

Rozprawa doktorska

**Zastosowanie cieczy jonowych w katalitycznym hydroborowaniu
nienasyconych wiązań węgiel-tlen i węgiel-azot**

Application of ionic liquids in catalytic hydroboration of unsaturated carbon-
oxygen and carbon-nitrogen bonds

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Promotor pomocniczy: dr Jakub Szyling

Uniwersytet im. Adama Mickiewicza w Poznaniu



UNIwersYTET
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W POZNANIU

Rozprawa doktorska w formie tematycznie spójnego cyklu artykułów
opublikowanych w czasopismach naukowych, przygotowana
w dziedzinie nauk ścisłych, w dyscyplinie nauk chemicznych

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Badania przedstawione w rozprawie doktorskiej pt. „Zastosowanie cieczy jonowych w katalitycznym hydroborowaniu nienasyconych wiązań węgiel-tlen i węgiel-azot” zostały sfinansowane ze środków Narodowego Centrum Nauki w ramach grantu Sonata Bis 9 (UMO-2019/34/E/ST4/00068)



N A R O D O W E C E N T R U M N A U K I

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Streszczenie w języku polskim

Celem niniejszej rozprawy doktorskiej pt. „Zastosowanie cieczy jonowych w katalitycznym hydroborowaniu nienasyconych wiązań węgiel-tlen i węgiel-azot” było opracowanie nowych i wydajnych układów katalitycznych dla reakcji hydroborowania nienasyconych wiązań węgiel-tlen ($C=O$) oraz węgiel-azot ($C=N$, $C\equiv N$). Kluczowym elementem badań było wykorzystanie cieczy jonowych – zarówno jako mediów do immobilizacji katalizatorów metali przejściowych, jak i jako organokatalizatorów.

Rozprawa obejmuje cykl trzech tematycznie spójnych artykułów naukowych (**P1–P3**) szczegółowo opisujących metody hydroborowania ketonów z udziałem kompleksu $[Pt(PPh_3)_4]$, immobilizowanego w cieczy jonowej (**P1**) oraz zastosowania cieczy jonowych jako organokatalizatorów w reakcjach hydroborowania związków karbonylowych (**P2**) i nienasyconych związków azotu (**P3**).

Odpowiedni dobór katalizatora i optymalizacja warunków reakcji (stężenie katalizatora, stosunek reagentów, temperatura, czas, rozpuszczalnik, atmosfera reakcji) pozwoliły na prowadzenie procesu w łagodnych warunkach oraz z wysoką wydajnością i selektywnością. W ramach badań przeprowadzono szeroki przegląd substratów obejmujący związki aromatyczne, heteroaromatyczne i alifatyczne – łącznie w trzech publikacjach opisano 99 przykładów. Wszystkie produkty zostały w pełni scharakteryzowane za pomocą spektroskopii magnetycznego rezonansu jądrowego oraz spektrometrii masowej. Wykazano również możliwość wielokrotnego wykorzystania katalizatora dzięki jego efektywnej immobilizacji w cieczy jonowej $[BMIM][NTf_2]$. Z kolei octan choliny, dzięki swojej strukturze umożliwiającej organokatalityczne działanie w reakcjach hydroborowania wiązań węgiel-heteroatom, z powodzeniem został wielokrotnie poddany recyklingowi z zachowaniem wysokiej aktywności.

Badania mechanistyczne przeprowadzono na podstawie analiz NMR, a w przypadku reakcji w obecności octanu choliny, dodatkowo wsparto je obliczeniami DFT. Zaproponowany mechanizm reakcji hydroborowania ketonów kompleksem platyny(0) opiera się na procesach utleniającej addycji i redukującej eliminacji. Natomiast dla reakcji katalizowanych cieczami jonowymi, połączenie metod eksperymentalnych i obliczeniowych, umożliwiło identyfikację aktywnych katalitycznie borowodorków oraz zaproponowanie mechanizmów reakcji. Wykazano, że zarówno kation, jak i anion cieczy jonowej odgrywają kluczową rolę w generowaniu

aktywnych form katalizatora, co stanowi istotny i nowatorski wkład w rozwój badań nad hydroborowaniem nienasyconych wiązań węgiel-heteroatom.

Ponadto, przeprowadzone badania wpisują się w założenia zielonej chemii, koncentrując się na procesach charakteryzujących się wysoką ekonomią atomową, ograniczonym zużyciem rozpuszczalników organicznych oraz możliwością recyklingu katalizatorów.

Streszczenie w języku angielskim

The aim of doctoral dissertation entitled *Application of ionic liquids in catalytic hydroboration of unsaturated carbon-oxygen and carbon-nitrogen bonds* is the development of novel, efficient, and sustainable catalytic systems for the hydroboration of unsaturated carbon-oxygen (C=O) and carbon–nitrogen (C=N, C≡N) bonds. A main focus of the research are the various applications of ionic liquids, serving both as media for the immobilization of transition-metal catalysts and as organocatalysts.

A series of thematically coherent articles (**P1-P3**) present a detailed description of catalytic protocols for the hydroboration of ketones employing the [Pt(PPh₃)₄] complex immobilized in an ionic liquid (**P1**) and applications of ionic liquids as organocatalysts in the hydroboration of carbonyl compounds (**P2**) and unsaturated nitrogen derivatives (**P3**).

Comprehensive optimization of reaction parameters, (catalyst concentration, reagent ratio, temperature, reaction time, solvent, and reaction atmosphere) enabled the transformations to proceed under mild conditions with excellent yields and high chemoselectivity. A broad substrate scope was investigated, including aromatic, heteroaromatic, and aliphatic compounds. The study included a broad substrate scope covering aromatic, heteroaromatic, and aliphatic compounds; in total, 99 examples were described across the three publications. All products were fully characterized by nuclear magnetic resonance spectroscopy and mass spectrometry. Subsequent recycling experiments demonstrated that the catalytic systems could be reused multiple times using two different approaches. For the transition metal-based system, this was enabled by effective immobilization of the platinum complex in the ionic liquid [BMIM][NTf₂]. In organocatalytic systems, choline acetate was successfully reused multiple times, benefiting from its low solubility in nonpolar solvents and its high catalytic activity in hydroboration reactions.

Mechanistic studies were conducted on the basis of NMR analyses, and in the case of reactions performed in the presence of choline acetate, these investigations were further supported by DFT calculations. The proposed mechanism for ketone hydroboration catalyzed by the platinum(0) complex is based on oxidative addition and reductive elimination processes. In contrast, for reactions catalyzed by ionic liquids, the combination of experimental and computational methods enabled the identification of catalytically active borohydride species and the proposal of reaction mechanisms. It was demonstrated that both the cation and the anion of the ionic liquid play a crucial role in generating the active catalytic species, representing a

significant and novel contribution to the development of research on the catalytic hydroboration of unsaturated carbon–heteroatom bonds.

Therefore, the conducted studies are in line with the principles of green chemistry, on processes characterized by high atom economy, reduced consumption of organic solvents, and the possibility of catalyst recycling.

Ankieta dorobku naukowego

A. Dane personalne

Imię i nazwisko Barbara Krupa

Data urodzenia 27.02.1996 r.

Numer ORCID  0000-0003-2661-2008

B. Edukacja

od 10/2020 **Uniwersytet im. Adama Mickiewicza w Poznaniu – Szkoła Doktorska Nauk Ścisłych, Centrum Zaawansowanych Technologii**

- Studia III stopnia w dyscyplinie nauk chemicznych.

2019–2020 **Politechnika Poznańska – Wydział Technologii Chemicznej**

- Studia II stopnia na kierunku Technologia Chemiczna
- Temat pracy magisterskiej: *Synteza i fitotoksyczność cieczy jonowych na bazie morfoliny z anionem o działaniu chwastobójczym*. Opiekun naukowy: dr inż. Anna Syguda.

2016–2019 **Politechnika Poznańska – Wydział Technologii Chemicznej**

- Studia I stopnia na kierunku Inżynieria Chemiczna i Procesowa.
- Temat pracy inżynierskiej: *Oznaczenie ołowiu i kadmu w płatkach owsianych powszechnie dostępnych na rynku*. Opiekun naukowy: dr hab. inż. Ewa Stanisław.

C. Publikacje naukowe będące przedmiotem rozprawy doktorskiej

P1

B. Krupa, J. Szyling, J. Walkowiak, *Pt(PPh₃)₄ and Pt(PPh₃)₄@IL catalyzed hydroboration of ketones*. *Scientific Reports* **2023**, *13*, 20237, doi: 10.1038/s41598-023-47518-6 (IF₂₀₂₃ = 3.8, IF_{5-years} = 4.3, MNI_{SW}₂₀₂₃ = 140, Percentyl₂₀₂₃ = 92, cytowania = 10);

P2

B. Krupa, M. Nowicki, P. Huninik, J. Szyling, J. Walkowiak, *Organocatalytic hydroboration of carbonyl compounds promoted by choline-based ionic liquids*. *ACS Sustainable Chemistry & Engineering* **2025**, 13, 41, 17510–17519 doi: 10.1021/acssuschemeng.5c07304 (IF₂₀₂₄ = 7.3, IF_{5-years} = 8.0, MNI_{SW}₂₀₂₅ = 140, Percentyl₂₀₂₄ = 93, cytowania = 2);

P3

B. Krupa, M. Nowicki, J. Szyling, J. Walkowiak, *Organocatalytic hydroboration of imines, nitriles, and amides using choline-based ionic liquids*. *Journal of Catalysis* **2025**, 116362, doi: 10.1016/j.jcat.2025.116362 (IF₂₀₂₄ = 6.5, IF_{5-years} = 6.8, MNI_{SW}₂₀₂₅ = 140, Percentyl₂₀₂₄ = 87, cytowania = 1).

Metryka (dane ze strony Scopus z dnia 31.05.2026 r.)

IF skumulowany	17.6
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MNI _{SW} skumulowane	420
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Sumaryczna liczba cytowań	13
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D. Publikacje naukowe nie będące przedmiotem rozprawy doktorskiej

1) M. Wojcieszak, B. Krupa, A. Syguda, F. Walkiewicz, M. Wilkowska, M. Kozak, K. Materna, *Surface activity and phytotoxicity of morpholinium herbicidal ionic liquids*. *Journal of Molecular Liquids*, **2022**, 362, 119750, doi: 10.1016/j.molliq.2022.119750, (IF₂₀₂₂ = 6.0, MNI_{SW}₂₀₂₂ = 100, Percentyl₂₀₂₂ = 91, cytowania = 18);

2) A. Szymańska, M. Nowicki, S. De, B. Krupa, J. Szyling, K. Leżaić, M-E. Moret, J. Walkowiak, *Catalytic hydroboration of ketones using Mn(CO)₅Br and Mn₂(CO)₁₀*. *Advanced Synthesis & Catalysis*, **2025**, 367, e70092, doi: 10.1002/adsc.70092, (IF₂₀₂₅ = 4.0, MNI_{SW}₂₀₂₅ = 140, Percentyl₂₀₂₄ = 83, cytowania = 2).

Podsumowanie parametrów dla wszystkich artykułów naukowych:

IF skumulowany	27.6
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MNI _{SW} skumulowane	660
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Sumaryczna liczba cytowań	33 ^{a)} (33) ^{b)}
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^{a)}dane z Scopus z dnia 31.05.2026 r.; ^{b)}dane z Google Scholar z dnia 31.05.2026 r.

E. Udział w projektach badawczych

od 10/2020

Grant **Sonata Bis 9** (NCN)

Nowe podejście do procesów hydroborowania wiązań nienasyconych węgiel-węgiel i węgiel-heteroatom w układach powtórzeniowych i przepływowych. (UMO-2019/34/E/ST4/00068).

Pełniona funkcja: wykonawca (stypendystka naukowa).

Kierownik projektu: dr hab. inż. Jędrzej Walkowiak, prof. UAM.

07/2024–02/2025

Grant **Beethoven Classic 3** (NCN)

Katalityczne hydrosililowanie w układzie SILP/scCO₂ – innowacyjne podejście do redukcji i funkcjonalizacji alkinów, imin oraz związków karbonylowych. (UMO-2018/31/G/ST4/04012).

Pełniona funkcja: wykonawca (stypendystka naukowa).

Kierownik projektu: dr hab. inż. Jędrzej Walkowiak, prof. UAM.

F. Uczestnictwo w konferencjach naukowych

Komunikaty ustane prezentowane osobiście:

- 1) B. Krupa, P. Huninik, J. Szyling, A. Franczyk, J. Walkowiak, *Catalytic hydroboration of unsaturated carbon-carbon and carbon-heteroatom bonds in ionic liquids.*
International Symposium on Synthesis and Catalysis 2021 (ISySyCat2021), 31.08–03.09.2021, Evora, Portugalia;
- 2) B. Krupa, J. Szyling, J. Walkowiak, *Application of platinum catalyst in hydroboration of carbonyl compounds and alternative protocol for catalyst recycling.*
I Doctoral Symposium in Exact Science, 04–05.12.2023, Dębina, Polska;
- 3) B. Krupa, M. Nowicki, P. Huninik, J. Szyling, J. Walkowiak, *Cholinowe ciecze jonowe jako efektywne organokatalizatory hydroborowania związków karbonylowych.*
II Ogólnopolska Konferencja Naukowa PUTChemikon, 18.05.2024, Poznań, Polska.

Współautorstwo 7 komunikatów ustnych prezentowanych na konferencjach krajowych i zagranicznych:

- 1) J. Walkowiak, J. Szyling, K. Stefanowska, T. Sokolnicki, B. Krupa, K. Stęsik, M. Kreik, *Green methods in the synthesis of organosilicon and organoboron compounds via catalytic hydrometallation and coupling reactions*.
Catalysis and Chemical Engineering Conferences (CCE Series), 22–24.02. 2021, San Francisco, USA;
- 2) J. Walkowiak, J. Szyling , K. Stefanowska, T. Sokolnicki, A. Franczyk, M. Kreik, B. Krupa, K. Stęsik, *The new catalytic and sustainable approach in the synthesis of unsaturated organosilicon and organoboron compounds*.
International Symposium on Synthesis and Catalysis 2021 (ISySyCat2021), 31.08–03.09.2021, Evora, Portugalia;
- 3) J. Walkowiak, J. Szyling, T. Sokolnicki, A. Franczyk, K. Stefanowska, B. Krupa, P. Huninik, *Green catalysis in organoboron and related compounds synthesis*.
9th European Conference on Boron Chemistry, 03–07.07.2022, Barcelona, Hiszpania;
- 4) J. Szyling, T. Sokolnicki, B. Krupa, A. Franczyk, J. Walkowiak, *Green solvents mediated synthesis of unsaturated organoboron and silicon compounds via trans-metallation: new tricks for old dogs*.
Swiss Summer School 2021, 05–09.09. 2021, Les Diablerets, Szwajcaria;
- 5) J. Walkowiak, P. Huninik, B. Krupa, A. Franczyk, J. Szyling, K. Stefanowska-Kątna, T. Sokolnicki, M. Nowicki, *Sustainable approaches to organoboron and organosilicon compounds*.
ACS Fall, 18–22.08.2024, Denver, USA;
- 6) J. Walkowiak, P. Huninik, B. Krupa, T. Sokolnicki, K. Stęsik, A. Szymańska, A. Franczyk, K. Stefanowska-Kątna, J. Szyling, S. De, *Transition metal vs. organic catalyzed hydrometallation reactions – the catalysts influence on process regio- and stereoselectivity*.

30th International Conference on Organometallic Chemistry (ICOMC), 14–18.07.2024, Agra, Indie;

- 7) J. Walkowiak, J. Szyling, B. Krupa, P. Huninik, A. Szymańska, *Transition metal vs. Organocatalyzed hydrometallation reactions*.
10th European Conference on Boron Chemistry, Łódź, Polska, 6–10.07.2025.

Komunikaty plakatowe prezentowane osobiście:

- 1) B. Krupa, J. Szyling, A. Franczyk, K. Stefanowska, J. Walkowiak, *Katalityczne hydroborowanie alkinów i związków karbonylowych w konwencjonalnych i niekonwencjonalnych mediach reakcyjnych*.
II Pomorskie Studenckie Sympozjum Chemiczne (IIPSSCh), 20–21.03.2021, Gdańsk, Polska;
- 2) B. Krupa, P. Huninik, J. Szyling, A. Franczyk, J. Walkowiak, *Catalytic hydroboration of alkynes and carbonyl compounds in green reaction media*.
Swiss Summer School 2021, 05–09.09. 2021, Les Diablerets, Szwajcaria;
- 3) B. Krupa, J. Szyling, J. Walkowiak, *Pt-Catalyzed Hydroboration Of Carbonyl Compounds*.
„Attilio Corbella” International Summer School on Organic Synthesis (ISOS 2022), 12–16.06.2022, Gargnano, Włochy;
- 4) B. Krupa, P. Huninik, J. Szyling, A. Franczyk, J. Walkowiak, *Catalytic hydroboration of carbonyl compounds in traditional and green reaction media*.
9th European Conference on Boron Chemistry, 03–07.07.2022, Barcelona, Hiszpania;
- 5) B. Krupa, J. Szyling, J. Walkowiak, *Hydroborowanie związków karbonylowych w obecności katalizatora platynowego*.
III Ogólnopolska Studencka Konferencja Naukowa „Bliżej Chemii” 2023, 07–08.01.2023, konferencja on-line;

- 6) B. Krupa, J. Szyling, J. Walkowiak, *Catalytic reduction of ketones in the presence of a Pt: traditional and green approach.*
International Conference on Phosphorus, Boron and Silicon – PBSi 2023, 22–24.03.2023, Berlin, Niemcy;
- 7) B. Krupa, J. Szyling, J. Walkowiak, *Katalityczna redukcja ketonów z wykorzystaniem tradycyjnych i „zielonych” mediów reakcyjnych.*
I Ogólnopolska Konferencja Naukowa PUTChemikon, 06.05.2023, Poznań, Polska;
- 8) B. Krupa, J. Szyling, J. Walkowiak, *Hydroboration of ketones in conventional and green reaction media.*
„Attilio Corbella” International Summer School on Organic Synthesis (ISOS 2023), 18–22.06.2023, Gargnano, Włochy;
- 9) B. Krupa, M. Nowicki, P. Huninik, J. Szyling, J. Walkowiak, *Carbonyl group hydroboration catalysed by cholinium-based ionic liquids.*
„Attilio Corbella” International Summer School on Organic Synthesis (ISOS 2024), 16–20.06.2024, Gargnano, Włochy;
- 10) B. Krupa, M. Nowicki, J. Szyling, J. Walkowiak, *Organocatalytic hydroboration of imines, nitriles, and amides using choline-based ionic liquids.*
Swiss Summer School 2025, 17-21.08. 2025, Haute-Nendaz, Szwajcaria.

Współautorstwo 5 komunikatów plakatowych prezentowanych na konferencjach krajowych i zagranicznych:

- 1) J. Szyling, P. Huninik, B. Krupa, T. Sokolnicki, J. Walkowiak, *TM-catalyzed diboration and hydroboration of 1,3-diynes – efficient access to boryl-functionalized enynes.*
9th European Conference on Boron Chemistry, 03–07.07.2022, Barcelona, Hiszpania;
- 2) J. Szyling, A. Szymańska, B. Krupa, P. Huninik, J. Walkowiak, *Functionalization of 1,3-diynes via catalytic diboration and protodeboration reactions.*

International Conference on Phosphorus, Boron and Silicon – PBSi 2023, 22–24.03.2023, Berlin, Niemcy;

- 3) A. Szymańska, M. Nowicki, S. De, B. Krupa, J. Szyling, J. Walkowiak, *Simple manganese complexes as efficient catalysts of ketone hydroboration*.
Swiss Summer School 2025, 17–21.08. 2025, Haute-Nendaz, Szwajcaria;
- 4) A. Szymańska, M. Nowicki, S. De, B. Krupa, J. Szyling, J. Walkowiak, *Catalytic hydroboration of ketones using $Mn(CO)_5Br$ and $Mn_2(CO)_{10}$* .
16th European Congress on Catalysis EuropaCat 2025, 31.08–5.09.2025, Trondheim, Norwegia;
- 5) J. Walkowiak, P. Huninik, B. Krupa, J. Szyling, M. Nowicki, H. Im, M-H. Baik, R. Zbořil, S. Kment, *New organic, boron and single atom catalysts for borylation and silylation reactions: towards typical and unusual selectivities*.
OMCOS XXII – 22nd International Symposium on Organometallic Chemistry Directed Towards Organic Synthesis, 01–05.09 2025, Kyoto, Japonia.

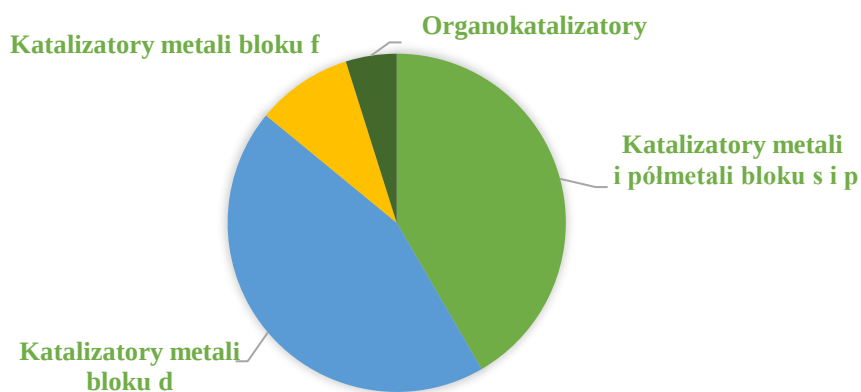
G. Stypendia, nagrody i wyróżnienia

- 1) Laureatka 7 konkursów organizowanych w ramach projektu *Inicjatywa Doskonałości – Uczelnia Badawcza* (2020-2026);
- 2) Pierwsza nagroda za najlepszy poster w *Sekcji Chemii Organicznej i Bioorganicznej* zaprezentowany podczas I Ogólnopolskiej Konferencji Naukowej PUTChemicon 2023.

1. Wprowadzenie i uzasadnienie podjęcia tematyki badawczej

1.1. Katalityczne hydroborowanie wiązań nienasyconych węgiel-heteroatom

Hydroborowanie to wydajna i wszechstronna metoda funkcjonalizacji związków polegająca na redukcji nienasyconych wiązań węgiel-węgiel lub węgiel-heteroatom poprzez addycję wiązania bor-wodór do wiązań wielokrotnych m.in. w olefinach, alkinach, związkach karbonylowych, iminach czy nitylach.^{1,2} W porównaniu z metodami opartymi na bardziej niebezpiecznych wodorkach nieorganicznych (np. glinowodorek litu [LAH])^{3,4} lub na klasycznym uwodornieniu⁵⁻⁷, reakcje hydroborowania przebiegają zwykle w łagodnych warunkach, z wykorzystaniem prostych i komercyjnie dostępnych czynników borylujących (np. pinakoloboran, katecholoboran, 9-borabicyklo[3.3.1]nonan).⁸ Proces ten charakteryzuje się 100% ekonomią atomową, a otrzymane produkty mogą w prosty sposób ulegać dalszym funkcjonalizacjom, takim jak: deborylacja⁹, sprzęganie Suzuki-Miyaura¹⁰, alkenylowanie czy cykloaddycja¹¹. Znakomita większość katalizatorów stosowanych w hydroborowaniu nienasyconych wiązań węgiel-węgiel i węgiel-heteroatom to kompleksy metali przejściowych lub związki nieorganiczne.^{8,12} Z kolei hydroborowanie związków karbonylowych przebiega na ogół w obecności katalizatorów metali grup głównych,¹² metali przejściowych,⁸ rzadziej przy udziale kompleksów metali bloku f¹³ lub organokatalizatorów (Wykres 1).¹⁴



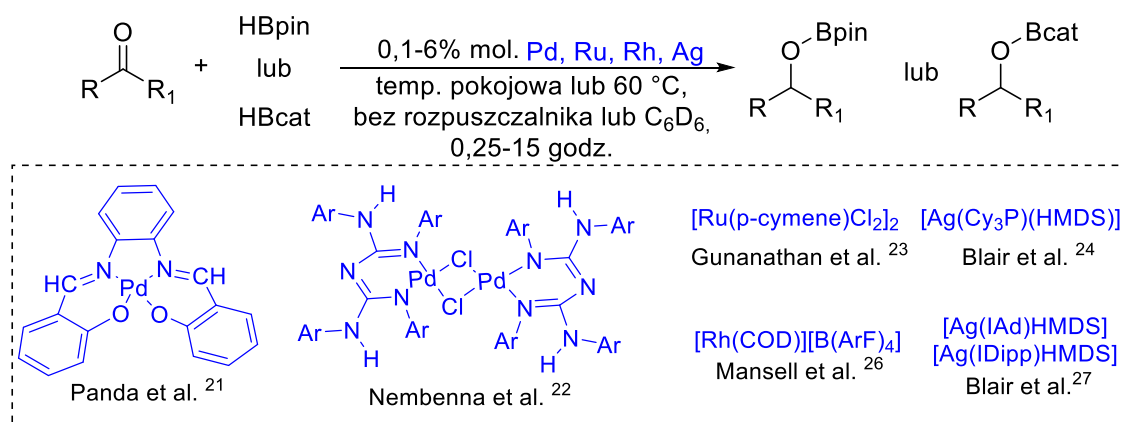
Wykres 1. Udział publikacji dot. hydroborowania ketonów i aldehydów podzielona ze względu na typ katalizatora (Scopus, maj 2026).

Hydroborowanie wiązań nienasyconych CO oraz CN, a następnie hydroliza powstałych produktów prowadzi do otrzymywania alkoholi lub amin, które stanowią ważne bloki budulcowe w syntezie organicznej.¹⁵⁻¹⁷ Zastosowanie kompleksów metali przejściowych pozwala na ogół prowadzić reakcje w łagodnych warunkach, zapewnia wysoką wydajność i selektywność procesu.

Dodatkowo proces często toleruje różne grupy funkcyjne, co pozwala na syntezę wartościowych bloków budulcowych. Z drugiej strony, kompleksy metali przejściowych – zwłaszcza metali szlachetnych – są kosztowne, a ich synteza oraz izolacja jest często wieloetapowa. Zastosowanie takich układów wymaga bezwodnych i beztlenowych warunków reakcji. Ponadto w przypadku katalizy homogenicznej ponowne wykorzystywanie katalizatorów jest często niemożliwe, co negatywnie wpływa na ekonomię procesu.¹⁷ Dlatego też poszukiwanie nowych i efektywnych protokołów uwzględniających wielokrotne wykorzystanie katalizatora oraz ograniczenie ilości lotnych rozpuszczalników organicznych jest w pełni uzasadnione i wpisuje się w najnowsze trendy współczesnej chemii.

1.1.1. Hydroborowanie aldehydów i ketów katalizowane kompleksami metali szlachetnych

Wykorzystanie kompleksów metali szlachetnych w katalitycznym hydroborowaniu wiązań nienasyconych węgiel-tlen ograniczone jest głównie do związków palladu, rutenu, srebra i rodu. Proces został opisany przede wszystkim dla aldehydów,¹⁸⁻²⁰ podczas gdy efektywna redukcja mniej reaktywnych ketonów w obecności katalizatorów metali szlachetnych została przedstawiona zaledwie w kilku przykładach (Schemat 1).²¹⁻²⁷

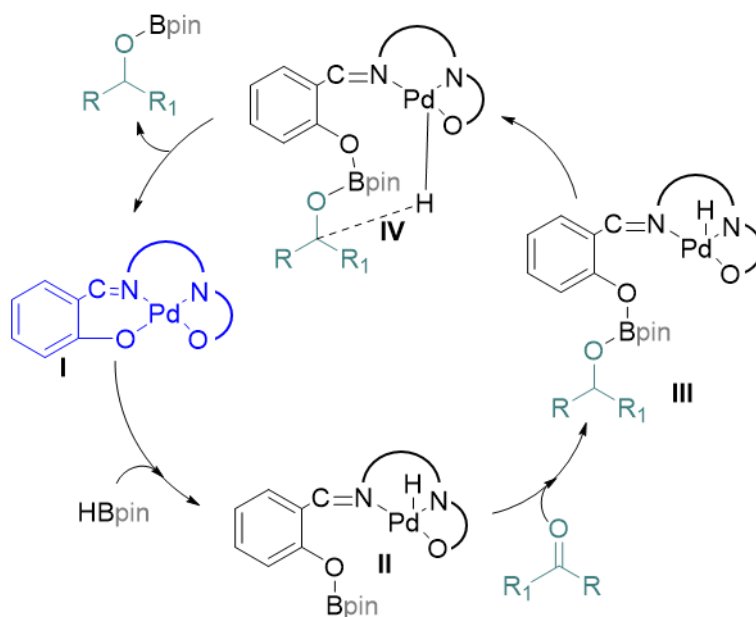


Schemat 1. Katalizatory metali szlachetnych zastosowane w hydroborowaniu ketonów.

Hydroborowanie aldehydów i ketonów katalizowane kompleksami palladu^{21,22} oraz przez dwurdzeniowy kompleks $[\text{Ru}(\text{p-cymen})\text{Cl}_2]_2$,²³ prowadzone było w warunkach bezrozpuszczalnikowych, a czynnikiem redukującym był pinakoloboran (HBpin). Aby uzyskać pełną konwersję ketonów reakcje prowadzono w temperaturze 60 °C przez 12–15 godzin w obecności 0,1–6% molowych katalizatora. Grupy elektronodonorowe i elektronoakceptorowe były dobrze tolerowane w procesie, podobnie jak związki alifatyczne i heterocykliczne, przy czym te ostatnie były niereaktywne w obecności $[\text{Ru}(\text{p-cymen})\text{Cl}_2]_2$.²¹⁻²³ Reakcje z udziałem

kompleksów palladu(II) były dodatkowo chemoselektywne względem wiązania C=O w obecności grup: estrowej, nitrowej, nitrylowej oraz nienasyconych wiązań węgiel-węgiel.^{21,22}

Mechanizm reakcji katalizowanej kompleksem palladu(II) z ligandem salenowym zakłada utworzenie wiązania Pd-H w wyniku reakcji z pinakoloboranem i przyłączenie się grupy borylowej do atomu tlenu liganda (**II**, Schemat 2). Umożliwia to w kolejnych etapach: i) koordynację grupy karbonylowej do atomu boru (**III**), ii) przeniesienie wodorku z atomu palladu na atom węgla grupy karbonylowej (**IV**), iii) regenerację katalizatora z wydzielaniem produktu (**I**).²¹ Wytworzenie wiązania Pd-H było również kluczowe dla reakcji hydroborowania związków karbonylowych w obecności liganda guanidynowego. Mechanizm reakcji dla tego układu katalitycznego zakłada insercję wiązania CO do wiązania Pd-H oraz metatezę wiązań σ między utworzonym alkoholem palladu oraz pinakoloboranem.²² Podobnie jak dla katalizatorów palladowych, mechanizm hydroborowania w obecności $[\text{Ru}(p\text{-cymen})\text{Cl}_2]_2$ również zakłada wytworzenie wiązania metal-wodór w pierwszym etapie (utleniająca addycja). Następnie, przeniesienie wodorku z centrum metalicznego na grupę karbonylową. Cykl zamyka uwolnienie hydroborowanego produktu i odtworzenie katalizatora.²³



Schemat 2. Prawdopodobny mechanizm reakcji hydroborowania związków karbonylowych katalizowanej kompleksem palladu(II) z ligandem salenowym.

W przypadku kompleksu srebra $[\text{Ag}(\text{PCy}_3)(\text{HMDS})]$ reakcję prowadzono w temperaturze pokojowej w deuterowanym benzenie. Zastosowanie 5% molowych katalizatora prowadziło do pełnej konwersji substratów w czasie od 15 minut do 6 godzin, w zależności od struktury reagenta.²⁴ Podobne warunki (temperatura pokojowa, deuterowany benzen) były zastosowane dla

kompleksu rodu (0,1% molowego) w reakcji z katecholoboranem. Czas prowadzenia procesu wynosił 30–60 minut. Substraty z podstawnikami halogenkowymi, alkilowymi i grupą nitrową były dobrze tolerowane. Zaproponowany protokół był odpowiedni także dla aldehydów i imin, jednak hydroborowanie wiązania węgiel-azot wymagało wyższego stężenia katalizatora oraz podniesienia temperatury procesu.²⁶ Mechanizmy reakcji hydroborowania dla obu kompleksów (srebra [Ag(PCy₃)(HMDS)] oraz rutenu z ligandem NHC) zakładały wytworzenie aktywnego wiązania metal-wodór, podobnie jak opisano powyżej.

Szymczak i Geri wykorzystali kompleks rutenu z kleszczowym N-heterocyklicznym ligandem w reakcji hydroborowania nitryli, który okazał się również skutecznym promotorem redukcji acetofenonu. Reakcja przebiegała w temperaturze pokojowej, w deuterowanym benzenie z udziałem 0,04% molowych katalizatora, a ilościowa konwersja substratu została osiągnięta po godzinie.²⁵

Należy zaznaczyć, że doniesienia literaturowe opisujące hydroborowanie ketonów i aldehydów w obecności kompleksów metali szlachetnych, nie uwzględniają możliwości ich wielokrotnego użycia. Najczęściej, wciąż aktywny katalizator jest dezaktywowany w poreakcyjnych procedurach oczyszczania produktu. Odsłania to potrzebę projektowania nowych protokołów reakcyjnych, które z jednej strony zapewniałyby wysoką aktywność kompleksu metalu, z drugiej zaś – zgodnie z zasadami zielonej chemii – umożliwiałyby recykling katalizatora i organicznie zużycia lotnych rozpuszczalników organicznych. Jedną ze strategii pozwalającą osiągnąć te cele jest zastosowanie przyjaznych dla środowiska tzw. „zielonych” rozpuszczalników, jakimi są m.in. ciecze jonowe. Mogą one służyć jako medium reakcji oraz nośnik do immobilizacji katalizatora. Podejście to jest ugruntowane w literaturze i zostało opisane w rozdziale 1.3, jednak dotychczas nie było zastosowane w hydroborowaniu wiązań nienasyconych węgiel-heteroatom.

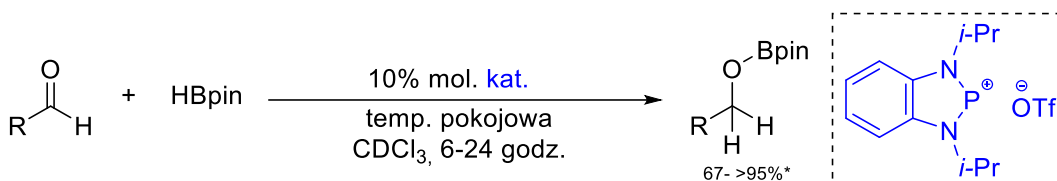
W 2023 roku opublikowano dwie prace dotyczące hydroborowania związków karbonylowych w obecności kompleksów metali szlachetnych, [Pt(PPh₃)₄] oraz [Ag(IDipp)HMDS], które zostały podane recyklingowi. Jedna z tych prac jest przedmiotem niniejszej rozprawy (**P1**), druga natomiast została opublikowana w grupie Blaira i stanowiła²⁷ kontynuację badań nad wykorzystaniem kompleksów srebra(I) z N-heterocyklicznymi ligandami w hydroborowaniu i hydrosililowania aldehydów i ketonów. Autorzy zastosowali 5% molowych kompleksu srebra, 50% nadmiar pinakoloboranu i deuterowany benzen jako rozpuszczalnik. Reakcja przebiegała w temperaturze pokojowej, jednak efektywność metody zależała od struktury

substratu. Grupy wyciągające elektrony znacząco wpływały na skrócenie czasu trwania reakcji, natomiast modelowy substrat (acetofenon) ulegał konwersji na poziomie 50 lub 61% w czasie 24 godzin w zależności od testowanego kompleksu. W związku z tym, badanie możliwości wielokrotnego użycia katalizatora przeprowadzono dla reaktywnego 2,2,2-trifluoracetofenofenonu. W pięciu kolejnych cyklach reakcyjnych uzyskano konwersję substratu $\geq 94\%$, a całkowita liczba obrotów katalizatora (TON) wynosiła 97, co wskazuje na jego niską aktywność. Warto zaznaczyć, że zastosowane katalizatory nie są dostępne komercyjnie, a ich synteza jest skomplikowana i czasochłonna.²⁷

1.1.2. Organokatalizatory w hydroborowaniu wiązań nienasyconych węgiel-tlen

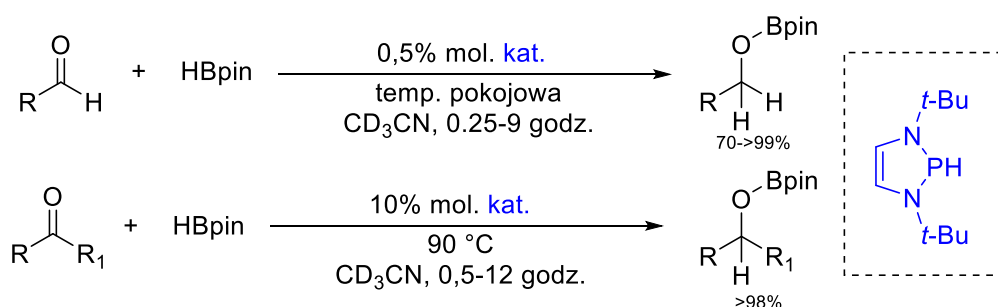
Koncepcja wykorzystywania małych cząsteczek organicznych jako katalizatorów reakcji do tej pory zdominowanych przez kompleksy metali przejściowych jest stosunkowo nową i popularną dziedziną przede wszystkim w obszarze syntezy związków chiralnych.²⁸ Choć pierwszy przykład reakcji organokatalitycznej pochodzi z 1860 roku, kiedy Justus Liebig opisał hydrolizę dicyjanu katalizowaną przez acetaldehyd,²⁹ to organokataliza dopiero w ciągu ostatnich dwóch dekad rozwinęła się w prężne pole badań w wiodących ośrodkach akademickich.³⁰ O potencjale tego podejścia do projektowania i syntezy związków organicznych świadczyć może chociażby Nagroda Nobla z 2021 roku przyznana Benjaminowi Listowi i Davidowi MacMillanowi za rozwój asymetrycznej organokatalizy.^{30,31} Obecnie ta koncepcja jest często wykorzystywana w wielu przemianach, które wcześniej zarezerwowane były jedynie dla katalizy metalami przejściowymi (TM, z ang. *transition metal*).^{32,33} Organokataliza znajduje zastosowanie w licznych transformacjach, takich jak reakcja Mannicha, reakcje aldolowe, cykloaddycje czy funkcjonalizacja wiązania C-H.³⁴ Jednak wykorzystanie tego typu katalizatorów w hydroborowaniu grup karbonylowych jest ograniczone do kilku przykładów.

Jednym z przykładów organokatalizatorów procesu hydroborowania wiązań podwójnych węgiel-tlen są związki P- i N-heterocykliczne. Melen i in. opisali zastosowanie soli składającej się z kationu fosfeniowego i anionu trifluorometanosulfonowego w hydroborowaniu aldehydów (Schemat 3). Stosując 10% mol. katalizatora, w czasie 6–24 godz. oraz w temperaturze pokojowej uzyskano wysokie konwersje substratów aromatycznych. Mechanizm reakcji jest analogiczny do mechanizmu zaproponowanego przez Kinjo³⁵ i zakłada aktywację wiązania B-H w reakcji soli organicznej z pinakoloboranem, a następnie przeniesienie wodorku z atomu fosforu na grupę karboksylową.³⁶



Schemat 3. Hydroborowanie aldehydów w obecności organicznej soli fosforu(III) jako katalizatora. *Wydajność na podstawie ^1H NMR.

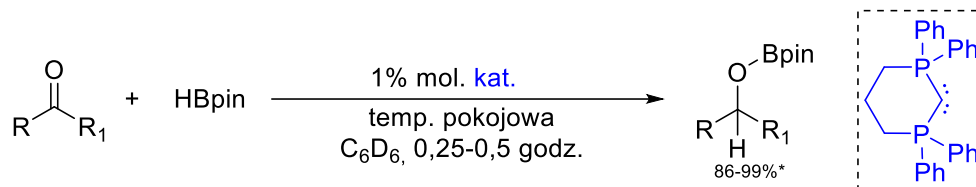
Niewielka ilość 1,3,2-diazafofolenu skutecznie promowała addycję wiązania B-H do wiązania karbonylowego aldehydów (Schemat 4). Substraty aromatyczne łatwo ulegały redukcji (konwersja >90% w czasie <15 min do 3 godzin), natomiast związki niearomatyczne wymagały wydłużenia czasu reakcji do 9 godzin. Większym wyzwaniem okazała się reakcja hydroborowania ketonów (Schemat 4). Aby efektywnie zredukować te związki wymagane było 20-krotnie wyższe stężenie katalizatora, podwyższona temperatura (90 °C), nadmiar pinakoloboranu oraz wydłużenie czasu reakcji (0,5–12 godz.). Stosując deuterowany pinakoloboran, zbadano również efekt izotopowy reakcji z benzofenonem. Wykazano, że kluczowym etapem procesu jest metateza wiązań sigma P-O (atom fosforu katalizatora – atom tlenu związku karbonylowego) i H-Bpin (pinakoloboran) w czterocząłowym stanie przejściowym. Potwierdziły to również obliczenia DFT.³⁷ Triazafofoleny zostały również opisane jako efektywne katalizatory hydroborowania aldehydów. Nawet relatywnie niewielka ilość katalizatora (0,1% molowego) umożliwiała chemoselektywną redukcję wiązań karbonylowych w α , β -nienasyconych aldehydach.³⁸



Schemat 4. Hydroborowanie aldehydów i ketonów w obecności 1,3,2-diazafofolenu jako katalizatora. *Wydajność na podstawie ^1H NMR.

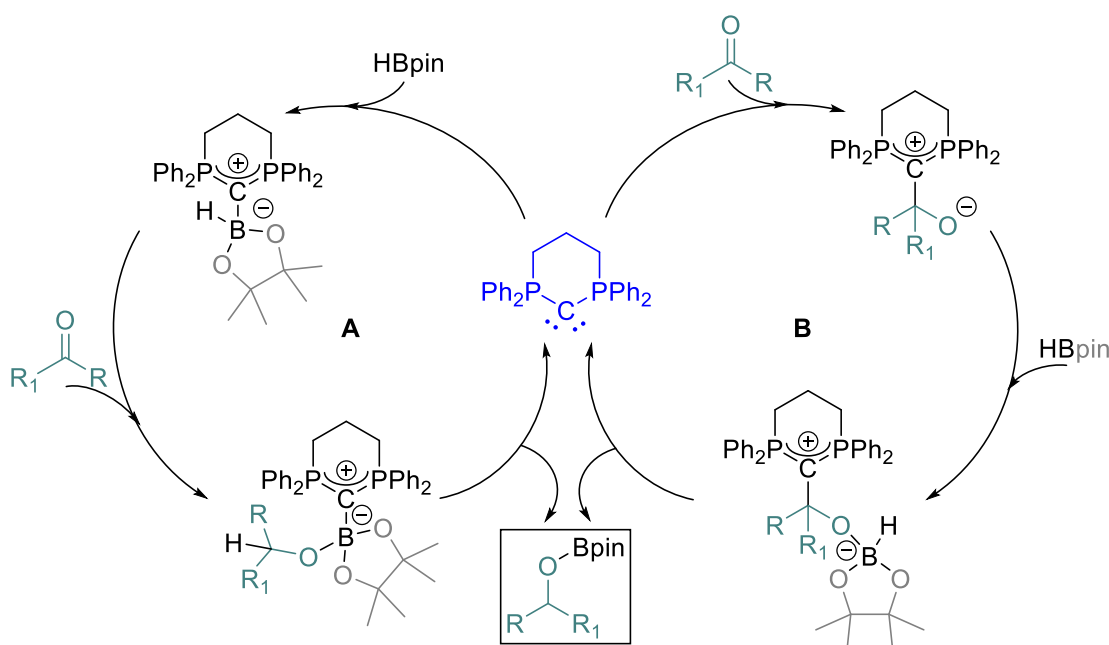
Liberman-Martin i in. zastosowali karbodifosforany, które przy stężeniu 1% molowego i niewielkim nadmiarze HBpin dawały wysokie konwersje ketonów i imin w czasie poniżej 30 minut (Schemat 5). Na podstawie badań stechiometrycznych katalizatora z substratami, monitorowanych techniką NMR, autorzy zaproponowali dwie możliwe ścieżki katalityczne. Pierwsza zakłada koordynację katalizatora do HBpin (Schemat 6), a następnie przeniesienie wodorku na atom węgla grupy karbonylowej i utworzenie wiązania B-O. Alternatywnie,

katalizator może najpierw koordynować do ketonu, po czym do układu przyłącza się cząsteczka pinakoloboranu, a przeniesienie wodorku na atom węgla grupy karbonylowej skutkuje powstaniem produktu – borylowanego eteru.³⁹

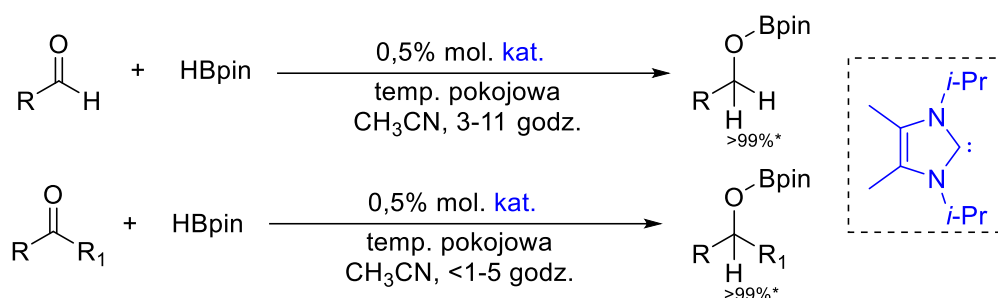


Schemat 5. Hydroborowanie ketonów w obecności katalizatora karbodifosforanowego. *Wydajność na podstawie ¹H NMR.

Podobnie jak karbodifosforany, N-heterocykliczne karbeny (NHC) skutecznie katalizują hydroborowanie ketonów i aldehydów, pozwalając na ilościową konwersję substratów w łagodnych warunkach i czasie od <1 do 13 godzin (Schemat 7). Warto zaznaczyć, że aldehydy ulegały redukcji wolniej niż ketony. Ponadto, w obydwu grupach związków zaobserwowano, że podstawniki elektronodonorowe były odpowiedzialne za wydłużenie czasu reakcji. Tendencja ta była szczególnie widoczna dla 3-metoksyacetofenonu i 3-metoksybenzaldehydu, dla których czas reakcji został wydłużony odpowiednio do 13 i 14 godzin. Mechanizm obejmował utworzenie kompleksu NHC-HBpin, transfer wodorku na atom węgla karbonylowego i przeniesienie grupy –Bpin na atom tlenu.⁴⁰

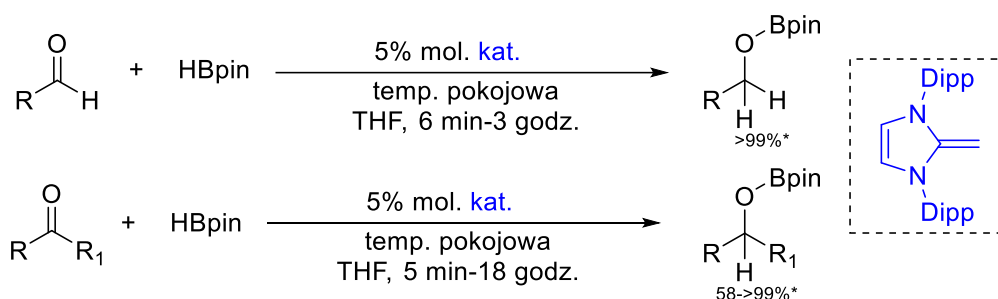


Schemat 6. Prawdopodobny mechanizm hydroborowania ketonów w obecności karbodifosforanu jako katalizatora.



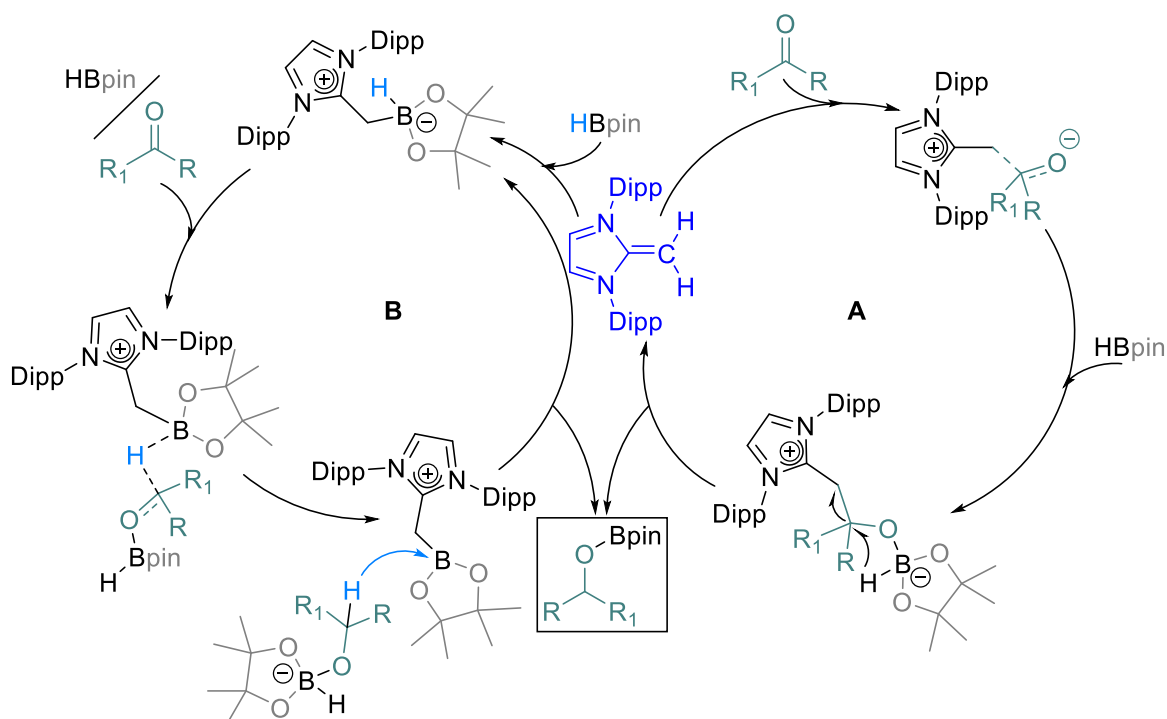
Schemat 7. Hydroborowanie ketonów i aldehydów w obecności katalizatora NHC. Schemat nie uwzględnia warunków dla 3-metoksyacetofenonu i 3-metoksybenzaldehydu.*Wydajność na podstawie ^1H NMR.

W hydroborowaniu ketonów i aldehydów sprawdzone zostały także N-heterocykliczne olefiny (NHO) (Schemat 8). Reakcja przebiegała przy relatywnie niskim stężeniu katalizatora (5% mol. NHO), w temperaturze pokojowej i rozpuszczalniku organicznym. Czas reakcji był zależny od budowy reagenta – redukcji łatwo ulegały związki aromatyczne z podstawnikami zarówno elektrodonorowymi, jak i elektronoakceptorowymi (poniżej 12 min.). Dłuższego czasu reakcji wymagały związki bez podstawników w pierścieniu aromatycznym i związki cykliczne. Autorzy zaproponowali dwie możliwe ścieżki katalityczne: w ścieżce A katalizator NHO najpierw reaguje ze związkiem karbonylowym, natomiast w ścieżce B w pierwszym etapie tworzy się addukt z HBpin (Schemat 9). W obu przypadkach kolejne etapy prowadzą do przeniesienia wodorku, utworzenia wiązania B–O oraz regeneracji aktywnego układu katalitycznego.⁴¹



Schemat 8. Hydroborowanie ketonów i aldehydów w obecności katalizatora NHO. *Wydajność na podstawie ^1H NMR.

Alternatywnie do opisanych powyżej przykładów, enancjoselektywne hydroborowanie ketonów zostało przeprowadzone w obecności od 5 do 10% molowych katalizatorów będących pochodnymi BINOL-u lub kompleksów tiomocznikowo-aminowych oraz z użyciem katecholoboranu (HBcat) jako czynnika redukującego. Reakcje przebiegały w ujemnych temperaturach (od -78 do -20 °C), w toluenie jako rozpuszczalniku, a uzyskane nadmiary enancjomeryczne sięgały 99%.⁴²⁻⁴⁴



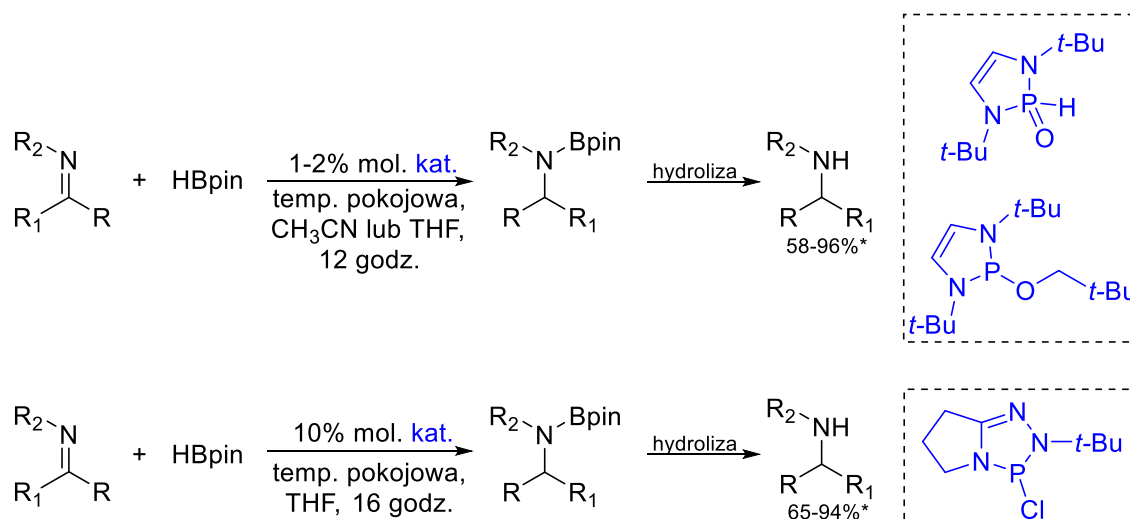
Schemat 9. Proponowane ścieżki katalityczne hydroborowania ketonów w obecności katalizatora NHO.

1.1.3. Organokatalizatory w hydroborowaniu wiązań nienasyconych węgiel-azot

Związki azotu zajmują szczególne miejsce w syntezie chemicznej. Dzięki swojej dużej aktywności biologicznej są kluczowe przy wytwarzaniu leków⁴⁵, agrochemikaliów⁴⁶ oraz w syntezie produktów naturalnych.⁴⁷ Redukcja nienasyconych wiązań węgiel-azot, niezmiennie od dekad, stanowi istotą strategię w otrzymywaniu wysokowartościowych chemikaliów (ang. *fine chemicals*).^{45,48} Reakcje hydroborowania imin, nityli i amidów są zdominowane przez katalizatory metaliczne.^{49,50} Jednakże w ostatnich latach można zaobserwować wzrost zainteresowania wykorzystaniem organokatalizatorów w tego typu transformacjach.

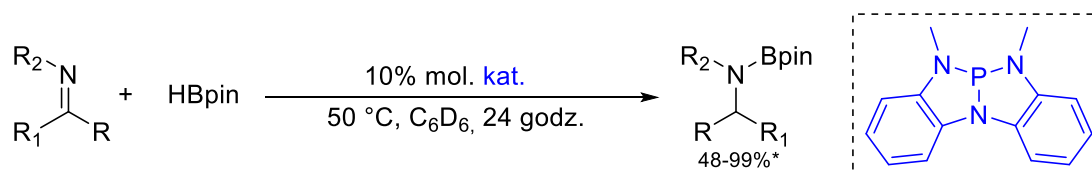
Podobnie jak dla hydroborowania związków karbonylowych, także w hydroborowaniu imin dominującą grupę katalizatorów stanowią związki P- i N-heterocykliczne, takie jak diazafosfoleny^{51,52} oraz triazafosfoleny (Schemat 10).³⁸ W obecności diazafosfolenów reakcja przebiegała efektywnie w czasie 12–16 godzin przy zastosowaniu równomolowej ilości pinakoloboranu lub jego niewielkiego nadmiaru. Możliwa była redukcja zarówno związków aromatycznych jak i alifatycznych. Proponowany mechanizm reakcji zakłada powstawanie wiązania P-H w reakcji z pinakoloboranem – prowadzące do wytworzenia aktywnego katalizatora umożliwiającego redukcję imin.^{51,52} Mimo podobnych warunków reakcji, badania mechanistyczne z udziałem triazafosfolenów nie dostarczyły dowodów na powstawanie wiązania P-H. Według autorów tych badań, cykl katalityczny rozpoczyna się od utworzenia kompleksu

katalizator-imina, który reaguje z pinakoloboranem, tworząc sześcioczłonowy pierścień w niskoenergetycznym stanie przejściowym, w którym zachodzi przeniesienie wodorku na cząsteczkę iminy. Cykl zamyka dysocjacja produktu i regeneracja katalizatora.³⁸



Schemat 10. Hydroborowanie imin w obecności di- i triazafosfolenów jako katalizatorów. *Wydajność izolacyjna.

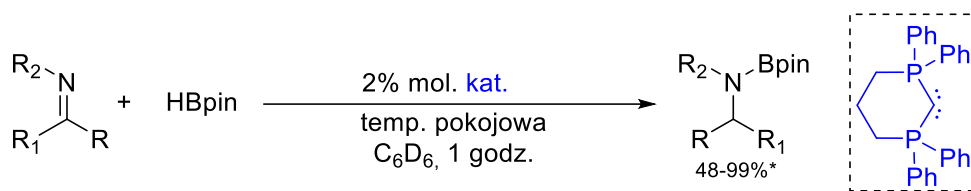
Radosevich i in. wykorzystali 10% molowych triamidu fosforu do hydroborowania imin przy równomolowym stosunku substratów, 50 °C, w czasie 24 godzin (Schemat 11). Aldiminy były dobrze tolerowane, niezależnie od rodzaju podstawników. Natomiast dla ketimin odnotowywane konwersje były niższe, prawdopodobnie wskutek efektów sterycznych. Mechanizm reakcji zakłada aktywację wiązania B–H przez elektrofilowy atom fosforu oraz nukleofilowy atom azotu ugrupowania *N*-metyloanilidowego. Rozerwanie wiązania B–H pinakoloboranu prowadzi do addycji wodorku do elektrofilowego atomu fosforu z wytworzeniem wiązania P–H oraz przeniesienia grupy –Bpin do nukleofilowego centrum *N*-metyloanilidowego. W kolejnym etapie zachodzi insercja iminy do wiązania wodór-fosfor, po czym wewnątrzcząsteczkowe przeniesienie grupy –Bpin prowadzi do powstania borylowanego produktu oraz regeneracji katalizatora, co zamyka cykl katalityczny.⁵³



Schemat 11. Hydroborowanie imin w obecności di- i triamidu fosforu jako katalizatora. *Wydajność na podstawie 1H NMR.

Również karbodifosforany były efektywnymi katalizatorami w reakcjach hydroborowania ketonów i imin (Schemat 12). Zoptymalizowane warunki reakcji dla *N*-benzylidenoaniliny, pozwoliły na osiągnięcie wydajności reakcji przekraczającej 95%. Przegląd imin został jednak

ograniczony do 6 przykładów.³⁹ Znane są również fotochemiczne metody hydroborowania imin, w których jako katalizatory zastosowano disiarczki difenylu w połączeniu z N-heterocyklicznymi boranami pełniącymi rolę czynników redukujących.⁵⁴



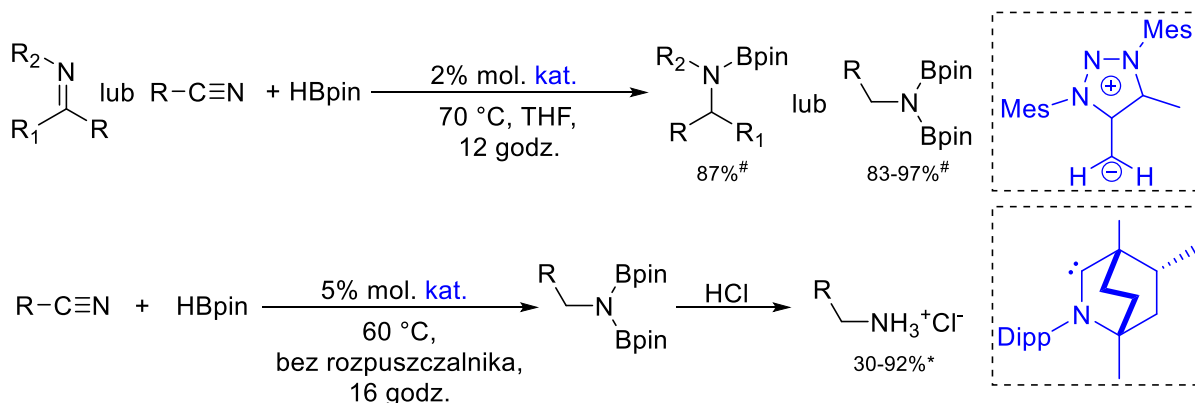
Schemat 12. Hydroborowanie imin w obecności karbodifosforanu jako katalizatora. *Wydajność na podstawie ^1H NMR.

Asymetryczna organokatalityczna redukcja ketimin została opisana z udziałem trzech organokatalizatorów. W obecności 5% molowych chiralnych katalizatorów będących pochodnymi BINOL-u i katecholoboranu jako czynnika redukcyjnego, uzyskano chiralne aminy z wysokimi wydajnościami i nadmiarem enancjomerycznym sięgającym 72%. Proces wymagał jednak zastosowania ujemnych temperatur ($-78\text{ }^{\circ}\text{C}$) oraz długiego czasu reakcji (24 godziny).⁵⁵ Speed i in. wykorzystali dwa organokatalizatory na bazie diazafosfolenów (0,2–2% molowych) do otrzymywania chiralnych amin. Reakcje prowadzone były w temperaturze pokojowej lub $-35\text{ }^{\circ}\text{C}$. Po 16 godzinach uzyskano wysokie konwersje substratów oraz nadmiary enancjomeryczne (90%).^{56,57}

Redukcja nitryli stanowi istotne wyzwanie syntetyczne, co wynika zarówno z wysokiej trwałości wiązania $\text{C}\equiv\text{N}$, jak i z trudności w kontrolowaniu selektywności procesu.⁵⁸ Dotychczas jako organokatalizatory w reakcji hydroborowania nitryli opisano jedynie N-heterocykliczne olefiny (NHO)⁵⁹ oraz bicykliczny (alkilo)(amino)karben (BICAAC) (Schemat 13).⁶⁰

W odróżnieniu od niezatłoczonych imin, hydroborowanie wiązań $\text{C}\equiv\text{N}$ przez N-heterocykliczne olefiny ograniczone jest jedynie do kilku substratów takich jak: benzonitryl, 4-fluorobenzonitryl oraz acetonitryl. Całkowity brak konwersji, pomimo nadmiaru pinakoloboranu oraz wysokiej temperatury reakcji ($70\text{ }^{\circ}\text{C}$), obserwowano dla substratów z grupą estrową, amidową lub nitrową, co według autorów prawdopodobnie wynikało z dezaktywacji katalizatora. Ponadto, w przypadku substratów zawierających zarówno wiązanie $\text{C}=\text{N}$, jak i $\text{C}\equiv\text{N}$, redukcji ulegało tylko wiązanie podwójne, co było zgodne z przewidywaniami. Proponowany mechanizm, opisany dla imin, zakłada oddziaływanie katalizatora z pinakoloboranem, zwiększające nukleofilowość wiązania B-H, które reaguje z atomem węgla wiązania $\text{C}=\text{N}$. Jednocześnie atom azotu reaguje z kolejną cząsteczką HBpin, a przeniesienie wodoru powoduje dysocjację

produktu i odtworzenie adduktu NHO-HBpin, analogicznie jak przy związkach karbonylowych (por. Schemat 9).⁵⁹

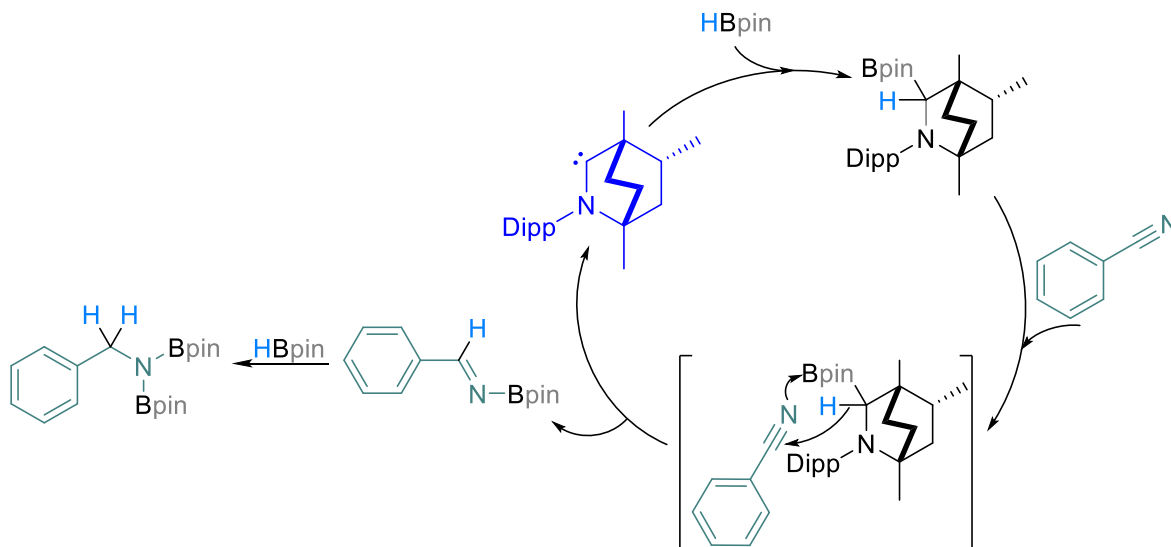


Schemat 13. Organokatalizatory zastosowane w hydroborowaniu imin i nityryli. #Wydajność na podstawie ¹H NMR. *Wydajność izolacyjna.

Zastosowanie 5% molowych bicyklicznego (alkilo)(amino)karbenu (BICAAC) umożliwiło hydroborowanie szerokiej gamy nityryli aromatycznych. Niższe wydajności otrzymano dla substratów heterocyklicznych i alifatycznych. Warto zaznaczyć, że dla identycznej reakcji w rozpuszczalniku organicznym (THF, DCM, acetonitryl, heksan, toluen, eter dietylowy) nie obserwowano powstawania produktu. Taki sam efekt został odnotowany w przypadku zmiany pinakoloboranu na 9-borabicyklo[3.3.1]nonan (9-BBN) lub addukt $\text{NH}_3 \cdot \text{BH}_3$. Na podstawie analiz NMR i DFT założono, że cykl katalityczny rozpoczyna się od reakcji katalizatora BICAAC z HBpin. Następnie wodorek jest przenoszony na elektrofilowy atom węgla wiązania $\text{C} \equiv \text{N}$, a grupa –Bpin oddziałuje z wolną parą elektronową na atomie azotu. Kolejna addycja wiązania B-H do nienasyconego wiązania C-N skutkuje utworzeniem *N,N*-diborylowanego produktu (Schemat 14).⁶⁰ Autorzy zbadali również możliwość wielokrotnego wykorzystania katalizatora. Spadek wydajności reakcji obserwowano już po drugim cyklu.⁶⁰

Nguyen i Doan zastosowali tetrafluoroboran tropyliowy $[\text{Trop}][\text{BF}_4]$ jako jonowy, uniwersalny prekatalizator dla hydroborowania imin, nityryli oraz amidów. Użyto go w ilości 10% molowych, a redukcja szerokiej gamy nityryli, w tym: aromatycznych z grupami dostarczającymi i wyciągającymi elektrony oraz związków heterocyklicznych i alifatycznych przebiegała z wysokimi wydajnościami ($\geq 90\%$) w temperaturze 70 °C w czasie 18–24 godzin. Proponowany mechanizm zachodzi poprzez „ukrytą” ścieżkę katalityczną zaproponowaną przez Thomasa.⁶¹ W pierwszym etapie pinakoloboran reaguje z tetrafluoroboranem tropyliowym, a następnie poprzez sekwencję przemian *in situ* powstaje aktywny katalitycznie (BH_2F). Ulega on 1,2-syn-addycji do wiązania wielokrotnego nityrylu po czym następuje etap transborylowania z HBpin,

prowadzący do monoboryloiminy. Kolejna 1,2-syn-addycja BH_2F do wiązania $\text{C}=\text{N}$ oraz drugie transborylowanie z HBpin, prowadzą do otrzymania *N,N*-diborylowanego produktu.⁶²



Schemat 14. Prawdopodobny mechanizm hydroborowania nityry w obecności katalizatora BICAAC.

Warto podkreślić, że Thomas i współpracownicy wykazali, że nukleofile mogą sprzyjać rozkładowi pinakoloboranu (HBpin) do prostych borowodorków, działających jako „prawdziwe” i jednocześnie „ukryte” katalizatory.⁶¹ Odkrycie to podkreśla, że skuteczność wielu opisanych dotychczas metod nie wynika bezpośrednio z aktywności katalitycznej zastosowanego katalizatora, lecz z powstających *in situ* borowodorków. Generuje to konieczność kompleksowej weryfikacji proponowanych mechanizmów reakcji, starannych badań eksperymentalnych jak i obliczeniowych, które umożliwiają weryfikację indywidualów katalitycznych odpowiedzialnych za przebieg procesu hydroborowania.

Mimo zadowalającej efektywności, większość opisanych układów organokatalitycznych cechuje ograniczona dostępność, skomplikowana procedura syntezy lub wrażliwość na tlen i wilgoć, co znacząco ogranicza ich praktyczne zastosowanie. W związku z tym istnieje potrzeba dalszych badań nad opracowaniem wydajnych, selektywnych, stabilnych, prostych w użyciu i łatwo dostępnych katalizatorów organicznych, które dodatkowo będą charakteryzowały się możliwie niskim negatywnym wpływem na środowisko. Istotne jest również by hydroborowanie nienasyconych wiązań węgiel-heteroatom zachodziło w łagodnych warunkach, ze stechiometryczną ilością reagentów oraz z możliwością recyklingu katalizatora. Takie podejście wpisuje się w obszar zrównoważonego rozwoju, a zwłaszcza zielonej chemii.

1.2. Ciecze jonowe

Ciecze jonowe (ang. *ionic liquids*, *ILs*) to sole o temperaturze topnienia poniżej 100 °C składające się zwykle z organicznego kationu i organicznego lub nieorganicznego anionu.⁶³ Ze względu na swoje unikalne właściwości, takie jak niska prężność par, niepalność, chemiczna i fizyczna stabilność, łatwość projektowania ich właściwości poprzez odpowiedni dobór jonów czy niską korozyjność sprawiają, że w literaturze są one często rozważane jako „zielone” lub „przyjazne dla środowiska” rozpuszczalniki.⁶⁴

Dla cieczy jonowych znaleziono wiele zastosowań, zarówno laboratoryjnych jak i przemysłowych,⁶⁵ m.in. jako: elektrolity w urządzeniach magazynujących energię,⁶⁶ adsorbenty w wychwytywaniu i przetwarzaniu dwutlenku węgla⁶⁷ czy siarkowodoru⁶⁸ oraz oczyszczaniu wody z zanieczyszczeń organicznych i metali ciężkich⁶⁹. Ciecze jonowe są znane również z zastosowania w rozpuszczaniu biomasy i jej przetwarzaniu^{70,71} oraz w medycynie jako elementy sensorów diagnostycznych, nośniki leków czy substancje czynne.^{72,73}

Zależnie od właściwości, ILs mogą być zastosowane w procesach katalitycznych przebiegających zarówno w układach homogenicznych jak i dwufazowych.^{74,75} Ciecze jonowe zapewniają dobrą rozpuszczalność wielu katalizatorów i reagentów, pozwalają prowadzić reakcje w wyższej temperaturze niż większość rozpuszczalników organicznych, stabilizują kompleksy metali i nanocząstki, ułatwiają izolacje produktów, a same mogą zostać wielokrotnie wykorzystane. Z drugiej strony, ich znaczna lepkość może utrudniać wymianę masy i ciepła.^{76,77} W zależności od swojej budowy, niektóre ciecze jonowe mogą wykazywać znaczną toksyczność, szczególnie w środowisku wodnym oraz nie ulegać biodegradacji.⁷⁸

Ciecze jonowe składające się wyłącznie z cząsteczek organicznych lub zawierając w swojej strukturze atomy metali znalazły zastosowanie jako katalizatory w syntezach organicznych^{79,80} m.in. w: halogenowaniu, alkilowaniu, estryfikacji, reakcjach Dielsa-Aldera,⁸¹ addycji Michaela, kondensacjach Knoevenagla i aldolowych⁸² oraz reakcjach multikomponentowych.⁸³ Ponadto układy oparte na cieczach jonowych mogą ulegać heterogenizacji poprzez ich osadzenie na nośnikach stałych, takich jak krzemionka, tlenek glinu czy węgiel aktywny,^{77,84} co jest kluczowe dla możliwości projektowania procesów przepływowych i zwiększania skali procesu.⁸⁵

W ostatnich latach szczególną uwagę przyciągają ciecze jonowe pochodzenia naturalnego ze względu na możliwość ich pozyskiwania z odnawialnych źródeł, biodegradowalność, a w wielu przypadkach, także niską toksyczność.^{86,87} Jonami w takich związkach są pochodne aminokwasów, cukrów, kwasów organicznych, kwasów tłuszczowych lub alkaloidów.⁸⁸

Przykładem mogą być katalizatory na bazie choliny, które zostały opisane w literaturze w wielu transformacjach organicznych, takich jak: addycje,^{89,90} kondensacje,^{91,92} depolimeryzacje,^{93,94} utlenienie⁹⁵ czy reakcje multikomponentowe.^{96,97}

1.2.1. Zastosowanie cieczy jonowych w reakcjach katalitycznego hydroborowania

W reakcjach katalitycznego hydroborowania ciecze jonowe znalazły zastosowanie jako rozpuszczalniki i czynniki immobilizujące kompleksy metali przejściowych,⁹⁸⁻¹⁰⁰ związki indukujące chiralność¹⁰¹ oraz katalizatory.¹⁰²⁻¹⁰⁷ Strategia immobilizacji katalizatora metaloorganicznego w cieczach jonowych ma wiele zalet. Przede wszystkim upraszcza rozdział kompleksu metalu od produktów reakcji, obniża zużycie katalizatora, a także ma pozytywny wpływ na produktywność procesu dzięki możliwości wielokrotnego wykorzystania katalizatora. W literaturze znane jest kilka przykładów zastosowania cieczy jonowych w reakcjach hydroborowania wiązań wielokrotnych jako rozpuszczalników i mediów do immobilizacji katalizatorów. Są one jednak ograniczone głównie do hydroborowania nienasyconych wiązań węgiel-węgiel.

Vaultier i in. opisali reakcję pinakoloboranu z alkinami, przeprowadzaną w obecności katalizatora Wilkinsona $[\text{RhCl}(\text{PPh}_3)_3]$ oraz kompleksu $[\text{NiCl}_2(\text{dppe})]$, rozpuszczonych w mieszaninie chlorku 1-butył-3-metyloimidazoliowego i chlorku cynku lub glinu. Ciecze jonowe z anionami chlorocynkowym lub chloroglinowym tworzyły się *in situ*. Prowadzenie reakcji hydroborowania heks-1-ynu w obecności układu katalitycznego $[\text{RhCl}(\text{PPh}_3)_3]@[\text{BMIM}][\text{Cl}]/\text{ZnCl}_2$ pozwoliło na przeprowadzenie 6 cykli powtórzeniowych, jednak odnotowano stopniowy spadek wydajności w każdym kolejnym cyklu (od 83% w 1. cyklu do 44% w 6. cyklu), co świadczy o niskiej stabilności zastosowanego układu katalitycznego.⁹⁸

Katalizator $[\text{Ru}(\text{CO})(\text{Cl})\text{H}(\text{PPh}_3)_3]$ immobilizowany był w szeregu różnych cieczy jonowych z kationami pirolidyniowymi $[\text{BMPyr}][\text{Cl}]$, $[\text{EMPyrr}][\text{OTf}]$, $[\text{EMPyrr}][\text{NTf}_2]$ oraz imidazoliowymi $[\text{BMIM}][\text{Cl}]$, $[\text{BMIM}][\text{PF}_6]$, $[\text{BMIM}][\text{BF}_4]$, $[\text{BMIM}][\text{NTf}_2]$, $[\text{BMIM}][\text{OTf}]$, $[\text{BMIM}][\text{TOS}]$. Reakcję hydroborowania alkinów prowadzono w dwóch różnych układach: w toluenie oraz w dwutlenku węgla w stanie nadkrytycznym. Najbardziej efektywnym układem katalitycznym był $[\text{Ru}(\text{CO})(\text{Cl})\text{H}(\text{PPh}_3)_3]@[\text{EMPyrr}][\text{NTf}_2]$. Stosując 2% molowe hydrydowego kompleksu rutenu(II), przeprowadzono 25 cykli powtórzeniowych, a liczba obrotów katalizatora wynosiła 1345.⁹⁹

Nanocząstki irydu(0) oraz ciecze jonowe: [THTdP][DBS] i [HMIM][CF₃SO₃] zostały zastosowane w reakcji hydroborowania/izomeryzacji liniowych alkenów, wykazując wysoką selektywność w kierunku tworzenia ω-borylopodstawionych produktów.¹⁰⁰

Ciecze jonowe w reakcjach hydroborowania wiązań C=C znalazły także zastosowanie jako promotory chiralności. W obecności kompleksu rodu oraz prolinowej cieczy jonowej z anionem bis(trifluorometylosulfonylo)imidkowym prowadzono reakcje hydroborowania i uwodornienia olefin. W zoptymalizowanych warunkach reakcji, (–50 °C, w 2-metylotetrahydrofuranie jako medium reakcji i w czasie 12 godzin), hydroborowanie styrenu katecholoboranem przebiegało z całkowitą konwersją substratu, doskonałą regioselektywnością do produktu zgodnego z regułą Markownikowa i nadmiarem enenacjomerycznym wynoszącym 86%.¹⁰¹

Efektywnym i selektywnym katalizatorem hydroborowania imin oraz aminowania redukcyjnego okazał się [BMIM][FeCl₄]. Dla przebiegu reakcji kluczową była struktura anionu. Stosując aniony octanowy, tetrafluoroboranowy, chlorkowy, tetrachlorokobaltowy oraz tetrachloroglinianowy z tym samym kationem, konwersja *N*-benzylidenoaniliny nie przekraczała 50%. Wykazano, że obecność atomu żelaza w anionie cieczy jonowej jest konieczna dla zachowania wysokiej efektywności procesu, co tłumaczy zaproponowany mechanizm reakcji, który opiera się na interakcjach substratów z atomem żelaza.¹⁰² Ponadto, [BMIM][FeCl₄] mógł zostać poddany recyklingowi, co zostało potwierdzone w 15 cyklach powtórzeniowych.

Ciecze jonowe mogą również pełnić funkcję organokatalizatorów. Terminalne oraz wewnętrzne alkeny i alkiny ulegały reakcji hydroborowania z poliboranami w układach dwufazowych ciecz jonowa/toluen, w obecności różnych soli organicznych z kationami amoniowymi oraz anionami halogenkowymi, tetrafluoroboranowymi, octanowymi oraz heksafluorofosforanowymi. Najbardziej efektywnymi były [BMIM][Cl] i [BMPy][BF₄], dla których w 125 °C w czasie, odpowiednio 12 i 20 godzin, obserwowano 90% wydajność produktów zgodnych z regułą Markownikowa.^{104,108}

Szczególnie interesującym przykładem jest możliwość sterowania selektywnością hydroborowania poprzez odpowiedni dobór struktury soli organicznej. W literaturze opisano dwa układy katalityczne, które mimo zbliżonych warunków prowadziły do odmiennych produktów hydroborowania olefin. Produkty o orientacji anty-Markownikowa otrzymano stosując trifluorometanosulfonian 1-etylo-1-metylopirolidyniowy ([EMPyr][OTf]) (40% mol. katalizatora, brak rozpuszczalnika, 20 godz., 100 °C). Układ charakteryzował się wysoką

stabilnością umożliwiającą jego ponowne wykorzystanie aż 31 razy.¹⁰⁶ Odminną selektywność uzyskano stosując czwartorzędową sól amoniową [TBA][OAc] (10% mol. katalizatora, brak rozpuszczalnika, 20 godz., 90 °C). Selektywność reakcji zgodna z regułą Markownikowa została wytłumaczona przez stabilizujący wpływ łańcucha alkilowego katalizatora na stan przejściowy w momencie tworzenia się wiązania C-H.¹⁰⁵

Octan tetrabutylamoniowy ([TBA][OAc]) został z powodzeniem zastosowany w hydroborowaniu dwutlenku węgla prowadząc do otrzymania trimetoksycyklotriboroksanu. Czynnikiem redukcyjnym był $\text{BH}_3 \cdot \text{SMe}_2$, a reakcja przebiegała w temperaturze pokojowej, pod ciśnieniem 1,5 atm. W eksperymentach mechanistycznych, $\text{BH}_3 \cdot \text{SMe}_2$ zastąpiono pinakoloboranem. Analizy NMR wykazały, że w pierwszym etapie następuje szybka koordynacja jonu octanowego do HBpin, a następnie reakcja wytworzonego borowodorku z dwutlenkiem węgla.¹⁰⁷

Należy zaznaczyć, że stosowanie cieczy jonowych jako „zielonych” rozpuszczalników do immobilizacji katalizatorów w reakcjach hydroborowania dotychczas było organiczne wyłącznie dla reakcji hydroborowania wiązań wielokrotnych węgiel-węgiel. Podobnie, wykorzystanie cieczy jonowych jako organokatalizatorów znane jest wyłącznie dla procesów hydroborowania olefin oraz dwutlenku węgla. W związku z powyższym, kierunkiem badań podjętych w ramach doktoratu było opracowanie nowych i selektywnych metod hydroborowania związków karbonylowych i nienasyconych związków azotu z użyciem prostych, efektywnych, możliwych do wielokrotnego wykorzystania i przyjaznych środowisku układów katalitycznych, obejmujących zarówno systemy oparte na metalach przejściowych, jak i organokatalizatory. Ciecze jonowe stanowią niejako wspólny mianownik dla przedstawionych w dysertacji badań (publikacje **P1–P3**), które uwzględniają zarówno immobilizację komercyjnie dostępnych kompleksów platyny, jak i zastosowanie cieczy jonowych jako selektywnych i wydajnych katalizatorów.

2. Cele pracy

Celem naukowym pracy doktorskiej pod tytułem „Zastosowanie cieczy jonowych w katalitycznym hydroborowaniu nienasyconych wiązań węgiel-tlen i węgiel-azot” było opracowanie nowych, wydajnych i zrównoważonych układów katalitycznych dla procesu hydroborowania wiązań nienasyconych $C=O$, $C=N$ i $C\equiv N$, charakteryzujących się wysoką aktywnością, selektywnością oraz stabilnością. Nacisk położony jest na poszukiwanie układów katalitycznych o prostej strukturze, komercyjnie dostępnych, których użycie nie wymaga stosowania wysublimowanych warunków reakcji. Istotnym elementem pracy jest wieloaspektowe wykorzystanie cieczy jonowych zarówno jako rozpuszczalników do immobilizacji katalizatorów opartych na metalach przejściowych oraz organokatalizatorów, które jednocześnie stosowane będą jako medium reakcyjne (Schemat 15).

Dane literaturowe	Luka badawcza	Cele pracy
- Złożone, często nietrwale i niedostępne komercyjnie katalizatory bez możliwości ich ponownego wykorzystania. - Brak lub sporadyczne zastosowania ILs w hydroborowaniu wiązań CO i CN; dominacja lotnych rozpuszczalników organicznych. - Ograniczona liczba praktycznych procedur syntetycznych.	- Brak prostych, wydajnych i trwałych układów katalitycznych opartych na łatwo dostępnych i wielokrotnie wykorzystywanych katalizatorach. - Niewykorzystany potencjał ILs, zwłaszcza pochodzenia naturalnego, jako medium reakcji do immobilizacji katalizatora, lub potencjalnych organokatalizatorów - Brak prostych, zintegrowanych metod syntezy i izolacji produktów.	- Opracowanie nowych, prostych, aktywnych i selektywnych układów katalitycznych do hydroborowania wiązań $C=O$, $C=N$ i $C\equiv N$ z możliwością recyklingu katalizatora. - Zastosowanie cieczy jonowych jako „zielonych” rozpuszczalników do immobilizacji katalizatorów oraz weryfikacja ich aktywności katalitycznej. - Uproszczenie procedur syntezy i izolacji produktów poprzez zastosowanie strategii <i>one-pot</i>.

Schemat 15. Kontekst naukowy i cele dysertacji.

Katalityczne hydroborowanie jest reakcją przebiegającą w łagodnych warunkach, charakteryzującą się 100% ekonomią atomową oraz możliwością precyzyjnego kontrolowania regio- i stereoselektywności dzięki odpowiedniemu doborowi katalizatorów i warunków procesu. Hydroborowanie związków karbonylowych i nienasyconych związków azotu, połączone z następczą hydrolizą, prowadzi do uzyskania odpowiednio pierwszo- i drugorzędowych alkoholi oraz amin, wykorzystywanych m.in. w przemyśle farmaceutycznym czy w syntezie środków agrochemicznych. Dostępne doniesienia literaturowe dotyczące tego procesu nie uwzględniają potrzeby opracowania protokołów syntetycznych, w których drogie katalizatory oparte na metalach szlachetnych mogłyby być wielokrotnie wykorzystywane lub zastępowane znacznie

tańszymi organokatalizatorami, a lotne rozpuszczalniki organiczne – bardziej przyjaznymi dla środowiska „zielonymi” odpowiednikami.

Mając na uwadze powyższe, cele szczegółowe dysertacji obejmują: i) opracowanie nowych protokołów hydroborowania związków karbonylowych w obecności prostych i komercyjnie dostępnych kompleksów metali przejściowych oraz ich efektywną immobilizację w cieczach jonowych, które jednocześnie pełnią rolę rozpuszczalnika. Taka strategia umożliwi prostą separację produktów z mieszaniny poreakcyjnej oraz wielokrotne wykorzystanie katalizatora, co pozytywnie wpływa na efektywność procesu na płaszczyźnie ekonomicznej i ekologicznej (**P1**). ii) Zastosowanie organokatalizatorów w formie cieczy jonowych pochodzenia naturalnego w reakcjach hydroborowania związków karbonylowych (**P2**) oraz nienasyconych związków azotu (iminy, nityle, amidy) (**P3**). iii) Uproszczenie procedury syntezy i rozdziału produktów: poprzez zastosowanie strategii *one-pot*, efektywną ekstrakcję produktów, wysoką selektywność procesu i jak najbardziej zbliżone do równomolowych stosunki reagentów.

Realizacja założeń dysertacji przyczyni się zatem do poszerzenia aktualnego stanu wiedzy dotyczącego addycji wiązania bor-wodór do wiązań węgiel-heteroatom prowadzonej z uwzględnieniem zasad zielonej chemii. Zastosowanie cieczy jonowych jako bezpiecznych i efektywnych mediów reakcyjnych lub organokatalizatorów, ich wielokrotne wykorzystanie i protokoły *one-pot* przyczynią się nie tylko do zapewnienia wysokiej wydajności i selektywności reakcji, ale także do redukcji zużycia surowców i energii oraz zmniejszenia ilości generowanych odpadów. Opracowane w pracy układy katalityczne łączyć będą wysoką aktywność, chemoselektywność i stabilność katalizatorów z możliwością ich recyklingu, co odpowiada wyzwaniom i trendom współczesnej chemii, a zwłaszcza katalizy.

3. Wyniki badań i ich omówienie

W ramach niniejszej pracy doktorskiej opracowano 3 efektywne protokoły katalitycznego hydroborowania wiązań nienasyconych węgiel-heteroatom. Elementem łączącym wszystkie artykuły jest zastosowanie cieczy jonowych, zarówno jako mediów do immobilizacji kompleksów metali przejściowych jak i organokatalizatorów tej przemiany. Publikacja **P1** dotyczy hydroborowania ketonów w obecności kompleksu platyny(0) immobilizowanej w cieczy jonowej. Publikacje **P2** i **P3** wpisują się natomiast w obszar zastosowania cieczy jonowych pochodzenia naturalnego jako organokatalizatorów w reakcjach hydroborowania wiązań C=O (**P2**) oraz C=N i C≡N (**P3**). Badania mechanistyczne przedstawione w **P2** i **P3** obejmowały zarówno część eksperymentalną, jak i teoretyczną (obliczenia DFT), jednakże obliczenia DFT nie są elementem niniejszej dysertacji.

3.1. Hydroborowanie ketonów w obecności kompleksu [Pt(PPh₃)₄] oraz jego immobilizacja w cieczach jonowych (P1)

Przedmiotem publikacji **P1** było opracowanie efektywnej metody katalitycznej hydroborowania ketonów w oparciu o kompleksy platyny, z jednoczesnym uwzględnieniem możliwości wielokrotnego wykorzystania katalizatora. Aspekt ten ma bezpośrednie znaczenie dla efektywności oraz ekonomii procesu. Wśród katalizatorów metali szlachetnych stosowanych w hydroborowaniu związków karbonylowych, kompleksy platyny nie były jak dotąd przedmiotem badań. Motywacja dotycząca zastosowania prostych i komercyjnie dostępnych katalizatorów platynowych w procesie hydroborowania, wynikała z innych analogicznych procesów hydrometalacji (np. hydrosililowania).^{109,110}

W pierwszym etapie przeprowadzono przegląd katalizatorów platynowych zarówno homogenicznych, jak i heterogenicznych w modelowej reakcji hydroborowania acetofenonu (**P1-1a**^{*}) pinakoloboranem (**P1-2**). Reakcję prowadzono w warunkach bezrozpuszczalnikowych, w atmosferze argonu, przy użyciu 0,5% molowego katalizatora, w temperaturze 60 °C przez 18 godzin (Tabela 1). W próbie kontrolnej sprawdzono możliwość niekatalitycznego hydroborowania, jednak wydajność produktu **P1-3a** była znikoma (Tabela 1, l.p. 1). Umiarkowaną aktywność zauważono dla heterogenicznej czerni platynowej i PtO₂ oraz dla związków PtCl₂ i [PtCl₂(PPh₃)₂] (Tabela 1, l.p. 2–5). Zauważono, że obecność atomu chloru w strukturze katalizatora sprzyja tworzeniu się produktów ubocznych (Tabela 1, l.p. 5–6). Znaczącą poprawę konwersji acetofenonu (**P1-1a**) odnotowano w obecności kompleksu [Pt(η²-

* Aby ułatwić śledzenie wyników zawartych w artykułach i materiałach uzupełniających **P1-P3**, zachowano analogiczną numerację jak publikacjach wchodzących w skład rozprawy, poprzedzoną jej symbolem

$C_2H_4)(PPh_3)]$, a ilościową wydajność produktu **P1-3a** uzyskano wyłącznie przy zastosowaniu komercyjnie dostępnego i stabilnego kompleksu $[Pt(PPh_3)_4]$, który został wybrany do dalszych badań (Tabela 1, l.p. 6–7).

Szczegółowa optymalizacja warunków reakcji wykazała, że całkowitą konwersję acetofenonu (**P1-1a**) można uzyskać już po 3 godzinach przy zastosowaniu 0,5% molowego $[Pt(PPh_3)_4]$. Skrócenie czasu reakcji do 2 godzin prowadziło do niepełnego przereagowania acetofenonu (Tabela 1, l.p. 8–9). Wydajność procesu była zbliżona w reakcjach prowadzonych w rozpuszczalniku organicznym (Tabela 1, l.p. 10–11). Obniżenie stężenia katalizatora o połowę, niższa temperatura czy zastosowanie równomolowej ilości pinakoloboranu powodowały spadek konwersji **P1-1a** (Tabela 1, l.p. 12–14).

Tabela 1. Przegląd katalizatorów platynowych w reakcji hydroborowania acetofenonu pinakoloboranem.

$P1-1a + P1-2 (HBpin) \xrightarrow[Ar, \text{bez rozpuszczalnika}]{0,5\% \text{ mol. kat.}, 60^\circ C} P1-3a + \text{produkty uboczne } P1-4$

L.p.	Katalizator	Czas (godz.)	Konwersja P1-1a ^{a)} [%]	Selektywność P1-3a:P1-4 ^{a)} [%]
1	-	18	17	100:0
2	Czerń platynowa	18	49	100:0
3	PtO ₂	18	45	100:0
4	PtCl ₂	18	47	0:100
5	$[PtCl_2(PPh_3)_2]$	18	61	87:13
6	$[Pt(\eta^2-C_2H_4)(PPh_3)_2]$	18	77	72:28
7	$[Pt(PPh_3)_4]$	18	>99	100:0
8	$[Pt(PPh_3)_4]$	3	>99	100:0
9	$[Pt(PPh_3)_4]$	2	96	100:0
10 ^{b)}	$[Pt(PPh_3)_4]$	3	99	100:0
11 ^{c)}	$[Pt(PPh_3)_4]$	3	99	100:0
12 ^{d)}	$[Pt(PPh_3)_4]$	3	97	100:0
13 ^{e)}	$[Pt(PPh_3)_4]$	3	41	100:0
14 ^{f)}	$[Pt(PPh_3)_4]$	3	94	100:0
15 ^{g)}	$[Pt(PPh_3)_4]$	3	95	100:0

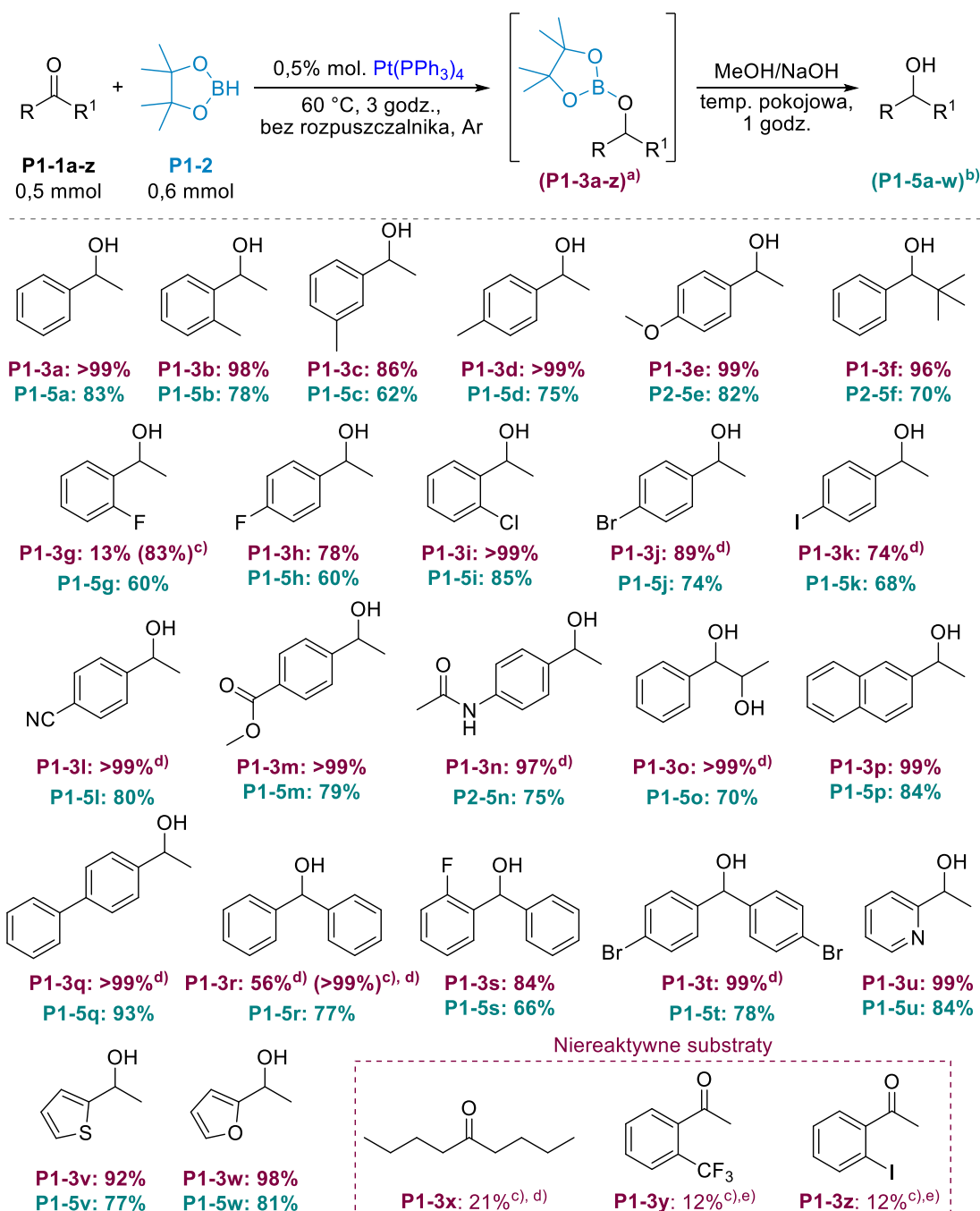
Warunki reakcji: [katalizator]:[acetofenon]:[pinakoloboran] = 0,005:1:1,2, 60 °C, atmosfera argonu. ^{a)} Wydajność i selektywność zostały określone na podstawie analizy GC-MS; ^{b)} reakcja w THF; ^{c)} reakcja w toluenie; ^{d)} katalizator w ilości 0,25% molowego; ^{e)} temperatura pokojowa; ^{f)} 50 °C; ^{g)} acetofenon (**P1-1a**) (0,5 mmol), pinakoloboran (**P1-2**) (0,5 mmol).

Zoptymalizowane warunki wykorzystano dla procesu hydroborowania ketonów o różnej strukturze, także tych zawierających grupy funkcyjne (Schemat 16). Wysokie konwersje odnotowano dla aromatycznych ketonów z grupami elektronodonorowymi (**P1-1b–e**). Zamiana grupy CH₃ acetofenonu na znacznie bardziej sterycznie zatłoczoną grupę *tert*-butylową (**P1-1f**) nie wpływała istotnie na przebieg reakcji. Znaczny spadek konwersji obserwowano dla *o*-fluoroacetofenonu (**P1-1g**), jednak wydłużenie czasu trwania reakcji do 18 godzin, pozwoliło na otrzymanie produktu **P1-3g** z wysoką wydajnością (83%). Nieco niższą konwersję odnotowano dla związków z podstawnikiem halogenowym w pozycji *para* (**P1-1h**, **P1-1j**, **P1-1k**), z kolei *o*-chloroacetofenon (**P1-1i**) reagował z pinakoloboranem ilościowo. Zbliżone wyniki uzyskano dla substratów z grupami: nitrylową, estrową czy amidową (**P1-1l–n**), a reakcja przebiegała chemoselektywnie względem grupy karbonylowej. Dodatkowo, w przypadku diketonu (**P1-1o**) redukcji ulegały obydwie grupy C=O. Cząsteczki zawierające w swojej budowie więcej niż jeden pierścień aromatyczny (**P1-1p–t**) oraz podstawniki heterocykliczne (**P1-1u–w**) reagowały z HBpin z wysokimi wydajnościami. Katalizator platynowy okazał się mniej aktywny w reakcjach z benzofenonem (**P1-1r**). Natomiast śladowe konwersje uzyskano dla liniowego 5-nonanonu (**P1-1x**) oraz aromatycznych związków z podstawnikami w pozycji *orto* (**P1-1y**, **P1-1z**), co prawdopodobnie było spowodowane względami sterycznymi.

Wszystkie *O*-borylowane etery (**P1-3a–w**) zostały przekształcone w odpowiadające im alkohole (**P1-5**) na drodze hydrolizy z użyciem 1M roztworu NaOH w metanolu. Reakcje hydrolizy prowadzono w tym samym naczyniu reakcyjnym (*one-pot*), bez konieczności izolowania produktów pośrednich **P1-3a–w**, co znacząco skraca czas syntezy oraz upraszcza procedury rozdziału (Schemat 16). Wszystkie otrzymane produkty **P1-3a–w** i **P1-5a–w** scharakteryzowano za pomocą spektroskopii protonowego magnetycznego rezonansu jądrowego (¹H NMR) i chromatografii gazowej sprzężonej ze spektrometrią mas (GC-MS).

W kolejnym etapie badań, aby zminimalizować koszty procesu, wynikające z zastosowania drogiego kompleksu platyny(0), zweryfikowano możliwość recyklingu katalizatora poprzez jego immobilizację w cieczach jonowych. Opierając się na wcześniejszych doniesieniach literaturowych dotyczących zastosowania soli organicznych w reakcjach hydroborowania i borylującego sprzęgania,^{99,111} do testów immobilizacji katalizatora platynowego wybrano kilka cieczy jonowych o temperaturach topnienia poniżej temperatury pokojowej (RTILs). Reakcja była prowadzona w układzie jednofazowym, ponieważ reagenty, jak i katalizator bardzo dobrze rozpuszczały się w cieczy jonowej. Po zakończeniu procesu do układu dodawano niemieszący się z solą organiczną *n*-heptan, co pozwoliło na efektywną ekstrakcję

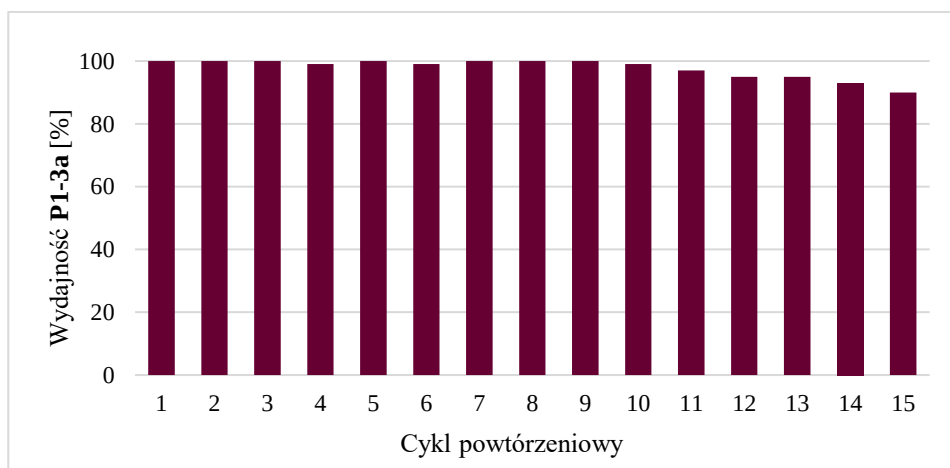
produktów. Roztwór po ekstrakcji analizowano za pomocą technik GC-MS i ^1H NMR, a IL suszono pod zmniejszonym ciśnieniem, w celu usunięcia pozostałości niepolarniej fazy.



Schemat 16. Hydroborowanie ketonów (**P1-1a-z**) w obecności $[\text{Pt(PPh}_3)_4]$. ^{a)} Wydajność określona na podstawie analizy ^1H NMR; ^{b)} wydajność izolacyjna; ^{c)} 18 godz.; ^{d)} HBpin (2 mmole); ^{e)} wydajność na podstawie analizy GC-MS.

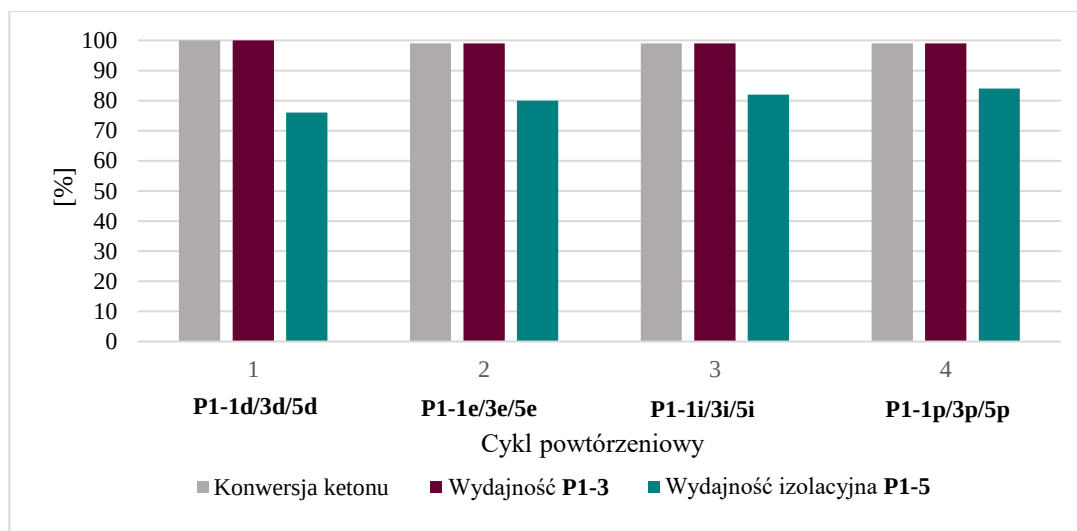
Dla układu katalitycznego $[\text{Pt(PPh}_3)_4]@[\text{BMIM}][\text{NTf}_2]$ obserwowano niemal ilościową konwersję **P1-1a** (>99%) w czasie 3 godz. Układ $[\text{Pt(PPh}_3)_4]@[\text{BMIM}][\text{NTf}_2]$ został wykorzystany w kolejnych reakcjach powtórzeniowych, dla których obserwowano powstawanie produktu **P1-3a** z bardzo wysoką wydajnością w pierwszych dziesięciu cyklach (Wykres 2).

W następnych reakcjach powtórzeniowych wydajność produktu stopniowo malała, prawdopodobnie na skutek wprowadzenia wilgoci lub tlenu oraz częściowe wymywanie katalizatora podczas kolejnych ekstrakcji. W układzie $[\text{Pt}(\text{PPh}_3)_4]@[\text{BMIM}][\text{NTf}_2]$ przeprowadzono łącznie 15 reakcji powtórzeniowych, osiągając sumaryczną wartość obrotów katalizatora (TON) równą 2934 (Wykres 2). Analizy ICP-MS wykonane po 1., 2. i 12. cyklu wykazały, że zawartość platyny w ekstraktach nie przekraczała 0,35 ppm. Wyniki te potwierdzają skuteczną fizyczną immobilizację katalizatora, stabilność układu oraz odpowiedni dobór rozpuszczalnika do ekstrakcji. Immobilizacja kompleksu platyny w cieczy jonowej zwiększyła efektywność procesu oraz umożliwiła wielokrotne wykorzystanie kosztownego metalu, co jest szczególnie istotne w przypadku pierwiastków o ograniczonej dostępności.



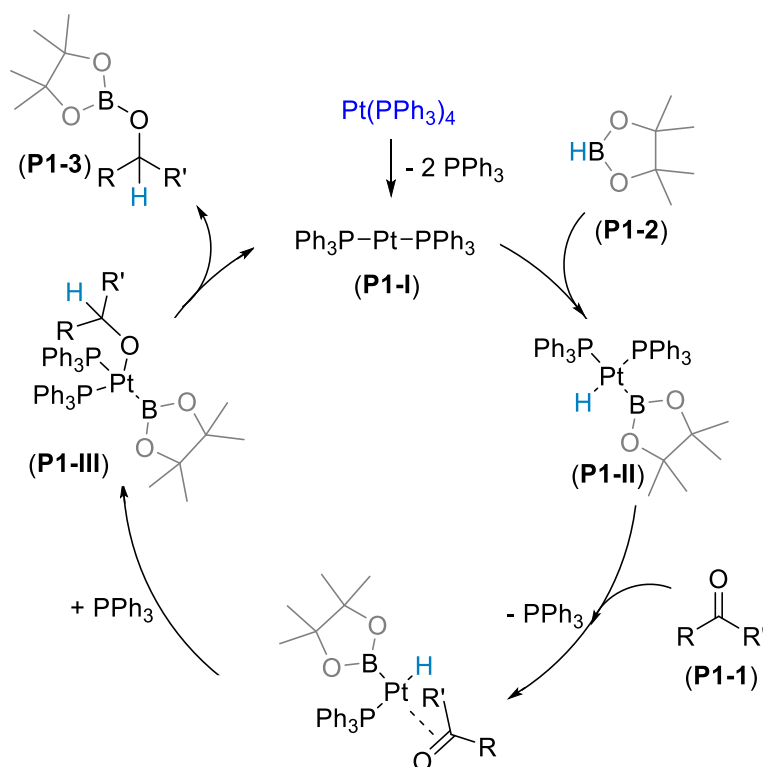
Wykres 2. Efektywność reakcji hydroborowania acetofenonu (**P1-1a**) w trybie reakcji powtórzeniowych w obecności $[\text{Pt}(\text{PPh}_3)_4]@[\text{BMIM}][\text{NTf}_2]$. Warunki reakcji: $[\text{Pt}(\text{PPh}_3)_4]:[\text{acetofenon}]:[\text{pinakoloboran}] = 0,005:1:1,2$, 60 °C, 3 godz., $[\text{BMIM}][\text{NTf}_2]$, atmosfera argonu. Wydajność została określona na podstawie analiz GC-MS i ^1H NMR.

W celu wykazania uniwersalności układu katalitycznego $[\text{Pt}(\text{PPh}_3)_4]@[\text{BMIM}][\text{NTf}_2]$, tę samą porcję katalizatora wykorzystano w kolejnych reakcjach hydroborowania różnych ketonów, kolejno: *p*-metyloacetofenonu (**P1-1d**), *p*-metoksyacetofenonu (**P1-1e**), *o*-chloroacetofenonu (**P1-1i**), oraz 2-acetylnaftalenu (**P1-1p**). Uzyskano niemal ilościowe wydajności oczekiwanych produktów (**P1-3d–e**, **P1-3i** oraz **P1-3p**) (Wykres 3). Warto podkreślić, że proces ekstrakcji był efektywny, a produkty z kolejnych cykli nie zawierały reagentów z poprzednich wsadów, co potwierdzono analizami ^1H NMR oraz GC-MS.



Wykres 3. Efektywność reakcji hydroborowania ketonów (**P1-1d-e**, **P1-1i** and **P1-1p**) w trybie powtórzeniowym w obecności $[\text{Pt}(\text{PPh}_3)_4]@[\text{BMIM}][\text{NTf}_2]$. Warunki reakcji: $[\text{Pt}(\text{PPh}_3)_4]:[\text{keton}]:[\text{pinakoloboran}] = 0,005:1:1,2$, $60\text{ }^\circ\text{C}$, 3 godz., $[\text{BMIM}][\text{NTf}_2]$, atmosfera argonu. Wydajność została określona na podstawie analiz GC-MS i ^1H NMR.

Ze względu na to, że kompleksy platyny nie były stosowane w procesie hydroborowania nienasyconych wiązań węgiel-tlen, przeprowadzono również badania mechanistyczne. Rozpoczęto je od sprawdzenia hipotezy badawczej postulującej fizyczną immobilizację katalizatora w cieczy jonowej. Mieszaninę $[\text{Pt}(\text{PPh}_3)_4]$ i $[\text{BMIM}][\text{NTf}_2]$ ogrzewano w $60\text{ }^\circ\text{C}$ przez 3 godziny i następnie przeprowadzono analizy ^1H i ^{31}P NMR. Uzyskane widma nie ujawniły nowych sygnałów, co sugeruje, że nie powstaje nowy addukt katalizator-ciecz jonowa, a katalizator jest jedynie fizycznie immobilizowany w $[\text{BMIM}][\text{NTf}_2]$. W związku z tym, dalsze badania mechanistyczne były prowadzone w deuterowanym rozpuszczalniku organicznym. Na podstawie obserwacji nowego sygnału odpowiadającego wolnej trifenylfosfinie (^{31}P NMR, $-6,3$ ppm), zaproponowano, że w pierwszym etapie następuje dysocjacja liganda PPh_3 . Następnie, zaobserwowano pojawienie się nowego sygnału przy ujemnych wartościach przesunięcia chemicznego ($\delta = -6,31$ ppm [$^1J_{(\text{Pt-H})} = 1215$ Hz]¹¹²) na niskotemperaturowym ($-40\text{ }^\circ\text{C}$) widmie ^1H NMR, sugerującego utleniającą addycję HBpin (**P1-2**) do atomu platyny (**P1-II**). Dysocjacja kolejnego liganda fosfinowego oraz koordynacja grupy karbonylowej, a następnie jej insercja do wiązania Pt-H, prowadzą do powstania produktu przejściowego (**P1-III**), a w wyniku redukującej eliminacji następuje uwolnienie produktu **P1-3** i regeneracja katalizatora, co potwierdza zanik sygnału od atomu wodoru wiązania Pt-H (Schemat 17).



Schemat 17. Proponowany mechanizmu reakcji hydroborowania ketonów katalizowanego przez $[\text{Pt}(\text{PPh}_3)_4]$.

W ramach publikacji **P1** opracowano nową i efektywną metodę katalizycznego hydroborowania ketonów przy użyciu prostego i komercyjnie dostępnego katalizatora platynowego $[\text{Pt}(\text{PPh}_3)_4]$. Wysoką wydajność produktów uzyskano przy niewielkim stężeniu katalizatora (0,5% molowego), dla ketonów z różnymi podstawnikami, w tym elektronodonorowymi, elektronoakceptorowymi oraz heterocyklicznymi. Otrzymane O-borylowane etery efektywnie przekształcono w odpowiednie alkohole w procedurze *one-pot*, bez konieczności izolacji produktów pośrednich, na drodze hydrolizy. Zaproponowano również mechanizm reakcji, który przebiega poprzez typowe procesy utleniającej addycji i redukującej eliminacji. Ponadto immobilizacja $[\text{Pt}(\text{PPh}_3)_4]$ w cieczy jonowej $[\text{BMIM}][\text{NTf}_2]$ pozwoliła na 15-krotne wykorzystanie tej samej porcji katalizatora bez znacznej utraty aktywności, co korzystnie wpływa na efektywność i ekonomię procesu.

3.2. Ciecze jonowe jako efektywne organokatalizatory hydroborowania związków karbonylowych (P2)

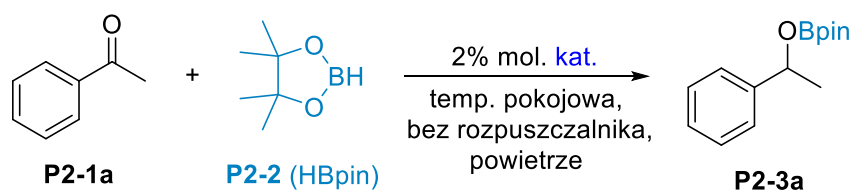
Przeprowadzony przegląd literaturowy, opisany w rozdziale 1.1.2, wykazał, że organokatalizatory były dotychczas stosowane w reakcjach hydroborowania związków karbonylowych jedynie w ograniczonym zakresie. Stanowią one klasę katalizatorów umożliwiających prowadzenie procesów bez udziału metali, co eliminuje ryzyko zanieczyszczenia produktów końcowych ich śladowymi ilościami, co ma bardzo duże znaczenie w syntezie m.in. farmaceutyków. W kontekście ich praktycznego zastosowania istotna jest dostępność, wysoka stabilność wobec tlenu i wilgoci oraz relatywnie niska cena, co przekłada się na łatwość stosowania, przechowywania i korzystną ekonomię procesu. W świetle zasad zielonej chemii warto podkreślić, że część organokatalizatorów, w tym niektóre ciecze jonowe, mogą być otrzymywane z surowców odnawialnych, wykazywać niską toksyczność, a także biodegradowalność.

Mając na uwadze ogromny potencjał aplikacyjny cieczy jonowych jak również ich aktywność katalityczną w hydroborowaniu wielokrotnych wiązań węgiel-węgiel,^{104,106,108} postawiono hipotezę badawczą zakładającą możliwość wykorzystania cieczy jonowych jako organokatalizatorów w reakcji addycji wiązań bor-wodór do nienasyconych wiązań węgiel-tlen. Poszukiwanie efektywnej metody organokatalitycznego hydroborowania wiązań węgiel-heteroatom w obecności prostej, stabilnej w warunkach atmosfery powietrza, możliwej do wielokrotnego wykorzystania cieczy jonowej, która dodatkowo byłaby przyjazna środowisku naturalnemu, wpisuje się w najnowsze trendy współczesnej chemii ukierunkowanej na realizację procesów zgodnie z założeniami zrównoważonego rozwoju.

Pracę nad organokatalitycznym hydroborowaniem wiązań karbonylowych rozpoczęto od przeglądu katalizatorów w formie cieczy jonowych zawierających jony naturalnie występujące w przyrodzie: kation cholinowy oraz aniony kwasów karboksylowych. Kation cholinowy wybrano ze względu na jego wysoką dostępność oraz korzystny profil środowiskowy. Dodatkowo istniejące doniesienia literaturowe wskazują, iż ciecze jonowe oparte na cholinie mogą wykazywać potencjał katalityczny w różnych przemianach organicznych. Z kolei aniony karboksylanowe uznano natomiast za szczególnie interesujące z uwagi na ich zasadowy charakter, który może sprzyjać aktywacji HBpin, a także możliwość tworzenia prostych i łatwo dostępnych cieczy jonowych.^{113,114} Ich aktywność katalityczną zweryfikowano w modelowej reakcji hydroborowania acetofenonu (**P2-1a**) pinakoloboranem (**P2-2**), prowadzonej w temperaturze pokojowej, bez rozpuszczalnika z udziałem 2% molowych katalizatora (Tabela 2).

Dla zasadowych cieczy jonowych z kationem choliny i anionami [OAc]⁻ (**IL1**), [Bz]⁻ (**IL2**) i [Oxa]²⁻ (**IL5**) (Tabela 2, l.p. 2–5, 8) obserwowano wysokie wydajności produktu hydroborowania **P2-3a**. Wyjątek stanowiła [Cho][TFA] (**IL3**), która wykazywała niższą aktywność katalityczną (Tabela 2, l.p. 6). Warto podkreślić, iż brak katalizatora nie prowadził do konwersji reagentów (< 5%) co jednoznacznie podkreśla konieczność jego stosowania, (Tabela 2, l.p. 1). Podobne rezultaty uzyskano dla cieczy jonowych o amfoterycznym charakterze [Cho][Oxa] (**IL4**) (Tabela 2, l.p. 7) lub z neutralnym i niekoordynującym anionem [NTf₂]⁻ (**IL6**) (Tabela 2, l.p. 9). Uzyskane wyniki sugerują, że kluczowym czynnikiem w procesie katalitycznym jest nukleofilowość anionu.¹¹⁵ Zmiana kationu z [Cho]⁺ (**IL1**) na [TBA]⁺ (**IL7**) również wpływa niekorzystnie na wydajność reakcji (Tabela 2, l.p. 4 vs. 7). Co istotne, nie zaobserwowano konkurencyjnej reakcji kondensacji aldolowej promowanej przez zasadowe ciecze jonowe,⁸² jednak w obecności kwasów, będącymi prekursorami ILs (m.in. HOAc, HBz, H₂Oxa) zaobserwowano powstawanie produktów ubocznych. W przeglądzie katalizatorów sprawdzono też analogiczne do soli organicznych, sole potasowe, m.in. octan i benzoetan potasu (KOAc, KBz). Ich zastosowanie w roli katalizatora pozwalało na selektywne prowadzenie procesu, jednak wydajność produktu **P2-3a** była zdecydowanie niższa niż w przypadku **IL1** i **IL2**.

Tabela 2. Przegląd cieczy jonowych jako katalizatorów hydroborowania ketonów.



L.p.	Katalizator	Czas [godz.]	Wydajność P2-3a ^{a)} [%]
1	-	2	śladowa
2	[Cho][OAc] IL1	0,5	93
3	[Cho][OAc] IL1	1	97
4	[Cho][OAc] IL1	2	99
5	[Cho][Bz] IL2	1	97
6	[Cho][TFA] IL3	1	20
7	[Cho][Oxa] IL4	1	4
8	[Cho] ₂ [Oxa] IL5	1	89
9	[Cho][NTf ₂] ^{b)} IL6	2	0
10	[TBA][OAc] IL7	2	87

Warunki reakcji: [katalizator]:[acetofenon]:[pinakoloboran] = 0,02:1:1,2, temperatura pokojowa, bez rozpuszczalnika, atmosfera powietrza. ^{a)} Wydajność produktu **P2-3a** została określona na podstawie analiz GC-MS i ¹H NMR; ^{b)} 8% molowych katalizatora.

Najbardziej efektywnym katalizatorem okazał się octan choliny (**IL1**), który został wybrany do dalszej optymalizacji warunków reakcji (Tabela 3). Reakcja przebiegała efektywnie zarówno w atmosferze powietrza, jak i gazu obojętnego i wymagała niewielkiego nadmiaru czynnika borylującego (Tabela 3, l.p. 1–3). Hydroborowanie acetofenonu (**P2-1a**) w rozpuszczalnikach organicznych, skutkowało osiągnięciem niższych konwersji substratu, niż bez rozpuszczalnika (Tabela 3, l.p. 4–7). Sprawdzone również wpływ obecności wody na efektywność procesu. Dodatek 10 μL wody całkowicie inhibitował reakcję (Tabela 3, l.p. 8), co potwierdza konieczność stosowania cieczy jonowych o jak najniższej zawartości wody. Ilościową wydajność produktu hydroborowania uzyskano w czasie 1 godziny, w temperaturze pokojowej, przy braku rozpuszczalnika, stosując 8% molowych octanu choliny (Tabela 3, l.p. 9). 4- lub 8-krotne zmniejszenie stężenia katalizatora wpływało na niewielkie obniżenie wydajności produktu **P2-3a** (Tabela 3, l.p. 10–11). Drastyczny spadek konwersji acetofenonu (**P2-1a**) następował, gdy ilość katalizatora została ograniczona do 0,5% molowych. (Tabela 3, l.p.12).

Tabela 3. Optymalizacja warunków reakcji dla hydroborowania acetofenonu pinakoloboranem w obecności [Cho][OAc] jako organokatalizatora.

$\text{P2-1a} + \text{P2-2 (HBpin)} \xrightarrow[\text{temp. pokojowa, 1 godz., powietrze}]{[\text{Cho}][\text{OAc}](\text{IL1})} \text{P2-3a}$

L.p.	HBpin [ekw.]	Rozpuszczalnik	IL1 [% mol.]	Wydajność P2-3a ^{a)} [%]
1	1,2	-	4	97 (97) ^{b)}
2	1,1	-	4	95
3	1,0	-	4	85
4	1,2	toluen	4	86
5	1,2	octan etylu	4	85
6	1,2	THF	4	79
7	1,2	DCM	4	90
8 ^{c)}	1,2	-	4	0
9	1,2	-	8	>99
10	1,2	-	2	96
11	1,2	-	1	92
12	1,2	-	0,5	14

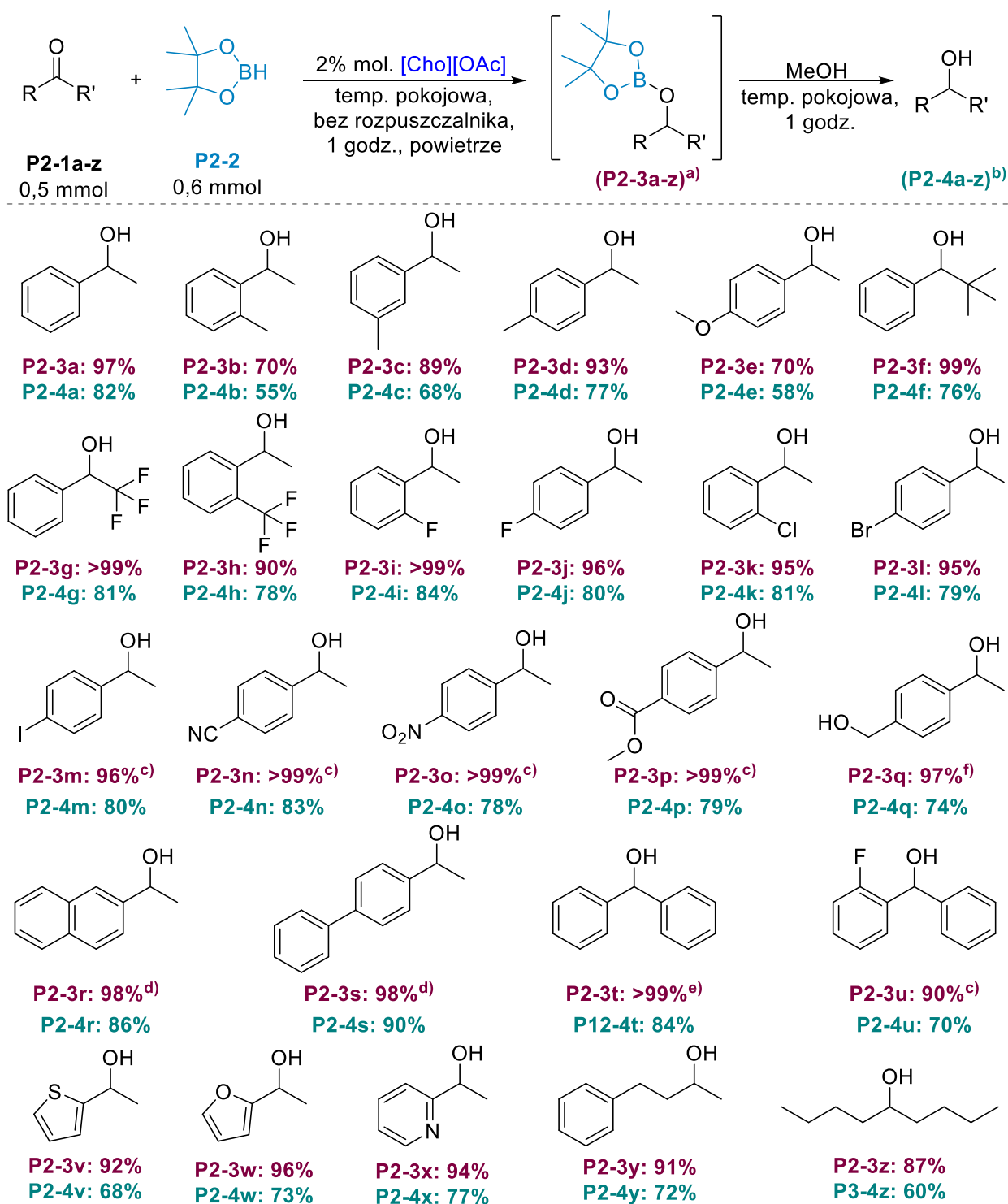
Warunki reakcji: [[Cho][OAc]]:[acetofenon]:[pinakoloboran] = 0.005–0.08:1:1.0–1.2, temperatura pokojowa, 1 godz., rozpuszczalnik (1 mL), atmosfera powietrza. ^{a)} Wydajność została określona na podstawie analiz GC-MS i ¹H NMR; ^{b)} atmosfera argonu; ^{c)} dodano 10 μL wody.

W kolejnym etapie badań, sprawdzono uniwersalność i chemoselektywność katalizatora w reakcjach hydroborowania ze zróżnicowanymi strukturalnie ketonami (Schemat 18).

Opracowany protokół był odpowiedni zarówno dla substratów z podstawnikami elektronodonorowymi (**P2-1b–e**), jak i elektronoakceptorowymi (**P2-1h–q**). Jedynie dla przestrzennie zatłoczonego reagenta z grupą $-\text{CF}_3$ w pozycji *orto*- (**P2-1h**) proces był mniej efektywny i wymagał wydłużenia czasu trwania reakcji (3 godz., 90%). Co ważne, **IL1** była selektywna względem grupy acetylowej, nie powodując redukcji podstawników: nitrylowego, nitrowego oraz estrowego (**P2-1n–p**). Obecność grupy aldehydowej (**P2-1q**) powodowała, że oba ugrupowania karbonylowe ulegały redukcji po zastosowaniu 2,2 ekwiwalentu HBpin (**P2-2**). Dla tego układu katalitycznego nie zaobserwowano wyraźnego efektu sterycznego. Substraty z zatłoczonymi grupami *tert*-butylową (**P2-1f**) lub trifluorometylową (**P2-1g**) efektywnie ulegały hydroborowaniu. Podobne wyniki uzyskano dla związków o rozbudowanych przestrzennie podstawnikach, takich jak grupa naftylowa lub bifenylowa (**P2-1r–u**), dla których konwersja była na poziomie 90%. Niezbędny był jednak większy nadmiar pinakoloboranu w celu zapewnienia całkowitej rozpuszczalności reagentów. Następnie przetestowano ketony z 5- lub 6-członowymi podstawnikami heterocyklicznymi (**P2-1v–x**) oraz grupami alifatycznymi (**P2-1y–z**), które ulegały redukcji z doskonałymi wydajnościami. Mimo uniwersalności octanu choliney jako katalizatora, w zoptymalizowanych warunkach reakcja hydroborowania nie zachodziła dla *m*-aminoacetofenonu, 2-acetylopirolu oraz 4,4'-dibromobenzofenonu.

Wszystkie otrzymane *O*-borylowane etery (**P2-3a–z**) zostały przekształcone w odpowiadające im alkohole (**P2-4a–z**) poprzez hydrolizę w metanolu w procedurze *one-pot*. Otrzymane związki **P2-3** i **P2-4** scharakteryzowano za pomocą spektroskopii magnetycznego rezonansu jądrowego (^1H NMR) oraz chromatografii gazowej ze spektrometrią mas (GC-MS).

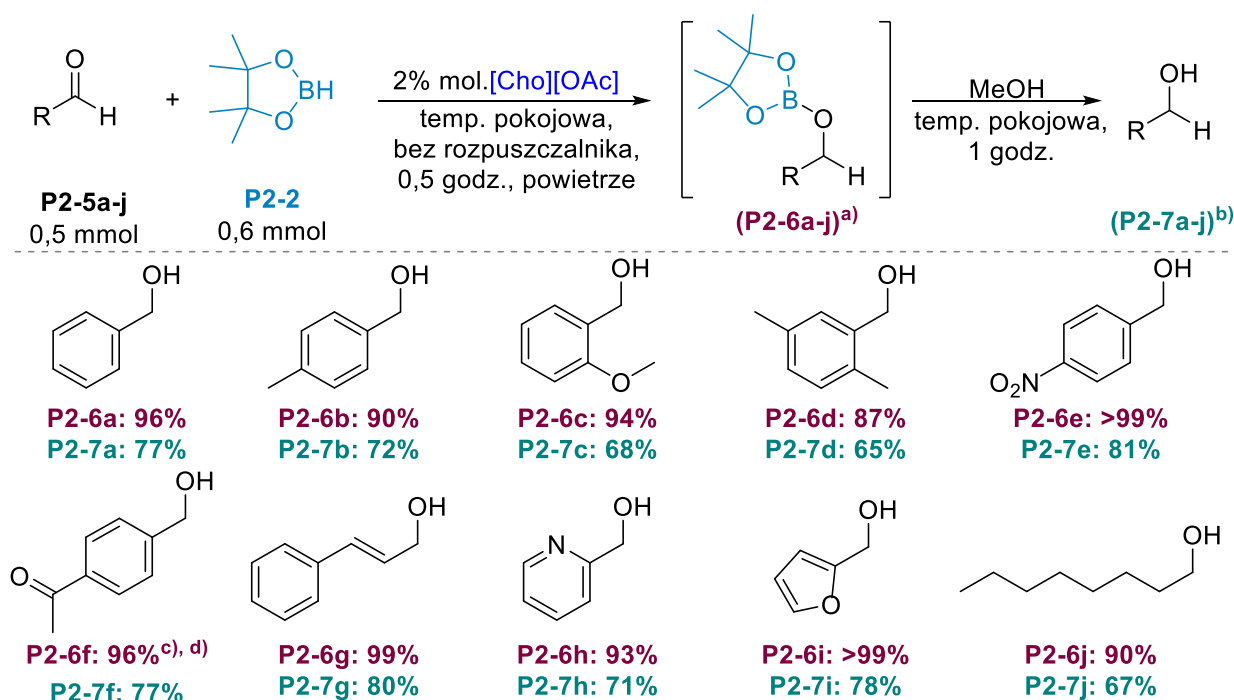
Pozytywne wyniki uzyskane w organokatalitycznym hydroborowaniu ketonów stanowiły podstawę do rozszerzenia badanego zakresu substratów o inne związki karbonylowe. Uwzględniając doniesienia literaturowe opisane w podrozdziałach 1.1.1. i 1.1.2 wskazujące, że hydroborowanie aldehydów zwykle przebiega w łagodniejszych warunkach, ponownie zoptymalizowano warunki, co pozwoliło na dwukrotne skrócenie czasu trwania reakcji.



Schemat 18. Hydroborowanie ketonów **P2-1a–z** w obecności katalizatora [Cho][OAc]. ^{a)} Wydajność określona na podstawie analizy ¹H NMR; ^{b)} wydajność izolacyjna; ^{c)} 1,5 ekwiwalentu HBpin; ^{d)} 2 ekwiwalenty HBpin; ^{e)} 4 ekwiwalenty HBpin; ^{f)} 2,2 ekwiwalentu HBpin.

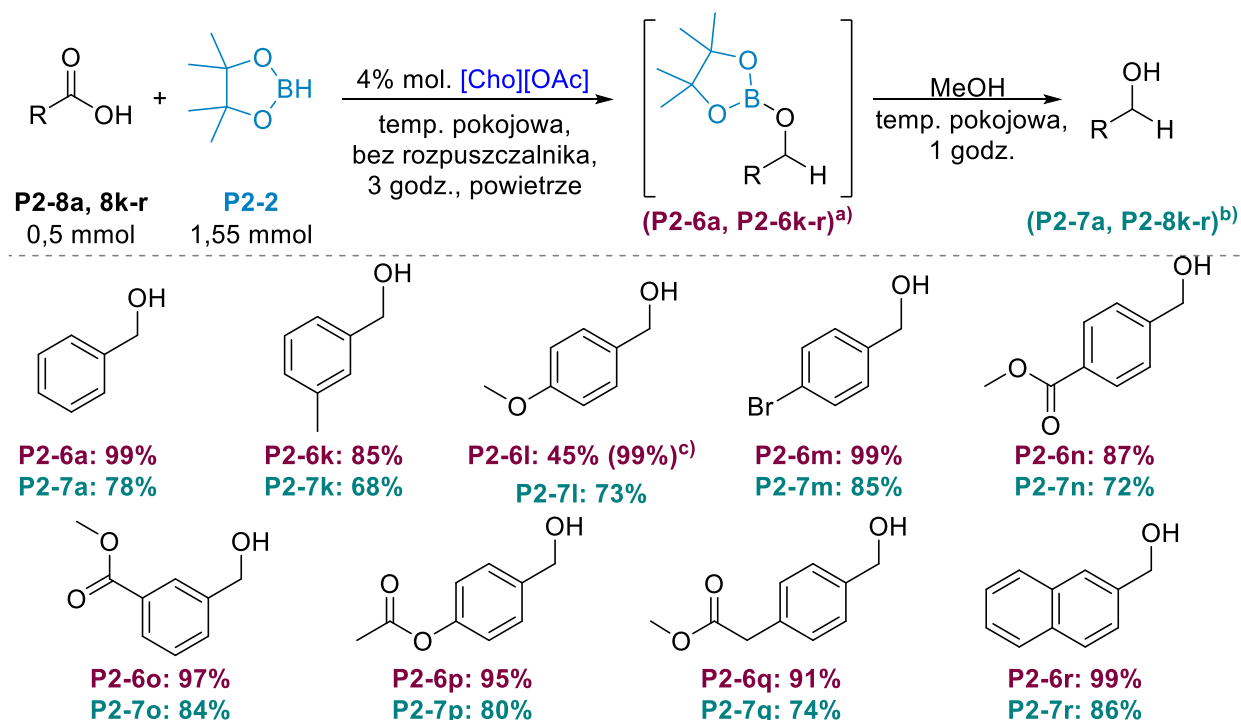
Dla aldehydów wpływ podstawników w pierścieniu aromatycznym był zbliżony do tego, który obserwowano dla ketonów (Schemat 19). Hydroborowanie substratów aromatycznych z grupami metylową lub metoksyową (**P2-5b–d**) skutkowało nieco niższymi wydajnościami produktów niż dla modelowego benzaldehydu (**P2-5a**). Z kolei obecność grup

elektronoakceptorowych, takich jak nitrowa czy acetylowa (**P2-6e-f**), miały pozytywny wpływ na wydajność reakcji. Warto zauważyć, że reakcja przebiegała chemoselektywnie względem grupy C=O w obecności wiązania podwójnego węgiel-węgiel w cząsteczce aldehydu cynamonowego (**P2-6g**). Selektowna redukcja grupy karbonylowej w cząsteczce 4-acetylobenzaldehydu (**P2-6f**) była możliwa po modyfikacji warunków reakcji (1,02 ekwiwalentu HBpin). Podobnie jak dla ketonów, substraty z podstawnikami heterocyklicznymi i alifatycznymi (**P2-5h-j**) ulegały redukcji prowadząc do pożądanych produktów z wysokimi wydajnościami.



Schemat 19. Hydroborowanie aldehydów **P2-5a-j** w obecności katalizatora [Cho][OAc]. ^{a)} Wydajność określona na podstawie analizy ¹H NMR; ^{b)} wydajność izolacyjna; ^{c)} 45 min.; ^{d)} 1,02 ekwiwalentu HBpin.

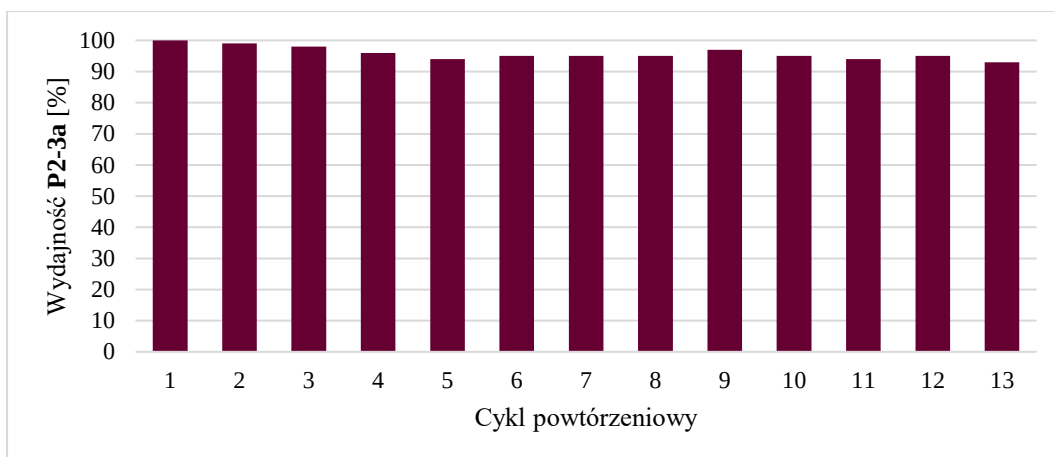
Analogicznie produkty otrzymywano w reakcji hydroborowania kwasów karboksylowych **P2-8** (Schemat 20), jednak konieczna była ponowna modyfikacja warunków prowadzenia procesu. Uzyskanie prawie ilościowej konwersji kwasu benzoesowego (**P2-8a**) wymagało wydłużenia czasu reakcji do 3 godzin oraz zwiększenia stężenia octanu choliny do 4% molowych. Obecność podstawników elektronodonorowych w pierścieniu aromatycznym (**P2-8k-l**), w szczególności grupy metoksyłowej, miała niekorzystny wpływ na wydajność reakcji. Natomiast kwas karboksylowy z podstawnikiem halogenowym (**P2-8m**), czy większe cząsteczki, takie jak kwas 2-naftoesowy (**P2-8r**), reagowały z pinakoloboranem (**P2-2**) z niemal ilościową wydajnością. Substraty z grupą estrową (**P2-8n-q**) również wykazywały wysoką efektywność i chemoselektywność względem grupy karboksylowej.



Schemat 20. Hydroborowanie kwasów karboksylowych **P2-8a** i **P2-8k-r** w obecności katalizatora **[Cho][OAc]**.

^{a)} Wydajność określona na podstawie analizy ^1H NMR; ^{b)} wydajność izolacyjna; ^{c)} 18 godz.

W ramach realizacji kolejnego celu niniejszej dysertacji oraz mając na uwadze zasady zielonej chemii, zweryfikowano możliwość wielokrotnego wykorzystania tej samej porcji katalizatora. W standardowych warunkach (temperatura pokojowa, bez rozpuszczalnika, 1 godz., 2% molowe **[Cho][OAc]**) przeprowadzono hydroborowanie acetofenonu (**P2-1a**) pinakoloboranem (**P2-2**). Po zakończeniu reakcji, w celu ekstrakcji produktów, do mieszaniny dodawano niepolarny *n*-heptan, w którym nie rozpuszczał się jonowy katalizator. Pozostałość po kilkukrotnym przemyciu (3×2 mL), suszono pod zmniejszonym ciśnieniem w celu odparowania resztek rozpuszczalnika organicznego przed dodaniem kolejnej porcji substratów. Zaproponowana procedura pozwoliła na efektywne wykorzystanie tej samej porcji katalizatora w 5 cyklach powtórzeniowych. Obserwowany w szóstym cyklu spadek wydajności był najprawdopodobniej spowodowany mechaniczną utratą katalizatora podczas odmywania produktów z naczynia reakcyjnego. W celu sprawdzenia tej tezy, w kolejnym eksperymencie zwiększono 4-krotnie stężenie **[Cho][OAc]**. Wysoka konwersja substratów utrzymywała się w trzynastu kolejnych cyklach powtórzeniowych (Wykres 4).



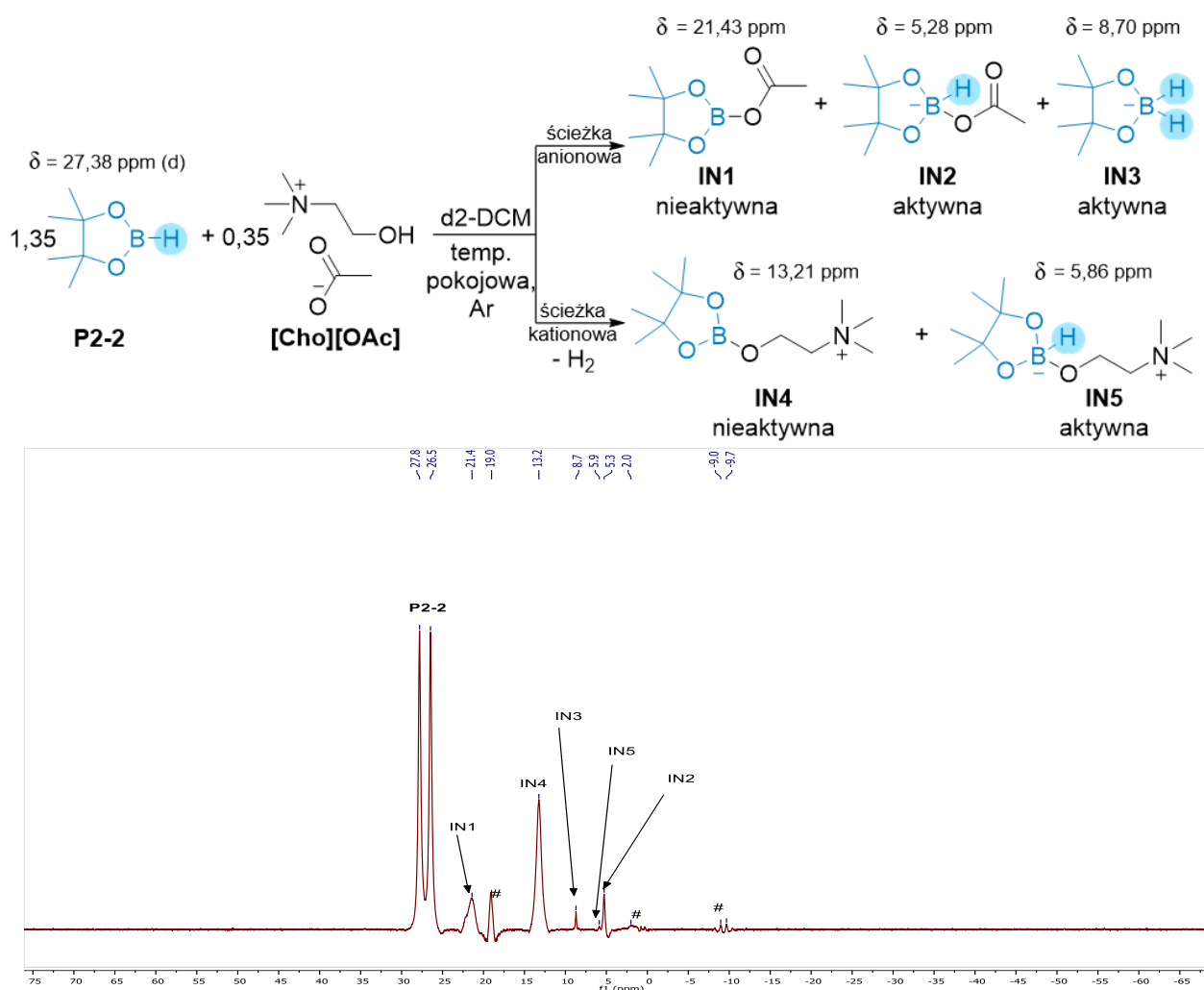
Wykres 4. Efektywność reakcji hydroborowania acetofenonu (**P2-3a**) w trybie powtórzeniowym w obecności [Cho][OAc]. Warunki reakcji: [[Cho][OAc]]:[acetofenon]:[pinakoloboran] = 0,08:1:1,2, temperatura pokojowa, 1 godz., bez rozpuszczalnika, atmosfera powietrza. Wydajność została określona na podstawie analiz GC-MS.

W związku z nieopisaną jak dotąd aktywnością katalityczną cieczy jonowych w reakcjach hydroborowania związków karbonylowych, szczegółowe zbadanie mechanizmu reakcji było kluczowe dla zrozumienia i wytłumaczenia natury tego procesu. Pierwszym etapem badań mechanistycznych było wykluczenie powstawania „ukrytego” katalizatora „BH₃” w wyniku rozkładu HBpin (**P2-2**). Zgodnie z doniesieniami Thomasa i in. przeprowadzono reakcję w obecności TMEDA (*N,N,N',N'*-tetrametyloetylenodiaminy),⁶¹ jednak nie zaobserwowano znaczącego spadku konwersji czy obecności sygnałów pochodzących od „ukrytego” katalizatora na widmach ¹H i ¹¹B NMR, co potwierdza, iż nie jest on właściwym promotorem tej przemiany.

Następnie, przeprowadzono szereg eksperymentów NMR mających na celu określenie mechanizmu procesu. W reakcjach acetofenonu (**P2-1a**) z **IL1** nie zauważono zmian na widmach ¹H i ¹³C NMR, niezależnie od stosunku molowego reagentów. Natomiast po zmieszaniu nadmiaru HBpin (**P2-2**) z [Cho][OAc] otrzymano skomplikowane widmo ¹¹B NMR, wskazujące na obecność kilku nowych cząsteczek zawierających w swojej strukturze atom boru: (δ = 21,43; 19,40; 12,06; 8,70; 5,85; 5,28; 2,03; -9,36 ppm). Potwierdza to wcześniejszą obserwację Clarka i in. dotyczącą występowania borowodorków w dynamicznej równowadze.¹¹⁶

Na podstawie literatury oraz referencyjnych widm NMR zidentyfikowano cząsteczki **IN1** (21,43 ppm), **IN2** (5,28 ppm,) oraz **IN3** (8,70 ppm) odpowiadające reakcji pinakoloboranu z anionem cieczy jonowej oraz **IN4** i **IN5** odpowiadające reakcji HBpin z kationem cieczy jonowej (Schemat 21).^{116,117} Dodatkowo, **IN1** został niezależnie zsyntezowany i zastosowany jako katalizator hydroborowania acetofenonu pinakoloboranem (**P2-2**), jednak nie zaobserwowano żadnego produktu tej reakcji. Co więcej, stechiometryczna reakcja **P2-2** z [Cho][OAc] prowadziła głównie do powstania obojętnego, O-borylowanego produktu **IN4**, który również nie wykazywał

aktywności katalitycznej w dalszej reakcji z acetofenonem (**P2-1a**). Uzyskana informacja sugeruje, że aktywnymi katalizatorami tej przemiany są najprawdopodobniej borowodorki, a nadmiar pinakoloboranu jest niezbędny do ich utworzenia. Jednocześnie liczba nowych indywiduów chemicznych obserwowanych na widmie ^{11}B NMR wskazuje, że badany proces katalityczny jest jeszcze bardziej złożony niż układ opisany wcześniej przez Clarka i in. wykorzystujący proste alkoholany jako katalizatory.¹¹⁶



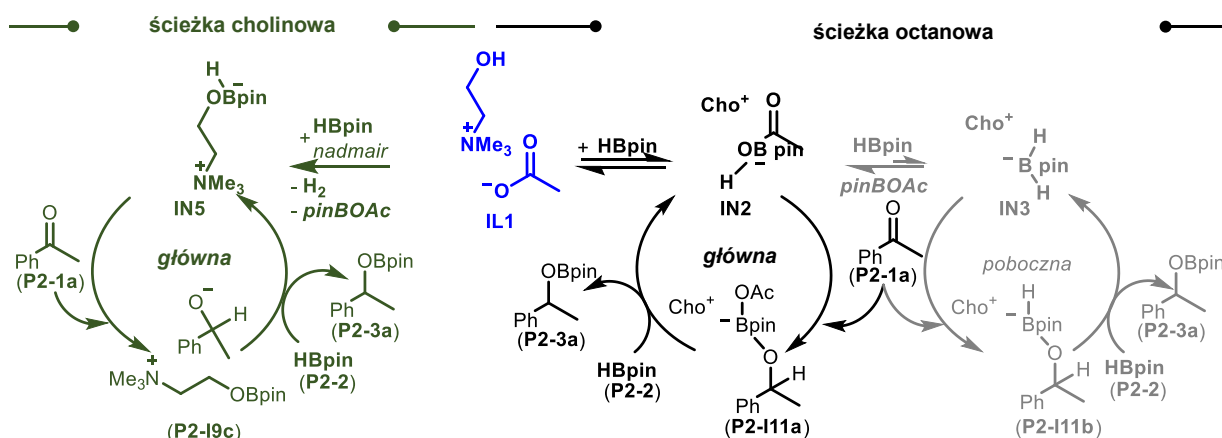
Schemat 21. Identyfikacja produktów reakcji pinakoloboranu (**P2-2**) z [Cho][OAc] (**IL1**). Na schemacie zaprezentowano wartości przesunięć chemicznych obecnych na widmie ^{11}B NMR oraz wskazano, które z utworzonych produktów przejściowych zostały określone jako aktywne lub nieaktywne katalitycznie. # Sygnał niezdefiniowany. Sygnał przy $\delta = -9.36$ ppm widoczny tylko na widmie wykonanym w d2-DCM (brak tego sygnału dla widm wykonywanych w deuterowanym toluenie).

Mechanizm reakcji został zaproponowany zarówno na podstawie badań eksperymentalnych, jak i obliczeń DFT, które wykonane zostały przez dr Mateusza Nowickiego (Schemat 22). W pierwszym etapie, reakcji katalizatora z HBpin (**P2-2**), powstają aktywne katalitycznie borowodorki, które mogą wytwarzać się zarówno z anionu, jak i kationu cieczy jonowej (odpowiednio ścieżka octanowa lub cholinowa). W ścieżce octanowej powstaje **IN2** (ΔG

= -2,6 kcal/mol), natomiast dalsze utworzenie **IN3** ($\Delta G = +11,1$ kcal/mol) jest najmniej korzystne energetycznie. Ścieżką o najniższej energii jest ta, w której powstaje aktywny katalitycznie borowodorek **IN5** ($\Delta G = -5,1$ kcal/mol).

W kolejnym etapie katalitycznie aktywne borowodorki reagują z acetofenonem (**P2-1a**). W ścieżce cholinowej, prowadzącej przez **IN5**, po transferze wodorku powstaje produkt przejściowy **P2-I9c**, a następnie reakcja z kolejną cząsteczką HBpin prowadzi do utworzenia produktu **P2-3a** i regeneracji katalizatora. Analogicznie, w ścieżce octanowej produkty przejściowe **P2-I11a** i **P2-I11b** prowadzą odpowiednio do produktu **P2-3a** z udziałem **IN2** oraz **IN3**. Obliczenia DFT wskazują, że wszystkie trzy cykle mogą zachodzić równoległe, a całkowita zmiana energii swobodnej dla każdego z nich wynosi -28,6 kcal/mol. Bariery dla etapów determinujących szybkość reakcji mieszczą się w zakresie 10,9–18,0 kcal/mol, przy czym największy udział w katalizie przypisano ścieżkom prowadzącym przez **IN2** i **IN5**, natomiast udział ścieżki z udziałem **IN3** jest najmniejszy (Schemat 22).

Warto podkreślić, że w przeciwieństwie do wcześniej opisanych układów katalitycznych opartych na borowodorkach,^{116,117} zastosowanie cieczy jonowej umożliwia współdziałanie zarówno anionu, jak i kationu w tworzeniu aktywnych katalitycznie cząsteczek, co przekłada się na zwiększoną efektywność procesu.



Schemat 22. Prawdopodobny, uproszczony mechanizm reakcji hydroborowania związków karbonylowych na podstawie reakcji modelowego acetofenonu (**P2-1a**) z pinakoloboranem (**P2-2**) w obecności octanu choliny jako katalizatora.

Podsumowując tę część badań, należy wskazać, że [Cho][OAc] jest aktywnym katalizatorem hydroborowania związków karbonylowych. Reakcje przebiegały w krótkim czasie oraz w łagodnych warunkach, zarówno dla związków aromatycznych z różnymi podstawnikami, jak i dla substratów sterycznie zatłoczonych czy układów heteroaromatycznych. Katalizator wykazał tolerancję wobec licznych grup funkcyjnych obecnych w strukturze substratów. Warto podkreślić, iż można było go poddać efektywnemu recyklingowi, bez wyraźnego spadku wydajności

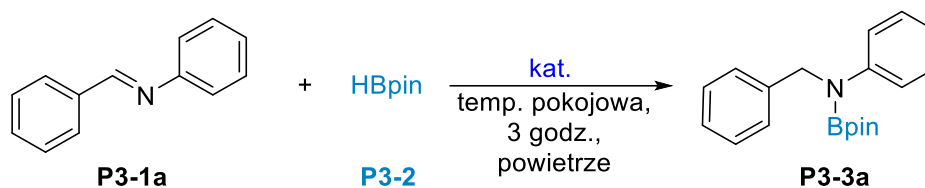
pożądanego produktu (**P2-3a**). Strategia ta, jak również naturalne pochodzenie choline wpisuje się w założenia zrównoważonego rozwoju. Przeprowadzono również szereg badań eksperymentalnych i teoretycznych, które wykazały, że aktywne katalitycznie są borowodorki pochodzące zarówno z kationu choline, jak i z anionu octanowego, natomiast rola „ukrytego” katalizatora jest marginalna lub praktycznie nieobecna. Otrzymane wyniki badań jednoznacznie wskazują na potencjał aplikacyjny cieczy jonowych w reakcjach hydroborowania nienasyconych wiązań węgiel-tlen. Możliwość recyklingu katalizatora, zastosowanie tanich i komercyjnie dostępnych układów oraz wysoka selektywność procesu mogą stanowić realną konkurencję dla katalizatorów opartych na pierwiastkach grup głównych i przejściowych.

3.3. Hydroborowanie imin, nitryli i amidów w obecności cieczy jonowych jako organokatalizatorów (P3)

Wyniki badań nad organokatalitycznym hydroborowaniem związków karbonylowych oraz doniesienia literaturowe, w których opisano możliwość zastosowania cieczy jonowych zawierających w swojej budowie atom metalu w hydroborowaniu imin (opisane w rozdziale 1.3), były inspiracją do rozszerzenia badań o redukcję związków azotu w obecności organicznych soli.

Badania wstępne nad hydroborowaniem imin, będące naturalną kontynuacją wcześniejszych badań nad redukcją ketonów, przeprowadzono z wykorzystaniem *N*-benzylidenoaniliny (**P3-1a**). Ze względu na stałą postać substratu konieczne było stosowanie rozpuszczalnika organicznego (zwykle tetrahydrofuranu). Przegląd katalizatorów obejmował ciecze jonowe zarówno z kationem cholinowym, jak i czwartorzędownymi kationami amoniowymi oraz z anionami kwasów karboksylowych i z $[\text{NTf}_2]^-$. Najskuteczniejszymi katalizatorami okazały się cholinowe ciecze jonowe o charakterze zasadowym, $[\text{Cho}][\text{OAc}]$ i $[\text{Cho}][\text{Bz}]$ (Tabela 4, l.p. 2 i 7). Zastosowanie anionu trifluorooctowego lub $[\text{NTf}_2]^-$ prowadziło do znacznego spadku konwersji **P3-1a** (Tabela 4, l.p. 3–4). Szczawiany, zarówno o charakterze amfoterycznym $[\text{Cho}][\text{Oxa}]$, jak i kwasowym $[\text{Cho}]_2[\text{Oxa}]$ skutkowały wydajnością **P3-3a** na poziomie 65% (Tabela 4, l. p. 5–6). Podobnie jak w przypadku związków karbonylowych, także i tu nie tylko rodzaj anionu, ale również kationu, miały wpływ na efektywność procesu. Zastąpienie kationu cholinowego w $[\text{Cho}][\text{OAc}]$ innym kationem, np. $[\text{TBA}]^+$ lub $[\text{TMA}]^+$, skutkowało znacznym spadkiem wydajności reakcji, zdecydowanie wyższym niż w przypadku ketonów.

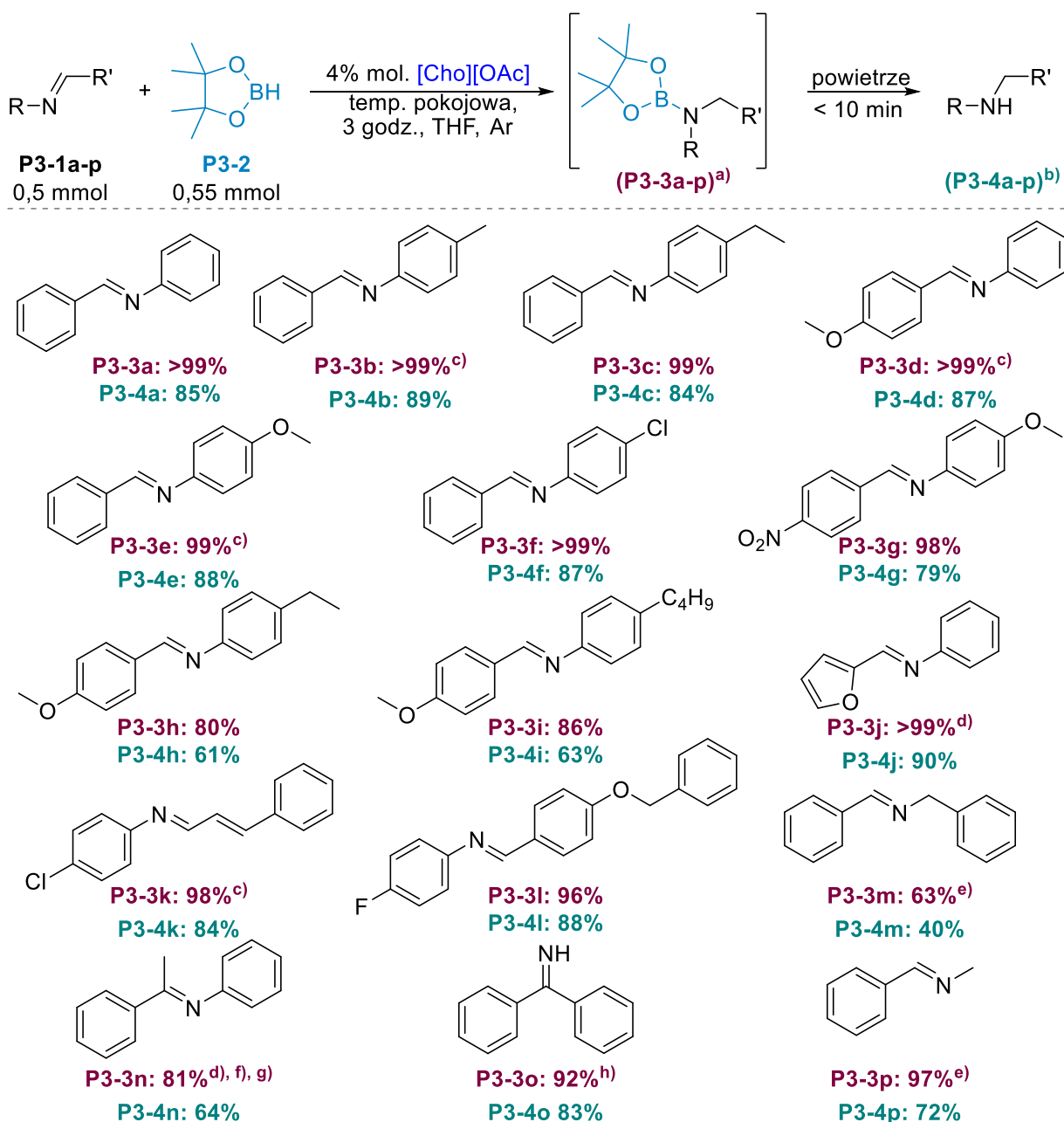
Optymalizacja warunków reakcji została przeprowadzona dla najbardziej aktywnego octanu choliny. Dwukrotne obniżenie ilości katalizatora skutkowało gwałtownym spadkiem konwersji **P3-1a**, natomiast zwiększenie stężenia $[\text{Cho}][\text{OAc}]$ z 4 do 6% molowych, nie powodowało wyraźnej zmiany konwersji (Tabela 4, l.p. 7–9). Pozytywny wpływ na wydajność procesu miały: nadmiar HBpin (**P3-2**) (Tabela 4, l.p. 10) oraz zmiana rozpuszczalnika z toluenu na THF lub octan etylu (Tabela 4, l.p. 11 i 13). W przeciwieństwie do związków karbonylowych, stosowanie dichlorometanu nie sprzyjało powstawaniu produktu **P3-3a** (Tabela 4, l.p. 12).

Tabela 4. Przegląd cieczy jonowych jako katalizatorów reakcji hydroborowania *N*-benzylidenoaniliny (**P3-1a**) pinakoloboranem (**P3-2**) i optymalizacja warunków procesu.

L.p.	Katalizator	% Molowy katalizatora	HBpin [ekw.]	Rozpuszczalnik	Wydajność P3-3a [%] ^{a)}
1	-	-	1,1	toluen	0
2	[Cho][Bz]	4	1,1	toluen	79
3	[Cho][TFA]	4	1,1	toluen	19
4	[Cho][NTf ₂]	4	1,1	toluen	22
5	[Cho][Oxa]	4	1,1	toluen	63
6	[Cho] ₂ [Oxa]	4	1,1	toluen	65
7	[Cho][OAc]	4	1,1	toluen	83 (96) ^{b)}
8 ^{b)}	[Cho][OAc]	2	1,1	toluen	38
9 ^{b)}	[Cho][OAc]	6	1,1	toluen	96
10 ^{b)}	[Cho][OAc]	4	1,5	toluen	>99
11 ^{b), c)}	[Cho][OAc]	4	1,1	THF	>99
12 ^{b)}	[Cho][OAc]	4	1,1	DCM	64
13 ^{b)}	[Cho][OAc]	4	1,1	octan etylu	>99

Warunki reakcji: [[Cho][OAc]]:[*N*-benzylidenoanilina]:[pinakoloboran] = 0,02–0,06:1:1,1–1,5, temperatura pokojowa, 3 godz., toluen, atmosfera powietrza. ^{a)}Wydajności zostały określone na podstawie analizy ¹H NMR; ^{b)} atmosfera argonu; ^{c)} 2 godz.

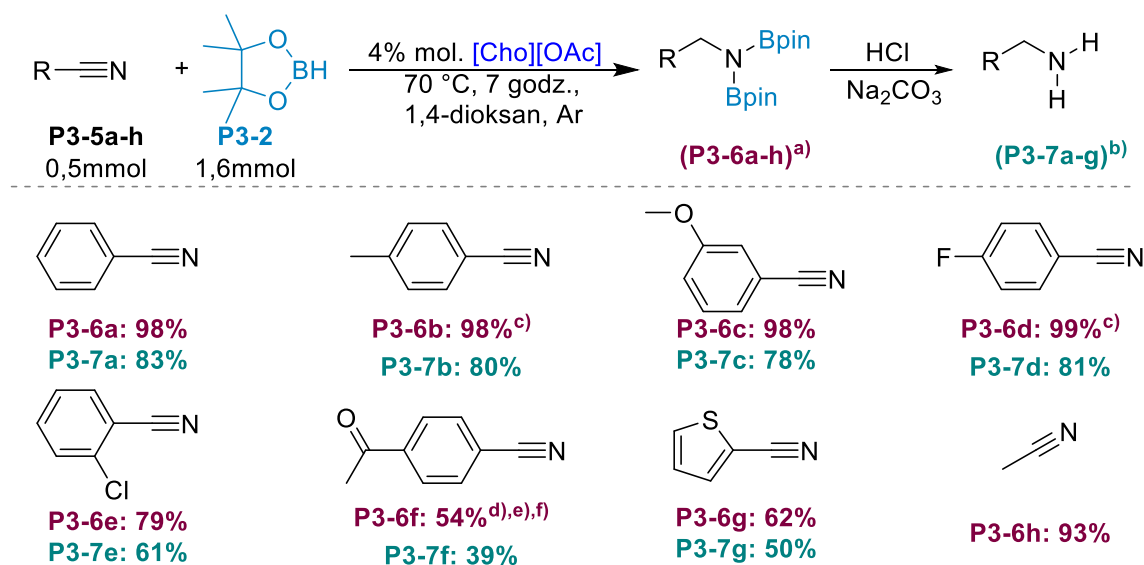
Przegląd imin został przeprowadzony w zoptymalizowanych warunkach reakcji: 1,1 ekwiwalentu HBpin (**P3-2**), 4% molowe [Cho][OAc], THF jako rozpuszczalnik, w atmosferze gazu obojętnego i w temperaturze pokojowej (Schemat 23). Zarówno podstawniki elektronodonorowe, jak i elektronoakceptorowe były dobrze tolerowane (**P3-1b–f**). Obecność grup –CH₃ oraz –OCH₃ wpłynęła na skrócenie czasu trwania reakcji (**P3-1b, d–e**). Co ciekawe, gdy w cząsteczce obecne były dwie grupy elektronodonorowe, odnotowano spadek wydajności produktów (**P3-3h–i**). Należy podkreślić, że hydroborowanie imin przebiegało chemoselektywnie nie powodując redukcji grupy nitrowej (**P3-3g**) oraz wiązania podwójnego węgiel–węgiel (**P3-3k**). Aby zapewnić wysoką wydajność produktów **P3-3j** i **P3-3m–n** konieczna była dodatkowa optymalizacja warunków reakcji obejmująca wydłużenie czasu reakcji oraz zwiększenie temperatury lub ilości HBpin. Natomiast *N*-benzylidenometyloamina (**3P-1p**), difenylometanimina (**P3-1o**) czy cząsteczki o wyższej masie, jak **P3-1l**, efektywnie ulegały hydroborowaniu w zoptymalizowanych warunkach reakcji.



Schemat 23. Hydroborowanie imin **P3-1a-p** w obecności katalizatora [Cho][OAc]. ^{a)} Wydajność określona na podstawie analizy ¹H NMR; ^{b)} wydajność izolacyjna; ^{c)} 1 godz.; ^{d)} 18 godz.; ^{e)} bez rozpuszczalnika; ^{f)} 60 °C; ^{g)} 2 ekwiwalenty HBpin; ^{h)} toluen.

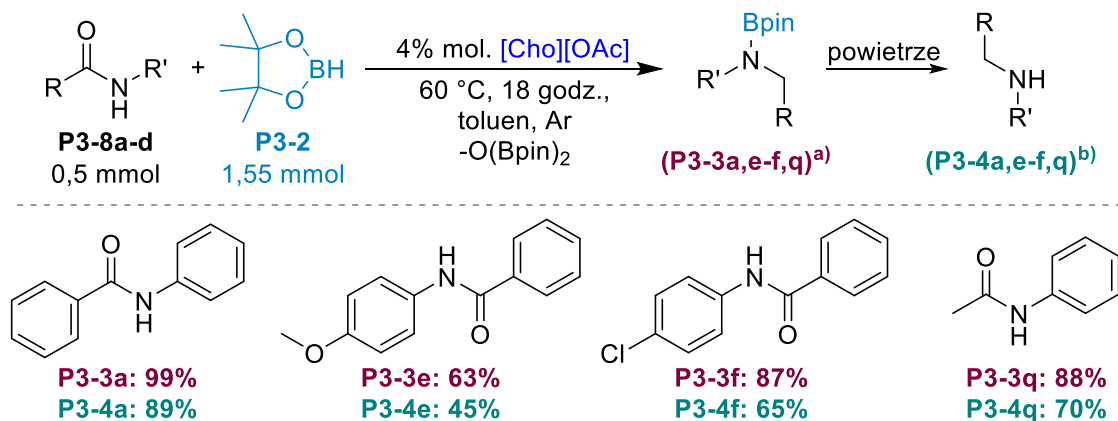
Uzyskane wyniki hydroborowania imin, obejmujące wysoką chemoselektywność i dobrą tolerancję grup funkcyjnych, stanowiły podstawę do rozszerzenia metodologii na inne substraty – nitryle i amidy. Ze względu na wysoką energię i znaczną stabilność wiązania C≡N,⁵⁸ niezbędne było podwyższenie temperatury do 70 °C, zwiększenie ilości czynnika borylującego do 3,2 ekwiwalentu oraz wydłużenie czasu trwania procesu (7 godz.). Reakcja najefektywniej przebiegała w 1,4-dioksanie i w atmosferze gazu obojętnego. W przeglądzie substratów nie odnotowano różnicy pomiędzy podstawnikami o zróżnicowanych efektach elektronowych (**P3-**

5b–d). Wyjątek stanowił *orto*-chlorobenzonitryl (**P3-5e**), dla którego odnotowano niższą konwersję, co może być wynikiem ograniczonej dostępności grupy nitrylowej. W cząsteczce acetylobenzonitrylu (**P3-5f**) addycja pinakoloboranu (**P3-2**) przebiegała do obu grup funkcyjnych z wydajnością równą 54%. Niższą konwersję obserwowano dla heteroaromatycznego substratu **P3-5g**, natomiast proces okazał się bardzo wydajny dla acetonitrylu (**P3-5h**). Produkty hydroborowania **P3-6a–g** poddawano reakcji z kwasem solnym, a następnie zobojętniano je węglanem sodu. Otrzymane aminy **P3-7a–g** izolowano poprzez ekstrakcję w niemieszających się fazach octan etylu-woda i woda-DCM (Schemat 24).



Schemat 24. Hydroborowanie nitryli **P3-5a–h** w obecności katalizatora $[\text{Cho}][\text{OAc}]$. ^{a)} Wydajność określona na podstawie analizy ^1H NMR; ^{b)} wydajność izolacyjna; ^{c)} 5 godz.; ^{d)} 18 godz.; ^{e)} 4 ekwiwalenty HBpin; ^{f)} konwersja **5f** = >99%.

Koleją testowaną grupą substratów były amidy, których redukcja prowadzi do amin. Włączenie amidów pozwalało więc sprawdzić, czy opracowany układ katalityczny nadaje się nie tylko do redukcji wiązań $\text{C}\equiv\text{N}$, lecz także szerzej do syntezy amin z różnych praktycznie istotnych prekursorów azotowych. Deoksygenacyjne hydroborowanie przebiegało ilościowo w obecności 4% molowych $[\text{Cho}][\text{OAc}]$, w temperaturze 60°C przez 18 godzin, prowadząc do otrzymywania drugorzędowych amin. Tolerowane były podstawniki $-\text{OMe}$ (**P3-8b**) oraz $-\text{Cl}$ (**P3-8c**). Wysoką wydajność reakcji redukcji obserwowano także dla *N*-fenyloacetamidu (**P3-8d**) (Schemat 25).

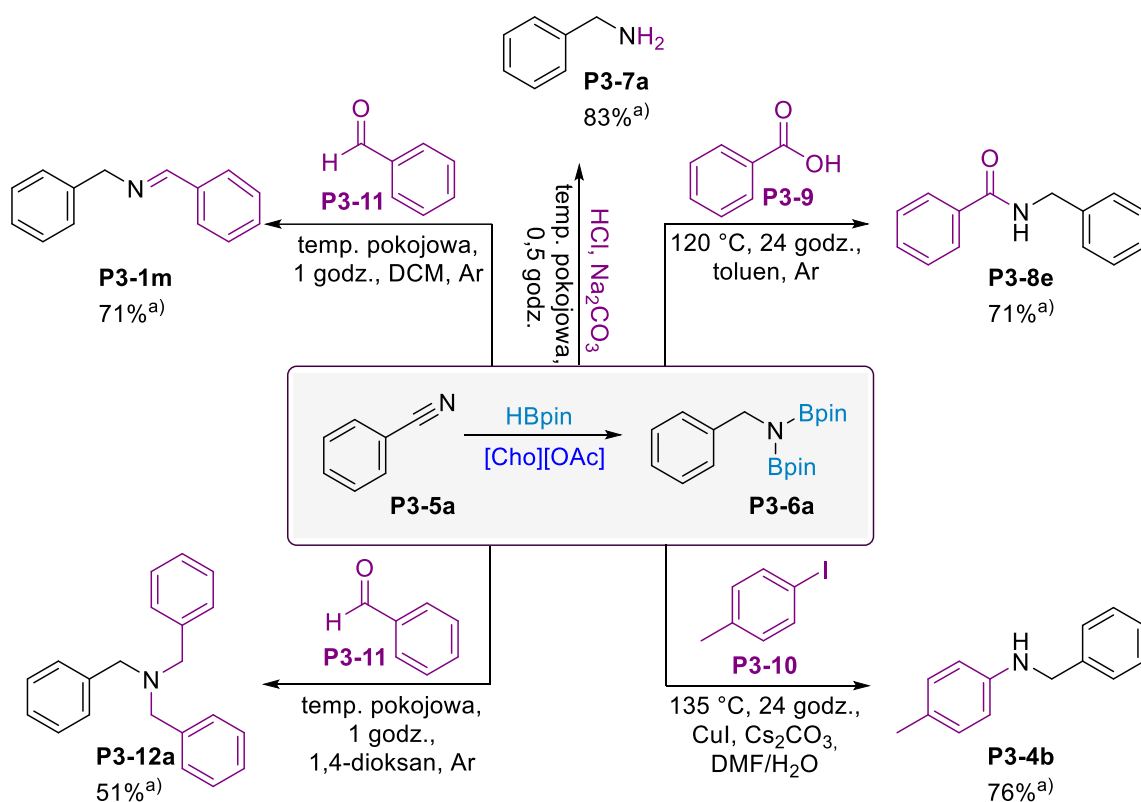


Schemat 25. Hydroborowanie amidów **P3-8a-d** w obecności katalizatora **[Cho][OAc]**. ^{a)} Wydajność określona na podstawie analizy ^1H NMR; ^{b)} wydajność izolacyjna.

N,N-Diborylowane aminy mogą stanowić wartościowe bloki budulcowe w syntezie organicznej, ze względu na możliwość ich dalszej funkcjonalizacji. Aplikacyjność tej klasy związków pokazano w reakcjach *one-pot*, w których pierwszym etapem jest hydroborowanie benzonitrylu (**P3-5a**) (Schemat 26). Pierwszorzędową aminę **P3-7a** otrzymano poprzez reakcję **P3-6a** najpierw z HCl, a następnie z Na_2CO_3 . Ponadto, opracowano trzyetapową syntezę aminy drugorzędowej **P3-4b**, z benzonitrylu (**P3-5a**) poprzez sekwencję reakcji: hydroborowania nitrylu, hydrolizy i sprzęgania otrzymanej aminy (**P3-7b**) z 4-jodotoluenem (**P3-10**) w obecności jodku miedzi(I) i węglanu cezu. Trzecią transformacją, tym razem pozwalającą na otrzymanie amidu **P3-8e**, było ogrzewanie mieszaniny poreakcyjnej zawierającej **P3-6a** z kwasem karboksylowym (**P3-9**) w toluenie. Przeprowadzono również syntezę iminy **P3-1m** poprzez reakcję **P3-6a** z benzaldehydem (**P3-11**). Optymalizacja warunków pokazała, że w zależności od stosunku molowego substratów oraz doboru rozpuszczalnika możliwe było selektywne otrzymanie iminy **P3-1m** lub aminy trzeciorzędowej **P3-12a** z zadowalającymi wydajnościami izolacyjnymi.

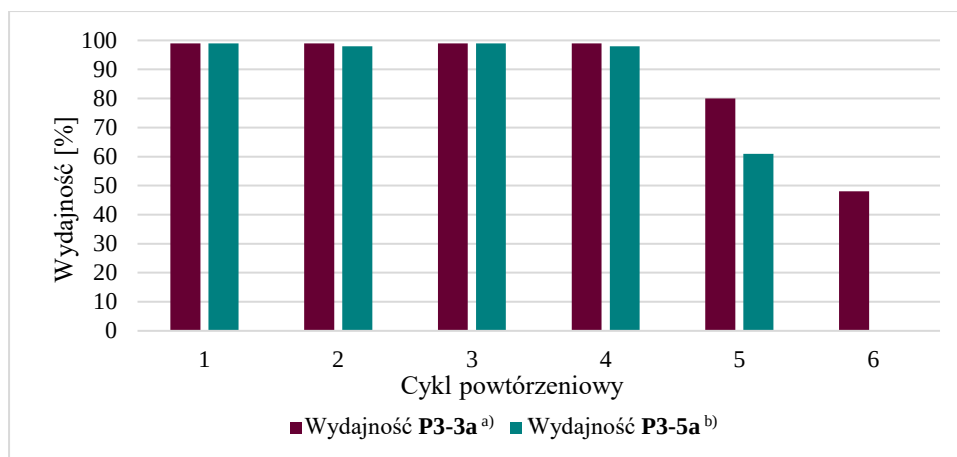
W pracach **P1** i **P2** udowodniono możliwość wielokrotnego użycia zarówno kompleksu platyny immobilizowanego w cieczy jonowej, jak i samej cieczy jonowej jako organokatalizatora w reakcji hydroborowania związków karbonylowych. W publikacji **P3** potwierdzono możliwość wielokrotnego wykorzystania katalizatora **[Cho][OAc]** w reakcjach hydroborowania *N*-benzylidenoaniliny (**P3-1a**) i benzonitrylu (**P3-5a**) (Wykres 5). Procedura była analogiczna jak w przypadku acetofenonu (**P2-1a**). Stosując 8% molowych octanu choliny, przeprowadzono reakcje powtórzeniowe. Dla iminy **P3-1a** w piątym cyklu uzyskana konwersja była już niższa (80%), podczas gdy dla reakcji z **P3-5a** wysoka wydajność procesu była utrzymywana przez cztery pierwsze cykle powtórzeniowe. W obu przypadkach, prawdopodobną przyczyną spadku

efektywności procesu było częściowe odmycie katalizatora w trakcie separacji produktów. Mimo, że stosowana ciecz jonowa jest nierozpuszczalna lub jest słabo rozpuszczalna w wielu rozpuszczalnikach organicznych, to powstające na skutek reakcji z HBpin (**P3-2**) potencjalnie aktywne katalityczne cząsteczki (**IN1-5**), wykazują znacznie lepszą rozpuszczalność w rozpuszczalnikach organicznych, co było odnotowane dla reakcji prowadzonych w toluenie, THF czy DCM.



Schemat 26. Synteza *one-pot* amin, imin i amidów, poprzez hydroborowanie nityli katalizowane przez [Cho][OAc].
^{a)} Wydajność izolacyjna.

Dopełnieniem przeprowadzonych badań było opracowanie mechanizmu reakcji, który w dużej mierze jest zbliżony do tego zaproponowanego dla związków karbonylowych. W tym celu przeprowadzono szereg badań eksperymentalnych (NMR) oraz obliczeniowych (DFT). W równomolowej reakcji octanu choliney z **P3-1a** (lub **P3-5a**) nie obserwowano żadnych zmian na widmach ¹H i ¹³C NMR. Stechiometryczne i substechiomertyczne reakcje octanu choliney z pinakolboranem (**P3-2**) zostały opisane w rozdziale 3.2. Powstające w tej reakcji produkty zostały zidentyfikowane jako **IN1-5**, jednak udowodniono, że **IN1** i **IN4** nie są aktywne katalitycznie (rozdział 3.2, Schemat 21). Hipoteza ta znalazła potwierdzenie w obliczeniach.

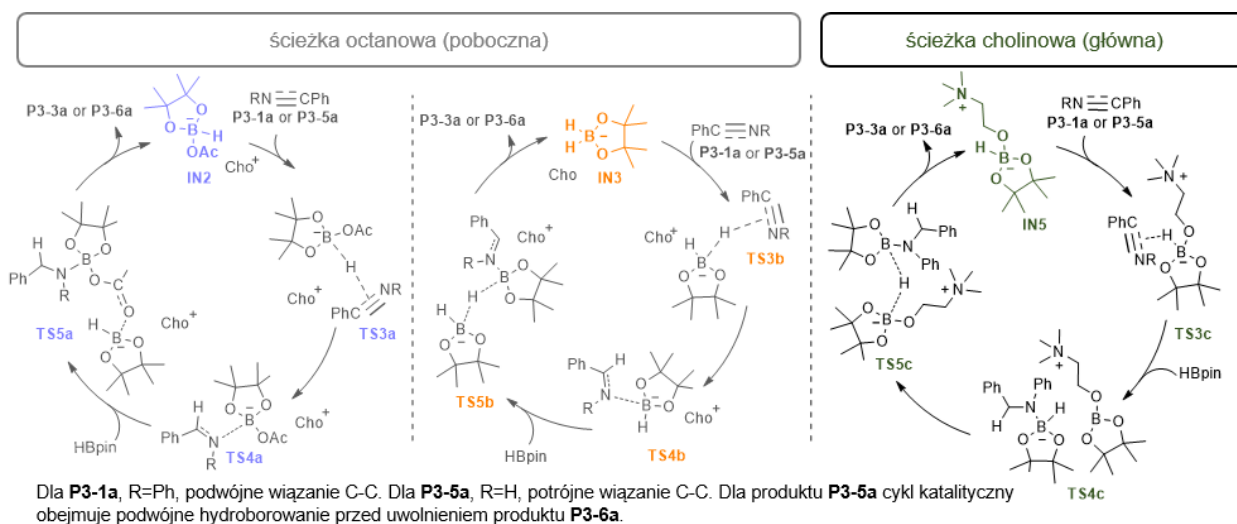


Wykres 5. Efektywność reakcji hydroborowania *N*-benzylidenoaniliny (**P3-1a**) i benzonitrylu (**P3-5a**) w trybie powtórzeniowym w obecności [Cho][OAc]. Warunki reakcji: ^{a)}[Cho][OAc]:[*N*-benzylidenoanilina]:[pinakoloboran] = 0,08:1:1,1, temperatura pokojowa, 2 godz., THF, atmosfera argonu; ^{b)}[Cho][OAc]:[benzonitryl]:[pinakoloboran] = 0,08:1:3,2, 70 °C, 7 godz., 1,4-dioksan, atmosfera argonu. Wydajność została określona na podstawie analiz GC-MS.

Na podstawie obliczeń DFT (wykonanych przez dr Mateusza Nowickiego), biorąc pod uwagę dwa główne czynniki – względne stężenia cząsteczek katalitycznych (**IN2**, **IN3** i **IN5**), występujących w równowadze oraz obliczone standardowe energie swobodne Gibbsa odpowiednich produktów pośrednich i stanów przejściowych – prawdopodobne jest, że ścieżka uwzględniająca **IN5** jest najkorzystniejsza. Niemniej ścieżki katalityczne z udziałem **IN2** i **IN3** również biorą udział w przebiegu całego procesu o czym świadczy szereg sygnałów na widmie ¹¹B NMR.¹¹⁶ Dla etapu tworzenia aktywnych borowodorków powstanie **IN2** w ścieżce octanowej jest energetycznie korzystne ($\Delta G = -4,9$ kcal/mol), natomiast przekształcenie **IN2** w **IN3** jest wyraźnie mniej korzystne ($\Delta G = +15,8$ kcal/mol). Z kolei ścieżka cholinowa, prowadząca ostatecznie do **IN5**, jest najbardziej uprzywilejowana energetycznie. Wszystkie opisane ścieżki (cholinowa i octanowa) przebiegają w analogiczny sposób. W pierwszym etapie następuje wytworzenie borowodorków, z których następuje przeniesienie wodorku na atom węgla przy wiązaniu C-N z następczym utworzeniem wiązania B-N. Przyłączenie kolejnej cząsteczki HBpin (**P3-2**) powoduje odtworzenie się katalizatora i uwolnienie produktu. W przypadku nitryli cykl katalityczny jest analogiczny i zakłada podwójne hydroborowanie, przy czym pierwsza reakcja jest znacznie mniej egzoenergetyczna niż dla imin ($\Delta G = -18,8$ kcal/mol wobec $\Delta G = -34,3$ kcal/mol), natomiast druga przebiega z większym efektem energetycznym ($\Delta G = -42,1$ kcal/mol). Różnice te wyjaśniają konieczność utrzymania wyższej temperatury reakcji dla nitryli (Schemat 27).

Przeprowadzono także eksperyment z udziałem TMEDA by wykluczyć ścieżkę z udziałem „ukrytego” katalizatora.⁶¹ Konwersja **P3-1a** po 3 godzinach reakcji pozostawała na poziomie $\geq 93\%$. W przypadku hydroborowania benzonitrylu (**P3-5a**), zaobserwowano silniejszy

wpływ TMEDA na przebieg reakcji, co może sugerować większe znaczenie „ukrytej” ścieżki katalitycznej niż w przypadku imin. Warto zaznaczyć, że zastosowanie TMEDA w reakcji hydroborowania **P3-5a** prowadzonej według mechanizmu „ukrytego” katalizatora skutkowało całkowitym brakiem pożądanego produktu.¹¹⁸



Schemat 27. Możliwe ścieżki katalityczne hydroborowania imin i nityli w obecności [Cho][OAc].

Powyższe wyniki badań opublikowane w artykule **P3** wnoszą istotne poszerzenie stanu wiedzy na temat wykorzystania cieczy jonowych, a w szczególności octanu choliny, jako organokatalizatora reakcji hydroborowania nienasyconych wiązań węgiel-azot. Ponadto, stanowią nową i atrakcyjną alternatywę dla obecnie stosowanych układów opartych na metalach przejściowych oraz pierwiastkach bloku s i p. Opracowany protokół był skuteczny dla szerokiego wachlarza związków aromatycznych, zawierających zarówno grupy elektronodonorowe, jak i elektronoakceptorowe, a także dla podstawników heterocyklicznych. Zaproponowano prostą metodę syntezy amidów, imin oraz amin z nityli poprzez hydroborowanie i następcze reakcje *one-pot*, bez konieczności izolowania produktów pośrednich. Wykorzystując ograniczoną rozpuszczalność katalizatora w rozpuszczalnikach niepolarnych, opracowano metodę jego recyklingu, co istotnie wpływa na poprawę efektywności procesu. Mechanizm reakcji, zaproponowany na podstawie badań NMR, wsparty obliczeniami DFT, wykazał, że w procesie hydroborowania nienasyconych wiązań węgiel-azot występują trzy ścieżki katalityczne, które przebiegają poprzez tworzenie różnych borowodorków. Wiodące znaczenie w procesie hydroborowania imin i nityli ma tzw. ścieżka cholinowa, dla której kluczowym borowodorkiem jest **IN5**, powstający z kationu [Cho][OAc].

4. Podsumowanie i wnioski

W niniejszej rozprawie doktorskiej przedstawiono nowe i efektywne metody hydroborowania nienasyconych wiązań węgiel-heteroatom. Przeprowadzone badania pozwalają stwierdzić, że ciecze jonowe stanowią skuteczne i wielofunkcyjne media w reakcjach hydroborowania wiązań wielokrotnych węgiel-heteroatom, pełniąc zarówno rolę ośrodka immobilizującego katalizator, jak i aktywnego komponenta katalitycznego. Wykorzystanie immobilizacji katalizatora platynowego w cieczy jonowej (**P1**) oraz zastosowanie cieczy jonowych jako organokatalizatorów (**P2** i **P3**) prowadzi do uzyskania układów o wysokiej aktywności, selektywności oraz możliwości wielokrotnego użycia, co potwierdza ich znaczenie w kontekście rozwoju bardziej zrównoważonych procesów katalitycznych.

W ramach publikacji **P1** wykazano, że:

- i) Komercyjnie dostępny kompleks $[Pt(PPh_3)_4]$ stanowi wysoce efektywny katalizator reakcji hydroborowania ketonów w warunkach bezropuszczalnikowych, przy jednoczesnej wysokiej tolerancji grup funkcyjnych (uzyskano 26 produktów z wysokimi wydajnościami).
- ii) O-borylowane produkty ulegały hydrolizie w przemianie *one-pot* (w jednym naczyniu reakcyjnym, bez konieczności izolacji produktów pośrednich) do alkoholi, które stanowią ważne bloki budulcowe w chemii organicznej, co znacząco upraszcza procedurę syntezy i ogranicza liczbę etapów izolacyjnych.
- iii) Immobilizacja katalizatora $[Pt(PPh_3)_4]$ w cieczy jonowej $[BMIM][NTf_2]$ umożliwia jego efektywny recykling i stabilność w 15 cyklach reakcyjnych, przy zachowaniu wysokiej aktywności katalitycznej (TON = 2934). Analiza ICP-MS potwierdziła niską zawartość platyny w uzyskanych ekstraktach ($\leq 0,35$ ppm), co świadczy o niewielkim stopniu wymywania katalizatora w trakcie procesu i potwierdza zarówno skuteczność strategii immobilizacji oraz odpowiedni dobór ekstrahenta. Dodatkowo możliwość stosowania tego samego układu katalitycznego w sekwencji reakcji z różnymi substratami podkreśla jego uniwersalność oraz wysoką funkcjonalność opracowanej metodologii rozdziału produktów.
- iv) Badania mechanistyczne oparte na spektroskopii NMR pozwoliły na zaproponowanie cyklu katalitycznego zakładającego utleniającą addycję pinakoloboroanu do centrum metalicznego, koordynację ketonu oraz redukującą eliminację borylowanego produktu z jednoczesnym odtworzeniem katalizatora.

Wyniki badań nad zastosowaniem komercyjnie dostępnych cieczy jonowych jako potencjalnych organokatalizatorów (**P2** i **P3**) w reakcjach hydroborowania nienasyconych wiązań węgiel-heteroatom dowodzą, że:

- i) ciecze jonowe pochodzenia naturalnego, w szczególności [Cho][OAc], mogą katalizować proces hydroborowania ketonów, aldehydów oraz kwasów karboksylowych (bez udziału rozpuszczalnika organicznego) oraz imin, nitryli i amidów (w THF), w krótkim czasie (od 0,5–3 godziny, w zależności od stosowanego substratu).
- ii) Optymalizacja warunków reakcji wykazała, iż kluczową rolę w procesie katalitycznym pełni nukleofilowość anionu. Octan choliney był najefektywniejszy spośród testowanych cieczy jonowych, podczas gdy zmiana kationu cholinowego na inne czwartorzędowe kationy amoniowe prowadziła do obniżenia aktywności katalitycznej.
- iii) Układy katalityczne bazujące na [Cho][OAc] odznaczały się wysoką tolerancją w stosunku do różnych struktur substratów, co potwierdza szeroka gama testowanych związków (dla związków karbonylowych łącznie 45 przykładów, a dla związków azotu 28 przykładów), które przekształcono poprzez hydrolizę w odpowiadające im alkohole lub aminy w procedurze *one-pot*.
- iv) Produkty hydroborowania nitryli mogą być efektywnie przekształcone, bez konieczności izolacji produktów pośrednich, w pierwszo-, drugo- i trzeciorzędowe aminy, iminy lub amidy w wyniku sekwencyjnych przemian katalitycznych lub/i niekatalitycznych.
- v) Organokatalizator może zostać efektywnie oddzielony od mieszaniny poreakcyjnej poprzez ekstrakcję produktów w niepolarnym rozpuszczalniku. Strategia ta pozwoliła na przeprowadzenie cykli powtórzeniowych (13 dla ketonów, 5 dla imin) bez wyraźnego spadku aktywności katalizatora, co pozytywnie wpływa na produktywność procesu hydroborowania.
- vi) Badania mechanistyczne, obejmujące eksperymenty NMR oraz obliczenia DFT wykazały, że aktywne katalitycznie borowodorki powstają zarówno z udziałem kationu, jak i anionu [Cho][OAc]. W hydroborowaniu związków karbonylowych istotną rolę odgrywają zarówno ścieżka octanowa oraz cholinowa, prowadzące odpowiednio do wytworzenia borowodorków **IN2** oraz **IN5**. Natomiast dla hydroborowania nienasyconych wiązań węgiel-azot dominującą rolę przypisano ścieżce cholinowej (**IN5**).
- vii) Proponowany mechanizm reakcji zakłada, że powstające borowodorki reagują z nienasyconym wiązaniem węgiel-tlen lub węgiel-azot, co skutkuje przeniesieniem wodorku na atom węgla przy wiązaniu wielokrotnym oraz utworzeniem wiązania O/N-B.

Przylączenie się cząsteczki pinakoloboranu pozwala na regenerację katalizatora i dysocjację produktu reakcji.

viii) Eksperymenty z TMEDA potwierdziły, że udział „ukrytego” katalizatora jest minimalny.

W przeciwieństwie do wcześniej opisanych układów katalitycznych opartych na solach nieorganicznych, zastosowanie cieczy jonowej umożliwia współdziałanie zarówno kationu, jak i anionu w tworzeniu aktywnych katalitycznie cząsteczek, co przekłada się na zwiększoną efektywność procesu.

Przedstawione w rozprawie wyniki, obejmujące opracowanie efektywnych protokołów hydroborowania z wykorzystaniem kompleksów platyny oraz cieczy jonowych, wskazują na potencjał tych układów jako funkcjonalnych środowisk reakcyjnych, wpisujących się w rozwój nowoczesnych strategii prowadzenia reakcji w niekonwencjonalnych układach. Zastosowanie cieczy jonowych umożliwiło nie tylko prowadzenie reakcji (rozpuszczalnik, katalizator), lecz także efektywny rozdział produktów i recykling katalizatora, co wpisuje się w aktualne dążenia do bardziej zrównoważonych procesów chemicznych. Uzupełniające badania mechanistyczne (NMR, DFT) pozwoliły lepiej zrozumieć przebieg reakcji hydroborowania wiązań węgiel-heteroatom. Uzyskane rezultaty wypełniają istotną lukę badawczą w kontekście lepszego zrozumienia i praktycznego wykorzystania cieczy jonowych jako medium reakcyjnego oraz organokatalizatorów, a także stanowią podstawę do dalszego rozwoju układów katalitycznych opartych na cieczach jonowych oraz ich zastosowania w innych transformacjach wiązań nienasyconych, w tym w kierunku funkcjonalizacji bardziej wymagających substratów.

5. Wykaz skrótów

^1H NMR – spektroskopia protonowego magnetycznego rezonansu jądrowego

^{13}C NMR – spektroskopia węglowego magnetycznego rezonansu jądrowego

^{31}P NMR – spektroskopia fosforowego magnetycznego rezonansu jądrowego

^{11}B NMR – spektroskopia borowego magnetycznego rezonansu jądrowego

EA – analiza elementarna

GC-MS – chromatografia gazowa sprzężona ze spektrometrią mas

ICP MS – spektrometria mas z plazmą indukcyjnie sprzężoną

DFT – teoria funkcjonału gęstości

API – substancja czynna (z ang. *active pharmaceutical ingredient*)

LAH – glinowodorek litu

IL (ILs) – ciecz jonowa (ciecze jonowe)

RTILs – ciecze jonowe o temperaturach topnienia poniżej temperatury pokojowej

scCO₂ – dwutlenek węgla w stanie nadkrytycznym

NHO – N-heterocykliczna olefina

THF – tetrahydrofuran

DCM – dichlorometan

DMF – dimetyloformamid

TON – liczba obrotów katalizatora (z ang. *turnover number*)

BH₃·SMe₂ – boran-siarczek dimetylu

HBpin – 4,4,5,5-tetrametylo-1,3,2 dioksoborolan, (pinakoloboran)

[Ag(PCy₃)(HMDS)] – [tricykloheksylofosfina(heksametylodisilazan)srebro(I)]

[Ag(IDipp)HMDS] – [1,3-bis(2,6-diizopropylfenylo)imidazol-2-yliden]heksametylodisilazan srebro(I)

[RhCl(PPh₃)₃] – [chlorotris(trifenylfosfina)rod(I)], (katalizatora Wilkinsona)

- [NiCl₂(dppe)] – [dichloro[1,2-bis(difenylofosfino)etan]nikiel(II)]
- [(cod)Rh(dppe)][BF₄] – tetrafluoroboran [1,2-bis(difenylofosfino)etano]bis(1,5-cyklooktadien)rodu(I)]
- nano-Ir(0)@IL – nanocząstki irydu(0) stabilizowane w cieczy jonowej
- [Ru(CO)(Cl)HPPPh₃]₃] – [chlorohydrydokarbonyltris(trifenylofosfina)ruten(II)]
- PtCl₂ – chlorek platyny(II)
- PtO₂ – tlenek platyny(IV)
- [PtCl₂(PPh₃)₂] – [dichlorobis(trifenylofosfina)platyna(II)]
- [Pt(η²-C₂H₄)(PPh₃)] – [hapto-2-etylenobis(trifenylofosfina)platyna(0)]
- [Pt(PPh₃)₄] – [tetrakis(trifenylofosfina)platyna(0)]
- [TBA][BF₄] – tetrafluoroboran tetrabutyloamoniowy
- [TBA][OAc] – octan tetrabutyloamoniowy
- [TBA][TFA] – trifluoroocatan tetrabutyloamoniowy
- [TMA][OAc] – octan tetrametyloamoniowy
- [THTdP][DBS] – dodecylobenzenosulfonian triheksylo(tetradecylo)fosfoniowy
- [HMIM][CF₃SO₃] – trifluorometanosulfonian 1-heksylo-3-metyloimidazoliowy
- [BMPy][BF₄] – tetrafluoroboran 1-butylo-4-metylopirydyniowy
- [BMPyrr][Cl] – chlorek 1-butylo-1-metylopirolidyniowy
- [EMPyrr][OTf] – trifluorometanosulfonian 1-etylo-1-metylopirolidyniowy
- [EMPyrr][NTf₂] – bis(trifluorometylosulfonylo)imidek 1-etylo-1-metylopirolidyniowy
- [BMIM][Cl] – chlorek 1-butylo-3-metyloimidazoliowy
- [BMIM][NTf₂] – bis(trifluorometylosulfonylo)imidek 1-butylo-3-metyloimidazoliowy
- [BMIM][OTf] – trifluorometanosulfonian 1-butylo-3-metyloimidazoliowy
- [BMIM][TOS] – *p*-toluenosulfonian 1-butylo-3-metyloimidazoliowy
- [BMIM][FeCl₄] – tetrachlorożelazian(III) 1-butylo-3-metyloimidazoliowy

ZnCl_2 – chlorek cynku(II)

[Trop][BF₄] – tetrafluoroboran tropyliowy

[Cho][OAc] – octan choliny

[Cho][TFA] – trifluorooctan choliny

[Cho]₂[Oxa] – szczawian dicholiny

[Cho][Oxa] – szczawian choliny

[Cho][Bz] – benzoesan choliny

[Cho][NTf₂] – bis(trifluorometylosulfonylo)imidek choliny

HOAc – kwas octowy

HBz – kwas benzoesowy

H₂Oxa – kwas szczawiowy

ChoCl – chlorek choliny

KOAc – octan potasu

KBz – benzoesan potasu

HCl – kwas solny

Na₂CO₃ – węglan sodu

Cs₂CO₃ – węglan cezu

CuI – jodek miedzi(I)

TMEDA – *N,N,N,N'*-tetrametyloetylenodiamina

6. Literatura

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7. Oświadczenia współautorów

Poznań, dnia 31.05.2026 r.

OŚWIADCZENIE

Niniejszym oświadczam, że w poniższych artykułach:

P1. B. Krupa, J. Szyling, J. Walkowiak, Pt(PPh₃)₄ and Pt(PPh₃)₄@IL catalyzed hydroboration of ketones. *Scientific Reports* **2023**, *13*, 20237, doi: 10.1038/s41598-023-47518-6

P2. B. Krupa, M. Nowicki, P. Huninik, J. Szyling, J. Walkowiak, Organocatalytic hydroboration of carbonyl compounds promoted by choline-based ionic liquids. *ACS Sustainable Chemistry & Engineering* **2025**, *13*, 41, 17510–17519 doi: 10.1021/acssuschemeng.5c07304

P3. B. Krupa, M. Nowicki, J. Szyling, J. Walkowiak, Organocatalytic hydroboration of imines, nitriles, and amides using choline-based ionic liquids. *Journal of Catalysis* **2025**, 116362, doi: 10.1016/j.jcat.2025.116362

mój wkład autorski obejmuje:

w publikacji **P1**:

- przegląd katalizatorów i optymalizacja warunków reakcji,
- synteza i charakterystyka produktów (**3a-m**, **3p**, **3r-s**, **3u-z**),
- izolacja i charakterystyka produktów (**3n-o**, **3q**, **3t**, **5a-w**) (GC-MS, NMR, EA),
- immobilizacja katalizatora w cieczach jonowych i prowadzenie reakcji w trybie powtórzeniowym,
- współudział w badaniu mechanizmu reakcji,
- współudział w tworzeniu oraz korektach manuskryptu i suplementu – przygotowanie oryginalnego tekstu publikacji, tabel i schematów, opis metod badawczych oraz analiz GC-MS, ¹H, ¹³C, ¹¹B NMR, analiza elementarna,
- współudział w opracowaniu koncepcji i metodyki badań,
- współudział w korespondencji z edytorem i recenzentami.

w publikacji **P2**:

- synteza cieczy jonowych (**IL2-IL5**), przegląd katalizatorów i optymalizacja warunków reakcji,
- synteza i charakterystyka produktów przejściowych (**3a-z**, **6a-r**) oraz synteza, charakterystyka i izolacja produktów końcowych (**5a-z**, **7a-r**) (GC-MS, NMR, analiza elementarna),
- prowadzenie reakcji w trybie powtórzeniowym,
- prowadzenie eksperymentów mających na celu zbadanie mechanizmu reakcji,
- współudział w tworzeniu manuskryptu, przygotowanie oryginalnego tekstu publikacji, tabel i schematów oraz ich dalsza korekta,
- współudział w tworzeniu suplementu do publikacji – przygotowanie oryginalnego tekstu tabel i schematów, opis metod badawczych, a także opis analiz GC-MS, ¹H, ¹³C, ¹¹B NMR, analiza elementarna,

Barbara Krupa
Wydział Chemii, Uniwersytet im. Adama Mickiewicza w Poznaniu
Centrum Zaawansowanych Technologii

- współudział w opracowaniu koncepcji i metodyki badań,
- współudział w korespondencji z edytorem i recenzentami.

w publikacji **P3**:

- synteza katalizatorów ([Cho][Bz], [Cho][Oxa], [Cho]₂[Oxa]) i przeprowadzenie przeglądu cieczy jonowych jako katalizatorów,
- optymalizacja warunków reakcji,
- synteza substratów **1c**, **1e-h**, **1j-k**, **8b-c**,
- otrzymywanie produktów przejściowych (**3a-q**, **6a-h**) oraz produktów końcowych oraz ich izolacja i charakterystyka **4a-p**, **7a-g**, **1m**, **8e**, **12a**) (GC-MS, NMR, analiza elementarna),
- prowadzenie reakcji w trybie powtórzeniowym,
- prowadzenie eksperymentów mających na celu zbadanie mechanizmu reakcji,
- współudział w tworzeniu manuskryptu – przygotowanie wersji wstępnej publikacji wraz ze schematami i tabelami,
- współudział w tworzeniu suplementu do publikacji – przygotowanie oryginalnego tekstu tabel i schematów, opis metod badawczych i analiz GC-MS, ¹H, ¹³C, ¹¹B NMR, analiza elementarna,
- współudział w korektach manuskryptu i suplementu publikacji,
- współudział w opracowaniu koncepcji i metodyki badań,
- współudział w korespondencji z edytorem i recenzentami.

Barbara Krupa

Poznań, 31-05-2026

OŚWIADCZENIE

Niniejszym oświadczam, że w poniższych artykułach:

P1. B. Krupa, J. Szyling, J. Walkowiak, $\text{Pt}(\text{PPh}_3)_4$ and $\text{Pt}(\text{PPh}_3)_4/\text{IL}$ catalyzed hydroboration of ketones. *Scientific Reports* **2023**, 13, 20237, doi: 10.1038/s41598-023-47518-6

P2. B. Krupa, M. Nowicki, P. Huninik, J. Szyling, J. Walkowiak, Organocatalytic hydroboration of carbonyl compounds promoted by choline-based ionic liquids. *ACS Sustainable Chemistry & Engineering* **2025**, 13, 41, 17510–17519 doi: 10.1021/acssuschemeng.5c07304

P3. B. Krupa, M. Nowicki, J. Szyling, J. Walkowiak, Organocatalytic hydroboration of imines, nitriles, and amides using choline-based ionic liquids. *Journal of Catalysis* **2025**, 116362, doi: 10.1016/j.jcat.2025.116362

mój wkład autorski obejmuje:

- współudział w interpretacji uzyskanych wyników,
- współudział w tworzeniu oraz korekcie manuskryptów,
- współudział w opracowaniu koncepcji pracy,
- współudział w korespondencji z edytorem i recenzentami,
- finansowanie badań zawartych w tych artykułach.



Podpisano przez/ Signed by:
Jędrzej
Walkowiak
Data/ Date: 31.05.2026 22:10
mSzofir

Poznań, 26-05-2026

OŚWIADCZENIE

Niniejszym oświadczam, że w poniższych artykułach:

P1. B. Krupa, J. Szyling, J. Walkowiak, $\text{Pt}(\text{PPh}_3)_4$ and $\text{Pt}(\text{PPh}_3)_4/\text{IL}$ catalyzed hydroboration of ketones. *Scientific Reports* **2023**, 13, 20237, doi: 10.1038/s41598-023-47518-6

P2. B. Krupa, M. Nowicki, P. Huninik, J. Szyling, J. Walkowiak, Organocatalytic hydroboration of carbonyl compounds promoted by choline-based ionic liquids. *ACS Sustainable Chemistry & Engineering* **2025**, 13, 41, 17510–17519 doi: 10.1021/acssuschemeng.5c07304

P3. B. Krupa, M. Nowicki, J. Szyling, J. Walkowiak, Organocatalytic hydroboration of imines, nitriles, and amides using choline-based ionic liquids. *Journal of Catalysis* **2025**, 116362, doi: 10.1016/j.jcat.2025.116362

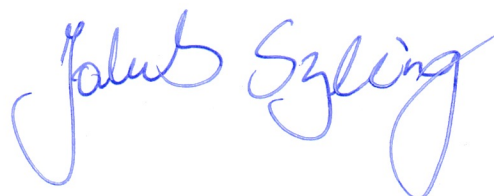
mój wkład autorski obejmuje:

w publikacji **P1**:

- współudział w prowadzeniu eksperymentów, analizie i interpretacji uzyskanych wyników dot. mechanizmu reakcji hydroborowania,
- współudział w interpretacji i analizie uzyskanych wyników,
- współudział w tworzeniu oraz korekcie manuskryptu,
- współudział w opracowaniu koncepcji pracy oraz zaplanowaniu syntez,
- korekta suplementu do publikacji;
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w publikacjach **P2–P3**:

- współudział w interpretacji i analizie uzyskanych wyników,
- współudział w tworzeniu oraz korekcie manuskryptu,
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- współudział w korekcie suplementu do publikacji;
- współudział w korespondencji z edytorem i recenzentami.



Poznań, dnia 1.06.2026

OŚWIADCZENIE

Niniejszym oświadczam, że w poniższych artykułach:

P2. B. Krupa, M. Nowicki, P. Huninik, J. Szyling, J. Walkowiak, Organocatalytic hydroboration of carbonyl compounds promoted by choline-based ionic liquids. *ACS Sustainable Chemistry & Engineering* **2025**, *13*, *41*, 17510–17519 doi: 10.1021/acssuschemeng.5c07304

P3. B. Krupa, M. Nowicki, J. Szyling, J. Walkowiak, Organocatalytic hydroboration of imines, nitriles, and amides using choline-based ionic liquids. *Journal of Catalysis* **2025**, 116362, doi: 10.1016/j.jcat.2025.116362

mój wkład autorski obejmuje:

- Przeprowadzenie i opracowanie badań mechanistycznych DFT,
- współudział w interpretacji i analizie uzyskanych wyników dotyczących mechanizmu reakcji,
- współtworzenie oraz korekta manuskryptu oraz suplementu publikacji,
- współudział w korespondencji z edytorem i recenzentami.



.....
dr Mateusz Nowicki

Poznań, dnia 02.06.2026✓

OŚWIADCZENIE

Niniejszym oświadczam, że w poniższych artykułach:

P2. B. Krupa, M. Nowicki, P. Huninik, J. Szyling, J. Walkowiak, Organocatalytic hydroboration of carbonyl compounds promoted by choline-based ionic liquids. *ACS Sustainable Chemistry & Engineering* **2025**, 13, 41, 17510–17519 doi: 10.1021/acssuschemeng.5c07304

mój wkład autorski obejmuje:

- współudział w planowaniu eksperymentów dot. poznania mechanizmu reakcji,
- współudział w interpretacji i analizie uzyskanych wyników dotyczących mechanizmu reakcji.

Paweł Huninik

8. Kopie publikacji naukowych będących przedmiotem rozprawy

Publikacja **P1**

B. Krupa, J. Szyling, J. Walkowiak,

Pt(PPh₃)₄ and Pt(PPh₃)₄@IL catalyzed hydroboration of ketones.

Scientific Reports **2023**, 13, 20237,

doi: 10.1038/s41598-023-47518-6



OPEN

Pt(PPh₃)₄ and Pt(PPh₃)₄@IL catalyzed hydroboration of ketones

Barbara Krupa^{1,2}, Jakub Szyling¹ & Jędrzej Walkowiak¹✉

An efficient method for the reduction of various ketones via [Pt(PPh₃)₄]-catalyzed hydroboration with HBpin has been successfully developed for the first time. The protocol is suitable for symmetrical and unsymmetrical derivatives possessing electron donating or withdrawing functional groups. O-borylated products were easily converted to 2° alcohols via hydrolysis with high isolated yields. According to the low-temperature NMR spectroscopy, a reaction mechanism was proposed. Additionally, effective immobilization of the catalyst in the ionic liquid [BMIM][NTf₂] was applied to increase the productivity of the process by carrying out reactions under the repetitive batch mode, obtaining higher TON values and limiting the amount of expensive Pt used. The catalyst stability and almost neglectable leaching were confirmed by ICP-MS analysis of the extracted mixture. A simple separation method via extraction with *n*-heptane, efficient catalyst immobilization, and the commercial availability of the Pt complex, make this protocol an attractive method for the hydroboration of ketones

Hydroboration is one of the most powerful methods for the incorporation of a boryl moiety into the structure of various compounds^{1–3}. This reaction occurs by the addition of the B–H bond to compounds possessing unsaturated carbon–carbon or carbon–heteroatom bonds (e.g., C≡C⁴, C=C^{1,5}, C=O⁶, C=N⁷). It is a versatile and straightforward synthetic tool that proceeds with high selectivity and excellent atom economy depending on the type of catalyst and reagents, as well as reaction conditions. Organoboron compounds obtained via the hydroboration process are characterized by high reactivity, low toxicity and possibilities for their further, simple functionalization in many catalytic and stoichiometric transformations, e.g., deborylation⁸, Suzuki–Miyaura cross-coupling⁹, cycloaddition¹⁰, alkenylation¹¹ or propargylation¹² making them important building blocks in the synthesis of fine chemicals^{13,14}.

Hydroboration of carbonyl compounds is one of the most useful strategies for the synthesis of alcohols, obtained by the subsequent hydrolysis of boronate ether intermediates¹⁵. The reduction of aldehydes and ketones generates 1° and 2° alcohols respectively. These compounds are important scaffolds for the synthesis of biologically active molecules in the pharmaceutical industry^{14,16}. Moreover, in contrast to conventional methods, which involve dangerous, highly reactive hydrides or flammable pressurized hydrogen gas, hydroboration often proceeds under mild conditions with 100% atomic economy which is in line with the principles of green chemistry. Moreover, the reduction might be carried out selectively, provided that the other unsaturated bonds are unreactive^{6,15,17,18}.

Catalytic hydroboration of carbonyl derivatives can be performed in the presence of main group metals^{19,20}, transition metals³, rare earth metal complexes²¹ and organocatalysts^{22–25}. This subject had been comprehensively reviewed^{6,8}. Transition metal-based catalysts are still very effective in hydroboration reactions including carbonyl compounds because of their ability to provide high reagent conversion, product yield and reaction selectivity. Their principle advantage over main group catalysts is low catalyst loading and the lack of any need to apply various additives or additional ligands^{24,26–28}. These processes are mainly performed under homogeneous conditions, which on the one hand assure excellent selectivity towards the desired products and on the other, generate important economic and ecological issues, such as the lack of any possibility of recycling precious TM-catalysts or the generation of a vast amount of contaminated volatile organic solvents (VOSs). Thus, alternative protocols for the hydroboration of ketones following green chemistry rules and enhancing process sustainability should be developed. For the hydroboration of carbonyl compounds, reusable protocols based on nanoparticles^{29,30}, metal–organic frameworks (MOF)^{31–39}, metal–coordination polymers^{40–42} or silica-supported metal catalysts^{43,44} have been reported. Very recently, Peters et al. reported the homogeneous cooperative Lewis acid–ammonium salt catalyzed hydroboration of ketones. The catalyst was recycled eleven times in the hydroboration reaction of acetophenone. For the first 9 runs, the product was obtained with a 99% yield, while in the last cycle, the conversion

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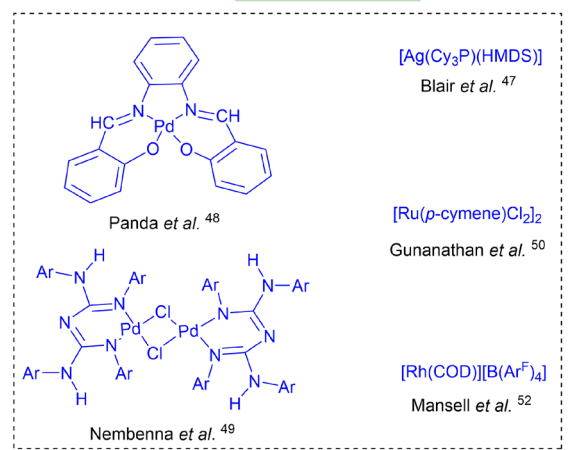
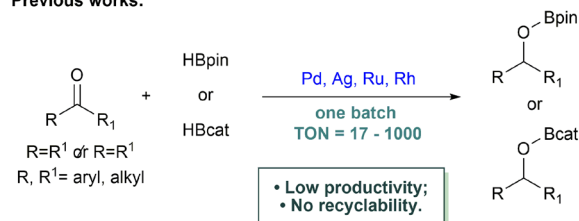
of ketone dropped to 75%. The accumulative TON value for this process was 2094⁴⁵. An ionic liquid with the organic cation [BMIM]⁺ and metallic anion [FeCl₄]⁻ has been used as an effective catalyst in the hydroboration of imines by Lin et al. The 15 repetitive batches with *N*-benzylideneaniline and pinacolborane were carried out with substrate conversion between 93 and 85%, giving an accumulative TON value of 449⁴⁶.

TM-catalyzed hydroboration of C=O bonds is a powerful synthetic strategy leading to the corresponding alcohol; however, it has mainly been utilized for aldehydes⁶. In contrast to aldehydes, the efficient hydroboration of ketones in the presence of noble metal catalysts based on Ag⁴⁷, Pd,^{48,49} Ru^{50,51} or Rh⁵² is limited to a few examples (Fig. 1). For the reaction catalyzed by silver, palladium and ruthenium compounds in solvent-free conditions, pinacolborane was used as the reducing agent. To achieve full reagents conversion, the reactions were carried out at 60 °C for 12–15 h with 0.1–6 mol% of the catalyst. For the rhodium complex, catecholborane was used as a boron source. The reaction was performed in deuterated benzene at room temperature for 30 or 60 min with 0.1 mol% of Rh catalyst. It should be pointed out that, hydroboration of ketones in the presence of precious metals has so far been conducted, in single batch mode, resulting in low productivity of the applied system. The TON (turnover numbers) values for the previously described protocols range from 17 for the palladium dimer complex to 1000 for the rhodium and ruthenium complexes (Fig. 1). Nevertheless, in each case an expensive and probably still active catalyst was sacrificed during the work-up procedure.

Platinum complexes have found application as effective catalysts in the hydroboration of alkenes^{53–56}, alkynes⁵³, allyl halides⁵⁷ and allens⁵⁸. Our group has already proved that platinum catalysts are effective promoters in hydrosilylation^{59–66}, hydroboration and diboration reactions of unsaturated C≡C bonds⁶⁷. However, the application of platinum complexes in the hydroboration of carbonyl compounds was unexplored until now.

The high activity of Pt catalysts in the functionalization of unsaturated C–C bonds and the lack of scientific reports concerning the application of Pt complexes in the hydroboration of ketones prompted us to explore this field. Herein, we present the results for the catalytic hydroboration of ketones in the presence of a commercially available and easily applied, stable platinum catalyst Pt(PPh₃)₄ followed by the efficient transformation of the obtained boronate ethers into secondary alcohols. Our main goal was to develop a simple and efficient protocol

Previous works:



This work:

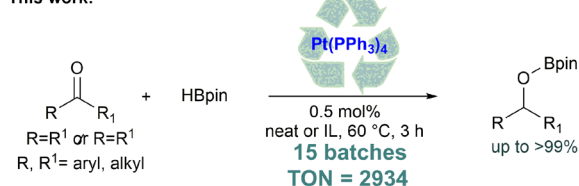


Figure 1. Hydroboration of ketones catalyzed by noble metal complexes.

for the hydroboration of ketones in the presence of Pt catalysts, which could be easily applied in each organic laboratory. Having in mind green chemistry rules, additionally, we proposed an alternative protocol based on the application of the ionic liquid (IL), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([BMIM][NTf₂]), as a greener alternative for VOSS, which are typically used in ketones hydroboration. This approach also permitted catalyst immobilization and its recycling, intensifying the process according to its productivity and effectivity.

Results and Discussion

In the first step of our study, a catalytic screening of various homogeneous and heterogeneous platinum catalysts (platinum black, PtO₂, PtCl₂, PtCl₂(PPh₃)₂, Pt(η²-C₂H₄)(PPh₃)₂ and Pt(PPh₃)₄) was performed in the model reaction of acetophenone (**1a**) with pinacolborane (HBpin) (**2**). The process was carried out without the solvent in an inert atmosphere with 0.5 mol% of Pt-catalyst loading in 18 h at 60 °C. To exclude non-catalytic hydroboration of **1a** with **2** under these conditions, the control experiment without the catalyst was carried out. The borylated ether **3a** was formed with a poor 17% yield (Table 1, entry 1). The non-catalytic hydroboration of ketones is also feasible^{68,69}. However, achieving high conversions requires harsh conditions: a high temperature (80 °C), a high excess of pinacolborane and a long reaction time (24 h)⁶⁹. Additionally, for halogen-substituted acetophenones, these non-catalytic conditions were not sufficient to achieve full conversion of substrates⁶⁹. The heterogeneous catalysts, such as platinum black and PtO₂, showed moderate activity (Table 1, entries 2–3). The hydroboration of **1** with **2a** in the presence of catalysts with the chlorine atom (PtCl₂ and PtCl₂(PPh₃)₂) also proceeded with the moderate conversion of **1a** however, a significant decrease in reaction selectivity was observed. For both systems, the undefined side-products **4** were detected (Table 1, entries 4–5). Pt(PPh₃)₄ and Pt(η²-C₂H₄)(PPh₃)₂ showed a great improvement in the conversion of acetophenone (**1a**). The full conversion and excellent selectivity towards **3a** were only observed for hydroboration of acetophenone (**1a**) with **2** in the presence of commercially available and air-stable Pt(PPh₃)₄ (Table 1, entry 7). For Pt(η²-C₂H₄)(PPh₃)₂, much lower selectivity was observed (Table 1, entry 6). In the next stage of process optimization, the influence of selected catalyst loading, substrates ratio, solvent type, time and temperature were verified (Table 1). The full conversion of **1a** was observed after 3 h with excellent product yield using 0.5 mol% of Pt(PPh₃)₄ (Table 1, entry 8). Shortening the time to 2 h resulted in the incomplete conversion of **1a** (Table 1, entry 9). Solvent choice had no significant influence on process efficiency. The reaction proceeded with quantitative yields in THF and toluene as well as without the solvent (Table 1, entries 10–11). It should be noted that the Pt(PPh₃)₄ was dissolved very well in the substrates mixture, so having in mind green chemistry principles to reduce the amount of solvents, for the next experiments solvent-free conditions

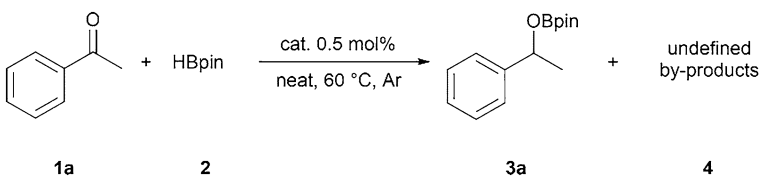
				
1a	2		3a	4
Entry	Catalyst	Time (h)	Conversion of 1a [%] ^a	Selectivity of 3a:4[%] ^a
1	none	18	17	100:0
2	Platinum black	18	49	100:0
3	PtO ₂	18	45	100:0
4	PtCl ₂	18	47	0:100
5	PtCl ₂ (PPh ₃) ₂	18	61	87:13
6	Pt(η ² -C ₂ H ₄)(PPh ₃) ₂	18	77	72:28
7	Pt(PPh ₃) ₄	18	> 99	100:0
8	Pt(PPh ₃) ₄	3	> 99	100:0
9	Pt(PPh ₃) ₄	2	96	100:0
10 ^b	Pt(PPh ₃) ₄	3	99	100:0
11 ^c	Pt(PPh ₃) ₄	3	99	100:0
12 ^d	Pt(PPh ₃) ₄	3	97	100:0
13 ^e	Pt(PPh ₃) ₄	3	41	100:0
14 ^f	Pt(PPh ₃) ₄	3	94	100:0
15 ^g	Pt(PPh ₃) ₄	3	95	100:0
16 ^h	Pt(PPh ₃) ₄	3	99	100:0

Table 1. Pt catalysts screening for hydroboration of acetophenone (**1a**) with pinacolborane (**2**). Reaction conditions: acetophenone (**1a**) (0.5 mmol), pinacolborane (**2**) (0.6 mmol), 60 °C, argon atmosphere ^aYield was determined using GC–MS analysis ^bReaction in THF ^cReaction in toluene ^dCatalyst loading 0.25 mol% ^eRoom temperature ^f50 °C ^gAcetophenone (**1a**) (0.5 mmol), pinacolborane (**2**) (0.5 mmol) ^hAcetophenone (**1a**) (0.5 mmol), catecholborane (**2'**) (0.6 mmol).

were applied. The reduction of catalyst loading from 0.5% to 0.25% provides a slightly lower conversion of **1a** (Table 1, entries 8 and 12). Similarly, lower yields of **3a** were observed when the reaction was performed at room temperature or 50 °C and using an equimolar ratio of reagents **1a** and **2** (Table 1, entries 13–15). Changing the reducing agent from pinacolborane (**2**) to catecholborane (**2'**), resulted in similar acetophenone (**1**) conversions in both cases (Table 1, entry 16).

