Supporting Information

Ligand-controlled regiodivergent Ni-catalyzed *trans*-hydroboration/carboboration of internal alkynes with B_2pin_2

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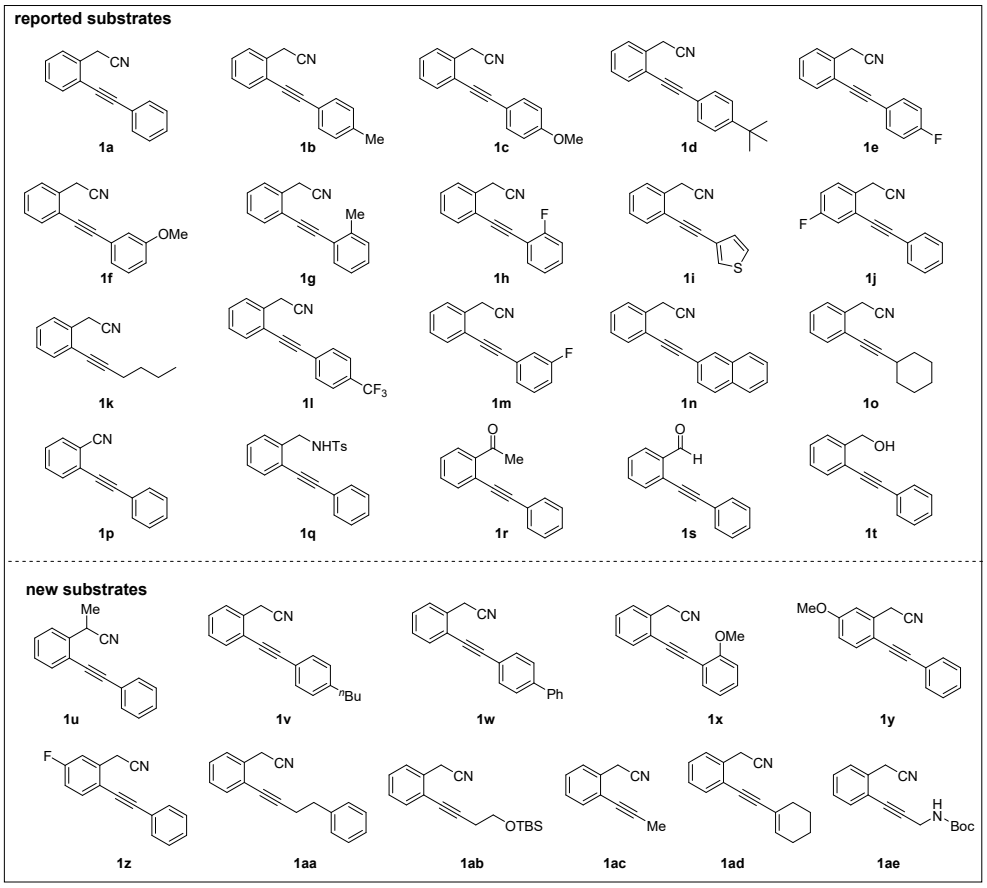
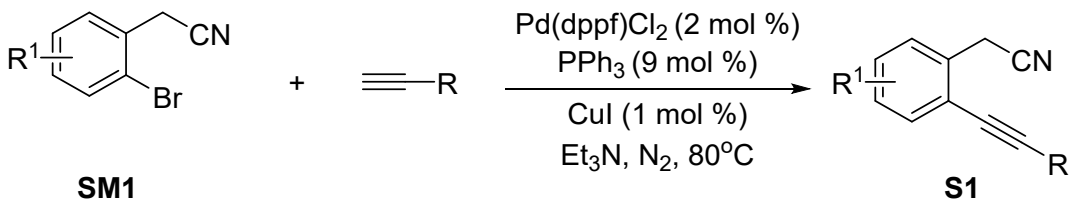
General information

^{1}H NMR, ^{13}C NMR, ^{11}B NMR and ^{19}F NMR spectra were recorded on a Bruker Ascend^{TM} 400M spectrometer at ambient temperature in chloroform-*d* and tetramethylsilane (TMS) as an internal standard unless otherwise noted, the chemical shifts of ^{1}H NMR, ^{13}C NMR are referenced to signals at 7.26 and 77.0 ppm, respectively. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Data for ^{11}B NMR and ^{19}F NMR are reported in terms of chemical shift (δ ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), td (triplet of doublets), dt (doublet of triplets), ddd (doublet of doublet of doublets). The data of HRMS were carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). Melting points were determined with Büchi Melting Point B-545 instrument. The data of X-ray were performed on a BRUKER Single Crystal X-Ray Diffractometer, Germany (model of the instrument-AXS D8 Quest System). TLC was performed by using commercially prepared 200-300 mesh silica gel plates and visualization effected at 254 nm. Unless stated otherwise, all reagents and solvents were purchased from commercial suppliers and used without further purification.

General procedure for the synthesis of reaction substrates

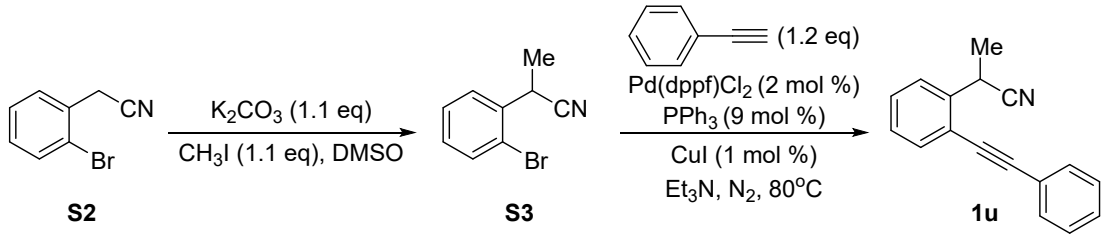
Synthetic methods and spectral data for 1a[1], 1b[2], 1c[1], 1d[3], 1e[1], 1f[4], 1g[2], 1h[2], 1i[5], 1j[3], 1k[1], 1l[2], 1m[5], 1n[5], 1o[6], 1p[7], 1q[8], 1r[9], 1s[10], 1t[11] were consistent with the methods and data reported in the literatures.





SM1 **S1**

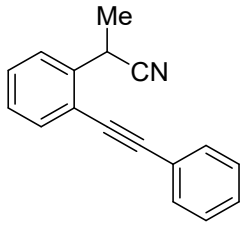
To a 25 mL sealed tube with magnetic stirrer bar, 2-(2-bromophenyl)acetonitrile (**SM1**, 5 mmol), alkyne(1.2 equiv), $Pd(dppf)Cl_2$ (2 mol %), PPh_3 (9 mol %), CuI (1 mol %), and Et_3N (15 mL) were successively added and vigorously stirred together in 80 °C oil bath under N_2 atmosphere. After the reaction was finished, the mixture was cooled to room temperature. The reaction was quenched with saturated NH_4Cl aq. and extracted with EtOAc (3 × 25 mL). The combined ethyl acetate layer was washed with brine (25 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The crude product was purified by flash column chromatography (eluting with petroleum ether/ethyl acetate) on silica gel to afford the product **S1**.



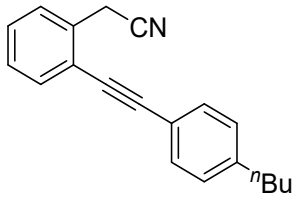
S2 **S3** **1u**

Step 1：In a 100 mL round-bottom flask with magnetic stirrer bar, 2-(2-bromophenyl)acetonitrile (**S2**, 5 mmol), DMSO (15 mL) and K_2CO_3 (1.1 equiv) were successively added, the mixture was stirred at room temperature for 20 minutes, then iodomethane (1.1 equiv) was slowly added to the reaction, the reaction was stopped when **S2** disappeared. After the reaction, the reaction was quenched with water and extracted with dichloromethane (3 × 25 mL). The combined ethyl acetate layer was washed with brine (25 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The crude product was purified by flash column chromatography (eluting with petroleum ether/ethyl acetate=20/1) on silica gel to afford the product **S3**.

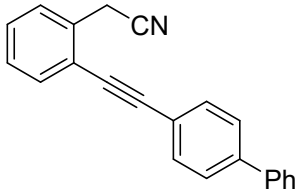
Step 2：The second synthesis step is performed in the same way as the general procedure for the synthesis of substrates.



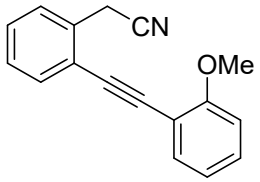
2-(2-(phenylethynyl)phenyl)propanenitrile (1u) yellow oil. ^1H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.53 (m, 5H), 7.37 (td, *J* = 6.2, 5.4, 2.6 Hz, 4H), 4.48 (q, *J* = 7.2 Hz, 1H), 1.69 (d, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.7, 132.7, 131.6, 129.3, 128.9, 128.6, 128.1, 126.7, 122.6, 121.8, 121.5, 95.0, 86.0, 30.0, 20.5. HRMS-ESI (m/z): calcd for $C_{20}H_{19}N$, $[M+H]^+$: 222.0953, found, 222.0969.



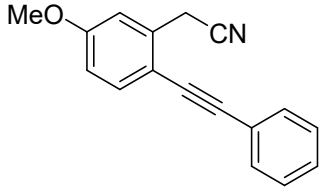
2-(2-((4-butylphenyl)ethynyl)phenyl)acetonitrile (1v) yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.56 (m, 1H), 7.51 (dd, *J* = 13.3, 8.2 Hz, 3H), 7.42 – 7.34 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 4.00 (s, 2H), 2.70 – 2.64 (m, 2H), 1.70 – 1.59 (m, 2H), 1.43 – 1.35 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.2, 133.1, 132.3, 131.5, 128.9, 128.7, 128.2, 128.1, 123.0, 119.60, 117.6, 96.0, 35.7, 33.4, 22.8, 22.4, 14.0. HRMS-ESI (m/z): calcd for $C_{20}H_{19}N$, $[M+H]^+$: 274.1596, found, 274.1596.



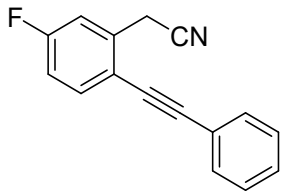
2-(2-([1,1'-biphenyl]-4-ylethynyl)phenyl)acetonitrile (1w) white solid, m.p. = 128-130 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.57 (m, 7H), 7.52 – 7.44 (m, 3H), 7.40 – 7.32 (m, 3H), 3.99 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.6, 140.2, 132.4, 132.1, 131.7, 129.1, 128.9, 128.2, 127.8, 127.2, 127.1, 122.9, 121.4, 117.5, 95.7, 86.7, 22.9. HRMS-ESI (m/z): calcd for $C_{22}H_{15}N$, $[M+H]^+$: 294.1283, found, 294.1271.



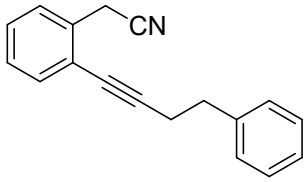
2-(2-((2-methoxyphenyl)ethynyl)phenyl)acetonitrile (1x) white solid, m.p. = 92-94 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.36 (ddd, *J* = 10.4, 7.9, 6.3 Hz, 3H), 6.95 (dd, *J* = 17.3, 8.0 Hz, 2H), 4.07 (s, 2H), 3.94 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.2, 133.1, 132.0, 131.9, 130.3, 128.8, 128.0, 128.0, 123.2, 120.6, 117.8, 111.8, 110.6, 92.2, 90.3, 55.8, 22.6. HRMS-ESI (m/z): calcd for $C_{17}H_{13}ON$, $[M+H]^+$: 248.1075, found, 248.1091.



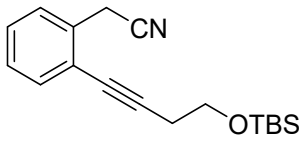
2-(5-methoxy-2-(phenylethynyl)phenyl)acetonitrile (1y) light yellow solid, m.p. = 43-45 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.69 (m, 3H), 7.58 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.29 – 7.23 (m, 1H), 7.09 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.19 (d, *J* = 4.9 Hz, 2H), 4.07 (d, *J* = 2.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.1, 133.8, 133.3, 133.3, 131.5, 128.5, 122.9, 117.5, 114.8, 113.9, 113.8, 94.1, 86.0, 55.6, 23.0. HRMS-ESI (m/z): $C_{17}H_{13}ON$, $[M+H]^+$: 248.1075, found, 248.1091.



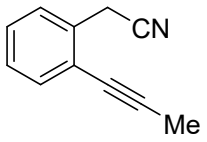
2-(5-fluoro-2-(phenylethynyl)phenyl)acetonitrile (1z) white solid, m.p. = 59-61 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.51 (m, 3H), 7.37 (dd, *J* = 6.5, 2.8 Hz, 3H), 7.27 – 7.24 (m, 1H), 7.06 (td, *J* = 8.3, 2.6 Hz, 1H), 3.97 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ162.5 (d, *J* = 251.7 Hz), 161.2, 134.3, 134.2, 131.6, 129.0, 128.6, 122.3, 118.9 (d, *J* = 3.6 Hz), 116.9, 115.7 (dd, *J* = 22.9, 16.4 Hz), δ 95.4 (d, *J* = 1.8 Hz), 85.0, 22.9. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -108.89. HRMS-ESI (m/z): calcd for $C_{16}H_{10}FN$, $[M+H]^+$: 236.0876, found, 236.0880.



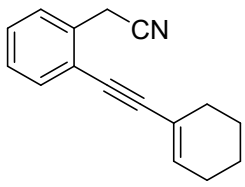
2-(2-(4-phenylbut-1-yn-1-yl)phenyl)acetonitrile (1aa) yellow oil. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.45 – 7.19 (m, 9H), 3.59 (s, 2H), 2.94 (t, J = 7.2 Hz, 2H), 2.79 (t, J = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 140.31, 132.17, 131.78, 128.58, 128.51, 128.36, 127.92, 127.81, 126.57, 123.25, 117.65, 96.02, 78.52, 34.72, 22.36, 21.45. HRMS-ESI (m/z): calcd for $C_{18}H_{15}N$, $[M+H]^+$: 246.1283, found, 246.1287.



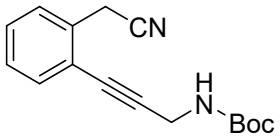
2-(2-(4-((tert-butyldimethylsilyl)oxy)but-1-yn-1-yl)phenyl)acetonitrile (1ab) yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.41 (m, 2H), 7.33 – 7.24 (m, 2H), 3.89 (s, 2H), 3.83 (t, *J* = 6.9 Hz, 2H), 2.68 (t, *J* = 6.9 Hz, 2H), 0.92 (s, 9H), 0.10 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.28, 131.73, 128.44, 128.00, 127.89, 123.26, 117.63, 94.09, 78.53, 61.73, 25.90, 23.97, 22.67, 18.36, -5.23. HRMS-ESI (m/z): calcd for $C_{18}H_{25}NOSi$, $[M+H]^+$: 300.1784, found, 300.1798.



2-(2-(prop-1-yn-1-yl)phenyl)acetonitrile (1ac) yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.40 (m, 2H), 7.32 – 7.23 (m, 2H), 3.87 (s, 2H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.3, 131.6, 128.3, 128.0, 127.9, 123.6, 117.7, 92.6, 76.8, 22.7, 4.5. HRMS-ESI (m/z): calcd for $C_{11}H_{9}N$, $[M+H]^+$: 156.0813, found, 156.0800.

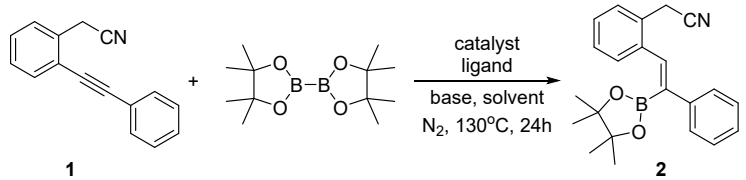


2-(2-(cyclohex-1-en-1-ylethynyl)phenyl)acetonitrile (1ad) yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (dd, *J* = 7.4, 1.6 Hz, 2H), 7.29 (pd, *J* = 7.5, 1.4 Hz, 2H), 6.26 (tt, *J* = 3.8, 1.7 Hz, 1H), 3.87 (s, 2H), 2.24 (ddq, *J* = 6.0, 4.6, 2.3 Hz, 2H), 2.15 (qd, *J* = 6.3, 5.0, 1.9 Hz, 2H), 1.65 (dddt, *J* = 24.3, 7.9, 5.8, 2.9 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.3, 132.1, 131.4, 128.5, 128.1, 128.0, 123.3, 120.3, 117.6, 97.8, 83.5, 29.1, 25., 22.7, 22.3, 21.4. HRMS-ESI (m/z): calcd for $C_{16}H_{15}N$, $[M+H]^+$: 222.1283, found, 222.1270.



tert-butyl (3-(2-(cyanomethyl)phenyl)prop- 2-yn-1-yl)carbamate (1ae) yellow soild. m. p. = 51-53°C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (dd, *J* = 7.3, 4.6 Hz, 2H), 7.36 (t, *J* = 7.1 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 4.91 (s, 1H), 4.19 (d, *J* = 5.5 Hz, 2H), 3.88 (s, 2H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.4, 132.5, 132.0, 129.1, 128.1, 122.3, 117.5, 92.1, 80.2, 79.9, 28.4, 22.7. HRMS-ESI (m/z): calcd for $C_{16}H_{15}N$, $[M+Na]^+$:293.1266, found, 293.1270.

Optimization of the *trans*-hydroboration reaction conditions

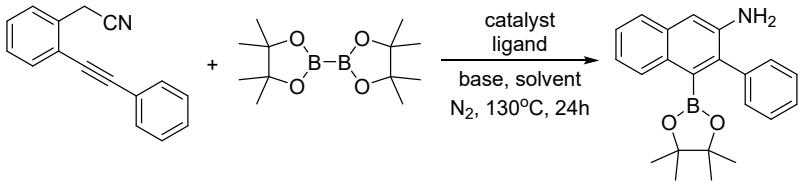


entry [a]	catalyst	ligand	base	solvent	yield of 2 (%)
1	**$Ni(PPh_3)_2Cl_2$**	**terpy**	**K_3PO_4**	**cyclohexane**	**88 (85)**
2	$Ni(PPh_3)_2Cl_2$	bpy	K_3PO_4	cyclohexane	N.D.
3	$Ni(PPh_3)_2Cl_2$	DAF	K_3PO_4	cyclohexane	70
4	$Ni(PPh_3)_2Cl_2$	1,10-phen	K_3PO_4	cyclohexane	22
5	$Ni(acac)_2$	terpy	K_3PO_4	cyclohexane	60
6	$Ni(OAc)_2$	terpy	K_3PO_4	cyclohexane	62
7	$Pd(OAc)_2$	terpy	K_3PO_4	cyclohexane	N.D.
8	$Ni(PPh_3)_2Cl_2$	terpy	Na_3PO_4	cyclohexane	N.D.
9	$Ni(PPh_3)_2Cl_2$	terpy	K_2CO_3	cyclohexane	41
10	$Ni(PPh_3)_2Cl_2$	terpy	MeOK	cyclohexane	20
11	$Ni(PPh_3)_2Cl_2$	terpy	^{t}BuOK	cyclohexane	42
12	$Ni(PPh_3)_2Cl_2$	terpy	K_3PO_4	toluene	68
13	$Ni(PPh_3)_2Cl_2$	terpy	K_3PO_4	acetone	<5
14	$Ni(PPh_3)_2Cl_2$	terpy	K_3PO_4	THF	15
15	$Ni(PPh_3)_2Cl_2$	terpy	K_3PO_4	MTBE	40
16[b]	$Ni(PPh_3)_2Cl_2$	terpy	K_3PO_4	cyclohexane	53
17[c]	$Ni(PPh_3)_2Cl_2$	terpy	K_3PO_4	cyclohexane	50
18[d]	$Ni(PPh_3)_2Cl_2$	terpy	K_3PO_4	cyclohexane	65

[a] Unless otherwise specified, the reactions were carried out with **1** (0.2 mmol), B_2pin_2 (1.5 equiv), catalyst (5 mol %), ligand (10 mol %), base (1.5 equiv), solvent (2.0 mL) under N_2 atmosphere in oil bath (130 °C) for 24 h in seal tube; Yields were determined by ^{1}H NMR with CH_2Br_2 as internal

standard; N.D. = not detected; Isolated yield is in the parentheses; [b] Under air atmosphere; [c] Under 80 °C; [d] Under 110 °C.

Optimization of the *trans*-carboboration reaction conditions

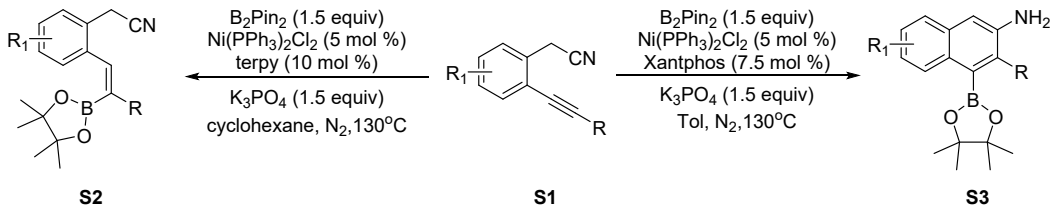


1 **3**

entry [a]	catalyst	ligand	base	solvent	yield of 3 (%)
1	**$Ni(PPh_3)_2Cl_2$**	**Xantphos**	**K_3PO_4**	**toluene**	**79 (74)**
2	$Ni(PPh_3)_2Cl_2$	dppp	K_3PO_4	toluene	25
3	$Ni(PPh_3)_2Cl_2$	Brettphos	K_3PO_4	toluene	31
4	$Ni(PPh_3)_2Cl_2$	Cy_3P	K_3PO_4	toluene	20
5	$Ni(acac)_2$	Xantphos	K_3PO_4	toluene	35
6	$Ni(OAc)_2{\cdot}4H_2O$	Xantphos	K_3PO_4	toluene	28
7	$Pd(OAc)_2$	Xantphos	K_3PO_4	toluene	N.D.
8	$Pd(PPh_3)_2Cl_2$	Xantphos	K_3PO_4	toluene	N.D.
9	$Ni(PPh_3)_2Cl_2$	Xantphos	Li_3PO_4	toluene	N.D.
10	$Ni(PPh_3)_2Cl_2$	Xantphos	Na_2CO_3	toluene	32
11	$Ni(PPh_3)_2Cl_2$	Xantphos	Cs_2CO_3	toluene	10
12	$Ni(PPh_3)_2Cl_2$	Xantphos	^{t}BuOK	toluene	45
13	$Ni(PPh_3)_2Cl_2$	Xantphos	K_3PO_4	cyclohexane	58
14	$Ni(PPh_3)_2Cl_2$	Xantphos	K_3PO_4	MTBE	50
15	$Ni(PPh_3)_2Cl_2$	Xantphos	K_3PO_4	DME	41
16	$Ni(PPh_3)_2Cl_2$	Xantphos	K_3PO_4	THF	38
17	$Ni(PPh_3)_2Cl_2$	Xantphos	K_3PO_4	CH_3CN	N.D.
18[b]	$Ni(PPh_3)_2Cl_2$	Xantphos	K_3PO_4	toluene	42
19[c]	$Ni(PPh_3)_2Cl_2$	Xantphos	K_3PO_4	toluene	30
20[d]	$Ni(PPh_3)_2Cl_2$	Xantphos	K_3PO_4	toluene	55
21[e]	$Ni(PPh_3)_2Cl_2$	Xantphos	K_3PO_4	toluene	78
22[f]	$Ni(PPh_3)_2Cl_2$	Xantphos	K_3PO_4	toluene	<5

[a] Unless otherwise specified, the reactions were carried out with **1** (0.2 mmol), B_2pin_2 (1.5 equiv), catalyst (5 mol %), ligand (7.5 mol %), base (1.5 equiv), solvent (2.0 mL) under N_2 atmosphere in oil bath (130 °C) for 24 h in seal tube; Yields were determined by ^{1}H NMR with CH_2Br_2 as internal standard; N.D. = not detected; Isolated yield is in the parentheses; [b] Under air atmosphere; [c] Under 80 °C; [d] Under 110 °C; [e] absolute dry toluene; [f] absolute dry toluene, H_2O (5 equiv).

General procedure for the synthesis of products 2 and 3



To a 25 mL sealed tube with magnetic stirrer bar, 2-(2-(phenylethynyl)phenyl)acetonitrile (**S1**, 0.2 mmol), B_2pin_2 (1.5 eq), $Ni(PPh_3)_2Cl_2$ (5 mol %), terpy (10 mol %) or Xantphos (7.5 mol %), K_3PO_4 (1.5 equiv), cyclohexane or toluene (2.0 mL) were successively added and vigorously stirred together in 130 °C oil bath under N_2 atmosphere. After the reaction was finished, the mixture was cooled to room temperature. The reaction was quenched with saturated NH_4Cl aq. and extracted with EtOAc (3 × 15 mL). The combined ethyl acetate layer was washed with brine (15 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The crude product was purified by flash column chromatography (eluting with petroleum ether/ethyl acetate) on silica gel to afford the product **S2** or **S3**.

Gram-scale reaction and the transformation of alkenyl boronate

Gram-scale reaction: To a 50 mL sealed tube with magnetic stirrer bar, 2-(2-(phenylethynyl)phenyl)acetonitrile (**S1**, 5 mmol), B_2pin_2 (1.5 equiv), $Ni(PPh_3)_2Cl_2$ (3 mol %), terpy (6 mol %), K_3PO_4 (1.5 equiv), cyclohexane (35 mL) were successively added and vigorously stirred together in 130 °C oil bath under N_2 atmosphere for 24 hours. Then the mixture was cooled to room temperature, the reaction was quenched with saturated NH_4Cl aq. and extracted with EtOAc (3 × 60 mL). The combined ethyl acetate layer was washed with brine (30 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The crude product was purified by flash column chromatography (eluting with petroleum ether/ethyl acetate = (12/1 - 10/1) on silica gel to afford product **2** as pale solid (1.24 g, 72% yield).

H_2O_2 oxidation of alkenyl boronate: To a 20 mL sealed tube with magnetic stirrer bar, alkenyl boronate **2** (0.5 mmol), THF (6 mL) and 30% H_2O_2 aq. (3.0 equiv) were successively added and vigorously stirred together in 75 °C oil bath under air atmosphere for 16 hours. Then the reaction was cooled to room temperature and quenched with saturated $Na_2S_2O_3$ aq.. The mixture was extracted with EtOAc (3 × 20 mL). The combined ethyl acetate layer was washed with brine (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The crude product was purified by flash column chromatography (eluting with petroleum ether/ethyl acetate = 4:1) on silica gel to afford the product **46**.

Suzuki cross-coupling: To a 20 mL sealed tube with magnetic stirrer bar, alkenyl boronate **2** (0.5 mmol), 4-Iodotoluene (1.5 equiv), $Pd(OAc)_2$ (5 mol %), $^tBu_3P{\cdot}HBF_4$ (5 mol %), K_2CO_3 (3.0 equiv), dioxane (5 mL) and H_2O (1 mL) were successively added and vigorously stirred together in 100 °C oil bath under N_2 atmosphere for 24 hours. Then the reaction was cooled to room temperature and quenched with saturated NH_4Cl aq.. The mixture was extracted with EtOAc (3 × 20 mL). The combined ethyl acetate layer was washed with brine (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The crude product was purified by flash column chromatography (eluting with petroleum ether/ethyl acetate = 6:1) on silica gel to

afford the product **47**.

Synthesis of 3-phenyl isoquinoline: To a 20 mL sealed tube with magnetic stirrer bar, alkenyl boronate **2** (0.5 mmol), $CuSO_4$ (0.6 equiv), MeOH (6 mL) and NaN_3 (3.0 equiv) were successively added and vigorously stirred together in 50 °C oil bath under air atmosphere for 20 hours. Then the reaction was cooled to room temperature and quenched with saturated NH_4Cl aqueous. The mixture was extracted with EtOAc (3 × 20 mL). The combined ethyl acetate layer was washed with brine (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The crude product was purified by flash column chromatography (eluting with petroleum ether/ethyl acetate = 6:1) on silica gel to afford the product **48**. The proposed mechanism for the formation of **48** was shown as follows:

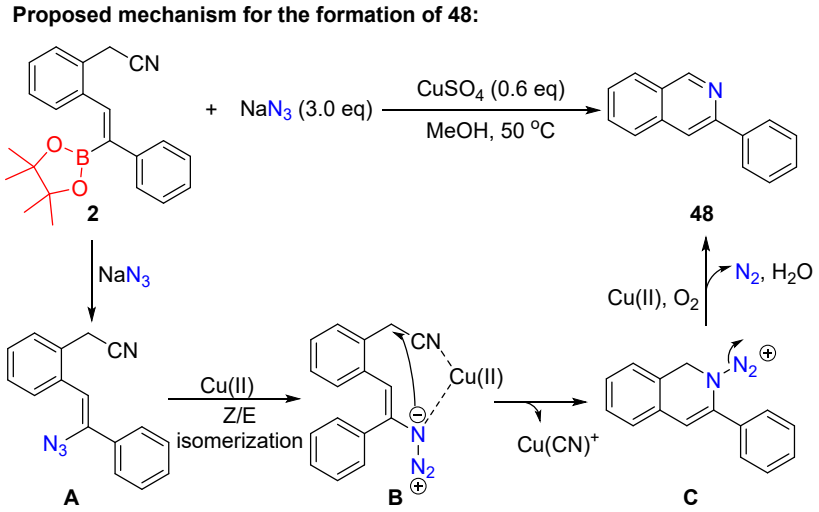


Figure S1 The proposed mechanism for the formation of **48**

Synthesis of 2-phenyl-3-naphthylamine: To a 20 mL sealed tube with magnetic stirrer bar, alkenyl boronate **2** (0.5 mmol), $[Rh(COD)Cl]_2$ (5 mol %), K_3PO_4 (1.5 equiv), dioxane (5 mL) and H_2O (2 mL) were successively added and vigorously stirred together in 80 °C oil bath under N_2 atmosphere for 8 hours. Then the reaction was cooled to room temperature and quenched with saturated NH_4Cl aq.. The mixture was extracted with EtOAc (3 × 20 mL). The combined ethyl acetate layer was washed with brine (20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. The crude product was purified by flash column chromatography (eluting with petroleum ether/ethyl acetate = 5:1) on silica gel to afford the product **49**.

Synthesis of *d*-50

To a 50 mL sealed tube with magnetic stirrer bar, 2-(2-(hex-1-yn-1-yl)phenyl)acetonitrile (**50**, 1.0 mmol), K_2CO_3 (2.2 equiv), anhydrous toluene (8 mL) and D_2O (10 equiv) were successively added and vigorously stirred together in 130 °C oil bath under N_2 atmosphere for 24 hours. Then the mixture was cooled to room temperature, the reaction was filtrated with celite and washed by EtOAc. The filtrate was concentrated and purified by flash column chromatography (eluting with petroleum ether/ethyl acetate = (12/1 - 10/1) on silica gel to afford product ***d*-50** (0.18 g, 90% yield) with 75% proportion deuterium.

Mechanism study with *meta*-CH_2CN diphenyl acetylene as substrate

We obtained the hydroboration products (**oil**) of *meta*-CH_2CN diphenyl acetylene **53** in 34% yield under $Ni(PPh_3)_2Cl_2$/terpy catalysis system (Figure S2). The ratio of two isomers was 16:84 (minor isomer: major isomer) determined by the integral value of ^1H NMR spectrum. However, the absolute configuration (*trans*- or *cis*-, α- or β-site) of hydroboration products couldn't be confirmed by NMR spectrum, and single crystals was also hard to form for the oily state. In the other hand, the mixed products (**solid**, 1:2 ratio) were produced under CuCl or CuCl(IMes) as catalyst, that were different with isomers producing under $Ni(PPh_3)_2Cl_2$/terpy catalysis system (Figure S3). Fortunately, the single crystals of isomers producing under CuCl(IMes) as catalyst were acquired from the wall and bottom of EP tube and confirmed as α-*cis*-isomer (CCDC: 2312562) and β-*cis*-isomer (CCDC: 2312563), the ratio of α-*cis*-isomer and β-*cis*-isomer is 1:2 (Figure S4). Logically, isomers producing under $Ni(PPh_3)_2Cl_2$/terpy catalysis system were α-*trans*-isomer and β-*trans*-isomer. Therefore, directing group was crucial for the regioselectivity and reactivity of internal alkynes.

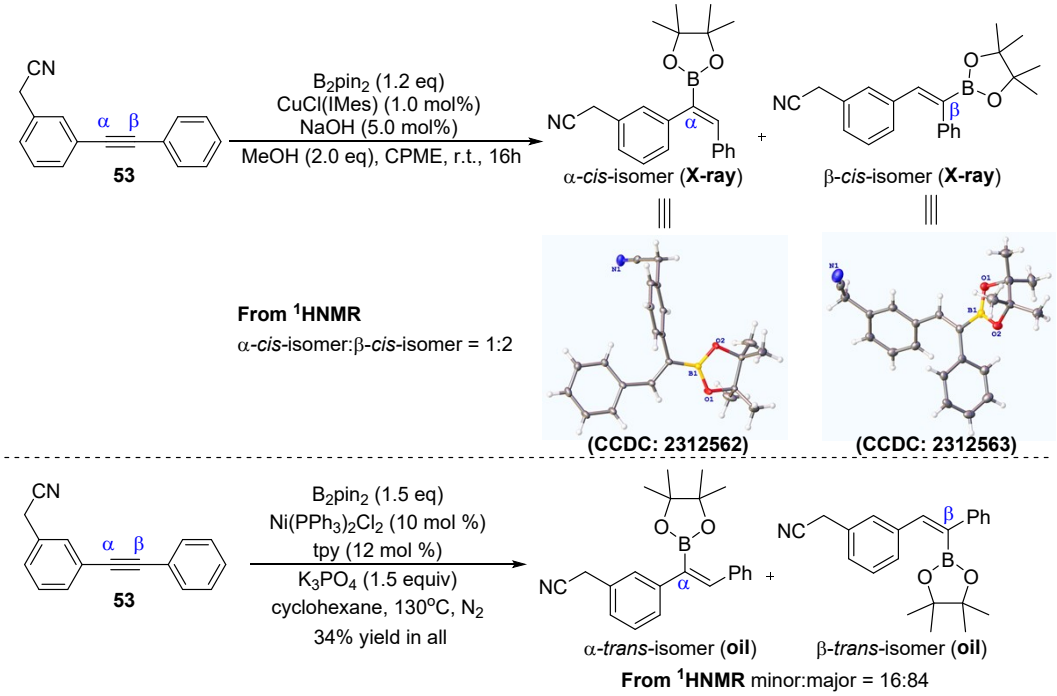


Figure S2 The hydroboration reaction of **53**

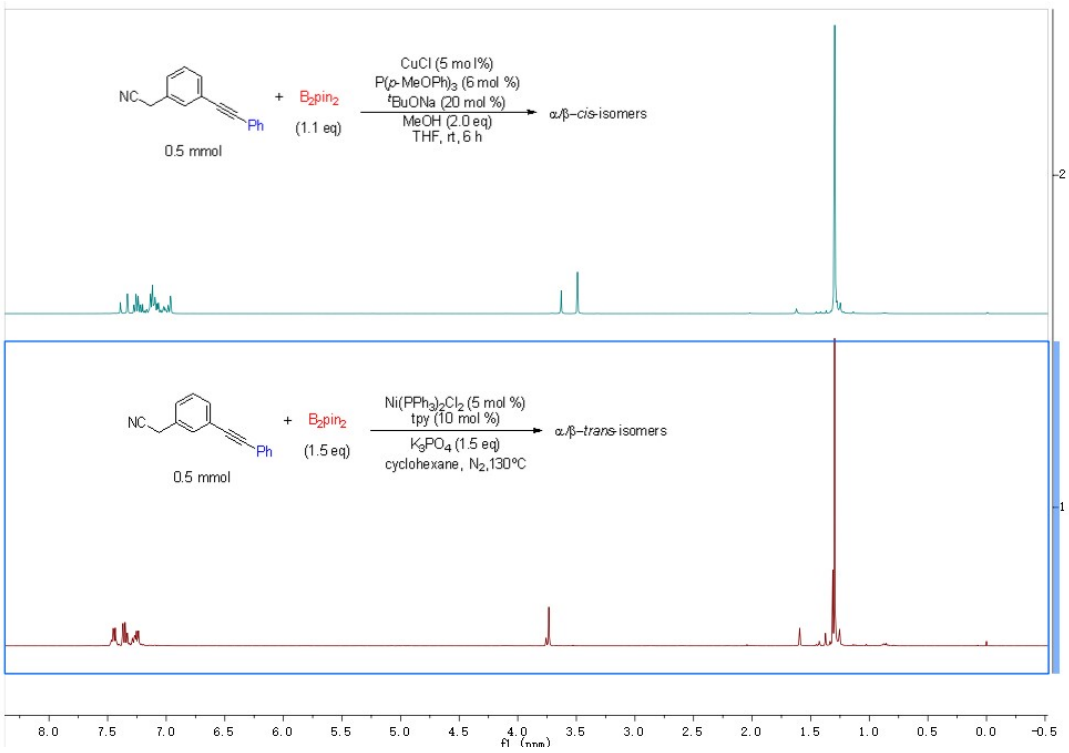


Figure S3 ^{1}HNMR of α/β-*cis*-isomers with α/β-*trans*-isomers

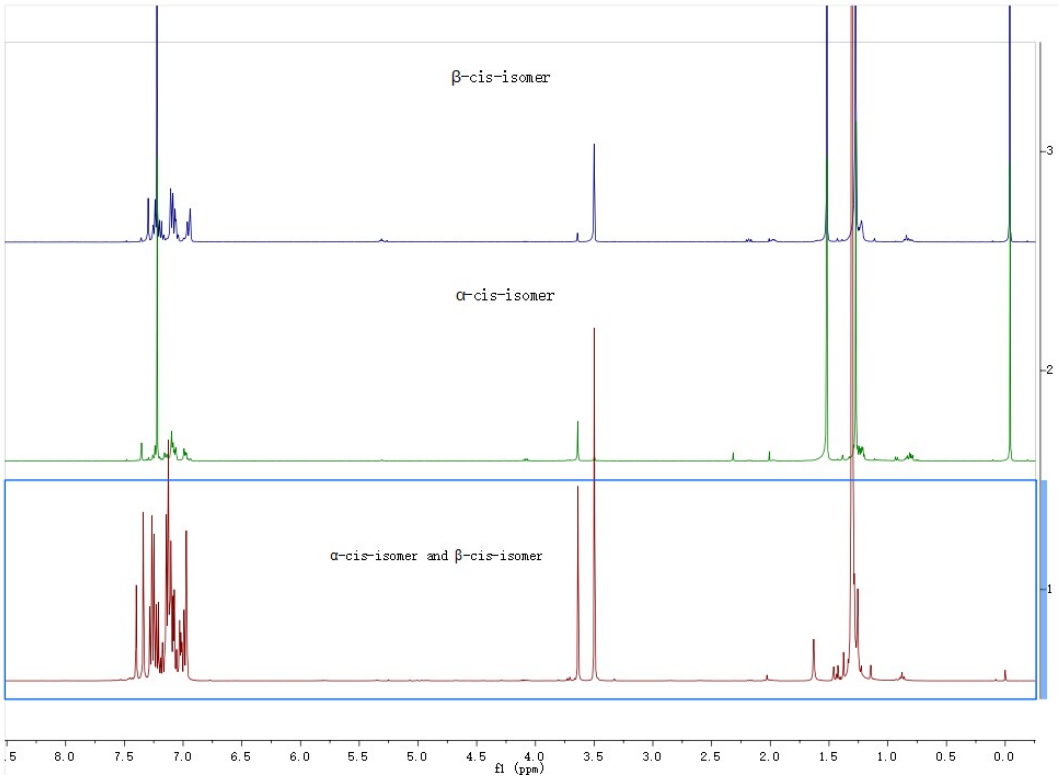


Figure S4 ^{1}HNMR of α-*cis*-isomer (CCDC: 2312562) and β-*cis*-isomer (CCDC: 2312563)

Primary DFT calculation on the *cis*-to-*trans* isomerization

Complete reference for Gaussian 09: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,

M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Version D. 01, Inc., Wallingford CT, 2009.

All electronic structure calculations in this work were performed using Gaussian 09 program. A combination of the PBE functional, along with the def2TZVP basis set (for the metal atom of Ni), and the def2SVP basis set (for the non-metals of C, N, B, O, H, Cl), was employed for the full parameter optimization of all stationary points (intermediates) and saddle points (transition states) studied in this work. This includes reactants, intermediates, transition states, and products. Subsequently, frequency analysis was carried out to ensure that all intermediates have no imaginary frequencies, while transition states (saddle points) have one and only one imaginary frequency. The SMD solvent model was used in the calculations to obtain results that are closer to experimental conditions, with cyclohexane as the solvent. Furthermore, to obtain more accurate relative energies, we performed single-point energy calculations using the M06-2X/Def2-TZVPP method on the above optimized geometries. Through these calculations, the Gibbs free energy reaction potential surface shown in Figure S3 was obtained. Two transient states **TS-A** (zwitterionic carbene-type species) and **TS-B** (metallacyclopropene) from **cis-Int-2** were evaluated via the comparison of free energy barrier. The calculated results demonstrate that **cis-Int-2** are prone to undergo zwitterionic carbene-type species **TS-A** cis-to-trans isomerization, achieving carbon-carbon double bond rotation. And **trans-Int-3** is more stable than **cis-Int-2** due to removal of the huge steric-hindrance between Bpin and tpy ligand, that may be the inherent driving force for selective formation of the trans-isomer.

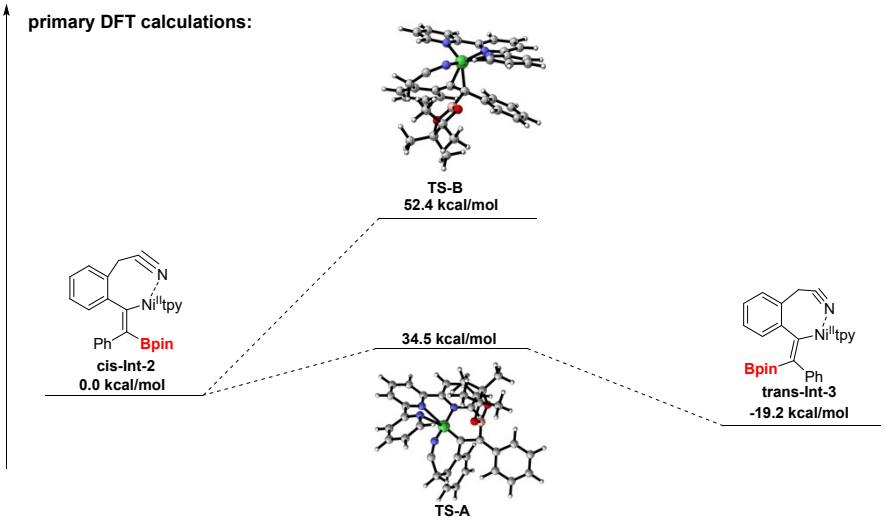


Figure S3 Free energy profile of the synthesis of *cis*-to-*trans* isomerization

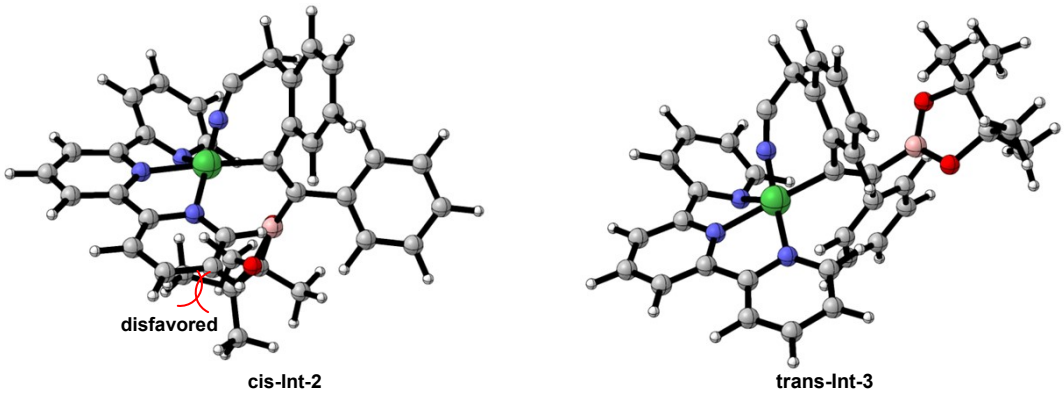


Table S4 Cartesian coordinates and energies of optimized structures

Species	Engrgy (in a.u.)	Cartesian coordinates		
cis-Int-2	B3LYP SCF energy: -3328.730677 B3LYP enthalpy: -3328.687687 B3LYP free energy: -3328.810564 M06 SCF energy in solution: -3332.8093	C	-2.64956100	3.84029700 -3.20136500
		C	-2.66416000	2.44723900 -3.35291100
		C	-2.21740700	1.63009000 -2.30831500
		C	-1.74814500	2.16782600 -1.08429000
		C	-1.74270400	3.59080300 -0.93774900
		C	-2.18580100	4.39705900 -2.00094800
		C	-1.32743600	1.19235800 -0.04530100
		C	-2.11643700	0.30977100 0.62060100
		C	-3.59340600	0.21108000 0.40837900
		C	-1.31137100	4.29081400 0.35173900
		C	-0.19689700	3.53644600 0.95243000
		N	0.22516700	2.42471900 0.87489200
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		C	-5.80813400	1.21956500 0.16872600
		C	-6.38786600	-0.05266500 0.03111800
		C	-5.57434700	-1.19497200 0.09191200
		C	-4.19190400	-1.06510500 0.28757900
		B	-1.54342700	-0.71985500 1.67334300
		O	-0.92658800	-1.89305000 1.30151000
		C	-0.45780100	-2.54603400 2.52866900
		C	-1.37133100	-1.87838400 3.63668900
		O	-1.71007400	-0.58522100 3.03027200
		C	-0.67072600	-1.63607300 4.96807100
		C	-2.69875600	-2.60867000 3.85332400
		C	-0.63869900	-4.05069300 2.37381400
		C	1.02320900	-2.18740600 2.67420900
		C	4.49520200	1.41792100 2.19314900

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C	4.59590500	0.03823500	0.21160300
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C	2.36700400	-0.62576600	-0.83933500
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		H -0.23719000 3.46308900 5.72020700
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		H -0.10987300 -2.57708100 -3.06641200
		H 2.38840300 -2.89139500 -3.40232200
		H 3.96895500 -1.62299800 -1.92064400
TS-A	B3LYP SCF energy: -3328.683209 B3LYP enthalpy: -3328.642565 B3LYP free energy: -3328.755605 M06 SCF energy in solution: -3332.7334	C 2.09251600 -3.69551500 2.89586100 C 2.07095300 -3.83625200 1.49804900 C 1.49300000 -2.83177900 0.70409100 C 0.93444500 -1.65716600 1.27214600 C 0.93783900 -1.53398800 2.70204600 C 1.51910300 -2.55230400 3.48499600 C 0.43271000 -0.60002500 0.30756400 C 1.54753300 0.35948600 -0.35667400 C 2.99876200 0.15133800 -0.32424900 C 0.39798200 -0.29478700 3.44629300 C -0.70479300 0.26191700 2.64245000 N -1.12964200 0.13758100 1.53695400 C 3.71927200 -0.41868600 0.76594500 C 5.11648500 -0.53984100 0.72194600 C 5.84295700 -0.09879700 -0.40342100 C 5.15418100 0.48473200 -1.48511000 C 3.75703400 0.61294600 -1.44408400 B 0.86411900 1.44939300 -1.26711400 O 0.59473400 1.23328400 -2.61036300 C -0.29321800 2.31685700 -3.05398000 C 0.00242000 3.45202500 -1.98498000 O 0.42591800 2.67587200 -0.80954800 C -1.21650400 4.29604300 -1.61005100 C 1.18930100 4.35191200 -2.36174600 C 0.06583500 2.68116200 -4.49424500 C -1.73008600 1.77627000 -2.97346100 C -5.60647500 -0.29140900 0.49043200 C -4.25444400 0.11251500 0.56978500 N -3.29876700 -0.49909600 -0.17395400 C -3.64507100 -1.46232000 -1.07142000 C -4.98018300 -1.89377000 -1.21109200 C -5.96782700 -1.31172700 -0.40151600 C -2.53019600 -1.97145700 -1.90888400 C -3.84691600 1.25477700 1.44503000 C -4.32231600 1.35205700 2.77311200 C -3.86288800 2.41328700 3.57186100

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TS-B	B3LYP SCF energy: -3328.652657	C 1.04371400 0.12203100 4.76688000

B3LYP enthalpy: -3328.612715

B3LYP free energy: -3328.727101

M06 SCF energy in solution: -3332.6557

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C	-0.22133500	0.51072000	0.71195100
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C	-1.02696300	4.57967200	-0.67668100
C	-0.69663400	3.27551700	-0.29248700
B	-2.60037300	-0.14723300	0.01273500
O	-3.48637200	-0.56984500	-0.93564500
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O	-2.98408200	-0.34782300	1.30736200
C	-4.59085300	-1.84656300	2.34308300
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C	-5.86732100	-1.06011300	-0.88477900
C	-4.14363000	-2.81236400	-0.37496100
C	3.67116200	3.16290100	-1.04809800
C	2.92696200	1.99442300	-0.80488000
N	1.80833700	1.73092600	-1.50634500
C	1.44788300	2.48301600	-2.56432400
C	2.14354200	3.66884100	-2.86803400
C	3.24595400	4.01878900	-2.07592700
C	0.34562300	1.89307400	-3.36321700
C	3.30193900	0.90021100	0.12262200
C	4.38928300	0.94799700	1.01227800
C	4.69564300	-0.18811000	1.77160200
C	3.90792100	-1.33902000	1.62358900
C	2.82122600	-1.29511500	0.74022200
N	2.52669700	-0.20989200	0.01372600
N	0.01175600	0.63230300	-2.99318000
C	-0.96477200	-0.01554600	-3.63908200
C	-1.65376000	0.55600000	-4.71846200
C	-1.31295200	1.85738000	-5.11766000
C	-0.30205600	2.54081700	-4.43051200
Ni	0.57578900	0.14470800	-0.88667300

		H	1.38524400	0.00153600	5.80561500
		H	1.30965900	2.28160500	4.76003000
		H	0.56882400	2.55780700	2.39890500
		H	0.65074600	-2.00033000	4.48981000
		H	-1.53243100	-2.01647100	2.15018900
		H	-0.02834100	-2.97839600	2.23706400
		H	-3.23788100	1.58002400	-1.84301700
		H	-3.82107600	3.90270600	-2.54180900
		H	-2.40854200	5.83824600	-1.79481600
		H	-0.39685300	5.42121600	-0.35032500
		H	0.20807800	3.09668300	0.30682700
		H	-4.43035600	-1.39209300	3.34040500
		H	-5.62523700	-2.24251500	2.31416100
		H	-3.89246200	-2.69722900	2.23488000
		H	-4.93956600	0.87519000	2.51170200
		H	-5.09460500	1.22040200	0.76179000
		H	-6.31674000	0.19313800	1.58778200
		H	-5.86167600	-1.44751600	-1.92241300
		H	-6.68415500	-1.57174100	-0.33808500
		H	-6.09557400	0.02084600	-0.92505200
		H	-4.90564600	-3.47648500	0.07667100
		H	-4.06838000	-3.05812500	-1.45209700
		H	-3.16115700	-3.03490700	0.08638600
		H	4.57994000	3.38634100	-0.47256000
		H	1.84827800	4.29508800	-3.72080000
		H	3.80479400	4.94185000	-2.28868300
		H	4.98690500	1.86481200	1.11013500
		H	5.54209500	-0.17416600	2.47381400
		H	4.12302500	-2.25708300	2.18841800
		H	2.14785500	-2.15950900	0.60459700
		H	-1.20341100	-1.02266900	-3.25549400
		H	-2.44485500	-0.00997000	-5.23071500
		H	-1.83846500	2.34252000	-5.95339800
		H	-0.03144000	3.56850600	-4.70900500
trans-Int-3	B3LYP SCF energy: -3328.7602 B3LYP enthalpy: -3328.718 B3LYP free energy: -3328.8412 M06 SCF energy in solution: -3332.8453	C	1.96626100	-3.71245300	3.00011500
		C	1.97751900	-3.90410400	1.61249200
		C	1.50467600	-2.89262900	0.76416200
		C	1.01107600	-1.66846900	1.27145600
		C	1.01625100	-1.47738400	2.68966500
		C	1.48542900	-2.50360800	3.52658600
		C	0.56128900	-0.61234200	0.31831300
		C	1.42518900	0.25145400	-0.28147000
		C	1.07646800	1.42844600	-1.10865700
		C	0.54890900	-0.17044100	3.33324000

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N	-1.12617300	0.13715900	1.53223400
C	-0.14235500	1.55770400	-1.81558600
C	-0.43915500	2.71600700	-2.54487000
C	0.47986200	3.77701800	-2.59766400
C	1.70217700	3.66360600	-1.91470300
C	1.99653100	2.50459400	-1.18536800
B	2.95493300	-0.02985900	0.00680200
O	3.63068300	0.53162900	1.06394100
C	4.94239500	-0.12316500	1.13289200
C	5.10919100	-0.70869300	-0.33179500
O	3.71932500	-0.85776300	-0.77561000
C	5.78722300	-2.07207600	-0.39654600
C	5.77096000	0.26851700	-1.30613200
C	5.98317300	0.91724200	1.52787100
C	4.83102600	-1.20573800	2.20781800
C	-5.59831500	0.18633500	0.60296100
C	-4.22248300	0.48502900	0.54470600
N	-3.36400000	-0.36577000	-0.06552300
C	-3.82746400	-1.45739400	-0.72975400
C	-5.18876200	-1.79924600	-0.71331800
C	-6.07830500	-0.97480900	-0.01255700
C	-2.78689700	-2.17266900	-1.49470400
C	-3.66540200	1.76522600	1.05838000
C	-4.17878400	2.39869700	2.20766100
C	-3.59705700	3.60707300	2.61599000
C	-2.54040300	4.13923000	1.86412000
C	-2.10474900	3.43432900	0.72753700
N	-2.64914600	2.27780300	0.33492500
N	-1.52620800	-1.66368300	-1.34699100
C	-0.52100500	-2.15980000	-2.09717500
C	-0.71375500	-3.20568300	-3.00575000
C	-1.99195200	-3.76671600	-3.13242100
C	-3.04175900	-3.23858800	-2.37158600
Ni	-1.37861200	-0.40088900	0.14370400
H	2.33073400	-4.49945600	3.67692200
H	2.35670200	-4.84367000	1.18321400
H	1.53076800	-3.04126600	-0.32417600
H	1.48180500	-2.34597400	4.61642400
H	1.32292400	0.62161900	3.20530900
H	0.38679900	-0.28761200	4.42158300
H	-0.87596700	0.73687000	-1.80533500
H	-1.40009900	2.78877700	-3.07640900
H	0.24719500	4.68505600	-3.17412000

H	2.43301500	4.48611200	-1.94822100
H	2.94569200	2.43698400	-0.63130700
H	5.84746900	-2.41227200	-1.44918400
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H	5.23196800	-2.83652700	0.17786400
H	5.67015600	-0.12482000	-2.33667000
H	5.28541900	1.26400100	-1.27644700
H	6.84930300	0.39710800	-1.09030400
H	5.77731100	1.28270600	2.55337700
H	6.99984300	0.47622700	1.52446500
H	5.97795900	1.78967700	0.84882400
H	5.79914400	-1.71710000	2.37220100
H	4.52628800	-0.73626200	3.16349900
H	4.07026000	-1.96438900	1.94335600
H	-6.28593100	0.88791100	1.09482000
H	-5.54917500	-2.69191800	-1.24150900
H	-7.14960500	-1.22029700	0.02320000
H	-4.99570800	1.94445300	2.78681500
H	-3.96284200	4.12321800	3.51648100
H	-2.05824400	5.08623500	2.14792600
H	-1.27833700	3.81768700	0.10379800
H	0.46303100	-1.69071400	-1.95119400
H	0.13599700	-3.56910300	-3.60023200
H	-2.17543900	-4.59921400	-3.82721000
H	-4.05922800	-3.64013300	-2.46913100

X-ray Crystallographic data of compounds 10, 24, 36, α- and β-*cis*-hydroboration of 53

Crystal of compound **10**, **24** and **36** were prepared in a solvent mixture of DCM and petroleum ether (v/v = 1/1) respectively. **10** (30 mg), **24** (30 mg) and **36** (27 mg) were firstly dissolved in DCM (1 mL) in a vial, then petroleum ether (1 mL) was added dropwise to it. The vial was not fully screwed down and the sample was carefully setting in room temperature. The crystal was obtained in about 96 h. The single crystals of **α- and β-*cis*-hydroboration of 53** were acquired from the wall and bottom of EP tube, respectively.

The X-ray crystallographic structure for **10**. ORTEP representation with 50% probability thermal ellipsoids. Crystal data have been deposited to CCDC number 2265346.

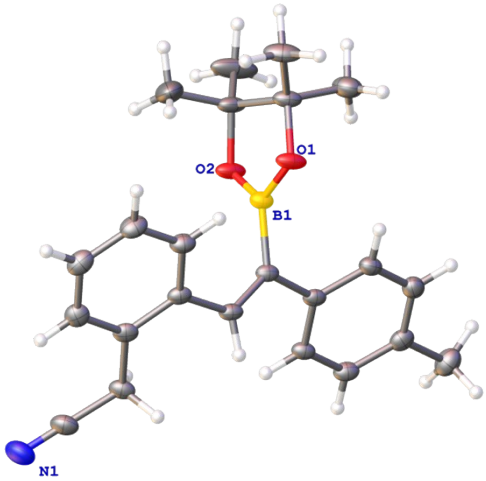


Table S1 Crystal data and structure refinements for **10**

Identification code	10
Empirical formula	$C_{23}H_{26}BNO_2$
Formula weight	359.26
Temperature/K	149.99(10)
Crystal system	Triclinic
Space group	P-1
a/Å	7.0732(3)
b/Å	12.8154(5)
c/Å	12.8838(5)
α/°	109.101(4)
β/°	103.862(4)
γ/°	102.475(4)
Volume/Å^3	1014.75(8)
Z	2
ρ_{calc}g/cm^3	1.176
μ/mm^{-1}	0.573
F(000)	384.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.708 to 143.196
Index ranges	-8 ≤ h ≤ 6, -15 ≤ k ≤ 15, -15 ≤ l ≤ 15
Reflections collected	10644
Independent reflections	3847 [R_{int} = 0.0683, R_{sigma} = 0.0677]
Data/restraints/parameters	3847/0/249
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0838, wR_2 = 0.2317
Final R indexes [all data]	R_1 = 0.0884, wR_2 = 0.2377
Largest diff. peak/hole / e Å^{-3}	0.58/-0.41

The X-ray crystallographic structure for **24** ORTEP representation with 50% probability thermal ellipsoids. Crystal data have been deposited to CCDC number 2265348.

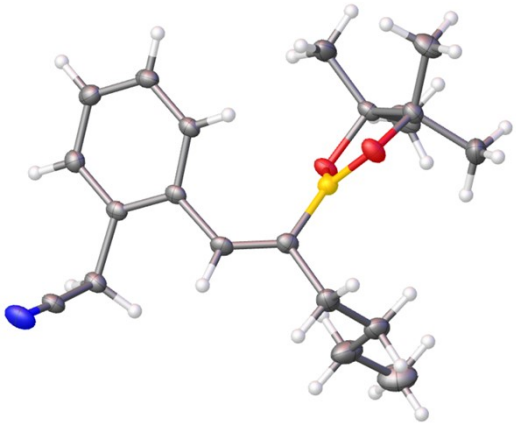


Table S2 Crystal data and structure refinements for **24**

Identification code	24
Empirical formula	$C_{20}H_{28}BNO_2$
Formula weight	325.24
Temperature/K	166(20)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.9832(5)
b/Å	9.6904(4)
c/Å	13.4858(4)
α/°	90
β/°	100.376(3)
γ/°	90
Volume/Å^3	1926.03(12)
Z	4
ρ_{calc}g/cm^3	1.122
μ/mm^{-1}	0.548
F(000)	704.0
Crystal size/mm^3	0.14 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.996 to 142.71
Index ranges	$-17 \le h \le 18$, $-11 \le k \le 11$, $-16 \le l \le 16$
Reflections collected	10323
Independent reflections	3658 [R_{int} = 0.0404, R_{sigma} = 0.0455]
Data/restraints/parameters	3658/0/226
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0634, wR_2 = 0.1697
Final R indexes [all data]	R_1 = 0.0795, wR_2 = 0.1779
Largest diff. peak/hole / e Å^{-3}	0.50/-0.22

The X-ray crystallographic structure for **36** ORTEP representation with 50% probability thermal ellipsoids. Crystal data have been deposited to CCDC number 2265345.

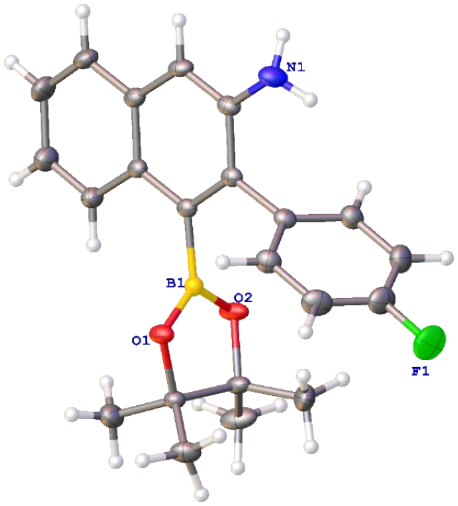


Table S3 Crystal data and structure refinements for **36**

Identification code	36
Empirical formula	$C_{22}H_{23}BFNO_2$
Formula weight	363.22
Temperature/K	169.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.8733(9)
b/Å	11.5417(10)
c/Å	17.0581(17)
α/°	90
β/°	95.130(9)
γ/°	90
Volume/Å^3	1936.1(3)
Z	4
ρ_{calc}g/cm^3	1.246
μ/mm^{-1}	0.085
F(000)	768.0
Crystal size/mm^3	0.14 × 0.12 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.266 to 49.992
Index ranges	$-9 \le h \le 11$, $-11 \le k \le 13$, $-20 \le l \le 17$
Reflections collected	8907
Independent reflections	3417 [R_{int} = 0.0250, R_{sigma} = 0.0340]
Data/restraints/parameters	3417/0/249
Goodness-of-fit on F^2	1.045

Final R indexes [I>=2σ (I)]	R_1 = 0.0475, wR_2 = 0.1094
Final R indexes [all data]	R_1 = 0.0627, wR_2 = 0.1198
Largest diff. peak/hole / e Å^{-3}	0.23/-0.21

The X-ray crystallographic structure for **α-*cis*-hydroboration of 53** ORTEP representation with 50% probability thermal ellipsoids. Crystal data have been deposited to CCDC number 2312562.

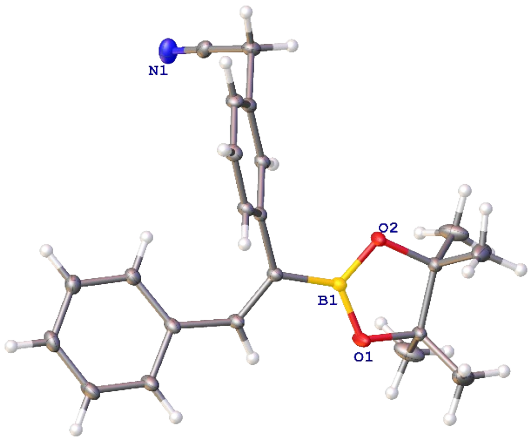


Table S4 Crystal data and structure refinement for **α-*cis*-hydroboration of 53**

Identification code	**α-*cis*-hydroboration of 53**
Empirical formula	$C_{22}H_{24}BNO_2$
Formula weight	345.23
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.1597(2)
b/Å	10.2937(2)
c/Å	11.2498(3)
α/°	79.933(2)
β/°	89.723(2)
γ/°	76.120(2)
Volume/Å^3	1123.73(4)
Z	2
ρ_{calc}g/cm^3	1.020
μ/mm^{-1}	0.501
F(000)	368.0
Crystal size/mm^3	0.15 × 0.13 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.988 to 153.098
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14
Reflections collected	13108
Independent reflections	4524 [R_{int} = 0.0166, R_{sigma} = 0.0139]
Data/restraints/parameters	4524/0/239

Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0649, wR_2 = 0.1629
Final R indexes [all data]	R_1 = 0.0665, wR_2 = 0.1641
Largest diff. peak/hole / e $Å^{-3}$	0.66/-0.56

The X-ray crystallographic structure for **β-*cis*-hydroboration of 53** ORTEP representation with 50% probability thermal ellipsoids. Crystal data have been deposited to CCDC number 2312563.

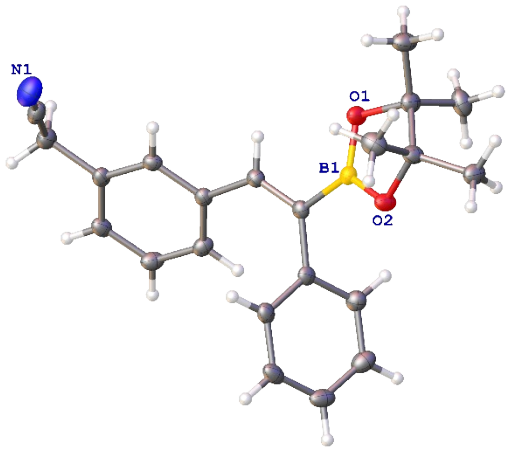
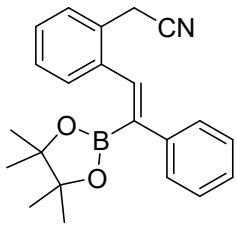


Table S5 Crystal data and structure refinement for **β-*cis*-hydroboration of 53**

Identification code	**β-*cis*-hydroboration of 53**
Empirical formula	$C_{22}H_{24}BNO_2$
Formula weight	345.23
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.6547(10)
b/Å	10.2621(13)
c/Å	10.6861(15)
α/°	102.169(11)
β/°	105.217(10)
γ/°	103.684(10)
Volume/$Å^3$	949.7(2)
Z	2
ρ_{calc}g/cm^3	1.207
μ/mm^{-1}	0.076
F(000)	368.0
Crystal size/mm^3	0.16 × 0.14 × 0.11
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.128 to 49.996
Index ranges	-11 ≤ h ≤ 10, -11 ≤ k ≤ 12, -8 ≤ l ≤ 12
Reflections collected	7165

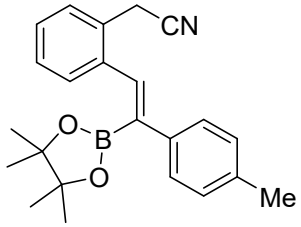
Independent reflections	3351 [R_{int} = 0.0254, R_{sigma} = 0.0415]
Data/restraints/parameters	3351/0/239
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0498, wR_2 = 0.1141
Final R indexes [all data]	R_1 = 0.0626, wR_2 = 0.1232
Largest diff. peak/hole / e $Å^{-3}$	0.53/-0.27

Characterization data for all products



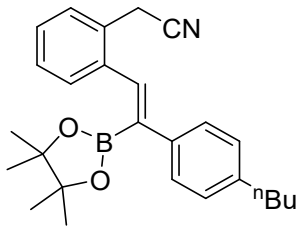
(E)-2-(2-(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetonitrile (2)

White solid (53.8 mg, 78%), m.p. = 141-143 °C.
^{1}H NMR (400 MHz, Chloroform-d) δ 7.51 – 7.43 (m, 3H), 7.42 – 7.26 (m, 7H), 3.80 (s, 2H), 1.14 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.2, 138.3, 136.7, 129.4, 128.7, 128.55, 128.3, 128.0, 127.8, 127.5, 126.9, 117.9, 84.1, 24.6, 22.0. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.51. HRMS-ESI (m/z): calcd for $C_{22}H_{24}BNO_2$, $[M+H]^+$: 346.1978, found, 346.1963.



(E)-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(p-tolyl)vinyl)phenyl)acetonitrile (10)

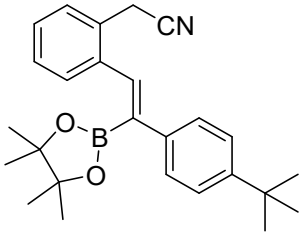
White solid (53.2 mg, 74%), m.p. = 142-144 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.0 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.21 (s, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 3.75 (s, 2H), 2.32 (s, 3H), 1.10 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.4, 138.4, 137.3, 135.8, 129.5, 129.4, 128.6, 128.2, 128.0, 127.8, 126.8, 117.9, 84.0, 24.7, 22.0, 21.2. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.30. HRMS-ESI (m/z): calcd for $C_{23}H_{26}BNO_2$, $[M+H]^+$: 360.2135, found, 360.2140.



(E)-2-(2-(2-(4-butylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetonitrile (11)

Yellow solid (56.2 mg, 70%), m.p. = 81-83 °C.

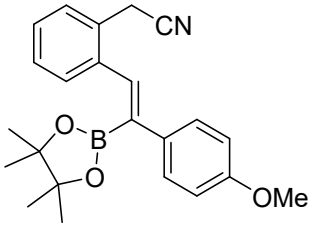
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 7.4 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 3H), 7.27 – 7.19 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 3.72 (s, 2H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.58 – 1.51 (m, 2H), 1.35 – 1.28 (m, 2H), 1.08 (s, 12H), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.4, 138.5, 138.4, 135.8, 129.5, 128.7, 128.6, 128.2, 128.0, 127.8, 126.8, 118.0, 84.0, 35.4, 33.6, 24.66, 22.4, 22.0, 14.0. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.24. HRMS-ESI (m/z): calcd for $C_{26}H_{32}BNO_2$, $[M+H]^+$: 402.2604, found, 402.2605.



(E)-2-(2-(2-(4-(tert-butyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetonitrile (12)

Yellow solid (57.8 mg, 72%), m.p. = 130-132 °C.

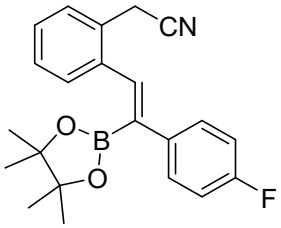
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.35 (m, 1H), 7.31 (dd, *J* = 7.5, 1.6 Hz, 5H), 7.26 – 7.17 (m, 3H), 3.70 (s, 2H), 1.25 (s, 9H), 1.06 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.5, 138.5, 138.2, 135.9, 129.5, 128.6, 128.2, 128.0, 127.8, 126.6, 125.6, 117.9, 84.0, 34.6, 31.4, 24.7, 22.0. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.40. HRMS-ESI (m/z): calcd for $C_{26}H_{32}BNO_2$, $[M+H]^+$: 402.2604, found, 402.2605.



(E)-2-(2-(2-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetonitrile (13)

Light yellow solid (51.8 mg, 69%), m.p. = 167-169 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.0 Hz, 1H), 7.32 (td, *J* = 6.6, 1.8 Hz, 3H), 7.27 – 7.20 (m, 2H), 7.14 (s, 1H), 6.86 – 6.80 (m, 2H), 3.75 (s, 3H), 3.72 (s, 2H), 1.07 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.2, 138.5, 134.9, 133.8, 129.5, 128.6, 128.2, 128.0, 128.0, 127.8 118.0, 114.1, 84.0, 55.3, 24.7, 22.0. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.72. HRMS-ESI (m/z): calcd for $C_{23}H_{26}BNO_3$, $[M+H]^+$:376.2084, found, 376.2097.

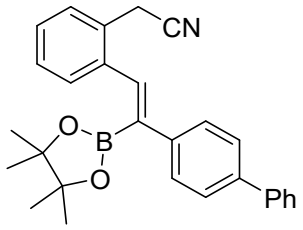


(E)-2-(2-(2-(4-fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetonitrile (14)

Light yellow solid (40.7 mg, 56%), m.p. = 145-147 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.33 (m, 3H), 7.29 (t, *J* = 6.4 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.17 (s, 1H), 6.97 (t, *J* = 8.5 Hz, 2H), 3.71 (s, 2H), 1.06 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.41 (d, *J* = 246.6 Hz), 138.1, 137.3 (d, *J* = 3.3 Hz), 136.9, 136.9, 129.5, 128.5,

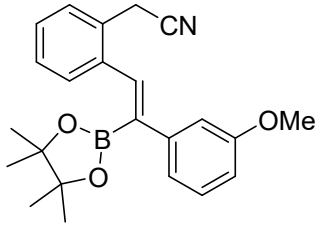
128.46, 128.4, 128.1, 127.9, 117.8, 115.6, 115.4, 84.1, 77.4, 77.1, 76.8, 24.6, 22.1. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.50. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -115.00. HRMS-ESI (m/z): calcd for $C_{22}H_{23}BFNO_2$, $[M+H]^+$: 364.1884, found, 364.1881.



