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Supporting Information for:

Probing B-X to B-H conversions and applications in Friedel-Crafts catalysis

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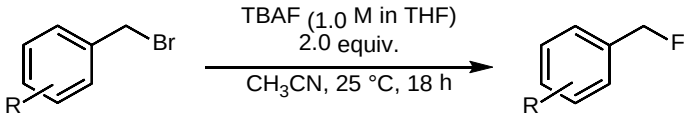
1 General

1.1 General Information

All preparative procedures were performed in an inert atmosphere of nitrogen using glovebox techniques or standard Schlenk line techniques, unless otherwise specified. Toluene, *n*-pentane, and dichloromethane (DCM, CH_2Cl_2) purchased from Sigma Aldrich were dried using a Grubbs-type Innovative Technologies solvent purification system. For benchtop purposes, anhydrous acetonitrile (purchased from Sigma Aldrich), DCM, *n*-pentane, hexanes (purchased from Fisher Chemical), ethyl acetate (purchased from Sigma Aldrich) were used without any further purification. Benzene, 1,2-difluorobenzene (*o*-DFB), 1,2-dichloroethane (1,2-DCE), fluorobenzene, fluorocyclohexane and hexafluorobenzene (C_6F_6) were purchased from Sigma Aldrich and dried by distillation from sodium-benzophenone or calcium hydride prior to use. All solvents were stored over activated 3 Ă molecular sieves. Deuterated solvents (C_6D_6, toluene-d_8, $CDCl_3$) were obtained from Cambridge Isotope Laboratories Inc. and distilled from sodium-benzophenone or calcium hydride prior to use. 9-Borabicyclo[3.3.1]nonane dimer (9-BBN), 9-bromo-9-borabicyclo[3.3.1]nonane (9-Br-9-BBN; 1.0 M DCM solution, Sure/Seal™), 2-chloro-1,3,2,-benzodioxaborole, chlorodicyclohexylborane, dichlorophenyl borane, *(+)*-B-chlorodiisopinocampheylborane (*(+)*-Ipc_2BCl), triethylsilane (Sure/Seal™), tris(trimethylsilyl)silane, tri*iso*porpylsilane, chlorodiphenylsilane, (difluoromethyl)benzene, 4-*tert*-butylbenzyl bromide, 2-methylbenzyl bromide, 3-methoxybenzyl bromide, 4-bromobenzyl bromide, naphthalene, 1,2,4,5-tetramethylbenzene, 1,2,3,4,5-pentamethylbenzene, 1-bromo-2,3,5,6-tetramethylbenzene, anisole, 1,3,5-trimethoxybenzene, furan, and thiophene were obtained from Sigma Aldrich and used without further purification. Triphenylcarbenium tetrakis(pentafluorophenyl)borate ($[Ph_3C][B(C_6F_5)_4]$; trityl; Boulder Scientific), dimesitylboron fluoride (TCI America), 4-bromomethylbiphenyl (TCI America), and tetrabutylammonium fluoride (TBAF; 1.0 M solution in THF; Alfa Aesar) were obtained from commercial sources and used without further purification. Haloboranes $RB(NiPr_2)Cl$ (R = Mes[1], *t*Bu[2], Ph[3]) and $(Me_3Si)_2NB(NiPr_2)Cl$[4], $Ph_2NB(NiPr_2)Cl$[5], and $((Me_3Si)_2N)_2BF$[6] were prepared following modified reported synthetic procedures. When applicable, substrates were purified by column chromatography using Silicycle Silia-P Flash Silica Gel. Thin-layer chromatography (TLC) was performed on EMD Silica Gel 60 F254 aluminum plates and visualization of the developed plates was achieved using a UV lamp (254 nm). Plastic syringes and disposable needles were used to dispense solvents. Prior to use inside the glovebox, plastic syringes and disposable needles were placed under vacuum inside the antechamber of the glovebox overnight. All NMR spectra were collected at 298 K on Bruker Avance III 400, Agilent DD2-500, or Varian VnmrS 400 spectrometers in 3- or 5-mm diameter NMR tubes. ^1H chemical shifts are reported relative to proteo-solvent signals[7] ($CDCl_3$, δ = 7.26 ppm and C_6D_6, δ = 7.16 ppm) or an internal standard (e.g., DCM). Data are reported as: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, br = broad), coupling constants (Hz), integration and *assignment*. $^{13}C\{^1H\}$ chemical shifts are reported relative to proteo-solvent signals ($CDCl_3$, δ = 77.00 ppm), while ^{11}B and ^{19}F NMR chemical shifts are reported relative to $(Et_2O)\cdot BF_3$ and $CFCl_3$ external standards, respectively. Departmental facilities were used for mass spectrometry (DART+: JEOL AccTOF or ESI: Agilent 6538 Q-TOF).

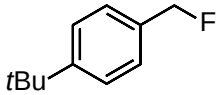
1.2 Preparation of Benzyl Fluorides

General Procedure



The procedures used were based on previously reported methods.[8,9] To a stirred solution of the benzyl bromide (10 mmol) in acetonitrile (15 mL), was added a solution of tetrabutylammonium fluoride in THF (1.0 M, 20 mL, 2 equiv.). The reaction mixture was stirred for 18 hr at room temperature. The reaction was subsequently quenched with water and extracted with diethyl ether. The combined organic extracts were washed with brine, dried with Na_2SO_4, filtered and concentrated under vacuum. The residue was purified by column chromatography (hexane or hexane/ethyl acetate eluent) on silica gel to afford the benzyl fluoride product.

4-(*Tert*-butyl)benzyl fluoride

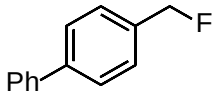


Following the general procedure and work-up, the crude product was purified by column chromatography (2% ethyl acetate in hexane eluent) on silica gel to afford the benzyl fluoride product as a colourless oil. Analytical data were in accordance with those previously reported.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 – 7.41 (m, 2H), 7.37 – 7.30 (m, 2H), 5.35 (d, $^2J_{HF}$ = 48.1 Hz, 2H), 1.35 (s, 9H).

^{19}F NMR (377 MHz, $CDCl_3$) δ: -204.34 (d, $^2J_{HF}$ = 48.0 Hz).

4-Phenylbenzyl fluoride

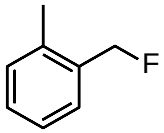


Following the general procedure and work-up, the crude product was purified by column chromatography (2% ethyl acetate in hexane eluent) on silica gel to afford the benzyl fluoride product as a colourless solid. Analytical data were in accordance with those previously reported.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 – 7.56 (m, 4H), 7.46 (t, $^3J_{HH}$ = 7.7 Hz, 4H), 7.37 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 5.43 (d, $^2J_{HF}$ = 47.9 Hz, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ: -206.18 (t, $^2J_{HF}$ = 47.9 Hz).

2-Methylbenzyl fluoride

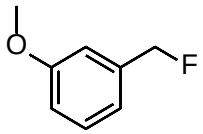


Following the general procedure and work-up, the crude product was purified by column chromatography (1% ethyl acetate in hexane eluent) on silica gel to afford the benzyl fluoride product as a colourless oil. Note that complete removal of solvent from the product under high vacuum leads to decomposition. Analytical data were in accordance with those previously reported.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (m, 1H), 7.33 – 7.26 (m, 1H), 7.24 (t, $^{3}J_{HH}$ = 6.8 Hz, 2H), 5.43 (d, $^{2}J_{HF}$ = 47.9 Hz, 2H), 2.40 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ: -209.12 (t, $^{2}J_{HF}$ = 47.8 Hz).

3-Methoxybenzyl fluoride

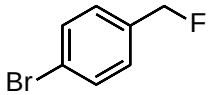


Following the general procedure and work-up, the crude product was purified by column chromatography (5% ethyl acetate in hexane eluent) on silica gel to afford the benzyl fluoride product as a colourless oil. Analytical data were in accordance with those previously reported.[12]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (t, $^{3}J_{HH}$ = 7.8 Hz, 1H), 7.03 – 6.84 (m, 3H), 5.36 (d, $^{2}J_{HF}$ = 47.7 Hz, 2H), 3.83 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ: -207.93 (t, $^{2}J_{HF}$ = 47.8 Hz).

4-Bromobenzyl fluoride

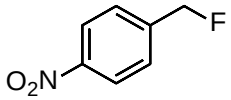


Following the general procedure and work-up, crude product was filtered through a silica plug (with hexane eluent) to afford the benzyl fluoride product as a crystalline colourless solid. Analytical data were in accordance with those previously reported.[11]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.53 (dd, $^{3}J_{HH}$ = 8.5 Hz, $^{5}J_{HF}$ = 1.2 Hz, 2H), 7.25 (dd, $^{3}J_{HH}$ = 8.5 Hz, $^{4}J_{HF}$ = 1.7 Hz, 2H), 5.33 (d, $^{2}J_{HF}$ = 47.6 Hz, 2H).

^{19}F NMR (377 MHz, $CDCl_3$) δ: -208.13 (t, $^{2}J_{HF}$ = 47.6 Hz).

4-Nitrobenzyl fluoride

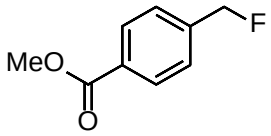


Following the general procedure and work-up, crude product was purified by column chromatography (10% ethyl acetate in hexane eluent) to afford the benzyl fluoride product as a crystalline yellow solid. Analytical data were in accordance with those previously reported.[8,11]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (d, $^{3}J_{HH}$ = 7.7 Hz, 2H), 7.53 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H), 5.51 (d, $^{2}J_{HF}$ = 46.8 Hz, 2H).

^{19}F NMR (282 MHz, $CDCl_3$) δ: -215.68 (t, $^{2}J_{HF}$ = 46.9 Hz).

Methyl 4-(fluoromethyl)benzoate



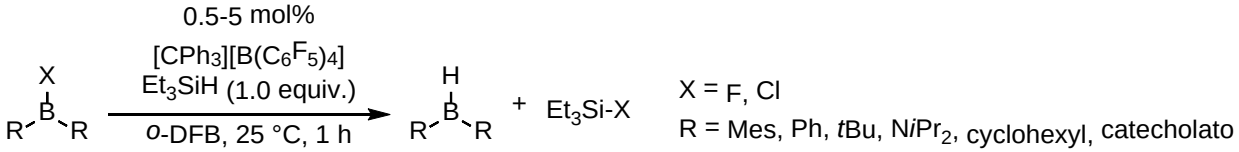
Using a modified procedure, the bright orange reaction mixture was refluxed at 85 °C. The reaction solution turned dark green after 18 hours. Following the general work-up procedure, crude product was purified by column chromatography (10% ethyl acetate in hexane eluent) to afford the benzyl fluoride product as a crystalline colourless solid. Analytical data were in accordance with those previously reported.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.06 (d, $^{3}J_{HH}$ = 7.4 Hz, 2H), 7.43 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 5.44 (d, $^{2}J_{HF}$ = 47.2 Hz, 2H), 3.92 (s, 3H).

^{19}F NMR (377 MHz, $CDCl_3$) δ: -212.88 (t, $^{2}J_{HF}$ = 47.3 Hz).

2 Reduction of Haloboranes

2.1 General Procedure



Under an inert atmosphere of a nitrogen glovebox, haloborane (1 equiv.) and triethylsilane (1 equiv.) were weighed into separate 1Dr vials. Triethylsilane was dissolved in *o*-DFB (0.5 mL). This solution was added to the haloborane and the mixture was transferred into an NMR tube. After an hour, the ^{1}H and ^{11}B NMR spectra of the reaction were collected to confirm the lack of reactivity in the absence of trityl initiator. The NMR tube was then brought back into the glovebox and the reaction mixture was added to a 1Dr vial containing triphenylcarbenium tetrakis(pentafluorophenyl)borate (0.005 or 0.05 equiv.). In the case of successful catalysis, this was followed by the disappearance of the yellow trityl colour. The reaction

mixture was then analyzed by ^{1}H and ^{11}B NMR spectroscopy. Note: two representative boranes were prepared on a larger scale and isolated, while other examples were generated in-situ and analyzed as a mixture with the triethylsilyl chloride by-product in o-DFB.

2.2 Optimization

2.2.1 Initiator Loading

Following the general procedure, Mes_2BF (15 mg, 0.06 mmol) and Et_3SiH (8 mg, 0.06 mmol) were dissolved in *o*-DFB (0.5 mL) and transferred to an NMR tube. To the reaction mixture was added triphenylcarbenium tetrakis(pentafluorophenyl)borate, using stock solutions of different concentrations. This was followed by the disappearance of the trityl colour. After an hour, the reaction mixture was analyzed by ^{1}H and ^{11}B NMR spectroscopy. The following trityl solutions were used for 0.01, 0.005, and 0.001 stoichiometries, respectively: 0.1 mL of a 5 mg/mL trityl solution in *o*-DFB (0.6 µmol), 0.3 mL of a 1 mg/mL trityl solution in *o*-DFB (0.3 µmol), and 50 µL of a 1 mg/mL trityl solution in *o*-DFB (0.06 µmol). While complete consumption of Mes_2BF was achieved at 0.5 mol% of initiator, to ensure reproducibility at the NMR scale for other haloboranes, 5.0 mol% of initiator was used.

2.2.2 Silane Screening

Following the general procedure, the model substrate Mes_2BF (15 mg, 0.06 mmol) was mixed with the silane (0.07 mmol, 1.2 equiv.) in *o*-DFB (0.55 mL). DCM (approx. 1 drop) was used as an internal standard and after 1 hour ^{1}H and ^{11}B NMR spectra of the sample were obtained to confirm the lack of reactivity between Mes_2BF and the silane. The NMR sample was brought back into the glovebox and the trityl initiator (0.3 mL of a 1 mg/mL stock solution, 0.3 µmol, 0.005 equiv.) was added to the reaction. The reaction was then monitored by ^{1}H and ^{11}B NMR spectroscopy.

Tris(trimethylsilyl)silane and Chlorodiphenylsilane
Neither silane showed any reactivity with Mes_2BF over an extended period of time (48 hr) at room temperature.

Tri*iso*propylsilane
Using tri*iso*propylsilane, the reaction was monitored by ^{1}H and ^{11}B NMR spectroscopy. After 14 hours, approximately 65% of the Mes_2BF had reacted (conversion obtained by integration of the Ar-CH_3 ^{1}H NMR signal of Mes_2BF against the DCM internal standard signal). Increasing reaction times resulted in no change in the maximum conversion.

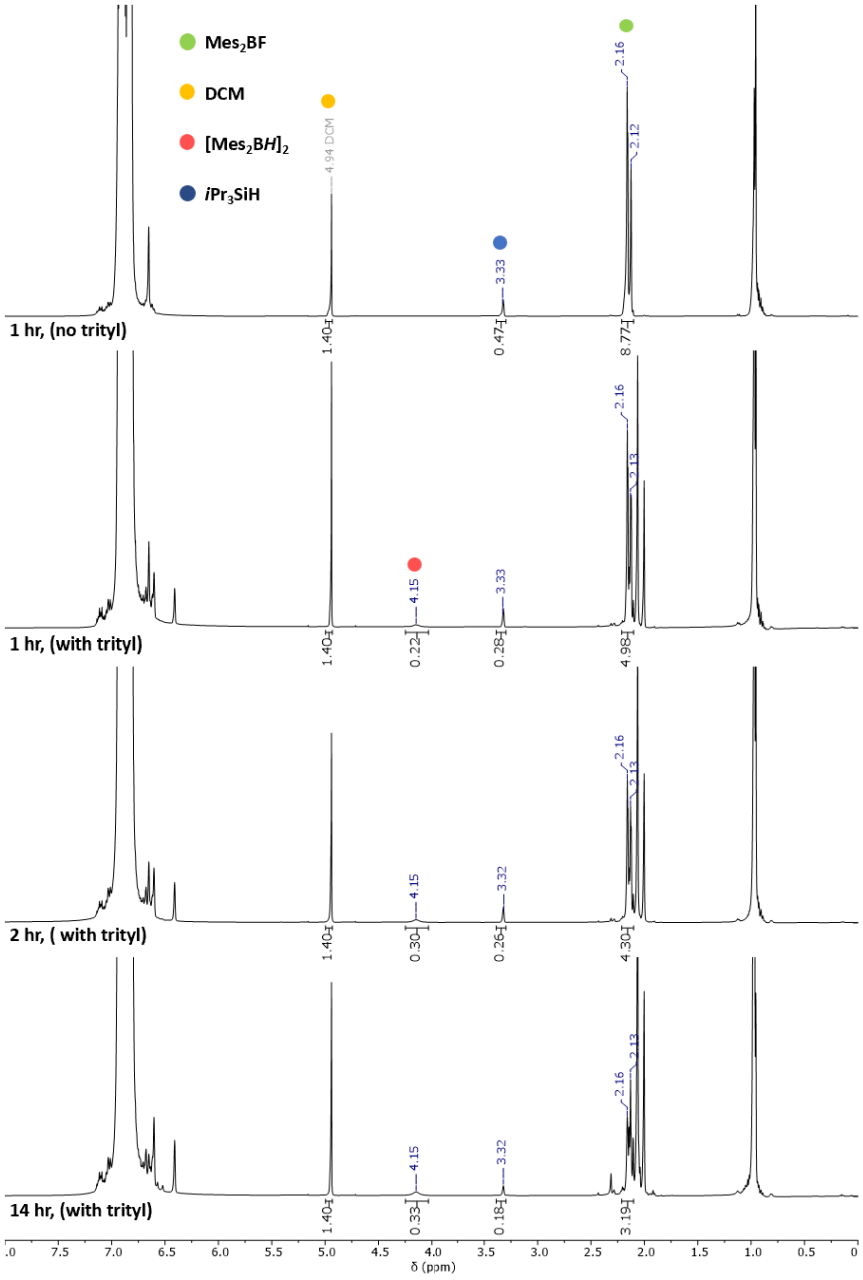


Figure S 1: ^{1}H NMR (400 MHz) spectra of the reaction between dimesitylboron fluoride and tri*iso*propylsilane. Top spectrum is the reaction mixture before the addition of the trityl salt. Time point after the addition of trityl is labeled accordingly on each spectrum. DCM was used as an internal standard.

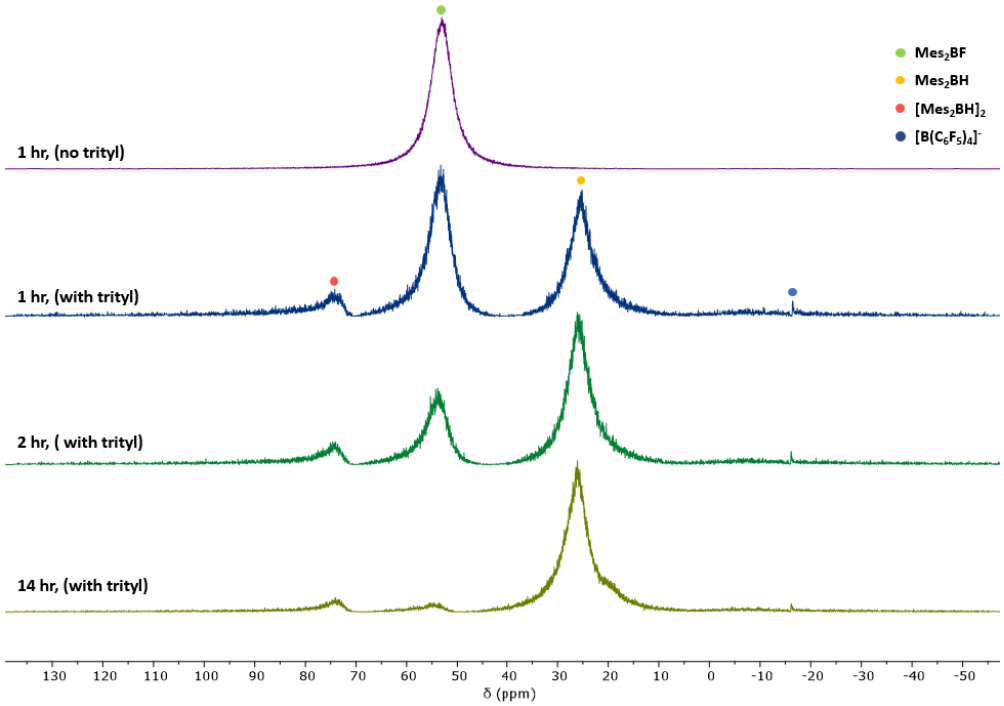
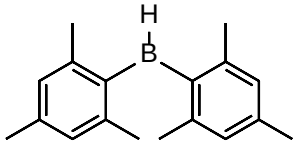


Figure S 2: ^{11}B NMR (126 MHz) spectra at different time point of the reaction between dimesitylboron fluoride and tri*iso*propylsilane.

2.3 Scope of Haloboranes

Synthesis of dimesitylborane[13]



Following the general procedure, Mes_2BF (403 mg, 1.5 mmol) was weighed into a 20 mL vial and dissolved in 2 mL of *o*-DFB. Next, Et_3SiH (175 mg, 1.5 mmol) was washed into the Mes_2BF vial using 1 mL of *o*-DFB. In a separate vial, 0.5 mol% of $[Ph_3C][B(C_6F_5)_4]$ (7 mg, 0.008 mmol) was dissolved in 0.2 mL of *o*-DFB. The trityl solution was, with stirring, added to the fluoroborane/silane mixture. The bright yellow colouration of trityl immediately disappeared, furnishing a clear and colourless solution. After 1 min, a white suspension was formed. The reaction was left to stir for an additional 30 minutes. The product Mes_2BH was isolated after adding 1 mL of *n*-pentane to the crude reaction mixture, decanting the supernatant, and drying the precipitate under reduced pressure, in approximately 70% yield (263 mg). Additional yield (up to 95% total conversion from Mes_2BF) may be obtained by removal of volatiles from the supernatant and extraction with *n*-pentane. The extract was filtered through a short plug of celite into a fresh vial and the volatiles were removed in vacuo to furnish Mes_2BH. The spectroscopic data for both batches of isolated material are in agreement with the reported data[14] for dimesitylborane and there are no detectable signals for $[B(C_6F_5)_4]$-containing salts in the isolated materials. Lack of reactivity between dimesitylboron fluoride and triethylsilane was confirmed in a separate NMR-scale experiment.

^{1}H NMR (400 MHz, C_6D_6) δ: 6.76 (s, 2H, $CH_{Ar,monomer}$), 6.69 (s, 4H, $CH_{Ar,dimer}$), 6.57 (s, 4H, $CH_{Ar,dimer}$), 4.31 (br, 2H, $BH_{,dimer}$), 2.28 (s, 6H, $CH_{3,Monomer}$), 2.22 (s, 12H, $CH_{3,dimer}$), 2.19 (s, 12H, $CH_{3,dimer}$), 2.13 (s, 3H, $CH_{3,Monomer}$), 2.05 (s, 12H, $CH_{3,dimer}$).

^{11}B NMR (128 MHz, C_6D_6) δ: 73.8 (br s, monomer), 26.5 (br s, dimer).

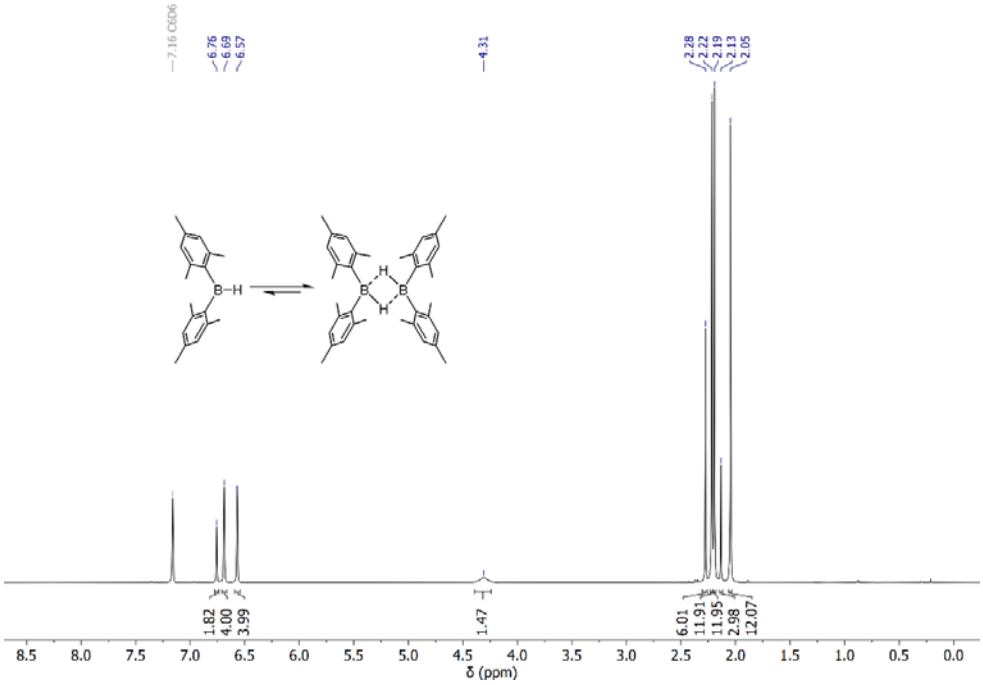


Figure S 3: ^{1}H NMR (400 MHz) spectrum of dimesitylborane in C_6D_6. A mixture of monomer and dimer are present in solution.

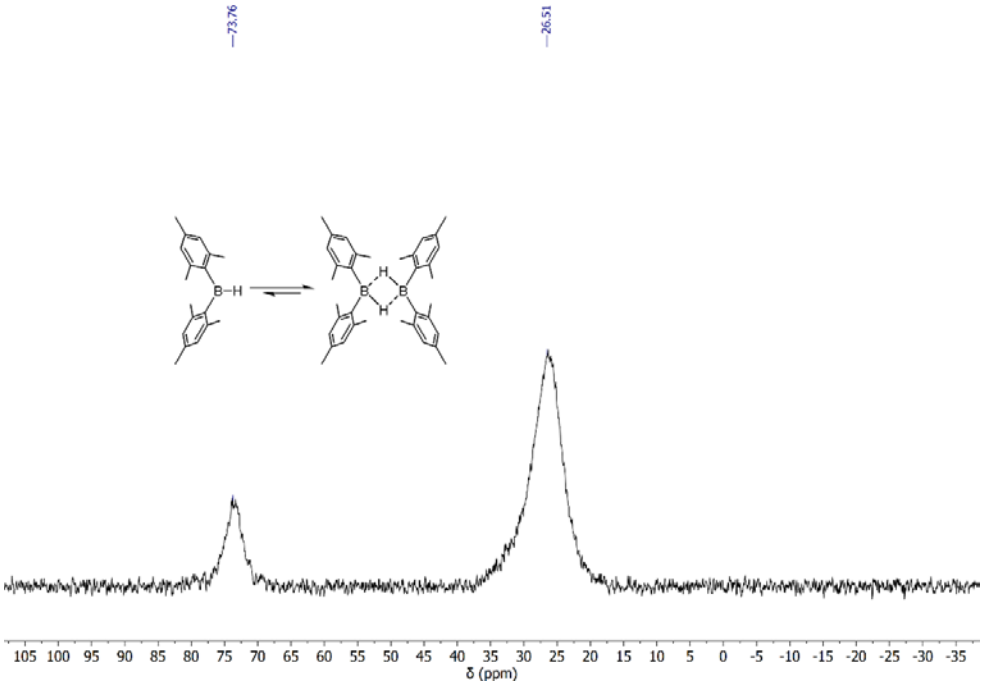
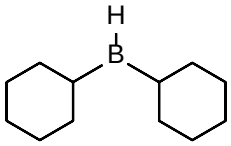


Figure S 4: ^{11}B NMR (128 MHz) spectrum of dimesitylborane in C_6D_6.

Synthesis of dicyclohexylborane



In an inert atmosphere of a nitrogen glovebox, Cy_2BCl (400. mg, 1.9 mmol) and Et_3SiH (241 mg, 2.0 mmol) were dissolved in 3 mL of *o*-DFB. In a separate vial, 0.5 mol% of $[Ph_3C][B(C_6F_5)_4]$ (9 mg) was dissolved in 0.2 mL of *o*-DFB. The trityl solution was added to the chloroborane/silane mixture. The bright orange colouration of trityl immediately turned light-yellow. After 1 min, a white suspension was formed. The reaction was left to stir for an addition hour. The product Cy_2BH was isolated after adding 2 mL of *n*-pentane to the crude reaction mixture and decanting the supernatant. The suspension was then washed with *n*-pentane (1 mL) three times, decanting after each wash. The suspension was dried under reduced pressure to afford a white solid in 78% yield (261 mg). Lack of reactivity between chlorodicyclohexylborane and triethylsilane was confirmed in a separate NMR-scale experiment.

^{1}H NMR (400 MHz, $CDCl_3$, partial) δ: 1.80 – 1.63 (m, 6H), 1.47 (br, 4H), 1.32 (br, 6H), 1.27 – 1.13 (m, 6H). *The B-H resonance was not observed.*

^{11}B NMR (128 MHz, $CDCl_3$) δ: 29.9.

EA calcd (%) $C_{12}H_{23}B$: C 80.92, H 13.02; Found: C 80.19, H 13.65

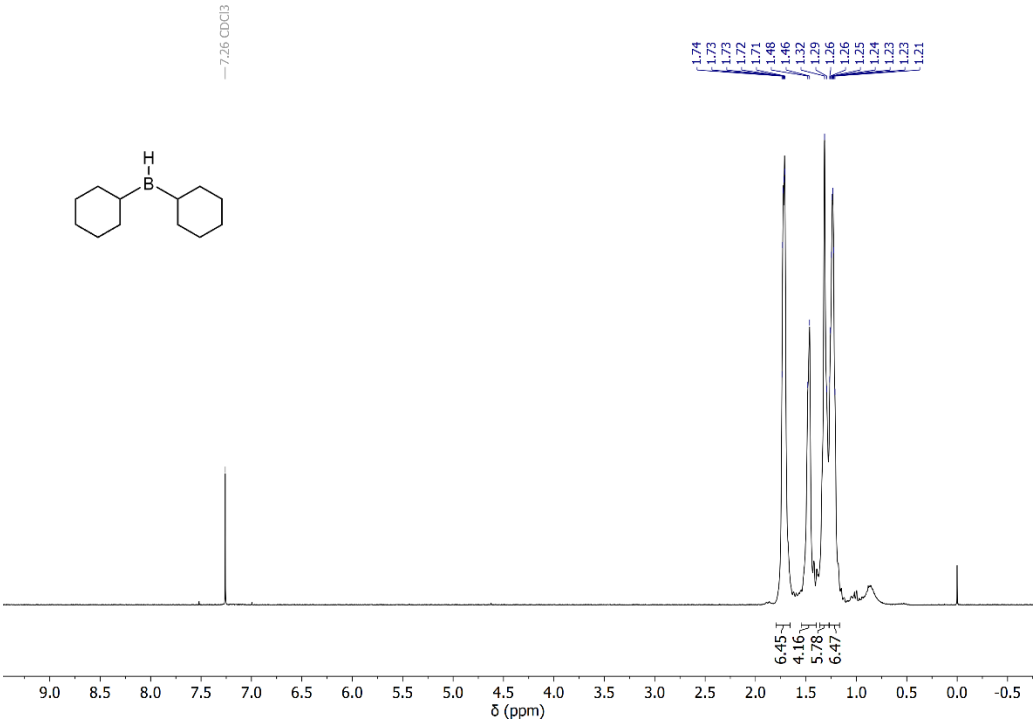


Figure S 5: ^{1}H NMR (400 MHz) spectrum of dicyclohexylborane in $CDCl_3$.