With the optimized reaction conditions in hand, the substrate scope was determined. Aromatic ketones with electron-donating groups (**1b–f**) were smoothly transformed into borylated ethers with high yields (> 86%). A slightly lower conversion was observed for 3-methylacetophenone (**1c**). The replacement of the methyl group with the sterically hindered *t*-Bu substituent had no significant influence on the conversion of ketone **1f**. The hydroboration of aromatic ketones with an electron-withdrawing group like nitriles (**1i**) proceeded with quantitative yield. Lower reactivity (74–89%) was observed for aryl ketones possessing halides in *para*-position **1h**, **1j**, **1k**. A significant decrease in product yield was observed for *o*-fluoroacetophenone (**1g**). Extending the time to 18 h, gave the expected product **3g** with very good yields. The hydroboration of another halogenated arylketone, 2-chloroacetophenone (**1i**), furnished product **3i** with quantitative yield. Pt(PPh₃)₄ was found to be the selective catalyst for the reduction of ketone, in the presence of nitrile (**3l**), ester (**3m**) and amide (**3n**) groups. The reactions proceeded with an excellent substrates conversion. To investigate the selectivity of hydroboration of carbonyl groups in both ketones and aldehydes, the equimolar ratio of acetophenone (**1a**), benzaldehyde, and pinacolborane (**2**) was used in the presence of a platinum catalyst. The experiment demonstrated that hydroboration of more reactive aldehyde is privileged (see Supplementary Information for details). In the case of diketones (**1o**), both C=O bonds were reduced to hydroxyl groups when 2 equiv. of pinacolborane were used. More bulky ketones with 2-naphthyl (**1p**) or 4-biphenyl (**1q**) substituents also provide products with 99% conversion of ketone and excellent selectivity for products **3p** and **3q** respectively. In the next step of our study, the substrate scope was extended to include diarylsubstituted ketones (**1r–1t**). Hydroboration of benzophenone (**1r**) in the optimized reaction conditions gave product **3r** with moderate reaction yield; however, extending the reaction time to 18 h provided **3r** in almost quantitative yield. Keeping in mind the moderate reactivity of 2-fluorosubstituted acetophenone **1g**, we were surprised to find that for analogue 2-fluorobenzophenone (**1s**) the reaction proceeded in 3 h with a high (84%) yield of **3s**. In turn, hydroboration of 4,4-dibromobenzophenone (**1t**) gave **3t** with excellent yield; however, twofold excess of **2** was needed. The catalytic method was effective for heteroaromatic compounds (**1u–1w**). Specifically, 2-acetylpyridine (**1u**) and 2-acetylfuran (**1w**) underwent hydroboration with nearly quantitative yields. However, for 2-acetylthiophene (**1v**), the reaction efficiency was slightly lower, reaching 92% yield. Notably, the developed catalytic system was less suitable for aliphatic compounds, which was exemplified by 5-nonanone (**1x**). Additionally, the reactions with aromatic substrates such as *o*-(trifluoromethyl)acetophenone and *o*-iodoacetophenone (**1y–z**) gave very low products yields. We attribute this limitation to the steric effects of the *ortho*-positioned groups on the phenyl ring in these substrates. All O-borylated ethers (**3**) were easily converted to the corresponding alcohols (**5**) via simple hydrolysis with 1 M NaOH solution in methanol. Moreover, it was possible to proceed hydrolysis in a one-pot procedure without isolation of borylated ether **3a–w** intermediates. This approach allowed the process time to be shortened by the elimination of time-consuming separation steps of intermediates and reduction of the amount of volatile organic solvents used for purification (Fig. 2). Final products were purified by column chromatography using 9:1 hexane/ethyl acetate, 3:7 hexane/ethyl acetate (in case of **5o**) or 7:3 hexane/ethyl acetate in case of (**5n**), as an eluent. All obtained products **3** and **5** were characterized by nuclear magnetic resonance (¹H NMR) and quantitative product extraction, the ionic liquid was dried under vacuum to remove any residual of the organic phase. The post-reaction mixture was characterized by GC–MS and ¹H NMR analyses.

Generally, the hydroboration of ketones under solvent-free conditions at 60 °C with other noble metal catalysts (palladium^{48,49} and ruthenium⁵⁰) has been described in the literature. However, by employing the platinum catalyst system, we were able to shorten the reaction time, and catalyst loading compared to the previously described systems.

In the next stage of our study, we verified the feasibility of the catalyst recycling by its immobilization in ILs. Based on our experience in the application of ILs in hydroboration and borylative coupling reactions^{70–72}, we examined several ILs with melting points below room temperature (RTILs), such as 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([BMIM][NTf₂]), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonfyl)imide ([BMPyrr][NTf₂]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF₄]) and 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate ([BMPyrr][OTf]), for catalyst immobilization. When the reaction of **1a** with **2** was carried out in the tested ionic liquids, without the addition of a platinum catalyst, no formation of reaction products was observed. The model reaction of acetophenone (**1a**) with pinacolborane (**2**), under standard reaction conditions (3 h at 60 °C, 0.5 mol% of Pt(PPh₃)₄) was used for the immobilization and catalyst recyclability test. Pt(PPh₃)₄ was immobilized in 150 mg of IL. A pale-yellow homogeneous solution was obtained after mixing the catalyst with the ionic liquid for 5 min. The reaction was carried out in a single-phase system since the reactants were highly soluble in the ionic liquid as well. After the reaction, the products were extracted with *n*-heptane. When the non-polar solvent was added, a two-phase system was formed. After quantitative product extraction, the ionic liquid was dried under vacuum to remove any residual of the organic phase. The post-reaction mixture was characterized by GC–MS and ¹H NMR analyses. For [BMPyrr][NTf₂], [BMPyrr][OTf], and [BMIM][BF₄], we were able to observe poor conversion of substrate **1a** after 3 h. The best results were obtained by immobilization of the platinum catalyst in [BMIM][NTf₂]. Almost quantitative (> 99%) formation of **3a** was observed in the first 10 cycles. Afterwards, an insignificant, gradual decrease in catalyst activity was noticed. To pinpoint the onset of catalyst deactivation, an experiment with a shorter reaction time of 2 h was conducted (Fig. 3). The catalyst's gradual deactivation became apparent around the 3rd batch. This suggests that the initial reaction rate slightly decreases after each subsequent run, likely due to catalyst deactivation. It may be caused by introducing moisture or oxygen during the extraction process, and the formation of an inactive

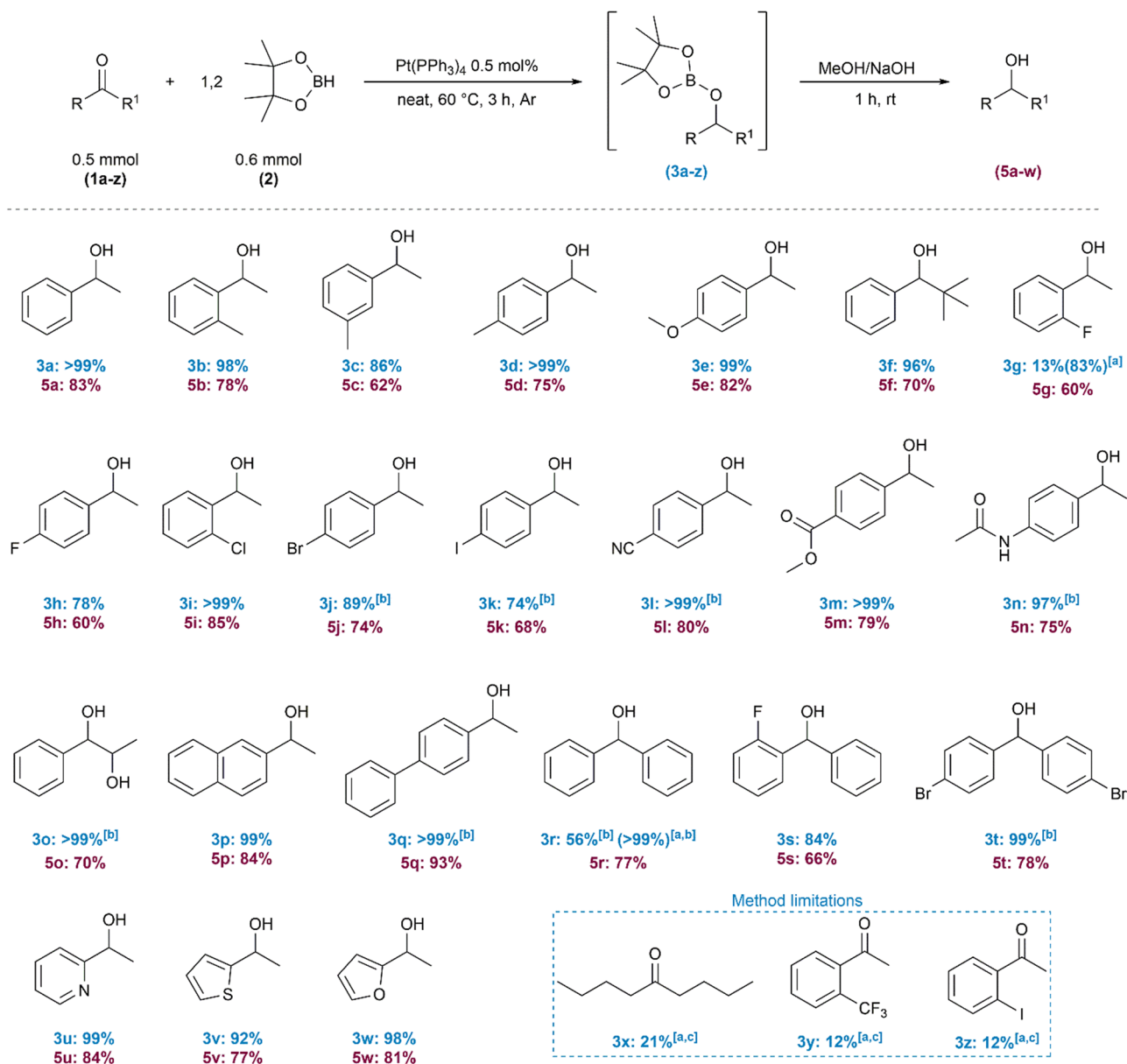


Figure 2. Substrate scope for hydroboration of ketones (**1a–z**) catalyzed by $\text{Pt(PPh}_3)_4$. Yields were based on ^1H NMR spectroscopy. (a) 18 h, (b) HBpin (2 mmol); (c) yield based on GC-MS analysis.

catalyst form (homogeneous or heterogeneous). However, we were unable to determine an inactive form of the catalyst. In total, 15 catalytic runs (3 h each) were conducted with the accumulative TON value 2934 (Fig. 3). Catalyst immobilization not only influences process effectivity but also allows for expensive catalyst reuse. It is especially important in the case of metals which have limited abundance. To determine the leaching of metal from the ionic liquid after the 1st, 2nd and 12th runs, ICP-MS analyses were carried out. The amount of platinum in the extracts was at an almost negligible level (not higher than 0.35 ppm), which proves sufficient catalyst immobilization and proper choice of the extractant.

In the next stage of the study, to demonstrate the versatility of our protocol, we utilized the catalyst immobilized within an ionic liquid for a series of repetitive batches. Each reaction run involved the reduction of a different substrate. The same procedure that had been previously employed for hydroboration of model acetophenone in the presence of $\text{Pt(PPh}_3)_4$ @[BMIM][NTf₂] was applied. The reaction runs were executed sequentially with various ketones: *p*-methylacetophenone (**1d**) in the 1st run, *p*-methoxyacetophenone (**1e**) in the 2nd run, *o*-chloroacetophenone (**1i**) in the 3rd and 2-acetylnaphthalene (**3p**) in the 4th run. Nearly quantitative yields of the expected products (**3d–e**, **3i** and **3p**) were achieved (Fig. 4). After each run, the reaction mixture was separated from the catalytic system by *n*-heptane extraction and drying of the catalytic system under vacuum to remove any residual of the organic phase. It is worth noting that the extraction process was highly effective. The extracted solutions were devoid of reactants from previous cycles, which ^1H NMR and GC-MS confirmed analyses.

To better understand catalyst immobilization nature and reaction mechanism the composition of the catalytic system was investigated. After mixing the catalyst with the ionic liquid, and heating the mixture for 3 h in 60 °C,

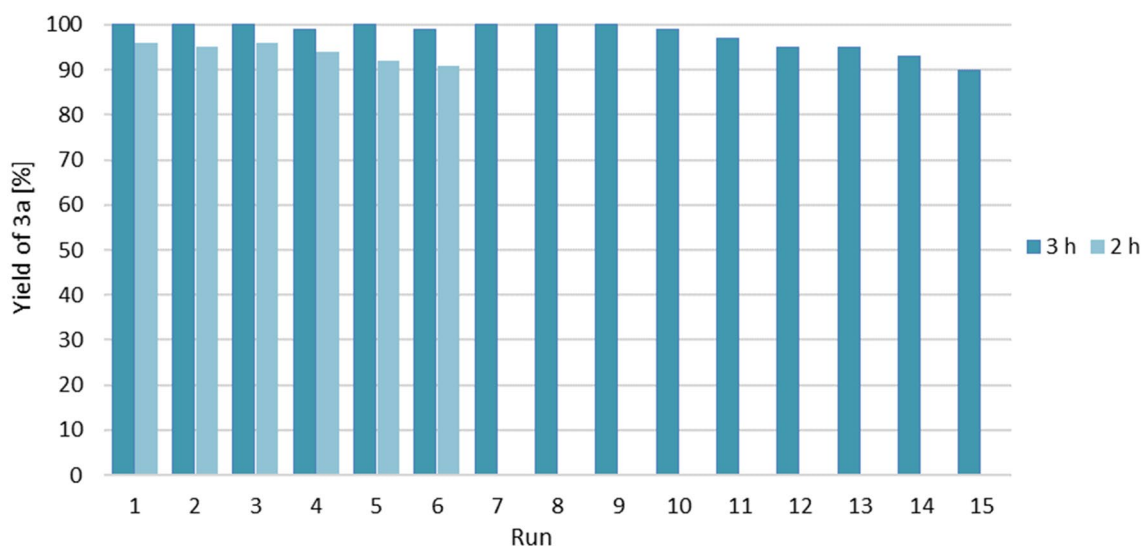


Figure 3. Yields of **3a** in the repetitive batch hydroboration of **1a** (0.5 mmol) with **2** (0.6 mmol) using 0.5 mol% $\text{Pt}(\text{PPh}_3)_4$ @ $[\text{BMIM}][\text{NTf}_2]$ at 60 °C in 2 and 3 h. Yields were determined by GC–MS and ^1H NMR analyses.

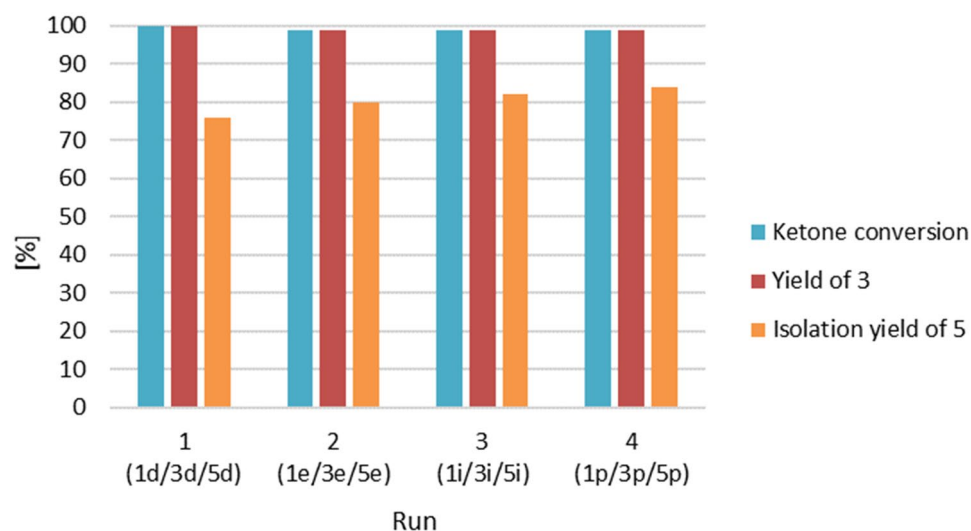


Figure 4. Hydroboration/extraction sequences performed in 0.5 mol% $\text{Pt}(\text{PPh}_3)_4$ @ $[\text{BMIM}][\text{NTf}_2]$ catalytic system for series of different aryl ketones (**1d–e**, **1i** and **1p**).

any new signals in the ^1H and ^{31}P NMR spectra were observed (See SI). This suggests that a new catalyst-ionic liquid adduct is not formed, and there is physical immobilization of $\text{Pt}(\text{PPh}_3)_4$ in $[\text{BMIM}][\text{NTf}_2]$. Therefore, the reaction mechanism was investigated in a deuterated organic solvent without the involvement of IL (Fig. 5). The first step of the mechanism is believed to proceed via the dissociation of PPh_3 (appearance of free PPh_3 signal at -6.3 ppm in ^{31}P NMR spectrum) followed by oxidative addition of HBpin to Pt center. The low temperature ^1H NMR spectrum of the reaction mixture contains a platinum-hydride, high-field shifted resonance at $\delta = -16.31$ ppm [$^1J_{(\text{Pt-H})} = 1215$ Hz]⁷³. The dissociation of another phosphine ligand and coordination of ketone followed by its insertion generates specie (specie III), which after reductive elimination gives O-borylated ether **3a** and regenerates the catalysts (disappearance of platinum-hydride signal) (See SI).

Conclusion

In conclusion, a new catalytic method for the hydroboration of ketones was developed using a simple and commercially available $\text{Pt}(\text{PPh}_3)_4$ catalyst for the first time. It was found that 0.5 mol% of the catalyst is required to obtain excellent or very good conversion of various ketones possessing both electron-withdrawing and electron-donating functional groups such as methyl, methoxy, halides, nitrile, ester and amide. Moreover, the reaction time was shortened by up to 3 h in comparison to non-catalytic processes, which required higher temperatures and much longer reaction times. The obtained borylated ethers were easily transformed to the corresponding alcohols, which are important building blocks in organic and medicinal chemistry. Moreover, solvent-free

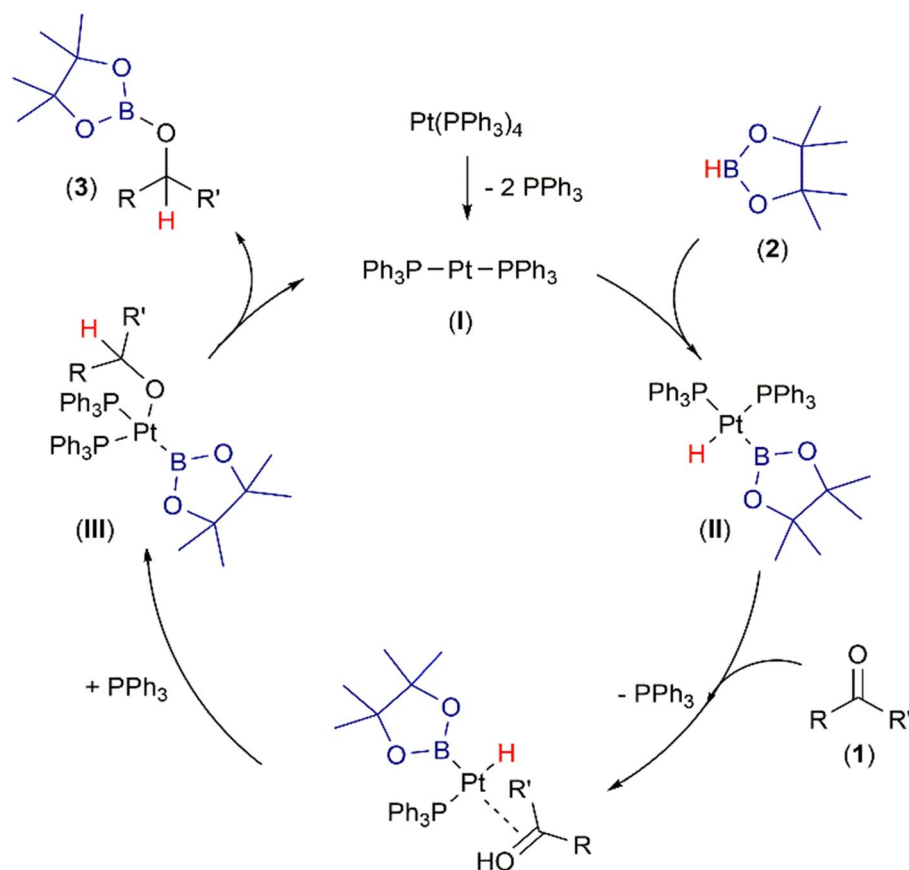


Figure 5. Proposed mechanism of $\text{Pt}(\text{PPh}_3)_4$ -catalyzed hydroboration of ketones.

conditions, as well as a one-pot procedure providing alcohols, without the isolation of the intermediates, are in line with the rules of green chemistry. The proposed reaction mechanism involves the oxidative addition of HBpin to the Pt center, followed by ketone coordination and reductive elimination of product (3) with the catalyst regeneration. Additionally, having in mind the costs of the catalyst as well as the limited abundance of platinum, the immobilization of $\text{Pt}(\text{PPh}_3)_4$ in ionic liquids was developed. $\text{Pt}(\text{PPh}_3)_4@[\text{BMIM}][\text{NTf}_2]$ allowed for effective catalyst recycling (up to 15 cycles with TON 2934) without a significant drop in catalyst activity and stability. Such strategy has a positive impact on process economy and efficiency.

Methods

Catalytic hydroboration of ketones with subsequent deborylation process – one pot procedure

A Schlenk vessel containing a magnetic stirring bar was charged with $\text{Pt}(\text{PPh}_3)_4$ (0.5 mol%, 3.22 mg). Then, the vessel was evacuated under vacuum and refilled with argon several times. Subsequently, pinacolborane (2) (1.2 eq., 0.6 mmol, 90 μL) or catecholborane (2') (1.2 eq., 0.6 mmol, 72 mg) and ketone (1a–z) (1 eq., 0.5 mmol) were added. The reaction was carried out for 3 h at 60 $^\circ\text{C}$. After this time, the crude reaction mixture was analysed by ^1H NMR and GC–MS analyses. Afterwards, the reaction mixture was quenched with 1 M solution of NaOH in methanol (1 mL) and allowed to stir for 1 h. Then methanol was evaporated, and 5 mL of water was added. The product was extracted with diethyl ether (3 $\times$ 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and purified by column chromatography using 9:1 hexane/ethyl acetate (for product 5o 3:7 hexane/ethyl acetate and for product 5n 7:3 hexane/ethyl acetate) as the eluent.

Hydroboration in a $\text{Pt}(\text{PPh}_3)_4@[\text{BMIM}][\text{NTf}_2]$ system under repetitive batch mode

Dry $[\text{BMIM}][\text{NTf}_2]$ (0.38 mol, 150 mg) and $\text{Pt}(\text{PPh}_3)_4$ (0.5 mol%, 3.22 mg) were added to a Schlenk vessel equipped with a magnetic stirring bar and vigorously stirred for 5 min. Then, pinacolborane (2) (0.6 mmol, 77 mg, 90 μL) and ketone (0.5 mmol) were added to the bright yellow $\text{Pt}(\text{PPh}_3)_4@[\text{BMIM}][\text{NTf}_2]$ solution. After 3 h, the products were extracted with dry *n*-heptane (4 $\times$ 1 mL) and analysed by GC–MS and ^1H NMR analyses. The solvent residues were evaporated under vacuum. The $\text{Pt}(\text{PPh}_3)_4@[\text{BMIM}][\text{NTf}_2]$ catalytic system was applied to the next batches according to the procedure described above.

Procedure of mechanistic studies

The Young's NMR tube was charged under the argon with $\text{Pt}(\text{PPh}_3)_4$ (0.0321 mmol, 40 mg) and approx. 0.6 mL of dry CDCl_3 was added. Subsequently, the 1.2 equiv. of HBpin (**2**) (0.0385 mmol, 4.9 mg) was added. The ^1H and ^{31}P NMR spectra were recorded at the low temperature (-40°C). Afterward, to the Young's NMR tube the 1 equiv. of acetophenone (**1a**) (0.0321 mmol, 3.9 mg) was added under the argon and the reaction mixture was stirred over 18 h at 55°C . After that, the low-temperature (-40°C) ^1H NMR was performed.

Data availability

All data generated or analyzed during this study are included in this published article and its supplementary information file.

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Author contributions

B.K.: investigation, methodology and writing original draft; J.S.: mechanistic study, review and editing, work supervision; J.W.: review and editing, work supervision.

Competing interests

The authors declare no competing interests.

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Supporting Information

Pt(PPh₃)₄ and Pt(PPh₃)₄@IL catalyzed hydroboration of ketones

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1. General information

1.1. Materials

Acetophenone, ($\geq 98.5\%$, Carlo Erba), 1-(*o*-tolyl)ethanone (98%, AmBeed), 3-methylacetophenone (97%, Alfa Aesar), 1-(*p*-tolyl)ethanone (97%, AmBeed), 2,2,2-trimethylacetophenone, (97%, Alfa Aesar), 4-methoxyacetophenone (98%, AmBeed), 2'-fluoroacetophenone (98%, AmBeed), 1-(4-fluorophenyl)ethanone (98%, AmBeed), 1-(2-chlorophenyl)ethanone (95%, AmBeed), 4-iodoacetophenone (98%, Sigma-Aldrich), 4-acetylbenzonitrile (97%, AmBeed), benzophenone ($\geq 99\%$, Acros-Organics), 2-fluorobenzophenone (98%, AmBeed), 4,4'-dibromobenzophenone (98%, abcr), 4-acetylbiphenyl (97%, AmBeed), 2-acetylnaphtalene (99%, abcr), methyl 4-acetylbenzoate (99.91%, AmBeed) *N*-(4-acetylphenyl)acetamide (98%, Fluorochem), 1-phenylpropane-1,2-diol (98%, Angene), 5-nonanone (Acros Organics, 98%), 2'-(trifluoromethyl)acetophenone (AmBeed, 98%), 2'-iodoacetophenone (Acros Organics, $>99\%$), 2-acetylpyridine (AmBeed, 98%), 2-acetylfuran (Thermo Scientific, 99%), 2-acetylthiophene (AmBeed, 98%), catecholborane (98%, Sigma-Aldrich), benzaldehyde (Alfa Aesar, $>99\%$), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (97%, Apollo Organics), ethylenebis(triphenylphosphine)platinum(0) (98%, AcrosOrganics), *cis*-dichlorobis(triphenylphosphine)platinum(II) (98%, Angene), platinum(II) chloride (99.9%, abcr), platinum(IV) oxide (Pt, 79-83%, Sigma-Aldrich), platinum black ($\geq 99.95\%$, Sigma-Aldrich), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($\geq 97\%$, Sigma-Aldrich), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (99%, Io-li-tec), 1-butyl-3-methylimidazolium tetrafluoroborate ($\geq 98\%$, Sigma-Aldrich), 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate (97%, Sigma-Aldrich), silica gel (pore size 60Å, 63-200 μm particle size, Sigma-Aldrich), sodium hydroxide (98.8%, Avantor Performance Materials Poland), sodium sulfate, anhydrous ($>99.9\%$, Eurochem), diethyl ether (99.5%, Avantor Performance Materials Poland), ethyl acetate (99%, Avantor Performance Materials Poland), methanol ($\geq 99.9\%$, Stanlab), *n*-heptane ($>99\%$, Sigma-Aldrich), *n*-pentane (99%, Lach-Ner), (chloroform- d_1 (99.8%, Deutero GmbH), dichloromethane- d_2 (99.6%, Deutero GmbH). All chemicals were used without further purification and purchased from commercial sources, except acetophenone, which was purified by vacuum distillation and *n*-pentane and *n*-heptane were dried over NaH and distilled. Ionic liquids were dried overnight under vacuum at 60 °C before use. Tetrakis(triphenylphosphine)platinum(0) was synthesized according to the previously described procedure¹.

1.2 Methods

1.2.1. Nuclear magnetic resonance

The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Ultrashield 300 MHz or Bruker Ascend 400 MHz spectrometers. The ^{11}B NMR spectra were received on Bruker Ascend 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm) with reference to the residual solvent peaks for ^1H and ^{13}C NMR or $\text{BF}_3\text{-Et}_2\text{O}$ for ^{11}B NMR, respectively. The multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), multiplet (m), and broad resonances (br).

1.2.2. Gas chromatography–mass spectrometry

The mass spectra of the products were obtained by GC-MS analysis on a Bruker Scion 436-GC with a 30 m Varian DB-5 0.25 mm capillary column and a Scion SQ-MS mass spectrometry detector (temperature program: 60 °C (3 min), 10 °C/min, 250 °C (20 min)).

1.2.3. Inductively coupled plasma mass spectrometry

In a 50 mL teflon beaker equipped with a stirrer, 150 mg of extract was placed and 2 mL of aqua regia was added. The mixture was heated for 1 h. The mixture was then diluted in demineralized water and filtered. Metal content was determined by inductively coupled plasma-mass spectroscopy (ICP-MS) with a NexION 350D (PerkinElmer).

1.2.4 Elemental analysis

Elemental analyzes were performed using a Vario EL III instrument.

2. Chemoselectivity test of Pt(PPh₃)₄ in hydroboration of ketones and aldehydes

A Schlenk vessel containing a magnetic stirring bar was charged with Pt(PPh₃)₄ (0.5 mol%, 3.22 mg). Then, the vessel was evacuated under vacuum and refilled with argon several times. Subsequently, pinacolborane (**2**) (1 eq., 0.5 mmol, 64 mg), acetophenone (**1a**) (1 eq., 0.5 mmol, 60 mg) and benzaldehyde (1 eq., 0.5 mmol, 53 mg) were added. The reaction was carried out for 3 hours at 60 °C. After this time, the crude reaction mixture was analyzed by ¹H NMR analysis.

3. Product yields in the hydroboration of ketones with pinacolborane (**2**) under repetitive batch mode

Table S1. Yields of **3a** and catalysts leaching for selected runs for the hydroboration of **1a** with **2** in the presence of Pt(PPh₃)₄@[BMIM][NTf₂] catalytic system (3 h, 60 °C).

Cycle number	Yield of 3a (%) ^a	Catalyst leaching [ppm] ^b
1	>99	0.35
2	>99	0.29
3	>99	
4	99	
5	>99	
6	99	
7	>99	
8	>99	
9	>99	
10	99	
11	97	
12	95	0.30
13	95	
14	93	
15	90	

^a Yields were determined by GC-MS and ¹H NMR analyzes. ^b Determined by ICP-MS.

Table S2. Yields of **3a** obtained under repetitive batch hydroboration of **1a** with **2** in the presence of $\text{Pt}(\text{PPh}_3)_4@[\text{BMIM}][\text{NTf}_2]$ catalytic system (2 h, 60 °C).

Cycle number	Conversion of 1a (%) ^a	Yield of 3a (%) ^a
1	96	96
2	95	95
3	96	96
4	94	94
5	92	92
6	91	91

^a Yields were determined by GC-MS and ¹H NMR analyzes.

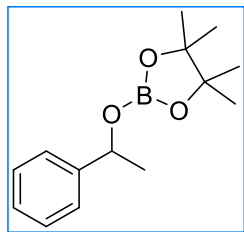
Table S3. Yields of **3a** obtained under repetitive batch hydroboration of **1a** with **2** in the presence of $\text{Pt}(\text{PPh}_3)_4@[\text{BMIM}][\text{NTf}_2]$ catalytic system (3 h, 60 °C).

Cycle number	Conversion of 1 (%) ^a	Yield of 3 (%) ^a	Isolated yield of 5 (%) ^a
1 (1d/3d/5d)	100	100	76
2 (1e/3e/5e)	99	99	80
3 (1i/3i/5i)	99	99	82
4 (1p/3p/5p)	99	99	84

^a Yields were determined by GC-MS and ¹H NMR analyzes.

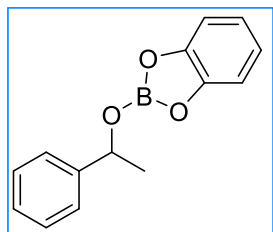
4. Products characterization

4,4,5,5-Tetramethyl-2-(1-phenylethoxy)-1,3,2-dioxaborolane (**3a**)



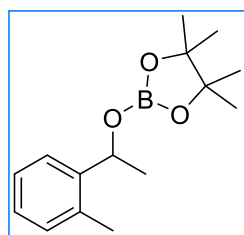
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.31 – 7.28 (m, 2H, Ph), 7.26 – 7.12 (m, 3H, Ph), 5.17 (q, *J*_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.42 (d, *J*_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.16 (s, 6H, C(CH₃)₂), 1.13 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 248(2), 233(27), 190(26), 129(17), 105(100), 77(21), 83(20), 80(16), 59(12), 55(8), 51(6). Characterized as a crude product. Analytical data are in agreement with the literature.^{2,3}

2-(1-Phenylethoxy)-1,3,2-benzodioxaborole (**3a'**)



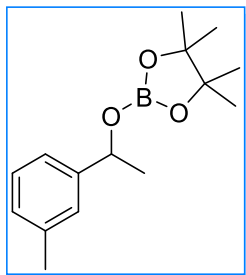
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.54 – 7.45 (m, 2H, Ph), 7.43 – 7.38 (m, 2H, Ph), 7.35 – 7.31 (m, 1H, Ph), 7.13 (m, 2H, Ph), 7.05 – 7.02 (m, 2H, Ph), 5.62 (q, *J*_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 1.70 (d, *J*_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **¹¹B NMR** (128 MHz, CDCl₃, δ, ppm): 23.20. Characterized as a crude product. Analytical data are in agreement with the literature.⁴

4,4,5,5-Tetramethyl-2-(1-(*o*-tolyl)ethoxy)-1,3,2-dioxaborolane (**3b**)



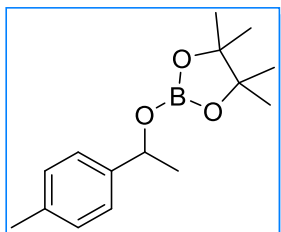
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.53 (d, *J*_{H-H} = 8.6 Hz, 1H, Ph), 7.22 – 7.07 (m, 3H, Ph), 5.43 (q, *J*_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 2.34 (s, 3H, *o*-CH₃), 1.46 (d, *J*_{H-H} = 6.4 Hz, 3H, CH(CH₃)), 1.23 (s, 6H, C(CH₃)₂), 1.20 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 262(1), 247(26), 189(9), 136(8), 129(10), 121(33), 115(12), 116(24), 118(100), 119(62), 93(75), 91(73), 83(20), 77(47), 65(18), 57(13), 55(12). Characterized as a crude product. The analytical data are in agreement with the literature and were additionally supplemented with MS analysis.⁵

4,4,5,5-Tetramethyl-2-(1-(*m*-tolyl)ethoxy)-1,3,2-dioxaborolane (3c**)**



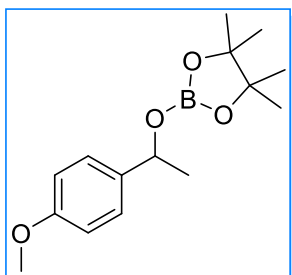
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.22 – 7.14 (m, 3H, Ph), 7.05 (d, *J*_{H-H} = 7.5 Hz, 1H, Ph), 5.22 (q, *J*_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 2.34 (s, 3H, *m*-CH₃), 1.48 (d, *J*_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.25 (s, 6H, C(CH₃)₂), 1.22 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 262(13), 247(52), 204(28), 188(15), 129(22), 119(100), 117(23), 91(31), 83(19), 59(7). Characterized as a crude product. Analytical data are in agreement with the literature.^{2,6}

4,4,5,5-Tetramethyl-2-(1-(*p*-tolyl)ethoxy)-1,3,2-dioxaborolane (3d**)**



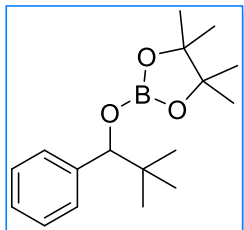
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.26 (d, *J*_{H-H} = 8.1 Hz, 2H, Ph), 7.13 (d, *J*_{H-H} = 7.9 Hz, 2H, Ph), 5.23 (q, *J*_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 2.33 (s, 3H, *p*-CH₃), 1.48 (d, *J*_{H-H} = 6.4 Hz, 3H, CH(CH₃)), 1.25 (s, 6H, C(CH₃)₂), 1.22 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 262(88), 261(17), 184(18), 183(100), 152(10), 115(6), 108(48), 107(25), 77(6), 51(13). Characterized as a crude product. Analytical data are in agreement with the literature.^{2,3}

2-(1-(4-Methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e**)**



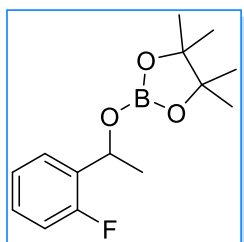
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.29 (d, *J*_{H-H} = 8.5 Hz, 2H, Ph), 6.85 (d, *J*_{H-H} = 8.8 Hz, 2H, Ph), 5.20 (q, *J*_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 3.79 (s, 3H, *p*-OCH₃), 1.47 (d, *J*_{H-H} = 6.4 Hz, 3H, CH(CH₃)), 1.24 (s, 6H, C(CH₃)₂), 1.21 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 278(4), 263(34), 181(8), 135(100), 129(13), 118(5), 105(10), 91(11), 83(7), 77(8), 59(4). Characterized as a crude product. Analytical data are data in agreement with a literature.^{2,3}

2-(2,2-Dimethyl-1-phenylpropoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**)



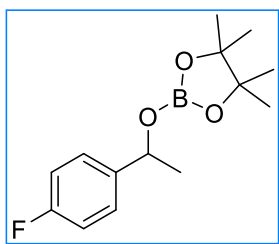
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.36 – 7.25 (m, 5H, Ph), 4.79 (s, 1H, CH(CH₃)), 1.23 (s, 6H, C(CH₃)₂), 1.17 (s, 6H, C(CH₃)₂), 0.93 (s, 9H, (C(CH₃)₃)). **MS (EI) [m/z (%)]**: 290(4), 233(100), 232(24), 151(12), 129(12), 105(14), 91(20), 83(31), 55(11). Characterized as a crude product. The analytical data are in agreement with the literature.⁷

2-(1-(2-Fluorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3g**)



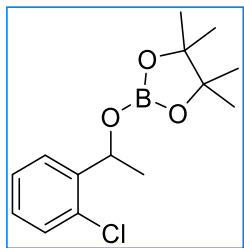
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.57 – 7.51 (m, 1H, Ph), 7.25 – 7.17 (m, 1H, Ph), 7.14 – 7.09 (m, 1H, Ph), 7.01 – 6.94 (m, 1H, Ph), 5.55 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.49 (d, J_{H-H} = 6.2 Hz, 3H, CH(CH₃)), 1.24 (s, 6H, C(CH₃)₂), 1.21 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 266(4), 251(30), 208(25), 207(9), 165(6), 149(47), 129(25), 123(100), 103(28), 96(6), 83(17), 77(17), 59(16), 55(6). Characterized as a crude product. Analytical data are in agreement with the literature and were additionally supplemented with MS analysis.⁸

2-(1-(4-Fluorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3h**)



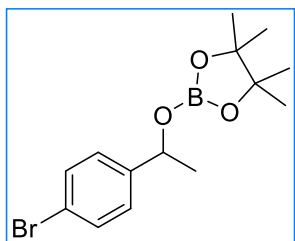
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.35 – 7.29 (m, 2H, Ph), 7.02 – 6.95 (m, 2H, Ph), 5.21 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.46 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.23 (s, 6H, C(CH₃)₂), 1.20 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 266(4), 251(17), 208(13), 193(10), 182(11), 151(5), 129(23), 123(100), 122(44), 103(23), 97(9), 83(24), 77(12), 69(5), 59 (11), 55(10). Characterized as a crude product. Analytical data are in agreement with the literature.^{2,3}

2-(1-(2-Chlorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i**)



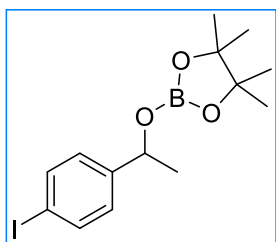
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.65 (dd, J_{H-H} = 7.8, 1.6 Hz, 1H, Ph), 7.34 – 7.26 (m, 2H, Ph), 7.19 (m, 1H, Ph), 5.60 (q, J_{H-H} = 6.3 Hz, 1H, CH(CH₃)), 1.50 (d, J_{H-H} = 6.3 Hz, 3H, CH(CH₃)), 1.27 (s, 6H, C(CH₃)₂), 1.24 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 283(4), 267(28), 247(30), 224(14), 189(46), 161(13), 147(11), 141(36), 139(100), 129(36), 103(54), 83(20), 77(32), 59(15), 55 (8). Characterized as a crude product. Analytical data are in agreement with the literature.^{2,6}

2-(1-(4-Bromophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3j**)



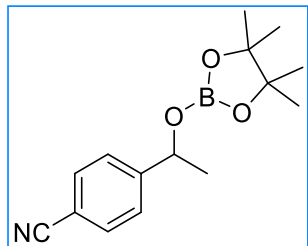
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.45 – 7.41 (m, 2H, Ph), 7.24 (d, J_{H-H} = 8.3 Hz, 2H, Ph), 5.19 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.46 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.24 (s, 6H, C(CH₃)₂), 1.21 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 327(15), 311(22), 268(18), 212(21), 202(40), 200(46), 185(100), 158(55), 147(32), 129(51), 120(13), 108(17), 99(17), 92(46), 82(10), 78(36), 70(30), 60(26). Characterized as a crude product. Analytical data are in agreement with the literature.^{2,3}

2-(1-(4-Iodophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3k**)



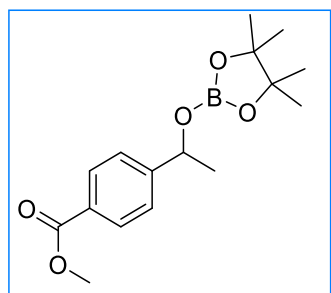
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.64 – 7.60 (m, 2H, Ph), 7.12 – 7.08 (m, 2H, Ph), 5.17 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.44 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.22 (s, 6H, C(CH₃)₂), 1.20 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 374(5), 359(19), 248(21), 233(68), 231(93), 204(9), 189(21), 160(50), 147(100), 129(67), 121(14), 117(16), 102(36), 91(10), 85(24), 78(82), 77(58), 63(6), 59(70), 58(41), 50(31). Characterized as a crude product. The analytical data are in agreement with the literature and were additionally supported with MS analysis.⁹

4-(1-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)benzonitrile (**3l**)



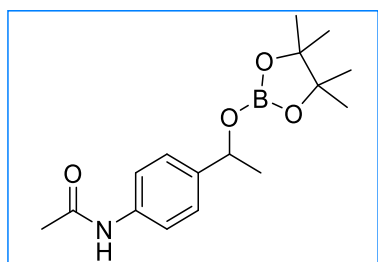
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.58 (d, *J*_{H-H} = 8.3 Hz, 2H, Ph), 7.43 (d, *J*_{H-H} = 8.2 Hz, 2H, Ph), 5.23 (q, *J*_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.44 (d, *J*_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.21 (s, 6H, C(CH₃)₂), 1.18 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 273(13), 258(21), 215(100), 200(22), 173(31), 158(15), 131(42), 130(91), 129(53), 103(25), 85(25), 83(24), 77(12), 59(45), 55(13). Characterized as a crude product. The analytical data are in agreement with the literature and were additionally supplemented with MS analysis.¹⁰

Methyl 4-(1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)benzoate (**3m**)



¹H NMR (300 MHz, CDCl₃, δ, ppm): δ 8.01 – 7.96 (m, 2H, Ph), 7.44 – 7.40 (m, 2H, Ph), 5.27 (q, *J*_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 3.89 (s, 3H, OCH₃), 1.48 (d, *J*_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.23 (s, 6H, C(CH₃)₂), 1.20 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 306(2), 291(37), 275(13), 263(19), 248(44), 223(12), 189(100), 175(13), 163(92), 147(21), 131(44), 129(44), 103(39), 91(20), 83(31), 78(19), 59(43). Characterized as a crude product. Analytical data are in agreement with the literature.¹¹

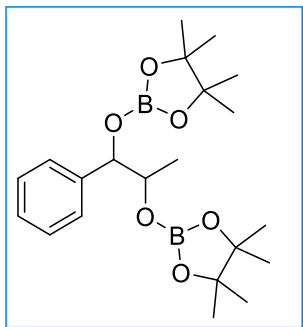
N-(4-(1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)phenyl)acetamide (**3n**)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.74 (s, 1H, NH), 7.47 – 7.42 (m, 2H, Ph), 7.30 – 7.25 (m, 2H, Ph), 5.19 (q, *J* = 6.4 Hz, 1H, CH(CH₃)), 2.13 (s, 3H, C(CH₃)), 1.45 (d, *J* = 6.5 Hz, 3H, CH(CH₃)), 1.23 (s, 6H, C(CH₃)₂), 1.20 (s, 6H, C(CH₃)₂). **¹³C NMR** (75 MHz, CDCl₃, δ, ppm): 168.66(CO), 140.55 (Ph), 137.10(Ph), 126.08(Ph), 119.89 (Ph), 83.28 (C(CH₃)₂), 72.34, (C(CH₃)), 24.67 C(CH₃), 24.64(C(CH₃)₂), 24.62 CH(CH₃). **¹¹B NMR** (128 MHz, CDCl₃, δ, ppm): 22.31. **MS (EI) [m/z (%)]**: 305(10), 290(100), 248(17), 237(43), 215(51), 161(39), 137(82), 129(39), 119(81), 91(20), 77(90), 59(67). **Elem. Anal.** calcd (%) for

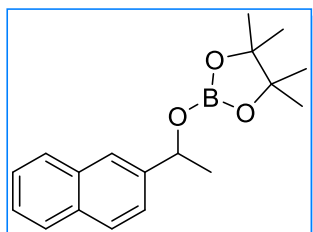
C₁₆H₂₄BNO₄: C, 62.97; H, 7.93; found C, 63.02; H, 7.99. Colorless liquid. Isolation yield 89% (150.7 mg).

2,2'-((1-Phenylpropane-1,2-diyl)bis(oxy))bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**3o**)



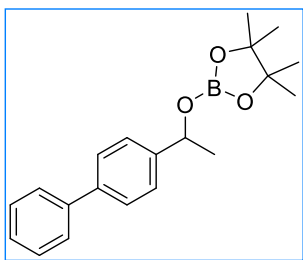
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.40 – 7.23 (m, 5H, Ph), 5.02 (d, *J*_{H-H} = 5.2 Hz, 0.82H, CHCH₂-*syn*), 4.87 (d, *J*_{H-H} = 7.4 Hz, 0.18H, CHCH₂-*anti*), 4.82 – 4.74 (m, 0.18H, CHCH₂-*anti*), 4.34 – 4.17 m, 0.82H, (CHCH₂-*syn*), 1.27 – 1.14 (m, 27H, CH(CH₃) overlap). **¹³C NMR** (101 MHz, CDCl₃, δ, ppm): 140.26 (Ph), 127.99(Ph), 127.49(Ph), 127.03(Ph), 82.98(C(CH₃)₂), 82.64 (C(CH₃)₂), 79.45 (CHCH₂), 74.27(CHCH₂), 24.75 (C(CH₃)₂), 24.69 (C(CH₃)₂), 24.63 (C(CH₃)₂), 24.56 (C(CH₃)₂), 17.01 (CH(CH₃)). **¹B NMR** (128 MHz, CDCl₃, δ, ppm): 22.20, 21.08. **MS (EI) [m/z (%)]**: 404(2), 346(3), 303(3), 289(4), 259(12), 241(12), 233(100), 185(13), 155(12), 129(5), 117(11), 82(8), 55(10), 43(9). **Elem. Anal.** calcd (%) for C₂₁H₃₄B₂O₆: C, 62.42; H, 8.48; found C, 62.29; H, 8.41. Colorless liquid. Isolation yield 90% (196.6 mg).

4,4,5,5-Tetramethyl-2-(1-(naphthalen-2-yl)ethoxy)-1,3,2-dioxaborolane (**3p**)



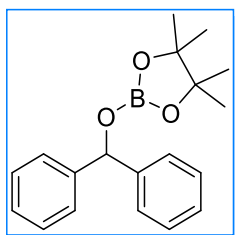
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.88 – 7.81 (m, 4H, napht), 7.54 – 7.43 (m, 3H, napht), 5.44 (q, *J*_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.60 (d, *J*_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.27 (s, 6H, C(CH₃)₂), 1.24 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 298(15), 283(37), 240(9), 215(6), 155(100), 154(24), 153(28), 129(22), 115(7), 83(7), 59(6). Characterized as a crude product. The analytical data are in agreement with the literature and were additionally supplemented with MS analysis².

2-(1-([1,1'-Biphenyl]-4-yl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3q**)



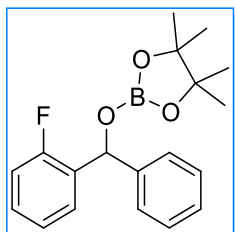
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.47 – 7.41 (m, 4H, Ph), 7.34 – 7.27 (m, 4H, Ph), 7.19 (m, 1H, Ph), 5.17 (q, *J*_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.41 (d, *J*_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.12 (s, 6H, C(CH₃)₂), 1.09 (s, 6H, C(CH₃)₂). **¹³C NMR** (101 MHz, CDCl₃, δ, ppm): 143.7 (Ph), 141.0 (Ph), 140.1 (Ph), 128.8 (Ph), 127.2 (Ph), 127.1 (Ph), 127.0 (Ph), 125.8 (Ph), 82.8 (C(CH₃)₂), 72.4 (CH(CH₃)), 25.5 (C(CH₃)₂), 24.6 (CH(CH₃)). **¹¹B NMR** (128 MHz, CDCl₃, δ, ppm): 22.24. **MS (EI) [m/z (%)]**: 324(4), 309(8), 262(81), 261(18), 198(12), 183(100), 181(19), 155(17), 152(19), 129(9), 108(35), 107(22), 77(14), 51(17). **Elem. Anal.** calcd (%) for C₂₀H₂₅BO₃: C, 74.09; H, 7.77; found C, 76.16; H, 7.61. White solid. Isolation yield 99% (160.1 mg). The compound **3q** was synthesized and characterized for the first time.

2-(Benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3r)



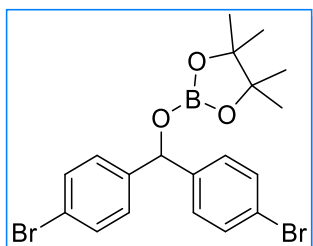
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.41 – 7.37 (m, 4H, Ph), 7.32 – 7.27 (m, 4H, Ph), 7.25 – 7.20 (m, 2H, Ph), 6.18 (s, 1H, CH(Ph)₂), 1.20 (s, 12H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 310(3), 252(23), 227(35), 210(17), 183(15), 167(100), 165(45), 152(21), 105(7), 84(22), 77(6), 59(7). Characterized as a crude product. Analytical data are in agreement with the literature.^{2,12}

2-((2-Fluorophenyl)(phenyl)methoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3s)



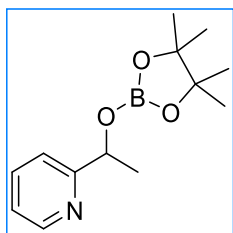
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.53 – 7.49 (m, 1H, Ph), 7.36 (dd, *J*_{H-H} = 7.5, 1.7 Hz, 2H, Ph), 7.25 – 7.21 (m, 2H, Ph), 7.19 – 7.12 (m, 2H, Ph), 7.07 – 7.04 (m, 1H, Ph), 6.93 – 6.90 (m, 1H, Ph), 6.44 (s, 1H, CH(Ph)₂), 1.13 (s, 12H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 328(4), 270(9), 245(18), 227(44), 201(9), 185(100), 183(38), 170(8), 165(50), 84(21), 59(9). Characterized as a crude product. The analytical data are in agreement with the literature and were additionally supplemented with MS analysis.¹³

2-(Bis(4-bromophenyl)methoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3t**)



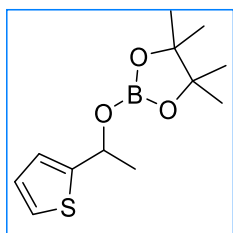
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.35 (d, *J*_{H-H} = 8.4 Hz, 4H, Ph), 7.14 (d, *J*_{H-H} = 8.4 Hz, 4H, Ph), 5.99 (s, 1H, CH(Ph)₂), 1.12 (s, 12H, C(CH₃)₂). **¹³C NMR** (101 MHz, CDCl₃, δ, ppm): 141.7 (C(COH)), 131.6 (Ph), 128.3 (Ph), 121.7 (CBr), 83.4 (C(CH₃)₂), 76.8 (PhCPh), 24.7 (C(CH₃)₂). **¹¹B NMR** (128 MHz, CDCl₃, δ, ppm): 22.42. **MS (EI) [m/z (%)]**: 468(5), 410(5), 278(44), 277(94), 201(28), 199(16), 185(35), 183(55), 165(23), 152(14), 129(11), 84(22), 82(19), 77(100), 63(11). **Elem. Anal.** calcd (%) for C₁₉H₂₁BBr₂O₃: C, 48.76; H, 4.52; found C, 59.09; H, 4.50. White solid. Isolation yield 99% (231.6 mg). The compound **3q** was synthesized and characterized for the first time.

2-(1-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)pyridine (**3u**)



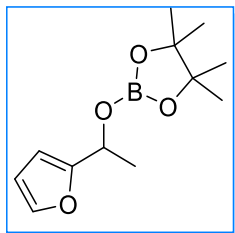
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.67 – 8.57 (m, 1H, Ph), 8.03 – 7.92 (m, 1H, Ph), 7.53 – 7.43 (m, 2H, Ph), 5.25 (q, *J*_{H-H} = 6.6 Hz, 1H, CH(CH₃)), 1.58 (d, *J*_{H-H} = 6.7 Hz, 3H, CH(CH₃)), 1.33 (s, 6H, C(CH₃)₂), 1.30 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 249(2), 234(11), 191(73), 190(32), 150(54), 149(87), 148(35), 133(40), 132(47), 105(100), 79(41), 78(65). Characterized as a crude product. The analytical data are in agreement with the literature and were additionally supplemented with MS analysis.¹⁴

4,4,5,5-Tetramethyl-2-(1-(thiophen-2-yl)ethoxy)-1,3,2-dioxaborolane (**3v**)



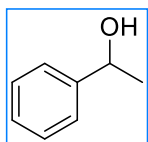
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.20 (dd, *J*_{H-H} = 4.9, 1.4 Hz, 1H, CHS), 6.98 – 6.91 (m, 2H, CHCH), 5.48 (q, *J*_{H-H} = 6.4, 1H, CH(CH₃)), 1.60 (d, *J*_{H-H} = 6.4 Hz, 3H, CH(CH₃)), 1.25 (s, 6H, C(CH₃)₂), 1.24 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 254(17), 239(100), 196(27), 171(52), 157(11), 128(26), 111(87), 84(11), 57(10), 43(27). Characterized as a crude product. Analytical data are in agreement with the literature and were additionally supplemented with MS analysis.¹⁵

2-(1-(Furan-2-yl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3w**)



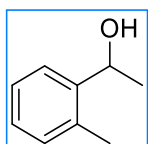
¹H NMR (400 MHz, CDCl₃, δ, ppm): δ 7.32 (s, 1H, CHO), 6.31 – 6.24 (m, 1H, CHCH), 6.24 – 6.18 (m, 1H, CHCH), 5.23 (q, *J*_{H-H} = 6.6 Hz, 1H, CH(CH₃)), 1.54 – 1.51 (m, 3H, CH(CH₃)), 1.24 (s, 12H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 254(15), 237(10), 223(62), 195(16), 155(52), 129(76), 95(100), 94(39), 67(22), 43(39). Characterized as a crude product. The analytical data are in agreement with the literature and were additionally supplemented with MS analysis.¹⁵

1-Phenylethan-1-ol (**5a**)



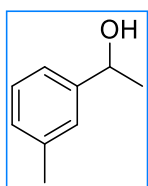
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.37 – 7.27 (m, 4H, Ph), 7.26 – 7.19 (m, 1H, Ph), 4.86 (q, *J*_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 1.77 (s, 1H, OH), 1.46 (d, *J*_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 122(21), 107(80), 105(12), 80(7), 79(100), 78(27), 77(63), 64(3), 52(6), 50(24). Colorless liquid. Isolation yield 83% (50.6 mg). Analytical data are in agreement with the literature.^{16,17}

1-(2-Tolyl)ethan-1-ol (**5b**)



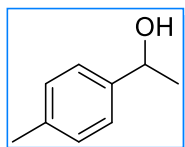
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.45 (d, *J*_{H-H} = 7.3 Hz, 1H, Ph), 7.20 – 7.15 (m, 1H, Ph), 7.14 – 7.05 (m, 2H, Ph), 5.06 (q, *J*_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 2.28 (s, 3H, *o*-CH₃), 1.80 (brs, 1H, OH), 1.40 (d, *J*_{H-H} = 6.4 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 136(5), 121(74), 118(64), 93(100), 91(91), 77 (47), 65(28), 63 (9), 51(14). Colorless liquid. Isolation yield 78% (53 mg). Analytical data are in agreement with the literature.¹⁶

1-(3-Tolyl)ethan-1-ol (**5c**)



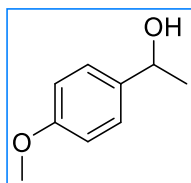
¹H NMR (300 MHz, CD₂Cl₂, δ, ppm): 7.30 – 7.12 (m, 4H, Ph), 4.82 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 2.82 (s, 1H, OH), 2.41 (s, 3H, *m*-CH₃), 1.47 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 136(27), 121(58), 93(100), 92(25), 91(75), 78(7), 65(22), 60(11), 51(11). Colorless liquid. Isolation yield 62% (42.2 mg). Analytical data are in agreement with the literature.^{16,18}

1-(4-Tolyl)ethan-1-ol (5d)



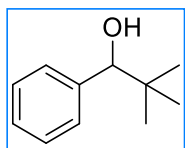
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.19 (d, J_{H-H} = 8.1 Hz 2H, Ph), 7.09 (d, J_{H-H} = 7.9 Hz, 2H, Ph), 4.78 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 2.28 (s, 3H, *p*-CH₃), 1.91 (s, 1H, OH), 1.41 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 136(30), 121(100), 118(8), 115(9), 93(82), 91(84), 78(14), 77(33), 65(22), 63(13), 51(20). Colorless liquid. Isolation yield 75% (51 mg). Analytical data are in agreement with the literature.¹⁶

1-(4-Methoxyphenyl)propan-1-ol (5e)



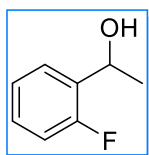
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.32 – 7.27 (m, 2H, Ph), 6.90 – 6.86 (m, 2H, Ph), 4.84 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 3.80 (s, 3H, *p*-OCH₃), 1.89 (brs, 1H, OH), 1.47 (d, J_{H-H} = 6.4 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 152(24), 137(100), 134(13), 119(9), 109(66), 94(39), 91(17), 77(38), 65(17), 51(9). Colorless liquid. Isolation yield 82% (62.4 mg). Analytical data are data in agreement with the literature.¹⁶

2,2-Dimethyl-1-phenylpropan-1-ol (5f)



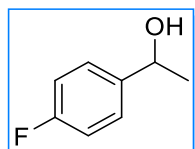
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.36 – 7.27 (m, 5H, Ph), 4.42 (s, 1H, CH(CH₃)), 1.85 (brs, 1H, OH), 0.95 (s, 9H, (C(CH₃)₃)). **MS (EI) [m/z (%)]**: 164(3), 107(100), 79(57), 77(26), 57(16), 51(6). Pale yellow solid. Isolation yield 70% (57.5 mg). Analytical data are in agreement with the literature.¹⁹

1-(2-Fluorophenyl)ethan-1-ol (5g)



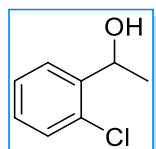
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.52 – 7.46 (m, 1H, Ph), 7.29 – 7.20 (m, 1H, Ph), 7.18 – 7.12 (m, 1H, Ph), 7.05 – 6.99 (m, 1H, Ph), 5.20 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 1.83 (s, 1H, OH), 1.52 (d, J_{H-H} = 6.9 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 140(18), 126(7), 124(100), 97(66), 96(11), 95(8), 77(34), 75(10), 62(4), 51(12). Colorless liquid. Isolation yield 60% (42.5 mg). Analytical data are in agreement with the literature.^{20,21}

1-(4-Fluorophenyl)ethan-1-ol (5h)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.25 – 7.14 (m, 4H, Ph), 4.78 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.75 (s, 1H, OH), 1.39 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 140(14), 125(100), 98(91), 96(44), 83(7), 77(44), 71(9), 57(13), 51 (18). Colorless liquid. Isolation yield 60% (42 mg). Analytical data are in agreement with the literature.^{16,22}

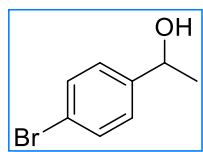
1-(2-Chlorophenyl)ethan-1-ol (5i)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.60 (dd, J_{H-H} = 7.6 Hz, 1.7 Hz, 1H, Ph), 7.35 – 7.27 (m, 2H, Ph), 7.23 – 7.17 (m, 1H, Ph), 5.30 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.85 (s, 1H, OH), 1.50 (d, J_{H-H} = 6.4 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 155(15), 141(86), 113(33), 77(100), 75 (12), 70(6), 51(25). Colorless liquid. Isolation yield 85% (66.6 mg). Analytical data are in agreement with the literature.^{3,23}

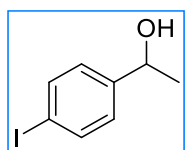
1-(4-Bromophenyl)ethan-1-ol

(5j)



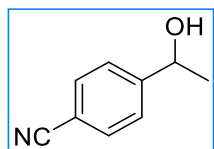
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.46 (d, J_{H-H} = 8.4 Hz, 2H, Ph), 7.23 (d, J_{H-H} = 8.4 Hz, 2H, Ph), 4.84 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 2.04 (s, 1H, OH), 1.46 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 202(25), 201(4), 200(25), 187(76), 185(85), 159(21), 157(25), 121(18), 104(6), 78(47), 77(100), 63(6), 51(34). Colorless liquid. Isolation yield 74% (74.4 mg). Analytical data are in agreement with the literature.^{19,24}

1-(4-Iodophenyl)ethan-1-ol (5k)



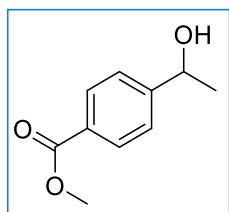
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.72-7.62 (m, 2H, Ph), 7.17-7.07 (m, 2H, Ph), 4.85 (q, $J_{H-H} = 6.5$ Hz, 1H, CH(CH₃)), 1.80 (s, 1H, OH), 1.46 (d, $J_{H-H} = 6.5$ Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 248(47), 233(90), 205(10), 127(9), 121(10), 116(8), 105(14), 91(7), 78(100), 77(37), 51(30), 50(21). Yellow solid. Isolation yield 68% (84.3 mg). Analytical data are in agreement with the literature.²⁵

4-(1-Hydroxyethyl)benzonitrile (5l)



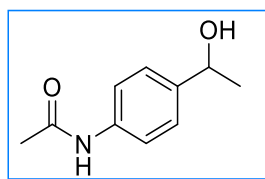
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.63 (d, $J_{H-H} = 8.3$ Hz, 2H, Ph), 7.48 (d, $J_{H-H} = 8.2$ Hz, 2H, Ph), 4.96 (q, $J_{H-H} = 6.5$ Hz, 1H, CH(CH₃)), 1.95 (s, 1H, OH), 1.49 (d, $J_{H-H} = 6.5$ Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 147(11), 132(100), 104(69), 77(21), 76(12), 51(14). Colorless liquid. Isolation yield 80% (58.9 mg). Analytical data are in agreement with the literature.²⁶

Methyl 4-(1-hydroxyethyl)benzoate (5m)



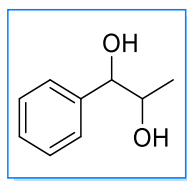
¹H NMR (400 MHz, CDCl₃, δ, ppm): δ 8.01 – 7.95 (m, 2H, Ph), 7.43 – 7.39 (m, 2H, Ph), 4.93 (q, $J_{H-H} = 6.5$ Hz, 1H, CH(CH₃)), 3.89 (s, 3H, OCH₃), 2.25 (brs, 1H, OH), 1.48 (d, $J_{H-H} = 6.5$ Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 180(2), 165(55), 149(16), 137 (94), 132(8), 121(13), 104(45), 91(49), 77(100), 63(7), 63(7), 56(68), 51(30). Colorless liquid. Isolation yield 79% (71.2 mg). Analytical data are in agreement with the literature.¹⁸

N-(4-(1-hydroxyethyl)phenyl)acetamide (5n)



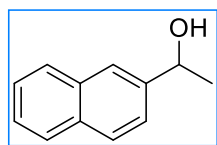
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.50 – 7.41 (m, 2H, Ph), 7.38 – 7.27 (m, 3H, Ph and NH(overlap)), 4.87 (q, $J_{H-H} = 6.4$ Hz, 1H, CH(CH₃)), 2.16 (s, 3H, CO(CH₃)), 1.79 (s, 1H, OH), 1.47 (d, $J_{H-H} = 6.4$ Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 179(2), 161(37), 119(100), 104(4), 91(40), 77(6), 65(19), 51(13). Colorless liquid. Isolation yield 75% (67.0 mg). Analytical data are in agreement with the literature.²⁷

1-Phenylpropane-1,2-diol (5o)



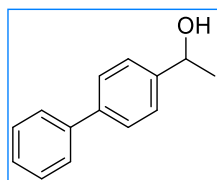
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.37 – 7.29 (m, 5H, Ph), 4.68 (d, J_{H-H} = 4.4 Hz, 0.72H, CHCH-*syn*), 4.38 (d, J_{H-H} = 7.3 Hz, 0.28H, CHCH-*anti*), 4.02 (m, 0.72H, CHCH-*syn*), 3.93 – 3.78 (m, 0.28H, CHCH-*anti*), 2.18 (s, 2H, OH), 1.08 (m, 2H, CCH₃). **MS (EI) [m/z (%)]**: 152(2), 149(3), 133(3), 119(3), 115(5), 108(54), 170(45), 90(8), 79(100), 77(55), 63(7), 51(24). Pale yellow solid. Isolation yield 70% (53.1 mg). Analytical data are in agreement with the literature.²⁸⁻³⁰

1-(Naphthalen-2-yl)ethan-1-ol (5p)



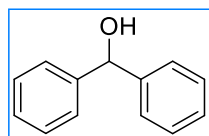
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.86 – 7.80 (m, 4H, Ph), 7.52 – 7.47 (m, 3H, Ph), 5.06 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 2.00 (s, 1H, OH), 1.59 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 170(43), 155(84), 127(100), 126(19), 101(8), 77(19), 63(15), 51(10). White solid. Isolation yield 84% (72.3 mg). Analytical data are in agreement with the literature.^{24,31}

1-([1,1'-Biphenyl]-4-yl)ethan-1-ol (5q)



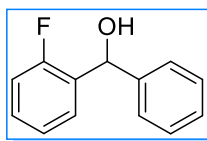
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.65 – 7.57 (m, 4H, Ph), 7.50 – 7.42 (m, 4H, Ph), 7.37 (t, J_{H-H} = 7.3 Hz, 1H, Ph), 4.96 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 2.05 (s, 1H, OH), 1.56 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 198(69), 183(100), 180(12), 155(99), 152(32), 115(9), 92(12), 77(31), 51(12). White solid. Isolation yield 93% (92.1 mg). Analytical data are in agreement with the literature.^{32,33}

Diphenylmethanol (5r)



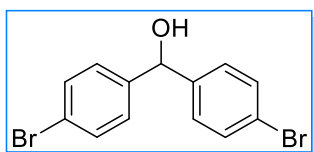
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.42 – 7.33 (m, 8H, Ph), 7.32 – 7.27 (m, 2H, Ph), 5.83 (s, 1H, CH(Ph)₂), 2.34 (s, 1H, OH). **MS (EI) [m/z (%)]**: 184(50), 183(16), 165(11), 152(4), 107(12), 105(100), 79(28), 78(41), 77(48), 51(18). White solid. Isolation yield 77% (70.9 mg). Analytical data are in agreement with the literature.^{9,17}

(2-Fluorophenyl)(phenyl)methanol (**5s**)



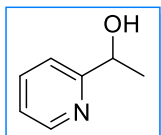
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.55 – 7.24 (m, 1H, Ph), 7.45 – 7.39 (m, 2H, Ph), 7.39 – 7.33 (m, 2H, Ph), 7.33 – 7.23 (m, 2H, Ph), 7.19 – 7.15 (m, 1H, Ph), 7.07 – 7.02 (m, 1H, Ph), 6.15 (s, 1H, CH(Ph)₂), 2.43 (s, 1H, OH). **MS (EI) [m/z (%)]**: 200(47), 180(7), 123(62), 105(100), 95(30), 77(58), 75(22), 51(23). Yellow liquid. Isolation yield 66% (66.7 mg). Analytical data are in agreement with the literature.^{13,34}

Bis-(4-bromophenyl)methanol (**5t**)



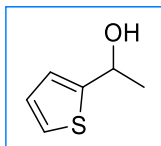
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.46 (d, J_{H-H} = 8.4 Hz, 4H, Ph), 7.22 (d, J_{H-H} = 8.4 Hz, 4H, Ph), 5.75 (s, 1H, CH(Ph)₂), 2.12 (brs, 1H, OH). **MS (EI) [m/z (%)]**: 342(11), 185(100), 183(99), 165(8), 157(17), 105(12), 78(20), 77(44), 76(20), 51(18). White solid. Isolation yield 78% (133.4 mg). Analytical data are in agreement with the literature.^{22,32}

1-(Pyridin-2-yl)ethan-1-ol (**5u**)



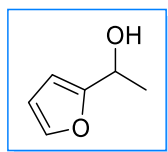
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.47 – 8.44 (m, 1H, Ar), 7.64 – 7.59 (m, 1H, Ar), 7.23 – 7.20 (m, 1H, Ar), 7.14 – 7.10 (m, 1H, Ar), 4.82 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 4.07 (s, 1H, OH), 1.43 (d, J_{H-H} = 6.6 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 124(14), 122(10), 108(100), 1006(42), 104(7), 81(7), 79(30), 78(33), 52(27), 51(24). Colorless liquid. Isolation yield 84% (50.7 mg). Analytical data are in agreement with the literature.³⁵

1-(Thiophen-2-yl)ethan-1-ol (**5v**)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.24 (dd, J_{H-H} = 4.7, 1.6 Hz, 1H, CHS), 7.02 – 6.91 (m, 2H, CHCH), 5.14 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.98 (bs, 1H, OH), 1.61 (d, J_{H-H} = 6.4 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 128(11), 113(45), 110(16), 95(13), 85(100), 84(10), 65(11), 59(8), 58(13), 51(10). Colorless oil. Isolation yield 77% (49.4 mg). Analytical data are in agreement with the literature.³⁵

1-(Furan-2-yl)ethan-1-ol (**5w**)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.33 (dd, $J_{H-H} = 1.8, 0.8$ Hz, 1H, CHO), 6.30 – 6.28 (m, 1H, CHCH), 6.19 – 6.18 (m, 1H, CHCH), 4.82 (q, $J_{H-H} = 6.5$ Hz, 1H, CH(CH₃)), 2.77 (bs, 1H, OH), 1.49 (d, $J_{H-H} = 6.6$ Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 112(23), 111(12), 97(66), 96(11), 95(100), 94(15), 84(10), 69(20), 43(22), 42(28). Colorless liquid. Isolation yield 81% (50.8 mg). Analytical data are in agreement with the literature.³⁶

5. NMR spectra of products

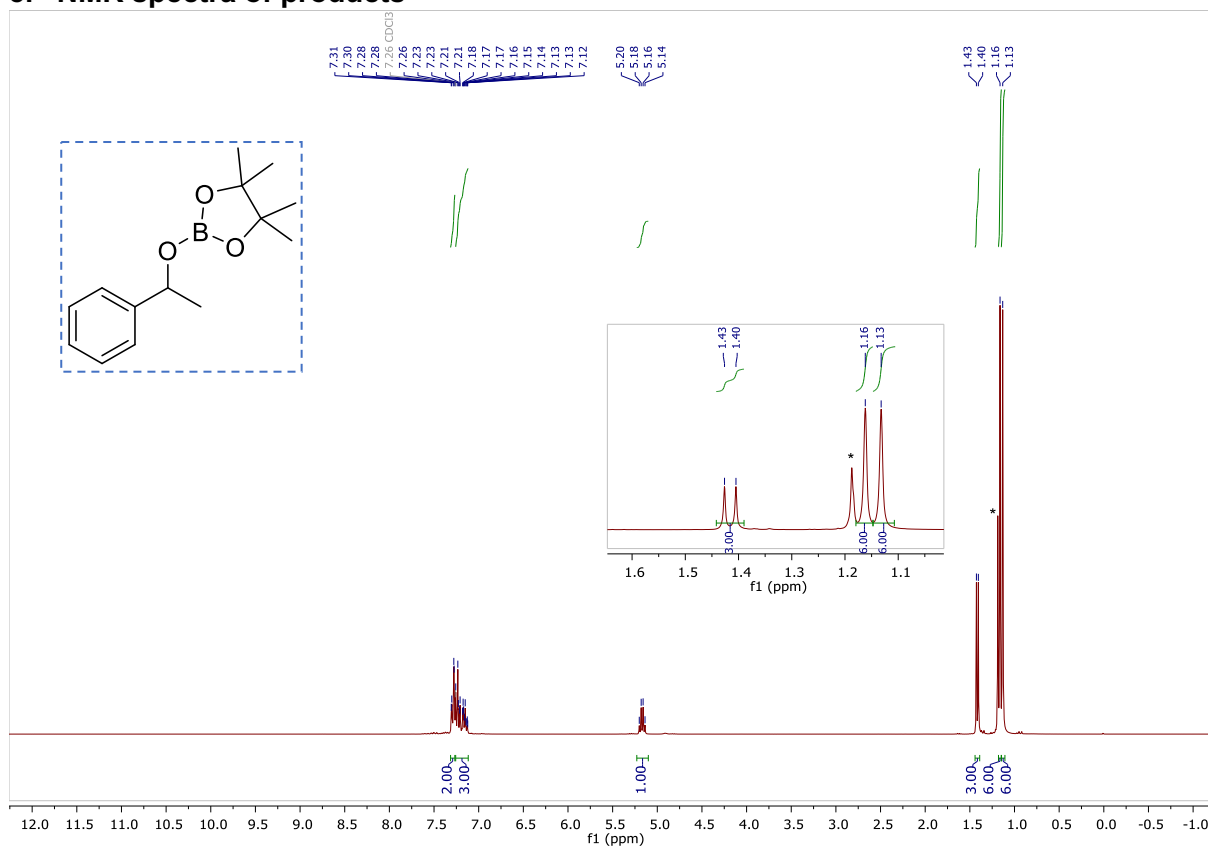


Figure S1 – ¹H NMR spectrum of **3a** from crude reaction mixture. *Excess of the HBpin.

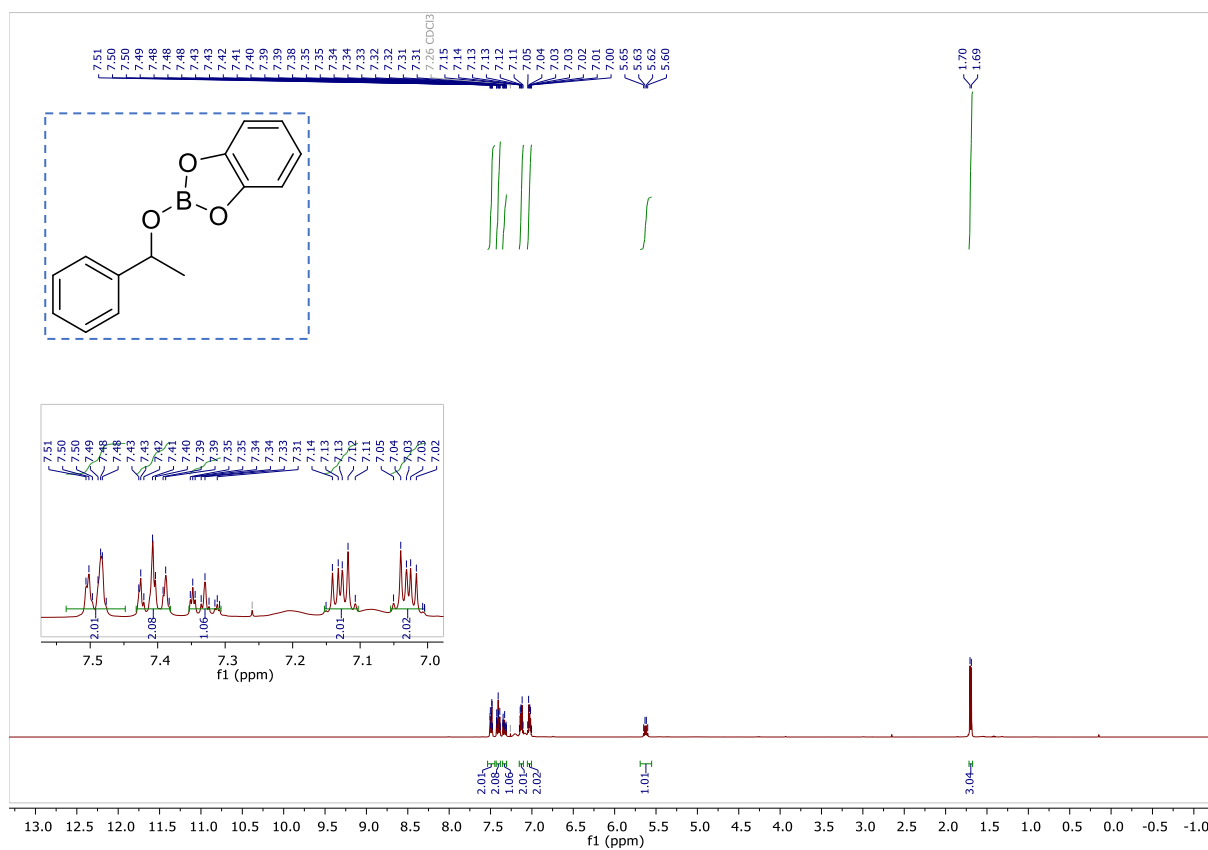


Figure S2 – ¹H NMR spectrum of **3a'**.

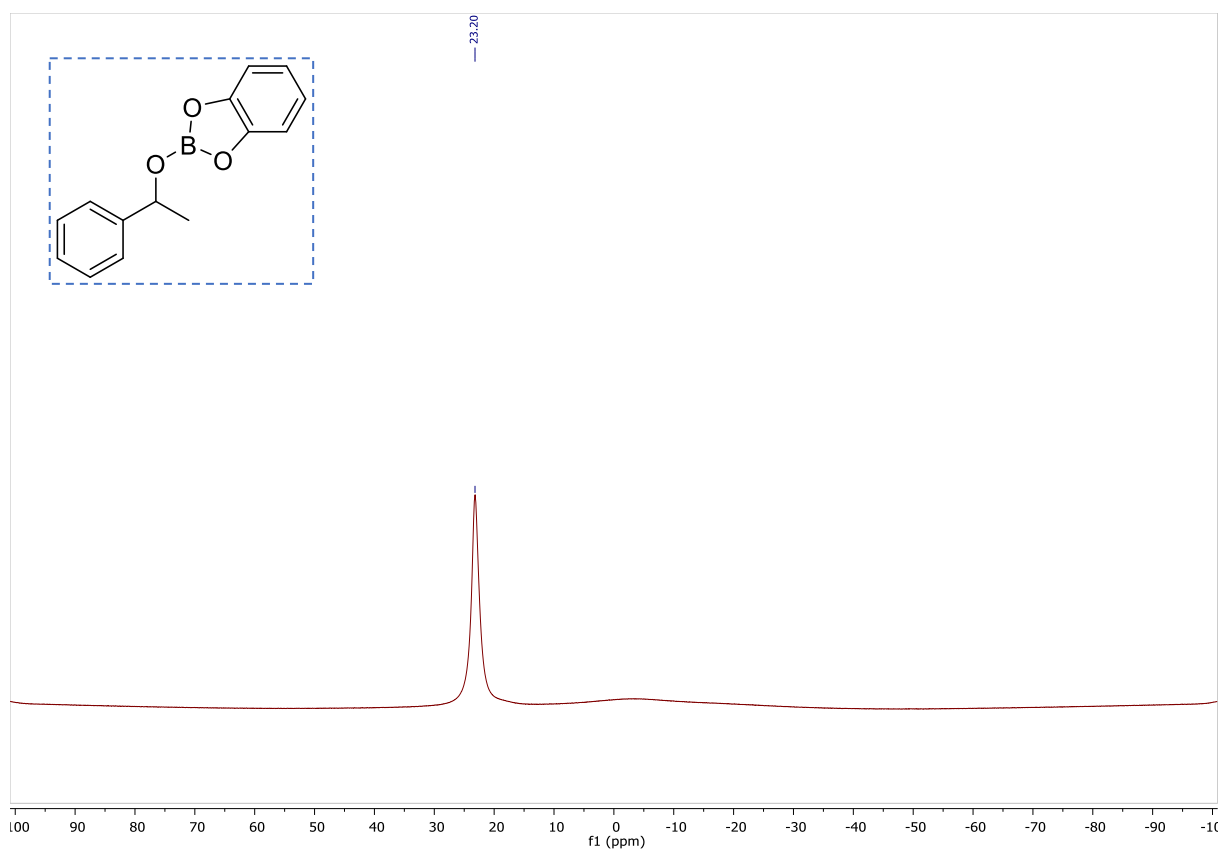


Figure S3 – ^{11}B NMR spectrum of **3a'**.

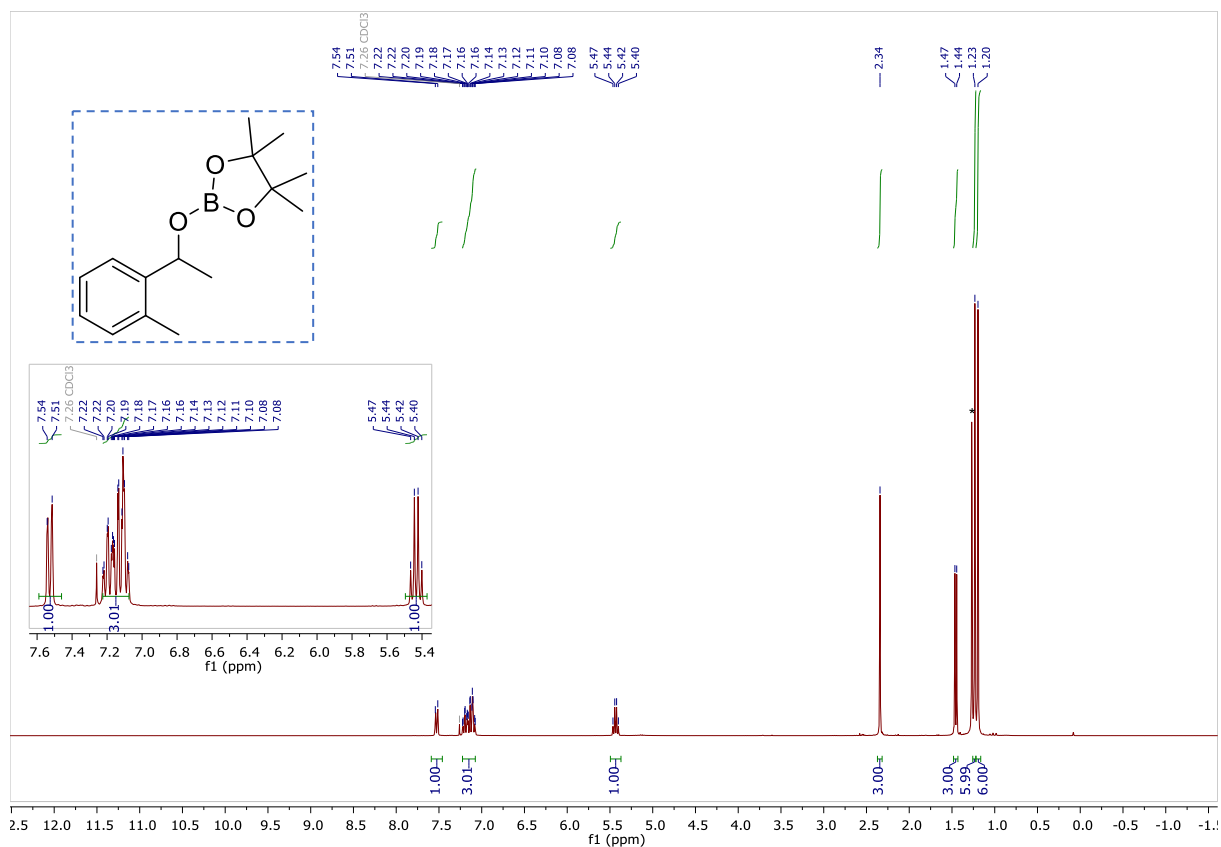


Figure S4 – ^1H NMR spectrum of **3b** from crude reaction mixture. *Excess of the HBpin.

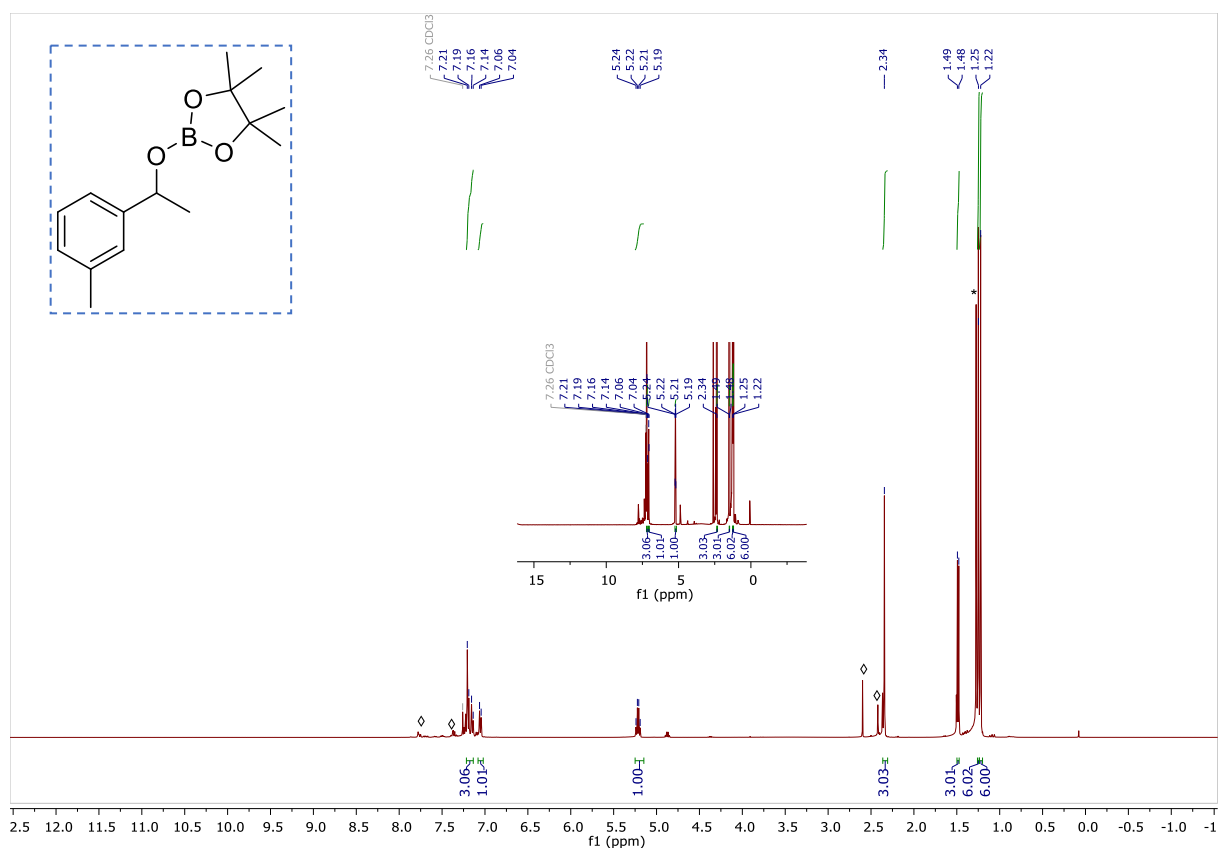


Figure S5 – ^1H NMR spectrum of **3c** from crude reaction mixture. *Excess of the HBpin. $\diamond$ Unreacted substrate. Conversion of **1c** = 86%.

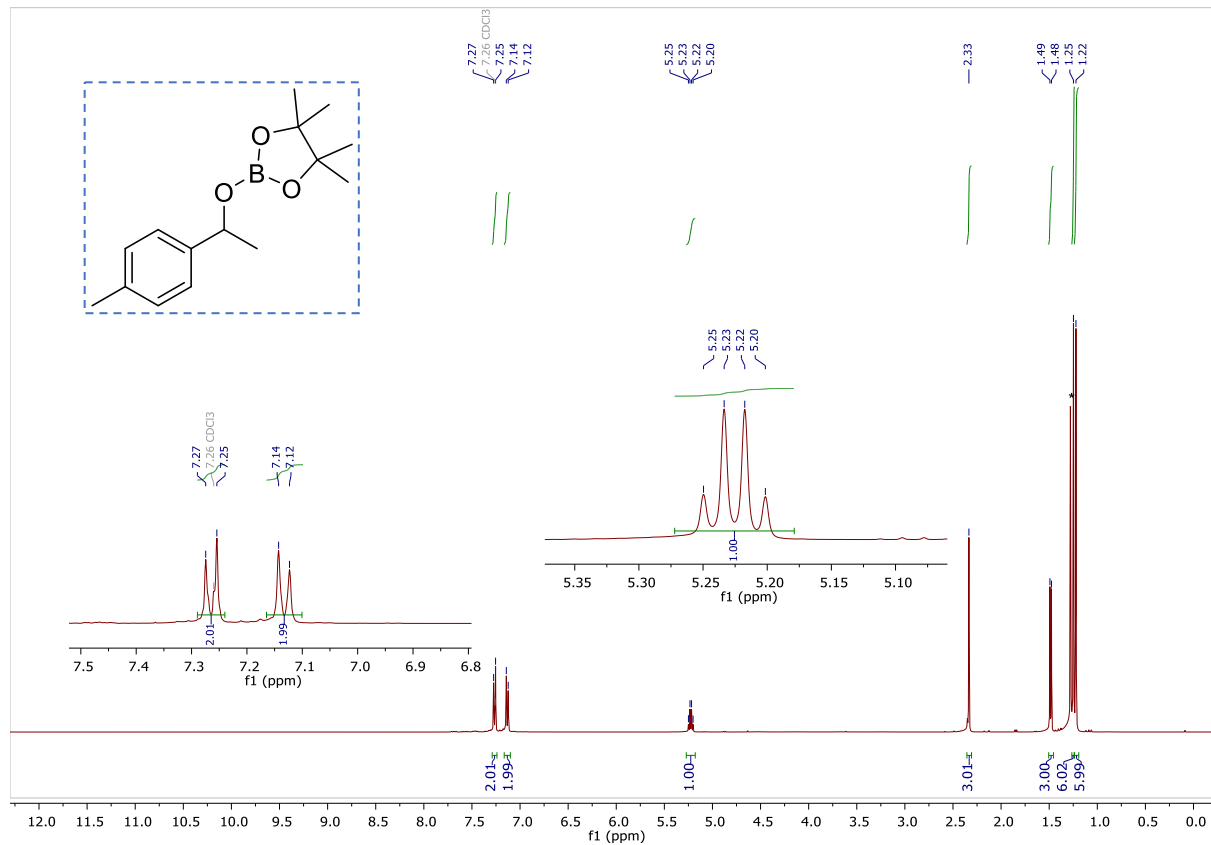


Figure S6 – ^1H NMR spectrum of **3d** from crude reaction mixture. *Excess of the HBpin.

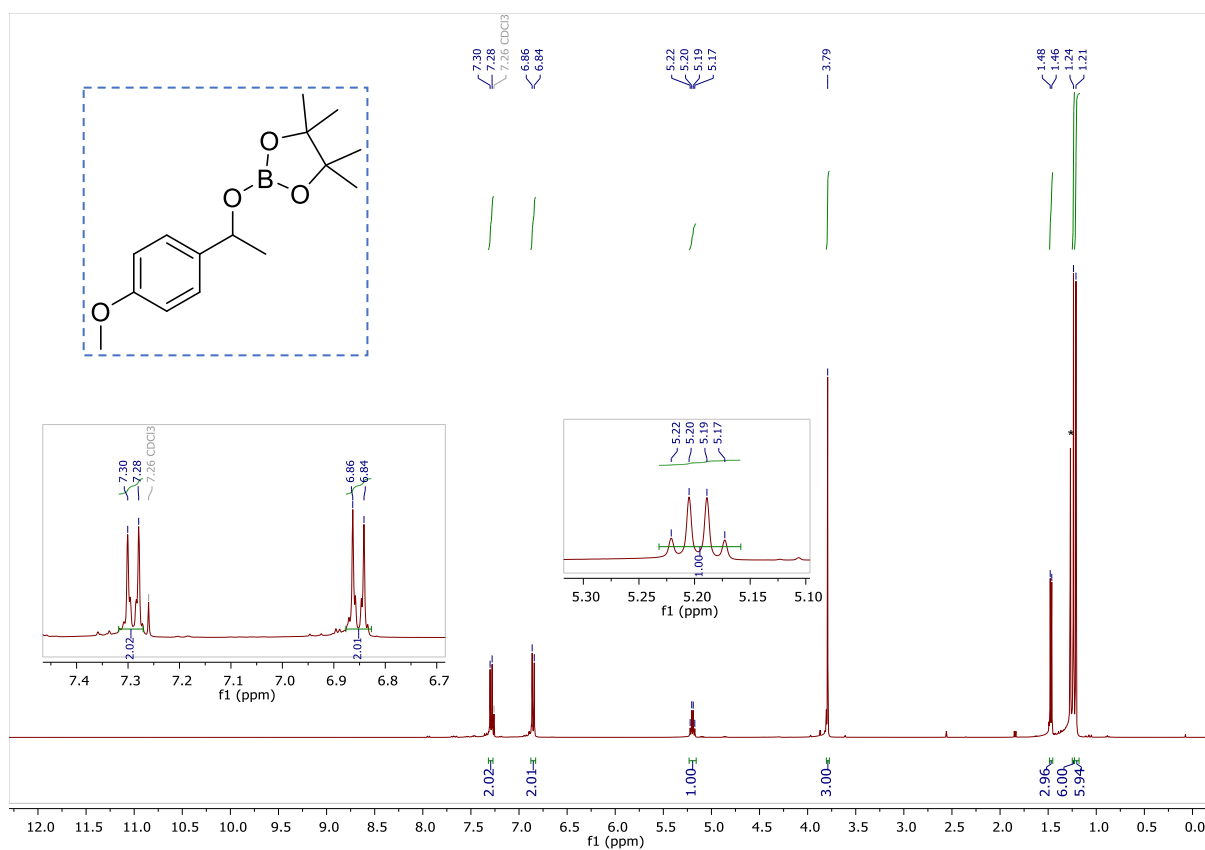


Figure S7 – ¹H NMR spectrum of **3e** from crude reaction mixture. *Excess of the HBpin.

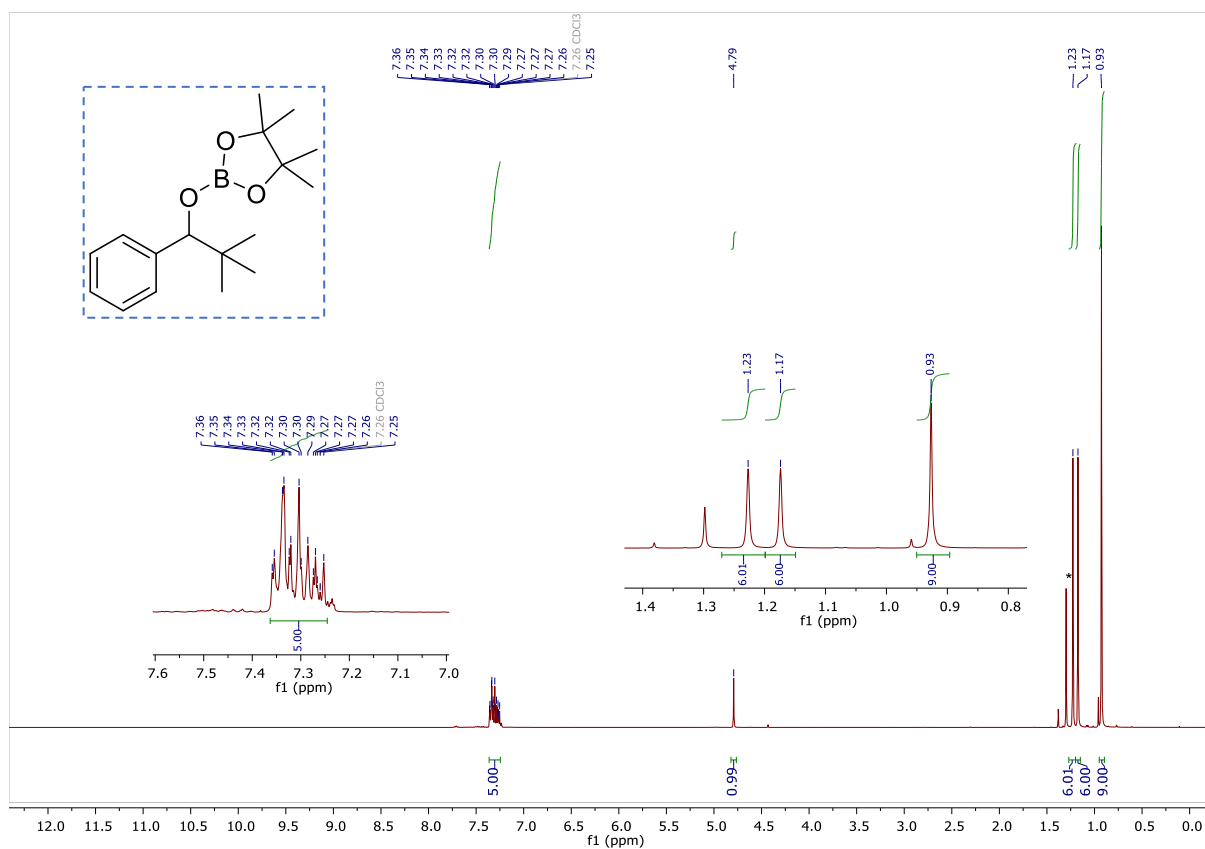


Figure S8 – ¹H NMR spectrum of **3f** from crude reaction mixture. *Excess of the HBpin.

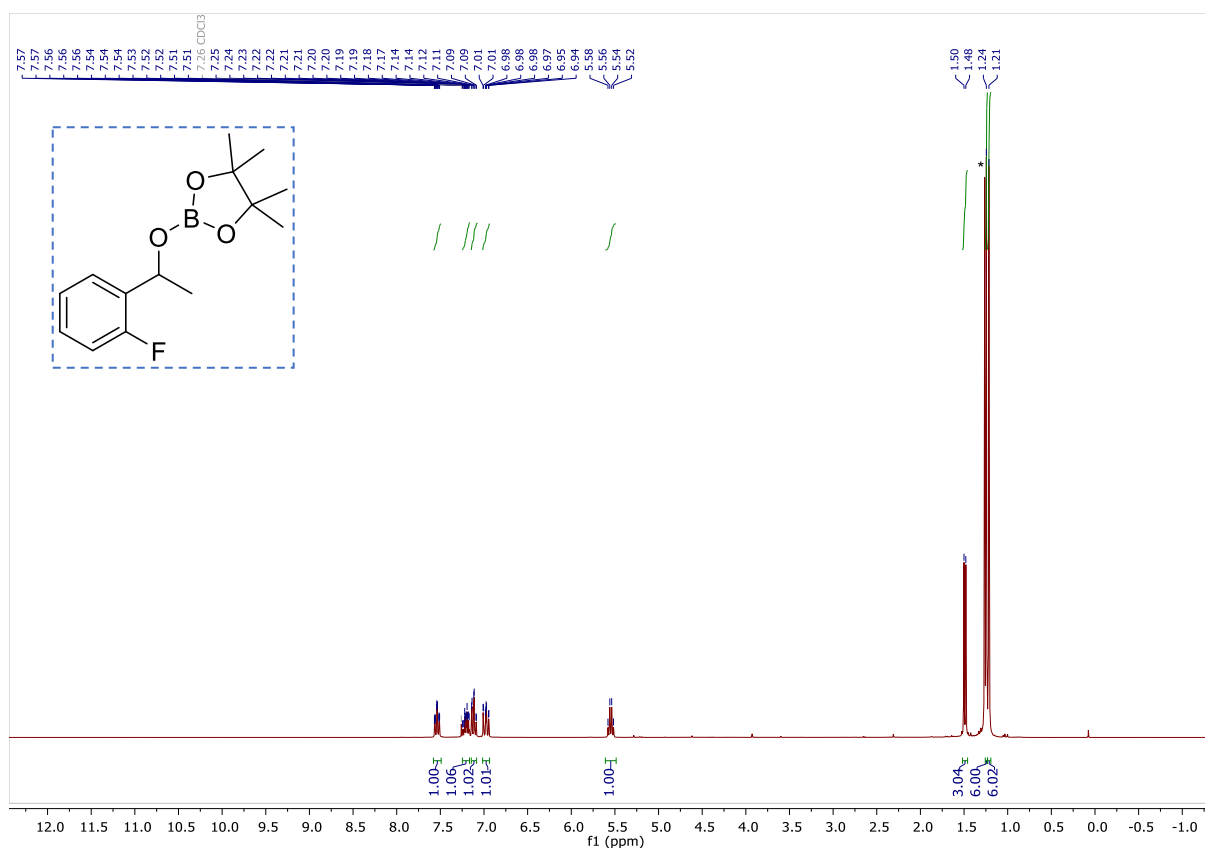


Figure S9 – ^1H NMR spectrum of **3g** from crude reaction mixture. *Excess of the HBpin.

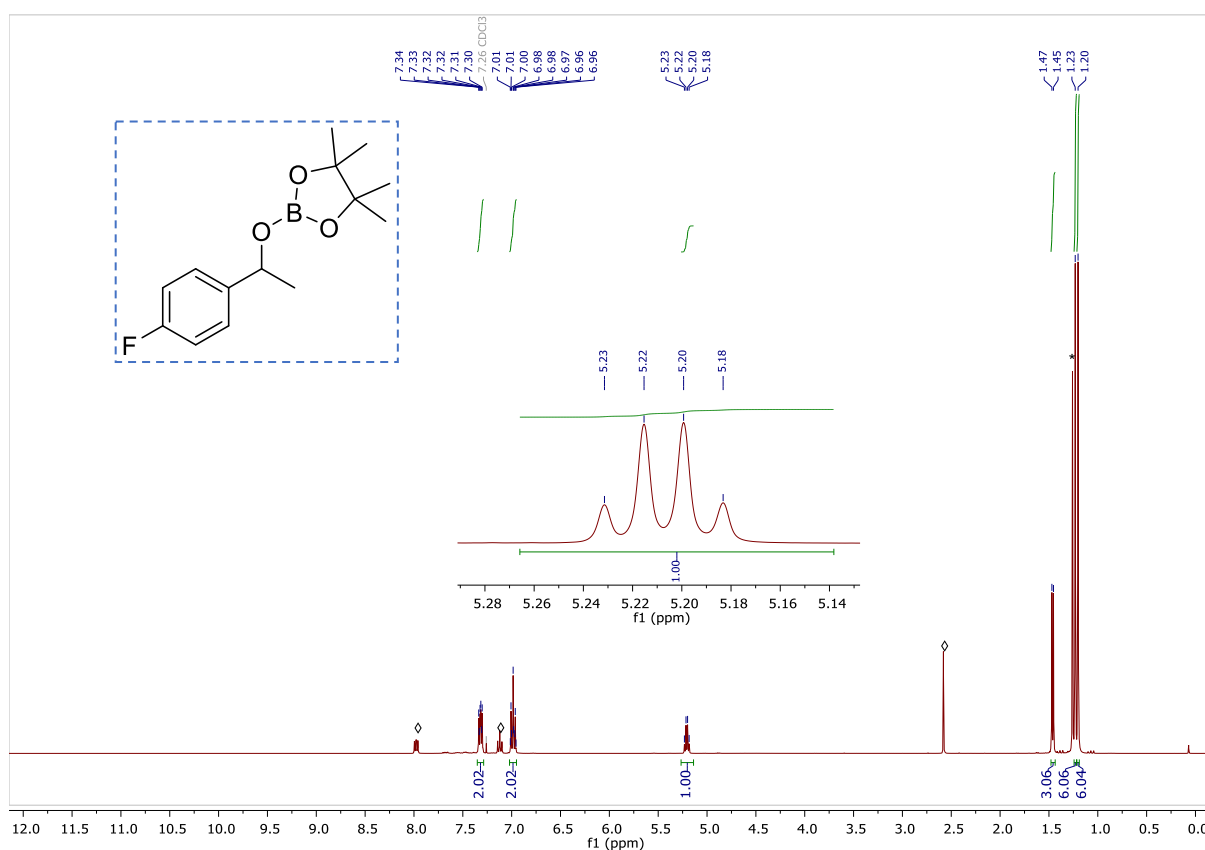
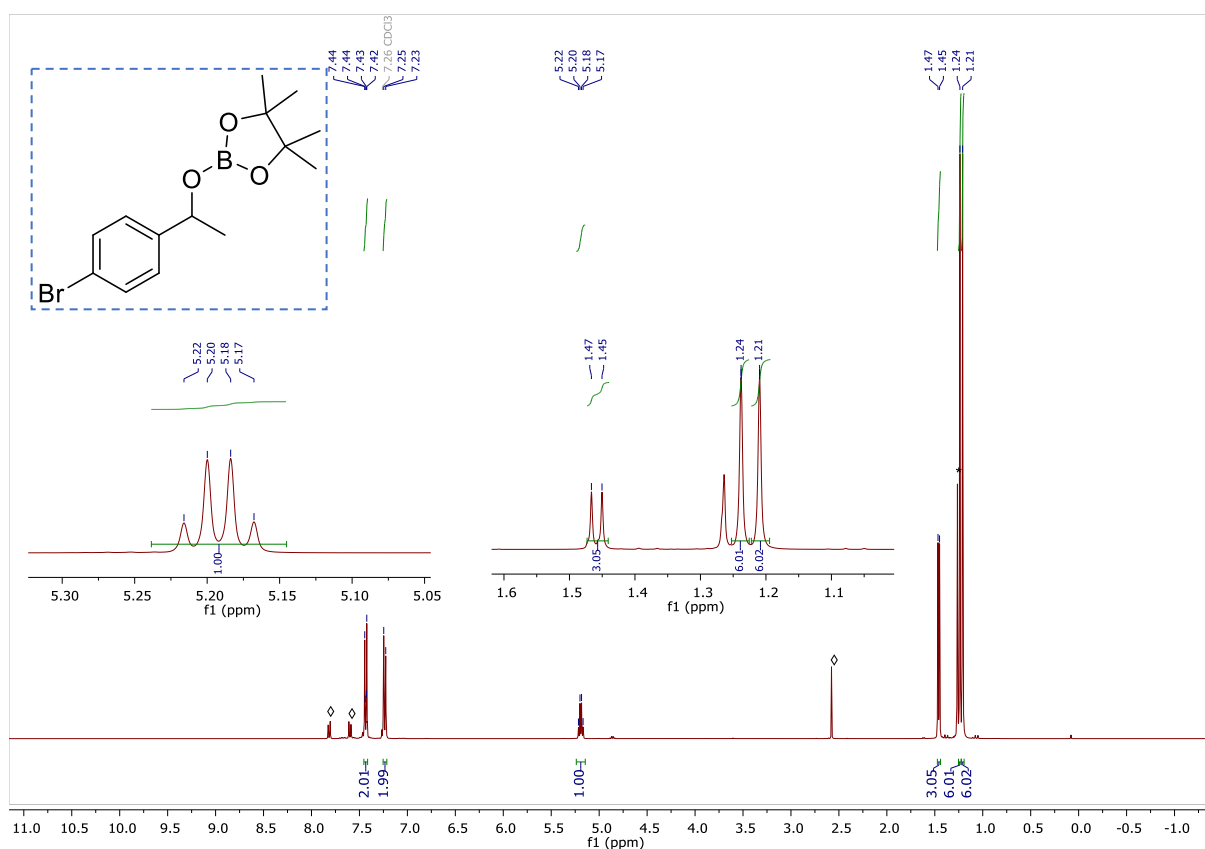
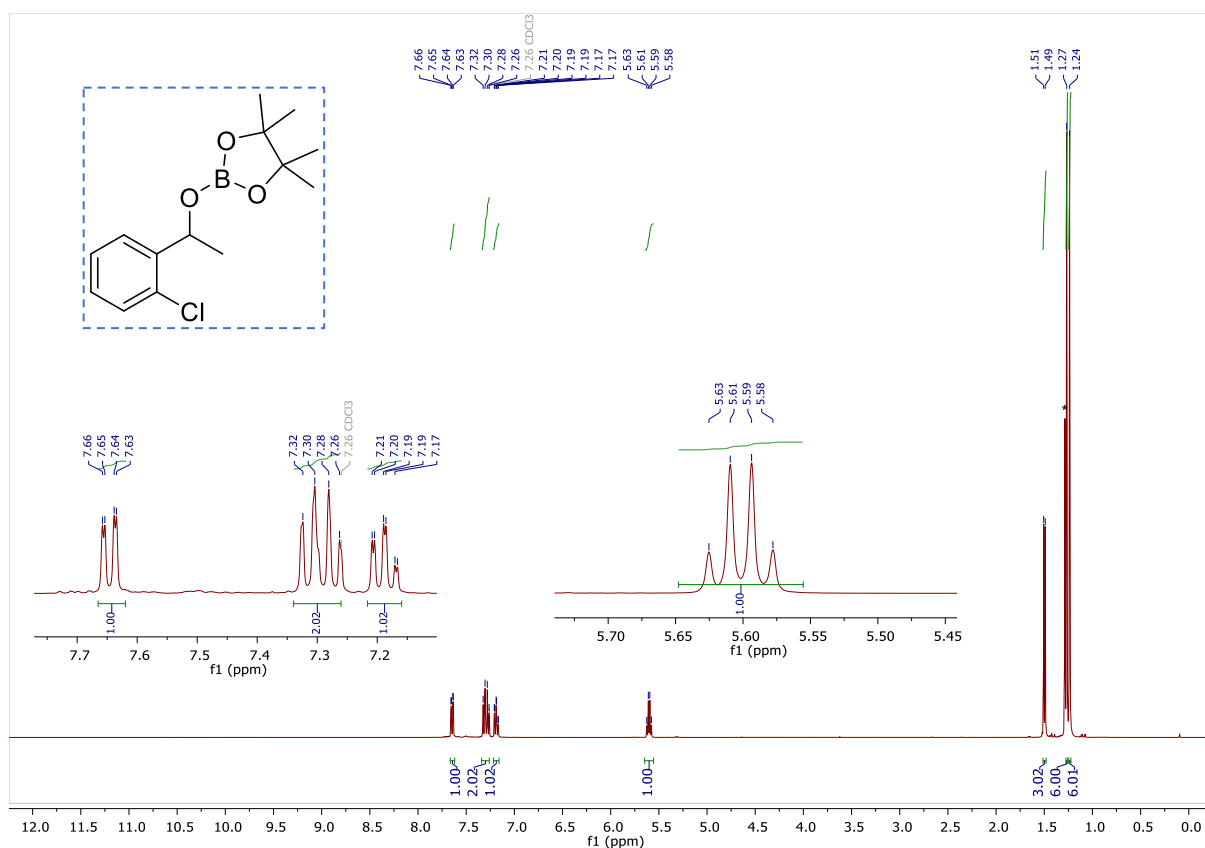


Figure S10 – ^1H NMR spectrum of **3h** from crude reaction mixture. *Excess of the HBpin. $\diamond$ Unreacted substrate. Conversion of **1h** = 78%.



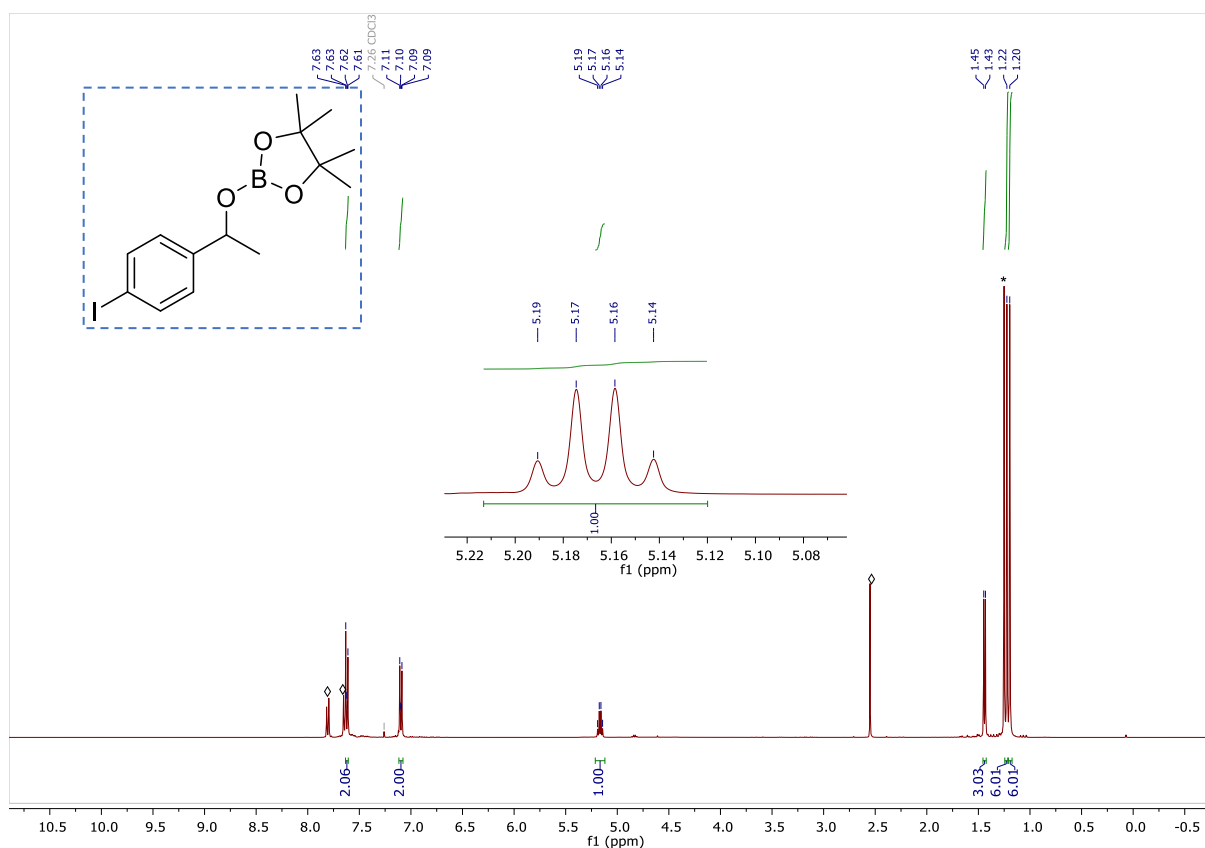


Figure S13 – ^1H NMR spectrum of **3k** from crude reaction mixture. *Excess of the HBpin.
 $\diamond$ Unreacted substrate. Conversion of **1k** = 74%.

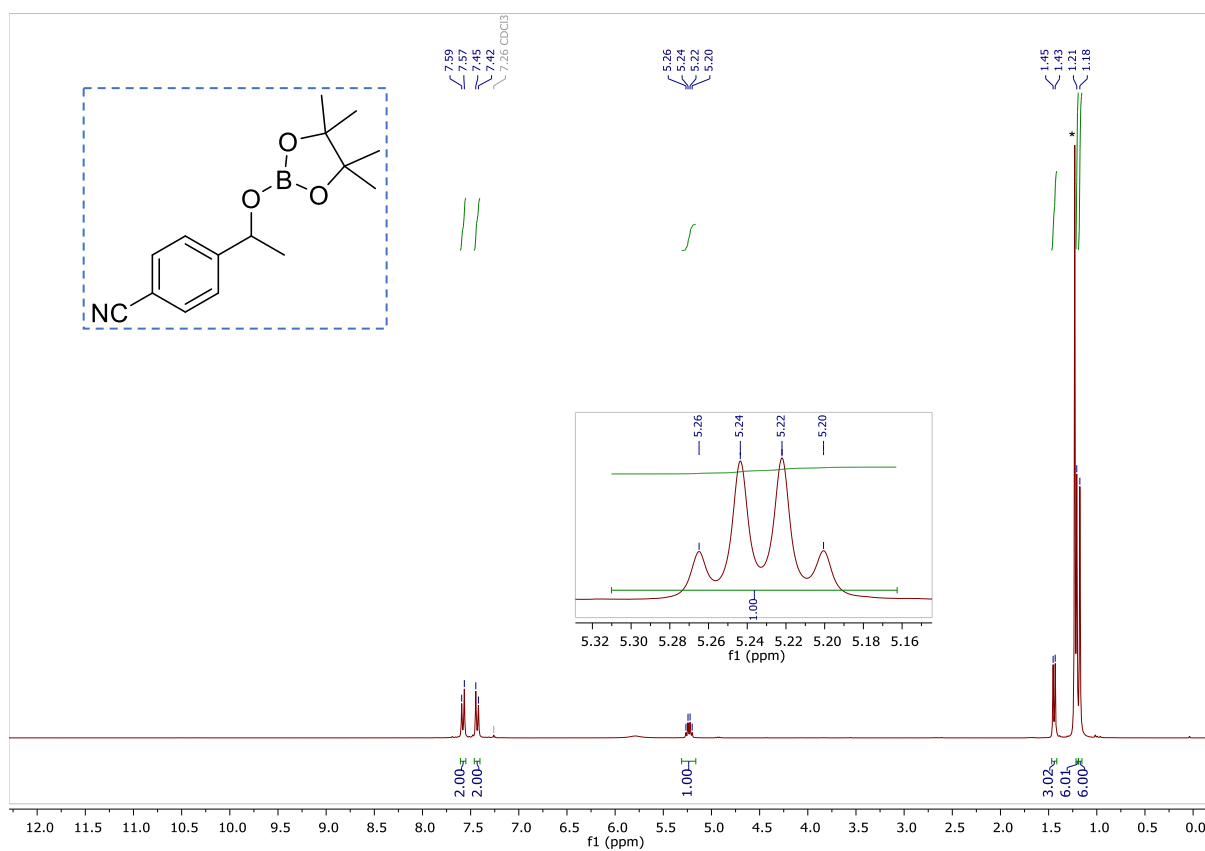


Figure S14 – ^1H NMR spectrum of **3l** from crude reaction mixture. *Excess of the HBpin.

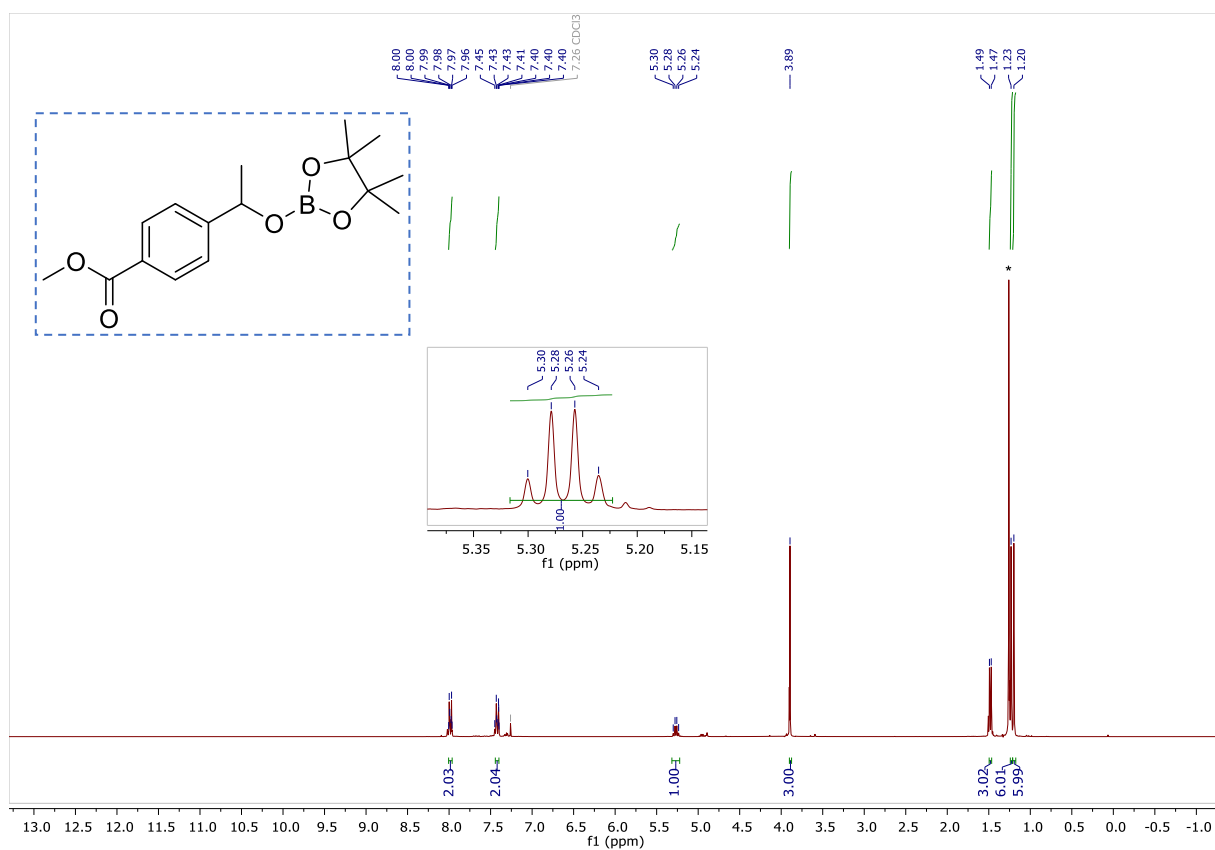


Figure S15 – ¹H NMR spectrum of **3m** from crude reaction mixture. *Excess of the HBpin.

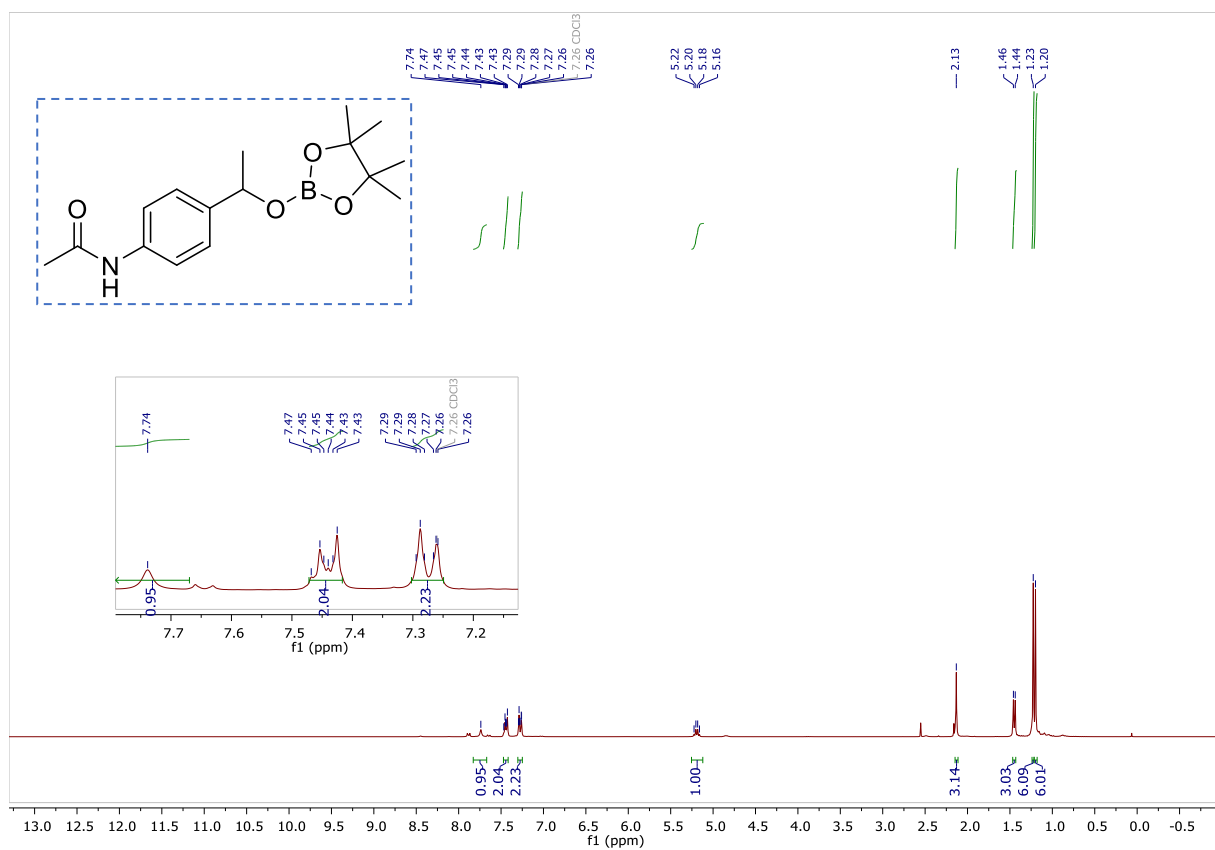


Figure S16 – ¹H NMR spectrum of **3n**.

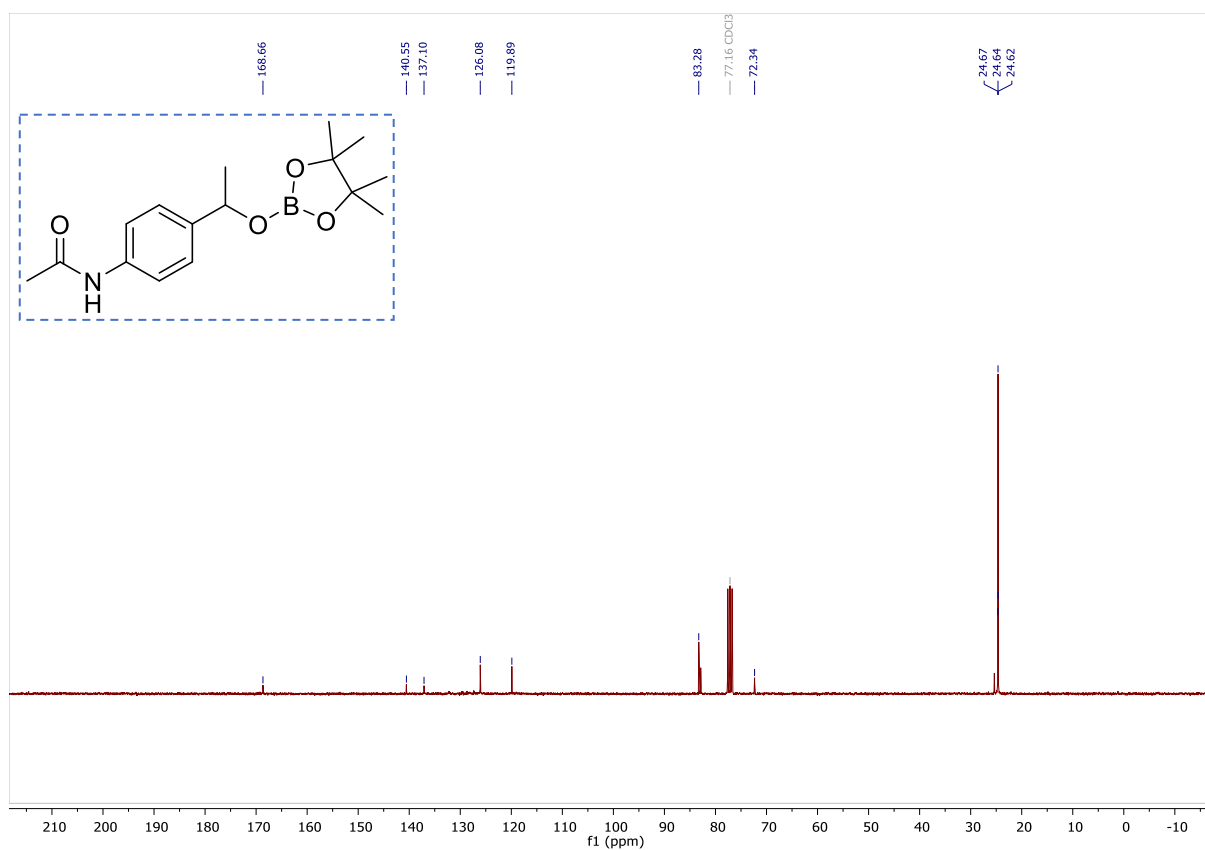


Figure S17 – ^{13}C NMR spectrum of **3n**.

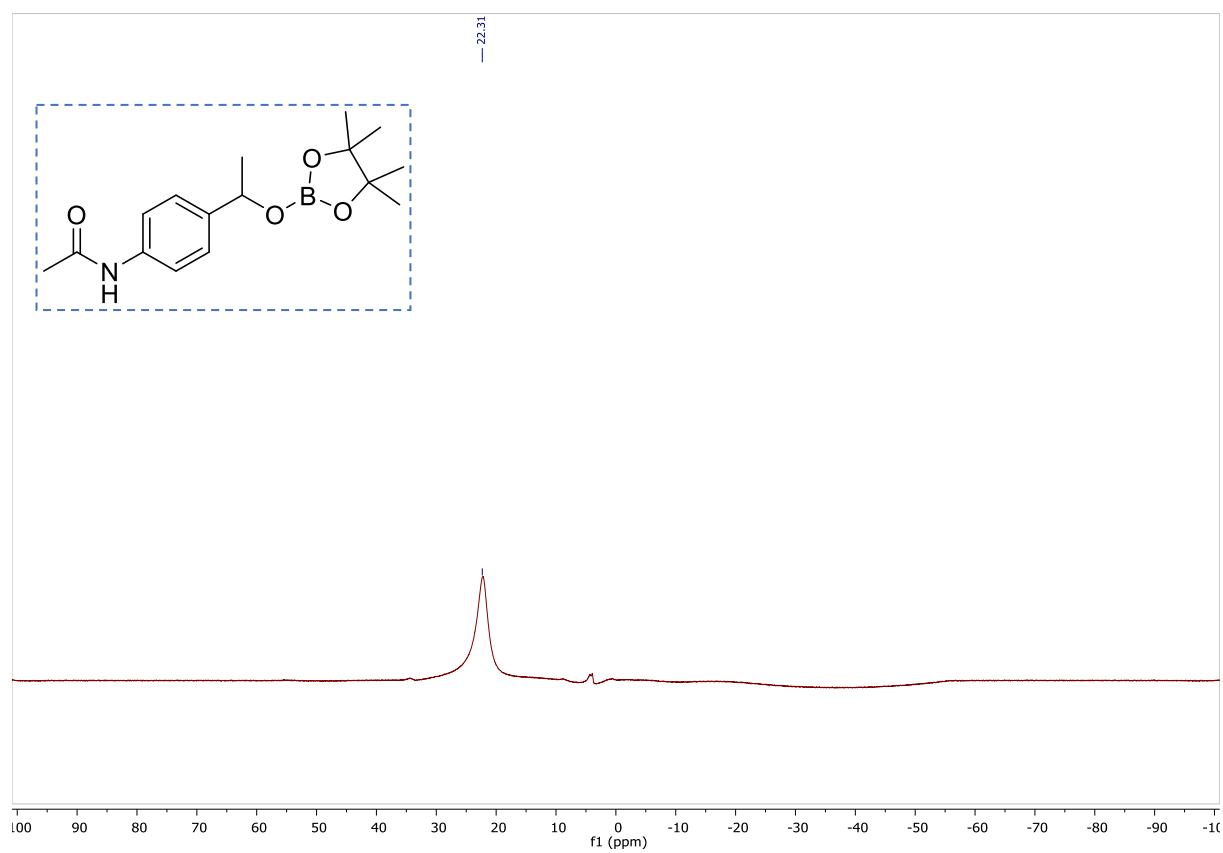
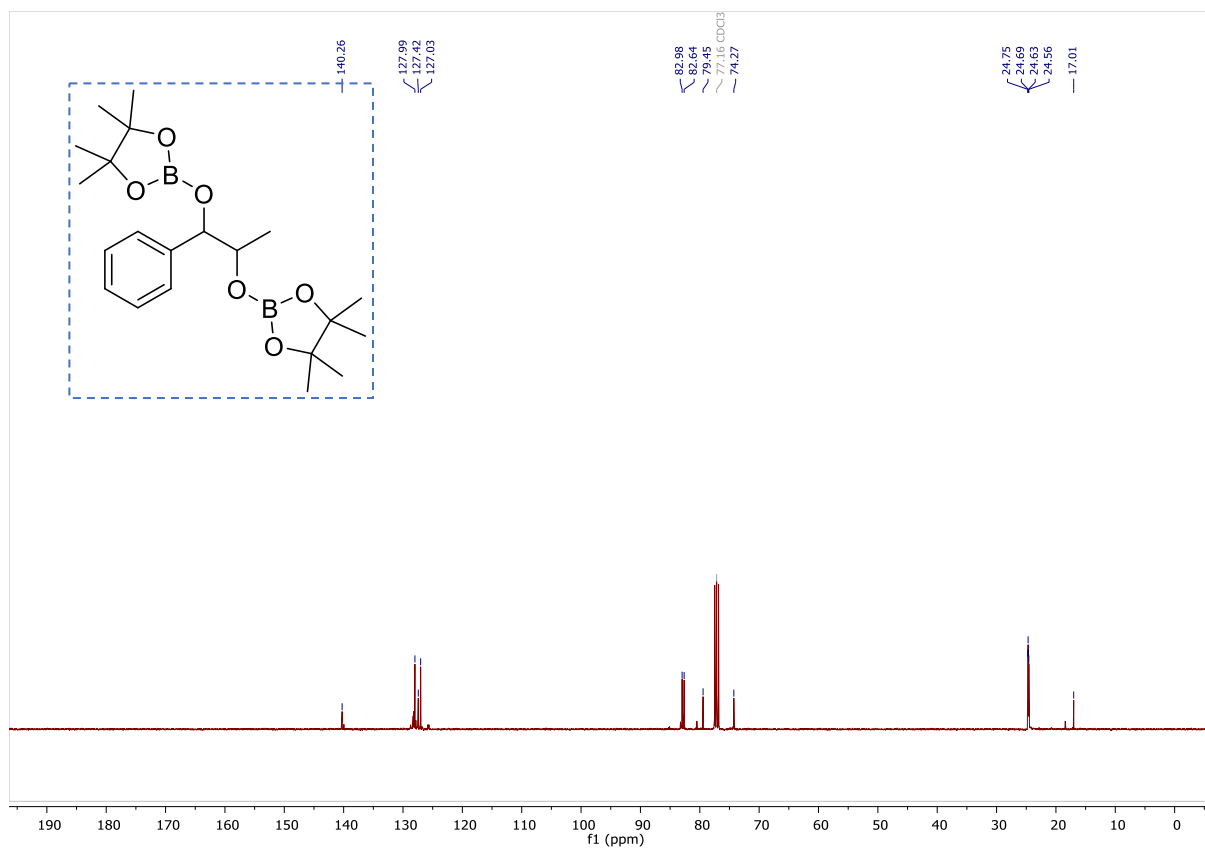
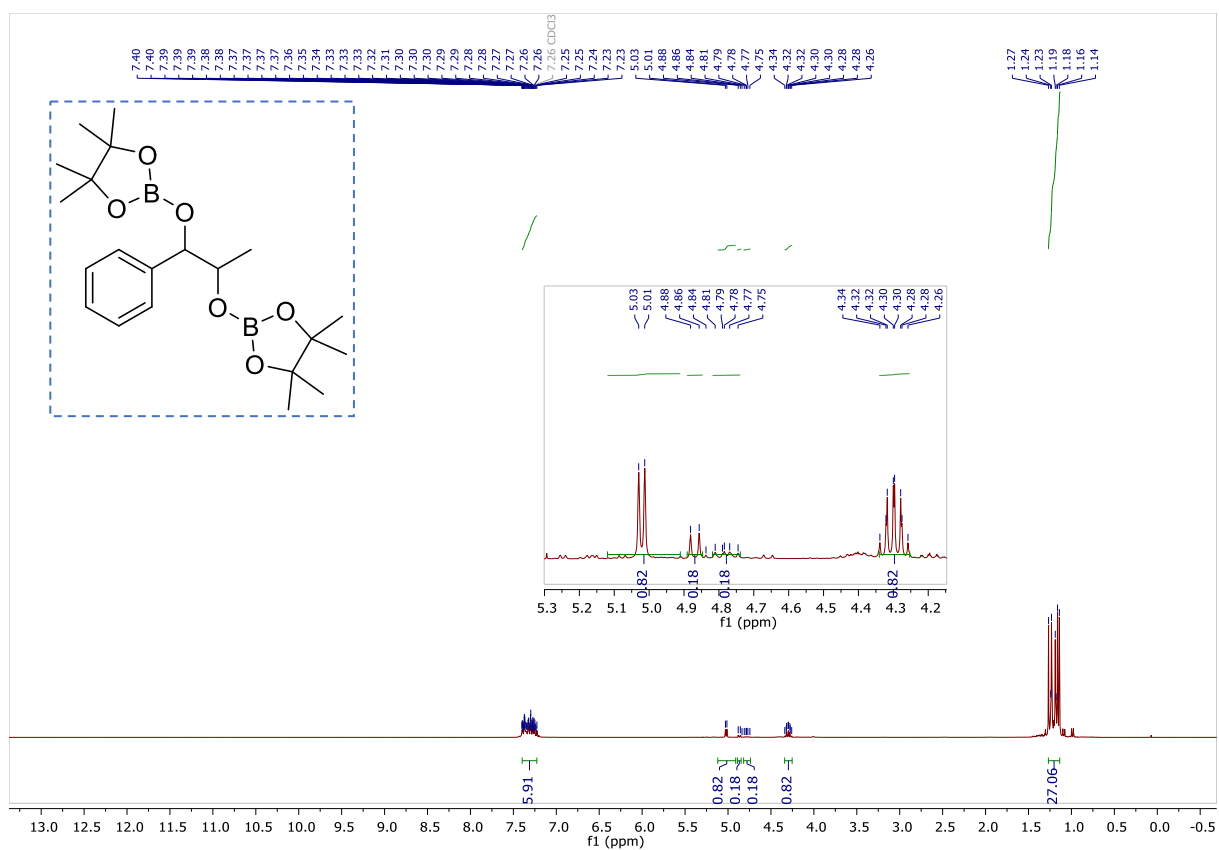


Figure S18 – ^{11}B NMR spectrum of **3n.**



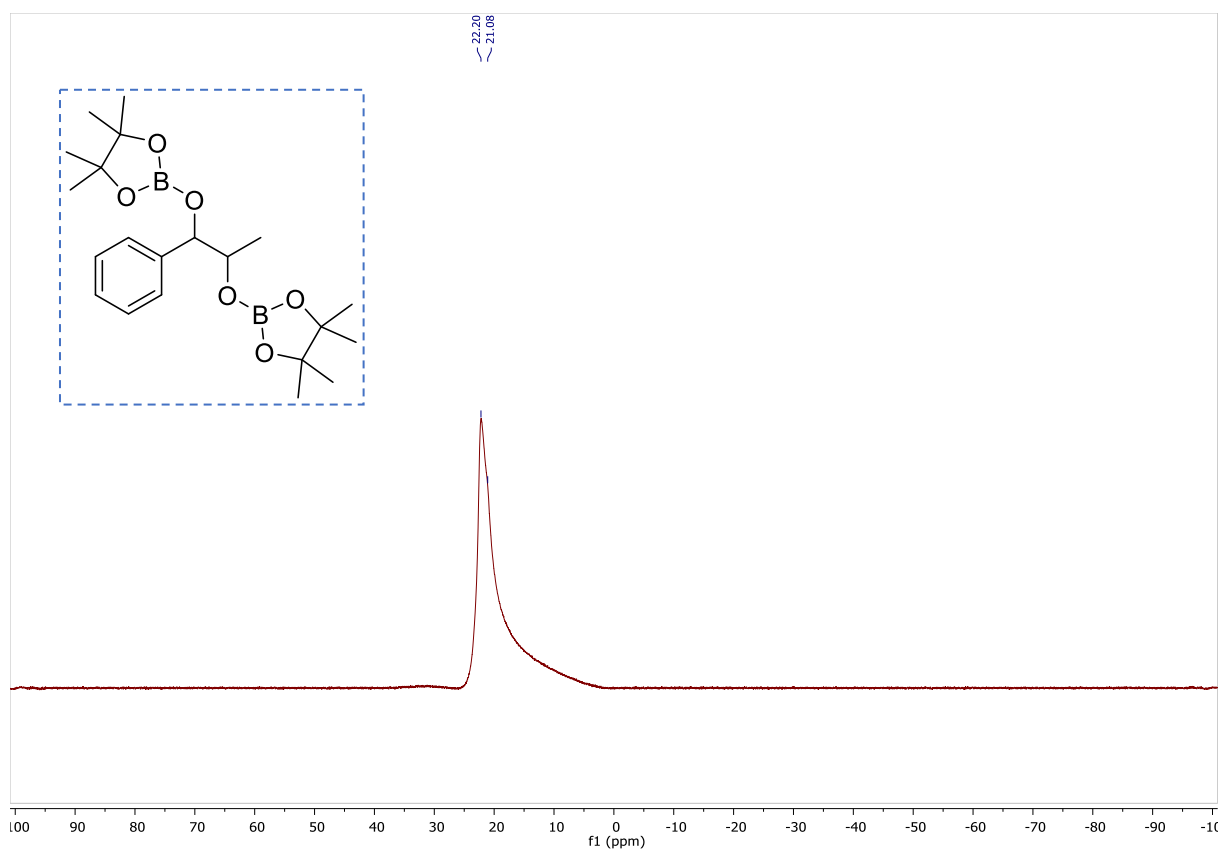


Figure S21 – ^{11}B NMR spectrum of **3o**.

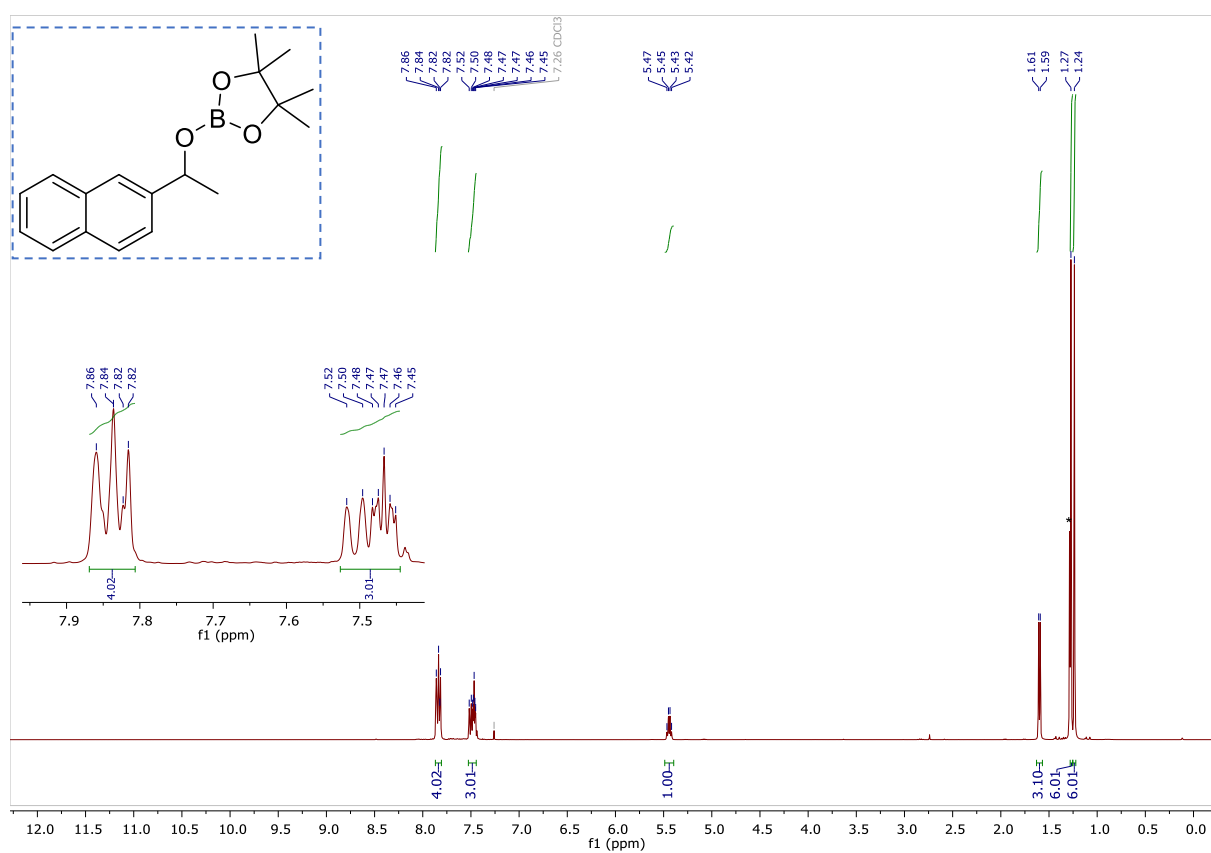


Figure S22 – ^1H NMR spectrum of **3p** from crude reaction mixture. *Excess of the HBpin.

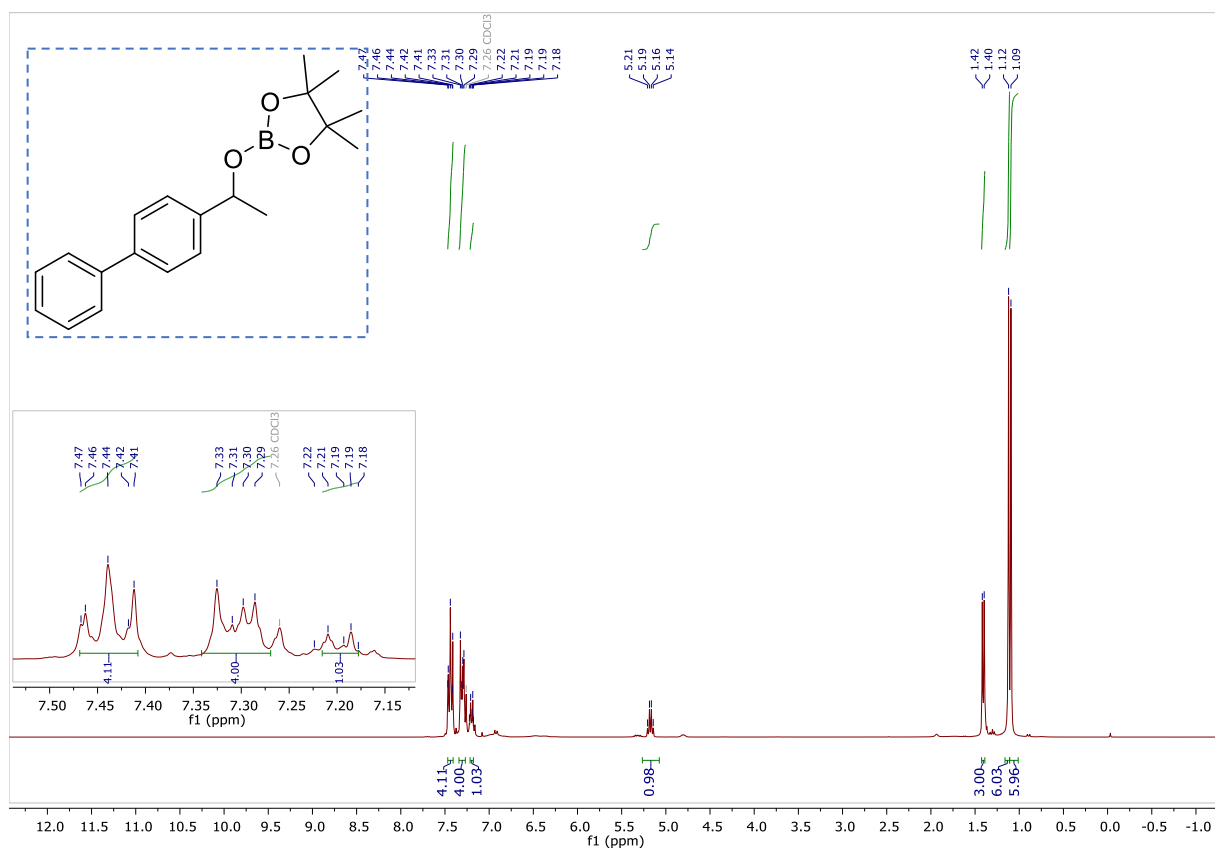


Figure S23 – ^1H NMR spectrum of **3q**.

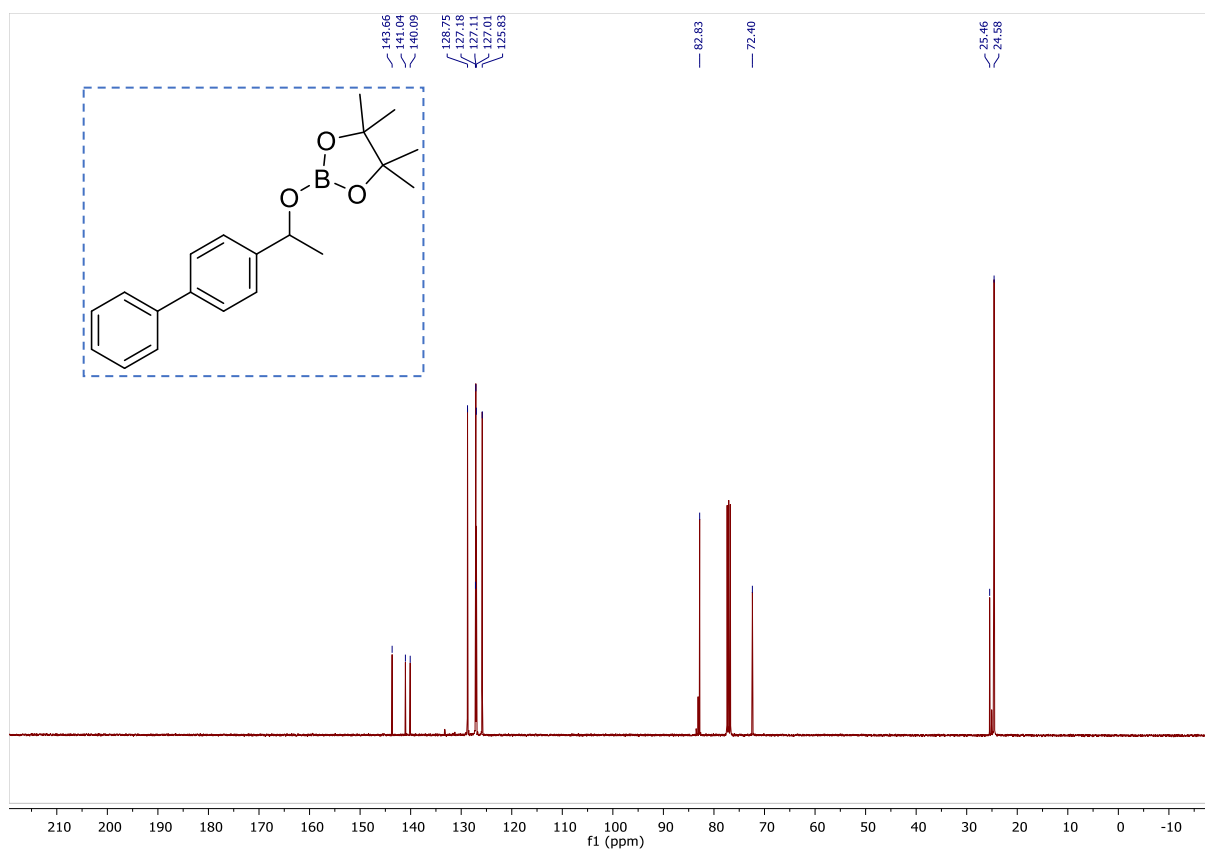


Figure S24 – ^{13}C NMR spectrum of **3q**.

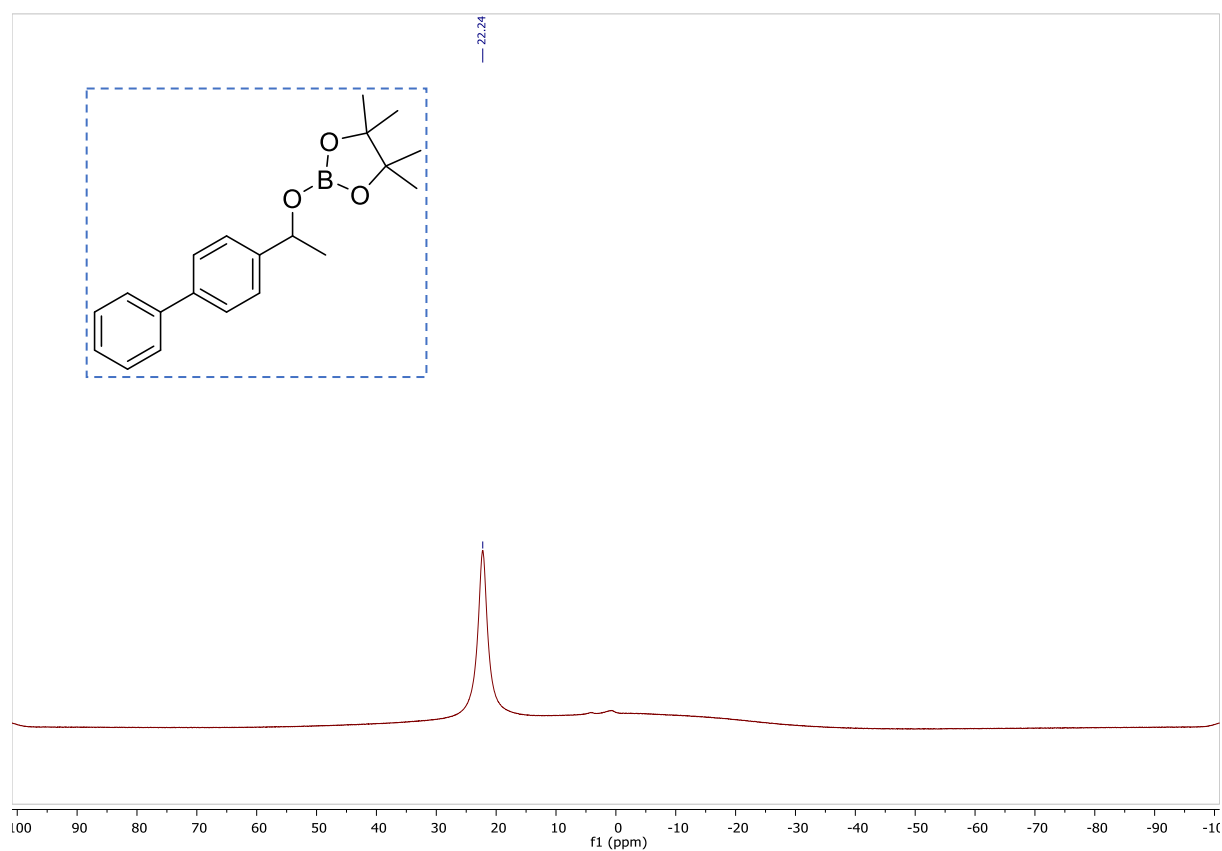


Figure S25 – ^{11}B NMR spectrum of **3q**.

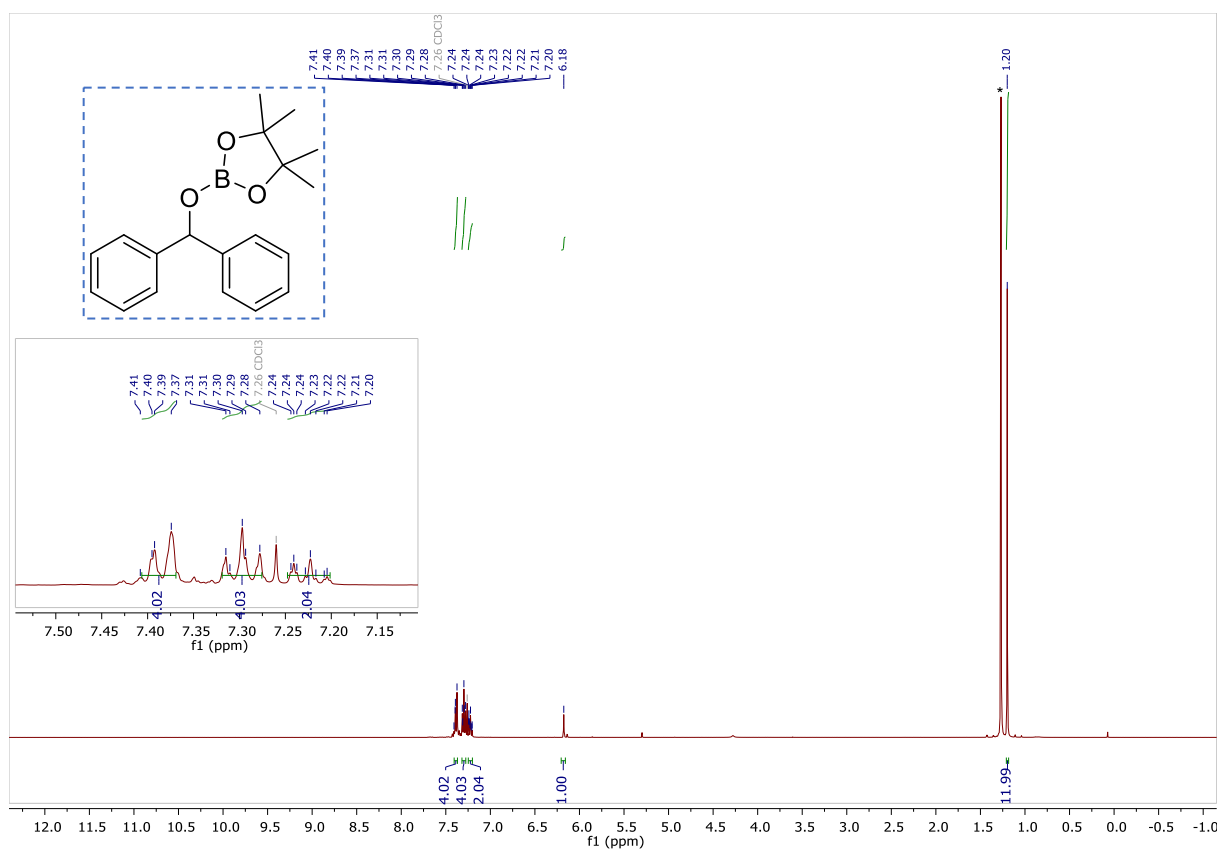


Figure S26 – ^1H NMR spectrum of **3r** from crude reaction mixture. *Excess of the HBpin.

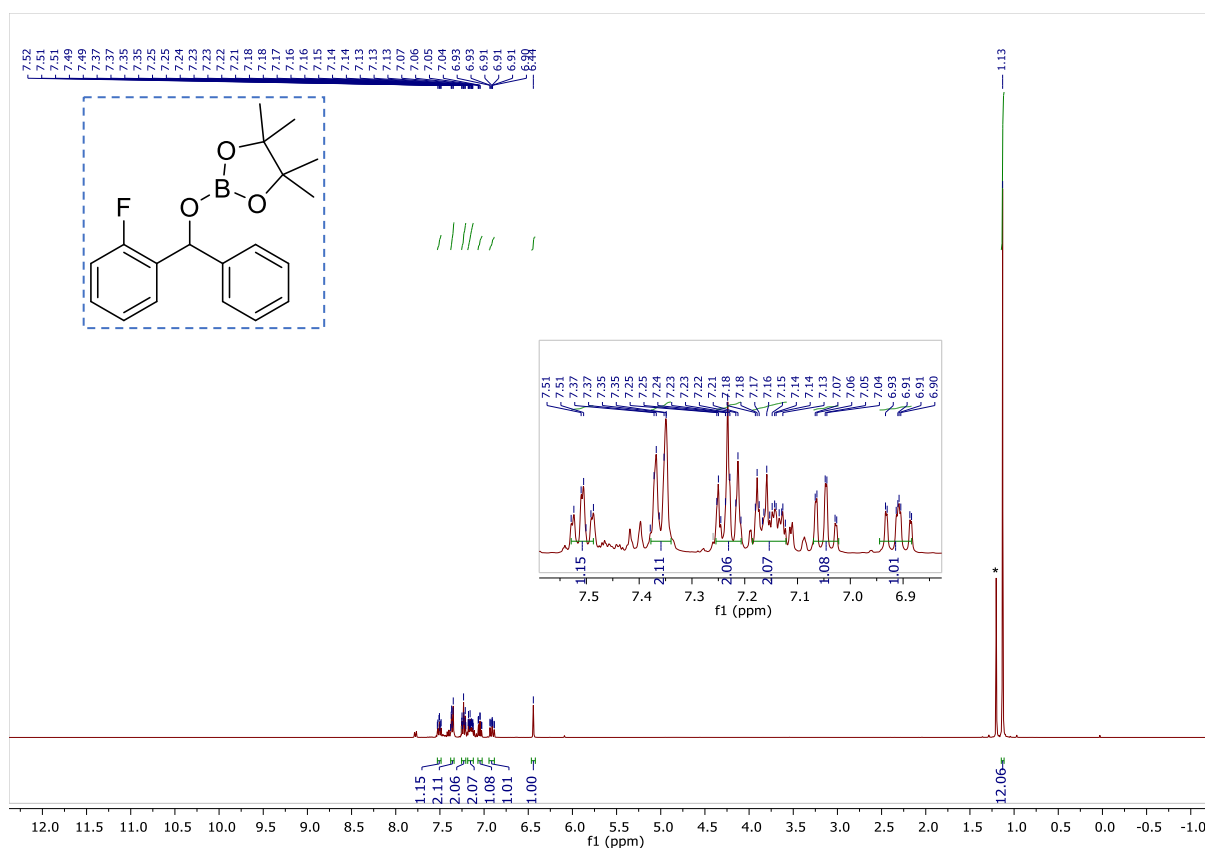


Figure S27 – ^1H NMR spectrum of **3s** from crude reaction mixture. *Excess of the HBpin.

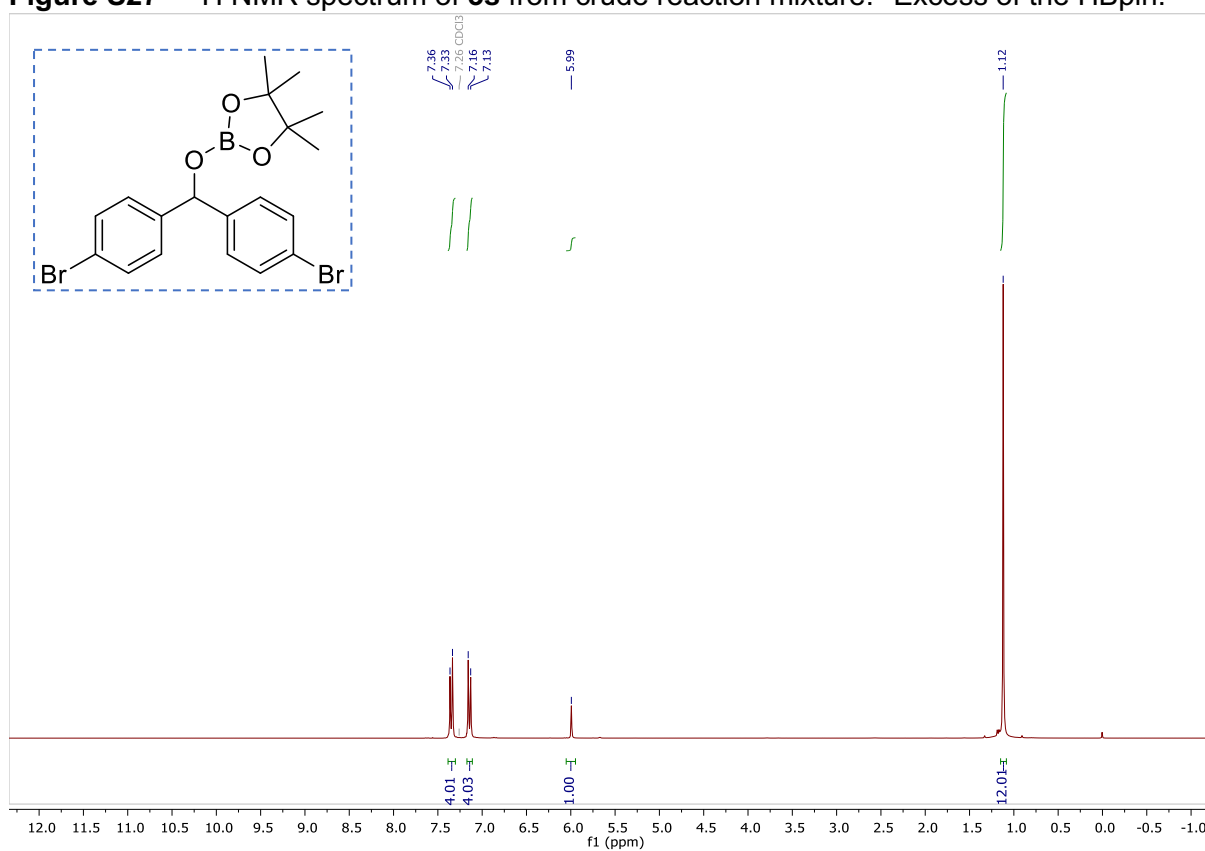


Figure S28 – ^1H NMR spectrum of **3t**.

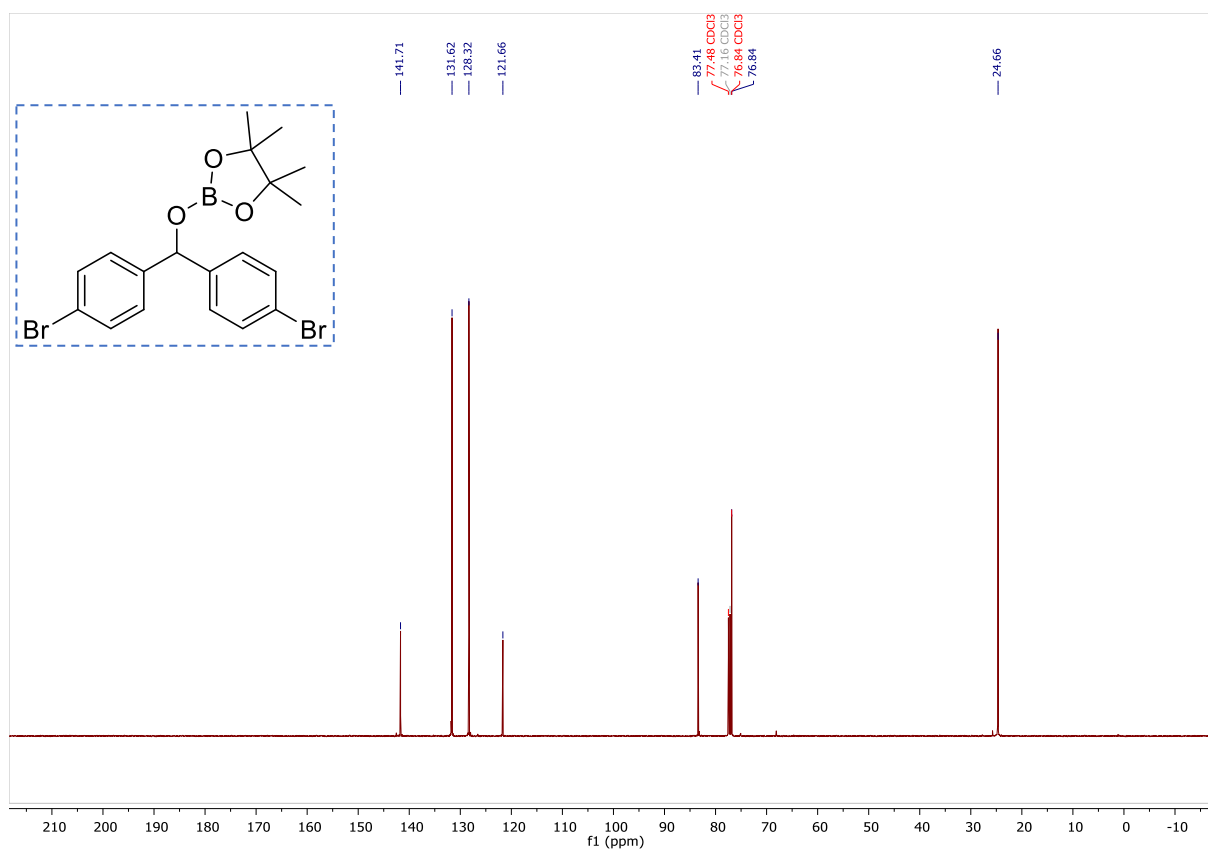


Figure S29 – ^{13}C NMR spectrum of **3t**.

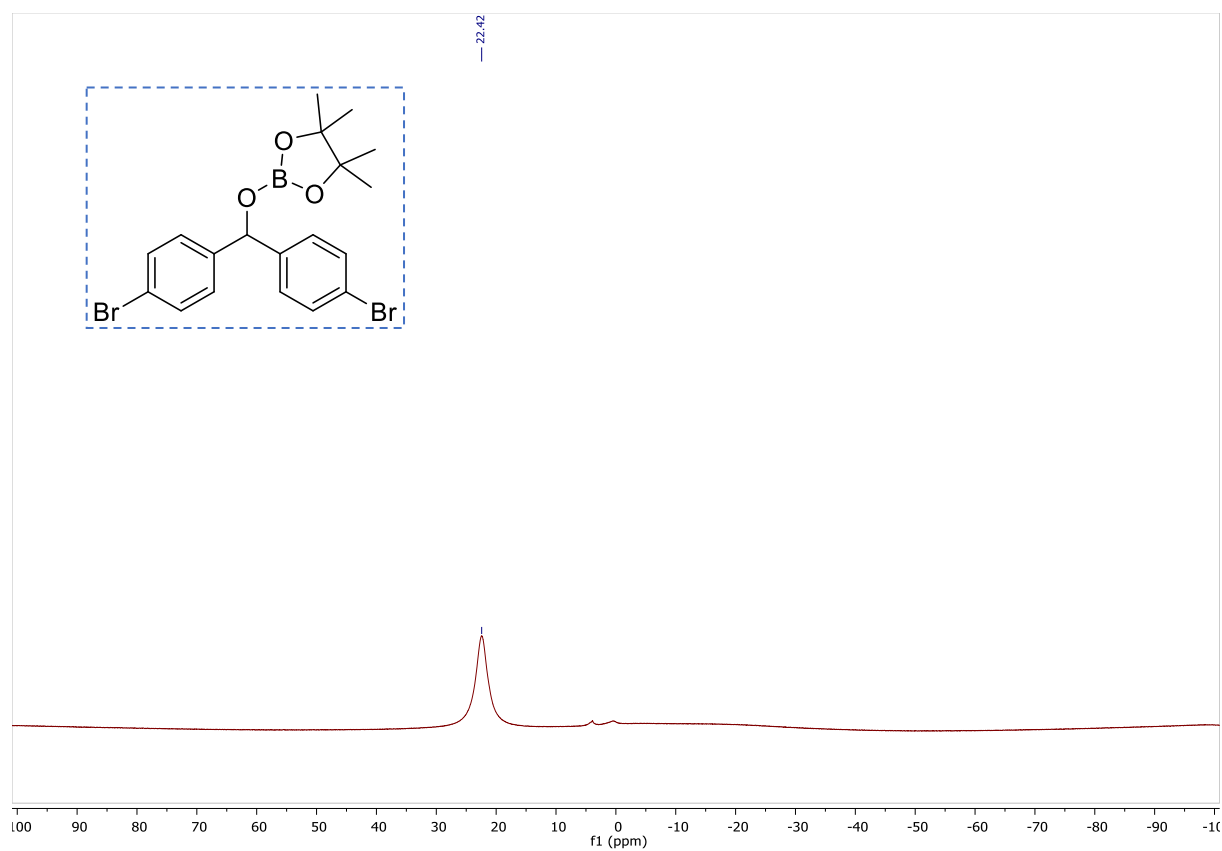


Figure S30 – ^{11}B NMR spectrum of **3t**.

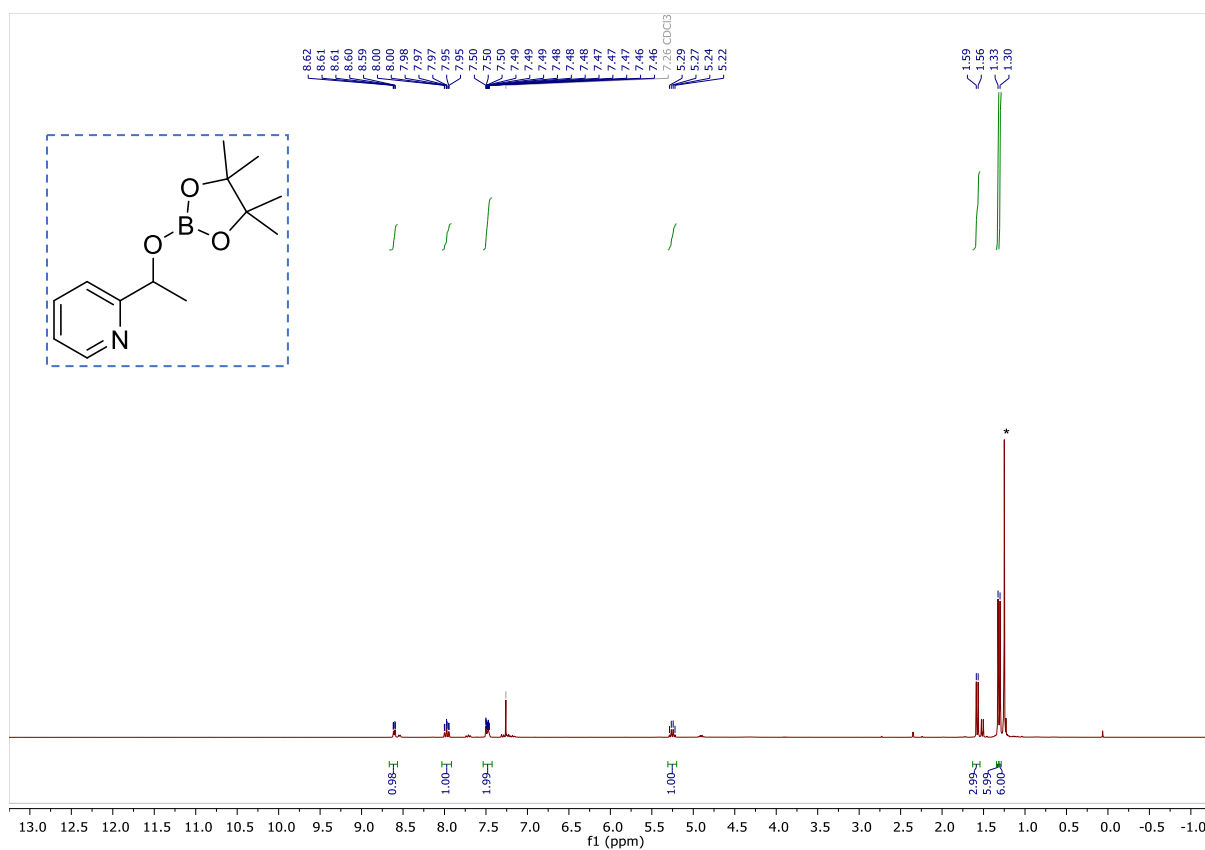


Figure S31 – ¹H NMR spectrum of **3u** from crude reaction mixture. *Excess of the HBpin.

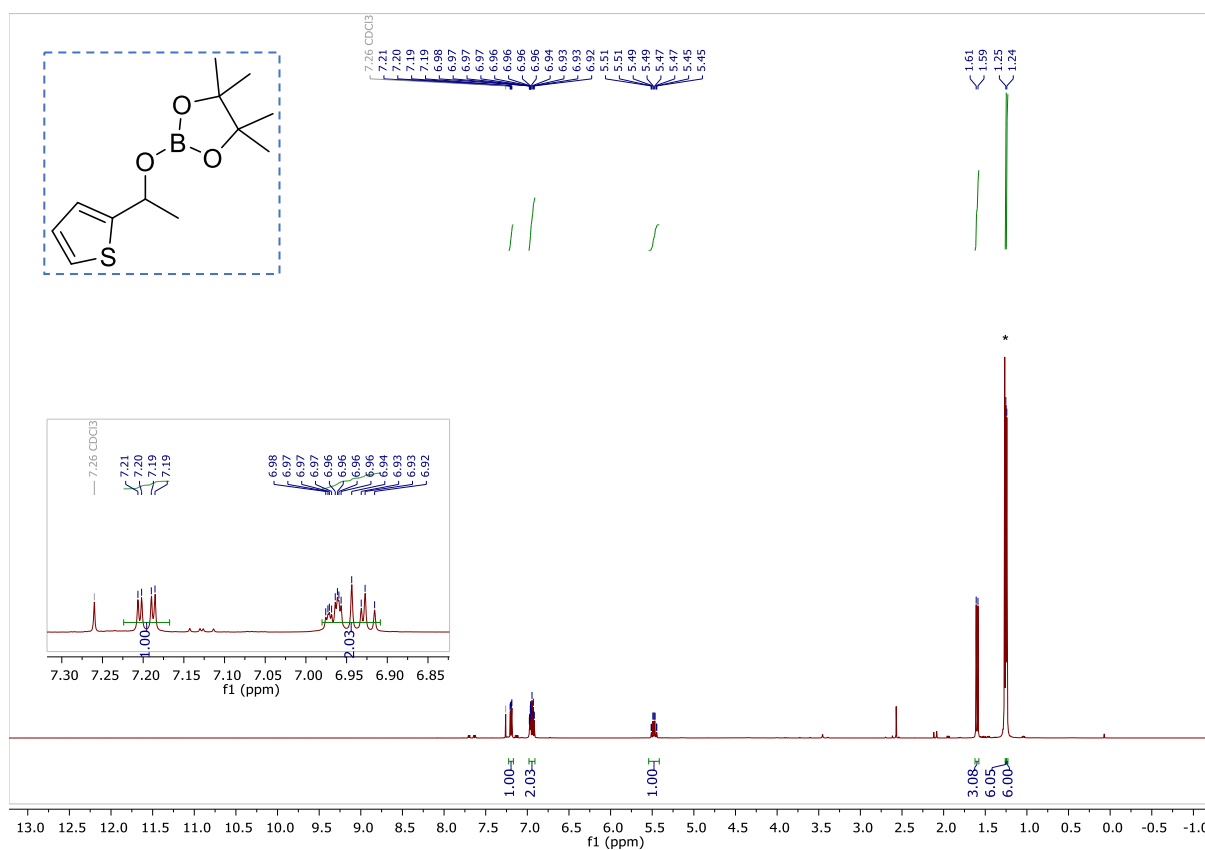


Figure S32 – ¹H NMR spectrum of **3v** from crude reaction mixture. *Excess of the HBpin.

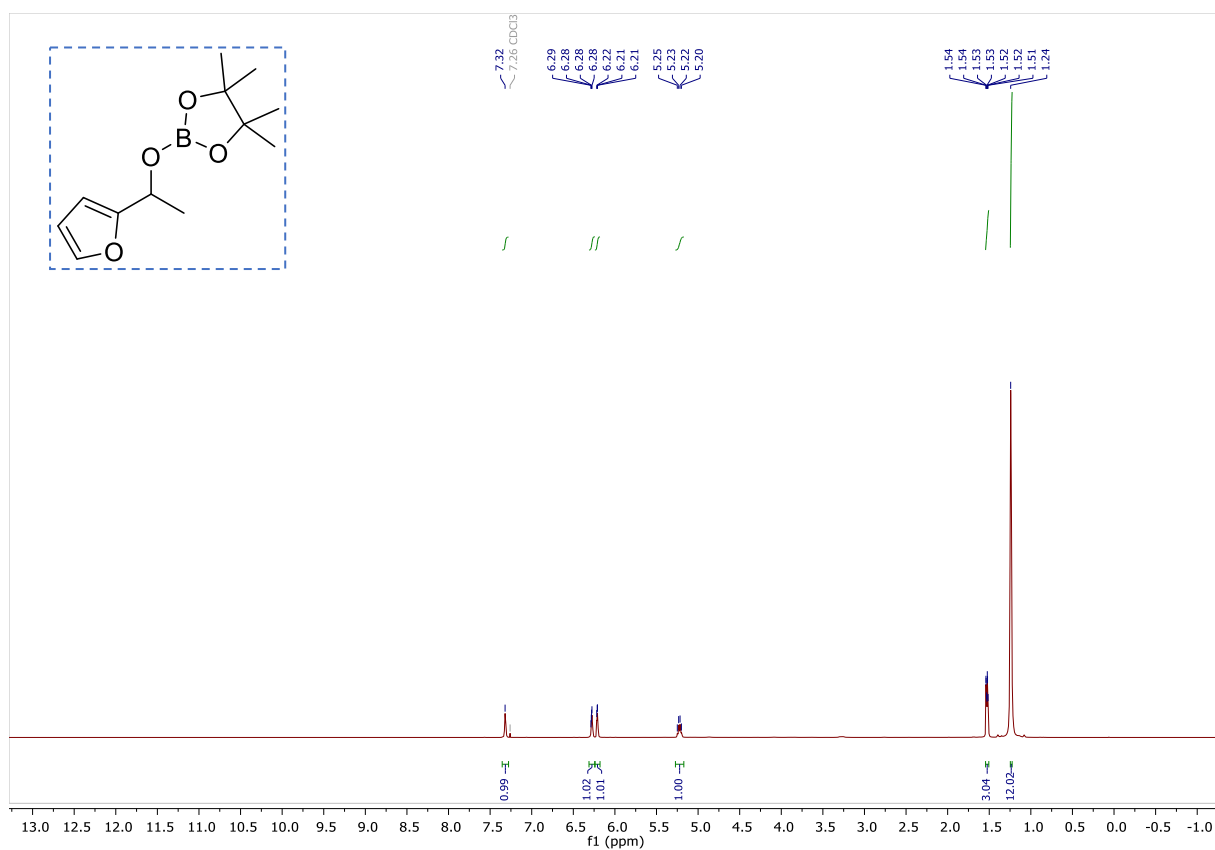


Figure S33 – ¹H NMR spectrum of **3w**.

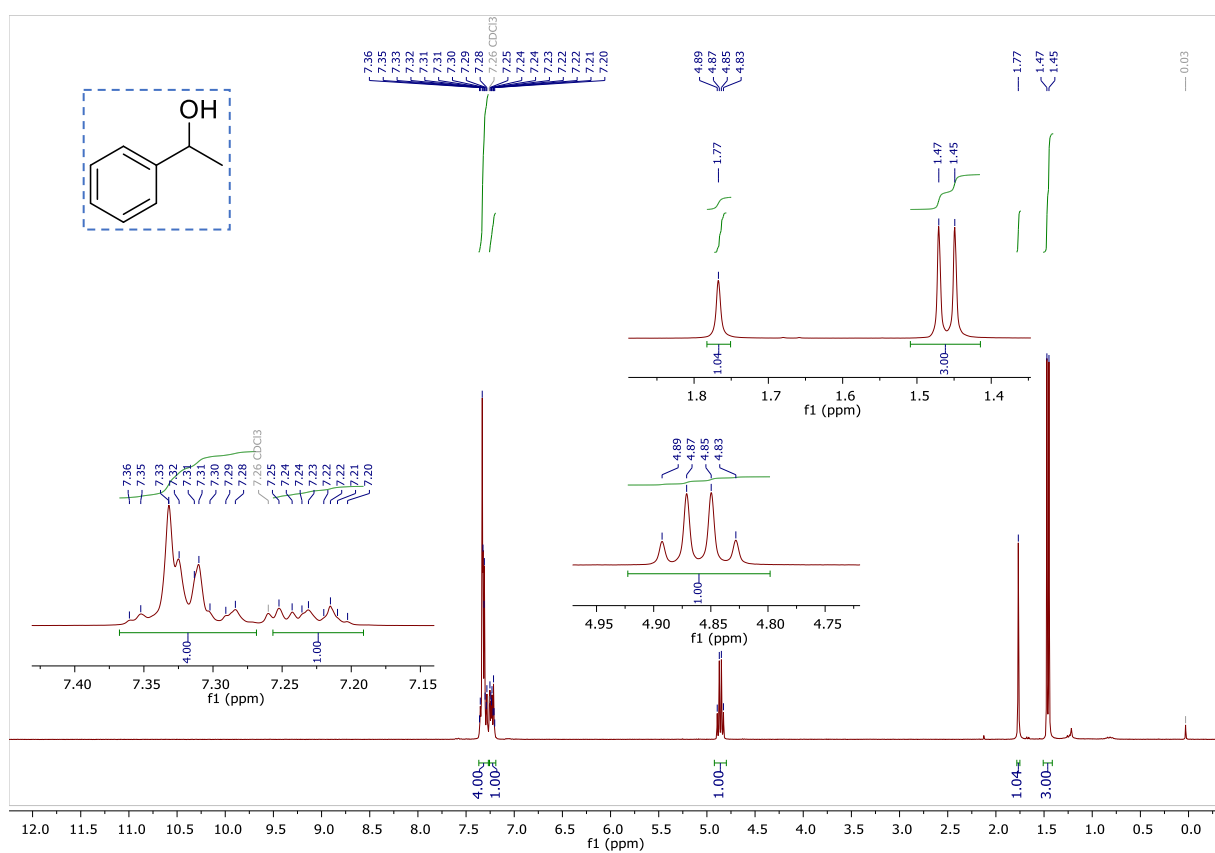


Figure S34 – ¹H NMR spectrum of **5a**.

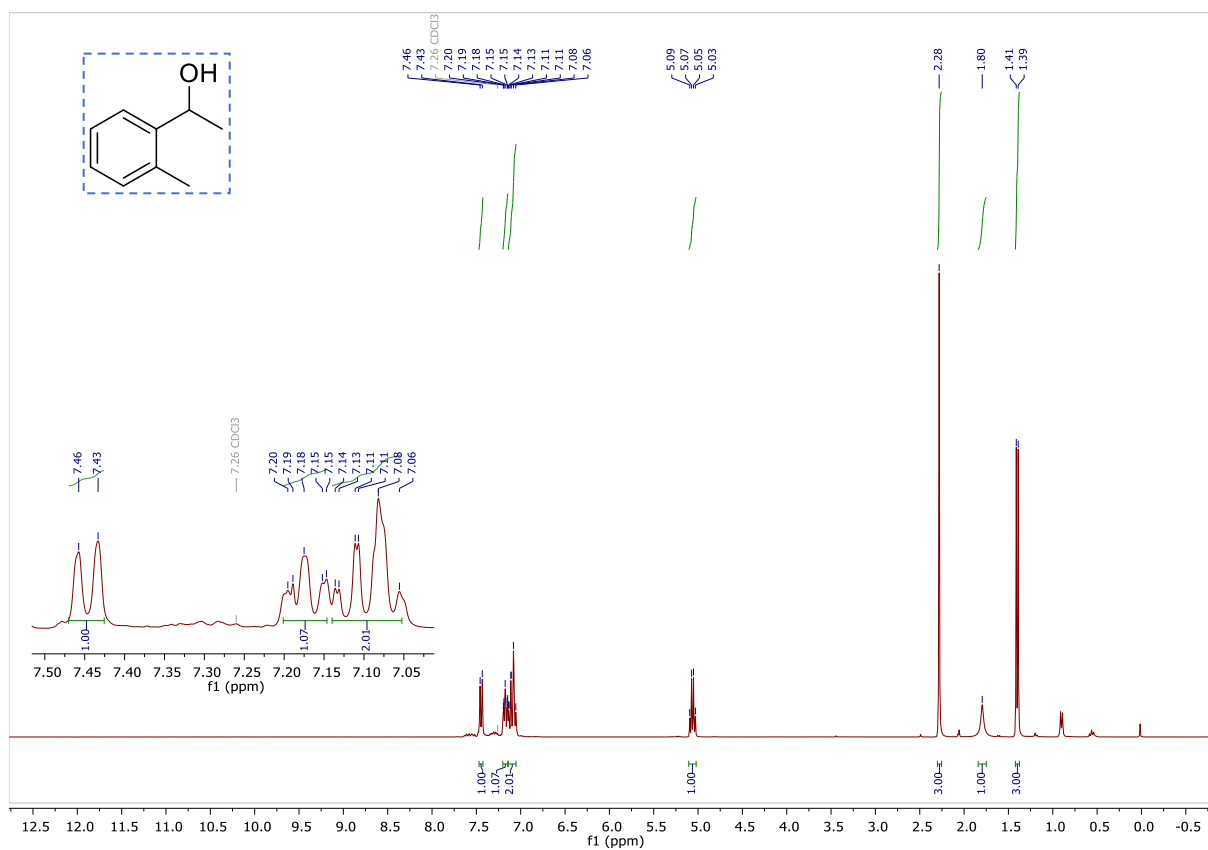


Figure S35 – ¹H NMR spectrum of **5b**.

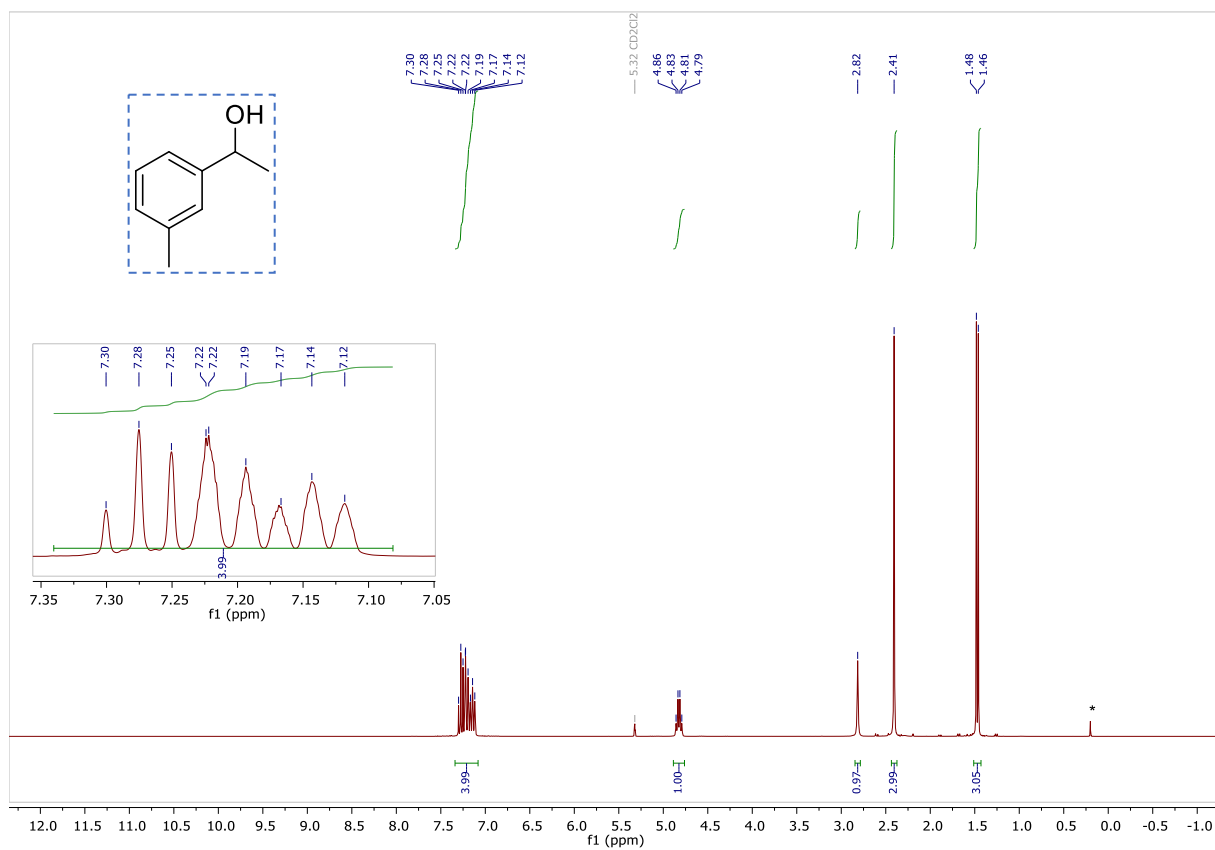


Figure S36 – ¹H NMR spectrum of **5c*** - Grease.

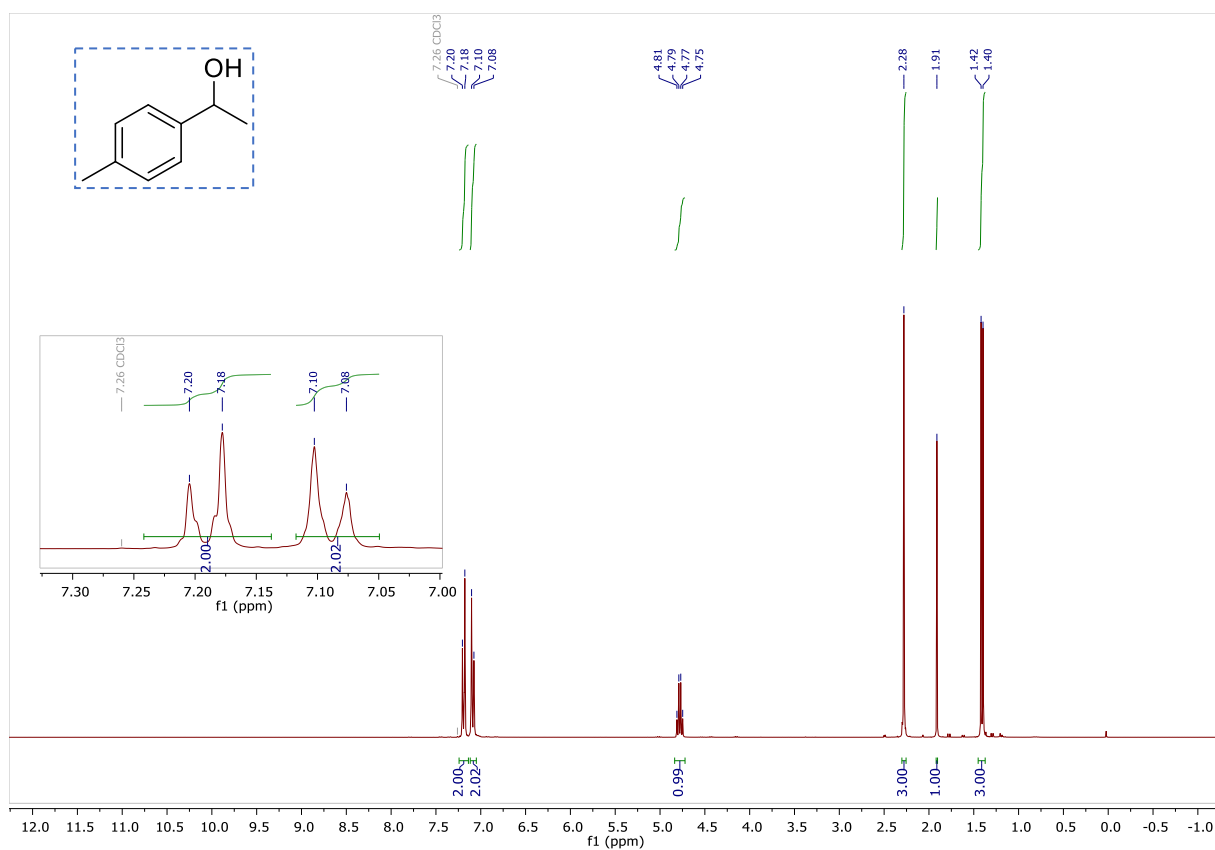


Figure S37 – ^1H NMR spectrum of **5d**.

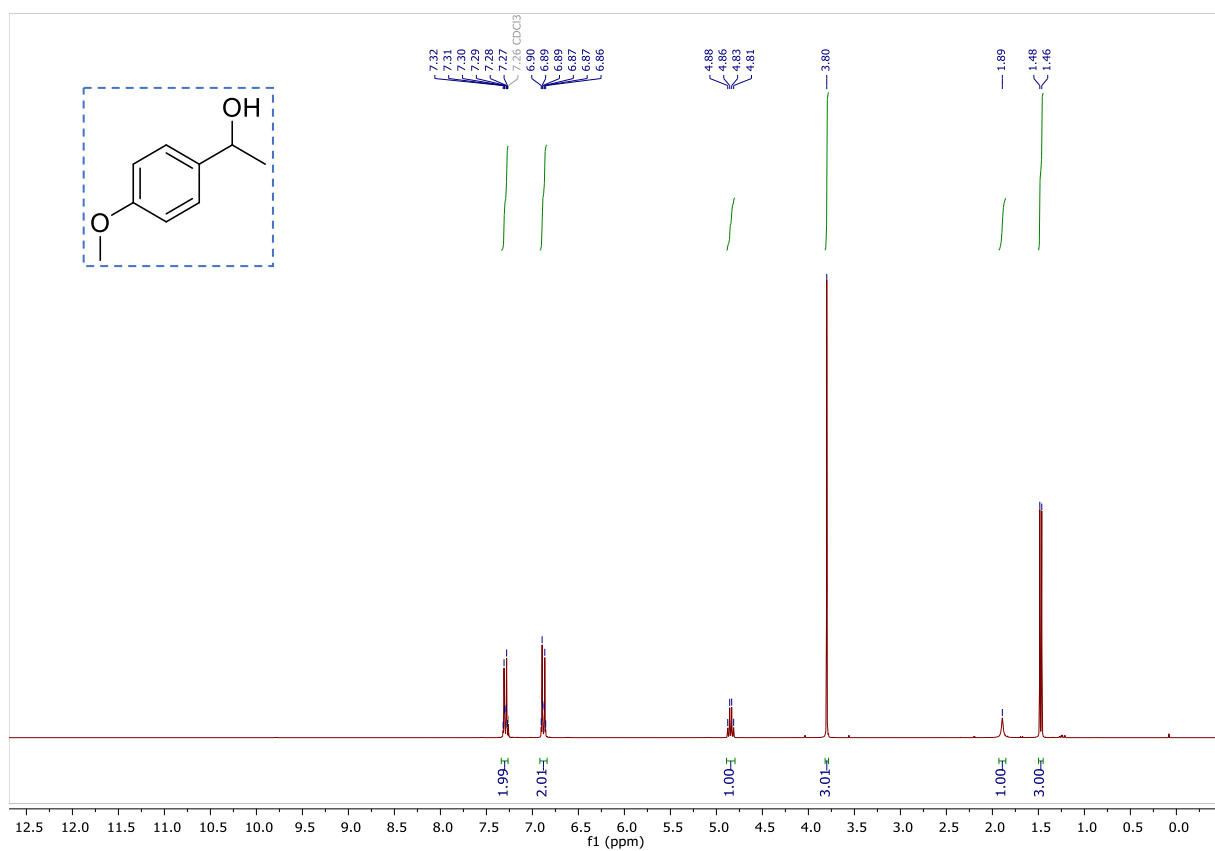


Figure S38 – ^1H NMR spectrum of **5e**.

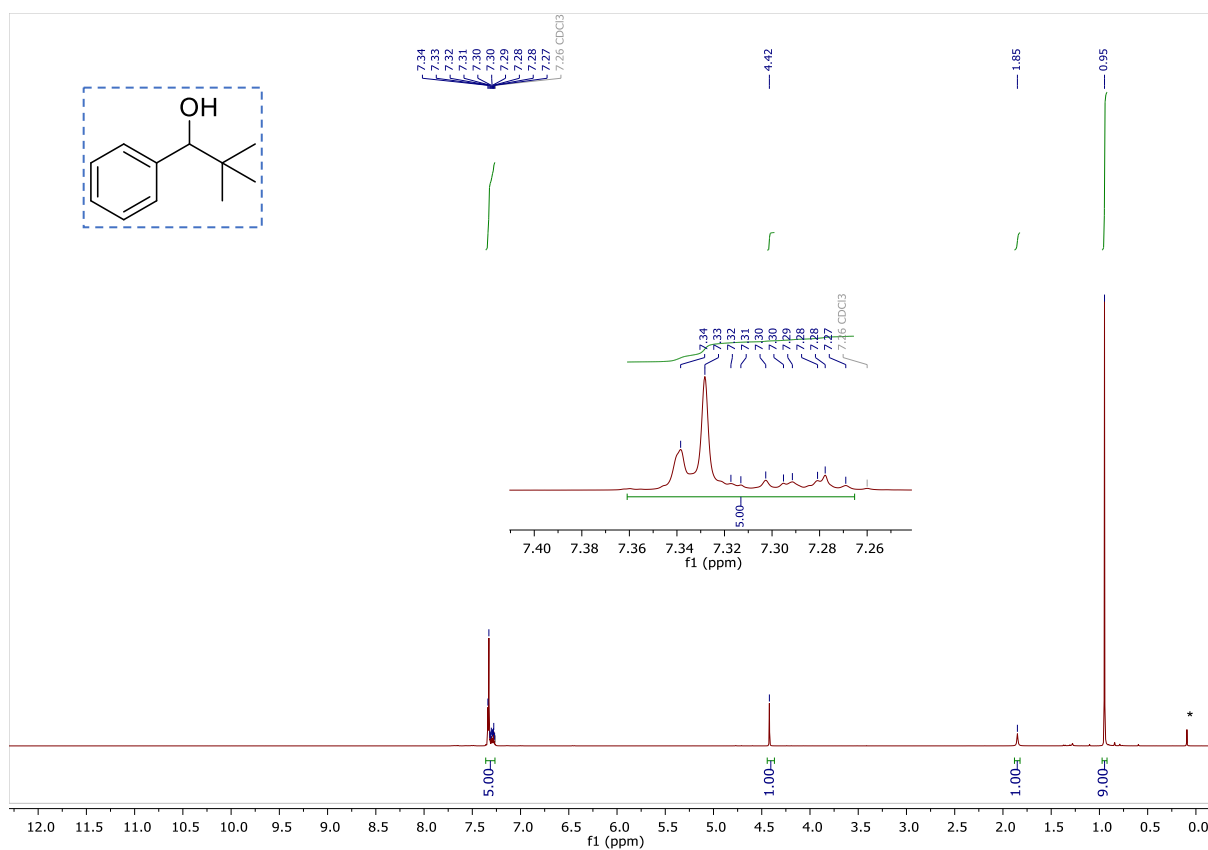


Figure S39 – ¹H NMR spectrum of 5f. * - Grease.

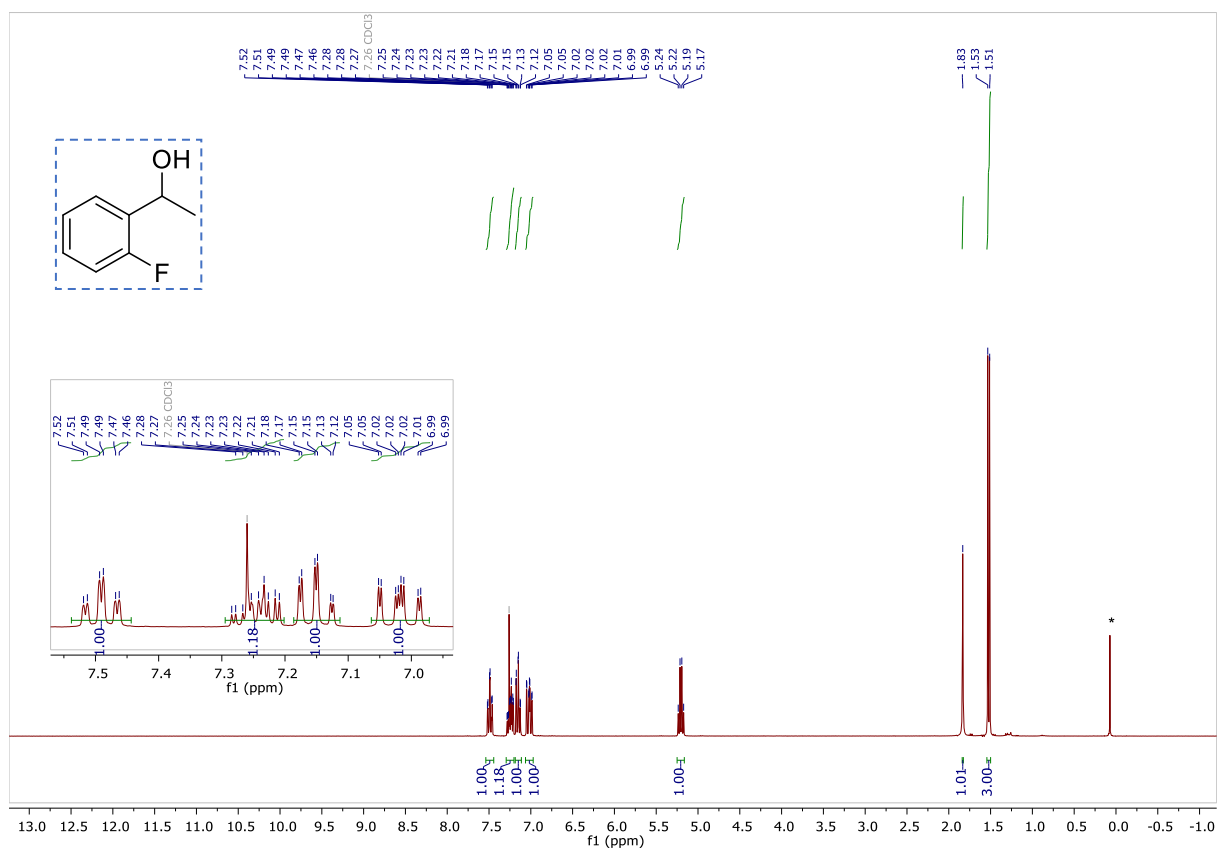


Figure S40 – ¹H NMR spectrum of 5g. * - Grease.

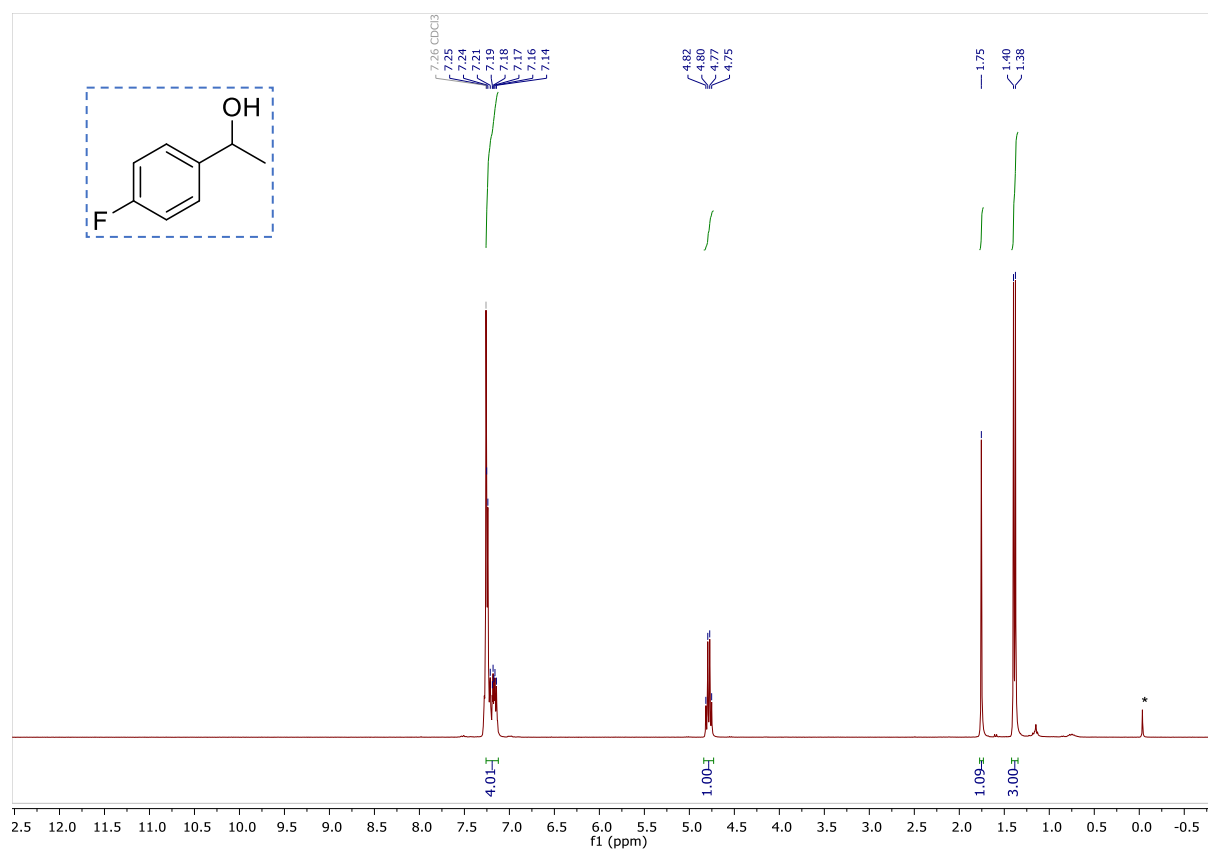


Figure S41 – ¹H NMR spectrum of **5h**. * - Grease.

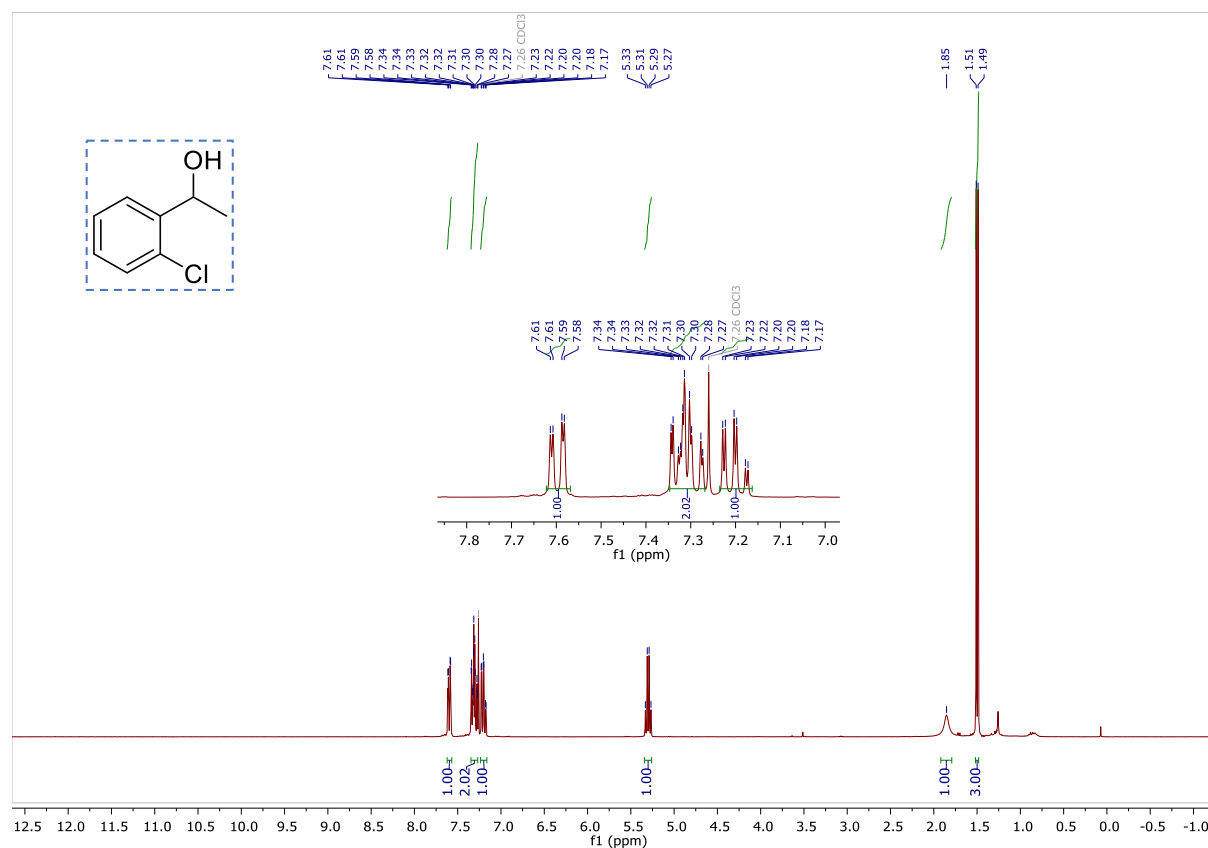


Figure S42 – ¹H NMR spectrum of **5i**.

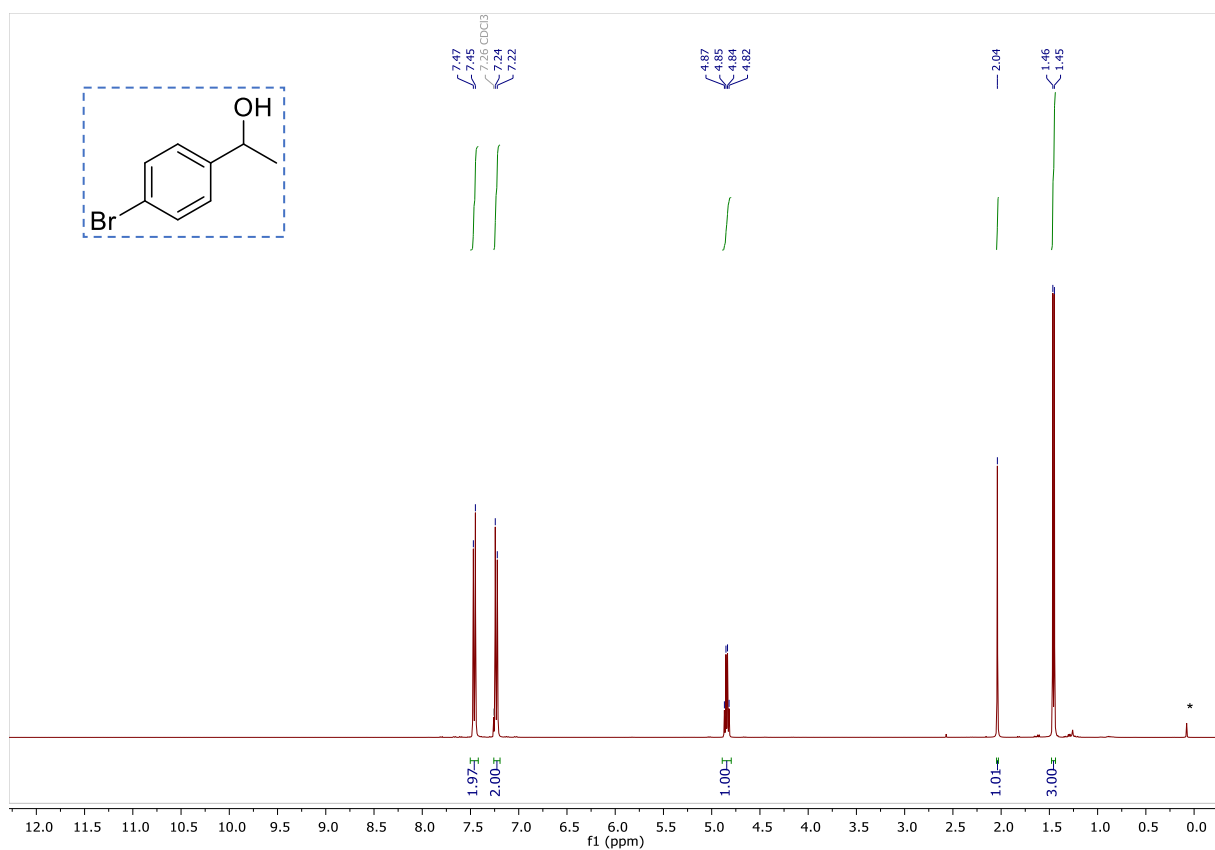


Figure S43 – ¹H NMR spectrum of 5j. * - Grease.

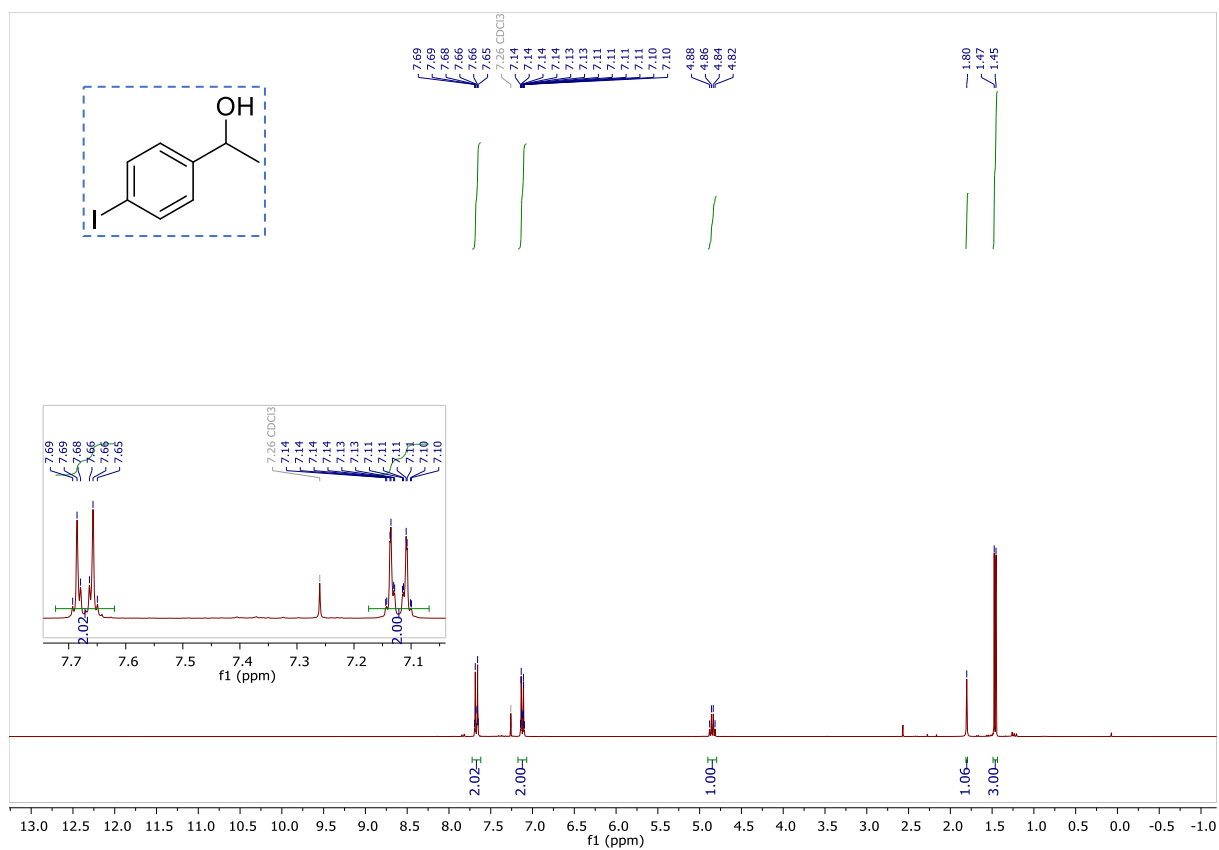


Figure S44 – ¹H NMR spectrum of 5k.

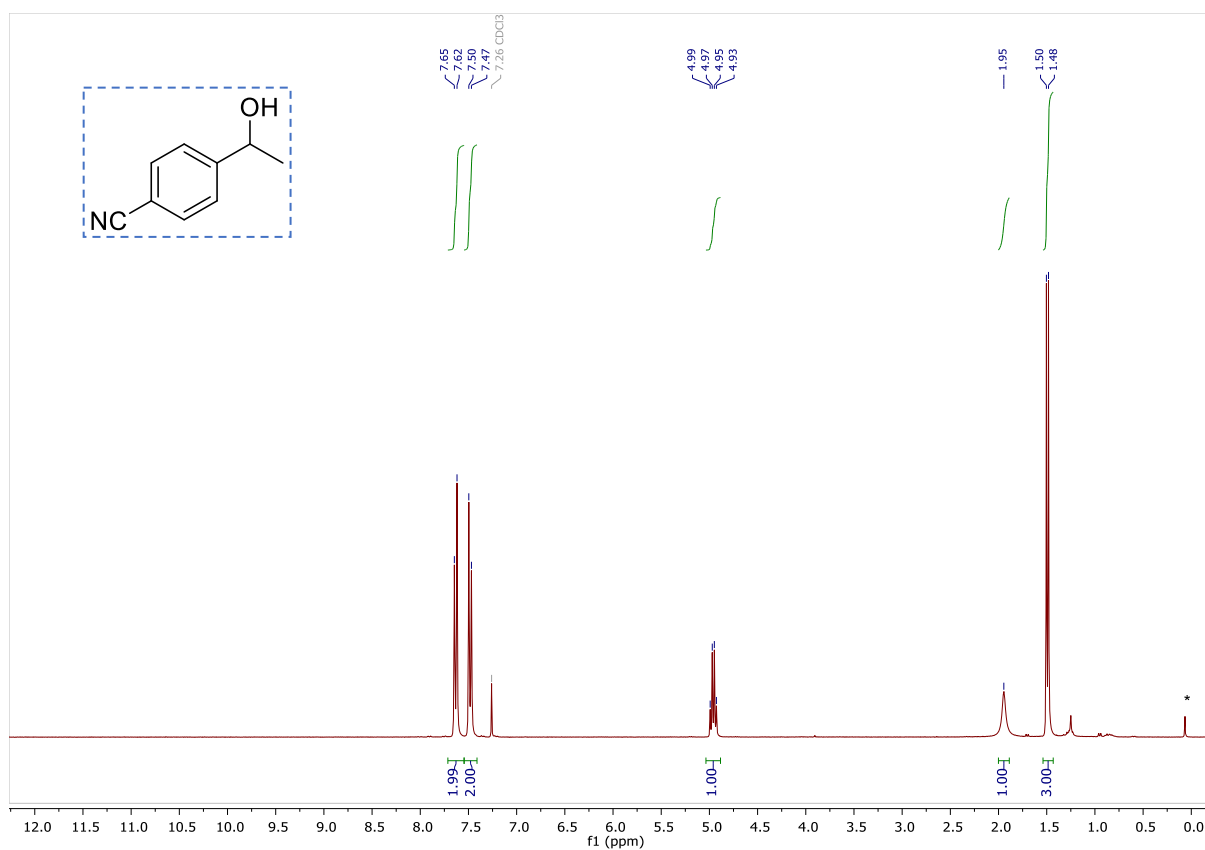


Figure S45 – ¹H NMR spectrum of 5l. * - Grease.

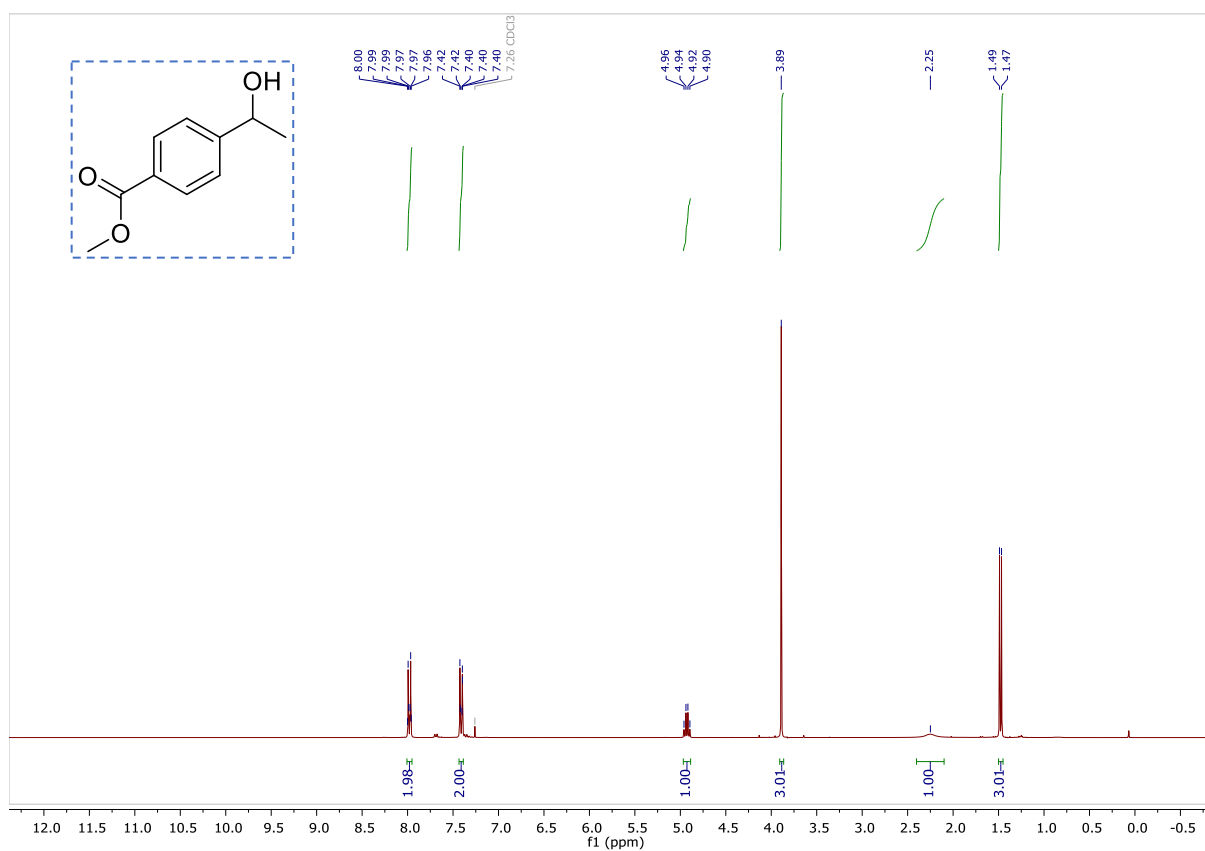


Figure S46 – ¹H NMR spectrum of 5m.