(E)-2-(2-(2-([1,1'-biphenyl]-4-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetonitrile (15)

Yellow solid (54.8 mg, 65%), m.p. = 172-174 °C.

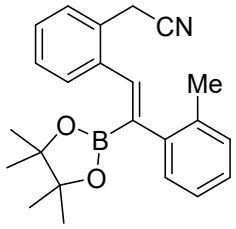
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.61 (m, 4H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.42 (m, 4H), 7.42 – 7.30 (m, 4H), 3.85 (s, 2H), 1.19 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-d) δ 140.8, 140.3, 140.2, 138.3, 136.7, 129.8, 128.8, 128.6, 128.4, 128.0, 127.8, 127.4, 127.3, 127.0, 117.9, 84.1, 24.7, 22.1. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.70. HRMS-ESI (m/z): calcd for $C_{28}H_{28}BNO_2$, $[M+H]^+$: 422.2291, found, 422.2291.



(E)-2-(2-(2-(3-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetonitrile (16)

Yellow solid (44.3 mg, 59%), m.p. = 92-94 °C.

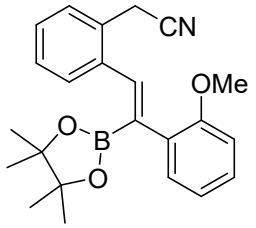
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.1 Hz, 1H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.25 – 7.17 (m, 4H), 6.99 – 6.93 (m, 2H), 6.77 (dd, *J* = 8.2, 2.4 Hz, 1H), 3.75 (s, 3H), 3.72 (s, 2H), 1.06 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.8, 142.6, 138.2, 136.8, 129.6, 129.4, 128.5, 128.4, 128.0, 127.8, 119.4, 117.9, 113.2, 112.3, 84.1, 55.3, 24.6, 22.0. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.53. HRMS-ESI (m/z): calcd for $C_{23}H_{26}BNO_3$, $[M+H]^+$: 376.2084, found, 376.2097.



(E)-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(o-tolyl)vinyl)phenyl)acetonitrile (17)

Yellow solid (51.0 mg, 71%), m.p. = 63-65 °C.

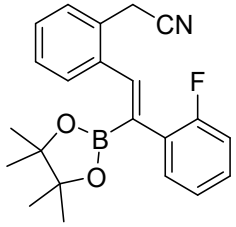
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 7.1 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.35 – 7.27 (m, 2H), 7.20 (q, *J* = 3.9 Hz, 4H), 7.01 (s, 1H), 3.78 (s, 2H), 2.37 (s, 3H), 1.09 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.3, 140.5, 138.2, 135.2, 130.1, 129.5, 128.7, 128.3, 128.3, 127.9, 127.7, 127.2, 126.1, 117.9, 83.8, 24.6, 22.1, 20.6. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.03. HRMS-ESI (m/z): calcd for $C_{23}H_{26}BNO_2$, $[M+H]^+$: 360.2135, found, 360.2140.



(E)-2-(2-(2-(2-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetonitrile (18)

Yellow solid (49.5 mg, 66%), m.p. = 144-146 °C.

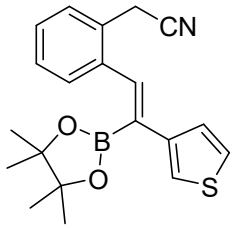
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, J = 7.3 Hz, 1H), 7.30 (dd, J = 7.5, 1.6 Hz, 1H), 7.28 – 7.18 (m, 4H), 7.11 (s, 1H), 6.91 (t, J = 7.4 Hz, 1H), 6.79 (d, J = 8.2 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 2H), 1.03 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.5, 138.3, 137.8, 131.8, 129.8, 129.0, 128.7, 128.2, 127.7, 127.5, 121.4, 118.1, 110.4, 83.5, 55.4, 24.9, 22.0. ^{11}B NMR (128 MHz, Chloroform-d) δ 30.11. HRMS-ESI (m/z): calcd for $C_{23}H_{26}BNO_3$, $[M+H]^+$: 376.2084, found, 376.2097.



(E)-2-(2-(2-(2-fluorophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetonitrile (19)

Light yellow solid (39.9 mg, 55%), m.p. = 114-116 °C.

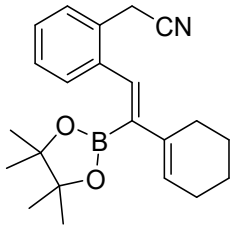
^{1}H NMR (400 MHz, Chloroform-d) δ 7.49 – 7.43 (m, 2H), 7.38 – 7.27 (m, 5H), 7.16 (t, J = 7.5 Hz, 1H), 7.06 (dd, J = 10.5, 8.3 Hz, 1H), 3.80 (s, 2H), 1.12 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-d) δ 160.14 (d, *J* = 246.0 Hz), 139.7 (d, *J* = 1.8 Hz), 137.9, 129.6, 129.3 (d, *J* = 8.3 Hz), 129.1 (d, *J* = 3.7 Hz), 128.6, 128.6, 128.0, 127.7, 124.6 (d, *J* = 3.4 Hz), 117.9, 115.5, 115.3, 84.0, 77.4, 77.1, 76.7, 24.6, 22.1. ^{11}B NMR (128 MHz, Chloroform-d) δ 30.53. ^{19}F NMR (377 MHz, Chloroform-d) δ -113.41. HRMS-ESI (m/z): calcd for $C_{22}H_{23}BFNO_2$, $[M+H]^+$: 364.1884, found, 364.1881.



(E)-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(thiophen-3-yl)vinyl)phenyl)acetonitrile (20)

Yellow solid (34.4 mg, 49%), m.p. = 104-106 °C.

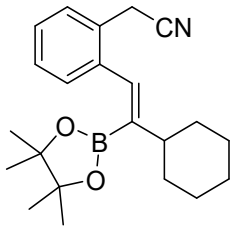
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.0 Hz, 1H), 7.42 (s, 1H), 7.41 – 7.29 (m, 6H), 3.81 (s, 2H), 1.18 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.3, 138.3, 135.5, 129.5, 128.5, 128.2, 128.0, 127.8, 125.9, 125.6, 122.3, 117.9, 84.0, 24.7, 22.0. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.35. HRMS-ESI (m/z): calcd for $C_{20}H_{22}BNO_2S$, $[M+H]^+$: 352.1543, found, 352.1544.



(E)-2-(2-(2-(cyclohex-1-en-1-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetonitrile (21)

Light yellow solid (35.6 mg, 51%), m.p. =105-107°C.

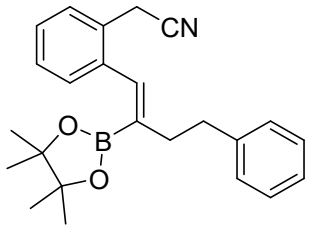
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.39 (m, 1H), 7.31 – 7.24 (m, 3H), 6.89 (s, 1H), 5.88 (t, *J* = 4.0 Hz, 1H), 3.75 (s, 2H), 2.29 (ddd, *J* = 7.7, 4.0, 1.6 Hz, 2H), 2.22 – 2.16 (m, 2H), 1.74 (ddt, *J* = 8.4, 6.1, 2.5 Hz, 2H), 1.66 – 1.62 (m, 2H), 1.06 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.1, 138.1, 130.5, 129.9, 129.7, 128.6, 127.8, 127.8, 127.7, 118.1, 83.9, 26.4, 25.5, 24.7, 22.7, 22.3, 22.0. HRMS-ESI (m/z): calcd for $C_{22}H_{28}BNO_2$, $[M+H]^+$: 350.2291, found, 350.2279.



(E)-2-(2-(2-cyclohexyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetonitrile (22)

White solid (42.2 mg, 63%), m.p. =66-68°C.

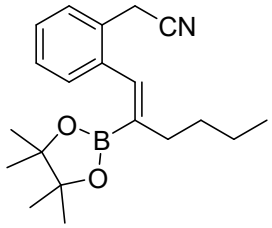
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 – 7.35 (m, 1H), 7.26 – 7.20 (m, 3H), 6.79 (s, 1H), 3.73 (s, 2H), 2.23 (m, 1H), 1.80 (dd, *J* = 16.1, 6.3 Hz, 4H), 1.74 – 1.66 (m, 1H), 1.37 – 1.21 (m, 5H), 1.07 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.0, 133.1, 129.6, 128.2, 127.7, 127.6, 127.6, 118.1, 83.5, 45.6, 33.0, 26.6, 26.2, 24.6, 21.9. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.70. HRMS-ESI (m/z): calcd for $C_{22}H_{30}BNO_2$, $[M+H]^+$: 352.2448, found, 352.2443.



(E)-2-(2-(4-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)phenyl)acetonitrile (23)

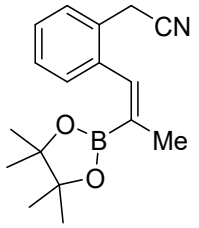
Yellow oil (47.0 mg, 63%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.33 (m, 3H), 7.29 – 7.20 (m, 6H), 6.72 (s, 1H), 3.38 (s, 2H), 2.87 (t, *J* = 7.4 Hz, 2H), 2.69 (t, *J* = 7.3 Hz, 2H), 1.16 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.6, 138.5, 138.4, 129.5, 128.9, 128.4, 128.0, 127.7, 127.5, 127.4, 125.9, 118.1, 83.5, 39.1, 35.7, 24.6, 21.5. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.62. HRMS-ESI (m/z): calcd for $C_{24}H_{28}BNO_2$, $[M+H]^+$: 374.2291, found, 374.2288.



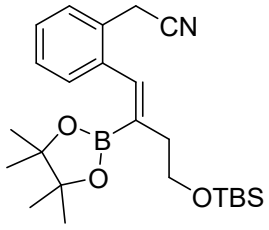
(E)-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-1-yl)phenyl)acetonitrile (24)

Yellow solid (41.6mg, 64%), m.p. = 146-148 °C.
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 (d, *J* = 7.2 Hz, 1H), 7.26 – 7.19 (m, 3H), 6.85 (s, 1H), 3.72 (s, 2H), 2.32 (t, *J* = 7.4 Hz, 2H), 1.50 – 1.43 (m, 2H), 1.37 (dd, *J* = 14.0, 6.3 Hz, 2H), 1.09 (s, 12H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.6, 136.2, 129.6, 127.8, 127.6, 127.6, 127.4, 118.0, 83.4, 36.9, 31.7, 24.4, 22.4, 21.8, 13.9. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.30. HRMS-ESI (m/z): calcd for $C_{20}H_{28}BNO_2$, $[M+H]^+$: 326.2291, found, 326.2288.



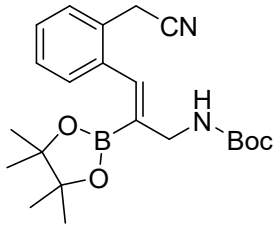
(E)-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)phenyl)acetonitrile (25)

Yellow oil (26.1 mg, 46%).
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 7.3 Hz, 1H), 7.26 (dt, *J* = 8.1, 4.3 Hz, 1H), 7.22 (d, *J* = 3.9 Hz, 2H), 6.92 (s, 1H), 3.73 (s, 2H), 1.99 (d, *J* = 1.7 Hz, 3H), 1.12 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.6, 137.7, 129.7, 127.8, 127.7, 127.5, 118.1, 83.5, 24.5, 22.8, 21.9. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.40. HRMS-ESI (m/z): calcd for $C_{17}H_{22}BNO_2$, $[M+H]^+$: 284.1822, found, 284.1833.



(E)-2-(2-(4-((tert-butyldimethylsilyl)oxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-1-en-1-yl)phenyl)acetonitrile (26)

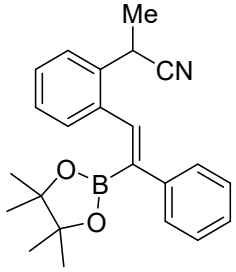
Yellow oil (58.1 mg, 68%)
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 7.4 Hz, 1H), 7.20 – 7.08 (m, 3H), 6.87 (s, 1H), 3.69 – 3.61 (m, 4H), 2.47 – 2.42 (m, 2H), 1.00 (s, 12H), 0.83 (s, 9H), 0.00 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.7, 138.5, 129.6, 127.8, 127.6, 127.4, 118.1, 83.4, 63.0, 40.8, 26.0, 24.5, 21.9, 18.4, -5.2. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.41. HRMS-ESI (m/z): calcd for $C_{24}H_{38}BNO_3Si$, $[M+H]^+$: 428.2792, found, 428.2817.



tert-butyl(E)-(3-(2-(cyanomethyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)allyl)carbamate (27)

Yellow solid (35.8 mg, 45%), m.p. = 95-97°C.

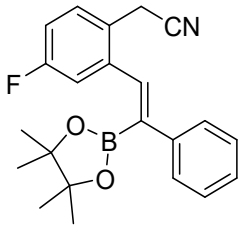
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, *J* = 7.5 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.25 – 7.19 (m, 2H), 7.04 (s, 1H), 4.85 (s, 1H), 3.97 (d, *J* = 5.7 Hz, 2H), 3.73 (s, 2H), 1.45 (s, 9H), 1.11 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.7, 138.4, 137.6, 129.6, 128.2, 128.0, 127.8, 127.5, 83.7, 28.4, 24.5, 21.8. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 29.81. HRMS-ESI (m/z): calcd for $C_{22}H_{31}BN_2O_4$, $[M+H]^+$: 399.2455, found, 399.2478.



(E)-2-(2-(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)propanenitrile (28)

Light yellow oil (36.6 mg, 51%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (dd, *J* = 6.6, 1.9 Hz, 1H), 7.33 (d, *J* = 7.4 Hz, 2H), 7.28 – 7.21 (m, 5H), 7.15 (q, *J* = 8.7, 8.1 Hz, 2H), 4.07 (q, *J* = 7.2 Hz, 1H), 1.45 (d, *J* = 7.3 Hz, 3H), 0.98 (d, *J* = 10.9 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.1, 137.5, 136.6, 135.8, 129.9, 128.7, 128.5, 127.6, 127.5, 126.9, 126.4, 122.1, 84.0, 28.8, 24.7, 24.6, 20.7. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.66. HRMS-ESI (m/z): calcd for $C_{23}H_{26}BNO_2$, $[M+H]^+$: 360.2135, found, 360.2140.

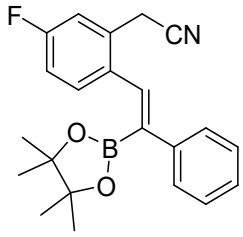


(E)-2-(4-fluoro-2-(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetonitrile (29)

Light yellow solid (42.1 mg, 58%), m.p. = 146-148 °C.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.30 (m, 6H), 7.17 – 7.11 (m, 2H), 6.97 (td, J = 8.3, 2.7 Hz, 1H), 3.69 (s, 2H), 1.13 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-d) δ 162.1 (d, J = 247.3 Hz), 140.9, 140.2 (d, J = 8.0 Hz), 135.5 (d, J = 1.8 Hz), 129.8 (d, J = 8.6 Hz), 128.7, 127.8, 126.9, 124.3 (d, J = 3.2 Hz), 117.7, 116.4 (d, J = 22.1 Hz), 114.9 (d, J = 21.5 Hz), 84.3, 77.4, 77.1, 76.8,

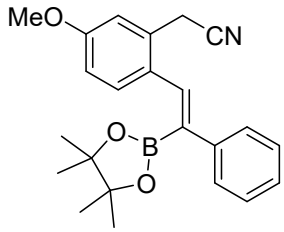
24.7, 21.4. ^{11}B NMR (128 MHz, Chloroform-d) δ 30.51. ^{19}F NMR (377 MHz, Chloroform-d) δ -114.49. HRMS-ESI (m/z): calcd for $C_{22}H_{23}BFNO_2$, $[M+H]^+$: 364.1884, found, 364.1881.



(E)-2-(5-fluoro-2-(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetonitrile (30)

Yellow solid (45.0 mg, 62%), m.p. = 118-120°C.

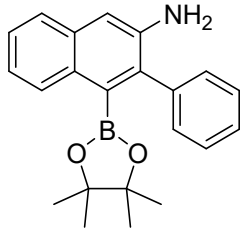
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 (dt, *J* = 8.2, 1.8 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.25 – 7.20 (m, 1H), 7.16 – 7.11 (m, 2H), 6.93 (td, *J* = 8.3, 2.5 Hz, 1H), 3.71 (s, 2H), 1.08 (s, 12H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.4 (d, *J* = 249.1 Hz), 141.0, 135.7, 134.3, 131.2 (d, *J* = 7.7 Hz), 130.8 (d, *J* = 7.7 Hz), 128.7, 127.6, 126.9, 117.3, 115.2 (d, *J* = 23.6 Hz), 114.6 (d, *J* = 20.8 Hz), 84.1, 24.6, 22.1. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.59. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -113.07. HRMS-ESI (m/z): calcd for $C_{22}H_{23}BFNO_2$, $[M+H]^+$: 364.1884, found, 364.1881.



(E)-2-(5-methoxy-2-(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetonitrile (31)

Yellow solid (53.3 mg, 71%), m.p. = 156-158 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.42 (m, 2H), 7.36 (dd, *J* = 8.2, 6.5 Hz, 3H), 7.30 – 7.27 (m, 1H), 7.20 (s, 1H), 7.02 (d, *J* = 2.5 Hz, 1H), 6.82 (dd, *J* = 8.4, 2.6 Hz, 1H), 3.85 (s, 3H), 3.77 (s, 2H), 1.18 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.7, 141.5, 136.4, 130.6, 130.6, 129.8, 128.6, 127.3, 126.9, 117.8, 113.6, 113.1, 84.0, 55.5, 24.7, 22.2. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.69. HRMS-ESI (m/z): calcd for $C_{23}H_{26}BNO_3$, $[M+H]^+$: 376.2084, found, 376.2079.

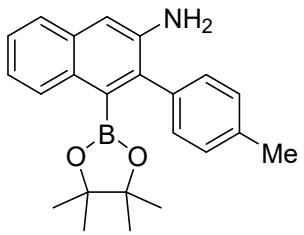


3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-amine (3)

Brown oil (49.7 mg, 72%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 8.3 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.31 (dtt, *J* = 8.0, 5.5, 2.6 Hz, 5H), 7.23 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.15 – 7.10 (m, 1H), 6.97 (s, 1H), 3.56 (s, 2H), 1.01 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.7, 139.4, 135.6, 134.3, 130.5, 130.3,

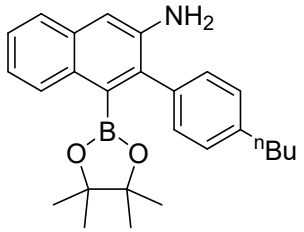
128.5, 127.7, 127.6, 126.0, 125.8, 122.7, 110.2, 83.9, 24.8. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.35. HRMS-ESI (m/z): calcd for $C_{22}H_{24}BNO_2$, $[M+H]^+$: 346.1978, found, 346.2001.



4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(p-tolyl)naphthalen-2-amine (32)

Yellow solid (51.7 mg, 72%), m.p. = 108-110 °C.

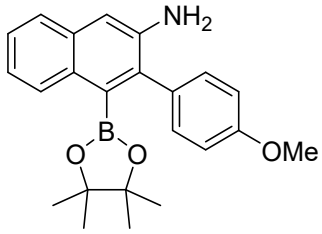
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.31 (dd, *J* = 16.0, 7.6 Hz, 3H), 7.22 (dd, *J* = 14.4, 7.4 Hz, 3H), 7.04 (s, 1H), 3.56 (s, 2H), 2.40 (s, 3H), 1.12 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.9, 137.3, 136.3, 135.6, 134.2, 130.5, 130.2, 129.1, 127.6, 125.9, 125.7, 122.6, 110.1, 83.8, 24.8, 21.3. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.40. HRMS-ESI (m/z): calcd for $C_{23}H_{26}BNO_2$, $[M+H]^+$: 360.2135, found, 360.2140.



3-(4-butylphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-amine (33)

Dark yellow solid (41.7 mg, 52%), m.p. = 82-84 °C.

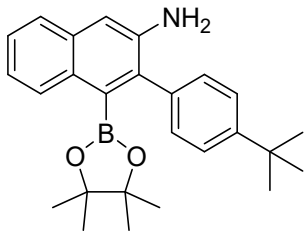
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.38 – 7.33 (m, 3H), 7.30 – 7.23 (m, 3H), 7.09 (s, 1H), 3.29 (s, 2H), 2.71 – 2.66 (m, 2H), 1.69 – 1.61 (m, 2H), 1.41 (dd, *J* = 14.8, 7.5 Hz, 2H), 1.15 (s, 12H), 0.97 (d, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.4, 141.8, 136.5, 135.7, 134.2, 130.5, 130.1, 128.6, 127.6, 126.0, 125.7, 122.6, 110.1, 83.8, 35.5, 34.0, 24.8, 22.3, 14.0. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.77. HRMS-ESI (m/z): calcd for $C_{26}H_{32}BNO_2$, $[M+H]^+$: 402.2604, found, 402.2605.



3-(4-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-amine (34)

Yellow solid (46.5 mg, 62%), m.p. = 139-141 °C.

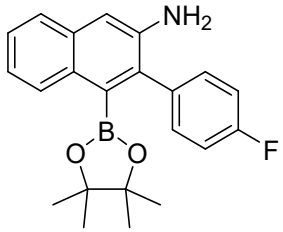
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.3 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.33 (td, *J* = 6.4, 1.6 Hz, 3H), 7.21 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.05 (s, 1H), 7.00 – 6.96 (m, 2H), 3.85 (s, 3H), 3.67 (s, 2H), 1.14 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.3, 142.1, 135.2, 134.2, 131.6, 131.5, 130.5, 127.6, 125.9, 125.7, 122.6, 113.9, 110.0, 83.8, 55.5, 24.8. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.94. HRMS-ESI (m/z): calcd for $C_{23}H_{26}BNO_3$, $[M+H]^+$: 376.2084, found, 376.2097.



3-(4-(tert-butyl)phenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-amine (35)

Dark yellow solid (36.9 mg, 46%), m.p. = 147-149 °C.

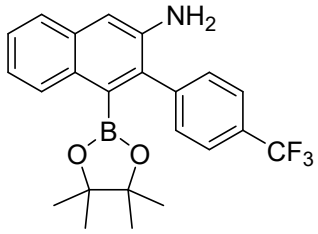
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.41 – 7.33 (m, 3H), 7.24 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.10 (s, 1H), 3.09 (s, 2H), 1.39 (s, 10H), 1.13 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.6, 141.7, 136.3, 135.7, 134.2, 130.5, 129.9, 127.6, 126.0, 125.7, 125.4, 122.7, 110.2, 83.8, 34.6, 31.4, 24.8. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.77. HRMS-ESI (m/z): calcd for $C_{26}H_{32}BNO_2$, $[M+H]^+$: 402.2604, found, 402.2605.



3-(4-fluorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-amine (36)

Dark yellow solid (42.9 mg, 59%), m.p. = 139-141 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.44 – 7.31 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 8.6 Hz, 2H), 7.07 (s, 1H), 3.62 (s, 2H), 1.14 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ162.5 (d, *J* = 246.3 Hz), 141.7, 135.3 (d, *J* = 3.3 Hz), 134.4, 134.3, 132.1 (d, *J* = 8.0 Hz), 130.4, 127.7, 126.0, 122.8, 115.4 (d, *J* = 21.3 Hz), 110.3, 83.9, 24.8. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.57. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -114.82. HRMS-ESI (m/z): calcd for $C_{22}H_{23}BFNO_2$, $[M+H]^+$: 364.1884, found, 364.1881.

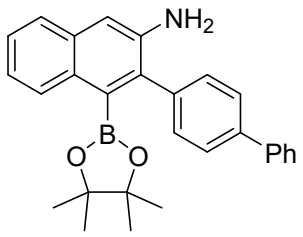


4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(4-(trifluoromethyl)phenyl)naphthalen-2-amine (37)

Yellow solid (40.5 mg, %), m.p. = 175-177 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 7.9 Hz, 2H), 7.40 – 7.33 (m, 1H), 7.27 – 7.22 (m, 1H), 7.10 (s, 1H), 3.61 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.5, 141.1, 134.4, 134.2, 130.9, 130.5, 130.0 (q, *J* = 32.5 Hz), 127.7, 126.2, 126.0, 125.4 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 272.1 Hz), 123.0, 110.7, 84.0, 24.6. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.62. ^{19}F NMR (377 MHz,

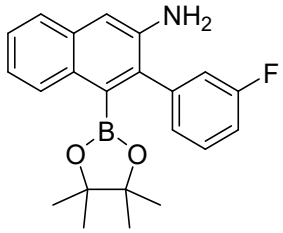
Chloroform-*d*) δ -62.54. HRMS-ESI (m/z): calcd for $C_{23}H_{23}BF_3NO_2$, $[M+H]^+$: 414.1852, found, 414.1861.



3-([1,1'-biphenyl]-4-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-amine (38)

Yellow solid (43.0 mg, 51%), m.p. = 177-179 °C.

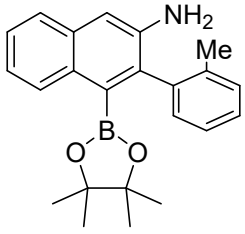
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.3 Hz, 1H), 7.68 – 7.59 (m, 5H), 7.49 (dd, *J* = 7.8, 2.7 Hz, 4H), 7.40 – 7.33 (m, 2H), 7.24 (ddd, *J* = 8.1, 6.0, 1.2 Hz, 1H), 7.09 (s, 1H), 3.72 (s, 2H), 1.12 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.7, 141.0, 140.6, 138.4, 135.2, 134.3, 130.8, 130.5, 128.9, 127.7, 127.4, 127.3, 127.1, 126.0, 125.9, 122.8, 110.3, 83.9, 24.8. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.95. HRMS-ESI (m/z): calcd for $C_{28}H_{28}BNO_2$, $[M+H]^+$: 422.2291, found, 346.2001.



3-(3-fluorophenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-amine (39)

Yellow oil (38.5 mg, 53%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.3 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.44 – 7.33 (m, 2H), 7.25 – 7.19 (m, 2H), 7.15 (dt, *J* = 9.5, 2.0 Hz, 1H), 7.08 (q, *J* = 3.6, 3.1 Hz, 2H), 3.66 (s, 2H), 1.15 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 164.0, 161.5, 141.6 (d, *J* = 7.6 Hz), 141.3, 134.3, 134.2 (d, *J* = 1.8 Hz), 130.4, 130.1, 130.0, 127.7, 126.1 (d, *J* = 3.0 Hz), 126.0 (d, *J* = 6.7 Hz), 122.9, 117.5 (d, *J* = 21.0 Hz), 114.5 (d, *J* = 20.9 Hz), 110.5, 84.0, 24.8. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.82. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -113.04. HRMS-ESI (m/z): calcd for $C_{23}H_{23}BF_3NO_2$, $[M+H]^+$: 364.1884, found, 364.1881.

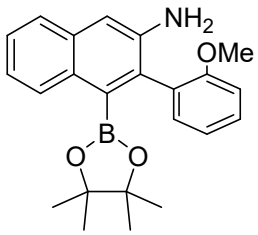


4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(o-tolyl)naphthalen-2-amine (40)

Yellow solid (48.9 mg, 68%), m.p. = 93-95 °C.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.30 – 7.28 (m, 2H), 7.27 – 7.23 (m, 3H), 7.09 (s, 1H), 2.15 (s, 3H), 1.11 (s, 6H), 1.05 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.7, 138.4, 138.2, 135.0, 134.3, 130.8, 130.4, 129.9, 128.0, 127.7, 126.0, 125.9, 125.7, 122.6, 109.8, 83.7, 24.7, 24.5, 19.8. ^{11}B NMR

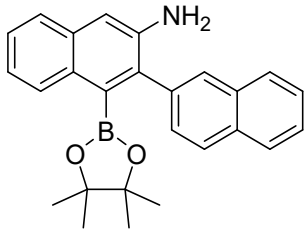
(128 MHz, Chloroform-*d*) δ 32.19. HRMS-ESI (m/z): calcd for $C_{23}H_{26}BNO_2$, $[M+H]^+$: 360.2135, found, 360.2140.



3-(2-methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-amine (41)

Yellow oil (41.3 mg, 55%).

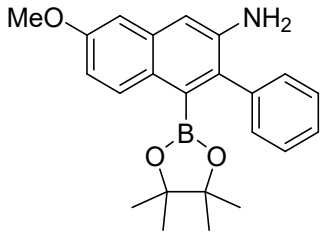
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.3 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.33 – 7.22 (m, 2H), 7.18 – 7.08 (m, 2H), 7.02 (s, 1H), 6.98 – 6.88 (m, 2H), 3.69 (s, 3H), 3.33 (s, 2H), 1.06 (s, 6H), 0.98 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.9, 142.2, 134.3, 132.9, 132.4, 130.7, 129.4, 128.4, 127.8, 126.0, 125.7, 122.5, 120.9, 111.4, 110.4, 83.6, 56.1, 24.9, 24.6. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.19. HRMS-ESI (m/z): calcd for $C_{23}H_{26}BNO_3$, $[M+H]^+$: 376.2084, found, 376.2097.



1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[2,2'-binaphthalen]-3-amine (42)

Yellow solid (50.6 mg, 64%), m.p. = 118-120 °C.

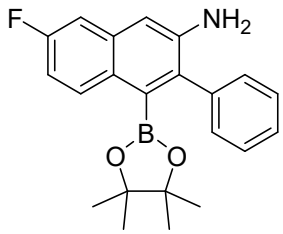
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.76 (m, 5H), 7.56 – 7.49 (m, 2H), 7.44 (dq, *J* = 6.7, 3.5 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.03 (s, 1H), 3.47 (s, 2H), 0.89 (d, *J* = 34.4 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.8, 137.1, 135.4, 134.4, 133.5, 132.8, 130.6, 129.4, 128.2, 128.0, 128.0, 127.7, 127.7, 126.3, 126.1, 126.0, 125.9, 122.8, 110.3, 83.8, 24.7, 24.6. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.89. HRMS-ESI (m/z): calcd for $C_{26}H_{26}BNO_2$, $[M+H]^+$: 396.2135, found, 396.2124.



7-methoxy-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-amine (43)

Dark yellow solid (30.0mg, 40%), m.p. = 155-157 °C.

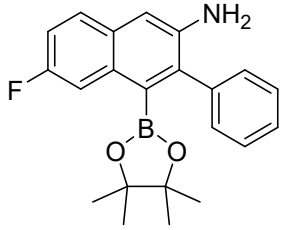
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.8 Hz, 1H), 7.38 – 7.28 (m, 5H), 6.91 (s, 1H), 6.83 (d, *J* = 9.3 Hz, 2H), 3.82 (s, 3H), 3.32 (s, 2H), 1.03 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.6, 142.2, 139.5, 135.5, 133.2, 130.5, 129.2, 128.5, 127.5, 125.9, 115.2, 109.5, 104.18, 83.8, 55.2, 24.8. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.50. HRMS-ESI (m/z): calcd for $C_{23}H_{26}BNO_3$, $[M+H]^+$: 376.2084, found, 376.2097.



7-fluoro-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-amine (44)

Yellow solid (37.8 mg, 52%), m.p. = 106-108 °C.

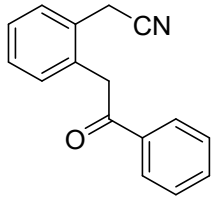
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (dd, *J* = 9.1, 5.7 Hz, 1H), 7.46 – 7.36 (m, 5H), 7.19 (dd, J = 10.4, 2.7 Hz, 1H), 7.02 – 6.96 (m, 2H), 3.72 (s, 2H), 1.11 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.0 (d, *J* = 244.2 Hz), 142.7, 139.1, 135.3 (d, *J* = 9.7 Hz), 134.8 (d, *J* = 2.8 Hz), 130.3, 130.0 (d, *J* = 9.4 Hz), 128.6, 127.8, 127.3, 112.6 (d, *J* = 25.1 Hz), 109.3 (d, *J* = 5.1 Hz), 108.8 (d, *J* = 20.6 Hz), 84.0, 24.7. ^{11}B NMR (128 MHz, Chloroform-d) δ 31.76. ^{19}F NMR (377 MHz, Chloroform-d) δ -115.91. HRMS-ESI (m/z): calcd for $C_{22}H_{23}BFNO_2$, $[M+H]^+$: 364.1884, found, 364.1881.



6-fluoro-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-2-amine (45)

Yellow solid (45.8 mg, 48%), m.p. = 116-118 °C.

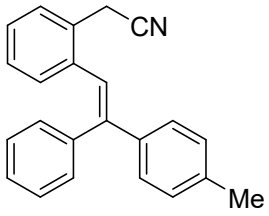
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 – 7.51 (m, 2H), 7.43 (d, *J* = 6.1 Hz, 2H), 7.41 – 7.38 (m, 3H), 7.17 – 7.12 (m, 1H), 7.08 (s, 1H), 3.64 (s, 2H), 1.12 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 158.8 (d, *J* = 240.6 Hz), 141.2 (d, *J* = 2.4 Hz), 139.2, 136.9, 131.2, 130.6 (d, *J* = 8.6 Hz), 130.1, 128.6, 127.9 (d, *J* = 8.7 Hz), 127.8, 116.0 (d, *J* = 25.2 Hz), 111.0 (d, *J* = 20.8 Hz), 110.4, 84.0, 24.7. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 31.77. ^{19}F NMR (377 MHz, Chloroform-*d*) δ -119.24. HRMS-ESI (m/z): calcd for $C_{22}H_{23}BFNO_2$, $[M+H]^+$: 364.1884, found, 364.1881.



2-(2-(2-oxo-2-phenylethyl)phenyl)acetonitrile (46)

White solid (101 mg, 86%), m.p. = 81-83 °C.

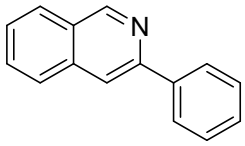
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.46 – 7.37 (m, 3H), 7.28 – 7.20 (m, 2H), 7.14 – 7.09 (m, 1H), 4.32 (s, 2H), 3.62 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.5, 136.3, 133.8, 133.1, 131.5, 129.7, 129.4, 128.9, 128.6, 128.4, 128.2, 117.8, 43.0, 22.0. HRMS-ESI (m/z): calcd for $C_{16}H_{13}ON$, $[M+Na]^+$: 258.0895, found, 258.0910.



(E)-2-(2-(2-phenyl-2-(p-tolyl)vinyl)phenyl)acetonitrile (47)

White soild (103.5 mg, 67%), m.p. = 101-103 °C.

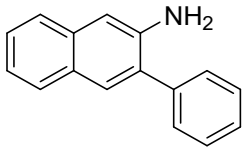
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (d, *J* = 6.2 Hz, 8H), 7.12 (s, 1H), 7.05 (d, *J* = 7.7 Hz, 1H), 6.95 (dd, *J* = 16.4, 7.8 Hz, 3H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.78 (s, 1H), 3.48 (s, 2H), 2.23 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.9, 143.0, 137.6, 137.1, 136.3, 130.7, 130.4, 129.0, 128.6, 128.3, 128.3, 128.3, 128.1, 127.9, 127.5, 124.6, 118.0, 22.1, 21.3. HRMS-ESI (m/z): calcd for $C_{23}H_{19}N$, $[M+H]^+$: 310.1596, found, 310.1593.



3-phenylisoquinoline (48)[12]

Light yellow oil (59.4 mg, 58%).

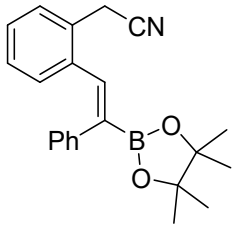
^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.35 (s, 1H), 8.15 – 8.12 (m, 2H), 8.08 (s, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.72 (dd, *J* = 6.9, 1.1 Hz, 1H), 7.59 (td, *J* = 8.0, 1.0 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.42 (tt, *J* = 6.7, 1.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.4, 151.3, 139.6, 136.7, 130.5, 128.8, 128.5, 127.8, 127.6, 127.1, 127.0, 126.9, 116.6.



2-amino-3-phenylnaphthalene (49)[13]

Brown oil (80.6 mg, 75%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.1 Hz, 1H), 7.53 (d, *J* = 6.4 Hz, 2H), 7.45 (dt, *J* = 7.8, 1.7 Hz, 2H), 7.43 – 7.37 (m, 2H), 7.34 – 7.26 (m, 2H), 7.15 (ddd, *J* = 8.0, 5.1, 1.1 Hz, 1H), 6.99 (s, 1H), 3.82 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.2, 139.1, 134.4, 130.8, 129.5, 129.3, 128.9, 128.0, 127.8, 127.6, 126.3, 125.4, 122.7, 109.0.

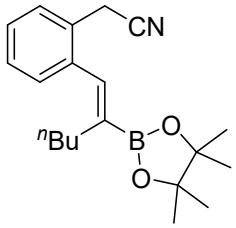


(Z)-2-(2-(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)acetonitrile (Z-2)

White solid (20.7mg, 30%), m.p. = 100-102 °C.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.40 (dd, J = 8.2, 2.7 Hz, 2H), 7.28 – 7.21 (m, 2H), 7.13 –

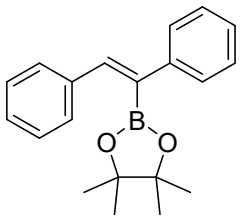
7.00 (m, 4H), 6.85 (d, J = 7.7 Hz, 2H), 3.61 – 3.29 (m, 2H), 1.22 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-d) δ 145.0, 140.1, 136.3, 129.6, 129.3, 128.6, 128.6, 128.3, 127.4, 127.1, 118.2, 84.1, 24.8, 21.7. ^{11}B NMR (128 MHz, Chloroform-d) δ 30.31.



(Z)-2-(2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-1-yl)phenyl)acetonitrile (Z-24)

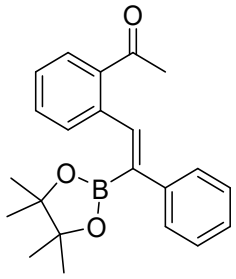
Yellow oil (40.3 mg, 62%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.46 (m, 1H), 7.30 (dt, *J* = 7.4, 3.7 Hz, 2H), 7.19 – 7.16 (m, 1H), 7.13 (s, 1H), 3.67 (s, 2H), 2.14 – 2.08 (m, 2H), 1.31 (s, 12H), 1.26 – 1.15 (m, 4H), 0.79 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.8, 137.2, 129.4, 128.1, 127.8, 127.8, 127.8, 117.9, 83.6, 32.0, 29.4, 24.8, 22.6, 21.7, 13.9. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 30.54.



(E)-2-(1,2-diphenylvinyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (51)[14]

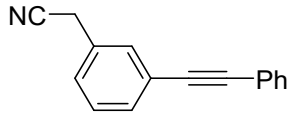
White solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47-7.44 (m, 4H), 7.33-7.21 (m,7H), 1.29 (s,12H) ppm; ^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.6, 140.7, 138.7, 128.4, 128.2, 128.1, 127.5, 126.9, 126.8, 84.0, 24.8. ^{11}B NMR (128 MHz, Chloroform-*d*) δ 32.18.



(E)-1-(2-(2-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl)phenyl)ethan-1-one (52)

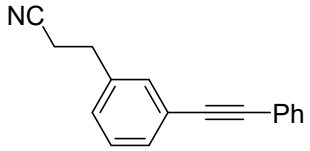
Yellow oil (35.8 mg, 53%).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.67 (d, J = 7.7 Hz, 1H), 7.61 (s, 1H), 7.44 (d, J = 7.8 Hz, 2H), 7.37 (dt, J = 14.7, 7.2 Hz, 3H), 7.29 (d, J = 8.6 Hz, 2H), 7.19 – 7.14 (m, 1H), 2.50 (s, 3H), 1.07 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-d) δ 201.0, 142.1, 141.35, 139.5, 137.4, 131.3, 130.5, 129.2, 128.5, 127.4, 127.1, 126.9, 83.8, 29.9, 24.7.^{11}B NMR (128 MHz, Chloroform-d) δ 30.88. HRMS-ESI (m/z): calcd for $C_{22}H_{25}BO_3$, $[M+H]^+$: 349.1975, found, 349.1977.



2-(3-(phenylethynyl)phenyl)acetonitrile (53)

Yellow oil.[1]H NMR (400 MHz, Chloroform-*d*) δ 7.55 (dd, *J* = 6.6, 2.8 Hz, 2H), 7.50 (d, *J* = 7.3 Hz, 2H), 7.37 (p, *J* = 4.4 Hz, 4H), 7.29 (d, *J* = 7.8 Hz, 1H), 3.74 (s, 2H). [13]C NMR (101 MHz, Chloroform-d) δ 131.7, 131.3, 131.0, 130.2, 129.2, 128.6, 128.5, 127.7, 124.3, 122.9, 117.6, 90.41, 88.5, 23.4.



3-(3-(phenylethynyl)phenyl)propanenitrile (54)

White oil. [1]H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.52 (m, 2H), 7.48 – 7.44 (m, 1H), 7.41 (s, 1H), 7.39 – 7.31 (m, 4H), 7.21 (d, *J* = 7.7 Hz, 1H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.63 (t, *J* = 7.4 Hz, 2H). [13]C NMR (101 MHz, Chloroform-*d*) δ 138.3, 131.7, 131.4, 130.5, 129.0, 128.5, 128.4, 128.3, 123.9, 123.1, 119.0, 89.8, 89.0, 31.4, 19.2.

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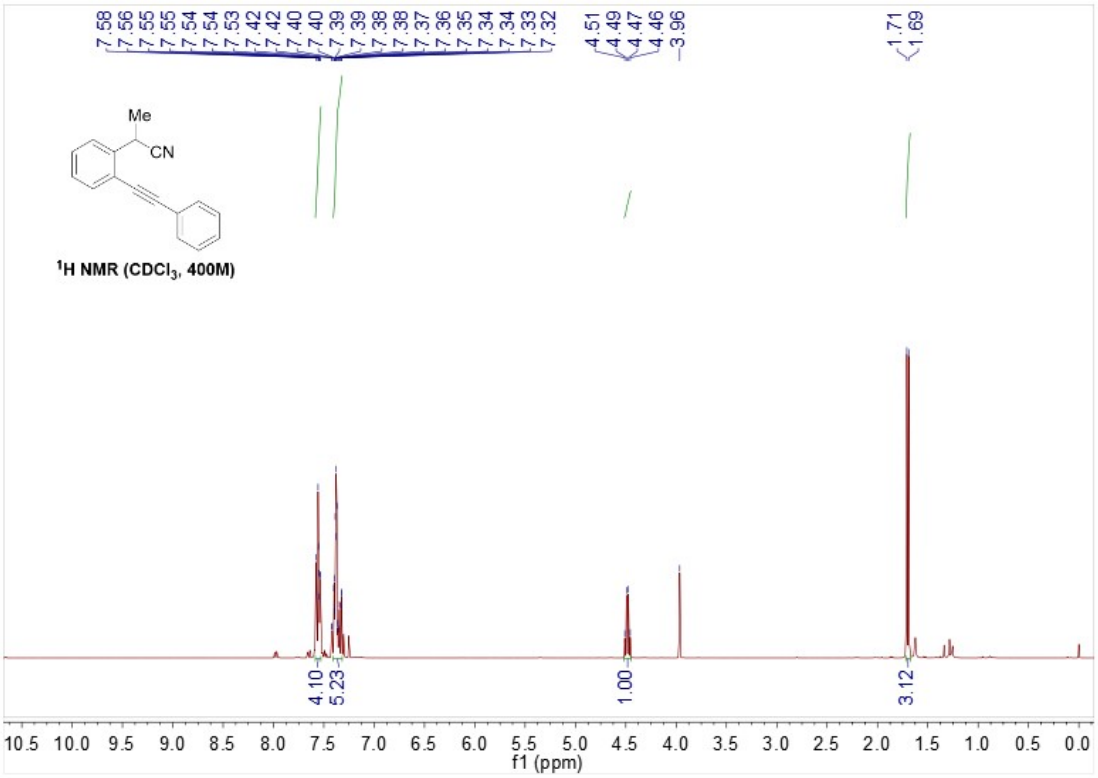
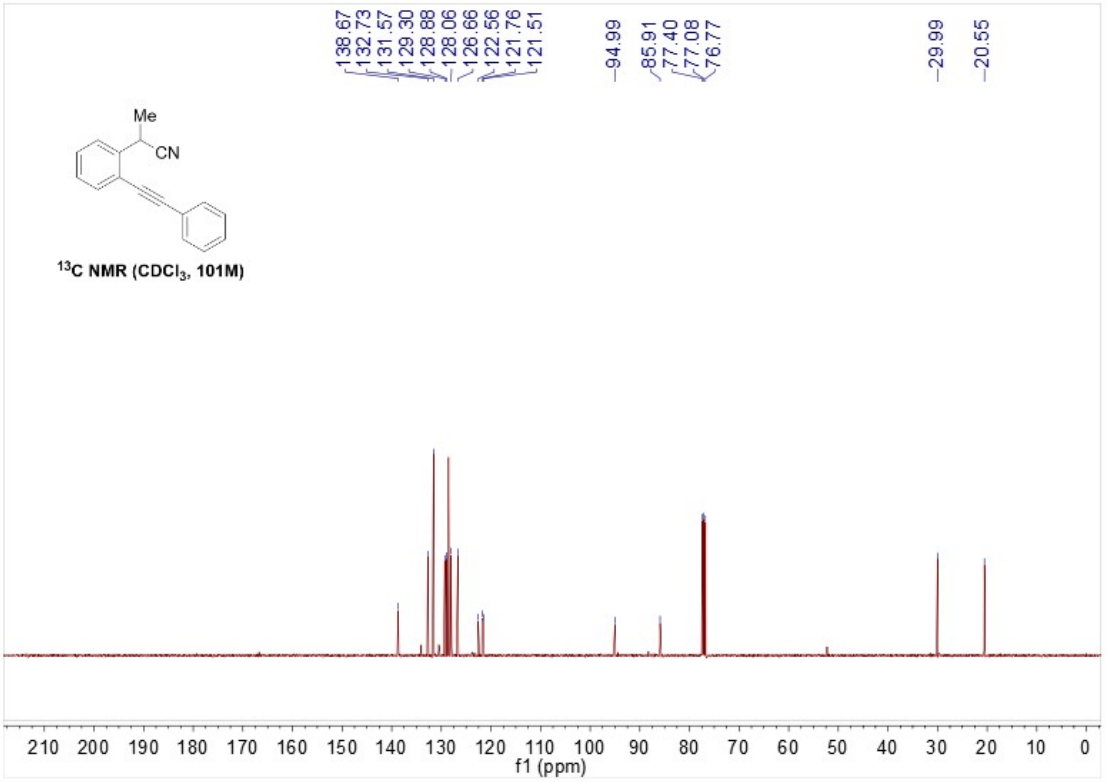
NMR Spectra for all compounds

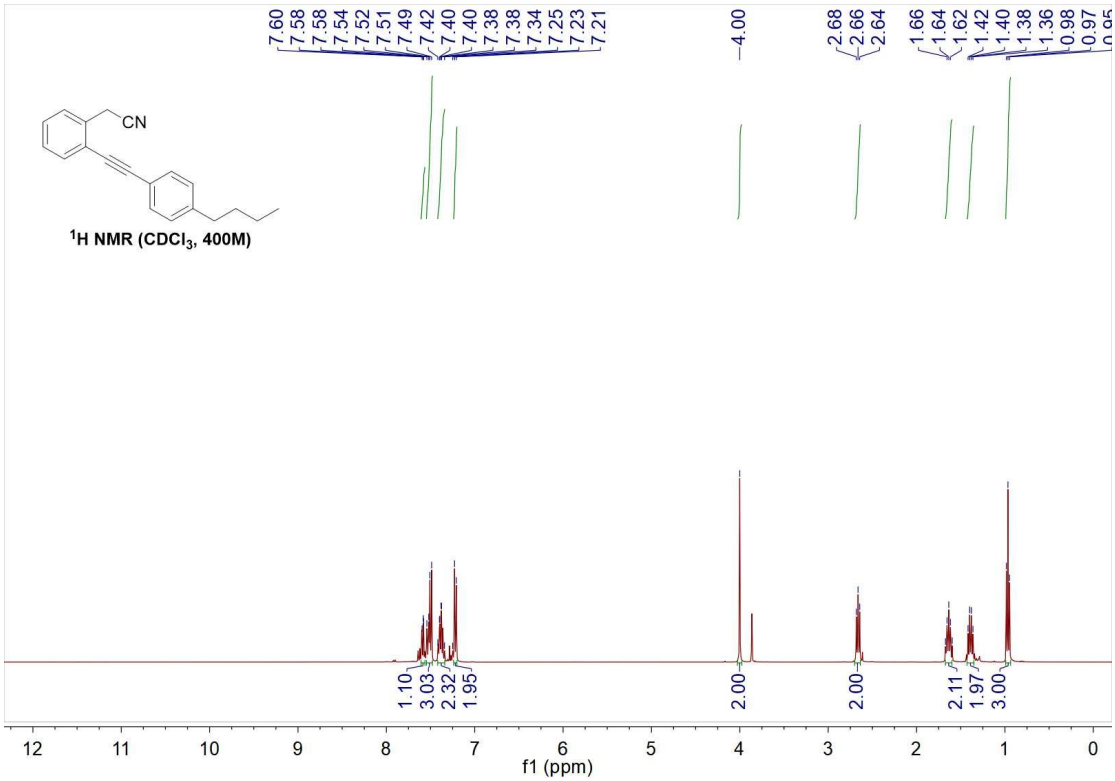
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 1u



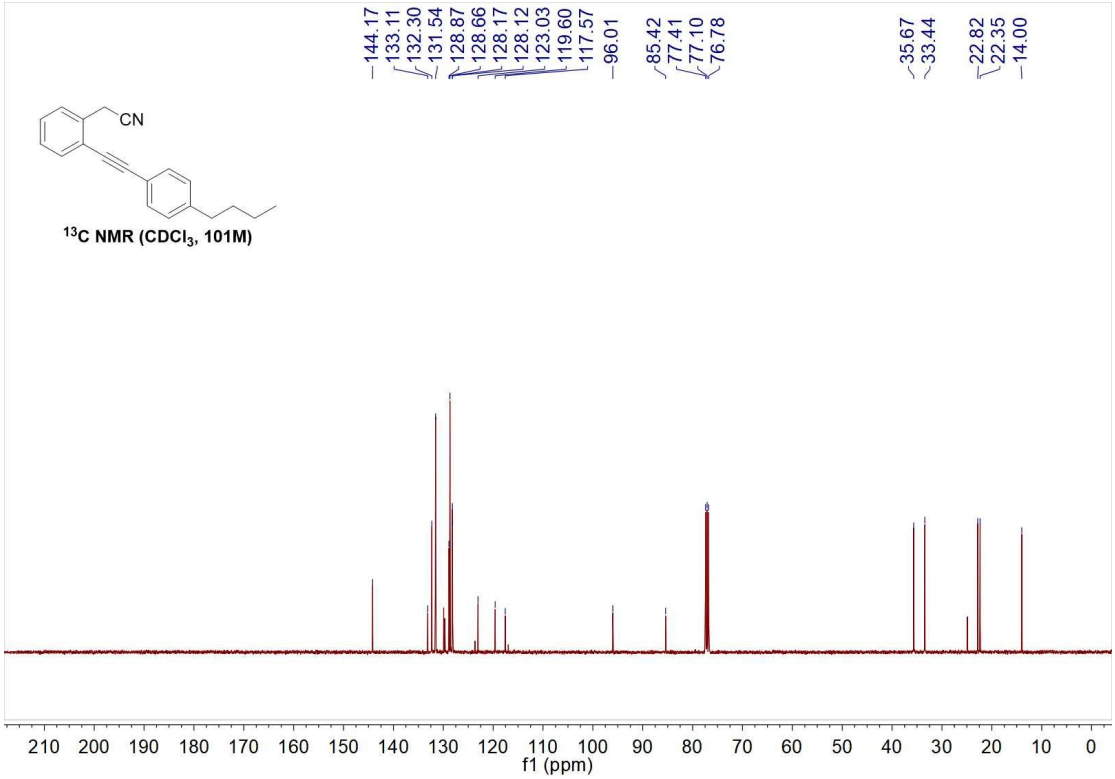
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 1u



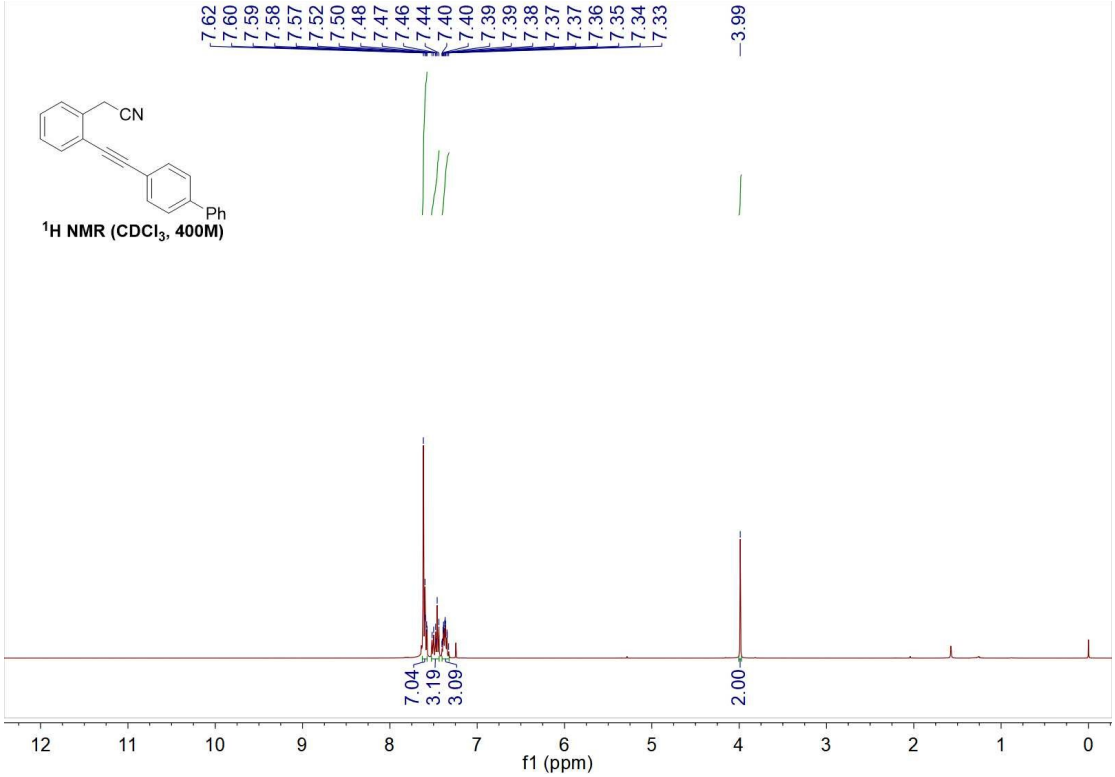
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 1v



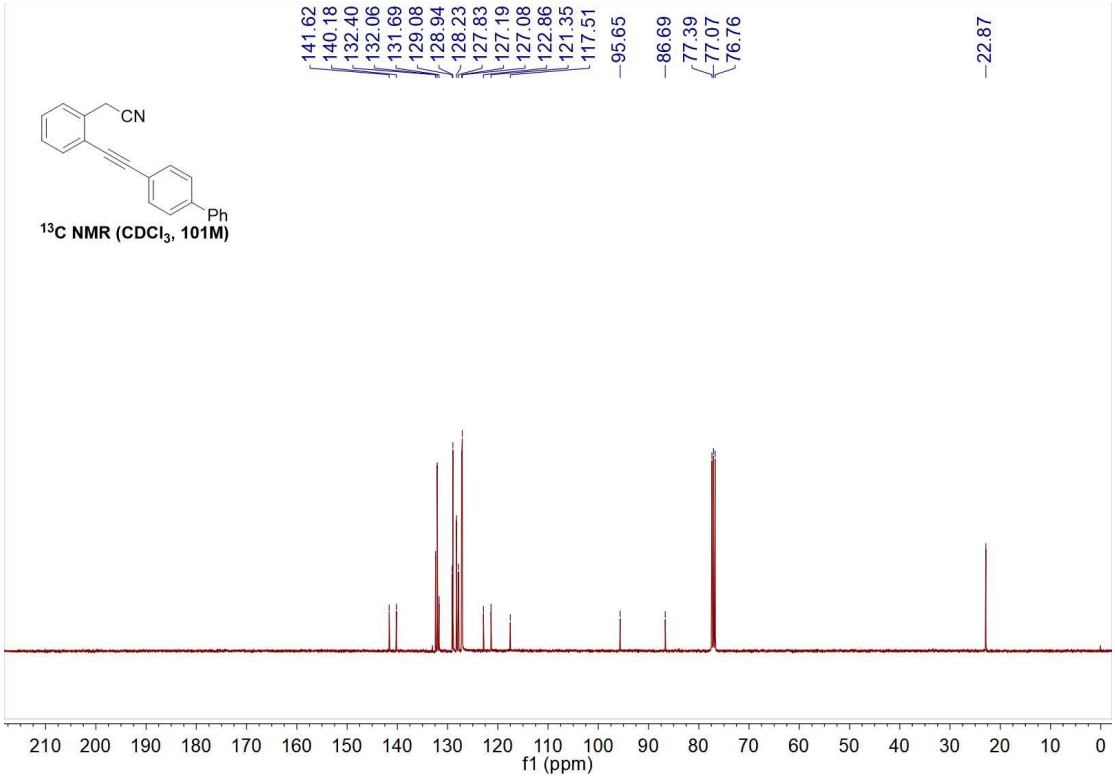
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 1v



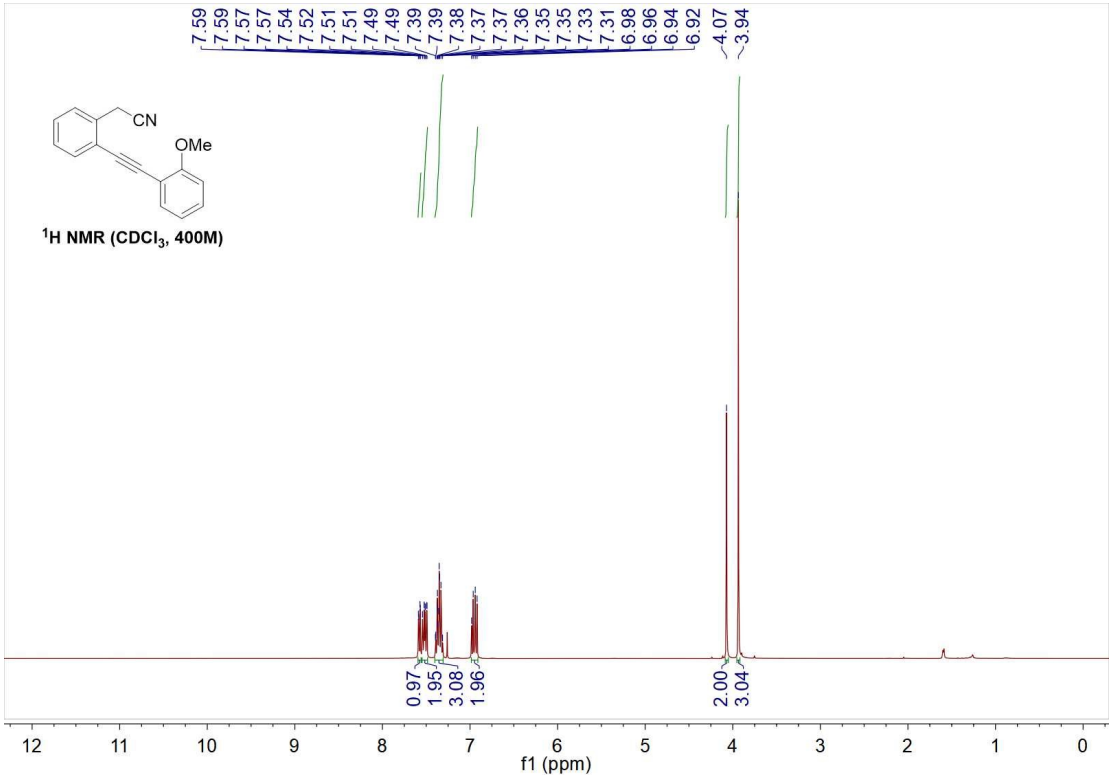
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 1w



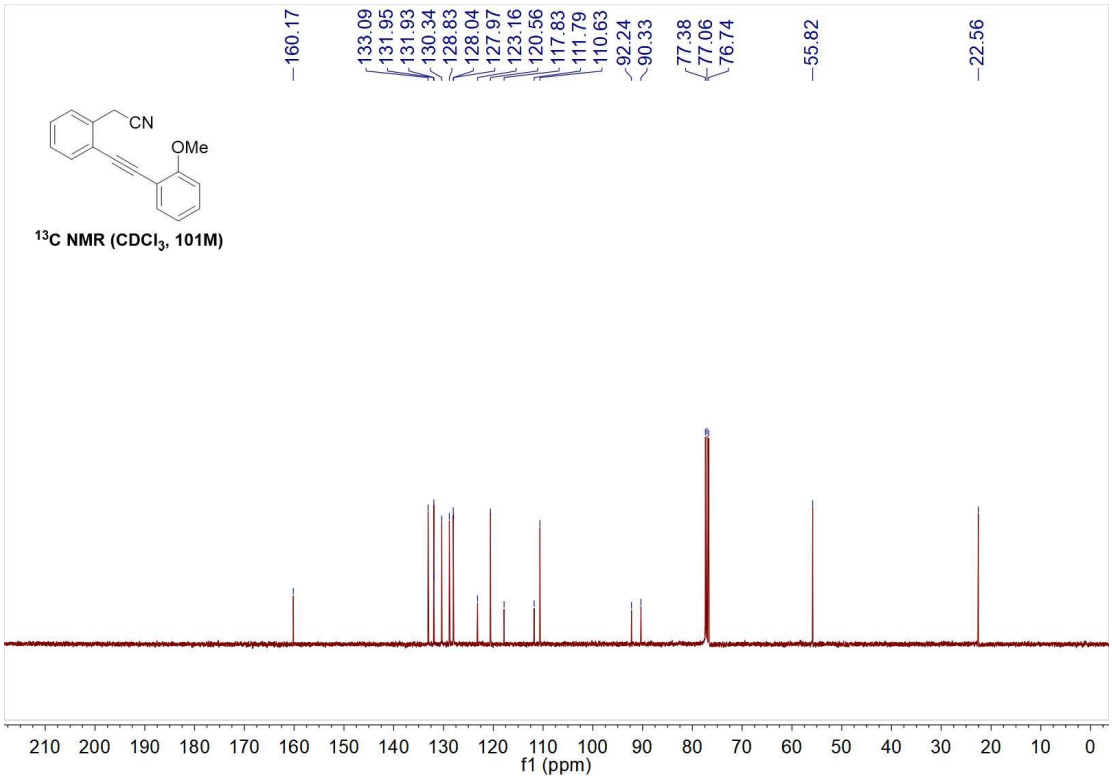
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 1w



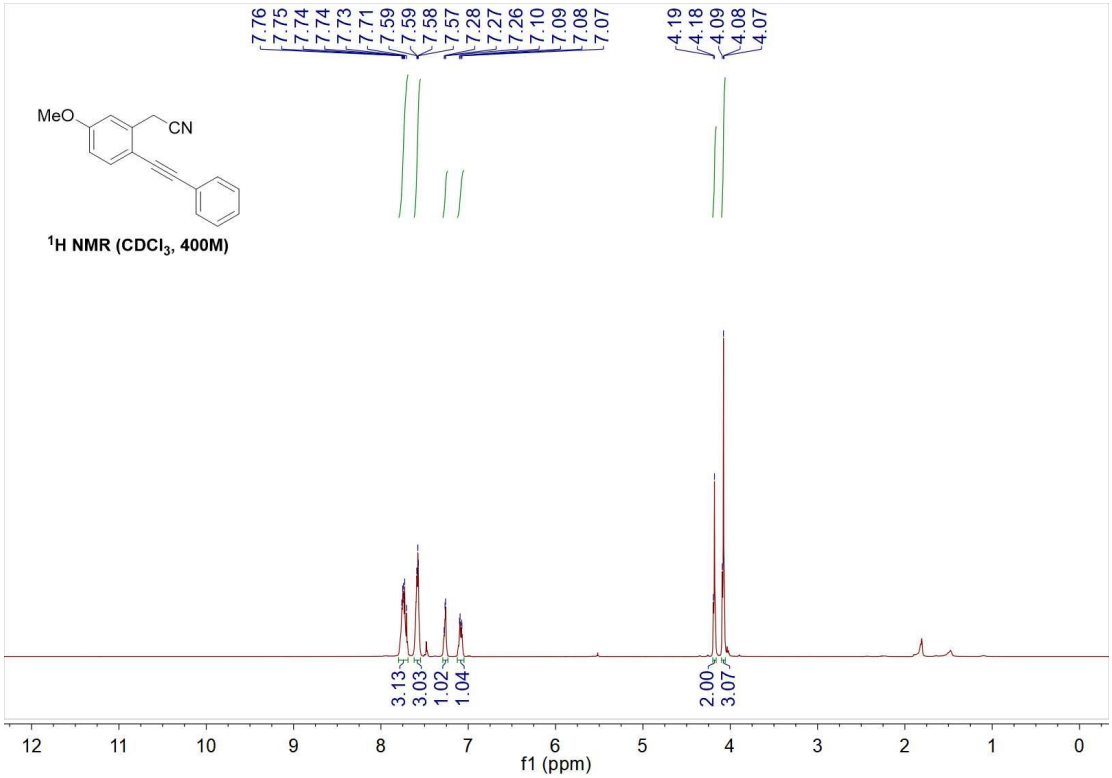
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 1x



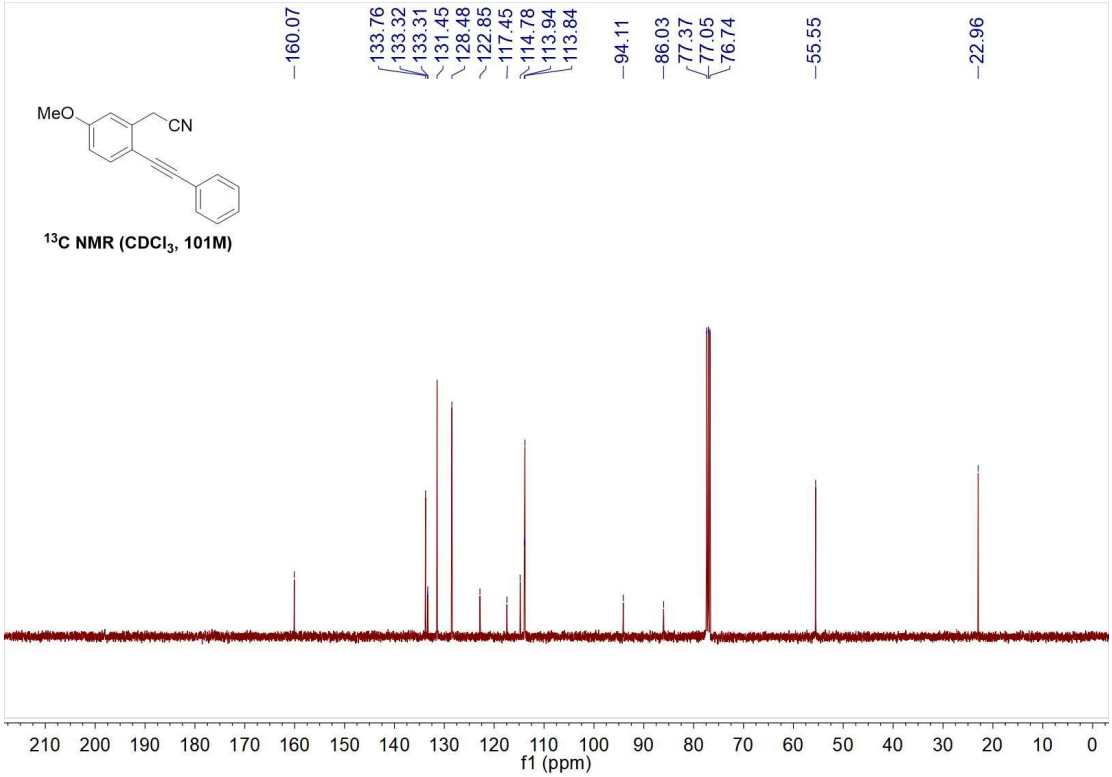
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 1x



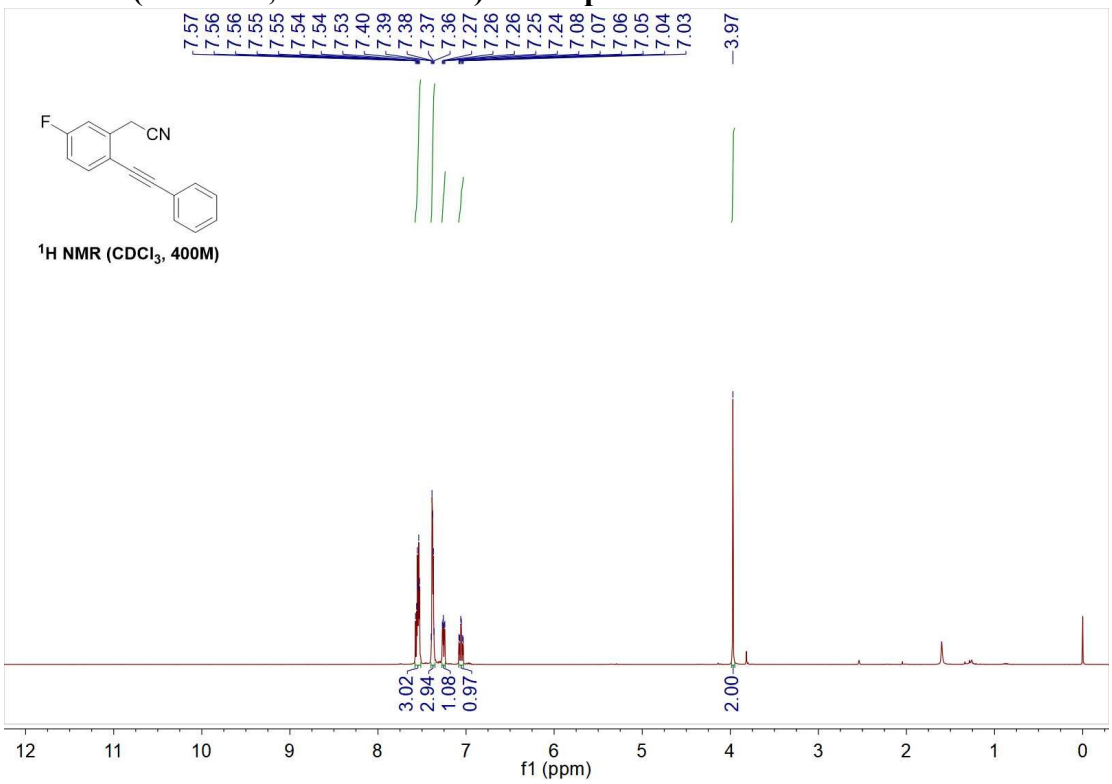
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 1y



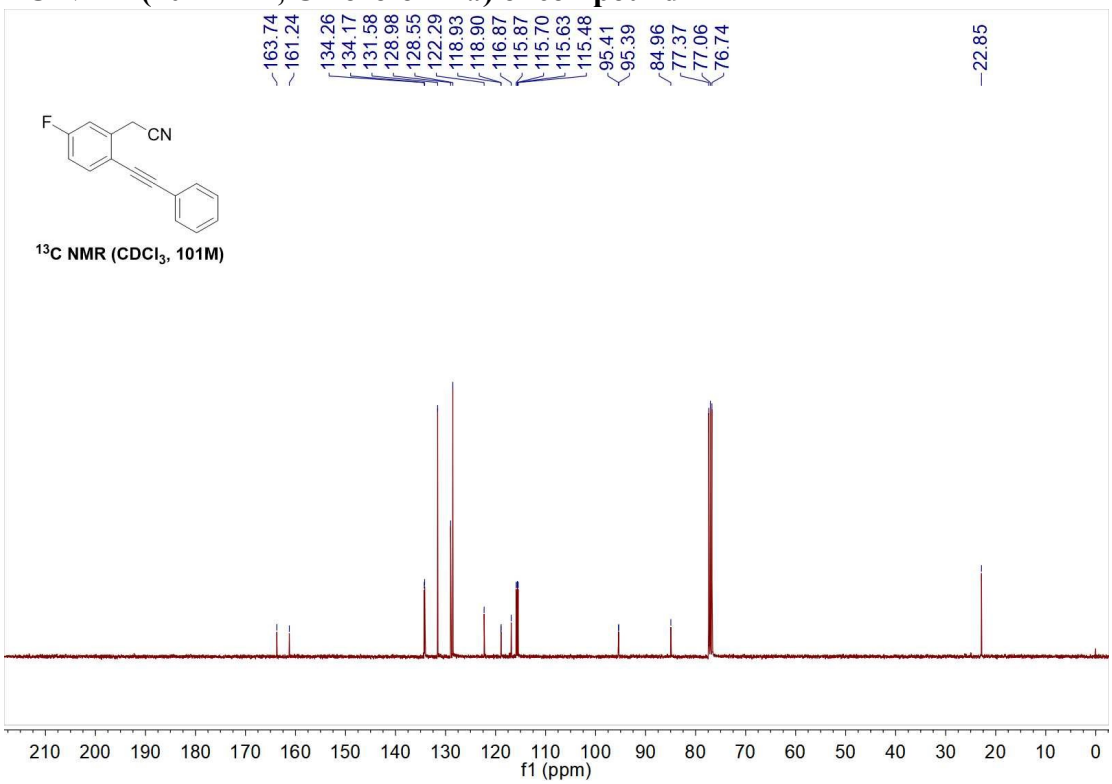
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 1y