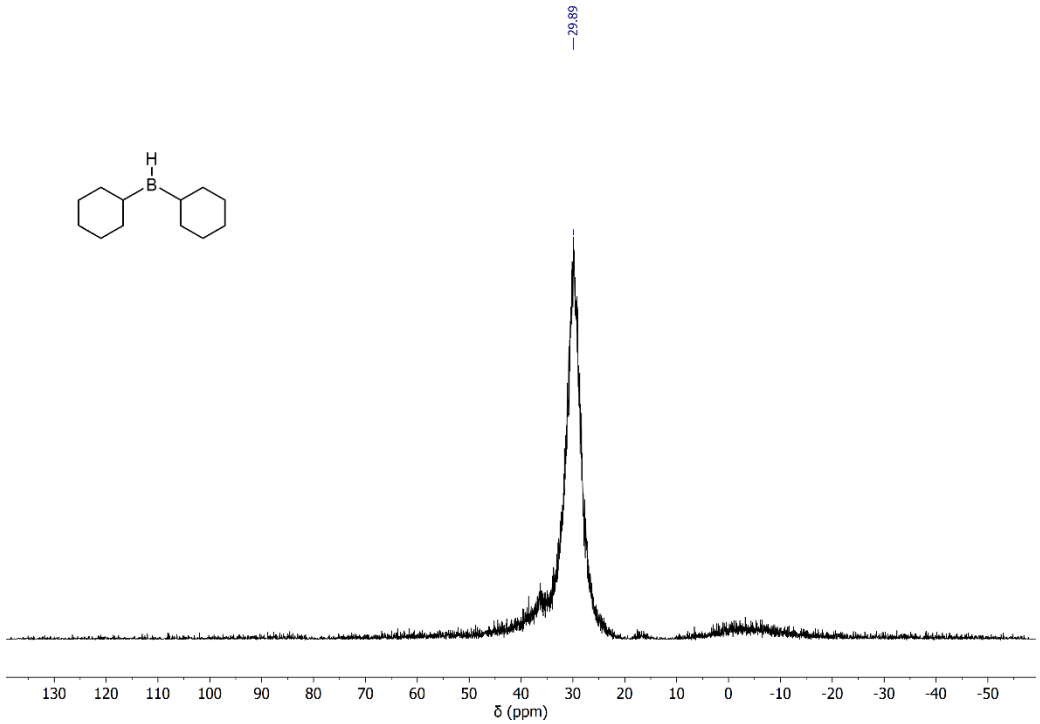
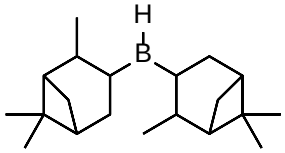


Figure S 6: ^{11}B NMR (128 MHz) spectrum of dicyclohexylborane in $CDCl_3$.

Generation of bis(2,6,6-trimethylbicyclo[3.1.1]heptan-3-yl)borane, (α-pinene)$_2$BH



Under an inert atmosphere of a nitrogen glovebox, *(+)*-B-chlorodiisopinocampheylborane (20 mg, 0.06 mmol) and triethylsilane (8 mg, 0.07 mmol, 1.1 equiv.) were dissolved in *o*-DFB (0.5 mL) and transferred to an NMR tube. After an hour, the ^{1}H and ^{11}B NMR spectra of the reaction were collected. The NMR tube was then brought back into the glovebox and to the reaction mixture was added triphenylcarbenium tetrakis(pentafluorophenyl)borate (2 mg, 0.002 mmol, 0.05 equiv.). This was followed by the disappearance of the trityl colour. After an hour, the reaction mixture was analyzed by ^{1}H and ^{11}B NMR spectroscopy.

^{1}H NMR (400 MHz, $CDCl_3$, partial) δ: 2.44 – 1.43 (br), 1.40 – 0.36 (br). *Further analysis of the ^{1}H NMR spectrum was not possible. The B-H resonance was not observed.*

^{11}B NMR (128 MHz, *o*-DFB) δ: 31.9, -16.1 ($[B(C_6F_5)_4]^-$) *Note: the $[B(C_6F_5)_4]$ anion peak assigned based on previous reports in the literature.*[15]

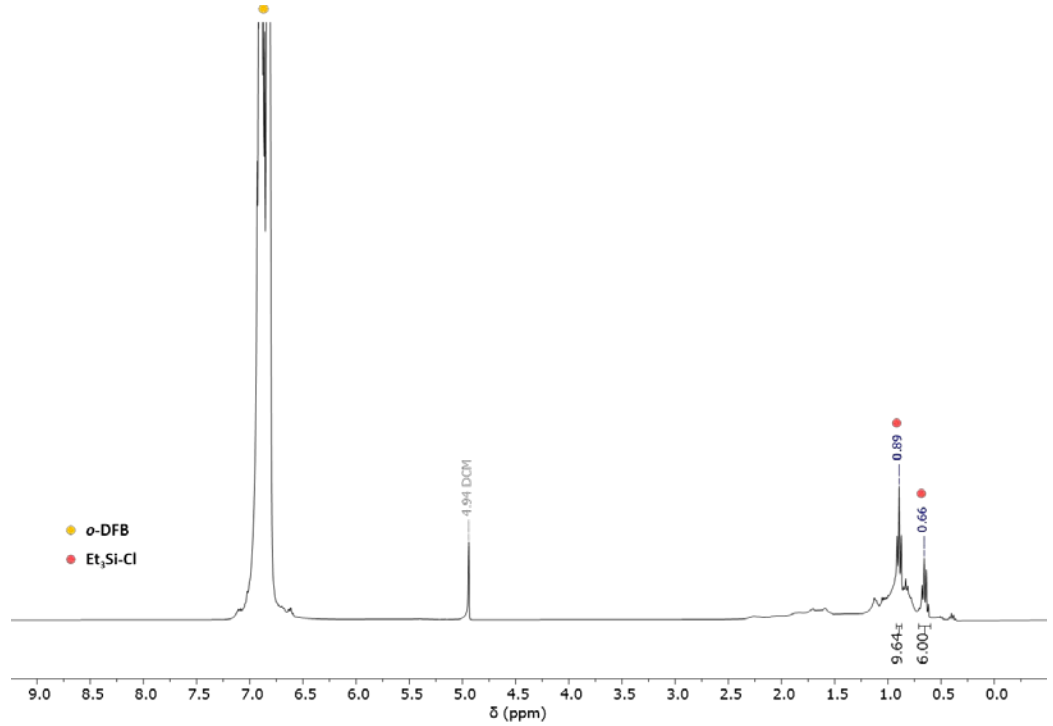


Figure S 7: ^{1}H NMR (400 MHz) spectrum of (α-pinene)$_2$BH generated in *o*-DFB. DCM was used to reference the spectrum. Signals corresponding to the triethylsilyl chloride by-product are labeled.

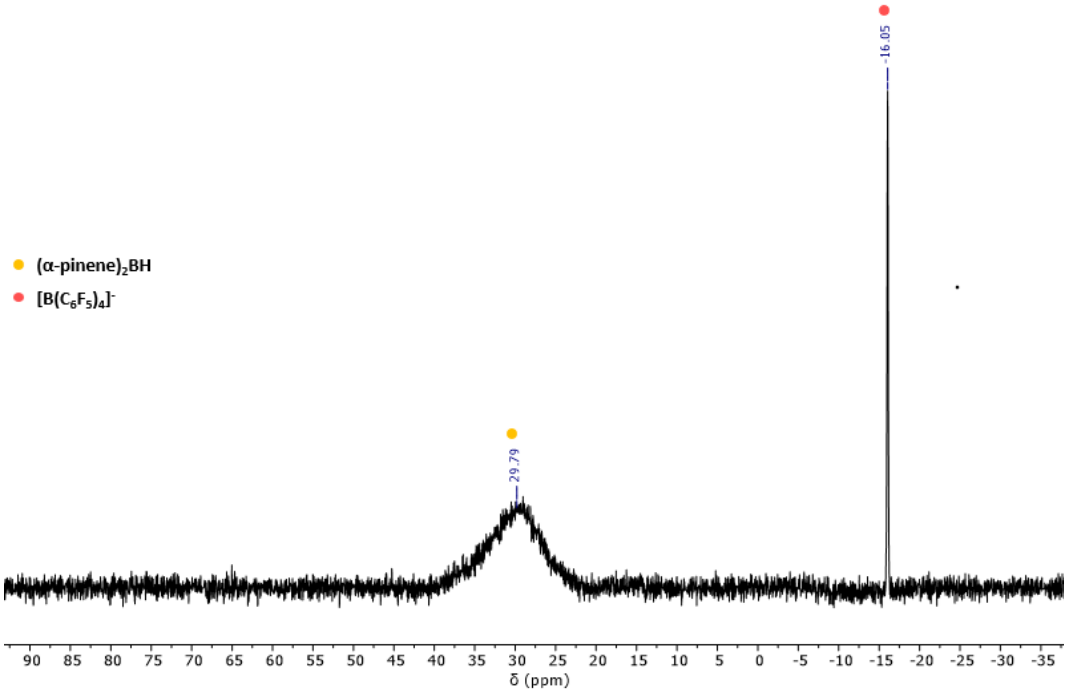
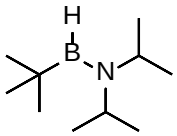


Figure S 8: ^{11}B NMR (128 MHz) spectrum of (α-pinene)$_2$BH generated in *o*-DFB.

Generation of 1-*tert*-butyl-*N,N*-di*iso*propylboranamine



Under an inert atmosphere of a nitrogen glovebox, *tert*-butyl-(*N,N*-diisopropylamino)chloroborane (10 mg, 0.05 mmol) and triethylsilane (6 mg, 0.05 mmol, 1 equiv.) were dissolved in *o*-DFB (0.5 mL) and transferred to an NMR tube. After an hour, the ^{1}H and ^{11}B NMR spectra of the reaction were collected. The NMR tube was then brought back into the glovebox and to the reaction mixture was added triphenylcarbenium tetrakis(pentafluorophenyl)borate (2 mg, 0.002 mmol, 0.05 equiv.). This was followed by the disappearance of the trityl colour. After an hour, the reaction mixture was analyzed by ^{1}H and ^{11}B NMR spectroscopy.

^{1}H NMR (400 MHz, *o*-DFB) δ: 4.04 (hept, $^{3}J_{HH}$ = 6.7 Hz, 1H, C*H*(CH$_3$)$_2$), 3.05 (hept, $^{3}J_{HH}$ = 6.9 Hz, 1H, C*H*(CH$_3$)$_2$), 1.09 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.99 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.93 (s, 9H, C(C*H*$_3$)$_3$), 0.90 (t, $^{3}J_{HH}$ = 8.1 Hz, 9H, (C*H*$_3$CH$_2$)$_3$SiCl), 0.67 (q, $^{3}J_{HH}$ = 7.9 Hz, 6H, (CH$_3$C*H*$_2$)$_3$SiCl). *Note: the B-H resonance was not observed.*

^{11}B NMR (128 MHz, *o*-DFB) δ: 42.5 (d, $^{1}J_{BH}$ = 144 Hz), -16.1 ([B(C$_6$F$_5$)$_4$]$^-$).

^{11}B{^{1}H} NMR (128 MHz, *o*-DFB) δ: 42.5, -16.1 ([B(C$_6$F$_5$)$_4$]$^-$).

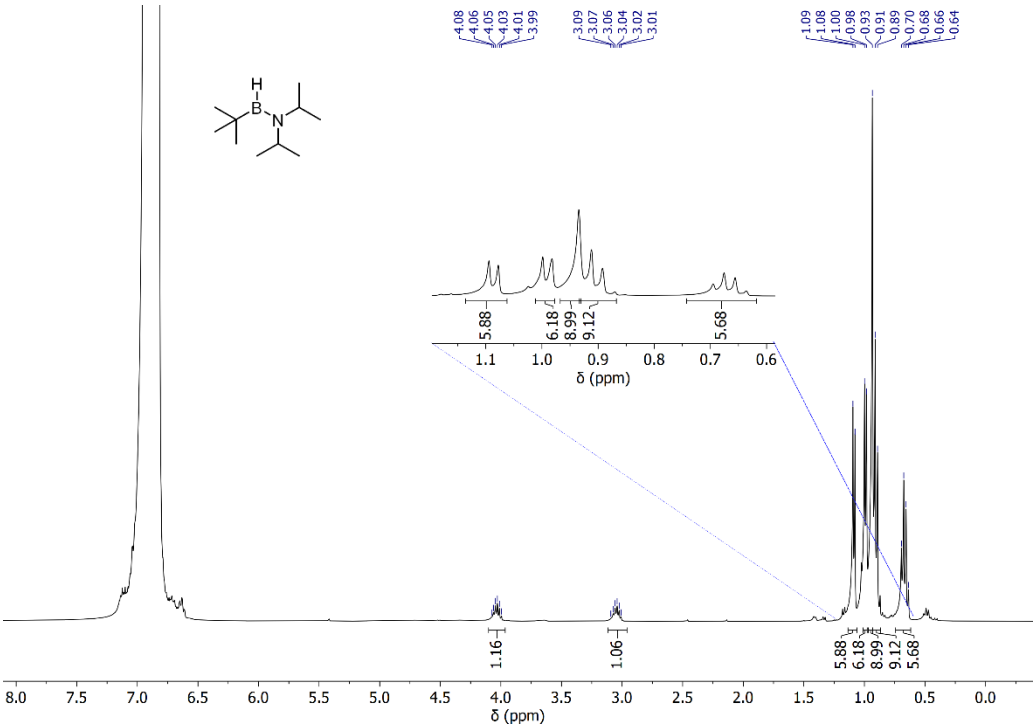


Figure S 9: ^{1}H NMR (400 MHz) spectrum of *t*Bu(*i*Pr$_2$N)BH generated in *o*-DFB.

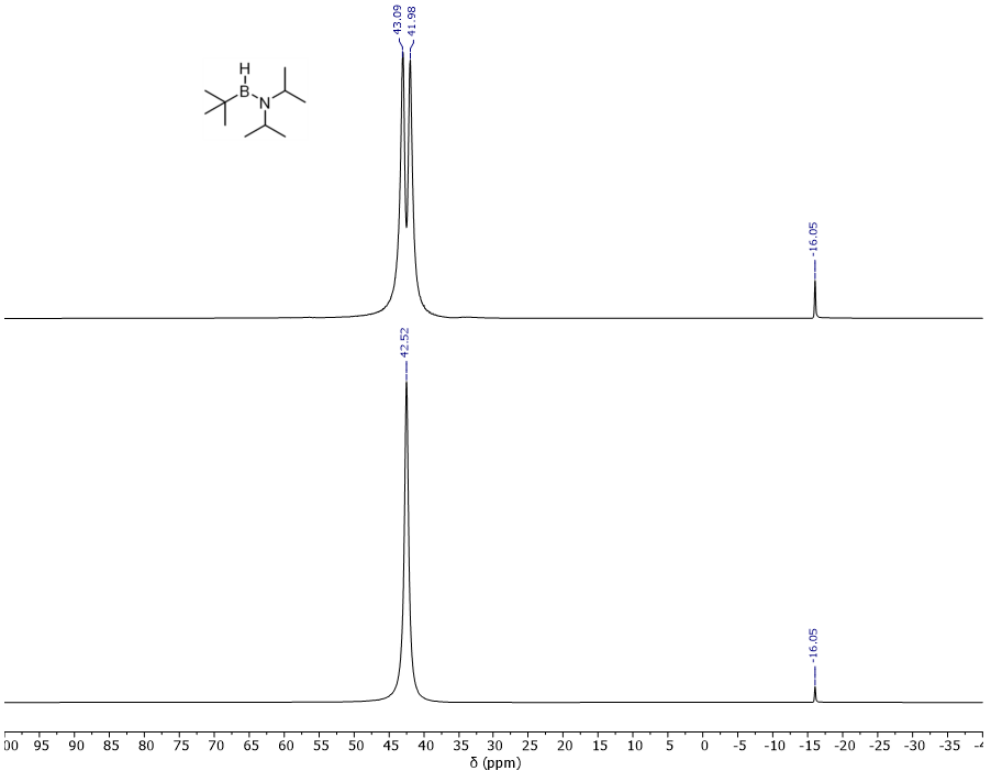
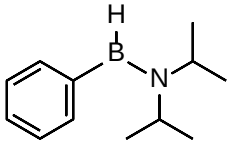


Figure S 10: ^{11}B (top, 128 MHz) and ^{11}B{^{1}H} (bottom, 128 MHz) NMR spectra of *t*Bu(*i*Pr$_2$N)BH generated in *o*-DFB.

Generation of *N,N*-di*iso*propyl-1-phenylboranamine



Under an inert atmosphere of a nitrogen glovebox, phenyl-(*N,N*-diisopropylamino)chloroborane (10 mg, 0.05 mmol) and triethylsilane (6 mg, 0.05 mmol, 1 equiv.) were dissolved in *o*-DFB (0.5 mL) and transferred to an NMR tube. After an hour, the ^{1}H and ^{11}B NMR spectra of the reaction was collected. The NMR tube was then brought back into the glovebox and to the reaction mixture was added triphenylcarbenium tetrakis(pentafluorophenyl)borate (2 mg, 0.002 mmol, 0.05 equiv.). This was followed by the disappearance of the trityl colour. After an hour, the reaction mixture was analyzed by ^{1}H and ^{11}B NMR spectroscopy.

^{1}H NMR (400 MHz, *o*-DFB) δ: 7.38 (d, J_{HH} = 7.9 Hz, 2H, H_{Ar}), 7.28 – 7.19 (m, 2H, H_{Ar}), 7.02 (d, J_{HH} = 8.5 Hz, 1H, H_{Ar}), 4.17 (hept, $^{3}J_{HH}$ = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 3.22 (hept, $^{3}J_{HH}$ = 6.7 Hz, 1H, C*H*(CH$_3$)$_2$), 1.22 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.98 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.91 (t, $^{3}J_{HH}$ = 7.9 Hz, 9H, (C*H*$_3$CH$_2$)$_3$SiCl), 0.67 (q, $^{3}J_{HH}$ = 7.8 Hz, 6H, (CH$_3$C*H*$_2$)$_3$SiCl). *Note: the B-H resonance was not observed.*

^{11}B NMR (128 MHz, *o*-DFB) δ: 38.3 (d, $^{1}J_{BH}$ = 147 Hz), -16.1 ([B(C$_6$F$_5$)$_4$]$^-$).

^{11}B{^{1}H} NMR (128 MHz, *o*-DFB) δ: 38.3, -16.1 ([B(C$_6$F$_5$)$_4$]$^-$).

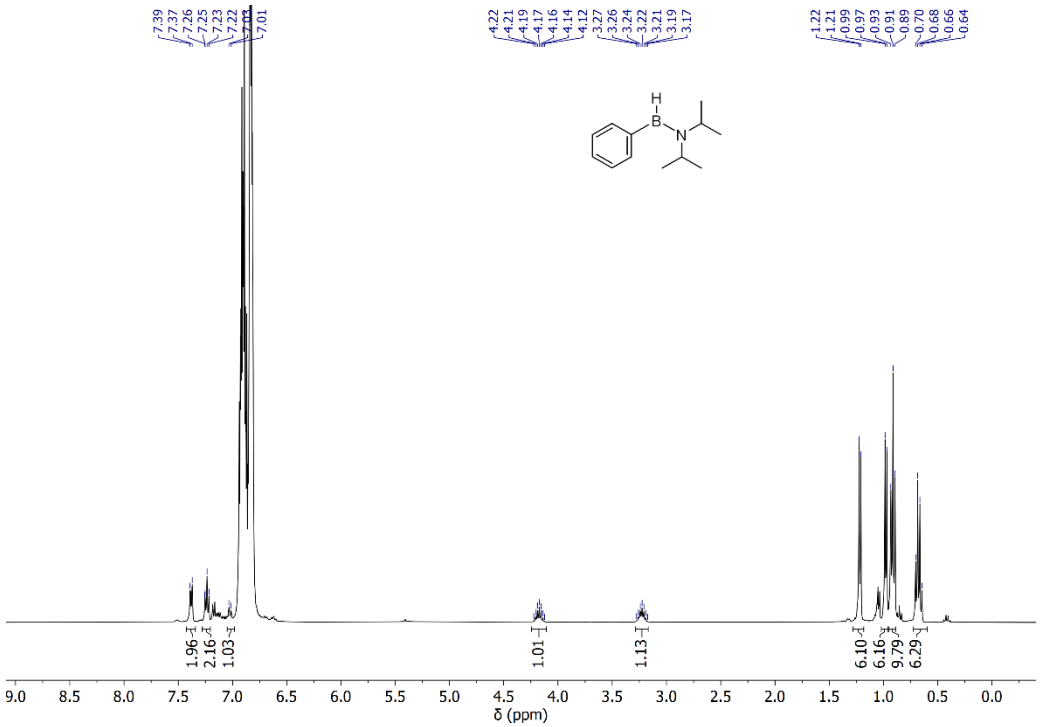


Figure S 11: ^{1}H NMR (400 MHz) spectrum of *t*Bu(*i*Pr$_2$N)BH generated in *o*-DFB.

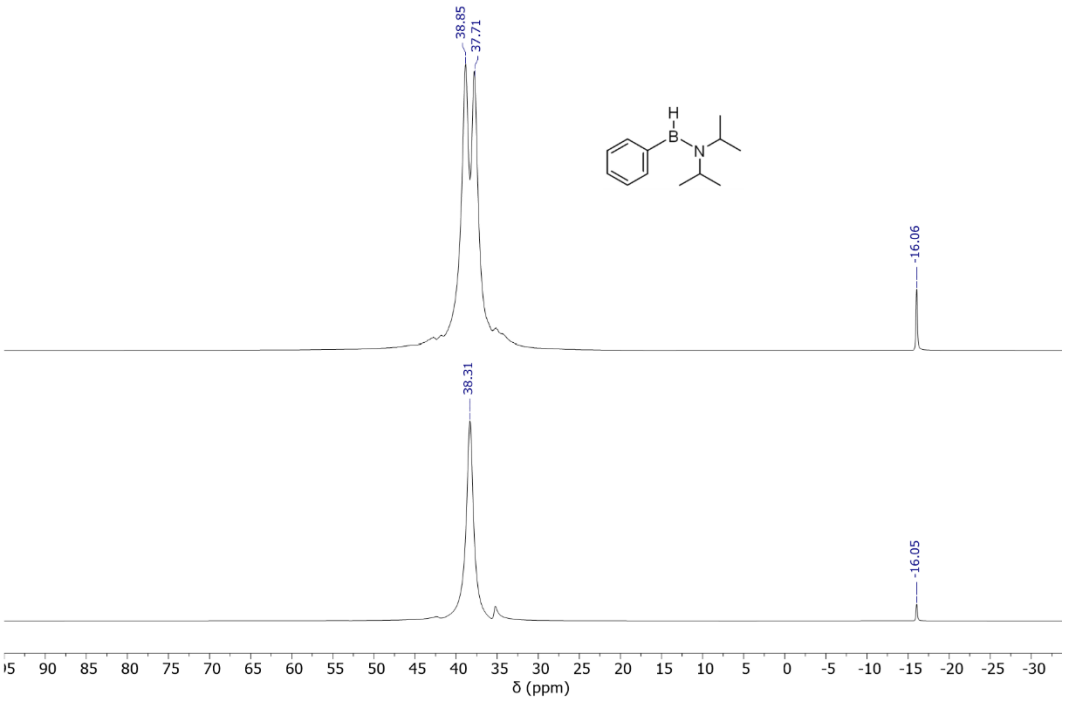
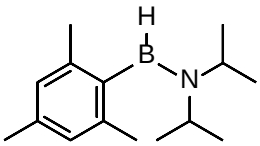


Figure S 12:^{11}B (top, 128 MHz) and ^{11}B{^{1}H} (bottom, 128 MHz) NMR spectra of Ph(*i*Pr$_2$N)BH generated in *o*-DFB.

Generation of *N,N*-di*iso*propyl-1-mesitylboranamine



Under an inert atmosphere of a nitrogen glovebox, mesityl-(*N,N*-diisopropylamino)chloroborane (10 mg, 0.05 mmol) and triethylsilane (6 mg, 0.05 mmol, 1 equiv.) were dissolved in *o*-DFB (0.5 mL) and transferred to an NMR tube. After an hour, the ^{1}H and ^{11}B NMR spectra of the reaction were collected. The NMR tube was then brought back into the glovebox and to the reaction mixture was added triphenylcarbenium tetrakis(pentafluorophenyl)borate (2 mg, 0.002 mmol, 0.05 equiv.). This was followed by the disappearance of the trityl colour. After an hour, the reaction mixture was analyzed by ^{1}H and ^{11}B NMR spectroscopy.

^{1}H NMR (400 MHz, *o*-DFB) δ: 6.66 (s, 2H, H_{Ar}), 3.55 (hept, $^{3}J_{HH}$ = 6.8 Hz, 1H, C*H*(CH$_3$)$_2$), 3.21 (hept, $^{3}J_{HH}$ = 6.7 Hz, 1H, C*H*(CH$_3$)$_2$), 2.15 (s, 3H, Ar-C*H*$_3$), 2.11 (s, 6H, Ar-C*H*$_3$), 1.24 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, CH(C*H*$_3$)$_2$), 0.90 (m, 15H, CH(C*H*$_3$)$_2$ and (C*H*$_3$CH$_2$)$_3$SiCl*)*, 0.66 (q, $^{3}J_{HH}$ = 7.8 Hz, 6H, (CH$_3$C*H*$_2$)$_3$SiCl). *Note: the B-H resonance was not observed.*

^{11}B NMR (128 MHz, *o*-DFB) δ: 39. 6 (d, $^{1}J_{BH}$ = 94 Hz), -16.0 ([B(C$_6$F$_5$)$_4$]$^-$).

^{11}B{^{1}H} NMR (128 MHz, *o*-DFB) δ: 39.6, -16.0 ([B(C$_6$F$_5$)$_4$]$^-$).

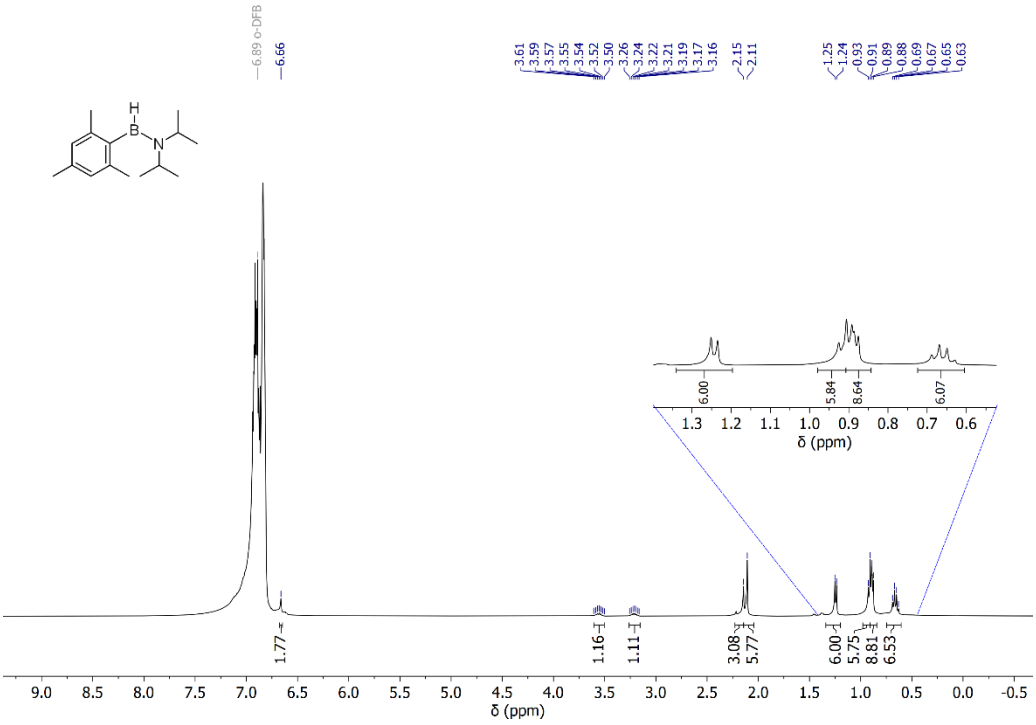


Figure S 13: ^{1}H NMR (400 MHz) spectrum of Mes(*i*Pr$_2$N)BH generated in *o*-DFB.

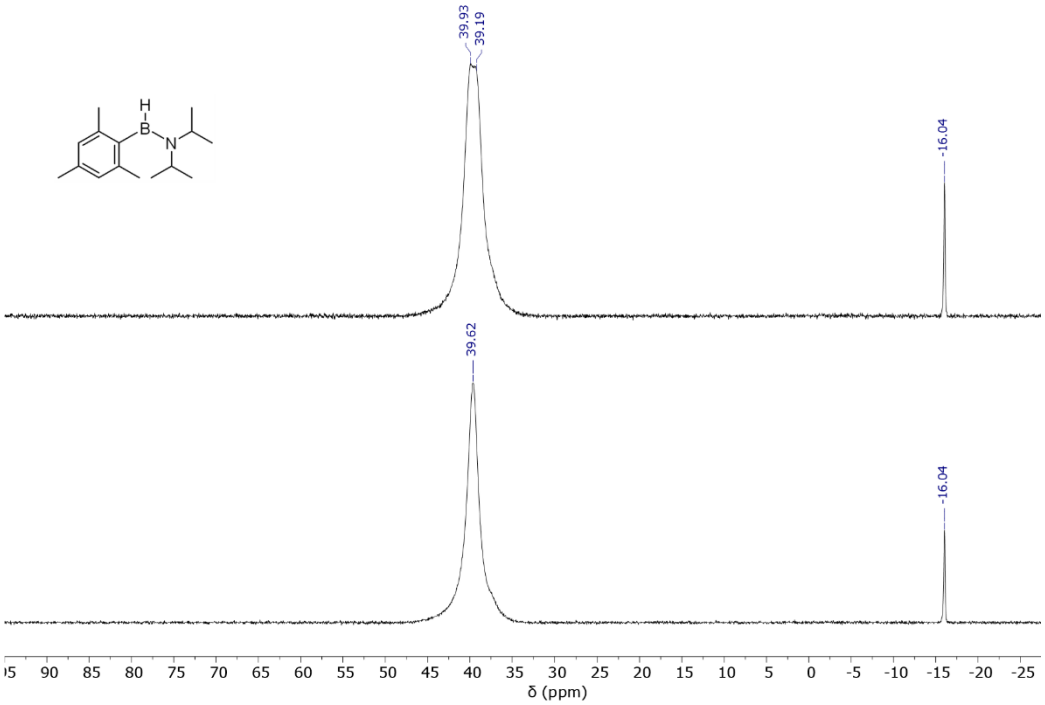
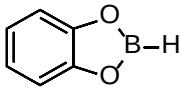


Figure S 14: ^{11}B (top, 128 MHz) and ^{11}B{^{1}H} (bottom, 128 MHz) NMR spectra of Mes(*i*Pr$_2$N)BH generated in *o*-DFB.