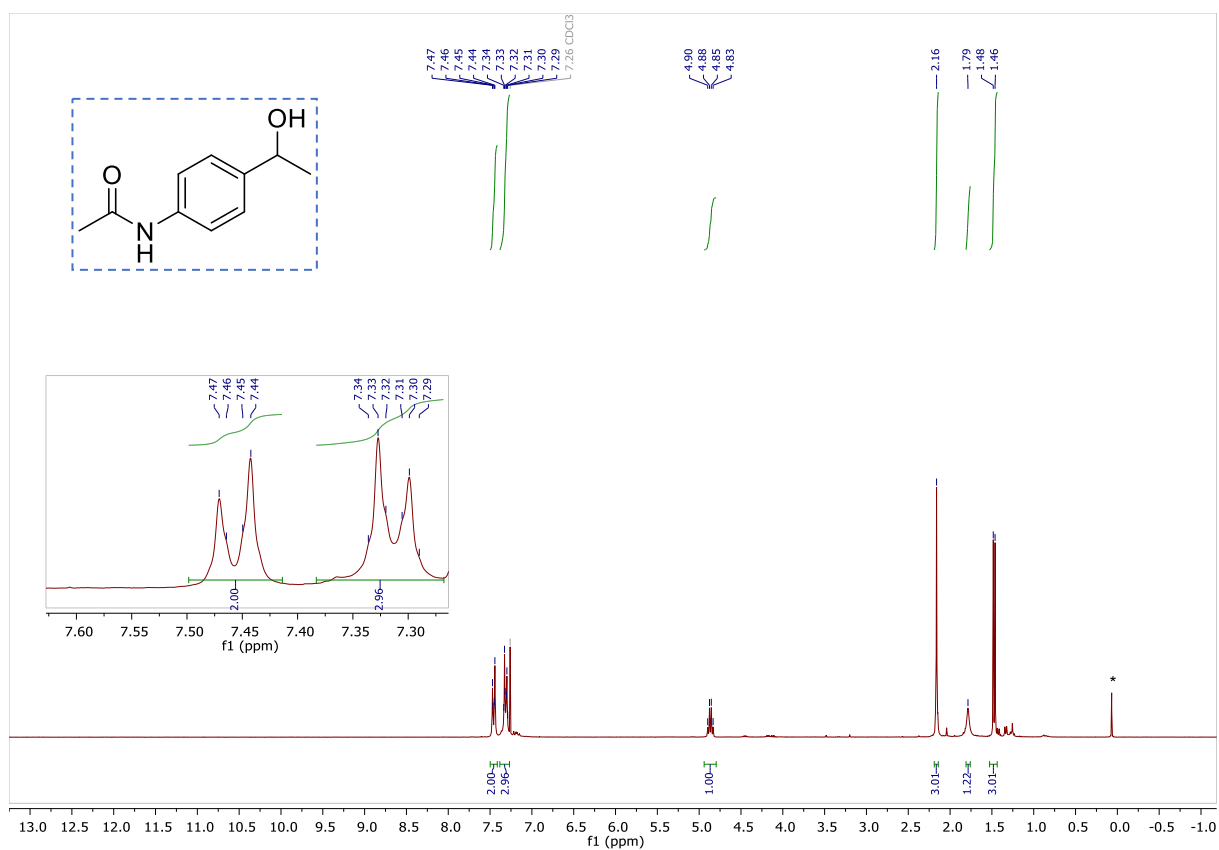


Figure S47 – ¹H NMR spectrum of 5n.

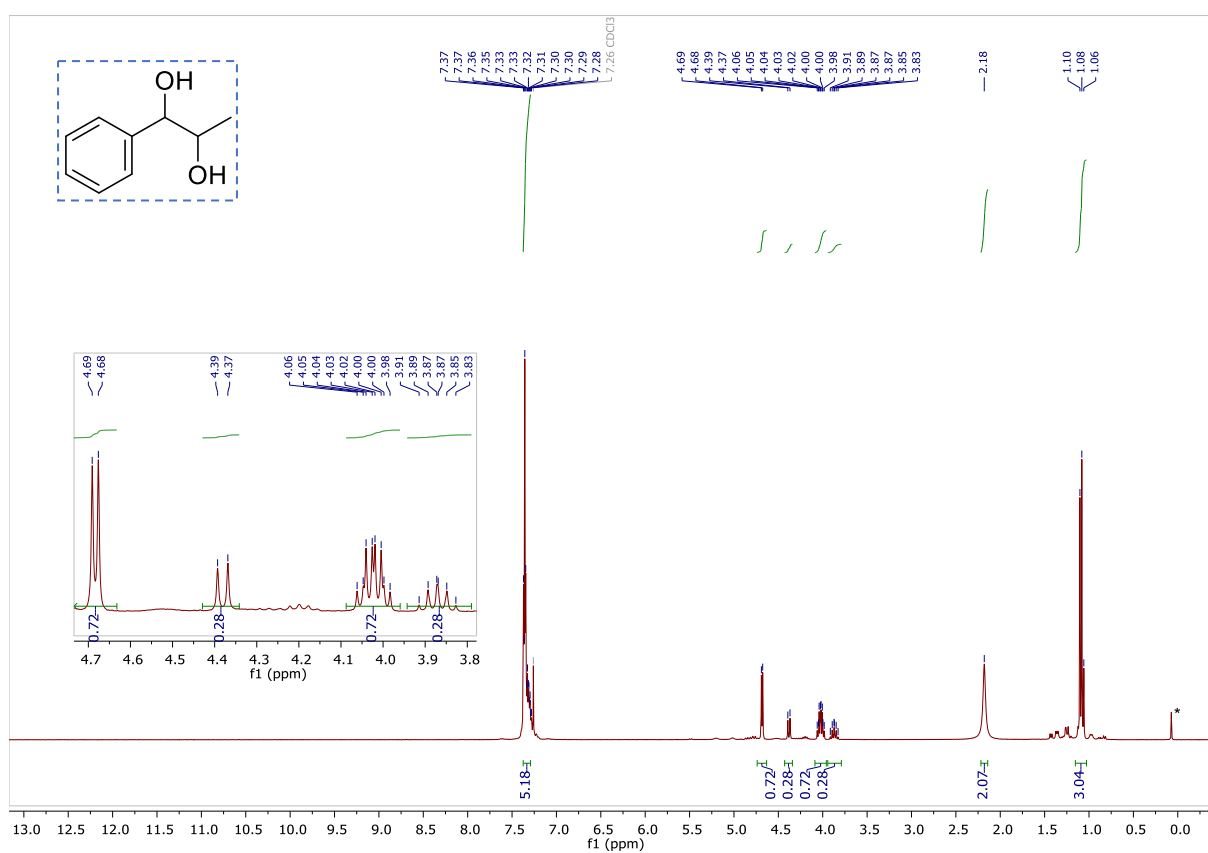


Figure S48 – ¹H NMR spectrum of 5o.

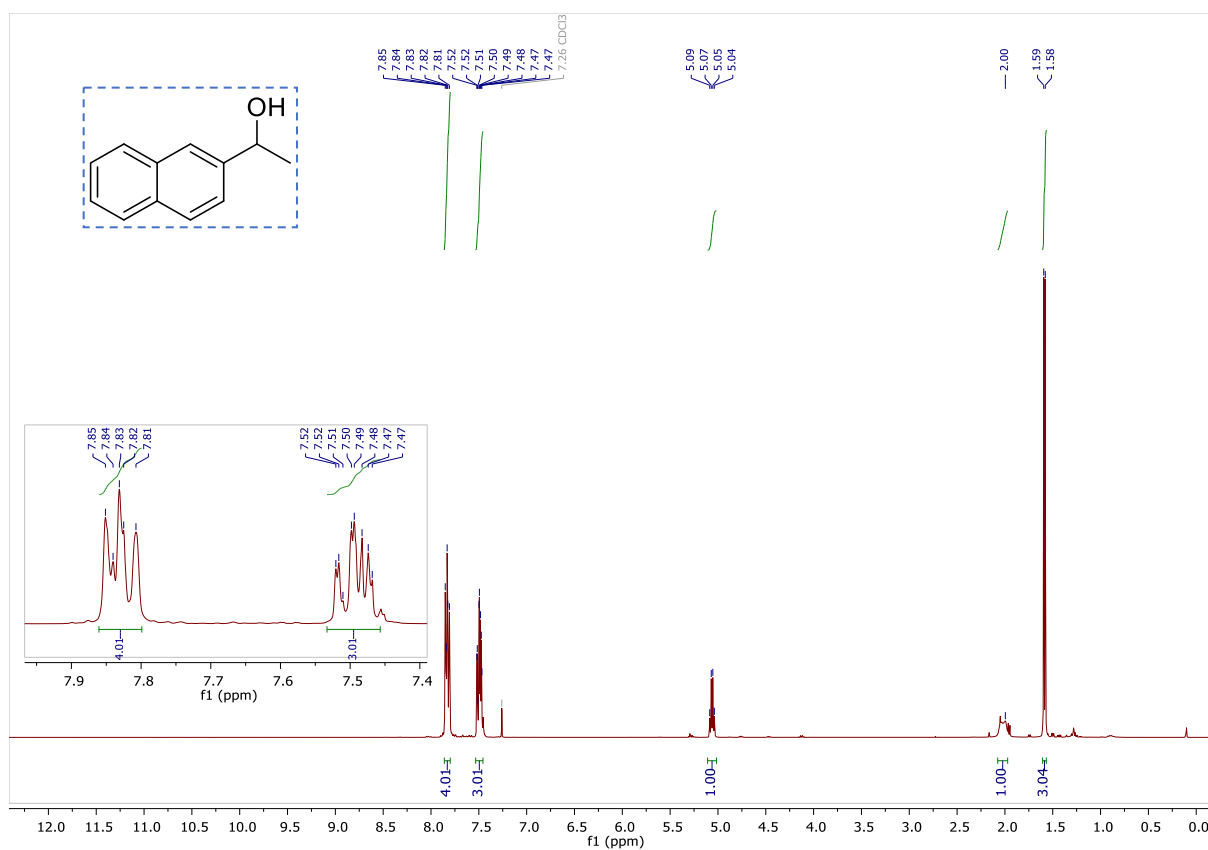


Figure S49 – ¹H NMR spectrum of 5p.

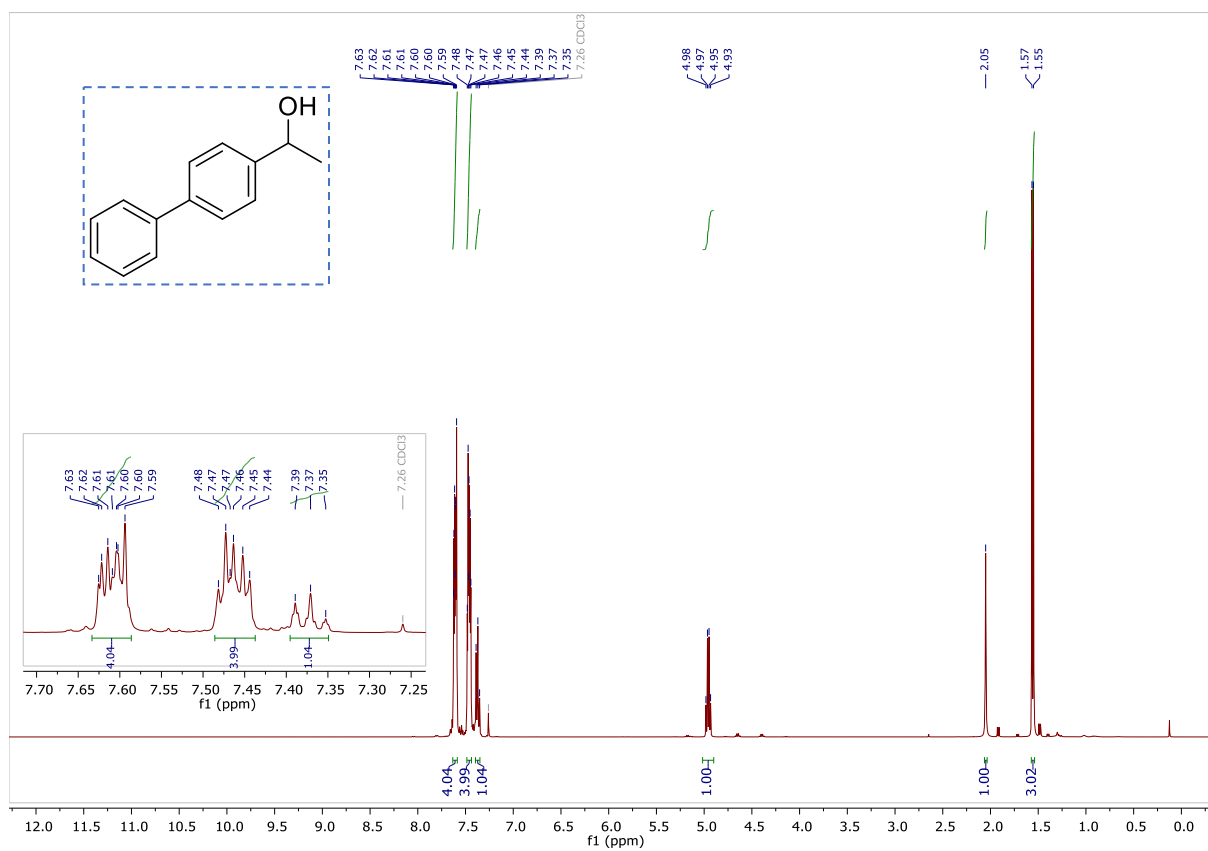


Figure S50 – ¹H NMR spectrum of 5q.

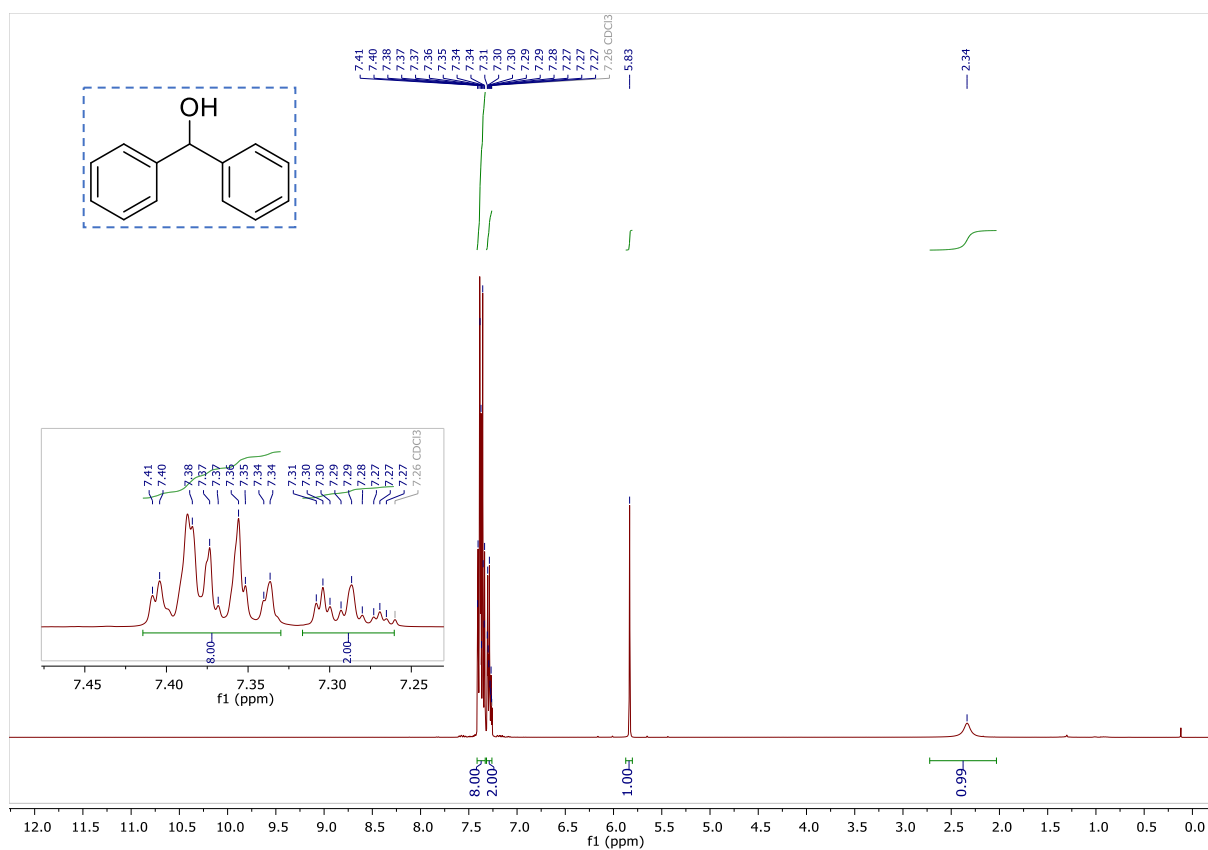


Figure S51 – ¹H NMR spectrum of 5r.

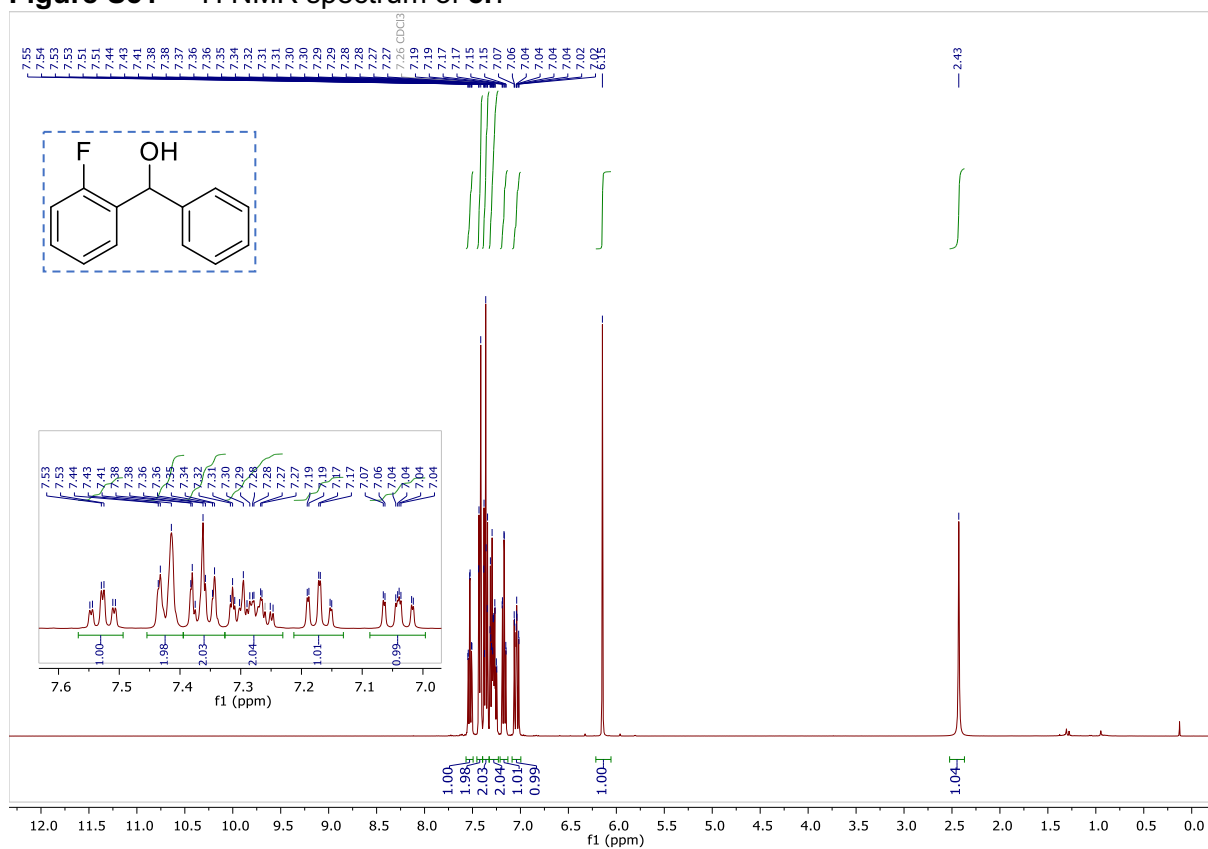


Figure S52 – ¹H NMR spectrum of 5s.

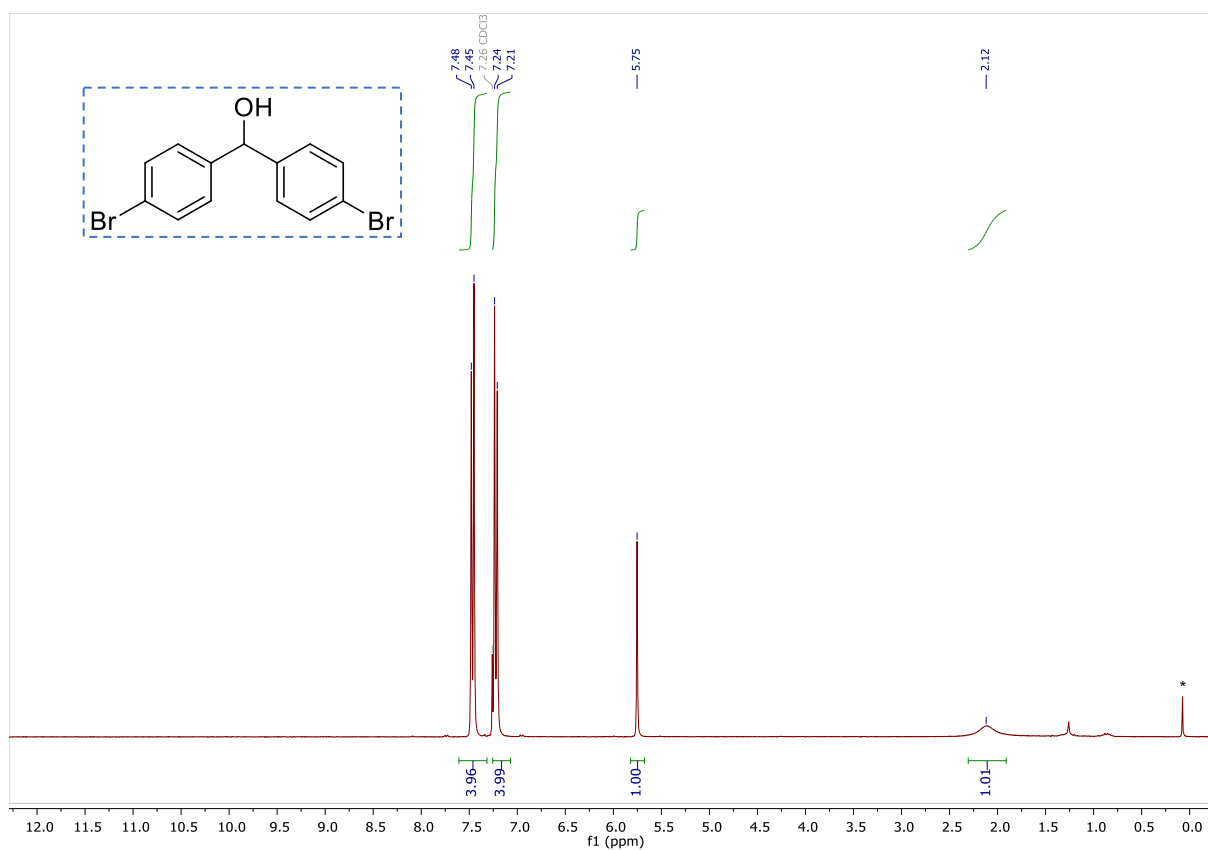


Figure S53 – ¹H NMR spectrum of 5t. * - Grease.

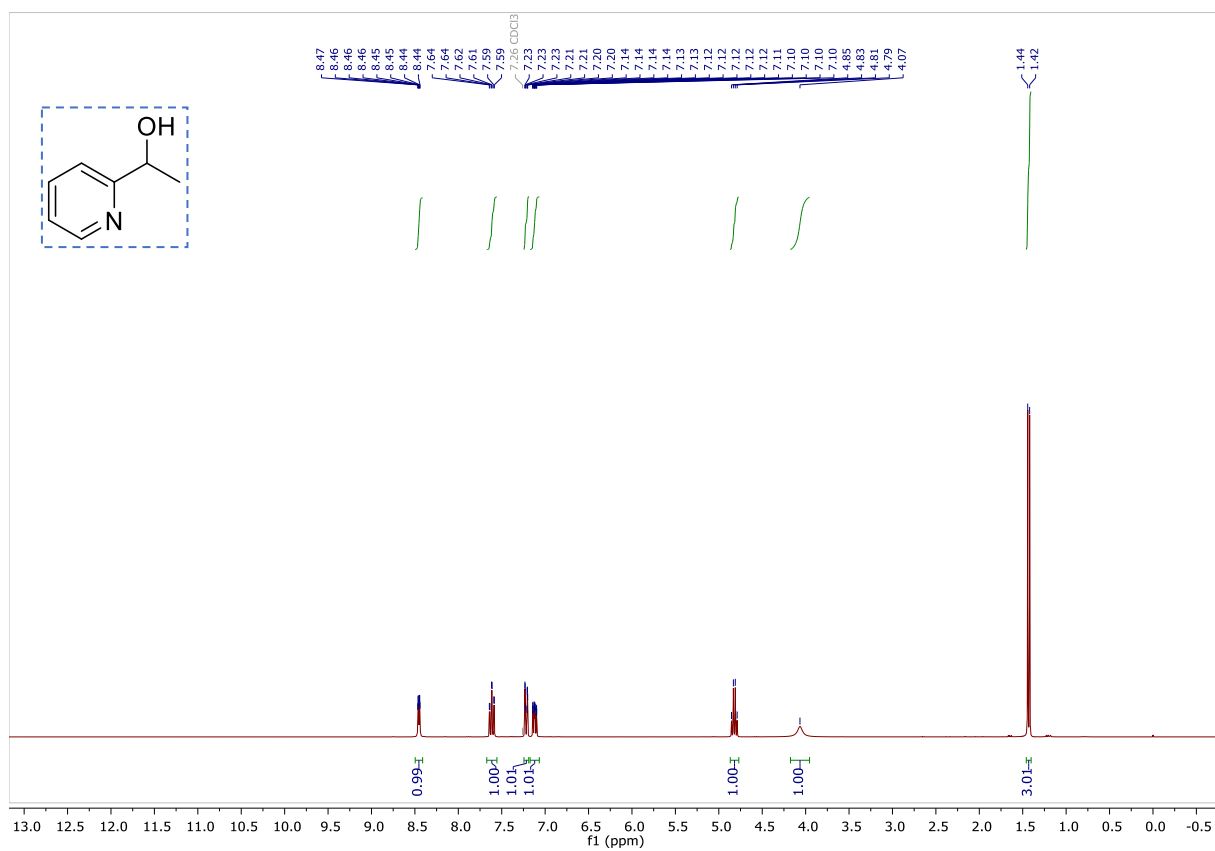


Figure S54 – ¹H NMR spectrum of 5u.

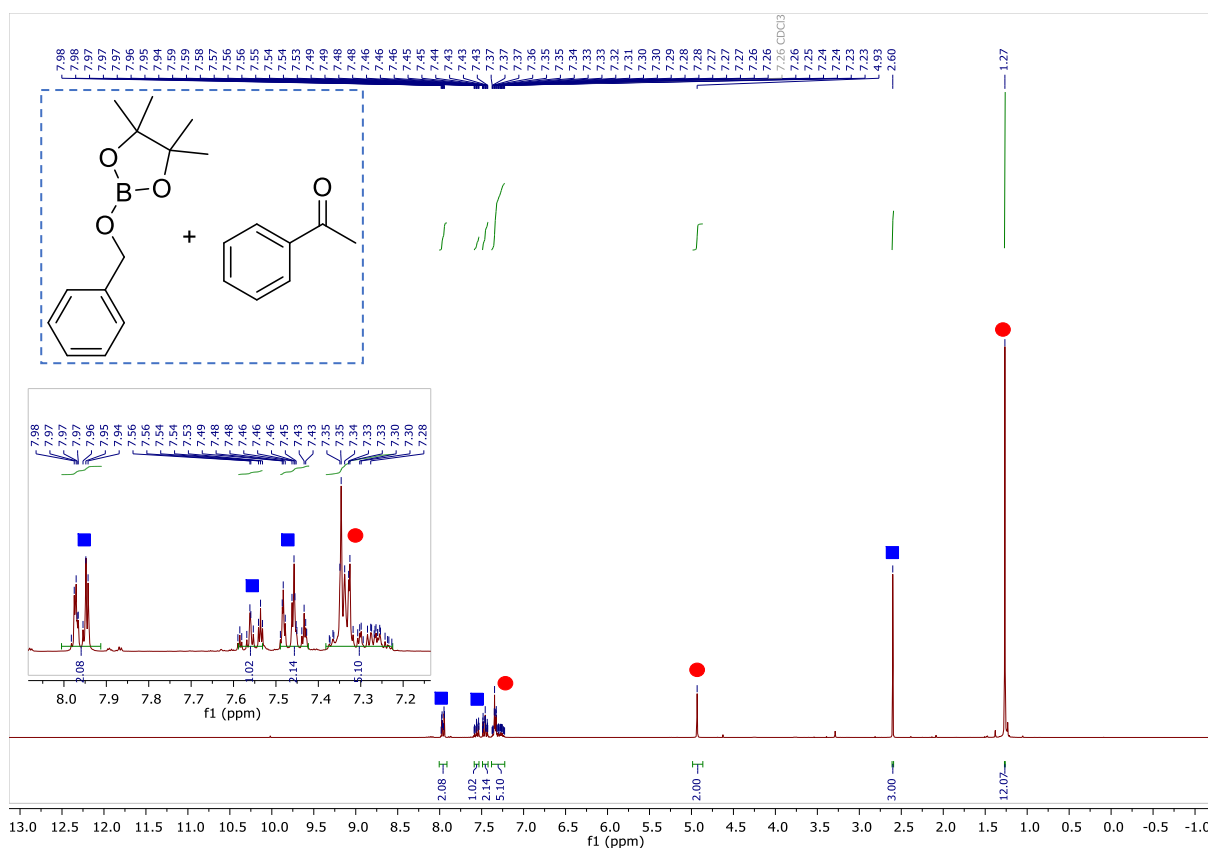


Figure S57 – ^1H NMR spectrum from the competitive hydroboration reaction of benzaldehyde and acetophenone (**1a**) with pinacolborane (**2**) as a reducing agent. Blue square (■) – signals from acetophenone; red circle (●) – signals from benzaldehyde hydroboration product.

6. Immobilization of $\text{Pt}(\text{PPh}_3)_4$ in $[\text{BMIM}][\text{NTf}_2]$

50 mg (11.9 mmol) of $[\text{BMIM}][\text{NTf}_2]$ was mixed with 10 mg (0.008 mmol) of $\text{Pt}(\text{PPh}_3)_4$. The mixture was stirred for 3 h at 60 °C under argon atmosphere. After this time, ^1H and ^{31}P NMR spectra were measured in CDCl_3 .

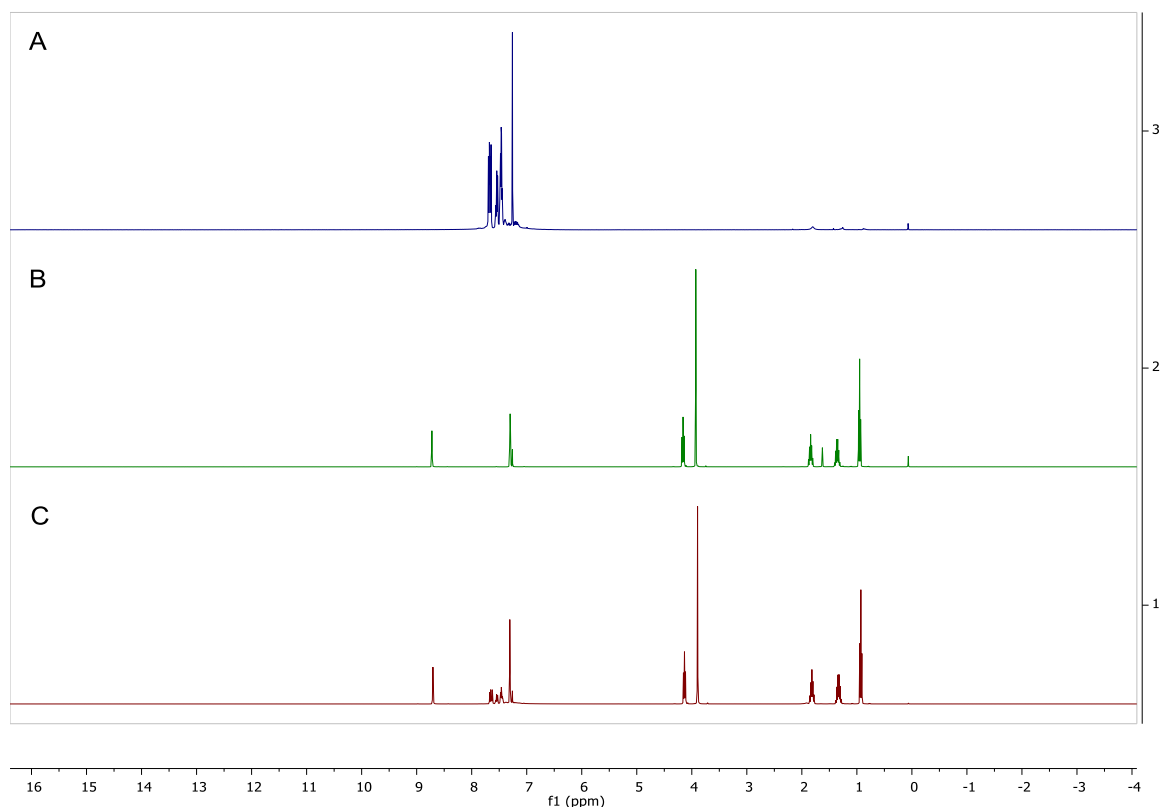


Figure S58 – ^1H NMR spectrum of $\text{Pt}(\text{PPh}_3)_4$ (A), $[\text{BMIM}][\text{NTf}_2]$ (B) and mixture of $\text{Pt}(\text{PPh}_3)_4$ and $[\text{BMIM}][\text{NTf}_2]$ (C) .

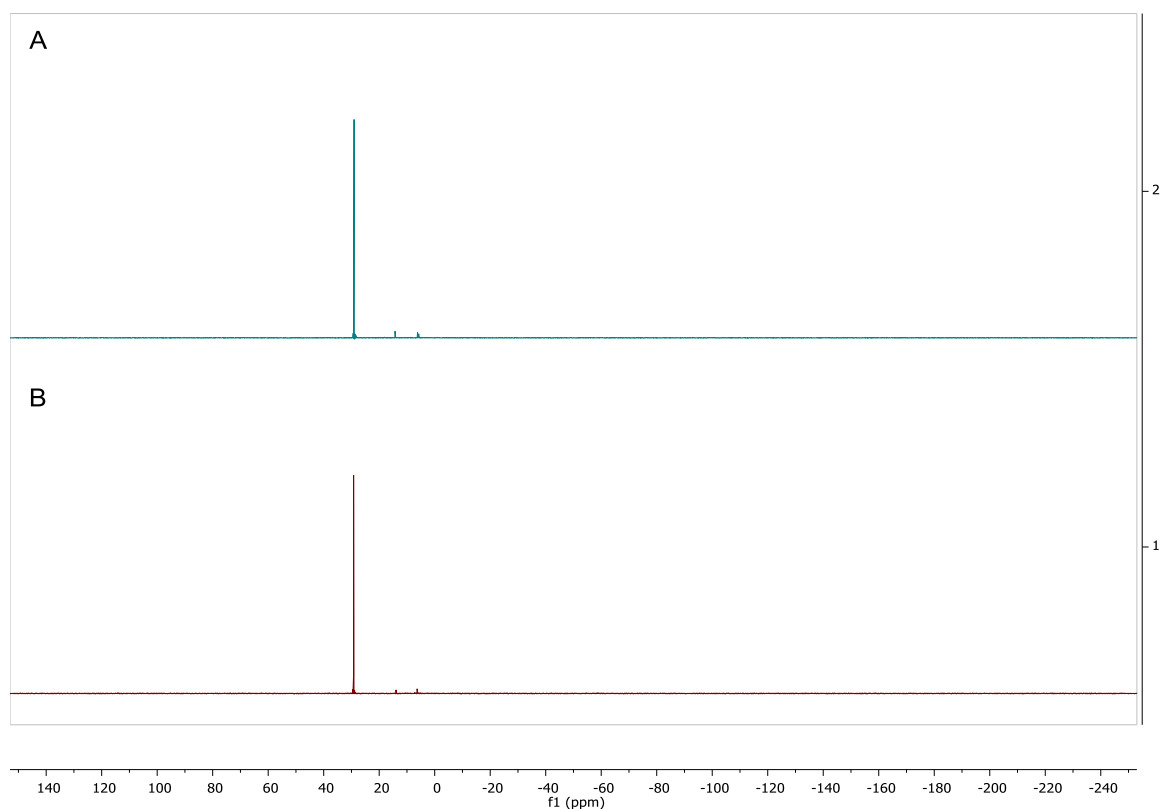


Figure S59 – ^{31}P NMR spectrum of $\text{Pt}(\text{PPh}_3)_4$ (A) and mixture of $\text{Pt}(\text{PPh}_3)_4$ and $[\text{BMIM}][\text{NTf}_2]$ (B).

7. Stability of HBpin in $[\text{BMIM}][\text{NTf}_2]$

To determine the stability of pinacolborane in the ionic liquid, pinacolborane (0.18 mmol, 32 mg) and $[\text{BMIM}][\text{NTf}_2]$ (0.18 mmol, 75.5 mg) were mixed in equimolar ratio. The mixture was stirred for 3 h at 60 °C under argon atmosphere and then ^1H and ^{11}B NMR spectra were performed in CDCl_3 . New signals or changes in the multiplicity of signals were not observed.

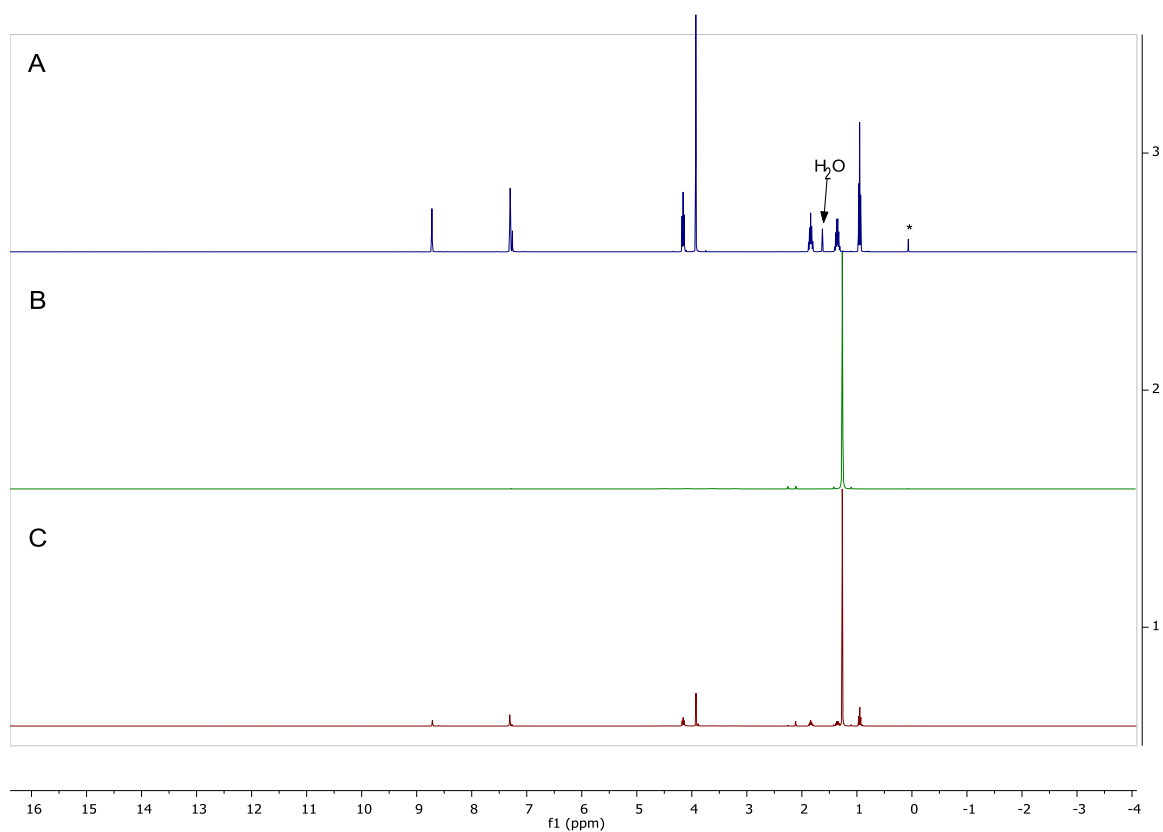


Figure S60 – ^1H NMR spectrum of [BMIM][NTf₂] (A), pinacolborane (B) and equimolar mixture of pinacolborane with [BMIM][NTf₂] (C). * - Grease.

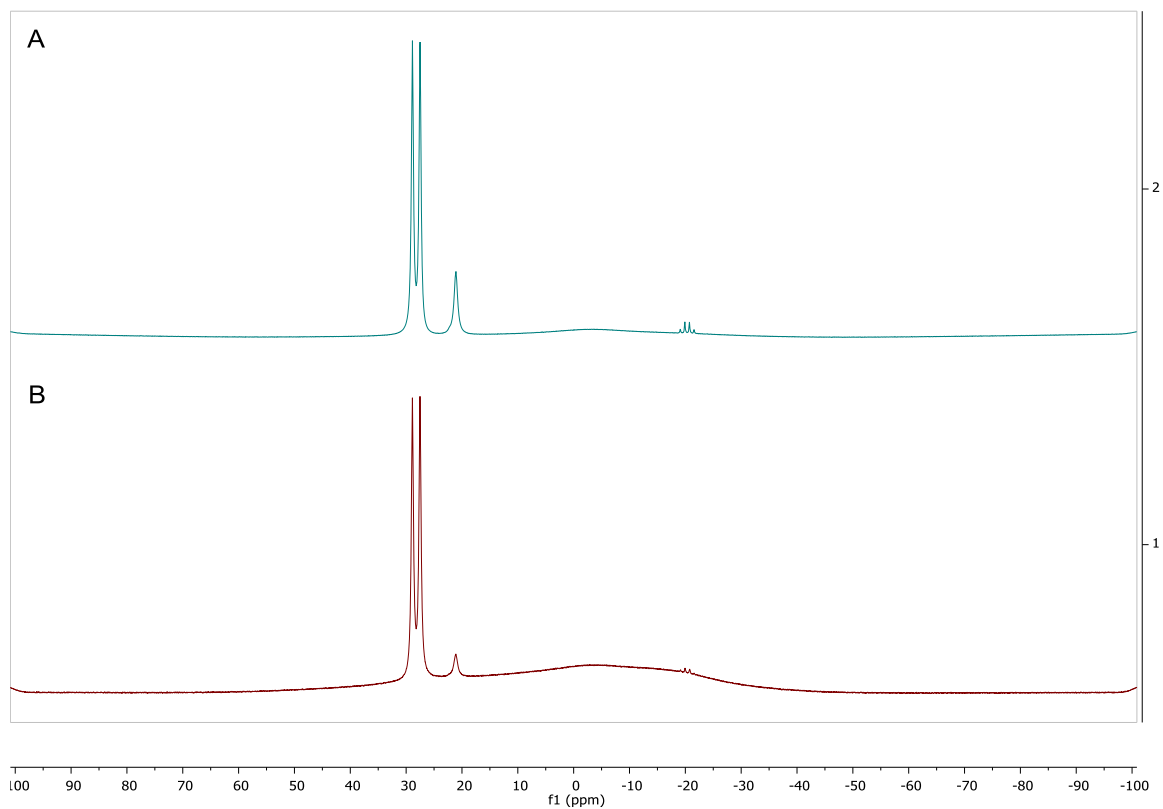


Figure S61 – ^{11}B NMR spectrum of pinacolborane (A) and an equimolar mixture of pinacolborane with [BMIM][NTf₂] (B)

8. Mechanistic studies

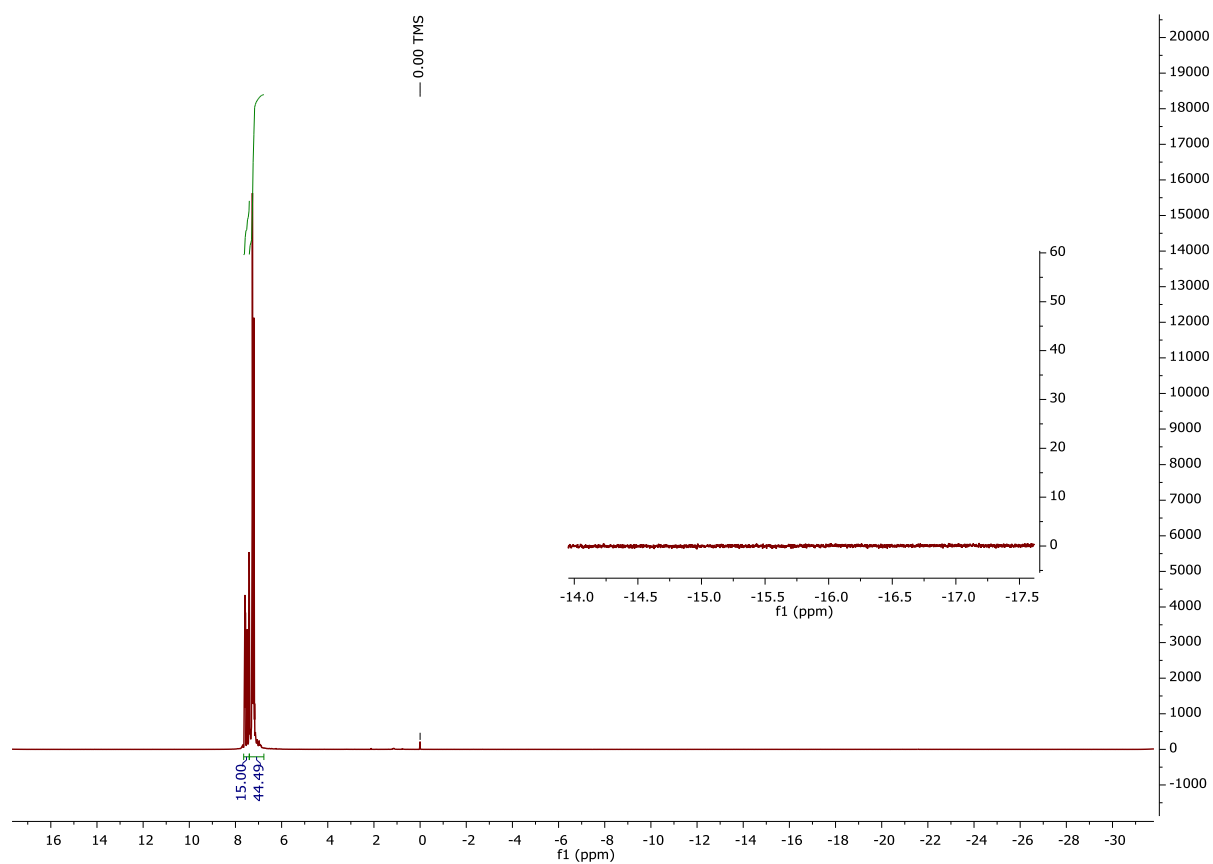
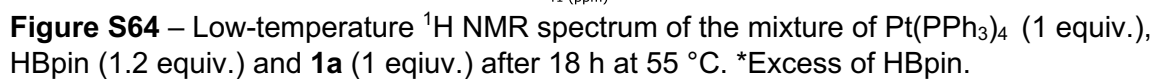
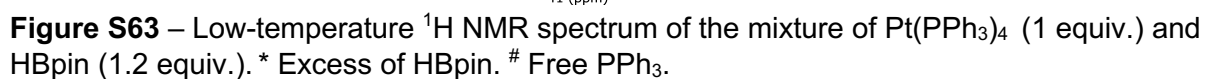


Figure S62 – Low-temperature ^1H NMR spectrum of $\text{Pt}(\text{PPh}_3)_4$.



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Publikacja **P2**

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Organocatalytic Hydroboration of Carbonyl Compounds Promoted by Choline-Based Ionic Liquids

Barbara Krupa, Mateusz Nowicki, Paweł Huninik, Jakub Szyling, and Jędrzej Walkowiak*

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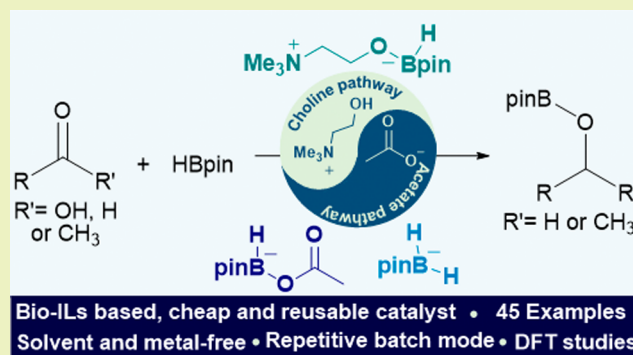
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Supporting Information

ABSTRACT: The organocatalytic activity of choline-based ionic liquids in the hydroboration of ketones, aldehydes, and carboxylic acids with pinacolborane was investigated. The employed method was based on a simple, inexpensive, biobased, reusable, and environmentally friendly [Cho][OAc] catalyst. Detailed studies on catalyst screening, optimization of reaction conditions, and substrate scope were carried out. [Cho][OAc] showed excellent tolerance to various functional groups and chemoselectivity toward C=O hydroboration, which occurred under mild conditions. Furthermore, it was shown that the reaction can be carried out under repetitive batch mode, allowing effective catalyst recycling and improving the process productivity. NMR studies and quantum-mechanical calculations based on density functional theory (DFT) were carried out to explore the reaction mechanism.

KEYWORDS: hydroboration, ionic liquids, choline acetate, organocatalysis, ketones, aldehydes, carboxylic acids, DFT calculations



INTRODUCTION

The hydroboration of carbonyl compounds is one of the most important and widely used methods not only for the synthesis of valuable boronate ethers but also for the large-scale preparation of primary or secondary alcohols that can be used, e.g., as building blocks for the synthesis of active pharmaceutical ingredients (APIs).¹ The process is an important alternative to the stoichiometric reduction of C=O using NaBH₄ and LiAlH₄ or the application of explosive H₂.² Hydroboration has commonly relied on transition-metal catalysts, which enable mild reaction conditions but are often sacrificed during workup procedures. They are difficult to recycle, and the amount of waste (e.g., some additives and volatile organic solvents) generated during the reaction and separation is often substantial.³ Many inorganic or organometallic compounds, such as *n*-BuLi,⁴ LiOt-Bu,⁵ LiBr,⁶ NaH,⁷ NaOH,⁸ NaOt-Bu,⁹ NaHBt₃,¹⁰ KF,¹¹ K₂CO₃,¹² MeMgCl,¹³ EtOMgCl,¹⁴ and MgI₂,¹⁵ have been described as effective hydroboration catalysts. However, Thomas and co-workers proved that these simple nucleophiles can promote HBpin decomposition and the generation of 'BH₃' as a hidden catalyst, responsible for process promotion.^{16,17}

In recent years, the use of organocatalysts has been a growing trend in the field of catalysis.^{18,19} Among several transformations catalyzed by organocatalysts, the hydroboration of carbonyl compounds remains relatively unexplored, with only a few reported examples (Scheme 1). Catalysts such as N-heterocyclic olefins (NCO)²⁰ or N-heterocyclic carbenes (NHC)²¹ have

proved to be efficient organocatalysts for the hydroboration of ketones and aldehydes, producing boronate ethers in 5 min to 24 h at catalyst loadings of 0.5–5.0 mol %. Similarly, P-containing heterocycles such as 1,3,2-diazaphospholene,²² phosphonium triflate,²³ triazaphospholene halides (TAP),²⁴ and carbodiphosphorane²⁵ have been applied in boron–hydrogen bond addition to C=O bonds. Enantioselective reduction of ketones has also been achieved using binol-derived phosphoric acids^{26,27} or the thiourea-amine complex.²⁸ However, in most cases, the catalysts are not commercially available, are difficult to prepare, or require the process to be carried out under an inert atmosphere.

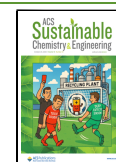
Inspired by the unique and tunable properties of ionic liquids (ILs), and based on our experience with hydroboration reactions,^{29–33} in particular, our recent work on IL-catalyzed hydroboration of olefins in the presence of [EMPyr][OTf]³⁴ as a proof of concept, we decided to use bio ionic liquids as potential organocatalysts for the hydroboration of carbonyl compounds. ILs are defined as salts with a melting point below 100 °C.³⁵ Due to the possibility of changing their properties by anion and cation exchange, low vapor pressure, nonflammability,

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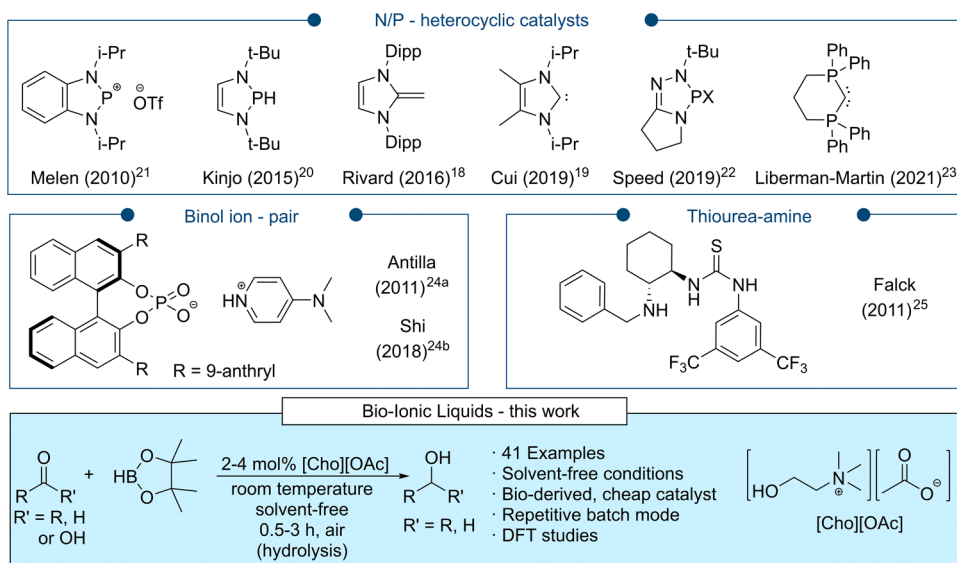
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Scheme 1. Organocatalysts Applied in the Hydroboration of Carbonyl Compounds



and electrical conductivity, ionic liquids have a wide range of applications, e.g., in organic synthesis and catalysis, electrochemical applications, extraction and separation, and biomass conversion, and are considered to be green solvents for chemical processes.^{36–38} Among the various classes of ionic liquids, bio-ILs, which only contain naturally derived compounds as components, have attracted particular attention due to their biodegradability and noncytotoxicity.^{39,40} In particular, choline-based ionic liquids, e.g., [Cho][OAc], have been used in various organic transformations, such as Knoevenagel reactions,⁴¹ cyclizations,^{42,43} polymerizations/depolymerizations,^{44–46} etherifications,⁴⁷ and oxidations.⁴⁸ Moreover, as choline is an essential nutrient for human health,⁴⁹ choline-based ionic liquids are considered a safer alternative to the other ILs and can be applied in drug delivery or the synthesis of biomaterials.⁵⁰

Despite the extensive use of traditional ionic liquids as solvents or immobilization media for transition-metal catalysts in hydroboration reactions,^{29,31,51–53} their application as organocatalysts in such reactions has been almost entirely neglected.^{34,54–56} As a result, the search for a novel and selective method for the hydroboration of carbonyl compounds with a simple, cheap, reusable, and environmentally friendly catalyst is of great importance.

Herein, we report for the first time an efficient and chemoselective protocol for the hydroboration of ketones, aldehydes, and carboxylic acids by employing simple and cheap bio-IL [Cho][OAc] in a single and repetitive batch mode. The subsequent one-pot hydrolysis process yielded primary and secondary alcohols in high yields. In addition to catalytic studies, the reaction mechanism was elucidated by a combination of NMR experiments and DFT calculations.

EXPERIMENTAL SECTION

General Procedure for the Hydroboration of Ketones and Aldehydes with Subsequent Deborylation Process. A 10 mL round-bottom flask containing a magnetic stirring bar was charged with [Cho][OAc] (2 mol %, 1.6 mg) and kept in an oil bath at 80 °C under vacuum for 30 min. After this time, the reaction vessel was allowed to cool to room temperature and IL solidified. Subsequently, ketone (**1a–z**) or aldehyde (**5a–j**) (0.5 mmol) and pinacolborane (**2**) (0.6 mmol, 77 mg) were added. The mixture was stirred for 1 or 0.5 h at room temperature. Then, the crude reaction mixture was analyzed by ¹H

NMR and GC–MS analyses. GC–MS samples were prepared in DCM with the addition of a drop of methanol. Afterward, the reaction mixture was quenched with 1 mL of methanol and allowed to stir for 1 h. After this time, the volatiles were removed under reduced pressure and the crude product was purified by column chromatography using 9:1 hexane/ethyl acetate (for products **4y**, **4z**, and **7j**, 95:5 hexane/ethyl acetate; for product **4w**, 7:3 hexane/ethyl acetate; for product **4q**, 1:1 hexane/ethyl acetate; and for products **4x**, **7f**, and **7h**, 3:7 hexane/ethyl acetate) as the eluent.

General Procedure for the Hydroboration of Carboxylic Acids with Subsequent Deborylation Process. A 10 mL round-bottom flask containing a magnetic stirring bar was charged with [Cho][OAc] (2 mol %, 1.6 mg) and kept in an oil bath at 80 °C under a vacuum for 30 min. After this time, the reaction vessel was allowed to cool down to room temperature and IL solidified. The reaction was carried out for 3 h with a 3.1-fold excess of pinacolborane (**2**) over carboxylic acid (**8a** and **8k–r**) (0.5 mmol) in a 10 mL round-bottom flask under an air atmosphere. Subsequently, the reaction mixture was quenched with 1 mL of methanol and allowed to stir for 1 h. Afterward, the volatiles were removed under reduced pressure. The crude product was dissolved in 5 mL of chloroform and washed with warm water (40–45 °C) (3 × 5 mL). If the phase separation took a long time, then 2 mL of brine was added. The organic layer was dried (Na₂SO₄) and purified by column chromatography using 9:1 hexane/ethyl acetate (for products **7p–r**, 8:2 hexane/ethyl acetate; for product **7o**, 6:4 hexane/ethyl acetate; and for product **7n**, 3:7 hexane/ethyl acetate) as the eluent.

Hydroboration of Acetophenone (1a) in the Presence of [Cho][OAc] under Repetitive Batch Mode. A 10 mL round-bottom flask containing a magnetic stirring bar was charged with [Cho][OAc] (8 mol %, 3.3 mg). The catalyst was kept in an oil bath at 80 °C under a vacuum for 30 min. After this time, the reaction vessel was allowed to cool and IL solidified. Subsequently, the acetophenone (**1a**) (1 mmol, 120 mg) and pinacolborane (**2**) (1.2 mmol, 154 mg) were added. The reaction mixture was stirred at room temperature for 1 h. After this time, the crude product was extracted with 3 × 2 mL of *n*-heptane and analyzed by GC–MS and ¹H NMR analyses. The remaining product in the reaction vessel [Cho][OAc] was dried under a vacuum for 1 h and reused in the next batch.

RESULTS AND DISCUSSION

We started our investigations with the screening of several ionic liquids based on choline or simple *n*-alkyl quaternary ammonium cations and carboxylic acids or bis-(trifluoromethylsulfonyl)imide anions (**IL1–8**) (Figure 1) in

the model reaction of acetophenone (**1a**) with pinacolborane (**2**). This was carried out under solvent-free conditions at room temperature with 2 mol % catalyst loading.

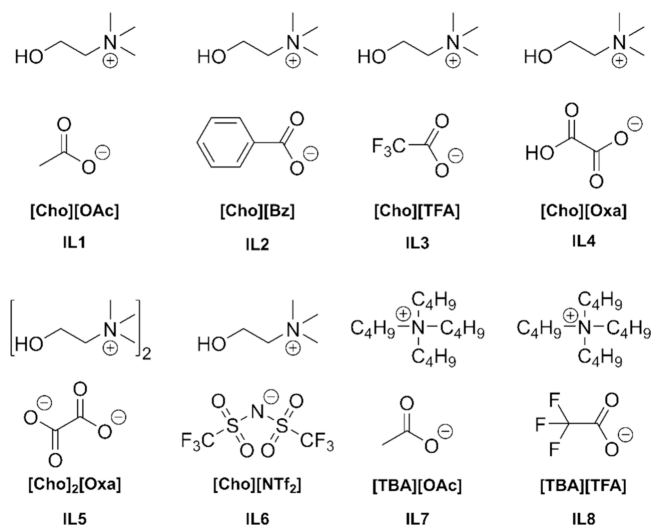


Figure 1. Structures of the ionic liquids used in the study.

Initially, the hydroboration of the ketone was examined in the absence of an IL to exclude the noncatalytic pathway. After 2 h at room temperature, only trace conversion of **1a** was observed (Table 1, entry 1). Subsequently, choline-based ILs with various

Table 1. Catalyst Screening for the Model Reaction of Acetophenone (**1a**) and Pinacolborane (**2**)

entry	catalyst	time [h]	yield of 3a ^a
1		2	trace
2	[Cho][OAc] IL1	0.5	93
3	[Cho][OAc] IL1	1	97
4	[Cho][OAc] IL1	2	99
5	[Cho][Bz] IL2	1	97
6	[Cho][TFA] IL3	1	20
7	[Cho][Oxa] IL4	1	4
8	[Cho] ₂ [Oxa] IL5	1	89
9	[Cho][NTf ₂] ^b IL6	2	0
10	[TBA][OAc] IL7	2	87
11	[TBA][TFA] ^b IL8	2	89

^aYield of **3a** was determined based on GC-MS and ¹H NMR analyses. ^b8 mol % catalyst.

anions were screened as potential organocatalysts in the reduction of carbonyl groups. High yields were obtained for the hydroboration of **1a** with HBpin (**2**) using basic ionic liquids. Almost quantitative yields were observed for choline ionic liquids with both [OAc][−] (IL1) and [Bz][−] (IL2) anions (Table 1, entries 2–5). A slightly lower but still satisfactory conversion of **1a** was observed when [Cho]₂[Oxa] (IL5) was applied (Table 1, entry 8). Contrary to the above-mentioned findings, [Cho][TFA] (IL3) had a poor catalytic effect (Table 1, entry 6). Similarly, the IL with amphoteric [Cho][Oxa] (IL4) or

the neutral anion [Cho][NTf₂] (IL6) showed no catalytic activity (Table 1, entries 7 and 9). Thus, we assumed that the nucleophilicity of the anion plays an important role in the catalytic process.⁵⁷ The competitive aldol condensation of **1a** promoted by basic ionic liquids was not observed.⁵⁸ In the next step of our study, we investigated the influence of the cation on the catalytic activity of acetate-based ionic liquids. Changing the cation from [Cho]⁺ (IL1) to [TBA]⁺ (IL7) resulted in a lower conversion of **1a** (Table 1, entry 10). A similar trend was observed for [TBA][TFA] (IL8) (Table 1, entry 11).

Next, we studied the catalytic activity of carboxylic acids (e.g., HOAc, HBz, and H₂Oxa) and salts (ChoCl, KOAc, and KBz) used as precursors for the synthesis of ILs to verify whether both the cation and the anion of the IL are necessary for its catalytic activity. The hydroboration of **1a** in the presence of all of the carboxylic acids used was not selective and led to a mixture of hydroboration and aldol condensation products. In contrast, when potassium salts were employed as catalysts, the hydroboration reactions gave **3a** exclusively, but the yields were significantly lower than those for IL catalysts with the same anions. Choline chloride did not catalyze the reaction even at a high catalyst loading (8 mol %) and with a prolonged reaction time (18 h) (for details, see ESI, Table S1).

Selecting [Cho][OAc] (IL1) as the most active catalyst, we carried out the optimization process (Table 2). Reducing the

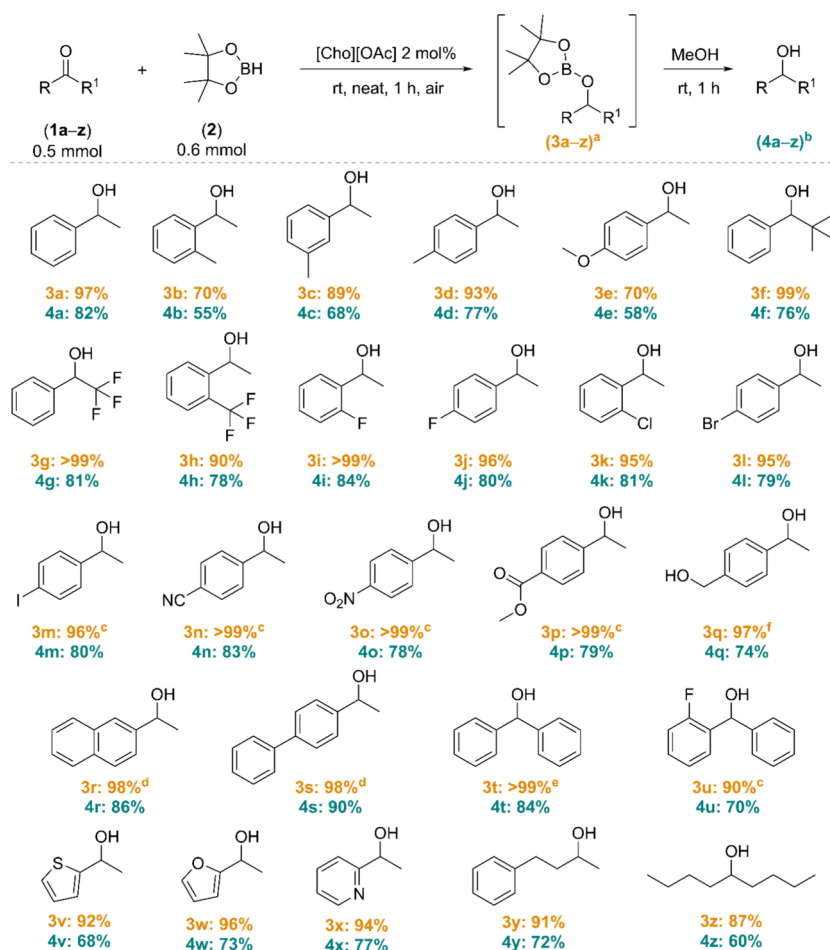
Table 2. Optimization of Conditions for the Model Reaction of Acetophenone (**1a**) and Pinacolborane (**2**)^a

entry	equiv of HBpin	solvent	IL1 [mol %]	yield of 3a [%] ^b
1	1.2	neat	4	97 (97 ^c)
2	1.1	neat	4	95
3	1.0	neat	4	85
4	1.2	toluene	4	86
5	1.2	ethyl acetate	4	85
6	1.2	THF	4	79
7	1.2	DCM	4	90
8 ^d	1.2	neat	4	0
9	1.2	neat	8	>99
10	1.2	neat	2	96
11	1.2	neat	1	92
12	1.2	neat	0.5	14

^aReaction conditions: [[Cho][OAc]]:[**1a**]:[**2**] = 0.005–0.08:1:1.0–1.2, solvent (1 mL), 1 h, rt, air. ^bYield of **3a** was determined based on GC-MS and ¹H NMR analyses. ^cUnder an argon atmosphere. ^d10 μL of water was added.

HBpin excess (1.2–1.0 equiv) resulted in a slight decrease in the yield of **3a** (Table 2, entries 1–3). The process proceeded smoothly under ambient conditions or an argon atmosphere (Table 2, entry 1) and under solvent-free conditions. Slightly lower yields of **3a** were observed when toluene, ethyl acetate, or THF was used as the solvent. A better yield was achieved when DCM was used (Table 2, entries 4–7). Moreover, the effect of moisture on the reaction efficiency was determined. The addition of 10 μL (0.56 mmol) of water to the reaction mixture completely inhibited the reaction (Table 2, entry 8).

Scheme 2. Hydroboration of Ketones (1a–z) Catalyzed by [Cho][OAc]



^aYields were based on ¹H NMR analysis. ^bIsolated yields. ^cHBpin 1.5 equiv. ^dHBpin 2.0 equiv. ^eHBpin 4.0 equiv. ^fHBpin 2.2 equiv.

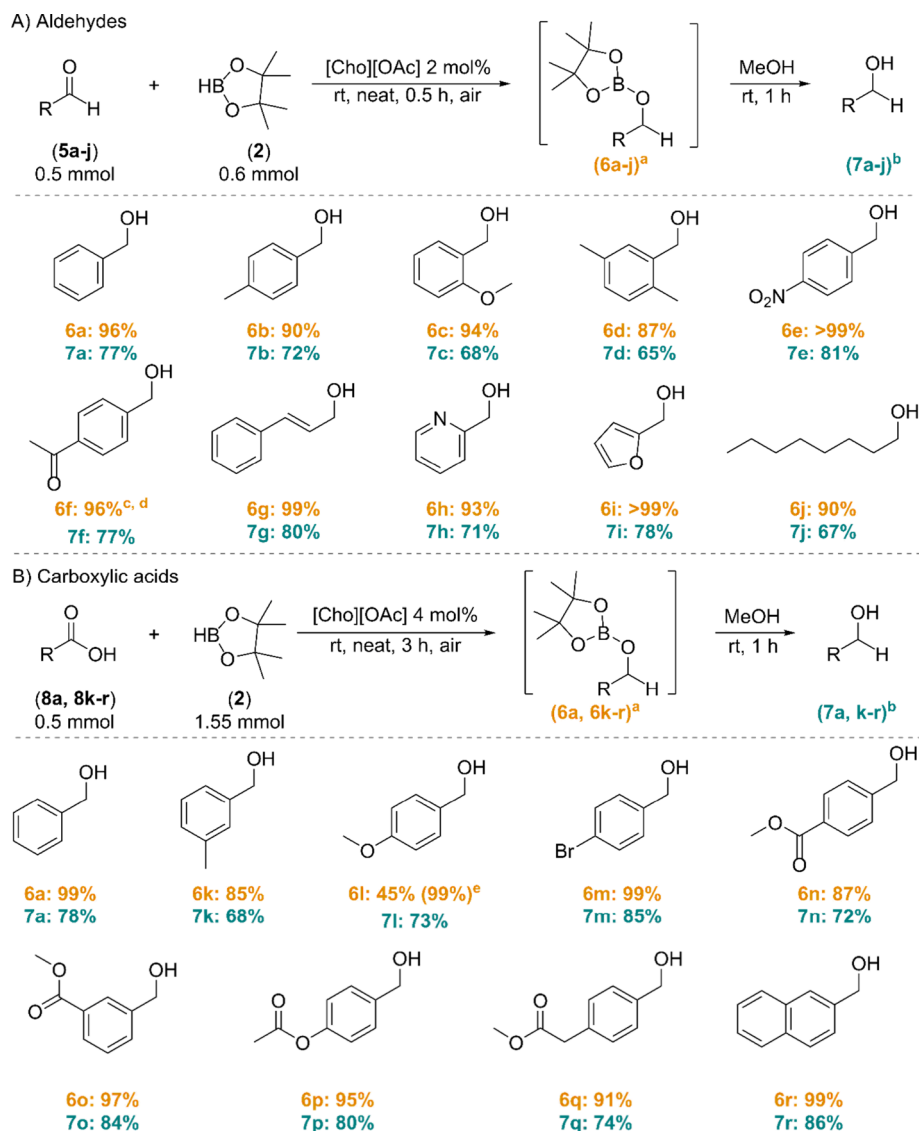
Quantitative conversion of **1a** was observed under solvent-free conditions with 8 mol % **IL1** in 1 h at room temperature (Table 2, entry 9). Reducing the catalyst loading to 2 or 1 mol % resulted in a slight decrease in **1a** conversion, but its further decrease to 0.5 mol % caused a significant drop in reagent conversion after 1 h (Table 2, entries 10–12).

The optimized reaction conditions were applied for the hydroboration of various ketones (Scheme 2). The yields for borylated ethers (**3b–e**) with electron-donating groups were a bit lower than those for the model reaction. Replacement of the methyl group in the acetophenone core with the sterically hindered *t*-Bu substituent (**1f**) or the trifluoromethyl group (**1g**) led to an almost quantitative conversion of the substrates. High catalytic activity of **IL1** was observed for *ortho*- and *meta*-halogen-substituted acetophenones (**1h–m**). Only for the more crowded $-\text{CF}_3$ group in the *ortho* position (**1h**) was the process less effective (**3h**, 90%). Notably, the [Cho][OAc]-catalyzed hydroboration of ketones possessing nitrile, nitro, and ester groups attached to the phenyl ring (**1n–p**) was chemoselective, leading to the reduction of the carbonyl group only. However, in the presence of an aldehyde group (**1q**), both groups were reduced when 2.2 equiv of HBpin (**2**) was applied. Ketones bearing 2-naphthyl (**1r**) or 4-biphenyl (**1s**) substituents and benzophenone (**1t**) underwent nearly quantitative conversion when an excess of **2** was used. The use of excess HBpin was essential to ensure complete solubility of reaction components during the process. A very good result was obtained for the

hydroboration of *o*-fluorobenzophenone (**1u**) under standard reaction conditions, but the conversion of **1u** was not complete. Subsequently, a series of heterocyclic ketones (**3v–x**) containing S, O, and N atoms were tested, leading to hydroboration products with excellent yields. The developed protocol was also effective for the reaction of aliphatic ketones such as 4-phenylbutan-2-one (**1y**) or 5-nonanone (**1z**) with HBpin (**2**), easily providing the corresponding products with high yields (87–91%). However, 3'-aminoacetophenone, 2-acetylpyrrole, and 4,4'-dibromobenzophenone could not be converted to hydroboration products (Scheme 2). All of the O-borylated ethers (**3a–z**) were readily converted to the corresponding alcohols (**4a–z**) in a one-pot procedure via simple hydrolysis with methanol, without the isolation of borylated intermediates (**3a–z**). This approach eliminated the time-consuming step of separating the intermediates and reduced the amount of volatile organic solvents used for additional purification procedures. The final products were purified by column chromatography using hexane/ethyl acetate as an eluent. All obtained products **3** and **4** were characterized by nuclear magnetic resonance (¹H NMR) and mass spectroscopy (GC-MS).

The successful organocatalytic hydroboration of ketones prompted us to extend the scope of the reagents to include other carbonyl compounds (aldehydes and acids). The optimization process is detailed in the ESI (Table S3).⁵⁹ A very high yield was observed in the hydroboration of benzaldehyde (**5a**) with

Scheme 3. Hydroboration of Aldehydes (5a–j) and Carboxylic Acids (8a and 8k–r) Catalyzed by [Cho][OAc]



^aYields were based on ¹H NMR analysis. ^bIsolated yields. ^c45 min. ^d1.02 equiv of HBpin. ^e18 h.

pinacolborane (2) after just 30 min in analogous reaction conditions for ketones, showing the higher reactivity of aldehydes. Various aldehydes (5) were converted to the corresponding O-borylated ethers (6) and primary alcohols (7) in a one-pot procedure using the same process conditions (Scheme 3A). The effects of electron-donating and electron-withdrawing substituents are similar to that observed in the hydroboration of ketones. For aromatic aldehydes with methyl and methoxy groups (5b–d), lower yields of the expected products were observed. Conversely, compounds with electron-withdrawing groups such as nitro or acetyl (6e–f) had a positive effect on reaction yields. However, to ensure chemoselectivity toward the aldehyde group in 4-acetylbenzaldehyde (6f), 1.02 equiv of HBpin was used. Furthermore, for cinnamaldehyde (5g), only the reduction of the C=O bond was observed, whereas the C=C bond was intact. The heteroaromatic and aliphatic substrates (5h–j) were also successfully applied, furnishing the corresponding boryl ethers and alcohols in excellent yields. The reduction of carboxylic acids with pinacolborane followed by hydrolysis with methanol, as with

aldehydes, gave primary alcohols (Scheme 3B). However, an extension of the reaction time to 3 h and increased catalyst loading to 4 mol % were necessary to achieve full conversion of benzoic acid (8a) (see ESI, Table S5). The benzoic acids substituted with electron-donating methyl and methoxy (8k–l) required a much longer reaction time (18 h) to obtain satisfactory conversion of these reagents. In contrast, carboxylic acids with electron-withdrawing substituents, e.g., bromo (8m) or bulky 2-naphthoic acid (8r), reacted with HBpin in almost quantitative yields. Substrates (8n–q) exhibited high efficiency and chemoselectivity toward the carboxyl group in the presence of the ester group.

In the next stage of our study, bearing in mind green chemistry principles and our previous research on catalyst recycling in the synthesis of organoboron compounds,^{31–33,31–33,60–62} we tested the possibility of recycling the catalyst, carrying out the process in repetitive batch mode. Hydroboration of acetophenone (1a) was performed under standard conditions (1 h, rt, 2 mol % IL1, neat). After the process, *n*-heptane was added to the postreaction mixture, causing precipitation of [Cho][OAc]. The

catalyst was washed three times (3×2 mL) with *n*-heptane to remove the product and then dried under vacuum for 1 h to evaporate the residual solvent before more substrate was added. This strategy allowed us to efficiently reuse ionic liquid up to 5 times. After the fifth cycle, the product yield dropped drastically (see ESI, Figure S2). This was likely caused by mechanical loss of the suspended catalyst during the extraction process, which was visible from the milky color of the filtrate. To minimize the effect of accidental sediment removal from the reaction vessel, the catalyst loading was increased in the next experiment. When an 8 mol % catalyst was used, 13 runs were carried out with stable and high reagent conversion (Figure 2). After that, the

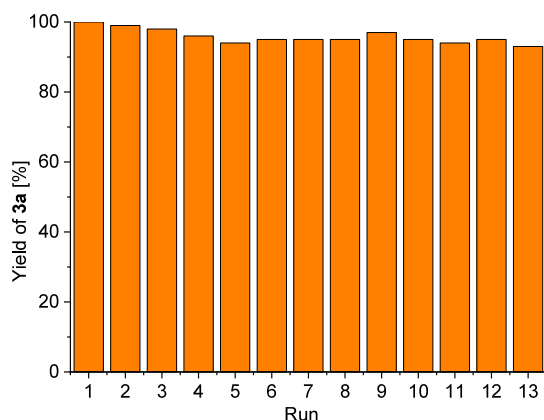


Figure 2. Repetitive batch hydroboration of **1a** (1 mmol) with **2** (1.2 mmol) using 8 mol % of [Cho][OAc] at room temperature for 1 h in air. Yields of compound **3a** were determined by GC-MS analysis.

catalyst was transferred to a vial and exposed to ambient conditions for 6 weeks. In the 14th and 15th runs, a high conversion of **1a** (72 and 81%) was observed and product **3a** was formed in a 53–75% yield. The postreaction mixture analysis revealed the presence of an aldol-condensation byproduct. This experiment showed that catalyst aging has a negative influence on the process efficiency. Moreover, in a new set of experiments, the catalyst was analyzed by NMR spectroscopy after the third reaction cycle. The ^1H NMR spectra showed no signals corresponding to unmodified [Cho][OAc], indicating its consumption or transformation during the reaction. Instead, the data revealed the presence of a choline-derived species [ChoOBpin][OAc] bearing an –OBpin moiety in place of the original –OH group—consistent with the formation of **IN4**, as proposed in the mechanistic pathway.

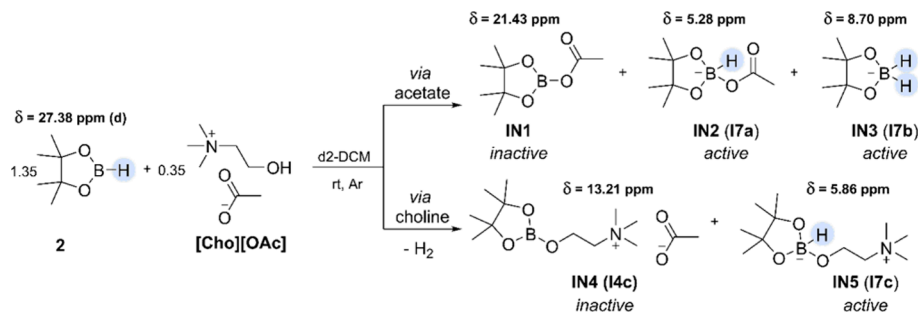
MECHANISM INVESTIGATIONS: EXPERIMENTAL AND DFT STUDIES

To exclude the formation of the ‘hidden’ BH_3 -catalyst during the possible decomposition of HBpin, we carried out a reaction in the presence of N,N,N',N' -tetramethylethylenediamine (TMEDA), as reported by Thomas and co-workers.^{16,17} The 6-fold excess of the amine over the catalyst (ESI, Table S6, entry 4) did not stop the reaction. However, the conversion achieved was slightly lower than in the absence of TMEDA (99 vs 83%) (see ESI, Figures S141 and S142). Furthermore, there were no signals in the ^1H and ^{11}B NMR spectra, indicating the formation of ‘ BH_3 ’. The reaction pathways proceeding with BH_3 and choline borohydride at the theoretical level are presented in ESI.

To further investigate the reaction mechanism, we conducted detailed NMR experiments. Initial reactions of acetophenone (**1a**) with [Cho][OAc] revealed no changes in the ^1H or ^{13}C NMR. However, combining excess of **2** with [Cho][OAc] yielded a complex ^{11}B NMR spectrum with signals corresponding to several boron-containing species ($\delta = 21.43, 19.40, 12.06, 8.70, 5.85, 5.28, 2.03$, and -9.36 ppm; see ESI, Figure S125). These findings align with earlier studies by Clark and co-workers, which documented the presence of dynamic equilibria involving boron hydride complexes.⁹ Based on literature data and reference compounds, we identified three species: **IN1** (21.43 ppm), **IN2** (5.28 ppm, corresponding to **17a**), and **IN3** (8.70 ppm, **17b**) (Scheme 4). All of these might be potential catalytic systems. We synthesized **IN1** and tested it in the hydroboration of **1a** with HBpin (**2**). However, no product formation was observed, suggesting that alkoxyborohydride species, rather than simple adducts, act as active catalysts.^{9,16} Nevertheless, the number of new species presented in ^{11}B NMR indicated that our catalyst is more complex than previously published systems. The formation of **IN2** and **IN3** might suggest a mechanism similar to that described by Clark, but on the other hand, we observed also the evolution of hydrogen during the reaction of HBpin with [Cho][OAc] (singlet at $\delta = 4.60$ ppm in the ^1H NMR spectrum). This suggests that HBpin reacts with the hydroxyl group of the choline cation (exothermic reaction). The equimolar reaction of HBpin with [Cho][OAc] predominantly yielded neutral O-borylated intermediate **IN4**, which exhibited no catalytic activity in the subsequent reaction with substrate **1a**. However, in the presence of an excess amount of HBpin, **IN4** can undergo further transformation into borohydride intermediate **IN5**. Notably, an excess of HBpin relative to [Cho][OAc] is crucial for the formation of all catalytically active borohydride species, including **IN2**, **IN3**, and **IN5** (see the ESI, Figures S137–S140).

The results of DFT calculations were consistent with NMR observations, confirming that the reaction of the choline hydroxyl group with **2** is feasible (Figure 3). It might lead to an intermediate **IN4** and potentially catalytically active trialkoxyborohydride intermediate **IN5** via hydride transfer from **IN2** to the boron atom of **IN4**. Additional computational data show that H_2Bpin^- (**IN3**), generated through hydride transfer from **IN2** to HBpin, is energetically less favorable; the amount of this species in the reaction mixture is significantly lower than that in **IN2** and **IN5**, indicating that **IN3** contributes minimally to the

Scheme 4. Identified Reaction Products of HBpin (**2**) with [Cho][OAc] (**IL1**)^a



^aThe chemical shifts for ^{11}B NMR are presented.

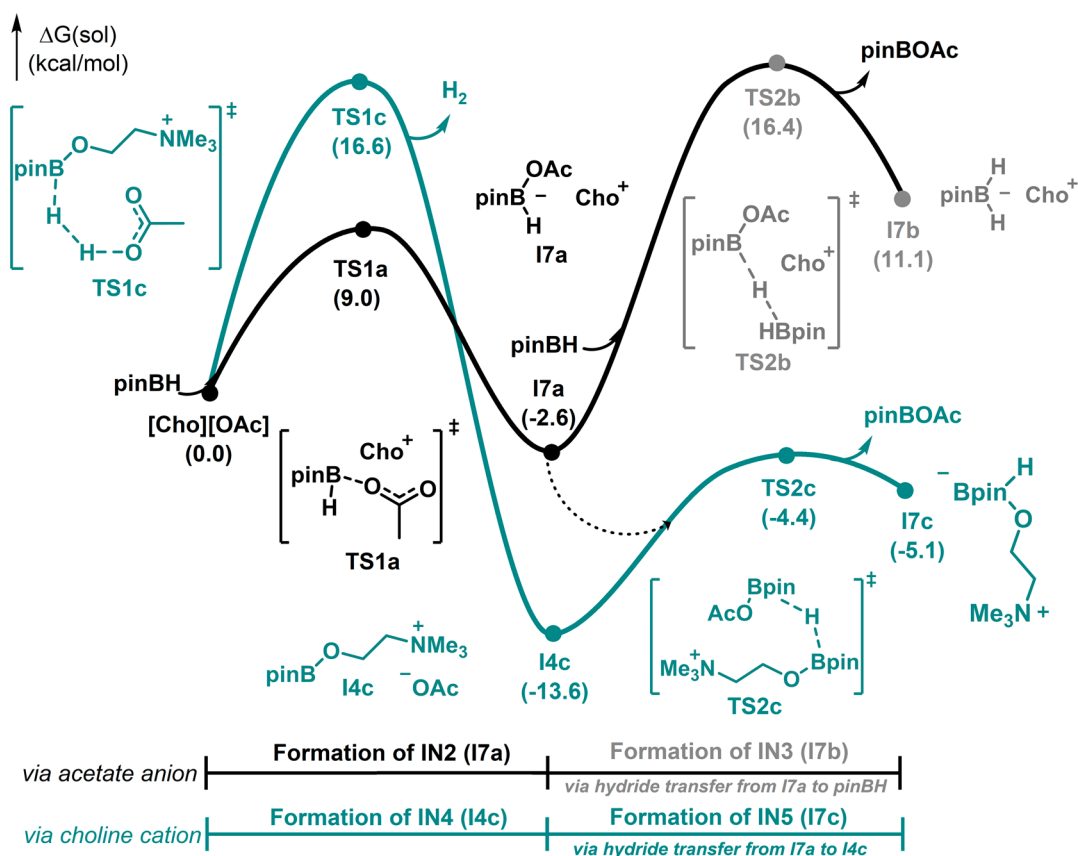


Figure 3. Gibbs free energy profiles of the reaction of $[\text{Cho}][\text{OAc}]$ (IL1) with pinacolborane (2) ($\omega\text{B97XD}/\text{def2-SVPD}$, 295 K, and dichloromethane as the PCM solvent).

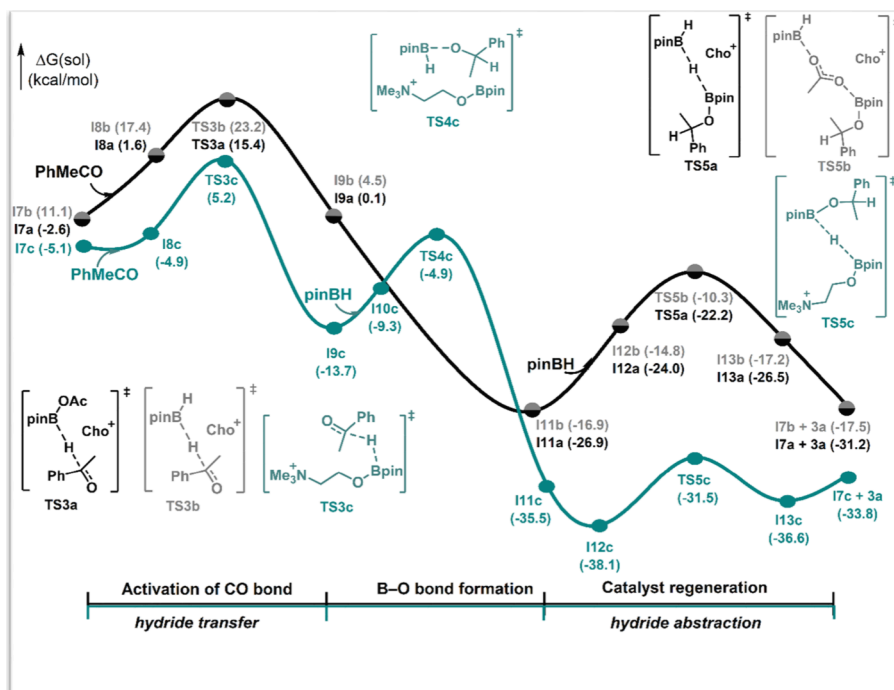
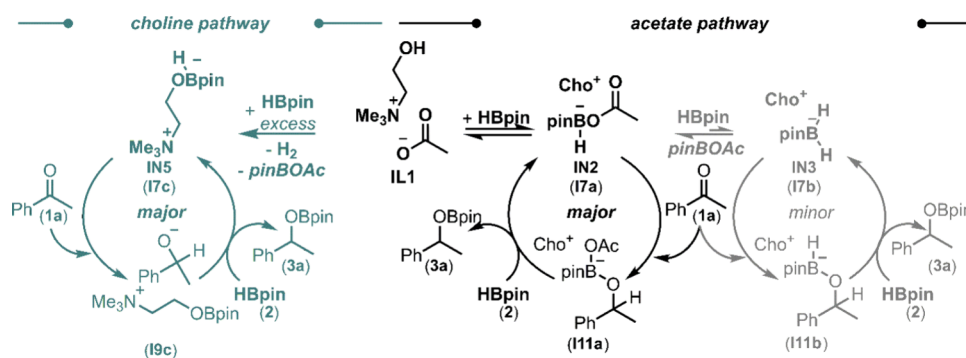


Figure 4. Gibbs free energy profiles of the reaction of catalytically active intermediates (I7) with acetophenone (1a) ($\omega\text{B97XD}/\text{def2-SVPD}$, 295 K, dichloromethane as the PCM solvent). The course of the curve for the acetate pathway, including I7a (black) and I7b (gray), was averaged.

overall catalytic process. In contrast, both IN2 and IN5 appear to play a significant role in catalysis, but to create IN5 in the reaction mixture, the existence of IN2 (acetate pathway) is crucial. This conclusion is

supported by the comparable ΔG barriers in their respective cycles and by control experiments, which indicated that the choline cation

Scheme 5. Proposed Mechanism for [Cho][OAc] Catalyzed Hydroboration of Carbonyl Compounds



increased the reaction yield but is not essential for the reaction to occur (for more details, see ESI).

Combining experimental insights with DFT calculations provides a comprehensive picture of catalyst formation. The generation of borohydrides is mandatory to course the hydroboration process. Based on the calculated energy profiles, it is proposed that all three catalytic cycles (a, b, and c) might occur in parallel, but with different contributions to the formation of the desired products. This depends both on the concentration of the individual active species in the solution and on the ΔG barriers that must be overcome (Figure 4). Each of the possible catalytic cycles involves the following steps: (i) activation of the acetophenone molecule via hydride transfer, (ii) formation of a B–O bond between HBpin and the 1-phenylethoxide ion, and (iii) hydride abstraction from the resulting anion to regenerate the catalyst. The overall Gibbs free energy change for each cycle is -28.6 kcal/mol, and the calculated barriers ($\Delta G^\ddagger$) for the rate-determining steps in all three pathways fall within the range of 10.9 – 18.0 kcal/mol—values accessible at room temperature.

Considering the obtained reaction energy profiles, it is presumed that all three of the described cycles (a, b, and c) contribute to the catalysis of the reaction and intersect during its progress; however, cycles a and c seem to be the most relevant (Scheme 5). Therefore, the reaction mechanism involves the formation of catalytically active borohydrides IN2, IN3, and IN5 from both the cation and anion of the ionic liquid (choline or acetate pathway), which enables activation of the CO bond and formation of the alkoxide anion. The reaction with HBpin regenerates the catalyst and releases the hydroboration product. It should be noted that, in contrast to previously reported borohydride-based catalytic systems, the use of an ionic liquid enables the cooperation of both the cation and anion in the formation of catalytically active species, which enhances reaction efficiency.

CONCLUSIONS

In conclusion, [Cho][OAc] is an efficient, inexpensive, and biobased organocatalyst for the hydroboration of various carbonyl compounds (aldehydes, ketones, and carboxylic acids). The process occurred very quickly (30 min for aldehydes, 1 h for ketones, and 3 h for carboxylic acids) under mild, ambient conditions. This metal-free hydroboration is feasible for aromatic compounds with electron-donating and electron-withdrawing substituents and also with sterically hindered, heteroaromatic, and aliphatic reagents. The system based on [Cho][OAc] is tolerant of many functional groups (e.g., nitro, nitrile, ester, and acetyl groups). Moreover, the recyclability of the catalyst was successfully demonstrated, with up to 13 cycles with excellent reaction yields. The elimination of transition-metal catalysts, which are commonly used in this transformation, and the reduction of the amount of organic solvents are in line with the rules of green chemistry. Based on the experimental studies and DFT calculations, the mechanism of this transformation was elucidated. Experimental mechanistic studies

revealed the formation of several catalytically active alkoxyborohydrides through the reaction of both the choline cation and the acetate anion. The formation of 'BH₃' as a significant 'hidden catalyst' was minimized by both DFT calculations and experiments involving TMEDA. The DFT calculations proved that H₂Bpin[−], HAcOBpin[−], and ChoHBpin can act as catalysts for the described process; however, the acetate- and choline-based trialkoxyborohydrides are pivotal catalytic species.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.5c07304>.

Additional experimental and DFT details; materials; methods; compounds characterization; and NMR spectra (PDF)

Cartesian coordinates (ZIP)

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Notes

The authors declare no competing financial interest.

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Supporting Information

Organocatalytic hydroboration of carbonyl compounds promoted by choline-based ionic liquids

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1. General information

1.1. Materials

Acetophenone, ($\geq 98.5\%$, Carlo Erba), 1-(*o*-tolyl)ethanone (98%, AmBeed), 3-methylacetophenone (97%, Alfa Aesar), 1-(*p*-tolyl)ethanone (97%, AmBeed), 2,2,2-trimethylacetophenone, (97%, Alfa Aesar), 4-methoxyacetophenone (98%, AmBeed), 2,2,2-trifluoroacetophenone (99%, Sigma-Aldrich), 1-(2-(trifluoromethyl)phenyl)ethanone (98%, AmBeed), 2'-fluoroacetophenone (98%, AmBeed), 1-(4-fluorophenyl)ethanone (98%, AmBeed), 1-(2-chlorophenyl)ethanone (95%, AmBeed), 4-bromoacetophenone (98%, Sigma-Aldrich), 4-iodoacetophenone (98%, Sigma-Aldrich), 4-acetylbenzonitrile (97%, AmBeed), 1-(4-nitrophenyl)ethanone (98%, AmBeed), methyl 4-acetylbenzoate (99.91%, AmBeed), 4-acetylbiphenyl (97%, AmBeed), 2-acetylNaphtalene (99%, abcr), benzophenone ($\geq 99\%$, Acros-Organics), 2-fluorobenzophenone (98%, AmBeed), 1-thiophen-2-yl-ethanone (98%, AmBeed), 1-furan-2-yl-ethanone (98%, Fluorochem), 1-(pyridin-2-yl)ethanone (98%, AmBeed), 4-phenyl-2-butanone, ($>95\%$, TCI), 5-nonanone (98%, Acros Organics), 3'-aminoacetophenone (98%, Angene), 2-acetylpyrrole (99.53%, AmBeed) and 4,4'-dibromobenzophenone (98%, abcr), benzaldehyde, ($>99\%$, Alfa Aesar), 4-methylbenzaldehyde (97%, Sigma-Aldrich), 2-methoxybenzaldehyde (98%, Acros-Organics), 2,5-dimethylbenzaldehyde (98%, Alfa Aesar), 4-nitrobenzaldehyde (98%, AmBeed), 4-acetylbenzaldehyde (98%, Angene), *trans*-cinnamaldehyde (97%, Sigma-Aldrich), 2-pyridinecarboxaldehyde (99%, Sigma-Aldrich), furfural (99%, Sigma-Aldrich), octanal (99%, Sigma-Aldrich), benzoic acid (98%, Angene), *m*-toluic acid (99%, Thermo Scientific), *p*-anisic acid (99.99%, AmBeed), 4-bromobenzoic acid (97.48%, AmBeed), 4-

(methoxycarbonyl)benzoic acid (99.65%, AmBeed), 2-naphtoic acid (97%, AmBeed), acetic anhydride (99%, Chempur), 3-(methoxycarbonyl)benzoic acid (Chemat, 97%), 4-acetoxybenzoic acid (AmBeed, 99,55%), 4-(Acetoxymethyl)benzoic acid (AmBeed, 98%), ethyl phenylacetate (99%, Acros Organics), 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (97%, Fluorochem), choline chloride (98%, Angene), choline acetate (98%, io-li-tec), choline bis(trifluoromethylsulfonyl)imide, (99%, io-li-tec), choline hydroxide, (46% w/w aq. soln, Thermo Scientific), trifluoroacetic acid (>99%, Fischer Chemical), benzoic acid ($\geq$ 99%, Chempur), oxalic acid dihydrate ($\geq$ 99%, Chempur), tetrabutylammonium acetate (98%, Angene), tetramethylammonium acetate (98%, Angene), tetrabutylammonium trifluoroacetate (98%, AmBeed), potassium benzoate (99%, AmBeed), potassium acetate (99%, Sigma Aldrich), *N,N*-dimethylethanolamine ($\geq$ 99,5%, Sigma-Aldrich), *N,N,N',N'*-tetramethylethylenediamine ($\geq$ 99,5%, Sigma-Aldrich), silica gel (pore size 60Å, 63-200 μ m particle size, Sigma-Aldrich), methanol ($\geq$ 99.9%, Stanlab), diethyl ether (99.5%, Avantor Performance Materials Poland), ethyl acetate (99%, Avantor Performance Materials Poland), *n*-hexane (99%, Stanlab), *n*-heptane (99%, Sigma-Aldrich), THF (>99%, Eurochem), toluene (>99%, Stanlab), DCM (>99%, anhydrous, TCI), acetonitrile (99%, anhydrous, Sigma-Aldrich), chloroform-*d*1 (99.8% stabilized with Ag, Deutero GmbH), dichloromethane-*d*2 (99.6%, Deutero GmbH), deuterium oxide (99%, Deutero GmbH), toluene-*d*8 (99.5%, Deutero GmbH), THF-*d*8 (99.5%, Deutero GmbH).

All chemicals were used without further purification and purchased from commercial sources, except acetophenone and pinacolborane, which were purified by vacuum distillation prior to use. THF, diethyl ether, and toluene were dried over Na/benzophenone or CaH₂ respectively and distilled. Ionic liquids were dried overnight under vacuum at 60 °C before use.

1.2. Methods

1.2.1. Nuclear magnetic resonance

The ^1H NMR and ^{13}C NMR spectra were recorded on the Bruker Ultrashield 300 MHz or Bruker Ascend 400 MHz spectrometers. The ^{11}B NMR spectra were recorded on the Bruker Ascend 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm) with reference to the residual solvent peaks for ^1H and ^{13}C NMR or $\text{BF}_3\text{-Et}_2\text{O}$ for ^{11}B NMR, respectively. The multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), multiplet (m), and broad singlet (brs).

1.2.2. Gas chromatography–mass spectrometry

The mass spectra of the products were obtained by GC-MS analysis on a Varian 431-GC with a 30 m Agilent J&W VF-200ms 0.25 mm capillary column and a Varian 220-MS mass spectrometry detector (temperature program: 60 °C (3 min), 60 to 280 °C (10 °C/min), 280 °C (8 min)).

1.2.3. Elemental analyzes

Elemental analyzes were performed using a Vario EL III instrument.

1.2.4. DFT calculations

The initial structures of all relevant species were systematically generated based on established values for bond lengths and valence angles.¹ This was followed by full geometry optimizations aimed at identifying potential energy minima. During these preliminary optimizations, the ωB97XD functional² and the 6-31+G(d) basis set³ were selected for their balance between computational efficiency and resource consumption, accommodating the extensive variety of potential pathways and the computational demands they entailed. To elucidate plausible reaction mechanisms, we executed relaxed potential energy surface scans, varying the distances between atoms poised for reaction (namely boron, hydridic hydrogen, carbonyl carbon and oxygen, hydroxyl oxygen and hydrogen, and carboxyl oxygen). Paths not culminating in a new minimum were discontinued; otherwise, the quadratic synchronous transit (QST)⁴ methods – both QST2 and QST3 – were employed to pinpoint transition state geometries, complemented by pseudo-IRC⁵ calculations to identify the potential energy minima linked by these transition states, thereby guiding the generation of subsequent structures representing energy minima. To validate these stationary points as either minima or first-order saddle points, we performed force constant calculations. We analyzed the vibrational modes, identifying none (for minima) or a single imaginary frequency (for transition states), corresponding to stretching the bonds being broken and formed (freq. calculations). Subsequent re-optimizations and frequency analyzes, including determinations of the nature of each stationary point, were conducted using the ωB97XD functional and the def2-SVPD basis set.⁶ Still, this time they assumed the solvation of molecules in dichloromethane, modeled as a continuum medium within the polarizable continuum model (PCM).⁷ This was a strategic compromise between computational demand and the fidelity of results, especially for the anionic species with hydridic hydrogen atoms. Thermochemical evaluations were standardized at a pressure of 1 atm and a temperature of 295 K to closely replicate experimental conditions. All quantum-chemical computations throughout the study were

performed using the Gaussian 16 program package.⁸ Basis Set Exchange resource was used to optimize the level of theory employed.⁹

2. Synthetic procedures

All glassware was vacuum dried at 120 °C prior to use.

2.1. General procedure for the synthesis of ionic liquids (IL2–IL5)

The synthesis was performed based on the literature-known procedure with modifications.¹⁰ An aqueous solution of choline hydroxide (7 mmol, 840 mg), 10 mL of methanol, and carboxylic acid (7 mmol or 3.5 mmol) were added to the 100 mL round-bottom flask equipped with a magnetic stirring bar. The reaction was allowed to proceed for 24 hours at room temperature. After this time, the solvent was evaporated using a rotary evaporator. The obtained products were dried for 48 hours under vacuum at 80 °C.

2.2. General procedure for the hydroboration of ketones with subsequent deborylation process

A 10 mL round-bottom flask containing a magnetic stirring bar was charged with [Cho][OAc] (2 mol%, 1.6 mg) and kept in an oil bath at 80 °C under vacuum for 30 min. After this time, the reaction vessel was allowed to cool down to room temperature and IL solidified. Subsequently, ketone (**1a–z**) (0.5 mmol) and pinacolborane (**2**) (0.6 mmol, 77 mg) were added. The mixture was stirred for 1 hour at room temperature. Then, the crude reaction mixture was analyzed by ¹H NMR and GC–MS analyzes. GC–MS samples were prepared in DCM with the addition of a drop of methanol. Afterward, the reaction mixture was quenched with 1 mL of methanol and allowed to stir for 1 hour. After this time the volatiles were removed under reduced pressure and the crude product was purified by column chromatography using 9:1 hexane/ethyl acetate (for products **4y** and **4z** 95:5 hexane/ethyl acetate; for product **4w** 7:3 hexane/ethyl acetate; for product **4q** 1:1 hexane/ethyl acetate; for product **4x** 3:7 hexane/ethyl acetate) as the eluent.

2.3. General procedure for the hydroboration of aldehydes with subsequent deborylation process

The procedure for hydroboration of aldehydes (**5a–j**) was analogous to that described in section 2.2. The reaction time was 30 min. The crude products were purified by column chromatography using 9:1 hexane/ethyl acetate (for product **7j** 95:5 hexane/ethyl acetate; for products **7f** and **7h** 3:7 hexane/ethyl acetate) as the eluent.

2.4. General procedure for the hydroboration of carboxylic acids with subsequent deborylation process

The procedure for the hydroboration of carboxylic acids was analogous to that described in section 2.2. The reaction was carried out for 3 h with a 3.1-fold excess of pinacolborane (**2**) over carboxylic acid (**8a** and **8k–r**) in a 10-mL screw capped vial under an air atmosphere. Hydroborated products were isolated by sublimation or the reaction mixture was quenched with 1 mL of methanol and allowed to stir for 1 hour. Afterwards, the volatiles were removed under reduced pressure. The crude product was dissolved in 5 mL of chloroform and washed with warm water (40–45 °C) (3 x 5 mL). If the phase separation took a long time, 2 mL of brine was added. The organic layer was dried (Na₂SO₄) and purified by column chromatography

using 9:1 hexane/ethyl acetate (for product **7p–r** 8:2 hexane/ethyl acetate, for product **7o** 6:4 hexane/ethyl acetate, for product **7n** 3:7 hexane/ethyl acetate) as the eluent.

2.5. Hydroboration of acetophenone (1a) in the presence of [Cho][OAc] under repetitive batch mode

The 10-mL round-bottom flask containing a magnetic stirring bar was charged with [Cho][OAc] (8 mol%, 3.3 mg). The catalyst was kept in an oil bath at 80 °C under vacuum for 30 min. After this time, the reaction vessel was allowed to cool down and IL solidified. Subsequently, the acetophenone (**1a**) (1 mmol, 120 mg) and pinacolborane (**2**) (1.2 mmol, 154 mg) were added. The reaction mixture was stirred at room temperature for 1 hour. After this time, the crude product was extracted with 3 × 2 mL of *n*-heptane and analyzed by GC–MS and ¹H NMR analyzes. The remaining in the reaction vessel [Cho][OAc] was dried under the vacuum for 1 hour and reused in the next batch.

2.6. General procedure for the equimolar reaction of acetophenone (1a) or pinacolborane (2) with [Cho][OAc]

The Young's NMR tube was charged under the argon with [Cho][OAc] (0.05 mmol, 8.2 mg) and approx. 0.6 mL of dry CD₂Cl₂ was added. Subsequently, acetophenone (**1a**) (0.05 mmol, 6 mg) or pinacolborane (**2**) (0.05 mmol, 6.4 mg) were added and the mixture was shaken vigorously, and the ¹H, ¹¹B, and ¹³C NMR spectra were recorded.

2.7. General procedure for the nonequimolar reaction of pinacolborane (2) with [Cho][OAc]

The Young's NMR tube was charged under the argon with [Cho][OAc] (0.35 equiv., 0.05 mmol, 8.2 mg) and approx. 0.6 mL of dry CD₂Cl₂ was added. Subsequently, pinacolborane (**2**) (1.35 equiv., 0.193 mmol, 24.7 mg) was added and the mixture was shaken vigorously, and the ¹H and ¹¹B NMR spectra were recorded.

2.8. General procedure for the nonequimolar reaction of pinacolborane (2) with [Cho][OAc] and acetophenone (1a)

The Young's NMR tube was charged under the argon with [Cho][OAc] (0.35 equiv., 0.05 mmol, 8.2 mg) and approx. 0.6 mL of dry CD₂Cl₂ was added. Subsequently, acetophenone (**1a**) (1 equiv., 0.142 mmol, 17 mg) and pinacolborane (**2**) (1.35 equiv., 0.193 mmol, 24.7 mg) were added and the mixture was shaken vigorously and left at room temperature for a specified time. After that, the ¹H and ¹¹B NMR spectra were then recorded.

2.9. General procedure for the synthesis of 2,2'-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

Pinacolborane (**2**) (0.1 mmol, 12.8 mg) was mixed with approx. 0.6 mL of dry CD₂Cl₂ in an NMR tube under the air atmosphere. Next, water (0.1 mmol, 1.8 mg) was added and the tube was shaken vigorously. After that, ¹H and ¹¹B NMR spectra were recorded. Caution: the reaction proceeds rapidly and with the release of hydrogen.

2.10. General procedure for the synthesis of 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl acetate

To the Young's NMR tube charged with argon pinacolborane (**2**) (0.1 mmol, 12.8 mg), approx. 0.6 mL of dry CD₂Cl₂ and acetic acid (0.1 mmol, 6 mg) were added. The mixture was shaken vigorously and left at room temperature for 1 h. After that, ¹¹B NMR spectra were recorded.

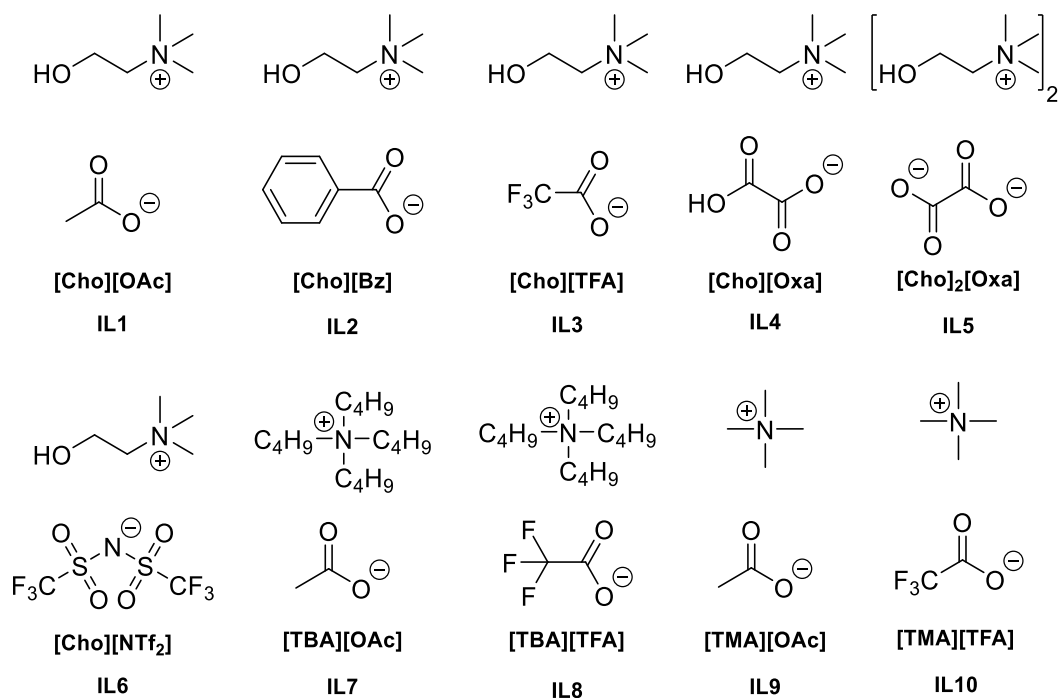
2.11. General procedure for the reaction of 2-(dimethylamino)ethan-1-ol (14**) with pinacolborane (**2**)**

To the Young's NMR tube charged under argon with pinacolborane (**2**) (0.1 mmol, 12.8 mg), approx. 0.6 mL of dry CD₂Cl₂ and 2-(dimethylamino)ethan-1-ol (**14**) (0.1 mmol, 8.9 mg). The mixture was shaken vigorously. After that, ¹H and ¹¹B NMR spectra were recorded.

2.12. General procedure for the [Cho][OAc]-catalyzed hydroboration of **1a with **2** in the presence of TMEDA**

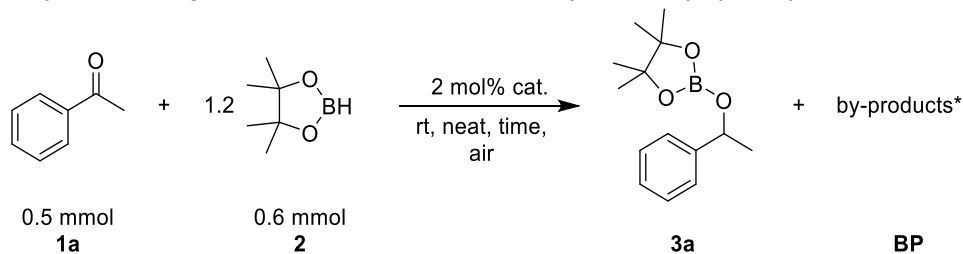
A 10-mL round-bottom flask containing a magnetic stirring bar was charged with [Cho][OAc] (10 mol%, 8.2 mg) and kept in an oil bath at 80 °C under vacuum for 30 min. After this time, the reaction vessel was allowed to cool down to room temperature and IL solidified. Subsequently, ketone (**1a**) (0.5 mmol, 60 mg), TMEDA (0.1–0.6 equiv.), and pinacolborane (**2**) (0.6 mmol, 77 mg) were added. The mixture was stirred for 1 hour at room temperature. Then, the crude reaction mixture was analyzed by GC–MS analysis. GC–MS samples were prepared in DCM with the addition of a drop of methanol.

3. Ionic liquids used as the catalysts in hydroboration of carbonyl compounds



FigureS1. Structures of ionic liquids used in the study. Catalyst screening for the hydroboration of ketones

Table S1. Catalyst screening for the model reaction of acetophenone (**1a**) and pinacolborane (**2**)



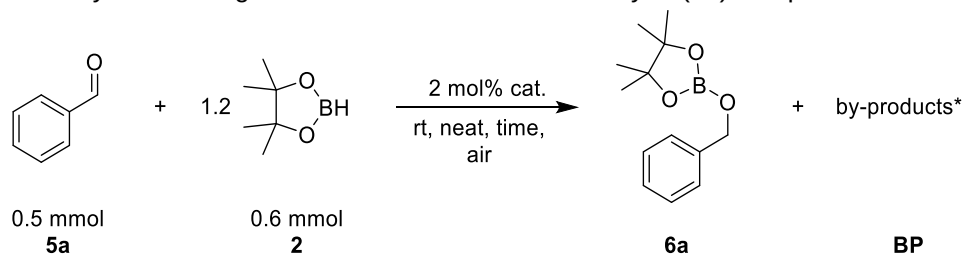
Entry	Cat.	Mol% of cat.	Time [h]	Conversion of 1a [%] ^{a)}	Selectivity of 3a [%] ^{a)}
1	-	-	1	0	n/d
2			2	trace	n/d
2	[Cho][OAc]	2	0.5	93	>99
3			1	97	>99
4			2	99	>99
5	[Cho][Bz]	2	0.5	93	>99
6			1	97	>99
7	[Cho][TFA]	2	0.5	0	n/d
8			1	20	>99
9	[Cho][Oxa]	2	0.5	0	n/d
10			1	4	>99
11	[Cho] ₂ [Oxa]	2	0.5	73	>99
12			1	89	>99

13	[Cho][NTf ₂]	8	2	0	>99
14			24	34	>99
15	[TBA][OAc]	8	2	97	>99
16			20	99	>99
17		2	1	84	>99
18			2	87	>99
19	[TBA][TFA]	8	2	89	>99
20	[TBA][TFA]	2	1	16	>99
21			2	37	>99
22	[TMA][OAc]	2	1	6	>99
23			2	10	>99
24	ChoCl	8	18	trace	n/d
25	[Cho][OH]	2	1	0	n/d
26	2-DMAE	2	1	0	n/d
27	HOAc	2	1	17	82
28		8	18	90	89
29	HBz	4	1	3	0
30	HTFA	4	1	80	97
31	H ₂ Oxa	4	1	>99	54
32	KOAc	8	1	60	>99
33	KBz	2	1	8	>99

^a) Conversion and selectivity were calculated based on GC-MS and ¹H NMR analyzes; n/d – not determined; *mainly aldol condensation products.

4. Catalyst screening for hydroboration of aldehydes

Table S2. Catalyst screening for model reaction of benzaldehyde (**5a**) and pinacolborane (**2**)



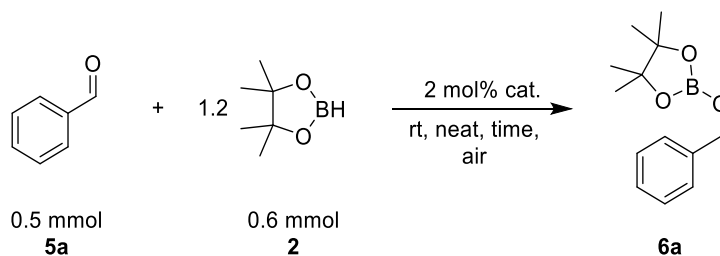
Entry	Cat.	Time [h]	Conversion of 5a [%] ^a	Selectivity 6a:BP [%] ^a
1	-	0.5	11	>99:<1
2		1	34	>99:<1
3	[Cho][OAc]	0.25	88	>99:<1
4		0.5	96	>99:<1
5	[Cho][Bz]	1	87	>99:<1
6		2	98	>99:<1
7	[Cho][TFA]	0.5	0	n/d
8		2	16	>99:<1
9	[Cho][Oxa]	0.5	0	n/d
10		2	24	>99:<1

11	[Cho] ₂ [Oxa]	0.25	91	>99:<1
12		0.5	96	>99:<1
13	[Cho][OH]	0.5	10	n/d
14	HOAc	1	99	96:4
15	HBz	1	96	97:3
16	HTFA	1	99	88:12
17	H ₂ Oxa	1	>99	11:89
18	KBz	0.5	93	>99:<1
19		1	98	>99:<1

^{a)} Conversion and selectivity were calculated based on GC-MS and ¹H NMR analyzes; n/d – not determined; *mainly aldol condensation products.

5. Optimization of conditions for hydroboration of aldehydes

Table S3. Optimization of conditions for the model reaction of benzaldehyde (**5a**) and pinacolborane (**2**)

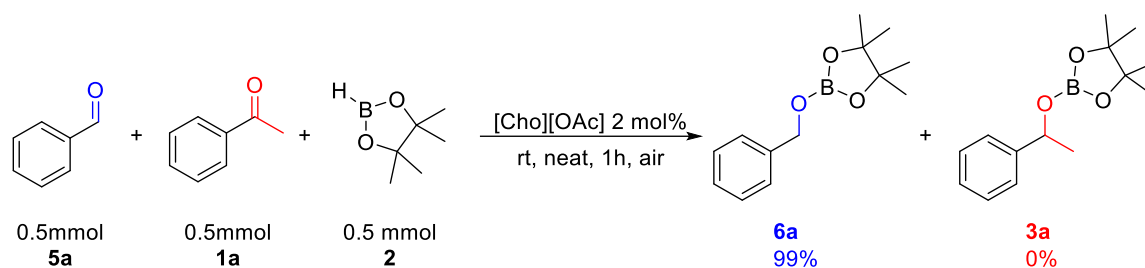


Entry	Mol % of IL	Time [min]	Solvent	2 [equiv.]	Conversion of 5a [%] ^{a)}	Selectivity of 6a [%] ^{a)}
1	4	5	neat	1.2	99	>99
2		15			>99	>99
3	4	15	DCM	1.2	79	>99
4		30			88	>99
5	4	15	toluene	1.2	94	>99
6		30			95	>99
7	4	15	acetonitrile	1.2	40	>99
8		30			45	>99
9	2	15	neat	1.2	88	>99
10		30			96	>99
11	1	15	neat	1.2	87	>99
12		30			91	>99
13	1	15	neat	1.2	67	>99
14		30			80	>99
15	0.5	15	neat	1.2	71	>99
16		30			89	>99

^{a)} The conversion and selectivity were calculated based on GC-MS analysis.

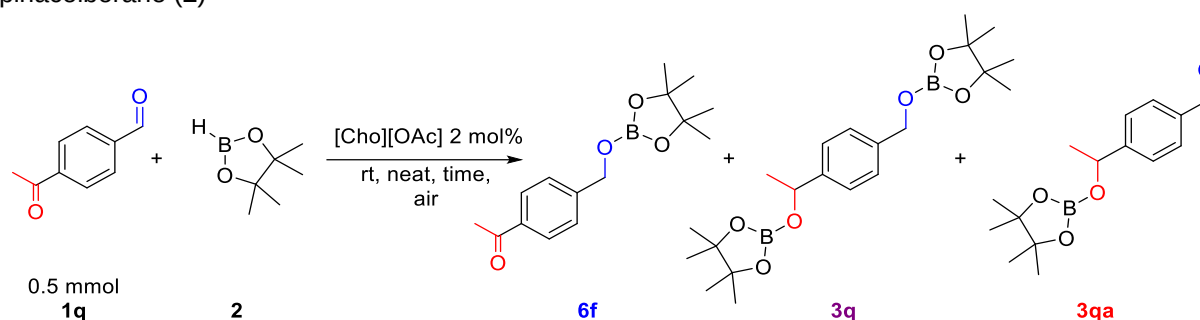
6. Competitive hydroboration reactions of ketones and aldehydes

a) Competitive hydroboration reaction of acetophenone (**1a**) and benzaldehyde (**5a**)



b) Hydroboration of 4-acetylbenzaldehyde (**1q**)

Table S4. Optimization of reaction conditions for the hydroboration of 4-acetylbenzaldehyde (**1q**) and pinacolborane (**2**)

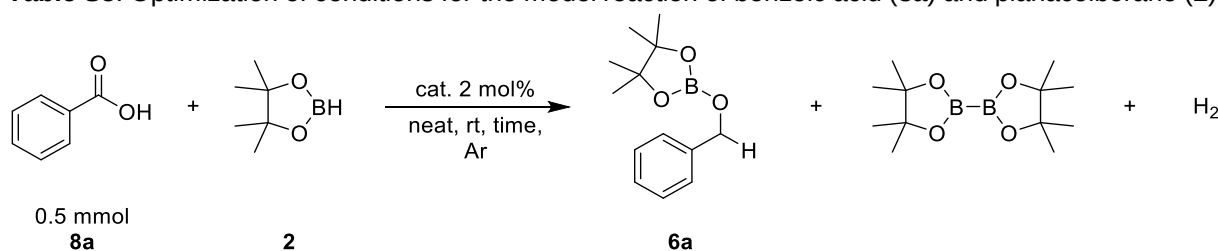


Entry	Time [h]	HBpin [equiv.]	Conversion of 1q [%] ^{a)}	Selectivity of 6f : 3q : 3qa [%] ^{a)}
1	0.5	1.2	>99	74:26:traces
2	0.5	1.0	81	97:3: traces
3	0.75	1.02	99	97:3:traces
4	1	2.2	>99	3:97:traces

^{a)} Conversion and selectivity were calculated based on GC-MS and ¹H NMR analyzes.

7. Optimization of the reaction conditions for the hydroboration of benzoic acid in the presence of [Cho][OAc]

Table S5. Optimization of conditions for the model reaction of benzoic acid (**8a**) and pinacolborane (**2**)



Entry	Mol%	Solvent	HBpin [equiv.]	Time [h]	Conversion of 8a [%] ^{a)}	Selectivity of 6a [%] ^{a)}
1	-	neat	3.1	3	0	>99
2	4	neat	3.1	2	86	>99
3				3	>99	>99
4	4	neat	3.5	2	87	>99
5				3	>99	>99
6	2	neat	3.1	2	80	>99
7				3	97	>99
8 ^{b)}	4	neat	3.1	2	89	>99
9 ^{b)}				3	99	>99

^{a)} The conversion and selectivity were calculated based on GC-MS analysis; ^{b)} under air.

8. The repetitive batch mode for the hydroboration of acetophenone (1a**) with pinacolborane (**2**)**

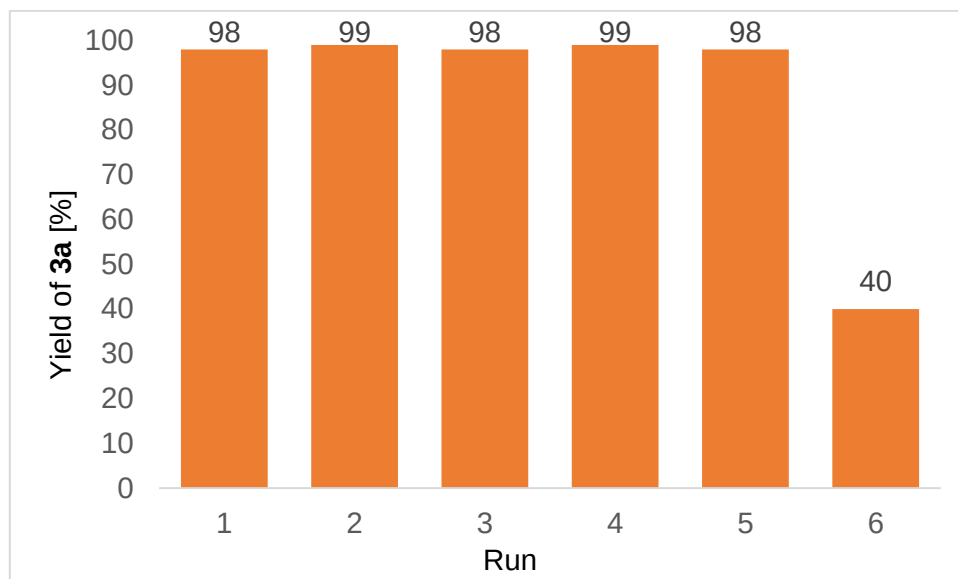
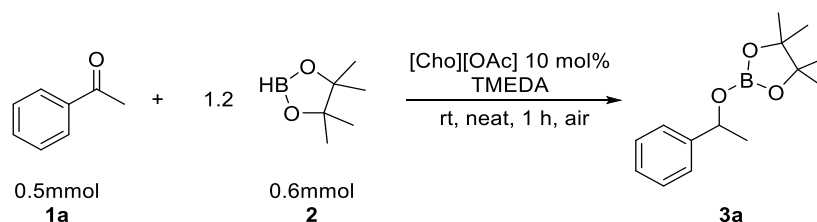


Figure S2. The repetitive batch reactions for the hydroboration of **1a** (1 mmol) with **2** (1.2 mmol) using 2 mol% of [Cho][OAc] at room temperature for 1 h under air atmosphere. The yields of **3a** were determined by GC-MS analysis.

9. [Cho][OAc]-catalyzed hydroboration of **1a with **2** in the presence of N,N,N',N'-tetramethylethylenediamine (TMEDA)**

Table S6. Hydroboration of acetophenone (**1a**) with pinacolborane (**2**) in the presence of [Cho][OAc] catalyst with the addition of TMEDA.



Entry	Mol% TMEDA	Conversion of 1a [%] ^{a)}	Selectivity of 3a [%] ^{a)}
1	0	>99	>99
2	10	95	>99
3	30	93	>99
4	45	83 ^{b)}	>99
5	60	86	>99

^{a)} The conversion and selectivity were calculated based on GC-MS analysis; ^{b)} reaction in NMR tube in DCM-d₂, with 15 mol % [Cho][OAc], under argon atmosphere; ^{b)} reaction in NMR tube in DCM-d₂, with 15 mol % [Cho][OAc], under argon atmosphere, yield were based on ¹H NMR analysis.

10. Further computational results

10.1 Detailed Gibbs free energy profiles for choline acetate

10.1.1. Formation of IN2 and IN3

First, we focused on the rate and yield of catalytically active anion formation from choline acetate (**IL1**). [Cho][OAc] (**IL1**) and HBpin (**2**) form two stable complexes **I1a** and **I2a**, with the latter leading *via* transition state **TS1a** to **I7a** (**IN2**) (**Figure S3**). This transformation occurs freely at room temperature, and the Gibbs free energies of the substrates and products are comparable. The formation of **I7b** (**IN3**) is more challenging, with a barrier from **I7a** through **TS2b** to **I6b** of 19.0 kcal/mol and a $\Delta G_{I7a \rightarrow I7b}$ of 13.7 kcal/mol. This shifts the equilibrium toward **I7a**, which is consistent with NMR investigations.

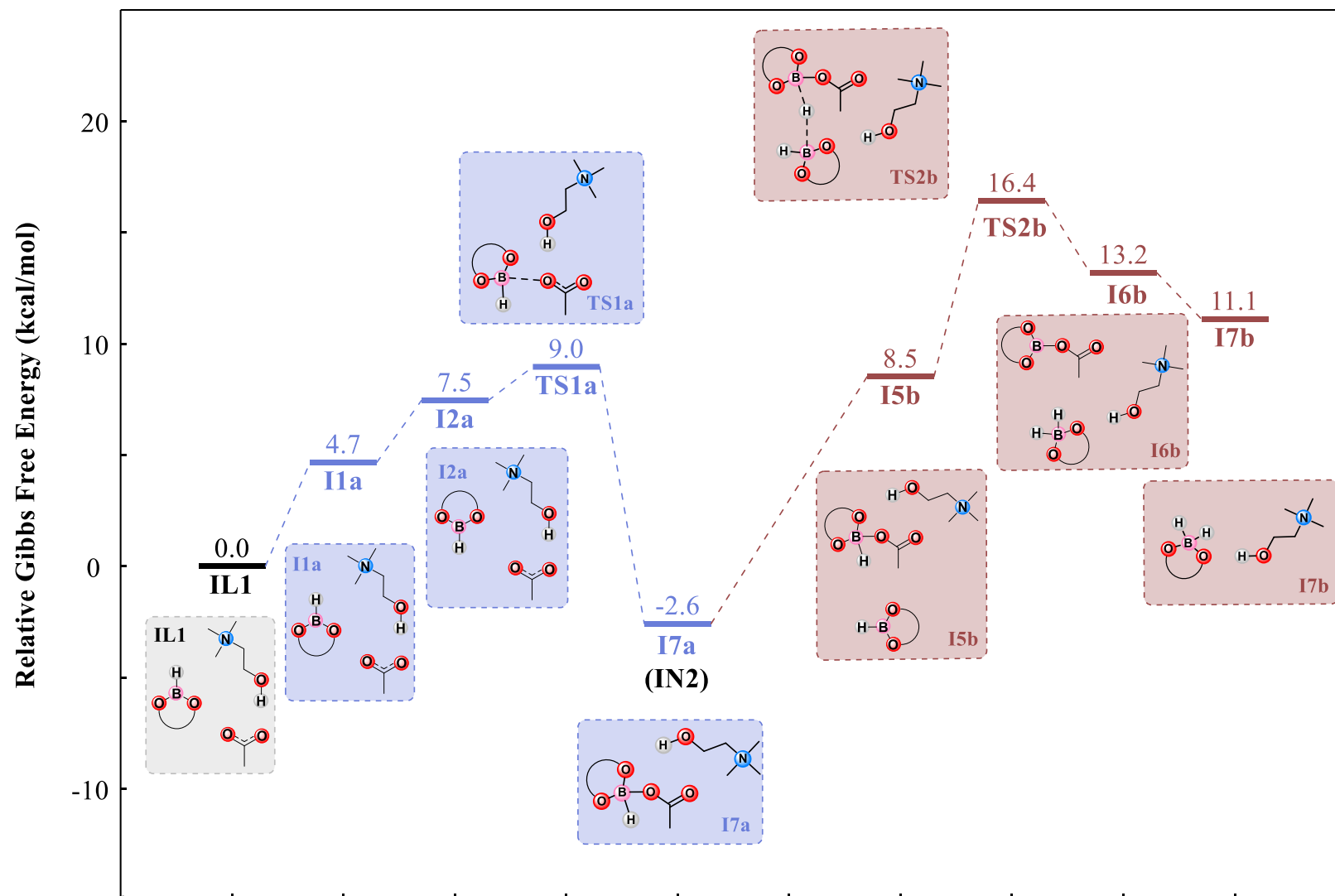


Figure S3. Gibbs free energy profile of the reaction of choline acetate (IL1) with pinacolborane – acetate pathway (ω B97XD/def2-SVPD, 295K, dichloromethane as PCM solvent).

10.1.2. Formation of IN5

Alternatively, the hydroxyl group of choline in **IL1** can react with boron atom of pinacolborane (**Figure S4**). As complex **I1c** is formed, boron is attacked by lone electron pair of oxygen and hydroxyl hydrogen is captured by acetate anion, forming **I2c**. Then, the hydrogen atom combines with another hydrogen from B-H bond (**TS1c**), leading to the release of hydrogen and formation of **I3c** and ultimately **I4c** (**IN4**). Although less accessible than pathway **a**, this reaction is irreversible due to the evolution of hydrogen. **I4c** and **I7a** can react together via **I5c** and **TS2c**; this leads to a weak complex **I6c** and then **I7c** (**IN5**). However, **I4c** can also be attacked by carboxylic oxygen of acetate (**TS2d** and **I7d**); this is easily reversible, but slows down the hydroboration reaction as **I7d** does not demonstrate catalytic properties.

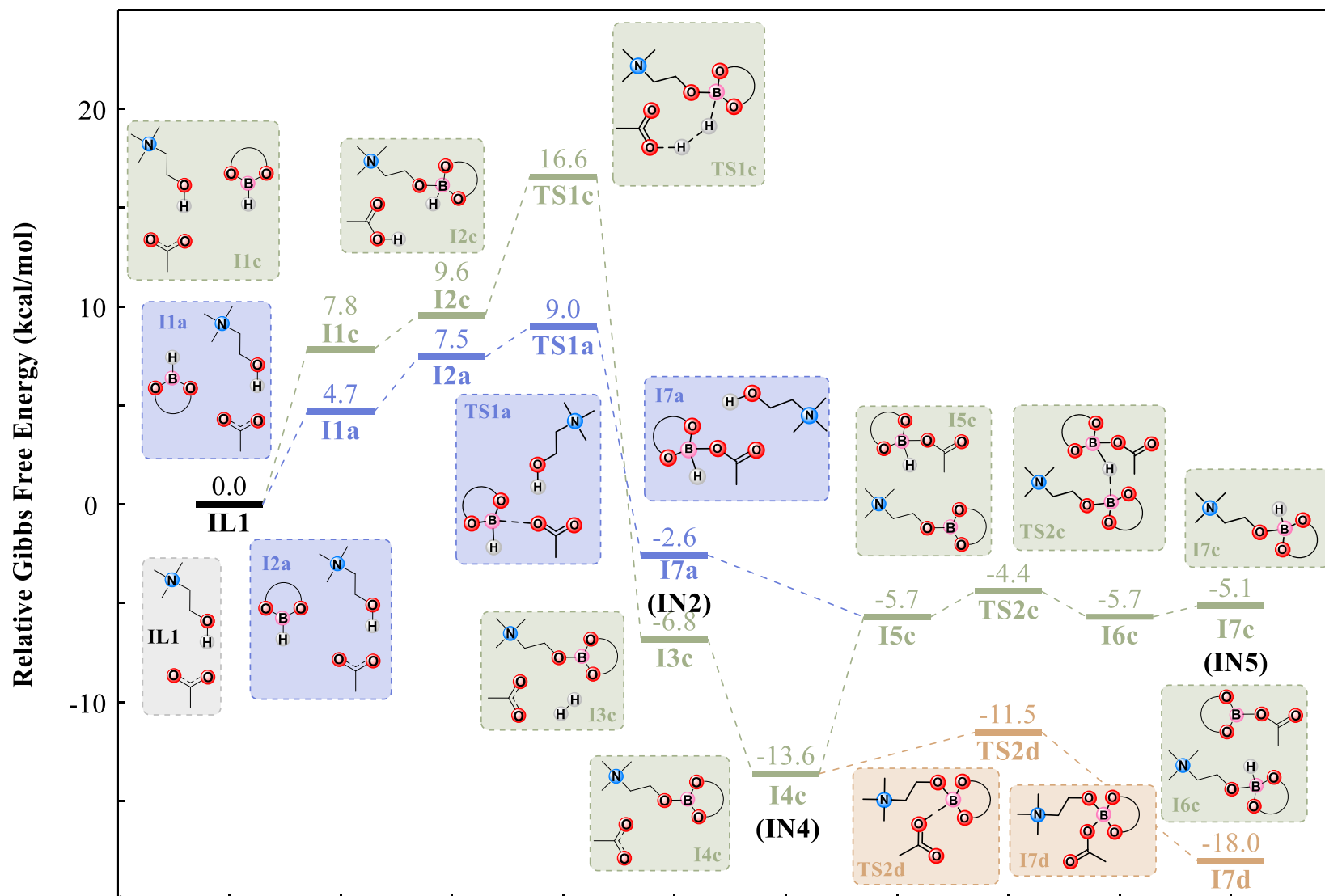


Figure S4. Gibbs free energy profile of the reaction of choline acetate (**IL1**) with pinacolborane – choline pathway (ω B97XD/6-31+G(d,p), 295K, dichloromethane as PCM solvent).

10.1.3. Catalytic cycle a (IN2)

As **I7a** is approached by acetophenone, a weak complex **I8a** is formed (**Figure S5**), followed by the attack of hydridic hydrogen of **IN2** on the carbonyl carbon of acetophenone (**TS3a**). The resulting **I9a** complex is very unstable, resulting in the attack of acetophenone's oxygen, now negatively charged, on the boron atom, which leads to **I11a**. To complete the catalytic cycle, a pinacolborane molecule approaches (**I12a**) and detaches the acetate moiety (**TS5a**), yielding a weak complex **I13a**, whose dissociation gives the product **3a** and regenerated **I7a**. The rate-determining step (RDS) of this cycle is the activation of acetophenone with $\Delta G^\ddagger = 18.0$ kcal/mol; the reaction is pushed especially by B-O bond formation, which is virtually irreversible in ambient conditions.

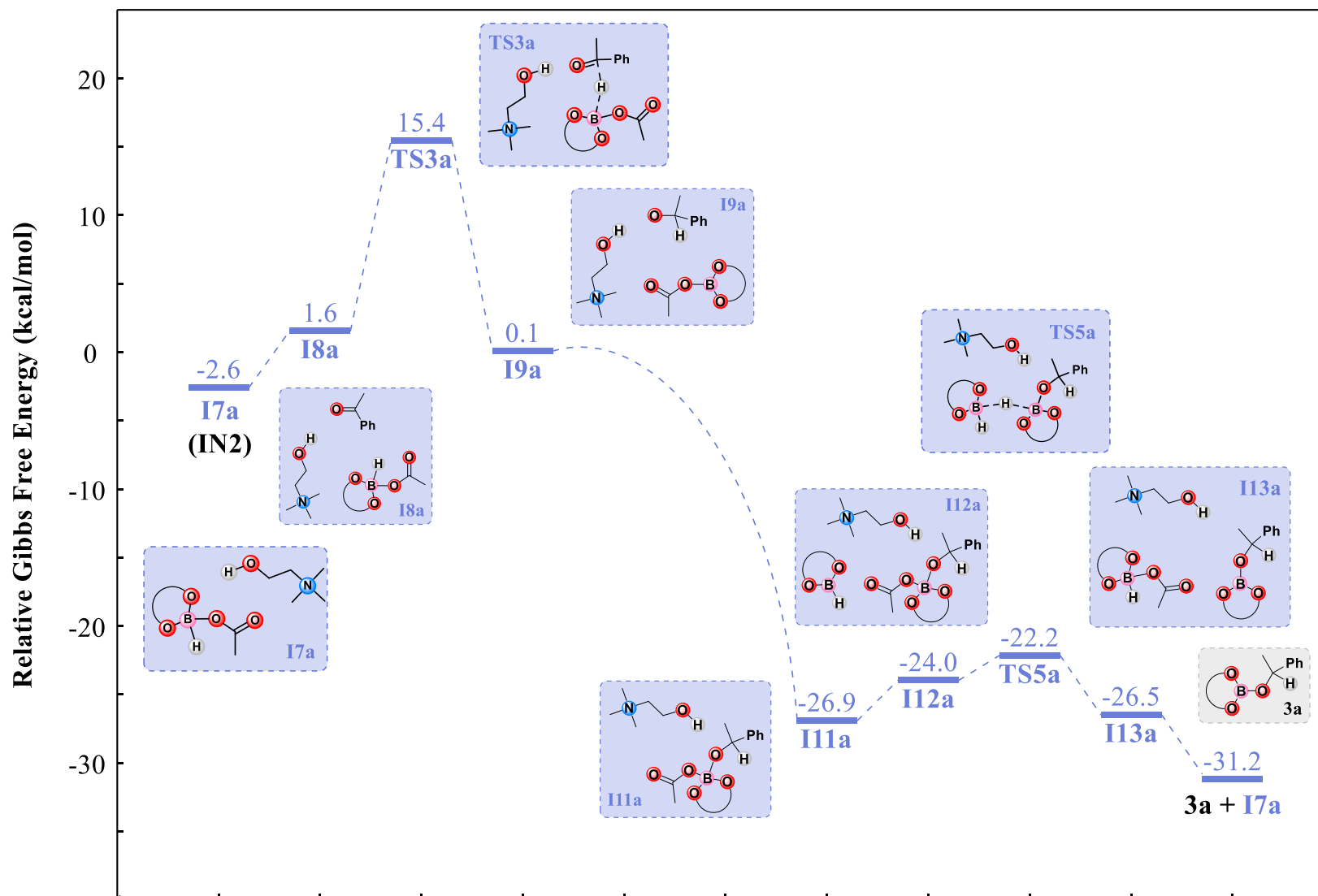


Figure S5. Gibbs free energy profile of the hydroboration of acetophenone with pinacolborane – catalytic cycle **a** (ω B97XD/def2-SVPD, 295K, dichloromethane as PCM solvent).

10.1.4. Catalytic cycle **b** (IN3)

Acetophenone and **I7b** form a weak complex **I8b** (Figure S6) with a subsequent attack of one of the two hydridic hydrogen atoms of **IN3** on the carbonyl carbon of acetophenone (**TS3b**). Again, the weak complex which results (**I9b**) rearranges to **I11b** with a negligible barrier as B-O bond is formed. Finally, a pinacolborane molecule joins (**I12b**) and the boron atom is attacked by hydridic hydrogen (**TS5b**), leading to a weak complex **I13b**, and the product **3a** along with regenerated **I7b**. The RDS of cycle **b** is accompanied by $\Delta G^\ddagger = 12.1$ kcal/mol.

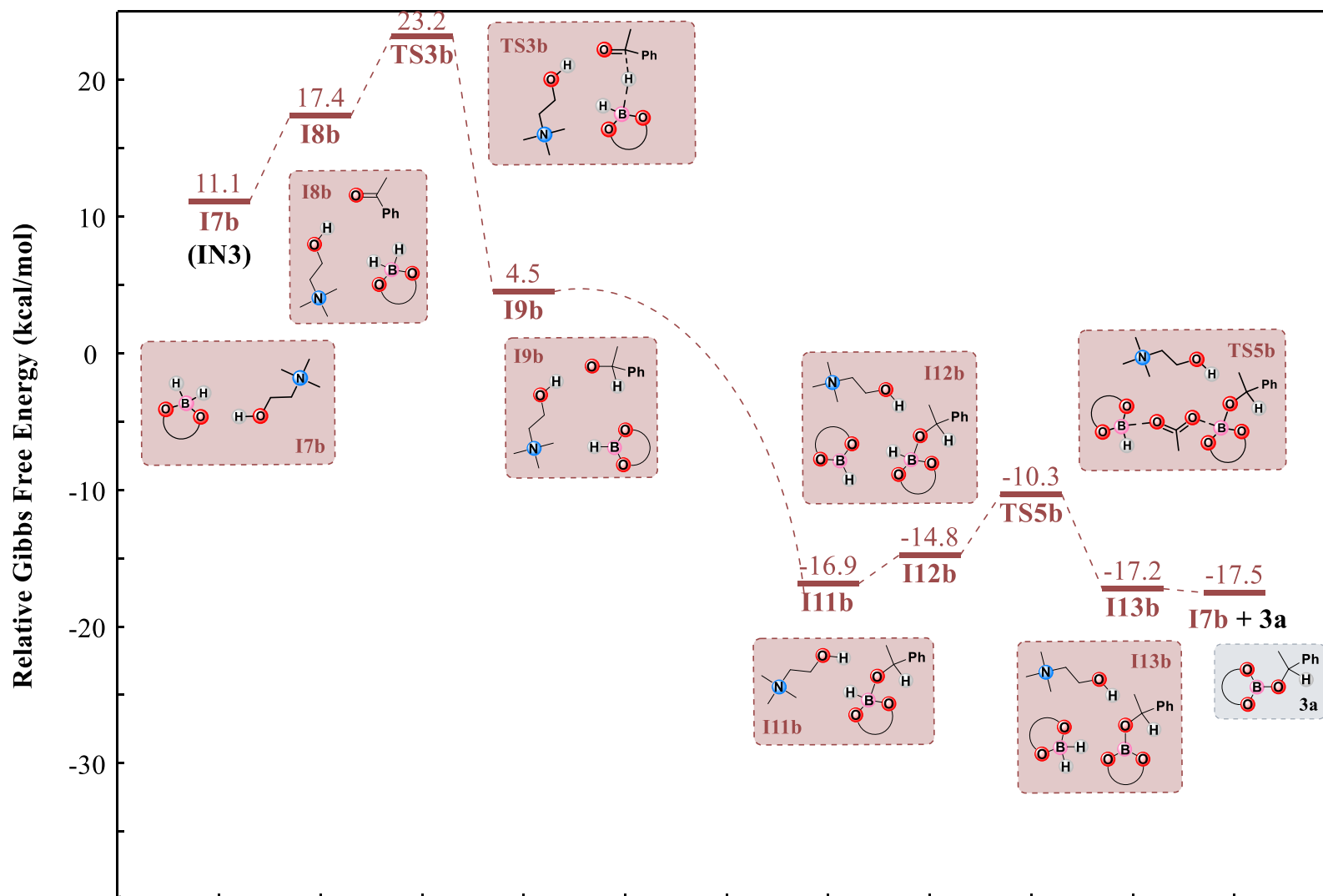


Figure S6. Gibbs free energy profile of the hydroboration of acetophenone with pinacolborane – catalytic cycle **b** (ω B97XD/def2-SVPD, 295K, dichloromethane as PCM solvent).

10.1.5. Catalytic cycle c (IN5)

I7c forms a weak complex **I8c** with acetophenone (**Figure S7**), leading to the transfer of the hydridic hydrogen from **IN5** on the carbonyl carbon of acetophenone (**TS3c**). **I9c** complex is formed; Contrary to cycles **a** and **b**, subsequent rearrangement within **I9c** – the formation of B-O bond – would block further reaction as the zwitterionic cholinic moiety in **I10e** is not a good leaving group. Instead, the reaction progresses when **I9c** is approached by a pinacolborane molecule (**I10c**), which is then attacked by the alkoxylate (**TS4c**). After the resulting **I11c** complex rearranges to **I12c**, hydride transfer via **TS5c** leads to **I13c**, which finally dissociates to produce **3c** and regenerated **I7c**. The rate-determining step (RDS) of this cycle is the activation of acetophenone with $\Delta G^\ddagger = 10.3$ kcal/mol.

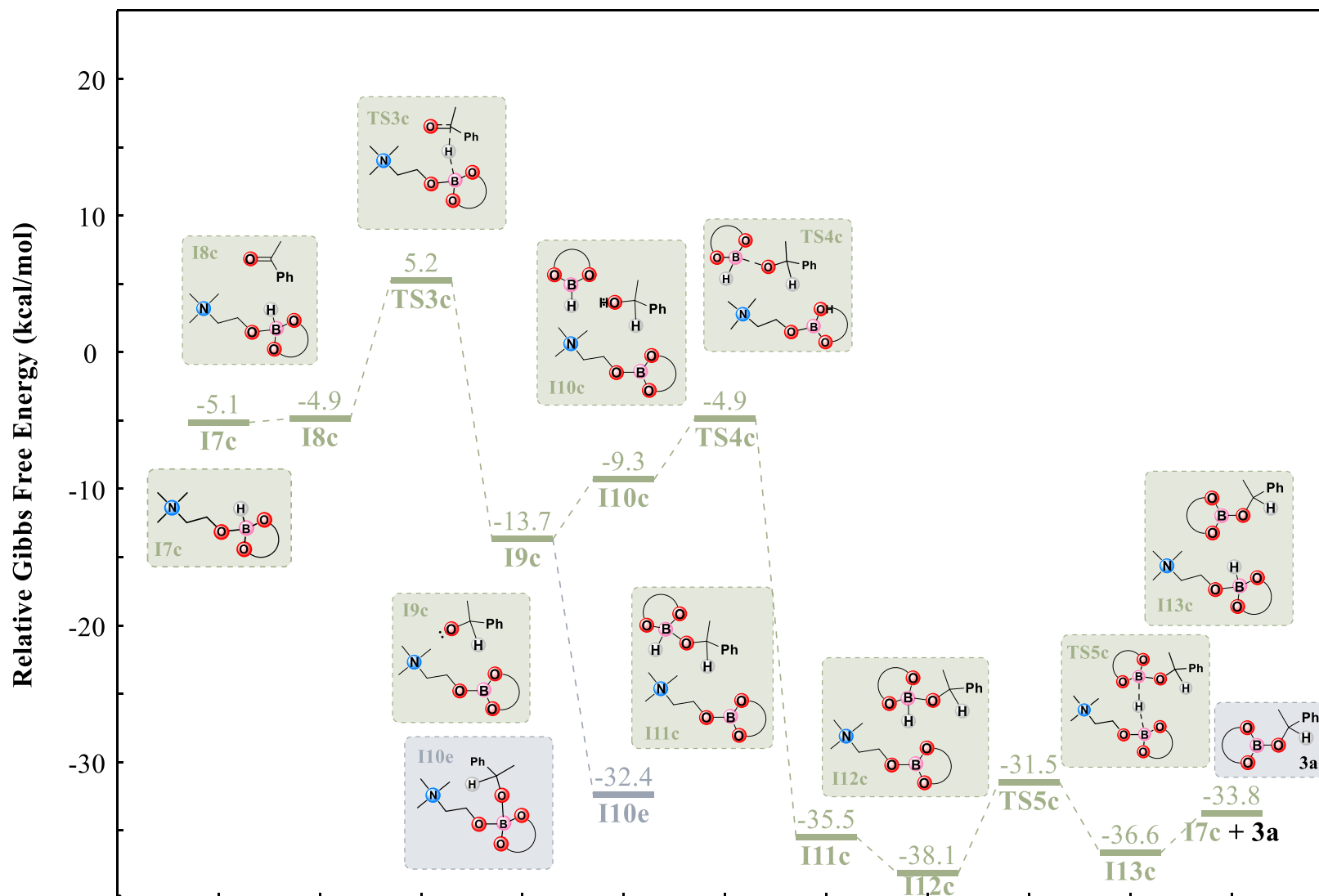


Figure S7. Gibbs free energy profile of the hydroboration of acetophenone with pinacolborane – catalytic cycle **c** (ω B97XD/def2-SVPD), 295K, dichloromethane as PCM solvent).

10.2. Gibbs free energy profiles of the reactions of other selected ILs

We investigated the formation of catalytic species from three other ionic liquids: choline trifluoroacetate (**IL3**), tetramethylammonium acetate, (**IL9**), and tetramethylammonium trifluoroacetate (**IL10**), with the use of computational methods. For trifluoroacetate-based ionic liquids (**IL3** and **IL10**), formation of not only **I7** (analogous to **IN3** in the model reaction), but even **I3** (analogous to **IN2** in the model reaction), was found to be disfavored by reaction equilibria ($\Delta G_{\text{IL} \rightarrow \text{I3}} = 5.9 \text{ kcal/mol}$ for **IL3** and 9.3 kcal/mol for **IL10**). This is consistent with the results of the experiment, where **IL3** and **IL10** are observed to perform less effectively than **IL1**. However, the computational model failed in predicting the reactivity of **IL9**, which it predicts to be transformed easily into **I3**. We suppose that the nature of the N-alkyl groups has such a significant effect on reactivity because of the solvent-free character of the reaction; these effects our model was not able to properly account for, producing results that would be more relevant to tetrabutylammonium acetate **IL7**.

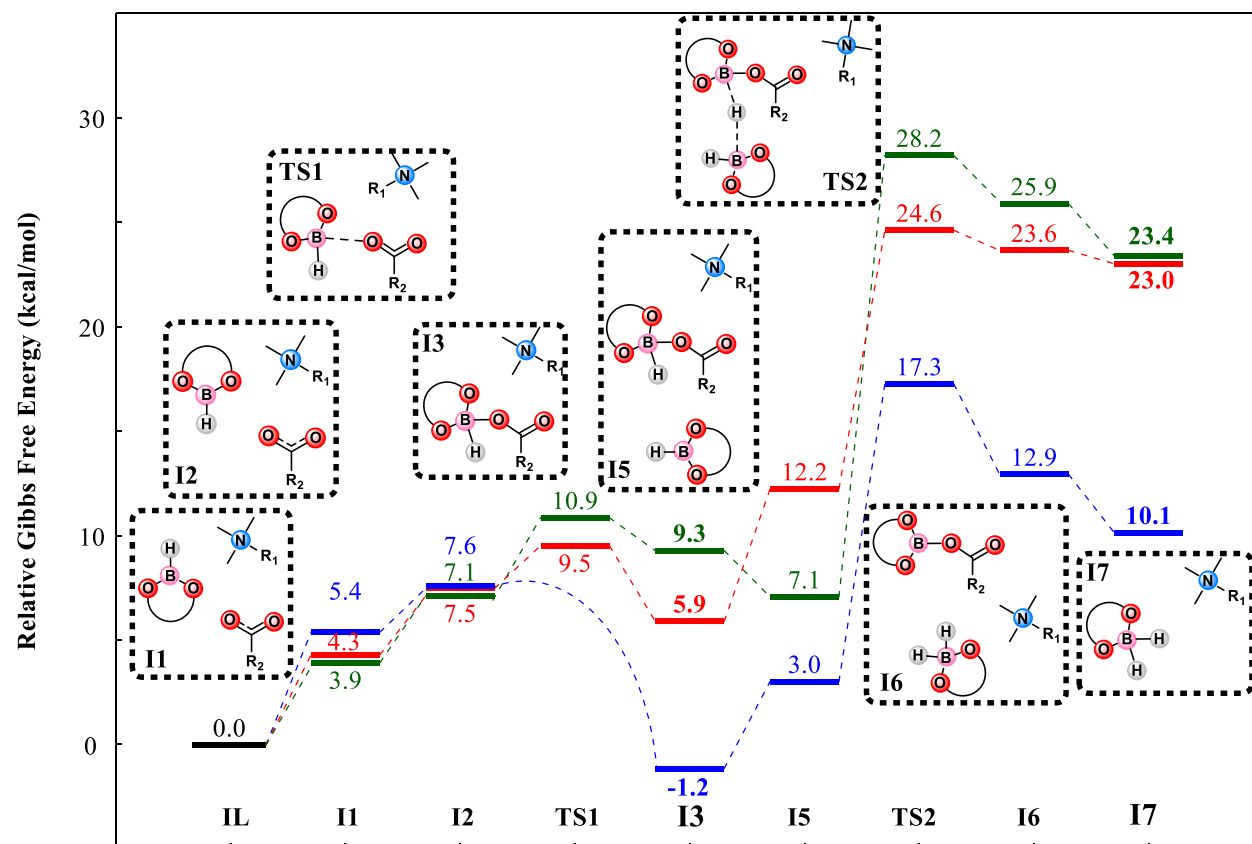


Figure S8. Gibbs free energy profiles of the reactions of selected ILs: **IL3** (red), **IL9** (blue), and **IL10** (green) with pinacolborane (ω B97XD/6-31+G(d,p), 295K, dichloromethane as PCM solvent).

10.3. Reaction pathway with BH₃ as catalyst

We investigated reaction pathways proceeding with BH₃ at theoretical level (**Figure S8**). Release of BH₃ through the opening of a 1,3,2-dioxaborolane ring requires the overcoming of Gibbs free energy barrier ($\Delta G^\ddagger$) of over 40 kcal/mol, which would be impossible under the applied conditions. However, as pinacolborane might be contaminated with this compound, this pathway was considered. It was found that although BH₃ easily attaches to the C=O bond of acetophenone, regeneration of 'hidden catalyst', through the reaction with HBpin, involves $\Delta G^\ddagger$ of 18.9 kcal/mol and is slightly endoenergetic (+3 kcal/mol). It suggests that the contribution of trace concentration of BH₃ to the catalysis, if any, is marginal. Choline borohydride, which could form in the presence of BH₃, is even less capable of acting as a catalyst, due to the high $\Delta G^\ddagger$ activation for the reaction with acetophenone (above 30 kcal/mol).

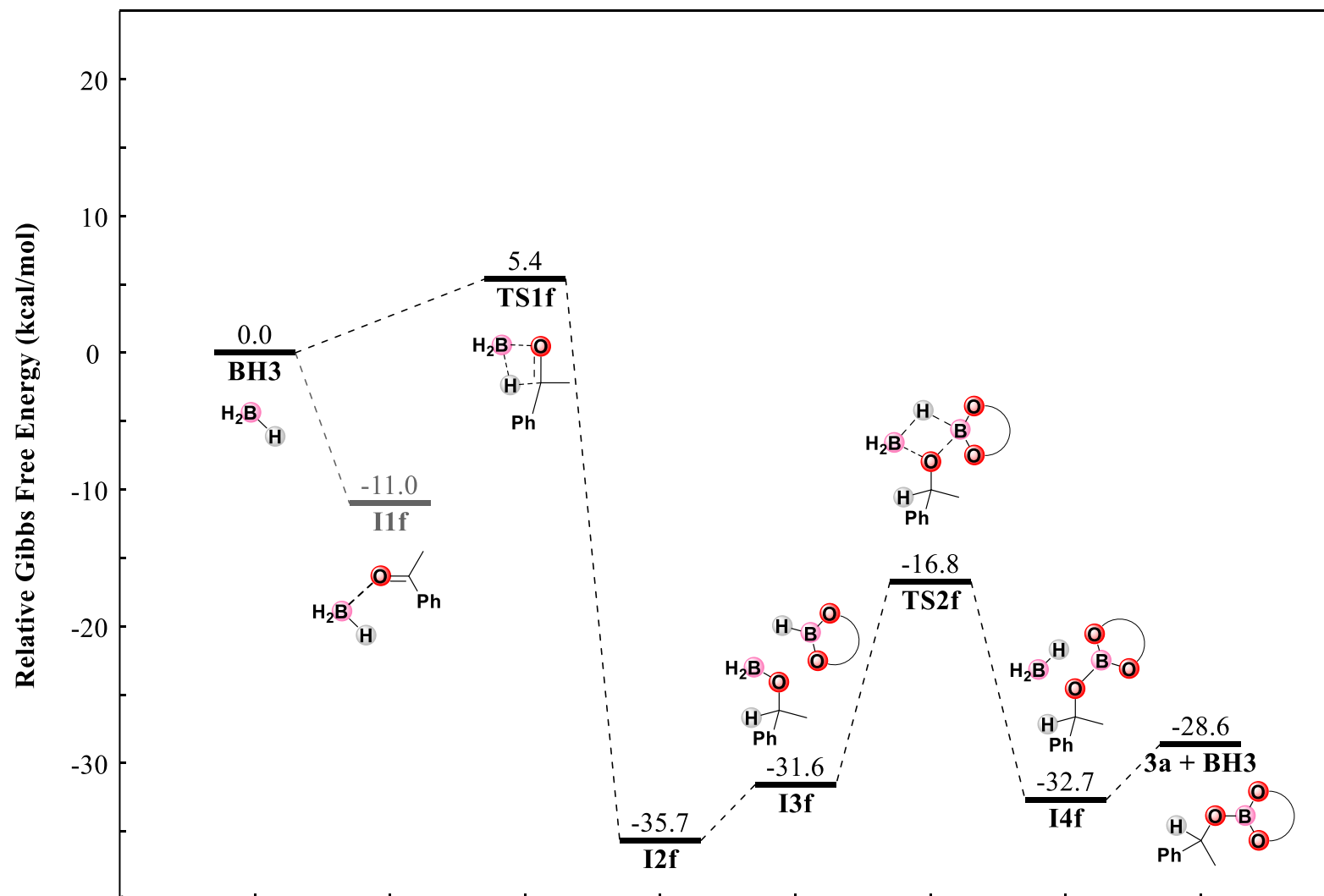


Figure S9. Gibbs free energy profile of the hydroboration of acetophenone with pinacolborane catalysed by BH₃ (ω B97XD/def2-SVPD, 295K, dichloromethane as PCM solvent).

10.4. Gibbs free energies of all structures

Table S7. Gibbs free energies of substrates and selected intermediates (ω B97XD/def2-SVPD, 1 atm, 295 K, dichloromethane solution, all energies given in Hartree).

Structure	Gibbs free energy	Structure	Gibbs free energy
HBpin	-411.322085	TFA ⁻	-525.843540
AcPh	-384.405946	[Cho][AcO]	-556.674579
BH ₃	-26.570770	[Cho][TFA]	-854.141884
H ₂	-1.173414	[TMA][TFA]	-739.745282
Cho ⁺	-328.284264	[TMA][AcO]	-442.275826
TMA ⁺	-213.897179	AcOBPin	-639.005862
AcO ⁻	-228.370775	TFABPin	-936.454207

Table S8. Gibbs free energies of structures in the reaction with [Cho][AcO] (ω B97XD/def2-SVPD, 1 atm, 295 K, dichloromethane solution, all energies given in Hartree).

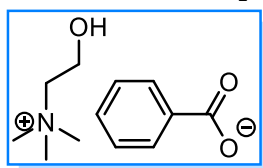
Structure	Gibbs free energy	Structure	Gibbs free energy
I1a	-967.989227	I3c	-968.007548
I2a	-967.984803	I4c	-966.844957
TS1a	-967.982396	I5c	-1378.175089
I7a	-968.000779	TS2c	-1378.152378
I8a	-1352.400139	I6c	-1378.154421
TS3a	-1352.377995	I7c	-739.147668
I9a	-1352.402486	I8c	-1123.553187
I11a	-1352.445492	TS3c	-1123.537101
I12a	-1763.762853	I9c	-1123.567230
TS5a	-1763.760016	I10e	-1123.597057
I13a	-1763.766898	I10c	-1534.882345
I5b	-1379.305186	TS4c	-1534.875333
TS2b	-1379.292585	I11c	-1534.924100
I6b	-1379.297733	I12c	-1534.928256
I7b	-740.295195	TS5c	-1534.917689
I8b	-1124.691146	I13c	-1534.925892
TS3b	-1124.681863	TS2d	-966.841623
I9b	-1124.711655	I7d	-966.851986
I11b	-1124.745713	I1f	-410.994253
I12b	-1536.064463	TS1f	-410.968139
TS5b	-1536.057394	I2f	-411.033574
I13b	-1536.068353	I3f	-822.349165
I1c	-967.984164	TS2f	-822.325509
I2c	-967.981420	I4f	-822.350885
TS1c	-967.970276	3a	-795.773653

Table S9. Gibbs free energies of structures in the reactions of HBpin with [Cho][TFA], [TMA][AcO] and [TMA][TFA] (suffixes 'k', 'm' and 'n', respectively; ω B97XD/def2-SVPD, 1 atm, 295 K, dichloromethane solution, all energies given in Hartree).

Structure	Gibbs free energy	Structure	Gibbs free energy
I1k	-1265.457134	TS2m	-1264.8925
I2k	-1265.452063	I6m	-1264.8994
TS1k	-1265.448817	I7m	-625.898001
I3k	-1265.454585	I1n	-1151.061136
I5k	-1676.766571	I2n	-1151.056039
TS2k	-1676.746844	TS1n	-1151.050078
I6k	-1676.748379	I3n	-1151.052588
I1m	-853.589351	I5n	-1562.378209
I2m	-853.585865	TS2n	-1562.344533
I3m	-853.59975	I6n	-1562.348219
I5m	-1264.915203		

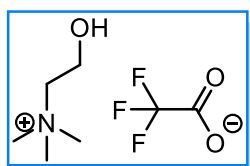
11. Characterization of synthesized ionic liquids

Choline benzoate [Cho][Bz] (IL2)



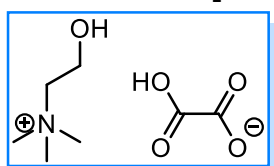
^1H NMR (300 MHz, D_2O , δ , ppm): 7.90 – 7.86 (m, 2H, Ph), 7.59 – 7.44 (m, 3H, Ph), 4.11 – 3.97 (m, 2H, $\text{CH}_2(\text{CH}_2)$), 3.52 – 3.43 (m, 2H, NCH_2), 3.16 (s, 9H, $\text{N}(\text{CH}_3)_3$). A hydrogen atom in hydroxyl group was not detected. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, D_2O , δ , ppm): 175.5 (COO^-), 136.1 (Ph), 131.3 (Ph), 128.8 (Ph), 128.3 (Ph), 67.4 (t, NCH_2), 55.6 ($\text{CH}_2(\text{CH}_2)$), 53.8 (t, $\text{N}(\text{CH}_3)_3$). The analytical data are in agreement with the literature.¹¹

Choline trifluoroacetate [Cho][TFA] (IL3)



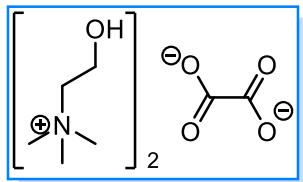
^1H NMR (300 MHz, D_2O , δ , ppm): 4.12 – 4.01 (m, 2H, $\text{CH}_2(\text{CH}_2)$), 3.56 – 3.47 (m, 2H, NCH_2), 3.20 (s, 9H, $\text{N}(\text{CH}_3)_3$). A hydrogen atom in hydroxyl group was not detected. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, D_2O , δ , ppm): 162.8 (q, $J_{\text{C-F}} = 35.4$ Hz, COO^-), 116.4 (q, $J_{\text{C-F}} = 292.0$ Hz, CF_3), 67.4 (t, NCH_2), 55.6 ($\text{CH}_2(\text{CH}_2)$), 53.8 (t, $\text{N}(\text{CH}_3)_3$). The analytical data are in agreement with the literature.¹²

Choline oxalate [Cho][Oxa] (IL4)



^1H NMR (300 MHz, D_2O , δ , ppm): 4.10 – 4.03 (m, 2H, $\text{CH}_2(\text{CH}_2)$), 3.56 – 3.47 (m, 2H, NCH_2), 3.20 (s, 9H, $\text{N}(\text{CH}_3)_3$). Hydrogen atoms in hydroxyl and carboxyl groups were not detected. **$^{13}\text{C}\{^1\text{H}\}$ NMR** (75 MHz, D_2O , δ , ppm): 165.6 (COO^-), 67.4 (t, NCH_2), 55.6 ($\text{CH}_2(\text{CH}_2)$), 53.8 (t, $\text{N}(\text{CH}_3)_3$). The analytical data are in agreement with the literature.¹³

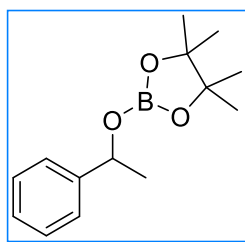
Di- choline oxalate [**Cho**]₂[**Oxa**] (**IL5**)



^1H NMR (300 MHz, D_2O , δ , ppm): 4.09 – 4.04 (m, 4H, $\text{CH}_2(\text{CH}_2)$), 3.57 – 3.48 (m, 4H, NCH_2), 3.21 (s, 18H, $\text{N}(\text{CH}_3)_3$). A hydrogen atom in hydroxyl group was not detected. **$^{13}\text{C}\{^1\text{H}\}$ NMR** (75 MHz, D_2O , δ , ppm): 173.1 (COO^-), 67.4 (t, NCH_2), 55.6 ($\text{CH}_2(\text{CH}_2)$), 53.8 (t, $\text{N}(\text{CH}_3)_3$). The analytical data are in agreement with the literature.¹⁴

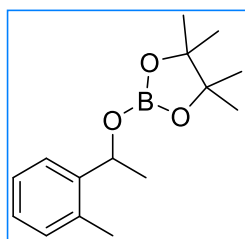
12. Products characterization

4,4,5,5-Tetramethyl-2-(1-phenylethoxy)-1,3,2-dioxaborolane (**3a**)



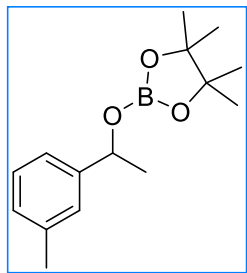
^1H NMR (300 MHz, CDCl_3 , δ , ppm): 7.31 – 7.28 (m, 2H, Ph), 7.26 – 7.12 (m, 3H, Ph), 5.17 (q, $J_{\text{H-H}} = 6.4$ Hz, 1H, $\text{CH}(\text{CH}_3)$), 1.42 (d, $J_{\text{H-H}} = 6.5$ Hz, 3H, $\text{CH}(\text{CH}_3)$), 1.16 (s, 6H, $\text{C}(\text{CH}_3)_2$), 1.13 (s, 6H, $\text{C}(\text{CH}_3)_2$). **MS (EI) [m/z (%)]**: 248(M^+ , 2), 233(100), 232(23), 190(47), 189(28), 175(20), 165(14), 129(15), 106(17), 103(13), 43(16). Characterized as a crude product. The analytical data are in agreement with the literature.¹⁵

4,4,5,5-Tetramethyl-2-(1-(*o*-tolyl)ethoxy)-1,3,2-dioxaborolane (**3b**)



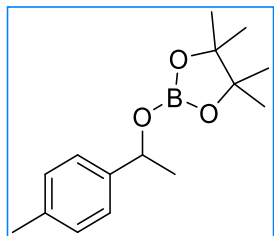
^1H NMR (300 MHz, CDCl_3 , δ , ppm): 7.53 (d, $J_{\text{H-H}} = 8.6$ Hz, 1H, Ph), 7.22 – 7.07 (m, 3H, Ph), 5.43 (q, $J_{\text{H-H}} = 6.4$ Hz, 1H, $\text{CH}(\text{CH}_3)$), 2.34 (s, 3H, *o*- CH_3 Ph), 1.46 (d, $J_{\text{H-H}} = 6.4$ Hz, 3H, $\text{CH}(\text{CH}_3)$), 1.23 (s, 6H, $\text{C}(\text{CH}_3)_2$), 1.20 (s, 6H, $\text{C}(\text{CH}_3)_2$). **MS (EI) [m/z (%)]**: 262(M^+ , 4), 248(10), 247(67), 246(19), 190(16), 129(10), 119(100), 118 (51), 117(34), 115(9), 43(10). Characterized as a crude product. The analytical data are in agreement with the literature.¹⁶

4,4,5,5-Tetramethyl-2-(1-(*m*-tolyl)ethoxy)-1,3,2-dioxaborolane (3c**)**



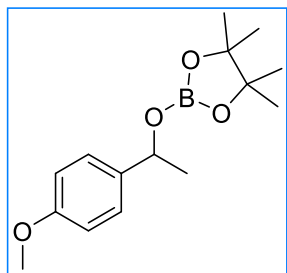
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.22 – 7.14 (m, 3H, Ph), 7.05 (d, J_{H-H} = 7.5 Hz, 1H, Ph), 5.22 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 2.34 (s, 3H, *m*-CH₃Ph), 1.48 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.25 (s, 6H, C(CH₃)₂), 1.22 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 262(M⁺, 16), 248(15), 247(49), 246(20), 204(24), 203(23), 189(15), 120(37), 119(100), 117(25). Characterized as a crude product. The analytical data are in agreement with the literature.^{15, 17}

4,4,5,5-Tetramethyl-2-(1-(*p*-tolyl)ethoxy)-1,3,2-dioxaborolane (3d**)**



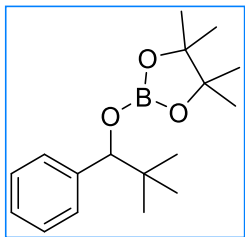
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.26 (d, J_{H-H} = 8.1 Hz, 2H, Ph), 7.13 (d, J_{H-H} = 7.9 Hz, 2H, Ph), 5.23 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 2.33 (s, 3H, *p*-CH₃Ph), 1.48 (d, J_{H-H} = 6.4 Hz, 3H, CH(CH₃)), 1.25 (s, 6H, C(CH₃)₂), 1.22 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 262(M⁺, 5), 261(7), 248(17), 247(49), 246(20), 179(9), 121(12), 120(37), 119(100), 117(21), 116(12). Characterized as a crude product. The analytical data are in agreement with the literature.¹⁵

2-(1-(4-Methoxyphenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3e**)**



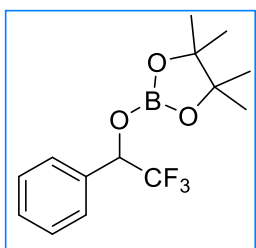
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.29 (d, J_{H-H} = 8.5 Hz, 2H, Ph), 6.85 (d, J_{H-H} = 8.8 Hz, 2H, Ph), 5.20 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 3.79 (s, 3H, *p*-OCH₃), 1.47 (d, J_{H-H} = 6.4 Hz, 3H, CH(CH₃)), 1.24 (s, 6H, C(CH₃)₂), 1.21 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 278(M⁺, 2), 264(14), 263(100), 262(8), 181(6), 129(6), 136(8), 135(23), 134(12), 91(6), 43(8). Characterized as a crude product. The analytical data are data in agreement with the literature.¹⁵

2-(2,2-Dimethyl-1-phenylpropoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3f**)



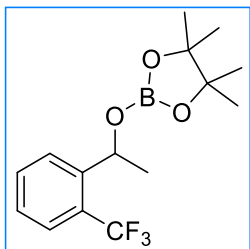
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.36 – 7.25 (m, 5H, Ph), 4.79 (s, 1H, CH(CH₃)), 1.23 (s, 6H, C(CH₃)₂), 1.17 (s, 6H, C(CH₃)₂), 0.93 (s, 9H, (C(CH₃)₃)). **MS (EI) [m/z (%)]**: 290(M⁺, 2), 234(14), 233(100), 232(24), 151(6), 129(8), 91(7), 83(9), 55(7), 44(8), 41(10). Characterized as a crude product. The analytical data are in agreement with the literature.¹⁸

4,4,5,5-Tetramethyl-2-(2,2,2-trifluoro-1-phenylethoxy)-1,3,2-dioxaborolane (**3g**)



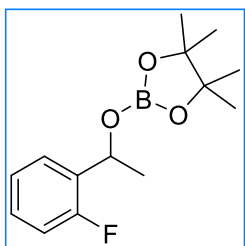
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.53 – 7.45 (m, 2H, Ph), 7.42 – 7.35 (m, 3H, Ph), 5.39 (q, *J*_{H-F} = 6.6 Hz, 1H, CH(CF₃)), 1.25 (s, 6H, C(CH₃)₂), 1.22 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 302(M⁺, 3), 301(26), 152(20), 151(93), 148(31), 147(100), 145(24), 144(15), 133(34), 131(29), 130(18). Characterized as a crude product. The analytical data are in agreement with the literature.¹⁹

4,4,5,5-Tetramethyl-2-(1-(2-(trifluoromethyl)phenyl)ethoxy)-1,3,2-dioxaborolane (**3h**)



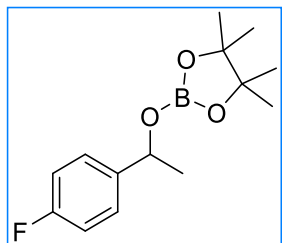
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.81 (d, *J*_{H-H} = 7.9 Hz, 1H, Ph), 7.60 – 7.51 (m, 2H, Ph), 7.33 (t, *J*_{H-H} = 7.6 Hz, 1H, Ph), 5.64 (q, *J*_{H-H} = 6.1 Hz, 1H, CH(CH₃)), 1.48 (d, *J*_{H-H} = 6.3 Hz, 3H, CH(CH₃)), 1.22 (s, 6H, C(CH₃)₂), 1.18 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 316(M⁺, 3), 301(41), 197(8), 173(27), 153(27), 151(29), 147(100), 133(40), 103(10), 83(7), 59(10). Characterized as a crude product. The analytical data are in agreement with the literature.²⁰

2-(1-(2-Fluorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3i**)



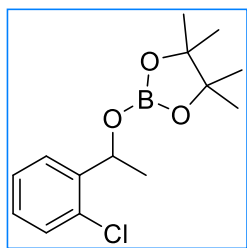
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.57 – 7.51 (m, 1H, Ph), 7.25 – 7.17 (m, 1H, Ph), 7.14 – 7.09 (m, 1H, Ph), 7.01 – 6.94 (m, 1H, Ph), 5.55 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.49 (d, J_{H-H} = 6.2 Hz, 3H, CH(CH₃)), 1.24 (s, 6H, C(CH₃)₂), 1.21 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 266(M⁺, 5), 234(20), 233(27), 220(20), 219(100), 218(35), 177(36), 176(29), 175(42), 92(30), 65(25). Characterized as a crude product. The analytical data are in agreement with the literature.²¹

2-(1-(4-Fluorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3j)



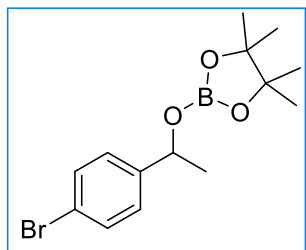
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.37 – 7.28 (m, 2H, Ph), 7.04 – 6.95 (m, 2H, Ph), 5.21 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.46 (d, J_{H-H} = 6.4 Hz, 3H, CH(CH₃)), 1.23 (s, 6H, C(CH₃)₂), 1.20 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 266(M⁺, 4), 251(100), 208(11), 207(12), 193(14), 129(10), 124(14), 123(39), 122(16), 103(13), 43(12). Characterized as a crude product. The analytical data are in agreement with the literature.¹⁵

2-(1-(2-Chlorophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3k)



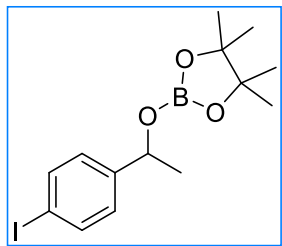
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.65 (dd, J_{H-H} = 7.8, 1.6 Hz, 1H, Ph), 7.34 – 7.26 (m, 2H, Ph), 7.19 (m, 1H, Ph), 5.60 (q, J_{H-H} = 6.3 Hz, 1H, CH(CH₃)), 1.50 (d, J_{H-H} = 6.3 Hz, 3H, CH(CH₃)), 1.27 (s, 6H, C(CH₃)₂), 1.24 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 283(M⁺, 2), 269(33), 267(100), 247(65), 189(56), 188(30), 141(21), 139(43), 138(23), 103(24), 43(22). Characterized as a crude product. The analytical data are in agreement with the literature.^{15, 17}

2-(1-(4-Bromophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3l)



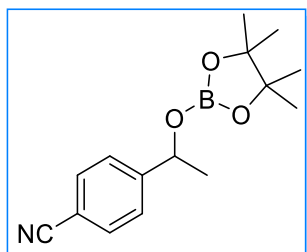
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.47 – 7.40 (m, 2H, Ph), 7.26 – 7.20 (m, 2H, Ph), 5.19 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.46 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.24 (s, 6H, C(CH₃)₂), 1.21 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 326(M⁺, 9), 313(81), 311(78), 186(46), 185(85), 184(73), 183(100), 182(80), 181(60), 180(49), 179(38). Characterized as a crude product. The analytical data are in agreement with the literature.¹⁵

2-(1-(4-Iodophenyl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3m**)



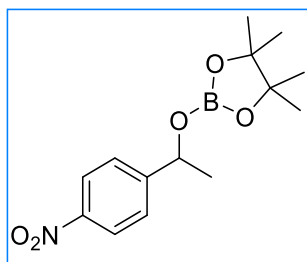
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.70 – 7.58 (m, 2H, Ph), 7.11 (d, J_{H-H} = 8.3 Hz, 2H, Ph), 5.17 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 1.45 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.23 (s, 6H, C(CH₃)₂), 1.21 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 374(M⁺, 4), 359(69), 358(17), 259(69), 291(32), 248(16), 232(20), 231(100), 189(29), 104(15), 103(15). Characterized as a crude product. The analytical data are in agreement with the literature.²²

4-(1-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)benzonitrile (**3n**)



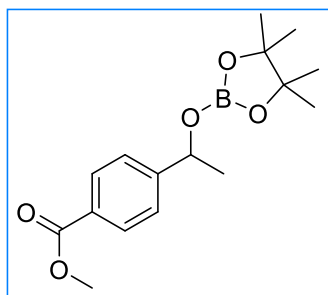
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.58 (d, J_{H-H} = 8.3 Hz, 2H, Ph), 7.43 (d, J_{H-H} = 8.2 Hz, 2H, Ph), 5.23 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.44 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.21 (s, 6H, C(CH₃)₂), 1.18 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 273(M⁺, 2), 256(25), 216(13), 215(100), 214(26), 200(10), 130(17), 129(15), 104(9), 103(9), 43(13). Characterized as a crude product. The analytical data are in agreement with the literature.²³

4,4,5,5-Tetramethyl-2-(1-(4-nitrophenyl)ethoxy)-1,3,2-dioxaborolane (**3o**)



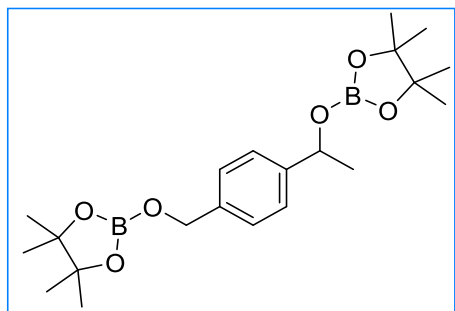
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.21 – 8.08 (m, 2H, Ph), 7.54 – 7.45 (m, 2H, Ph), 5.29 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 1.47 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.22 (s, 6H, C(CH₃)₂), 1.19 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 293(M⁺, 4), 278(35), 245(12), 235(100), 218(29), 150(14), 129(10), 103(15), 77(19), 60(5). Characterized as a crude product. The analytical data are in agreement with the literature.²³

Methyl 4-(1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)benzoate (3p)



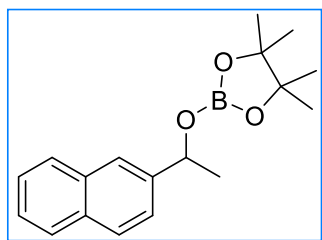
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.01 – 7.96 (m, 2H, Ph), 7.44 – 7.40 (m, 2H, Ph), 5.27 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 3.89 (s, 3H, OCH₃), 1.48 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.23 (s, 6H, C(CH₃)₂), 1.20 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 306(M⁺, 4), 291(37), 248(44), 189(100), 163(92), 147(21), 131(44), 129(44), 103(39), 91(20), 83(31). Characterized as a crude product. The analytical data are in agreement with the literature.²⁴

4,4,5,5-Tetramethyl-2-((4-(1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)benzyl)oxy)-1,3,2-dioxaborolane (3q)



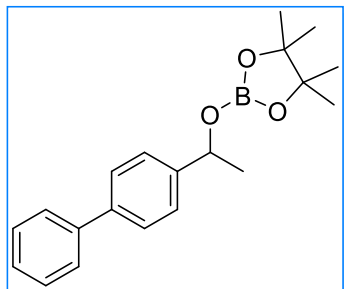
¹H NMR: (300 MHz, CDCl₃, δ, ppm): 7.35 – 7.29 (m, 4H, Ph), 5.23 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 4.90 (s, 2H, CH₂Ph), 1.47 (d, J_{H-H} = 6.4 Hz, 3H, CH(CH₃)), 1.26 (s, 12H, CH(CH₃)₂), 1.23 (s, 6H, CH(CH₃)), 1.21 (s, 6H, CH(CH₃)). **MS (EI) [m/z]**: 404(M⁺, 9), 403(18), 390(16), 263(32), 262(100), 261(68), 260(32), 258(20), 257(15), 256(15), 117(16). Characterized as a crude product. The analytical data are in agreement with the literature.²⁵

4,4,5,5-Tetramethyl-2-(1-(naphthalen-2-yl)ethoxy)-1,3,2-dioxaborolane (3r)



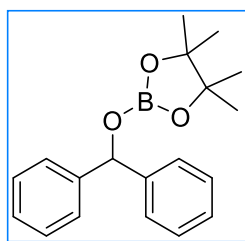
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.88 – 7.81 (m, 4H, napht), 7.54 – 7.43 (m, 3H, napht), 5.44 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.60 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.27 (s, 6H, C(CH₃)₂), 1.24 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 298(M⁺, 30), 297(10), 284(17), 283(100), 282(14), 156(10), 155(28), 154(18), 153(12), 43(8). Characterized as a crude product. The analytical data are in agreement with the literature.¹⁵

2-([1,1'-Biphenyl]-4-yl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3s**)



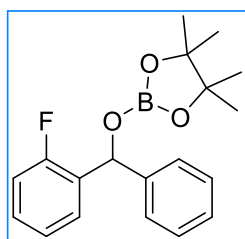
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.62 – 7.56 (m, 4H, Ph), 7.47 – 7.41 (m, 4H, Ph), 7.37 – 7.31 (m, 1H, Ph), 5.31 (q, *J*_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.55 (d, *J*_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.27 (s, 6H, C(CH₃)₂), 1.24 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 324(M⁺, 2), 199(13), 198(92), 183(100), 181(52), 180(28), 156(19), 155(62), 153 (24), 152(19), 43(22). Characterized as a crude product. The analytical data are in agreement with the literature.²⁶

2-(Benzhydryloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3t**)



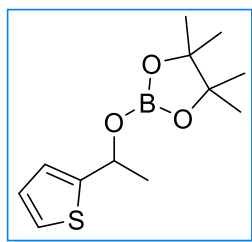
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.41 – 7.37 (m, 4H, Ph), 7.32 – 7.27 (m, 4H, Ph), 7.25 – 7.20 (m, 2H, Ph), 6.18 (s, 1H, CH(Ph)₂), 1.20 (s, 12H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 310(M⁺, 3), 252(100), 251(52), 228(19), 227(99), 226(28), 209(20), 183(17), 167(47), 165(30), 43(24). Characterized as a crude product. The analytical data are in agreement with the literature.^{15, 27}

2-((2-Fluorophenyl)(phenyl)methoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3u**)



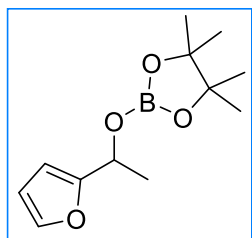
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.53 – 7.49 (m, 1H, Ph), 7.36 (m, 2H, Ph), 7.25 – 7.21 (m, 2H, Ph), 7.19 – 7.12 (m, 2H, Ph), 7.07 – 7.04 (m, 1H, Ph), 6.93 – 6.90 (m, 1H, Ph), 6.44 (s, 1H, CH(Ph)₂), 1.13 (s, 12H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 328(M⁺, 2), 245(84), 228(39), 227(100), 202(36), 201(29), 185(53), 123(30), 77(30), 51(25), 43(27). Characterized as a crude product. The analytical data are in agreement with the literature.²⁸

4,4,5,5-Tetramethyl-2-(1-(thien-2-yl)ethoxy)-1,3,2-dioxaborolane (3v)



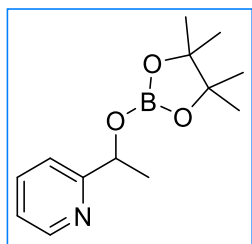
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.21 – 7.19 (m, 1H, thienyl), 6.98 – 6.91 (m, 2H, thienyl), 5.48 (q, J_{H-H} = 6.4, 1H, CH(CH₃)), 1.60 (d, J_{H-H} = 6.4 Hz, 3H, CH(CH₃)), 1.25 (s, 6H, C(CH₃)₂), 1.24 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 254(M⁺, 17), 239(100), 196(27), 171(52), 157(11), 128(26), 111(87), 84(11), 57(10), 43(27). Characterized as a crude product. The analytical data are in agreement with the literature.²⁹

2-(1-(Furan-2-yl)ethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3w)



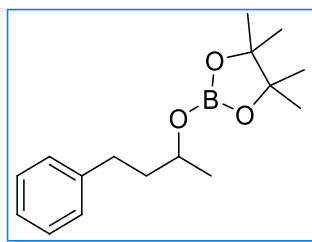
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.33 (m, 1H, furanyl), 6.29 (m, 1H, furanyl), 6.22 (d, J_{H-H} = 3.2 Hz, 1H, furanyl), 5.23 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 1.54 (d, J_{H-H} = 6.6 Hz, 3H, CH(CH₃)), 1.25 (s, 12H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 238(17, M⁺), 237(100), 236(20), 175(24), 131(14), 118(40), 117(29), 91(27), 89(16), 77(15). Characterized as a crude product. The analytical data are in agreement with the literature.¹⁵

2-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethylpyridine (3x)



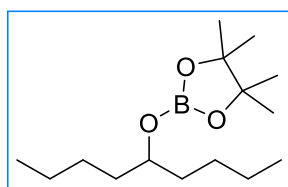
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.67 – 8.57 (m, 1H, Ar), 8.03 – 7.92 (m, 1H, Ar), 7.53 – 7.43 (m, 2H, Ar), 5.25 (q, J_{H-H} = 6.6 Hz, 1H, CH(CH₃)), 1.58 (d, J_{H-H} = 6.7 Hz, 3H, CH(CH₃)), 1.33 (s, 6H, C(CH₃)₂), 1.30 (s, 6H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 249(M⁺, 2), 191(73), 190(32), 150(54), 149(87), 148(35), 133(40), 132(47), 105(100), 79(41), 78(65). Characterized as a crude product. The analytical data are in agreement with the literature.¹⁵

4,4,5,5-Tetramethyl-2-((4-phenylbutan-2-yl)oxy)-1,3,2-dioxaborolane (**3y**)



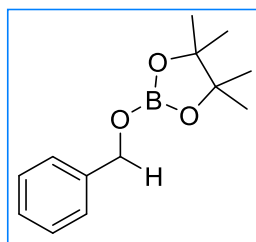
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.32 – 7.23 (m, 2H, Ph), 7.21 – 7.14 (m, 3H, Ph), 4.26 – 4.16 (m, 1H, CH(CH₃)), 2.79 – 2.57 (m, 2H, CH₂CH₂), 1.92 – 1.64 (m, 2H, CH₂CH₂), 1.27 (s, 12H, C(CH₃)₂), 1.23 (d, *J*_{H-H} = 6.2 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 276(M⁺, 3), 261(17), 247(2), 109(16), 176(7), 145(36), 132(100), 129(18), 117(53), 91(14). Characterized as a crude product. The analytical data are in agreement with the literature.²⁰

4,4,5,5-Tetramethyl-2-(nonan-5-yloxy)-1,3,2-dioxaborolane (**3z**)



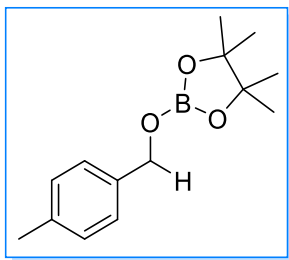
¹H NMR (300 MHz, CDCl₃, δ, ppm): 4.02 – 3.94 (m, 1H, (CH₂)₂CH), 1.46 – 1.37 (m, 4H, (CH₂)₂CH), 1.32 – 1.23 (m, 8H, CH₂CH₃), 1.22 (s, 12H, C(CH₃)₂), 0.90 – 0.82 (m, 6H, CH₂CH₃). **¹³C{¹H} NMR** (75 MHz, CDCl₃, δ, ppm): δ 82.4 (C(CH₃)₂), 74.7 ((CH₂)₂CH), 36.3, 27.7, 24.6 (C(CH₃)₂), 22.7 (CH₂CH₃), 14.1 (CH₂CH₃). **¹¹B NMR** (128 MHz, CDCl₃, δ, ppm): 22.04. **MS (EI) [m/z (%)]**: 270(M⁺, 2), 213(84), 171(18), 157(14), 145(31), 129(29), 101(17), 83(51), 69(100), 57(46), 55(33). **Elem. Anal.** calcd (%) for C₁₅H₃₁BO₃: C, 66.67; H, 11.56; found C, 66.72; H, 11.65. Colorless liquid. Isolation yield 95% (144.1 mg). The compound **3z** was synthesized and characterized for the first time.

2-(Benzyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6a**)



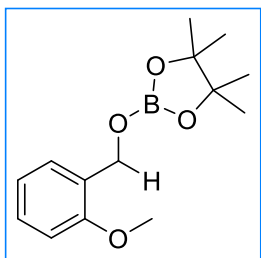
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.37 – 7.23 (m, 5H, Ph), 4.93 (s, 2H, C(CH₂)), 1.27 (s, 12H, C(CH₃)₂). **MS (EI) [m/z]**: 234(M⁺, 16), 219(100), 218(26), 176(42), 175(43), 133(19), 117(10), 91(90), 65(23), 43(21). Characterized as a crude product. The analytical data are in agreement with the literature.²³

4,4,5,5-Tetramethyl-2-((4-methylbenzyl)oxy)-1,3,2-dioxaborolane (6b)



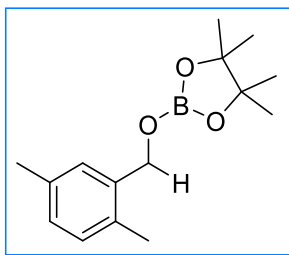
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.28 – 7.16 (m, 2H, Ph), 7.16 – 7.11 (m, 2H, Ph), 4.88 (s, 2H, C(CH₂)), 2.34 (s, 3H, pCH₃Ph), 1.26 (s, 12H, C(CH₃)₂). **MS (EI) [m/z]**: 248(M⁺, 24), 233(62), 190(49), 175(21), 165(27), 129(14), 106(25), 105(100), 103(22), 43(19). Characterized as a crude product. The analytical data are in agreement with the literature.²²

2-((2-Methoxybenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6c)



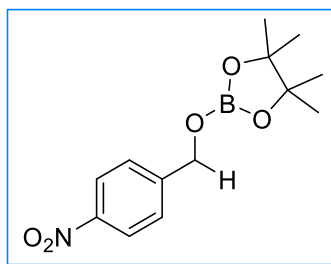
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.43 – 7.39 (m, 1H, Ph), 7.27 – 7.20 (m, 1H, Ph), 6.95 (td, *J*_{H-H} = 7.5, 1.1 Hz, 1H, Ph), 6.84 (dd, *J*_{H-H} = 8.2, 1.1 Hz, 1H, Ph), 4.98 (s, 2H, C(CH₂)), 3.81 (s, 3H o-OCH₃Ph), 1.27 (s, 12H, C(CH₃)₂). **MS (EI) [m/z]**: 264(M⁺, 84), 263(62), 249(11), 241(29), 190(7), 147(59), 135(11), 121(44), 119(100), 91(14). Characterized as a crude product. The analytical data are in agreement with the literature.³⁰

2-((2,5-Dimethylbenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6d)



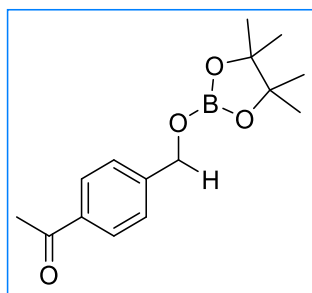
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.25 (s, 1H, Ph), 7.05 – 6.99 (m, 2H, Ph), 4.92 (s, 2H, C(CH₂)), 2.33 (s, 3H, C(CH₃)), 2.27 (s, 3H, C(CH₃)), 1.29 (s, 12H, C(CH₃)₂). **¹³C{¹H} NMR** (101 MHz, CDCl₃, δ, ppm): 137.0 (Ph), 135.4 (Ph), 132.4 (Ph), 130.0 (Ph), 128.1 (Ph), 127.9 (Ph), 83.0 (C(CH₃)₂), 65.0 (C(CH₂)), 24.7 (C(CH₃)₂), 21.1 (Ph(CH₃)), 18.3 (Ph(CH₃)). **¹¹B NMR** (128 MHz, CDCl₃, δ, ppm): 22.38. **MS (EI) [m/z]**: 262(M⁺, 5), 247(15), 237(19), 162(14), 147(5), 129(7), 119(84), 118(100), 117(38), 91(7). **Elem. Anal.** calcd (%) for C₁₅H₂₃BO₃: C, 68.72; H, 8.84; found C, 68.70; H, 8.91. Colorless liquid. Isolation yield 96% (123.6 mg). The compound **6d** was synthesized and characterized for the first time.

4,4,5,5-Tetramethyl-2-((4-nitrobenzyl)oxy)-1,3,2-dioxaborolane (6e)



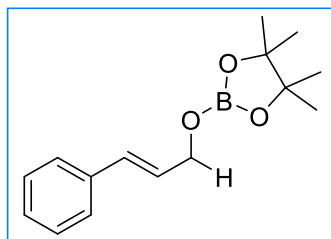
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.21 – 8.13 (m, 2H, Ph), 7.52 – 7.45 (m, 2H, Ph), 5.00 (s, 2H, C(CH₂)), 1.25 (s, 12H, C(CH₃)₂). **MS (EI) [m/z]**: 279(M⁺, 12), 265(13), 264(100), 236(17), 221(11), 179(15), 107(9), 89(32), 78(7), 43(6). Characterized as a crude product. The analytical data are in agreement with the literature.²²

1-(4-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)phenyl)ethan-1-one (6f)



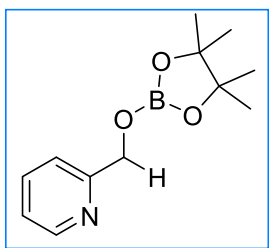
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.95 – 7.91 (m, 2H, Ph), 7.43 (d, *J*_{H-H} = 8.6 Hz, 2H, Ph), 4.98 (s, 2H, C(CH₂)), 2.60 (s, 3H, C(CH₃)), 1.27 (s, 12H, C(CH₃)₂). **MS (EI) [m/z]**: 277((M+1)⁺, 26), 276(M⁺, 54), 261(100), 218(69), 219(26), 175(35), 133(48), 132(20), 105(42), 43(34). Characterized as a crude product. The analytical data are in agreement with the literature.³¹

2-(Cinnamyloxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6g)



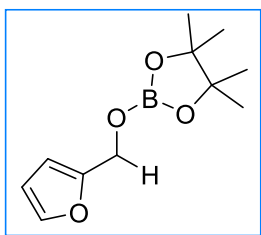
¹H NMR: (300 MHz, CDCl₃, δ, ppm) 7.39 – 7.20 (m, 5H, Ph), 6.63 (d, *J*_{H-H} = 15.9, 1H, CHCHCH₂), 6.29 (dt, *J*_{H-H} = 15.9, 5.3 Hz, 1H, CHCHCH₂), 4.54 (dd, *J*_{H-H} = 5.4, 1.7 Hz, 2H, CHCHCH₂), 1.27 (s, 12H, C(CH₃)₂). **MS (EI) [m/z]**: 260(M⁺, 4), 245(5), 177(7), 160(13), 145(31), 133(14), 117(100), 116(76), 115(72), 91(25), 84(32), 69(12), 59(17). Characterized as a crude product. The analytical data are in agreement with the literature.³⁰

2-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)pyridine (**6h**)



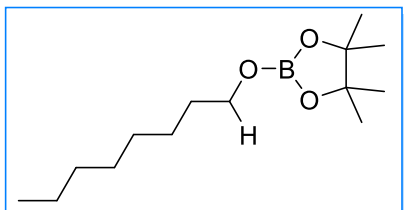
¹H NMR: (300 MHz, CDCl₃, δ, ppm): 8.59 – 8.55 (m, 1H, NCH), 7.98 – 7.85 (m, 1H, Ar), 7.47 – 7.38 (m, 2H, Ar), 5.06 (s, 2H, C(CH₂)), 1.28 (s, 12H, C(CH₃)₂). Characterized as a crude product. The analytical data are in agreement with the literature.³²

2-(Furan-2-ylmethoxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6i**)



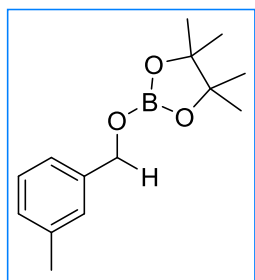
¹H NMR: (300 MHz, CDCl₃, δ, ppm): 7.37 – 7.36 (m, 1H, furanyl), 6.32 – 6.28 (m, 2H, furanyl), 4.81 (s, 2H, C(CH₂)), 1.25 (s, 12H, C(CH₃)₂). **MS (EI) [m/z]:** 224(M⁺, 4), 209(3), 181(6), 166(9), 141(5), 124(12), 84(10), 81(100), 69(4), 59(11), 53(16). Characterized as a crude product. The analytical data are in agreement with the literature.³³

4,4,5,5-Tetramethyl-2-(octyloxy)-1,3,2-dioxaborolane (**6j**)



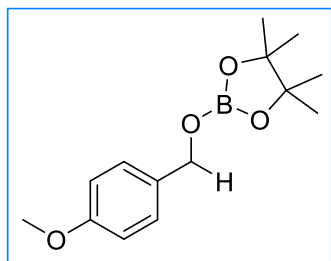
¹H NMR: (300 MHz, CDCl₃, δ, ppm): 3.82 (t, *J*_{H-H} = 6.6 Hz, 2H, O(CH₂)), 1.59 – 1.50 (m, 2H, CH₂(CH₂)), 1.26 (s, 10H, CH₂(CH₂)), 1.24 (s, 12H, C(CH₃)₂), 0.89 – 0.84 (m, 3H, CH₂(CH₃)). **MS (EI) [m/z]:** 256(M⁺, 2), 241(55), 157(36), 145(40), 129(47), 110(48), 83(73), 69(78), 59(71), 57(83), 55(100). Characterized as a crude product. The analytical data are in agreement with the literature.³²

4,4,5,5-Tetramethyl-2-((3-methylbenzyl)oxy)-1,3,2-dioxaborolane (6k)



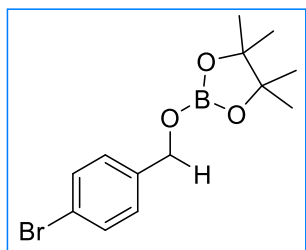
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.26 – 6.99 (m, 4H, Ph), 4.89 (s, 2H, C(CH₂)), 2.33 (s, 3H, *m*-CH₃Ph), 1.26 (s, 12H, C(CH₃)₂). **MS (EI) [m/z]**: 248(6, M⁺), 233(56), 191(34), 190(100), 189(30), 175(26), 148(18), 105(78), 103(19), 77(20). Characterized as a crude product. The analytical data are in agreement with the literature.³²

2-((4-Methoxybenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6l)



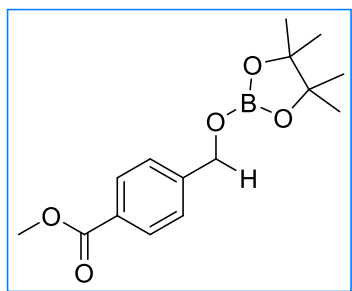
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.32 – 7.24 (m, 2H, Ph), 6.91 – 6.81 (m, 2H, Ph), 4.85 (s, 2H, C(CH₂)), 3.80 (s, 3H, *p*-OCH₃Ph), 1.26 (s, 12H, C(CH₃)₂). **MS (EI) [m/z]**: 264(M⁺, 33), 263(19), 207(14), 206(17), 181(38), 180(10), 122(14), 121(100), 77(7), 43(10). Characterized as a crude product. The analytical data are in agreement with the literature.³⁴

2-((4-Bromobenzyl)oxy)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6m)



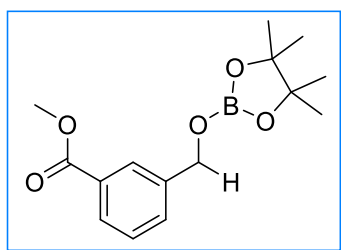
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.47 – 7.42 (m, 2H, Ph), 7.27 – 7.16 (m, 2H, Ph), 4.86 (s, 2H, C(CH₂)), 1.26 (s, 12H, C(CH₃)₂). **MS (EI) [m/z]**: 313(M⁺, 3), 297(44), 256(47), 175(65), 171(67), 169(60), 107(56), 89(48), 79(92), 77(100), 43(57). Characterized as a crude product. The analytical data are in agreement with the literature.³⁴

Methyl 4-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzoate (6n)



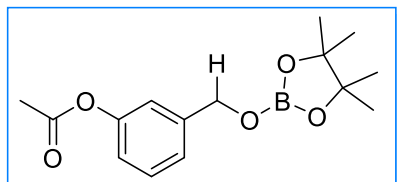
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.05 – 7.97 (m, 2H, Ph), 7.41 (d, *J*_{H-H} = 8.5 Hz, 2H, Ph), 4.98 (s, 2H, C(CH₂)), 3.91 (s, 3H, OCH₃), 1.27 (s, 12H, C(CH₃)₂). **MS (EI) [m/z]**: 292(M⁺, 8), 277(53), 234(100), 175(62), 149(62), 77(58), 59(36), 44(51). Characterized as a crude product. The analytical data are in agreement with the literature.³⁴

Methyl 3-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)benzoate (6o)



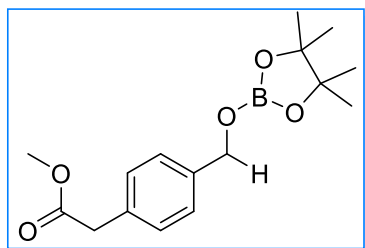
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.02 (s, 1H, Ph), 7.93 (d, *J*_{H-H} = 7.7 Hz, 1H, Ph), 7.54 (d, *J*_{H-H} = 7.7 Hz, 1H, Ph), 7.40 (t, *J*_{H-H} = 7.7 Hz, 1H, Ph), 4.95 (s, 2H, C(CH₂)), 3.90 (s, 3H, C(CH₃)), 1.26 (s, 12H, C(CH₃)₂). **¹³C{¹H} NMR** (101 MHz, CDCl₃, δ, ppm): 167.2 (C(O)OCH₃), 139.7 (Ph), 131.4 (Ph), 130.3 (Ph), 128.8 (Ph), 128.5 (Ph), 128.0 (Ph), 83.3 (C(CH₃)₂), 66.3 (C(CH₂)), 52.2 (C(O)OCH₃), 24.7 (C(CH₃)₂). **¹¹B NMR** (128 MHz, CDCl₃, δ, ppm): 22.39. **MS (EI) [m/z]**: 292(M⁺, 16), 234(24), 192(36), 191(29), 149(100), 119(21), 118(21), 91(21), 90(29), 89(31). **Elem. Anal.** calcd (%) for C₁₅H₂₁BO₅: C, 61.67; H, 7.25; found C, 61.72; H, 7.30. Colorless liquid. Isolation yield 91% (132.6 mg). The compound **6o** was synthesized and characterized for the first time.

3-(((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)phenyl acetate (6p)



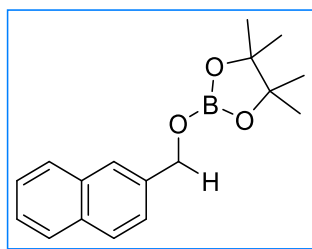
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.34 (d, *J*_{H-H} = 8.7 Hz, 2H, Ph), 7.04 (d, *J*_{H-H} = 8.6 Hz, 2H, Ph), 4.90 (s, 2H, C(CH₂)), 2.28 (s, 3H, C(O)OCH₃), 1.25 (s, 12H, C(CH₃)₂). **MS (EI) [m/z]**: 292(M⁺, 3), 250(35), 193(15), 192(31), 167(31), 149(12), 129(31), 107(100), 84(15), 78(16), 77(13). Characterized as a crude product. The analytical data are in agreement with the literature.²³

Methyl 2-(((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)methyl)phenyl)acetate (**6q**)



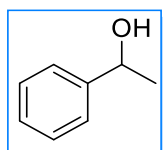
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.37 – 7.28 (m, 4H, Ph), 5.08 (s, 2H, C(CH₂)), 4.91 (s, 2H, C(CH₂)), 2.08 (s, 3H, C(O)OCH₃), 1.25 (s, 12H, C(CH₃)₂). **¹³C{¹H} NMR** (101 MHz, CDCl₃, δ, ppm): 171.0 (C(O)OCH₃), 139.5 (Ph), 135.1 (Ph), 128.4 (Ph), 127.0 (Ph), 83.1 (C(CH₃)₂), 66.4 (C(CH₂)), 66.2 (C(CH₂)), 24.7 (C(CH₃)₂), 21.1 (O(CH₃)). **¹¹B NMR** (128 MHz, CDCl₃, δ, ppm): 22.37. **MS (EI) [m/z]**: 306(M⁺, 3), 246(49), 231(46), 188(100), 163(80), 146(35), 103(73), 91(74), 84(32), 77(30), 59(35). **Elem. Anal.** calcd (%) for C₁₆H₂₃BO₅: C, 62.77; H, 7.57; found C, 62.84; H, 7.61. Colorless liquid. Isolation yield 90% (137.8 mg). The compound **6q** was synthesized and characterized for the first time.

4,4,5,5-Tetramethyl-2-(naphthalen-2-ylmethoxy)-1,3,2-dioxaborolane (**6r**)



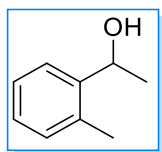
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.85 – 7.77 (m, 4H, napht), 7.50 – 7.41 (m, 3H, napht), 5.09 (s, 2H, C(CH₂)), 1.28 (s, 12H, C(CH₃)₂). **MS (EI) [m/z]**: 285((M+1)⁺, 19), 284(M⁺, 100), 283(31), 270(85), 269(32), 227(35), 226(85), 225(29), 142(27), 141(86), 115(27). Characterized as a crude product. The analytical data are in agreement with the literature.³⁵

1-Phenylethan-1-ol (**4a**)



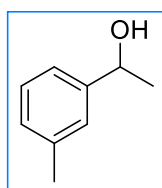
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.37 – 7.27 (m, 4H, Ph), 7.26 – 7.19 (m, 1H, Ph), 4.86 (q, *J*_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 1.77 (s, 1H, OH), 1.46 (d, *J*_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 122(M⁺, 19), 121(7), 107(83), 106(13), 105(100), 79(15), 77(11), 51(6), 45(12), 43(12). Colorless liquid. Isolation yield 82% (50.2 mg). The analytical data are in agreement with the literature.³⁶

1-(2-Tolyl)ethan-1-ol (**4b**)



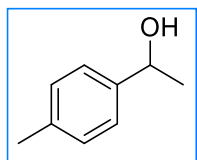
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.45 (d, J_{H-H} = 7.3 Hz, 1H, Ph), 7.20 – 7.15 (m, 1H, Ph), 7.14 – 7.05 (m, 2H, Ph), 5.06 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 2.28 (s, 3H, o-CH₃Ph), 1.80 (brs, 1H, OH), 1.40 (d, J_{H-H} = 6.4 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 136(M⁺, 5), 121(74), 118,(64), 93(100), 91(91), 77(47), 65(28), 63(9), 51(14). Colorless liquid. Isolation yield 55% (57.4 mg). The analytical data are in agreement with the literature.³⁶

1-(3-Tolyl)ethan-1-ol (**4c**)



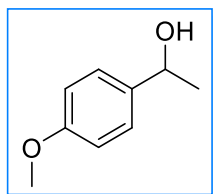
¹H NMR (300 MHz, CD₂Cl₂, δ, ppm): 7.30 – 7.12 (m, 4H, Ph), 4.82 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 2.82 (s, 1H, OH), 2.41 (s, 3H, m-CH₃Ph), 1.47 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 136(M⁺, 7), 121(100), 119(19), 93(58), 92(24), 91(53), 78(8), 77(19), 65(10), 43(22). Colorless liquid. Isolation yield 68% (46.1 mg). The analytical data are in agreement with the literature.³⁷

1-(4-Tolyl)ethan-1-ol (**4d**)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.19 (d, J_{H-H} = 8.1 Hz 2H, Ph), 7.09 (d, J_{H-H} = 7.9 Hz, 2H, Ph), 4.78 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 2.28 (s, 3H, p-CH₃Ph), 1.91 (s, 1H, OH), 1.41 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 136(M⁺, 8), 121(100), 118(42), 115(9), 93(82), 92(20), 91(84), 90(12), 77(12), 65(8), 43(19). Colorless liquid. Isolation yield 77% (52.2 mg). The analytical data are in agreement with the literature.²⁰

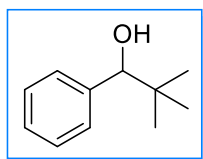
1-(4-Methoxyphenyl)propan-1-ol (**4e**)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.32 – 7.27 (m, 2H, Ph), 6.90 – 6.86 (m, 2H, Ph), 4.84 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 3.80 (s, 3H, p-OCH₃), 1.89 (brs, 1H, OH), 1.47 (d, J_{H-H} = 6.4 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 152(M⁺, 29), 137(100), 134(58), 119(11), 110(10), 109(43),

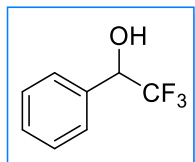
94(9), 91(14), 77(9), 43(12). Colorless liquid. Isolation yield 58% (44.2 mg). The analytical data are data in agreement with the literature.³⁶

2,2-Dimethyl-1-phenylpropan-1-ol (4f)



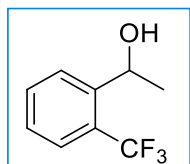
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.36 – 7.27 (m, 5H, Ph), 4.42 (s, 1H, CH(CH₃)), 1.85 (brs, 1H, OH), 0.95 (s, 9H, C(CH₃)₃). **MS (EI) [m/z (%)]**: 164(M⁺, 3), 107(100), 79(57), 77(26), 57(16), 51(6). Pale yellow solid. Isolation yield 76% (61.3 mg). The analytical data are in agreement with the literature.³⁸

2,2,2-Trifluoro-1-phenylethan-1-ol (4g)



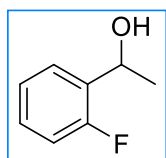
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.51 – 7.40 (m, 5H, Ph), 5.03 – 4.95 (m, 1H, CH(CF₃)), 2.84 (s, 1H, OH). **MS (EI) [m/z (%)]**: 176(M⁺, 17), 109(13), 107(61), 104(6), 89(5), 79(100), 74(5), 63(6), 53(8), 51(57). Colorless liquid. Isolation yield 81% (71.5 mg). The analytical data are in agreement with the literature.³⁸⁻³⁹

1-(2-(Trifluoromethyl)phenyl)ethan-1-ol (4h)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.82 (d, *J*_{H-H} = 7.3 Hz, 1H, Ph), 7.65 – 7.52 (m, 2H, Ph), 7.41 – 7.33 (m, 1H, Ph), 5.33 (q, *J*_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 2.00 (s, 1H, OH), 1.48 (d, *J*_{H-H} = 6.3 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 190(M⁺, 2), 175(7), 173(100), 155(28), 153(4), 131(2), 127(12), 174(9), 156(5), 125(4). Pale yellow solid. Isolation yield 78% (73.8 mg). The analytical data are in agreement with the literature.³⁸

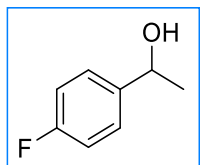
1-(2-Fluorophenyl)ethan-1-ol (4i)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.52 – 7.46 (m, 1H, Ph), 7.29 – 7.20 (m, 1H, Ph), 7.18 – 7.12 (m, 1H, Ph), 7.05 – 6.99 (m, 1H, Ph), 5.20 (q, *J*_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 1.83 (s, 1H, OH), 1.52 (d, *J*_{H-H} = 6.9 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 140(M⁺, 3), 126(8), 124(100),

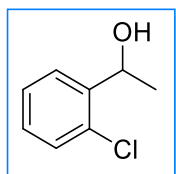
123(23), 105(6), 97(23), 96(7), 77(3), 165(11), 45(8), 43(12). Colorless liquid. Isolation yield 84% (59.0 mg). The analytical data are in agreement with the literature.³⁸

1-(4-Fluorophenyl)ethan-1-ol (4j)



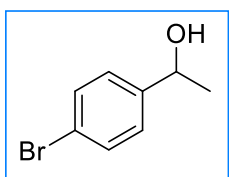
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.40 – 7.29 (m, 2H, Ph), 7.08 – 6.98 (m, 2H, Ph), 4.89 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 1.72 (s, 1H, OH), 1.48 (d, J_{H-H} = 6.4 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 140(M⁺, 3), 126(6), 125(100), 123(13), 98(8), 97(39), 95(11), 77(19), 75(9), 51(6), 43(12). Colorless liquid. Isolation yield 80% (56.4 mg). The analytical data are in agreement with the literature.³⁰

1-(2-Chlorophenyl)ethan-1-ol (4k)



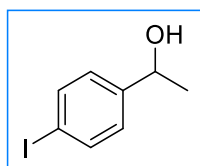
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.60 (dd, J_{H-H} = 7.6 Hz, 1.7 Hz, 1H, Ph), 7.35 – 7.27 (m, 2H, Ph), 7.23 – 7.17 (m, 1H, Ph), 5.30 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.85 (s, 1H, OH), 1.50 (d, J_{H-H} = 6.4 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 156(M⁺, 2), 143(20), 142(8), 141(100), 138(9), 113(17), 78(7), 77(14), 52(7), 45(8), 43(9). Colorless liquid. Isolation yield 81% (63.0 mg). The analytical data are in agreement with the literature.²²

1-(4-Bromophenyl)ethan-1-ol (4l)



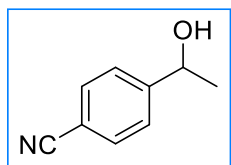
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.53 – 7.32 (m, 2H, Ph), 7.31 – 7.20 (m, 2H, Ph), 4.87 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 1.85 (s, 1H, OH), 1.47 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 202((M+2)⁺, 2), 200(M⁺, 2), 187(69), 185(100), 159(18), 157(22), 121(13), 79(14), 78(29), 77(33), 51(16), 43(27). Colorless liquid. Isolation yield 79% (128.2 mg). The analytical data are in agreement with the literature.³⁷

1-(4-Iodophenyl)ethan-1-ol (4m)



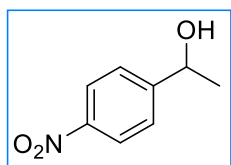
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.72 – 7.62 (m, 2H, Ph), 7.17 – 7.07 (m, 2H, Ph), 4.85 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 1.80 (s, 1H, OH), 1.46 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI)** [*m/z* (%): 248(M⁺, 19), 233(100), 232(47), 121(16), 80(15), 79(15), 78(39), 77(20), 51(14), 43(40). Yellow solid. Isolation yield 68% (84.3 mg). The analytical data are in agreement with the literature.³⁷

4-(1-Hydroxyethyl)benzonitrile (4n)



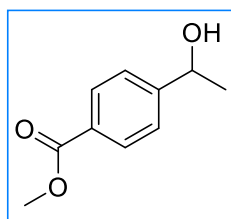
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.63 (d, J_{H-H} = 8.3 Hz, 2H, Ph), 7.48 (d, J_{H-H} = 8.2 Hz, 2H, Ph), 4.96 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 1.95 (s, 1H, OH), 1.49 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI)** [*m/z* (%): 147(M⁺, 25), 132(100), 130(12), 105(18), 104(91), 102(11), 77(23), 75(12), 51(13), 43(26). Colorless liquid. Isolation yield 83% (60.7 mg). The analytical data are in agreement with the literature.³⁶

1-(4-Nitrophenyl)ethan-1-ol (4o)



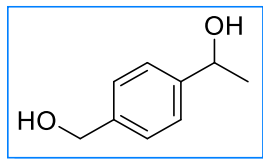
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.25 – 8.15 (m, 2H, Ph), 7.58 – 7.50 (m, 2H, Ph), 5.02 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 1.91 (s, 1H, OH), 1.52 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI)** [*m/z* (%): 167(M⁺, 2), 152(92), 125(8), 122(17), 107(75), 105(25), 94(41), 78(80), 77(100), 66(39), 52(23). Yellow solid. Isolation yield 78% (64.8 mg). The analytical data are in agreement with the literature.³⁰

Methyl 4-(1-hydroxyethyl)benzoate (4p)



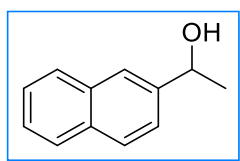
¹H NMR (400 MHz, CDCl₃, δ, ppm): 8.01 – 7.95 (m, 2H, Ph), 7.43 – 7.39 (m, 2H, Ph), 4.93 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 3.89 (s, 3H, OCH₃), 2.25 (brs, 1H, OH), 1.48 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI)** [*m/z* (%): 180(M⁺, 2), 165(55), 149(16), 137 (94), 132(8), 121(13), 104(45), 91(49), 77(100), 56(68), 51(30). Colorless liquid. Isolation yield 79% (70.3 mg). The analytical data are in agreement with the literature.³⁷

1-(4-(Hydroxymethyl)phenyl)ethan-1-ol (**4q**)



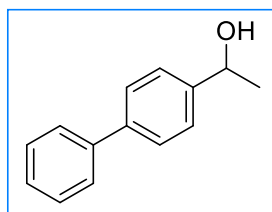
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.41 – 7.32 (m, 4H, Ph), 4.91 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 4.69 (s, 2H, C(CH₂)), 1.72 (s, 2H, OH), 1.50 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 152(M⁺, 2), 151(15), 150(3), 136(9), 135(100), 133(5), 107(4), 89(6), 51(3), 43(9). Yellow oil. Isolation yield 71% (54.7 mg). The analytical data are in agreement with the literature.⁴⁰

1-(Naphthalen-2-yl)ethan-1-ol (**4r**)



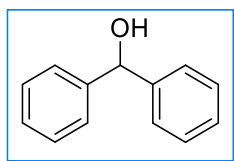
¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.86 – 7.80 (m, 4H, napht), 7.52 – 7.47 (m, 3H, napht), 5.06 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 2.00 (brs, 1H, OH), 1.59 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 173((M+1)⁺, 11), 172(M⁺, 100), 171(7), 157(11), 156(8), 155(31), 130(9), 129(29), 127(10), 43(5). White solid. Isolation yield 84% (73.2 mg). The analytical data are in agreement with the literature.²²

1-([1,1'-Biphenyl]-4-yl)ethan-1-ol (**4s**)



¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.65 – 7.57 (m, 4H, Ph), 7.50 – 7.42 (m, 4H, Ph), 7.37 (t, J_{H-H} = 7.3 Hz, 1H, Ph), 4.96 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 2.05 (s, 1H, OH), 1.56 (d, J_{H-H} = 6.5 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 199((M+1)⁺, 11), 198(M⁺, 76), 183(20), 182(14), 181(100), 180(25), 155(24), 153(13), 152(10), 43(11). White solid. Isolation yield 90% (89.4 mg). The analytical data are in agreement with the literature.⁴¹

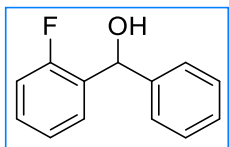
Diphenylmethanol (**4t**)



¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.42 – 7.33 (m, 8H, Ph), 7.32 – 7.27 (m, 2H, Ph), 5.83 (s, 1H, CH(Ph)₂), 2.34 (s, 1H, OH). **MS (EI) [m/z (%)]**: 184(M⁺, 67), 183(31), 106(12), 105(100),

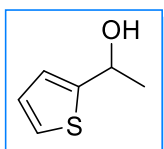
104(10), 79(27), 78(38), 77(48), 51(27), 50(14). White solid. Isolation yield 84% (77.0 mg). The analytical data are in agreement with the literature.²²

(2-Fluorophenyl)(phenyl)methanol (4u)



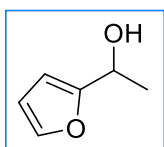
¹H NMR (400 MHz, CDCl₃, δ , ppm): 7.55 – 7.24 (m, 1H, Ph), 7.45 – 7.39 (m, 2H, Ph), 7.39 – 7.33 (m, 2H, Ph), 7.33 – 7.23 (m, 2H, Ph), 7.19 – 7.15 (m, 1H, Ph), 7.07 – 7.02 (m, 1H, Ph), 6.15 (s, 1H, CH(Ph)₂), 2.43 (s, 1H, OH). **MS (EI) [m/z (%)]**: 202(M⁺, 13), 201(32), 200(100), 180(28), 123(57), 106(21), 105(75), 77(33), 75(19), 51(28). Yellow liquid. Isolation yield 70% (70.3 mg). The analytical data are in agreement with the literature.²⁸

1-(Thien-2-yl)ethan-1-ol (4v)



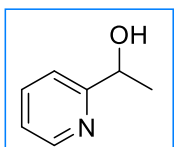
¹H NMR (300 MHz, CDCl₃, δ , ppm): 7.24 (dd, J_{H-H} = 4.7, 1.6 Hz, 1H, thienyl), 7.02 – 6.91 (m, 2H, thienyl), 5.14 (q, J_{H-H} = 6.4 Hz, 1H, CH(CH₃)), 1.98 (brs, 1H, OH), 1.61 (d, J_{H-H} = 6.4 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 128(M⁺, 11), 113(45), 110(16), 95(13), 85(100), 84(10), 65(11), 59(8), 58(13), 51(10). Colorless oil. Isolation yield 66% (42.0 mg). The analytical data are in agreement with the literature.³⁰

1-(Furan-2-yl)ethan-1-ol (4w)



¹H NMR (300 MHz, CDCl₃, δ , ppm): 7.33 (dd, J_{H-H} = 1.8, 0.8 Hz, 1H, furanyl), 6.30 – 6.28 (m, 1H, furanyl), 6.19 – 6.18 (m, 1H, furanyl), 4.82 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 2.77 (bs, 1H, OH), 1.49 (d, J_{H-H} = 6.6 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 112(M⁺, 23), 111(12), 97(66), 96(11), 95(100), 94(15), 84(10), 69(20), 43(22), 42(28). Colorless liquid. Isolation yield 73% (40.1 mg). The analytical data are in agreement with the literature.⁴²

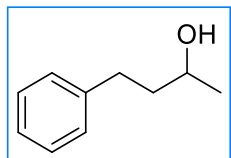
1-(Pyridin-2-yl)ethan-1-ol (4x)



¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.47 – 8.44 (m, 1H, Ar), 7.64 – 7.59 (m, 1H, Ar), 7.23 – 7.20 (m, 1H, Ar), 7.14 – 7.10 (m, 1H, Ar), 4.82 (q, J_{H-H} = 6.5 Hz, 1H, CH(CH₃)), 4.07 (brs, 1H,

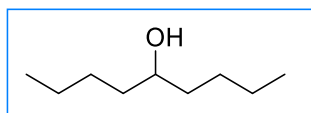
OH), 1.43 (d, $J_{H-H} = 6.6$ Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 124(M⁺, 14), 122(10), 108(100), 106(42), 104(7), 79(30), 78(33), 52(27), 51(24). Colorless liquid. Isolation yield 77% (47.5 mg). The analytical data are in agreement with the literature.⁴³

4-Phenylbutan-2-ol (**4y**)



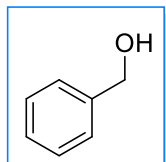
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.32 – 7.23 (m, 2H, Ph), 7.20 – 7.09 (m, 3H, Ph), 3.88 – 3.71 (m, 1H, CH(CH₃)), 2.73 – 2.63 (m, 2H, CH₂CH₂), 1.86 – 1.64 (m, 2H, CH₂CH₂), 1.42 (s, 1H, OH), 1.20 (d, $J_{H-H} = 6.2$ Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 150(M⁺, 7), 132(34), 117(87), 105(10), 92(46), 91(100), 78(28), 77(20), 65(24), 51(17). Colorless oil. Isolation yield 72% (54.1 mg). The analytical data are in agreement with the literature.⁴⁴

Nonan-5-ol (**4z**)



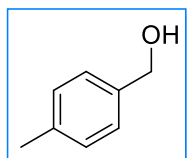
¹H NMR (300 MHz, CDCl₃, δ, ppm): 3.68 – 3.50 (m, 1H, OCH(CH₂)₂), 1.50 – 1.26 (m, 13H, CH₂(CH₂) and OH), 0.90 (t, $J_{H-H} = 7.1$ Hz, 6H, CH₂CH₃). **MS (EI) [m/z (%)]**: 144(M⁺, 1), 87(5), 70(7), 69(100), 68(12), 67(7), 43(3), 42(3), 41(25), 40(6). Colorless liquid. Isolation yield 60% (42.9 mg). The analytical data are in agreement with the literature.³⁹

Phenylmethanol (**7a**)



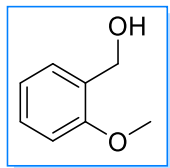
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.37 – 7.17 (m, 5H, Ph), 4.57 (s, 2H, C(CH₂)), 2.69 (s, 1H, OH). **MS (EI) [m/z (%)]**: 108(M⁺, 67), 107(43), 91(13), 79(100), 78(14), 77(66), 65(9), 63(8), 53(8), 51(30). Colorless liquid. Isolation yield 77% (41.2 mg). The analytical data are in agreement with the literature.²⁸

p-Tolylmethanol (**7b**)



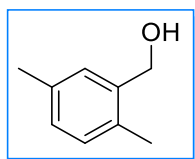
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.26 (d, $J_{H-H} = 8.1$ Hz, 2H, Ph), 7.18 (d, $J_{H-H} = 7.9$ Hz, 2H, Ph), 4.65 (s, 2H, C(CH₂)), 2.36 (s, 3H, o-CH₃Ph), 1.71 (s, 1H, OH). **MS (EI) [m/z (%)]**: 122(M⁺, 68), 121(23), 107(100), 106(41), 92(12), 91(27), 79(27), 77(23), 64(9), 51(9). White solid. Isolation yield 72% (44.2 mg). The analytical data are in agreement with the literature.²⁸

(2-Methoxyphenyl)methanol (**7c**)



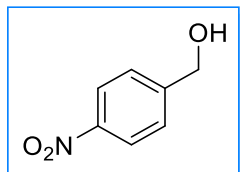
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.32 – 7.24 (m, 2H, Ph), 6.98 – 6.87 (m, 2H, Ph), 4.69 (s, 2H, C(CH₂)), 3.87 (s, 3H, o-OCH₃Ph), 2.16 (s, 1H, OH). **MS (EI) [m/z (%)]**: 138(M⁺, 100), 137(25), 121(60), 109(18), 107(19), 106(16), 105(32), 91(11), 77(16), 51(10). Colorless liquid. Isolation yield 68% (44.6 mg). The analytical data are in agreement with the literature.⁴⁵

(2,5-Dimethylphenyl)methanol (**7d**)



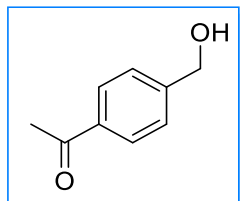
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.23 – 6.99 (m, 3H, Ph), 4.67 (s, 2H, C(CH₂)), 2.33 (s, 3H, C(CH₃)), 2.32 (s, 3H, C(CH₃)), 1.94 (s, 1H, OH). **MS (EI) [m/z (%)]**: 136(M⁺, 3), 121(11), 119(32), 118(100), 117(40), 105(8), 92(8), 91(22), 90(11), 77(9). Colorless liquid. Isolation yield 65% (44.2 mg). The analytical data are in agreement with the literature.²⁸

(4-Nitrophenyl)methanol (**7e**)



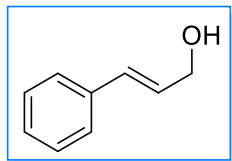
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.26 – 8.19 (m, 2H, Ph), 7.57 – 7.50 (m, 2H, Ph), 4.84 (s, 2H, C(CH₂)), 1.60 (brs, 1H, OH). **MS (EI) [m/z (%)]**: 153(M⁺, 11), 137(22), 136(24), 108(38), 107(100), 106(25), 89(25), 79(24), 78(42), 77(65), 51(27). Yellow solid. Isolation yield 81% (62.0 mg). The analytical data are in agreement with the literature.²⁸

1-(4-(Hydroxymethyl)phenyl)ethan-1-one (**7f**)



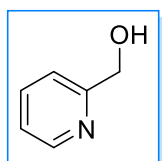
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.01 – 7.91 (m, 2H, Ph), 7.51 – 7.42 (m, 2H, Ph), 4.78 (s, 2H, C(CH₂)), 2.61 (s, 3H, C(O)CH₃), 1.76 (brs, 1H, OH). **MS (EI) [m/z (%)]**: 151(M⁺, 15), 150(3), 136(9), 135(100), 133(5), 107(3), 105(3), 89(6), 43(9), 51(3). White solid. Isolation yield 77% (57.9 mg). The analytical data are in agreement with the literature.⁴⁵

(E)-3-Phenylprop-2-en-1-ol (**7g**)



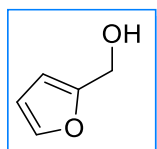
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.44 – 7.28 (m, 5H, Ph), 6.65 (d, J_{H-H} = 15.9 Hz, 1H, CHCHCH₂), 6.40 (dt, J_{H-H} = 15.9, 5.7 Hz, 1H, CHCHCH₂), 4.35 (dd, J_{H-H} = 5.7, 1.5 Hz, 2H, CHCHCH₂), 2.09 (s, 1H, OH). **MS (EI) [m/z (%)]**: 134(M⁺, 43), 115(38), 105(43), 103(26), 92(100), 91(86), 78(71), 77(62), 63(20), 51(38). Yellow liquid. Isolation yield 80% (53.8 mg). The analytical data are in agreement with the literature.⁴⁶

Pyridin-2-ylmethanol (**7h**)



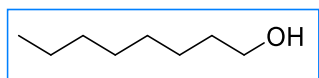
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.48 (d, J_{H-H} = 5.0 Hz, 1H, NCH), 7.62 (m, 1H, Ar), 7.21 (d, J_{H-H} = 7.7 Hz, 1H, Ar), 7.18 – 7.09 (m, 1H, Ar), 4.70 (s, 2H, C(CH₂)), 4.13 (s, 1H, OH). **MS (EI) [m/z (%)]**: 109(M⁺, 2), 108(8), 107(100), 105(57), 80(7), 79(28), 77(20), 76(6), 52(11), 50(6), 43(13). Yellow liquid. Isolation yield 71% (38.5 mg). The analytical data are in agreement with the literature.⁴⁵

Furan-2-ylmethanol (**7i**)



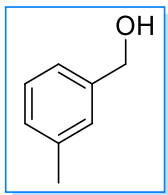
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.40 – 7.39 (m, 1H, furanyl), 6.64 – 6.33 (m, 1H, furanyl), 6.38 – 6.25 (m, 2H, furanyl), 4.61 (s, 2H, C(CH₂)), 1.85 (s, 1H, OH). **MS (EI) [m/z (%)]**: 98(M⁺, 100), 97(51), 97(51), 95(6), 81(58), 70(37), 69(44), 53(53), 52(16), 51(21). Colorless liquid. Isolation yield 78% (37.1 mg). The analytical data are in agreement with the literature.⁴⁶

Octan-1-ol (**7j**)



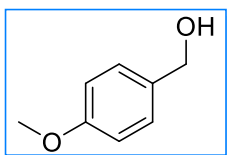
¹H NMR (300 MHz, CDCl₃, δ, ppm): 3.62 (t, J_{H-H} = 6.6 Hz, 2H, CH₂(OH)), 1.74 (brs, 1H, OH), 1.55 (p, J_{H-H} = 7.1, 6.7 Hz, CH₂CH₂), 1.36 – 1.23 (m, 10H, CH₂(CH₂)), 0.90 – 0.84 (m, 3H, CH₂CH₃). **MS (EI) [m/z (%)]**: 130(M⁺, 2), 97(4), 84(39), 83(22), 70(63), 69(53), 68(19), 59(9), 57(44), 56(100), 55(89). Colorless liquid. Isolation yield 67% (43.3 mg). The analytical data are in agreement with the literature.⁴⁵

m-Tolylmethanol (**7k**)



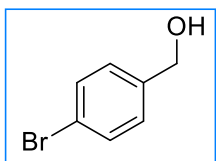
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.26 – 7.07 (m, 4H, Ph), 4.67 (s, 2H, C(CH₂)), 2.37 (s, 3H, *m*-CH₃Ph). A hydrogen atom in hydroxyl group is not detected. **MS (EI) [m/z (%)]**: 122(M⁺, 83), 121(21), 107(100), 105(32), 104(24), 93(29), 91(47), 79(49), 77(40), 65(17). Colorless liquid. Isolation yield 68% (41.5 mg). The analytical data are in agreement with the literature.⁴⁷

(4-Methoxyphenyl)methanol (**7l**)



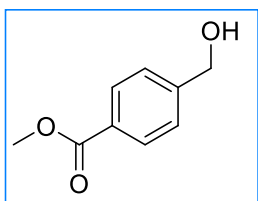
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.32 – 7.26 (m, 2H, Ph), 6.92 – 6.86 (m, 2H, Ph), 4.61 (s, 2H, C(CH₂)), 3.81 (s, 3H, *o*-OCH₃Ph), 1.72 (brs, 1H, OH). **MS (EI) [m/z (%)]**: 138(M⁺, 100), 137(43), 121 (59), 109(65), 105(12), 94(11), 79(10), 78(9), 77(20), 51(11). Colorless liquid. Isolation yield 73% (50.1 mg). The analytical data are in agreement with the literature.²⁸

(4-Bromophenyl)methanol (**7m**)



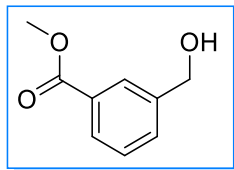
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.52 – 7.45 (m, 2H, Ph), 7.26 – 7.19 (m, 2H, Ph), 4.65 (s, 2H, C(CH₂)), 1.72 (s, 1H, OH). **MS (EI) [m/z (%)]**: 188((M+2)⁺, 97), 186(M⁺, 100), 171(37), 169(32), 107(92), 80(17), 79(90), 77(53), 51(25). Yellow solid. Isolation yield 85% (79.4 mg). The analytical data are in agreement with the literature.²⁸

Methyl 4-(hydroxymethyl)benzoate (**7n**)



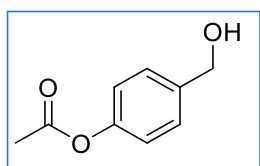
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.01 (d, *J*_{H-H} = 8.3 Hz, 2H, Ph), 7.42 (d, *J*_{H-H} = 8.3 Hz, 2H, Ph), 4.76 (s, 2H, C(CH₂)), 3.91 (s, 3H, O(CH₃)), 2.00 (brs, 1H, OH). **MS (EI) [m/z (%)]**: 167((M+1)⁺, 9), 166(M⁺, 100), 165(13), 148(12), 136(18), 134(41), 106(19), 104(13), 88(7), 78(6). White solid. Isolation yield 72% (59.9 mg). The analytical data are in agreement with the literature.⁴⁶

Methyl 3-(hydroxymethyl)benzoate (7o)



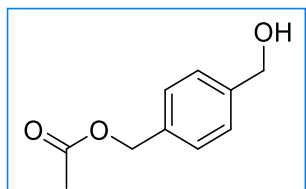
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.05 – 7.98 (m, 1H, Ph), 7.94 (d, J_{H-H} = 7.7 Hz, 1H, Ph), 7.55 (d, J_{H-H} = 7.6 Hz, 1H, Ph), 7.41 (t, J_{H-H} = 7.7 Hz, 1H, Ph), 4.72 (s, 2H, C(CH₂)), 3.90 (s, 3H, O(CH₃)), 2.19 (s, 1H, OH). **MS (EI) [m/z (%)]**: 167((M+1)⁺,33), 166(M⁺,81), 137(69), 135(100), 107(95), 105(51), 89(51), 79(41), 77(64), 51(29). Colorless liquid. Isolation yield 84% (69.4 mg). The analytical data are in agreement with the literature.⁴⁸

4-(Hydroxymethyl)phenyl acetate (7p)



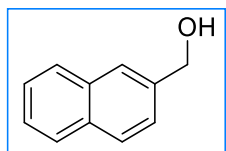
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.38 (d, J_{H-H} = 8.8 Hz, 2H, Ph), 7.08 (d, J_{H-H} = 8.5 Hz, 2H, Ph), 4.69 (s, 2H, C(CH₂)), 2.30 (s, 3H, O(CH₃)). A hydrogen atom in hydroxyl group was not detected. **MS (EI) [m/z (%)]**: 166(M⁺,11), 124(100), 123 (48), 121(13), 107(27), 106(26), 95(65), 78(19), 77(30), 67(8). Colorless liquid. Isolation yield 80% (74.5 mg). The analytical data are in agreement with the literature.⁴⁹

4-(Hydroxymethyl)phenyl acetate (7q)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.37 (s, 4H, Ph), 5.10 (s, 2H, C(CH₂)), 4.71 (s, 2H, C(CH₂)), 2.10 (s, 3H, OCH₃), 1.66 (s, 1H, OH). **MS (EI) [m/z (%)]**: 180(M⁺, 30), 138(52), 121(20), 119(44), 107(100), 92(20), 91(97), 89(22), 79(21), 77(51). Colorless liquid. Isolation yield 74% (66.9 mg). The analytical data are in agreement with the literature.⁵⁰

Naphthalen-2-ylmethanol (7r)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.89 – 7.78 (m, 4H, napht), 7.54 – 7.43 (m, 3H, napht), 4.86 (d, J_{H-H} = 0.8 Hz, 2H, C(CH₂)), 1.83 (s, 1H, OH). **MS (EI) [m/z (%)]**: 158(M⁺, 46), 157(12), 141(12), 129(100), 128(42), 127(24), 115(12), 77(8), 51(7), 63(8). White solid. Isolation yield 86% (68.2 mg). The analytical data are in agreement with the literature.⁴⁵

13. NMR spectra of products

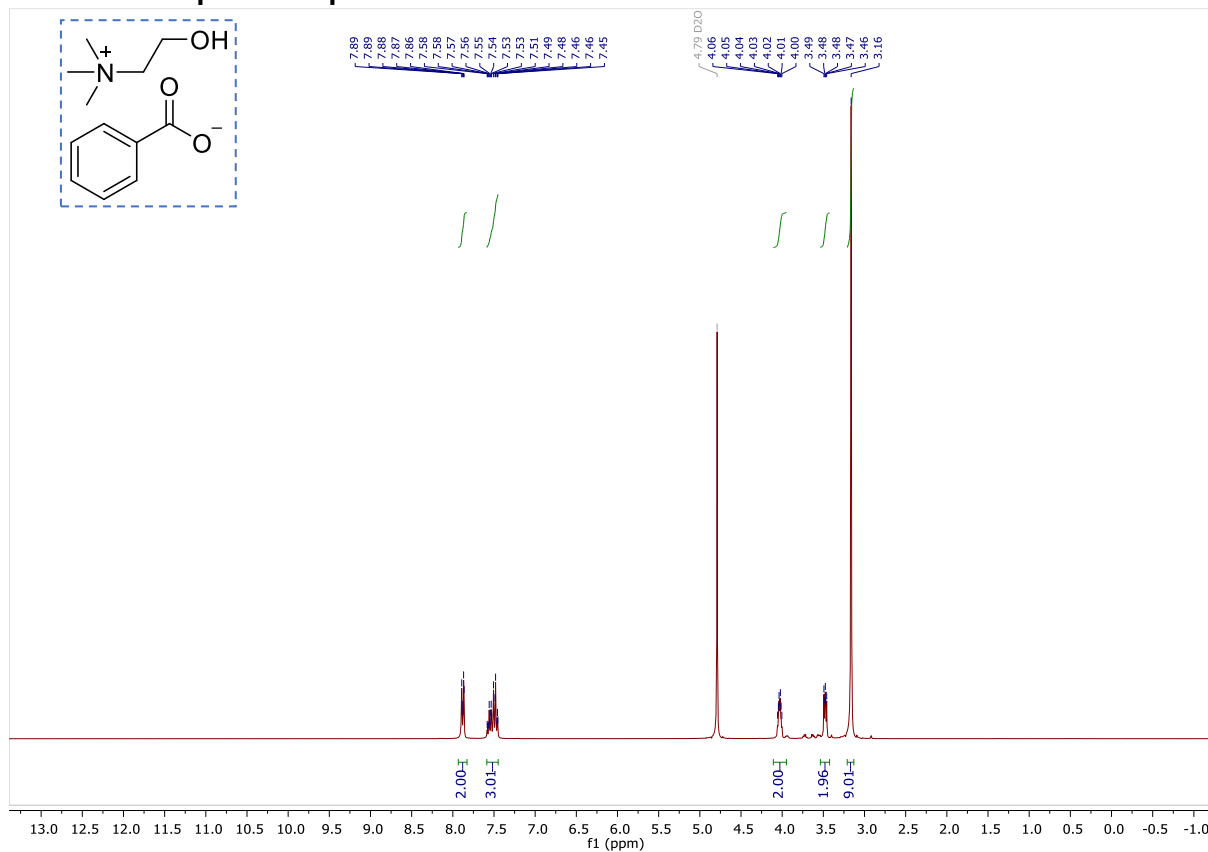


Figure S10 – ¹H NMR spectrum of IL2 [Cho][Bz].