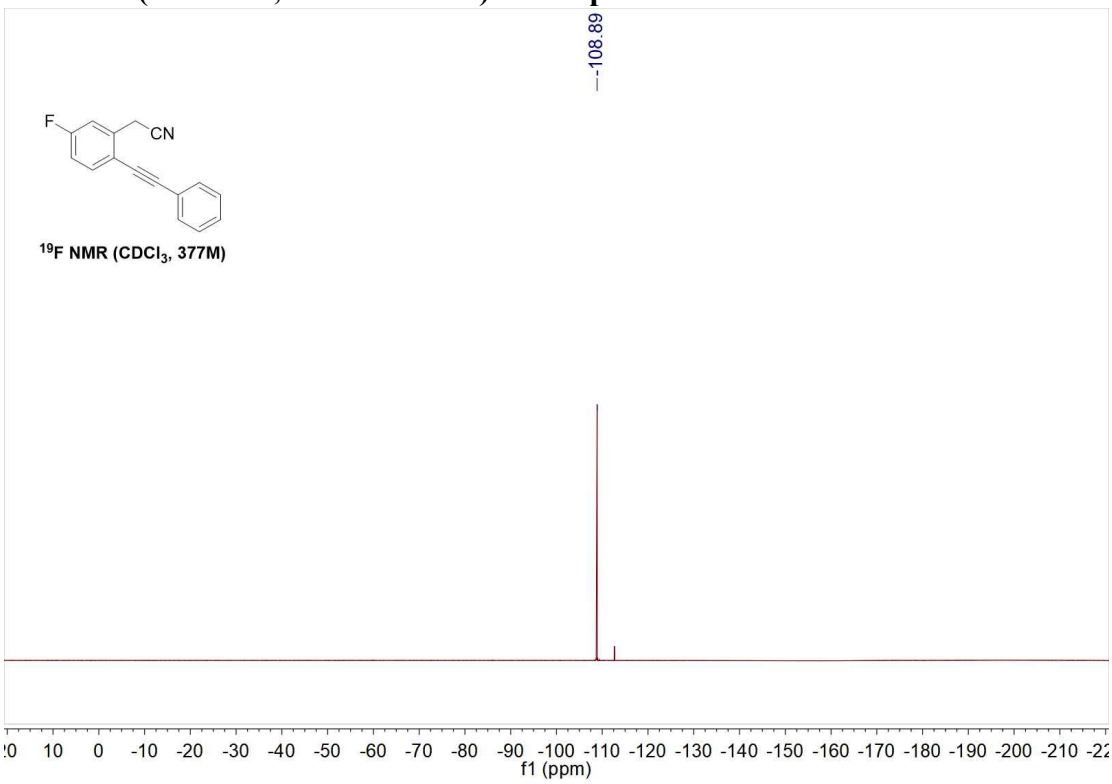
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 1z



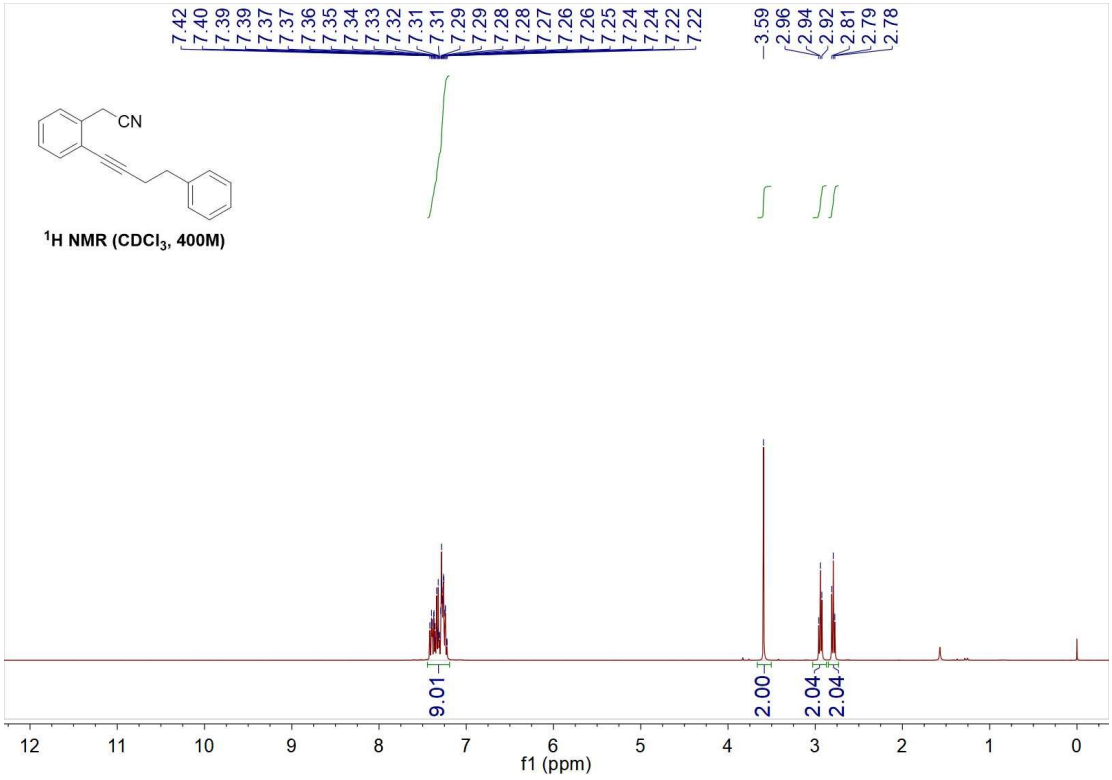
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 1z



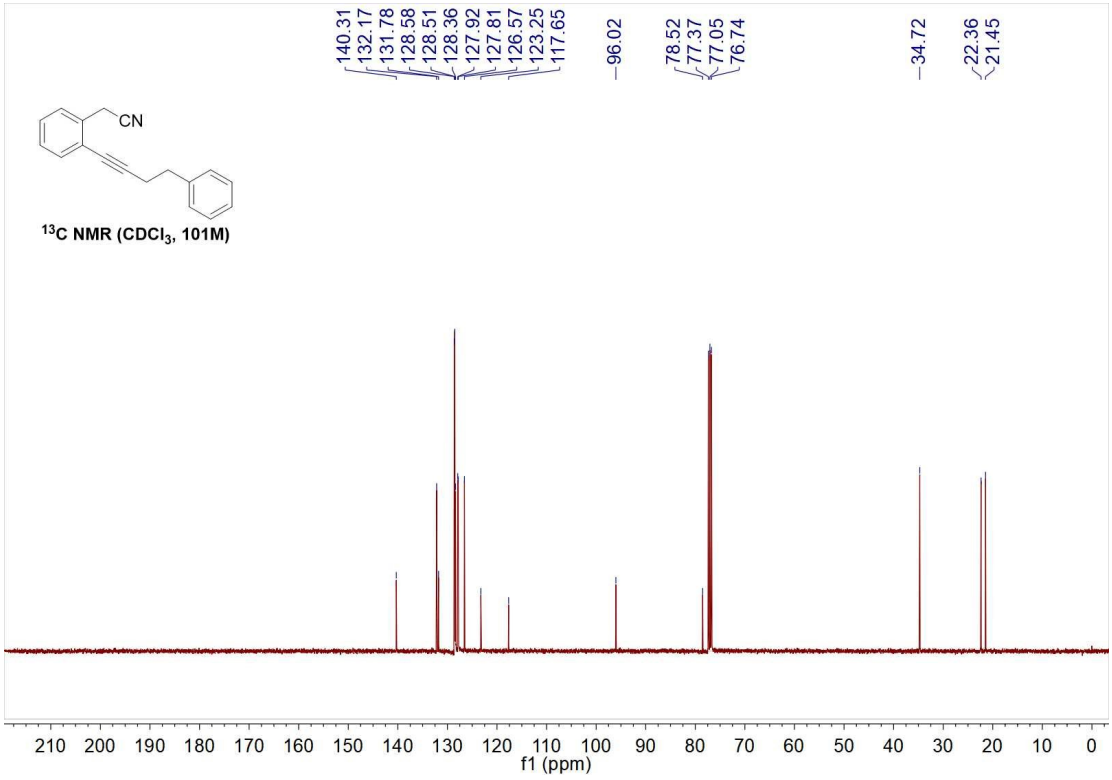
^{19}F NMR (377 MHz, Chloroform-*d*) of compound 1z



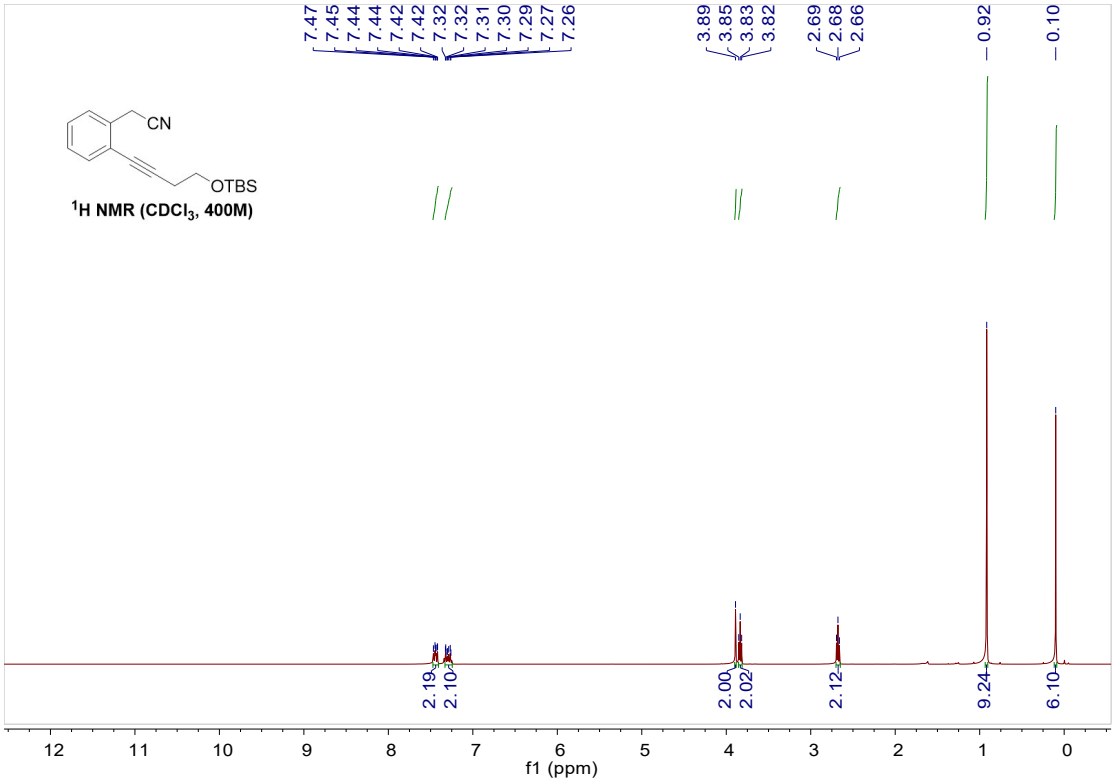
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 1aa



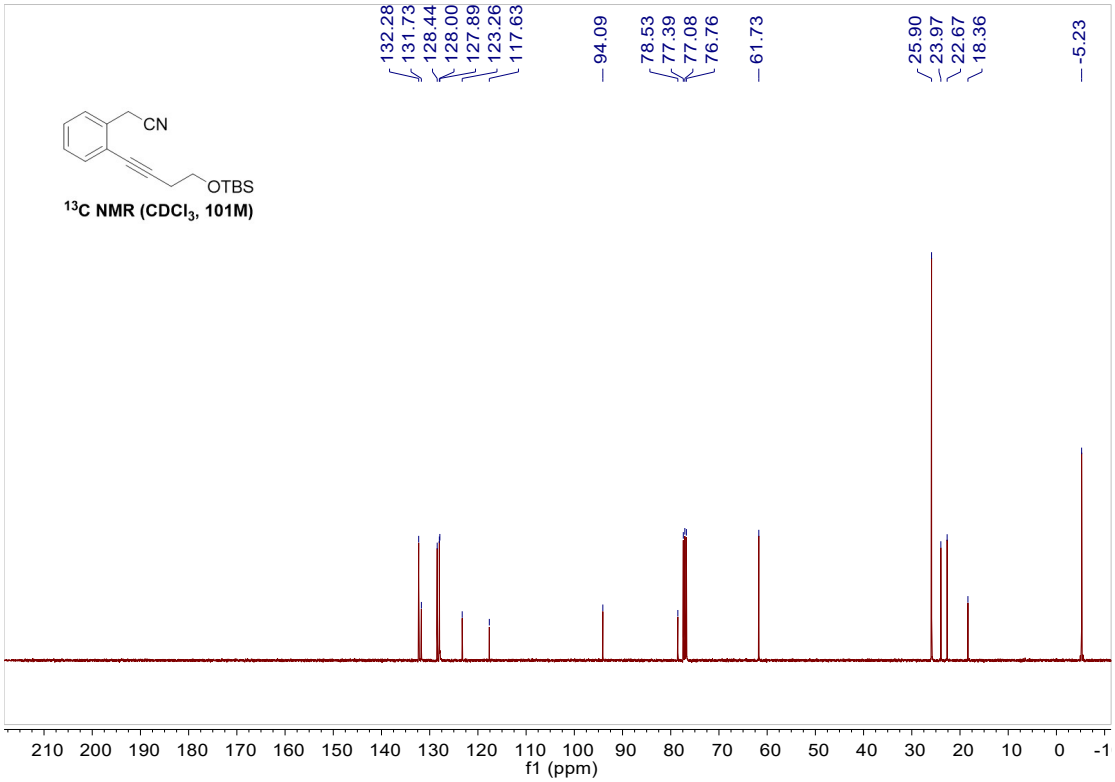
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 1aa



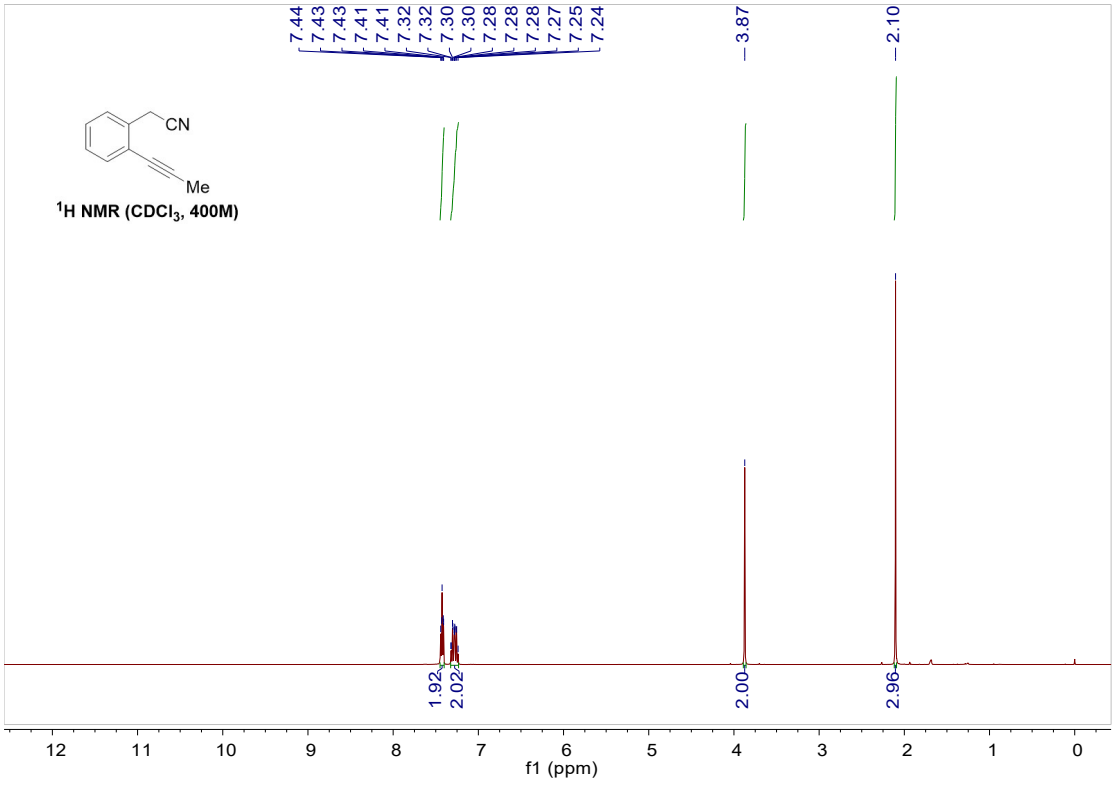
^{1}H NMR (400 MHz, Chloroform-d) of compound 1ab



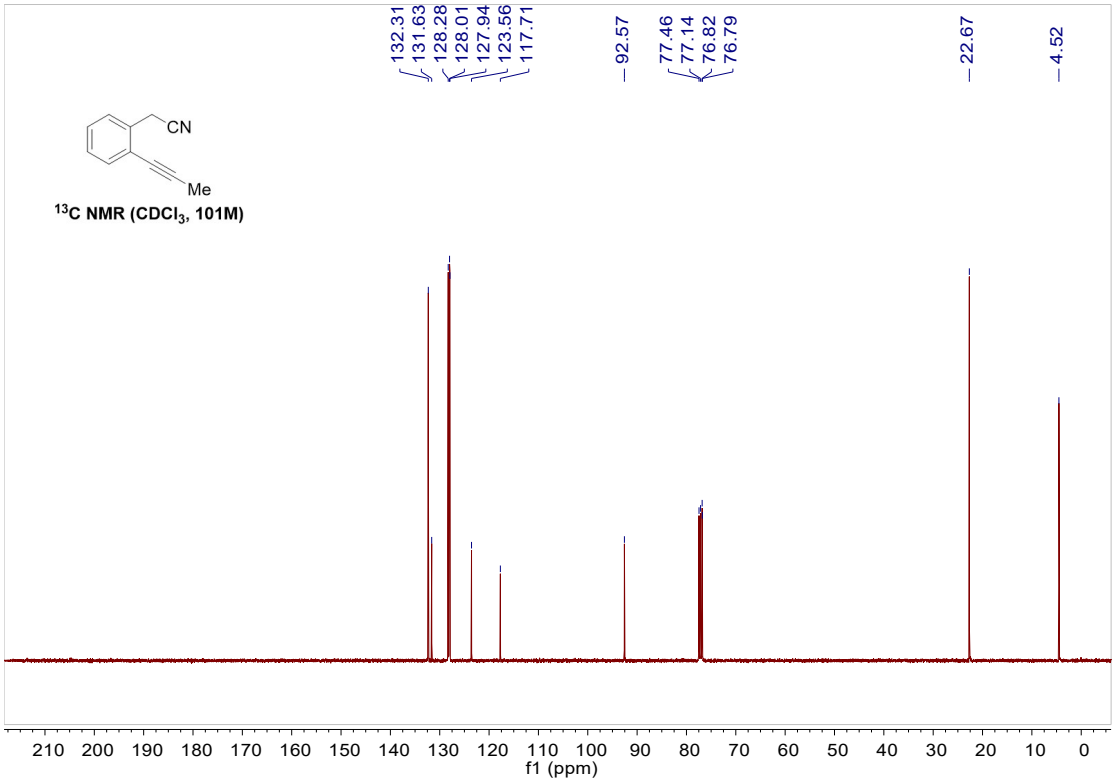
^{13}C NMR (101 MHz, Chloroform-d) of compound 1ab



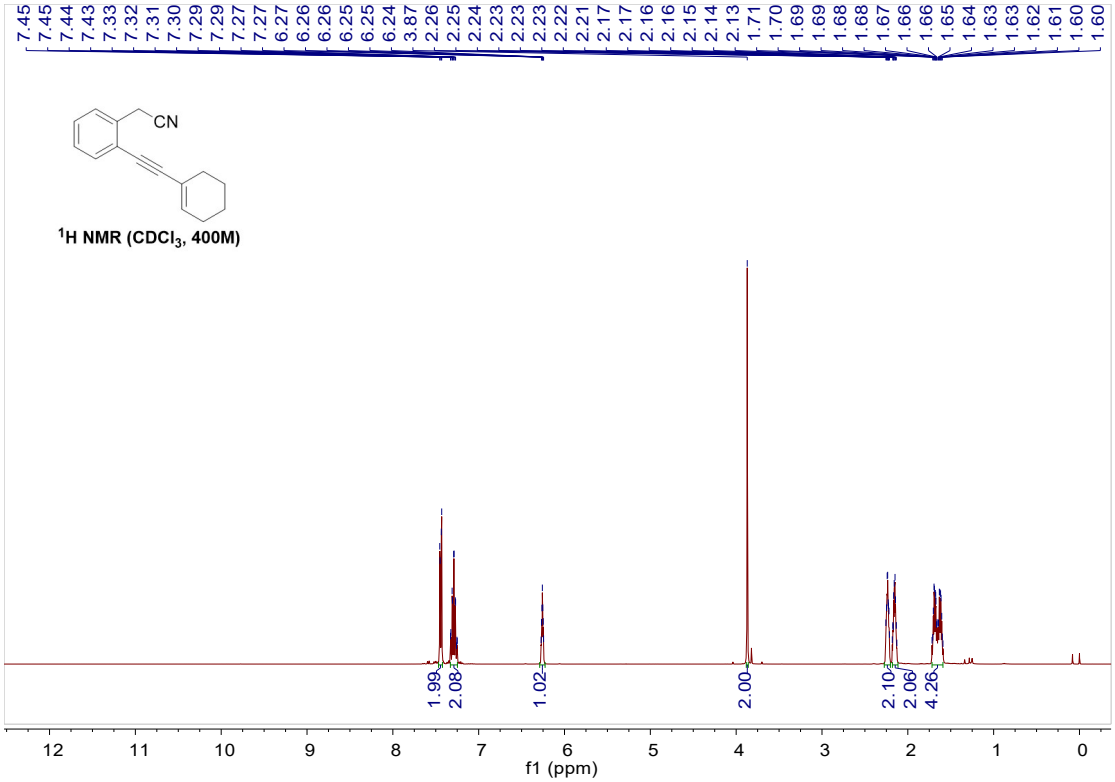
^{1}H NMR (400 MHz, Chloroform-d) of compound 1ac



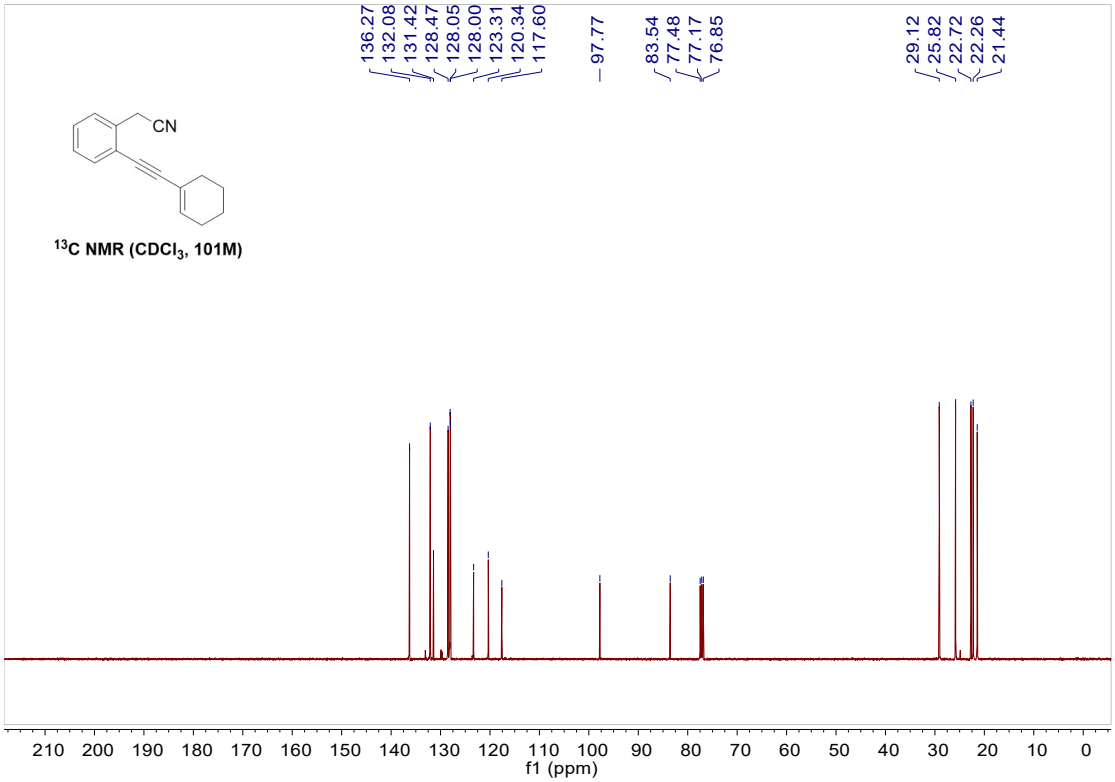
^{13}C NMR (101 MHz, Chloroform-d) of compound 1ac



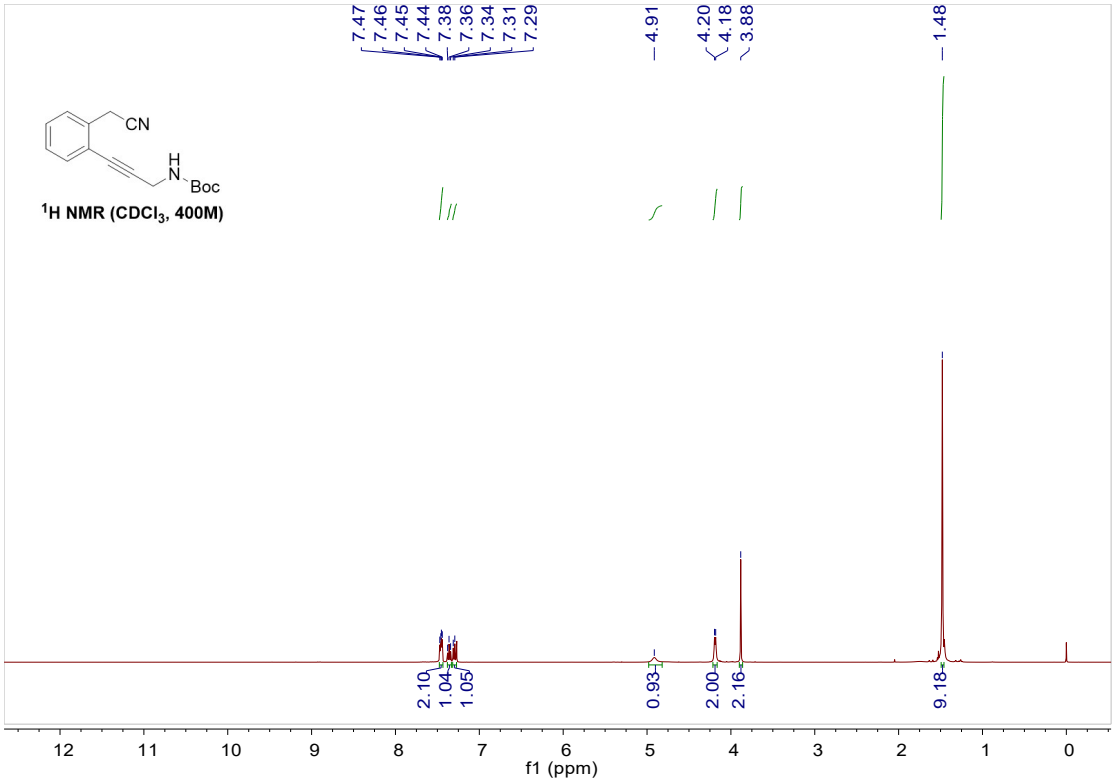
^{1}H NMR (400 MHz, Chloroform-d) of compound 1ad



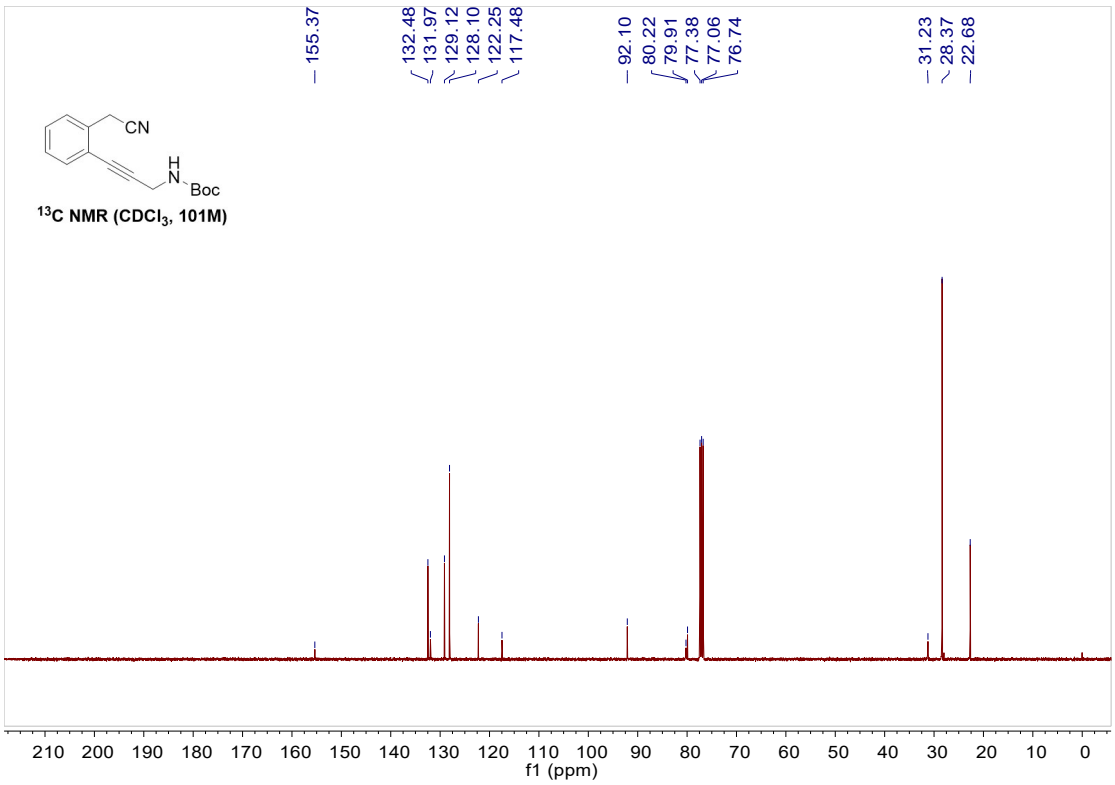
^{13}C NMR (101 MHz, Chloroform-d) of compound 1ad



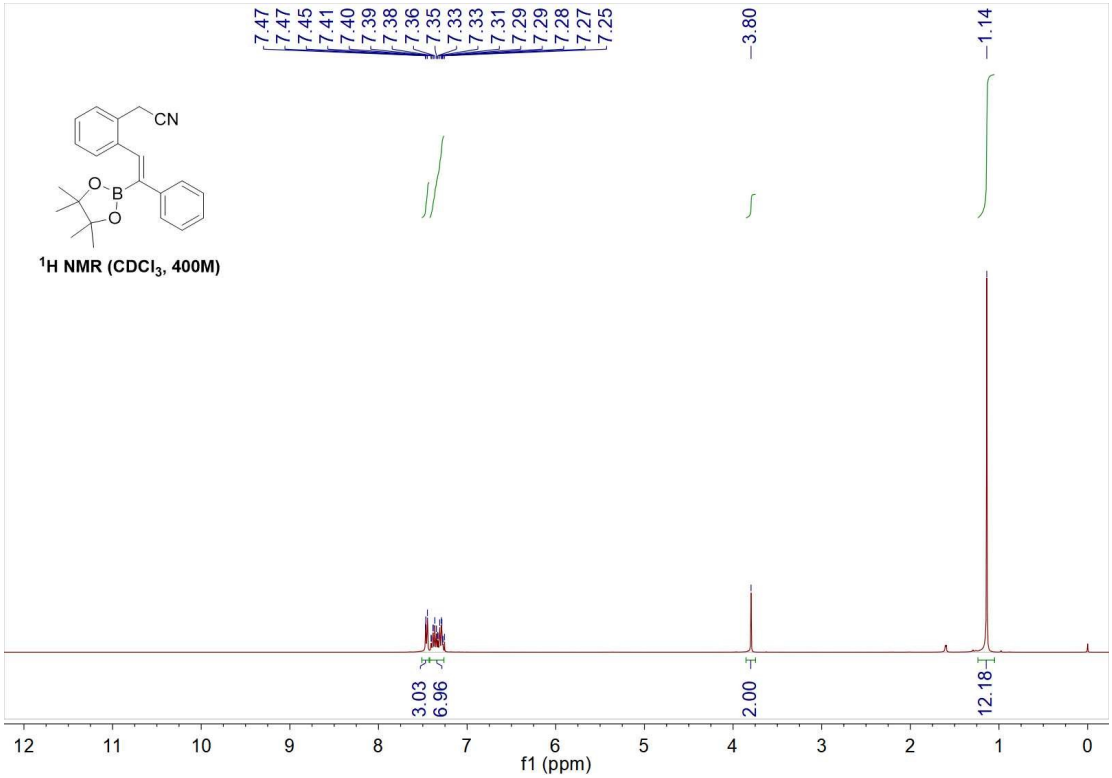
^{1}H NMR (400 MHz, Chloroform-d) of compound 1ae



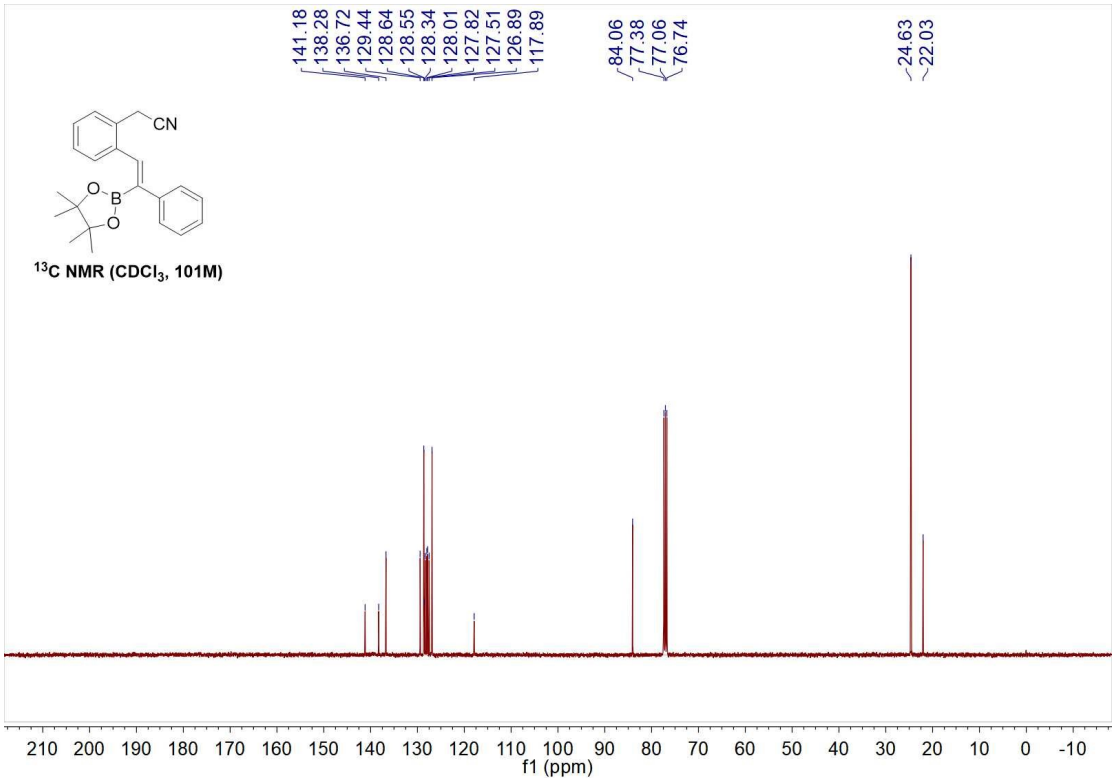
^{13}C NMR (101 MHz, Chloroform-d) of compound 1ae



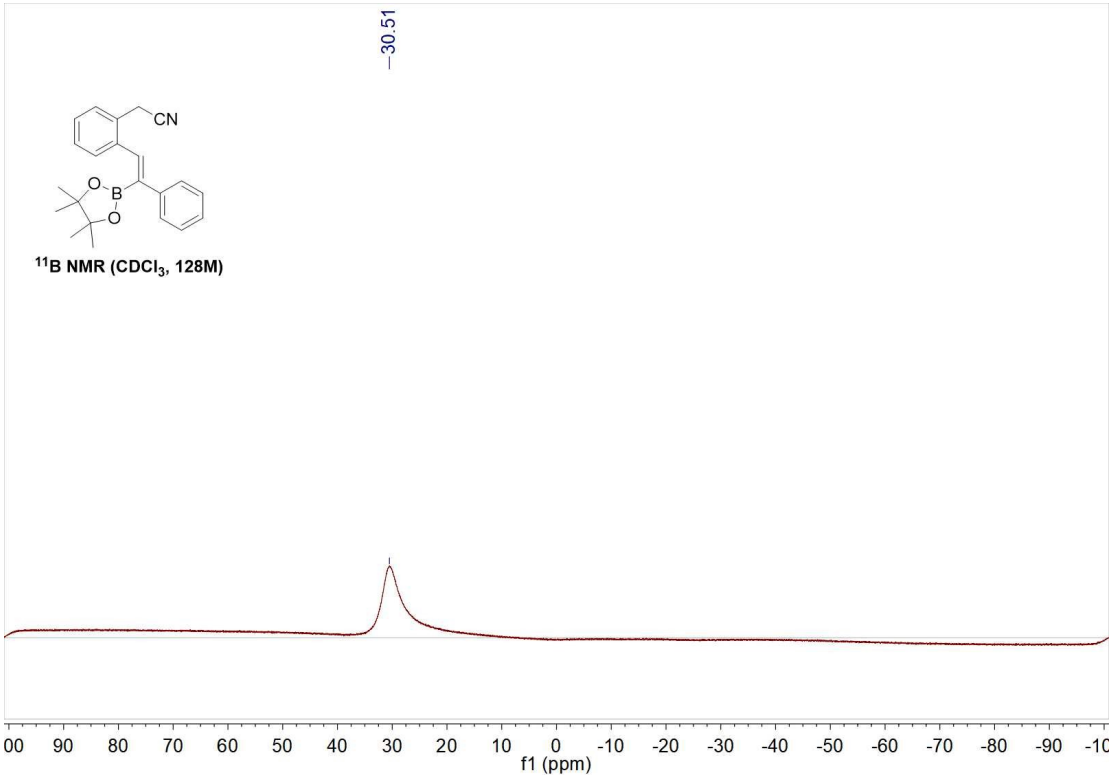
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 2



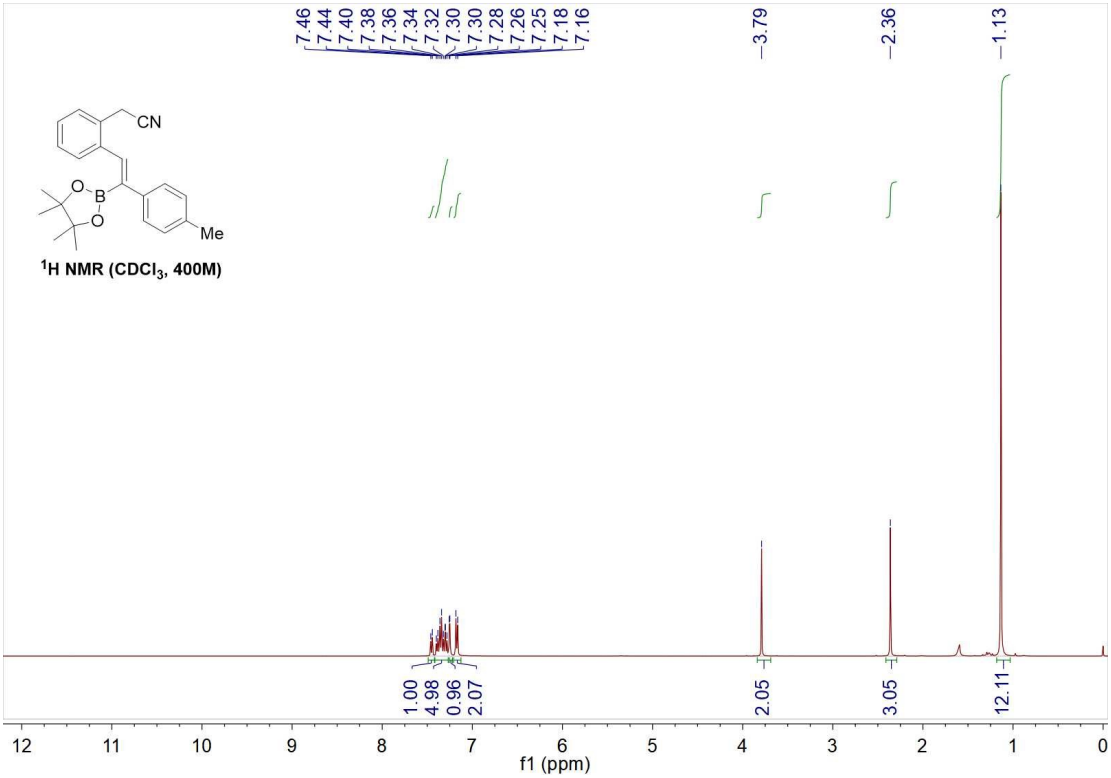
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 2



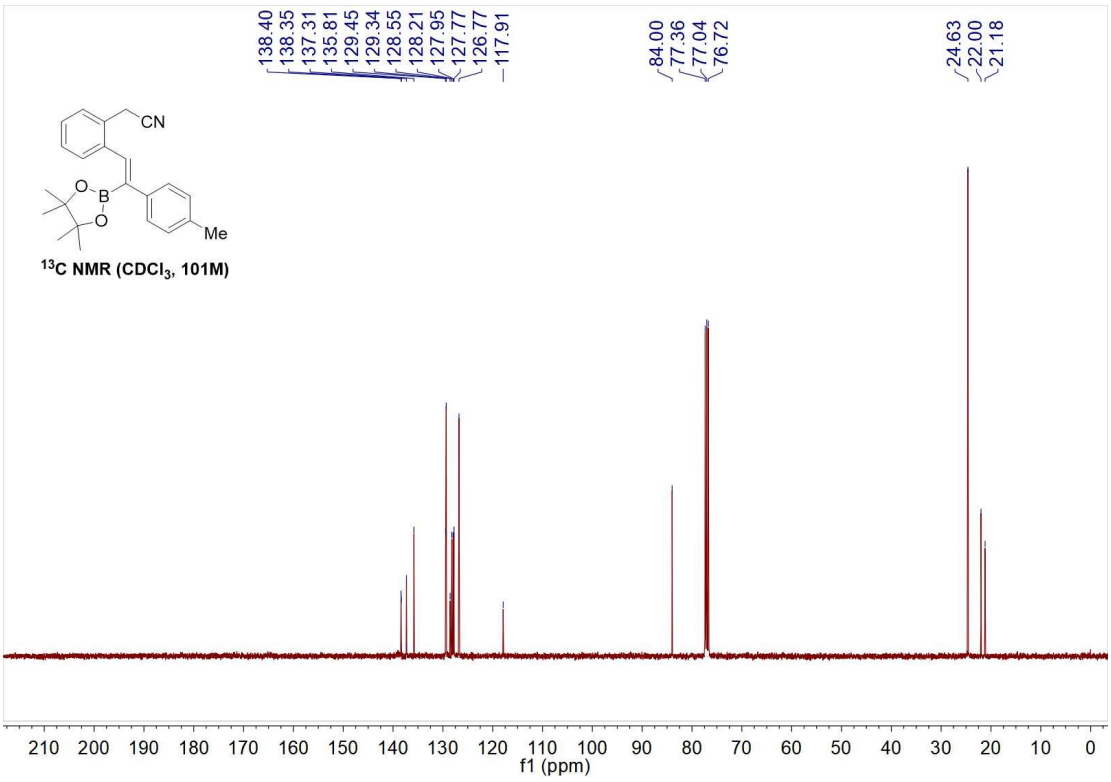
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 2



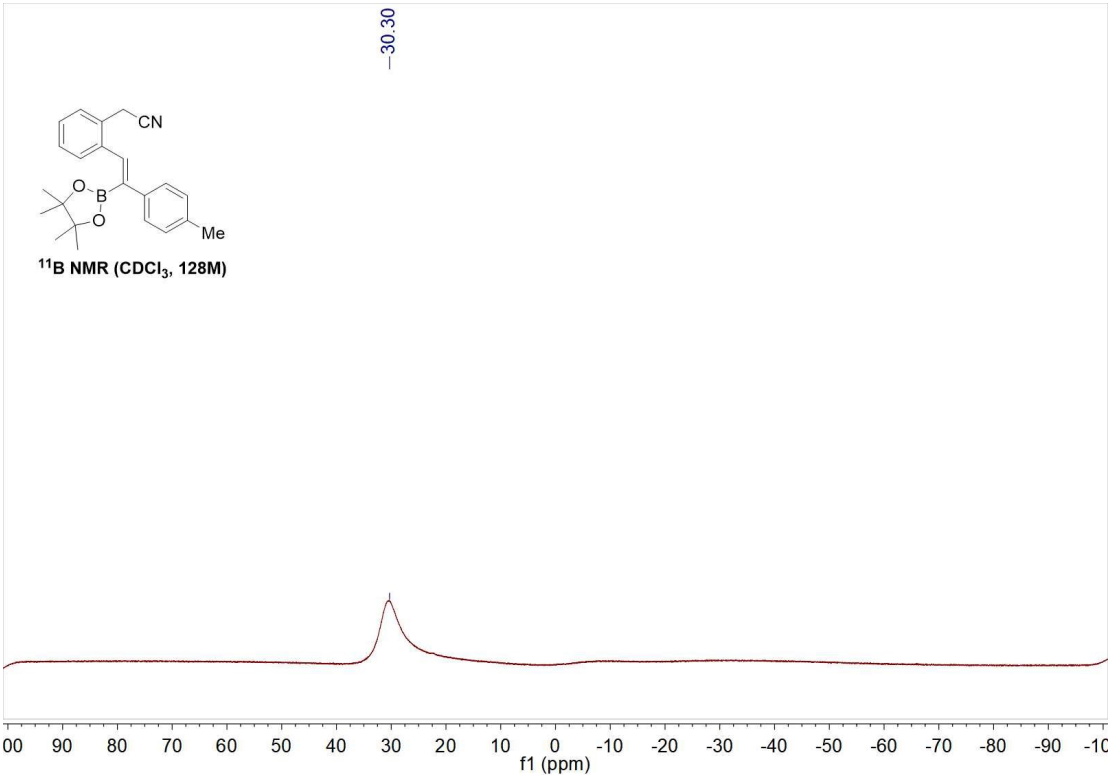
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 10



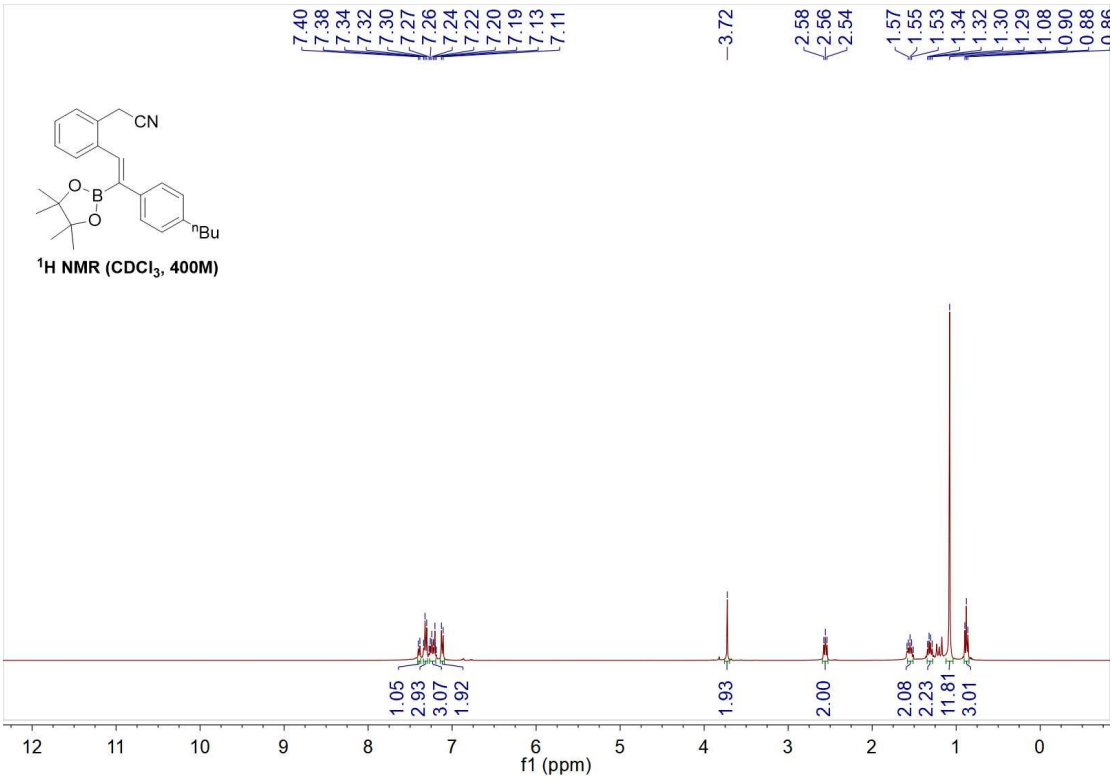
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 10



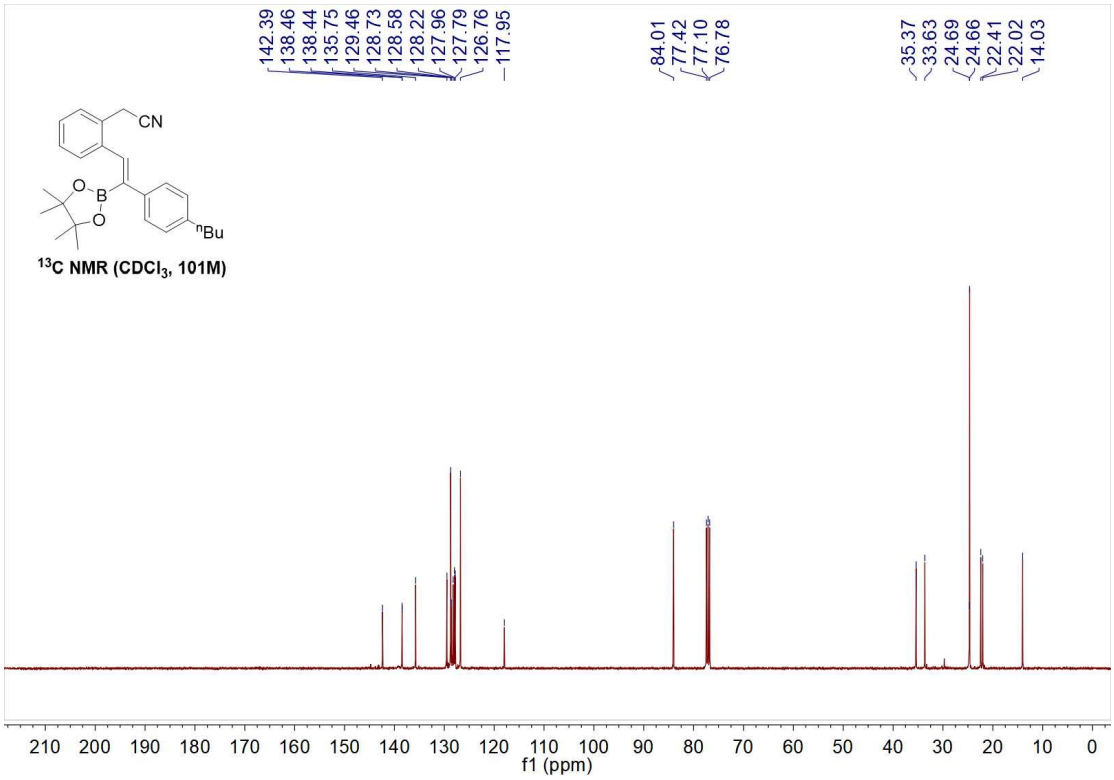
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 10



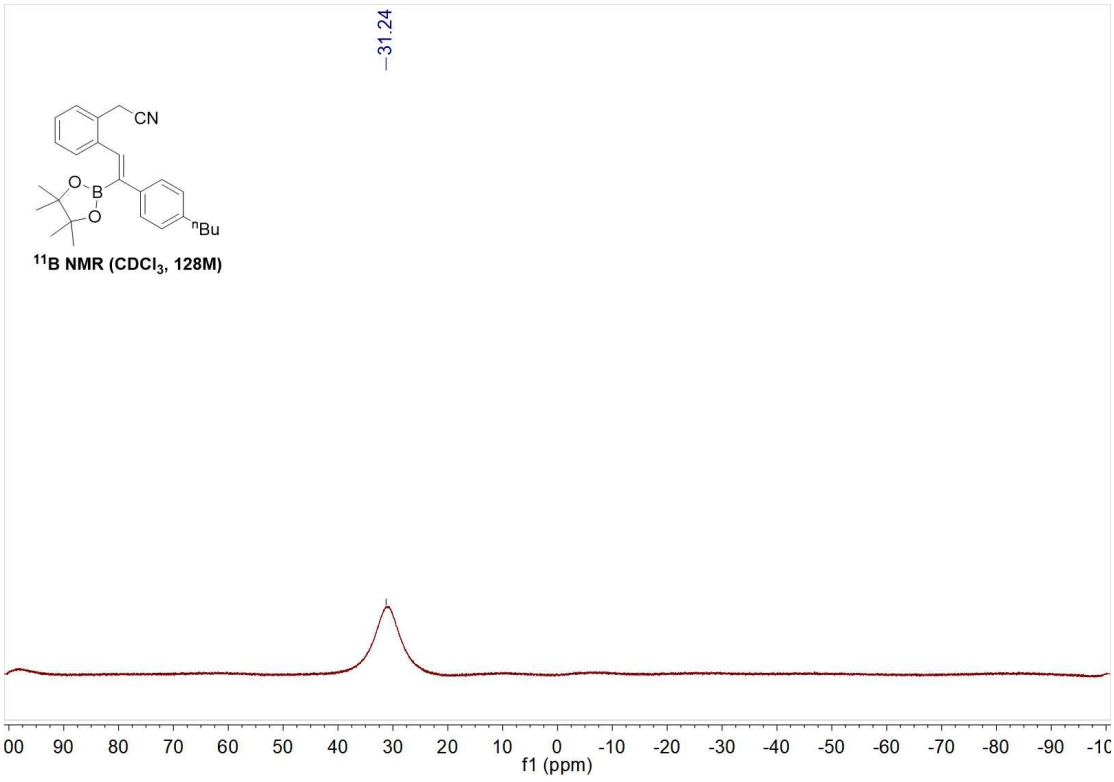
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 11



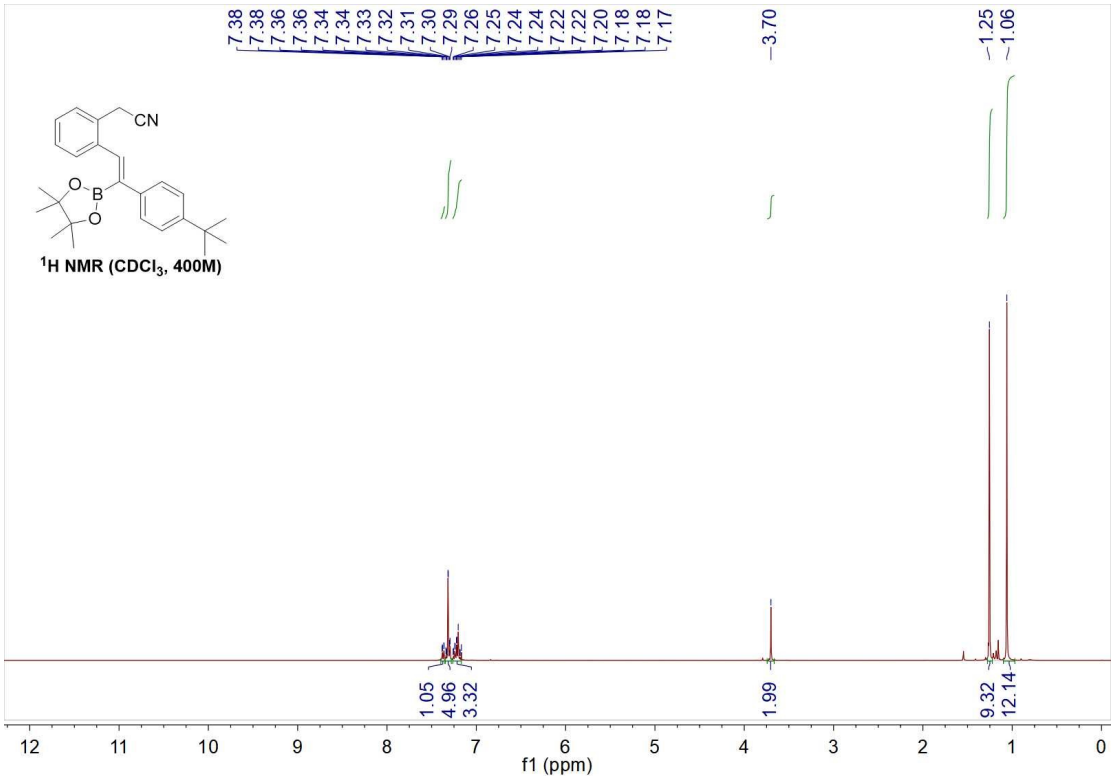
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 11



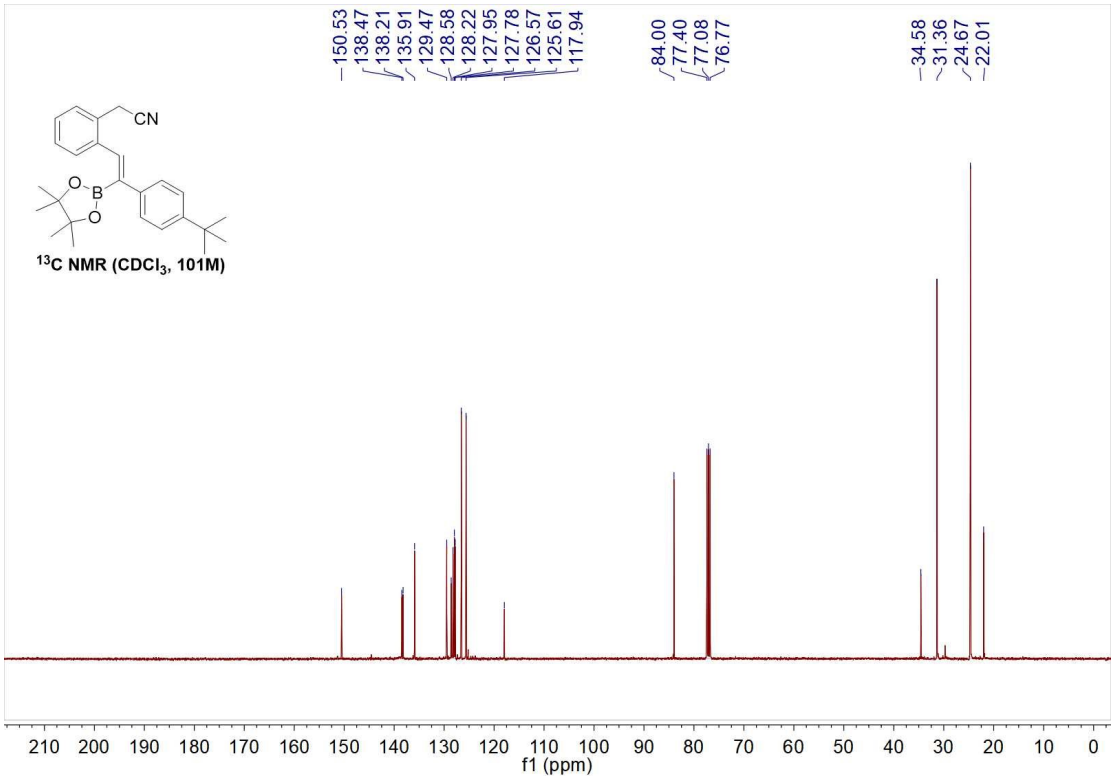
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 11



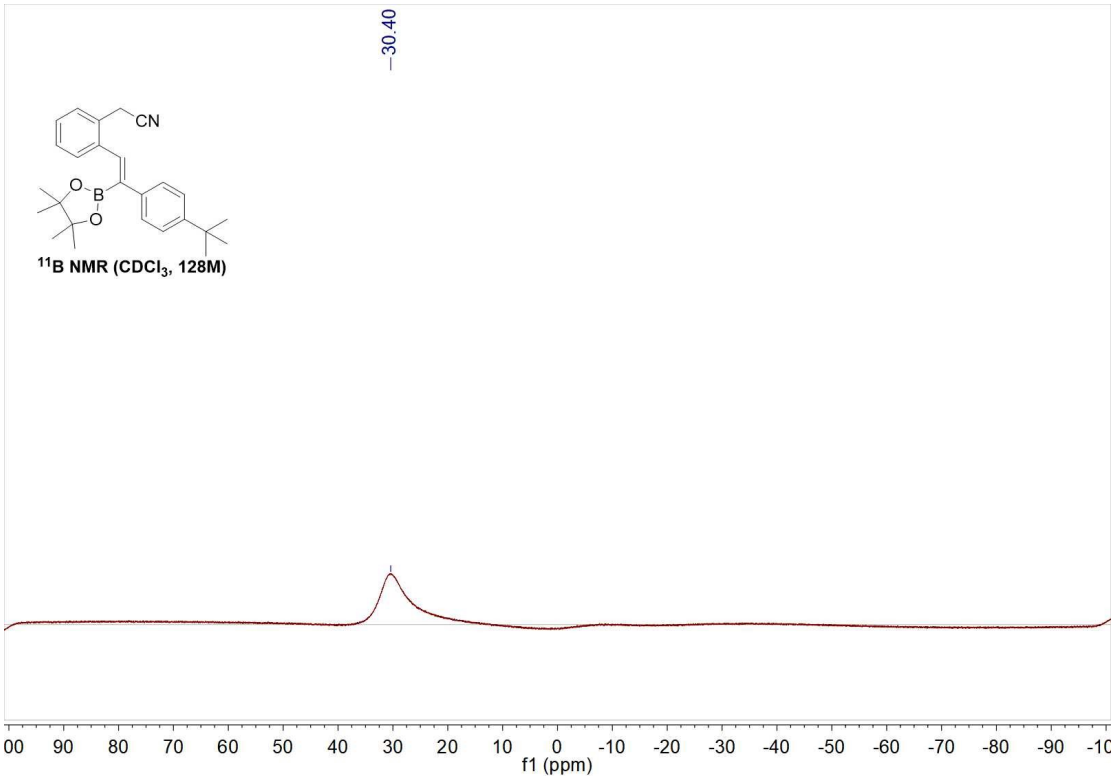
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 12



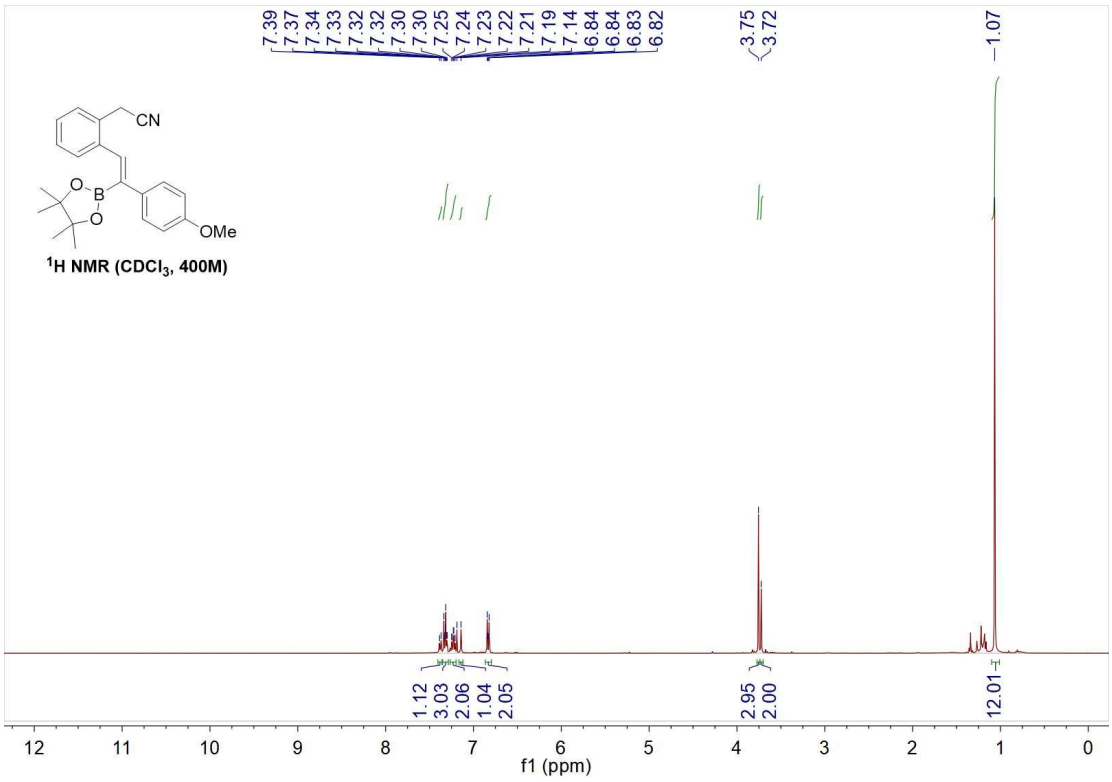
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 12



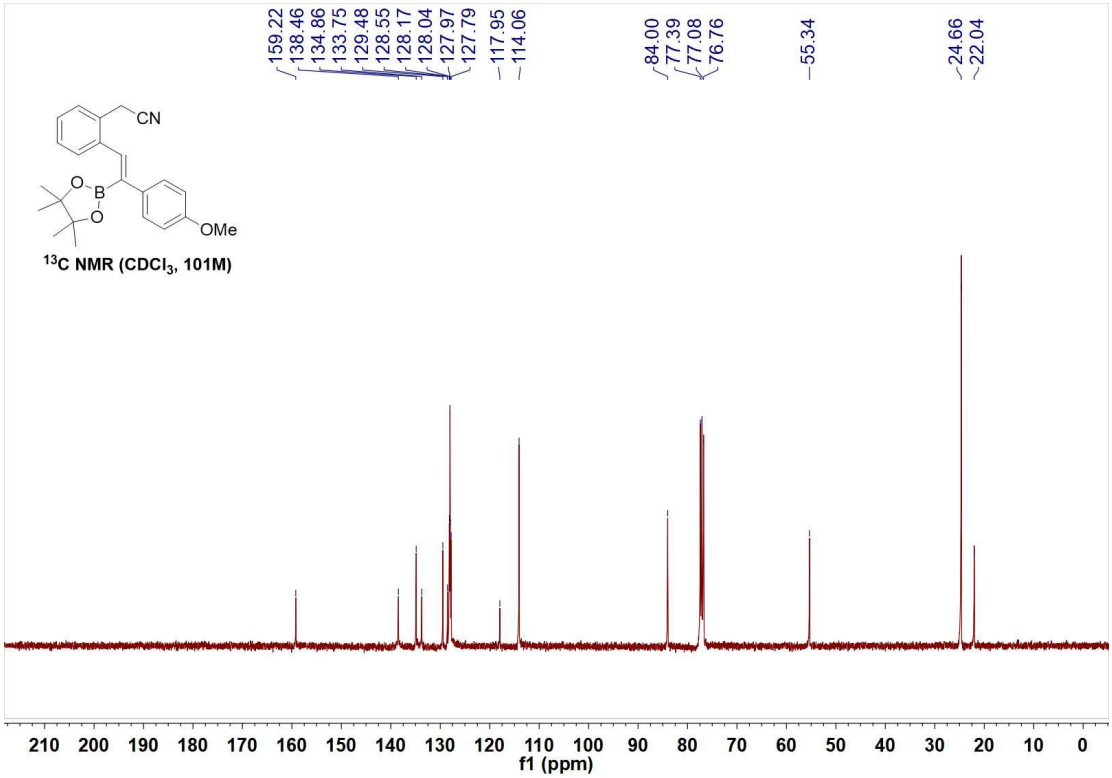
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 12



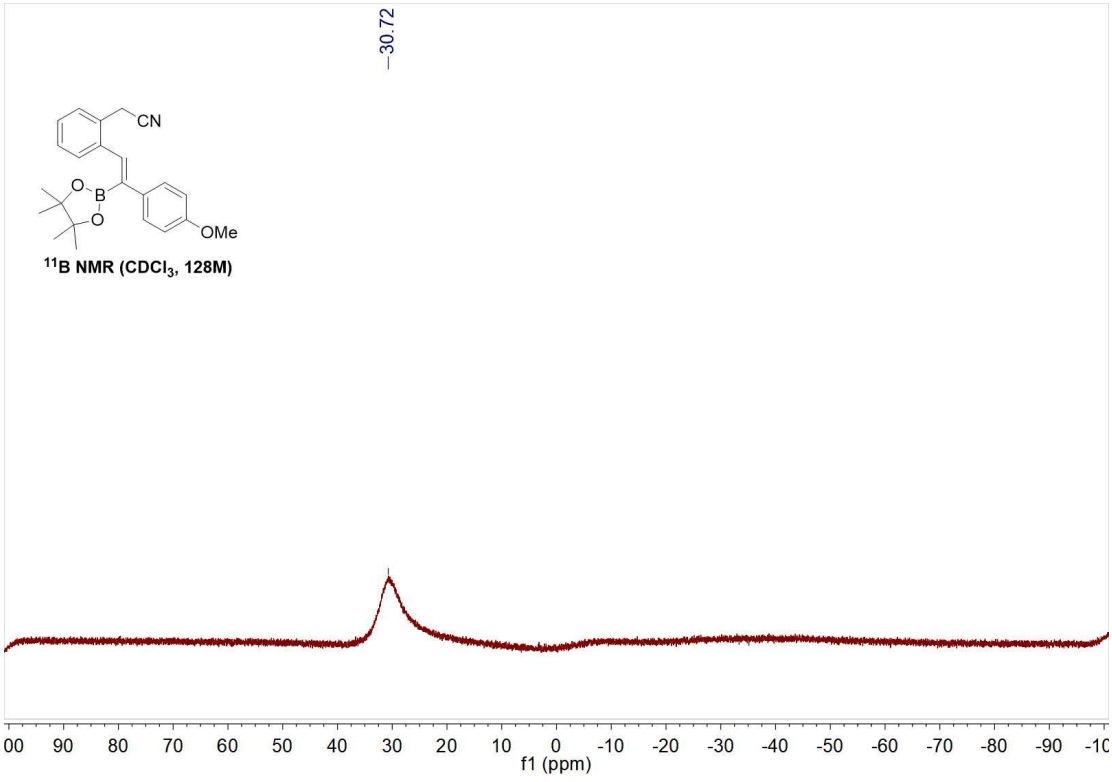
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 13



