Programmable late-stage functionalization of bridge-substituted BCP bis-boronates

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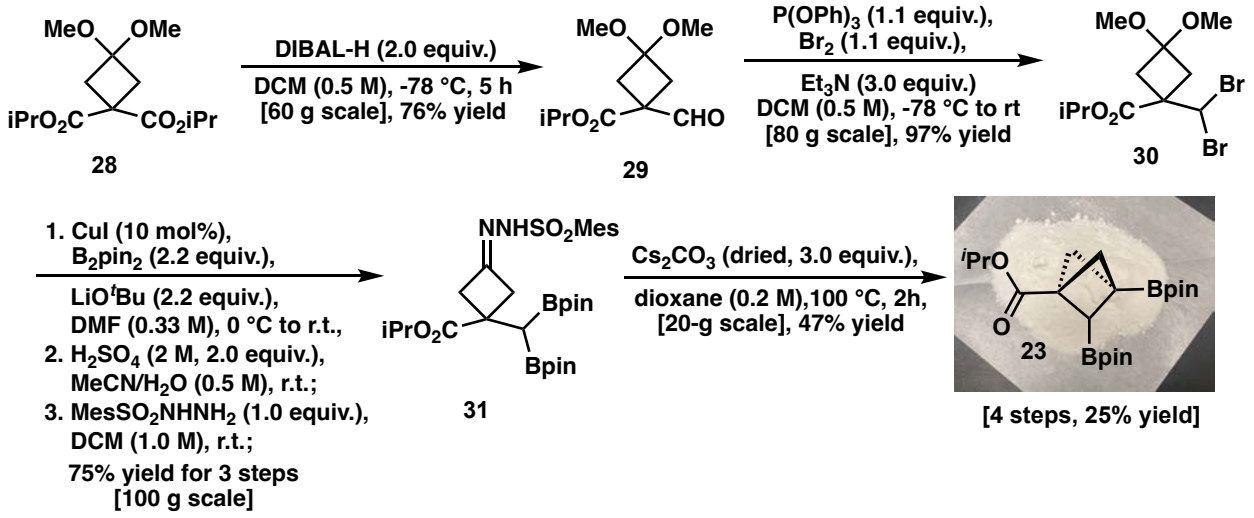
General Experimental

Tetrahydrofuran (THF), diethyl ether (Et_2O), toluene and dichloromethane (CH_2Cl_2) were obtained by passing the previously degassed solvents through an activated alumina column. Dioxane and reagents were purchased at the highest commercial quality and used without further purification. All of the rest reagents were purchased from BLD Pharmatech Co., Sigma-Aldrich, TCI, Synthonix and Combi-Blocks, which were used without further purification. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous material. Reactions were monitored by GC-MS (Rtx-5MS, 30 m, 0.25 mm ID, 0.25 μm), GC-FID (SH-Rxi-5Sil MS, 30m, 0.25 mm ID, 0.25 μm), LC/MS, and thin layer chromatography (TLC). TLC was performed using 0.25 mm E. Merck silica plates (60F-254), using short-wave UV light as the visualizing agent, and phosphomolybdic acid and CAM (H_2SO_4, ammonium molybdate and cerric ammonium sulfate), or $KMnO_4$ and heat as developing agents. NMR spectra were recorded on Bruker Ascend-600 spectrometers, Varian Inova-400 spectrometers and Bruker Ascend-400 spectrometers instruments and are calibrated using residual undeuterated solvent ($CHCl_3$ at 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR; acetone at 2.05 ppm ^{1}H NMR, 29.84, 206.26 ppm ^{13}C NMR; DMSO at 2.50 ppm ^{1}H NMR, 39.52 ppm ^{13}C NMR; methanol at 3.31 ppm ^{1}H NMR, 49.00 ppm ^{13}C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. ^{13}C signals adjacent to boron are generally not observed due to quadrupolar relaxation. Column chromatography was performed using E. Merck silica (60, particle size 0.043–0.063 mm), and preparative TLC was performed on Merck silica plates (60F-254). Melting points were recorded on a Fisher Scientific™ melting point apparatus (12-144) and are uncorrected. Optical rotation data was recorded on a JAS DIP-360 digital polarimeter.

Multi-gram Scale Preparation of BCP BisBoronates (13, 23-27)

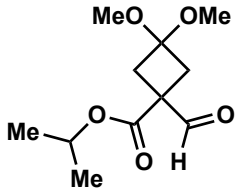
Decagram-scale synthesis of BCP BisBoronates 23 ($R^1 = CO_2{}^iPr$)



Step 1: Synthesis of compound 29

A 2-L three-necked (24/40 joint) round-bottomed flask, equipped with a 6.4 cm Teflon-coated magnetic stir bar, was flame-dried under vacuum, and then cooled to 23 ºC under an atmosphere of argon. Then the flask was charged with diisopropyl 3,3-dimethoxycyclobutane-1,1-dicarboxylate, compound **28**, (103.8 g, 360 mmol, 1.0 equiv.). Methylene chloride (720 mL) was added into the flask and the mixture was cooled in a dried ice-acetone bath (-78 °C) and stirred for 15 minutes. Next a solution of DIBAL-H (720 mL, 1 M in hexanes, 2.0 equiv., pre-cooled at -78 °C) was added dropwise into the flask through a dropping funnel at -78 °C in 2 hours and the mixture was allowed to stir at -78 °C for another 3 hours. After it was confirmed that the starting material, **28**, was consumed through TLC analysis, the reaction was quenched at -78 °C with methanol (24 mL, 720 mmol, 2.0 equiv.). After the reaction was slowly warmed to room temperature, water (29 mL), 20 % NaOH (29 mL) and water (72 mL) was slowly added into the reaction mixture in sequence and the mixture was allowed to stir for another 30 minutes. Next, excess Na_2SO_4 was added to dry the reaction mixture and the suspension was filtered through Celite. Solvents was removed under vaccum and the crude product was purified through flash chromatography (hexanes: ethyl acetate, 5:1) on silica gel to afford 63 g (76%) of the title compound **29**. [1]

Compound 29



***isopropyl 1-formyl-3,3-dimethoxycyclobutane-1-carboxylate* (29)**

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.69 (s, 1H), 5.09 (hept, *J* = 6.3 Hz, 1H), 3.16 (s, 3H), 3.13 (s, 3H), 2.65 (d, *J* = 12.1 Hz, 2H), 2.61 (d, *J* = 11.8 Hz, 2H), 1.25 (d, *J* = 6.3 Hz, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 196.06, 170.25, 98.28, 69.74, 49.73, 48.79, 48.72, 37.30, 21.80 ppm.

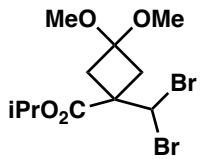
HRMS (ESI-TOF): calc'd for $C_{11}H_{18}O_5$ $[M+Na]^+$: 253.1047, found: 253.1035.

TLC: R_f = 0.31 (5:1 hexanes: ethyl acetate).

Step 2: Synthesis of compound 30

A 2-L three-necked (24/40 joint) round-bottomed flask, equipped with a 6.4 cm Teflon-coated magnetic stir bar, was flame-dried under vacuum, and then cooled to 23 ºC under an atmosphere of argon. Then the flask was charged with triphenyl phosphite (78 mL, 300 mmol, 1.1 equiv.). Methylene chloride (340 mL) was added into the flask and the mixture was cooled to -78°C. Then bromine (15 mL, 300 mmol, 1.1 equiv.) was added slowly into the flask, followed by addition of triethyl amine (140 mL, 1.0 mol, 3.3 equiv.). (*Note: a suspension of the mixture was formed.*) Next, the solution of **29** (63 g, 270 mmol, 1.0 equiv.) in 160 mL methylene chloride was added into the mixture and the reaction was warmed up to room temperature. After it was confirmed that the starting material, **29**, was consumed through TLC analysis, solvent was removed by rotary evaporator and the crude product was purified through flash chromatography (hexanes: ethyl acetate, 20:1) on silica gel to afford 87 g (97%) of the title compound **30**. [2]

Compound 30



***isopropyl 1-(dibromomethyl)-3,3-dimethoxycyclobutane-1-carboxylate* (30)**

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.03 (s, 1H), 5.10 (hept, *J* = 6.3 Hz, 1H), 3.16 (s, 3H), 3.15 (s, 3H), 2.72 – 2.66 (m, 2H), 2.48 – 2.42 (m, 2H), 1.28 (d, *J* = 6.3 Hz, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.41, 96.85, 69.77, 49.87, 48.79, 48.75, 48.57, 40.13, 21.74. ppm.

HRMS (ESI-TOF): calc'd for $C_{11}H_{18}Br_2O_4$ $[M+Na]^+$: 394.9464, found: 394.9457.

TLC: R_f = 0.32 (10:1 hexanes: ethyl acetate).

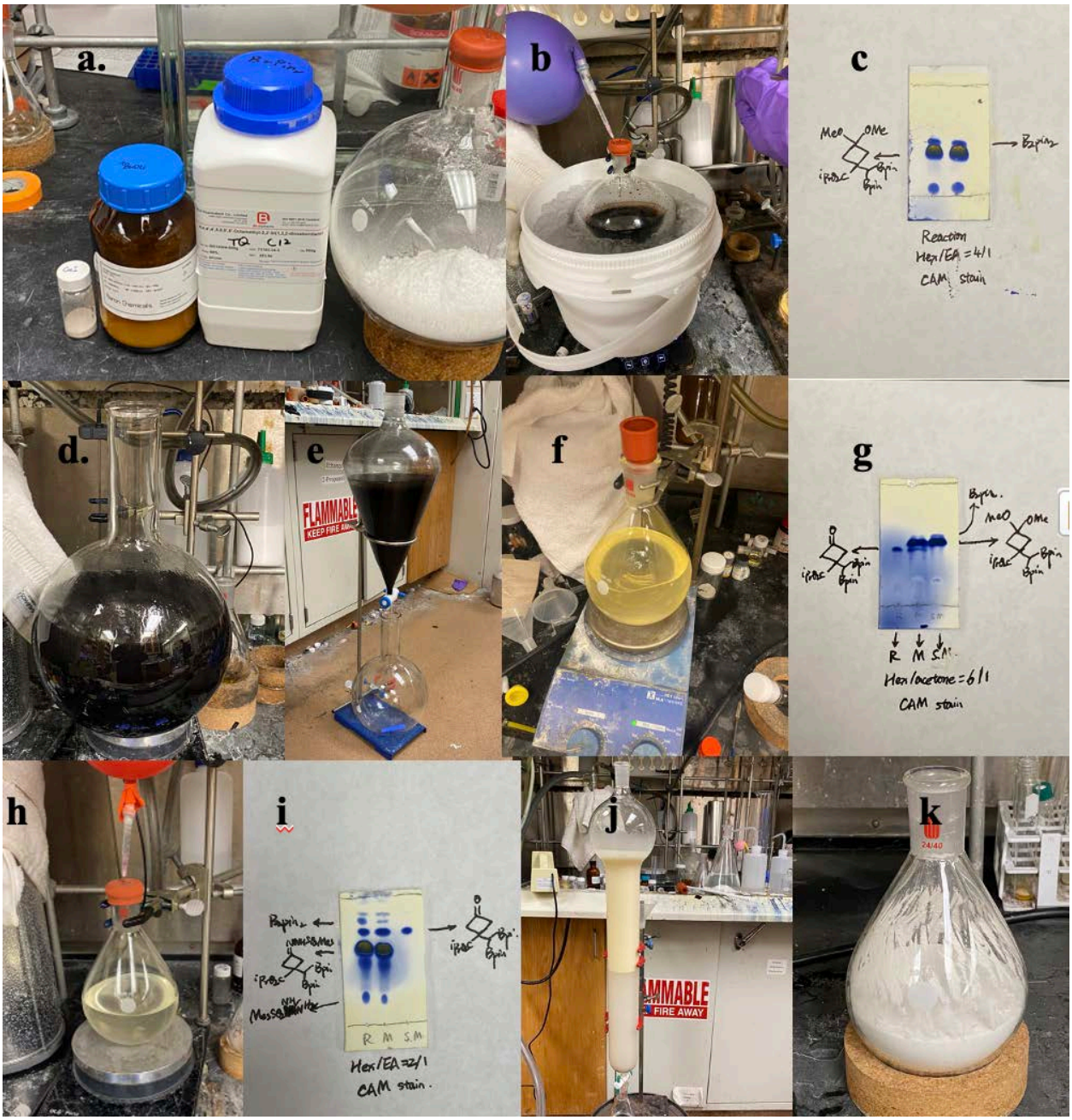
Step 3: Synthesis of compound 31

A 2-L one-necked (24/40 joint) round-bottomed flask, equipped with a 6.4 cm Teflon-coated magnetic stir bar, was flame-dried under vacuum, and then cooled to 23 ºC under an atmosphere of argon. Then the flask was charged with copper(I) iodide (4.88 g, 25.6 mmol, 0.1 equiv.), B_2pin_2 (140 g, 550 mmol, 2.2 equiv.), and lithium tert-butoxide (44.0 g, 550 mmol, 2.2 equiv.). After being evacuated and backfilled with argon from a balloon 3 times, DMF (500 mL) was added into the flask at 0 °C. Then a solution of compound **30** (256 mmol, 95.6 g, 1.0 equiv.) in DMF (250 mL) was added slowly into the mixture at 0 °C in 15 minutes and the reaction mixture was allowed to slowly warm to room temperature and stir for another 1 hour. After it was confirmed that the starting material, **30**, was consumed through TLC analysis, the reaction was filtered through Celite, washed with diethyl ether (200 mL) and quenched at 0 °C with water (500 mL) (*Caution: the quenching process is exothermic*). The mixture was transferred into a 6-L flask and diluted with water (1.5 L) and diethyl ether (300 mL). After the mixture was stirred for 30 minutes at room temperature, the two-phase solution was transferred into a 3-L separation funnel. The aqueous phase is separated and extracted with two 200-mL portions of diethyl ether. The combined organic layers are washed with the mixture of 200 mL water and 200 mL saturated NaCl solution twice, dried over Na_2SO_4, and filtered through Celite. [3]

After solvent was removed by rotary evaporator, the crude product was redissolved in 250 mL acetonitrile in a 1-L flask. 2M H_2SO_4 (256 mL, 2.0 equiv.) was added into the mixture at room temperature and the reaction was allowed to stir for another 1.5 hours. After it was confirmed that the ketal intermediate was consumed through TLC analysis, the crude reaction is concentrated to remove excess acetonitrile. Then diethyl ether (400 mL) and saturated brine (150 mL) is added to

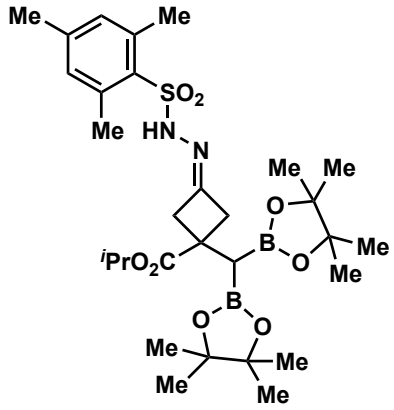
the reaction mixture and the mixture is transferred to a 1-L separatory funnel. The aqueous layer is separated and further extracted with diethyl ether (3 × 150 mL). The combined organic layers are dried over Na_2SO_4, filtered through Celite. Excess solvent was removed by rotary evaporator. The crude product was redissolved in 250 mL methylene chloride in a 500 mL-flask and mesitylene sulfonyl hydrazide (54.9 g, 256 mmol, 1.0 equiv.) was added. The mixture was allowed to stir at room temperature for another 2 hours. After it was confirmed that the ketone intermediate was consumed through TLC analysis, the crude reaction is concentrated to remove excess solvent. The crude product was purified through flash chromatography (hexanes: ethyl acetate, 4:1 to 2:1) on silica gel to afford 116 g (73%) of the title compound **31**.[1]

Graphic Suppoting Information for Synthesis of 31 (step 3)



(a) Reaction equipment setup charged with copper(I) iodide, B_2pin_2, and tBuOLi reagent; (b) The solution of **30** was added into the reaction mixture; (c) TLC plate of the borylation process; (d) The reaction was quenched by water and diluted with diethyl ether; (e) Extraction; (f) Hydrolysis of the crude ketal; (g) TLC plate of hydrolysis process; (h) Condensation of sulfonyl hydrazide; (i) TLC plate of the sulfonyl hydrazone; (j) Purification by column chromatography; (k) The final sulfonyl hydrazone product after being dried.

Compound 31



Isopropyl 1-(bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3-(2-(mesitylsulfonyl)-hydrazineylidene)cyclobutane-1-carboxylate **(31)**

Physical State: white solid.

m.p.: 85-87 °C.

^{1}H NMR (600 MHz, Acetone-d_6) δ 9.17 (s, 1H), 7.02 (s, 2H), 4.90 (hept, J = 6.2 Hz, 1H), 3.23 (ddd, J = 17.6, 3.3, 1.7 Hz, 1H), 3.12 (dt, J = 17.0, 2.5 Hz, 1H), 3.05 – 2.98 (m, 1H), 2.94 (ddd, J = 17.1, 3.4, 1.5 Hz, 1H), 2.65 (s, 6H), 2.28 (s, 3H), 1.22 (s, 1H), 1.19 (d, J = 6.3 Hz, 3H), 1.18 (d, J = 6.6 Hz, 3H), 1.17 (s, 6H), 1.16 (s, 6H), 1.13 (s, 12H) ppm.

^{13}C NMR (151 MHz, Acetone-d_6) δ 176.43, 154.40, 143.07, 140.75, 134.85, 132.46, 83.83, 83.78, 68.79, 45.17, 43.93, 40.62, 25.18, 25.06, 24.74, 23.44, 21.80, 21.76, 20.85 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.98 ppm.

HRMS (ESI-TOF): calc'd for $C_{30}H_{48}B_2N_2O_8S$ $[M+H]^+$: 619.3390, found: 619.3402.

TLC: R_f = 0.30 (3:1 hexanes: ethyl acetate).

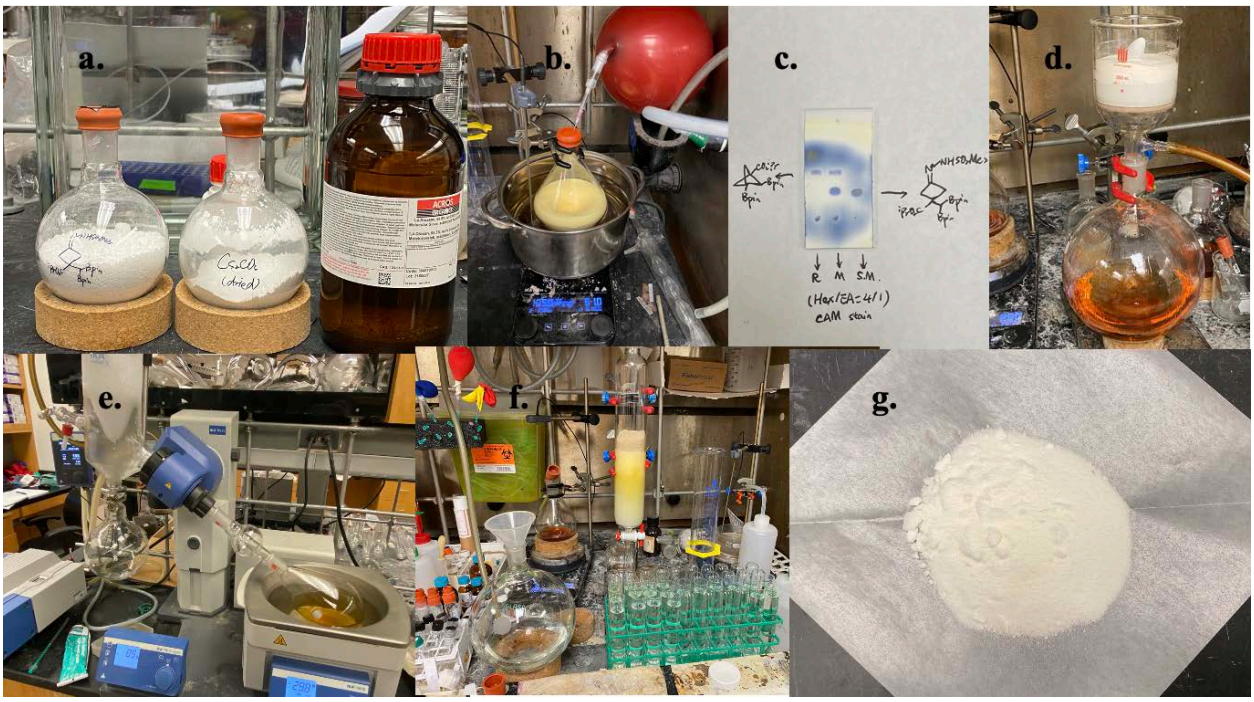
Step 4: Synthesis of 23

A 1-L one-necked (24/40 joint) round-bottomed flask, equipped with a 6.4 cm Teflon-coated magnetic stir bar, was flame-dried under vacuum, and then cooled to 23 ºC under an atmosphere of argon. Then the flask was charged with **31** (61.8 g, 100 mmol, 1.0 equiv.) and dried cesium carbonate (100 g, 300 mmol, 3.0 equiv.). (*Note: Cesium carbonate was dried at 120 °C under vaccum for 18 hours.*) After being evacuated and backfilled with argon from a balloon 3 times, dioxane (500 mL) was added into the flask and the reaction mixture was allowed to stir at 100 °C for 40 minutes. After it was confirmed that the starting material, **31**, was consumed through TLC analysis, the reaction was cooled to room temperature, filtered through Celite, washed with hexanes (500 mL), and concentrated to remove excess solvents. The crude reaction was purified through flash chromatography (hexanes: ethyl acetate, 10:1) on silica gel to afford the title compound **23**, which was further purified through recrystallization in hexanes at -40 °C, affording 19.0 g product (47% yield) with >99% purity as white solids.[1]

Recrystallization procedure: The product (around 21 g) after chromatography was dissolved in hexanes (10 mL) at room temperature and then cooled to -40 °C. After the solution of the product was slowly stirred at -40 °C for 1 h, the suspension was filtered and the white solid was washed with cooled hexanes (5 mL) quickly and dried under vaccum for 1 hour.

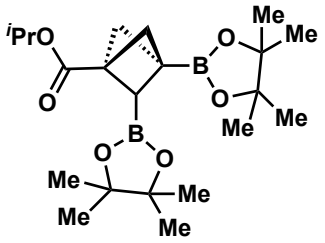
In the second run, following procedures in **step 4** on 87 mmol scale with the rest sulfonyl hydrazone **31**. Purification by flash chromatography (hexanes: ethyl acetate, 10:1) and trituration afforded 18.0 g (47%) of the title compound **23**.

Graphic Supporting Information for Synthesis of 23 (step 4)



(a) Sulfonyl hydrazone **31**, dried cesium carbonate and dioxane; (b) The reaction mixture was stirred at 100 °C; (c) TLC plate of the cyclization reaction; (d) The reaction crude was filtered through Celite; (e) The reaction was concentrated; (f) Purification by column chromatography; (g) The final BCP bisboronate product after recrystallization.

Compound 23



***isopropyl 2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentane-1-carboxylate* (23)**

Physical State: white solid.

m.p.: 41-43 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.93 (hept, *J* = 6.3 Hz, 1H), 2.71 (dd, *J* = 9.4, 2.3 Hz, 1H), 2.14 – 2.08 (m, 2H), 2.03 (dd, *J* = 8.1, 2.2 Hz, 1H), 1.88 (dd, *J* = 8.2, 0.9 Hz, 1H), 1.22 (s, 12H), 1.21 (s, 6H), 1.20 (s, 6H), 1.19 (d, *J* = 2.9 Hz, 3H), 1.18 (d, *J* = 3.0 Hz, 3H) ppm.

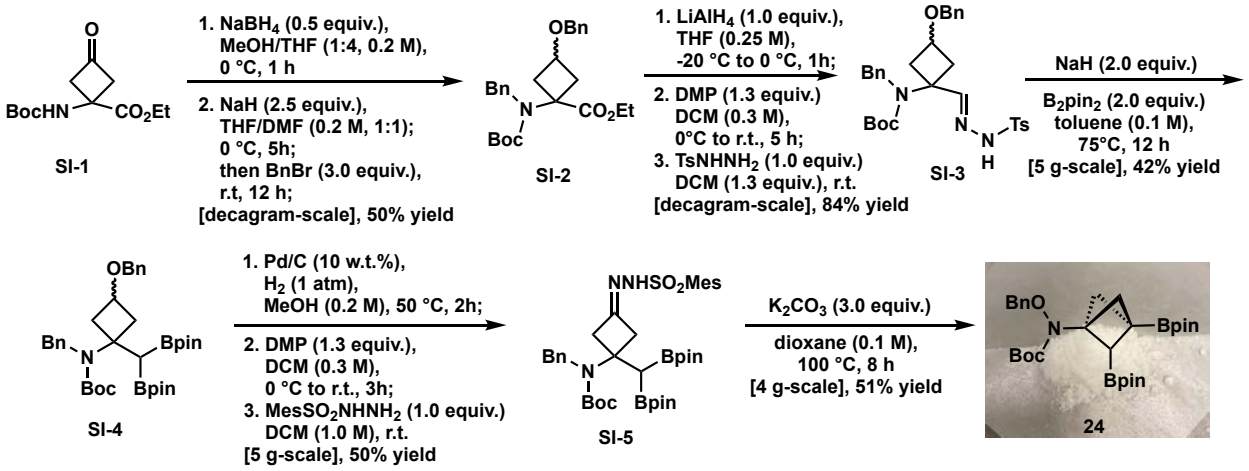
^{13}C NMR (151 MHz, $CDCl_3$) δ 169.49, 83.55, 83.10, 67.44, 55.81, 50.75, 44.87, 24.89, 24.87, 24.84, 24.79, 21.93 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.18 ppm.

HRMS (ESI-TOF): calc'd for $C_{21}H_{36}B_2O_6$ $[M+H]^+$: 407.2771, found: 407.2778.

TLC: R_f = 0.32 (5:1 hexanes: ethyl acetate).

Gram-scale synthesis of BCP BisBoronates 24 (R^1 = NBnBoc)



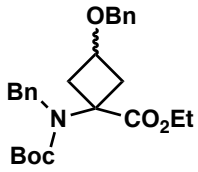
Step 1: Synthesis of SI-2.

A flame-dried 1-L round-bottom flask charged with ethyl 1-([(tert-butoxy)carbonyl]amino)-3-oxocyclobutane-1-carboxylate, **SI-1** (25 g, 100 mmol, 1.0 equiv.) dissolved in THF/methanol (500 mL, 4:1) was cooled to 0 °C. Then $NaBH_4$ (1.9 g, 50 mmol, 0.5 equiv.) was added slowly to the mixture at 0 °C and the reaction was allowed to stir at the same temperature for 1 h. After it was confirmed that the starting material, **SI-1**, was consumed totally, the reaction was quenched by water (1.0 mL). After excess solvent was removed, the mixture was diluted with ethyl acetate (200 mL) and water (200 mL) and transferred into a 1-L separatory funnel. The aqueous layer is separated and further extracted with ethyl acetate (3 × 100 mL). The combined organic layers are dried over Na_2SO_4, filtered through Celite. Excess solvent was removed by rotary evaporator. The crude alcohol was used without further purification.

The crude alcohol was dissolved in THF/DMF (500 mL, 1:1) and the mixture was cooled to 0 °C. NaH (10.0 g, 250 mmol, 2.5 equiv.) was added slowly to the reaction at 0 °C and the mixture was warmed to room temperature and stirred for 3 hours. After there is no bubble released, benzyl bromide (36 mL, 300 mmol, 3.0 equiv.) was added to the reaction at 0 °C and the mixture was allowed to stir at room temperature for around 12 hours. After it was confirmed that the alcohol intermediate was consumed totally, water (5.4 mL) was added to quench the reaction. Excess solvent was removed by rotary evaporator and the mixture was diluted with water (500 mL) and diethyl ether (200 mL) and then transferred into a 1-L separation funnel. The aqueous phase is separated and extracted with two 100-mL portions of diethyl ether. The combined organic layers

are washed with the mixture of 100 mL water and 100 mL saturated NaCl solution twice, dried over Na_2SO_4, and filtered through Celite. The crude product was purified through flash chromatography (hexanes: ethyl acetate, 4:1) on silica gel to afford 21.9 g (50%) of the title compound **SI-2**.

Compound SI-2



ethyl 1-(benzyl(tert-butoxycarbonyl)amino)-3-(benzyloxy)cyclobutane-1-carboxylate **(SI-2)**

Note: ^{1}H NMR showed the presence of diastereoisomers and rotamers.

Physical State: yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 – 7.14 (m, 10H), 4.49 (brs, 2H), 4.17 (brs, 2H), 4.12 – 4.06 (m, 2H), 3.65 (brs, 1H), 2.52 (brs, 4H), 1.35 (s, 9H), 1.24 – 1.13 (m, 3H) ppm. *Note: The complexity of the ^{1}H NMR is attributed to the diastereomerism and rotating isomerism*.

HRMS (ESI-TOF): calc'd for $C_{26}H_{33}NO_5$ $[M+H]^+$: 440.2432, found: 440.2428.

TLC: R_f = 0.68 (3:1 hexanes: ethyl acetate).

Step 2: Synthesis of SI-3.

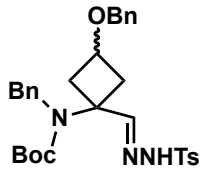
A flame-dried round-bottom flask charged with **SI-2** (11.5 g, 25 mmol, 1.0 equiv.) dissolved in THF (100 mL) was cooled to -20 °C. $LiAlH_4$ (1.0 g, 26 mmol, 1.05 equiv.) was added slowly to the solution at -20 °C and the reaction was allowed to warm to 0 °C and stir at 0 °C for 1 hour. After it was confirmed that **SI-2** was consumed totally, the reaction was quenched at 0 °C with water (1.0 mL), followed by 20% NaOH (1.0 mL) and water (3.0 mL) and the mixture was stirred at 0 °C for 30 min. Then excess Na_2SO_4 was added, and the suspended solution was stirred at room temperature for another 1 hour. The mixture was filtered through Celite, and the solvent was removed under high vacuum. The crude alcohol was used without further purification.

The crude alcohol was redissolved in methylene chloride (75 mL) and Dess–Martin periodinane (13.8 g, 32.5 mmol, 1.3 equiv.) was added to mixture at 0 °C. The reaction was allowed to warm to room temperature and stir for 2 hours. After it was confirmed that the alcohol intermediate was

consumed totally, the reaction was quenched by excess saturated $NaHCO_3$ solution and $Na_2S_2O_3$ solution and extracted with methylene chloride (100 mL) three times. The organic phase was separated, washed with brine, dried over Na_2SO_4 and evaporated. The crude aldehyde was used without further purification.

The aldehyde was dissolved in 25 mL methylene chloride and then p-toluenesulfonyl hydrazide (5.2 g, 27.5 mmol, 1.1 equiv.) was added. The mixture was allowed to stir at room temperature for another 1 hours. After it was confirmed that the aldehyde was consumed through TLC analysis, the crude reaction is concentrated to remove excess solvent. The crude product was purified through flash chromatography (hexanes: ethyl acetate, 3:1) on silica gel to afford 12.0 g (85%) of the title compound **SI-3**.

Compound SI-3



***tert-butyl benzyl(3-(benzyloxy)-1-((2-tosylhydrazineylidene)methyl)cyclobutyl)carbamate* (SI-3)**

Note: ^{1}H NMR showed the presence of diastereoisomers (1/0.4) and trans/cis isomers. The ^{1}H NMR of the main isomer is given.

Physical State: yellow oil.

^{1}H NMR (600 MHz, Acetone-*d*^{6}): δ 9.81 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.58 (s, 1H), 7.38 – 7.14 (m, 12H), 4.25 (s, 2H), 4.15 (s, 2H), 3.87 (tt, *J* = 7.0, 4.2 Hz, 1H), 2.58 (dd, *J* = 13.7, 6.9 Hz, 2H), 2.34 (s, 3H), 2.29 (dd, *J* = 13.8, 4.1 Hz, 2H), 1.31 (s, 9H) ppm.

HRMS (ESI-TOF): calc'd for $C_{31}H_{37}N_3O_5S$ $[M+Na]^+$: 586.2346, found: 586.2344.

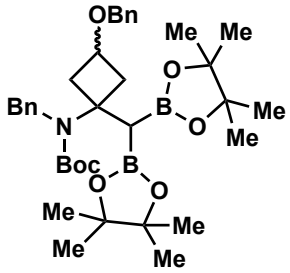
TLC: R_f = 0.32 (3:1 hexanes: ethyl acetate).

Step 3: Synthesis of SI-4

A dry round-bottom 500-mL flask charged with **SI-3** (12.0 g, 21 mmol, 1.0 equiv.), 60% NaH (1.68 g, 42 mmol, 2.0 equiv.) and B_2pin_2 (10.6 g, 42 mmol, 2.0 equiv.) was degassed and filled with argon for three times. Toluene (210 mL) was added, and the mixture was heated at 75 °C for 5 h.

After it was confirmed that the starting material **SI-3** was consumed totally, the reaction was cooled to room temperature and the suspension was filtered by Celite and washed by diethyl ether (200 mL). After solvent was removed by rotary evaporator from the filtrate, the crude product was flash chromatography (hexanes: ethyl acetate, 4:1) on silica gel to afford 5.3 g (42%) of the title compound **SI-4**.[4]

Compound SI-4



***tert-butyl benzyl(3-(benzyloxy)-1-(bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclobutyl)carbamate* (SI-4)**

Note: the main isomer was isolated and characterized.

Physical State: white solid.

m.p.: 99-101 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25 – 7.04 (m, 10H), 4.59 (s, 2H), 4.07 (s, 2H), 3.48 – 3.33 (m, 1H), 2.69 – 2.63 (m, 2H), 2.36 – 2.28 (m, 2H), 2.09 (s, 1H), 1.38 (s, 9H), 1.17 (s, 12H), 1.17 (s, 12H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.90, 138.80, 128.37, 128.22, 127.81, 127.29, 126.44, 126.40, 83.18, 69.66, 68.77, 49.84, 28.64, 25.05, 24.88 ppm. *Note: C*H(Bpin)$_2$*,* N*C*(cBu)(CH(Bpin)$_2$)*,* N*C*(O)OtBu*,* N*C*H$_2$Ph *and* Me$_3$*C were not observed*.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.66 ppm.

HRMS (ESI-TOF): calc'd for $C_{36}H_{53}B_2NO_7$ $[M+H]^+$: 634.4081, found: 634.4096.

TLC: R_f = 0.68 (3:1 hexanes: ethyl acetate).

Step 4: Synthesis of SI-5

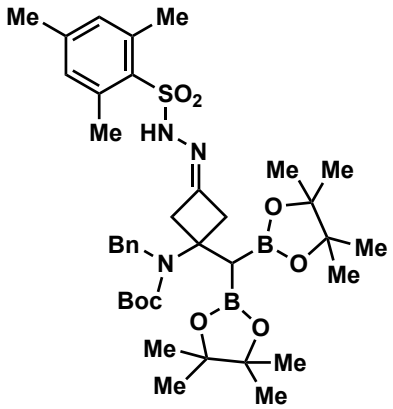
A dry 250-mL round-bottom flask was charged with **SI-4** (7 g, 11 mmol, 1.0 equiv.) and Pd/C (10 w.t.%, 350 mg) and methanol (70 mL) was added then. After the flask was degassed and refilled with hydrogen for three times. The reaction mixture was heated at 50 °C for 2 h. After it was

confirmed that the starting material, **SI-4**, was consumed totally, the mixture was cooled to room temperature, filtered through Celite and concentrated. The crude alcohol was used without further purification.

The crude alcohol was redissolved in methylene chloride (40 mL) and Dess–Martin periodinane (6.4 g, 15 mmol, 1.3 equiv.) was added to mixture at 0 °C. The reaction was allowed to warm to room temperature and stir for 2 hours. After it was confirmed that the alcohol intermediate was consumed totally, the reaction was quenched by excess saturated Na_2CO_3 solution and $Na_2S_2O_3$ solution and extracted with methylene chloride (50 mL) three times. The organic phase was separated, washed with brine, dried over Na_2SO_4 and evaporated. The crude ketone was used without further purification.

The ketone was dissolved in 25 mL methylene chloride and then mesitylsulfonyl hydrazide (2.6 g, 12 mmol, 1.1 equiv.) was added. The mixture was allowed to stir at room temperature for another 3-5 hours. After it was confirmed that the aldehyde was consumed through TLC analysis, the crude reaction is concentrated to remove excess solvent. The crude product was purified through flash chromatography (hexanes: ethyl acetate, 3:1) on silica gel to afford 4.48 g (55%) of the title compound **SI-5**.

Compound SI-5



tert-butyl benzyl(1-(bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3-(2-(mesityl sulfonyl)hydrazineylidene)cyclobutyl)carbamate **(SI-5)**

Physical State: white solid.

m.p.: 161-163 °C.

^{1}H NMR (600 MHz, Acetone-d_6): δ 9.08 (s, 1H), 7.27 (t, J = 7.6 Hz, 2H), 7.22 – 7.15 (m, 3H), 6.98 (s, 2H), 4.71 – 4.52 (m, 2H), 3.28 – 3.01 (m, 4H), 2.57 (s, 6H), 2.28 (s, 3H), 2.10 (s, 1H), 1.55 – 1.29 (m, 9H), 1.25 – 1.12 (m, 24H) ppm.

^{13}C NMR (151 MHz, Acetone-d_6): δ 142.98, 141.79, 140.73, 140.71, 135.00, 134.96, 132.44, 129.24, 127.21, 126.32, 84.09, 84.03, 50.70, 28.53, 25.21, 25.04, 25.01, 24.96, 23.43, 20.85 ppm. *Note: C*H(Bpin)$_2$*,* N*C*(cBu)(CH(Bpin)$_2$)*,* N*C*(O)OtBu*,* N*C*H$_2$Ph *and* Me$_3$*C were not observed*.

^{11}B NMR (128 MHz, CDCl$_3$): δ 37.71 ppm.

HRMS (ESI-TOF): calc'd for $C_{38}H_{57}B_2N_3O_8S$ $[M+H]^+$: 738.4125, found: 738.4148.

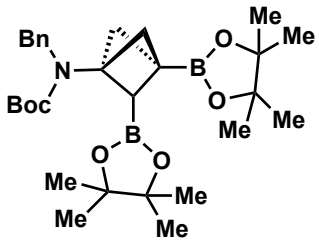
TLC: R_f = 0.40 (3:1 hexanes: ethyl acetate).

Step 5: Synthesis of 24

A 250-mL one-necked (24/40 joint) round-bottomed flask, equipped with a Teflon-coated magnetic stir bar, was flame-dried under vacuum, and then cooled to 23 ºC under an atmosphere of argon. Then the flask was charged with **SI-5** (4.48 g, 6 mmol, 1.0 equiv.) and dried potassium carbonate (2.76 g, 20 mmol, 3.3 equiv.). (*Note: Potassium carbonate was ground and dried at 120 °C under vaccum for 18 hours.*) After being evacuated and backfilled with argon from a balloon 3 times, dioxane (60 mL) was added into the flask and the reaction mixture was allowed to stir at 105 °C for 8 hours. After it was confirmed that the starting material, **SI-5**, was consumed through TLC analysis, the reaction was cooled to room temperature, filtered through Celite, washed with diethyl ether (200 mL), and concentrated to remove excess solvents. The crude reaction was purified through flash chromatography (hexanes: ethyl acetate, 6:1) on silica gel to afford the title compound **24**, which was further purified through recrystallization in hexanes at -40 °C. affording 1.8 g product (57% yield) with >99% purity as white solids.[1]

Recrystallization procedure: The product (around 2.5 g) after chromatography was dissolved in hexanes (2.0 mL) at room temperature and then cooled to -40 °C. After the solution of the product was slowly stirred at -40 °C for 40 minutes, the suspension was filtered and the white solid was washed with cooled hexanes (1.0 mL) quickly and dried under vaccum for 1 hour.

Compound 24



***tert-butyl benzyl(2,3-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)carbamate* (24)**

Physical State: white solid.

m.p.: 89-91 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 – 7.12 (m, 5H), 4.47 (brs, 2H), 2.56 (s, 1H), 2.12 (dd, *J* = 9.5, 1.4 Hz, 1H), 2.06 – 1.97 (m, 3H), 1.47 (s, 9H), 1.21 (s, 12H), 1.20 (s, 12H) ppm.

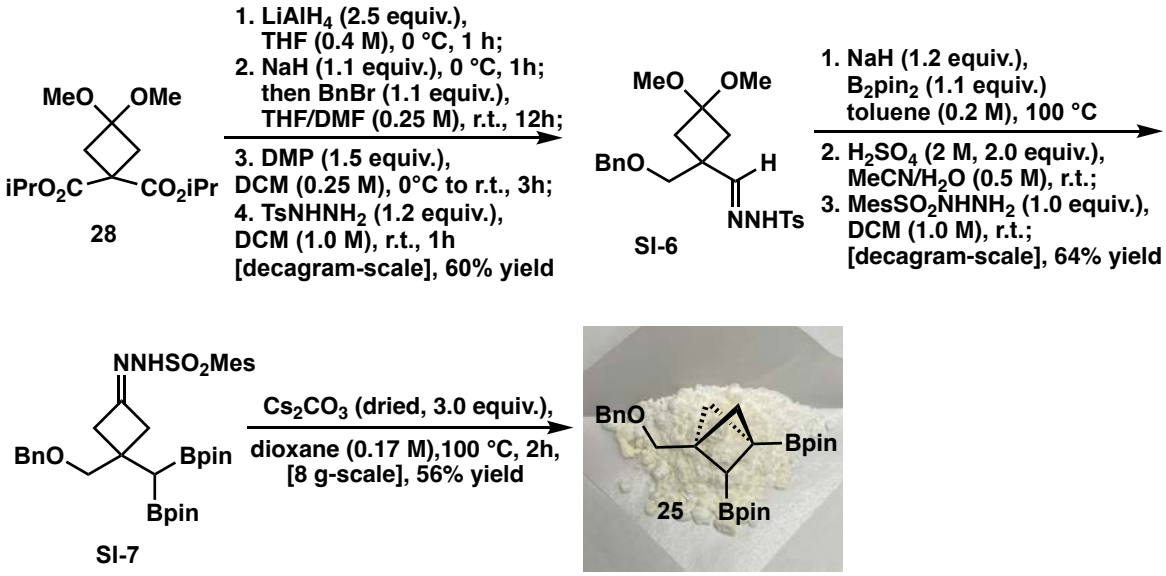
^{13}C NMR (151 MHz, $CDCl_3$) δ 140.12, 128.26, 126.92, 126.51, 83.48, 83.07, 79.83, 52.68, 48.28, 28.69, 25.00, 24.95, 24.84, 24.81 ppm. *Note:* N*C*(O)OtBu*,* BocBnN*C,* N*C*H_2Ph*,* Bpin*C*H*, and* Bpin*C were not observed*.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.94 ppm.

HRMS (ESI-TOF): calc'd for $C_{29}H_{46}B_2NO_6$ $[M+H]^+$: 526.3506, found: 526.3518.

TLC: R_f = 0.68 (3:1 hexanes: ethyl acetate).

Gram-scale synthesis of BCP BisBoronates 25 (R^1 = CH_2OBn)



Step 1: Synthesis of SI-6

To a solution of diisopropyl 3,3-dimethoxycyclobutane-1,1-dicarboxylate, **28**, (115.2 g, 400 mmol, 1.0 equiv.) in dried THF (1.0 L) was added $LiAlH_4$ (38 g, 1.0 mmol, 2.5 equiv.) at 0 °C. The mixture was allowed to warm up to room temperature and stirred for 3 hours. After it was confirmed that the start material, **SI-6**, was totally consumed, water (38 mL) was slowly added at 0 °C, followed by 20% w.t. NaOH (38 mL) and water (95 mL), and the mixture was stirred at 0 °C for 30 min. Then excess Na_2SO_4 was added, and the suspended solution was stirred at room temperature for another 1 hour. The mixture was filtered through Celite, and the solvent was removed under high vacuum. The crude alcohol was used without further purification. The crude yield (90% from **28**) was calculated by ^{1}H NMR with dibromomethane as inner standard.

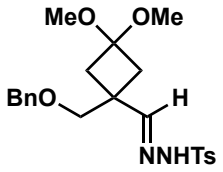
To a solution of the crude alcohol in THF/DMF (800 mL, 1:1) was added NaH (16.0 g, 400 mmol, 1.0 equiv.) slowly at 0 °C. (*Caution: Hydrogen was released.*) After the reaction was stirred for 1 hour at room temperature, benzyl bromide (52 mL, 440 mmol, 1.1 equiv.) was added and the mixture was allowed to stir for 12 hours at room temperature. After it was confirmed that the diol intermediate was totally consumed, the reaction was quenched with water (10 mL) at 0 °C. Excess solvent was removed by rotary evaporator and the mixture was diluted with water (500 mL) and diethyl ether (200 mL) and then transferred into a 1-L separation funnel. The aqueous phase is separated and extracted with two 200-mL portions of diethyl ether. The combined organic layers

are washed with the mixture of 200 mL water and 200 mL saturated NaCl solution twice, dried over Na_2SO_4, and filtered through Celite. The crude yield (75% from **28**) was calculated by ^1H NMR with dibromomethane as inner standard.

After solvent was removed by rotary evaporator, the crude product was redissolved in methylene chloride (1.0 L) and Dess–Martin periodinane (153.5 g, 360 mmol, 0.9 equiv.) was added to mixture at 0 °C. The reaction was allowed to warm to room temperature and stir for 2 hours. After it was confirmed that the alcohol intermediate was consumed totally, the reaction was quenched by excess saturated Na_2CO_3 solution and $Na_2S_2O_3$ solution and extracted with methylene chloride (200 mL) three times. The organic phase was separated, washed with brine, dried over Na_2SO_4 and evaporated. The crude aldehyde was used without further purification. The crude yield (62.5% from **28** was calculated by ^1H NMR with dibromomethane as inner standard.

The aldehyde was dissolved in 100 mL methylene chloride and then p-toluenesulfonyl hydrazide (56 g, 300 mmol, 0.75 equiv.) was added. The mixture was allowed to stir at room temperature for another 1 hours. After it was confirmed that the aldehyde was consumed through TLC analysis, the crude reaction is concentrated to remove excess solvent. The crude product was purified through flash chromatography (hexanes: ethyl acetate, 3:1) on silica gel to afford 103.0 g (60% from **28**) of the title compound **SI-6**. *Cis/trans-isomerism (1/1.8) was observed. The 1H NMR characterization of main isomer was provided.*

Compound SI-6



N'-((1-((benzyloxy)methyl)-3,3-dimethoxycyclobutyl)methylene)-4-methylbenzenesulfono-hydrazide **(SI-6)**

Physical State: yellow oil.

^1H NMR (600 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.09 (m, 8H), 4.43 (s, 2H), 3.52 (s, 2H), 3.06 (s, 3H), 3.02 (s, 3H), 2.37 (s, 3H), 2.24 (d, *J* = 9.0 Hz, 2H), 2.11 (d, *J* = 13.3 Hz, 2H) ppm.

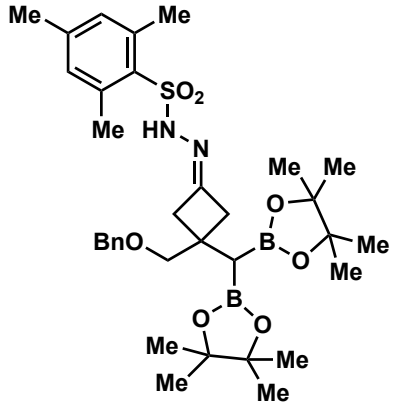
HRMS (ESI-TOF): calc'd for $C_{22}H_{28}N_2O_5S$ $[M+H]^+$: 433.1792, found: 433.1786.
TLC: R_f = 0.23 (2:1 hexanes: ethyl acetate).

Step 2: Synthesis of SI-7

A dry 1.0-L round-bottom flask charged with **SI-6** (103.0 g, 238 mmol, 1.0 equiv.) was degassed and filled with argon for three times. Toluene (1.0 L) was added, then 60% NaH (10.5 g, 262 mmol, 1.1 equiv.) was added in small portions and the mixture was stirred at room temperature for 1 h. A solution of B_2pin_2 (90 g, 357 mmol, 1.5 equiv.) in toluene (200 mL) was added. Then the reaction mixture was heated at 100 °C for 1 h.[4] After cooling to room temperature, the suspension was filtered by Celite, and washed by diethyl ether (500 mL). After solvent was removed by rotary evaporator from the filtrate, the crude product was redissolved in 250 mL acetonitrile in a 1-L flask. 2 M H_2SO_4 (250 mL, 2.0 equiv.) was added into the mixture at room temperature and the reaction was allowed to stir for another 2 hours. After it was confirmed that the ketal intermediate was totally consumed, the crude reaction is concentrated to remove excess acetonitrile. Then diethyl ether (600 mL) and saturated brine (500 mL) is added to the reaction mixture and the mixture is transferred to a separatory funnel. The aqueous layer is separated and further extracted with diethyl ether (3 × 250 mL). The combined organic layers are dried over Na_2SO_4, filtered through Celite. Excess solvent was removed by rotary evaporator.

The crude ketone was redissolved in 250 mL methylene chloride in a 500 mL-flask and mesitylene sulfonyl hydrazide (55 g, 262 mmol, 1.1 equiv.) was added. The mixture was allowed to stir at room temperature for another 3-5 hours. After it was confirmed that the ketone intermediate was consumed through TLC analysis, the crude reaction is concentrated to remove excess solvent. The crude product was purified through flash chromatography (hexanes: ethyl acetate, 4:1) on silica gel to afford 100 g (64%) of the title compound **SI-7**.

Compound SI-7



***N'-(3-((benzyloxy)methyl)-3-(bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)cyclobutylidene)-2,4,6-trimethylbenzenesulfonohydrazide* (SI-7)**

Physical State: white solid.

m.p.: 198-200 °C.

^{1}H NMR (600 MHz, Acetone-d_6) δ 9.02 (s, 1H), 7.36 – 7.30 (m, 4H), 7.29 – 7.23 (m, 1H), 7.00 (s, 2H), 4.50 (s, 2H), 3.35 (d, J = 8.9 Hz, 1H), 3.33 (d, J = 8.9 Hz, 1H), 2.88 – 2.81 (m, 1H), 2.81 – 2.77 (m, 1H), 2.74 (ddd, J = 17.3, 3.1, 2.1 Hz, 1H), 2.66 (ddd, J = 17.3, 3.1, 2.1 Hz, 1H),2.63 (s, 6H), 2.27 (s, 3H), 1.15 (s, 6H), 1.15 (s, 6H), 1.14 (s, 1H), 1.12 (s, 6H), 1.11 (s, 6H) ppm.

^{13}C NMR (151 MHz, Acetone-d_6) δ 156.62, 142.96, 140.67, 139.71, 134.90, 132.41, 129.07, 128.36, 128.17, 83.67, 83.65, 78.27, 73.50, 43.34, 42.10, 36.28, 25.20, 25.08, 24.74, 23.39, 20.84 ppm.

^{11}B NMR (128 MHz, Acetone-d_6): δ 33.11 ppm.

HRMS (ESI-TOF): calc'd for $C_{34}H_{50}B_2N_2O_7S$ $[M+H]^+$: 653.3598, found: 653.3602.

TLC: R_f = 0.37 (3:1 hexanes: ethyl acetate).

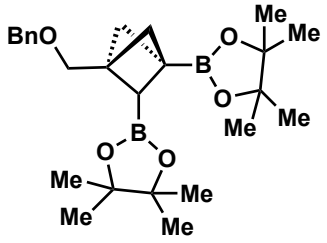
Step 3: Synthesis of 25

A 500-mL one-necked (24/40 joint) round-bottomed flask, equipped with a Teflon-coated magnetic stir bar, was flame-dried under vacuum, and then cooled to 23 ºC under an atmosphere of argon. Then the flask was charged with **SI-7** (22 g, 33 mmol, 1.0 equiv.) and dried cesium carbonate (33 g, 100 mmol, 3.0 equiv.). (*Note: Cesium carbonate was dried at 120 °C under vaccum for 18 hours.*) After being evacuated and backfilled with argon from a balloon 3 times, dioxane (200 mL) was added into the flask and the reaction mixture was allowed to stir at 100 °C

for 2 hours. After it was confirmed that the starting material, **SI-7**, was consumed through TLC analysis, the reaction was cooled to room temperature, filtered through Celite, washed with hexanes (500 mL), and concentrated to remove excess solvents. The crude reaction was purified through flash chromatography (hexanes: ethyl acetate, 10:1) on silica gel to afford the title compound **25**, which was further purified through recrystallization in hexanes at -40 °C. affording 8.3 g product (56% yield) with >99% purity as white solids.[1]

Recrystallization procedure: The product (around 10 g) after chromatography was dissolved in hexanes (6 mL) at room temperature and then cooled to -40 °C. After the solution of the product was slowly stirred at -40 °C for 30 minutes, the suspension was filtered, and the white solid was washed with cooled hexanes (4 mL) quickly and dried under vaccum for 1 hour.

Compound 25



***2,2'-(3-((benzyloxy)methyl)bicyclo[1.1.1]pentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)* (25)**

Physical State: colorless crystal.

m.p.: 65-67 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 – 7.28 (m, 4H), 7.24 (dd, *J* = 8.2, 5.9 Hz, 1H), 4.52 (s, 2H), 3.38 (d, *J* = 11.0, 1H), 3.36 (d, *J* = 11.0, 1H), 2.38 (dd, *J* = 9.7, 2.3 Hz, 1H), 1.93 (dd, *J* = 9.7, 1.5 Hz, 1H), 1.88 (s, 1H), 1.82 (dd, *J* = 8.3, 2.3 Hz, 1H), 1.67 (d, *J* = 8.2 Hz, 1H), 1.23 (s, 12H), 1.20 (s, 6H), 1.19 (s, 6H) ppm.

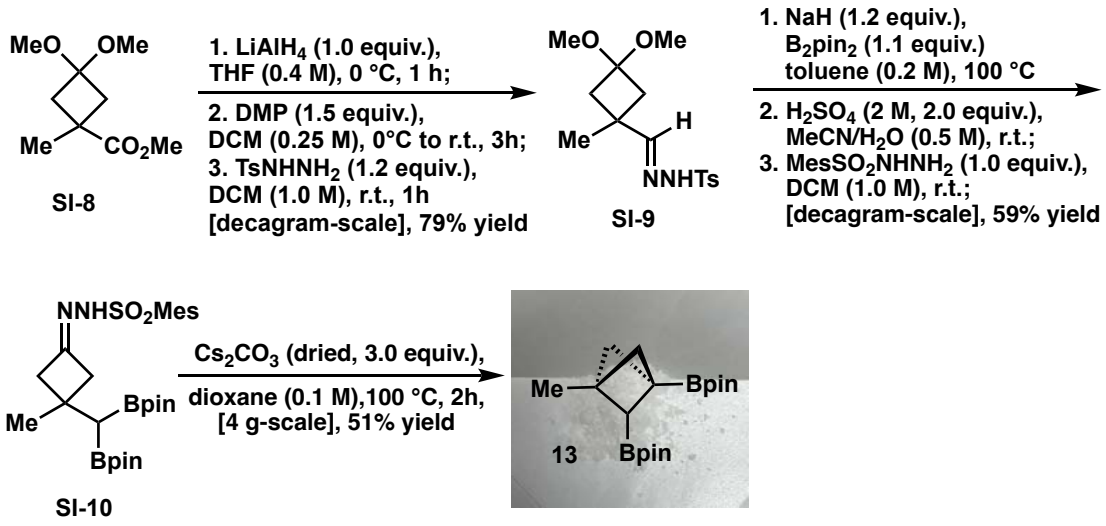
^{13}C NMR (151 MHz, $CDCl_3$) δ 139.14, 128.32, 127.55, 127.37, 83.35, 82.91, 72.88, 71.28, 54.69, 49.02, 46.50, 24.99, 24.90, 24.87, 24.84 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.92 ppm.

HRMS (ESI-TOF): calc'd for $C_{25}H_{38}B_2O_5$ $[M+H]^+$: 441.2978, found: 441.2996.

TLC: R_f = 0.54 (5:1 hexanes: ethyl acetate).

Gram-scale synthesis of BCP BisBoronates 13 (R^1 = Me)



Step 1: Synthesis of SI-9

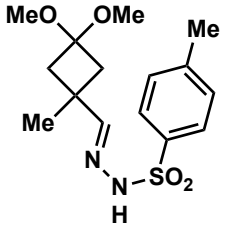
To a solution of methyl 3,3-dimethoxy-1-methyl-cyclobutanecarboxylate, **SI-8**, (10.8 g, 57 mmol, 1.0 equiv.) in diethyl ether (160 mL) was added $LiAlH_4$ (3.3 g, 85.5 mmol, 1.5 equiv.) at 0 °C. The mixture was allowed to warm up to room temperature. After it was confirmed that the start material, **SI-8**, was totally consumed, water (3.3 mL) was slowly added at 0 °C, followed by 20% w.t. NaOH (3.3 mL) and water (10 mL), and the mixture was stirred at 0 °C for 30 min. Then excess Na_2SO_4 was added, and the suspended solution was stirred at room temperature for another 1 hour. The mixture was filtered through Celite, and the solvent was removed under high vacuum. The crude alcohol was used without further purification.

To a solution of the crude alcohol in methylene chloride (250 mL) was added Dess–Martin periodinane (25 g, 60 mmol, 1.05 equiv.) at 0 °C and the reaction mixture was allowed to warm to room temperature and stir for 2 hours. Then after it was confirmed that the alcohol was consumed totally, the reaction was quenched by excess saturated Na_2CO_3 solution and $Na_2S_2O_3$ solution and extracted with methylene chloride (100 mL) three times. The organic phase was separated, washed with brine, dried over Na_2SO_4 and evaporated. The crude aldehyde was used without further purification.

The aldehyde was dissolved in methylene chloride (60 mL) and then p-toluenesulfonyl hydrazide (11.2 g, 60 mmol, 1.05 equiv.) was added. The mixture was allowed to stir at room temperature

for another 1 hour. After it was confirmed that the aldehyde was consumed through TLC analysis, the crude reaction is concentrated to remove excess solvent. The crude product was purified through flash chromatography (hexanes: ethyl acetate, 3:1) on silica gel to afford 14.7 g (79%) of the title compound **SI-9**.

Compound SI-9



N'-((3,3-dimethoxy-1-methylcyclobutyl)methylene)-4-methylbenzenesulfonohydrazide **(SI-9)**

Physical State: white solid.

m.p.: 85-87 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.42 (*br.*, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.25 (s, 1H), 3.12 (s, 3H), 3.04 (s, 3H), 2.43 (s, 3H), 2.28 (d, *J* = 13.1 Hz, 2H), 1.99 (d, *J* = 13.3 Hz, 2H), 1.28 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.68, 144.25, 135.30, 129.65, 128.16, 98.70, 48.46, 48.37, 41.94, 32.11, 24.46, 21.76 ppm.

HRMS (ESI-TOF): calc'd for $C_{15}H_{22}N_2O_4S$ $[M+H]^+$: 327.1273, not found.

LC-MS (ESI, m/z): calcd for $[M+Na]^+$ 349.1; found:349.2.

TLC: R_f = 0.20 (2:1 hexanes: ethyl acetate).

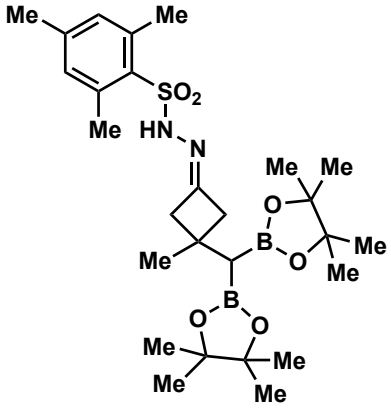
Step 2: Synthesis of SI-10

A dry round-bottom flask charged with **SI-9** (14.7 g, 45 mmol, 1.0 equiv.), 60% NaH (2.2 g, 54 mmol, 1.2 equiv.) was degassed and filled with argon for three times. Toluene (200 mL) was added, and the mixture was stirred at room temperature for 1 h. A solution of B_2pin_2 (17.0 g, 67 mmol, 1.5 equiv.) in toluene (50 mL) was added via syringe. Then the reaction flask was heated at 100 °C for 1 h.[4] After cooling to room temperature, the suspension was filtered by Celite, and washed by diethyl ether (200 mL). After solvent was removed by rotary evaporator from the filtrate, the crude product was redissolved in 45 mL acetonitrile in a 100-mL flask. 2M H_2SO_4 (45 mL, 2.0 equiv.) was added into the mixture at room temperature and the reaction was allowed to stir for another 2

hours. After it was confirmed that the ketal intermediate was totally consumed, the crude reaction is concentrated to remove excess acetonitrile. Then diethyl ether (150 mL) and saturated brine (150 mL) is added to the reaction mixture and the mixture is transferred to a separatory funnel. The aqueous layer is separated and further extracted with diethyl ether (3 × 50 mL). The combined organic layers are dried over Na_2SO_4, filtered through Celite. Excess solvent was removed by rotary evaporator.

The crude ketone was redissolved in 50 mL methylene chloride in a 100 mL-flask and mesitylene sulfonyl hydrazide (10.7 g, 50 mmol, 1.1 equiv.) was added. The mixture was allowed to stir at room temperature for another 3-5 hours. After it was confirmed that the ketone intermediate was consumed through TLC analysis, the crude reaction is concentrated to remove excess solvent. The crude product was purified through flash chromatography (hexanes: ethyl acetate, 4:1) on silica gel to afford 14.5 g (59%) of the title compound **SI-10**.

Compound SI-10



N'-(3-(bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3-methylcyclobutylidene)-2,4,6-trimethylbenzenesulfonohydrazide **(SI-10)**

Physical State: white solid.

m.p.: 111-113 °C.

^{1}H NMR (600 MHz, Acetone-*d*^{6}): δ 8.93 (s, 1H), 7.01 (s, 2H), 2.85 (dd, *J* = 18.1, 3.3 Hz, 1H), 2.80 (dd, *J* = 16.5, 2.2 Hz, 1H), 2.63 (s, 6H), 2.53 (dt, *J* = 17.1, 2.9 Hz, 1H), 2.43 (dt, *J* = 16.5, 3.0 Hz, 1H), 2.28 (s, 3H), 1.23 (s, 3H), 1.18 (s, 6H), 1.18 (s, 6H), 1.16 (s, 6H), 1.16 (s, 6H), 0.93 (s, 1H) ppm.

^{13}C NMR (151 MHz, Acetone-*d*^{6}): δ 156.80, 143.01, 140.69, 134.87, 132.42, 83.62, 83.61, 48.06, 46.69, 32.54, 30.04, 25.20, 25.12, 24.80, 24.79, 23.38, 20.86 ppm.

^{11}B NMR (128 MHz, Acetone-*d*^{6}): δ 32.87 ppm.

HRMS (ESI-TOF): calc'd for $C_{27}H_{44}B_2N_2O_6S$ $[M+H]^+$: 547.3179, found: 547.3177.

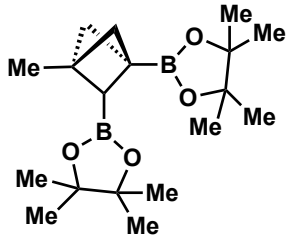
TLC: R_f = 0.40 (3:1 hexanes: ethyl acetate).

Step 3: Synthesis of 13

A 500-mL one-necked (24/40 joint) round-bottomed flask, equipped with a Teflon-coated magnetic stir bar, was flame-dried under vacuum, and then cooled to 23 ºC under an atmosphere of argon. Then the flask was charged with **SI-10** (14.5 g, 26.5 mmol, 1.0 equiv.) and dried cesium carbonate (25.4 g, 78 mmol, 3.0 equiv.). (*Note: Cesium carbonate was dried at 120 °C under vaccum for 18 hours.*) After being evacuated and backfilled with argon from a balloon 3 times, dioxane (250 mL) was added into the flask and the reaction mixture was allowed to stir at 100 °C for 2 hours. After it was confirmed that the starting material, **SI-10**, was consumed through TLC analysis, the reaction was cooled to room temperature, filtered through Celite, washed with hexanes (500 mL), and concentrated to remove excess solvents. The crude reaction was purified through flash chromatography (hexanes: ethyl acetate, 30:1) on silica gel to afford the title compound **13**, which was further purified through recrystallization in hexanes at -40 °C. affording 4.5 g product (51% yield) with >99% purity as white solids.[1]

Recrystallization procedure: The product (around 6 g) after chromatography was dissolved in hexanes (5 mL) at room temperature and then cooled to -40 °C. After the solution of the product was slowly stirred at -40 °C for 40 minutes, the suspension was filtered and the white solid was washed with cooled hexanes (3 mL) quickly and dried under vaccum for 1 hour.

Compound 13



2,2'-(-3-methylbicyclo[1.1.1]pentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(13)**

Physical State: colorless crystal.

m.p.: 35-37 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 2.22 (dd, *J* = 9.7, 2.2 Hz, 1H), 1.86 – 1.81 (m, 1H), 1.76 (s, 1H), 1.69 (dd, *J* = 8.4, 2.2 Hz, 1H), 1.57 (d, *J* = 8.4 Hz, 1H), 1.230 (s, 6H), 1.228 (s, 6H), 1.22 (s, 12H), 1.10 (s, 3H) ppm.

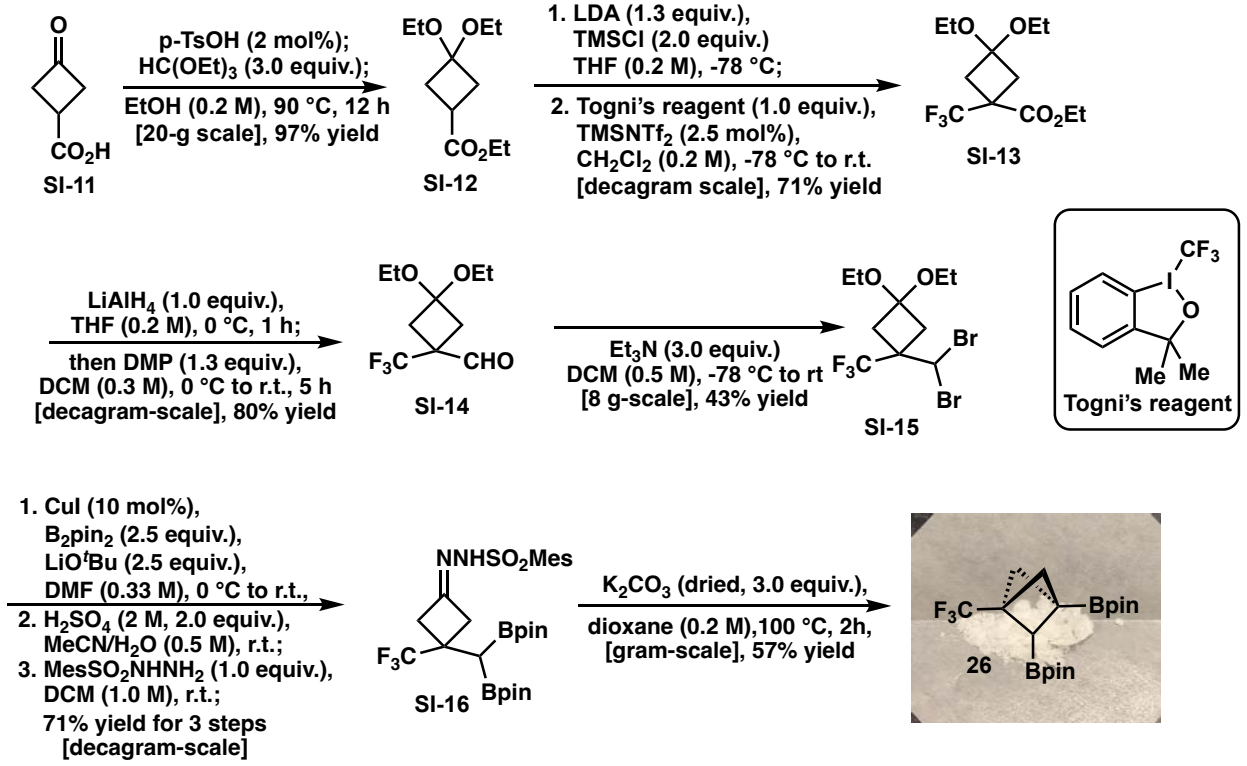
^{13}C NMR (151 MHz, $CDCl_3$): δ 83.22, 82.81, 57.14, 51.38, 44.81, 25.07, 24.95, 24.85, 24.83, 20.37 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.89, 30.77 ppm.

HRMS (ESI-TOF): calc'd for $C_{18}H_{32}B_2O_4$ $[M+H]^+$: 335.2560, found: 335.2574.

TLC: R_f = 0.33 (10:1 hexanes: ethyl acetate).

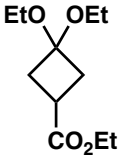
Gram-scale synthesis of BCP BisBoronates 26 ($R^1 = CF_3$)



Step 1: Synthesis of SI-12

A 500-mL round-bottomed flask, equipped with a Teflon-coated magnetic stir bar, was added **SI-11** (22.8 g, 200 mmol, 1.0 equiv.) and TsOH•H_2O (760 mg, 4.0 mmol, 0.02 equiv.). Then EtOH (600 mL) and $HC(OEt)_3$ (67 mL, 400 mmol, 2.0 equiv.) were added, and the reaction mixture was refluxed at 90 °C for 12 h. The reaction was cooled to room temperature and concentrated under vaccum. The residue was purified through flash chromatography (hexanes: ethyl acetate, 10:1) on silica gel to afford 41.9 g (97%) of the title compound **SI-12**.

Compound SI-12



ethyl 3,3-diethoxycyclobutane-1-carboxylate **(SI-12)**

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.14 (q, *J* = 7.2 Hz, 2H), 3.46 – 3.37 (m, 4H), 2.88 (p, *J* = 8.6 Hz, 1H), 2.48 – 2.35 (m, 4H), 1.24 (d, *J* = 7.3 Hz, 3H), 1.20 – 1.16 (m, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 175.06, 99.29, 60.75, 56.87, 56.59, 36.49, 29.40, 15.48, 15.30, 14.35 ppm.

HRMS (ESI-TOF): calc'd for $C_{11}H_{20}O_4$ $[M+Na]^+$: 239.1254, found: 239.1257.

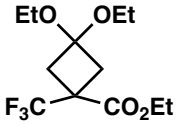
TLC: R_f = 0.28 (10:1 hexanes: ethyl acetate).