Generation of catecholborane



Under an inert atmosphere of a nitrogen glovebox, B-chlorocatecholborane (10 mg, 0.06 mmol) and triethylsilane (8 mg, 0.07 mmol, 1.1 equiv.) were dissolved in 1,2-difluorbenzene (0.5 mL) and transferred to an NMR tube. After an hour, the ^{1}H and ^{11}B NMR spectra of the reaction were collected. The NMR tube was then brought back into the glovebox and to the reaction mixture was added triphenylcarbenium tetrakis(pentafluorophenyl)borate (3 mg, 0.003 mmol, 0.05 equiv.). This was followed by the disappearance of the trityl colour. After an hour, the reaction mixture was analyzed by ^{1}H and ^{11}B NMR spectroscopy.

^{1}H NMR: *Signals corresponding to HBcat are overlapped by the proteo-solvent signals. The B-H resonance was not observed.*

^{11}B NMR (128 MHz, *o*-DFB) δ: 28.7 (d, $^{1}J_{BH}$ = 206 Hz), -16.2 ([B(C$_6$F$_5$)$_4$]$^-$).

^{11}B{^{1}H} NMR (128 MHz, *o*-DFB) δ: 28.7, -16.2 ([B(C$_6$F$_5$)$_4$]$^-$).

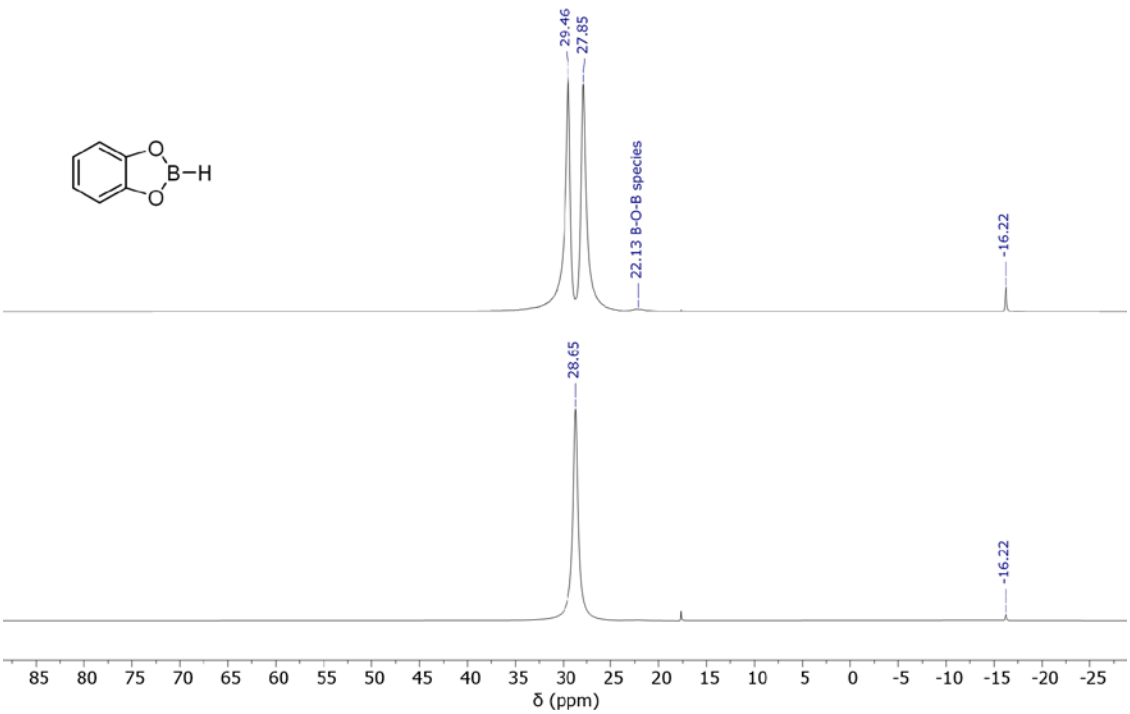


Figure S 15: ^{11}B (top, 128 MHz) and ^{11}B{^{1}H} (bottom, 128 MHz) NMR spectra of HBcat generated in *o*-DFB. Signal at 22.1 ppm corresponds to minor oxidization side-product.[15]

3 Friedel-Crafts Benzylation

3.1 Optimization

3.1.1 Arene equivalents

***General procedure for arene equivalent screening*:**

Under an inert atmosphere of a nitrogen glovebox, 4-*tert*-butylbenzyl fluoride (30 mg, 0.20 mmol, 1.0 equiv.), triethylsilane (21 mg, 0.20 mmol, 1.0 equiv.), the corresponding amount of C_6D_6 (0-25 equiv.) and 9-H-9-BBN (1 mg, 0.001 mmol, 0.05 equiv.) were weighed into separate 1Dr vials. The vials were rinsed with 1,2-DCE (0.4 mL) one into another in the order listed above and transferred into a Schlenk tube. The Schlenk tube was immediately transferred out of the glove box and placed in a pre-heated 60°C oil bath and was stirred for 4 hours. The reaction flask was removed from the oil bath after 4 hours and was allowed to cool down to room temperature (approx. 15 min).

Work-up procedure: Reaction mixture was placed in a 2Dr vial and the Schlenk tube was washed with *n*-pentane (0.6 mL) and the washings were also transferred into the 2Dr vial. The mixture was filtered over a silica filter pipette into a pre-weighed 2Dr vial. The filter cake was washed with *n*-pentane (0.3 mL) into the pre-weighed 2Dr vial. All volatiles were removed in vacuo.

Analysis: ^{1}H NMR spectra of dried products were measured in $CDCl_3$ (0.4 mL).

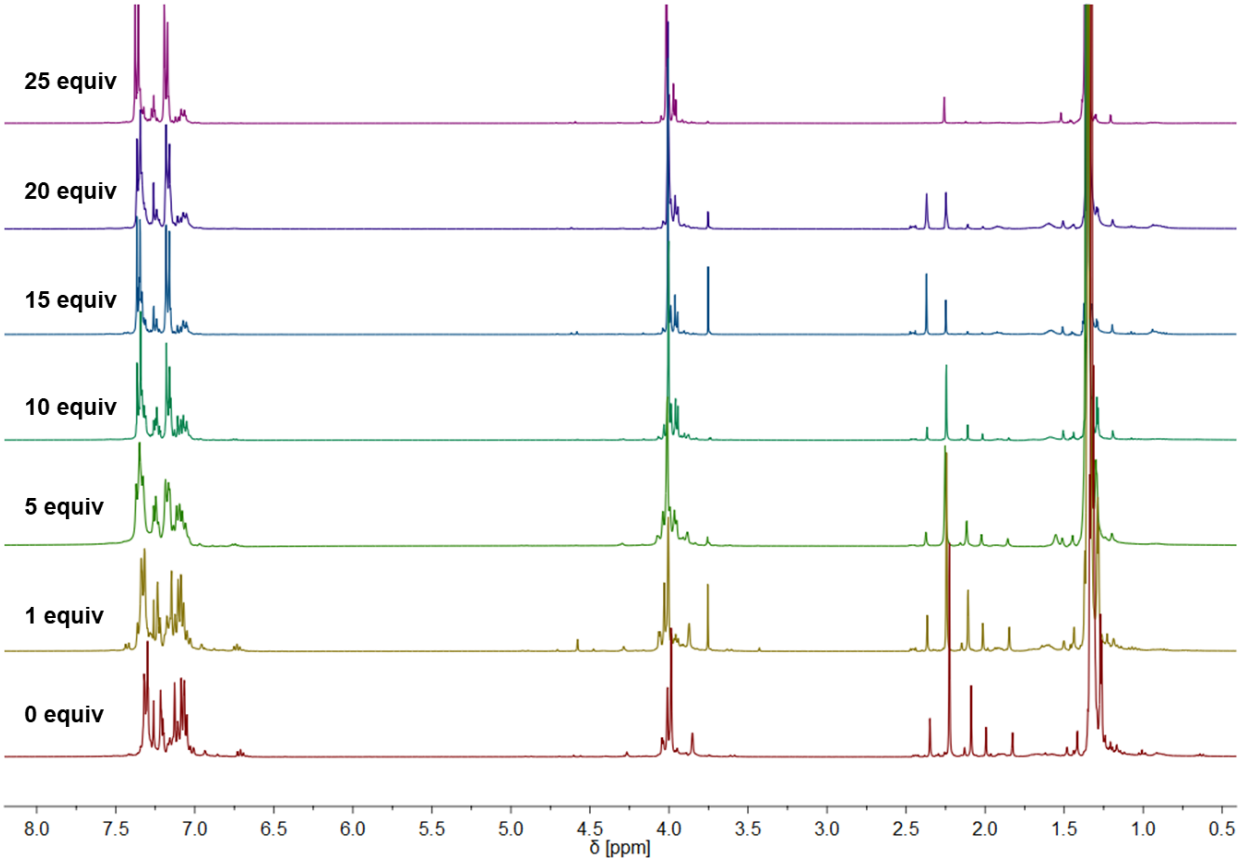


Figure S 16: Stacked ^{1}H NMR (400 MHz) spectra of products of arene equivalent screening after work-up procedure ($CDCl_3$). Amount of arene equivalents indicated on the left-hand side of each spectrum.

The ^{1}H NMR spectra of the products after the work-up procedure show that by-products get significantly reduced when increasing the amount of C_6D_6 (Figure S 16). *By-products originate from Friedel-Crafts benzylation of the 4-tert-butylbenzyl fluoride substrate leading to regioisomers of dimers and oligomers of 4-tert-butylbenzylfluoride (cf. reaction with 0 equiv. of C_6D_6,* Figure S 16).

3.1.2 Temperature optimization

***General procedure for temperature screening*:**

Under an inert atmosphere of a nitrogen glovebox, 4-*tert*-butylbenzyl fluoride (30 mg, 0.20 mmol, 1.0 equiv.), triethylsilane (21 mg, 0.20 mmol, 1.0 equiv.), C_6D_6 (379 mg, 4.5 mmol, 25 equiv.) and 9-H-9-BBN (1 mg, 0.001 mmol, 0.05 equiv.) were weighed into separate 1Dr vials. The vials were rinsed with 1,2-DCE (0.4 mL) one into another in the order listed above and transferred into a Schlenk tube. The Schlenk tube was immediately transferred out of the glove box and placed in a pre-heated oil bath at the corresponding temperature (room temperature, 40 °C, 50 °C, 60 °C) and was stirred for 4 hours. The reaction flask was removed from the oil bath after 4 hours and was allowed to cool down to room temperature (approx. 15 min).

Work-up procedure: Reaction mixture was placed in a 2Dr vial and the Schlenk tube was washed with *n*-pentane (0.6 mL) and the washings were also transferred into the 2Dr vial. The mixture was filtered over a silica filter pipette into a pre-weighed 2Dr vial. The filter cake was washed with *n*-pentane (0.3 mL) into the pre-weighed 2Dr vial. All volatiles were removed in vacuo.

Analysis: ^{1}H NMR spectra of dried products were measured in $CDCl_3$ (0.4 mL).

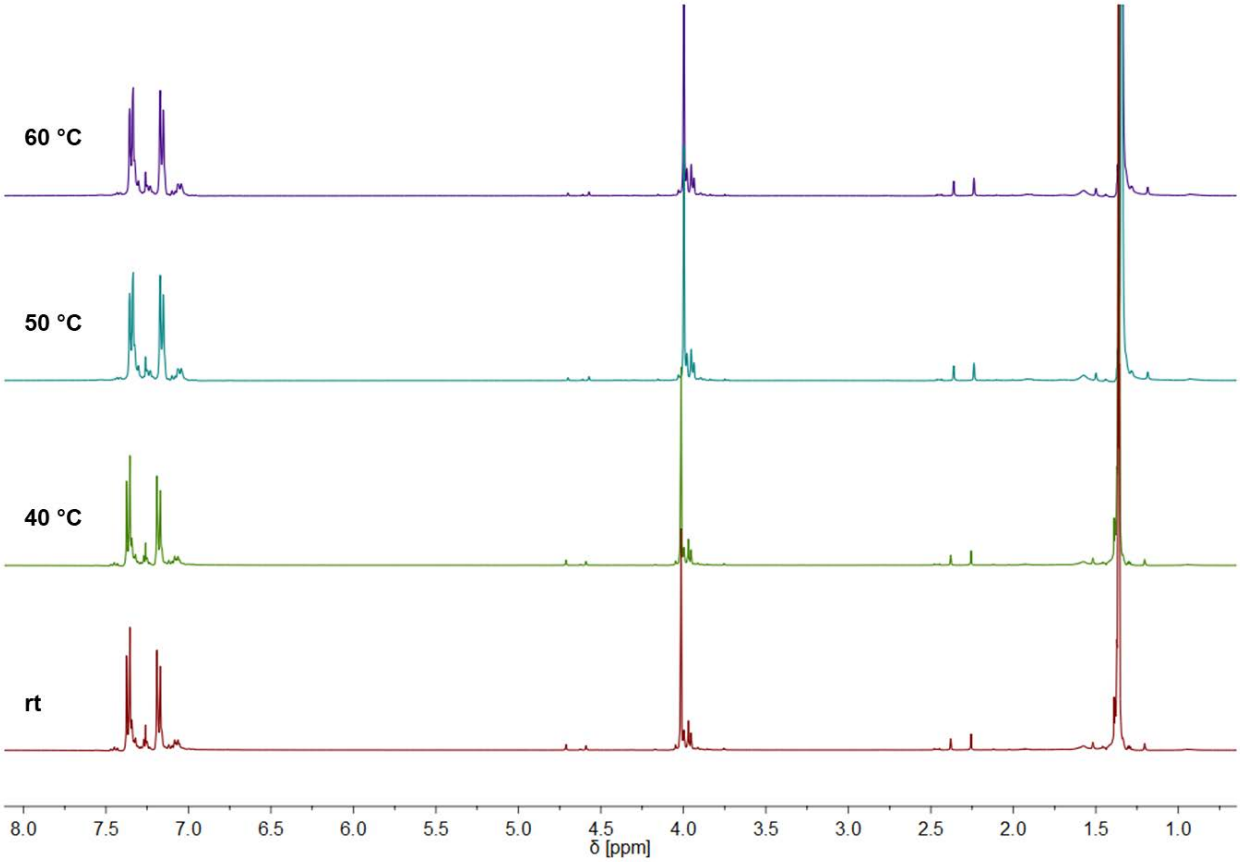
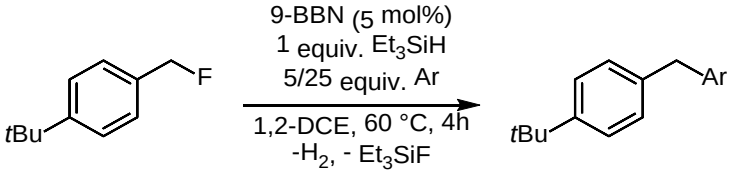


Figure S 17: Stacked ^{1}H NMR (400 MHz) spectra of products of temperature screening after work-up procedure ($CDCl_3$). Reaction temperature indicated on the left-hand side of each spectrum.

While we did not observe a change in by-products by ^{1}H NMR spectroscopy after work-up for the different temperatures, we noticed a drop in the yield of soluble material of the reactions when changing from 60 °C (72 %), to 50 °C (68 %), to 40 °C (62 %) and to room temperature (50 %). This is assumed to be due to the increased formation of oligomeric or polymeric by-products due to self-Friedel-Crafts benzylation of the substrate 4-tert-butylbenzyl fluoride. These less soluble oligomeric and polymeric by-products get separated during the work-up procedure.

3.2 General Procedure



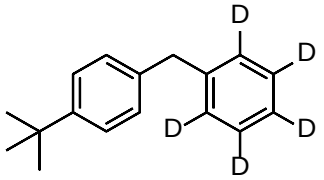
Under an inert atmosphere of a nitrogen glovebox, benzyl fluoride (1 equiv.), triethylsilane (1 equiv.), corresponding arene (5 or 25 equiv.) and 9-H-9-BBN (0.05 equiv.) were weighed into separate 1Dr vials. The vials were washed out with 1,2-DCE (0.4 mL) one into another in the order listed above and transferred into a Schlenk tube. The Schlenk tube was immediately transferred out of the glove box and placed in a pre-heated 60 °C oil bath and was stirred for 4 hours. The reaction flask was removed from the oil bath after 4 hours and was allowed to cool down to room temperature (approx. 15 min).

Work-up procedure: the reaction mixture was transferred to a 2Dr vial and the Schlenk tube was washed with *n*-pentane or DCM (1.8 mL) and the washings were added to the 2Dr vial. The mixture was filtered over a silica filter pipette into a pre-weighed 2Dr vial. The filter cake was washed with *n*-pentane or DCM (0.9 mL) into the pre-weighed 2Dr vial. The filtered reaction mixture was dried under vacuum to remove solvent and excess arene. In the case of non-volatile arenes, excess arene was removed through sublimation under vacuum. Yield of the isolated product was obtained and $CDCl_3$ (0.2 mL, 3 mm tube) was used to measure ^1H and $^{13}C\{^1H\}$ NMR spectra. The same NMR solution was used for ESI/DART-MS analysis.

^1H NMR analysis: where possible, integrations for isomer peaks have been reported as a portion of the total integration.

3.3 Arene Scope

1-(4-(*Tert*-butyl)benzyl)benzene-2,3,4,5,6-d_5, 1



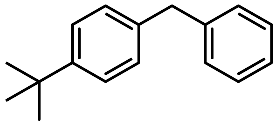
4-*Tert*-butylbenzyl fluoride (30 mg, 0.20 mmol), triethylsilane (21 mg, 0.20 mmol, 1.0 equiv.), C_6D_6 (379 mg, 4.5 mmol, 25 equiv.) and 9-H-9-BBN (1 mg, 0.01 mmol, 0.05 equiv.) were dissolved in 1,2-DCE (0.4 mL) in a Schlenk tube. Following work-up with *n*-pentane and removal of volatiles under vacuum product **1** was isolated as a colourless oil (27 mg, 64% yield).

^1H NMR (400 MHz, $CDCl_3$) δ: 7.39 – 7.32 (m, 2H), 7.20 – 7.09 (m, 2H), 3.99 (s, 2H), 1.35 (s, 9H).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ: 148.9, 141.2, 138.2, 128.7, 125.5, 41.5, 34.5, 31.6. *Note: C_{Ar}–D resonances were not observed.*

HRMS (DART Ionization, *m/z*): Calcd. for $C_{17}H_{19}ND_5$ ($[M+NH_4]^+$): 247.22171; Found: 247.22231.

1-(4-(*Tert*-butyl)benzyl)benzene, 2



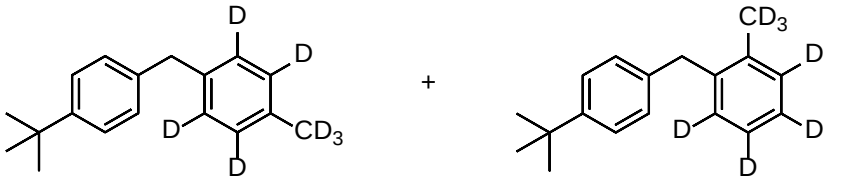
4-*Tert*-butylbenzyl fluoride (90 mg, 0.54 mmol), triethylsilane (63 mg, 0.54 mmol, 1.0 equiv.), benzene (1.055 g, 13.5 mmol, 25 equiv.) and 9-H-9-BBN (3 mg, 0.03 mmol, 0.05 equiv.) were dissolved in 1,2-DCE (1.2 mL) in a Schlenk tube. Following work-up with *n*-pentane and removal of volatiles under vacuum product **2** was isolated as a colourless oil (99 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 – 7.27 (m, 4H), 7.25 – 7.19 (m, 3H), 7.17 – 7.12 (m, 2H), 3.98 (s, 2H), 1.33 (s, 9H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ: 148.9, 141.4, 138.2, 129.1, 128.7, 128. 6, 126.1, 125.5, 41.6, 34.5, 31.6.

HRMS (DART Ionization, *m/z*): Calcd. for $C_{17}H_{24}N$ ($[M+NH_4]^+$): 242.19033; Found: 242.19083.

1-(4-(*Tert*-butyl)benzyl)-4-(methyl-d_3)-benzene-2,3,5,6-d_4 and 1-(4-(*tert*-butyl)benzyl)-2-(methyl-d_3)-benzene-2,3, 5,6-d_4, 3



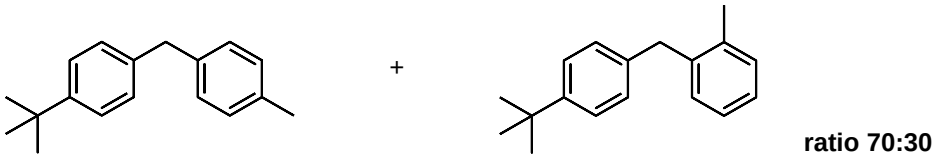
4-*Tert*-butylbenzyl fluoride (30 mg, 0.2 mmol), triethylsilane (21 mg, 0.20 mmol, 1.0 equiv.), toluene-d_8 (450 mg, 4.5 mmol, 25 equiv.) and 9-H-9-BBN (1 mg, 0.01 mmol, 0.05 equiv.) were dissolved in 1,2-DCE (0.4 mL) in a Schlenk tube. Following work-up with *n*-pentane and removal of volatiles under vacuum product **3** was isolated as a colourless oil (33 mg, 74% yield). Isolated product is a mixture of regioisomers (2.3:1) with 1-(4-(*tert*-butyl)benzyl)-4-(methyl-d_3)-benzene-2,3, 5,6-d_4 as the major isomer.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38 – 7.26 (m, 2H, isomer mixture), 7.16 – 7.11 (m, 1.38H), 7.10 – 7.05 (m, 0.54H), 3.97 (s, 1.42H), 3.93 (s, 0.57H), 1.32 (9H, isomer mixture).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ: 148.81, 148.78, 138.5, 137.4, 128.6, 128.5, 125.44, 125.39, 41.1 (CH_2), 39.0, 34.5 (C-CH_3), 31.6 (CH_3), 20.2 (q, J = 38.5 Hz, *p*-CD_3), 19.6 – 18.4 (m, *o*-CD_3). *Note: C_{Ar}-D resonances were not observed.*

HRMS (DART Ionization, *m/z*): Calcd. for $C_{18}H_{19}ND_7$ ($[M+NH_4]^+$): 263.24991; Found: 263.24990.

1-(*Tert*-butyl)-4-(4-methylbenzyl)benzene and 1-(4-(*tert*-butyl)benzyl)-2-methylbenzene, 4



ratio 70:30

4-*Tert*-butylbenzyl fluoride (90 mg, 0.54 mmol), triethylsilane (63 mg, 0.54 mmol, 1.0 equiv.), toluene (1.244 g, 13.5 mmol, 25 equiv.) and 9-H-9-BBN (3 mg, 0.03 mmol, 0.05 equiv.) were dissolved in 1,2-DCE (1.2 mL) in a Schlenk tube. Following work-up with DCM and removal of volatiles under vacuum product **4** was isolated as a colourless oil (122 mg, 95% yield). Isolated product is a mixture of regioisomers (2.3:1) with 1-(*tert*-butyl)-4-(4-methylbenzyl)benzene as the major isomer.

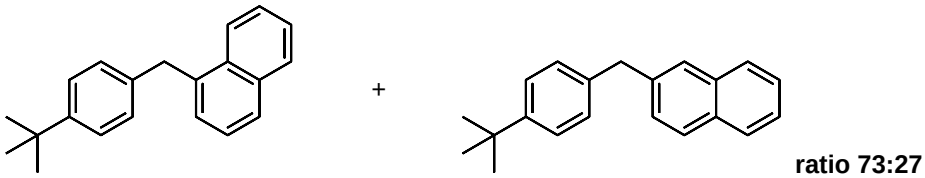
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 (m, 2H, isomer mixture), 7.30 – 7.26 (m, 1H, isomer mixture), 7.24 (br, 2H), 7.22 (d, *J* = 1.6 Hz, 2H, isomer mixture), 7.19 (d, *J* = 8.0 Hz, 1H), 4.08 (s, 0.59H), 4.04 (s, 1.41H), 2.44 (s, 2.04H), 2.38 (s, 0.92H), 1.43 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 148.83, 148.79, 139.3, 138.5, 138.4, 137.4, 136.7, 135.5, 130.4, 130.1, 129.3, 129.0, 128.6, 128.5, 126.5, 126.1, 125.5, 125.4, 41.2, 39.0, 34.5, 31.6, 21.2, 19.8.

HRMS (DART Ionization, *m/z*): Calcd. for $C_{18}H_{26}N$ ($[M+NH_4]^+$): 256.20598; Found: 256.20563.

Analytical data were in accordance with those previously reported. Data from compound **10** was used to analyze the ^{13}C{^{1}H} NMR spectrum.

1-(4-(*Tert*-butyl)benzyl)naphthalene and 2-(4-(*tert*-butyl)benzyl)naphthalene, 5



ratio 73:27

4-*Tert*-butylbenzyl fluoride (90 mg, 0.54 mmol), triethylsilane (63 mg, 0.54 mmol, 1.0 equiv.), naphthalene (346 mg, 2.7 mmol, 5.0 equiv.) and 9-H-9-BBN (3 mg, 0.03 mmol, 0.05 equiv.) were dissolved in 1,2-DCE (1.2 mL) in a Schlenk tube. Following work-up with DCM, the excess naphthalene was sublimed out at 80 °C under vacuum (0.003 mbar). Product **5** was isolated as a colourless solid (124 mg, 84% yield). Isolated product is a mixture of regioisomers (3:1) with 1-(4-(*tert*-butyl)benzyl)naphthalene as the major isomer.

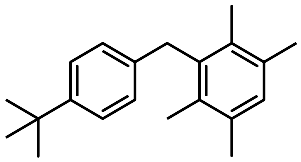
^{1}H NMR (500 MHz, $CDCl_3$), δ: 8.12 – 8.05 (m, 0.72H), 7.93 – 7.88 (m, 0.68H), 7.84 (d, *J = 9.8Hz*, 0.33H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.70 (s, 0.25H), 7.54 – 7.39 (m, 2.64H), 7.38 – 7.30 (m, 3H), 7.21 (d, J_{HH} = 8.3 Hz, 0.53H), 7.18 (d, J_{HH} = 8.1 Hz, 1.64H), 4.47 (s, 1.47H), 4.16 (s, 0.54H), 1.36 (s, 2.53H), 1.34 (s, 6.44H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 149.1, 149.0, 138.9, 138.1, 137.7, 137.0, 134.1, 133.8, 132.3, 132.2, 128.8, 128.7, 128.5, 128.2, 127.9, 127.8, 127.7, 127.4, 127.22, 127.18, 126.07, 126.05, 125.71, 125.66, 125.53, 125.47, 125.42, 124.5, 41.8, 38.7, 38.6, 34.52, 34.49, 31.5.

HRMS (DART Ionization, *m/z*): Calcd. for $C_{21}H_{26}N$ ($[M+NH_4]^+$): 292.20598; Found: 292.20661.

Analytical data were in accordance with those previously reported.[10]

3-(4-(*Tert*-butyl)benzyl)-1,2,4,5-tetramethylbenzene, 6



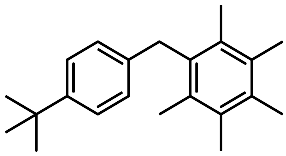
4-*Tert*-butylbenzyl fluoride (90 mg, 0.54 mmol), triethylsilane (63 mg, 0.54 mmol, 1.0 equiv.), 1,2,4,5-tetramethylbenzene (362 mg, 2.7 mmol, 5.0 equiv.) and 9-H-9-BBN (3 mg, 0.03 mmol, 0.05 equiv.) were dissolved in 1,2-DCE (1.2 mL) in a Schlenk tube. Following work-up with DCM, the excess arene was sublimed out at 75 °C under vacuum (0.003 mbar). Product **6** was isolated as a colourless solid (120 mg, 79% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.27 (d, $^3J_{HH}$ = 8.5 Hz, 2H, *peak overlapped by solvent signal*), 6.97, (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.94 (s, 1H), 4.08 (s, 2H), 2.27 (s, 6H), 2.15 (s, 6H), 1.31 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 148.5, 137.3, 137.0, 133.8, 133.2, 130.1, 127.8, 125.3, 35.3, 34.4, 31.6, 20.8, 16.0.

HRMS (DART Ionization, *m/z*): Calcd. for $C_{21}H_{32}N$ ($[M+NH_4]^+$): 298.25293; Found: 298.25239.

1-(4-(*Tert*-butyl)benzyl)-2,3,4,5,6-pentamethylbenzene, 7



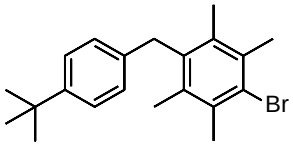
4-*Tert*-butylbenzyl fluoride (90 mg, 0.54 mmol), triethylsilane (63 mg, 0.54 mmol, 1.0 equiv.), 3-bromo-1,2,3,4,5-pentamethylbenzene (400 mg, 2.7 mmol, 5.0 equiv.) and 9-H-9-BBN (3 mg, 0.03 mmol, 0.05 equiv.) were dissolved in 1,2-DCE (1.2 mL) in a Schlenk tube. Following work-up with DCM, the excess arene was sublimed out at 80 °C under vacuum (0.003 mbar) and product **7** was isolated as a colourless solid (149 mg, 93% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.27 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 7.00 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 4.10 (s, 2H), 2.30 (s, 3H), 2.27 (s, 6H), 2.21 (s, 6H), 1.31 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 148.4, 137.6, 134.3, 133.1, 132.9, 132.6, 127.7, 125.3, 35.8, 34.4, 31.6, 17.10, 17.05, 17.02.

HRMS (DART Ionization, *m/z*): Calcd. for $C_{22}H_{31}N$ ($[M+NH_4]^+$): 295.24203; Found: 295.24186.

1-Bromo-4-(4-(*tert*-butyl)benzyl)-2,3,5,6-tetramethylbenzene, 8



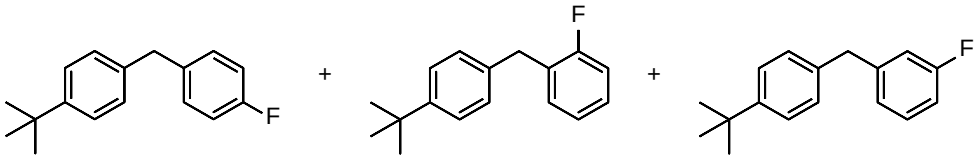
4-*Tert*-butylbenzyl fluoride (90 mg, 0.54 mmol), triethylsilane (63 mg, 0.54 mmol, 1.0 equiv.), 3-bromo-1,2,4,5-tetramethylbenzene (575 mg, 2.7 mmol, 5.0 equiv.) and 9-H-9-BBN (3 mg, 0.03 mmol, 0.05 equiv.) were dissolved in 1,2-DCE (1.2 mL) in a Schlenk tube. Following work-up with DCM, the excess arene was sublimed out at 80 °C under vacuum (0.003 mbar) and product **8** was isolated as a colourless solid (144 mg, 74% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.26 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 6.94 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 4.06 (s, 2H), 2.47 (s, 6H), 2.23 (s, 6H), 1.30 (s, 9H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ: 148.7, 136.7, 136.0, 134.8, 134.0, 127.8, 127.6, 125.4, 35.7, 34.5, 31.5, 21.7, 17.9.

HRMS (DART Ionization, *m/z*): Calcd. for $C_{21}H_{31}NBr$ ($[M+NH_4]^+$): 376.16344; Found: 376.16296.