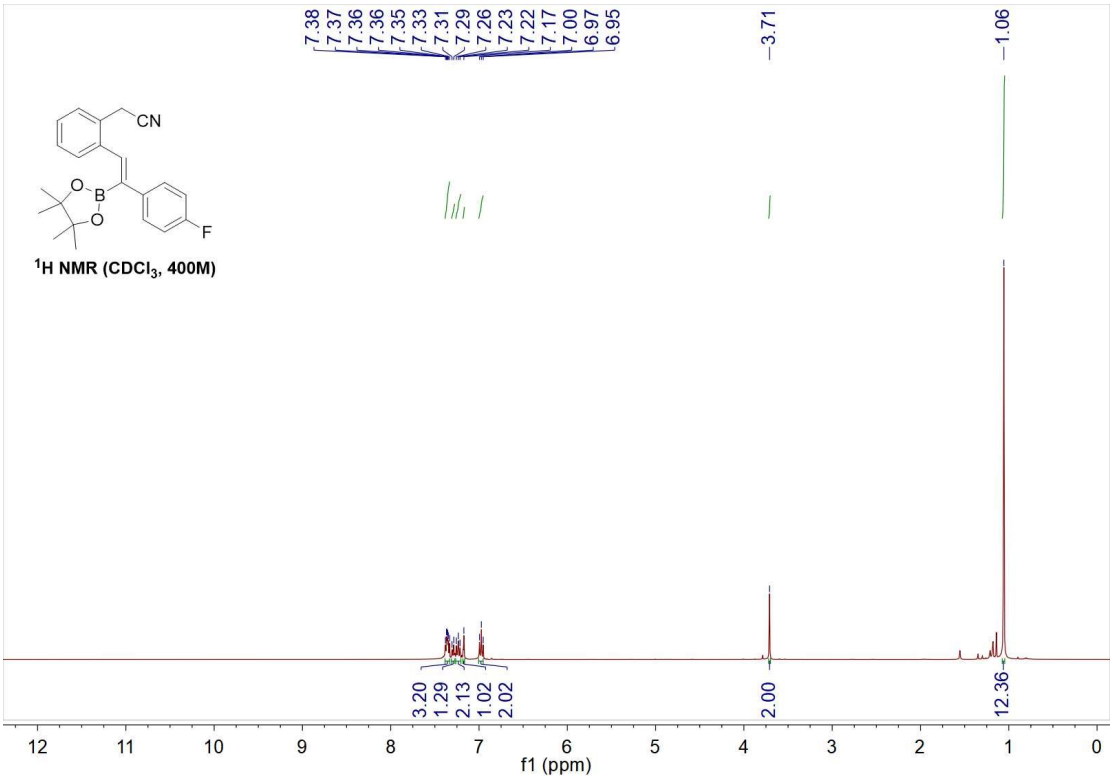
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 13



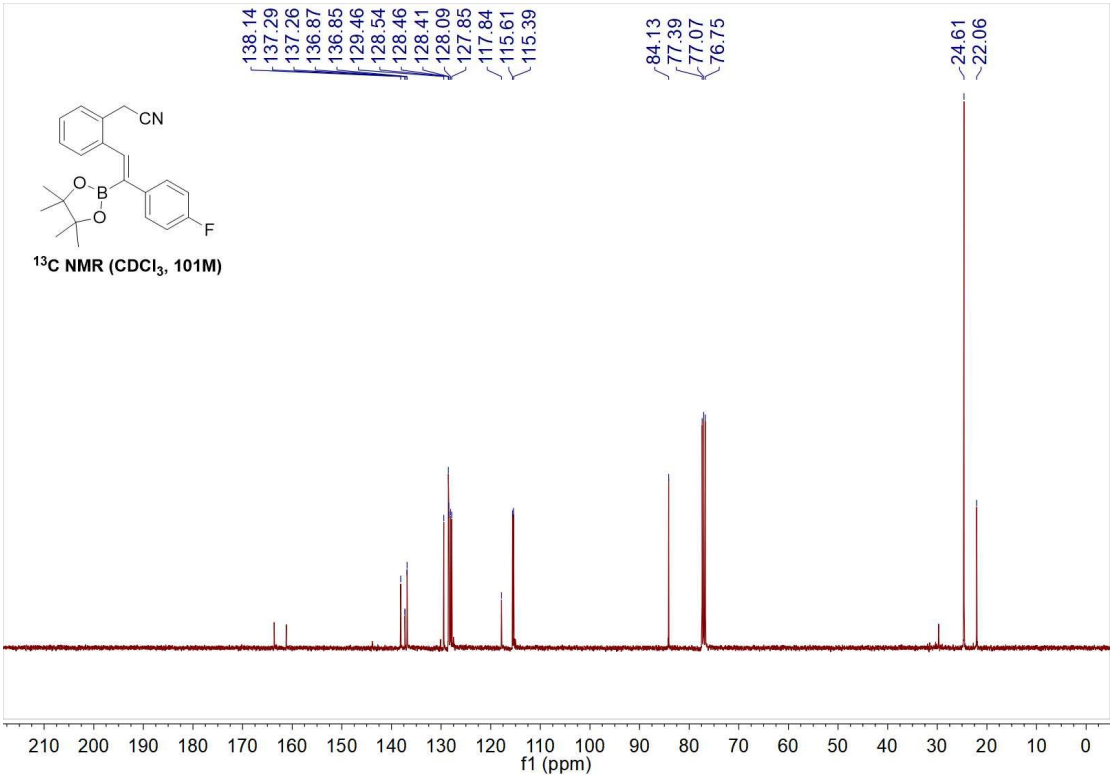
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 13



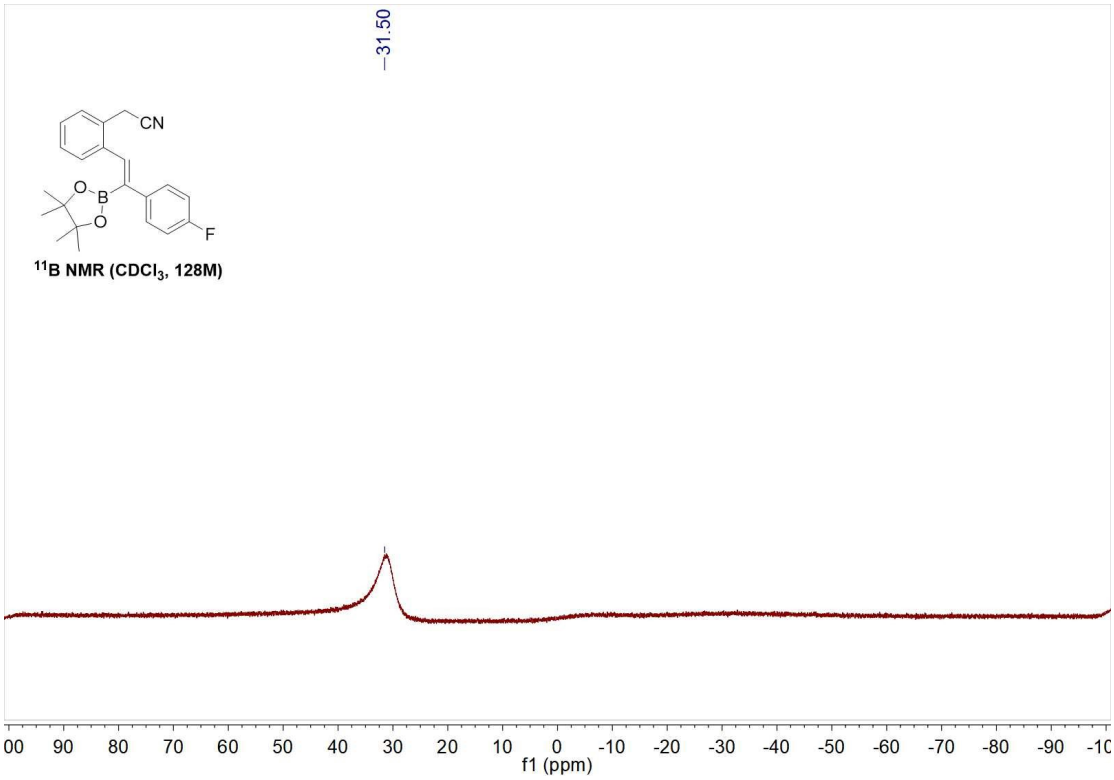
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 14



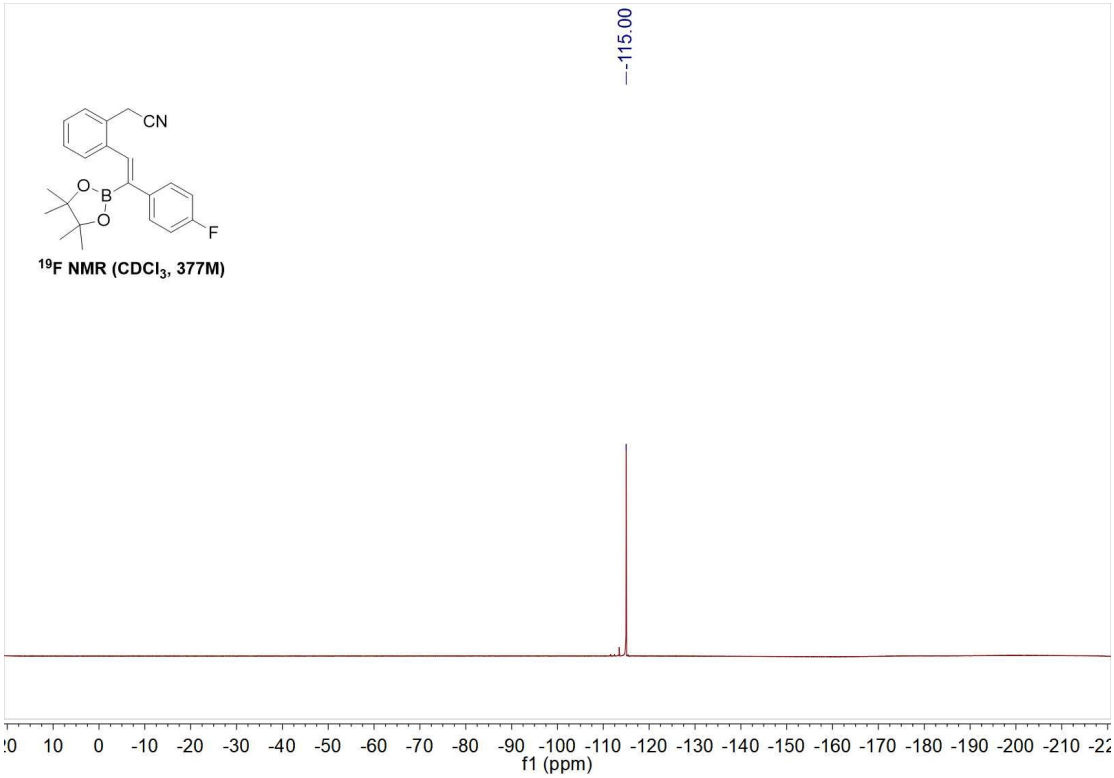
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 14



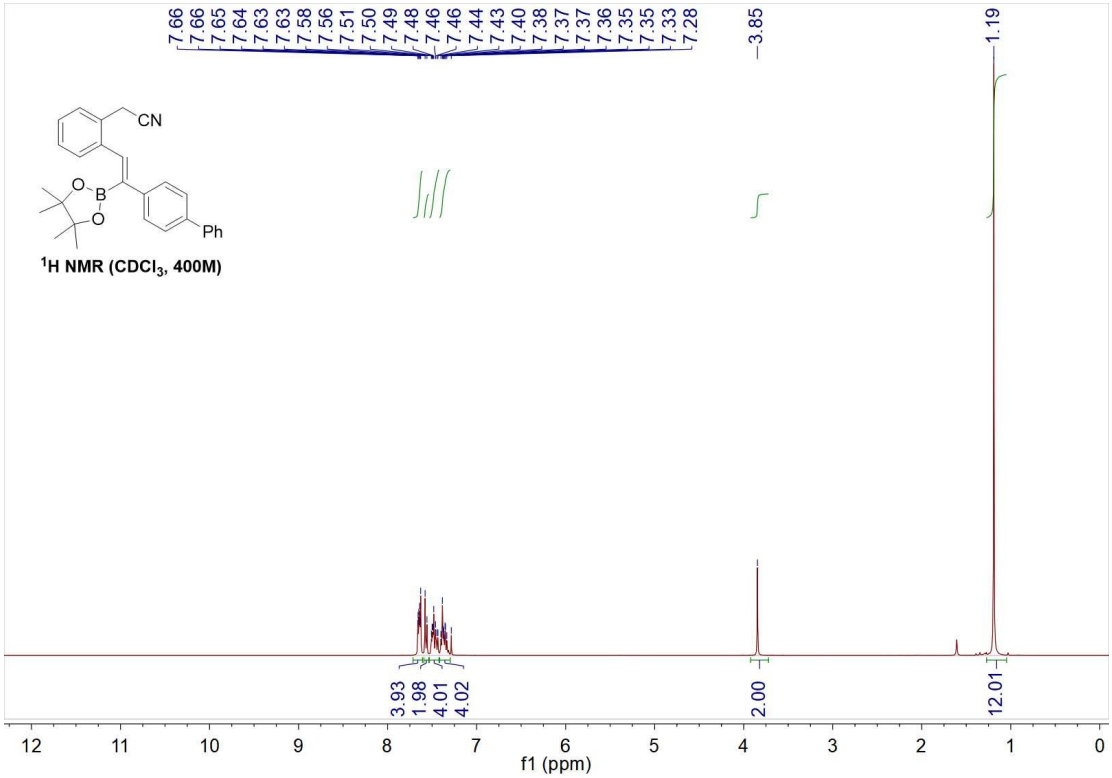
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 14



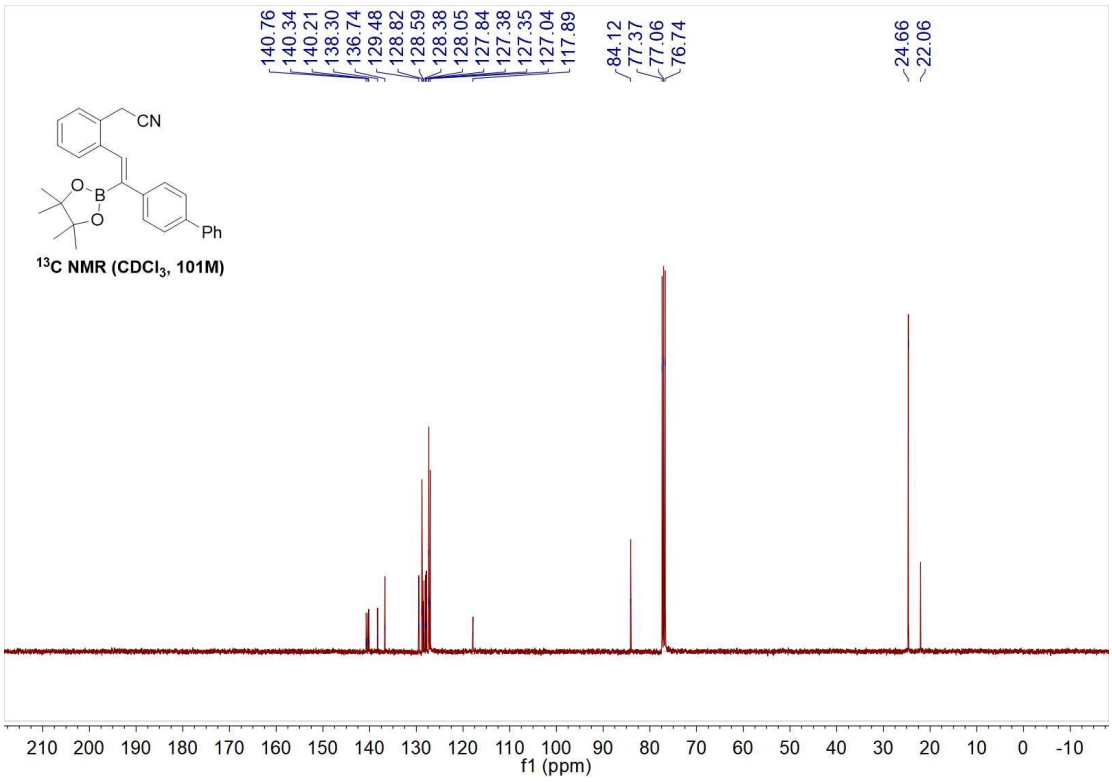
^{19}F NMR (377 MHz, Chloroform-*d*) of compound 14



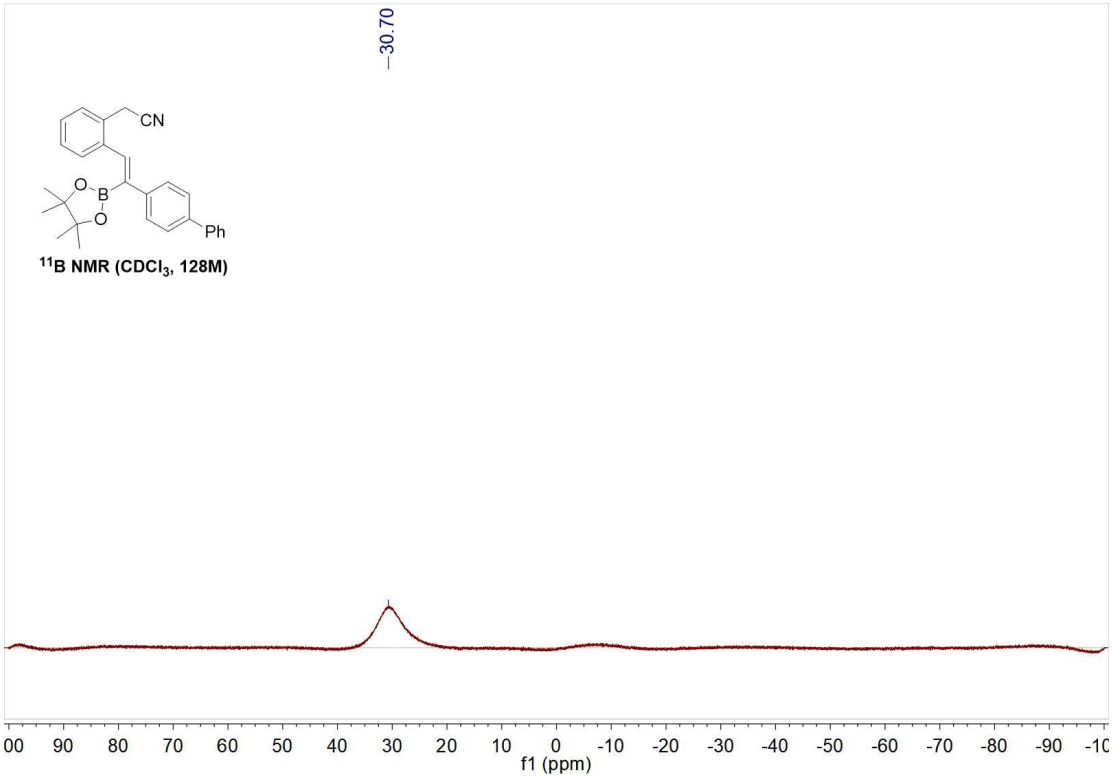
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 15



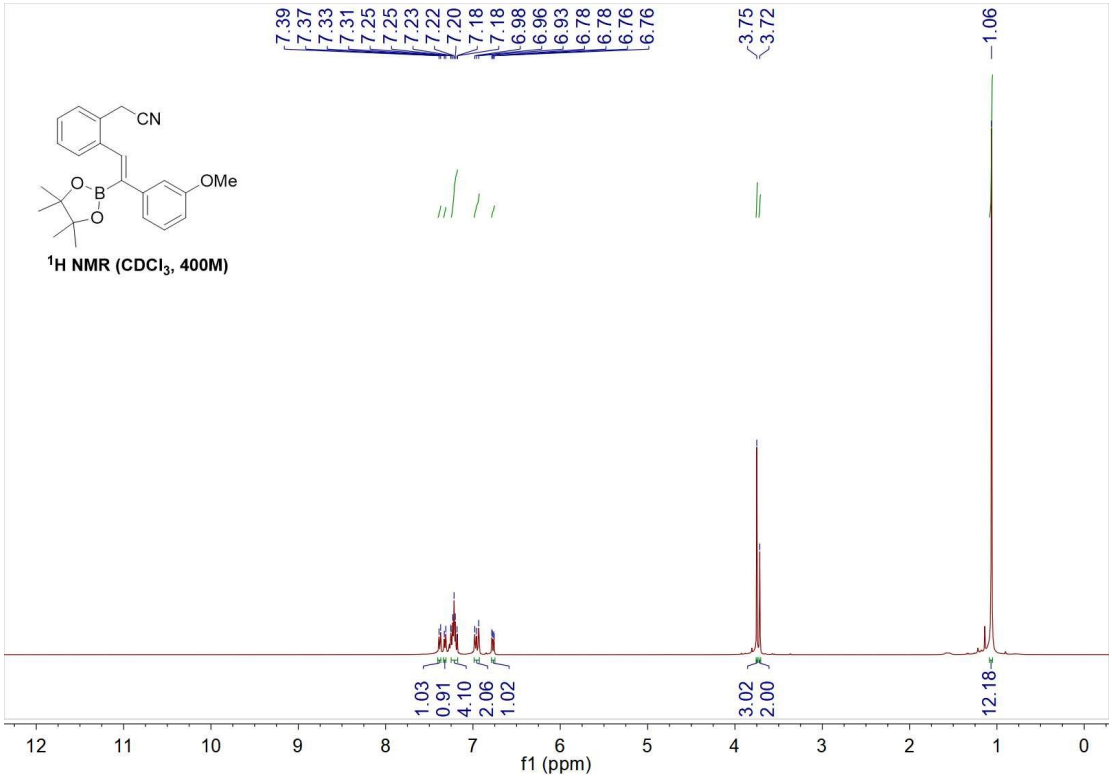
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 15



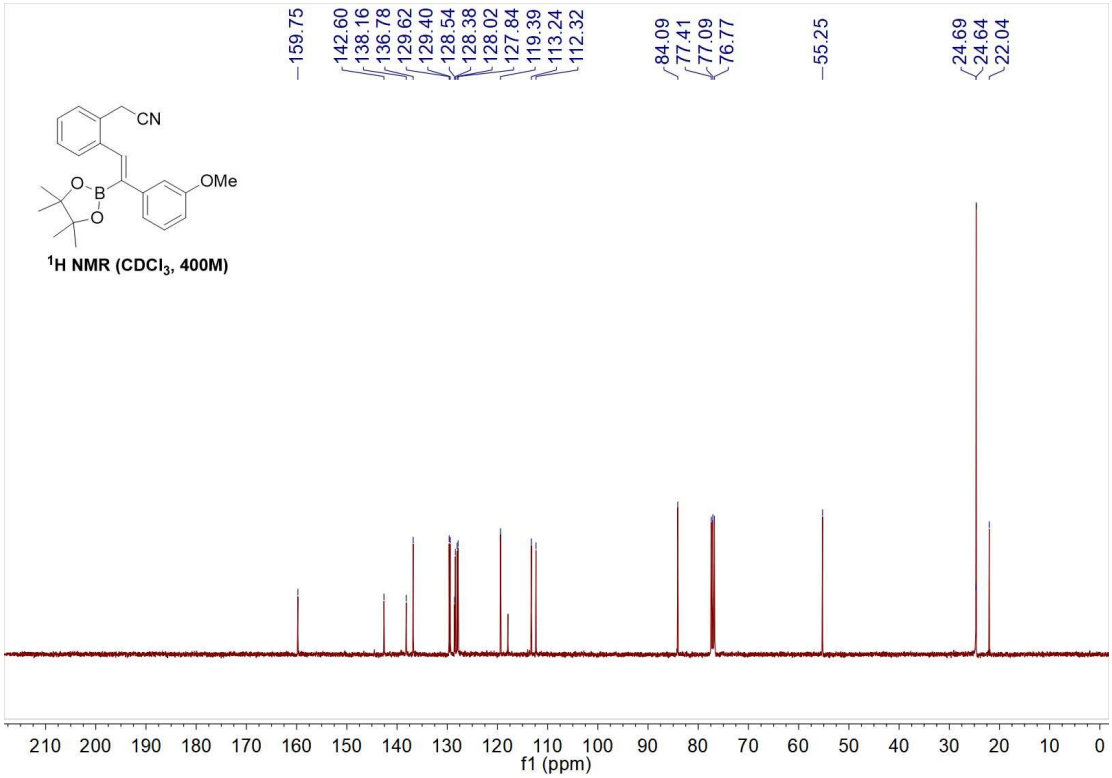
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 15



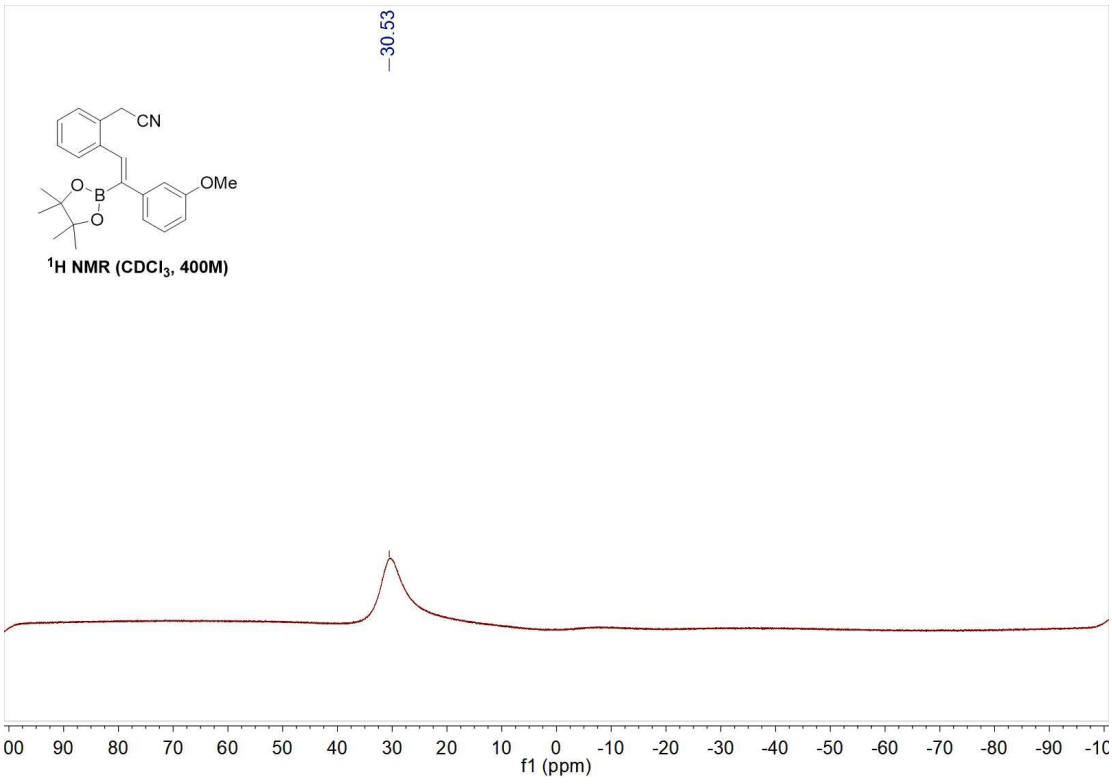
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 16



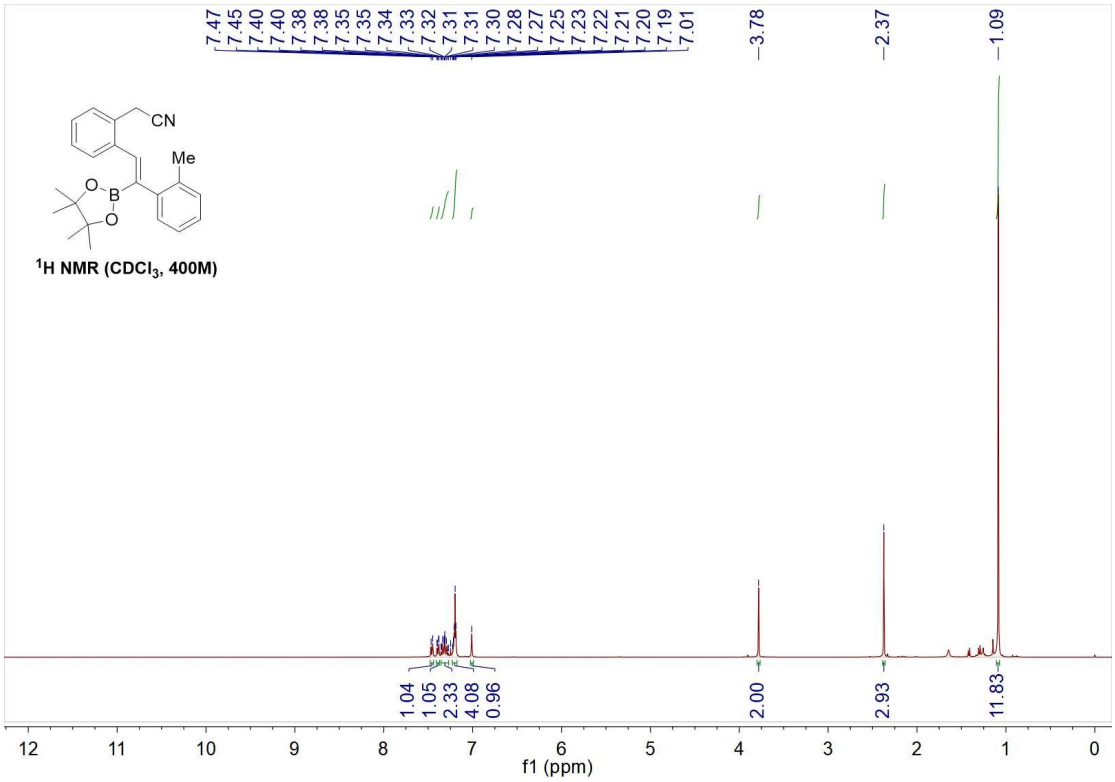
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 16



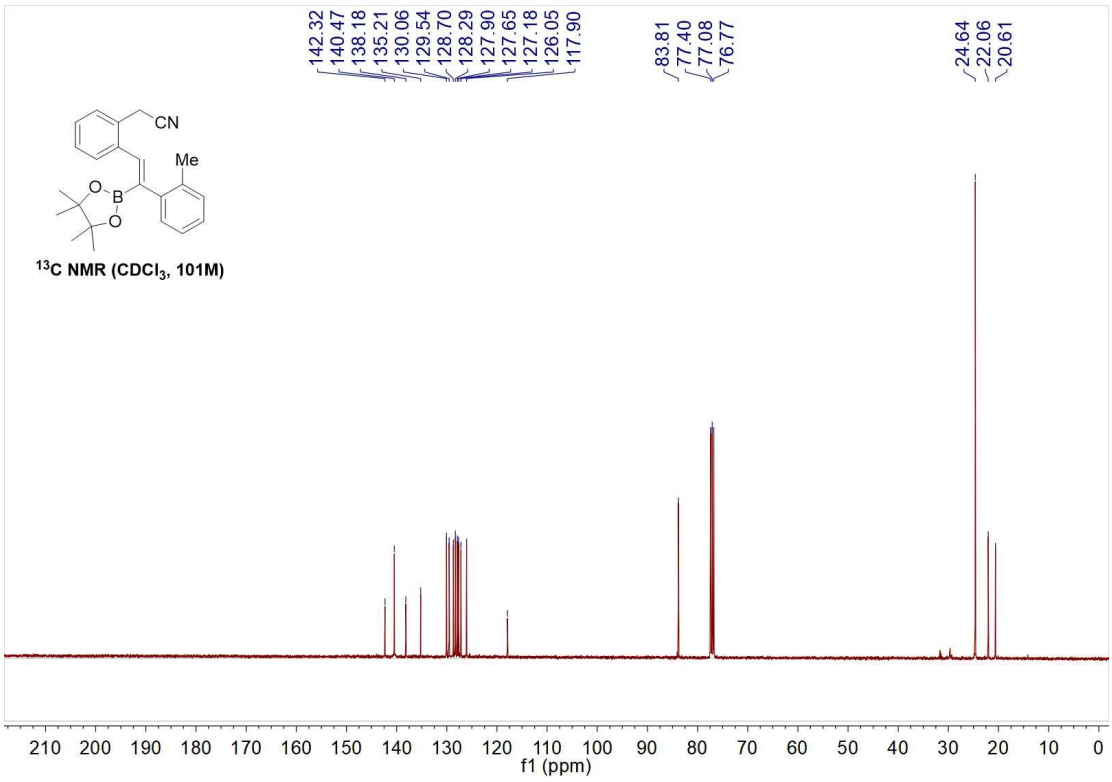
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 16



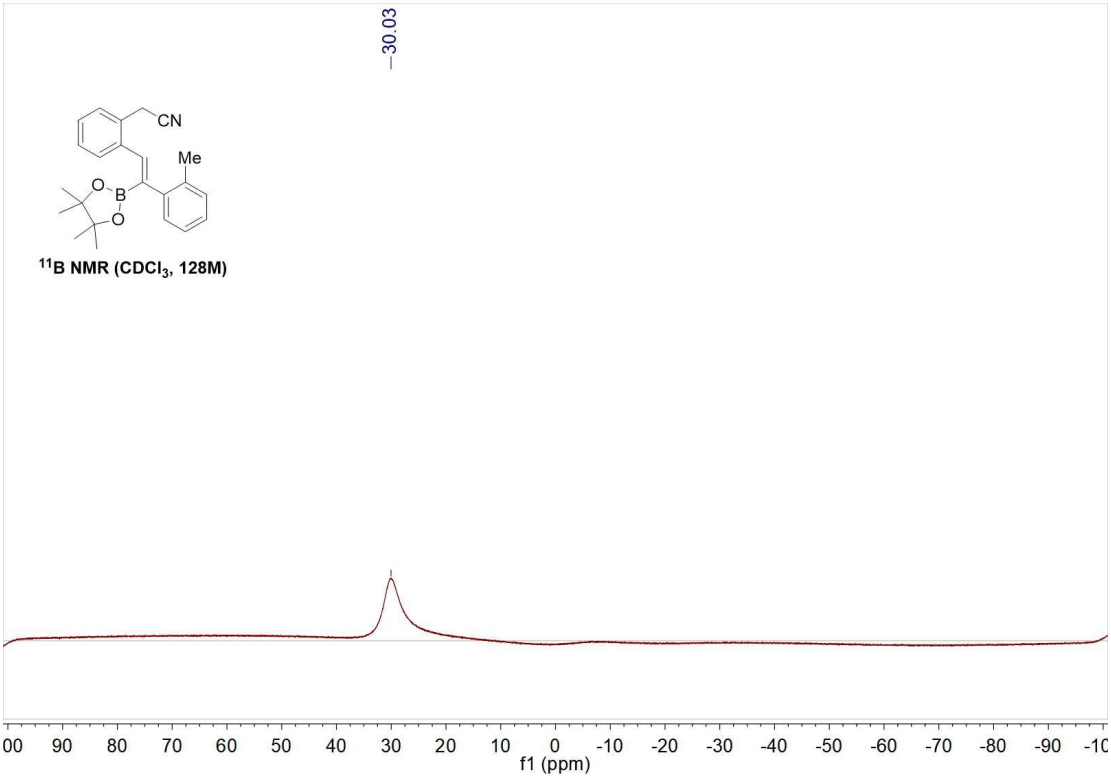
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 17



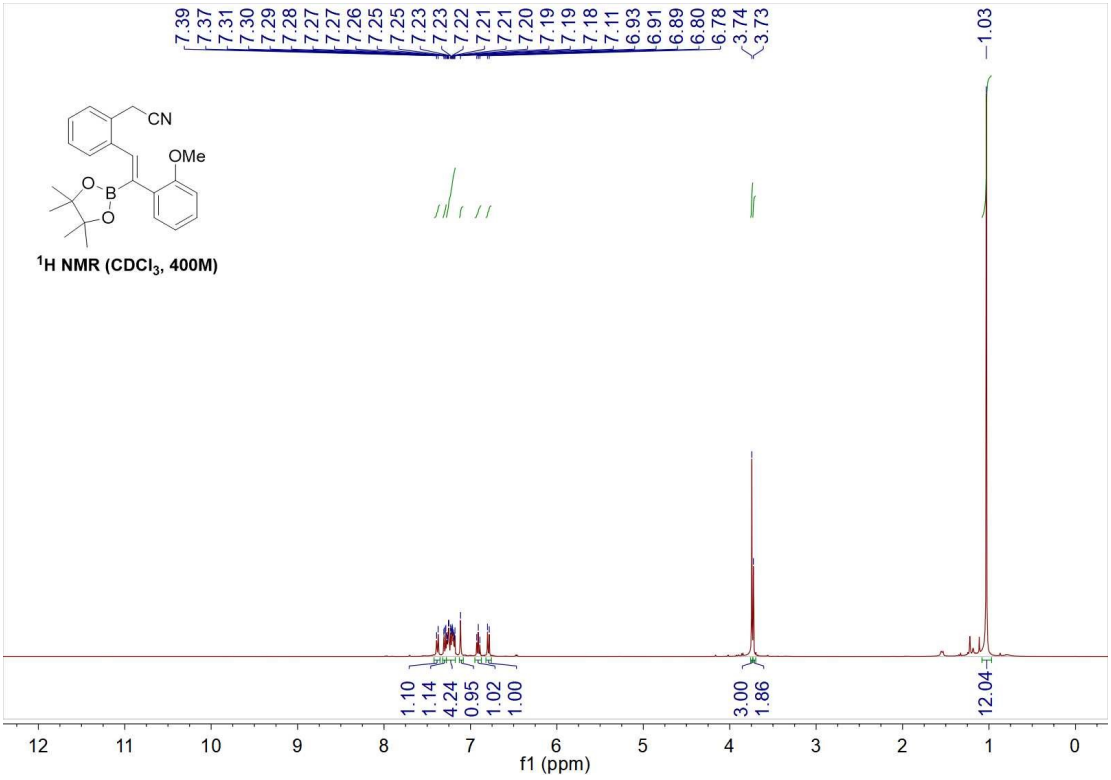
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 17



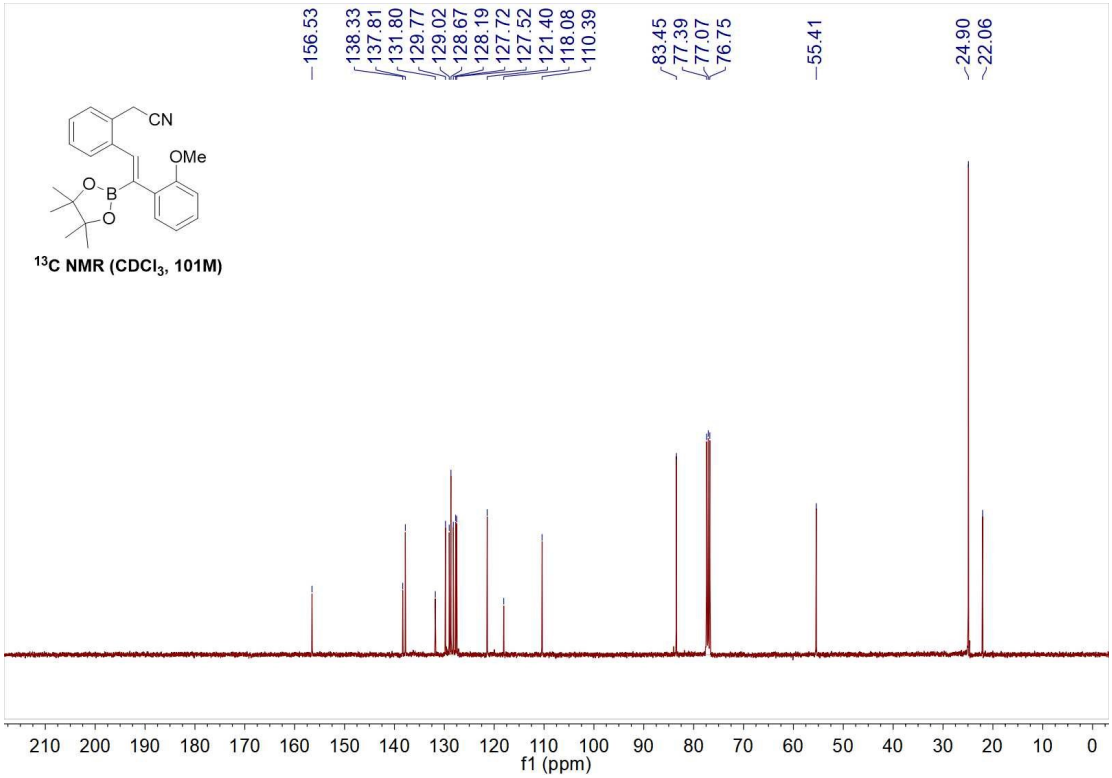
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 17



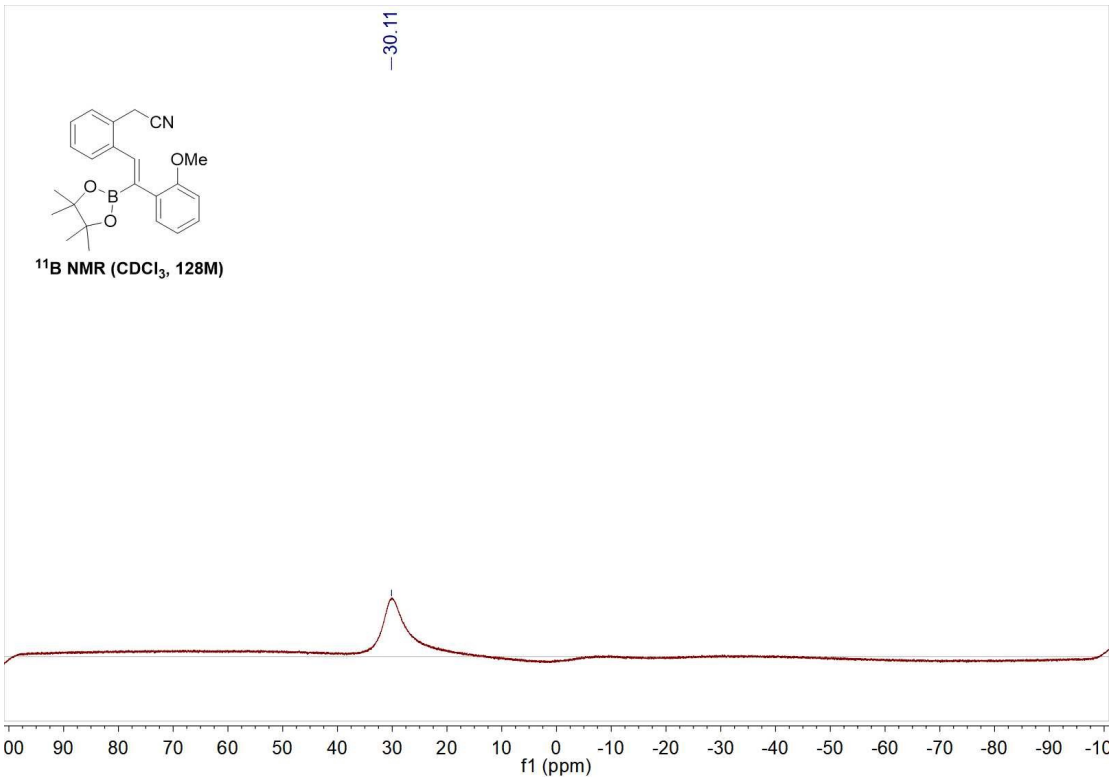
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 18



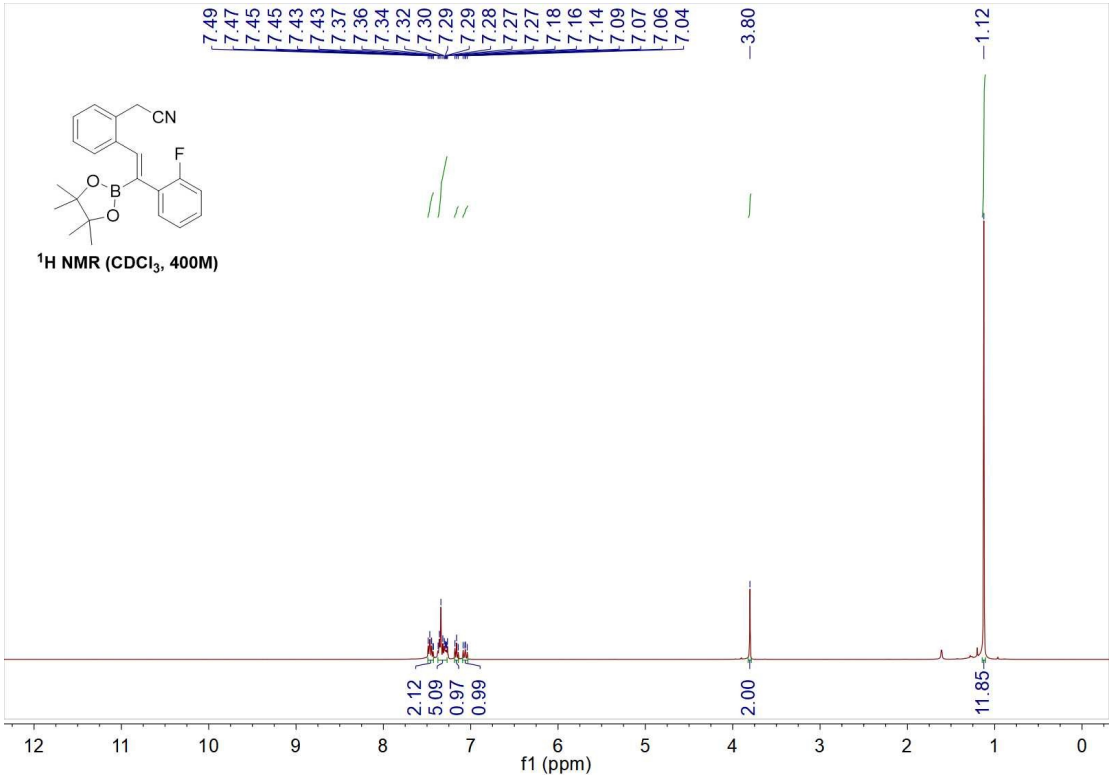
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 18



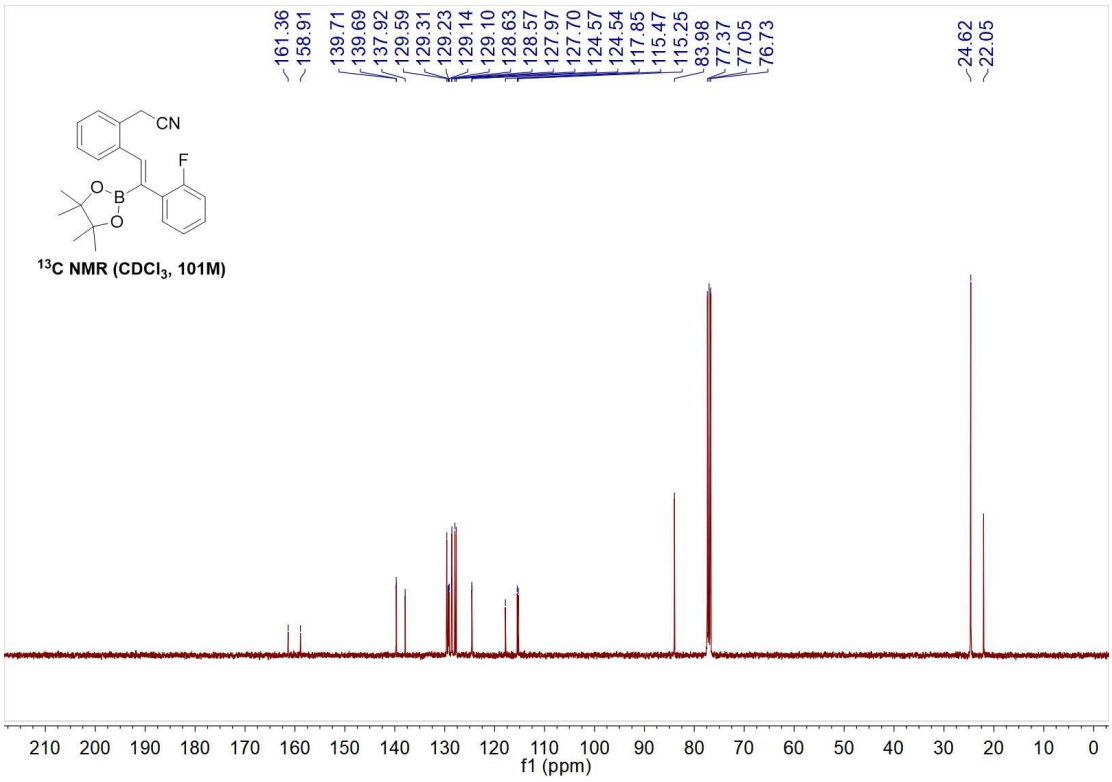
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 18



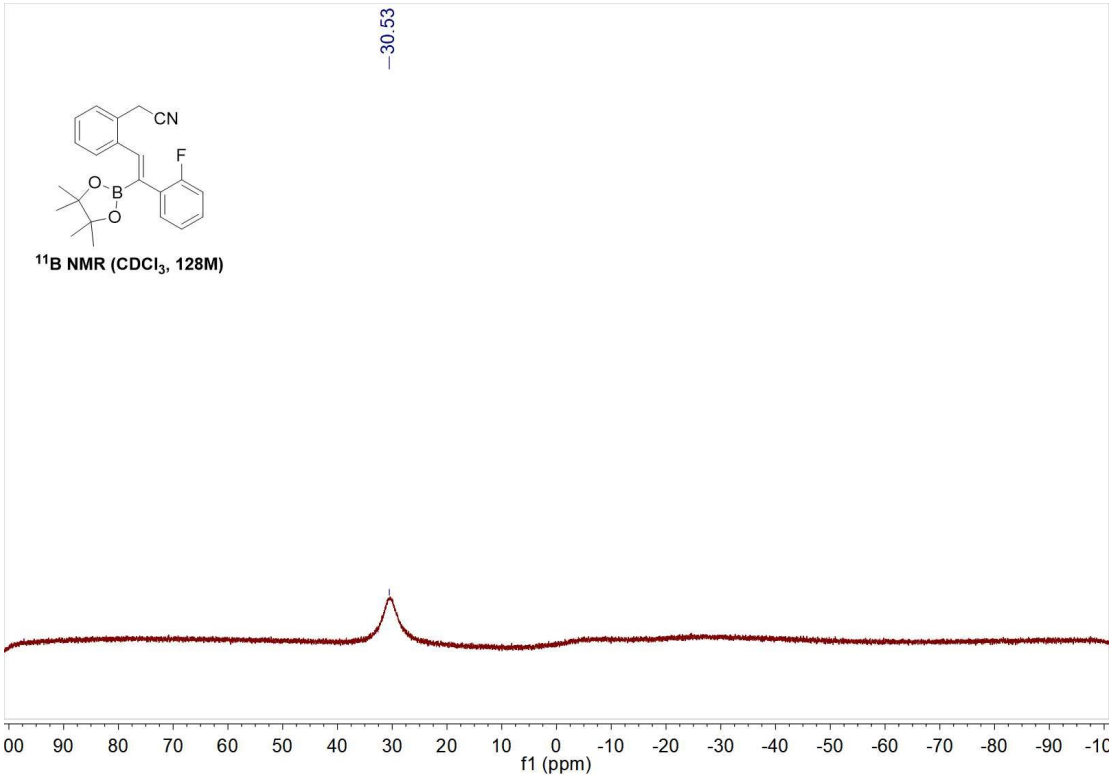
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 19



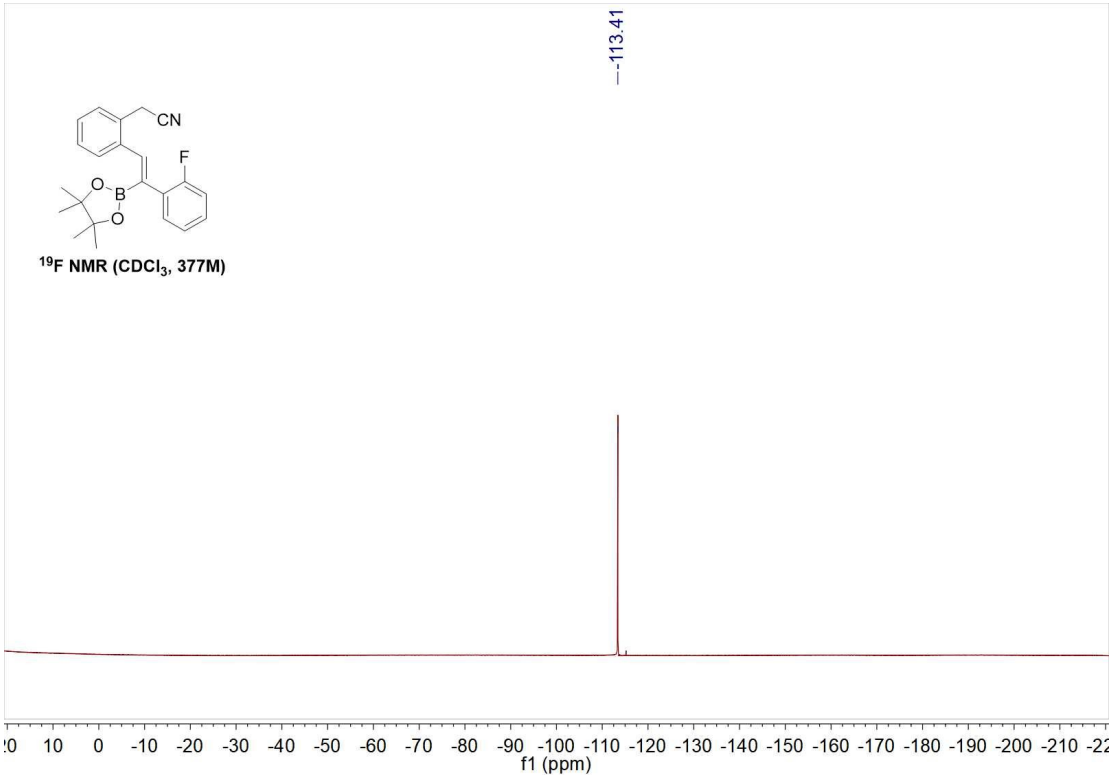
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 19



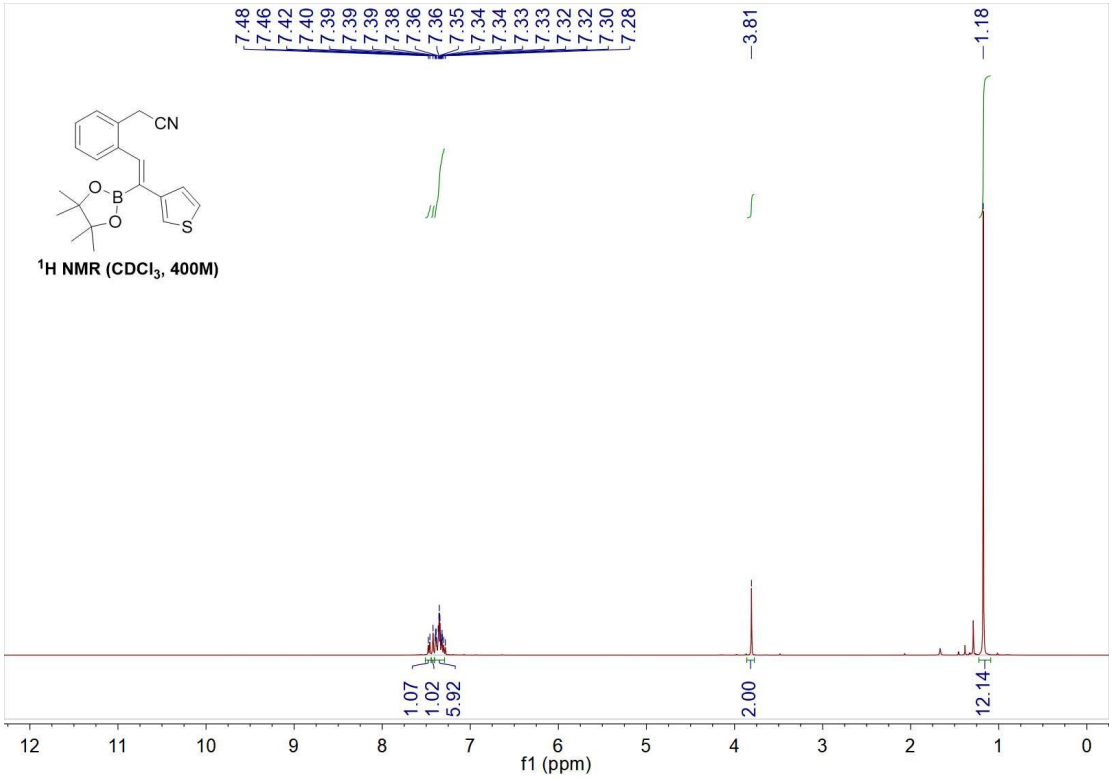
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 19



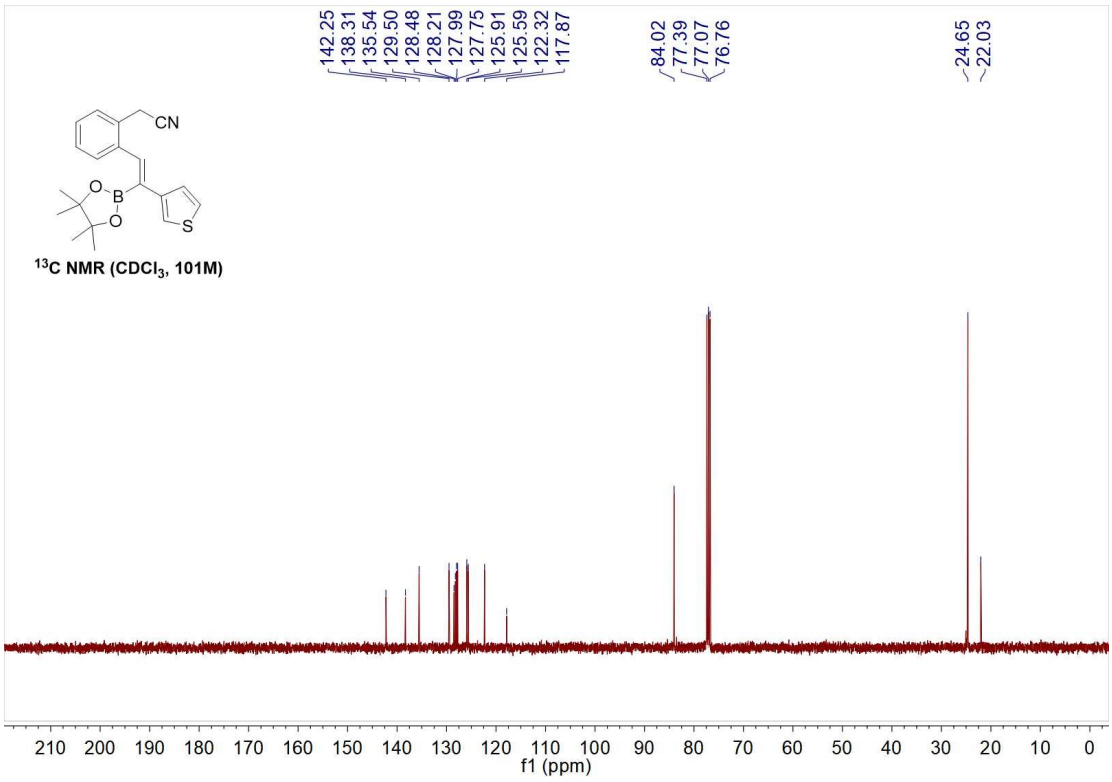
^{19}F NMR (377 MHz, Chloroform-*d*) of compound 19



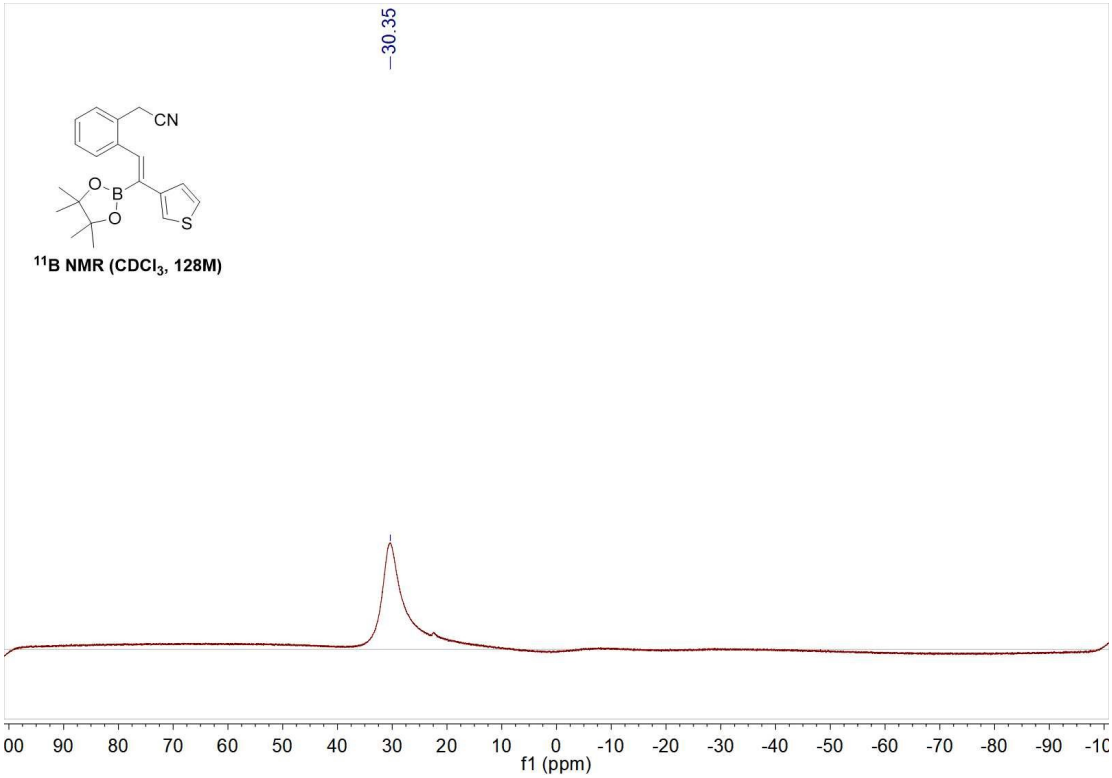
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 20



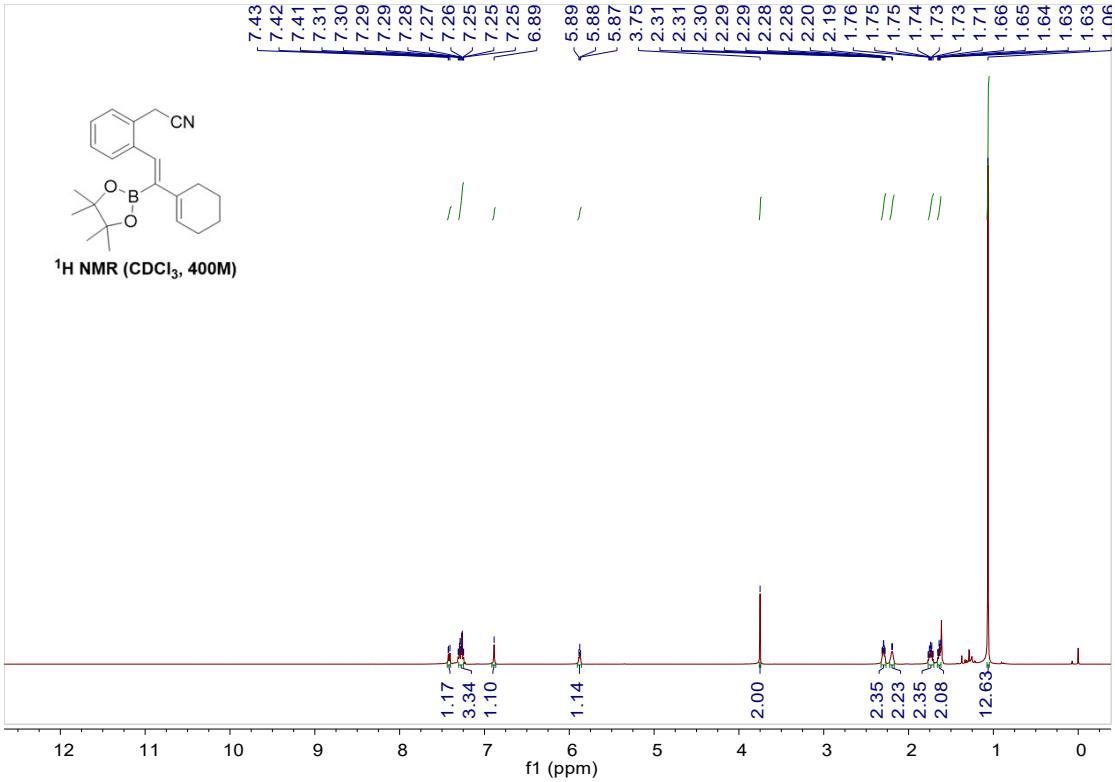
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 20



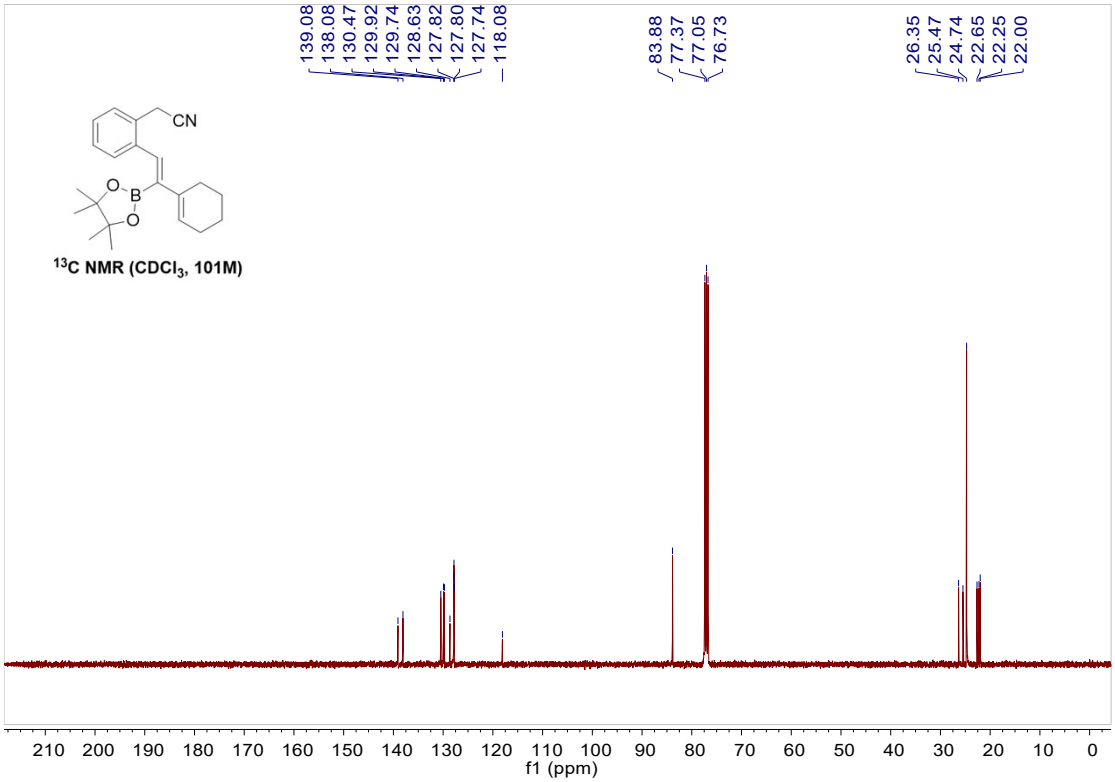
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 20



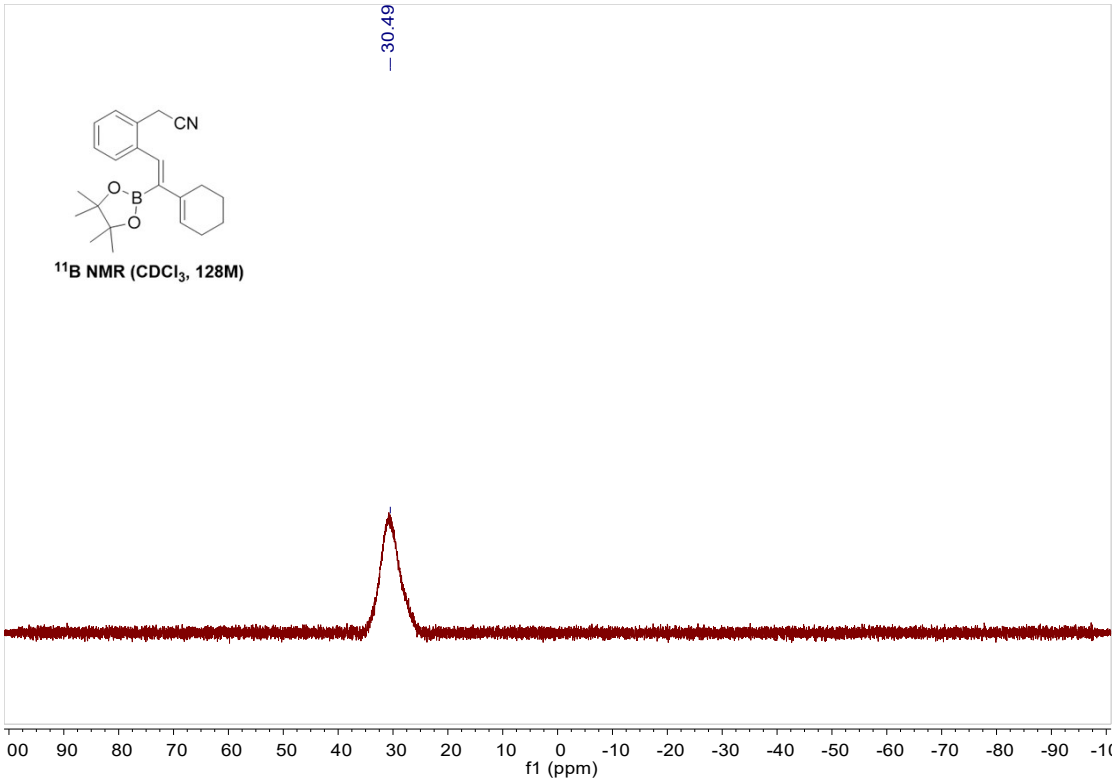
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 21



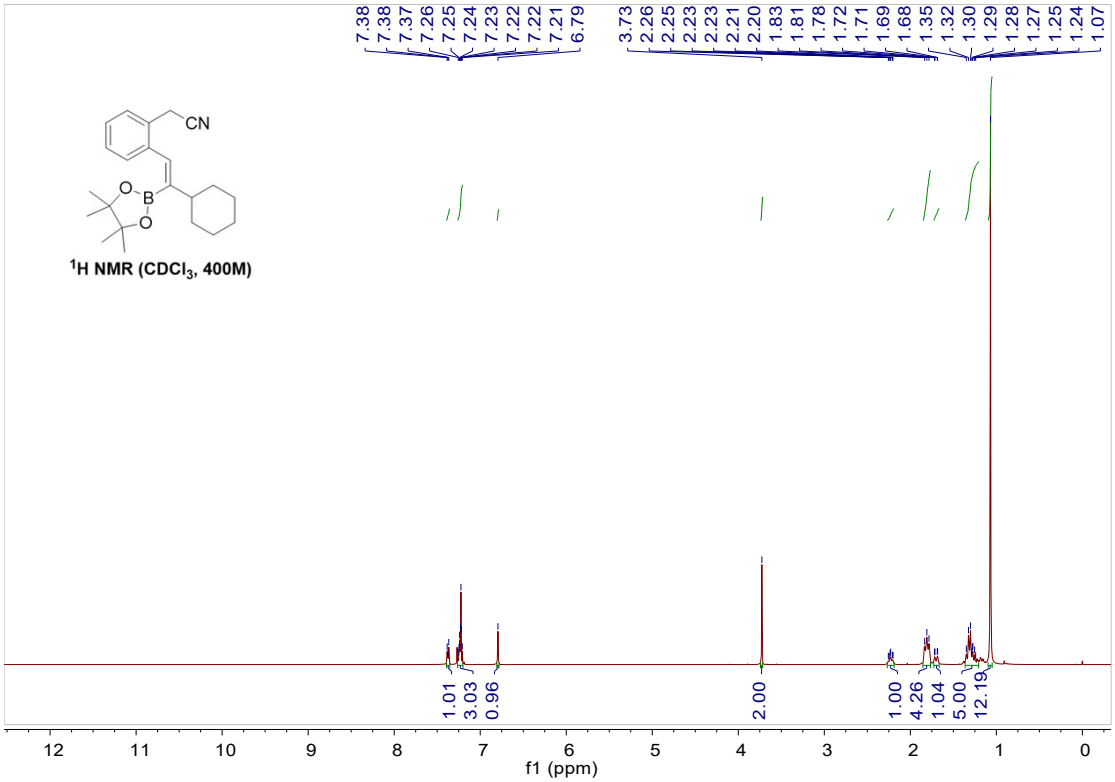
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 21