Step 2: Synthesis of SI-13

A flame-dried 1-L flask equipped with rubber septum and magnetic stirring bar was charged under argon atmosphere subsequently with diisopropylamine (27.7 mL, 198 mmol, 1.1 equiv.) and anhydrous THF (500 mL). To this well-stirred solution held at -78 °C was added within 20 minutes via a dropping funnel a solution of n-BuLi (86.4 mL, 2.5M in hexanes, 1.2 equiv.). The resulting solution was stirred at this temperature for 30 minutes. A solution of the **SI-12** (38.9 g, 180 mmol, 1.0 equiv.) in anhydrous THF (100 mL) was slowly introduced dropwise via a dropping funnel within 20 minutes. After stirring at -78 °C for 2 h, neat trimethylchlorosilane (39 mL; 306 mmol; 1.7 equiv.) was introduced at once. The resultant reaction mixture was allowed to gradually warm up to room temperature and stir overnight. The turbid solution was concentrated in vacuo in the reaction flask. To the remaining white slurry hexane (200 mL) was introduced and the mixture was cooled to 0 °C. The resulting suspension was poured into ice water and hexanes, and extracted with hexanes. The combined organic solution was dried with Na_2SO_4, filtered and concentrated. The residue was purified by distillation to afford the desired trimethylsilylketene acetal 43 g (83%) as colorless oil.

In a flame-dried 2-L flask equipped with rubber septum and magnetic stirring bar, trimethylsilyl ketene acetal (34.6 g, 120 mmol, 1.0 equiv.) was added under argon atmosphere. Then anhydrous methylene chloride (1.3 L) was added, and the reaction mixture was cooled to -78 °C (dry ice/acetone bath). $TMSNTf_2$ (424 mg; 1.2 mmol; 0.01 equiv) was added via a syringe at once. To the resulting well-stirred solution was added solid 1-trifluoromethyl-1,3-dihydro-3,3-dimethyl-1,2-benziodoxole (39.6 g, 120 mmol, 1.0 equiv.). The mixture was allowed to reach room temperature with stirring for 4 h. $NaHCO_3$ (50 mL) aqueous solution was added. The organic phase was separated and dried by Na_2SO_4. The solvent was concentrated, and the residue was purified through flash chromatography (hexanes: ethyl acetate, 10:1) on silica gel to afford 24.2 g (71%) of the title compound **SI-13**.[5]

Compound SI-13



ethyl 3,3-diethoxy-1-(trifluoromethyl)cyclobutane-1-carboxylate **(SI-13)**

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.26 (q, *J* = 7.1 Hz, 2H), 3.40 (q, *J* = 7.1 Hz, 2H), 3.40 (q, *J* = 7.1 Hz, 2H), 2.83 – 2.72 (m, 2H), 2.61 – 2.52 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.15 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.86, 125.22 (q, *J* = 279.5 Hz), 97.02, 62.26, 56.91, 56.82, 44.13 (q, *J* = 30.1 Hz), 38.07, 15.11, 15.06, 13.96 ppm.

^{19}F NMR (565 MHz, $CDCl_3$): δ -73.10 ppm.

HRMS (ESI-TOF): calc'd for $C_{12}H_{19}F_3O_4$ $[M+Na]^+$: 307.1128, found: 307.1130.

TLC: R_f = 0.59 (10:1 hexanes: ethyl acetate).

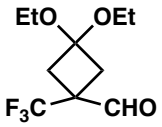
Step 3: Synthesis of SI-14

A 1-L one-necked (24/40 joint) round-bottomed flask, equipped with a 6.4 cm Teflon-coated magnetic stir bar, was flame-dried under vacuum, and then cooled to 23 ºC under an atmosphere of argon. Then the flask was charged with **SI-13** (20.2 g, 71 mmol, 1.0 equiv.). Dried THF (400 mL) was added into the flask and the mixture was cooled to 0 °C. Then $LiAlH_4$ (2.7 g, 71 mmol, 1.0 equiv.) was added into the flask slowly at 0 °C and the reaction mixture was allowed to stir at 0 °C for 1 hour. After it was confirmed that the start material, **SI-13**, was totally consumed, water (2.7 mL) was slowly added at 0 °C, followed by 20% w.t. NaOH (2.7 mL) and water (8.0 mL), and the mixture was stirred at 0 °C for 30 min. Then excess Na_2SO_4 was added, and the suspended solution was stirred at room temperature for another 1 hour. The mixture was filtered through Celite, and the solvent was removed under high vacuum. The crude alcohol was used without further purification.

To a solution of the crude alcohol in methylene chloride (280 mL) was added Dess–Martin periodinane (42.4 g, 100 mmol, 1.4 equiv.) at 0 °C and the reaction mixture was allowed to warm to room temperature and stir for 2 hours. Then after it is confirmed by TLC analysis that the alcohol

was consumed totally, the reaction was quenched by excess saturated $NaHCO_3$ solution and $Na_2S_2O_3$ solution and extracted with methylene chloride (100 mL) three times. The organic phase was separated, washed with brine, dried over Na_2SO_4 and evaporated. The crude product was purified through flash chromatography (hexanes: ethyl acetate, 10:1) on silica gel to afford 13.0 g (80%) of the title compound **SI-14**.

Compound SI-14



3,3-diethoxy-1-(trifluoromethyl)cyclobutane-1-carbaldehyde **(SI-14)**

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.73 (s, 1H), 3.44 – 3.39 (m, 2H), 3.40 – 3.36 (m, 2H), 2.67 – 2.62 (m, 2H), 2.50 (dt, *J* = 11.5, 1.6 Hz, 2H), 1.19 (tt, *J* = 7.1, 1.1 Hz, 3H), 1.15 (tt, *J* = 7.1, 1.2 Hz, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.87, 125.64 (q, *J* = 279.3 Hz), 96.55, 56.95, 56.86, 47.30 (q, *J* = 27.8 Hz), 34.98, 15.13 (2C) ppm.

^{19}F NMR (565 MHz, $CDCl_3$): δ -72.10 ppm.

HRMS (ESI-TOF): calc'd for $C_{10}H_{15}F_3O_3$ $[M+H]^+$: 241.1046, found: 241.1039.

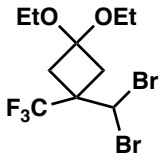
TLC: R_f = 0.53 (10:1 hexanes: ethyl acetate).

Step 4: Synthesis of SI-15

A 250-mL one-necked (24/40 joint) round-bottomed flask, equipped with a Teflon-coated magnetic stir bar, was flame-dried under vacuum, and then cooled to 23 ºC under an atmosphere of argon. Then the flask was charged with triphenyl phosphite (21 mL, 80 mmol, 1.5 equiv.). Methylene chloride (50 mL) was added into the flask and the mixture was cooled to -78°C. Then bromine (4 mL, 78 mmol, 1.4 equiv.) was added slowly into the flask, followed by addition of triethyl amine (23 mL, 162 mmol, 3.0 equiv.). Next, the solution of **SI-14** (13.0 g, 54 mmol, 1.0 equiv.) in 40 mL methylene chloride was added into the mixture and the reaction was warmed up to room temperature. After it was confirmed that the starting material, **SI-14**, was consumed through TLC analysis, solvent was removed by rotary evaporator and the crude product was

purified through flash chromatography (hexanes: ethyl acetate, 20:1) on silica gel to afford 8.6 g (43%) of the title compound **SI-15**.[2]

Compound SI-15



1-(dibromomethyl)-3,3-diethoxy-1-(trifluoromethyl)cyclobutane **(SI-15)**

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.96 (s, 1H), 3.43 (q, *J* = 7.1 Hz, 2H), 3.40 (q, *J* = 7.1 Hz, 2H), 2.66 – 2.59 (m, 2H), 2.42 – 2.36 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 126.09 (q, *J* = 281.8 Hz), 95.57, 57.10, 56.88, 45.76, 45.48 (q, *J* = 27.8 Hz), 39.60 (q, *J* = 2.3 Hz),15.40, 15.17 ppm.

^{19}F NMR (565 MHz, $CDCl_3$): δ -68.99 ppm.

HRMS (ESI-TOF): calc'd for $C_{10}H_{15}Br_2F_3O_2$ $[M+H]^+$: 382.9464, not found.

MS (GCMS, EI): m/z = 341 (5%), 339 (10%), 337 (5%), 311 (9%), 211 (30%), 116 (100%).

TLC: R_f = 0.69 (10:1 hexanes: ethyl acetate).

Step 5: Synthesis of SI-16

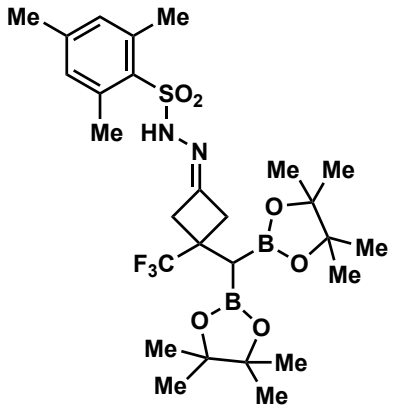
A 250-mL one-necked (24/40 joint) round-bottomed flask, equipped with a Teflon-coated magnetic stir bar, was flame-dried under vacuum, and then cooled to 23 ºC under an atmosphere of argon. Then the flask was charged with copper(I) iodide (437 mg, 2.3 mmol, 0.1 equiv.), B_2pin_2 (12.9 g, 51 mmol, 2.2 equiv.), and lithium tert-butoxide (4.4 g, 55 mmol, 2.4 equiv.). After being evacuated and backfilled with argon from a balloon 3 times, DMF (23 mL) was added into the flask at 0 °C. Then a solution of **SI-15** (23 mmol, 8.6 g, 1.0 equiv.) in DMF (46 mL) was added slowly into the mixture at 0 °C and the reaction mixture was allowed to slowly warm to room temperature and stir for another 1 hour. After it was confirmed that the starting material, **SI-15**, was consumed through TLC analysis, the reaction was filtered through Celite, washed with diethyl ether (100 mL) and quenched at 0 °C with water (300 mL) (*Caution: the quenching process is exothermic*). The mixture was then transferred into a 1-L separation funnel. The aqueous phase is separated and extracted with two 100-mL portions of diethyl ether. The combined organic layers

are washed with the mixture of 100 mL water and 100 mL saturated NaCl solution twice, dried over Na_2SO_4, and filtered through Celite. [3]

After solvent was removed by rotary evaporator, the crude product was redissolved in 23 mL acetonitrile in a 100-mL flask. 2M H_2SO_4 (23 mL, 2.0 equiv.) was added into the mixture at room temperature and the reaction was allowed to stir for another 1.5 hours. After it was confirmed that the ketal intermediate was consumed through TLC analysis, the crude reaction is concentrated to remove excess acetonitrile. Then diethyl ether (100 mL) and saturated brine (50 mL) is added to the reaction mixture and the mixture is transferred to a 125-mL separatory funnel. The aqueous layer is separated and further extracted with diethyl ether (3 × 50 mL). The combined organic layers are dried over Na_2SO_4, filtered through Celite. Excess solvent was removed by rotary evaporator.

The crude product was redissolved in 20 mL methylene chloride in a 100 mL-flask and mesitylene sulfonyl hydrazide (4.93 g, 23 mmol, 1.0 equiv.) was added. The mixture was allowed to stir at room temperature for another 2 hours. After it was confirmed that the ketone intermediate was consumed through TLC analysis, the crude reaction is concentrated to remove excess solvent. The crude product was purified through flash chromatography (hexanes: ethyl acetate, 4:1) on silica gel to afford 9.8 g (71%) of the title compound **SI-16**.

Compound SI-16



N'-(3-(bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3-(trifluoromethyl)cyclobutylidene)-2,4,6-trimethylbenzenesulfonohydrazide **(SI-16)**

Physical State: white solid.

m.p.: 186-188 °C.

^{1}H NMR (600 MHz, Acetone-d_6): δ 9.34 (s, 1H), 7.03 (s, 2H), 3.22 (dd, *J* = 18.1, 3.3 Hz, 1H), 3.11 (dd, *J* = 17.6, 3.2 Hz, 1H), 3.06 (ddd, *J* = 18.2, 3.3, 1.9 Hz, 1H), 3.00 (ddd, *J* = 17.7, 3.3, 1.9 Hz, 1H), 2.64 (s, 6H), 2.29 (s, 3H), 1.28 (s, 1H), 1.19 (s, 6H), 1.18 (s, 6H), 1.17 (s, 6H), 1.14 (s, 6H) ppm.

^{13}C NMR (151 MHz, Acetone-d_6) δ 151.49, 143.20, 140.78, 134.71, 132.49, 130.17 (q, *J* = 279.7 Hz), 84.32, 84.28, 41.54 (q, *J* = 2.8 Hz), 40.49 (q, *J* = 2.7 Hz), 39.96 (q, *J* = 27.4 Hz), 25.17, 24.98, 24.66, 24.64, 23.40, 20.85 ppm.

^{19}F NMR (565 MHz, Acetone-d_6): δ -78.92 ppm.

^{11}B NMR (128 MHz, Acetone-d_6): δ 32.51 ppm.

HRMS (ESI-TOF): calc'd for $C_{27}H_{41}B_2F_3N_2O_6S$ $[M+H]^+$: 601.2896, found: 601.2903.

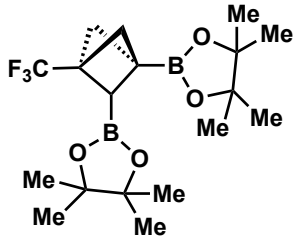
TLC: R_f = 0.47 (10:1 hexanes: ethyl acetate).

Step 6: Synthesis of 26

A 250-mL one-necked (24/40 joint) round-bottomed flask, equipped with a Teflon-coated magnetic stir bar, was flame-dried under vacuum, and then cooled to 23 ºC under an atmosphere of argon. Then the flask was charged with **SI-16** (6.0 g, 10 mmol, 1.0 equiv.) and dried potassium carbonate (4.14 g, 30 mmol, 3.0 equiv.). (*Note: Potassium carbonate was dried at 120 °C under vaccum for 18 hours.*) After being evacuated and backfilled with argon from a balloon 3 times, dioxane (60 mL) was added into the flask and the reaction mixture was allowed to stir at 105 °C for 2 hours. After it was confirmed that the starting material, **SI-16**, was consumed through TLC analysis, the reaction was cooled to room temperature, filtered through Celite, washed with hexanes (200 mL), and concentrated to remove excess solvents. The crude reaction was purified through flash chromatography (hexanes: ethyl acetate, 20:1) on silica gel to afford the title compound **26**, which was further purified through recrystallization in hexanes at -40 °C, affording 2.2 g product (57% yield) with >99% purity as white solids.[1]

Recrystallization procedure: The product (around 3 g) after chromatography was dissolved in hexanes (2.0 mL) at room temperature and then cooled to -40 °C. After the solution of the product was slowly stirred at -40 °C for 40 minutes, the suspension was filtered and the white solid was washed with cooled hexanes (1.0 mL) quickly and dried under vaccum for 1 hour.

Compound 26



2,2'-(3-(trifluoromethyl)bicyclo[1.1.1]pentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **(26)**

Physical State: white solid.

m.p.: 49-51 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 2.68 (dd, *J* = 9.6, 2.3 Hz, 1H), 2.07 (dd, *J* = 9.6, 1.7 Hz, 1H), 2.02 (d, *J* = 1.7 Hz, 1H), 1.96 (dd, *J* = 8.2, 2.3 Hz, 1H), 1.84 (d, *J* = 8.1 Hz, 1H), 1.25 – 1.18 (m, 24H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 121.70 (q, *J* = 278.4 Hz), 83.82, 83.44, 53.05 (q, *J* = 2.7 Hz), 47.47 (q, *J* = 2.4 Hz), 43.37 (q, *J* = 36.9 Hz), 24.88, 24.85, 24.81, 24.73 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ -74.97 ppm.

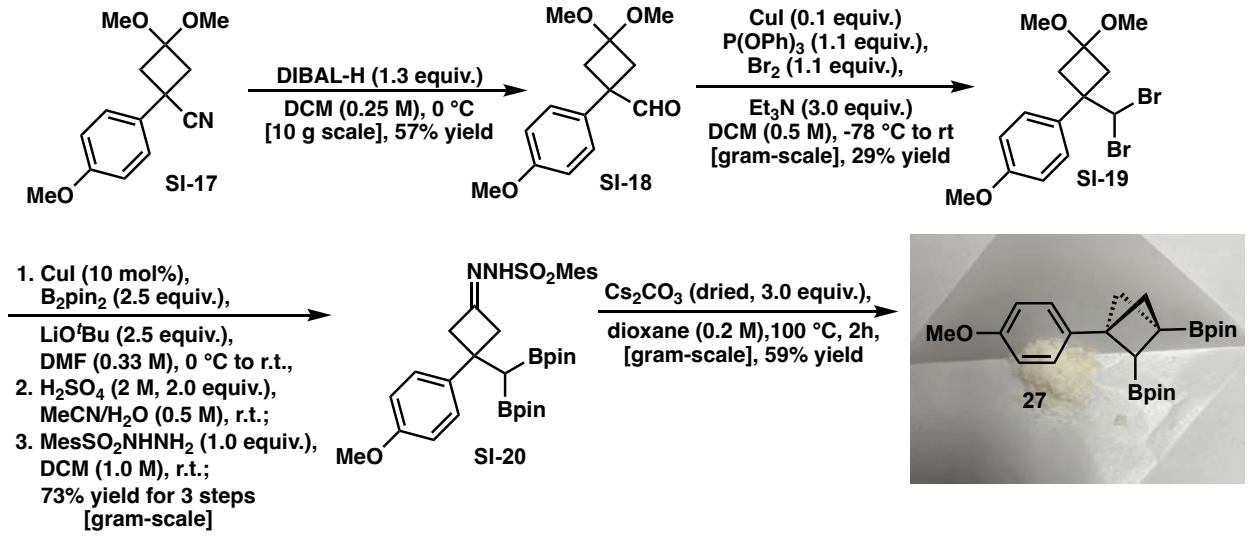
^{11}B NMR (128 MHz, $CDCl_3$): δ 30.96 ppm.

HRMS (ESI-TOF): calc'd for $C_{18}H_{29}B_2F_3O_4$ $[M+H]^+$: 389.2277, not found.

MS (GCMS, EI): m/z = 387 (0.1%), 373 (0.4%), 288 (1%), 231 (5%), 131 (15%), 83 (100%).

TLC: R_f = 0.28 (15:1 hexanes: ethyl acetate).

Gram-scale synthesis of BCP BisBoronates 27 (R^1 = 4-MeOPh)

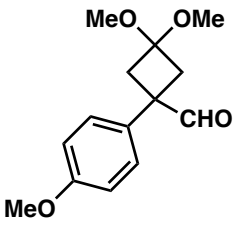


Compound **SI-17** was prepared according to previous literature.[6]

Step 1: Synthesis of SI-18

A 500-mL round-bottomed flask, equipped with a Teflon-coated magnetic stir bar, was flame-dried under vacuum, and then cooled to 23 ºC under an atmosphere of argon. Then the flask was charged with compound **SI-17** (12.5 g, 50 mmol, 1.0 equiv.). Then methylene chloride (200 mL) was added and the reaction mixture was cooled to 0 °C. Next, DIBAL-H (65 mL, 1.0 M, 1.3 equiv.) was added at 0 °C and the mixture was stirred at 0 °C for 3 hours. The cool mixture was added under vigorous stirring to saturated Rochelle salt solution at 0 °C and stirred overnight. The organic phase was separated, washed with brine, dried over Na_2SO_4 and evaporated. The crude product was purified through flash chromatography (hexanes: ethyl acetate, 4:1) on silica gel to afford 7.1 g (57%) of the title compound **SI-18**.

Compound SI-18



3,3-dimethoxy-1-(4-methoxyphenyl)cyclobutane-1-carbaldehyde **(SI-18)**

Physical State: white solid.

m.p.: 56-58 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.49 (s, 1H), 7.11 – 7.06 (m, 2H), 6.94 – 6.87 (m, 2H), 3.80 (s, 3H), 3.17 (s, 3H), 3.14 (s, 3H), 3.02 – 2.96 (m, 2H), 2.48 – 2.42 (m, 2H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.24, 158.95, 131.30, 128.25, 114.49, 98.60, 55.45, 48.77, 48.68, 48.21, 38.95 ppm.

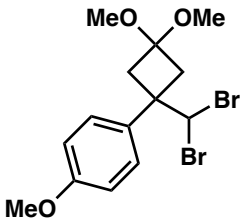
HRMS (ESI-TOF): calc'd for $C_{14}H_{18}O_4$ $[M+H]^+$: 251.1278, found: 251.1278.

TLC: R_f = 0.17 (10:1 hexanes: ethyl acetate).

Step 2: Synthesis of SI-19

A 250-mL one-necked (24/40 joint) round-bottomed flask, equipped with a Teflon-coated magnetic stir bar, was flame-dried under vacuum, and then cooled to 23 ºC under an atmosphere of argon. Then the flask was charged with triphenyl phosphite (5.8 mL, 22 mmol, 1.1 equiv.). Methylene chloride (25 mL) was added into the flask and the mixture was cooled to -78°C. Then bromine (1.1 mL, 22 mmol, 1.1 equiv.) was added slowly into the flask, followed by addition of triethyl amine (8.4 mL, 60 mmol, 3.0 equiv.). Next, the solution of **SI-18** (5.0 g, 20 mmol, 1.0 equiv.) in 25 mL methylene chloride was added into the mixture and the reaction was warmed up to room temperature. After it was confirmed that the starting material, **SI-18**, was consumed through TLC analysis, solvent was removed by rotary evaporator and the crude product was purified through flash chromatography (hexanes: ethyl acetate, 20:1) on silica gel to afford 2.31 g (29%) of the title compound **SI-19**.[2]

Compound SI-19



1-(1-(dibromomethyl)-3,3-dimethoxycyclobutyl)-4-methoxybenzene **(SI-19)**

Physical State: white solid.

m.p.: 59-61 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.33 – 7.26 (m, 2H), 6.92 – 6.86 (m, 2H), 6.22 (s, 1H), 3.82 (s, 3H), 3.22 (s, 3H), 3.10 (s, 3H), 2.71 – 2.60 (m, 4H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.79, 133.80, 130.48, 112.67, 97.64, 58.64, 55.36, 48.81, 48.65, 45.40, 43.67 ppm.

HRMS (ESI-TOF): calc'd for $C_{14}H_{18}Br_2O_3$ $[M+Na]^+$: 414.9515, found: 414.9508.

TLC: R_f = 0.45 (10:1 hexanes: ethyl acetate).

Step 3: Synthesis of SI-20

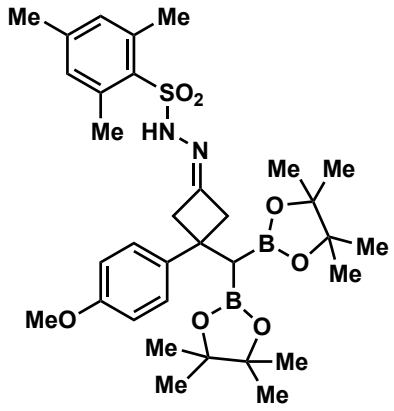
A 100-mL one-necked (24/40 joint) round-bottomed flask, equipped with a Teflon-coated magnetic stir bar, was flame-dried under vacuum, and then cooled to 23 ºC under an atmosphere of argon. Then the flask was charged with copper(I) iodide (114 mg, 0.6 mmol, 0.1 equiv.), B_2pin_2 (3.7 g, 14.5 mmol, 2.5 equiv.), and lithium tert-butoxide (1.16 g, 14.5 mmol, 2.5 equiv.). After being evacuated and backfilled with argon from a balloon 3 times, DMF (5 mL) was added into the flask at 0 °C. Then a solution of **SI-19** (5.8 mmol, 2.3 g, 1.0 equiv.) in DMF (10 mL) was added slowly into the mixture at 0 °C and the reaction mixture was allowed to slowly warm to room temperature and stir for another 1 hour. After it was confirmed that the starting material, **SI-19**, was consumed through TLC analysis, the reaction was filtered through Celite, washed with diethyl ether (50 mL) and quenched at 0 °C with water (100 mL) (*Caution: the quenching process is exothermic*). The mixture was then transferred into a 250-mL separation funnel. The aqueous phase is separated and extracted with two 50-mL portions of diethyl ether. The combined organic layers are washed with the mixture of 50 mL water and 50 mL saturated NaCl solution twice, dried over Na_2SO_4, and filtered through Celite. [3]

After solvent was removed by rotary evaporator, the crude product was redissolved in 10 mL acetonitrile in a 50-mL flask. 2M H_2SO_4 (6 mL, 2.0 equiv.) was added into the mixture at room temperature and the reaction was allowed to stir for another 1.5 hours. After it was confirmed that the ketal intermediate was consumed through TLC analysis, the crude reaction is concentrated to remove excess acetonitrile. Then diethyl ether (40 mL) and saturated brine (15 mL) is added to the reaction mixture and the mixture is transferred to a 125-mL separatory funnel. The aqueous layer is separated and further extracted with diethyl ether (3 × 30 mL). The combined organic layers are dried over Na_2SO_4, filtered through Celite. Excess solvent was removed by rotary evaporator.

The crude product was redissolved in 20 mL methylene chloride in a 50 mL-flask and mesitylene sulfonyl hydrazide (1.24 g, 5.8 mmol, 1.0 equiv.) was added. The mixture was allowed to stir at room temperature for another 2 hours. After it was confirmed that the ketone intermediate was

consumed through TLC analysis, the crude reaction is concentrated to remove excess solvent. The crude product was purified through flash chromatography (hexanes: ethyl acetate, 4:1 to 2:1) on silica gel to afford 2.72 g (73%) of the title compound **SI-20**.

Compound SI-20



N'-(3-(bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-3-(4-methoxyphenyl)cyclo-butylidene)-2,4,6-trimethylbenzenesulfonohydrazide **(SI-20)**

Physical State: white solid.

m.p.: 155-157 °C.

^{1}H NMR (600 MHz, Acetone-d_6) δ 9.04 (s, 1H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.98 (s, 2H), 6.89 – 6.64 (m, 2H), 3.74 (s, 3H), 3.40 (ddd, *J* = 17.8, 3.4, 1.9 Hz, 1H), 3.32 (ddd, *J* = 17.1, 3.4, 1.9 Hz, 1H), 3.16 (ddd, *J* = 17.7, 3.5, 1.6 Hz, 1H), 3.09 (ddd, *J* = 17.0, 3.5, 1.6 Hz, 1H), 2.63 (s, 6H), 2.26 (s, 3H), 1.31 (s, 1H), 1.11 (s, 12H), 1.10 (s, 12H) ppm.

^{13}C NMR (151 MHz, Acetone-d_6) δ 158.50, 156.01, 143.72, 142.96, 140.72, 134.91, 132.40, 128.11, 113.93, 83.78, 83.71, 55.41, 47.78, 46.21, 39.47, 25.21, 25.03, 24.88, 24.84, 23.44, 20.84 ppm.

^{11}B NMR (128 MHz, Acetone-d_6): δ 32.77 ppm.

HRMS (ESI-TOF): calc'd for $C_{33}H_{48}B_2N_2O_7S$ $[M+H]^+$: 639.3441, found: 639.3447.

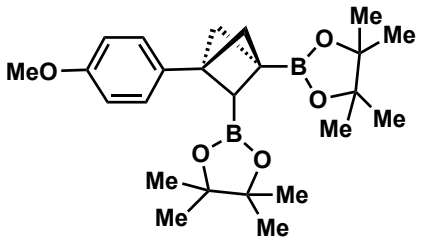
TLC: R_f = 0.30 (3:1 hexanes: ethyl acetate).

Step 4: Synthesis of 21

A 100-mL one-necked (24/40 joint) round-bottomed flask, equipped with a Teflon-coated magnetic stir bar, was flame-dried under vacuum, and then cooled to 23 ºC under an atmosphere

of argon. Then the flask was charged with **SI-20** (2.7 g, 4.2 mmol, 1.0 equiv.) and dried cesium carbonate (4.1 g, 12.6 mmol, 3.0 equiv.). (*Note: Cesium carbonate was dried at 120 °C under vaccum for 18 hours.*) After being evacuated and backfilled with argon from a balloon 3 times, dioxane (40 mL) was added into the flask and the reaction mixture was allowed to stir at 100 °C for 40 minutes. After it was confirmed that the starting material, **SI-20**, was consumed through TLC analysis, the reaction was cooled to room temperature, filtered through Celite, washed with hexanes (200 mL), and concentrated to remove excess solvents. The crude reaction was purified through flash chromatography (hexanes: ethyl acetate, 20:1) on silica gel to afford the title compound **21**, which was further purified through recrystallization in hexanes at -20 °C, affording 1.05 g product (59% yield) with >99% purity as white solids.[1]

Compound 27



***2,2'-(3-(4-methoxyphenyl)bicyclo[1.1.1]pentane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)* (27)**

Physical State: white solid.

m.p.: 89-91 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.22 – 7.17 (m, 2H), 6.85 – 6.78 (m, 2H), 3.77 (s, 3H), 2.73 (dd, *J* = 9.7, 2.2 Hz, 1H), 2.17 (dd, *J* = 9.7, 1.5 Hz, 1H), 2.15 – 2.12 (m, 1H), 2.04 (dd, *J* = 8.2, 2.2 Hz, 1H), 1.93 (dd, *J* = 8.2, 0.9 Hz, 1H), 1.25 (d, *J* = 1.3 Hz, 12H), 1.24 (s, 6H), 1.23 (s, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.23, 135.32, 127.21, 113.47, 83.41, 83.05, 56.34, 55.40, 51.87, 49.01, 25.02, 24.92, 24.91, 24.87 ppm.

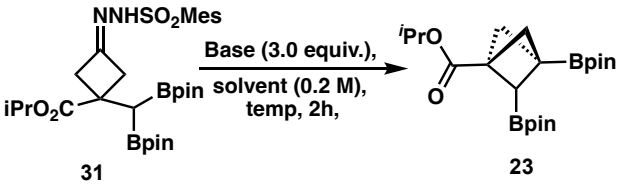
^{11}B NMR (128 MHz, $CDCl_3$): δ 32.00 ppm.

HRMS (ESI-TOF): calc'd for $C_{24}H_{36}B_2O_5$ $[M+H]^+$: 427.2822, found: 427.2819.

TLC: R_f = 0.43 (5:1 hexanes: ethyl acetate).

Optimization of Synthesis & Functionalizations of BCP Bisboronates

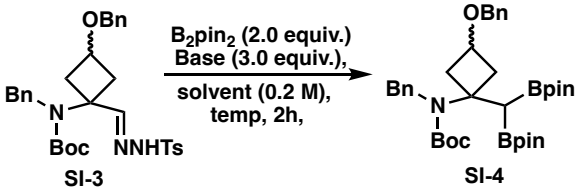
I. Synthesis of BCP BisBoronates



31 23

base	solvent	temp	Yield[a]
Cs_2CO_3[b]	dioxane	100 °C	66%
NaH	benzene	100 °C	56%
Cs_2CO_3	toluene	100 °C	37%
Cs_2CO_3	benzene	80 °C	20%
Cs_2CO_3	dioxane	80 °C	28%
NaH	toluene	80 °C	57%
Cs_2CO_3	toluene	80 °C	40%
K_2CO_3[b]	dioxane	100 °C	50%
Cs_2CO_3[c]	dioxane	100 °C	61%

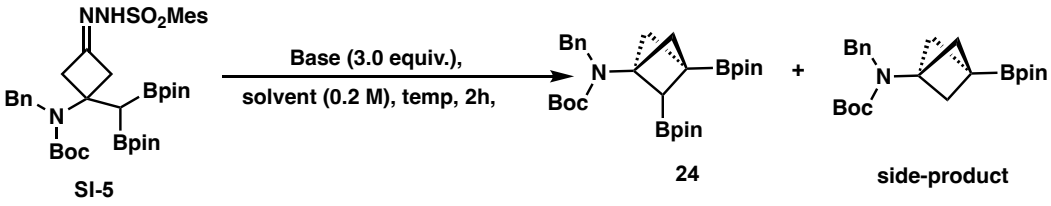
Table S1: Optimization of synthesis of 23



SI-3 SI-4

base	solvent	temp	Yield[a]
Cs_2CO_3[b]	dioxane	100 °C	< 10%
Cs_2CO_3[b]	toluene	100 °C	< 10%
NaH	toluene	80 °C	38%
NaH	benzene	80 °C	< 10%
K_3PO_4	dioxane	80 °C	< 10%
K_2CO_3	dioxane	80 °C	< 10%
NaH	toluene	70 °C	40%
NaH	toluene	75 °C	50%
NaH	toluene	90 °C	19%

Table S2: Optimization of synthesis of SI-4



SI-5 24 side-product

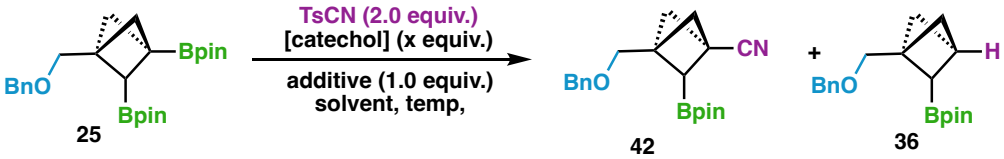
base	solvent	temp	yield of 24[a]	side-product[a]
Cs_2CO_3[b]	dioxane	100 °C	30%	20%
Cs_2CO_3[b]	toluene	100 °C	26%	56%
NaH	toluene	100 °C	41%	28%
Cs_2CO_3[b]	benzene	100 °C	19%	63%
NaH	toluene	80 °C	46%	25%
K_2CO_3	dioxane	100 °C	35%	20%
Cs_2CO_3[c]	dioxane	100 °C	22%	57%
K_2CO_3[b]	dioxane	100 °C	65%	trace

Note: *a*. Yield determined by ^1H NMR analysis with trimethoxybenzene as an internal standard;
b. The base was dried at 120 °C for 18 hours;
c. 99.995% from Sigma-aldrich.

Table S3: Optimization of synthesis of 24

II. Selective C_3-Functionalization of BCP BisBoronates

[Cyanation]

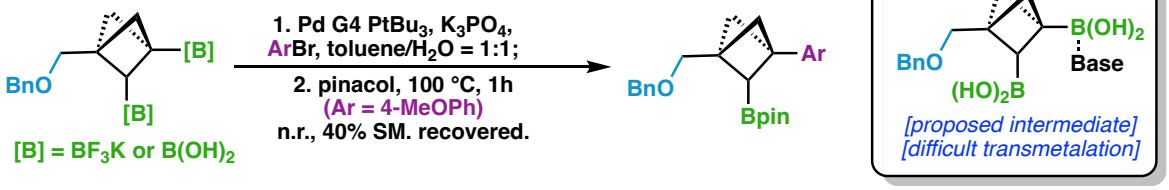


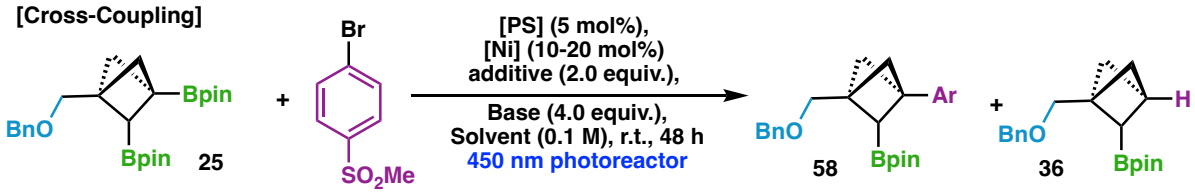
Entry	[catechol]	x	additive	solvent	temp	42[a]	36[a]
1	TBC	0.5	none	toluene	100 °C	45%	23%
2	catechol	0.5	none	toluene	100 °C	36%	12%
3	4-Cl catechol	0.5	none	toluene	100 °C	37%	35%
4	TBC	0.5	DMPU	toluene	100 °C	36%	21%
5	TBC	0.5	MeOH	toluene	100 °C	30%	16%
6	TBC	0.5	MeOD	toluene	100 °C	33%	10%
7	TBC	0.5	H_2O	toluene	100 °C	33%	12%
8	TBC	0.5	none	toluene	r.t.	33%	17%
9	TBC	0.5	none	toluene	40 °C	39%	29%
10	TBC	0.5	none	toluene	70 °C	48%	29%
11	TBC	0.5	none	toluene	120 °C	38%	15%
12	TBC	1.0	none	toluene	100 °C	26%	20%
13	TBC	2.0	none	toluene	100 °C	16%	25%
14	TBC	0.2	none	toluene	100 °C	49%	7%
15	TBC	0.01	none	toluene	70 °C	23%	3%
16	TBC	0.05	none	toluene	70 °C	43%	5%
17	TBC	0.1	none	toluene	70 °C	43%	10%
18	TBC	0.2	none	toluene	70 °C	60%	6%
19	TBC	0.2	none	benzene	70 °C	50%	13%
20	TBC	0.2	none	DCE	70 °C	34%	< 5%
21	TBC	0.2	none	dioxane	70 °C	0%	0%
22	TBC	0.2	none	THF	70 °C	0%	0%
23	TBC	0.2	pyrogallol	toluene	70 °C	32%	23%
24	TBC	0.2	guaiacol	toluene	70 °C	70%	6%
25	TBC	0.2	1,2-naphthoquinone	toluene	70 °C	43%	9%
26	TBC	0.2	1,4-naphthoquinone	toluene	70 °C	36%	10%
27	TBC	0.2	$B(OMe)_3$[b]	toluene	70 °C	41%	7%
28	TBC	0.2	$B(OMe)_3$[c]	toluene	70 °C	29%	10%
29	TBC	0.2	MeOBcat	toluene	70 °C	60%	3%
30	TBC	0.2	TMSOTf	toluene	70 °C	50%	3%

Note: *a.* Yield determined by 1H NMR analysis with trimethoxybenzene as an internal standard;
b. $B(OMe)_3$ (0.1 equiv.); c. $B(OMe)_3$ (0.5 equiv.).

Table S4: Optimization of cyanation of BCP 25

[Cross-Coupling]

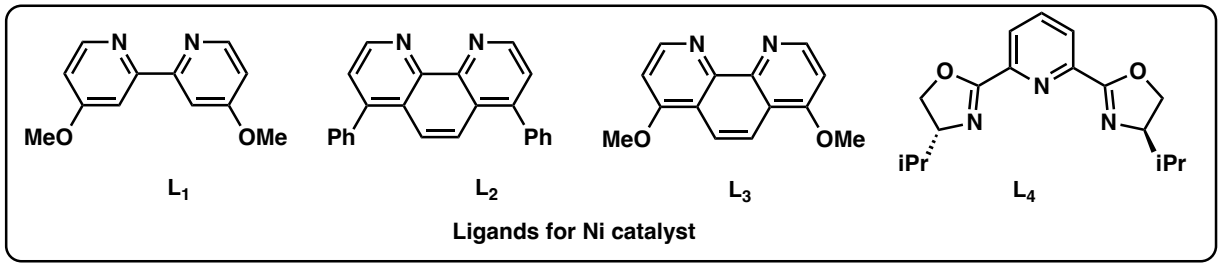


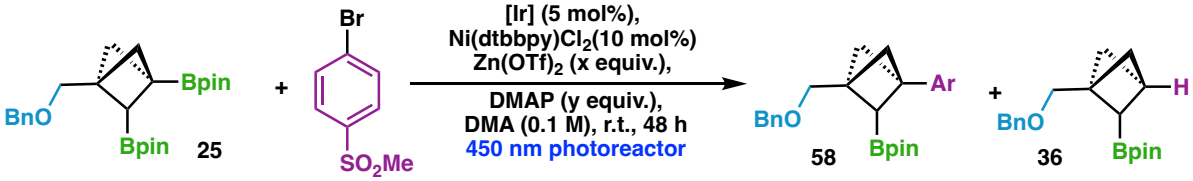


Entry	[PS]	[Ni]	additive	Base	solvent	58[a]	36[a]	25[a]
1	[Ir]	$Ni(dtbbpy)Cl_2$	none	DMAP	DMA	0%	0%	main
2	[Ir]	$Ni(dtbbpy)Cl_2$	$ZnBr_2$	DMAP	DMA	25%	6%	10%
3	[Ir]	$Ni(dtbbpy)Cl_2$	$ZnBr_2$	DMAP	DMSO	0%	0%	0%
4	[Ir]	$Ni(dtbbpy)Cl_2$	$ZnBr_2$	DMAP	DMF	trace	0%	0%
5	[Ir]	$Ni(dtbbpy)Cl_2$	$ZnBr_2$	DMAP	dioxane	0%	0%	main
6	[Ir]	$Ni(dtbbpy)Cl_2$	$ZnBr_2$	DMAP	acetone	0%	10%	main
7[b]	[Ir]	$Ni(dtbbpy)Cl_2$	$ZnBr_2$	DMAP	DMA	2%	0%	0%
8	[Ir]	$NiBr_2$·glyme + dtbbpy	$ZnBr_2$	DMAP	DMA	10%	20%	trace
9	[Ir]	$NiBr_2$·glyme + dtbbpy[c]	$ZnBr_2$	DMAP	DMA	14%	23%	trace
10	[Ir]	$NiBr_2$·glyme + L_1	$ZnBr_2$	DMAP	DMA	10%	29%	trace
11	[Ir]	$NiBr_2$·glyme + L_2	$ZnBr_2$	DMAP	DMA	10%	15%	trace
12	[Ir]	$NiBr_2$·glyme + L_3	$ZnBr_2$	DMAP	DMA	5%	20%	trace
13	[Ir]	$NiBr_2$·glyme + L_4	$ZnBr_2$	DMAP	DMA	trace	25%	trace
14	[Ir]	$Ni(TMHD)_2$	$ZnBr_2$	DMAP	DMA	0%	0%	trace%
15	[Ir]	$Ni(dtbbpy)Cl_2$	$ZnBr_2$	CsF	DMA	17%	24%	10%
16	[Ir]	$Ni(dtbbpy)Cl_2$	$ZnBr_2$	PhONa	DMA	22%	13%	7%
17	[Ir]	$Ni(dtbbpy)Cl_2$	$Zn(OTf)_2$	DMAP	DMA	40%	18%	10%
18	[Ir]	$Ni(dtbbpy)Cl_2$	$Zn(ClO)_4$·$6H_2O$	DMAP	DMA	25%	20%	10%
19	[Ir]	$Ni(dtbbpy)Cl_2$	$In(OTf)_3$	DMAP	DMA	23%	13%	38%
20	[Ir]	$Ni(cod)_2$+dtbbpy	$Zn(OTf)_2$	DMAP	DMA	39%	20%	trace
21	4-CzIPn	$Ni(dtbbpy)Cl_2$	$Zn(OTf)_2$	DMAP	DMA	50%	22%	trace
22	Acr-Mes	$Ni(dtbbpy)Cl_2$	$Zn(OTf)_2$	DMAP	DMA	trace	0%	0%

Table S5: Optimization of cross-coupling reaction of BCP 25

Note: *a.* Yield determined by 1H NMR analysis with trimethoxybenzene as an internal standard;
b. The reaction was runned under light from 468-nm blue LED;
c. $NiBr_2$·glyme:dtbbpy = 1:2
d. [Ir] = $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$; dtbbpy = 4,4′-Di-tert-butyl-2,2′-dipyridyl.

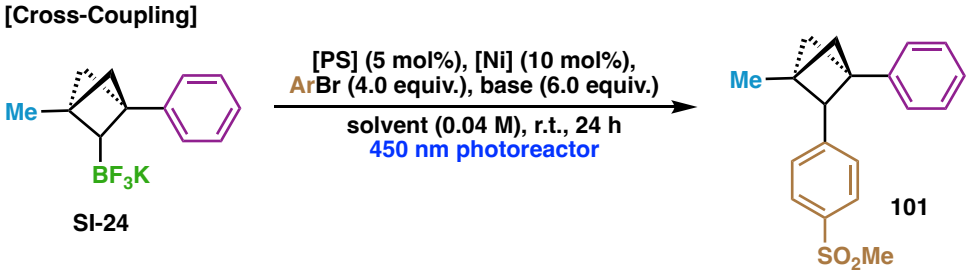




x	y	58[a]	36[a]	25[a]	x	y	58[a]	36[a]	25[a]
0.5	4.0	7%	11%	56%	2.0	2.0	21%	20%	13%
1	4.0	25%	13%	20%	2.0	3.0	33%	19%	16%
4.0	4.0	22%	21%	20%	2.0	4.0	50%	22%	trace

Table S5: Optimization of cross-coupling reaction of BCP 25 (continued)

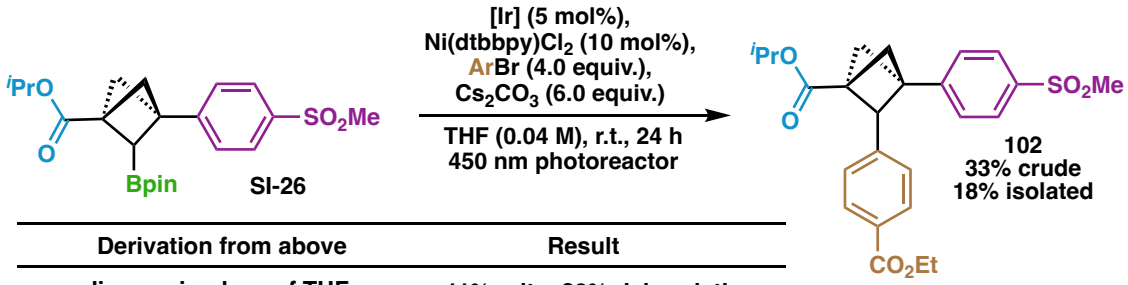
III. Late-stage C_2-Functionalization of BCP BisBoronates



Entry	[PS]	[Ni]	Base	solvent	Result[a]
1	[Ir]	$Ni(dtbbpy)Cl_2$	Cs_2CO_3	Dioxane/DMA (4:1)	trace
2	[Ir]	$Ni(TMHD)_2$	CS_2CO_3	Dioxane/DMA (4:1)	n.d.
3	4-CzIPn	$Ni(dtbbpy)Cl_2$	Cs_2CO_3	Dioxane/DMA (4:1)	n.d.
4	[Ir]	$Ni(dtbbpy)Cl_2$	K_3PO_4	Dioxane/DMA (4:1)	40% yield
5	[Ir]	$Ni(dtbbpy)Cl_2$	Cs_2CO_3	Dioxane	50% yield
6	[Ir]	$Ni(dtbbpy)Cl_2$	Cs_2CO_3	DMA	23% yield
7	4-CzIPn	$Ni(TMHD)_2$	Cs_2CO_3	Dioxane/DMA (4:1)	n.d.

Table S6: Optimization of cross-coupling reaction of BCP SI-24

Note: *a.* Yield determined by ^1H NMR analysis with trimethoxybenzene as an internal standard; *b.* [Ir] = $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$; dtbbpy = 4,4′-Di-tert-butyl-2,2′-dipyridyl.

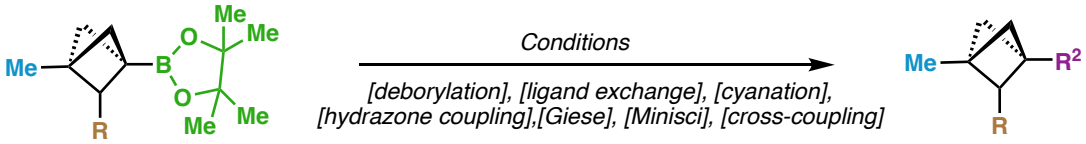


Derivation from above	Result
dioxane in place of THF	11% pdt + 23% deborylation
dioxane/DMA (5:1) in place of THF	12% pdt + 20% deborylation
DMA in place of THF	n.d.
K_3PO_4 in place of Cs_2CO_3	0% pdt + 23% deborylation
K_2CO_3 in place of Cs_2CO_3	n.d.
MeONa in place of Cs_2CO_3	n.d.
$Zn(OTf)_2$ as additive	n.d.
$ZnBr_2$ as additive	n.d.
4-CzIPn in place of [Ir]	n.d.

Table S7: Optimization of cross-coupling reaction of BCP SI-26

Note: *a.* Yield determined by ^1H NMR analysis with trimethoxybenzene as an internal standard; *b.* [Ir] = $[Ir(dF(CF_3)ppy)_2(dtbpy)]PF_6$; dtbbpy = 4,4′-Di-tert-butyl-2,2′-dipyridyl.

C_2 control of Selective C_3-Functionalization of BCP Boronates



Conditions	R	pdt/%	SM/%
TBC, C_6D_6, 100 °C, 5 h *[deborylation]*	**R = cPent**	**17**	**63**
	Bpin	**63**	**23**
1,8-diamino-naphthalene, toluene, 100 °C, 12 h *[ligand exchange]*	**R = cPent**	**7**	**85**
	Bpin	**60**	**28**
sulfonyl hydrazone Cs_2CO_3, toluene, 70 °C, 48 h *[hydrazone coupling]*	**R = cPent**	**14**	**80**
	Bpin	**42**	**23**
TsCN, TBC, toluene, 70 °C, 16 h *[cyanation]*	**R = cPent**	**0**	**78**
	Bpin	**50**	**30**
[Ir], DMAP, MVK, acetone/MeOH, 450 nm hv *[Giese]*	**R = cPent**	**0**	**54**
	Bpin	**26**	**44**
2,6-diClpyrazine $Mn(OAc)_3$, TFA, $AcOH/H_2O$, 50 °C, 18 h *[Minisci]*	**R = cPent**	**52**	**0**
	Bpin	**52**	**0**
[Ir], [Ni], 4-CF_3PhBr $Zn(OTf)_2$, DMAP, DMA, 450 nm hv, 24 h *[cross-coupling]*	**R = cPent**	**20**	**40**
	Bpin	**40**	**0**

Table S8 : C_2-control of 1st functionalization of BCP boronate

Troubleshooting:

For Synthesis and Chemistry of BCP Bisboronates:

Question 1:

Are BCP bis-boronates stable at room temperature? If not, how could we store them?

Answer:

Most of the BCP bis-boronates could be stable in air at room temperature for several days. But they would decompose for staying under air atmosphere at room temperature longer. Usually the BCP bisboronates are stored at -20 °C for several months.

Question 2:

Is the intramolecular coupling sensitive to moisture? Could this type of reaction work with cesium carbonate which is not dried at high temperature under vacuum?

Answer:

BCP bisboronates **13**, **25**, **27** are relatively stable and the coupling reaction will work under existence of trace water, although the yield will drop a little. BCP **13** was synthesized through a procedure with sulfonyl hydrazone formed in situ (where water was formed as the by-product). However, BCP **23**, **24**, **26** are more sensitive to moisture at high temperature and the yield of the hydrazone coupling will drop a lot if the cesium carbonate is not dried. Details are listed in the optimization of BCP synthesis.

Question 3:

Any tips for purification of BCP bisboronates?

Answer:

All of the BCP bisboronates are not very stable on the column so purification of BCP bisBpins through chromatography on silica gel should be finished in one hour at most.

For 1st functionalization of BCP Bisboronates:

Question 1:

In the transformations of 1st functionalization of BCP bisboronates, is there any by-product with C_2-functionalization observed?

Answer:

No, owing to lower reactivity of C_2-Bpin, no C_2-functionalized by-product with C_3-Bpin retained was observed in all type of transformations in Figure 4. However, sometimes over functionalization happened with more harsh conditions, which transformed C_2-Bpin into other functional groups (like H, SPh).

Question 2:

In the hydrazone coupling, did the tertiary Bpin formed in the product react with excess sulfonyl hydrazones?

Answer:

No, the reactivity of alkyl Bpin is lower and no by-product through double hydrazone coupling was observed. Thus, excess sulfonyl hydrazones could be added into the reaction mixture if they were consumed faster than BCPs.

Question 3:

In the protodeborylation of BCP bisboronates, what is the by-product of the reaction?

Answer:

The C_2-Bpin could also be deborylated after C_3-Bpin was transformed into hydrogen thus trace double deborylation product (R^2, R^3 = H) was observed in this transformation. It is necessary to choose a proper temperature for reaction and a proper time to stop it with the yield went to the highest.

Question 4:

What are the by-products in other transformations of BCP bisboronates including cyanation and C-X (X = S or N) formation, Giese-type reaction and cross-coupling?

Answer:

Owing to the use of catalytic tertbutyl catechol, deborylation will also happen in the cyanation and C-S, C-N formation of BCPs. Also, the same byproduct was observed in the Giese reaction and cross-coupling thus photo-induced deborylation was utilized in the synthesis of compound **36**.

Question 5:

Do I need a glovebox to run these transformations?

Answer:

We do not set up or run the reaction in a glovebox unless extra details like that $Ni(cod)_2$ was charged in a glovebox were included. A glovebox is not necessary to run these reactions. The reaction tubes were purged under argon atmosphere for more than 10 seconds when it is needed.

Question 6:

Could BCP bisboronates react with quinolines and pyridines to install 2-quinolyl and 2-pyridyl groups through Minisci-type reaction?

Answer:

Yes, the Minisci reaction actually happened when quinolines and pyridines was added into the reaction. However, the quinolyl and 2-pyridyl group motivated the hydrolysis of C_2-Bpin and a mixture of boronic acid and boronic pinacol ester was obtained in this transformation.

For 2nd functionalization of BCP Bisboronates:

Question 1:

Could all BCP C_2-Bpin be oxidized into the alcohol?

Answer:

According to our result, whether BCPs are able to contain a hydroxyl group on C_2 position depends on substituents on C_1, C_3-position. If there are some polar functional groups like esters, the BCP core could easily be opened to form a cyclobutanone product if the C_2-Bpin is oxidized into the alcohol. See details in the Limitation Part.

Question 2:

Are all BCP C_2-BF_3Ks and BCP C_2-boronic acids stable?

Answer:

According to our observation, all of BCP C_2-BF_3Ks are stable at room temperature for months. However, the BCP C_2-boronic acids containing alkyl groups at C_1, C_3-positions like compound **82** is stable at room temperature for several days after they are recrystalized. Usually, such boronic acids should be stored at -20 °C in case of its decomposition. However, other boronic acids containing some electron-withdrawing group like esters and cyanides are not very stable, which should be used intermediately in following transformations.

Question 3:

There are several conditions for the cross-coupling with aryl bromide step. What condition do you recommend to choose for a specific substrate?

Answer:

Owing to effect from C_1, C_3-substituents, optimization of cross-coupling for each substrate is needed. Usually it is recommended that K_3PO_4 and Cs_2CO_3 are used as bases while dioxane and THF as solvents.

Question 4:

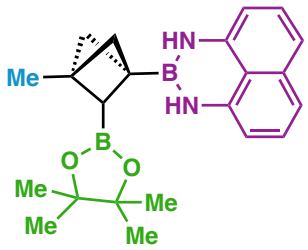
Is the ate-complex formed from BCP C_2-Bpin with PhLi stable?

Answer:

The ate complex is stable for several hours without any solvent under vacuum or argon atmosphere. Usually it is used intermediately in the following transformation rather than stored for days.

General Experimental Procedures and Characterization Data of substrates in Selective C_3-Bpin Functionalization of BCP BisBoronates

Compound 15



2-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine **(15)**

A flame-dried 13×100 mm pyrex culture tube was charged with BCP bis-boronate **13** (33.4 mg, 0.1 mmol, 1.0 equiv.) and 1,8-diaminonaphthalene (31.6 mg, 0.2 mmol, 2.0 equiv.). Then the tube was evacuated and backfilled with argon for three times, followed by addition of toluene (1.0 mL, 0.1 M) via a syringe. After stirring for at 100 °C for 12 hours, the reaction mixture was cooled to room temperature. Next, the solvent was removed under high vacuum, and the crude residue was purified by chromatography on silica gel (50:1, hexanes: ethyl acetate) to afford 22.4 mg (60%) of the title compound **15**.

Physical State: white solid.

m.p.: 162-164 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.08 (dd, *J* = 8.2, 7.3 Hz, 2H), 6.97 (dd, *J* = 8.3, 0.9 Hz, 2H), 6.28 – 6.23 (m, 4H), 2.07 (dd, *J* = 9.8, 2.5 Hz, 1H), 1.79 (s, 1H), 1.77 (dd, *J* = 9.8, 1.3 Hz, 1H), 1.73 (dd, *J* = 8.8, 2.5 Hz, 1H), 1.55 (d, *J* = 8.7 Hz, 1H), 1.35 (s, 12H), 1.19 (s, 3H) ppm.

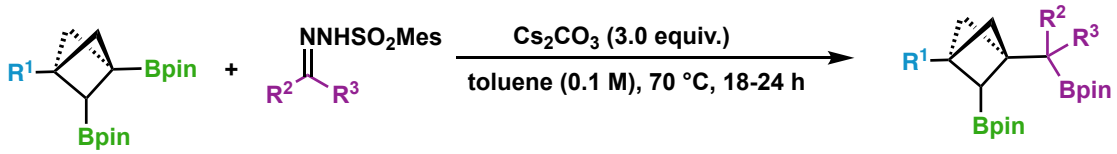
^{13}C NMR (151 MHz, $CDCl_3$): δ 141.70, 136.56, 127.65, 119.93, 117.14, 105.36, 83.45, 55.08, 54.21, 44.23, 25.27, 25.05, 20.12 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.50, 29.75 ppm.

HRMS (ESI-TOF): calc'd for $C_{22}H_{28}B_2N_2O_2$ $[M+H]^+$: 375.2410, found: 375.2421.

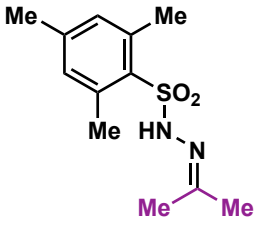
TLC: R_f = 0.40 (10:1 hexanes: ethyl acetate).

General Procedure A for Hydrazone Coupling of BCP BisBoronates

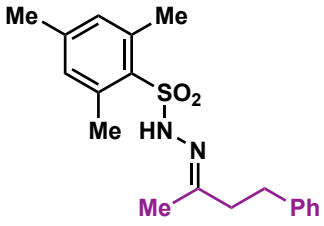


A screw-capped 13×100 mm pyrex culture tube was charged with cesium carbonate (3.0 equiv.), 2-mesitylsulfonyl hydrazone (2.0 equiv.) and BCP bis-boronate (1.0 equiv.). Then the tube was evacuated and backfilled with argon for three times, followed by addition of toluene (0.1 M) via a syringe. After stirring for at 70 °C for 18-48 hours when it is confirmed that the BCP bis-boronate was totally consumed, the reaction mixture was cooled to room temperature. Next, the suspended solution was then filtered over Celite and washed with diethyl ether. The solvent was removed under high vacuum, and the crude residue was purified by chromatography on silica gel.[7]

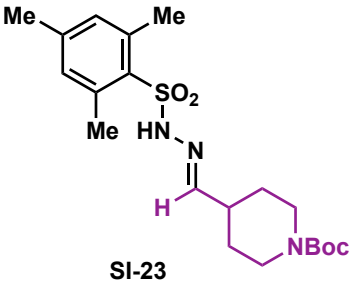
The sulfonyl hydrazones were prepared through the procedure in literatures:[7]



17

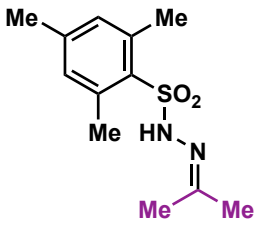


SI-22



SI-23

Compound 17



***2,4,6-trimethyl-N'-(propan-2-ylidene)benzenesulfonohydrazide* (17).**

Physical State: white solid.

m.p.: 149-152 °C.

^{1}H NMR (600 MHz, Acetone-d_6): δ 8.80 (s, 1H), 7.01 (s, 2H), 2.64 (s, 6H), 2.28 (s, 3H), 1.86 (s, 3H), 1.82 (s, 3H) ppm.

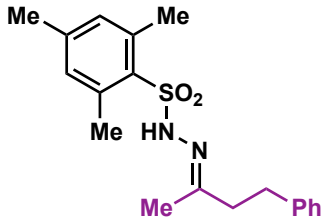
^{13}C NMR (151 MHz, Acetone-d_6): δ 154.87, 143.10, 140.91, 134.78, 132.37, 25.15, 23.38, 20.84,

16.94 ppm.

HRMS (ESI-TOF): calc'd for $C_{12}H_{18}N_2O_2S$ $[M+H]^+$: 255.1162, found: 255.1170.

TLC: R_f = 0.42 (2:1 hexanes : ethyl acetate).

Compound SI-22



2,4,6-trimethyl-N'-(4-phenylbutan-2-ylidene)benzenesulfonohydrazide **(SI-22).**

Physical State: white solid.

m.p.: 105-107 °C.

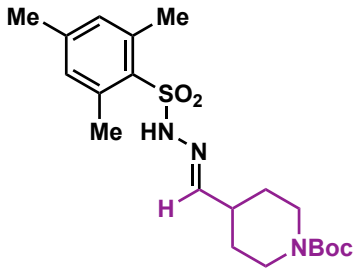
^{1}H NMR (600 MHz, Acetone-d_6): δ 8.87 (br., 1H), 7.21 – 7.15 (m, 2H), 7.14 – 7.10 (m, 1H), 7.08 – 7.06 (m, 2H), 7.02 (s, 2H), 2.74 – 2.69 (m, 2H), 2.66 (s, 6H), 2.49 – 2.43 (m, 2H), 2.29 (s, 3H), 1.86 (s, 3H) ppm.

^{13}C NMR (151 MHz, Acetone-d_6): δ 156.52, 143.10, 142.42, 140.91, 134.66, 132.40, 129.11, 129.03, 126.56, 40.84, 32.51, 23.42, 23.41, 20.89, 16.53 ppm.

HRMS (ESI-TOF): calc'd for $C_{19}H_{24}N_2O_2S$ $[M+H]^+$: 345.1631, found: 345.1625.

TLC: R_f = 0.27 (5:1 hexanes : ethyl acetate).

Compound SI-23



tert-butyl-4-((2-(mesitylsulfonyl)hydrazineylidene)methyl)piperidine-1-carboxylate **(SI-23).**

Physical State: white solid.

m.p.: 165-167 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.05 (d, J = 4.1 Hz, 1H), 6.96 (s, 2H), 4.03 – 3.83

(m, 2H), 2.80 – 2.68 (m, 2H), 2.64 (s, 6H), 2.34 – 2.23 (m, 1H), 2.30 (s, 3H), 1.71 – 1.62 (m, 2H), 1.43 (s, 9H), 1.36 – 1.25 (m, 2H) ppm.

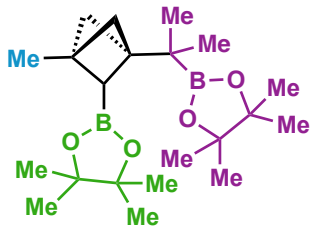
^{13}C NMR (151 MHz, $CDCl_3$): δ 154.83, 152.46, 143.12, 140.28, 132.25, 132.00, 79.71, 43.48 *(approx.)*, 38.76, 28.71, 28.56, 23.32, 21.15 ppm.

HRMS (ESI-TOF): calc'd for $C_{20}H_{31}N_3O_4S$ $[M+H]^+$: 410.2108, found: 410.2104.

TLC: R_f = 0.56 (2:1 hexanes : ethyl acetate).

Characterization of Substrates in Hydrazone Coupling (18, 32-35)

Compound 18



4,4,5,5-tetramethyl-2-(2-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)propan-2-yl)-1,3,2-dioxaborolane **(18)**

Following **General Procedure A** on 0.1 mmol scale with BCP bisboronate **13** and 2-mesityl sulfonyl hydrazone **17** reacting for 48 h. Purification by flash chromatography (hexanes: diethyl ether, 20:1) and afforded 16.0 mg (42%) of the title compound **18**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 2.27 (dd, *J* = 9.7, 1.8 Hz, 1H), 1.52 (dd, *J* = 9.7, 1.1 Hz, 1H), 1.43 (s, 1H), 1.37 (dd, *J* = 8.1, 1.8 Hz, 1H), 1.28 (d, *J* = 8.0 Hz, 1H), 1.22 (s, 12H), 1.21 (s, 12H), 1.15 (s, 3H), 0.86 (s, 3H), 0.85 (s, 3H) ppm.

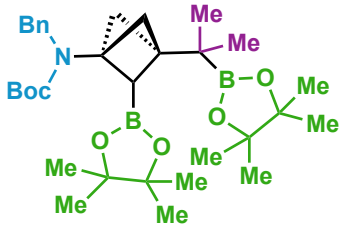
^{13}C NMR (151 MHz, $CDCl_3$): δ 82.94, 82.54, 54.70, 48.90, 47.59, 37.02, 24.98, 24.94, 24.89, 22.04, 21.85, 18.79 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.30 ppm.

HRMS (ESI-TOF): calc'd for $C_{21}H_{38}B_2O_4$ $[M+H]^+$: 377.3029, found: 377.3040.

TLC: R_f = 0.35 (15:1 hexanes: ethyl acetate).

Compound 32



***tert-butyl benzyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(2-(4,4,5,5-tetra methyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)bicyclo[1.1.1]pentan-1-yl)carbamate* (32)**

Following **General Procedure A** on 0.05 mmol scale with BCP bisboronate **24** and 2-mesityl sulfonyl hydrazone **SI-21** reacting for 24 h. Purification by flash chromatography (hexanes: ethyl acetate, 4:1) and afforded 17.5 mg (62%) of the title compound **27**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.22 – 7.14 (m, 4H), 7.11 (t, J = 7.0 Hz, 1H), 4.46 – 4.24 (m, 2H), 2.58 (s, 1H), 1.85 (d, J = 9.5 Hz, 1H), 1.78 (d, J = 7.9 Hz, 1H), 1.67 (s, 1H), 1.66 (s, 1H), 1.38 (s, 9H), 1.139 (s, 6H), 1.136 (s, 6H) 1.11 (s, 12H), 0.80 (s, 3H), 0.79 (s, 3H) ppm.

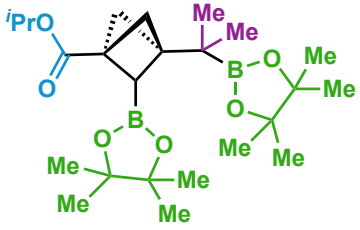
^{13}C NMR (151 MHz, $CDCl_3$): δ 140.28, 128.22, 126.85, 126.47, 83.06, 82.80, 49.14, 48.76, 45.90, 28.61, 25.07, 24.92, 24.90, 22.40, 22.16 ppm. *Note:* BnN*C*(O*)*, BocBnN*C*, N*C*H$_2$Ph, Me$_3$*C*O, B*C*H *and* B*C*Me$_2$ *were not observed*.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.08 ppm.

HRMS (ESI-TOF): calc'd for $C_{32}H_{51}BNO_6$ $[M+H]^+$: 568.3975, found: 568.3975.

TLC: R_f = 0.56 (5:1 hexanes: ethyl acetate).

Compound 33



***isopropyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)bicyclo[1.1.1]pentane-1-carboxylate* (33)**

Following **General Procedure A** on 0.1 mmol scale with BCP bisboronate **23** and 2-mesityl sulfonyl hydrazone **17** reacting for 18 h. Purification by flash chromatography (hexanes: ethyl

acetate, 4:1) and afforded 27.7 mg (62%) of the title compound **33**.

Physical State: white solid.

m.p.: 74-76 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.97 (hept, *J* = 6.3 Hz, 1H), 2.69 (dd, *J* = 9.5, 1.8 Hz, 1H), 1.89 – 1.85 (m, 2H), 1.81 (dd, *J* = 7.9, 1.8 Hz, 1H), 1.66 (d, *J* = 7.8 Hz, 1H), 1.23 (s, 6H), 1.22 (s, 6H), 1.20 (s, 12H), 1.195 (d, *J* = 7.0 Hz, 6H), 0.88 (s, 3H), 0.87 (s, 3H) ppm.

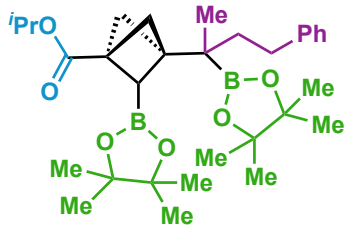
^{13}C NMR (151 MHz, $CDCl_3$): δ 170.85, 83.14, 82.91, 67.44, 54.10, 49.29, 47.75, 38.82, 24.96, 24.94, 24.92, 24.86, 22.00, 21.80, 21.66 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 33.04 ppm.

HRMS (ESI-TOF): calc'd for $C_{24}H_{42}B_2O_6$ $[M+H]^+$: 449.3240, found: 449.3259.

TLC: R_f = 0.54 (5:1 hexanes: ethyl acetate).

Compound 34



***isopropyl 3-(4-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentane-1-carboxylate* (34)**

Following **General Procedure A** on 0.1 mmol scale with BCP bisboronate **23** and 2-mesityl sulfonyl hydrazone **SI-22** reacting for 18 h. Purification by flash chromatography (hexanes: ethyl acetate, 4:1) and afforded 30.6 mg (57%) of the title compound **34**.

Note: two diastereoisomers (1/1) were observed. NMR characterization for the mixture was given.

Physical State: pale yellow solid.

m.p.: 53-55 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.27 – 7.09 (m, 5H), 4.96 (hept, *J* = 6.3 Hz, 1H), 2.75 (dd, *J* = 9.6, 1.9 Hz, 1H), 2.56 (tdd, *J* = 12.9, 5.1, 2.7 Hz, 1H), 2.49 – 2.38 (m, 1H), 1.92 (ddd, *J* = 5.6, 4.3, 1.4 Hz, 1H), 1.89 – 1.78 (m, 3H), 1.67 (dd, *J* = 7.8, 4.4 Hz, 1H), 1.26 (s, 6H), 1.26 (s, 6H), 1.21 – 1.19 (m, 7H), 1.18 (s, 3H), 1.17 (s, 3H), 1.12 (s, 3H), 1.11 (s, 3H), 0.97 (s, 1.5H), 0.96 (s, 1.5H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 170.70, 170.69, 143.66, 143.62, 128.54, 128.52, 128.30, 128.28, 125.60, 83.44, 82.93, 67.51, 67.50, 54.19, 54.13, 49.17, 49.03, 48.18, 48.12, 39.23, 39.15, 39.07,

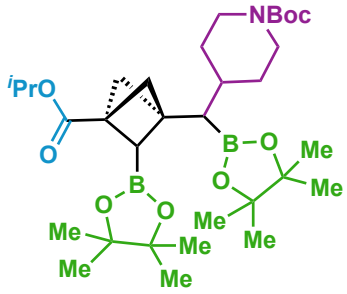
38.61, 33.54, 33.49, 25.37, 25.33, 25.07, 25.03, 24.90, 24.86, 24.78, 24.75, 21.99, 18.35, 18.31 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.84 ppm.

HRMS (ESI-TOF): calc'd for $C_{31}H_{48}B_2O_6$ $[M+H]^+$: 539.3710, found: 539.3705.

TLC: R_f = 0.52 (5:1 hexanes: ethyl acetate).

Compound 35



***tert-butyl 4-((3-(isopropoxycarbonyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)piperidine-1-carboxylate* (35)**

Following **General Procedure A** on 0.1 mmol scale with BCP bisboronate **23** and 2-mesityl sulfonyl hydrazone **SI-23** reacting for 24 h. Purification by flash chromatography (hexanes: ethyl acetate, 4:1) and afforded 45.1 mg (75%) of the title compound **35**.

