Supporting Information

Synthesis of Secondary and Tertiary Alkylboranes via Formal Hydroboration of Terminal and 1,1-Disubstituted Alkenes

Hilary A. Kerchner and John Montgomery*

Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055

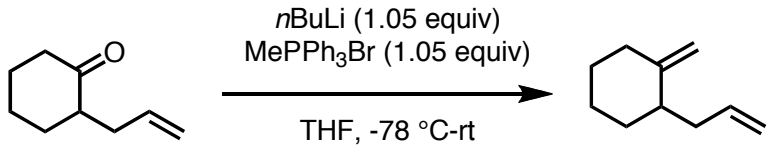
jmontg@umich.edu

All reactions were conducted in a flame-dried or oven dried (120 °C) glassware with magnetic stirring under an atmosphere of dry nitrogen. Solvents were purified under nitrogen using a solvent purification system (Innovative Technology, Inc. Model # Sps-400-3 and PS-400-3). Unless otherwise noted all reagents were used as received. Allyltrimethylsilane, and allylbenzene were distilled. Copper salts (Sigma Aldrich, Strem Chemicals, Inc), *N*-heterocyclic carbene salts (Sigma Aldrich, Strem), t-BuOK (Strem), t-BuONa (Strem) B_2Pin_2 (Combi Blocks, recrystallized from pentanes) were stored and weighed in an inert atmosphere. IPrCuCl was synthesized[1], stored, and weighed in an inert atmosphere. MeOH was distilled from CaH_2 and stored under nitrogen.

^1H and ^{13}C were obtained in $CDCl_3$ at rt in a Varian Mercury 400 MHz instrument, a Varian Unity 500 MHz, or a Varian Unity 700 MHz instrument. Chemical shifts of ^1H NMR spectra were recorded in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.24 ppm). Chemical shifts of ^{13}C NMR spectra were recorded in ppm from the central peak of $CDCl_3$ (77.0 ppm) on the δ scale. High-resolution mass spectra (HRMS) were obtained at the University of Michigan Mass Spectrometry Laboratory on a VG-70-250-s spectrometer manufactured by Micromass Corp. (Manchester UK). Regioisomeric ratios were determined on crude reaction mixtures using GC. GCMS analysis was carried out on a HP 6980 Series GC System with HP-5MS column (30 m x 0.250 mm x 0.25 μm). GCFID analysis was carried out on a HP 6980N Series GC system with a HP-5 column (30 m x 0.32 mm x 0.25 μm).

The following substrates were prepared according to literature procedures:
tert-Butyldimethyl(pent-4-enyloxy)silane,[2]
(*R*)-4,8-Dimethylnona-1,7-diene,[3]
((Hex-5-enyloxy)methyl)benzene,[4,5]
1-Allyl-1*H*-indole,[6]
(3-methylbut-3-enyl)benzene[3,7]
(3-methylenepentyl)benzene[3,8]

1-Allyl-2-methylenecyclohexane



Methyltriphenylphosphonium bromide (2.7 g, 7.6 mmol) was added to a flask and backfilled with N_2. THF (18 mL, 0.4 M) was added and the reaction was cooled to 0 °C. *n*-butyllithium solution (3.0 mL, 2.5M, 7.6 mmol) was added dropwise. The mixture was allowed to stir at 0 °C for 30 minutes before being cooled to -78 °C. 2-allyl-cylcohexanone (0.68 mL, 7.2 mmol) was added dropwise. The reaction was allowed to stir overnight, gradually warming to rt. 75 mL saturated NH_4Cl was added. The aqueous layer was washed with Et_2O (3x75 mL). The organic layers were combined, washed with brine dried over $MgSO_4$, filtered, and concentrated. The reaction mixture was purified via column chromatography (100 % hexanes) (442 mg, 3.2 mmol, 45 % yield).

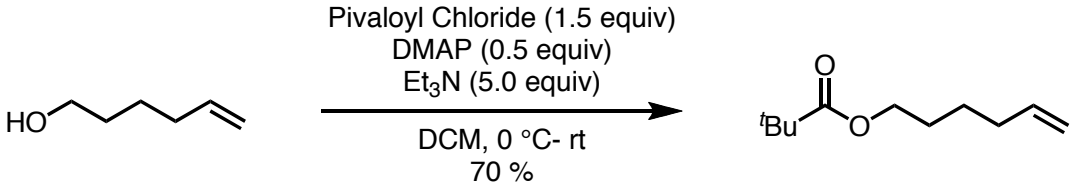
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.87 – 5.72 (m, 1H), 5.08 – 4.93 (m, 2H), 4.67 (s, 1H), 4.58 (s, 1H), 2.43 – 2.33 (m, 1H), 2.30 – 2.21 (m, 1H), 2.12 – 1.97 (m, 3H), 1.84 – 1.74 (m, 1H), 1.72 – 1.61 (m, 2H), 1.51 – 1.40 (m, 2H), 1.25 – 1.12 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 152.64, 137.80, 115.38, 105.38, 42.83, 36.89, 35.36, 33.49, 28.75, 24.72.

IR (thin film): v 2926, 2854, 1642, 1446, 992, 909, 889, 495, 416 cm^{-1}.

HRMS (EI) (m/z): [M^+] calculated for $C_{10}H_{16}$, 136.1252 found, 136.1253.

Hex-5-enyl pivalate



DMAP (611 mg, 5.0 mmol) was added to a flask and backfilled with N_2. DCM (44 mL 0.2 M) was added and the reaction was cooled to 0 °C. 5-hexen-1-ol (1.2 mL, 10 mmol) and freshly distilled Et_3N (7.0 mL, 50.0 mmol) were added. Pivaloyl chloride (2.0 mL, 15.0 mmol) was added dropwise. The reaction was allowed to stir overnight, gradually warming to rt. 30 mL saturated $NaHCO_3$ was added. The aqueous layer was washed with EtOAc (3x50 mL). The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated. The reaction mixture was purified via column chromatography (5 % EtOAc in hexanes) (1.29 g, 7.01 mmol, 70 % yield).

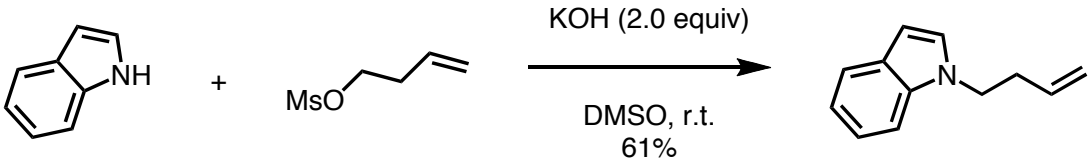
^{1}H NMR (500 MHz, $CDCl_3$): δ 5.80 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.09 – 4.89 (m, 2H), 4.06 (t, *J* = 6.6 Hz, 2H), 2.13 – 2.04 (m, 2H), 1.69 – 1.59 (m, 2H), 1.51 – 1.39 (m, 2H), 1.19 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 178.63, 138.40, 114.75, 64.21, 38.73, 33.27, 28.05, 27.20, 25.20.

IR (thin film): v 2975, 2938, 2871, 1728, 1480, 1459, 1283, 1036, 994, 910 cm^{-1}.

HRMS (EI) (m/z): [M^+] calculated for $C_{11}H_{20}O_2$, 184.1463 found, 184.1467.

1-(But-3-enyl)-1*H*-indole



Indole (562 mg, 4.8 mmol) and crushed KOH pellets (539 mg, 9.6 mmol) were added to a flask and backfilled with N_2. DMSO (20 mL, 0.25 M) and then but-3-enyl methanesulfonate (1.44 g, 9.6 mmol) were added. The reaction mixture was allowed to stir at rt overnight. 100 mL H_2O was added. The reaction mixture was extracted with EtOAc (3x100 mL). The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered, and concentrated. The reaction was purified via column chromatography (100 % hexanes) (505 mg, 2.95 mmol, 61%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.16 – 7.06 (m, 2H), 6.50 (s, 1H), 5.80 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1H), 5.09 (d, *J* = 17.0 Hz, 1H), 5.07 (d, *J* = 10.0 Hz, 1H), 4.20 (t, *J* = 7.2 Hz, 2H), 2.60 (q, *J* = 7.1, 6.7 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 135.84, 134.65, 128.60, 127.70, 121.36, 120.95, 119.24, 117.36, 109.30, 101.03, 45.98, 34.54.

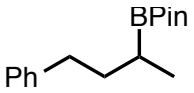
IR (thin film): v 2927, 1641, 1612, 1510, 1463, 1313, 913, 735, 714 cm^{-1}.

HRMS (EI) (m/z): [M^+] calculated for $C_{12}H_{13}N$, 171.1048 found, 171.1049.

General procedures for copper-catalyzed hydroboration of alkenes:

1.5 mL of acetonitrile was added to a solid mixture of IPrCuCl (0.03 mmol) and t-BuOK (0.45 mmol) under N_2. The reaction was allowed to stir at rt for 10 minutes. B_2Pin_2 (0.6 mmol) was added under N_2 and the reaction was allowed to stir for an additional 30 minutes at rt. The alkene (0.3 mmol) and MeOH (0.6 mmol) were added to the mixture by syringe. The reaction mixture was allowed to stir at rt for 2 h and was then filtered through silica gel, eluting with 50% v/v EtOAc/hexanes. The solvent was removed *in vacuo*, and the crude residue was purified via flash chromatography on silica gel to afford the desired product.

4,4,5,5-Tetramethyl-2-(4-phenylbutan-2-yl)-1,3,2-dioxaborolane; compound 2,



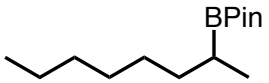
The title compound was prepared from IPrCuCl (14.6 mg, 0.03 mmol), t-BuOK (50 mg, 0.45 mmol), B_2Pin_2 (152 mg, 0.6 mmol), 4-phenyl-1-butene (40 mg, 0.3 mmol) and MeOH (19 mg, 0.6 mmol) by following the general procedure. The crude residue was purified via flash chromatography (100% hexanes to 4% EtOAc in hexanes) to afford the desired product as a 92:8 mixture of regioisomers (63 mg, 0.24 mmol, 81% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.23 (m, 2H), 7.23 – 7.13 (m, 3H), 2.69 – 2.57 (m, 2H), 1.85 – 1.74 (m, 1H), 1.64 – 1.54 (m, 1H), 1.27 (s, 12H), 1.14 – 0.99 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 143.08, 128.42, 128.18, 125.48, 82.87, 35.31, 35.29, 24.79, 24.74, 15.41.

The spectral data matched the literature.[9]

4,4,5,5-Tetramethyl-2-(octan-2-yl)-1,3,2-dioxaborolane; compound 3



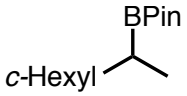
The title compound was prepared from IPrCuCl (14.6 mg, 0.03 mmol), t-BuOK (50 mg, 0.45 mmol), B_2Pin_2 (152 mg, 0.6 mmol), 1-octene (34 mg, 0.3 mmol) and MeOH (19 mg, 0.6 mmol) by following the general procedure**.** The crude residue was purified via flash chromatography (100% hexanes to 4% EtOAc in hexanes) to afford the desired product as a 95:5 mixture of regioisomers (56 mg, 0.23 mmol, 77% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.47 – 1.39 (m, 1H), 1.33 – 1.18 (m, 21H), 1.03 – 0.92 (m, 4H), 0.92 – 0.82 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 82.73, 33.25, 31.87, 29.54, 28.94, 24.74, 24.71, 22.65, 15.52, 14.11.

The spectral data matched the literature.[10]

2-(1-Cyclohexylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; compound 4



The title compound was prepared from IPrCuCl (14.6 mg, 0.03 mmol), t-BuOK (50 mg, 0.45 mmol), B_2Pin_2 (152 mg, 0.6 mmol), vinylcyclohexane (33 mg, 0.3 mmol) and MeOH (19 mg, 0.6 mmol) by following the general procedure**.** The crude residue was purified via flash chromatography (100% hexanes to 4% EtOAc in hexanes) to afford the desired product as an 87:13 mixture of regioisomers (70 mg, 0.29 mmol, 98% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.83 – 1.57 (m, 5H), 1.40 – 1.19 (m, 15H), 1.19 – 1.08 (m, 1H), 1.08 – 0.83 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 82.68, 40.46, 32.68, 31.81, 26.75, 26.70, 24.80, 24.72, 12.50.

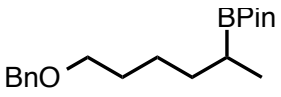
^{11}B NMR (128 MHz, $CDCl_3$): δ 34.29.

IR (thin film): v 2978, 2921, 2851, 1378, 1370, 1357, 1308, 1143, 863, 845 cm^{-1}.

HRMS (EI) (m/z): [M^+] calculated for $C_{14}H_{27}BO_2$, 238.2104 found, 238.2113.

The spectral data matched the literature.[10]

2-(6-(Benzyloxy)hexan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; compound 5



The title compound was prepared from IPrCuCl (14.6 mg, 0.03 mmol), t-BuOK (50 mg, 0.45 mmol), B_2Pin_2 (152 mg, 0.6 mmol), ((hex-5-enyloxy)methyl)benzene (57 mg, 0.3 mmol) and MeOH (19 mg, 0.6 mmol) by following the general procedure**.** The crude residue was purified via

flash chromatography (100% hexanes to 4% EtOAc in hexanes) to afford the desired product as a 92:8 mixture of regioisomers (79 mg, 0.25 mmol, 83% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 – 7.33 (m, 4H), 7.33 – 7.25 (m, 1H), 4.51 (s, 2H), 3.48 (t, *J* = 6.7 Hz, 2H), 1.64 (m, 2H), 1.55 – 1.44 (m, 1H), 1.44 – 1.35 (m, 2H), 1.35 – 1.20 (m, 14H), 1.07 – 0.94 (m, 4H).

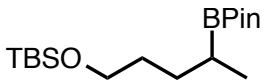
^{13}C NMR (126 MHz, $CDCl_3$): δ 138.75, 128.27, 127.54, 127.37, 82.77, 72.76, 70.50, 32.99, 29.95, 25.49, 24.73, 24.70, 15.44.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.34.

IR (thin film): v 2930, 2856, 1455, 1370, 1213, 1143, 1103, 732 cm^{-1}.

HRMS (EI) (m/z): [M^+] calculated for $C_{19}H_{31}BO_3$, 318.2366, found, 318.2370.

***tert*-Butyldimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyloxy)silane; compound 6**



The title compound was prepared from IPrCuCl (14.6 mg, 0.03 mmol), t-BuOK (50 mg, 0.45 mmol), B_2Pin_2 (152 mg, 0.6 mmol), *tert*-butyldimethyl(pent-4-enyloxy)silane (60 mg, 0.3 mmol) and MeOH (19 mg, 0.6 mmol) by following the general procedure**.** The crude residue was purified via flash chromatography (100% hexanes to 5% EtOAc in hexanes) to afford the desired product as a 90:10 mixture of regioisomers (91 mg, 0.28 mmol, 92% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.61 – 3.51 (m, 2H), 1.55 – 1.46 (m, 2H), 1.46 – 1.37 (m, 1H), 1.31 – 1.24 (m, 1H), 1.20 (m, 12H), 1.01 – 0.91 (m, 4H), 0.86 (m, 9H), 0.01 (m, 6H).

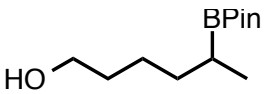
^{13}C NMR (126 MHz, $CDCl_3$): δ 82.78, 63.60, 32.27, 29.26, 25.99, 24.75, 24.71, 18.38, 15.53, -5.24.

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.95.

IR (thin film): v 2929, 2858, 1462, 1386, 1314, 1251, 1145, 1096, 833, 773 cm^{-1}.

HRMS (EI) (m/z): [$M+H^+$] calculated for $C_{17}H_{38}BO_3Si$, 329.2678 found, 329.2680.

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-ol; compound 7



The title compound was prepared from IPrCuCl (14.6 mg, 0.03 mmol), t-BuOK (50 mg, 0.45 mmol), B_2Pin_2 (152 mg, 0.6 mmol), 5-hexen-1-ol (30 mg, 0.3 mmol) and MeOH (19 mg, 0.6 mmol) by following the general procedure**.** The crude residue was purified via flash chromatography (100% hexanes to 20% EtOAc in hexanes) to afford the desired product observed as a single isomer (64 mg, 0.28 mmol, 93% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 3.63 (t, *J* = 6.5 Hz, 2H), 1.56 (quint, *J* = 6.9 Hz, 2H), 1.49 – 1.26 (m, 6H), 1.23 (s, 12H), 1.06 – 0.88 (m, 4H).

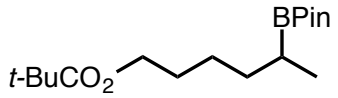
^{13}C NMR (126 MHz, $CDCl_3$): δ 82.86, 62.83, 32.77, 32.61, 24.91, 24.74, 24.69, 15.46.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.11.

IR (thin film): v 3362, 2977, 2928, 2872, 1462, 1370, 1313, 1143, 858 cm^{-1}.

HRMS (EI) (m/z): [M+H^+] calculated for $C_{12}H_{25}BO_3$, 229.1970 found, 229.1970.

5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl pivalate; compound 8



The title compound was prepared from IPrCuCl (14.6 mg, 0.03 mmol), t-BuOK (50 mg, 0.45 mmol), B_2Pin_2 (152 mg, 0.6 mmol), hex-5-enyl pivalate (55 mg, 0.3 mmol) and MeOH (19 mg, 0.6 mmol) by following the general procedure**.** The crude residue was purified via flash chromatography (100% hexanes to 4% EtOAc in hexanes) to afford the desired product as a 96:4 mixture of regioisomers (73 mg, 0.23 mmol, 78% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.09 – 3.97 (m, 2H), 1.66 – 1.55 (m, 2H), 1.51 – 1.41 (m, 1H), 1.39 – 1.27 (m, 3H), 1.23 (s, 12H), 1.18 (s, 9H), 1.03 – 0.93 (m, 4H).

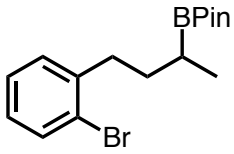
^{13}C NMR (126 MHz, $CDCl_3$): δ 178.62, 82.82, 64.50, 38.70, 32.81, 28.86, 27.20, 25.27, 24.74, 24.70, 15.43.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.35.

IR (thin film): v 2975, 2932, 2871, 1727, 1370, 1315, 1284, 1144, 859 cm^{-1}.

HRMS (EI) (m/z): [M+H^+] calculated for $C_{17}H_{34}BO_4$, 313.2545 found, 313.2546.

2-(4-(2-Bromophenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; compound 9



The title compound was prepared from IPrCuCl (14.6 mg, 0.03 mmol), t-BuOK (50 mg, 0.45 mmol), B_2Pin_2 (152 mg, 0.6 mmol), 4-(2-bromophenyl)-1-butene (63 mg, 0.3 mmol) and MeOH (19 mg, 0.6 mmol) by following the general procedure**.** The crude residue was purified via flash chromatography (100% hexanes to 4% EtOAc in hexanes) to afford the desired product as a 90:10 mixture of regioisomers (94 mg, 0.28 mmol, 92% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.24 – 7.15 (m, 2H), 7.00 (dt, *J* = 8.3, 4.1 Hz, 1H), 2.79 – 2.67 (m, 2H), 1.79 – 1.67 (m, 1H), 1.62 – 1.52 (m, 1H), 1.24 (s, 12H), 1.13 – 0.99 (m, 4H).

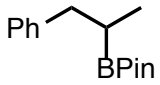
^{13}C NMR (126 MHz, $CDCl_3$): δ 142.29, 132.64, 130.31, 127.28, 127.24, 124.37, 82.94, 35.54, 33.55, 24.83, 24.78, 15.41

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.29.

IR (thin film): v 2976, 1469, 1369, 1315, 1142, 747, 411 cm^{-1}.

HRMS (EI) (m/z): [M^+] calculated for $C_{16}H_{24}BBrO_2$, 338.1053 found, 338.1051.

4,4,5,5-Tetramethyl-2-(1-phenylpropan-2-yl)-1,3,2-dioxaborolane; compound 10



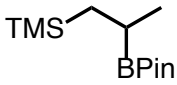
Following a modified procedure 1.5 mL of acetonitrile was added to a solid mixture of IPrCuCl (14.6 mg, 0.03 mmol), t-BuOK (50 mg 0.45 mmol), and B_2Pin_2 (152 mg, 0.6 mmol). Allylbenzene (35 mg, 0.3 mmol) and MeOH (19 mg 0.6 mmol) were immediately added to the mixture by syringe. The reaction mixture was allowed to stir at rt for 2 h and was then filtered through silica gel, eluting with 50% v/v EtOAc/hexanes. The solvent was removed *in vacuo*, and the crude residue was purified via flash chromatography on silica gel to afford the desired product. The crude residue was purified via flash chromatography (100% hexanes to 4% EtOAc in hexanes) to afford the desired product as a 95:5 mixture of regioisomers (72 mg, 0.29 mmol, 98% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 – 7.13 (m, 5H), 2.82 (dd, *J* = 13.6, 7.5 Hz, 1H), 2.55 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.38 (m, 1H), 1.19 (m, 12H), 0.98 (d, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz $CDCl_3$): δ 142.28, 128.86, 127.96, 125.51, 82.94, 38.94, 24.69, 24.67, 15.17.

The spectral data matched the literature.[11]

Trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane; compound 11



Following a modified procedure 1.5 mL of acetonitrile was added to a solid mixture of IPrCuCl (14.6 mg, 0.03 mmol), t-BuOK (50 mg 0.45 mmol), and B_2Pin_2 (152 mg, 0.6 mmol). Allyltrimethylsilane (34 mg, 0.3 mmol) and MeOH (19 mg 0.6 mmol) were immediately added to the mixture by syringe. The reaction mixture was allowed to stir at rt for 2 h and was then filtered through silica gel, eluting with 50% v/v EtOAc/hexanes. The solvent was removed *in vacuo*, and the crude residue was purified via flash chromatography on silica gel to afford the desired product. The crude residue was purified via flash chromatography (100% hexanes to 4% EtOAc in hexanes) to afford the desired product as a single regioisomers (52 mg, 0.23 mmol, 77% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.21 (s, 12H), 1.10 – 1.04 (m, 1H), 0.99 (d, *J* = 7.2 Hz, 3H), 0.77 (dd, *J* = 14.6, 7.4 Hz, 1H), 0.40 (dd, *J* = 14.6, 6.9 Hz, 1H), -0.04 (s, 9H).

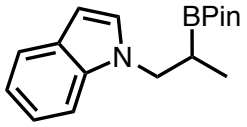
^{13}C NMR (126 MHz, $CDCl_3$): δ 82.78, 24.78, 24.76, 19.88, 19.35, -0.86.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.36.

IR (thin film): v 2952, 1459, 1378, 1315, 1246, 1226, 1144, 834, 689 cm^{-1}.

HRMS (EI) (m/z): [M-CH_3^+] calculated for $C_{11}H_{23}BO_2Si$, 227.1639 found, 227.1637.

1-(2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1*H*-indole; compound 12



The title compound was prepared from IPrCuCl (29.2 mg, 0.06 mmol), t-BuOK (50 mg, 0.45 mmol), B_2Pin_2 (152 mg, 0.6 mmol), 1-allyl-1*H*-indole (47 mg, 0.3 mmol) and MeOH (19 mg, 0.6 mmol) by following the general procedure**.** The crude residue was purified via flash chromatography (100% hexanes to 4% EtOAc in hexanes) to afford the desired product as a 94:6 mixture of regioisomers (48 mg, 0.17 mmol, 56% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.9, 1.1 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.22 – 7.12 (m, 2H), 7.07 (td, *J* = 7.5, 7.0, 1.0 Hz, 1H), 6.46 (d, *J* = 3.0 Hz, 1H), 4.31 (dd, *J* = 14.1, 6.7 Hz, 1H), 4.00 (dd, *J* = 14.1, 9.1 Hz, 1H), 1.77 – 1.63 (m, 1H), 1.23 – 1.17 (m, 14H), 0.94 (d, *J* = 7.4 Hz, 3H).