1-(*Tert*-butyl)-4-(4-fluorobenzyl)benzene, 1-(4-(*tert*-butyl)benzyl)-2-fluorobenzene, and 1-(4-(*tert*-butyl)benzyl)-3-fluorobenzene, 9



ratio 78:15:7

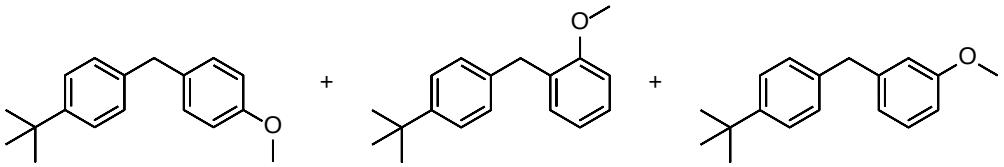
4-*Tert*-butylbenzyl fluoride (90 mg, 0.54 mmol), triethylsilane (63 mg, 0.54 mmol, 1.0 equiv.), fluorobenzene (1.297 g, 13.5 mmol, 25 equiv.) and 9-H-9-BBN (3 mg, 0.03 mmol, 0.05 equiv.) were dissolved in 1,2-DCE (1.2 mL) in a Schlenk tube. Following work-up with DCM and removal of volatiles under vacuum, product **9** was isolated as a colourless solid (107 mg, 82% yield). Isolated product is a mixture of regioisomers (16:3:1) with 1-(*tert*-butyl)-4-(4-fluorobenzyl)benzene as the major isomer.

^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.36 – 7.31 (m, 2H), 7.19 – 7.08 (m, 4H), 6.97 (m, 2H), 3.98 (s, 0.31H), 3.93 (s, 1.56H), 3.87 (s, 0.13H), 1.33 (s, 9H).

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, *partial*) δ: 162.5, 160.6, 149.1, 138.03, 138.03, 137.1, 137.0, 133.8, 130.5, 130.4, 128.6, 128.33, 128.29, 125.6, 125.4, 125.3, 115.4, 115.2, 40.7, 39.5, 39.2, 37.8, 34.5, 31.5. *Note: although the minor isomer was observed in the ^{1}H and ^{19}F NMR spectra, it was not fully detected in the $^{13}C\{^{1}H\}$ spectrum.*

HRMS (DART Ionization, *m/z*): Calcd. for $C_{17}H_{23}NF$ ($[M+NH_4]^+$): 260.18090; Found: 260.18132.

1-(*Tert*-butyl)-4-(4-methoxybenzyl)benzene, 1-(4-(*tert*-butyl)benzyl)-2-methoxybenzene, 1-(4-(*tert*-butyl)benzyl)-3-methoxybenzene, 10



ratio 50:44:6

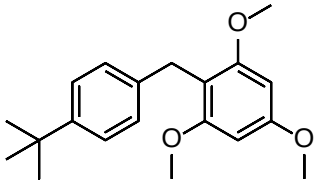
4-*Tert*-butylbenzylfluoride (90 mg, 0.54 mmol), triethylsilane (63 mg, 0.54 mmol, 1.0 equiv.), anisole (292 mg, 2.7 mmol, 5.0 equiv.) and 9-H-9-BBN (3 mg, 0.03 mmol, 0.05 equiv.) were dissolved in 1,2-DCE (1.2 mL) in a Schlenk tube. The mixture was stirred for 4 hours at 60 °C. After 4 hours the mixture was cooled down to room temperature. Following the work-up procedure with DCM and removal of volatiles under vacuum (0.003 mbar), **10** was isolated as a white oil (115 mg, 83% yield). Isolated product is a mixture of regioisomers (8.3:7.3:1) with 1-(*tert*-butyl)-4-(4-methoxybenzyl)benzene as the major isomer. Pure fraction of 1-(4-(*tert*-butyl)benzyl)-2-methoxybenzene was isolated using column chromatography (silica, 5% EtOAc/ 95% hexane). Reported NMR and HRMS data are of an isolated pure fraction of 1-(4-(*tert*-butyl)benzyl)-2-methoxybenzene.[16] ^{1}H NMR spectrum of the isolated mixture of products is also provided.

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.33 – 7.29 (m, 2H, H_{ar}), 7.23 – 7.21 (m, 1H, H_{ar}), 7.19 – 7.16 (m, 2H, H_{ar}), 7.11 – 7.09 (m, 1H, H_{ar}), 6.91 – 6.88 (m, 2H, H_{ar}), 3.97 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3), 1.32 (s, 9 H, *t*Bu).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$), δ: 157.5, 148.6, 138.1, 130.5, 130.0, 128.7, 127.4, 125.3, 120.6, 110.5, 55.5, 35.4, 34.5, 31.6.

HRMS (DART Ionization, *m/z*): Calcd. for $C_{18}H_{22}O$ ($[M+NH_4]^+$): 272.20089; found: 272.20078.

2-(4-(*Tert*-butyl)benzyl)-1,3,5-trimethoxybenzene, 11



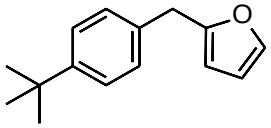
4-*Tert*-butylbenzyl fluoride (90 mg, 0.54 mmol), triethylsilane (63 mg, 0.54 mmol, 1.0 equiv.), 3-bromo-1,3,5-trimethoxybenzene (454 mg, 2.7 mmol, 5.0 equiv.) and 9-H-9-BBN (3 mg, 0.03 mmol, 0.05 equiv.) were dissolved in 1,2-DCE (1.2 mL) in a Schlenk tube. Following work-up with DCM and sublimation at 80 °C under vacuum (0.003 mbar), product **11** was isolated as a colourless solid (130 mg, 76% yield).

^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.26 – 7.15 (m, 4H), 6.16 (d, *J* = 2.5 Hz, 2H), 3.91 (s, 2H), 3.81 (t, *J* = 1.7 Hz, 3H), 3.82 – 3.78 (m, 6H), 1.29 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 159.7, 159.0, 147.9, 139.3, 128.2, 125.0, 110.6, 90.8, 55.8, 55.5, 34.4, 31.6, 27.8.

HRMS (DART Ionization, *m/z*): Calcd. for $C_{20}H_{27}O_3$ ($[M+H]^+$): 315.19547; Found: 315.19564.

2-(4-(*Tert*-butyl)benzyl)furan, 12



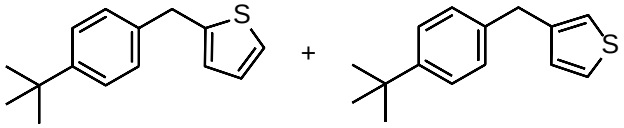
4-*Tert*-butylbenzyl fluoride (90 mg, 0.54 mmol), triethylsilane (63 mg, 0.54 mmol, 1.0 equiv.), furan (735 mg, 2.7 mmol, 20 equiv.) and 9-H-9-BBN (3 mg, 0.03 mmol, 0.05 equiv.) were dissolved in 1,2-DCE (1.2 mL) in a Schlenk tube. Following work-up with DCM and removal of volatiles under vacuum product **12** was isolated as a light-yellow oil (114 mg, 98% yield). Due to the low boiling point of the substrate, the reaction was additionally performed at 30°C and the same yield was obtained.

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.39 – 7.30 (m, 3H), 7.18 (d, *J* = 8.6 Hz, 2H), 6.30 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.03 (dd, *J* = 3.1, 0.9 Hz, 1H), 3.96 (s, 2H), 1.32 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 154.9, 149.4, 141.5, 135.3, 128.4, 125.5, 110.4, 106.3, 34.5, 34.1, 31.5.

HRMS (DART Ionization, *m/z*): Calcd. for $C_{15}H_{19}O$ ($[M+H]^+$): 215.14304; Found: 215.14304.

2-(4-(*Tert*-butyl)benzyl)thiophene and 3-(4-(*tert*-butyl)benzyl)thiophene, 13



ratio 70:30

4-*Tert*-butylbenzyl fluoride (90 mg, 0.54 mmol), triethylsilane (63 mg, 0.54 mmol, 1.0 equiv.), thiophene (1.1360 g, 2.7 mmol, 25 equiv.) and 9-H-9-BBN (3 mg, 0.03 mmol, 0.05 equiv.) were dissolved in 1,2-DCE (1.2 mL) in a Schlenk tube. Following work-up with DCM and removal of volatiles under vacuum, product **13** was isolated as a light-yellow oil (124 mg, 99% yield). Isolated product is a mixture of regioisomers (2.3:1) with 2-(4-(*tert*-butyl)benzyl)thiophene as the major isomer.

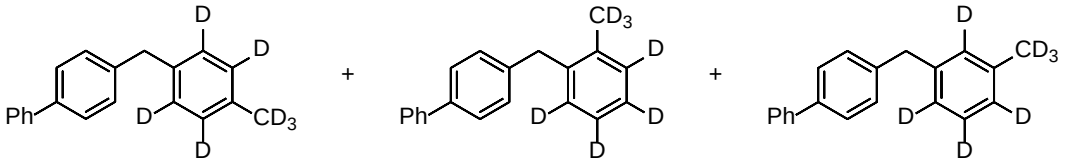
^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.35 (m, 2.19H), 7.23 – 7.12 (m, 2.90H), 6.96 – 6.92 (m, 1.23H), 6.85 – 6.80 (m, 0.67H), 4.15 (s, 1.40H), 3.97 (s, 0.60H), 1.34 (s, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 149.4, 149.1, 144.3, 141.8, 137.7, 137.5, 128.7, 128.5, 128.3, 126.9, 125.64, 125.56, 125.48, 125.2, 123.9, 121.3, 36.1, 35.6, 34.54, 34.51, 31.54, 31.53.

HRMS (DART Ionization, *m/z*): Calcd. for $C_{15}H_{19}S$ ($[M+H]^+$): 231.12020; Found: 231.11930.

3.4 Benzyl Fluoride Scope

4-(CH_2-(2-CD_3-C_6D_5))-1,1´-biphenyl, 4-(CH_2-(3-CD_3-C_6D_5))-1,1´-biphenyl, and 4-(CH_2-(4-CD_3-C_6D_5))-1,1´-biphenyl, 14



ratio 64:30:6

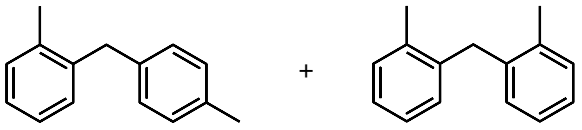
4-Phenylbenzylfluoride (34 mg, 0.2 mmol), triethylsilane (21 mg, 0.2 mmol, 1.0 equiv.), toluene-d_8 (450 mg, 4.5 mmol, 25 equiv.) and 9-H-9-BBN (1 mg, 0.01 mmol, 0.05 equiv.) were dissolved in 1,2-DCE (0.4 mL) in a Schlenk tube. The mixture was stirred for 4 hours at 60 °C. After 4 hours the mixture was cooled down to room temperature. Following work-up with *n*-pentane and removal of volatiles under vacuum, product **14** was isolated as a mixture of regioisomers (10.7:5:1) in 94 % yield (45 mg). 4-(CH_2-(2-CD_3-C_6D_5))-1,1´-biphenyl was determined to be the major isomer.

^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.69-7.66 (m, 2H, H_{ar}), 7.63 – 7.60 (m, 2H, H_{ar})7.53 - 7.50 (m, 2H, H_{ar}), 7.43 – 7.40 (m, 1H, H_{ar}), 7.37 – 7.34 (m, 1.3H, H_{ar}), 7.31 - 7.29 (m, 0.6H, H_{ar}), 4.12 (s, 0.6 H, CH_2), 4.08 (s, 1.3H, CH_2), 3.77 (s, 0.14H, CH_2).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, *partial*) δ: 141.2, 141.1, 140.7, 139.7, 139.1, 139.0, 129.4, 129.3, 128.84, 128.83, 127.30, 127.23, 127.17, 127.16, 127.12, 127.10, 43.6, 41.2, 39.2, 20.2 (m, *CD_3*), 19.0 (*CD_3*). *Note: although the minor isomers were observed in the ^{1}H NMR spectrum, they were not fully detected in the ^{13}C spectrum.*

HRMS (DART Ionization, *m/z*): Calcd. for $C_{20}H_{15}ND_7$ ([M+NH_4]$^+$): 283.21861; found: 283.21849.

1-Methyl-2-(4-methylbenzyl)benzene and 1-methyl-2-(2-methylbenzyl)benzene, 15



ratio 70:30

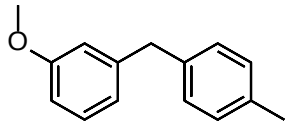
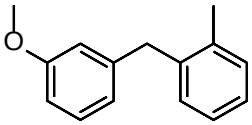
2-Methylbenzyl fluoride (67 mg, 0.54 mmol), triethylsilane (63 mg, 0.54 mmol, 1.0 equiv.), toluene (1.240 g, 13.5 mmol, 25 equiv.) and 9-H-9-BBN (3 mg, 0.03 mmol, 0.05 equiv.) were dissolved in 1,2-DCE (1.2 mL) in a Schlenk tube. The mixture was stirred for 4 hours at 60 °C. After 4 hours the mixture was cooled down to room temperature. Following work-up with *n*-pentane and removal of volatiles under vacuum, product **15** was isolated as a colourless oil (81 mg, 76% yield). Isolated product is a mixture of regioisomers (2.2:1) with 1-methyl-2-(4-methylbenzyl)benzene as the major isomer.

^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.25 – 7.17 (m, 3H), 7.17 – 7.09 (m, 3H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 3.99 (s, 1.38H), 3.96 (s, 0.62H), 2.35 (s, 1.96H), 2.31 (s, 1.65H), 2.29 (s, 2.06H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 139.3, 138.5, 137.4, 136.70, 136.69, 135.5, 130.4, 130.2, 130.0, 129.3, 129.2, 128.8, 126.5, 126.4, 126.2, 126.1, 39.1, 36.8, 21.1, 19.8, 19.7.

HRMS (DART Ionization, *m/z*): Calcd. for $C_{15}H_{20}N$ ([M+NH_4]$^+$): 214.15903; Found: 214.15986.

1-Methoxy-3-(4-methylbenzyl)benzene and 1-(3-methoxybenzyl)-2-methylbenzene, 16


+

ratio 58:42

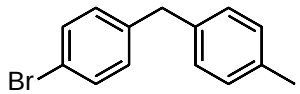
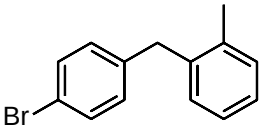
3-Methoxybenzyl fluoride (250 mg, *1.8 mmol*), triethylsilane (210 mg, *1.8 mmol*, 1.0 equiv.), toluene (4.150 g, *45 mmol*, 25 equiv.) and 9-H-9-BBN (10 mg, *0.09 mmol*, 0.05 equiv.) were dissolved in 1,2-DCE (4.0 mL) in a Schlenk tube. Following work-up with DCM and removal of volatiles under vacuum, product **16** was isolated as a colourless oil (335 mg, 88% yield). Isolated product is a mixture of regioisomers (1.4:1) with 1-(3-methoxybenzyl)-4-methylbenzene as the major isomer.

^{1}H NMR (500 MHz, $CDCl_3$), δ: 7.39 – 7.27 (m, 3H, H_{ar}), 7.26 (s, 2H, H_{ar}), 6.98 – 6.83 (m, 3H, H_{ar}), 4.13 (s, 0.83H, CH_2), 4.08 (s, 1.15H, CH_2), 3.92 (s, 1.69H, OCH_3), 3.91 (s, 1.18H, OCH_3), 2.48 (s, 1.63H, CH_3), 2.42 (s, 1.20H, CH_3).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 159.82, 159.81, 143.1, 142.2, 138.8, 138.0, 136.7, 135.6, 130.4, 130.0, 129.5, 129.4, 129.3, 128.9, 126.6, 126.1, 121.4, 121.3, 114.82, 114.77, 111.3, 111.2, 55.16, 55.15, 41.6, 39.6, 21.1, 19.8.

HRMS (DART Ionization, *m/z*): Calcd. for $C_{15}H_{17}O$ ($[M+H]^+$): 213.12739; Found: 213.12675.

1-Bromo-4-(4-methylbenzyl)benzene & 1-(4-bromobenzyl)-2-methylbenzene, 17


+

ratio 55:45

4-Bromobenzyl fluoride (102 mg, 0.54 mmol), triethylsilane (63 mg, 0.54 mmol, 1.0 equiv.), toluene (1.240 g, 13.5 mmol, 25 equiv.) and 9-H-9-BBN (3 mg, 0.03 mmol, 0.05 equiv.) were dissolved in 1,2-DCE (1.2 mL) in a Schlenk tube. Following work-up with DCM and removal of volatiles under vacuum, product **17** was isolated as a colourless oil (139 mg, 98% yield). Isolated product is a mixture of regioisomers (1.2:1) with 1-(4-bromobenzyl)-4-methylbenzene as the major isomer.

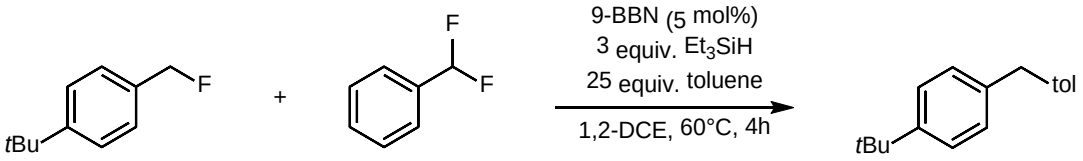
^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.51 – 7.41 (m, 2H, H_{ar}), 7.27 – 7.15 (m, 3H, H_{ar}), 7.15 – 7.09 (m, 2H, H_{ar}), 7.08 – 7.03 (m, 1H, H_{ar}), 4.00 (s, 0.90H, CH_2), 3.96 (s, 1.10H, CH_2), 2.40 (s, 1.56H, CH_3), 2.30 (s, 1.37H, CH_3).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 140.5, 139.5, 138.4, 137.5, 136.6, 135.9, 131.6, 131.5, 130.7, 130.54, 130.52, 130.0, 129.4, 128.9, 126.8, 126.2, 120.0, 119.9, 41.0, 39.0, 21.1, 19.7.

HRMS (DART Ionization, *m/z*): Calcd. for $C_{14}H_{17}NBr$ ($[M+NH_4]^+$): 278.05389; Found: 278.05468.

3.5 Mechanistic Considerations

3.5.1 Competition Experiment with (Difluoromethyl)benzene



Following the general procedure, 4-*tert*-butylbenzyl fluoride (30 mg, 0.2 mmol), (difluoromethyl)benzene (23 mg, 0.2 mmol, 1.0 equiv.), triethylsilane (65 mg, 0.56 mmol, *3.1 equiv.*), and toluene (415 mg, 4.5 mmol, 25 equiv.) were dissolved in 1,2-DCE (0.4 mL) and transferred to a J-Young NMR tube. Using DCM and C_6F_6 as internal standards, ^{1}H and ^{19}F NMR spectra of the sample were collected. Next, 9-H-9-BBN (1 mg, 0.01 mmol, 0.05 equiv.) was added and the reaction was stirred for 4 hours at 60 °C. After 4 hours the reaction mixture was cooled down to room temperature and ^{1}H and ^{19}F NMR spectra were measured again.

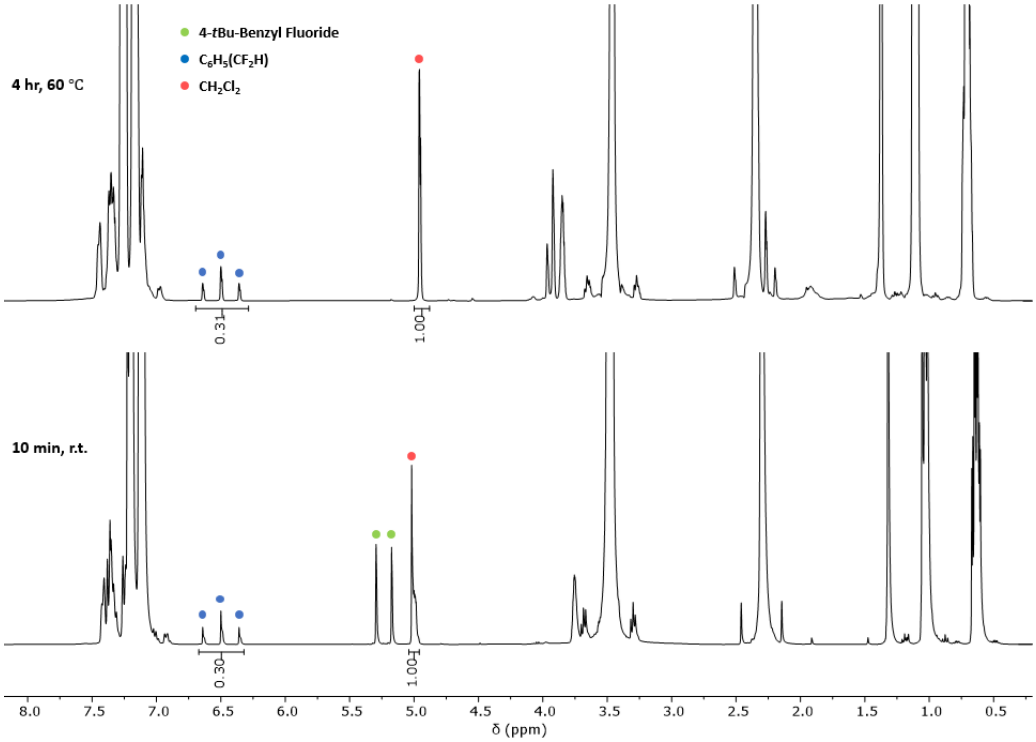


Figure S 18: ^{1}H NMR (400 MHz) spectra of competition study between 4-*tert*-butylbenzyl fluoride and (difluoromethyl)benzene at zero-point (bottom, no catalyst) and after 4 hours of heating (top).

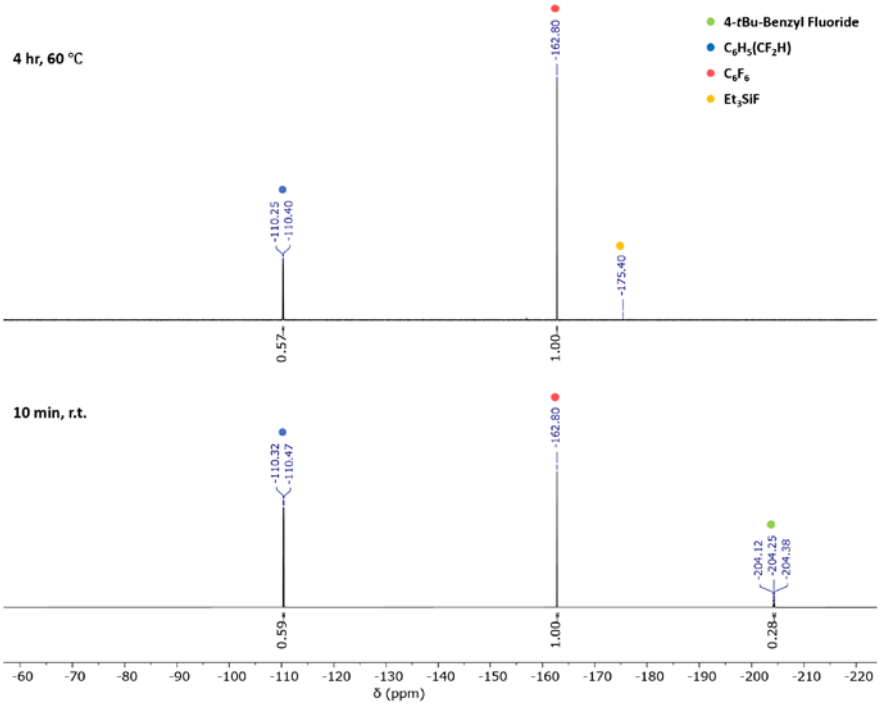
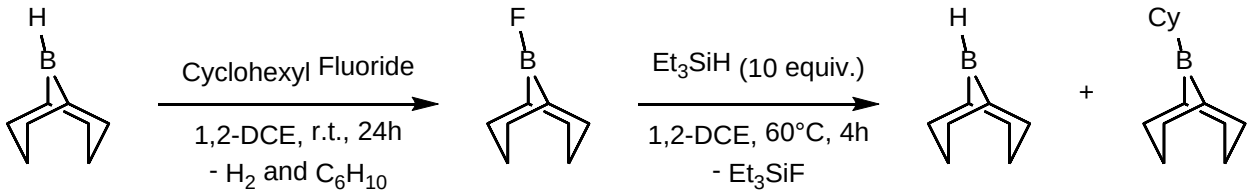


Figure S 19: ^{19}F NMR (377 MHz) spectra of competition study between 4-*tert*-butylbenzyl fluoride and (difluoromethyl)benzene at zero-point (bottom, no catalyst) and after 4 hours of heating (top). Spectra referenced to the C_6F_6 internal standard.

Based on the exclusive disappearance of the benzyl fluoride signal, the boron-mediated catalysis is selective towards the benzyl fluoride. In such an experiment, the reported silylium-mediated activation of benzylic C–F bonds[17] *would result in the conversion of both substrates, given that sufficient amount of triethylsilane (3.0 equiv.) is present in solution.*

3.5.2 Catalyst regeneration through reaction with triethyl silane



9-H-9-BBN (22 mg, 0.2 mmol), cyclohexyl fluoride (18 mg, 0.2 mmol, 1.0 equiv.) and C_6F_6 internal standard were dissolved in 1,2-DCE (0.6 mL) and transferred to a J-Young NMR tube. Slow bubbling of H_2 gas was observed. ^{11}B and ^{19}F NMR spectra of the reaction mixture was collected after 24 hours. Next, triethylsilane (210 mg, 2.0 mmol, 10 equiv.) was added to the reaction mixture and the J-Young NMR tube was placed in a 60 °C oil bath for 4 hours. Reaction mixture was then analyzed by ^{11}B and ^{19}F NMR spectroscopy.

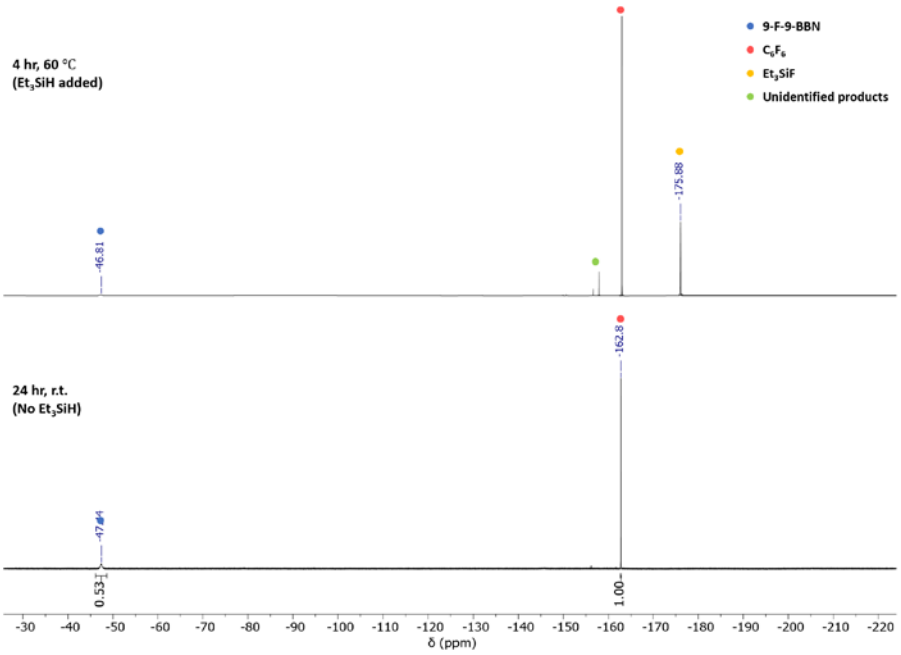


Figure S 20: ^{19}F NMR (377 MHz) spectra of the reaction of *in situ*-generated 9-F-9-BBN with triethyl silane at zero-point (bottom, no silane) and after 4 hours of heating (top, silane added). Spectra referenced to the C_6F_6 internal standard.

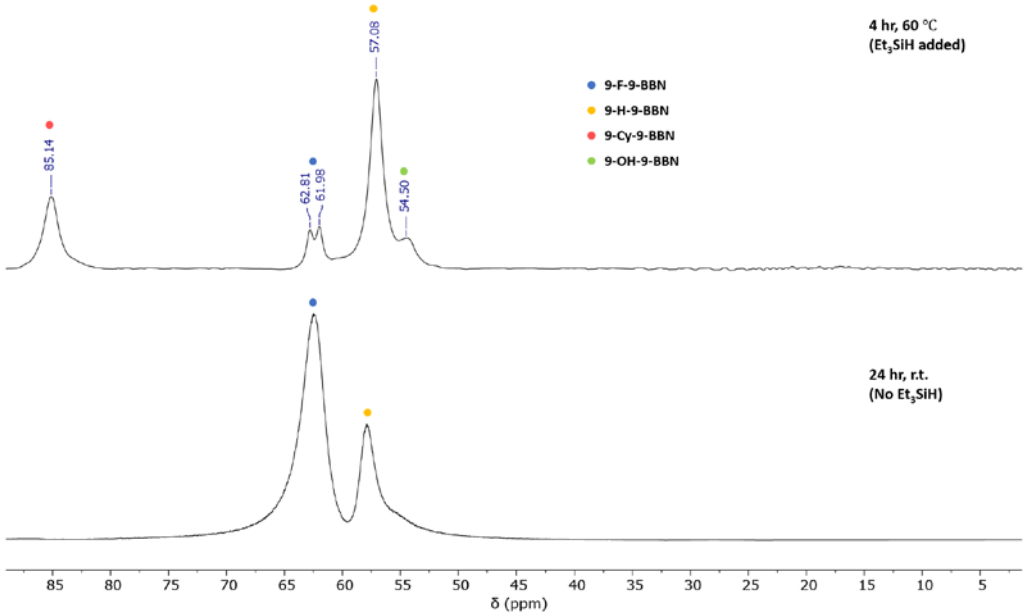


Figure S 21: ^{11}B NMR (128 MHz) spectra of the reaction of in situ-generated 9-F-9-BBN with triethyl silane at zero-point (bottom, no silane) and after 4 hours of heating (top, silane added).[18,19]

Based on the reported reaction of 9-H-9-BBN with cyclohexyl fluoride,[18] 9-F-9-BBN was generated in-situ and was then subjected to similar conditions as the Friedel-Crafts catalysis (10 equivalents of silane). The ^{19}F and ^{11}B NMR spectra show that the catalyst can be regenerated via the direct reaction with triethylsilane. 9-cyclohexyl-9-BBN was generated due to the side reaction between the re-generated 9-H-9-BBN and the cyclohexene formed as by-product of the first step.