Note: two diastereoisomers (1/1) were observed. NMR characterization for the mixture was given.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.96 (hept, J = 6.3, 1.1 Hz, 1H), 4.03 (br., 2H), 2.69 – 2.56 (m, 3H), 2.06 – 1.93 (m, 3H), 1.90 – 1.83 (m, 1H), 1.72 (d, J = 8.0 Hz, 1H), 1.69 – 1.58 (m, 3H), 1.46 – 1.42 (m, 11H), 1.24 (s, 3H), 1.23 (s, 3H), 1.23 (s, 6H), 1.22 (s, 12H), 1.21 – 1.18 (m, 6H) ppm.

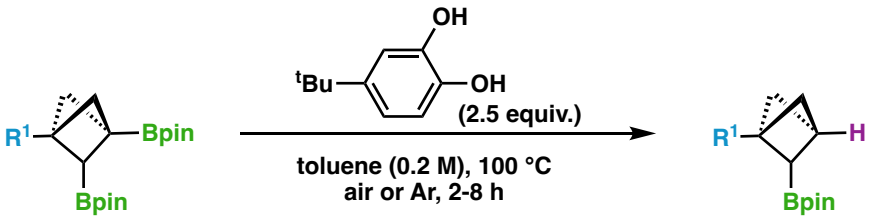
^{13}C NMR (151 MHz, $CDCl_3$): δ 170.09, 155.06, 155.04, 83.31, 83.24, 83.10, 83.08, 79.20, 67.56, 56.10, 51.94, 42.97, 42.84, 40.75, 40.72, 36.60, 36.47, 28.60, 25.28, 25.24, 25.16, 25.10, 25.08, 24.84, 24.83, 21.99, 21.97 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.78 ppm.

HRMS (ESI-TOF): calc'd for $C_{32}H_{55}B_2NO_8$ $[M+H]^+$: 604.4187, found: 604.4194.

TLC: R_f = 0.32 (5:1 hexanes: ethyl acetate).

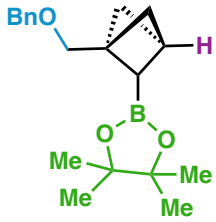
General Procedure B for Deborylation of BCP Bisboronates



A screw-capped 13×100 mm Pyrex culture tube or a flame-dried 100-mL Pyrex flask was charged with BCP bisboronate (1.0 equiv.) and tert-butyl catechol (2.5 equiv.). Then the tube or the flask was evacuated and backfilled with argon or air (as details below showed) for three times, followed by addition of toluene (0.1 M) via a syringe. After stirring for at 100 °C for 2-12 hours when it is confirmed that the starting material was consumed totally, the reaction mixture was cooled to room temperature. Next, the solvent was removed under high vacuum, and the crude residue was purified by chromatography on silica gel.[8]

Characterization of Substrates in Protodeborylation (36-41)

Compound 36



***2-(1-((benzyloxy)methyl)bicyclo[1.1.1]pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (36)**

Following **General Procedure B** on 0.1 mmol scale with BCP bisboronate **25** under argon atmosphere heating for 12 hours. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 22.0 mg (70%) of the title compound **36**.

Following **General Procedure B** on 2.0 mmol scale with BCP bisboronate **25** under argon atmosphere heating for 5 hours. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 528 mg (84%) of the title compound **36**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 – 7.30 (m, 4H), 7.28 – 7.24 (m, 1H), 4.54 (s, 2H), 3.45 (s, 2H), 2.69 (s, 1H), 2.22 (dd, *J* = 9.8, 2.2 Hz, 1H), 1.82 (d, *J* = 9.0 Hz, 2H), 1.78 (dd, *J* = 8.3, 2.2 Hz, 1H), 1.61 (d, *J* = 8.3 Hz, 1H), 1.225 (s, 6H), 1.222 (s, 6H) ppm.

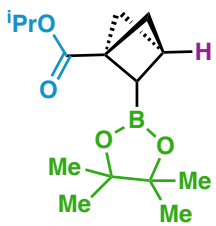
^{13}C NMR (151 MHz, $CDCl_3$): δ 139.04, 128.37, 127.60, 127.45, 83.06, 72.96, 70.74, 53.55, 48.90, 46.48, 30.49, 24.94(2C) ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.21 ppm.

HRMS (ESI-TOF): calc'd for $C_{19}H_{27}BO_3$ $[M+H]^+$: 315.2126, found: 315.2134.

TLC: R_f = 0.46 (10:1 hexanes: ethyl acetate).

Compound 37



isopropyl 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentane-1-carboxylate

(37)

Following **General Procedure B** on 0.1 mmol scale with BCP bisboronate **23** under air atmosphere heating for 3 h. Purification by flash chromatography (hexanes: ethyl acetate, 10:1) and afforded 20.2 mg (72%) of the title compound **37**.

Following **General Procedure B** on 3.0 mmol scale with BCP bisboronate **23** under air atmosphere heating for 2 h 20 minutes. Purification by flash chromatography (hexanes: ethyl acetate, 10:1) and afforded 630.7 mg (75%) of the title compound **37**.

Following **General Procedure B** on 10.0 mmol scale with BCP bisboronate **23** under air atmosphere heating for 2.5 h. Purification by flash chromatography (hexanes: ethyl acetate, 10:1) and afforded 2.09 g (75%) of the title compound **37**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.97 (hept, *J* = 6.3 Hz, 1H), 2.58 (dd, *J* = 9.5, 2.2 Hz, 1H), 2.55 (s, 1H), 2.10 – 2.04 (m, 2H), 2.02 (dd, *J* = 8.2, 2.3 Hz, 1H), 1.89 (dd, *J* = 8.2, 1.0 Hz, 1H), 1.25 (s, 12H), 1.22 (d, *J* = 3.9 Hz, 3H), 1.20 (d, *J* = 3.9 Hz, 3H) ppm.

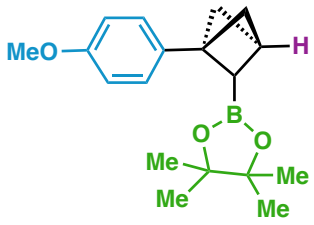
^{13}C NMR (151 MHz, $CDCl_3$): δ 169.38, 83.32, 67.59, 55.03, 50.46, 44.96, 29.72, 25.01, 24.88, 21.96, 21.95 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.65 ppm.

HRMS (ESI-TOF): calc'd for $C_{15}H_{25}BO_4$ $[M+H]^+$: 289.1919, found: 289.1933.

TLC: R_f = 0.36 (10:1 hexanes: ethyl acetate).

Compound 38



2-(1-(4-methoxyphenyl)bicyclo[1.1.1]pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **(38)**

Following **General Procedure B** on 0.1 mmol scale with BCP bisboronate **27** under argon atmosphere heating for 6 h. Purification by flash chromatography (hexanes: ethyl acetate, 4:1) and afforded 19.6 mg (65%) of the title compound **38**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 3.78 (s, 3H),

2.68 (s, 1H), 2.61 (dd, J = 9.7, 2.1 Hz, 1H), 2.08 (d, J = 9.6 Hz, 1H), 2.05 (s, 1H), 2.00 (dd, J = 8.2, 2.1 Hz, 1H), 1.89 (d, J = 8.2 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 158.23, 134.47, 127.43, 113.45, 83.15, 55.65, 55.39, 51.39, 49.27, 28.71, 24.99, 24.96 ppm.

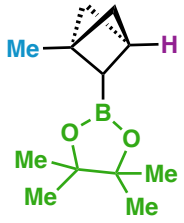
^{11}B NMR (128 MHz, $CDCl_3$): δ 32.18 ppm.

HRMS (ESI-TOF): calc'd for $C_{18}H_{25}BO_3$ $[M+H]^+$: 301.1970, not found.

MS (GCMS, EI): m/z = 300 (14%), 200 (18%), 172 (90%), 133 (100%), 84 (54%).

TLC: R_f = 0.50 (10:1 hexanes: ethyl acetate).

Compound 39



***4,4,5,5-tetramethyl-2-((1s,3s)-1-methylbicyclo[1.1.1]pentan-2-yl)-1,3,2-dioxaborolane* (39)**

Following **General Procedure B** on 0.1 mmol scale with BCP bisboronate **13** under argon atmosphere heating for 5 hours. Purification by flash chromatography (hexanes: ethyl acetate, 40:1) and afforded 12.6 mg (61%) of the title compound **39**. *Note: The compound is volatile.*

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 2.59 (s, 1H), 2.07 (dd, J = 9.7, 2.2 Hz, 1H), 1.71 (dd, J = 9.7, 1.4 Hz, 1H), 1.69 (s, 1H), 1.64 (dd, J = 8.4, 2.2 Hz, 1H), 1.49 (dd, J = 8.4, 1.1 Hz, 1H), 1.258 (s, 6H), 1.256 (s, 6H), 1.17 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 82.96, 55.95, 51.30, 44.81, 29.44, 25.04, 24.95, 19.39 ppm.

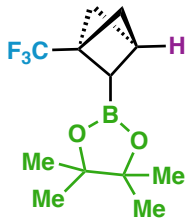
^{11}B NMR (128 MHz, $CDCl_3$): δ 32.16 ppm.

HRMS (ESI-TOF): calc'd for $C_{12}H_{21}BO_2$ $[M+H]^+$: 209.1707, not found.

MS (GCMS, EI): m/z = 193 (7%), 151 (8%), 135 (7%), 108 (100%), 67 (62%).

TLC: R_f = 0.50 (20:1 hexanes: ethyl acetate).

Compound 40



***4,4,5,5-tetramethyl-2-(1-(trifluoromethyl)bicyclo[1.1.1]pentan-2-yl)-1,3,2-dioxaborolane* (40)**

Following **General Procedure B** on 0.1 mmol scale with BCP bisboronate **26** under argon atmosphere in benzene solution heating at 100 °C for 12 hours. Purification by flash chromatography (hexanes: ethyl acetate, 40:1) and afforded 17.4 mg (66%) of the title compound **40**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 2.67 (s, 1H), 2.58 (dd, *J* = 9.5, 2.3 Hz, 1H), 2.03 – 1.98 (m, 2H), 1.96 (dd, *J* = 8.2, 2.3 Hz, 1H), 1.84 (d, *J* = 8.2 Hz, 1H), 1.254 (s, 6H), 1.252 (s, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 122.03 (q, *J* = 277.2 Hz), 83.46, 52.13, 47.33, 43.36 (q, *J* = 37.5 Hz), 29.72, 24.70, 24.69 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.45 ppm.

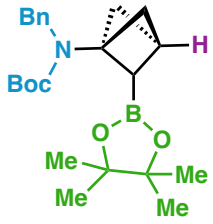
^{19}F NMR (565 MHz, $CDCl_3$): δ -73.45 ppm.

HRMS (ESI-TOF): calc'd for $C_{12}H_{18}BF_3O_2$ $[M+H]^+$: 263.1425, not found.

MS (GCMS, EI): m/z = 247 (11%), 153 (9%), 131 (29%), 83 (52%), 59 (100%).

TLC: R_f = 0.50 (20:1 hexanes: ethyl acetate).

Compound 41



***tert-butyl benzyl(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)carbamate* (41)**

In a 5 mL screw-capped culture tube was added **24** (0.1 mmol), DMAP (30 mol%), MeOBcat (30 mol%) and $(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$ (5 mol%). CH_3OH (0.5 mL) and acetone (0.5 mL) was

added, and the tube was sealed. The reaction was stirred under irradiation by blue LED for 2 hours when TLC analysis showed the consume of the starting material. The solvent was concentrated and the residue was purified by flash chromatography (hexanes: ethyl acetate, 10:1) and afforded 20.5 mg (53%) of the title compound **41**.

Note: the protodeboralation product of bis-Bpins was observed as the reaction time is extended.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 – 7.26 (m, 2H), 7.24 – 7.21 (m, 2H), 7.19 (td, *J* = 7.1, 1.4 Hz, 1H), 4.57 – 4.33 (m, 2H), 2.80 – 2.28 (m, 2H), 2.04 (dd, *J* = 9.6, 1.3 Hz, 1H), 2.00 – 1.91 (m, 3H), 1.45 (br., 9H), 1.23 (s, 12H) ppm.

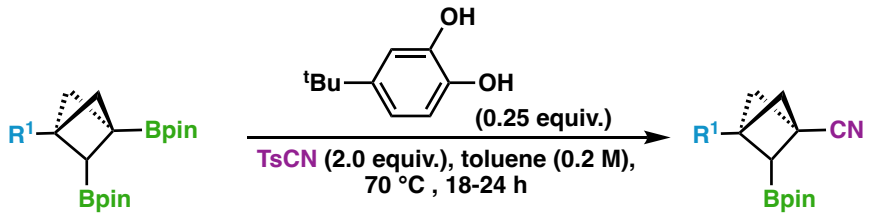
^{13}C NMR (151 MHz, $CDCl_3$): δ 140.09, 128.29, 126.76, 126.57, 83.16, 52.11, 48.88, 28.58, 25.79, 25.00 ppm. *Note:* BnN*C*(O)*,* BocBnN*C,* N*C*H_2Ph*,* Me_3*C, and* Bpin*C were not observed*.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.29 ppm.

HRMS (ESI-TOF): calc'd for $C_{23}H_{34}BNO_4$ $[M+H]^+$: 400.2653, found: 400.2655.

TLC: R_f = 0.39 (10:1 hexanes: ethyl acetate).

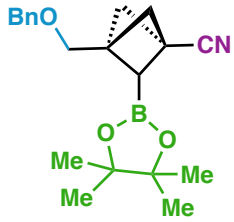
General Procedures C for Cyanation of BCP Bisboronates



A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with BCP bisboronate (1.0 equiv.), p-toluenesulfonyl cyanide (2.0 equiv.) and tert-butyl catechol (0.25 equiv.). Then the tube or the flask was evacuated and backfilled with argon for three times, followed by addition of toluene (0.2 M) via a syringe. After stirring for at 70°C for 18-24 hours when it is confirmed that the starting material was consumed totally, the reaction mixture was cooled to room temperature. Next, the solvent was removed under high vacuum, and the crude residue was purified by chromatography on silica gel.[8]

Characterization of Substrates in Cyanation (42, 43)

Compound 42



***3-((benzyloxy)methyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentane-1-carbonitrile* (42)**

Following **General Procedure C** on 0.1 mmol scale with BCP bisboronate **25**, p-toluenesulfonyl cyanide and guaiacol (1.0 equiv.) as additive. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 19.5 mg (57%) of the title compound **42**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 – 7.24 (m, 4H), 7.24 – 7.21 (m, 1H), 4.45 (s, 2H), 3.39 (s, 2H), 2.69 (dd, *J* = 9.9, 2.3 Hz, 1H), 2.19 – 2.14 (m, 2H), 2.10 (dd, *J* = 8.2, 2.3 Hz, 1H), 1.98 (d, *J* = 8.2 Hz, 1H), 1.19 (s, 6H), 1.18 (s, 6H) ppm.

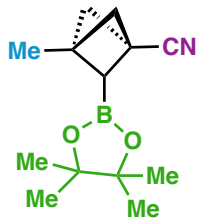
^{13}C NMR (151 MHz, $CDCl_3$): δ 138.26, 128.44, 127.71, 127.61, 118.00, 83.85, 73.17, 68.93, 57.33, 52.55, 45.48, 26.01, 24.87, 24.84 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.02 ppm.

HRMS (ESI-TOF): calc'd for $C_{20}H_{26}BNO_3$ $[M+H]^+$: 340.2079, found: 340.2088.

TLC: R_f = 0.28 (10:1 hexanes: ethyl acetate).

Compound 43



***3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentane-1-carbonitrile* (43)**

Following **General Procedure C** on 0.2 mmol scale with BCP bisboronate **13**, and p-toluenesulfonyl cyanide. Purification by flash chromatography (hexanes: ethyl acetate, 50:1) and

afforded 23.0 mg (50%) of the title compound **43**.

Physical State: white solid.

m.p.: 44-46 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 2.56 (dd, *J* = 9.7, 2.3 Hz, 1H), 2.14 – 2.11 (m, 2H), 2.05 (dd, *J* = 8.4, 2.4 Hz, 1H), 1.92 (d, *J* = 8.3 Hz, 1H), 1.26 (s, 12H), 1.19 (s, 3H) ppm.

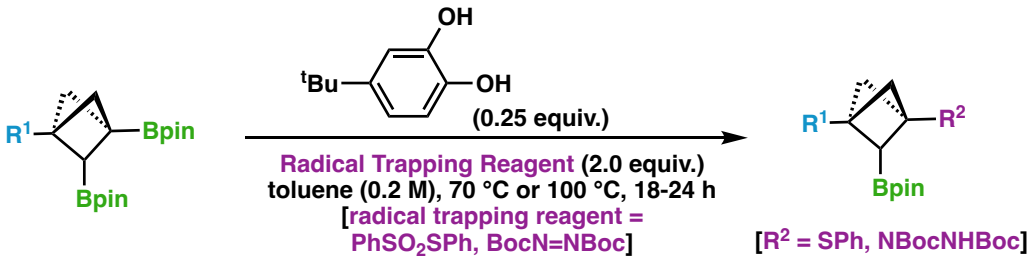
^{13}C NMR (151 MHz, $CDCl_3$): δ 118.13, 83.79, 59.60, 54.83, 43.87, 25.19, 24.96, 24.93, 17.82 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.12 ppm.

HRMS (ESI-TOF): calc'd for $C_{13}H_{20}BNO_2$ $[M+H]^+$: 234.1660, found: 234.1667.

TLC: R_f = 0.28 (10:1 hexanes: ethyl acetate).

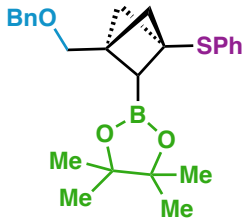
General Procedures D for C-S & C-N Formation of BCP Bisboronates



A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with BCP bisboronate (1.0 equiv.), radical trapping reagent (2.0 equiv., $PhSO_2SPh$ or DBAD) and tert-butyl catechol (0.25 equiv.). Then the tube or the flask was evacuated and backfilled with argon for three times, followed by addition of toluene (0.2 M) via a syringe. After stirring for at 70 °C or 100 °C (as details showed) for 18-24 hours when it is confirmed that the starting material was consumed totally, the reaction mixture was cooled to room temperature. Next, the solvent was removed under high vacuum, and the crude residue was purified by chromatography on silica gel.[8]

Characterization of Substrates in C-S & C-N Formation (44-47)

Compound 44



***2-(1-((benzyloxy)methyl)-3-(phenylthio)bicyclo[1.1.1]pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (44)**

Following **General Procedure D** on 0.1 mmol scale with BCP bisboronate **25**, and $PhSO_2SPh$ reacting at 100 °C for 24 h. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 29.6 mg (70%) of the title compound **44**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.46 – 7.41 (m, 2H), 7.32 – 7.16 (m, 8H), 4.46 (s, 2H), 3.44 (s, 2H), 2.54 (dd, *J* = 9.5, 1.9 Hz, 1H), 1.87 (dd, *J* = 8.1, 1.9 Hz, 1H), 1.85 – 1.81 (m, 2H), 1.67 (d, *J* = 8.0 Hz, 1H), 1.142 (s, 6H), 1.138 (s, 6H) ppm.

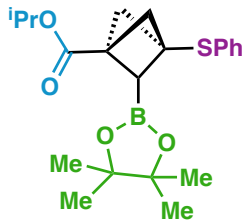
^{13}C NMR (151 MHz, $CDCl_3$): δ 138.67, 134.17, 134.12, 128.78, 128.40, 127.60, 127.57, 127.55, 83.22, 72.96, 69.71, 57.80, 52.05, 45.30, 42.19, 24.92, 24.87 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.13 ppm.

HRMS (ESI-TOF): calc'd for $C_{25}H_{31}BO_3S$ $[M+H]^+$: 423.2160, found: 423.2173.

TLC: R_f = 0.48 (10:1 hexanes: ethyl acetate).

Compound 45



***isopropyl 3-(phenylthio)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentane-1-carboxylate* (45)**

Following **General Procedure D** on 0.1 mmol scale with BCP bisboronate **23**, and $PhSO_2SPh$ reacting at 70 °C for 24 h. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and

afforded 13.6 mg (35%) of the title compound **45**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.48 – 7.43 (m, 2H), 7.31 – 7.27 (m, 3H), 4.95 (hept, *J* = 6.3 Hz, 1H), 2.90 (dd, *J* = 9.4, 1.9 Hz, 1H), 2.20 – 2.13 (m, 1H), 2.12 (s, 1H), 2.12 – 2.07 (m, 1H), 2.01 – 1.92 (m, 1H), 1.22 (s, 6H), 1.21 (s, 6H), 1.18 (d, *J* = 6.3 Hz, 6H) ppm.

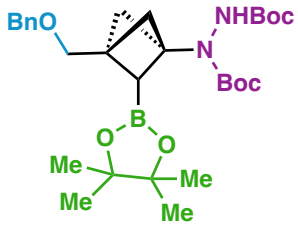
^{13}C NMR (151 MHz, $CDCl_3$): δ 168.60, 134.51, 133.16, 128.95, 128.04, 83.50, 68.10, 59.22, 53.67, 45.08, 41.21, 25.02, 24.82, 21.90 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.01 ppm.

HRMS (ESI-TOF): calc'd for $C_{21}H_{29}BO_4S$ $[M+H]^+$: 389.1952, found: 389.1959.

TLC: R_f = 0.45 (10:1 hexanes: ethyl acetate).

Compound 46



***di-tert-butyl 1-(3-((benzyloxy)methyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo [1.1.1]pentan-1-yl)hydrazine-1,2-dicarboxylate* (46)**

Following **General Procedure D** on 0.1 mmol scale with BCP bisboronate **25**, and and di-*tert*-butyl azodicarboxylate (DBAD) reacting at 100 °C for 24 h. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 27.2 mg (50%) of the title compound **46**.

Physical State: red oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 – 7.23 (m, 5H), 6.66 (s, 0.5H), 6.15 (s, 0.5H), 4.54 (s, 2H), 3.61 (s, 2H), 2.57 – 1.68 (m, 5H), 1.46 (s, 9H), 1.45 (s, 9H), 1.21 (s, 12H) ppm.

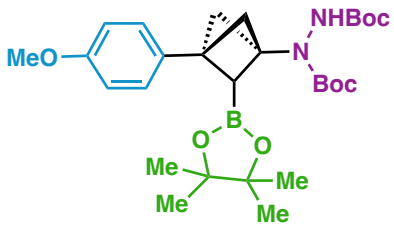
^{13}C NMR (151 MHz, $CDCl_3$): δ 138.82, 128.40, 127.61, 127.52, 83.37, 72.97, 69.05, 28.45, 28.34, 24.95, 24.90 ppm. *Note:* Me_3C, CNC(O), NNHC(O) *and all the carbon of BCP skeleton were not observed*.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.76 ppm.

HRMS (ESI-TOF): calc. for $C_{29}H_{45}BN_2O_7$ $[M+H]^+$: 545.3393, found: 545.3374.

TLC: R_f = 0.59 (2:1 hexanes: ethyl acetate).

Compound 47



***di-tert-butyl 1-(3-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo [1.1.1]pentan-1-yl)hydrazine-1,2-dicarboxylate* (47)**

Following **General Procedure D** on 0.1 mmol scale with BCP bisboronate **27**, and di-*tert*-butyl azodicarboxylate (DBAD) reacting at 100 °C for 24 h. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 23.9 mg (45%) of the title compound **47**.

Physical State: light yellow foam.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.21 (d, *J* = 8.1 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 6.65 (br., 0.5H), 6.16 (br., 0.5H), 3.78 (s, 3H), 2.98 – 2.60 (m, 1H), 2.52 – 2.25 (m, 2H), 2.20 – 1.97 (m, 2H), 1.54 – 1.44 (m, 18H), 1.24 (s, 12H) ppm.

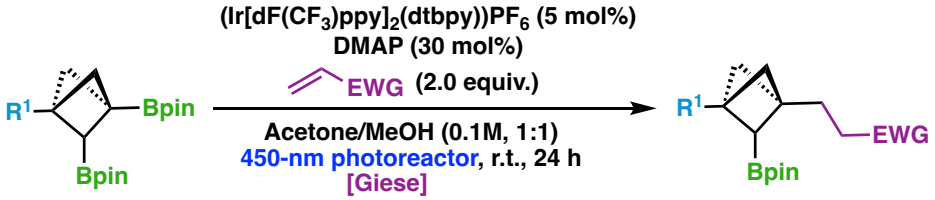
^{13}C NMR (151 MHz, $CDCl_3$): δ 158.44, 131.80, 127.93, 113.59, 83.45, 55.41, 28.46, 28.34, 25.03, 24.92 ppm. *Note:* Me_3C, CN*C*(O), NNH*C*(O) *and all the carbon of BCP skeleton were not observed*.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.11 ppm.

HRMS (ESI-TOF): calc. for $C_{28}H_{43}BN_2O_7$ $[M+H]^+$: 531.3236, found: 531.3235.

TLC: R_f = 0.59 (2:1 hexanes: ethyl acetate).

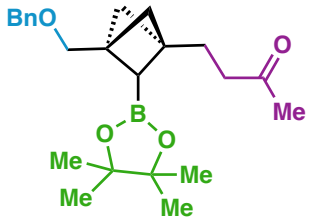
General Procedure E for Giese-type reaction of BCP Bisboronates



A screw-capped 13×100 mm pyrex culture tube was charged with (Ir[dF(CF_3)ppy]$_2$(dtbpy))PF_6 (5 mol%), DMAP (30 mol%), BCP bisboronate (1.0 equiv.) and Michael acceptor (2.0 equiv.). Then the tube or the flask was evacuated and backfilled with argon for three times, followed by addition of methanol/acetone (0.1 M, 1:1) solvent via a syringe. Then the headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds. After stirring in a 450-nm photoreactor for 24 hours when it is confirmed that the starting material was consumed totally, the reaction mixture was concentrated under high vacuum, and the crude residue was purified by chromatography on silica gel. [9]

Characterization of Substrates in Giese reaction (48-54)

Compound 48



***4-(3-((benzyloxy)methyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)butan-2-one* (48)**

Following **General Procedure E** on 0.05 mmol scale with BCP bisboronate **25**, and methyl vinyl ketone. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 13.5 mg (70%) of the title compound **48**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 – 7.29 (m, 4H), 7.27 – 7.23 (m, 1H), 4.53 (s, 2H), 3.47 (s, 2H), 2.42 (dd, J = 8.6, 6.9 Hz, 2H), 2.14 (s, 3H), 2.11 (dd, J = 9.9, 2.0 Hz, 1H), 1.79 (t, J = 7.7 Hz, 2H), 1.61 – 1.58 (m, 2H), 1.55 (dd, J = 8.2, 2.0 Hz, 1H), 1.44 – 1.38 (m, 1H), 1.21 (s, 12H) ppm.

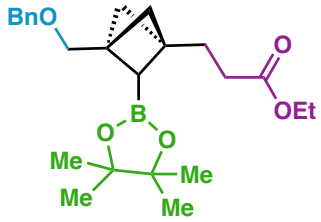
^{13}C NMR (151 MHz, $CDCl_3$): δ 209.17, 139.00, 128.36, 127.57, 127.44, 82.96, 72.93, 70.40, 53.49, 48.17, 42.45, 41.01, 40.72, 29.93, 26.48, 24.96, 24.95 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.69 ppm.

HRMS (ESI-TOF): calc'd for $C_{23}H_{33}BO_4S$ $[M+H]^+$: 385.2545, found: 385.2547.

TLC: R_f = 0.32 (4:1 hexanes: ethyl acetate).

Compound 49



***ethyl 3-(3-((benzyloxy)methyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)propanoate* (49)**

Following **General Procedure E** on 0.1 mmol scale with BCP bisboronate **25**, and ethyl acrylate. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 15.7 mg (38%)

of the title compound **49**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 – 7.30 (m, 4H), 7.29 – 7.23 (m, 1H), 4.53 (s, 2H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.48 (s, 2H), 2.29 (td, *J* = 7.5, 1.8 Hz, 2H), 2.12 (dd, *J* = 9.8, 2.0 Hz, 1H), 1.85 (t, *J* = 7.8 Hz, 2H), 1.63 – 1.59 (m, 2H), 1.57 (dd, *J* = 8.3, 2.0 Hz, 1H), 1.42 (d, *J* = 8.2 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.21 (s, 12H) ppm.

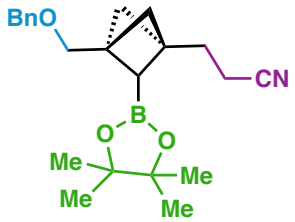
^{13}C NMR (151 MHz, $CDCl_3$): δ 173.95, 139.01, 128.36, 127.58, 127.44, 82.96, 72.94, 70.41, 60.34, 53.40, 48.12, 42.46, 40.69, 31.71, 27.58, 24.95, 24.93, 14.35 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.62 ppm.

HRMS (ESI-TOF): calc'd for $C_{24}H_{35}BO_5$ $[M+H]^+$: 415.2650, found: 415.2656.

TLC: R_f = 0.54 (4:1 hexanes: ethyl acetate).

Compound 50



***3-(3-((benzyloxy)methyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)propanenitrile* (50)**

Following **General Procedure E** on 0.1 mmol scale with BCP bisboronate **25**, and acrylonitrile. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 20.0 mg (55%) of the title compound **50**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 – 7.30 (m, 4H), 7.30 – 7.23 (m, 1H), 4.53 (s, 2H), 3.50 (s, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 2.13 (dd, *J* = 10.0, 2.2 Hz, 1H), 1.89 (t, *J* = 7.5 Hz, 2H), 1.73 – 1.69 (m, 2H), 1.66 (dd, *J* = 8.3, 2.1 Hz, 1H), 1.47 (d, *J* = 8.2 Hz, 1H), 1.213 (s, 6H), 1.208 (s, 6H) ppm.

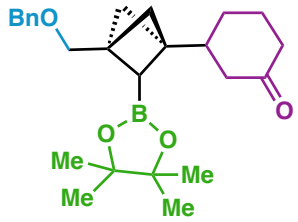
^{13}C NMR (151 MHz, $CDCl_3$): δ 138.88, 128.37, 127.57, 127.49, 120.28, 83.19, 72.99, 70.07, 53.51, 48.42, 41.61, 40.95, 28.16, 24.95 (2C), 14.52 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.66 ppm.

HRMS (ESI-TOF): calc'd for $C_{22}H_{30}BNO_3$ $[M+H]^+$: 368.2392, found: 368.2400.

TLC: R_f = 0.39 (4:1 hexanes: ethyl acetate).

Compound 51



***3-(3-((benzyloxy)methyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)cyclohexan-1-one* (51)**

Following **General Procedure E** on 0.1 mmol scale with BCP bisboronate **25**, and cyclohexenone. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 22.8 mg (56%) of the title compound **51**.

Note: two diastereoisomers (1/1) were observed. NMR spectroscopy of the mixture was given.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 – 7.28 (m, 4H), 7.29 – 7.21 (m, 1H), 4.53 (s, 2H), 3.49 (s, 2H), 2.36 – 2.28 (m, 2H), 2.24 – 2.15 (m, 2H), 2.10 – 1.98 (m, 2H), 1.90 (tt, J = 12.3, 3.7 Hz, 1H), 1.86 – 1.79 (m, 1H), 1.66 – 1.51 (m, 4H), 1.41 (dd, J = 11.1, 8.1 Hz, 1H), 1.34 – 1.27 (m, 1H), 1.20 (s, 6H), 1.19 (s, 6H) ppm.

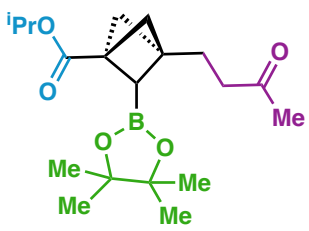
^{13}C NMR (151 MHz, $CDCl_3$): δ 212.61, 138.90, 128.37, 127.58, 127.47, 83.02, 83.00, 72.98, 70.37, 70.35, 51.37, 51.24, 46.22, 46.20, 46.09, 46.07, 44.87, 44.85, 41.38, 41.34, 40.57, 40.50, 39.97, 39.95, 28.08, 28.00, 25.59, 25.48, 24.91, 24.87 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.00 ppm.

HRMS (ESI-TOF): calc'd for $C_{25}H_{35}BO_4$ $[M+H]^+$: 411.2701, found: 411.2700.

TLC: R_f = 0.36 (4:1 hexanes: ethyl acetate).

Compound 52



***isopropyl 3-(3-oxobutyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentane-1-carboxylate* (52)**

Following **General Procedure E** on 0.1 mmol scale with BCP bisboronate **23**, and methyl vinyl ketone. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 12.9 mg (37%) of the title compound **52**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 4.97 (hept, *J* = 6.3 Hz, 1H), 2.47 (dd, *J* = 9.9, 2.1 Hz, 1H), 2.44 – 2.38 (m, 2H), 2.13 (s, 3H), 1.87 – 1.83 (m, 2H), 1.82 (dd, *J* = 8.1, 2.1 Hz, 1H), 1.78 (ddd, *J* = 11.2, 6.7, 3.4 Hz, 2H), 1.67 (d, *J* = 8.1 Hz, 1H), 1.241 (s, 6H), 1.238 (s, 6H), 1.21 (d, *J* = 2.9 Hz, 3H), 1.20 (d, *J* = 2.9 Hz, 3H) ppm.

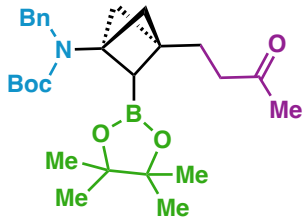
^{13}C NMR (151 MHz, $CDCl_3$): δ 208.53, 169.90, 83.26, 67.64, 55.18, 50.05, 41.72, 40.64, 39.95, 29.98, 25.85, 25.01, 24.89, 21.96, 21.95 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.62 ppm.

HRMS (ESI-TOF): calc'd for $C_{19}H_{31}BO_5$ $[M+H]^+$: 351.2337, found: 351.2347.

TLC: R_f = 0.29 (4:1 hexanes: ethyl acetate).

Compound 53



***tert-butyl benzyl(3-(3-oxobutyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)carbamate* (53)**

Following **General Procedure E** on 0.1 mmol scale with BCP bisboronate **24**, and methyl vinyl ketone. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 13.6 mg (29%) of the title compound **53**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 – 7.22 (m, 2H), 7.23 – 7.16 (m, 3H), 4.52 – 4.41 (m, 2H), 2.37 (t, *J* = 7.7 Hz, 2H), 2.10 (s, 3H), 1.84 (dd, *J* = 9.6, 1.2 Hz, 1H), 1.82 – 1.71 (m, 5H), 1.57 – 1.32 (m, 10H), 1.22 (s, 12H) ppm.

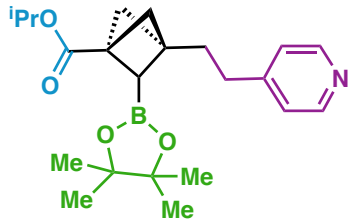
^{13}C NMR (151 MHz, $CDCl_3$): δ 208.73, 140.05, 128.29, 126.73, 126.59, 83.11, 79.83 (br.), 51.62, 49.08 (br.), 41.25, 38.27, 29.93, 28.58, 25.05, 25.00, 24.44 ppm. *Note:* BnN*C*(O), BnBocN*C*, BocN*C*H_2Ph *and* Bpin*C were not observed*.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.06 ppm.

HRMS (ESI-TOF): calc. for $C_{27}H_{40}BNO_5$ $[M+H]^+$: 470.3072, found: 470.3069.

TLC: R_f = 0.32 (4:1 hexanes: ethyl acetate).

Compound 54



***isopropyl 3-(2-(pyridin-4-yl)ethyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo [1.1.1]pentane-1-carboxylate* (54)**

Following **General Procedure E** on 0.1 mmol scale with BCP bisboronate **23**, and 4-vinylpyridine. Purification by flash chromatography (hexanes: ethyl acetate, 2:1) and afforded 20.5 mg (53%) of the title compound **54**.

Scale-up preparation: A flame-dried screw-capped 50-mL pyrex flask was charged with BCP bisboronate **23** (810 mg, 2.0 mmol, 1.0 equiv.), 4-CzlPn (78.8 mg, 0.1 mmol, 0.05 equiv.) and DMAP (73.2 mg, 0.6 mmol, 0.3 equiv.). Then the flask was evacuated and backfilled with argon for three times, followed by addition of 4-vinyl pyridine (0.43 mL, 4.0 mmol, 2.0 equiv.), and acetone/methanol (20 mL, 1:1). Next, the reaction tube was irradiated under a 40 W Kessil blue LED lamp (468 nm) for 24 hours with a fan running to cool the reaction down. After it is confirmed that the starting material was consumed totally, the reaction mixture was concentrated under high vacuum. The crude residue was purified by chromatography on silica gel (hexanes: ethyl acetate, 2:1) and that afforded 578 mg (75%) product **54** as pale-yellow oil.

Physical State: pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.49 (br., 2H), 7.14 (br., 2H), 4.97 (hept, J = 6.2 Hz, 1H), 2.59 (td, J = 7.7, 4.4 Hz, 2H), 2.50 (dd, J = 9.9, 2.0 Hz, 1H), 1.90 – 1.87 (m, 2H), 1.87 – 1.83 (m, 3H), 1.72 (d, J = 8.1 Hz, 1H), 1.240 (s, 6H), 1.238 (s, 6H), 1.21 (d, J = 2.8 Hz, 3H), 1.20 (d, J = 2.8 Hz, 3H) ppm.

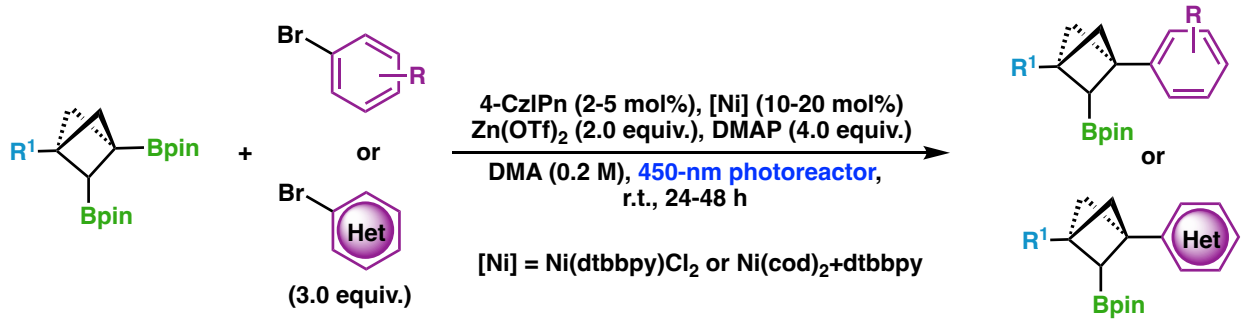
^{13}C NMR (151 MHz, $CDCl_3$): δ 169.84, 151.88, 149.29, 124.15, 83.28, 67.70, 55.28, 50.27, 42.07, 40.04, 32.25, 32.20, 24.99, 24.92, 21.94 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.50 ppm.

HRMS (ESI-TOF): calc'd for $C_{22}H_{32}BNO_4$ $[M+H]^+$: 386.2497, found: 386.2498.

TLC: R_f = 0.23 (1:1 hexanes: ethyl acetate).

General Procedure F for Cross-Coupling of BCP Bisboronates



General Procedure F1:

A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with BCP bisboronate (1.0 equiv.), aryl bromide (3.0 equiv.), 4-CzlPn (5 mol%), Ni(dtbbpy)Cl_2 (10 mol%), Zn(OTf)$_2$ (2.0 equiv.) and DMAP (4.0 equiv.). Then the tube was evacuated and backfilled with argon three times, followed by addition of DMA (0.2 M) solvent via a syringe. Next, the headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was allowed to stir in a 450-nm PennPhD integrated photoreactor (M2) for 24-60 hours. After it is confirmed that the starting material was consumed totally, the reaction mixture quenched with water, extracted with ethyl acetate or diethyl ether, washed with brine, dried by Na_2SO_4, and concentrated under high vacuum. The crude residue was purified by chromatography on silica gel.

General Procedure F2:

Preparation of [Ni] catalyst: A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with Ni(cod)$_2$ (0.2 mmol, 55 mg) and dtbbpy (0.24 mmol, 64.4 mg). Then the tube was evacuated and backfilled with argon three times, followed by addition of DMA (4.0 mL) solvent via a syringe. Next, the tube was then sonicated for 20 minutes to dissolve the catalyst.

A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with BCP bisboronate (1.0 equiv.), aryl bromide (3.0 equiv.), Zn(OTf)$_2$ (2.0 equiv.) and DMAP (4.0 equiv.). Then the tube was evacuated and backfilled with argon for three times, followed by addition of 4-CzlPn solution (0.02 equiv., 0.02 M) in DMA and [Ni] catalyst solution (0.2 equiv., 0.05 M) in DMA via a syringe. Next, the headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was allowed to stir in a 450-nm PennPhD integrated photoreactor (M2) for 24-60 hours. After it is confirmed that the starting material was consumed

totally, the reaction mixture quenched with water, extracted with ethyl acetate or diethyl ether, washed with brine, dried by Na_2SO_4, and concentrated under high vacuum. The crude residue was purified by chromatography on silica gel.

Scale-up of cross-coupling of BCP boronate 13 & 23:

Preparation of [Ni] catalyst: A flame-dried screw-capped 20×150 mm pyrex culture tube was charged with $Ni(cod)_2$ (0.4 mmol, 110 mg) and dtbbpy (0.48 mmol, 128.8 mg). Then the tube was evacuated and backfilled with argon for three times, followed by addition of DMA (8.0 mL) solvent via a syringe. Next, the tube was then sonicated for 20 minutes to form a dark purple solution of Ni catalyst.

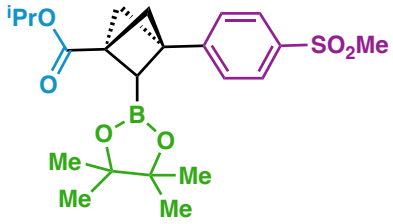
Scale-up preparation of BCP boronate 65: A flame-dried 20×150 mm pyrex screw-capped culture tube was charged with BCP bisboronate **13** (668 mg, 2.0 mmol, 1.0 equiv.), $Zn(OTf)_2$ (1.46 mg, 4.0 mmol, 2.0 equiv.) and DMAP (977.6 mg, 8.0 mmol, 4.0 equiv.). Then the tube was evacuated and backfilled with argon for three times, followed by addition of phenyl bromide (0.62 mL, 6.0 mmol, 3.0 equiv.), 4-CzlPn solution (1.0 mL, 0.05 equiv., 0.05 M) in DMA and [Ni] catalyst solution (8.0 mL, 0.2 equiv., 0.05 M) in DMA via a syringe. Next, the headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction tube was sealed and then irradiated under a 40 W Kessil blue LED lamp (468 nm) for 60 hours with a fan running to cool the reaction down. After it is confirmed that the starting material was consumed totally, the reaction mixture quenched with water (30 mL), extracted with ethyl acetate (10 mL × 2) and diethyl ether (10 mL × 2), washed with brine (10 mL × 2), dried by Na_2SO_4, and concentrated under high vacuum. The crude residue was purified by chromatography on silica gel and that afforded 209.6 mg (37%) product as colorless oil.

Scale-up preparation of BCP boronate 55: A flame-dried screw-capped 20×150 mm pyrex culture tube was charged with BCP bisboronate **23** (406 mg, 1.0 mmol, 1.0 equiv.), 4-bromophenyl methyl sulfone (705 mg, 3.0 mmol, 3.0 equiv.), $Zn(OTf)_2$ (732 mg, 2.0 mmol, 2.0 equiv.) and DMAP (488.8 mg, 4.0 mmol, 4.0 equiv.). Then the tube was evacuated and backfilled with argon for three times, followed by addition of 4-CzlPn solution (1.0 mL, 0.02 equiv., 0.02 M) in DMA and [Ni] catalyst solution (4.0 mL, 0.2 equiv., 0.05 M) in DMA via a syringe. Next, the headspace

of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was sealed and then irradiated under a 40 W Kessil blue LED lamp (468 nm) for 48 hours with a fan running to cool the reaction down. After it is confirmed that the starting material was consumed totally, the reaction mixture quenched with water (30 mL), extracted with ethyl acetate (10 mL × 2) and diethyl ether (10 mL × 2), washed with brine (10 mL × 2), dried by Na_2SO_4, and concentrated under high vacuum. The crude residue was purified by chromatography on silica gel and that afforded 200.0 mg (46%) product as colorless oil.

Characterization of Substrates in Cross-Coupling (55-69)

Compound 55



***isopropyl 3-(4-(methylsulfonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo [1.1.1]pentane-1-carboxylate* (55)**

Following **General Procedure F2** on 0.1 mmol scale with BCP bisboronate **23**, and 4-bromophenyl methyl sulfone reacting for 60 hours. Purification by flash chromatography (methylene chloride: ethyl acetate, 50:1 to 20:1) afforded 22.4 mg (52%) of the title compound **55**. Following **Scale-up of preparation of BCP boronate 55** on 1.0 mmol scale with BCP bisboronate **23**, and 4-bromophenyl methyl sulfone reacting for 48 hours. Purification by flash chromatography (methylene chloride: ethyl acetate, 50:1 to 20:1) afforded 200.0 mg (46%) of the title compound **55**.

Physical State: white solid.

m.p.: 114-116 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.88 – 7.84 (m, 2H), 7.49 – 7.45 (m, 2H), 5.04 (hept, J = 6.3 Hz, 1H), 3.05 (dd, J = 10.0, 1.9 Hz, 1H), 3.03 (s, 3H), 2.37 – 2.32 (m, 2H), 2.27 (dd, J = 8.1, 2.0 Hz, 1H), 2.15 (d, J = 8.0 Hz, 1H), 1.26 (d, J = 2.5 Hz, 3H), 1.25 – 1.24 (m, 15H) ppm.

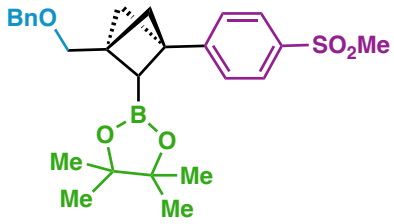
^{13}C NMR (151 MHz, $CDCl_3$): δ 169.58, 146.67, 138.89, 127.54, 127.45, 83.68, 68.13, 56.72, 52.42, 44.72, 43.53, 39.60, 24.96, 24.91, 21.98 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.90 ppm.

HRMS (ESI-TOF): calc'd for $C_{22}H_{31}BO_6S$ $[M+H]^+$: 435.2007, found: 435.2000.

TLC: R_f = 0.20 (2:1 hexanes: ethyl acetate).

Compound 56



***2-(1-((benzyloxy)methyl)-3-(4-(methylsulfonyl)phenyl)bicyclo[1.1.1]pentan-2-yl)-4,4,5,5-tetra methyl-1,3,2-dioxaborolane* (56)**

Following **General Procedure F1** on 0.1 mmol scale with BCP bisboronate **25**, and 4-bromophenyl methyl sulfone reacting for 48 hours. Purification by flash chromatography (methylene chloride: ethyl acetate, 50:1 to 20:1) afforded 19.8 mg (42%) of the title compound **56**.

Physical State: pale yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.51 – 7.46 (m, 2H), 7.40 – 7.31 (m, 4H), 7.30 – 7.27 (m, 1H), 4.58 (s, 2H), 3.58 (s, 2H), 3.03 (s, 3H), 2.74 – 2.69 (m, 1H), 2.09 (d, *J* = 8.9 Hz, 2H), 2.00 (dd, *J* = 8.0, 1.7 Hz, 1H), 1.87 (d, *J* = 8.1 Hz, 1H), 1.20 (s, 12H) ppm.

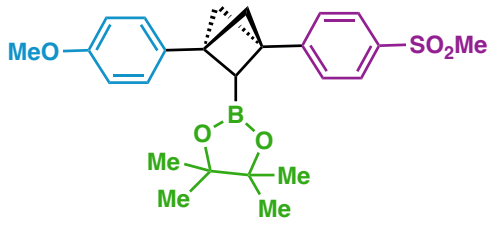
^{13}C NMR (151 MHz, $CDCl_3$): δ 147.83, 138.77, 138.35, 128.43, 127.64, 127.59, 127.52, 127.30, 83.37, 73.14, 70.06, 55.30, 50.64, 44.75, 44.42, 40.55, 24.93, 24.91 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.32 ppm.

HRMS (ESI-TOF): calc'd for $C_{26}H_{33}BO_5S$ $[M+H]^+$: 469.2215, found: 469.2222.

TLC: R_f = 0.25 (2:1 hexanes: ethyl acetate).

Compound 57



***2-(1-(4-methoxyphenyl)-3-(4-(methylsulfonyl)phenyl)bicyclo[1.1.1]pentan-2-yl)-4,4,5,5-tetra methyl-1,3,2-dioxaborolane* (57)**

Following **General Procedure F2** on 0.1 mmol scale with BCP bisboronate **27**, and 4-bromophenyl methyl sulfone reacting for 48 hours. Purification by flash chromatography (methylene chloride: ethyl acetate, 50:1) and afforded 22.2 mg (31%) of the title compound **57**.

Physical State: white solid.

m.p.: 155-157 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.90 – 7.85 (m, 2H), 7.56 – 7.51 (m, 2H), 7.29 – 7.24 (m, 2H), 6.88 – 6.83 (m, 2H), 3.80 (s, 3H), 3.11 (dd, *J* = 9.6, 1.9 Hz, 1H), 3.04 (s, 3H), 2.37 (dd, *J* = 9.6, 1.2 Hz, 1H), 2.32 (s, 1H), 2.24 (dd, *J* = 8.1, 1.9 Hz, 1H), 2.16 (d, *J* = 7.9 Hz, 1H), 1.22 (s, 6H), 1.21 (s, 6H) ppm.

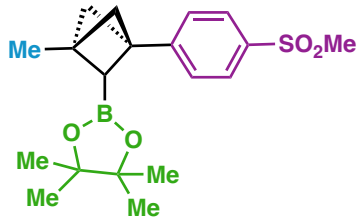
^{13}C NMR (151 MHz, $CDCl_3$): δ 158.57, 147.87, 138.42, 133.02, 127.57(2C), 127.35, 113.65, 83.49, 57.64, 55.43, 52.84, 44.77, 43.36, 42.82, 25.00, 24.92 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.22 ppm.

HRMS (ESI-TOF): calc'd for $C_{25}H_{31}BO_5S$ $[M+H]^+$: 455.2058, found: 455.2058.

TLC: R_f = 0.28 (2:1 hexanes: ethyl acetate).

Compound 58



***4,4,5,5-tetramethyl-2-(1-methyl-3-(4-(methylsulfonyl)phenyl)bicyclo[1.1.1]pentan-2-yl)-1,3,2-dioxaborolane* (58)**

Following **General Procedure F2** on 0.1 mmol scale with BCP bisboronate **13**, and 4-bromophenyl methyl sulfone reacting for 48 hours. Purification by flash chromatography (hexanes: methylene chloride, 1:1) and afforded 15.7 mg (43%) of the title compound **58**.

Physical State: white solid.

m.p.: 88-90 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.85 – 7.80 (m, 2H), 7.49 – 7.44 (m, 2H), 3.02 (s, 3H), 2.55 (dd, *J* = 9.7, 2.0 Hz, 1H), 2.01 – 1.96 (m, 2H), 1.89 (dd, *J* = 8.3, 2.0 Hz, 1H), 1.77 (d, *J* = 8.3 Hz, 1H), 1.29 (s, 3H), 1.24 (s, 12H) ppm.

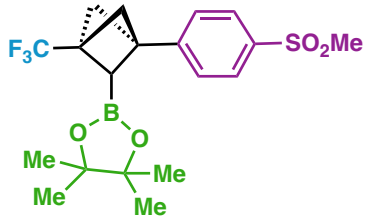
^{13}C NMR (151 MHz, $CDCl_3$): δ 148.14, 138.10, 127.53, 127.24, 83.28, 57.75, 53.02, 44.77, 43.56, 38.54, 25.01, 24.97, 18.36 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.95 ppm.

HRMS (ESI-TOF): calc'd for $C_{19}H_{27}BO_4S$ $[M+H]^+$: 361.1800, found: 361.1801.

TLC: R_f = 0.38 (2:1 hexanes: ethyl acetate).

Compound 59



***4,4,5,5-tetramethyl-2-(1-(4-(methylsulfonyl)phenyl)-3-(trifluoromethyl)bicyclo[1.1.1]pentan-2-yl)-1,3,2-dioxaborolane* (59)**

Following **General Procedure F2** on 0.1 mmol scale with BCP bisboronate **26**, and 4-bromophenyl methyl sulfone reacting for 48 hours. Purification by flash chromatography (hexanes: methylene chloride, 1:1) and afforded 13.0 mg (31%) of the title compound **59**.

Physical State: white solid.

m.p.: 95-97 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92 – 7.85 (m, 2H), 7.51 – 7.44 (m, 2H), 3.08 (dd, *J* = 9.6, 2.1 Hz, 1H), 3.04 (s, 3H), 2.30 (dd, *J* = 9.6, 1.5 Hz, 1H), 2.27 (s, 1H), 2.21 (dd, *J* = 8.1, 2.1 Hz, 1H), 2.11 (d, *J* = 8.1 Hz, 1H), 1.24 (s, 12H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.53, 139.28, 127.56, 127.54, 123.04 (q, *J* = 276.4 Hz), 83.97, 54.16, 49.22, 44.69, 43.31, 38.91 (q, *J* = 38.5 Hz), 24.83, 24.78 ppm.

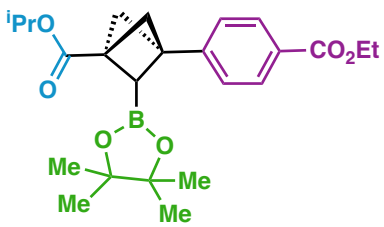
^{19}F NMR (376 MHz, $CDCl_3$): δ -72.73 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.29 ppm.

HRMS (ESI-TOF): calc'd for $C_{19}H_{24}BF_3O_4S$ $[M+H]^+$: 417.1513, found: 417.1510.

TLC: R_f = 0.35 (2:1 hexanes: ethyl acetate).

Compound 60



isopropyl 3-(4-(ethoxycarbonyl)phenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo

***[1.1.1]pentane-1-carboxylate* (60)**

Following **General Procedure F2** on 0.1 mmol scale with BCP bisboronate **23**, and ethyl 4-bromo-benzoate reacting for 48 hours. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 15.0 mg (35%) of the title compound **60**.

Physical State: white solid.

m.p.: 54-56 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.98 – 7.94 (m, 2H), 7.35 – 7.30 (m, 2H), 5.03 (hept, *J* = 6.3 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.06 (dd, *J* = 9.9, 2.0 Hz, 1H), 2.32 (d, *J* = 8.8 Hz, 2H), 2.26 (dd, *J* = 8.1, 1.9 Hz, 1H), 2.13 (d, *J* = 7.9 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.25 (d, *J* = 2.2 Hz, 3H), 1.24 (d, *J* = 2.2 Hz, 3H), 1.24 (s, 6H), 1.23 (s, 6H) ppm.

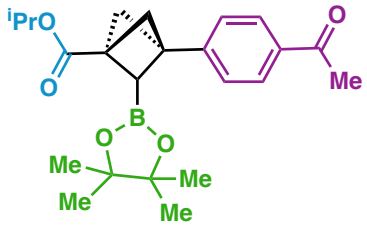
^{13}C NMR (151 MHz, $CDCl_3$): δ 169.90, 166.73, 145.44, 129.56, 128.98, 126.47, 83.52, 67.98, 61.01, 56.83, 52.29, 43.87, 39.54, 24.96, 24.89, 22.00, 14.49 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.40 ppm.

HRMS (ESI-TOF): calc'd for $C_{24}H_{33}BO_6$ $[M+H]^+$: 429.2443, found: 429.2451.

TLC: R_f = 0.66 (3:1 hexanes: ethyl acetate).

Compound 61



***isopropyl 3-(4-acetylphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1] pentane-1-carboxylate* (61)**

Following **General Procedure F2** on 0.1 mmol scale with BCP bisboronate **23**, and 4′-Bromoacetophenone reacting for 48 hours. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 12.9 mg (32%) of the title compound **61**.

Physical State: white solid.

m.p.: 39-41 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.91 – 7.86 (m, 2H), 7.38 – 7.33 (m, 2H), 5.03 (hept, *J* = 6.3 Hz, 1H), 3.06 (dd, *J* = 9.8, 2.0 Hz, 1H), 2.58 (s, 3H), 2.33 (d, *J* = 9.0 Hz, 2H), 2.27 (dd, *J* = 8.1, 2.0 Hz, 1H), 2.13 (d, *J* = 8.0 Hz, 1H), 1.26 (d, *J* = 2.3 Hz, 3H), 1.25 – 1.23 (m, 15H) ppm.

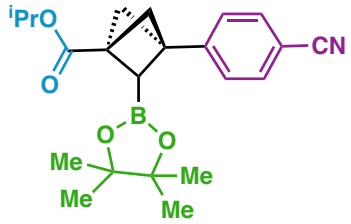
^{13}C NMR (151 MHz, $CDCl_3$): δ 198.00, 169.84, 145.82, 135.75, 128.43, 126.72, 83.55, 68.01, 56.81, 52.32, 43.83, 39.57, 26.79, 24.97, 24.89, 21.99 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.88 ppm.

HRMS (ESI-TOF): calc'd for $C_{23}H_{31}BO_5$ $[M+H]^+$: 399.2337, found: 399.2342.

TLC: R_f = 0.50 (3:1 hexanes: ethyl acetate).

Compound 62



***isopropyl 3-(4-cyanophenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentane-1-carboxylate* (62)**

Following **General Procedure F2** on 0.1 mmol scale with BCP bisboronate **23**, and 4-bromobenzonitrile reacting for 48 hours. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 14.7 mg (39%) of the title compound **62**.

Physical State: white solid.

m.p.: 57-59 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, J = 8.3 Hz, 2H), 7.39 – 7.36 (m, 2H), 5.03 (hept, J = 6.3 Hz, 1H), 3.02 (dd, J = 9.8, 2.0 Hz, 1H), 2.34 – 2.30 (m, 2H), 2.25 (dd, J = 8.1, 2.0 Hz, 1H), 2.13 (d, J = 8.0 Hz, 1H), 1.25 (d, J = 2.5 Hz, 3H), 1.24 (d, J = 2.6 Hz, 3H), 1.24 (s, 6H) 1.23 (s, 6H) ppm.

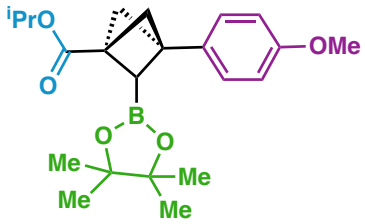
^{13}C NMR (151 MHz, $CDCl_3$): δ 169.58, 145.66, 132.13, 127.33, 119.17, 110.60, 83.65, 68.11, 56.72, 52.24, 43.64, 39.56, 24.95, 24.88, 21.98, 21.97 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.54 ppm.

HRMS (ESI-TOF): calc'd for $C_{22}H_{28}BNO_4$ $[M+H]^+$: 382.2184, found: 382.2201.

TLC: R_f = 0.56 (3:1 hexanes: ethyl acetate).

Compound 63



***isopropyl 3-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1] pentane-1-carboxylate* (63)**

Following **General Procedure F2** on 0.1 mmol scale with BCP bisboronate **23**, and 4-bromo-anisole reacting for 48 hours. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 12.8 mg (33%) of the title compound **63**.

Physical State: white solid.

m.p.: 38-40 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.22 – 7.17 (m, 2H), 6.85 – 6.80 (m, 2H), 5.07 – 4.98 (hept, *J* = 6.3 Hz, 1H), 3.78 (s, 3H), 3.01 (dd, *J* = 9.5, 1.9 Hz, 1H), 2.29 – 2.24 (m, 2H), 2.20 (dd, *J* = 8.1, 1.9 Hz, 1H), 2.07 (d, *J* = 7.9 Hz, 1H), 1.27 – 1.19 (m, 18H) ppm.

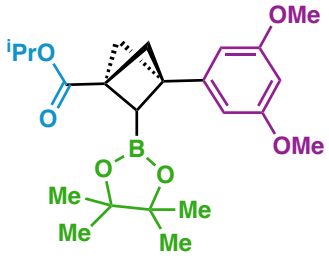
^{13}C NMR (151 MHz, $CDCl_3$): δ 170.28, 158.61, 132.83, 127.57, 113.63, 83.36, 67.80, 56.76, 55.42, 52.38, 43.67, 39.28, 24.99, 24.89, 22.01 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.64 ppm.

HRMS (ESI-TOF): calc'd for $C_{22}H_{31}BO_5$ $[M+H]^+$: 387.2337, found: 387.2347.

TLC: R_f = 0.63 (3:1 hexanes: ethyl acetate).

Compound 64



***isopropyl 3-(3,5-dimethoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo [1.1.1]pentane-1-carboxylate* (64)**

Following **General Procedure F2** on 0.1 mmol scale with BCP bisboronate **23**, and 3,5-dimethoxylbromobenzene reacting for 48 hours. Purification by flash chromatography (hexanes:

ethyl acetate, 20:1) and afforded 14.2 mg (34%) of the title compound **64**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.46 (d, *J* = 2.3 Hz, 2H), 6.33 (t, *J* = 2.3 Hz, 1H), 5.03 (hept, *J* = 6.3 Hz, 1H), 3.78 (s, 6H), 3.00 (dd, *J* = 9.5, 1.9 Hz, 1H), 2.28 (s, 1H), 2.26 (dd, *J* = 9.5, 1.4 Hz, 1H), 2.20 (dd, *J* = 8.1, 1.9 Hz, 1H), 2.07 (d, *J* = 7.6 Hz, 1H), 1.28 – 1.23 (m, 18H) ppm.

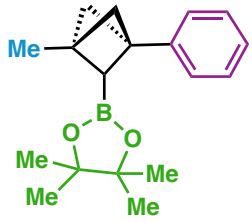
^{13}C NMR (151 MHz, $CDCl_3$): δ 170.10, 160.83, 142.92, 104.43, 99.22, 83.41, 67.86, 56.41, 55.42, 52.61, 44.10, 39.22, 25.06, 24.93, 22.01, 21.99 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.75 ppm.

HRMS (ESI-TOF): calc'd for $C_{23}H_{33}BO_6$ $[M+H]^+$: 417.2443, found: 417.2462.

TLC: R_f = 0.56 (3:1 hexanes: ethyl acetate).

Compound 65



***4,4,5,5-tetramethyl-2-(1-methyl-3-phenylbicyclo[1.1.1]pentan-2-yl)-1,3,2-dioxaborolane* (65)**

Following **General Procedure F2** on 0.1 mmol scale with BCP bisboronate **13**, and bromobenzene reacting for 48 hours. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 12.0 mg (42%) of the title compound **65**.

Following **Scale-up of preparation of BCP boronate 65** on 2.0 mmol scale with BCP bisboronate **13**, and bromobenzene reacting for 60 hours. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) afforded 209.6 mg (37%) of the title compound **65**.

[Note: The protodeborylated side-product (R^3 = H) was removed by high vaccum.]

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.30 – 7.22 (m, 4H), 7.16 (tt, *J* = 6.6, 1.9 Hz, 1H), 2.56 (dd, *J* = 9.9, 1.9 Hz, 1H), 1.93 (d, *J* = 9.3 Hz, 2H), 1.83 (dd, *J* = 8.2, 1.9 Hz, 1H), 1.72 (d, *J* = 8.2 Hz, 1H), 1.26 (s, 3H), 1.230 (s, 6H), 1.225 (s, 6H) ppm.

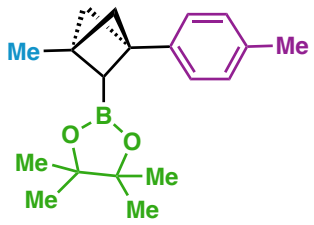
^{13}C NMR (151 MHz, $CDCl_3$): δ 141.89, 128.01, 126.45, 126.12, 83.01, 57.73, 52.75, 44.02, 38.05, 25.00, 24.98, 18.55 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.18 ppm.

HRMS (ESI-TOF): calc'd for $C_{18}H_{25}BO_2$ $[M+H]^+$: 285.2020, found: 285.2029.

TLC: R_f = 0.38 (15:1 hexanes: ethyl acetate).

Compound 66



***4,4,5,5-tetramethyl-2-(1-methyl-3-(p-tolyl)bicyclo[1.1.1]pentan-2-yl)-1,3,2-dioxaborolane* (66)**

Following **General Procedure F2** on 0.1 mmol scale with BCP bisboronate **13**, and 4-bromo-toluene reacting for 48 hours. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 11.2 mg (37%) of the title compound **66**.

[Note: The deborolated side-product (R^3 = H) was removed by high vaccum]

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20 – 7.15 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 2H), 2.55 (dd, *J* = 10.0, 1.9 Hz, 1H), 2.31 (s, 3H), 1.94 – 1.90 (m, 2H), 1.82 (dd, *J* = 8.2, 1.9 Hz, 1H), 1.71 (d, *J* = 8.1 Hz, 1H), 1.27 (s, 3H), 1.244 (s, 6H), 1.240 (s, 6H) ppm.

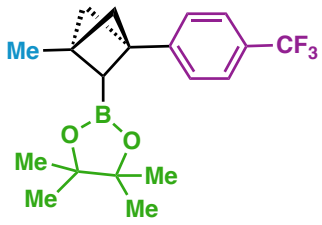
^{13}C NMR (151 MHz, $CDCl_3$): δ 138.96, 135.59, 128.71, 126.36, 82.97, 57.75, 52.79, 43.81, 37.99, 25.01, 24.98, 21.25, 18.56 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.23 ppm.

HRMS (ESI-TOF): calc'd for $C_{19}H_{27}BO_2$ $[M+H]^+$: 299.2177, found: 299.2187.

TLC: R_f = 0.38 (15:1 hexanes: ethyl acetate).

Compound 67



***4,4,5,5-tetramethyl-2-(1-methyl-3-(4-(trifluoromethyl)phenyl)bicyclo[1.1.1]pentan-2-yl)-1,3,2-dioxaborolane* (67)**

Following **General Procedure F2** on 0.1 mmol scale with BCP bisboronate **13**, and 4-bromo-trifluorotoluene reacting for 48 hours. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 13.7 mg (39%) of the title compound **67**.

[Note: The deborolated side-product (R^3 = H) was removed by high vaccum]

Physical State: colorless crystal.

m.p.: 31-33 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 2.56 (dd, *J* = 9.6, 1.9 Hz, 1H), 2.01 – 1.94 (m, 2H), 1.87 (dd, *J* = 8.2, 1.9 Hz, 1H), 1.76 (d, *J* = 8.3 Hz, 1H), 1.29 (s, 3H), 1.243 (s, 6H) ,1.241 (s, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.76,128.32 (q, *J* = 32.4 Hz), 126.84, 124.98 (q, *J* = 3.9 Hz), 124.59 (q, *J* = 272.0 Hz), 83.18, 57.75, 52.87, 43.60, 38.36, 25.00, 24.98, 18.42 ppm.

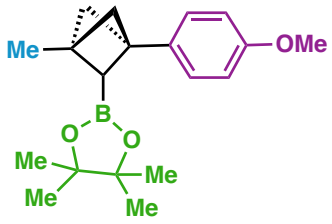
^{19}F NMR (376 MHz, $CDCl_3$) δ -62.28 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.01 ppm.

HRMS (ESI-TOF): calc'd for $C_{19}H_{25}BF_3O_2$ $[M+H]^+$: 353.1894, found: 353.1899.

TLC: R_f = 0.38 (15:1 hexanes: ethyl acetate).

Compound 68



***2-(1-(4-methoxyphenyl)-3-methylbicyclo[1.1.1]pentan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (68)**

Following **General Procedure F2** on 0.1 mmol scale with BCP bisboronate **13**, and 4-bromo-anisole reacting for 48 hours. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 7.6 mg (24%) of the title compound **68**.

[Note: The deborolated side-product (R^3 = H) was removed by high vaccum]

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.23 – 7.18 (m, 2H), 6.83 – 6.78 (m, 2H), 3.78 (s, 3H), 2.53 (dd, *J* = 9.7, 1.9 Hz, 1H), 1.94 – 1.89 (m, 2H), 1.81 (dd, *J* = 8.2, 1.9 Hz, 1H), 1.70 (d, *J* = 8.2 Hz, 1H), 1.26 (s, 3H), 1.243 (s, 6H), 1.238 (s, 6H) ppm.

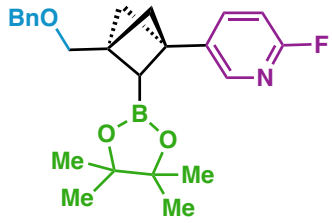
^{13}C NMR (151 MHz, $CDCl_3$): δ 158.11, 134.36, 127.53, 113.45, 82.98, 57.76, 55.40, 52.83, 43.57, 37.91, 25.01, 24.99, 18.53 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.15 ppm.

HRMS (ESI-TOF): calc'd for $C_{19}H_{27}BO_3$ $[M+H]^+$: 315.2126, found: 315.2142.

TLC: R_f = 0.31 (15:1 hexanes: ethyl acetate).

Compound 69



***5-(3-((benzyloxy)methyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)-2-fluoropyridine* (69)**

Following **General Procedure F1** on 0.1 mmol scale with BCP bisboronate **25**, and 3-bromo-6-fluoropyridine reacting for 48 hours. Purification by flash chromatography (hexanes: ethyl acetate, 5:1) and afforded 9.0 mg (22%) of the title compound **69**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12 (d, *J* = 2.5 Hz, 1H), 7.72 (td, *J* = 8.1, 2.5 Hz, 1H), 7.35 (d, *J* = 7.0 Hz, 4H), 7.31 – 7.24 (m, 1H), 6.83 (dd, *J* = 8.4, 2.8 Hz, 1H), 4.57 (s, 2H), 3.57 (s, 2H), 2.66 (dd, *J* = 9.7, 2.0 Hz, 1H), 2.10 – 2.06 (m, 2H), 1.98 (dd, *J* = 8.2, 2.1 Hz, 1H), 1.85 (d, *J* = 8.1 Hz, 1H), 1.20 (s, 12H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 162.61 (d, *J* = 237.1 Hz), 145.89 (d, *J* = 14.5 Hz), 139.60 (d, *J* = 7.7 Hz), 138.80, 134.58, 128.43, 127.64, 127.58, 108.73 (d, *J* = 37.4 Hz), 83.37, 73.12, 70.03, 55.14, 50.74, 41.98, 40.88, 24.94, 24.91 ppm.

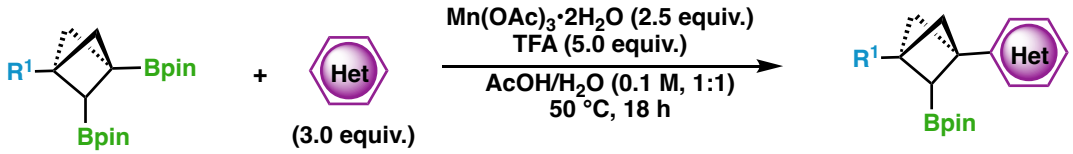
^{11}B NMR (128 MHz, $CDCl_3$): δ 31.62 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ -71.46 ppm.