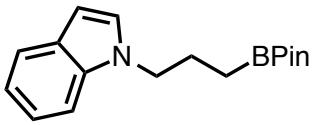
^{13}C NMR (126 MHz, $CDCl_3$): δ 136.13, 128.46, 128.24, 121.03, 120.69, 118.96, 109.75, 100.53, 83.40, 48.98, 24.72, 24.68, 13.30

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.35.

IR (thin film): v 2975, 2931, 2873, 1512, 1462, 1371, 1317, 1216, 1142, 966, 853, 714 cm^{-1}.

HRMS (EI) (m/z): [M+H$^+$] calculated for $C_{17}H_{25}BNO_2$, 286.1973 found, 286.1975.

1-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1*H*-indole



The title compound was synthesized according to a literature procedure for use as an authentic standard for the analysis of entry 12.[10]

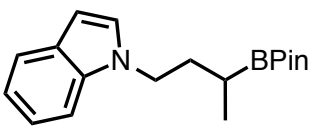
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.16 (m, 1H), 7.14 – 7.04 (m, 2H), 4.12 (t, *J* = 7.3, 5.5 Hz, 2H), 2.00 – 1.88 (m, 2H), 1.25 (s, 13H), 0.80 (t, *J* = 7.7 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 135.95, 128.52, 127.94, 121.16, 120.81, 119.05, 109.51, 100.70, 83.17, 48.28, 24.90, 24.84.

IR (thin film): v 2976, 1463, 1370, 1314, 1219, 1142, 967, 845, 737 cm^{-1}.

HRMS (EI) (m/z): [M+H$^+$] calculated for $C_{17}H_{25}BNO_2$, 286.1973 found, 286.1976.

1-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-1*H*-indole, compound 13



The title compound was prepared from IPrCuCl (21.9 mg, 0.045 mmol), t-BuOK (50 mg, 0.45 mmol), B_2Pin_2 (152 mg, 0.6 mmol), 1-(but-3-enyl)-1*H*-indole (51 mg, 0.3 mmol) and MeOH (19 mg, 0.6 mmol) by following the general procedure. The crude residue was purified via flash chromatography (100% hexanes to 4% EtOAc in hexanes) to afford the desired product as a 94:6 mixture of regioisomers (71 mg, 0.24 mmol, 79% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.14 – 7.06 (m, 2H), 6.50 – 6.47 (m, 1H), 4.22 – 4.09 (m, 2H), 2.05 – 1.95 (m, 1H), 1.87 – 1.77 (m, 1H), 1.28 (s, 12H), 1.12 – 1.00 (m, 4H).

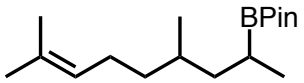
^{13}C NMR (126 MHz, $CDCl_3$): δ 135.94, 128.52, 127.80, 121.14, 120.81, 119.03, 109.50, 100.72, 83.15, 45.78, 33.67, 24.83, 24.77, 15.46.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.37.

IR (thin film): v 2975, 2871, 1463, 1387, 1369, 1315, 1142, 737 cm^{-1}.

HRMS (EI) (m/z): [M+H$^+$] calculated for $C_{18}H_{27}BNO_2$, 300.2129 found, 300.2131.

2-((4*R*)-4,8-Dimethylnon-7-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane compound 14.



The title was prepared from IPrCuCl (14.6 mg, 0.03 mmol), t-BuOK (50 mg, 0.45 mmol), B_2Pin_2 (152 mg, 0.6 mmol), ((*R*)-4,8-dimethylnona-1,7-diene (46 mg, 0.3 mmol) and MeOH (19 mg, 0.6 mmol) by following the general procedure**.** The crude residue was purified via flash chromatography (100% hexanes to 4% EtOAc in hexanes) to afford the desired product observed as a single isomer (1:1 diastereomeric ratio) (69 mg, 0.24 mmol, 81% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.07 (m, 1H), 2.04 – 1.82 (m, 2H), 1.65 (s, 3H), 1.57 (s, 3H), 1.49 – 1.35 (m, 1H), 1.35 – 1.16 (m, 14H), 1.13 – 0.98 (m, 2H), 0.91 (m, 3H), 0.83 (m, 3H).

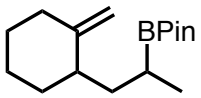
^{13}C NMR (126 MHz, $CDCl_3$): δ 130.84, 130.82, 125.12, 125.11, 82.73, 82.70, 41.04, 40.27, 37.29, 37.26, 31.62, 31.02, 25.71, 25.58, 25.54, 24.74, 24.71, 24.70, 24.66, 19.75, 19.33, 17.64, 17.62, 16.11, 15.39.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.28.

IR (thin film): v 2957, 2914, 1460, 1370, 1314, 1144, 861, 688 cm^{-1}.

HRMS (EI) (m/z): [M$^+$] calculated for $C_{17}H_{33}BO_2$, 280.2574 found, 280.2579.

4,4,5,5-tetramethyl-2-(1-(2-methylenecyclohexyl)propan-2-yl)-1,3,2-dioxaborolane; compound 15



The title compound was prepared from IPrCuCl (14.6 mg, 0.03 mmol), t-BuOK (50 mg, 0.45 mmol), B_2Pin_2 (152 mg, 0.6 mmol), 1-allyl-2-methylenecyclohexane (41 mg, 0.3 mmol) and MeOH (19 mg, 0.6 mmol) by following the general procedure**.** The crude residue was purified via flash

chromatography (100% hexanes to 4% EtOAc in hexanes) to afford the desired product observed as a single isomer (66 mg, 0.25 mmol, 83% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.63 (s, 1H), 4.58 (d, *J* = 7.6, 1.5 Hz, 1H), 2.22 (m, 1H), 2.17 – 2.08 (m, 1H), 2.04 – 1.95 (m, 1H), 1.80 (dt, *J* = 13.4, 7.9 Hz, 1H), 1.76 – 1.62 (m, 2H), 1.58 – 1.34 (m, 5H), 1.31 – 1.18 (m, 14H), 1.11 – 1.00 (m, 1H), 0.99 – 0.93 (m, 3H).

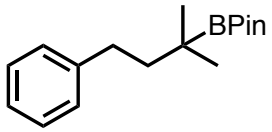
^{13}C NMR (126 MHz, $CDCl_3$): δ 105.96, 105.74, 82.73, 42.08, 41.99, 35.59, 35.38, 34.44, 34.41, 33.78, 33.52, 28.85, 28.84, 24.75, 24.75, 24.71, 24.68, 23.87, 15.96, 15.78.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.48.

IR (thin film): v 2976, 2926, 2854, 1462, 1370, 1312, 1144, 859, 688 cm^{-1}.

HRMS (EI) (m/z): [M^+] calculated for $C_{16}H_{29}BO_2$, 264.2261 found, 264.2274.

4,4,5,5-tetramethyl-2-(2-methyl-4-phenylbutan-2-yl)-1,3,2-dioxaborolane; compound 16



The title compound was prepared from a modified general procedure. 1.5 mL of dichloromethane was added to a solid mixture of IPrCuCl (14.6 mg, 0.03 mmol) and t-BuONa (29 mg, 0.3 mmol) under N_2. The reaction was allowed to stir at rt for 10 minutes. B_2Pin_2 (152 mg, 0.6 mmol) was added under N_2 and the reaction was allowed to stir for an additional 30 minutes at rt. (3-methylbut-3-enyl)benzene (44 mg, 0.3 mmol) and MeOH (19 mg, 0.6 mmol) were added to the mixture by syringe. The reaction mixture was allowed to stir at rt for 2 h and was then filtered through silica gel, eluting with 50% v/v EtOAc/hexanes. The crude residue was purified via flash chromatography (100% hexanes to 4% EtOAc in hexanes) to afford the desired product as a 91:9 mixture of regioisomers (72 mg, 0.26 mmol, 87% yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 – 7.24 (m, 2H), 7.22 – 7.14 (m, 3H), 2.61 – 2.54 (m, 2H), 1.63 – 1.56 (m, 2H), 1.27 (s, 12H), 1.02 (s, 6H).

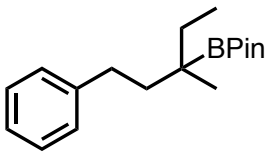
^{13}C NMR (126 MHz, $CDCl_3$): δ 143.63, 128.31, 128.19, 125.42, 82.96, 43.50, 33.06, 24.76, 24.74.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.80.

IR (thin film): v 2937, 2861, 1474, 1388, 1365, 1306, 1134, 854, 693 cm^{-1}.

HRMS (EI) (m/z): [$M+H^+$] calculated for $C_{17}H_{27}BO_2$, 274.2104 found, 274.2110.

4,4,5,5-tetramethyl-2-(3-methyl-1-phenylpentan-3-yl)-1,3,2-dioxaborolane, compound 17



The title compound was prepared from a modified general procedure. 1.5 mL of dichloromethane was added to a solid mixture of IPrCuCl (14.6 mg, 0.03 mmol) and t-BuONa (29 mg, 0.3 mmol) under N_2. The reaction was allowed to stir at rt for 10 minutes. B_2Pin_2 (152 mg, 0.6 mmol) was

added under N_2 and the reaction was allowed to stir for an additional 30 minutes at rt. (3-methylenepentyl)benzene (48 mg, 0.3 mmol) and MeOH (19 mg, 0.6 mmol) were added to the mixture by syringe. The reaction mixture was allowed to stir at rt for 2 h and was then filtered through silica gel, eluting with 50% v/v EtOAc/hexanes. The crude residue was purified via flash chromatography (100% hexanes to 4% EtOAc in hexanes) to afford the desired product as a 93:7 mixture of regioisomers (51 mg, 0.26 mmol, 59% yield).

^{1}H NMR (700 MHz, $CDCl_3$): δ 7.28 – 7.25 (m, 2H), 7.20 – 7.18 (m, 2H), 7.16 (td, *J* = 7.2, 1.4 Hz, 1H), 2.58 (td, *J* = 13.0, 5.0 Hz, 1H), 2.52 (td, *J* = 13.0, 4.7 Hz, 1H), 1.71 (td, *J* = 13.0, 4.7 Hz, 1H), 1.56 – 1.45 (m, 2H), 1.33 – 1.23 (m, 13H), 0.98 (s, 3H), 0.88 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (176 MHz, $CDCl_3$): δ 143.76, 128.32, 128.20, 125.42, 82.98, 41.35, 32.43, 31.38, 24.90, 24.84, 20.83, 10.05.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.49.

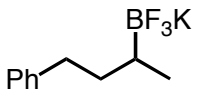
IR (thin film): v 2974, 2931, 1456, 1370, 1306, 1260, 1138, 852, 698 cm^{-1}.

HRMS (EI) (m/z): [M+H^+] calculated for $C_{18}H_{20}BO_2$, 289.2333 found, 289.2335.

General Procedure for Synthesis of Trifluoroborate Salts[13]

Acetone (0.5 M) was added to the boronic ester (1.0 equiv) and cooled in an ice bath. KHF_2 (3.0 equiv) and deionized water (1.5 M) were added. The reaction was capped with a septum, and a nitrogen line was inserted. The ice bath was removed, and the reaction was allowed to stir at rt. After 30 min the reaction mixture was concentrated. The pinacol and water were azeotroped with toluene, and the residual solvent was removed on high vacuum. The crude material was extracted with hot acetone (4x20 mL) and filtered. The mixture was concentrated to < 1 mL and copious amounts of hexanes were added. The mixture was sonicated for ~2 min, and the suspension was placed in the freezer (-20 °C) overnight. The resulting white crystalline solid was collected via vacuum filtration washing with hexanes.

Potassium (4-phenylbutan-2-yl)trifluoroborate



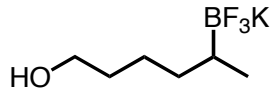
Following the general procedure, KHF_2 (618 mg, 8.70 mmol) and deionized H_2O (1.9 mL) were added to acetone (5.8 mL) and 4,4,5,5-tetramethyl-2-(4-phenylbutan-2-yl)-1,3,2-dioxaborolane (780 mg, 2.90 mmol). The white solid was precipitated from 200 mL of hexanes affording the desired product (495 mg, 2.06 mmol, 71 % yield).

^{1}H NMR (500 MHz, Acetone-d_6): δ 7.22 – 7.12 (m, 4H), 7.09 – 7.03 (m, 1H), 2.71 – 2.62 (m, 1H), 2.58 – 2.47 (m, 1H), 1.77 – 1.66 (m, 1H), 1.36 – 1.23 (m, 1H), 0.82 (d, *J* = 7.2 Hz, 3H), 0.32 (s, 1H).

^{13}C NMR (126 MHz, Acetone-d_6): δ 145.79, 128.92, 128.42, 125.31, 36.93, 36.16, 16.16.

The spectral data matched the literature.[14]

Potassium trifluoro(6-hydroxyhexan-2-yl)borate



Following the general procedure, KHF_2 (351 mg, 4.5 mmol) and deionized H_2O (1.0 mL) were added to acetone (3.0 mL) and 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-ol (342 mg, 1.5 mmol). The white solid was precipitated from 150 mL of hexanes affording the desired product (217 mg, 1.04 mmol, 70 % yield).

^{1}H NMR (500 MHz, Acetone-d_6): δ 3.50 (q, *J* = 6.2 Hz, 2H), 3.23 (t, *J* = 5.4 Hz, 1H), 1.50 – 1.38 (m, 4H), 1.31 – 1.20 (m, 1H), 1.06 – 0.94 (m, 1H), 0.74 (d, *J* = 7.6 Hz, 3H), 0.26 (s, 1H).

^{13}C NMR (126 MHz, Acetone-d_6): δ 62.98, 34.74, 34.37, 26.01, 16.39.

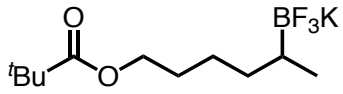
^{11}B NMR (128 MHz, Acetone-d_6): δ 5.50.

^{19}F NMR (377 MHz, Acetone-d_6): δ -147.33.

IR (KBr pellet): v 3594, 3430, 2934, 2853, 1459, 1276, 1087, 1067, 1003, 904 cm^{-1}.

HRMS (EI) (m/z): [M-K^-] calculated for $C_6H_{13}BF_3O$, 169.1017 found, 169.1016.

Potassium trifluoro(6-(pivaloyloxy)hexan-2-yl)borate



Following the general procedure, KHF_2 (169 mg, 2.16 mmol) and deionized H_2O (0.5 mL) were added to acetone (1.4 mL) and 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl pivalate (225 mg, 0.72 mmol). The white solid was precipitated from 150 mL of hexanes affording the desired product (144 mg, 0.49 mmol, 69 % yield).

^{1}H NMR (500 MHz, Acetone-d_6): δ 4.01 (t, *J* = 6.8 Hz, 2H), 1.64 – 1.48 (m, 2H), 1.48 – 1.41 (m, 2H), 1.32 – 1.25 (m, 1H), 1.16 (s, 9H), 1.07 – 0.99 (m, 1H), 0.75 (d, *J* = 7.2 Hz, 3H), 0.26 (s, 1H).

^{13}C NMR (126 MHz, Acetone-d_6): δ 178.28, 65.23, 39.14, 33.95, 27.45, 25.85, 25.21, 16.19.

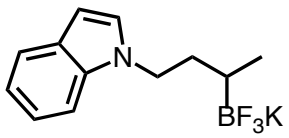
^{11}B NMR (128 MHz, Acetone-d_6): δ 5.52.

^{19}F NMR (377 MHz, Acetone-d_6): δ -147.39.

IR (KBr pellet): v 3432, 2970, 2938, 2868, 1720, 1480, 1463, 1290, 1179 cm^{-1}.

HRMS (EI) (m/z): [M-K^-] calculated for $C_{11}H_{21}BF_3O_2$ 253.1592 found, 253.1595.

Potassium (4-(1*H*-indol-1-yl)butan-2-yl)trifluoroborate



Following the general procedure, KHF_2 (234 mg, 3.0 mmol) and deionized H_2O (0.67 mL) were added to acetone (2.0 mL) and **17** (300 mg, 1.0 mmol). The white solid was precipitated from 150 mL of hexanes affording the desired product (182 mg, 0.65 mmol, 65 % yield).

^{1}H NMR (500 MHz, Acetone-d_6): δ 7.55 – 7.47 (m, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.24 (d, *J* = 3.2, 1.1 Hz, 1H), 7.08 (ddt, *J* = 8.3, 6.9, 1.2 Hz, 1H), 6.95 (ddt, *J* = 9.1, 7.8, 1.6 Hz, 1H), 6.36 – 6.33 (m, 1H), 4.28 – 4.13 (m, 2H), 1.95 – 1.81 (m, 1H), 1.61 – 1.51 (m, 1H), 0.85 (d, *J* = 7.2 Hz, 3H), 0.37 (s, 1H).

^{13}C NMR (126 MHz, Acetone-d_6): δ 137.30, 129.89, 129.31, 121.73, 121.47, 119.60, 110.84, 100.92, 47.30, 35.80, 16.89.

^{11}B NMR (128 MHz, Acetone-d_6): δ 5.09.

^{19}F NMR (377 MHz, Acetone-d_6): δ -146.71.

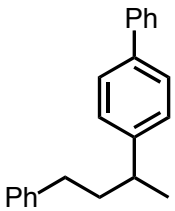
IR (KBr plate): v 3621, 3052, 2933, 2868, 1890, 1612, 1464, 751 cm^{-1}.

HRMS (EI) (m/z): [M-K$^-$] calculated for $C_{12}H_{14}BF_3N$, 240.1177 found, 2410.1179.

General Procedure for Photocatalytic Cross-Couplings[13a]

Following the Molander procedure, to a thin threaded culture tube, $NiCl_2$·dme (2.2 mg, 0.01 mmol) and 4,4'-di-*tert*-2,2'-bipyridine (2.7 mg, 0.01 mmol) were added under N_2. THF (0.4 mL, 0.5 M) was added and vial was heated with a heat gun until the solids were fully dissolved. The reaction mixture was concentrated *in vacuo* leaving behind a blue/green solid. The aryl bromide (0.2 mmol), potassium trifluoroborate salt (0.3 mmol), $Ir[dFCF_3ppy]_2(bpy)PF_6$[11a] (5.0 mg, 0.005 mmol) and Cs_2CO_3 (98 mg, 0.3 mmol) were added. The reaction vial was sealed with a septum and purged with N_2 four times. 4.0 mL (0.05 M) dioxanes (freeze, pumped, thawed three times) were added. The reaction was stirred ~4 cm away from two 23 W compact fluorescent (CFL) light bulbs while a fan was blown across to keep constant temperature. After ~22 h the reaction was filtered through a Celite plug with 20 mL EtOAc. The solvent was removed *in vacuo*, and the crude residue was purified via flash chromatography on silica gel to afford the desired product.

4-(4-Phenylbutan-2-yl)biphenyl; compound 21



The general procedure was followed using $NiCl_2$·dme (2.2 mg, 0.01 mmol), 4,4'-di-*tert*-2,2'-bipyridine (2.7 mg, 0.01 mmol), 4-bromobiphenyl (47 mg, 0.2 mmol), potassium (4-phenylbutan-2-yl)trifluoroborate (63 mg, 0.3 mmol), $Ir[dFCF_3ppy]_2(bpy)PF_6$ (5.0 mg, 0.005 mmol), and Cs_2CO_3 (98 mg, 0.3 mmol) in 4 mL dioxanes. The crude residue was purified via column chromatography (5% EtOAc in hexanes) to afford the desired product (54 mg, 0.190 mmol, 95 % yield).

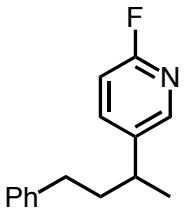
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 – 7.60 (m, 2H), 7.60 – 7.53 (m, 2H), 7.50 – 7.42 (m, 2H), 7.37 – 7.32 (m, 1H), 7.32 – 7.25 (m, 4H), 7.22 – 7.15 (m, 3H), 2.84 – 2.75 (m, 1H), 2.61 – 2.55 (m, 2H), 2.05 – 1.89 (m, 2H), 1.34 (d, *J* = 7.4 Hz, 3H), 1.29 – 1.25 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 146.41, 142.48, 141.10, 138.87, 128.69, 128.37, 128.26, 127.47, 127.11, 126.98, 126.97, 125.65, 39.94, 39.15, 33.93, 22.48.

IR (thin film): v 3025, 29.21, 1601, 1485, 1452, 836, 763, 731, 695 cm^{-1}.

HRMS (EI) (m/z): [M^+] calculated for $C_{22}H_{22}$, 286.1722 found, 286.1727.

2-Fluoro-5-(4-phenylbutan-2-yl)pyridine; compound 22



The general procedure was followed using $NiCl_2$·dme (2.2 mg, 0.01 mmol), 4,4'-di-*tert*-2,2'-bipyridine (2.7 mg, 0.01 mmol), 5-bromo-2-fluoropyridine (35 mg, 0.2 mmol), potassium (4-phenylbutan-2-yl)trifluoroborate (63 mg, 0.3 mmol), $Ir[dFCF_3ppy]_2(bpy)PF_6$ (5.0 mg, 0.005 mmol), and Cs_2CO_3 (98 mg, 0.3 mmol) in 4 mL dioxanes. The crude residue was purified via column chromatography (5% EtOAc in hexanes) to afford the desired product (43 mg, 0.189 mmol, 95% yield).

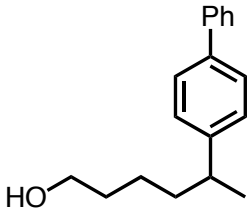
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.61 (td, *J* = 8.1, 2.5 Hz, 1H), 7.31 – 7.23 (m, 2H), 7.23 – 7.15 (m, 1H), 7.15 – 7.08 (m, 2H), 6.88 (dd, *J* = 8.4, 2.9 Hz, 1H), 2.82 – 2.71 (m, 1H), 2.57 – 2.47 (m, 2H), 2.01 – 1.84 (m, 2H), 1.29 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 162.32 (d, *J* = 236.8 Hz), 146.29 (d, *J* = 14.2 Hz), 141.65, 139.84 (d, *J* = 4.9 Hz), 139.33 (d, *J* = 7.6 Hz), 128.38 , 128.26 , 125.89 , 109.23 (d, *J* = 37.2 Hz), 39.61 , 36.06 , 33.64 , 22.23.

IR (thin film): v 3026, 2921, 1594, 1481, 1454, 1400, 1249, 831, 731, 698 cm^{-1}.

HRMS (EI) (m/z): [$M+H^+$] calculated for $C_{15}H_{16}FN$, 230.1340 found, 230.1337.

5-(Biphenyl-4-yl)hexan-1-ol; compound 23



The general procedure was followed using $NiCl_2$·dme (2.2 mg, 0.01 mmol), 4,4'-di-*tert*-2,2'-bipyridine (2.7 mg, 0.01 mmol), 4-bromobiphenyl (35 mg, 0.2 mmol), potassium trifluoro(6-hydroxyhexan-2-yl)borate (62 mg, 0.3 mmol), $Ir[dFCF_3ppy]_2(bpy)PF_6$ (5.0 mg, 0.005 mmol), and Cs_2CO_3 (98 mg, 0.3 mmol) in 4 mL dioxanes. The crude residue was purified via column chromatography (10% EtOAc in hexanes) to afford the desired product (31 mg, 0.122 mmol, 60 % yield).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, *J* = 10.0 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.30 (m, 1H), 7.27 – 7.24 (m, 2H), 3.61 (t, *J* = 6.7 Hz, 2H), 2.75 (sextet, *J* = 7.0

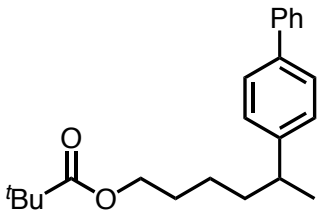
Hz, 1H), 1.68 – 1.60 (m, 2H), 1.60 – 1.53 (m, 2H), 1.41 – 1.31 (m, 1H), 1.29 (d, *J* = 6.9 Hz, 4H), 1.27 – 1.18 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 146.70, 141.09, 138.77, 128.66, 127.36, 127.04, 126.96, 126.94, 62.93, 39.61, 38.17, 32.85, 23.91, 22.29.