4 NMR Spectra of Benzyl Fluorides and Diarylmethanes

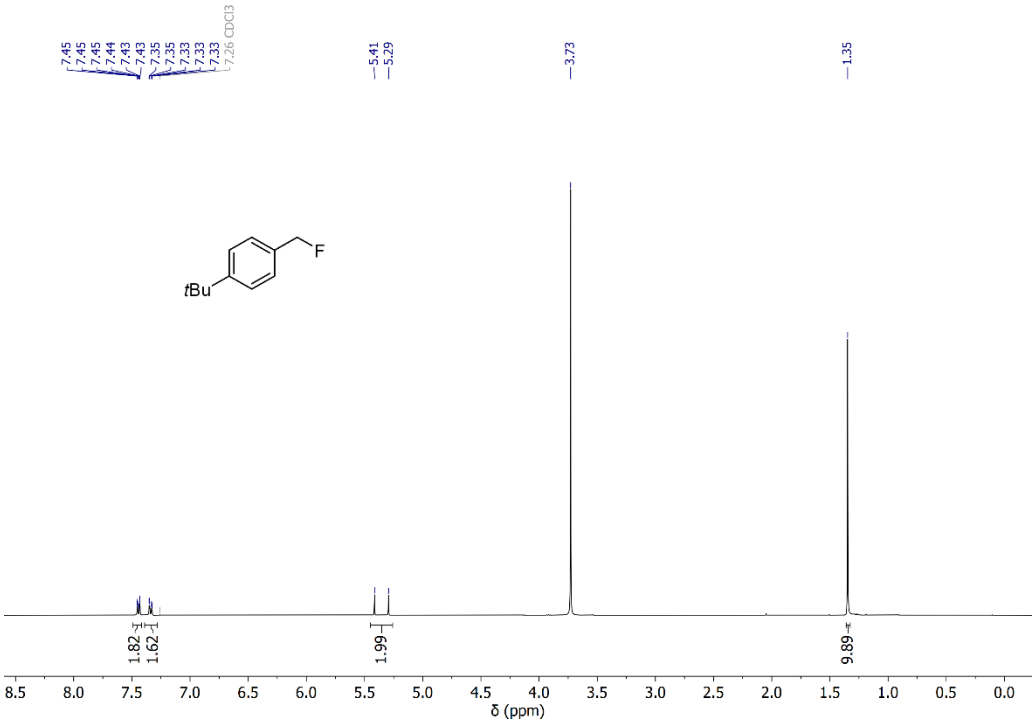


Figure S 22: ^{1}H NMR (400 MHz) spectrum of 4-(*tert*-butyl)benzyl fluoride ($CDCl_3$).

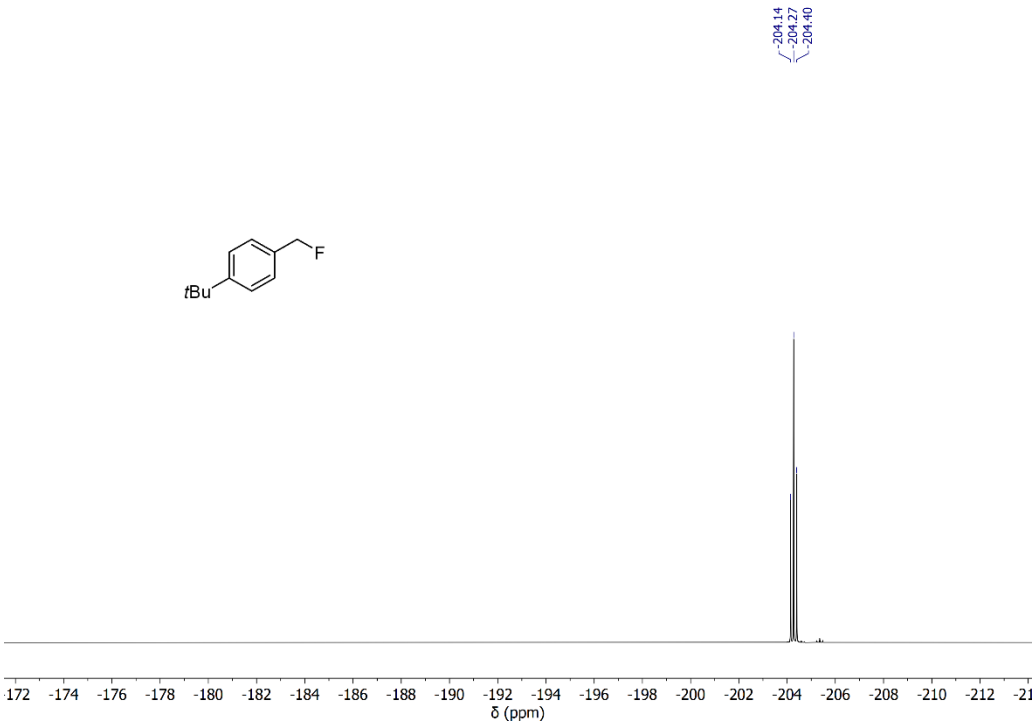


Figure S 23: ^{19}F NMR (377 MHz) spectrum of compound 4-(*tert*-butyl)benzyl fluoride ($CDCl_3$).

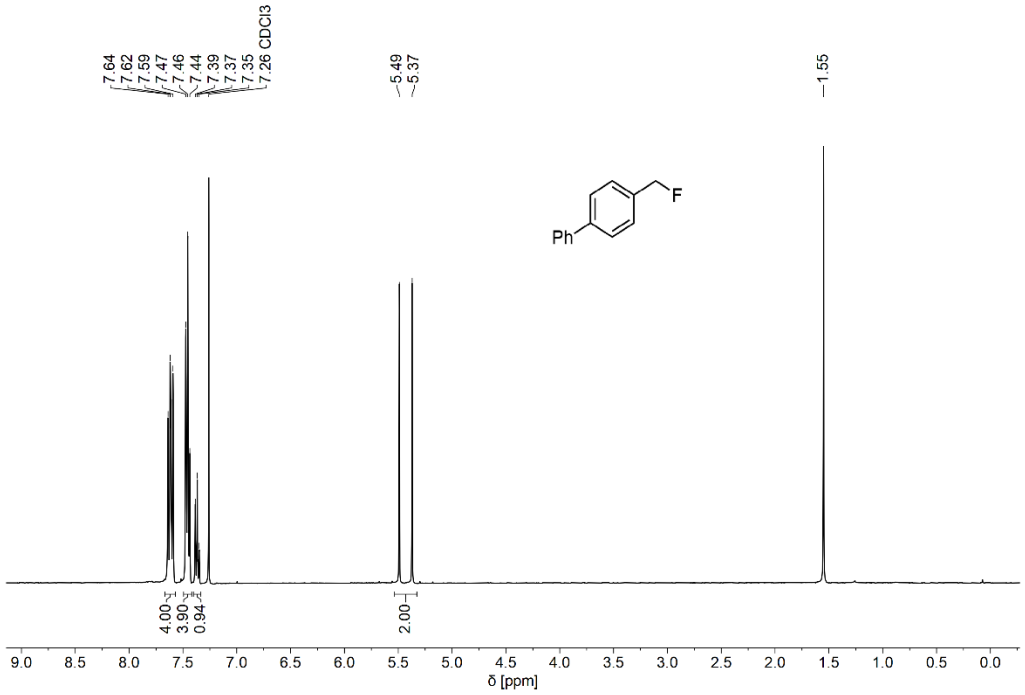


Figure S 24:^{1}H NMR (400 MHz) spectrum of compound 4-phenylbenzyl fluoride ($CDCl_3$).

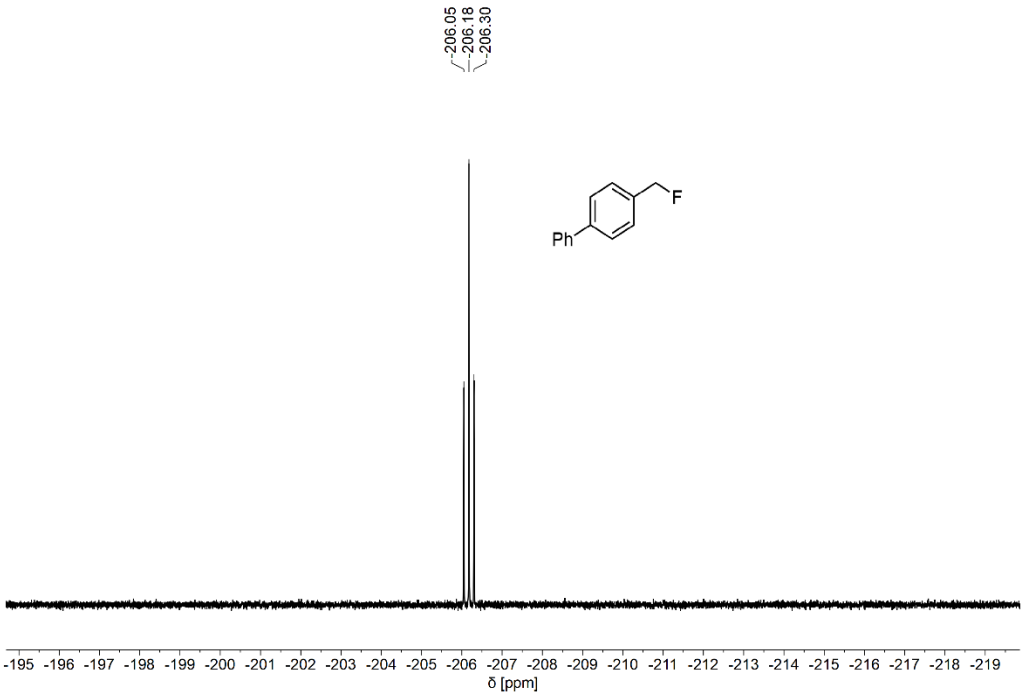


Figure S 25: ^{19}F NMR (377 MHz) spectrum of compound 4-phenylbenzyl fluoride ($CDCl_3$).

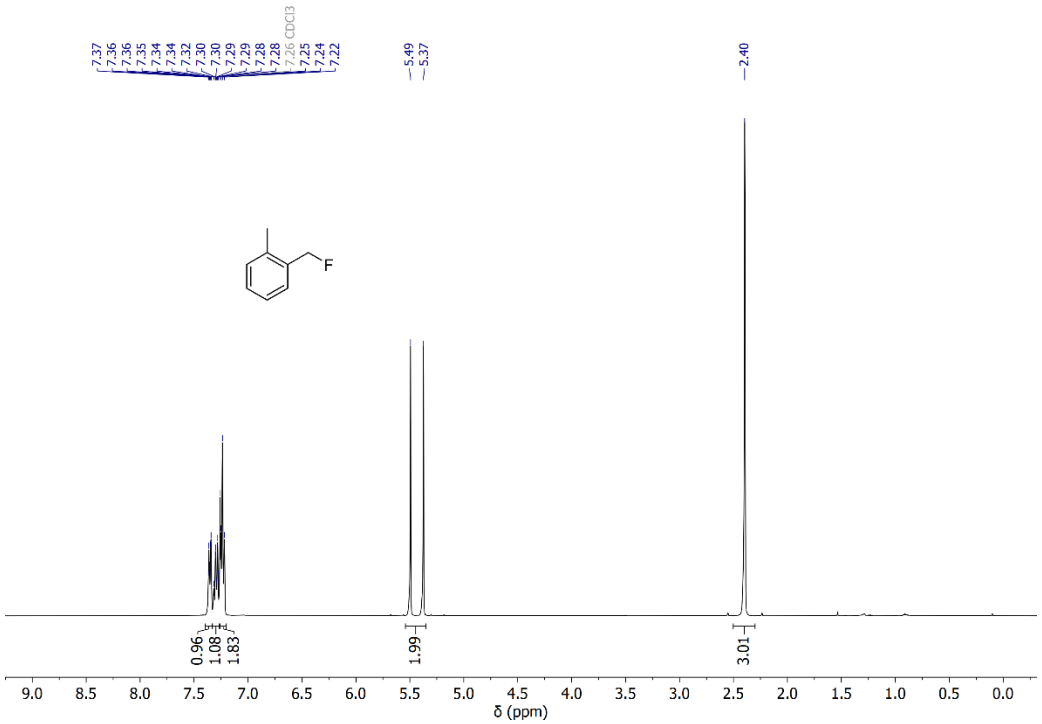


Figure S 26: ^{1}H NMR (400 MHz) spectrum of 2-methylbenzyl fluoride ($CDCl_3$).

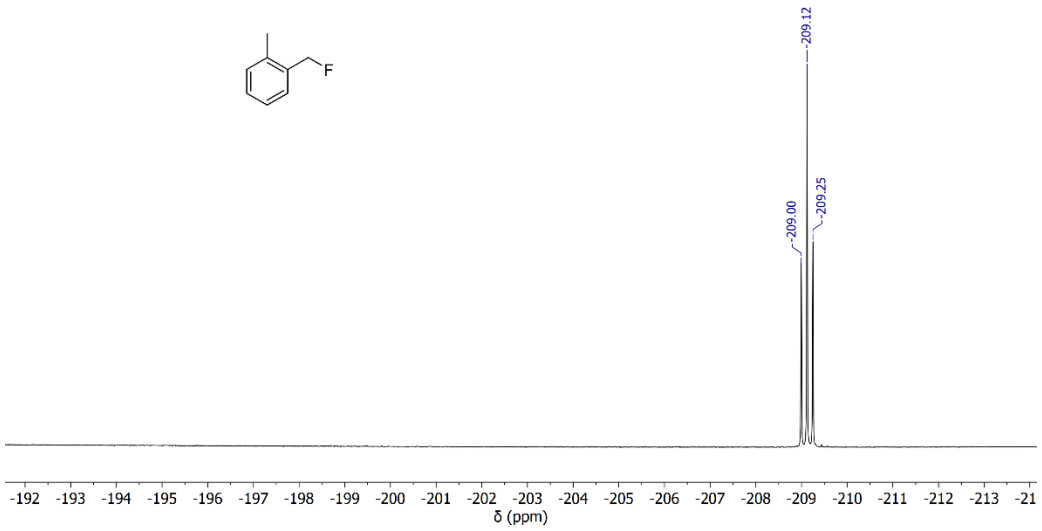


Figure S 27: ^{19}F NMR (377 MHz) spectrum of 2-methylbenzyl fluoride ($CDCl_3$).

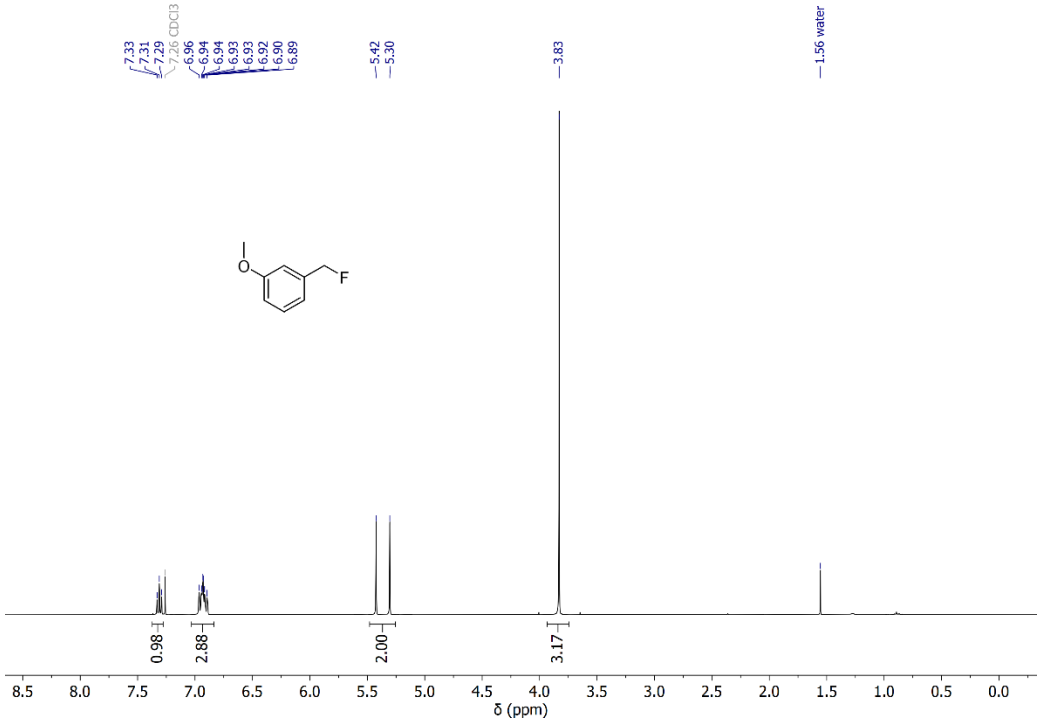


Figure S 28: ^{1}H NMR (400 MHz) spectrum of 3-methoxybenzyl fluoride ($CDCl_3$).

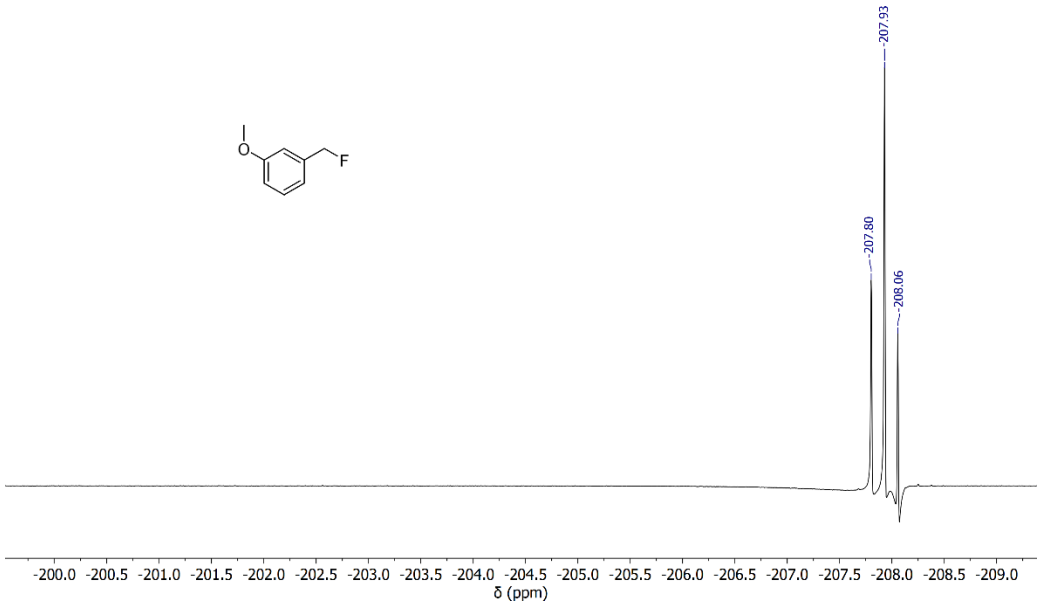


Figure S 29: ^{19}F NMR (377 MHz) spectrum of 3-methoxybenzyl fluoride ($CDCl_3$).

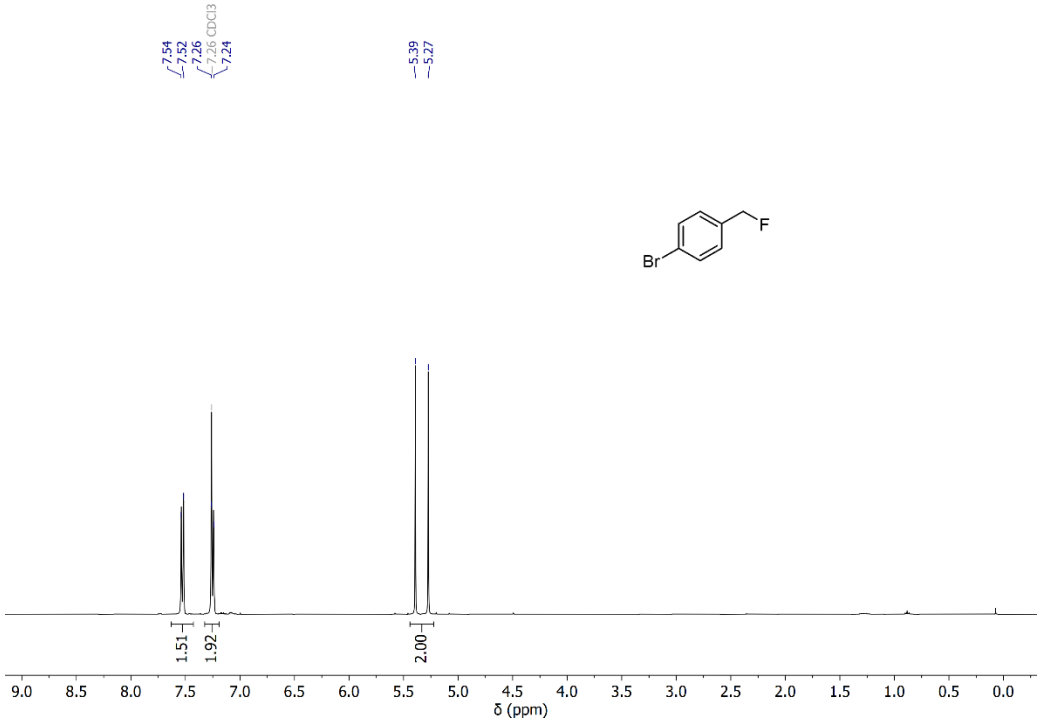


Figure S 30: ^{1}H NMR (400 MHz) spectrum of 4-bromobenzyl fluoride ($CDCl_3$).

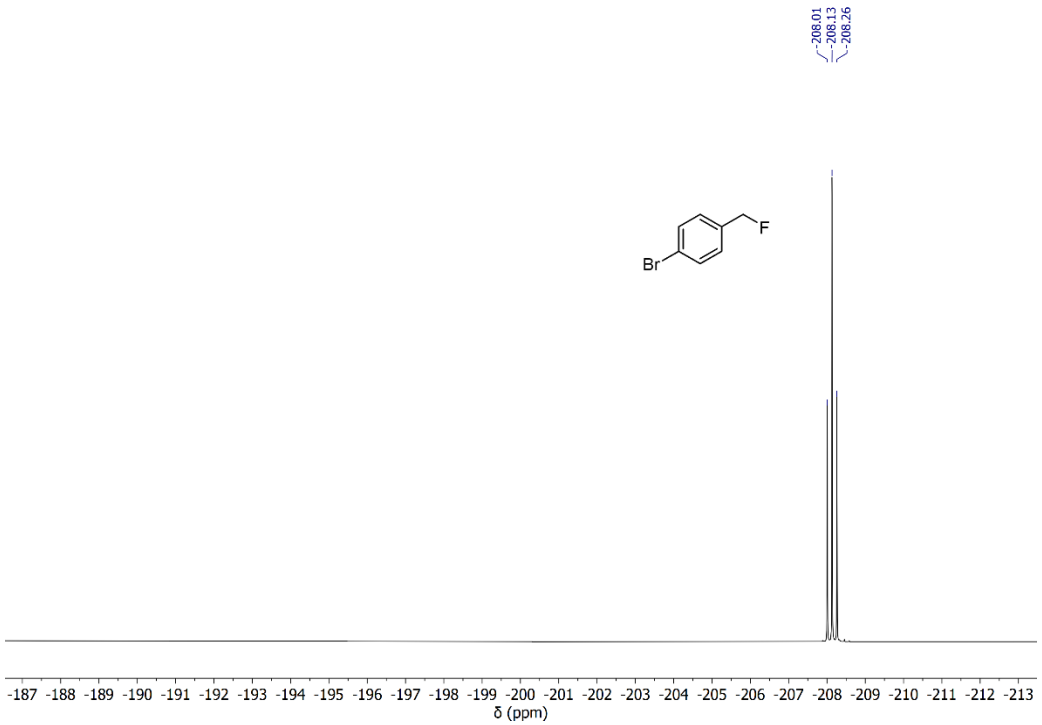


Figure S 31: ^{19}F NMR (377 MHz) spectrum of 4-bromobenzyl fluoride ($CDCl_3$).

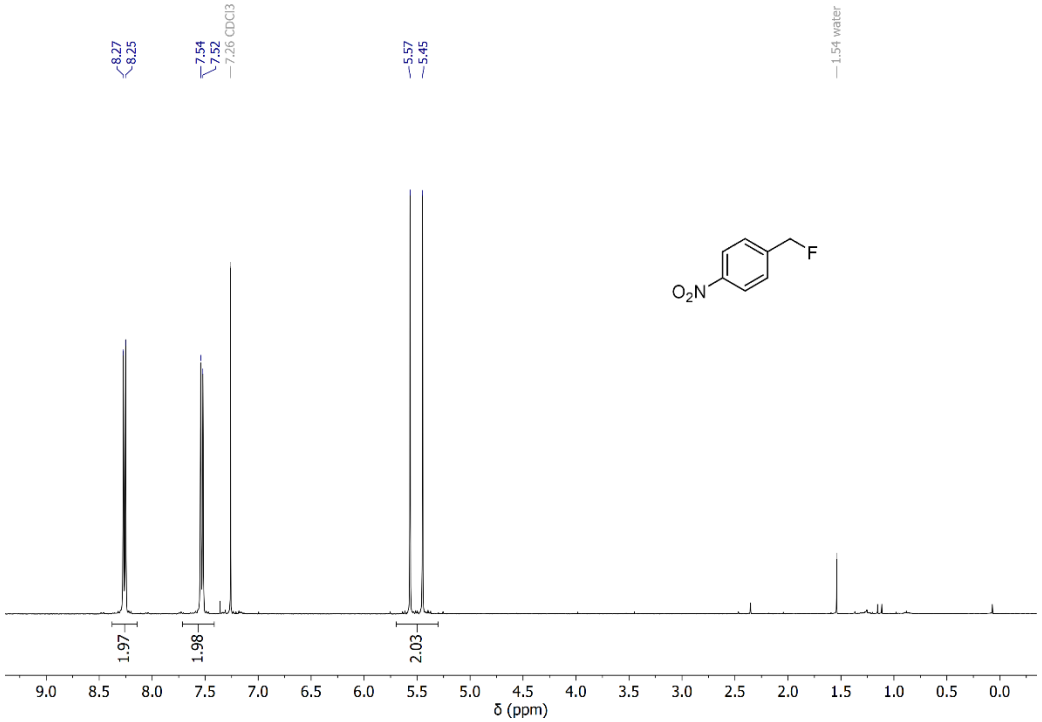


Figure S 32: ^{1}H NMR (400 MHz) spectrum of 4-nitrobenzyl fluoride ($CDCl_3$).

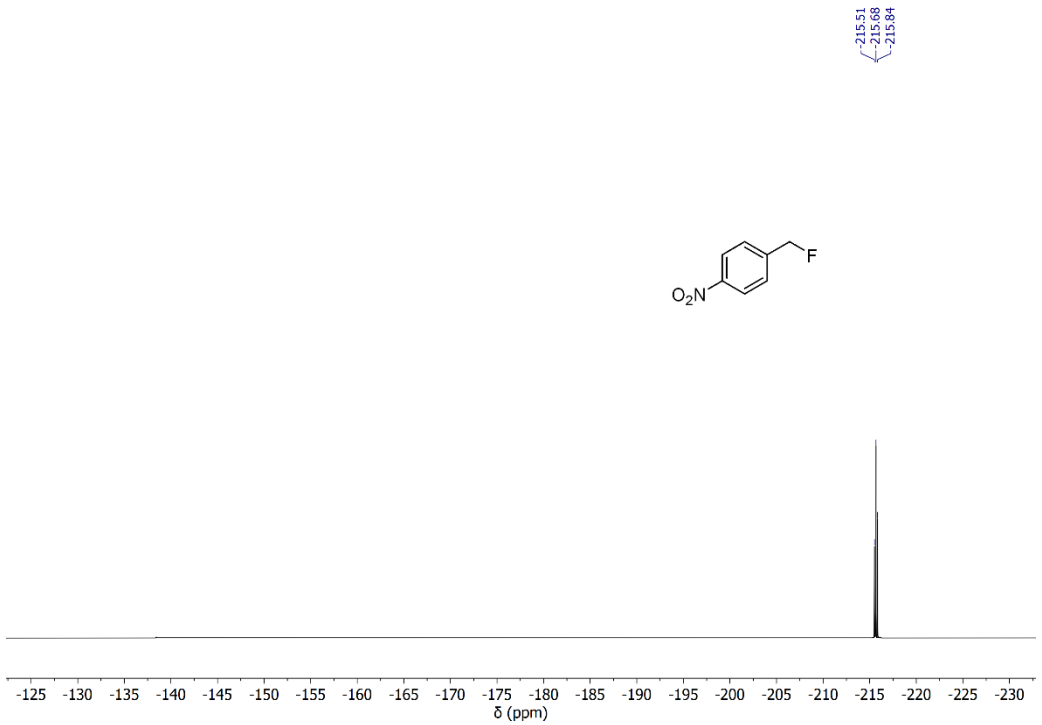


Figure S 33: ^{19}F NMR (282 MHz) spectrum of 4-nitrobenzyl fluoride ($CDCl_3$).

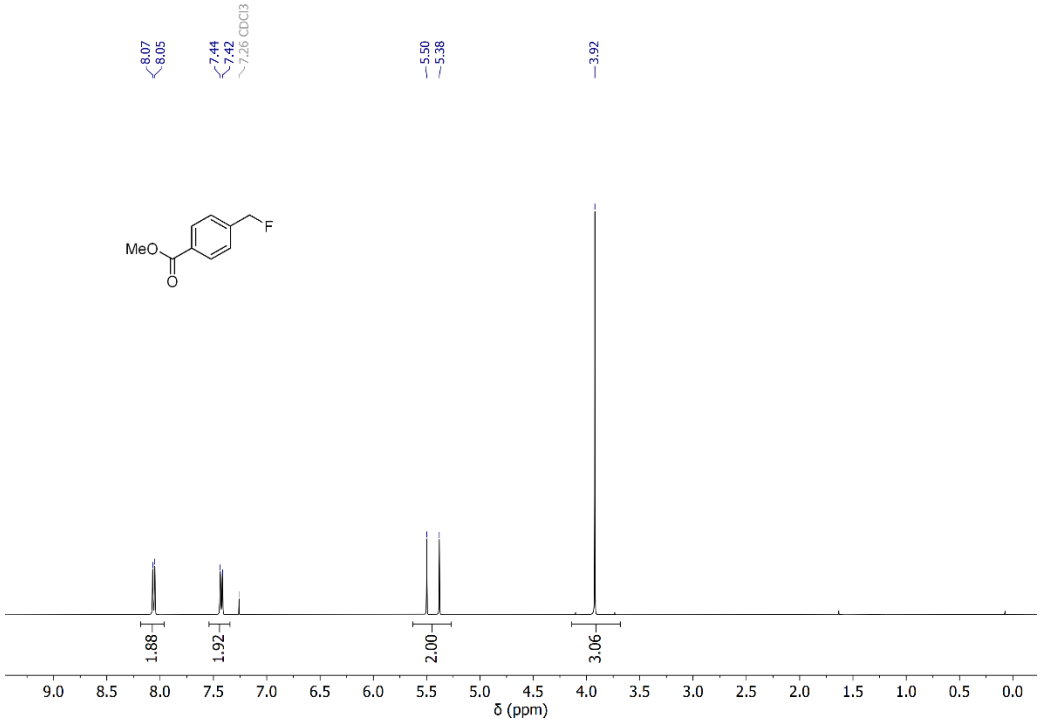


Figure S 34: ^{1}H NMR (400 MHz) spectrum of methyl 4-(fluoromethyl)benzoate ($CDCl_3$).