HRMS (ESI-TOF): calc'd for $C_{24}H_{29}BFNO_3$ $[M+H]^+$: 410.2297, found: 410.2294.

TLC: R_f = 0.59 (3:1 hexanes: ethyl acetate).

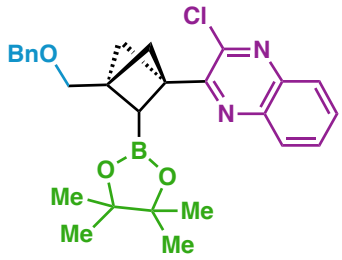
General Procedure G for Minisci reaction of BCP Bisboronates



A screw-capped 13×100 mm pyrex culture tube was charged with BCP bisboronate (1.0 equiv.), heteroarene (3.0 equiv.) and $Mn(OAc)_3•2H_2O$ (2.5 equiv.). Then the tube or the flask was evacuated and backfilled with argon for three times, followed by addition of acetic acid/water (0.1 M, 1:1) solvent via a syringe. Next, trifluoroacetic acid (5.0 equiv.) was added into the reaction. Then the headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was stirred at 50 °C for 18 hours. After it is confirmed that the starting material was consumed totally, the reaction mixture was concentrated under high vacuum to remove excess acetic acid, quenched with Na_2CO_3 solution, extracted with ethyl acetate, dried with Na_2SO_4, and concentrated under high vacuum. The crude residue was purified by chromatography on silica gel. [10]

Characterization of Substrates in Hydrazone Coupling (70-79)

Compound 70



***2-(3-((benzyloxy)methyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)-3-chloroquinoxaline* (70)**

Following **General Procedure G** on 0.1 mmol scale with BCP bisboronate **25**, and 2-chloroquinoxaline. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 23.2 mg (49%) of the title compound **70**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.06 – 8.00 (m, 1H), 7.99 – 7.94 (m, 1H), 7.74 – 7.68 (m, 2H), 7.41 – 7.33 (m, 4H), 7.30 – 7.27 (m, 1H), 4.61 (s, 2H), 3.62 (s, 2H), 2.94 (dd, J = 9.5, 1.9 Hz, 1H), 2.56 (s, 1H), 2.53 (dd, J = 8.0, 1.9 Hz, 1H), 2.28 (dd, J = 9.5, 1.3 Hz, 1H), 2.17 (d, J = 7.9 Hz, 1H), 1.22 (s, 6H), 1.18 (s, 6H) ppm.

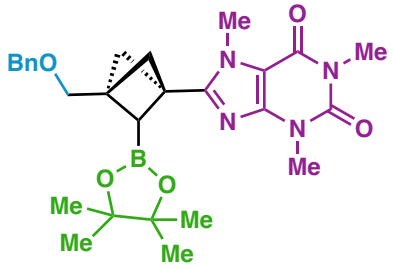
^{13}C NMR (151 MHz, $CDCl_3$): δ 152.16, 146.94, 141.17, 141.10, 138.80, 130.21, 129.94, 128.97, 128.44, 128.11, 127.64, 127.56, 83.11, 73.09, 70.19, 56.77, 50.50, 45.40, 42.03, 24.88, 24.81 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 32.52 ppm.

HRMS (ESI-TOF): calc'd for $C_{27}H_{30}BClN_2O_3$ $[M+H]^+$: 477.2111, found: 477.2124.

TLC: R_f = 0.25 (10:1 hexanes: ethyl acetate).

Compound 71



***8-(3-((benzyloxy)methyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)-1,3,7-trimethyl-3,7-dihydro-1H-purine-2,6-dione* (71)**

Following **General Procedure G** on 0.1 mmol scale with BCP bisboronate **25**, and caffeine. Purification by flash chromatography (hexanes: ethyl acetate, 2:1) and afforded 27.7 mg (55%) of the title compound **71**.

Physical State: white solid.

m.p.: 124-126 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (d, *J* = 4.4 Hz, 4H), 7.30 – 7.26 (m, 1H), 4.56 (s, 2H), 4.01 (s, 3H), 3.55 (s, 3H), 3.55 (s, 2H), 3.38 (s, 3H), 2.90 (dd, *J* = 9.6, 2.1 Hz, 1H), 2.33 (dd, *J* = 9.6, 1.5 Hz, 1H), 2.29 – 2.24 (m, 2H), 2.12 (d, *J* = 8.1 Hz, 1H), 1.200 (s, 6H), 1.196 (s, 6H) ppm.

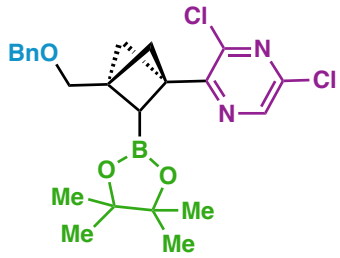
^{13}C NMR (151 MHz, $CDCl_3$): δ 155.53, 151.82, 151.10, 147.59, 138.56, 128.45, 127.66, 127.64, 107.55, 83.55, 73.17, 69.63, 56.53, 50.85, 43.43, 38.06, 32.60, 30.03, 28.00, 24.89, 24.85 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.53 ppm.

HRMS (ESI-TOF): calc'd for $C_{27}H_{35}BN_4O_5$ $[M+H]^+$: 507.2773, found: 507.2778.

TLC: R_f = 0.30 (1:1 hexanes: ethyl acetate).

Compound 72



***2-(3-((benzyloxy)methyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)-3,5-dichloropyrazine* (72)**

Following **General Procedure G** on 0.1 mmol scale with BCP bisboronate **25**, and 2,6-Dichloropyrazine. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 28.3 mg (61%) of the title compound **72**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.39 (s, 1H), 7.38 – 7.31 (m, 4H), 7.29 – 7.26 (m, 1H), 4.57 (s, 2H), 3.58 (s, 2H), 2.81 (dd, *J* = 9.6, 2.0 Hz, 1H), 2.38 – 2.33 (m, 2H), 2.25 (dd, *J* = 9.5, 1.4 Hz, 1H), 2.09 (d, *J* = 8.0 Hz, 1H), 1.19 (s, 6H), 1.17 (s, 6H) ppm.

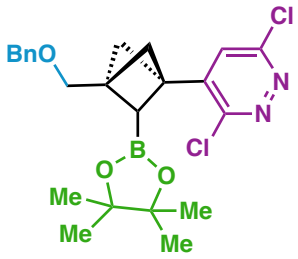
^{13}C NMR (151 MHz, $CDCl_3$): δ 150.83, 146.22, 144.99, 141.56, 138.72, 128.43, 127.64, 127.58, 83.23, 73.11, 69.96, 56.33, 50.17, 43.96, 42.12, 24.84, 24.79 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.26 ppm.

HRMS (ESI-TOF): calc'd for $C_{23}H_{27}BCl_2N_2O_3$ $[M+H]^+$: 461.1565, found: 461.1558.

TLC: R_f = 0.32 (10:1 hexanes: ethyl acetate).

Compound 73



***4-(3-((benzyloxy)methyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)-3,6-dichloropyridazine* (73)**

Following **General Procedure G** on 0.1 mmol scale with BCP bisboronate **25**, and 3,6-dichloropyridazine. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 21.6 mg (47%) of the title compound **73**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, Acetone-*d*^{6}): δ 7.70 (s, 1H), 7.41 – 7.32 (m, 4H), 7.31 – 7.24 (m, 1H), 4.57 (s, 2H), 3.61 (s, 2H), 2.60 (dd, *J* = 9.6, 2.1 Hz, 1H), 2.37 (dd, *J* = 8.3, 2.1 Hz, 1H), 2.35 (d, *J* = 1.2 Hz, 1H), 2.31 (dd, *J* = 9.5, 1.4 Hz, 1H), 2.16 (dd, *J* = 8.3, 1.0 Hz, 1H), 1.201 (s, 6H), 1.198 (s, 6H) ppm.

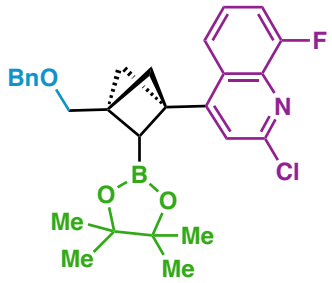
^{13}C NMR (151 MHz, Acetone-*d*^{6}): δ 156.74, 156.28, 142.53, 139.85, 130.21, 129.05, 128.25, 128.17, 84.22, 73.44, 70.07, 56.72, 50.51, 42.97, 42.92, 25.08 (2C) ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.58 ppm.

HRMS (ESI-TOF): calc'd for $C_{23}H_{27}BCl_2N_2O_3$ $[M+H]^+$: 461.1565, found: 461.1560.

TLC: R_f = 0.18 (10:1 hexanes: ethyl acetate).

Compound 74



***4-(3-((benzyloxy)methyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)-2-chloro-8-fluoroquinoline* (74)**

Following **General Procedure G** on 0.1 mmol scale with BCP bisboronate **25**, and 2,6-Dichloropyrazine. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 18.6 mg (38%) of the title compound **74**.

Physical State: red oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.4 Hz, 1H), 7.46 (td, *J* = 8.1, 5.2 Hz, 1H), 7.42 – 7.39 (m, 1H), 7.39 – 7.33 (m, 4H), 7.31 (s, 1H), 7.30 – 7.28 (m, 1H), 4.60 (s, 2H), 3.63 (s, 2H), 2.91 (dd, *J* = 9.6, 2.2 Hz, 1H), 2.45 – 2.42 (m, 1H), 2.40 (dd, *J* = 8.2, 2.2 Hz, 1H), 2.36 (dd, *J* = 9.5, 1.6 Hz, 1H), 2.17 (d, *J* = 8.1 Hz, 1H), 1.18 (s, 12H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 157.57 (d, *J* = 257.2 Hz), 151.32, 149.76 (d, *J* = 2.5 Hz), 138.65, 138.43 (d, *J* = 11.5 Hz), 128.49, 128.15, 127.69, 127.68, 126.21 (d, *J* = 8.1 Hz), 122.77, 121.03, 114.32 (d, *J* = 18.7 Hz), 83.55, 73.23, 69.79, 57.86, 51.30, 44.56, 41.97, 24.91, 24.83 ppm.

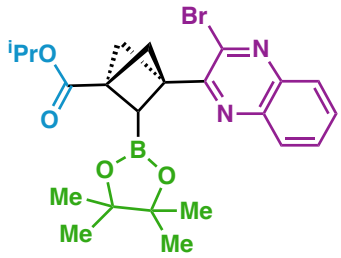
^{11}B NMR (128 MHz, $CDCl_3$): δ 31.32 ppm.

^{19}F NMR (376 MHz, $CDCl_3$): δ -123.05 ppm.

HRMS (ESI-TOF): calc'd for $C_{28}H_{30}BClFNO_3$ $[M+H]^+$: 494.2064, found: 494.2063.

TLC: R_f = 0.36 (5:1 hexanes: ethyl acetate).

Compound 75



isopropyl 3-(3-bromoquinoxalin-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo

[1.1.1]pentane-1-carboxylate **(75)**

Following **General Procedure G** on 0.1 mmol scale with BCP bisboronate **23**, and 2-bromoquinoxaline. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 22.5 mg (46%) of the title compound **75**.

Physical State: pale red solid.

m.p.: 102-103 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 – 7.97 (m, 2H), 7.76 – 7.69 (m, 2H), 5.05 (hept, *J* = 6.3 Hz, 1H), 3.24 (dd, *J* = 9.4, 1.9 Hz, 1H), 2.95 (d, *J* = 1.2 Hz, 1H), 2.89 (dd, *J* = 8.0, 1.9 Hz, 1H), 2.51 (dd, *J* = 9.4, 1.4 Hz, 1H), 2.42 (d, *J* = 8.0 Hz, 1H), 1.29 – 1.26 (m, 9H), 1.26 (d, *J* = 4.0 Hz, 3H), 1.23 (s, 6H) ppm.

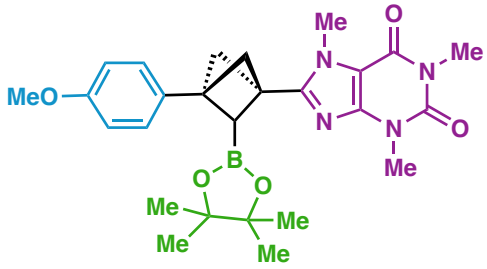
^{13}C NMR (151 MHz, $CDCl_3$): δ 169.74, 152.38, 142.10, 140.93, 138.58, 130.53, 130.31, 129.05, 128.25, 83.36, 68.12, 58.13, 52.77, 45.26, 40.91, 24.94, 24.81, 22.03, 22.01 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.05 ppm.

HRMS (ESI-TOF): calc'd for $C_{23}H_{28}BBrN_2O_4$ $[M+H]^+$: 487.1398, found: 487.1399.

TLC: R_f = 0.36 (5:1 hexanes: ethyl acetate).

Compound 76



8-(3-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)-1,3,7-trimethyl-3,7-dihydro-1H-purine-2,6-dione **(76)**

Following **General Procedure G** on 0.1 mmol scale with BCP bisboronate **27**, and caffeine Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 17.1 mg (35%) of the title compound **76**.

Physical State: yellow solid.

m.p.: >200 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25 – 7.21 (m, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 4.05 (s, 3H), 3.80 (s, 3H), 3.56 (s, 3H), 3.40 (s, 3H), 3.26 (dd, *J* = 9.6, 2.0 Hz, 1H), 2.58 (dd, *J* = 9.6, 1.5 Hz, 1H),

2.52 (t, J = 1.2 Hz, 1H), 2.49 (dd, J = 8.1, 2.0 Hz, 1H), 2.38 (dd, J = 8.1, 1.0 Hz, 1H), 1.23 (s, 6H), 1.22 (s, 6H) ppm.

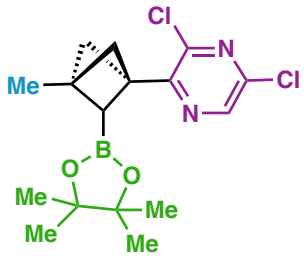
^{13}C NMR (151 MHz, $CDCl_3$): δ 158.77, 155.58, 151.89, 151.45, 147.88, 132.23, 127.49, 113.73, 107.69, 83.65, 58.58, 55.43, 53.21, 46.12, 36.71, 32.66, 29.92, 28.01, 24.92 (2C) ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.50 ppm.

HRMS (ESI-TOF): calc'd for $C_{26}H_{33}BN_4O_5$ $[M+H]^+$: 493.2617, found: 493.2597.

TLC: R_f = 0.40 (1:1 hexanes: ethyl acetate).

Compound 77



***3,5-dichloro-2-(3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)pyrazine* (77)**

Following **General Procedure G** on 0.1 mmol scale with BCP bisboronate **13**, and 2,6-dichloropyrazine. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 26.1 mg (74%) of the title compound **77**.

Following **General Procedure G** on 2.0 mmol scale with BCP bisboronate **13**, and 2,6-dichloropyrazine in a 50-mL pyrex flask. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 465.7 mg (65%) of the title compound **77**.

Physical State: white solid.

m.p.: 32-33 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.38 (s, 1H), 2.66 (dd, J = 9.6, 2.1 Hz, 1H), 2.25 – 2.20 (m, 2H), 2.17 (dd, J = 9.6, 1.2 Hz, 1H), 2.01 (dd, J = 8.1, 1.0 Hz, 1H), 1.29 (s, 3H), 1.22 (s, 6H), 1.21 (s, 6H) ppm.

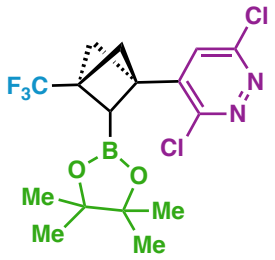
^{13}C NMR (151 MHz, $CDCl_3$): δ 151.11, 146.19, 144.73, 141.51, 83.17, 58.64, 52.33, 43.13, 40.18, 24.92, 24.87, 18.35 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.87 ppm.

HRMS (ESI-TOF): calc'd for $C_{16}H_{21}BCl_2N_2O_2$ $[M+H]^+$: 355.1146, found: 355.1152.

TLC: R_f = 0.46 (10:1 hexanes: ethyl acetate).

Compound 78



***3,6-dichloro-4-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trifluoromethyl)bicyclo [1.1.1]pentan-1-yl)pyridazine* (78)**

Following **General Procedure G** on 0.1 mmol scale with BCP bisboronate **26**, and 2,6-Dichloropyrazine. Purification by flash chromatography (hexanes: ethyl acetate, 20:1) and afforded 13.6 mg (33%) of the title compound **78**.

Physical State: white solid.

m.p.: 77-79 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (s, 1H), 2.94 (dd, *J* = 9.6, 2.2 Hz, 1H), 2.61 – 2.59 (m, 1H), 2.57 (dd, *J* = 8.2, 2.2 Hz, 1H), 2.47 (dd, *J* = 9.6, 1.7 Hz, 1H), 2.33 (d, *J* = 8.1 Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 156.15, 155.34, 139.82, 129.17, 122.48 (q, *J* = 276.1 Hz), 84.39, 55.23, 49.07, 41.20, 40.38 (q, *J* = 39.1 Hz). 24.80, 24.76 ppm.

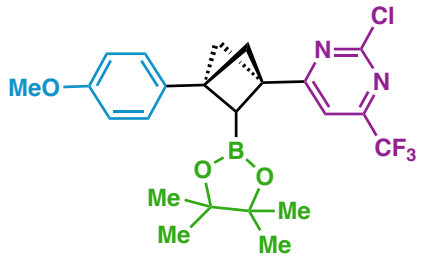
^{19}F NMR (376 MHz, $CDCl_3$): δ -72.73 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.91 ppm.

HRMS (ESI-TOF): calc'd for $C_{16}H_{18}BCl_2F_3N_2O_2$ $[M+H]^+$: 409.0863, found: 409.0860.

TLC: R_f = 0.30 (10:1 hexanes: ethyl acetate).

Compound 79



***2-chloro-4-(3-(4-methoxyphenyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)-6-(trifluoromethyl)pyrimidine* (79)**

Following **General Procedure G** on 0.1 mmol scale with BCP bisboronate **27**, and 2-chloro-4-(trifluoromethyl)pyrimidine. Purification by flash chromatography (hexanes: ethyl acetate, 10:1) and afforded 17.6 mg (37%) of the title compound **79**.

Physical State: yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.73 (s, 1H), 7.29 – 7.24 (m, 2H), 6.90 – 6.84 (m, 2H), 3.81 (s, 3H), 3.12 (dd, *J* = 9.6, 1.9 Hz, 1H), 2.50 (d, *J* = 1.3 Hz, 1H), 2.48 – 2.43 (m, 1H), 2.37 (dd, *J* = 8.2, 1.9 Hz, 1H), 2.25 – 2.21 (m, 1H), 1.27 (s, 6H), 1.26 (s, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 174.79, 161.98, 158.83, 157.62 (q, *J* = 37.0 Hz), 132.13, 127.64, 120.06 (q, *J* = 275.3 Hz), 113.76, 113.40 (q, *J* = 2.8 Hz), 83.87, 56.61, 55.45, 54.22, 44.16, 43.12, 25.03, 24.87 ppm.

^{19}F NMR (565 MHz, $CDCl_3$): δ -69.81 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.28 ppm.

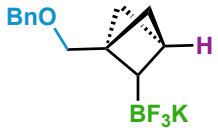
HRMS (ESI-TOF): calc'd for $C_{23}H_{25}BClF_3N_2O_3$ $[M+H]^+$: 481.1672, found: 481.1669.

TLC: R_f = 0.36 (10:1 hexanes: ethyl acetate).

Experimental Procedures and Characterization Data of substrates in Late-stage Functionalization of BCP C_2-Boronates

Experimental Procedures and Characterization of C1, C2-disubstituted BCPs (80-94)

Compound 80



***(1-((benzyloxy)methyl)bicyclo[1.1.1]pentan-2-yl)trifluoro-λ⁴-borane, potassium salt* (80)**

BCP boronate **36** (1.1 g, 3.3 mmol) was suspended in methanol (6.6 mL), and a saturated aqueous solution of KHF_2 (5 mL, 25 mmol) was added dropwise. The suspended solution was stirred at room temperature for 2 hours and then concentrated to dryness. (Note: removing the pinacol by azeotrope with methanol and water under high vacuum 5 times facilitate the subsequent crystallization). The residue was extracted with hot acetone (3 × 30 mL), and the combined filtered extracts were concentrated to approximately 5 mL. Diethyl ether was added, and the resultant precipitate was collected and dried to afford the 750 mg (73%) of the potassium trifluoroborate **80**.

Physical State: white solid.

m.p.: 88-90 °C.

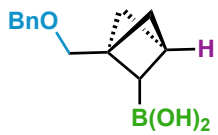
^{1}H NMR (600 MHz, acetone-*d*^{6}): δ 7.34 (d, *J* = 7.1 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.20 (m, 1H), 4.51 (d, *J* = 12.3 Hz, 1H), 4.47 (d, *J* = 12.3 Hz, 1H), 3.48 (d, *J* = 10.7 Hz, 1H), 3.39 (d, *J* = 10.7 Hz, 1H), 2.49 (d, *J* = 9.4 Hz, 1H), 2.36 (s, 1H), 1.70 (s, 1H), 1.54 (d, *J* = 8.0 Hz, 1H), 1.52 (d, *J* = 9.4 Hz, 1H), 1.23 – 1.15 (m, 1H) ppm.

^{13}C NMR (151 MHz, acetone-*d*^{6}): δ 140.80, 128.88, 128.09, 127.75, 72.91, 72.33, 54.06, 47.92, 46.61, 31.15 (q, *J* = 3.3 Hz) ppm.

^{19}F NMR (376 MHz, acetone-*d*^{6}): δ -136.15 ppm.

^{11}B NMR (128 MHz, Acetone-*d*^{6}): δ 3.77 (q, *J* = 75.1 Hz) ppm.

Compound 81



***(1-((benzyloxy)methyl)bicyclo[1.1.1]pentan-2-yl)boronic acid* (81)**

A screw-capped 20×150 mm pyrex culture tube was charged with **80** (294 mg, 1.0 mmol) and water (5.0 mL), followed by addition of silica gel (500 mg) under argon atmosphere. The mixture was stirred at room temperature for 1 hour. Ethyl ether (10 mL) was added, and the suspended solution was filtered by Celite. The organic phase was separated, and the water phase was extracted with diethyl ether (3 × 5 mL). The combined organic solvent was washed with brine and dried by anhydrous $MgSO_4$. The solvent was removed under vacuum to afford the desire boronic acid **81** (230 mg, 99%) without further purification.

A screw-capped 20×150 mm pyrex culture tube was charged with **36** (314 mg, 1.0 mmol, 1.0 equiv.) and Na_5IO_6 (855.6 mg, 4.0 mmol, 4.0 equiv.), followed by addition of THF/H_2O (5 mL, 1:1). Then 12 M HCl (0.17 mL, 2.0 mmol, 2.0 equiv.) was added to reaction tube at 0 °C. The reaction mixture was allowed to stir at 0 °C for 3 hours. After it was confirmed by TLC analysis that **36** was totally consumed, the suspended reaction mixture was filtered via Celite to remove excess Na_5IO_6, and the organic phase was separated, and the water phase was extracted with diethyl ether (3 × 5 mL). The combined organic solvent was washed with brine and dried by anhydrous Na_2SO_4. The solvent was removed under vacuum to afford the desire boronic acid **81** (157.8 mg, 68%) without further purification.

Physical State: white solid.

m.p.: 64-66 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 – 7.35 (m, 2H), 7.34 – 7.30 (m, 3H), 6.05 (br., 2H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.56 (d, *J* = 12.0 Hz, 1H), 3.52 (dd, *J* = 9.9, 1.5 Hz, 1H), 3.48 (dd, *J* = 9.7, 1.2 Hz, 1H), 2.71 (s, 1H), 2.12 (dd, *J* = 9.8, 2.5 Hz, 1H), 1.76 – 1.71 (m, 3H), 1.68 (d, *J* = 8.7 Hz, 1H) ppm.

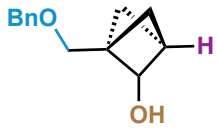
^{13}C NMR (151 MHz, $CDCl_3$): δ 136.97, 128.75, 128.31, 128.12, 73.79, 71.83, 52.42, 49.98, 44.48, 31.14 ppm.

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.19 ppm.

HRMS (ESI-TOF): calc'd for $C_{13}H_{17}BO_3$ $[M+H]^+$: 233.1344, found: 233.1350.

TLC: R_f = 0.68 (2:1 hexanes: ethyl acetate).

Compound 82



***1-((benzyloxy)methyl)bicyclo[1.1.1]pentan-2-ol* (82)**

To a solution of BCP boronate **36** (314.2 mg, 1.0 mmol) and NaOAc (164 mg, 2.0 mmol) in THF (10 mL) at 0 °C was added H_2O_2 (35 wt.% in water, 1.0 mL) dropwise. The resulting mixture was stirred at 0 °C for 1.5 hours. $Na_2S_2O_3$ was added and the mixture was stirred at 0 °C for 10 min. Diethyl ether was added, the layers were separated, and the aqueous phase was extracted with diethyl ether. The combined organic layers were washed with water and brine, dried over anhydrous $MgSO_4$, concentrated, and purified by column chromatography (hexanes: ethyl acetate, 2:1) on silica gel to obtain the 150 mg (75%) of the alcohol **82**.

Physical State: colorless oil.

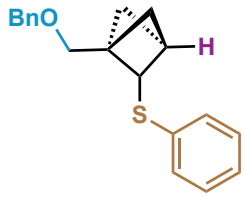
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 – 7.31 (m, 4H), 7.30 – 7.27 (m, 1H), 4.51 (s, 2H), 4.08 (d, *J* = 6.2 Hz, 1H), 3.46 (d, *J* = 12.0 Hz, 1H), 3.44 (d, *J* = 12.0 Hz, 1H), 2.65 (dd, *J* = 9.7, 2.6 Hz, 1H), 2.55 (s, 1H), 2.22 (br., 1H), 1.76 (dd, *J* = 6.2, 2.5 Hz, 1H), 1.62 (d, *J* = 2.9 Hz, 1H), 1.25 (dd, *J* = 9.7, 2.9 Hz, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 138.52, 128.54, 127.74, 127.66, 82.73, 73.29, 68.76, 49.09, 43.46, 39.48, 35.23 ppm.

HRMS (ESI-TOF): calc'd for $C_{13}H_{16}O_2$ $[M+H]^+$: 205.1223, found: 205.1220.

TLC: R_f = 0.41 (2:1 hexanes: ethyl acetate).

Compound 83



***(1-((benzyloxy)methyl)bicyclo[1.1.1]pentan-2-yl)(phenyl)sulfane* (83)**

A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with BCP boronate **36** (31.4 mg, 0.1 mmol, 1.0 equiv.), $PhSO_2SPh$ (50 mg, 0.2 mmol, 2.0 equiv.), and tert-butyl catechol (4.8 mg, 0.03 mmol, 0.3 equiv.), MeOBcat (6.0 mg, 0.04 mmol, 0.4 equiv.). Then the tube was

evacuated and backfilled with argon for three times, followed by addition of toluene (0.5 mL, 0.2 M) solvent via a syringe. Next, the headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was allowed to stir at 100 °C for 36 hours. After it is confirmed that the starting material was consumed totally, the reaction mixture was concentrated under high vacuum and the crude residue was purified by chromatography on silica gel to give 15.8 mg (53%) of the desired product **83**. [8]

Physical State: colorless oil.

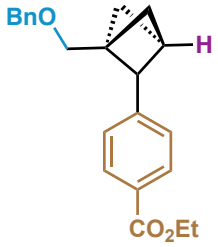
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 – 7.37 (m, 2H), 7.37 – 7.31 (m, 4H), 7.30 – 7.27 (m, 1H), 7.23 (dd, *J* = 8.5, 7.0 Hz, 2H), 7.18 – 7.12 (m, 1H), 4.51 (d, *J* = 12.2 Hz, 1H), 4.48 (d, *J* = 12.2 Hz, 1H), 3.72 – 3.67 (m, 1H), 3.46 (d, *J* = 10.8 Hz, 1H), 3.42 (d, *J* = 10.7 Hz, 1H), 2.76 (s, 1H), 2.63 (dd, *J* = 10.0, 3.0 Hz, 1H), 2.03 (d, *J* = 2.5 Hz, 1H), 1.89 – 1.82 (m, 2H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 138.51, 137.52, 129.10, 128.92, 128.48, 127.66, 127.61, 125.69, 73.23, 68.36, 64.74, 49.32, 47.80, 47.04, 34.68 ppm.

HRMS (ESI-TOF): calc'd for $C_{19}H_{20}OS$ $[M+H]^+$: 297.1308, found: 297.1319.

TLC: R_f = 0.57 (10:1 hexanes: ethyl acetate).

Compound 84



***ethyl 4-(1-((benzyloxy)methyl)bicyclo[1.1.1]pentan-2-yl)benzoate* (84)**

A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with BCP boronate **36** (31.4 mg, 0.1 mmol, 1.0 equiv.). Then the tube was evacuated and backfilled with argon three times, followed by addition of THF (0.5 mL, 0.2 M) solvent via a syringe. Next, PhLi (68 μL, 1.75 M in hexanes, 0.12 mmol, 1.2 equiv.) was added into the reaction mixture at -78 °C and the reaction was allowed to stir at -78 °C for 30 minutes. Then the mixture was allowed to warm up to room temperature and stir for another 30 minutes. A solution of 4-CzlPn (3.9 mg, 0.005 mmol, 0.05 equiv.), Ni(dtbbpy)Cl_2 (8.0 mg, 0.02 mmol, 0.2 equiv.) and ethyl 4-bromobenzoate (49 μL, 0.3 mmol, 3.0 equiv.) in DMA (0.5 mL) was added into the reaction mixture. Next, the headspace of

the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was allowed to stir in a 450-nm photoreactor for 12 hours. After it is confirmed that the starting material was consumed totally, the reaction mixture was quenched with water, extracted with diethyl ether, washed by saturated brine, dried with Na_2SO_4 and concentrated under high vacuum and the crude residue was purified by chromatography on silica gel to give 21.2 mg (63%) of the desired product **84**.

Physical State: colorless oil.

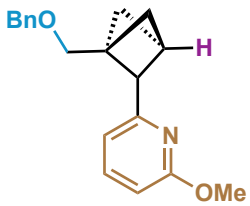
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.34 (m, 4H), 7.31 (ddd, *J* = 8.6, 5.5, 2.4 Hz, 1H), 7.23 (d, *J* = 7.9 Hz, 2H), 4.59 (d, *J* = 12.1 Hz, 1H), 4.53 (d, *J* = 12.2 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.50 (d, *J* = 10.7 Hz, 1H), 3.47 – 3.42 (m, 2H), 2.92 (s, 1H), 2.07 – 2.02 (m, 1H), 1.88 (dd, *J* = 9.7, 1.9 Hz, 1H), 1.86 (d, *J* = 1.8 Hz, 1H), 1.78 (dd, *J* = 6.9, 2.7 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.88, 145.42, 138.48, 129.35, 128.92, 128.52, 128.23, 127.85, 127.79, 73.28, 68.86, 62.78, 60.93, 47.61, 47.34, 46.51, 31.22, 14.50 ppm.

HRMS (ESI-TOF): calc'd for $C_{22}H_{24}O_3$ $[M+H]^+$: 337.1798, found: 337.1800.

TLC: R_f = 0.46 (10:1 hexanes: ethyl acetate).

Compound 85



***2-(1-((benzyloxy)methyl)bicyclo[1.1.1]pentan-2-yl)-6-methoxypyridine* (85)**

A solution of 2-bromo-6-methoxypyridine (17 µL, 0.14 mmol, 1.4 equiv.) in THF:diethyl ether:pentane (4:1:1, 0.3 M) was cooled to –78 °C and treated with *n*-BuLi (0.06 mL, 0.14 mmol, 1.3 eq., 2.32 M in hexanes) and the mixture was stirred at this temperature for 30 min. BCP boronate **36** (31.4 mg, 0.1 mmol, 1.0 equiv.) was added dropwise as a solution in THF (0.5 mL). The mixture was stirred at –78 °C for 30 min. The mixture was warmed to room temperature. and the solvents were removed under high vacuum at room temperature. The crude was redissolved in MeOH (1.0 mL) and the mixture was cooled to 0 °C. A solution of 1,3-dibromo-5,5-dimethylhydantoin (56 mg, 0.2 mmol, 2.0 eq.) in MeOH (1.5 mL) was added dropwise. After 1

hour at 0 °C saturated aqueous solution of $Na_2S_2O_3$ was added and the reaction mixture was allowed to warm to room temperature. The reaction mixture was diluted with ethyl acetate (1.5 mL) and water (1.5 mL). The layers were separated, and the aqueous layer was extracted with ethyl acetate twice. The combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated under vacuum. The crude material was adsorbed on silica and purified by flash column chromatography (hexanes: ethyl acetate, 20:1) on silica gel to give 15.6 mg (53%) of the desired product **85**.[12]

Physical State: colorless oil.

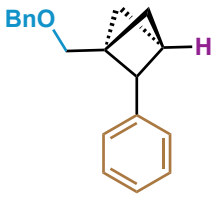
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49 (t, *J* = 7.7 Hz, 1H), 7.37 – 7.30 (m, 4H), 7.29 – 7.25 (m, 1H), 6.75 (d, *J* = 7.3 Hz, 1H), 6.57 (d, *J* = 8.2 Hz, 1H), 4.61 (d, *J* = 12.2 Hz, 1H), 4.58 (d, *J* = 12.2 Hz, 1H), 3.83 (s, 3H), 3.72 (d, *J* = 10.9 Hz, 1H), 3.67 (d, *J* = 10.8 Hz, 1H), 3.40 (d, *J* = 6.9 Hz, 1H), 2.91 (s, 1H), 2.14 (dd, *J* = 9.5, 2.6 Hz, 1H), 1.91 – 1.84 (m, 2H), 1.83 (dd, *J* = 6.9, 2.6 Hz, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 163.37, 157.95, 138.87, 138.70 (br.), 128.43, 127.68, 127.58, 115.95, 107.76, 73.21, 69.46, 63.87 (br.), 53.45, 47.68, 47.49, 46.78, 32.06 ppm.

HRMS (ESI-TOF): calc'd for $C_{19}H_{21}NO_2$ $[M+H]^+$: 296.1645, found: 296.1648.

TLC: R_f = 0.54 (10:1 hexanes: ethyl acetate).

Compound 86



***1-((benzyloxy)methyl)-2-phenylbicyclo[1.1.1]pentane* (86)**

On the benchtop, BCP BF_3K **80** (14.7 mg, 0.05 mmol, 1.0 equiv.), $(Ir[dF(CF_3)ppy]_2(dtbbpy))PF_6$ (2.8 mg, 0.0025 mmol, 0.05 equiv.), $Ni(dtbbpy)Cl_2$ (4.0 mg, 0.01 mmol, 0.20 equiv.) and Cs_2CO_3 (100 mg, 0.3 mmol, 6.0 equiv.) were added to a flame-dried 13×100 mm pyrex culture tube equipped with a stir bar. The test tube was evacuated and backfilled with argon three times. Then PhBr (26 µL, 0.25 mmol, 5.0 equiv.), and distilled dioxane (0.5 mL) was added into the tube. Then the tube was purged with a gentle stream of argon for 10 seconds, then sealed and stirred at room temperature in 450-nm photoreactor for 24 hours. Next, the reaction mixture was quenched with

water (1.0 mL) and extracted with diethyl ether (1.0 mL) three times. The combined organic layers were dried over Na_2SO_4, filtered through Celite, concentrated under reduced pressure, and purified by pTLC (hexanes: diethyl ether, 10:1) on silica gel to obtain 5.3 mg (40%) of the desired coupling product **86**. [13]

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 – 7.33 (m, 4H), 7.32 – 7.26 (m, 3H), 7.22 – 7.18 (m, 1H), 7.16 (dt, *J* = 8.1, 1.1 Hz, 2H), 4.60 (d, *J* = 12.1 Hz, 1H), 4.53 (d, *J* = 12.2 Hz, 1H), 3.53 (d, *J* = 10.7 Hz, 1H), 3.47 – 3.41 (m, 2H), 2.89 (s, 1H), 2.10 (dd, *J* = 10.1, 2.6 Hz, 1H), 1.86 (dq, *J* = 4.0, 1.9 Hz, 2H), 1.78 (dd, *J* = 6.8, 2.6 Hz, 1H) ppm.

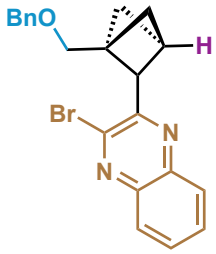
^{13}C NMR (151 MHz, $CDCl_3$): δ 139.99, 138.66, 128.94, 128.49, 128.09, 127.83, 127.70, 125.94, 73.24, 69.05, 62.79, 47.59, 47.00, 46.50, 31.13 ppm.

HRMS (ESI-TOF): calc'd for $C_{19}H_{20}O$ $[M+H]^+$: 265.1587, not found.

MS (GCMS, EI): m/z = 264 (0.2%), 173 (2%), 155 (16%), 115 (30%), 91 (100%).

TLC: R_f = 0.54 (10:1 hexanes : ethyl acetate).

Compound 87



***2-(1-((benzyloxy)methyl)bicyclo[1.1.1]pentan-2-yl)-3-bromoquinoxaline* (87)**

A screw-capped 13×100 mm pyrex culture tube was charged with BCP BF_3K **80** (29.4 mg, 0.1 mmol, 1.0 equiv.), 2-bromoquinoxaline (62.4 mg, 0.3 mmol, 3.0 equiv.) and $Mn(OAc)_3$•$2H_2O$(80.4 mg, 0.3 mmol, 3.0 equiv.). Then the tube or the flask was evacuated and backfilled with argon for three times, followed by addition of acetic acid/water (1.0 mL, 0.1 M, 1:1) solvent via a syringe. Next, trifluoroacetic acid (23 μL, 0.5 mmol, 5.0 equiv.) was added into the reaction. Then the headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was stirred at 50 °C for 18 hours. After it is confirmed that the starting material was consumed totally, the reaction mixture was concentrated under high vacuum to remove excess acetic acid, quenched with K_2CO_3 solution, extracted with ethyl acetate, dried with Na_2SO_4, and

concentrated under high vacuum. The crude residue was purified by pTLC (hexanes: diethyl ether, 5:1) on silica gel to obtain 12.1 mg (31%) of the desired coupling product **87**. [10]

Physical State: red oil.

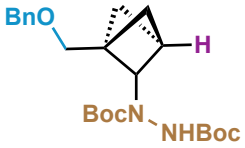
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (dd, *J* = 7.7, 2.0 Hz, 2H), 7.78 – 7.70 (m, 2H), 7.29 – 7.27 (m, 4H), 7.23 (dq, *J* = 7.8, 2.6 Hz, 1H), 4.59 (d, *J* = 12.2 Hz, 1H), 4.53 (d, *J* = 12.2 Hz, 1H), 3.93 (d, *J* = 10.6 Hz, 1H), 3.82 (d, *J* = 10.6 Hz, 1H), 3.72 (d, *J* = 6.2 Hz, 1H), 3.16 (s, 1H), 2.38 (dd, *J* = 9.8, 2.9 Hz, 1H), 2.05 – 1.98 (m, 1H), 1.92 (d, *J* = 1.9 Hz, 1H), 1.87 (dd, *J* = 6.2, 2.9 Hz, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 154.97, 141.81, 141.52, 138.75, 130.21, 130.10, 129.27, 128.39, 128.28, 127.82, 127.64, 127.54, 73.19, 69.30, 63.69, 48.32, 48.09, 46.13, 33.54 ppm.

HRMS (ESI-TOF): calc'd for $C_{21}H_{19}BrN_2O$ $[M+H]^+$: 395.0754, found: 395.0750.

TLC: R_f = 0.43 (10:1 hexanes: ethyl acetate).

Compound 88



***di-tert-butyl 1-(2-((benzyloxy)methyl)cyclobutyl)hydrazine-1,2-dicarboxylate* (88)**

A screw-capped 20×150 mm pyrex culture tube was added boronic acid **81** (116 mg, 0.5 mmol), TBC (30 mol%), DBAD (1.0 mmol) and toluene (2.5 mL). The headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was allowed to stir at 70 °C for 2 h. The solvent was concentrated, and the residue was directly purified by flash column chromatography (hexanes: ethyl acetate, 10:1) on silica gel to give 199 mg (95%) of the desired product **88**.[8]

Physical State: colorless oil.

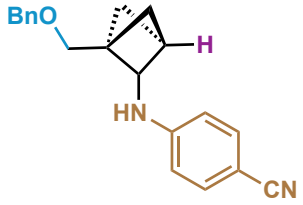
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 – 7.26 (m, 5H), 6.99 (br., 0.5H), 6.51 (br., 0.5H), 4.50 (s, 2H), 3.82 (br., 1H), 3.43 (br., 2H), 2.97 – 2.60 (m, 1H), 2.39 – 2.29 (m, 1H), 1.90 – 1.68 (m, 2H), 1.54 – 1.38 (m, 19H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 138.21, 128.51, 127.92, 127.77, 81.16 (br.), 73.48 (br.), 73.08 (br.), 69.32 (br.), 44.87, 28.40, 28.37 ppm. *Note: bridge-head* CH *and C, bridge* NCH *and* CH_2 BocNN*C*(O)OtBu *and* BocHNN*C*(O)OtBu *were not observed.*

HRMS (ESI-TOF): calc'd for $C_{23}H_{34}N_2O_5$ $[M+H]^+$: 419.2541, found: 419.2541.

TLC: R_f = 0.39 (2:1 hexanes: ethyl acetate).

Compound 89



***4-((1-((benzyloxy)methyl)bicyclo[1.1.1]pentan-2-yl)amino)benzonitrile* (89)**

A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with boronic acid **81** (23.2 mg, 0.1 mmol), 4-nitrobenzonitrile (14.8 mg, 0.1 mmol) and 1,2,2,3,4,4 hexamethylphosphetane 1-oxide (15 mol%) under argon atmosphere, followed by addition of m-xylene (0.2 mL) and $PhSiH_3$ (0.2 mmol). The reaction mixture was stirred at 120 °C for 8 hours. The mixture was directly purified by flash column chromatography (hexanes: ethyl acetate, 10:1) on silica gel to give 20.0 mg (66%) of the desired product **89**.[14]

Physical State: colorless oil.

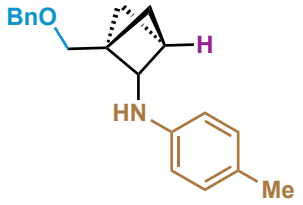
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40 – 7.35 (m, 4H), 7.32 (td, *J* = 6.7, 6.3, 1.7 Hz, 3H), 6.59 – 6.54 (m, 2H), 5.29 (br., 1H), 4.50 (s, 2H), 3.60 (d, *J* = 6.3 Hz, 1H), 3.51 (d, *J* = 10.3 Hz, 1H), 3.47 (d, *J* = 10.3 Hz, 1H), 2.77 (s, 1H), 2.56 (dd, *J* = 9.8, 2.9 Hz, 1H), 1.83 – 1.78 (m, 2H), 1.61 (dd, *J* = 9.7, 2.7 Hz, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 151.62, 138.21, 133.76, 128.64, 127.96, 127.64, 120.78, 112.25, 98.53, 73.50, 70.09, 68.50, 47.23, 44.82, 43.47, 33.23 ppm.

HRMS (ESI-TOF): calc'd for $C_{20}H_{20}N_2O$ $[M+H]^+$: 305.1648, found: 305.1684.

TLC: R_f = 0.46 (10:1 hexanes: ethyl acetate).

Compound 90



***1-((benzyloxy)methyl)-N-(p-tolyl)bicyclo[1.1.1]pentan-2-amine* (90)**

A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with boronic acid **81** (23.2 mg, 0.1 mmol), 4-nitrotoluene (13.7 mg, 0.1 mmol) and 1,2,2,3,4,4 hexamethylphosphetane 1-oxide (15 mol%) under argon atmosphere, followed by addition of m-xylene (0.2 mL) and $PhSiH_3$ (0.2 mmol). The reaction mixture was stirred at 120 °C for 8 hours. The mixture was directly purified by flash column chromatography (hexanes: ethyl acetate, 10:1) on silica gel to give 18.0 mg (61%) of the desired product **90**.[14]

Physical State: red oil.

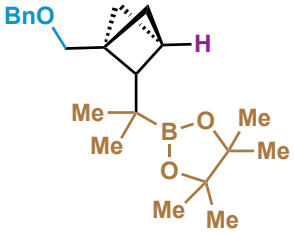
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 – 7.28 (m, 5H), 7.01 – 6.96 (m, 2H), 6.59 – 6.54 (m, 2H), 4.53 (d, *J* = 12.1 Hz, 1H), 4.50 (d, *J* = 12.1 Hz, 1H), 3.60 (d, *J* = 6.2 Hz, 1H), 3.48 (s, 2H), 2.72 (s, 1H), 2.61 (dd, *J* = 9.7, 2.6 Hz, 1H), 2.25 (s, 3H), 1.79 (dd, *J* = 6.3, 2.6 Hz, 1H), 1.76 (d, *J* = 2.5 Hz, 1H), 1.58 (dd, *J* = 9.7, 2.5 Hz, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.16, 138.55, 129.81, 128.55, 127.73, 127.61, 126.22, 112.66, 73.32, 69.83, 69.76, 47.46, 44.80, 43.54, 33.29, 20.53 ppm.

HRMS (ESI-TOF): calc'd for $C_{20}H_{23}NO$ $[M+H]^+$: 294.1852, found: 294.1856.

TLC: R_f = 0.68 (5:1 hexanes: ethyl acetate).

Compound 91



***2-(2-(1-((benzyloxy)methyl)bicyclo[1.1.1]pentan-2-yl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (91)**

A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with BCP boronic acid **81** (23.2 mg, 0.1 mmol, 1.0 equiv.) and sulfonyl hydrazone **17** (30.5 mg, 0.12 mmol, 1.0 equiv.), and cesium carbonate (97.5 mg, 0.3 mmol, 3.0 equiv.) Then the tube was evacuated and backfilled with argon for three times, followed by addition of chlorobenzene (1.0 mL) via a syringe. After stirring for at 100 °C for 2 hours, the reaction mixture was cooled to room temperature. Next, pinacol (118 mg, 1.0 mmol, 5.0 equiv.) was added, and the reaction was stirred at 100 °C for another 1 hour. The suspended solution was then filtered over Celite and washed with diethyl ether.

The solvent was removed under high vacuum, and the crude residue was purified by chromatography (hexanes: ethyl acetate, 15:1) on silica gel to afford 22.1 mg (62%) of the desired product **91**.[7]

Physical State: white solid.

m.p.: 27-29 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 – 7.31 (m, 4H), 7.29 – 7.24 (m, 1H), 4.52 (s, 2H), 3.56 (d, *J* = 10.6 Hz, 1H), 3.52 (d, *J* = 10.6 Hz, 1H), 2.51 (s, 1H), 2.07 (dd, *J* = 9.9, 3.3 Hz, 1H), 1.86 (d, *J* = 7.1 Hz, 1H), 1.76 (dd, *J* = 7.2, 3.2 Hz, 1H), 1.71 (d, *J* = 1.6 Hz, 1H), 1.46 (dd, *J* = 9.9, 1.7 Hz, 1H), 1.21 (s, 6H), 1.20 (s, 6H), 0.97 (s, 3H), 0.95 (s, 3H) ppm.

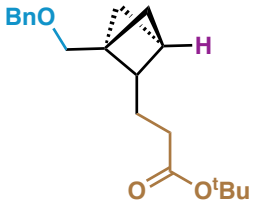
^{13}C NMR (151 MHz, $CDCl_3$): δ 139.12, 128.39, 127.60, 127.44, 82.96, 73.20, 73.07, 69.87, 48.13, 47.65, 47.08, 31.84, 27.12, 26.43, 24.86, 24.84 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 34.77 ppm.

HRMS (ESI-TOF): calc'd for $C_{22}H_{33}BO_3$ $[M+H]^+$: 357.2596, found: 357.2597.

TLC: R_f = 0.50 (10:1 hexanes: ethyl acetate).

Compound 92



***tert-butyl 3-(1-((benzyloxy)methyl)bicyclo[1.1.1]pentan-2-yl)propanoate* (92)**

A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with BCP boronate **36** (31.4 mg, 0.1 mmol, 1.0 equiv.). Then the tube was evacuated and backfilled with argon three times, followed by addition of THF (0.2 mL, 0.5 M) solvent via a syringe. Next, PhLi (68 μL, 1.75 M in hexanes, 0.12 mmol, 1.2 equiv.) was added into the reaction mixture at -78 °C and the reaction was allowed to stir at -78 °C for 30 minutes. Then the mixture was allowed to warm up to room temperature and stir for another 30 minutes. A solution of 4-CzIPn (3.9 mg, 0.005 mmol, 0.05 equiv.), tert-butylacrylate (29 μL, 0.2 mmol, 2.0 equiv.) and tert-butanol (28 μL, 0.3 mmol, 3.0 equiv.) in acetonitrile (1.0 mL) was added into the reaction mixture. Next, the headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was allowed to stir in a 450-nm photoreactor for 12 hours. The reaction mixture was concentrated under

high vacuum and the crude residue was purified by chromatography on silica gel to give 28.8 mg (91%) of the desired product **92**.

Physical State: colorless oil.

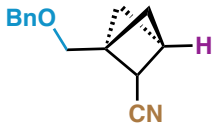
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.16 (m, 5H), 4.42 (s, 2H), 3.27 (s, 2H), 2.32 (s, 1H), 2.23 (dd, *J* = 9.8, 2.9 Hz, 1H), 2.16 (ddd, *J* = 8.4, 6.9, 5.2 Hz, 2H), 2.01 (dt, *J* = 7.8, 6.2 Hz, 1H), 1.87 – 1.70 (m, 2H), 1.69 – 1.64 (m, 2H), 1.48 (dd, *J* = 9.8, 1.7 Hz, 1H), 1.37 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 173.38, 138.79, 134.87, 128.45, 127.57, 80.10, 73.12, 69.51, 60.31, 48.89, 46.38, 45.36, 34.94, 31.12, 28.26, 21.25 ppm.

HRMS (ESI-TOF): calc'd for $C_{20}H_{28}O_3$ $[M+H]^+$: 317.2111, found: 317.2113.

TLC: R_f = 0.54 (10:1 hexanes: ethyl acetate).

Compound 93



***1-((benzyloxy)methyl)bicyclo[1.1.1]pentane-2-carbonitrile* (93)**

A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with BCP boronate **36** (31.4 mg, 0.1 mmol, 1.0 equiv.). Then the tube was evacuated and backfilled with argon three times, followed by addition of THF (0.2 mL, 0.5 M) solvent via a syringe. Next, PhLi (68 µL, 1.75 M in hexanes, 0.12 mmol, 1.2 equiv.) was added into the reaction mixture at -78 °C and the reaction was allowed to stir at -78 °C for 30 minutes. Then the mixture was allowed to warm up to room temperature and stir for another 30 minutes. A solution of 4-CzIPn (3.9 mg, 0.005 mmol, 0.05 equiv.) and TsCN (36 mg, 0.2 mmol, 2.0 equiv.) in acetonitrile (1.0 mL) was added into the reaction mixture. Next, the headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was allowed to stir in a 450-nm photoreactor for 12 hours. The reaction mixture was concentrated under high vacuum and the crude residue was purified by chromatography on silica gel to give 14 mg (66%) of the desired product **93**.

Physical State: colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.26 (m, 5H), 4.55 (d, *J* = 12.4 Hz, 1H), 4.51 (d, *J* = 12.4 Hz, 1H), 3.50 (d, *J* = 11.0 Hz, 1H), 3.45 (d, *J* = 11.0 Hz, 1H), 2.91 (s, 1H), 2.76 (d, *J* = 7.6 Hz, 1H), 2.53 (dd, *J* = 9.9, 3.4 Hz, 1H), 1.94 (dd, *J* = 7.6, 3.4 Hz, 1H), 1.87 (dd, *J* = 9.9, 2.7 Hz, 1H),

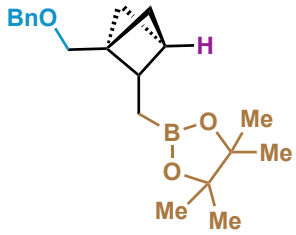
1.81 (d, J = 2.7 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ 138.11, 128.58, 127.86, 127.63, 119.43, 73.40, 68.17, 48.49, 48.32, 47.87, 45.90, 33.10 ppm.

HRMS (ESI-TOF): calc'd for $C_{14}H_{15}NO$ $[M+H]^+$: 214.1226, found: 214.1235.

TLC: R_f = 0.63 (2:1 hexanes: ethyl acetate).

Compound 94



***2-((1-((benzyloxy)methyl)bicyclo[1.1.1]pentan-2-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane* (94)**

BCP boronate **36** (31.4 mg, 0.1 mmol, 1.0 equiv.) and bromoiodomethane (15 µL, 0.2 mmol, 2.0 eq.) were dissolved in anhydrous THF (1.0 mL) and cooled to –78 °C. *n*-BuLi (2.5 M in n-hexane, 0.08 mL, 0.2 mmol, 2.0 equiv.) was added dropwise and the solution was stirred 10 minutes at –78 °C, and then warmed up to room temperature and stir overnight. The reaction mixture was quenched with saturated NH_4Cl solution and dissolved in ethyl acetate. The aqueous phase was extracted with ethyl acetate twice. The combined organic phase was washed with brine, dried over Na_2SO_4 and evaporated to afford the crude residue, which was purified by flash chromatography (hexane: ethyl acetate, 20:1) on silica gel to give 28.0 mg (85%) of the desired product **94**.[11]

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 – 7.30 (m, 4H), 7.29 – 7.24 (m, 1H), 4.52 – 4.46 (m, 2H), 3.34 (s, 2H), 2.36 (s, 1H), 2.32 – 2.24 (m, 2H), 1.79 (d, J = 1.7 Hz, 1H), 1.73 (dd, J = 6.3, 2.9 Hz, 1H), 1.60 (dd, J = 9.8, 1.7 Hz, 1H), 1.22 (s, 12H), 1.09 – 10.6 (m, 2H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 138.95, 128.39, 127.48, 127.46, 83.04, 72.99, 69.35, 55.93, 49.10, 46.79, 45.04, 32.56, 24.95, 24.94 ppm.

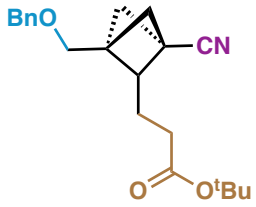
^{11}B NMR (128 MHz, $CDCl_3$): δ 33.77 ppm.

HRMS (ESI-TOF): calc'd for $C_{20}H_{29}BO_3$ $[M+H]^+$: 329.2283, found: 329.2289.

TLC: R_f = 0.50 (10:1 hexanes: ethyl acetate).

Experimental Procedures and Characterization of C1, C2, C3-trisubstituted BCPs (96-105)

Compound 96



***tert-butyl 3-(1-((benzyloxy)methyl)-3-cyanobicyclo[1.1.1]pentan-2-yl)propanoate* (96)**

A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with BCP boronate **42** (33.9 mg, 0.1 mmol, 1.0 equiv.). Then the tube was evacuated and backfilled with argon three times, followed by addition of THF (0.2 mL, 0.5 M) solvent via a syringe. Next, PhLi (68 µL, 1.75 M in hexanes, 0.12 mmol, 1.2 equiv.) was added into the reaction mixture at -78 °C and the reaction was allowed to stir at -78 °C for 30 minutes. Then the mixture was allowed to warm up to room temperature and stir for another 30 minutes. A solution of 4-CzlPn (3.9 mg, 0.005 mmol, 0.05 equiv.), tert-butylacrylate (29 µL, 0.2 mmol, 2.0 equiv.) and tert-butanol (28 µL, 0.3 mmol, 3.0 equiv.) in acetonitrile (1.0 mL) was added into the reaction mixture. Next, the headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was allowed to stir in a 450-nm photoreactor for 12 hours. The reaction mixture was concentrated under high vacuum and the crude residue was purified by chromatography on silica gel to give 15 mg (44%) of the desired product **96**.

Physical State: colorless oil.

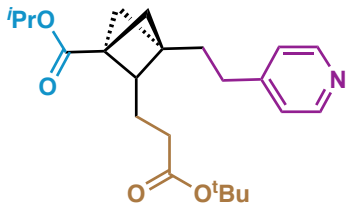
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 – 7.32 (m, 2H), 7.32 – 7.26 (m, 3H), 4.47 (d, J = 12.2 Hz, 1H), 4.45 (d, J = 12.2 Hz, 1H), 3.39 – 3.34 (m, 2H), 2.70 (dd, J = 9.7, 3.1 Hz, 1H), 2.48 (q, J = 6.7 Hz, 1H), 2.43 – 2.27 (m, 2H), 2.18 – 2.15 (m, 2H), 2.07 – 1.83 (m, 3H), 1.45 (s, 9H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.44, 138.04, 128.58, 127.90, 127.67, 117.47, 80.67, 73.39, 67.76, 64.28, 53.00, 49.28, 45.51, 33.53, 28.25, 26.98, 20.43 ppm.

HRMS (ESI-TOF): calc'd for $C_{21}H_{27}NO_3$ $[M+H]^+$: 342.2064, found: 342.2061.

TLC: R_f = 0.29 (10:1 hexanes: ethyl acetate).

Compound 97



***isopropyl 2-(3-(tert-butoxy)-3-oxopropyl)-3-(2-(pyridin-4-yl)ethyl)bicyclo[1.1.1]pentane-1-carboxylate* (97)**

A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with BCP boronate **54** (41.9 mg, 0.1 mmol, 1.0 equiv.). Then the tube was evacuated and backfilled with argon three times, followed by addition of THF (0.2 mL, 0.5 M) solvent via a syringe. Next, PhLi (68 µL, 1.75 M in hexanes, 0.12 mmol, 1.2 equiv.) was added into the reaction mixture at -78 °C and the reaction was allowed to stir at -78 °C for 30 minutes. Then the mixture was allowed to warm up to room temperature and stir for another 30 minutes. A solution of 4-CzlPn (3.9 mg, 0.005 mmol, 0.05 equiv.), tert-butylacrylate (29 µL, 0.2 mmol, 2.0 equiv.) and tert-butanol (28 µL, 0.3 mmol, 3.0 equiv.) in acetonitrile (1.0 mL) was added into the reaction mixture. Next, the headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was allowed to stir in a 450-nm photoreactor for 12 hours. The reaction mixture was concentrated under high vacuum and the crude residue was purified by chromatography on silica gel to give 36 mg (85%) of the desired product **97**.

Physical State: colorless oil.

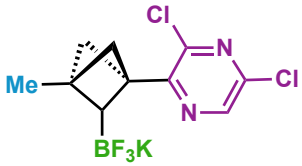
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 – 8.43 (m, 2H), 7.13 – 7.06 (m, 2H), 4.95 (hept, J = 6.3 Hz, 1H), 2.56 – 2.47 (m, 2H), 2.41 – 2.13 (m, 4H), 1.98 – 1.77 (m, 4H), 1.75 (ddd, J = 8.0, 6.9, 2.5 Hz, 2H), 1.67 (dd, J = 9.7, 1.7 Hz, 1H), 1.43 (s, 9H), 1.20 (d, J = 6.2 Hz, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.93, 169.43, 151.09, 149.73, 123.85, 80.34, 67.77, 62.08, 51.21, 46.61, 42.50, 41.04, 34.23, 31.90, 30.07, 28.22, 21.90, 20.40 ppm.

HRMS (ESI-TOF): calc'd for $C_{23}H_{33}NO_4$ $[M+H]^+$: 388.2482, found: 388.2513.

TLC: R_f = 0.17 (2:1 hexanes: ethyl acetate).

Compound SI-24



***3,5-dichloro-2-(3-methyl-2-(trifluoro-λ4-boraneyl)bicyclo[1.1.1]pentan-1-yl)pyrazine, potassium salt* (SI-24)**

BCP boronate **77** (355 mg, 1.0 mmol) was suspended in methanol (5 mL), and a saturated aqueous solution of KHF_2 (1 mL, 4 mmol) was added dropwise. The suspended solution was stirred at room temperature for 2 hours and then concentrated to dryness. The residue was extracted with hot acetone (3 × 20 mL), and the combined filtered extracts were concentrated. Methylene chloride was added, and the resultant precipitate was collected and dried to afford the 245 mg (73%) of the potassium trifluoroborate **SI-24**.

Physical State: white solid.

m.p.: >200 °C.

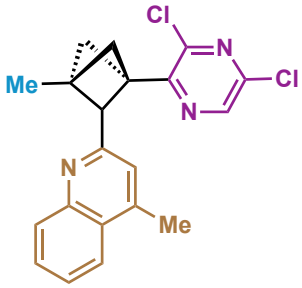
^{1}H NMR (600 MHz, Acetone-*d*^{6}): δ 8.52 (s, 1H), 2.82 (d, *J* = 9.5 Hz, 1H), 2.09 (dd, *J* = 9.7, 2.6 Hz, 1H), 1.88 (t, *J* = 6.3 Hz, 2H), 1.80 (dq, *J* = 11.2, 5.8 Hz, 1H), 1.19 (s, 3H) ppm.

^{13}C NMR (151 MHz, Acetone-*d*^{6}): δ 154.86, 146.56, 143.79, 142.24, 58.90, 50.70, 43.69 (q, *J* = 3.3 Hz), 39.67 (q, *J* = 2.8 Hz), 18.61 ppm.

^{19}F NMR (376 MHz, Acetone-*d*^{6}): δ -136.10 ppm.

^{11}B NMR (128 MHz, Acetone-*d*$_{6}$): δ 3.63 ppm.

Compound 98



***2-(1-(3,5-dichloropyrazin-2-yl)-3-methylbicyclo[1.1.1]pentan-2-yl)-4-methylquinoline* (98)**

A screw-capped 13×100 mm pyrex culture tube was charged with BCP BF_3K **SI-24** (31.9 mg, 0.1 mmol, 1.0 equiv.), lepidine (40 μL, 0.3 mmol, 3.0 equiv.) and $Mn(OAc)_3$•$2H_2O$(80.4 mg, 0.3 mmol,

3.0 equiv.). Then the tube or the flask was evacuated and backfilled with argon for three times, followed by addition of acetic acid/water (1.0 mL, 0.1 M, 1:1) solvent via a syringe. Next, trifluoroacetic acid (23 μL, 0.5 mmol, 5.0 equiv.) was added into the reaction. Then the headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was stirred at 50 °C for 18 hours. Then the reaction mixture was concentrated under high vacuum to remove excess acetic acid, quenched with Na_2CO_3 solution, extracted with ethyl acetate, dried with Na_2SO_4, and concentrated under high vacuum. The crude residue was purified by pTLC (hexanes: diethyl ether, 5:1) on silica gel to obtain 11.0 mg (30%) of the desired coupling product **98**. [10]

Physical State: pale yellow solid.

m.p.: 49-51 °C.

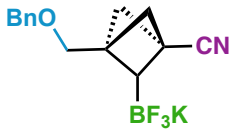
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.47 (s, 1H), 7.92 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 6.95 (s, 1H), 4.08 (d, *J* = 6.8 Hz, 1H), 2.73 (dd, *J* = 9.8, 2.8 Hz, 1H), 2.62 (s, 3H), 2.42 (dd, *J* = 9.8, 1.5 Hz, 1H), 2.26 (dd, *J* = 6.9, 2.8 Hz, 1H), 2.12 (s, 1H), 1.49 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 158.81, 150.73, 147.81, 146.56, 144.83, 143.60, 141.63, 130.08, 128.97, 126.91, 125.78, 123.64, 121.85, 68.15, 53.90, 49.43, 44.81, 42.43, 18.98, 16.66 ppm.

HRMS (ESI-TOF): calc'd for $C_{20}H_{17}Cl_2N_3$ $[M+H]^+$: 370.0872, found: 370.0870.

TLC: R_f = 0.55 (5:1 hexanes: ethyl acetate).

Compound SI-25



***3-((benzyloxy)methyl)-2-(trifluoro-λ^4-boraneyl)bicyclo[1.1.1]pentane-1-carbonitrile, potassium salt* (SI-25)**

BCP boronate **42** (678 mg, 2.0 mmol) was suspended in methanol (10 mL), and a saturated aqueous solution of KHF_2 (2 mL, 8 mmol) was added dropwise. The suspended solution was stirred at room temperature for 2 hours and then concentrated to dryness. The residue was extracted with hot acetone (3 × 30 mL), and the combined filtered extracts were concentrated. Methylene chloride was added, and the resultant precipitate was collected and dried to afford the 517 mg (81%) of the

potassium trifluoroborate **SI-25**.

Physical State: white solid.

m.p.: 122-124 °C.

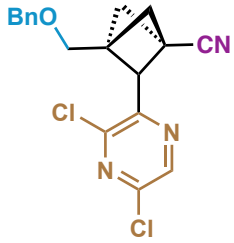
^{1}H NMR (600 MHz, Acetone-*d*^{6}): δ 7.35 – 7.29 (m, 4H), 7.28 – 7.21 (m, 1H), 4.49 (d, *J* = 12.2 Hz, 1H), 4.45 (d, *J* = 12.3 Hz, 1H), 3.50 (d, *J* = 10.8 Hz, 1H), 3.42 (d, *J* = 10.9 Hz, 1H), 2.85 (d, *J* = 9.2 Hz, 1H), 2.09 (s, 1H), 1.95 (d, *J* = 8.1 Hz, 1H), 1.91 (d, *J* = 9.3 Hz, 1H), 1.59 (dq, *J* = 10.2, 5.2 Hz, 1H) ppm.

^{13}C NMR (151 MHz, Acetone-*d*^{6}): δ 140.18, 128.92, 128.11, 127.92, 120.54, 73.12, 70.53, 57.40, 51.52, 45.32 (q, *J* = 2.2 Hz), 26.47 (q, *J* = 3.4 Hz) ppm.

^{19}F NMR (376 MHz, Acetone-*d*^{6}): δ -137.30 ppm.

^{11}B NMR (128 MHz, Acetone-*d*$_{6}$): δ 2.94 (q, *J* = 62.8 Hz) ppm.

Compound 99



***3-((benzyloxy)methyl)-2-(3,5-dichloropyrazin-2-yl)bicyclo[1.1.1]pentane-1-carbonitrile* (99)**

A screw-capped 13×100 mm pyrex culture tube was charged with BCP BF_3K **SI-25** (31.9 mg, 0.1 mmol, 1.0 equiv.), 2,6-dichloropyrazine (44.7 mg, 0.3 mmol, 3.0 equiv.) and $Mn(OAc)_3•2H_2O$(80.4 mg, 0.3 mmol, 3.0 equiv.). Then the tube or the flask was evacuated and backfilled with argon for three times, followed by addition of acetic acid/water (1.0 mL, 0.1 M, 1:1) solvent via a syringe. Next, trifluoroacetic acid (23 μL, 0.5 mmol, 5.0 equiv.) was added into the reaction. Then the headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was stirred at 50 °C for 18 hours. Then the reaction mixture was concentrated under high vacuum to remove excess acetic acid, quenched with K_2CO_3 solution, extracted with ethyl acetate, dried with Na_2SO_4, and concentrated under high vacuum. The crude residue was purified by pTLC (hexanes: diethyl ether, 5:1) on silica gel to obtain 9.3 mg (28%) of the desired coupling product **99**. [10]

Physical State: colorless oil.

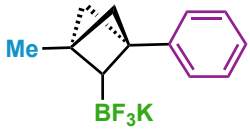
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.51 (s, 1H), 7.36 – 7.26 (m, 3H), 7.23 – 7.18 (m, 2H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.41 (d, *J* = 11.9 Hz, 1H), 3.92 (d, *J* = 6.4 Hz, 1H), 3.63 (d, *J* = 10.7 Hz, 1H), 3.59 (d, *J* = 10.7 Hz, 1H), 2.80 (dd, *J* = 9.7, 3.1 Hz, 1H), 2.33 (dd, *J* = 9.8, 2.3 Hz, 1H), 2.29 (d, *J* = 2.3 Hz, 1H), 2.25 (dd, *J* = 6.5, 3.1 Hz, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 148.50, 148.32, 146.22, 141.56, 137.80, 128.53, 127.96, 127.77, 116.76, 73.51, 67.83, 64.18, 51.67, 50.03, 48.17, 28.12 ppm.

HRMS (ESI-TOF): calc'd for $C_{18}H_{15}Cl_2N_3O$ $[M+H]^+$: 360.0665, found: 360.0671.

TLC: R_f = 0.36 (5:1 hexanes: ethyl acetate).

Compound SI-26



trifluoro(1-methyl-3-phenylbicyclo[1.1.1]pentan-2-yl)-λ^4-borane, potassium salt **(SI-26)**

BCP boronate **65** (284 mg, 1.0 mmol) was suspended in methanol (5 mL), and a saturated aqueous solution of KHF_2 (1 mL, 4 mmol) was added dropwise. The suspended solution was stirred at room temperature for 2 hours and then concentrated to dryness. The residue was extracted with hot acetone (3 × 20 mL), and the combined filtered extracts were concentrated. Methylene chloride was added, and the resultant precipitate was collected and dried to afford the 201 mg (76%) of the potassium trifluoroborate **SI-26**.

Physical State: white solid.

m.p.: 191-193 °C.

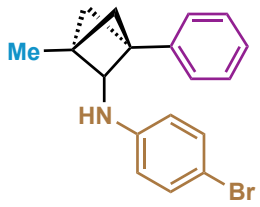
^{1}H NMR (600 MHz, Acetone-*d*^{6}): δ 7.34 – 7.29 (m, 2H), 7.14 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.06 – 7.00 (m, 1H), 2.74 (d, *J* = 9.5 Hz, 1H), 1.78 (s, 1H), 1.63 (d, *J* = 9.4 Hz, 1H), 1.57 (d, *J* = 8.0 Hz, 1H), 1.27 (dd, *J* = 7.7, 5.7 Hz, 1H), 1.18 (s, 3H) ppm.

^{13}C NMR (151 MHz, Acetone-*d*^{6}): δ 145.49, 128.03, 127.66, 125.51, 58.94, 52.08, 44.22 (q, *J* = 2.8 Hz), 37.47 (q, *J* = 2.9 Hz), 18.95 ppm.

^{19}F NMR (376 MHz, Acetone-*d*^{6}): δ -134.94 ppm.

^{11}B NMR (128 MHz, Acetone-*d*$_6$): δ 4.01 (q, *J* = 65.8 Hz) ppm.