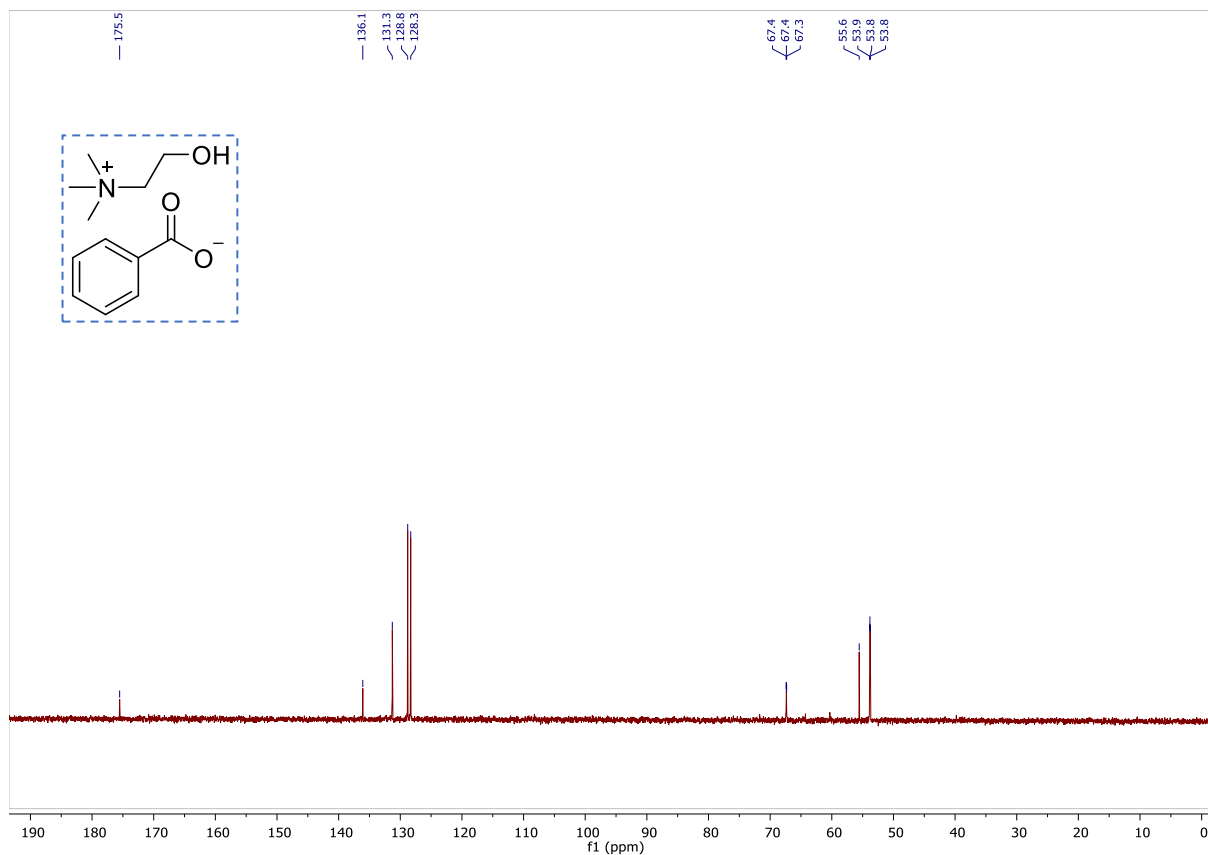


Figure S11 – ¹³C{¹H} NMR spectrum of IL2 [Cho][Bz].

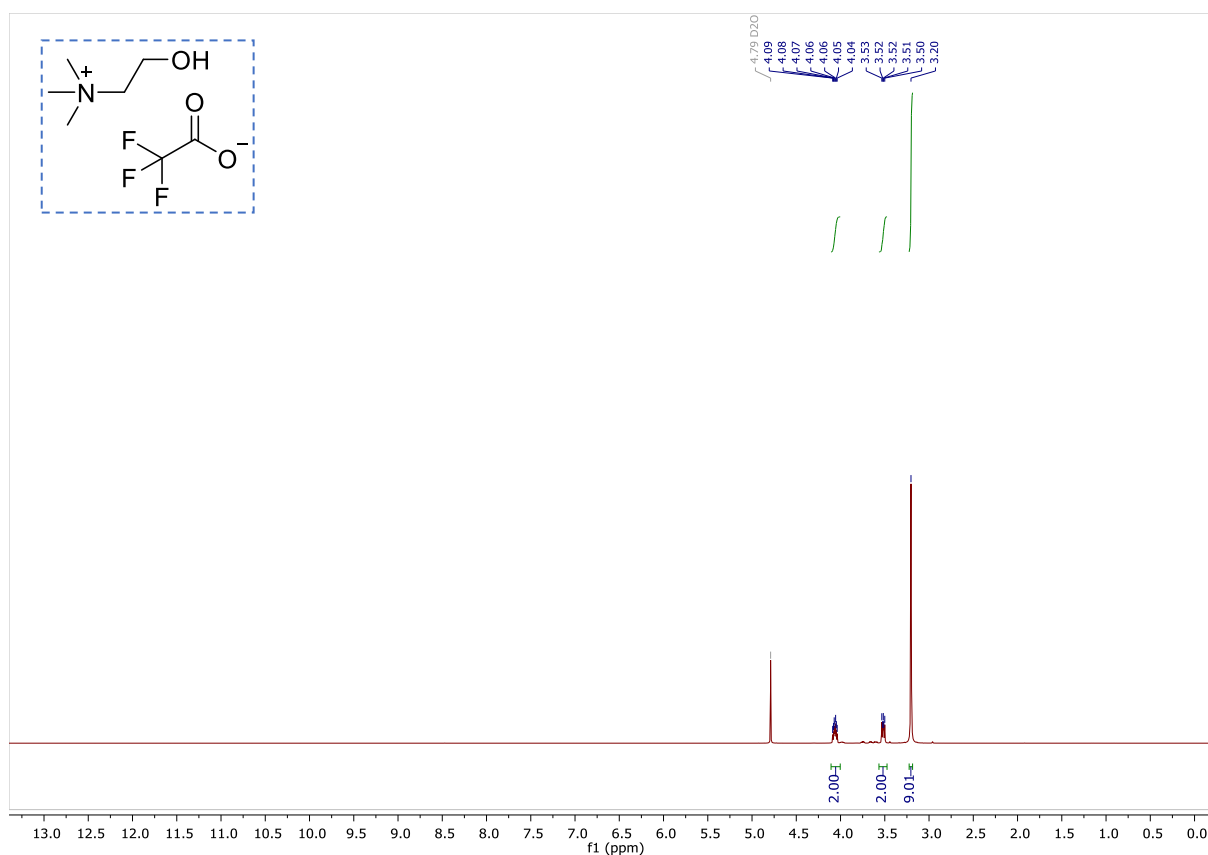


Figure S12 – ¹H NMR spectrum of IL3 [Cho][TFA].

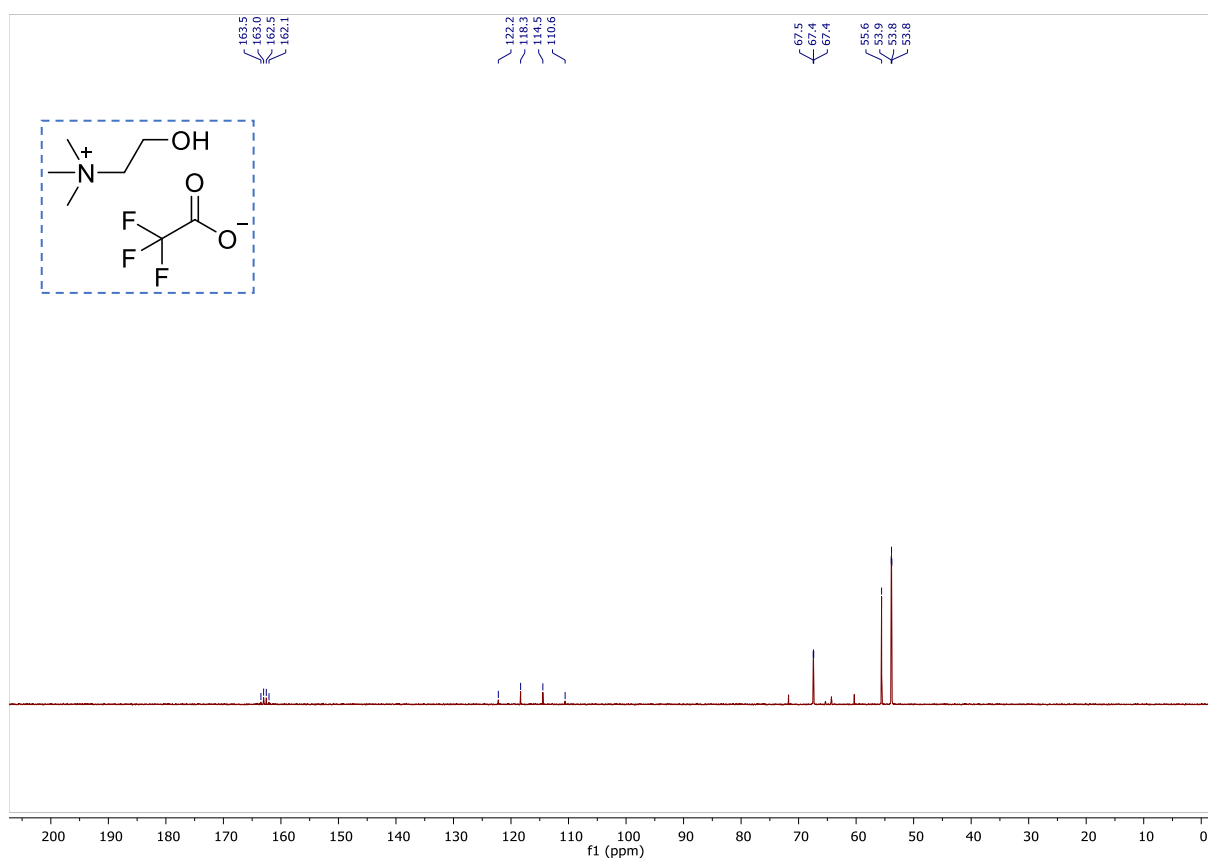


Figure S13 – ¹³C{¹H} NMR spectrum of IL3 [Cho][TFA].

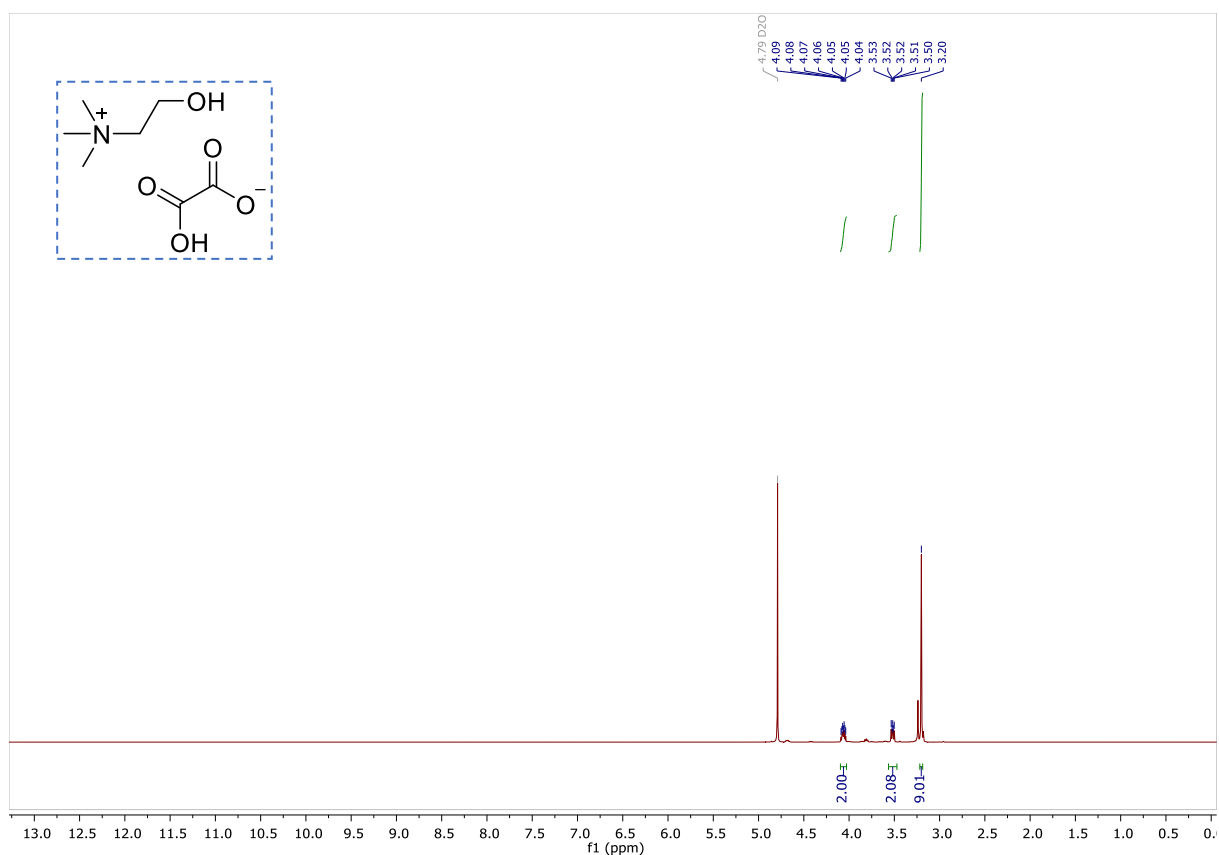


Figure S14 – ¹H NMR spectrum of IL4 [Cho][Oxa].

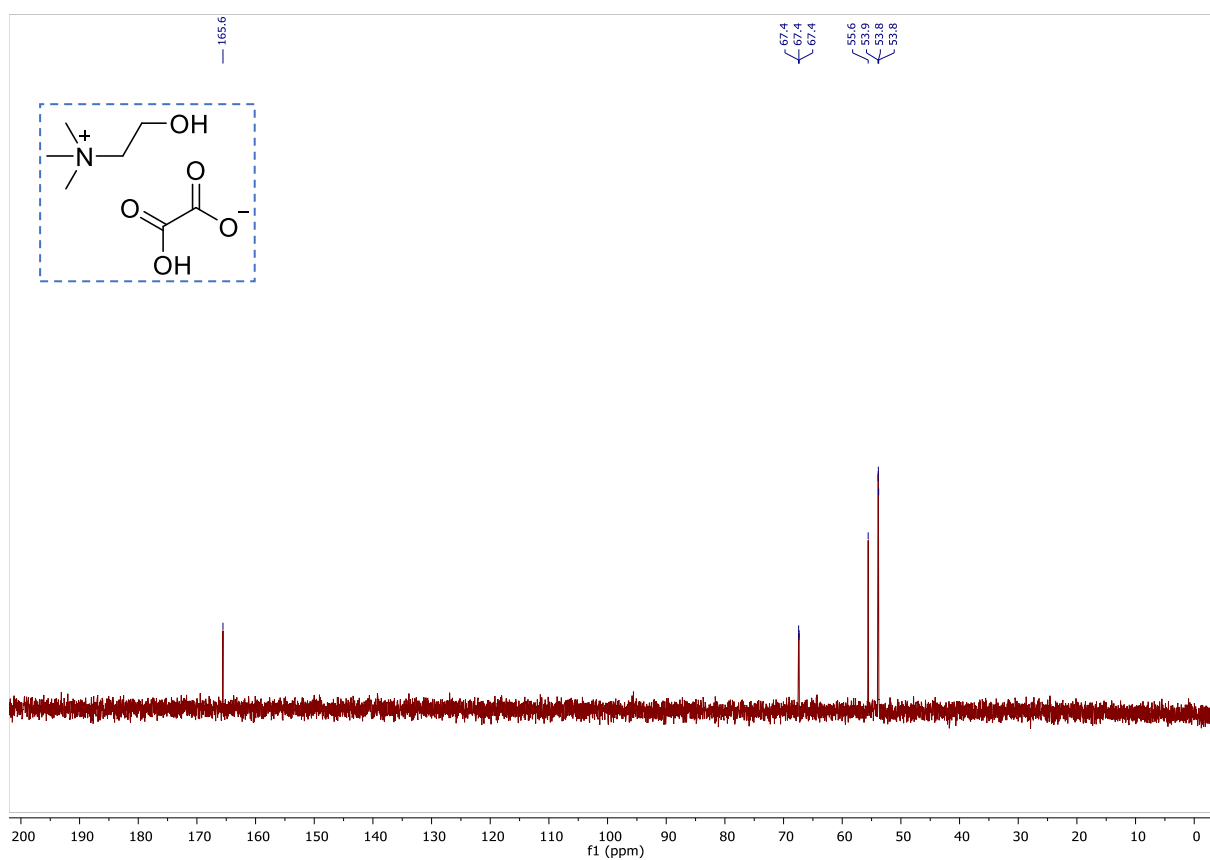


Figure S15 – ¹³C{¹H} NMR spectrum of IL4 [Cho][Oxa].

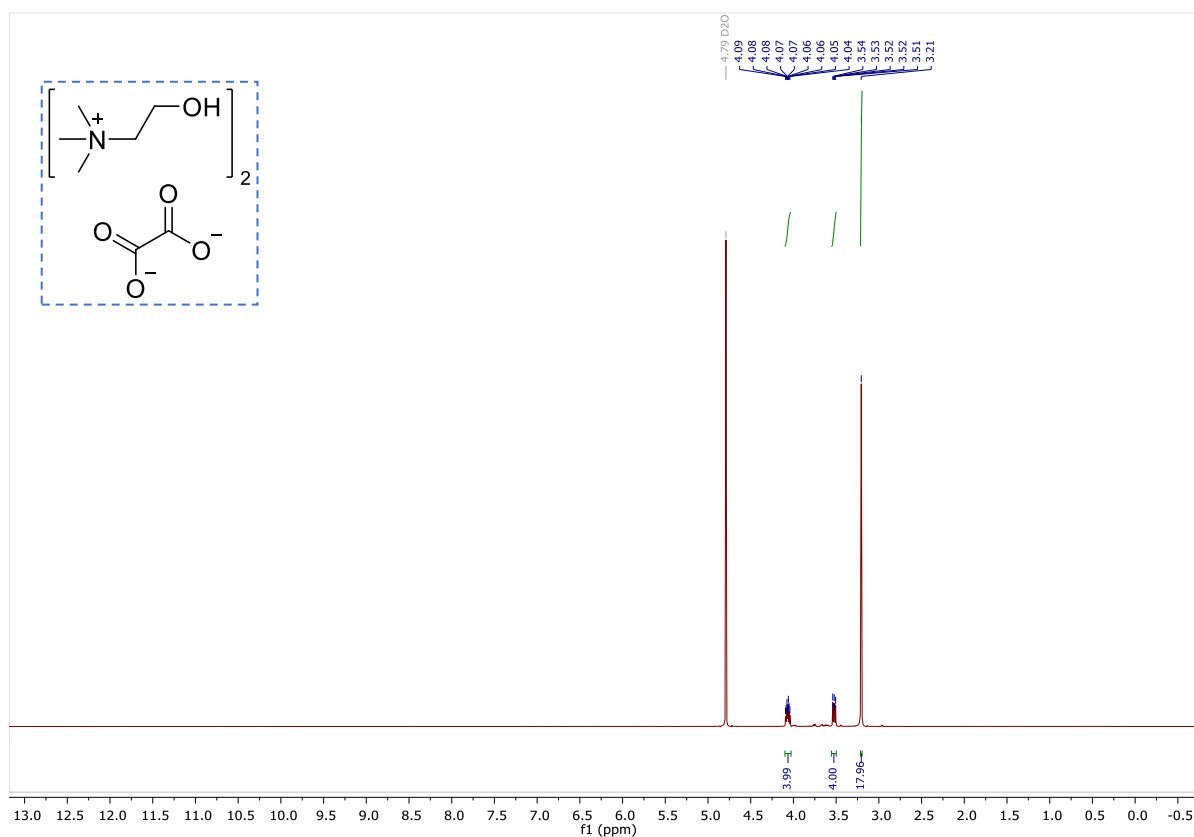


Figure S16 – ¹H NMR spectrum of IL5 [Cho]₂[Oxa].

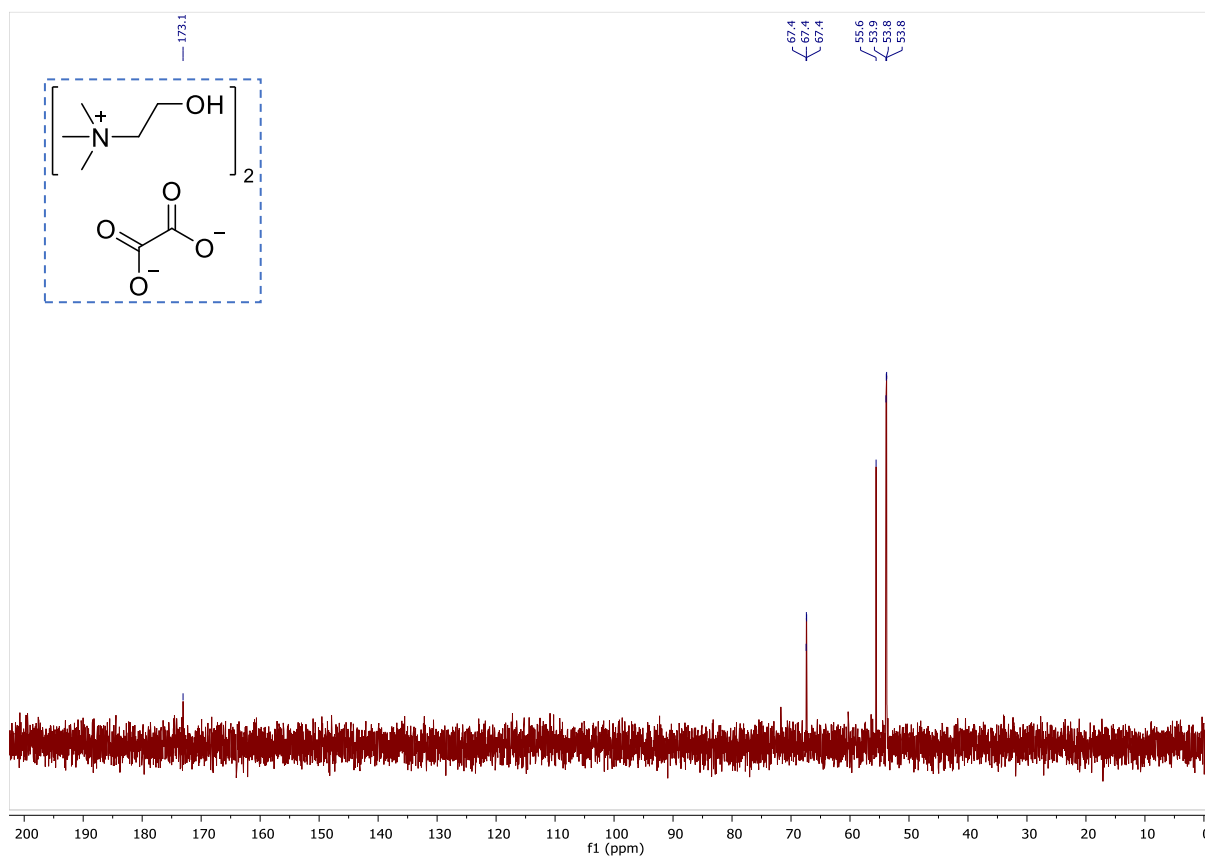


Figure S17 – ¹³C{¹H} NMR spectrum of IL5 [Cho]₂[Oxa].

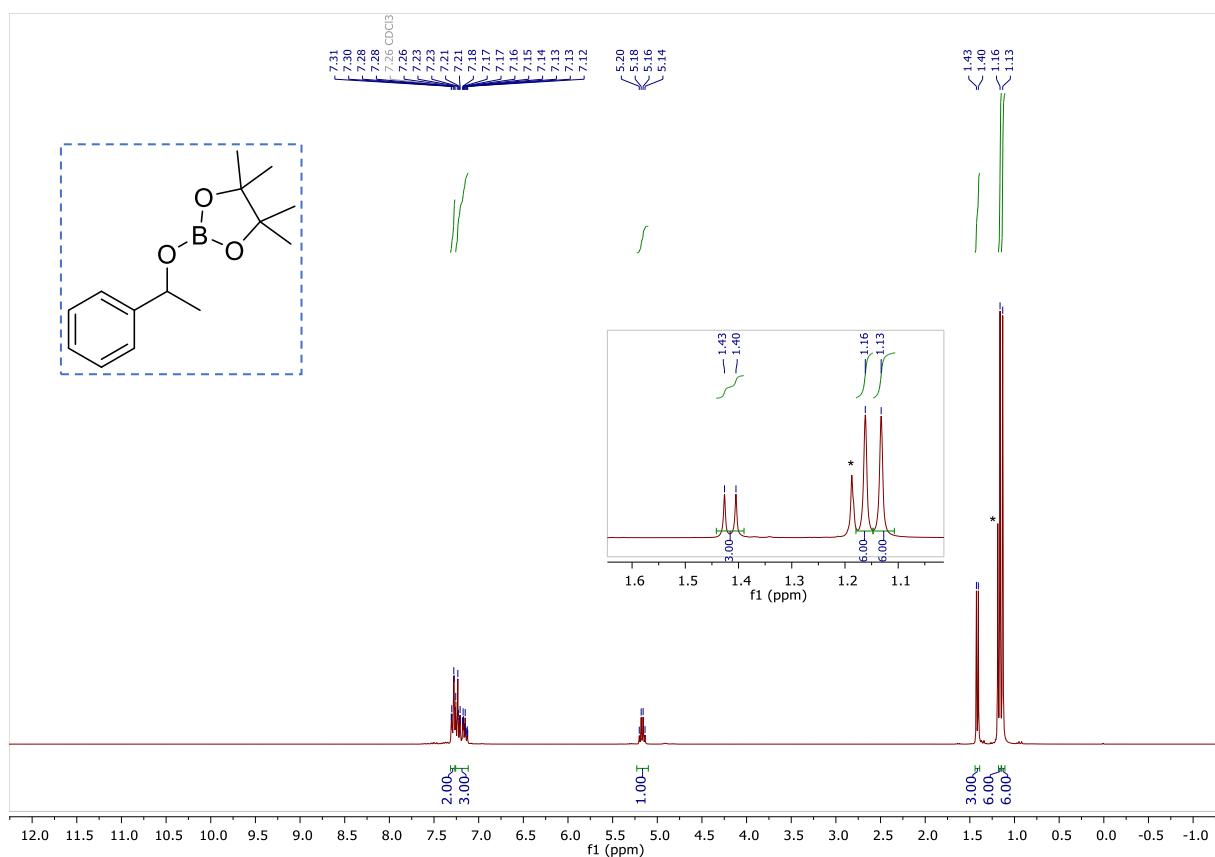


Figure S18 – ^1H NMR spectrum of **3a** from crude reaction mixture. *Excess of the HBpin.

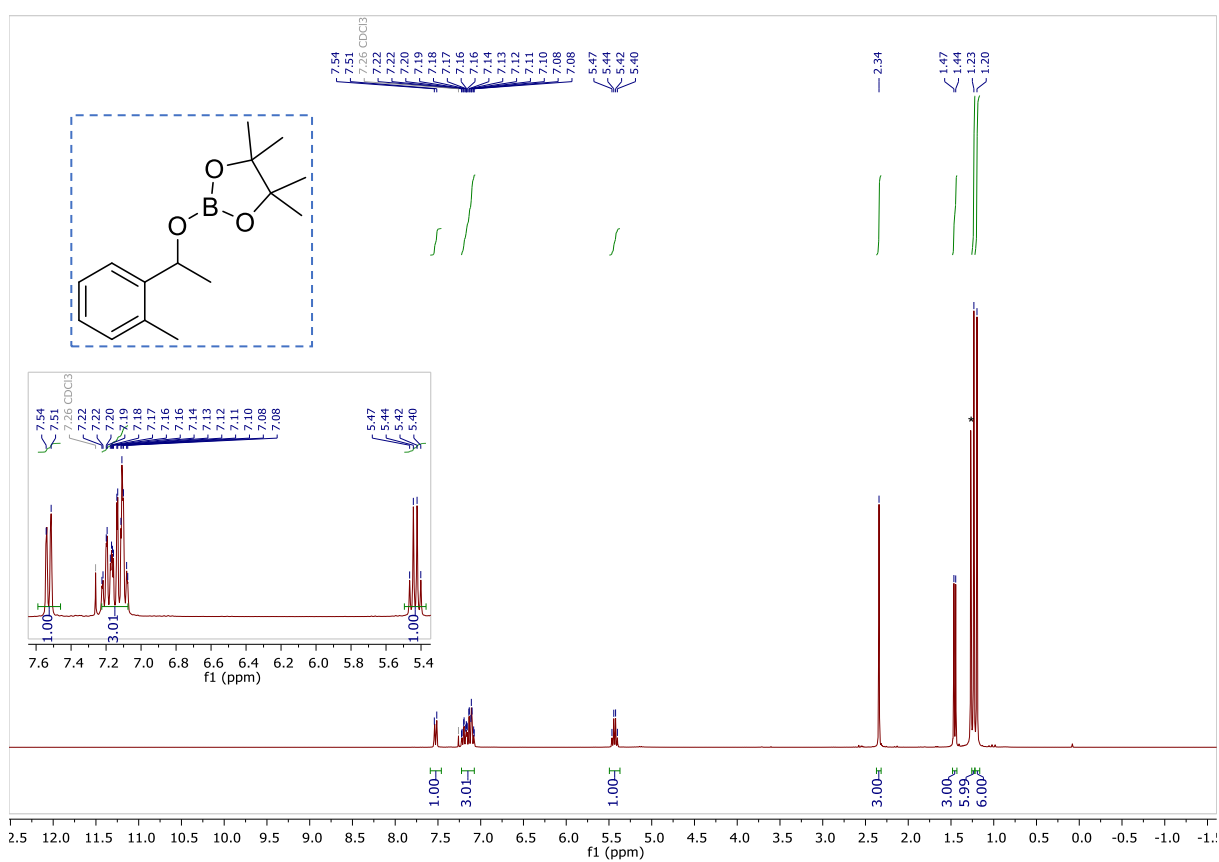


Figure S19 – ^1H NMR spectrum of **3b** from crude reaction mixture. *Excess of the HBpin.

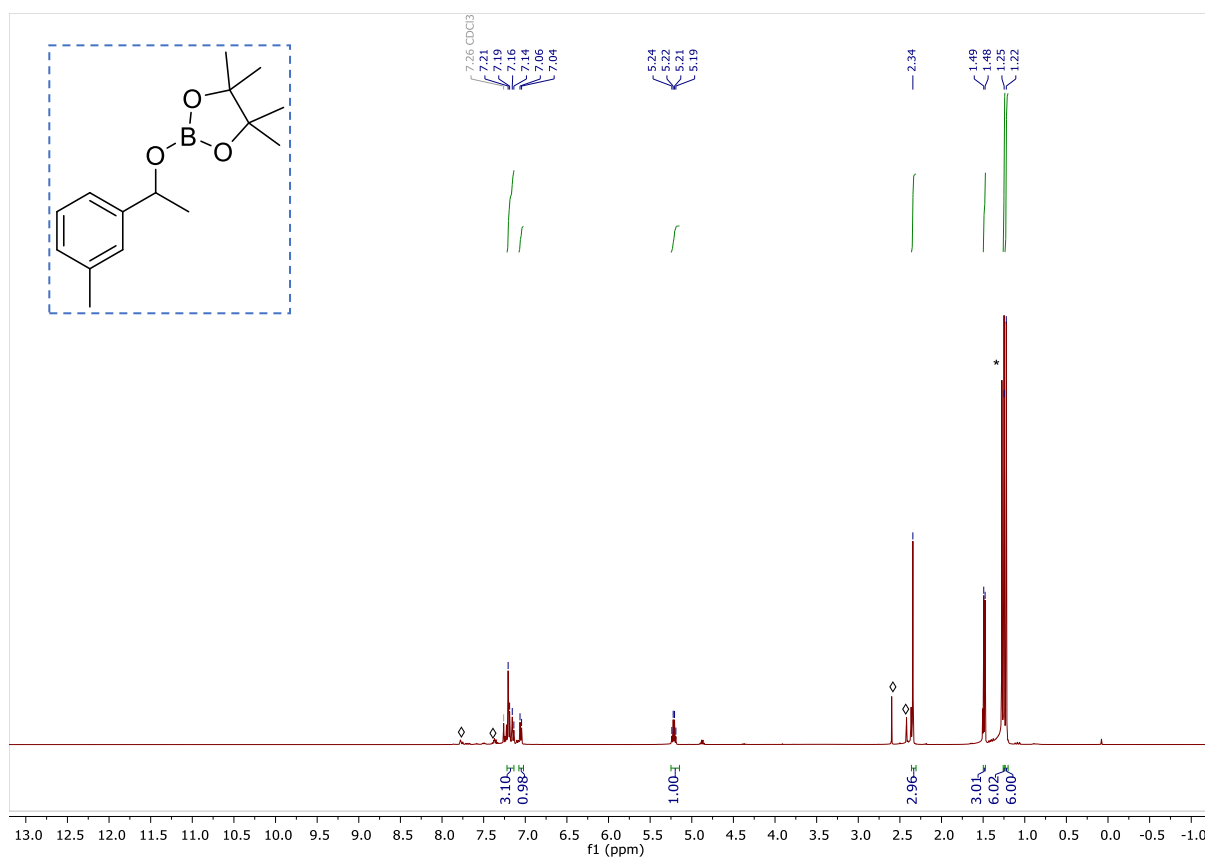


Figure S20 – ¹H NMR spectrum of **3c** from crude reaction mixture. *Excess of the HBpin.
 ◇ Unreacted substrate (**1c**). Conversion of **1c** = 90%.

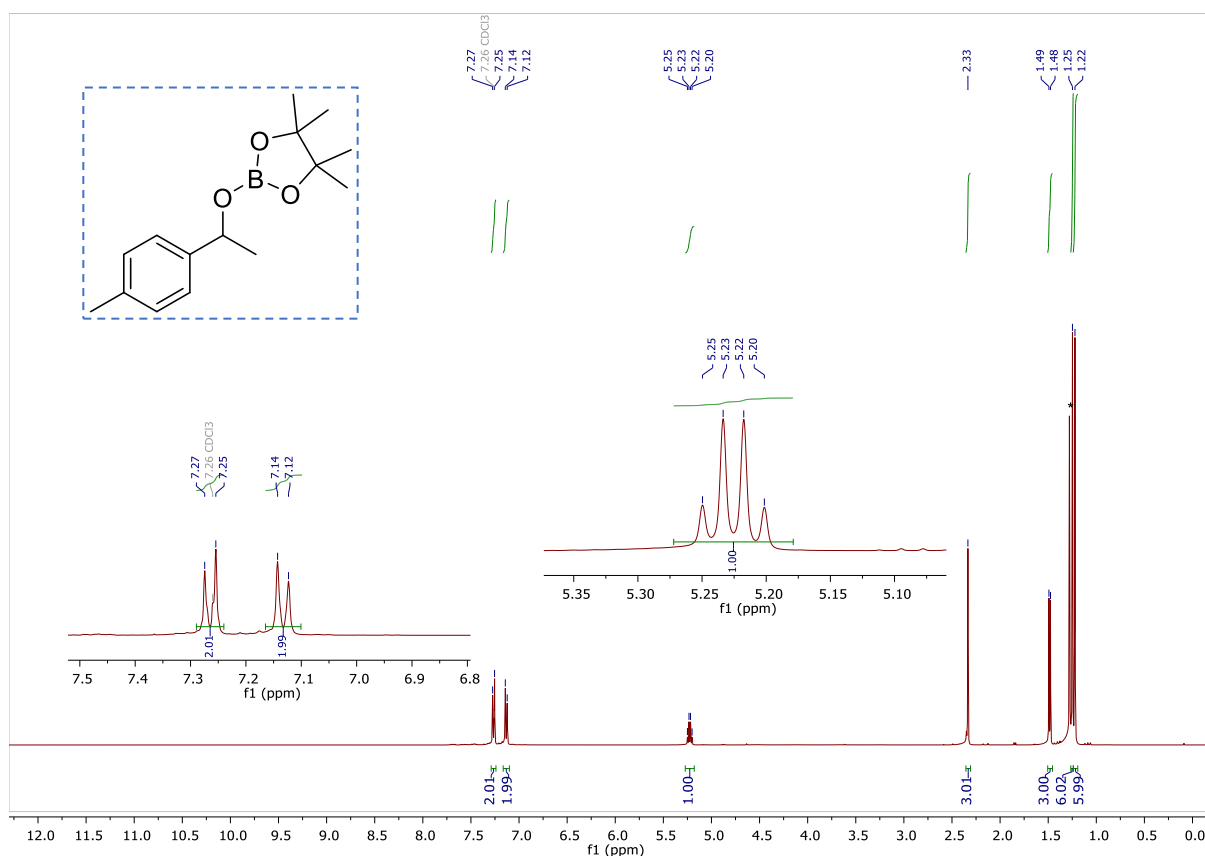


Figure S21 – ¹H NMR spectrum of **3d** from crude reaction mixture. *Excess of the HBpin.

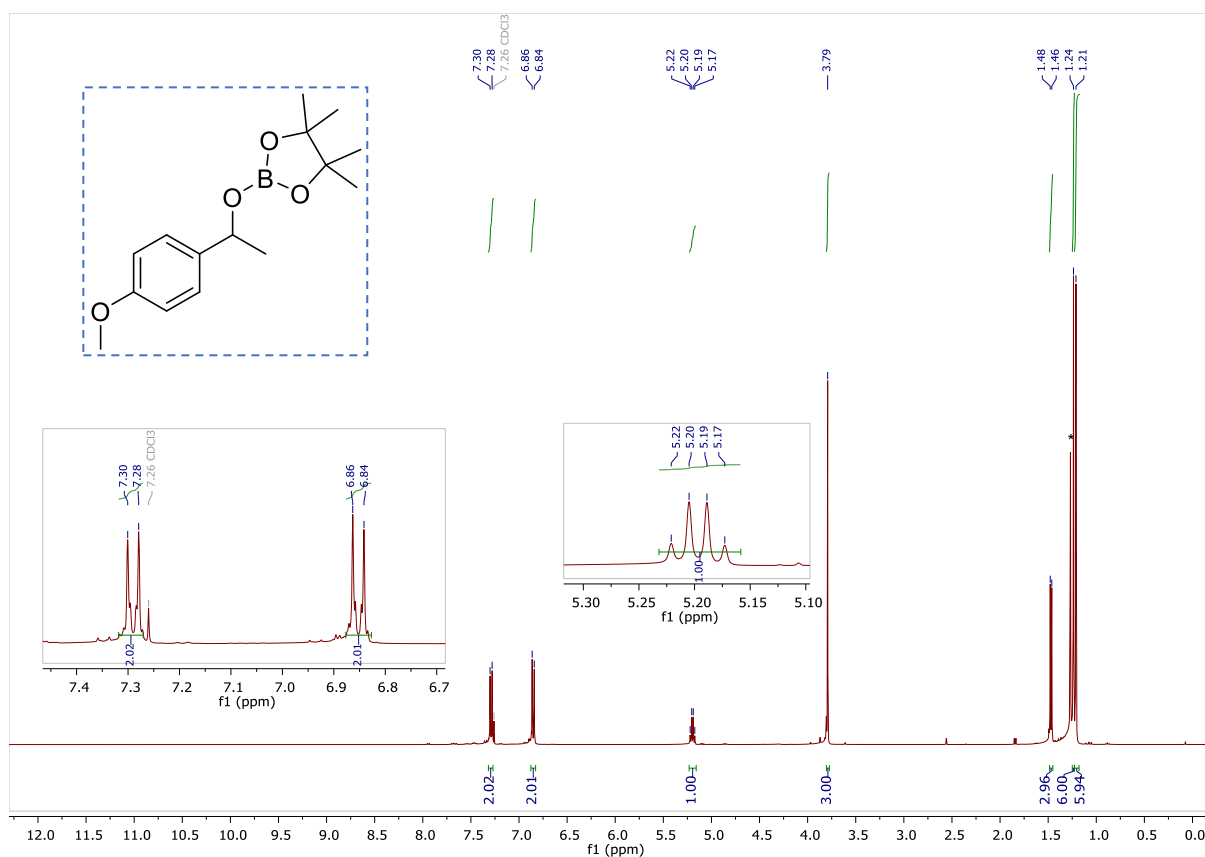


Figure S22 – ^1H NMR spectrum of **3e** from crude reaction mixture. *Excess of the HBpin.

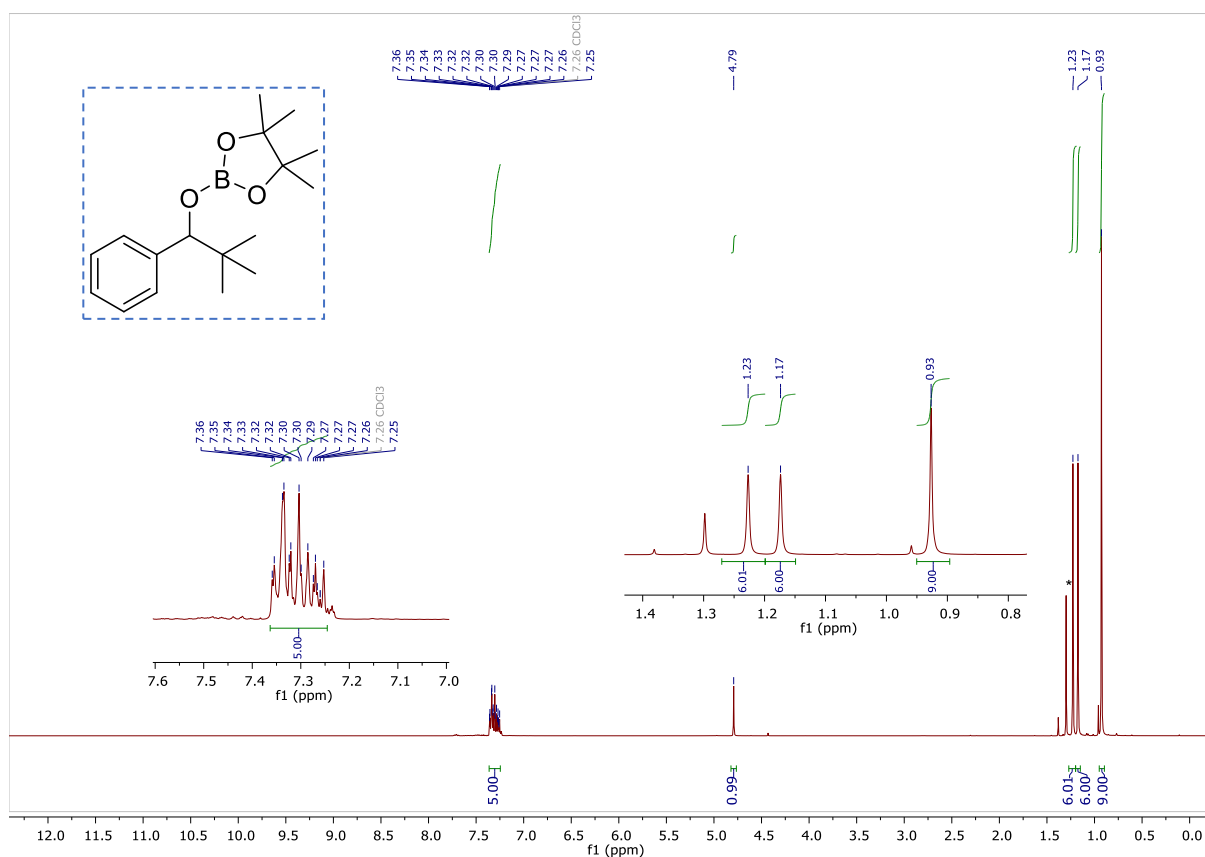


Figure S23 – ^1H NMR spectrum of **3f** from crude reaction mixture. *Excess of the HBpin.

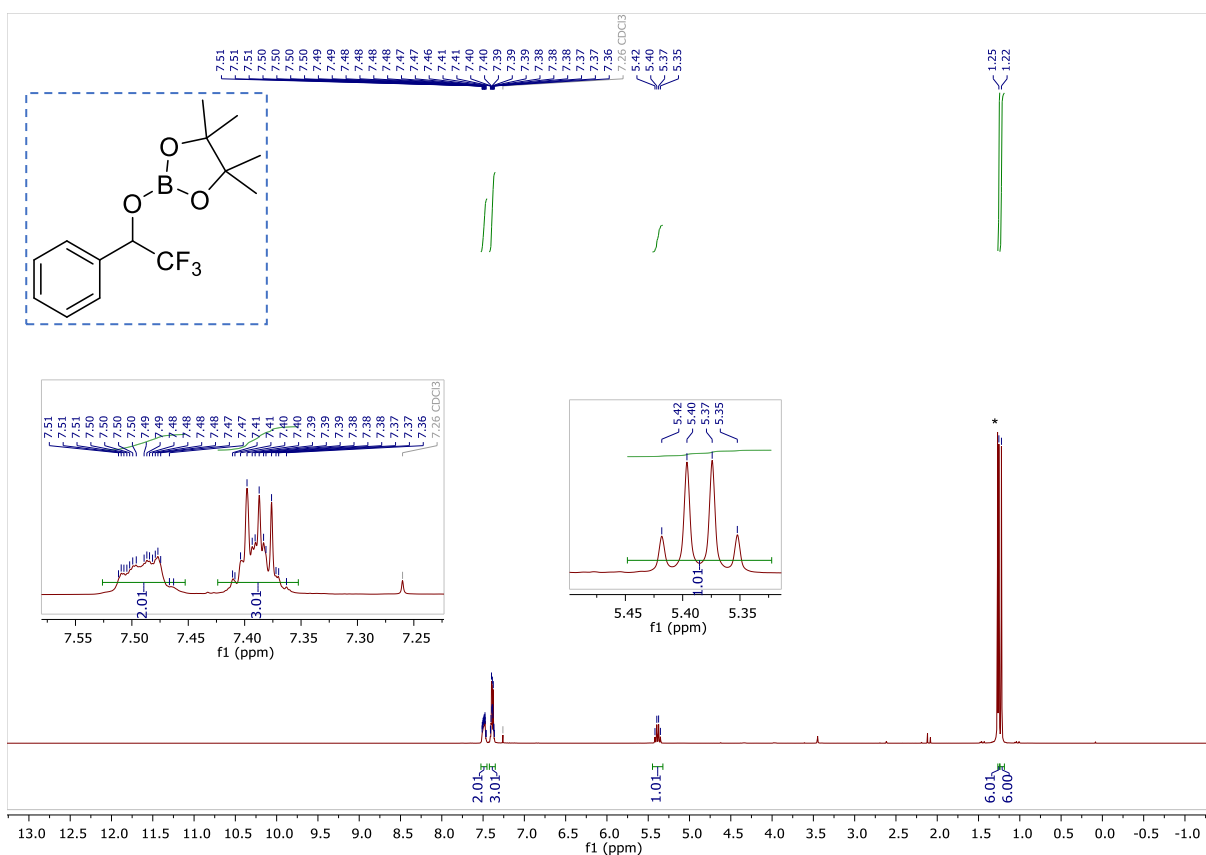


Figure S24 – ¹H NMR spectrum of **3g** from crude reaction mixture. *Excess of the HBpin.

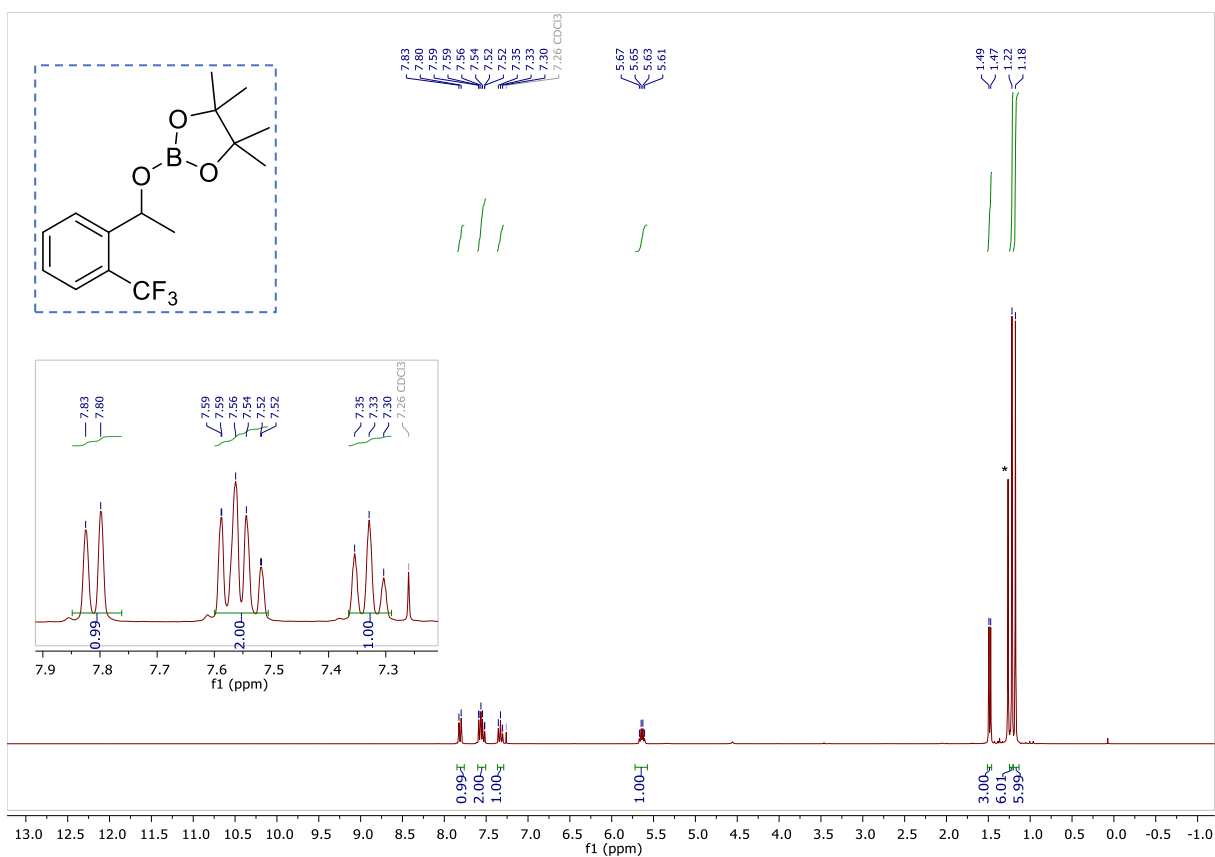


Figure S25 – ¹H NMR spectrum of **3h** from crude reaction mixture. *Excess of the HBpin.

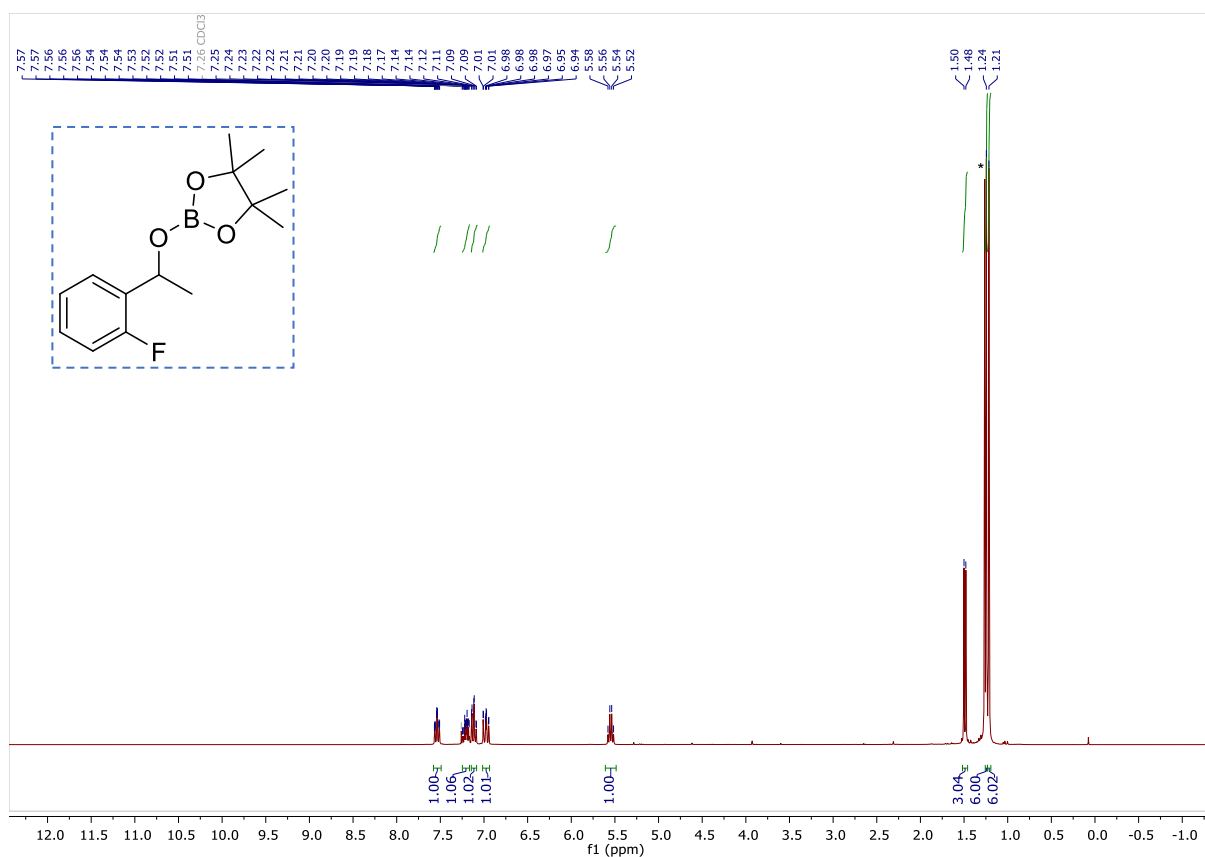


Figure S26 – ¹H NMR spectrum of **3i** from crude reaction mixture. *Excess of the HBpin.

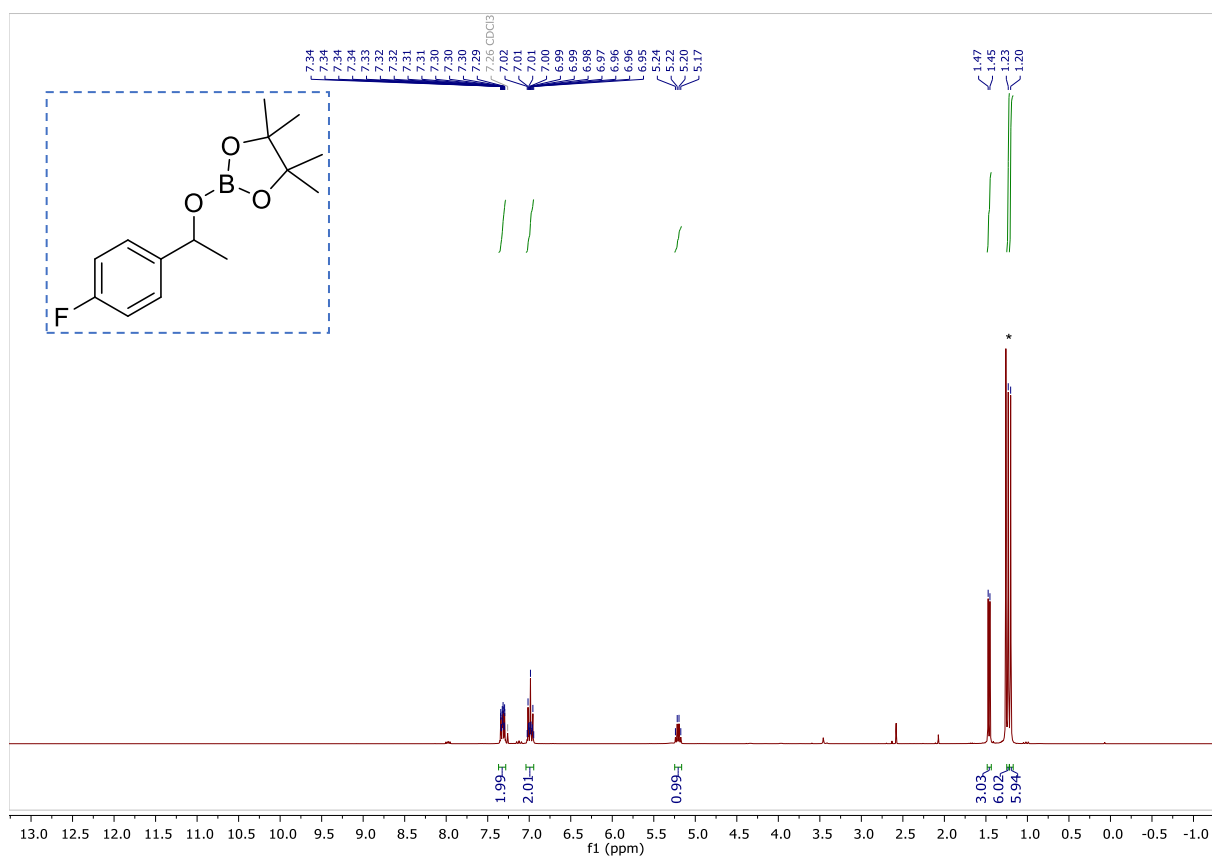


Figure S27 – ¹H NMR spectrum of **3j** from crude reaction mixture. *Excess of the HBpin.

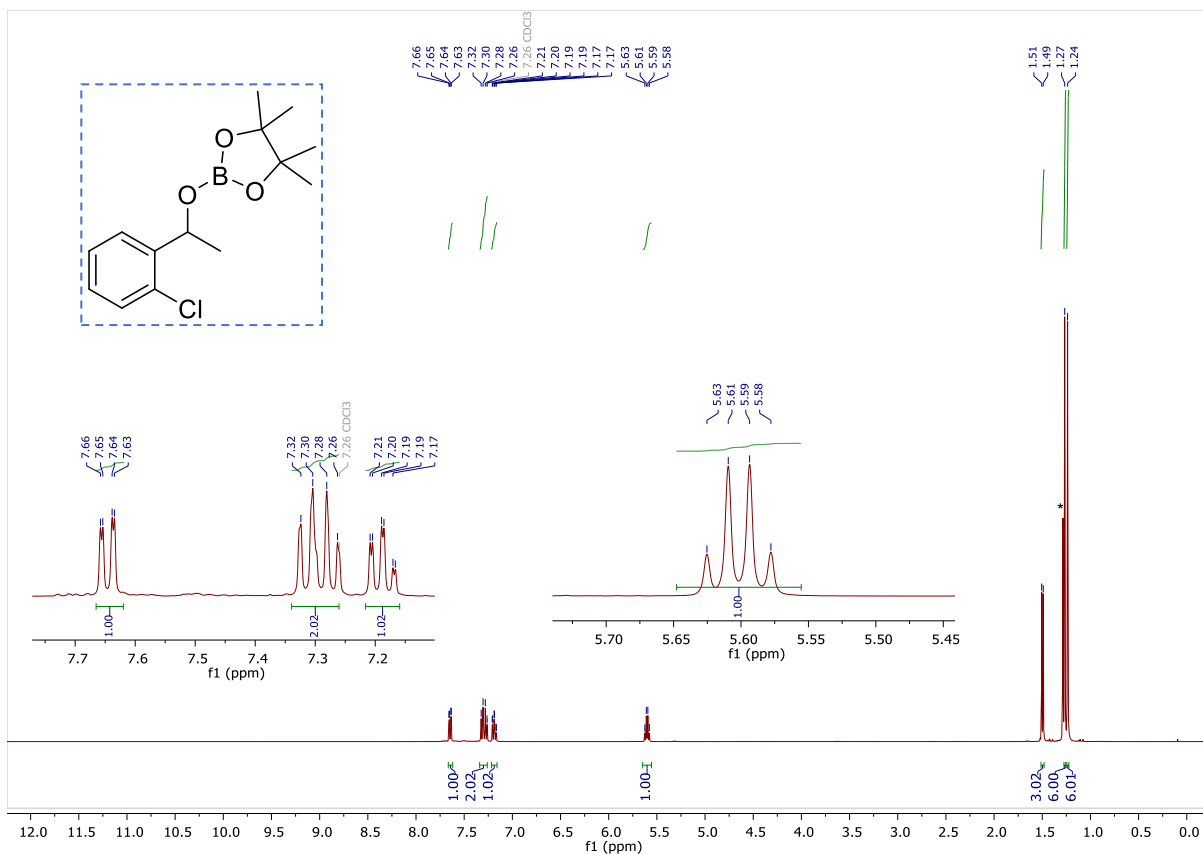


Figure S28 – ¹H NMR spectrum of **3k** from crude reaction mixture. *Excess of the HBpin.

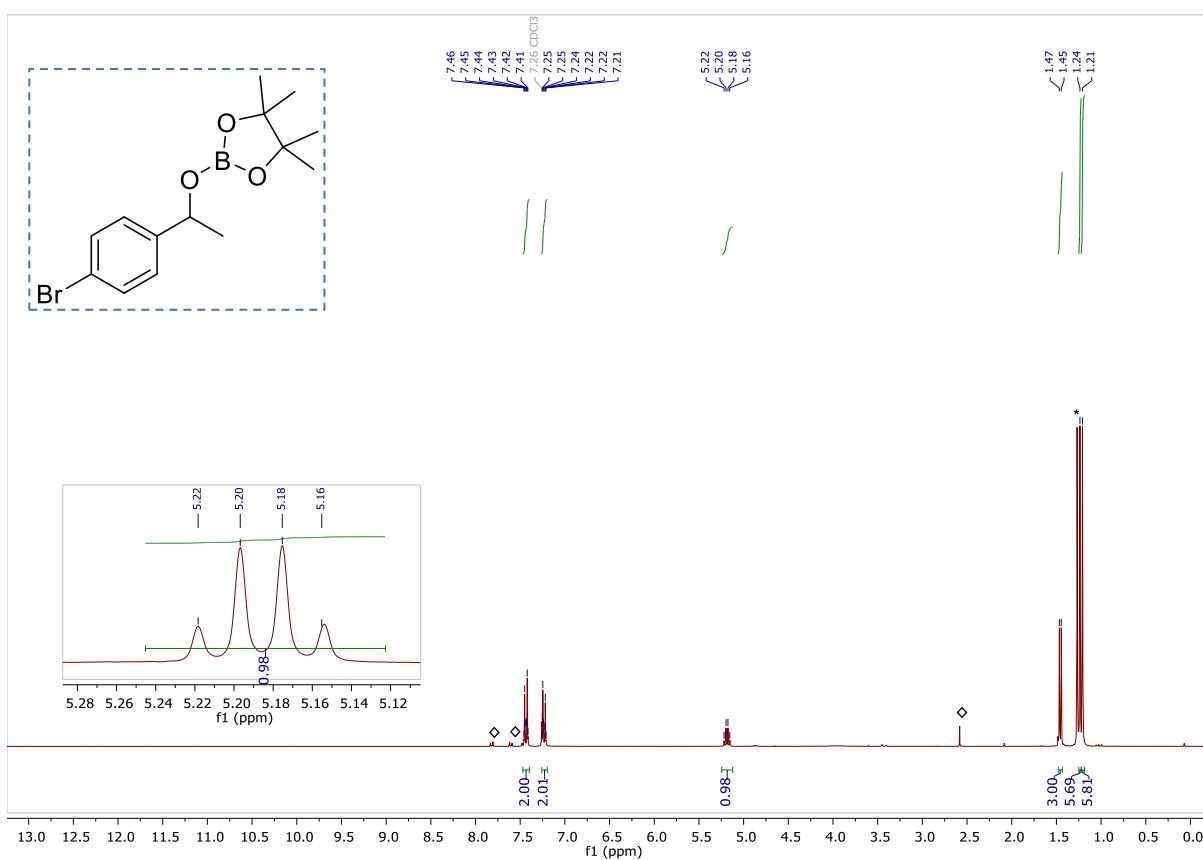


Figure S29 – ¹H NMR spectrum of **3l** from the crude reaction mixture. *Excess of the HBpin.
 ◇ Unreacted substrate (**1l**). Conversion of **1l** = 96%.

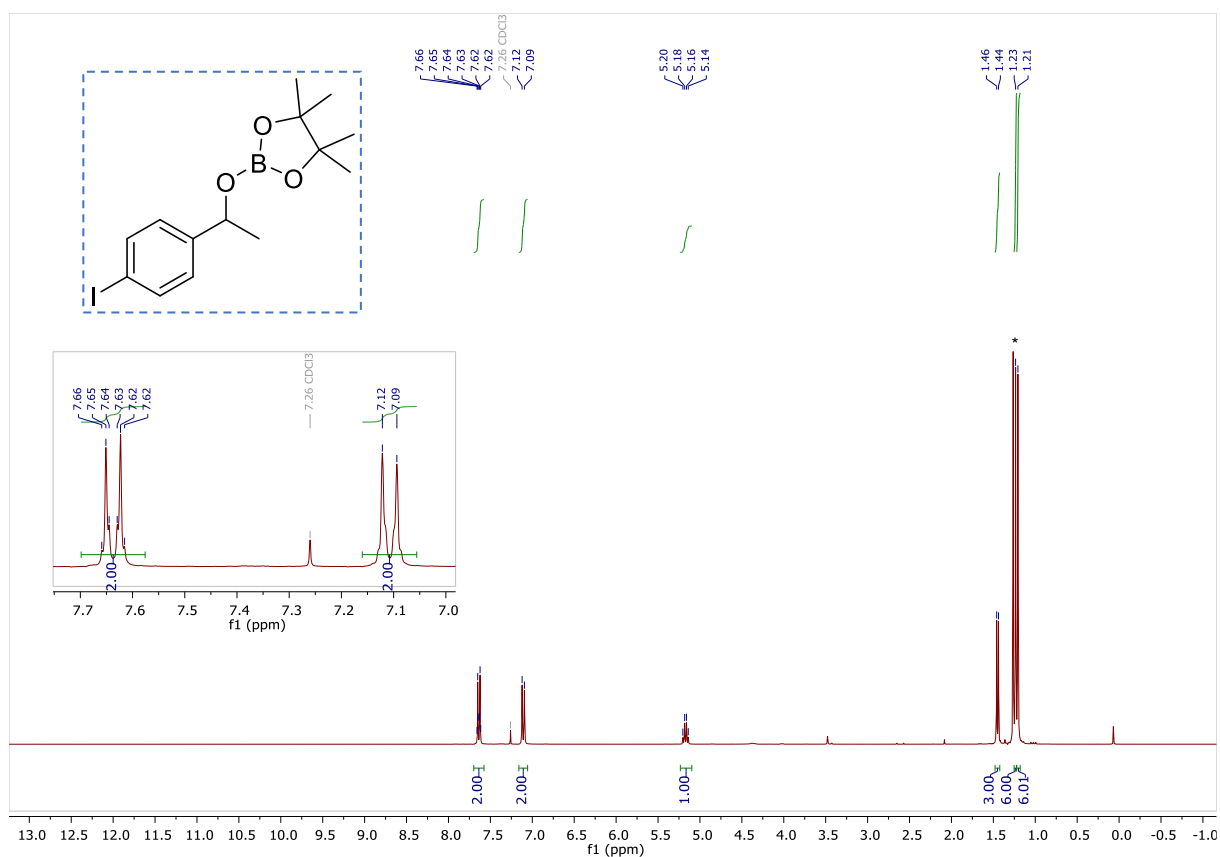


Figure S30 – ¹H NMR spectrum of **3m** from crude reaction mixture. *Excess of the HBpin.

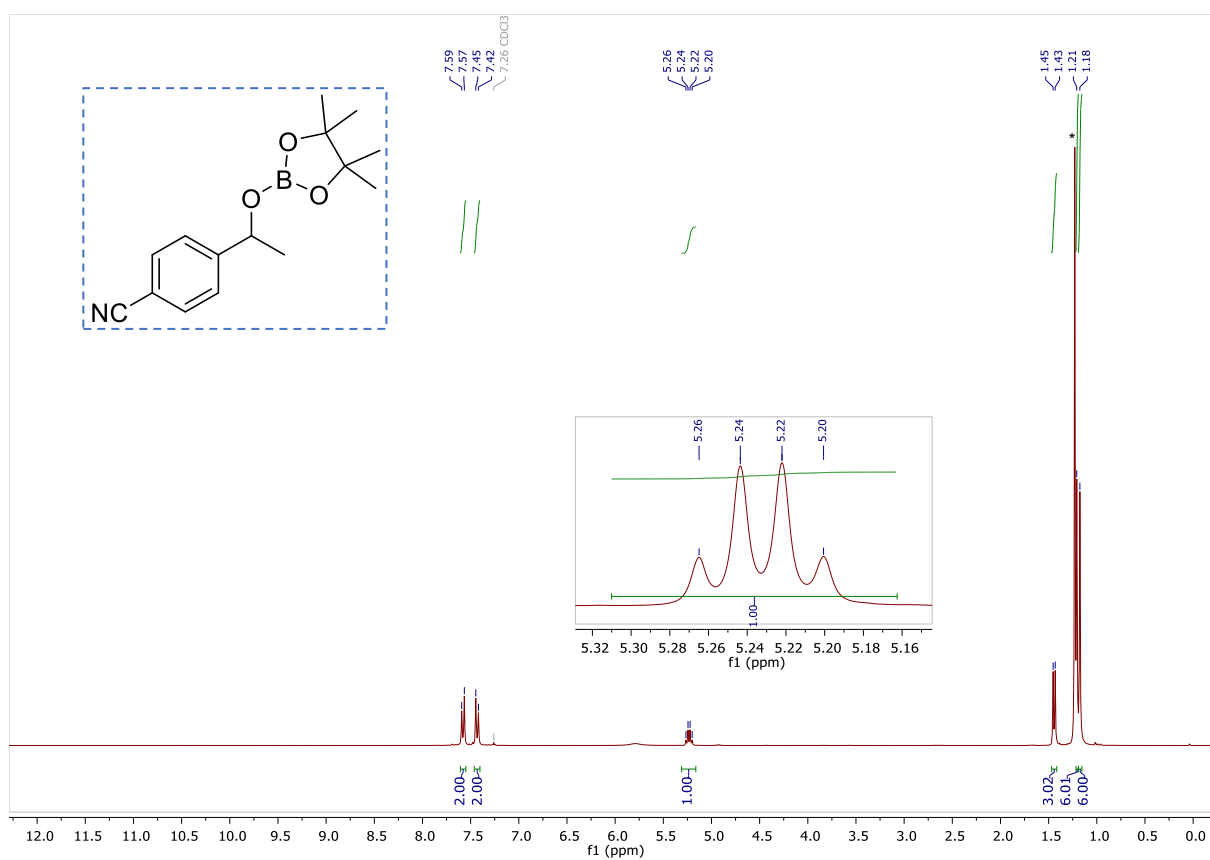
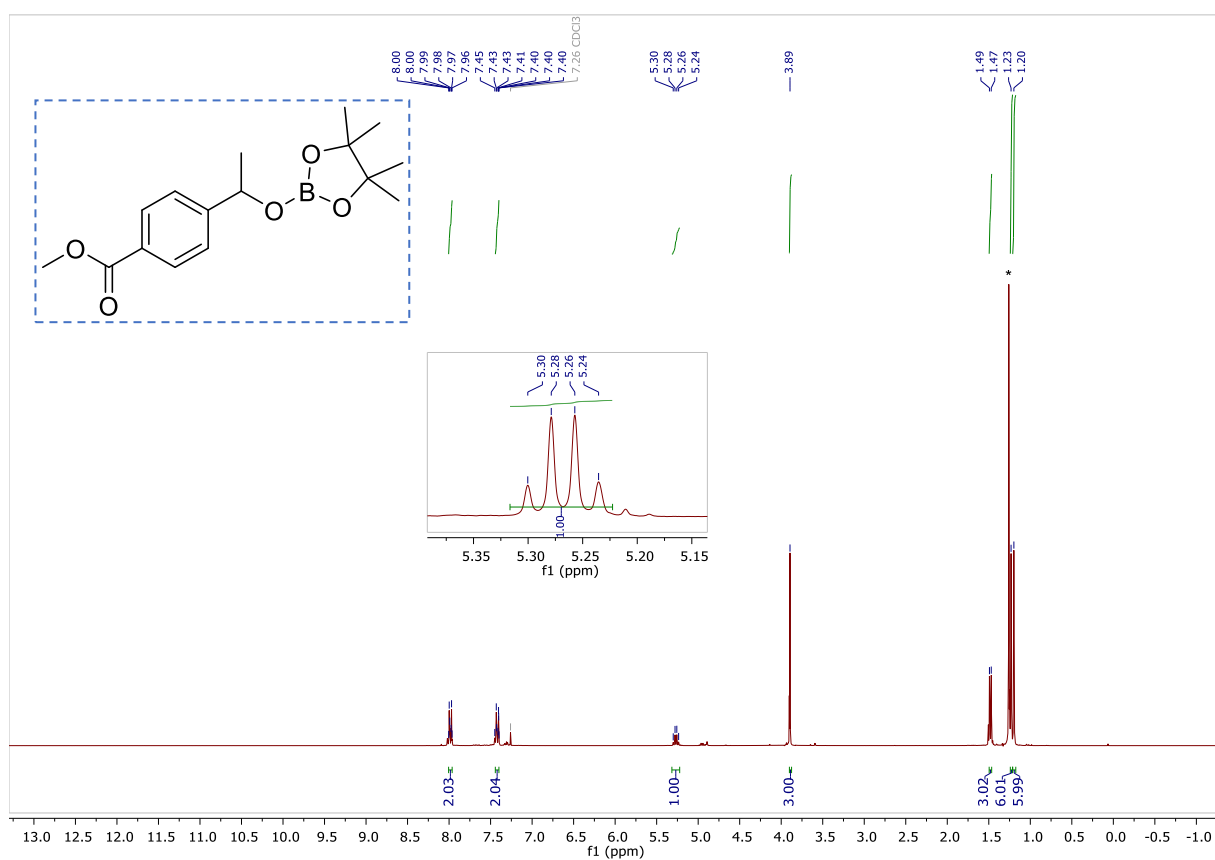
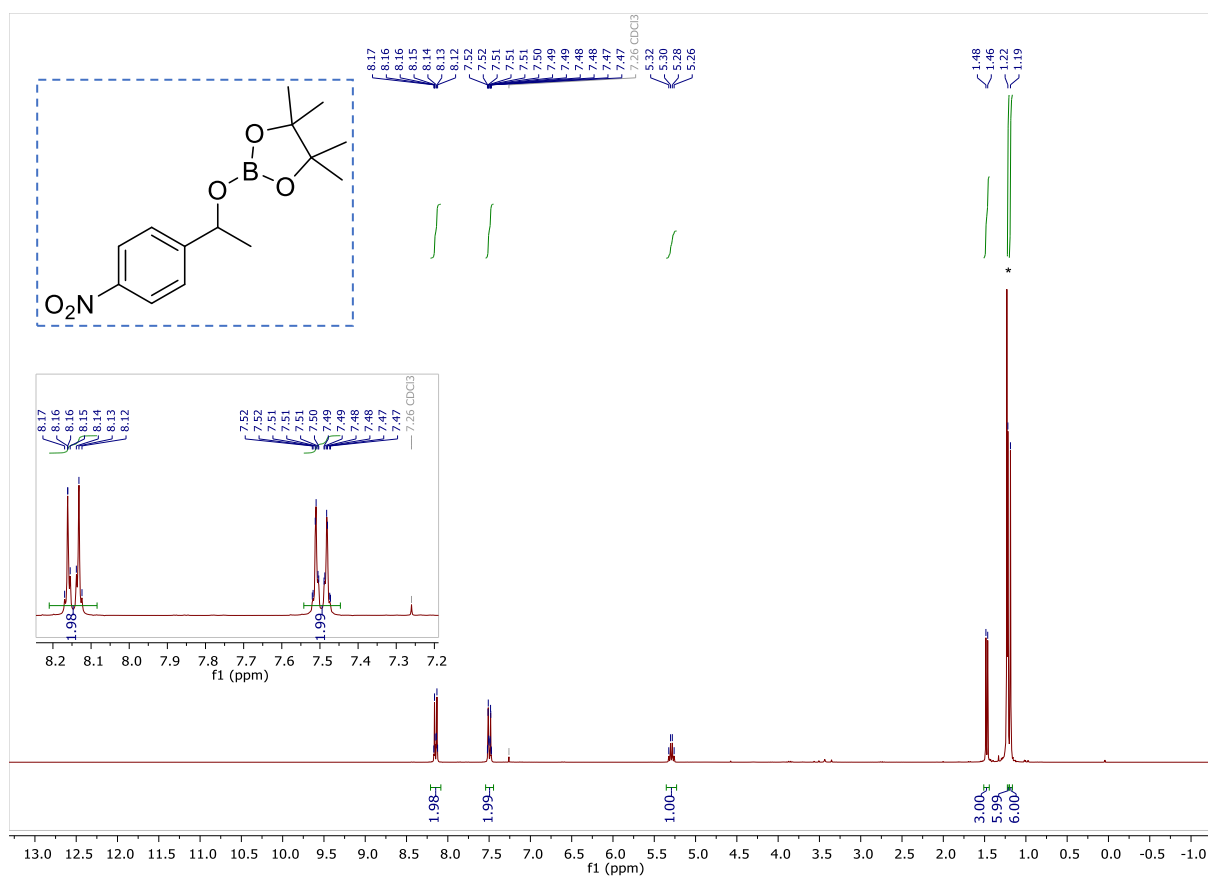


Figure S31 – ¹H NMR spectrum of **3n** from crude reaction mixture. *Excess of the HBpin.



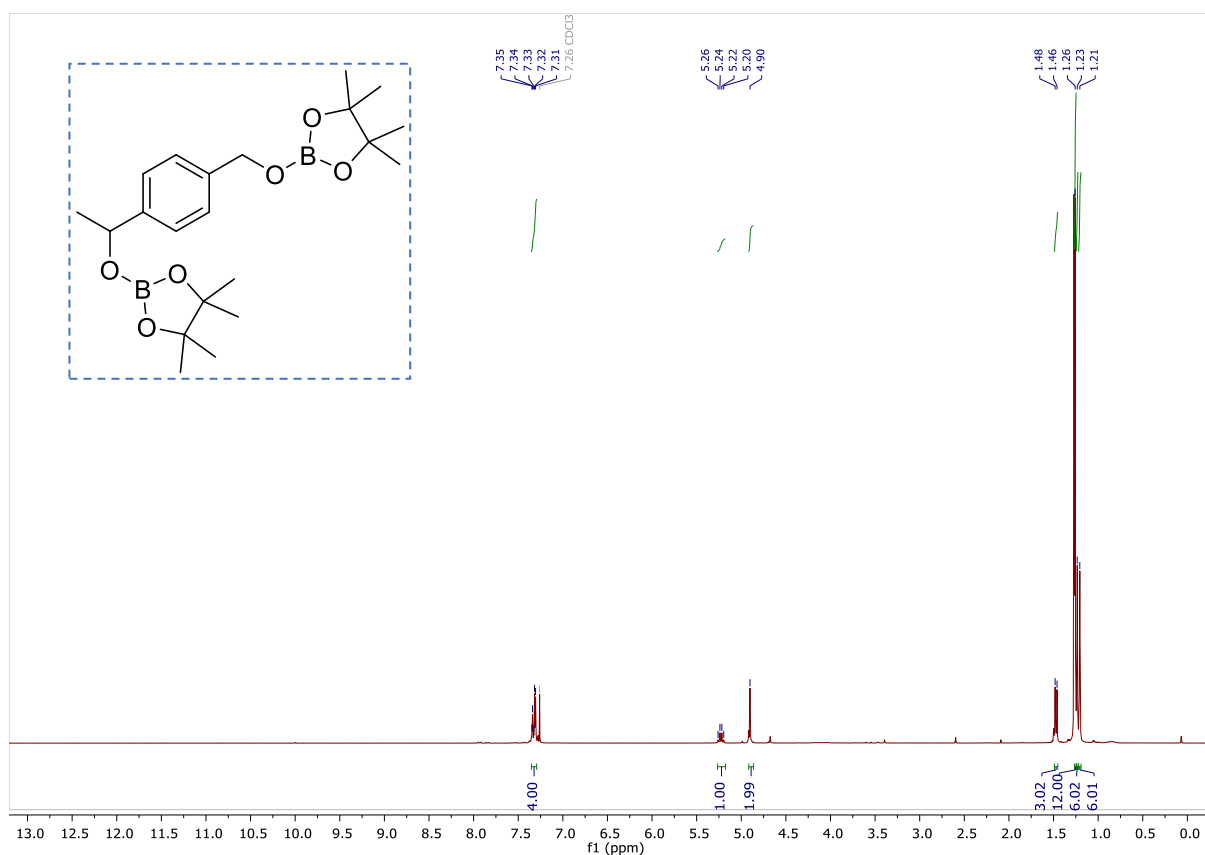


Figure S34 – ^1H NMR spectrum of **3q** from crude reaction mixture. *Excess of the HBpin.

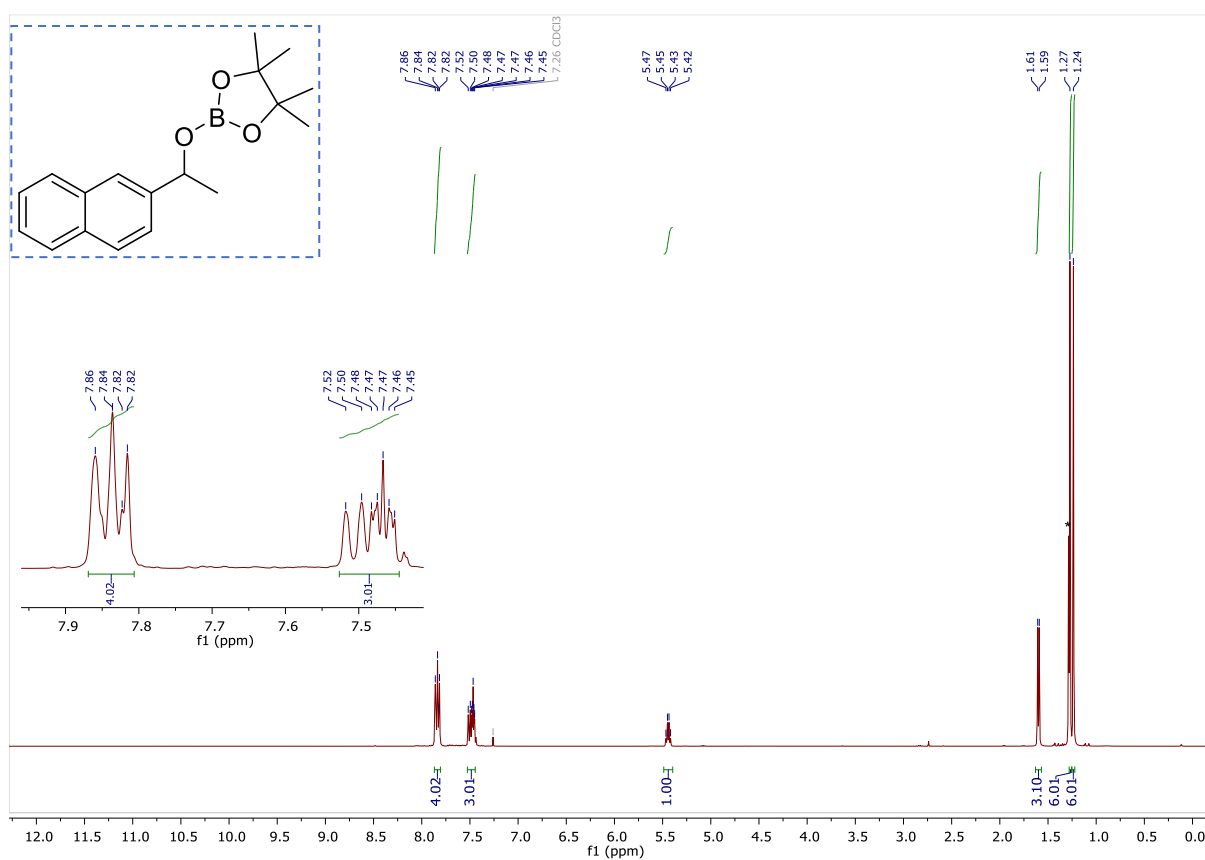


Figure S35 – ^1H NMR spectrum of **3r** from crude reaction mixture. *Excess of the HBpin.

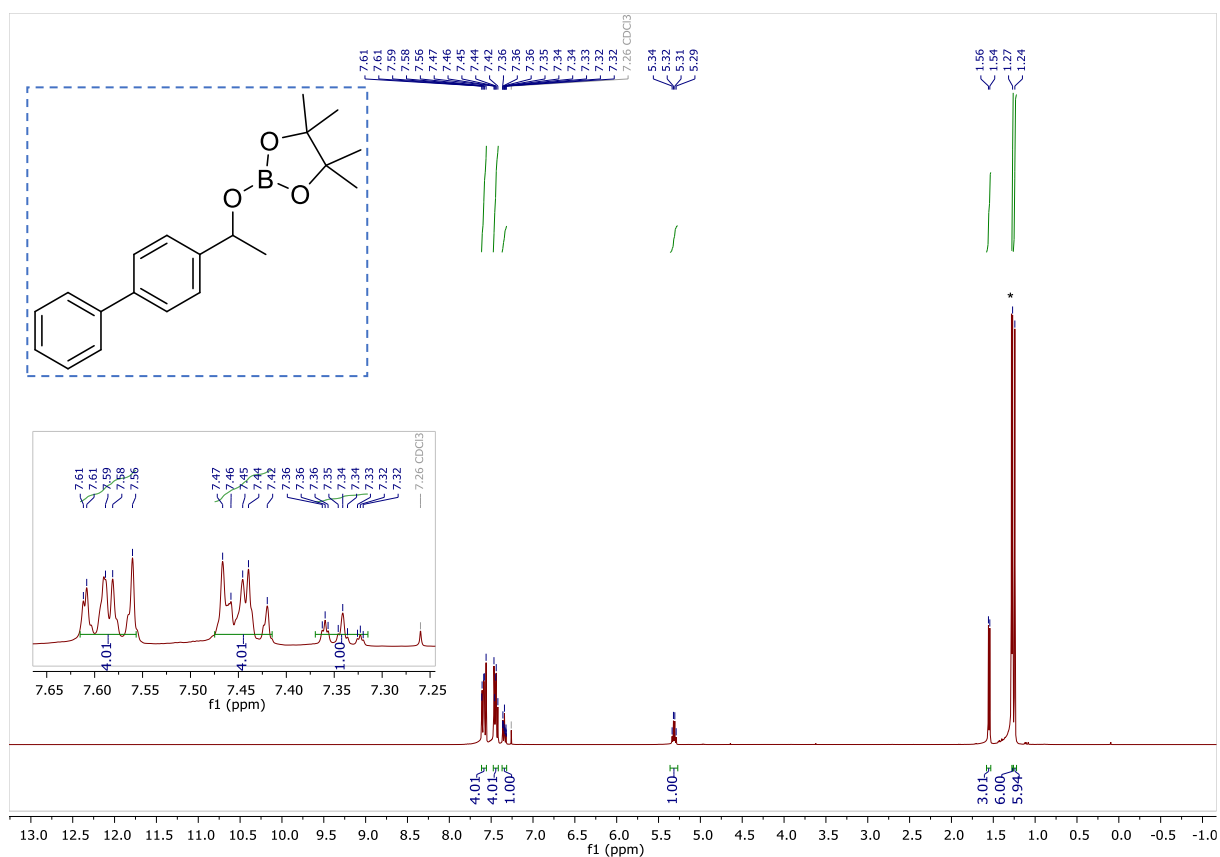


Figure S36 – ^1H NMR spectrum of **3s**. *Excess of the HBpin.

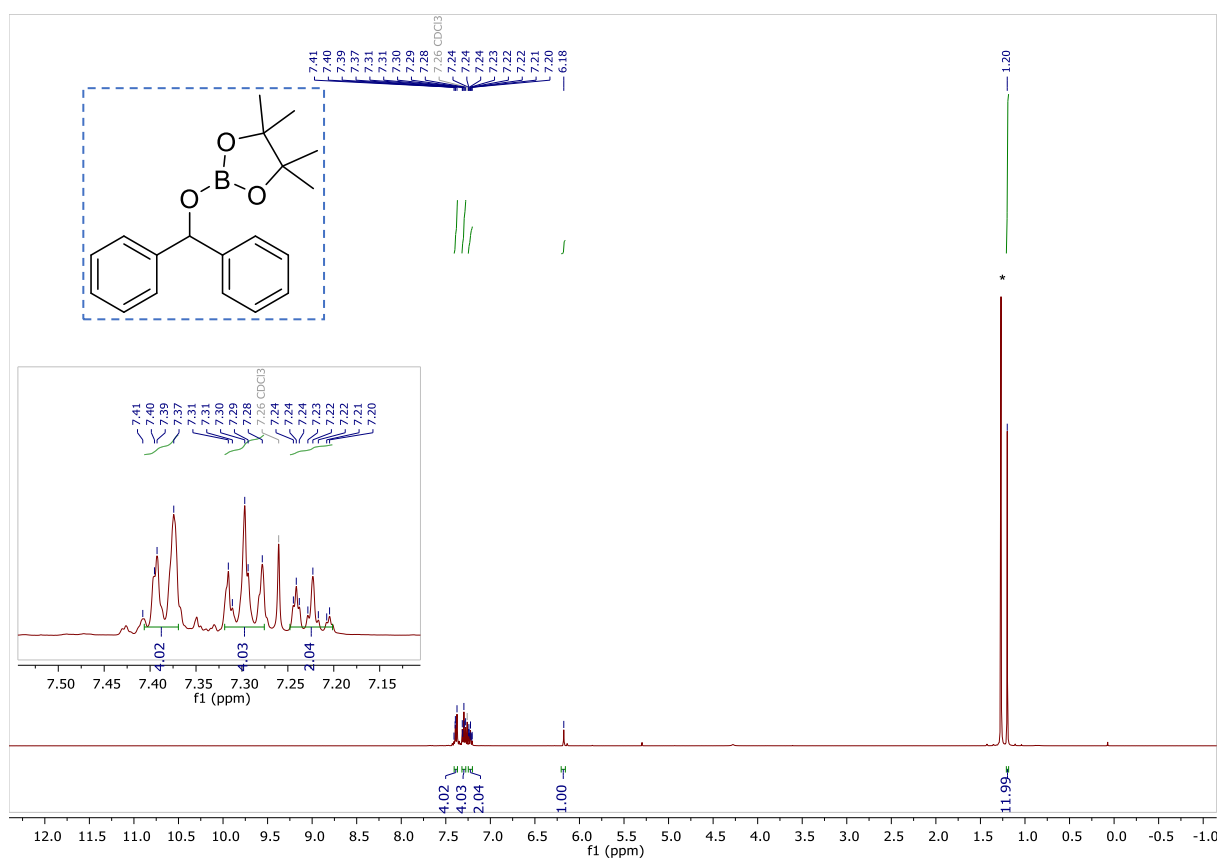


Figure S37 – ^1H NMR spectrum of **3t** from crude reaction mixture. *Excess of the HBpin.

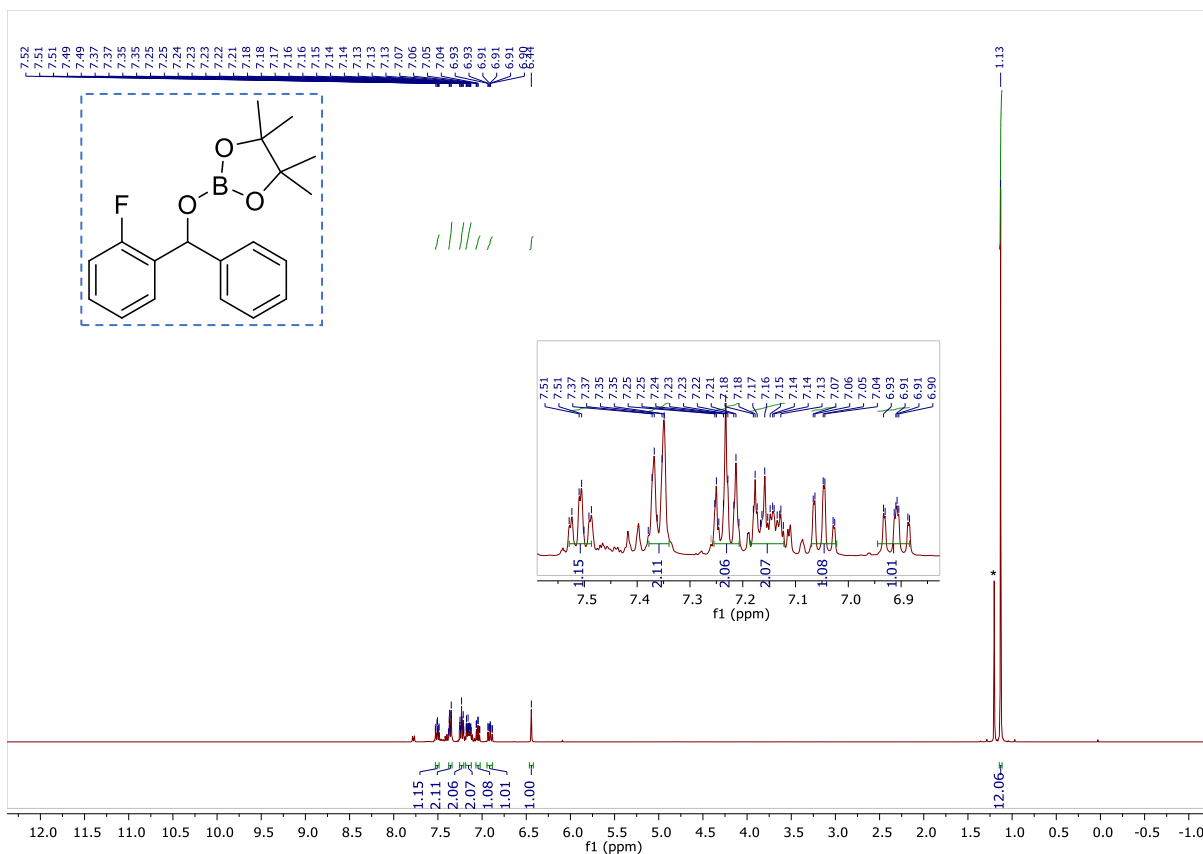


Figure S38 – ^1H NMR spectrum of **3u** from crude reaction mixture. *Excess of the HBpin.

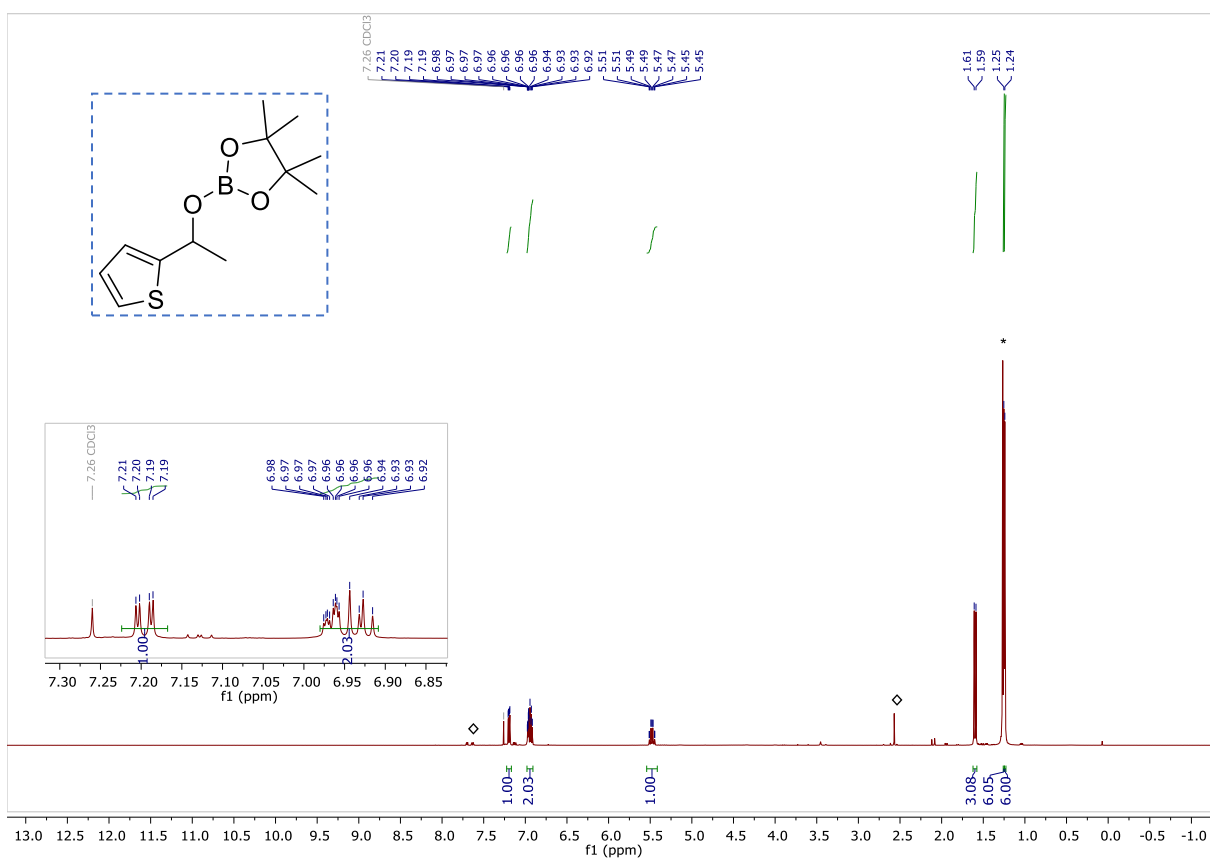
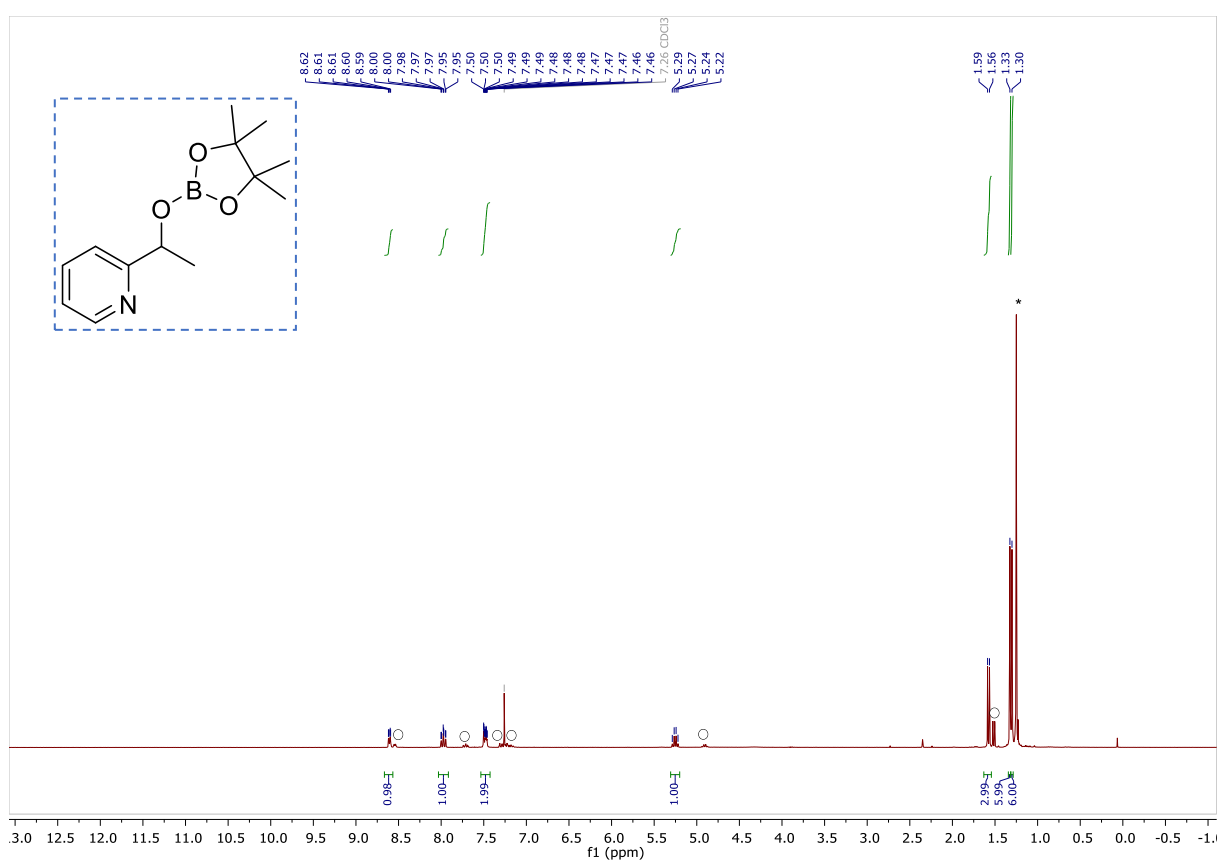
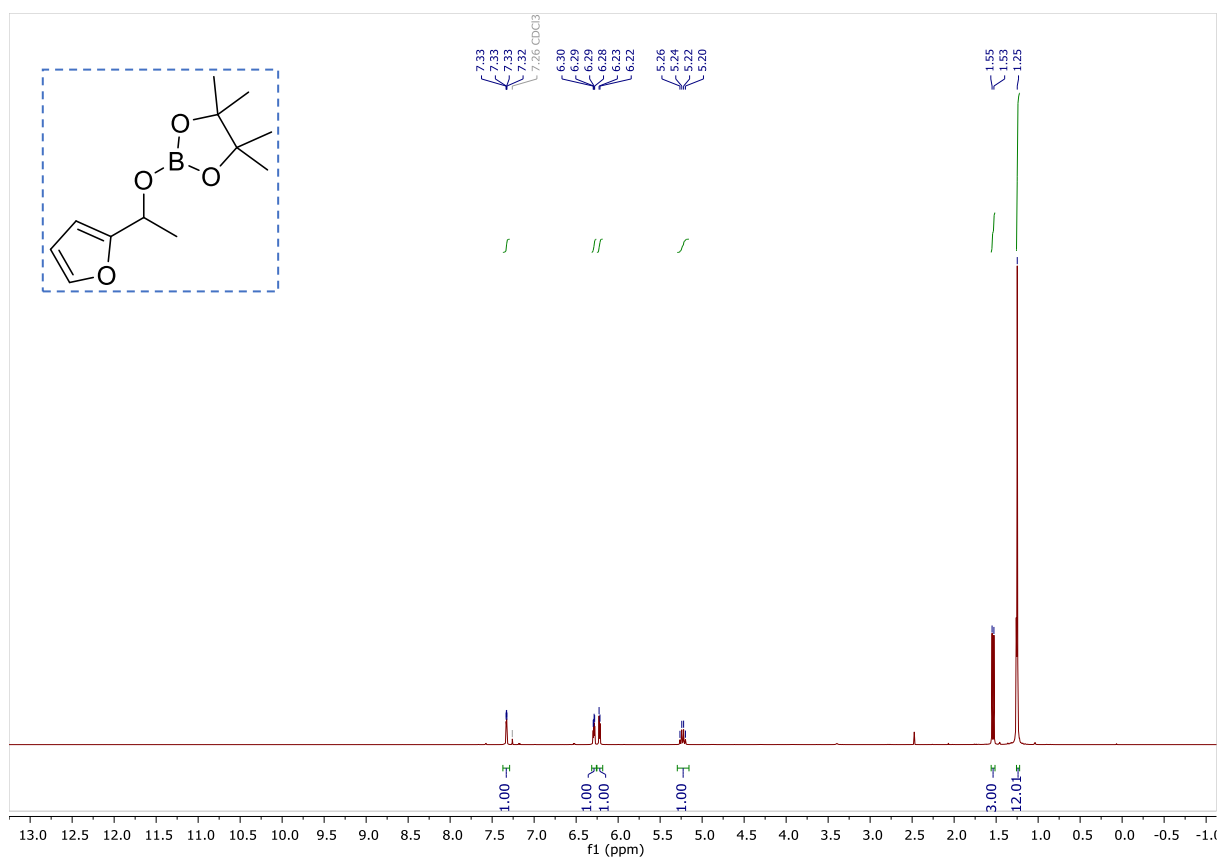
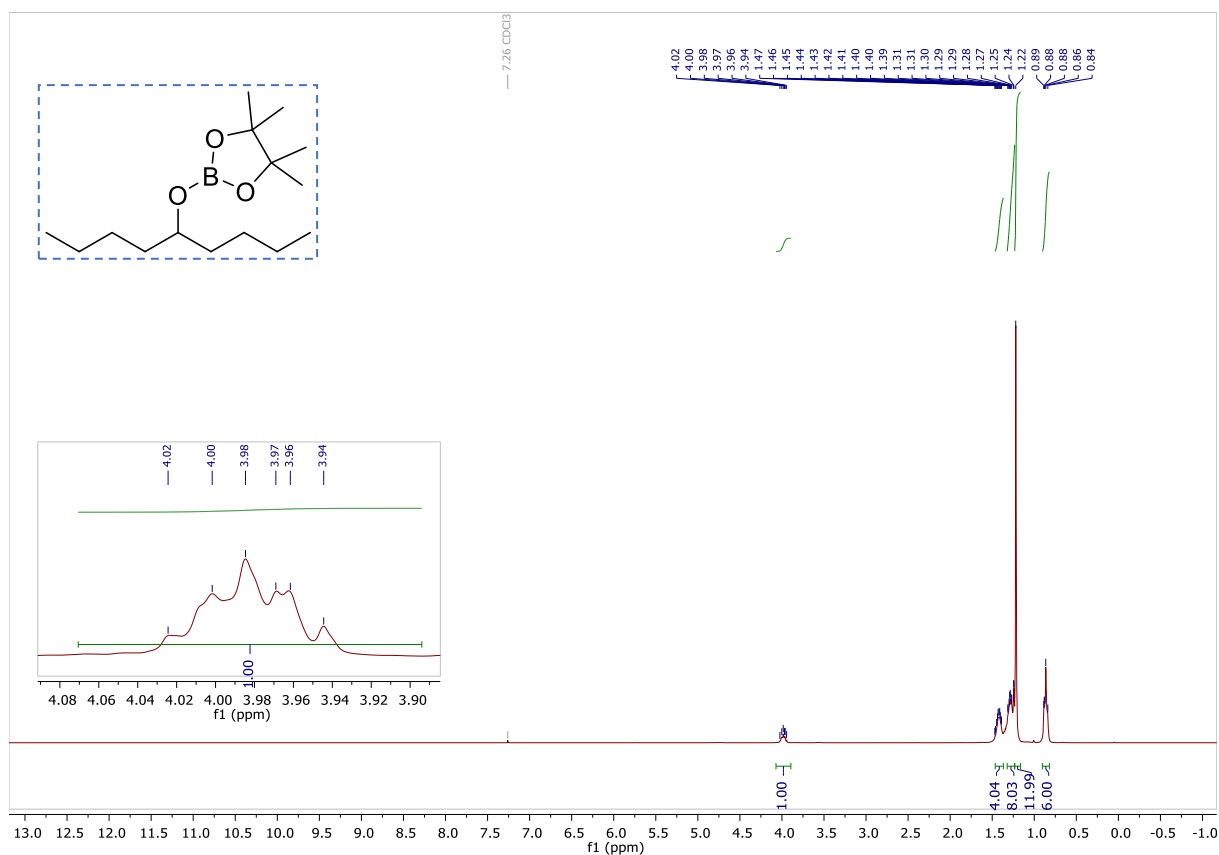
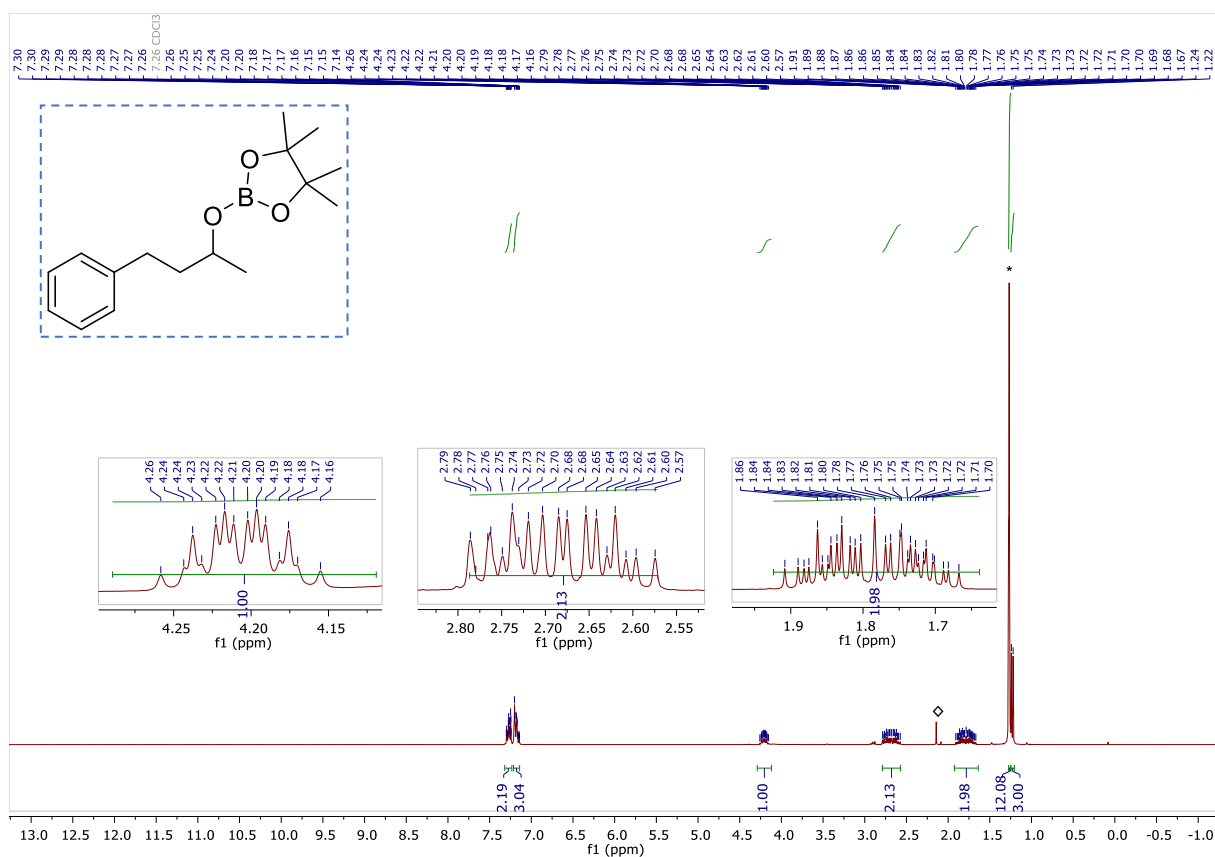


Figure S39 – ^1H NMR spectrum of **3v** from crude reaction mixture. *Excess of the HBpin.
 ◊ Unreacted substrate (**1v**). Conversion of **1v** = 92%.





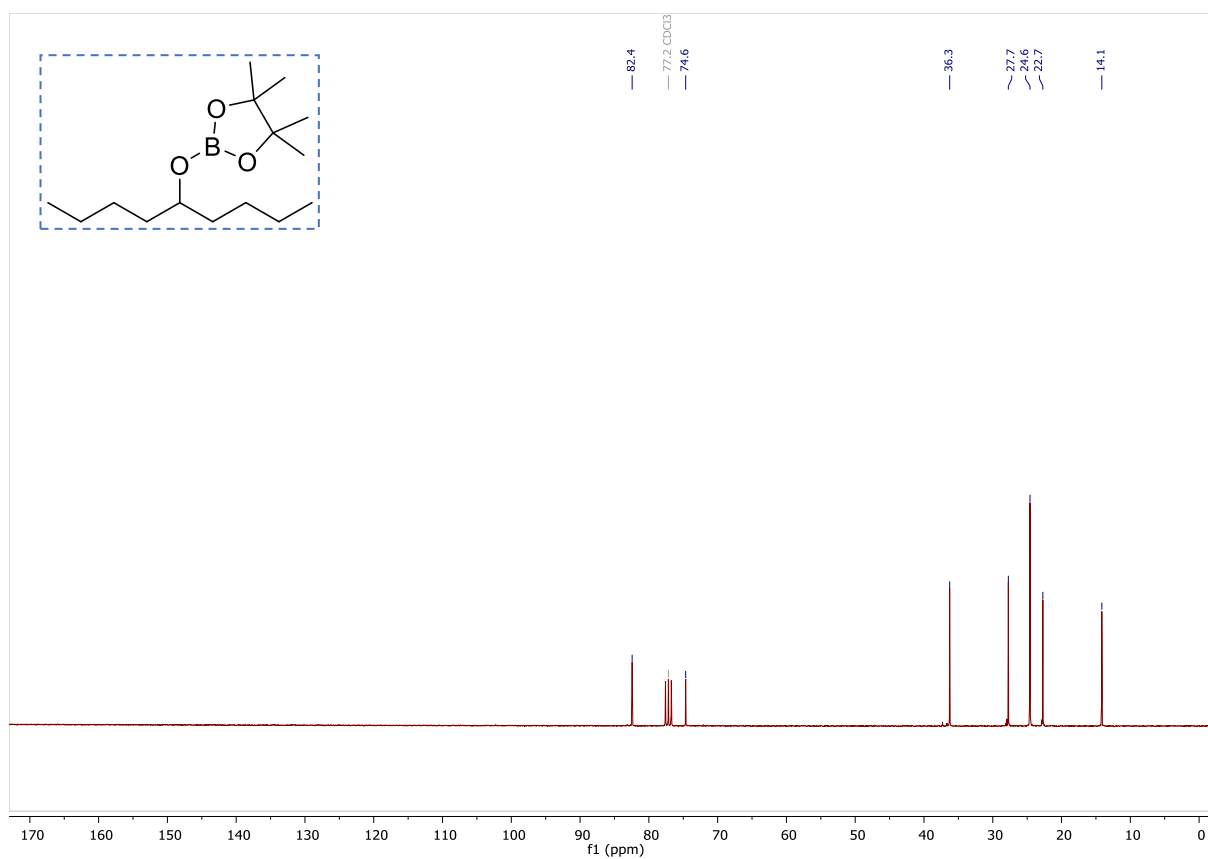


Figure S44 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3z**.

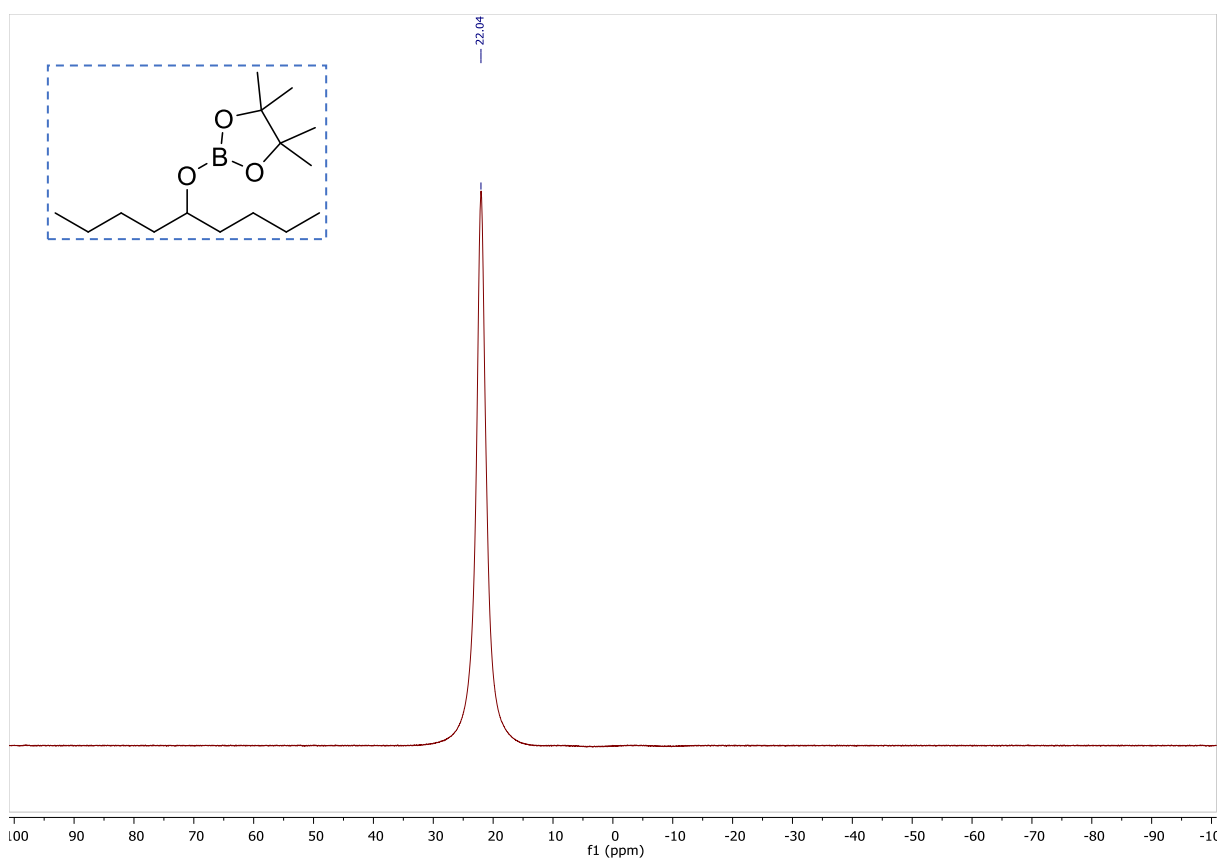


Figure S45 – ^{11}B NMR spectrum of **3z**.

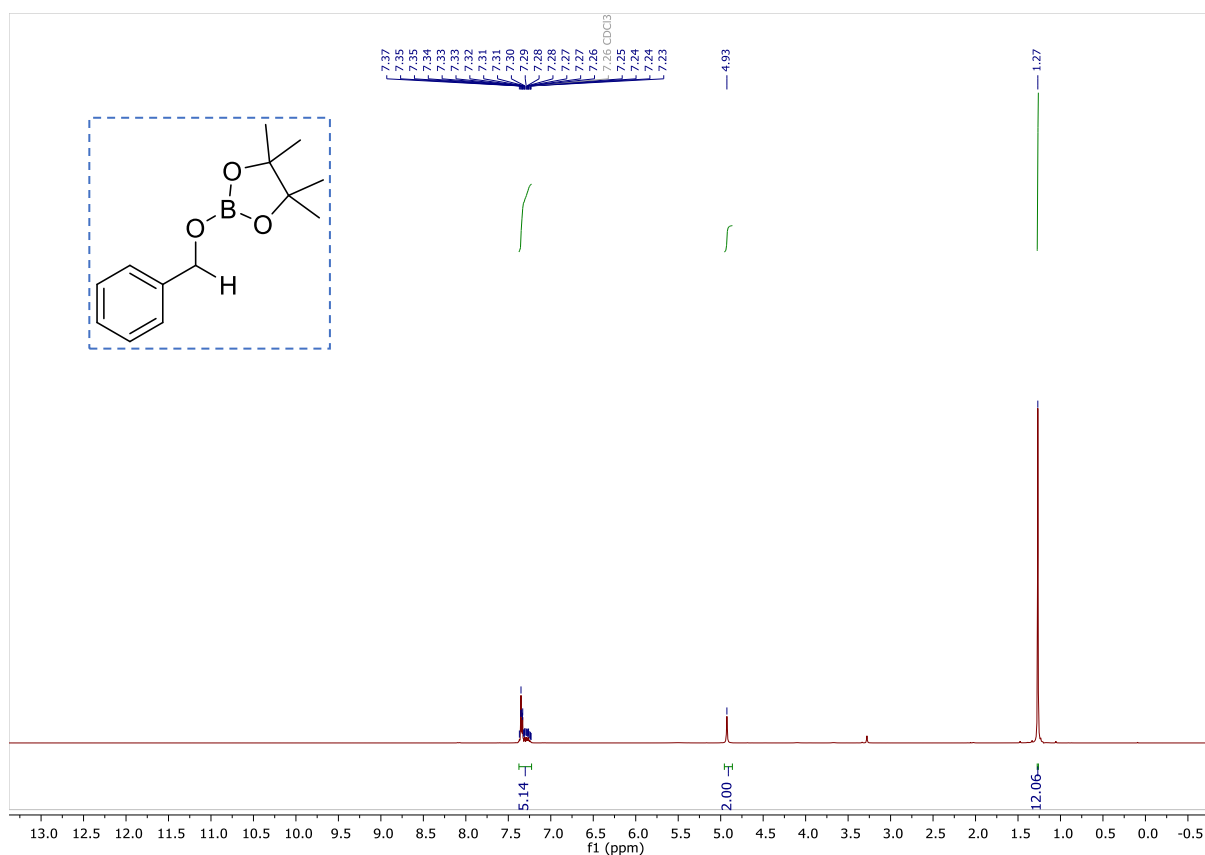


Figure S46 – ¹H NMR spectrum of **6a** from crude reaction mixture. *Excess of the HBpin.

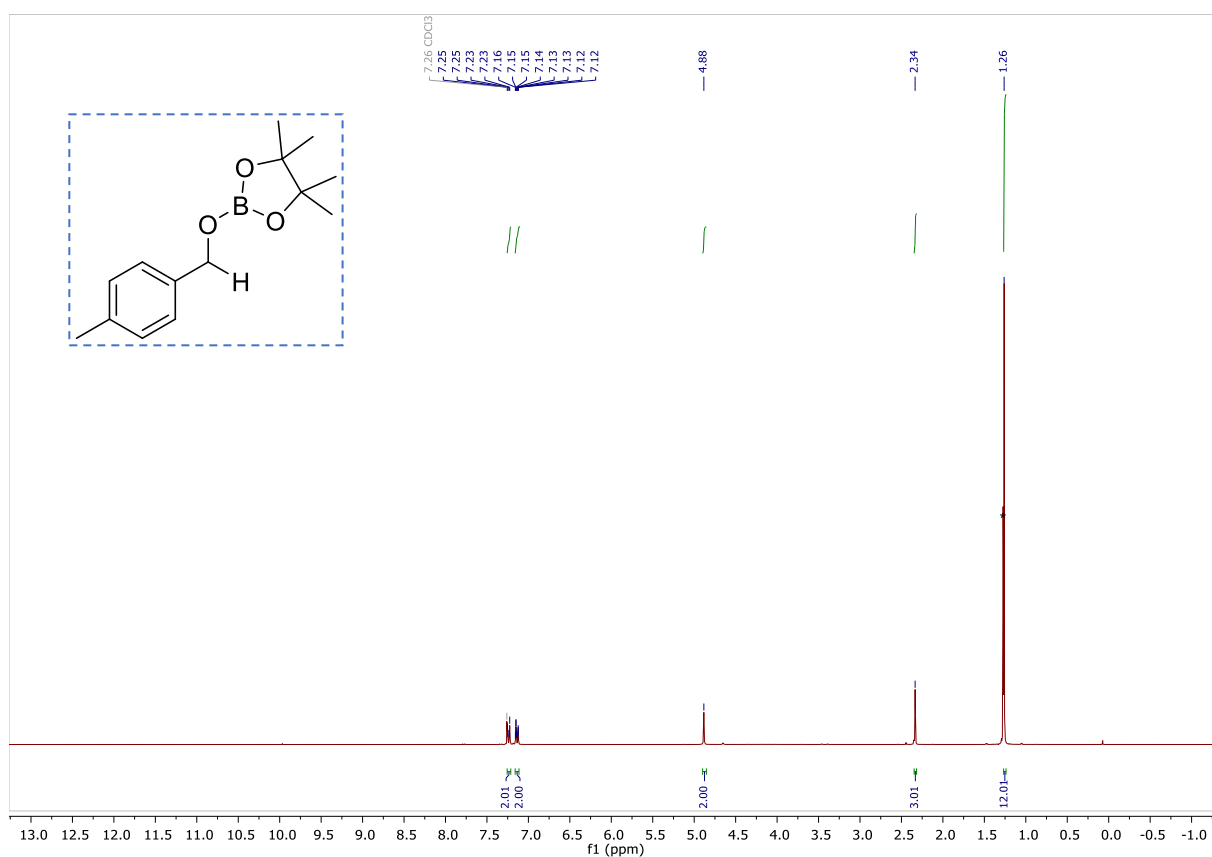


Figure S47 – ¹H NMR spectrum of **6b** from crude reaction mixture. *Excess of the HBpin.

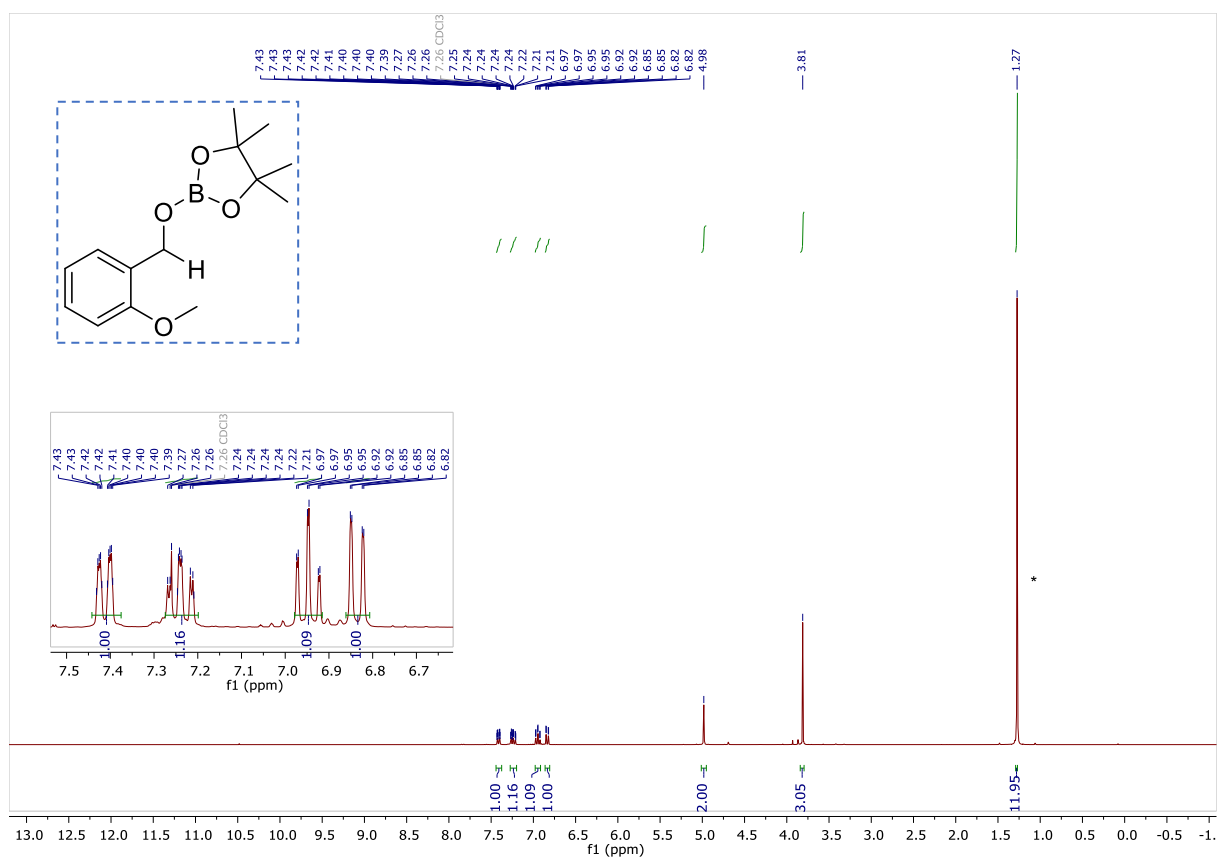


Figure S48 – ^1H NMR spectrum of **6c** from crude reaction mixture. *Excess of the HBpin.

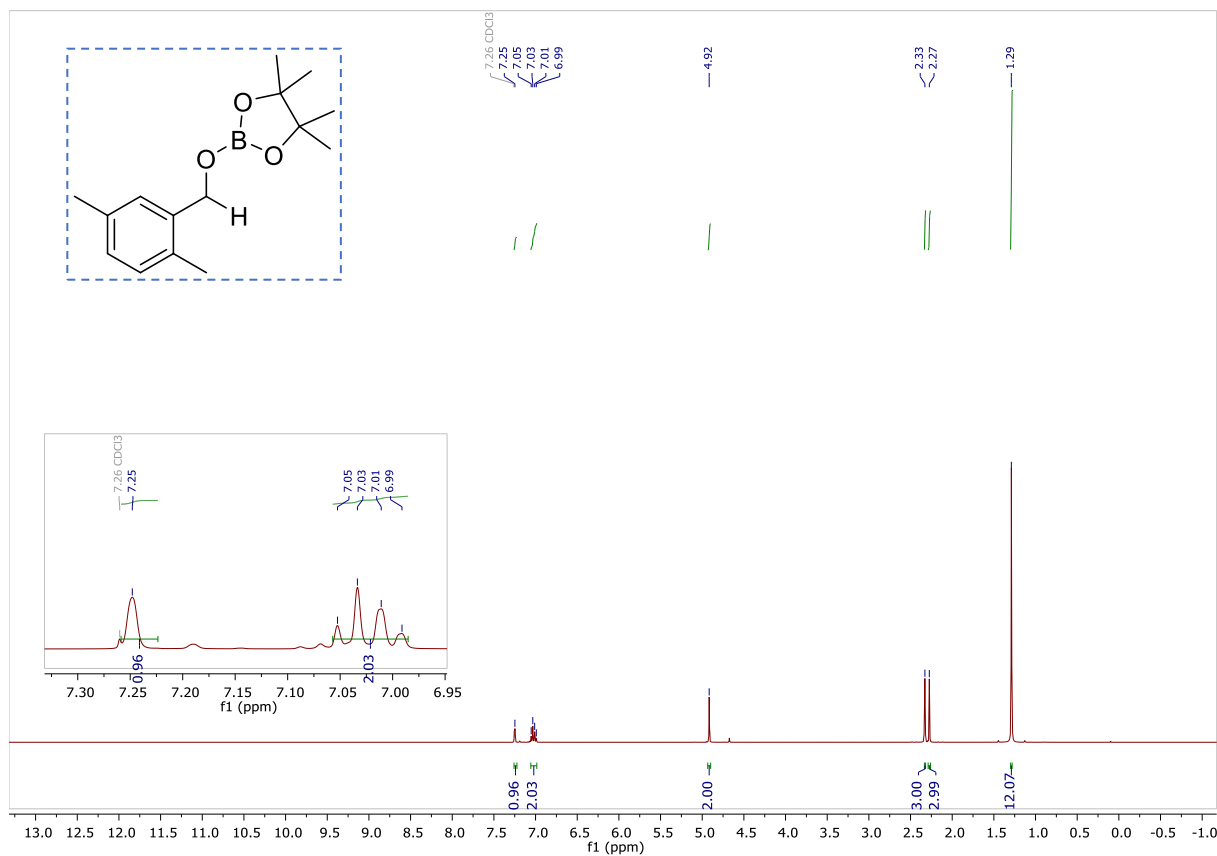


Figure S49 – ^1H NMR spectrum of **6d** from crude reaction mixture. *Excess of the HBpin.

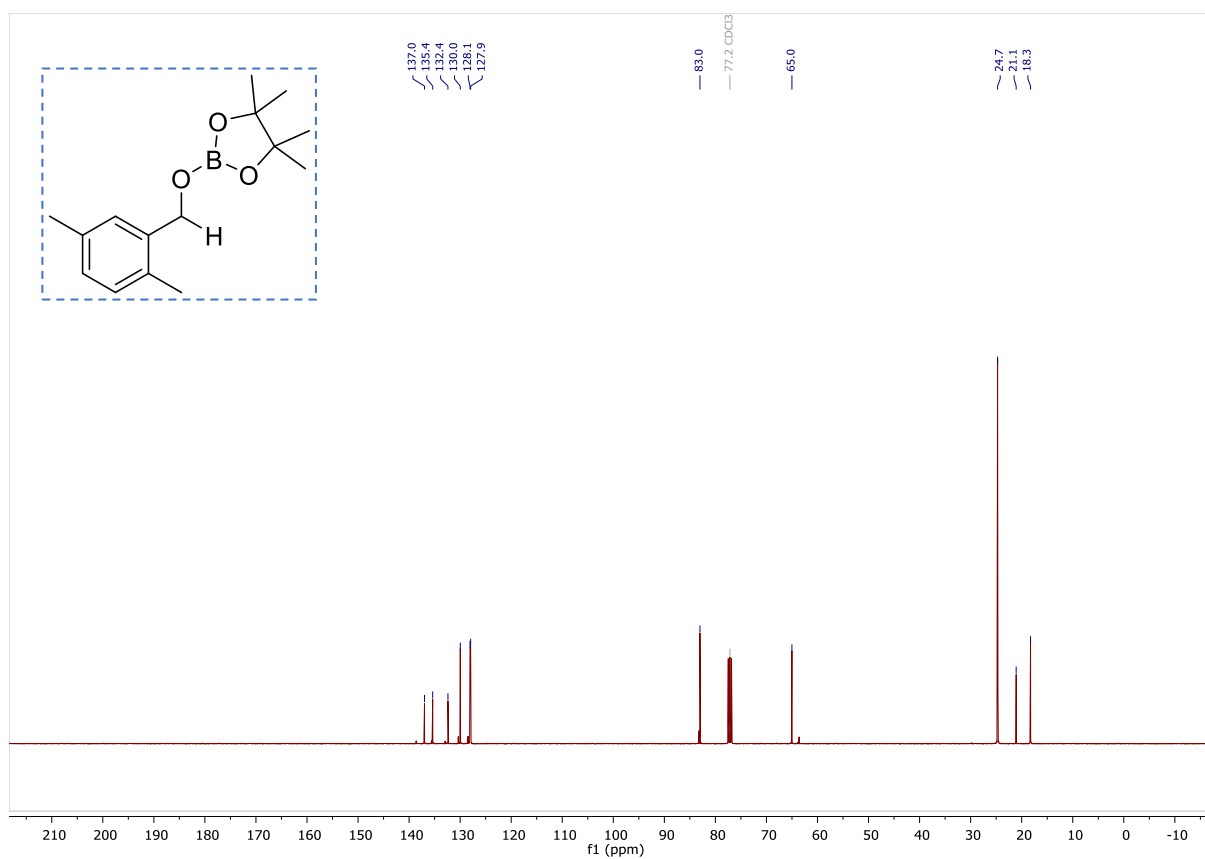


Figure S50 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6d**.

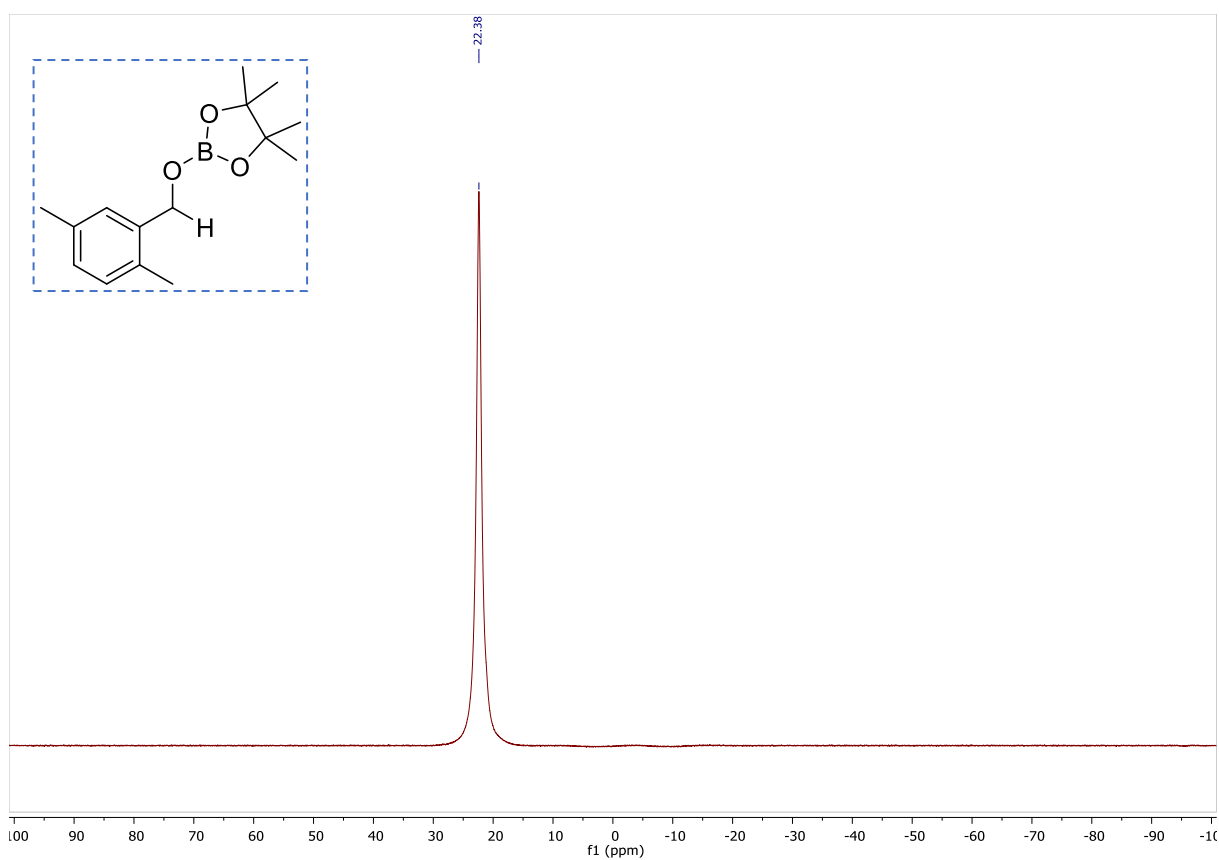


Figure S51 – ^{11}B NMR spectrum of **6d**.

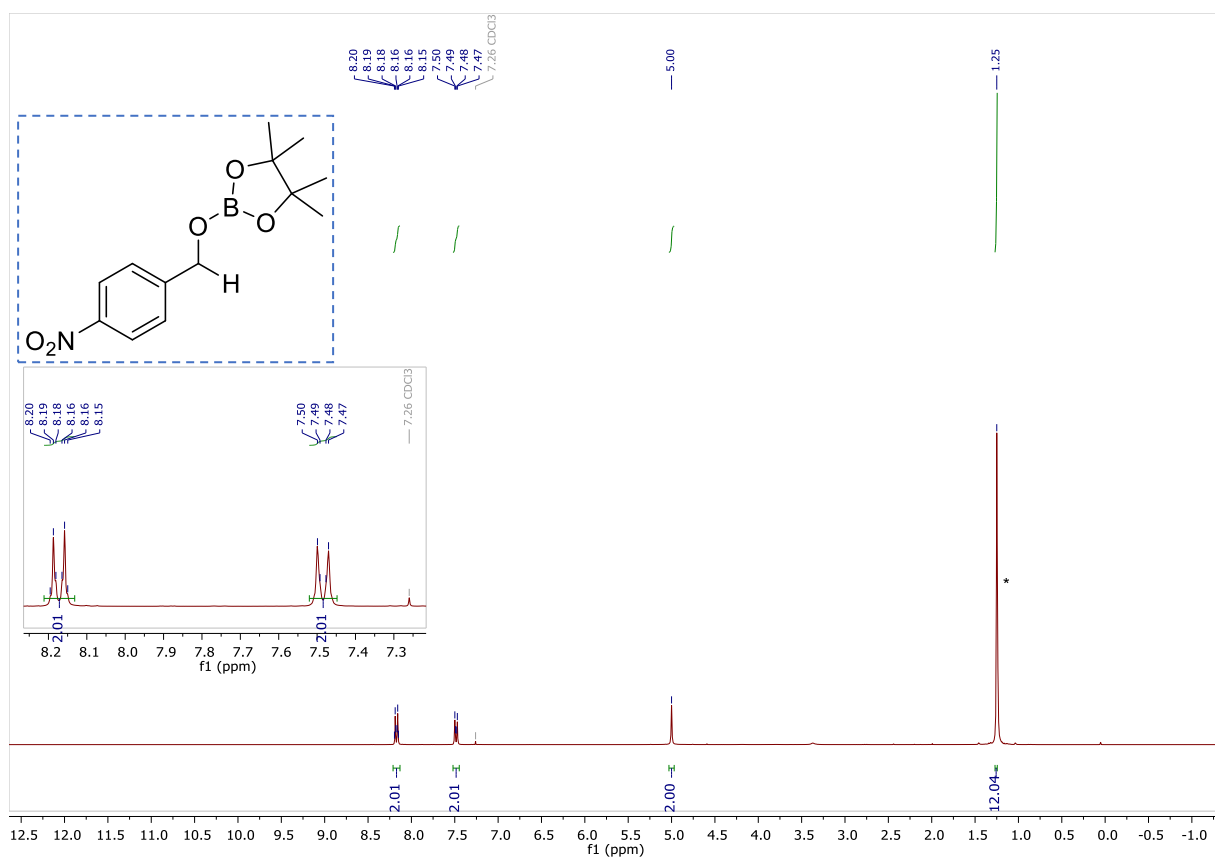


Figure S52 – ^1H NMR spectrum of **6e** from crude reaction mixture. *Excess of the HBpin.

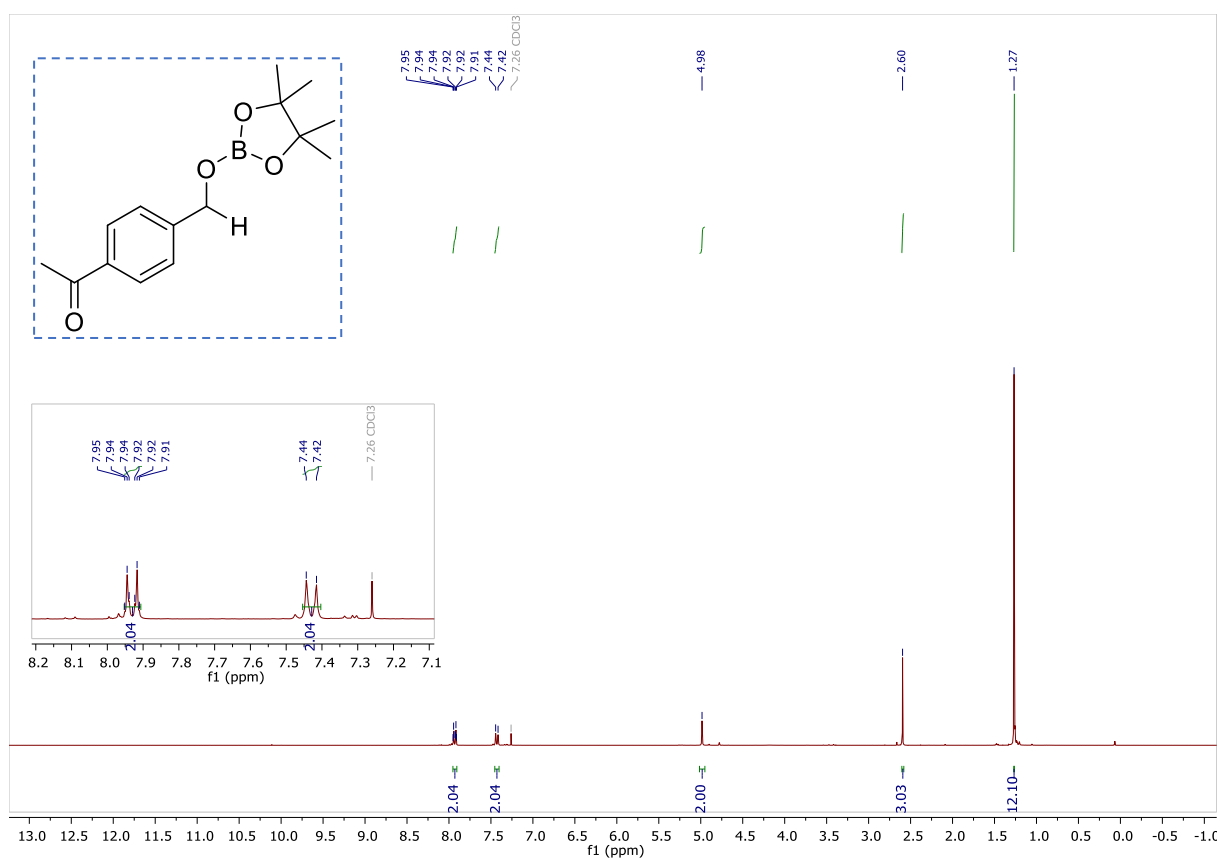


Figure S53 – ^1H NMR spectrum of **6f** from crude reaction mixture.

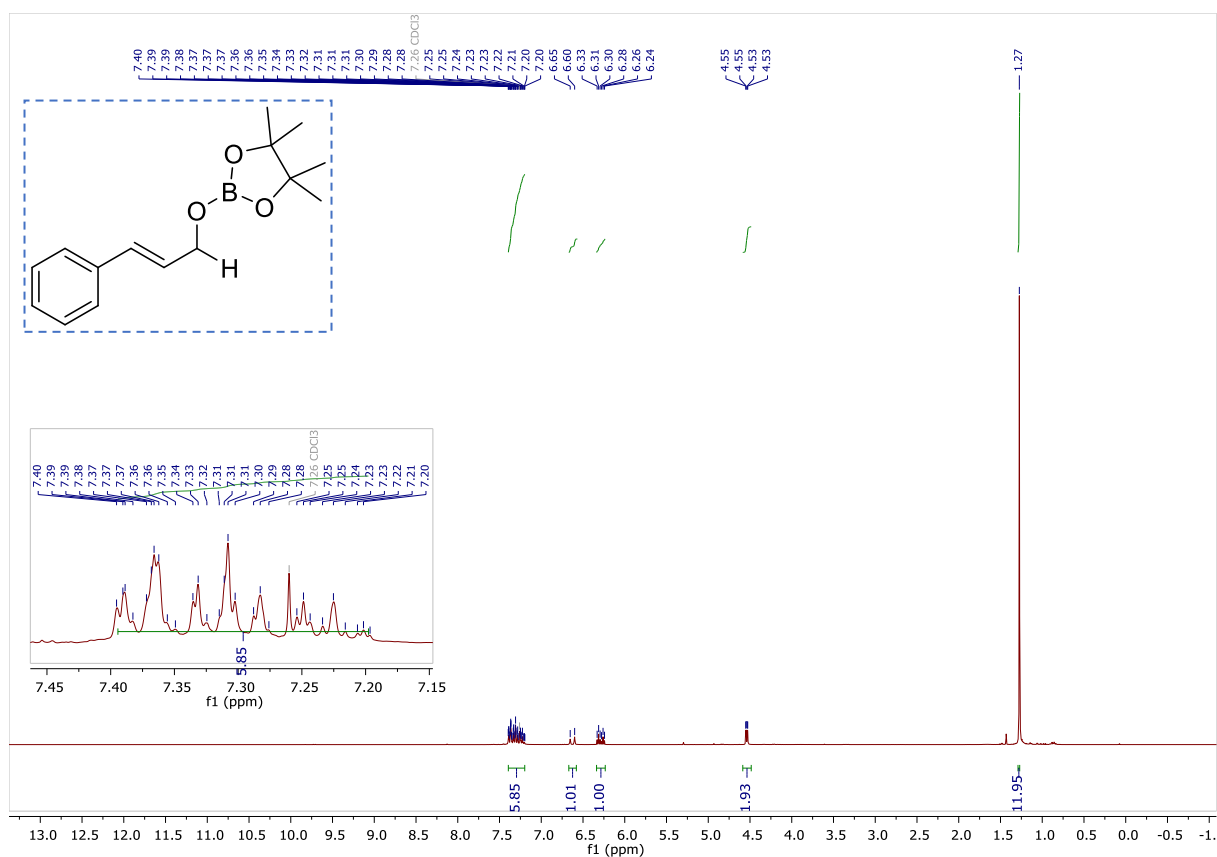


Figure S54 – ¹H NMR spectrum of **6g** from crude reaction mixture.

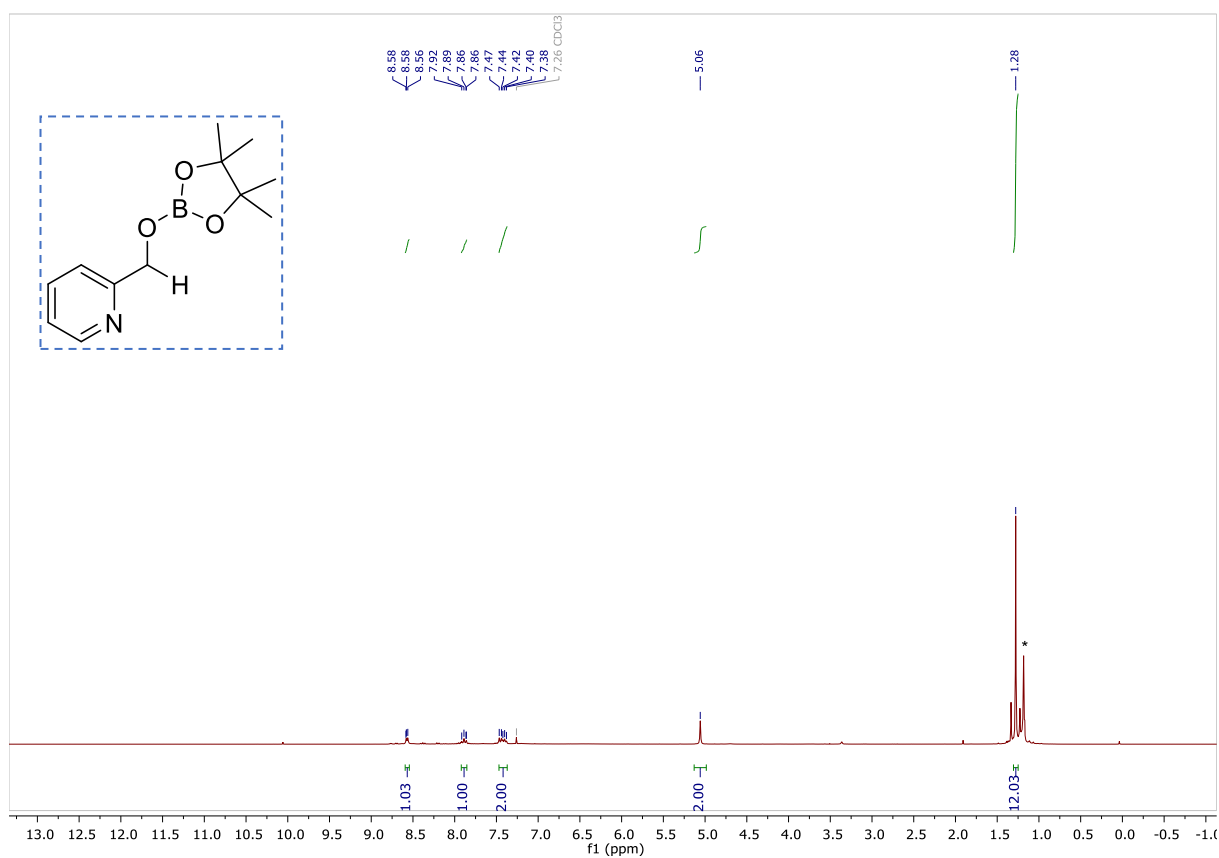


Figure S55 – ¹H NMR spectrum of **6h** from crude reaction mixture. *Excess of the HBpin.f

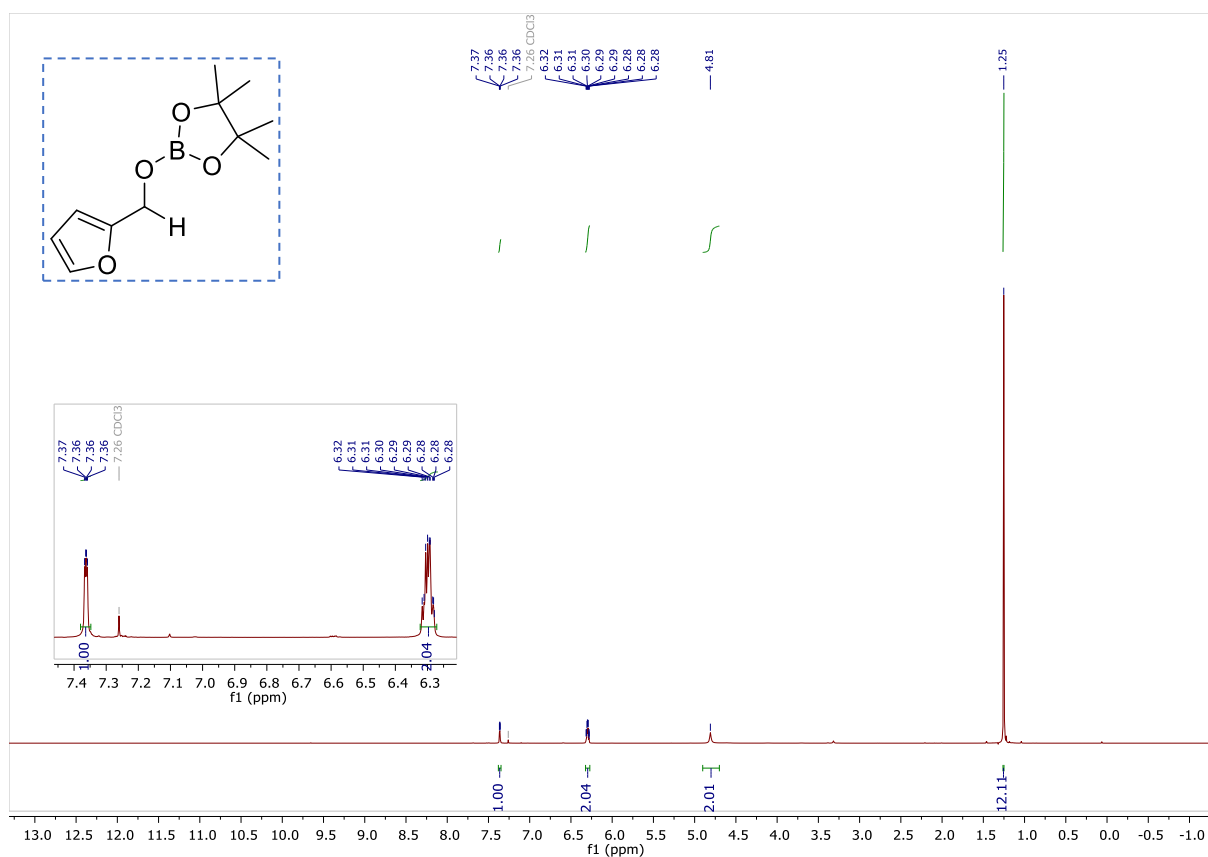


Figure S56 – ¹H NMR spectrum of **6i** from crude reaction mixture.

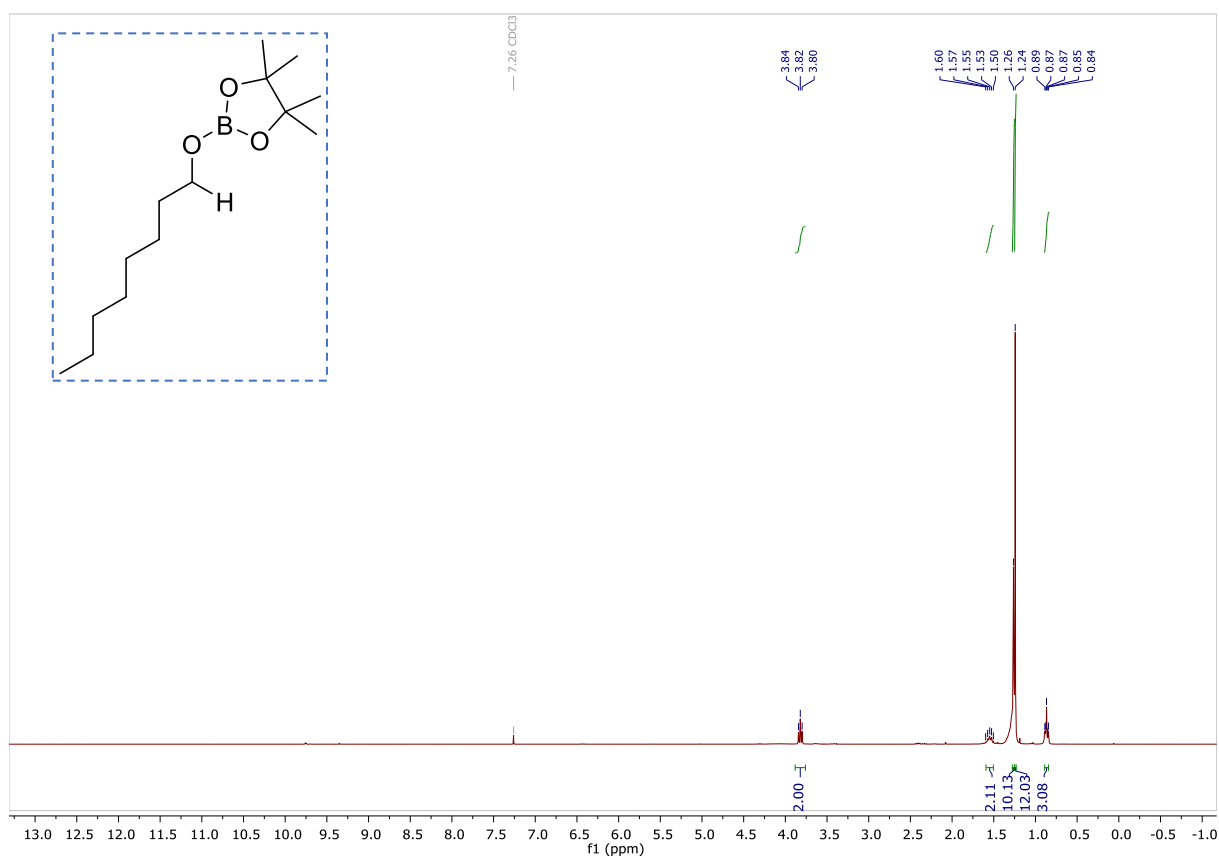


Figure S57 – ¹H NMR spectrum of **6j** from crude reaction mixture.

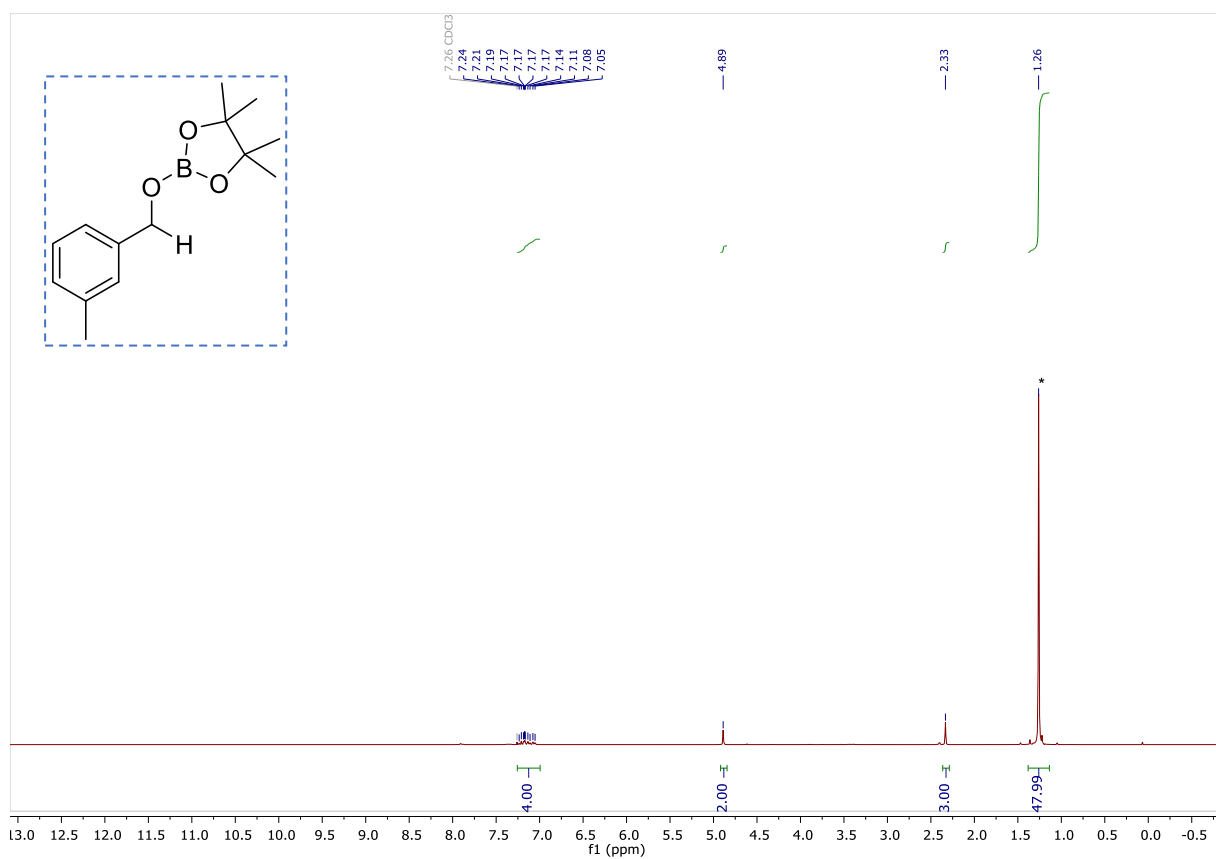


Figure S58 – ^1H NMR spectrum of **6k** from crude reaction mixture. *OB₂pin overlapped

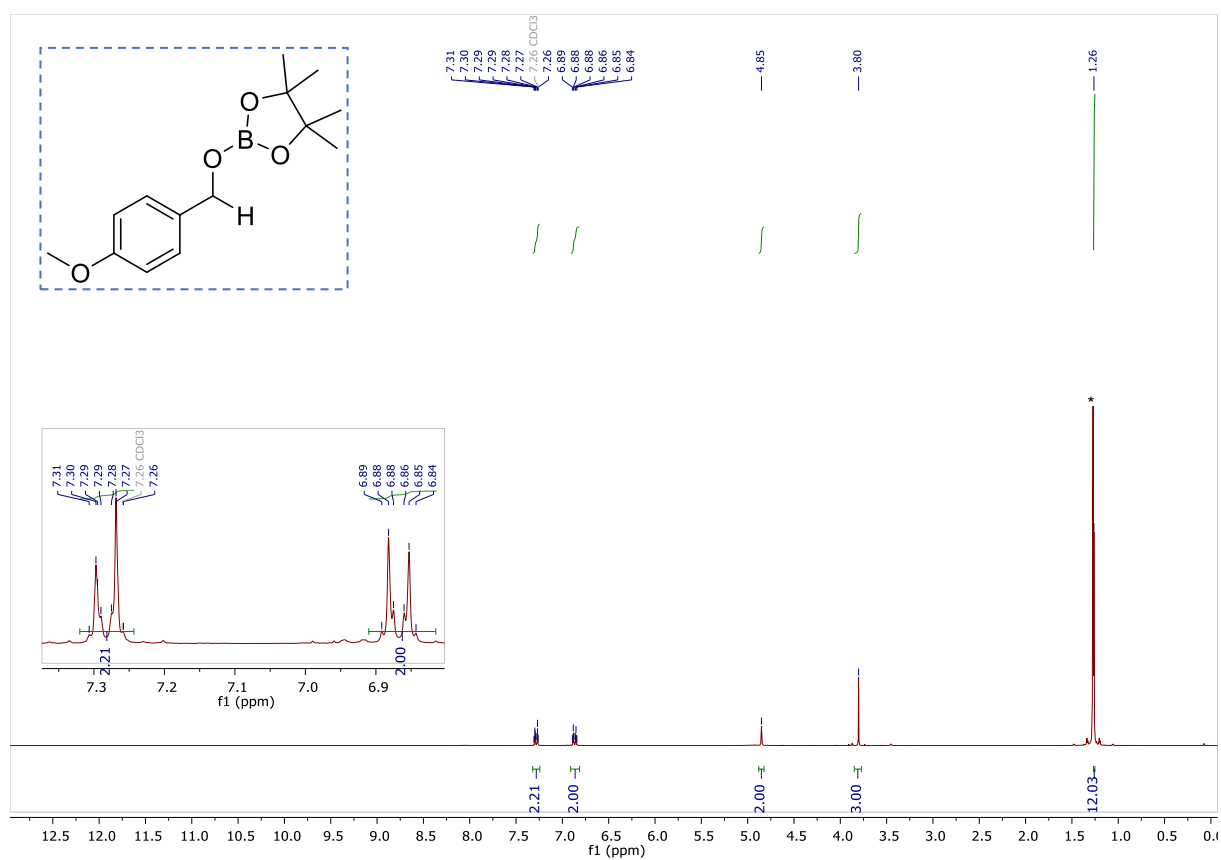


Figure S59 – ^1H NMR spectrum of **6l** from crude reaction mixture. *O(Bpin)₂

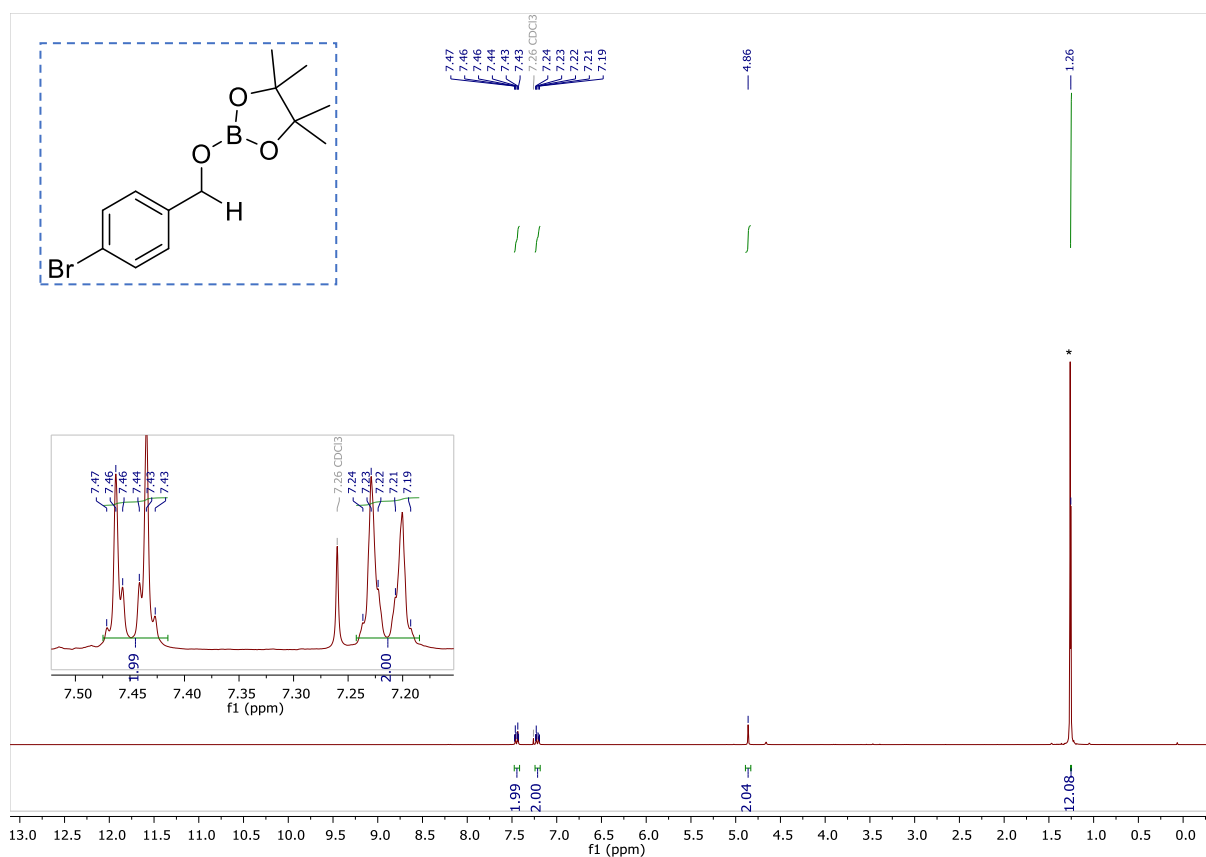


Figure S60 – ¹H NMR spectrum of **6m** from crude reaction mixture. *O(Bpin)₂

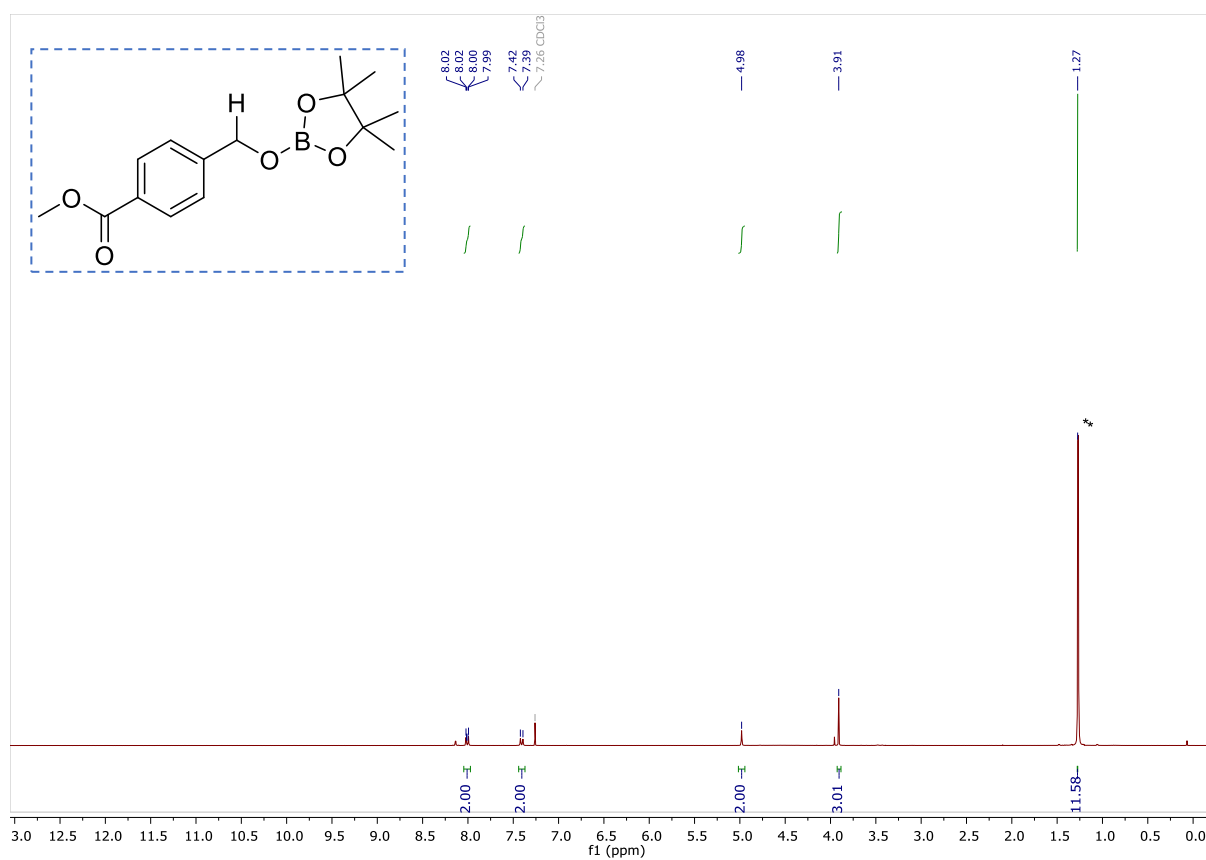


Figure S61 – ¹H NMR spectrum of **6n** from crude reaction mixture. *O(Bpin)₂

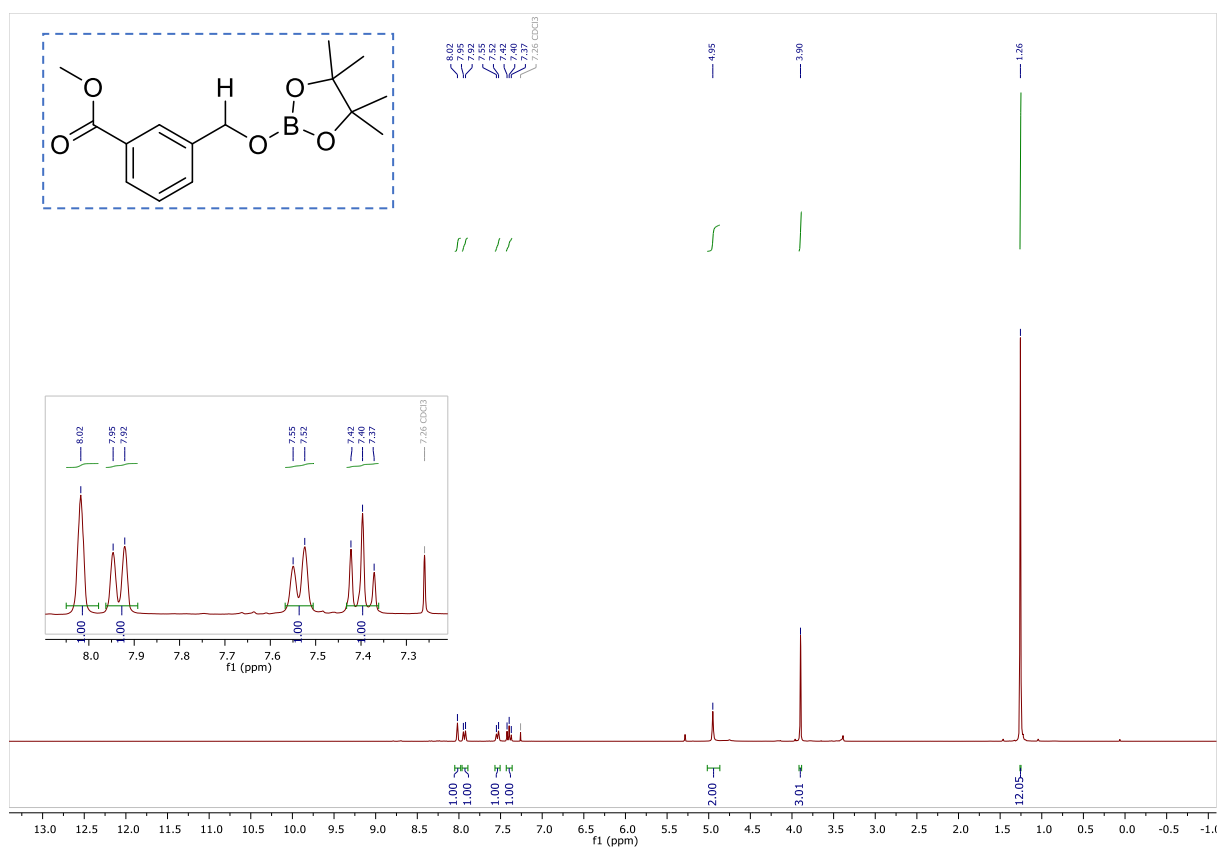


Figure S62 – ¹H NMR spectrum of **6o**.

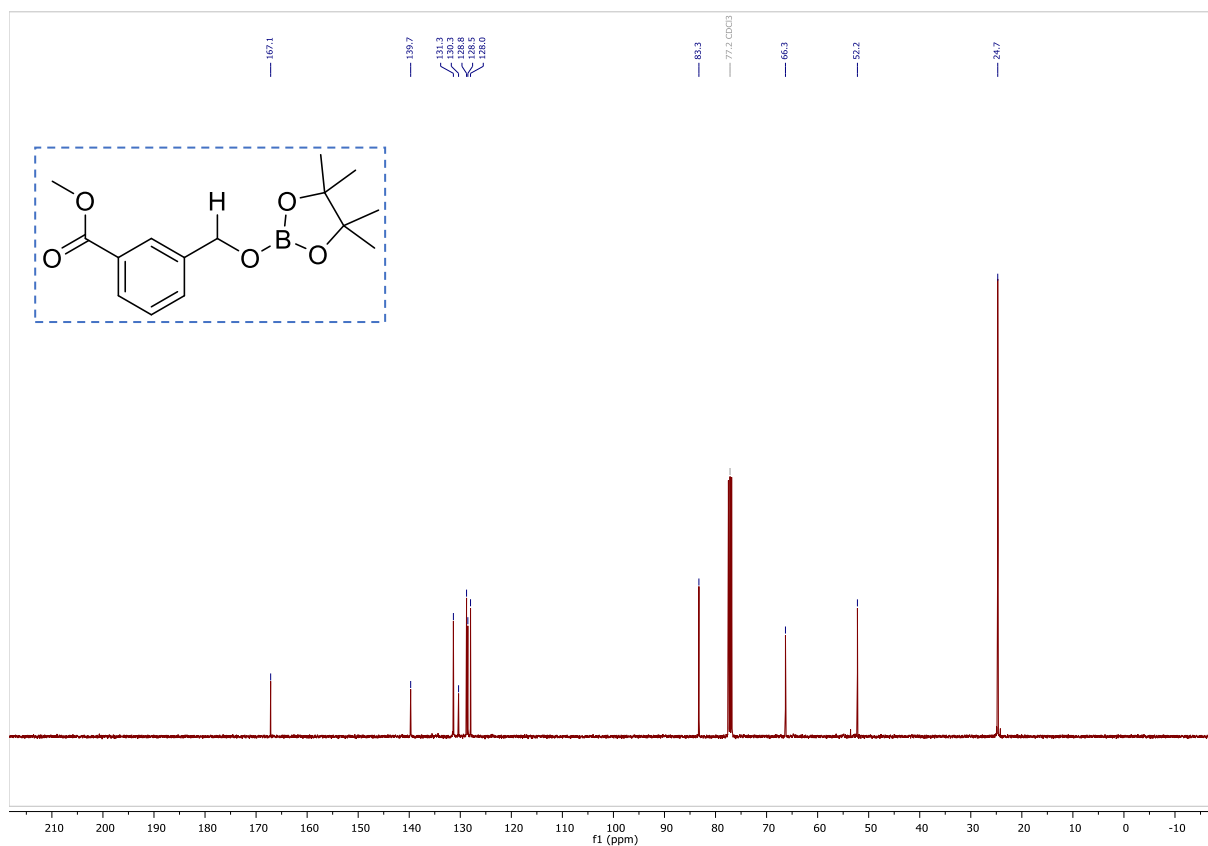


Figure S63 – ¹³C{¹H} NMR spectrum of **6o**.

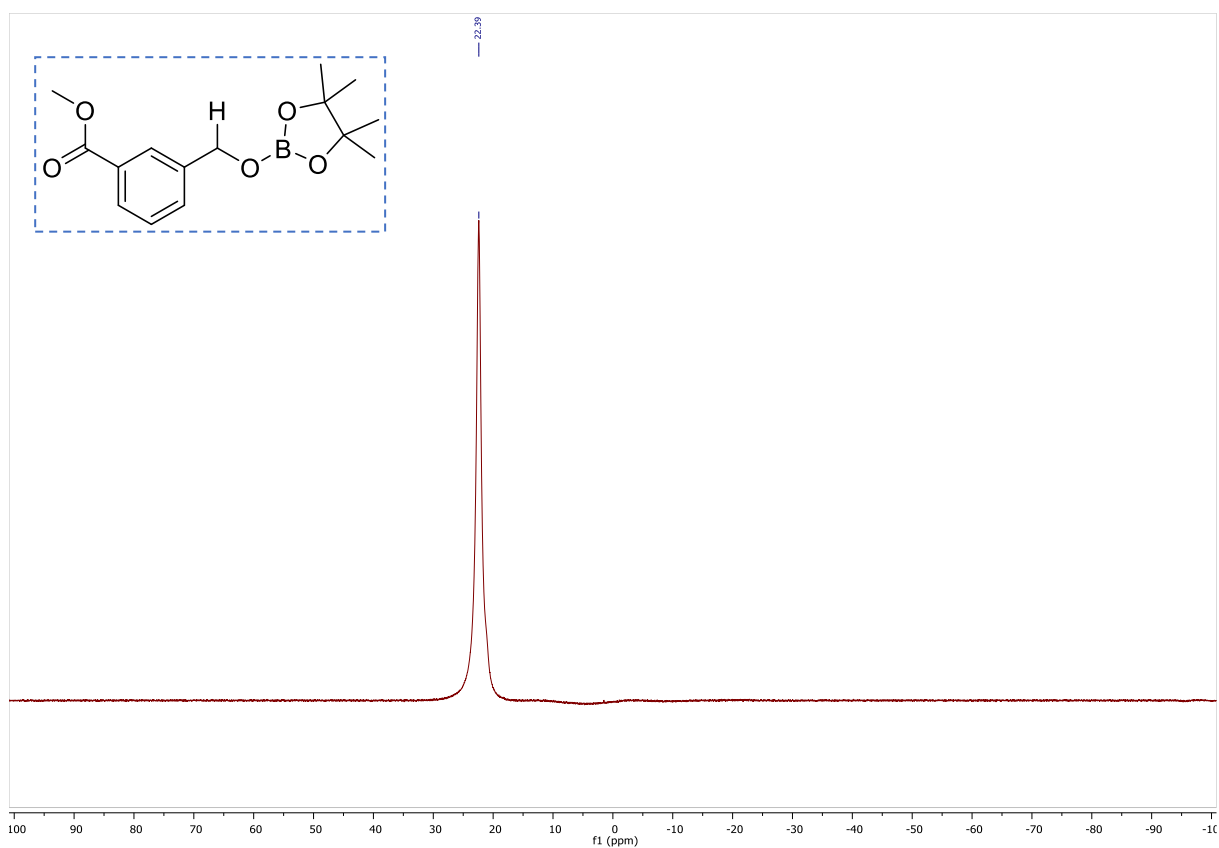


Figure S64 – ^{11}B NMR spectrum of **6o**.

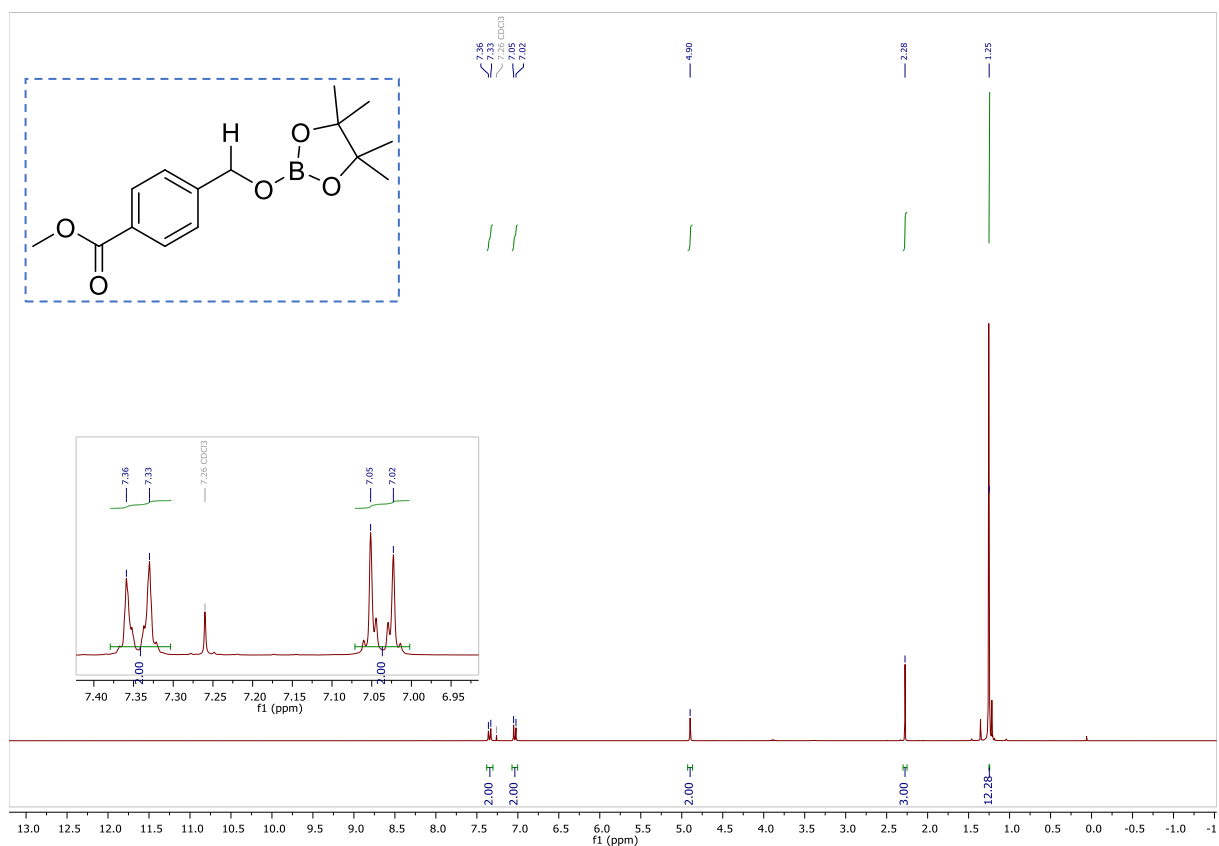


Figure S65 – ^1H NMR spectrum of **6p** from crude reaction mixture.

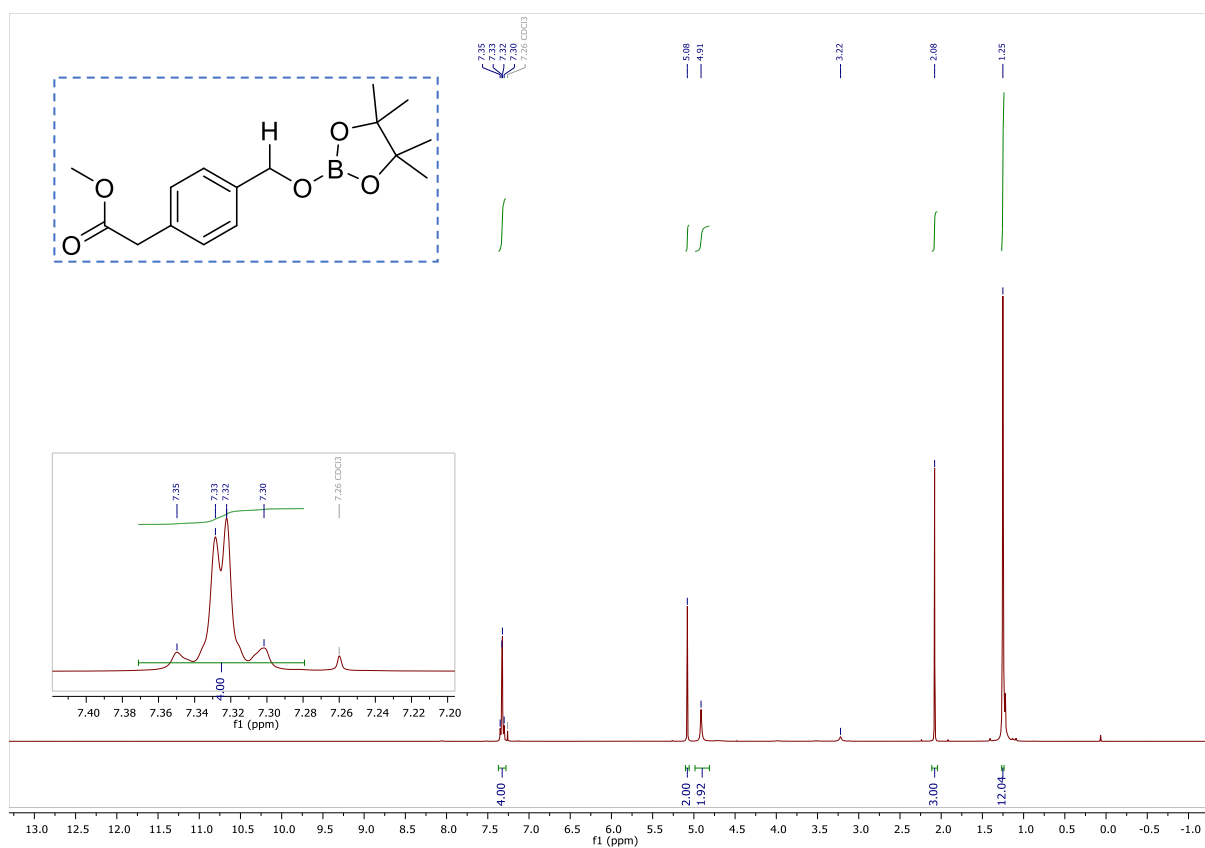


Figure S66 – ¹H NMR spectrum of **6q**.

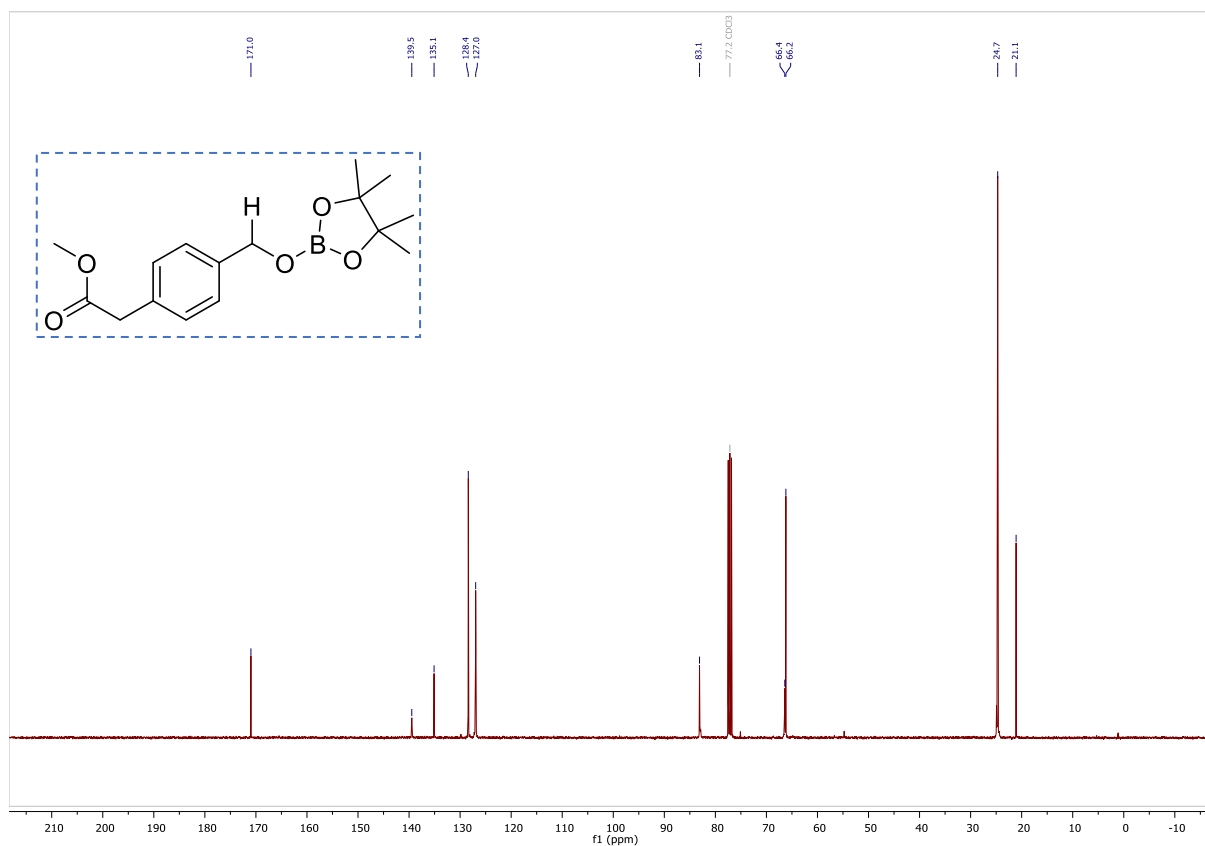


Figure S67 – ¹³C{¹H} NMR spectrum of **6q**.

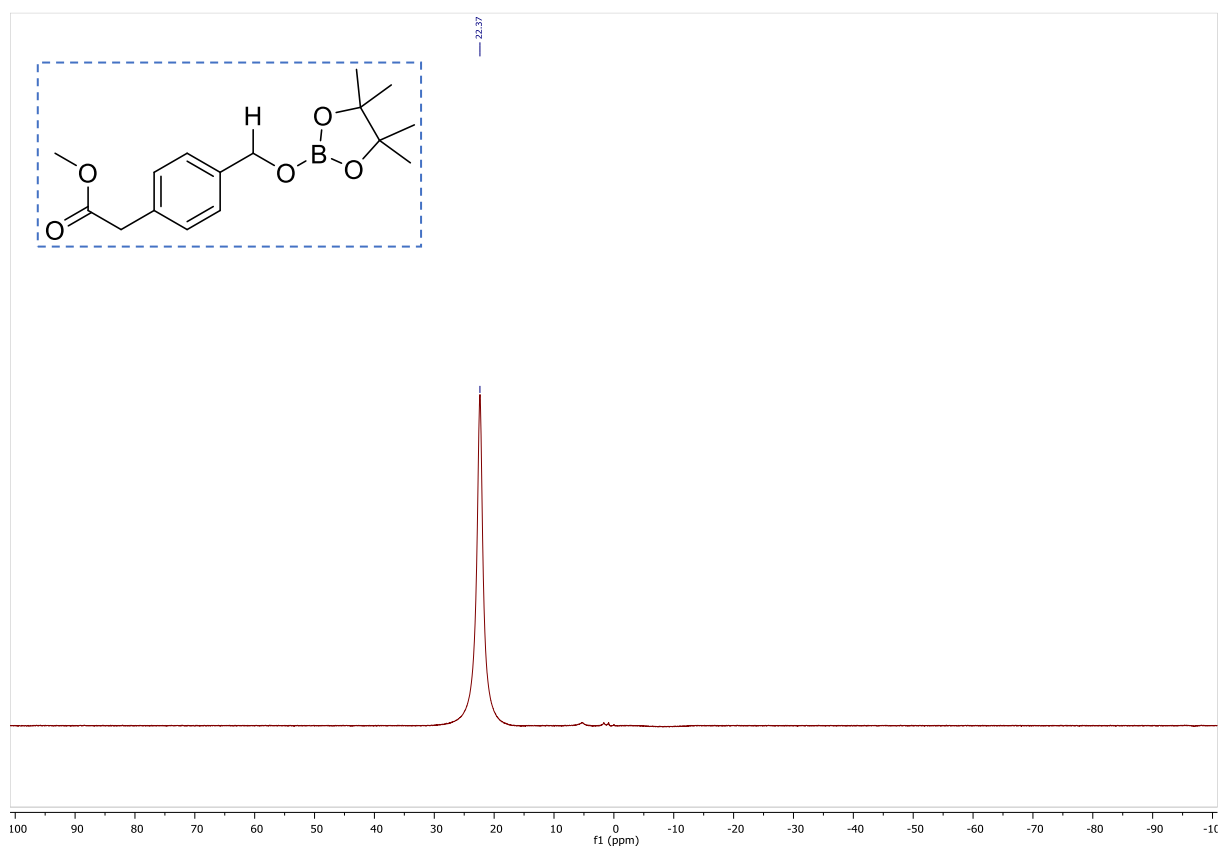


Figure S68 – ^{11}B NMR spectrum of **6q**.

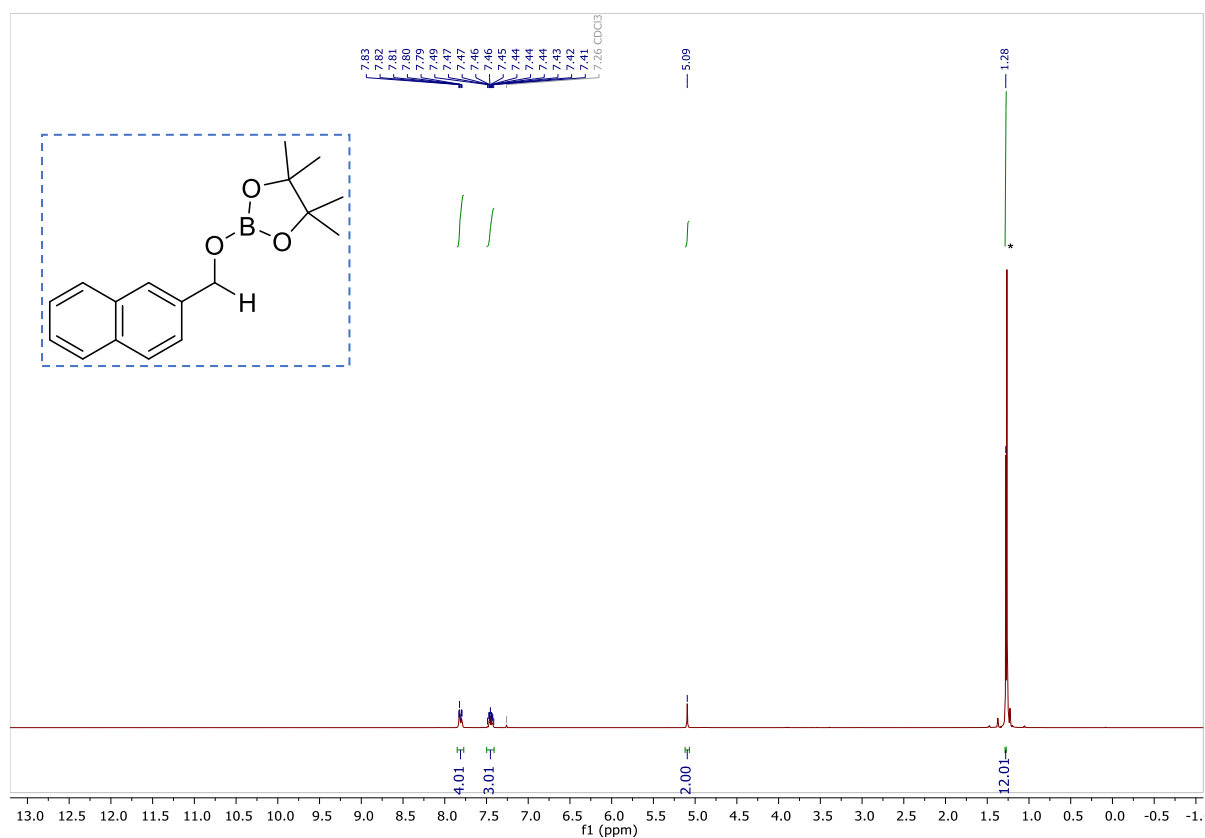


Figure S69 – ^1H NMR spectrum of **6r** from crude reaction mixture. * $\text{O}(\text{Bpin})_2$.

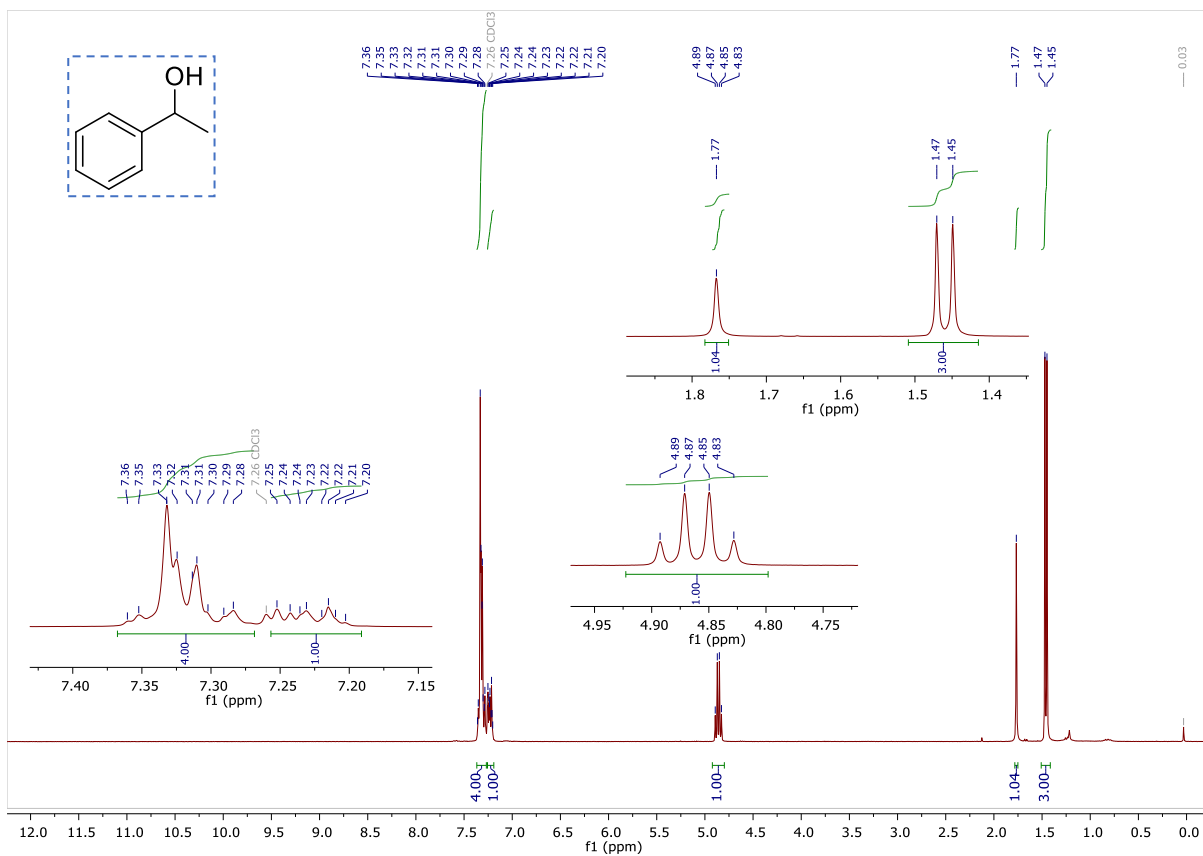


Figure S70 – ¹H NMR spectrum of 4a.

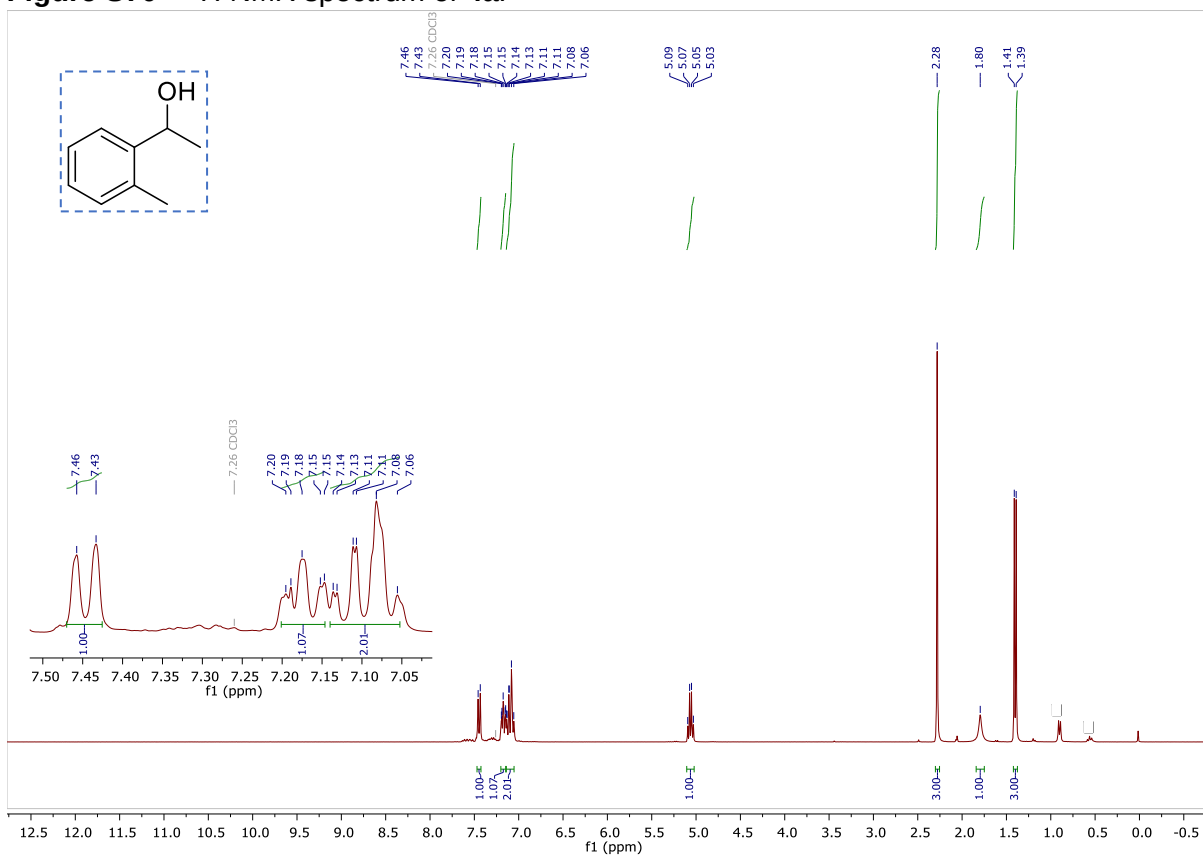


Figure S71 – ¹H NMR spectrum of 4b. □ Undefined impurities

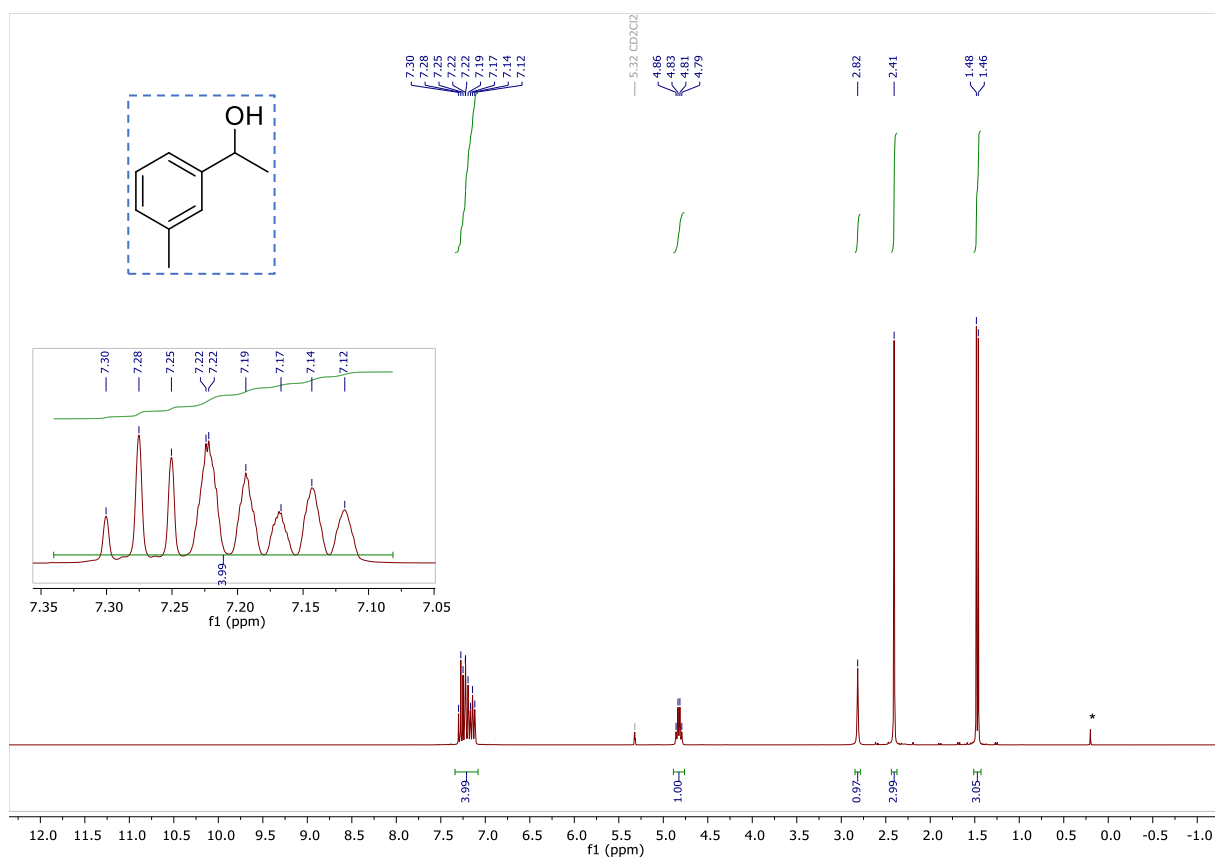


Figure S72 – ^1H NMR spectrum of **4c.*** - Grease.