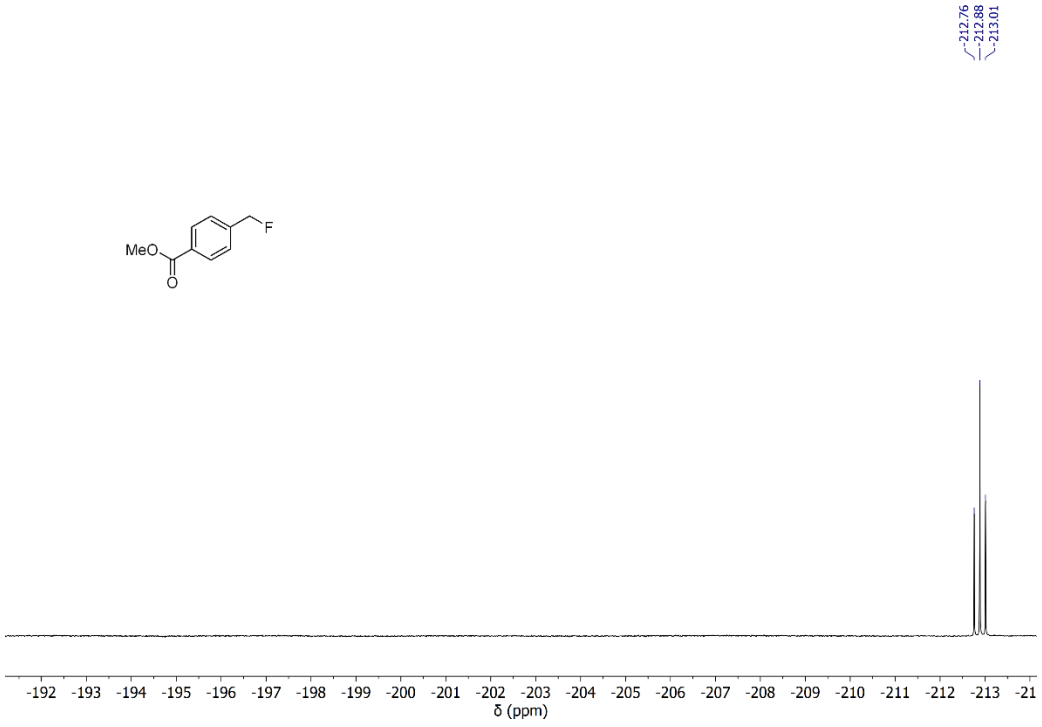


Figure S 35: ^{19}F NMR (377 MHz) spectrum of methyl 4-(fluoromethyl)benzoate ($CDCl_3$).

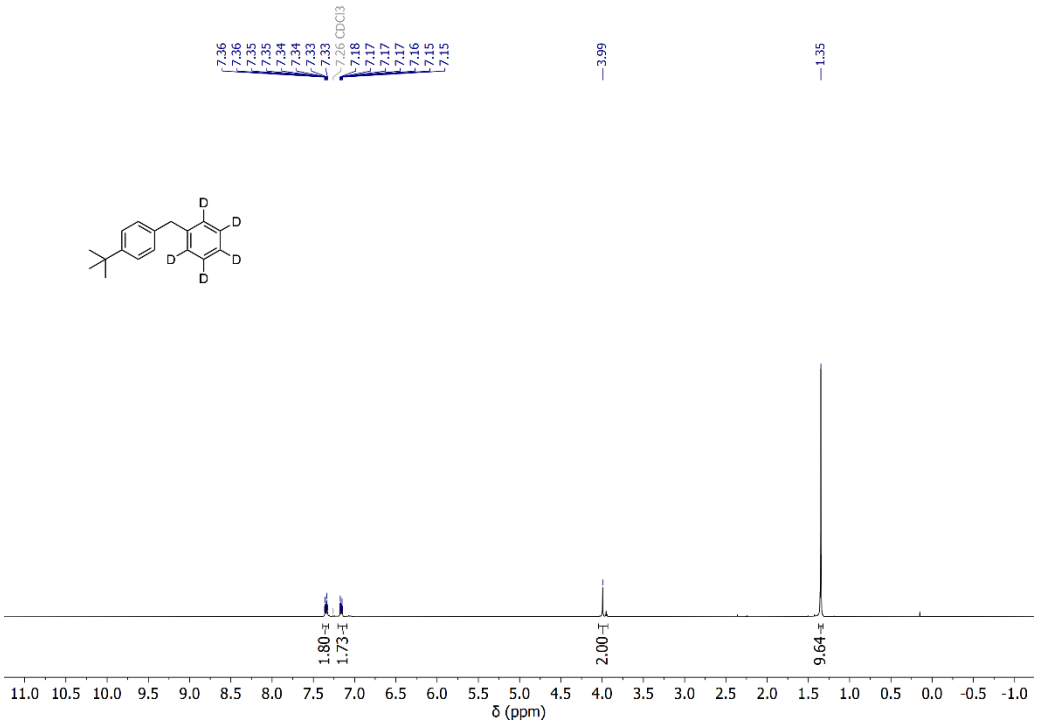


Figure S 36: ^{1}H NMR (400 MHz) spectrum of compound 1 ($CDCl_3$).

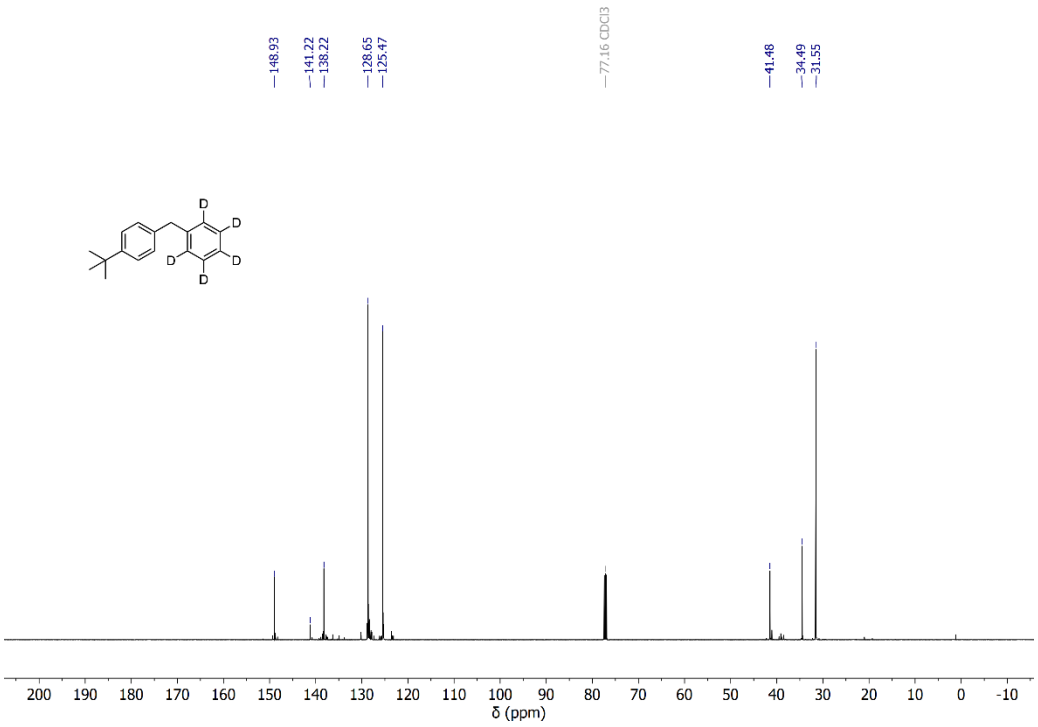


Figure S 37: $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound 1 ($CDCl_3$).

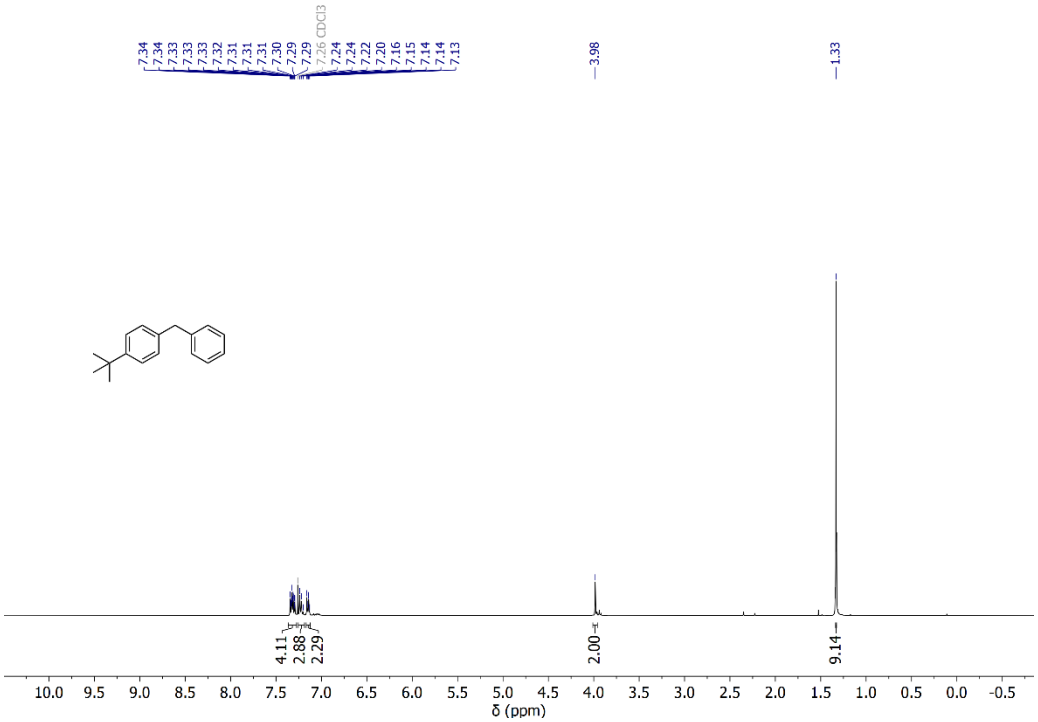


Figure S 38: ^{1}H NMR (400 MHz) spectrum of compound 2 ($CDCl_3$).

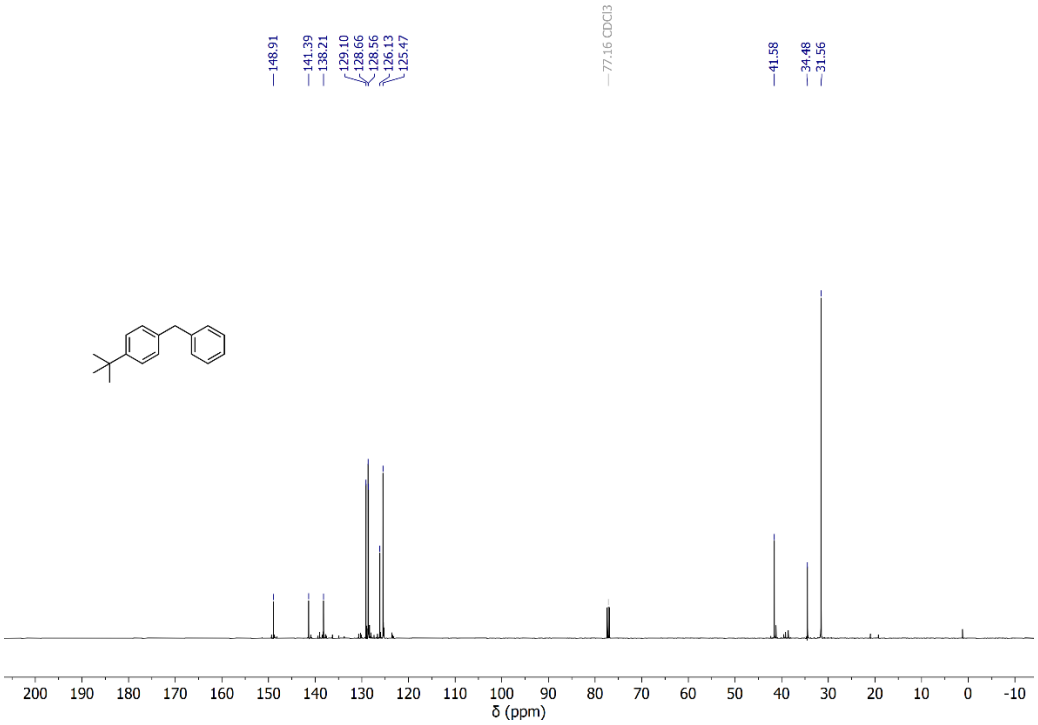


Figure S 39: $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound 2 ($CDCl_3$).

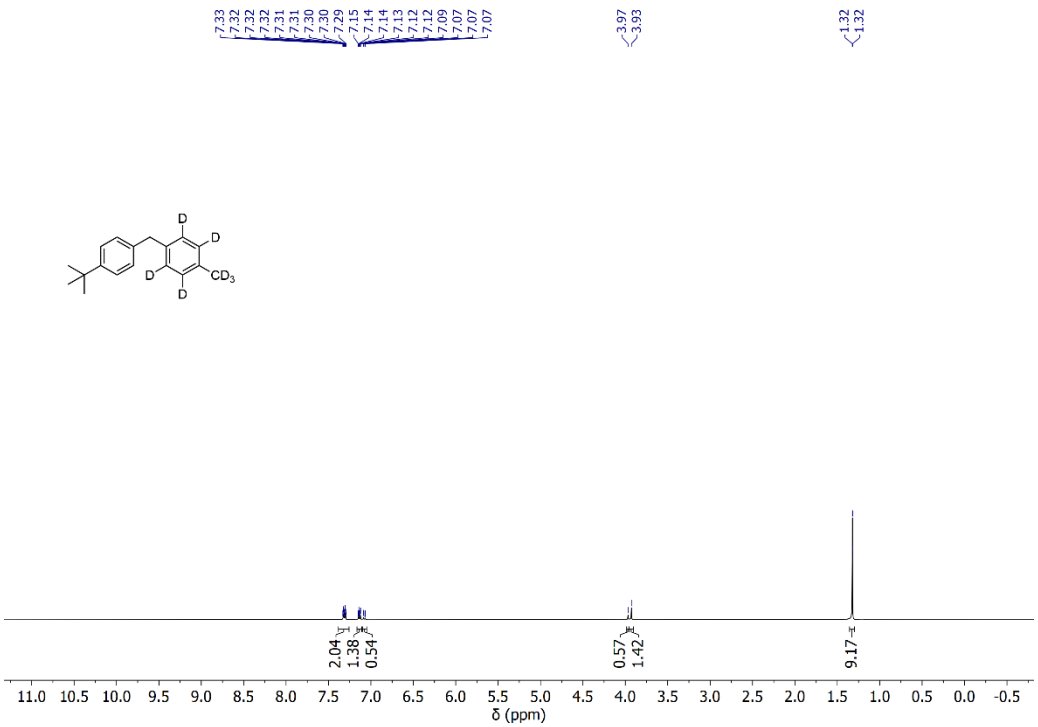


Figure S 40: ^{1}H NMR (400 MHz) spectrum of compound 3 ($CDCl_3$).

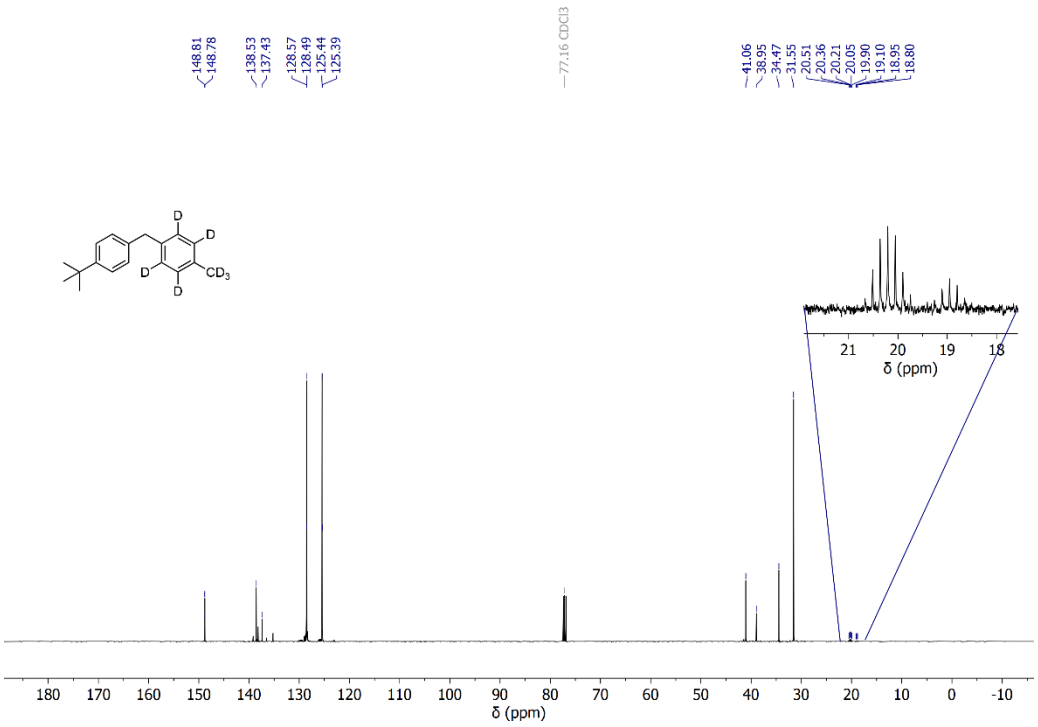


Figure S 41: ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound 3 ($CDCl_3$).

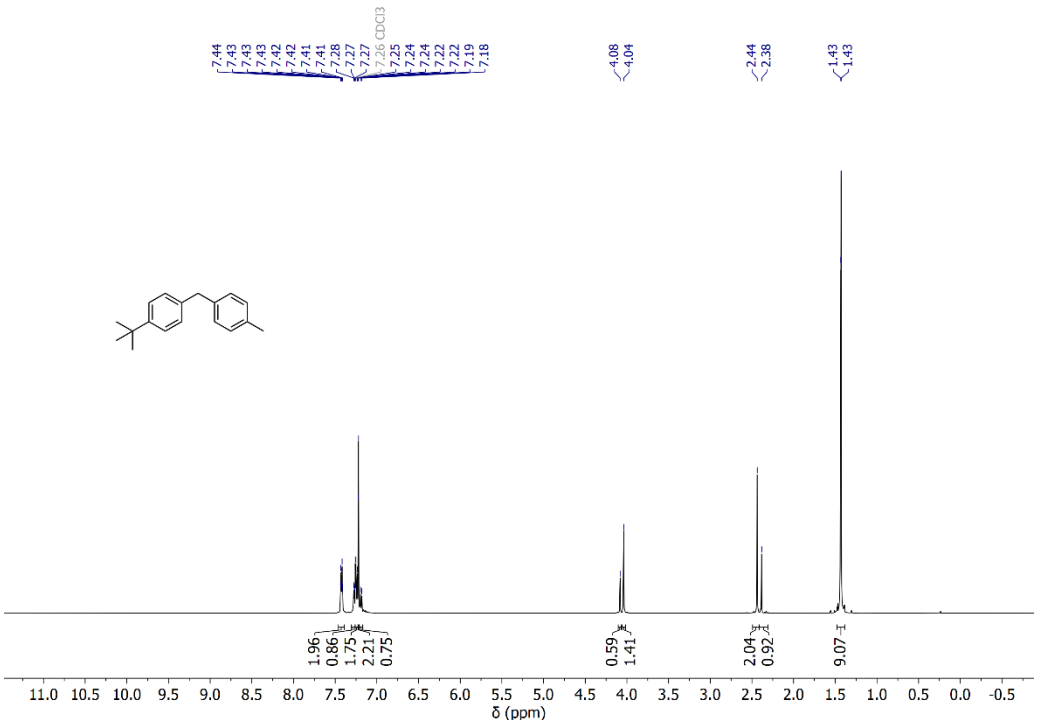


Figure S 42: ^{1}H NMR (500 MHz) spectrum of compound 4 ($CDCl_3$).

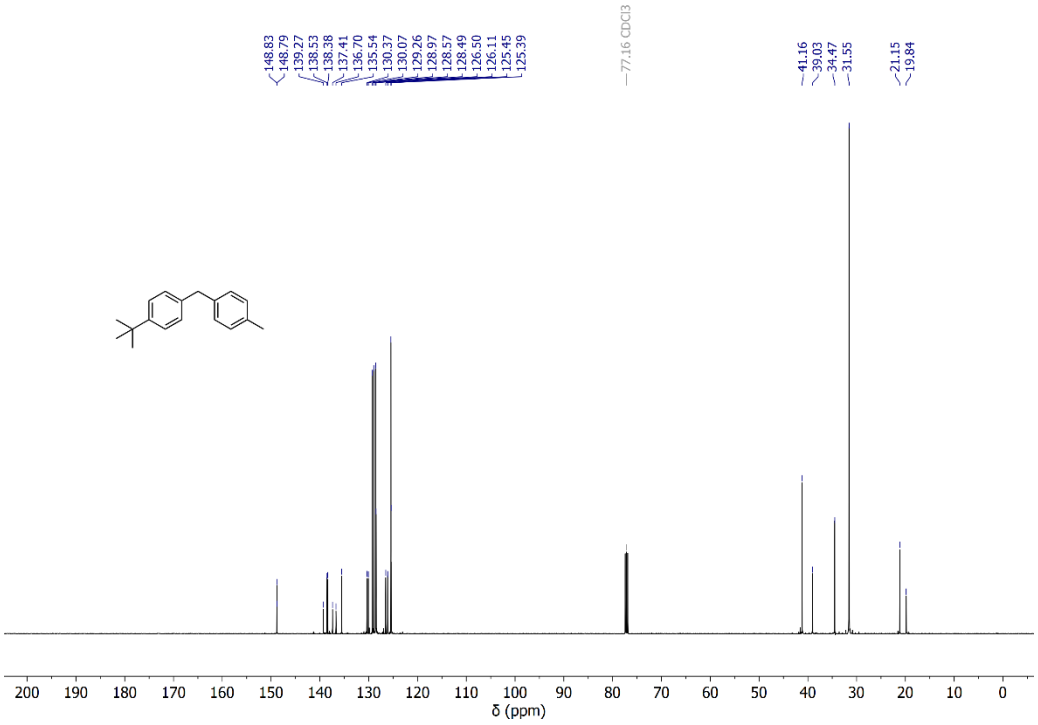


Figure S 43: ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound 4 ($CDCl_3$).

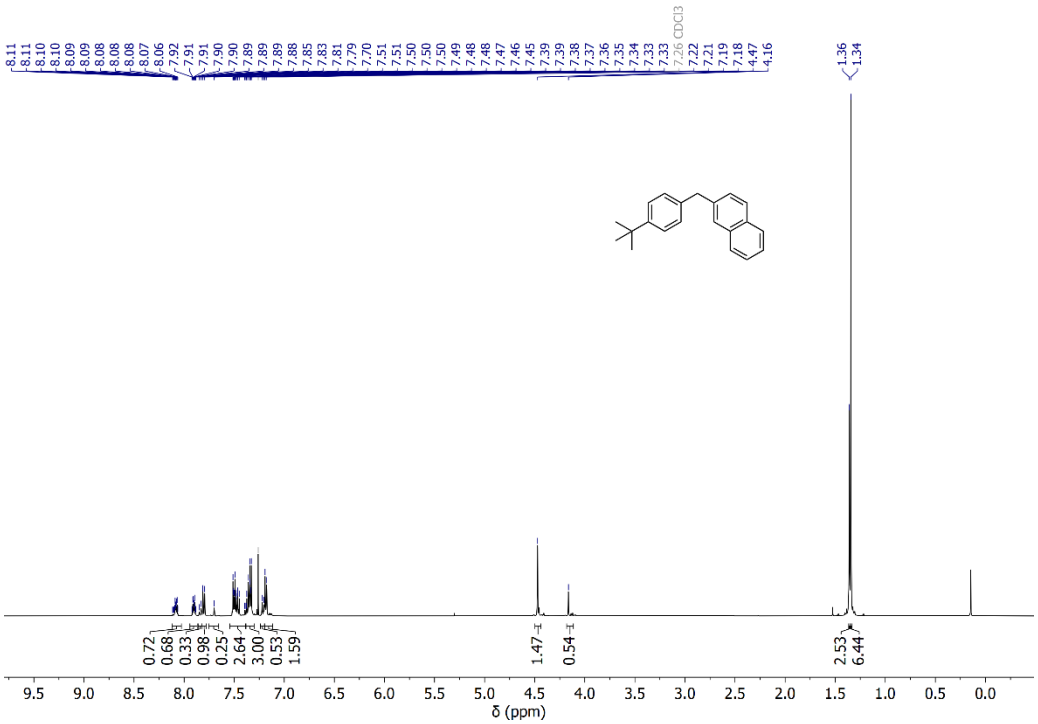


Figure S 44: ^{1}H NMR (500 MHz) spectrum of compound 5 ($CDCl_3$).

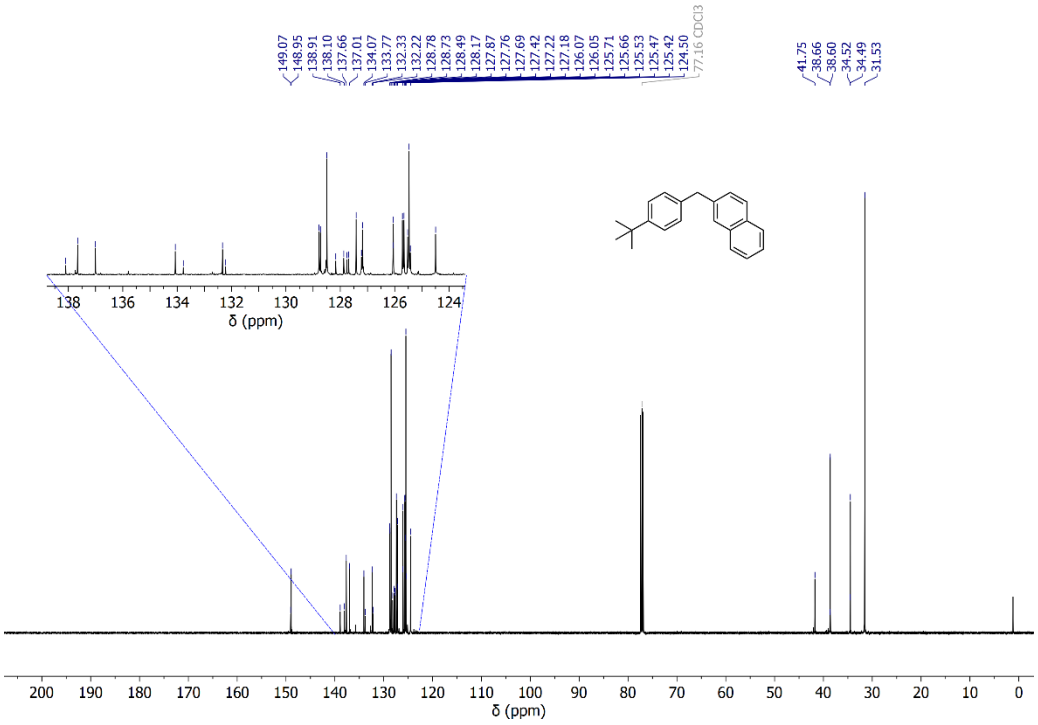


Figure S 45: $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound 5 ($CDCl_3$).

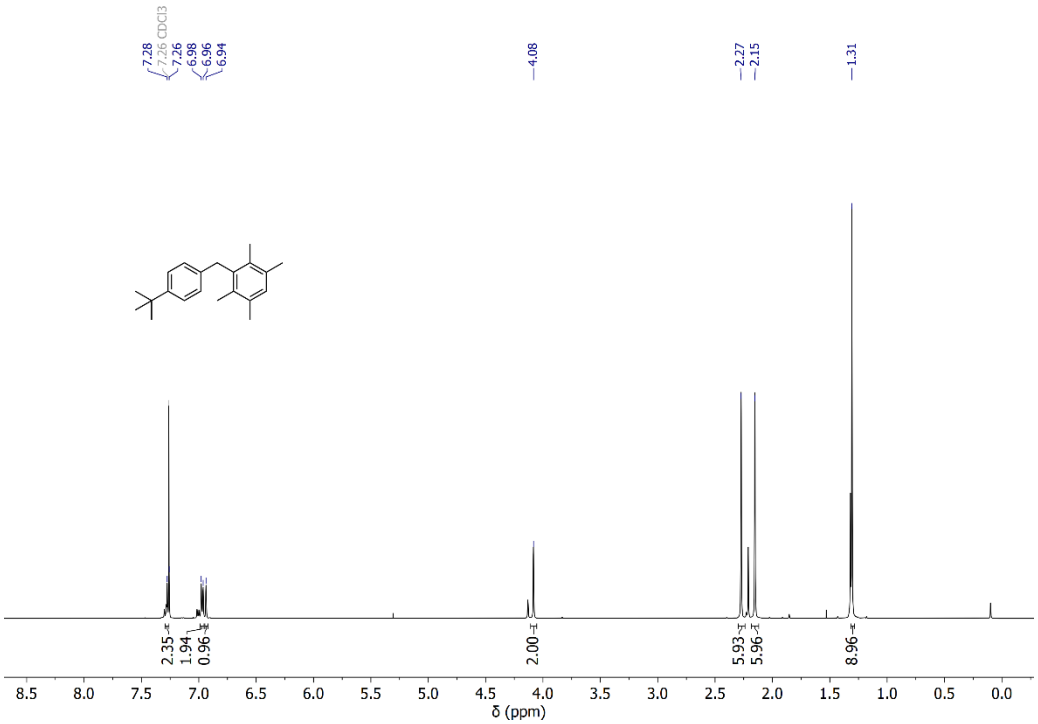


Figure S 46: ^{1}H NMR (500 MHz) spectrum of compound 6 ($CDCl_3$).

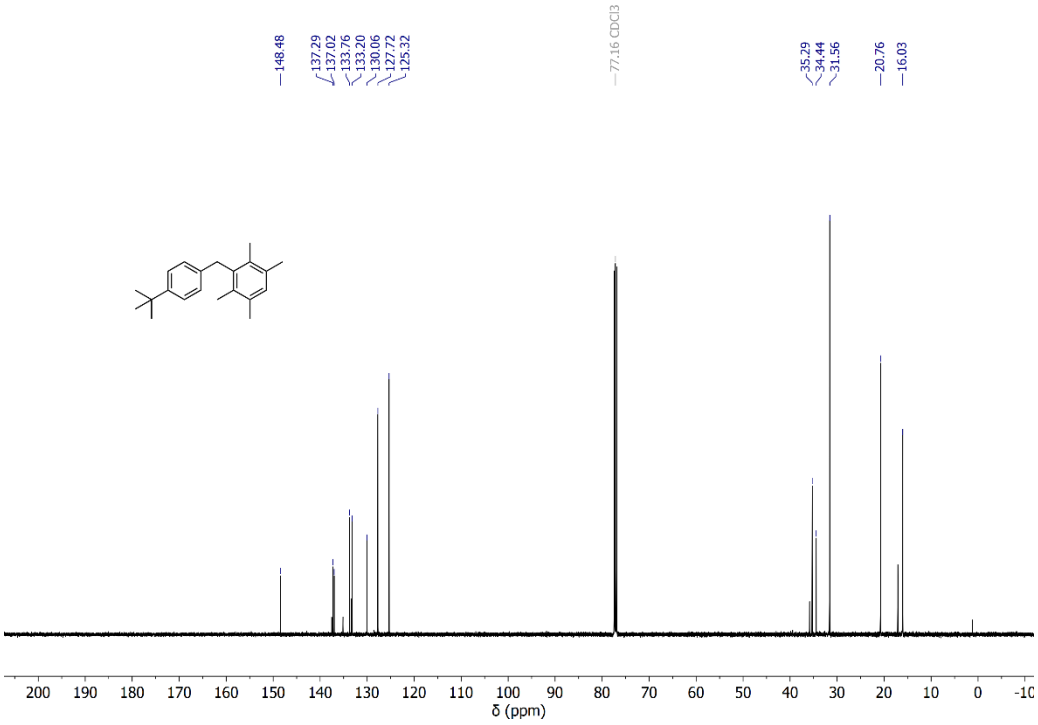


Figure S 47: $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound 6 ($CDCl_3$).