IR (thin film): v 3341, 2925, 1485, 1452, 1408, 1312, 1073, 1039, 1007, 836 cm^{-1}.

HRMS (EI) (m/z): [M^+] calculated for $C_{18}H_{22}O$, 254.1671 found, 254.1666.

5-(Biphenyl-4-yl)hexyl pivalate; compound 24



The general procedure was followed using $NiCl_2$·dme (2.2 mg, 0.01 mmol), 4,4'-di-*tert*-2,2'-bipyridine (2.7 mg, 0.01 mmol), 4-bromobiphenyl (35 mg, 0.2 mmol), potassium trifluoro(6-(pivaloyloxy)hexan-2-yl)borate (88 mg, 0.3 mmol), $Ir[dFCF_3ppy]_2(bpy)PF_6$ (5.0 mg, 0.005 mmol), and Cs_2CO_3 (98 mg, 0.3 mmol) in 4 mL dioxanes. The crude residue was purified via column chromatography (5% EtOAc in hexanes) to afford the desired product (58 mg, 0.173 mmol, 86% % yield).

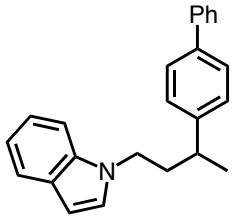
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 – 7.56 (m, 2H), 7.55 – 7.50 (m, 2H), 7.47 – 7.40 (m, 2H), 7.35 – 7.30 (m, 1H), 7.28 – 7.23 (m, 2H), 4.03 (t, *J* = 6.6 Hz, 2H), 2.78 – 2.68 (m, 1H), 1.71 – 1.54 (m, 4H), 1.39 – 1.26 (m, 5H), 1.16 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 178.54, 146.54, 141.13, 138.83, 128.66, 127.34, 127.05, 126.97, 126.94, 64.14, 39.48, 38.69, 37.87, 28.64, 27.15, 23.96, 22.29.

IR (thin film): v 2958, 1725, 1485, 1283, 1152, 837, 765, 732, 696 cm^{-1}.

HRMS (EI) (m/z): [$M+H^+$] calculated for $C_{23}H_{31}O_2$, 339.2319 found, 339.2316.

1-(3-(Biphenyl-4-yl)butyl)-1*H*-indole; compound 25



The general procedure was followed using $NiCl_2$·dme (2.2 mg, 0.01 mmol), 4,4'-di-*tert*-2,2'-bipyridine (2.7 mg, 0.01 mmol), 4-bromobiphenyl (35 mg, 0.2 mmol), potassium (4-(1*H*-indol-1-yl)butan-2-yl)trifluoroborate (88 mg, 0.3 mmol), $Ir[dFCF_3ppy]_2(bpy)PF_6$ (5.0 mg, 0.005 mmol), and Cs_2CO_3 (98 mg, 0.3 mmol) in 4 mL dioxanes. The crude residue was purified via column chromatography (1% EtOAc in hexanes) to afford the desired product (43 mg, 0.131 mmol, 65% % yield).

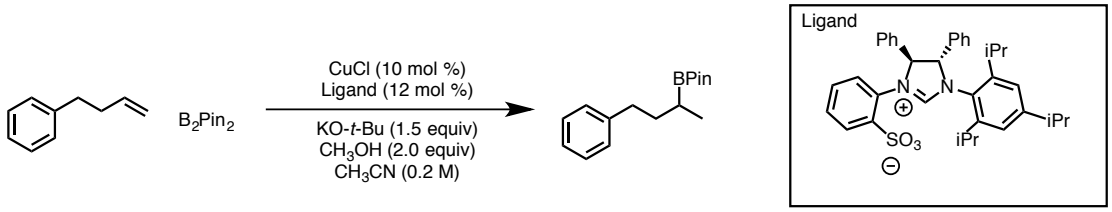
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 – 7.56 (m, 5H), 7.46 (td, *J* = 7.8, 2.0 Hz, 2H), 7.36 (dd, *J* = 8.3, 6.3 Hz, 1H), 7.29 (dd, *J* = 8.2, 1.9 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.13 – 7.09 (m, 1H), 7.06 – 7.03 (m, 1H), 6.51 – 6.46 (m, 1H), 4.11 – 3.97 (m, 2H), 2.82 – 2.72 (m, 1H), 2.27 – 2.12 (m, 2H), 1.32 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 145.09, 140.91, 139.35, 135.82, 128.75, 128.60, 127.68, 127.46, 127.37, 127.13, 127.00, 121.30, 120.93, 119.20, 109.36, 100.97, 44.57, 38.04, 37.11, 22.87.

IR (thin film): v 2956, 2157, 1510, 1485, 1462, 1315, 1262, 1007, 763, 731 cm^{-1}.

HRMS (EI) (m/z): [M+H^+] calculated for $C_{24}H_{23}N$, 326.1903 found, 326.1900.

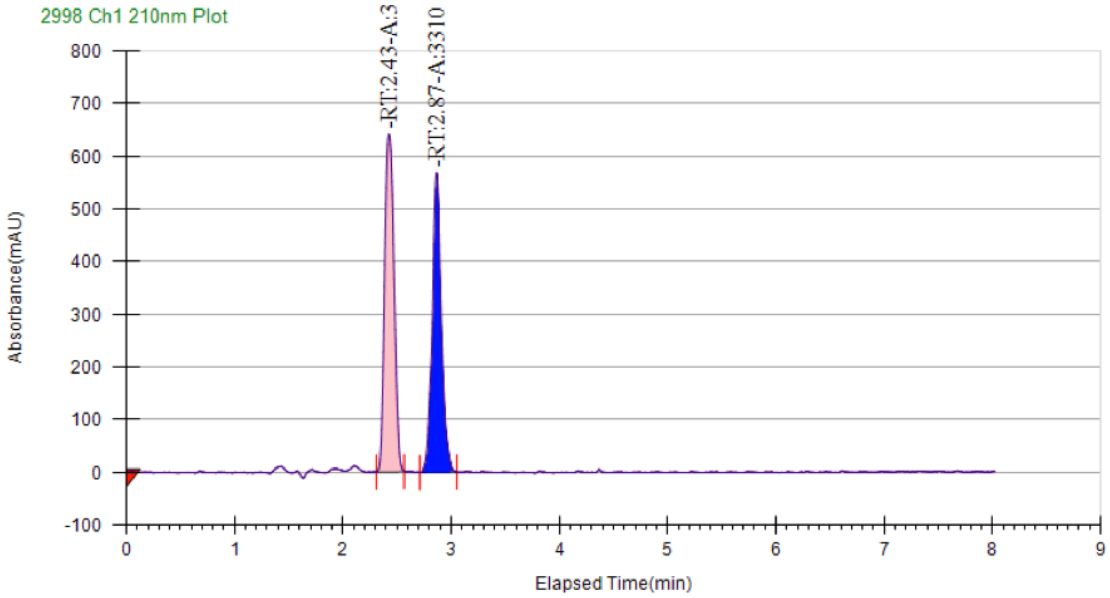
Enantioselectivity Investigation



1.5 mL of acetonitrile was added to a solid mixture of CuCl (2.0 mg, 0.02 mmol), Ligand (11.6 mg, 0.024 mmol), and t-BuOK (34 mg, 0.3 mmol) under N_2. The reaction was allowed to stir at rt for 10 minutes. B_2Pin_2 (102 mg, 0.4 mmol) was added under N_2 and the reaction was allowed to stir for an additional 30 minutes at rt. 4-Phenyl-1-butene (26 mg, 0.2 mmol) and MeOH (13 mg, 0.4 mmol) were added to the mixture by syringe. The reaction mixture was allowed to stir at rt for 2 h and was then filtered through silica gel, eluting with 50% v/v EtOAc/hexanes. The solvent was removed *in vacuo*. The crude residue was purified via flash chromatography (100% hexanes to 4% EtOAc in hexanes) to afford the desired product as an 86:14 mixture of regioisomers (29 mg, 0.11 mmol, 56% yield). Following literature precedent, conversion of the secondary alkylborane to the secondary alcohol was performed for enantioselectivity determination.[11]

The enantioselectivity was determined by SFC analysis: OD-H column, 3 mL/min, 20% *i*-PrOH, 120 bar, 40 °C.

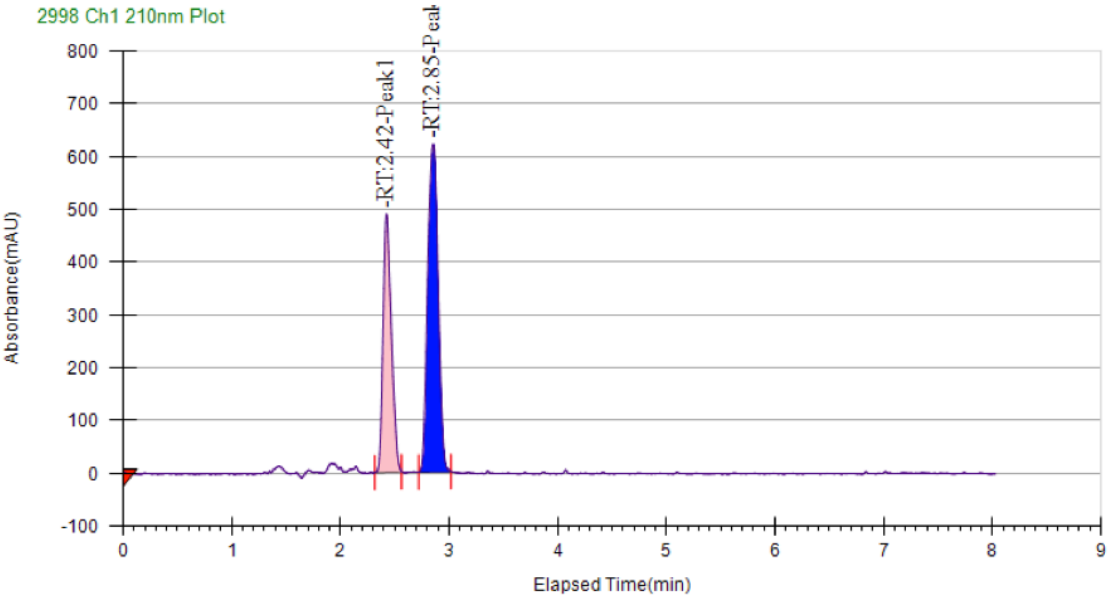
Racemic



Peak Information

Peak No	% Area	Area	Ret. Time	Height	Cap. Factor
1	53.5611	3818.2731	2.43 min	640.5723	0
2	46.4389	3310.5496	2.87 min	568.0121	0

Reaction with Chiral Ligand



Peak Information

Peak No	% Area	Area	Ret. Time	Height	Cap. Factor
1	38.2337	2550.1034	2.42 min	488.6584	0
2	61.7663	4119.684	2.85 min	620.9428	0

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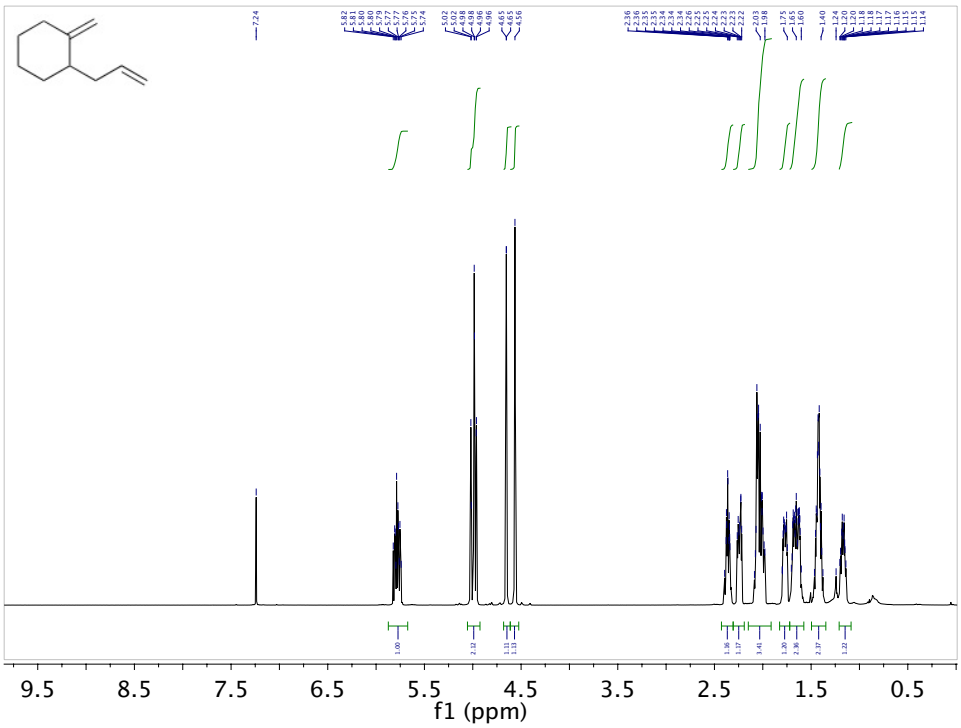
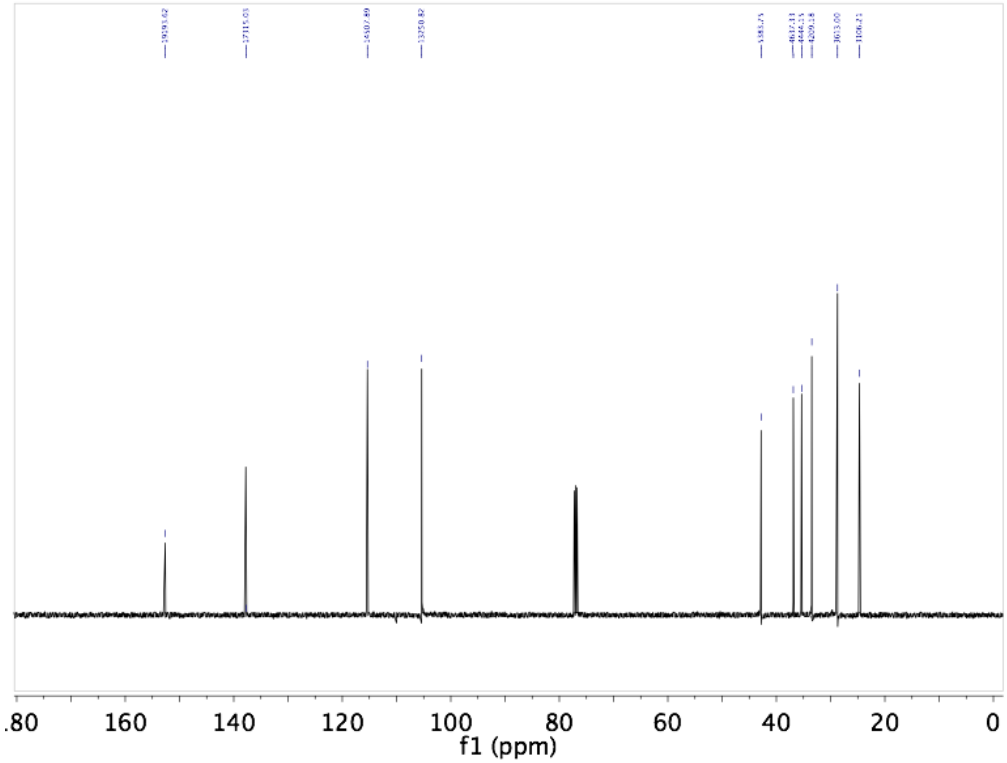
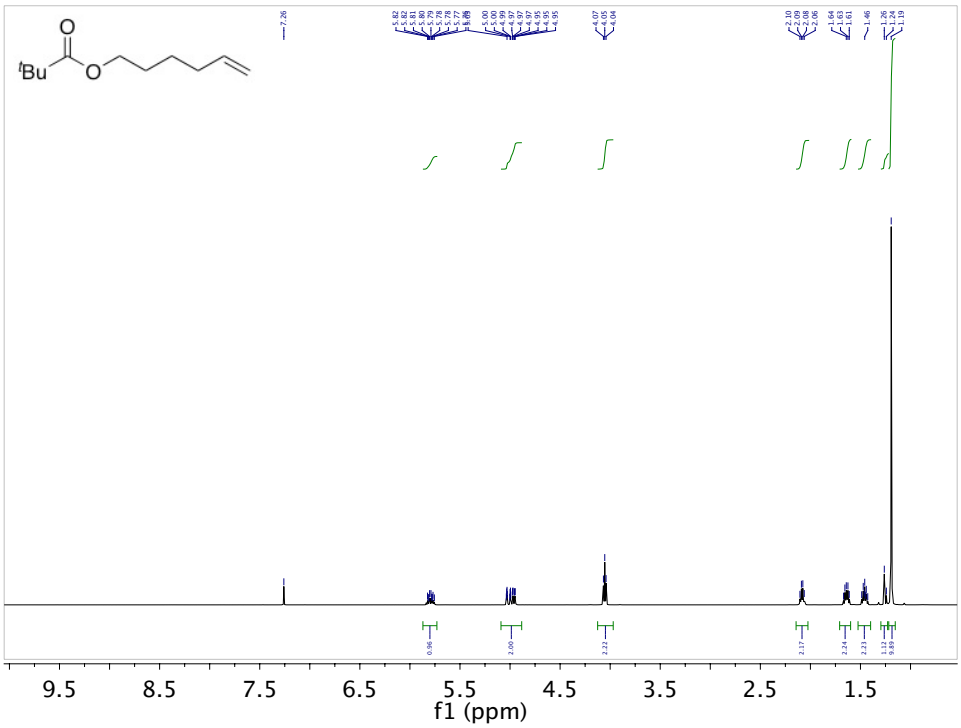
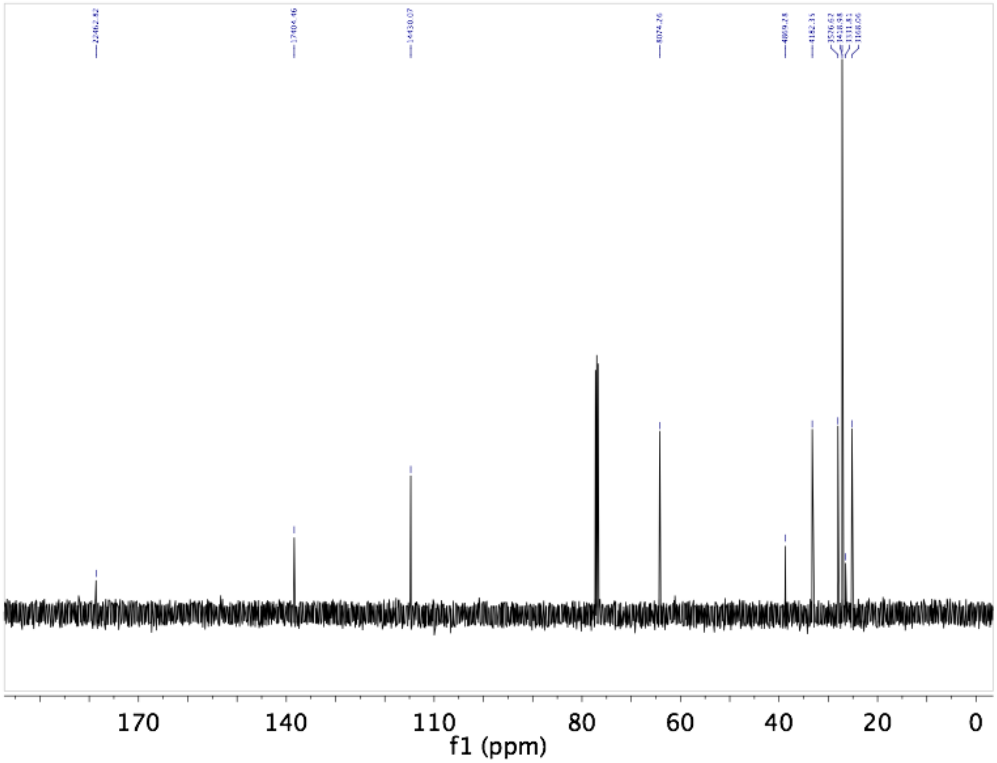
1-Allyl-2-methylenecyclohexane