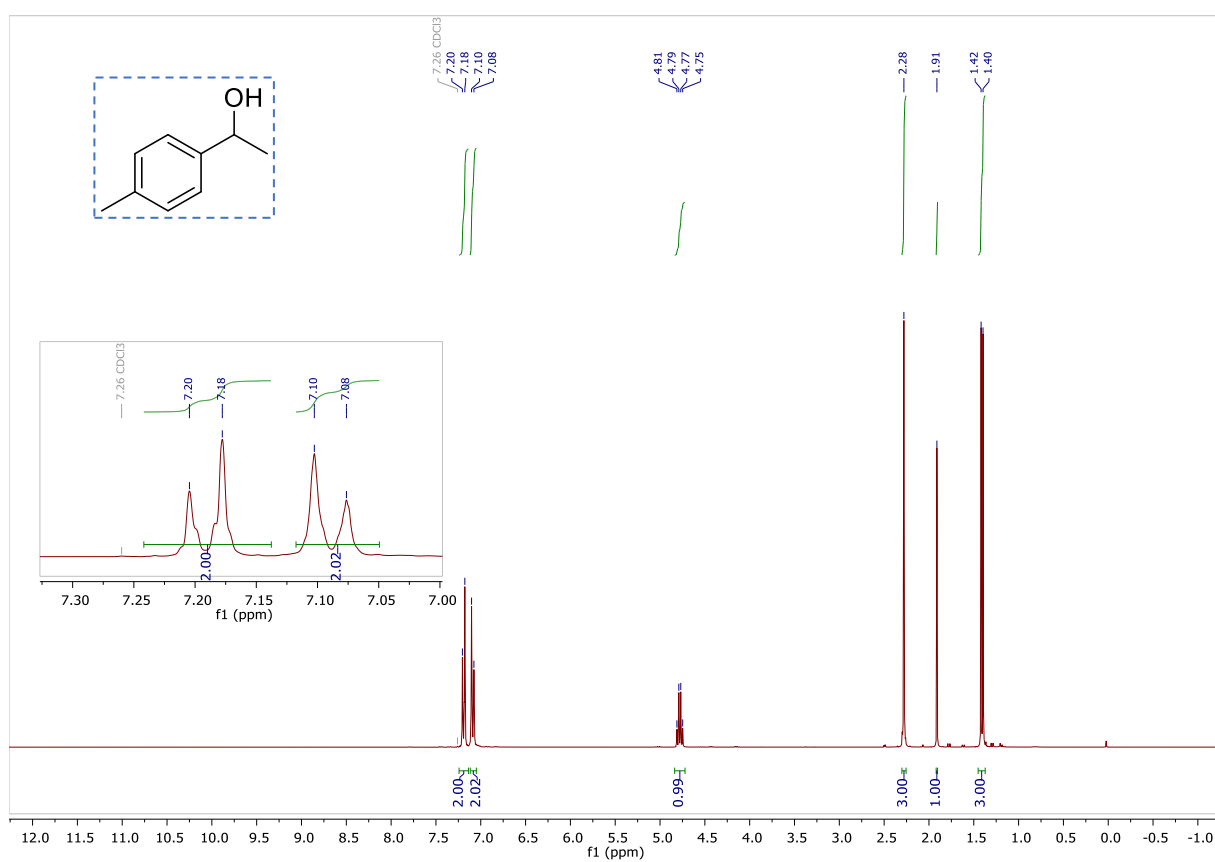


Figure S73 – ^1H NMR spectrum of **4d**.

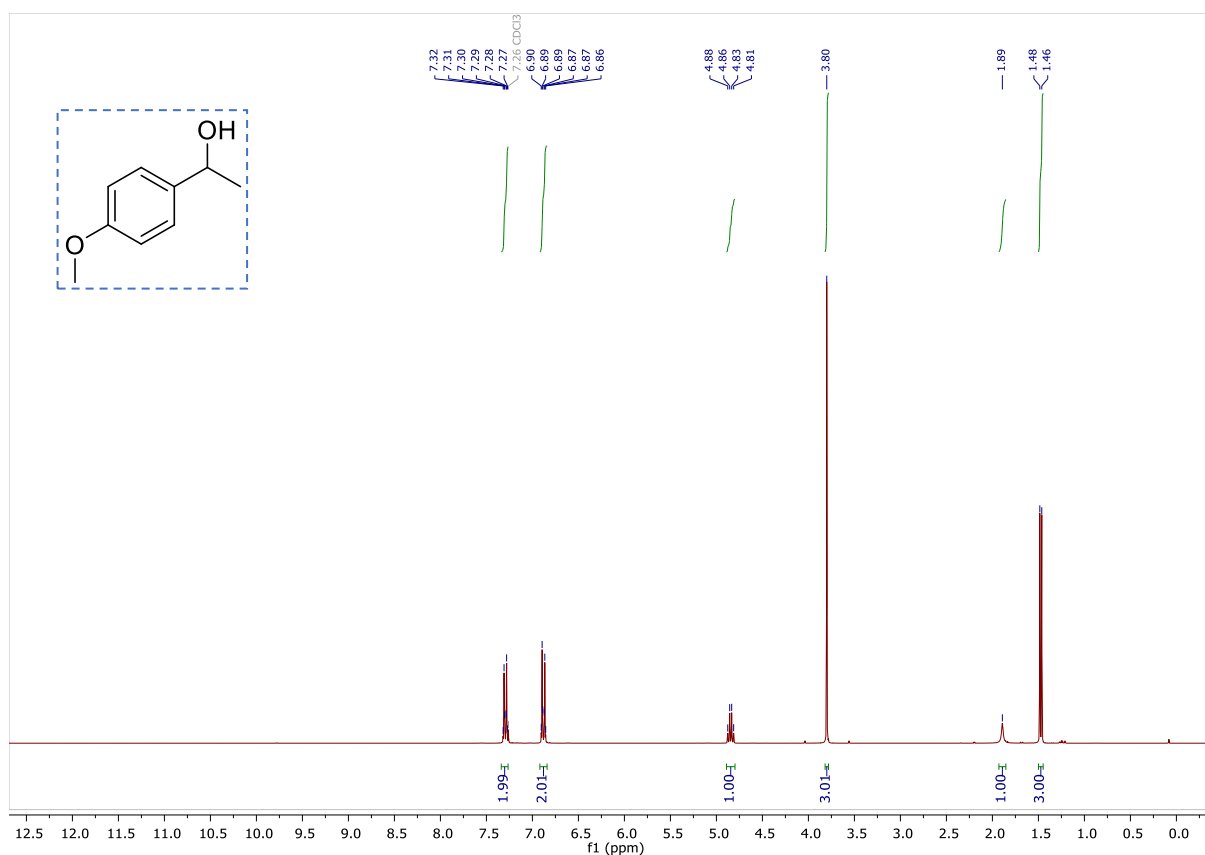


Figure S74 – ¹H NMR spectrum of 4e.

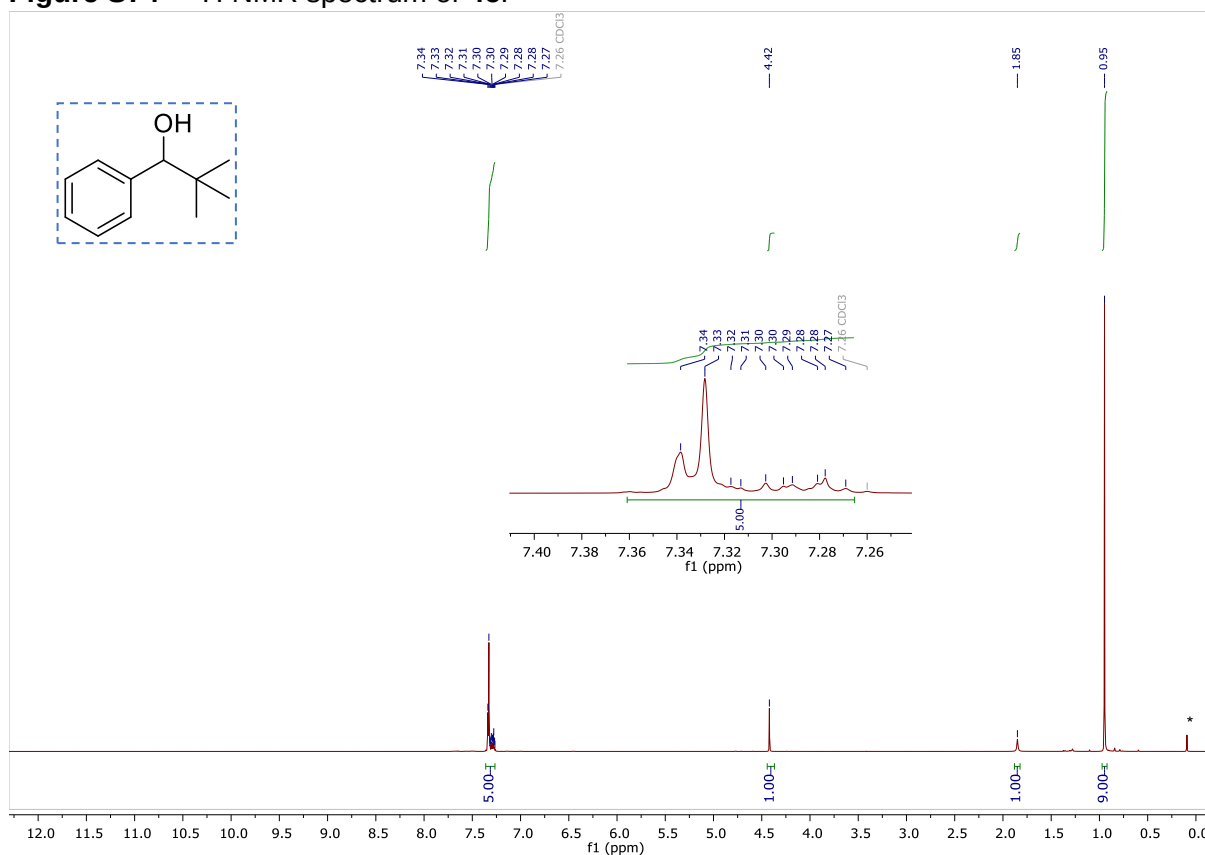


Figure 75 – ¹H NMR spectrum of 4f. * - Grease.

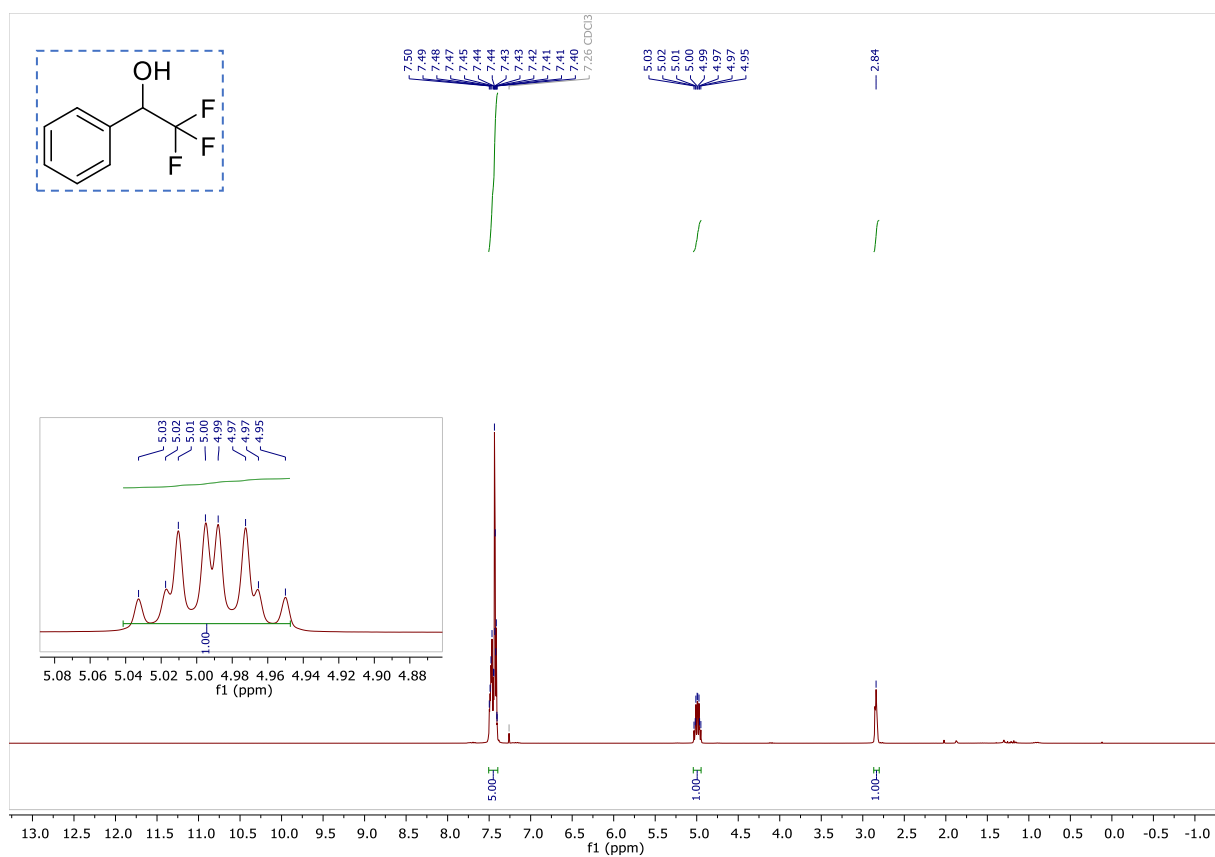


Figure S76 – ¹H NMR spectrum of 4g.

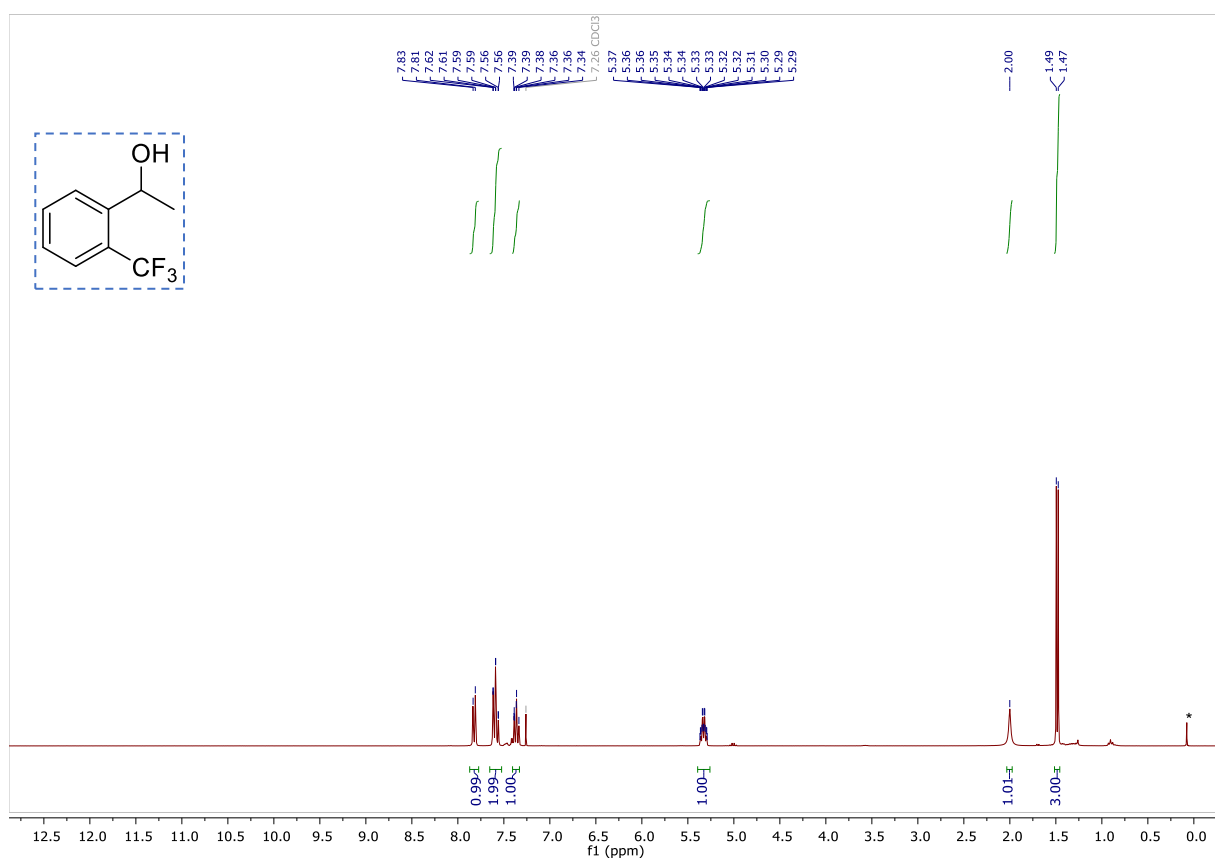


Figure S77 – ¹H NMR spectrum of 4h. * - Grease.

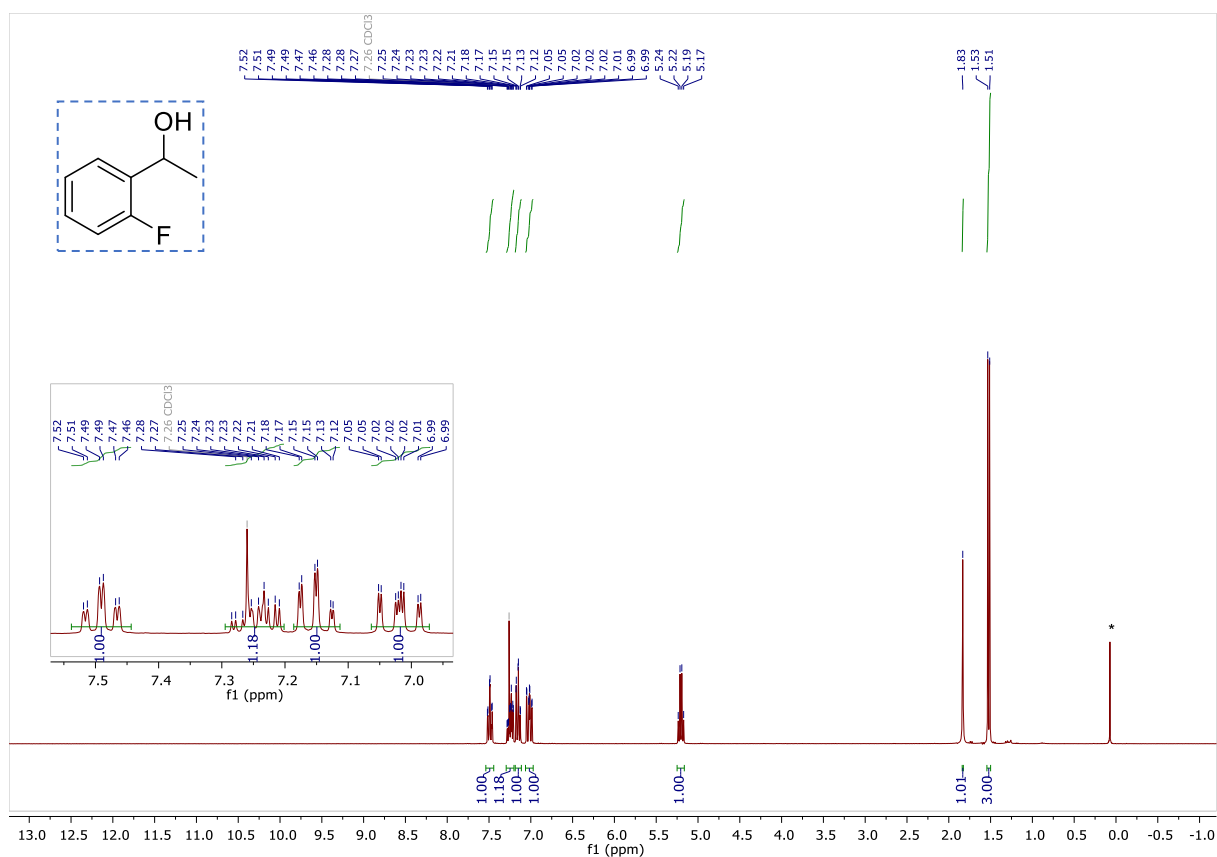


Figure S78 – ¹H NMR spectrum of **4i**. * - Grease.

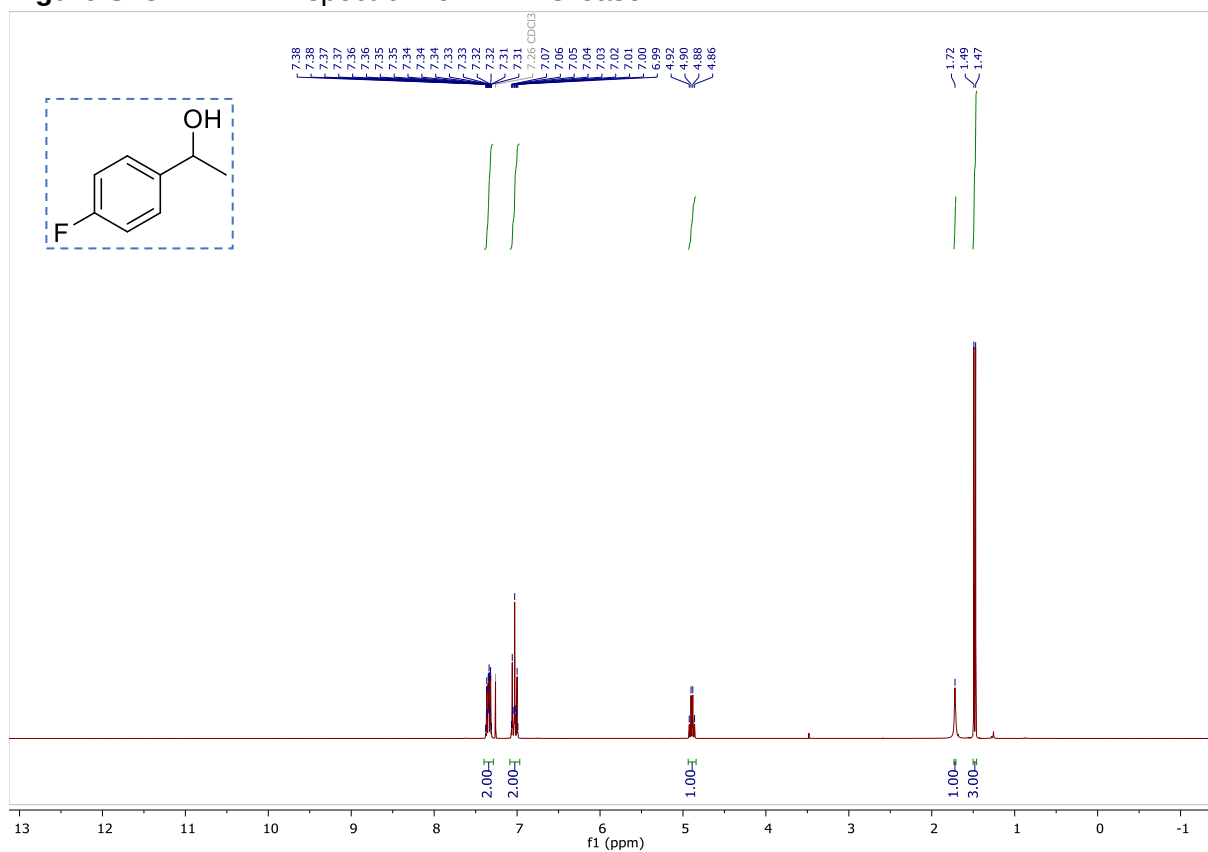
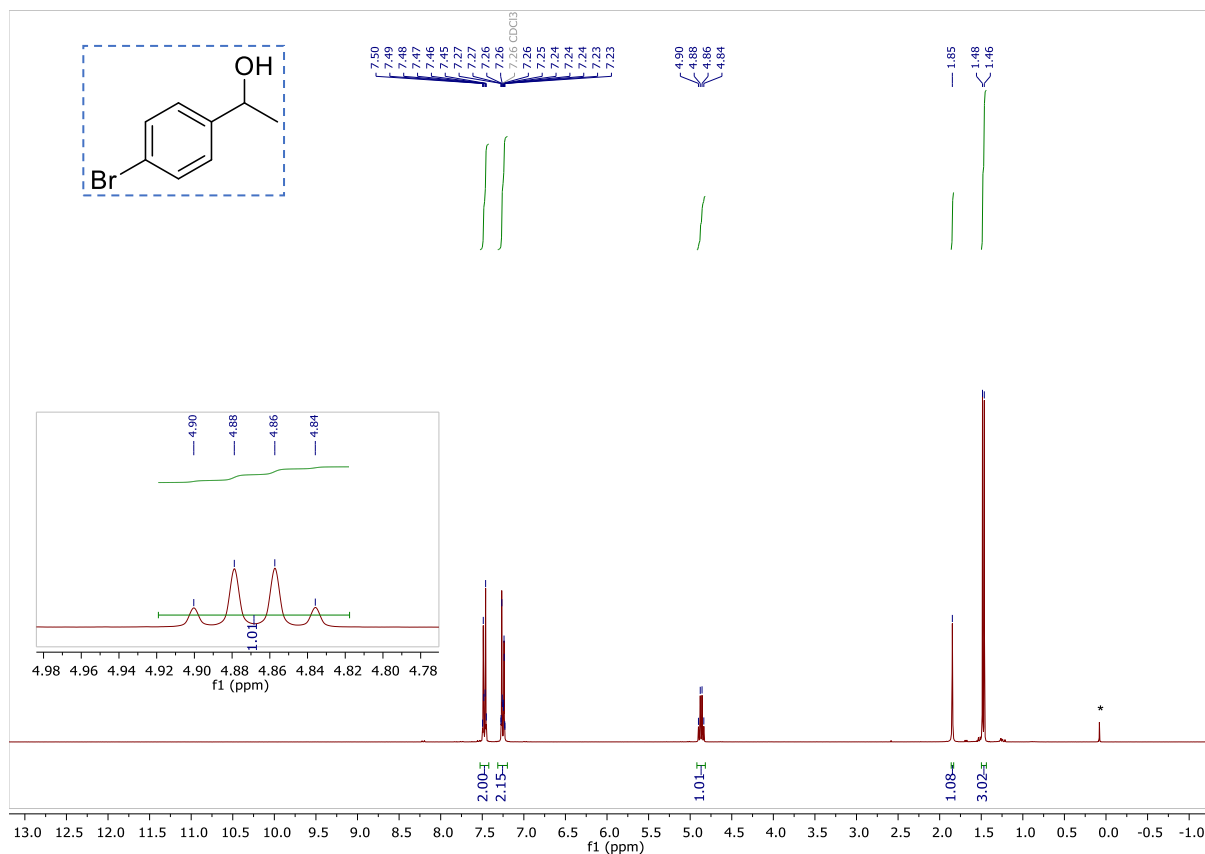
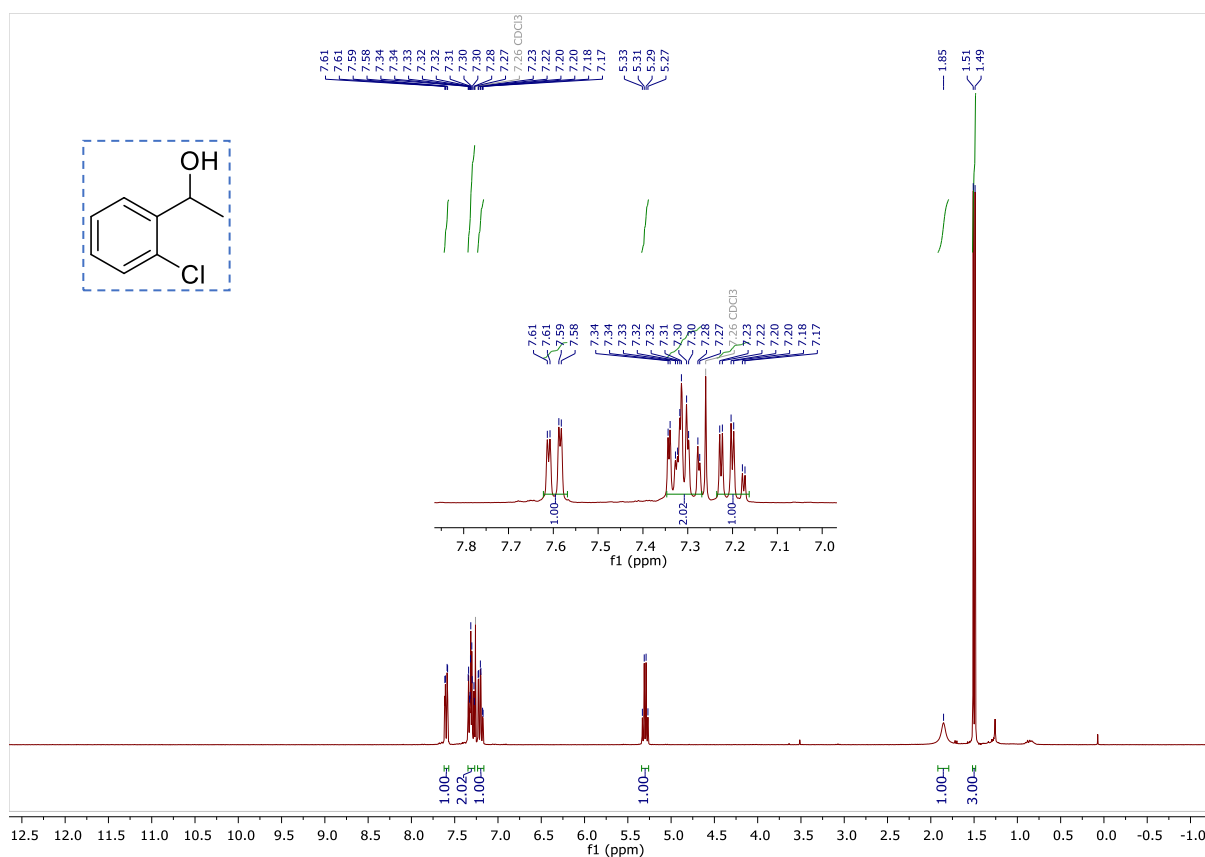


Figure S79 – ¹H NMR spectrum of **4j**. * - Grease.



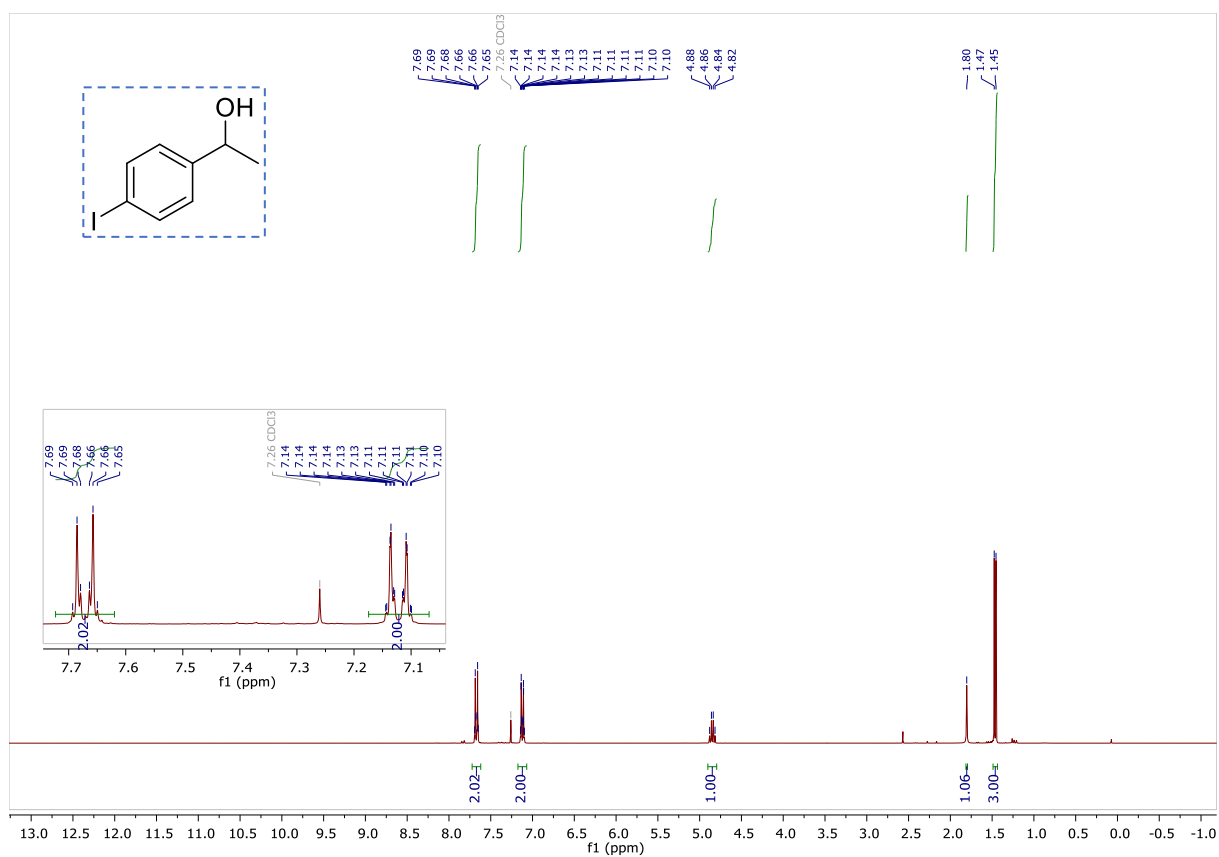


Figure S82 – ¹H NMR spectrum of 4m.

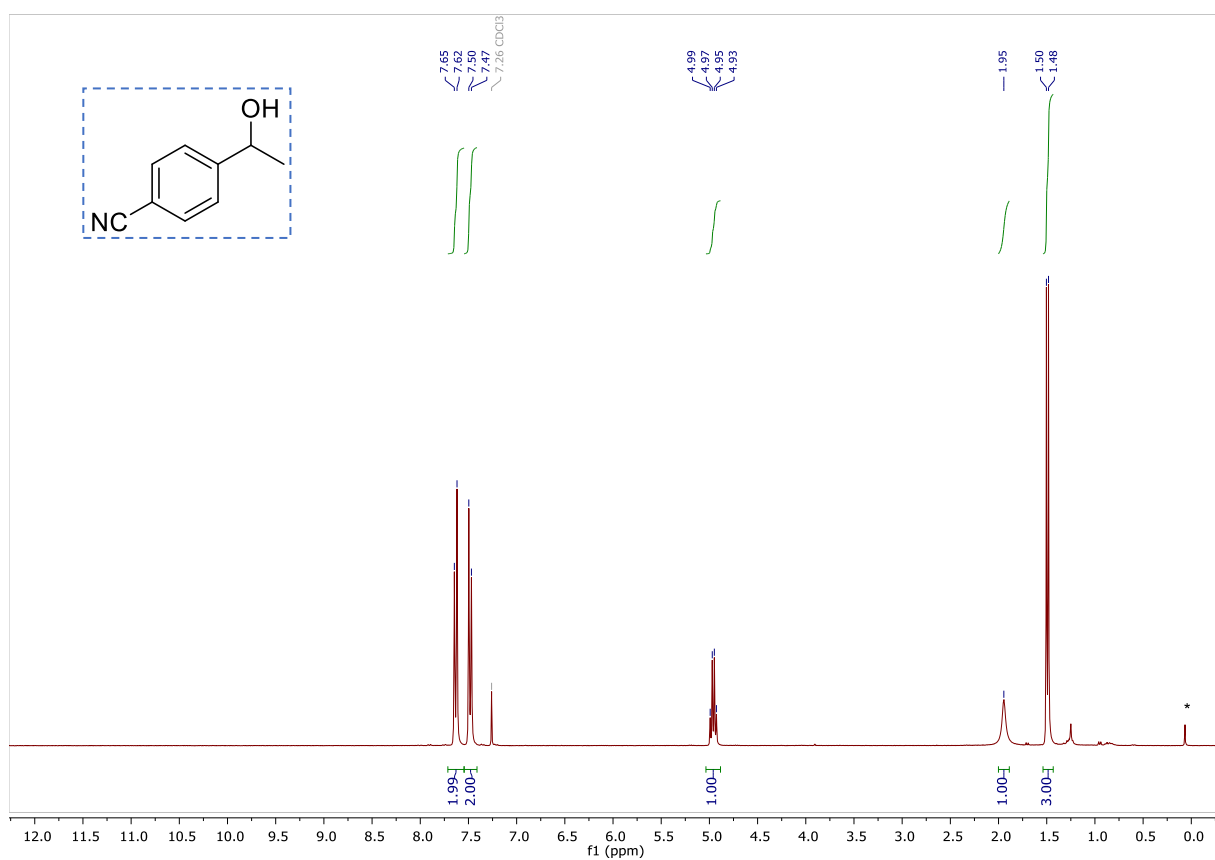


Figure S83 – ¹H NMR spectrum of 4n. * - Grease.

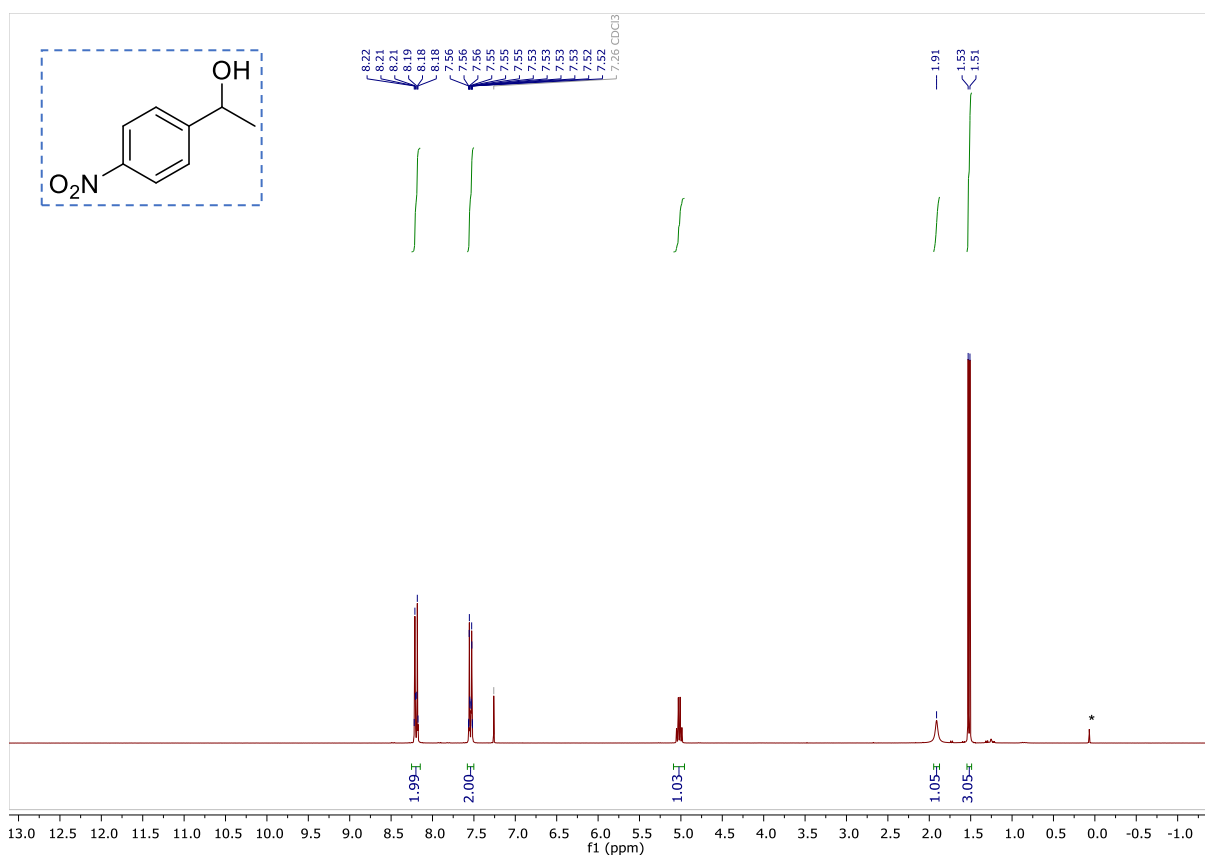


Figure S84 – ¹H NMR spectrum of 4o. * - Grease.

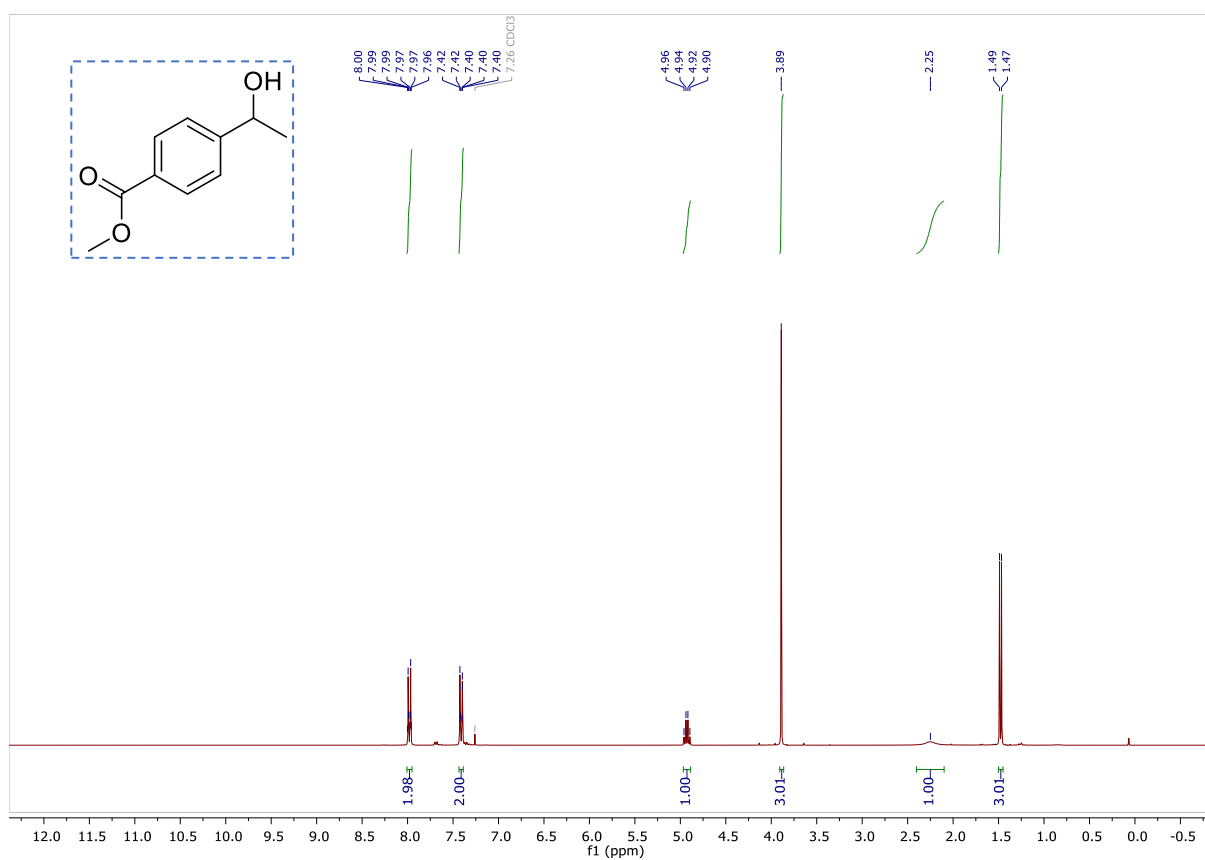


Figure S85 – ¹H NMR spectrum of 4p.

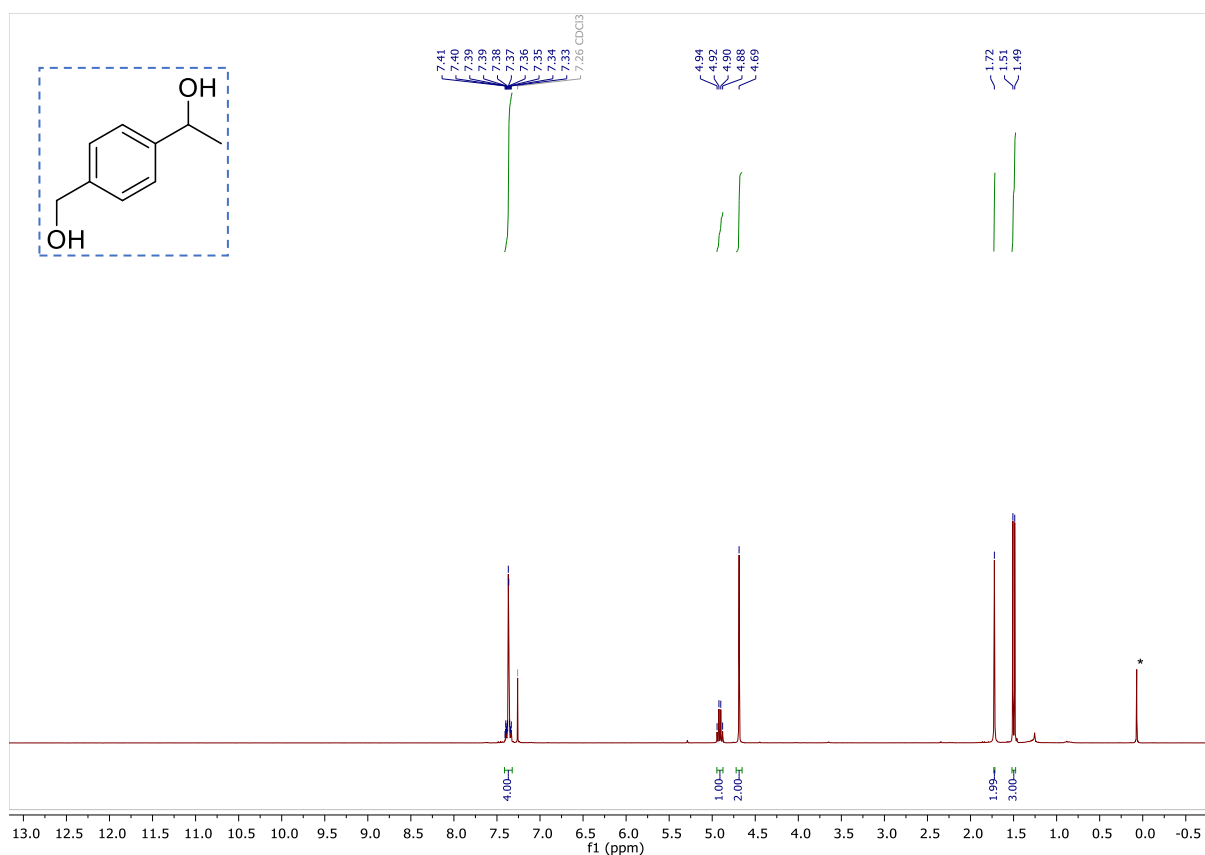


Figure S86 – ¹H NMR spectrum of 4q. * - Grease

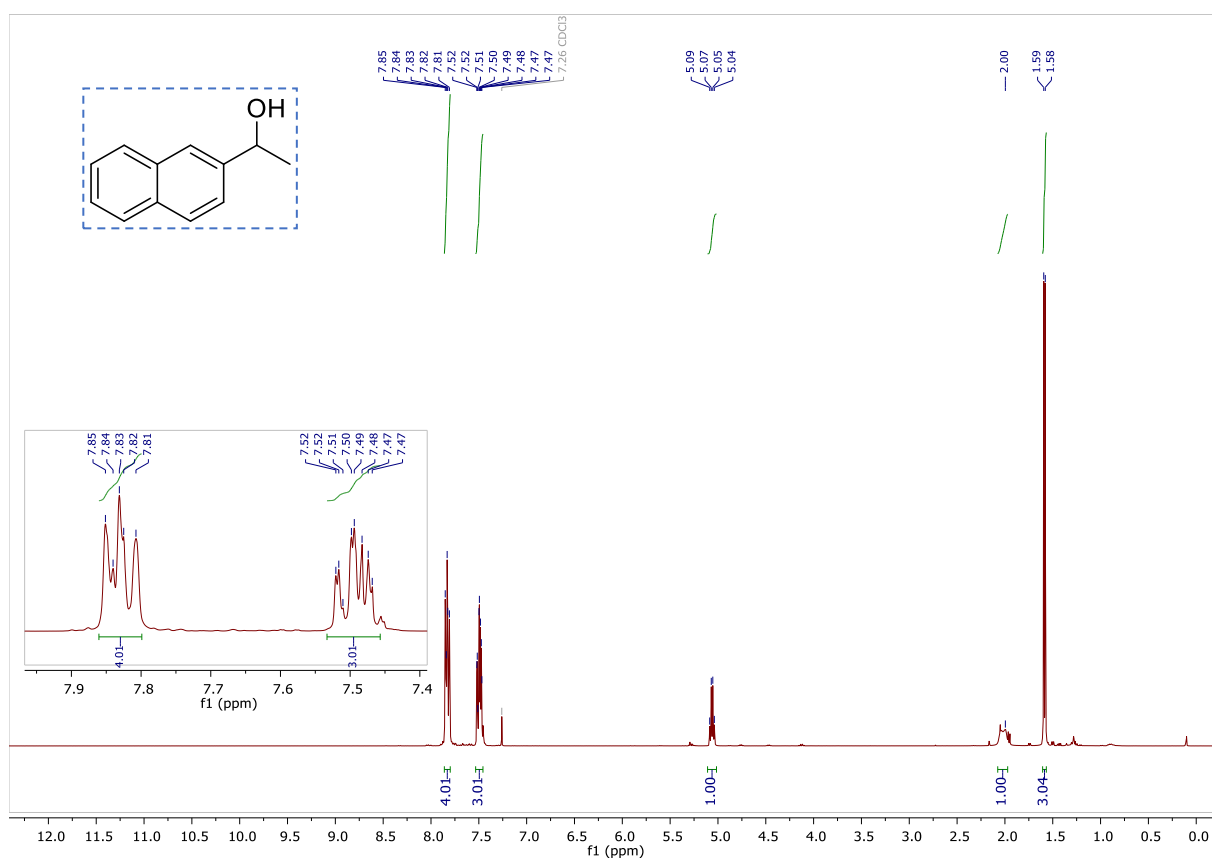


Figure S87 – ¹H NMR spectrum of 4r.

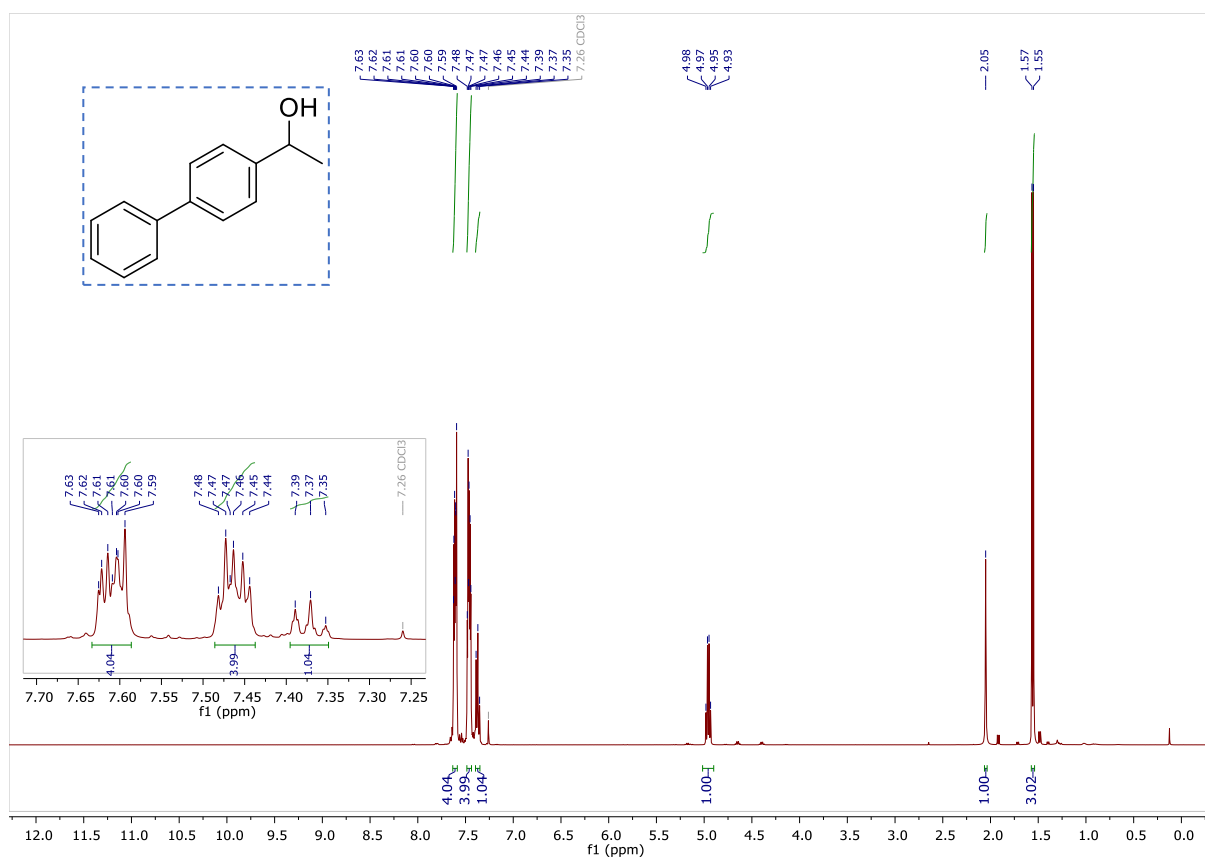


Figure S88 – ¹H NMR spectrum of **4s**.

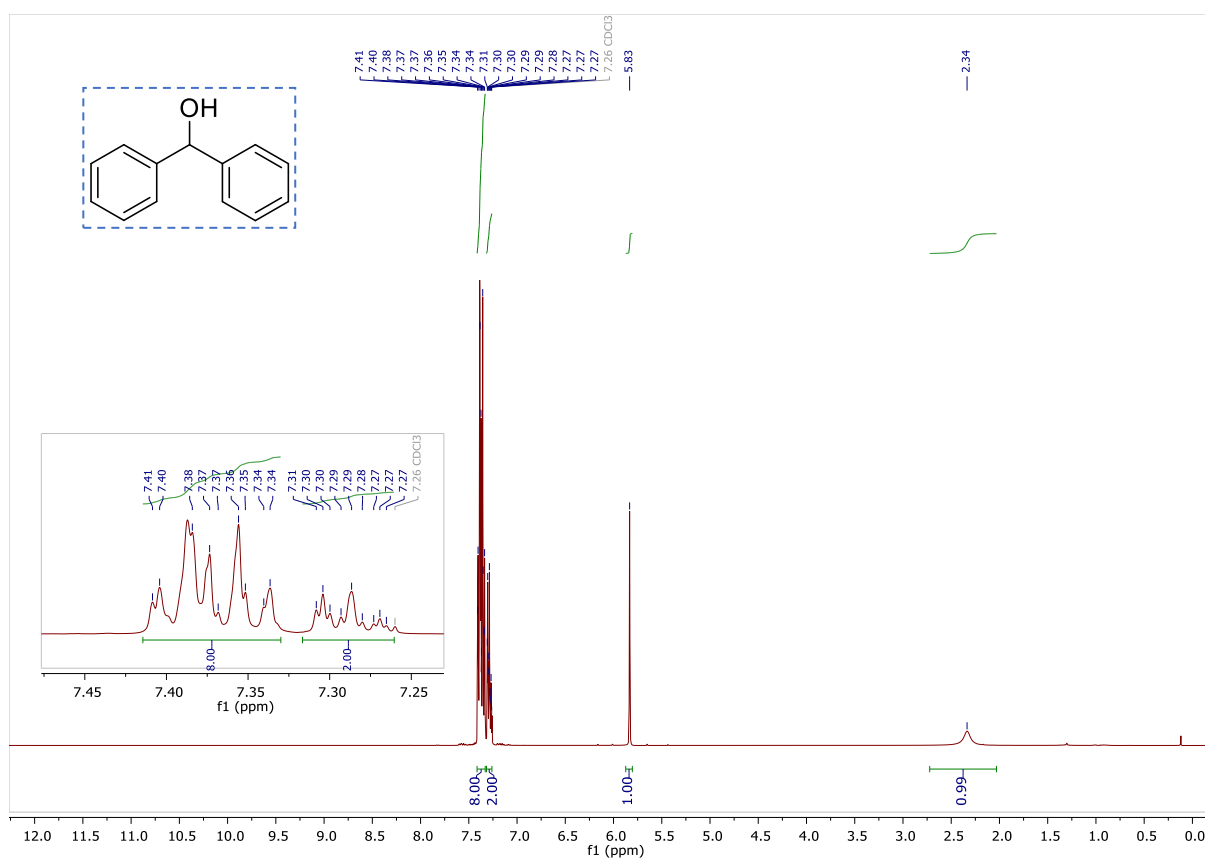


Figure S89 – ¹H NMR spectrum of **4t**.

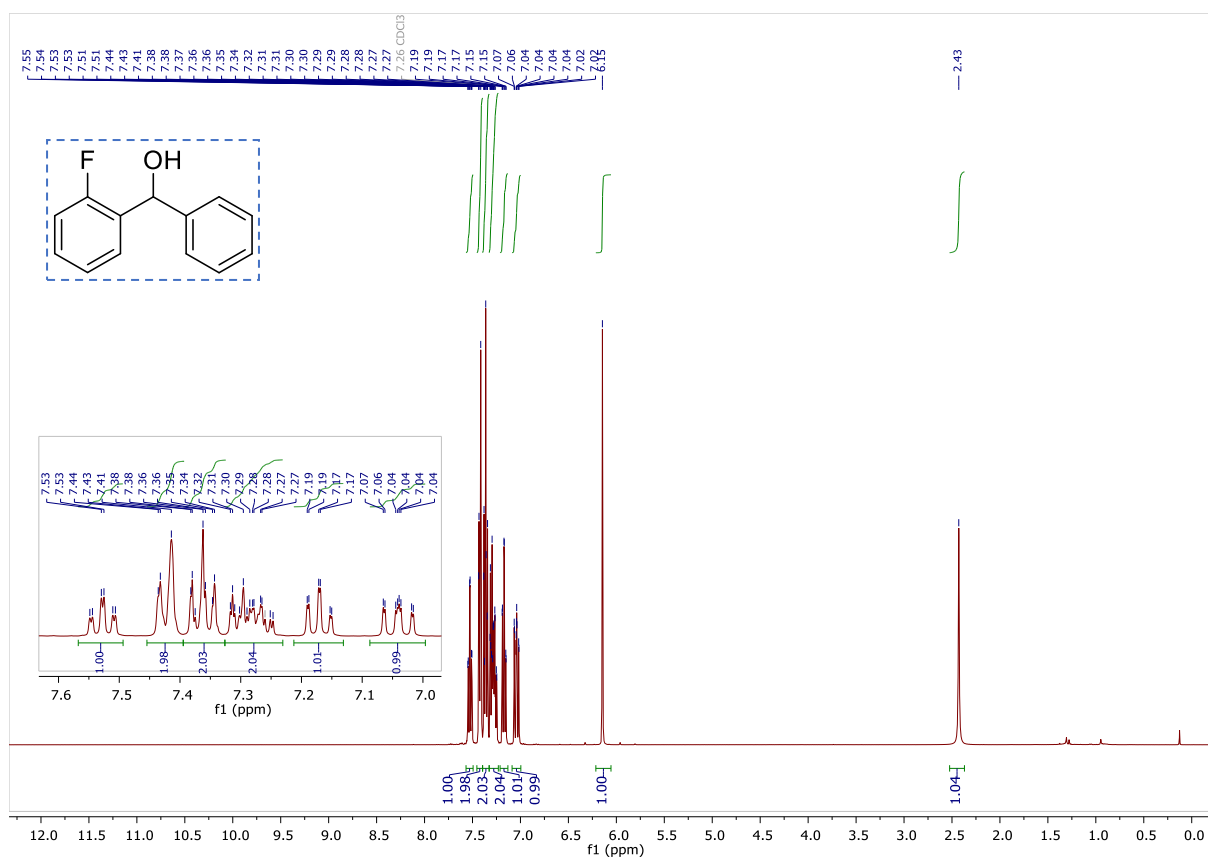


Figure S90 – ¹H NMR spectrum of 4u.

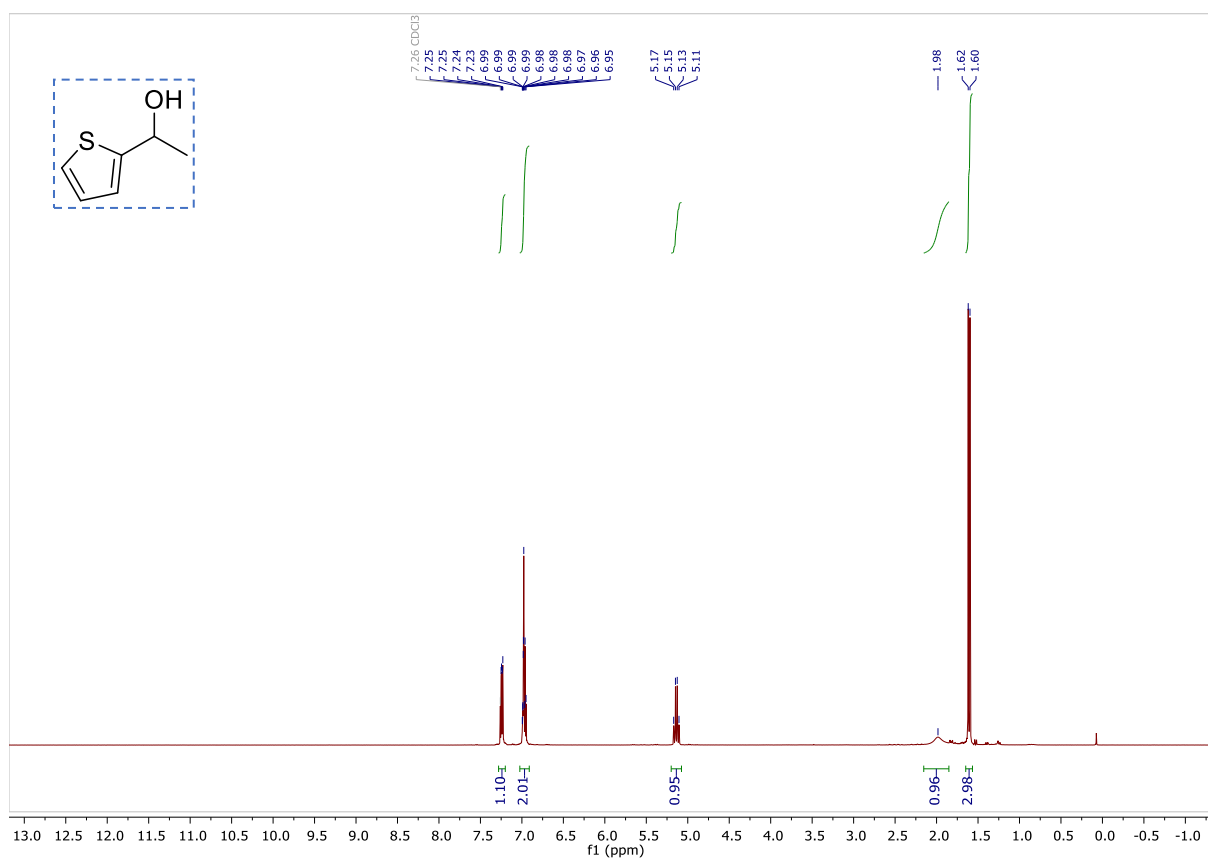


Figure S91 – ¹H NMR spectrum of 4v.

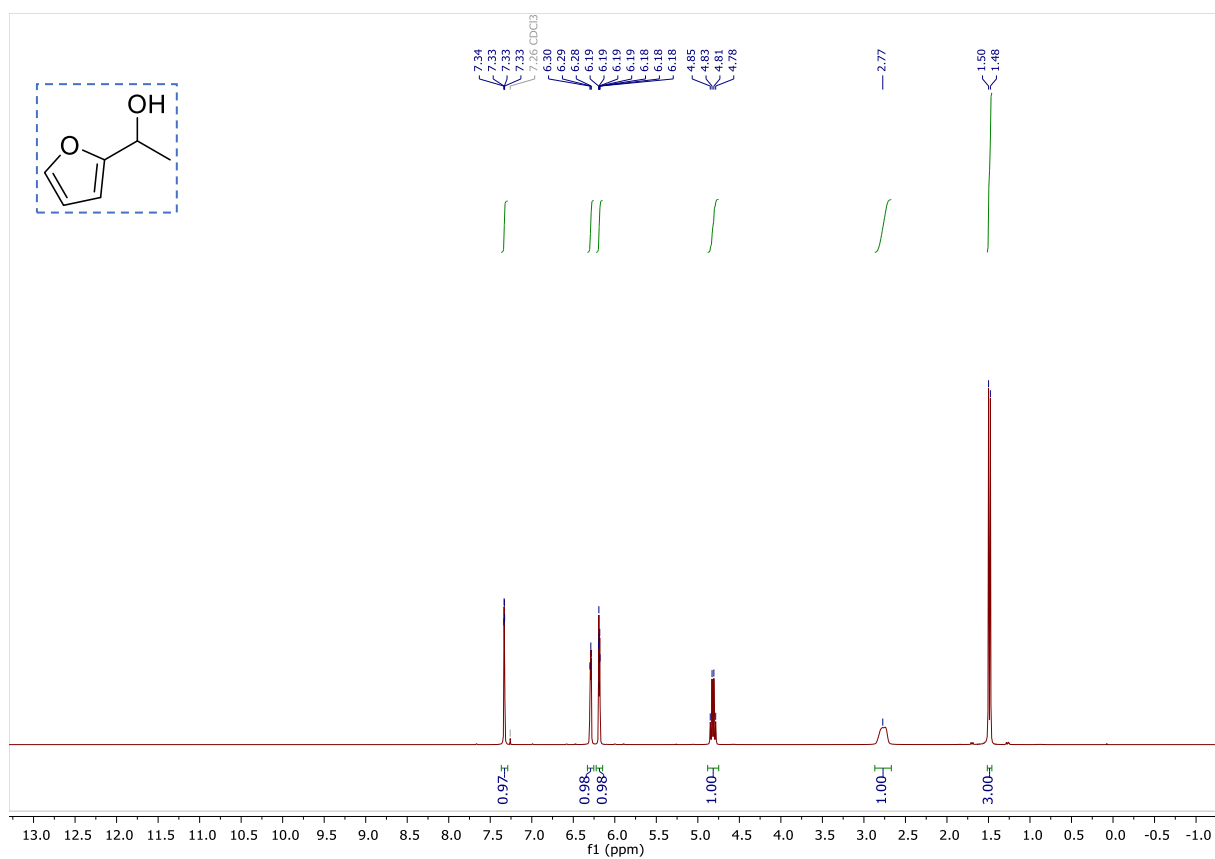


Figure S92 – ^1H NMR spectrum of 4w.

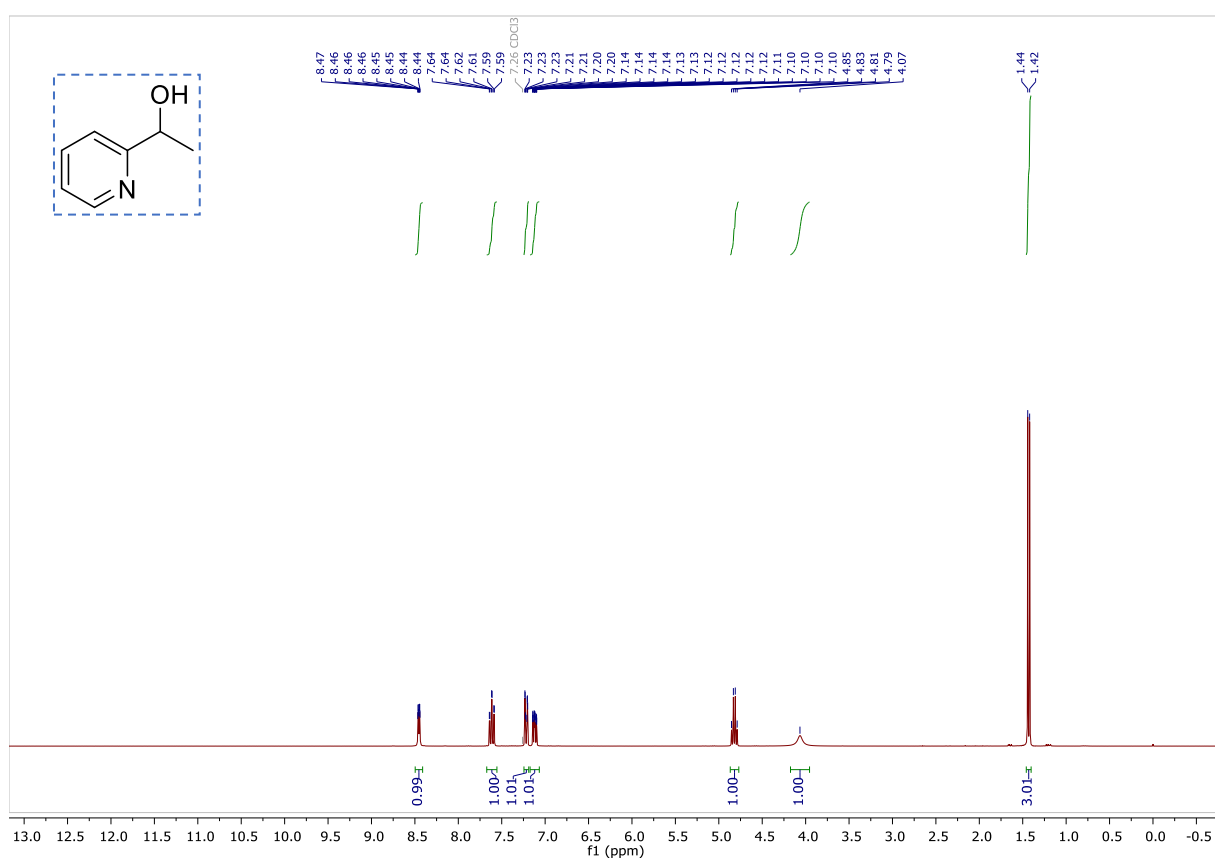


Figure S93 – ^1H NMR spectrum of **4x**.

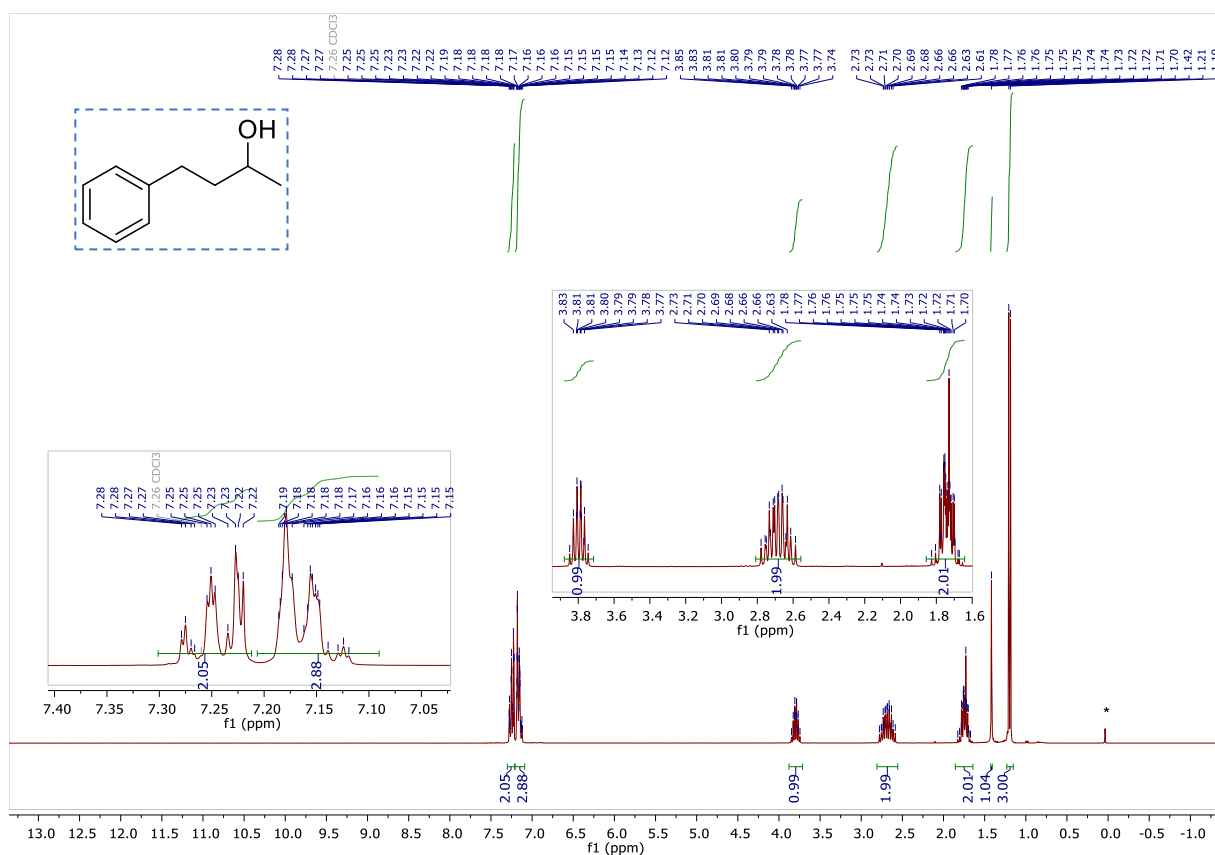


Figure S94 – ¹H NMR spectrum of 4y. * - Grease

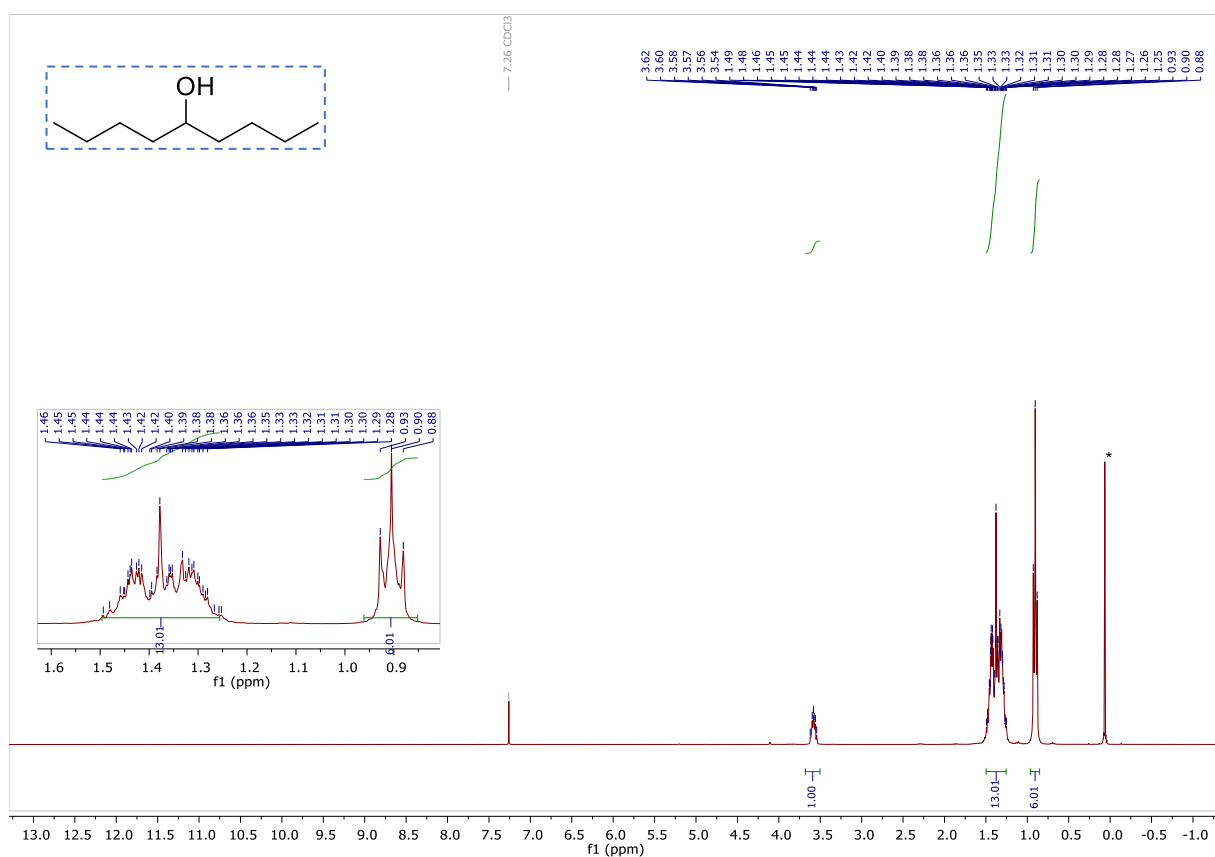


Figure S95 – ¹H NMR spectrum of 4z. * - Grease

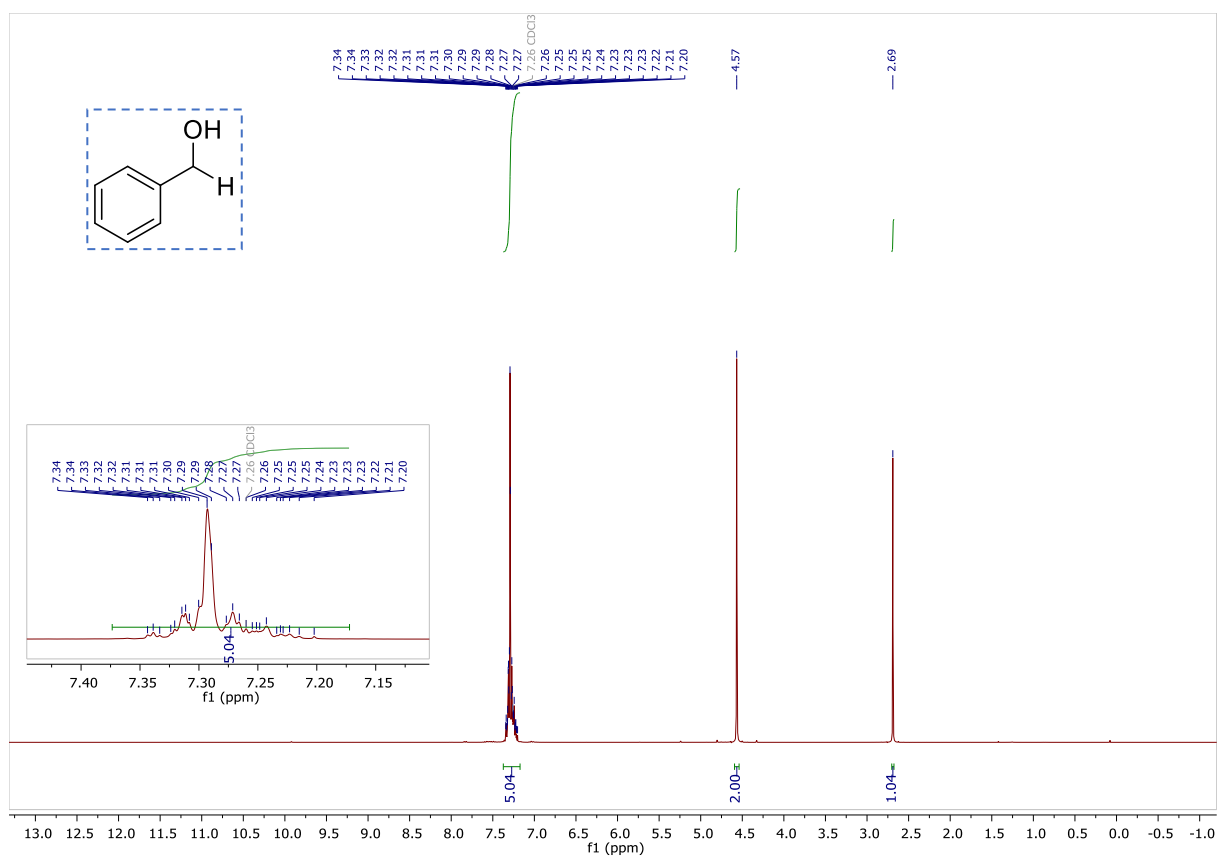


Figure S96 – ¹H NMR spectrum of **7a**.

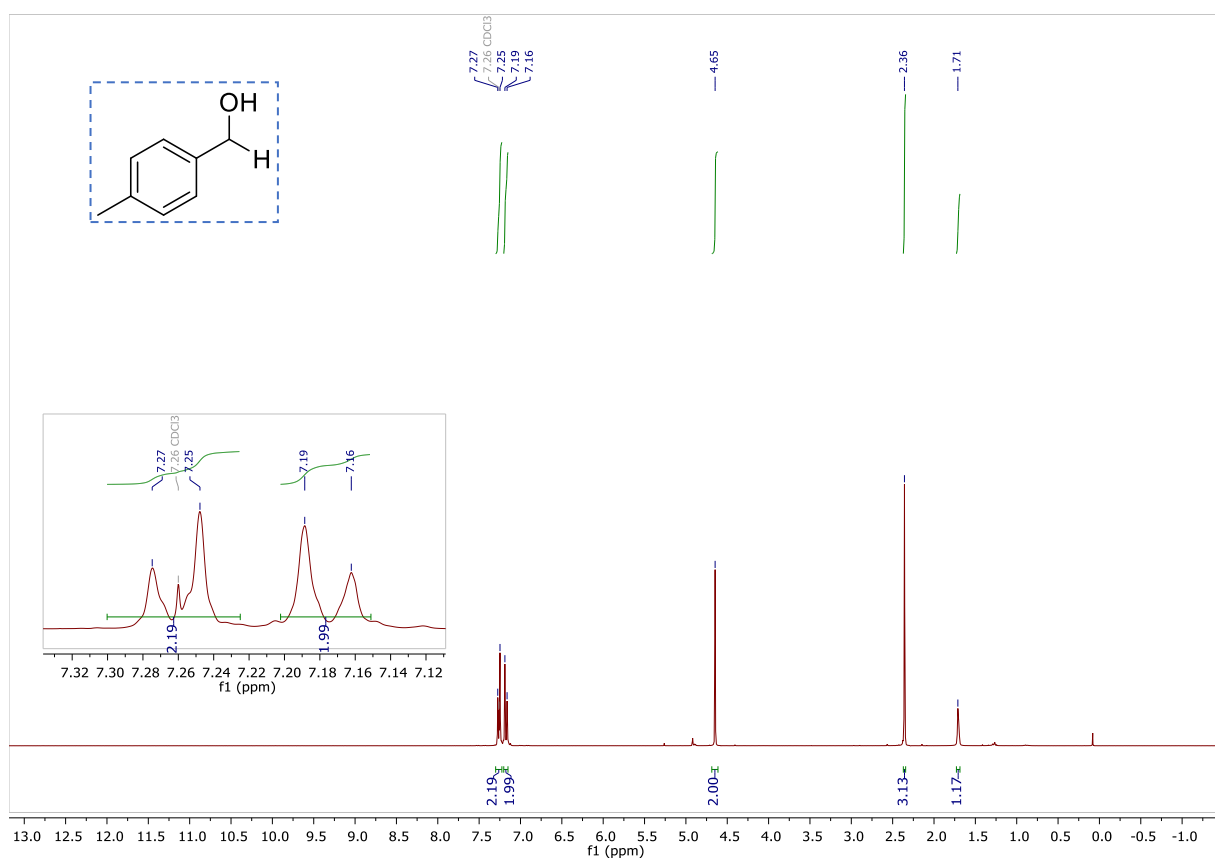


Figure S97 – ¹H NMR spectrum of **7b**.

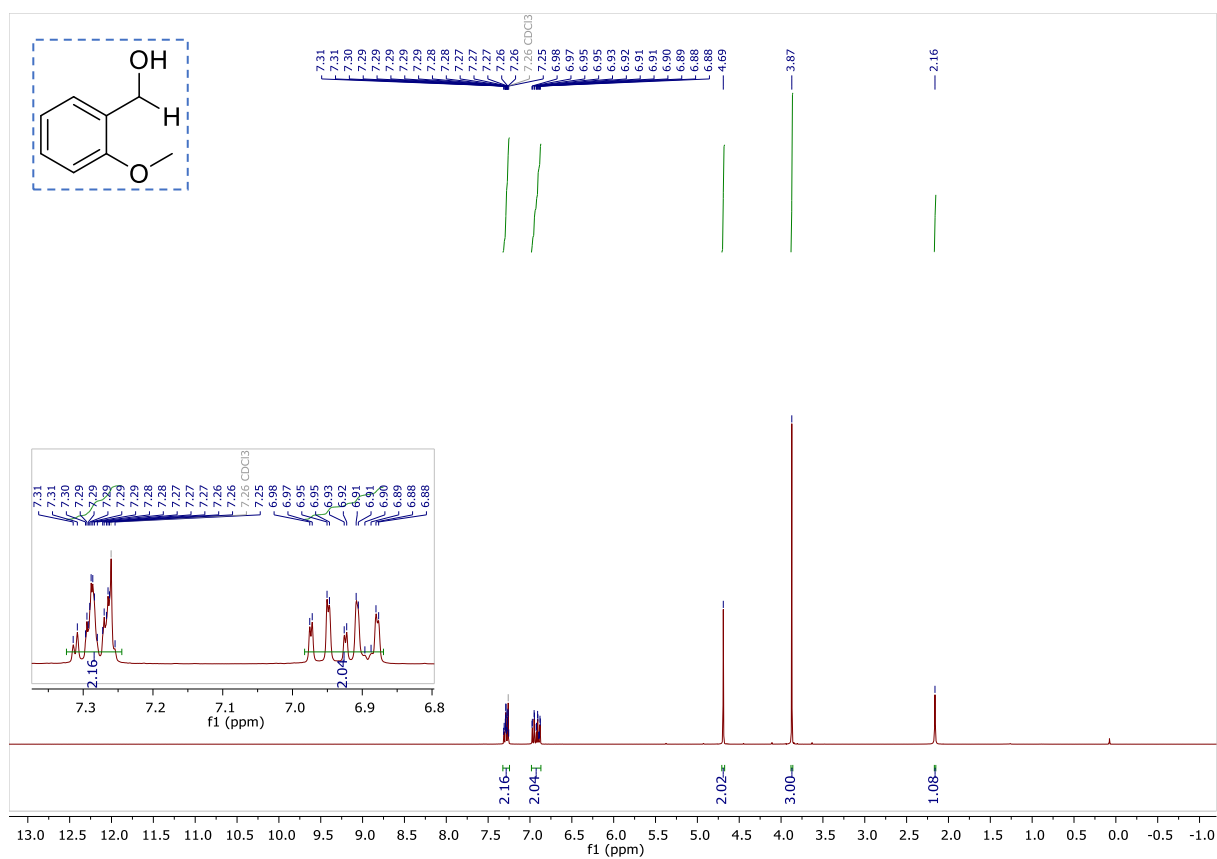


Figure S98 – ¹H NMR spectrum of 7c.

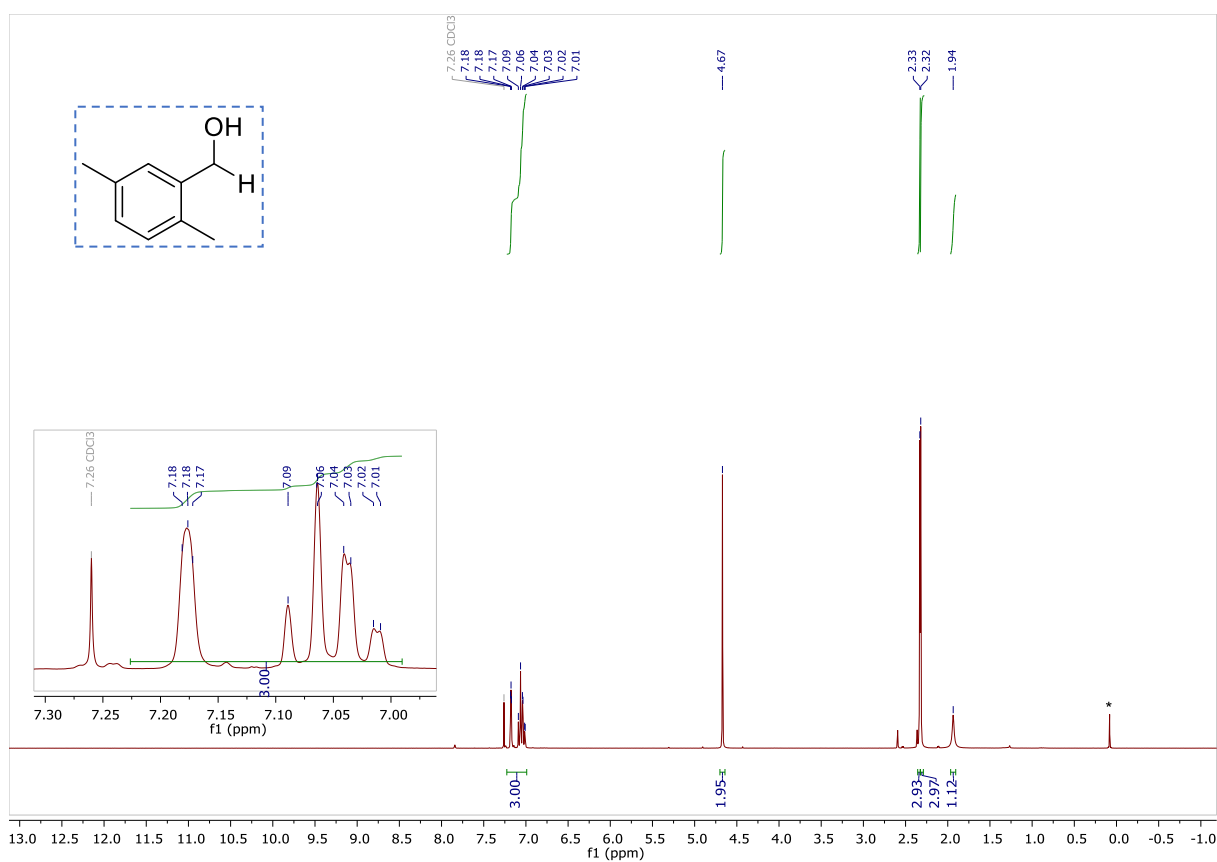


Figure S99 – ¹H NMR spectrum of 7d. * - Grease.

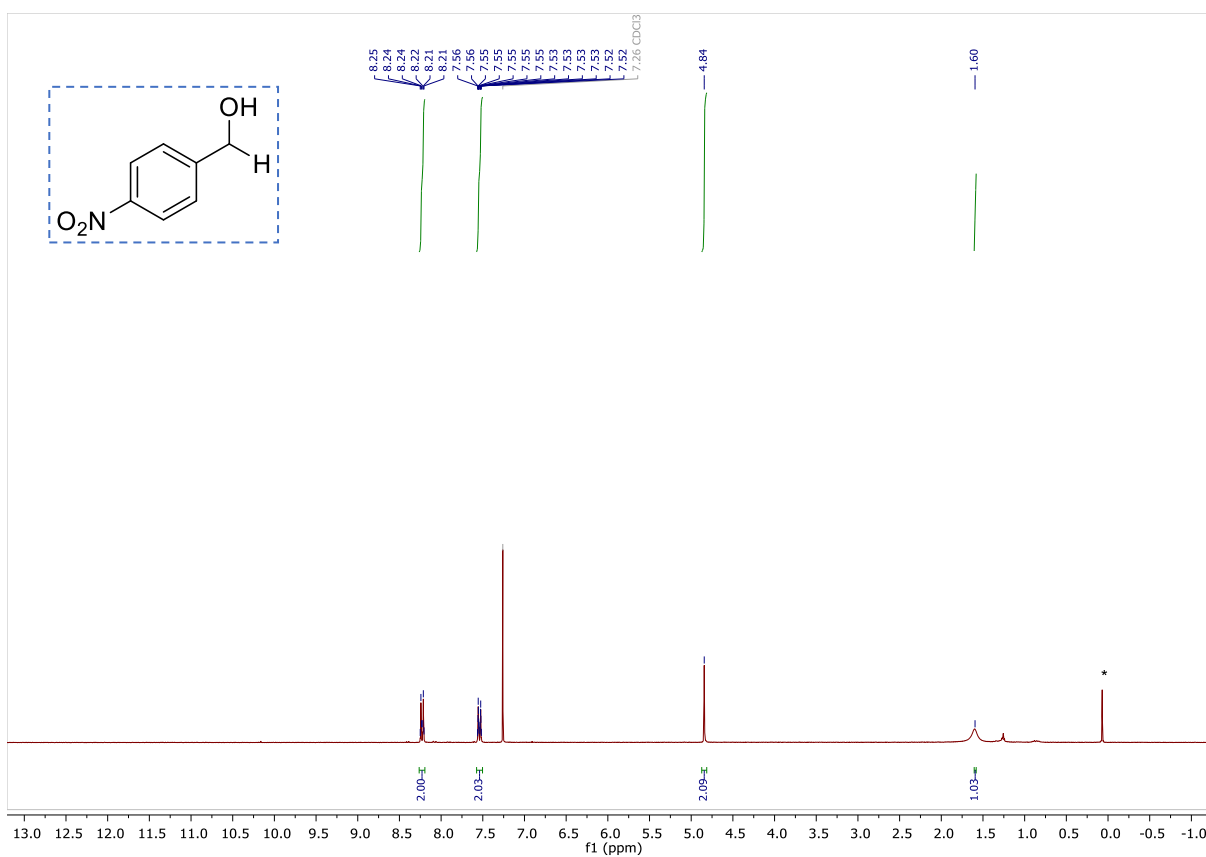


Figure S100 – ¹H NMR spectrum of 7e. * - Grease.

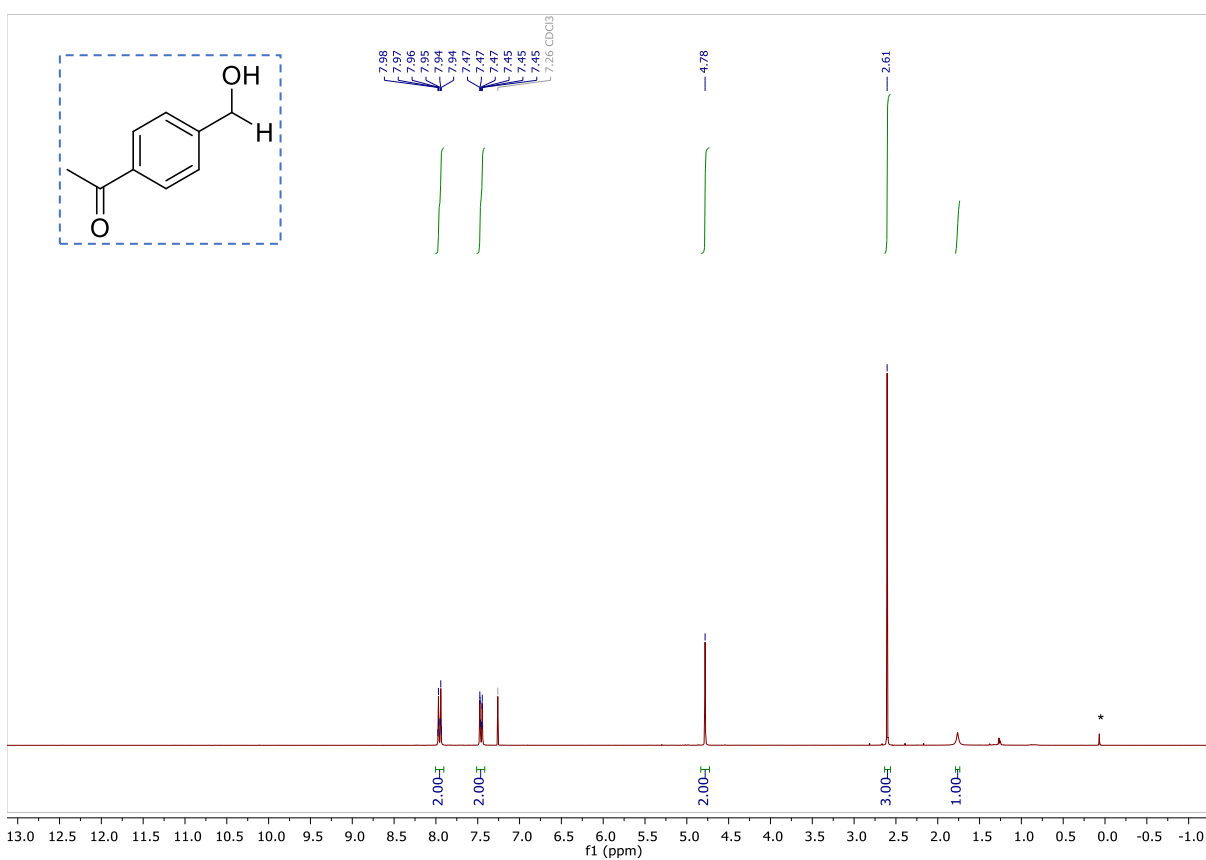


Figure S101 – ¹H NMR spectrum of 7f. * - Grease.

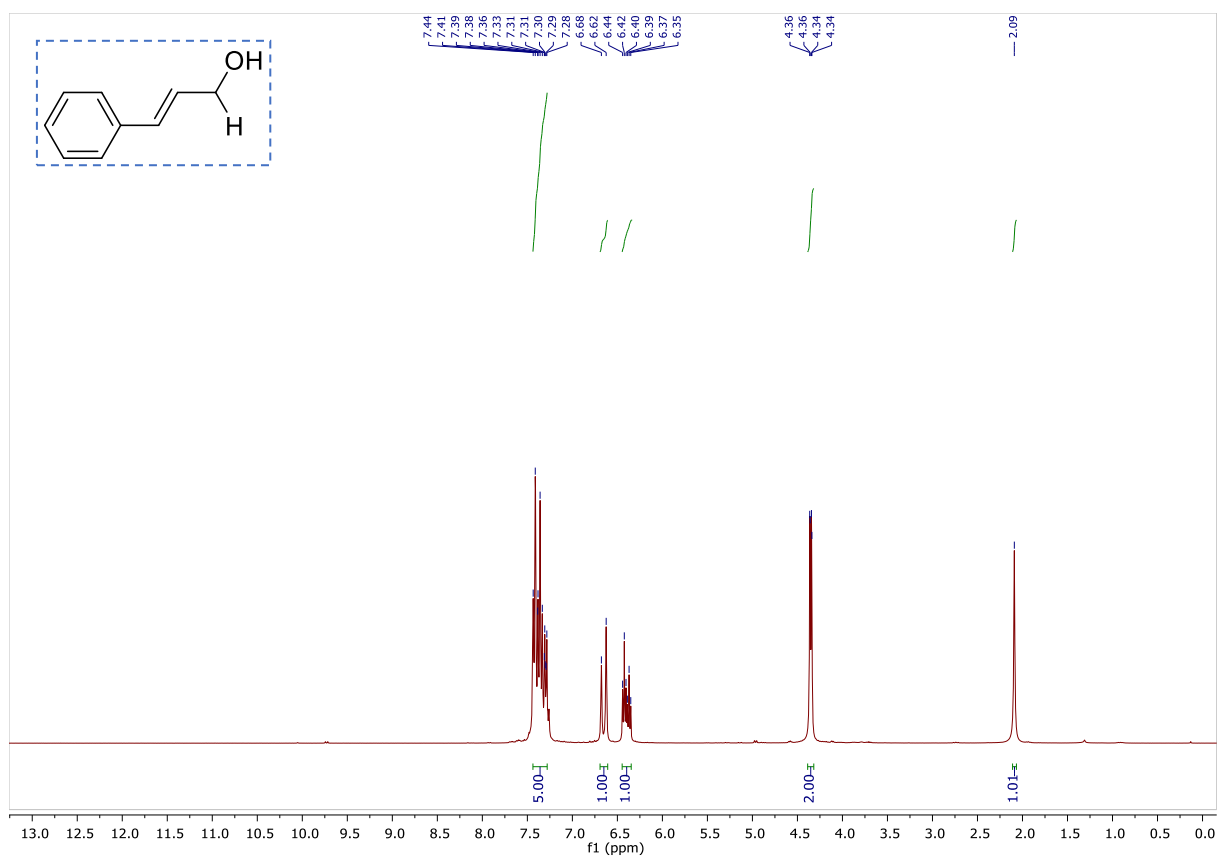


Figure S102 – ¹H NMR spectrum of **7g**.

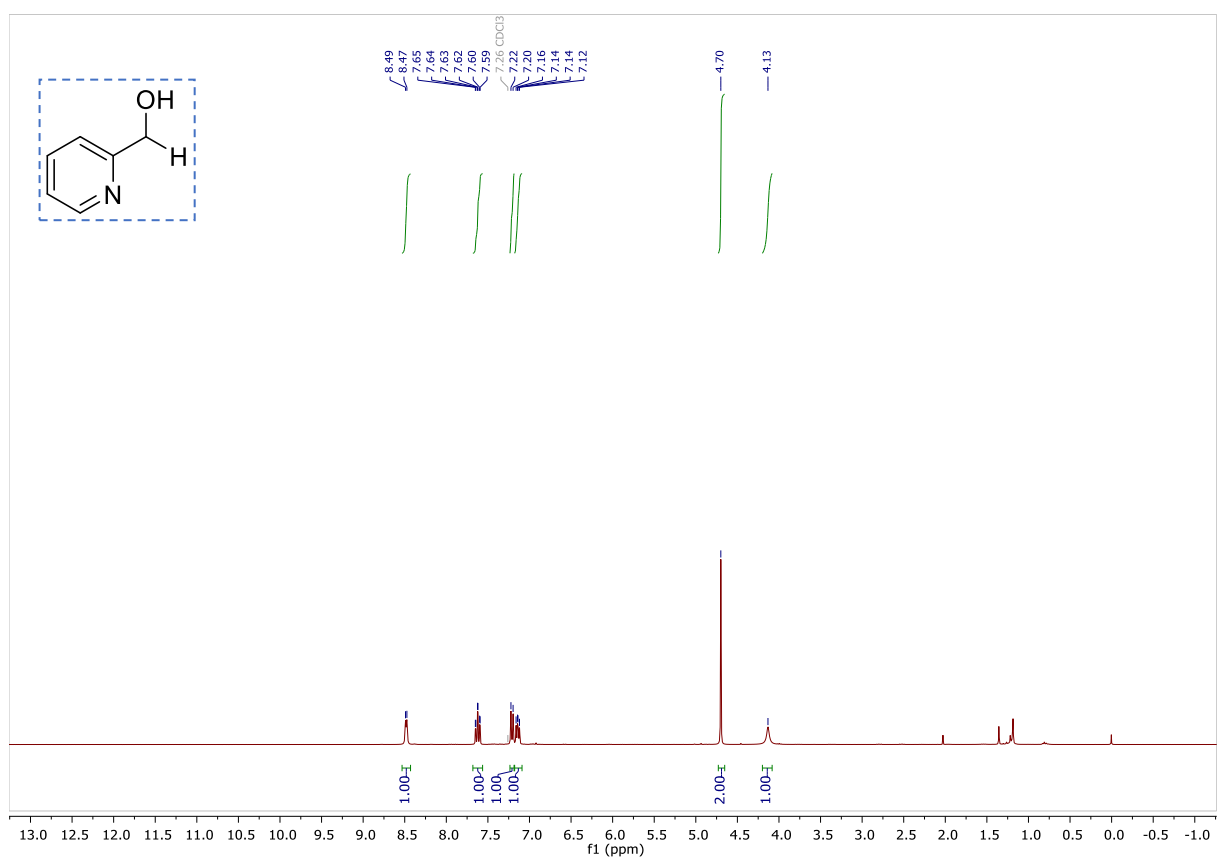


Figure S103 – ¹H NMR spectrum of **7h**.

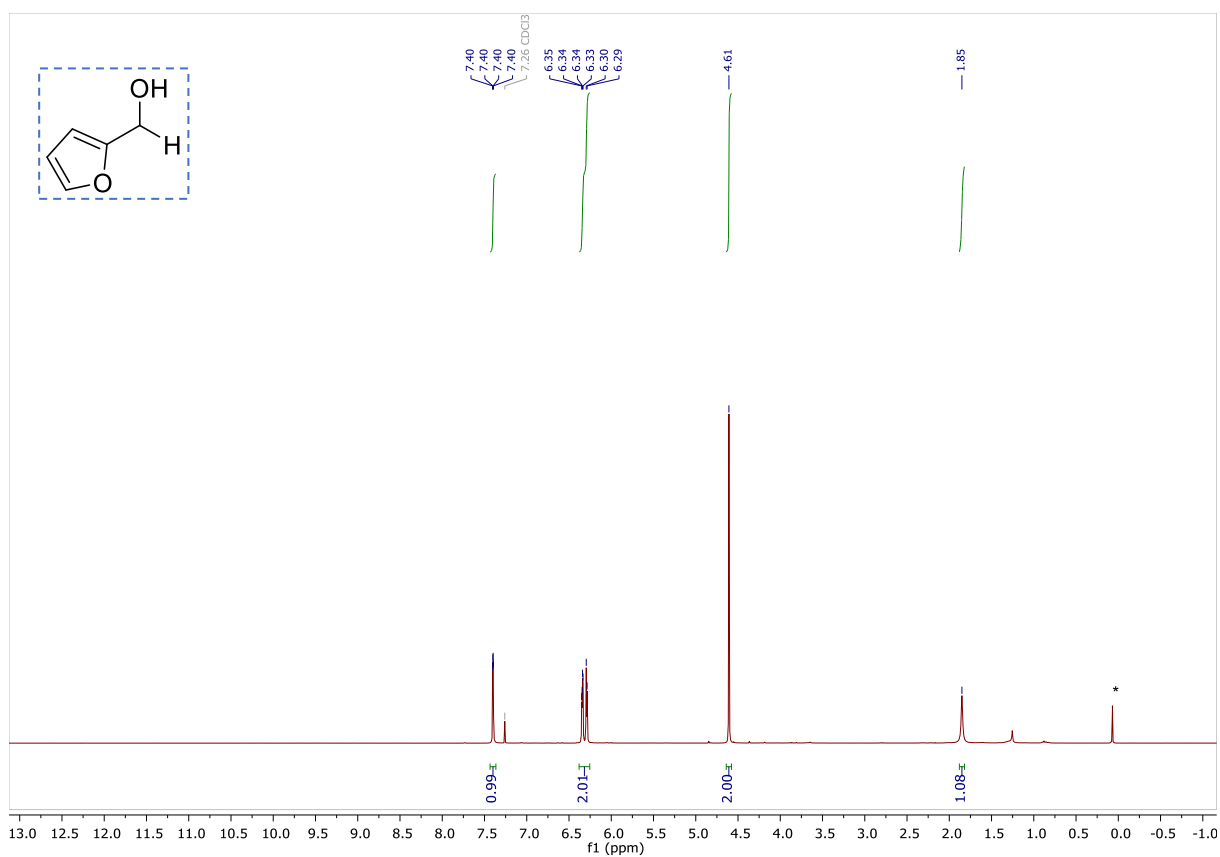


Figure S104 – ¹H NMR spectrum of 7i. * - Grease.

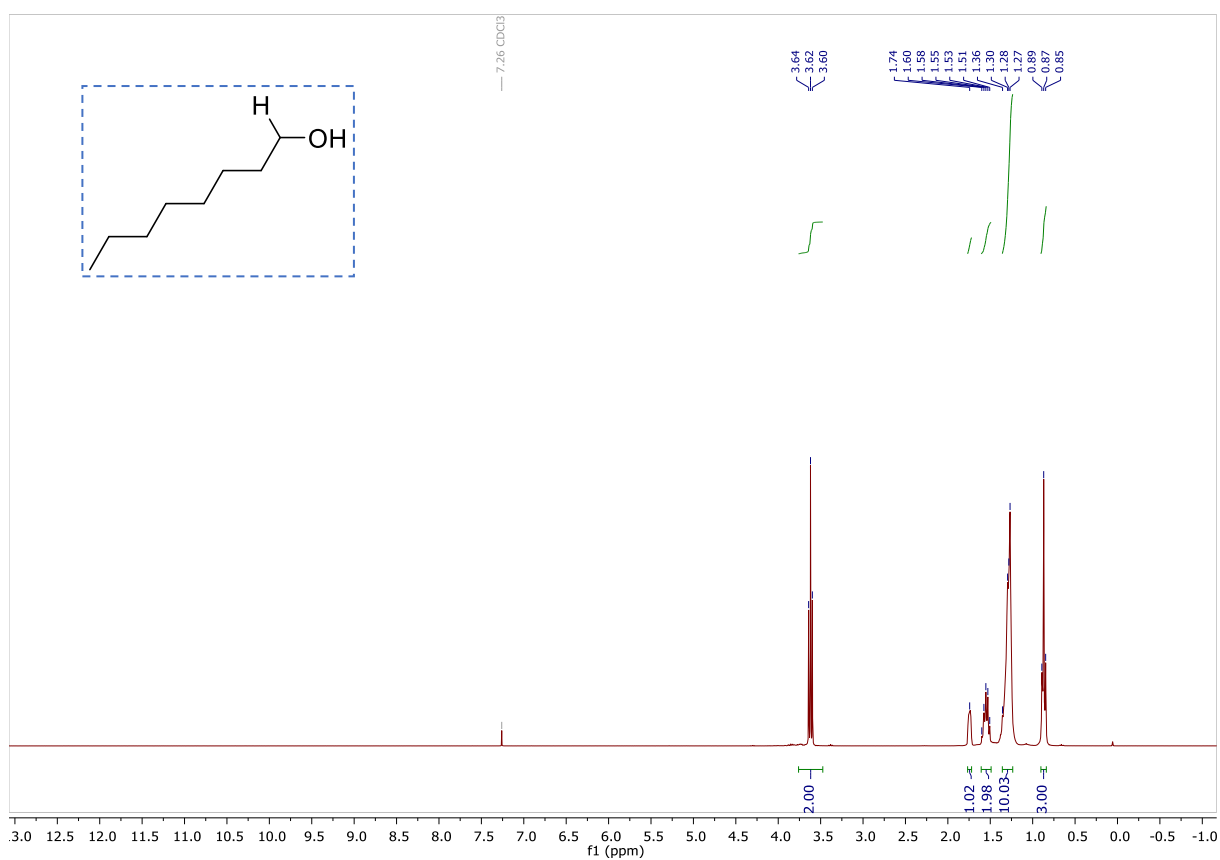


Figure S105 – ¹H NMR spectrum of 7j.

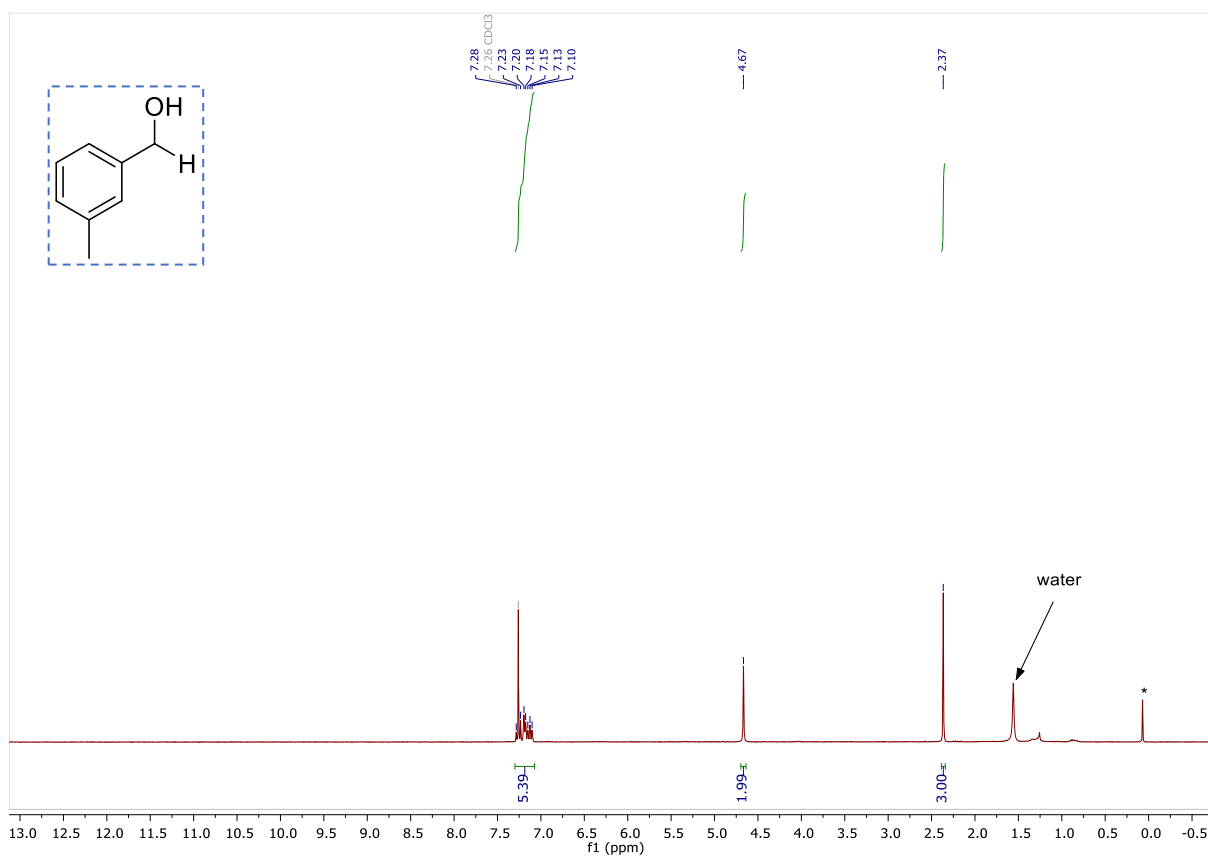


Figure S106 – ¹H NMR spectrum of 7k. * - Grease.

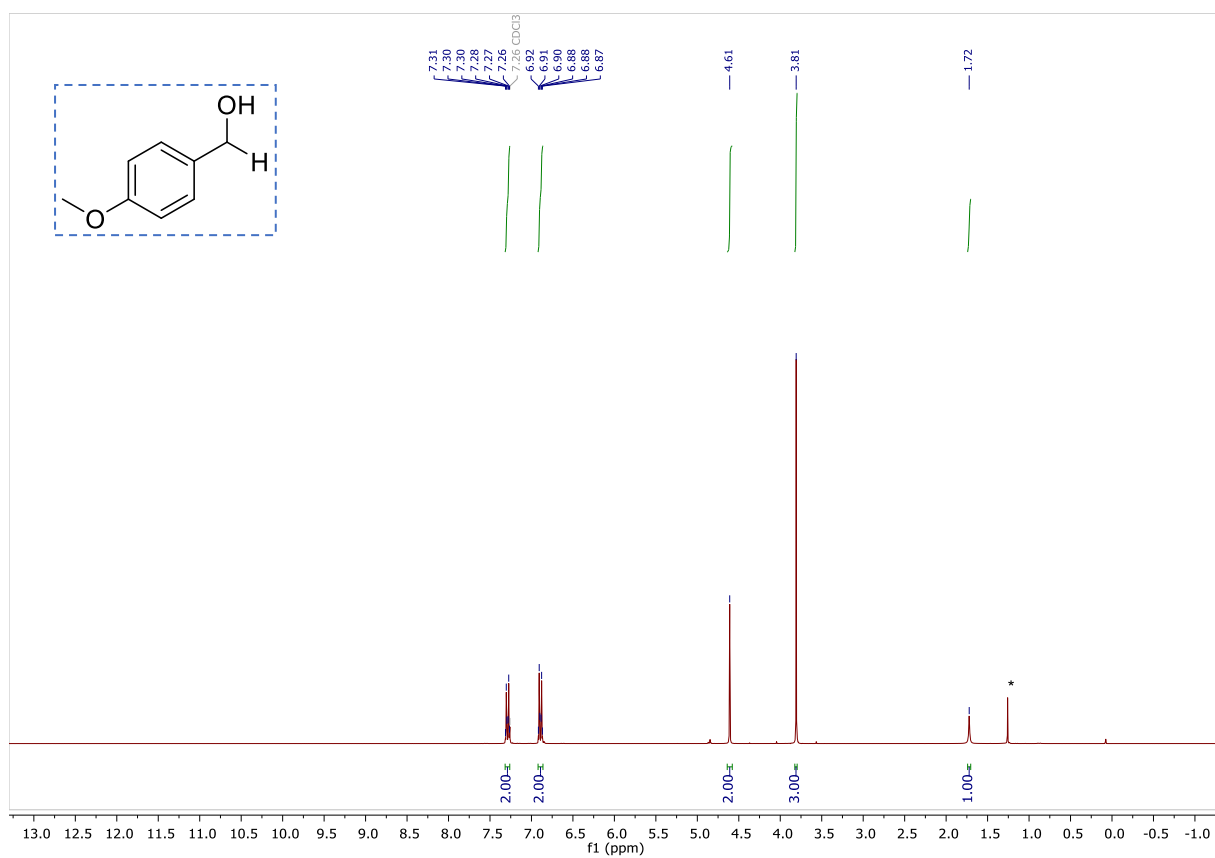


Figure S107 – ¹H NMR spectrum of 7l. * - Pinacol – impurity.

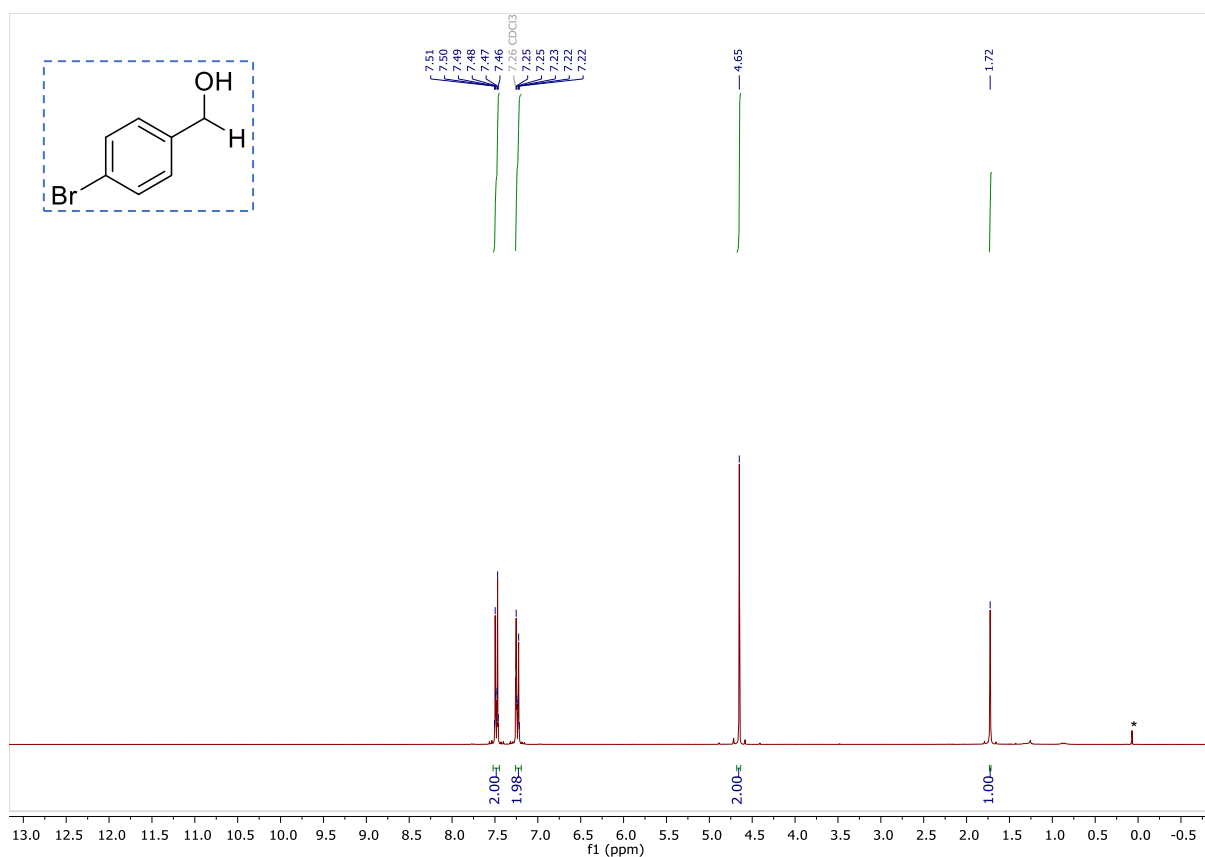


Figure S108 – ¹H NMR spectrum of **7m**. * - Grease.

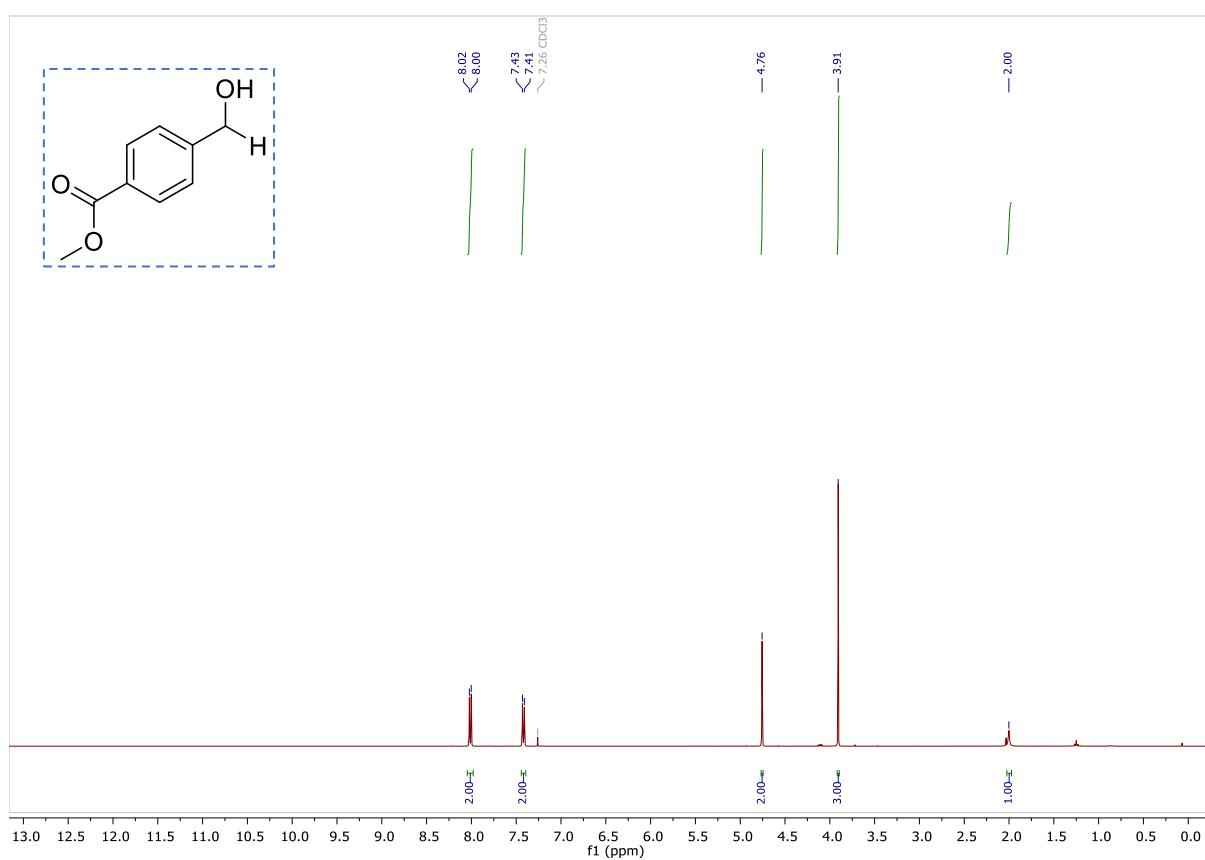


Figure S109 – ¹H NMR spectrum of **7n**.

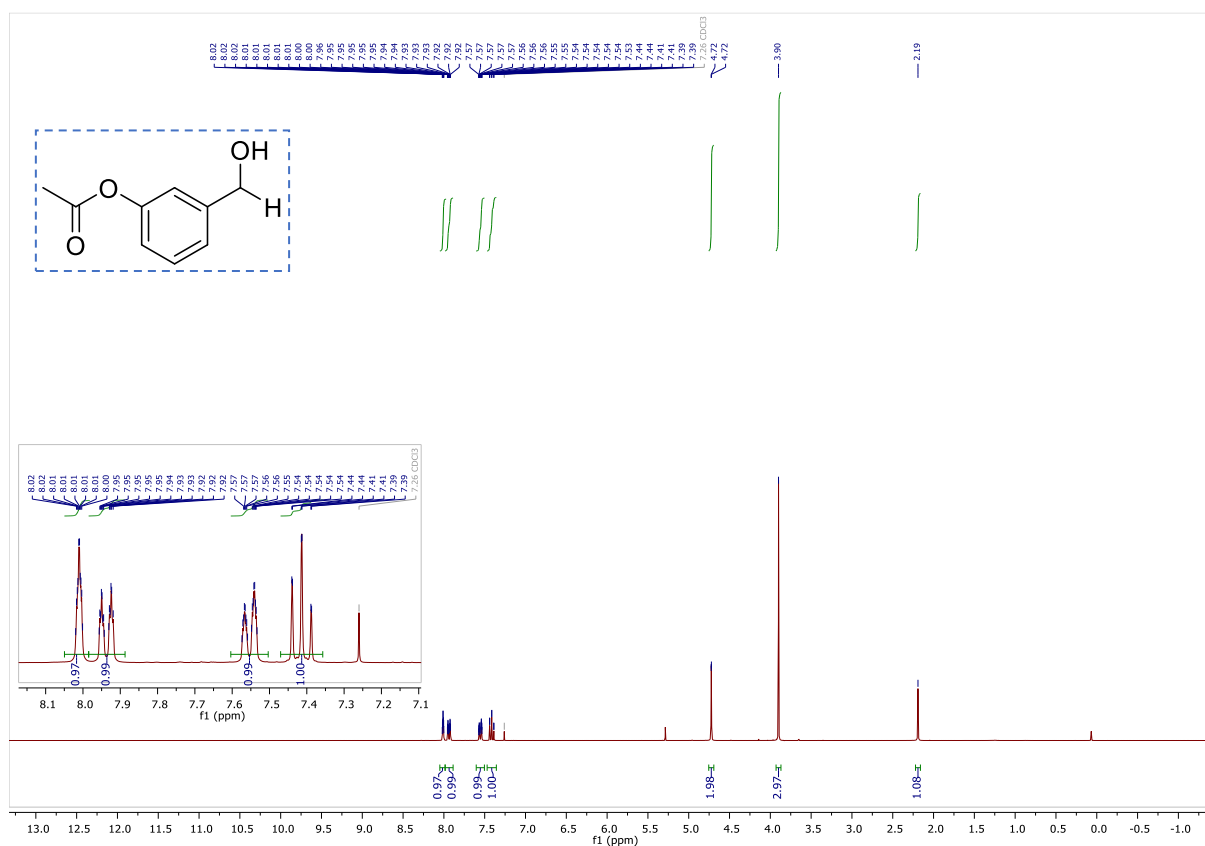


Figure S110 – ^1H NMR spectrum of **7o**.

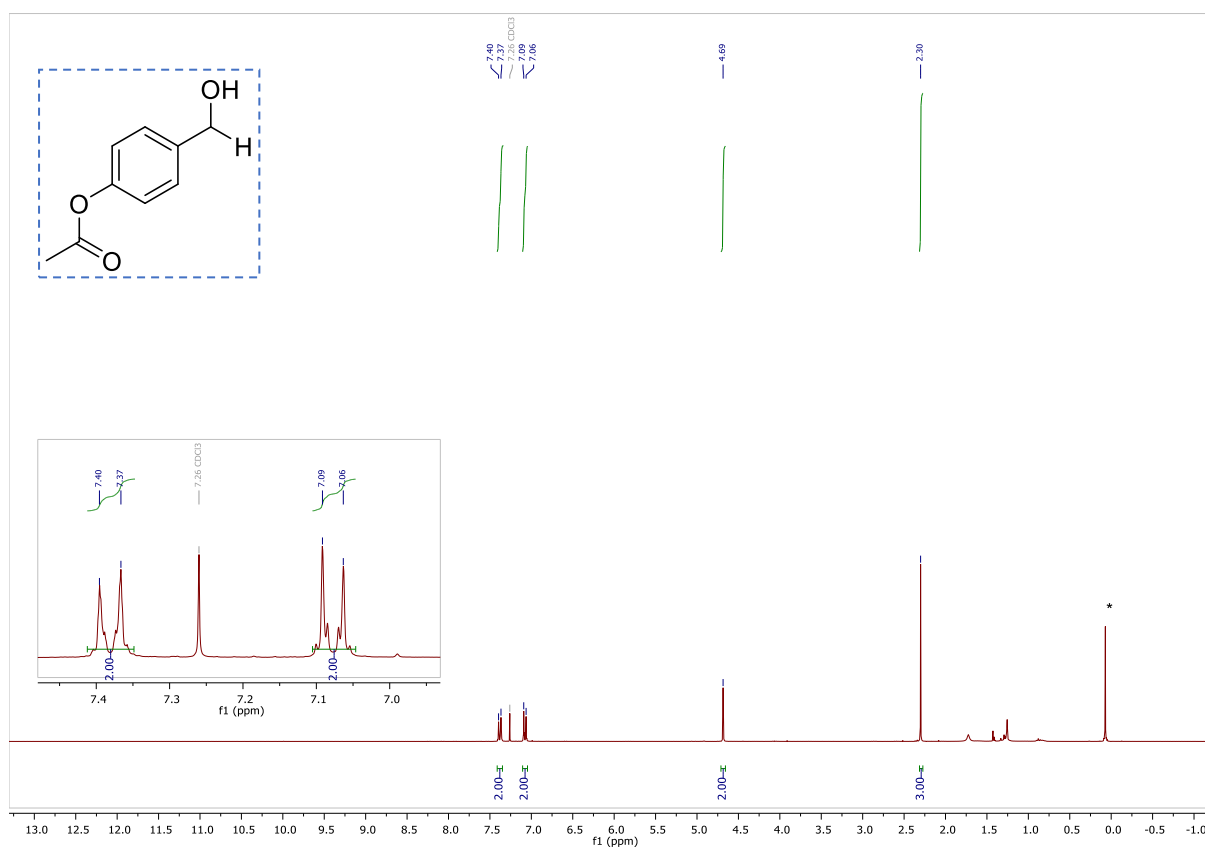


Figure S111 – ^1H NMR spectrum of **7p**. * - Grease.

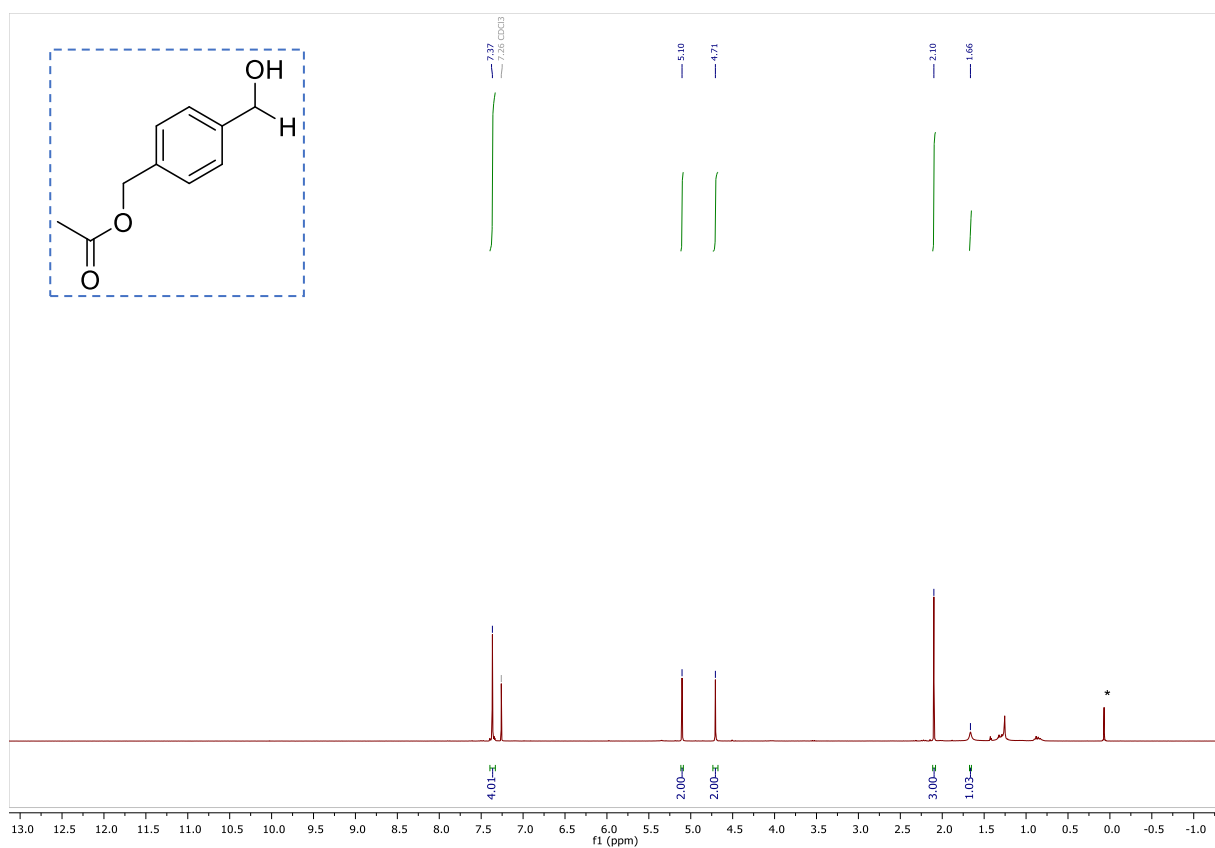


Figure S112– ¹H NMR spectrum of 7q. * - Grease.

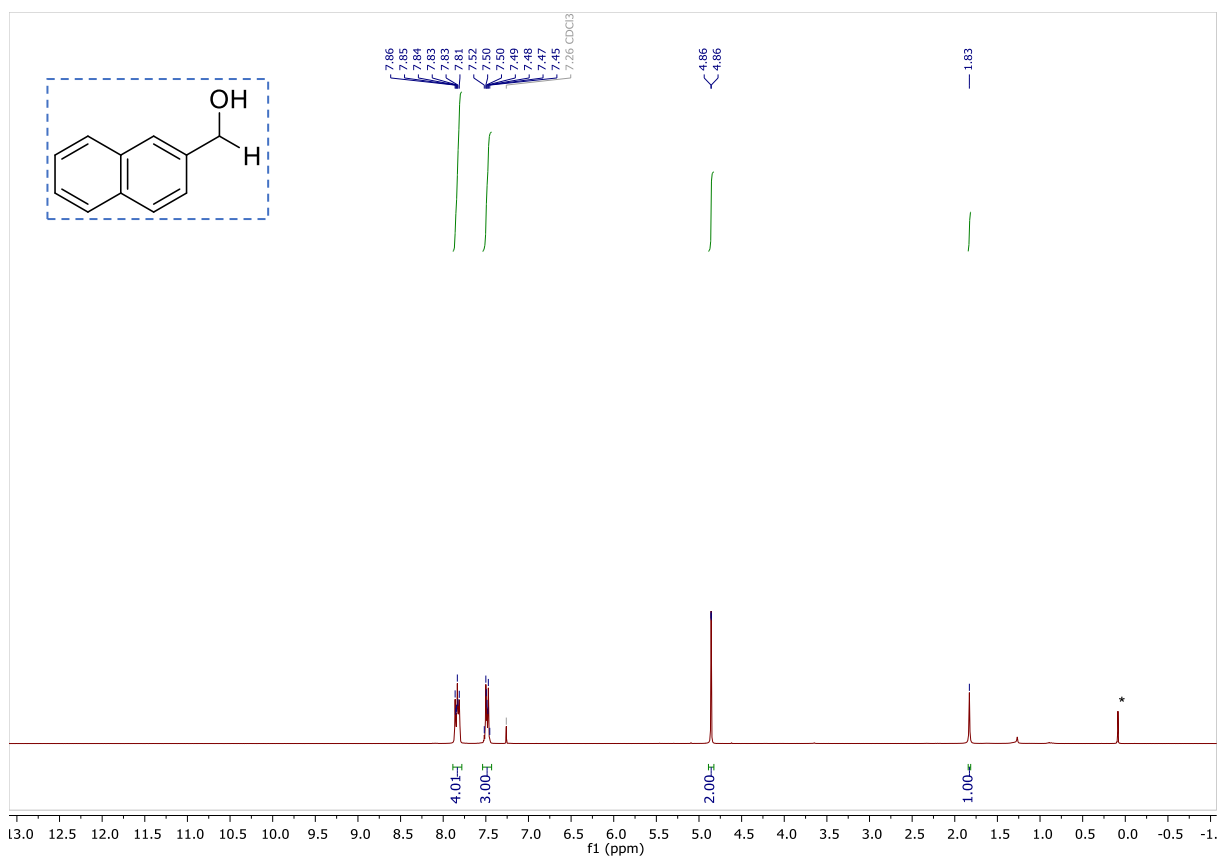
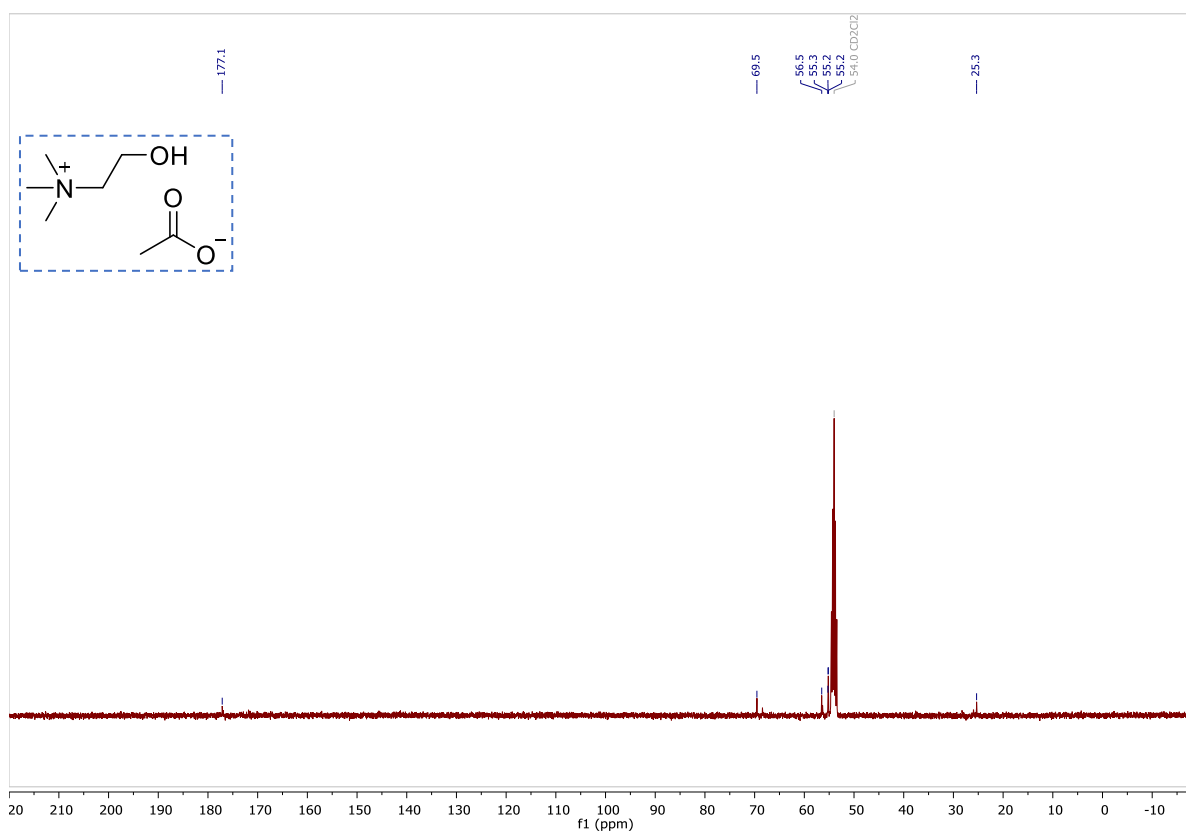
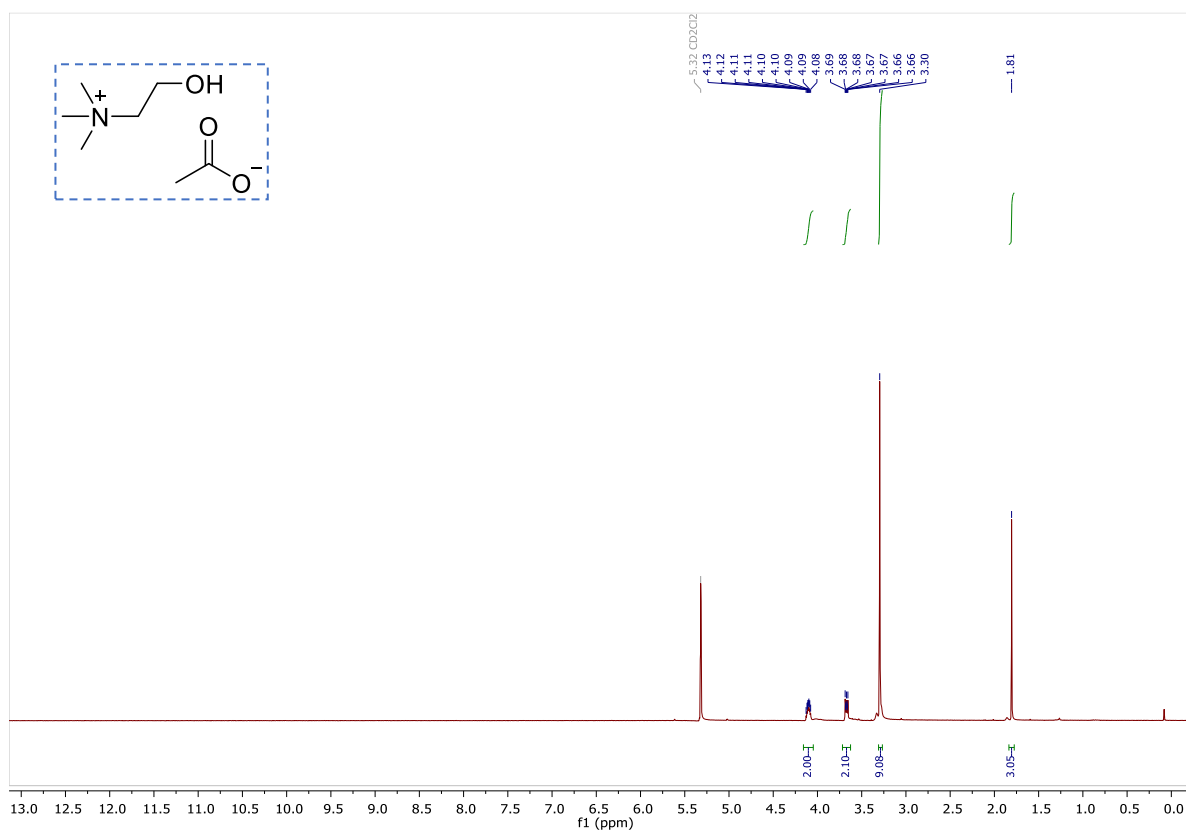


Figure S113 – ¹H NMR spectrum of 7r. * - Grease.



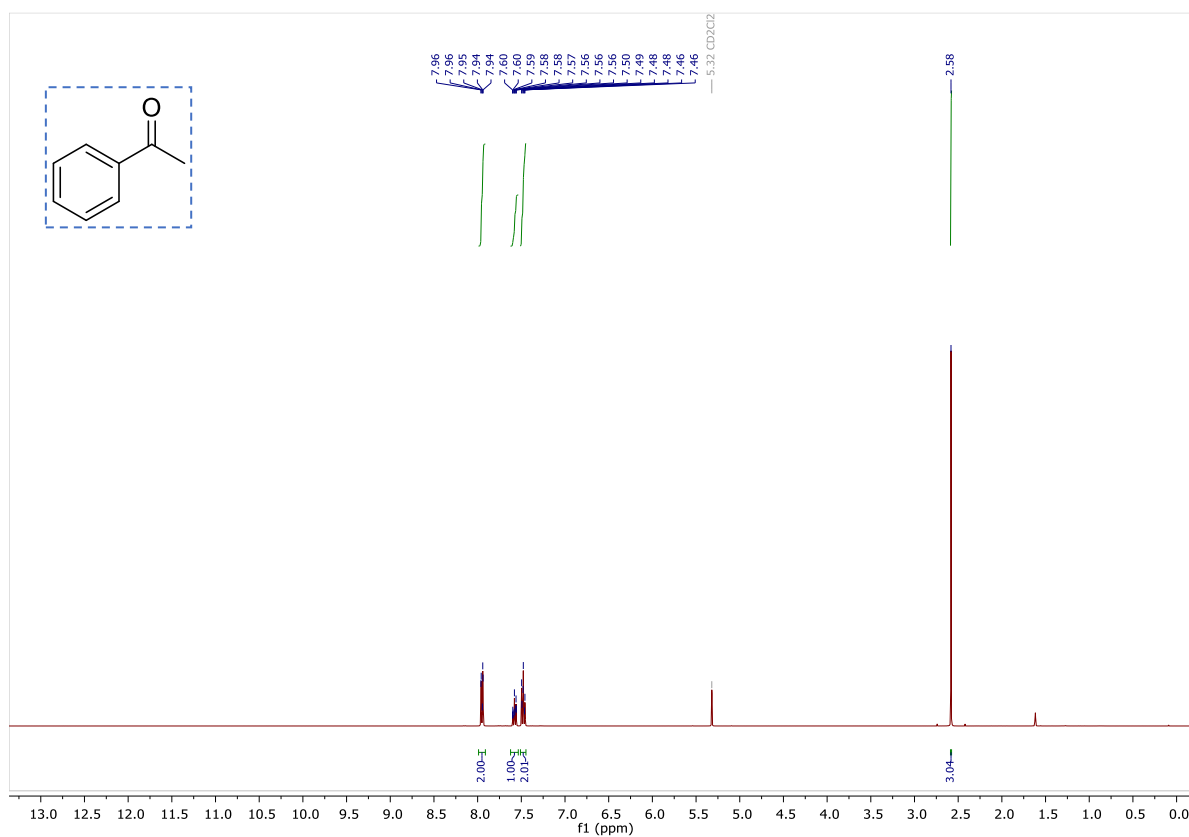


Figure S116 – ¹H NMR spectrum of acetophenone (**1a**) in DCM-d₂.

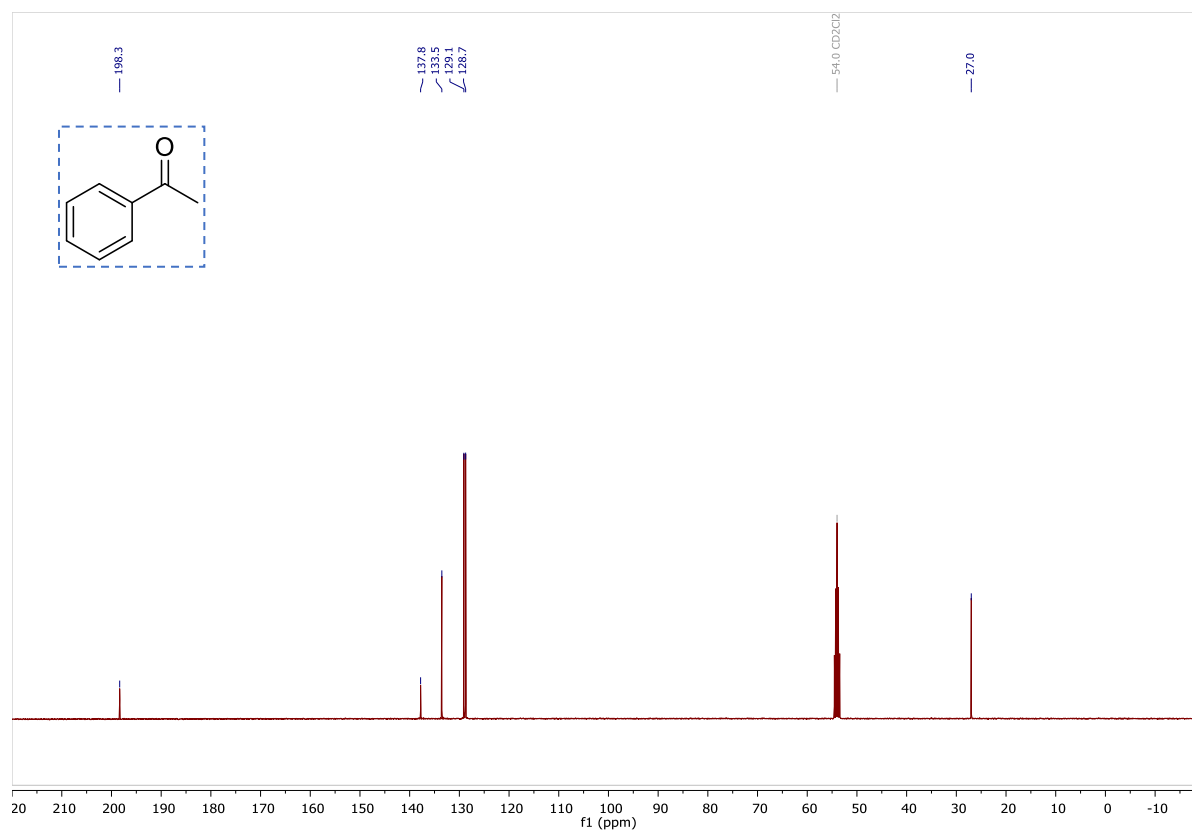


Figure S117 – ¹³C{¹H} NMR spectrum of acetophenone (**1a**) in DCM-d₂.

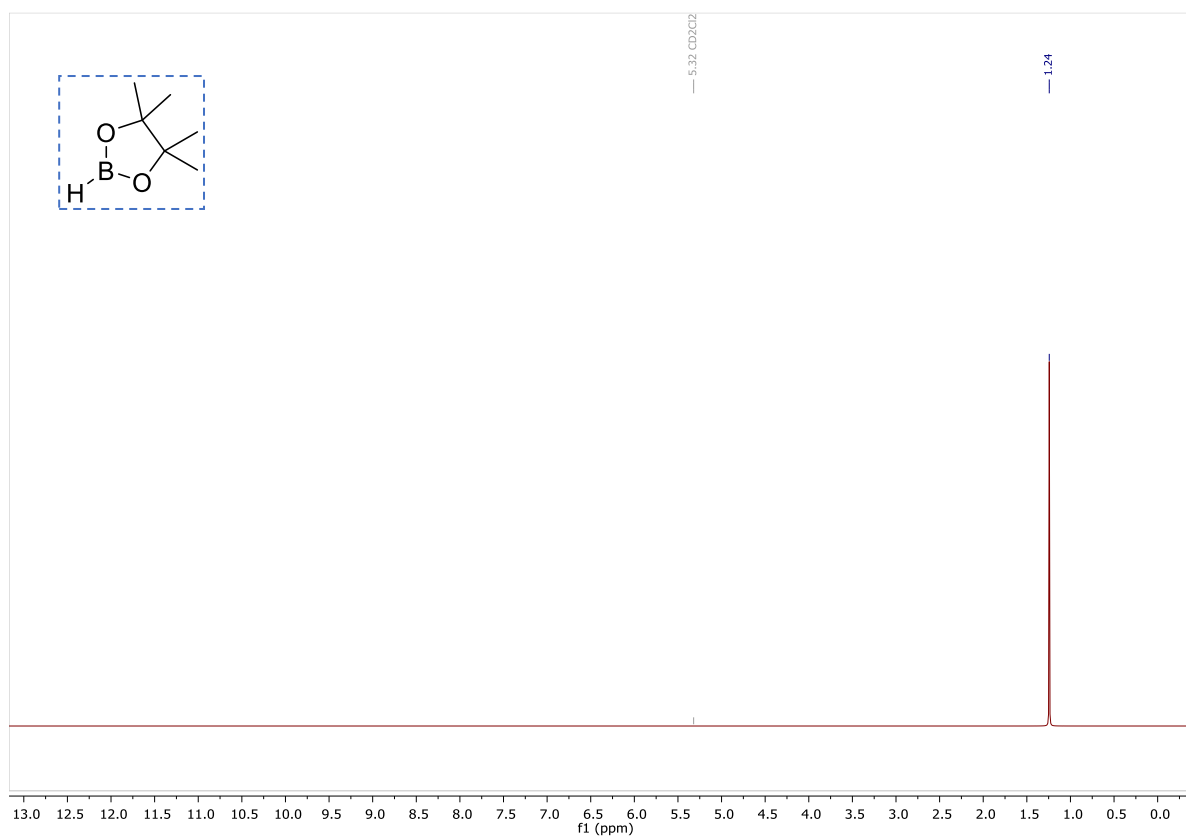


Figure S118 – ¹H NMR spectrum of pinacolborane (**2**) in DCM-d₂.

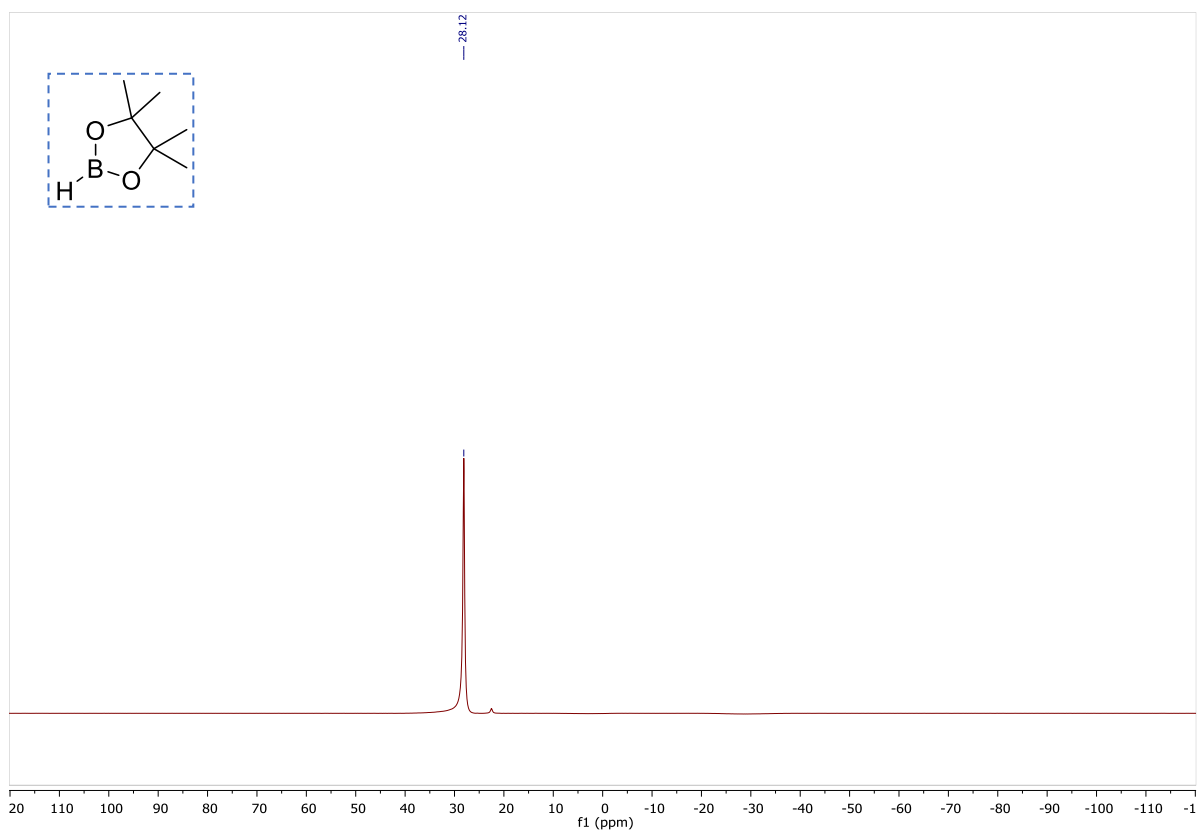
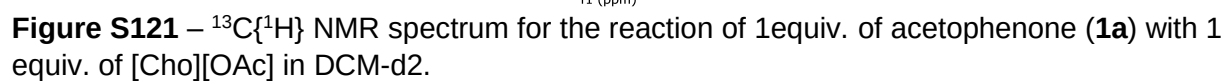
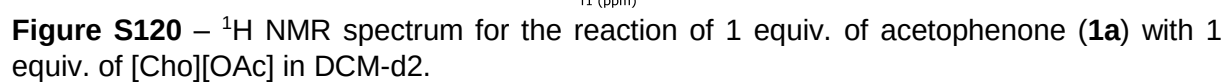


Figure S119 – ¹¹B {¹H} NMR spectrum of pinacolborane (**2**) in DCM-d₂.



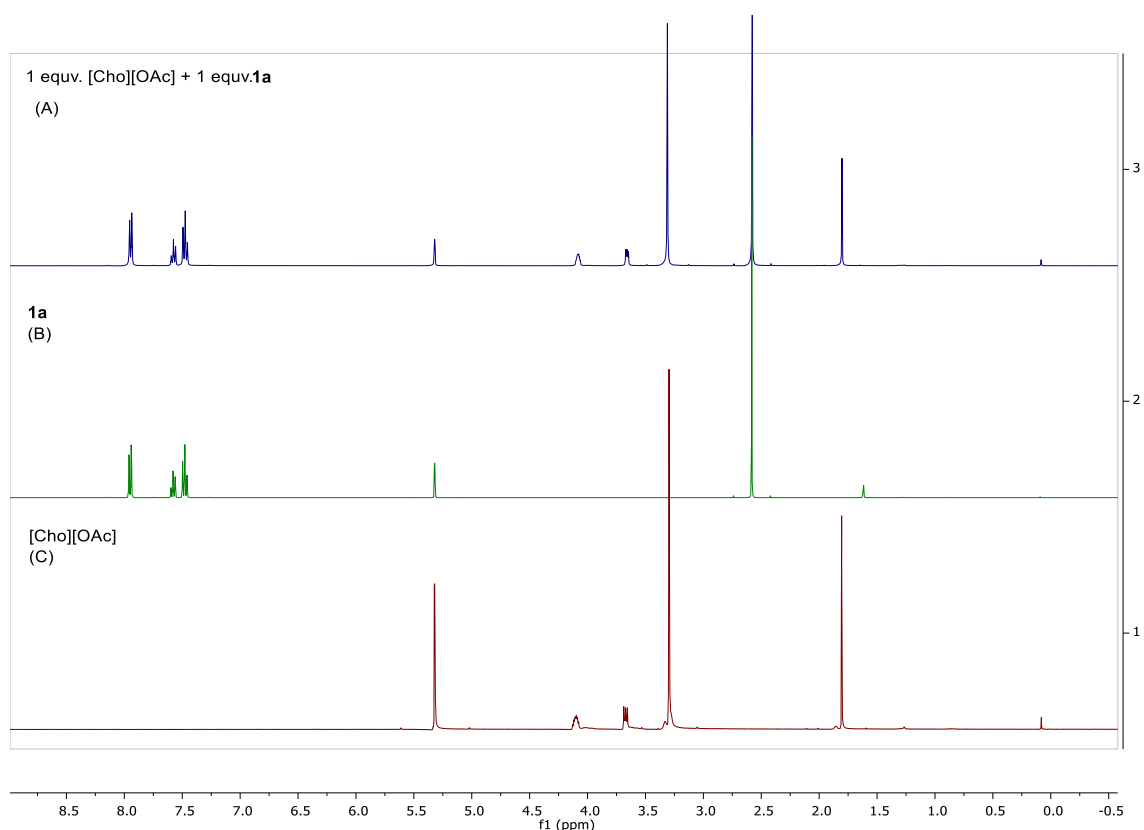


Figure S122 – Stacked ^1H NMR spectra: (A) the reaction of 1equiv. of acetophenone (**1a**) with 1 equiv. of [Cho][OAc], (B) acetophenone (**1a**) and (C) [Cho][OAc]. Solvent: DCM-d_2 .

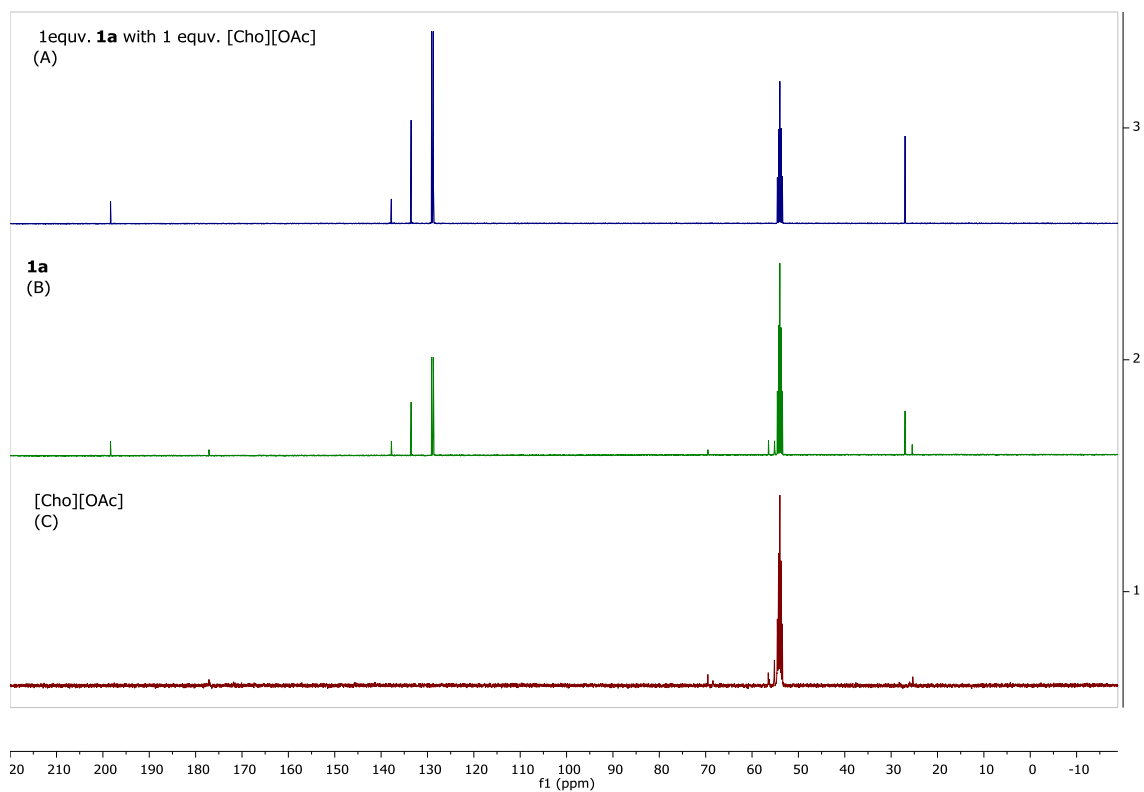


Figure S123 – Stacked $^{13}\text{C}\{^1\text{H}\}$ NMR spectra: (A) the reaction of 1 equiv. of acetophenone (**1a**) with 1 equiv. of [Cho][OAc], (B) acetophenone (**1a**) and (C) [Cho][OAc]. Solvent: DCM-d_2 .

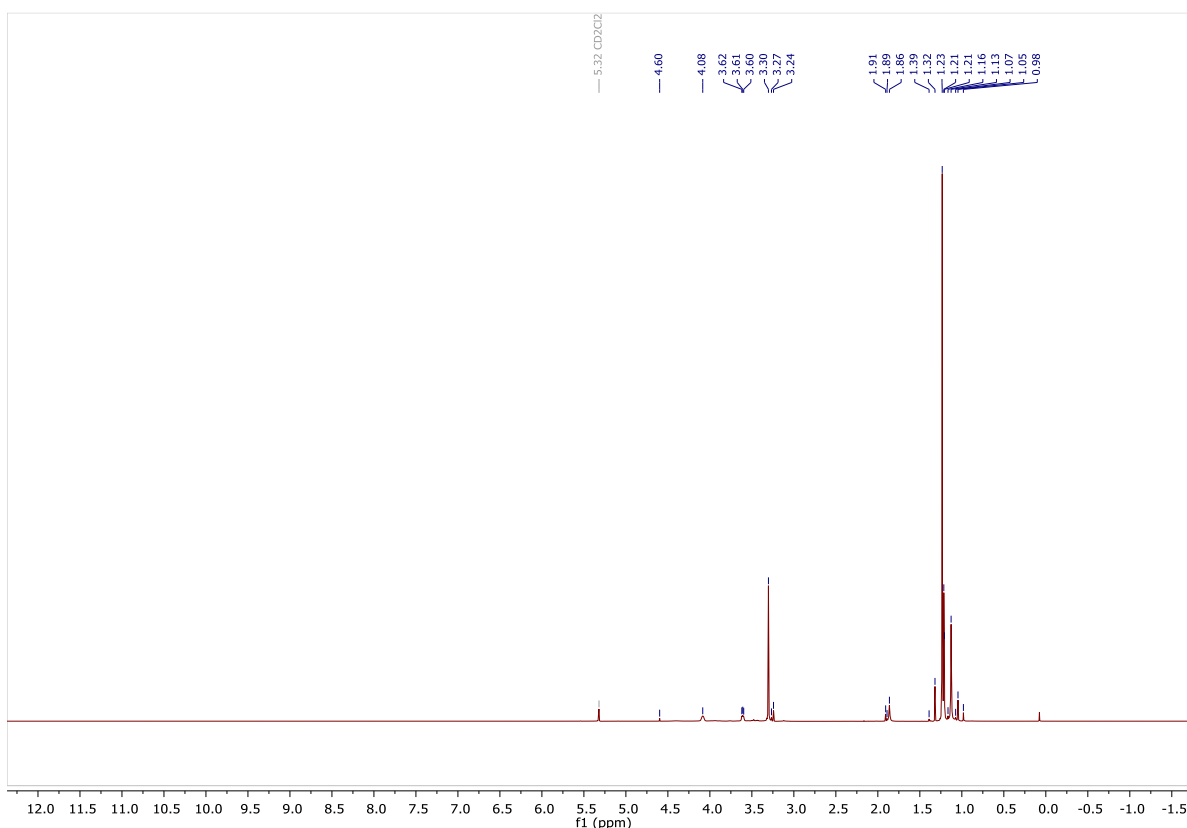


Figure S124 – ^1H NMR spectrum for the reaction of 1.35 equiv. of HBpin (**2**) with 0.35 equiv. of [Chol][OAc] in CDCl_3 .

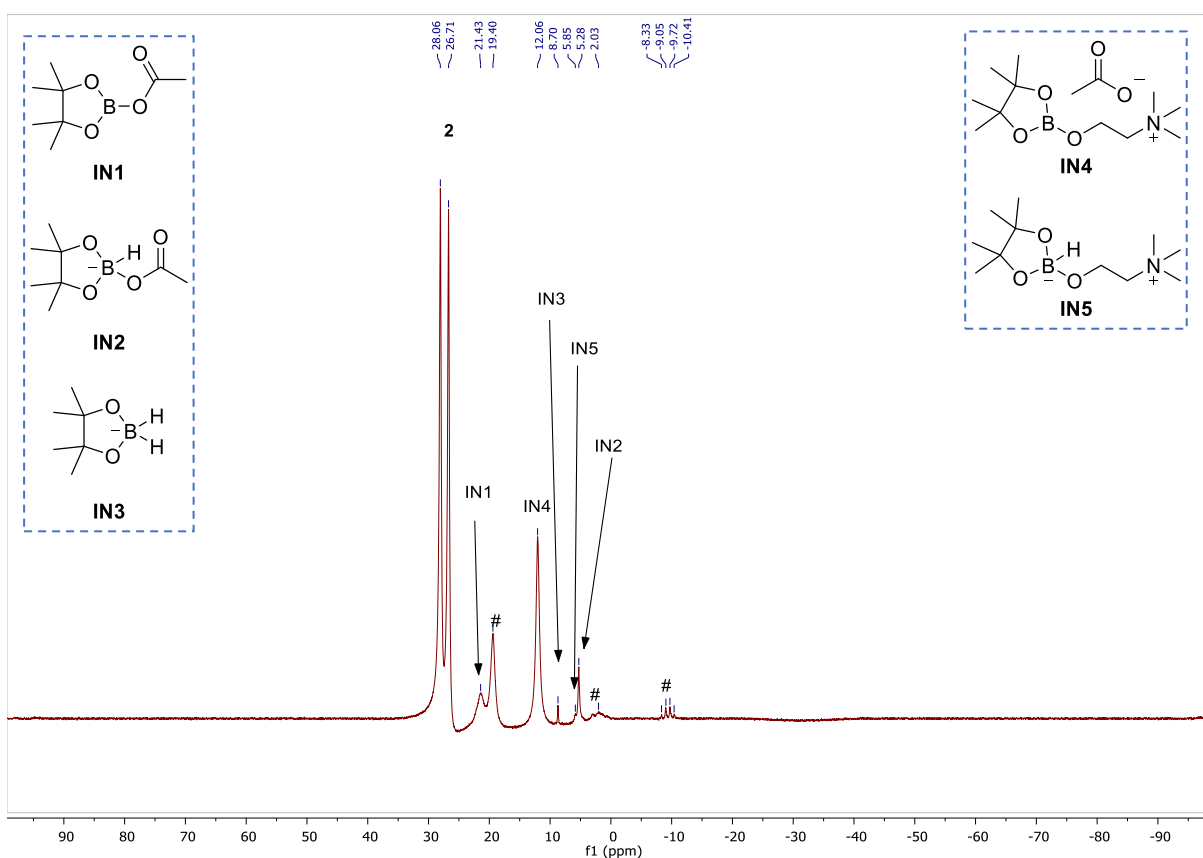


Figure S125 – ^{11}B NMR spectrum for the reaction of 1.35 equiv. of HBpin (**2**) with 0.35 equiv. of [Chol][OAc] in CDCl_3 . # Undefined signals. The signal at $\delta = -9.36$ ppm is visible only in

DCM-d2. For the spectrum in the toluene-d8 quartet at $\delta = -9.36$ ppm was not observed. For comparison, see Fig. S126.

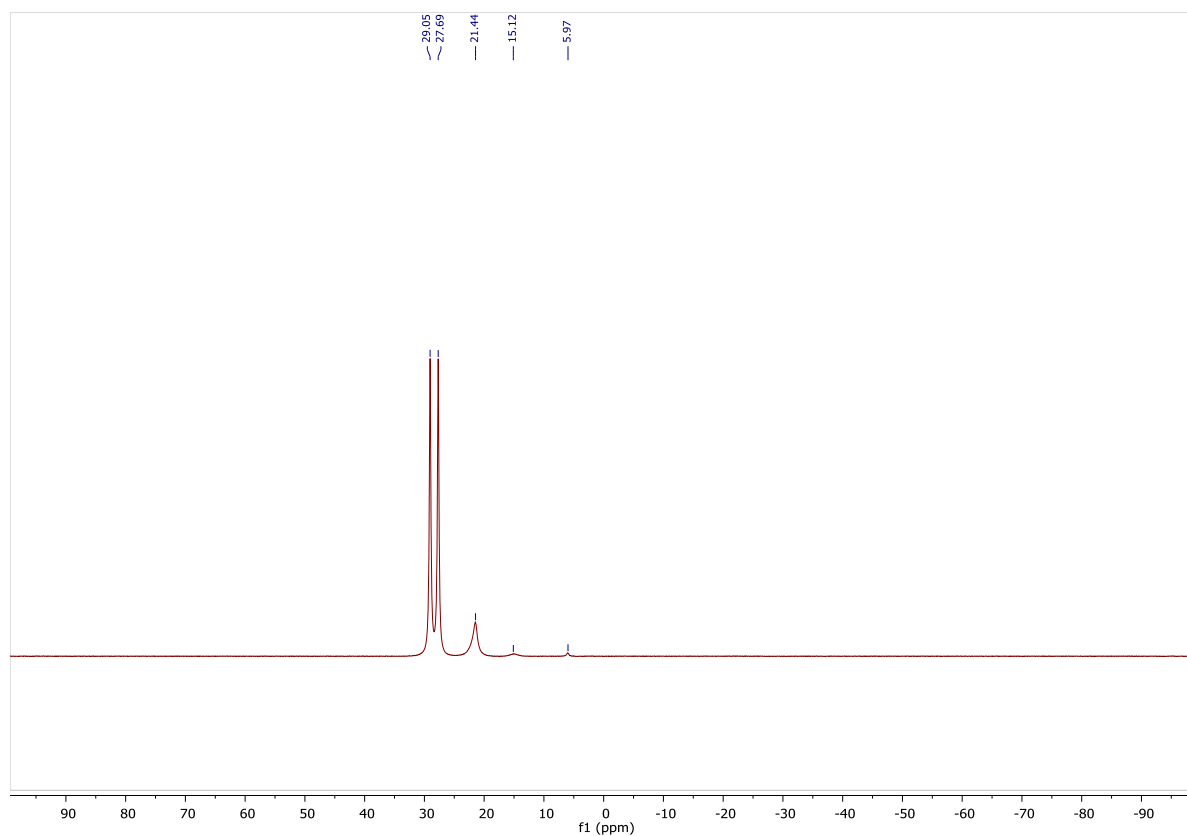


Figure S126 – ^{11}B NMR spectrum for the reaction of 1.35 equiv. of HBpin (**2**) with 0.35 equiv. of [Cho][OAc] in toluene-d8.

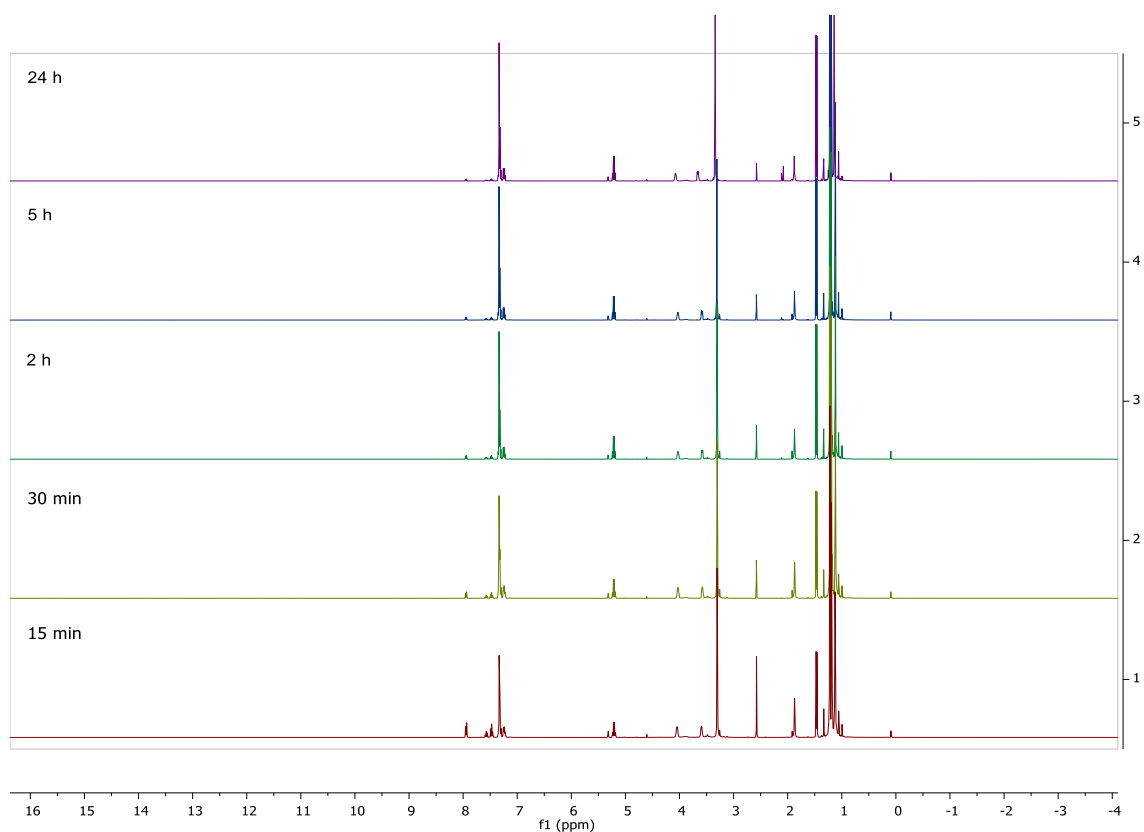


Figure S127 – Time-dependent stacked ^1H NMR spectra for the reaction of 1.35 equiv. of HBpin (**2**) with 1 equiv. of acetophenone (**1a**) in the presence of 0.35 equiv. of [Chol][OAc] in DCM-d_2 .

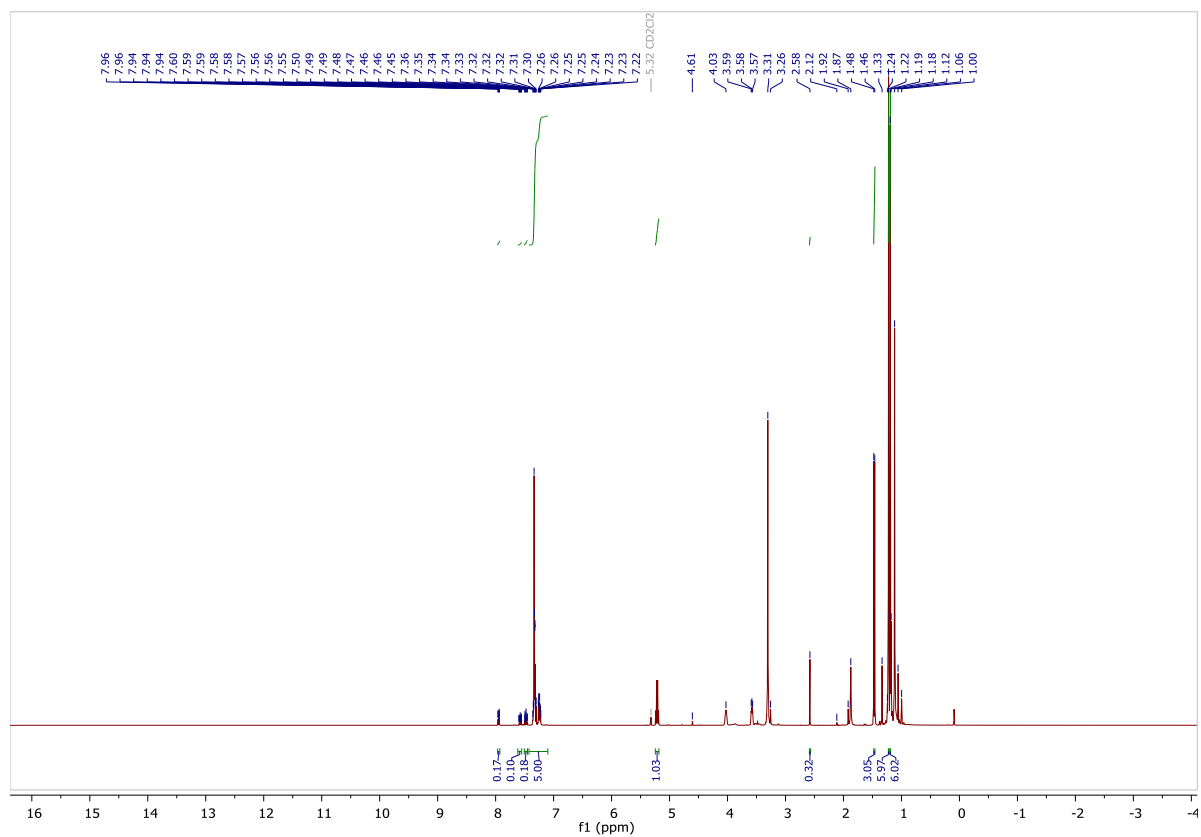


Figure S128 – ^1H NMR spectrum for the reaction of 1.35 equiv. of HBpin (**2**) with 1 equiv. of

acetophenone (**1a**) in the presence of 0.35 equiv. of [Cho][OAc] in DCM-d2 after 2 h. For clarity, only signals from **1a** and **3a** have been integrated.

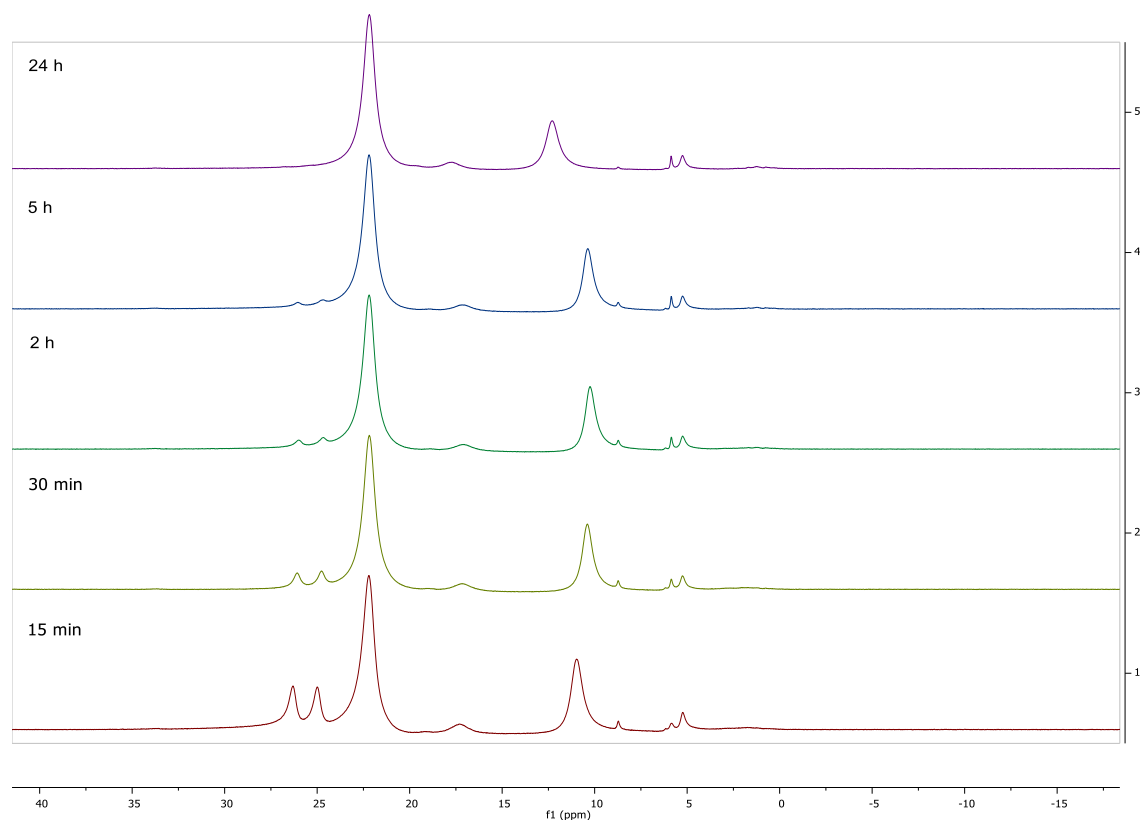


Figure S129 – Time-dependent stacked ^{11}B NMR spectrum for the reaction of 1.35 equiv. HBpin (**2**) with 1 equiv. of acetophenone (**1a**) in the presence of 0.35 equiv. of [Cho][OAc] in DCM-d2.

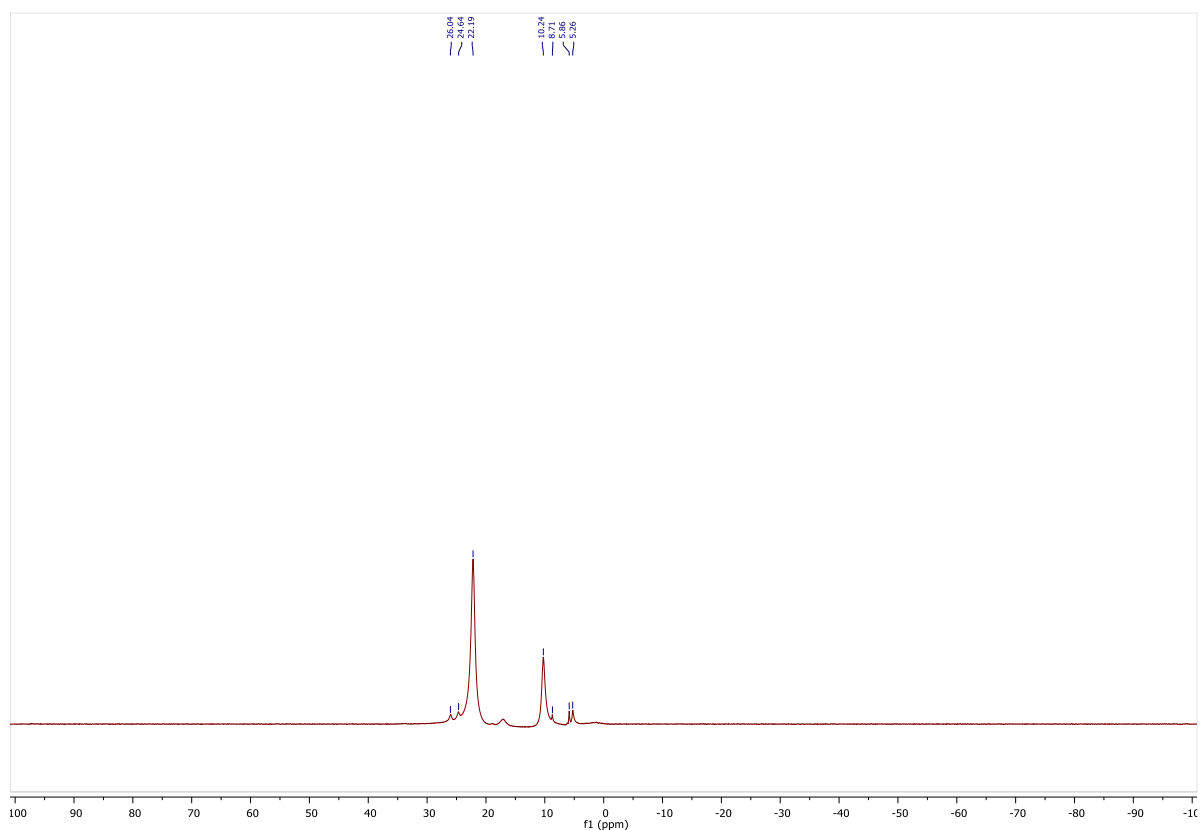


Figure S130 – ^{11}B NMR spectrum for the reaction of 1.35 equiv. of HBpin (**2**) with 1 equiv. of acetophenone (**1a**) in the presence of 0.35 equiv. of [Cho][OAc] after 2 h in DCM- d_2 .

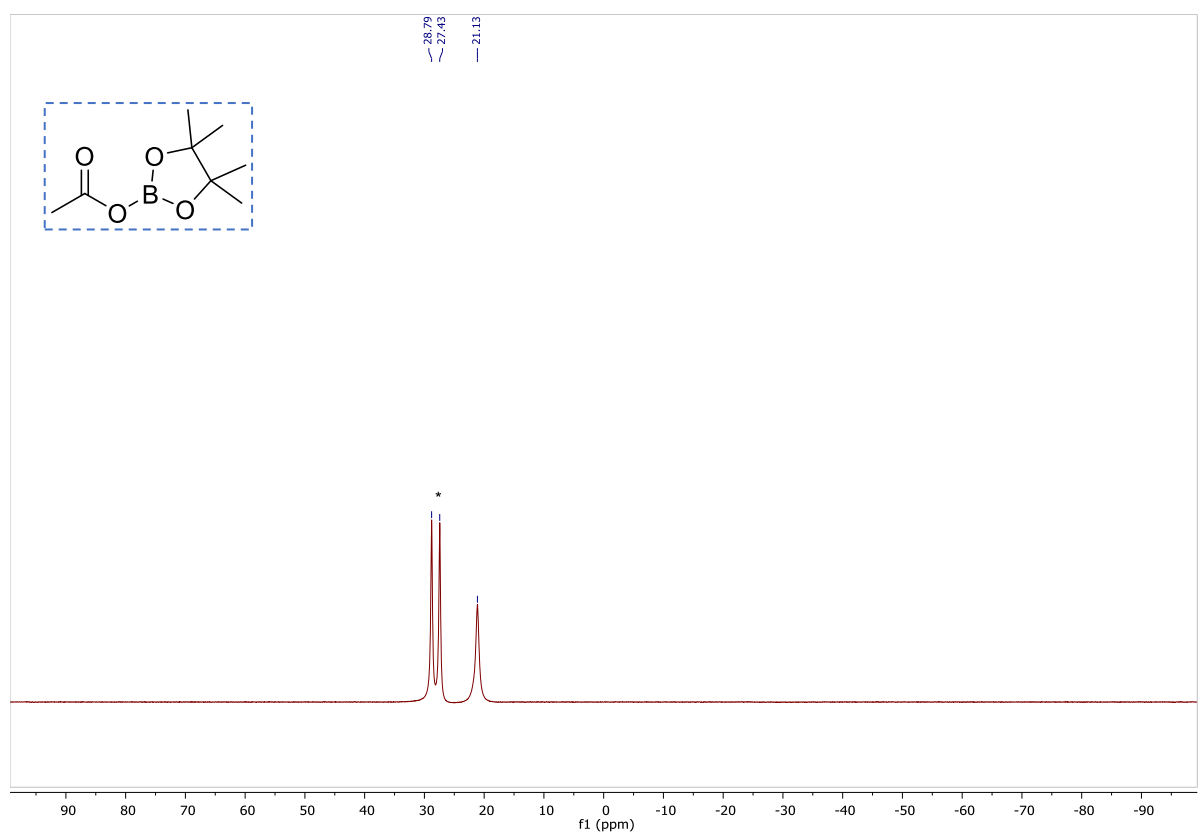


Figure S131 – ^{11}B NMR spectrum of OAcBpin (**IN1**) obtained in equimolar reaction of acetic acid with pinacolborane (**2**) in DCM- d_2 . *HBpin.

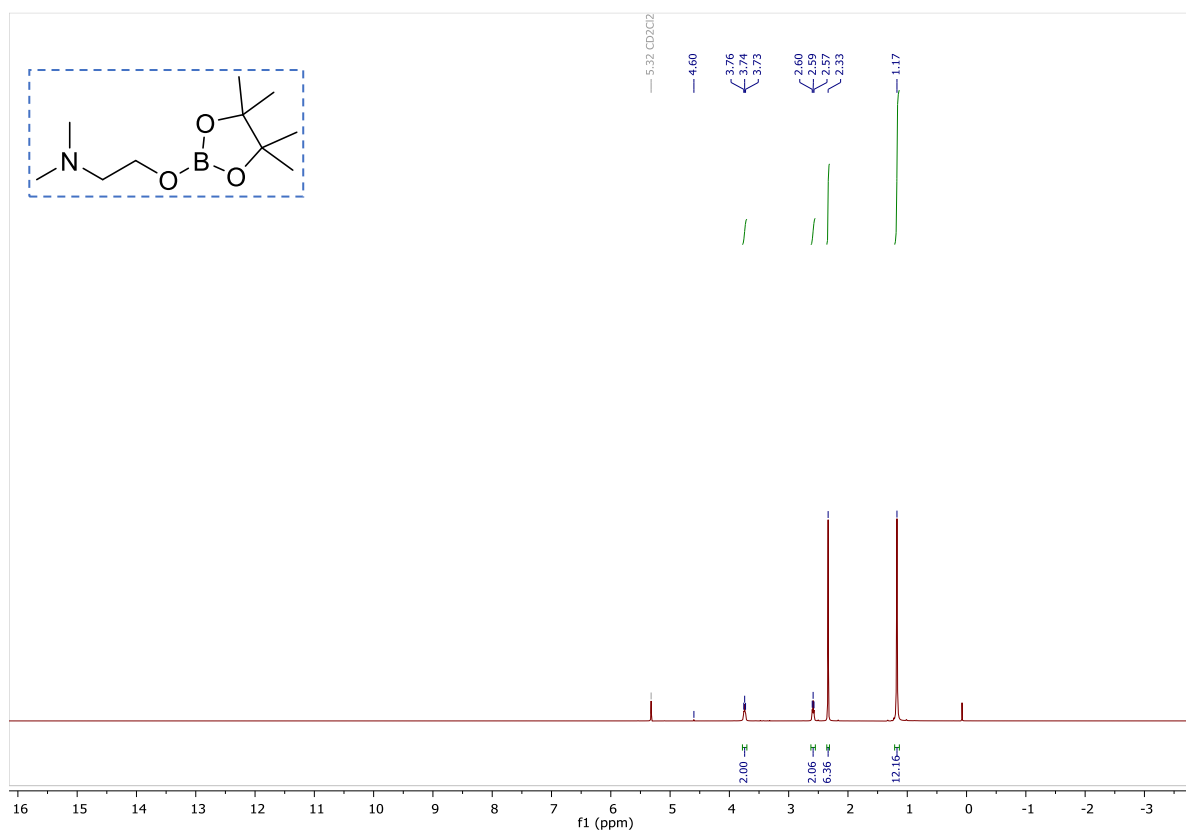


Figure S132 – ¹H NMR spectrum for the equimolar reaction of 2-(dimethylamino)ethan-1-ol with pinacolborane (**2**) in DCM-d₂.

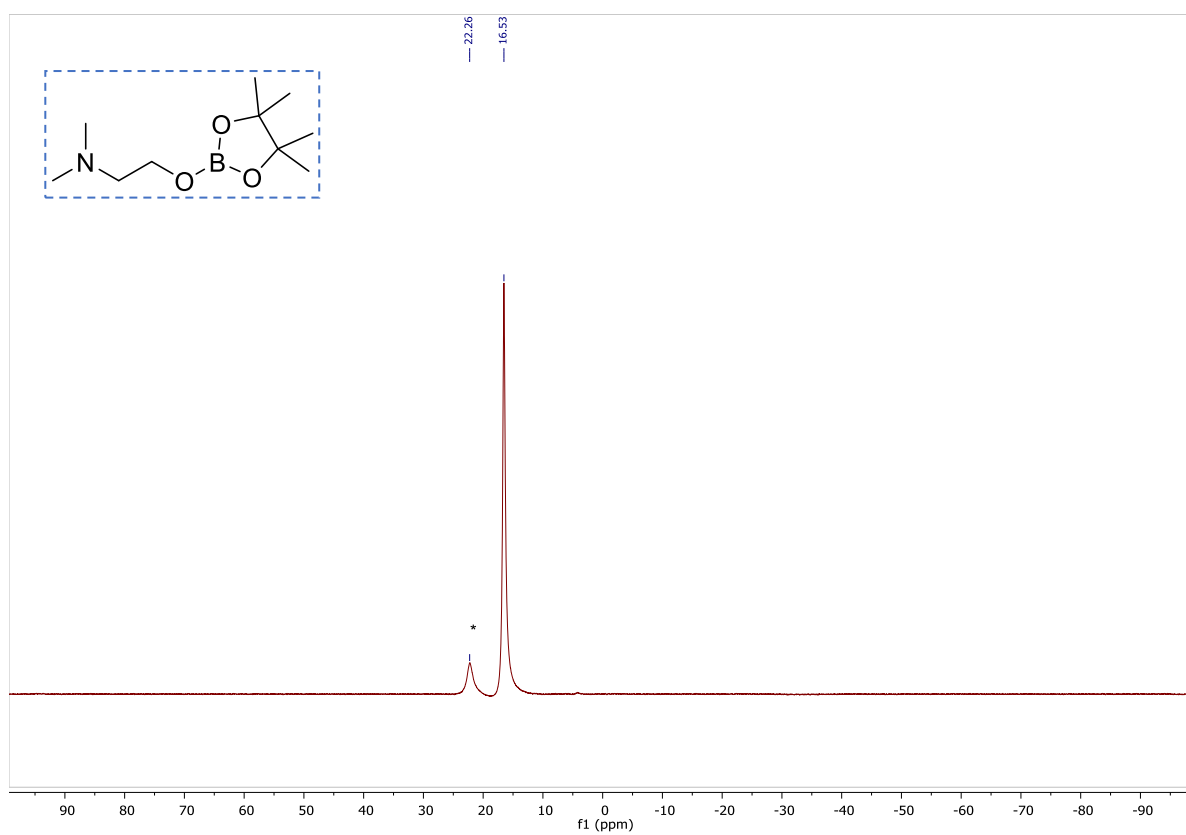


Figure S133 – ¹¹B NMR spectrum for the equimolar reaction of 2-(dimethylamino)ethan-1-ol with pinacolborane (**2**) in DCM-d₂. *O(Bpin)₂.

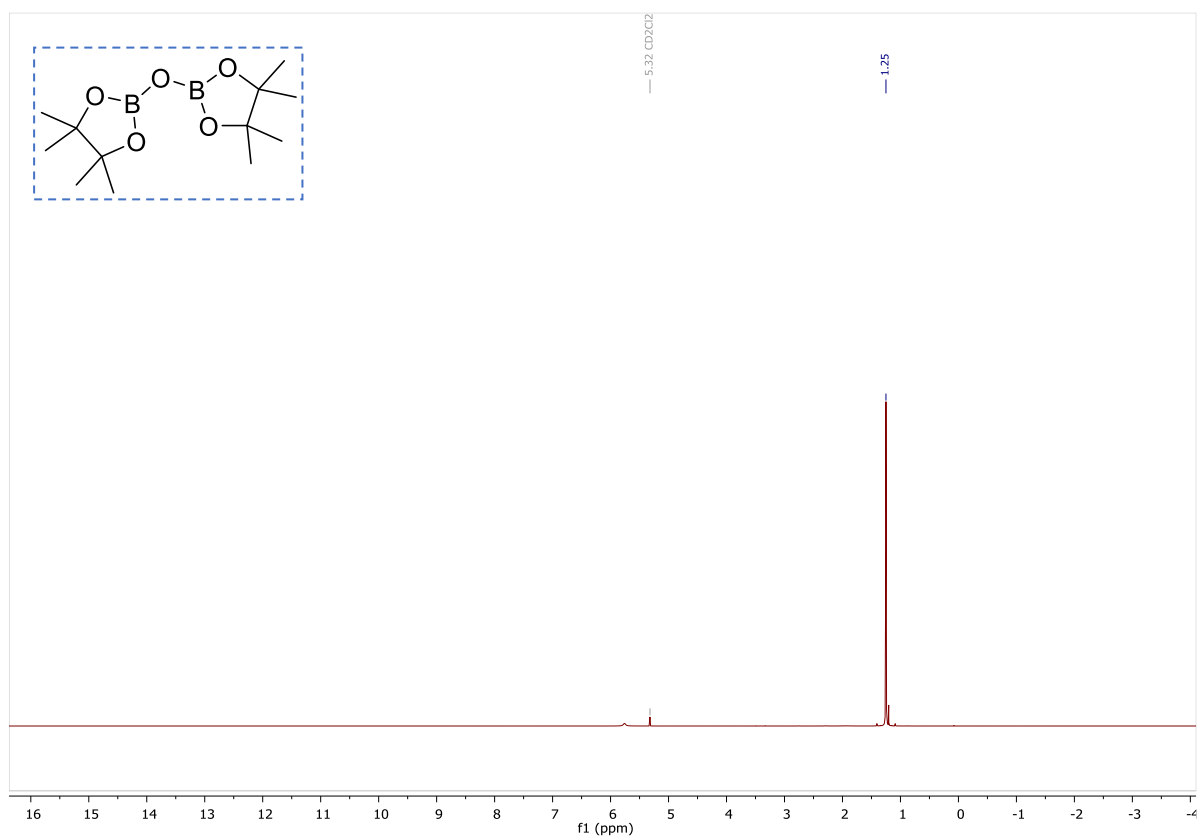


Figure S134 – ^1H NMR spectrum of $\text{O}(\text{Bpin})_2$ obtained in equimolar reaction of water with pinacolborane (**2**) in DCM-d_2 .

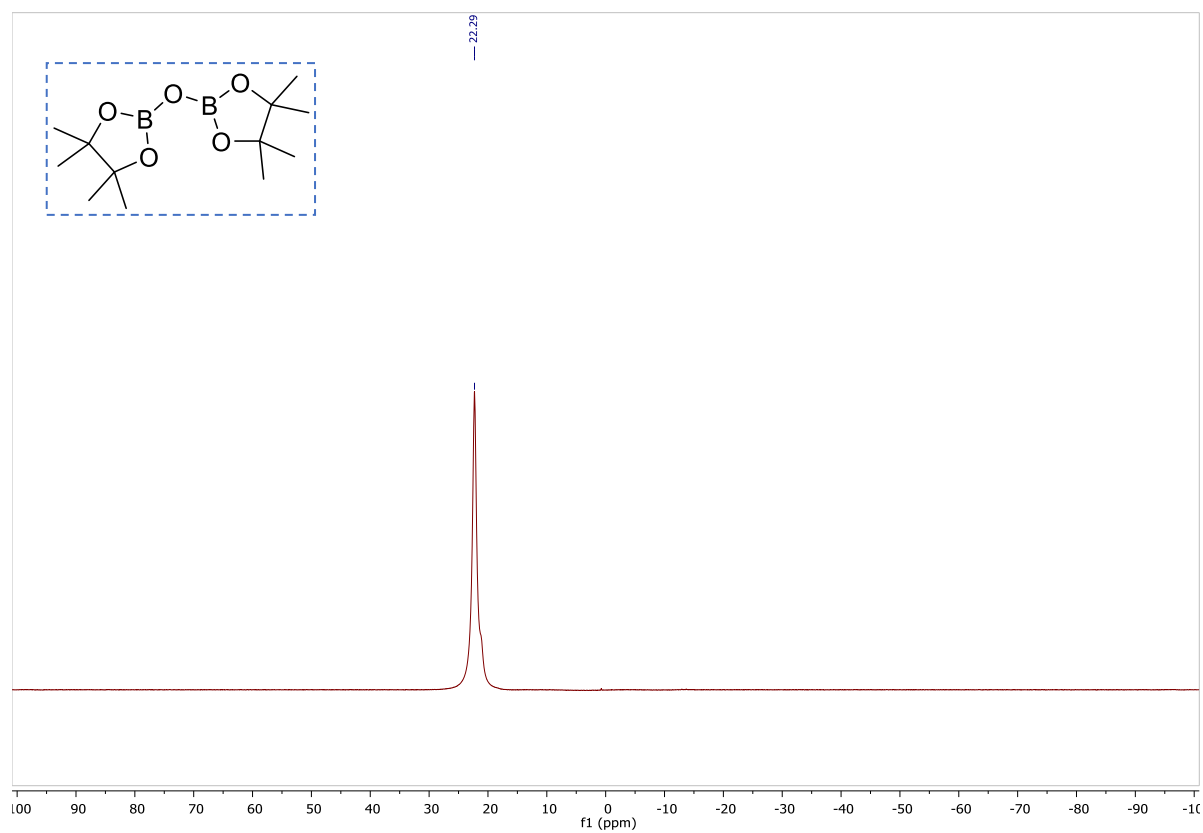


Figure S135 – ^{11}B NMR spectrum of $\text{O}(\text{Bpin})_2$ obtained in equimolar reaction of water with pinacolborane (**2**) in DCM-d_2 .

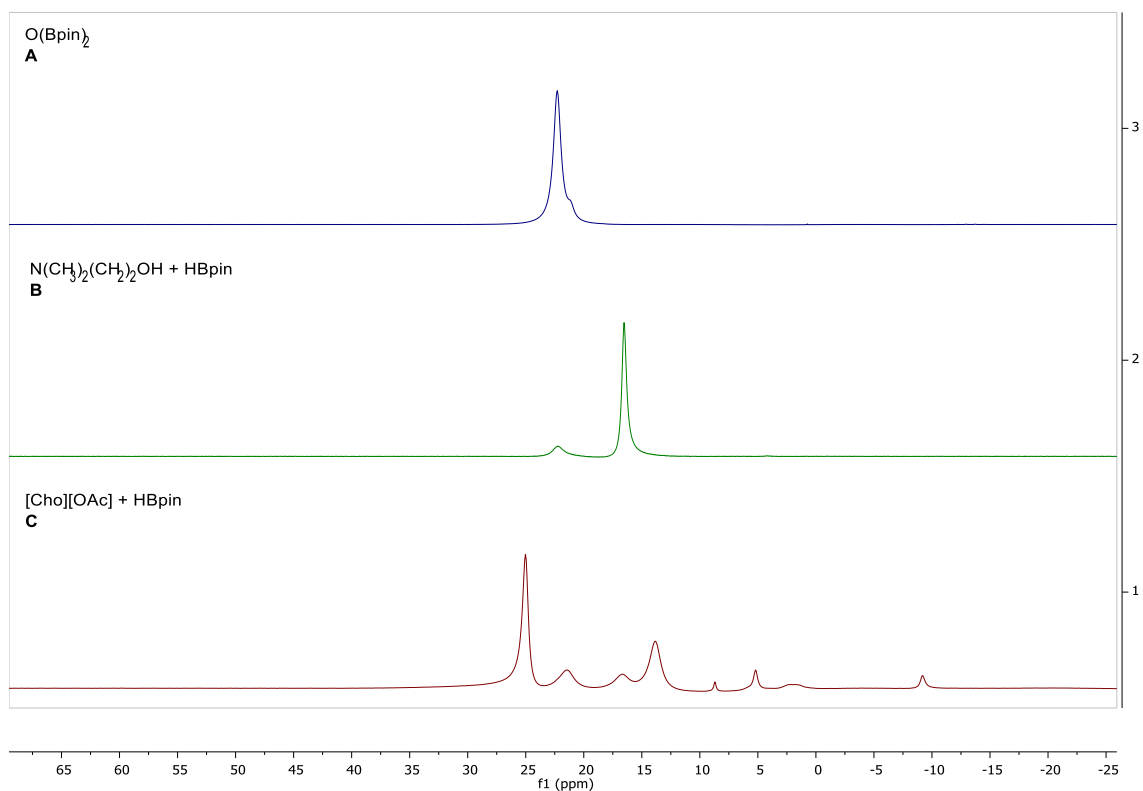


Figure S136 – Stacked ^{11}B NMR spectra: (A) $\text{O}(\text{Bpin})_2$, (B) the equimolar reaction of 2-(dimethylamino)ethan-1-ol with pinacolborane (**2**) and (C) reaction of pinacolborane (**2**) with $[\text{Cho}][\text{OAc}]$.

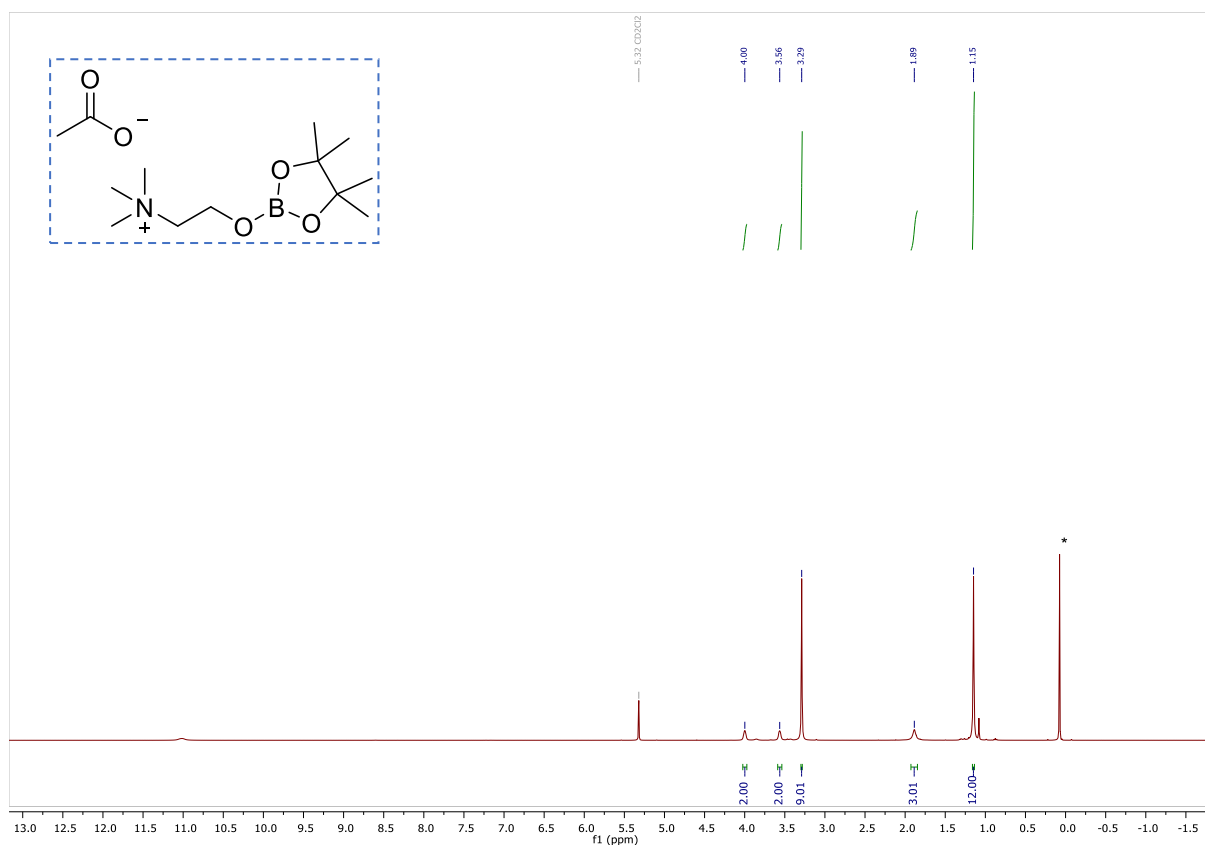


Figure S137 – ^1H NMR spectrum for the IN4 synthesized in equimolar reaction of $[\text{Cho}][\text{OAc}]$ with pinacolborane (**2**) in DCM-d_2 . * - Grease.

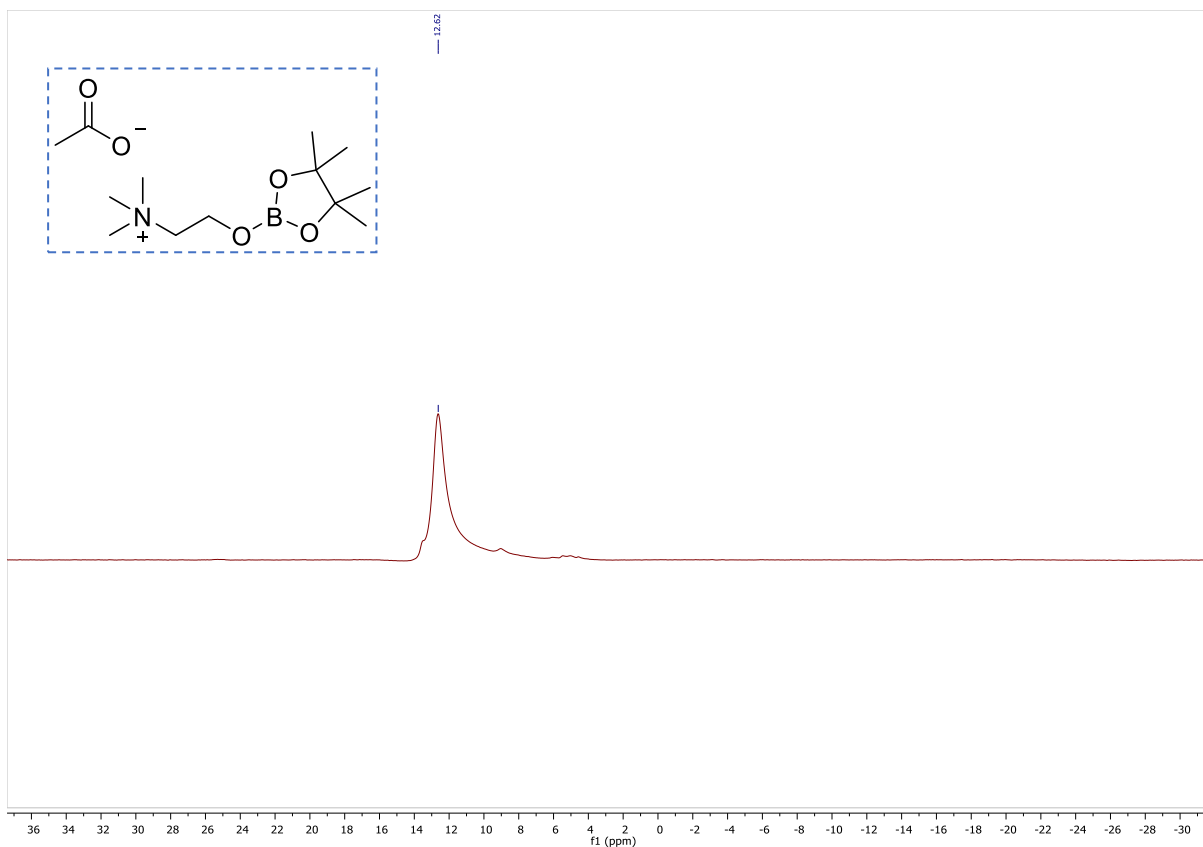


Figure S138 – ¹¹B NMR spectrum for the IN4, synthesized in equimolar reaction of [Cho][OAc] with pinacolborane (**2**) in DCM-d₂.

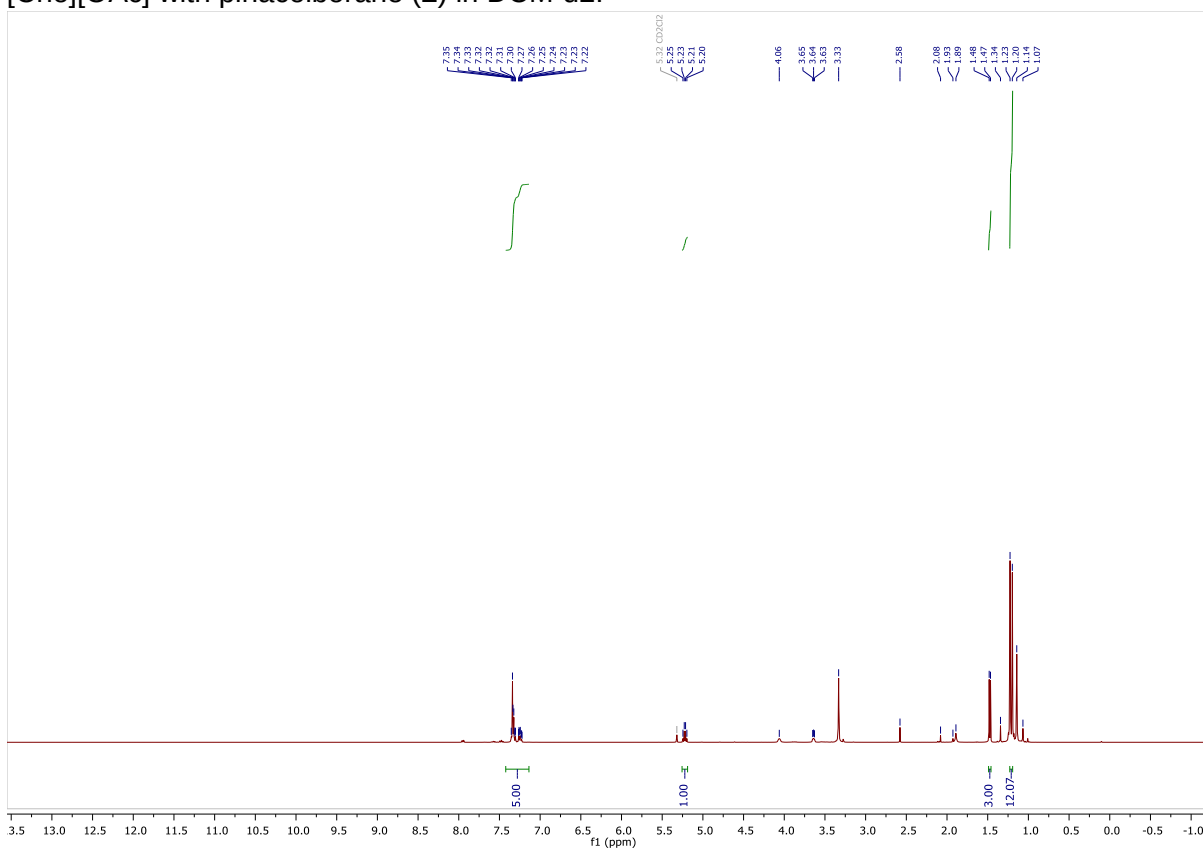


Figure S139 – ¹H NMR spectrum for the reaction of 1.2 equiv. of pinacolborane (**2**), 1 equiv. of acetophenone (**1a**), 20 mol% of IN4 after 1 h in DCM-d₂. For clarity, only signals **3a** have been integrated.

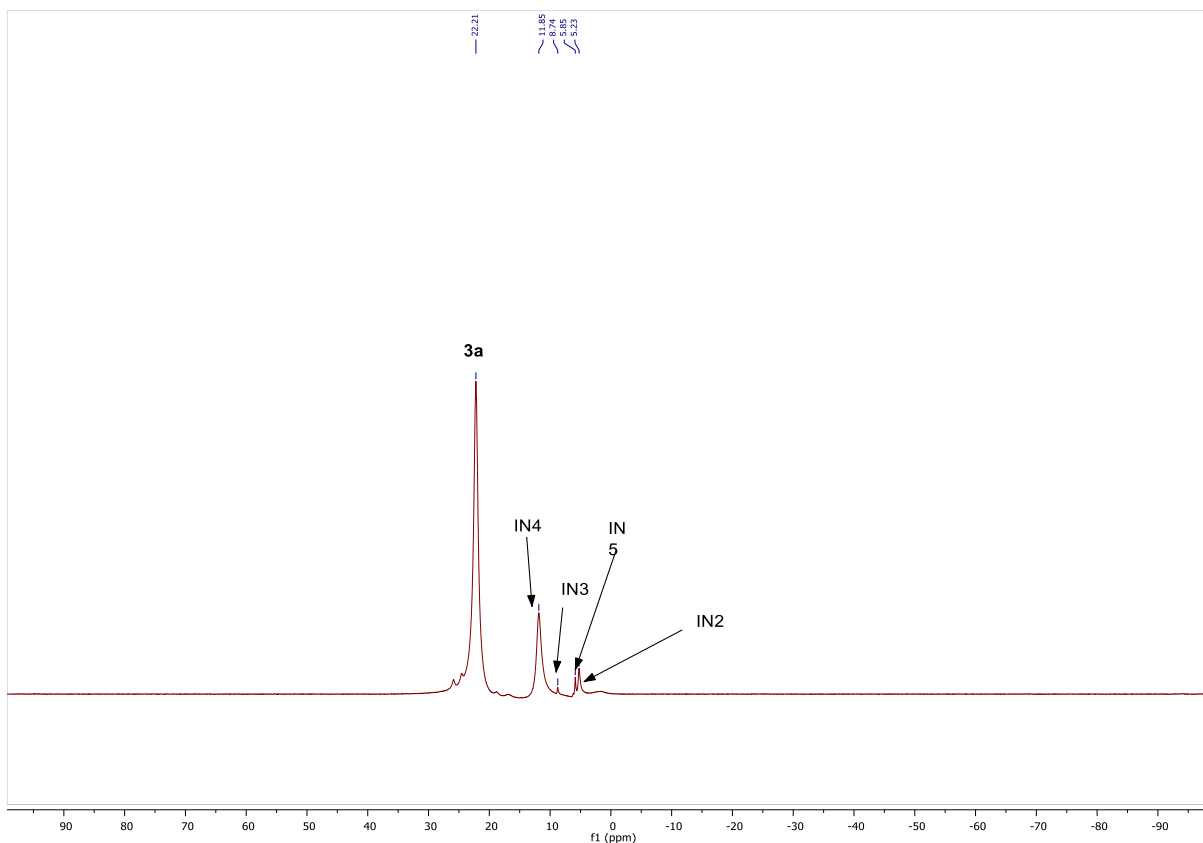


Figure S140 – ^{11}B NMR spectrum for the reaction of 1.2 equiv. of pinacolborane (**2**), 1 equiv. of acetophenone (**1a**), 20 mol% of IN4 after 1 h in DCM-d₂.

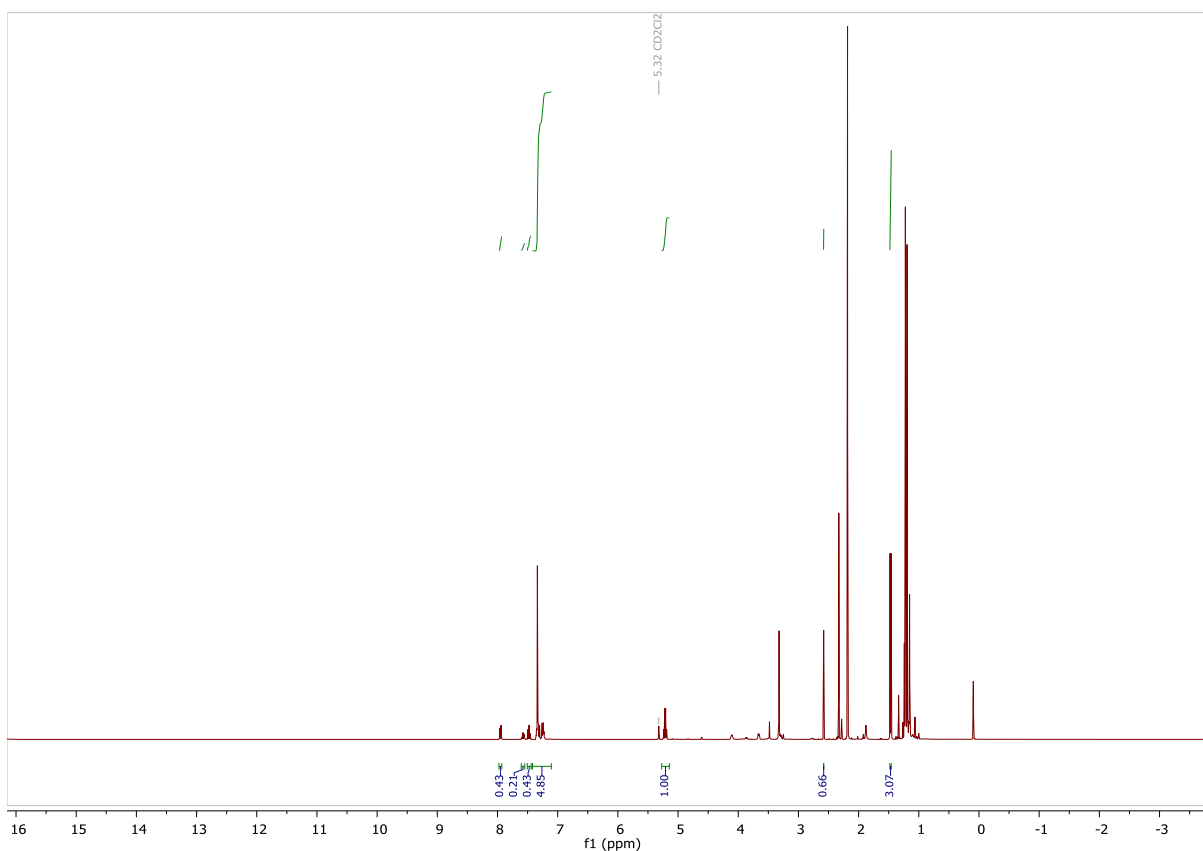


Figure S141 – ^1H NMR spectrum for the reaction of 1.2 equiv. of pinacolborane (**2**), 1 equiv. of acetophenone (**1a**), 15 mol% of [Cho][OAc], and 45 mol% of TMEDA under argon

atmosphere at room temperature after 1 h in DCM-d₂. For clarity, only signals from **1a** and **3a** have been integrated.

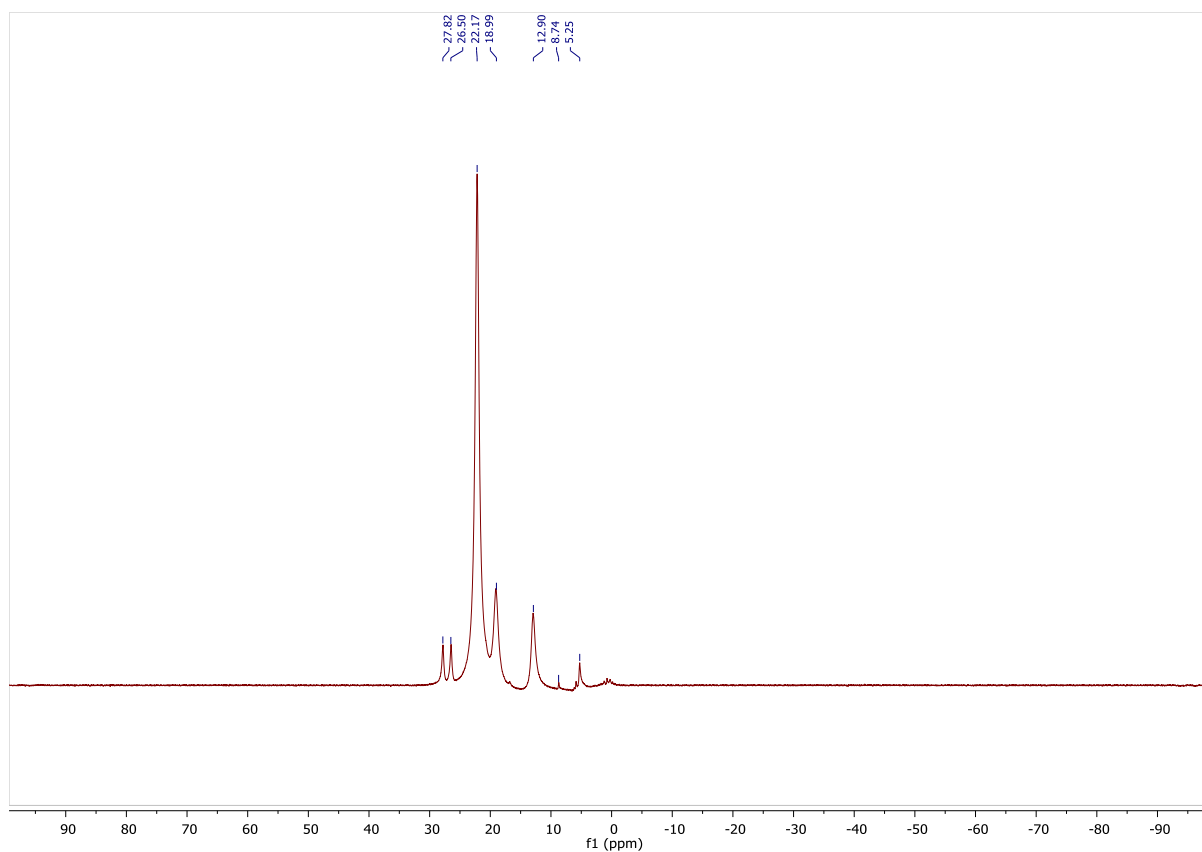


Figure S142 – ¹¹B NMR spectrum for the reaction of 1.2 equiv. of pinacolborane (**2**), 1 equiv of acetophenone (**1a**), 15mol% of [Cho][OAc], and 45 mol% of TMEDA under argon atmosphere at room temperature after 1 h in DCM-d₂.