Compound 100



***N-(4-bromophenyl)-1-methyl-3-phenylbicyclo[1.1.1]pentan-2-amine* (100)**

A screw-capped 13×100 mm pyrex culture tube was charged with **SI-26** (132 mg, 0.5 mmol) and water (2.5 mL), followed by addition of silica gel (250 mg) under argon atmosphere. The mixture was stirred at room temperature for 1 hour. Ethyl ether (5 mL) was added, and the suspended solution was filtered by Celite. The organic phase was separated, and the water phase was extracted with diethyl ether (3 × 2 mL). The combined organic solvent was washed with brine and dried by anhydrous $MgSO_4$. The solvent was removed under vacuum to afford the desire boronic acid without further purification.

A flame dried screw-capped culture tube was charged with boronic acid (20.2 mg, 0.1 mmol), 1-bromo-4-nitrobenzene (20.2 mg, 0.1 mmol) and 1,2,2,3,4,4-hexamethylphosphetane-1-oxide (15 mol%) under argon atmosphere, followed by addition of m-xylene (0.2 mL) and $PhSiH_3$ (0.2 mmol) were added. The reaction mixture was stirred at 120 °C for 8 hours. The mixture was directly purified by flash column chromatography (hexanes: ethyl acetate, 10:1) on silica gel to give 14.1 mg (43%) of the desired product **100**.[14]

Physical State: red oil.

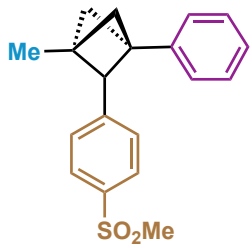
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.28 (dd, *J* = 8.1, 6.8 Hz, 2H), 7.25 – 7.19 (m, 1H), 7.16 (ddd, *J* = 10.2, 7.5, 1.8 Hz, 4H), 6.45 – 6.40 (m, 2H), 3.64 (d, *J* = 6.3 Hz, 1H), 2.65 (dd, *J* = 9.8, 2.7 Hz, 1H), 1.91 (dd, *J* = 6.3, 2.7 Hz, 1H), 1.89 (d, *J* = 2.4 Hz, 1H), 1.84 (dd, *J* = 9.8, 2.5 Hz, 1H), 1.25 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 147.23, 138.46, 131.88, 128.48, 126.93, 126.54, 114.47, 108.89, 72.32, 49.00, 47.00, 46.95, 40.85, 15.98 ppm.

HRMS (ESI-TOF): calc'd for $C_{18}H_{18}BrN$ $[M+H]^+$: 328.0695, found: 328.0694.

TLC: R_f = 0.27 (5:1 hexanes: ethyl acetate).

Compound 101



***1-methyl-2-(4-(methylsulfonyl)phenyl)-3-phenylbicyclo[1.1.1]pentane* (101)**

On the benchtop, BCP BF_3K **SI-26** (14.7 mg, 0.05 mmol, 1.0 equiv.), 4-bromophenyl methyl sulfone (47 mg, 0.2 mmol, 4.0 equiv.), $(Ir[dF(CF_3)ppy]_2(dtbbpy))PF_6$ (2.8 mg, 0.0025 mmol, 0.05 equiv.), $Ni(dtbbpy)Cl_2$ (4.0 mg, 0.01 mmol, 0.20 equiv.) and Cs_2CO_3 (100 mg, 0.3 mmol, 6.0 equiv.) were added to a flame-dried 13×100 mm pyrex culture tube equipped with a stir bar. The test tube was evacuated and backfilled with argon three times. Then dried dioxane (0.5 mL) was added into the tube. Then the tube was purged with a gentle stream of argon for 10 seconds, then sealed and stirred at room temperature in 450-nm photoreactor for 24 hours. Next, the reaction mixture was quenched with water (1.0 mL) and extracted with diethyl ether (1.0 mL) three times. The combined organic layers were dried over Na_2SO_4, filtered through Celite, concentrated under reduced pressure, and purified by pTLC (hexanes: diethyl ether, 10:1) on silica gel to obtain 8.1 mg (52%) of the desired coupling product **96**. [13]

Physical State: colorless oil.

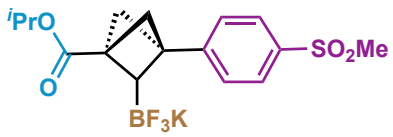
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.81 – 7.77 (m, 2H), 7.35 – 7.29 (m, 2H), 7.29 – 7.23 (m, 3H), 7.21 – 7.16 (m, 2H), 3.52 (d, J = 6.7 Hz, 1H), 3.02 (s, 3H), 2.35 (dd, J = 9.8, 2.8 Hz, 1H), 2.05 (dd, J = 9.8, 1.8 Hz, 1H), 2.02 (dd, J = 6.8, 2.8 Hz, 1H), 2.00 – 1.94 (m, 1H), 1.37 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 146.42, 139.35, 138.05, 129.76, 128.53, 127.08, 126.83, 126.59, 65.08, 55.55, 47.75, 45.40, 44.68, 39.71, 16.71 ppm.

HRMS (ESI-TOF): calc'd for $C_{19}H_{20}O_2S$ $[M+H]^+$: 313.1257, found: 313.1258.

TLC: R_f = 0.58 (2:1 hexanes: ethyl acetate).

Compound SI-27



***isopropyl 3-(4-(methylsulfonyl)phenyl)-2-(trifluoro-λ4-boraneyl)bicyclo[1.1.1]pentane-1-carboxylate, potassium salt* (SI-27)**

BCP boronate **56** (217 mg, 0.5 mmol) was suspended in methanol (3 mL), and a saturated aqueous solution of KHF_2 (0.7 mL, 2.8 mmol) was added dropwise. The suspended solution was stirred at room temperature for 2 hours and then concentrated to dryness. The residue was extracted with hot acetone (3 × 10 mL), and the combined filtered extracts were concentrated. Methylene chloride was added, and the resultant precipitate was collected and dried to afford the 147 mg (71%) of the potassium trifluoroborate **SI-27**.

Physical State: white solid.

m.p.: >200 °C.

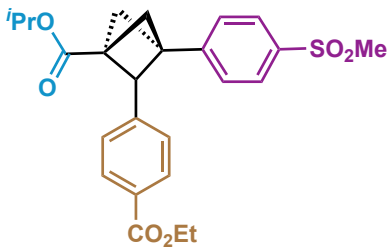
^{1}H NMR (600 MHz, DMSO-*d*$_6$): δ 7.79 – 7.75 (m, 2H), 7.50 – 7.45 (m, 2H), 4.83 (hept, *J* = 6.3 Hz, 1H), 3.14 (s, 3H), 2.91 (d, *J* = 9.2 Hz, 1H), 2.06 (s, 1H), 2.01 (d, *J* = 9.2 Hz, 1H), 1.88 (d, *J* = 7.9 Hz, 1H), 1.64 (dq, *J* = 10.1, 5.2 Hz, 1H), 1.15 (d, *J* = 6.2 Hz, 6H) ppm.

^{13}C NMR (151 MHz, DMSO-*d*$_6$): δ 170.71, 148.80, 138.11, 127.59, 126.53, 66.17, 56.94, 48.83, 43.84, 42.87, 21.79, 21.76 ppm.

^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ -133.31 ppm.

^{11}B NMR (128 MHz, DMSO-*d*$_6$): δ 2.57 ppm.

Compound 102



***isopropyl 2-(4-(ethoxycarbonyl)phenyl)-3-(4-(methylsulfonyl)phenyl)bicyclo[1.1.1]pentane-1-carboxylate* (102)**

On the benchtop, BCP BF_3K **SI-27** (20.1 mg, 0.05 mmol, 1.0 equiv.), ethyl 4-bromobenzoate (49 μL , 0.3 mmol, 6.0 equiv.), (Ir[dF(CF_3)ppy]$_2$(dtbbpy))PF_6 (2.8 mg, 0.0025 mmol, 0.05 equiv.), Ni(dtbbpy)Cl_2 (4.0 mg, 0.01 mmol, 0.20 equiv.) and Cs_2CO_3 (100 mg, 0.3 mmol, 6.0 equiv.) were added to a flame-dried 13×100 mm pyrex culture tube equipped with a stir bar. The test tube was evacuated and backfilled with argon three times. Then dried THF (0.5 mL) was added into the tube.

Then the tube was purged with a gentle stream of argon for 10 seconds, then sealed and stirred at room temperature in 450-nm photoreactor for 24 hours. Next, the reaction mixture was quenched with water (1.0 mL) and extracted with diethyl ether (1.0 mL) three times. The combined organic layers were dried over Na_2SO_4, filtered through Celite, concentrated under reduced pressure, and purified by pTLC (hexanes: diethyl ether, 2:1) on silica gel to obtain 4.1 mg (18%) of the desired coupling product **102**. [13]

Physical State: colorless oil.

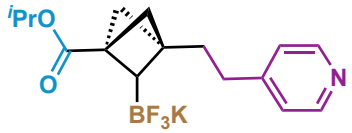
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.92 (d, *J* = 3.0 Hz, 2H), 7.90 (d, *J* = 2.9 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 5.11 (hept, *J* = 6.3 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 4.03 (d, *J* = 6.7 Hz, 1H), 3.07 (s, 3H), 2.76 (dd, *J* = 9.6, 2.9 Hz, 1H), 2.51 (dd, *J* = 9.6, 1.8 Hz, 1H), 2.40 (dd, *J* = 6.8, 2.8 Hz, 1H), 2.35 (d, *J* = 1.8 Hz, 1H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.30 (d, *J* = 4.1 Hz, 3H), 1.29 (d, *J* = 4.0 Hz, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 168.86, 166.52, 144.42, 142.00, 139.50, 129.51, 129.18, 128.66, 127.84, 127.79, 68.73, 67.51, 61.10, 53.78, 47.12, 45.07, 44.67, 41.09, 21.98, 21.96, 14.45 ppm.

HRMS (ESI-TOF): calc'd for $C_{25}H_{28}O_6S$ $[M+H]^+$: 457.1679, found: 457.1677.

TLC: R_f = 0.35 (2:1 hexanes: ethyl acetate).

Compound SI-28



isopropyl 3-(2-(pyridin-4-yl)ethyl)-2-(trifluoro-λ^4-boraneyl)bicyclo[1.1.1]pentane-1-carboxylate, potassium salt **(SI-28)**

BCP boronate **54** (385 mg, 1.0 mmol) was suspended in methanol (5 mL), and a saturated aqueous solution of KHF_2 (1 mL, 4 mmol) was added dropwise. The suspended solution was stirred at room temperature for 2 hours and then concentrated to dryness. The residue was extracted with hot acetone (3 × 40 mL), and the combined filtered extracts were concentrated. Methylene chloride was added, and the resultant precipitate was collected and dried to afford the 274 mg (75%) of the potassium trifluoroborate **SI-28**.

Physical State: white solid.

m.p.: >200 °C.

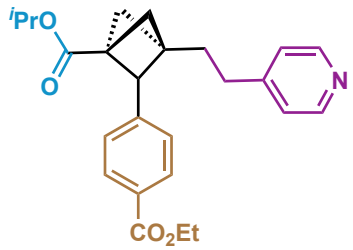
^{1}H NMR (600 MHz, DMSO-*d*$_6$): δ 8.42 – 8.38 (m, 2H), 7.20 – 7.16 (m, 2H), 4.75 (hept, *J* = 6.3 Hz, 1H), 2.54 – 2.50 (m, 2H), 2.44 (d, *J* = 9.3 Hz, 1H), 1.69 (td, *J* = 7.2, 1.6 Hz, 2H), 1.57 (s, 1H), 1.53 (d, *J* = 9.3 Hz, 1H), 1.44 (d, *J* = 7.9 Hz, 1H), 1.22 (dq, *J* = 10.3, 5.3 Hz, 1H), 1.10 (d, *J* = 6.3 Hz, 6H) ppm.

^{13}C NMR (151 MHz, DMSO-*d*$_6$): δ 170.87, 151.89, 149.37, 123.89, 65.80, 55.34, 46.90, 40.96, 40.94, 31.96, 31.65, 21.79, 21.76 ppm.

^{19}F NMR (376 MHz, DMSO-*d*$_6$): δ -133.29 ppm.

^{11}B NMR (128 MHz, DMSO-*d*$_6$): δ 2.99 ppm.

Compound 103



***ethyl 4-(1-((benzyloxy)methyl)bicyclo[1.1.1]pentan-2-yl)benzoate* (103)**

A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with BCP boronate **54** (31.4 mg, 0.1 mmol, 1.0 equiv.). Then the tube was evacuated and backfilled with argon three times, followed by addition of THF (0.5 mL, 0.2 M) solvent via a syringe. Next, PhLi (68 μL, 1.75 M in hexanes, 0.12 mmol, 1.2 equiv.) was added into the reaction mixture at -78 °C and the reaction was allowed to stir at -78 °C for 30 minutes. Then the mixture was allowed to warm up to room temperature and stir for another 30 minutes. A solution of 4-CzlPn (3.9 mg, 0.005 mmol, 0.05 equiv.), Ni(dtbbpy)Cl_2 (8.0 mg, 0.02 mmol, 0.2 equiv.) and ethyl 4-bromobenzoate (49 μL, 0.3 mmol, 3.0 equiv.) in DMA (0.5 mL) was added into the reaction mixture. Next, the headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was allowed to stir in a 450-nm photoreactor for 12 hours. After it is confirmed that the starting material was consumed totally, the reaction mixture was quenched with water, extracted with diethyl ether, washed by saturated brine, dried with Na_2SO_4 and concentrated under high vacuum and the crude residue was purified by pTLC on silica gel (hexane: acetone, 3:1) to give 10.2 mg (25%) of the desired product **103**.

On the benchtop, BCP BF_3K **SI-27** (18.3 mg, 0.05 mmol, 1.0 equiv.), ethyl 4-bromobenzoate (48

μL , 0.3 mmol, 4.0 equiv.), (Ir[dF(CF_3)ppy]$_2$(dtbbpy))PF_6 (2.8 mg, 0.0025 mmol, 0.05 equiv.), Ni(dtbbpy)Cl_2 (4.0 mg, 0.01 mmol, 0.20 equiv.) and Cs_2CO_3 (100 mg, 0.3 mmol, 6.0 equiv.) were added to a flame-dried 13×100 mm pyrex culture tube equipped with a stir bar. The test tube was evacuated and backfilled with argon three times. Then dried THF (0.5 mL) was added into the tube. Then the tube was purged with a gentle stream of argon for 10 seconds, then sealed and stirred at room temperature in 450-nm photoreactor for 24 hours. Next, the reaction mixture was quenched with water (1.0 mL) and extracted with diethyl ether (1.0 mL) three times. The combined organic layers were dried over Na_2SO_4, filtered through Celite, concentrated under reduced pressure, and purified by pTLC (hexanes: diethyl ether, 1:3) on silica gel to obtain 4.8 mg (24%) of the desired coupling product **103**.

Physical State: colorless oil.

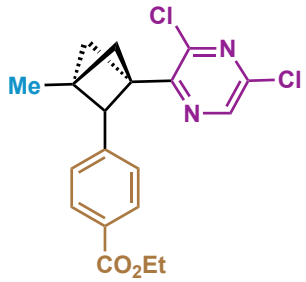
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.50 (d, *J* = 5.0 Hz, 2H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 5.0 Hz, 2H), 5.06 (hept, *J* = 6.2 Hz, 1H), 4.37 (q, *J* = 7.1 Hz, 2H), 3.60 (d, *J* = 6.6 Hz, 1H), 2.63 (qdd, *J* = 14.2, 10.3, 6.1 Hz, 2H), 2.33 (dd, *J* = 9.7, 3.0 Hz, 1H), 2.01 – 1.94 (m, 3H), 1.94 – 1.86 (m, 2H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.25 (dd, *J* = 7.7, 6.3 Hz, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 169.13, 166.65, 151.19, 149.56, 143.16, 129.57, 128.83, 128.68, 123.98, 68.34, 65.00, 61.08, 51.04, 47.02, 43.75, 41.46, 31.91, 30.20, 21.95, 14.49 ppm.

HRMS (ESI-TOF): calc'd for $C_{25}H_{29}NO_4$ $[M+H]^+$: 408.2169, found: 408.2167.

TLC: R_f = 0.13 (2:1 hexanes: ethyl acetate).

Compound 104



***ethyl 4-(1-(3,5-dichloropyrazin-2-yl)-3-methylbicyclo[1.1.1]pentan-2-yl)benzoate* (104)**

A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with BCP boronate **77** (35.5 mg, 0.1 mmol, 1.0 equiv.). Then the tube was evacuated and backfilled with argon for three times, followed by addition of THF (0.5 mL, 0.2 M) solvent via a syringe. Next, PhLi (68 μL, 1.75

M in hexanes, 0.12 mmol, 1.2 equiv.) was added into the reaction mixture at -78 °C and the reaction was allowed to stir at -78 °C for 30 minutes. Then the mixture was allowed to warm up to room temperature and stir for another 30 minutes. A solution of 4-CzlPn (3.9 mg, 0.005 mmol, 0.05 equiv.), Ni(dtbbpy)Cl_2 (8.0 mg, 0.02 mmol, 0.2 equiv.) and ethyl 4-bromobenzoate (49 μL, 0.3 mmol, 3.0 equiv.) in DMA (0.5 mL) was added into the reaction mixture. Next, the headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was allowed to stir in a 450-nm photoreactor for 12 hours. After it is confirmed that the starting material was consumed totally, the reaction mixture was quenched with water, extracted with diethyl ether, washed by saturated brine, dried with Na_2SO_4 and concentrated under high vacuum and the crude residue was purified by chromatography on silica gel to give 8.2 mg (22%) of the desired product **104**.

Physical State: red oil.

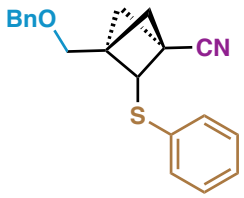
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.46 (s, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.95 (d, *J* = 6.7 Hz, 1H), 2.59 (dd, *J* = 9.8, 3.0 Hz, 1H), 2.36 (dd, *J* = 9.8, 1.7 Hz, 1H), 2.24 (dt, *J* = 7.4, 3.7 Hz, 1H), 2.14 (d, *J* = 1.6 Hz, 1H), 1.42 – 1.32 (m, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.68, 149.87, 146.46, 145.42, 143.96, 141.99, 129.47, 128.59, 128.52, 66.18, 60.99, 54.18, 48.84, 44.58, 41.70, 16.40, 14.47 ppm.

HRMS (ESI-TOF): calc'd for $C_{19}H_{18}Cl_2N_2O_2$ $[M+H]^+$: 377.0818, found: 377.0816.

TLC: R_f = 0.46 (10:1 hexanes: ethyl acetate).

Compound 105



3-((benzyloxy)methyl)-2-(phenylthio)bicyclo[1.1.1]pentane-1-carbonitrile **(105)**

A screw-capped 13×100 mm pyrex culture tube was charged with BCP Bpin **42** (17.0 mg, 0.05 mmol, 1.0 equiv.), $PhSO_2SPh$ (50.0 mg, 0.2 mmol, 4.0 equiv.) and tert-butylcatechol (2.5 mg, 0.015 mmol, 0.3 equiv.). Then the tube or the flask was evacuated and backfilled with argon for three times, followed by addition of MeOBcat (0.05 mmol, 1.0 equiv.) and toluene (0.25 mL, 0.2 M) via syringes. Next, the headspace of the tube was purged with a gentle stream of argon for

approximately 10 seconds and the reaction was stirred at 80 °C for 24 hours. Then the reaction mixture was concentrated under high vacuum to remove excess solvent and purified by pTLC (hexanes: methylene chloride, 1:1) on silica gel to obtain 14.9 mg (93%) of the desired coupling product **105**. [8]

Physical State: colorless oil.

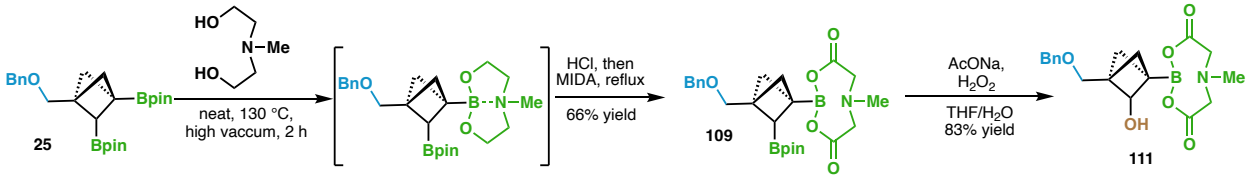
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 – 7.47 (m, 2H), 7.39 – 7.24 (m, 8H), 4.49 (s, 2H), 3.90 (d, *J* = 7.6 Hz, 1H), 3.52 (d, *J* = 11.0 Hz, 1H), 3.46 (d, *J* = 11.0 Hz, 1H), 2.94 (dd, *J* = 9.8, 3.1 Hz, 1H), 2.40 (d, *J* = 2.6 Hz, 1H), 2.26 (dd, *J* = 7.6, 3.1 Hz, 1H), 2.20 (dd, *J* = 9.7, 2.6 Hz, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 137.90, 134.28, 131.63, 129.31, 128.58, 127.95, 127.68, 127.49, 116.34, 73.46, 70.61, 66.47, 51.68, 50.80, 48.75, 30.94 ppm.

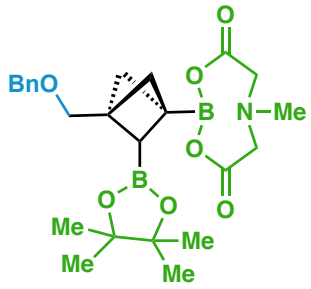
HRMS (ESI-TOF): calc'd for $C_{20}H_{19}NOS$ $[M+H]^+$: 322.1260, found: 322.1275.

TLC: R_f = 0.41 (5:1 hexanes: ethyl acetate).

Reverse Reactivity of BCP Bis-boronates



Compound 109



2-(3-((benzyloxy)methyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione **(109)**

A flame-dried reaction flask was charged with **25** (880 mg, 2.0 mmol, 1.0 equiv.) and methyl diethanolamine (0.35 mL, 3.0 mmol, 1.5 equiv.). Then the mixture was stirred at 140 °C for 2 hours under high vaccum (*note: pinacol was removed under high vaccum to drive the reaction forward*). It was confirmed that starting material **25** was totally consumed through NMR analysis, the reaction was cooled to room temperature, the reaction was quenched with 1 M HCl, extracted with diethyl ether, dried with Na_2SO_4, and concentrated under high vacuum. Methyliminodiacetic acid (441 mg, 3 mmol, 1.5 equiv.) was added into the reaction crude, followed by toluene (10 mL) and DMSO (1 mL). The reaction mixture was stirred at reflux using dean stark apparatus to remove water for 2 hours. After it was confirmed that boronic acid was totally consumed through TLC analysis, the reaction was cooled to room temperature and quenched with water, extracted with ethyl acetate, dried with Na_2SO_4, and concentrated under high vacuum. The reaction crude was finally purified by column chromatography (pure ethyl acetate) on silica gel to obtain 619.4 mg (66%) of the desired coupling product **109**.

Physical State: white solid.

m.p.: 103-105 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 – 7.29 (m, 4H), 7.29 – 7.23 (m, 1H), 4.55 (d, *J* = 12.4 Hz, 1H), 4.52 (d, *J* = 12.3 Hz, 1H), 3.87 (d, *J* = 15.8 Hz, 1H), 3.83 (d, *J* = 16.2 Hz, 1H), 3.75 (dd, *J* = 16.0, 2.7 Hz, 2H), 3.45 (d, *J* = 10.7 Hz, 1H), 3.40 (d, *J* = 10.7 Hz, 1H), 3.04 (s, 3H), 2.17 (dd, *J* =

9.8, 2.4 Hz, 1H), 1.87 (d, *J* = 1.6 Hz, 1H), 1.83 (dd, *J* = 8.7, 2.1 Hz, 2H), 1.57 (d, *J* = 8.4 Hz, 1H), 1.21 (s, 12H) ppm.

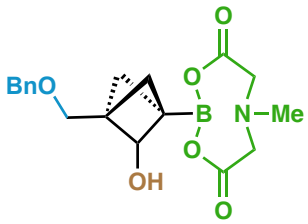
^{13}C NMR (151 MHz, $CDCl_3$): δ 167.37, 167.07, 138.99, 128.38, 127.57, 127.49, 83.51, 73.03, 70.96, 62.80, 62.29, 53.46, 49.21, 46.33, 45.86, 25.26, 24.52 ppm.

^{11}B NMR (128 MHz, $CDCl_3$) δ 32.71, 10.07 ppm.

HRMS (ESI-TOF): calc'd for $C_{24}H_{33}B_2NO_7$ $[M+H]^+$: 470.2516, found: 470.2532.

TLC: R_f = 0.33 (pure ethyl acetate).

Compound 111



***2-(3-((benzyloxy)methyl)-2-hydroxybicyclo[1.1.1]pentan-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione* (111)**

To a solution of **109** (24 mg, 0.05 mmol) and NaOAc (16.4 mg, 0.2 mmol) in THF (0.5 mL) at 0 °C was added H_2O_2 (50 wt.% in water, 0.05 mL) dropwise. The resulting mixture was stirred at 0 °C for 3 hours. $Na_2S_2O_3$ was added and the mixture was stirred at 0 °C for 10 min. Ethyl acetate was added, the layers were separated, and the aqueous phase was extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over anhydrous $MgSO_4$, concentrated, and purified by column chromatography (pure ethyl acetate) on silica gel to obtain the 15.3 mg (83%) of alcohol **111**.

Physical State: colorless oil.

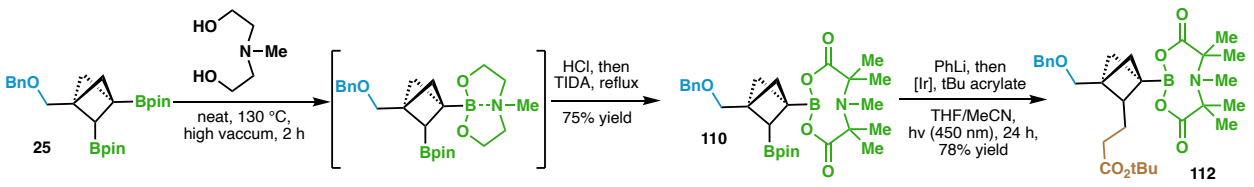
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 – 7.30 (m, 2H), 7.31 – 7.26 (m, 3H), 4.47 (s, 2H), 4.00 (d, *J* = 6.1 Hz, 1H), 3.92 – 3.81 (m, 3H), 3.65 (d, *J* = 16.7 Hz, 1H), 3.39 (d, *J* = 2.0 Hz, 2H), 3.17 (br., 1H), 3.03 (s, 3H), 2.56 (dd, *J* = 9.8, 2.4 Hz, 1H), 1.76 (dd, *J* = 6.3, 2.4 Hz, 1H), 1.65 (d, *J* = 2.9 Hz, 1H), 1.28 – 1.21 (m, 1H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 168.81, 167.98, 138.42, 128.57, 127.82, 127.72, 82.01, 73.32, 69.48, 62.10, 61.45, 49.01, 46.44, 43.13, 40.49 ppm.

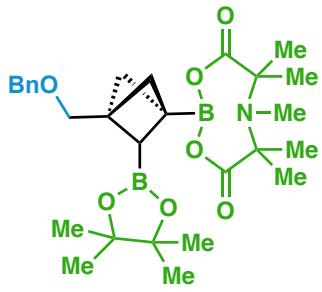
^{11}B NMR (128 MHz, $CDCl_3$) δ 10.08 ppm.

HRMS (ESI-TOF): calc'd for $C_{18}H_{22}BNO_6$ $[M+Na]^+$: 382.1432, found: 382.1441.

TLC: R_f = 0.20 (pure ethyl acetate).



Compound 110



2-(3-((benzyloxy)methyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)-5,5,6,7,7-pentamethyl-1,3,6,2-dioxazaborocane-4,8-dione **(110)**

A flame-dried reaction flask was charged with **25** (880 mg, 2.0 mmol, 1.0 equiv.) and methyl diethanolamine (0.35 mL, 3.0 mmol, 1.5 equiv.). Then the mixture was stirred at 140 °C for 2 hours under high vaccum (*note: pinacol was removed under high vaccum to drive the reaction forward*). It was confirmed that starting material **25** was totally consumed through NMR analysis, the reaction was cooled to room temperature, the reaction was quenched with 1 M HCl, extracted with diethyl ether, dried with Na_2SO_4, and concentrated under high vacuum. 2,2'-(Methylazanediyl)bis(2-methylpropanoic acid) (609 mg, 3 mmol, 1.5 equiv.) prepared via Burke's procedure[15] was added into the reaction crude, followed by toluene (10 mL) and DMSO (1 mL). The reaction mixture was stirred at reflux using dean stark apparatus to remove water for 2 hours. After it was confirmed that boronic acid was totally consumed through TLC analysis, the reaction was cooled to room temperature and quenched with water, extracted with ethyl acetate, dried with Na_2SO_4, and concentrated under high vacuum. The reaction crude was finally purified by column chromatography (pure ethyl acetate) on silica gel to obtain 790 mg (75%) of the desired coupling product **110**.

Physical State: white solid.

m.p.: 115-117 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 – 7.29 (m, 4H), 7.26 – 7.22 (m, 1H), 4.53 (d, *J* = 12.4 Hz, 1H), 4.50 (d, *J* = 12.3 Hz, 1H), 3.41 (d, *J* = 10.6 Hz, 1H), 3.37 (d, *J* = 10.6 Hz, 1H), 2.62 (s, 3H), 2.49 – 2.44 (m, 1H), 1.81 – 1.78 (m, 2H), 1.76 (dd, *J* = 8.2, 2.0 Hz, 1H), 1.69 (s, 3H), 1.67 (s, 3H), 1.57 (s, 3H), 1.55 (s, 3H), 1.54 (d, *J* = 8.1 Hz, 1H), 1.23 (s, 6H), 1.21 (s, 6H) ppm.

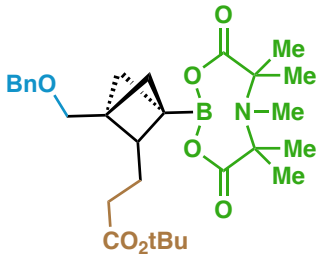
^{13}C NMR (151 MHz, $CDCl_3$): δ 174.49, 174.07, 138.99, 128.35, 127.54, 127.43, 83.09, 72.96, 71.09, 54.23, 48.91, 47.90(*br.*), 44.28, 36.51, 25.26, 24.63 ppm. *Note:* B*C,* N*C*Me_2 *were not detected.*

^{11}B NMR (128 MHz, $CDCl_3$) δ 31.53, 8.41 ppm.

HRMS (ESI-TOF): calc'd for $C_{28}H_{41}B_2NO_7$ $[M+H]^+$: 526.3142, found: 526.3154.

TLC: R_f = 0.45 (pure ethyl acetate).

Compound 112



***tert-butyl 3-(1-((benzyloxy)methyl)-3-(5,5,6,7,7-pentamethyl-4,8-dioxo-1,3,6,2-dioxaza borocan-2-yl)bicyclo[1.1.1]pentan-2-yl)propanoate* (112)**

A flame-dried screw-capped 13×100 mm pyrex culture tube was charged with **110** (52.5 mg, 0.1 mmol, 1.0 equiv.). Then the tube was evacuated and backfilled with argon three times, followed by addition of THF (0.5 mL, 0.2 M) solvent via a syringe. Next, PhLi (68 µL, 1.75 M in hexanes, 0.12 mmol, 1.2 equiv.) was added into the reaction mixture at -78 °C and the reaction was allowed to stir at -78 °C for 30 minutes. Then the mixture was allowed to warm up to room temperature and stir for another 30 minutes. A solution of 4-CzIPn (3.9 mg, 0.005 mmol, 0.05 equiv.), tert-BuOH (28 µL, 3.0 equiv.) and tert-butylacrylate (29 µL, 0.2 mmol, 2.0 equiv.) in acetonitrile (0.5 mL) was added into the reaction mixture. Next, the headspace of the tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was allowed to stir in a 450-nm photoreactor for 12 hours. The reaction mixture was concentrated under high vacuum and the crude residue was purified by chromatography on silica gel to give 41.1 mg (78%) of the desired product **112**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.35 – 7.28 (m, 4H), 7.28 – 7.24 (m, 1H), 4.49 (d, *J* = 12.2 Hz, 1H), 4.46 (d, *J* = 12.2 Hz, 1H), 3.30 (d, *J* = 1.8 Hz, 2H), 2.54 (s, 3H), 2.36 – 2.21 (m, 3H), 2.09 – 2.03 (m, 1H), 1.94 – 1.87 (m, 2H), 1.71 – 1.63 (m, 2H), 1.70 (s, 3H), 1.67 (s, 3H), 1.58 – 1.53 (m, 1H), 1.56 (s, 3H), 1.55 (s, 3H), 1.43 (s, 9H) ppm.

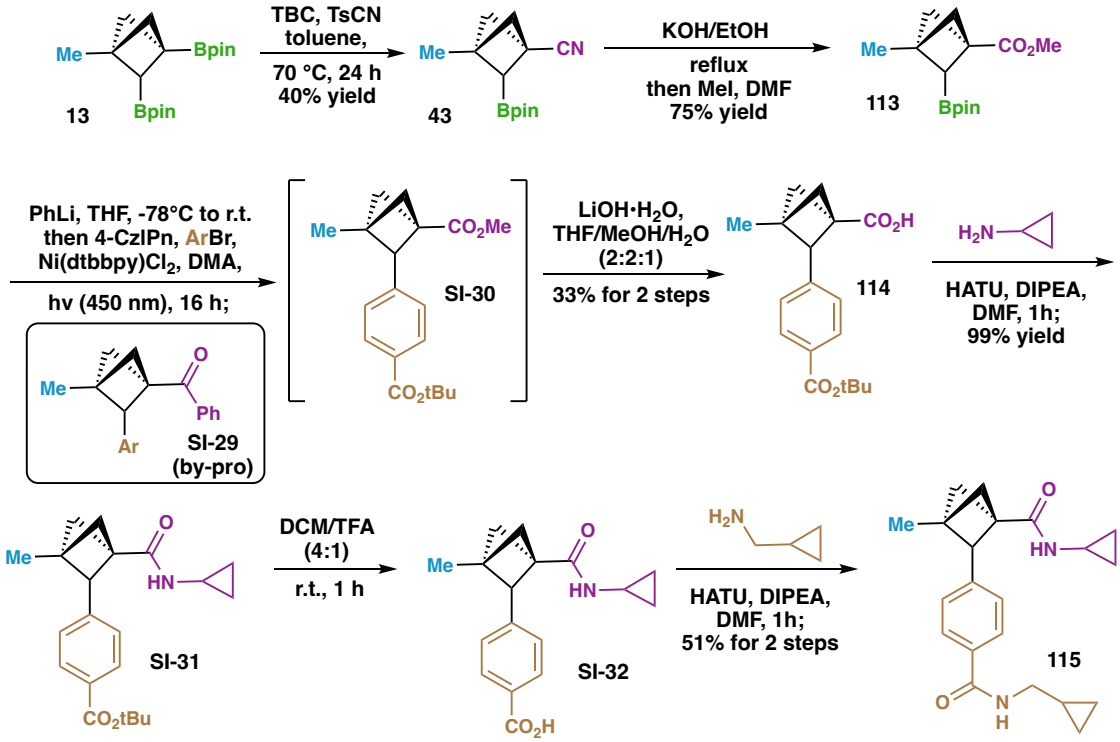
^{13}C NMR (151 MHz, $CDCl_3$): δ 174.31, 173.54, 138.67, 128.44, 127.61, 127.59, 79.97, 73.20, 73.07, 71.09, 69.79, 61.28, 50.38, 45.83, 45.39, 36.48, 36.36, 34.91, 28.28, 21.30 ppm.

^{11}B NMR (128 MHz, $CDCl_3$) δ 8.19 ppm.

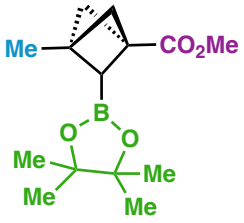
HRMS (ESI-TOF): calc'd for $C_{29}H_{42}NO_7$ $[M+H]^+$: 528.3127, found: 528.3128.

TLC: R_f = 0.52 (pure ethyl acetate).

Experimental Procedures and Characterization Data of BCP Analogue 115 and Bioactive Arene 116



Compound 113



methyl-3-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentane-1-carboxylate **(113)**

A 50 mL flask was charged with BCP **13** (3.34 g, 10.0 mmol, 1.0 equiv.). EtOH (20.0 mL) was added into the reaction, followed by addition of KOH (5 mL, 6N in H_2O). Then the reaction was stirred at 90 °C for 24 hours. The reaction mixture was acidified by 1 M HCl to pH < 1, extracted by Et_2O and dried by Na_2SO_4. The mixture was filtered and concentrated under vacuum to give the crude residue that was used directly without further purification.

In a 50 mL flask was added the crude carboxylic acid, K_2CO_3 (2.76 g, 20 mmol, 2.0 equiv.) and

DMF (20 mL) under argon atmosphere. MeI (1.25 mL, 20 mmol, 2.0 equiv.) was added and the mixture was stirred at room temperature for 12h. Et_2O and H_2O were added, and the organic layer was washed by H_2O, Brine and dried by Na_2SO_4. The mixture was filtered and concentrated under vacuum. The crude residue was purified by column chromatography (hexanes: diethyl ether, 10:1) on silica gel to obtain 2.0 g (75%) of the desired ester **113**.

Physical State: colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 3.64 (s, 3H), 2.54 (dd, J = 9.5, 2.0 Hz, 1H), 1.95 – 1.90 (m, 2H), 1.87 (dd, J = 8.2, 2.0 Hz, 1H), 1.72 (d, J = 8.1 Hz, 1H), 1.25 (s, 12H), 1.20 (s, 3H) ppm.

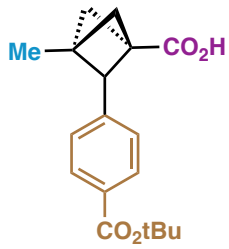
^{13}C NMR (151 MHz, $CDCl_3$): δ 170.78, 83.23, 57.26, 52.11, 51.59, 39.68, 39.27, 24.94, 24.86, 18.22 ppm.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.68 ppm.

HRMS (ESI-TOF): calc'd for $C_8H_{11}O_2$ $[M+H]^+$: 267.1762, found: 267.1777.

TLC: R_f = 0.50 (5:1 hexanes: ethyl acetate).

Compound 114



***2-(4-(tert-butoxycarbonyl)phenyl)-3-methylbicyclo[1.1.1]pentane-1-carboxylic acid* (114)**

A flame-dried screw-capped 20×150 mm pyrex culture tube was charged with BCP boronate **113** (470 mg, 1.8 mmol, 1.0 equiv.). Then the tube was evacuated and backfilled with argon three times, followed by addition of THF (5.0 mL, 0.36 M) solvent via a syringe. Next, PhLi (1.2 mL, 175 M in hexanes, 2.1 mmol, 1.17 equiv.) was added into the reaction mixture at -78 °C and the reaction was allowed to stir at -78 °C for 30 minutes. Then the mixture was allowed to warm up to room temperature and stir for another 30 minutes. Next, the THF solvent was removed under high vacuum and DMA (5.0 mL) was added into the reaction to dissolve the reaction crude. The crude solution of BCP ate complex in DMA (5.0 mL) was added into another flame-dried screw-capped culture tube charged with 4-CzlPn (71.0 mg, 0.09 mmol, 0.05 equiv.), Ni(dtbbpy)Cl_2 (143.4 mg, 0.36 mmol, 0.2 equiv.) and ethyl 4-bromobenzoate (1.29 g, 5.4 mmol, 3.0 equiv.). The first tube

containing BCP ate complex was then rinsed with DMA (2.0 mL) twice and the DMA solutions were transferred into the reaction tube. Next, the headspace of the reaction tube was purged with a gentle stream of argon for approximately 10 seconds and the reaction was irradiated under a 40 W Kessil blue LED lamp (468 nm) for 16 hours.

After it is confirmed that the starting material was consumed totally, the reaction mixture was quenched with water (50 mL), extracted with diethyl ether (20 mL × 3), washed by saturated brine (50 mL), dried with Na_2SO_4 and concentrated under high vacuum. The crude residue was purified by chromatography on silica gel to remove the rest aryl bromide and obtain a mixture of compound **SI-30** and **SI-29** (310 mg, 1:4). The mixture of **SI-29** and **SI-30** was used without further purification.

The mixture of **SI-29** and **SI-30** (310 mg) was dissolved in THF/MeOH/H_2O (5.0 mL, 2:2:1) and LiOH•H_2O (84 mg, 2 mmol) was added into the solution. The reaction mixture was stirred at room temperature for 2.5 hours. The solvent was evaporated, and the reaction crude was dissolved in water (50 mL) and extracted with diethyl ether (20 mL) twice. Then 1 M HCl (2.5 mL) was added into the water phase which was then extracted with methylene chloride (20 mL × 3). The combined methylene chloride phase was dried with Na_2SO_4 and concentrated under high vacuum, affording the pure carboxylic acid (180 mg, 33% yield) without further purification.

Physical State: white solid.

m.p.: 123-125 °C.

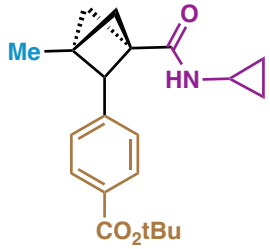
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 3.56 (d, *J* = 6.7 Hz, 1H), 2.38 (dd, *J* = 9.7, 2.9 Hz, 1H), 2.08 (s, 1H), 2.05 (dd, *J* = 9.7, 1.7 Hz, 1H), 1.98 (dd, *J* = 6.8, 2.9 Hz, 1H), 1.59 (s, 9H), 1.27 (s, 3H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 175.63, 165.93, 142.86, 130.24, 129.44, 128.42, 81.05, 66.03, 53.40, 48.68, 41.11, 40.83, 28.34, 16.31 ppm.

HRMS (ESI-TOF): calc'd for $C_{18}H_{22}O_4$ $[M+H]^+$: 303.1591, found: 303.1605.

TLC: R_f = 0.23 (1:1 hexanes: ethyl acetate).

Compound SI-31



***tert-butyl 4-(1-(cyclopropylcarbamoyl)-3-methylbicyclo[1.1.1]pentan-2-yl)benzoate* (SI-31)**

A screw-capped 20×150 mm pyrex culture tube was charged with BCP **107** (150 mg, 0.5 mmol, 1.0 equiv.), cyclopropylamine (52 μL, 0.75 mmol, 1.5 equiv.) and HATU (285.2 mg, 0.75 mmol, 1.5 equiv.). Next, DMF (2.5 mL, 0.2 M) was added into the reaction to dissolve the solids, followed by dropwise addition of DIPEA (0.17 mL, 1.0 mmol, 2.0 equiv.). Then the reaction was allowed to stir at room temperature for 2 hours. After it is confirmed that the starting material was consumed totally, the reaction mixture was quenched with water (50 mL), extracted with diethyl ether (20 mL × 3), washed by saturated brine (50 mL), dried with Na_2SO_4 and concentrated under high vacuum. The crude residue was purified by column chromatography (hexanes: ethyl acetate, 2:1) on silica gel to obtain 169.2 mg (99%) of the desired amide **SI-31**.

Physical State: colorless foam.

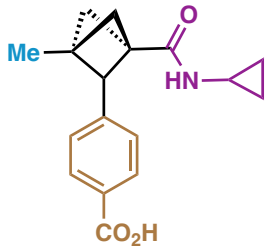
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.95 – 7.90 (m, 2H), 7.28 (d, J = 8.1 Hz, 2H), 5.58 (br., 1H), 3.46 (d, J = 6.7 Hz, 1H), 2.71 (tq, J = 7.2, 3.7 Hz, 1H), 2.24 (dd, J = 9.7, 2.6 Hz, 1H), 1.95 (dd, J = 9.7, 1.8 Hz, 1H), 1.93 (s, 1H), 1.84 (dd, J = 6.8, 2.6 Hz, 1H), 1.58 (s, 9H), 1.27 (s, 3H), 0.81 – 0.73 (m, 2H), 0.52 – 0.44 (m, 2H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 170.88, 165.88, 143.23, 130.21, 129.40, 128.48, 81.03, 65.43, 52.94, 47.82, 42.89, 39.64, 28.33, 22.57, 16.48, 6.82, 6.78 ppm.

HRMS (ESI-TOF): calc'd for $C_{21}H_{27}NO_3$ $[M+H]^+$: 342.2063, found: 342.2068.

TLC: R_f = 0.38 (1:1 hexanes: ethyl acetate).

Compound SI-32



***4-(1-(cyclopropylcarbamoyl)-3-methylbicyclo[1.1.1]pentan-2-yl)benzoic acid* (SI-32)**

A screw-capped 20×150 mm pyrex culture tube was charged with BCP **SI-31** (136.4 mg, 0.4 mmol, 1.0 equiv.), and then methylene chloride (1.6 mL) and TFA (0.40 mL) was added into the reaction. Then the reaction was allowed to stir at room temperature for 2 hours. Then the reaction mixture was concentrated under high vacuum to remove excess solvent, affording 114.2 mg (100%) of the desired carboxylic acid **SI-32** without further purification.

Physical State: white solid.

m.p.: 177-179 °C.

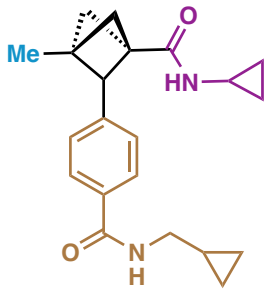
^{1}H NMR (600 MHz, $CDCl_3$): δ 12.08 (br., 1H), 8.05 – 7.98 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.05 (br., 1H), 3.52 (d, *J* = 6.6 Hz, 1H), 2.75 (tq, *J* = 7.2, 3.7 Hz, 1H), 2.27 (dd, *J* = 9.7, 2.7 Hz, 1H), 2.00 (dd, *J* = 9.8, 1.8 Hz, 1H), 1.96 (s, 1H), 1.88 (dd, *J* = 6.9, 2.7 Hz, 1H), 1.29 (s, 3H), 0.79 (qd, *J* = 5.6, 5.1, 3.4 Hz, 2H), 0.53 (ddd, *J* = 6.6, 5.0, 3.8 Hz, 2H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.39, 171.68, 144.35, 130.24, 128.61, 127.76, 65.58, 53.05, 47.74, 42.75, 39.86, 22.91, 16.37, 6.83, 6.76 ppm.

HRMS (ESI-TOF): calc'd for $C_{17}H_{19}NO_3$ $[M+H]^+$: 286.1438, found: 286.1447.

TLC: R_f = 0.15 (1:2 hexanes: ethyl acetate).

Compound 115



***N*-cyclopropyl-2-(4-((cyclopropylmethyl)carbamoyl)phenyl)-3-methylbicyclo[1.1.1]pentane-1-carboxamide (115)**

A screw-capped 13×100 mm pyrex culture tube was charged with BCP **SI-32** (100 mg, 0.35 mmol, 1.0 equiv.), cyclopropylmethylamine (43 μL, 0.52 mmol, 1.5 equiv.) and HATU (197.6 mg, 0.52 mmol, 1.5 equiv.). Next, DMF (1.5 mL, 0.2 M) was added into the reaction to dissolve the solids, followed by dropwise addition of DIPEA (0.17 mL, 1.0 mmol, 3.0 equiv.) . Then the reaction was allowed to stir at room temperature for 2 hours. After it is confirmed that the starting material was consumed totally, the reaction mixture was quenched with water (10 mL), extracted with diethyl ether (5 mL × 3), washed by saturated brine (5 mL), dried with Na_2SO_4 and concentrated under high vacuum. The crude residue was purified by column chromatography (hexanes: ethyl acetate, 2:1) on silica gel to obtain 60.0 mg (51%) of the desired amide **115**.

Physical State: white solid.

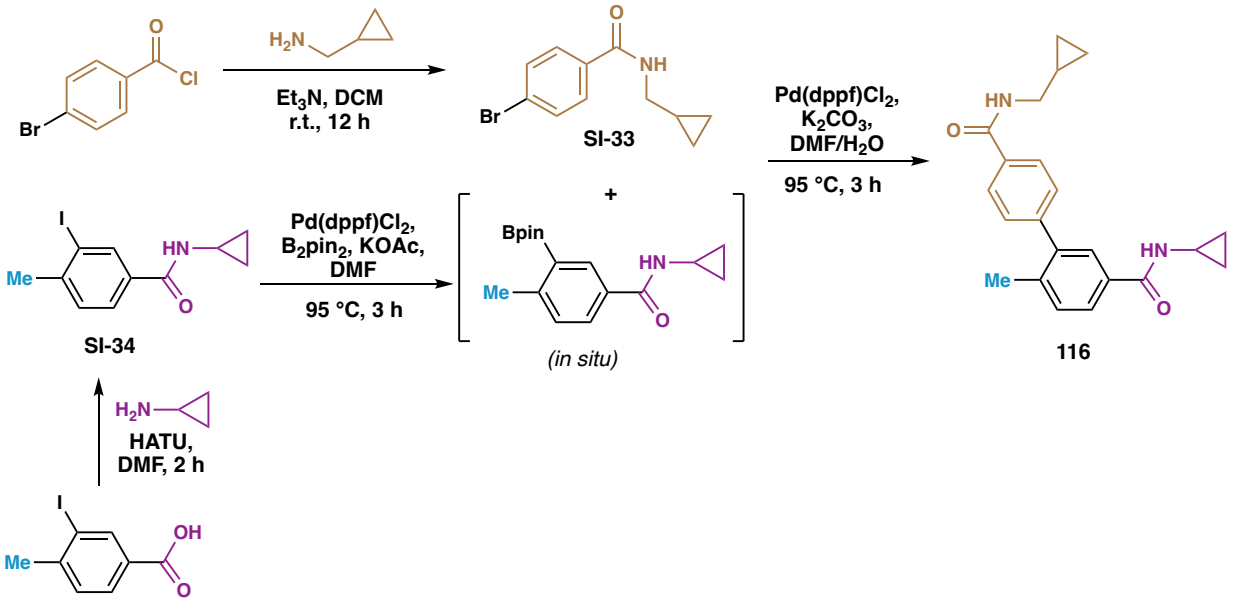
m.p.: 158-160 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 2H), 6.19 (br., 1H), 5.55 (br., 1H), 3.46 (d, *J* = 6.7 Hz, 1H), 3.32 (dd, *J* = 7.2, 5.4 Hz, 2H), 2.72 (tq, *J* = 7.1, 3.7 Hz, 1H), 2.25 (dd, *J* = 9.7, 2.7 Hz, 1H), 1.96 (dd, *J* = 9.7, 1.7 Hz, 1H), 1.94 (s, 1H), 1.85 (dd, *J* = 6.8, 2.6 Hz, 1H), 1.28 (s, 3H), 1.12 – 1.00 (m, 1H), 0.83 – 0.75 (m, 2H), 0.59 – 0.52 (m, 2H), 0.50 – 0.45 (m, 2H), 0.28 (dt, *J* = 6.0, 4.6 Hz, 2H) ppm.

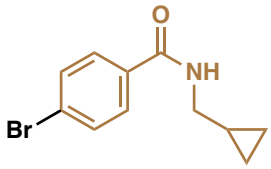
^{13}C NMR (151 MHz, $CDCl_3$): δ 170.91, 167.45, 142.09, 132.94, 128.85, 126.89, 65.35, 52.92, 47.87, 45.07, 42.90, 39.61, 22.58, 16.51, 10.89, 6.86, 6.81, 3.63 ppm.

HRMS (ESI-TOF): calc'd for $C_{21}H_{26}N_2O_2$ $[M+H]^+$: 339.2067, found: 339.2073.

TLC: R_f = 0.15 (1:2 hexanes: ethyl acetate).



Compound SI-33



4-bromo-N-(cyclopropylmethyl)benzamide **(SI-33)**

A reaction flask was charged with 4-bromobenzoyl chloride (5.0 g, 22.8 mmol, 1.0 equiv.) and cyclopropylmethylamine (1.62 g, 22.8 mmol, 1.0 equiv.), followed by addition of THF (40 mL). Next, triethylamine (3.5 mL, 25 mmol, 1.1 equiv.) was added dropwise to the reaction. Then the reaction was allowed to stir at room temperature for 12 hours. After it was confirmed that starting materials was totally consumed through TLC analysis, the reaction was concentrated under high vacuum. The reaction crude was then purified by column chromatography (hexanes: diethyl ether, 5:1) on silica gel to obtain 5.0 g (86%) of the desired coupling product **SI-33**.

Physical State: white solid.

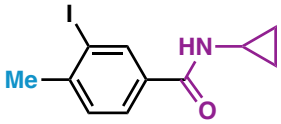
m.p.: 89-91 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.68 – 7.63 (m, 2H), 7.59 – 7.54 (m, 2H), 6.20 (br., 1H), 3.30 (dd, *J* = 7.2, 5.3 Hz, 2H), 1.05 (tt, *J* = 7.6, 4.8 Hz, 1H), 0.60 – 0.52 (m, 2H), 0.27 (dt, *J* = 6.3, 4.6 Hz, 2H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 166.56, 133.68, 131.90, 128.67, 126.14, 45.21, 10.80, 3.68 ppm.

HRMS (ESI-TOF): calc'd for $C_{11}H_{12}BrNO$ $[M+H]^+$: 254.0150, found: 254.0180.

Compound SI-34



***N-cyclopropyl-3-iodo-4-methylbenzamide* (SI-34)**

A reaction flask was charged with 3-iodo-4-methylbenzoic acid (1.3 g, 5.0 mmol, 1.0 equiv.), cyclopropylamine (360 mg, 6.0 mmol, 1.2 equiv.), HOBt (675 mg, 5.0 mmol, 1.0 equiv.) and HATU (2.28 g, 6.0 mmol, 1.2 equiv.). Next, DMF (6.5 mL) was added into the reaction to dissolve the solids, followed by dropwise addition of DIPEA (0.65 mL, 15 mmol, 3.0 equiv.) . Then the reaction was allowed to stir at room temperature for 12 hours. After it is confirmed that the starting material was consumed totally, the reaction mixture was quenched with water (50 mL), extracted with diethyl ether (20 mL × 3), washed by saturated brine (20 mL), dried with Na_2SO_4 and concentrated under high vacuum. The crude residue was purified by column chromatography (hexanes: ethyl acetate, 2:1) on silica gel to obtain 1.08 g (72%) of the desired amide **SI-34**.

Physical State: white solid.

m.p.: 102-104 °C.

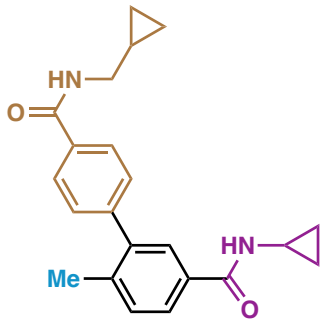
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14 (d, J = 1.9 Hz, 1H), 7.61 (dd, J = 7.9, 1.9 Hz, 1H), 7.26 (d, J = 7.9 Hz, 1H), 6.21 (s, 1H), 2.88 (tq, J = 7.1, 3.6 Hz, 1H), 2.45 (s, 3H), 0.91 – 0.82 (m, 2H), 0.65 – 0.59 (m, 2H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 167.30, 145.33, 137.39, 133.68, 129.79, 126.85, 101.02, 28.28, 23.30, 6.95 ppm.

HRMS (ESI-TOF): calc'd for $C_{11}H_{12}INO$ $[M+H]^+$: 302.0036, found: 302.0043.

TLC: R_f = 0.65 (1:1 hexanes: ethyl acetate).

Compound 116



***N*³-cyclopropyl-*N*⁴′-(cyclopropylmethyl)-6-methyl-[1,1′-biphenyl]-3,4′-dicarboxamide (116)**

A flame-dried screw-capped culture tube was charged with **SI-34** (301 mg, 1.0 mmol, 1.0 equiv.), B_2pin_2 (305 mg, 2.4 mmol, 1.2 equiv.), $PdCl_2$(dppf) (36.6 mg, 0.05 mmol, 0.05 equiv.) and KOAc (295 mg, 3.0 mmol, 3.0 equiv.). Then the tube was evacuated and backfilled with argon three times, followed by addition of DMF (3.0 mL) solvent via a syringe. Next, the reaction was allowed to stir at 95 °C for 3 hours. After it was confirmed that starting materials was totally consumed through TLC analysis and the reaction was cooled to room temperature, **SI-34** (254 mg, 1.0 mmol, 1.0 equiv.) and K_2CO_3 (414.6 mg, 3.0 mmol, 3.0 equiv.) was added into the reaction. the reaction was allowed to stir at 95 °C for another 3 hours. The reaction was quenched with water, extracted with diethyl ether, dried with Na_2SO_4, and concentrated under high vacuum. The reaction crude was then purified by pTLC (hexanes: diethyl ether, 1:1) on silica gel to obtain 35 mg (10%) of the desired coupling product **116**.

*Note: This synthetic route for preparation of **116** was conducted without any further optimization. Previous synthesis of **116** see ref. 16.*

Physical State: white solid.

m.p.: 171-173 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.87 – 7.82 (m, 2H), 7.65 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.58 (d, *J* = 1.9 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.32 (d, *J* = 7.9 Hz, 1H), 6.45 – 6.19 (*br.*, 2H), 3.34 (dd, *J* = 7.3, 5.3 Hz, 2H), 2.90 (tq, *J* = 7.1, 3.6 Hz, 1H), 2.27 (s, 3H), 1.13 – 1.03 (m, 1H), 0.86 (td, *J* = 7.0, 5.2 Hz, 2H), 0.64 – 0.59 (m, 2H), 0.59 – 0.55 (m, 2H), 0.29 (dt, *J* = 6.1, 4.5 Hz, 2H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 168.66, 167.26, 144.29, 141.26, 139.33, 133.70, 132.23, 130.85, 129.45, 128.17, 127.03, 126.23, 45.16, 23.26, 20.59, 10.89, 6.93, 3.67 ppm.

HRMS (ESI-TOF): calc'd for $C_{22}H_{24}N_2O_2$ $[M+H]^+$: 349.1911, found: 349.1916.

TLC: R_f = 0.28 (1:1 hexanes: ethyl acetate).

ADME Protocols of BCP 115 & Arene 116

HT HPLC log D (pH 7) Determination

The high throughput (HT) HPLC log D (pH 7) value was determined by the following method.

The chromatographic system consists of an Agilent 1290 UPLC/DAD system and ChemStation software, both from Agilent Technologies, USA.

The separations are carried out on a Supelco Ascentis Express C18, 30 mm x 3.0 mm I.D., 2.7 μm (Sigma-Aldrich, USA). The mobile phase consists of 10 mM Potassium phosphate buffered at pH 7 (mobile phase A) and acetonitrile (mobile phase B). The column oven temperature is set to 30°C. The HPLC analysis consists of a gradient. The injection cycle time is 1.6 minutes. The injection volume is 2 μL and the spectrophotometric detection is set to 215 and 238 nm.

The chromatographic system is calibrated with a set of standards with published shake-flask log D (pH 7) values. Linear regression is used to determine the calibration line relating the retention time to log D for the calibration standards. This best-fit line is then used to determine the HT HPLC log D (pH 7) value of API (active pharmaceutical ingredient) from its measured retention time by the HPLC/DAD analysis of a solution of the API.

High-Throughput (HT) Solubility Determination

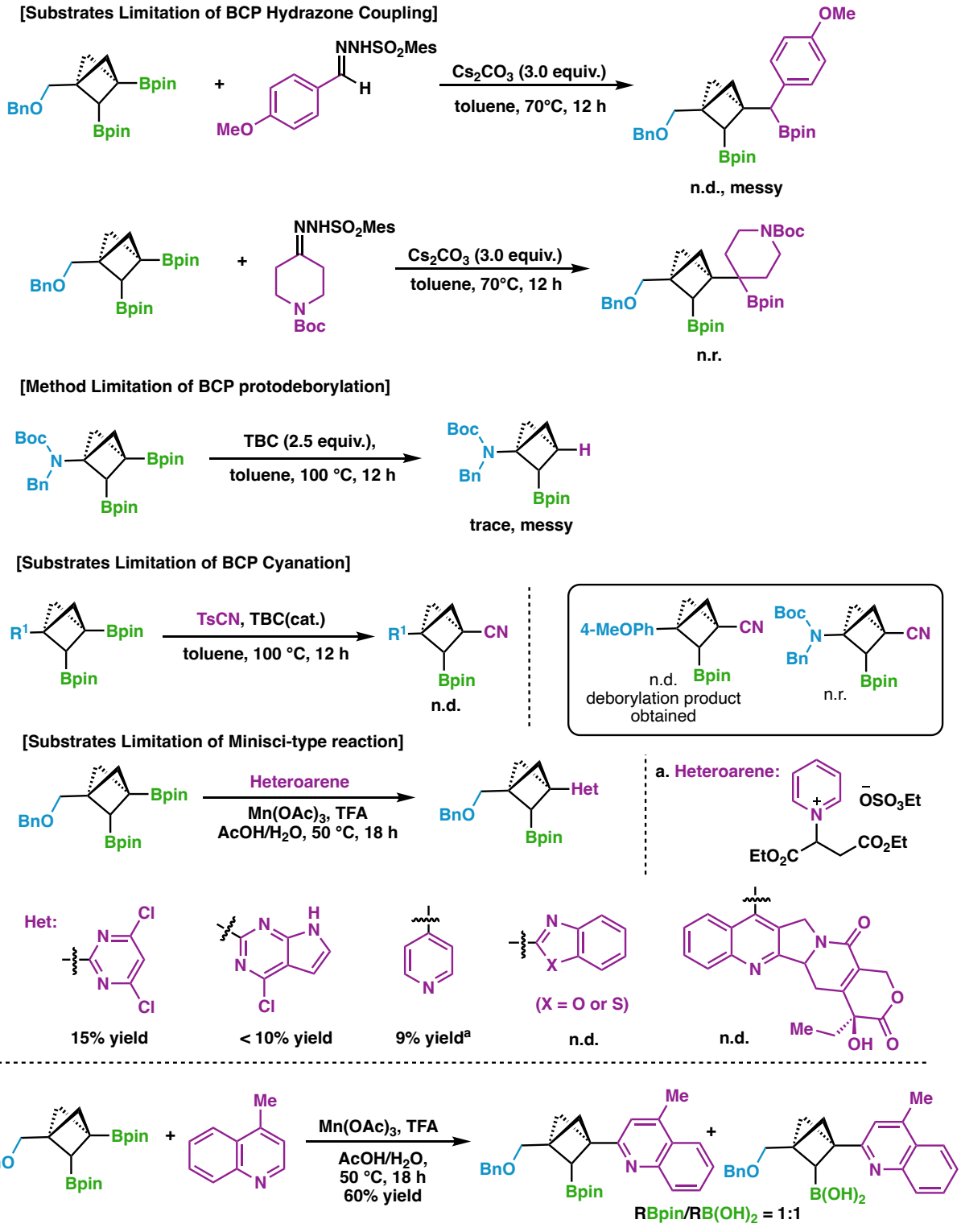
The chromatographic system consists of an Agilent 1290 UPLC/DAD system and ChemStation software, both from Agilent Technologies, USA. The separations are carried out on a Supelco Ascentis Express C18, 30 mm x 3.0 mm I.D., 2.7 μm HPLC column. The mobile phase consists of 10 mM Potassium phosphate buffered at pH 7 (mobile phase A) and acetonitrile (mobile phase B). The column oven temperature is set to 30°C and the UPLC analysis consists of a gradient. The injection volume is 2 μL and the spectrophotometric detection is set to 215 and 238 nm.

A 10 mM stock solution of the compound in DMSO is supplied for analysis. From the DMSO stock solution a single standard solution at 100 μM is created. The solubility solutions are created in phosphate buffered saline (PBS) (pH 7), phosphate buffered saline (PBS) (pH 2), and FaSSIF (pH 6.5). Based on the dilution

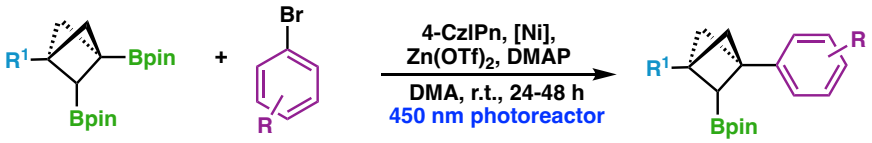
factor that was used to create the solubility solutions, the maximum attainable solubility is about 200 μM. The solubility solutions equilibrate with shaking in a stability chamber for 24 hours at 25°C. The equilibrated solubility solutions are filtered by centrifugation using a filter (0.45 μm, polypropylene). Analysis of the standard solution and the filtered equilibrated solubility solutions occurs by UPLC/DAD. The solubility is calculated based on the ratio of peak area of the sample solution to the standard solution then multiplied by the concentration of the standard solution.