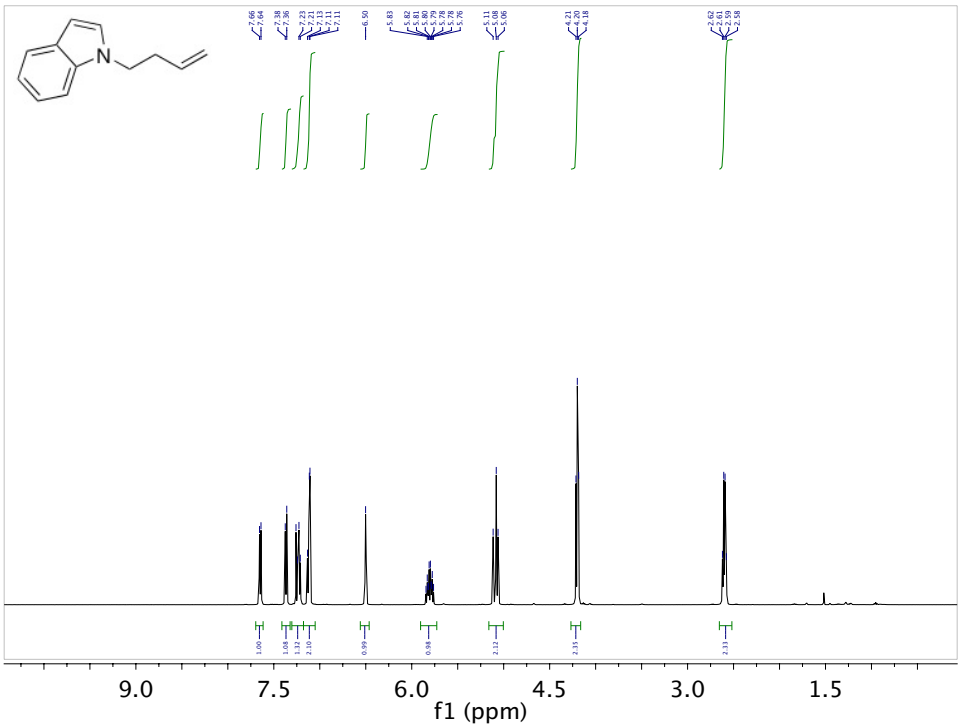


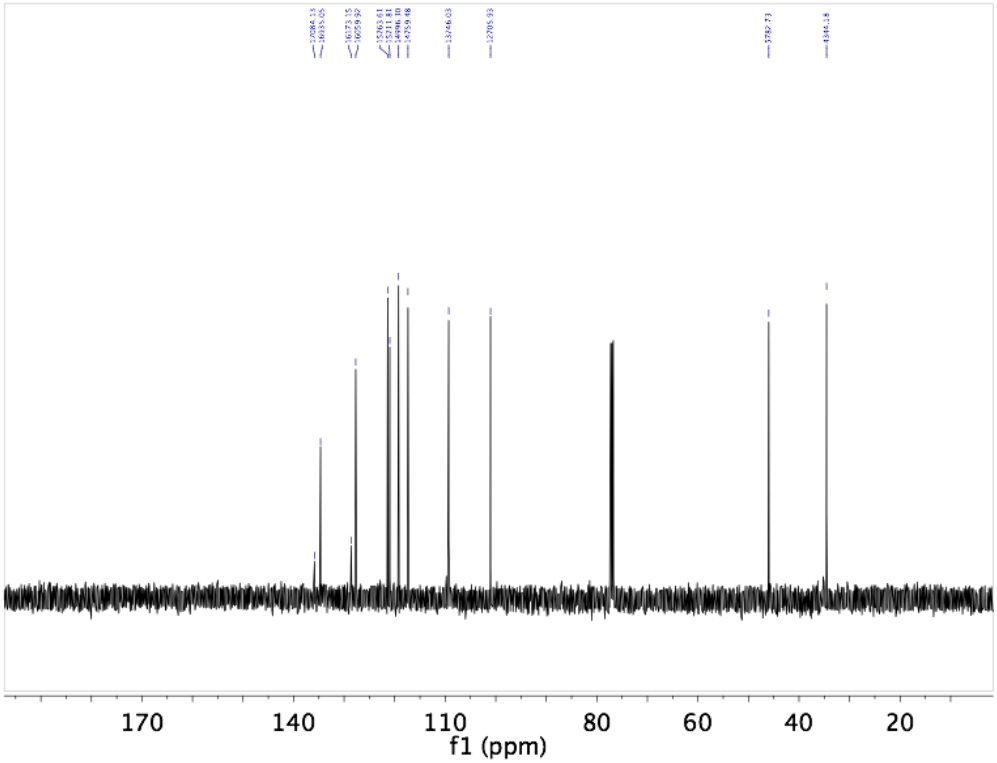
hex-5-enyl pivalate



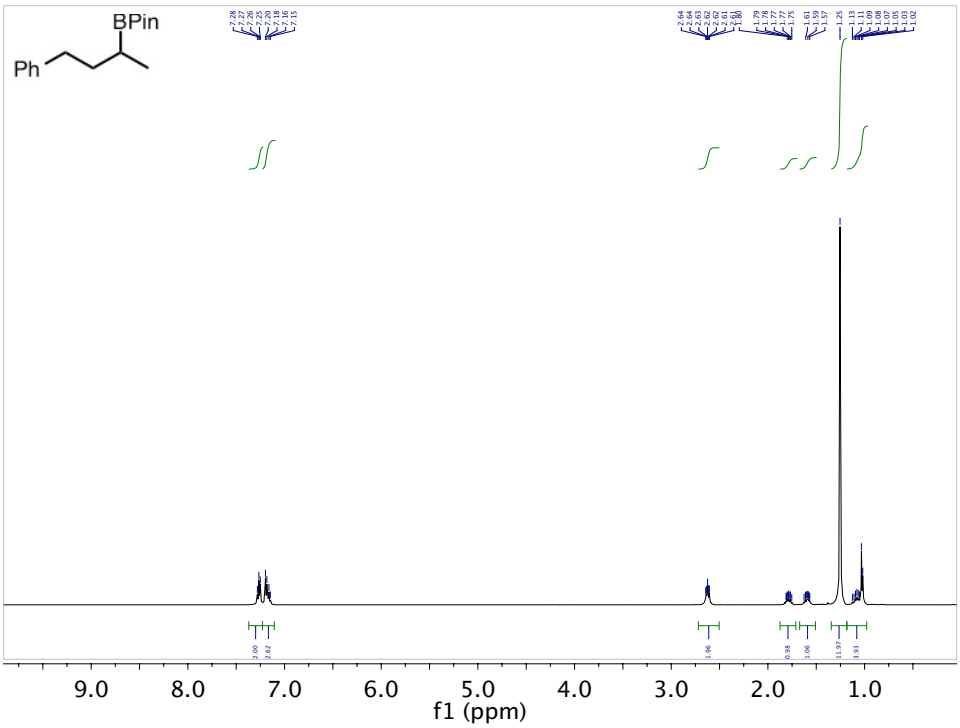


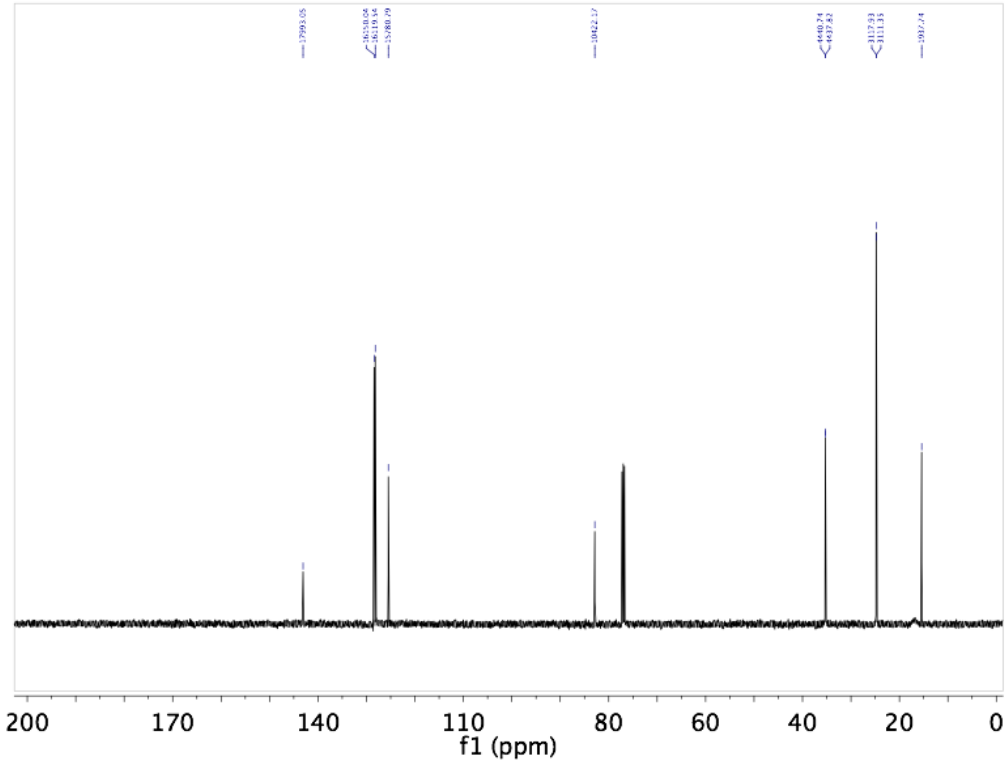
1-(but-3-enyl)-1*H*-indole



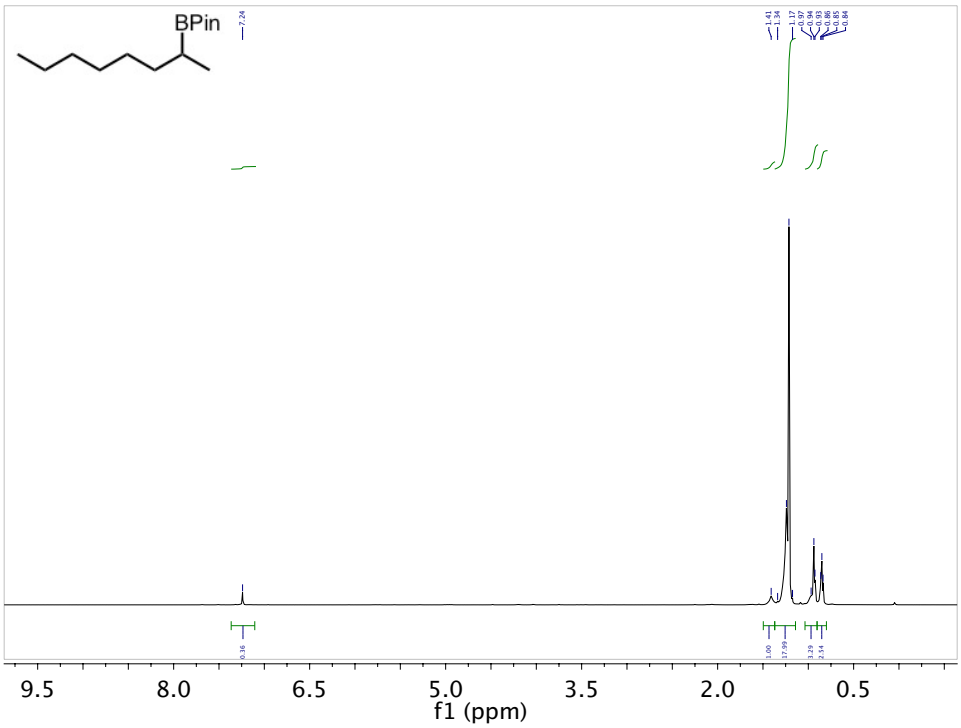


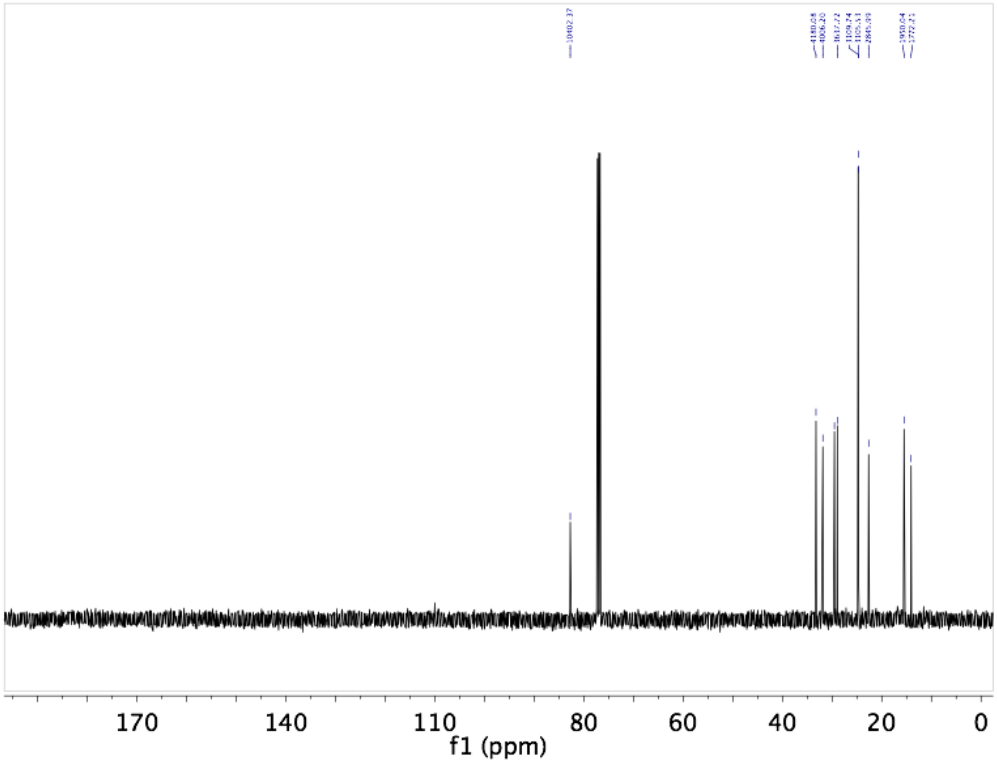
4,4,5,5-tetramethyl-2-(4-phenylbutan-2-yl)-1,3,2-dioxaborolane; compound 2



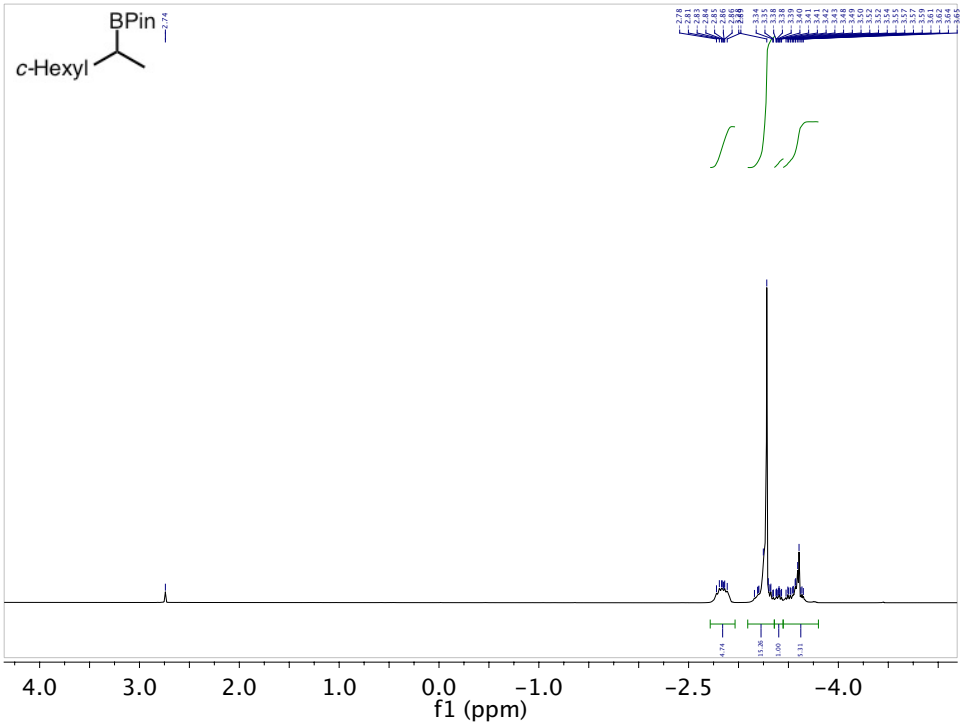


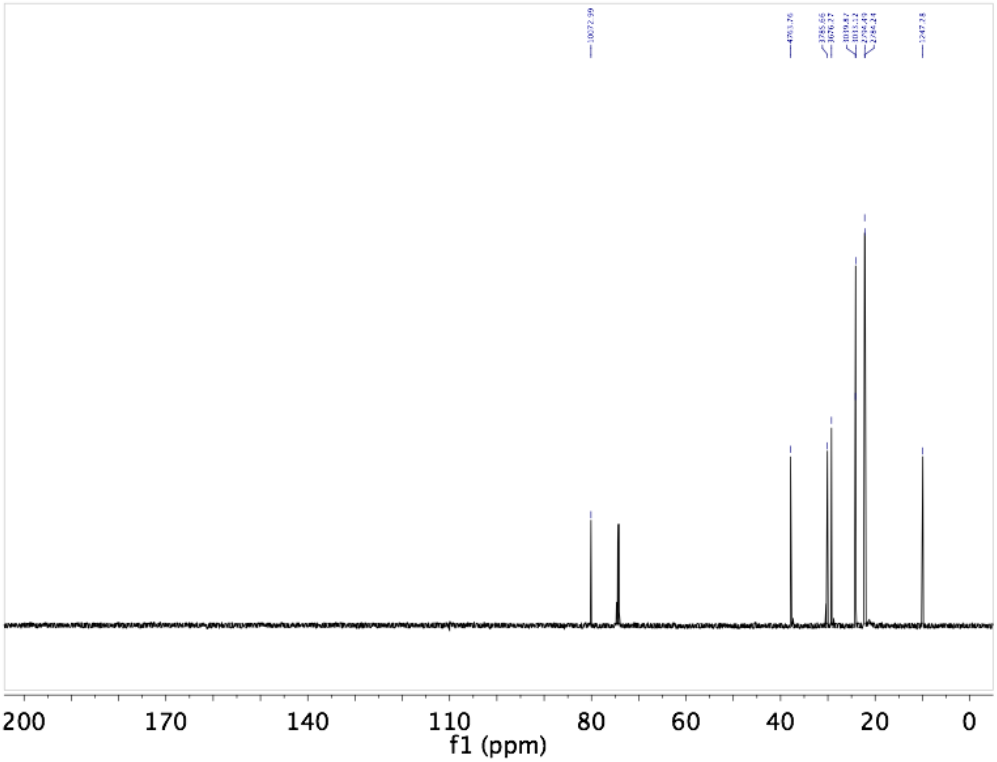
4,4,5,5-tetramethyl-2-(octan-2-yl)-1,3,2-dioxaborolane; compound 3



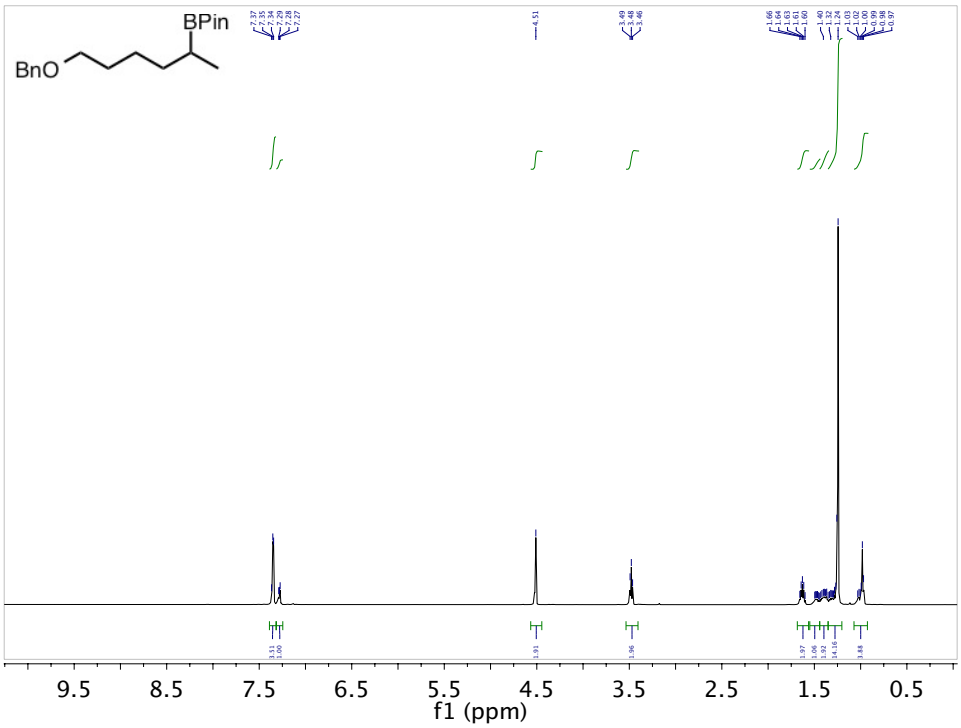


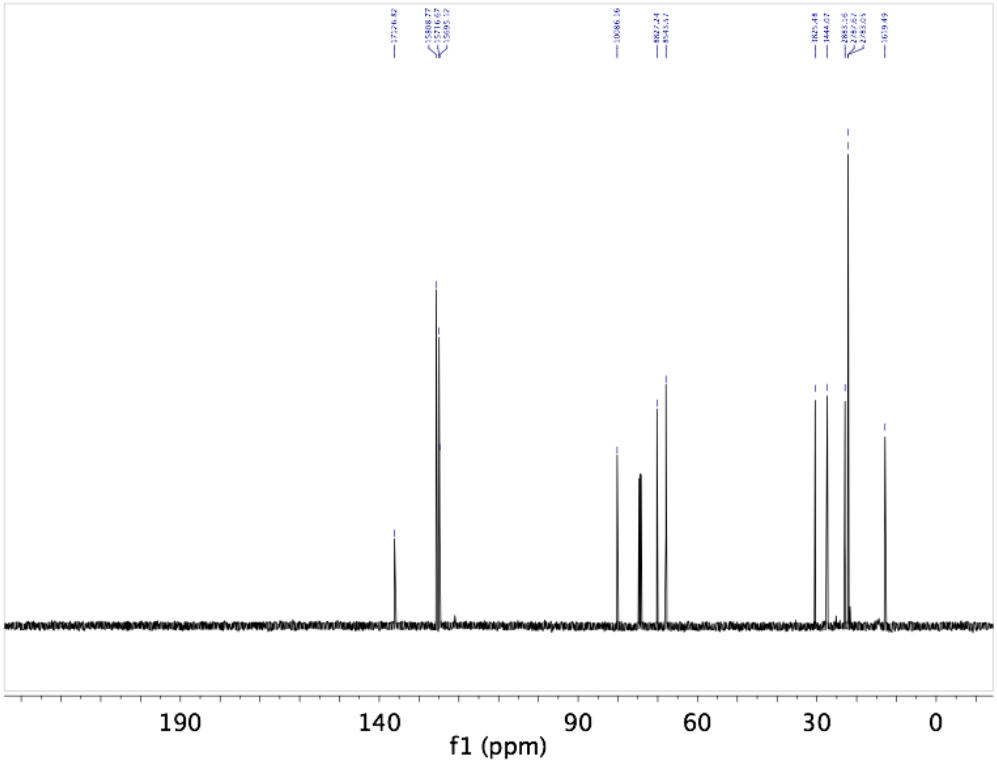
2-(1-cyclohexylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; compound 4



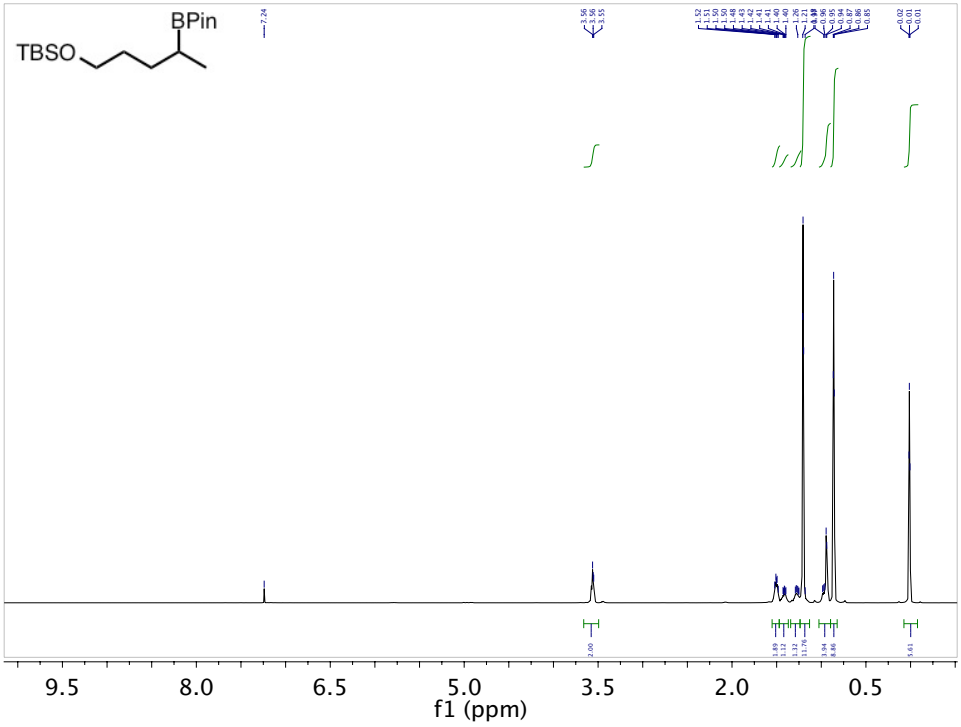


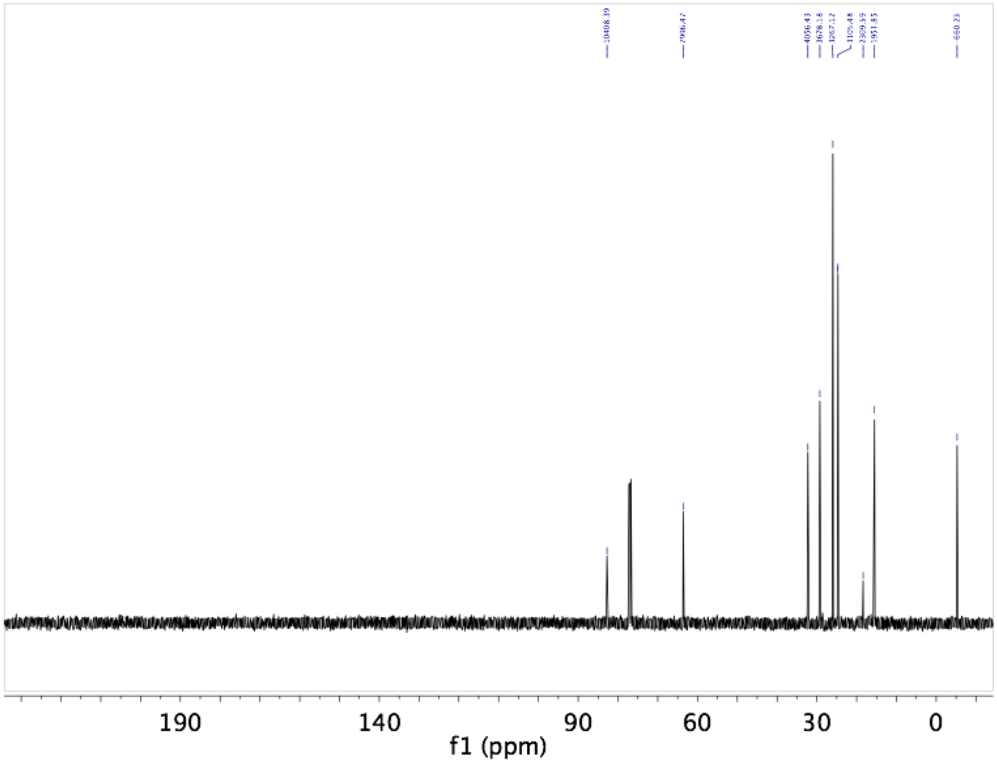
2-(6-(benzyloxy)hexan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; compound 5