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Organocatalytic hydroboration of imines, nitriles, and amides using choline-based ionic liquids

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ABSTRACT

This study reports the application of choline-based ionic liquids as organocatalysts in the hydroboration of imines, nitriles, and amides. The best results characterized by mild reaction conditions and low catalyst loading, were obtained for choline acetate, which showed high functional groups tolerance. Moreover, the one-pot hydroboration sequence and coupling reactions enabled the synthesis of amides, imines, and primary, secondary, and tertiary amines from nitriles with high yields. In these studies, the recyclability of the catalyst was proved by carrying out repetitive batch experiments. The NMR studies and DFT calculations revealed that the choline and acetate borohydrides are catalytically active species in this process.

1. Introduction

Ionic liquids are salts usually consisting of an organic cation and an inorganic or organic anion, with a melting point below 100 °C. They are currently being considered as a green alternative to many chemical and physical processes, due to their unique properties, such as low vapor pressure, non-flammability, very low corrosivity relative to mineral acids and bases, and physical and chemical stability [1–3]. Ionic liquids have multiple applications, in extraction and separation, electrochemistry and catalysis [4–7]. They are also used as organocatalysts [8,9]. Ionic liquids derived from natural resources attract significant interest due to their low toxicity and biodegradability [10,11]. Choline-based ionic liquids, of natural origin [12] with simple carboxylic acid anion have been established as effective organocatalysts. They have been applied in a wide range of organic transformations, such as Knoevenagel, [13] polymerization, [14] glycolysis of poly(ethylene terephthalate), [15] cycloaddition, [16] oxidation of alcohols [17,18] and multicomponent reactions [19,20]. These results have encouraged us to evaluate the use of choline-based ionic liquids as a potential organocatalyst for the hydroboration of imines, nitriles, and amides.

The chemistry of nitrogen compounds plays a critical role in industry due to their great biological importance. They are key compounds in the synthesis of e.g., pharmaceuticals, [21] agrochemicals, [22] and natural products [23]. Among these compounds, amines are the most widely used building blocks in the synthesis of APIs (active pharmaceutical

ingredients), [24] and the reduction of unsaturated carbon–nitrogen bonds has been of great importance in the synthesis of fine chemicals and natural products for decades [21,25]. Catalytic hydroboration is a powerful synthetic method for reducing unsaturated carbon–carbon and carbon–heteroatom bonds [26,27]. In contrast to reduction with more hazardous inorganic hydrides (e.g., LAH) [28,29] or hydrogen gas, [30–32] hydroboration of imines, nitriles, or amides occurs under mild conditions, with easy-to-handle borates, and avoids generating stoichiometric amounts of inorganic waste. However, the hydroboration of the unsaturated C–N bonds is still dominated by metal-based organic or inorganic catalysts [33–36].

In recent years, the number of organocatalysts employed in this transformation has increased (Scheme 1). In the hydroboration of imines, the diazaphospholenes [37–41] and triazaphospholenes, [42] have been used most frequently, but heterocyclic compounds like carbodiphosphorane, [43] N-heterocyclic olefins (NHO), [44] and N-triflyl phosphoramidate [45] have also proven to be effective catalysts in this process. In addition, light-activated organocatalysts – diphenyl disulfide with NHC-boranes as reducing agents have been used in imine hydroboration [46]. The hydroboration of nitriles is more challenging, due to the high bond dissociation energy of the triple carbon–nitrogen bond [47]. To date, only bicyclic (alkyl)(amino)carbene (BICAAC) [48] and N-heterocyclic olefins (NHO) have been reported as organocatalysts for this process [44]. Nguyen and Doan have employed tropylium tetrafluoroborate as an ionic, universal catalyst for the hydroboration of

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imines, nitriles, and amides, but high catalyst loading (10 mol%) was required [49]. Almost all previously described catalysts demand several synthesis steps and the systems are sensitive to moisture and air. Multiple uses of the catalyst have only been described by Mandal *et al.* for BICAAC in the hydroboration of nitriles [48]. Recycling of the catalyst affects the productivity of the process, and thus its economy. The search for easy-to-handle, readily available, and recyclable organocatalysts that are stable in moisture and air for the hydroboration of unsaturated carbon–nitrogen bonds is of great importance.

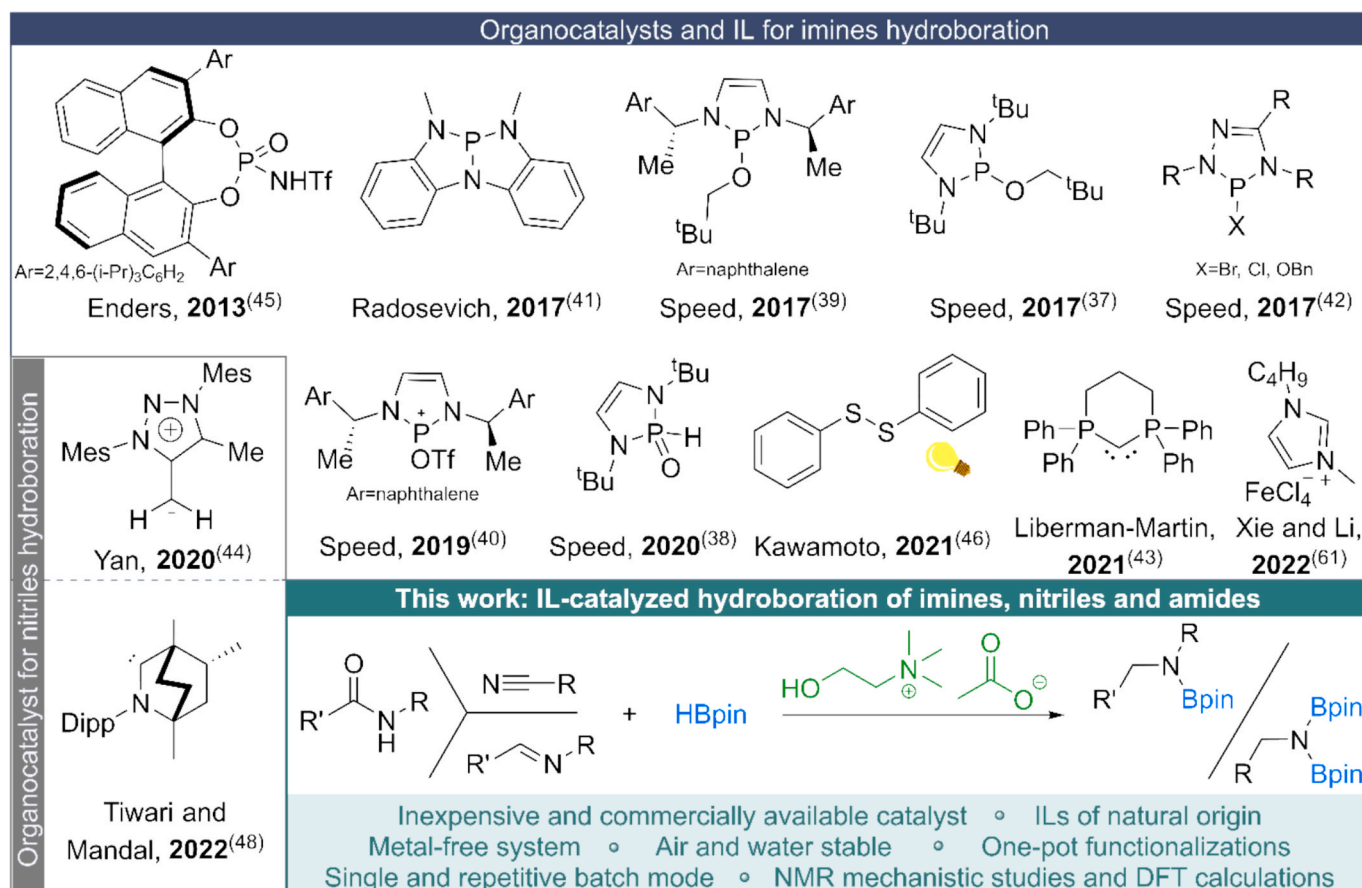
Ionic liquids have mainly been used as media for immobilization TM – catalysts or just as solvents [50–57]. The application of ILs as organocatalysts in hydroboration is limited to a few examples, including the hydroboration of CO₂, [58] the hydroboration of alkenes in the presence of pyrrolidinium salts, [59] and the hydroboration of olefins with polyboranes [60]. The hydroboration of imines has only been performed in the presence of a metallic imidazolium-based ionic liquid, in which a transition metal was responsible for catalytic activity [61]. Compared to the iron-containing IL catalyst reported by Xie and Li *et al.*, the [Cho][OAc] system offers several notable advantages: i) it represents the first metal-free ionic liquid used for hydroboration of unsaturated C–N bonds; ii) our mechanistic studies (NMR and DFT) support an ionic pathway involving borohydrides, in contrast to mechanism based on metal coordination; iii) [Cho][OAc] enables efficient hydroboration not only of imines but also of more challenging substrates such as nitriles and amides.

Herein, we present the application of choline acetate as an organocatalyst in the hydroboration of imines, nitriles, and secondary amides under mild conditions. This organocatalyst is simple, inexpensive, commercially available, naturally derived, stable, and recyclable, and it can be used in both single and repetitive batch modes. Both NMR experiments and DFT calculations were used to investigate the reaction

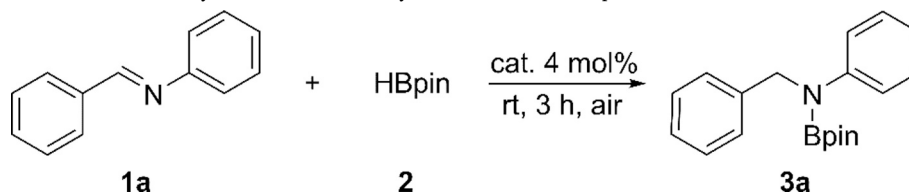
mechanism, which is complex, and to propose different pathways that occur simultaneously during the process.

2. Results and discussion

Based on our experience in the synthesis of organoboron compounds in green solvents, [53,54,62–67] as well as the application of ionic liquids as effective organocatalysts in the C=C reduction, [59] we tested the catalytic potential of choline or *n*-alkyl quaternary ammonium-based ionic liquids with carboxylic acids or bis(trifluoromethylsulfonyl)imide anions in the hydroboration reaction of imines (see ESI, Table S1). The catalyst and reaction conditions were screened using a model reaction of *N*-benzylidenaniline (**1a**) with a 10 % excess of pinacolborane (**2**), 4 mol % of the ionic liquid, and toluene as a solvent under air at room temperature. Keeping in mind that the hydroboration of imines is feasible without a catalyst, [68] a non-catalytic pathway was first excluded (Table 1, entry 1). Among several ionic liquids with choline cation, the highest conversion was observed for salts with benzyl and acetate anion (Table 1, entries 2 and 7). Changing the anion to [TFA] or [NTf₂][−] resulted in a significant drop in **2a** conversion (Table 1, entries 3–4). When ILs with oxalic anions were used (both amphoteric [Cho][Oxa] and acidic [Cho]₂[Oxa]) moderate reaction yields were achieved (Table 1, entries 5–6). Our study revealed that both the anion and the cation strongly influence the properties of the ionic liquids. [Cho][OAc] exhibited the highest catalytic activity in the process studied. Changing the cation to [TBA]⁺ or [TMA]⁺ resulted in lower process yields 39 % and 57 %, respectively. The precursors of the most efficient ionic liquids (acetic acid, benzoic acid, and potassium benzoate) were also tested, but the observed conversion of **2a** was lower in each case (see ESI, Table S1). It is worth mentioning that no by-products were formed regardless of the catalyst used.



Scheme 1. Previously employed organocatalysts and ionic liquid in the hydroboration reaction of imines and nitriles vs. this work.

Table 1Catalyst screening optimization of conditions for hydroboration of *N*-benzylidenaniline (**1a**) with pinacolborane (**2**).

Entry	IL	Mol% of IL	HBpin [equiv.]	Solvent	Yield of 3a [%] ^a
1	—	—	1.1	toluene	0
2	[Cho][Bz]	4	1.1	toluene	79
3	[Cho][TFA]	4	1.1	toluene	19
4	[Cho][NTf ₂]	4	1.1	toluene	22
5	[Cho][Oxa]	4	1.1	toluene	63
6	[Cho] ₂ [Oxa]	4	1.1	toluene	65
7	[Cho][OAc]	4	1.1	toluene	83 (96) ^b
8 ^b	[Cho][OAc]	2	1.1	toluene	38
9 ^b	[Cho][OAc]	6	1.1	toluene	96
10 ^b	[Cho][OAc]	4	1.5	toluene	>99
11 ^{b,c}	[Cho][OAc]	4	1.1	THF	>99
12 ^b	[Cho][OAc]	4	1.1	DCM	64
13 ^b	[Cho][OAc]	4	1.1	ethyl acetate	>99

Reaction conditions: [cat]:[**1a**]:[**2**] = 0.04:1:1.1–1.5, solvent (1 mL), 3 h, rt, air.^a The yield was based on GC–MS and ¹H NMR analyses.^b Under argon atmosphere.^c 2 h.

Furthermore, the yield of **3a** increased when the reaction was carried out under an argon atmosphere instead of air (Table 1, entry 7). Interestingly, a higher catalyst concentration (6 mol%) did not improve the conversion of **1a** after 3 h, but reducing the catalyst loading from 4 to 2 mol% resulted in a significant decrease in reaction yield (Table 1, entries 7–9). A considerable improvement, including quantitative conversion to the borylamine product (**3a**), was achieved either by using 1.5 equivalents of HBpin or by changing the solvent to THF or ethyl acetate (Table 1, entries 10–11 and 13). Using DCM as the reaction medium, resulted in moderate conversion of **1a** (Table 1, entry 12) (for more data see ESI, Table S2).

With the optimized conditions in hand, using 4 mol% of [Cho][OAc], 1.1 equivalents of HBpin (**2**), THF as a solvent, and an argon atmosphere, we explored the scope of imines (Scheme 2). Substituted imines with electron-donating groups such as –Me or –OMe (**1b** and **1d–e**) reacted faster than the model *N*-benzylidenaniline (**1a**), achieving quantitative conversion after 1 h. When the ethyl substituent was introduced, a reaction progress similar to **1a** was observed (**1c**). The introduction of electron-withdrawing groups (**1f**) or both electron-withdrawing and electron-donating groups in one molecule (**1g**) did not significantly affect the progress of the hydroboration reaction. However, the presence of an alkyl chain and methoxy group as a substituents at slightly decreased the yield of the product **3h–i**. It should be noted that imine hydroboration is chemoselective, leaving the nitro group and the double carbon–carbon bond (**3g** and **3k**) intact under the applied reaction conditions. Quantitative reduction of heteroaromatic imine (**1j**) and *N*-benzylidenbenzylamine (**1m**) required an extension of the reaction time to 18 h. The more sterically hindered *N*-(1-phenylethylidene)benzenamine (**1n**) reacted under harsher conditions to give the product **3n** in good yield. Similarly, more bulky imines (**1l**), diphenylmethanimine (**1o**), and *N*-methyl-1-phenylethanamine (**1p**) reacted smoothly with HBpin to form the corresponding products (**3l** and **3o–p**) in excellent yields (see ESI, Table S3).

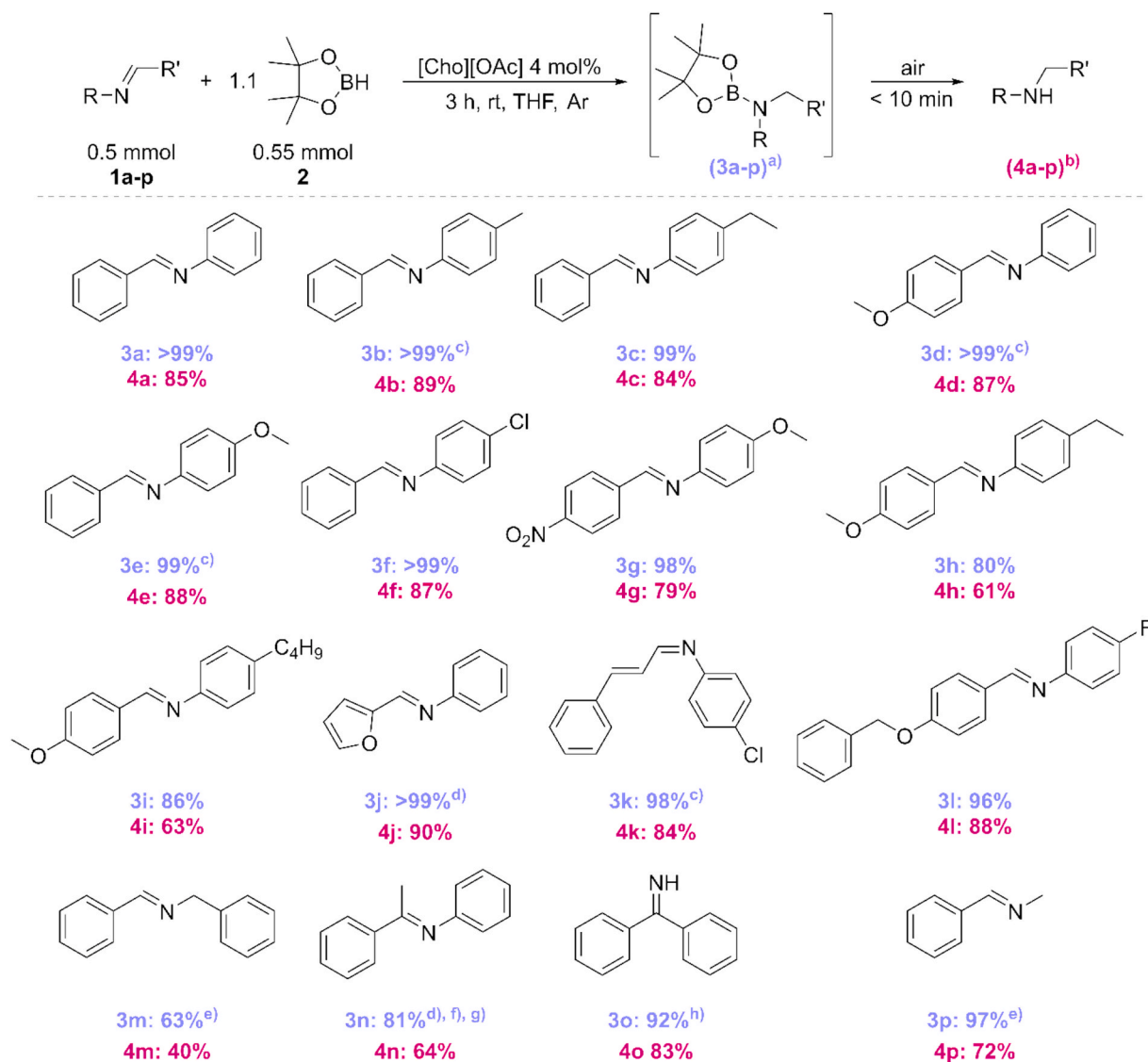
Amines (**4a–p**) were isolated from the crude reaction mixture by column chromatography technique using hexane/ethyl acetate as the eluent. It should be noted that products **3a–p** decomposed rapidly to the

corresponding amines (**4a–p**) in an air atmosphere (<10 min). For this reason, only peaks assigned to the amines (**4**) were observed in the GC–MS and ¹H NMR spectra when the samples were prepared under air. The NMR spectra of the hydroboration products were obtained when the reactions were carried out in Young's NMR tubes under an argon atmosphere using deuterated toluene (see ESI, section 2.4).

After the successful application of imines, we examined the hydroboration of more challenging nitriles [33] in the presence of [Cho][OAc]. The reduction of nitriles required additional optimization of the reaction conditions (see ESI, Tables S4 and S5). Our initial investigations were carried out in toluene, but quantitative conversion of benzonitrile (**5a**) was not achieved even at 100 °C, with 4 equivalents of HBpin (**2**) and 6 mol% of the [Cho][OAc] after 18 h. As observed with imines, the reaction proceeds much more effectively in THF. At 70 °C, 6 mol% of IL, and 3.2 equivalents of **2**, we observed a 94 % yield of corresponding *N,N*-diborylamines in 7 h. Interestingly, by applying 1,4-dioxane instead of THF, it was possible to reduce the catalyst loading to 4 mol% and obtain an almost quantitative conversion (98 %) of model benzonitrile (**5a**) with 3.2 equiv. of HBpin (**2**) in 7 h at 70 °C. (see ESI, Table S4).

With the optimized conditions established, the hydroboration reaction of various functionalized nitriles was investigated (Scheme 3, A). The reaction proceeded smoothly with nitriles substituted with electron-donating or electron-withdrawing groups attached to the phenyl ring (**5b–5d**). In the case of the nitrile with chlorine in the *ortho*-position (**5e**), we observed a decrease in the yield of **6e**. The hydroboration of benzonitrile functionalized with an acetyl group with 4 equivalents of HBpin (**2**) over 18 h resulted in full conversion of **5f**, with a 54 % yield of aminoalcohol **6f**. Moreover, [Cho][OAc] catalyzed the hydroboration of 2-thiophenecarbonitrile (**5g**) with 62 % substrate conversion and acetonitrile (**5h**) with excellent yield. The *N,N*-diborylamines **6a–h** were more stable than *N*-borylamines, allowing for analysis under air. The primary amines **7a–g** were isolated by double extraction in ethyl acetate–water and water–DCM systems.

Choline-based ionic liquids were also applied as catalysts for the deoxygenative hydroboration of secondary amides (for catalysts screening see ESI, Table S8). When an equimolar amount of HBpin was



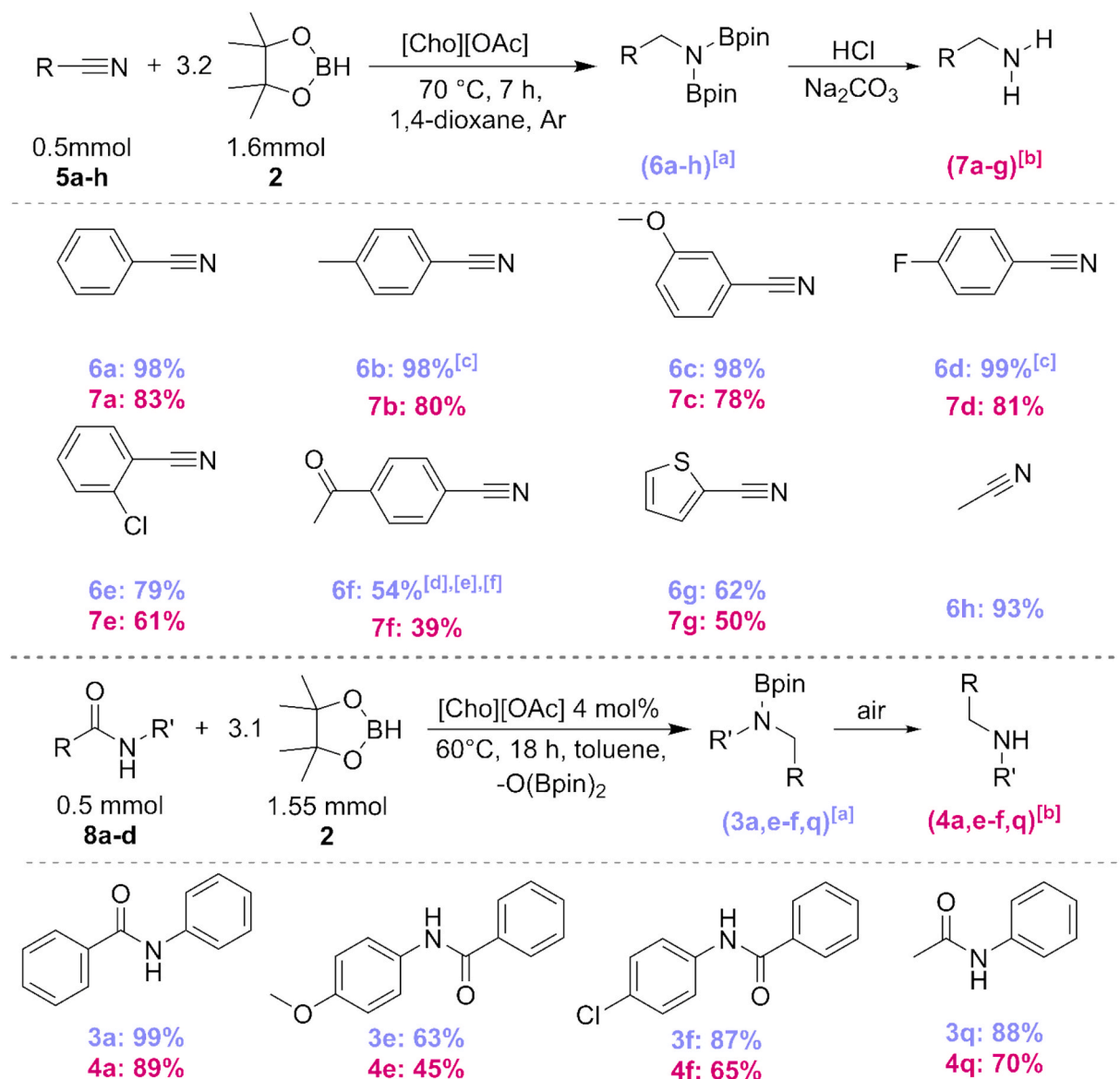
Scheme 2. Substrate scope for the hydroboration of imines (**1a-p**) catalyzed by $[\text{Cho}][\text{OAc}]$. ^{a)} The yields were based on GC-MS and ^1H NMR analyzes; ^{b)} isolation yields; ^{c)} 1 h; ^{d)} 18 h; ^{e)} neat; ^{f)} 60 °C; ^{g)} 2 equiv. of HBpin; ^{h)} toluene.

used, the corresponding imine was observed as a by-product. To avoid the formation of imine, a slight excess of HBpin was used in optimal conditions. The hydroboration of **8a** in the presence of 4 mol% of $[\text{Cho}][\text{OAc}]$ proceeded with a full amide conversion at 60 °C, in toluene under an argon atmosphere (see ESI, Table S7). The protocol was also suitable for secondary amides with methoxy- or chloro -substituents (**8b-8c**) and for *N*-phenylacetamide (**8d**) (Scheme 3, B). The amines were purified by column chromatography technique with hexane/ethyl acetate as the eluent.

Given the value of *N,N*-borylamines as building blocks in organic synthesis, the possibility of their one-pot functionalization was investigated (Scheme 4). Following the hydroboration of **5a**, the product was easily hydrolyzed in the presence of HCl, yielding an aniline hydrochloride. Subsequent neutralization with Na_2CO_3 , resulted in the primary amine **7a** with quantitative yield. Next, by heating the post-hydroboration mixture of **6a** with carboxylic acid (**9**) in toluene, *N*-benzylbenzamide (**8e**) was obtained in high yield; however, when **9** was added directly to the post-reaction-mixture in 1,4-dioxane, a competitive hydrolysis reaction of *N,N*-diborylamine was observed (see ESI, Table S9). Further, a three-step one-pot synthesis of secondary amine (**4b**) from nitrile (**5a**) hydroboration followed by the hydrolysis of *N,N*-diborylamine (**6b**) and subsequent cross-coupling of amine (**7b**) and

with aryl iodide (**10**) in the presence of copper iodide and cesium carbonate was carried out. (see ESI, Table S10). The resulting amine (**4b**) was purified by column chromatography using hexane/ethyl acetate as the eluent in 76 % yield. Previously, secondary amines have been prepared by the hydroboration of nitriles in a four-step one-pot reaction by double hydroboration of nitriles, transformation of *N,N*-diborylamine to an amide or imine, another hydroboration, and hydrolysis, as reported by Nguyen *et al.* [49] *N,N*-Diborylamine **6a** could also be coupled with benzaldehyde (**11**) in mild conditions and with a short reaction time. It is worth noting that the imine (**1m**) or tertiary amine (**12a**) could be selectively obtained depending on substrate ratio and solvent choice. The reaction in dichloromethane in an equimolar ratio of **6a** and **11** led smoothly to the quantitative yield of imine **1m**, whereas the application of 1,4-dioxane and a 2-fold excess of benzaldehyde gave **12a** with 51 % yield (see ESI, Table S11).

In the last stage of our experimental investigation, the versatility and recyclability of the catalyst $[\text{Cho}][\text{OAc}]$ were examined in the reaction of *N*-benzylidenaniline (**1a**) with pinacolborane (**2**) (Fig. 1). After the first run, the solvent was evaporated under vacuum, and then a non-polar solvent was added (*n*-heptane), resulting in the precipitation of the catalyst as a white solid. The precipitate was washed with *n*-heptane (3x3 mL) to remove the product, and the residue was dried for 1 h under



Scheme 3. A) Substrate scope for hydroboration of nitriles (**5a–h**) catalyzed by [Cho][OAc]. B) Substrate scope for hydroboration of amides (**8a–d**) catalyzed by [Cho][OAc]. ^{a)} The yields were based on ¹H NMR analysis; ^{b)} isolation yields; ^{c)} 5 h; ^{d)} 18 h; ^{e)} 4 equiv. of HBpin; ^{f)} conversion of **5f** = >99 %.

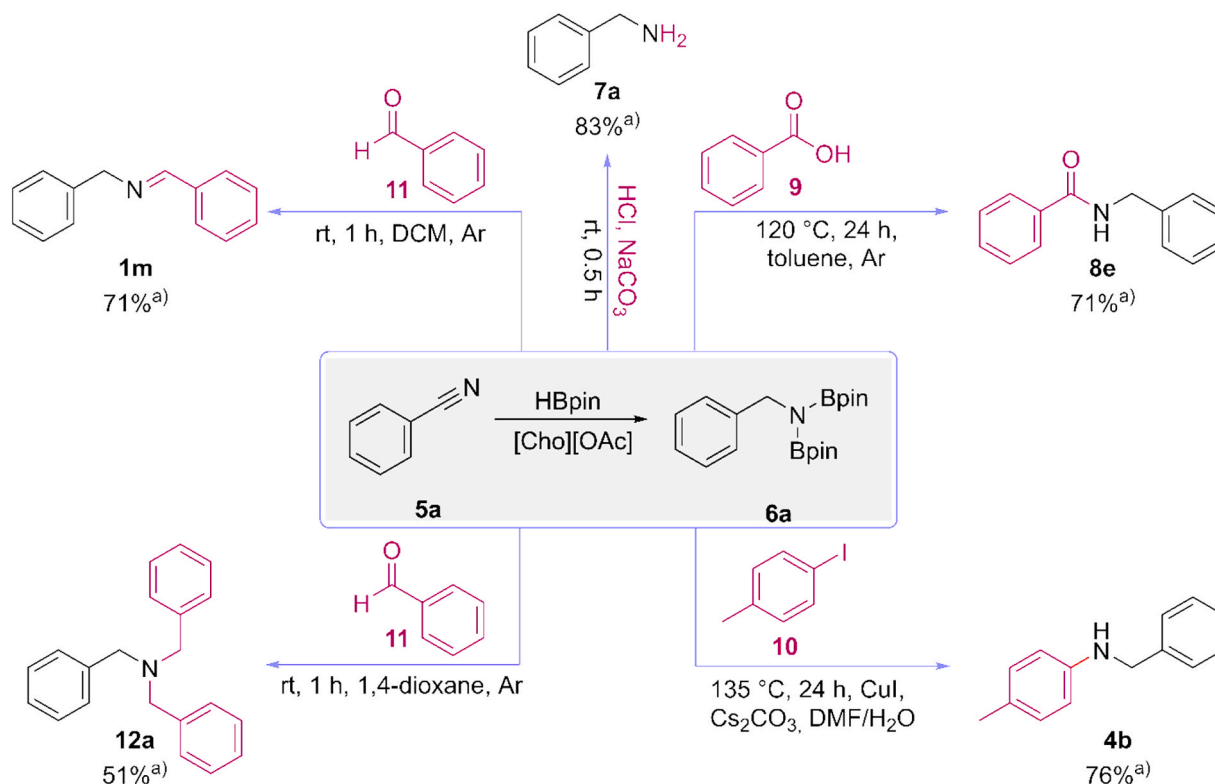
vacuum. Following the preparation of the catalyst, the next portion of substrates was added. Using 8 mol% of the [Cho][OAc], four catalytic runs were completed without any loss of IL activity. The fifth run resulted in a slightly lower hydroboration yield (80 %), while in the sixth, the conversion of **1a** did not exceed 50 % (Fig. 1). Similar results were observed when benzonitrile **5a** was used (see ESI Fig. S3). Recycling experiments with 4 mol% of [Cho][OAc] achieved excellent process efficiency for three cycles, while a significant drop in **1a** conversion was noted in the fourth cycle (see ESI Fig. S2). The decrease in reaction progress likely occurred due to the leaching of the catalyst. Choline acetate is insoluble or slightly soluble in many organic solvents; however, by following the reaction with HBpin (**2**) its solubility increases, which can be observed for reactions in DCM, toluene, or THF.

2.1. Mechanism investigations

To understand the mechanism of the reaction several experimental (NMR) and computational (DFT) studies were performed. In the first stage, (sub)stoichiometric reactions of [Cho][OAc] with *N*-benzylideneaniline (**1a**) or HBpin (**2**) were performed. Based on the optimization

of the reaction conditions and sufficient solubility of the catalyst, deuterated DCM or toluene (at elevated temperature) was chosen for NMR investigations. The equimolar reaction of the catalyst with imine **1a**, caused no changes in the ¹H and ¹³C NMR spectra (see ESI Figs. S116 and S117).

Subsequently, the stoichiometric reaction between [Cho][OAc] and HBpin (**2**) was conducted. It was accompanied by gas evolution and dissolution of the solid. ¹H NMR spectroscopy showed a signal at 4.6 ppm, indicative of molecular hydrogen formation. In the ¹¹B NMR spectrum, a major signal was observed at 12.63 ppm (**IN4**) (see ESI Fig. S118 and S119). However, no product formation was detected after the addition of **1a**. We hypothesized that the hydroxyl group of choline cation reacts with HBpin (**2**), which could explain why the hydroboration did not occur after the addition of the imine (**1a**), as the HBpin may have been fully consumed through reaction with the –OH group, accompanied by hydrogen release. The signal corresponding to **IN4** was identified based on its chemical shift similarity to a reference compound formed by the reaction of 2-(dimethylamino)ethan-1-ol with pinacolborane (**2**) (see ESI, Fig. S136 and S137), and by comparison with data reported in the literature [69].



Scheme 4. One-pot synthesis of primary, secondary, and tertiary amines, imines, and amides via hydroboration of nitriles. ^{a)} Isolation yields.

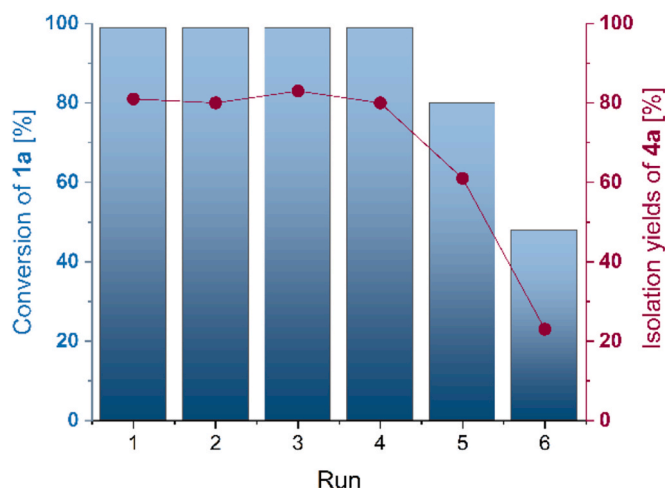


Fig. 1. The repetitive batch hydroboration of **1a** (0.5 mmol) with **2** (0.55 mmol) using 8 mol% of [Cho][OAc] at room temperature for 2 h in THF under an argon atmosphere. The yields of **4a** and **1a** conversion were determined by GC-MS analysis.

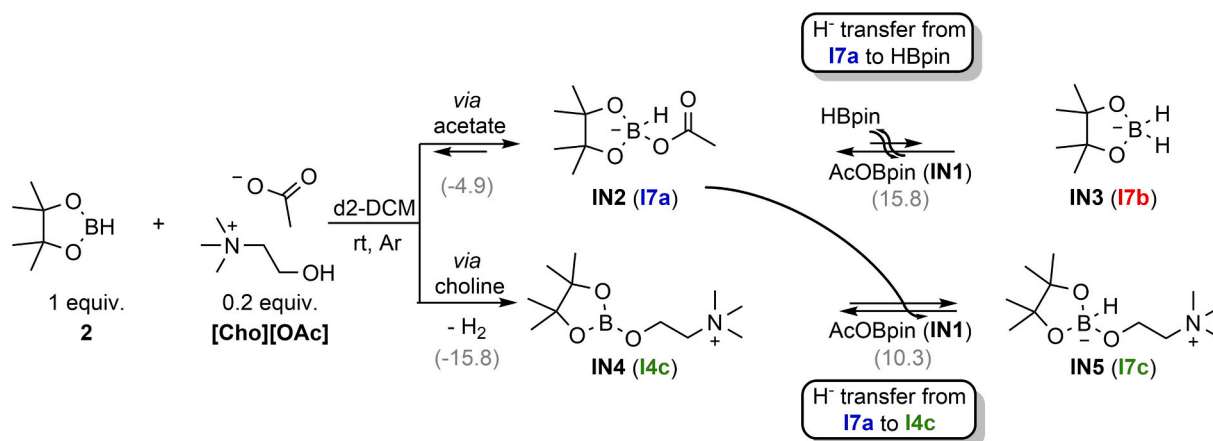
Then, we performed the reaction of [Cho][OAc] and HBpin (**2**, 5 equiv.). No signals corresponding to unreacted choline acetate were observed in the ¹H NMR spectrum. Several new signals were observed in the ¹¹B NMR spectrum, at 22.15, 20.12, 12.78, 9.42, 6.57, 6.00, 2.75, and -8.31 (q) ppm (see ESI Fig. S125). Taking into account the chemical shifts described in the literature and the established reactivity of nucleophiles toward pinacolborane, these newly formed species were identified as borohydrides. Moreover, borohydrides occur in equilibrium, which explains the complex ¹¹B and ¹H NMR spectra [70,71]. Based on previous reports, the signals at 9.42 ppm and 6.00 ppm were assigned to H₂Bpin⁻ (IN3) and AcO(H)Bpin⁻ (IN2), respectively

[70–73]. According to the similarity in chemical shift, the signal at $\delta = 6.57$ ppm was assigned as AcO(H)Bpin⁻ (IN5) (Scheme 5).

Among the proposed intermediates (IN1–IN5), we successfully synthesized IN1 (pinBOAc) and assessed its catalytic activity; however, it proved inactive in the hydroboration of **1a**. Furthermore, the equimolar reaction between HBpin (**2**) and [Cho][OAc] predominantly yielded IN4 (see ESI, Figs. S118–119). When *in situ* generated IN4 was subsequently employed as a catalyst for the hydroboration of **1a**, new signals corresponding to IN2, IN3 and IN5, appeared in the ¹¹B NMR spectrum (see ESI, Fig. S121). The results suggest that IN4 is not catalytically active itself but rather acts as a precatalyst, which is transformed under the reaction conditions into borohydride species.

Based on both literature reports [69–71] and our experimental findings, we hypothesize that these borohydride species are the catalytically active intermediates. To support this hypothesis, we employed computational methods based on density functional theory (DFT). Our investigation initially focused on the kinetics and efficiency of catalytically active anion generation from [Cho][OAc] (Figs. 2 and S4). The quantitative results differed slightly depending on the temperature; however, the qualitative conclusions were identical. [Cho][OAc] and HBpin (**2**) react with each other in two ways. One pathway is the formation of a bond between the acetate oxygen and the boron atom, leading, through weak complexes **I1a** and **I2a** and the transition state **TS1a**, to the intermediate product **I7a**. This process readily takes place under ambient conditions, with substrates and products exhibiting comparable Gibbs free energies. **I7a** can then interact with another HBpin molecule (**I5b**), and transfer a hydride anion to it (**TS2b**), giving **I6b** and finally, as AcOBpin leaves, **I7b**. The equilibrium between **I7a** and **I7b** is strongly shifted towards the former, with ΔG of the transformation being + 15.8 kcal/mol.

The second pathway arises from the reactivity of the hydroxyl group of choline (Figs. 2 and S5). As pinacolborane approaches choline acetate (**I1c**), a hydrogen cation is first transferred to the acetate group, while choline's hydroxyl oxygen atom attacks pinacolborane to form a tetra-coordinate boron species (**I2c**). Then, a hydrogen molecule is eliminated



Scheme 5. Formation of catalytically active borohydrides species (IN2, IN3 and IN5) in the reaction of excess of HBpin with [Cho][OAc]. The counter anions for each path are omitted for clarity. In paratheses ΔG values are given in kcal/mol for the formation of intermediates I7a-c, I4d.

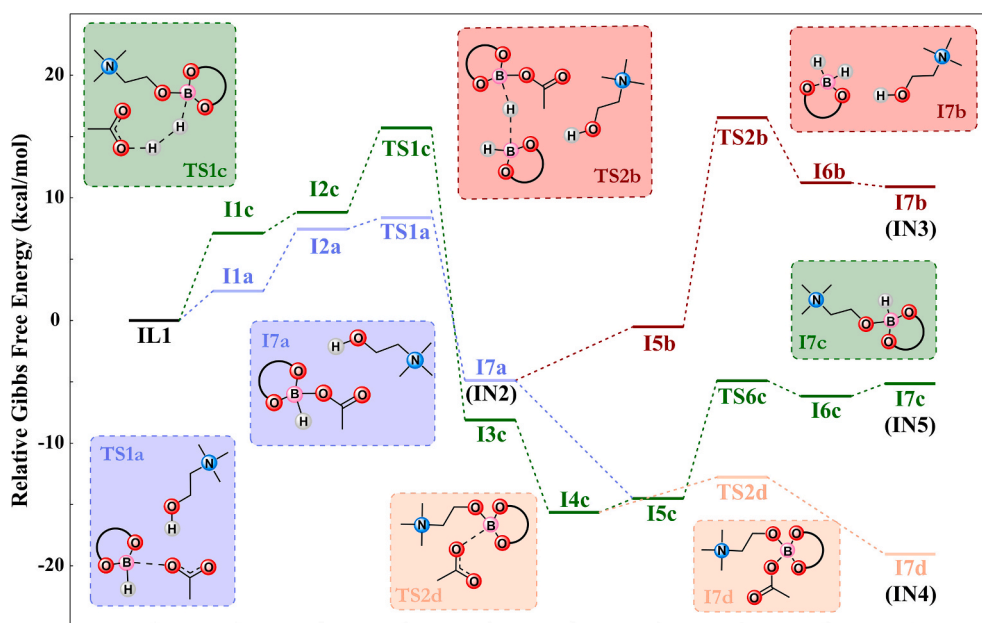
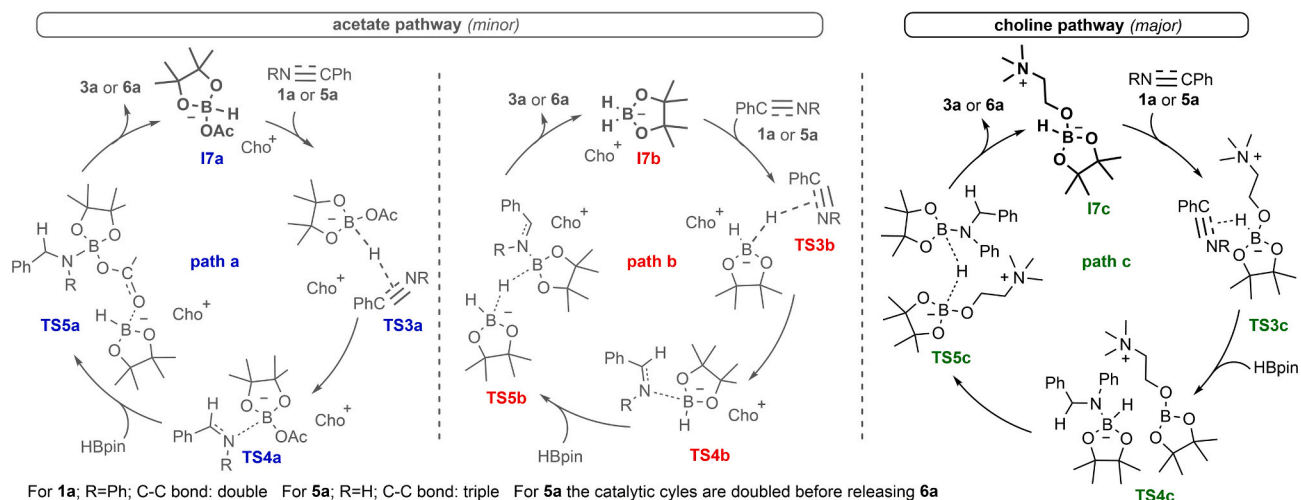


Fig. 2. ω B97XD/def2-SVPD Gibbs free energy profile of the reaction of [Cho][OAc] with pinacolborane (2) (333 K, 1 atm).



For 1a; R=Ph; C-C bond: double For 5a; R=H; C-C bond: triple For 5a the catalytic cycles are doubled before releasing 6a

Scheme 6. Plausible catalytic pathways for the hydroboration of imines and nitriles catalyzed by borohydrides IN2 (I7a), IN3 (I7b), and IN5 (I7c).

(TS1c to I3c) and released, leaving I4c. The transition state of this transformation lies considerably higher than TS1a; however, as the removal of hydrogen makes it irreversible, the contribution of this pathway can be expected to increase in time, especially in the elevated temperature which accompanies the hydroboration of nitriles. The cation and anion in I4c can recombine, yielding I7d; the two remain in an equilibrium, separated by a low transition state TS2d. However, the cation of I4c can also interact further with the anion of I7a, yielding I5c. There, a hydride is transferred from one boron atom to the other (TS2c), producing I6d, which dissociates to I7c and the original choline acetate. A total of three structures with potential catalytic properties may be formed, with one of them (I7b) expected to be present at a much lower concentration than the others (I7a and I7c), as corroborated by NMR studies (Fig. 2).

Further computations, aligned with experimental observations, confirmed the possible existence of corresponding catalytic cycles a–c for the hydroboration of both *N*-benzylideneaniline and benzonitrile, all of them comprising three analogous, major steps (Scheme 6). First, one of the species I7a–c attacks the unsaturated carbon atom of the imine or the nitrile (TS3), transferring the anionic hydrogen. This leads to an intermediate with a negatively charged nitrogen atom, which swiftly attacks the boron atom of HBpin, typically with a very low Gibbs free energy barrier (TS4). Finally, the abstraction of a hydride from the resulting anion regenerates the catalyst (TS5). Considering two principal factors – the relative concentrations of the catalytic species, governed by equilibria among I7a–c, and the computed standard Gibbs free energies of the relevant intermediates and transition states – it is likely that cycle c is the most favored pathway. Nevertheless, cycles a and b are also expected to contribute to the overall catalytic activity. This interpretation is consistent with experimental results obtained in the presence of [TBA][OAc] and [TMA][OAc], where the absence of cycle c leads to a significant decrease in reaction yield, although conversion still reaches moderate levels.

The overall transformation of pinacolborane (2) and *N*-benzylideneaniline (1a) into the product (3a) is associated with an energy release of -34.3 kcal/mol (see ESI, Figs. S6–S8). For benzonitrile (5a), the first cycle (single hydroboration) offers significantly lower exoergicity – -18.8 kcal/mol, roughly half that of imines – and proceeds through generally higher energy barriers (see ESI, Figs. S9, S11, and S13). These differences explain the need to maintain higher reaction temperature to achieve conversions comparable to those observed with imines. However, the second cycle – hydroboration of the resulting *N*-pinacolbor-ylbenzylimine (P') – proceeds through analogous intermediates and transition states, with lower energy barriers and a significantly greater change in Gibbs free energy ($\Delta G = -42.1$ kcal/mol) (see ESI, Figs. S10, S12, and S14), which aligns well with experimental observations (double hydroboration is preferred).

To check the catalytic activity of the IL as a 'true' catalyst, a reaction with TMEDA (*N,N,N',N'*-tetramethylethylenediamine) was carried out, as reported by Thomas et al. [72,74] The presence of TMEDA (10–60 mol%) did not significantly reduce reaction efficiency and 1a conversions were ≥ 93 % after 3 h (see ESI, Table S12 and Figs. S110–S113). A control experiment indicated that the 'BH₃' pathway, if present, is negligible, and the [Cho][OAc] can effectively promote the hydroboration of imines. It was further revealed by computational studies that despite borane's propensity to coordinate with the nitrogen atom of *N*-benzylideneaniline (1a), its regeneration through reaction with HBpin (2) entails a Gibbs free energy barrier of 25.1 kcal/mol, substantially higher than any barrier observed in other catalytic cycles (see ESI, Table S13). However, for the hydroboration of benzonitrile (5a) a significant drop in conversion (from 54 % to 24 %) was observed. The stronger effect of TMEDA on the efficiency of the hydroboration of 5a suggests a greater influence of the BH₃ pathway than for imines (see ESI Fig. S154). Although the free energy barrier for the rate-determining step in the BH₃-catalyzed pathway remains significantly higher than that in the IN5-mediated cycle for nitriles, the overall simplicity of the

BH₃ mechanism sets it apart. This, together with the exergonic character of both steps, suggests that even trace amounts of BH₃ (e.g., present as an impurity in pinacolborane) might still contribute to catalysis under the reaction conditions. Nevertheless, incomplete inhibition of reaction progress and ¹¹B NMR analysis suggest that catalytically active species such as borohydrides generated via the reaction of HBpin with the choline cation and acetate anion also contribute to product formation. Notably, the use of TMEDA in the moisture-assisted benzonitrile (5a) hydroboration reaction, catalyzed by the BH₃ pathway, resulted in a complete lack of conversion [75].

The catalytically active species in the [Cho][OAc]-mediated hydroboration of unsaturated carbon–nitrogen bonds are tetracoordinate intermediates derived from pinacolborane, similar to those described by Clark and co-workers. Notably, in our system, both the choline cation and the acetate anion play essential roles in generating the active borohydride species. This cooperative action of the ionic liquid components has been confirmed through experimental data and computational analysis. Beyond mechanistic aspects, we believe that employing bio-based [Cho][OAc] provides clear advantages and represents an innovative, green strategy for the hydroboration of nitrogen-containing compounds. Choline acetate is biodegradable, non-toxic, and produced from renewable resources, offering a greener alternative to conventional strong inorganic bases such as NaOH or KOtBu.

3. Conclusion

In summary, this study has described the hydroboration of imines, nitriles, and amides with HBpin to the corresponding amines, catalyzed by a cost-efficient, naturally sourced, and commercially available bio-ionic liquid – choline acetate. The developed protocol is effective for a wide range of aromatic compounds with both electron-donating and electron-withdrawing groups, as well as heterocyclic compounds. A straightforward method for the synthesis of amides and primary, secondary, and tertiary amines from nitriles via hydroboration and subsequent one-pot reactions – without the need to isolate intermediate products – was proposed. Taking advantage of the poor solubility of the catalyst in non-polar solvents, a recycling method was developed, notably increasing the efficiency of the process. A reaction mechanism was proposed based on NMR methods supported by DFT calculations. Mechanistic studies revealed that several alkoxyborohydrides, including H₂Bpin[−], AcO(H)Bpin[−], and Cho(H)Bpin, are catalytically active species. Moreover, the TMEDA experiment and DFT calculations demonstrated that the hidden 'BH₃' catalyzed hydroboration pathway plays a negligible role.

CCRediT authorship contribution statement

Barbara Krupa: Writing – original draft, Visualization, Methodology, Investigation, Data curation, Conceptualization. **Mateusz Nowicki:** Writing – original draft, Visualization, Methodology, Investigation. **Jakub Szyling:** Writing – review & editing, Visualization, Supervision, Methodology. **Jędrzej Walkowiak:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcat.2025.116362>.

Data availability

Data available within the article and its [supplementary materials](#)

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Supporting Information

Organocatalytic hydroboration of imines, nitriles, and amides using choline-based ionic liquids

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1. General information

1.1. Materials

4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (97%, Fluorochem), choline chloride (98%, Angene), choline acetate (98%, Io-li-tec), choline bis(trifluoromethylsulfonyl)imide, (99%, Io-li-tec), choline hydroxide, (46% w/w aq. soln., Thermo Scientific), acetic acid (>99.5%, Chempur) trifluoroacetic acid (>99%, Fischer Chemical), benzoic acid ($\geq 99\%$, Chempur), oxalic acid dihydrate ($\geq 99\%$, Chempur), tetrabutylammonium acetate (98%, Angene), tetramethylammonium acetate (98%, Angene), potassium acetate (99%, Chempur), *N*-benzylideneaniline (>98.0%, TCI Chemicals), *N*-benzylidene-*p*-toluidine ($\geq 96\%$, Sigma-Aldrich), *N*-(4-methoxybenzylidene)aniline (97%, Sigma-Aldrich), *N*-(4-methoxybenzylidene)-4-butaniline (98%, TCI Chemicals), *N*-(4-benzyloxy)benzylidene-4-fluoroaniline (95%, Fluorochem), *N*-benzylidenebenzylamine (99%, Sigma-Aldrich), phenyl-(1-phenylethylidene)amine (98%, Sigma-Aldrich), benzophenoneimine (98%, AmBeed), *N*-benzylidenemethylamine (97%, Sigma-Aldrich), aniline ($\geq 99.0\%$, Sigma-Aldrich), *p*-anisidine (99%, Thermo Scientific), 4-chloroaniline (98%, Thermo Scientific), 4-ethylaniline (98%, Sigma-Aldrich), benzaldehyde (>99%, Alfa Aesar), *trans*-cinnamaldehyde ($\geq 98\%$, Sigma-Aldrich), 4-nitrobenzaldehyde (98%, AmBeed), 4-methoxybenzaldehyde (98%, Sigma-Aldrich) furfural (99%, Sigma-Aldrich), benzonitrile (98%, Thermo Scientific), *p*-tolunitrile, (>98%, Thermo Scientific), 3-methoxybenzonitrile (98,65%, AmBeed), 4-fluorobenzonitrile (99,56%, AmBeed), 2-chlorobenzonitrile ($\geq 98\%$, TCI Chemicals), 4-acetylbenzonitrile (97%, AmBeed), 3-thiophenecarbonitrile (95%, AmBeed), 4-iodotoluene (99%, Sigma-Aldrich), benzanilide (98%, Angene), acetanilid (99%, Chempur), cesium carbonate, (99%, Fluorochem), copper(I) iodide (98%, Sigma-Aldrich), silica gel (pore size 60Å, 63-200 µm particle size, Sigma-Aldrich), sodium sulfate anhydrous (>99%, Eurochem), sodium carbonate (>99%, Eurochem), sodium chloride (>99%, Eurochem), methanol ($\geq 99.9\%$, Stanlab), ethanol (99.9%, Stanlab) diethyl ether (99.5%, Avantor Performance Materials Poland), ethyl acetate (99%, Avantor Performance Materials Poland), *n*-hexane (99%, Stanlab), *n*-heptane (99%, Sigma-Aldrich), tetrahydrofuran (>99%, Eurochem), toluene (>99%, Stanlab), dichloromethane (>99%, anhydrous, TCI), dichloromethane (99%, Stanlab), acetonitrile, (99%, anhydrous, Sigma-Aldrich), 1,4-dioxane (>99.8%, anhydrous, Sigma-Aldrich), *N,N*-dimethylformamide ($\geq 99.8\%$, anhydrous), hydrochloric acid (36–38%, Stanlab), sodium carbonate ($\geq 99.9\%$, Stanlab), chloroform-d1 (99.8% stabilized with Ag, Deutero GmbH), dichloromethane-d2 (99.6%, Deutero GmbH), deuterium oxide (99%, Deutero GmbH), toluene-d8 (99.5%, Deutero GmbH), DMSO-d6 (99,9%, Sigma-Aldrich), benzene-d6 (99,6%, Sigma-Aldrich).

All chemicals were used without further purification and purchased from commercial sources, except pinacolborane, which was purified by vacuum distillation prior use. THF, diethyl ether, and toluene were dried over Na/benzophenone or CaH₂ and distilled. Benzonitrile was dried over molecular sieves before use. Ionic liquids were dried overnight under a vacuum at 80 °C before use.

1.2 Methods

1.2.1. Nuclear magnetic resonance

The ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Ultrashield 300 MHz or Bruker Ascend 400 MHz spectrometer. The ¹¹B NMR spectra were recorded on Bruker Ascend 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm) with reference to the residual solvent peaks for ¹H and ¹³C NMR or BF₃-Et₂O for ¹¹B NMR, respectively. The multiplicities are reported as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), triplet of triplets (tt), multiplet (m), and broad resonances (br).

1.2.2. Gas chromatography–mass spectrometry

The mass spectra of the products were obtained by GC-MS analysis on a Varian 431-GC with a 30 m Agilent J&W VF-200ms 0.25 mm capillary column and a Varian 220-MS mass spectrometry detector (temperature program: 60 °C (3 min), 10 °C/min, 280 °C (30 min)).

1.2.3 Elemental analysis

Elemental analyses were performed using a Vario EL III instrument.

1.2.4. DFT calculations

The initial structures of all relevant species were systematically generated based on established values for bond lengths and valence angles.^[1] This was followed by full geometry optimizations aimed at identifying potential energy minima. During these preliminary optimizations, the ωB97XD functional^[2] and the 6-31+G(d) basis set^[3-7] were selected for their balance between computational efficiency and resource consumption, accommodating the extensive variety of potential pathways and the computational demands they entailed. To elucidate plausible reaction mechanisms, we executed relaxed potential energy surface scans, varying the distances between atoms poised for reaction (namely boron, hydridic hydrogen, imine carbon and oxygen, nitrile carbon and oxygen, hydroxyl oxygen and hydrogen, and

carboxyl oxygen). Paths not culminating in a new minimum were discontinued; otherwise, the quadratic synchronous transit (QST)^[8] methods – both QST2 and QST3 – were employed to pinpoint transition state geometries, complemented by pseudo-IRC^[9] calculations to identify the potential energy minima linked by these transition states, thereby guiding the generation of subsequent structures representing energy minima. To validate these stationary points as either minima or first-order saddle points, we performed force constant calculations and analyzed the vibrational modes, identifying none (for minima) or a single imaginary frequency (for transition states), corresponding to stretching the bonds being broken and formed (freq calculations). Subsequent re-optimizations and frequency analyzes, including determinations of the nature of each stationary point, were conducted using the ω B97XD functional and the def2-SVPD^[10-11] basis set, but this time they assumed the solvation of molecules in dichloromethane (for the reaction of imines) or toluene (for the reaction of nitriles), modeled as a continuum medium within the polarizable continuum model (PCM).^[12-15] This choice represented a deliberate balance between computational cost and the accuracy of the results, particularly in the case of anionic species bearing hydridic hydrogen atoms. Thermochemical evaluations were standardized at a pressure of 1 atm and a temperature of 295 K (imines) or 333 K (nitriles) to closely replicate experimental conditions. All quantum-chemical computations throughout the study were performed using the Gaussian 16 program package.^[16] Basis Set Exchange resource was used to optimize the level of theory employed.^[17]

2. Synthetic procedures

All glassware was vacuum dried at 120 °C prior to use.

2.1. General procedure for the synthesis of ionic liquids (IL2–5)

The synthesis of ILs was performed according to the literature procedure with some modifications.^[18] A 100 mL round-bottom flask equipped with a magnetic stirring bar was charged with an aqueous solution of choline hydroxide (7 mmol, 840 mg), carboxylic acid (7 mmol or 3.5 mmol for **IL5**), and 10 mL of methanol. The reaction was allowed to proceed for 24 hours at room temperature. After this time, the solvent was evaporated using a rotary evaporator. The resulting products were dried for 48 hours under vacuum at 80 °C.

2.2. General procedure for the synthesis of imines (1c, 1e–h, 1j–k)

The synthesis was performed according to the literature procedure with some modifications.^[19-20] Amine (1.55 mmol), aldehyde (1.5 mmol), and 10 mL of ethanol were placed in a 50 mL round-bottom flask containing a stirring bar. Subsequently, acetic acid (0.1 mmol, 9 mg) was

added to the reaction mixtures and refluxed for 5 h. After this time, the flask was cooled to room temperature and pre-dried over sodium sulfate. The reaction mixture was then filtered and concentrated on a rotary evaporator. The crude product was recrystallized from ethanol (**1e–h**) or purified by column chromatography using hexane-triethylamine 49:1 (**1j–k**) or hexane-ethyl acetate -triethylamine 45:4:1 (**1c**) as the eluent.

2.3. General procedure for the synthesis of amides (**8b–c**)

The synthesis was performed according to the literature procedure.^[21] In a 50 mL round-bottom flask equipped with a magnetic stirring bar, iodine (1.96 mmol) was dissolved in DCM (6 mL). The solution was cooled down to 0 °C and PPh₃ (1.96 mmol) was added at once. Then, amine (1.96 mmol) was added and stirred for 5 min. After this time, benzoic acid (1.64 mmol) was added and the reaction mixture was stirred for 5 min. Subsequently, triethylamine (3.28 mmol) was added. The reaction mixture was then warmed to room temperature and stirred for 10 min. The crude mixture was concentrated and purified by column chromatography using hexane-ethyl acetate 4:1 as eluent.

2.4. General procedure for the synthesis of compounds (**3a–q**)

Due to the rapid decomposition of product **3a–q** to an amine (**4a–q**), to collect NMR spectra of **3a–q**, the reaction was carried out in an NMR tube under an argon atmosphere. [Cho][OAc] (4 mol%, 0.83 mg) was placed into a Young NMR tube and kept in an oil bath at 80 °C under vacuum for 30 min. After that, the tube was refilled with argon. Next, imine (**1a–p**) or amide (**8q**) (0.125 mmol), approximately 0.6 mL of deuterated toluene, and pinacolborane (0.14 mmol, 17.9 mg or 0.39 mmol, 49.9 mg) were added. The reaction vessel was tightly closed, shaken vigorously, and heated in an oil bath at 40 °C for 3 h (for imines) or at 60 °C for 18 h (for amides). After this time, the NMR analyses were performed.

2.5. General procedure for the synthesis of compounds (**3a–p**) with subsequent deborylation process (**4a–p**) – one-pot procedure

A Schlenk vessel containing a magnetic stirring bar was charged with [Cho][OAc] (4 mol%, 3.3 mg) and kept in an oil bath at 80 °C under vacuum for 30 min. After this time, the reaction vessel was allowed to cool down to room temperature and IL solidified. Then, imine (**1a–p**) (0.5 mmol) and pinacolborane (**2**) (0.55 mmol, 70.4 mg) were added. After 1, 3, or 18 h the crude reaction mixture was analyzed by ¹H NMR and/or GC-MS analyses. Afterward, the reaction mixture was exposed to air for 10 min. After this time the volatiles were removed under

reduced pressure. The crude product was purified by column chromatography using 9:1 hexane-ethyl acetate or 19:1 hexane-ethyl acetate (for product **4i**) as the eluent.

2.6. General procedure for the synthesis of compounds (6a–h) with subsequent deborylation process (7a–h) – one-pot procedure

A Schlenk vessel equipped with a magnetic stirring bar was filled with [Cho][OAc] (4 mol%, 3.3 mg). The catalyst was kept in an oil bath at 80 °C under vacuum for 30 min. After this time, the reaction vessel was allowed to cool down to room temperature and IL solidified. Subsequently, nitrile (**5a–h**) (0.5 mmol), 1,4-dioxane (1 mL), and pinacolborane (**2**) (1.6 mmol, 205 mg) were added. The mixture was heated in an oil bath at 70 °C for 5 or 7 h. Then, the crude reaction mixture was analyzed by ¹H NMR and GC–MS analyses, and the reaction mixture was quenched by adding 5 mL of 0.25M HCl aqueous solution and mixed for 1 h at 70 °C. The aqueous phase was extracted with ethyl acetate (3x10 mL). The volatiles were removed under reduced pressure at 75 °C. An aqueous solution of Na₂CO₃ was then added to the amine chloride and the excess of HCl, to obtain a slightly alkaline pH. The aqueous phase was extracted with DCM (3x10 mL) and then dried over Na₂SO₄, filtered, and evaporated to dryness to give the corresponding amine.

2.7. General procedure for the hydroboration of amides with subsequent deborylation process – a one-pot procedure

[Cho][OAc] (4 mol%, 3.3 mg) was added to the Schlenk vessel equipped with a magnetic stirring bar. The catalyst was kept in an oil bath at 80 °C under vacuum for 30 min. After this time, the reaction vessel was allowed to cool down to room temperature and the IL solidified. Next, the amide (**8a–d**) (0.5 mmol), toluene (1 mL) and pinacolborane (**2**) (1.55 mmol, 198.4 mg) were added. The reaction mixture was stirred in an oil bath at 60 °C for 18 h, after this time the solution was exposed to air for 10 min. The amines formed were isolated by column chromatography using hexane-ethyl acetate 9:1 as eluent.

2.8. General procedure for the one-pot synthesis of *N*-benzylbenzamide (8e)

The synthesis was performed according to the literature procedure with some modifications.^[22] After completion of the hydroboration of benzonitrile (0.5 mmol, 51.5 mg), as described in section 2.5, benzoic acid (0.5 mmol, 61.1 mg) was added directly to the post-reaction mixture containing *N,N*-diborylamine. Then, the mixture was heated in an oil bath at 120 °C for 24 h. The crude product was purified by column chromatography using hexane-ethyl acetate 8:2 as eluent.

2.9. General procedure for the one-pot synthesis of *N*-benzyl-1-phenylmethanimine (**1m**)

The synthesis was performed according to the literature procedure with some modifications.^[23] After completion of the hydroboration of benzonitrile (0.5 mmol, 51.5 mg), as described in section 2.5, benzaldehyde (0.5 mmol, 53.1 mg) was added directly to the post-reaction mixture containing *N,N*-diborylamine. Afterwards, the reaction was carried out at 50 °C for 3 h. The pure product was obtained after column chromatography using hexane-ethyl acetate-trimethylamine 95:4:1 as eluent.

2.10. General procedure for the one-pot synthesis of tribenzylamine (**9a**)

After completion of the hydroboration of benzonitrile (0.5 mmol, 51.5 mg), as described in section 2.5., benzaldehyde (1 mmol, 106.1 mg) was directly added to the post-reaction mixture containing *N,N*-diborylamine. After stirring at 50 °C for 24 h, the crude product was purified by column chromatography using hexane-ethyl acetate-trimethylamine 95:4:1.

2.11. General procedure for the one-pot synthesis of *N*-benzyl-4-methyl aniline (**4b**)

The synthesis was performed according to the literature procedure with some modifications.^[24] After completion of the hydroboration of benzonitrile (0.5 mmol, 51.5 mg), as described in section 2.5, the volatiles were evaporated. Subsequently, DMF (1.5 mL) and water (1.1 mmol, 19.8 mg) were added, followed by the addition of copper iodide (10 mol%, 9.5 mg), cesium carbonate (0.6 mmol, 195.5 mg) and 4-iodotoluene (0.6 mmol, 130.8 mg). The Schlenk was then heated in an oil bath at 135 °C. The crude reaction mixture was analyzed by GC-MS. The resulting amines were isolated by column chromatography using hexane-ethyl acetate 9:1 as eluent.

2.12. General procedure for the repetitive batch hydroboration of *N*-benzylidenaniline (**1a**)

A Schlenk vessel containing a magnetic stirring bar was charged with [Cho][OAc] (4 mol%, 3.3 mg or 8 mol% 6.6 mg) and kept in an oil bath at 80 °C under vacuum for 30 min. After this time, the reaction vessel was allowed to cool down to room temperature and IL solidified. Next, the *N*-benzylidenaniline (**1a**) (0.5 mmol, 90.6 mg), THF (1 mL) and pinacolborane (**2**) (0.55 mmol, 70.4 mg) were added. The reaction mixture was stirred in an oil bath at room temperature for 2 hours. The THF was then evaporated on a vacuum and *n*-heptane (2 mL) was added, which resulted in the precipitation of the catalyst as a white solid. The catalyst was washed with *n*-heptane (4x2 mL) and dried under vacuum. The Schlenk vessel was then filled with argon and the next portion of substrates was added.

2.13. General procedure for the repetitive batch hydroboration of benzonitrile (**5a**)

A Schlenk vessel containing a magnetic stirring bar was charged with [Cho][OAc] (4 mol%, 3.3 mg or 8 mol% 6.6 mg) and kept in an oil bath at 80 °C under vacuum for 30 min. After this time, the reaction vessel was allowed to cool down to room temperature and IL solidified. Next, benzonitrile (**5a**) (0.5 mmol, 51.5 mg), 1,4-dioxane (1 mL), and pinacolborane (**2**) (1.6 mmol, 204.8 mg) were added. The reaction mixture was stirred in an oil bath at 70 °C for 7 h. The 1,4-dioxane was then evaporated under vacuum and *n*-heptane (3 mL) was added, which resulted in the precipitation of the catalyst as a white solid. The catalyst was washed with *n*-heptane (3x3 mL) and subsequently dried under vacuum. The Schlenk vessel was then filled with argon and the next portion of substrates was added.

2.14. General procedure for the equimolar reaction of *N*-benzylideneaniline (**1a**) or pinacolborane (**2**) with [Cho][OAc]

The Young's NMR tube was charged under the argon with [Cho][OAc] (0.1 mmol, 16.3 mg) and approx. 0.6 mL of dry toluene-*d*8 or CD₂Cl₂ was added. Subsequently, *N*-benzylideneaniline (**1a**) (0.1 mmol, 18.1 mg) or pinacolborane (**2**) (0.1 mmol, 12.8 mg) was added and the mixture was shaken vigorously, and the ¹H, ¹¹B, and ¹³C NMR spectra were recorded.

2.15. General procedure for the nonequimolar reaction of pinacolborane (**2**) with [Cho][OAc]

The Young's NMR tube was charged under the argon with [Cho][OAc] (0.2 equiv., 0.05 mmol, 8.2 mg) and approx. 0.6 mL of dry toluene-*d*8 or CD₂Cl₂ was added. Subsequently, pinacolborane (**2**) (1 equiv., 0.25 mmol, 32 mg) was added, the mixture was shaken vigorously, and the ¹H and ¹¹B NMR spectra were recorded.

2.16. General procedure for the nonequimolar reaction of pinacolborane (**2**) and *N*-benzylideneaniline (**1a**) with [Cho][OAc]

The Young's NMR tube was charged under the argon with [Cho][OAc] (0.2 equiv., 0.05 mmol, 8.2 mg) and approx. 0.6 mL of dry toluene-*d*8 or CD₂Cl₂ was added. Subsequently, *N*-benzylideneaniline (**1a**) (1 equiv., 0.25 mmol, 45.3 mg) and pinacolborane (**2**) (1.0 equiv., 0.25 mmol, 32 mg) were added and the mixture was shaken vigorously and left at room temperature for a specified time. After that, the ¹H, ¹³C, and ¹¹B NMR spectra were then recorded.

2.17. General procedure for the synthesis of 2,2'-oxybis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)

Caution: The reaction proceeds rapidly with the release of hydrogen.

Approximately 0.6 mL of dry CD₂Cl₂ and pinacolborane (**2**) (0.1 mmol, 12.8 mg) were placed in an NMR tube under the air atmosphere. Next, water (0.1 mmol, 1.8 mg) was added. After that, the ¹¹B NMR spectra were recorded.

2.18. General procedure for the synthesis of 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl acetate

To the Young's NMR tube charged with argon approx. 0.6 mL of dry CD₂Cl₂ and acetic acid (0.1 mmol, 6 mg) were placed. Next, pinacolborane (**2**) (0.1 mmol, 12.8 mg) was dropped in. The mixture was shaken vigorously and left at room temperature for 1 h. After that, ¹¹B NMR spectra was recorded.

2.19. General procedure for the [Cho][OAc]-catalyzed hydroboration of 1a with 2 in the presence of TMEDA

The Young's NMR tube was charged under the argon with [Cho][OAc] (0.2 equiv., 0.05 mmol, 8.2 mg) and approx. 0.6 mL of dry toluene-d₈ or CD₂Cl₂ was added. Subsequently, *N*-benzylideneaniline (**1a**) (1 equiv., 0.25 mmol, 45.3 mg), TMEDA (0.2 mmol, 0.05 mmol, 5.8 mg), and pinacolborane (**2**) (1 equiv., 0.25 mmol, 32 mg) were added. Next, the NMR tube was heated in an oil bath at 60 °C (for toluene) or 40 °C (for DCM) for 20 min. After that, the ¹H, ¹³C, and ¹¹B NMR spectra were recorded.

2.20. General procedure for the equimolar reaction of benzonitrile (5a) with [Cho][OAc]

The Young's NMR tube was charged under the argon with [Cho][OAc] (0.1 mmol, 16.3 mg) and approx. 0.6 mL of dry toluene-d₈ was added. Subsequently, benzonitrile (**5a**) (0.1 mmol, 10.3 mg) was added and the mixture was shaken vigorously, and the ¹H and ¹³C NMR spectra were recorded. Then, the reaction mixture was heated in an oil bath at 70 °C for 24 hours and NMR spectra were carried out again.

2.21. General procedure for the nonequimolar reaction of pinacolborane (2) and benzonitrile (5a) with [Cho][OAc].

The Young's NMR tube was charged under the argon with [Cho][OAc] (0.2 equiv., 0.05 mmol, 8.2 mg) and approx. 0.6 mL of dry toluene-d8 was added. Subsequently, benzonitrile (**5a**) (1 equiv., 0.25 mmol, 25.8 mg) and pinacolborane (**2**) (3.2 equiv., 0.8 mmol, 102.4 mg) were added and the mixture was shaken vigorously and the ^1H , ^{11}B and ^{13}C NMR spectra were recorded. Then, the reaction mixture was heated in an oil bath at 70 °C for 24 hours and NMR spectra were carried out again.

2.22. General procedure for the [Cho][OAc]-catalyzed hydroboration of **5a** with **2** in the presence of TMEDA

The Young's NMR tube was charged under the argon with [Cho][OAc] (0.2 equiv., 0.05 mmol, 8.2 mg) and approx. 0.6 mL of dry toluene-d8 was added. Subsequently, benzonitrile (**5a**) (1 equiv., 0.25 mmol, 25.8 mg), TMEDA (0.2 mmol, 0.05 mmol, 5.8 mg), and pinacolborane (**2**) (3.2 equiv., 0.8 mmol, 102.4 mg) were added and the mixture was shaken vigorously and the ^1H and ^{11}B spectra were recorded. Then, the reaction mixture was heated in an oil bath at 70 °C for 24 hours and NMR spectra were carried out again.

3. Ionic liquids used in catalyst screening process

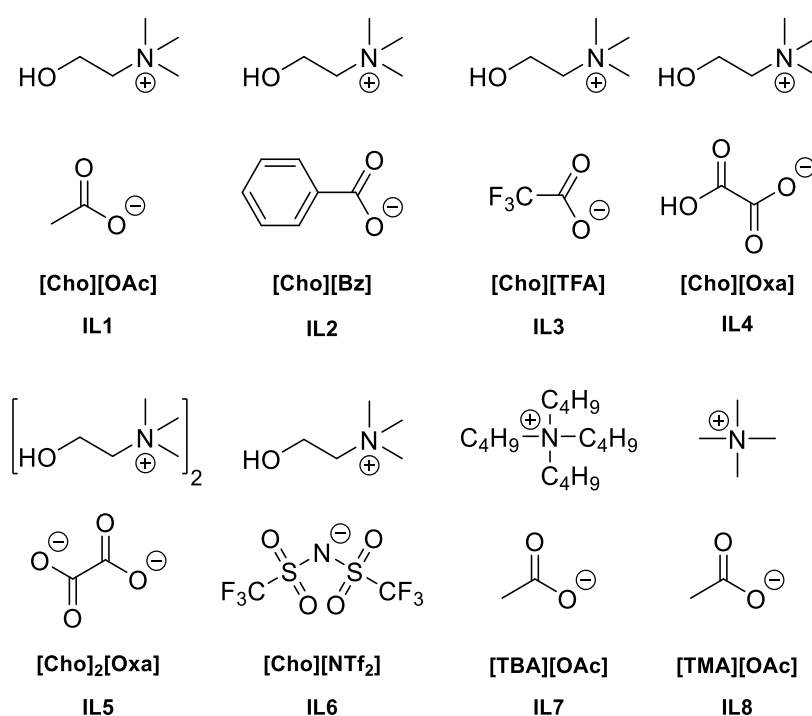
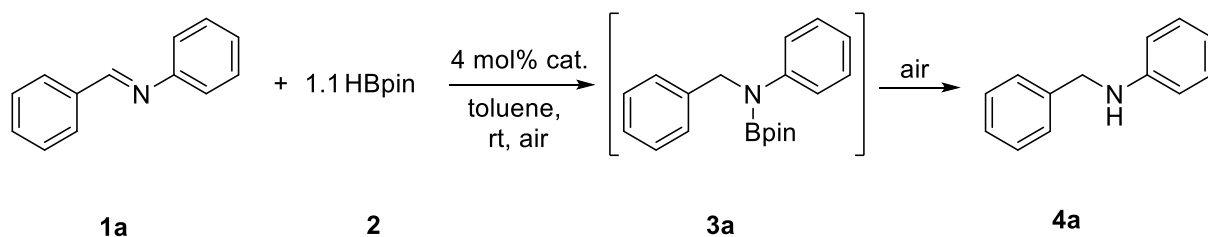


Figure S1. Structures of ionic liquids used in the catalyst screening process.

4. Catalyst screening for hydroboration of imines

Table S1. Catalyst screening for hydroboration of *N*-benzylidenaniline (**1a**) with pinacolborane (**2**).

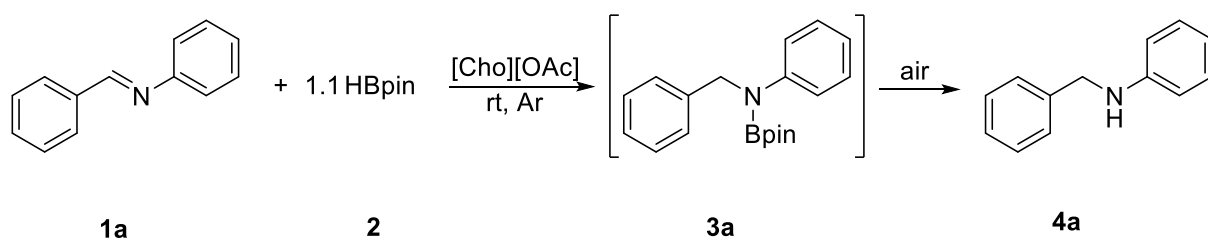


Entry	Cat.	Time [h]	Conversion of 1a [%] ^{a)}	Selectivity of 4a [%] ^{a)}
1	[Cho][OAc]	1	53	>99
2		3	83	>99
3	[Cho][Bz]	1	73	>99
4		3	79	>99
5	[Cho][TFA]	1	18	>99
6		3	19	>99
7	[Cho][Oxa]	1	45	>99
8		3	63	>99
9	[Cho] ₂ [Oxa]	1	30	>99
10		3	65	>99
11	[Cho][NTf ₂]	1	14	>99
12		3	22	>99
13	[TMA][OAc]	1	21	>99
14		3	39	>99
15	[TBA][OAc]	1	22	>99
16		3	57	>99
17	HOAc	1	31	>99
18		3	55	>99
19	HBz	1	62	>99
20		3	74	>99
21	HTFA	3	0	n.d.
22	KBz	1	45	>99
23		3	46	>99

Reaction conditions: [cat]:[**1a**]:[**2**] = 0.04:1:1.1, solvent (1 mL), 1–3 h, rt, air. ^{a)} The conversion and selectivity were based on GC-MS and ¹H NMR analyses; n.d. – not determined.

5. Optimization of conditions for hydroboration of imines

Table S2. Optimization of conditions for hydroboration of *N*-benzylidenaniline (**1a**) with pinacolborane (**2**).

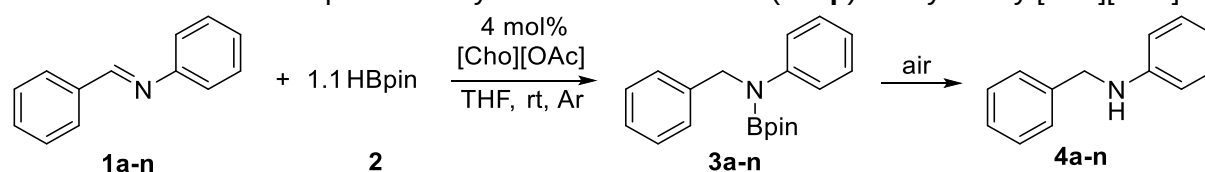


Entry	Mol% of IL	Time [h]	Solvent	Conversion of 1a [%] ^{a)}	Selectivity of 4a [%] ^{a)}
1	-	3	toluene	trace	n.d.
2	4	1	toluene	86	>99
3		3		96	>99
4 ^{b)}	4	1	toluene	57	>99
5 ^{b)}		3		83	>99
6	2	1	toluene	26	>99
7		3		38	>99
8	6	1	toluene	86	>99
9		3		96	>99
10	4	1	toluene	92	>99
11		3		>99	>99
12	4	1	DCM	58	>99
13		3		64	>99
14	4	1	THF	92	>99
15		3		>99	>99
16	-	1	THF	7	>99
17		3		10	>99
18 ^{c)}	4	1	THF	23	>99
19 ^{c)}		3		24	>99
20 ^{d)}	4	1	THF	48	>99
21	4	1	acetonitrile	62	>99
22		3		80	>99
23	4	1	ethyl acetate	88	>99
24		3		>99	>99
25	4	0.5	methanol	60	60

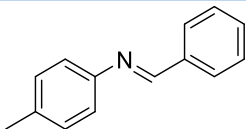
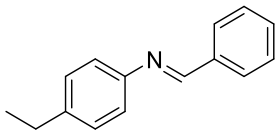
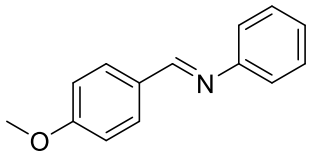
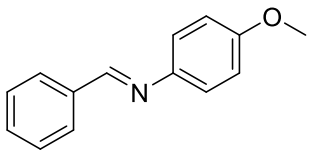
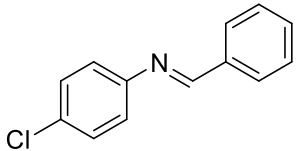
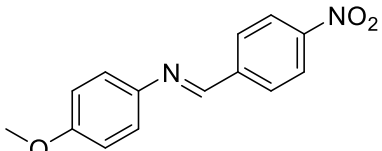
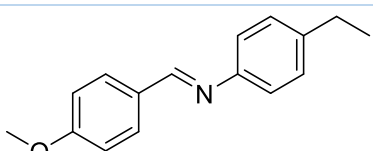
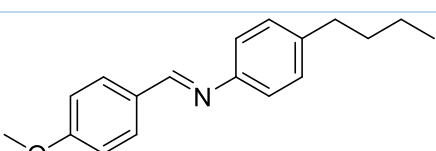
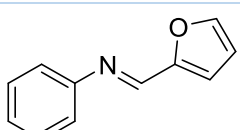
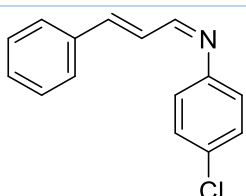
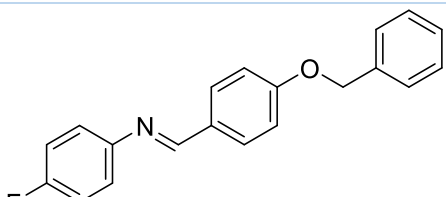
Reaction conditions: [Cho][OAc]:[1a]:[2] = 0.02–0.06:1:1.1, solvent (1 mL), 0.5–3 h, rt, Ar. ^{a)} The conversion and selectivity were based on GC-MS and ¹H NMR analyses; ^{b)} air atmosphere; ^{c)} 10 μl of water was added; ^{d)} 1 μl of water was added; n.d. – not determined.

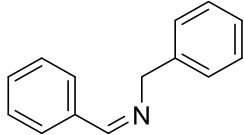
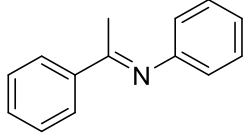
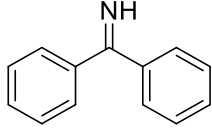
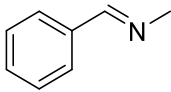
6. Hydroboration of imines - substrate scope. Additional information

Table S3. Substrate scope for the hydroboration of imines (**1a–p**) catalyzed by [Cho][OAc].



Substrate		Time [h]	Conversion of 1a–n [%] ^{a)}	Selectivity of 3a–n [%] ^{a)}
1a		1	92	>99
		2	>99	>99
		3	>99	>99

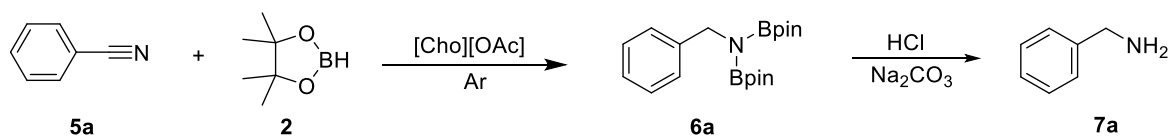
1b		1	>99	>99
1c		1	97	>99
		3	>99	>99
1d		1	>99	>99
1e		1	99	>99
1f		1	88	>99
		3	>99	>99
1g		1	76	>99
		3	98	>99
1h		1	64	>99
		3	80	>99
1i		1	59	>99
		3	86	>99
1j		1	30	>99
		18	>99	>99
1k		1	98	>99
		3	>99	>99
1l		1	75	>99
		3	96	>99

1m^{b)}		1	57	>99
		3	63	>99
1n^{c),d)}		1	49	>99
		18	81	>99
1o^{e)}		1	87	>99
		3	92	>99
1p^{b)}		1	71	>99
		3	92	>99

Reaction conditions: [Cho][OAc]:[**1a**]:[**2**] = 0.02–0.06:1:1.1, THF (1 mL), 1–18 h, rt, Ar. ^{a)} The yields were based on GC-MS and ¹H NMR analyzes; ^{b)} neat; ^{c)} 60 °C; ^{d)} 2 equiv. of HBpin; ^{e)} toluene.

7. Optimization of conditions for hydroboration of nitriles

Table S4. Optimization of conditions for hydroboration of benzonitrile (**5a**) with pinacolborane (**2**).



Entry	Solvent	Temp. [°C]	HBpin [equiv.]	Mol% of [Cho][OAc]	Time [h]	Conversion of 5a [%] ^{a)}	Selectivity of 6a [%] ^{a)}
1	toluene	100	2.4	6	18	69	>99
2	toluene	100	4.0	6	18	89	>99
3	ethyl acetate	80	4.0	6	18	89	>99
4	neat	100	4.0	6	18	>99	>99
5	neat	100	2.4	6	18	88	>99
6	neat	80	4.0	6	18	98	>99
7	THF	80	4.0	6	18	>99	>99
8	THF	80	4.0	4	18	>99	>99
9	THF	70	3.7	4	18	>99	>99
10	THF	70	3.5	4	5	85	>99
11					7	93	>99
12					18	>99	>99
13	THF	70	3.2	6	5	91	>99
14					7	94	>99

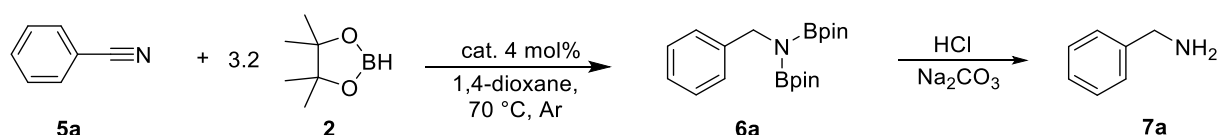
15					18	>99	>99
16	THF	60	4.0	6	5	78	>99
17					7	87	>99
18					18	98	>99
19	THF	60	3.5	6	5	80	>99
20					7	88	>99
21 ^{b)}	THF	60	3.5	6	5	79	>99
22 ^{b)}					7	87	>99
23	THF	60	3.5	4	18	95	>99
24	1,4-dioxane	80	4.0	6	18	>99	>99
25	1,4-dioxane	70	4.0	6	5	96	>99
26					7	>99	>99
27					18	>99	>99
28	1,4-dioxane	70	3.5	6	5	96	>99
29					7	>99	>99
30					18	>99	>99
31	1,4-dioxane	70	3.5	4	5	94	>99
32					7	98	>99
33					18	>99	>99
34	1,4-dioxane	70	3.2	6	5	95	>99
35					7	99	>99
36					18	>99	>99
37	1,4-dioxane	70	3.2	4	5	94	>99
38					7	98	>99
39					18	>99	>99
40 ^{b),*}	1,4-dioxane	70	3.2	4	5	94	>99
41 ^{b),*}					7	98	>99
42	1,4-dioxane	70	3.2	-	5	40	>99
43 ^{b)}	1,4-dioxane	70	3.2	-	5	0	n.d.
44 ^{c)}	1,4-dioxane	70	3.2	4	5	0	n.d.
45 ^{d)}	1,4-dioxane	70	3.2	4	5	58	>99
46	1,4-dioxane	70	3.0	4	5	71	>99
47					7	82	>99
48					18	96	>99
49	1,4-dioxane	60	3.5	6	18	>99	>99
50	1,4-dioxane	60	3.2	6	18	97	>99
51	1,4-dioxane	60	3.0	6	18	89	>99
52	1,4-dioxane	50	3.2	6	18	93	>99

Reaction conditions: [Cho][OAc]:[5a]:[2] = 0.04–0.06:1:2.2–4.0, solvent (1 mL), 60–100 °C, 5–24 h, Ar.

^{a)} The conversion and selectivity were based on GC-MS and ¹H NMR analyses; ^{b)} air atmosphere;

^{c)} 10 µL of water was added; ^{d)} 1 µL of water was added; n.d. – not determined; * Significant amounts of O(Bpin)₂ was observed.

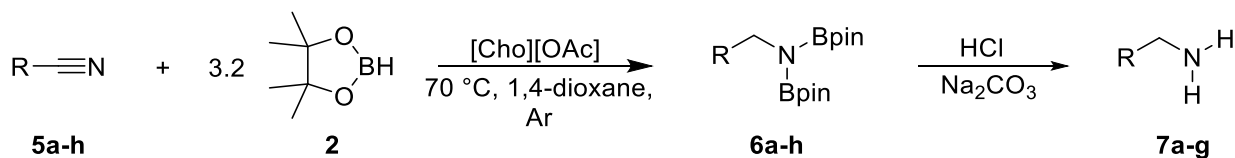
8. Catalyst screening for hydroboration of nitriles

Table S5. Catalyst screening for hydroboration of benzonitrile (**5a**) with pinacolborane (**2**).

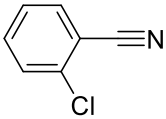
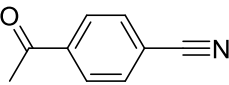
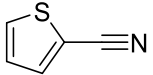
Entry	Mol% of cat.	Time [h]	Conversion of 5a [%] ^{a)}	Selectivity of 6a [%] ^{a)}
1	[Cho][OAc]	5	93	>99
2		7	97	>99
3	[Cho][Bz]	5	92	>99
4		7	98	>99
5	[Cho][Oxa]	5	70	>99
6		7	89	>99
7	[Cho] ₂ [Oxa]	5	90	>99
8		7	98	>99
9	[Cho][TFA]	5	89	>99
10		7	93	>99

Reaction conditions: [Cho]:**5a**:**2** = 0.04:1:3.2, solvent (1 mL), 70 °C, 5–7 h, Ar. ^{a)} The conversion and selectivity were based on GC-MS and ¹H NMR analyses.

9. Hydroboration of nitriles – substrate scope. Additional information

Table S6. Substrate scope for the hydroboration of nitriles (**5a–h**) catalyzed by [Cho][OAc].

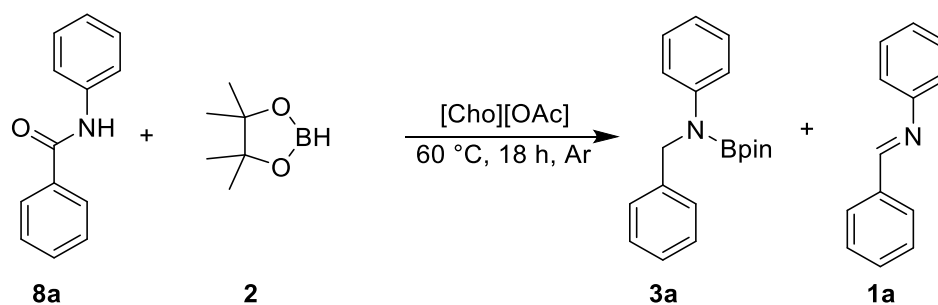
	Substrate	Time [h]	Conversion of 5a–h [%] ^{a)}	Selectivity of 6a–h [%] ^{a)}
5a		5	94	>99
		7	98	>99
5b		5	98	>99
		7	>99	>99
5c		5	83	>99
		7	98	>99
5d		5	99	>99
		7	>99	>99

5e		5	58	>99
		7	79	>99
5f ^{b)}		7	>99	54
5g		5	49	>99
		7	62	>99
5h		5	82	>99
		7	93	>99

Reaction conditions: [cat]:[5a]:[2] = 0.04:1:3.2, 4-dioxane (1 mL), 70 °C, 5–7 h, Ar. ^{a)} The yields were based on GC-MS and ¹H NMR analyzes; ^{b)} 4 equiv. of HBpin.

10. Optimization of conditions for hydroboration of amides

Table S7. Optimization of conditions for hydroboration of *N*-phenylbenzamide (**8a**) with pinacolborane (**2**)

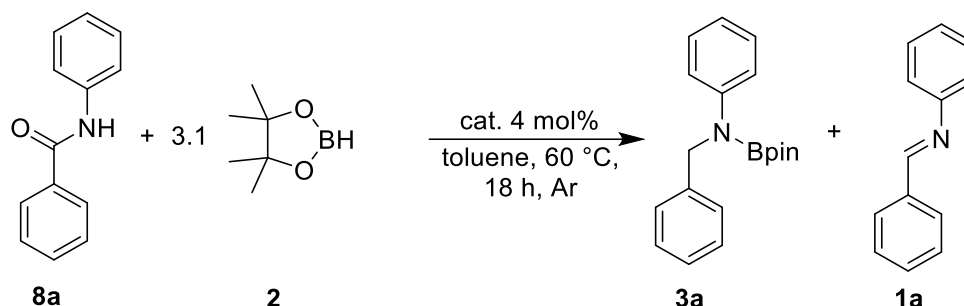


Entry	Solvent	Mol% of [Cho][OAc]	HBpin [equiv.]	Conversion of 8a [%] ^{a)}	Selectivity of 3a [%] ^{a)}
1	toluene	-	3	<1	n.d
2	neat	6	3	86	98
3	neat	6	3.5	83	>99
4	THF	6	3	77	98
5	ethyl acetate	6	3	47	73
6	dioxane	6	3	92	89
7	toluene	6	3	89	98
8	toluene	6	2	51	88
9	toluene	6	3.1	97	>99
10 ^{b)}	toluene	6	3.1	41	>99
11	toluene	5	3	86	98
12	toluene	4	3	86	98
13	toluene	4	3.1	97	>99
14	toluene	4	3.1	95	>99

Reaction conditions: [cat]:[**8a**]:[**2**] = 0–0.06:1:2–3.5, solvent (1 mL), 60 °C, 18 h, Ar ^a) The conversion and selectivity were based on GC-MS and ¹H NMR analyses; ^b) 2 mL of solvent.

11. Catalyst screening for hydroboration of amides

Table S8. Catalyst screening for hydroboration of *N*-phenylbenzamide (**8a**) with pinacolborane (**2**).

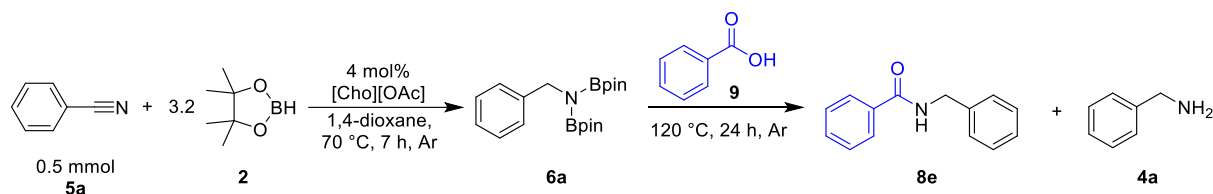


Entry	Cat.	Conversion of 8a [%] ^a	Selectivity of 3a [%] ^a
1	[Cho][OAc]	97	>99
2	[Cho][Bz]	97	89
3	[Cho][TFA]	97	96
4	[Cho][Oxa]	91	91
5	[Cho] ₂ [Oxa]	87	77

Reaction conditions: [cat]:[**8a**]:[**2**] = 0.04:1:3.1, solvent (1 mL), 60 °C, 18 h, Ar. ^a) The conversion and selectivity were based on GC-MS and ¹H NMR analyses.

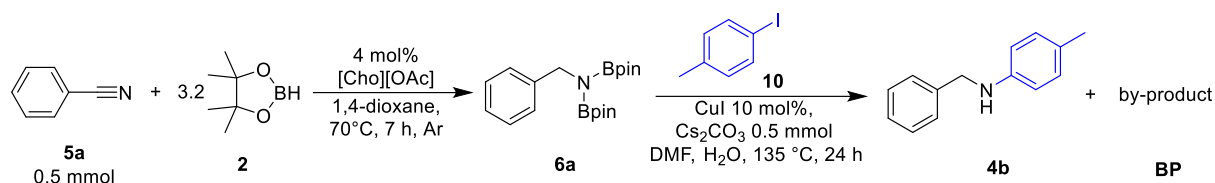
12. Functionalization of nitriles by hydroboration and subsequent reactions in a one-pot manner

Table S9. Optimization of conditions for the reaction of **6a** with benzoic acid (**9**)



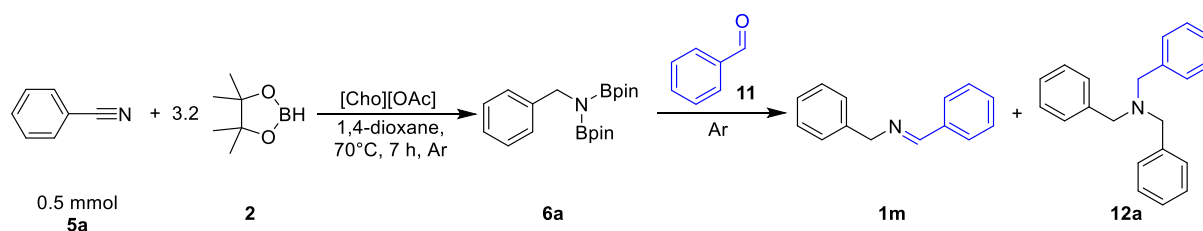
Entry	Solvent (II step)	Conversion of 6a [%] ^a	Selectivity of 8e [%] ^a
1	1,4-dioxane	>99	86
2	toluene	>99	>99

Reaction conditions: I step: [cat]:[**5a**]:[**2**] = 0.04:1: 3.2, 1,4-dioxane (1 mL), 70 °C, 7 h, Ar, II step: [**9**]=1.0, solvent (1 mL), 120 °C, 24 h, Ar ^a) The conversion and selectivity were based on GC-MS analysis.

Table S10. Optimization of conditions for the reaction **6a** with 4-iodotoluene (**10**)

Entry	10 [equiv.]	H ₂ O [equiv.]	Conversion of 6a [%] ^{a)}	Selectivity of 4b [%] ^{a)}
1	2	6.4 (1.6 mmol)	>99	81
2	2	44 (11.1 mmol)	>99	89
3	2	4.4 (1.1 mmol)	>99	84
4	1.2	4.4 (1.1 mmol)	>99	92

Reaction conditions: I step: [cat]:[**5a**]:[**2**] = 0.04:1: 3.2, 1,4-dioxane (1 mL), 70 °C, 7 h, Ar; II step: [**10**]:[CuI]:[Cs₂CO₃]:[H₂O]=1.2–2:0.1:1.2–2:4.4–44, DMF (1.5 mL), 135 °C, 24 h. ^{a)} The conversion and selectivity were based on GC-MS analysis.

Table S11. Optimization of conditions for the reaction **6a** with benzaldehyde (**11**)

Entry	11 [equiv.]	Solvent	Time [h]	Temp. [°C]	Conversion of 6a [%] ^{a)}	Ratio 1m : 12a [%] ^{a)}
1	1	DCM	3	50	>99	>99:<1
2	1	DCM	1	rt	>99	>99:<1
3	2	DCM	1	rt	>99	97:3
4	1	1,4-dioxane	3	50	>99	83:17
5	2	1,4-dioxane	1	rt	>99	50:50
6^{b)}	2	1,4-dioxane	3	rt	>99	54:46
7	2	1,4-dioxane	1	50	>99	49:51
8			3		>99	49:51
9			72		>99	49:51
10	2	1,4-dioxane	3	100	>99	78:22
11	2.5	1,4-dioxane	1	rt	>99	46:54
12	4	1,4-dioxane	1	rt	>99	84:16
13	2	THF	3	50	>99	92:8

Reaction conditions: I step: [cat]:[**5a**]:[**2**] = 0.04:1:3.2, 1,4-dioxane (1 mL), 70 °C, 7 h, Ar; II step: [**11**]=1–4, solvent (1 mL), rt–80 °C, 1–3 h; ^{a)} The conversion and selectivity were based on GC-MS analysis; ^{b)} 10 mol% of acetic acid was added.

13. The repetitive batch hydroboration

13.1. Hydroboration of imines

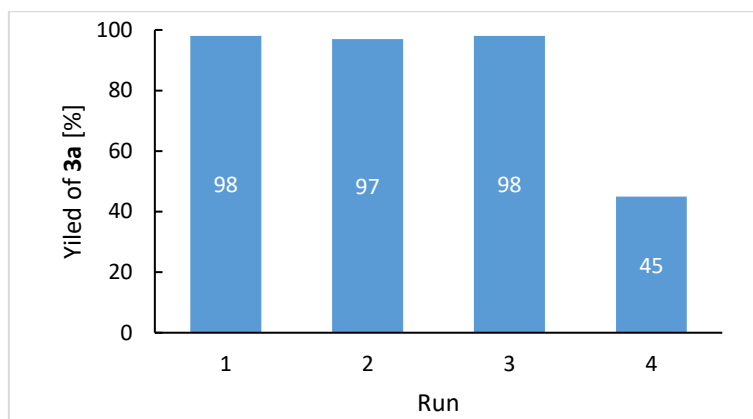


Figure S2. The repetitive batch hydroboration of **1a** (0.5 mmol) with **2** (0.55 mmol) using 4 mol% of [Cho][OAc] at room temperature for 2 h in THF under argon atmosphere. The yield of **3a** was determined by GC-MS analysis.

13.2. Hydroboration of nitriles

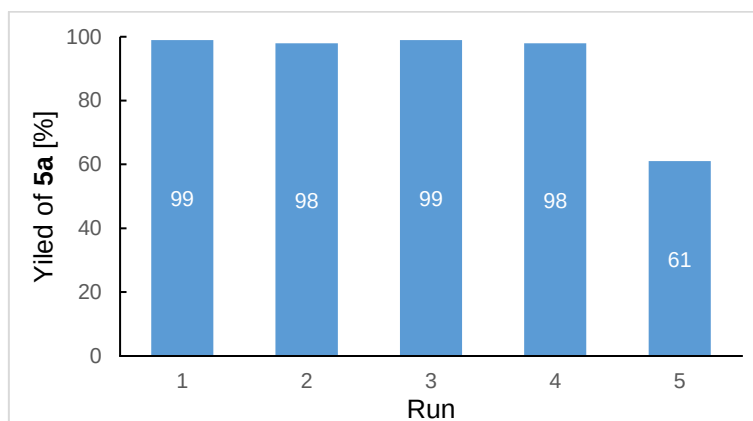
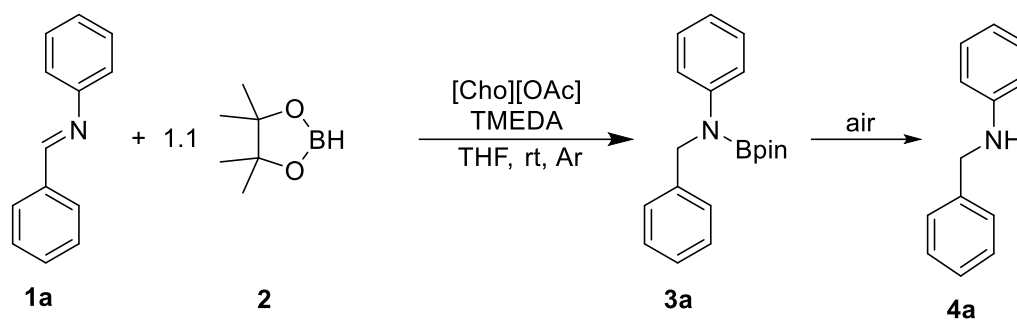


Figure S3. The repetitive batch hydroboration of **5a** (0.5 mmol) with **2** (1.6 mmol) using 8 mol% of [Cho][OAc] at 70 °C for 7 h in 1,4-dioxane under argon atmosphere. The yield of **5a** was determined by GC-MS analysis.

14. Control experiment with TMEDA

Table S12. Control experiments with TMEDA and for hydroboration of *N*-benzylidenaniline (**1a**) with pinacolborane (**2**)



Entry	[Cho][OAc] [mol%]	TMEDA [mol%]	Time [h]	Conversion of 1a [%] ^{a)}	Selectivity of 4a [%] ^{a)}
1	4	-	1	92	>99
			3	>99	>99
2	-	-	1	15	>99
			3	27	>99
3 ^{b)}	-	-	1	0	n.d.
			3	traces	n.d.
4	20	-	1	81	>99
			3	82	>99
5	10	10	1	93	>99
			3	99	>99
6	10	30	1	85	>99
			3	96	>99
7	10	60	1	75	>99
			3	93	>99
8 ^{c)}	4	-	1	23	>99
			3	24	>99

Reaction conditions: [cat]:[1a]:[2]:[TMEDA] = 0-0.2:1:1.1:0-0.6, solvent (1 mL), rt, 1-3 h, Ar. ^{a)} The conversion and selectivity were based on GC-MS and ¹H NMR analyses; ^{b)} solvent: toluene; ^{c)} addition of 10 μ L of water; n.d. – not determined.

15. Further computational results

Table S13. ω B97XD/def2-SVPD Gibbs free energy barriers of rate-determining steps in [Cho][AcO]-catalyzed hydroboration of N-benzylideneaniline (**1a**; DCM, 295 K) and benzonitrile (**5a**; toluene, 333 K)

Reagent	Catalytic species			
	I7a	I7b	I7c	BH ₃
N-benzylideneaniline (1a)	15.9	7.5	12.1	19.4
benzonitrile (5a) (1st cycle)	29.3	15.8	16.5	21.1
benzonitrile (5a) (2nd cycle)	19.2	10.9	10.0	18.6

15.1. Generation of catalytically active borohydrides

Choline acetate (**IL1**) readily reacts with pinacolborane (Figure S4) via two intermediate structures ($\Delta G^\ddagger = 8.4$ [9.0 for elevated temperature] kcal/mol), yielding **I7a** (**IN2**); this process is reversible and favors the formation of **I7a** ($\Delta G = -2.6$ [-4.9] kcal/mol). The latter can form a weak complex **I5b** with an additional HBpin molecule, which then reacts via **TS2b** to give **I6b** and ultimately **I7b** (**IN3**) along with inactive AcOBpin (**IN1**). This subsequent transformation is strongly shifted toward **I7a** ($\Delta G = 13.7$ [15.8] kcal/mol).

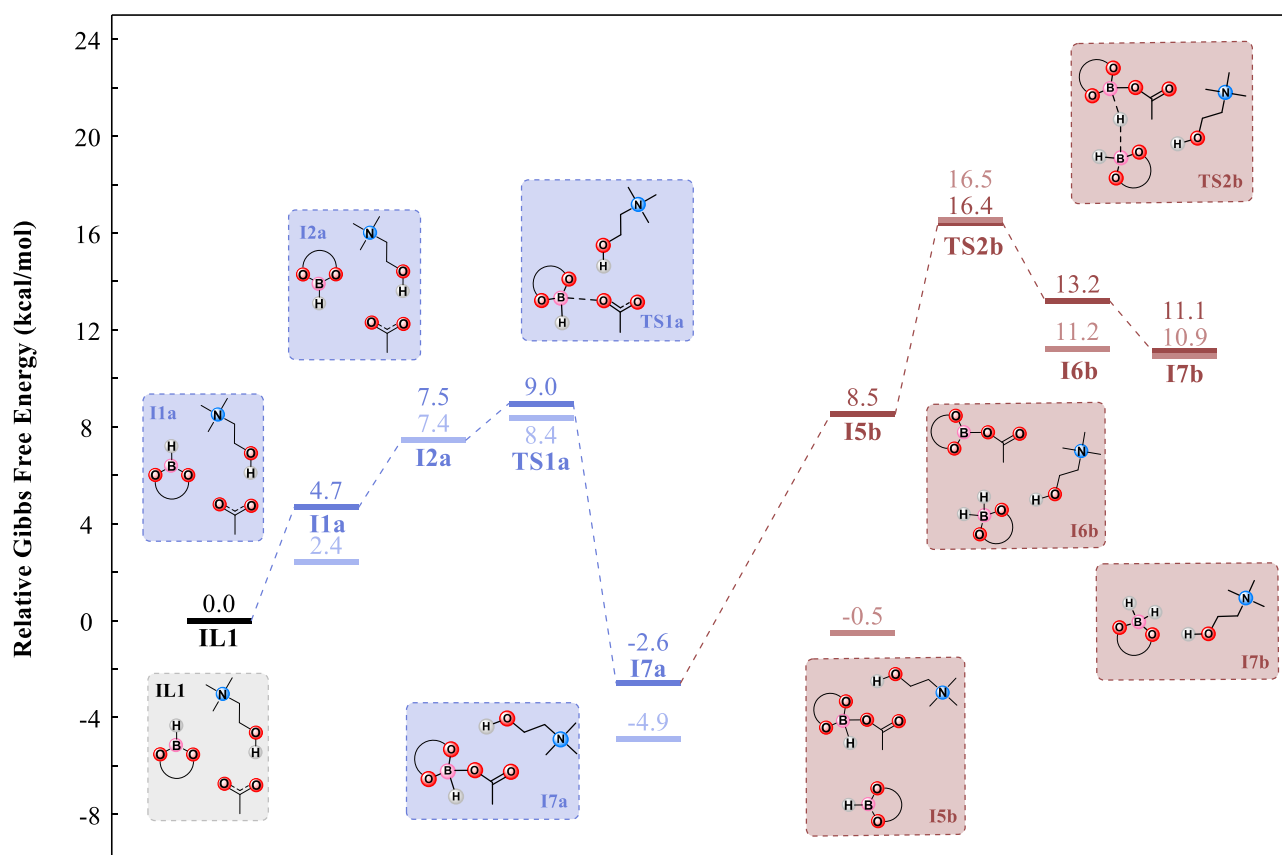


Figure S4. Gibbs free energy profile of the reaction of [Cho][OAc] with pinacolborane – pathways **a** and **b** (darker pathway: ω B97XD/def2-SVPD, 295K, DCM as solvent, lighter pathway: ω B97XD/def2-SVPD, 333K, toluene).

Although **TS1c** lies significantly higher than **TS1a** ($\Delta\Delta G^\ddagger = 7.6$ kcal/mol, Figure S5), it is still readily accessible even at room temperature and leads, via **I3c** and with the release of hydrogen, irreversibly to **I4c** (**IN4**). **I4c** remains in equilibrium with **I7d** (with the equilibrium shifted toward the latter) through a low transition state **TS2d**. The combination of the cation from **I4c** and the anion from **I7a** gives **I5c**, in which a hydride transfer from the anion to the cation can occur, also via a very low barrier. This yields **I6c**, which can dissociate into AcOBpin (**IN1**) and **I7c** (**IN5**).

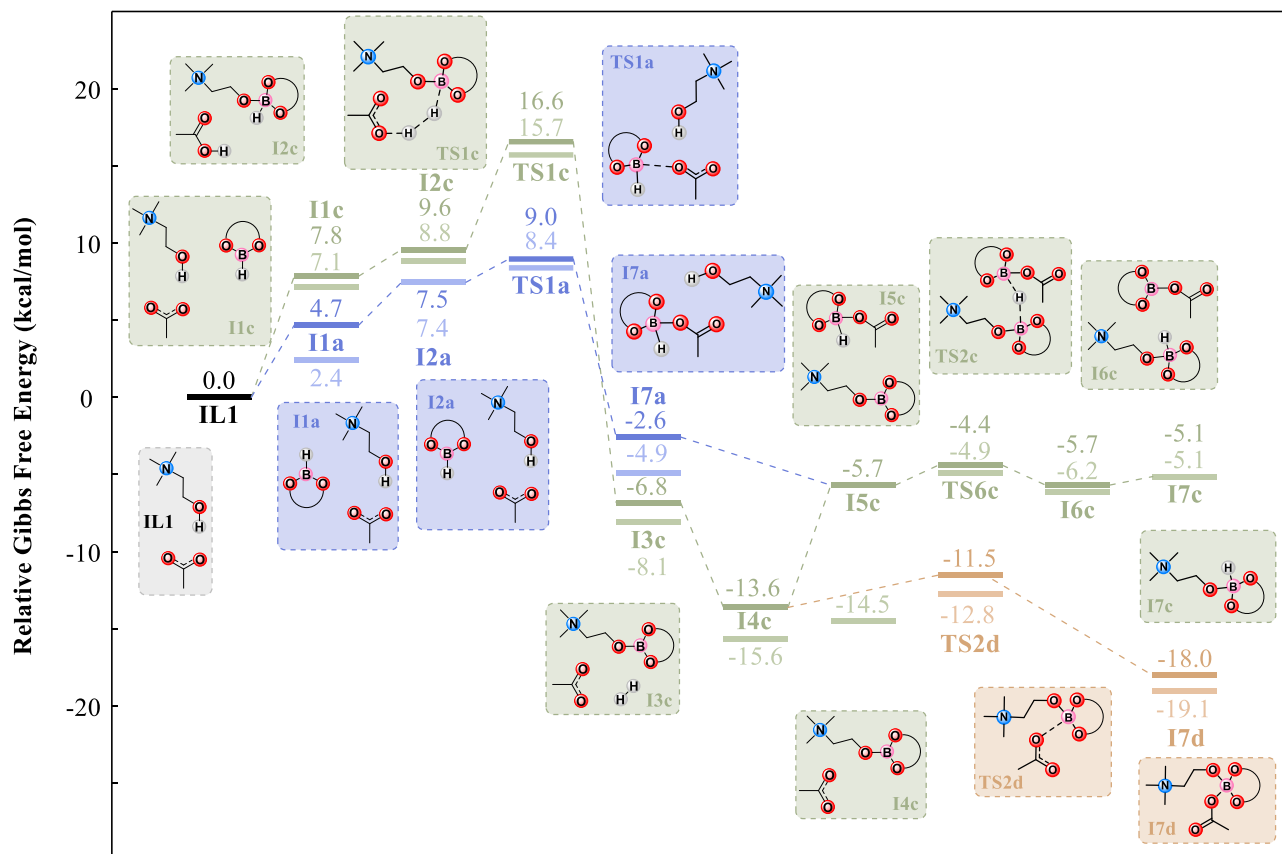


Figure S5. Gibbs free energy profile of the reaction of [Cho][OAc] with pinacolborane – pathways **a** and **c** (darker pathway: ω B97XD/def2-SVPD, 295K, DCM as solvent, lighter pathway: ω B97XD/def2-SVPD, 333K, toluene).

15.2. Hydroboration of imines

The attack of **IN2** on the C=N carbon atom of N-benzylideneaniline, involving hydride transfer, constitutes the rate-determining step (RDS) of catalytic cycle **a** ($\Delta G^\ddagger = 15.9$ kcal/mol, Figure S6). This step yields **I9a**, comprising **IN1** and the N-phenylbenzylamide anion; a slight rotation within this complex leads to **I10a**, which smoothly evolves into **I11a** via intramolecular attack of the nitrogen atom on boron (so facile that no distinct transition state could be located). Addition of another HBpin molecule affords **I12a**, which, again without a discernible barrier, transforms into **I13a** through acetate transfer to HBpin, ultimately generating the product **3a** and regenerating **I7a**.

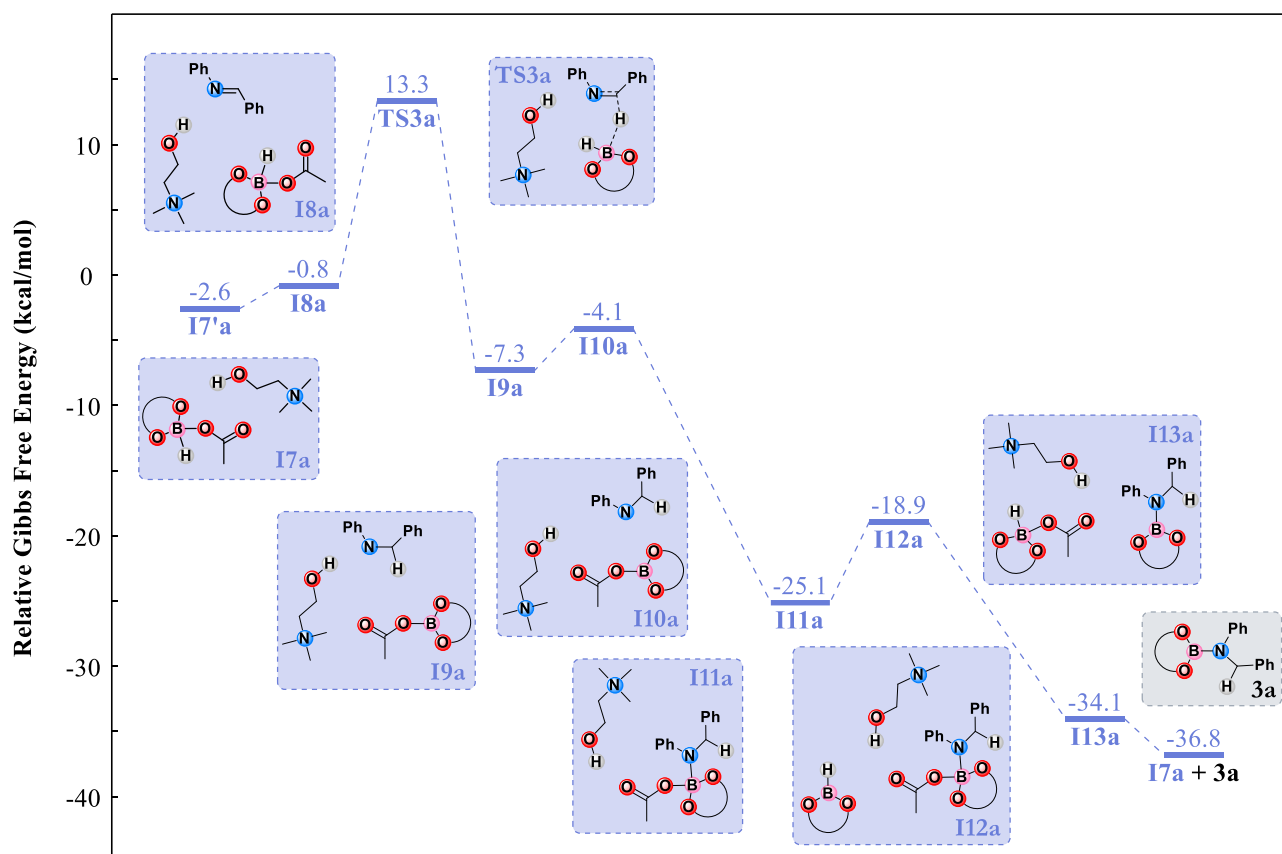


Figure S6. Gibbs free energy profile of the hydroboration of N-benzylideneaniline with pinacolborane – catalytic cycle **a** (ω B97XD/def2-SVPD, 295K, DCM as solvent).

In contrast, in cycle **b**, all three key steps – the hydride attack on the C=N carbon of the imine, the nucleophilic attack of the anionic nitrogen on the boron atom of HBpin, and the subsequent hydride release with regeneration of the catalytic species – proceed through identifiable, yet low, free energy barriers, corresponding to **TS3b**, **TS4b**, and **TS5b**, respectively ($\Delta G^\ddagger = 7.5$ kcal/mol).

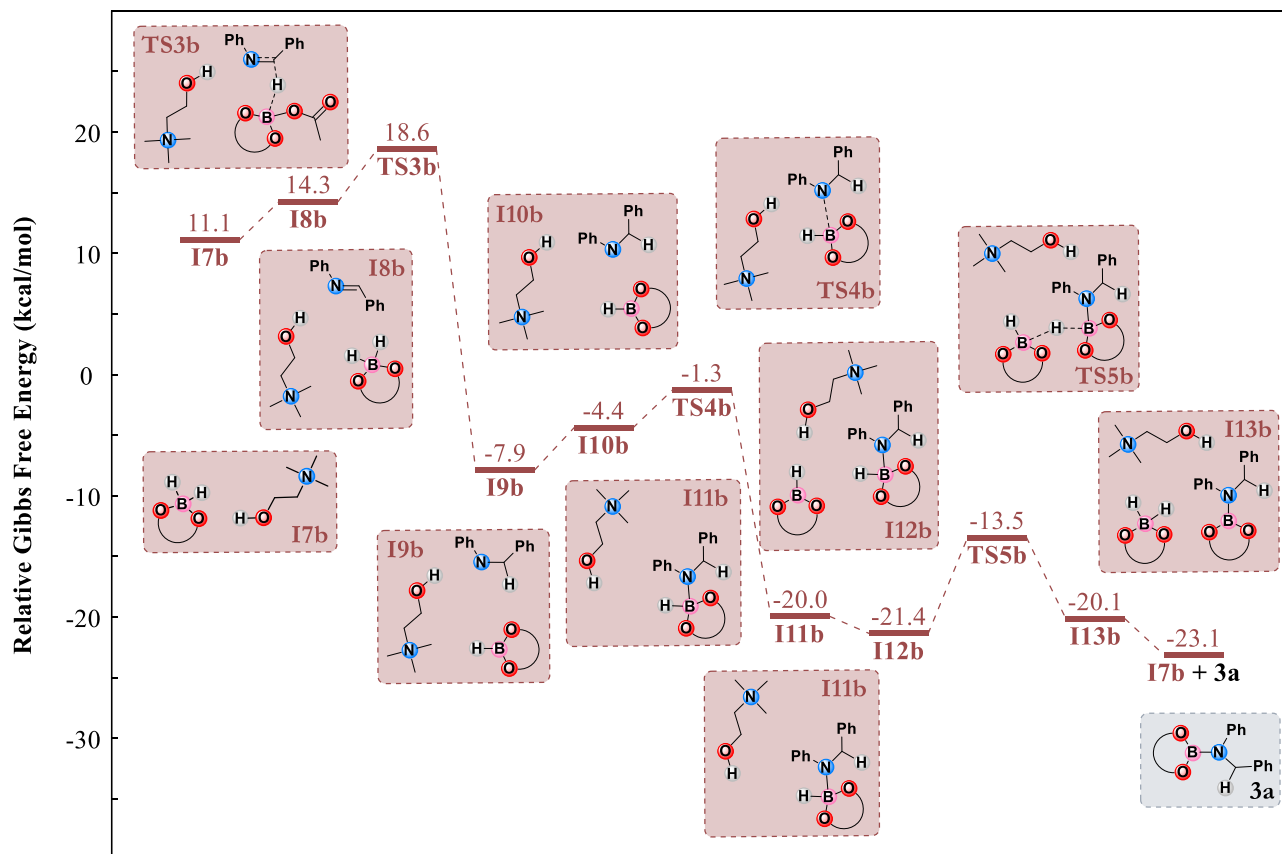


Figure S7. Gibbs free energy profile of the hydroboration of N-benzylideneaniline with pinacolborane – catalytic cycle **b** (ω B97XD/def2-SVPD, 295K, DCM as solvent).

A similar pattern is observed in cycle **c**, with barriers corresponding to **TS3c** ($\Delta G^\ddagger = 12.1$ kcal/mol), **TS4c**, and **TS5c**. Notably, the intermediate product **I9c** can proceed along two competing pathways: nucleophilic attack of the anionic nitrogen on the boron atom from which the hydride originated leads, via **TS4e** ($\Delta G^\ddagger = 4.0$ kcal/mol), to **I11e** – a dead-end species that precludes further reaction. However, **I11e** remains in equilibrium with **I9c**, which can alternatively undergo attack on a new HBpin molecule (**TS4c**). Subsequent hydride abstraction from the resulting intermediate by **IN4** leads to product formation with concurrent regeneration of **I7c**.

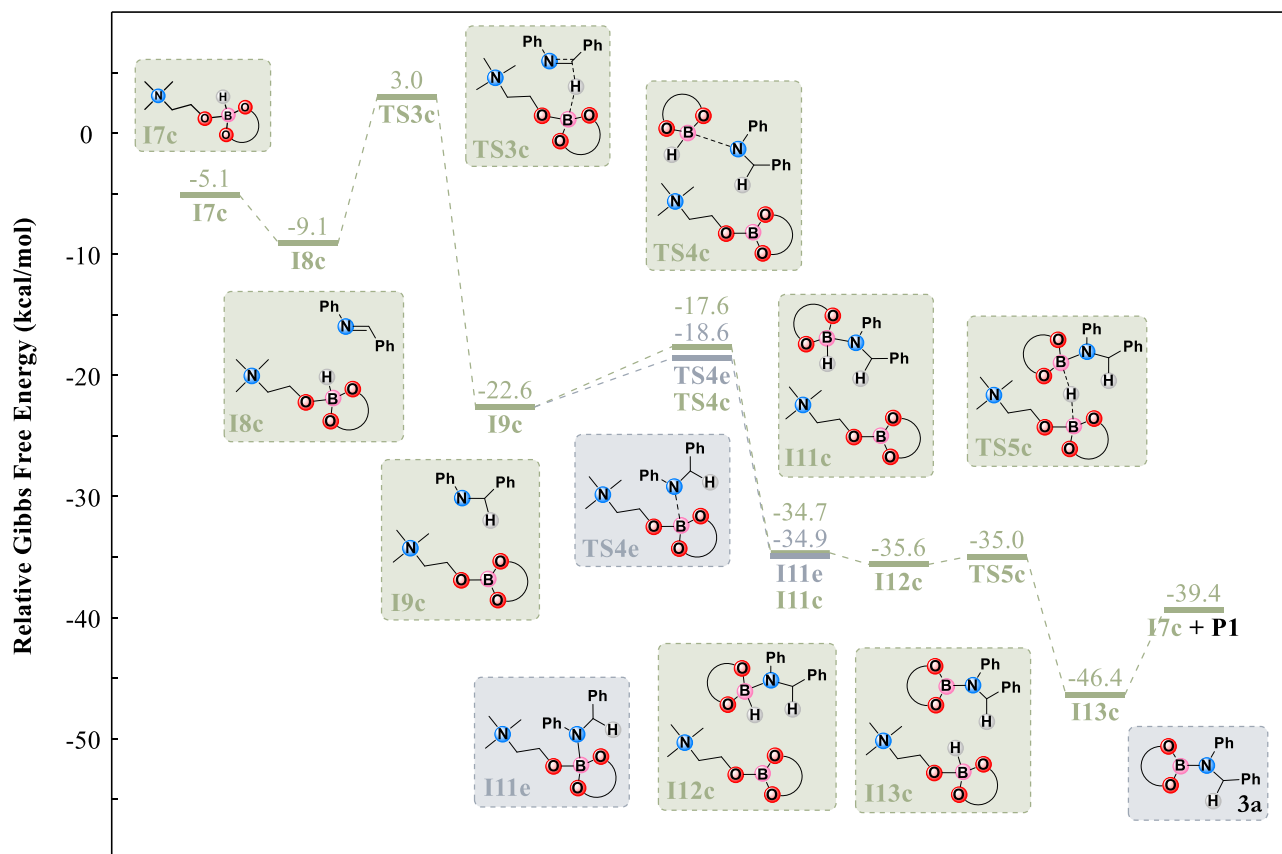


Figure S8. Gibbs free energy profile of the hydroboration of N-benzylideneaniline with pinacolborane – catalytic cycle **c** (ω B97XD/def2-SVPD, 295K, DCM as solvent).

15.3. Hydroboration of nitriles

The overall mechanistic outline is similar in the reaction of benzonitrile with HBpin (Figure 9). A relatively high barrier is observed for **TS3'a**, corresponding to hydride transfer from **IN2** to the sp-hybridized carbon of the nitrile ($\Delta G^\ddagger = 29.3$ kcal/mol). As in the case of imines, a slight rotation within complex **I9'a** leads to **I10'a**, and the subsequent attack of the nitrogen atom on boron proceeds without an additional energy barrier. Acetate abstraction by HBpin (**TS5'a**, $\Delta G^\ddagger = 10.5$ kcal/mol) yields complex **I13'a**, which may dissociate into **I7'a** and **P'1**, but can also undergo further transformation (Figure 10), ultimately leading to the double hydroboration product. The catalytic cycle then repeats; although the RDS barrier is lower in this second stage ($\Delta G^\ddagger = 19.2$ kcal/mol for **TS6'a**), the final hydride release and regeneration of the catalyst ($\Delta G_{I17a \rightarrow I9a} = 16.1$ kcal/mol) is more difficult than in the first cycle, mainly due to steric effects.

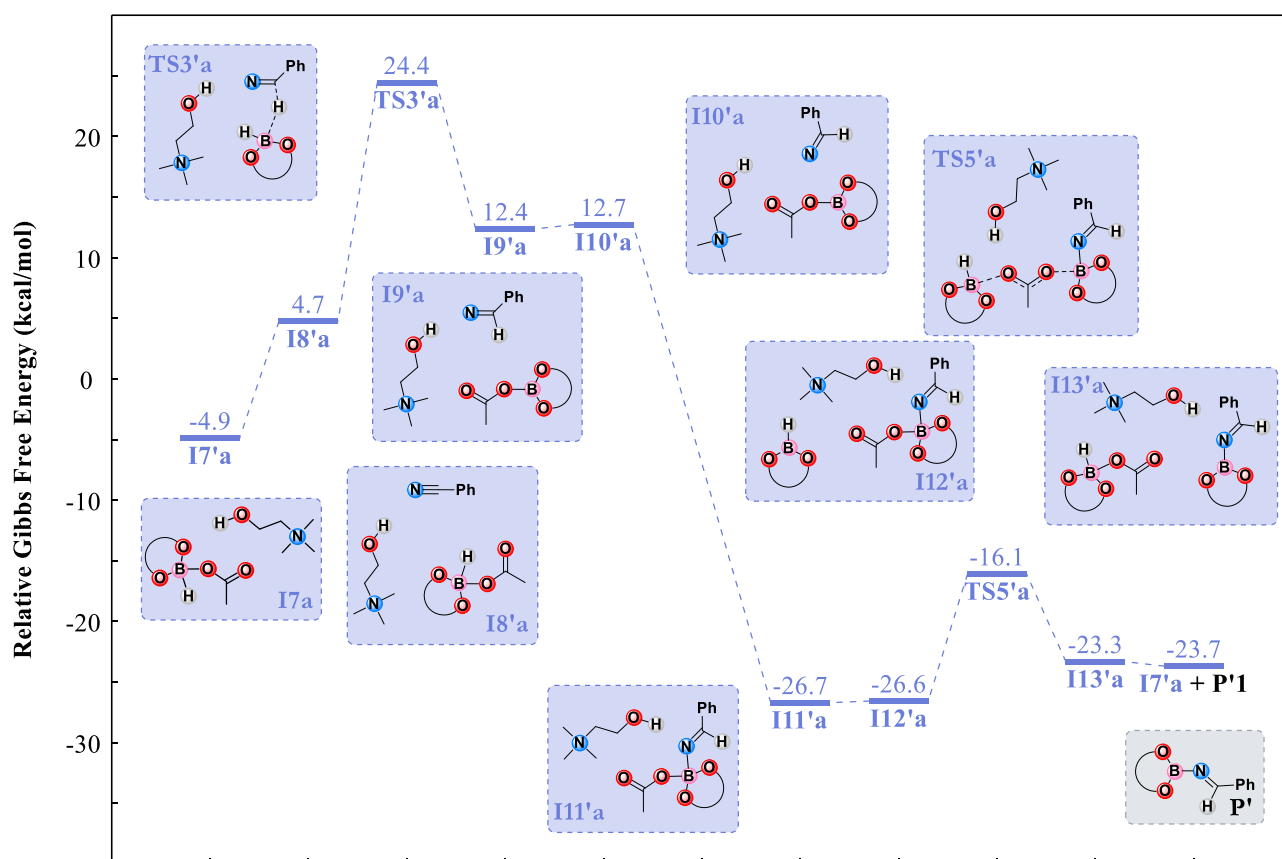


Figure S9. Gibbs free energy profile of the hydroboration of benzonitrile with pinacolborane – catalytic cycle **a**, first hydroboration (ω B97XD/def2-SVPD, 333K, toluene as solvent).

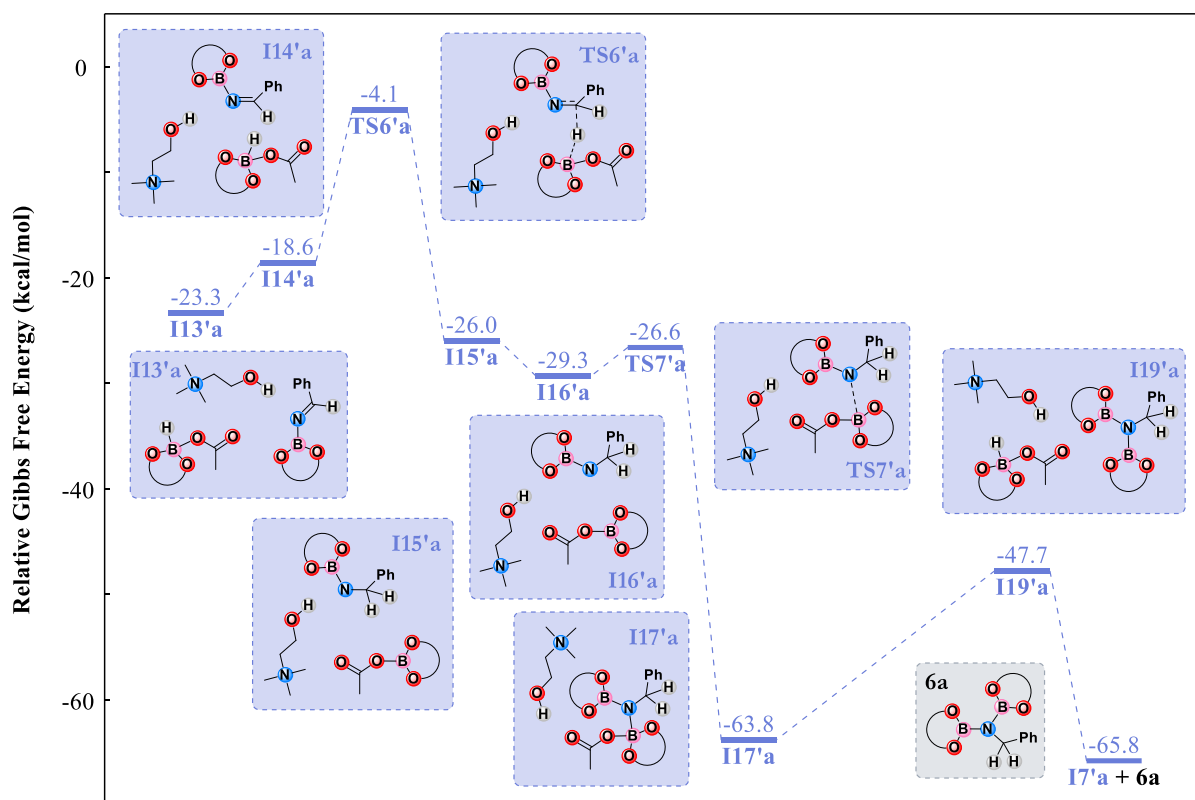


Figure S10. Gibbs free energy profile of the hydroboration of benzonitrile with pinacolborane – catalytic cycle **a**, second hydroboration (ω B97XD/def2-SVPD, 333K, toluene as solvent).

The energy profiles of catalytic cycle **b** closely resemble those of cycle **a** (Figures S11–S12). In the rate-determining step, the barrier ($\Delta G^\ddagger = 15.9$ kcal/mol for **TS'3b**) is significantly lower than that of cycle **a**, which appears to largely compensate for the $\text{I7a} \rightleftharpoons \text{I7b}$ equilibrium being unfavourable toward the formation of the latter. The remaining barriers have no significant impact on the overall reaction rate. The second hydroboration proceeds even more readily, with a lower rate-determining barrier ($\Delta G^\ddagger = 10.9$ kcal/mol for **TS'6b**).

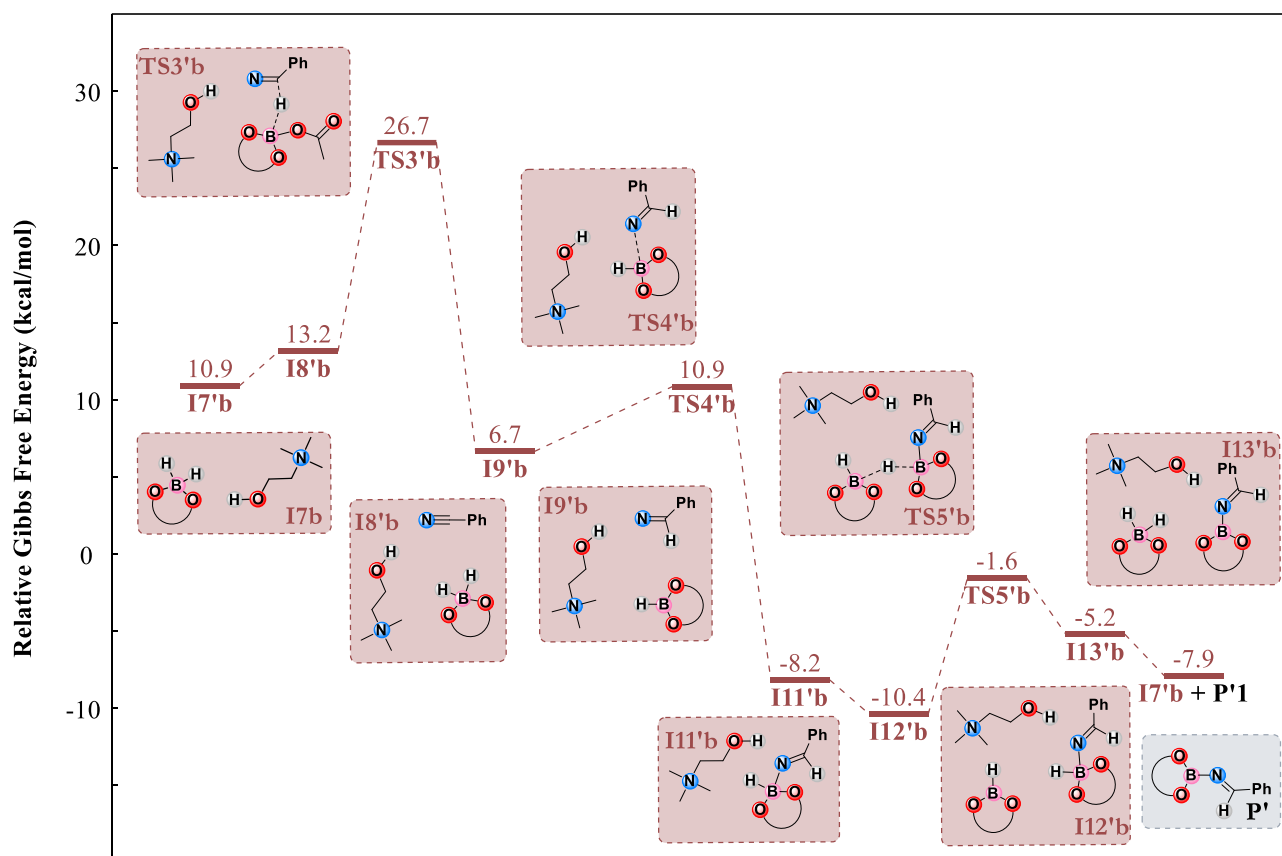


Figure S11. Gibbs free energy profile of the hydroboration of benzonitrile with pinacolborane – catalytic cycle **b**, first hydroboration ($\omega\text{B97XD/def2-SVPD}$, 333K, toluene as solvent).

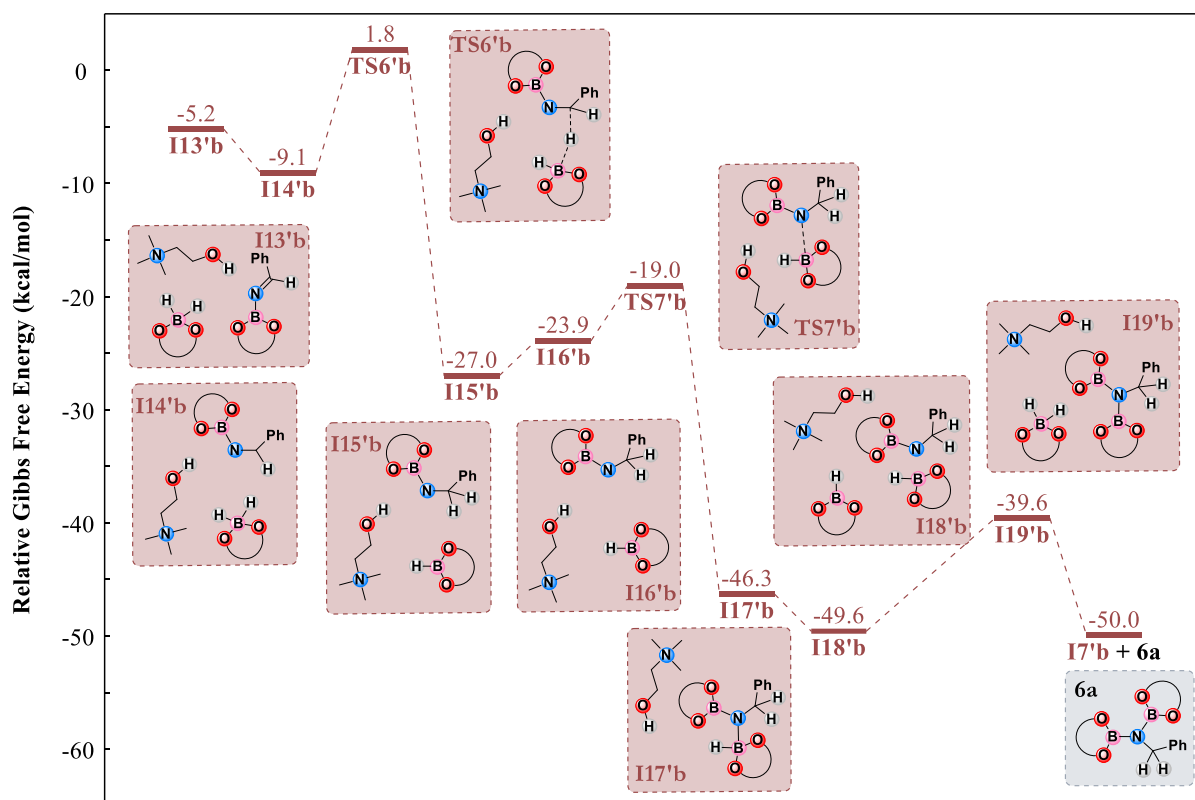


Figure S12. Gibbs free energy profile of the hydroboration of benzonitrile with pinacolborane – catalytic cycle **b**, first hydroboration (ω B97XD/def2-SVPD, 333K, toluene as solvent).

The scenario is similar for cycle **c**, where the rate-determining step again corresponds to the hydride transfer to the sp-type carbon of the nitrile, with the associated $\Delta G^\ddagger = 16.5$ kcal/mol (**TS3'c**). As observed for imines, the immediate back-attack of the negatively charged nitrogen on the boron atom can occur readily; yet, unlike in cycles **a** and **b**, this leads to a dead-end intermediate (**I11'e**) that inhibits the reaction ($\Delta G_{\text{I17a} \rightarrow \text{I19a}} = -23.8$ kcal/mol). Instead, the nitrogen must attack a new HBpin molecule, forming **I11'c** via **TS4'c**. Subsequent reorganization of the complex gives **I12'c**, which proceeds through **TS5'c** to yield the product and regenerate the catalyst. Once again, the reaction does not stop at this stage, but the cycle repeats with lower-energy transition states, ultimately affording product **6a** and regenerating **IN5**.

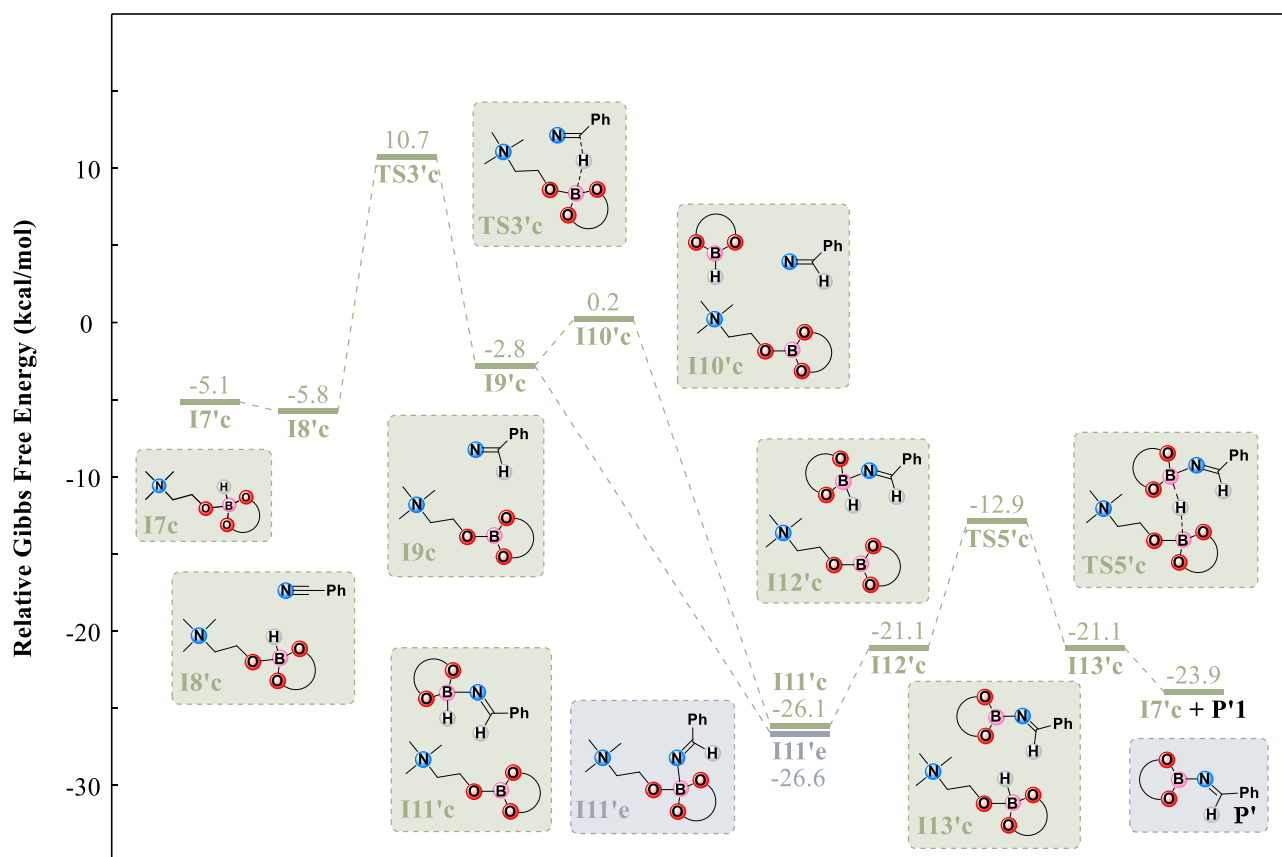


Figure S13. Gibbs free energy profile of the hydroboration of benzonitrile with pinacolborane – catalytic cycle **c**, first hydroboration (ω B97XD/def2-SVPD, 333K, toluene as solvent).

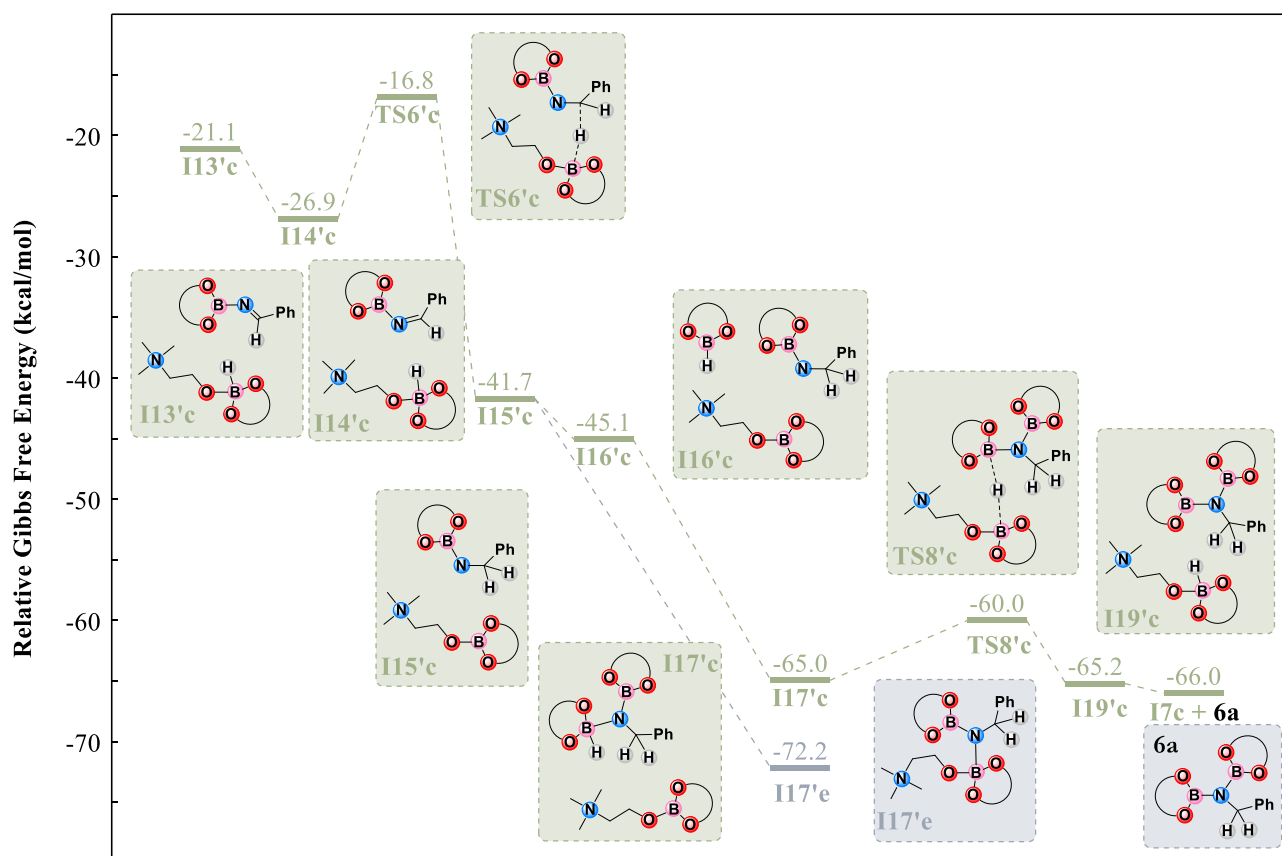


Figure S14. Gibbs free energy profile of the hydroboration of benzonitrile with pinacolborane – catalytic cycle **c**, first hydroboration (ω B97XD/def2-SVPD, 333K, toluene as solvent).

15.4. Gibbs free energies

Table S14. Gibbs free energies of substrates and selected intermediates (ω B97XD/def2-SVPD, 295 K, dichloromethane solution, all energies given in Hartree).

Structure	Gibbs free energy	Structure	Gibbs free energy
HBpin	-411.322090	Cho ⁺	-328.284264
PhCHNPh	-556.018549	AcO ⁻	-228.370785
BH ₃	-26.570775	ChoAcO	-556.674579
H ₂	-1.173414	AcOBPin	-639.005862

Table S15. Raw and corrected Gibbs free energies of substrates and selected intermediates (ω B97XD/def2-SVPD, 1 atm, 333 K, toluene solution, all energies given in Hartree).

Structure	Gibbs free energy	Structure	Gibbs free energy
HBpin	-411.324435	Cho ⁺	-328.267363
PhCN	-324.086793	AcO ⁻	-228.339431
BH ₃	-26.572978	ChoAcO	-556.665310
H ₂	-1.175107	AcOBPin	-639.008346

Table S16. Gibbs free energies of structures in the reaction of *N*-phenylbenzylimine (ω B97XD/def2-SVPD, 1 atm, 295 K, dichloromethane solution, all energies given in Hartree)

Structure	Gibbs free energy	Structure	Gibbs free energy
I1a	-967.989227	TS1c	-967.970276
I2a	-967.984803	I3c	-968.007548
TS1a	-967.982396	I4c	-966.844957
I7a	-968.000779	I5c	-1378.154421
I8a	-1524.016556	TS2c	-1378.152378
TS3a	-1523.993968	I6c	-1378.154421
I9a	-1524.026869	I7c	-739.147668
I10a	-1524.021777	I8c	-1295.172529
I11a	-1524.055268	TS2d	-966.841623
I12a	-1935.367503	I7d	-966.851986
I13a	-1935.391595	TS3c	-1295.153260
I5b	-1379.305186	I9c	-1295.194064
TS2b	-1379.292585	TS4c	-1706.508202
I6b	-1379.297733	I11c	-1706.535362
I7b	-740.295195	I12c	-1706.536885
I8b	-1296.308735	TS5c	-1706.535857
TS3b	-1296.301829	I13c	-1706.554005
I9b	-1296.343990	TS4e	-1295.187637
I10b	-1296.338441	I11e	-1295.213696
TS4b	-1296.333490	I1f	-582.627509
I11b	-1296.363243	TS1f	-582.583560
I12b	-1707.687576	I2f	-582.664312
TS5b	-1707.674973	I3f	-993.977286
I13b	-1707.685641	TS2f	-993.946363
I1c	-967.984164	I4f	-993.973325
I2c	-967.981420	3a	-967.395228

Table S17. Gibbs free energies of structures in the reaction of benzonitrile (ω B97XD/def2-SVPD, 1 atm, 333 K, toluene solution, all energies given in Hartree)

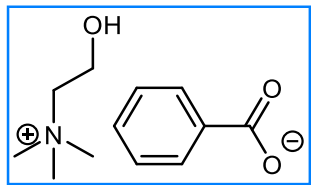
Structure	Gibbs free energy	Structure	Gibbs free energy
I1a	-967.985923	I1c	-967.978398
I2a	-967.977885	I2c	-967.975693
TS1a	-967.976385	TS1c	-967.964720
I7a	-967.997540	I3c	-968.002671
I8a	-1292.068983	I4c	-966.839560
TS3a	-1292.037586	I5c	-1378.162200
I9a	-1292.056824	TS2c	-1378.146893
I10a	-1292.056256	I6c	-1378.148900
TS4a	-1292.070696	I7c	-739.138931
I11a	-1292.119101	TS2d	-1063.226702
I12a	-1703.443325	I7d	-1063.200389

TS5a	-1703.426617	I8c	-1063.226702
I13a	-1703.438146	TS3c	-1063.200389
I14a	-1703.430565	I9c	-1063.221980
TS6a	-1703.407483	I10c	-1474.541581
I15a	-1703.442345	I11c	-1474.583626
I16a	-1703.447676	I12c	-1474.575532
TS7a	-1703.443373	TS5c	-1474.562481
I17a	-1703.502692	I13c	-1474.575600
I19a	-2114.801500	I14c	-1474.584771
I5b	-1379.314997	TS6c	-1474.568793
TS2b	-1379.287822	I15c	-1474.608422
I6b	-1379.296282	I17c	-1885.969896
I7b	-740.288452	TS8c	-1885.962023
I8b	-1064.371664	I19c	-1885.970315
TS3b	-1064.350137	I17e	-1474.657000
I9b	-1064.382022	I1f	-350.682686
TS4b	-1064.375332	TS1f	-350.644915
I11b	-1064.405646	I2f	-350.715440
I12b	-1475.733593	I3f	-762.032360
TS5b	-1475.719534	TS2f	-761.998804
I13b	-1475.725363	I4f	-762.047090
I14b	-1475.731511	I5f	-762.045010
TS6b	-1475.714146	TS3f	-762.008000
I15b	-1475.760074	I6f	-762.095910
I16b	-1475.755152	I7f	-1173.415000
TS7b	-1475.747397	TS4f	-1173.390651
I17b	-1475.790846	I8f	-1173.409984
I18b	-1887.120504	P'1	-735.441190
I19b	-1887.104605	6a	-1146.832657

16. Products characterization

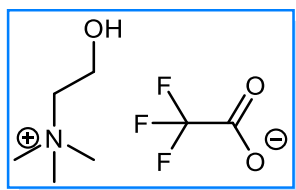
16.1. Characterization of synthesized ionic liquids

Choline benzoate [Cho][Bz] (IL2)



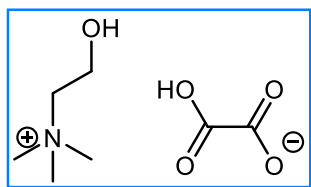
^1H NMR (300 MHz, D_2O , δ , ppm): 7.90 – 7.86 (m, 2H, Ph), 7.59 – 7.44 (m, 3H, Ph), 4.11 – 3.97 (m, 2H, $\text{CH}_2(\text{CH}_2)$), 3.52 – 3.43 (m, 2H, NCH_2), 3.16 (s, 9H, $\text{N}(\text{CH}_3)_3$). Hydrogen atom in hydroxyl group is not detected $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, D_2O , δ , ppm): 175.5 (COO^-), 136.1 (Ph), 131.3 (Ph), 128.8 (Ph), 128.3 (Ph), 67.4 (t, NCH_2), 55.6 ($\text{CH}_2(\text{CH}_2)$), 53.8 (t, $\text{N}(\text{CH}_3)_3$). Yellow solid. Isolation yield 94% (1.48 g). The analytical data are in agreement with the literature.^[25]

Choline trifluoroacetate [Cho][TFA] (IL3)



^1H NMR (300 MHz, D_2O , δ , ppm): 4.12 – 4.01 (m, 2H, $\text{CH}_2(\text{CH}_2)$), 3.56 – 3.47 (m, 2H, NCH_2), 3.20 (s, 9H, $\text{N}(\text{CH}_3)_3$). Hydrogen atom in hydroxyl group is not detected. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, D_2O , δ , ppm): 162.8 (q, $J_{\text{C-F}} = 35.4$ Hz, COO^-), 116.4 (q, $J_{\text{C-F}} = 292.0$ Hz, CF_3), 67.4 (t, NCH_2), 55.6 ($\text{CH}_2(\text{CH}_2)$), 53.8 (t, $\text{N}(\text{CH}_3)_3$). Yellow solid. Isolation yield 95% (1.44 g). The analytical data are in agreement with the literature.^[26]

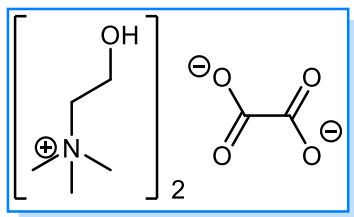
Choline oxalate [Cho][Oxa] (IL4)



^1H NMR (300 MHz, D_2O , δ , ppm): 4.10 – 4.03 (m, 2H, $\text{CH}_2(\text{CH}_2)$), 3.56 – 3.47 (m, 2H, NCH_2), 3.20 (s, 9H, $\text{N}(\text{CH}_3)_3$). Hydrogen atoms in hydroxyl and carboxyl group are not detected. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, D_2O , δ , ppm): 165.6 (COO^-), 67.4 (t, NCH_2), 55.6 ($\text{CH}_2(\text{CH}_2)$), 53.8 (t,

$N(CH_3)_3$. Yellow solid. Isolation yield 95% (1.28 g). The analytical data are in agreement with the literature.^[27]

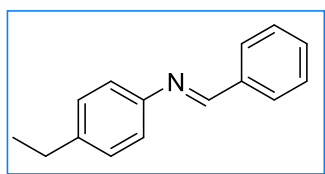
Dicholine oxalate [Cho]₂[Oxa] (IL5)



¹H NMR (300 MHz, D₂O, δ, ppm): 4.09 – 4.04 (m, 4H, CH₂(CH₂)), 3.57 – 3.48 (m, 4H, NCH₂), 3.21 (s, 18H, N(CH₃)₃). Hydrogen atom in hydroxyl group is not detected. ¹³C{¹H} NMR (75 MHz, D₂O, δ, ppm): 173.1 (COO⁻), 67.4 (t, NCH₂), 55.6 (CH₂(CH₂)), 53.8 (t, N(CH₃)₃). Yellow solid. Isolation yield 93% (0.96 g). The analytical data are in agreement with the literature.^[28]

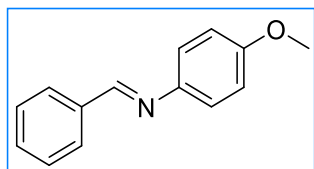
16.2. Characterization of synthesized imines

N-(4-Ethylphenyl)-1-phenylmethanimine (**1c**)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.38 (s, 1H, C(CH)), 7.84 – 7.77 (m, 2H, Ph), 7.44 – 7.30 (m, 3H, Ph), 7.19 – 7.03 (m, 4H, Ph), 2.58 (q, *J*_{H-H} = 7.6 Hz, 2H, CH₂(CH₃)), 1.17 (t, *J*_{H-H} = 7.6 Hz, 3H, CH₂(CH₃)). ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 159.7 (C(CH)), 149.7 (Ph), 142.4 (Ph), 136.5 (Ph), 131.3 (Ph), 128.9 (Ph), 128.7 (Ph), 121.0 (Ph), 28.6 (CH₂(CH₃)), 15.8 (CH₂(CH₃)). **MS (EI) [m/z (%)]**: 210 (M⁺, 35), 209 (M⁺, 100), 208 (13), 196 (3), 195 (15), 194 (47), 193 (9), 103 (4), 90 (3), 89 (5), 51 (4). Pale yellow liquid. Isolation yield 72% (226.5 mg). The analytical data are in agreement with the literature.^[29]

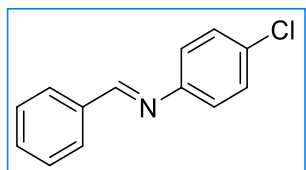
N-(4-Methoxyphenyl)-1-phenylmethanimine (**1e**)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.49 (s, 1H, C(CH)), 7.95 – 7.85 (m, 2H, Ph), 7.51 – 7.42 (m, 3H, Ph), 7.25 (d, *J*_{H-H} = 9.0 Hz, 2H, Ph), 6.94 (d, *J*_{H-H} = 9.0 Hz, 2H, Ph), 3.84 (s, 3H, *p*-OCH₃Ph). ¹³C{¹H} NMR (75 MHz, CDCl₃, δ, ppm): 158.5 (C(CH)), 145.0 (Ph), 136.6 (Ph), 131.2 (Ph), 128.9 (Ph), 128.7 (Ph), 122.3 (Ph), 114.5 (Ph), 55.6 (*p*-OCH₃Ph). **MS (EI) [m/z (%)]**: 211 (M⁺, 19), 210 (15), 197 (14), 196 (100), 167 (13), 141 (11), 115 (5), 77 (9), 63 (15), 51 (7). Pale

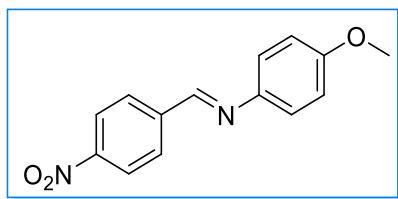
yellow solid. Isolation yield 71% (224.6 mg). The analytical data are in agreement with the literature.^[29]

N-(4-Chlorophenyl)-1-phenylmethanimine (**1f**)



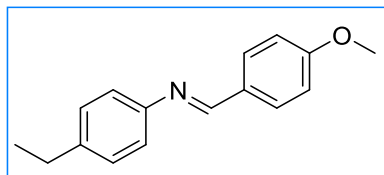
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.44 (s, 1H, C(CH)), 7.94 – 7.85 (m, 2H, Ph), 7.50 – 7.45 (m, 3H, Ph), 7.41 – 7.30 (m, 2H, Ph), 7.21 – 7.10 (m, 2H, Ph). **¹³C{¹H} NMR** (75 MHz, CDCl₃, δ, ppm): 160.9 (C(CH)), 150.7 (Ph), 136.1 (Ph), 131.8 (Ph), 131.6 (Ph), 129.4 (Ph), 129.0 (Ph), 129.0 (Ph), 122.4 (Ph). **MS (EI) [m/z (%)]**: 216(M⁺, 100), 215(71), 214(52), 213(11), 78(11), 77(14), 76(14), 75(13), 51(14), 50(11). White solid. Isolation yield 68% (218.6 mg). The analytical data are in agreement with the literature.^[29-30]

N-(4-Methoxyphenyl)-1-(4-nitrophenyl)methanimine (**1g**)



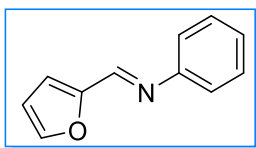
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.58 (s, 1H, C(CH)), 8.32 (d, *J*_{H-H} = 8.7 Hz, 2H, Ph), 8.06 (d, *J*_{H-H} = 8.8 Hz, 2H, Ph), 7.31 (d, *J*_{H-H} = 9.0 Hz, 2H, Ph), 6.96 (d, *J*_{H-H} = 8.9 Hz, 2H, Ph), 3.85 (s, 3H, *p*-OCH₃Ph). **¹³C{¹H} NMR** (75 MHz, CDCl₃, δ, ppm): 159.4 (Ph), 154.9 (C(CH)), 149.2 (Ph), 143.8 (Ph), 142.1 (Ph), 129.2 (Ph), 124.2 (Ph), 122.8 (Ph), 114.7 (Ph), 55. (*p*-OCH₃Ph). **MS (EI) [m/z (%)]**: 256(M⁺, 100), 242(9), 241(28), 240(17), 239(7), 195(5), 193(5), 165(5), 64(5), 63(6). Yellow-orange solid. Isolation yield 88% (336.8 mg). The analytical data are in agreement with the literature.^[31]

N-(4-Ethylphenyl)-1-(4-methoxyphenyl)methanimine (**1h**)



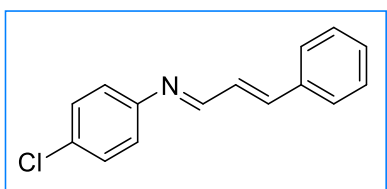
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.40 (s, 1H, C(CH)), 7.89 (d, *J*_{H-H} = 8.4 Hz, 2H, Ph), 7.21 (m, 4H, Ph), 6.99 (d, *J*_{H-H} = 8.9 Hz, 2H, Ph), 3.88 (s, 3H, *p*-OCH₃Ph), 2.67 (q, *J*_{H-H} = 7.6 Hz, 2H, CH₂(CH₃)), 1.26 (t, *J*_{H-H} = 7.6 Hz, 3H, CH₂(CH₃)). **MS (EI) [m/z (%)]**: 240(M⁺, 61), 239(M⁺, 100), 238(19), 237(4), 224(11), 223(32), 222(15), 221(6), 181(3), 180(3). White solid. Isolation yield 83% (296.9 mg). The analytical data are in agreement with the literature.^[32]

1-(Furan-2-yl)-N-phenylmethanimine (1j)



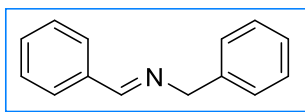
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.28 (s, 1H, C(CH)), 7.61 (d, *J*_{H-H} = 1.6 Hz, 1H, furyl), 7.41 – 7.35 (m, 2H, Ph), 7.26 – 7.19 (m, 3H, Ph), 6.95 (d, *J*_{H-H} = 3.4 Hz, 1H, furyl), 6.55 (dd, *J*_{H-H} = 3.5, 1.8 Hz, 1H, furyl). **¹³C{¹H} NMR** (75 MHz, CDCl₃, δ, ppm): 152.3, 151.6, 147.9, 145.8, 129.3, 126.4, 121.2, 116.5, 112.3. **MS (EI) [m/z (%)]**: 171(M⁺, 100), 170(26), 143(11), 142(14), 141(6), 116(7), 115(14), 114(8), 77(5), 51(13). Yellow liquid. Isolation yield 58% (149.2 mg). The analytical data are in agreement with the literature.^[33-34]

N-(4-Chlorophenyl)-3-phenylprop-2-en-1-imine (1k)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.25 (d, *J*_{H-H} = 7.9 Hz, 1H, N(CH)), 7.59 – 7.51 (m, 2H, Ph), 7.41 – 7.33 (m, 5H, Ph), 7.22 – 7.07 (m, 4H, Ph and CH(CH), overlapped). **¹³C{¹H} NMR** (75 MHz, CDCl₃, δ, ppm): 162.1 (CN), 145.0, 135.5, 131.9, 130.0, 129.4, 129.3, 129.1, 128.3, 127.8, 122.4. **MS (EI) [m/z (%)]**: 242(M⁺, 85), 241(100), 240(30), 128(7), 127(6), 126(6), 103(5), 77(7), 76(8), 75(7), 51(7). Yellow solid. Isolation yield 42% (154.0 mg). The analytical data are in agreement with the literature.^[35-36]

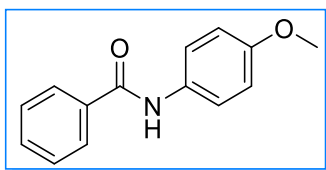
N-Benzyl-1-phenylmethanimine (1m)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.32 (s, 1H, C(CH)), 7.76 – 7.72 (m, 2H, Ph), 7.39 – 7.26 (m, 7H, Ph), 7.24 – 7.17 (m, 1H, Ph), 4.77 (s, 2H, C(CH₂)). **MS (EI) [m/z (%)]**: 195(M⁺, 19), 194(39), 117(10), 92(26), 91(100), 89(13), 77(9), 65(24), 63(10), 51(16). Colorless liquid. Isolation yield 71% (68.8 mg). The analytical data are in agreement with the literature.^[37]

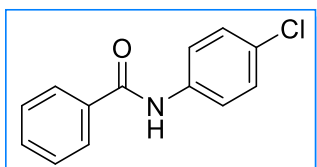
16.3. Characterization of synthesized amides

N-(4-Methoxyphenyl)benzamide (**8b**)



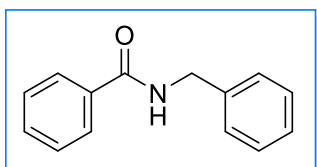
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.89 – 7.76 (m, 3H, Ph and NH, overlapped), 7.56 – 7.43 (m, 5H, Ph), 6.93 – 6.87 (m, 2H, Ph), 3.81 (s, 3H, *p*-OCH₃Ph). **¹³C{¹H} NMR** (75 MHz, CDCl₃, δ, ppm): 165.8 (C=O), 156.8 (Ph), 135.2 (Ph), 131.8 (Ph), 131.1 (Ph), 128.9 (Ph), 127.1 (Ph), 122.3 (Ph), 114.4 (Ph), 55.6 (*p*-OCH₃Ph). **MS (EI) [m/z (%)]**: 227(M⁺, 71), 124(6), 122(6), 106(8), 105(100), 95(5), 78(6), 77(43), 52(7), 50(6). White solid. Isolation yield 46% (169.8 mg). The analytical data are in agreement with the literature.^[38-39]

N-(4-Chlorophenyl)benzamide (**8c**)



¹H NMR (300 MHz, DMSO, δ, ppm): 10.12 (s, 1H, NH), 7.70 – 7.65 (m, 2H, Ph), 7.57 – 7.51 (m, 2H, Ph), 7.35 – 7.22 (m, 3H, Ph), 7.15 – 7.10 (m, 2H, Ph). **¹³C{¹H} NMR** (75 MHz, DMSO, δ, ppm): 166.0 (C=O), 138.3 (Ph), 134.8 (Ph), 132.0 (Ph), 128.7 (Ph), 128.7 (Ph), 127.9 (Ph), 127.6 (Ph), 122.2 (Ph). **MS (EI) [m/z (%)]**: 233(M+1)⁺, 11), 232(M⁺, 6), 231(35), 106(7), 105(100), 99(5), 78(3), 77(42), 63(5), 51(15). White solid. Isolation yield 48% (182.1 mg). The analytical data are in agreement with the literature.^[39-40]

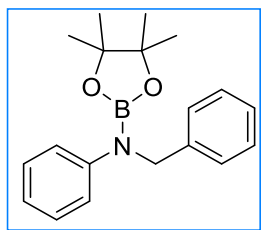
N-Benzylbenzamide (**8e**)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.83 – 7.76 (m, 2H, Ph), 7.53 – 7.39 (m, 3H, Ph), 7.38 – 7.27 (m, 5H, Ph), 6.50 (brs, 1H, NH), 4.64 (d, *J*_{H-H} = 5.7 Hz, 2H, C(CH₂)). **MS (EI) [m/z (%)]**: 211(M⁺, 81), 210(32), 106(29), 105(100), 104(15), 91(12), 77(88), 51(36). White solid. Isolation yield 71% (74.7 mg). The analytical data are in agreement with the literature.^[41]

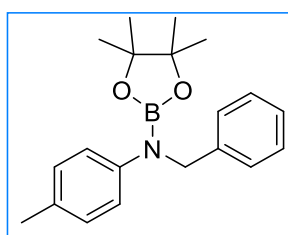
16.4. Characterization of hydroboration products

N-Benzyl-4,4,5,5-tetramethyl-*N*-phenyl-1,3,2-dioxaborolan-2-amine (**3a**)



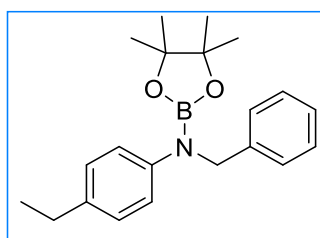
¹H NMR (300 MHz, toluene-*d*₈, δ, ppm): 7.44 – 7.36 (m, 2H, Ph), 7.24 – 7.15 (m, 2H, Ph), 7.15 – 6.98 (m, 5H, Ph), 6.83 – 6.73 (m, 1H, Ph), 4.71 (s, 2H, C(CH₂)), 1.08 (s, 12H, C(CH₃)₂). Characterized as a crude product. The analytical data are in agreement with the literature.^[42]

N-Benzyl-4,4,5,5-tetramethyl-*N*-(*p*-tolyl)-1,3,2-dioxaborolan-2-amine (**3b**)



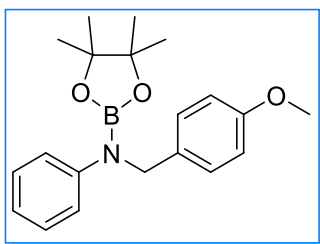
¹H NMR (300 MHz, toluene-*d*₈, δ, ppm): 7.33 – 7.27 (m, 2H, Ph), 7.24 – 7.21 (m, 2H, Ph), 7.14 – 7.08 (m, 2H, Ph), 7.03 – 6.97 (m, 1H, Ph), 6.87 (d, *J*_{H-H} = 8.1 Hz, 2H, Ph), 4.72 (s, 2H, C(CH₂)), 2.06 (s, 3H, *p*-CH₃Ph), 1.09 (s, 12H, C(CH₃)₂). Characterized as a crude product. The analytical data are in agreement with the literature.^[22]

N-Benzyl-*N*-(4-ethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine (**3c**)



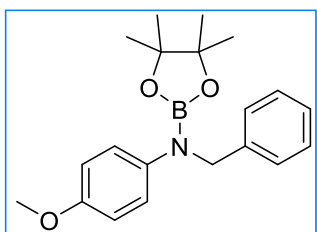
¹H NMR (400 MHz, toluene-*d*₈, δ, ppm): 7.37 – 7.27 (m, 2H, Ph), 7.22 (d, *J*_{H-H} = 7.2 Hz, 2H, Ph), 7.13 – 7.07 (m, 3H, Ph), 6.89 (d, *J*_{H-H} = 8.6 Hz, 2H, Ph), 4.72 (s, 2H, C(CH₂)), 2.39 (q, *J*_{H-H} = 7.6 Hz, 2H, CH₂(CH₃)), 1.10 (s, 12H, C(CH₃)₂), 1.05 (t, *J*_{H-H} = 7.6 Hz, 3H, CH₂(CH₃)). Characterized as a crude product.

N-(4-Methoxybenzyl)-4,4,5,5-tetramethyl-*N*-phenyl-1,3,2-dioxaborolan-2-amine (**3d**)



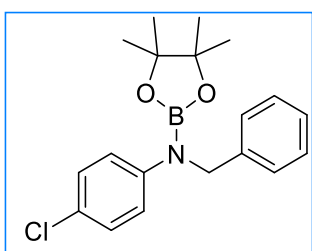
^1H NMR (300 MHz, toluene- d_8 , δ , ppm): 7.47 – 7.38 (m, 2H, Ph), 7.14 – 7.07 (m, 4H, Ph), 6.85 – 6.75 (m, 1H, Ph), 6.68 (d, $J_{H-H} = 8.7$ Hz, 2H, Ph), 4.69 (s, 2H, C(CH_2)), 3.28 (s, 3H, $p\text{-OCH}_3$ Ph), 1.10 (s, 12H, C(CH_3) $_2$). Characterized as a crude product. The analytical data are in agreement with the literature.^[43]

N-Benzyl-*N*-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine (**3e**)



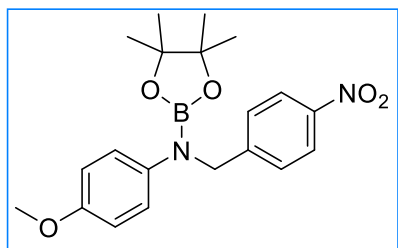
^1H NMR (400 MHz, toluene- d_8 , δ , ppm): 7.34 (m, 4H, Ph), 7.25 – 7.21 (m, 2H, Ph), 7.14 (d, $J_{H-H} = 7.3$ Hz, 1H, Ph), 6.73 (d, $J_{H-H} = 9.0$ Hz, 2H, Ph), 4.80 (s, 2H, C(CH_2)), 3.39 (s, 3H, $p\text{-OCH}_3$ Ph), 1.22 (s, 12H, C(CH_3) $_2$). Characterized as a crude product. The analytical data are in agreement with the literature.^[44]

N-Benzyl-*N*-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine (**3f**)



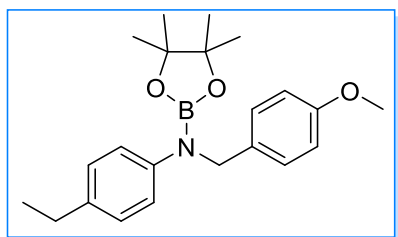
^1H NMR (400 MHz, toluene- d_8 , δ , ppm): 7.18 (d, $J_{H-H} = 8.9$ Hz, 2H, Ph), 7.15 – 7.06 (m, 4H, Ph), 7.02 – 6.95 (m, 3H, Ph), 4.60 (s, 2H, C(CH_2)), 1.06 (s, 12H, C(CH_3) $_2$). Characterized as a crude product. The analytical data are in agreement with the literature.^[22]

N-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-*N*-(4-nitrobenzyl)-1,3,2-dioxaborolan-2-amine (**3g**)



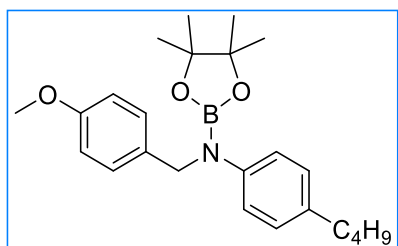
¹H NMR (400 MHz, toluene-*d*₈, δ , ppm): 7.76 (d, J_{H-H} = 8.7 Hz, 2H, Ph), 7.10 (d, J_{H-H} = 9.1 Hz, 2H, Ph), 6.94 (d, J_{H-H} = 8.8 Hz, 2H, Ph), 6.66 (d, J_{H-H} = 9.1 Hz, 2H, Ph), 4.50 (s, 2H, C(CH₂)), 3.30 (s, 3H, *p*-OCH₃Ph), 1.10 (s, 12H, C(CH₃)₂). **¹³C{¹H} NMR** (101 MHz, toluene-*d*₈, δ , ppm): 156.1 (Ph), 148.7 (Ph), 147.6 (Ph), 139.3 (Ph), 127.8 (Ph), 124.0 (Ph), 123.24 (Ph), 114.6 (Ph), 83.5 (C(CH₃)₂), 55.2 (*p*-OCH₃Ph), 52.0 (C(CH₂)), 25.0 (C(CH₃)₂). **¹¹B NMR** (128 MHz, toluene-*d*₈, δ , ppm): 25.08. The compound **3f** was characterized for the first time as a crude product.

N-(4-Ethylphenyl)-*N*-(4-methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine (**3h**)



¹H NMR (400 MHz, toluene-*d*₈, δ , ppm): 7.35 (d, J_{H-H} = 8.6 Hz, 2H, Ph), 7.14 (d, J_{H-H} = 8.6 Hz, 2H, Ph), 6.93 (d, J_{H-H} = 8.6 Hz, 2H, Ph), 6.69 (d, J_{H-H} = 8.6 Hz, 2H, Ph), 4.71 (s, 2H, C(CH₂)), 3.28 (s, 3H, *p*-OCH₃Ph), 2.40 (q, J_{H-H} = 7.6 Hz, 2H, CH₂(CH₃)), 1.12 (s, 12H, C(CH₃)₂), 1.07 (t, J_{H-H} = 7.6 Hz, 3H, CH₂(CH₃)). Characterized as a crude product.

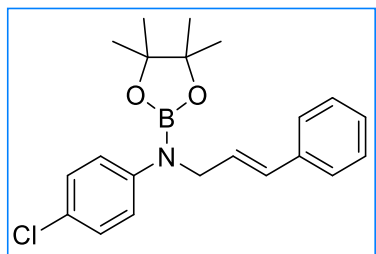
N-(4-Butylbenzyl)-*N*-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine (**3i**)



¹H NMR (400 MHz, toluene-*d*₈, δ , ppm): 7.36 (d, J_{H-H} = 8.6 Hz, 2H, Ph), 7.15 (d, J_{H-H} = 8.6 Hz, 2H, Ph), 6.94 (d, J_{H-H} = 8.5 Hz, 2H, Ph), 6.69 (d, J_{H-H} = 8.6 Hz, 2H, Ph), 4.71 (s, 2H, C(CH₂)), 3.29 (s, 3H, *p*-OCH₃Ph), 2.43 – 2.38 (m, 2H, CH₂(CH₂)), 1.48 – 1.40 (m, 2H, CH₂(CH₂)), 1.25 – 1.19 (m, 2H, CH₂(CH₂)), 1.12 (s, 12H, C(CH₃)₂), 0.83 (t, J_{H-H} = 7.3 Hz, 3H, CH₂(CH₃)). **¹³C{¹H} NMR** (101 MHz, toluene-*d*₈, δ , ppm): 159.3 (Ph), 144.8 (Ph), 136.2 (Ph), 133.4 (Ph), 131.1

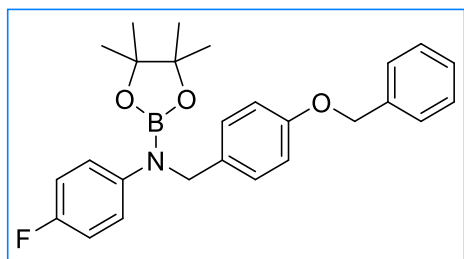
(Ph), 129.7 (Ph), 121.8 (Ph), 114.5 (Ph), 83.2 ($\underline{\text{C}}(\text{CH}_3)_2$), 54.9 ($p\text{-OCH}_3\text{Ph}$), 51.5 ($\text{C}(\underline{\text{C}}\text{H}_2)$), 35.7 ($\text{CH}_2(\underline{\text{C}}\text{H}_2)$), 34.5 ($\text{CH}_2(\underline{\text{C}}\text{H}_2)$), 25.0 ($\text{C}(\underline{\text{C}}\text{H}_3)_2$), 23.1 ($\underline{\text{C}}\text{H}_2(\text{CH}_3)$), 14.5 ($\text{CH}_2(\text{CH}_3)$). **^{11}B NMR** (128 MHz, toluene- d_8 , δ , ppm): 25.28. The compound **3g** was characterized for the first time as a crude product.

N-(4-Chlorophenyl)-*N*-cinnamyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine (**3k**)



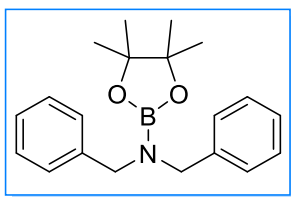
^1H NMR: (400 MHz, toluene- d_8 , δ , ppm): 7.26 (d, $J_{\text{H-H}} = 9.0$ Hz, 2H, Ph), 7.11 – 7.02 (m, 7H, Ph), 6.39 (d, $J_{\text{H-H}} = 16.0$ Hz, 1H, $\text{CH}(\underline{\text{C}}\text{H})$), 6.07 (dt, $J_{\text{H-H}} = 15.9, 5.0$ Hz, 1H, $\text{CH}(\underline{\text{C}}\text{H})$), 4.13 (d, $J_{\text{H-H}} = 5.1$ Hz, 2H, $\text{C}(\underline{\text{C}}\text{H}_2)$), 1.07 (s, 12H, $\text{C}(\underline{\text{C}}\text{H}_3)_2$). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, toluene- d_8 , δ , ppm) 145.4, 137.5, 130.5, 128.8, 128.7, 127.4, 126.6, 126.5, 121.7, 83.1 ($\underline{\text{C}}(\text{CH}_3)_2$), 49.5, 24.5 ($\text{C}(\underline{\text{C}}\text{H}_3)_2$). **^{11}B NMR** (128 MHz, toluene- d_8 , δ , ppm): 24.97. The compound **3i** was characterized for the first time as a crude product.

N-(4-(Benzyloxy)benzyl)-*N*-(4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine (**3l**)



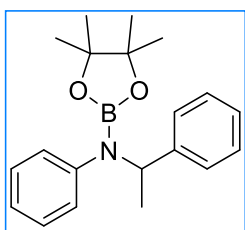
^1H NMR (400 MHz, toluene- d_8 , δ , ppm): 7.24 – 7.17 (m, 4H, Ph), 7.14 – 7.05 (m, 5H, Ph), 6.78 (d, $J_{\text{H-H}} = 8.7$ Hz, 2H, Ph), 6.75 – 6.68 (m, 2H, Ph), 4.62 (s, 2H, $\text{C}(\underline{\text{C}}\text{H}_2)$), 4.60 (s, 2H, $\text{C}(\underline{\text{C}}\text{H}_2)$), 1.10 (s, 12H, $\text{C}(\underline{\text{C}}\text{H}_3)_2$). **$^{13}\text{C}\{^1\text{H}\}$ NMR** (101 MHz, toluene- d_8 , δ , ppm): 158.7 (Ph), 138.2 (Ph), 133.2 (Ph), 129.0 (Ph), 182.4 (Ph), 182.2 (Ph), 127.9 (Ph), 123.3 (d, $J_{\text{C-F}} = 7.6$ Hz) (Ph), 115.5 (d, $J_{\text{C-F}} = 22.0$ Hz, Ph), 115.5 (Ph), 83.4 ($\underline{\text{C}}(\text{CH}_3)_2$), 70.3 ($\text{C}(\underline{\text{C}}\text{H}_2)$), 51.7 ($\text{C}(\underline{\text{C}}\text{H}_2)$), 24.9 ($\text{C}(\underline{\text{C}}\text{H}_3)_2$). **^{11}B NMR** (128 MHz, CDCl_3 , δ , ppm): 22.40. The compound **3j** characterized for the first time as a crude product.

N,N-Dibenzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine (**3m**)



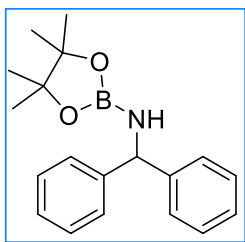
¹H NMR (300 MHz, toluene-*d*₈), δ , ppm): 7.23 – 7.08 (m, 10H, Ph), 4.06 (s, 4H, C(CH₂)), 1.17 (s, 12H, C(CH₃)₂). Characterized as a crude product. The analytical data are in agreement with the literature.^[45]

4,4,5,5-Tetramethyl-*N*-phenyl-*N*-(1-phenylethyl)-1,3,2-dioxaborolan-2-amine (**3n**)



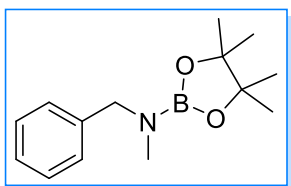
¹H NMR (300 MHz, CDCl₃, δ , ppm) 7.42 – 7.26 (m, 4H, Ph), 7.25 – 7.18 (m, 1H, Ph), 7.08 (m, 2H, 1H, Ph), 6.63 (m, 1H, Ph), 6.57 – 6.44 (m, 2H, Ph), 4.48 (q, $J_{H-H} = 6.6$ Hz, 1H, CH₂(CH₃)), 1.51 (d, $J_{H-H} = 6.7$ Hz, 3H, CH₂(CH₃)), 1.27 (s, 12H, C(CH₃)₂). Characterized as a crude product. The analytical data are in agreement with the literature.^[46]

N-Benzhydryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-amine (**3o**)



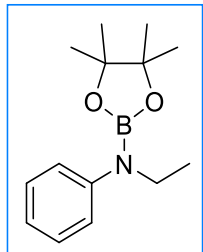
¹H NMR (300 MHz, CDCl₃, δ , ppm) 7.14 – 7.10 (m, 4H, Ph), 7.09 – 6.97 (m, 6H, Ph), 5.64 (d, $J_{H-H} = 11.0$ Hz, 1H, C(CH)), 2.87 (d, $J = 11.0$ Hz, 1H, NH), 1.08 (s, 12H, C(CH₃)₂). Characterized as a crude product. The analytical data are in agreement with the literature.^[47]

N-Benzyl-*N*,4,4,5,5-pentamethyl-1,3,2-dioxaborolan-2-amine (**3p**)



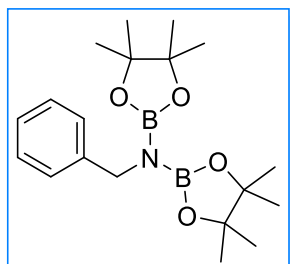
¹H NMR (300 MHz, C₆D₆, δ, ppm): 7.15 – 7.03 (m, 5H, Ph), 4.03 (s, 2H, C(CH₂)), 2.46 (s, 3H, N(CH₃)), 1.03 (s, 12H, C(CH₃)₂). Characterized as a crude product. The analytical data are in agreement with the literature.^[48]

N-Ethyl-4,4,5,5-tetramethyl-*N*-phenyl-1,3,2-dioxaborolan-2-amine (**3q**)



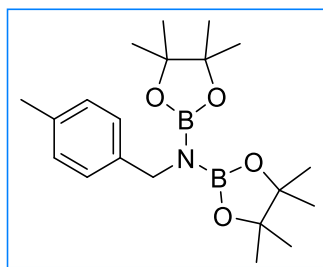
¹H NMR (400 MHz, C₆D₆, δ, ppm): 7.40 (dd, $J_{H-H} = 8.7, 1.0$ Hz, 2H, Ph), 7.19 (dd, $J_{H-H} = 8.7, 7.4$ Hz, 2H, Ph), 6.87 (tt, $J_{H-H} = 7.3, 1.2$ Hz, 1H, Ph), 3.58 (q, $J_{H-H} = 7.0$ Hz, 2H, CH₂(CH₃)), 1.09 (m, 15H, CH₂(CH₃) and C(CH₃)₂ overlap). Characterized as a crude product. The analytical data are in agreement with the literature.^[49]

N-Benzyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**6a**)



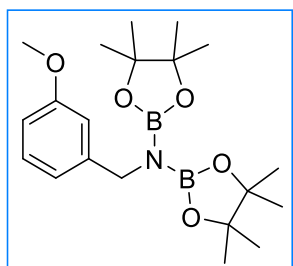
¹H NMR (300 MHz, C₆D₆, δ, ppm): 7.55 (d, $J_{H-H} = 7.1$ Hz, 2H, Ph), 7.24 (t, $J_{H-H} = 7.5$ Hz, 2H, Ph), 7.11 (t, $J_{H-H} = 7.4$ Hz, 2H, Ph), 4.57 (s, 2H, C(CH₂)), 1.02 (s, 24H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 359(M⁺, 31), 344(45), 343(20), 304(19), 303(100), 302(72), 300(29), 276(6), 275(33), 233(27). Characterized as a crude product. The analytical data are in agreement with the literature.^[22]

4,4,5,5-Tetramethyl-N-(4-methylbenzyl)-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (6b)



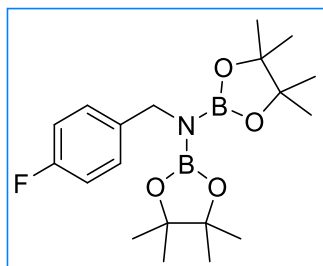
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.19 (d, *J*_{H-H} = 8.0 Hz, 2H, Ph), 7.04 (d, *J*_{H-H} = 7.8 Hz, 2H, Ph), 4.18 (s, 2H, C(CH₂)), 2.30 (s, 3H, *p*-CH₃Ph), 1.20 (s, 24H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 373(M⁺, 8), 358(29), 316(96), 315(49), 290(100), 289(54), 247(89), 246(27), 232(43), 105(52). Characterized as a crude product. The analytical data are in agreement with the literature.^[50]

N-(3-Methoxybenzyl)-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (6c)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.15 (t, *J*_{H-H} = 7.7 Hz, 1H, Ph), 6.91 – 6.87 (m, 2H, Ph), 6.73 – 6.69 (m, 1H, Ph), 4.20 (s, 2H, C(CH₂)), 3.78 (s, 3H, *m*-OCH₃Ph), 1.27 (s, 24H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 389(M⁺, 70), 388(38), 332(83), 331(100), 330(38), 306(40), 262(62), 248(56), 274(34), 55(25). Characterized as a crude product. The analytical data are in agreement with the literature.^[51]

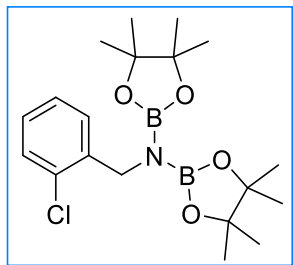
N-(4-Fluorobenzyl)-4,4,5,5-tetramethyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (6d)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.31 – 7.23 (m, 2H, Ph), 6.95 – 6.88 (m, 2H, Ph), 4.17 (s, 2H, C(CH₂)), 1.19 (s, 24H, C(CH₃)₂). **MS (EI) [m/z (%)]**: 377(M⁺, 17), 362(37), 320(100),

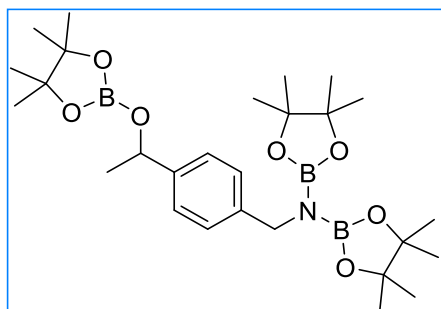
319(52), 294(86), 293(40), 281(11), 250(38), 237(24), 109(38). Characterized as a crude product. The analytical data are in agreement with the literature.^[50]

N-(2-Chlorobenzyl)-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**6e**)



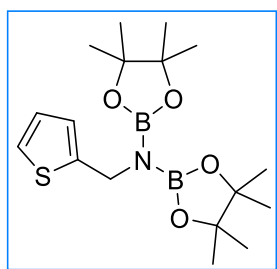
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.30 – 7.06 (m, 4H, Ph), 4.33 (s, 2H, C(CH₂)), 1.18 (s, 24H, C(CH₃)₂). MS (EI) [m/z (%): 394(M⁺, 21), 378(26), 359(19), 358(100), 357(44), 336(27), 317(21), 301(44), 300(26), 252(26). Characterized as a crude product. The analytical data are in agreement with the literature.^[52]

4,4,5,5-Tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(4-(1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)benzyl)-1,3,2-dioxaborolan-2-amine (**6f**)



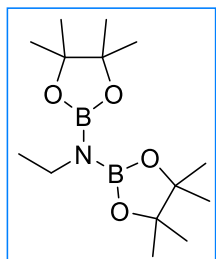
¹H NMR (400 MHz, Toluene-*d*₈, δ, ppm): 7.43 (d, *J* = 8.2 Hz, 2H, Ph), 7.30 (d, *J*_{H-H} = 8.1 Hz, 2H, Ph), 5.33 (q, *J*_{H-H} = 6.4 Hz, 1H, C(CH₂)), 4.43 (s, 2H, C(CH₂)), 1.43 (d, *J*_{H-H} = 6.5 Hz, 3H, CH(CH₃)), 1.02 (s, 12H, C(CH₃)₂), 1.00 (s, 24H, C(CH₃)₂). Characterized as a crude product. The analytical data are in agreement with the literature.^[53]

4,4,5,5-Tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-*N*-(thiophen-2-ylmethyl)-1,3,2-dioxaborolan-2-amine (**6g**)



^1H NMR (300 MHz, CDCl_3 , δ , ppm): 7.16 – 7.14 (m, 1H, thienyl), 7.08 – 7.05 (m, 1H, thienyl), 7.05 – 7.03 (m, 1H, thienyl), 4.19 (s, 2H, $\text{C}(\text{CH}_2)$), 1.26 (s, 24H, $\text{C}(\text{CH}_3)_2$). **MS (EI) [m/z (%)]**: 365(M^+ , 100), 364(45), 308(27), 307(38), 306(18), 298(23), 266(16), 224(23), 182(16), 97(22). Characterized as a crude product. The analytical data are in agreement with the literature.^[54-55]

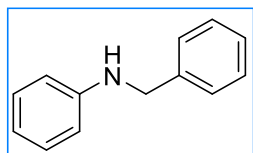
N-Ethyl-4,4,5,5-tetramethyl-*N*-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolan-2-amine (**6h**)



^1H NMR (300 MHz, CDCl_3 , δ , ppm): 3.02 (q, $J_{\text{H-H}} = 7.0$ Hz, 2H, $\text{CH}_3(\text{CH}_2)$), 1.19 (s, 24H, $\text{C}(\text{CH}_3)_2$), 0.99 (t, $J_{\text{H-H}} = 7.0$ Hz, 3H, $\text{CH}_2(\text{CH}_3)$). **MS (EI) [m/z (%)]**: 297(M^+ , 8), 283(14), 282(100), 281(47), 240(8), 112(47), 83(10), 69(8), 55(9), 41(11). Characterized as a crude product. The analytical data are in agreement with the literature.^[56]

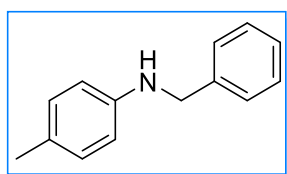
16.5. Characterization of synthesized amines

N-Benzylaniline (**4a**)



^1H NMR (300 MHz, CDCl_3 , δ , ppm): 7.42 – 7.27 (m, 5H, Ph), 7.24 – 7.17 (m, 2H, Ph), 6.76 (m, 1H, Ph), 6.72 – 6.61 (m, 2H, Ph), 4.36 (s, 2H, $\text{C}(\text{CH}_2)$). The hydrogen atom attached to N atom is not observed on ^1H NMR spectrum. **MS (EI) [m/z (%)]**: 183(M^+ , 100), 182(12), 181(3), 180(2), 106(3), 104(2), 92(2), 91(3), 90(2), 65(2). Colorless liquid. Isolation yield 85% (78.5 mg). The analytical data are in agreement with the literature.^[46, 57]

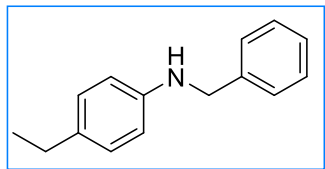
N-Benzyl-4-methylaniline (**4b**)



^1H NMR (400 MHz, CDCl_3 , δ , ppm): 7.41 – 7.27 (m, 5H, Ph), 7.02 (d, $J_{\text{H-H}} = 8.0$ Hz, 2H, Ph), 6.60 (d, $J_{\text{H-H}} = 8.3$ Hz, 2H, Ph), 4.34 (s, 2H, $\text{C}(\text{CH}_2)$), 4.16 (s, 1H, NH), 2.27 (s, 3H, $p\text{-CH}_3\text{Ph}$).

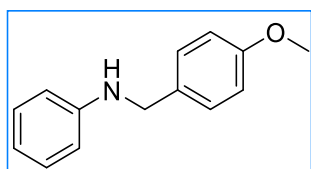
MS (EI) [m/z (%)]: 197(M^+ , 100), 196(28), 120(11), 92(16), 91(55), 90(9), 78(6), 77(9), 65(11), 51(7). Pale yellow oil. Isolation yield 89% (88.5 mg). The analytical data are in agreement with the literature.^[58-59]

N-Benzyl-4-ethylaniline (**4c**)



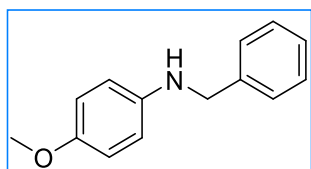
^1H NMR (300 MHz, CDCl_3 , δ , ppm): 7.39 – 7.19 (m, 5H, Ph), 7.00 (d, $J_{\text{H-H}} = 8.6$ Hz, 2H, Ph), 6.58 (d, $J_{\text{H-H}} = 8.5$ Hz, 2H, Ph), 4.29 (s, 2H, $\text{C}(\text{CH}_2)$), 3.97 (brs, 1H, NH), 2.53 (q, $J_{\text{H-H}} = 7.6$ Hz, 2H, $\text{CH}_2(\text{CH}_3)$), 1.18 (t, $J = 7.6$ Hz, 3H, $\text{CH}_2(\text{CH}_3)$). **MS (EI) [m/z (%)]**: 212(M^{+1} , 37), 211(M^+ , 100), 210(9), 197(5), 196(20), 195(10), 194(5), 192(3), 91(3), 90(2). Pale yellow liquid. Isolation yield 84% (84.5 mg). The analytical data are in agreement with the literature.^[60]

N-(4-Methoxybenzyl)aniline (**4d**)



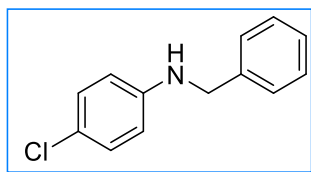
^1H NMR (300 MHz, CDCl_3 , δ , ppm): 7.31 (d, $J_{\text{H-H}} = 8.7$ Hz, 2H, Ph), 7.22 – 7.14 (m, 2H, Ph), 6.93 – 6.84 (m, 2H, Ph), 6.72 (t, $J_{\text{H-H}} = 7.3$ Hz, 1H, Ph), 6.65 (dd, $J_{\text{H-H}} = 8.6, 1.0$ Hz, 2H, Ph), 4.26 (s, 2H, $\text{C}(\text{CH}_2)$), 3.81 (s, 3H, $p\text{-OCH}_3\text{Ph}$). The hydrogen atom attached to N atom is not observed on ^1H NMR spectrum. **MS (EI) [m/z (%)]**: 213(M^+ , 60), 122(12), 121(100), 119(7), 91(9), 92(7), 77(25), 65(9), 51(15), 50(6). Pale yellow liquid. Isolation yield 87% (92.4 mg). The analytical data are in agreement with the literature.^[46, 61]

N-Benzyl-4-methoxyaniline (**4e**)



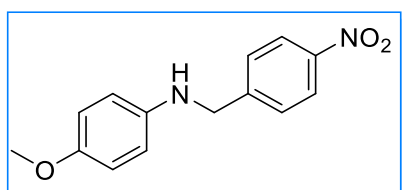
^1H NMR (300 MHz, CDCl_3 , δ , ppm): 7.40 – 7.27 (m, 5H, Ph), 6.81 – 6.75 (m, 2H, Ph), 6.65 (d, $J_{\text{H-H}} = 8.9$ Hz, 2H, Ph), 4.29 (s, 2H, $\text{C}(\text{CH}_2)$), 3.74 (s, 3H, $p\text{-OCH}_3\text{Ph}$). The hydrogen atom attached to N atom is not observed on ^1H NMR spectrum. **MS (EI) [m/z (%)]**: 213(M^+ , 100), 212(8), 122(63), 95(12), 91(61), 77(8+), 65(20), 63(8), 52(8), 51(8). Pale yellow solid. Isolation yield 88% (93.3 mg). The analytical data are in agreement with the literature.^[58, 62]

N-Benzyl-4-chloroaniline (**4f**)



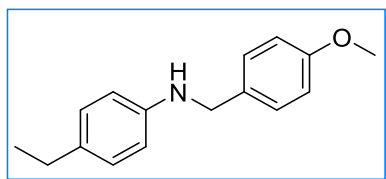
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.38 – 7.20 (m, 5H, Ph), 7.12 – 7.02 (m, 2H, Ph), 6.55 – 6.45 (m, 2H, Ph), 4.25 (s, 2H, C(CH₂)), 4.03 (br, 1H, NH). **MS (EI) [m/z (%)]**: 219(M+1)⁺, 37), 218(M⁺, 21), 217(100), 92(23), 91(71), 90(17), 89(6), 65(10), 63(7), 51(6). White solid. Isolation yield 87% (95.0 mg). The analytical data are in agreement with the literature.^[57]

4-Methoxy-*N*-(4-nitrobenzyl)aniline (**4g**)



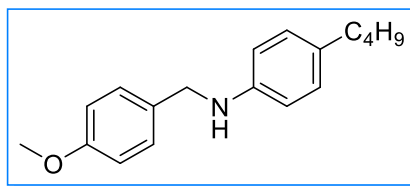
¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.18 (d, *J*_{H-H} = 8.8 Hz, 2H, Ph), 7.54 (d, *J*_{H-H} = 8.8 Hz, 2H, Ph), 6.77 (d, *J*_{H-H} = 9.0 Hz, 2H, Ph), 6.59 (d, *J*_{H-H} = 8.9 Hz, 2H, Ph), 4.43 (s, 2H, C(CH₂)), 3.74 (s, 3H, *p*-OCH₃Ph). The hydrogen atom attached to N atom is not observed on ¹H NMR spectrum. **MS (EI) [m/z (%)]**: 258(M⁺, 100), 124(4), 123(10), 122(25), 121(8), 120(3), 95(3), 90(4), 89(6), 63(3). Orange solid. Isolation yield 79% (113.5 mg). The analytical data are in agreement with the literature.^[63]

4-Ethyl-*N*-(4-methoxybenzyl)aniline (**4h**)



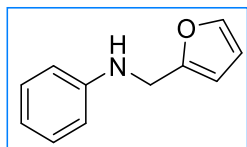
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.25 (d, *J*_{H-H} = 8.7 Hz, 2H, Ph), 6.99 (d, *J*_{H-H} = 8.5 Hz, 2H, Ph), 6.84 (d, *J*_{H-H} = 8.7 Hz, 2H, Ph), 6.55 (d, *J*_{H-H} = 8.4 Hz, 2H, Ph), 4.19 (s, 2H, C(CH₂)), 3.75 (s, 3H, *p*-OCH₃Ph), 2.52 (q, *J*_{H-H} = 7.6 Hz, 2H, CH₂(CH₃)), 1.17 (t, *J*_{H-H} = 7.6 Hz, 3H, CH₂(CH₃)). **MS (EI) [m/z (%)]**: 242(M⁺, 17), 241(M⁺, 100), 240(13), 239(3), 123(3), 122(9), 121(60), 120(8), 119(3), 91(2). Pale yellow liquid. Isolation yield 61% (73.7 mg). The analytical data are in agreement with the literature.^[60]

N-(4-Butylbenzyl)-4-methoxyaniline (**4i**)



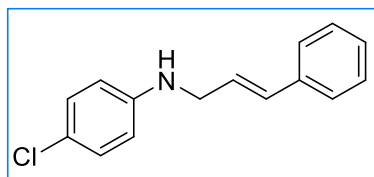
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.35 – 7.27 (m, 2H, Ph), 7.02 – 6.96 (m, 2H, Ph), 6.91 – 6.82 (m, 2H, Ph), 6.64 – 6.54 (m, 2H, Ph), 4.23 (s, 2H, C(CH₂)), 3.81 (s, 3H, *p*-OCH₃Ph), 2.56 – 2.45 (m, 2H, CH₂(CH₂)), 1.60 – 1.50 (m, 2H, CH₂(CH₂)), 1.39 – 1.30 (m, 2H, CH₂(CH₂)), 0.91 (t, *J*_{H-H} = 7.3 Hz, 3H, CH₂(CH₃)). The hydrogen atom attached to N atom is not observed on ¹H NMR spectrum. **¹³C{¹H} NMR** (75 MHz, CDCl₃, δ, ppm) 159.0 (Ph), 146.2 (Ph), 132.2 (Ph), 131.7 (Ph), 129.3 (Ph), 129.0 (Ph), 114.1 (Ph), 113.1 (Ph), 55.4 (*p*-OCH₃Ph), 48.3 (CH₂(CH₂)), 34.9 (C(CH₂)), 34.1 (CH₂(CH₂)), 22.5 (CH₂(CH₂)), 14.1 (CH₂(CH₃)). **MS (EI) [m/z (%)]**: 269(M⁺, 100), 268(11), 267(4), 123(5), 122(8), 121(12), 120(9), 119(7), 118(5), 117(4). **Elem. Anal.** calcd (%) for C₁₈H₂₃NO: C, 80.26; H, 8.61; found C, 82.25; H, 8.65. Yellow oil. Isolation yield 63% (85.2 mg). The compound **4g** was characterized for the first time.^[64]

N-(Furan-2-ylmethyl)aniline (**4j**)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.38 (dd, *J*_{H-H} = 1.8, 0.9 Hz, 1H, furyl), 7.24 – 7.17 (m, 2H, Ph), 6.79 – 6.67 (m, 3H, Ph), 6.33 (dd, *J*_{H-H} = 3.2, 1.9 Hz, 1H, furyl), 6.26 – 6.24 (m, 1H, furyl), 4.33 (s, 2H, C(CH₂)), 4.12 (bs, 1H, NH). **MS (EI) [m/z (%)]**: 173(M⁺, 54), 172(56), 171(5), 144(4), 83(7), 82(14), 81(100), 80(10), 53(12), 51(5). Yellow liquid. Isolation yield 90% (77.6 mg). The analytical data are in agreement with the literature.^[61, 65]

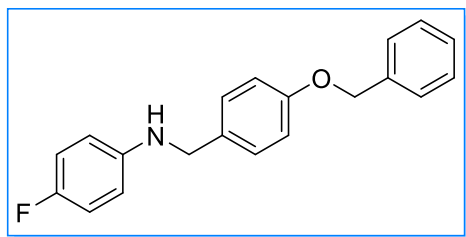
4-Chloro-*N*-cinnamylaniline (**4k**)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.38 – 7.20 (m, 5H, Ph), 7.17 – 7.10 (m, 2H, Ph), 6.67 – 6.57 (m, 3H, Ph and CH(CH), overlap), 6.30 (dt, *J*_{H-H} = 15.9, 5.8 Hz, 1H, CH(CH)), 3.92 (dd, *J*_{H-H} = 5.8 Hz, 1.2 Hz, 2H, C(CH₂)). The hydrogen atom attached to N atom is not observed on ¹H NMR spectrum. **MS (EI) [m/z (%)]**: 245(M+1)⁺, 32), 244(M⁺, 21), 243(100), 242(10),

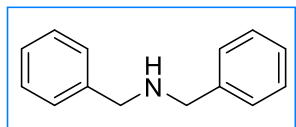
118(14), 117(51), 115(17), 114(6), 91(5), 63(3). White solid. Isolation yield 84% (102.8 mg). The analytical data are in agreement with the literature.^[66-67]

N-(4-(Benzyloxy)benzyl)-4-fluoroaniline (**4l**)



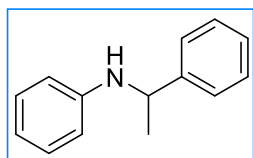
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.47 – 7.26 (m, 7H, Ph), 6.96 – 6.85 (m, 4H, Ph), 6.68 – 6.64 (m, 2H, Ph), 5.05 (s, 2H, C(CH₂)), 4.22 (s, 2H, C(CH₂)). The hydrogen atom attached to N atom is not observed on ¹H NMR spectrum. **MS (EI) [m/z (%)]**: 307(M⁺,100), 306(12), 198(13), 197(28), 196(13), 193(6), 192(5), 191(5), 190(4), 95(7). White solid. Isolation yield 88% (135.6 mg). The analytical data are in agreement with the literature.^[68]

Dibenzylamine (**4m**)



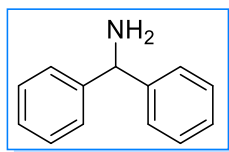
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.39 – 7.27 (m, 10H, Ph), 3.82 (s, 4H, C(CH₂)), 1.97 (s, 1H, NH). **MS (EI) [m/z (%)]**: 197(M⁺, 100), 196(11), 120(3), 107(4), 106(29), 93(3), 92(8), 91(13), 90(4), 65(3). Pale yellow solid. Isolation yield 40% (39.8 mg). The analytical data are in agreement with the literature.^[69]

N-(1-Phenylethyl)aniline (**4n**)



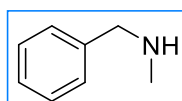
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.41 – 7.29 (m, 4H, Ph), 7.25 – 7.19 (m, 1H, Ph), 7.14 – 7.07 (m, 2H, Ph), 6.66 (tt, *J*_{H-H} = 7.3, 1.1 Hz, 1H, Ph), 6.53 (m, 2H, Ph), 4.50 (q, *J*_{H-H} = 6.7 Hz, 1H, CH(CH₃)), 4.22 (bs, 1H, NH) 1.53 (d, *J*_{H-H} = 6.7 Hz, 3H, CH(CH₃)). **MS (EI) [m/z (%)]**: 197(M⁺, 100), 196(8), 183(12), 182(52), 106(10), 105(26), 104(14), 103(10), 95(5), 94(9). Isolation yield 64% (63.2 mg). Colorless liquid. The analytical data are in agreement with the literature.^[59, 70]

Diphenylmethanamine (4o)



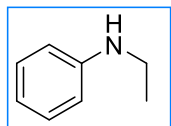
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.39 – 7.33 (m, 4H, Ph), 7.32 – 7.27 (m, 4H, Ph), 7.23 – 7.17 (m, 2H, Ph), 5.19 (s, 1H, C(CH₂)), 1.89 (s, 2H, NH₂). **MS (EI) [m/z (%)]**: 183(M⁺, 40), 182(32), 181(8), 168(9), 106(8), 105(100), 77(38), 76(4), 51(25), 50(10). Isolation yield 83% (75.5 mg). Pale yellow solid. The analytical data are in agreement with the literature.^[71-72]

N-Methyl-1-phenylmethanamine (4p)



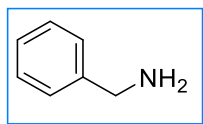
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.36 – 7.22 (m, 5H, Ph), 3.75 (s, 2H, C(CH₂)), 2.45 (s, 3H, N(CH₃)), 1.85 (s, 1H, NH). **MS (EI) [m/z (%)]**: 121(M⁺, 20), 120(100), 92(7), 91(23), 90(9), 65(8), 51(10), 50(6), 44(26), 42(27). Colorless liquid. Isolation yield 72% (43.7 mg). The analytical data are in agreement with the literature.^[69]

N-Ethylaniline (4q)



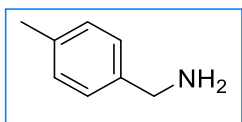
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.24 – 7.12 (m, 2H, Ph), 6.73 – 6.68 (m, 1H, Ph), 6.66 – 6.55 (m, 2H, Ph), 3.54 (brs, 1H, NH), 3.17 (q, *J*_{H-H} = 7.1 Hz, 2H, CH₂CH₃), 1.27 (t, *J*_{H-H} = 7.1 Hz, 3H, CH₂CH₃). **MS (EI) [m/z (%)]**: 121(M⁺, 50), 120(7), 107 (7), 106(100), 79(17), 78(5), 77(17), 65(6), 51(11), 43(14). Colorless liquid. Isolation yield 70% (42.1 mg). The analytical data are in agreement with the literature.^[73]

Phenylmethanamine (7a)



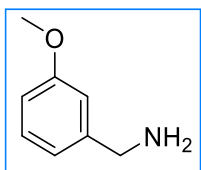
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.37 – 7.04 (m, 5H, Ph), 3.78 (s, 2H, C(CH₂)), 1.37 (s, 2H, NH). **MS (EI) [m/z (%)]**: 107(M⁺, 26), 106(100), 92(3), 91(12), 90(4), 79(6), 78(3), 77(4), 51(4), 50(3). Colorless liquid. Isolation yield 83% (89.4 mg). The analytical data are in agreement with the literature.^[74-75]

p-Tolylmethanamine (**7b**)



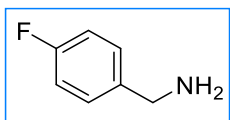
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.22 – 7.14 (m, 4H, Ph), 3.84 (s, 2H, C(CH₂)), 2.34 (s, 3H, *p*-CH₃Ph), 1.26 (s, 2H). **MS (EI) [m/z (%)]**: 121 (M⁺, 15), 120 (55), 106(46), 104(100), 93(52), 91(63), 79(33), 77(45), 65(20), 51(22). Pale yellow liquid. Isolation yield 80% (48.2 mg). The analytical data are in agreement with the literature.^[76]

(3-Methoxyphenyl)methanamine (**7c**)



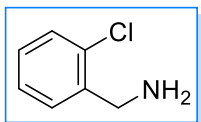
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.24 (t, *J*_{H-H} = 7.8 Hz, 1H, Ph), 6.92 – 6.85 (m, 2H, Ph), 6.78 (dd, *J*_{H-H} = 7.9, 2.4 Hz, 1H, Ph), 3.84 (s, 2H, NH₂), 3.80 (s, 3H, *m*-OCH₃Ph). **MS (EI) [m/z (%)]**: 137(M⁺, 30), 136(100), 112(22), 119(22), 109(42), 106(51), 94(35), 77(36), 79(21), 65(20). Pale yellow liquid. Isolation yield 78% (53.5 mg). The analytical data are in agreement with the literature.^[76]

(4-Fluorophenyl)methanamine (**7d**)



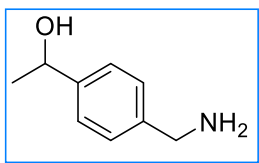
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.35 – 7.20 (m, 2H, Ph), 7.06 – 6.97 (m, 2H, Ph), 3.84 (s, 2H, C(CH₂)), 1.68 (s, 2H, NH₂). **MS (EI) [m/z (%)]**: 125(M⁺, 23), 124(100), 110(5), 109(36), 180(5), 107(7), 106(16), 105(28), 104(13), 97(4). Colorless liquid. Isolation yield 81% (50.8 mg). The analytical data are in agreement with the literature.^[77-78]

(2-Chlorophenyl)methanamine (**7e**)



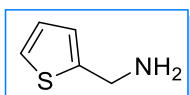
¹H NMR (300 MHz, DMSO-*d*₆, δ, ppm): 7.40 (d, *J*_{H-H} = 7.6 Hz, 1H, Ph), 7.27 – 7.08 (m, 3H, Ph), 3.64 (s, 2H, C(CH₂)). **MS (EI) [m/z (%)]**: 143(M+1)⁺, 6), 142(M⁺, 6), 140(63), 125(9), 113(5), 107(9), 106(100), 104(4), 77(4), 51(5). White solid. Isolation yield 61% (43.4 mg). The analytical data are in agreement with the literature.^[76]

1-(4-(Aminomethyl)phenyl)ethan-1-ol (**7f**)



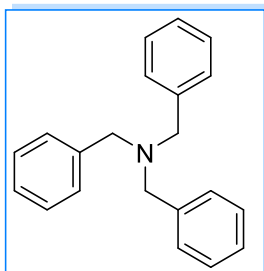
¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.35 (d, J_{H-H} = 8.2 Hz, 2H, Ph), 7.28 (d, J_{H-H} = 8.1 Hz, 2H, Ph), 4.89 (q, J_{H-H} = 6.5 Hz, 1H, (CH(CH₃))), 3.84 (s, 2H, C(CH₂)), 1.78 (s, 3H, NH₂ and OH, overlapped), 1.49 (d, J_{H-H} = 6.4 Hz, 3H, (CH(CH₃))). **MS (EI) [m/z (%)]**: 151(M⁺, 3), 150(13), 132(17), 119(21), 106(100), 105(17), 91(34), 79(29), 77(26), 51(13), 43(14). White solid. Isolation yield 39% (29.4 mg). The analytical data are in agreement with the literature.^[79]

Thiophen-2-ylmethanamine (**7g**)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.29 (dd, J_{H-H} = 4.9, 3.0 Hz, 1H, thienyl), 7.12 – 7.11(m, 1H, thienyl), 7.04 (dd, J_{H-H} = 4.9, 1.2 Hz, 1H, thienyl), 3.89 (s, 2H, C(CH₂)), 1.74 (s, 2H, NH₂). **MS (EI) [m/z (%)]**: 113(M⁺, 60), 112(100), 97(34), 85(71), 80(9), 69(7), 58(10), 57(5), 53(12), 45(46). Yellow liquid. Isolation yield 60% (33.9 mg). The analytical data are in agreement with the literature.^[74]

Tribenzylamine (**9a**)



¹H NMR (300 MHz, CDCl₃, δ, ppm): 7.41 (d, J_{H-H} = 7.2 Hz, 6H, Ph), 7.31 (t, J_{H-H} = 7.4 Hz, 6H, Ph), 7.22 (t, J_{H-H} = 7.2 Hz, 3H, Ph), 3.55 (s, 6H, C(CH₂)). **MS (EI) [m/z (%)]**: 287(M⁺, 61), 286(26), 211(13), 210(79), 208(9), 197(10), 196(47), 92(10), 91(100), 65(24). White solid. Isolation yield 51% (73.1 mg). The analytical data are in agreement with the literature.^[80-81]

17. NMR spectra of products

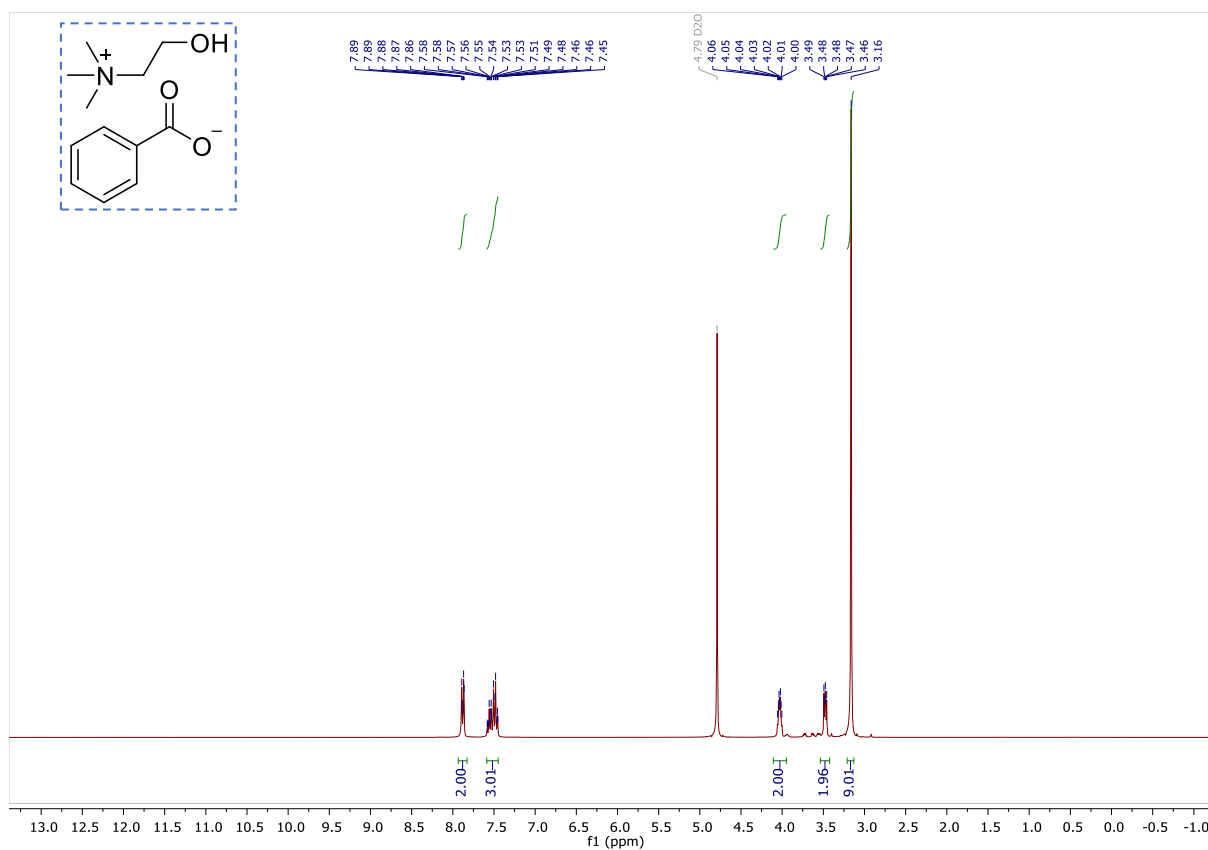


Figure S15 – ¹H NMR spectrum of IL2 [Cho][Bz].