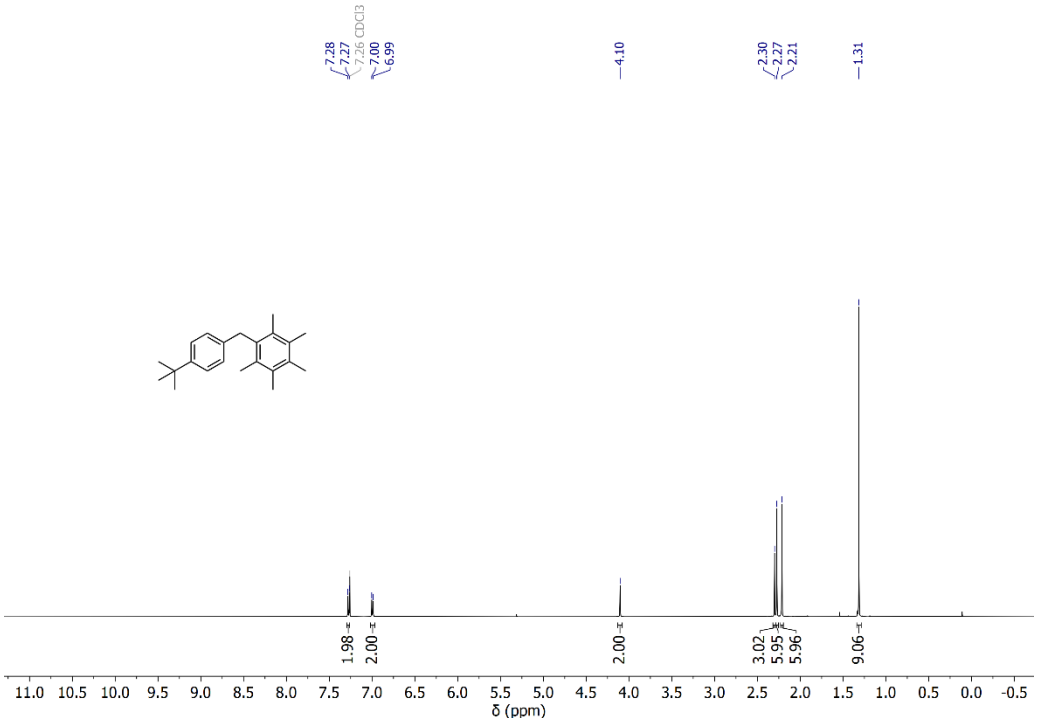


Figure S 48: ^{1}H NMR (500 MHz) spectrum of compound 7 ($CDCl_3$).

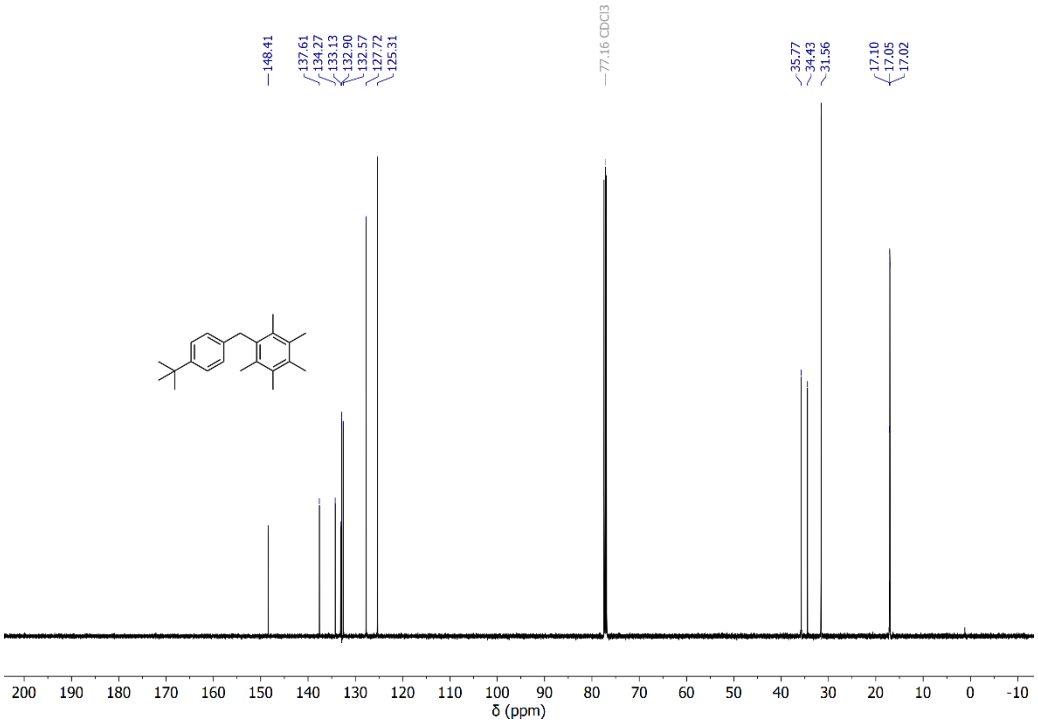


Figure S 49: $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound 7 ($CDCl_3$).

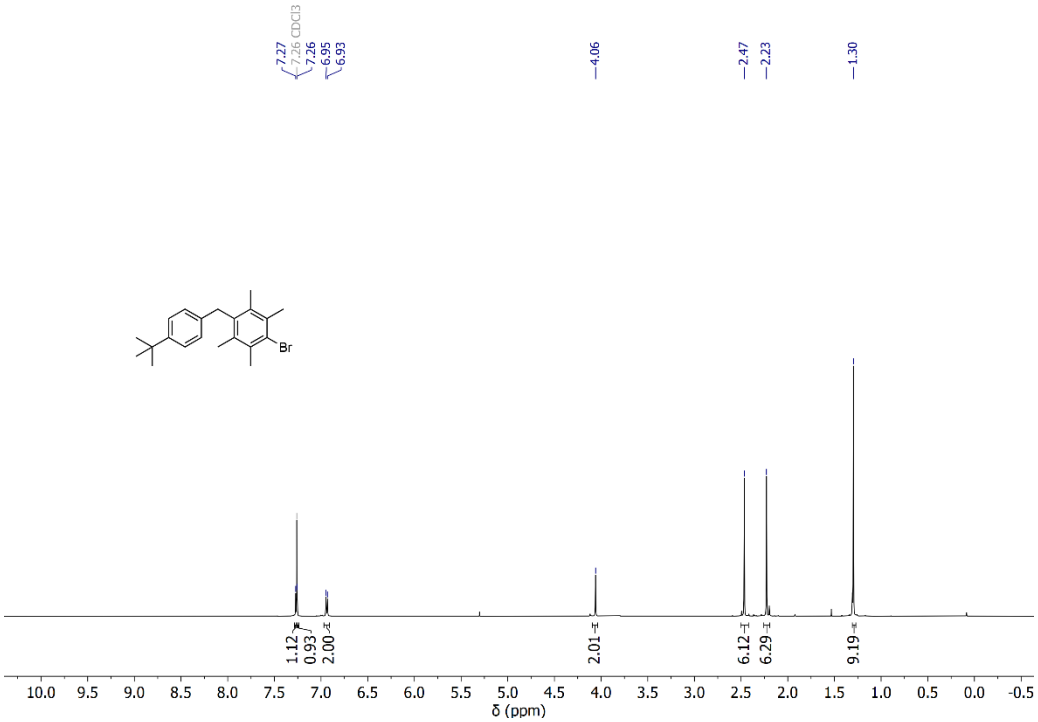


Figure S 50: ^{1}H NMR (500 MHz) spectrum of compound 8 ($CDCl_3$).

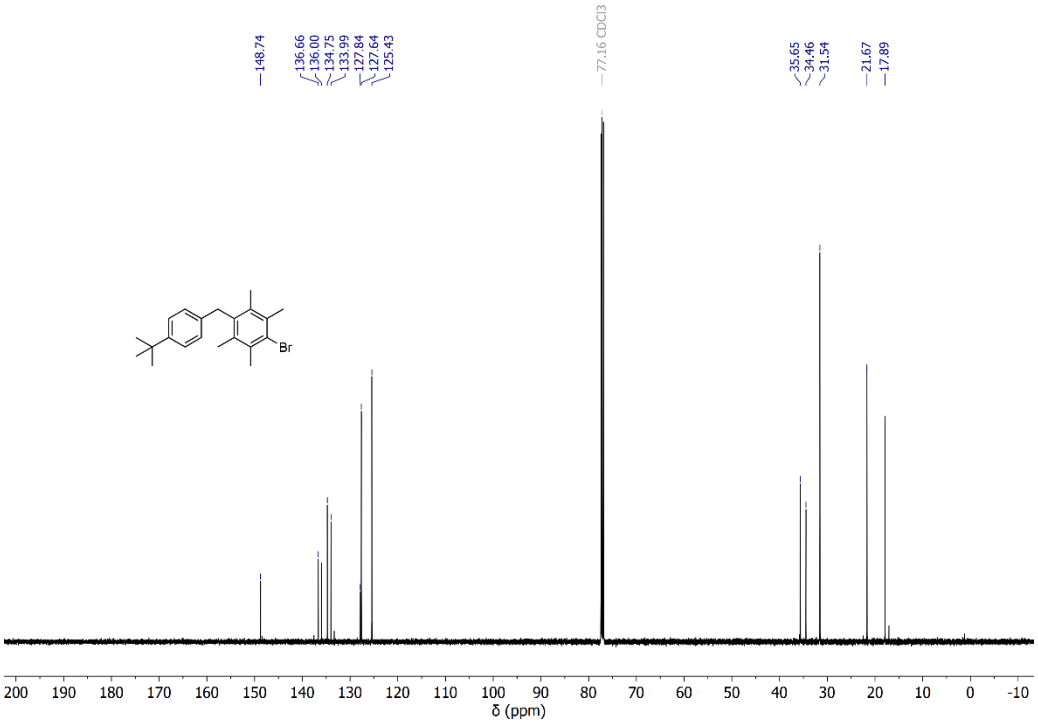


Figure S 51: $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound 8 ($CDCl_3$).

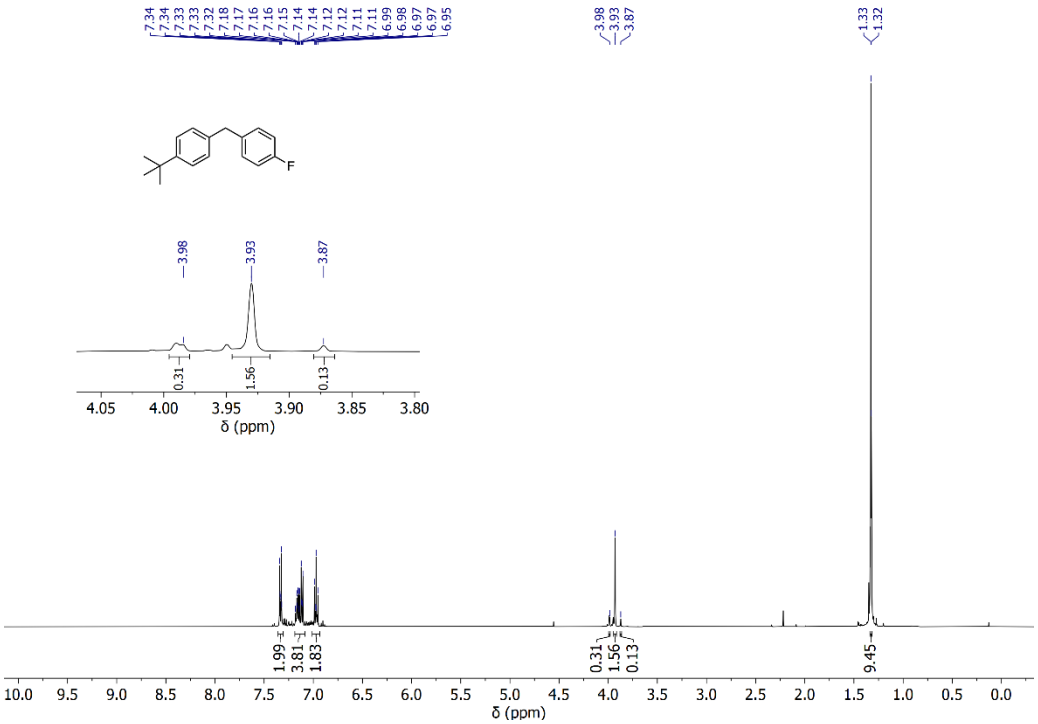


Figure S 52: ^{1}H NMR (500 MHz) spectrum of compound 9 ($CDCl_3$).

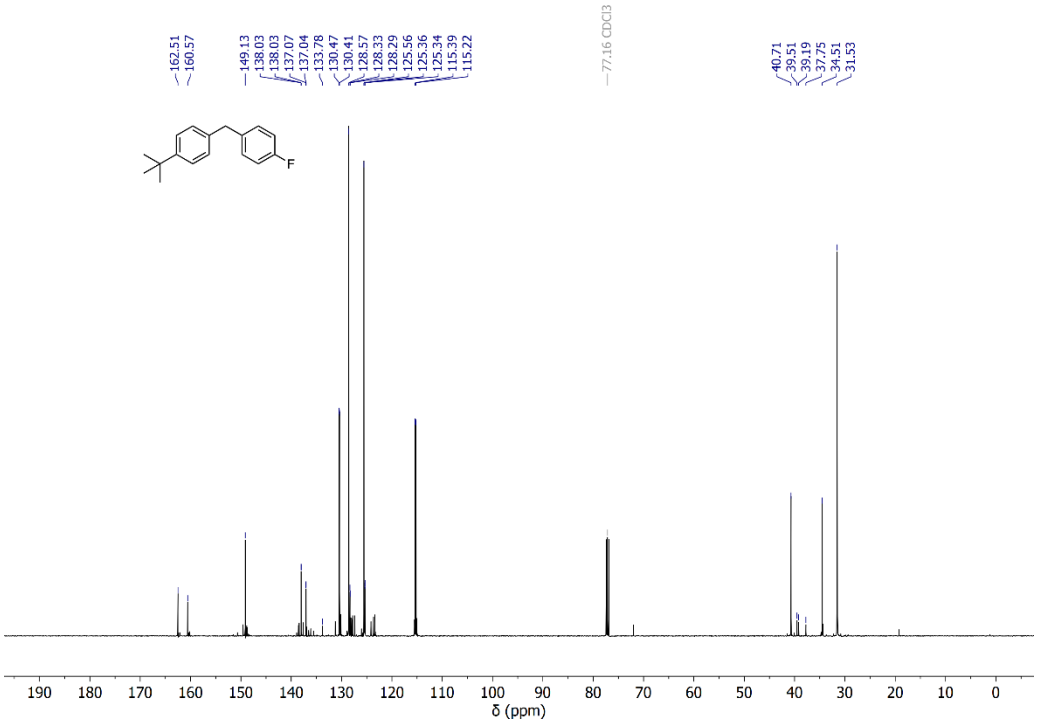


Figure S 53: $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound 9 ($CDCl_3$).

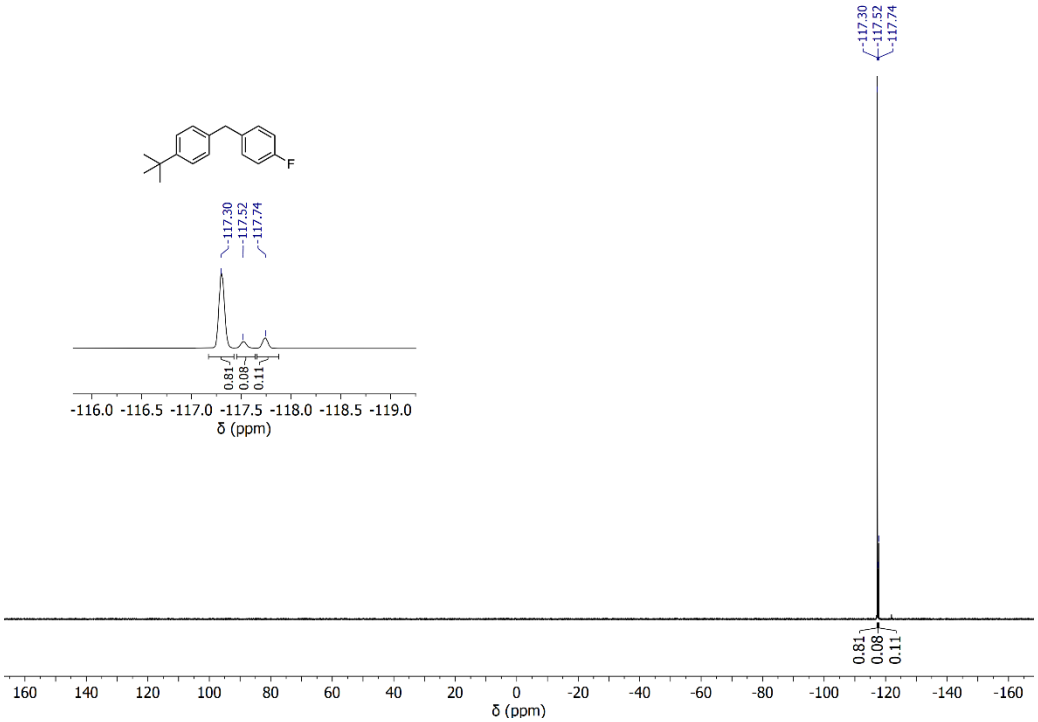


Figure S 54: ^{19}F NMR (377 MHz) spectrum of compound 9 ($CDCl_3$).

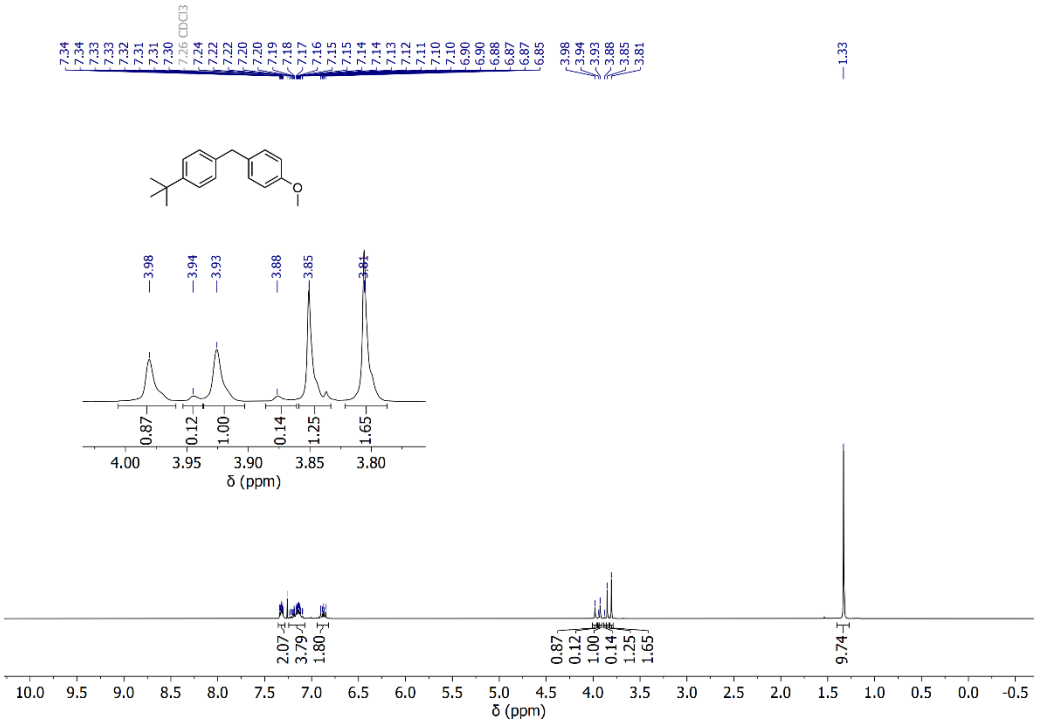


Figure S 55: ^{1}H NMR (400 MHz) spectrum of compound 10 ($CDCl_3$).

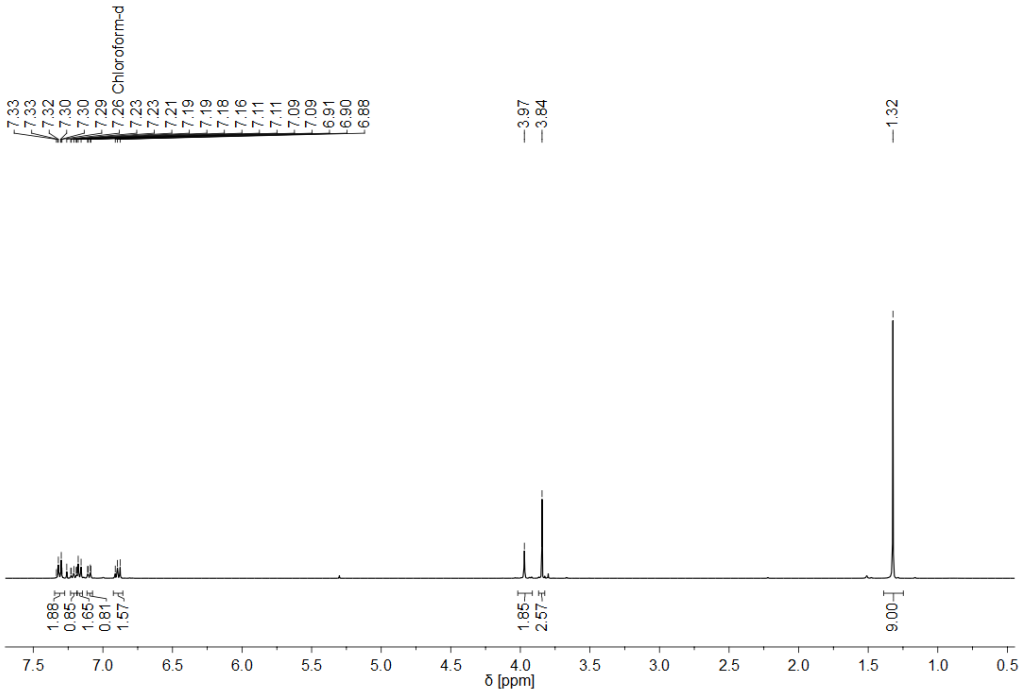


Figure S 56: ^{1}H NMR (400 MHz) spectrum of a pure fraction of 1-(4-(*tert*-butyl)benzyl)-2-methoxybenzene ($CDCl_3$).

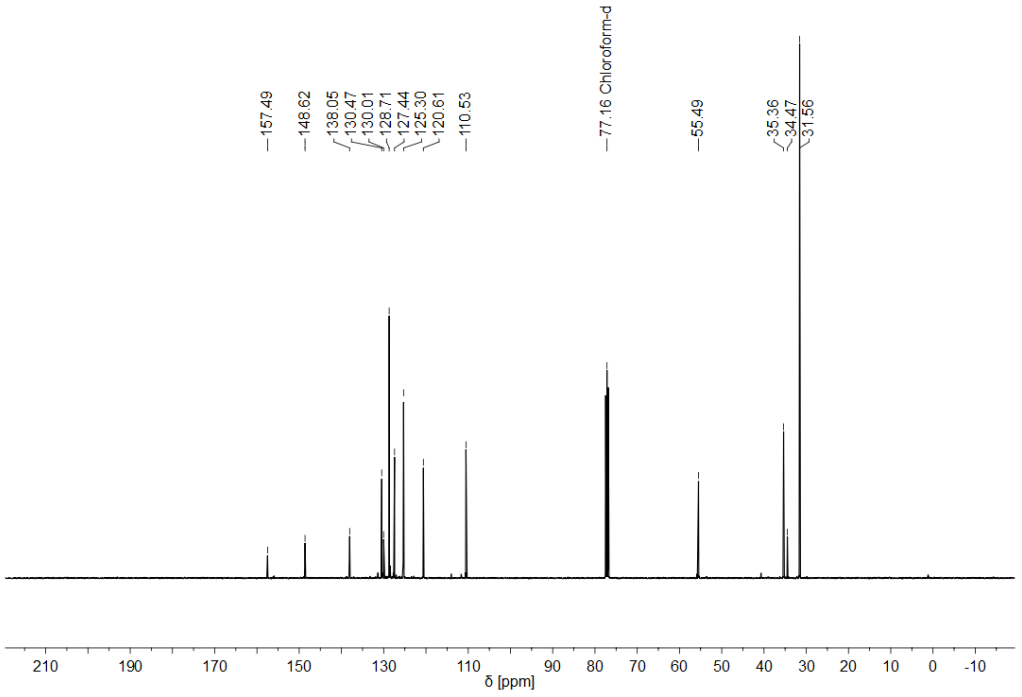


Figure S 57: $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of a pure fraction of 1-(4-(*tert*-butyl)benzyl)-2-methoxybenzene ($CDCl_3$).

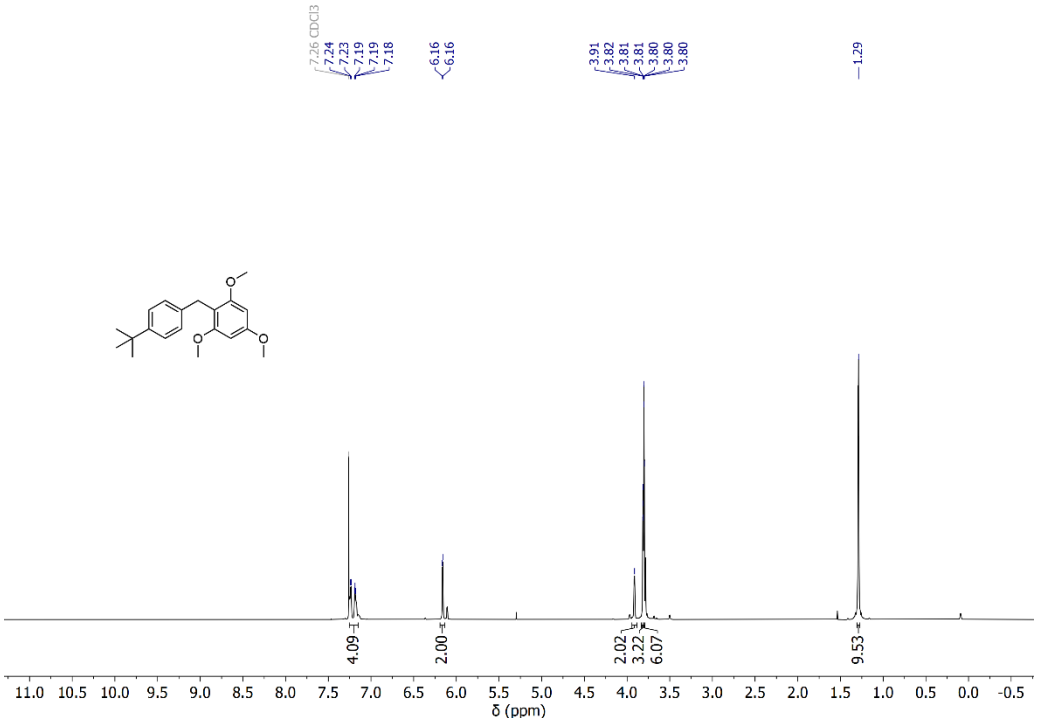


Figure S 58: ^{1}H NMR (500 MHz) spectrum of compound 11 ($CDCl_3$).

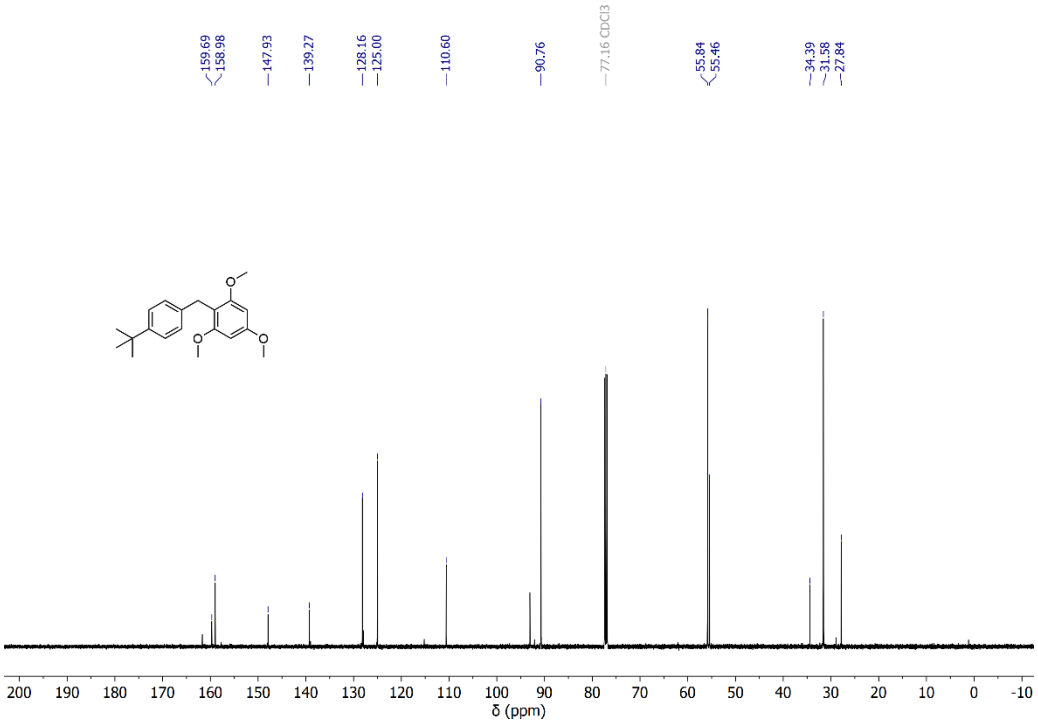


Figure S 59: $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound 11 ($CDCl_3$).