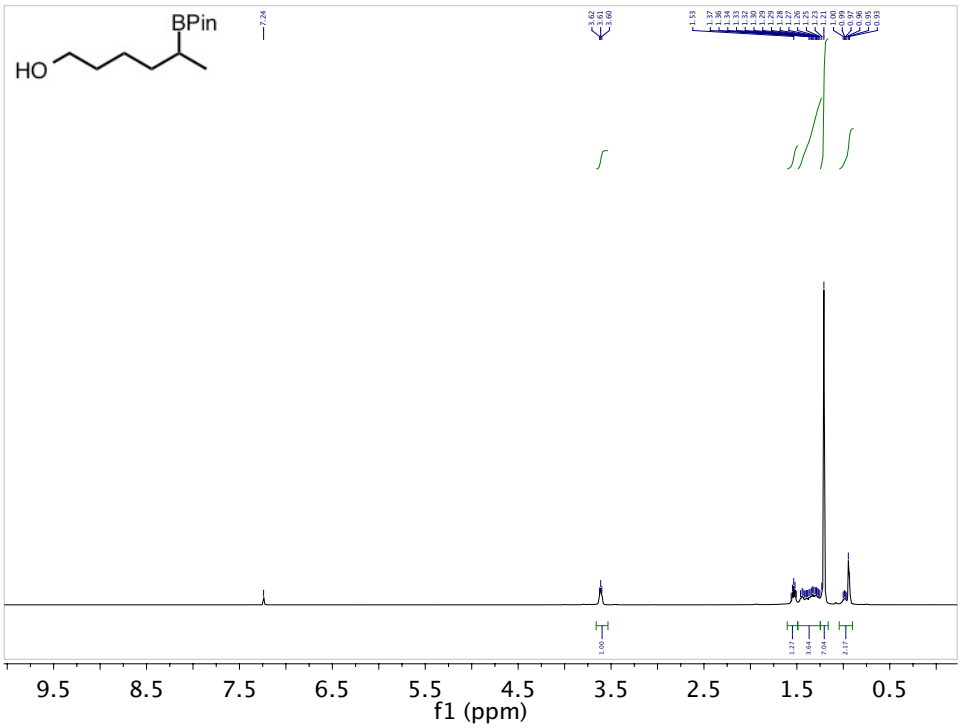


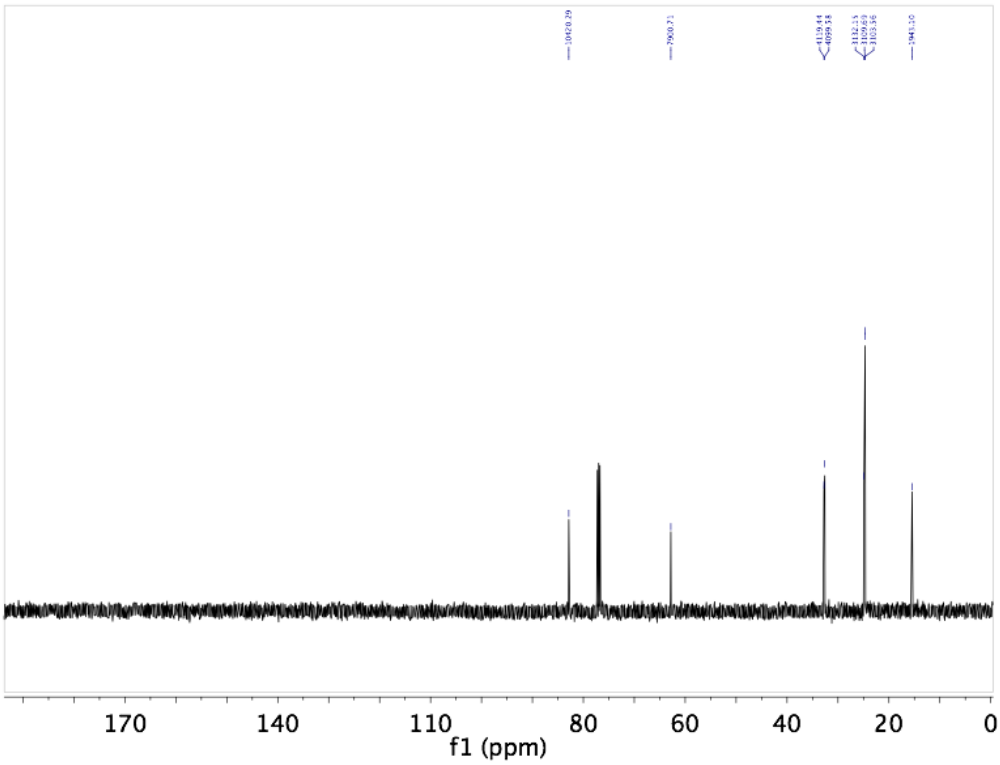
***tert*-butyldimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentyloxy)silane; compound 6**



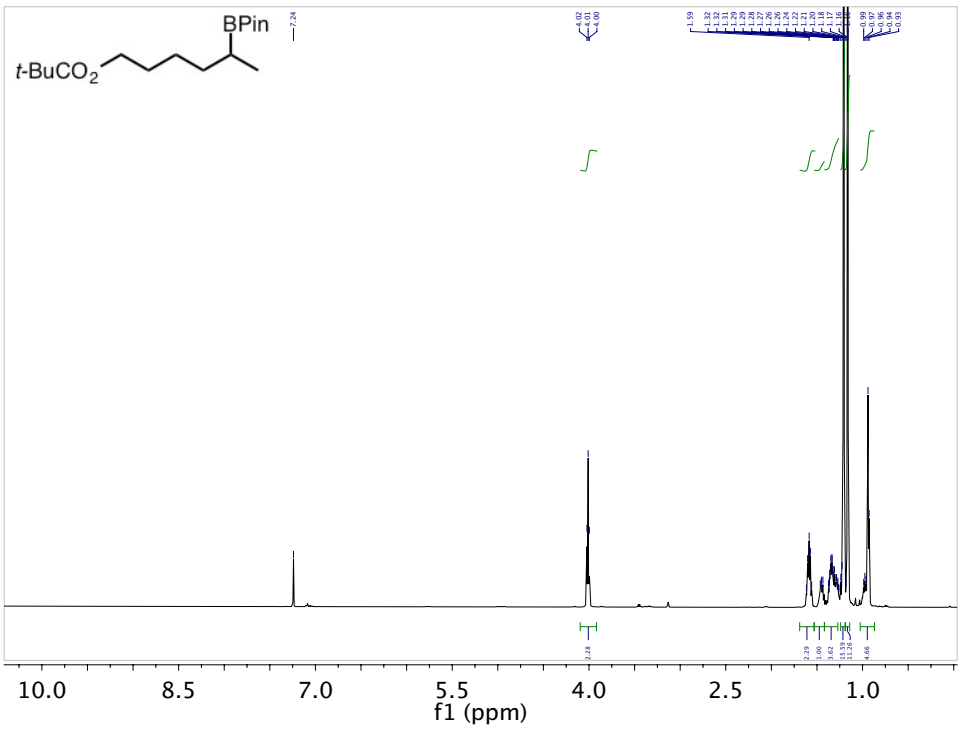


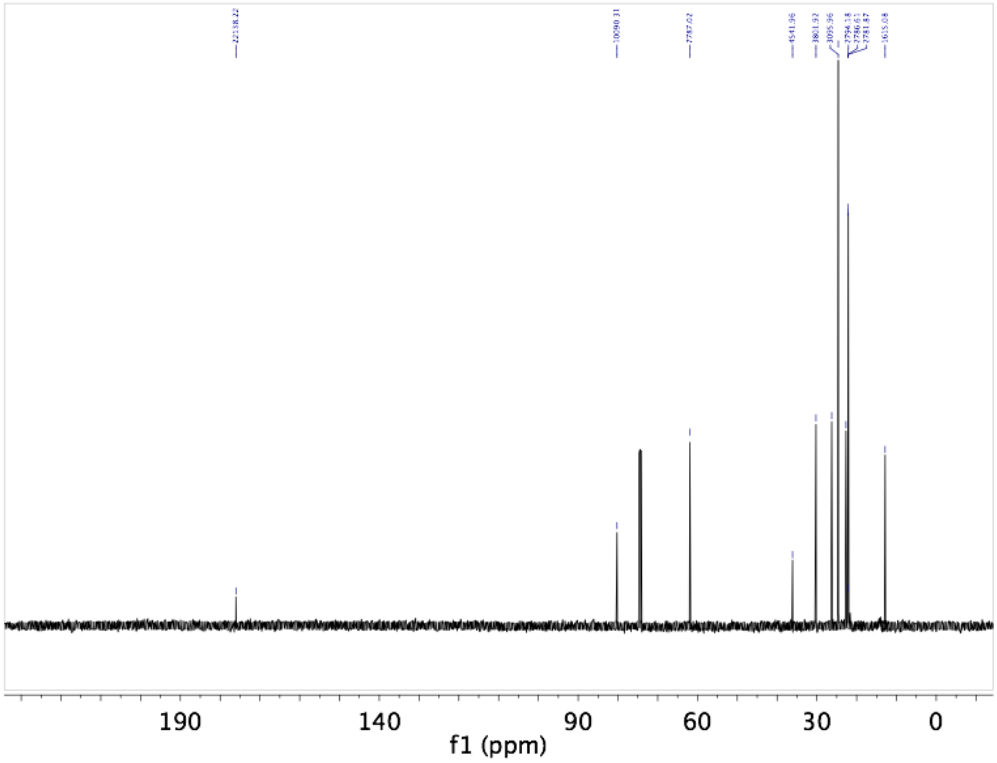
5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-1-ol; compound 7



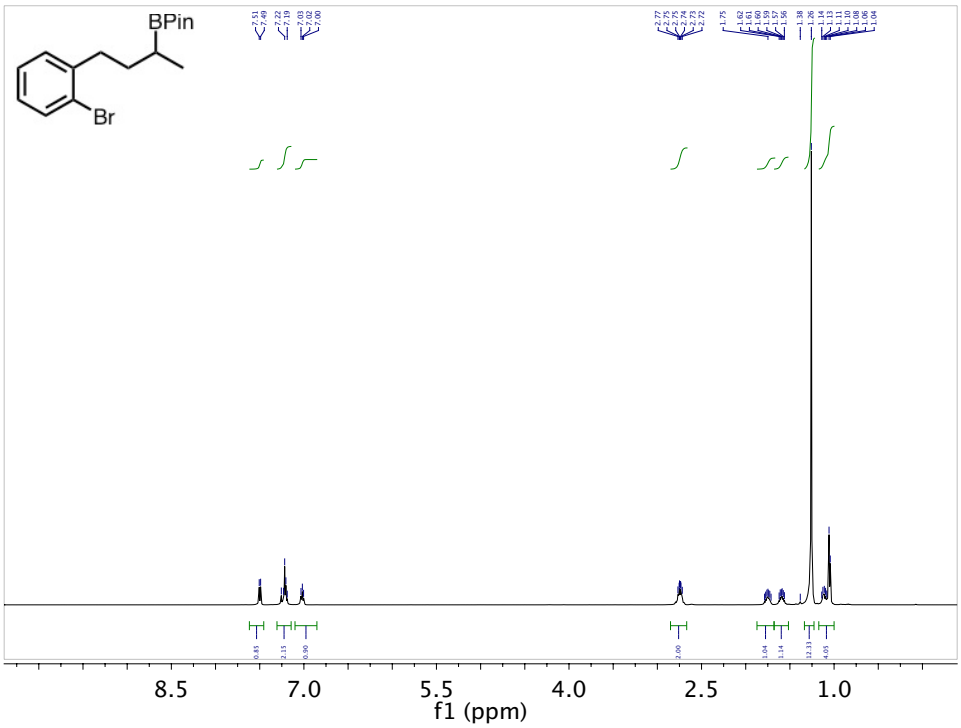


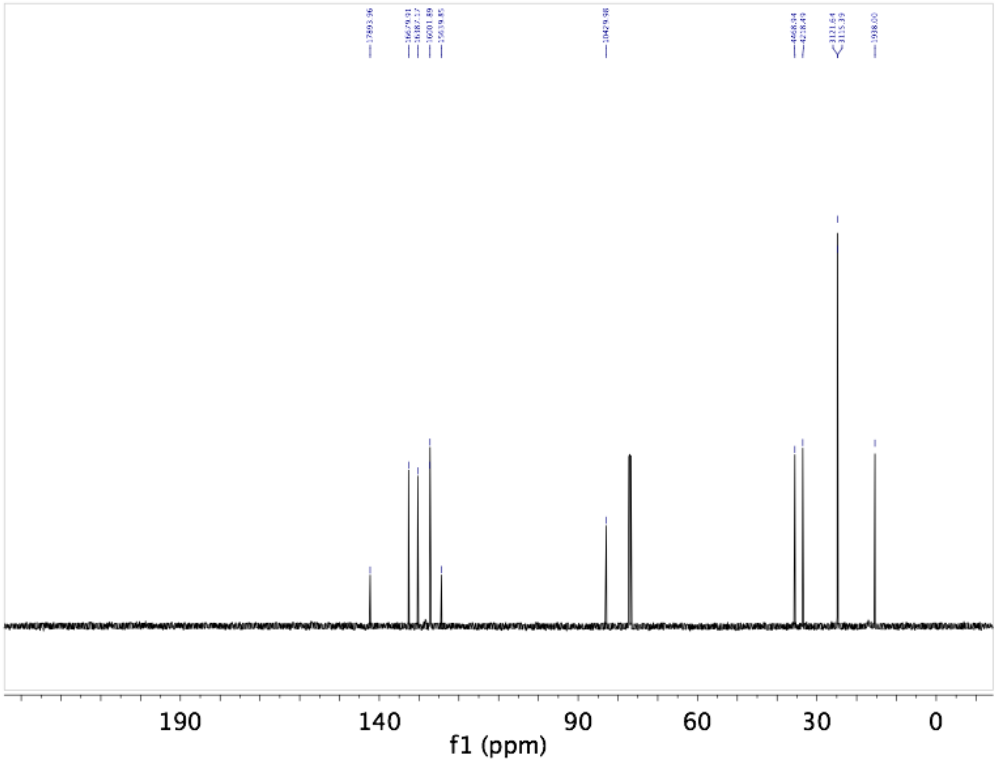
5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexyl pivalate; compound 8



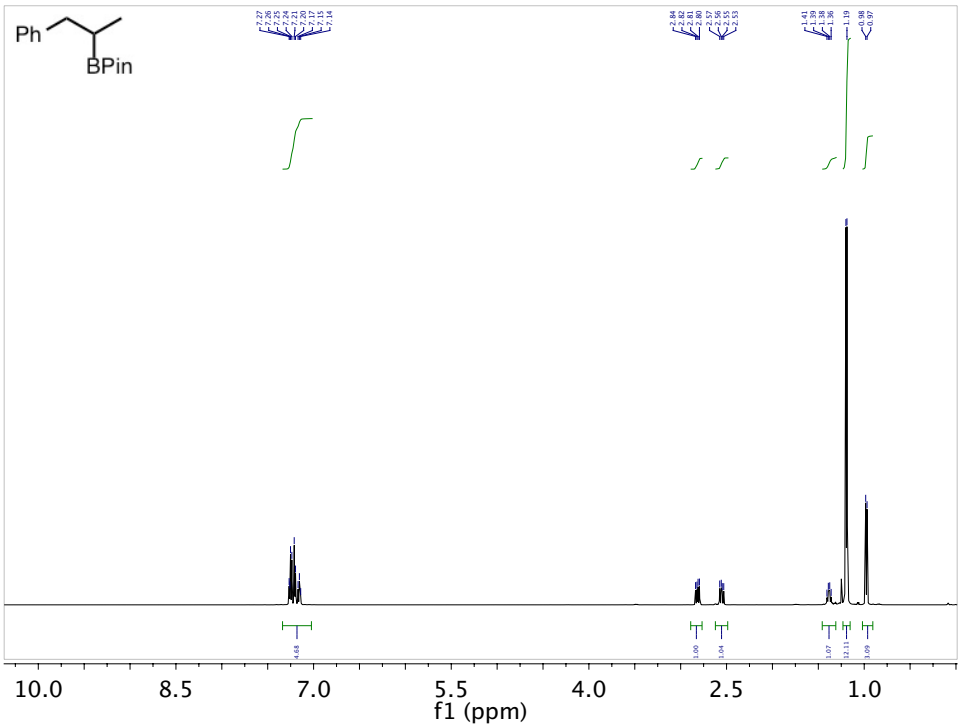


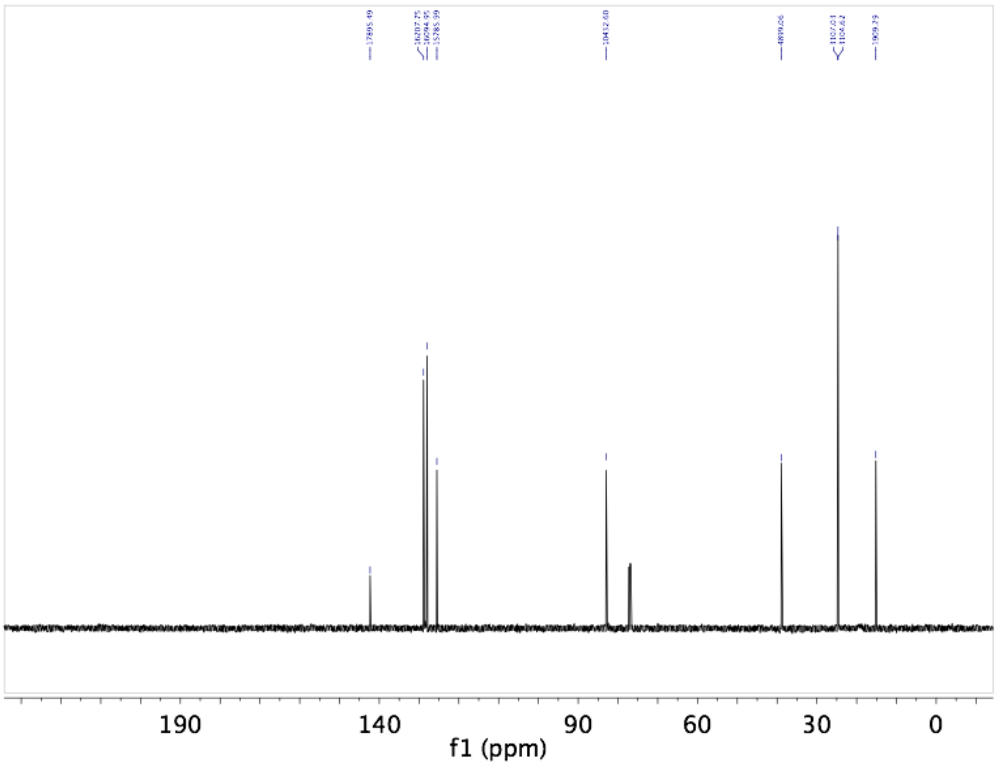
2-(4-(2-bromophenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; compound 9



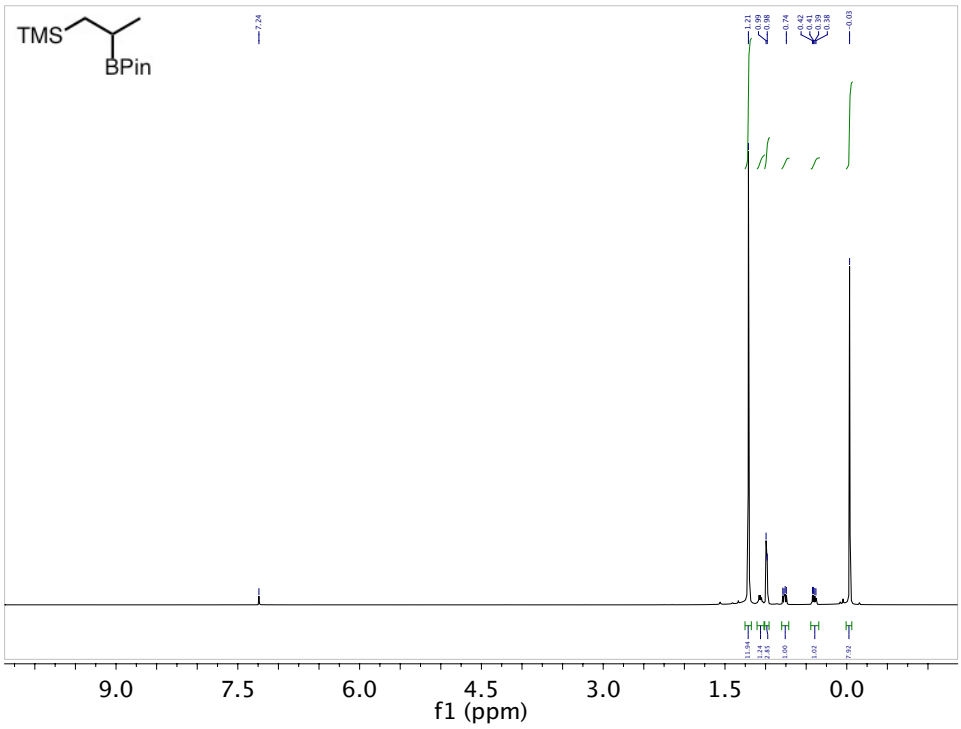


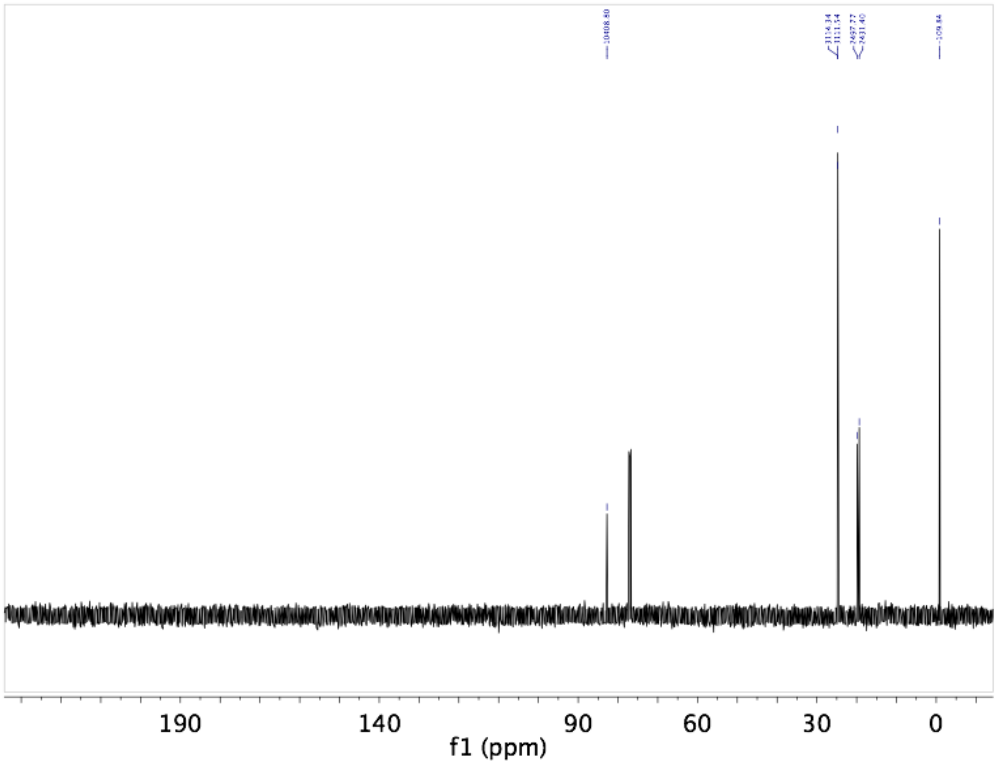
4,4,5,5-tetramethyl-2-(1-phenylpropan-2-yl)-1,3,2-dioxaborolane; compound 10