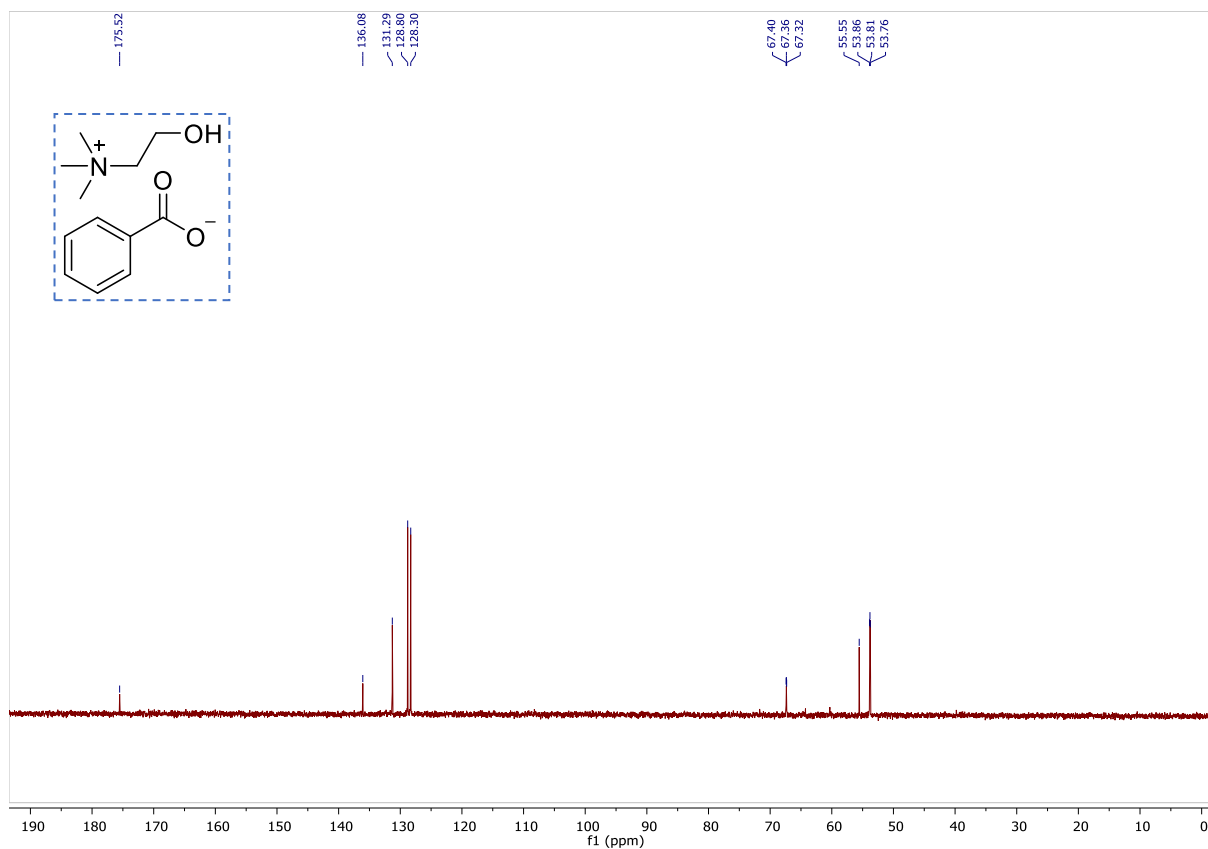


Figure S16 – ¹³C{¹H} NMR spectrum of IL2 [Cho][Bz].

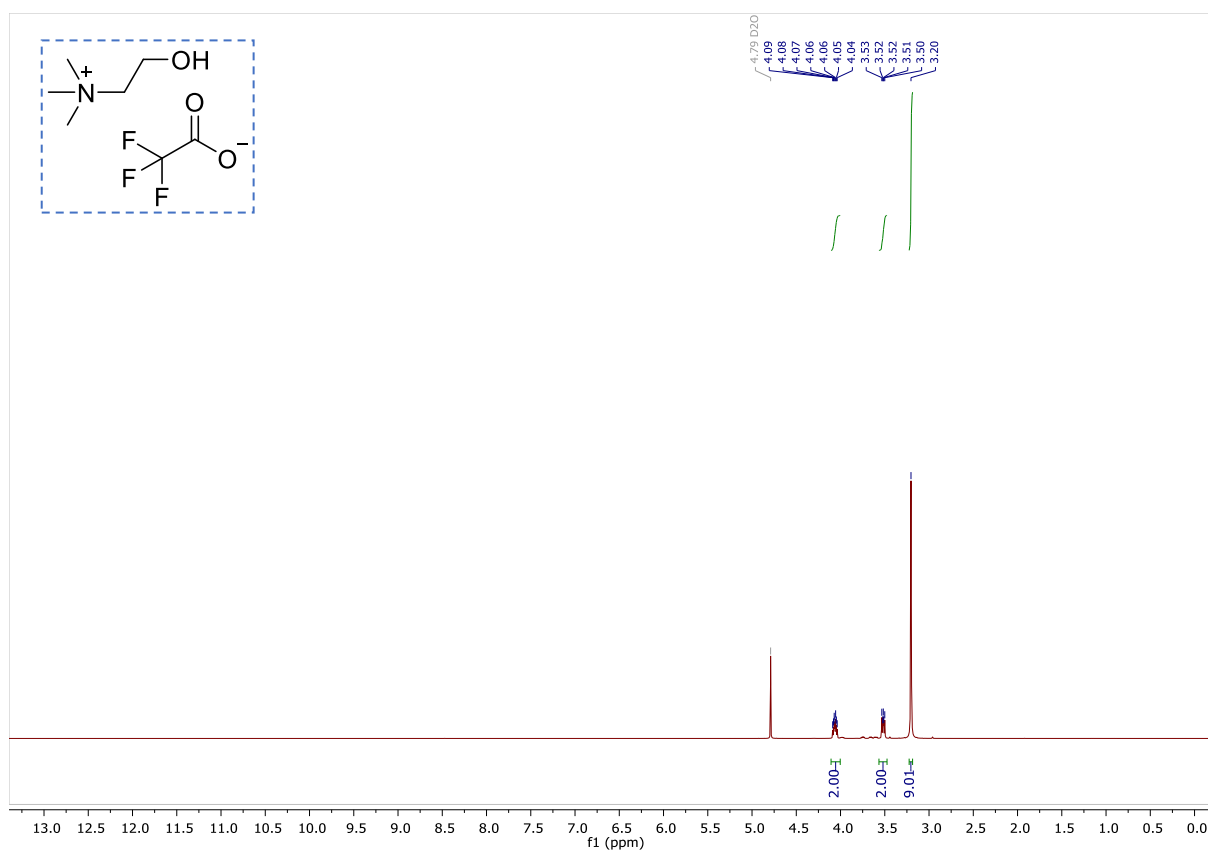


Figure S17 – ¹H NMR spectrum of IL3 [Cho][TFA].

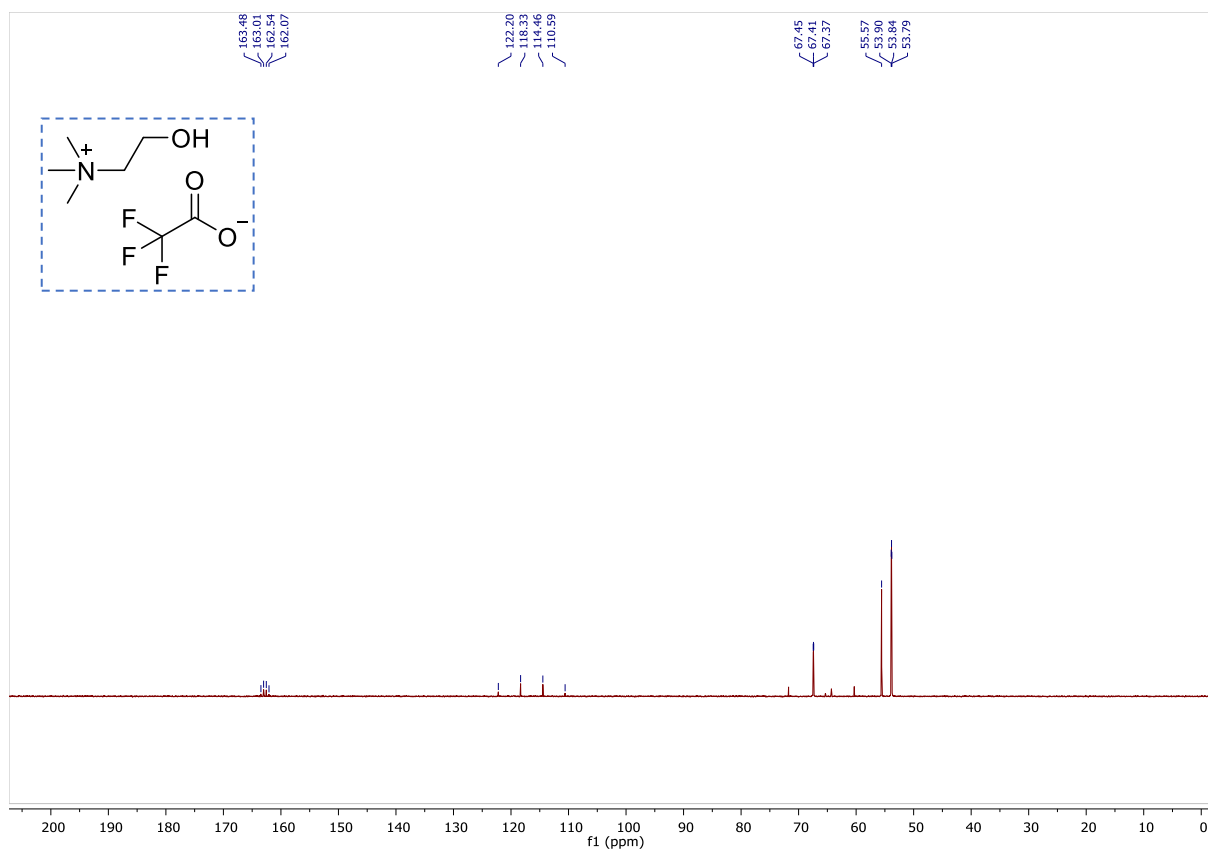


Figure S18 – ¹³C{¹H} NMR spectrum of IL3 [Cho][TFA].

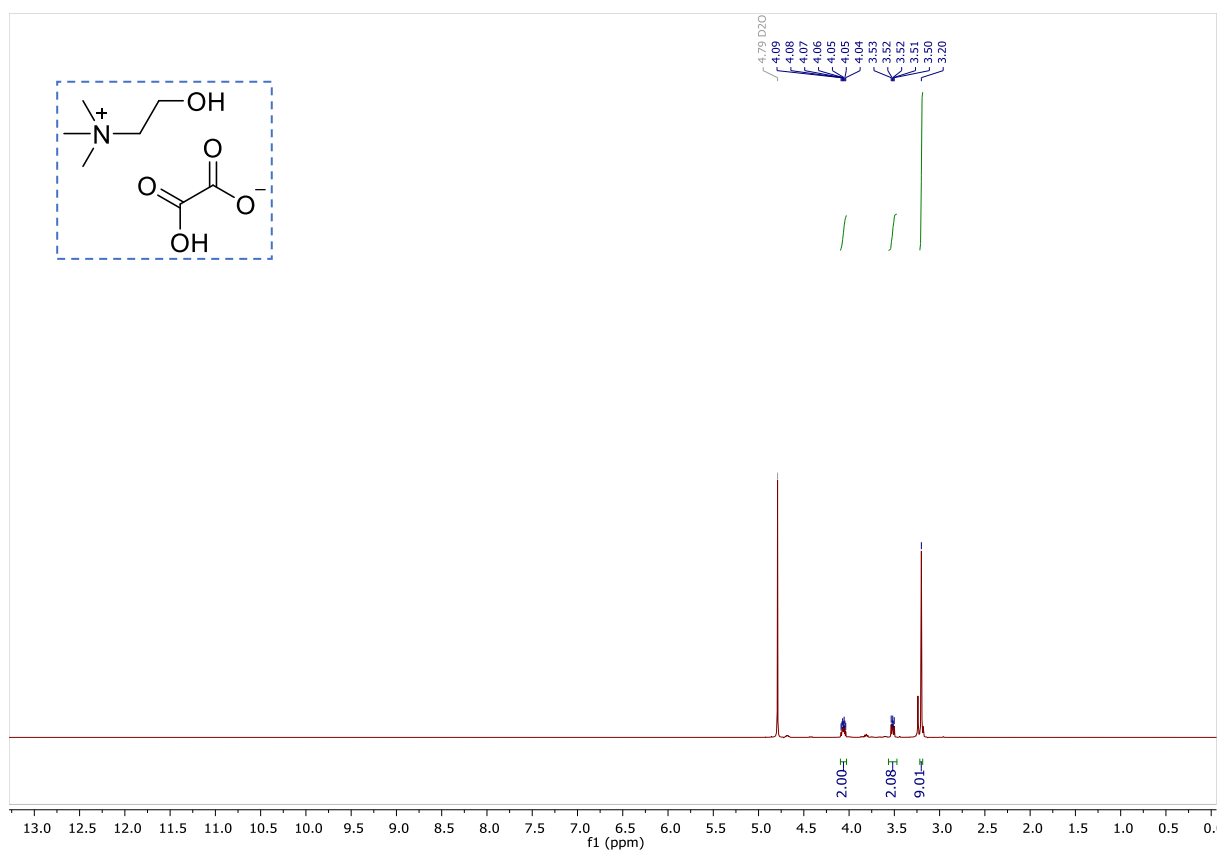


Figure S19 – ^1H NMR spectrum of IL4 [Cho][Oxa].

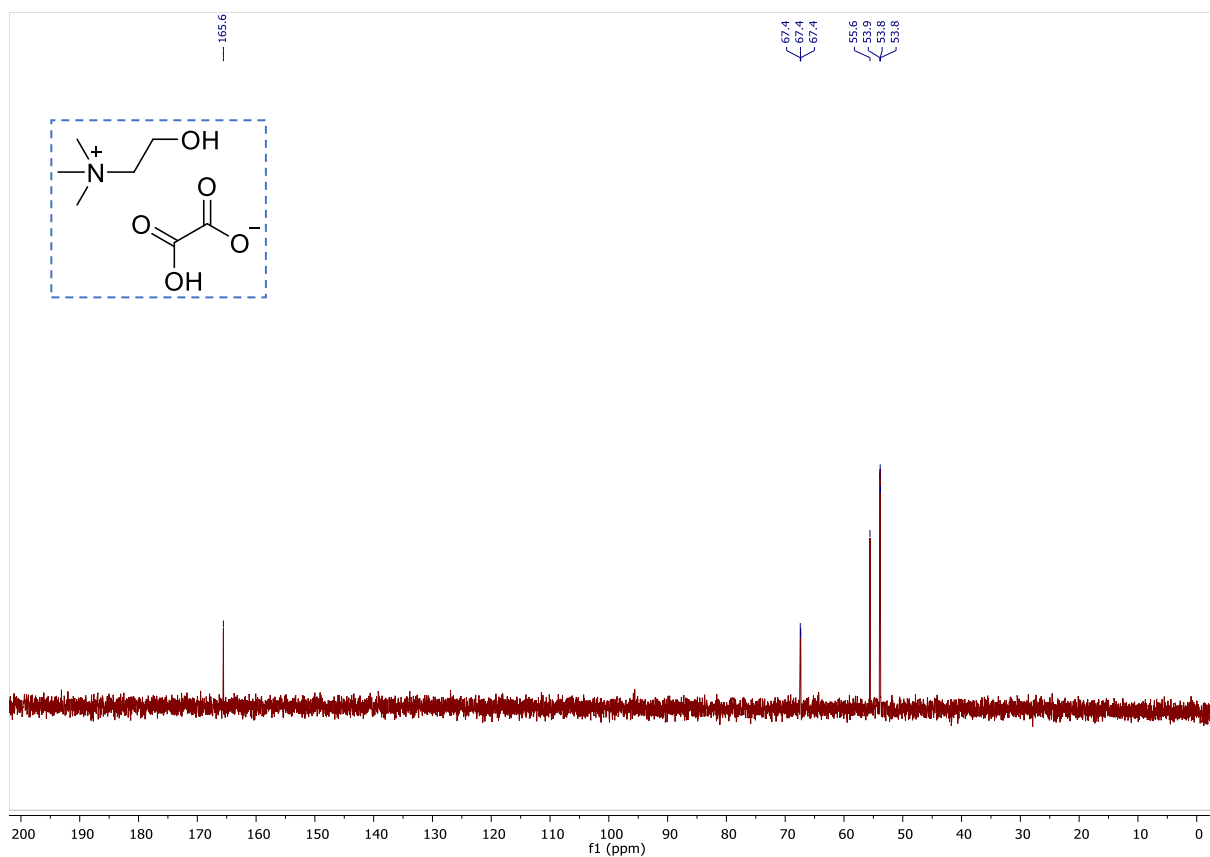


Figure S20 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of IL4 [Cho][Oxa].

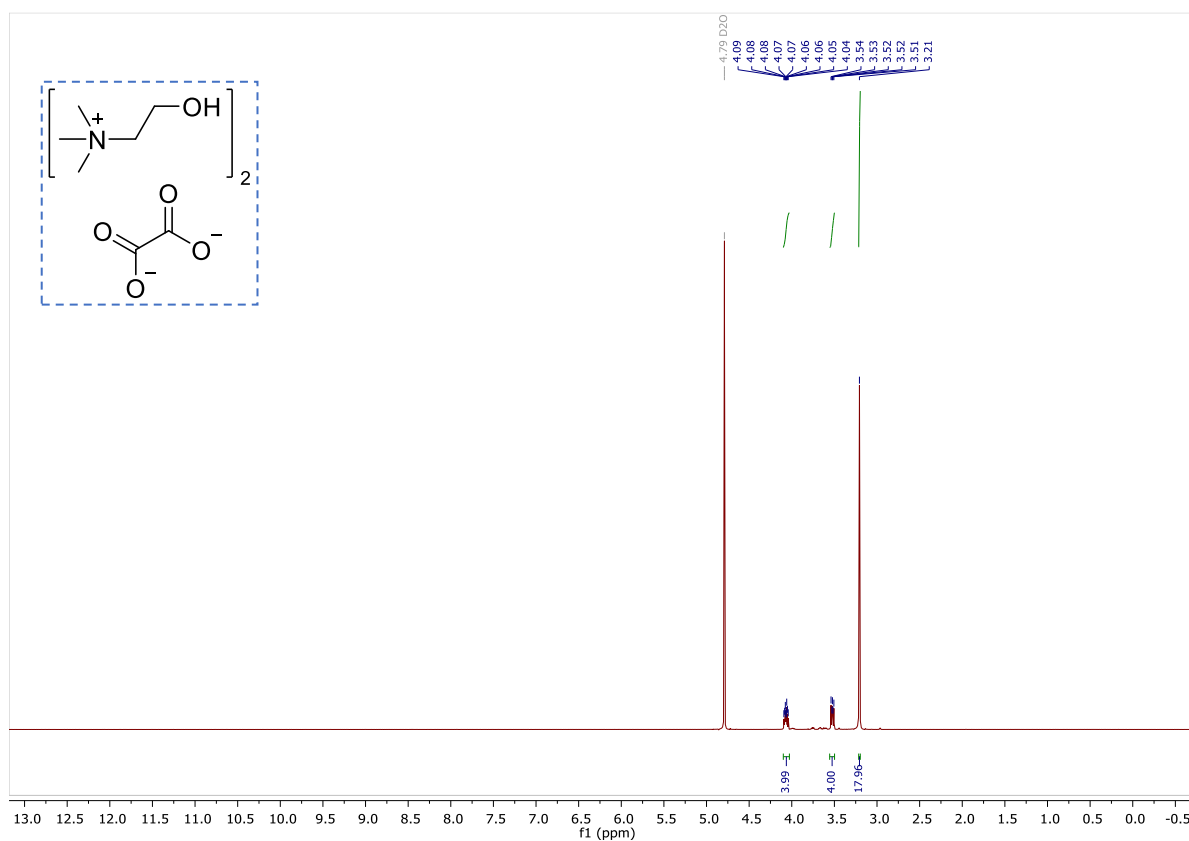


Figure S21 – ¹H NMR spectrum of IL5 [Cho]₂[Oxa].

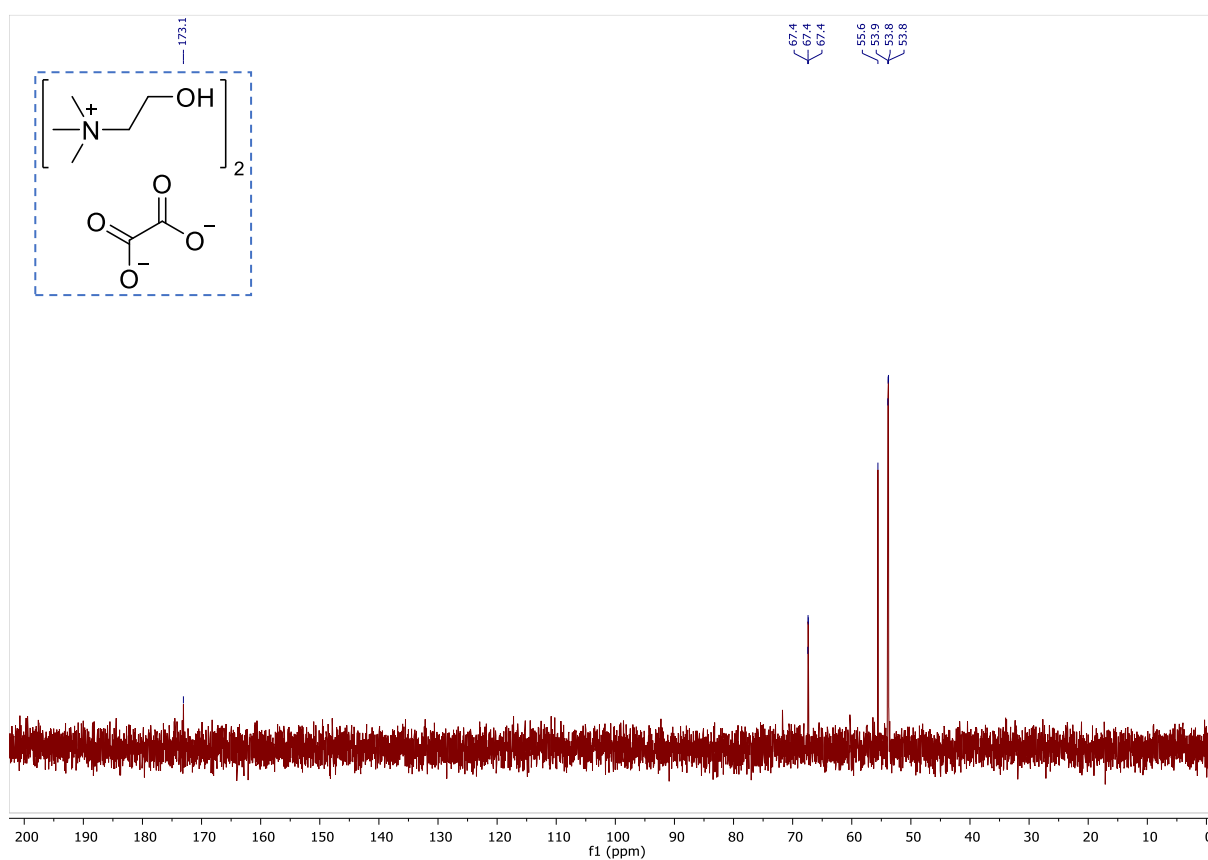


Figure S22 – ¹³C{¹H} NMR spectrum of IL5 [Cho]₂[Oxa].

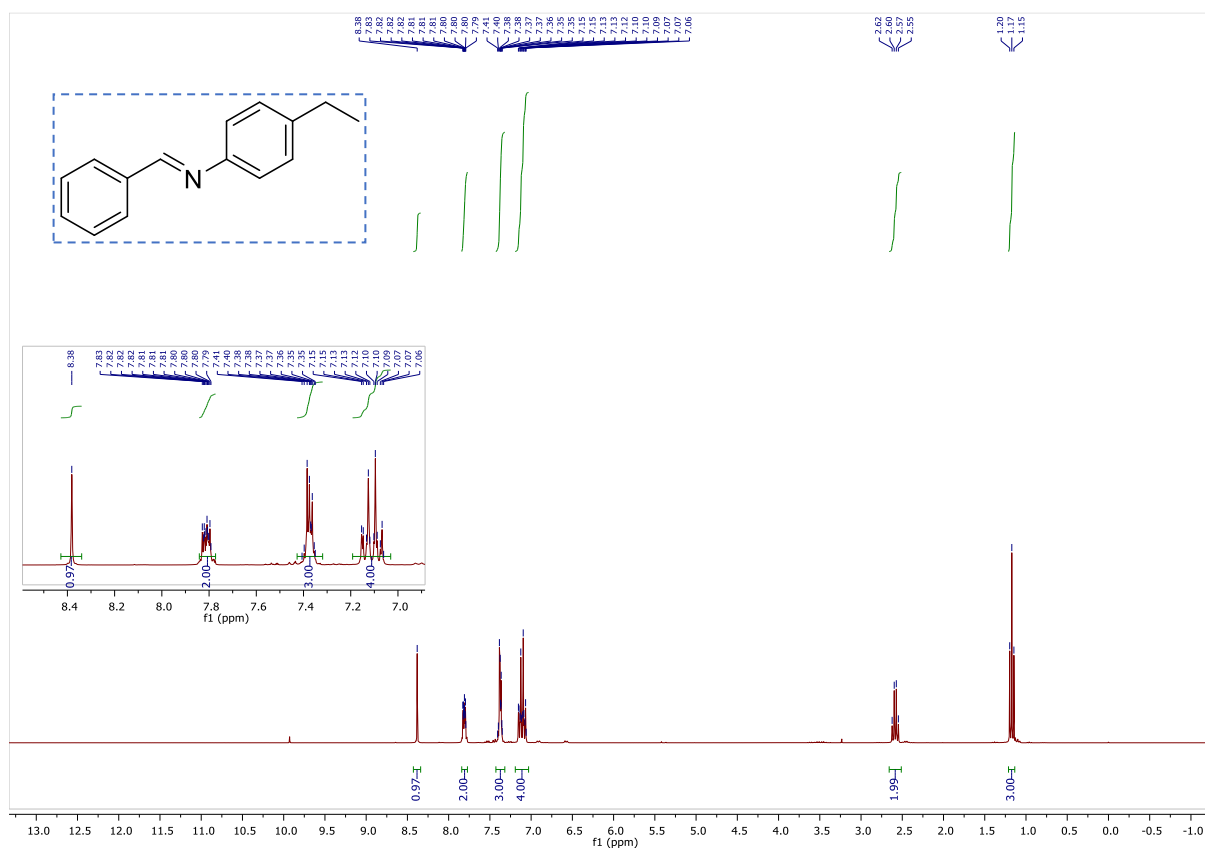


Figure S23 – ^1H NMR spectrum of **1c**.

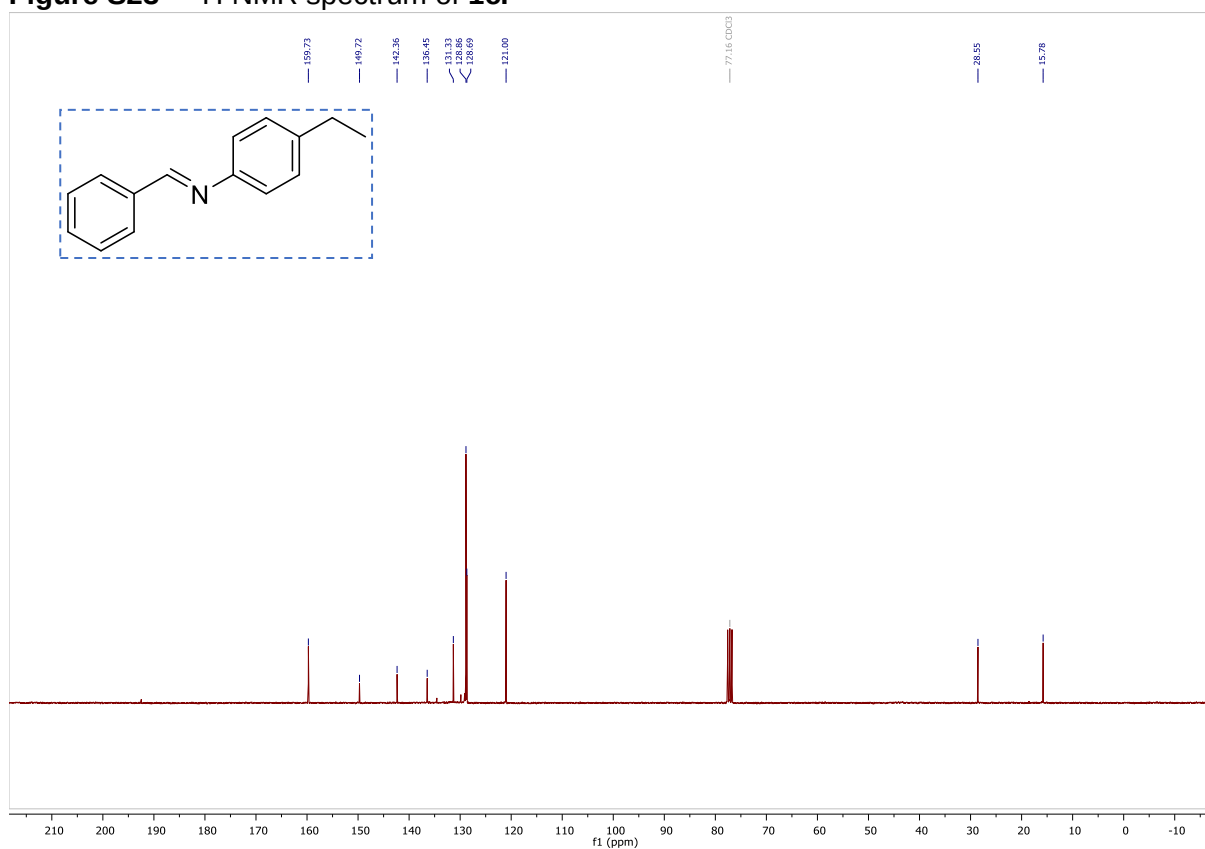


Figure S24 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1c**.

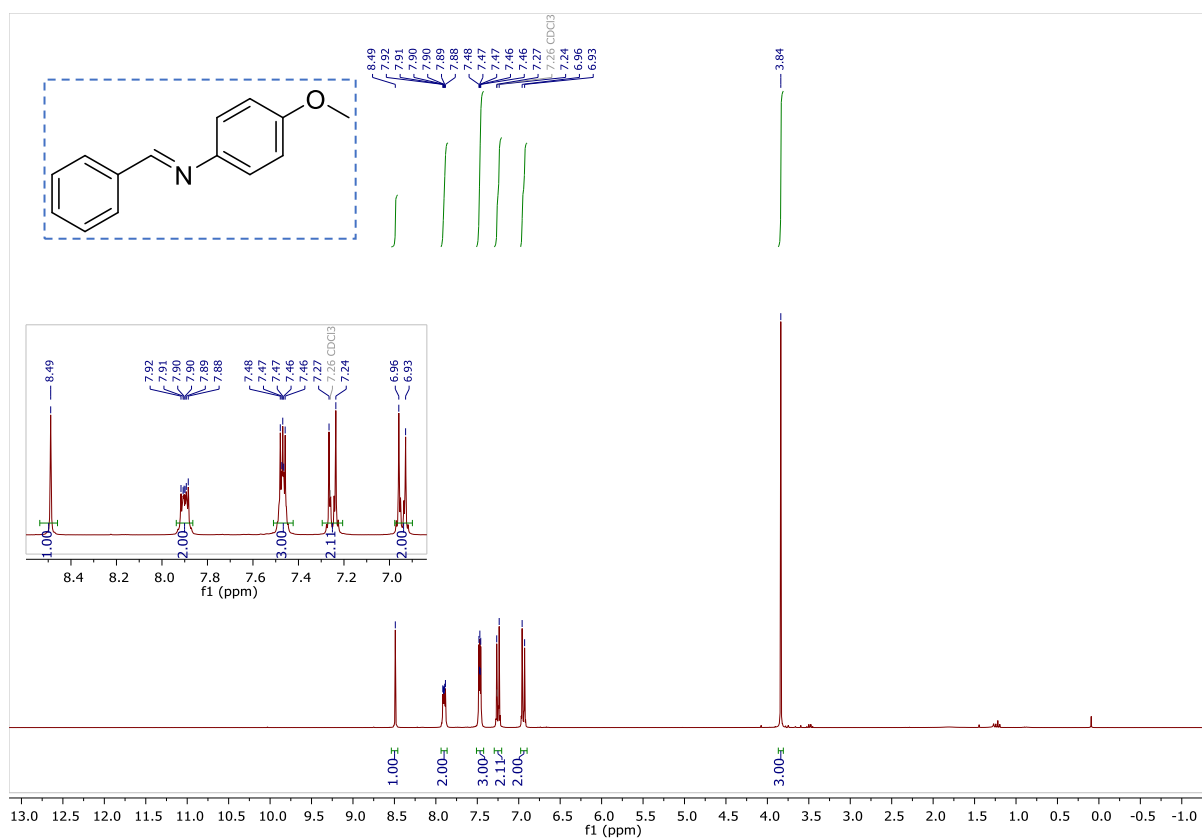


Figure S25 – ¹H NMR spectrum of 1e.

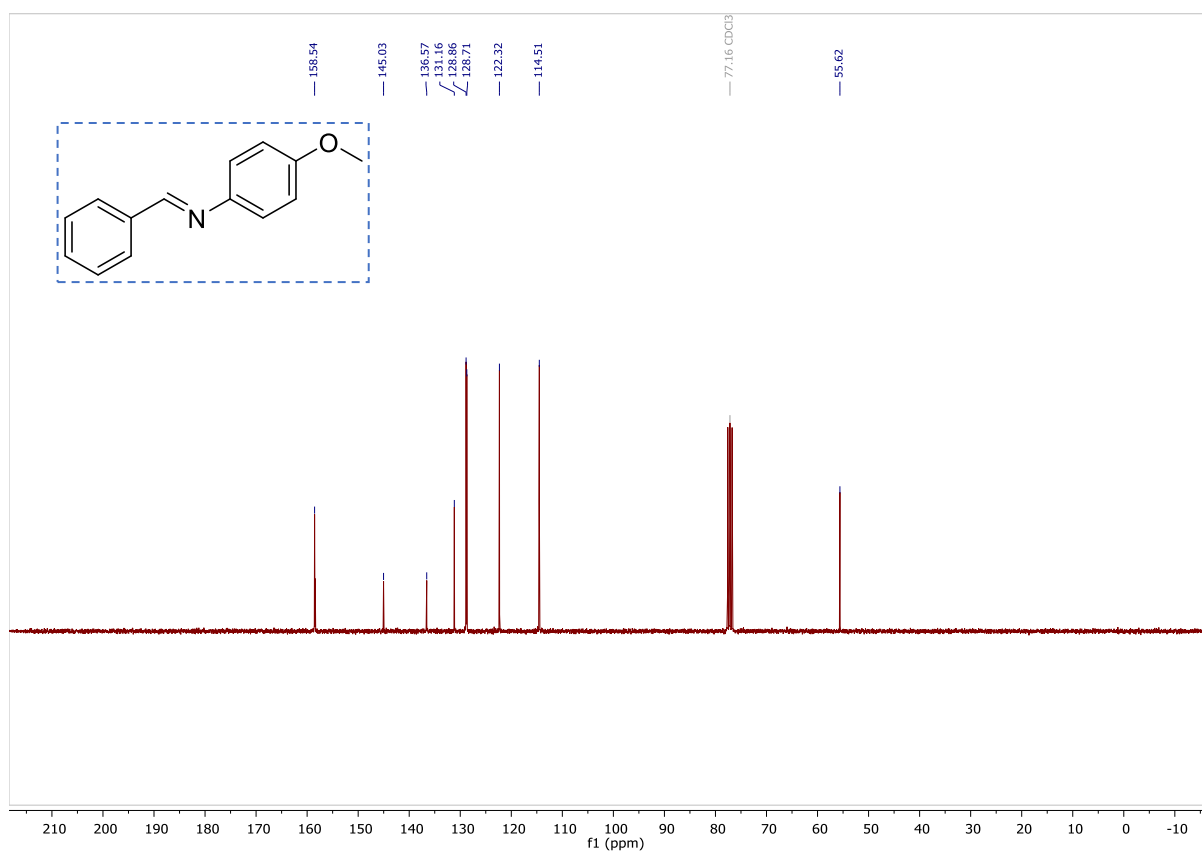


Figure S26 – ¹³C{¹H} NMR spectrum of 1e.

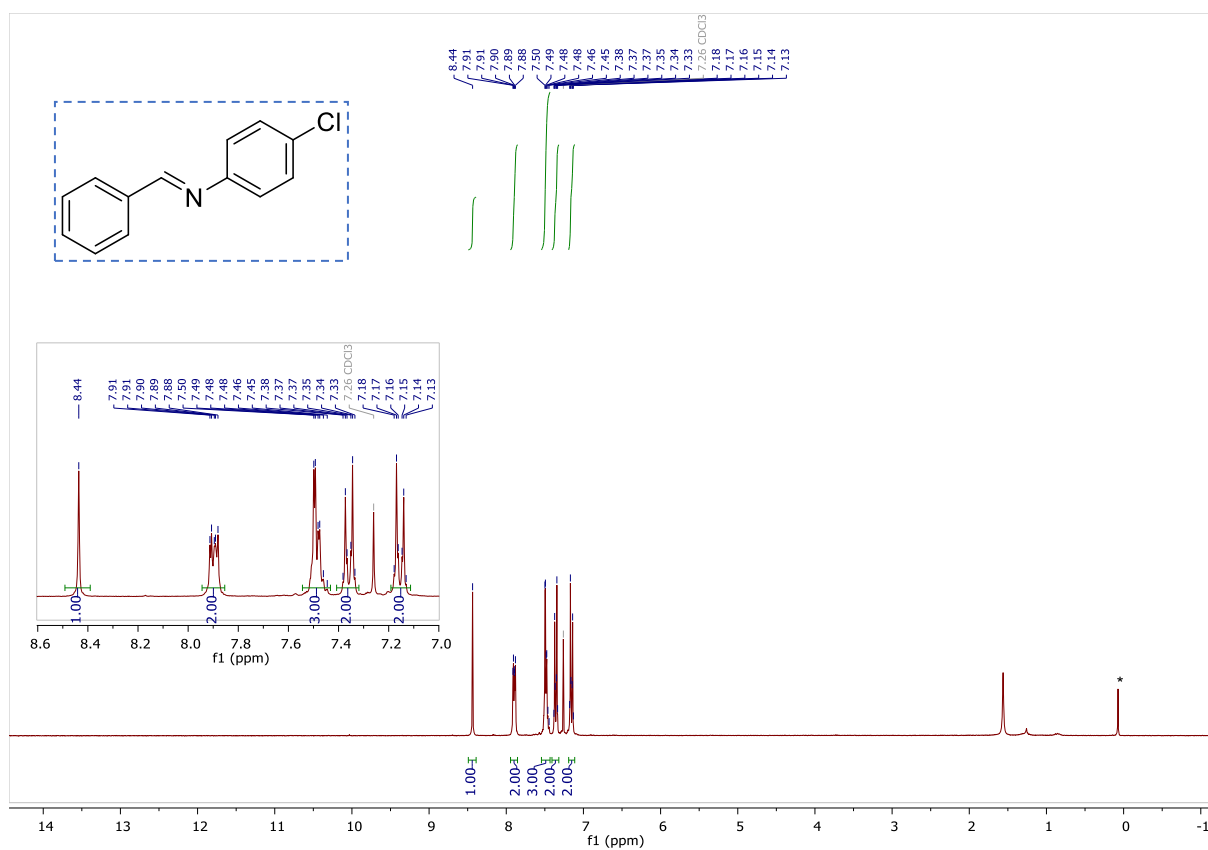


Figure S27 – ¹H NMR spectrum of 1f. *Grease.

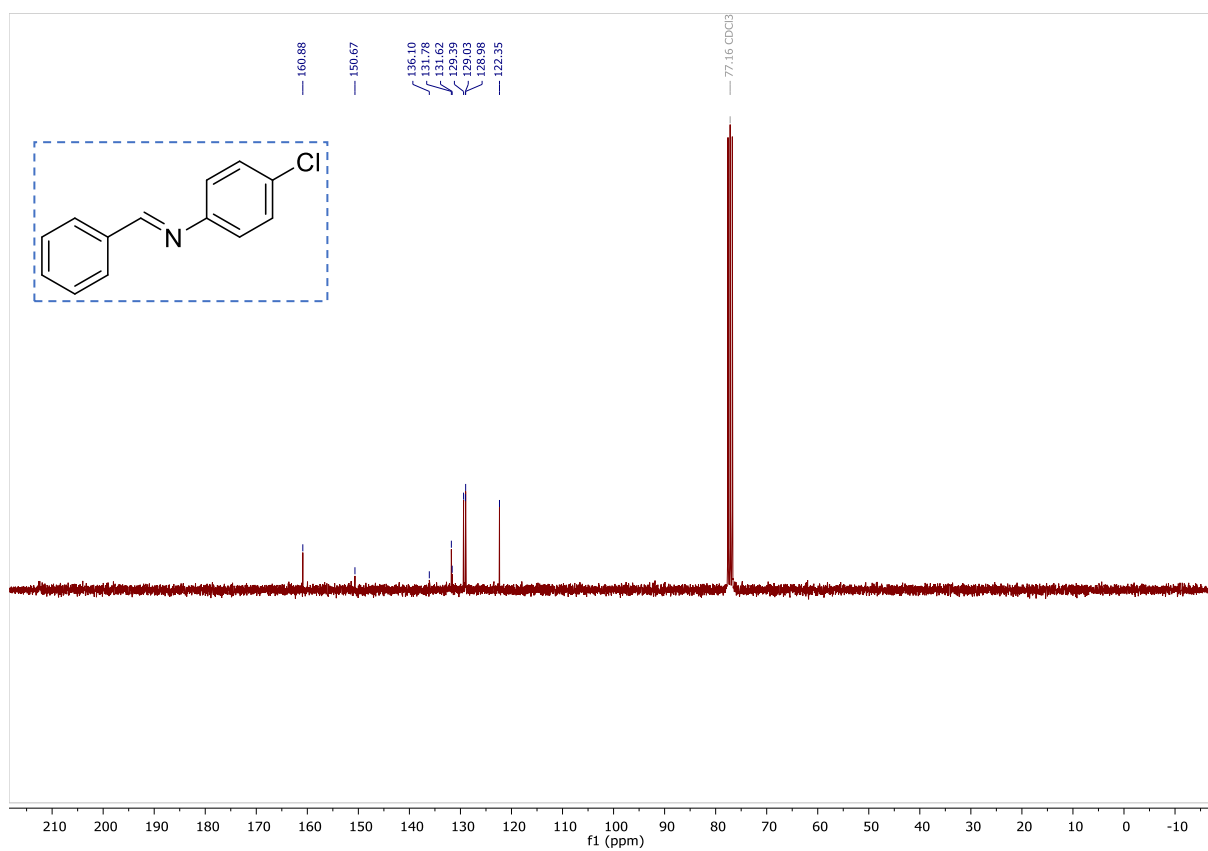


Figure S28 – ¹³C{¹H} NMR spectrum of 1f.

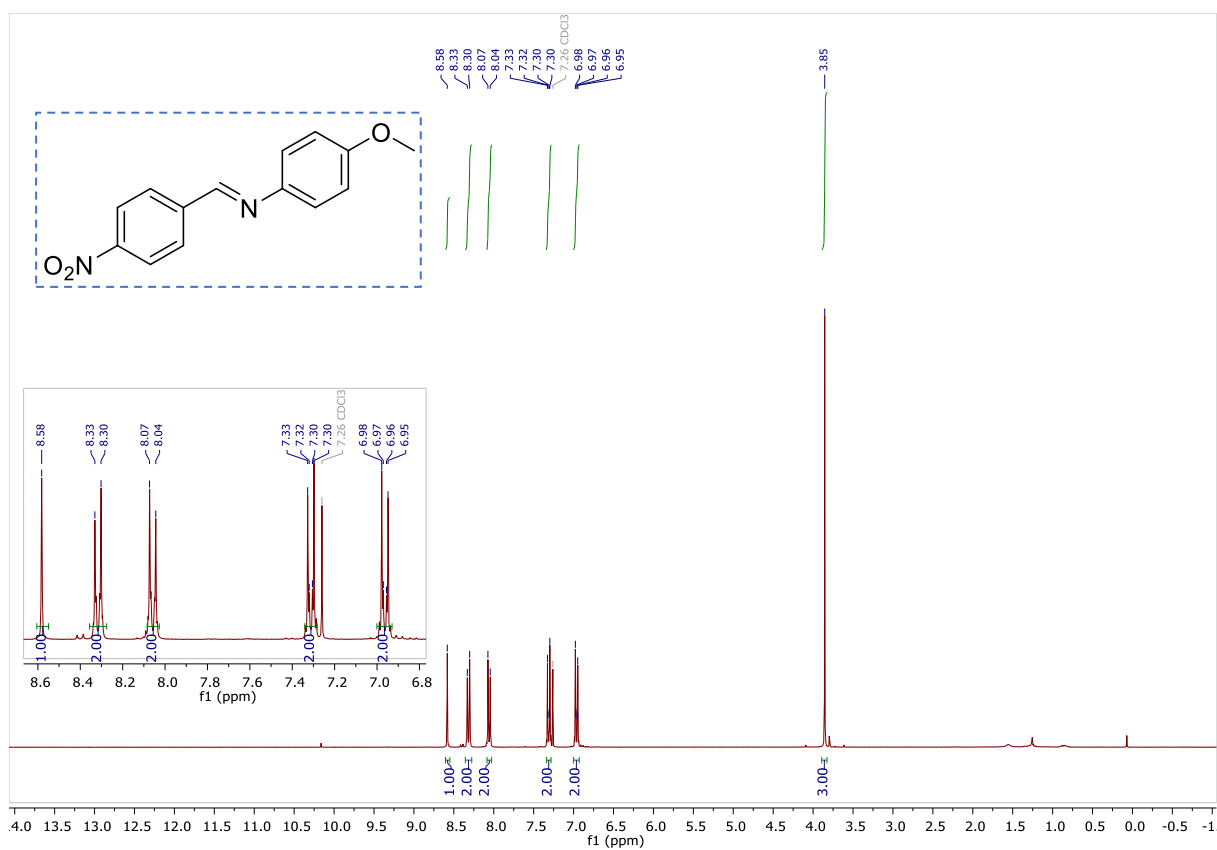


Figure S29 – ¹H NMR spectrum of **1g**.

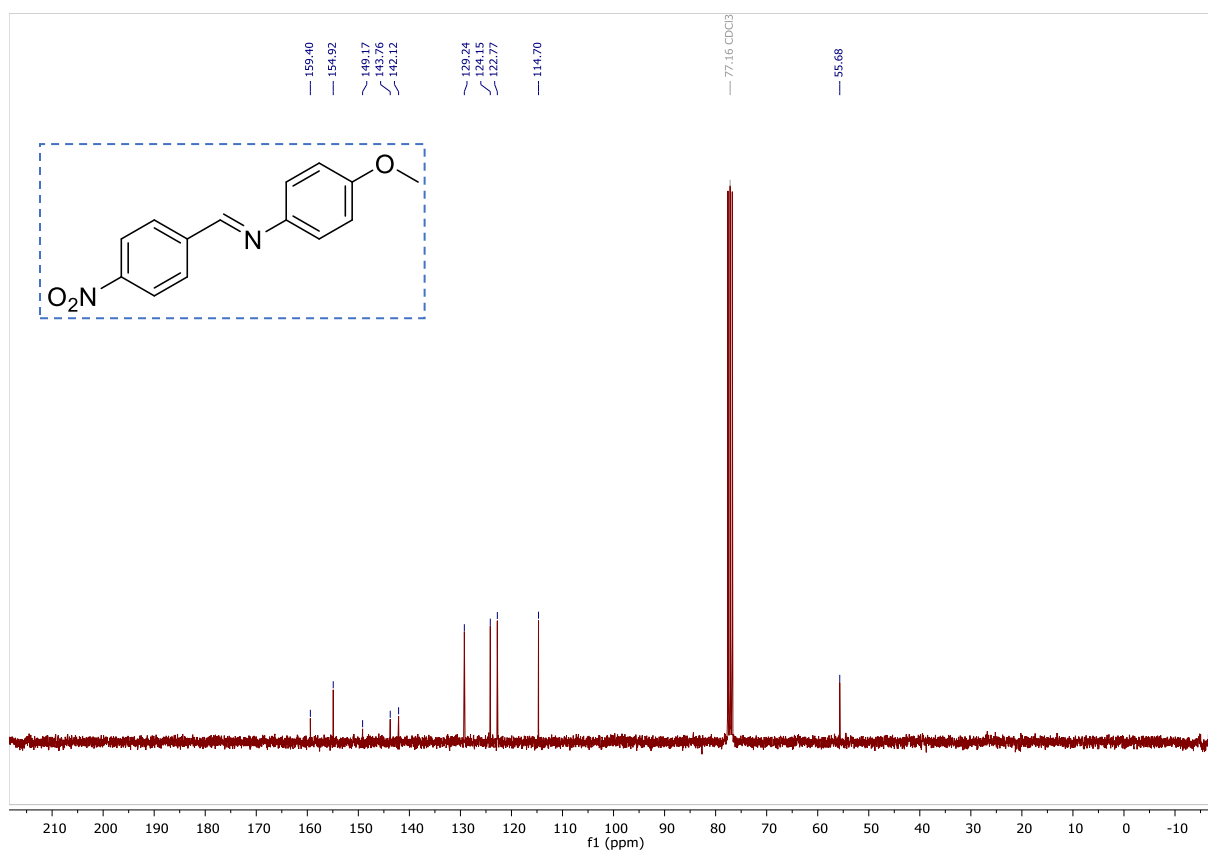


Figure S30 – ¹³C{¹H} NMR spectrum of **1g**.

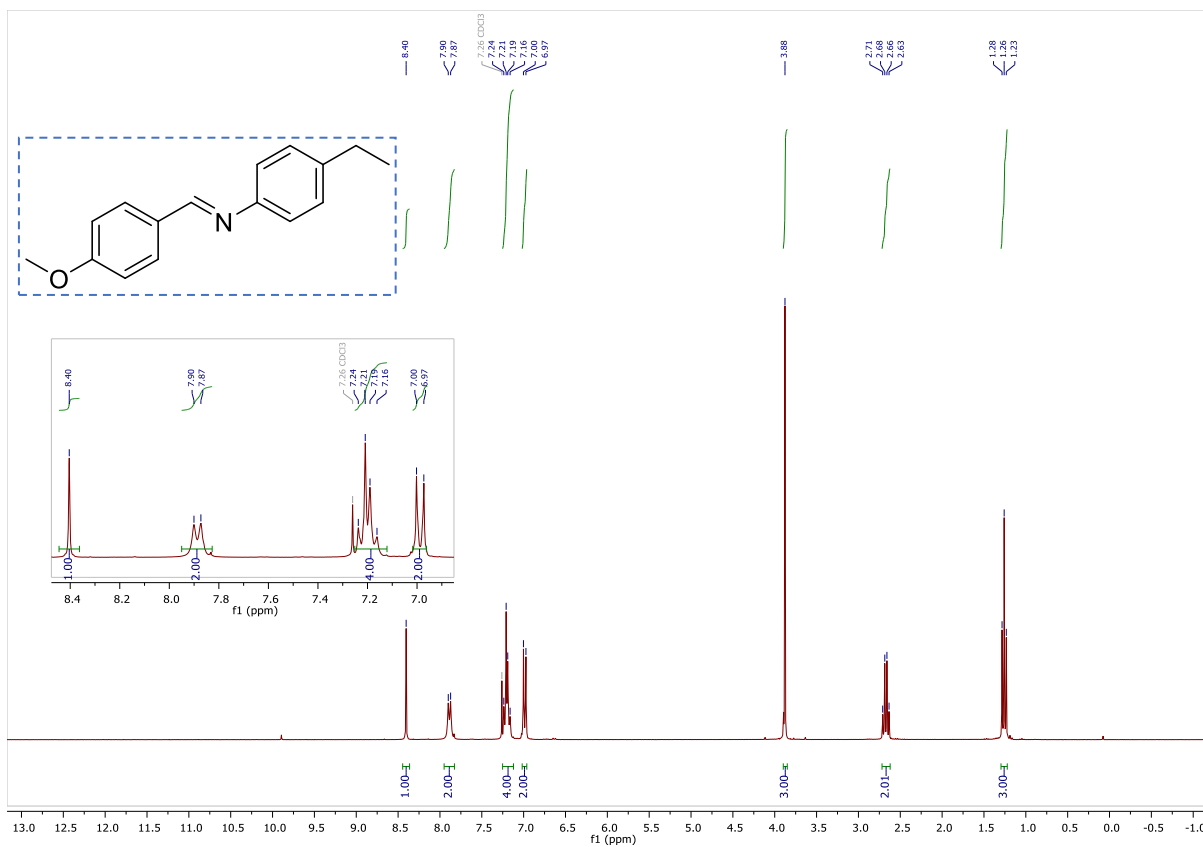


Figure S31 – ¹H NMR spectrum of **1h**.

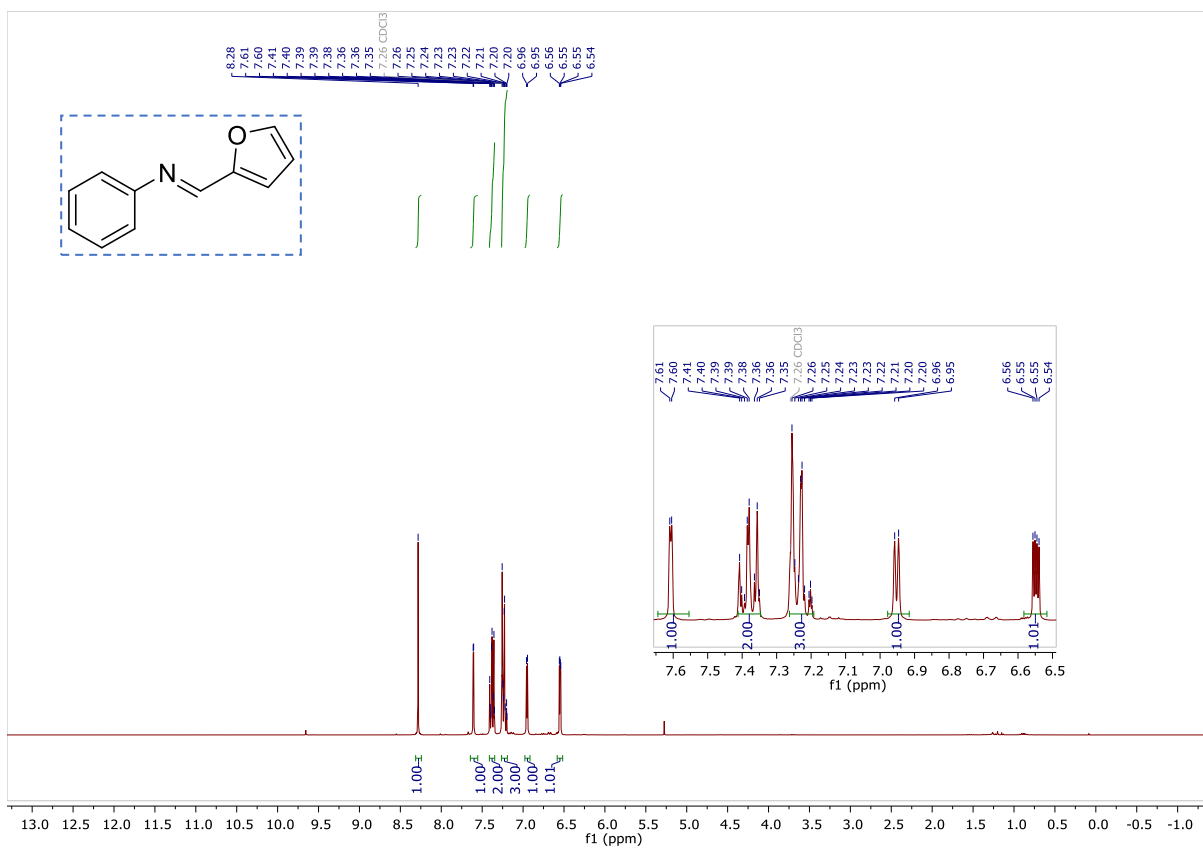


Figure S32 – ¹H NMR spectrum of **1i**.

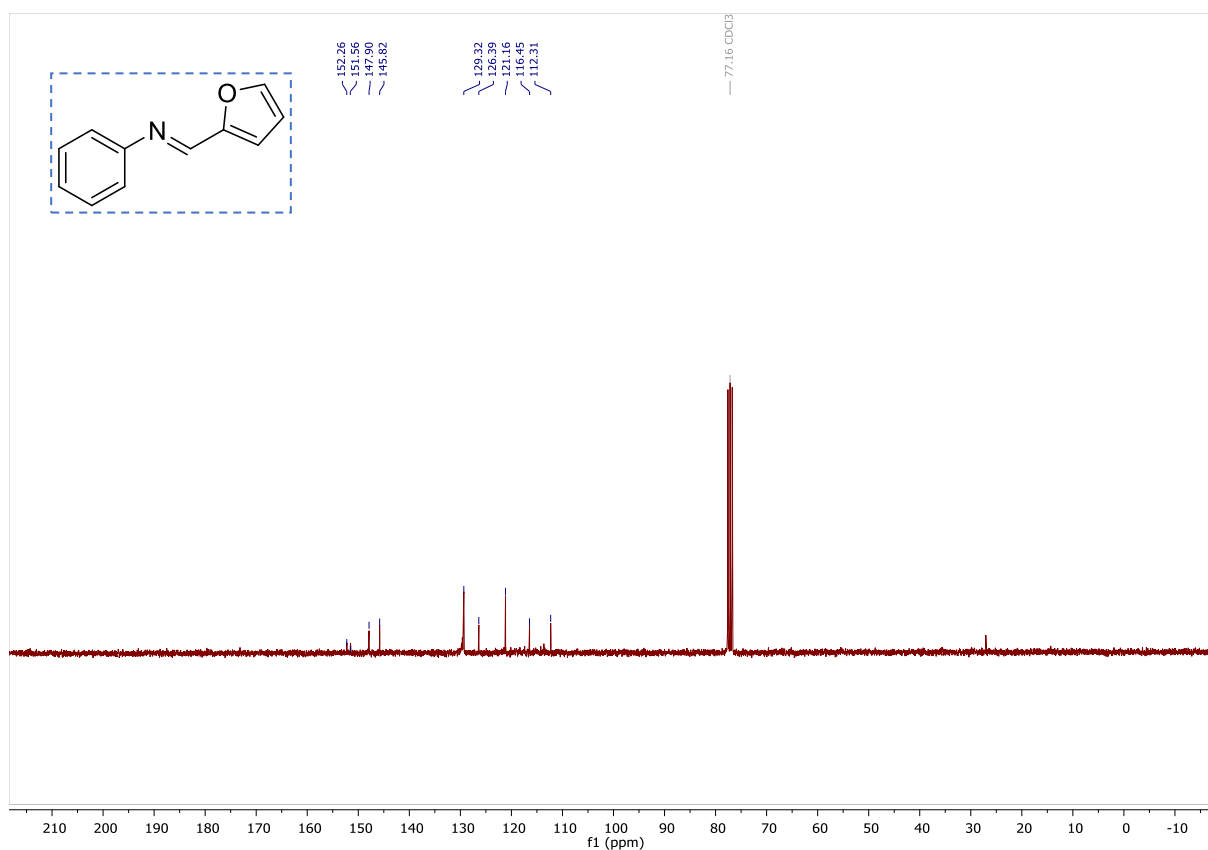


Figure S33 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1i**.

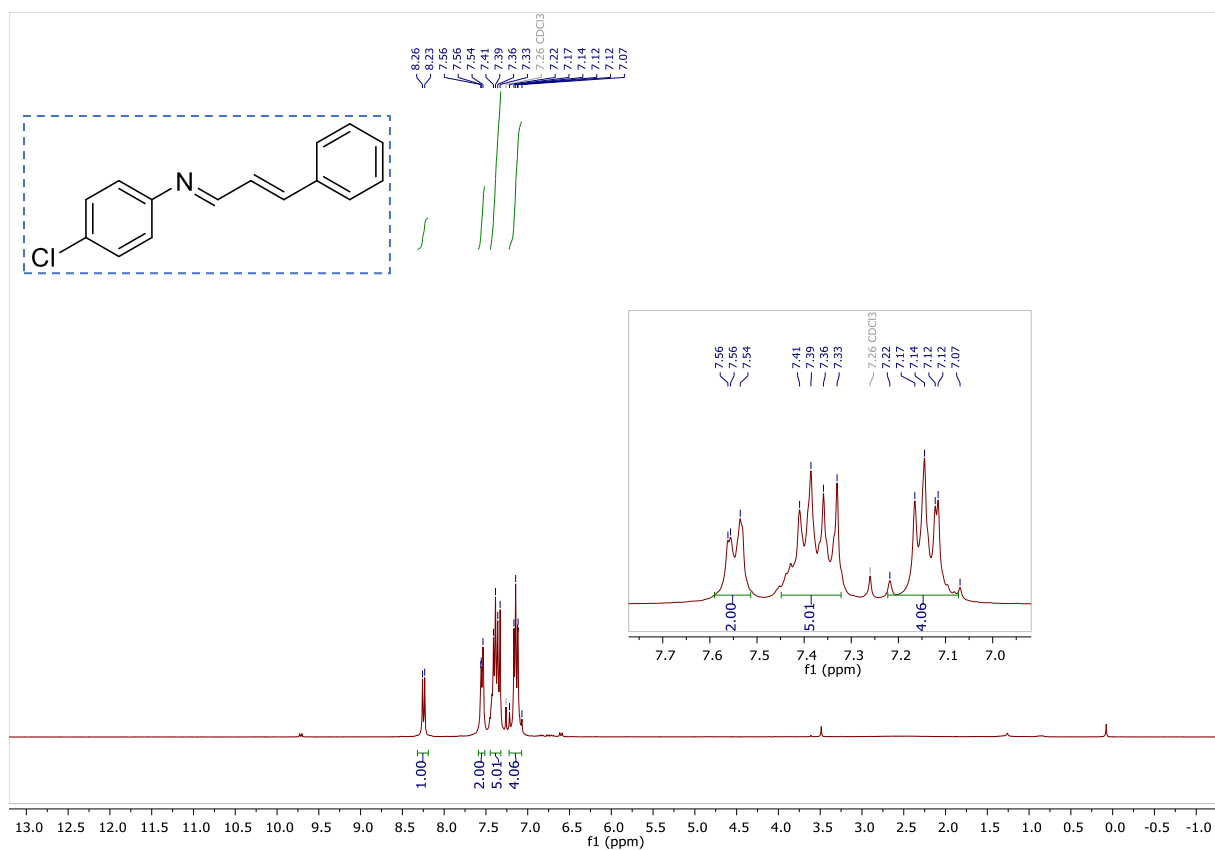


Figure S34 – ^1H NMR spectrum of **1j**.

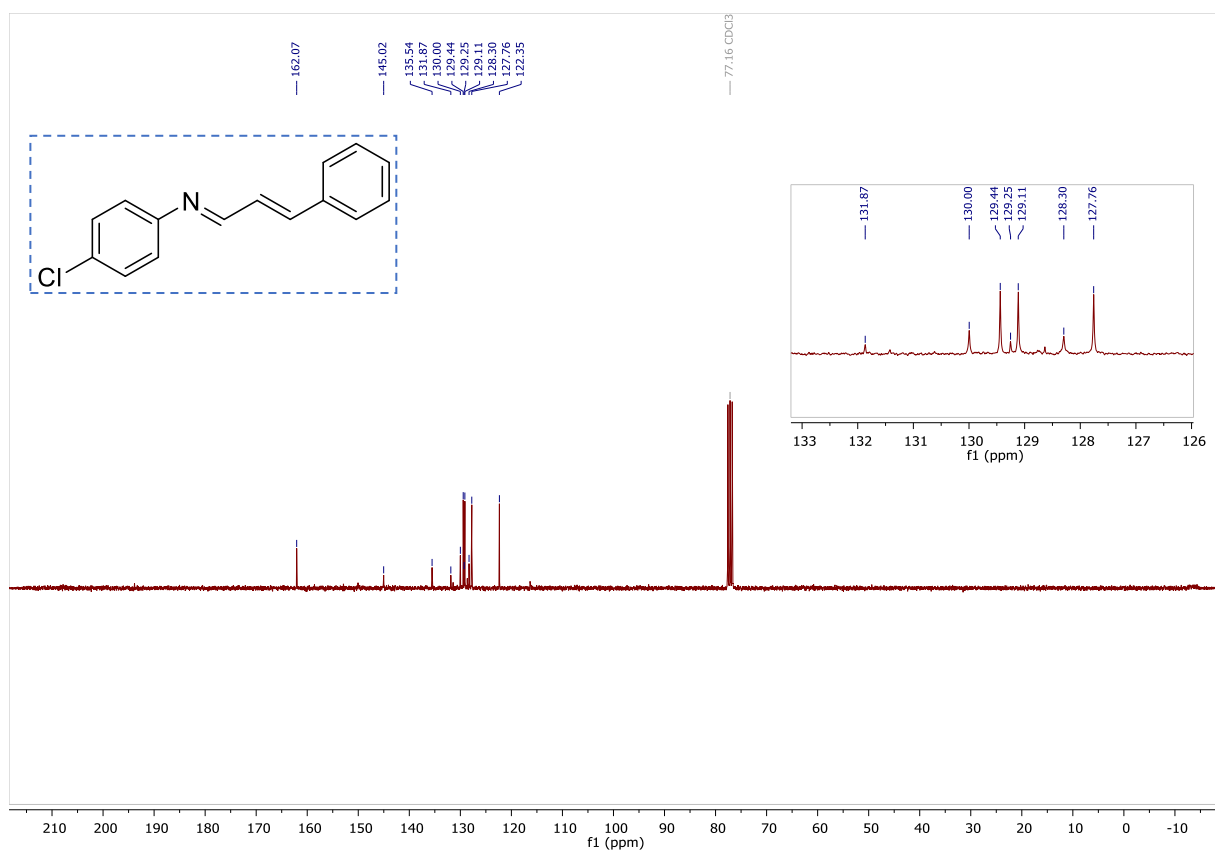


Figure S35 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **1j**.

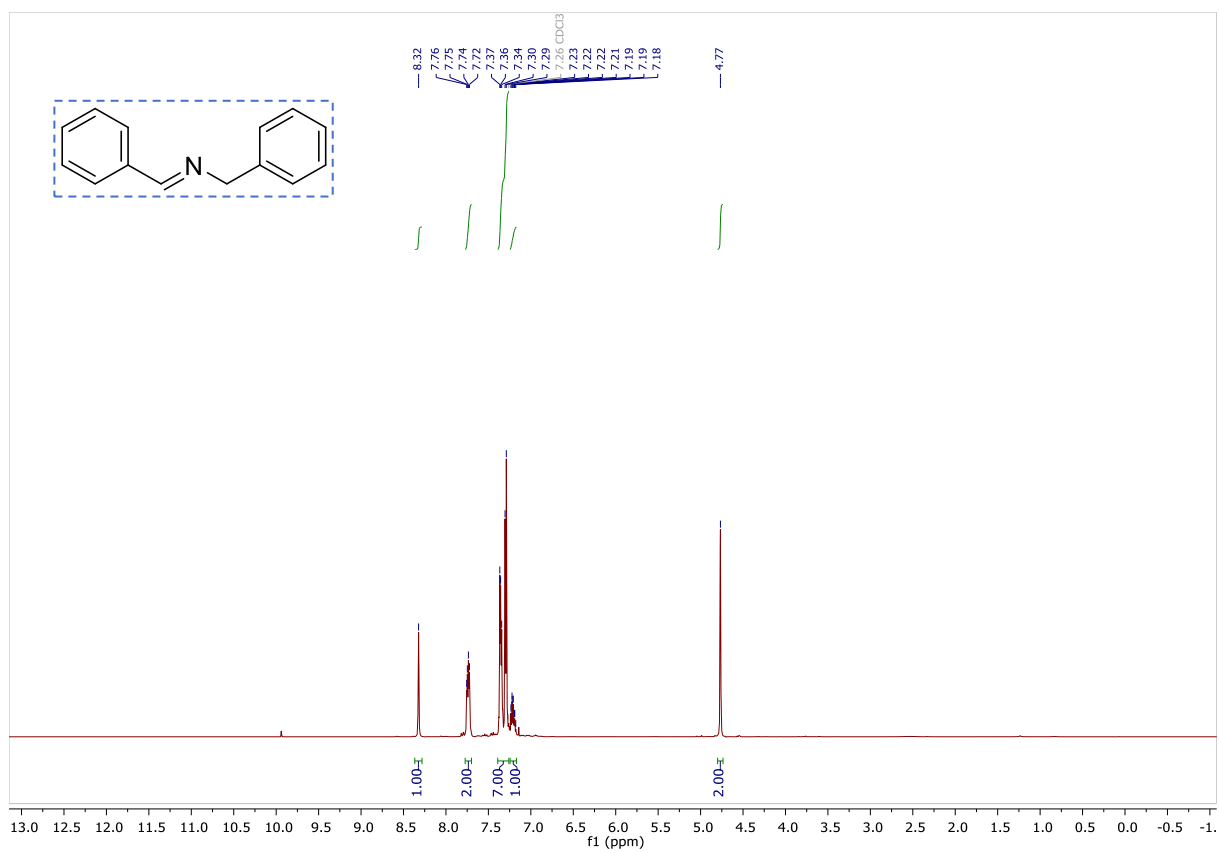


Figure S36 – ^1H NMR spectrum of **1m**.

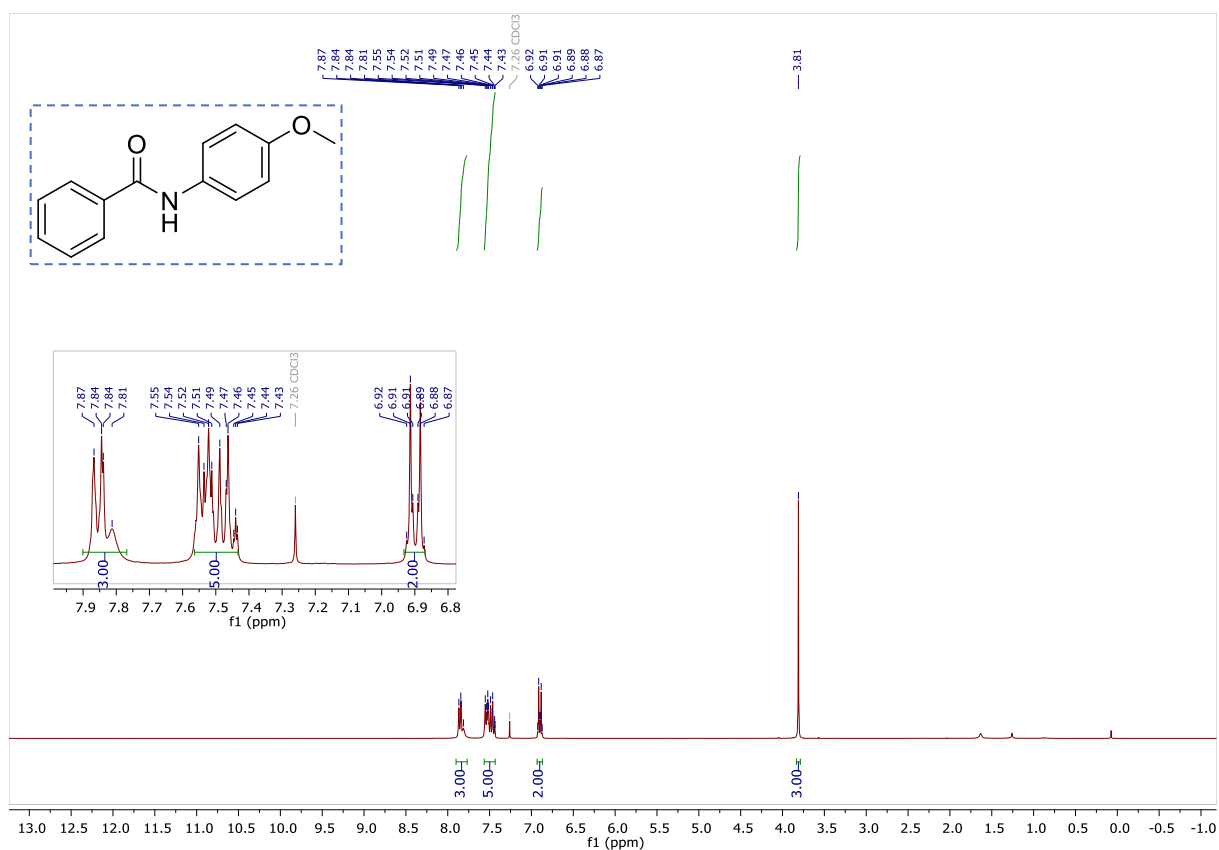


Figure S37 – ¹H NMR spectrum of **8b**.

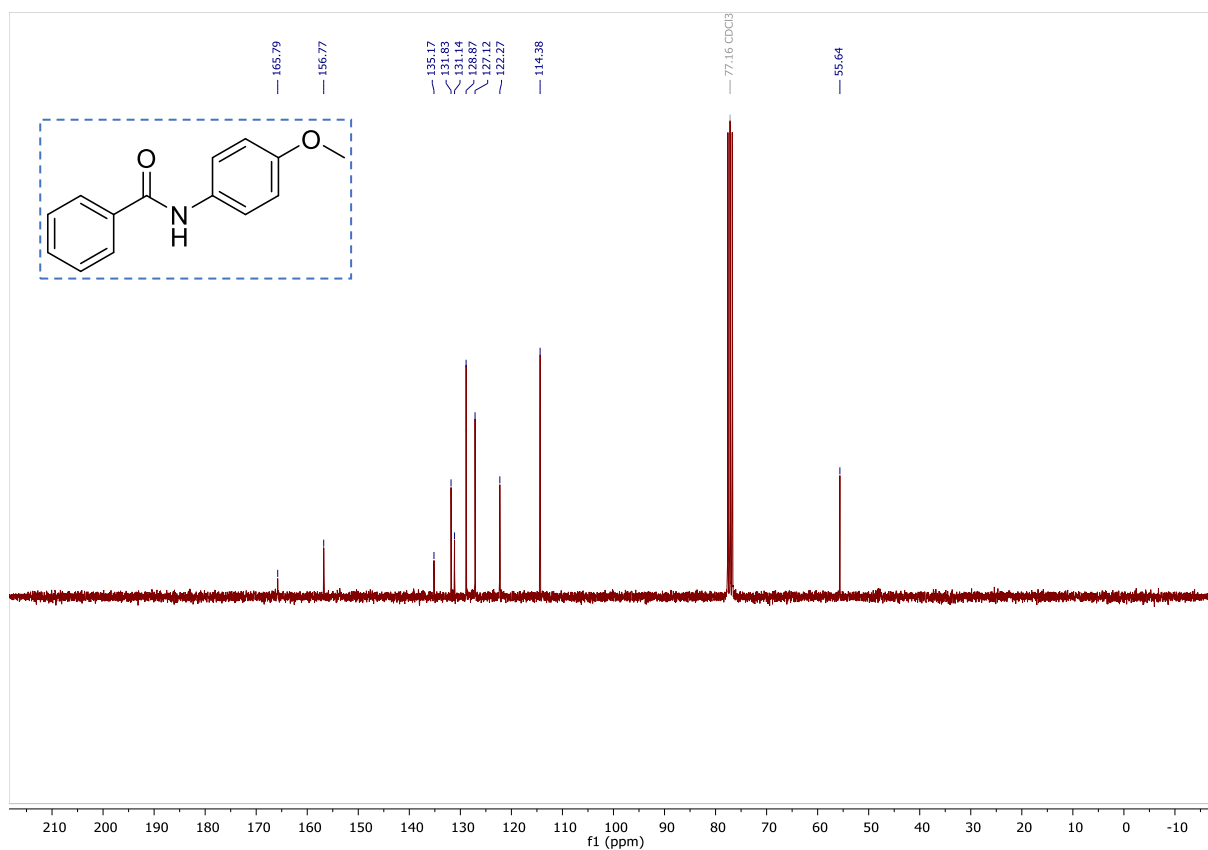


Figure S38 – ¹³C{¹H} NMR spectrum of **8b**.

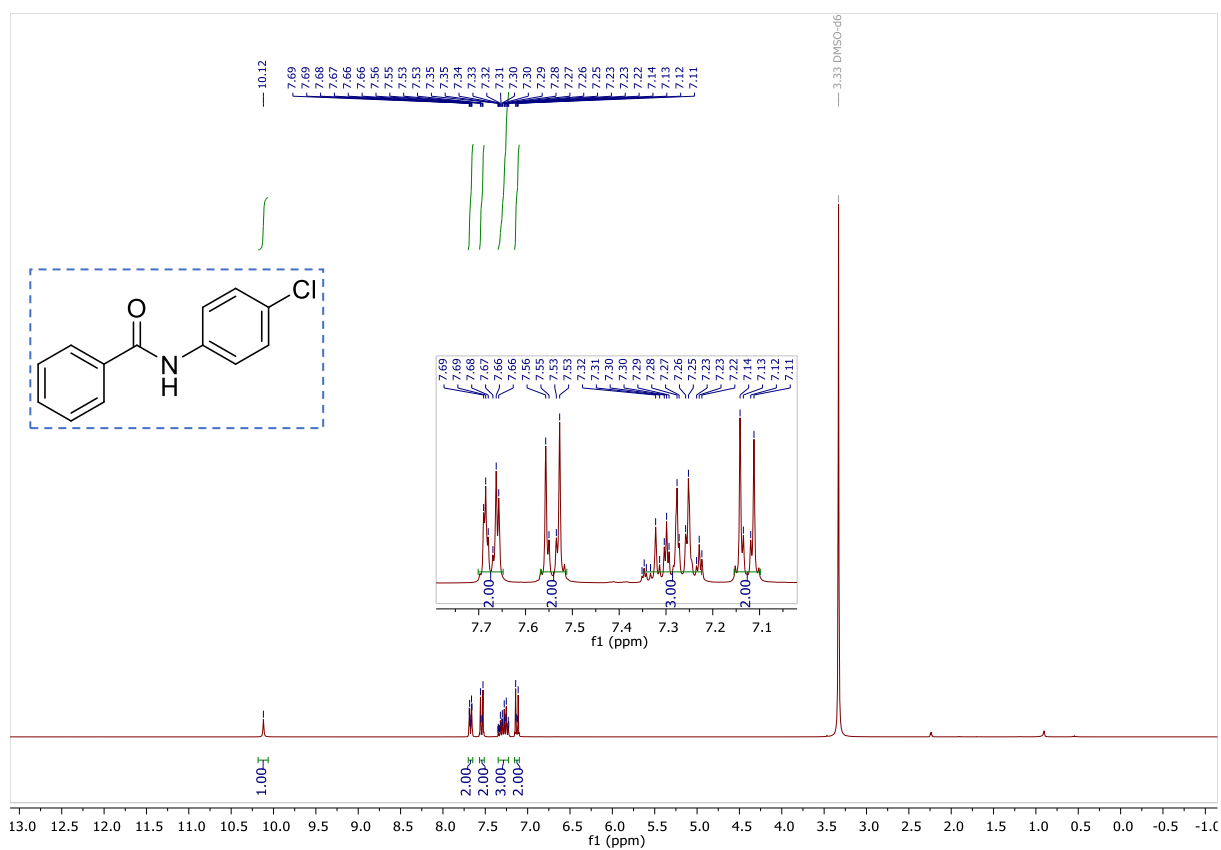


Figure S39 – ¹H NMR spectrum of **8c**.

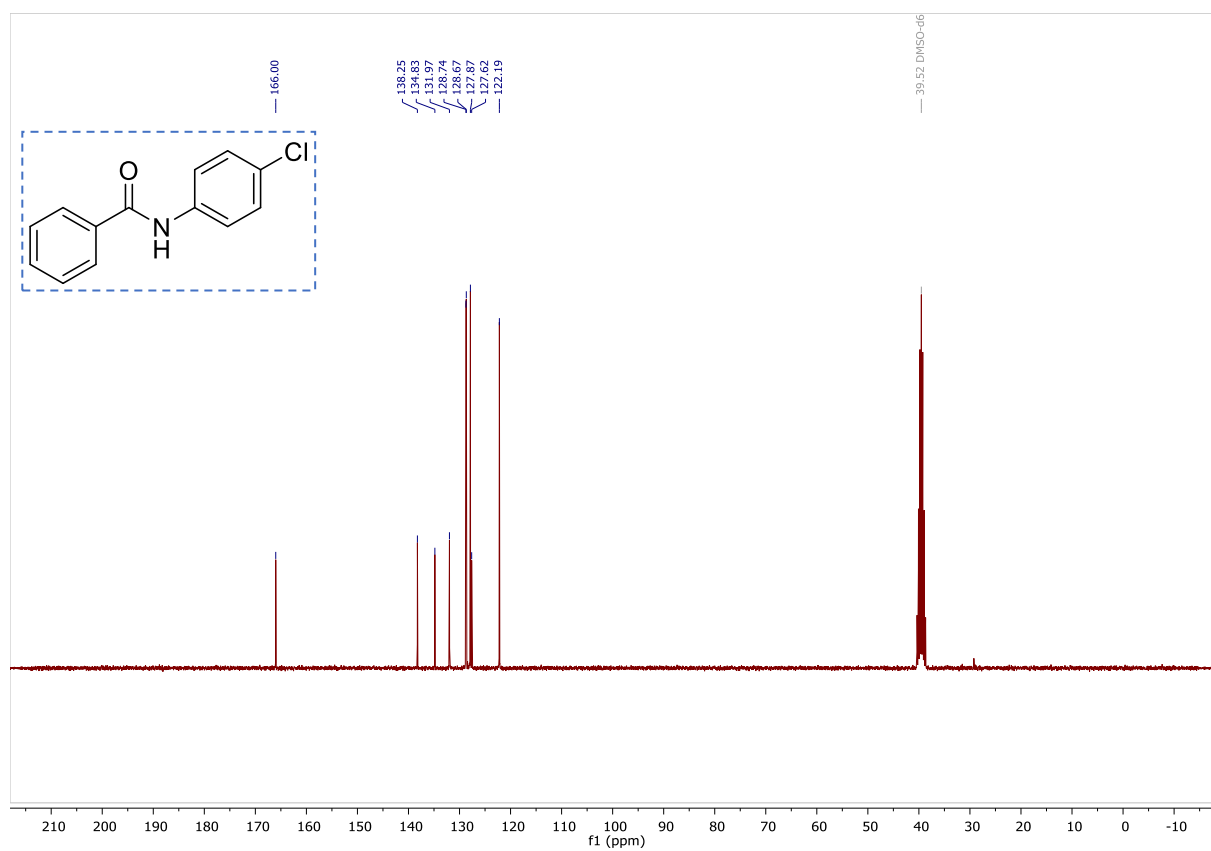


Figure S40 – ¹³C{¹H} NMR spectrum of **8c**.

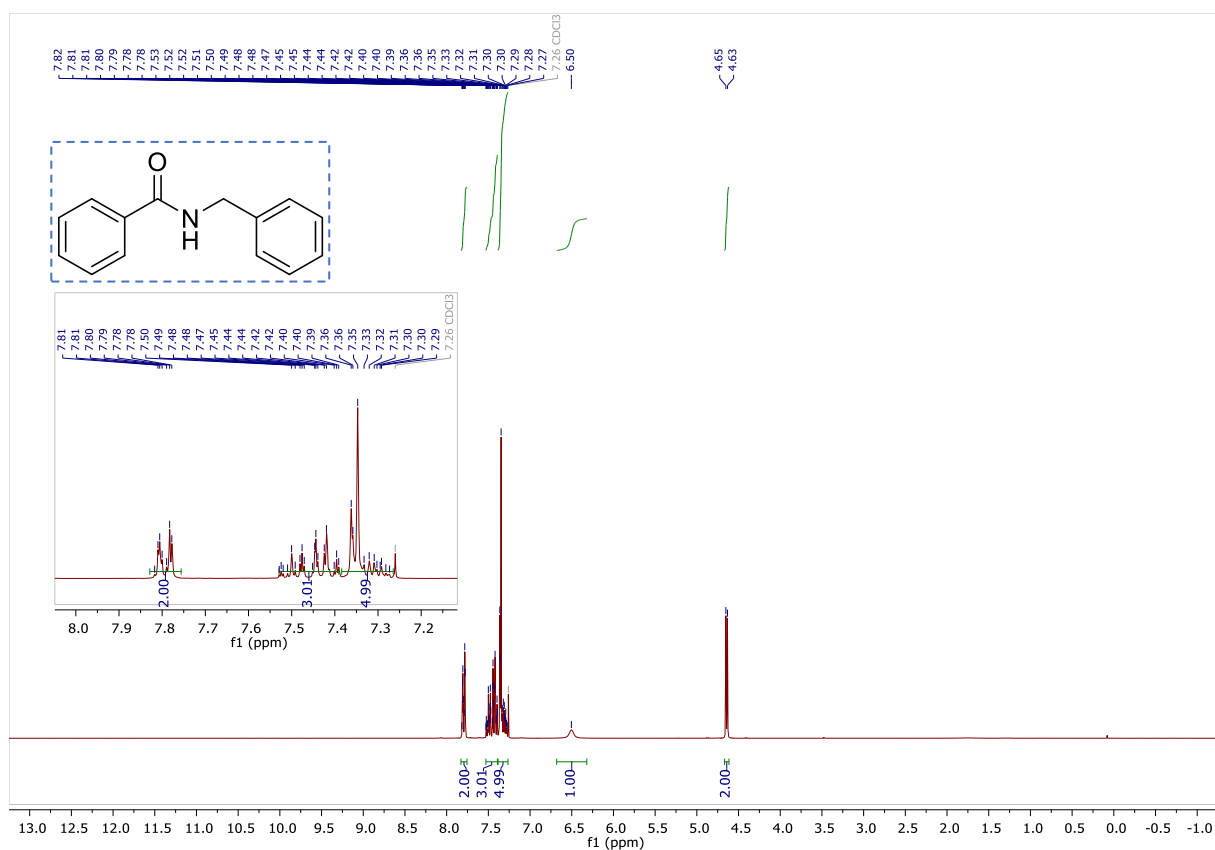


Figure S41 – ¹H NMR spectrum of **8e**.

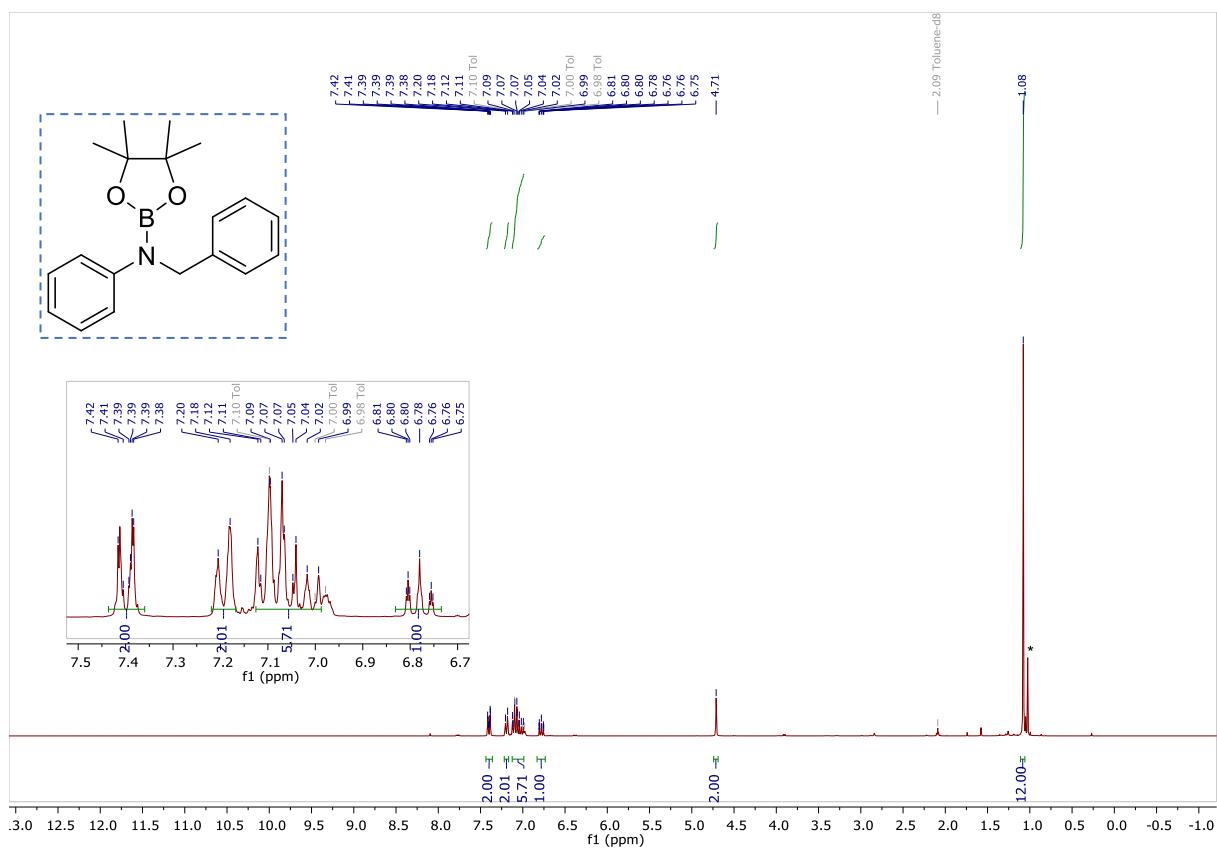


Figure S42 – ¹H NMR spectrum of **3a** from crude reaction mixture. *Excess of the HBpin.

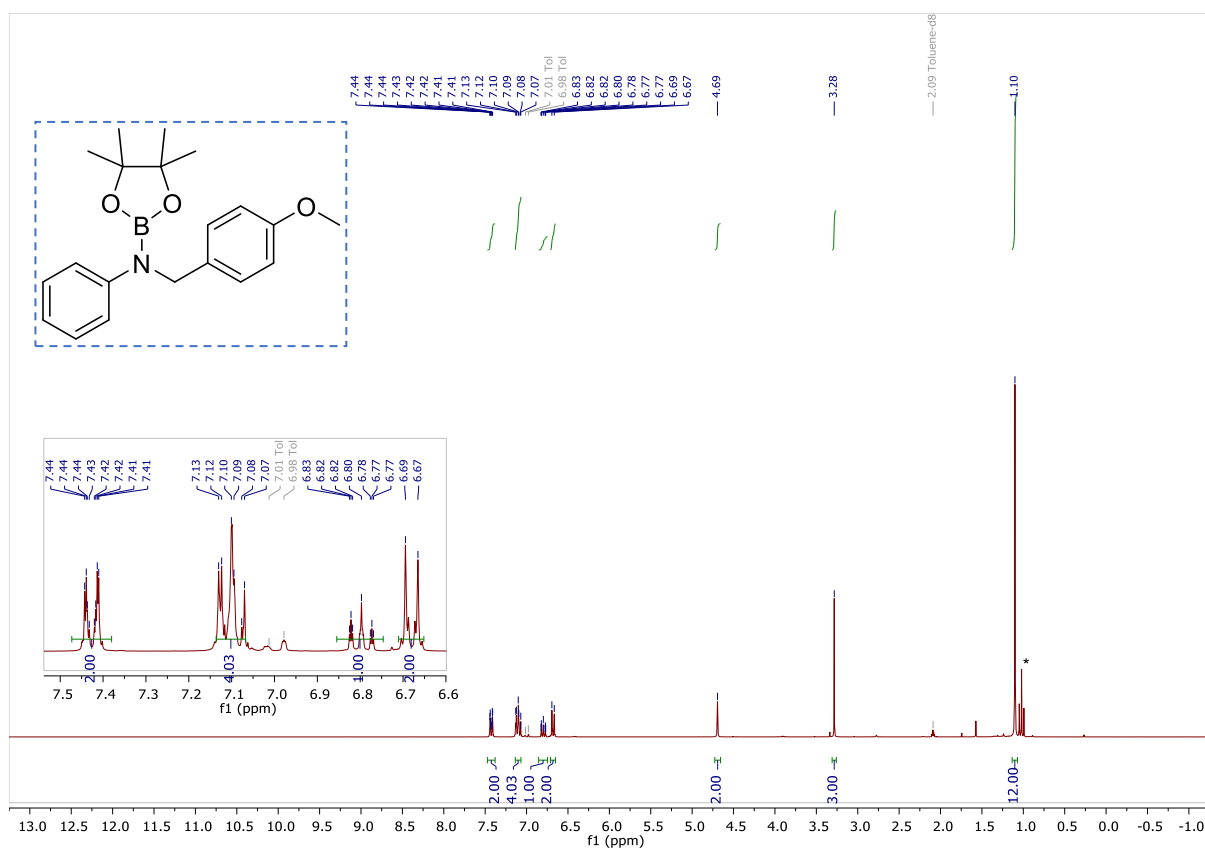


Figure S45 – ¹H NMR spectrum of **3d** from crude reaction mixture. *Excess of the HBpin.

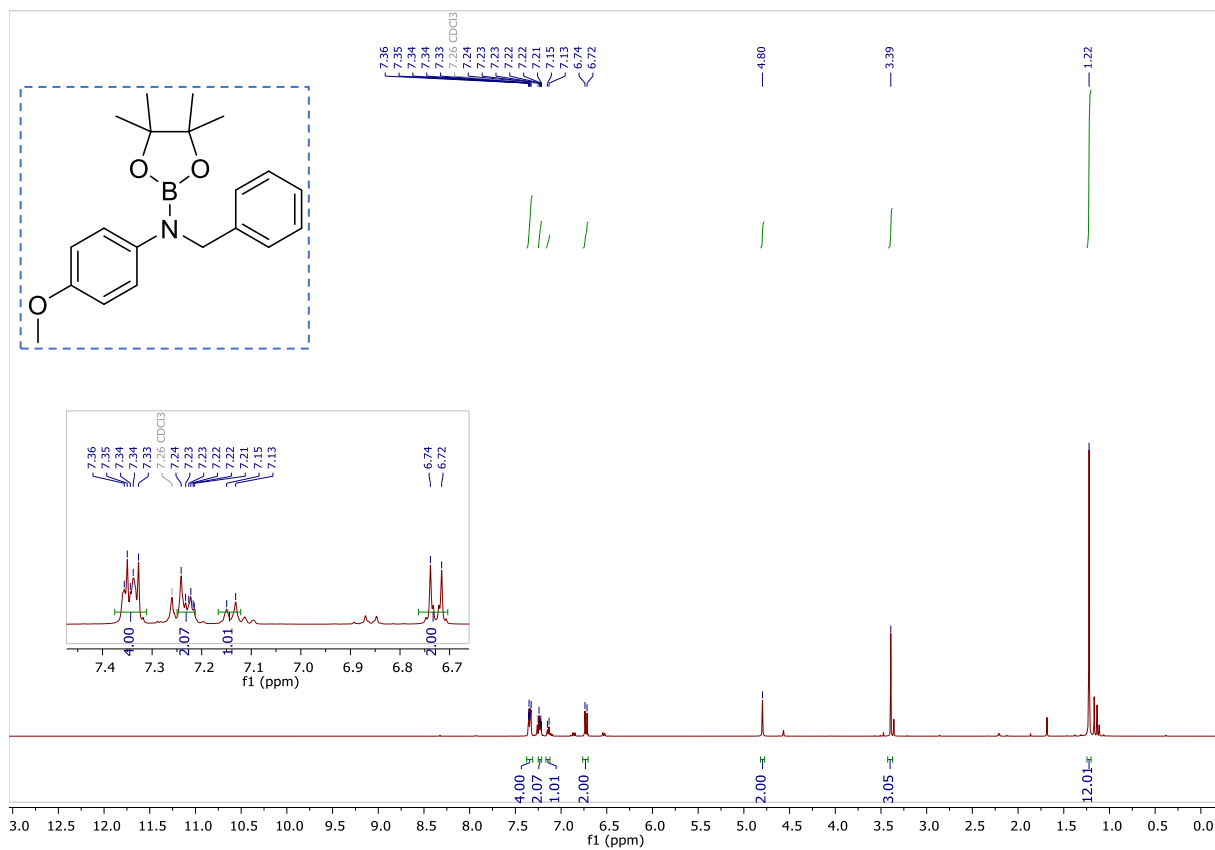


Figure S46 – ¹H NMR spectrum of **3e** from crude reaction mixture.

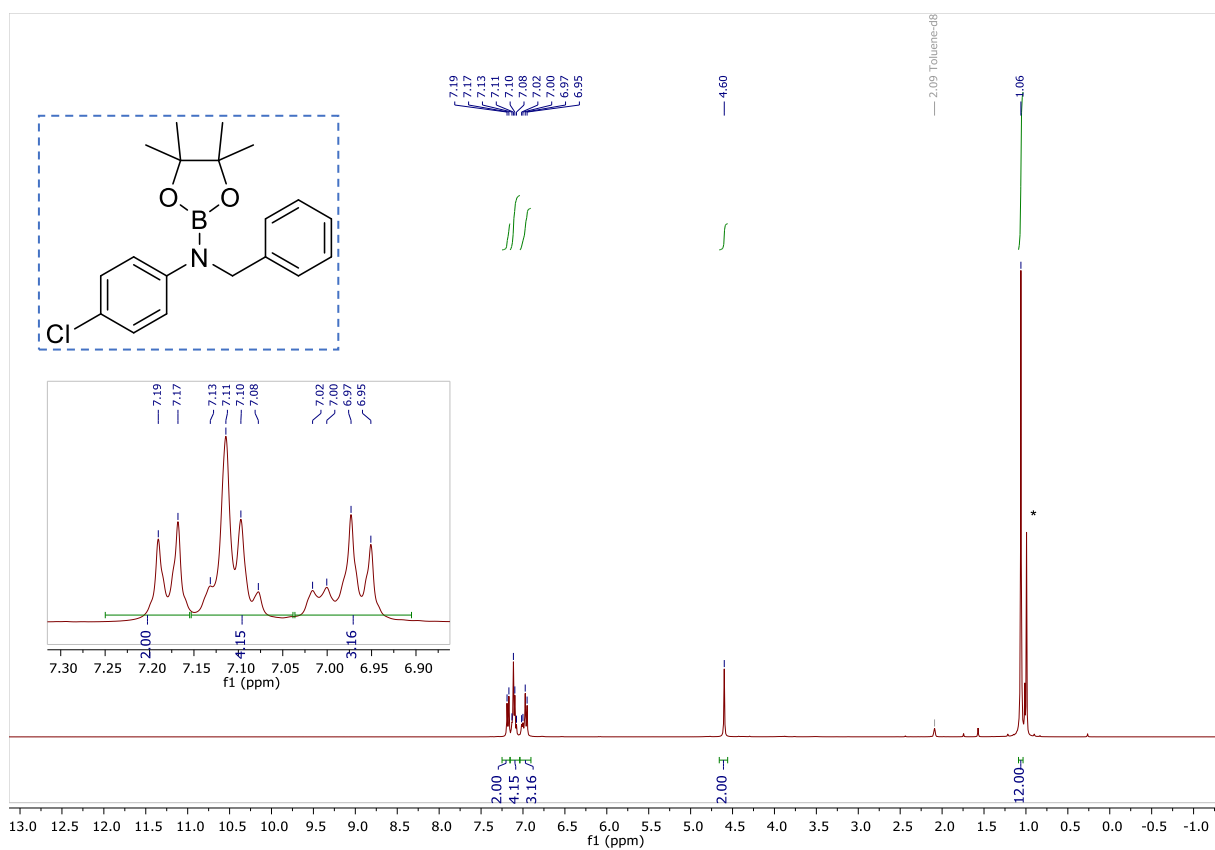


Figure S47 – ¹H NMR spectrum of **3f** from crude reaction mixture. *Excess of the HBpin.

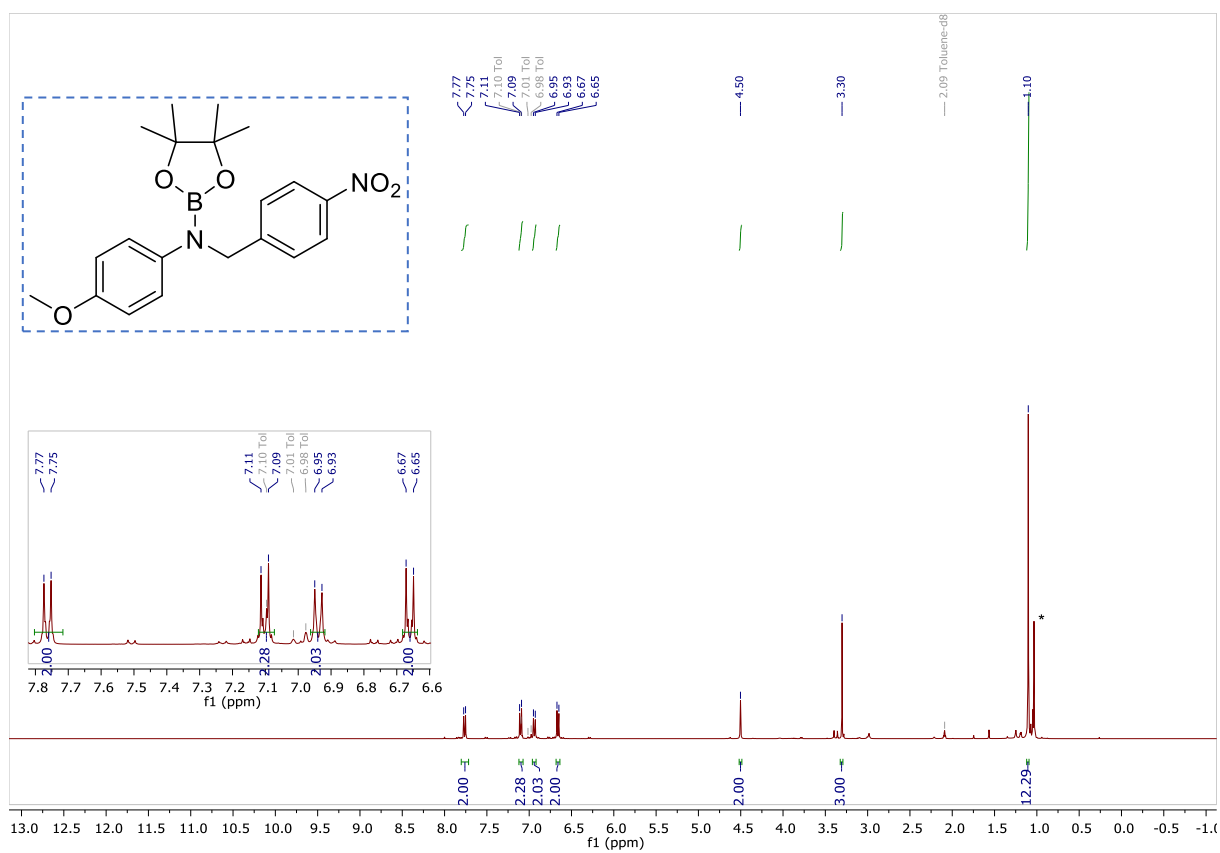


Figure S48 – ¹H NMR spectrum of **3g** from crude reaction mixture. *Excess of the HBpin.

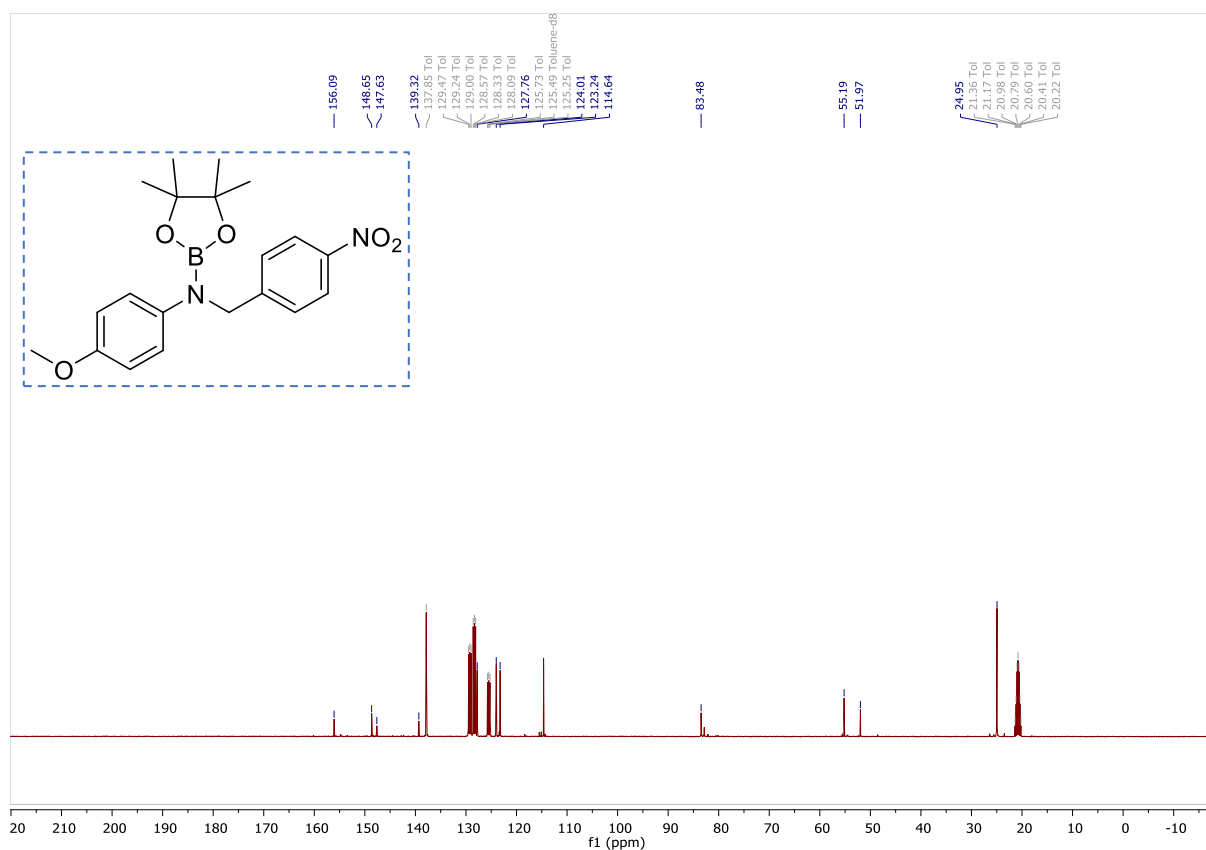


Figure S49 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3g** from crude reaction mixture.

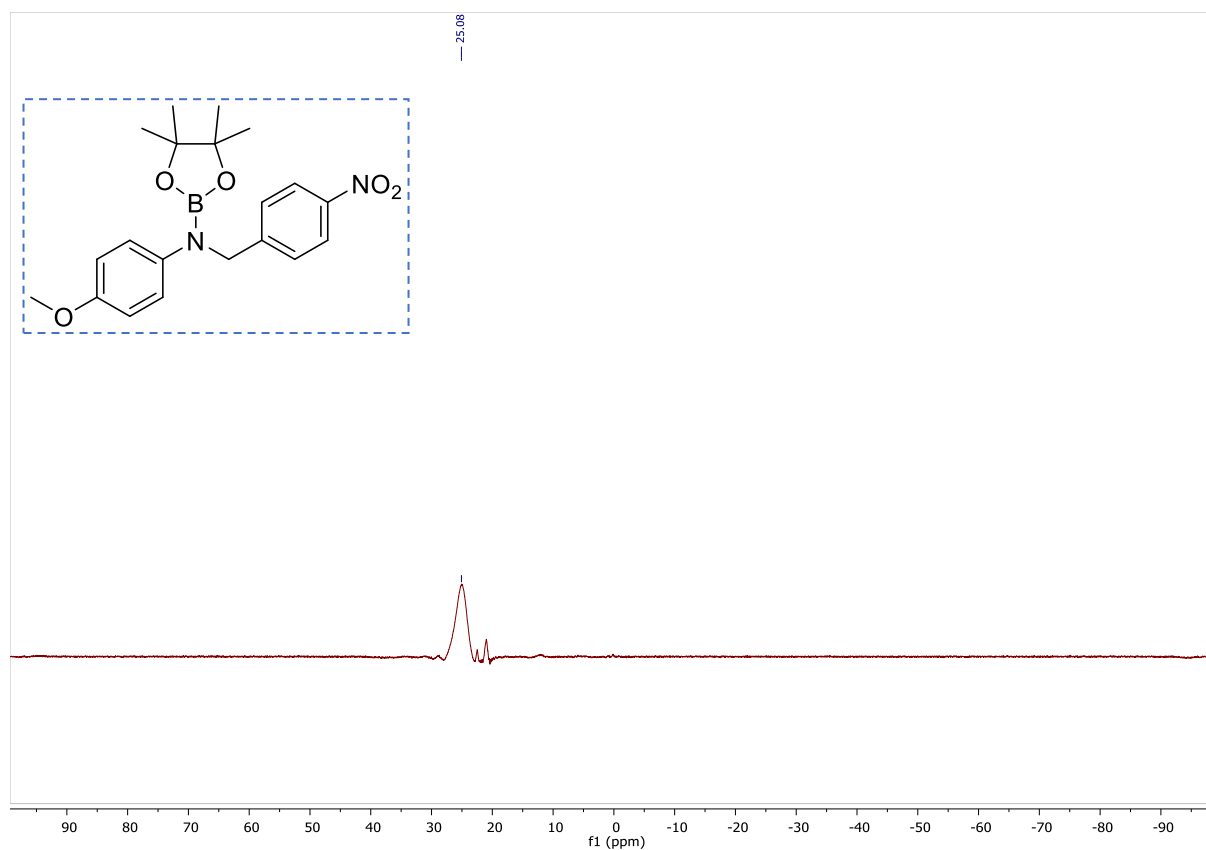


Figure S50 – ^{11}B NMR spectrum of **3g** from crude reaction mixture.

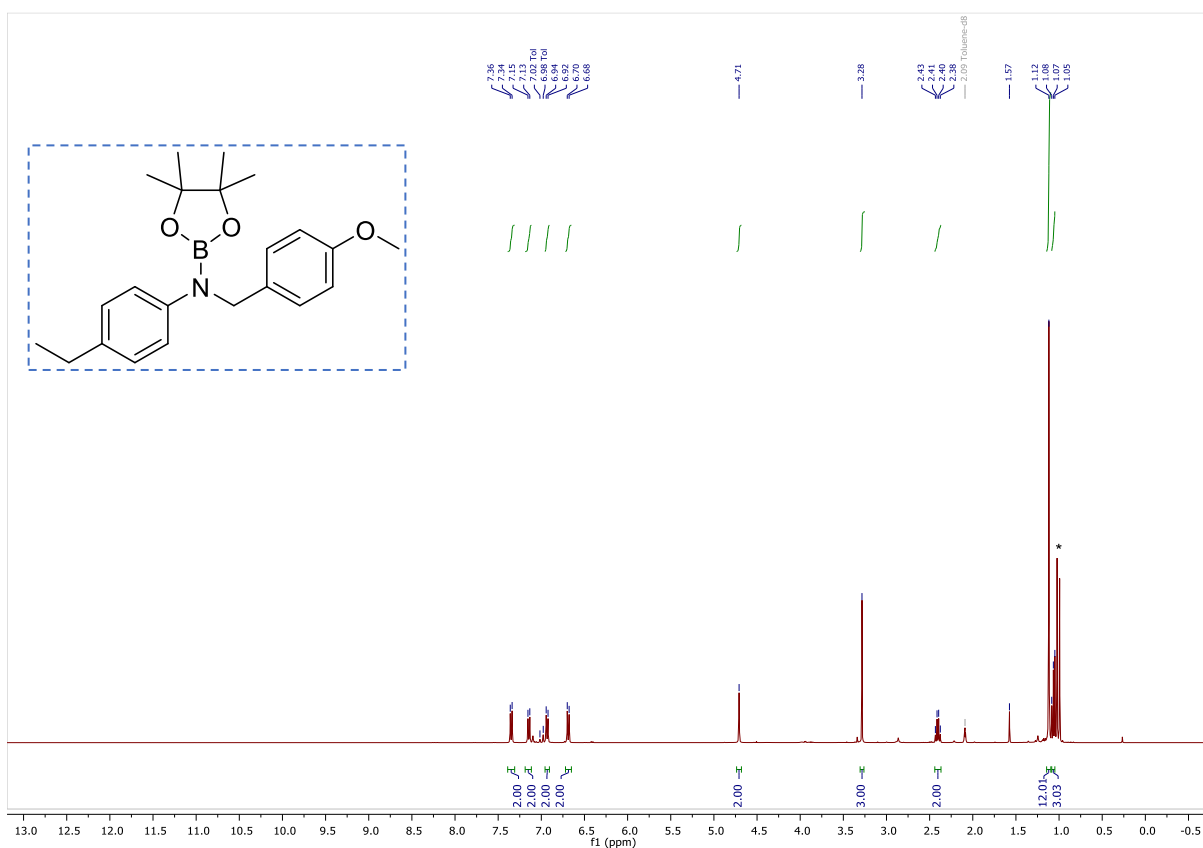


Figure S51 – ^1H NMR spectrum of **3h** from crude reaction mixture.

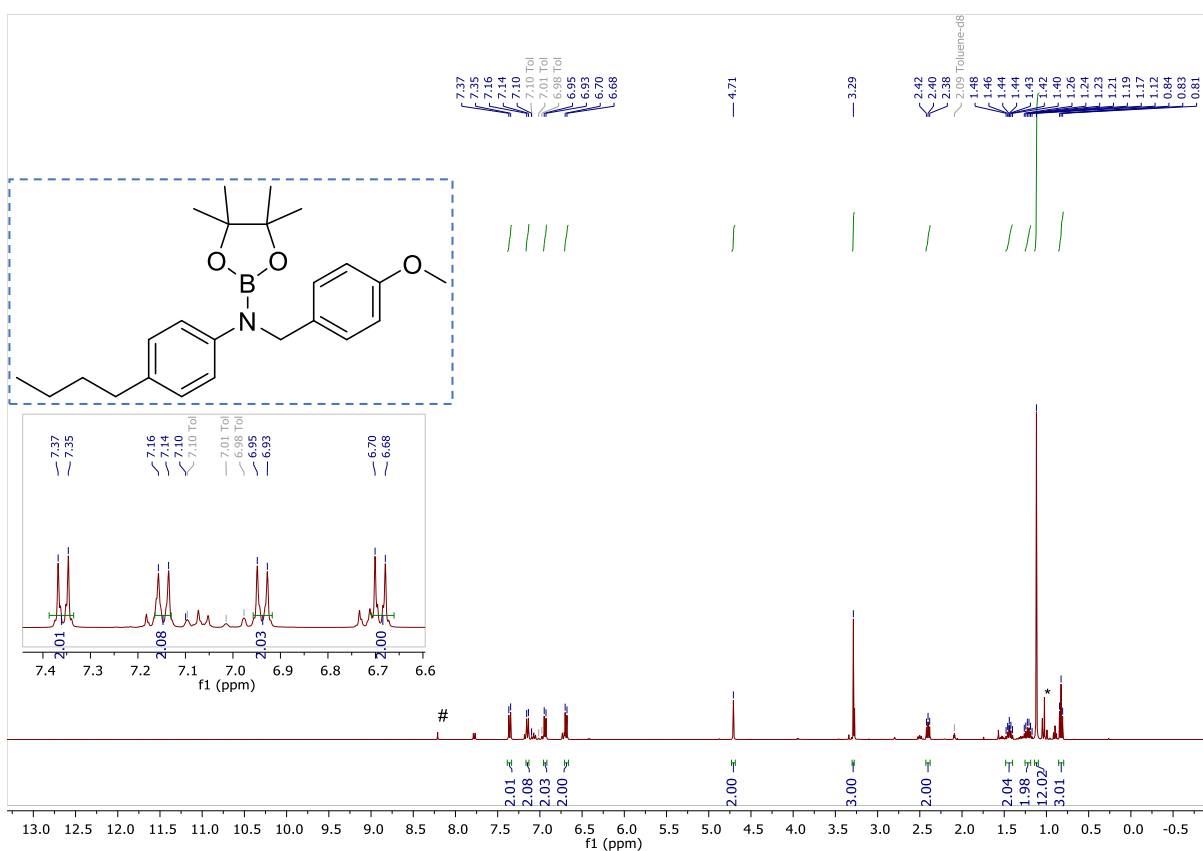
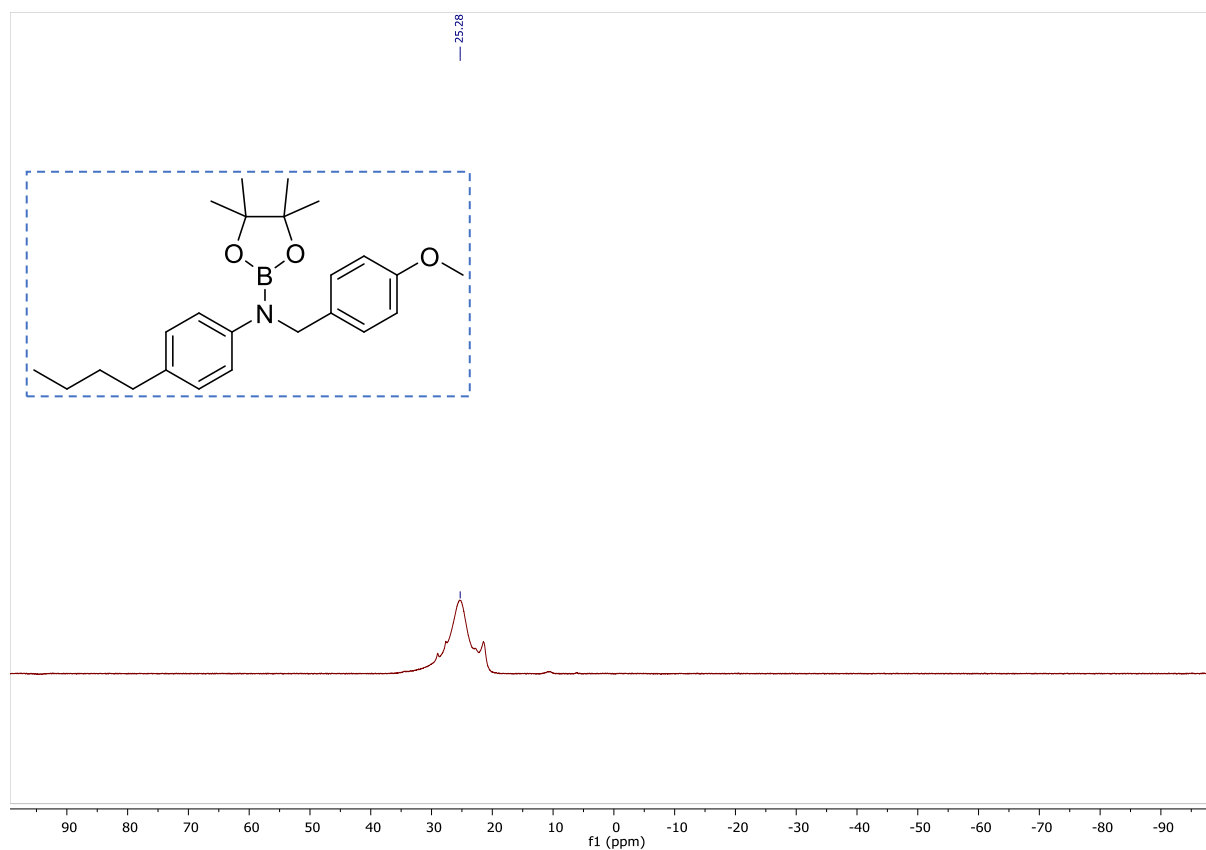
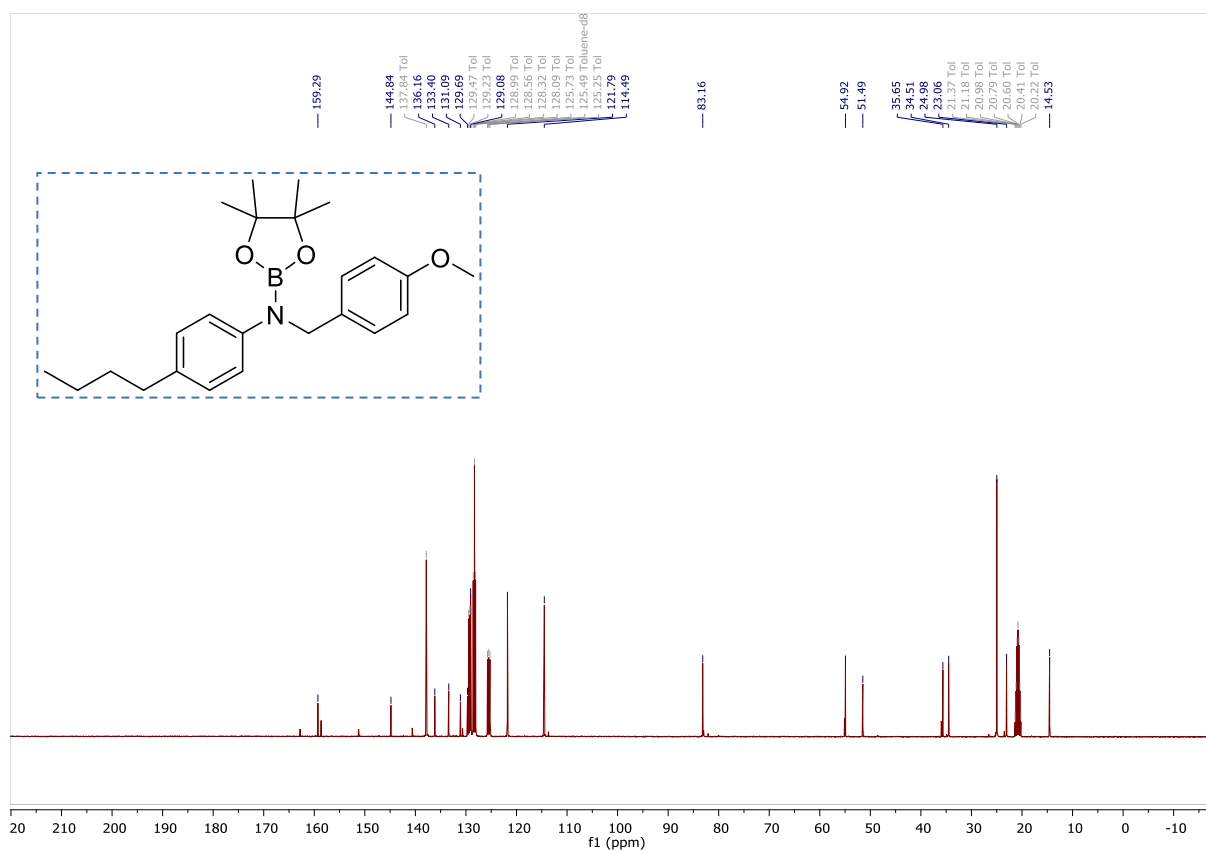


Figure S52 – ^1H NMR spectrum of **3i** from crude reaction mixture. *Excess of the HBpin **1i**.



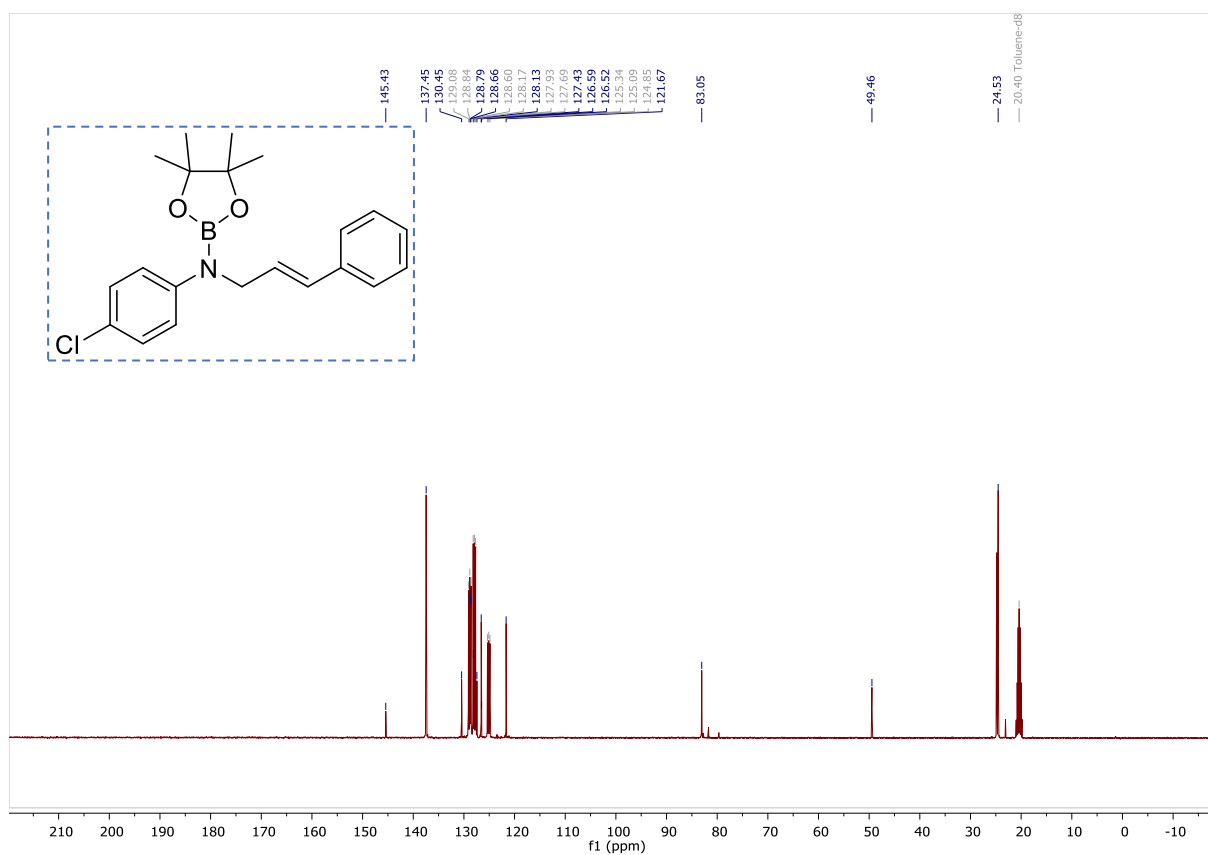


Figure S57 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3k** from crude reaction mixture.

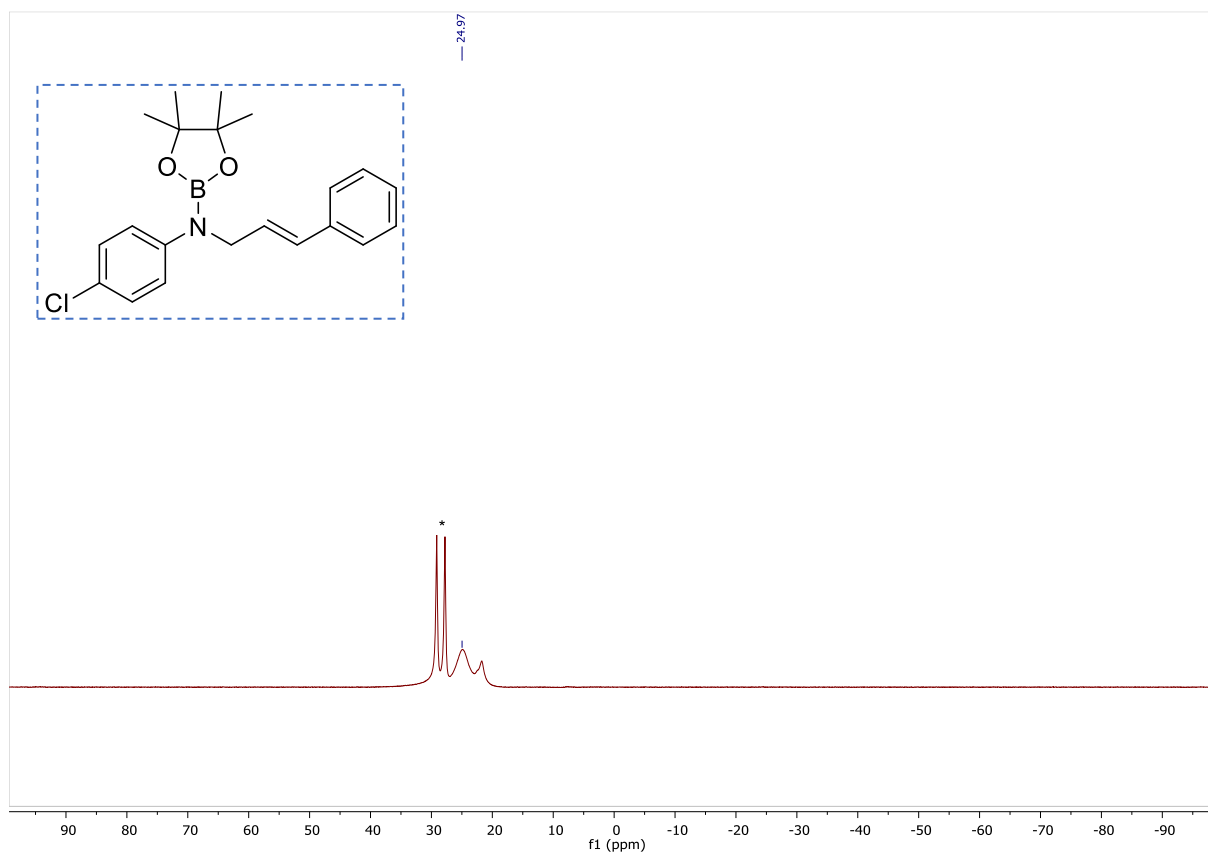


Figure S58 – ^{11}B NMR spectrum of **3k** from crude reaction mixture. *Excess of the HBpin

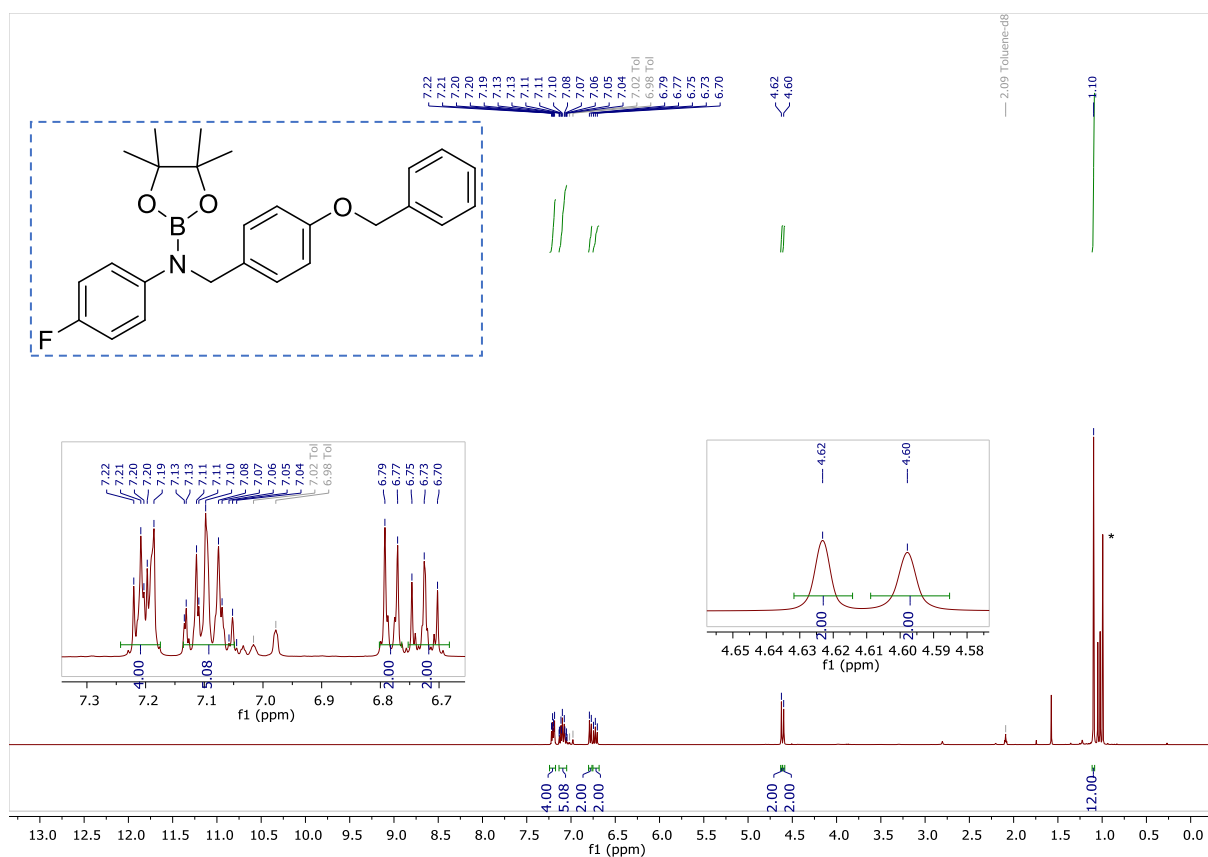


Figure S59 – ¹H NMR spectrum of **3I** from crude reaction mixture. *Excess of the HBpin.

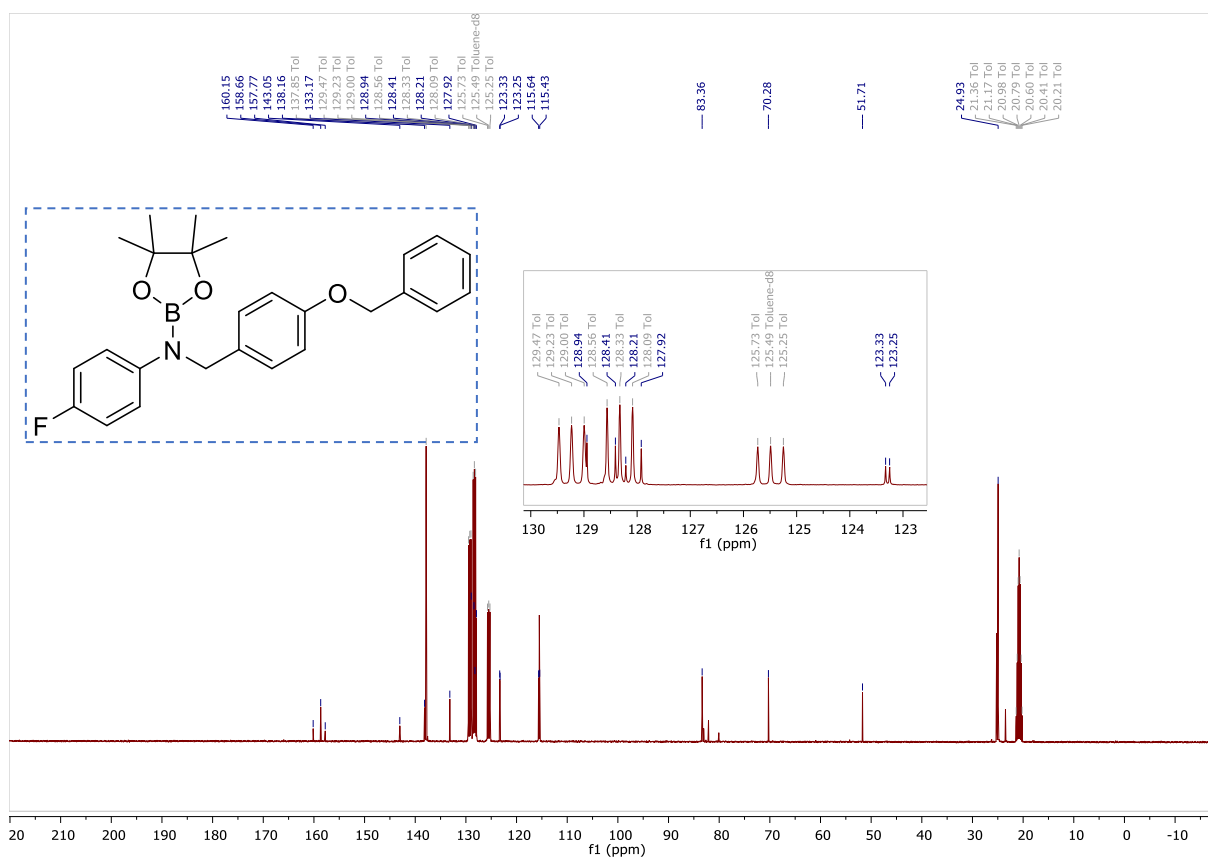


Figure S60 – ¹³C{¹H} NMR spectrum of **3I** from crude reaction mixture.

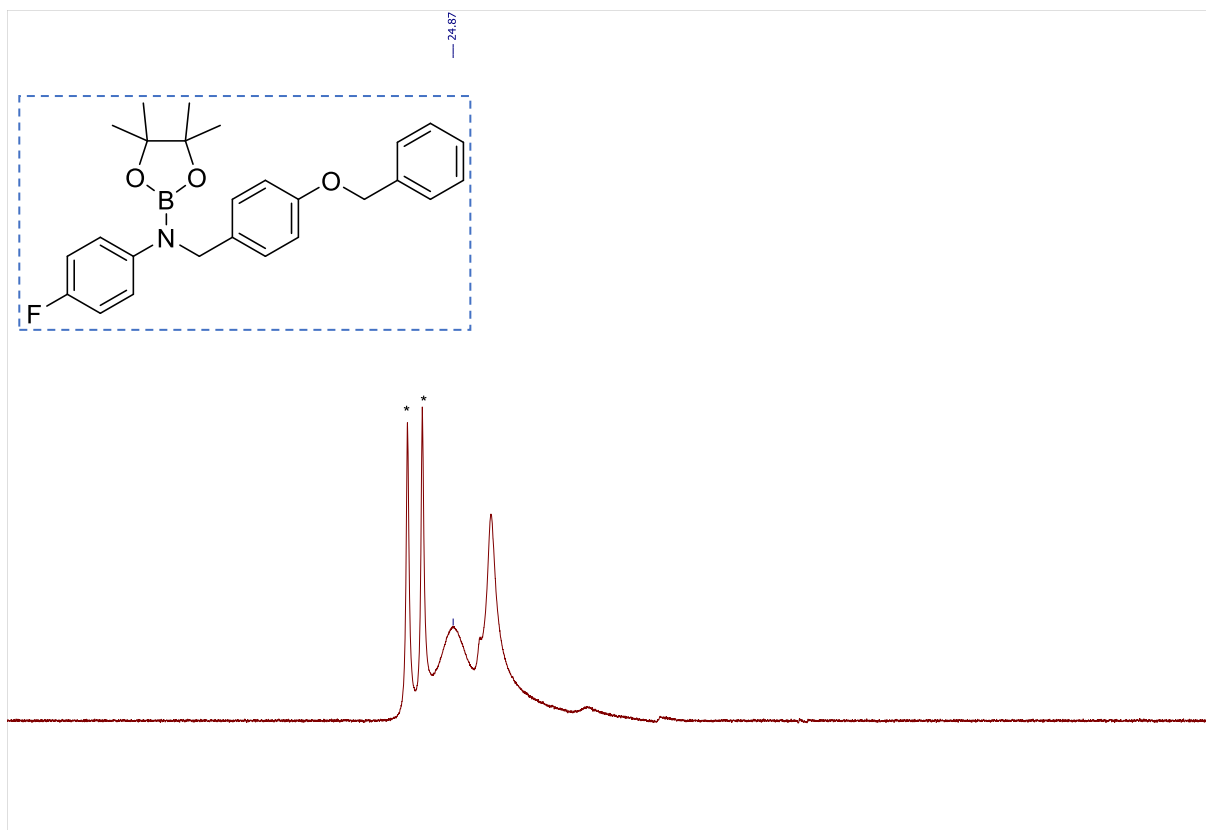


Figure S61 – ^{11}B NMR spectrum of **3l** from crude reaction mixture. *Excess of the HBpin.

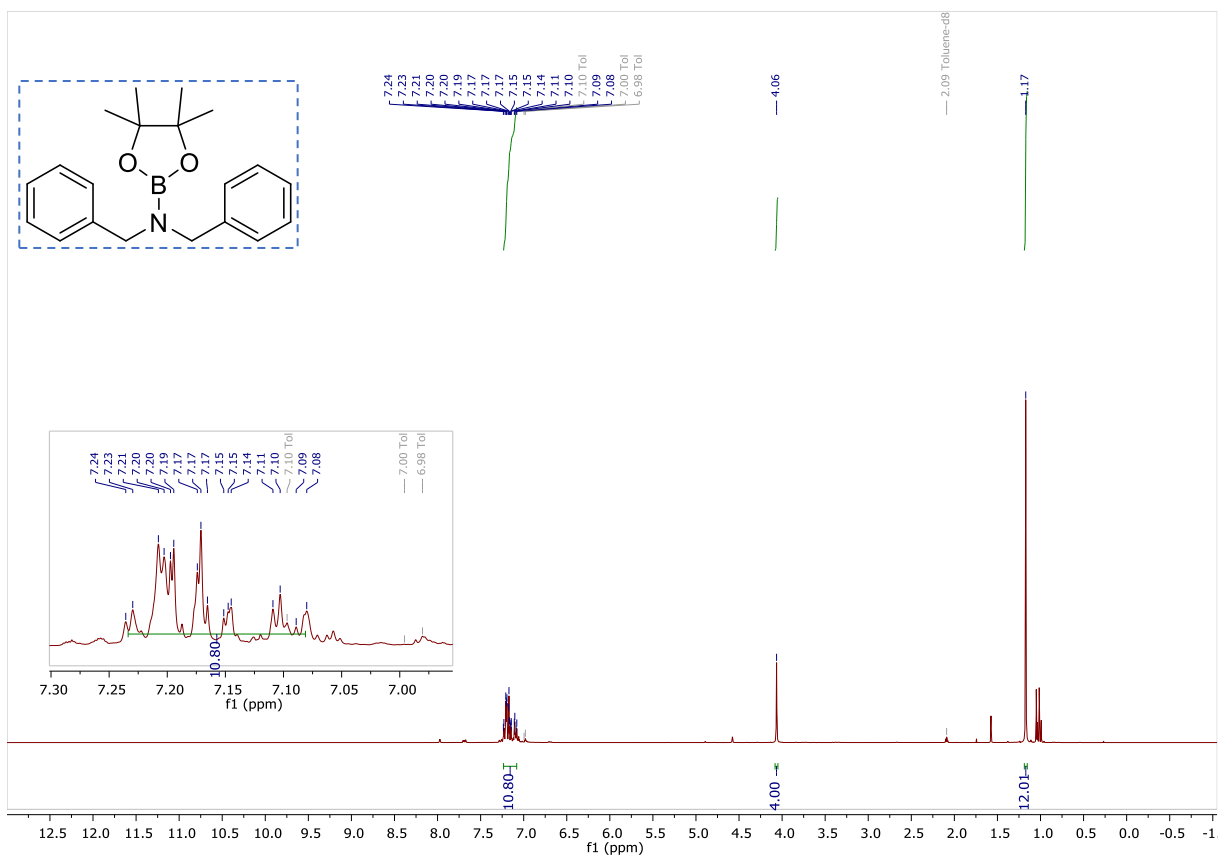


Figure S62 – ^1H NMR spectrum of **3m** from crude reaction mixture.

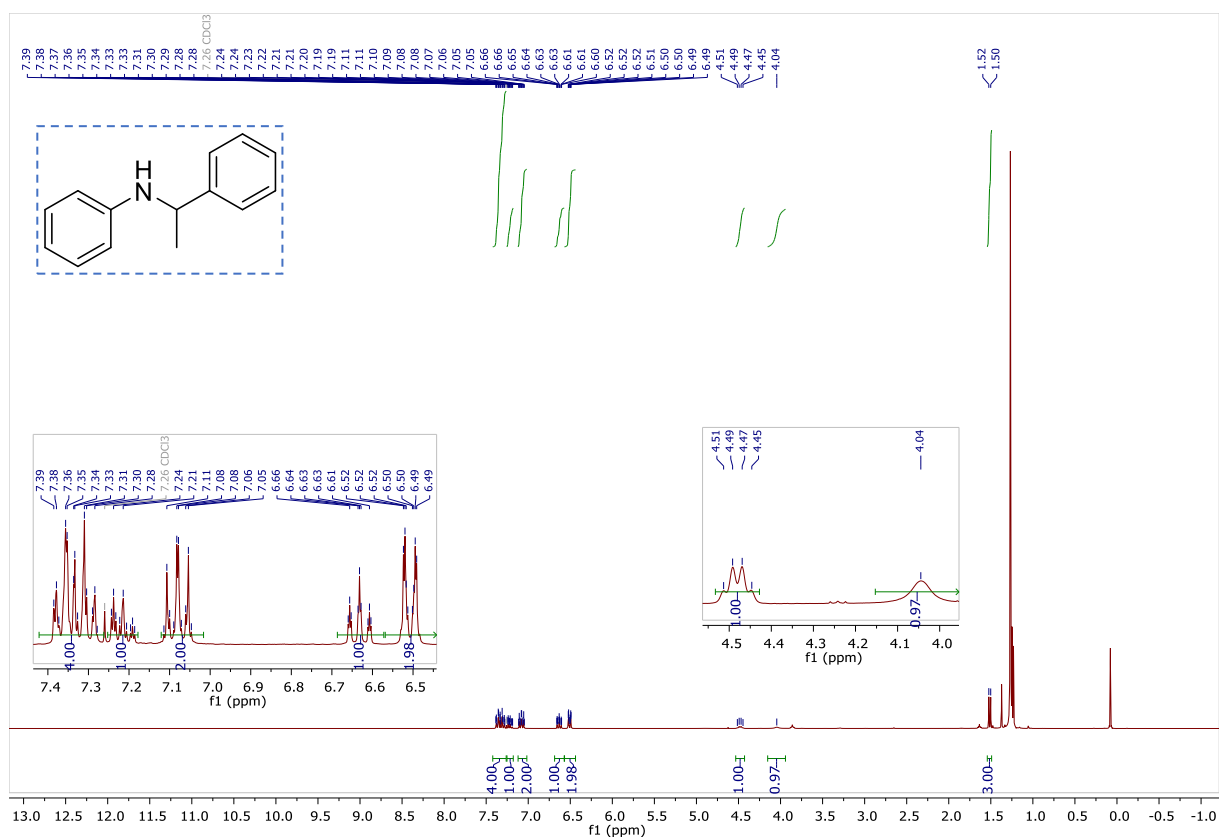


Figure S63 – ^1H NMR spectrum from crude reaction mixture after hydroboration reaction of **1n** with **2**. Sample was prepared in the air atmosphere.

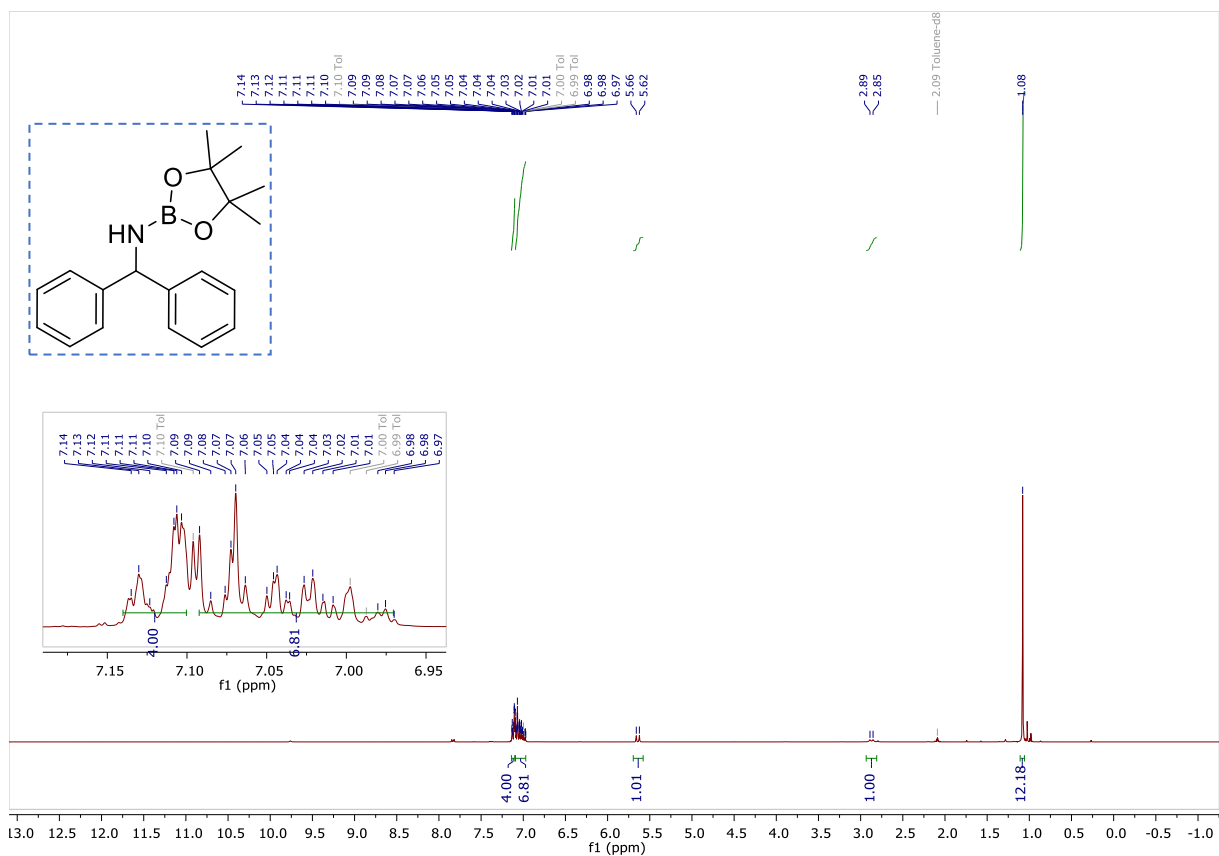
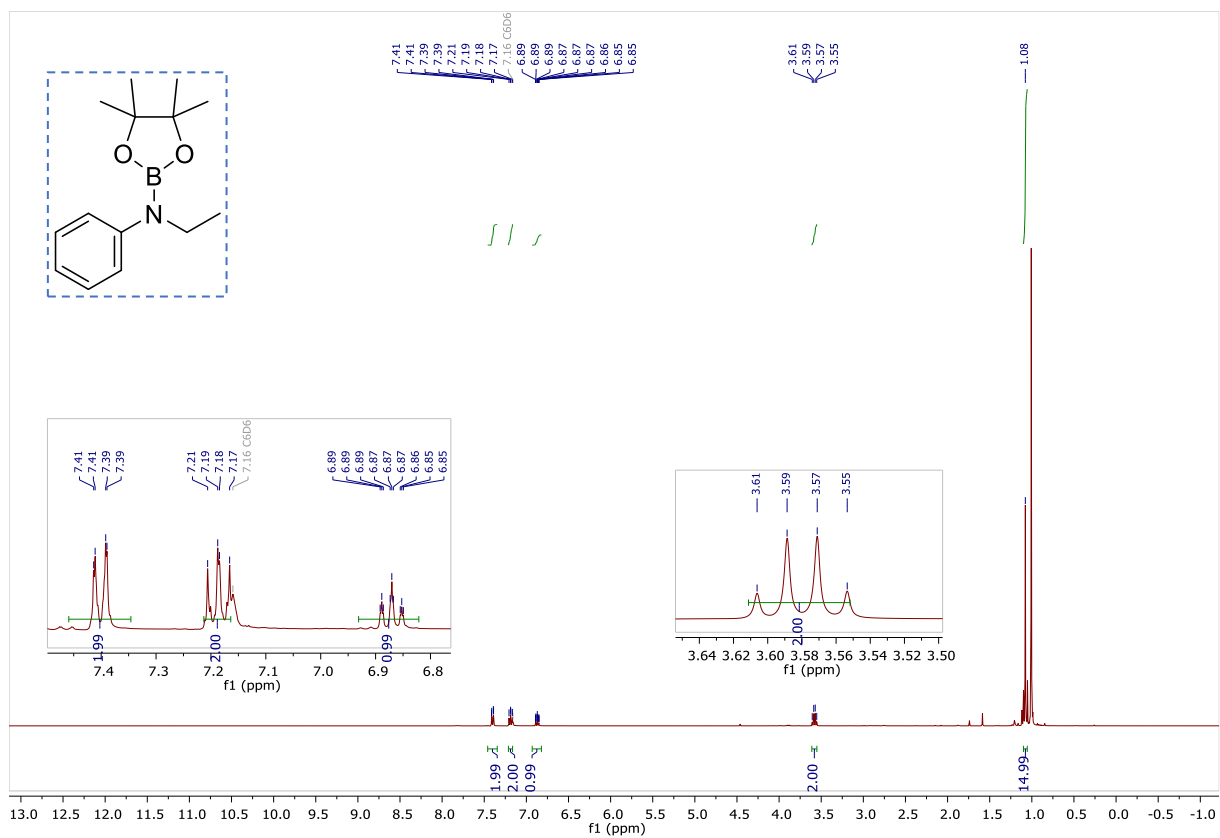
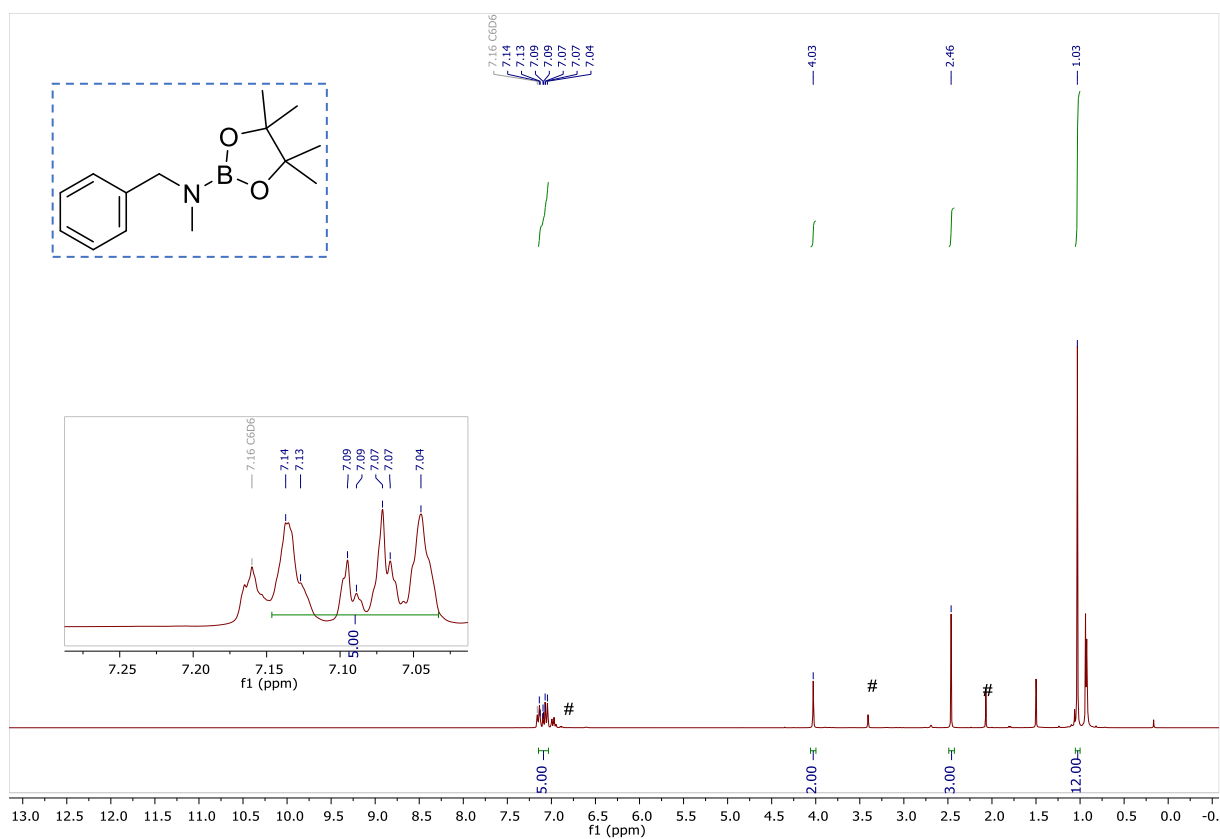


Figure S64 – ^1H NMR spectrum of **3o** from crude reaction mixture.



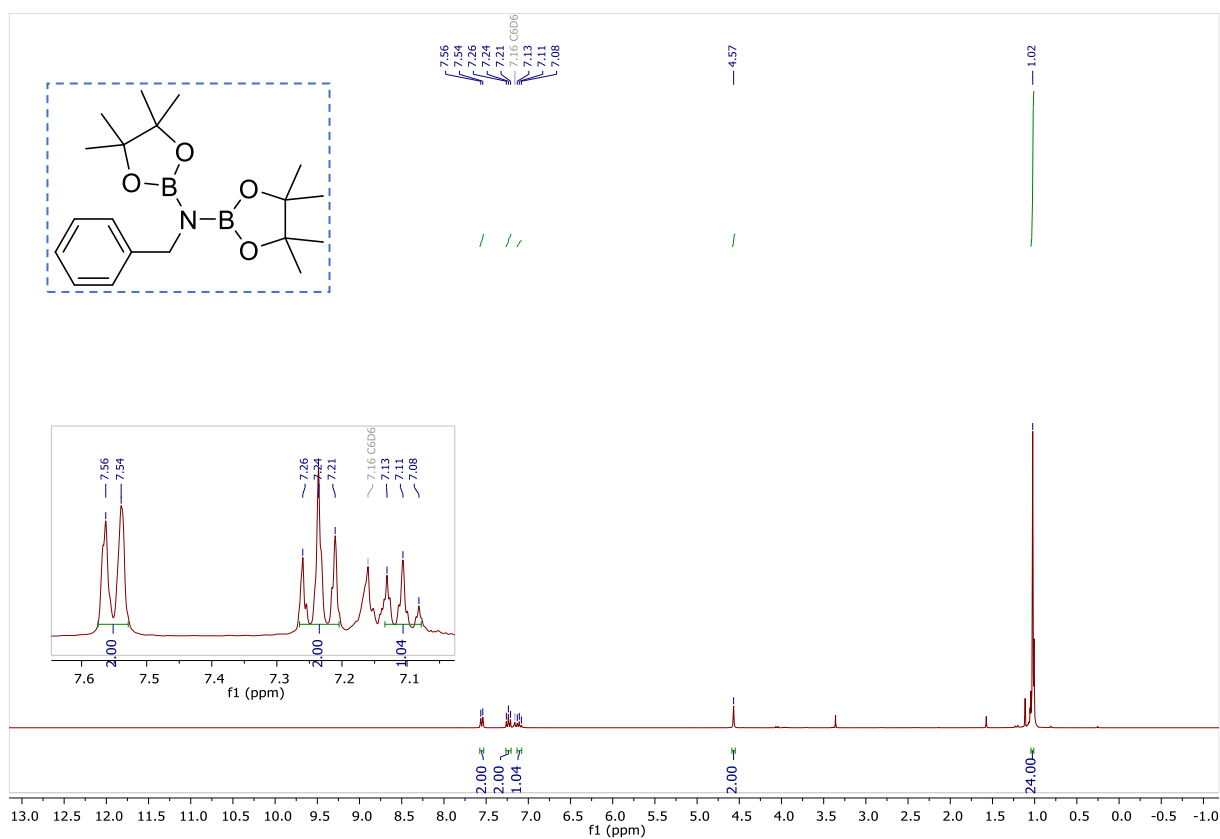


Figure S67 – ¹H NMR spectrum of **6a** from crude reaction mixture.

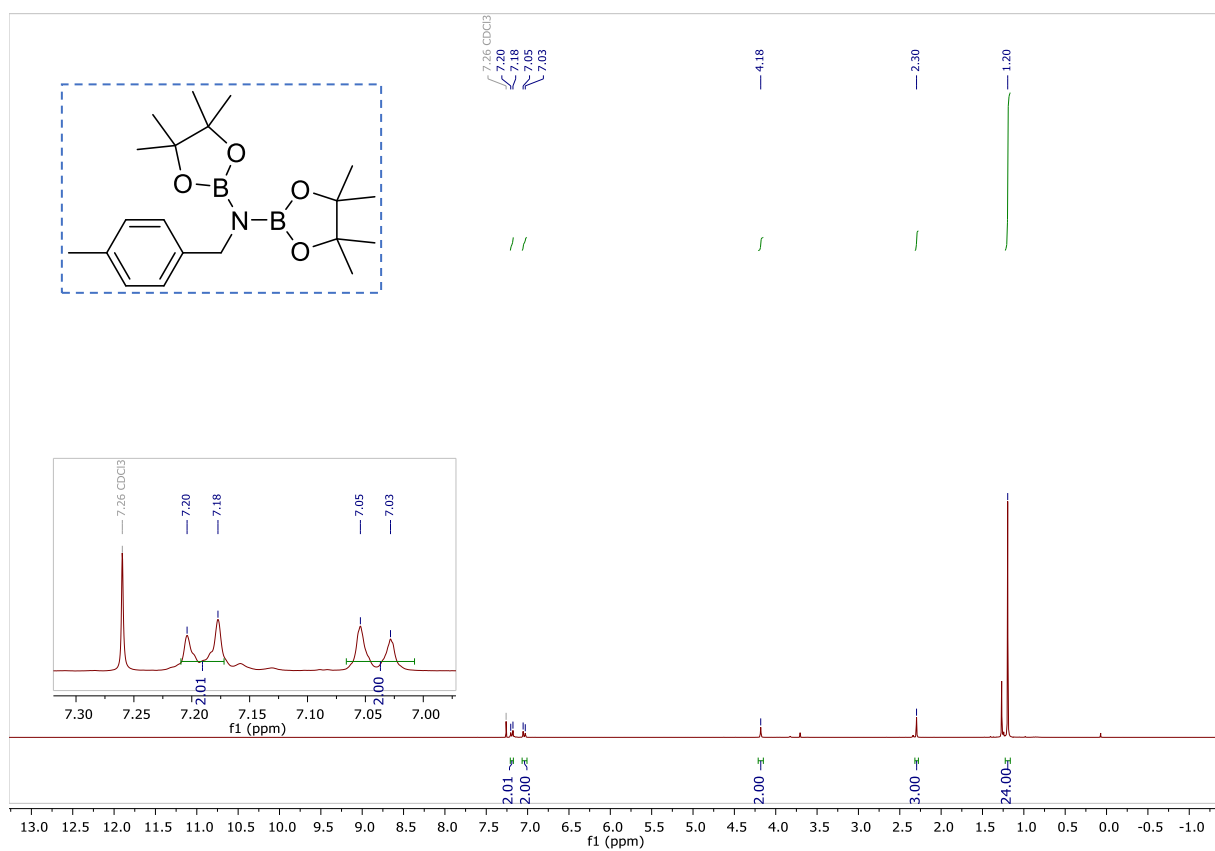


Figure S68 – ¹H NMR spectrum of **6b** from crude reaction mixture.

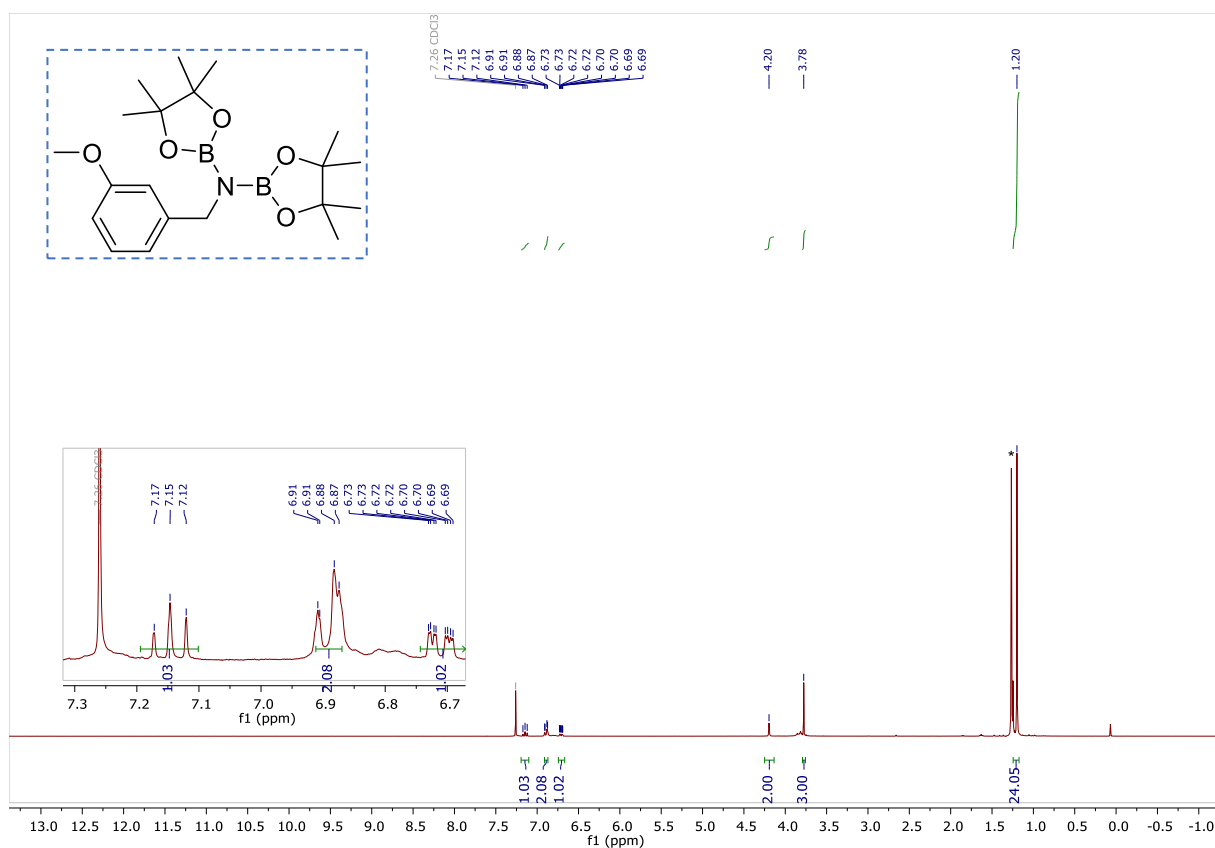


Figure S69 – ¹H NMR spectrum of **6c** from crude reaction mixture. *Excess of the HBpin.

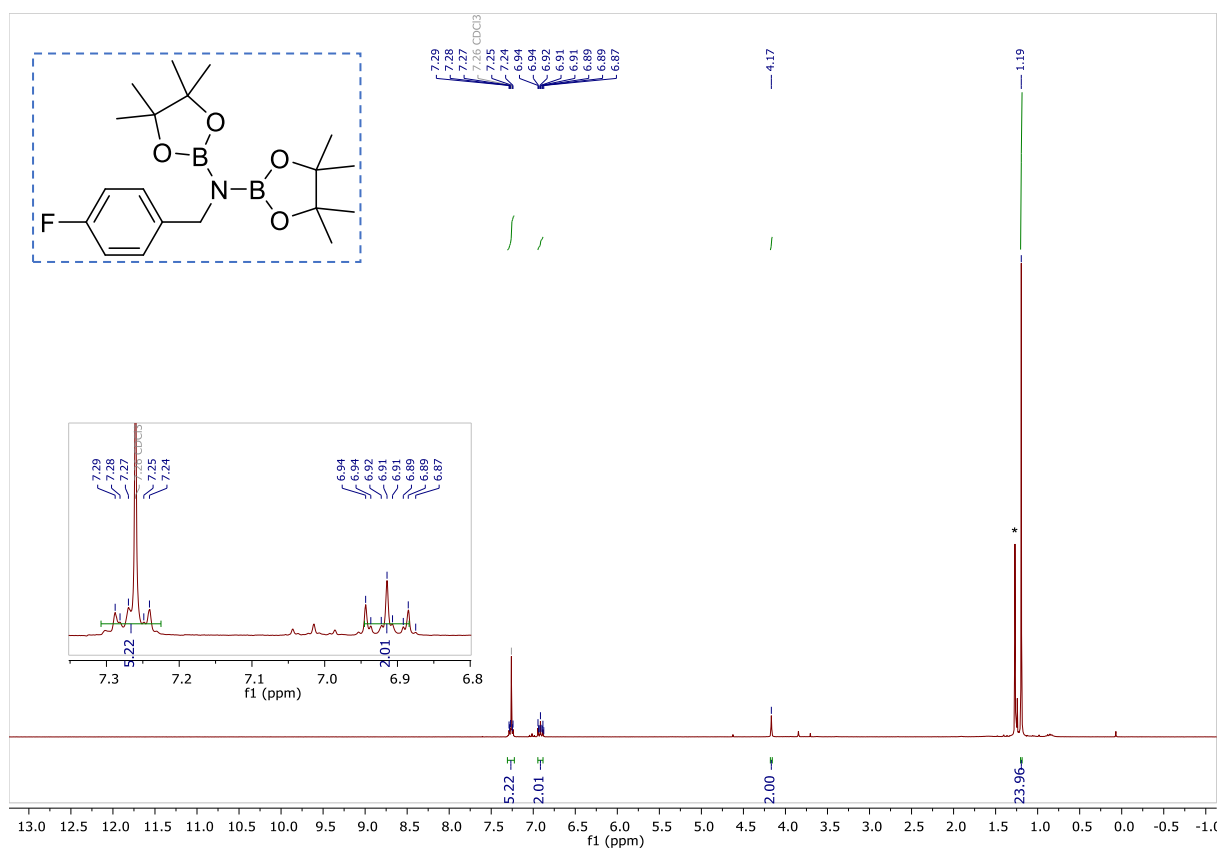


Figure S70 – ¹H NMR spectrum of **6d** from crude reaction mixture. *Excess of the HBpin.

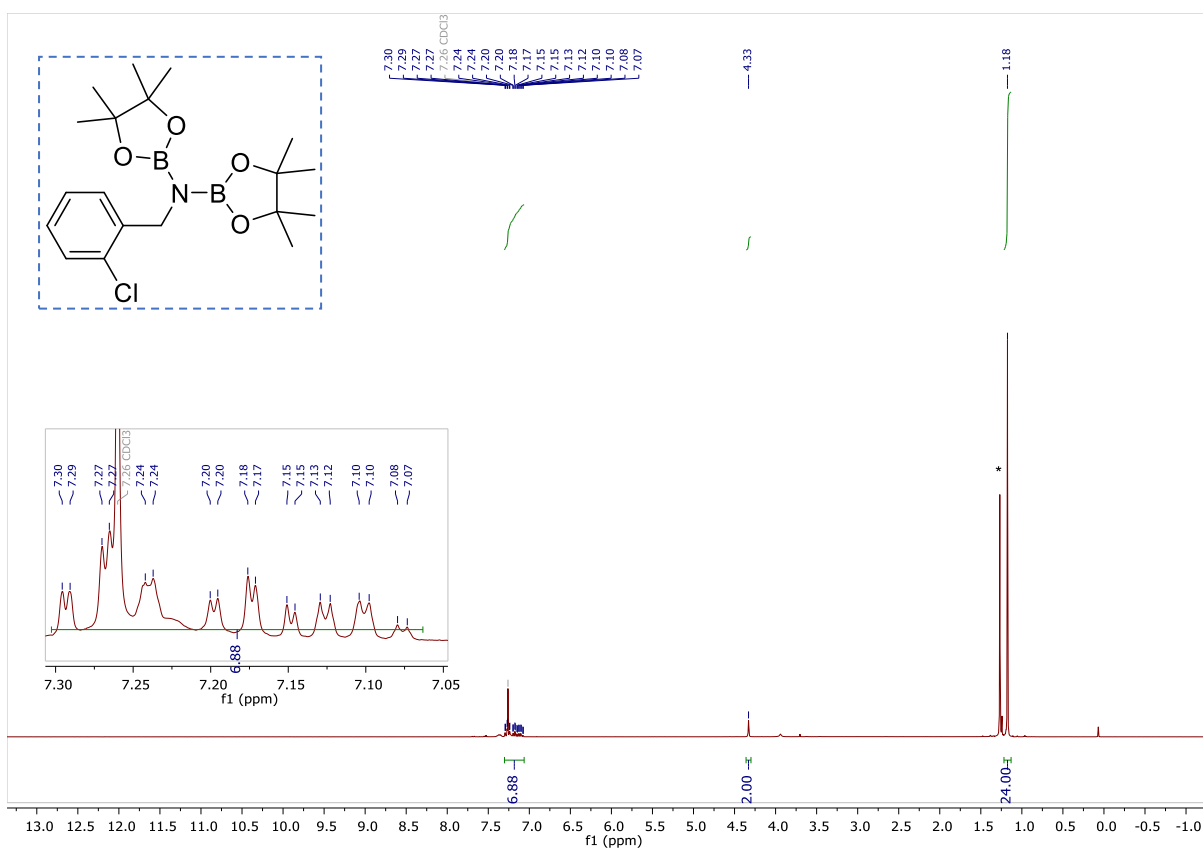


Figure S71 – ¹H NMR spectrum of **6e** from crude reaction mixture. *Excess of the HBpin.

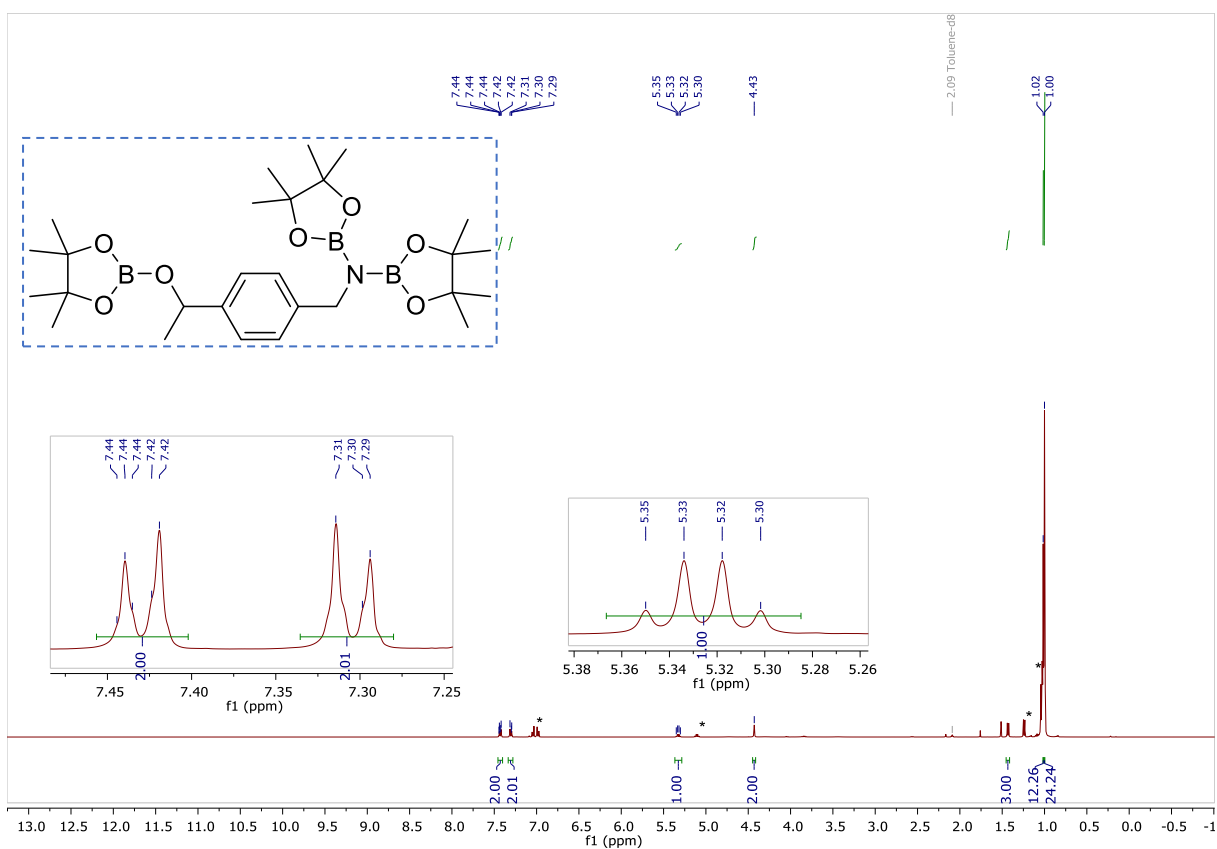


Figure S72 – ¹H NMR spectrum of **6f** from crude reaction mixture. * – 4-(1-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxy)ethyl)benzonitrile.

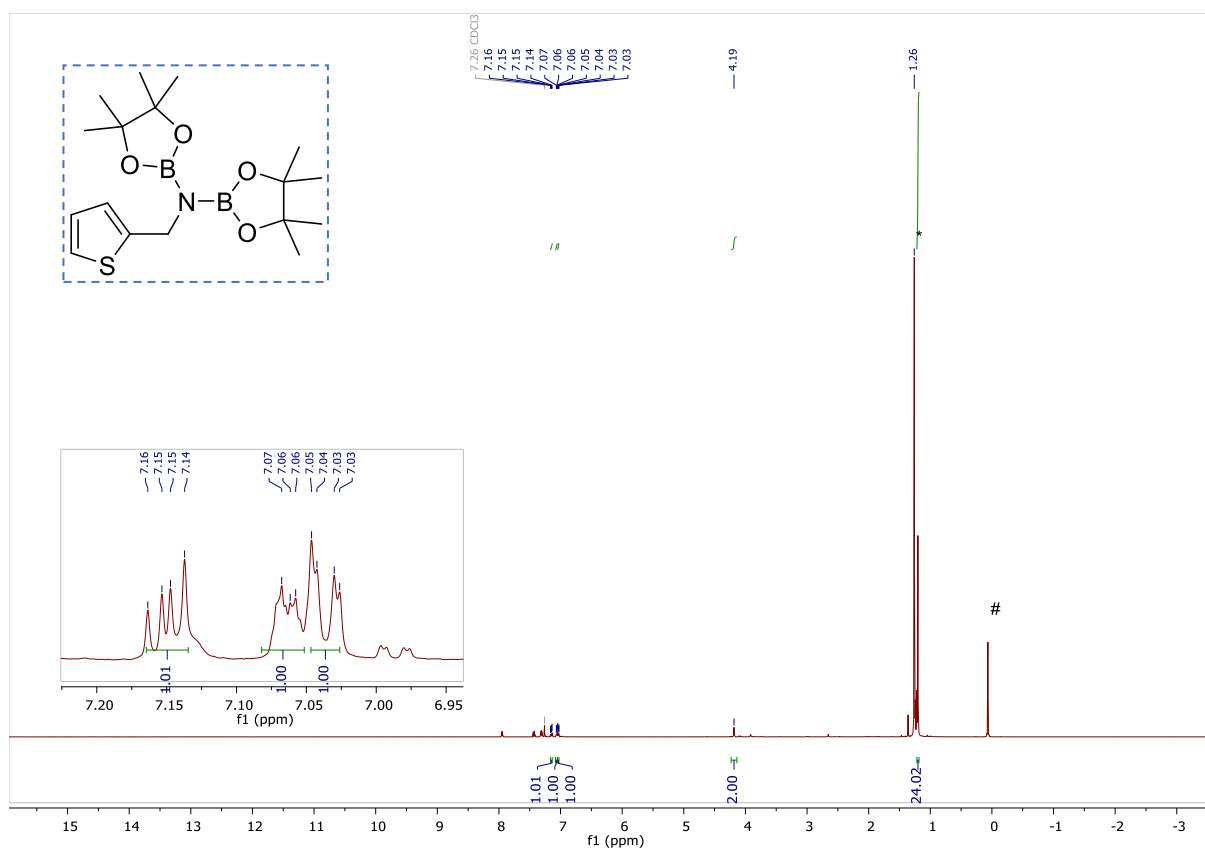


Figure S73 – ^1H NMR spectrum of **6g** from crude reaction mixture. *Excess of the HBpin.
#Grease.

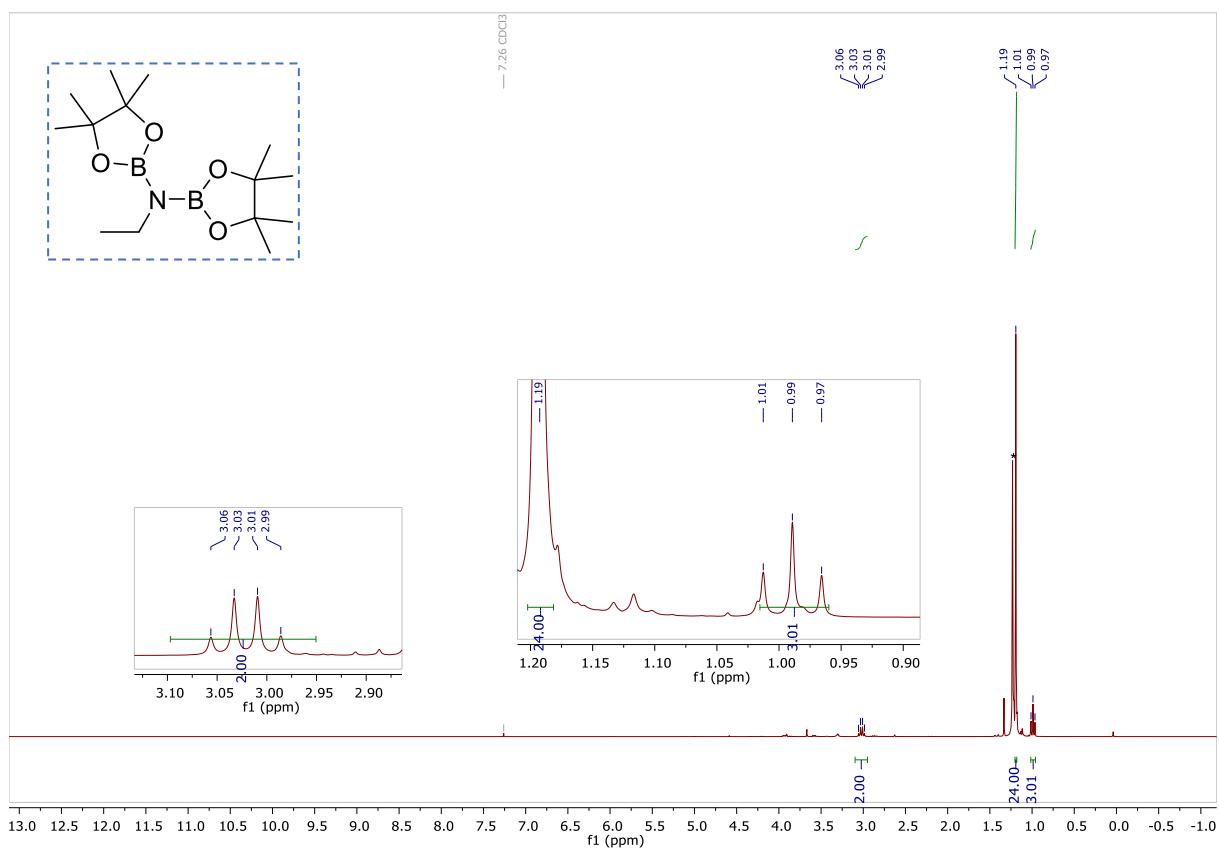


Figure S73 – ^1H NMR spectrum of **6h** from crude reaction mixture. *Excess of the HBpin.

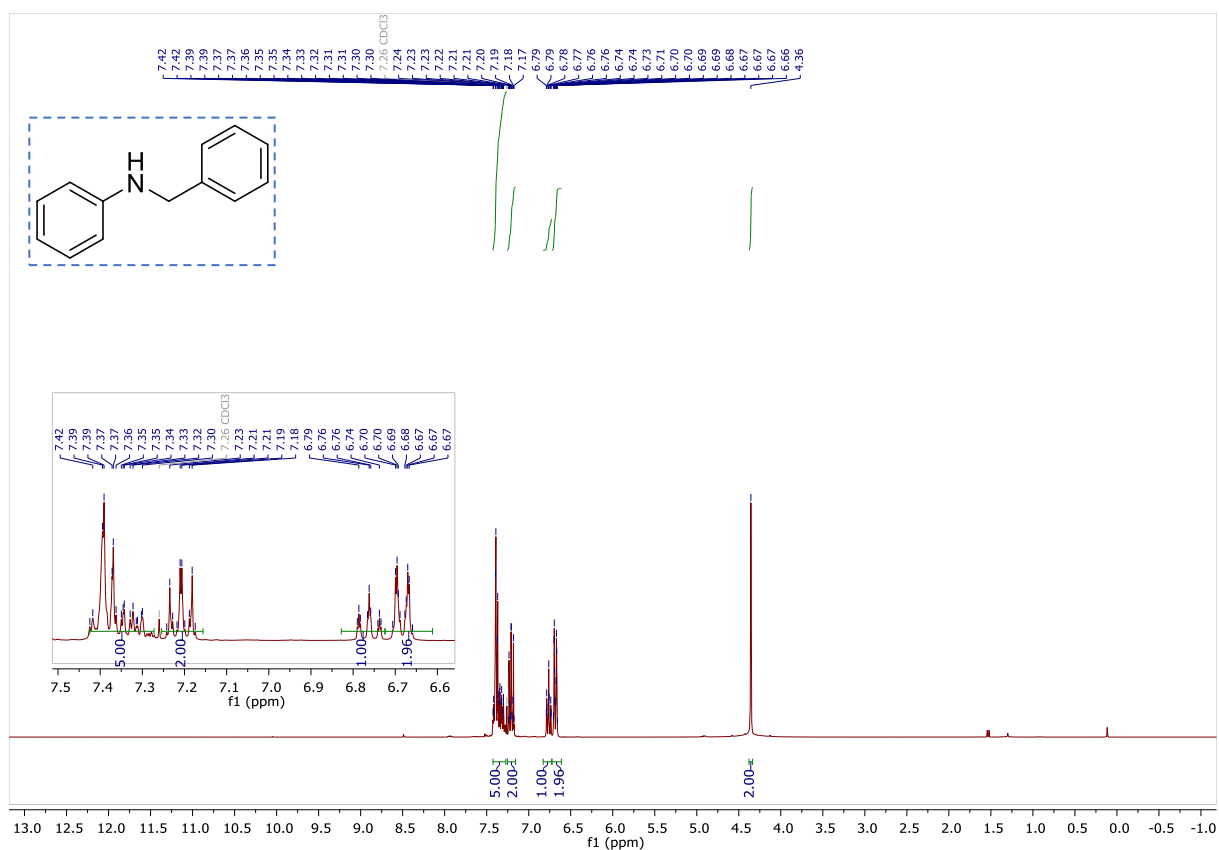


Figure S74 – ¹H NMR spectrum of **4a**.

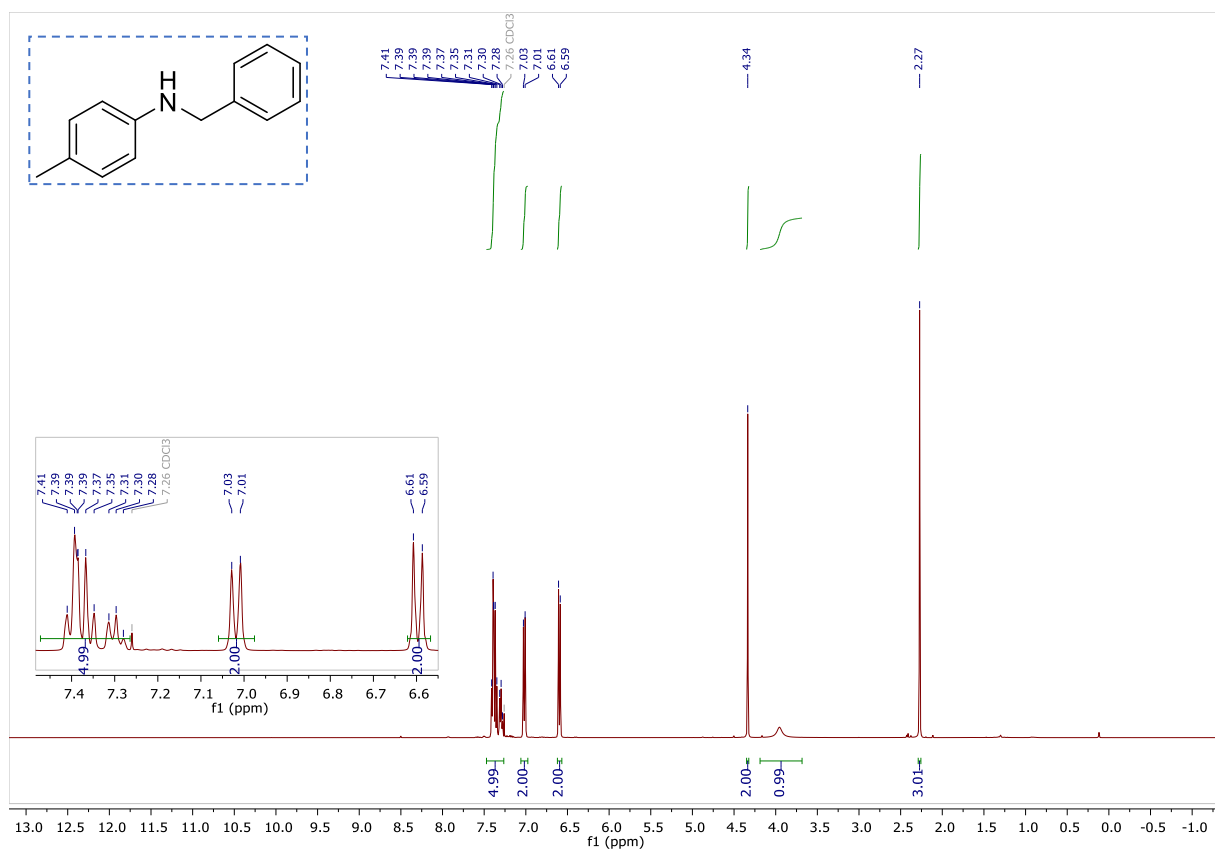


Figure S75 – ¹H NMR spectrum of **4b**.

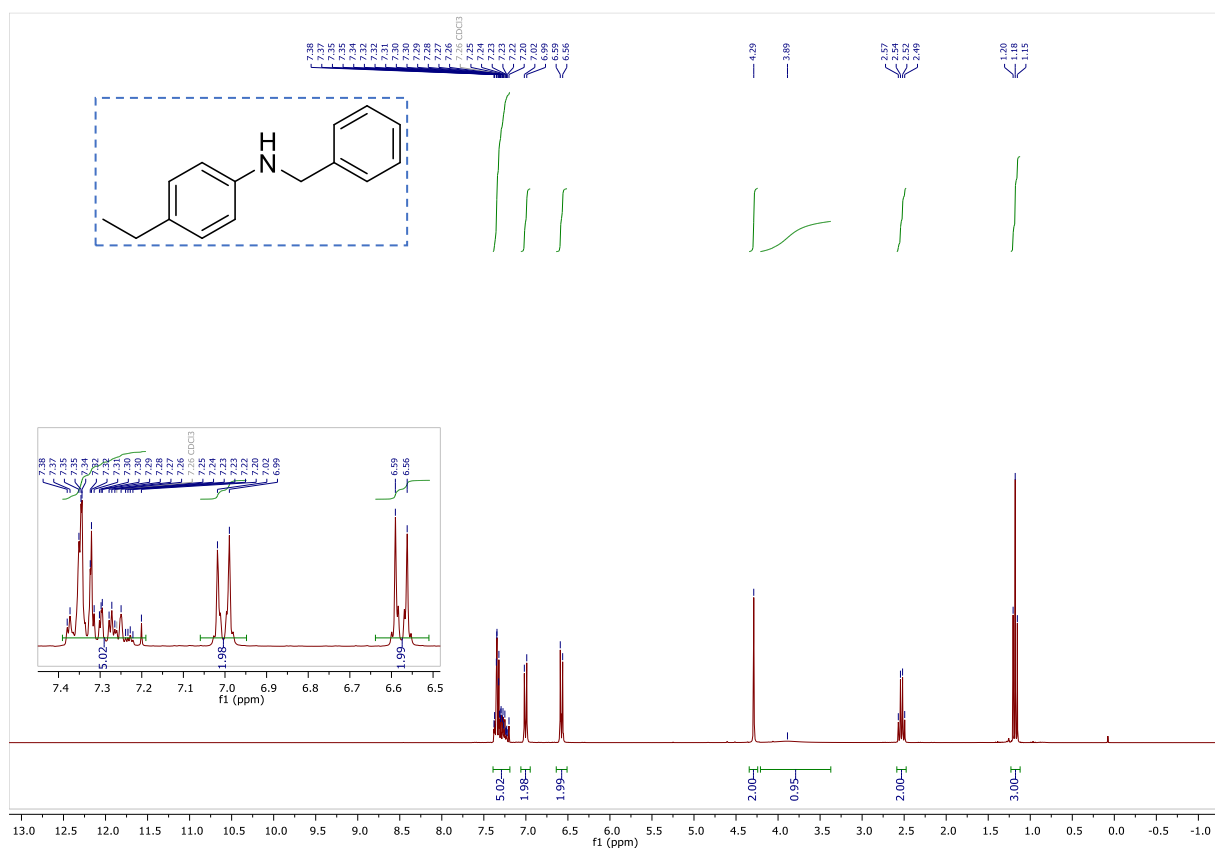


Figure S76 – ¹H NMR spectrum of **4c**.

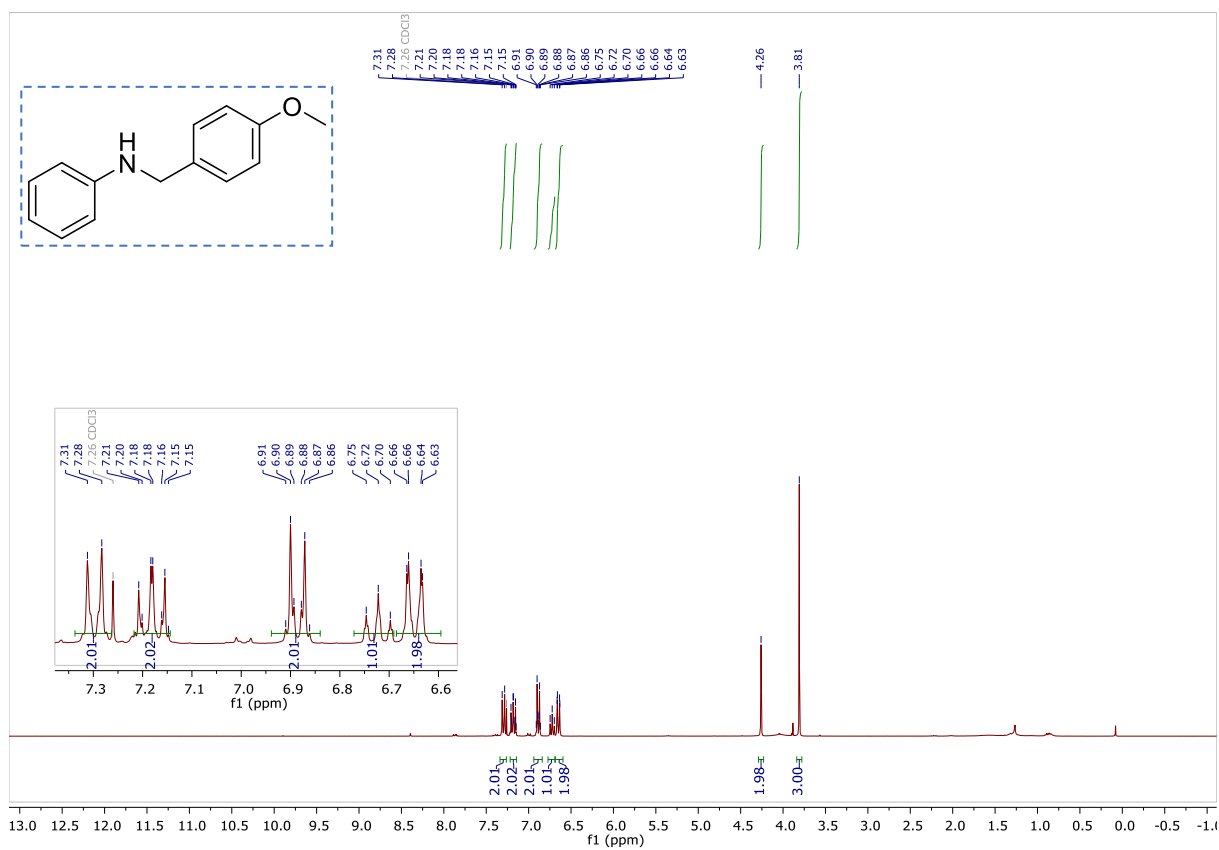


Figure S77 – ¹H NMR spectrum of **4d**.

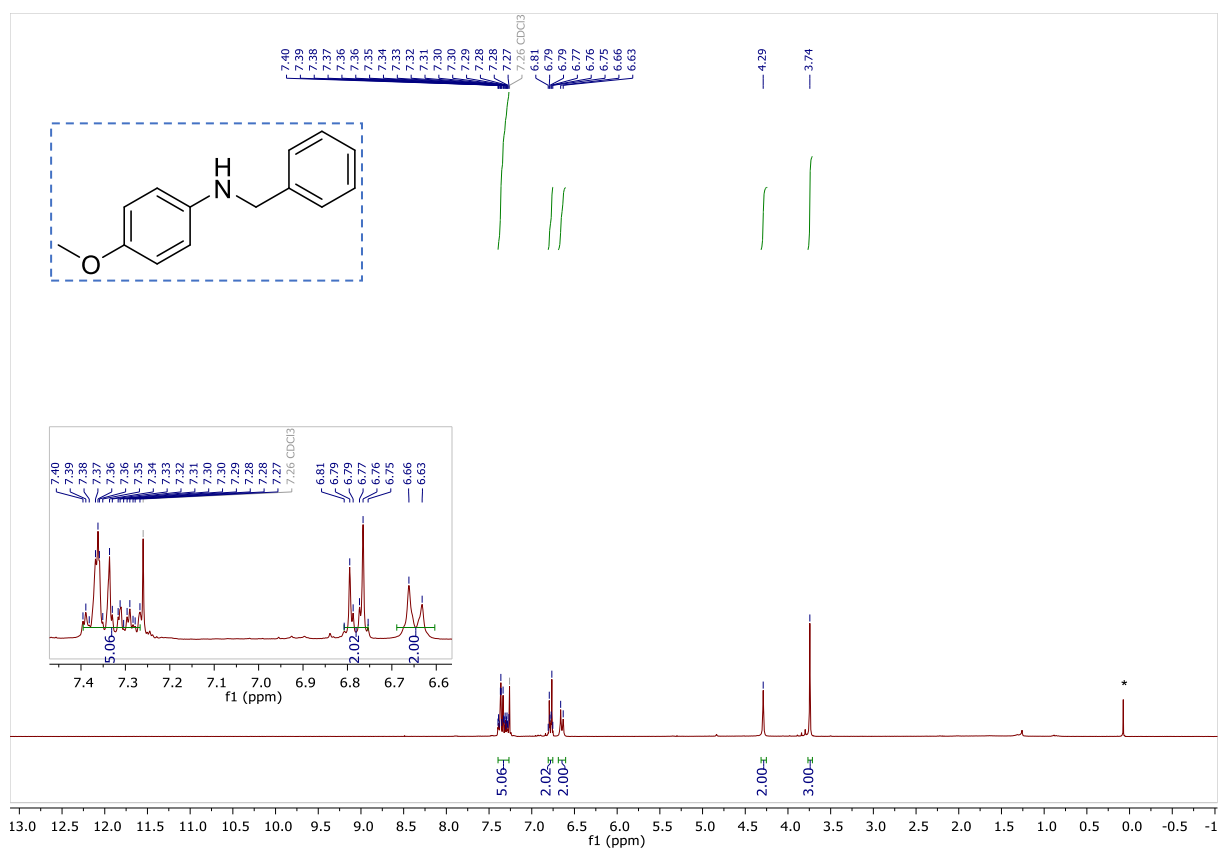


Figure S78 – ¹H NMR spectrum of 4e. *Grease.

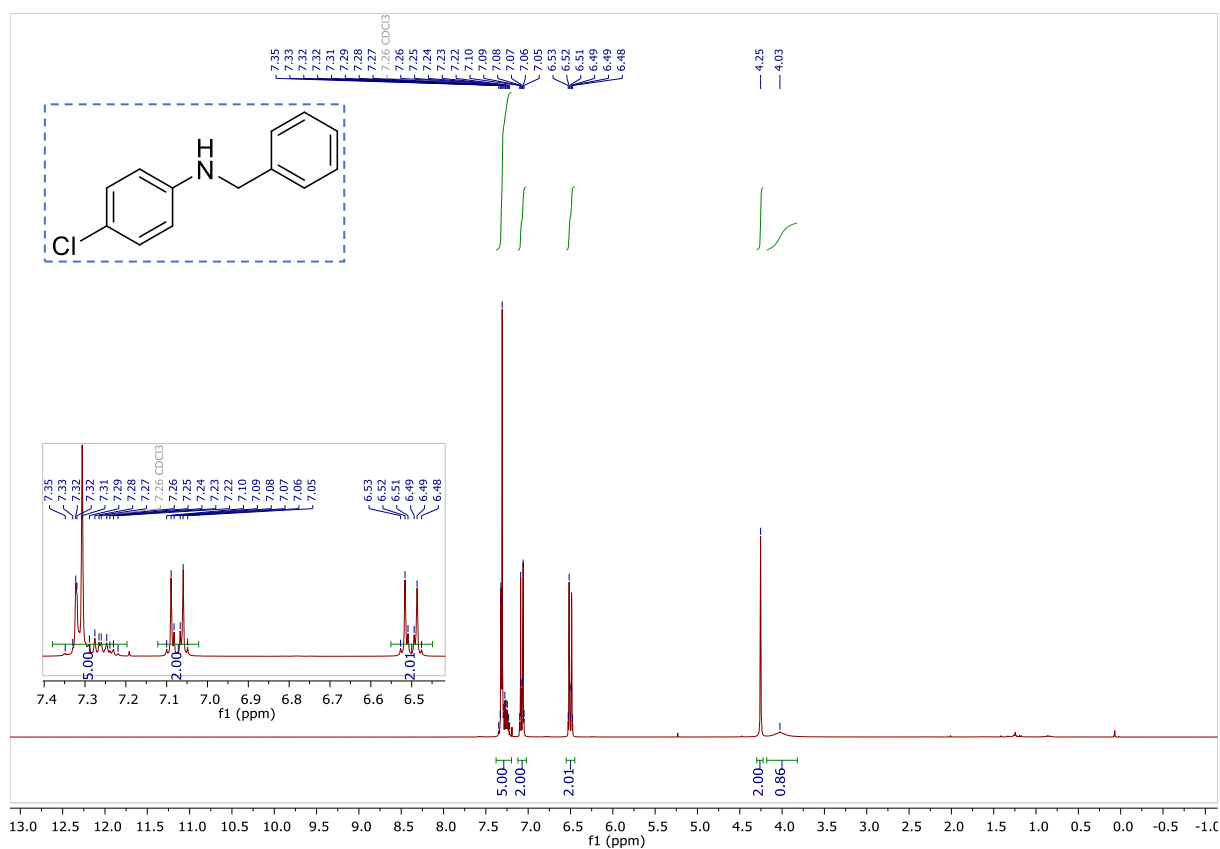


Figure S79 – ¹H NMR spectrum of 4f.

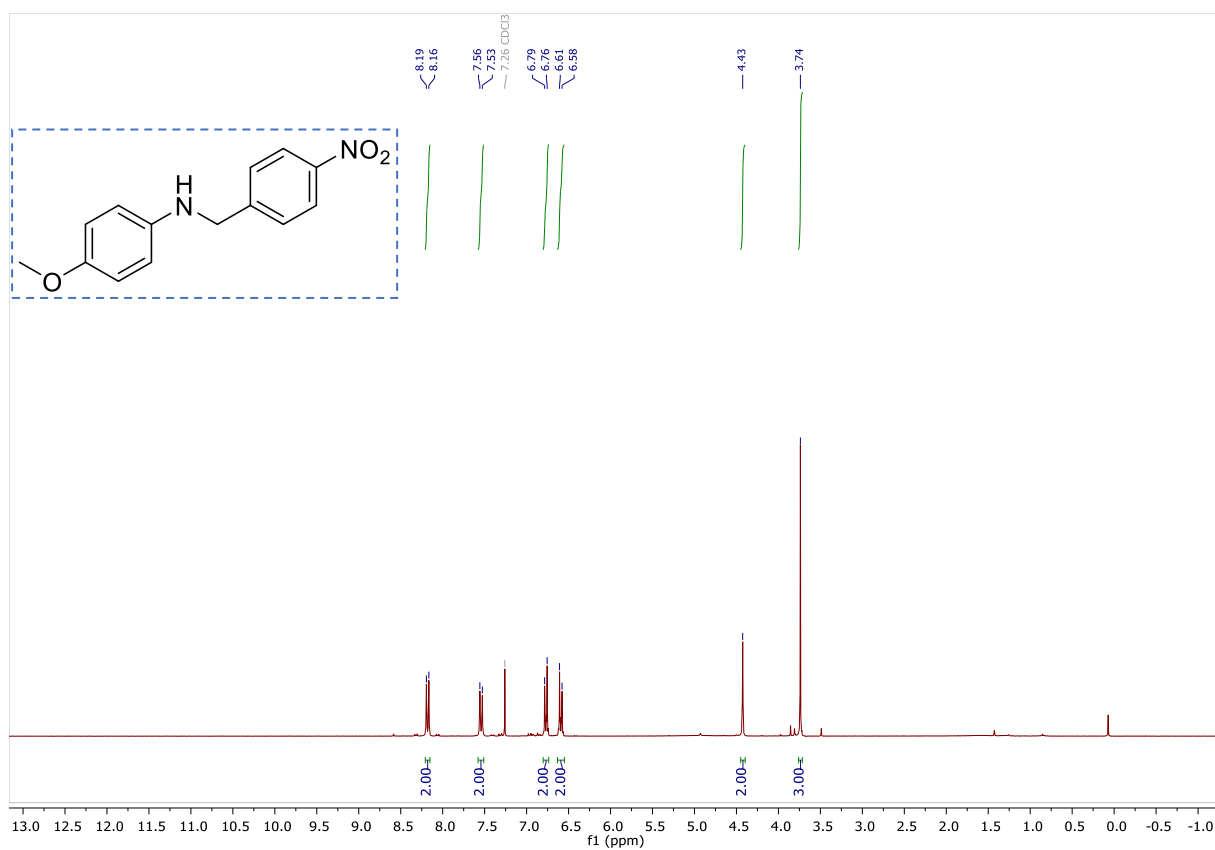


Figure S80 – ¹H NMR spectrum of 4g.

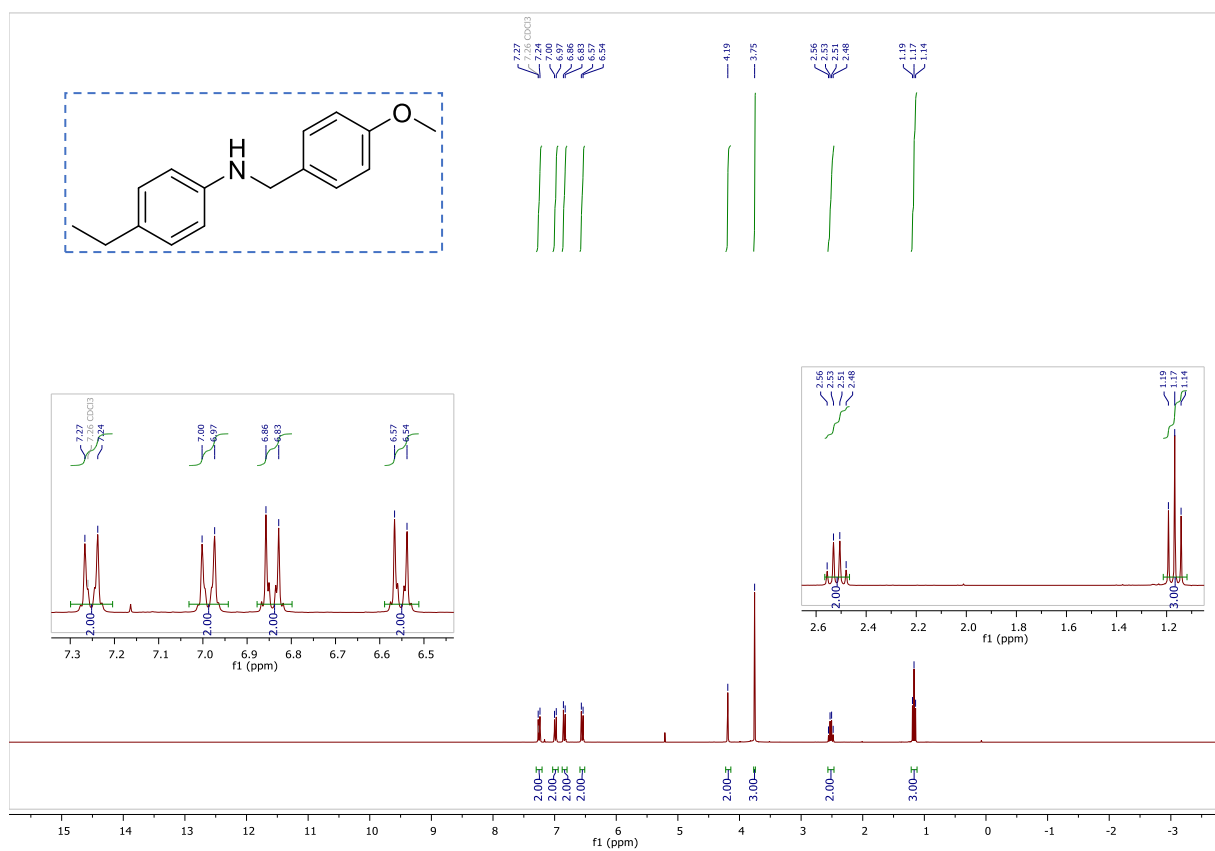


Figure S81 – ¹H NMR spectrum of 4h.

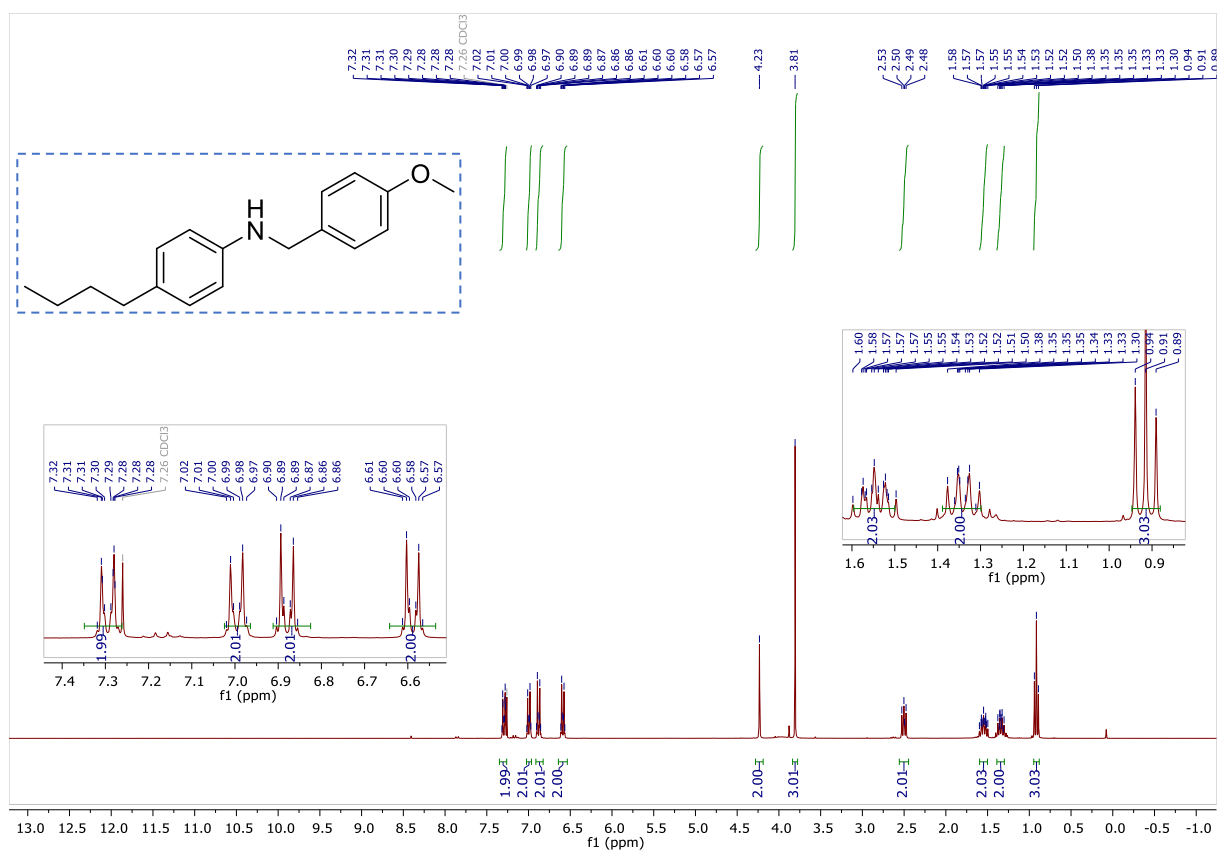


Figure S82 – ¹H NMR spectrum of 4i.

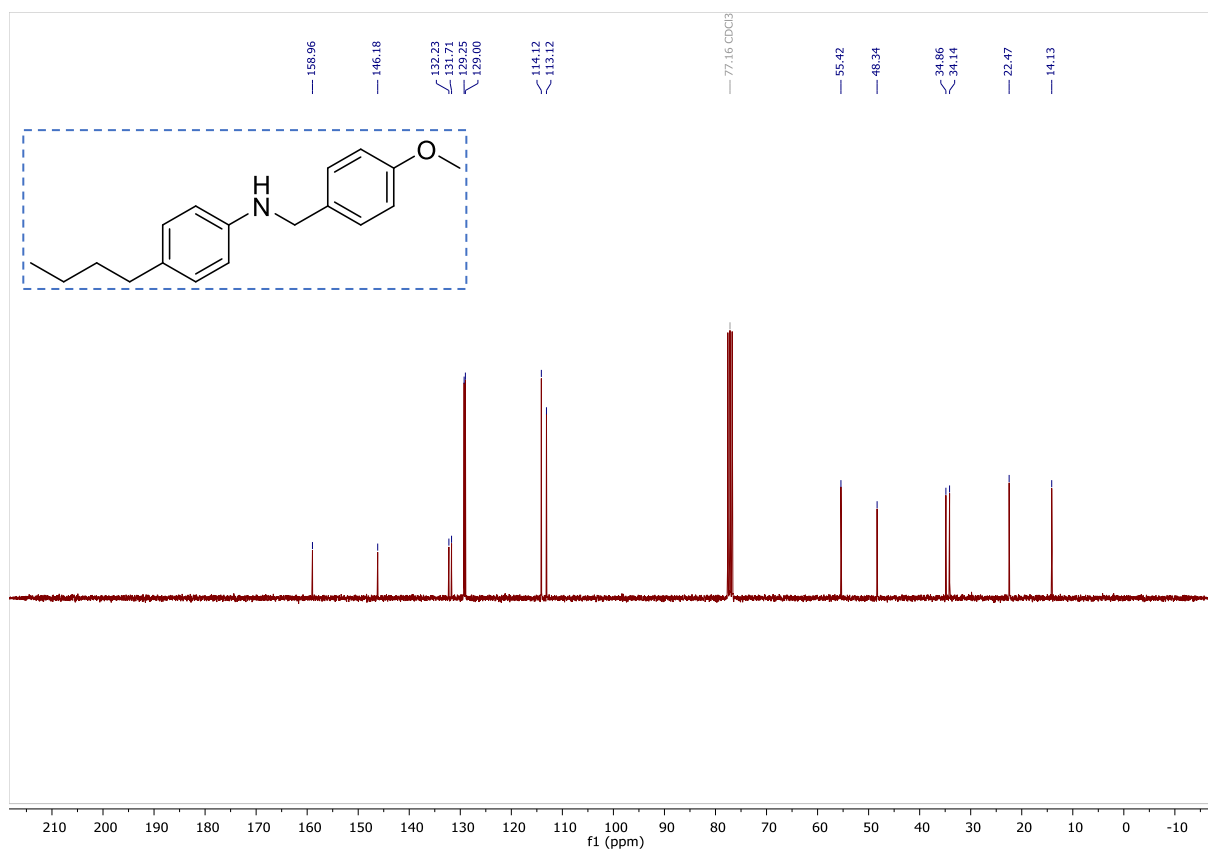


Figure S83 – ¹³C{¹H} NMR spectrum of 4i.

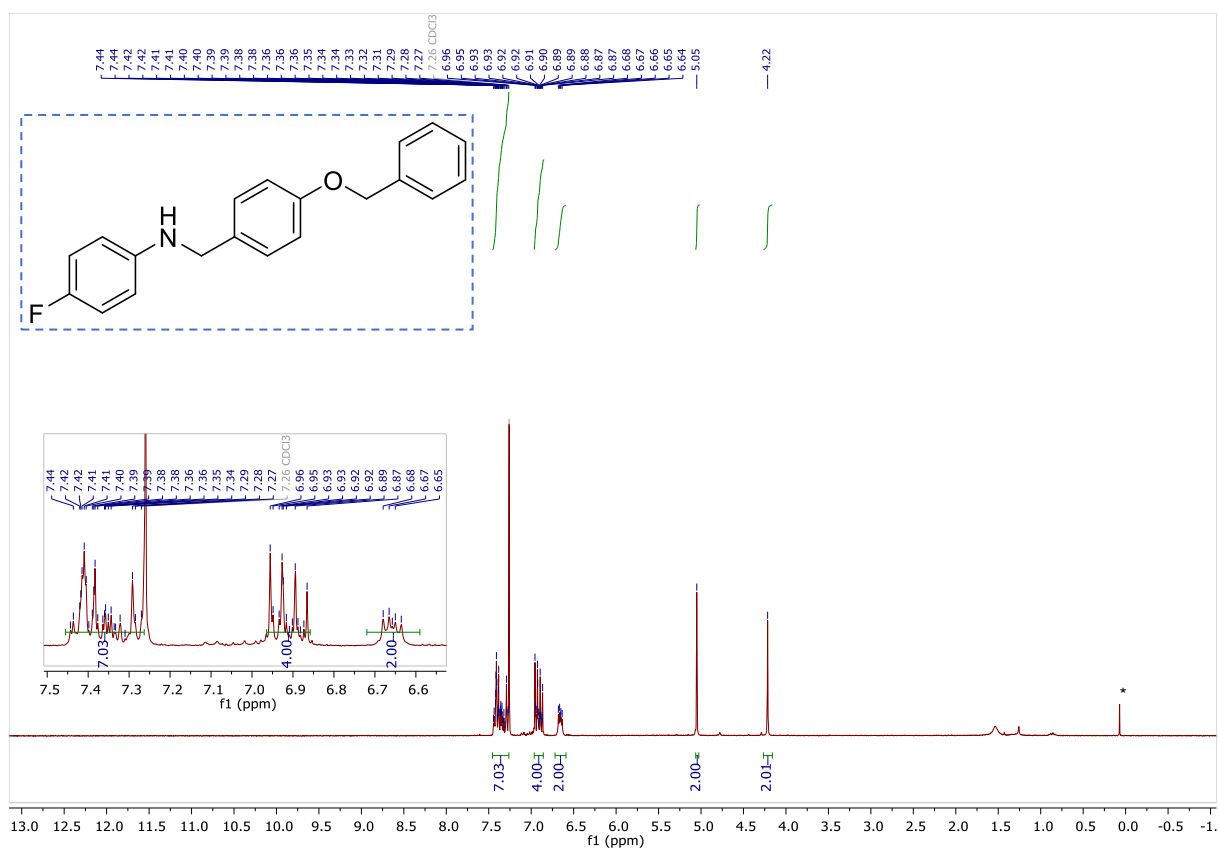


Figure S86 – ¹H NMR spectrum of 4l. *Grease.

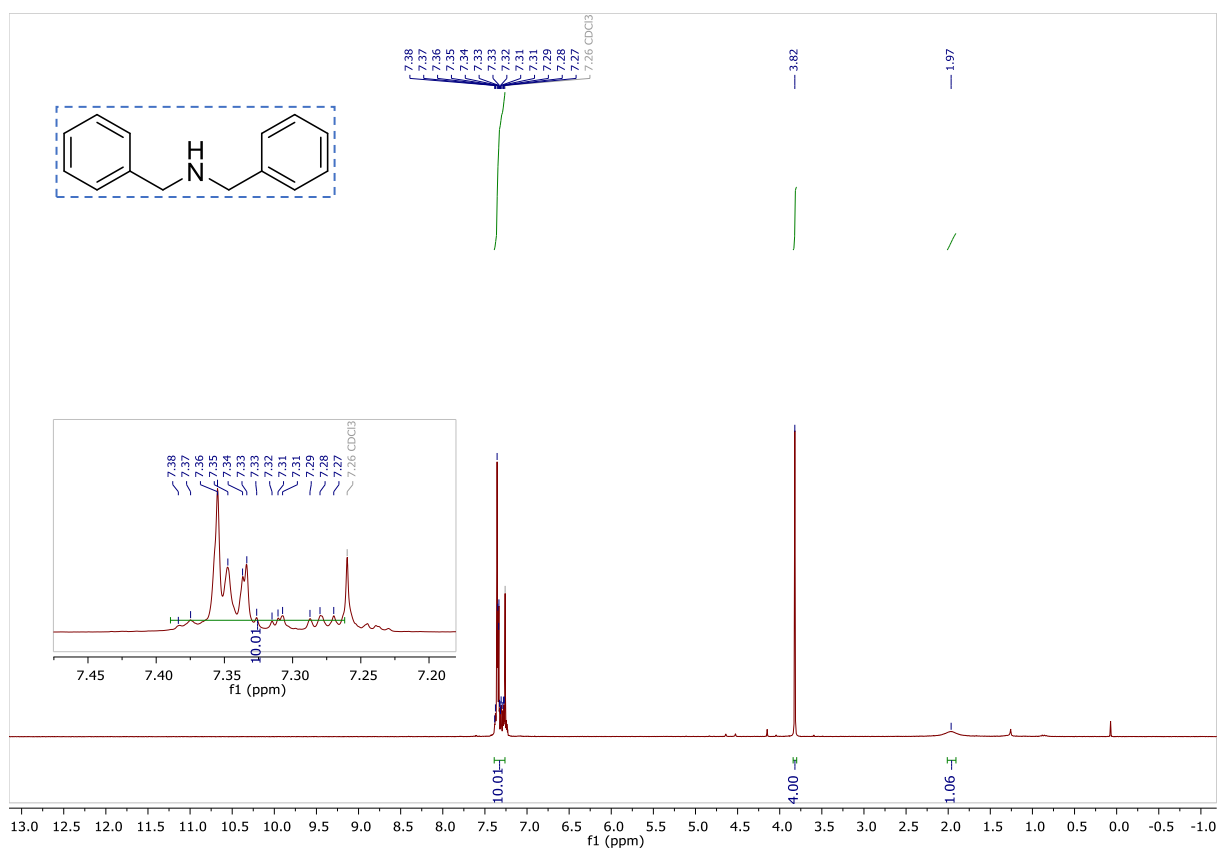


Figure S87 – ¹H NMR spectrum of 4m.