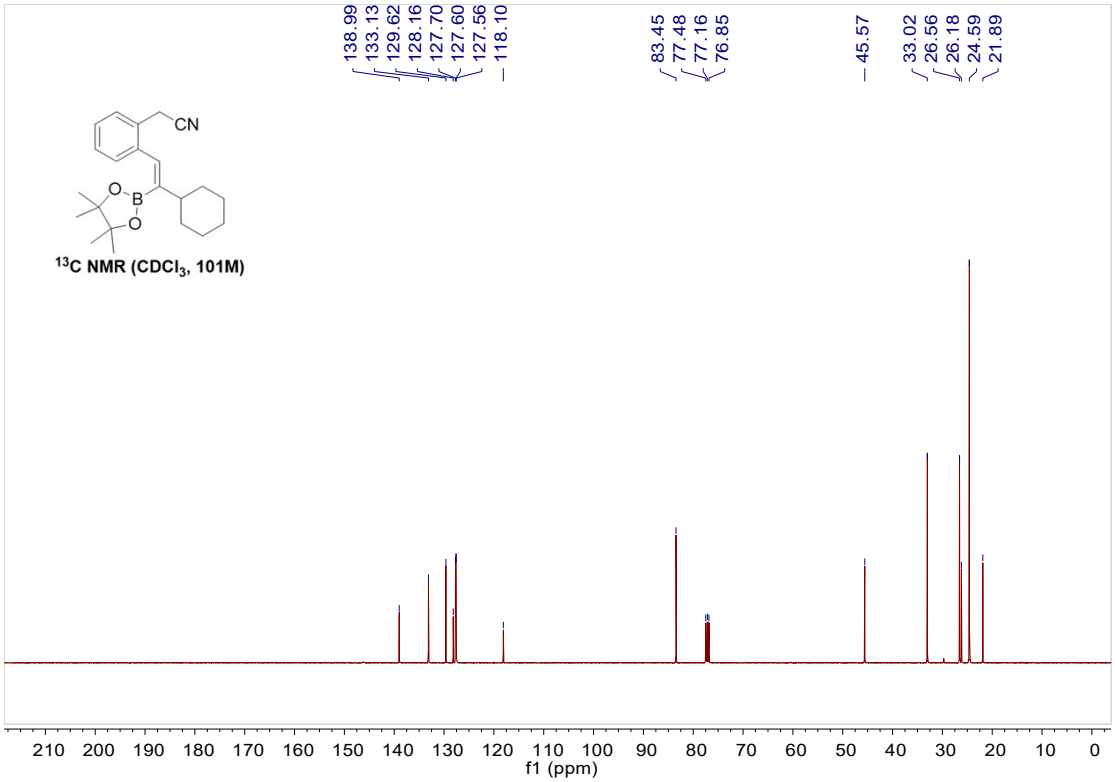
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 21



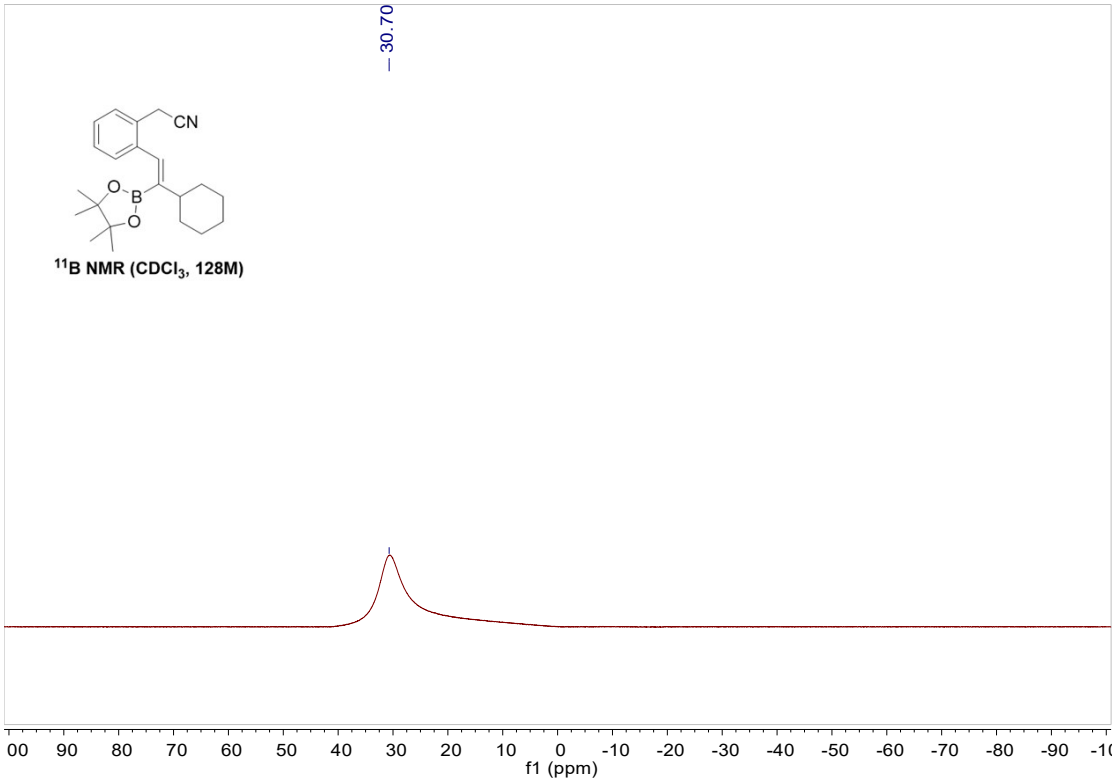
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 22



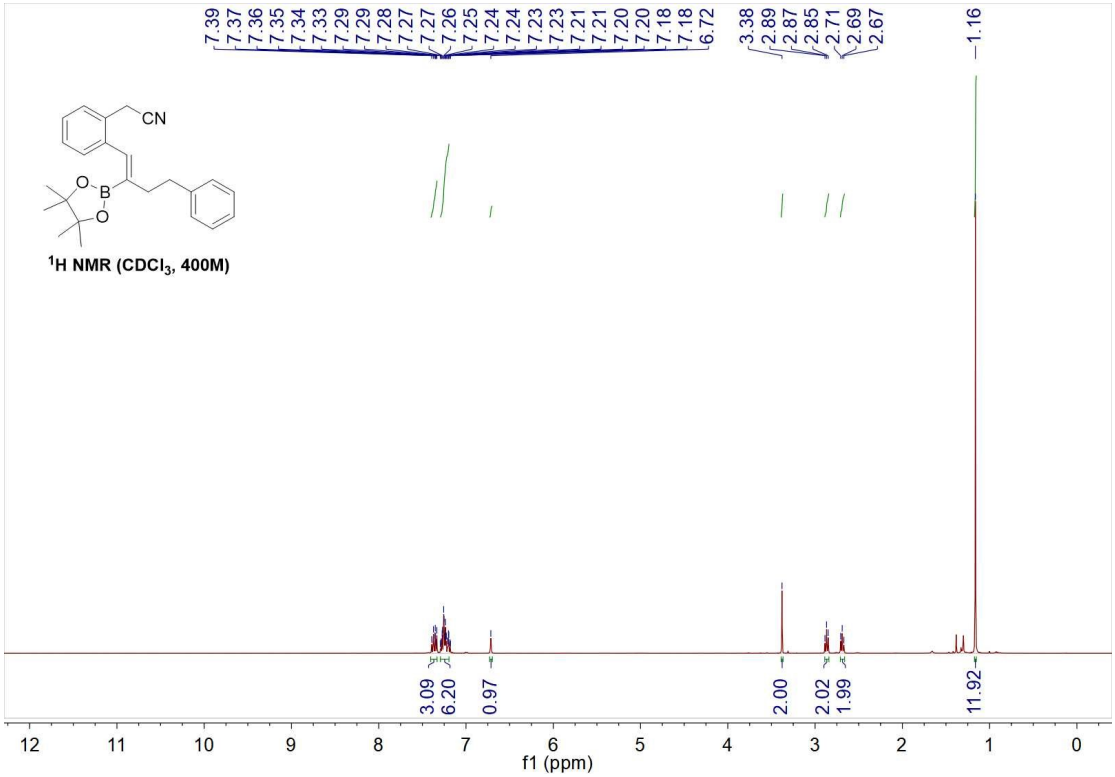
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 22



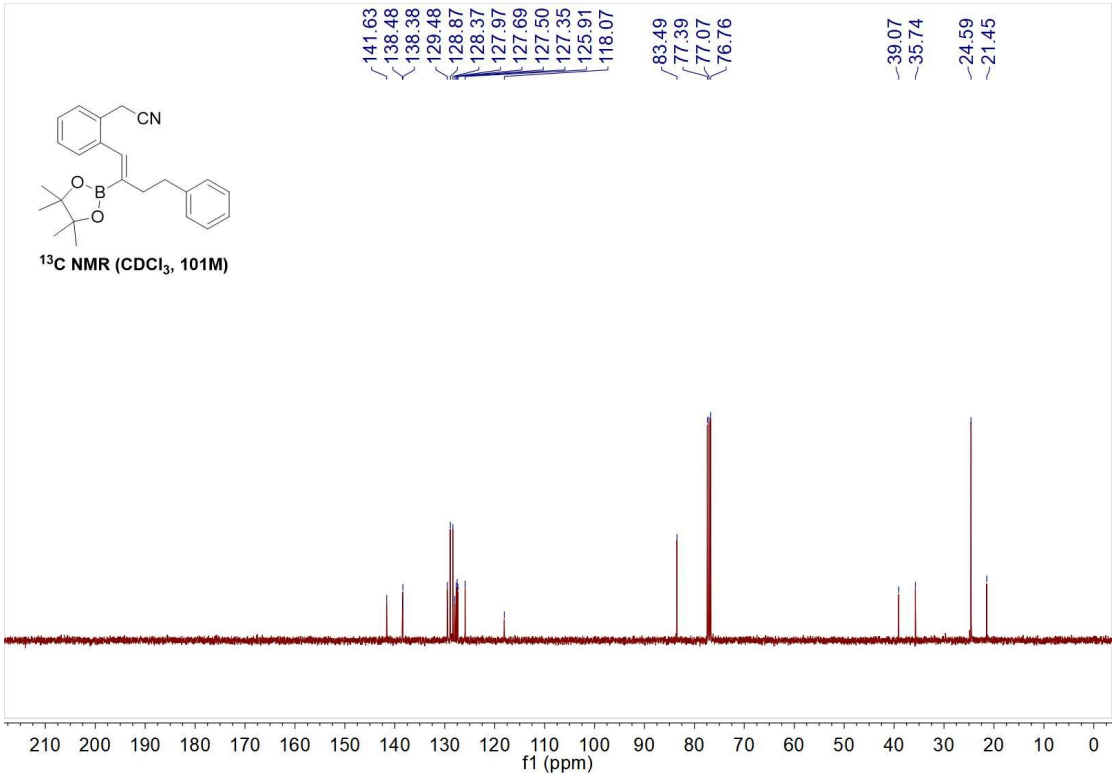
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 22



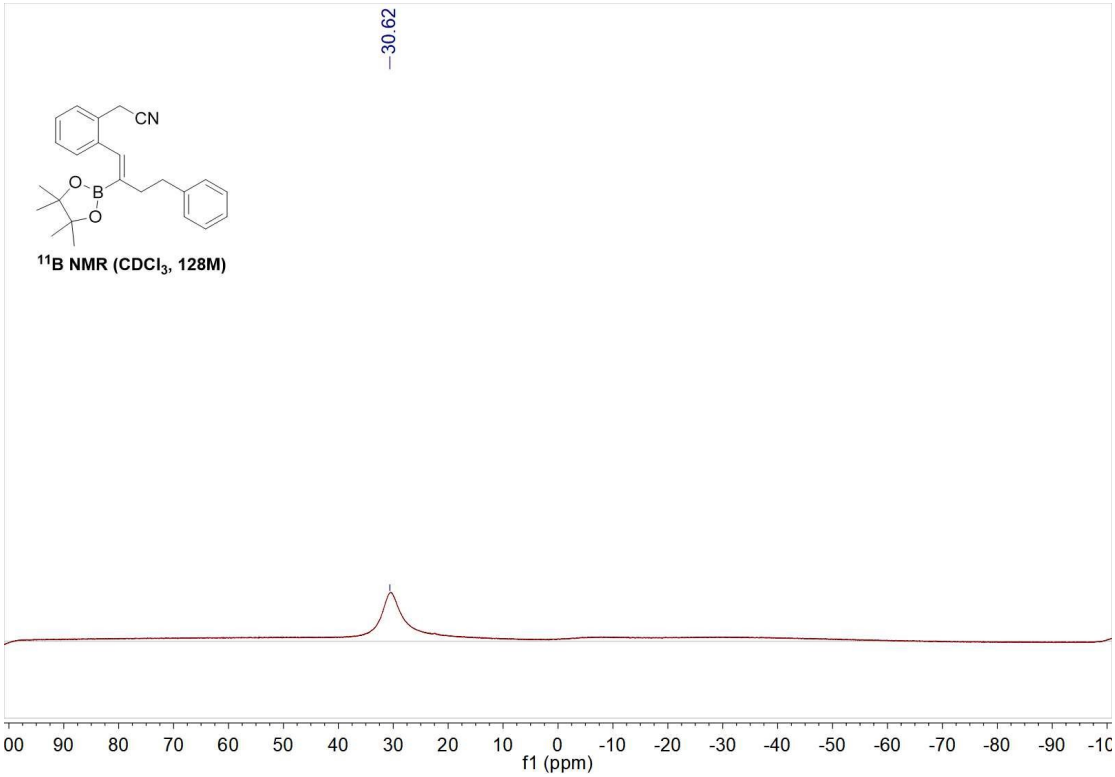
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 23



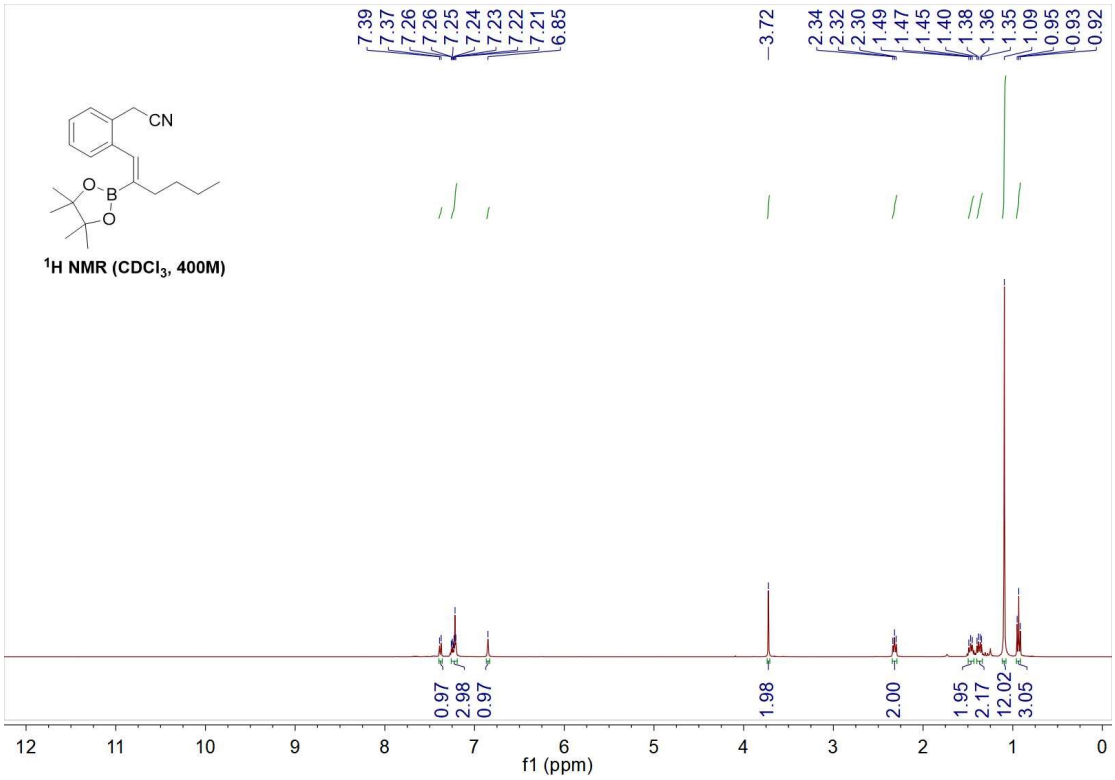
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 23



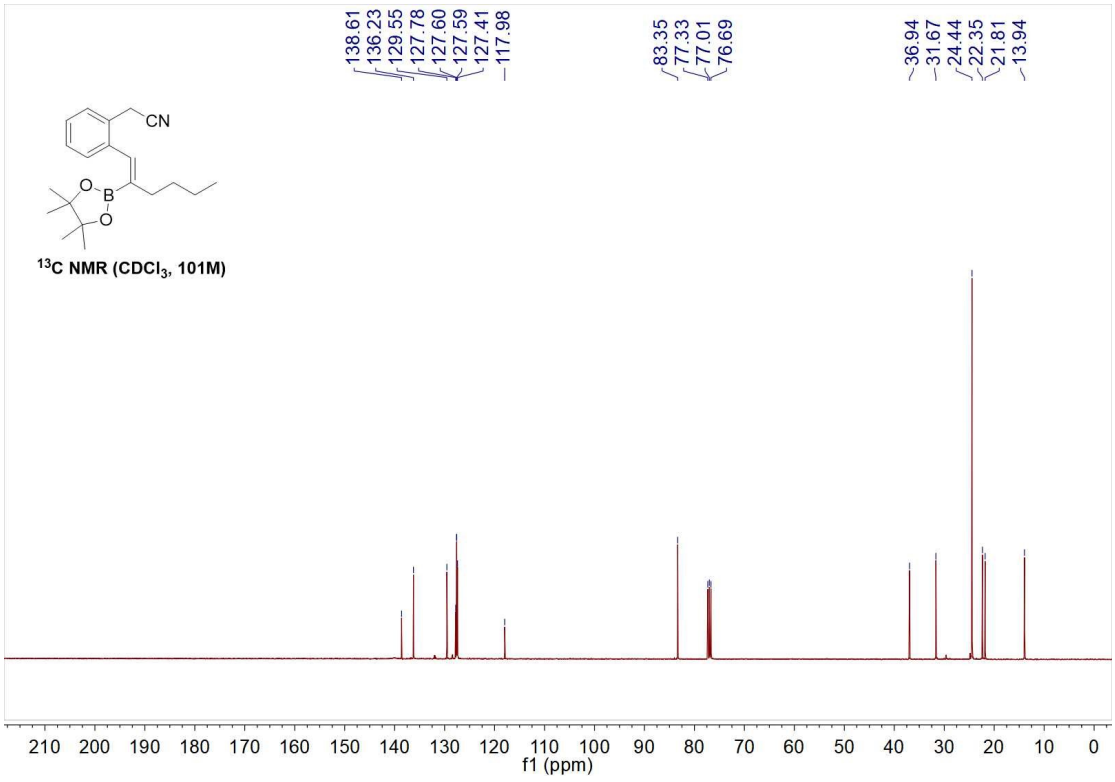
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 23



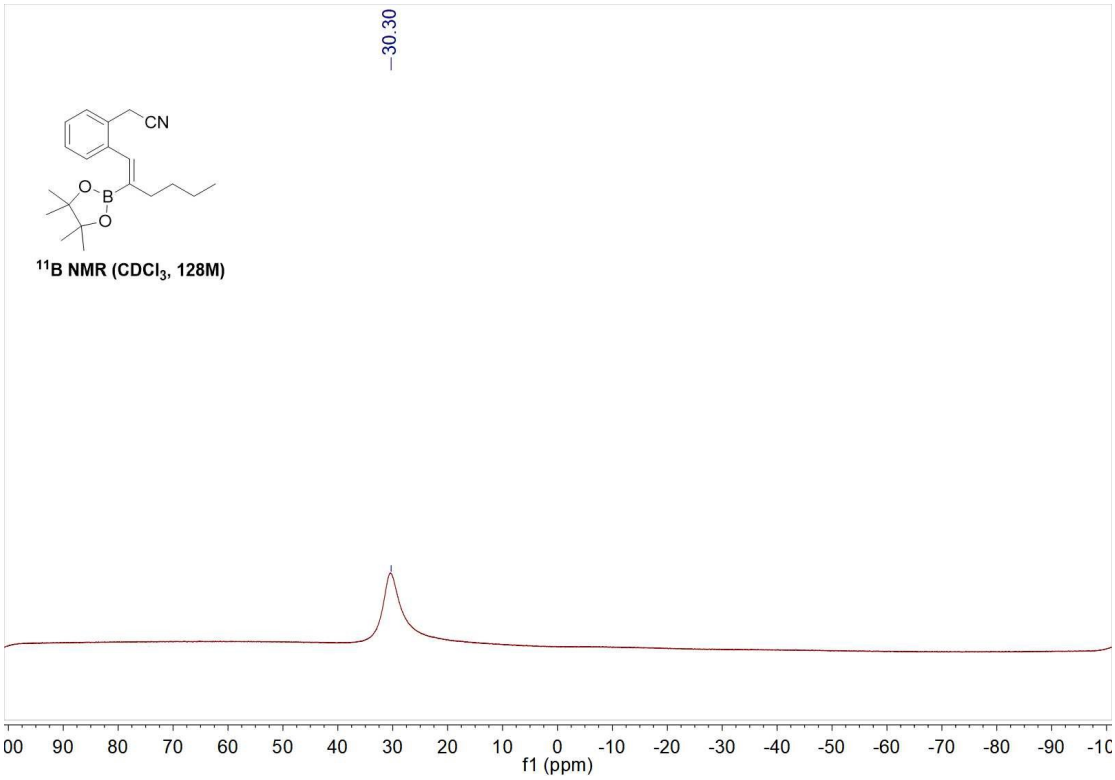
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 24



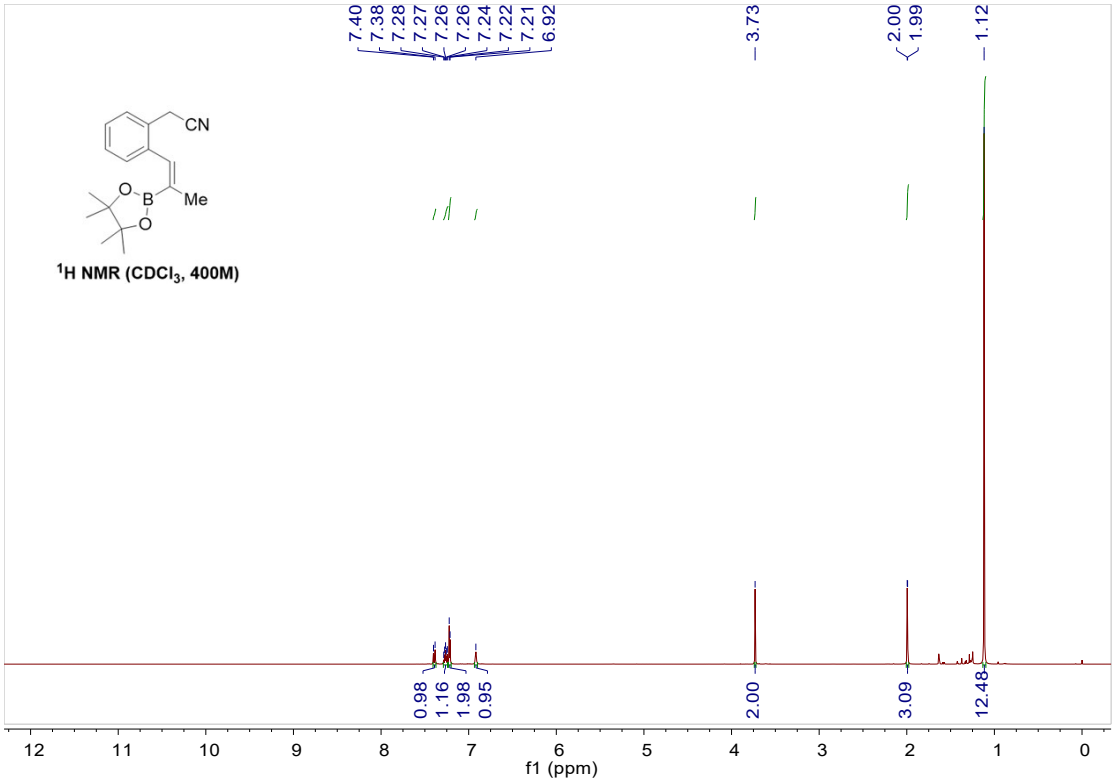
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 24



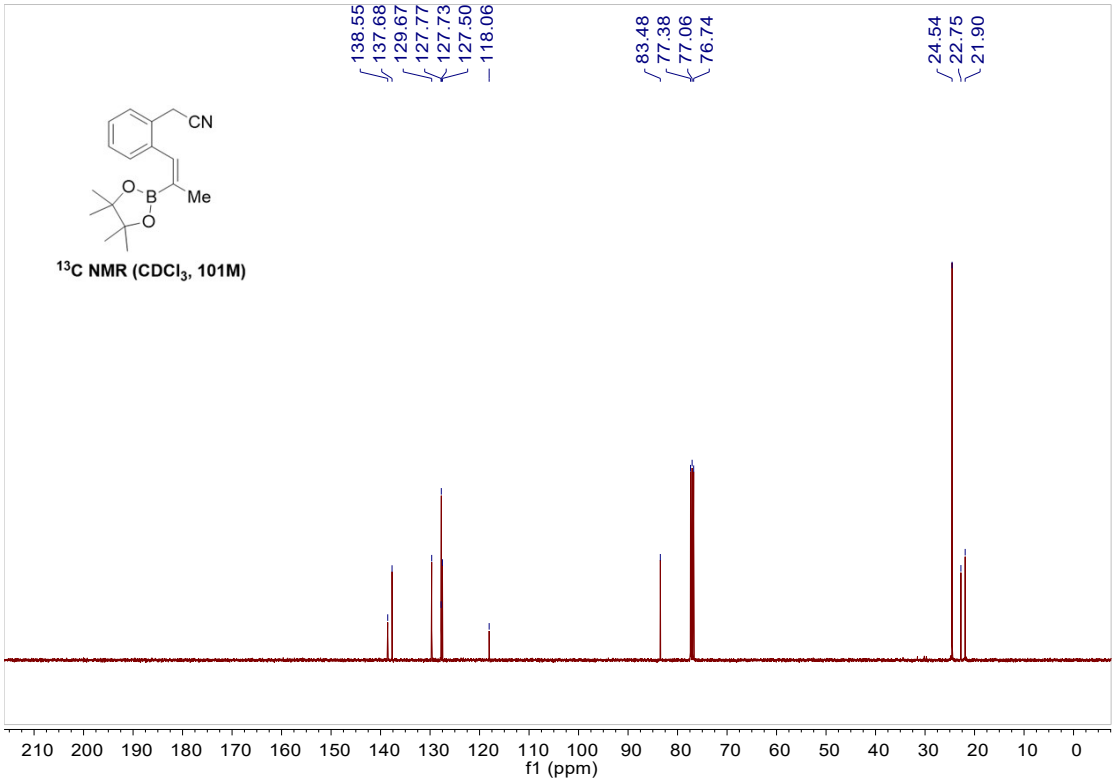
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 24



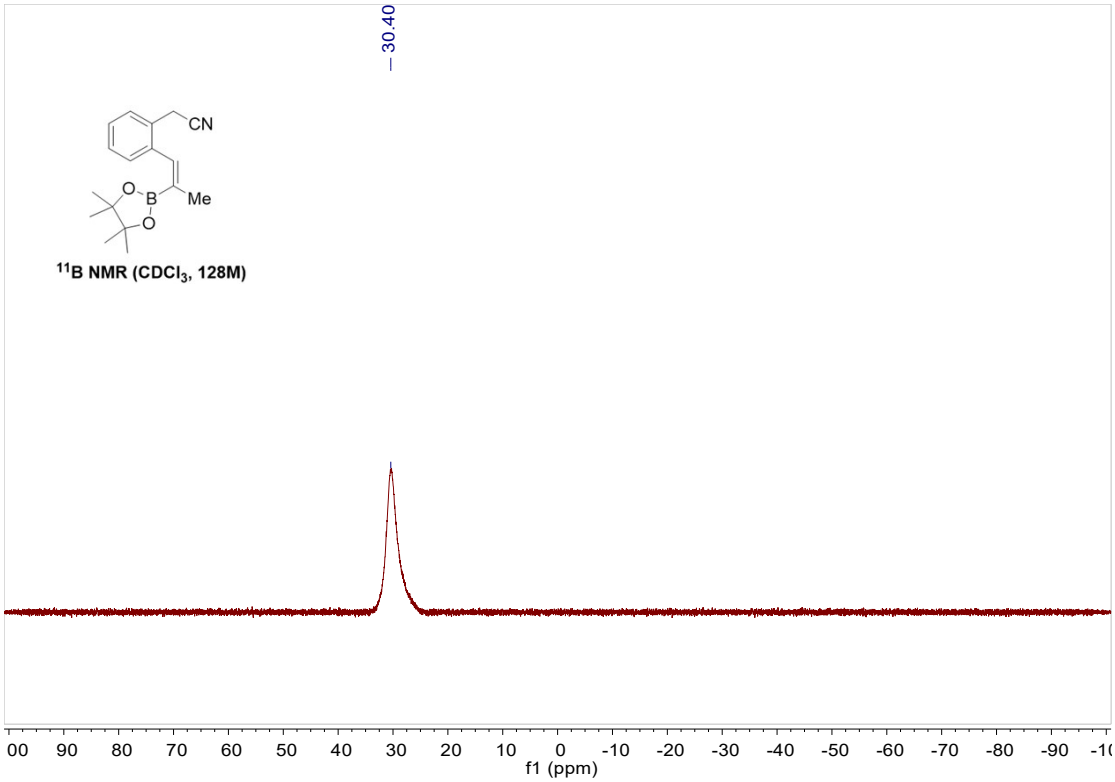
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 25



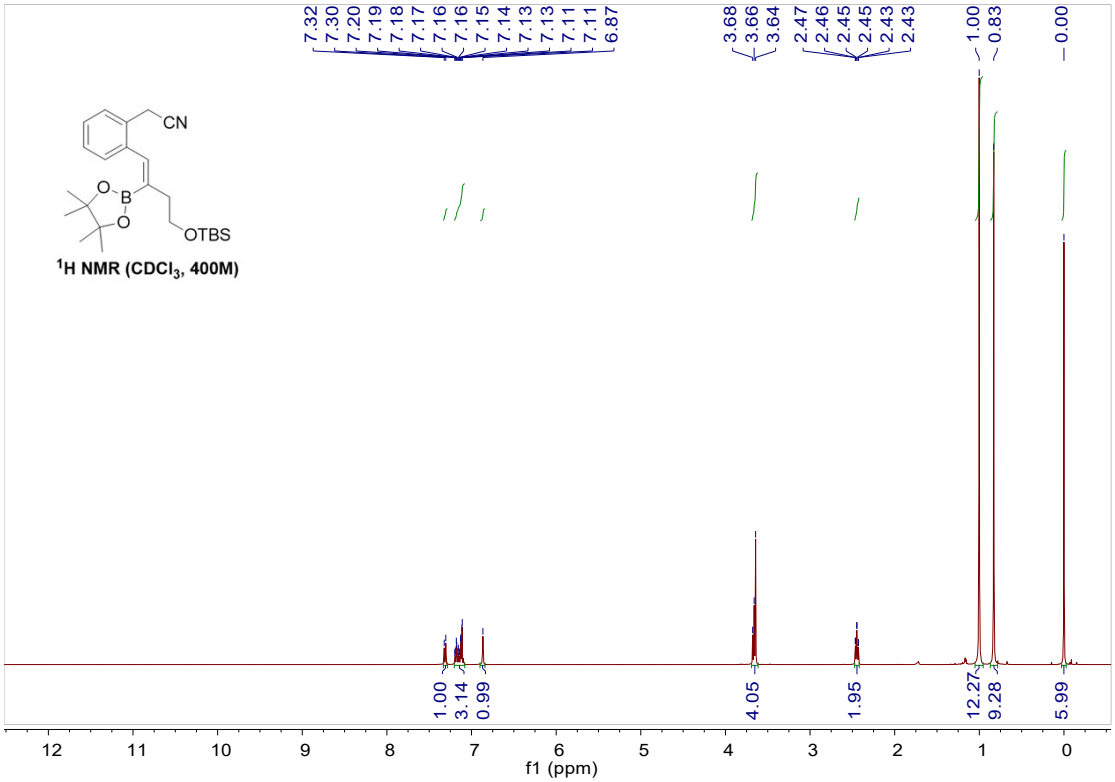
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 25



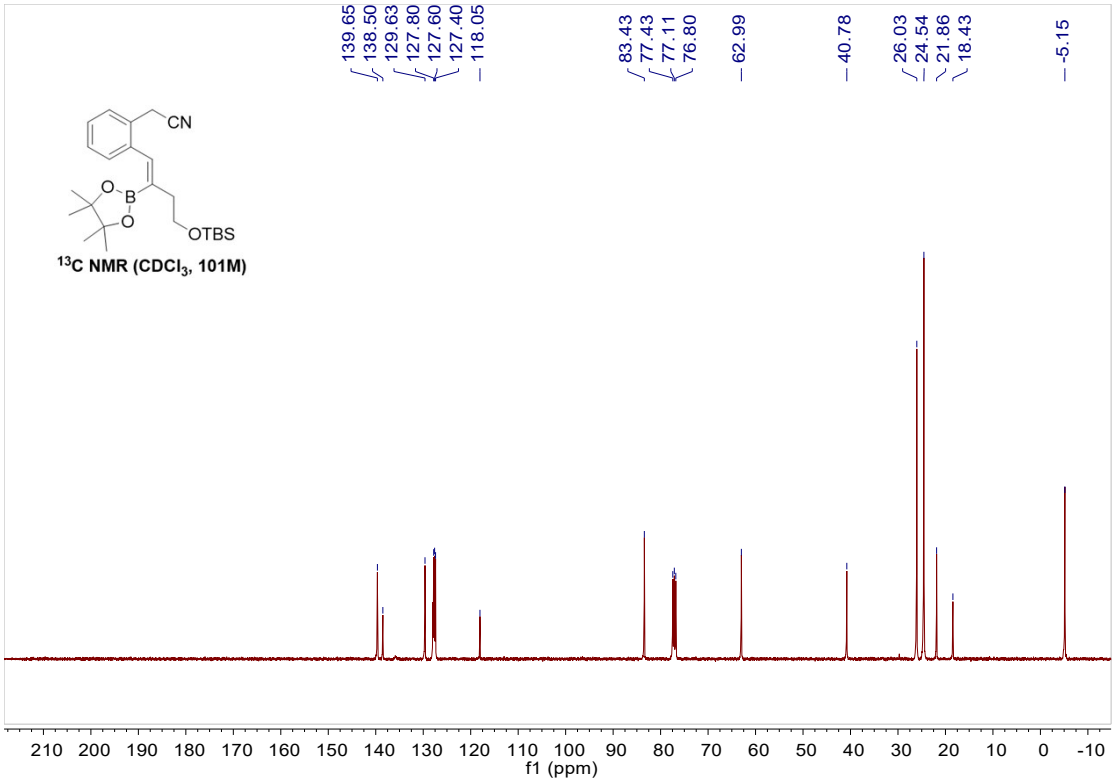
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 25



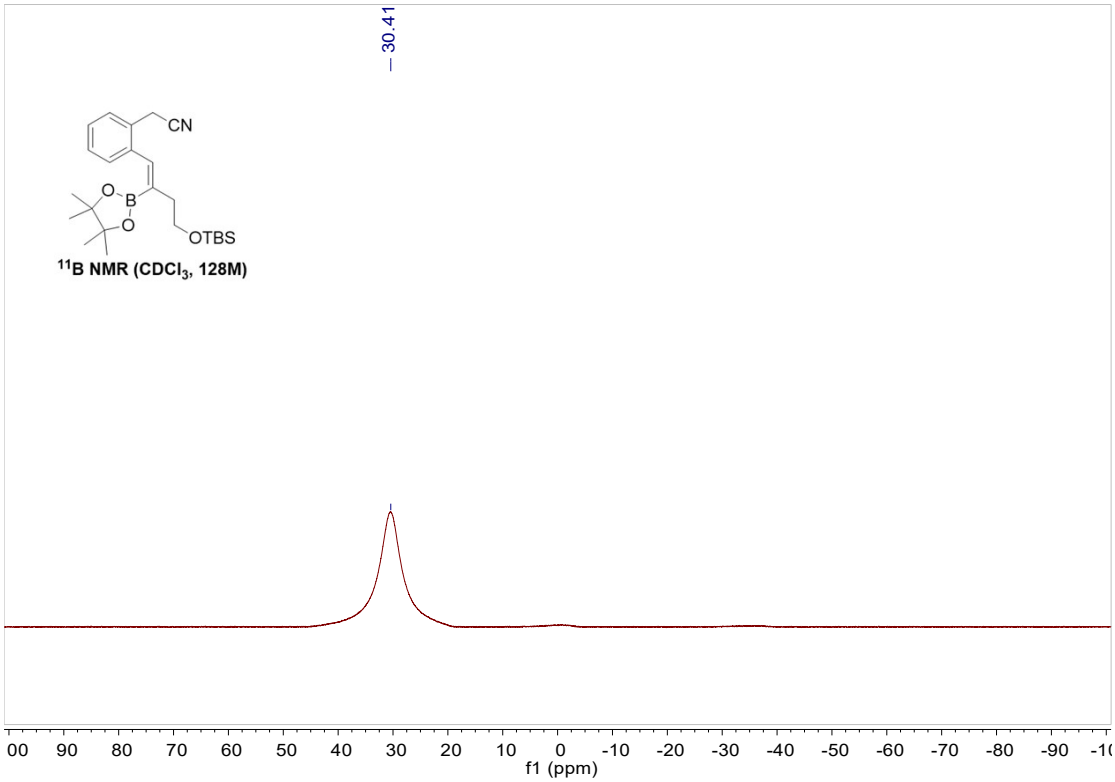
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 26



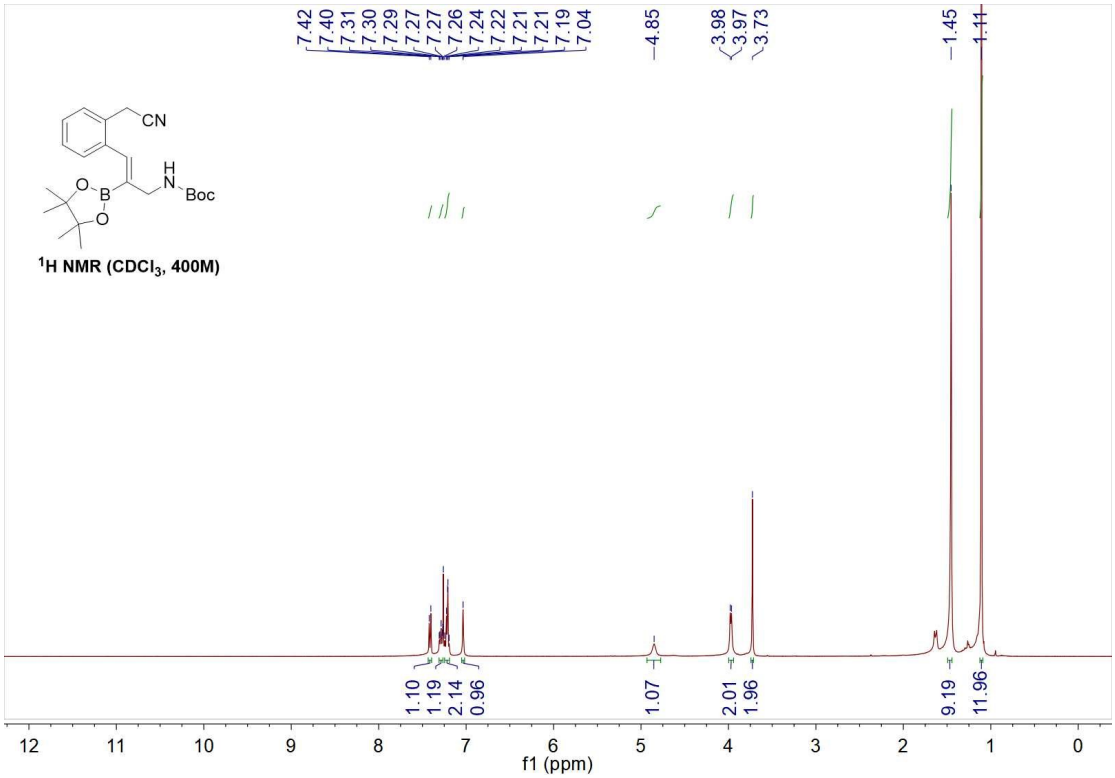
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 26



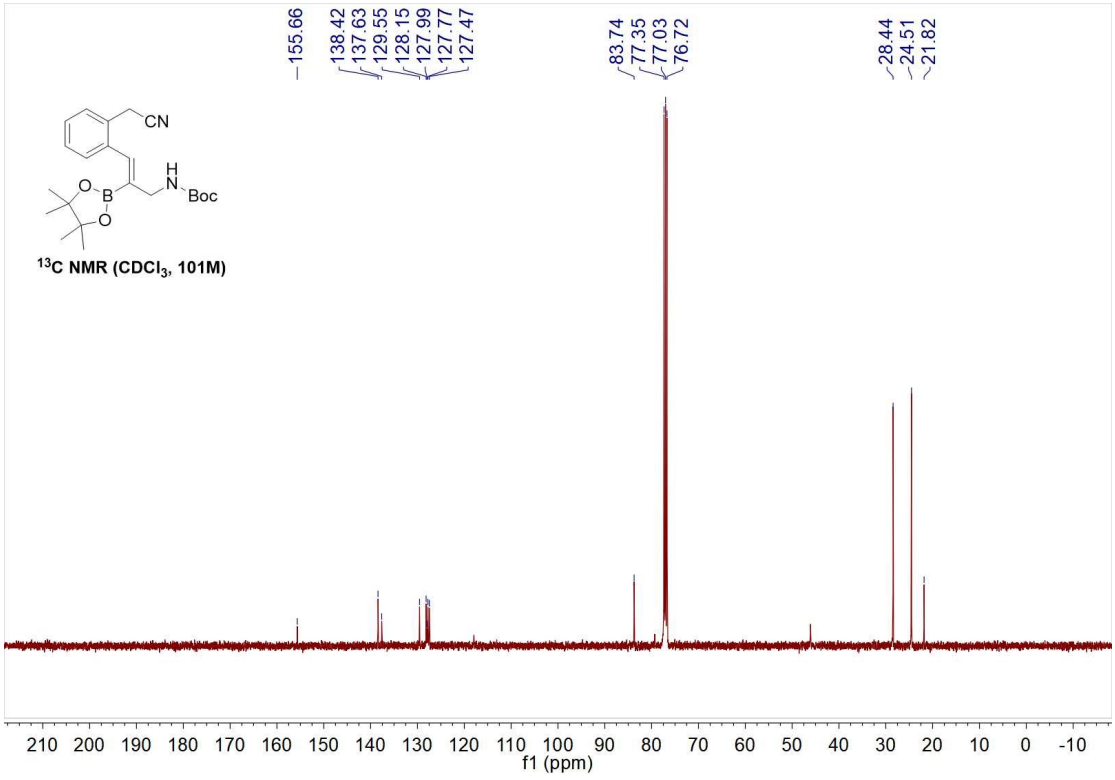
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 26



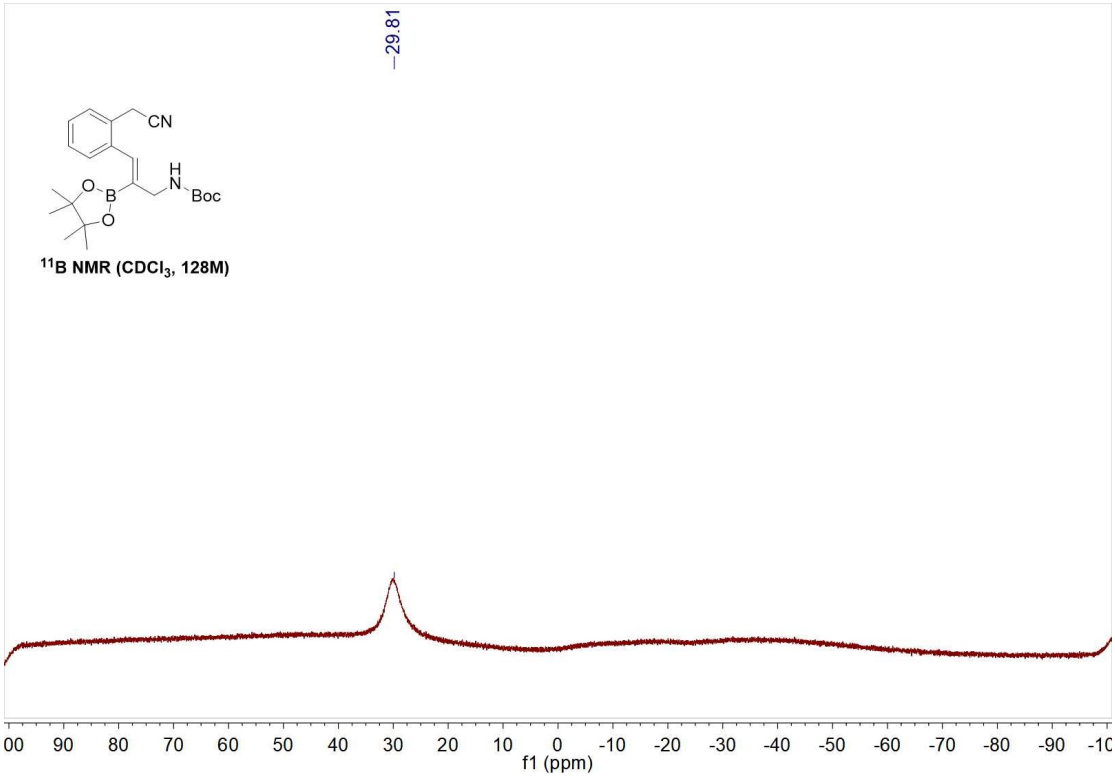
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 27



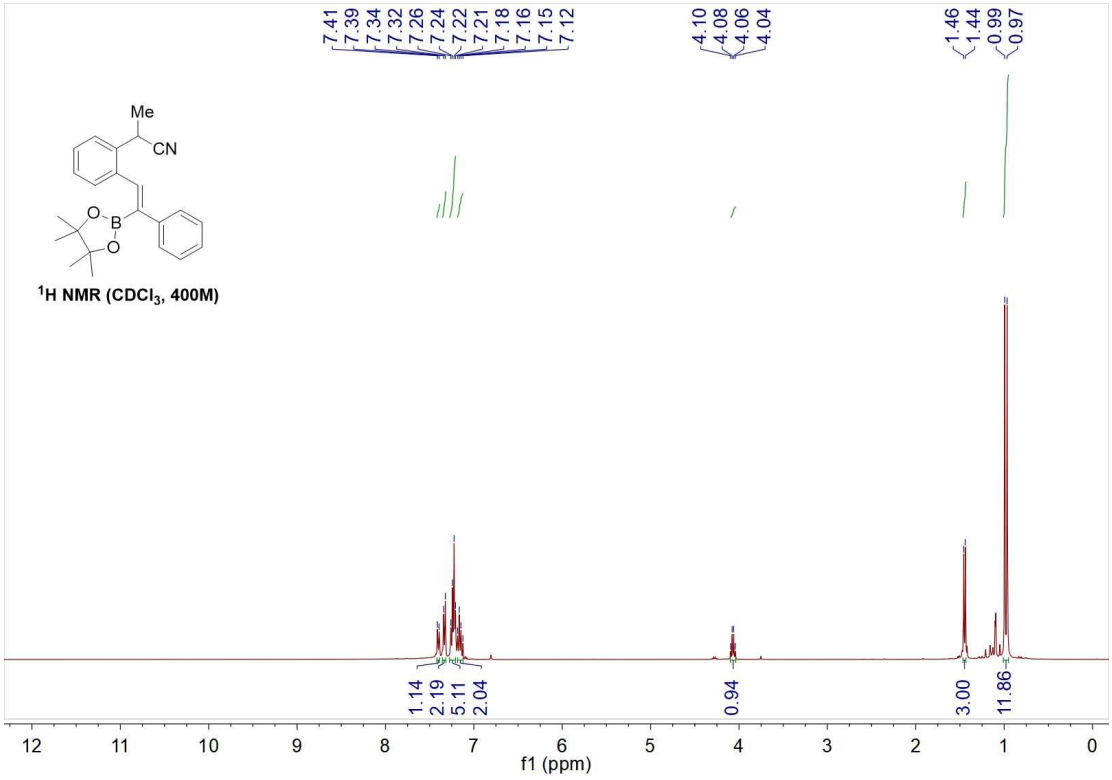
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 27



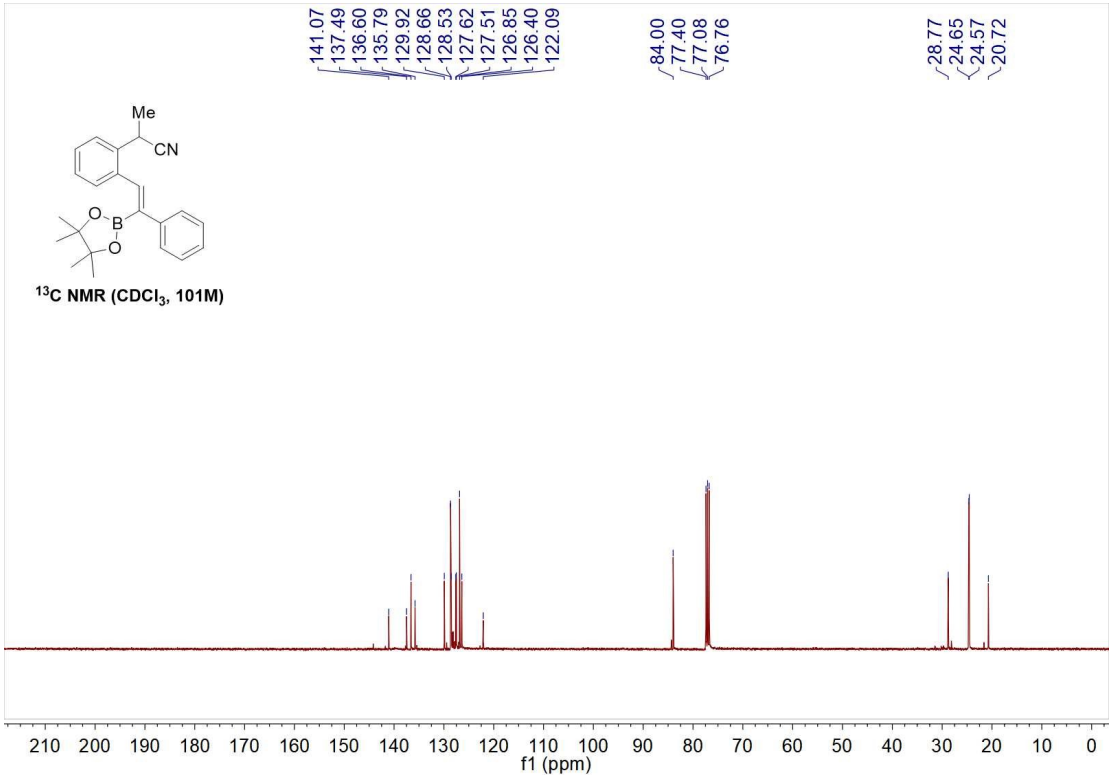
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 27



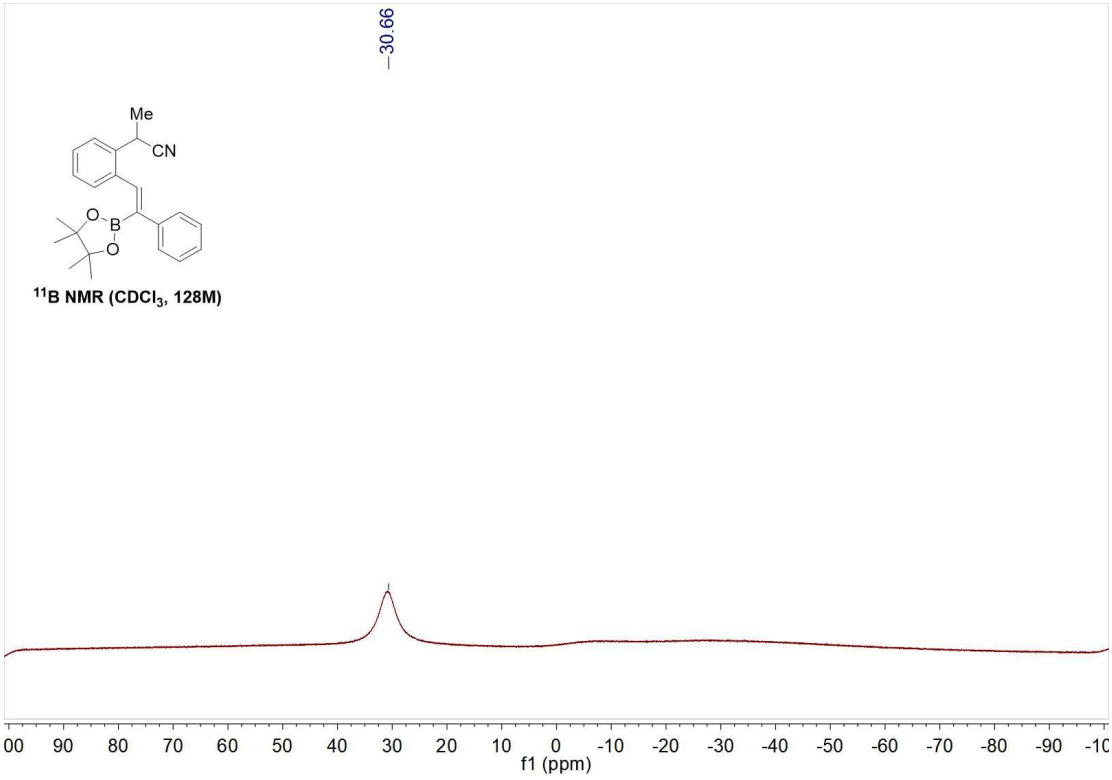
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 28



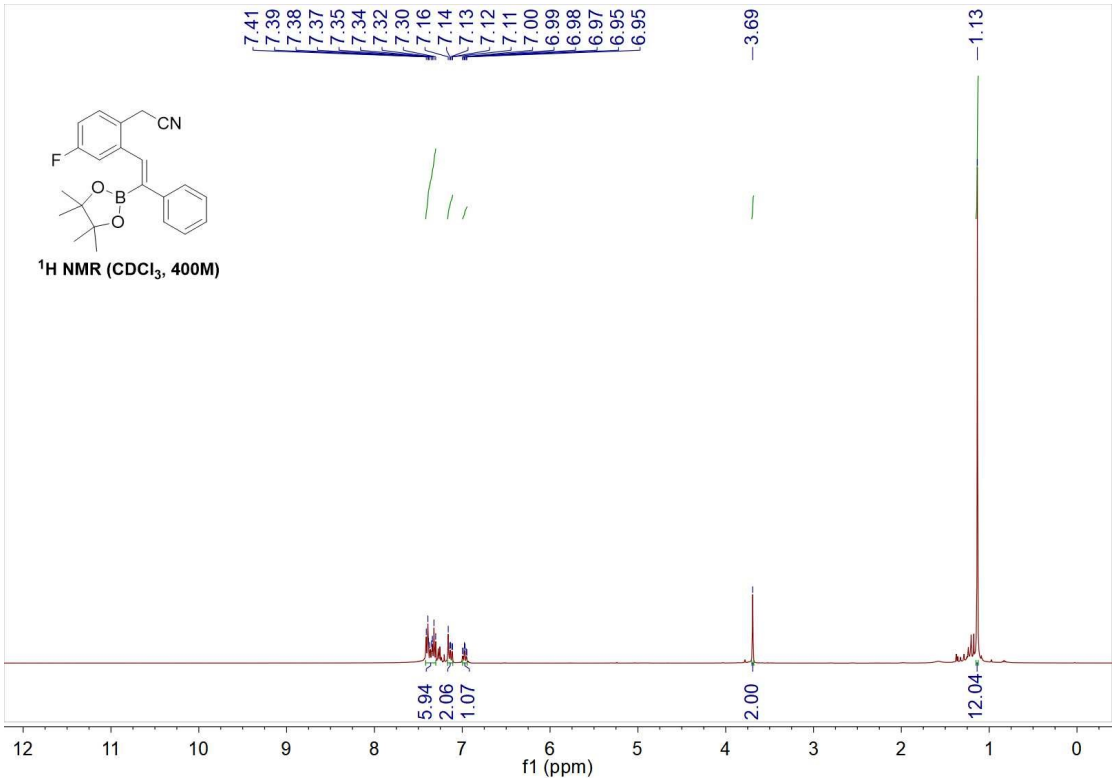
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 28



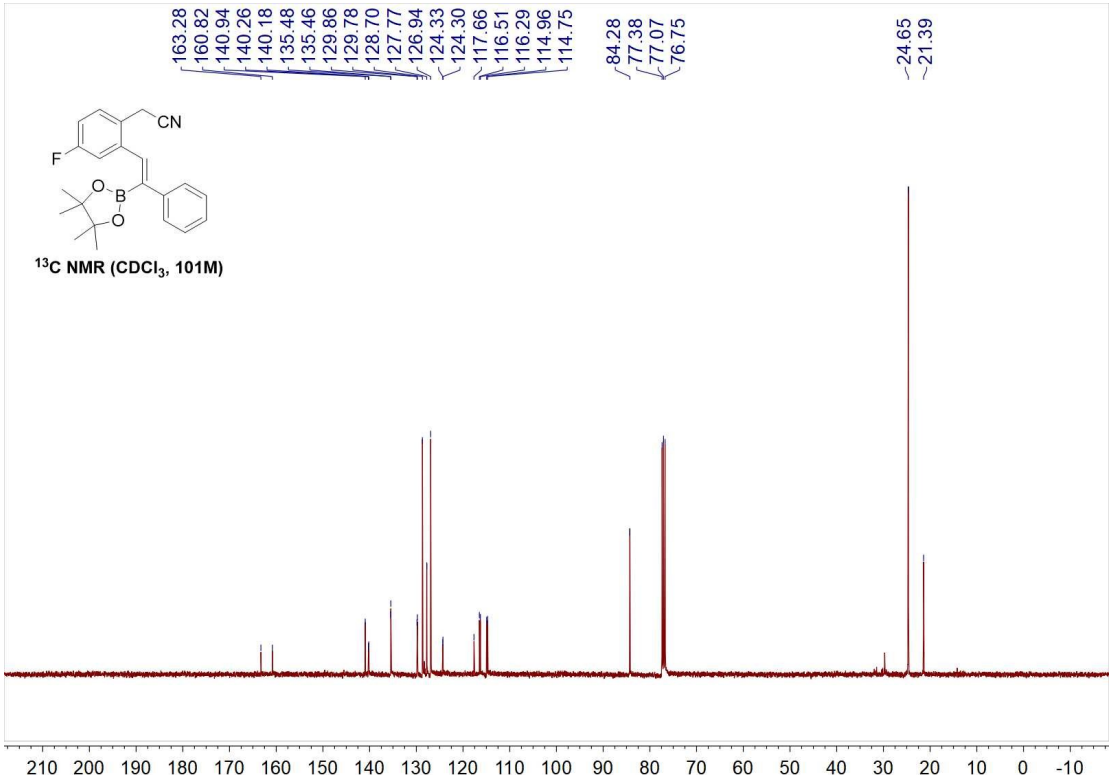
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 28



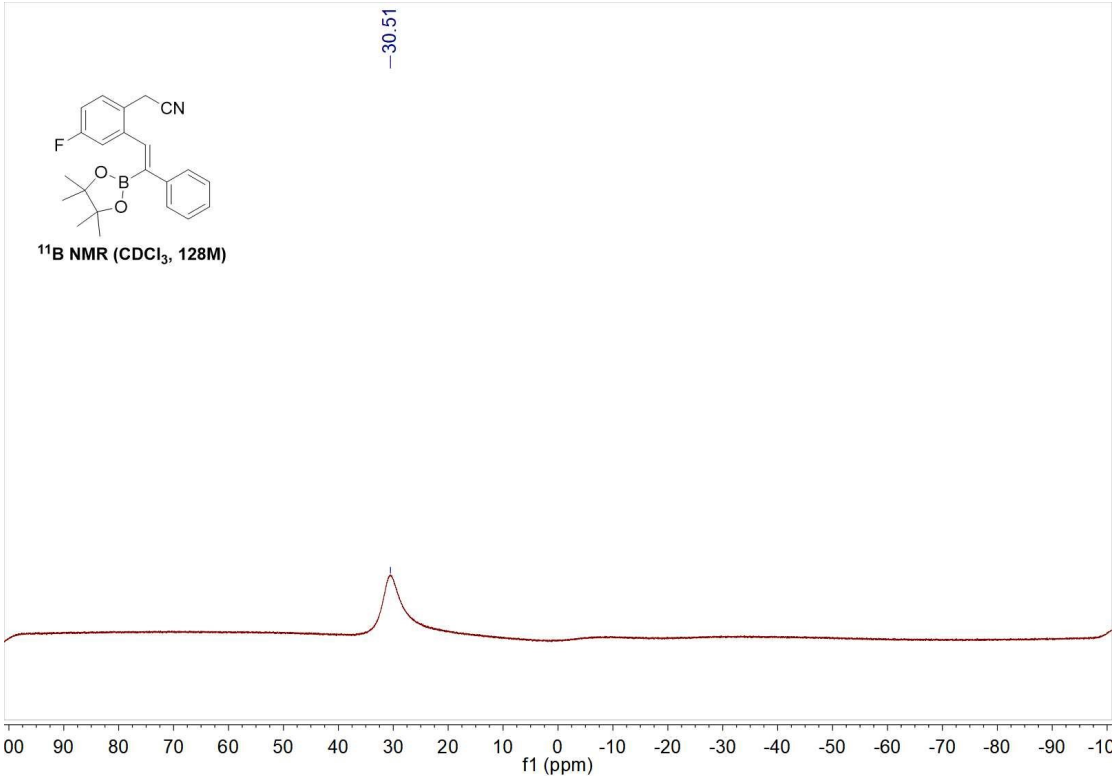
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 29



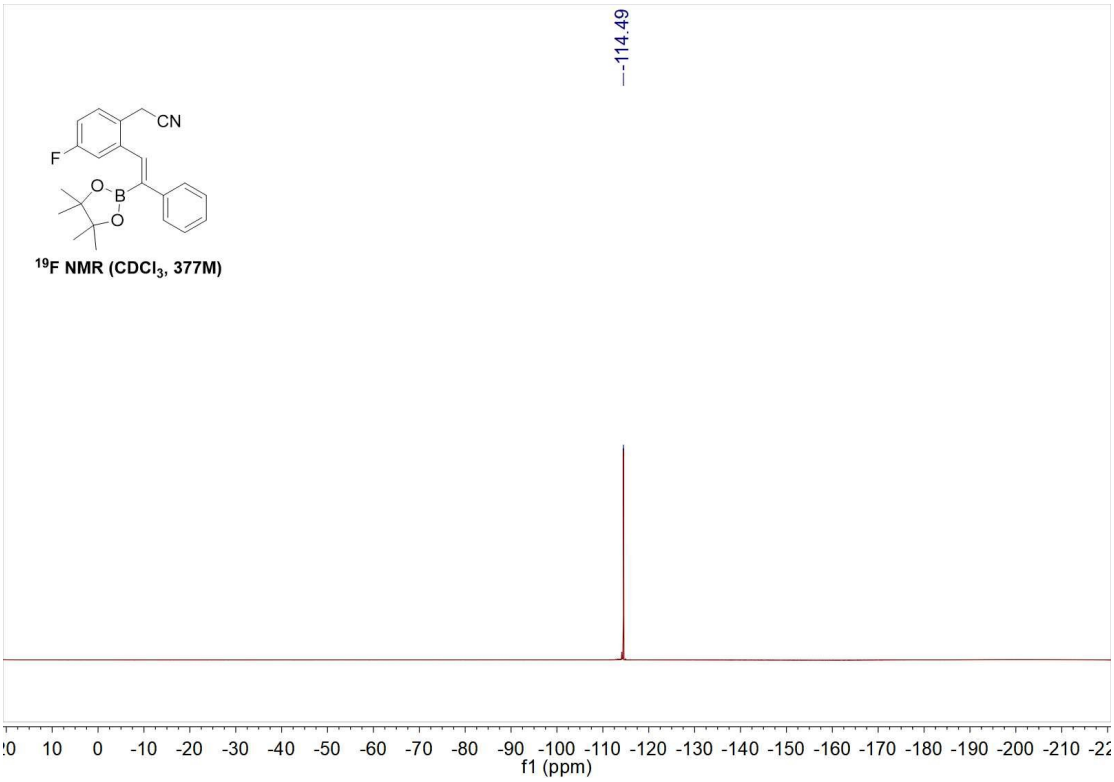
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 29



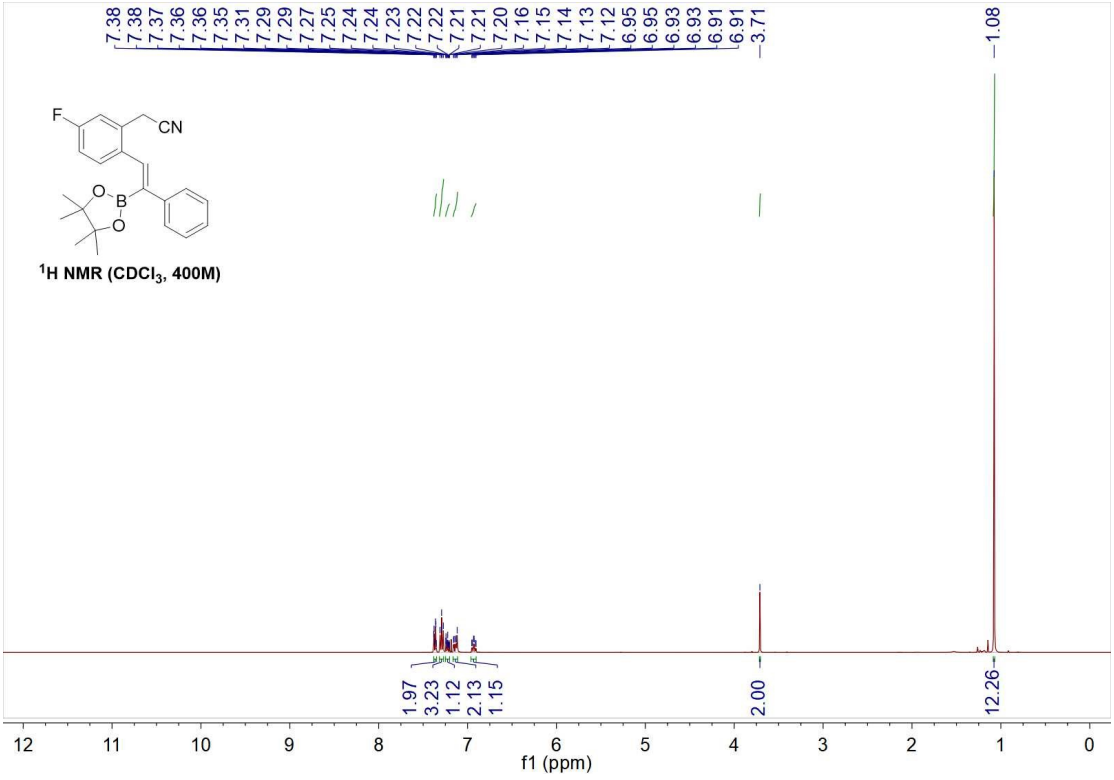
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 29



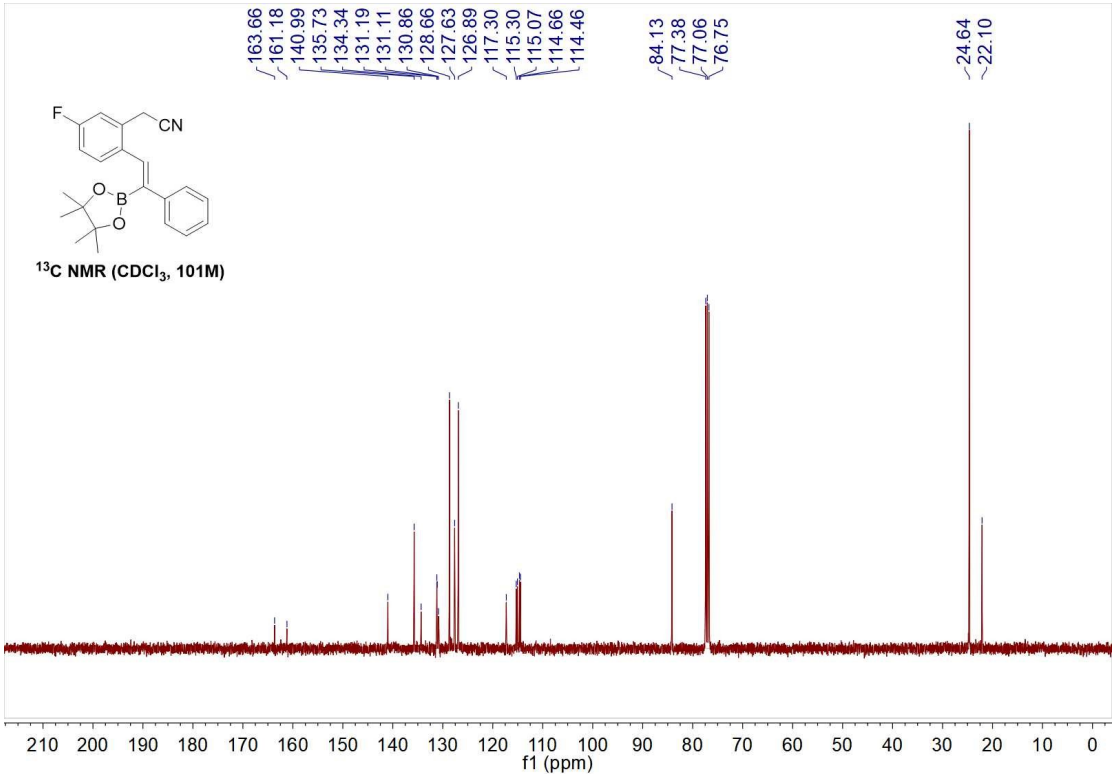
^{19}F NMR (377 MHz, Chloroform-*d*) of compound 29



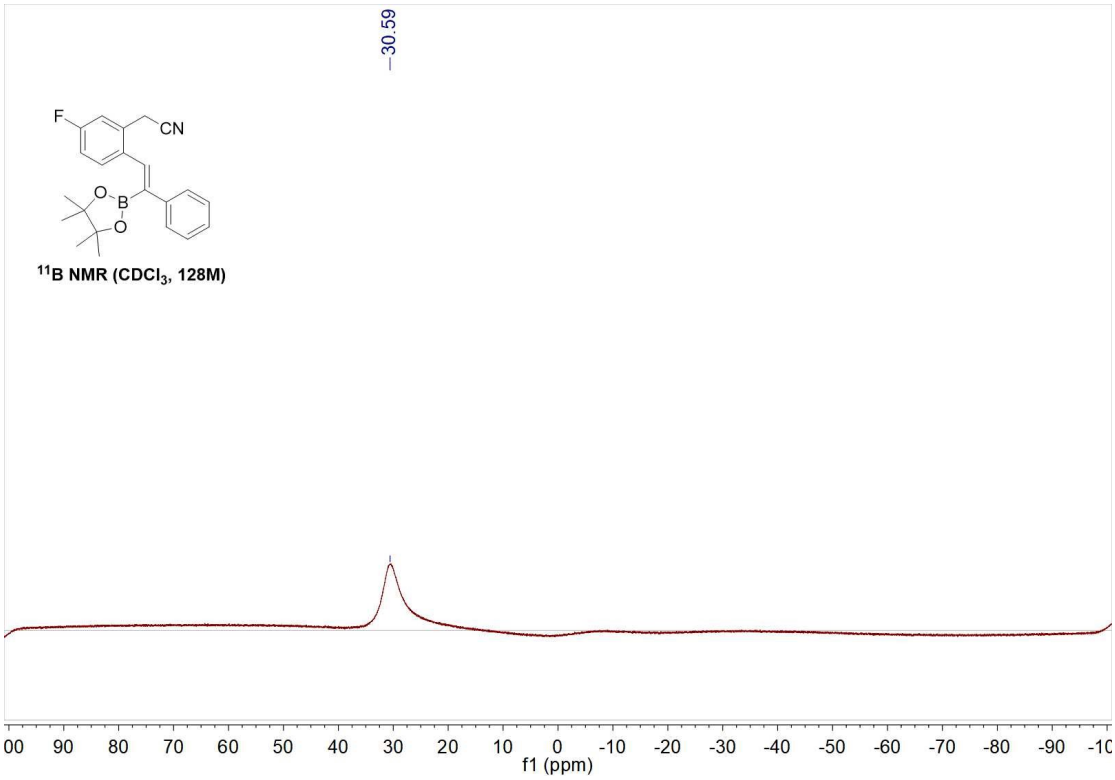
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 30