Current Methods and Substrates Limitation of BCP Bisboronates Functionalizations

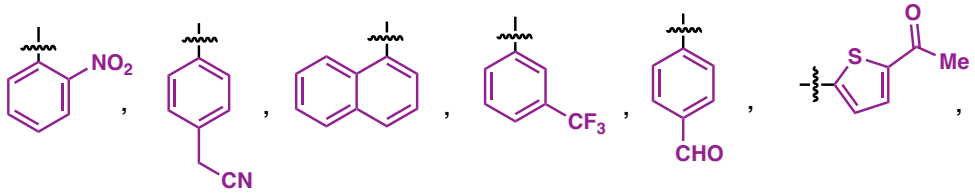
I. Selective C_3-Bpin Functionalization



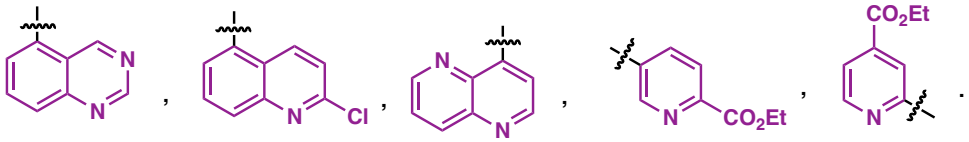
[Substrates Limitation of BCP Cross-Coupling]



R^1 = $CO_2{}^iPr$, Ar:

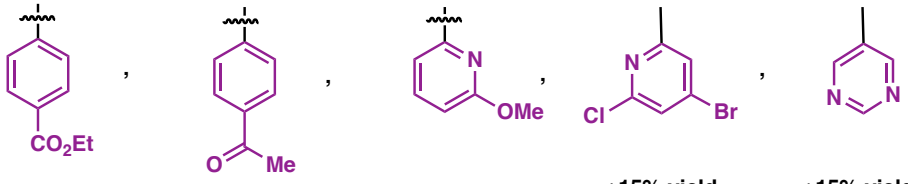


n.d. | n.d. | < 10% yield (crude) | < 10% yield (crude) | < 20% yield (crude) | < 20% yield (crude)



n.d. | n.d. | n.d. | < 15% yield (crude) | < 15% yield (crude)

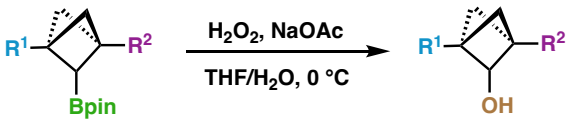
R^1 = Me, Ar:

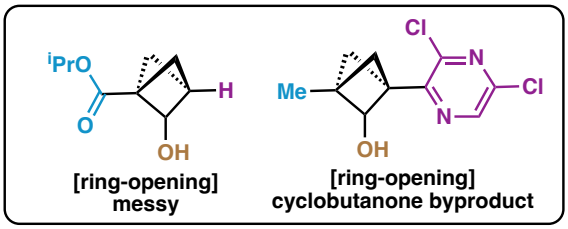


19% yield | 18% yield | n.d. | < 15% yield (crude) | < 15% yield (crude)

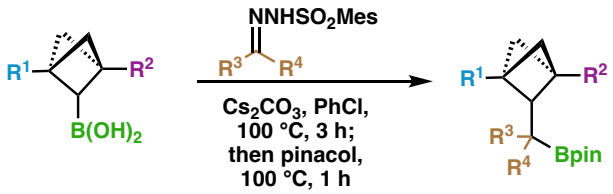
II. Late-stage C_2-Functionalization

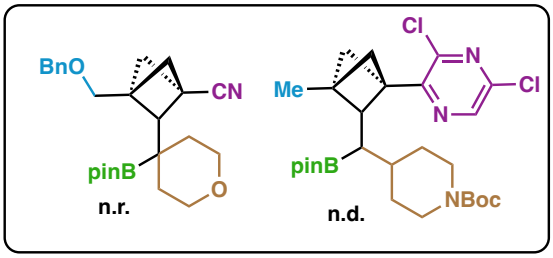
[Substrate Limitation of BCP Oxidation]



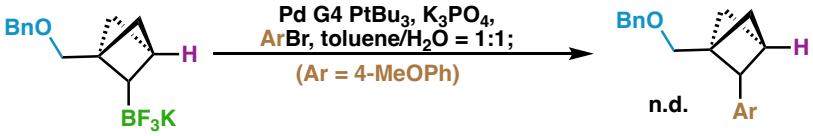


[Substrate Limitation of BCP Hydrazone Coupling]

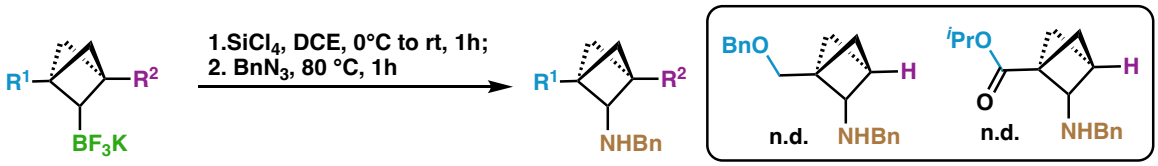


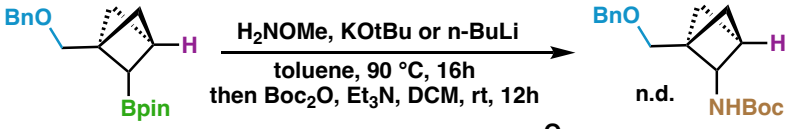


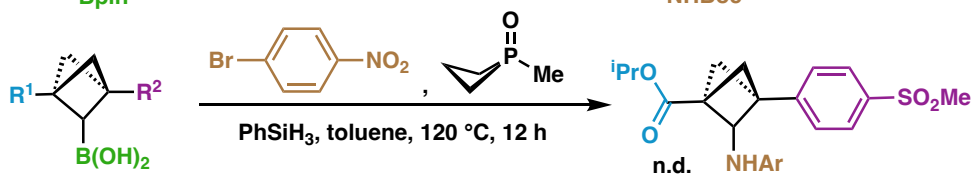
[Method Limitation of BCP C_2-Cross-Coupling]

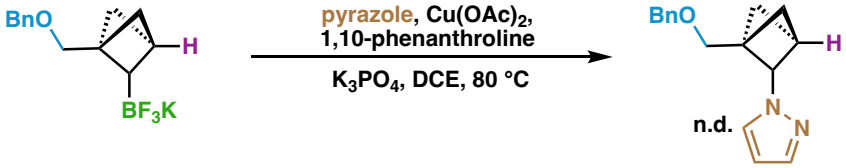


[Method Limitation of BCP Amination]

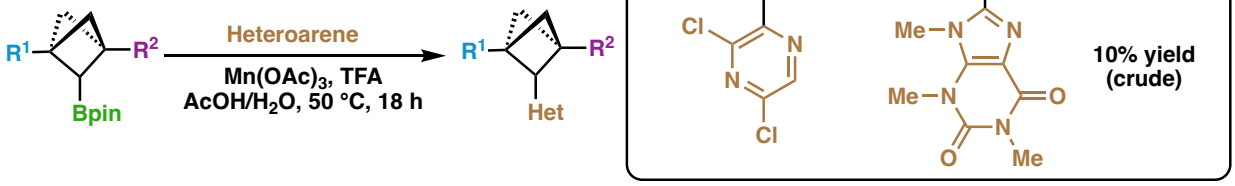




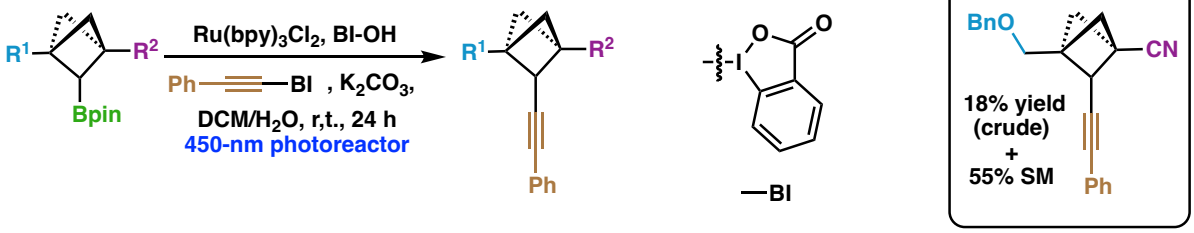




[Substrate Limitation of Minisci-type reaction]

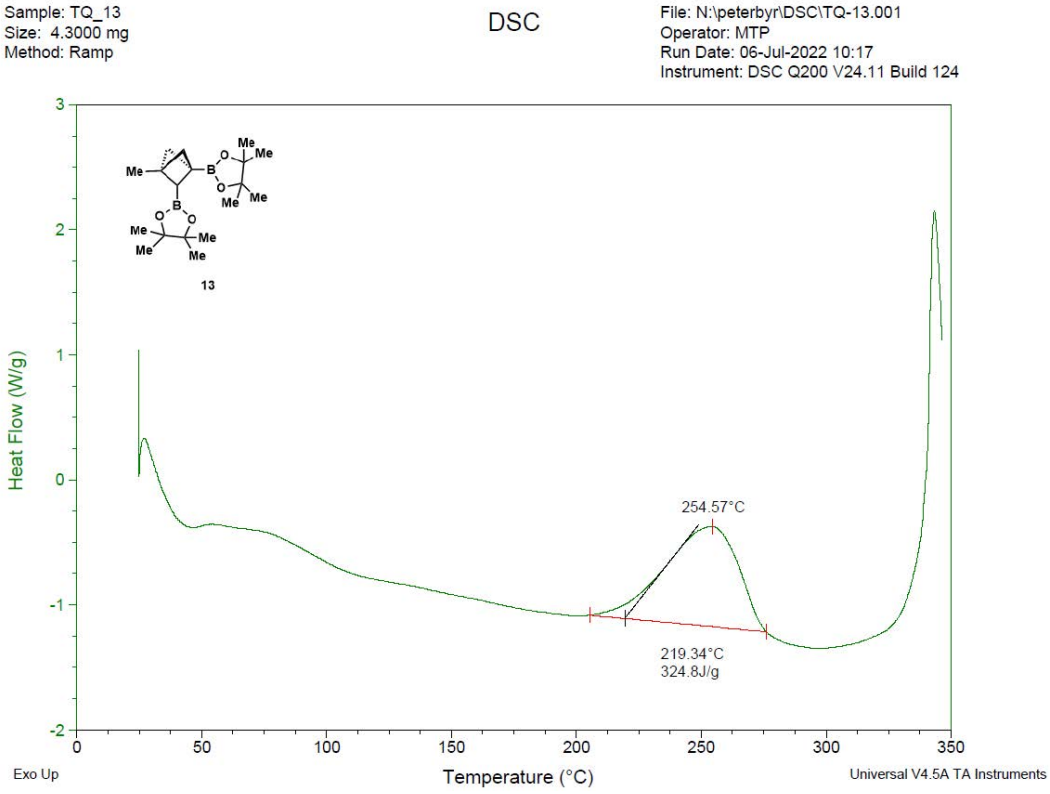


[Substrate Limitation of BCP Alkynylation]

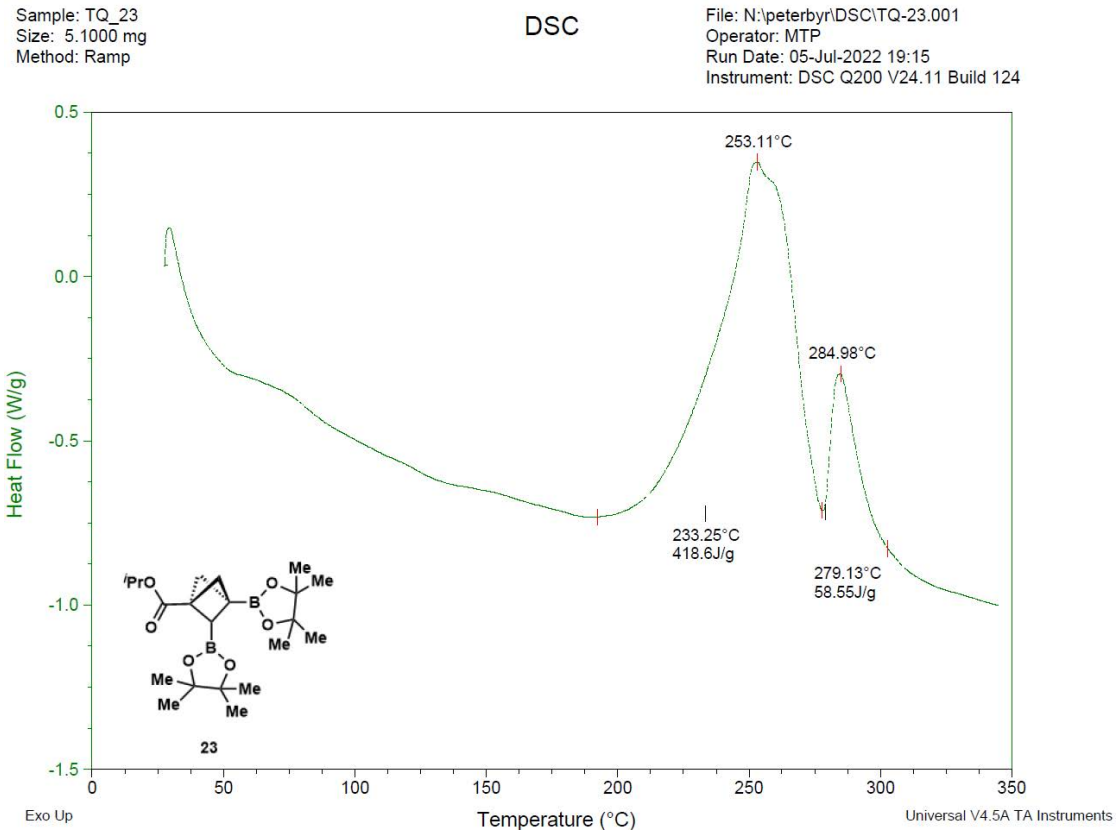


Differential Scanning Calorimetry (DSC) Experiments of Compound 13, 23-26, SI-5, SI-7 & SI-16

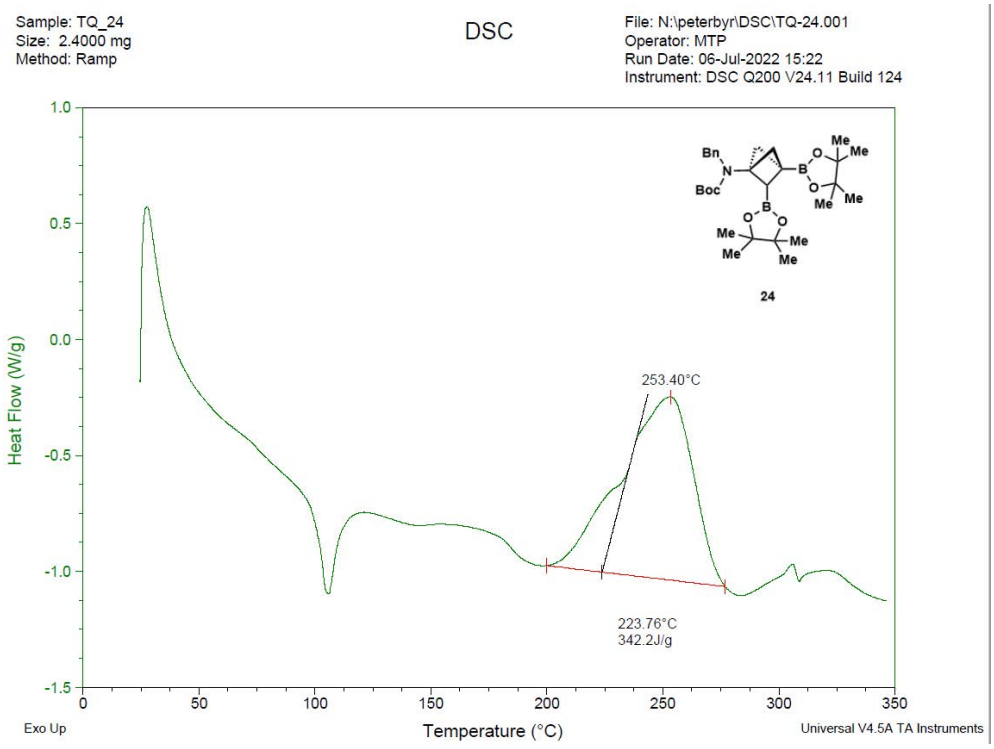
Compound 13



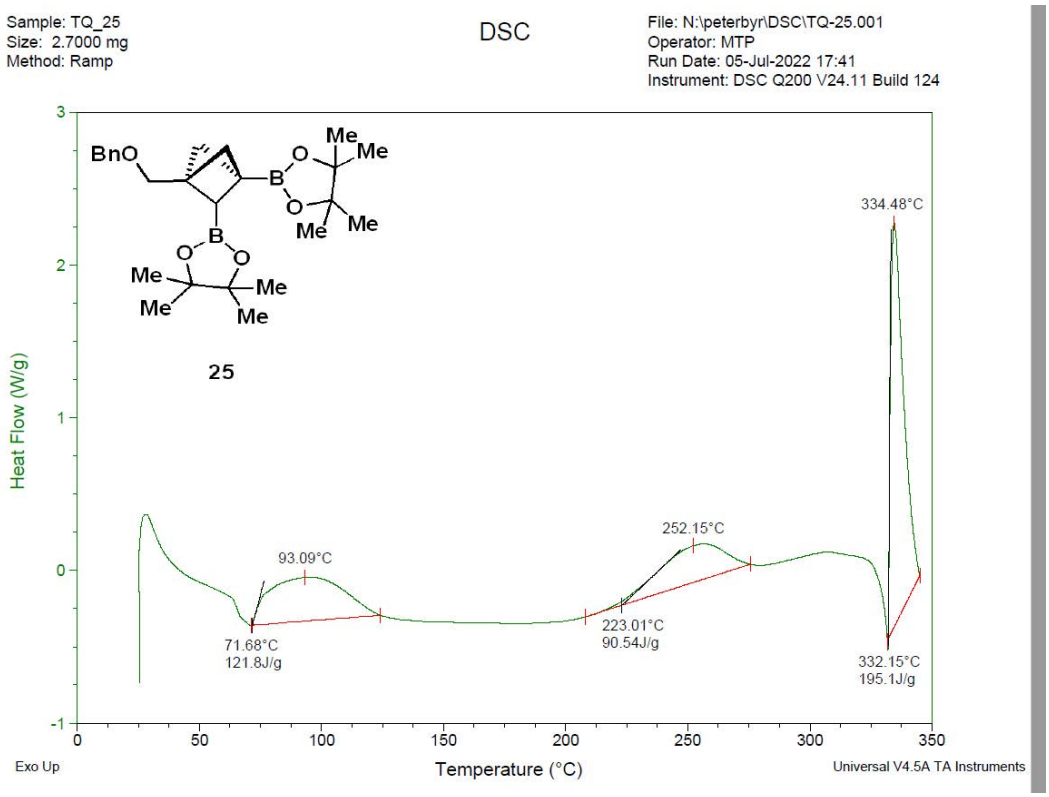
Compound 23



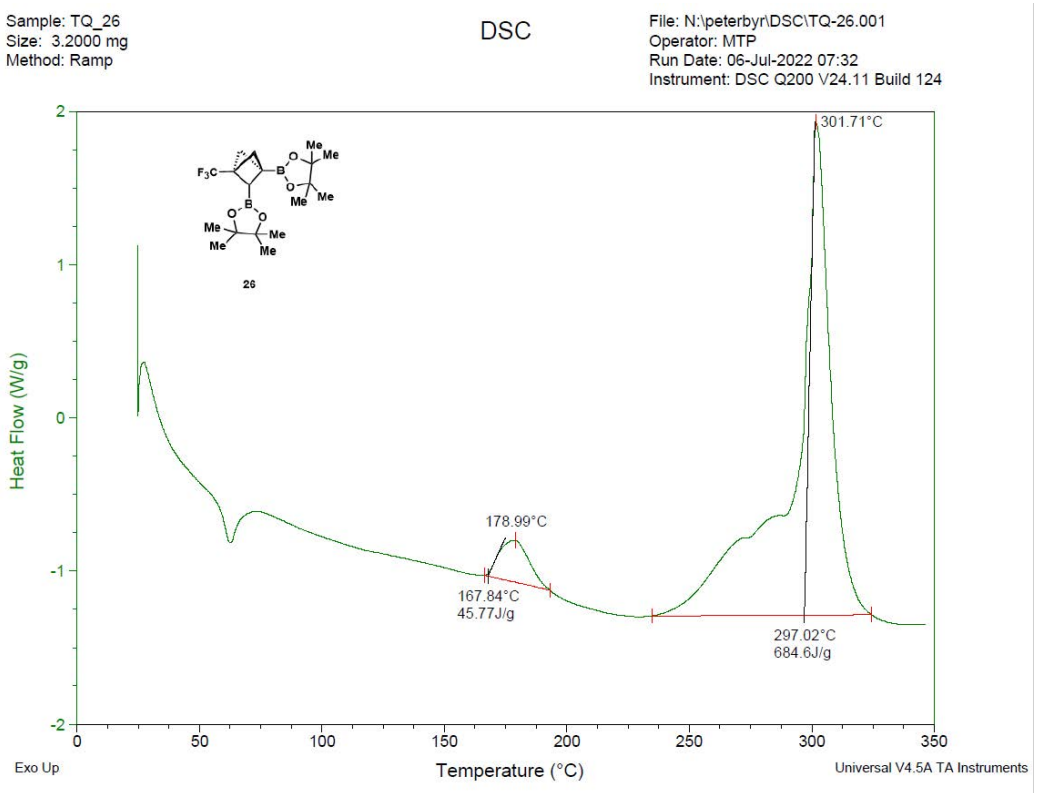
Compound 24



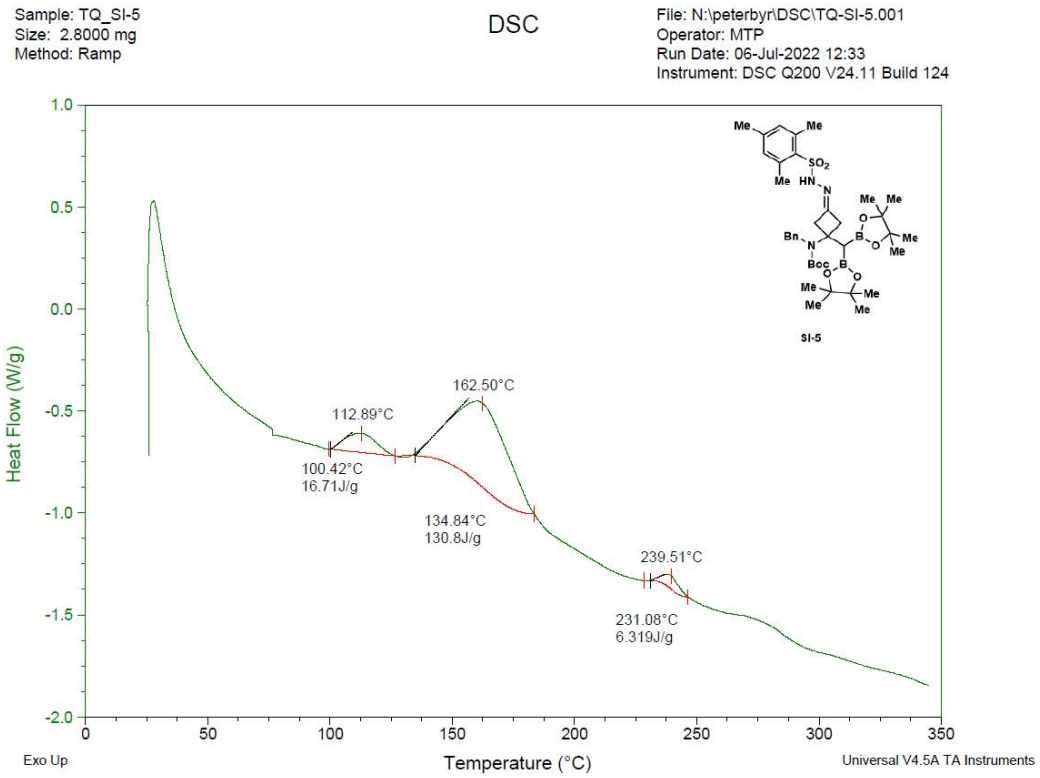
Compound 25



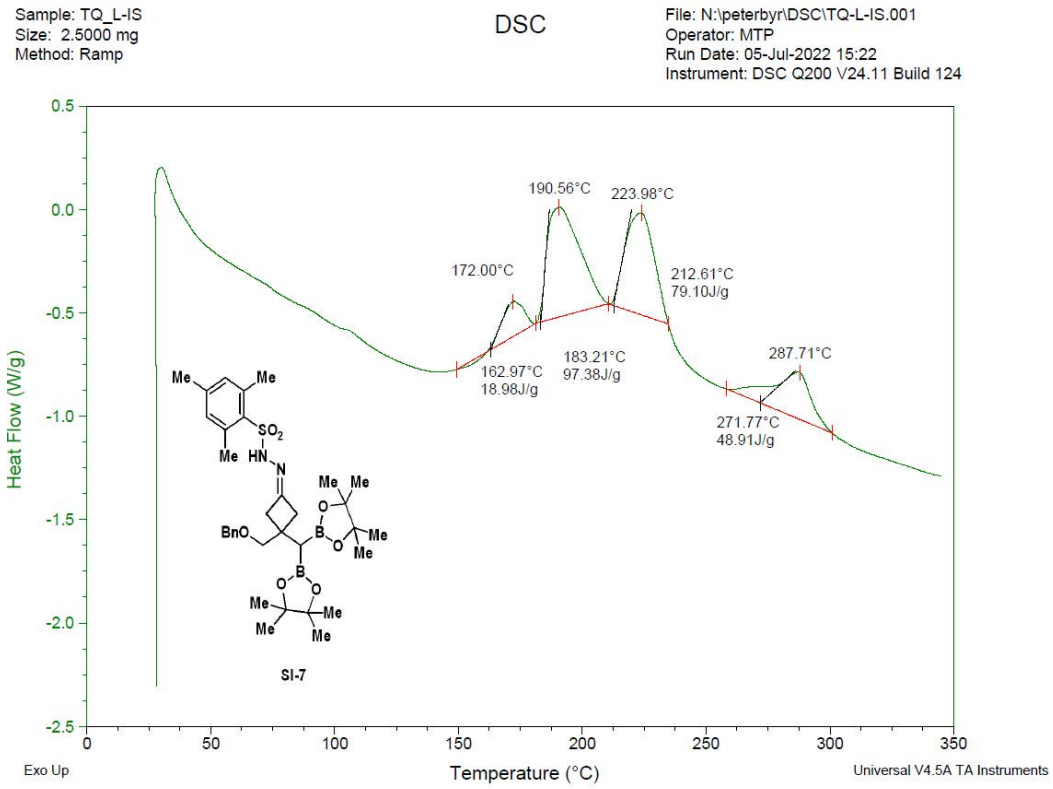
Compound 26



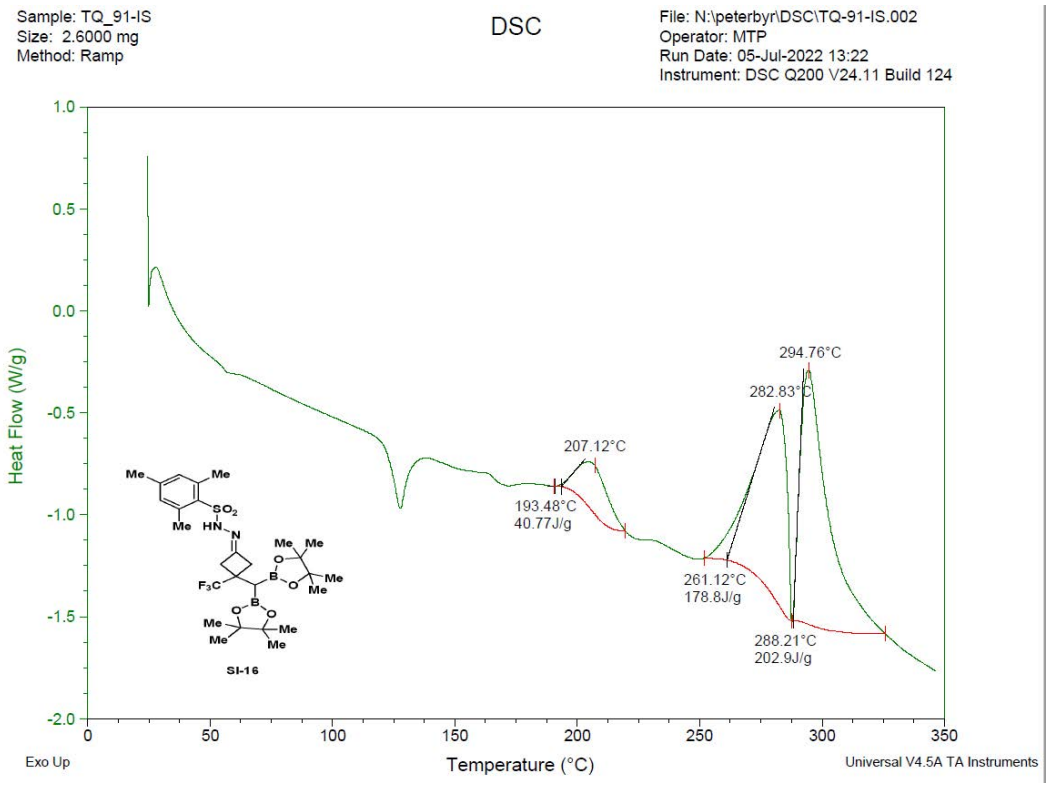
Compound SI-5



Compound SI-7



Compound SI-16



Yoshida Correlations are used to correlate a material's onset temperature (T) and energy (Q) from a DSC experiment to its ability to propagate an explosion and/or be shock sensitive.

- For explosive propagation (EP): $EP = \log (Q_{DSC}) - 0.38 \times \log (T_{DSC} - 25) - 1.67$
- For shock sensitivity (SS): $SS = \log (Q_{DSC}) - 0.72 \times \log (T_{DSC} - 25) - 0.98$

Q_{DSC} = energy of the exotherm in cal/g

T_{DSC} = onset temperature of exotherm in ^{o}C

If EP or SS ≤ 0, then the material is predicted NOT to demonstrate the ability to propagate an explosion or be shock sensitive.

Compound	Exotherm	Q (J/g)	Q (cal/g)	T (°C)	Explosive Propagation (EP)	Shock Sensitivity (SS)
13	1	324.8	77.57715	254	-0.677003678	-0.789347742
23	1	418.6	99.98089	253	-0.566098233	-0.677796081
	2	50.55	12.07366	285	-1.505850927	-1.636941865
24	1	342	81.6853	253	-0.653871351	-0.765569199
25	1	121.8	29.09143	93	-0.902588313	-0.835641344
	2	90.54	21.62511	252	-1.23033155	-1.341380342
	3	195.1	46.59883	334	-0.947809168	-1.104395051
26	1	45.77	10.93198	179	-1.462559176	-1.516316221
	2	684.6	163.5139	301	-0.383990771	-0.523899859
SI-5	1	16.71	3.991115	112	-1.805923081	-1.775359627
	2	130.8	31.24104	162	-0.987228286	-1.023713279
	3	6.319	1.509267	239	-2.376791093	-2.479131776
SI-7	1	18.98	4.533295	172	-1.837166594	-1.884054488
	2	183.21	43.75896	190	-0.871576939	-0.93552148
	3	79.1	18.89271	223	-1.266438504	-1.357304668
	4	48.91	11.68195	287	-1.521439043	-1.653661482
SI-16	1	40.77	9.737747	207	-1.540368631	-1.618792903
	2	178.8	42.70565	282	-0.955289287	-1.084666549
	3	202.9	48.46183	294	-0.907906034	-1.044021809

Conclusion:

All 8 compounds are predicted NOT to demonstrate the ability to propagate an explosion or be shock sensitive based on the DSC data collected.

Reference:

Yoshida, T.; Yoshizawa, F.; Itoh, M.; Matsunaga, T.; Watanabe, M. Prediction of Fire and Explosion Hazard for Reactive Chemicals (I): Estimation of Explosive Properties of Self-Reactive Chemicals from SC-DSC Data. Kogyo Kayaku 1987, 48, 311−316.

X-ray Crystallographic Data for BCP Compounds

Compound 15

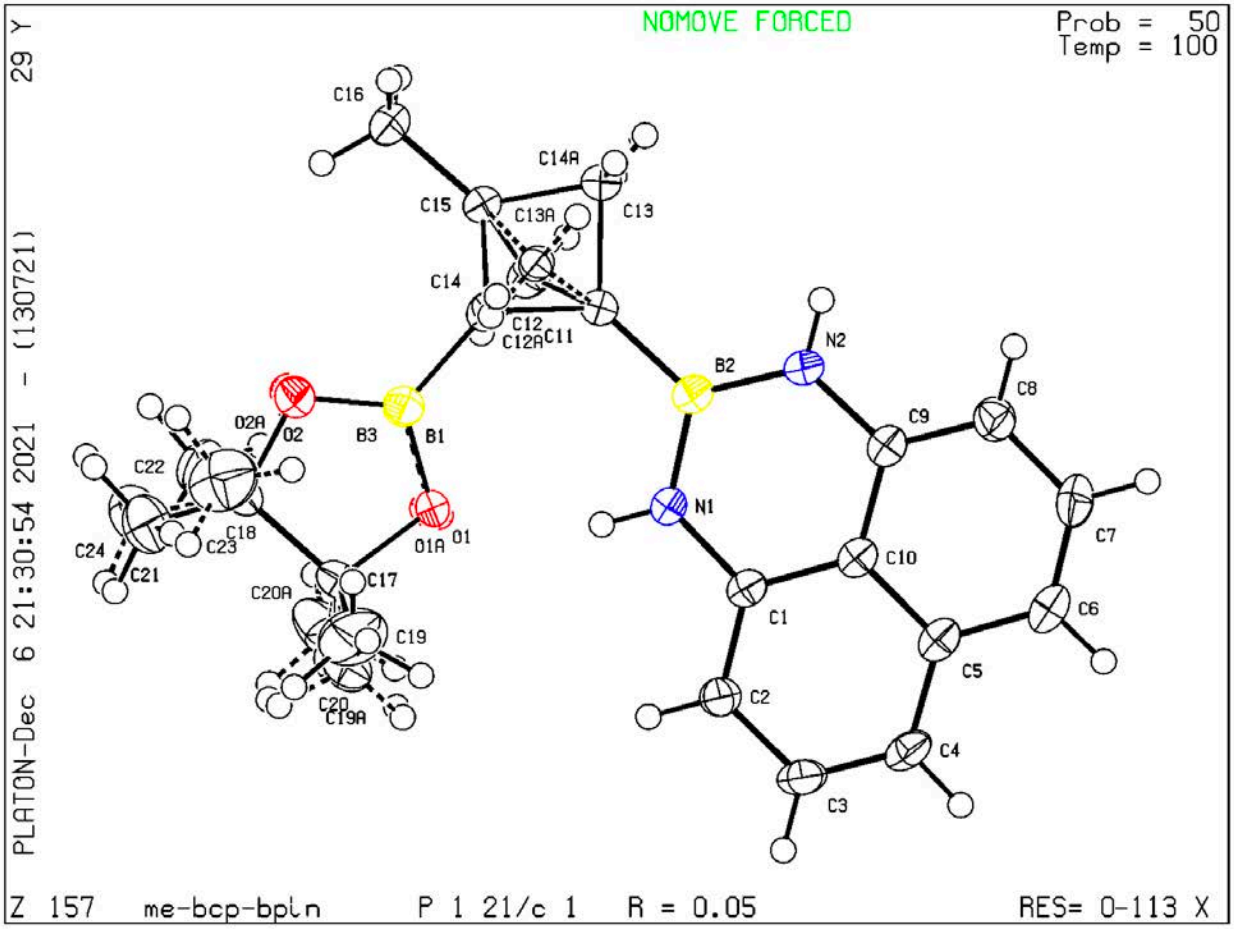


Table S9. Crystal data and structure refinement for compound **15**. CCDC reference number: 2158998.

Empirical formula	C22 H28 B2 N2 O2	
Formula weight	374.08	
Temperature	100.01(11) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 9.47573(16) Å	α= 90°.
	b = 10.73100(19) Å	β= 99.0998(15)°.
	c = 20.9064(3) Å	γ = 90°.
Volume	2099.09(6) Å^3	
Z	4	
Density (calculated)	1.184 Mg/m^3	

Absorption coefficient	0.578 mm^{-1}
F(000)	800
Crystal size	0.41 x 0.25 x 0.14 mm^3
Theta range for data collection	4.283 to 73.370°.
Index ranges	-11<=h<=11, -13<=k<=13, -25<=l<=25
Reflections collected	11994
Independent reflections	4105 [R(int) = 0.0246]
Completeness to theta = 67.684°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.88926
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4105 / 39 / 353
Goodness-of-fit on F^2	1.099
Final R indices [I>2sigma(I)]	R1 = 0.0488, wR2 = 0.1287
R indices (all data)	R1 = 0.0522, wR2 = 0.1316
Extinction coefficient	n/a
Largest diff. peak and hole	0.277 and -0.248 e.$Å^{-3}$

Table S10. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N1	2334(1)	6798(1)	2618(1)	23(1)
N2	560(1)	8336(1)	2763(1)	25(1)
C1	1666(1)	6538(1)	1991(1)	22(1)
C2	2192(2)	5657(1)	1607(1)	28(1)
C3	1505(2)	5457(2)	968(1)	32(1)
C4	311(2)	6112(2)	719(1)	29(1)
C5	-283(2)	7006(1)	1099(1)	25(1)
C6	-1535(2)	7689(1)	860(1)	30(1)
C7	-2060(2)	8547(2)	1246(1)	33(1)
C8	-1374(2)	8783(1)	1882(1)	30(1)
C9	-160(2)	8134(1)	2133(1)	23(1)
C10	406(1)	7222(1)	1746(1)	22(1)
C11	2660(1)	7938(1)	3721(1)	23(1)
C15	3693(2)	8174(1)	4573(1)	27(1)
C16	4506(2)	8338(2)	5246(1)	41(1)
C17	6497(2)	5607(2)	3277(1)	37(1)
C18	7402(2)	5924(1)	3944(1)	29(1)
B2	1829(2)	7697(2)	3025(1)	23(1)
O1	5191(9)	6303(6)	3308(4)	26(1)
O2	6758(2)	7065(2)	4149(1)	30(1)
C12	2818(3)	6979(2)	4288(1)	30(1)
C13	2423(3)	8934(3)	4240(1)	32(1)
C14	4316(2)	8186(2)	3929(1)	27(1)
C19	7124(8)	6387(5)	2732(3)	65(2)
C20	6278(6)	4340(6)	3089(2)	47(1)
C21	8986(3)	6138(3)	3970(2)	50(1)
C22	7186(3)	4929(3)	4438(1)	40(1)
B1	5435(3)	7166(3)	3798(1)	27(1)
O1A	5047(16)	6002(11)	3356(7)	44(3)
O2A	6354(3)	6356(4)	4335(2)	40(1)
C12A	3697(4)	7014(3)	4173(2)	18(1)

C13A	3818(4)	8958(3)	3920(2)	22(1)
C14A	2046(4)	8307(5)	4353(2)	26(1)
C23	8259(7)	7089(6)	3832(3)	61(2)
C24	8383(7)	4979(6)	4307(3)	62(2)
B3	5069(4)	6491(4)	3947(2)	18(1)
C20A	6059(13)	4088(11)	3318(6)	75(3)
C19A	7037(9)	5785(9)	2692(5)	62(2)

Compound 23

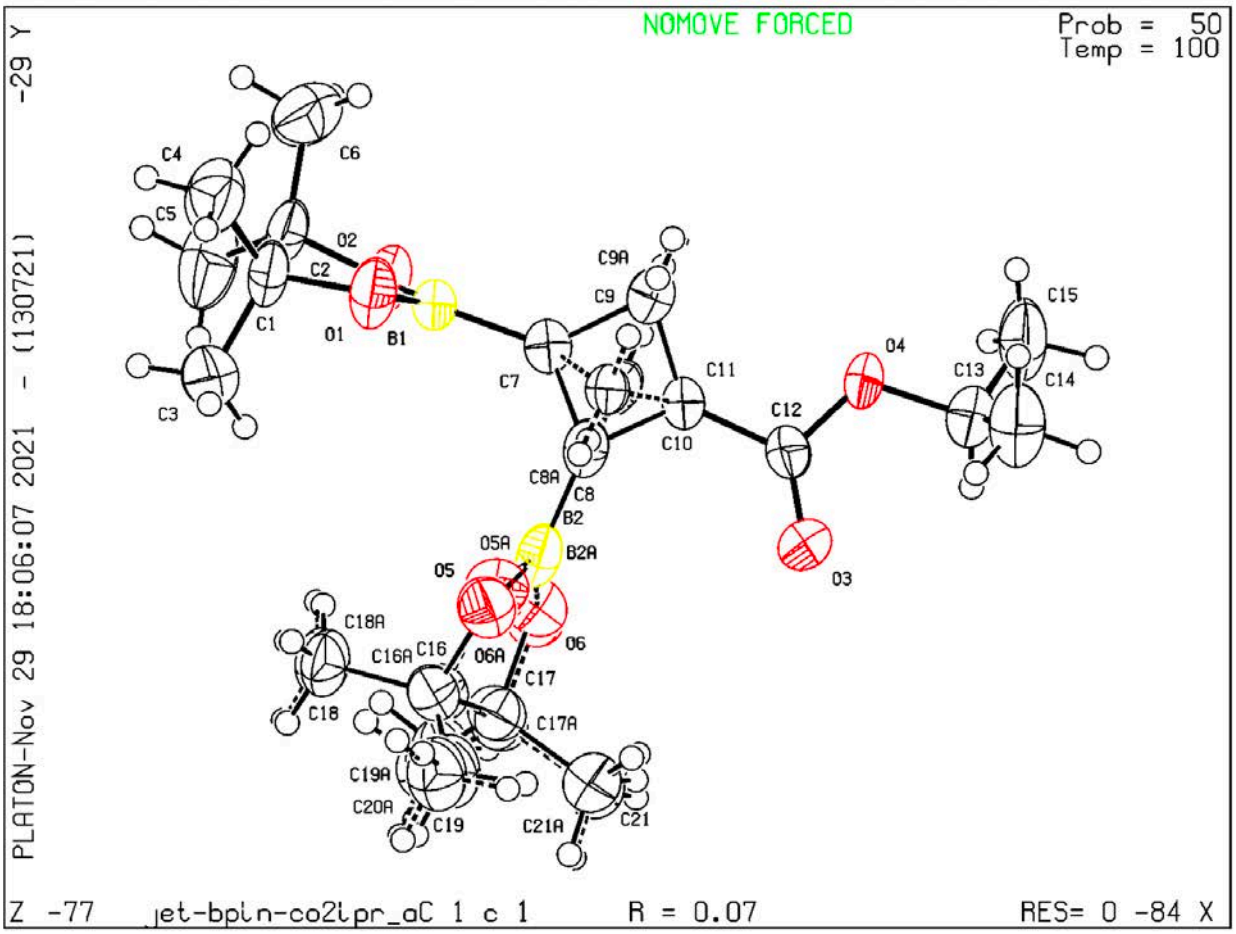


Table S11. Crystal data and structure refinement for compound **23**. CCDC reference number: 2159002.

Empirical formula	C21 H36 B2 O6	
Formula weight	406.12	
Temperature	100.04(15) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	C 1 c 1	
Unit cell dimensions	a = 9.8439(9) Å	α= 90°.
	b = 16.3337(19) Å	β= 90.304(8)°.
	c = 14.8019(9) Å	γ = 90°.
Volume	2379.9(4) $Å^3$	
Z	4	
Density (calculated)	1.133 Mg/m^3	
Absorption coefficient	0.642 mm^{-1}	
F(000)	880	

Crystal size	0.2 x 0.14 x 0.055 mm^3
Theta range for data collection	5.246 to 76.734°.
Index ranges	-9<=h<=12, -20<=k<=20, -18<=l<=9
Reflections collected	6562
Independent reflections	2980 [R(int) = 0.0566]
Completeness to theta = 67.684°	96.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.60810
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2980 / 248 / 340
Goodness-of-fit on F^2	1.064
Final R indices [I>2sigma(I)]	R1 = 0.0707, wR2 = 0.1960
R indices (all data)	R1 = 0.0919, wR2 = 0.2156
Absolute structure parameter	0.3(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.480 and -0.309 $e.Å^{-3}$

Table S12. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
B1	6913(6)	6690(4)	3443(4)	50(1)
C1	6524(6)	7115(4)	2018(4)	61(2)
C2	7739(7)	6534(4)	2026(4)	62(2)
C3	5213(9)	6730(6)	1681(6)	97(3)
C4	6766(10)	7921(4)	1504(6)	86(2)
C5	7704(12)	5842(6)	1336(6)	103(3)
C6	9115(8)	6955(6)	2011(7)	99(3)
C7	6719(6)	6572(4)	4477(4)	56(1)
C11	6433(5)	6374(3)	5719(4)	50(1)
C12	6171(5)	6190(3)	6685(4)	48(1)
C13	7198(7)	6177(4)	8168(4)	67(2)
C14	6572(9)	6857(6)	8659(6)	89(2)
C15	8641(8)	5995(6)	8434(5)	87(2)
O1	6344(5)	7309(3)	2970(3)	68(1)
O2	7629(5)	6158(3)	2923(3)	71(1)
O3	5129(4)	5897(3)	6976(3)	67(1)
O4	7250(4)	6377(3)	7210(2)	58(1)
B2	4240(20)	5903(14)	4737(11)	54(4)
C8	5376(10)	6519(6)	4997(7)	49(2)
C9	7355(15)	6990(9)	5301(10)	56(3)
C10	7097(11)	5697(7)	5038(7)	55(2)
C16	2250(30)	5565(12)	4070(20)	56(4)
C17	2840(30)	4793(11)	4560(20)	58(4)
C18	2420(40)	5536(18)	3090(30)	63(5)
C19	1000(80)	5720(50)	4390(50)	78(7)
C20	2890(50)	4010(20)	4060(30)	67(6)
C21	2220(80)	4640(30)	5490(60)	71(6)
O5	3045(11)	6221(7)	4431(8)	65(3)
O6	4245(12)	5090(9)	4707(8)	66(3)
B2A	4642(16)	5523(16)	4687(9)	38(3)
C8A	6071(11)	5852(7)	4918(8)	45(2)

C9A	7740(12)	6654(9)	5257(9)	39(3)
C10A	5741(11)	7120(7)	5133(7)	42(2)
C16A	2480(30)	5367(17)	4120(30)	56(4)
C17A	2910(40)	4562(15)	4570(30)	58(4)
C18A	2630(50)	5330(20)	3010(40)	63(5)
C19A	850(100)	5800(60)	4290(60)	78(7)
C20A	2700(60)	3850(30)	3950(40)	67(6)
C21A	2300(100)	4460(40)	5510(70)	71(6)
O5A	3596(16)	5969(7)	4450(11)	58(3)
O6A	4362(12)	4694(7)	4703(8)	51(3)

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT340_ALERT_3_B Low Bond Precision on C-C Bonds ..... 0.01013 Ang.

Author Response: There is a considerable amount of disorder in this molecule that contributes to the low bond precision.

Compound 24

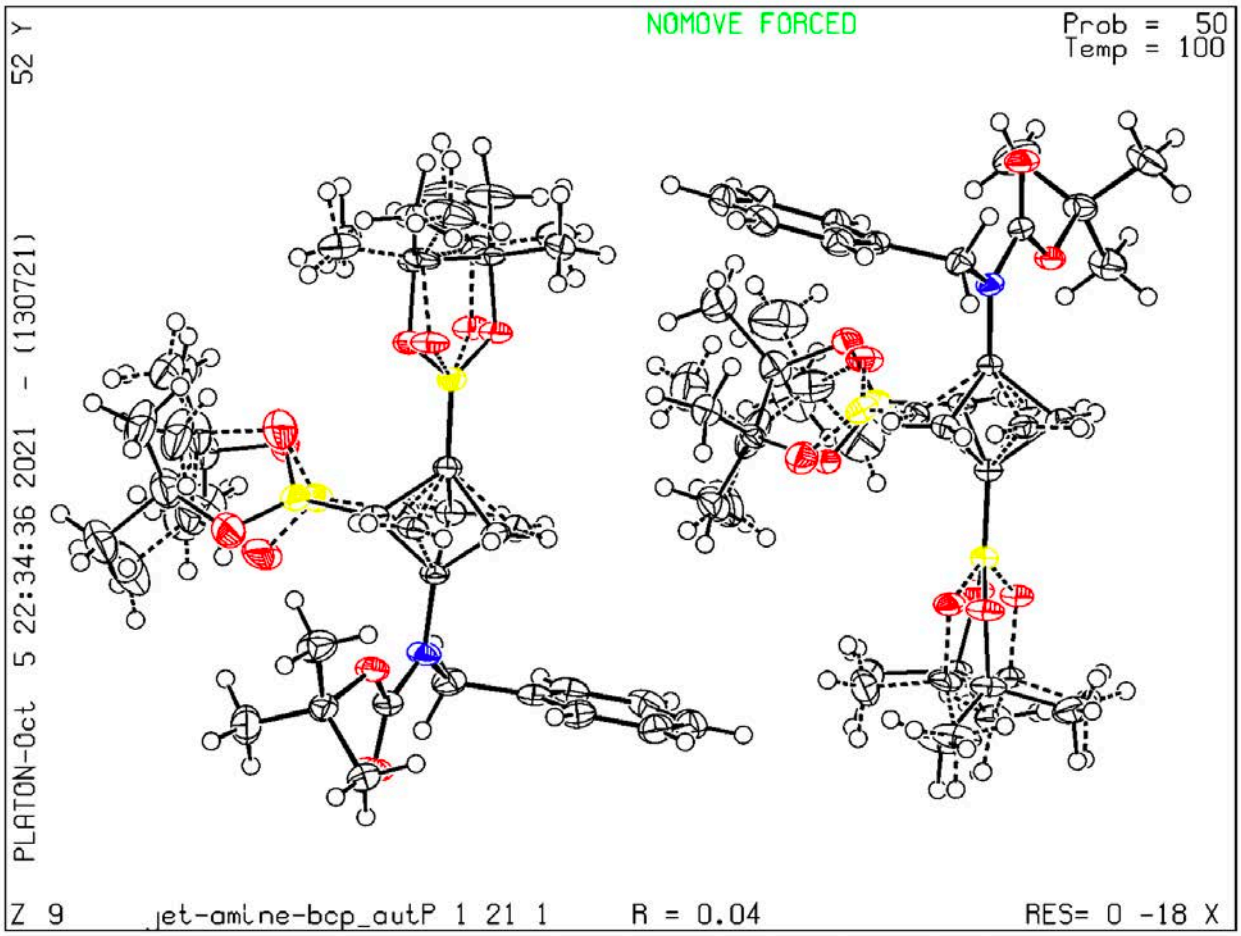


Table S13. Crystal data and structure refinement for compound **24**. CCDC reference number: 2158995.

Empirical formula	C29 H45 B2 N O6	
Formula weight	525.28	
Temperature	100.02(12) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 15.4484(4) Å	α= 90°.
	b = 12.6264(2) Å	β= 102.262(2)°.
	c = 15.9625(4) Å	γ = 90°.
Volume	3042.57(11) $Å^3$	
Z	4	
Density (calculated)	1.147 Mg/m^3	
Absorption coefficient	0.077 mm^{-1}	

F(000)	1136
Crystal size	0.44 x 0.23 x 0.23 mm^3
Theta range for data collection	2.319 to 33.170°.
Index ranges	-22<=h<=22, -18<=k<=18, -22<=l<=23
Reflections collected	64772
Independent reflections	19333 [R(int) = 0.0441]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.65168
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	19333 / 750 / 1059
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0439, wR2 = 0.1030
R indices (all data)	R1 = 0.0606, wR2 = 0.1103
Absolute structure parameter	0.1(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.391 and -0.299 $e.Å^{-3}$

Table S14. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O1	10352(2)	2841(2)	2916(2)	31(1)
O2	8946(2)	2778(1)	2104(2)	29(1)
O3	8091(2)	4755(2)	3193(2)	26(1)
O4	7492(2)	6210(3)	2422(3)	30(1)
O5	9517(1)	8766(1)	1383(1)	32(1)
O6	8949(1)	7198(1)	812(1)	25(1)
N1	9828(1)	7222(1)	2116(1)	22(1)
C1	10119(2)	1714(2)	2827(2)	28(1)
C2	9094(2)	1758(2)	2548(2)	25(1)
C3	10556(3)	1272(3)	2130(3)	41(1)
C4	10458(3)	1172(5)	3668(5)	45(1)
C5	8683(9)	892(12)	1949(11)	32(1)
C6	8635(3)	1828(2)	3299(3)	42(1)
C7	7386(4)	5124(3)	3598(3)	23(1)
C8	6839(2)	5864(3)	2905(2)	32(1)
C9	6901(4)	4167(5)	3853(4)	38(1)
C10	7838(2)	5726(2)	4408(2)	33(1)
C11	6124(2)	5278(4)	2271(2)	61(1)
C12	6464(2)	6836(3)	3263(2)	52(1)
C13	9700(1)	4612(1)	2292(1)	24(1)
C14	8866(1)	5386(2)	1996(1)	21(1)
C15	10078(2)	5427(2)	2985(1)	23(1)
C16	10153(2)	5233(2)	1665(1)	23(1)
C17	9750(1)	6085(1)	2170(1)	19(1)
C18	10416(1)	7770(1)	2811(1)	25(1)
C19	9432(1)	7811(1)	1425(1)	22(1)
C20	8404(1)	7681(2)	44(1)	30(1)
C21	8004(1)	6715(2)	-465(1)	36(1)
C22	8980(2)	8302(2)	-449(1)	42(1)
C23	7689(2)	8365(2)	291(2)	51(1)
C24	9984(1)	8152(1)	3523(1)	24(1)

C25	10527(1)	8404(1)	4319(1)	31(1)
C26	10164(2)	8814(2)	4974(1)	37(1)
C27	9267(2)	8975(2)	4847(1)	40(1)
C28	8720(2)	8720(2)	4063(1)	35(1)
C29	9080(1)	8305(1)	3403(1)	28(1)
B1	9670(1)	3396(1)	2432(1)	24(1)
B2	8150(3)	5467(2)	2552(3)	21(1)
O7	6380(3)	7006(4)	5910(3)	25(1)
O8	6978(3)	7253(4)	7334(3)	28(1)
O9	5077(3)	5694(3)	7748(3)	34(1)
O10	5784(2)	4825(2)	8977(1)	43(1)
O11	6814(1)	1376(1)	8199(1)	40(1)
O12	7517(1)	2951(1)	8526(1)	30(1)
N2	6553(1)	2782(1)	7283(1)	28(1)
C30	6583(3)	8128(5)	6010(3)	22(1)
C31	6700(4)	8299(6)	6989(4)	26(1)
C32	5854(3)	8774(3)	5469(3)	42(1)
C33	7446(3)	8300(2)	5705(2)	33(1)
C34	5849(4)	8542(3)	7278(4)	50(1)
C35	7411(3)	9102(3)	7382(3)	36(1)
C36	4460(3)	5639(3)	8330(2)	38(1)
C37	5052(2)	5390(3)	9201(2)	43(1)
C38	3824(3)	4719(4)	7995(3)	54(1)
C39	3952(7)	6671(8)	8201(4)	45(1)
C40	4636(4)	4716(4)	9794(3)	54(1)
C41	5422(3)	6420(4)	9666(3)	60(1)
C42	6707(1)	5338(1)	6861(1)	22(1)
C43	6628(2)	4847(2)	7754(2)	22(1)
C44	7401(2)	4468(2)	6807(2)	25(1)
C45	5983(2)	4524(2)	6424(2)	26(1)
C46	6651(1)	3895(1)	7112(1)	22(1)
C47	6951(1)	2291(1)	8026(1)	29(1)
C48	7930(1)	2659(2)	9417(1)	31(1)
C49	8447(2)	3657(2)	9741(1)	42(1)
C50	7226(2)	2445(2)	9922(1)	45(1)
C51	8560(1)	1738(2)	9420(1)	36(1)

C52	5951(1)	2167(1)	6638(1)	30(1)
C53	6327(1)	1848(1)	5875(1)	26(1)
C54	5756(1)	1669(1)	5088(1)	31(1)
C55	6078(2)	1342(2)	4384(1)	38(1)
C56	6980(2)	1185(2)	4461(1)	38(1)
C57	7553(1)	1366(2)	5240(1)	35(1)
C58	7230(1)	1698(1)	5945(1)	30(1)
B3	6705(1)	6557(1)	6698(1)	22(1)
B4	5819(2)	5107(2)	8156(2)	26(1)
C64	10622(4)	5357(5)	2396(5)	23(2)
C61	5883(4)	4641(5)	6910(5)	26(2)
C60	7017(5)	4391(5)	6322(5)	29(2)
C59	7219(4)	4730(4)	7676(4)	24(2)
C62	9419(5)	5520(5)	2892(4)	18(1)
C63	9339(5)	5285(5)	1522(4)	23(2)
O2A	9275(5)	2681(4)	1842(4)	25(1)
O1A	10109(6)	2962(5)	3184(5)	29(2)
C1A	9845(7)	1843(6)	3166(5)	34(2)
C3A	10690(11)	1252(17)	3637(17)	45(1)
C4A	9122(9)	1778(8)	3678(7)	46(3)
C5A	10258(8)	1244(9)	1773(8)	36(3)
C6A	8730(30)	910(30)	1940(30)	32(1)
C2A	9531(4)	1629(5)	2193(4)	22(2)
O13	5123(5)	4232(5)	8189(6)	79(3)
B5	5377(5)	4937(6)	7629(6)	31(2)
C66	4503(5)	4784(7)	8608(6)	48(2)
C65	4788(6)	6000(8)	8581(5)	37(2)
C67	4565(13)	4263(15)	9463(10)	87(5)
O17	5299(9)	5962(10)	7925(9)	66(3)
C68	3508(7)	4529(11)	8043(9)	54(1)
C70	4053(18)	6760(20)	8417(13)	45(1)
C69	5501(7)	6219(9)	9289(7)	60(1)
C34A	6336(14)	8615(8)	7642(10)	55(4)
C31A	6931(12)	8373(18)	7043(10)	27(4)
C35A	7718(11)	9116(10)	7146(11)	48(4)
C30A	6439(11)	8265(15)	6116(10)	37(5)

C32A	5578(8)	8855(8)	5832(12)	46(3)
C33A	6992(13)	8346(8)	5452(8)	47(3)
O4A	7731(6)	5977(7)	2387(8)	35(2)
O3A	8127(7)	4883(8)	3512(6)	37(2)
C7A	7175(10)	5105(12)	3466(9)	55(6)
C9A	6720(15)	4097(16)	3619(13)	57(5)
C10A	7184(9)	5937(9)	4169(8)	67(3)
C8A	6902(6)	5538(7)	2539(7)	47(2)
C12A	6216(7)	6372(9)	2418(11)	83(4)
C11A	6671(7)	4632(9)	1881(7)	62(3)
B6	8407(7)	5464(7)	2911(8)	28(2)
O15	7272(8)	7271(11)	7266(10)	29(2)
O14	6172(10)	7084(13)	6065(10)	29(2)

Compound 25

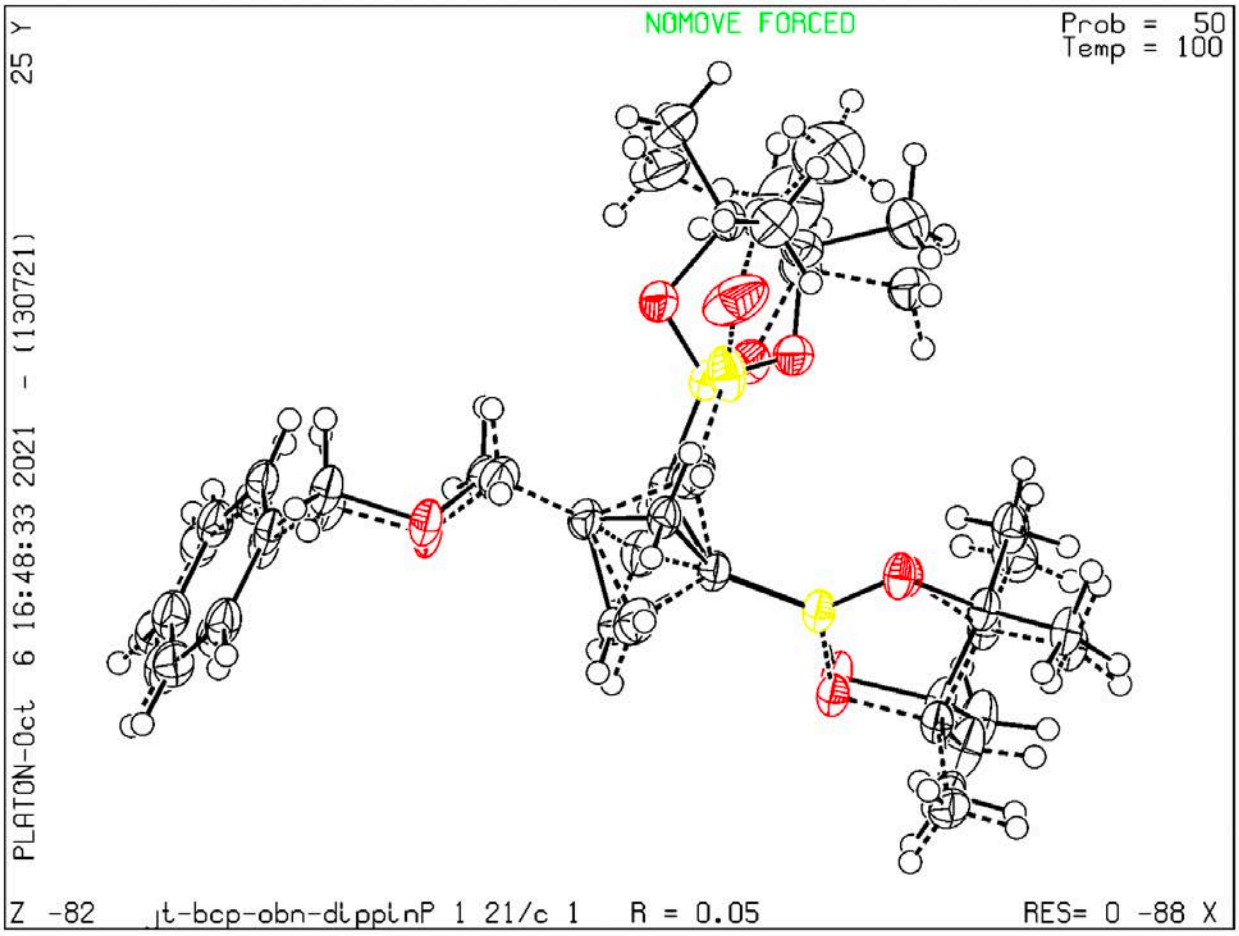


Table S15. Crystal data and structure refinement for compound **25**. CCDC reference number: 2159016.

Empirical formula	C25 H38 B2 O5	
Formula weight	440.17	
Temperature	100.01(11) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 15.7568(3) Å	α= 90°.
	b = 10.60872(17) Å	β= 93.4675(14)°.
	c = 14.8400(2) Å	γ = 90°.
Volume	2476.11(7) $Å^3$	
Z	4	
Density (calculated)	1.181 Mg/m^3	
Absorption coefficient	0.626 mm^{-1}	

F(000)	952
Crystal size	0.392 x 0.202 x 0.111 mm^3
Theta range for data collection	5.029 to 77.049°.
Index ranges	-16<=h<=19, -6<=k<=13, -17<=l<=18
Reflections collected	13236
Independent reflections	4940 [R(int) = 0.0257]
Completeness to theta = 67.684°	98.7 %
Absorption correction	Gaussian and multi-scan
Max. and min. transmission	1.000 and 0.625
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4940 / 849 / 548
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)]	R1 = 0.0501, wR2 = 0.1365
R indices (all data)	R1 = 0.0551, wR2 = 0.1409
Extinction coefficient	n/a
Largest diff. peak and hole	0.351 and -0.277 $e.Å^{-3}$

Table S16. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C8	2188(1)	5284(1)	3754(1)	27(1)
C12	2420(1)	5272(2)	2512(1)	34(1)
B1	1978(1)	5155(1)	4761(1)	27(1)
O1	1239(4)	4665(8)	4995(2)	33(1)
O2	2556(3)	5433(5)	5462(3)	28(1)
O3	3576(1)	2798(2)	4147(1)	36(1)
O4	4083(1)	3623(1)	2869(1)	35(1)
O5	2406(1)	6305(1)	1080(1)	31(1)
C2	2217(4)	4834(4)	6262(3)	27(1)
C3	1246(4)	4766(7)	5980(3)	31(1)
C4	2616(5)	3534(5)	6371(5)	36(1)
C5	2441(6)	5673(8)	7067(5)	30(1)
C6	768(6)	3638(9)	6321(6)	45(2)
C7	773(7)	5981(9)	6188(8)	37(2)
C9	2511(1)	4124(2)	3162(1)	25(1)
C10	2859(1)	6099(2)	3250(1)	27(1)
C11	1566(1)	5580(2)	2910(1)	28(1)
C14	4424(3)	2248(5)	4081(5)	35(1)
C15	4834(2)	3159(3)	3390(2)	31(1)
C16	4256(4)	908(5)	3692(4)	43(1)
C17	4858(2)	2215(3)	5018(2)	50(1)
C18	5412(2)	2525(3)	2760(2)	41(1)
C19	5263(2)	4286(2)	3842(2)	43(1)
C20	2569(1)	5137(2)	1516(1)	31(1)
C21	2493(2)	6233(2)	128(1)	33(1)
C22	1768(2)	5548(2)	-367(2)	30(1)
C23	1806(2)	4249(2)	-521(1)	30(1)
C24	1114(2)	3611(2)	-913(2)	34(1)
C25	378(2)	4266(3)	-1185(2)	38(1)
C26	340(3)	5572(3)	-1068(3)	41(1)
C27	1033(2)	6191(3)	-651(3)	36(1)

B2	3405(2)	3520(3)	3400(2)	26(1)
O1A	1139(6)	4926(8)	4991(6)	27(1)
O2A	2502(7)	5237(11)	5522(6)	27(1)
O3A	3455(5)	2870(9)	3759(5)	52(2)
O4A	4470(5)	4308(6)	3589(5)	66(2)
O5A	2064(5)	5552(8)	1093(4)	35(2)
C2A	2031(8)	4822(11)	6287(7)	27(1)
C3A	1099(8)	4953(11)	5978(7)	27(1)
C4A	2341(15)	3465(14)	6445(13)	54(4)
C5A	2284(12)	5600(20)	7131(11)	30(1)
C6A	549(13)	3840(16)	6238(15)	46(4)
C7A	708(17)	6195(19)	6228(19)	37(3)
C9A	3060(5)	5323(8)	3446(5)	42(2)
C10A	1899(6)	6344(9)	3126(5)	49(2)
C11A	1899(6)	4319(8)	3037(5)	47(2)
C14A	4243(13)	2267(18)	4090(20)	35(1)
C15A	4885(9)	3077(13)	3672(6)	31(1)
C16A	4439(16)	980(30)	3880(19)	77(7)
C17A	4269(7)	2285(11)	5114(5)	59(2)
C18A	5050(8)	2747(12)	2688(9)	56(3)
C19A	5724(7)	3335(15)	4227(9)	92(4)
C20A	2786(8)	5760(14)	1685(7)	38(2)
C21A	2206(9)	5787(14)	135(9)	37(3)
C22A	1538(11)	5224(15)	-399(12)	32(2)
C23A	1495(11)	3944(15)	-580(11)	31(2)
C24A	820(10)	3414(18)	-1036(12)	36(2)
C25A	134(12)	4105(19)	-1321(13)	36(2)
C26A	197(18)	5290(20)	-1153(18)	38(3)
C27A	822(15)	5952(19)	-712(18)	33(2)
B2A	3710(6)	4162(8)	3592(6)	40(2)

Compound 27

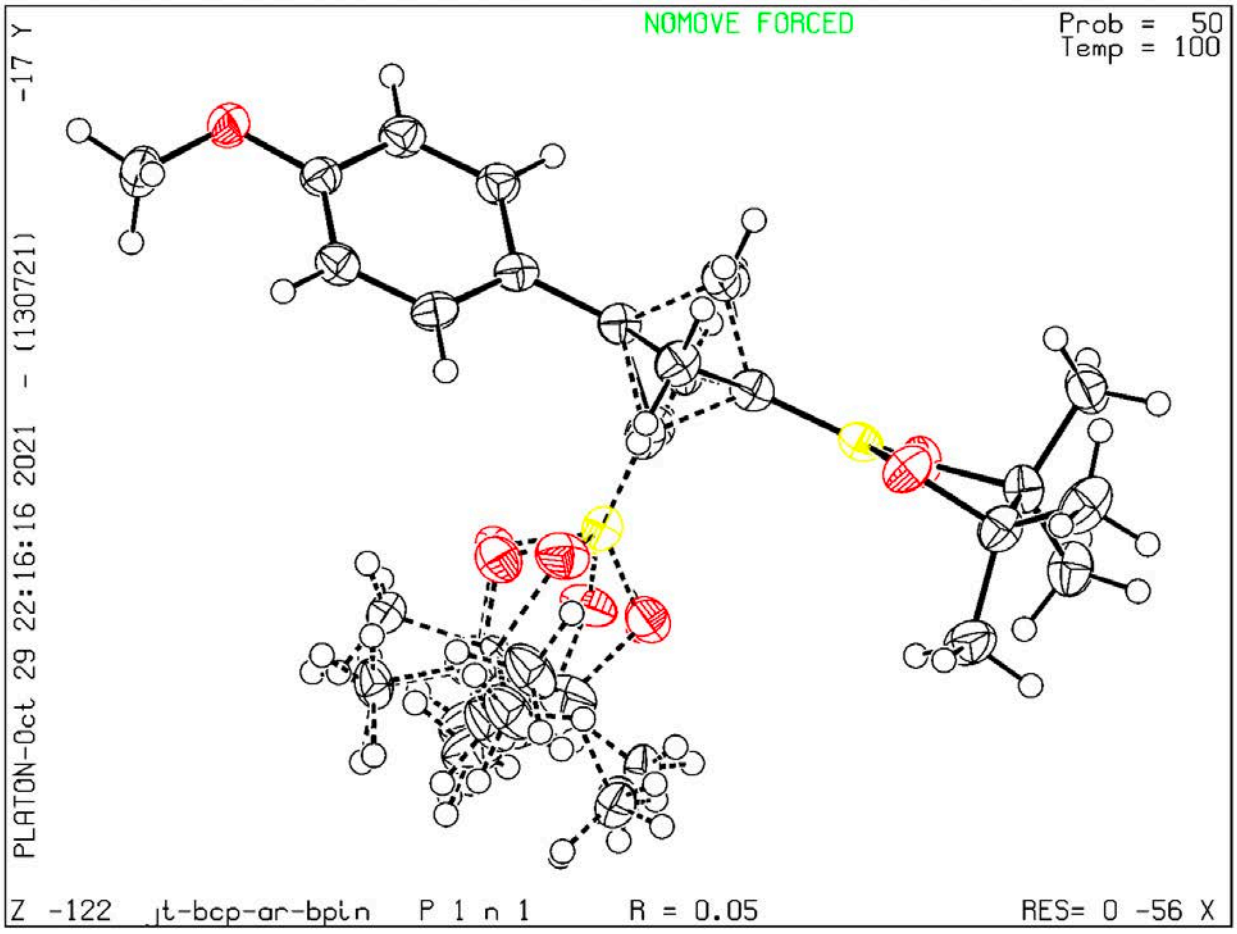


Table S17. Crystal data and structure refinement for compound **27**. CCDC reference number: 2159001.

Empirical formula	C24 H35.99 B2 O5	
Formula weight	426.08	
Temperature	100.01(11) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 1 n 1	
Unit cell dimensions	a = 12.02588(16) Å	α= 90°.
	b = 6.61763(11) Å	β= 93.5949(13)°.
	c = 14.9926(2) Å	γ = 90°.
Volume	1190.81(3) $Å^3$	
Z	2	
Density (calculated)	1.188 Mg/m^3	
Absorption coefficient	0.635 mm^{-1}	

F(000)	460
Crystal size	0.398 x 0.314 x 0.239 mm^3
Theta range for data collection	4.576 to 76.923°.
Index ranges	-11<=h<=15, -7<=k<=8, -18<=l<=18
Reflections collected	11284
Independent reflections	3931 [R(int) = 0.0230]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.37195
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3931 / 466 / 409
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0530, wR2 = 0.1448
R indices (all data)	R1 = 0.0535, wR2 = 0.1454
Absolute structure parameter	0.13(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.676 and -0.388 $e.Å^{-3}$

Table S18. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O1	2501(2)	5819(4)	6840(2)	36(1)
O2	3006(2)	2933(4)	6139(2)	34(1)
O3	9312(2)	11515(4)	4396(2)	36(1)
C1	1577(3)	4393(5)	6916(2)	36(1)
C2	2142(3)	2337(5)	6729(2)	33(1)
C3	1150(4)	4579(7)	7848(3)	48(1)
C4	683(3)	4972(6)	6201(3)	45(1)
C5	2743(3)	1414(6)	7559(2)	42(1)
C6	1387(4)	793(5)	6250(3)	41(1)
C7	4260(3)	6047(5)	5964(2)	31(1)
C11	5534(3)	7416(5)	5559(2)	29(1)
C12	6524(3)	8504(5)	5252(2)	28(1)
C13	7589(3)	7661(5)	5318(2)	32(1)
C14	8497(3)	8700(5)	5037(2)	33(1)
C15	8367(3)	10626(5)	4672(2)	28(1)
C16	7315(3)	11506(5)	4607(2)	32(1)
C17	6406(3)	10442(5)	4894(2)	32(1)
C18	9184(3)	13382(6)	3924(3)	40(1)
B1	3241(3)	4913(6)	6309(2)	30(1)
O4	3406(6)	6690(9)	3540(4)	44(2)
O5	3515(5)	9485(9)	4407(4)	42(2)
C8	4588(4)	6318(6)	4971(3)	29(1)
C9	5521(4)	5534(7)	6195(3)	34(1)
C10	4610(4)	8307(7)	6124(3)	34(1)
C19	2587(7)	8129(12)	3120(5)	30(1)
C20	3028(6)	10189(10)	3514(4)	18(1)
C21	2718(12)	7970(30)	2107(8)	52(3)
C22	1440(8)	7489(18)	3365(8)	43(3)
C23	3958(7)	11150(13)	3033(6)	38(2)
C24	2112(10)	11691(15)	3745(7)	46(2)
B2	3833(13)	7507(19)	4261(8)	25(1)

C8A	4239(14)	8140(30)	5396(10)	32(3)
C9A	5042(15)	5290(30)	5227(11)	29(3)
C10A	5315(15)	6780(30)	6509(11)	29(3)
O5A	4117(8)	9282(19)	3806(8)	52(3)
O6A	2666(7)	7752(16)	4302(6)	42(2)
B2A	3810(18)	7590(30)	4307(12)	25(1)
C20A	3254(14)	9100(20)	2950(9)	68(5)
C23A	3020(20)	7710(40)	2147(14)	52(3)
C24A	3385(15)	11380(20)	2607(10)	35(3)
C19A	2289(11)	9140(20)	3578(10)	64(4)
C21A	1153(12)	8340(30)	3186(12)	39(2)
C22A	2387(15)	11330(20)	4047(9)	46(2)
O6B	2854(8)	6883(14)	3975(6)	32(2)
O5B	3840(9)	10010(15)	3979(7)	47(3)
C19B	2471(8)	8069(15)	3218(6)	30(1)
C20B	2984(10)	10201(12)	3285(6)	18(1)
C21B	1225(8)	8220(30)	3182(11)	39(2)
C22B	2796(15)	7065(18)	2376(6)	52(3)
C23B	3455(15)	10804(18)	2421(7)	35(3)
C24B	2133(15)	11734(18)	3523(10)	46(2)
B2B	3683(9)	8356(17)	4575(5)	25(1)

Compound 33

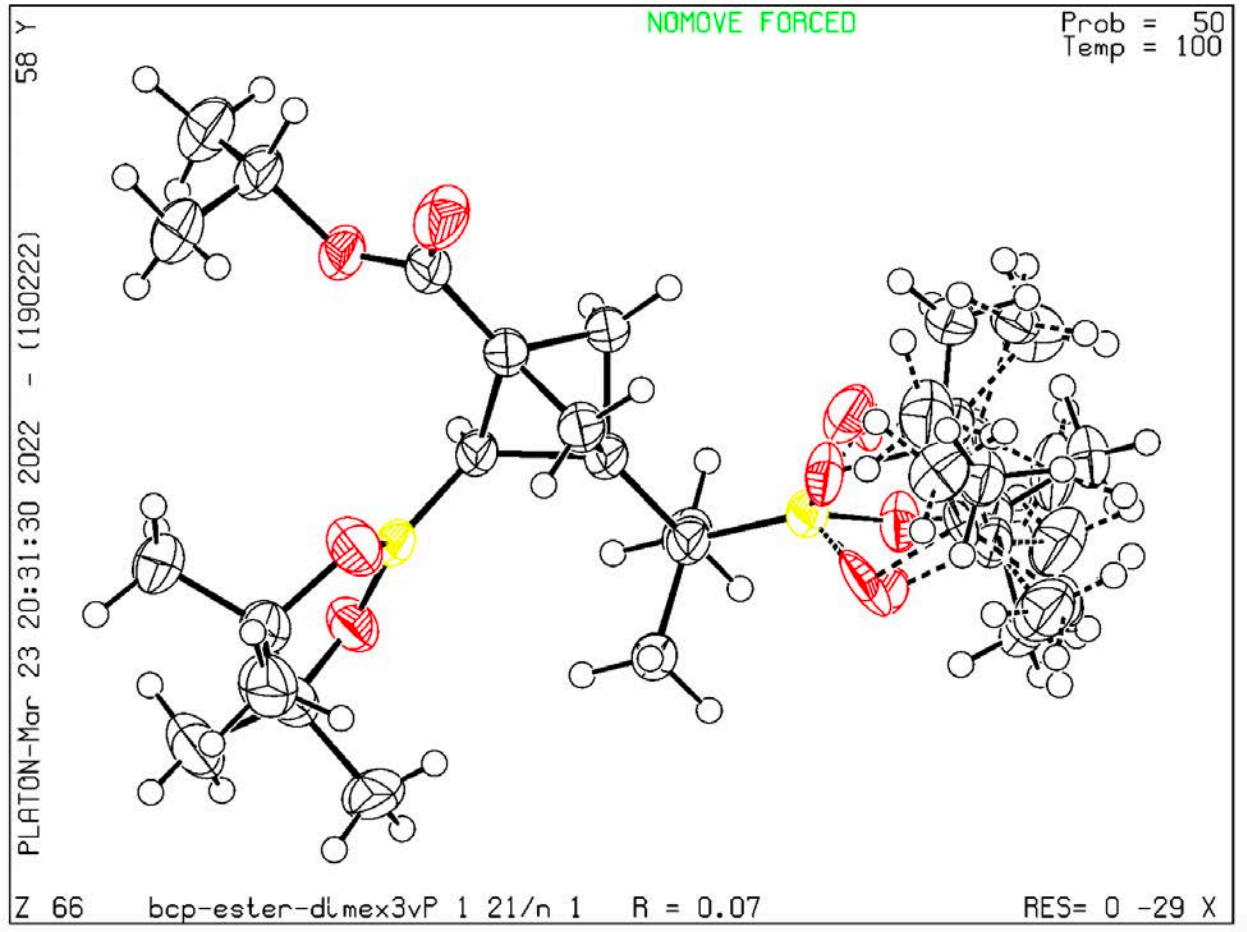


Table S19. Crystal data and structure refinement for compound **33**. CCDC reference number: 2162135.