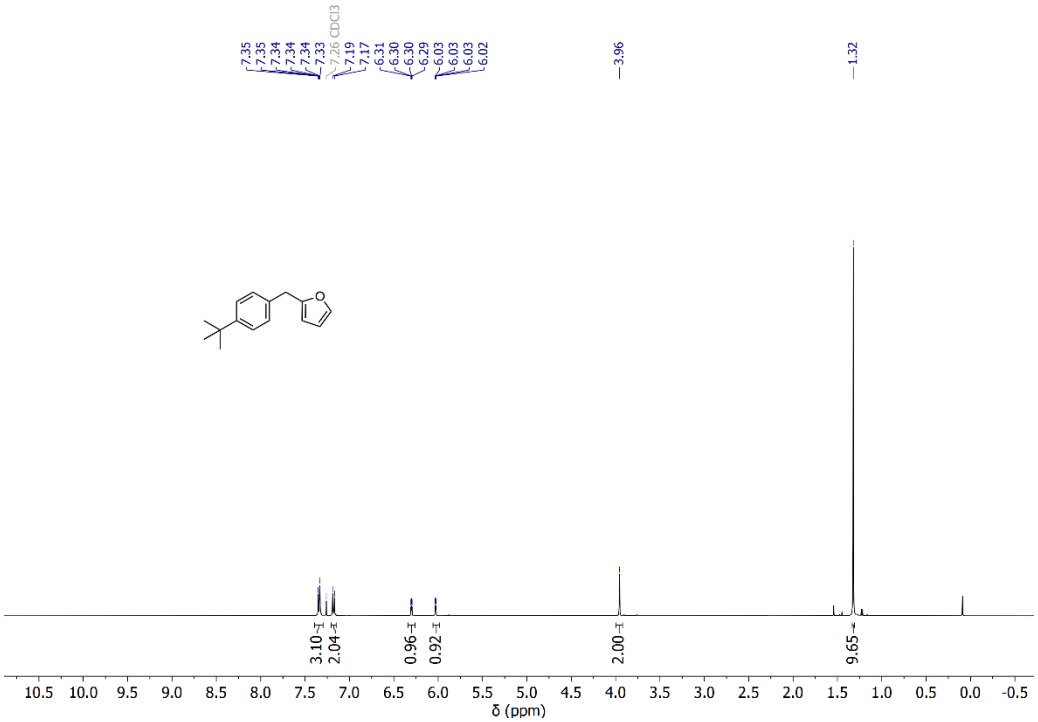


Figure S 60: ^{1}H NMR (400 MHz) spectrum of compound 12 ($CDCl_3$).

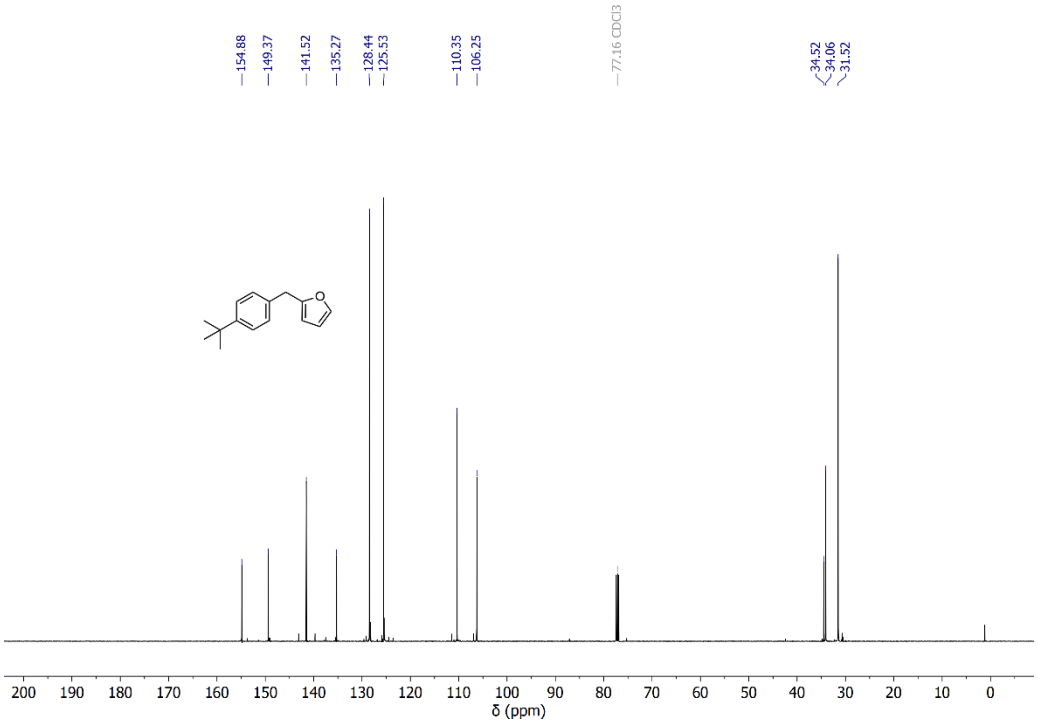


Figure S 61: $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound 12 ($CDCl_3$).

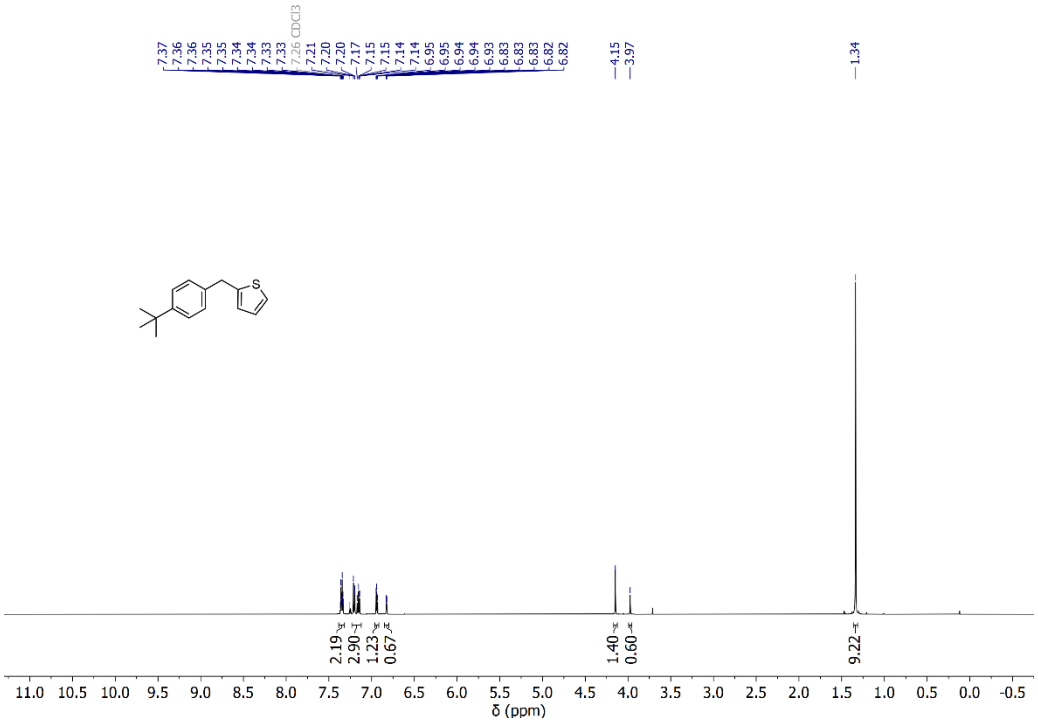


Figure S 62: ^{1}H NMR (500 MHz) spectrum of compound 13 ($CDCl_3$).

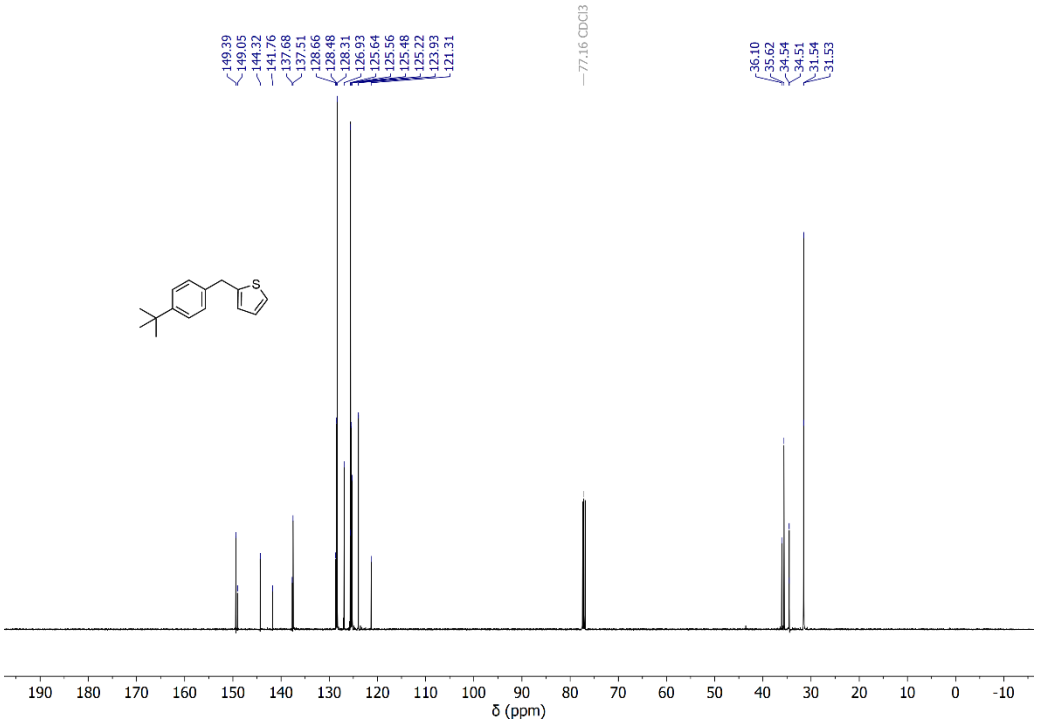


Figure S 63: ^{13}C{^{1}H} NMR (126 MHz) spectrum of compound 13 ($CDCl_3$).

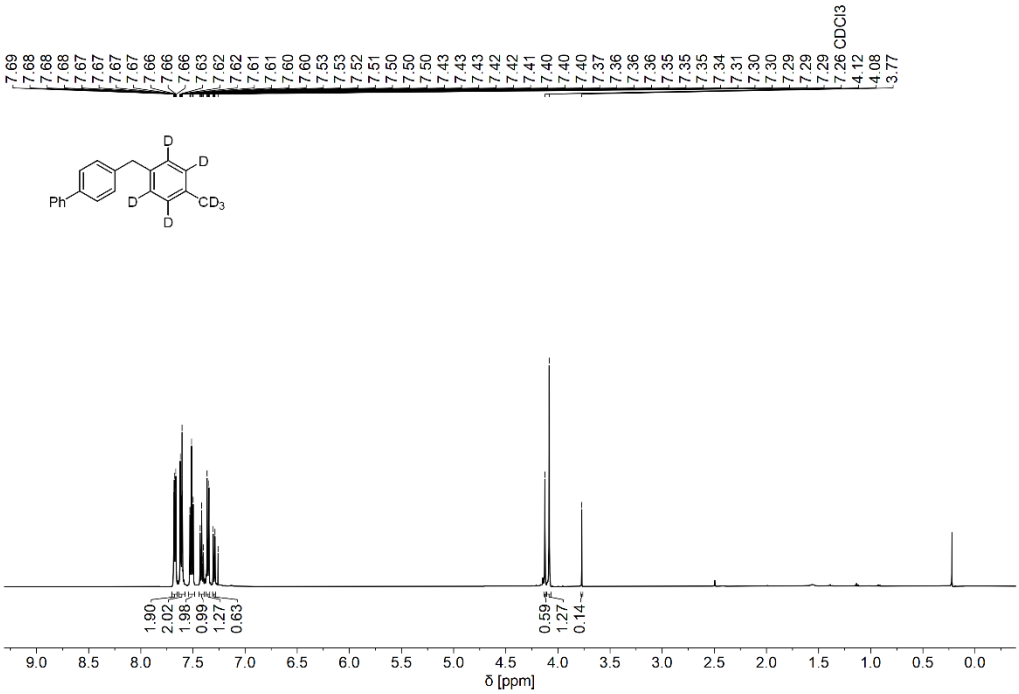


Figure S 64: ^{1}H NMR (500 MHz) spectrum of compound 14 ($CDCl_3$).

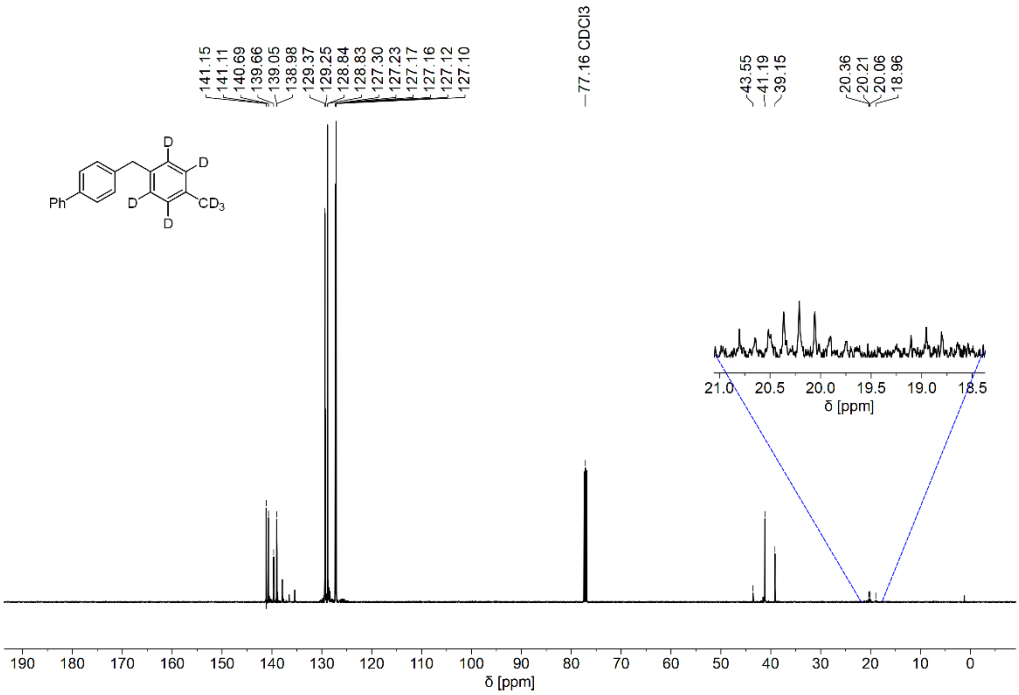


Figure S 65: $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound 14 ($CDCl_3$).

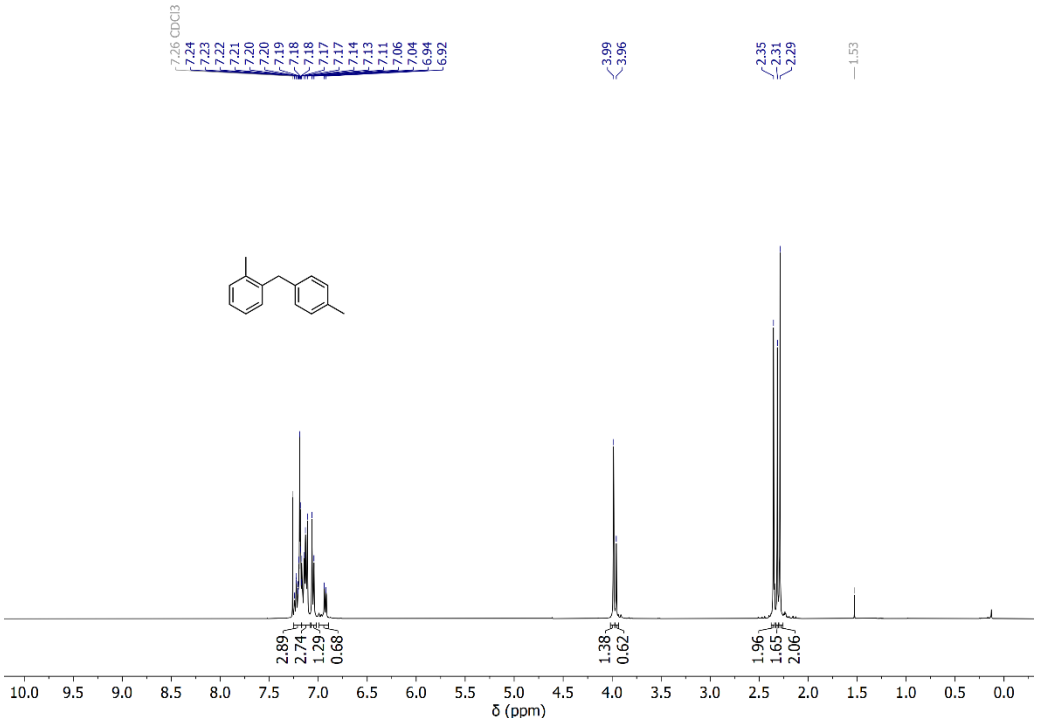


Figure S 66: ^{1}H NMR (400 MHz) spectrum of compound 15 ($CDCl_3$).

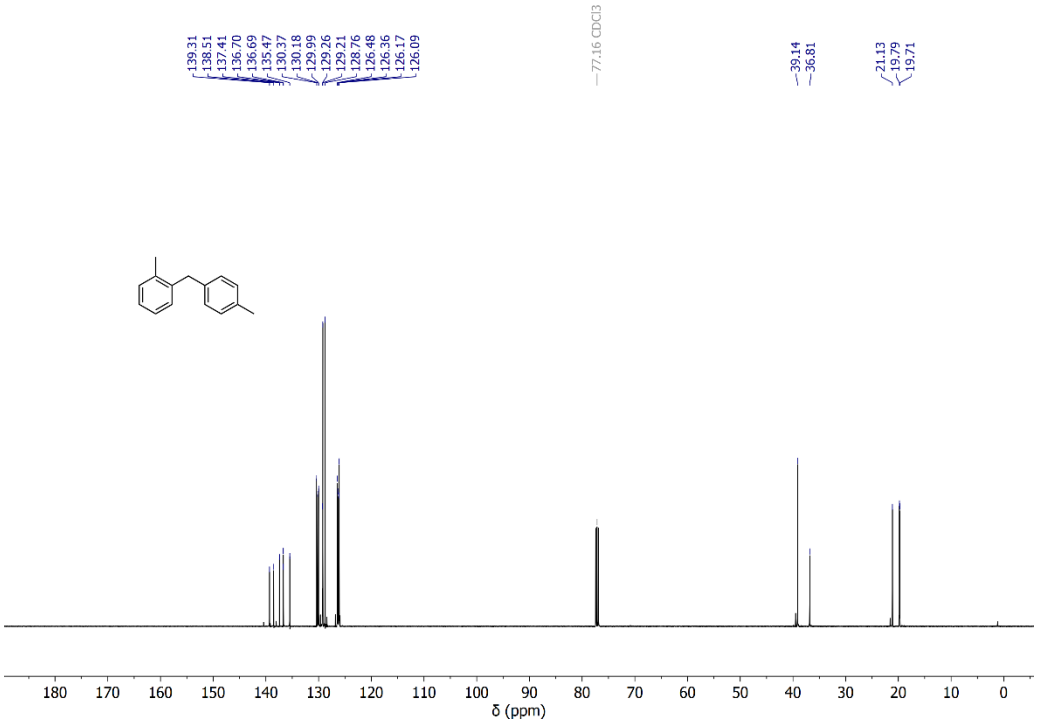


Figure S 67: $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of compound 15 ($CDCl_3$).

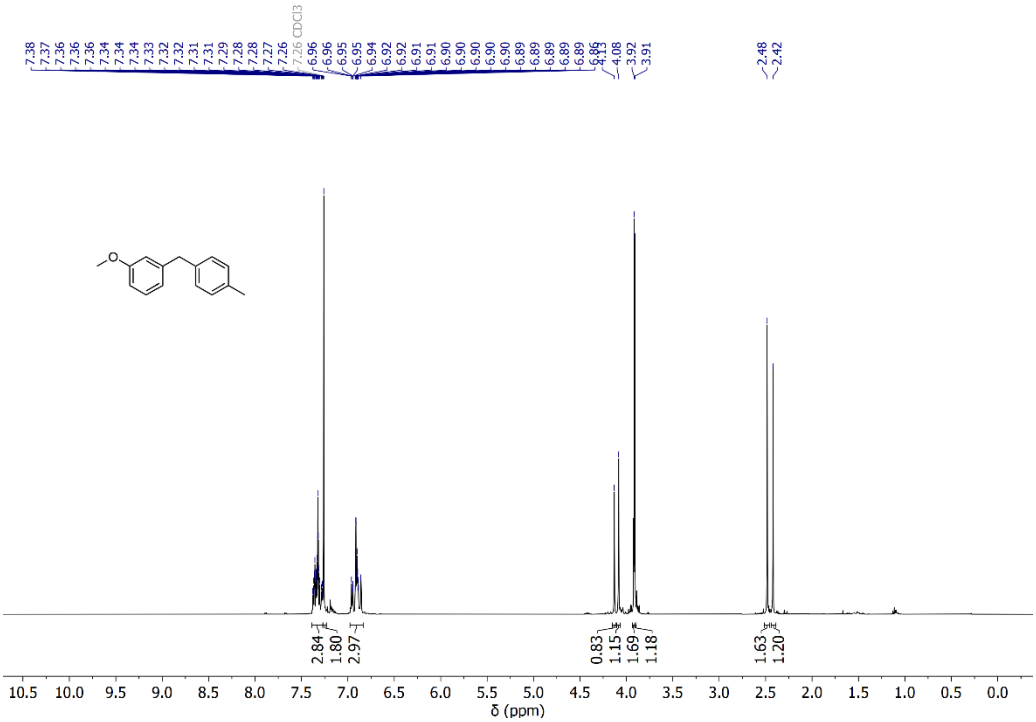


Figure S 68: ^{1}H NMR (500 MHz) spectrum of compound 16 ($CDCl_3$).

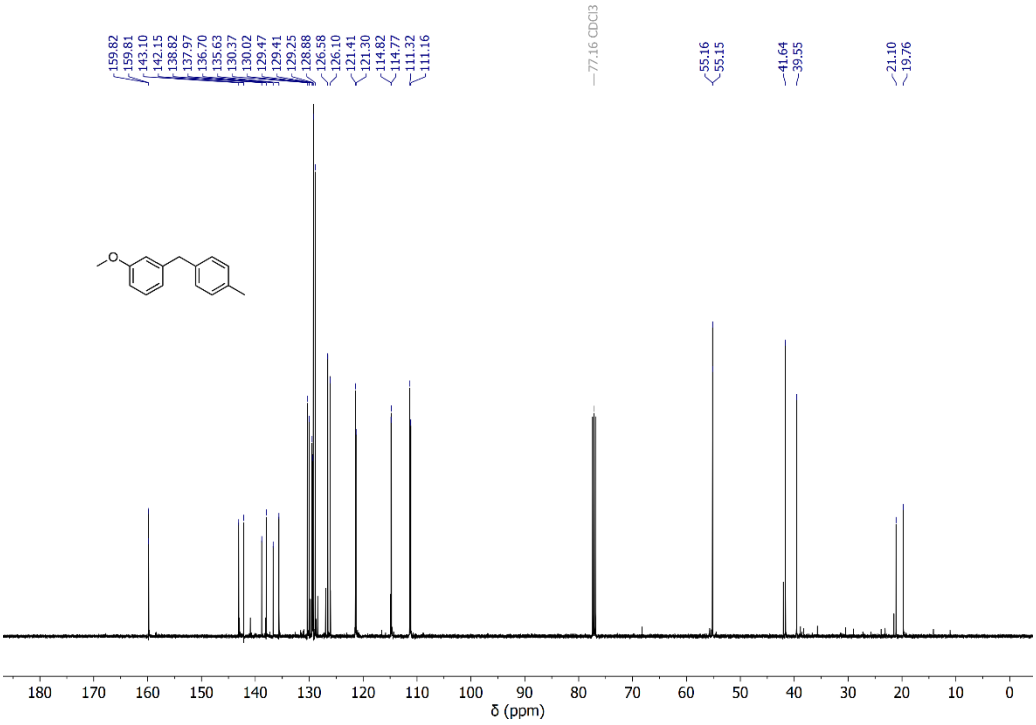


Figure S 69: $^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of compound 16 ($CDCl_3$).

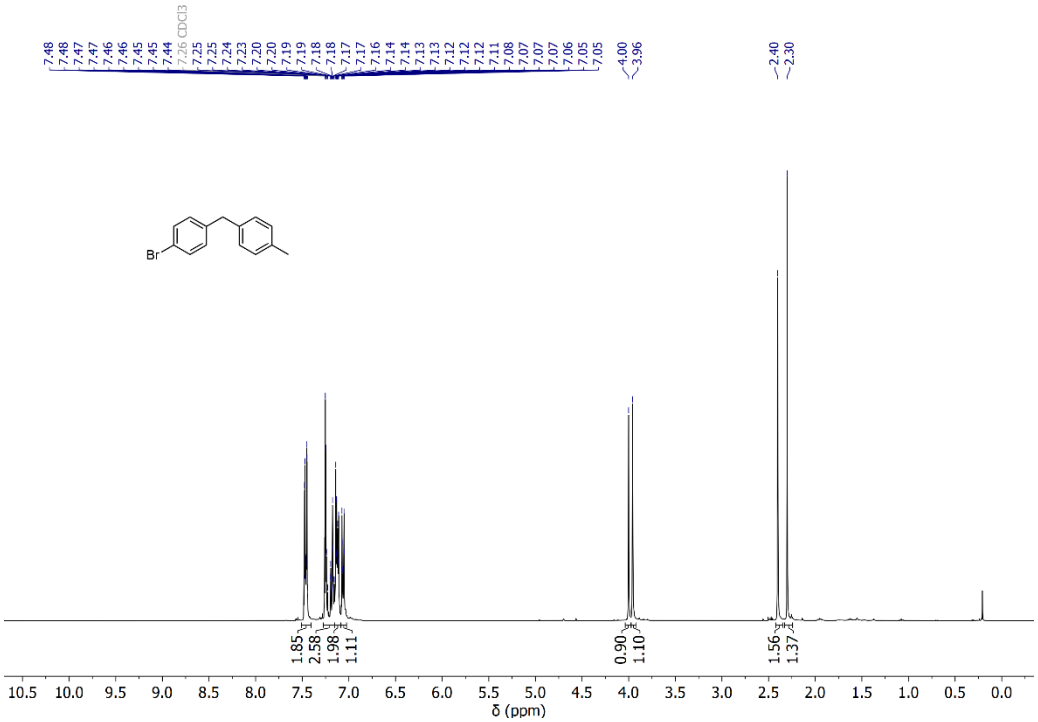


Figure S 70: ^{1}H NMR (400 MHz) spectrum of compound 17 ($CDCl_3$).

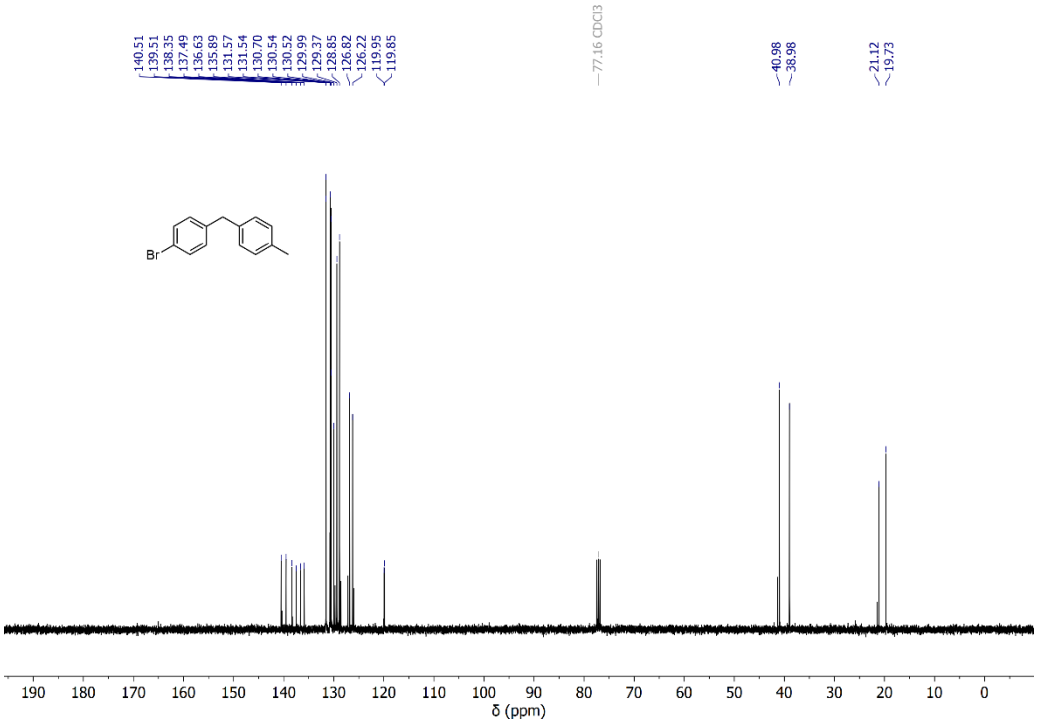


Figure S 71: ^{13}C{^{1}H} NMR (100 MHz) spectrum of compound 17 ($CDCl_3$).

5 References

[1] K. L. Bamford, D. W. Stephan, *Dalton Trans.* **2020**, *49*, 17571–17577.

[2] H. Schulz, G. Gabbert, H. Pritzkow, W. Siebert, *Chem. Ber.* **1993**, *126*, 1593–1595.

[3] R. H. Cragg, T. J. Miller, *J. Organomet. Chem.* **1982**, *232*, 201–214.

[4] P. Geymayer, E. G. Rochow, *Monatshefte für Chemie* **1966**, *97*, 437–443.

[5] W. Maringgele, U. Seebold, A. Meller, S. Dielkus, E. Pohl, R. Herbst-Irmer, G. M. Sheldrick, *Chem. Ber.* **1992**, *125*, 1559–1564.

[6] S. V. Sysoev, L. D. Nikulina, B. A. Gostevskii, I. S. Merenkov, R. V. Pushkarev, V. I. Rakhlin, M. L. Kosinova, *Glas. Phys. Chem.* **2014**, *40*, 261–266.

[7] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176–2179.

[8] P. A. Champagne, Y. Benhassine, J. Desroches, J. F. Paquin, *Angew. Chem. Int. Ed.* **2014**, *53*, 13835–13839.

[9] J. Zhu, M. Pérez, D. W. Stephan, *Angew. Chem. Int. Ed.* **2016**, *55*, 8448–8451.

[10] D. R. Willcox, G. S. Nichol, S. P. Thomas, *ACS Catal.* **2021**, *11*, 3190–3197.

[11] G. Blessley, P. Holden, M. Walker, J. M. Brown, V. Gouverneur, *Org. Lett.* **2012**, *14*, 2754–2757.

[12] C. Houle, P. R. Savoie, C. Davies, D. Jardel, P. A. Champagne, B. Bibal, J. F. Paquin, *Chem. – A Eur. J.* **2020**, *26*, 10620–10625.

[13] K. L. Bamford, Synthesis and Reactivity of Electron-Deficient Boron Species, Doctoral dissertation, University of Toronto, Toronto, **2021**.

[14] C. D. Entwistle, T. B. Marder, P. S. Smith, J. A. K. Howard, M. A. Fox, S. A. Mason, *J. Organomet. Chem.* **2003**, *680*, 165–172.

[15] A. Del Grosso, R. G. Pritchard, C. A. Muryn, M. J. Ingleson, *Organometallics* **2010**, *29*, 241–249.

[16] J. Guo, K. L. Bamford, D. W. Stephan, *Org. Biomol. Chem.* **2019**, *17*, 5258–5261.

[17] C. Douvris, O. V. Ozerov, *Science* **2008**, *321*, 1188–1190.

[18] K. L. Bamford, S. S. Chitnis, Z. wang Qu, D. W. Stephan, *Chem. Eur. J.* **2018**, *24*, 16014–16018.

[19] J. M. Farrell, R. T. Posaratnanathan, D. W. Stephan, *Chem. Sci.* **2015**, *6*, 2010–2015.