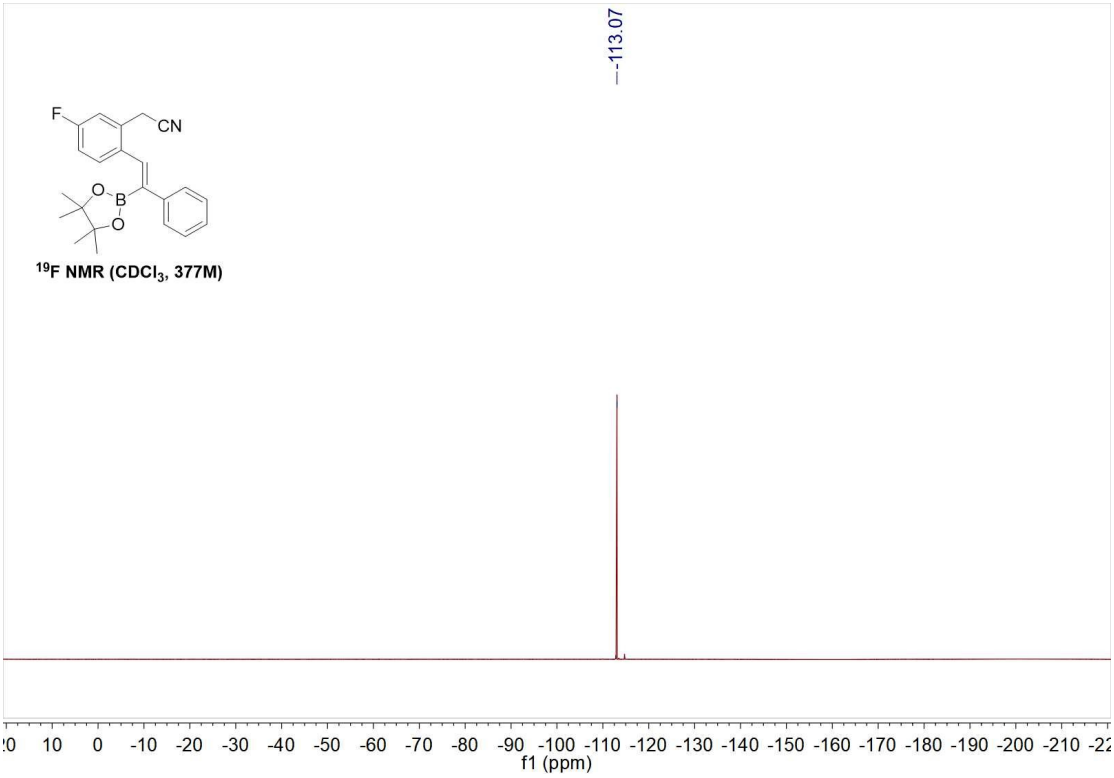
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 30



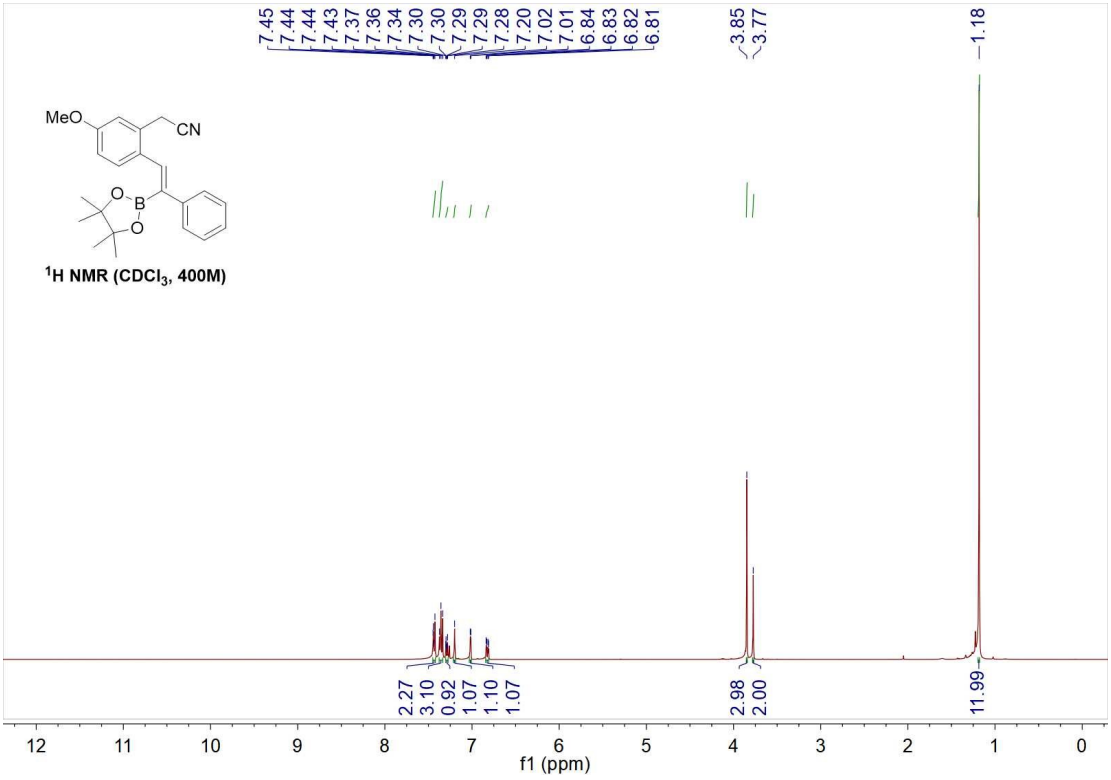
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 30



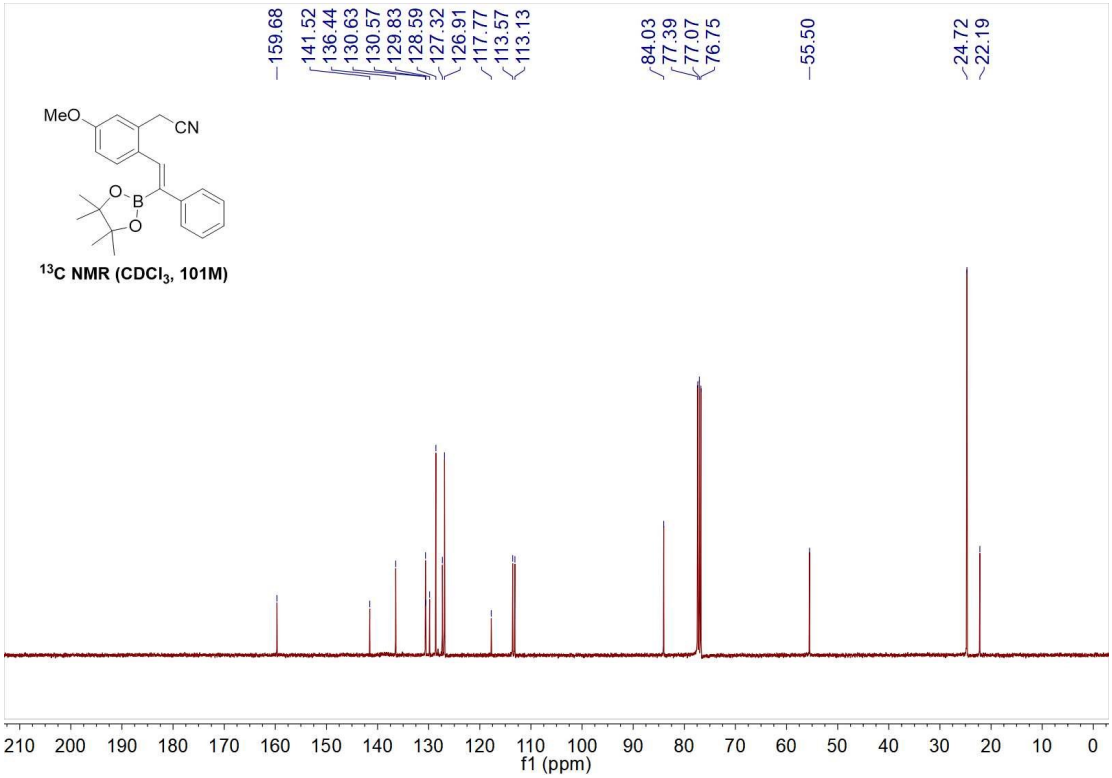
^{19}F NMR (377 MHz, Chloroform-*d*) of compound 30



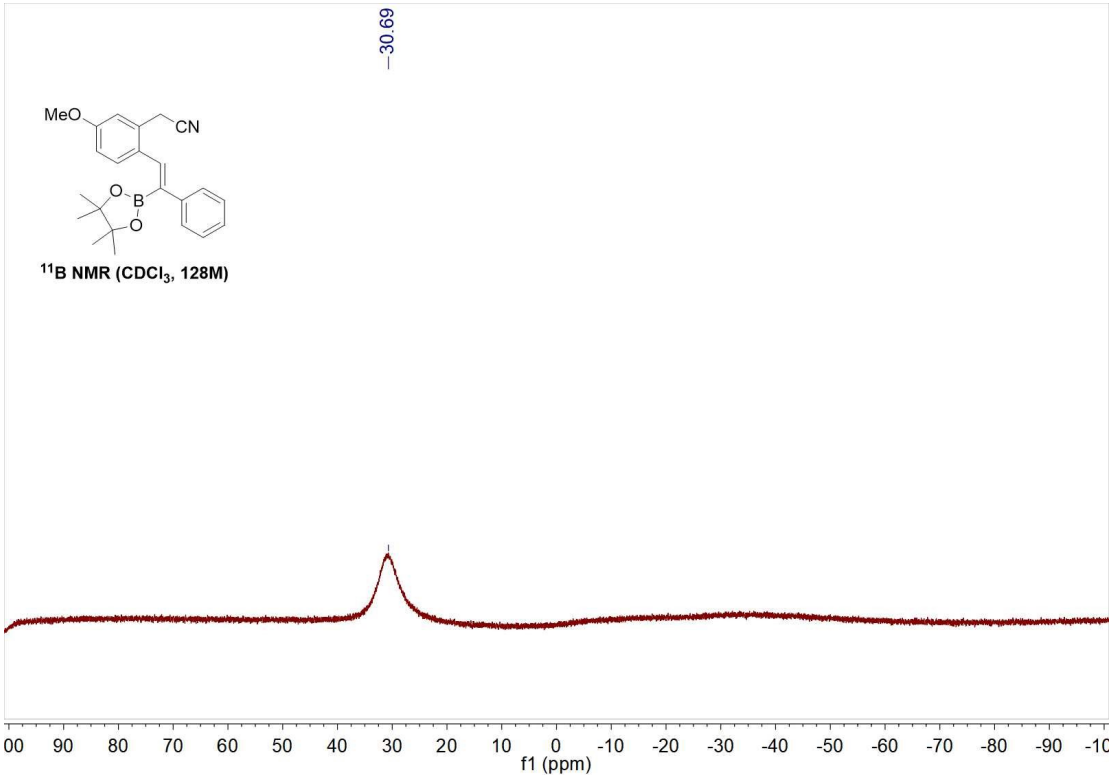
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 31



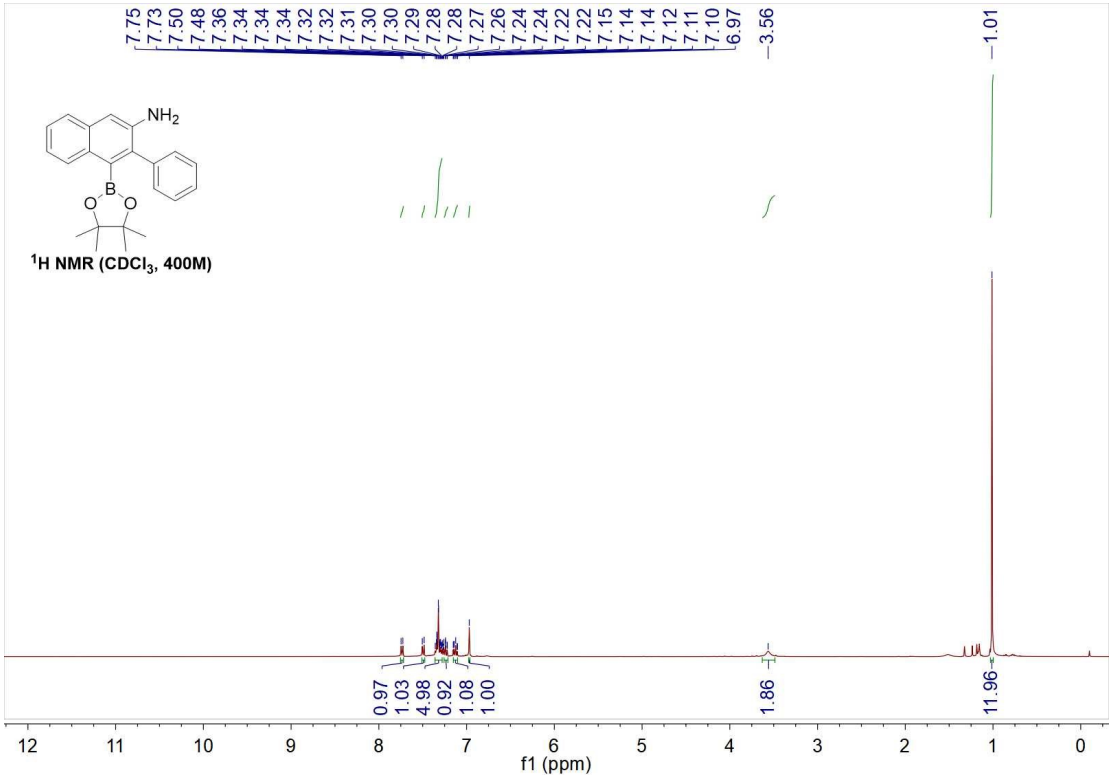
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 31



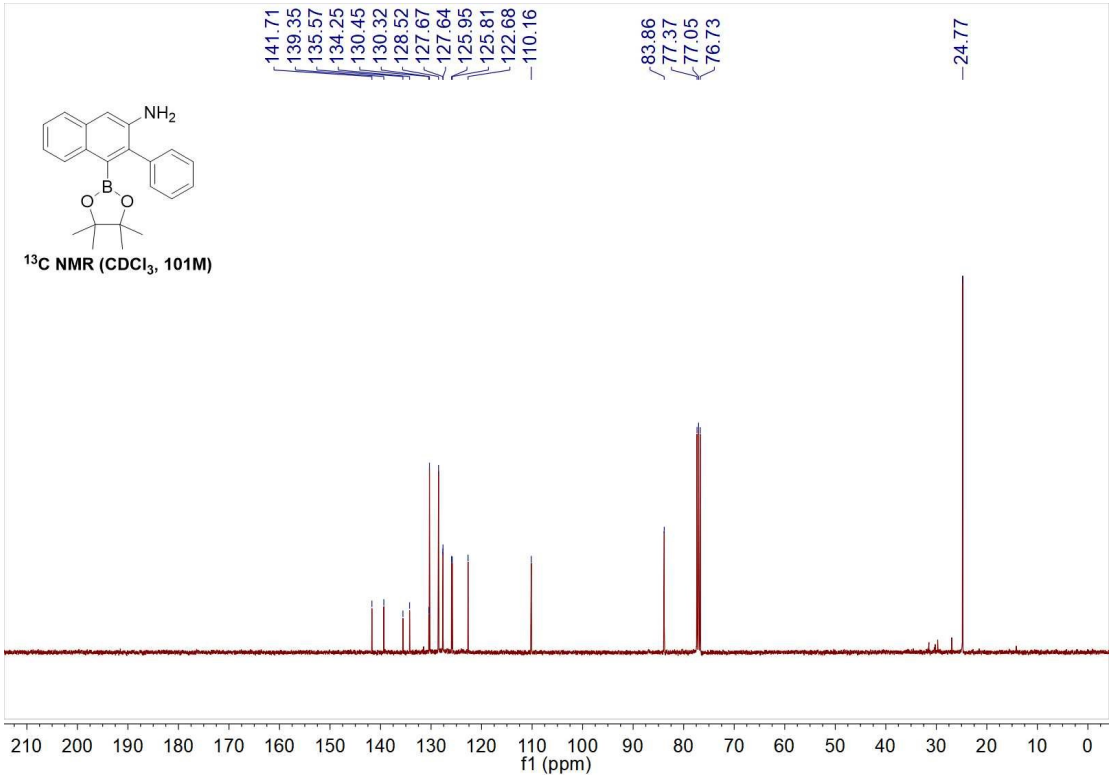
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 31



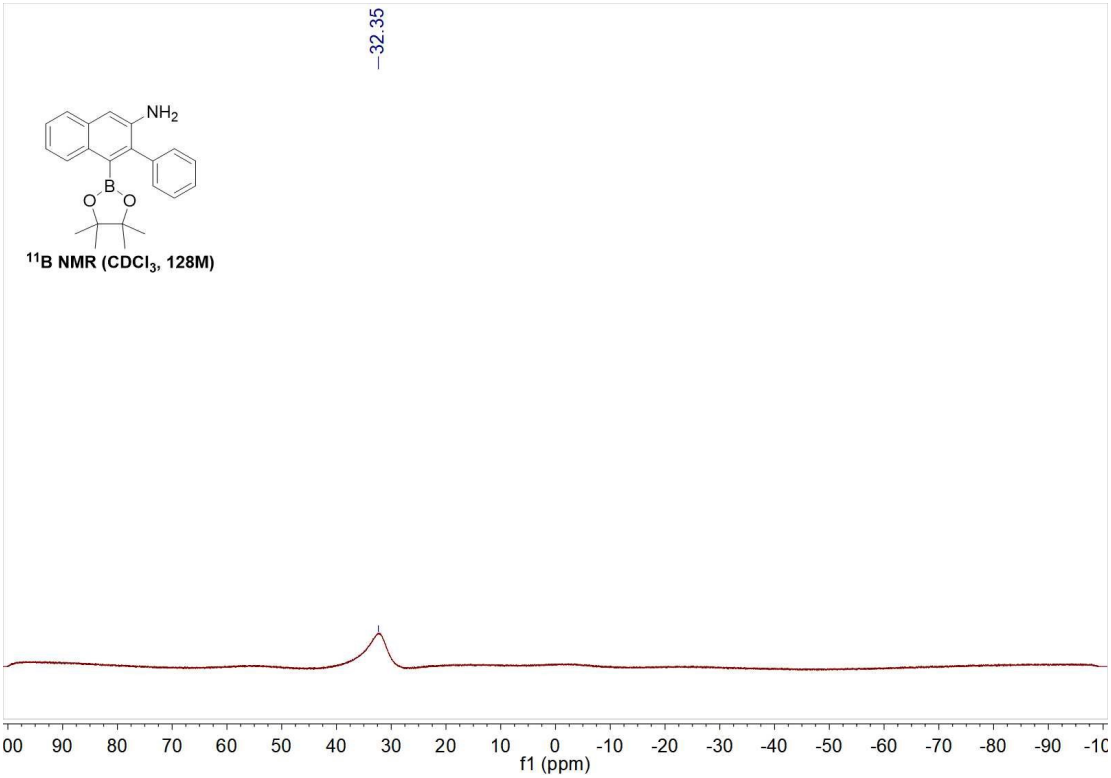
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 3



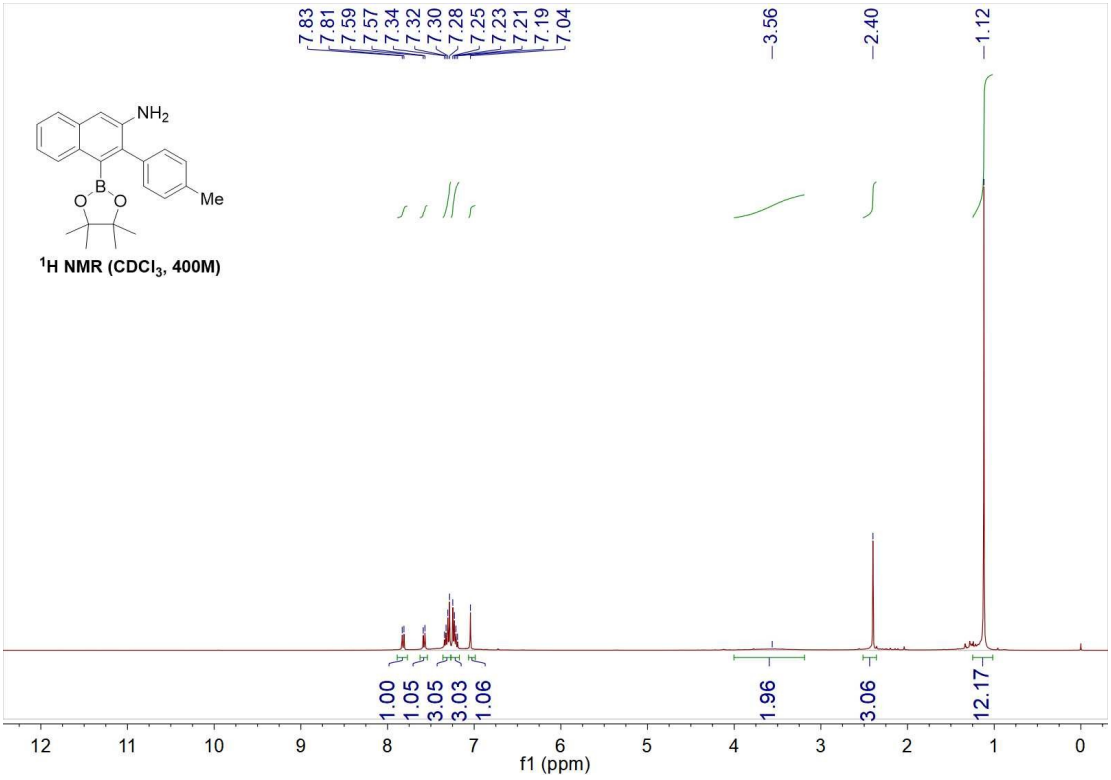
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 3



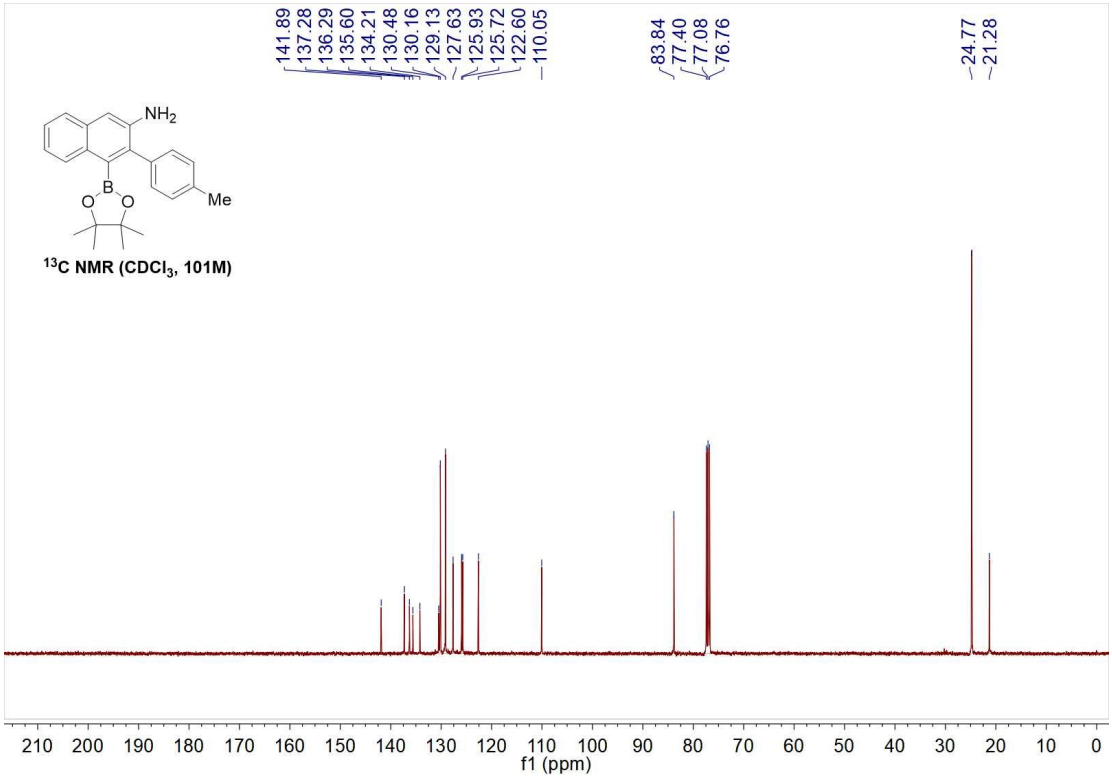
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 3



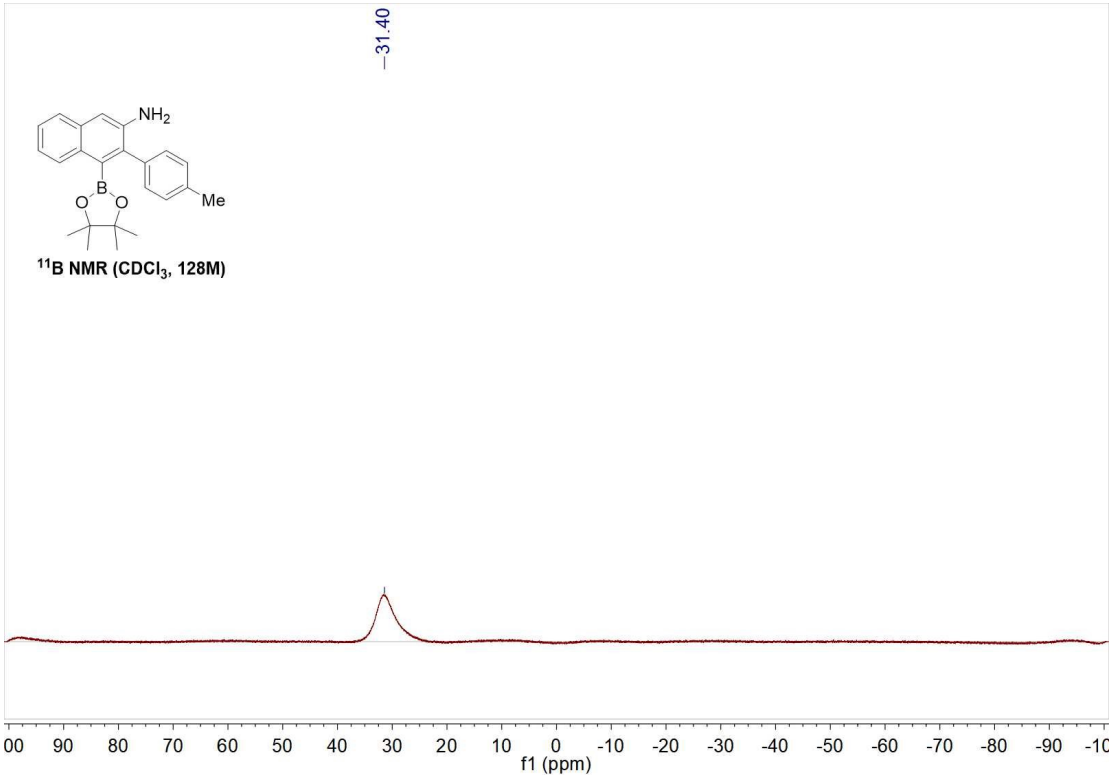
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 32



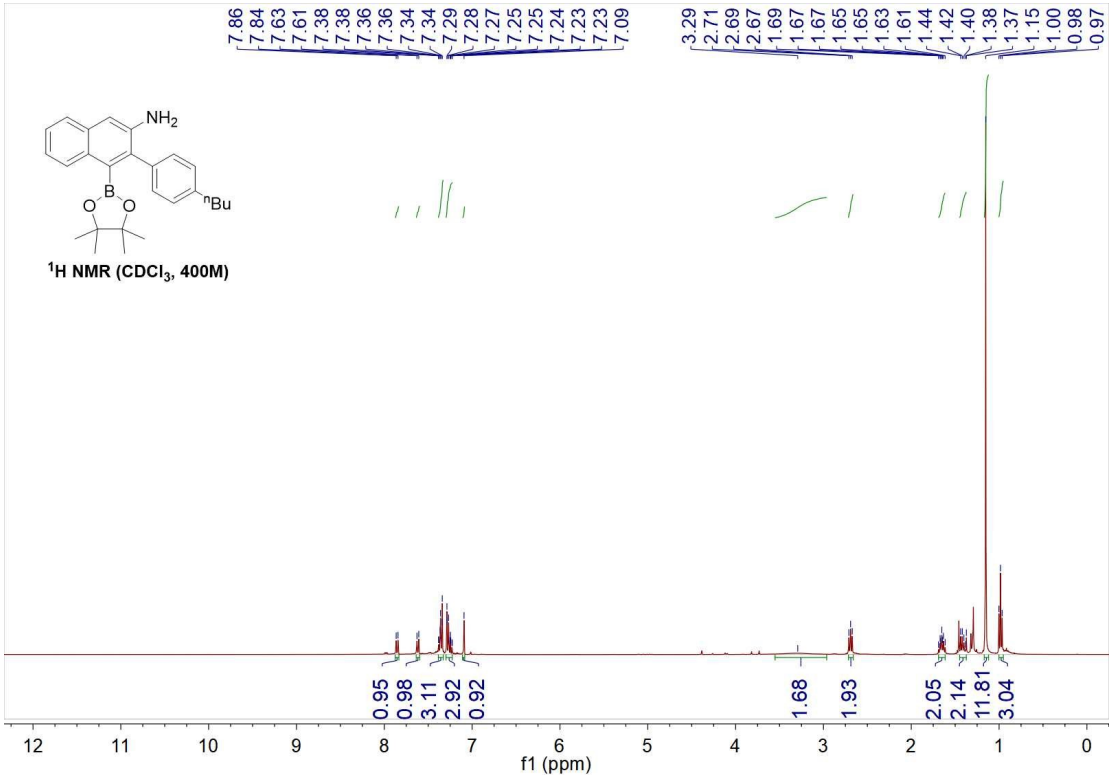
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 32



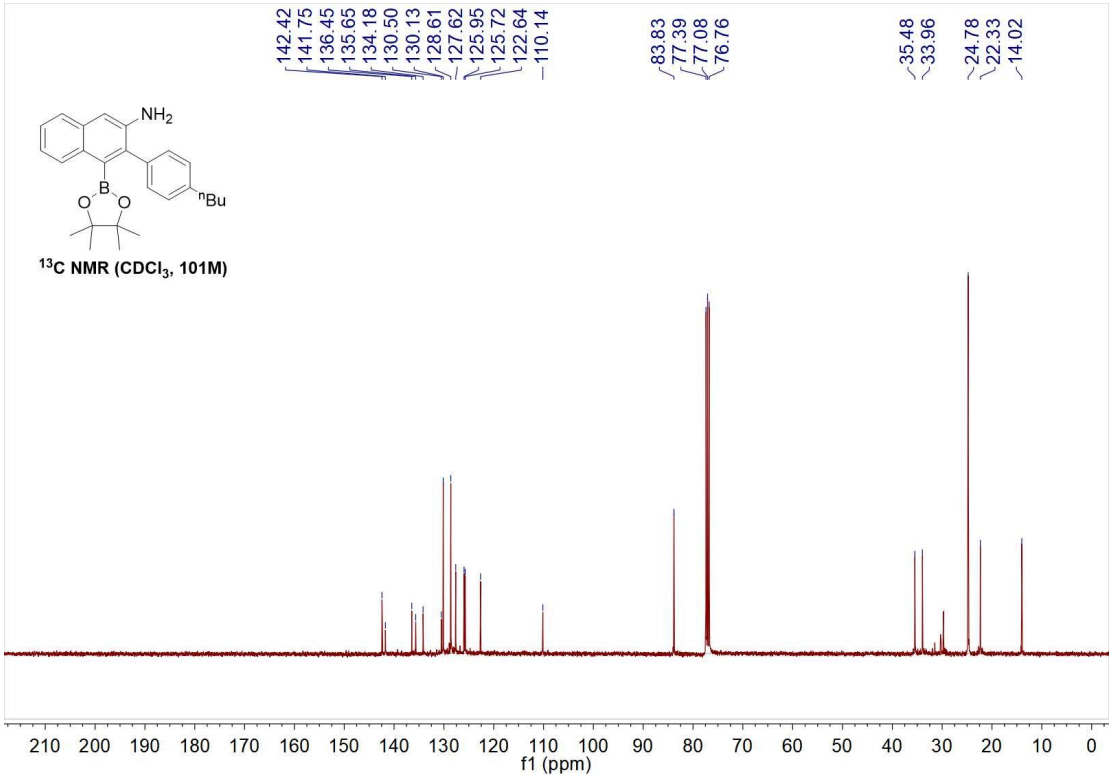
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 32



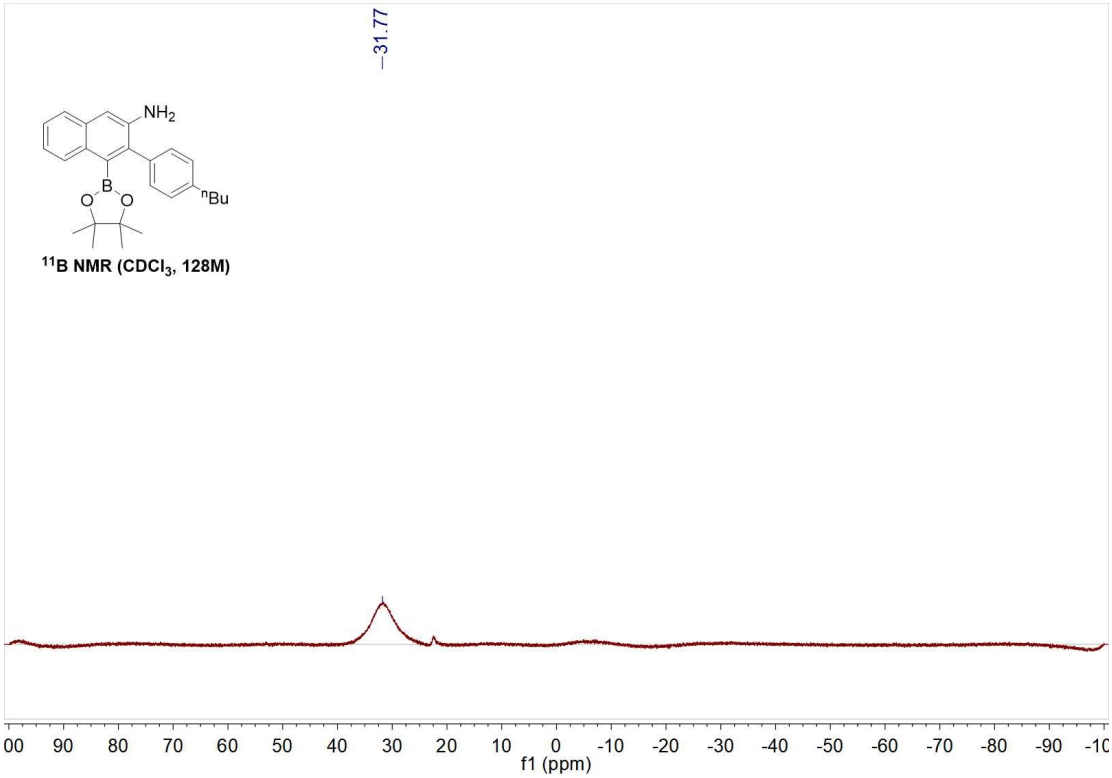
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 33



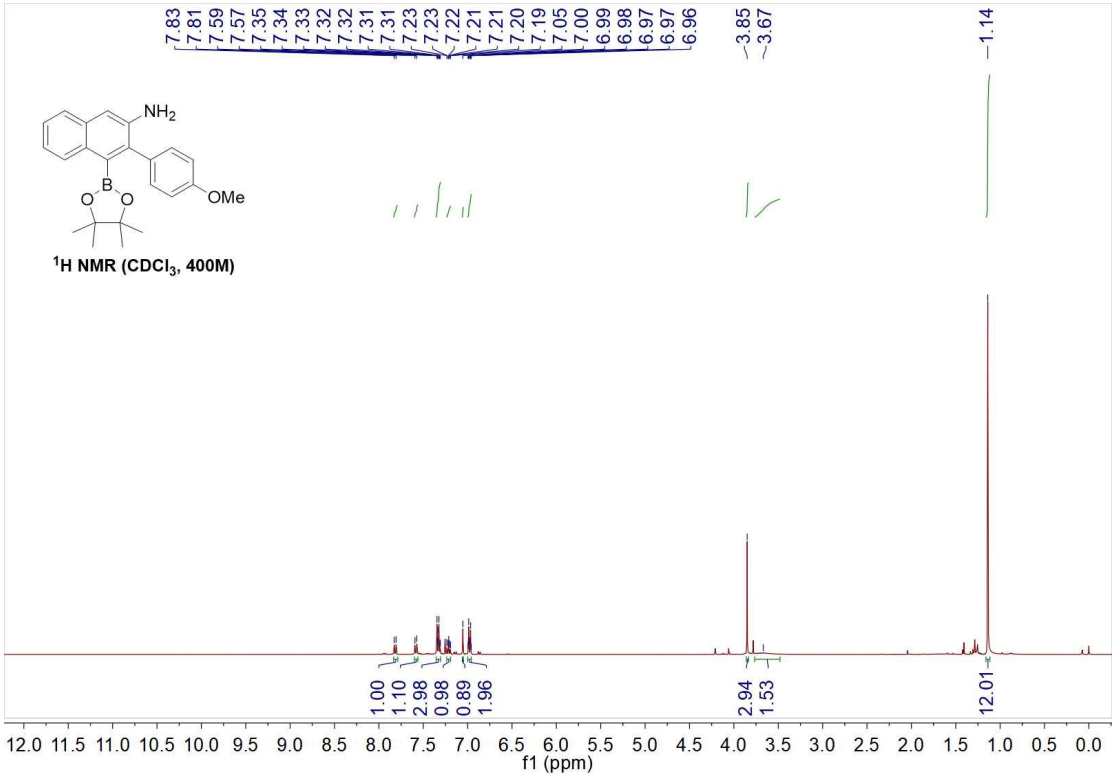
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 33



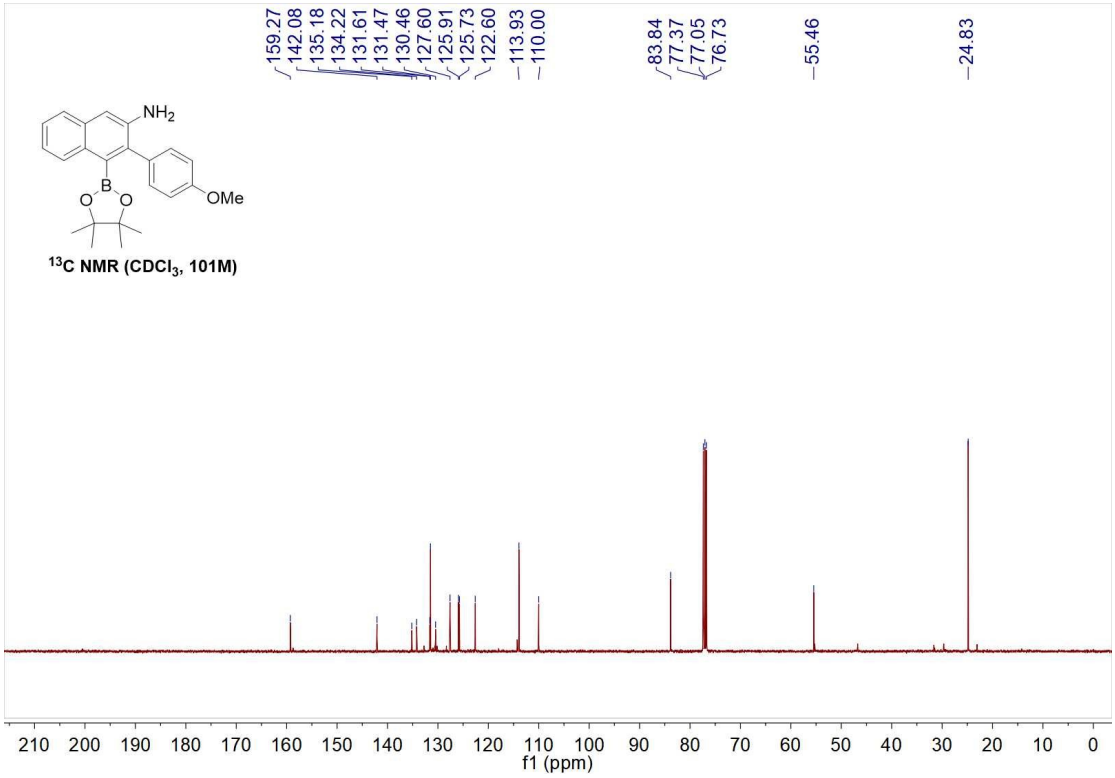
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 33



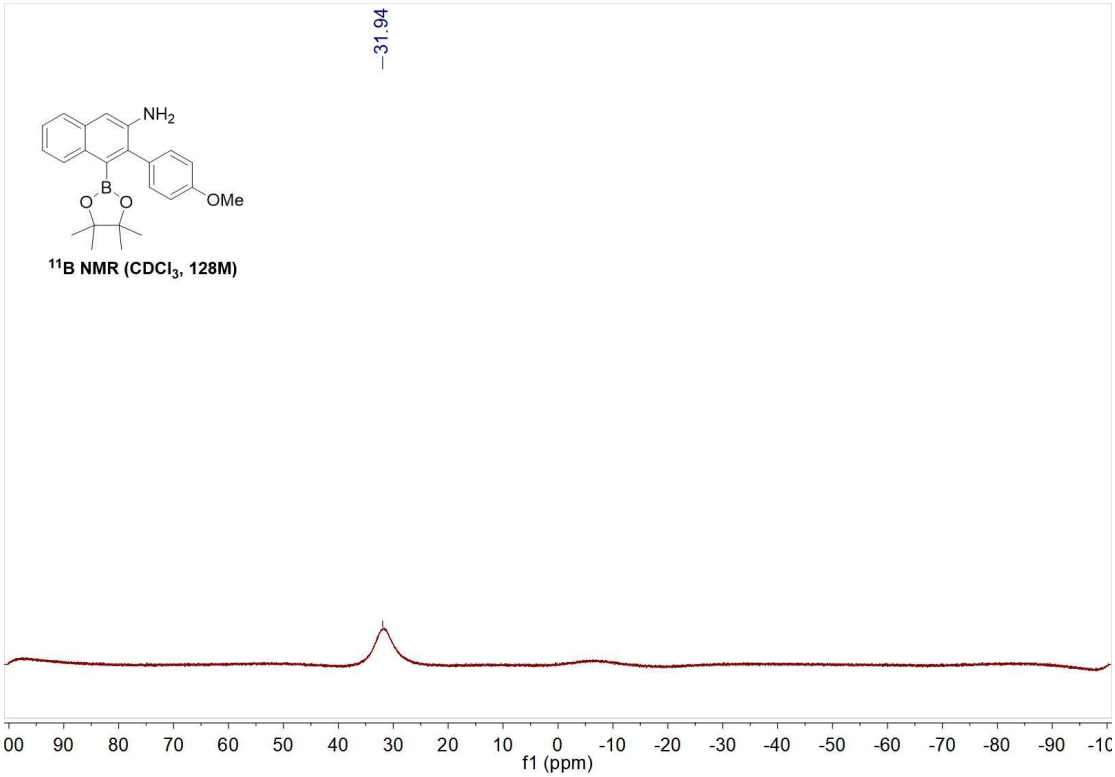
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 34



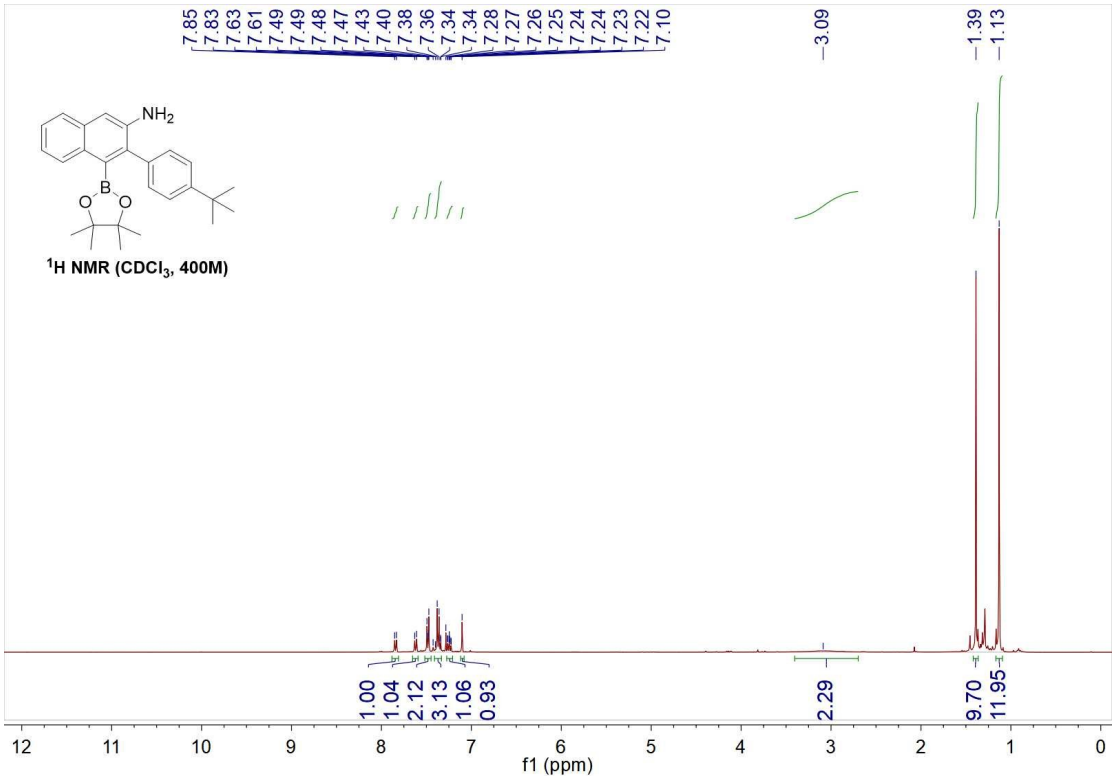
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 34



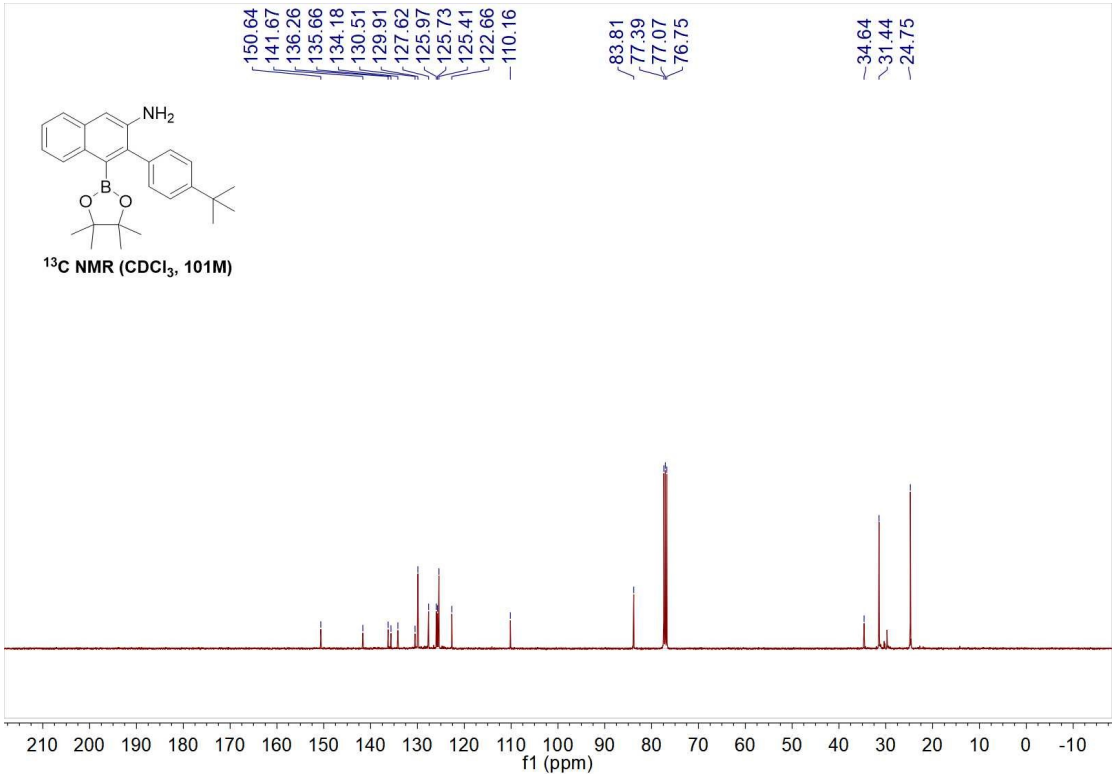
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 34



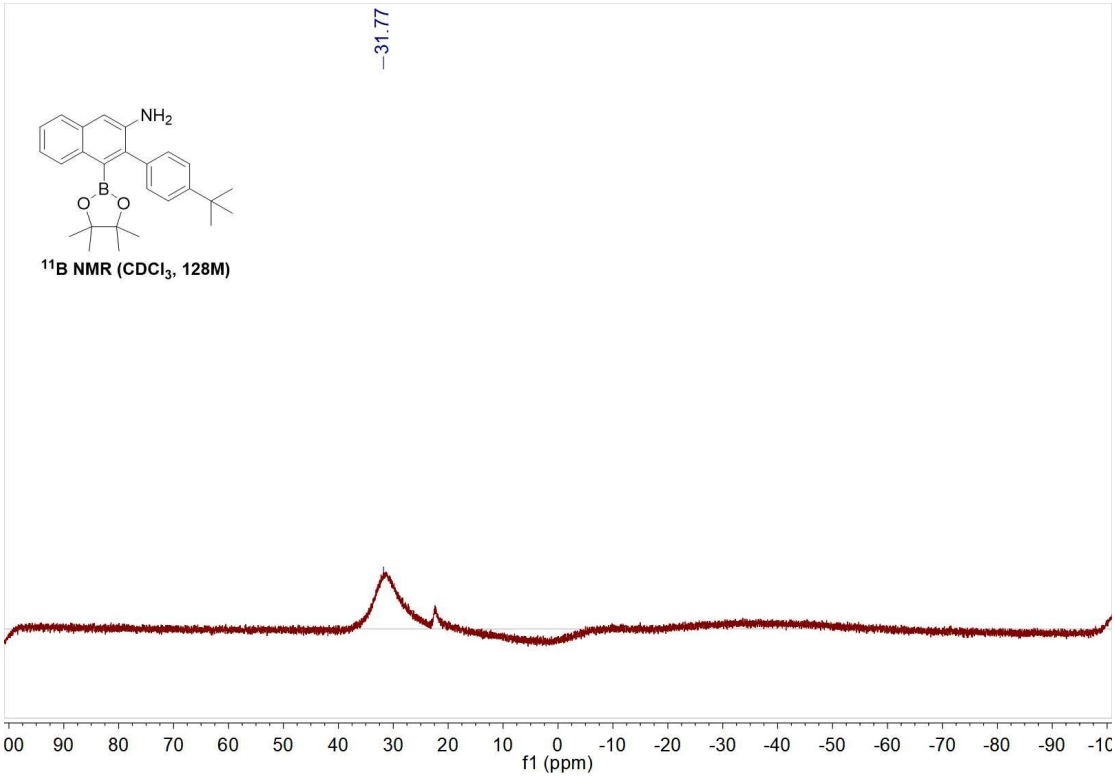
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 35



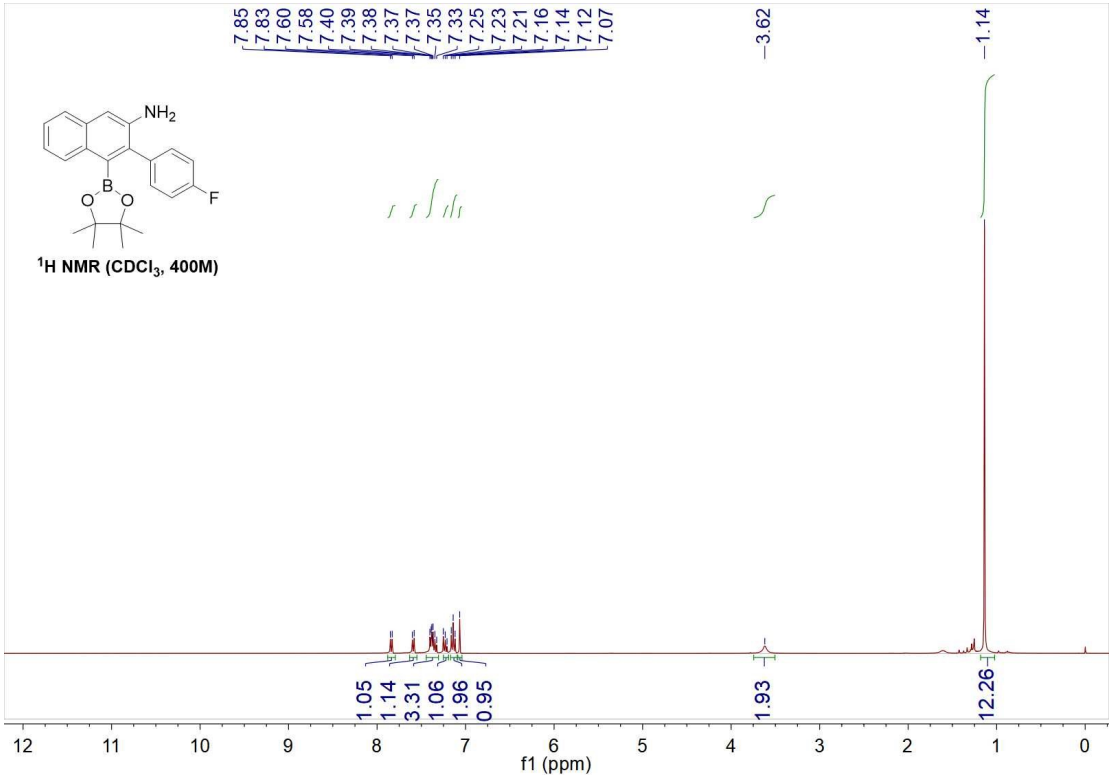
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 35



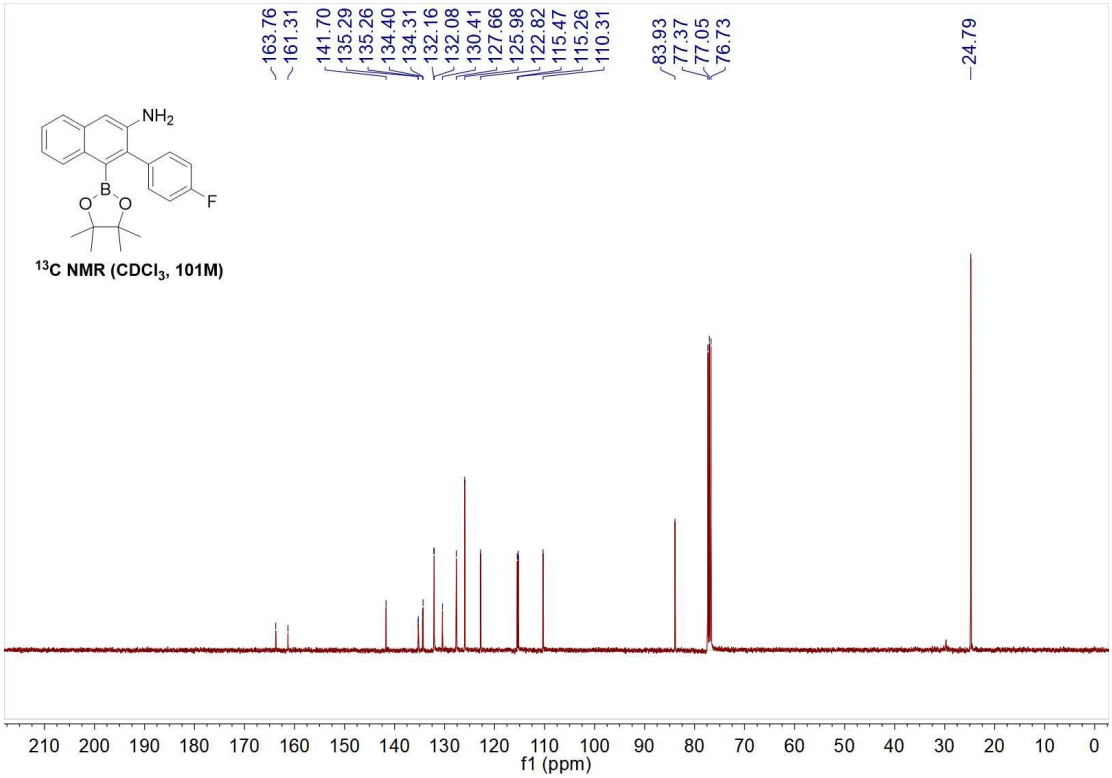
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 35



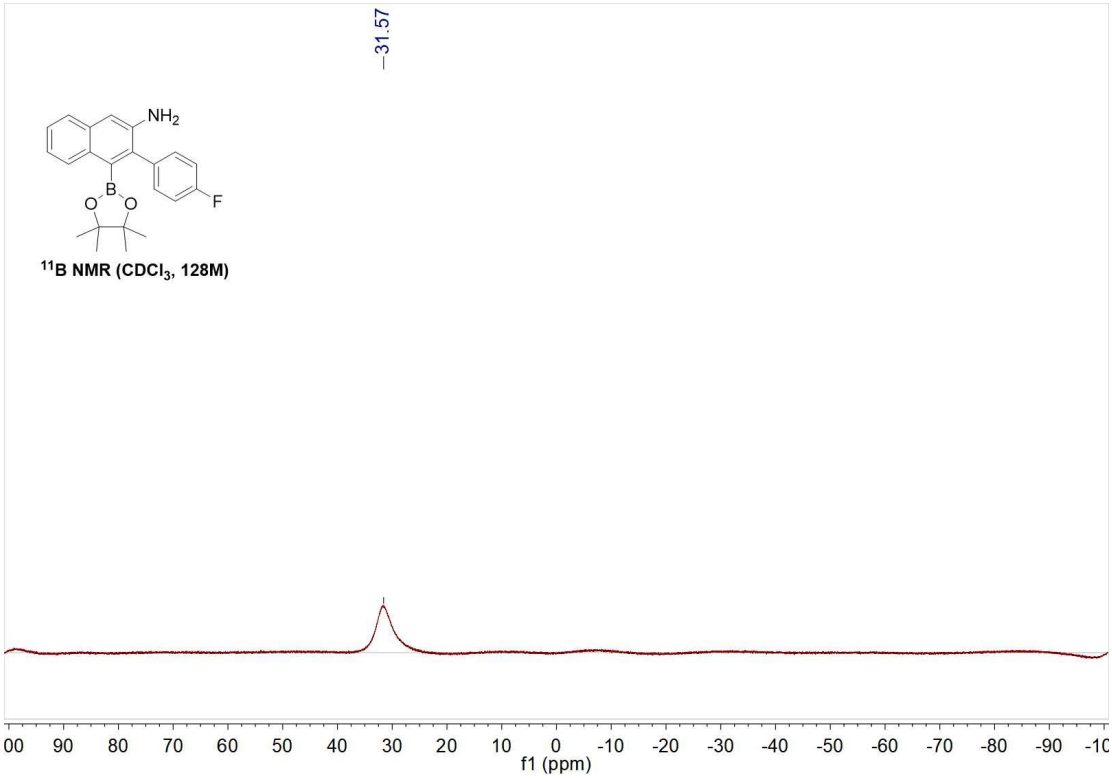
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 36



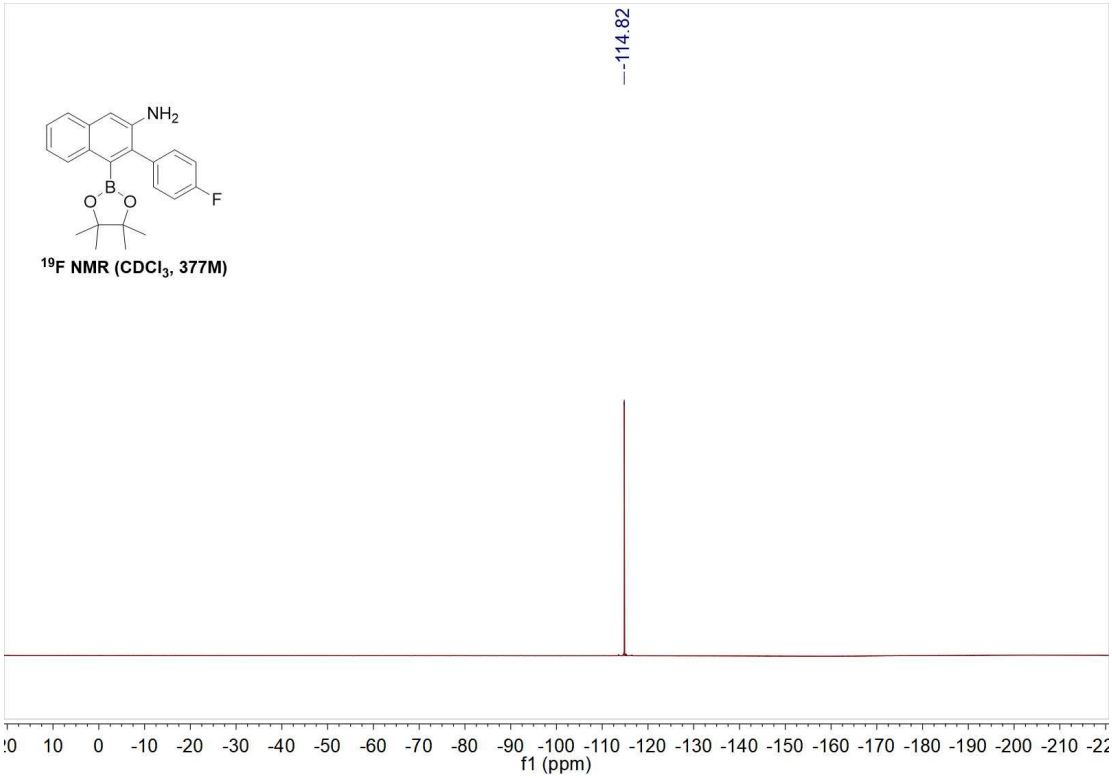
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 36



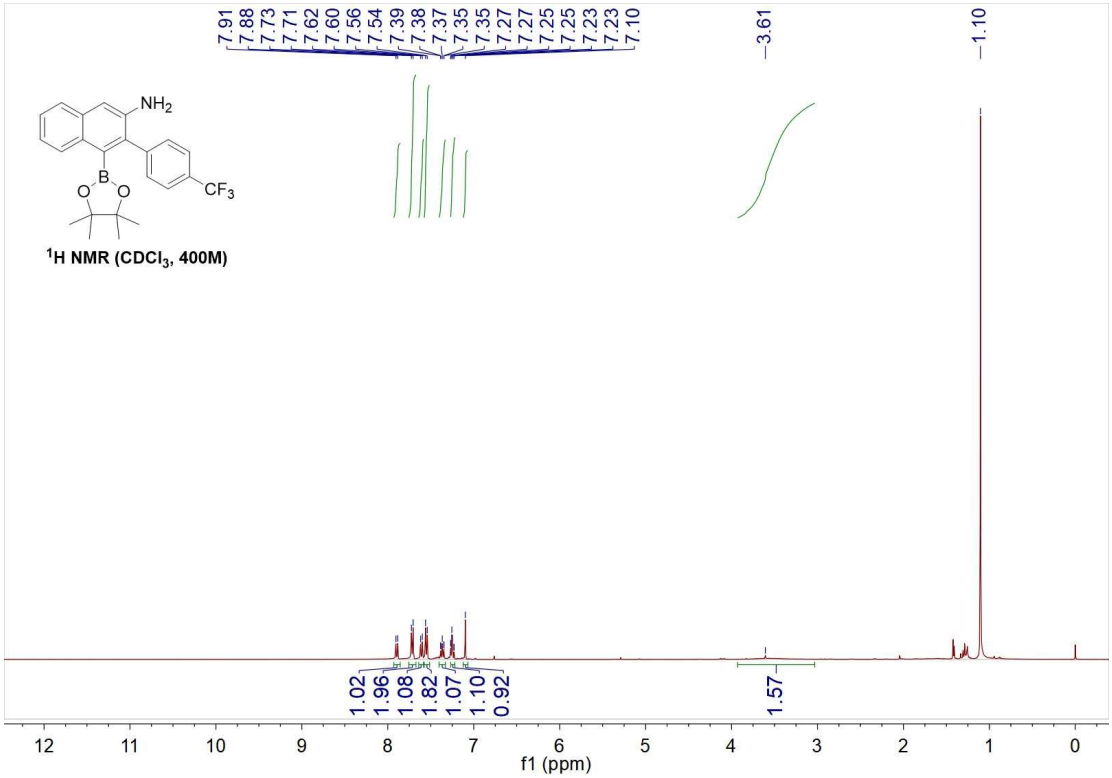
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 36



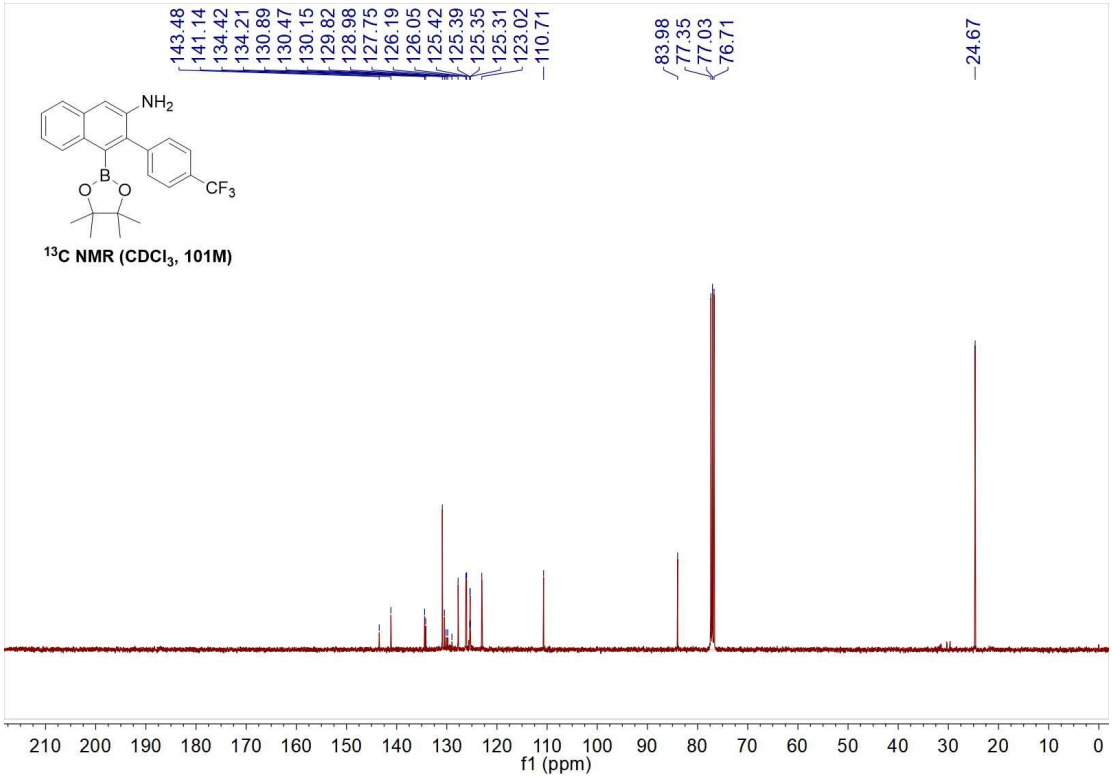
^{19}F NMR (377 MHz, Chloroform-*d*) of compound 36



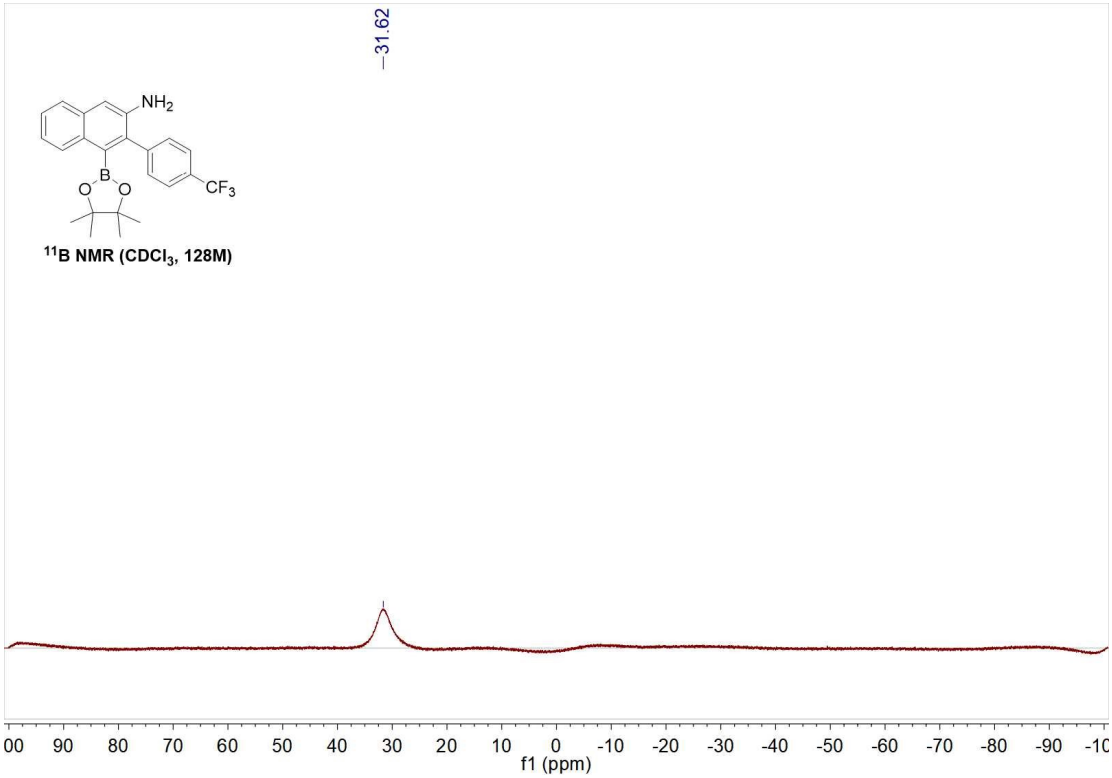
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 37



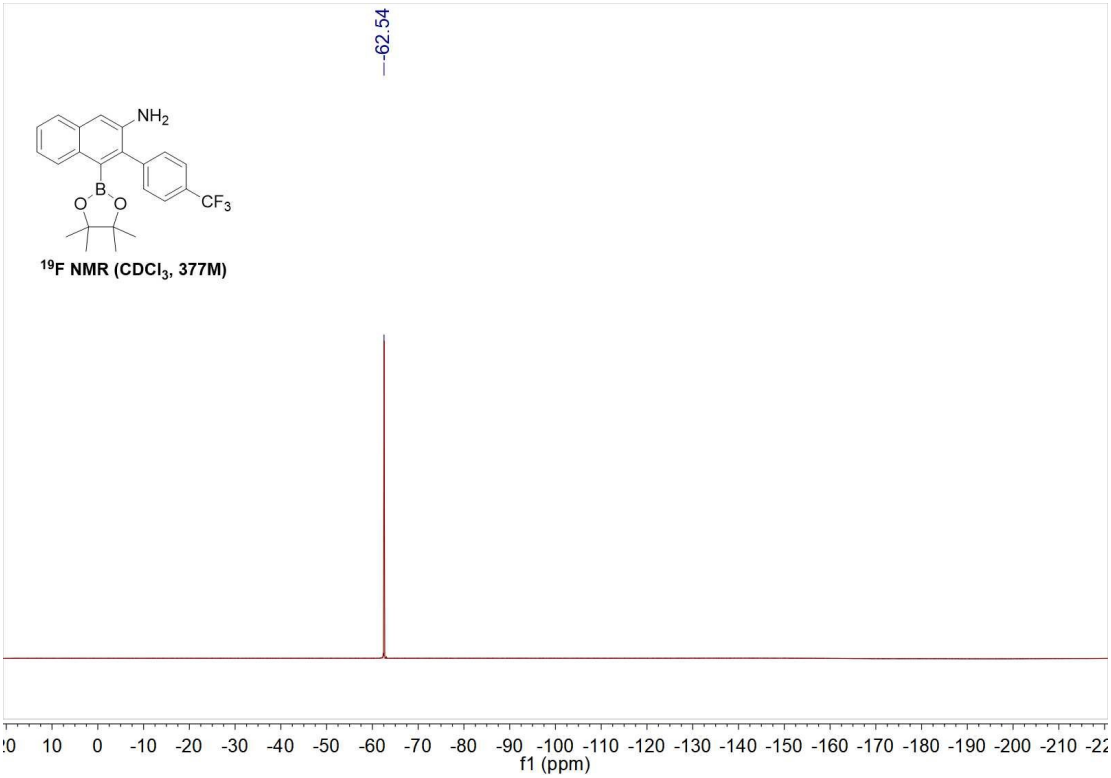
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 37