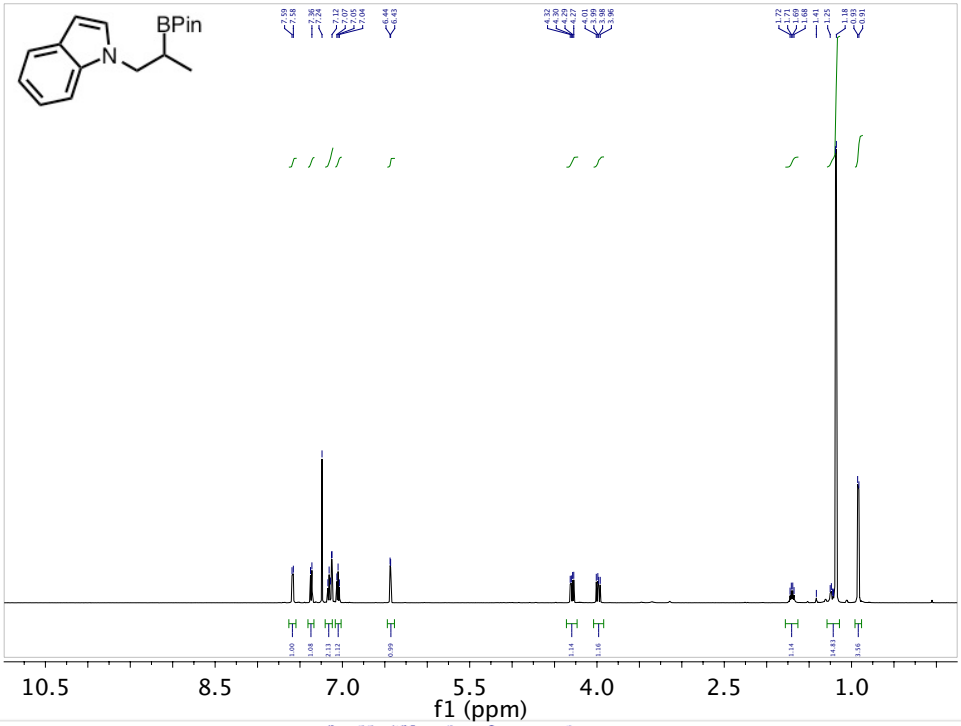


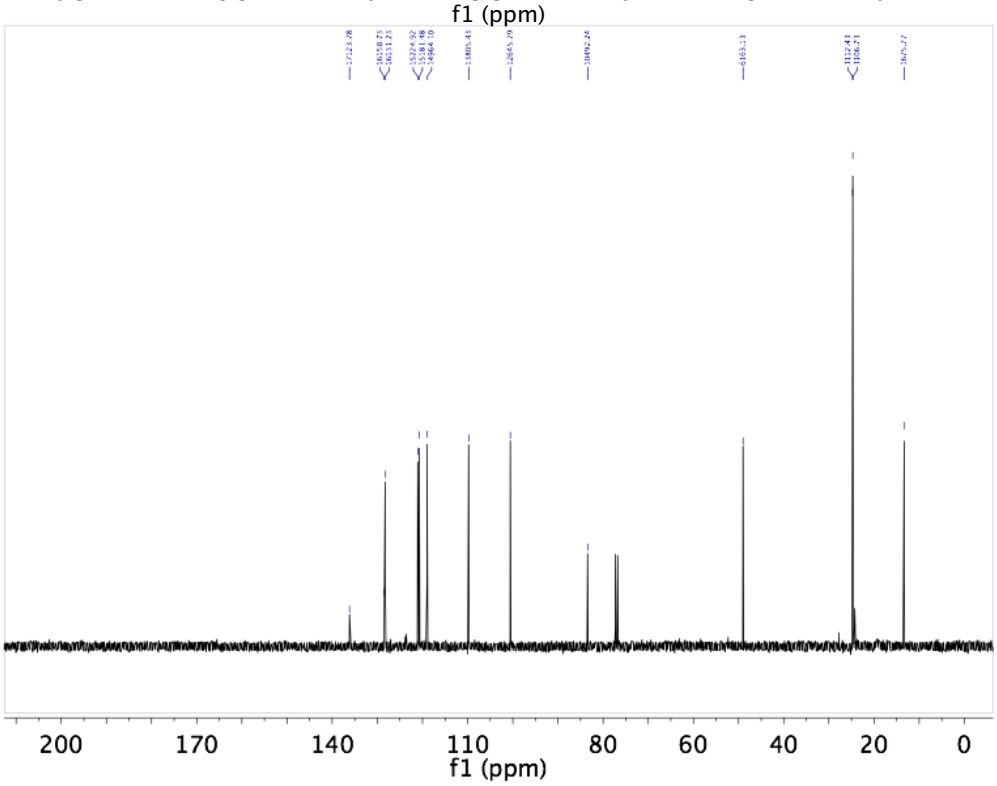
trimethyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)silane; compound 11



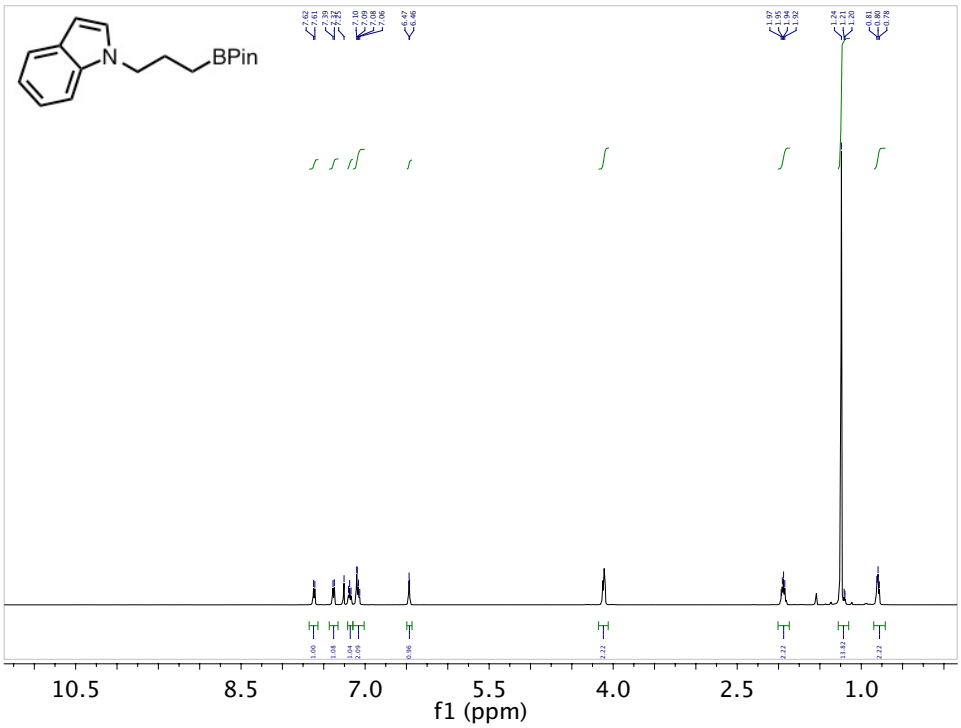


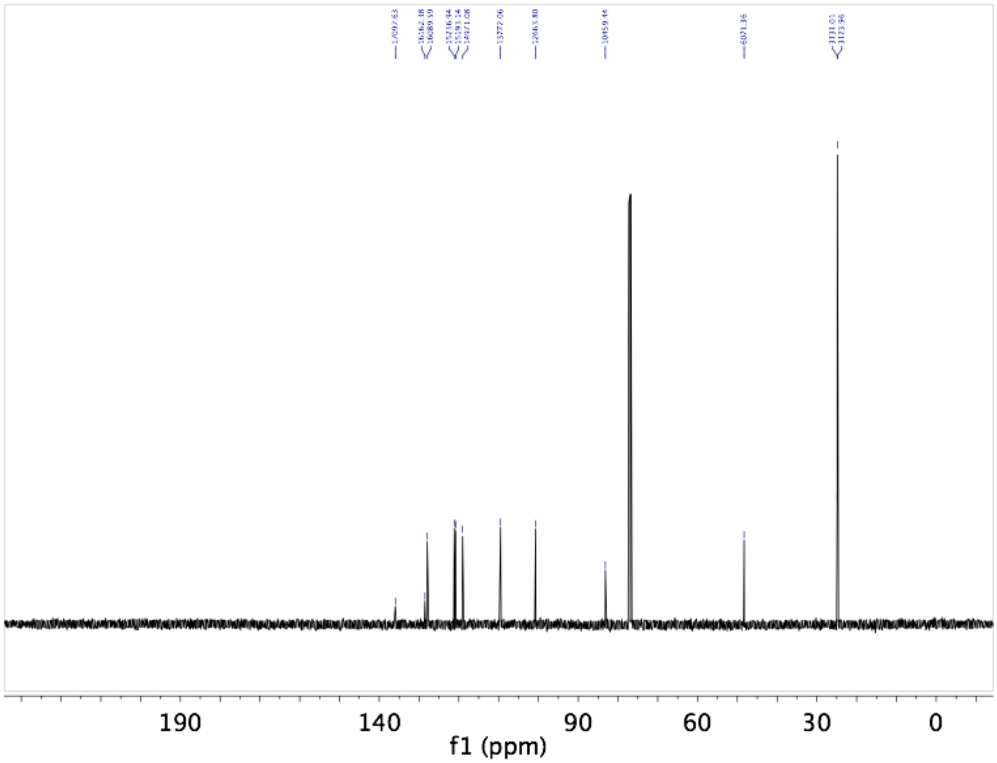
1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1*H*-indole; compound 12



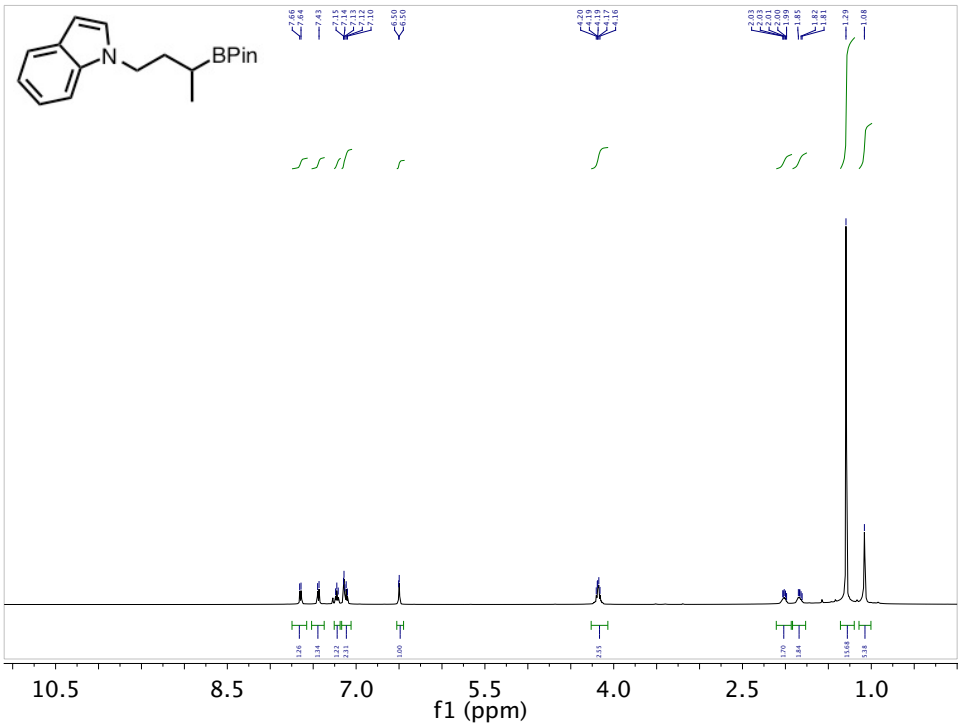


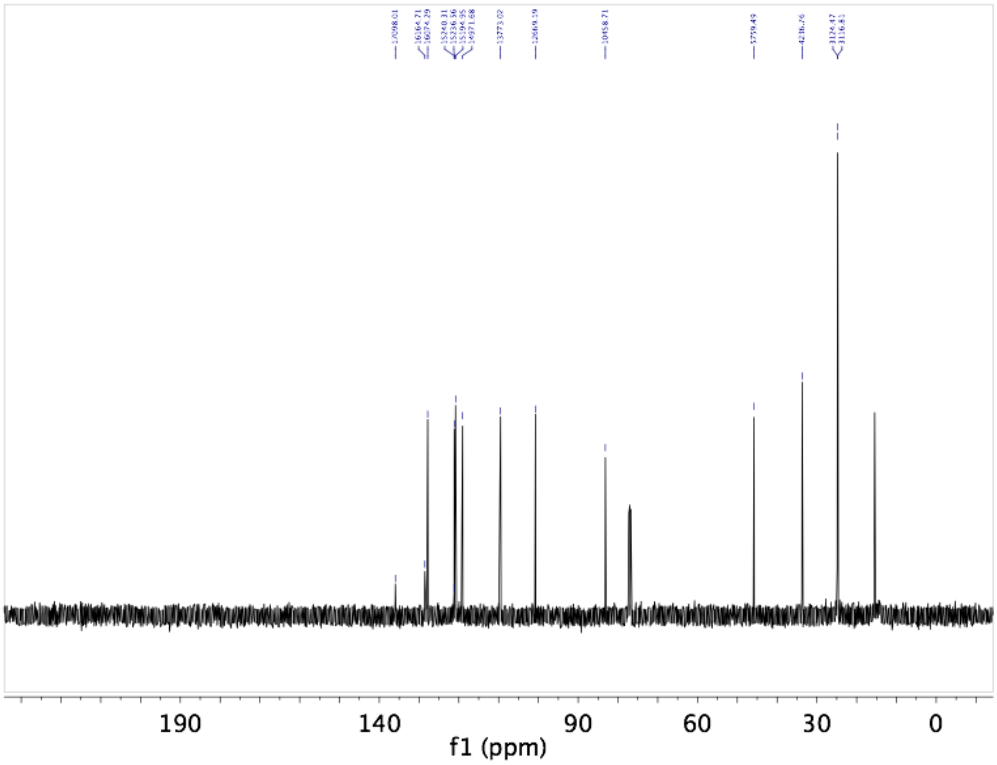
1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-1*H*-indole



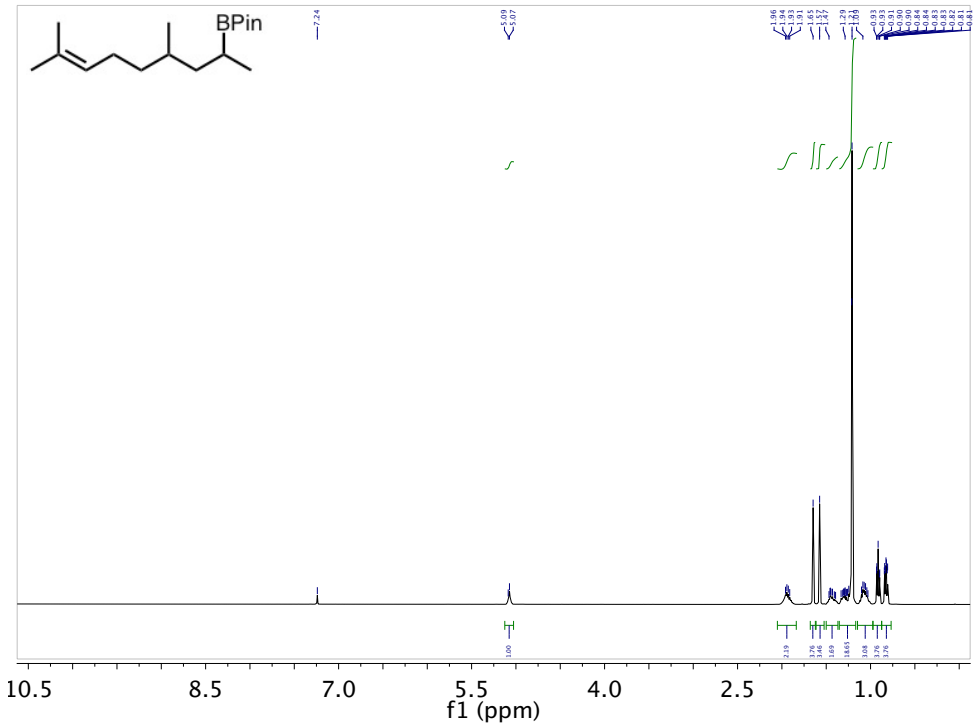


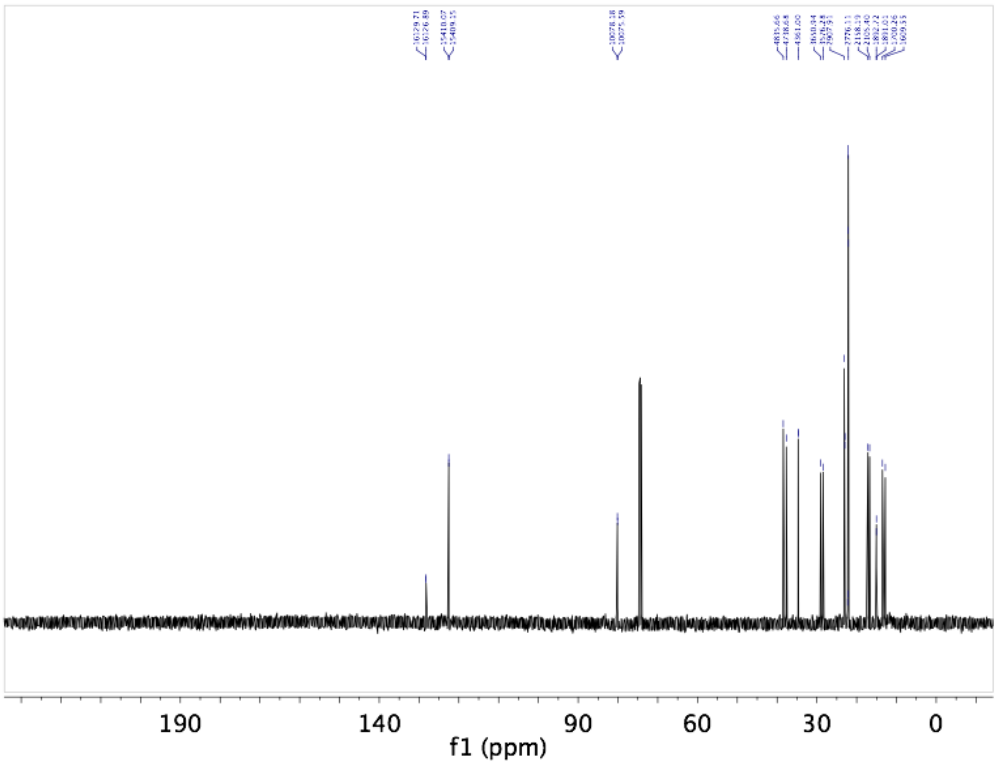
1-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-1*H*-indole; compound 13



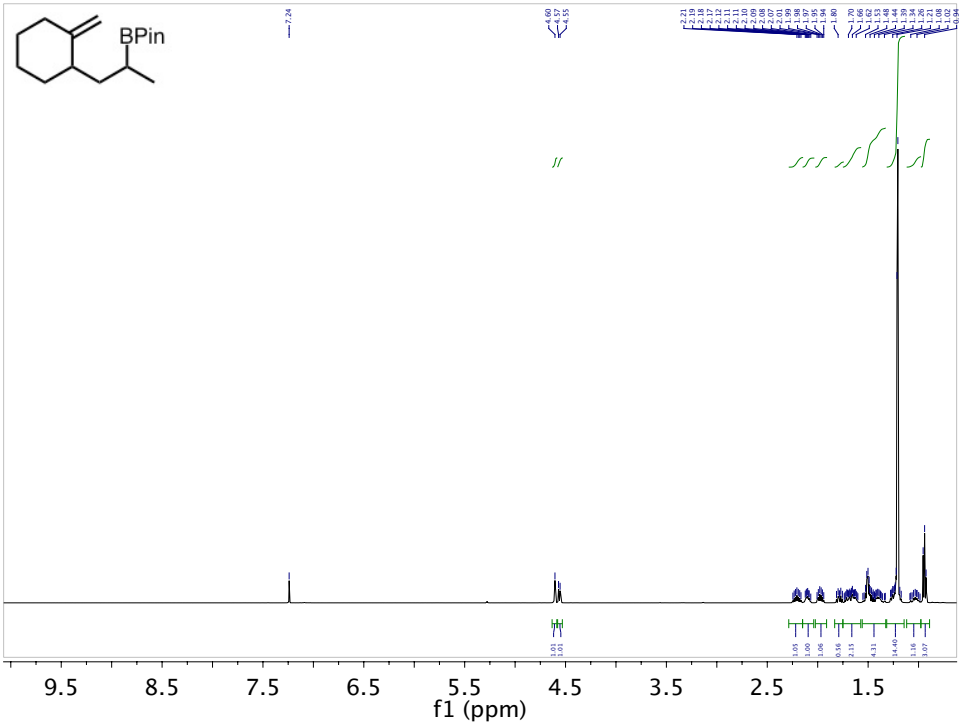


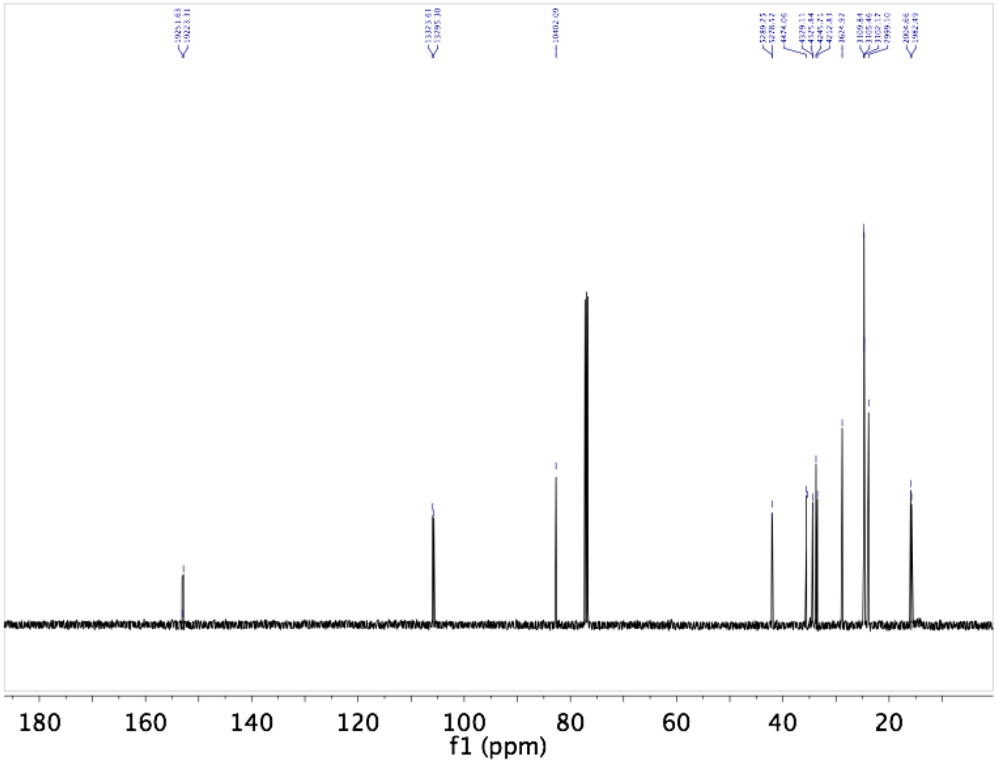
2-((4*R*)-4,8-dimethylnon-7-en-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; compound 14