Empirical formula	C24.04 H42.08 B2 O6.01	
Formula weight	448.92	
Temperature	100.0(3) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 6.1700(2) Å	α= 90°.
	b = 34.5169(12) Å	β= 96.682(3)°.
	c = 12.2637(4) Å	γ = 90°.
Volume	2594.05(15) $Å^3$	
Z	4	
Density (calculated)	1.149 Mg/m^3	
Absorption coefficient	0.632 mm^{-1}	

F(000)	978
Crystal size	0.176 x 0.069 x 0.046 mm^3
Theta range for data collection	3.848 to 68.237°.
Index ranges	-7<=h<=6, -41<=k<=41, -14<=l<=14
Reflections collected	19006
Independent reflections	4632 [R(int) = 0.0688]
Completeness to theta = 67.684°	97.5 %
Absorption correction	Gaussian and multi-scan
Max. and min. transmission	1.000 and 0.842
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4632 / 410 / 438
Goodness-of-fit on F^2	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0684, wR2 = 0.1847
R indices (all data)	R1 = 0.0841, wR2 = 0.1962
Extinction coefficient	n/a
Largest diff. peak and hole	0.548 and -0.201 $e.Å^{-3}$

Table S20. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O1	7417(4)	4281(1)	8063(2)	64(1)
O2	4755(3)	3833(1)	7921(1)	52(1)
O3	8954(3)	3199(1)	6842(2)	54(1)
O4	6576(3)	2844(1)	5692(1)	49(1)
O5	9103(6)	4418(1)	3635(2)	43(1)
O5A	7450(19)	4565(2)	3442(7)	51(2)
O5B	6556(14)	4535(2)	3039(10)	41(3)
O6	6763(5)	4320(1)	2094(2)	40(1)
O6A	8785(15)	4186(2)	2215(6)	41(2)
O6B	9640(16)	4209(2)	2683(14)	60(3)
C1	4502(6)	3881(1)	9089(2)	57(1)
C2	6118(6)	3616(1)	9743(2)	70(1)
C3	2174(6)	3781(1)	9203(3)	70(1)
C4	6308(5)	4048(1)	7529(2)	46(1)
C5	6398(4)	3969(1)	6335(2)	40(1)
C6	5832(4)	3580(1)	5714(2)	37(1)
C7	5125(4)	4187(1)	5356(2)	40(1)
C8	8451(4)	4009(1)	5738(2)	40(1)
C9	6572(4)	3882(1)	4850(2)	37(1)
C10	9463(5)	2796(1)	7120(2)	52(1)
C11	8336(5)	2579(1)	6098(2)	54(1)
C12	11905(5)	2750(1)	7318(3)	61(1)
C13	8430(6)	2705(1)	8151(2)	67(1)
C14	9883(7)	2550(1)	5188(2)	74(1)
C15	7368(6)	2190(1)	6298(3)	66(1)
C16	6685(4)	3812(1)	3629(2)	38(1)
C17	8243(5)	3474(1)	3487(2)	46(1)
C18	4388(4)	3710(1)	3081(2)	46(1)
C19	9320(10)	4763(2)	2965(5)	34(1)
C20	8311(9)	4616(2)	1801(4)	34(1)
C21	11713(14)	4872(3)	3028(7)	42(2)

C22	7936(10)	5083(2)	3400(6)	47(1)
C23	9970(10)	4419(2)	1169(4)	49(1)
C24	7044(13)	4927(2)	1115(7)	45(2)
C25	7330(20)	4626(5)	836(9)	64(3)
C26	9103(17)	4573(3)	1812(8)	34(1)
C27	11390(30)	4597(8)	1514(17)	63(6)
C28	8670(20)	4823(3)	2846(9)	34(1)
C29	7380(30)	5194(5)	2519(16)	66(5)
C30	10720(30)	4886(5)	3641(11)	67(4)
C31	11600(30)	4792(8)	3378(15)	47(5)
C32	11040(30)	4655(6)	1314(16)	37(5)
C33	7742(14)	4797(2)	2368(8)	25(3)
C34	10076(13)	4611(2)	2445(8)	29(3)
C35	7850(30)	5214(5)	2861(16)	35(4)
C36	6590(30)	4786(7)	1172(14)	54(5)
B1	7159(5)	3205(1)	6077(2)	37(1)
B2	7580(4)	4191(1)	3101(2)	36(1)

Compound 55

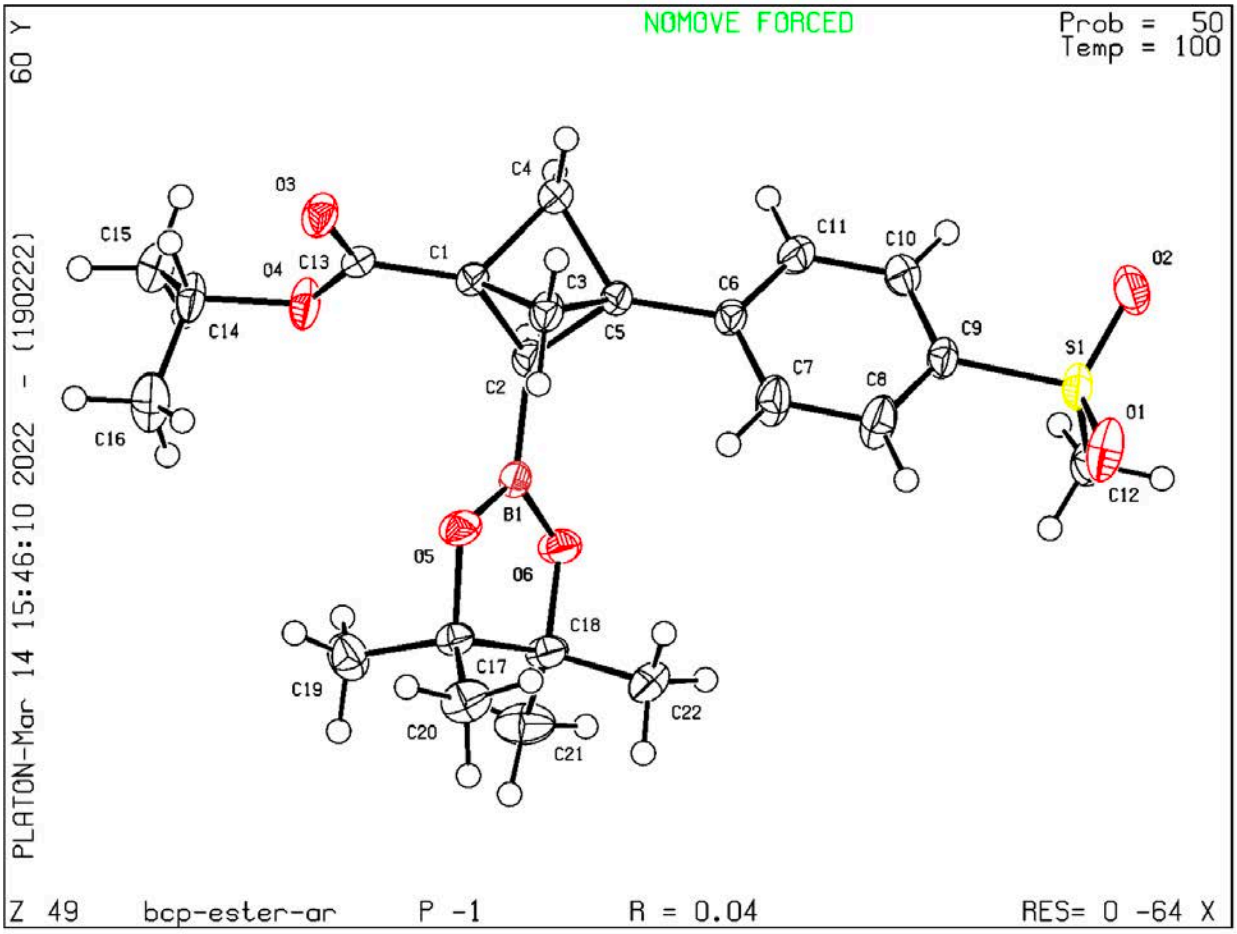


Table S21. Crystal data and structure refinement for compound **55**. CCDC reference number: 2160325.

Empirical formula	C22 H31 B O6 S	
Formula weight	434.34	
Temperature	100.03(12) K	
Wavelength	1.54184 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 5.95874(10) Å	α= 83.5200(10)°.
	b = 9.81535(13) Å	β= 87.3338(11)°.
	c = 20.1087(2) Å	γ = 74.1704(13)°.
Volume	1124.12(3) $Å^3$	
Z	2	
Density (calculated)	1.283 Mg/m^3	
Absorption coefficient	1.572 mm^{-1}	

F(000)	464
Crystal size	0.22 x 0.14 x 0.06 mm^3
Theta range for data collection	2.212 to 77.052°.
Index ranges	-7<=h<=7, -12<=k<=12, -25<=l<=22
Reflections collected	20714
Independent reflections	4625 [R(int) = 0.0315]
Completeness to theta = 67.684°	100.0 %
Absorption correction	Gaussian and multi-scan
Max. and min. transmission	1.00 and 0.498
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4625 / 0 / 278
Goodness-of-fit on F^2	1.068
Final R indices [I>2sigma(I)]	R1 = 0.0433, wR2 = 0.1115
R indices (all data)	R1 = 0.0447, wR2 = 0.1125
Extinction coefficient	n/a
Largest diff. peak and hole	0.600 and -0.306 e.$Å^{-3}$

Table S22. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S1	7203(1)	6990(1)	4245(1)	27(1)
O1	9681(2)	6683(2)	4327(1)	43(1)
O2	6109(3)	8004(1)	3702(1)	40(1)
O3	240(2)	10704(1)	8568(1)	30(1)
O4	-1103(2)	8763(1)	8624(1)	32(1)
O5	4542(2)	6292(1)	8264(1)	28(1)
O6	3320(2)	5097(1)	7506(1)	29(1)
C1	1058(3)	9240(2)	7670(1)	21(1)
C2	1446(3)	7777(2)	7391(1)	22(1)
C3	3568(3)	9267(2)	7421(1)	25(1)
C4	195(3)	9988(2)	6967(1)	28(1)
C5	2414(3)	8775(2)	6839(1)	21(1)
C6	3566(3)	8369(2)	6191(1)	21(1)
C7	5889(3)	7597(2)	6181(1)	34(1)
C8	7016(3)	7181(2)	5591(1)	37(1)
C9	5796(3)	7555(2)	4999(1)	24(1)
C10	3464(4)	8304(2)	4995(1)	38(1)
C11	2359(3)	8709(2)	5594(1)	38(1)
C12	6515(3)	5379(2)	4174(1)	32(1)
C13	41(3)	9667(2)	8331(1)	21(1)
C14	-2092(3)	9008(2)	9295(1)	29(1)
C15	-4497(3)	8810(2)	9296(1)	34(1)
C16	-499(3)	7975(3)	9795(1)	43(1)
C17	5561(3)	4784(2)	8482(1)	22(1)
C18	5277(3)	4056(2)	7851(1)	26(1)
C19	4124(3)	4425(2)	9087(1)	35(1)
C20	8056(3)	4580(2)	8678(1)	33(1)
C21	4586(4)	2668(2)	8000(1)	40(1)
C22	7380(4)	3855(2)	7378(1)	39(1)
B1	3135(3)	6374(2)	7732(1)	22(1)

Compound 59

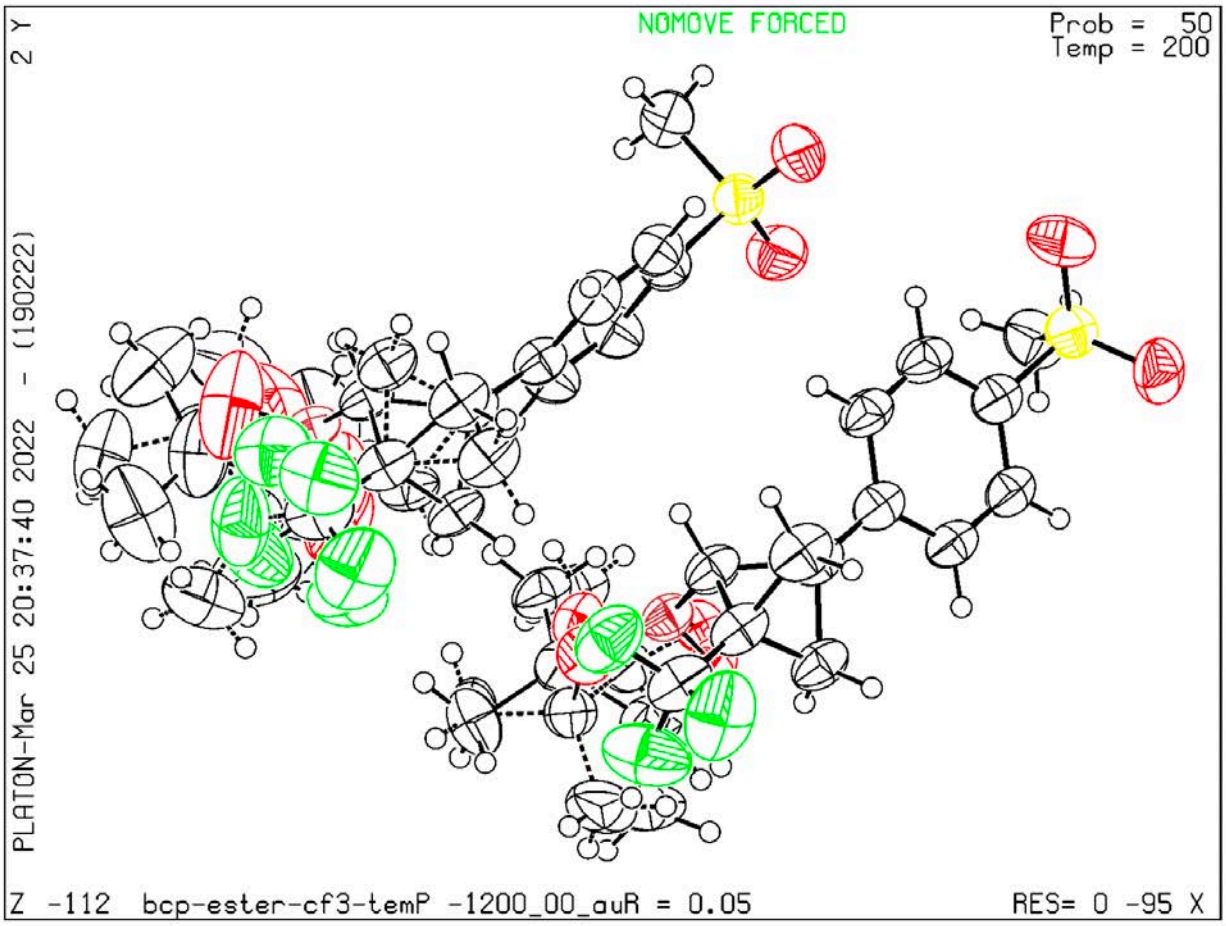


Table S23. Crystal data and structure refinement for **59**. CCDC reference number: 2160336.

Empirical formula	C19 H24 B F3 O4 S	
Formula weight	416.25	
Temperature	200.0(3) K	
Wavelength	1.54184 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.92218(20) Å	α= 78.1946(16)°.
	b = 10.05349(18) Å	β= 81.8000(16)°.
	c = 22.9971(5) Å	γ = 65.9117(18)°.
Volume	2045.46(7) $Å^3$	
Z	4	
Density (calculated)	1.352 Mg/m^3	
Absorption coefficient	1.847 mm^{-1}	
F(000)	872	

Crystal size	0.25 x 0.19 x 0.15 mm^3
Theta range for data collection	3.936 to 76.943°.
Index ranges	-12<=h<=12, -11<=k<=12, -27<=l<=28
Reflections collected	23689
Independent reflections	8231 [R(int) = 0.0209]
Completeness to theta = 67.684°	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 and 0.85389
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8231 / 324 / 729
Goodness-of-fit on F^2	1.077
Final R indices [I>2sigma(I)]	R1 = 0.0548, wR2 = 0.1596
R indices (all data)	R1 = 0.0603, wR2 = 0.1649
Extinction coefficient	n/a
Largest diff. peak and hole	0.498 and -0.445 $e.Å^{-3}$

Table S24. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
S1	4473(1)	1404(1)	6014(1)	61(1)
F1	1504(2)	8302(2)	2211(1)	100(1)
F2	89(3)	7228(2)	2184(1)	123(1)
F3	-603(2)	8982(2)	2672(1)	130(1)
O1	3271(2)	1447(2)	6446(1)	81(1)
O2	5603(2)	1788(2)	6167(1)	87(1)
O3	2333(4)	2953(5)	2956(2)	58(1)
O4	3544(4)	3995(4)	2208(2)	61(1)
C1	3744(2)	2567(2)	5355(1)	56(1)
C2	4542(2)	3310(2)	4991(1)	62(1)
C3	3965(2)	4216(2)	4476(1)	61(1)
C4	2582(2)	4407(2)	4311(1)	54(1)
C5	1801(2)	3645(2)	4683(1)	56(1)
C6	2371(2)	2722(2)	5199(1)	56(1)
C7	1972(2)	5420(2)	3763(1)	55(1)
C8	2691(2)	5349(2)	3109(1)	58(1)
C9	455(2)	5792(2)	3509(1)	63(1)
C10	1589(3)	7115(2)	3633(1)	71(1)
C11	1191(2)	6753(2)	3080(1)	61(1)
C12	556(3)	7806(2)	2547(1)	73(1)
C13	5314(3)	-371(3)	5825(1)	75(1)
C14	2344(5)	2359(4)	2420(2)	56(1)
C15	3602(5)	2664(4)	2020(2)	55(1)
C16	820(7)	3286(10)	2190(4)	101(3)
C17	2640(17)	712(17)	2579(6)	78(3)
C18	3350(18)	3105(19)	1350(5)	86(3)
C19	5117(7)	1474(8)	2137(3)	70(2)
B1	2873(2)	4091(2)	2756(1)	54(1)
S2	8667(1)	1695(1)	4316(1)	60(1)
F4	5655(9)	7502(9)	315(3)	111(2)
F5	6316(8)	8949(7)	617(2)	111(2)

F6	4091(6)	9094(7)	819(4)	132(2)
O5	8082(2)	567(2)	4450(1)	80(1)
O6	8493(2)	2564(2)	4765(1)	77(1)
O7	7482(9)	3356(8)	1138(3)	122(2)
O8	8957(10)	4247(8)	632(3)	150(3)
C20	7909(2)	2900(2)	3665(1)	55(1)
C21	7645(2)	4380(2)	3607(1)	58(1)
C22	7163(2)	5310(2)	3080(1)	59(1)
C23	6956(2)	4776(2)	2604(1)	53(1)
C24	7198(3)	3285(2)	2674(1)	62(1)
C25	7665(3)	2347(2)	3202(1)	64(1)
C26	6510(2)	5777(2)	2034(1)	54(1)
C27	7461(3)	5717(3)	1425(2)	50(1)
C28	5143(4)	6094(4)	1670(2)	59(1)
C29	6083(5)	7464(4)	1924(2)	64(1)
C30	5935(2)	7093(2)	1329(1)	62(1)
C31	5467(3)	8161(3)	777(2)	83(1)
C32	10569(3)	877(3)	4108(1)	71(1)
C33	8417(7)	2174(5)	778(2)	81(1)
C34	8990(11)	3107(10)	352(4)	118(3)
C35	7512(12)	1650(12)	444(5)	143(3)
C36	9284(12)	1000(7)	1239(4)	154(3)
C37	8387(14)	3893(11)	-192(4)	166(4)
C38	10764(8)	2315(10)	316(5)	147(3)
B2	7970(6)	4406(5)	1064(2)	54(1)
O9	2992(7)	2757(7)	2972(3)	55(1)
O10	2863(8)	4477(7)	2151(3)	69(2)
C40	2674(8)	3266(7)	1953(3)	64(2)
C44	3298(8)	1984(6)	2453(3)	56(1)
C43	4969(12)	1185(13)	2388(5)	67(2)
C41	1025(12)	3761(19)	1888(6)	109(5)
C39	2490(30)	960(30)	2589(9)	75(4)
C42	3540(30)	2920(30)	1361(9)	95(6)
C28A	7409(6)	6642(6)	1605(3)	68(1)
C27A	6052(7)	5493(6)	1466(3)	64(1)
C29A	5169(7)	7296(6)	1968(3)	74(2)

B2A	7216(9)	4316(9)	1081(3)	62(2)
O12	6978(10)	3247(12)	1028(5)	126(3)
O11	8774(13)	4077(13)	869(5)	137(3)
C45	9360(10)	2767(11)	494(4)	83(2)
CN	7865(10)	2702(10)	519(4)	91(2)
C49	10510(12)	1456(10)	815(5)	118(3)
C46	6871(13)	3633(13)	-1(5)	135(3)
C48	9744(14)	3017(12)	-231(4)	125(3)
C47	7947(18)	1072(12)	749(6)	132(4)
F5A	5402(19)	9505(8)	813(5)	109(3)
F4A	6090(20)	7730(20)	286(7)	129(6)
F6A	3993(11)	8498(15)	721(6)	110(3)

Compound 76

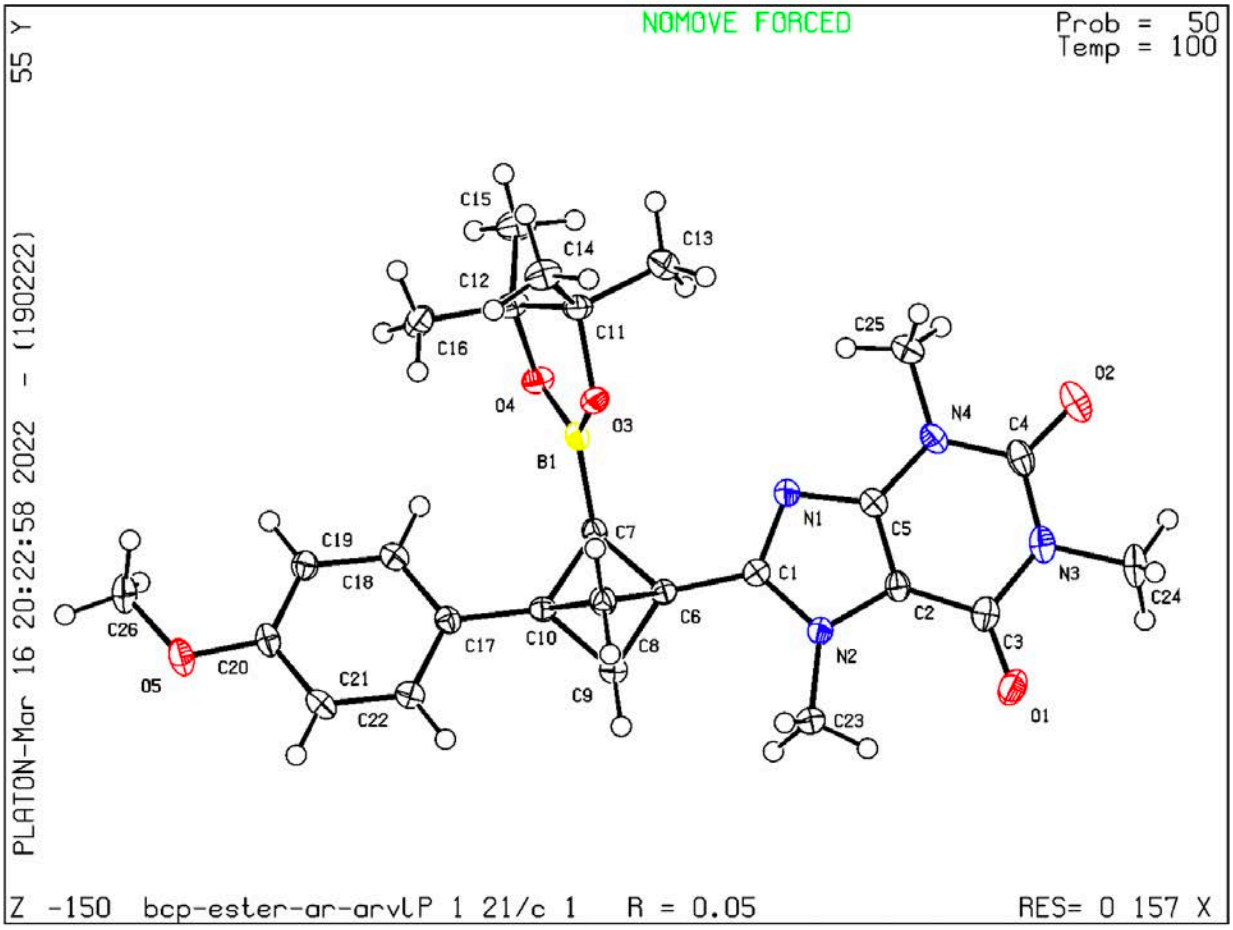


Table S25. Crystal data and structure refinement for compound **76**. CCDC reference number: 2162136.

Empirical formula	C26 H33 B N4 O5	
Formula weight	492.37	
Temperature	100.03(13) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 11.5499(3) Å	α= 90°.
	b = 18.6825(4) Å	β= 98.064(2)°.
	c = 11.5251(3) Å	γ = 90°.
Volume	2462.30(10) $Å^3$	
Z	4	
Density (calculated)	1.328 Mg/m^3	
Absorption coefficient	0.749 mm^{-1}	

F(000)	1048
Crystal size	0.42 x 0.09 x 0.043 mm^3
Theta range for data collection	3.865 to 77.027°.
Index ranges	-14<=h<=14, -23<=k<=23, -14<=l<=14
Reflections collected	5008
Independent reflections	5008 [R(int) = ?]
Completeness to theta = 67.684°	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.56923
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5008 / 0 / 335
Goodness-of-fit on F^2	1.202
Final R indices [I>2sigma(I)]	R1 = 0.0505, wR2 = 0.1325
R indices (all data)	R1 = 0.0541, wR2 = 0.1339
Extinction coefficient	$3.8(6)x10^{-7}$
Largest diff. peak and hole	0.277 and -0.282 e.$Å^{-3}$

Table S26. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for 1. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O1	2933(2)	3779(1)	-319(2)	29(1)
O2	3010(2)	6230(1)	-584(2)	31(1)
O3	7945(1)	5377(1)	4304(1)	20(1)
O4	7134(1)	5709(1)	5923(2)	21(1)
O5	9709(2)	2871(1)	9443(2)	26(1)
N1	5172(2)	5069(1)	2627(2)	18(1)
N2	4672(2)	3966(1)	1976(2)	18(1)
N3	2946(2)	5010(1)	-402(2)	24(1)
N4	4081(2)	5728(1)	1011(2)	21(1)
C1	5280(2)	4364(1)	2832(2)	17(1)
C2	4118(2)	4446(1)	1157(2)	18(1)
C3	3309(2)	4347(1)	117(2)	22(1)
C4	3330(2)	5690(1)	-27(2)	23(1)
C5	4459(2)	5108(1)	1596(2)	18(1)
C6	5984(2)	4074(1)	3892(2)	17(1)
C7	6355(2)	4534(1)	5016(2)	18(1)
C8	7255(2)	3767(1)	4025(2)	20(1)
C9	5700(2)	3456(1)	4719(2)	21(1)
C10	6901(2)	3769(1)	5288(2)	16(1)
C11	8366(2)	6106(1)	4591(2)	20(1)
C12	8149(2)	6174(1)	5890(2)	21(1)
C13	7610(2)	6611(1)	3767(2)	27(1)
C14	9635(2)	6155(1)	4399(2)	25(1)
C15	7845(2)	6920(1)	6275(3)	29(1)
C16	9139(2)	5858(1)	6756(2)	27(1)
C17	7627(2)	3549(1)	6396(2)	17(1)
C18	7966(2)	4040(1)	7279(2)	19(1)
C19	8672(2)	3843(1)	8312(2)	19(1)
C20	9032(2)	3135(1)	8465(2)	20(1)
C21	8694(2)	2636(1)	7584(2)	21(1)
C22	7996(2)	2839(1)	6565(2)	20(1)

C23	4680(2)	3186(1)	1856(2)	22(1)
C24	2112(2)	4970(2)	-1494(2)	30(1)
C25	4462(2)	6432(1)	1476(2)	26(1)
C26	10074(2)	3359(2)	10371(2)	28(1)
B1	7161(2)	5215(1)	5049(2)	18(1)

Computational Investigation on BCP BisBoronates

General Remarks

All optimizations of intermediates and transition states were calculated without constraints using dispersion corrected unrestricted (UB3LYP-D3)/def2-SVP level of the theory in implicit solvent (PhCl) using CPCM as the solvation model with the "guess=mix" keyword, as implemented in Gaussian 16, Revision C.01. Frequency calculations, at the same level of theory, were used to obtain thermal corrections (at 298K) and to characterize optimized structures as transition states (only a single imaginary frequency) or intermediate (if no imaginary frequencies were found). Single point energy calculations in implicit solvent using and B3LYP-D3/def2-TZVPP-CPCM(DMSO) were also performed. All energy decomposition analysis (EDA) was done using the second-generation absolutely-localized molecular orbital EDA available in Q-Chem version 5.3. These calculations were performed at the same level of theory used for single point energy calculations but in the gas phase. All 3-D structures were generated using CYLview20. NBO analysis was preformed using NBO version 3.1 as available in the Gaussian software package. Orbitals visualizied using GaussView 6. Non-covalent interaction (NCI) analysis was preformed using the Multiwfn software with the isosurfaces visualized using VMD and colored scatter plots made with Multiwfn scripts and gnuplot 5.4.

Full reference for Gaussian 16 Software:

Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.;

Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

Full reference for Q-Chem 5.0 Software:

Y. Shao, Z. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. Feng, D. Ghosh, M. Goldey P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Khaliullin, T. Kús, A. Landau, J. Liu, E. I. Proynov, Y. M. Rhee, R. M. Richard, M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. Woodcock III, P. M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G. J. O. Beran, Y. A. Bernard, E. Berquist, K. Brandhorst, K. B. Bravaya, S. T. Brown, D. Casanova, C.-M. Chang, Y. Chen, S. H. Chien, K. D. Closser, D. L. Crittenden, M. Diedenhofen, R. A. DiStasio Jr., H. Dop, A. D. Dutoi, R. G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M. W. D. Hanson-Heine, P. H. P. Harbach, A. W. Hauser, E. G. Hohenstein, Z. C. Holden, T.-C. Jagau, H. Ji, B. Kaduk, K. Khistyaev, J. Kim, J. Kim, R. A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C. M. Krauter, K. U. Lao, A. Laurent, K. V. Lawler, S. V. Levchenko, C. Y. Lin, F. Liu, E. Livshits, R. C. Lochan, A. Luenser, P. Manohar, S. F. Manzer, S.-P. Mao, N. Mardirossian, A. V. Marenich, S. A. Maurer, N. J. Mayhall, C. M. Oana, R. Olivares-Amaya, D. P. O'Neill, J. A. Parkhill, T. M. Perrine, R. Peverati, P. A. Pieniazek, A. Prociuk, D. R. Rehn, E. Rosta, N. J. Russ, N. Sergueev, S. M. Sharada, S. Sharmaa, D. W. Small, A. Sodt, T. Stein, D. Stück, Y.-C. Su, A. J. W. Thom, T. Tsuchimochi, L. Vogt, O. Vydrov, T. Wang, M. A. Watson, J. Wenzel, A. White, C. F. Williams, V. Vanovschi, S. Yeganeh, S. R. Yost, Z.-Q. You, I. Y. Zhang, X. Zhang, Y. Zhou, B. R. Brooks, G. K. L. Chan, D. M. Chipman, C. J. Cramer, W. A. Goddard III, M. S. Gordon, W. J. Hehre, A. Klamt, H. F. Schaefer III, M. W. Schmidt, C. D. Sherrill, D. G. Truhlar, A. Warshel, X. Xua, A. Aspuru-Guzik, R. Baer, A. T. Bell, N. A. Besley, J.-D. Chai, A. Dreuw, B. D. Dunietz, T. R. Furlani, S. R. Gwaltney, C.-P. Hsu, Y. Jung, J. Kong, D. S. Lambrecht, W. Liang, C. Ochsenfeld, V. A. Rassolov, L. V. Slipchenko, J. E. Subotnik, T. Van Voorhis, J. M. Herbert, A. I. Krylov, P. M. W. Gill, and M. Head-Gordon

Reference GaussView 6:

GaussView, Version 6.1, Roy Dennington, Todd A. Keith, and John M. Millam, Semichem Inc., Shawnee Mission, KS, 2016.

Reference CYLview20:

CYLview20; Legault, C. Y., Université de Sherbrooke, 2020 (http://www.cylview.org)

Reference NBO 3.1:

NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold.

Multiwfn 3.8:

Tian Lu, Feiwu Chen, *J. Comput. Chem.*, 33, 580-592 (2012).

VMD:

Humphrey, W., Dalke, A. and Schulten, K., "VMD - Visual Molecular Dynamics", J. Molec. Graphics, 1996, vol. 14, pp. 33-38.

GNUplot

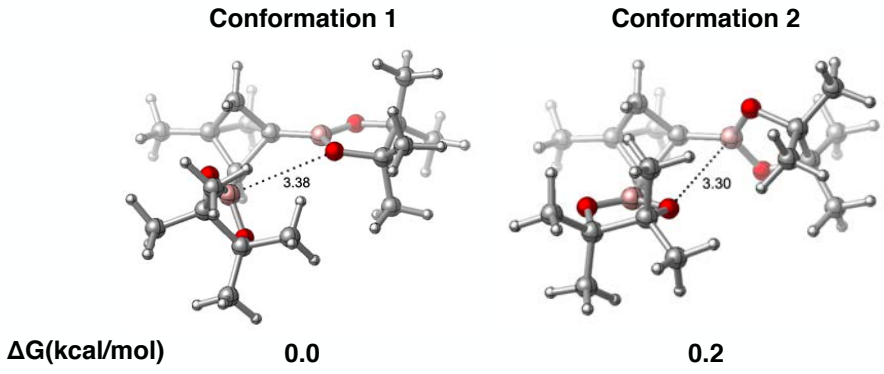
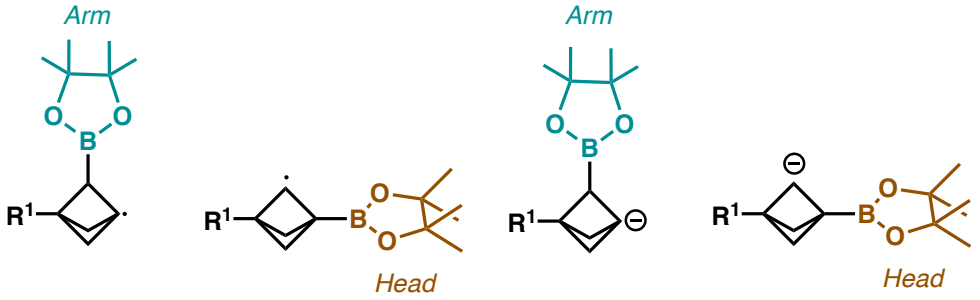


Figure S1: Lowest energy conformations obtained from conformational search of the BCP bis-

14. NBO energies reported in kcal/mol.



0.0	-3.0	0.0	1.8
0.0	-2.7	0.0	1.7
0.0	-0.8	0.0	1.8
0.0	-2.9	0.0	1.5

ΔG(kcal/mol)

B3LYP-D3/def2-SVP-CPCM(PhCl)

B3LYP-D3/def2-SVPD-CPCM(PhCl)

uM06-2X/def2-SVPD-CPCM(PhCl)

uWB97XD/def2-SVPD-CPCM(PhCl)

Figure S2: Relative free energies of both the radical and anionic intermediates that could be formed from 1 and $2e^{-}$ pathways. All free energies were obtained from optimizations done at the indicated level of theory at the bottom of the figure.

Initially, the stability of both the radical and anionic intermediate at both the head and arm position of **14** were modeled (Figure S2 and S2). All calculations suggested that the radical was thermodynamically preferred at the arm while the anion was preferred at the head of **14**. As both 1 and $2e^{-}$ pathways were shown to react exclusively at the head Bpin of the bis-boronate BCPs, the relative stability of the putative radical and anionic intermediates does not correlate with observed reactivity. As such, we then explored the full reaction profile of a model reaction (see below) to gain insights into the factors controlling reactivity and selectivity.

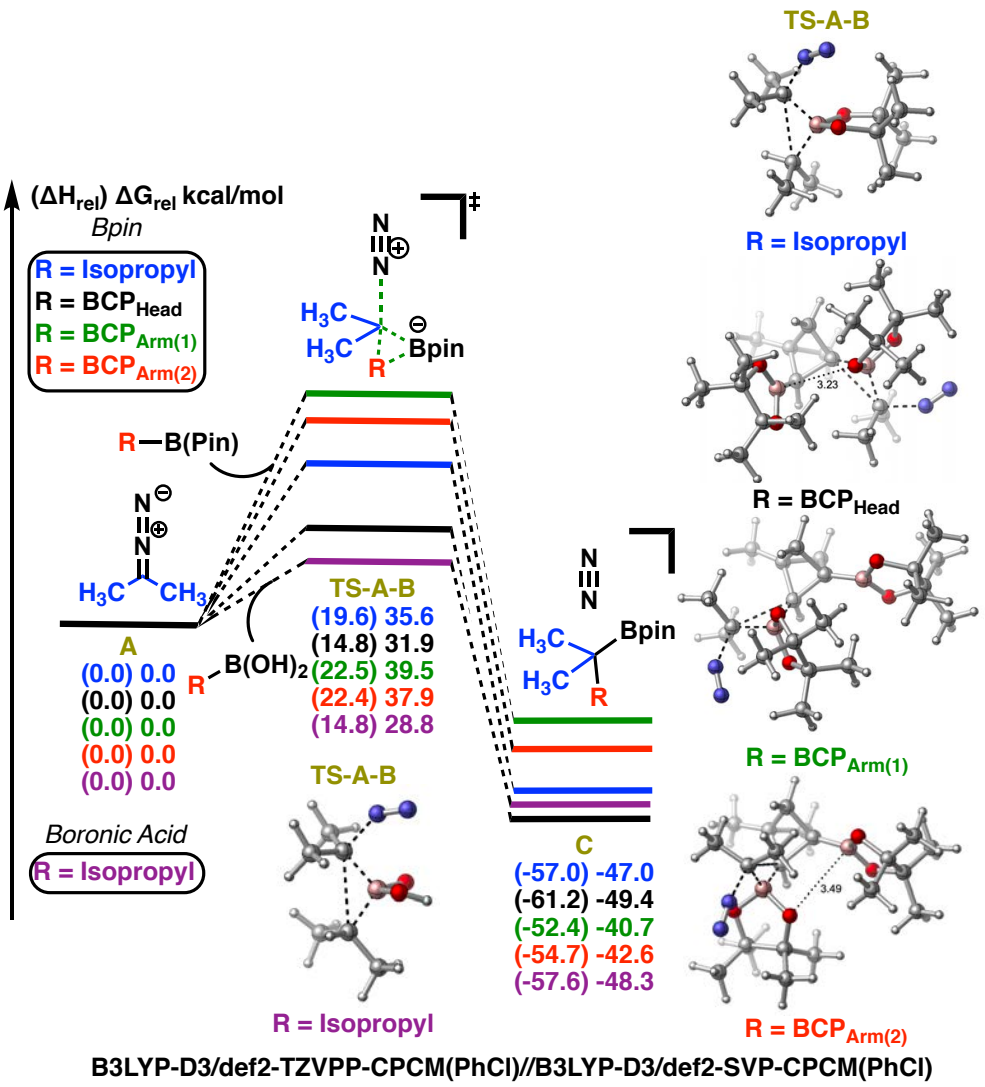


Figure S3: Reaction coordinate diagrams of concerted boron insertion pathways with bis-boronate BCP **14** at both the head and arm boronate. R = Isopropyl included for comparison. All pathways made relative to lowest energy conformation.

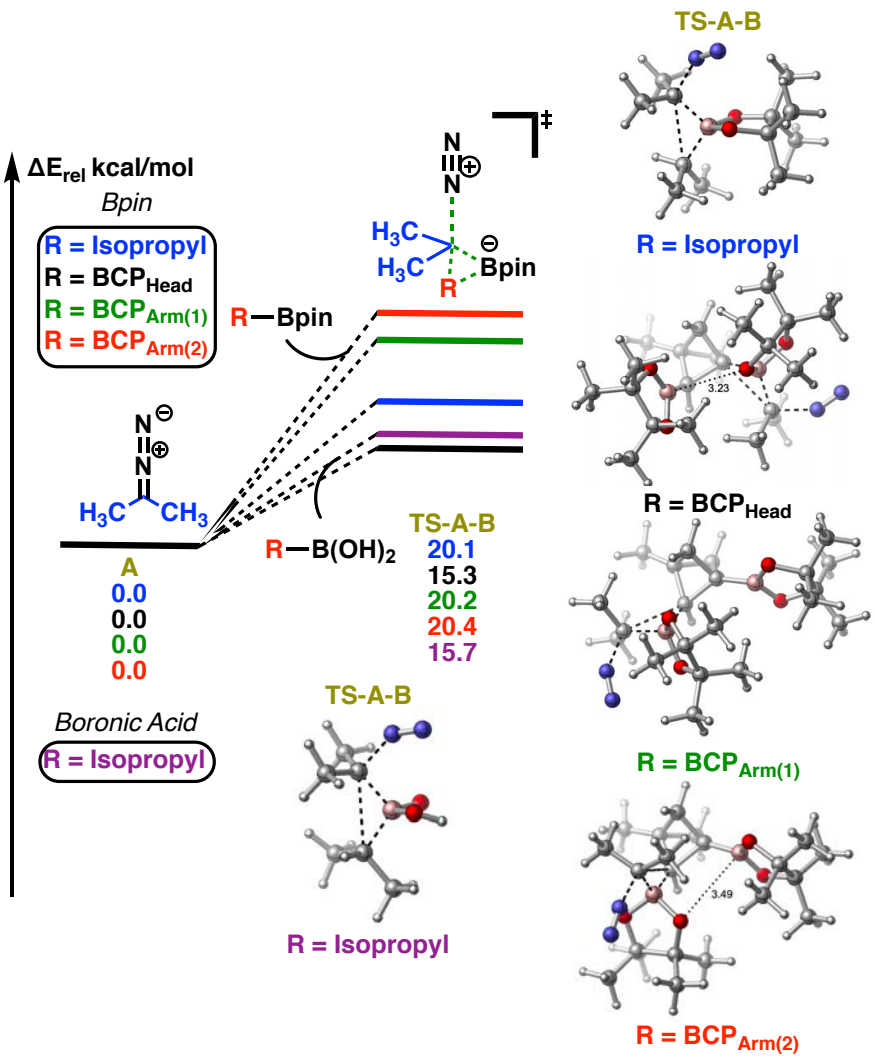


Figure S4: Reaction coordinate diagrams of concerted boron insertion pathways with bis-boronate BCP **14** at both the head and arm boronate in terms of total energy (E). R = Isopropyl included for comparison.

Modeling the reaction coordinate diagram of the boron insertion reaction which shows a preference in reactivity for the head Bpin in **14** (Figure 2A in the manuscript). Preliminary calculations of the boron insertion pathway revealed that this transformation proceeds via a concerted transition state. All attempts at locating putative intermediates previously proposed for these transformations failed (i.e., optimizations lead to either lead to reactants or products). Pathways were modeled for reactions at the head and arm of **14** from both conformations 1 and 2 (Figure S3). An additional pathway where the alkyl boronic ester with the alkyl group as an isopropyl is also shown as a

reference for the barriers of these transformations, which was not reported in the previous publication.[1] The alkyl model system has a barrier of 35.6 kcal/mol. The computed barrier via the head of **14** is 31.9 kcal/mol which is much closer to the barrier of 28.8 kcal/mol of the alkyl boronic acid. However, reactions at the arm from conformations **1** and **2** ($BCP_{Arm(1)}$ and $BCP_{Arm(2)}$) are substantially higher in free energy, 39.5 and 37.9 kcal/mol respectfully. These results reveal that the experimentally observed regioselectivity of these reactions are *kinetically* controlled. The relative barriers of the total energy of these calculations (Figure S4) retained similar trends, making energy decomposition analysis a viable next step in further interpretation of these results.

Equation Energy Decomposition Analysis

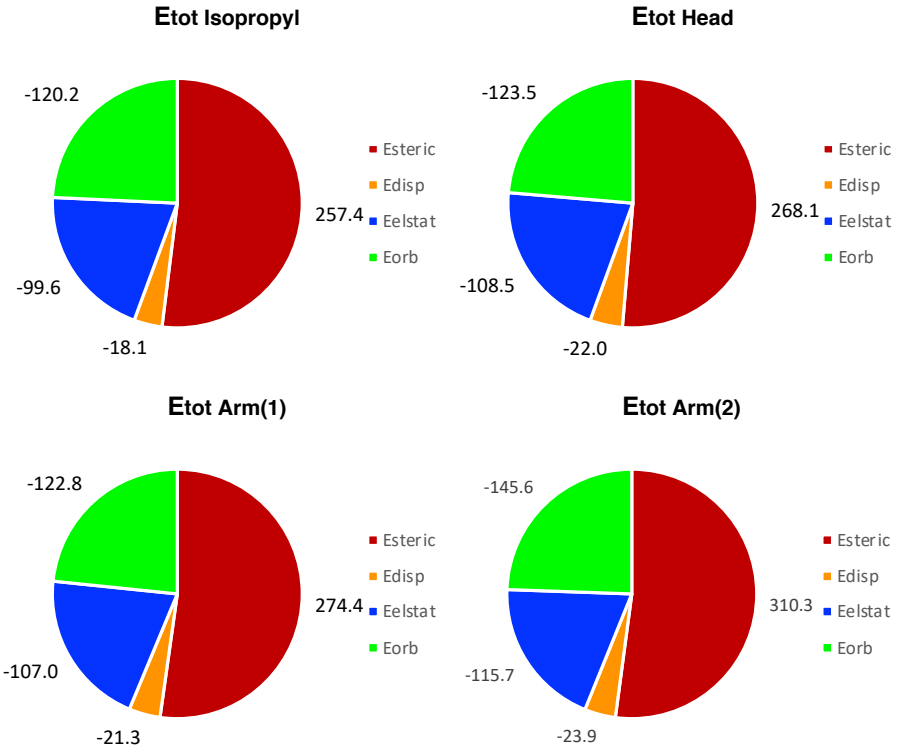
$$\Delta E_{act} = \Delta E_{dist} + \Delta E_{int}$$

$$\Delta E_{int} = \Delta E_{Pauli} + \Delta E_{elstat} + \Delta E_{pol} + \Delta E_{ct} + \Delta E_{disp}$$

$$\Delta E_{Sterics} = \Delta E_{Pauli} + \Delta E_{dist}$$

$$\Delta E_{Orb} = \Delta E_{pol} + \Delta E_{ct}$$

Total Energy Decomposition Analysis



B3LYP-D3/def2-TZVPP-gas//B3LYP-D3/def2-SVP-CPCM(PhCl)

Figure S5: Energy decomposition analysis of indicated transition states using the second-generation ALMO-EDA.

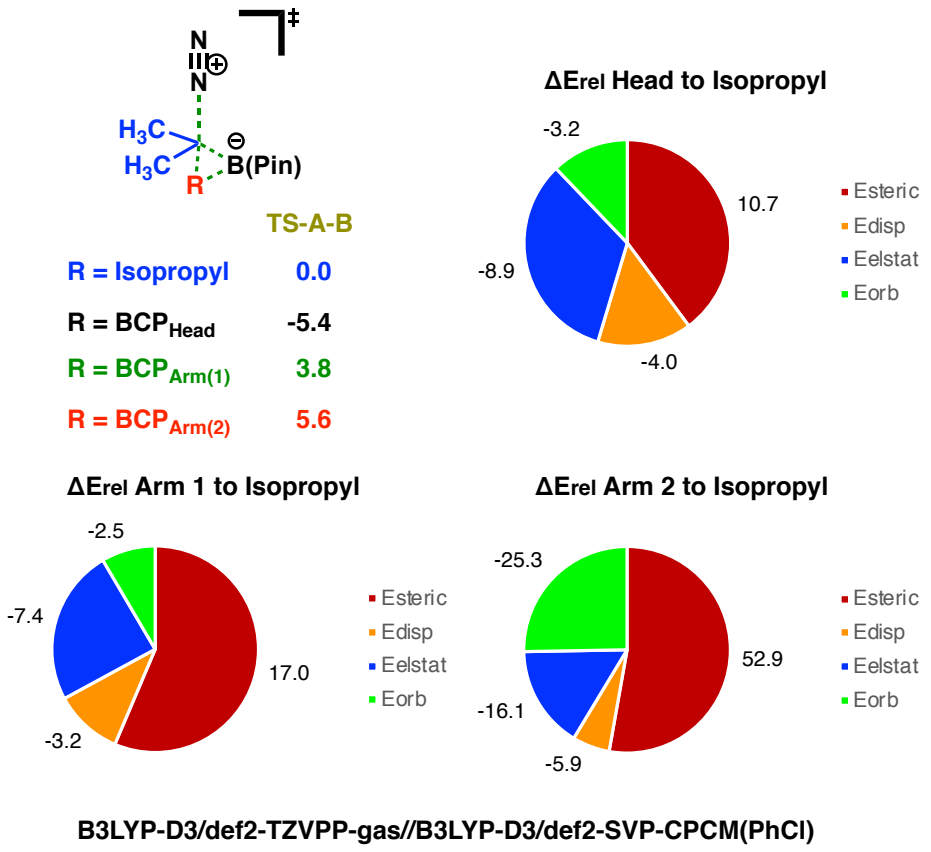


Figure S6: Energy decomposition analysis of indicated transition states made relative to R=Isopropyl transition state.

Energy decomposition analysis (EDA) using the second generation ALMO-EDA decomposes the activation energy into one unfavorable E_{steric} and three favorable E_{disp}, E_{elstat}, and E_{orb}, electronic interactions where disp = dispersion, elstat = electrostatic and orb = orbital (Figure S5). The EDA of the transition states were made relative to R = Isopropyl (Figure S6) to highlight the change in the decomposed energies between the transition states modeled at the head and arm Bpin of the BCP. Reactions through the head Bpin of BCP (ΔE_{rel} Head; Figure S6) has an increase in favorable electronic interactions which overcome the increase in disfavorable steric interactions; resulting in a lower barrier (~5.4 kcal/mol) with respect to the R = Isopropyl transition state. Transition states at the arm Bpin of BCP (ΔE_{rel} Arm 1 and ΔE_{rel} Arm 2) have larger increase in steric interactions which outweigh the change in favorable electronic interactions, resulting in higher barriers (~3.8 kcal/mol) through R = $BCP_{Arm(1)}$ and $BCP_{Arm(2)}$.

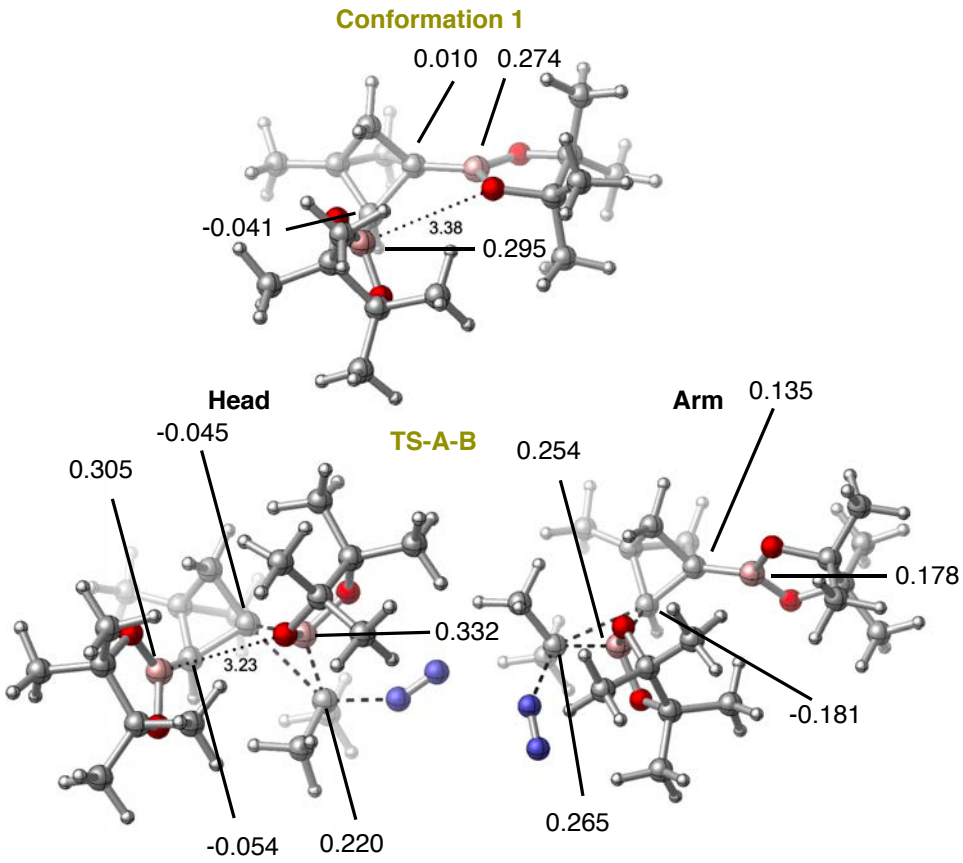
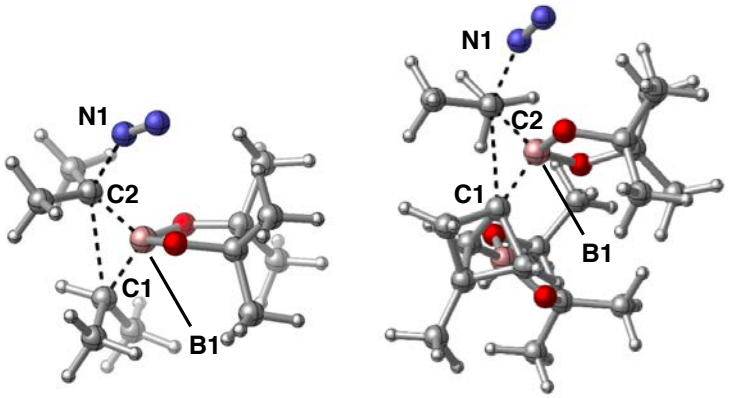


Figure S7: Mulliken charges labeled at head and arm boron and carbon for conformation 1 and additionally at the carbene carbon through TS-A-B for both arm and head transition states.

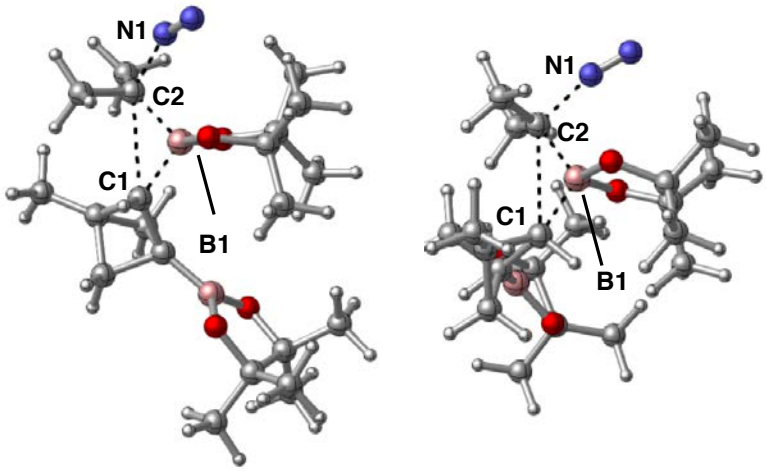
Moreover, analysis of the Mulliken charges (Figure S7) of the lowest energy intermediate of **14** show that there is more negative charge at the arm carbon than at the bridgehead carbon (-0.041 vs. 0.10). Preforming the same analysis of the lowest energy transition states shows a larger quantity of negative charge building up through TS-A-B Arm then through TS-A-B Head on the reacting BCP carbon (-0.181 vs. -0.045). Overall, these results suggest that the hybridization of the bridgehead carbon $sp^{2.0}$ reduces the negative charge through TS-A-B which corresponds to the lower barrier.

TS-A-B



R = Isopropyl R = BCP_{Head}

Bond	Distance	Distance	Distance(rel)
B1-C2	1.68743	1.70969	0.02226
C1-N5	1.75364	1.77047	0.01683
C2-C1	2.57488	2.62439	0.04951
B1-C1	1.72005	1.65654	-0.06351
Angle	**Degrees**	**Degrees**	**Degrees(rel)**
C1-B1-C2	98.51224	102.44058	3.92814



R = $BCP_{Arm(1)}$ R = $BCP_{Arm(2)}$

Bond	Distance	Distance(rel)	Distance	Distance(rel)
B1-C2	1.69545	0.00802	1.66660	-0.02083
C1-N5	1.76429	0.01065	1.76531	0.01167
C2-C1	2.60583	0.03095	2.77832	0.20344
B1-C1	1.69214	-0.02791	1.66136	-0.05869
Angle	**Degrees**	**Degrees(rel)**	**Degrees**	**Degrees(rel)**
C1-B1-C2	100.56923	2.05679	113.1988	14.68636

Figure S8: Bond lengths (Å) and angles (°) of the boron insertion transition states for TS-A-B. All bond distances and angles were made relative to the isopropyl system under Distance(rel) and Angle(rel).

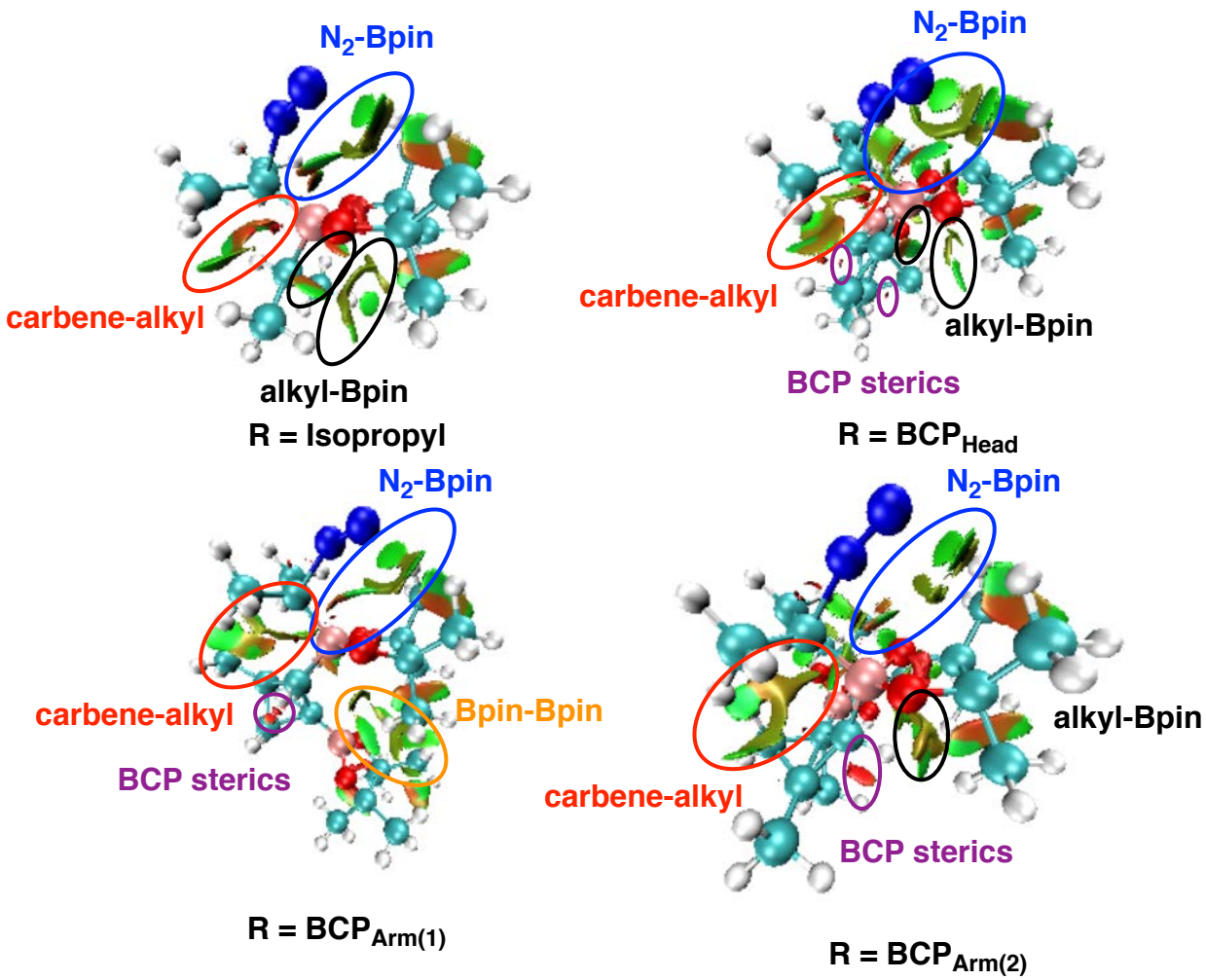
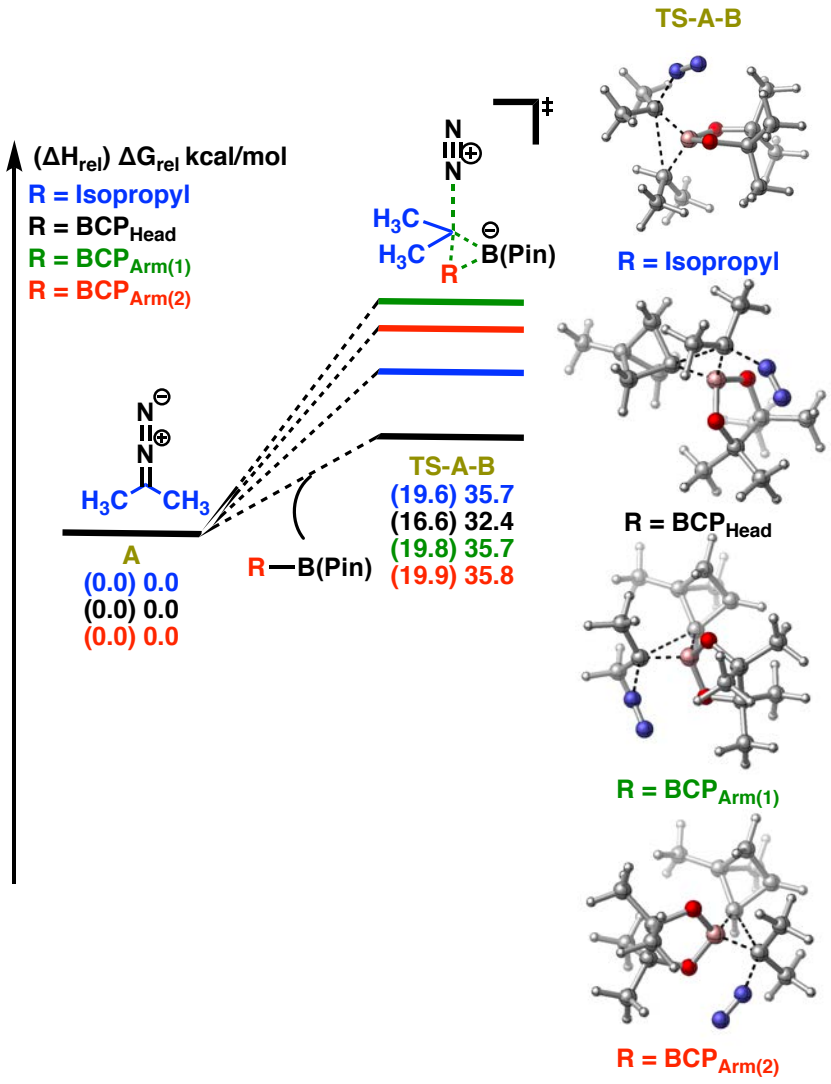


Figure S9: Non-covalent interaction analysis of TS-A-B as available in Multiwfn. Blue indicates attractive non-covalent interactions, green indicates dispersion interactions while red indicates repulsive interactions.

To better understand the results of the EDA, the bond distances and bond angles of the decomposed transition states as well as weak non-covalent interaction analysis (NCI) of BCP **14** were compared to the isopropyl system (Figure S8 and S9). As observed from the EDA, all transition states with the BCP have increases steric and favorable electronic interactions through TS-A-B when compared to the isopropyl system. NCI analysis reveals that the increase in C1-C2 distance of the BCP transition states results in lower steric interaction between the alkyl and carbene (red to brown color from alkyl to BCP system) while all BCP systems show a steric interaction within the BCP scaffold (red color between arms of BCP; circled in purple). The BCP transition state with the least BCP steric interactions is the head transition state (R = BCP_{Head}) while the transition state with the

largest BCP steric interaction is the second arm transition state (R= $BCP_{Arm(2)}$), in agreement with the EDA. As the NCI analysis was for weak electronic interactions (RDG ≤ 0.5 used for constructing isosurfaces), the stronger electrostatic interactions were not visualized using this method, as can be seen in Figure S11.



B3LYP-D3/def2-TZVPP-CPCM(PhCl)//B3LYP-D3/def2-SVP-CPCM(PhCl)

Figure S10: Reaction coordinate diagram of boron insertions for mono-boronate BCP. All barriers are relative to the lowest energy conformations.

To evaluate the influence of the additional boron on the barriers of boron insertion of the bis-boronate BCP, the mono-boronate BCP of **14** was modeled (Figure S10) for both the Bpin substituted at the head and arm position of the BCP. The trends in reactivity is still observed

without the additional Bpin: TS-A-B has a lower barrier (32.4 kcal/mol) than the transition states at the arm BCP (~ 35.7 kcal/mol), reinforcing that the *BCP scaffold* is responsible for the observed reactivity.

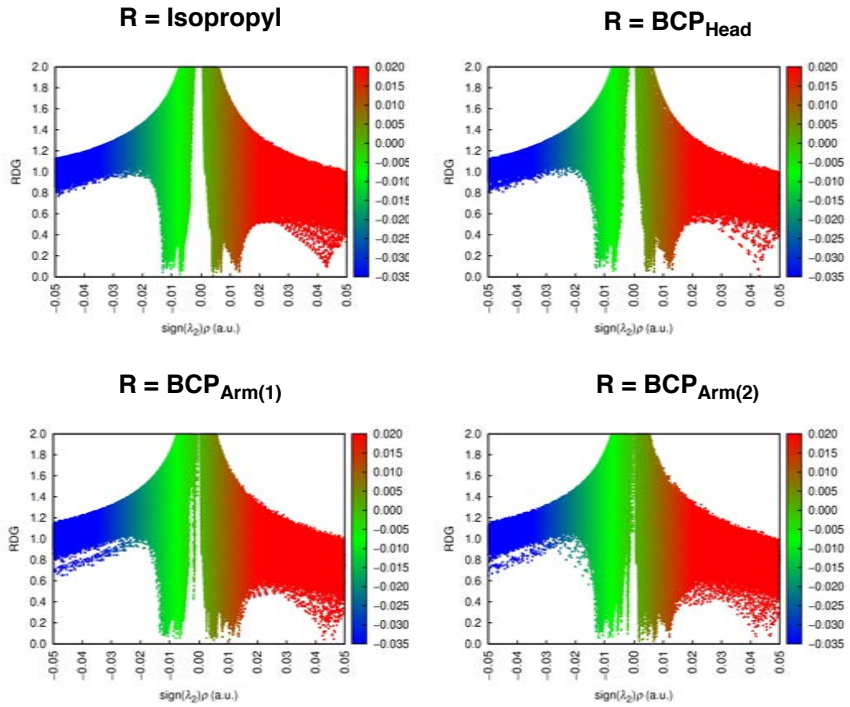


Figure S11: Scatter graphs of TS-A-B for the indicated transition states. The RDG isosurface cutoff is set to 0.5.

Procedure for Compound Enumeration.

The "Enumerate Combinatorial Reaction" component in Pipeline Pilot (version 18.1.100.11) from Dassault Systèmes (Vélizy-Villacoublay, France) was used to enumerate 2D structures of BCP compounds. 3D structures of these BCP compounds were generated with force field minimized conformations in Pipeline Pilot. These 3D structures were used to compute the topology-dependent properties, including PMI and 3D scores.