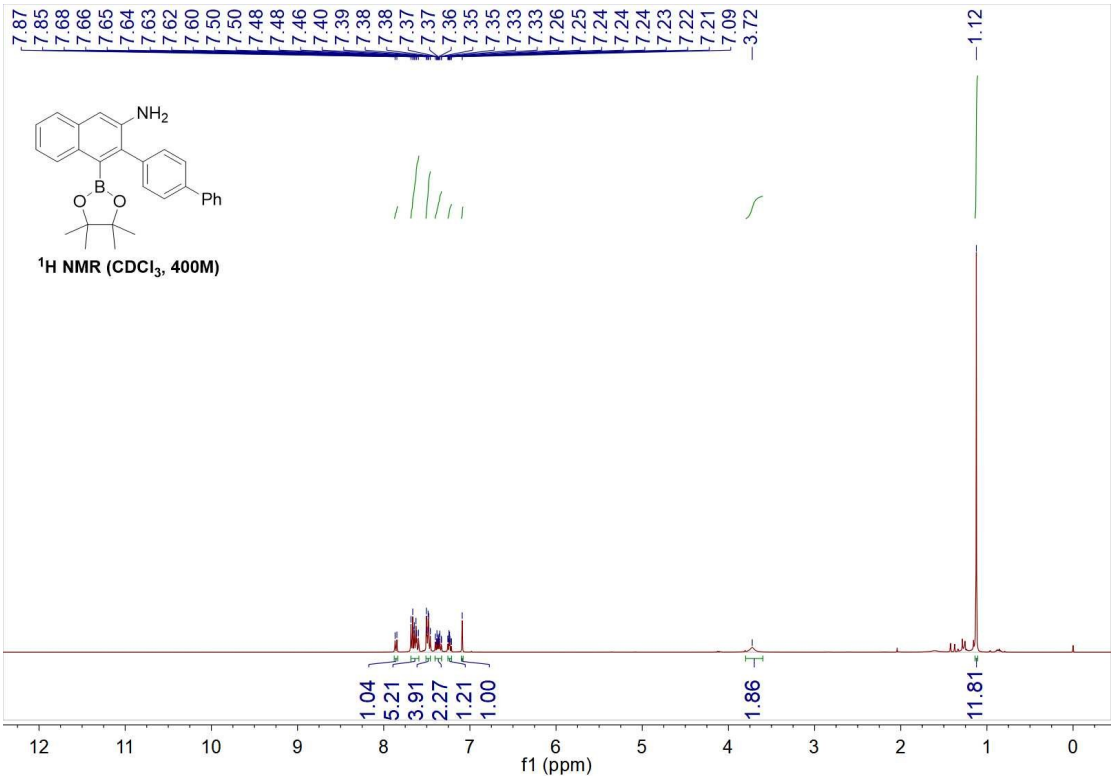
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 37



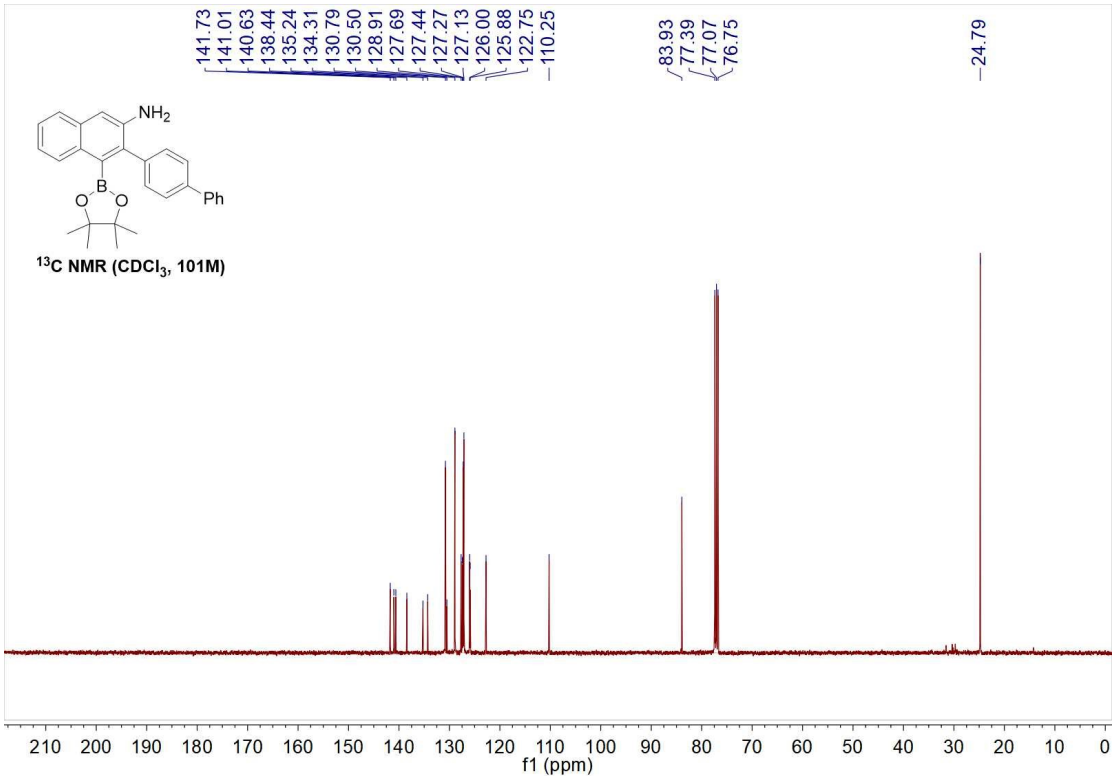
^{19}F NMR (377 MHz, Chloroform-*d*) of compound 37



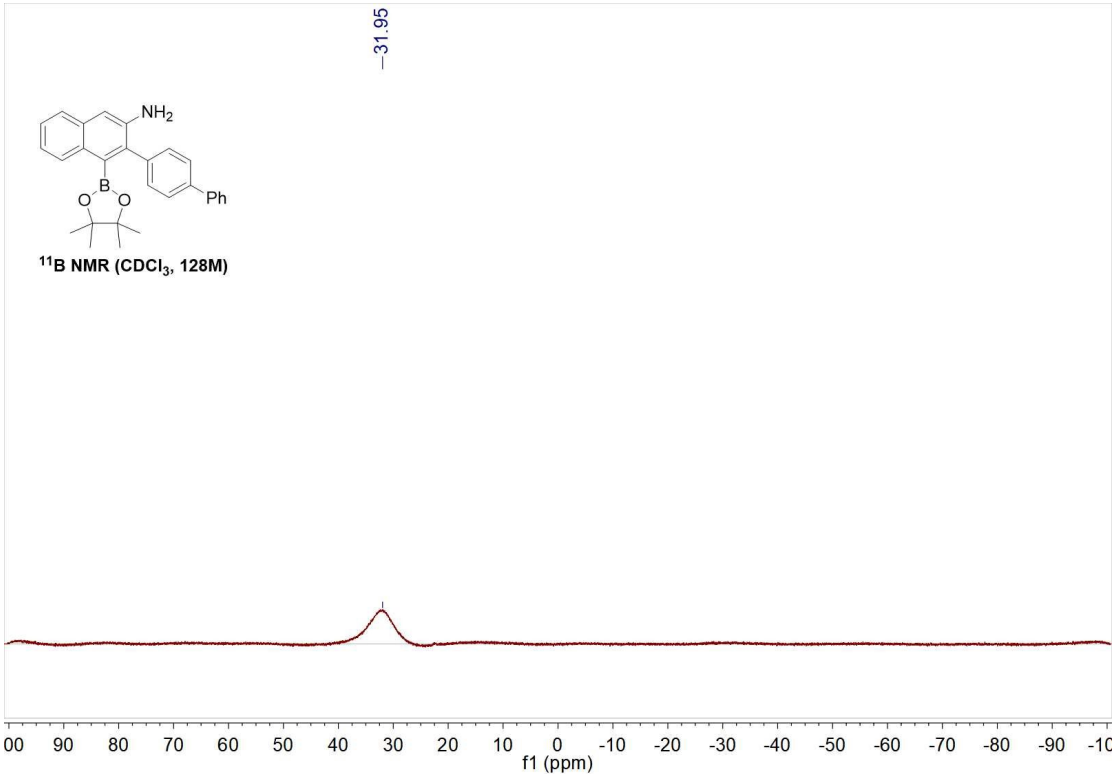
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 38



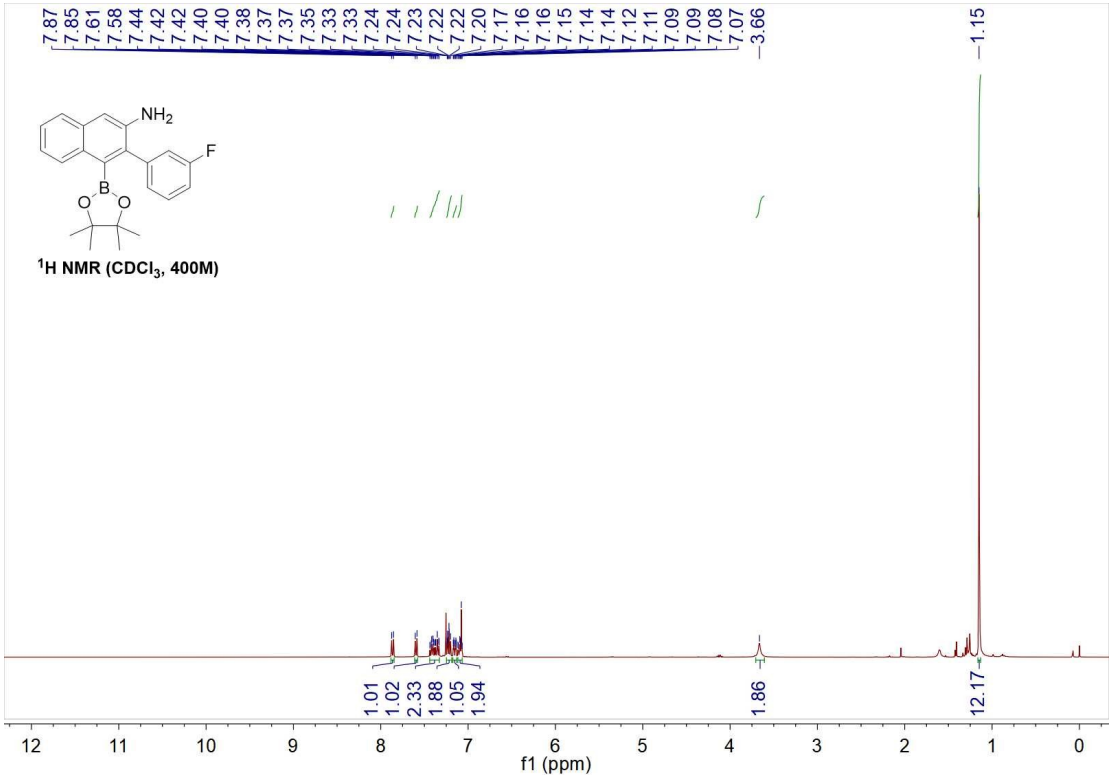
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 38



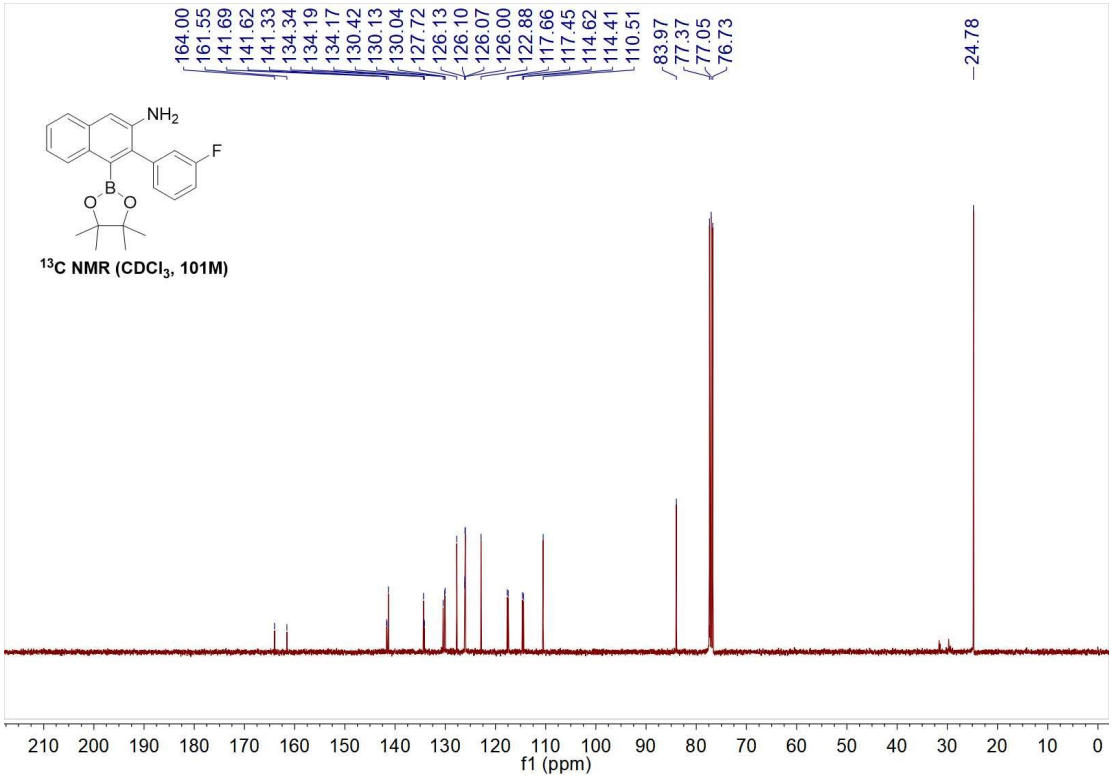
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 38



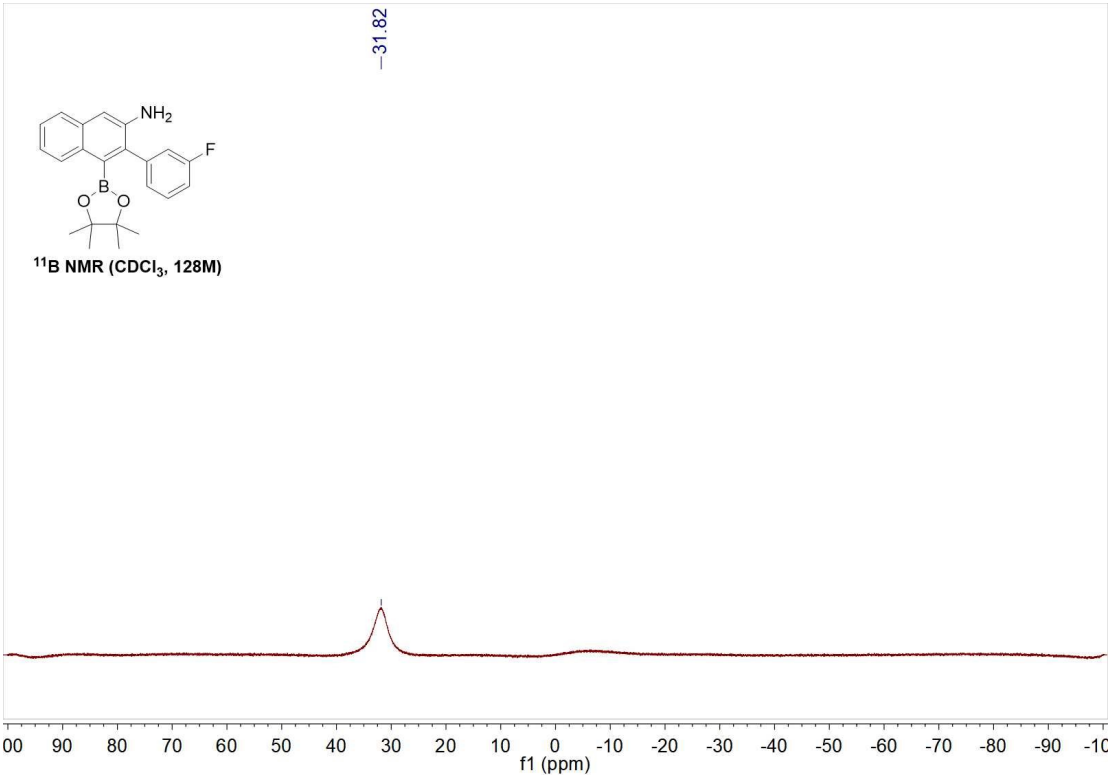
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 39



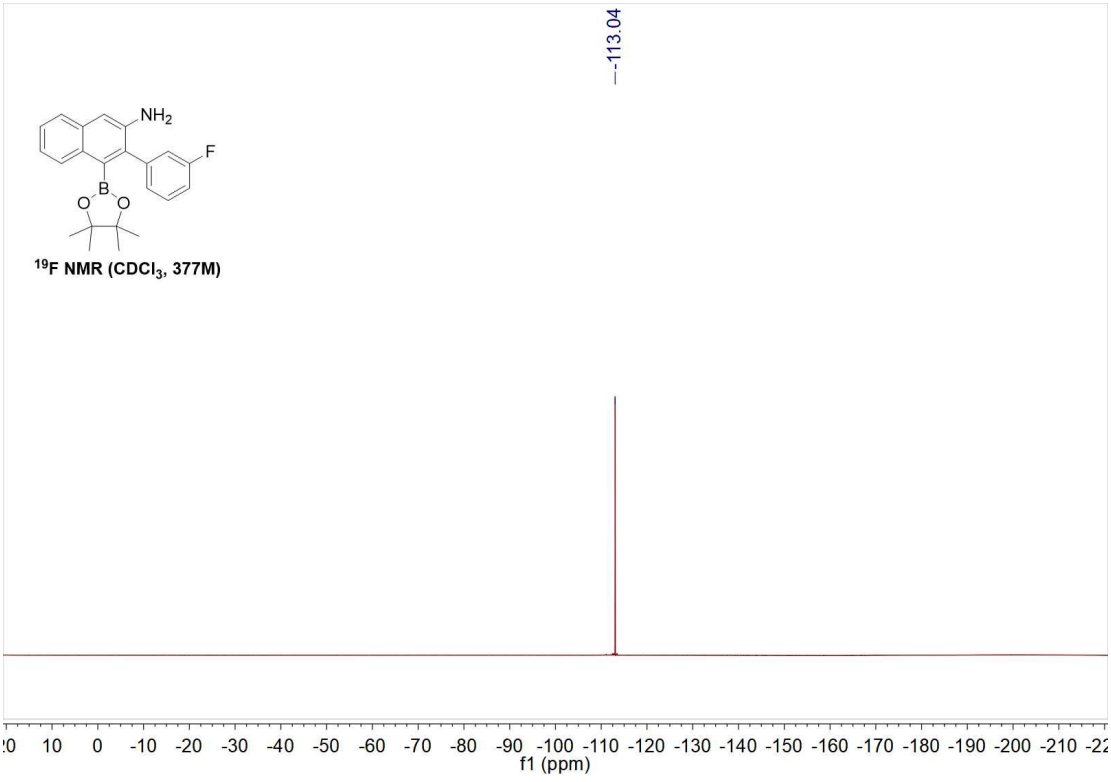
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 39



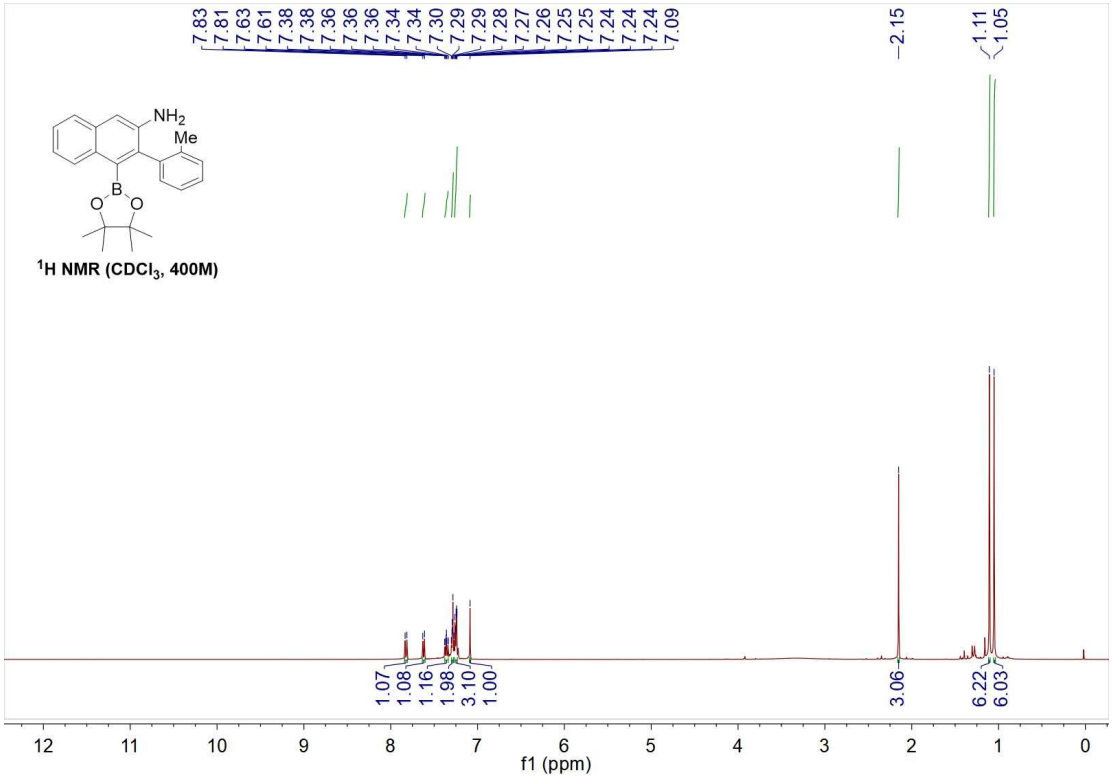
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 39



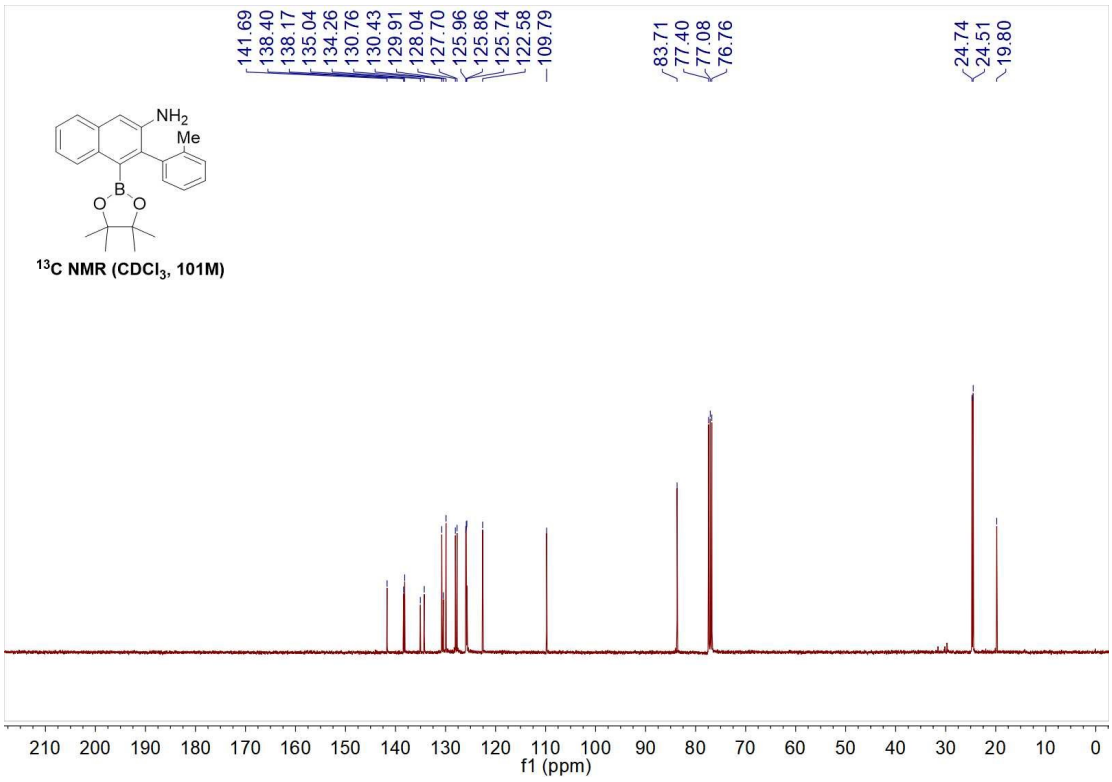
^{19}F NMR (377 MHz, Chloroform-*d*) of compound 39



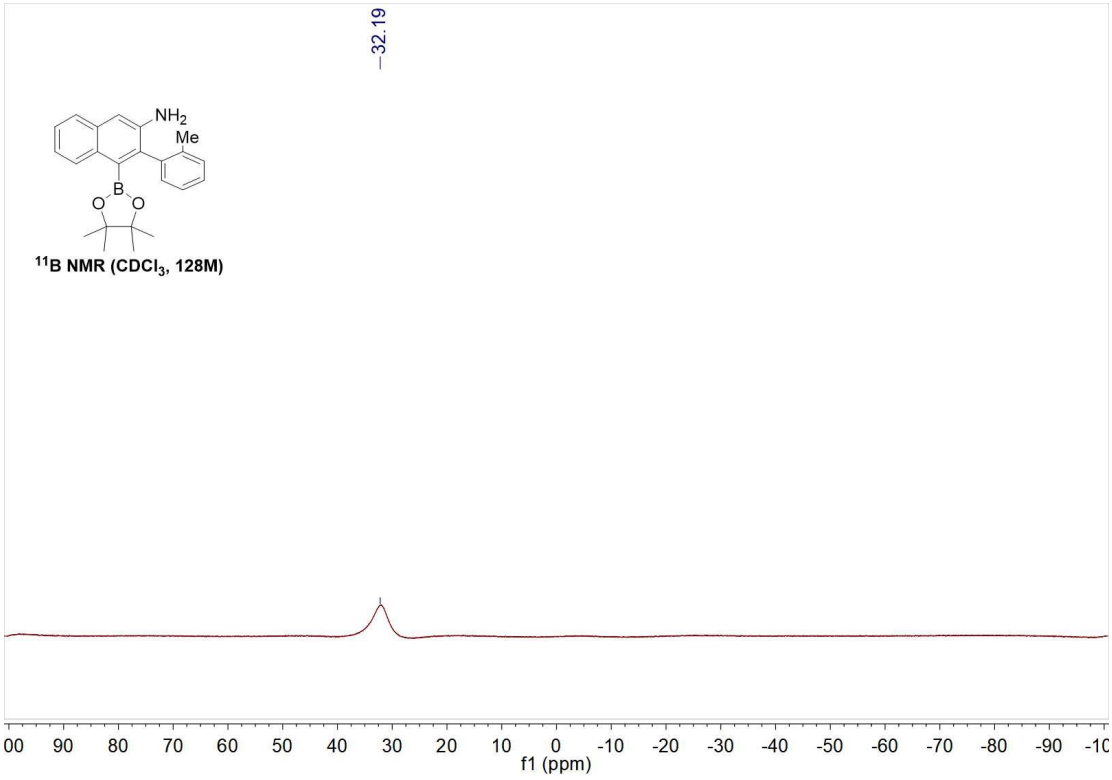
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 40



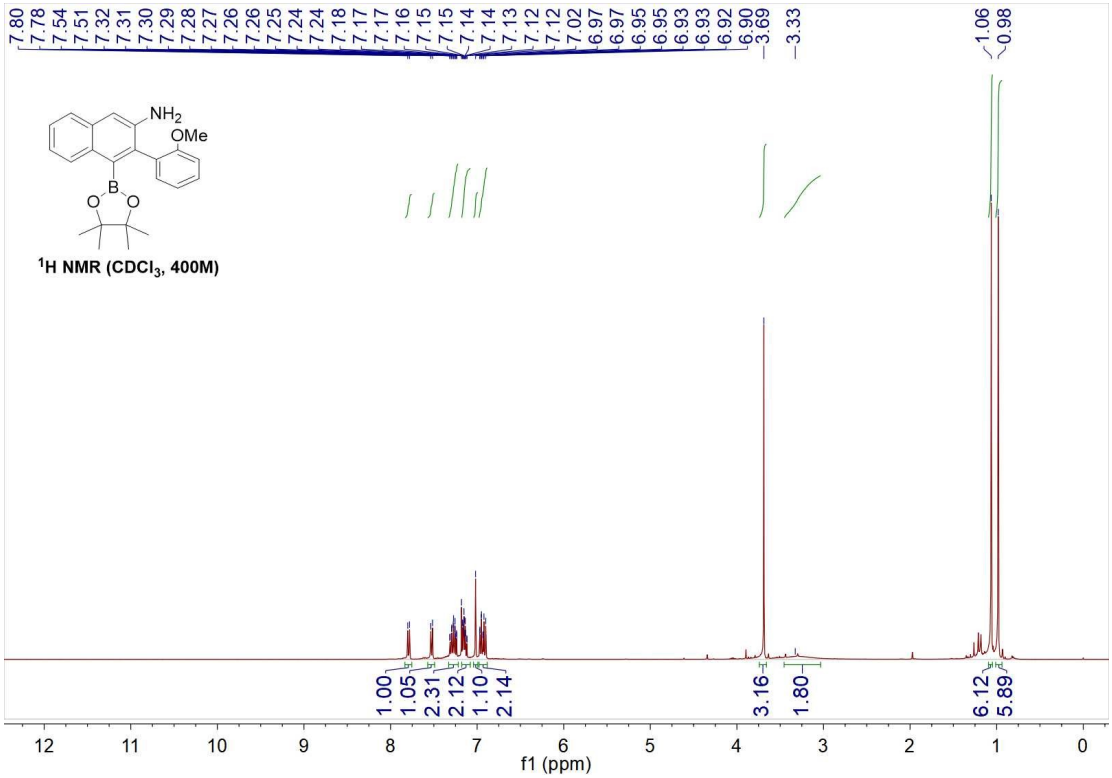
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 40



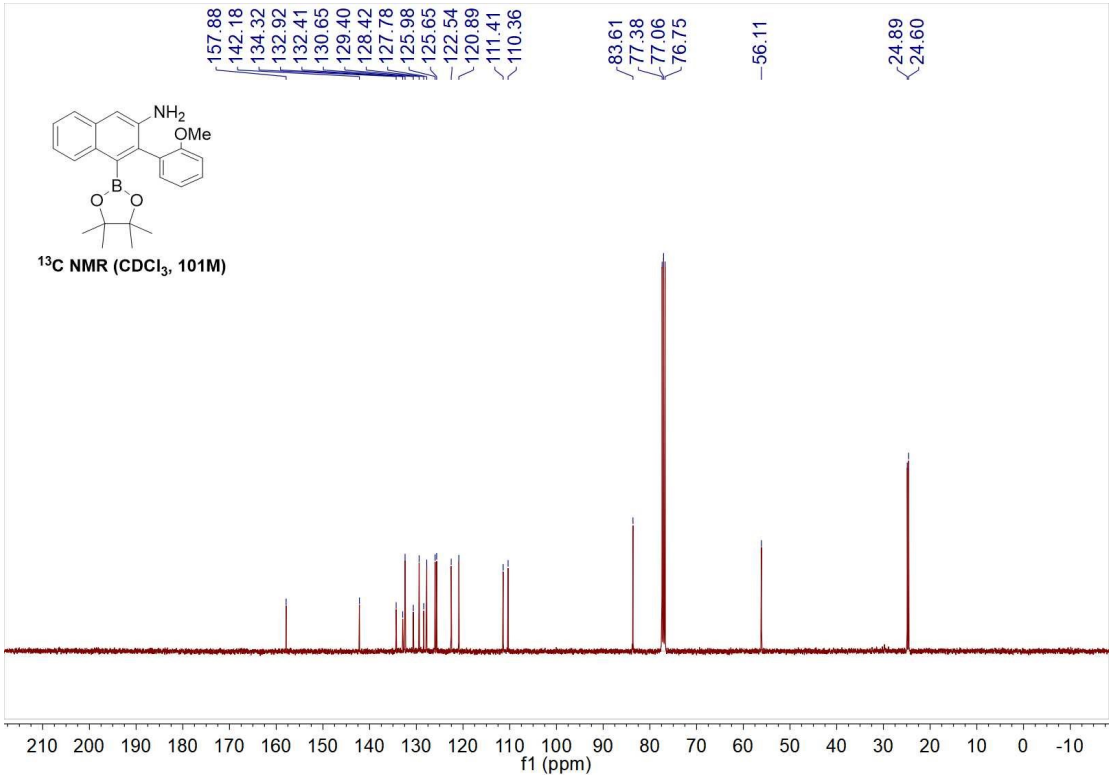
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 40



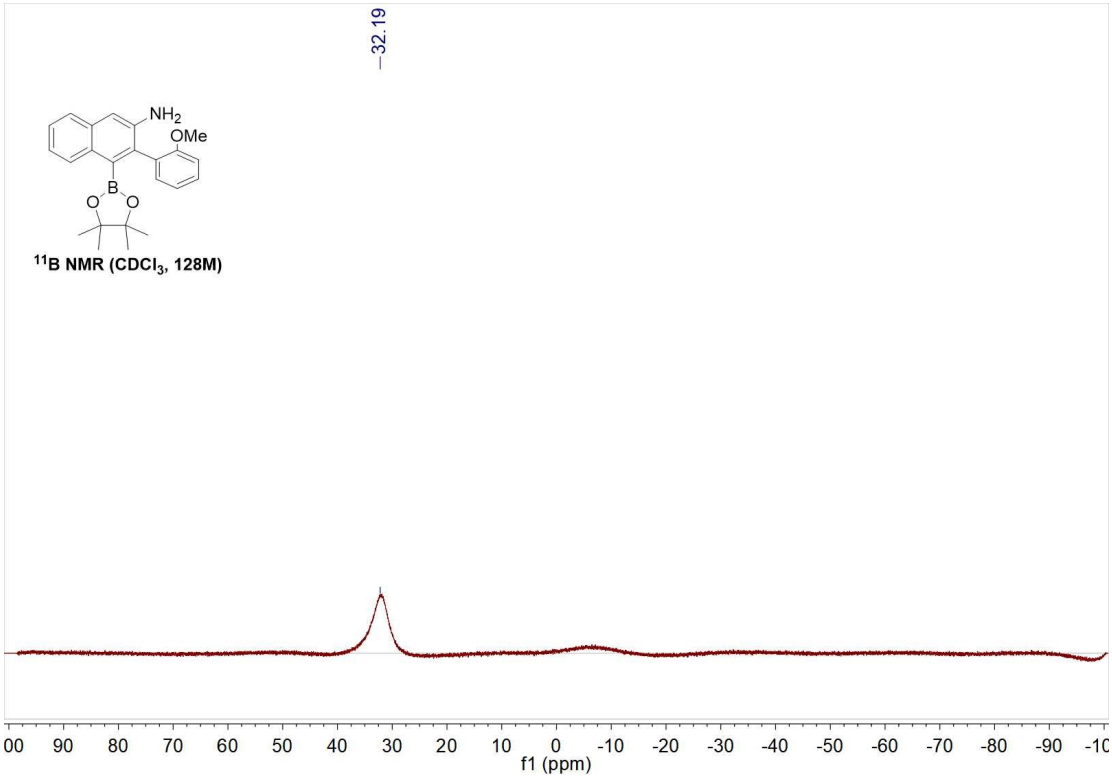
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 41



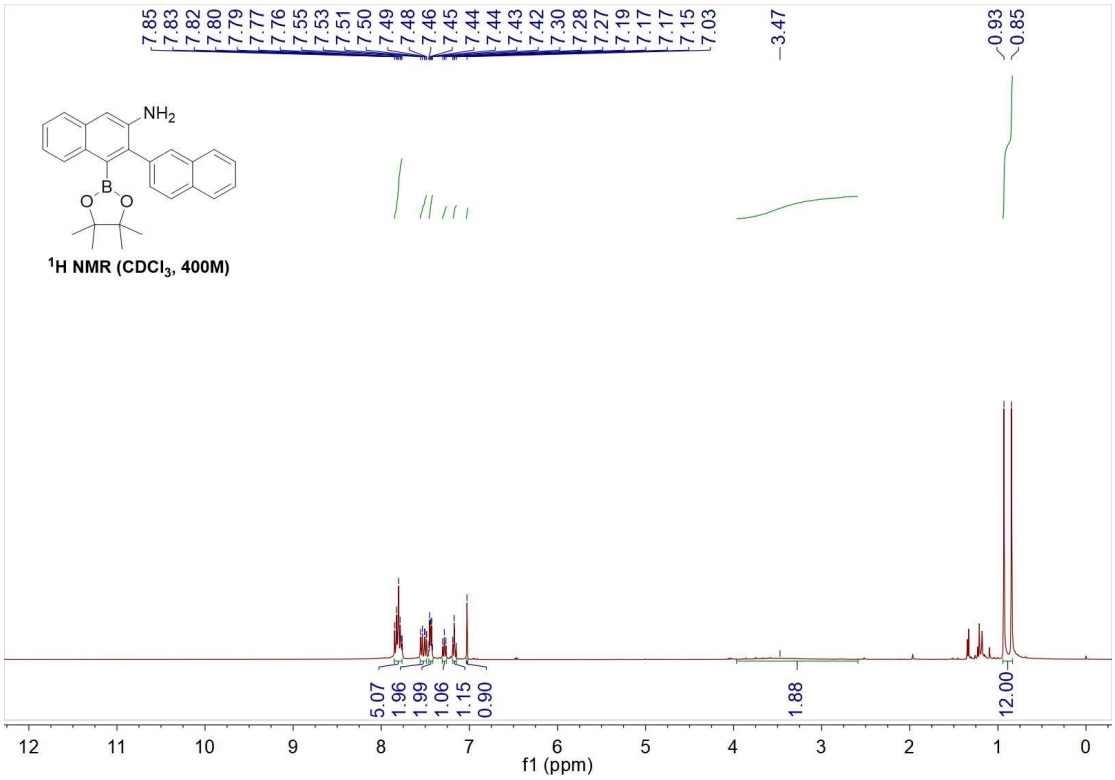
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 41



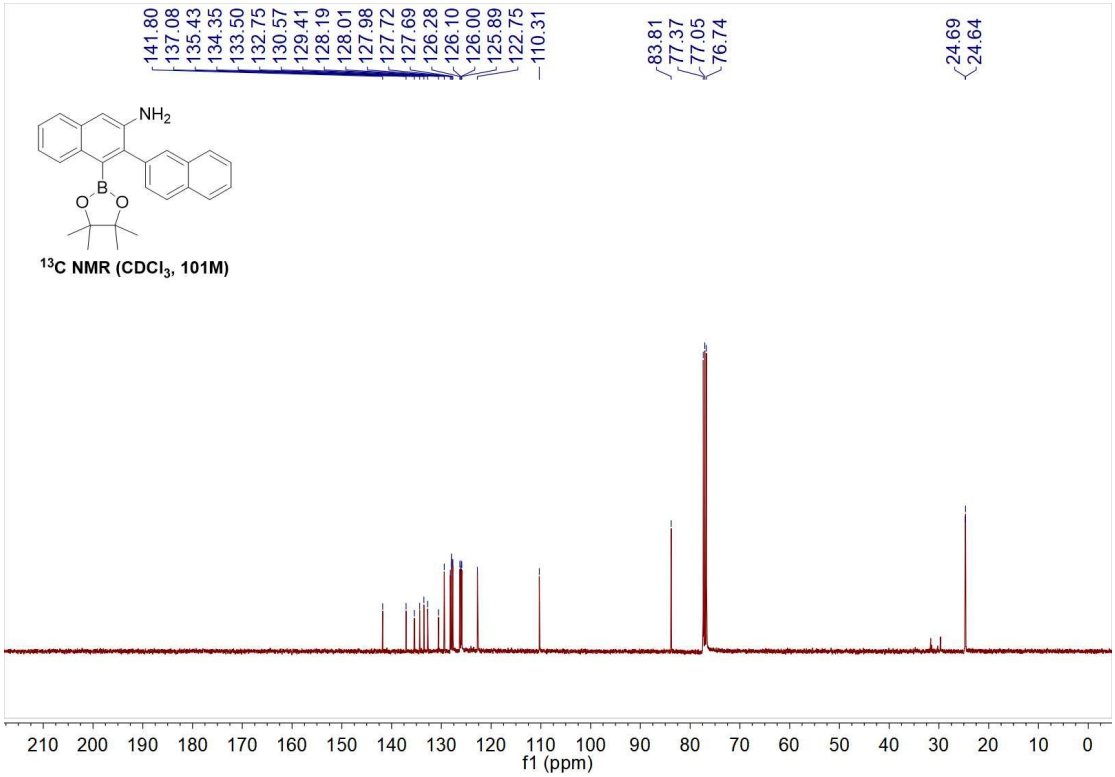
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 41



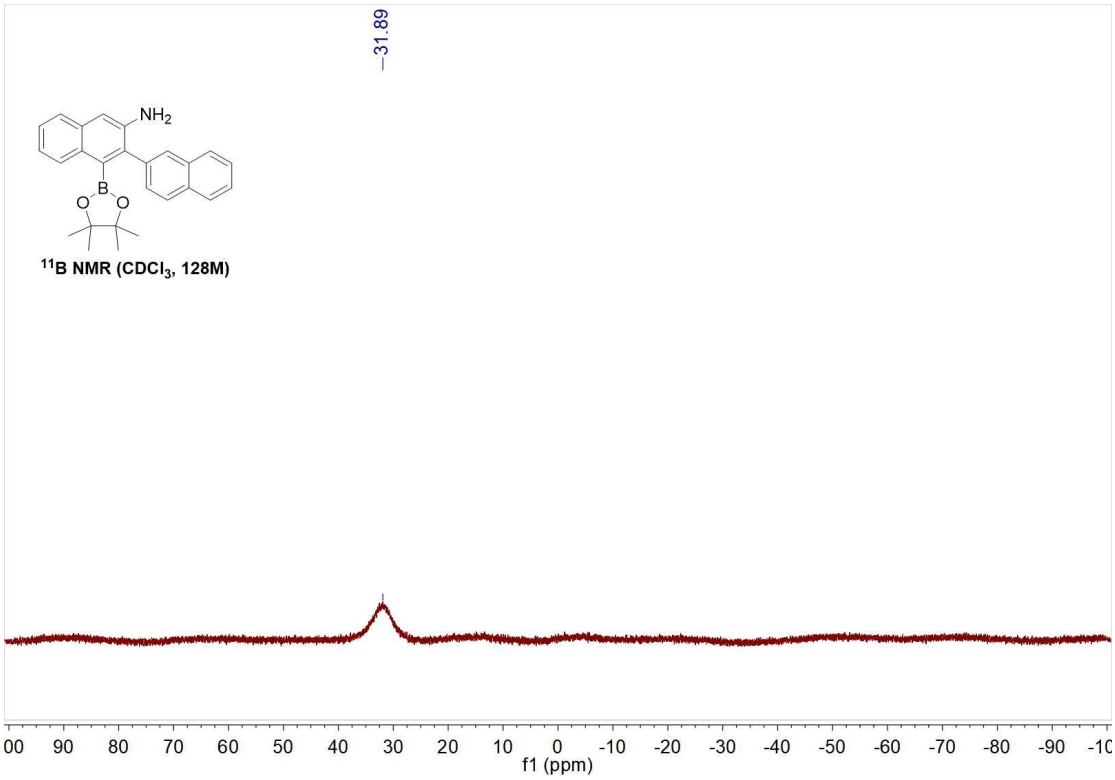
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 42



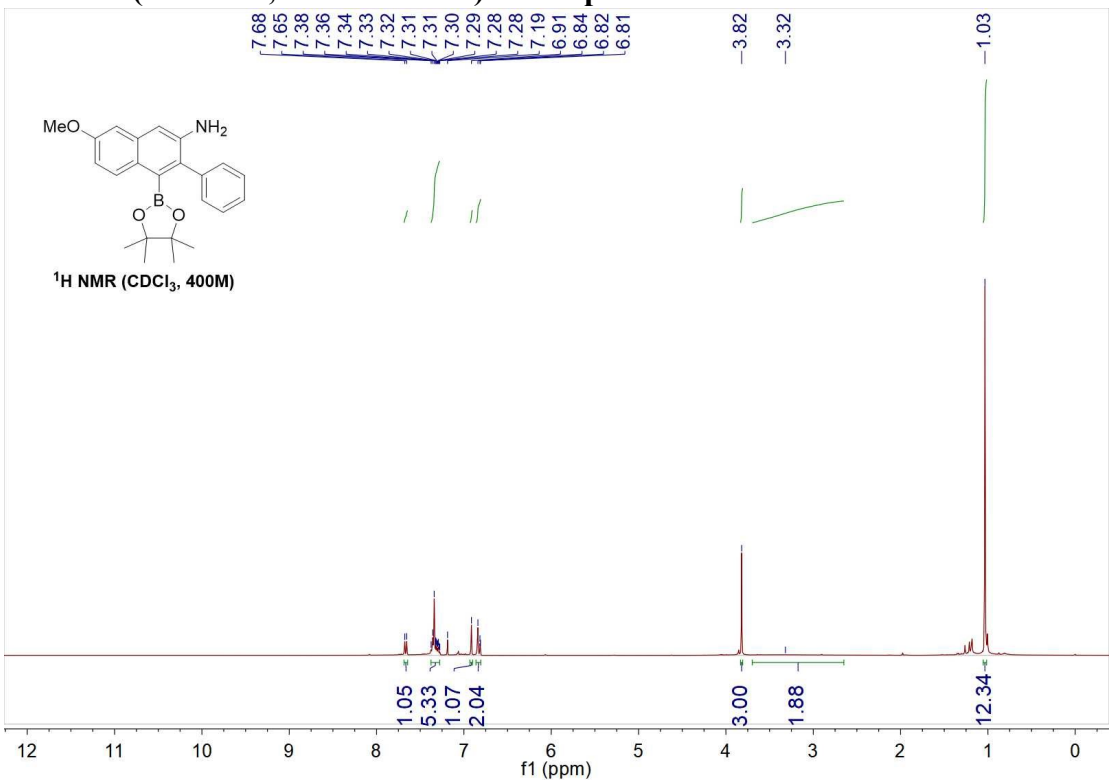
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 42



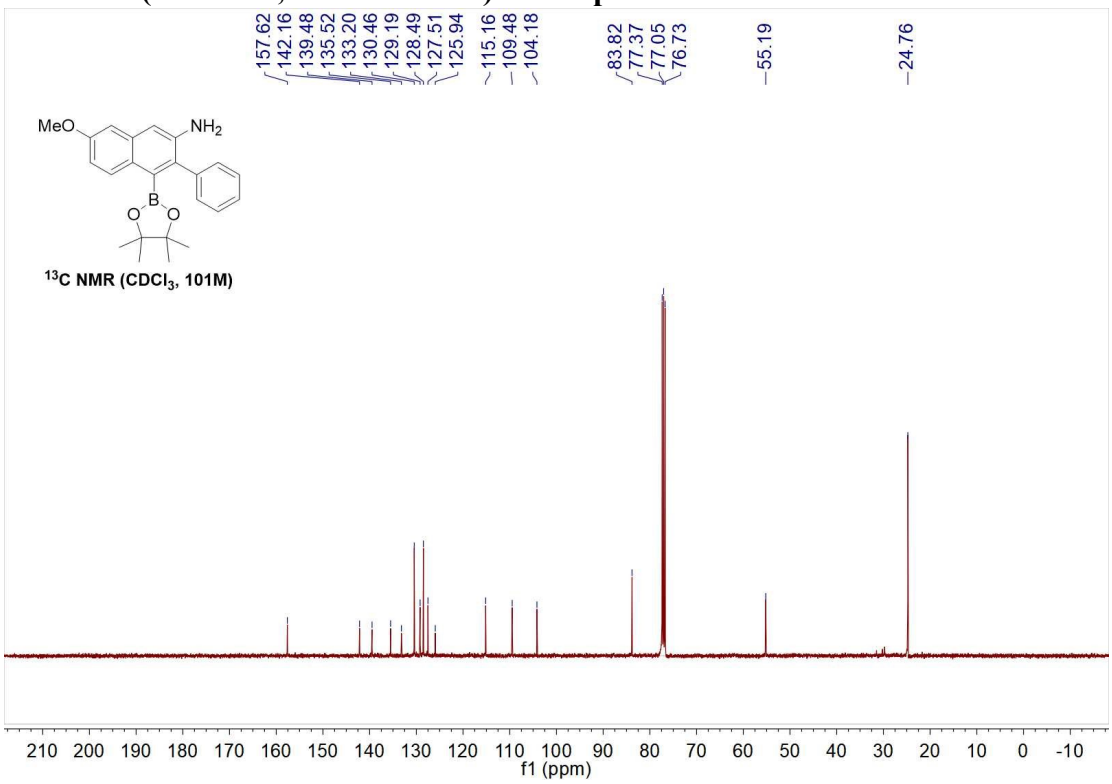
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 42



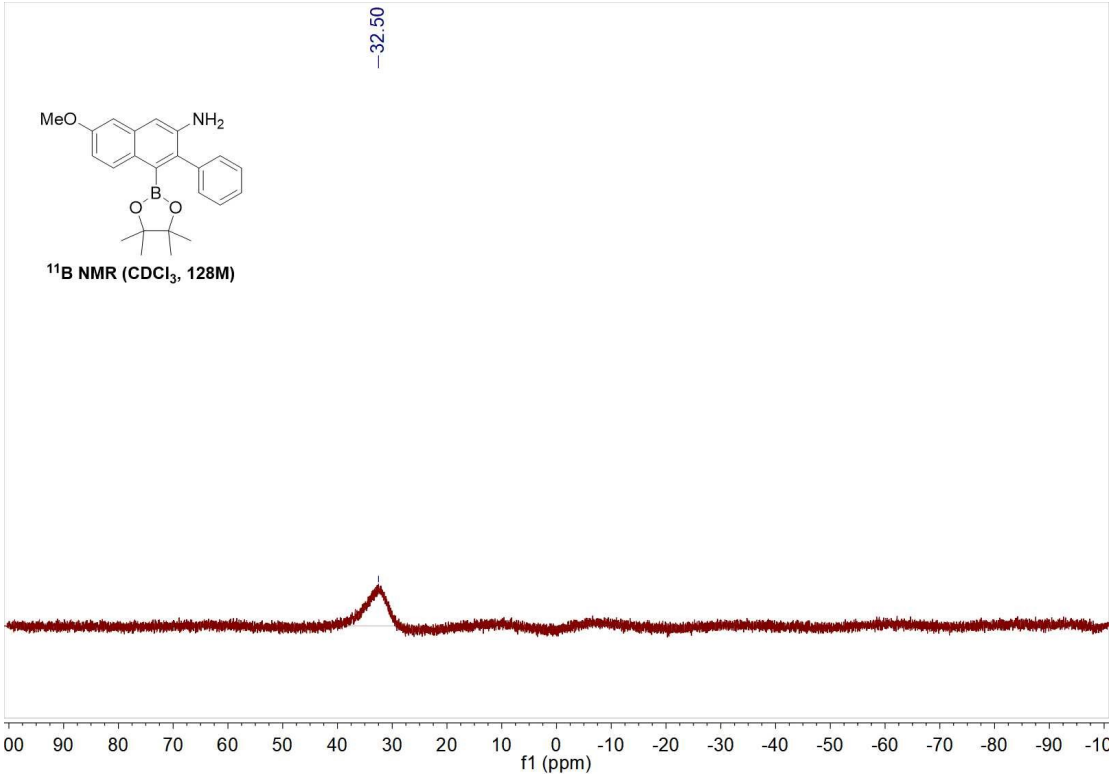
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 43



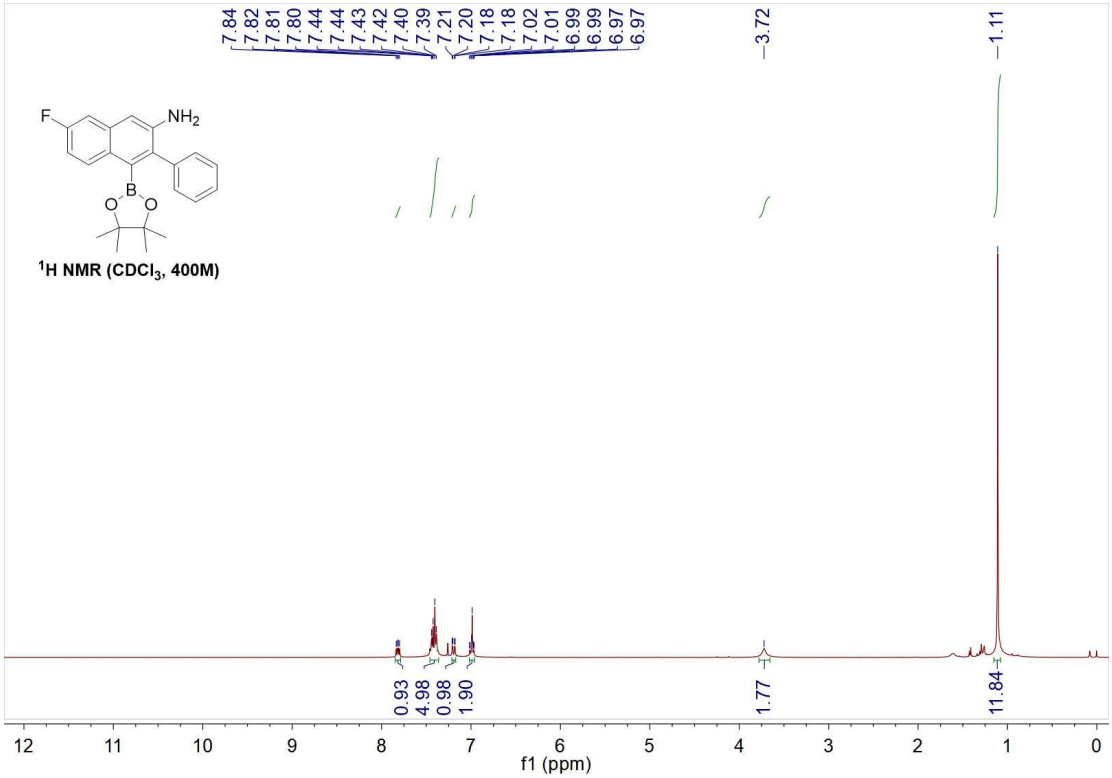
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 43



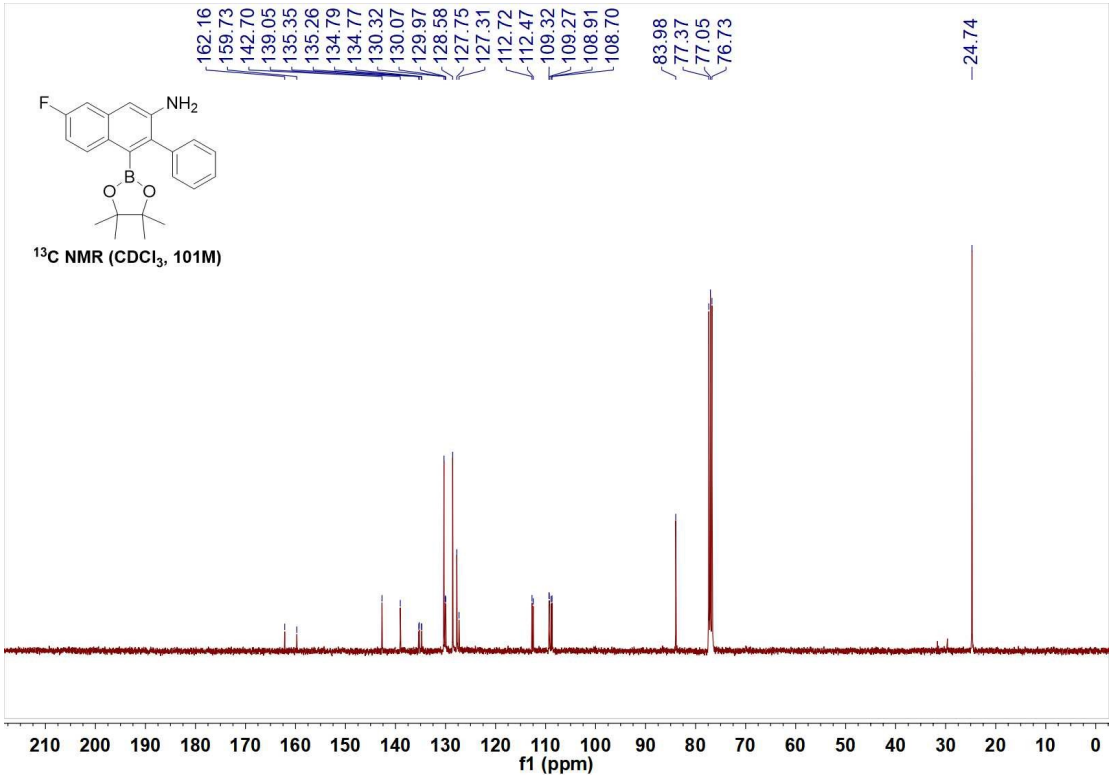
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 43



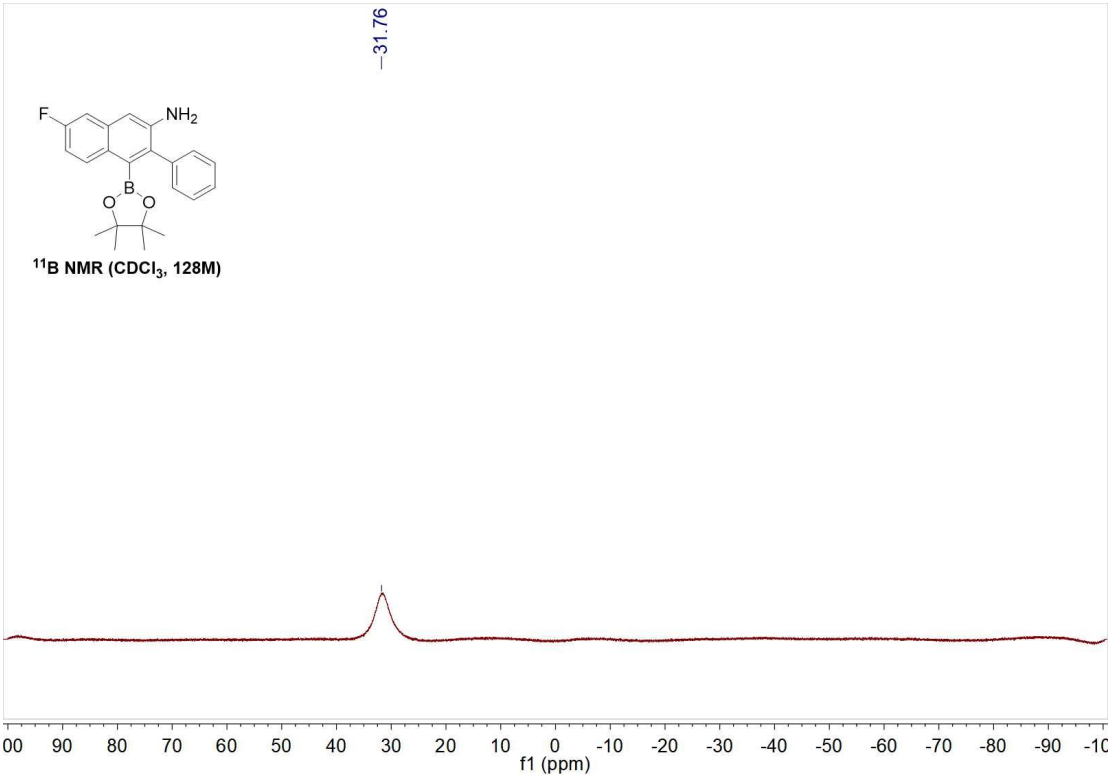
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 44



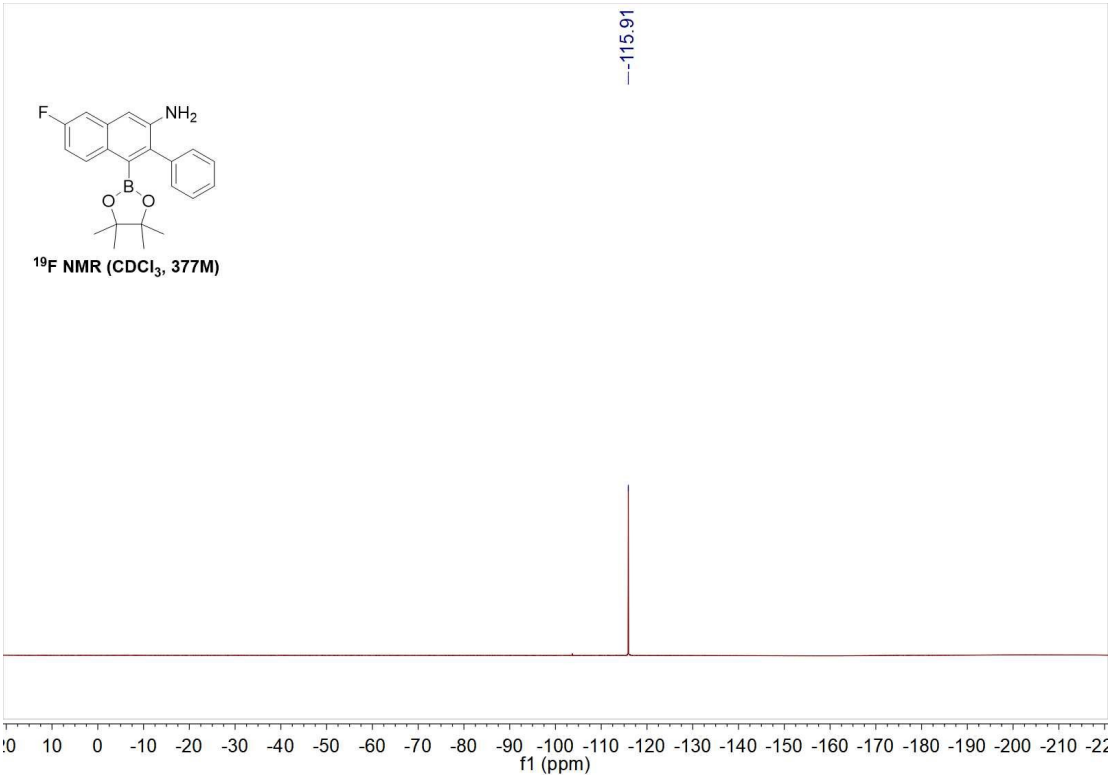
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 44



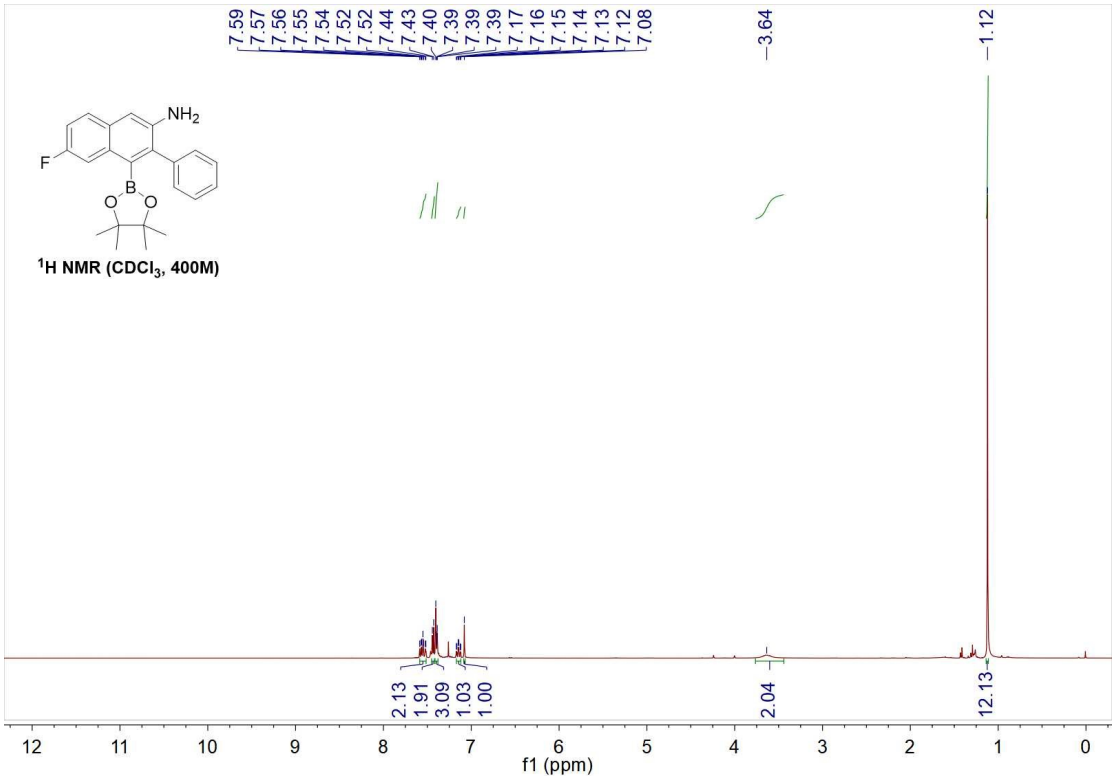
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 44



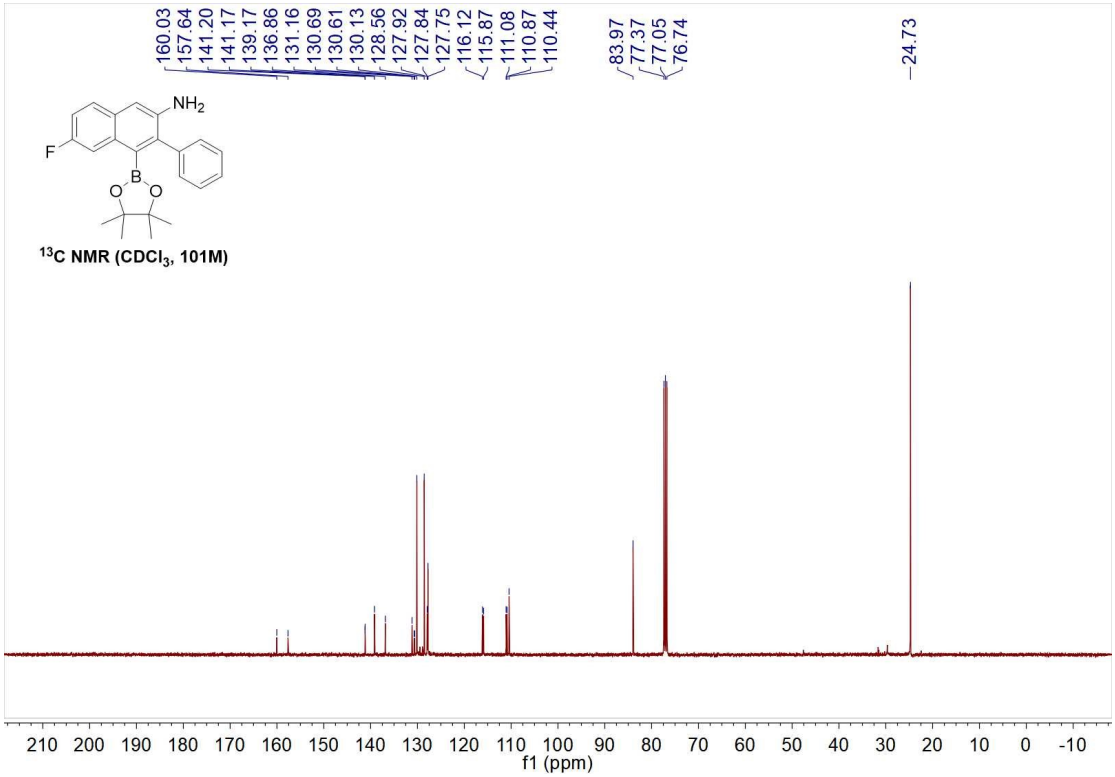
^{19}F NMR (377 MHz, Chloroform-*d*) of compound 44



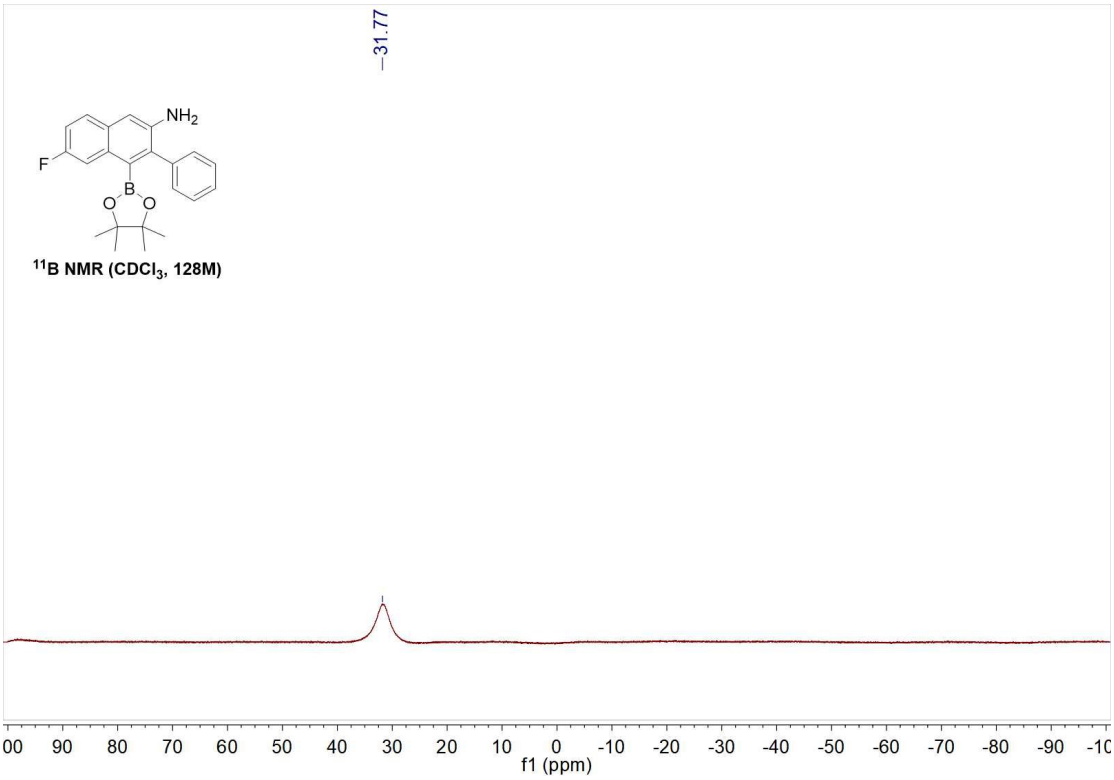
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 45



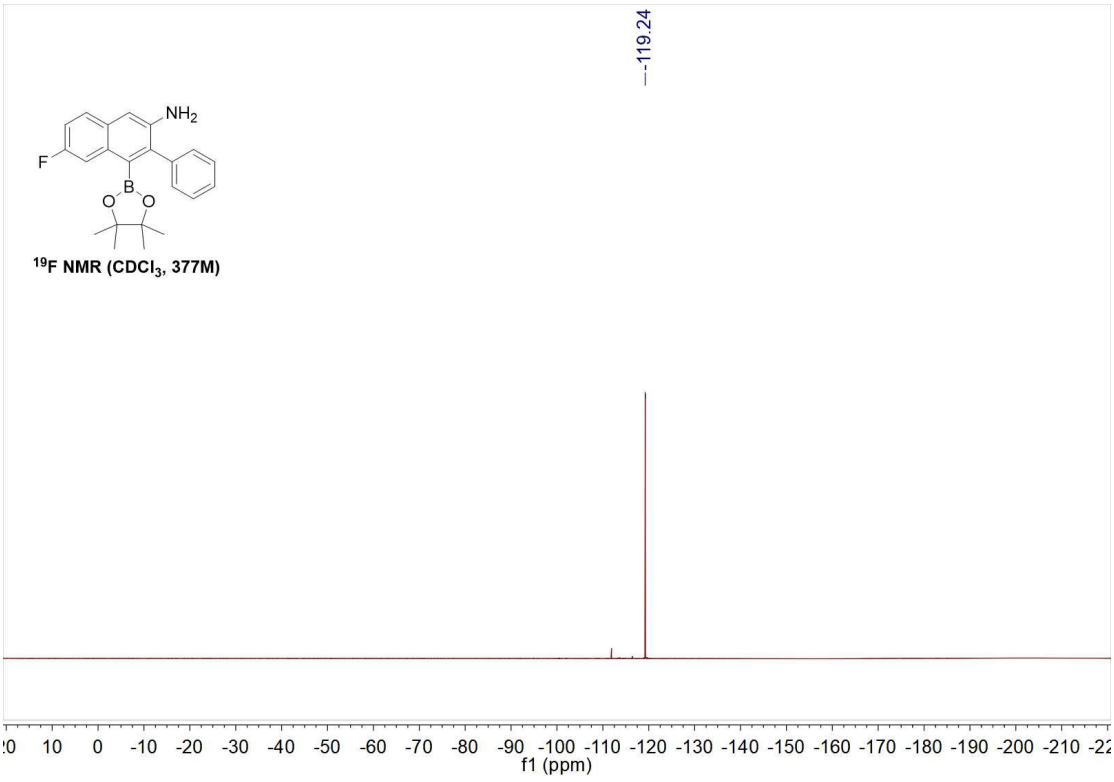
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 45