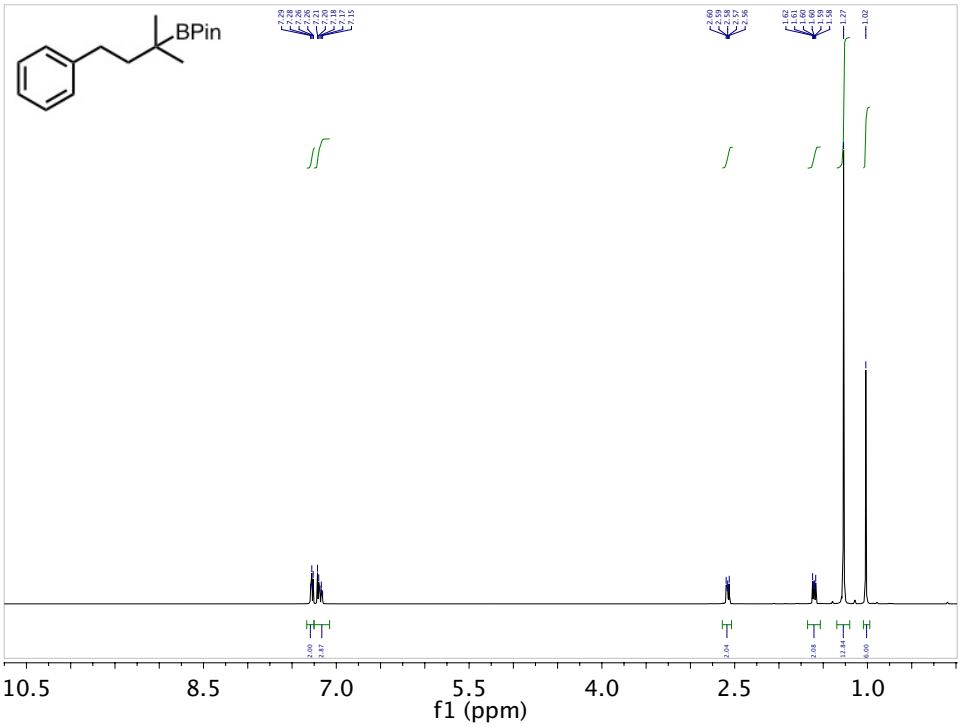


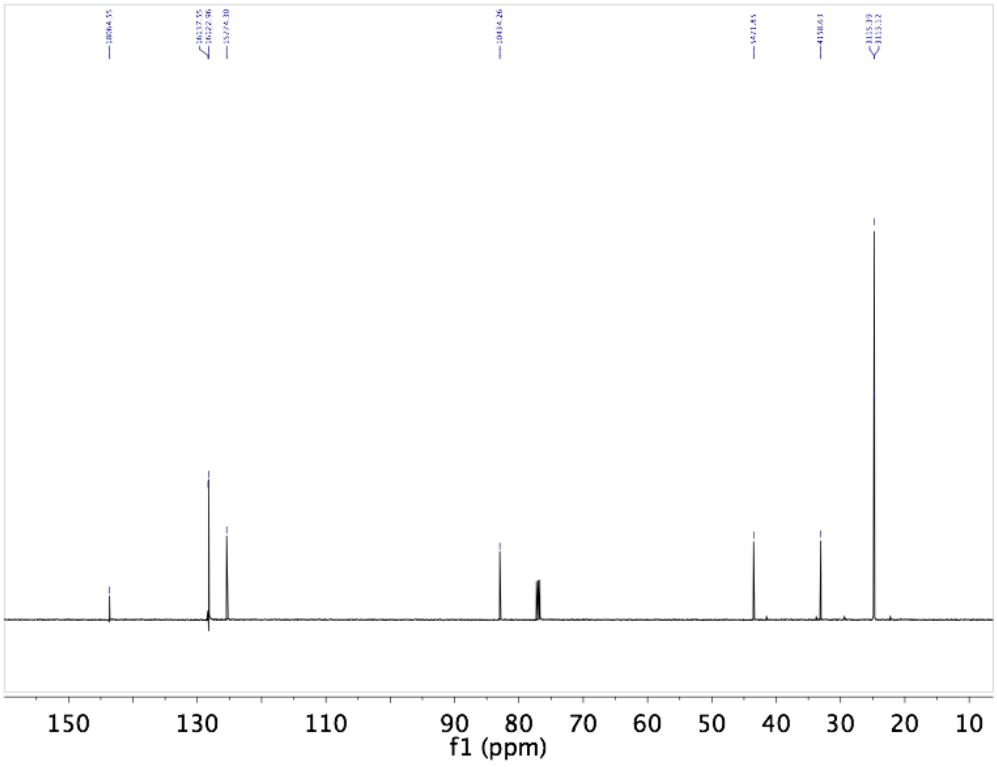
4,4,5,5-tetramethyl-2-(1-(2-methylenecyclohexyl)propan-2-yl)-1,3,2-dioxaborolane; compound 15



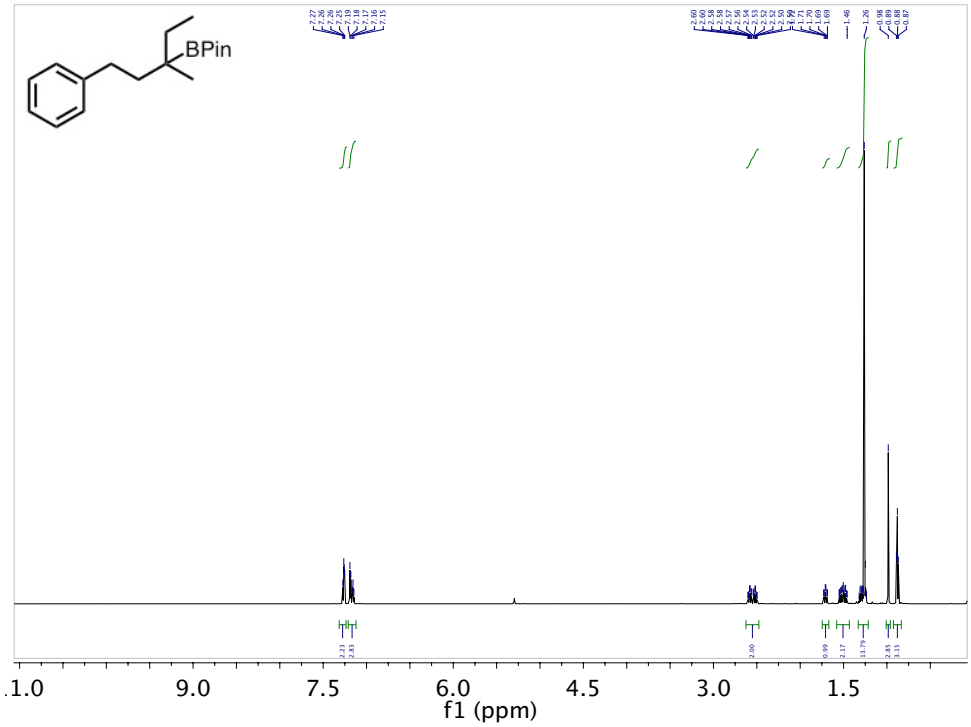


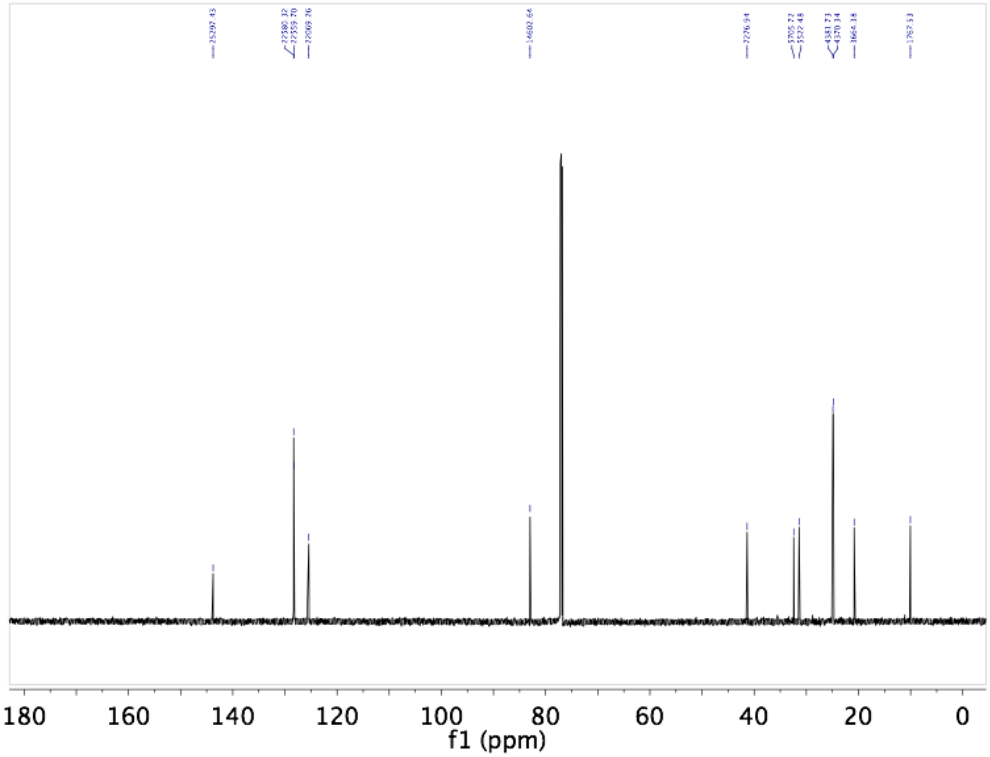
4,4,5,5-tetramethyl-2-(2-methyl-4-phenylbutan-2-yl)-1,3,2-dioxaborolane; compound 16



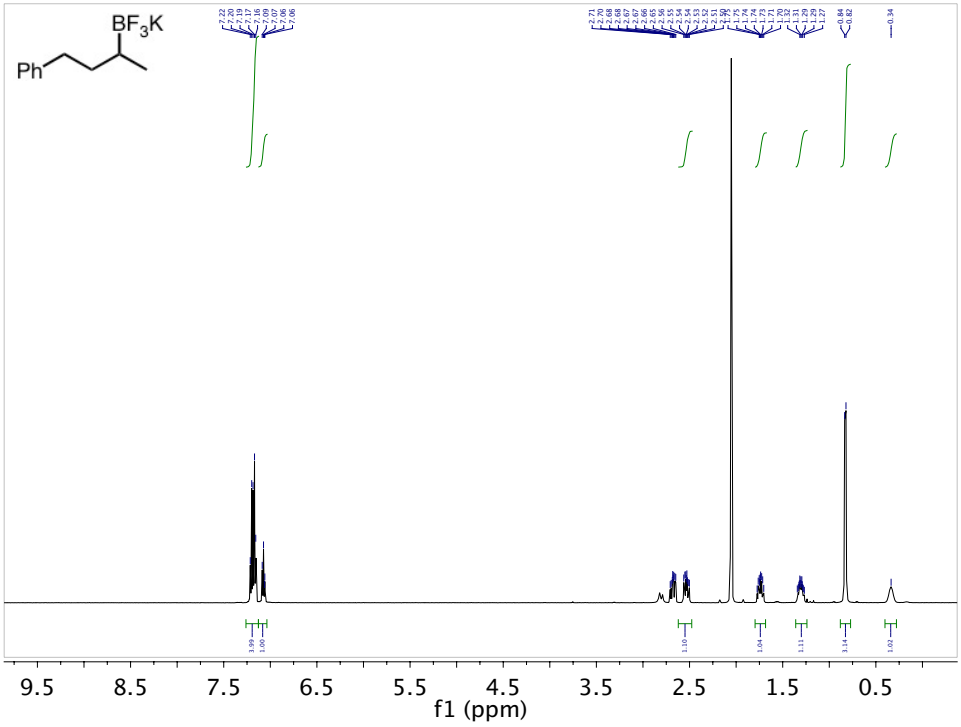


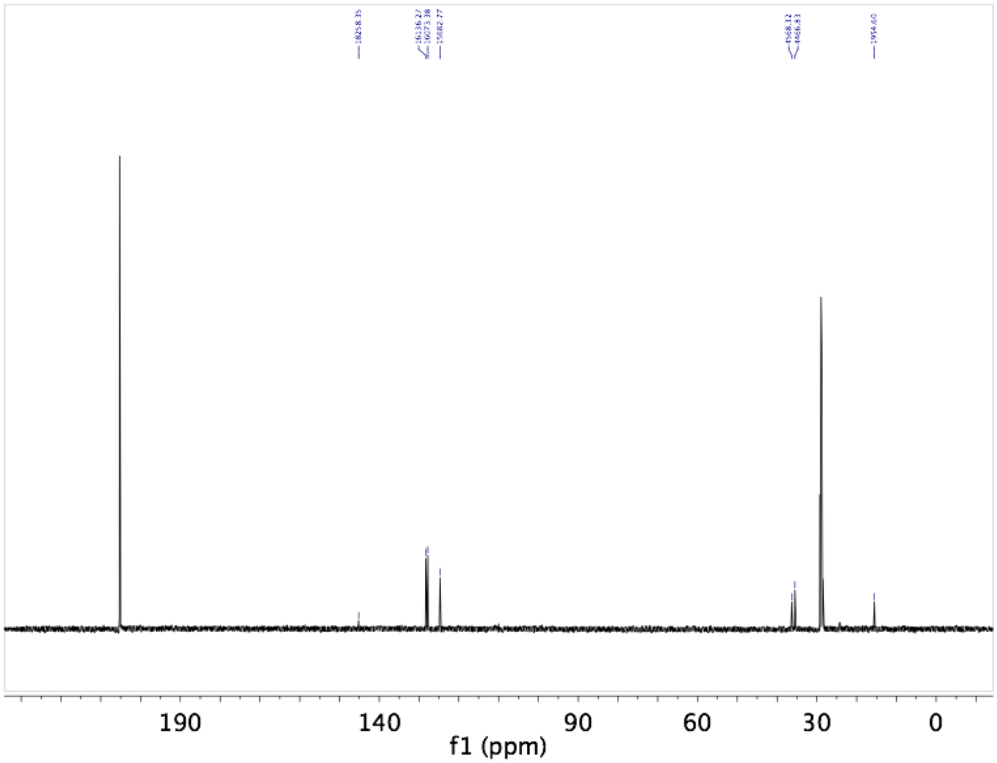
4,4,5,5-tetramethyl-2-(3-methyl-1-phenylpentan-3-yl)-1,3,2-dioxaborolane, compound 17



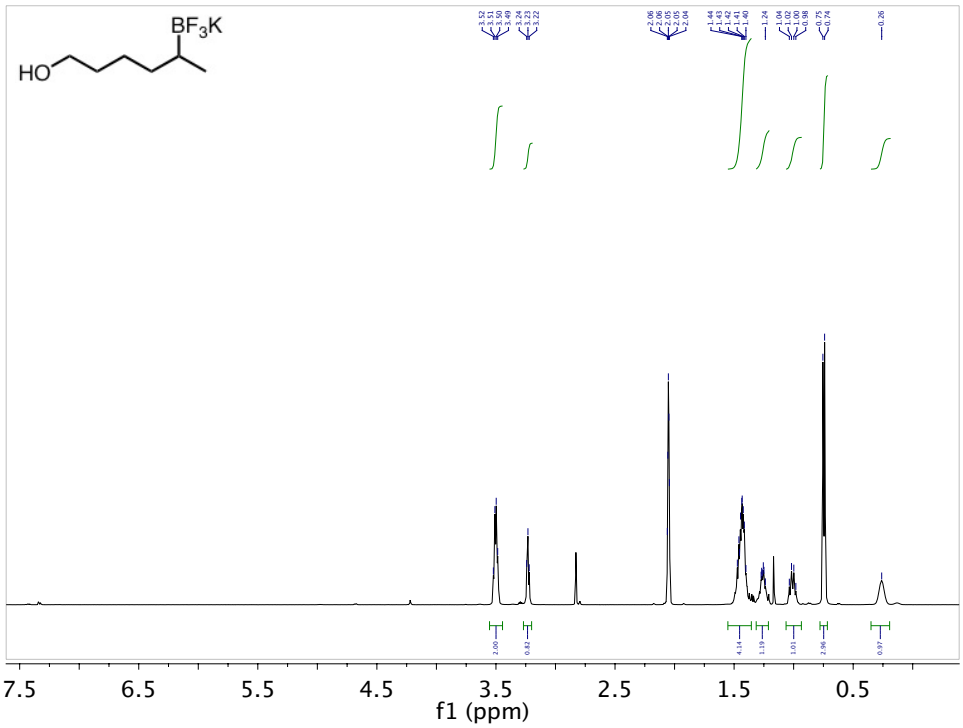


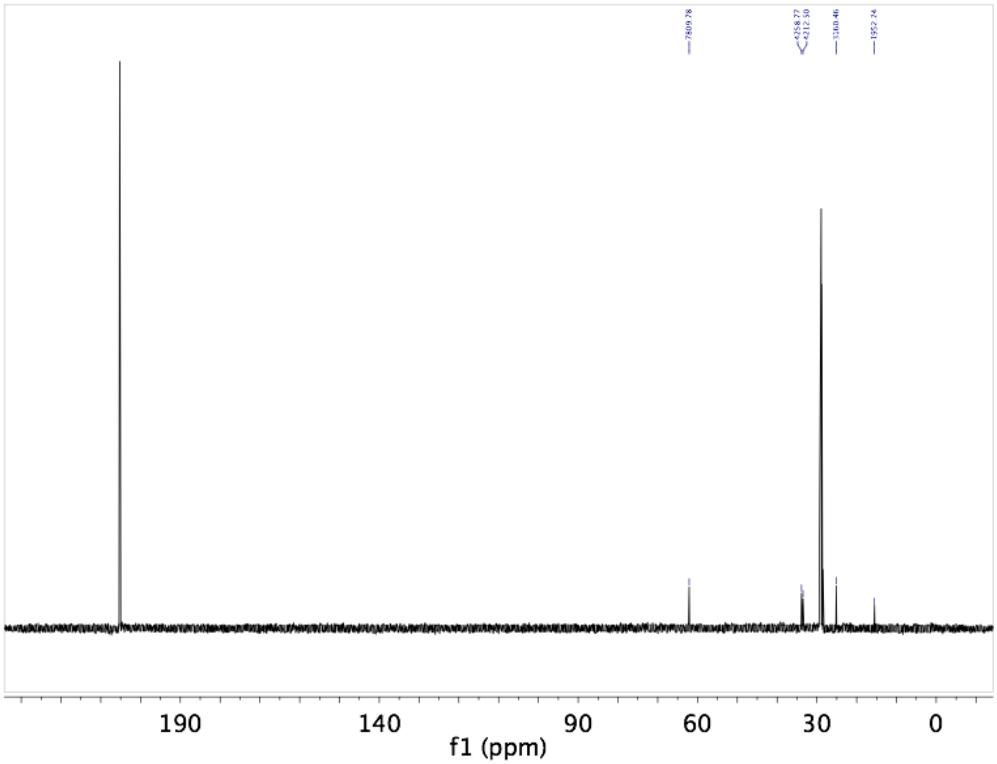
Potassium (4-phenylbutan-2-yl)trifluoroborate



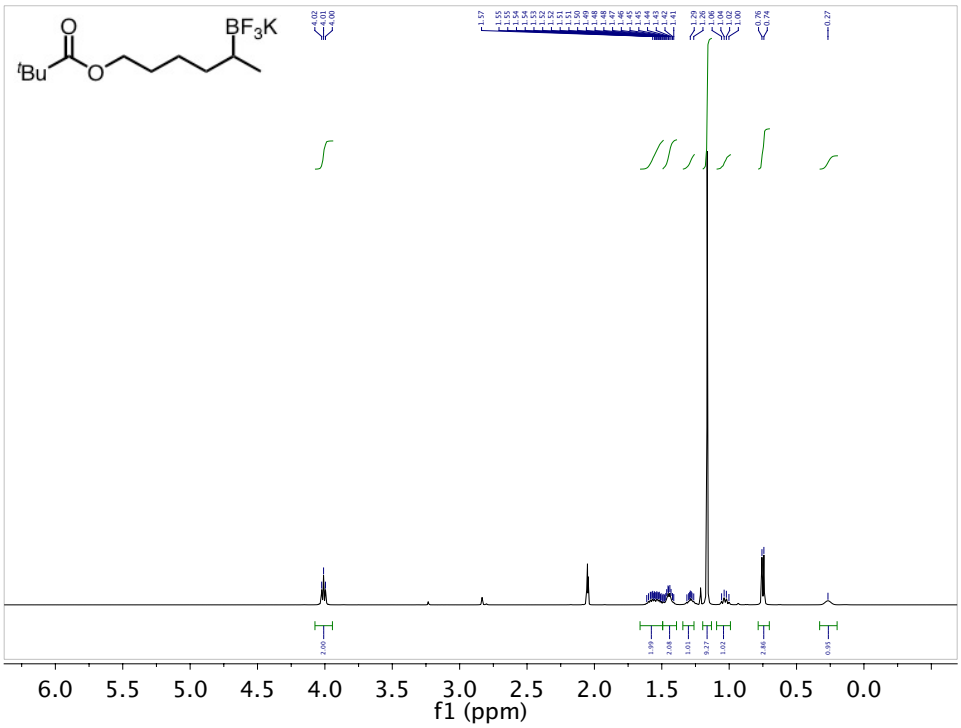


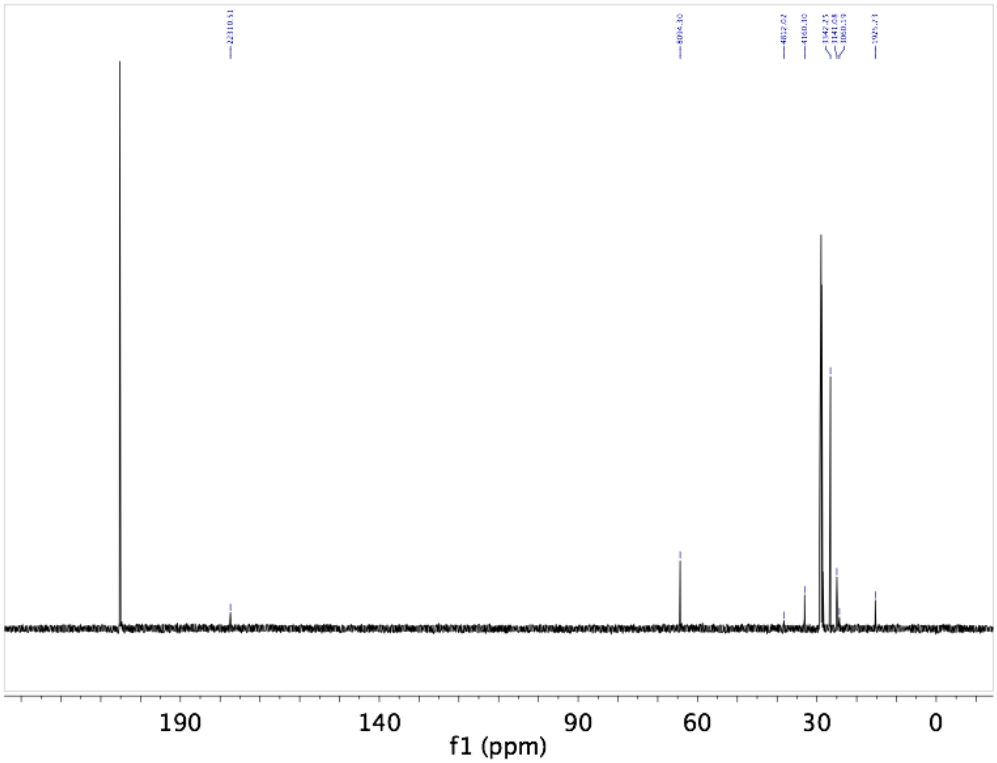
Potassium trifluoro(6-hydroxyhexan-2-yl)borate