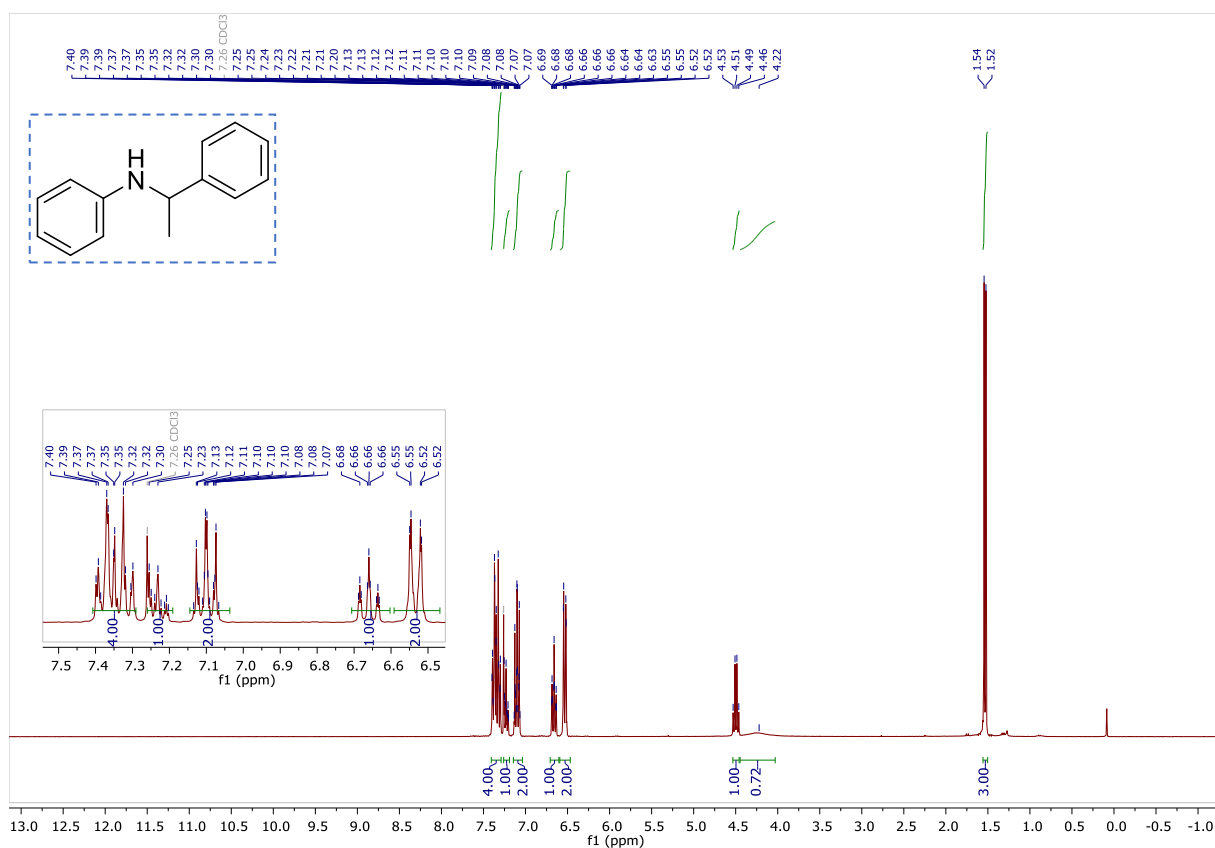


Figure S88 – ¹H NMR spectrum of **4n**. *Grease.

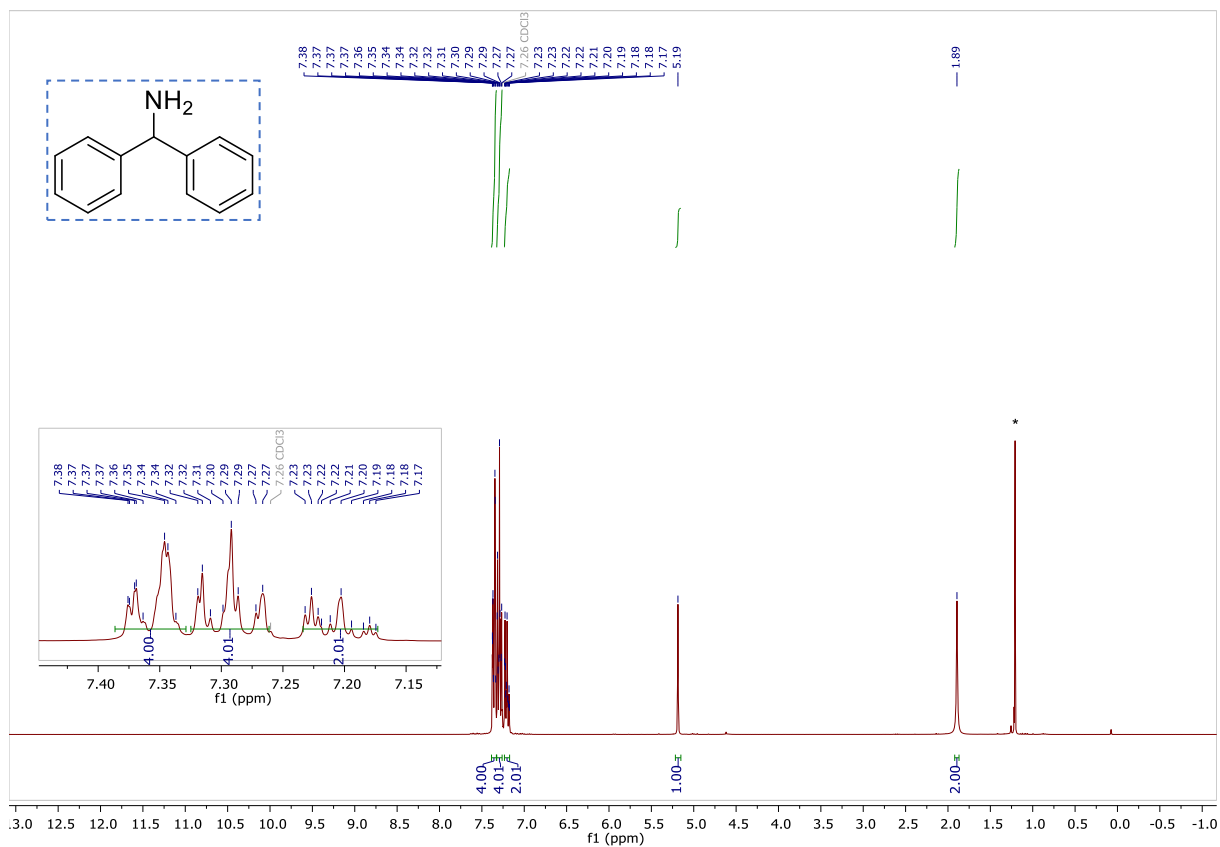


Figure S89 – ¹H NMR spectrum of **4o**. *Impurity – pinacol.

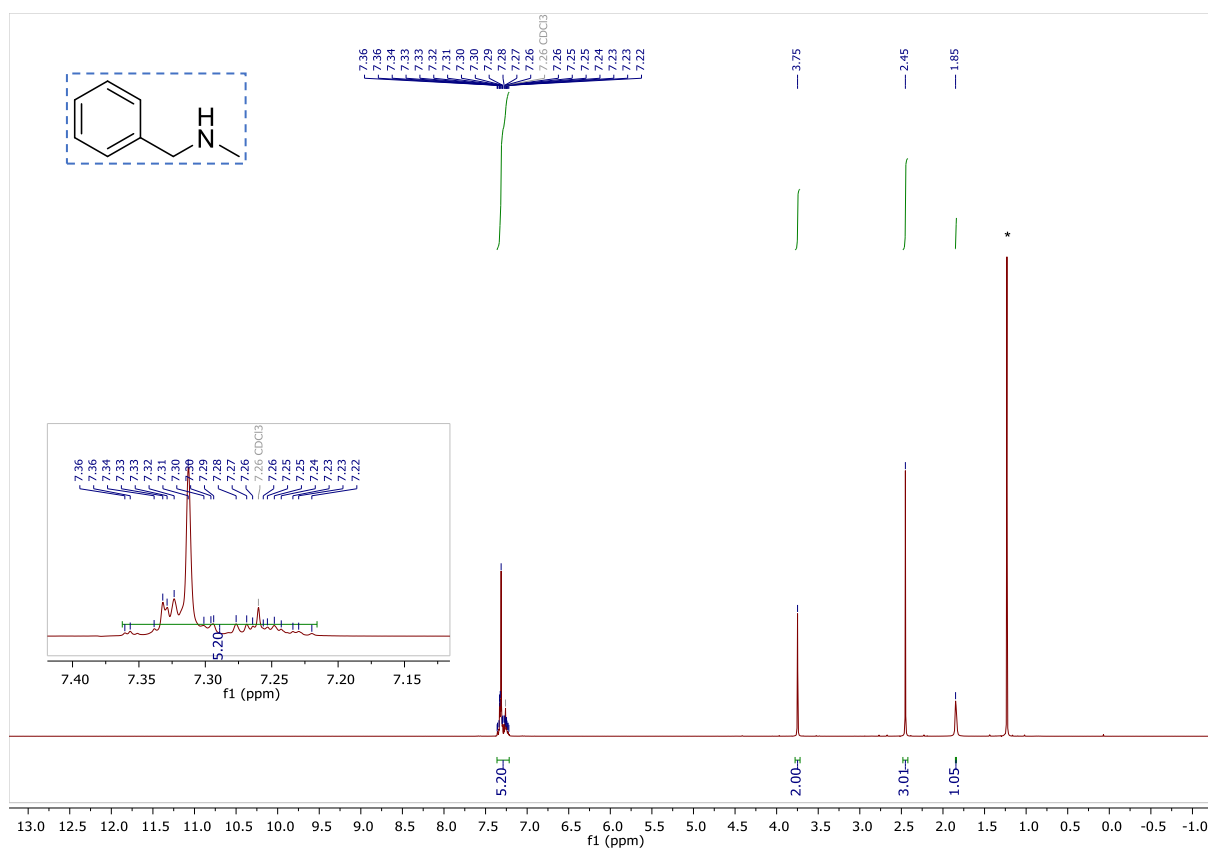


Figure S90 – ¹H NMR spectrum of **4p**. *Impurity – pinacol.

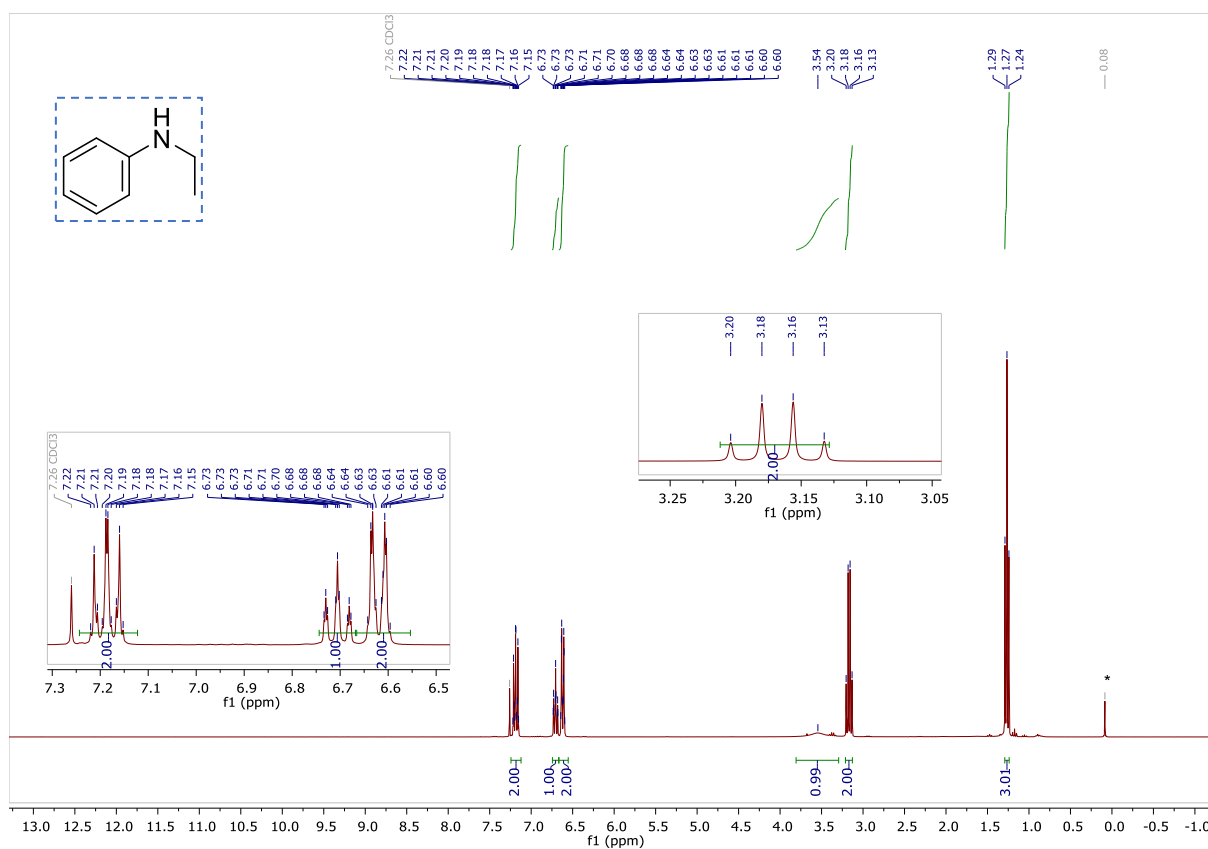


Figure S91 – ¹H NMR spectrum of **4q**. *Grease.

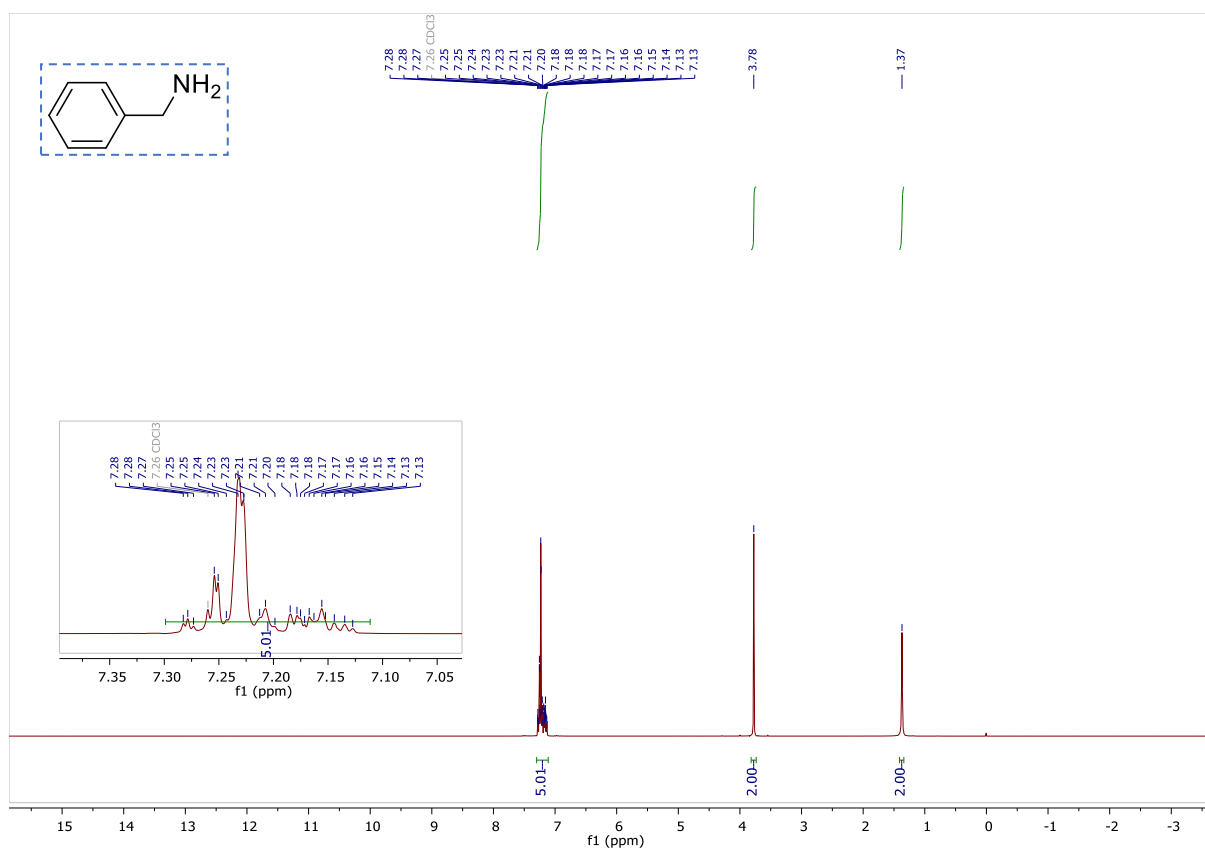


Figure S92 – ¹H NMR spectrum of **7a**.

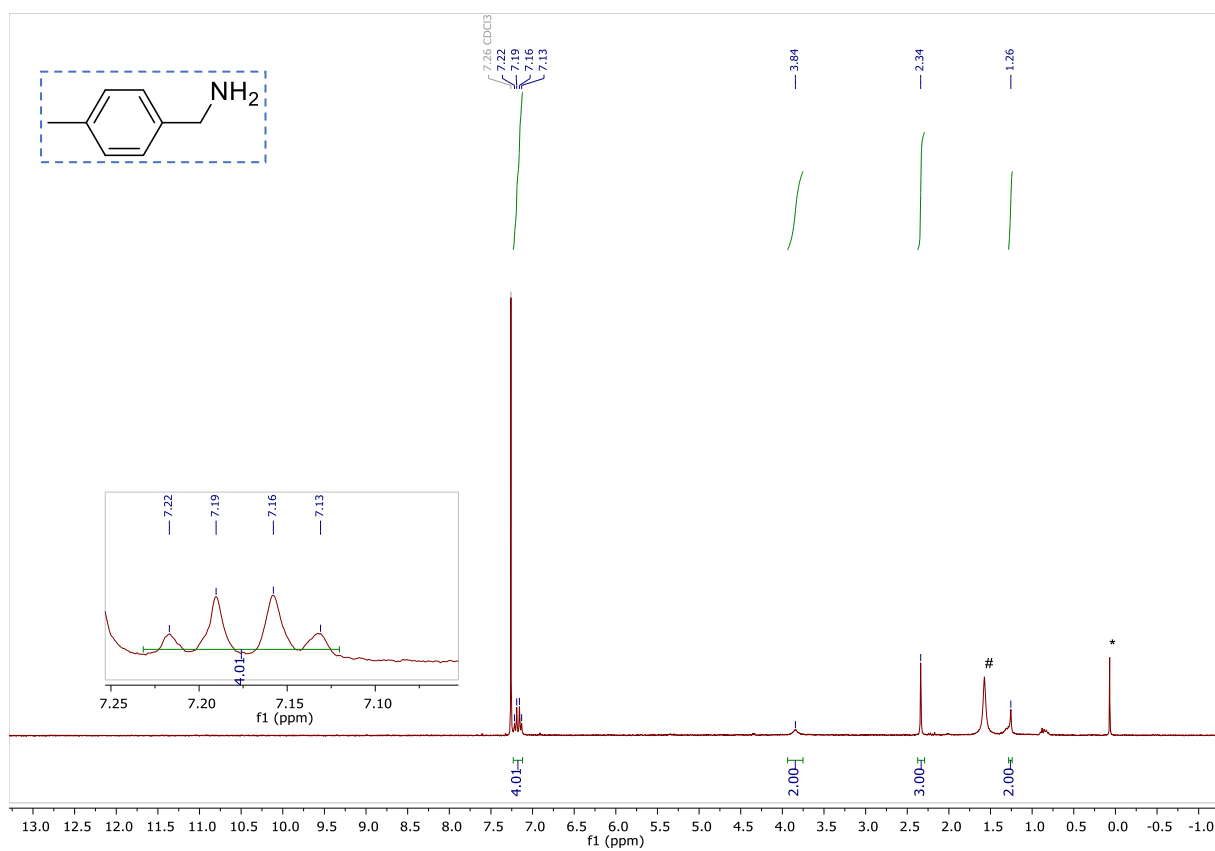


Figure S93 – ¹H NMR spectrum of **7b**. *Grease # – Impurity: water.

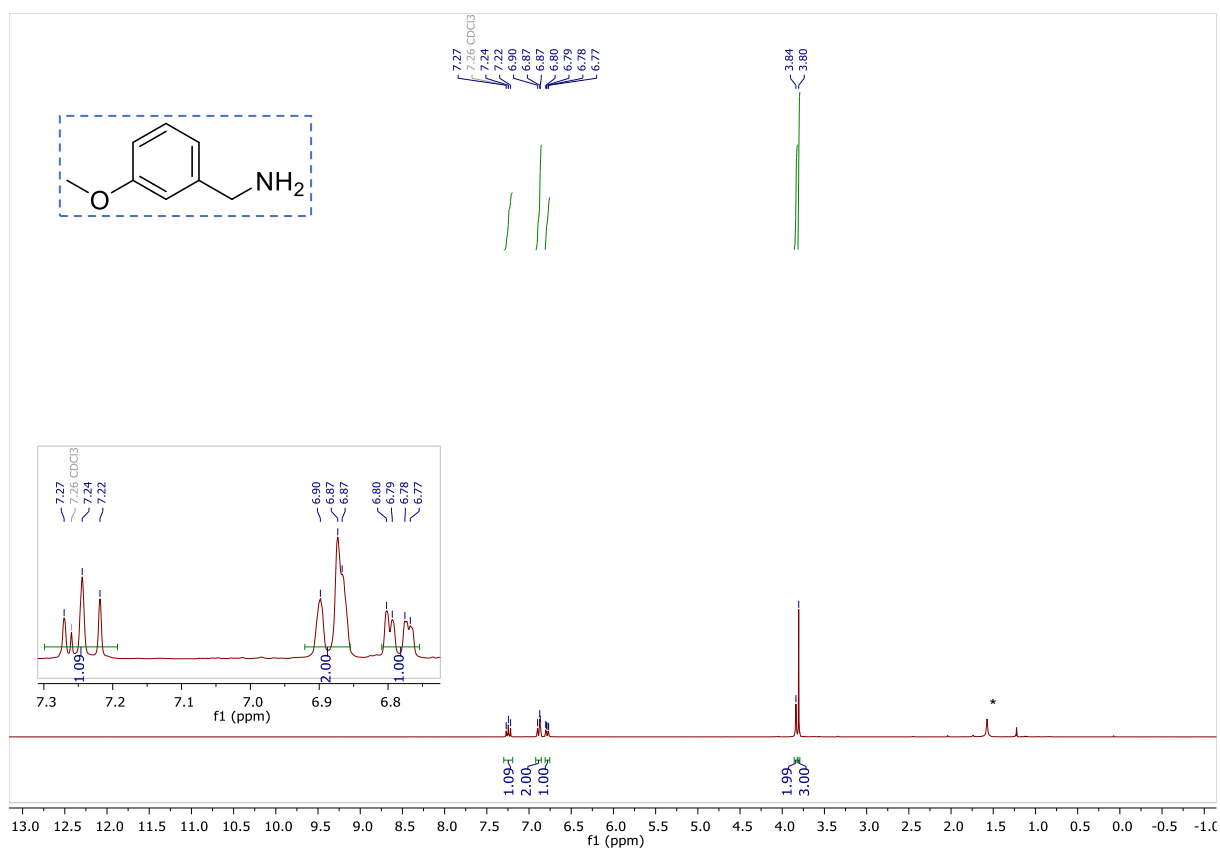


Figure S94 – ¹H NMR spectrum of 7c. * – Impurity: water.

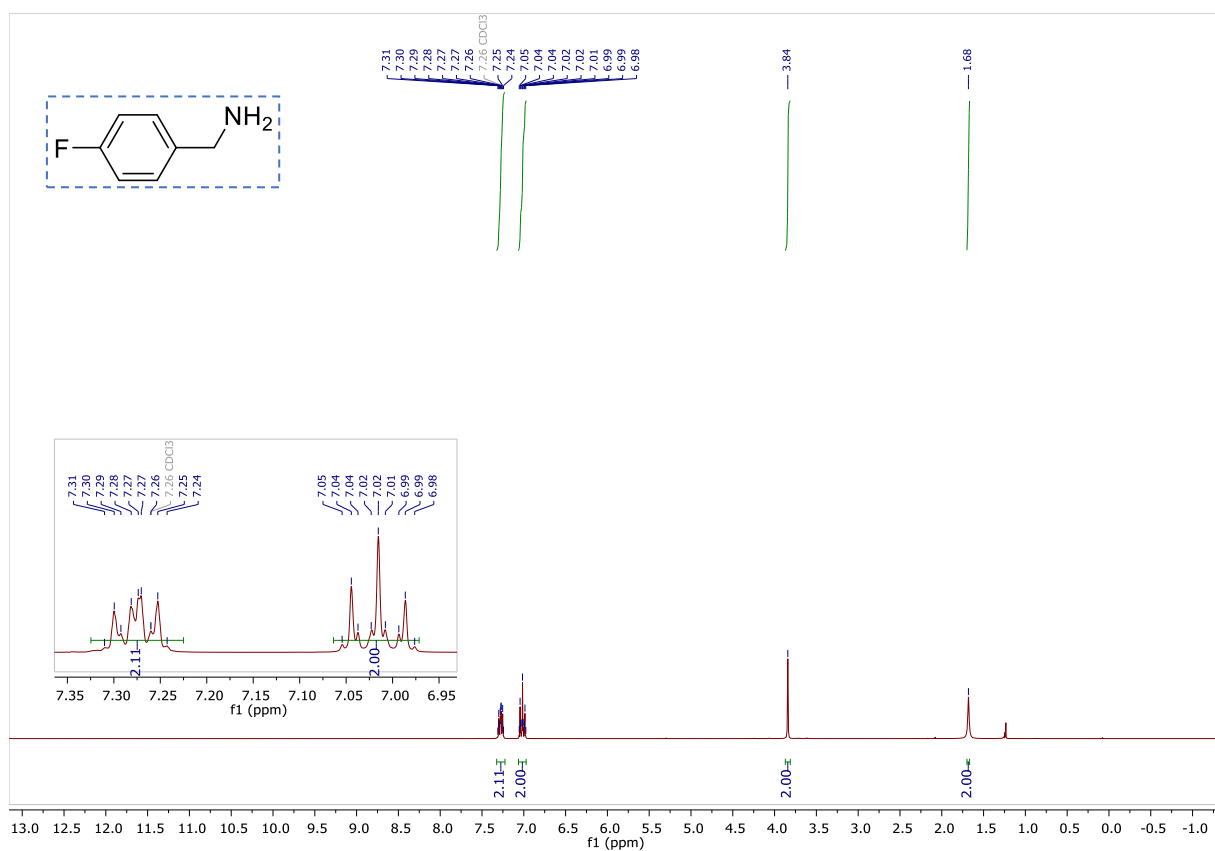


Figure S95 – ¹H NMR spectrum of 7d.

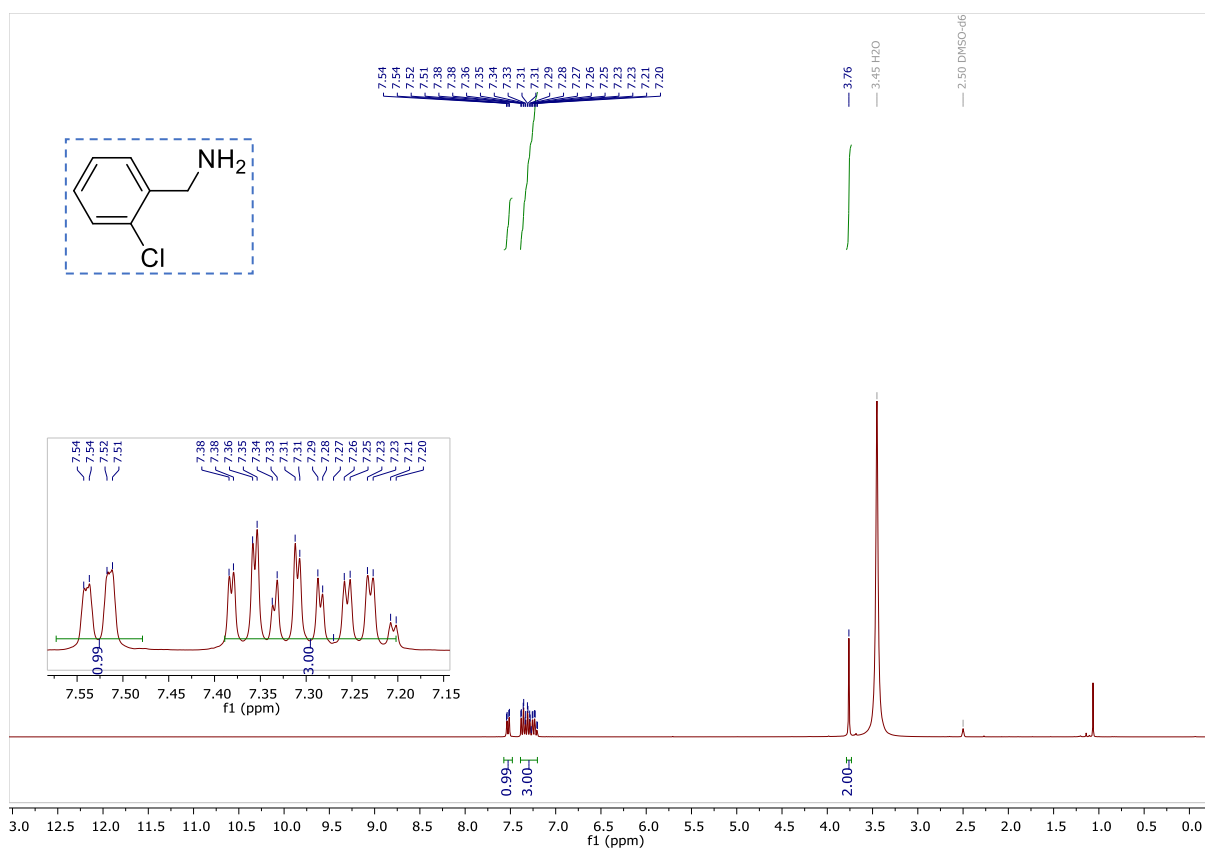


Figure S96 – ¹H NMR spectrum of 7e.

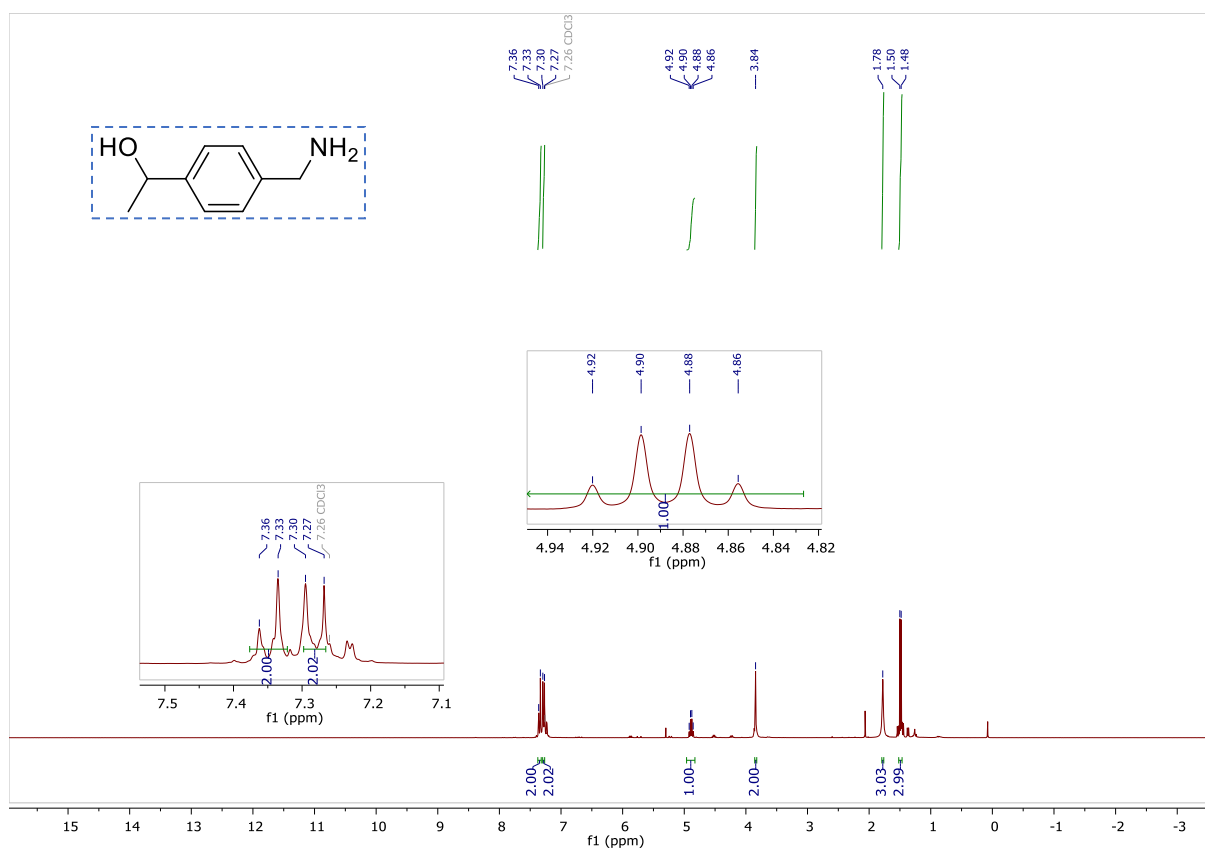


Figure S97 – ¹H NMR spectrum of 7f.

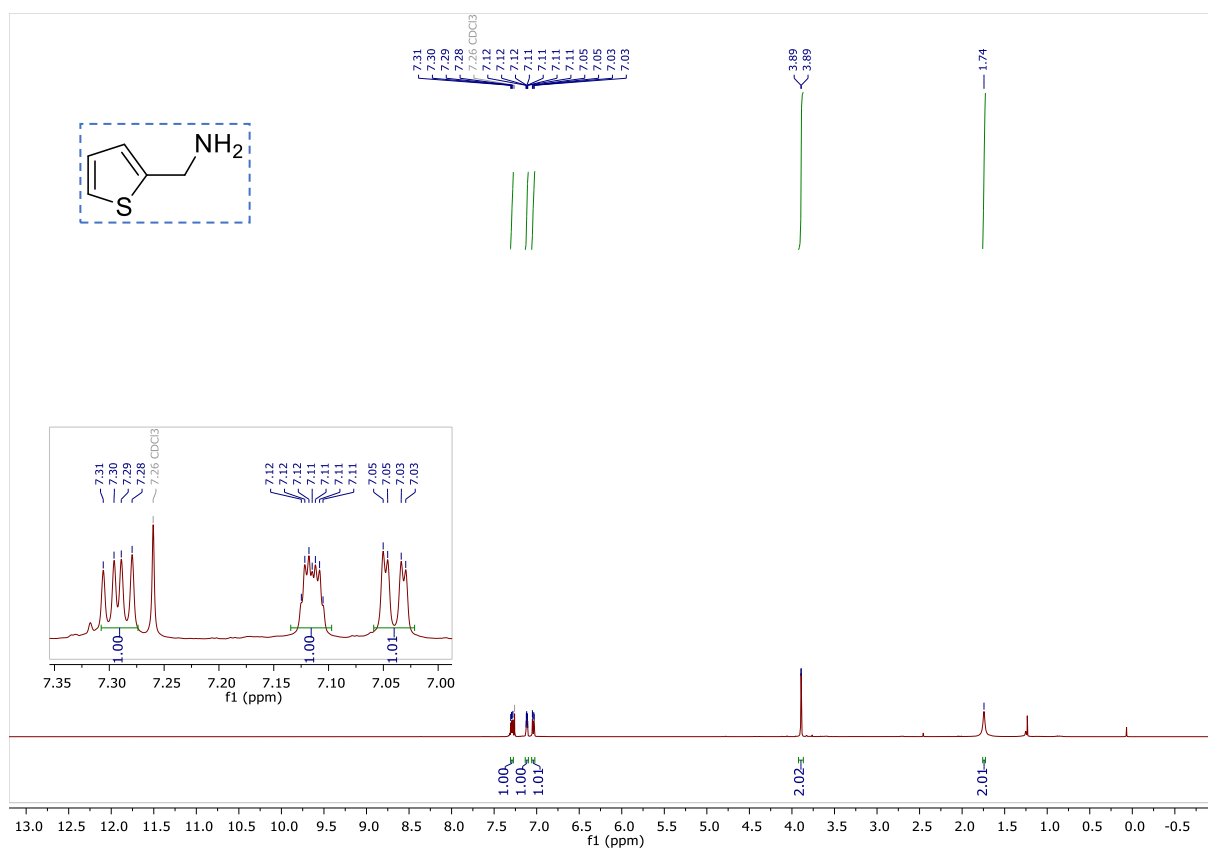


Figure S98 – ¹H NMR spectrum of **7g**.

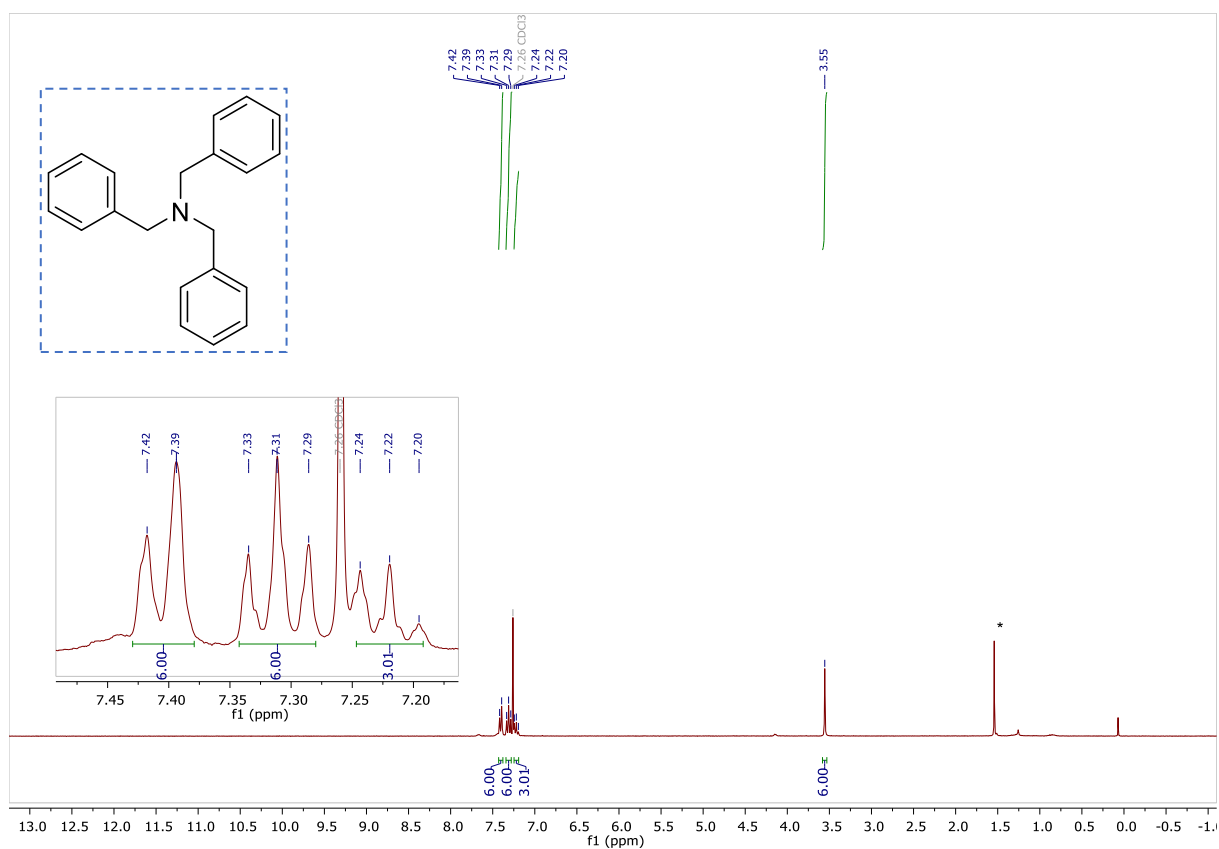


Figure S99 – ¹H NMR spectrum of **12a**. * – Impurity – pinacol.

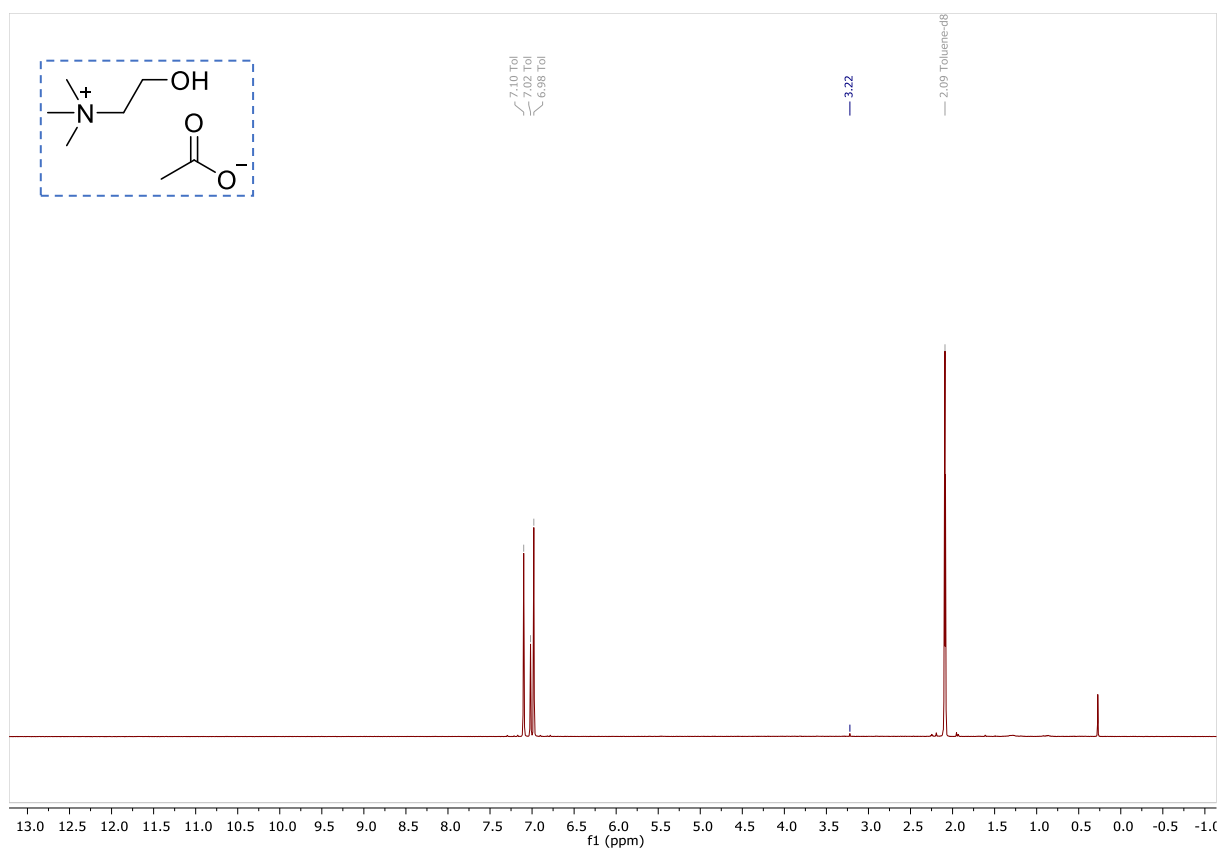


Figure S100– ¹H NMR spectrum of [Cho][OAc] in toluene-d₈.

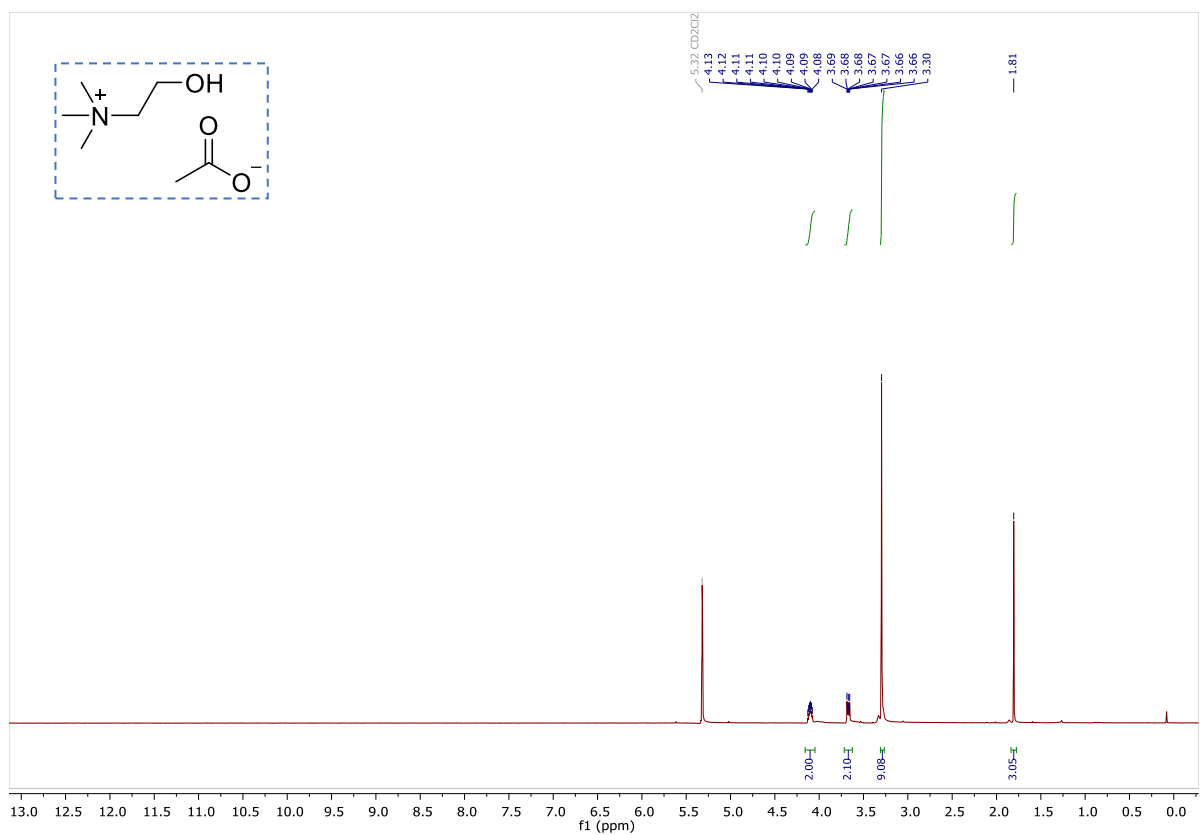


Figure S101 – ¹H NMR spectrum of [Cho][OAc] in DCM-d₂.

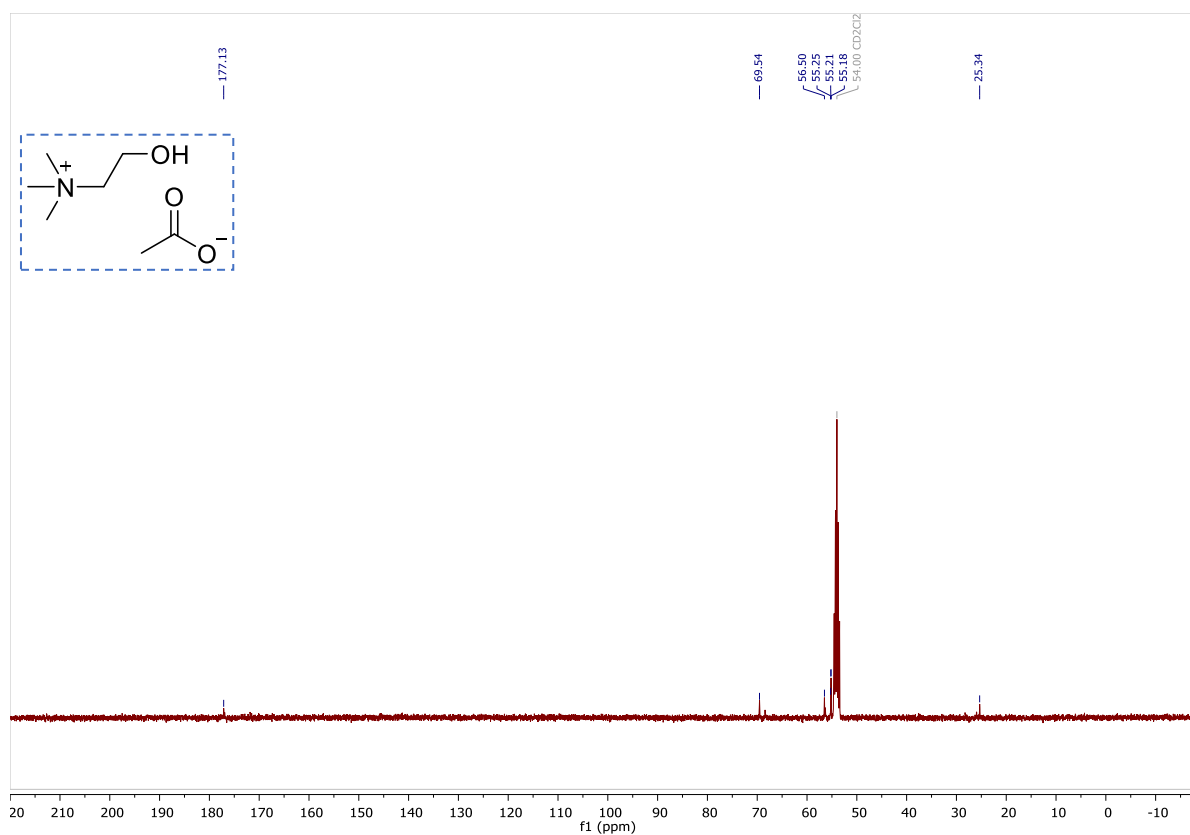


Figure S102 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of [Cho][OAc] in DCM-d₂.

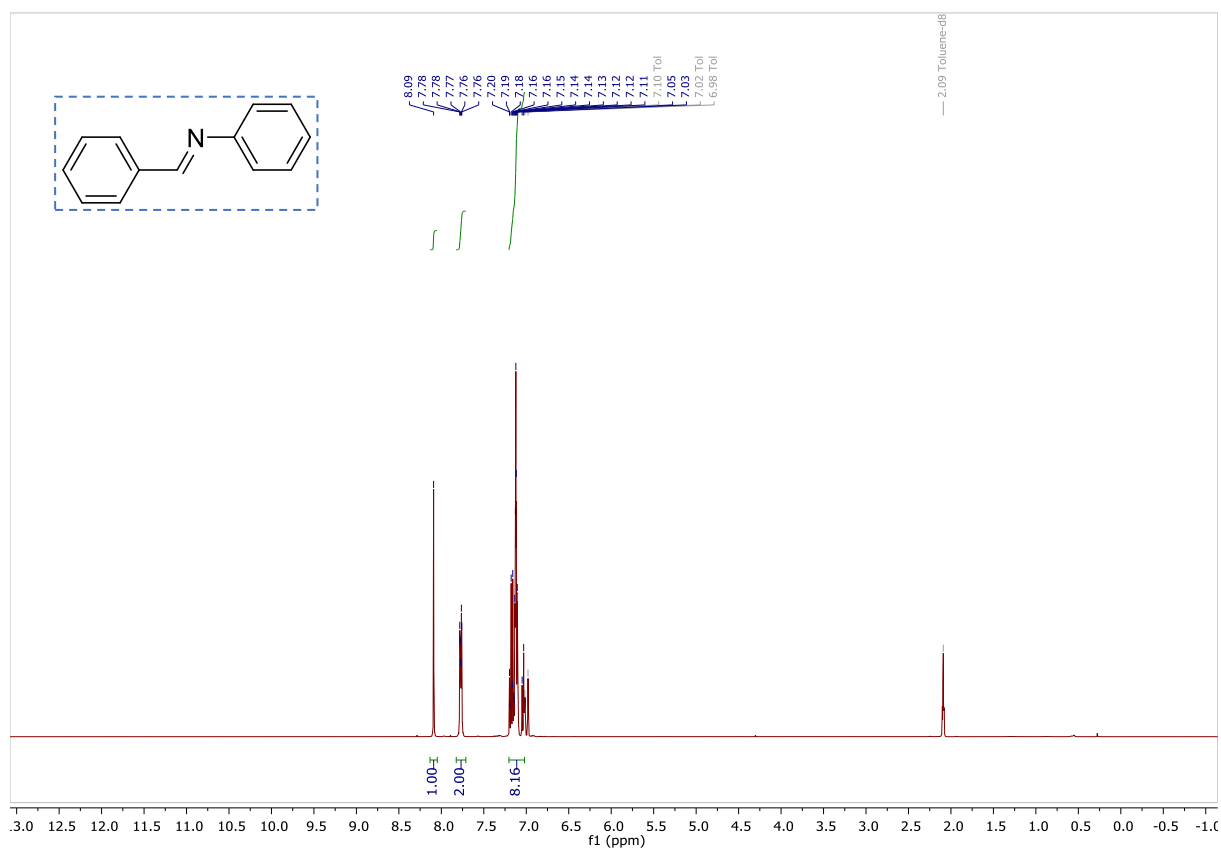


Figure S103 – ^1H NMR spectrum of *N*-benzylideneaniline (**1a**) in toluene-d₈.

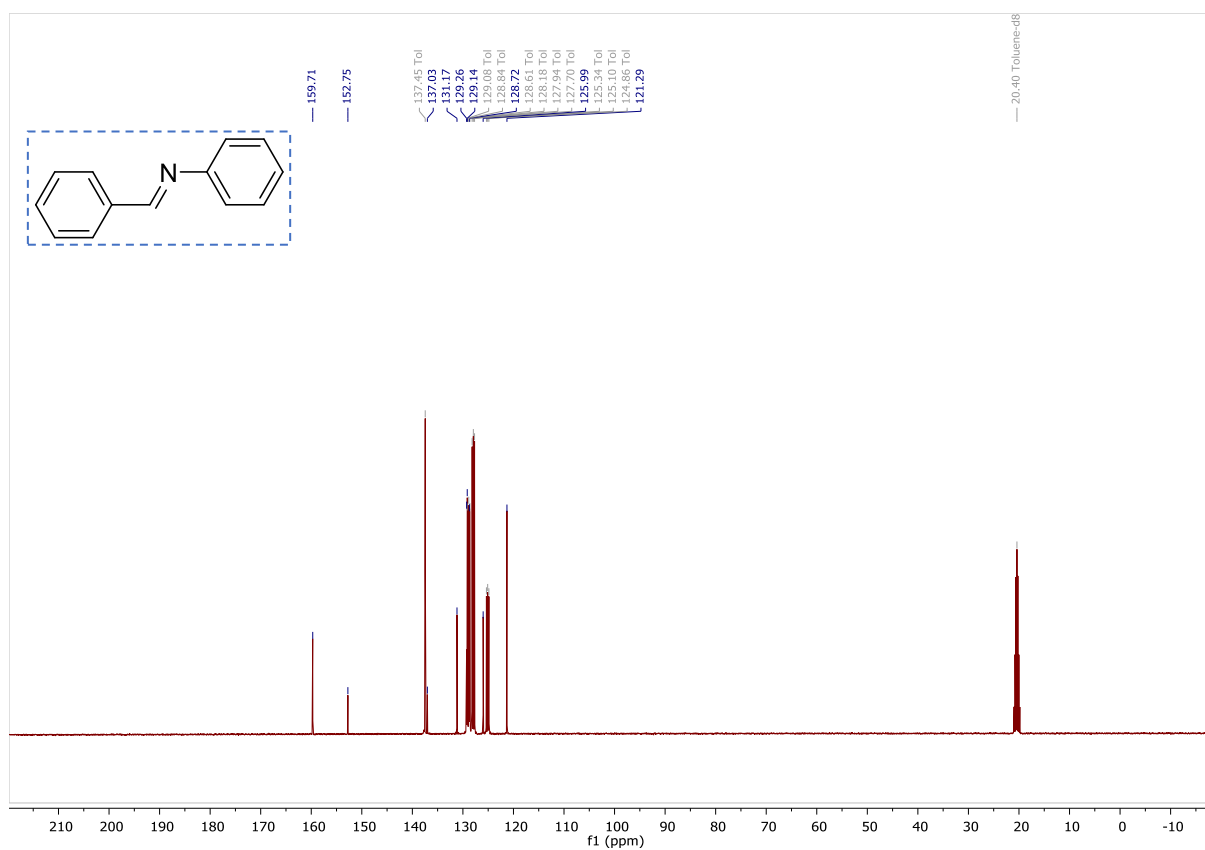


Figure S104 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of N-benzylideneaniline (1a) in toluene-d8.

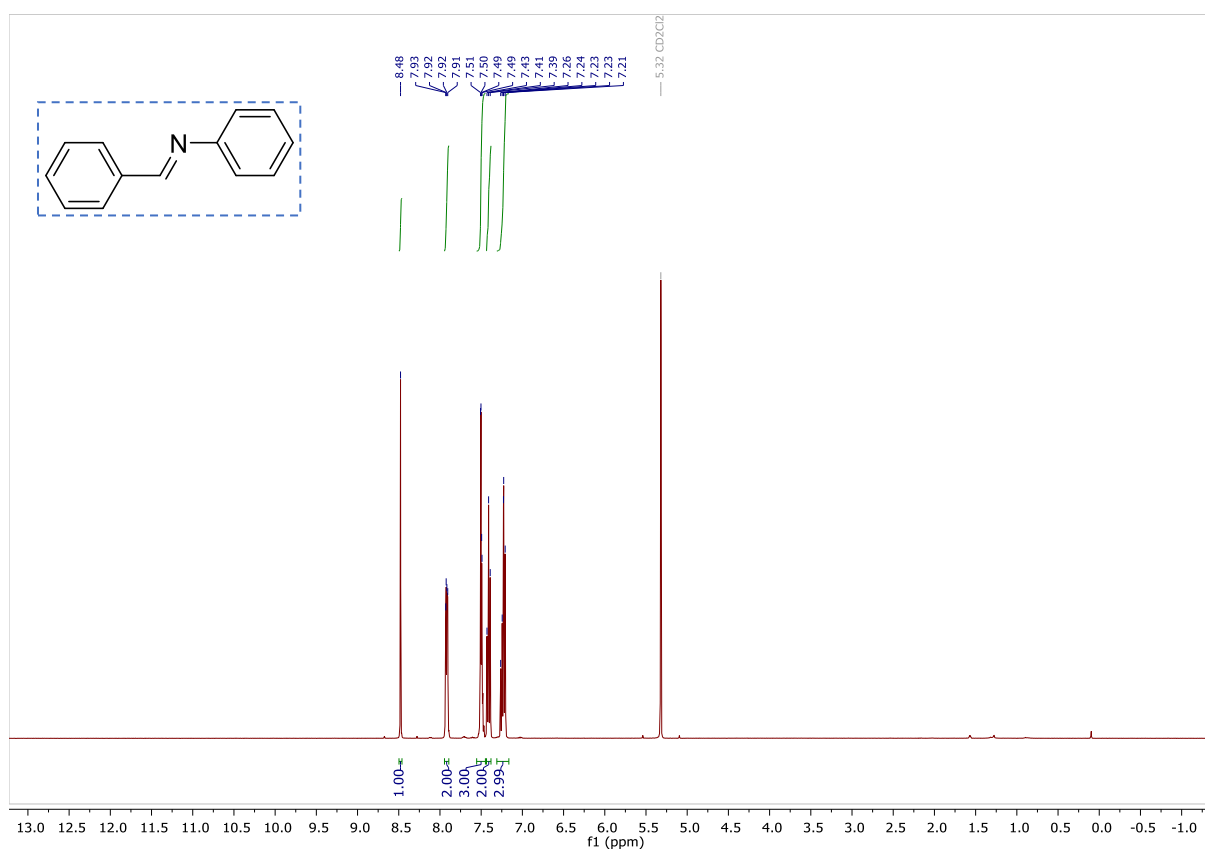


Figure S105 – ^1H NMR spectrum of N-benzylideneaniline (1a) in DCM-d2.

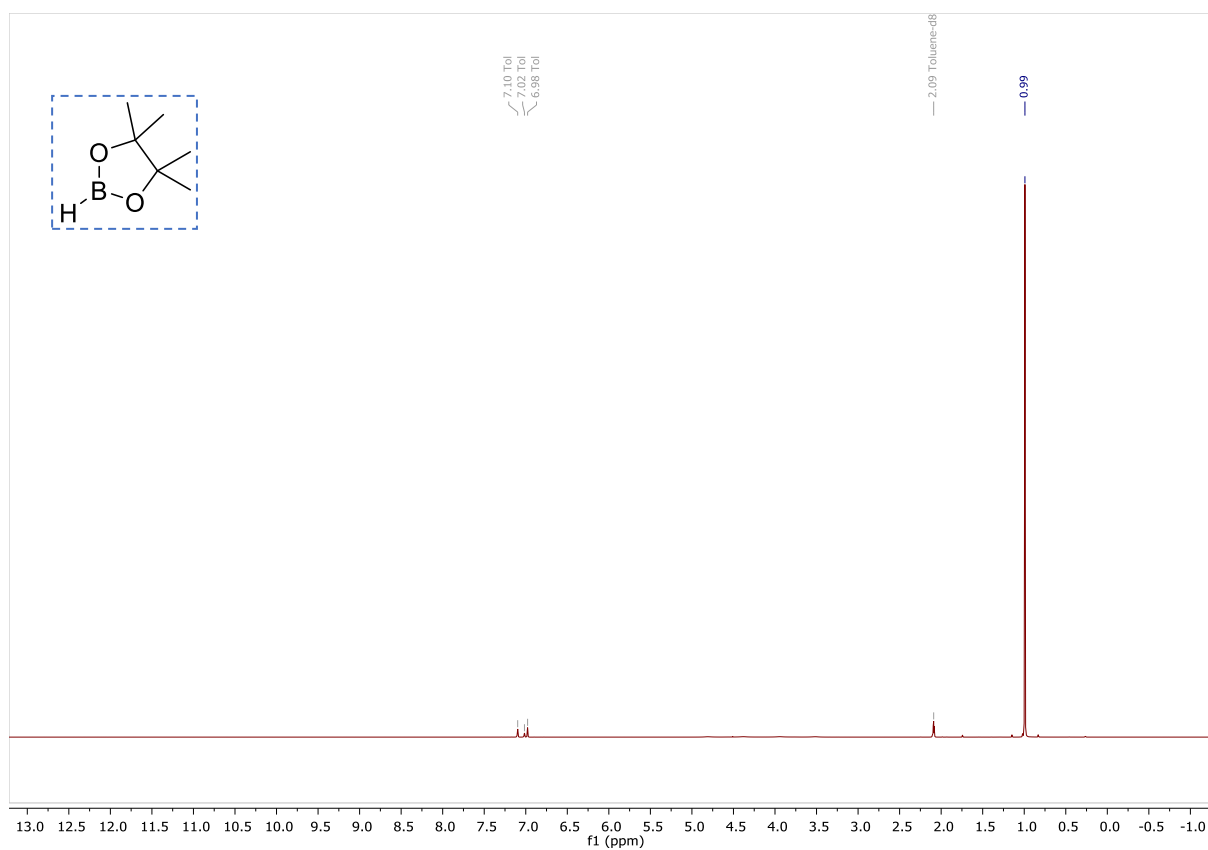


Figure S106 – ¹H NMR spectrum of pinacolborane (**2**) in toluene-d₈.

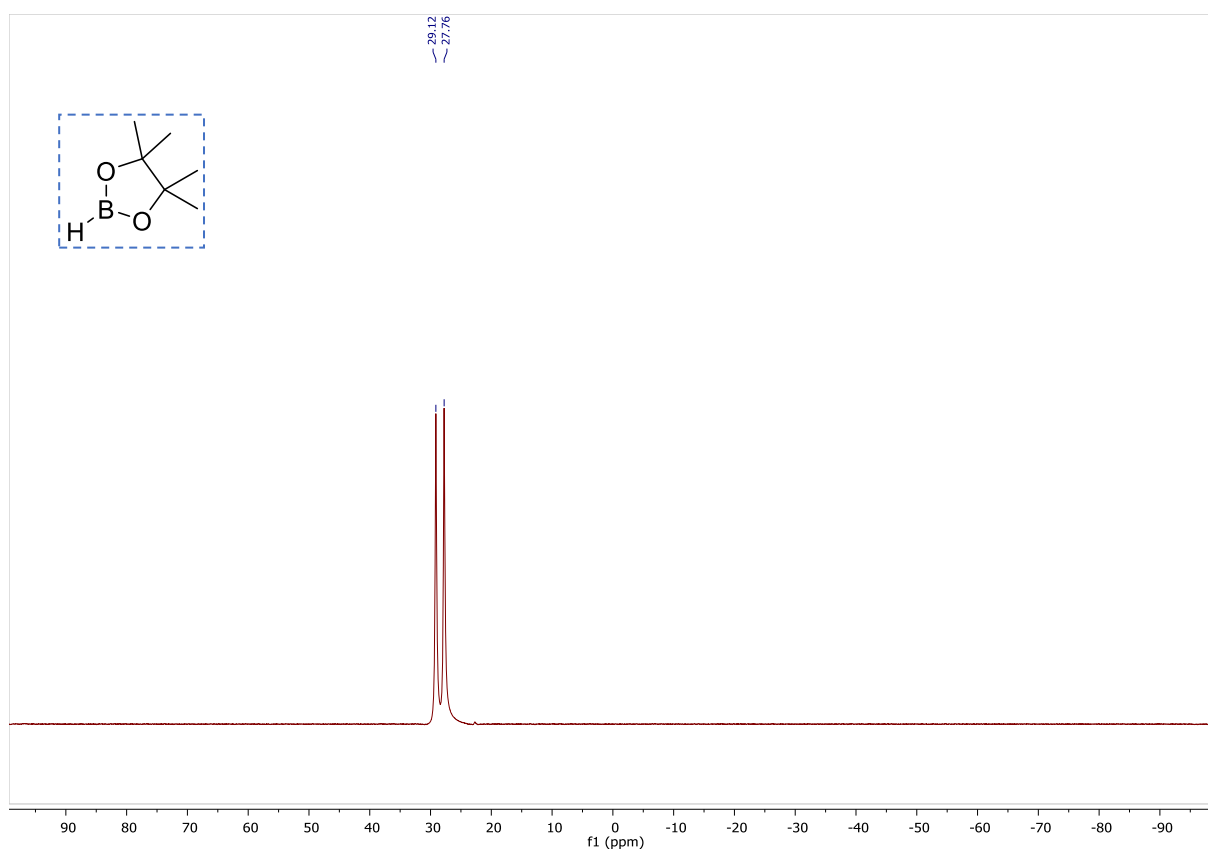


Figure S107 – ¹¹B {¹H} NMR spectrum of pinacolborane (**2**) in toluene-d₈.

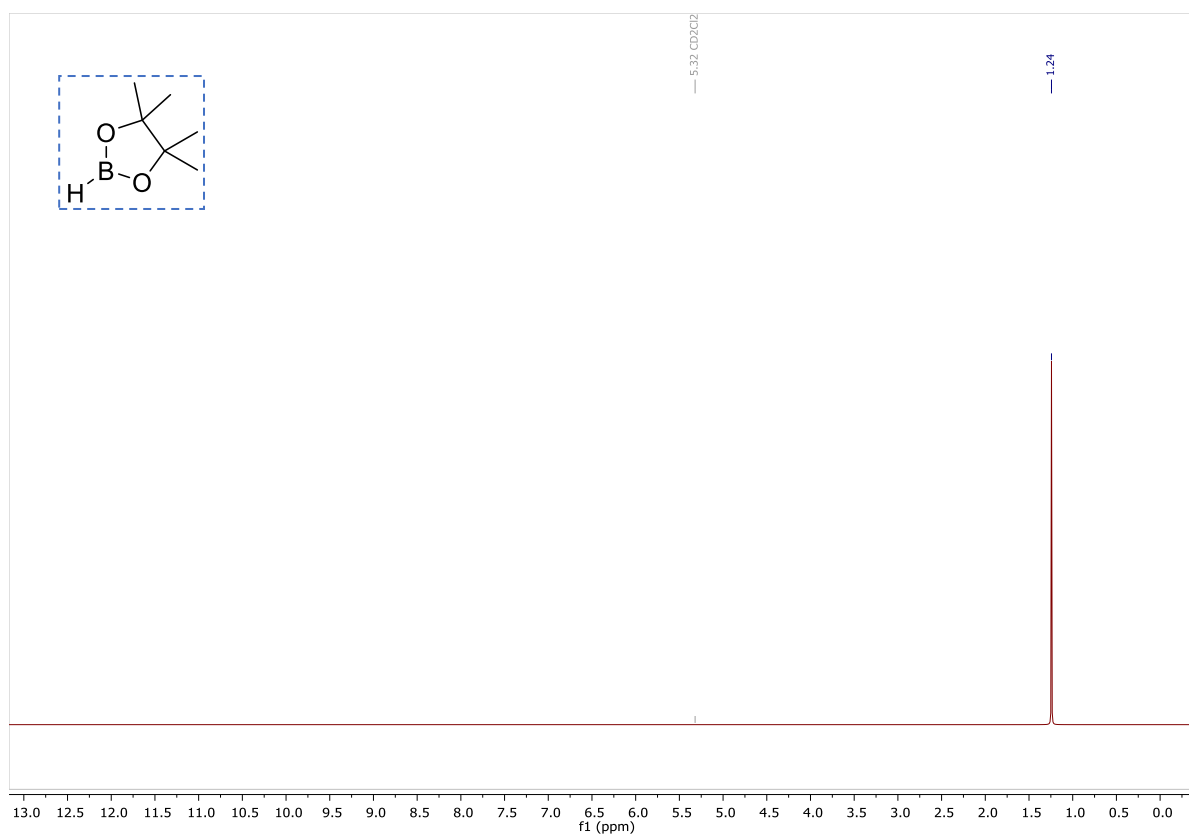


Figure S108 – ¹H NMR spectrum of pinacolborane (2) in DCM-d₂.

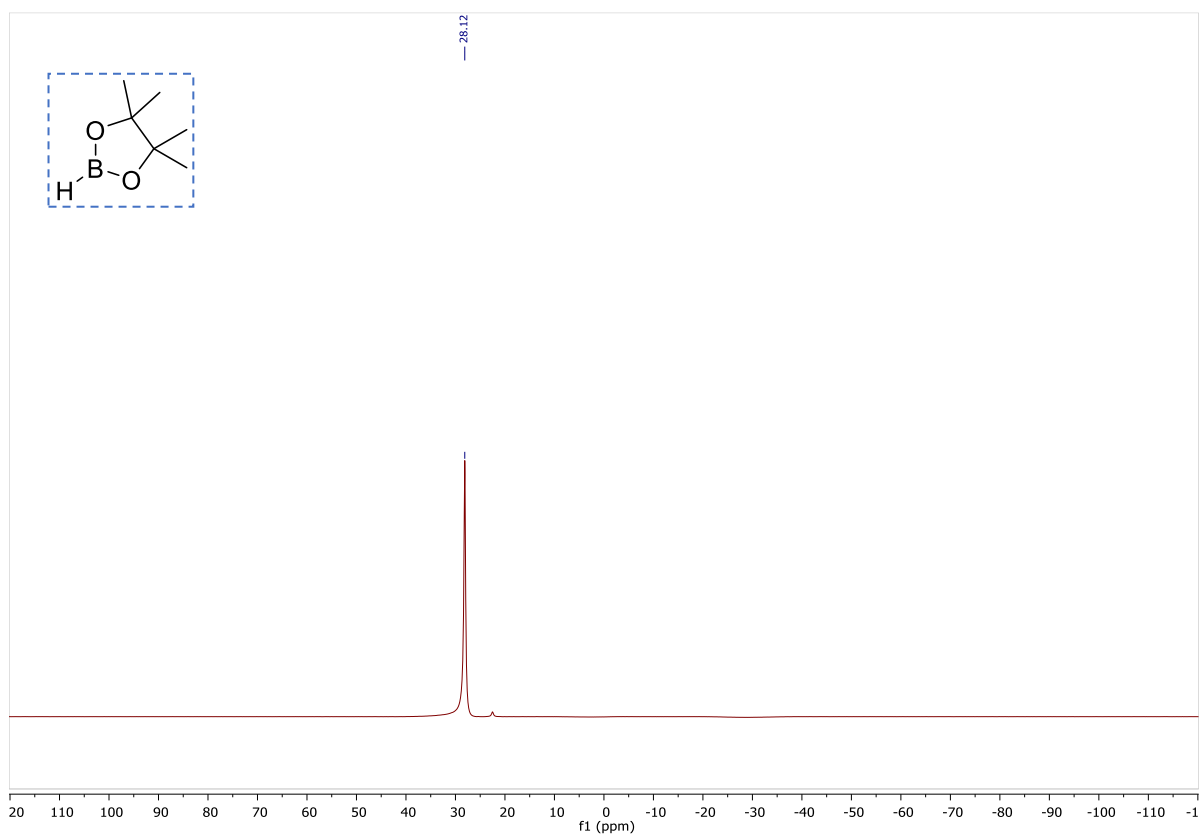


Figure S109 – ¹¹B NMR spectrum of pinacolborane (2) in DCM-d₂.

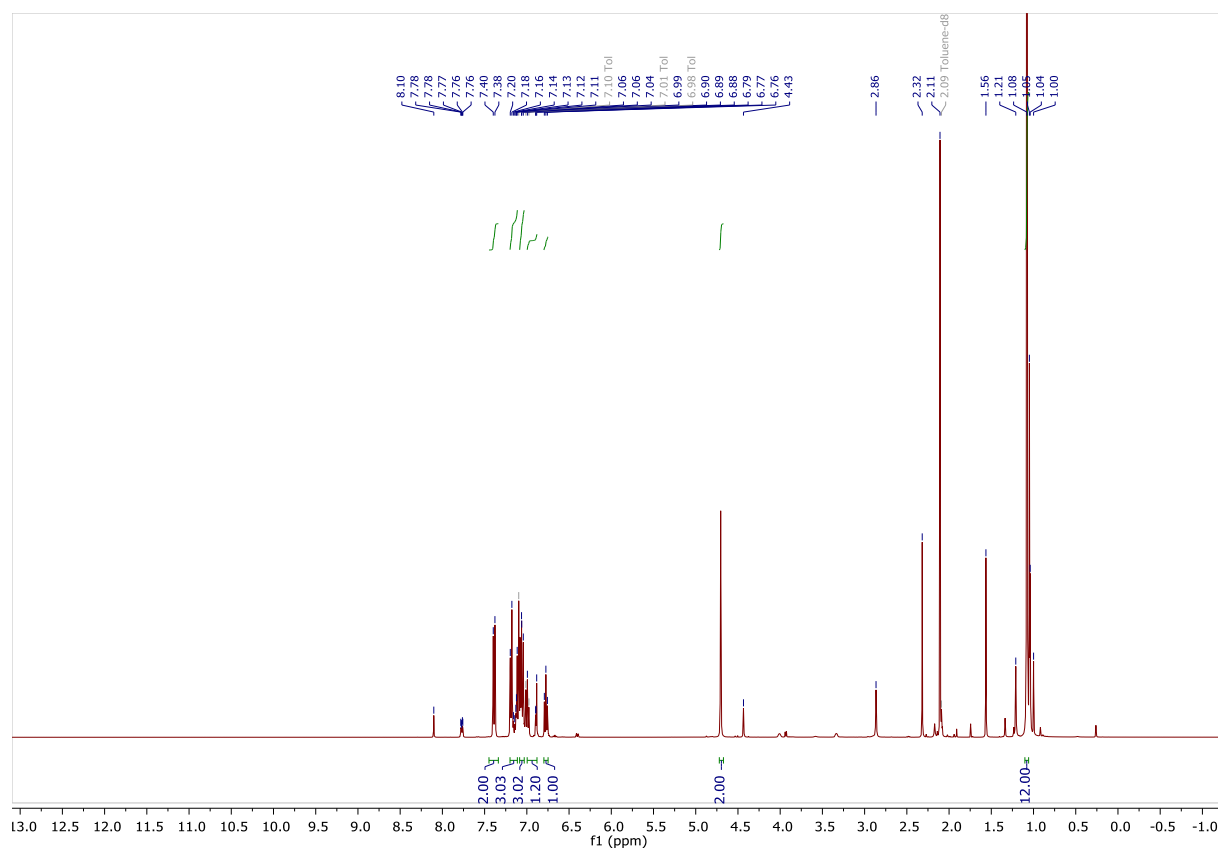


Figure S110 – ^1H NMR spectrum for the reaction of 1 equiv. of HBpin (**2**), 1 equiv. of *N*-benzylideneaniline (**1a**), 0.2 equiv. of [Cho][OAc] and 0.2 equiv. of TMEDA in toluene- d_8 . For clarity, only the **3a** signals were integrated.

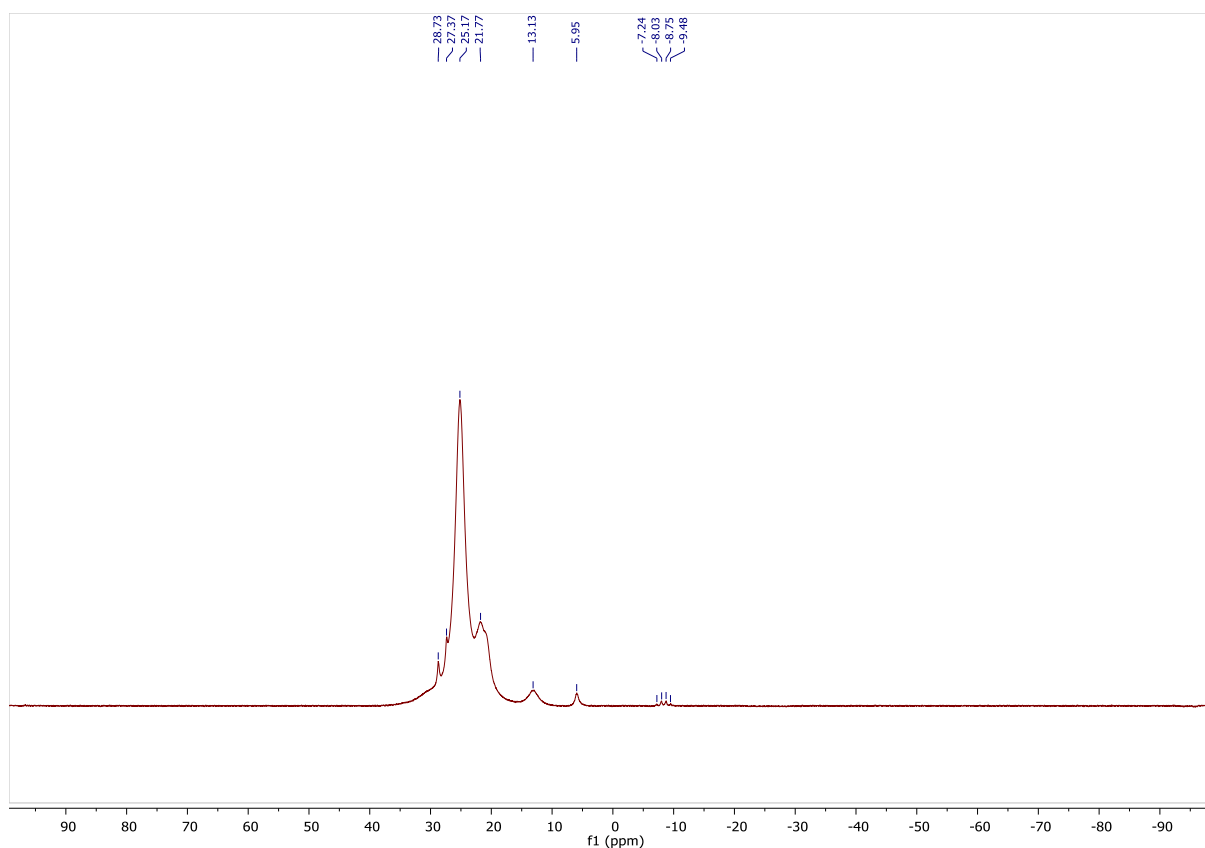


Figure S111 – ^{11}B NMR spectrum for the reaction of 1 equiv. of HBpin (**2**), 1 equiv. of *N*-benzylideneaniline (**1a**), 0.2 equiv. of [Cho][OAc] and 0.2 equiv. of TMEDA in toluene- d_8 .

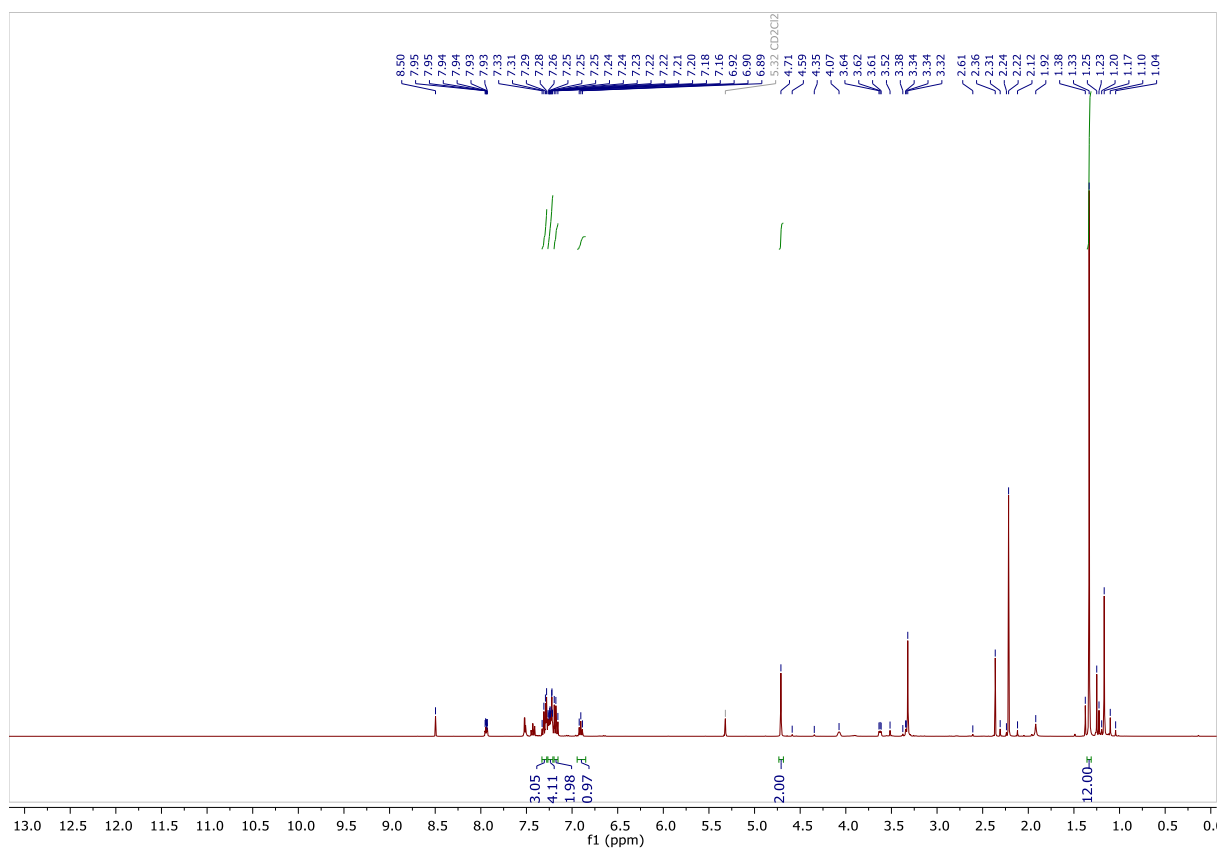


Figure S112 – ^1H NMR spectrum for the reaction of 1 equiv. of HBpin (**2**), 1 equiv. of *N*-benzylideneaniline (**1a**), 0.2 equiv. of [Cho][OAc] and 0.2 equiv. of TMEDA in toluene- d_8 .

benzylideneaniline (**1a**), 0.2 equiv. of [Cho][OAc] and 0.2 equiv. of TMEDA in DCM-d2. For clarity, only the **3a** signals were integrated.

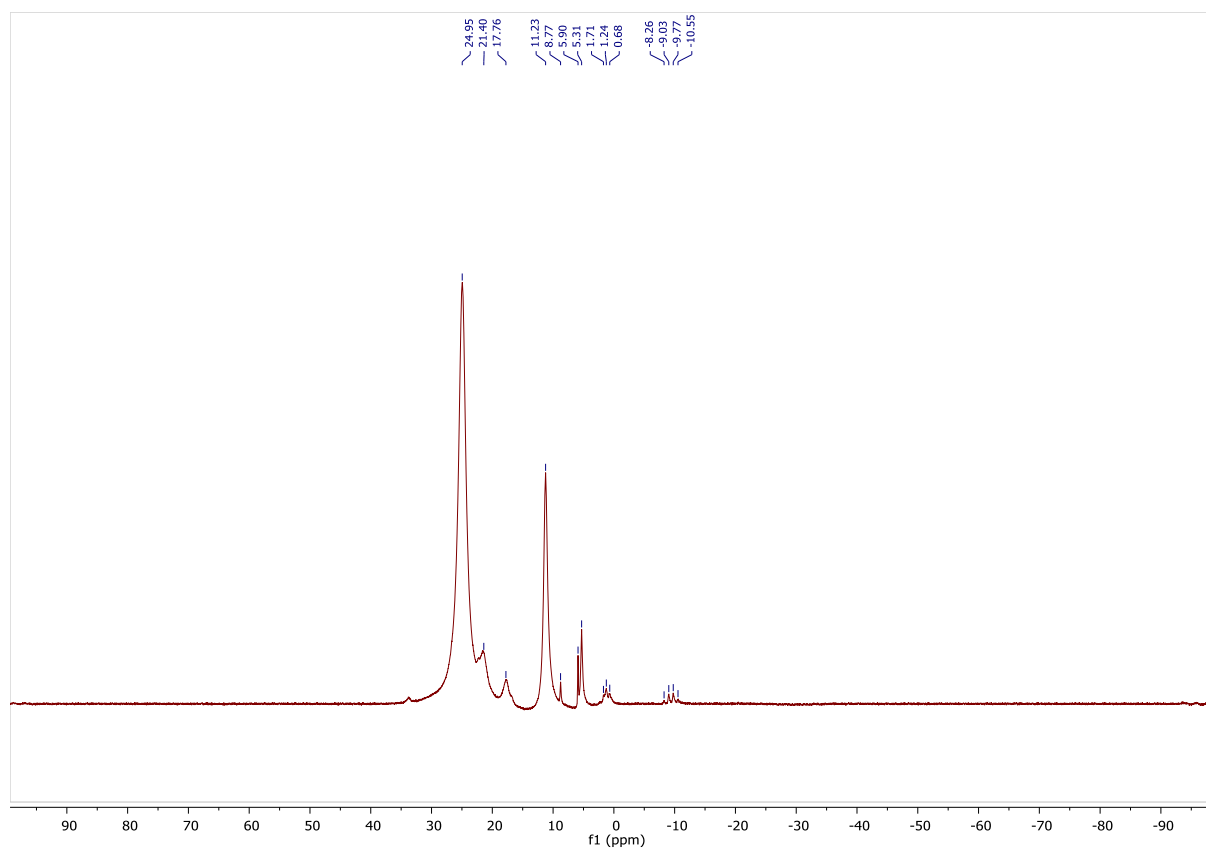


Figure S113 – ^{11}B NMR spectrum for the reaction of 1 equiv. of HBpin (**2**), 1 equiv. of *N*-benzylideneaniline (**1a**), 0.2 equiv. of [Cho][OAc] and 0.2 equiv. of TMEDA in DCM-d2.

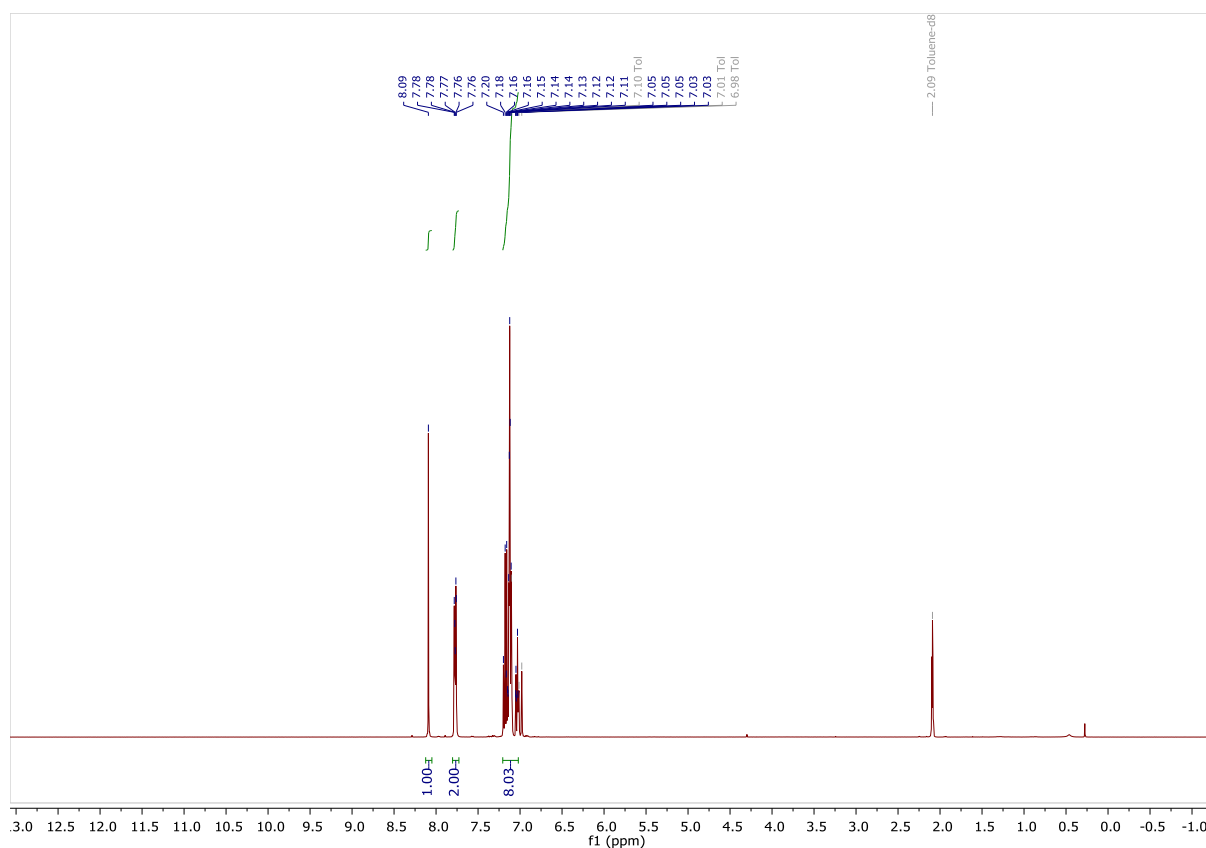


Figure S114– ¹H NMR spectrum for the reaction of 1 equiv. of *N*-benzylideneaniline (**1a**) with 1 equiv. of [Cho][OAc] in toluene-d₈.

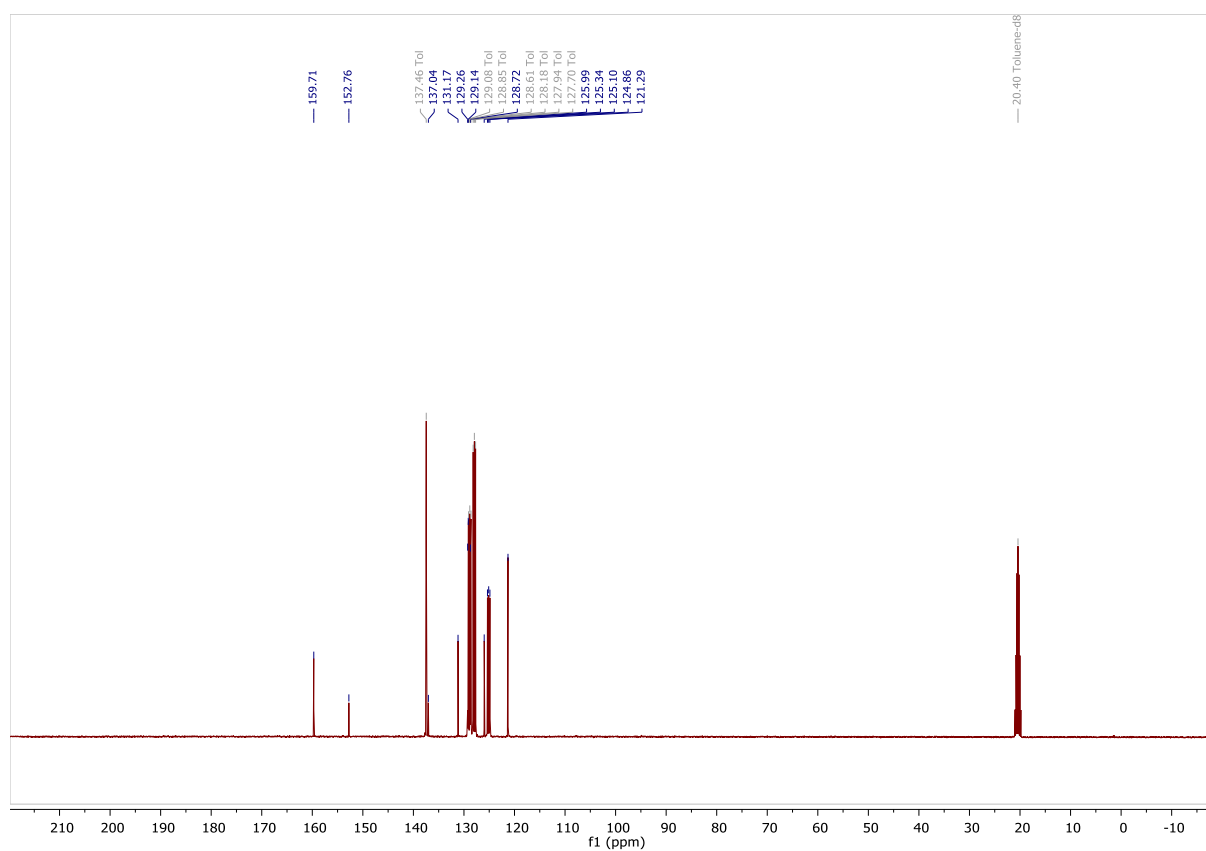


Figure S115 – ¹³C{¹H} NMR spectrum for the reaction of 1equiv. of *N*-benzylideneaniline (**1a**) with 1 equiv. of [Cho][OAc] in toluene-d₈.

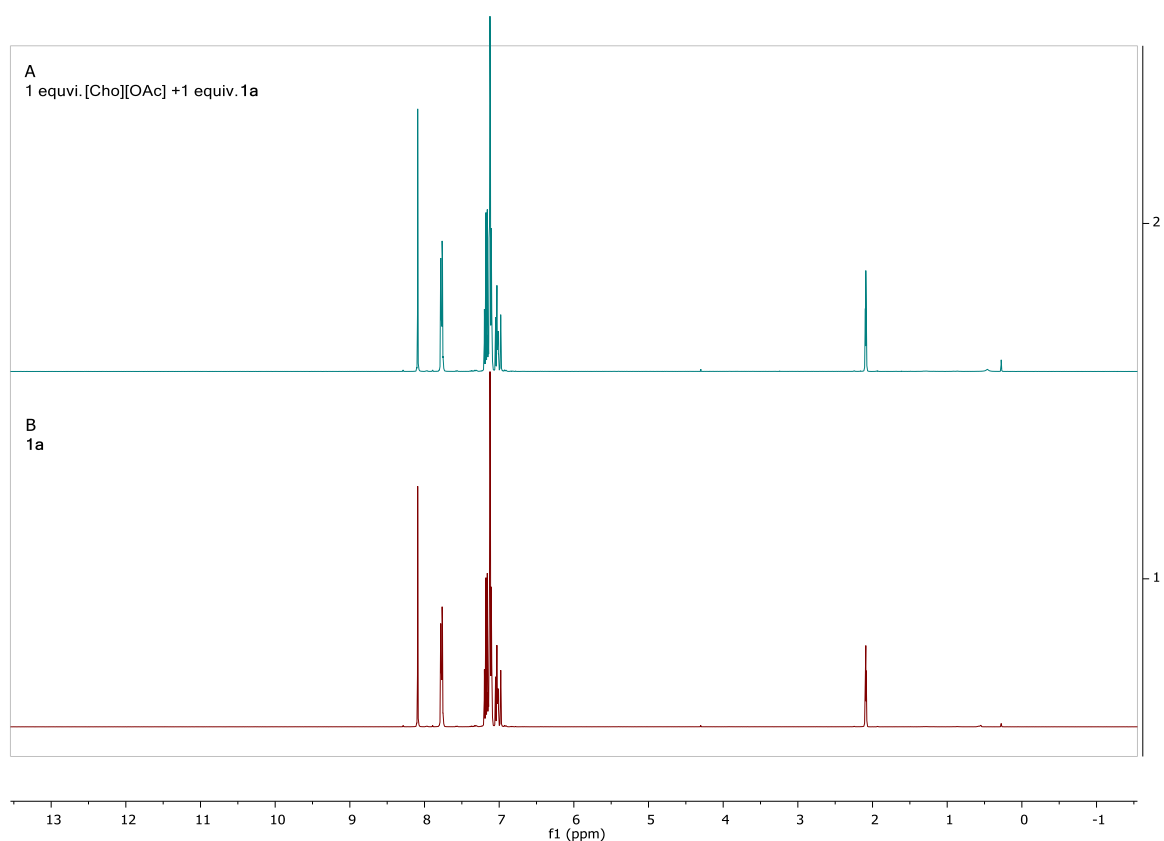


Figure S116 – Stacked ^1H NMR spectra: (A) the reaction of 1equiv. of *N*-benzylideneaniline (**1a**) with 1 equiv. of [Cho][OAc], (B) *N*-benzylideneaniline (**1a**). Solvent: toluene- d_8 .

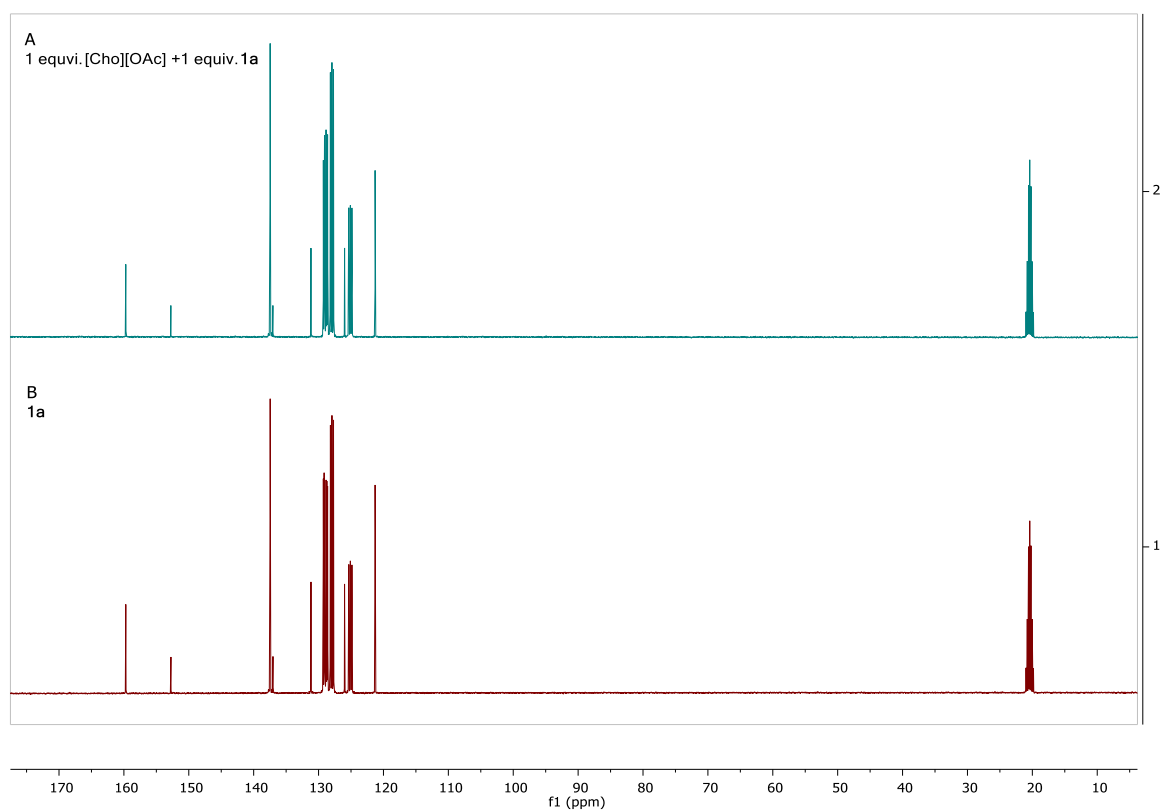
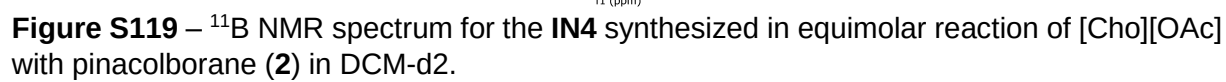
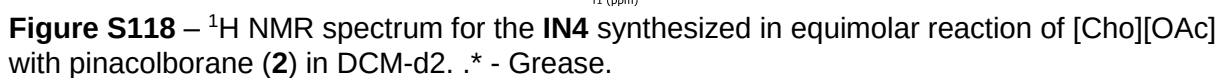


Figure S117 – Stacked $^{13}\text{C}\{^1\text{H}\}$ NMR spectra: (A) the reaction of 1 equiv. of *N*-benzylideneaniline (**1a**) with 1 equiv. of [Cho][OAc], (B) *N*-benzylidenaniline (**1a**). Solvent: toluene- d_8 .



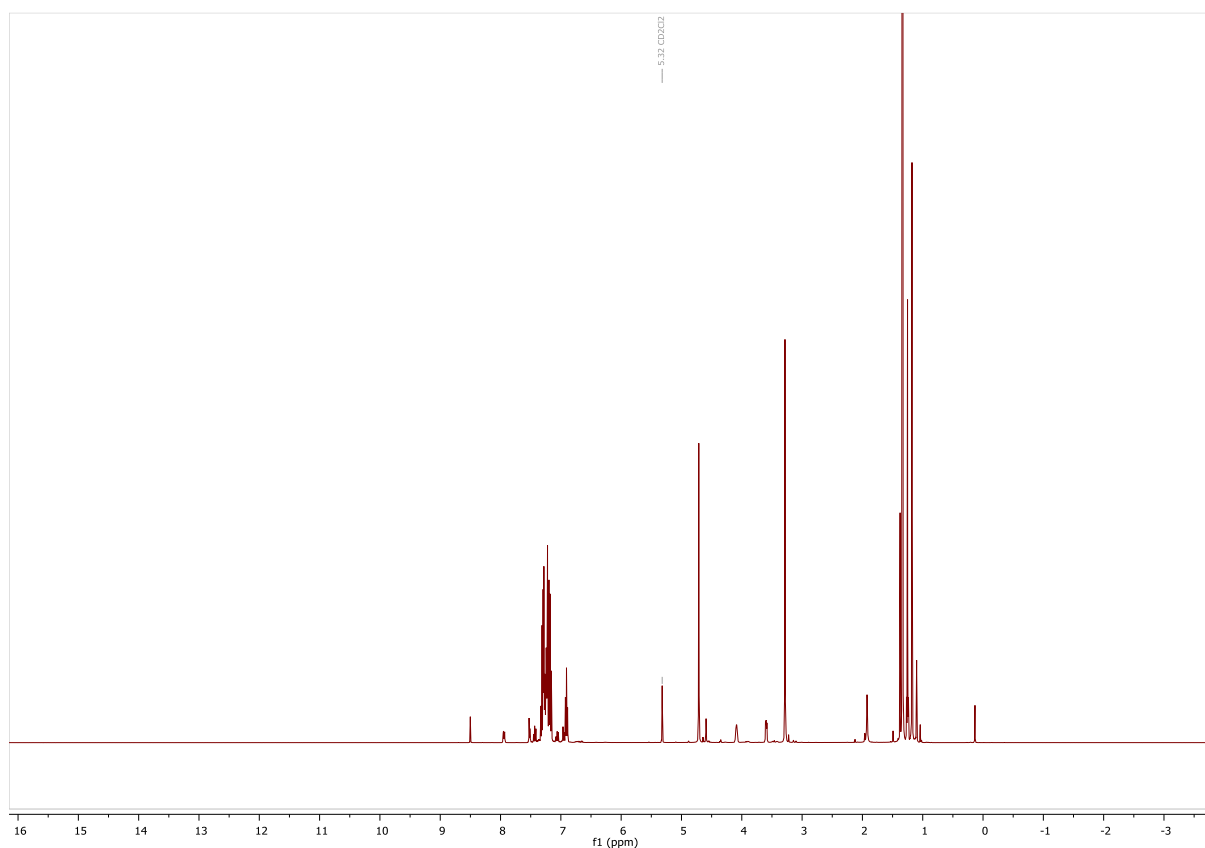


Figure S120 – ^1H NMR spectrum for the reaction of 1.2 equiv. of pinacolborane (**2**), 1 equiv. of *N*-benzylideneaniline (**1a**), 20 mol% of IN4 after 1 h in DCM-d_2 .

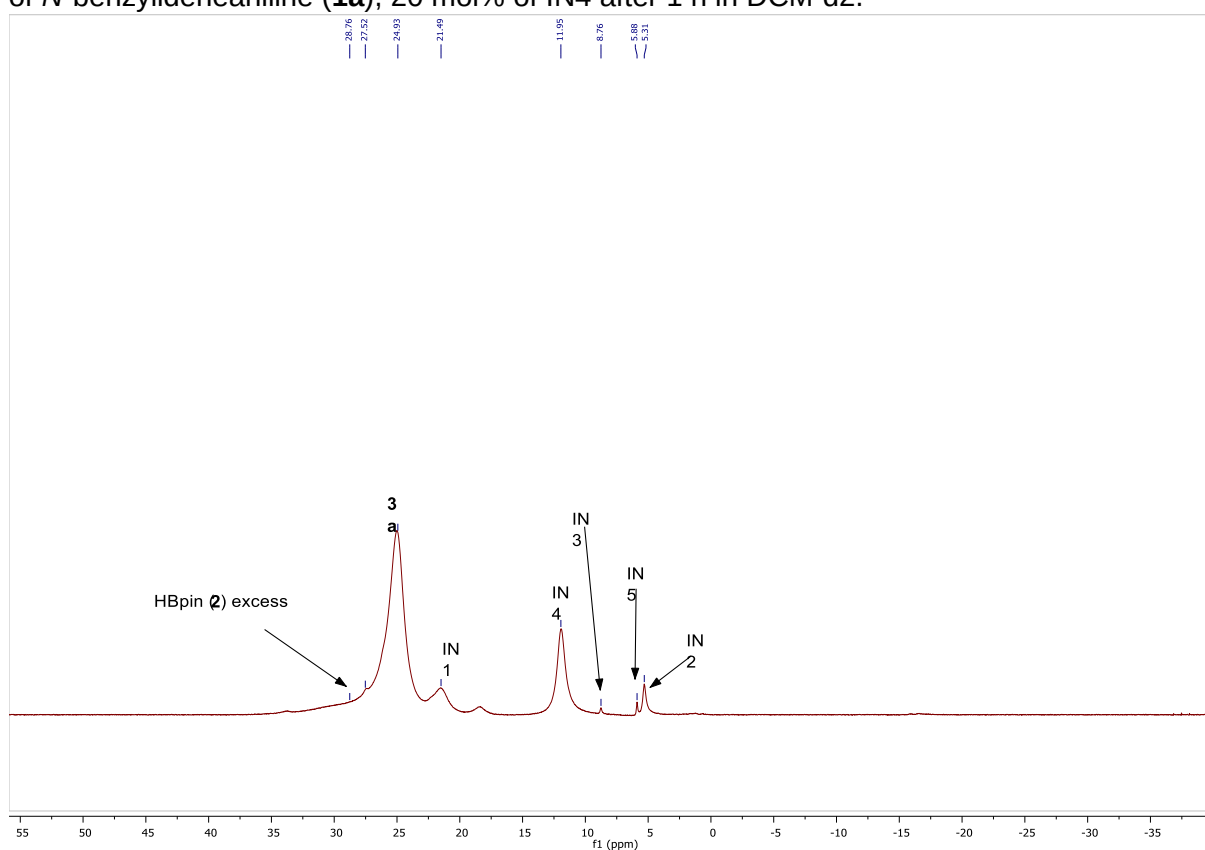


Figure S121 – ^{11}B NMR spectrum for the reaction of 1.2 equiv. of pinacolborane (**2**), 1 equiv. of *N*-benzylideneaniline (**1a**), 20 mol% of IN4 after 1 h in DCM-d_2 .

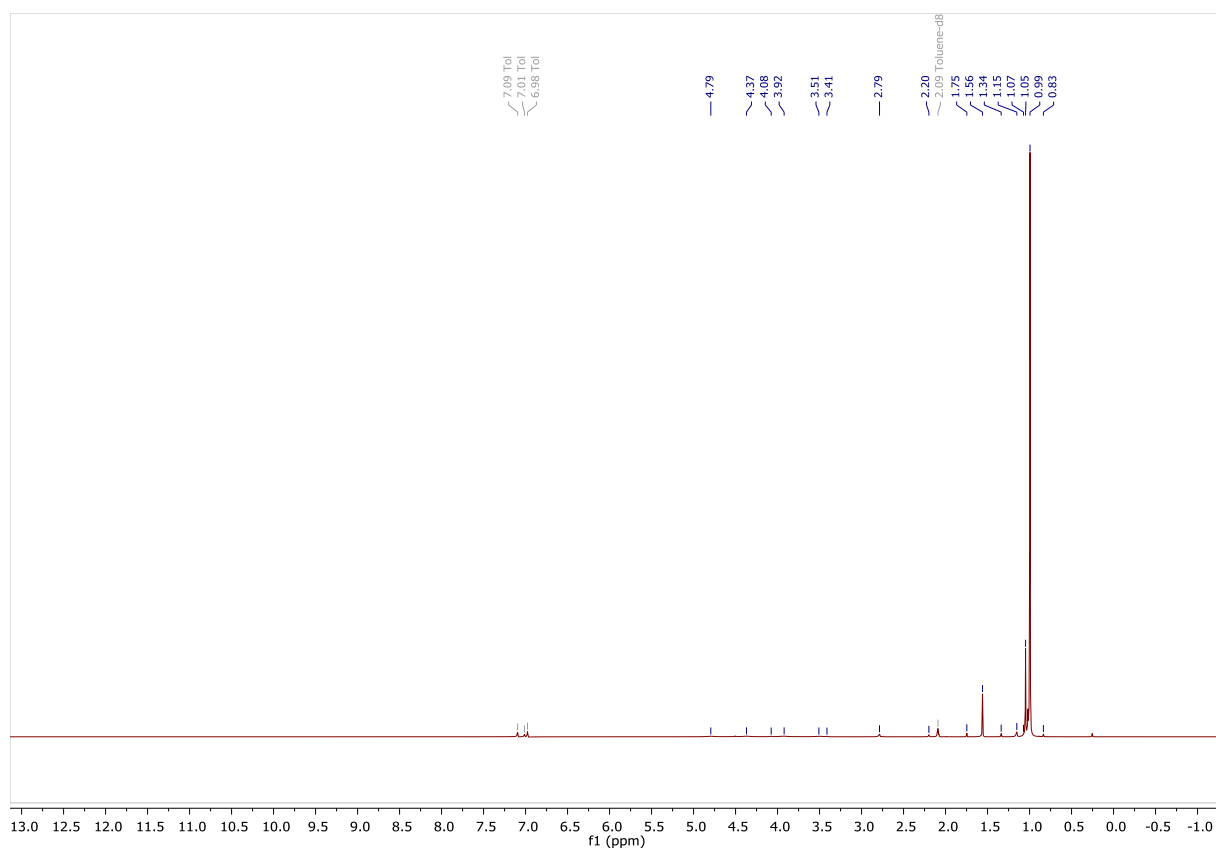


Figure S122 – ^1H NMR spectrum for the reaction of 1 equiv. of HBpin (**2**) with 0.2 equiv. of [Cho][OAc] in toluene- d_8 .

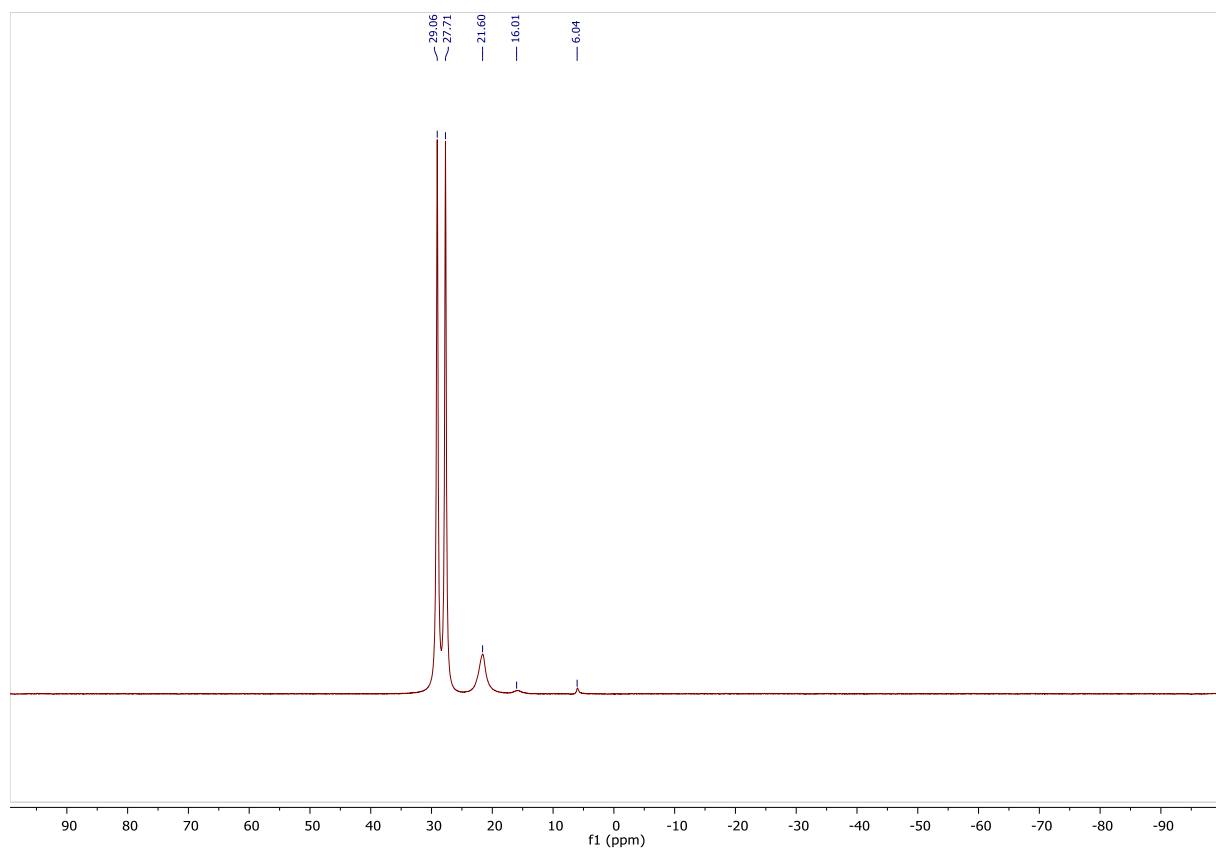


Figure S123 – ^{11}B NMR spectrum for the reaction of 1 equiv. of HBpin (**2**) with 0.2 equiv. of [Cho][OAc] in toluene- d_8 .

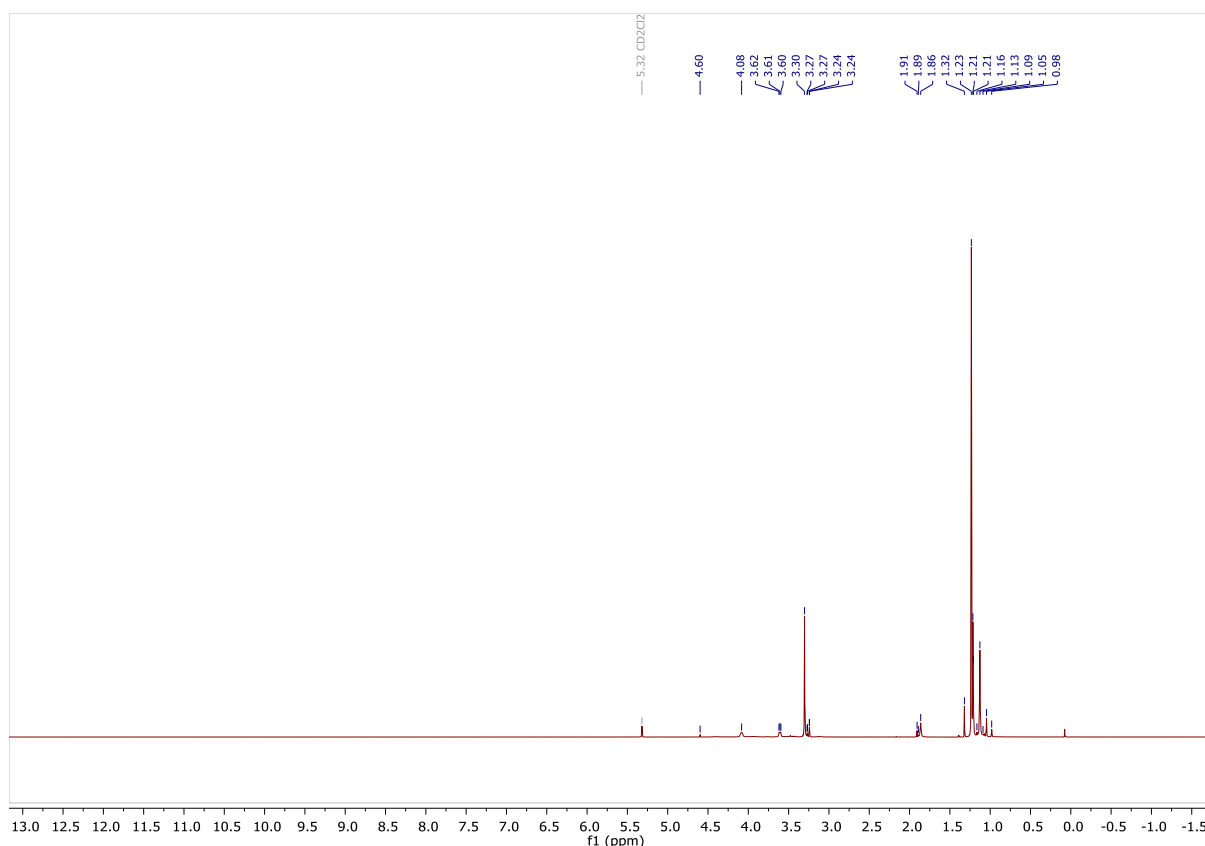


Figure S124 – ^1H NMR spectrum for the reaction of 1 equiv. of HBpin (**2**) with 0.2 equiv. of [Cho][OAc] in CDCl_3 .

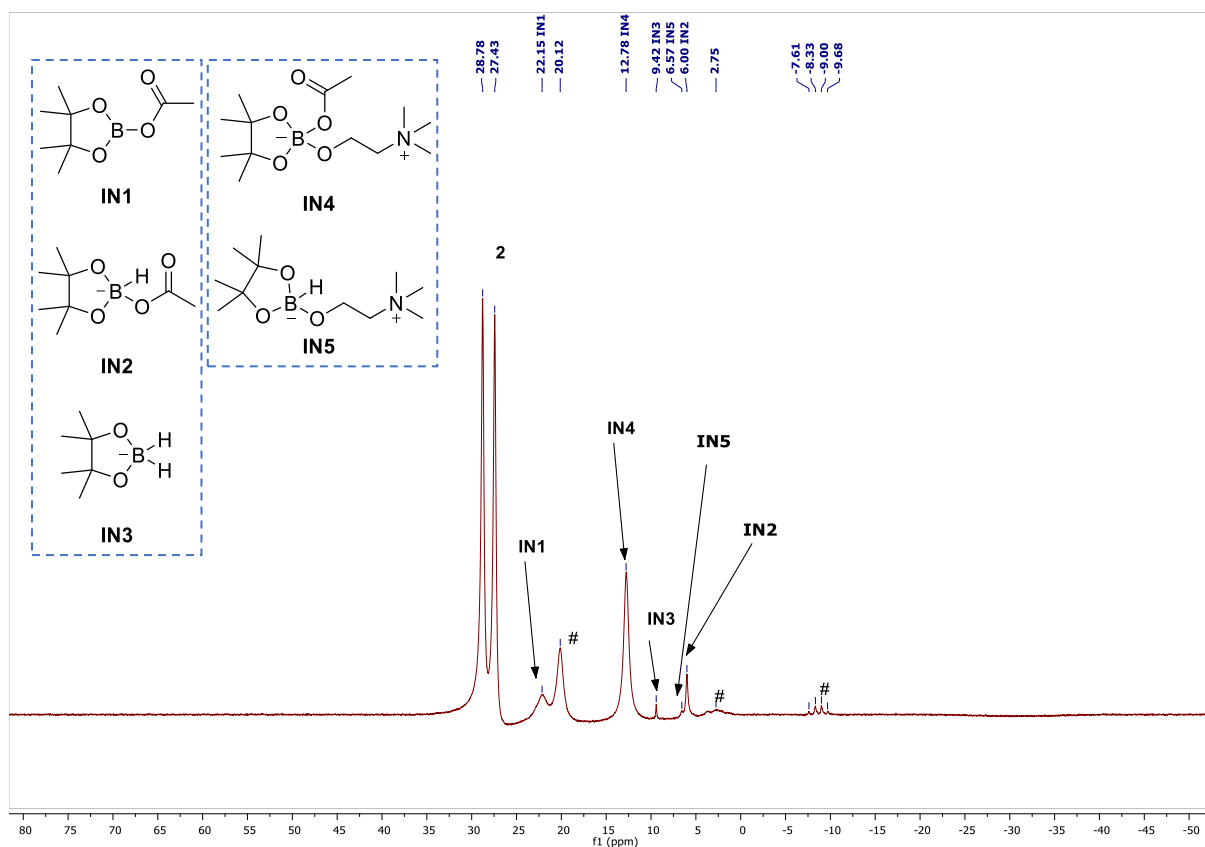


Figure S125 – ^{11}B NMR spectrum for the reaction of 1 equiv. of HBpin (**2**) with 0.2 equiv. of [Cho][OAc] in CDCl_3 . # Undefined signals. The signal at $\delta = -9.03$ ppm is visible only in CDCl_3 .

d2. For the spectrum in the toluene-d8 quartet at $\delta = -9.03$ ppm was not observed (for comparison see Figures S121)

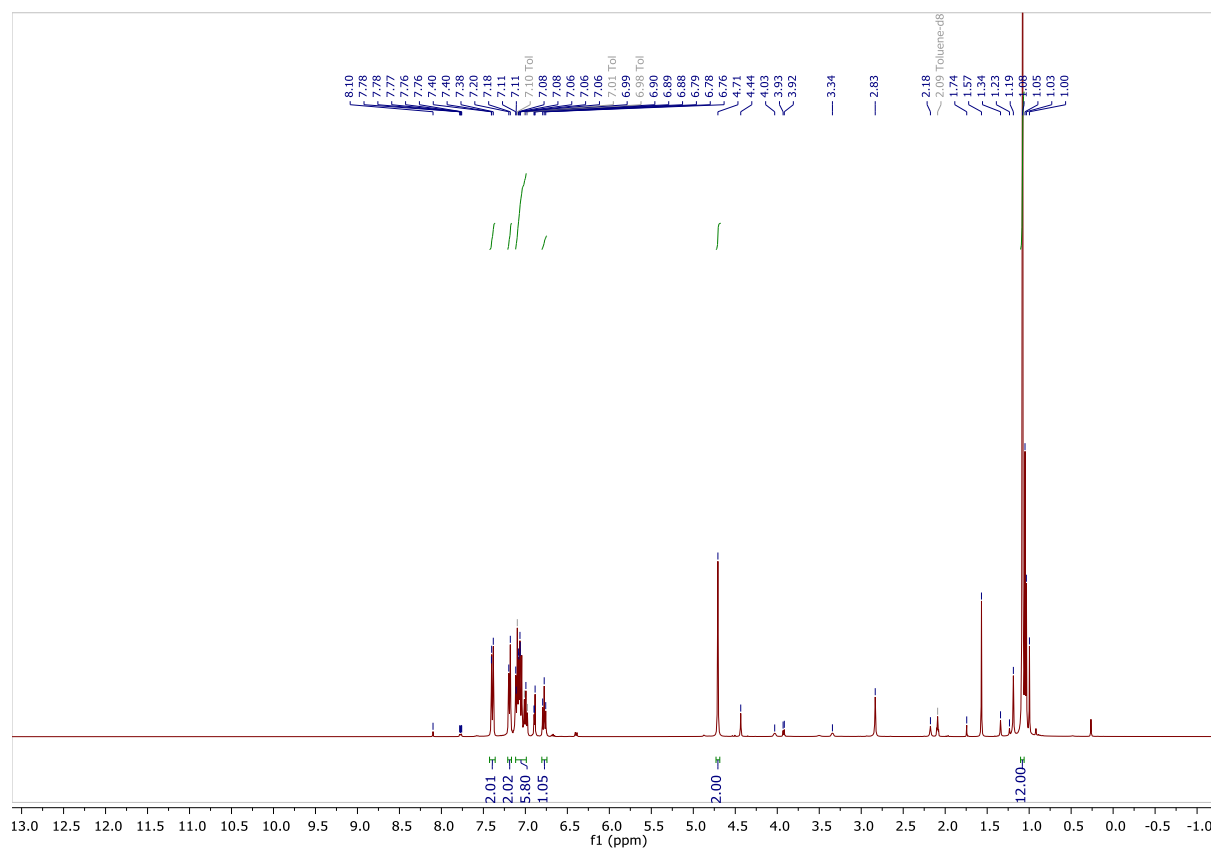


Figure S126 – ^1H NMR spectrum for the reaction of 1 equiv. of HBpin (**2**), 1 equiv. of *N*-benzylideneaniline (**1a**) and 0.2 equiv. of [Chol][OAc] in toluene-d8. For clarity, only the **3a** signals were integrated.

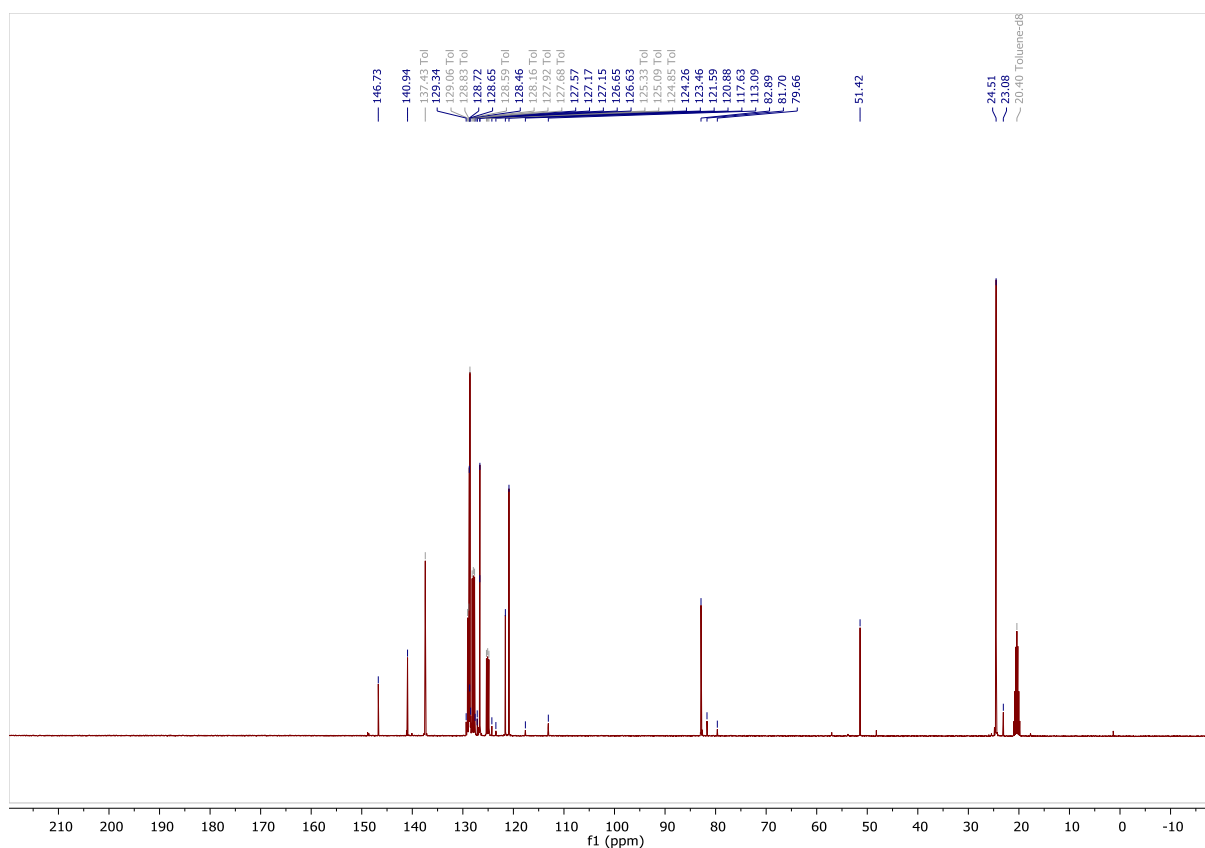


Figure S127 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for the reaction of 1 equiv. of HBpin (**2**), 1 equiv. of *N*-benzylideneaniline (**1a**) and 0.2 equiv. of [Cho][OAc] in toluene-d8.

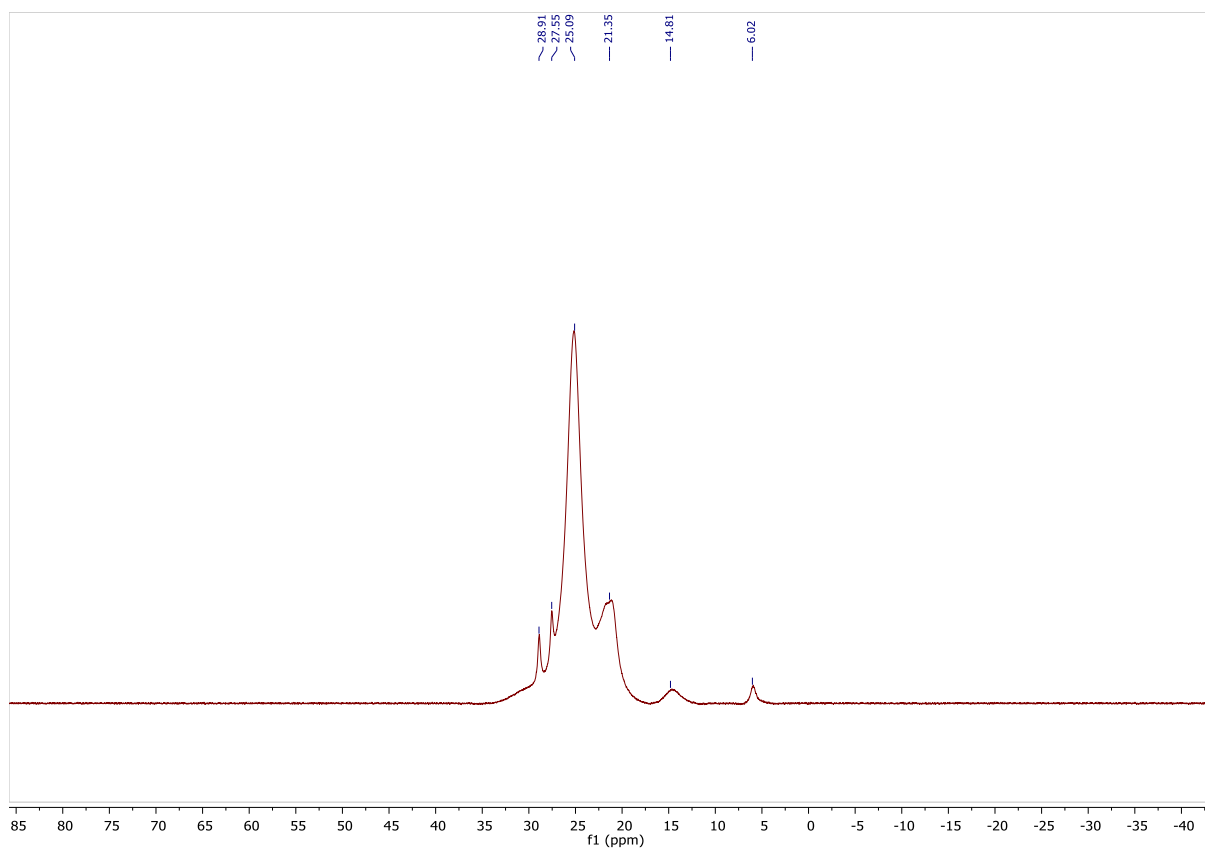


Figure S128 – ^{11}B NMR spectrum for the reaction of 1 equiv. of HBpin (**2**), 1 equiv. of *N*-benzylideneaniline (**1a**) and 0.2 equiv. of [Cho][OAc] in toluene-d8.

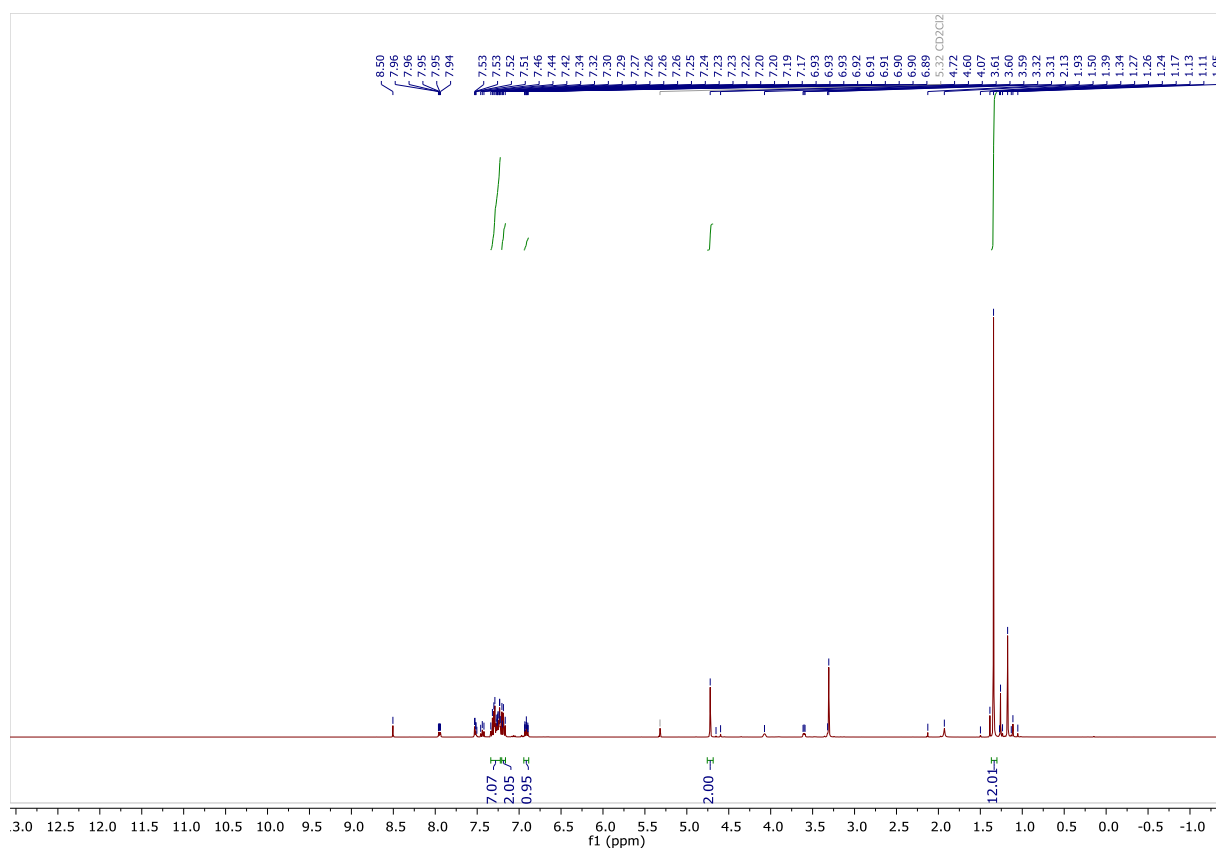


Figure S129 – ^1H NMR spectrum for the reaction of 1 equiv. of HBpin (**2**), 1 equiv. of *N*-benzylideneaniline (**1a**) and 0.2 equiv. of [Cho][OAc] in DCM- d_2 . For clarity, only the **3a** signals were integrated.

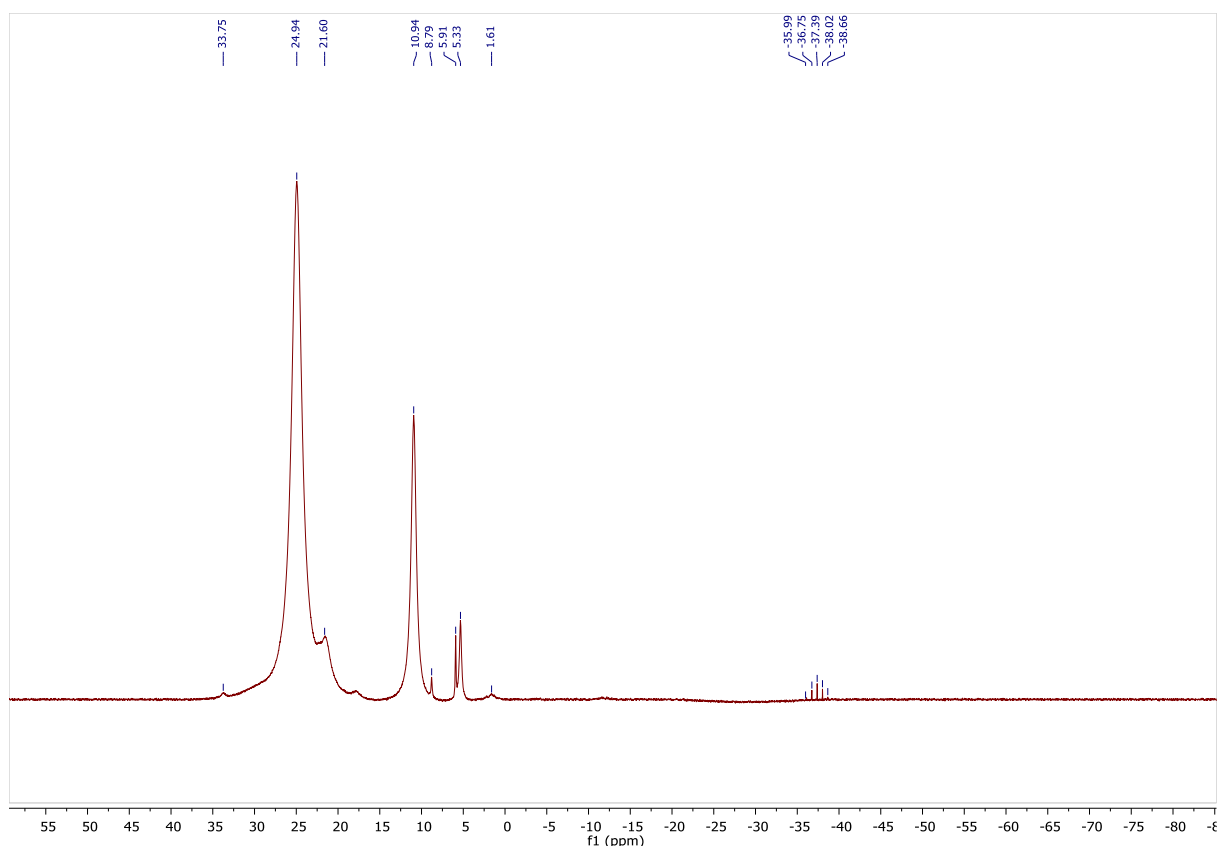


Figure S130 – ¹¹B NMR spectrum for the reaction of 1 equiv. of HBpin (**2**), 1 equiv. of *N*-benzylideneaniline (**1a**) and 0.2 equiv. of [Cho][OAc] in DCM-d₂.

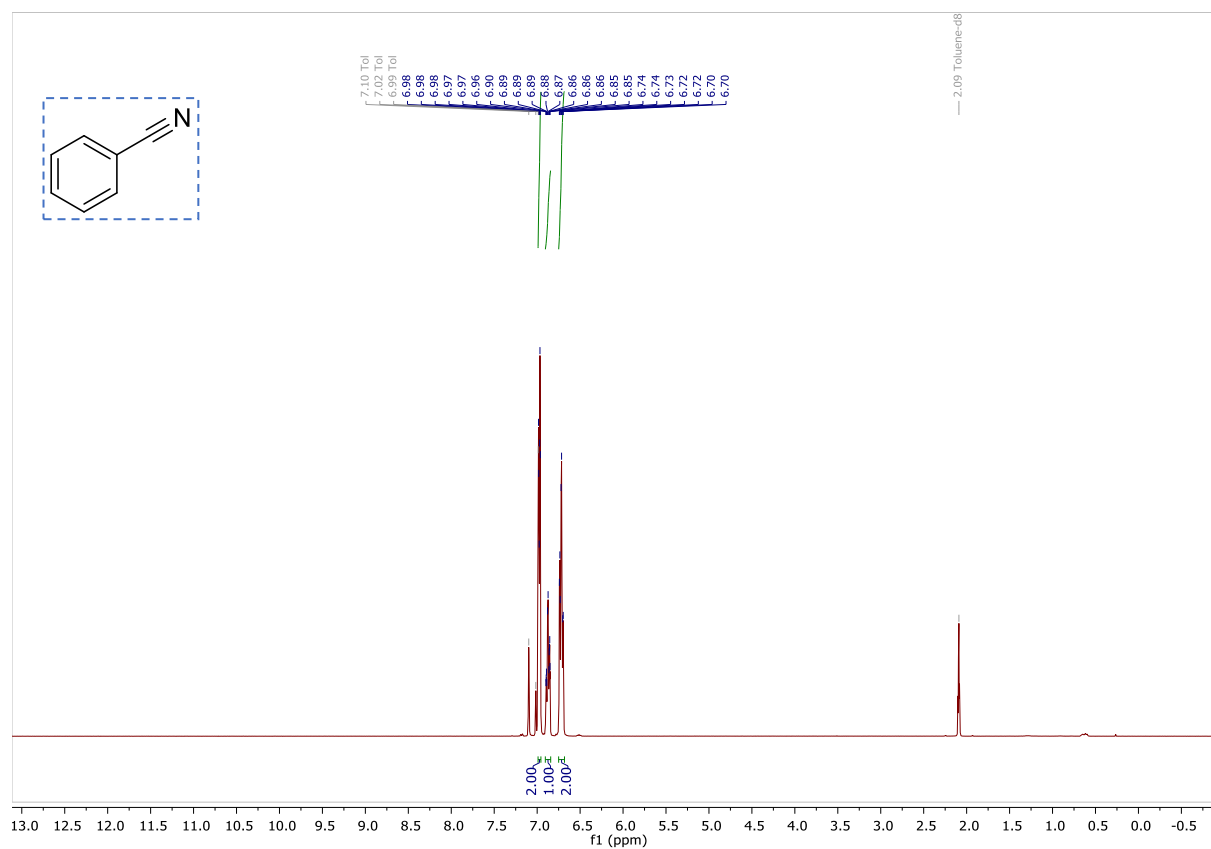


Figure S131 – ¹H NMR spectrum of benzonitrile (**5a**) in toluene-d₈.

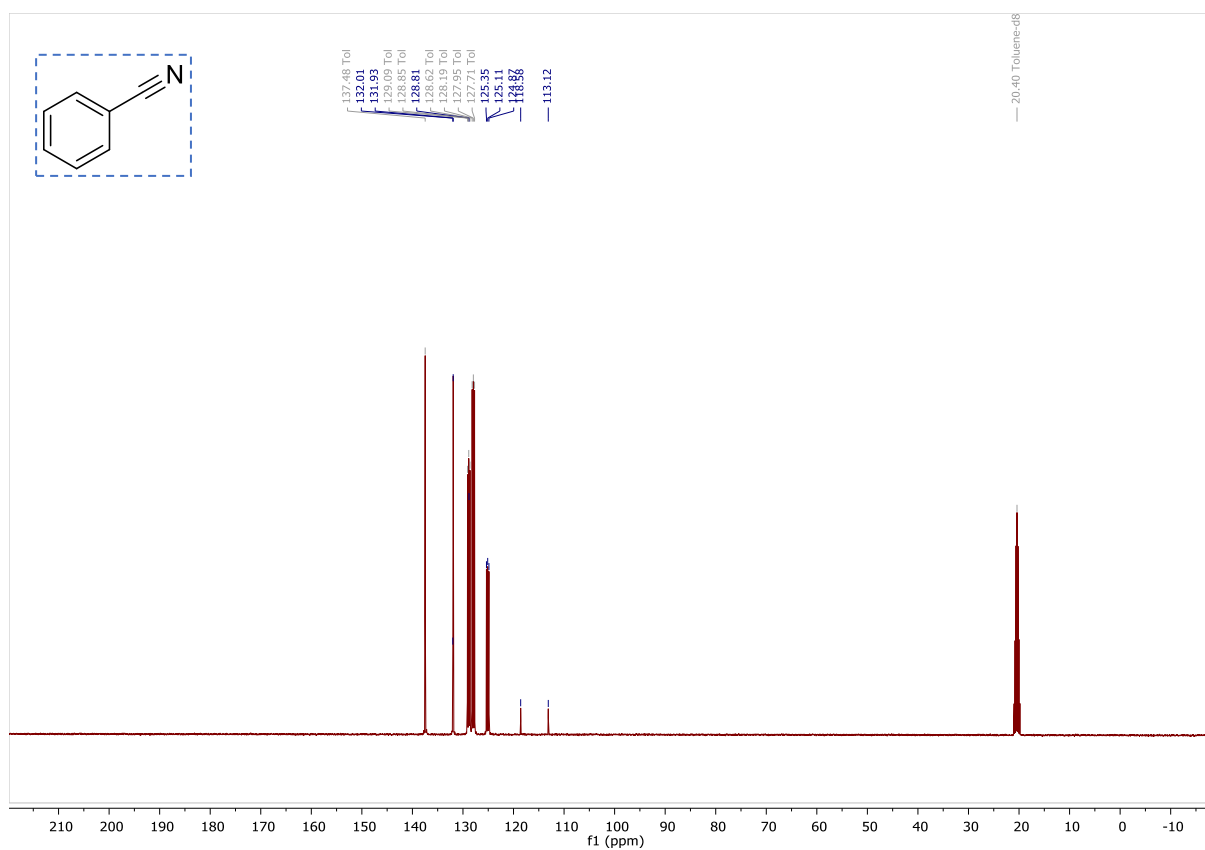


Figure S132 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of benzonitrile (5a) in toluene- d_8 .

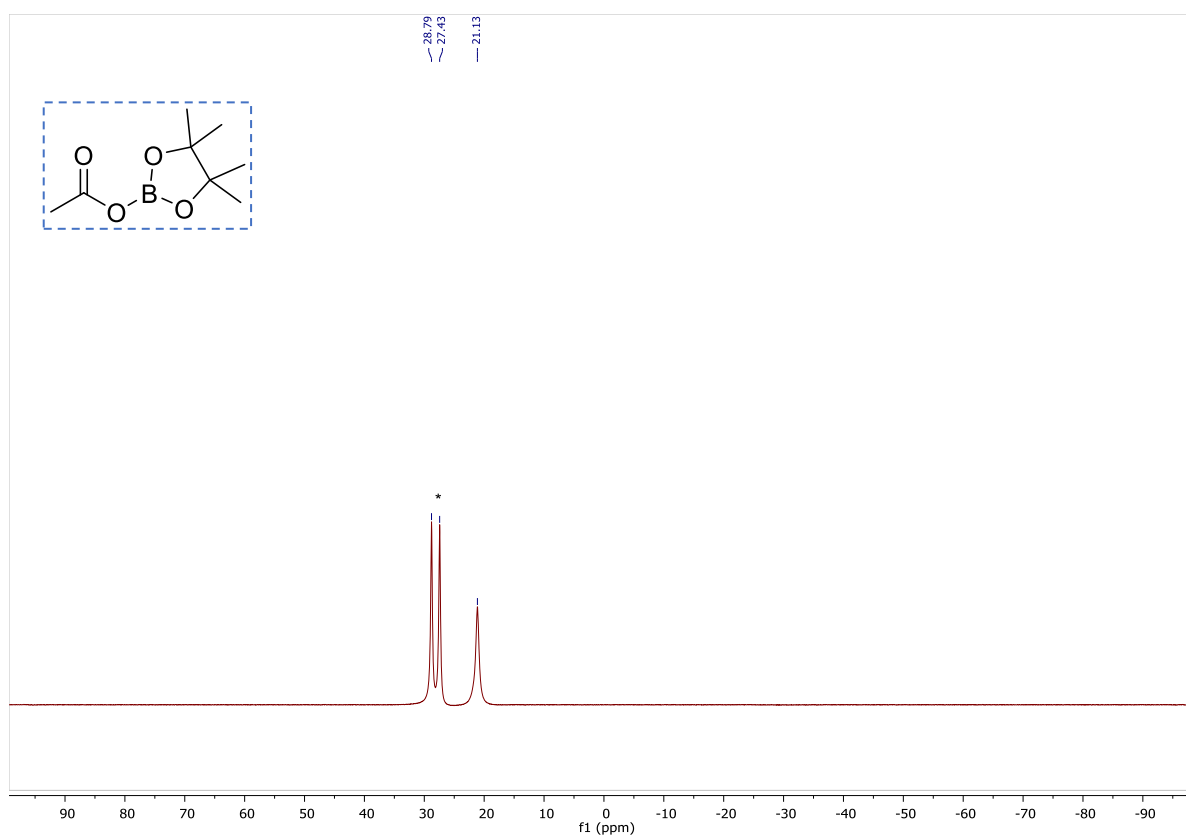


Figure S133 – ^{11}B NMR spectrum of OAcBpin (IN1) obtained in equimolar reaction of acetic acid with pinacolborane (2) in $\text{DCM-}d_2$. *HBpin.

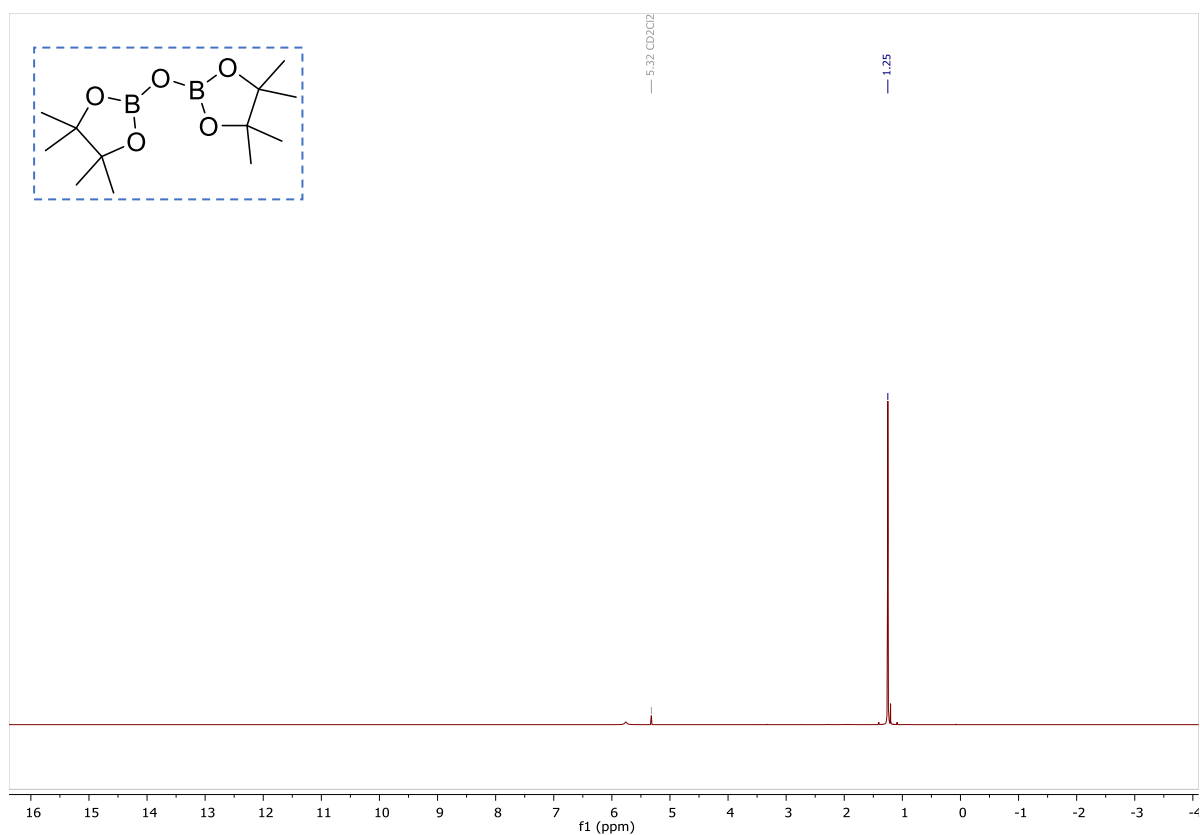


Figure S134 – ^1H NMR spectrum of $\text{O}(\text{Bpin})_2$ obtained in equimolar reaction of water with pinacolborane (**2**) in DCM-d_2 .

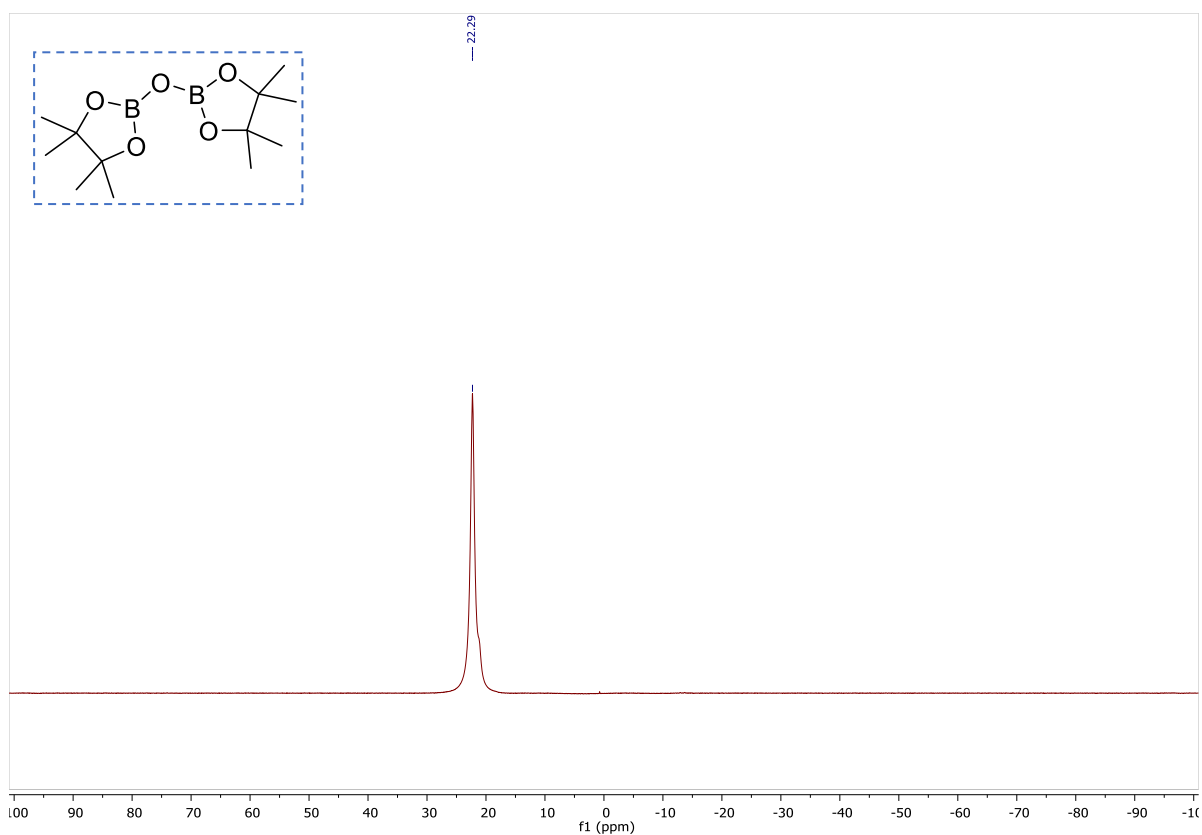


Figure S135 – ^{11}B NMR spectrum of $\text{O}(\text{Bpin})_2$ obtained in equimolar reaction of water with pinacolborane (**2**) in DCM-d_2 .

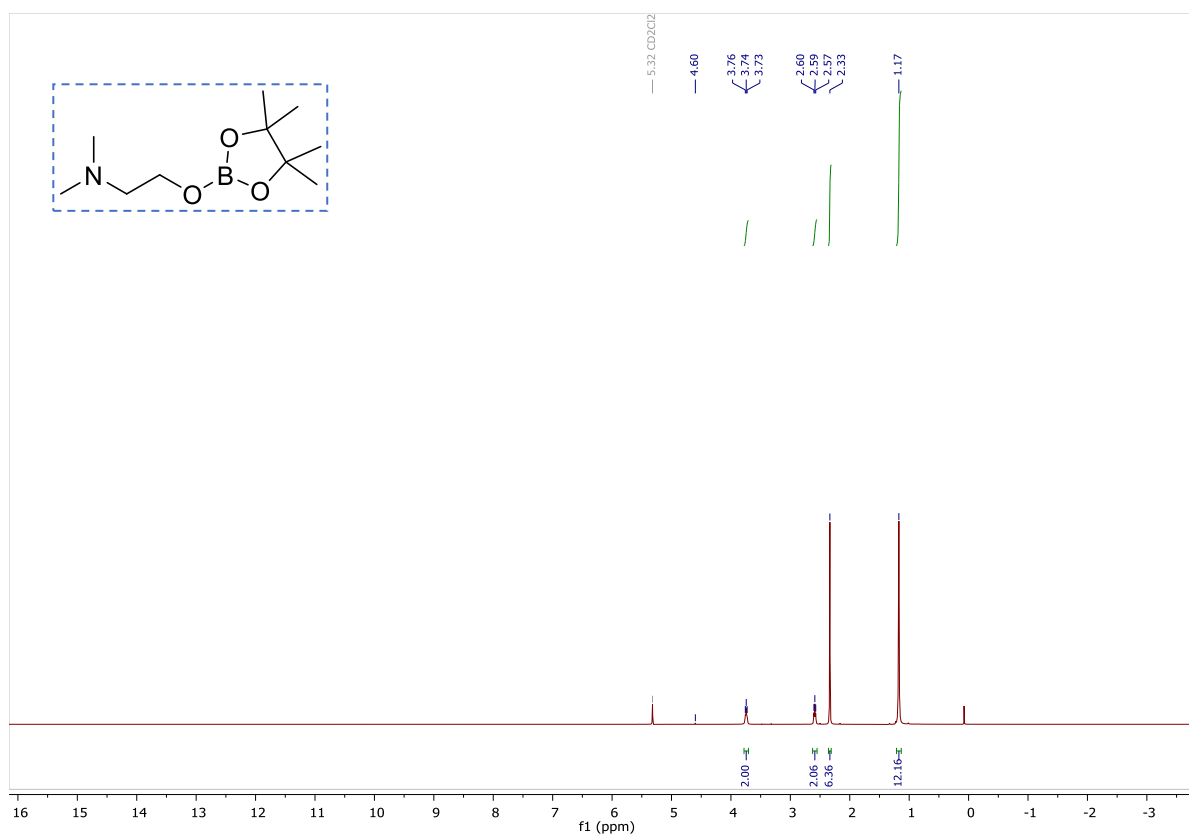


Figure S136 – ^1H NMR spectrum of Cho(OBpin) obtained in equimolar reaction of 2-(dimethylamino)ethan-1-ol with pinacolborane (**2**) in DCM- d_2 .

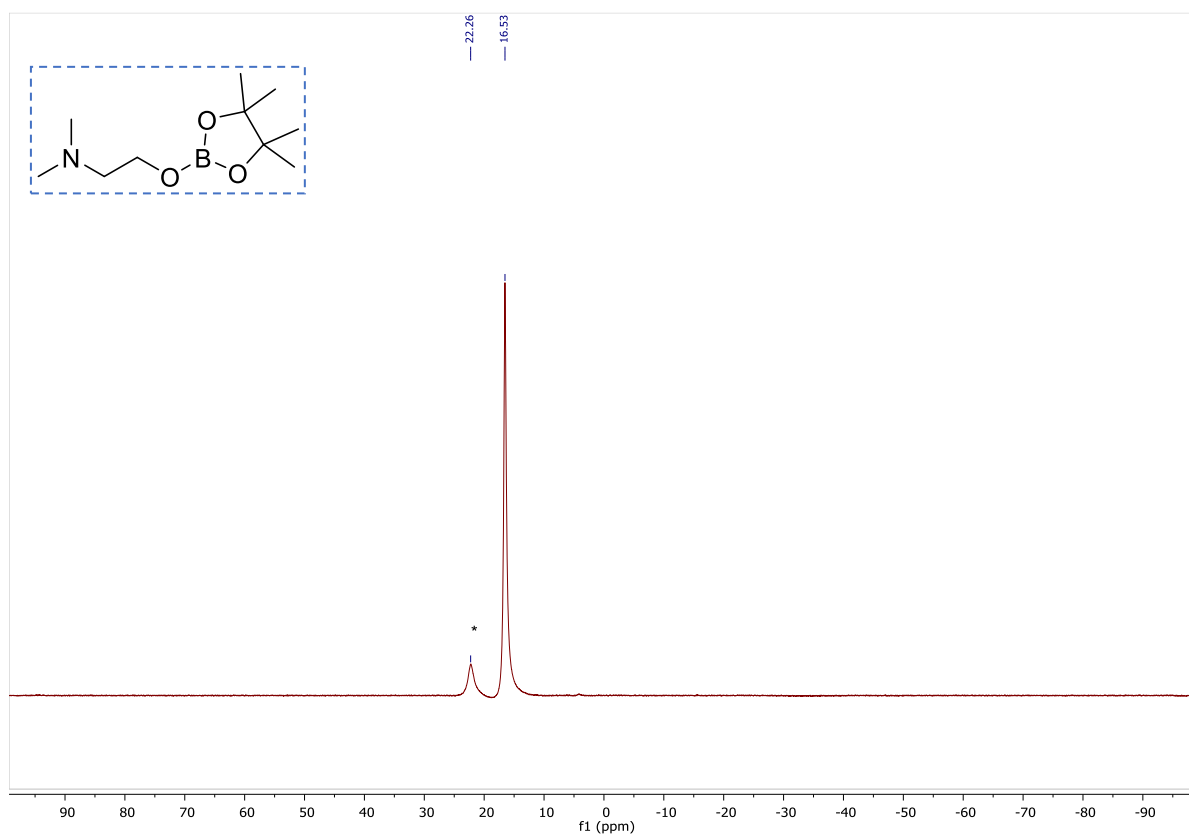


Figure S137 – ^{11}B NMR spectrum of Cho(OBpin) obtained in equimolar reaction of 2-(dimethylamino)ethan-1-ol with pinacolborane (**2**) in DCM- d_2 . *O(Bpin) $_2$.

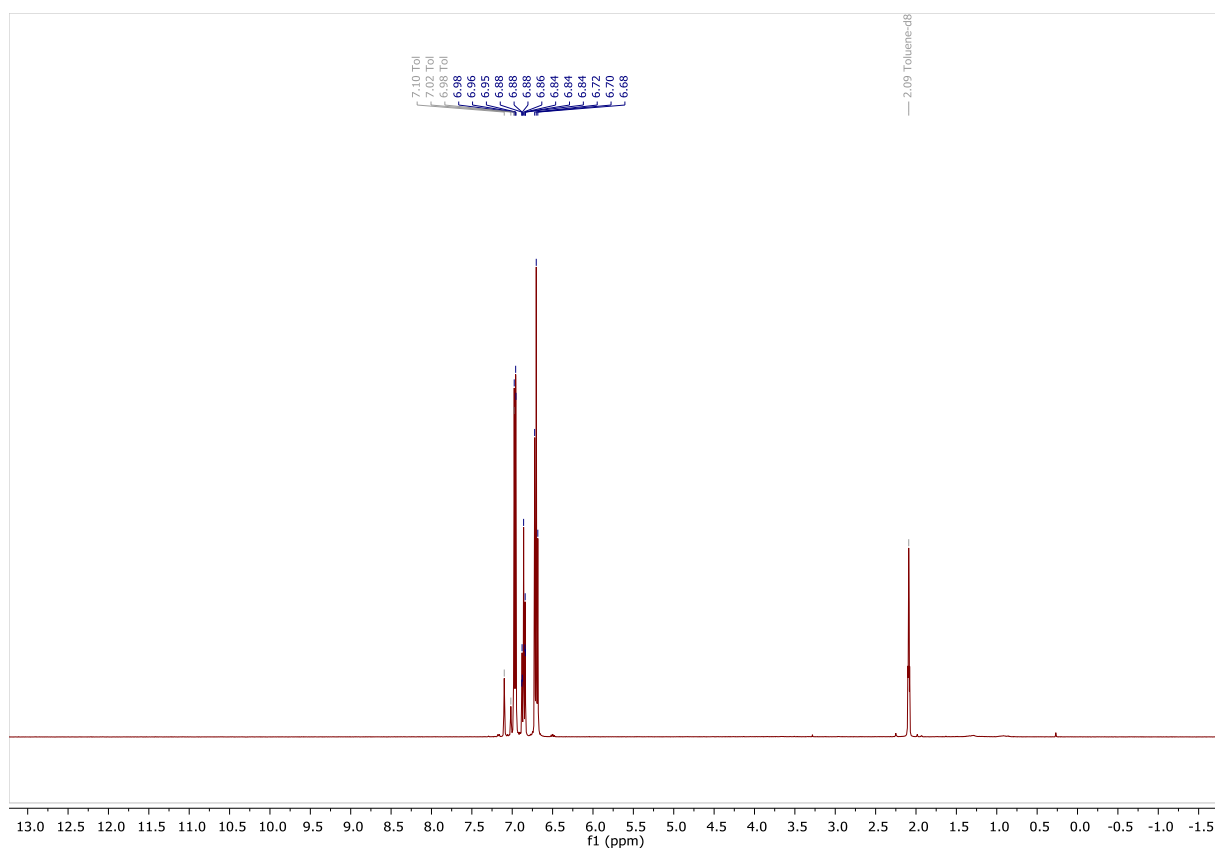


Figure S138 – ¹H NMR spectrum for the reaction of 1 equiv. of benzonitrile (**5a**) and 1 equiv. of [Cho][OAc] in toluene-d₈, shortly after mixing the reagents.

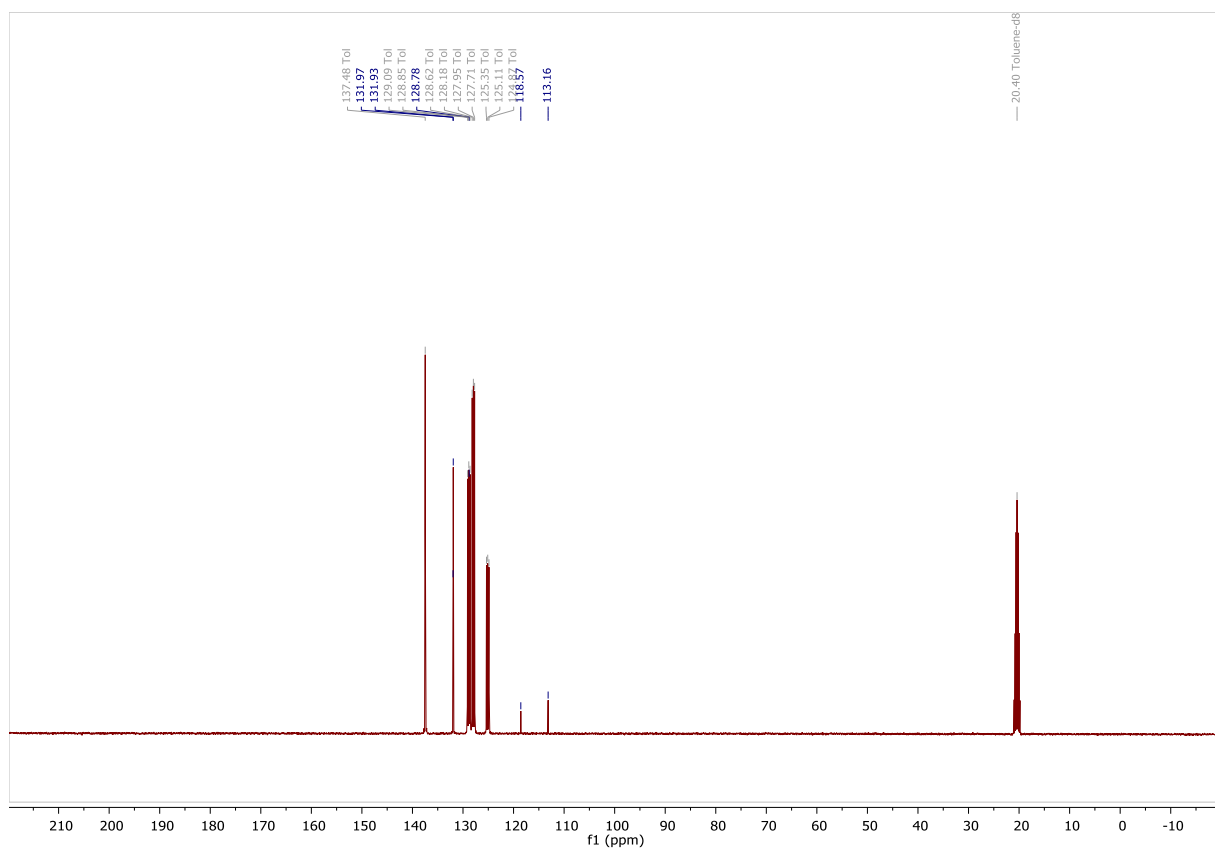


Figure S139 – ¹³C{¹H} NMR spectrum for the reaction of 1 equiv. of benzonitrile (**5a**) and 1 equiv. of [Cho][OAc] in toluene-d₈, shortly after mixing the reagents.

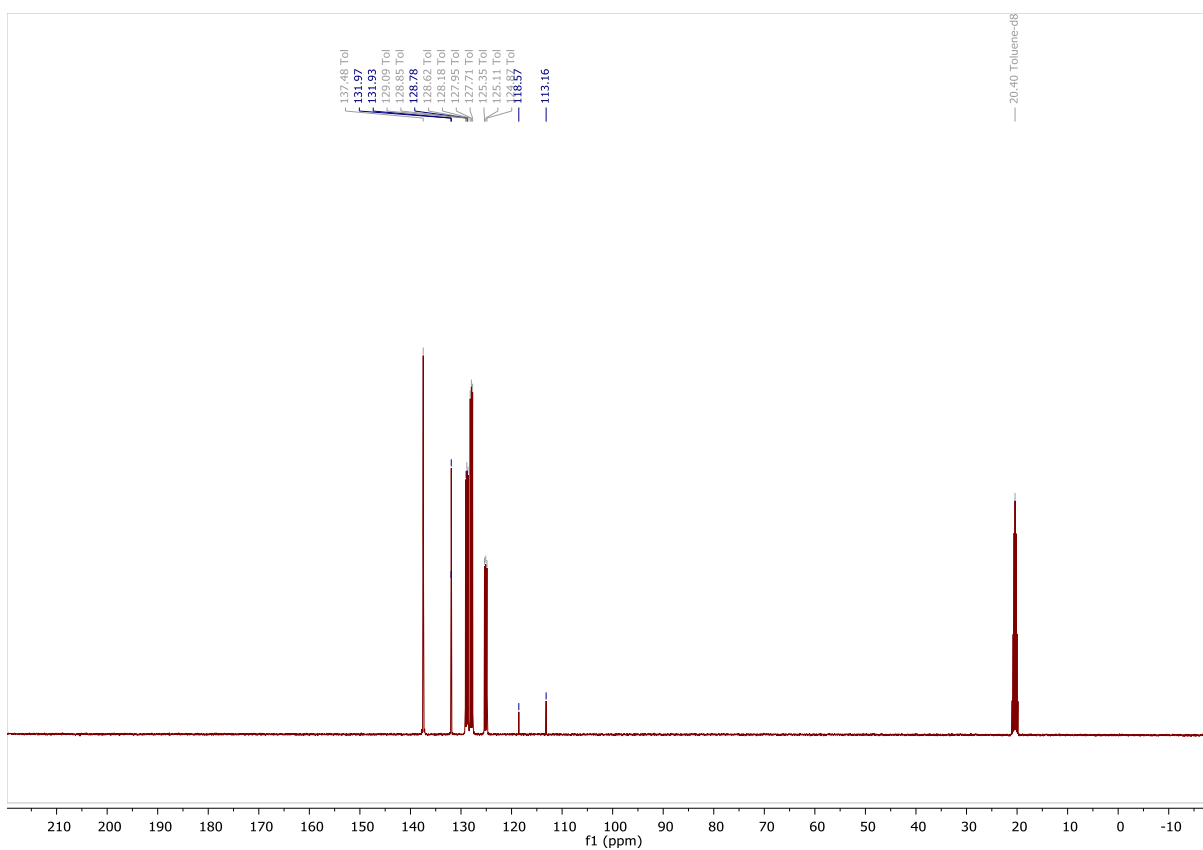


Figure S140 – ^1H NMR spectrum for the reaction of 1 equiv. of benzonitrile (**5a**) and 1 equiv. of [Cho][OAc] in toluene- d_8 , after heating in an oil bath in 70 °C for 24 h.

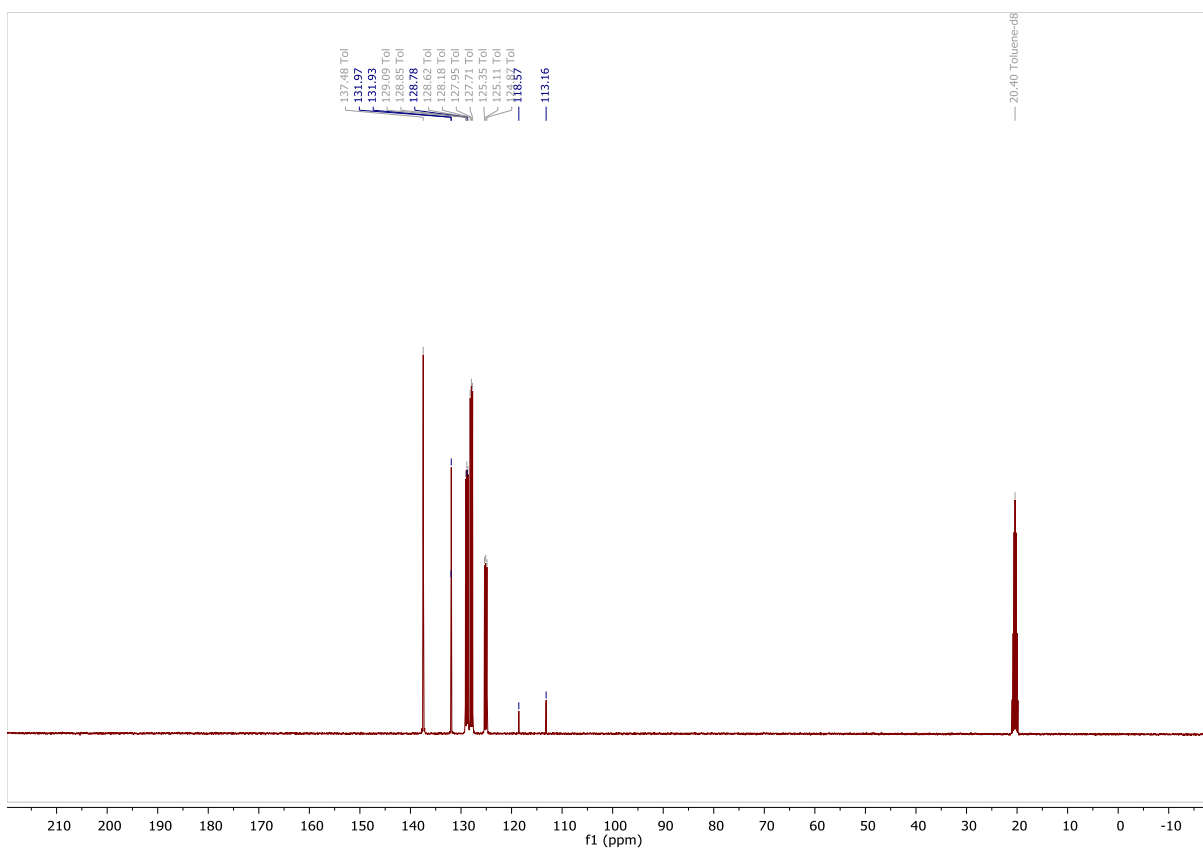


Figure S141 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for the reaction of 1 equiv. of benzonitrile (**5a**) and 1 equiv. of [Cho][OAc] in toluene- d_8 , after heating in an oil bath in 70 °C for 24h.

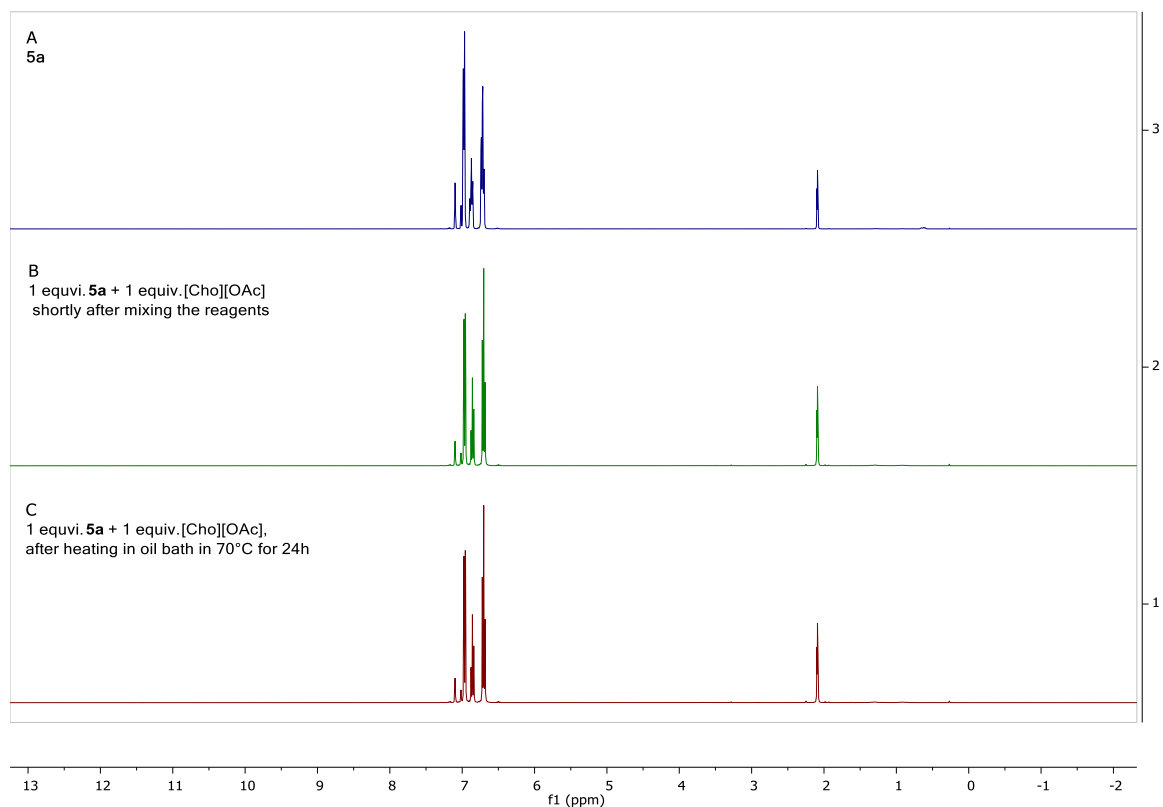


Figure S142 – Stacked ¹H NMR spectra: (A) benzonitrile (**5a**), (B) the reaction of 1 equiv. of benzonitrile (**5a**) with 1 equiv. of [Cho][OAc], shortly after mixing the reagents, (C) the reaction of 1 equiv. of benzonitrile (**5a**) with 1 equiv. of [Cho][OAc], after heating in an oil bath in 70 °C for 24 h. Solvent: toluene-d₈.

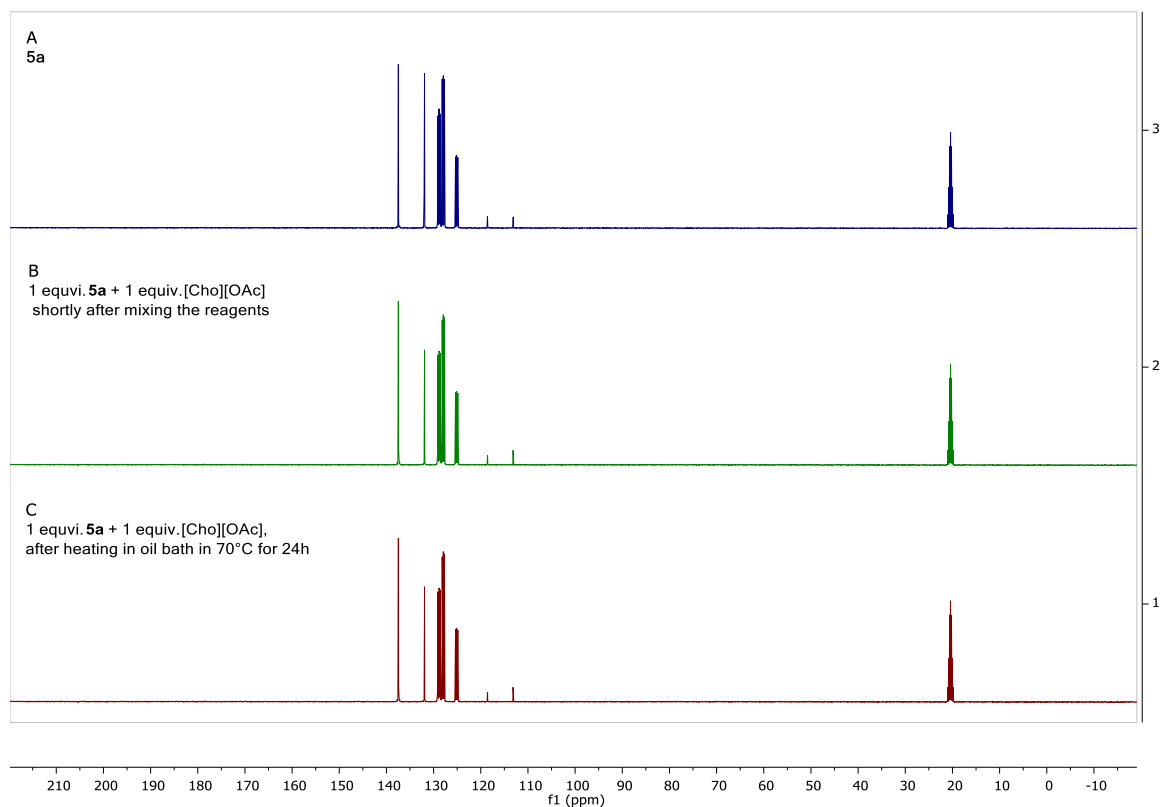


Figure S143 – Stacked $^{13}\text{C}\{^1\text{H}\}$ NMR spectra: (A) benzonitrile (**5a**), (B) the reaction of 1 equiv. of benzonitrile (**5a**) with 1 equiv. of [Cho][OAc], shortly after mixing the reagents, (C) the reaction of 1 equiv. of benzonitrile (**5a**) with 1 equiv. of [Cho][OAc], after heating in oil bath in 70 °C for 24 h. Solvent: toluene- d_8 .

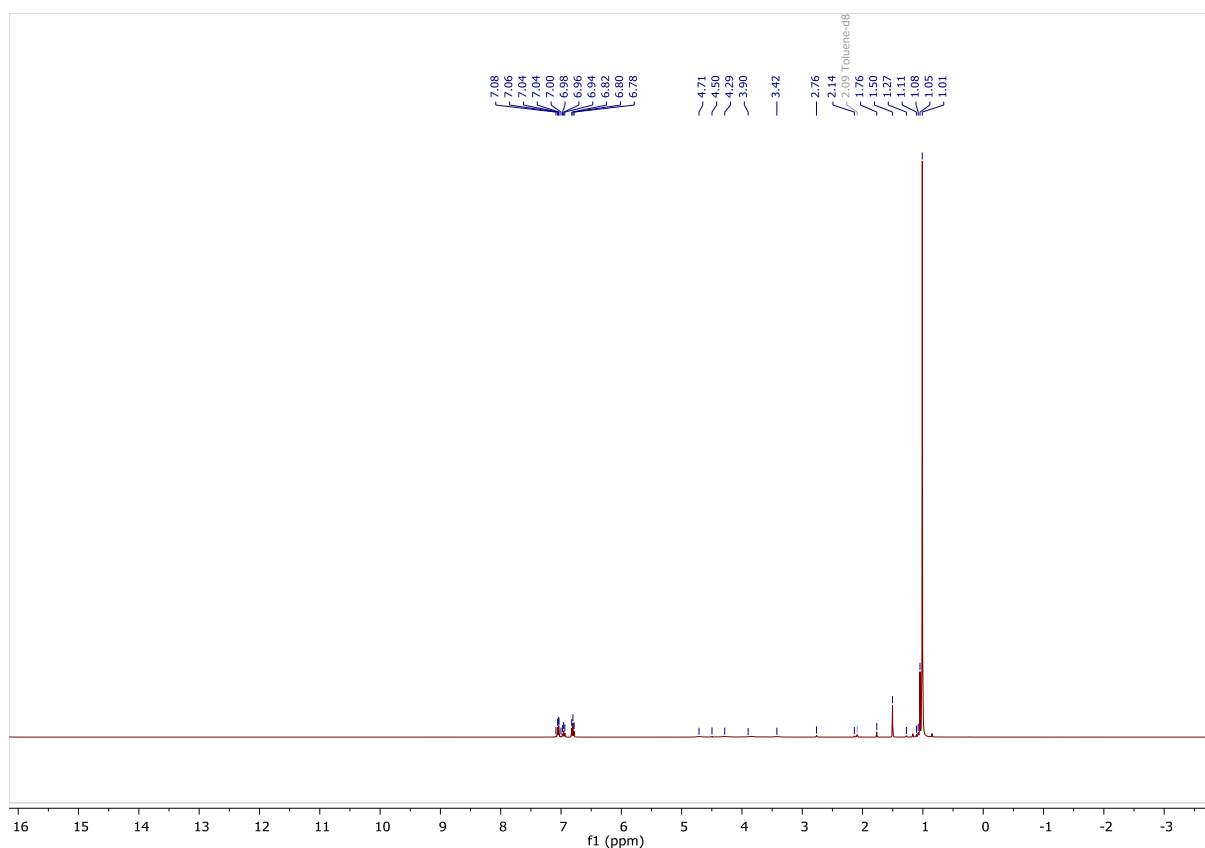


Figure S144 – ¹H NMR spectrum for the reaction of 3.2 equiv. of HBpin (**2**), 1 equiv. of benzonitrile (**5a**) and 0.2 equiv. of [Cho][OAc] in toluene-d₈, shortly after mixing the reagents.

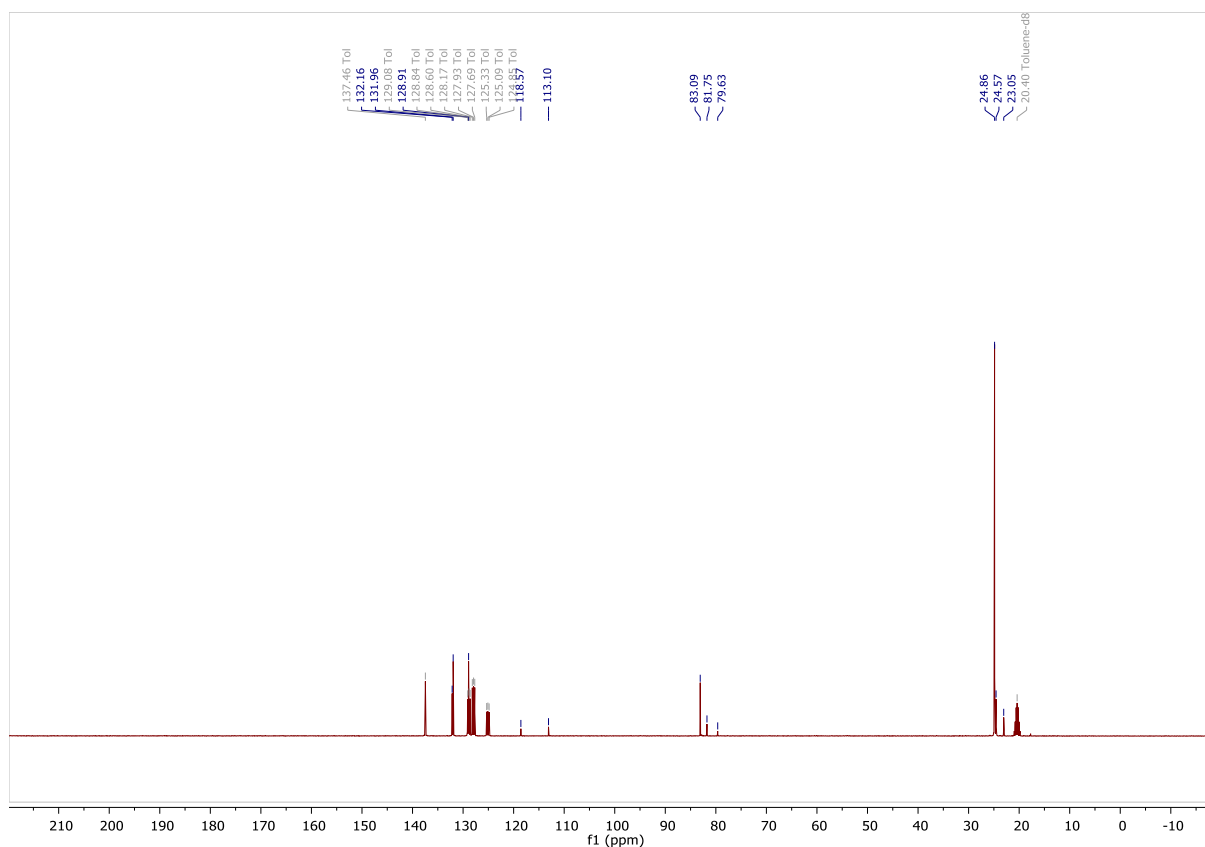


Figure S145 – ¹³C{¹H} NMR spectrum for the reaction of 3.2 equiv. of HBpin (**2**), 1 equiv. of benzonitrile (**5a**) and 0.2 equiv. of [Cho][OAc] in toluene-d₈, shortly after mixing the reagents.

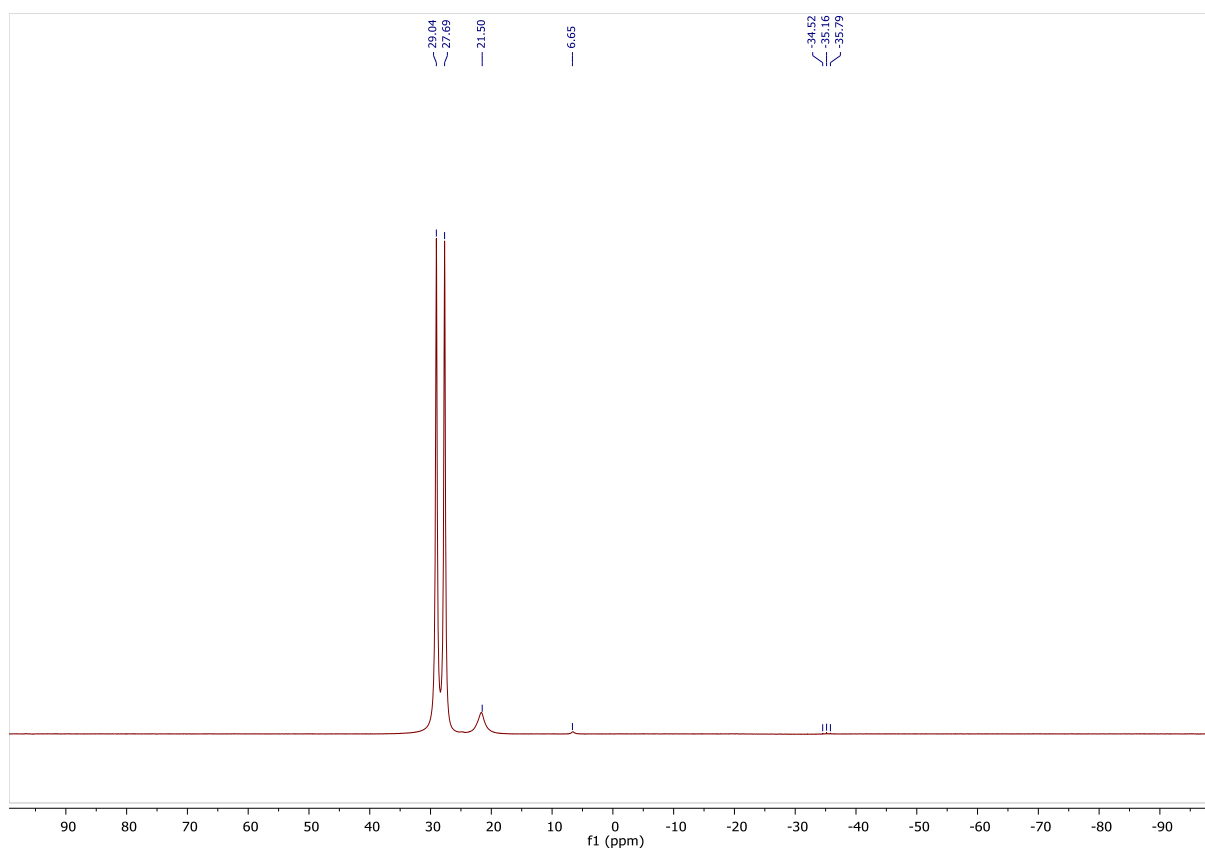


Figure S146 – ^{11}B NMR spectrum for the reaction of 3.2 equiv. of HBpin (**2**), 1 equiv. of benzonitrile (**5a**) and 0.2 equiv. of $[\text{Cho}][\text{OAc}]$ in toluene- d_8 , shortly after mixing the reagents.

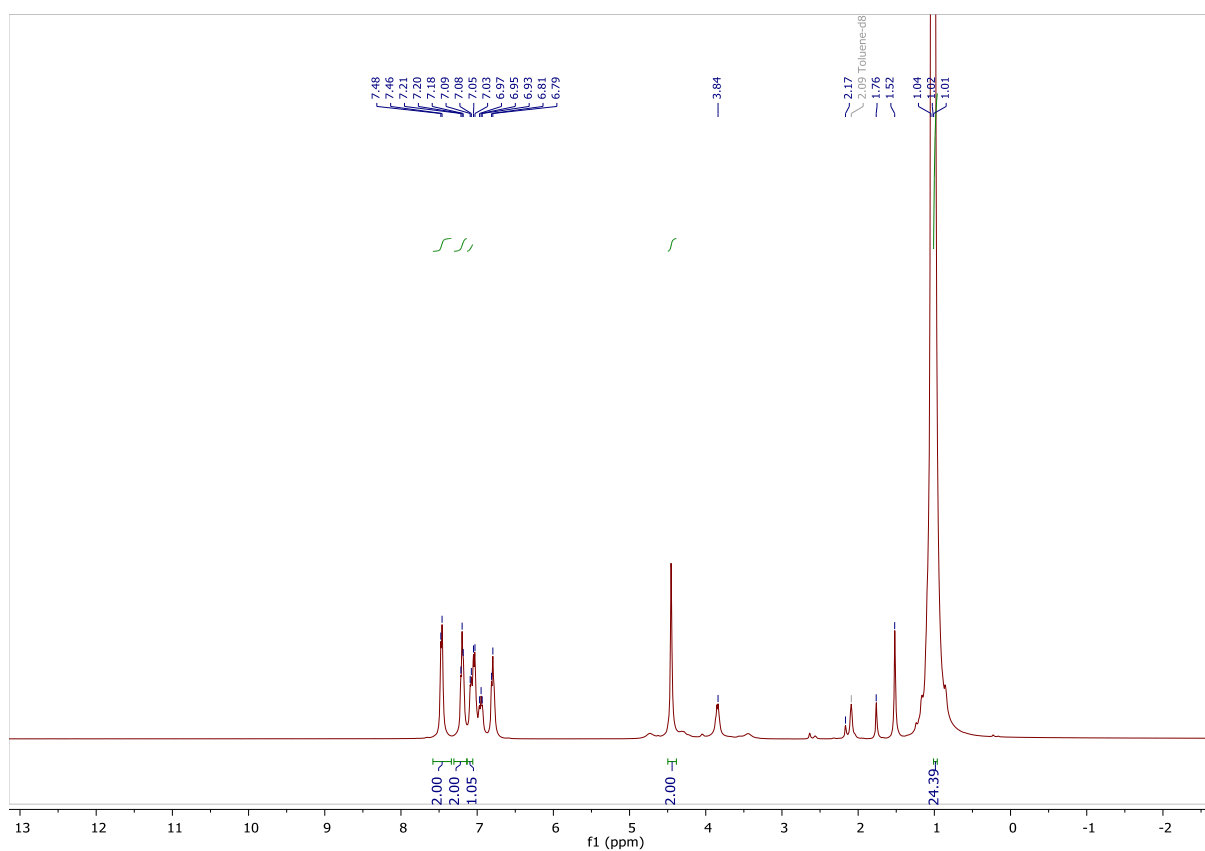


Figure S147 – ^1H NMR spectrum for the reaction of 3.2 equiv. of HBpin (**2**), 1 equiv. of

benzonitrile (**5a**) and 0.2 equiv. of [Cho][OAc] in toluene-d₈, after heating in an oil bath in 70 °C for 24 h. For clarity, only the **6a** signals were integrated.

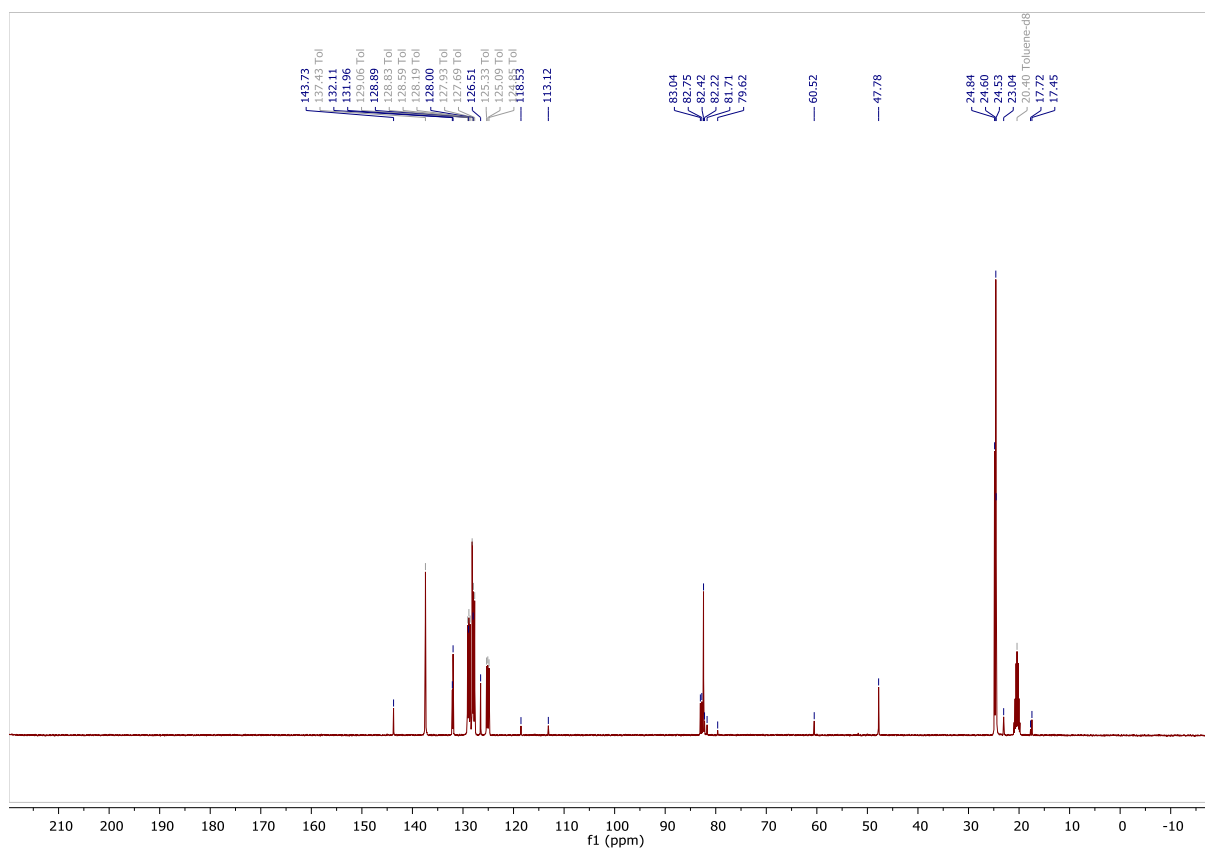


Figure S148 – $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum for the reaction of 3.2 equiv. of HBpin (**2**), 1 equiv. of benzonitrile (**5a**) and 0.2 equiv. of [Cho][OAc] in toluene-d₈, after heating in an oil bath in 70 °C for 24 h.

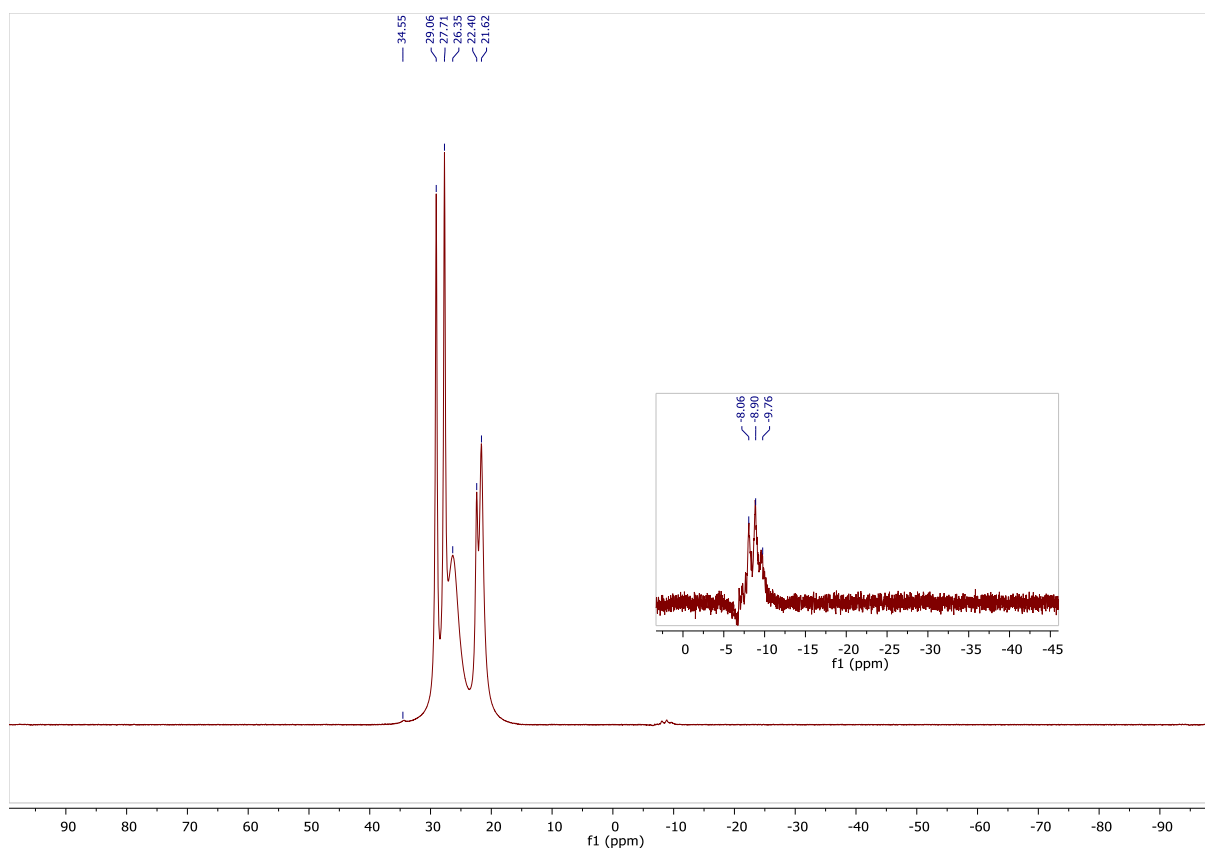


Figure S149 – ^{11}B NMR spectrum for the reaction of 3.2 equiv. of HBpin (**2**), 1 equiv. of benzonitrile (**5a**) and 0.2 equiv. of $[\text{Cho}][\text{OAc}]$ in toluene- d_8 , after heating in an oil bath in 70 °C for 24h.

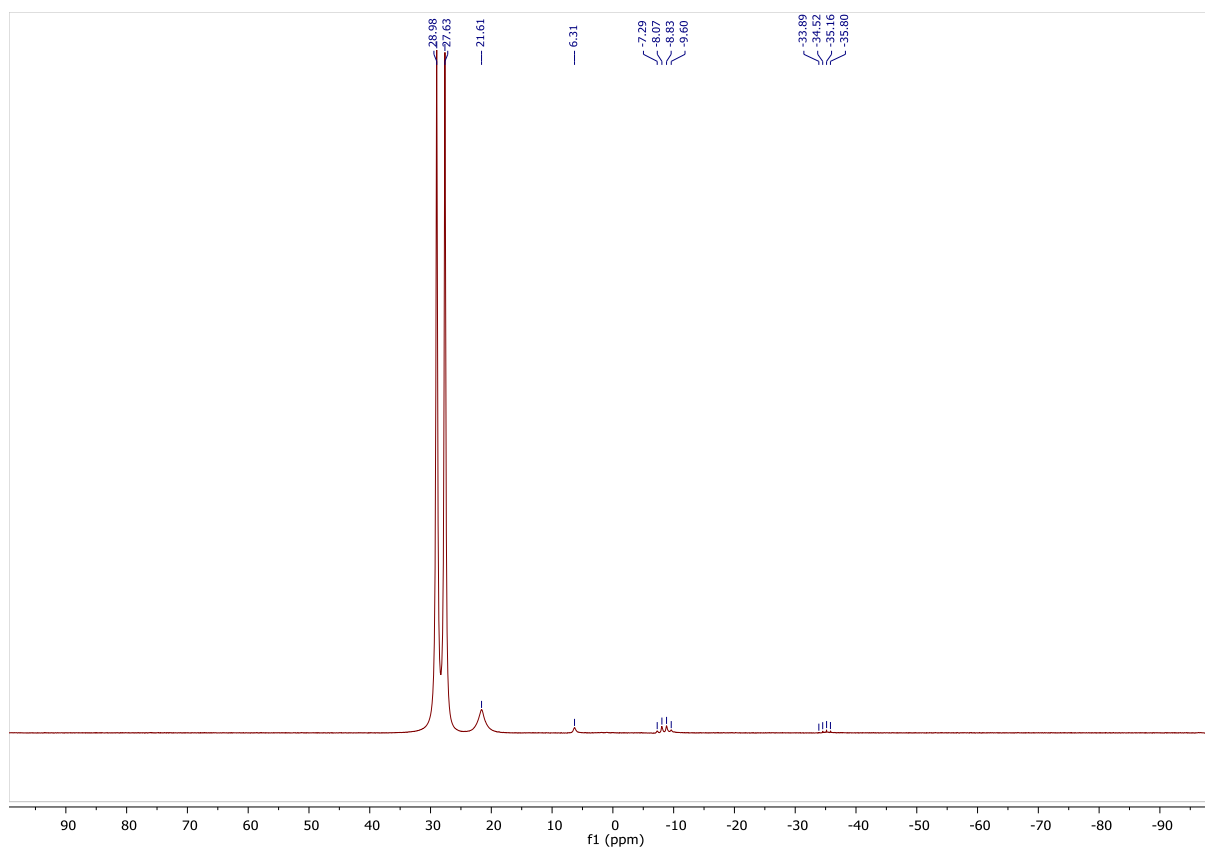


Figure S150 – ^{11}B NMR spectrum for the reaction of 3.2 equiv. of HBpin (**2**), 1 equiv. of

benzonitrile (**5a**), 0.2 equiv. of [Cho][OAc] and 0.2 equiv. of TMEDA in toluene-d₈, shortly after mixing the reagents.

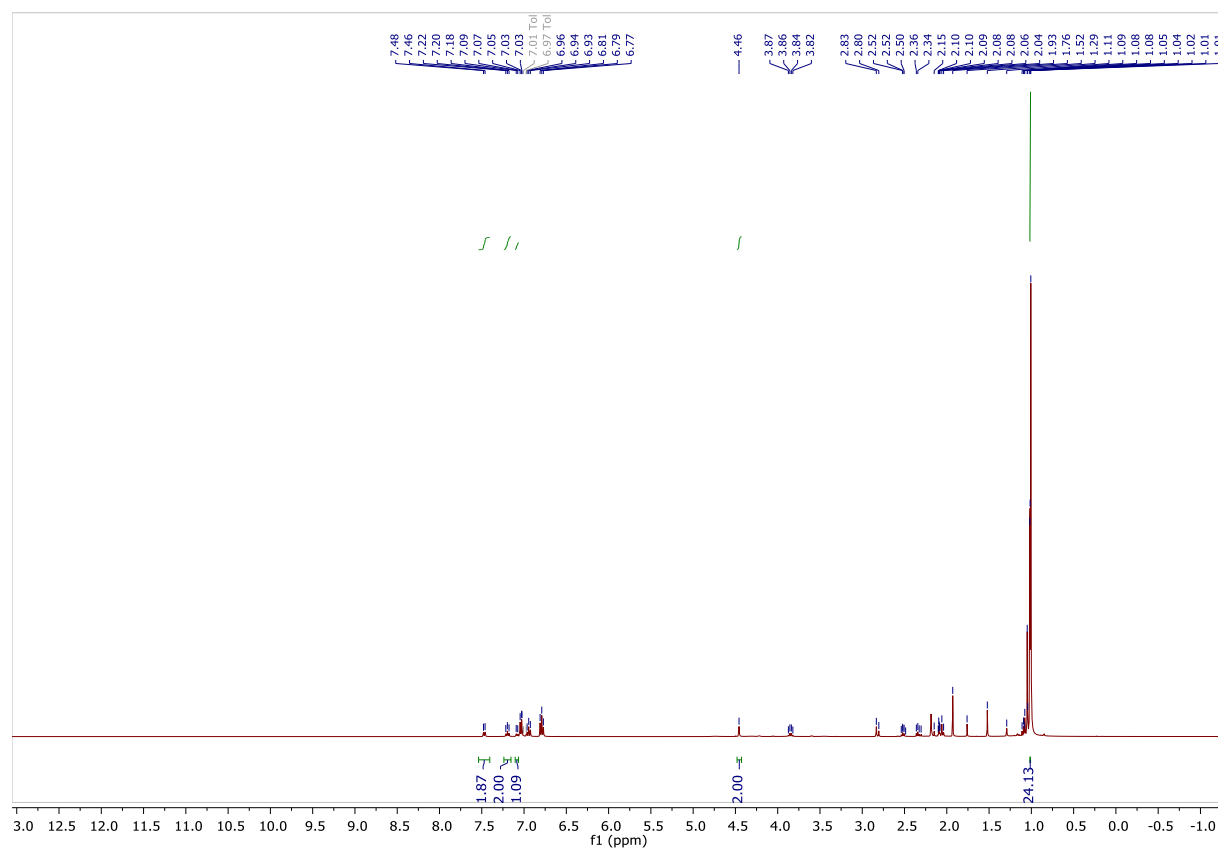


Figure S151 – ¹H NMR spectrum for the reaction of 3.2 equiv. of HBpin (**2**), 1 equiv. of benzonitrile (**5a**), 0.2 equiv. of [Cho][OAc] and 0.2 equiv. of TMEDA in toluene-d₈, after heating in an oil bath in 70 °C for 24 h. For clarity, only the **6a** signals were integrated.

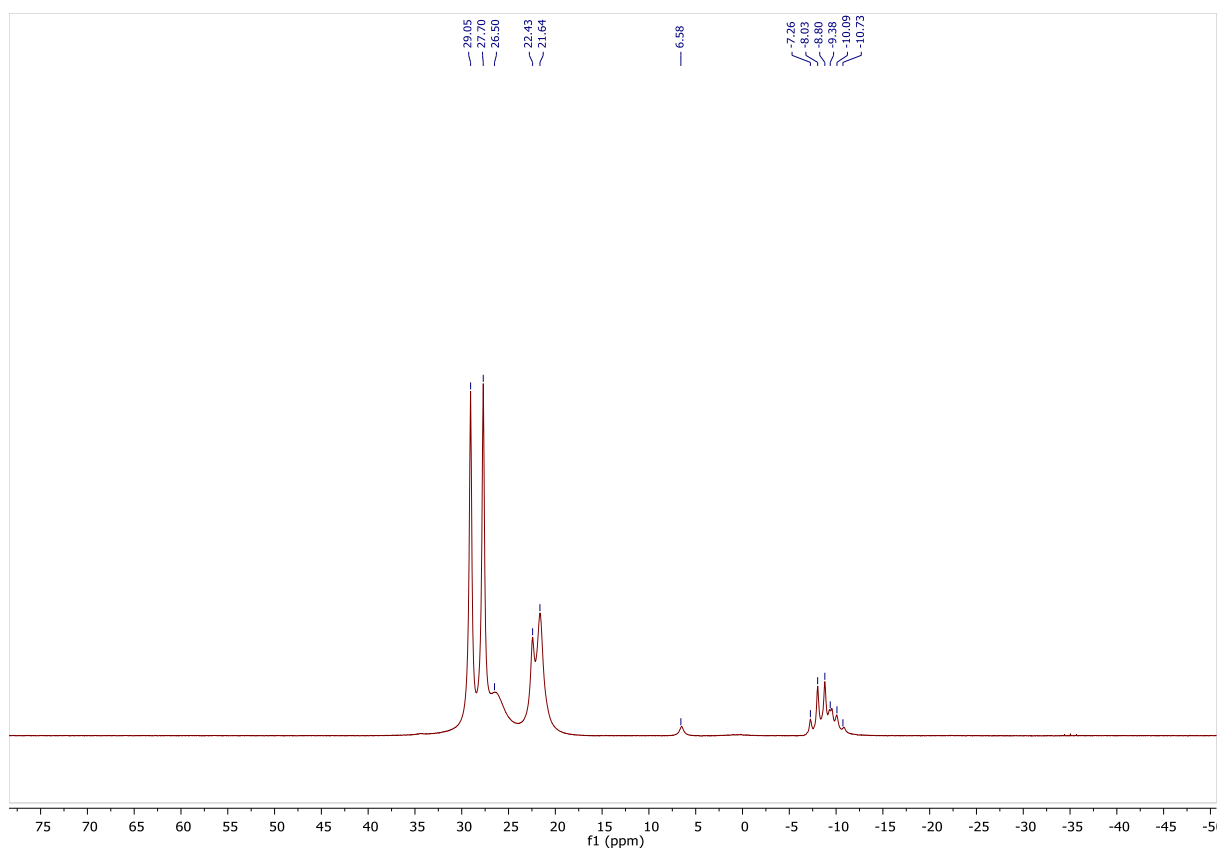


Figure S152 – ^{11}B NMR spectrum for the reaction of 3.2 equiv. of HBpin (**2**), 1 equiv. of benzonitrile (**5a**), 0.2 equiv. of $[\text{Cho}][\text{OAc}]$ and 0.2 equiv. of TMEDA in toluene- d_8 , after heating in an oil bath in 70 °C for 24 h.

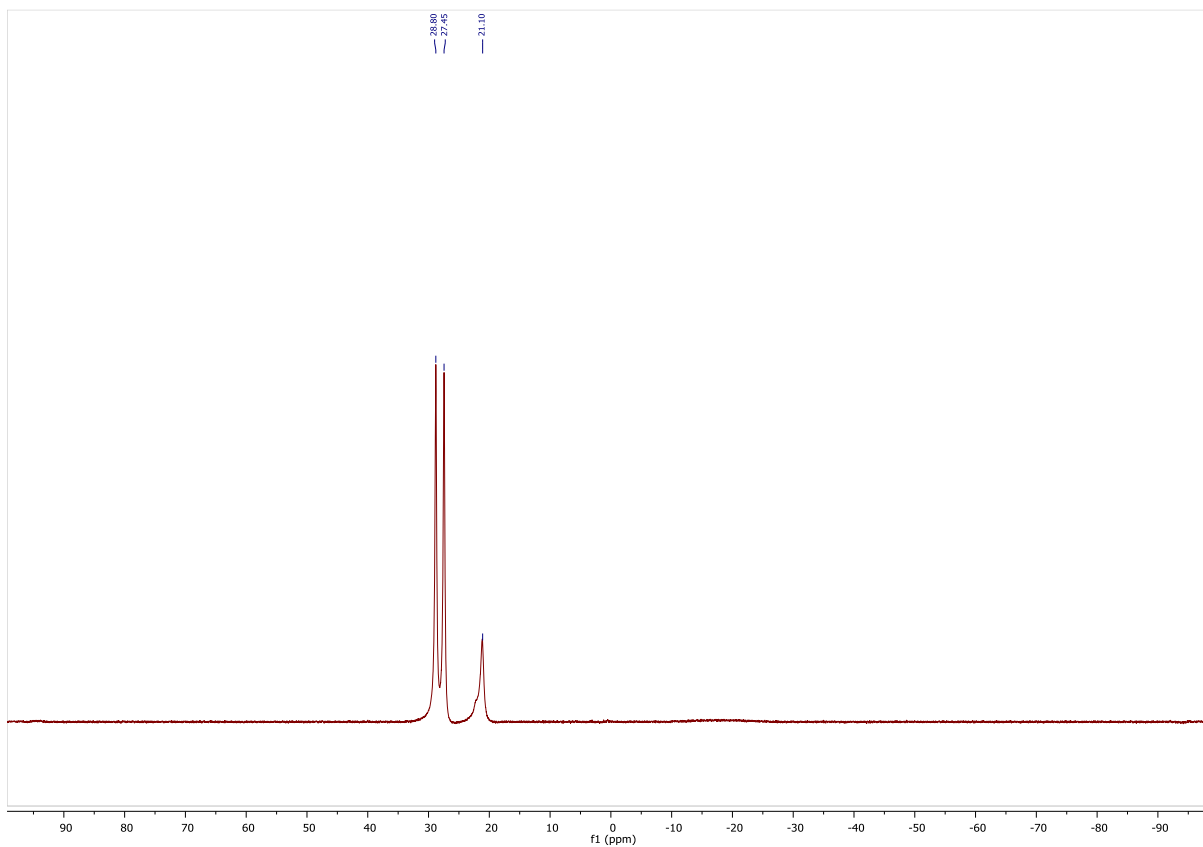


Figure S153 – ^{11}B NMR spectrum for the reaction of 1.2 equiv. of pinacolborane (**2**) and 0.2 equiv. of [Cho][OAc] after 7 days, rt in DCM-d_2 .

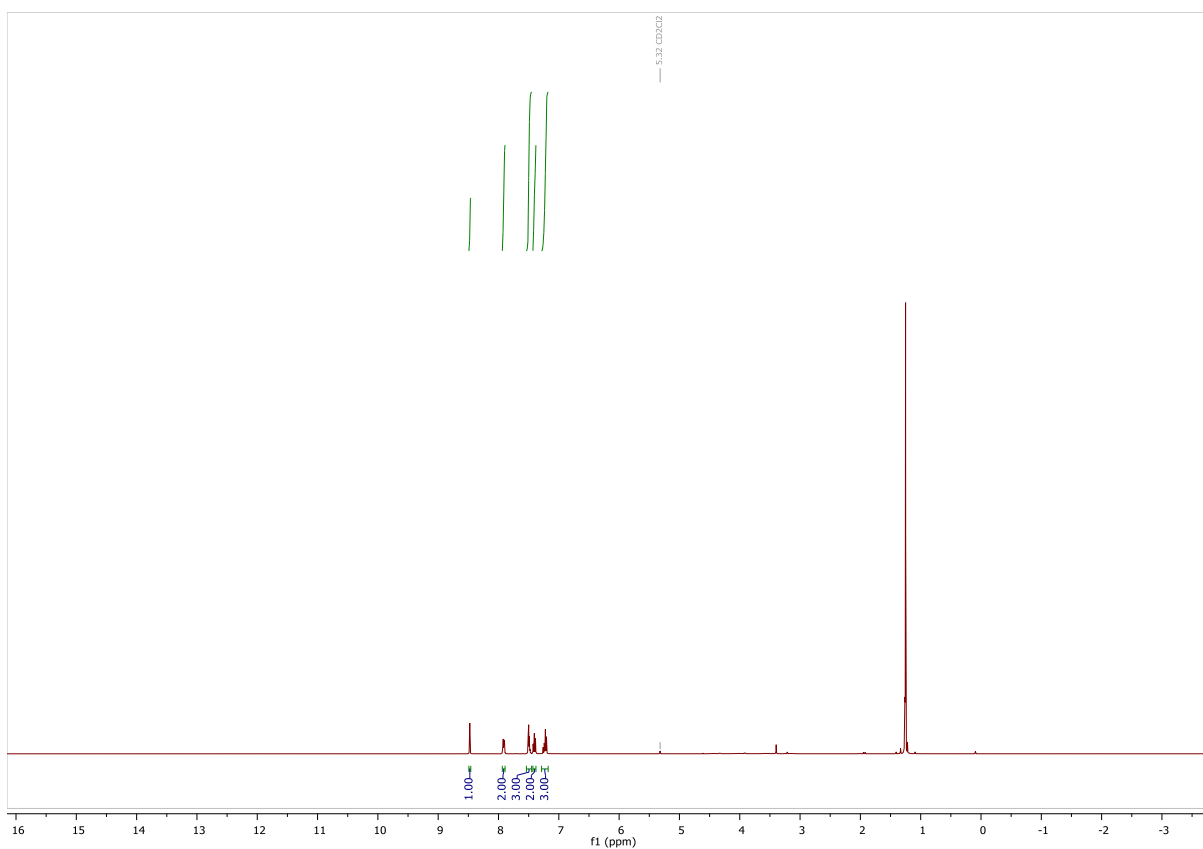


Figure S154 – ^1H NMR spectrum for the reaction mixture after addition of 1 equiv. of *N*-benzylideneaniline (**1a**) to the solution of the catalyst, 3h, rt, DCM-d_2 . The catalyst was

prepped as follows: 1.2 equiv. of pinacolborane (**2**) and 0.2 equiv. of [Cho][OAc] after 7 days, rt in DCM-d₂, and analysed in Figure S153. For clarity, only the **1a** signals were integrated.

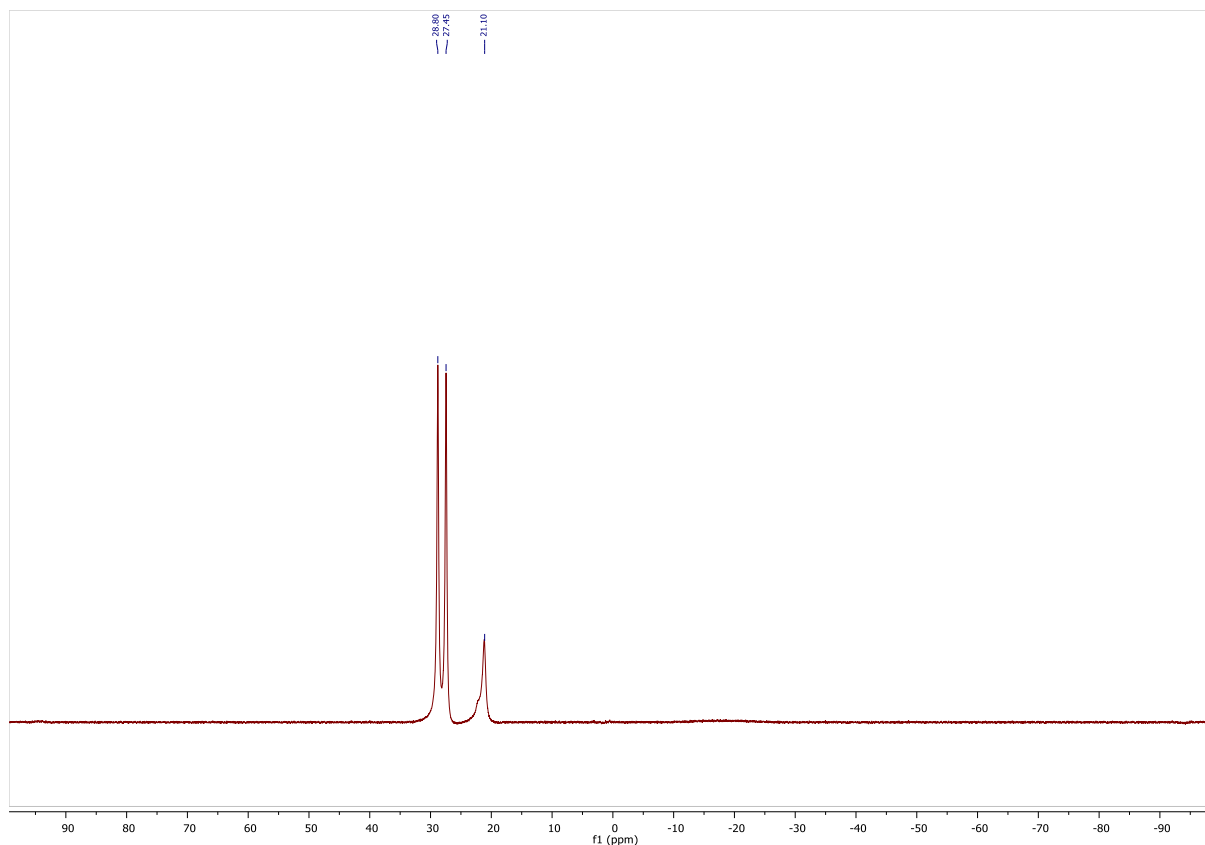


Figure S155 – ¹¹B NMR spectrum for the reaction mixture after addition of 1 equiv. of *N*-benzylideneaniline (**1a**) to the solution of the catalyst, 3h, rt, DCM-d₂. The catalyst was prepped as follows: 1.2 equiv. of pinacolborane (**2**) and 0.2 equiv. of [Cho][OAc] after 7 days, rt in DCM-d₂, and analysed in Figure S153.

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