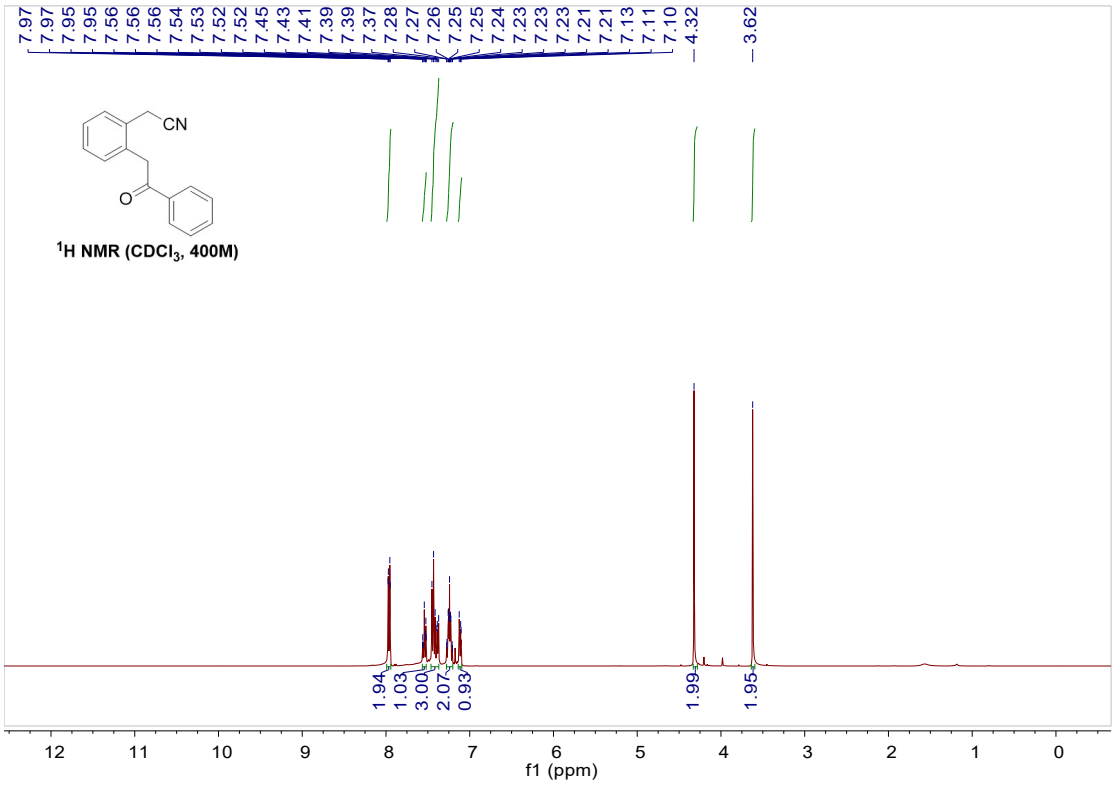
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 45



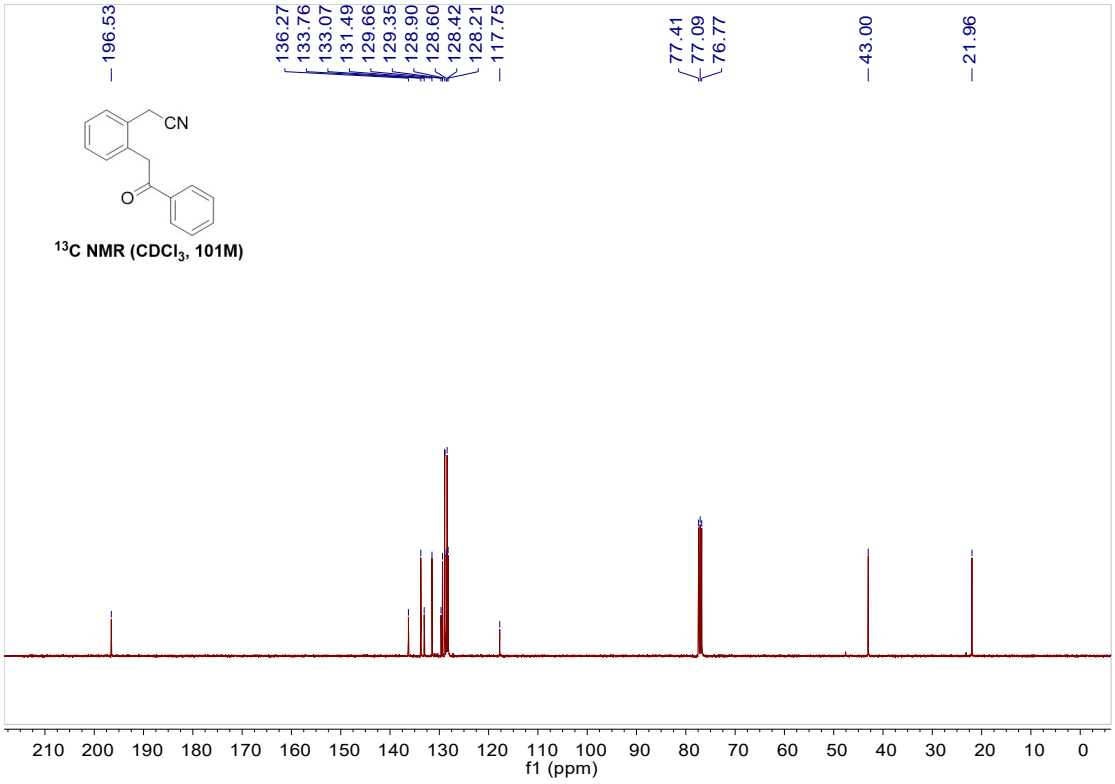
^{19}F NMR (377 MHz, Chloroform-*d*) of compound 45



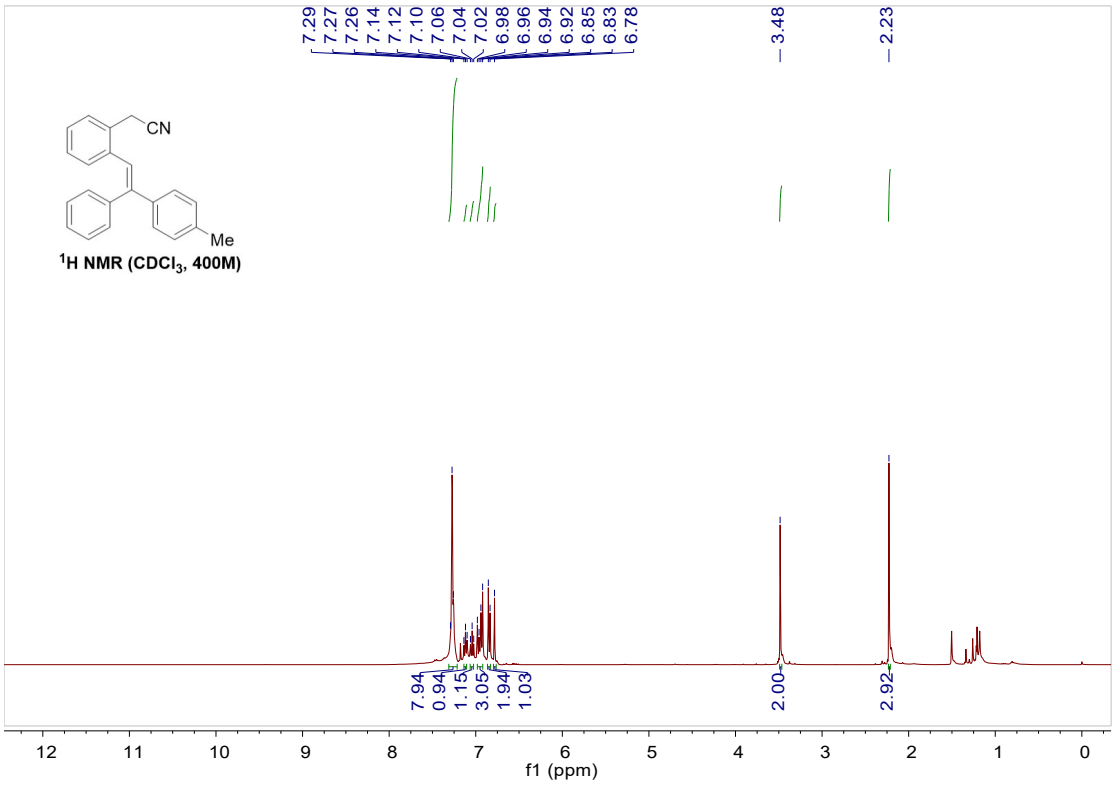
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 46



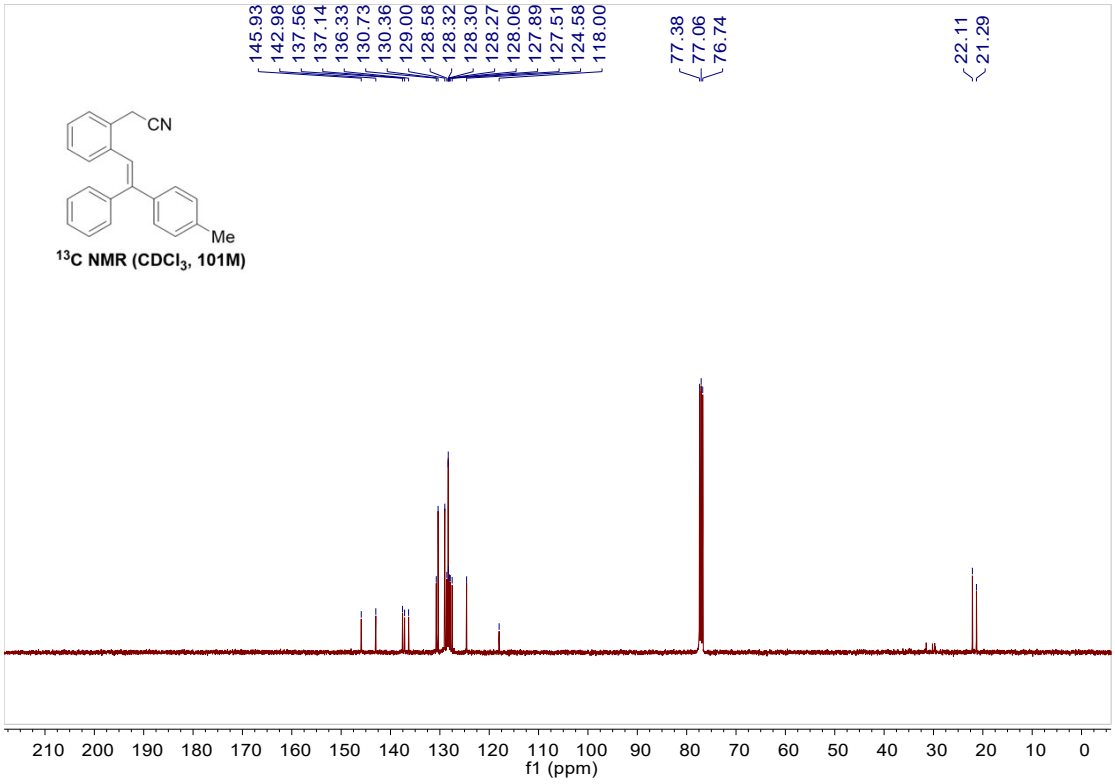
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 46



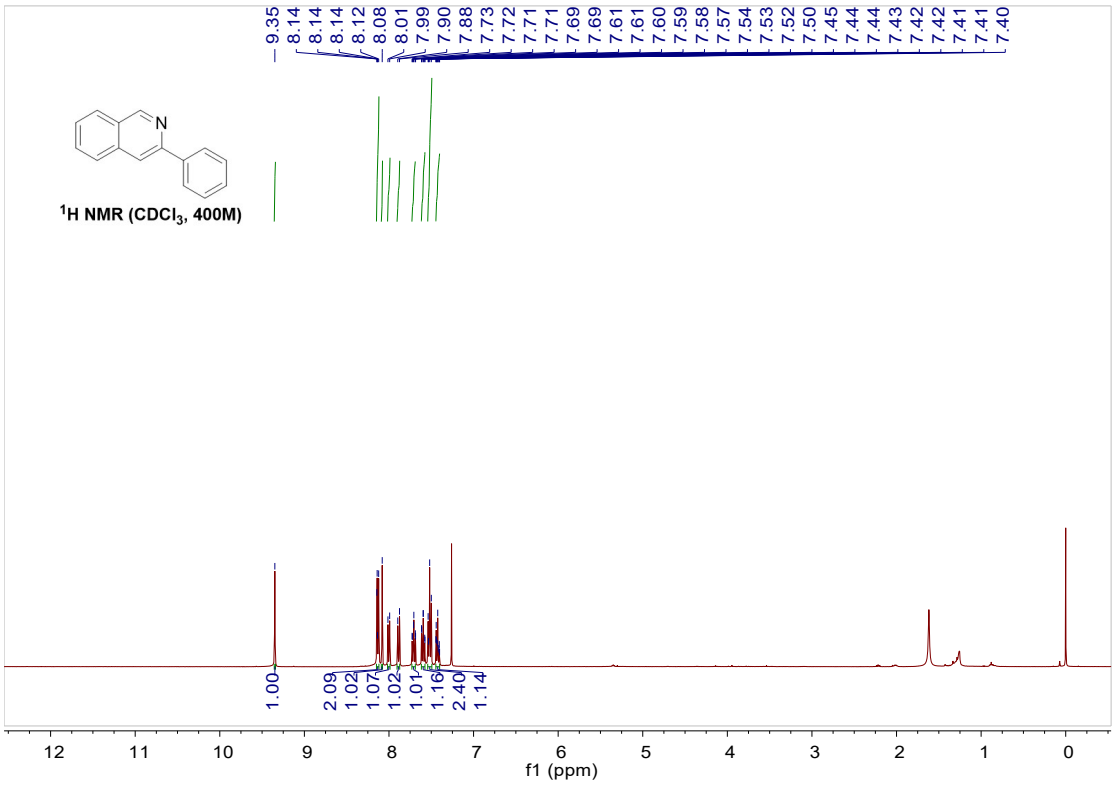
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 47



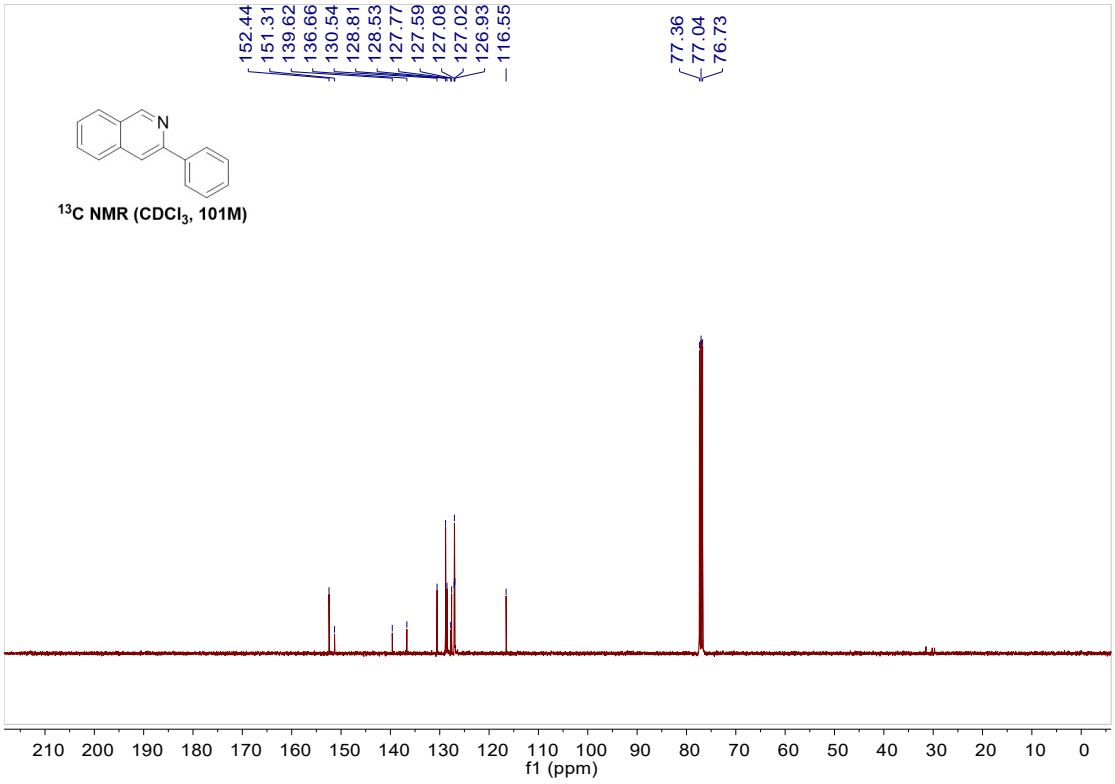
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 47



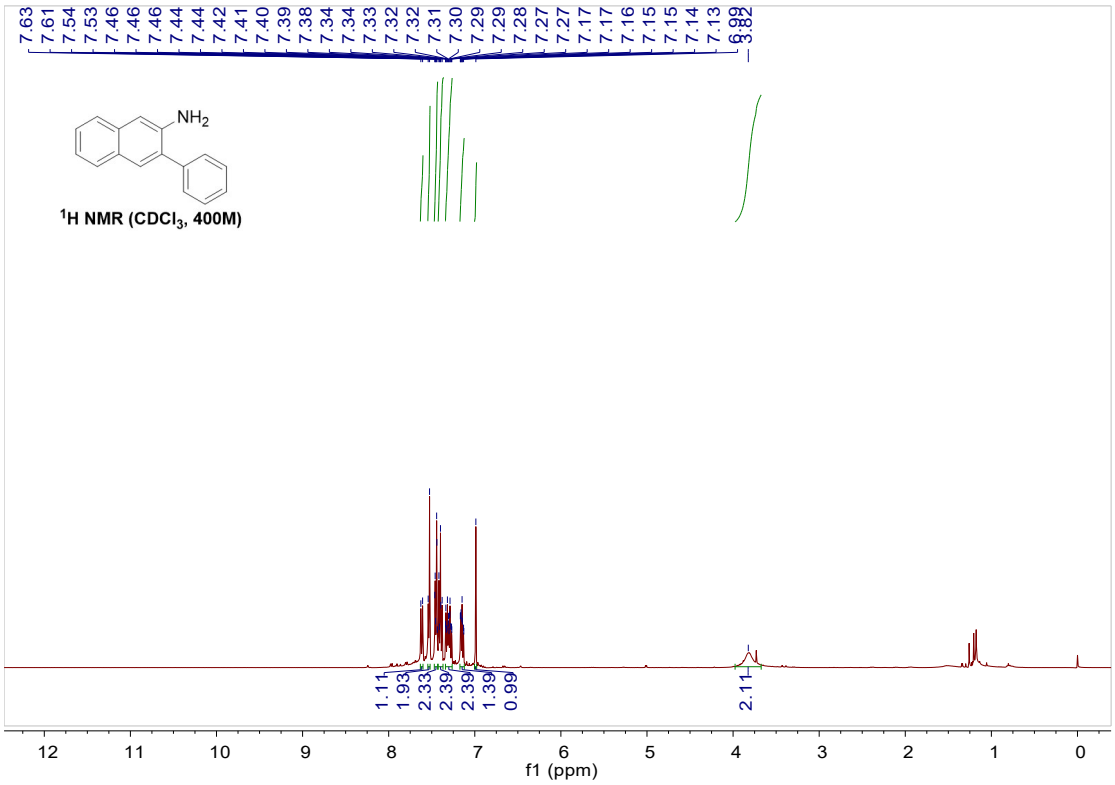
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 48



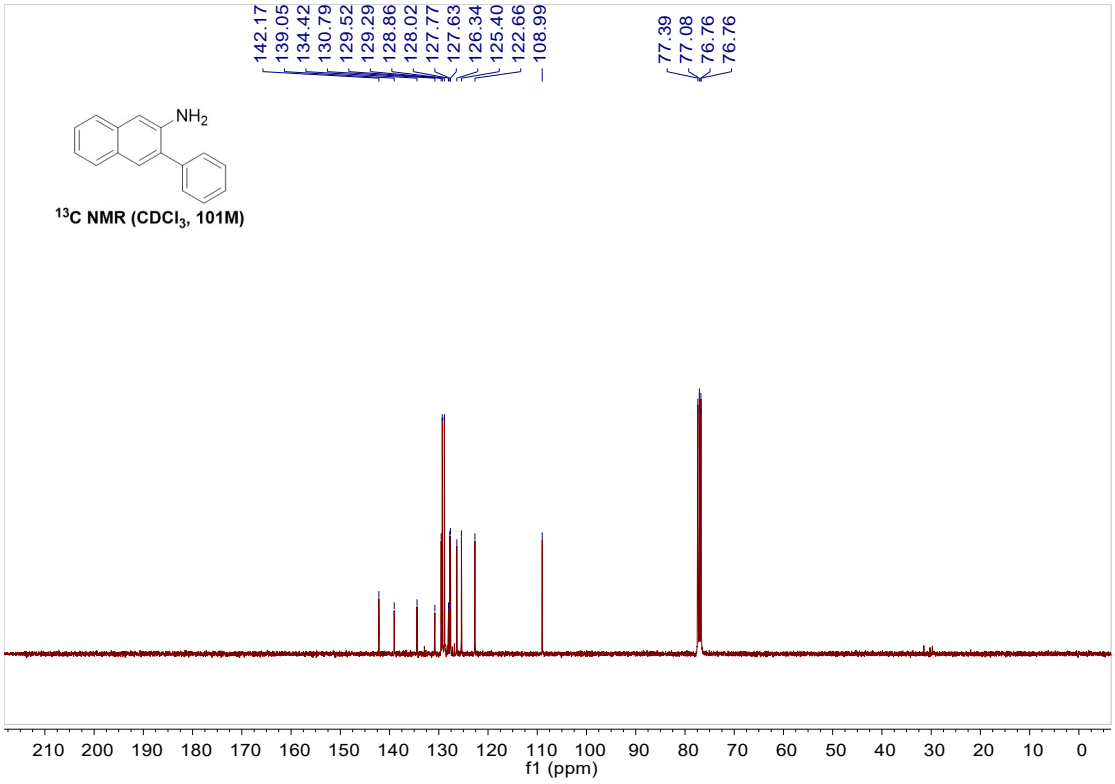
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 48



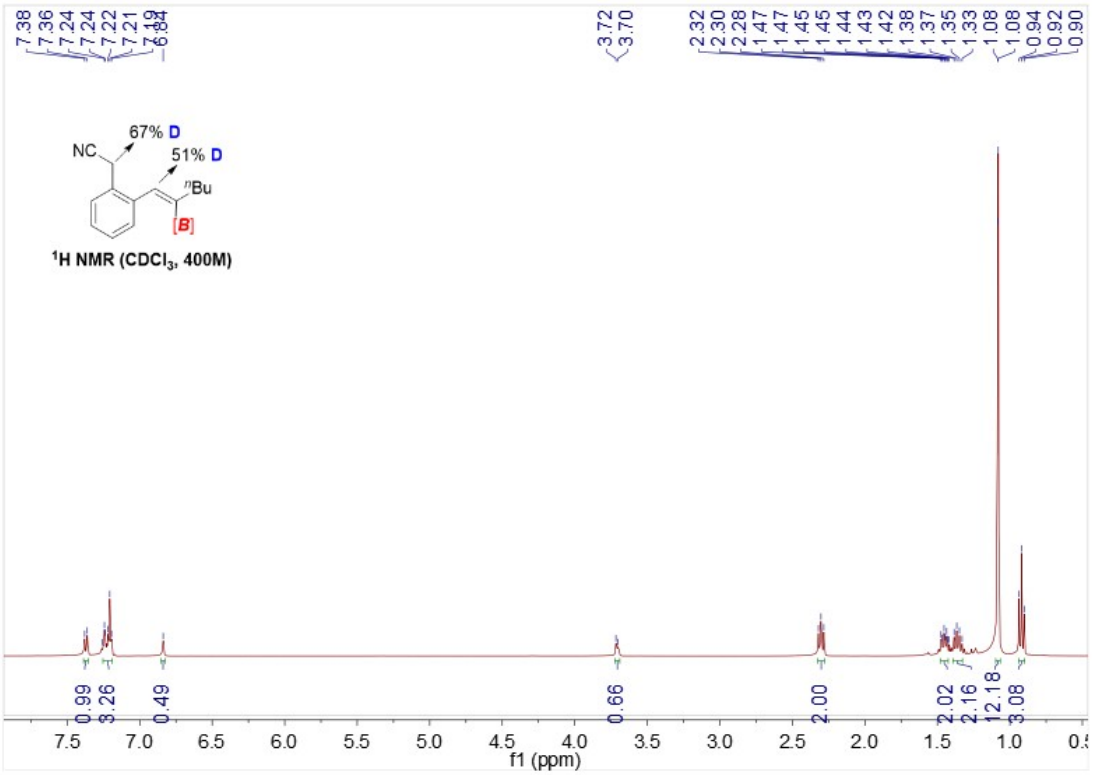
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 49



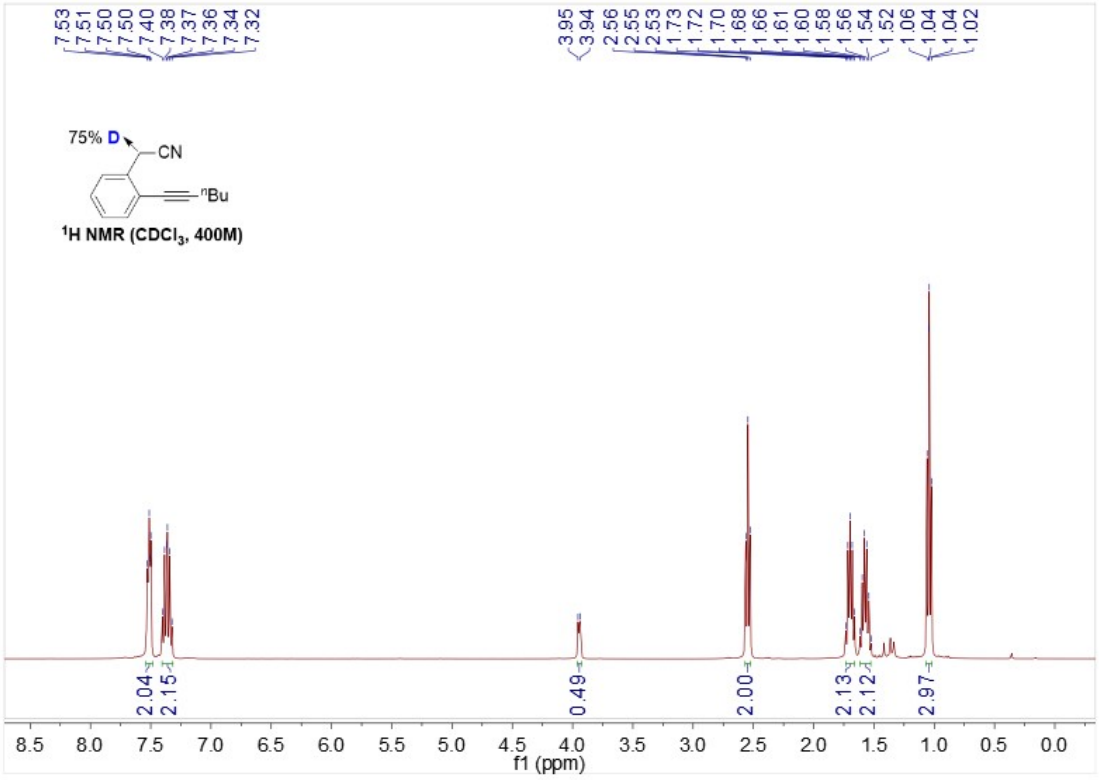
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 49



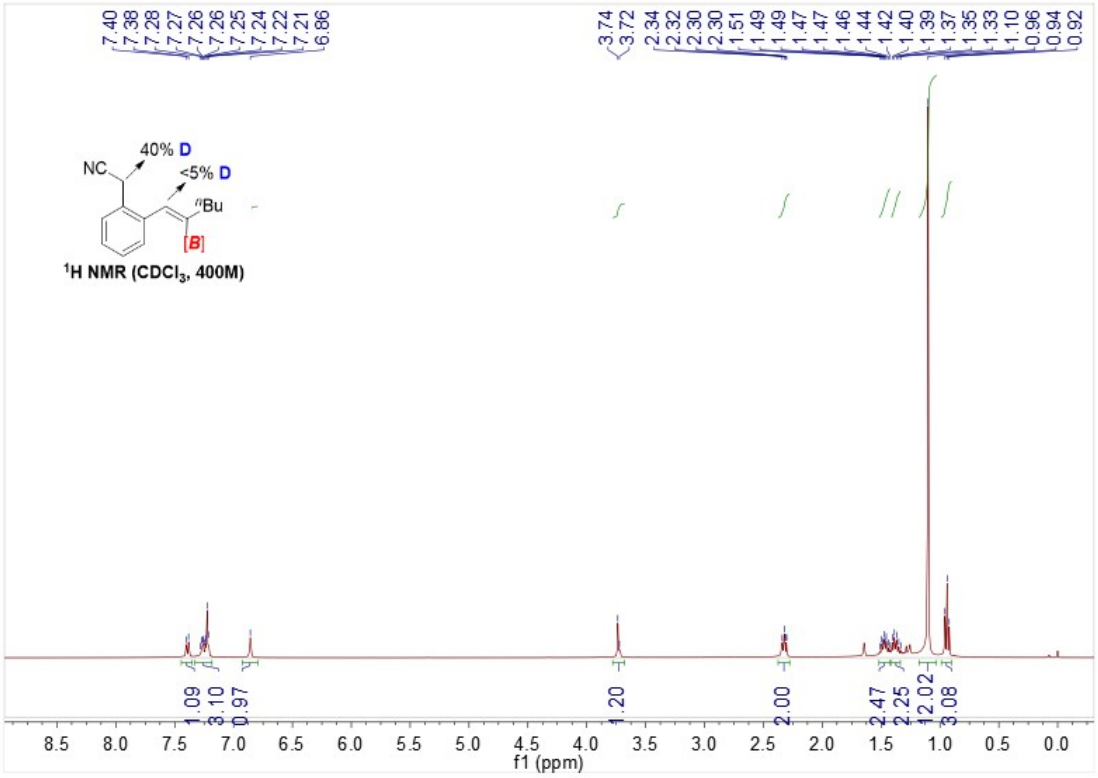
^{1}H NMR (400 MHz, Chloroform-*d*) of compound *d*-24



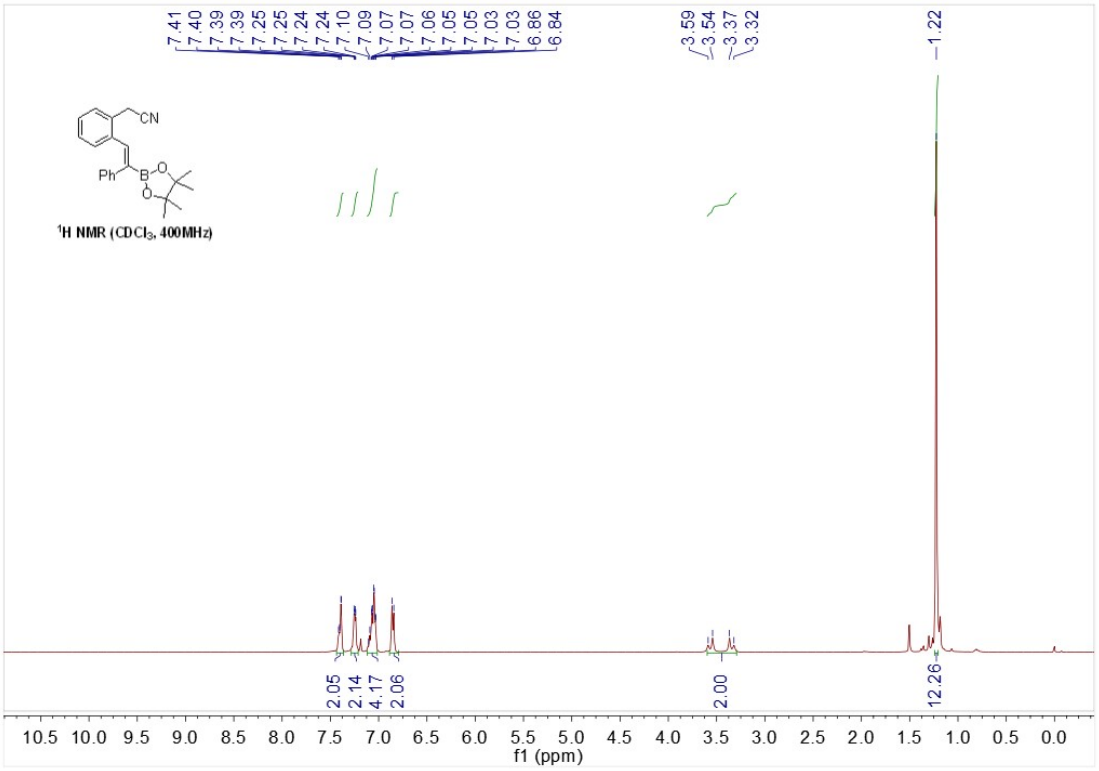
^{1}H NMR (400 MHz, Chloroform-*d*) of compound *d*-50



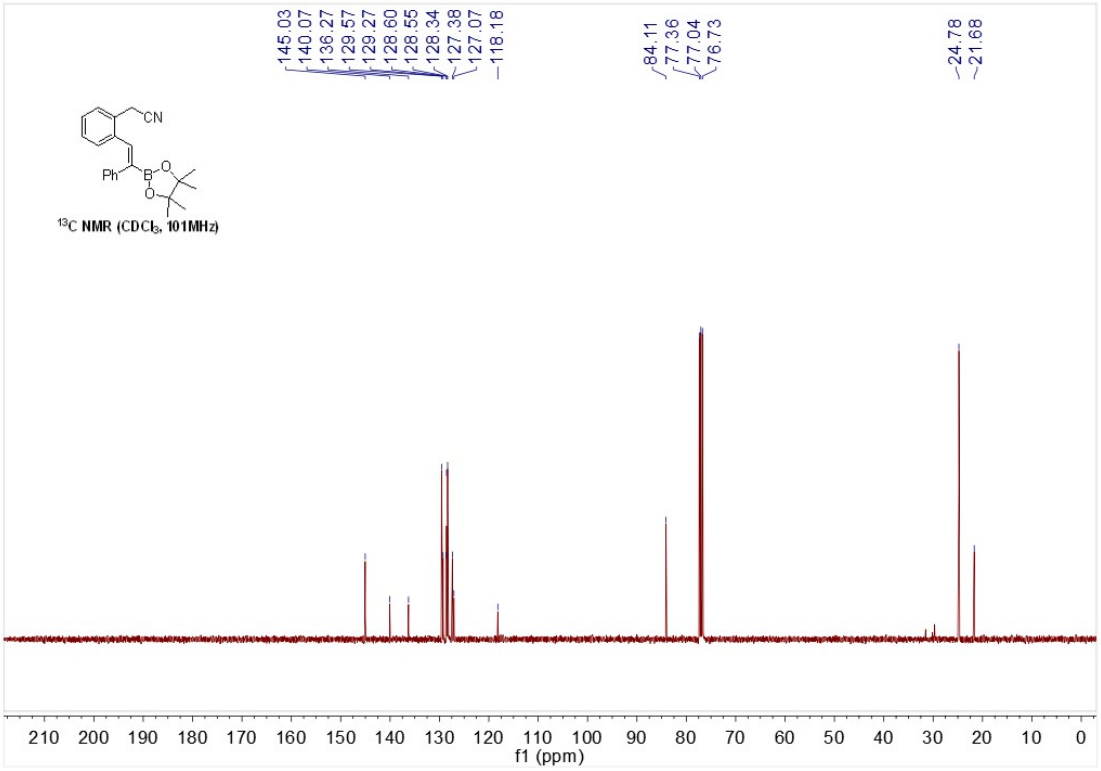
^{1}H NMR (400 MHz, Chloroform-*d*) of compound *d*-24 (from *d*-50)



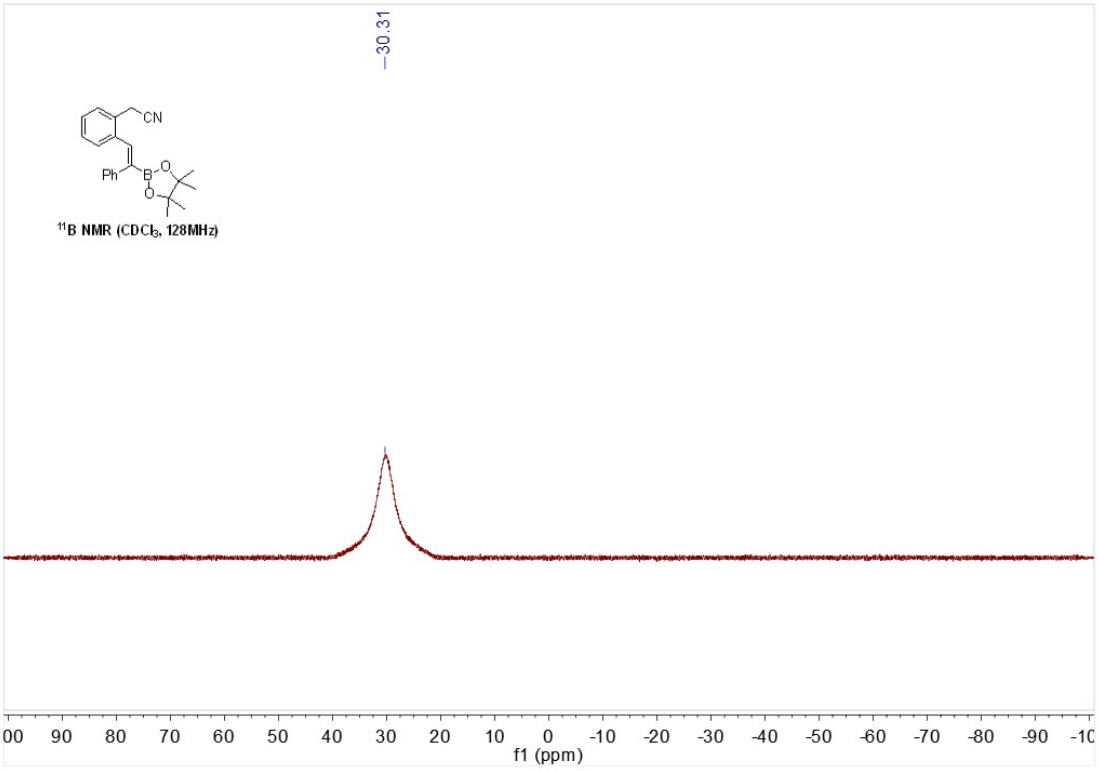
^{1}H NMR (400 MHz, Chloroform-*d*) of compound Z-2



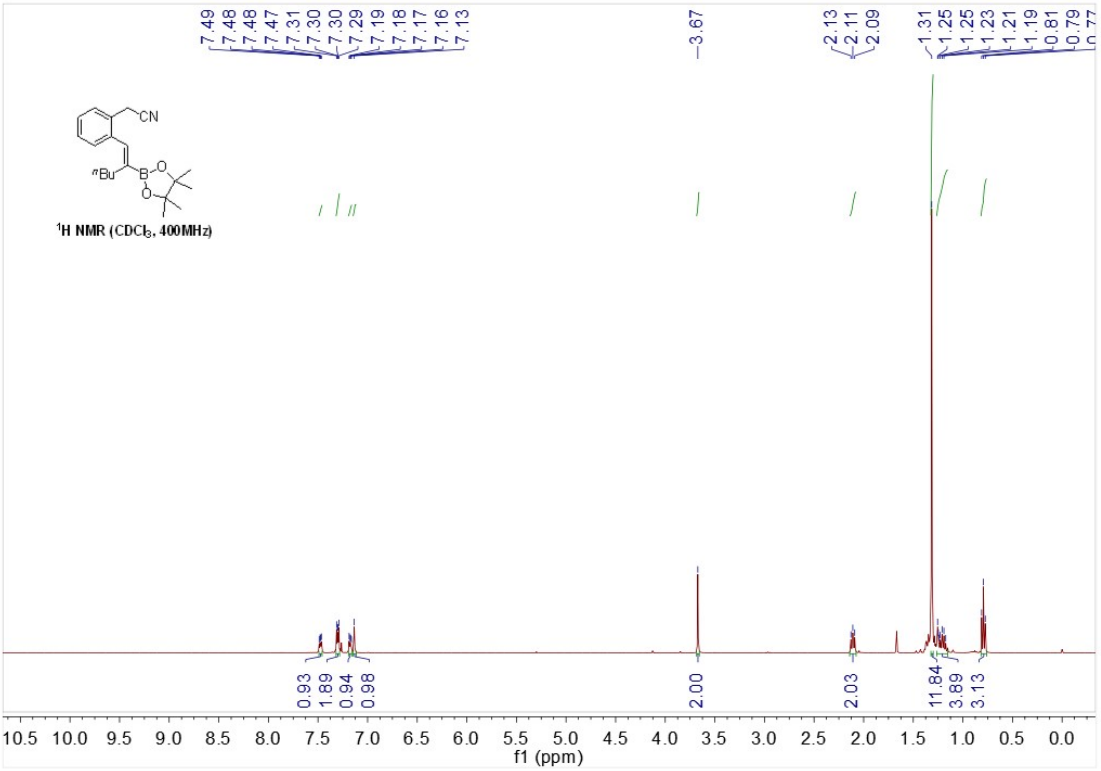
^{13}C NMR (101 MHz, Chloroform-*d*) of compound Z-2



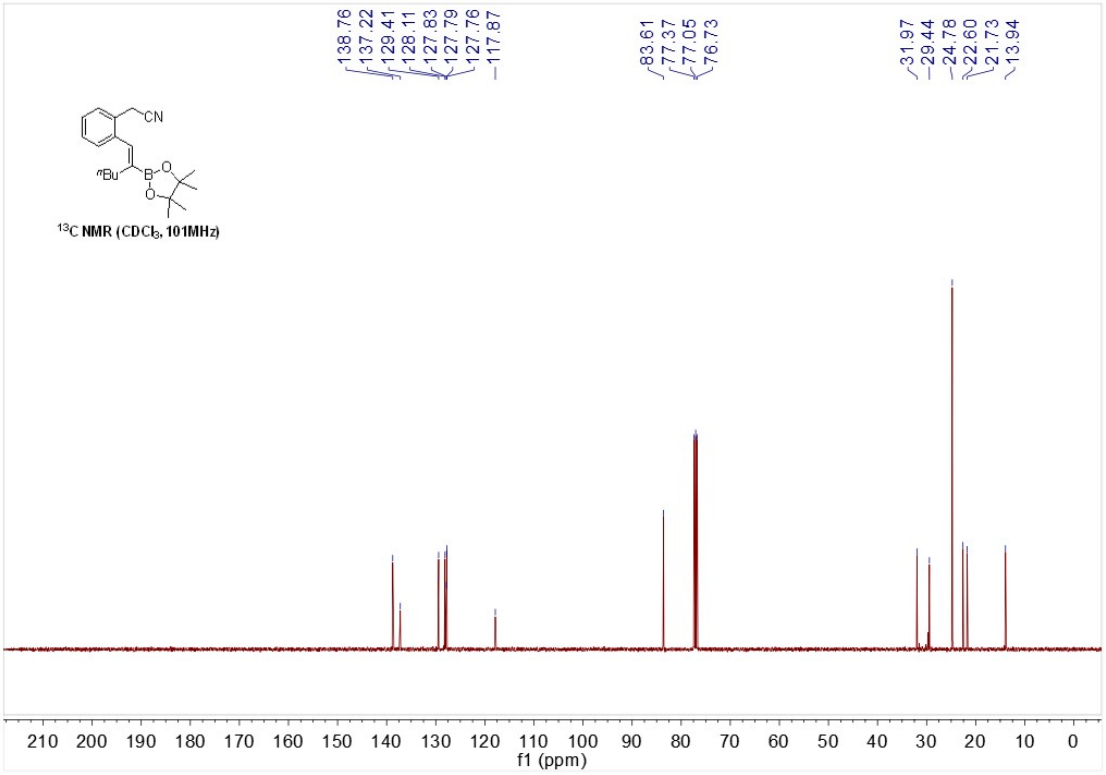
^{11}B NMR (128 MHz, Chloroform-*d*) of compound Z-2



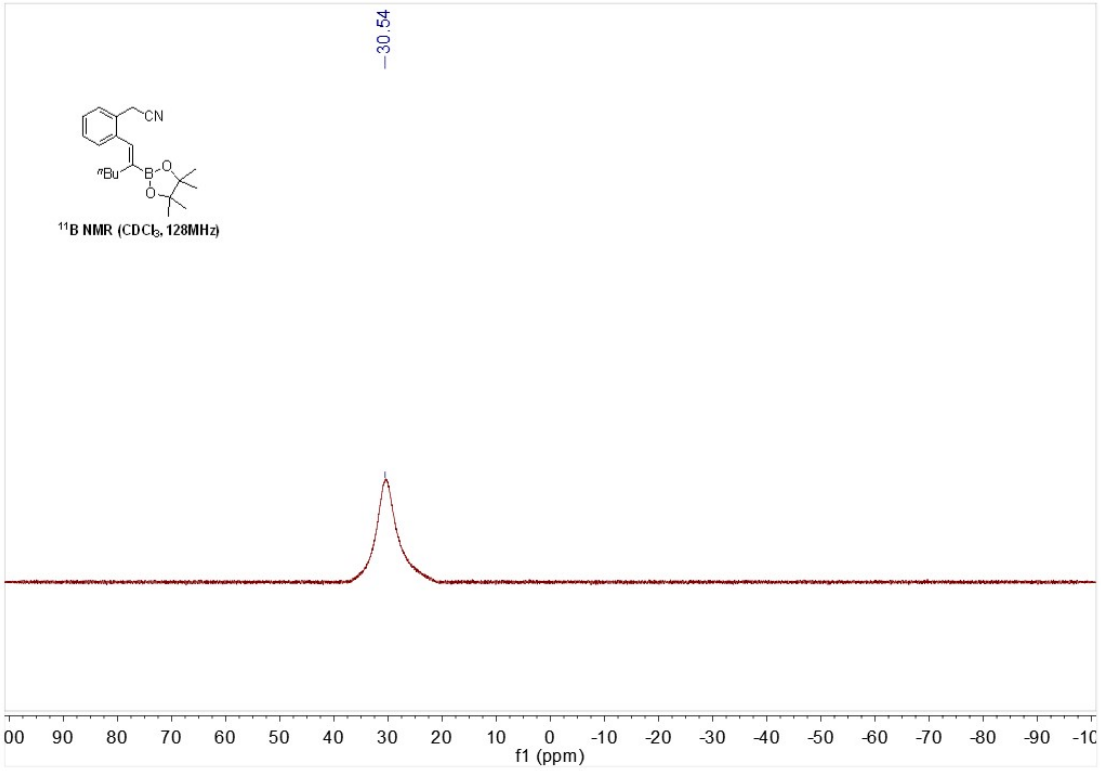
^{1}H NMR (400 MHz, Chloroform-*d*) of compound Z-24



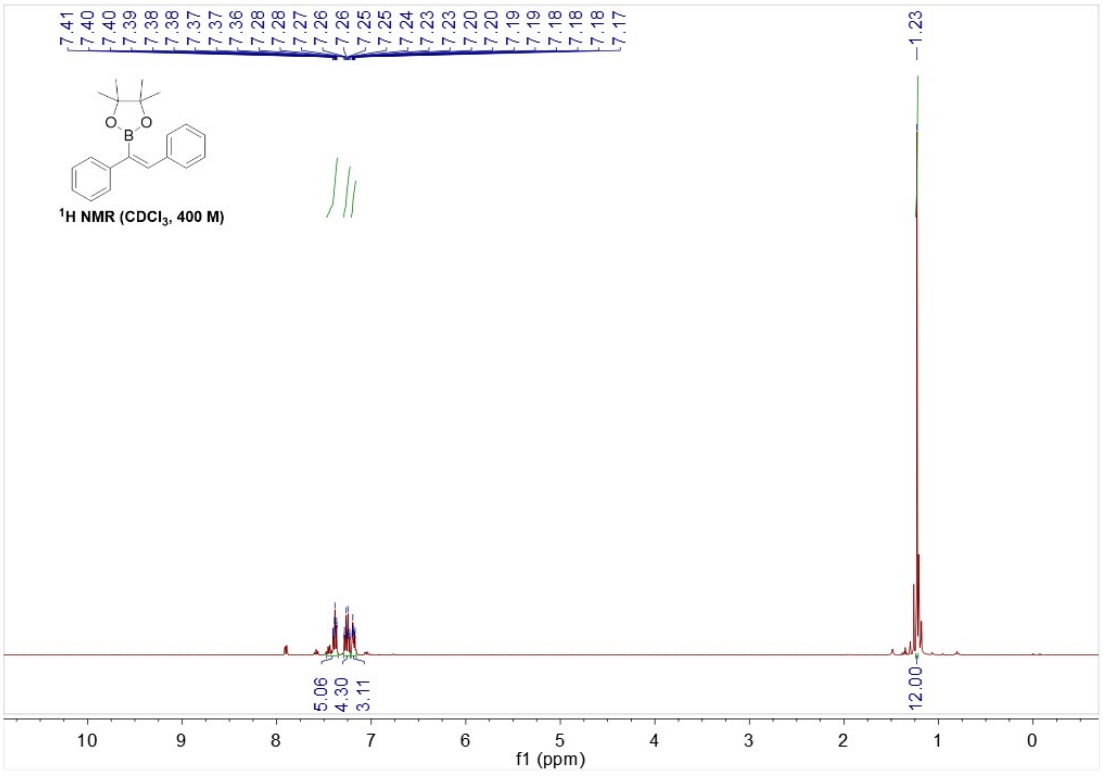
^{13}C NMR (101 MHz, Chloroform-*d*) of compound Z-24



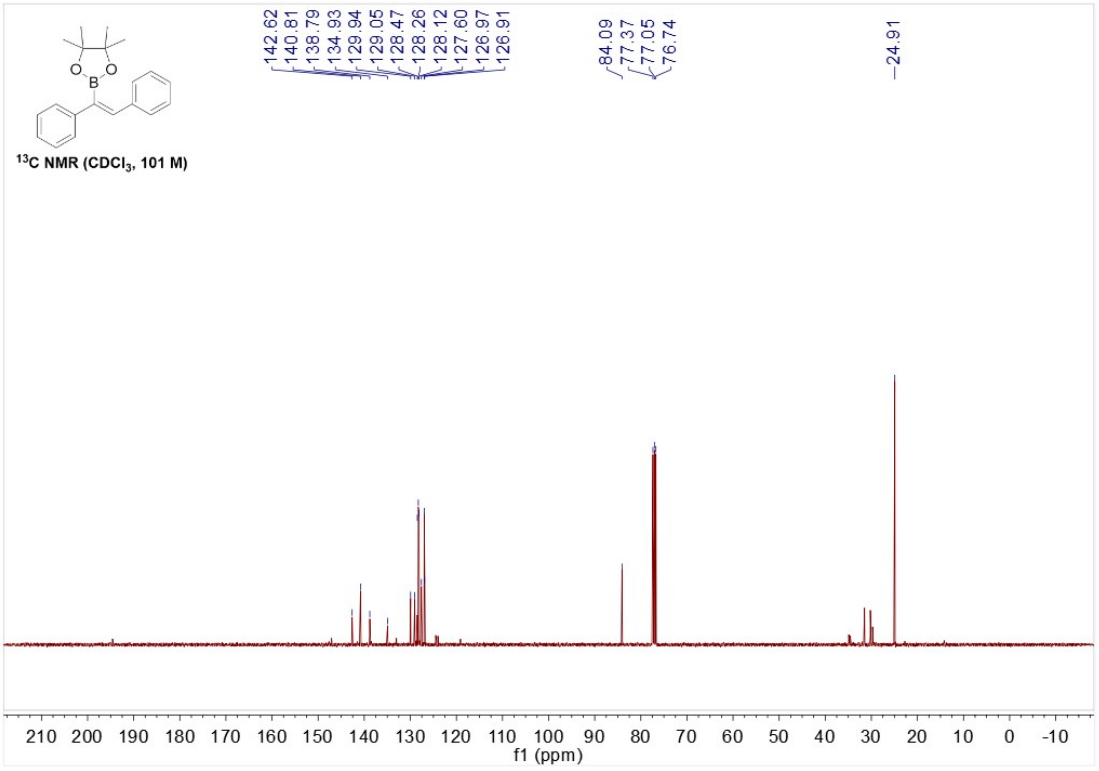
^{11}B NMR (128 MHz, Chloroform-*d*) of compound Z-24



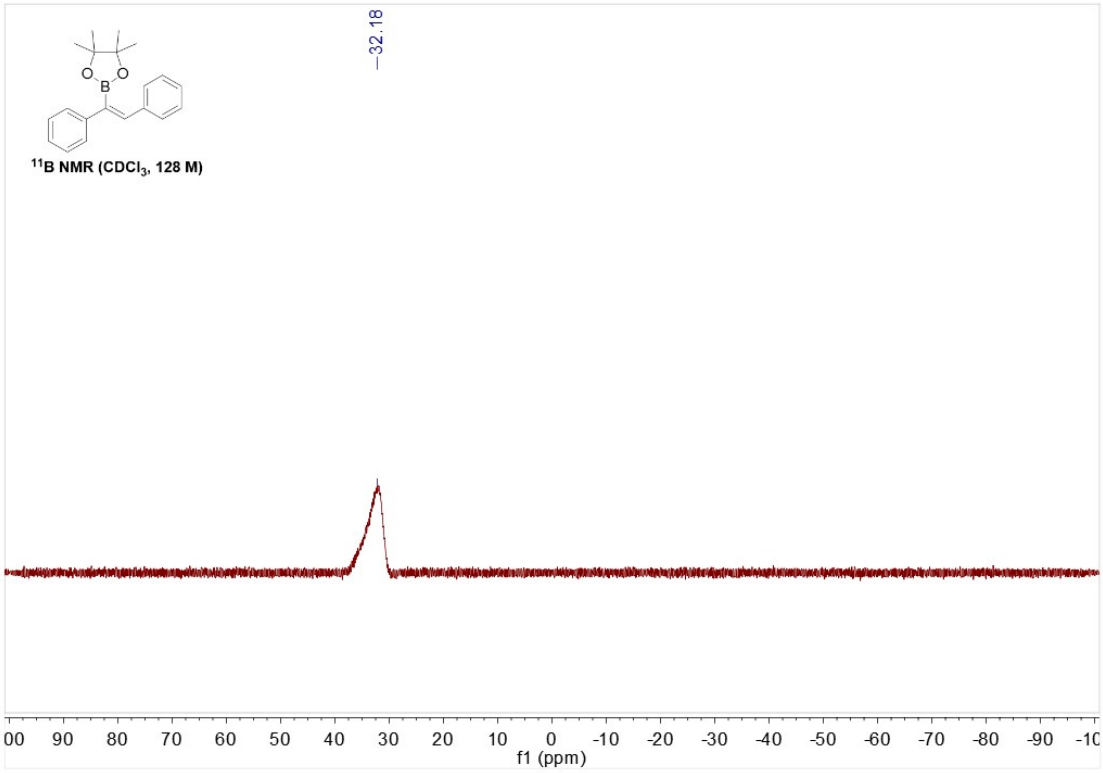
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 51



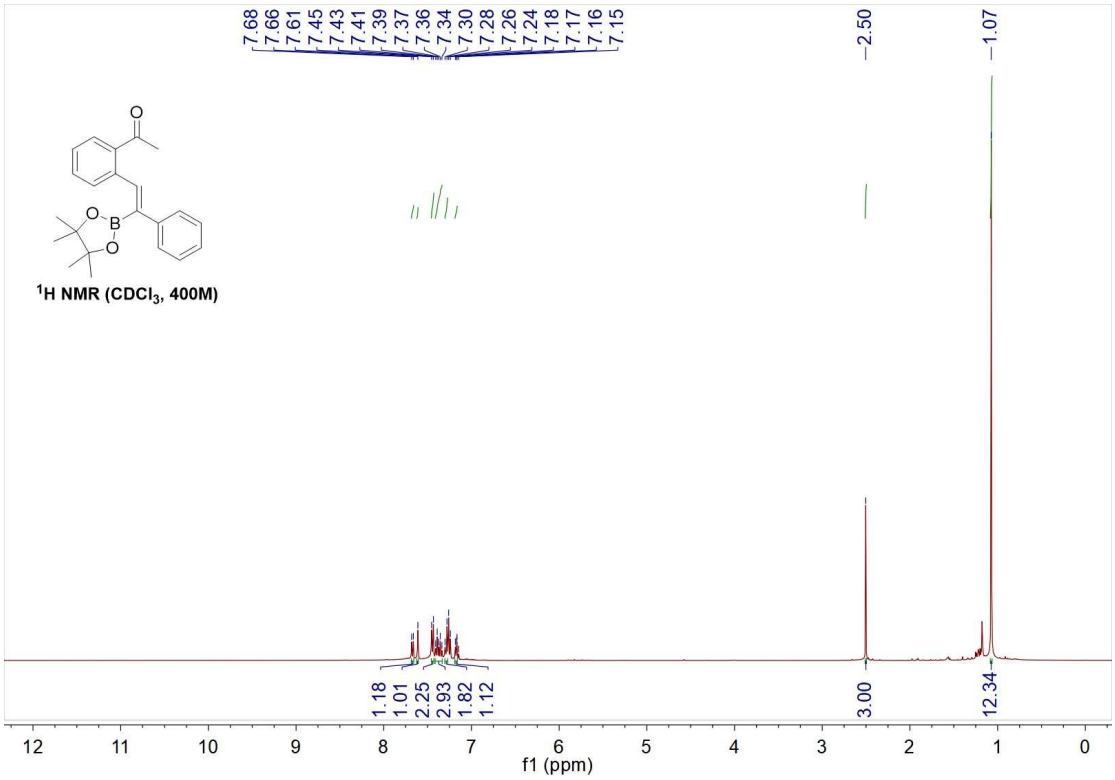
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 51



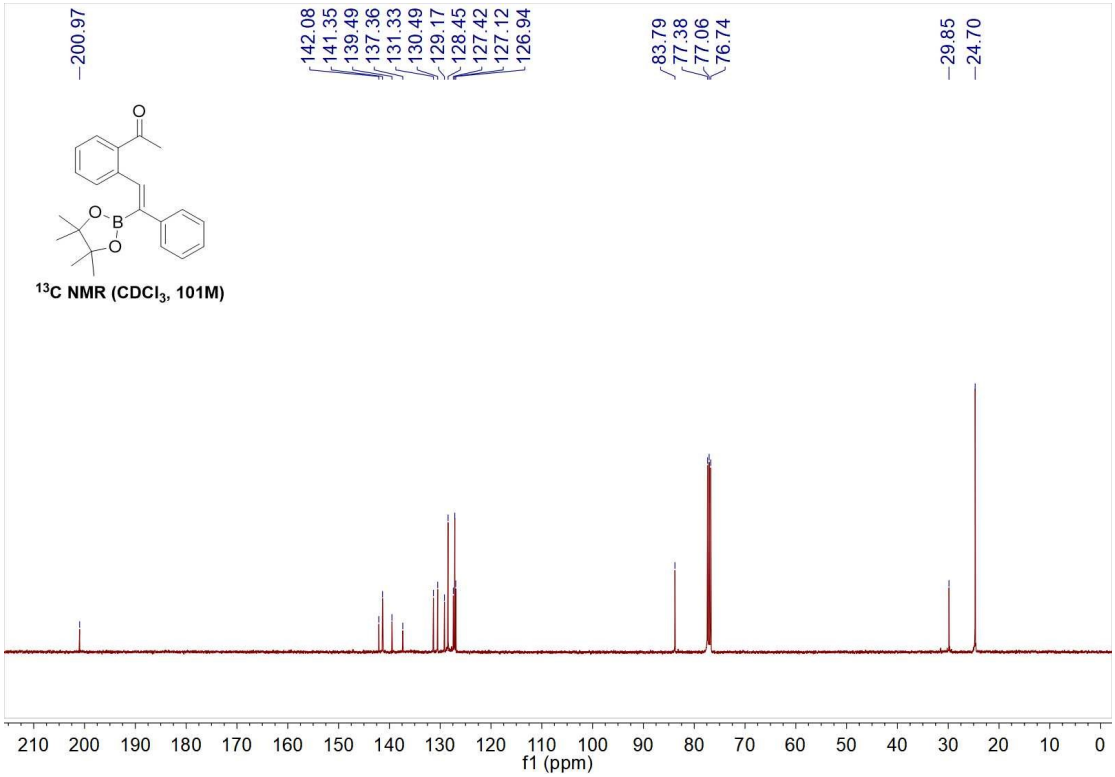
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 51



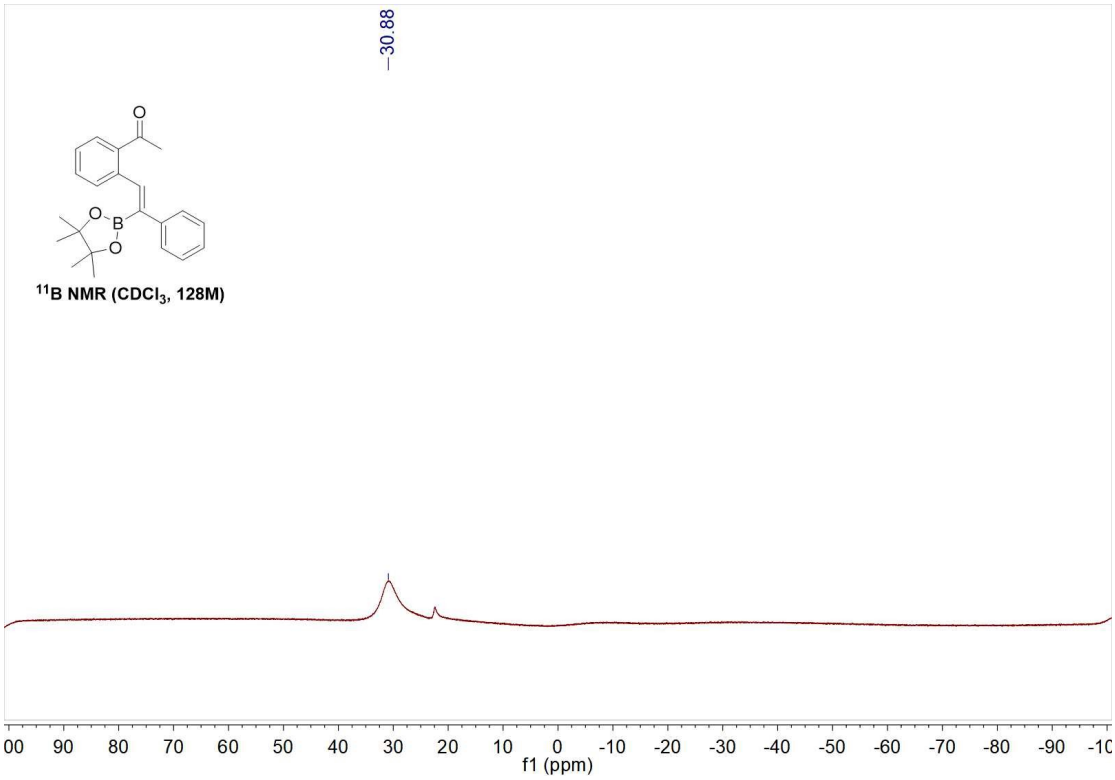
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 52



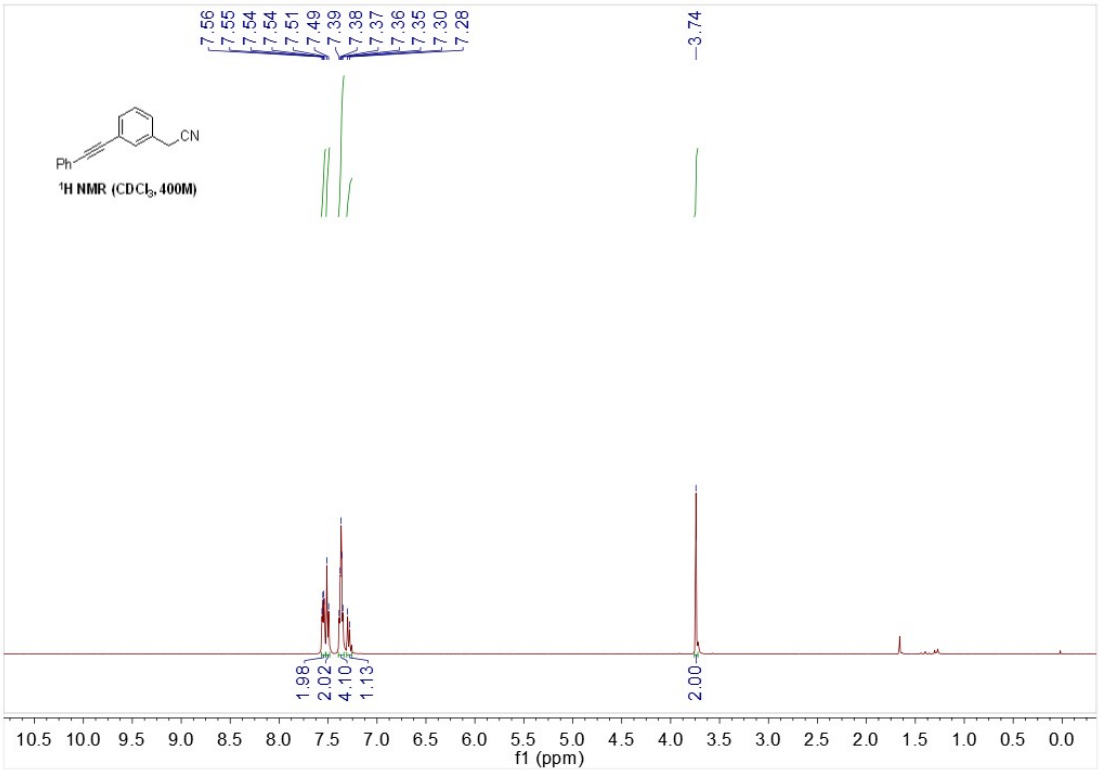
^{13}C NMR (101 MHz, Chloroform-*d*) of compound 52



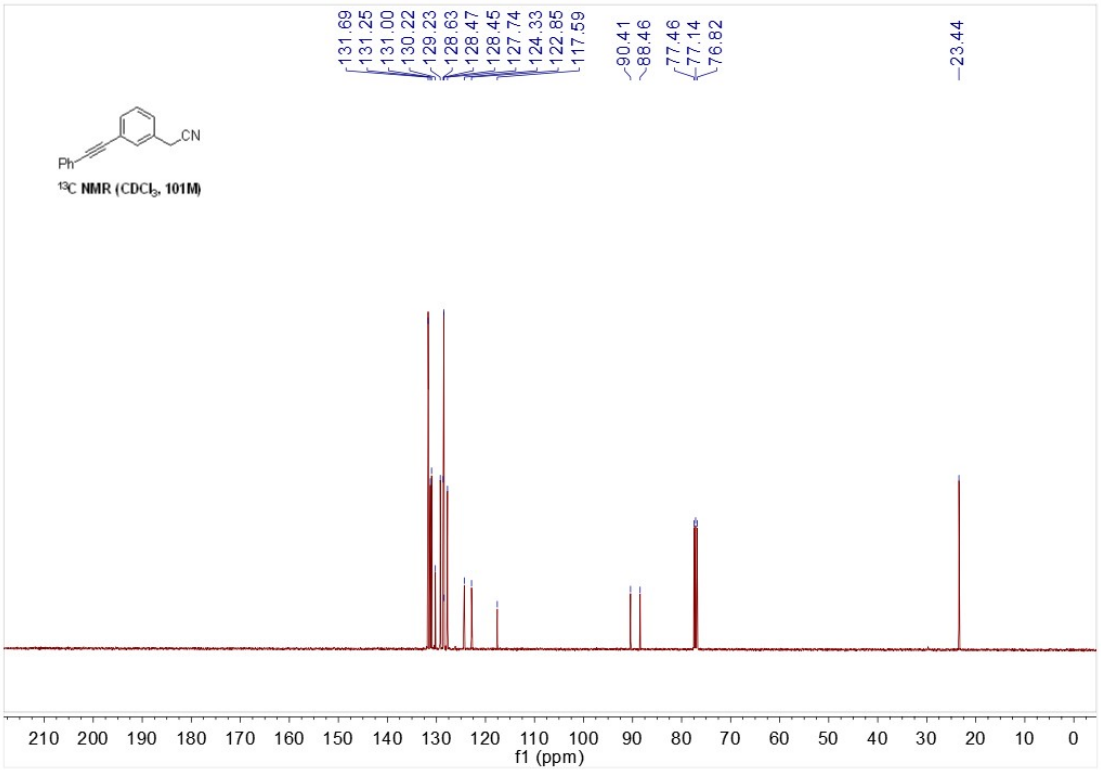
^{11}B NMR (128 MHz, Chloroform-*d*) of compound 52



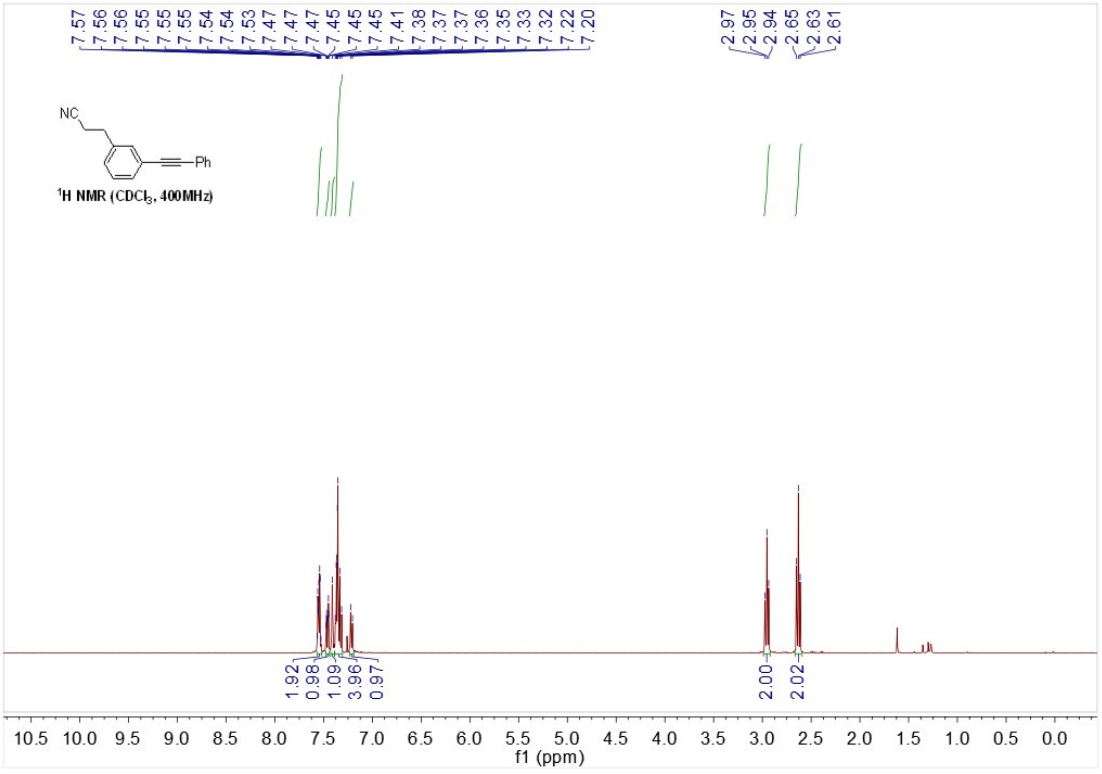
^{1}H NMR (400 MHz, Chloroform-*d*) of compound 53



^{13}C NMR (101 MHz, Chloroform-*d*) of compound 53



^{1}H NMR (400 MHz, Chloroform-*d*) of compound 54



^{13}C NMR (101 MHz, Chloroform-*d*) of compound 54