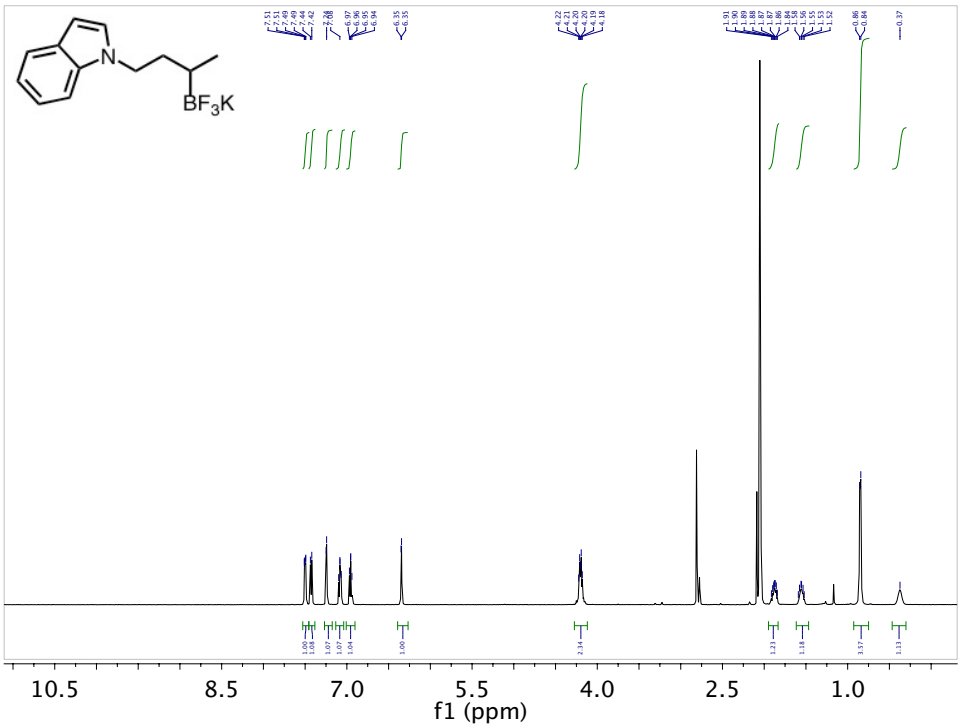


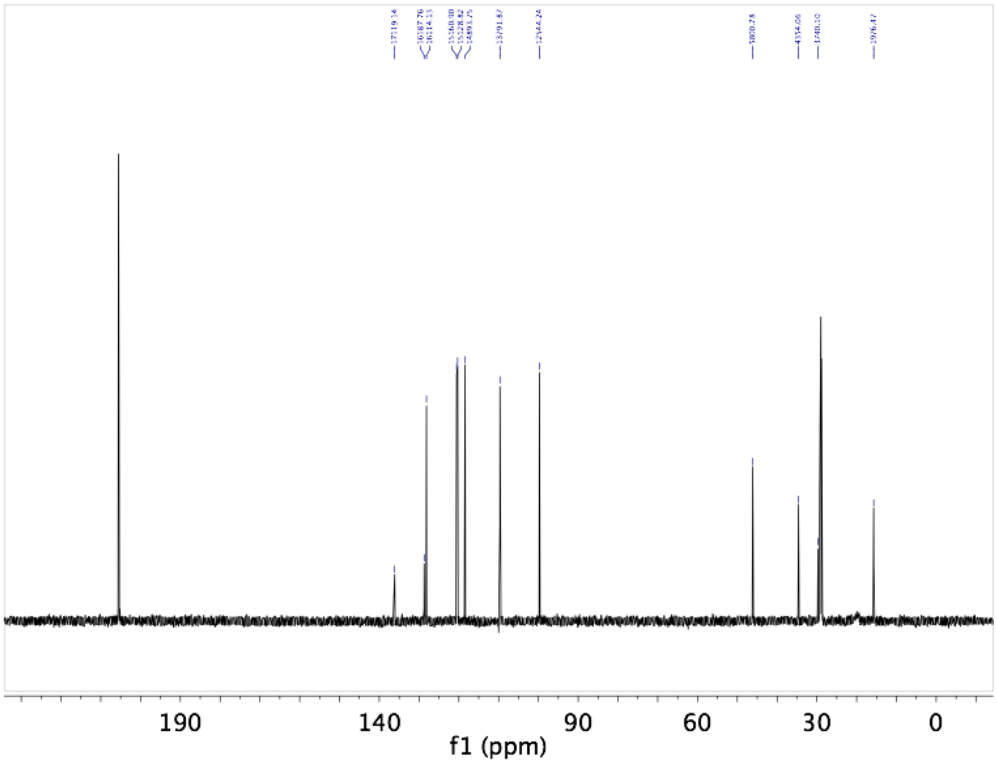
Potassium trifluoro(6-(pivaloyloxy)hexan-2-yl)borate



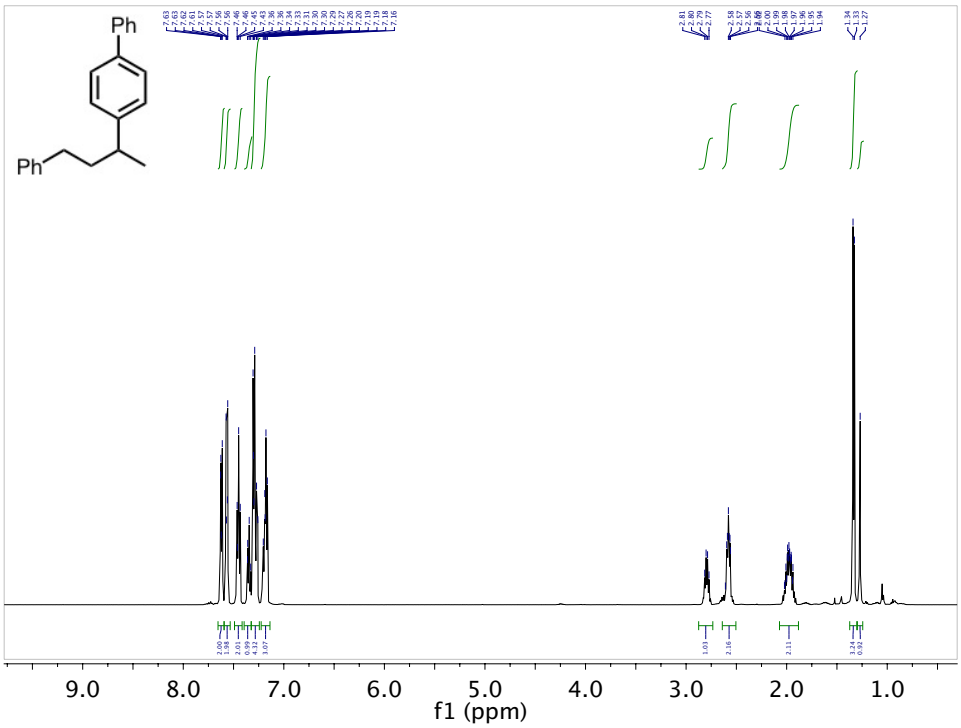


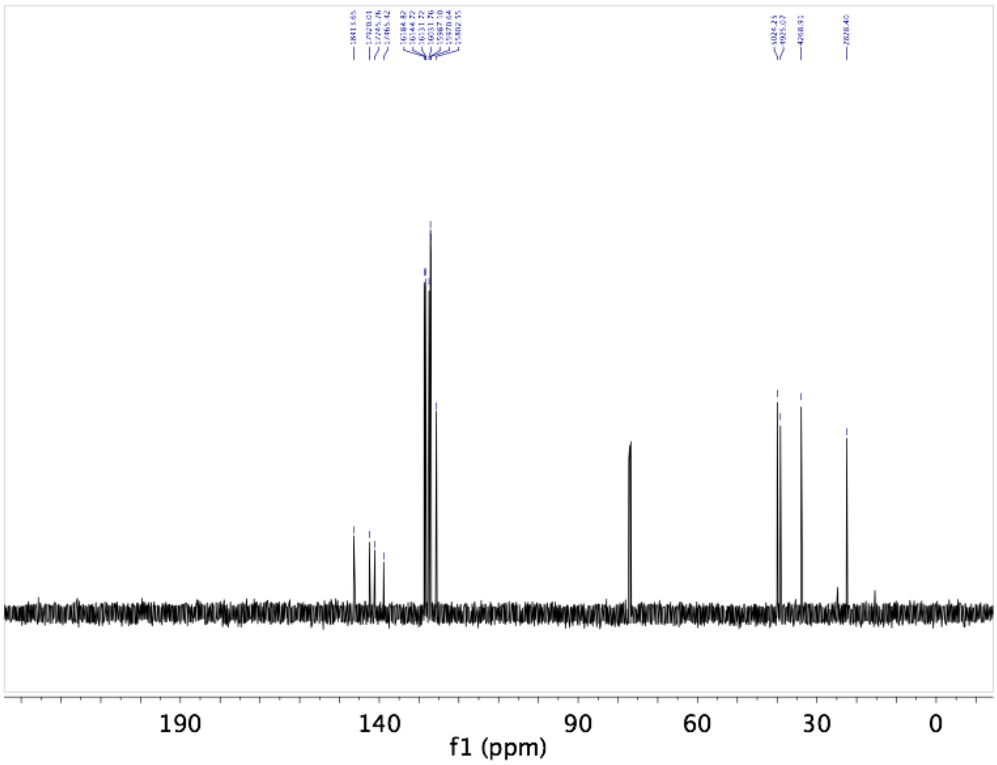
Potassium (4-(1*H*-indol-1-yl)butan-2-yl)trifluoroborate



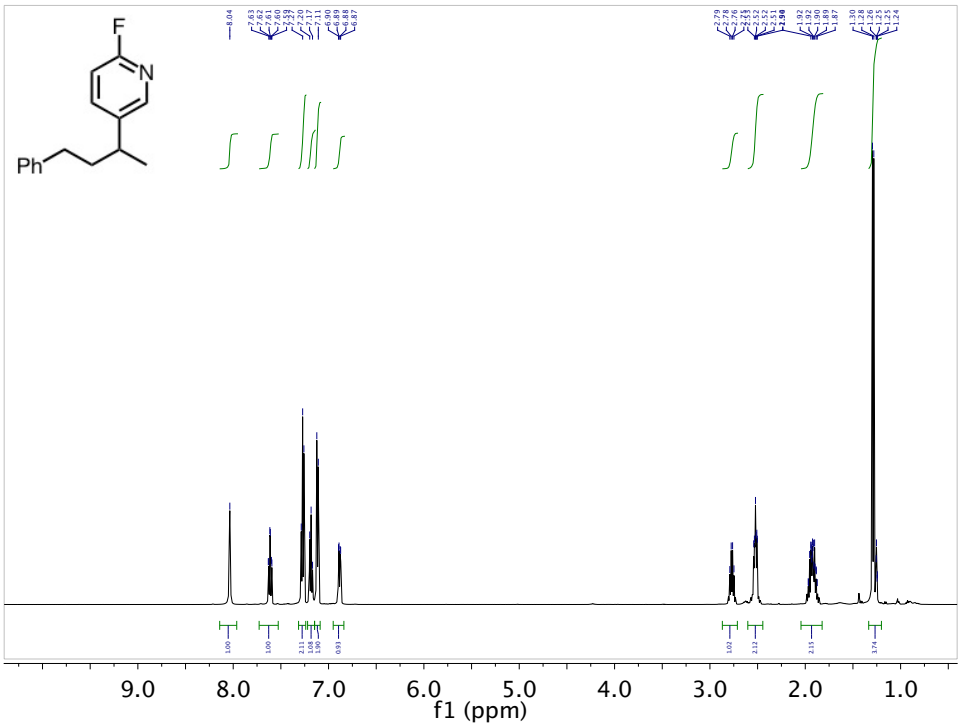


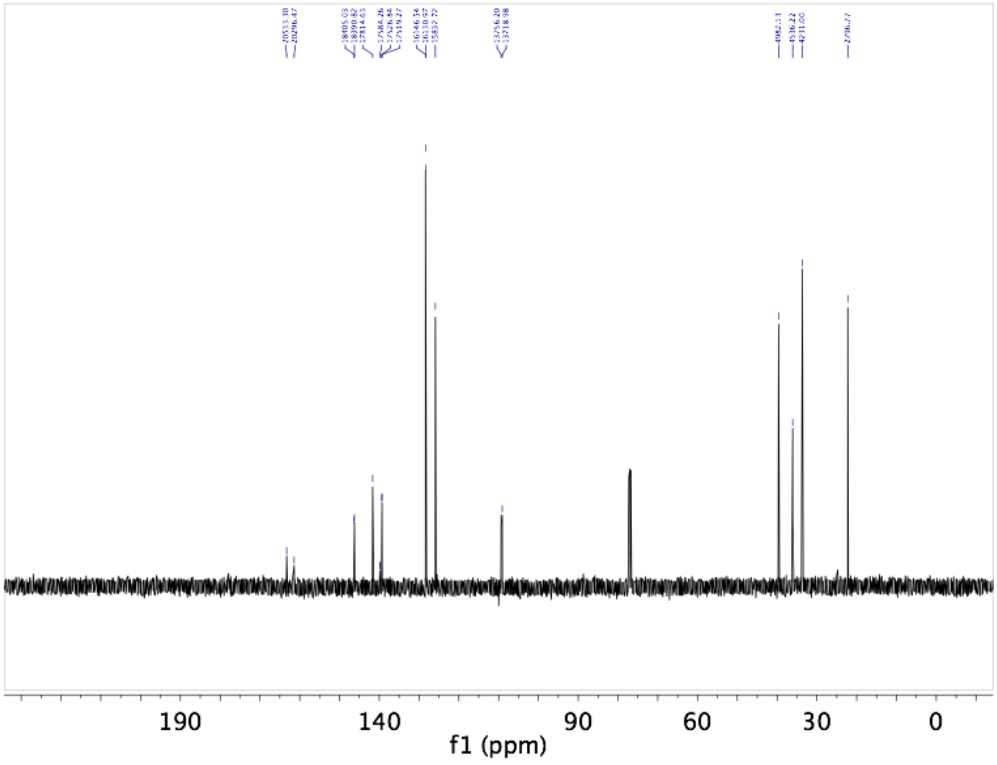
4-(4-phenylbutan-2-yl)biphenyl; compound 21



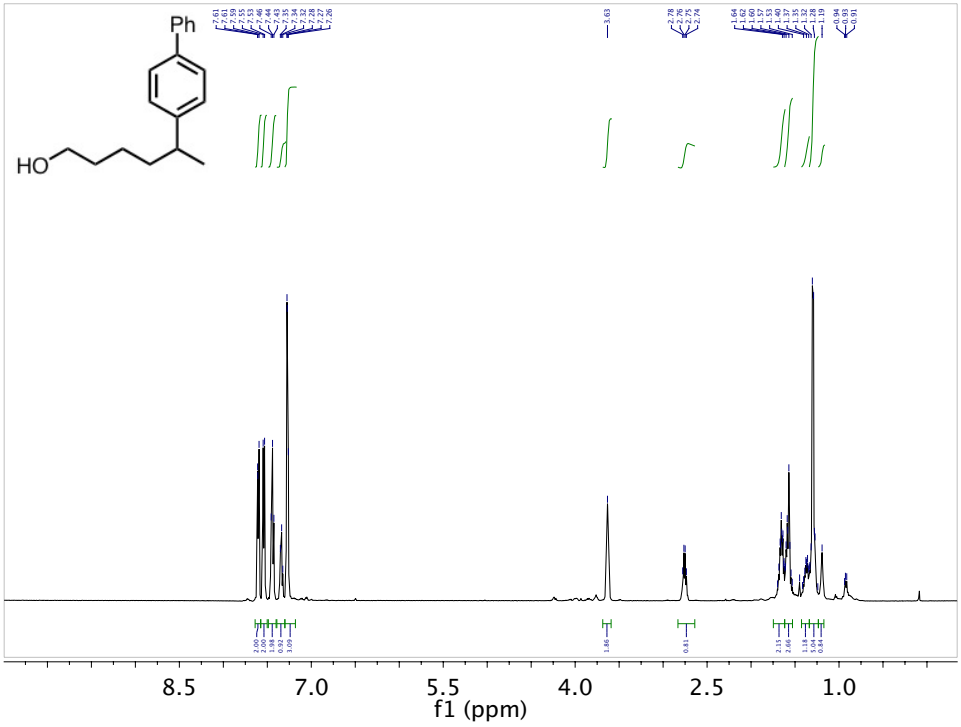


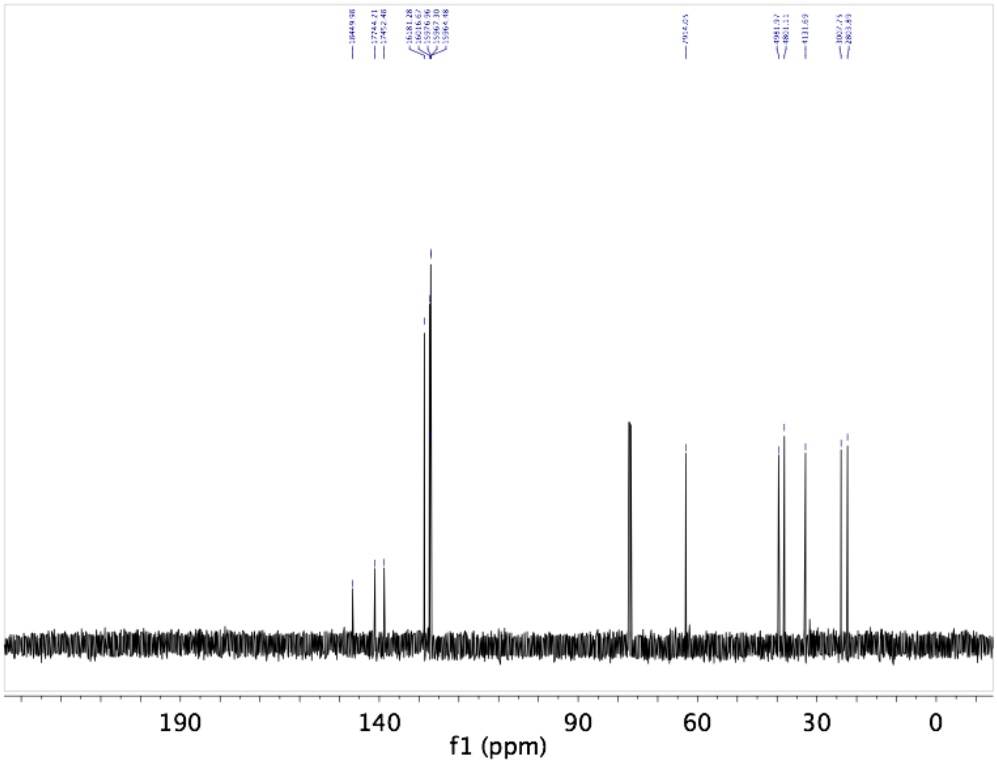
2-fluoro-5-(4-phenylbutan-2-yl)pyridine; compound 22



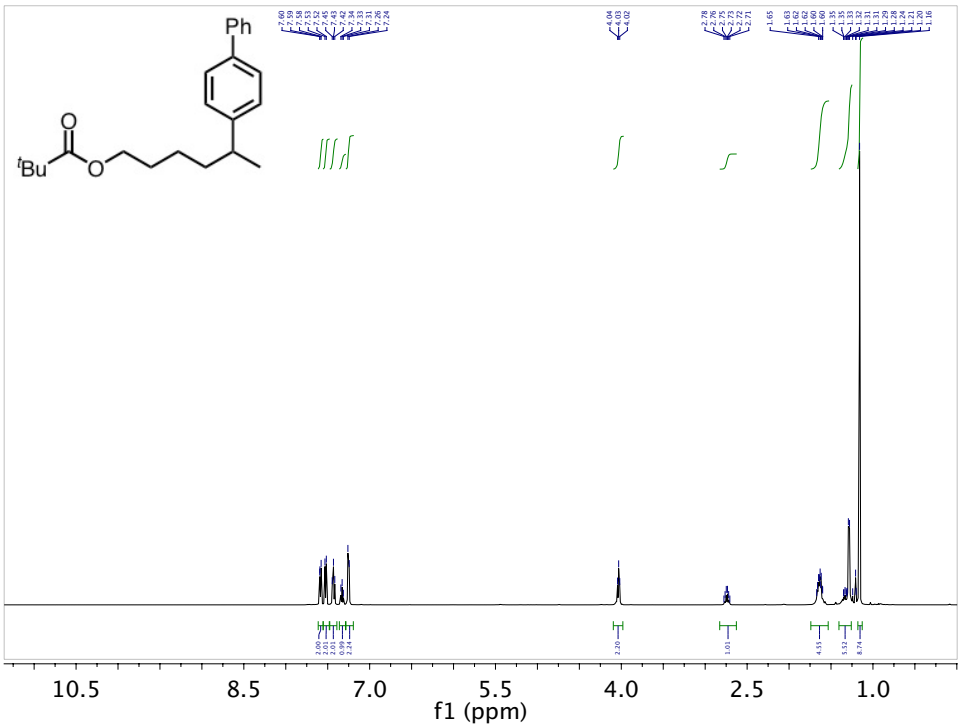


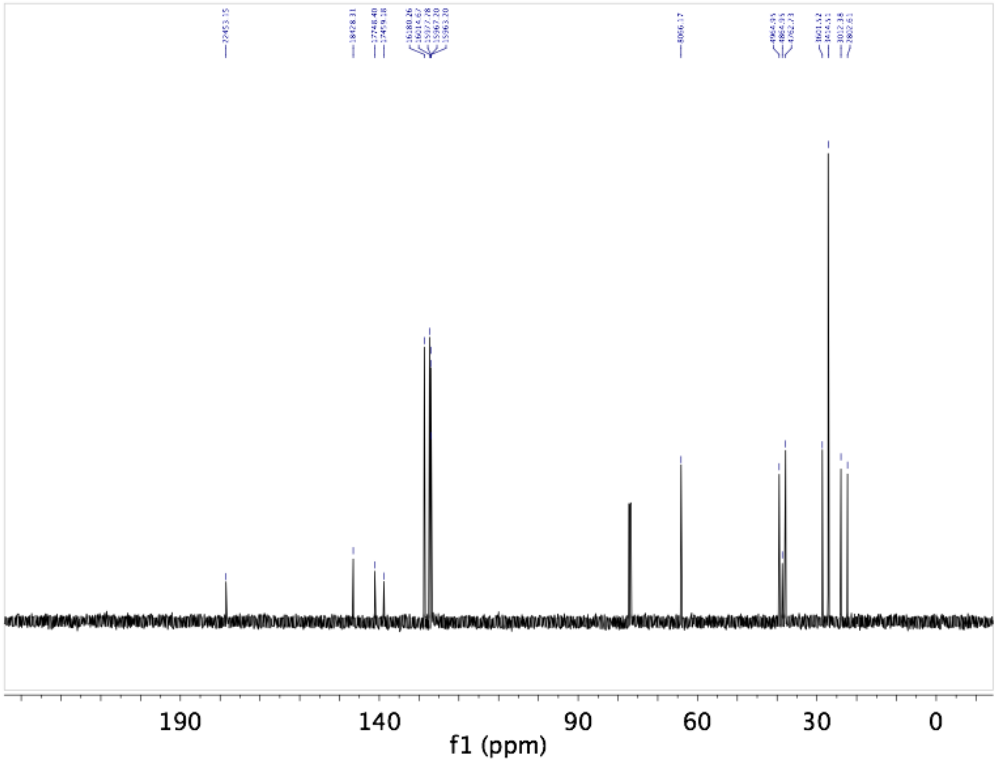
5-(biphenyl-4-yl)hexan-1-ol; compound 23





5-(biphenyl-4-yl)hexyl pivalate; compound 24





1-(3-(biphenyl-4-yl)butyl)-1*H*-indole; compound 25