Enumeration of tri-substituted BCP and arenes

C_1, C_2 and C_3 substituents on 1,2,3-trisubstituted BCP compounds, 1, 2, 4- and 1, 3, 4-trisubstituted arenes were selected based on the experimental outcomes from Fig.4 and Fig.5 (Figure S12). Protecting groups from the output products were removed to remove influence on topology (Figure S13).

Enumeration of 1,2- and 1,3-disubstituted BCP and arenes

C_1, C_2 and C_3 substituents disubstituted BCP compounds and arenes were conducted based on the experimental outcomes from Fig.4 and Fig.5, where only functional groups successfully afforded with both C_2-Bpin and C_3-Bpin functionalization methods were selected (Figure S14). Protecting groups from the output products were removed to remove influence on topology (Figure S13).

Calculation of Principal Moments of Inertia (PMI) and 3D Scores

I_1, I_2 and I_3 are the three principal moments of inertia in an ascending order ($I_1 \leq I_2 \leq I_3$) for each given molecule calculated with Pipeline Pilot (version 18.1.100.11) from Dassault Systèmes (Vélizy-Villacoublay, France). 3D scores were calculated as 3D score = npr1 + npr2, where npr1 = I_1/I_3, and npr2 = I_2/I_3.

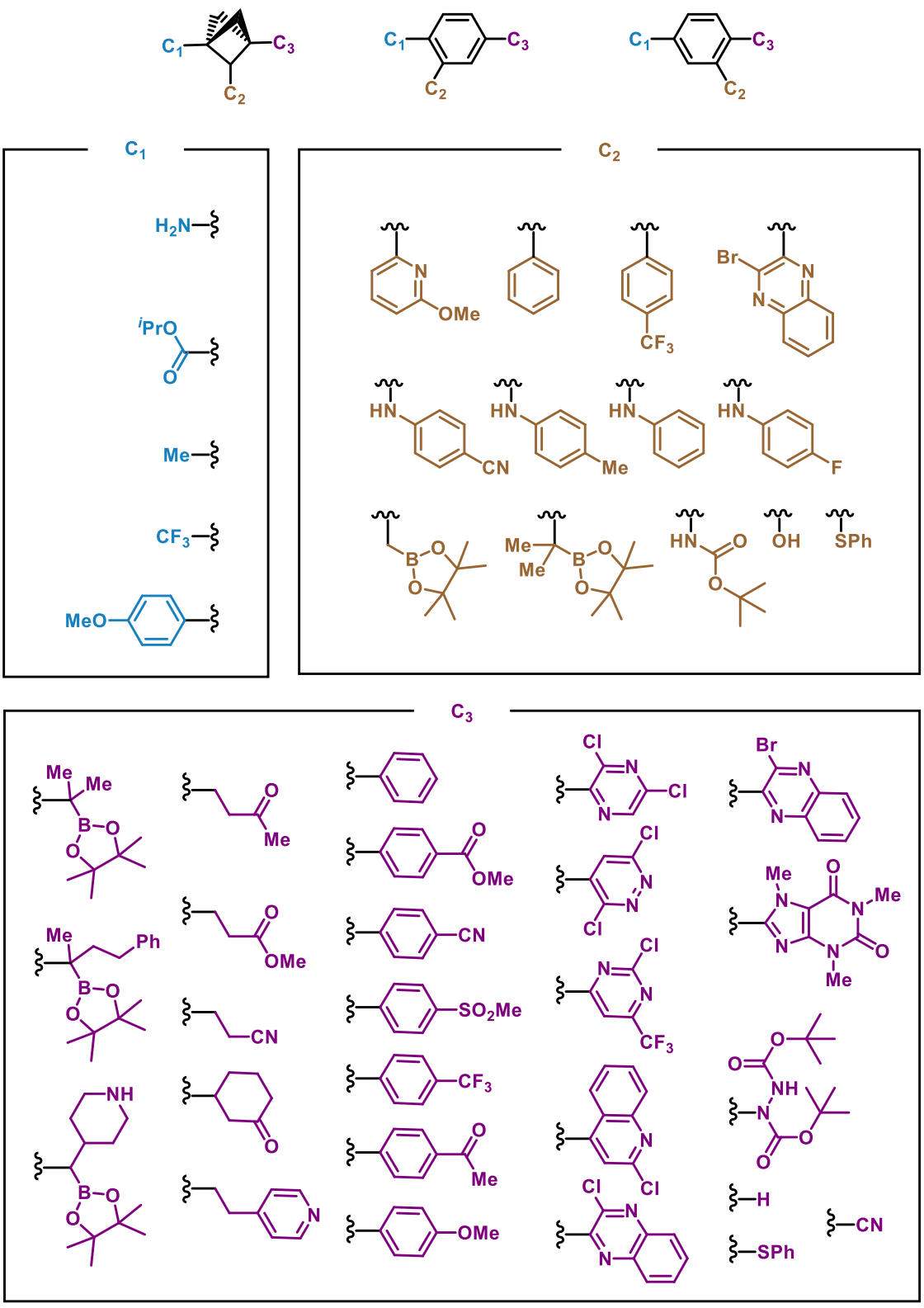


Figure S12: Enumeration of 1,2,3-trisubstituted BCP compounds, 1, 2, 4- and 1, 3, 4-trisubstituted arenes with selected substituents.

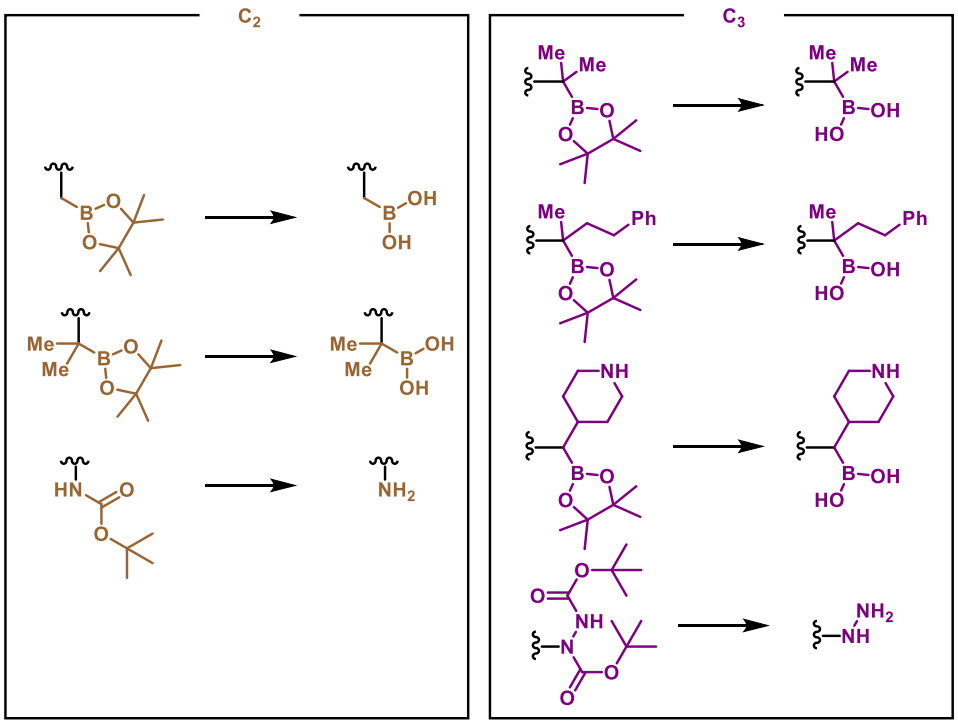


Figure S13: Deprotection of selected enumerated substituents.

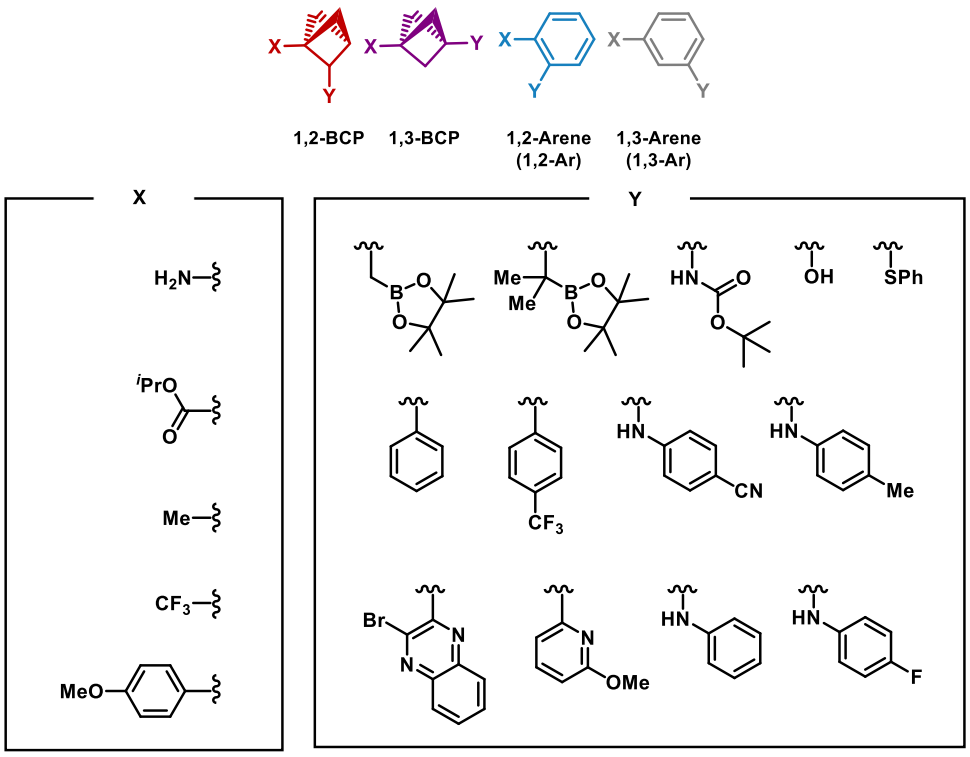


Figure S14: Enumeration of 1,2- and 1, 3-disubstituted BCP compounds and arenes with selected substituents.

Reference

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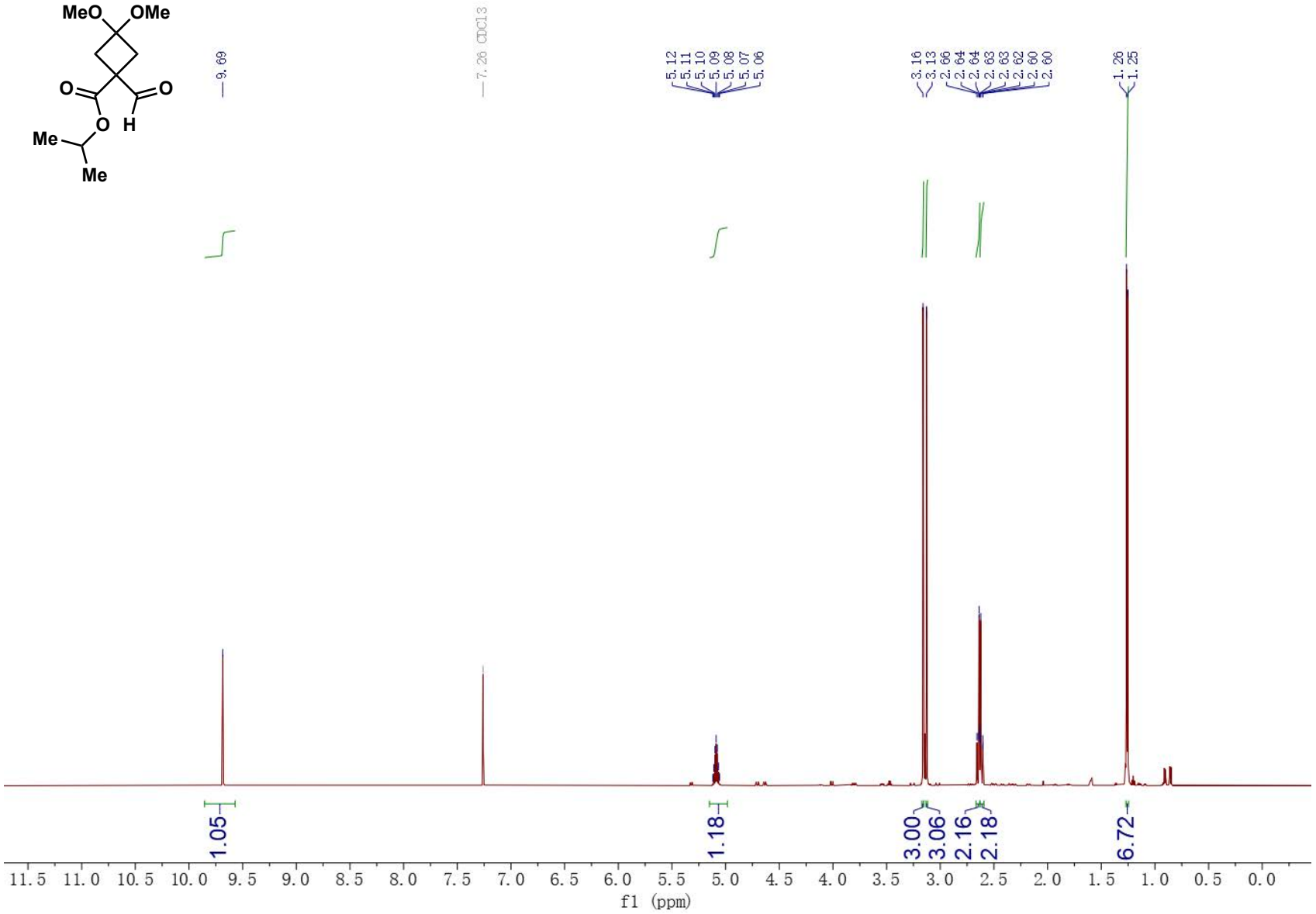
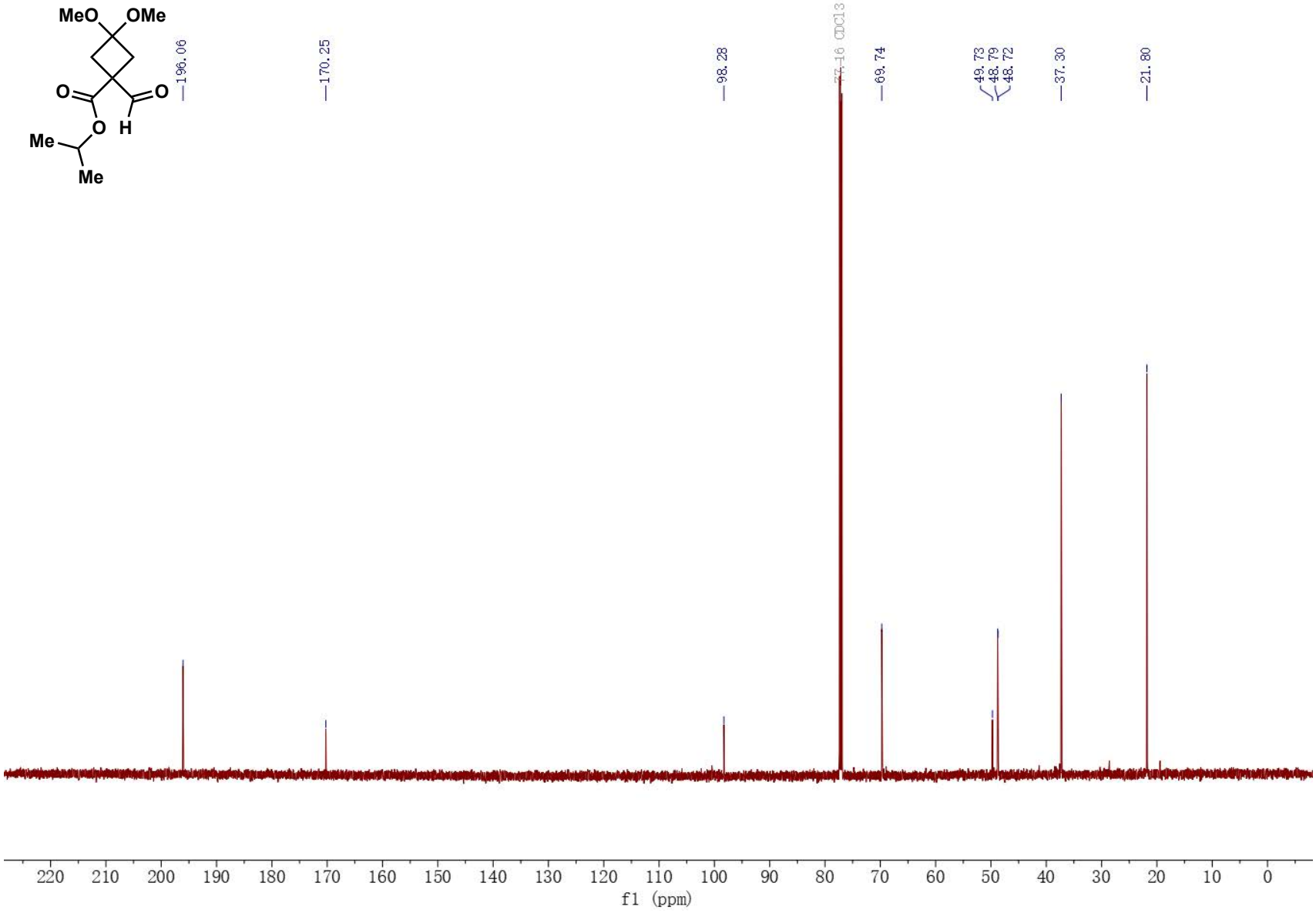
NMR Spectra

Compound 29 ^{1}H NMR



Compound 29 ^{13}C NMR



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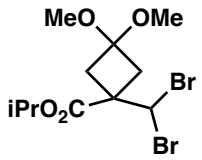

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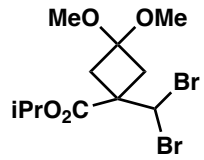

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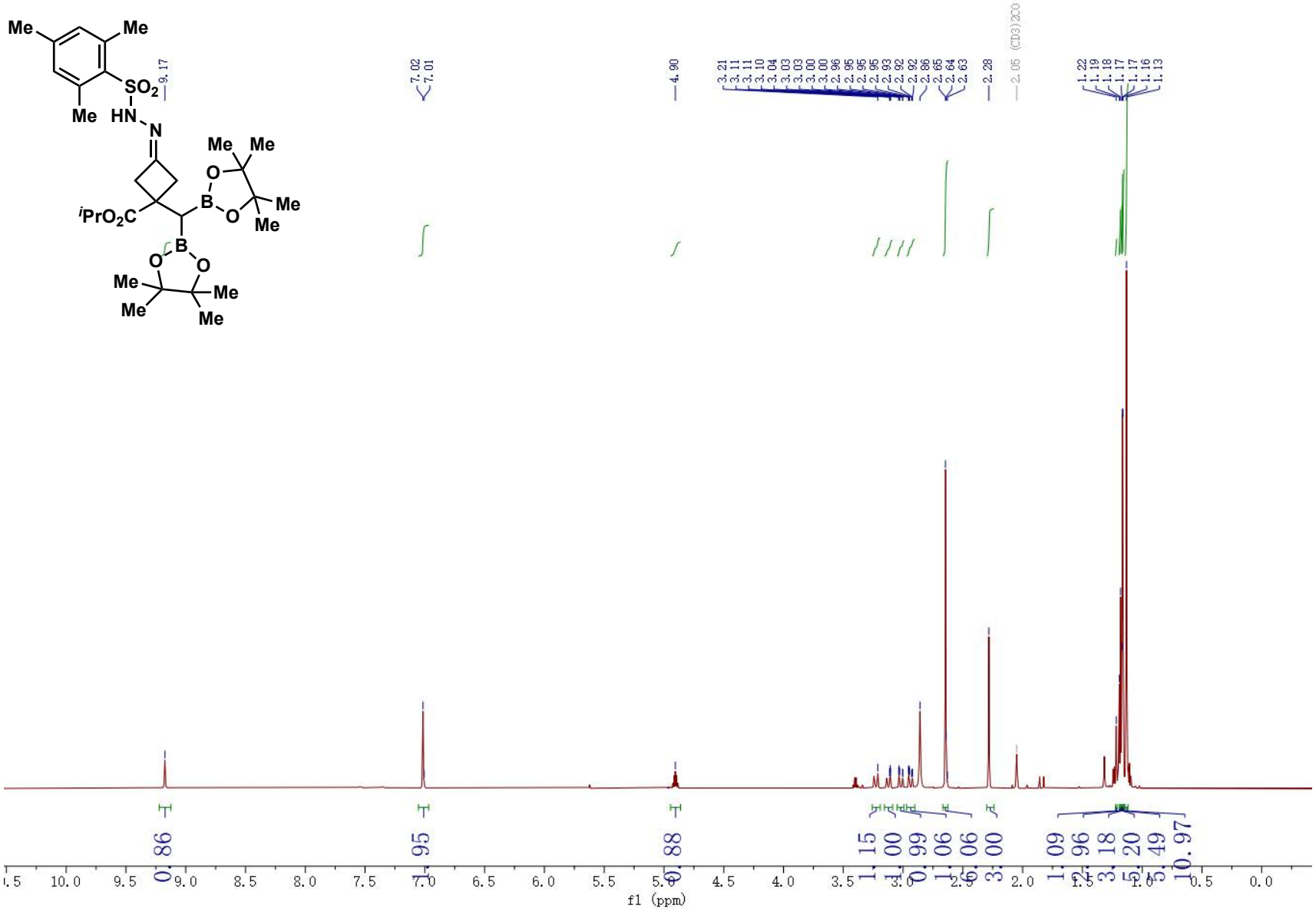

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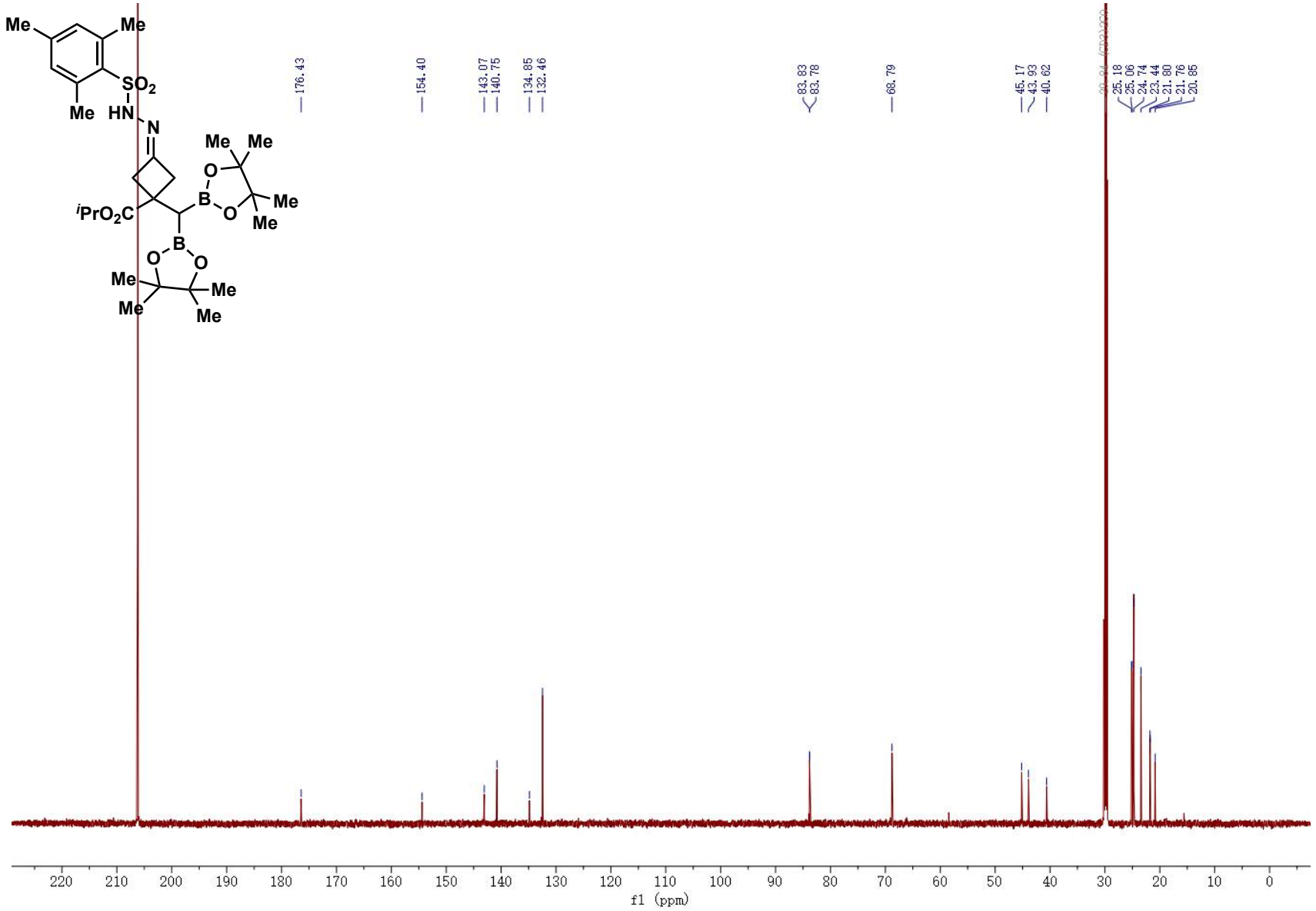
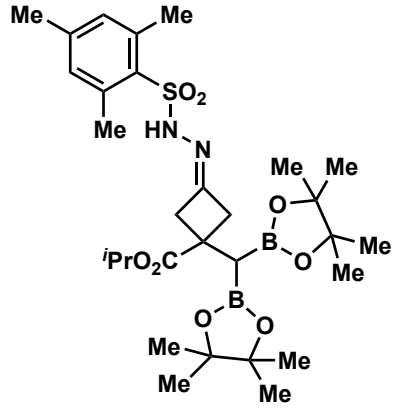
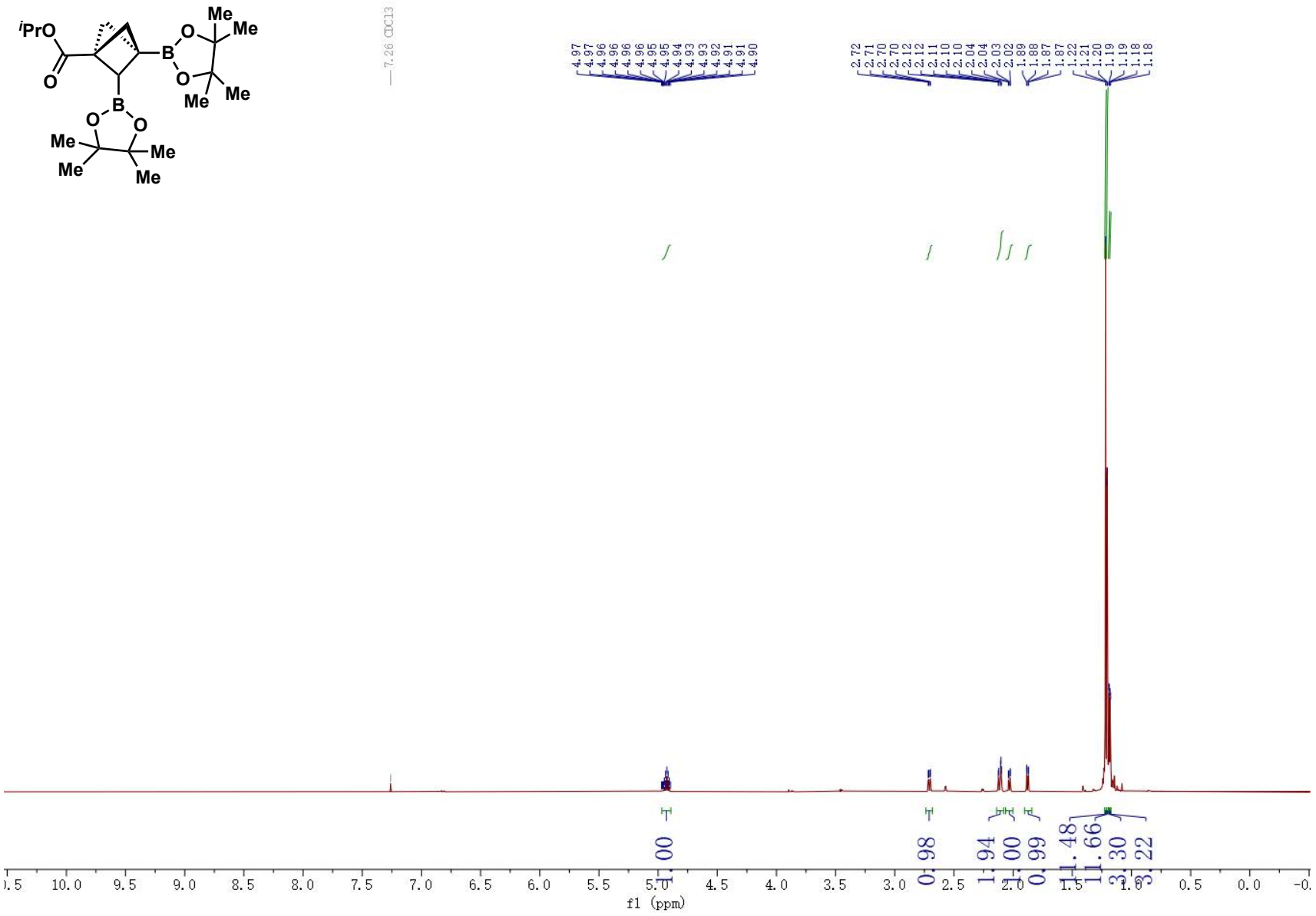


Compound 31 ^{11}B NMR



Compound 23 ^{1}H NMR



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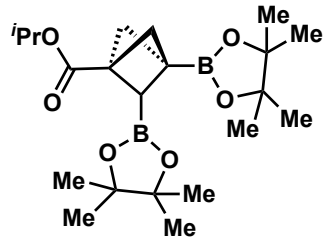
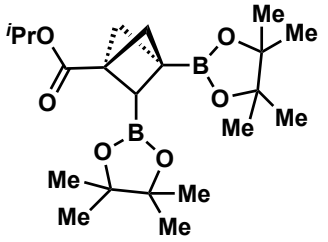
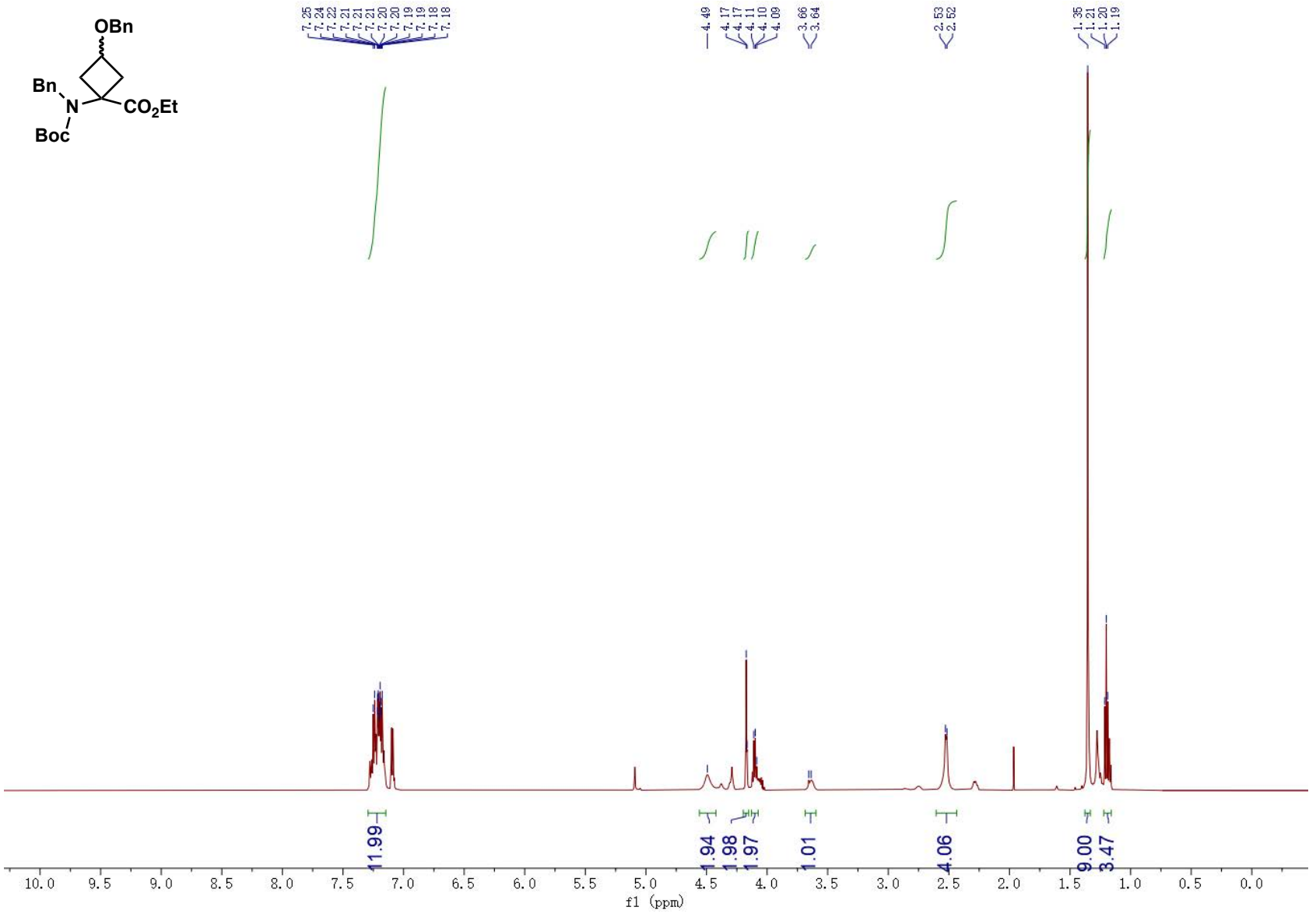


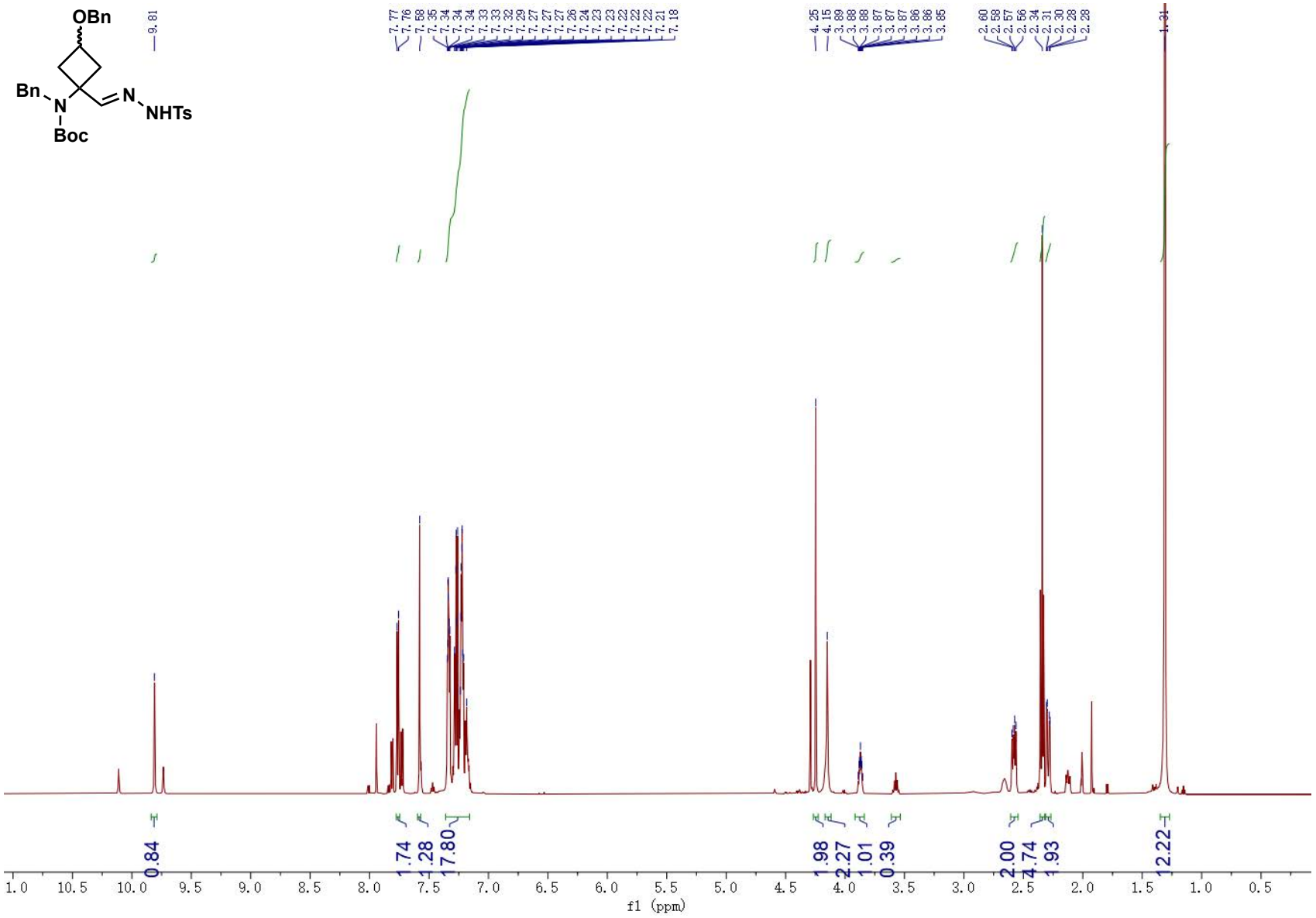
Compound 23 ^{11}B NMR



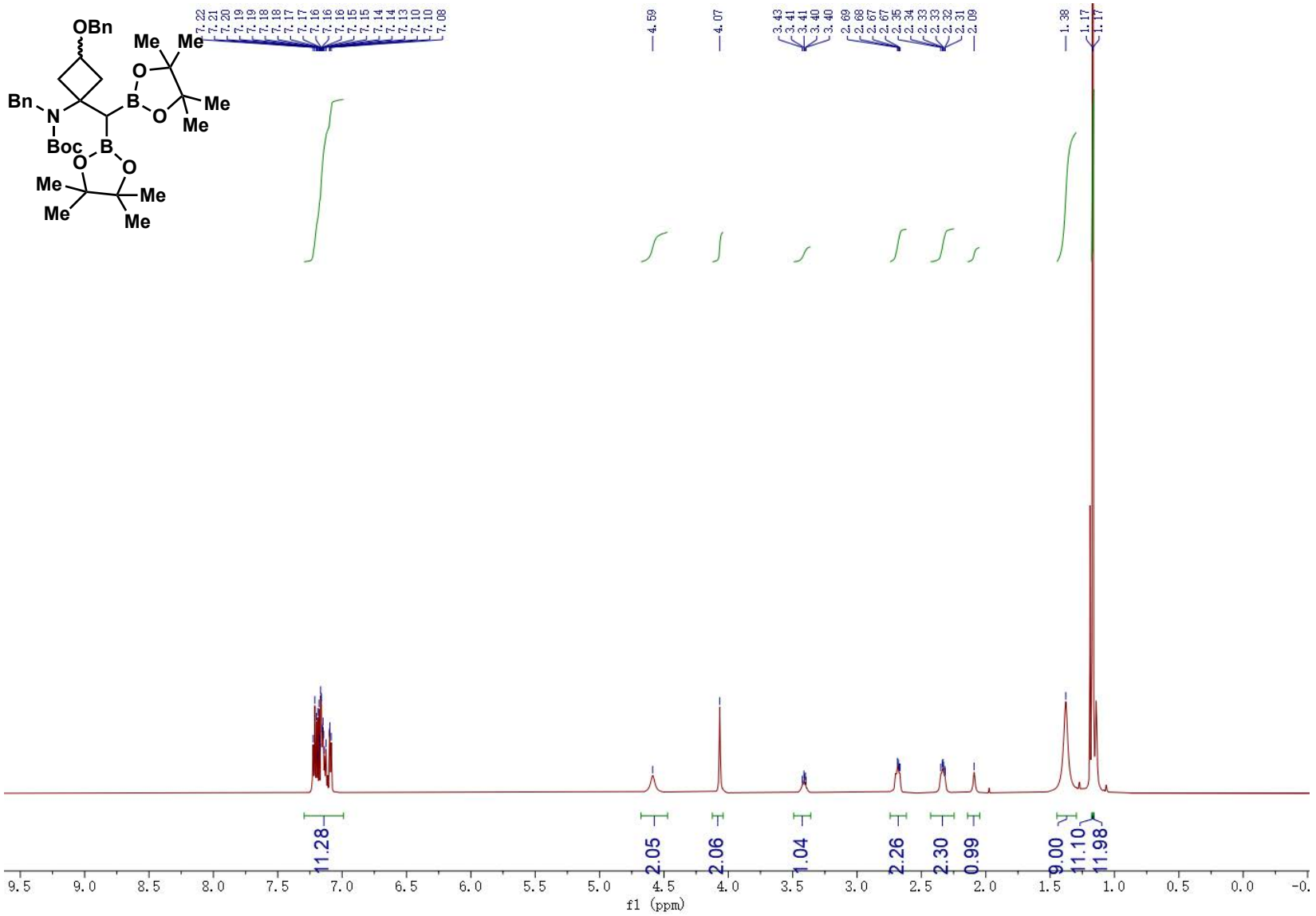
Compound SI-2 ^{1}H NMR



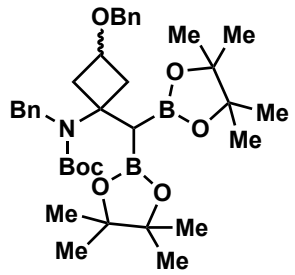
Compound SI-3 ^{1}H NMR



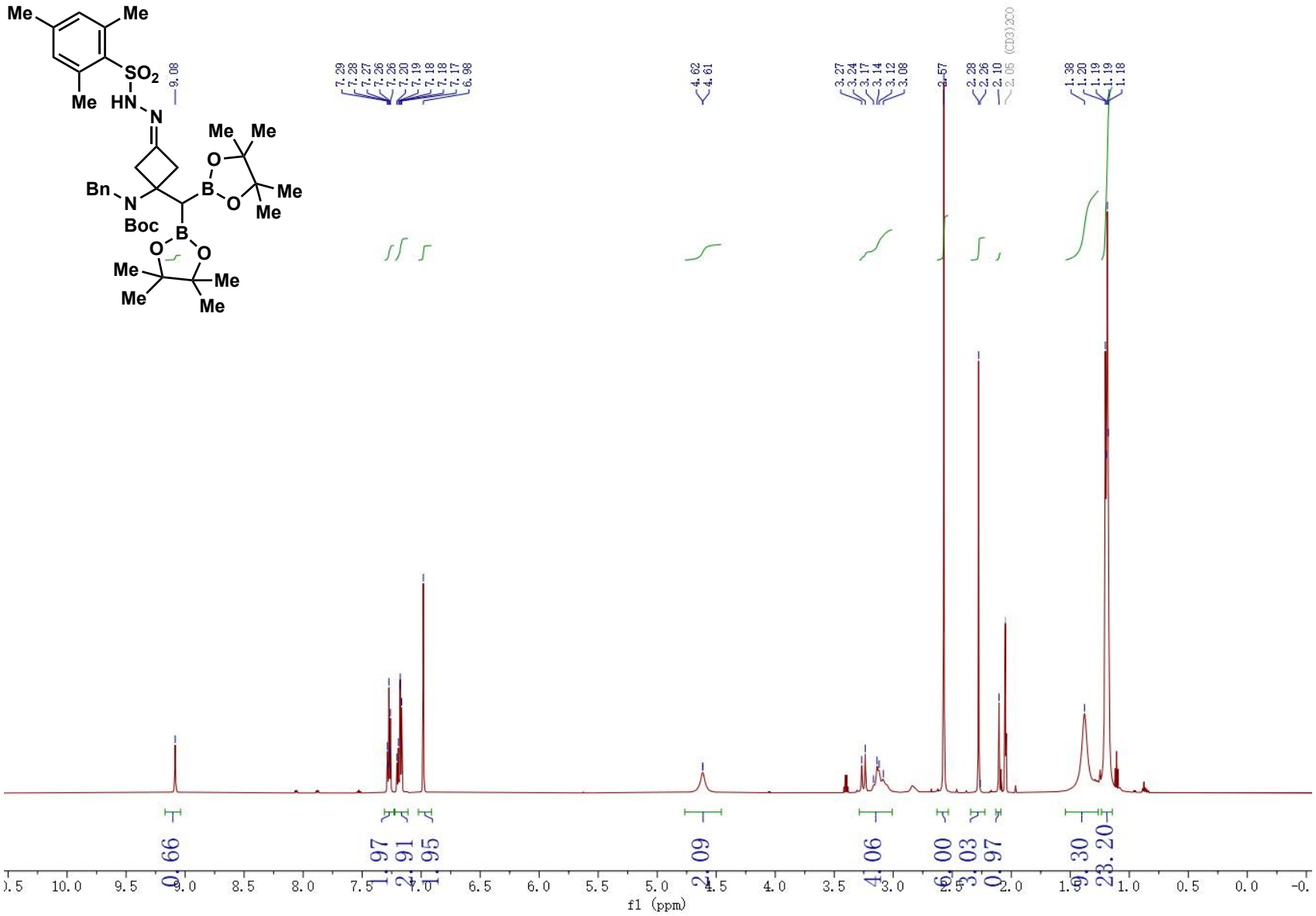
Compound SI-4 ^{1}H NMR



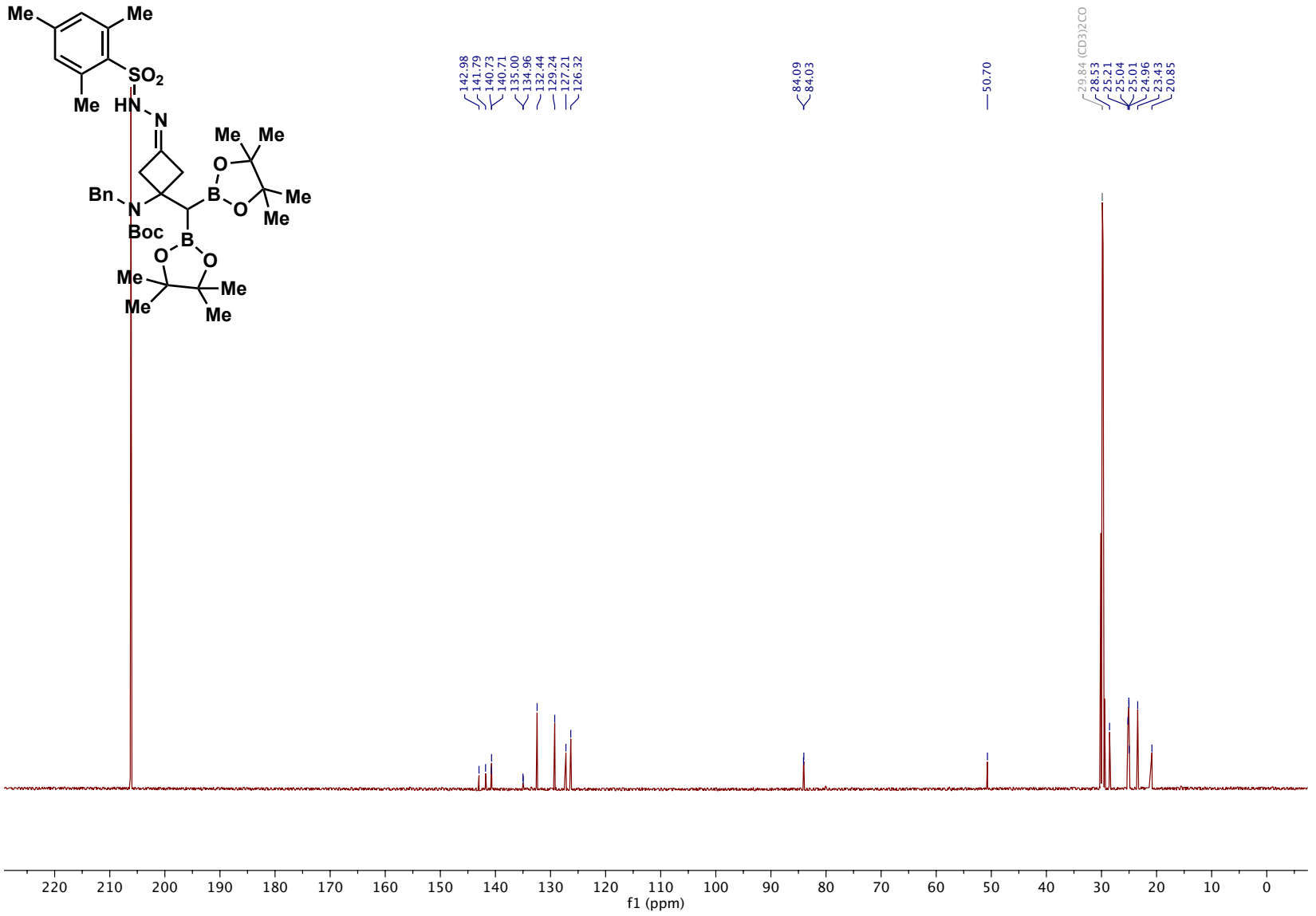
Compound SI-4 ^{13}C NMR



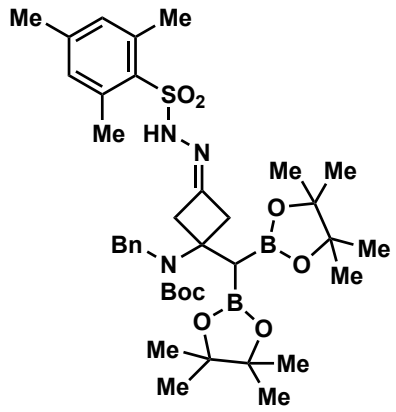
Compound SI-5 ^{1}H NMR



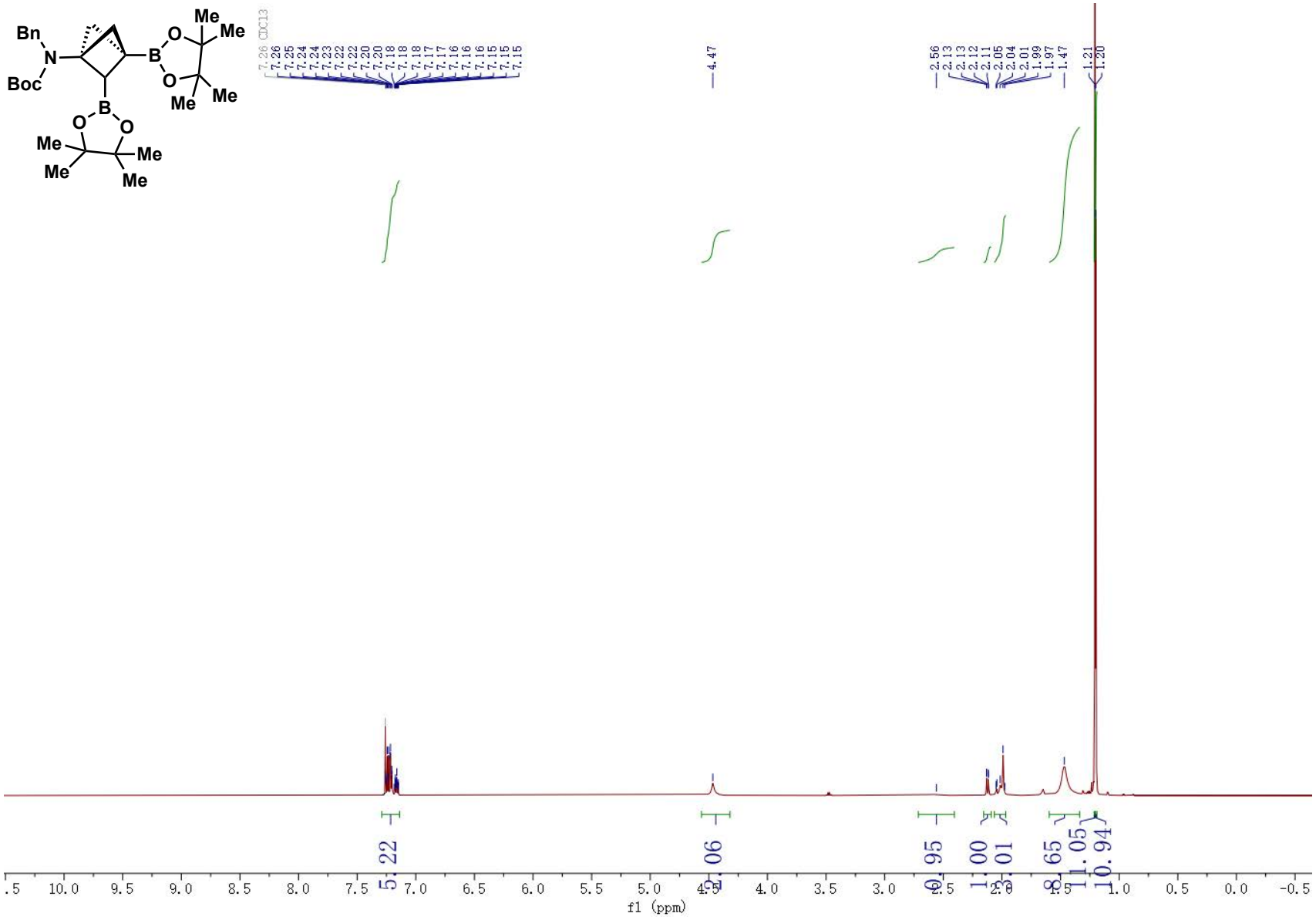
Compound SI-5 ^{13}C NMR



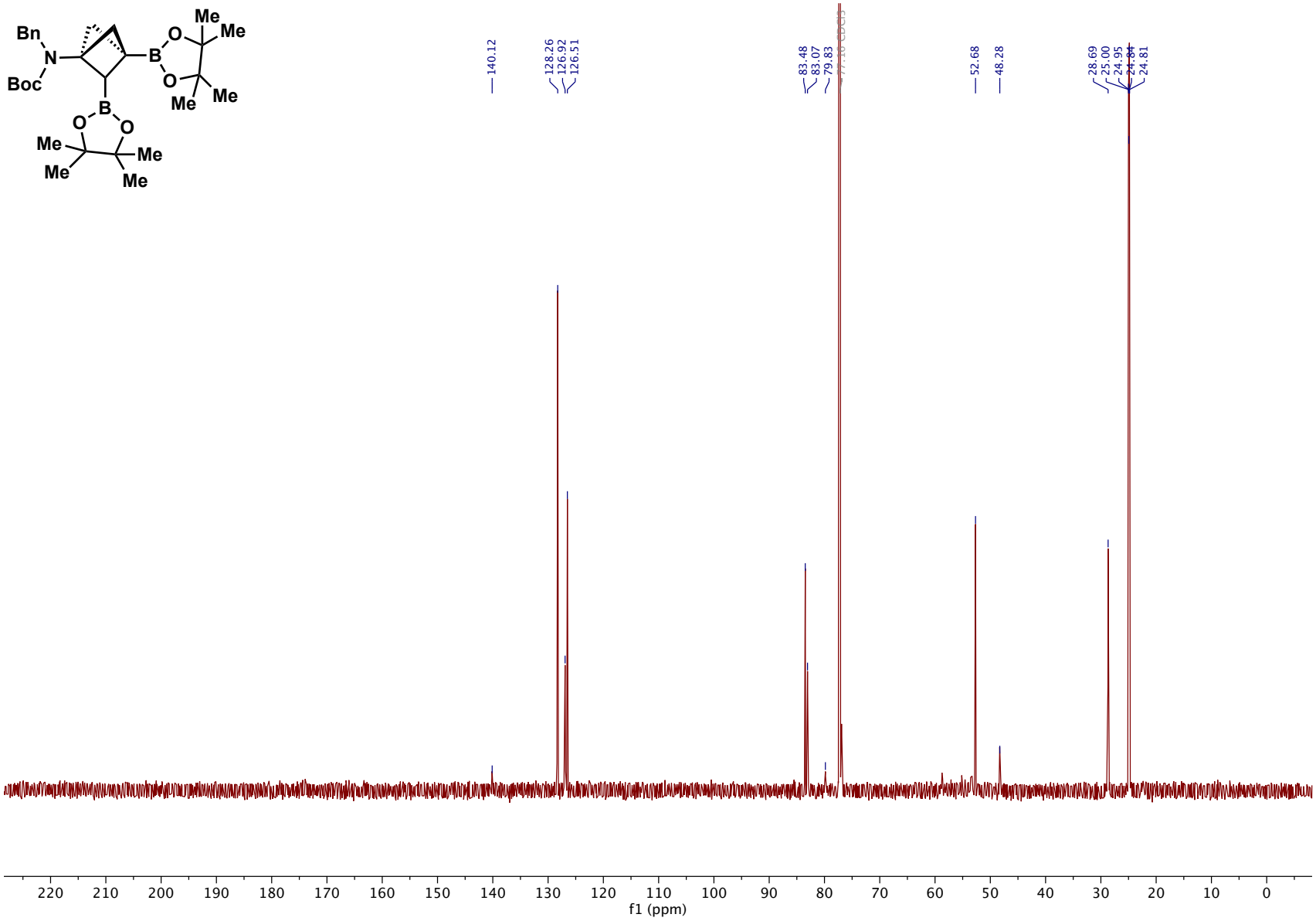
Compound SI-5 ^{11}B NMR



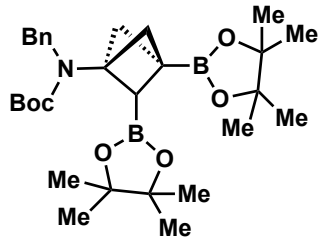
Compound 24 ^{1}H NMR



Compound 24 ^{13}C NMR



Compound 24 ^{11}B NMR



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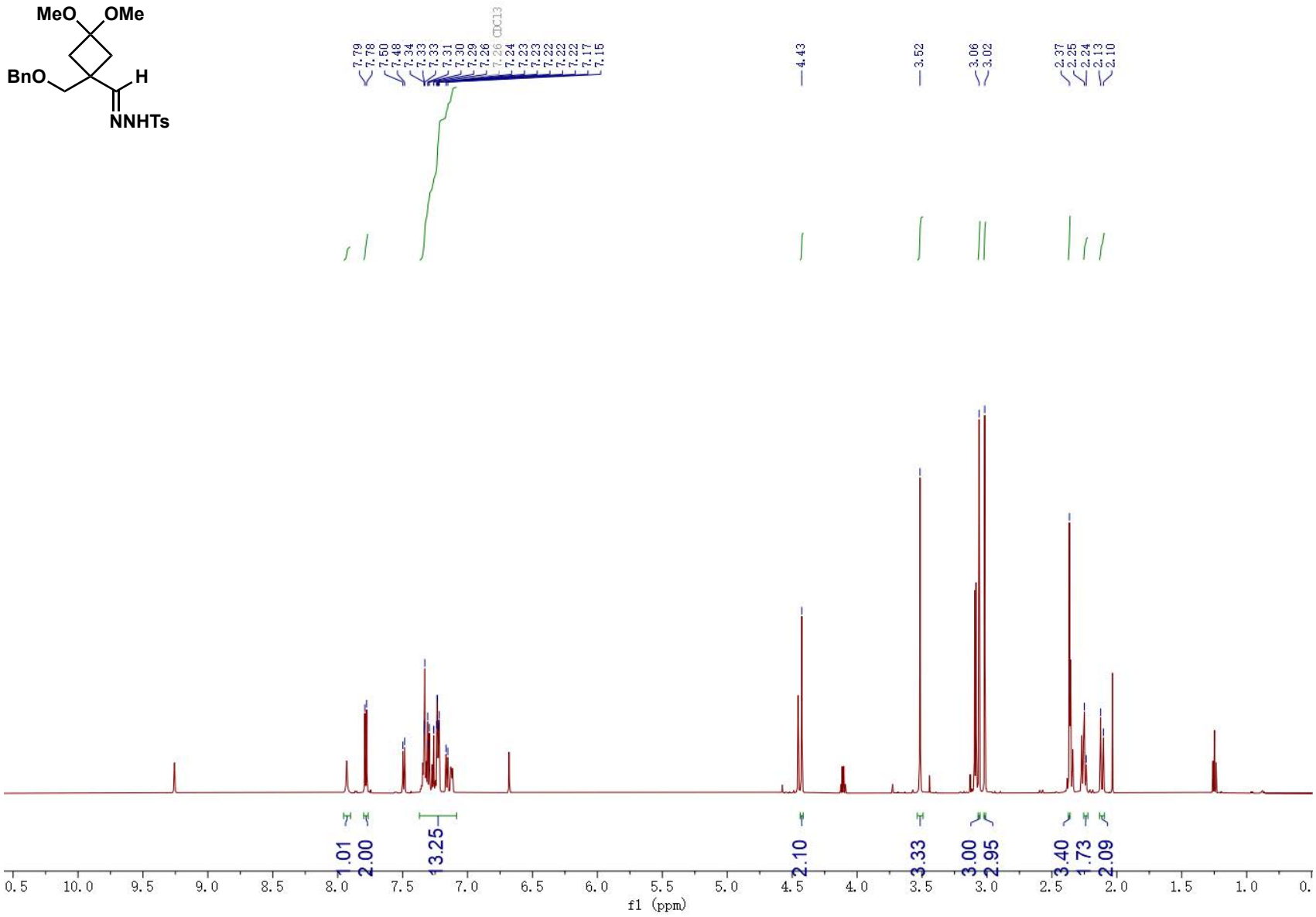
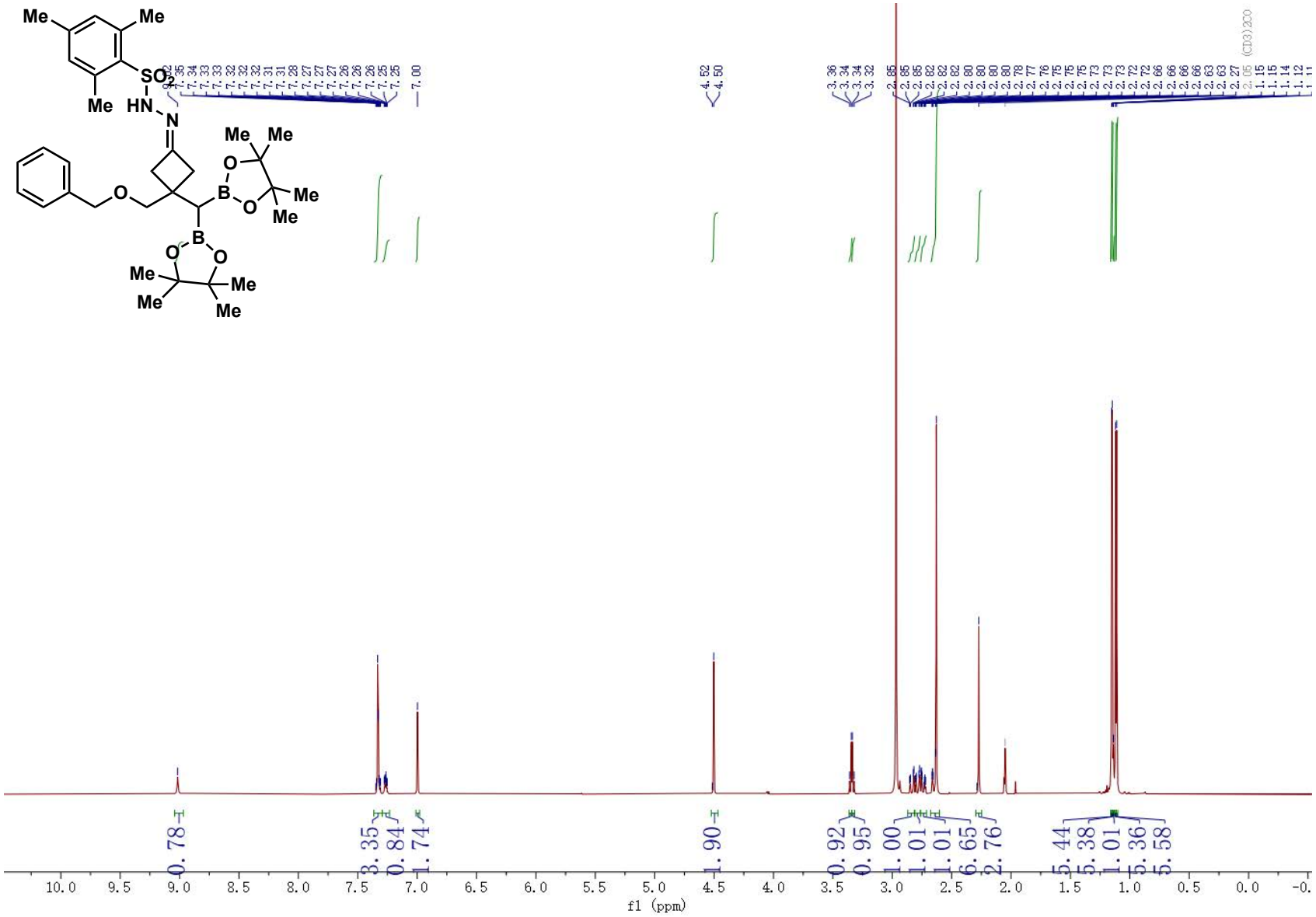
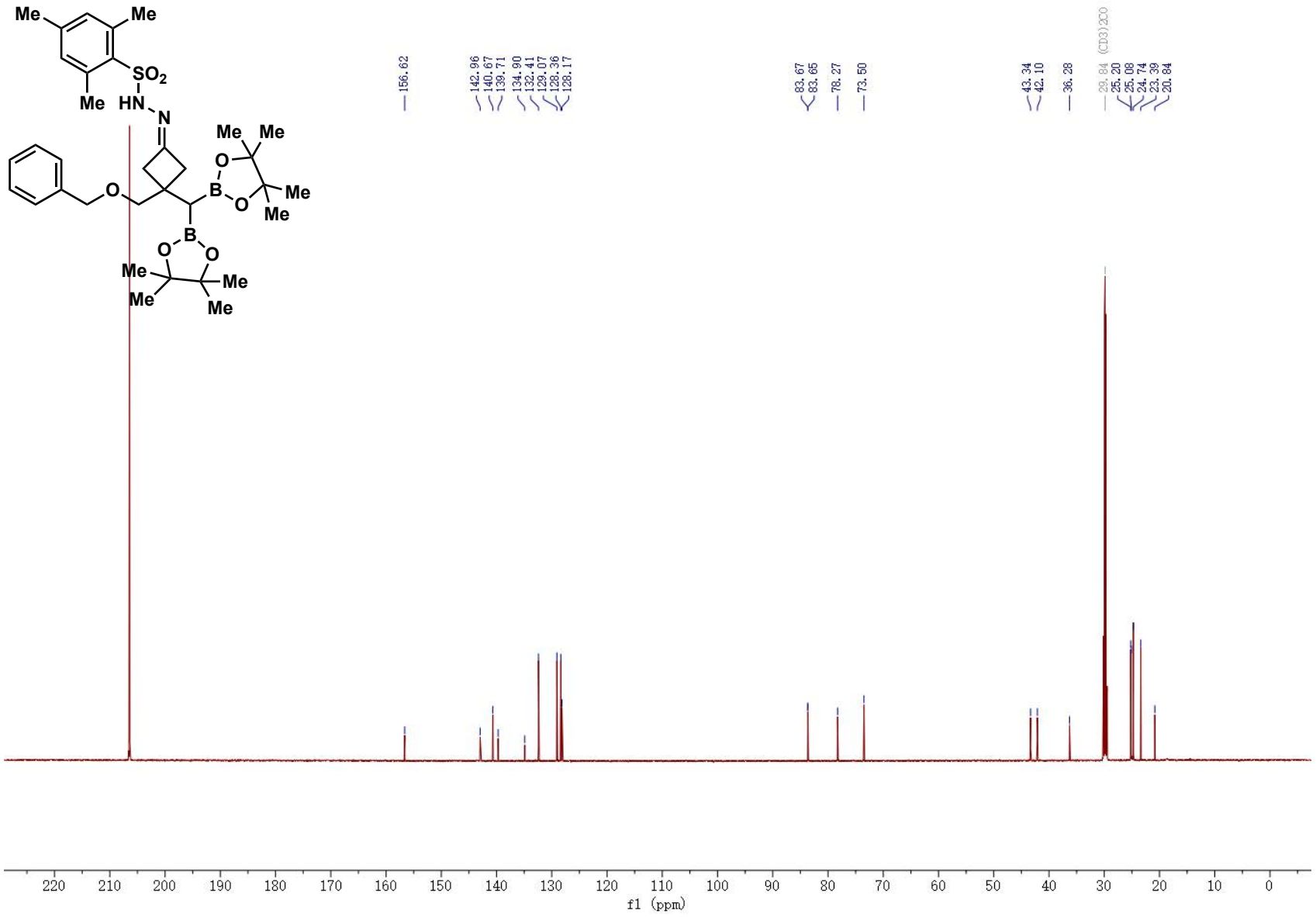


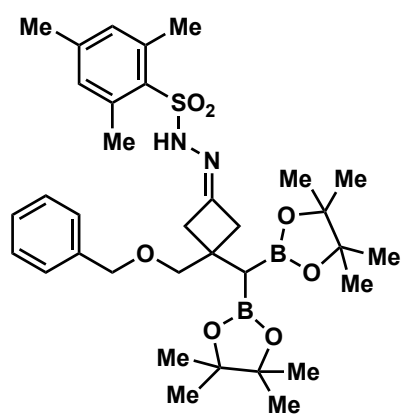
Compound SI-7 ^{1}H NMR



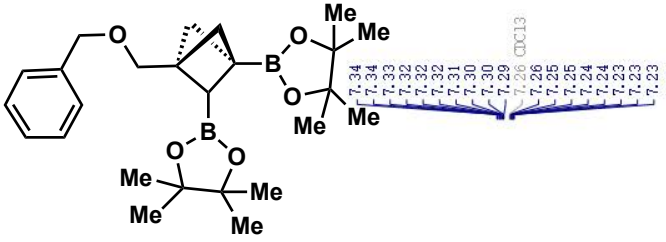
Compound SI-7 ^{13}C NMR



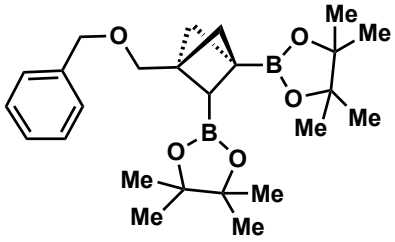
Compound SI-7 ^{11}B NMR



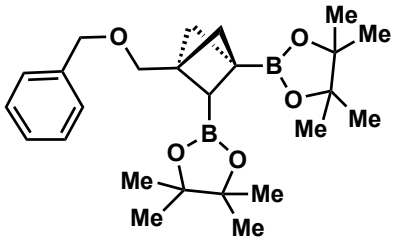
Compound 25 ^{1}H NMR



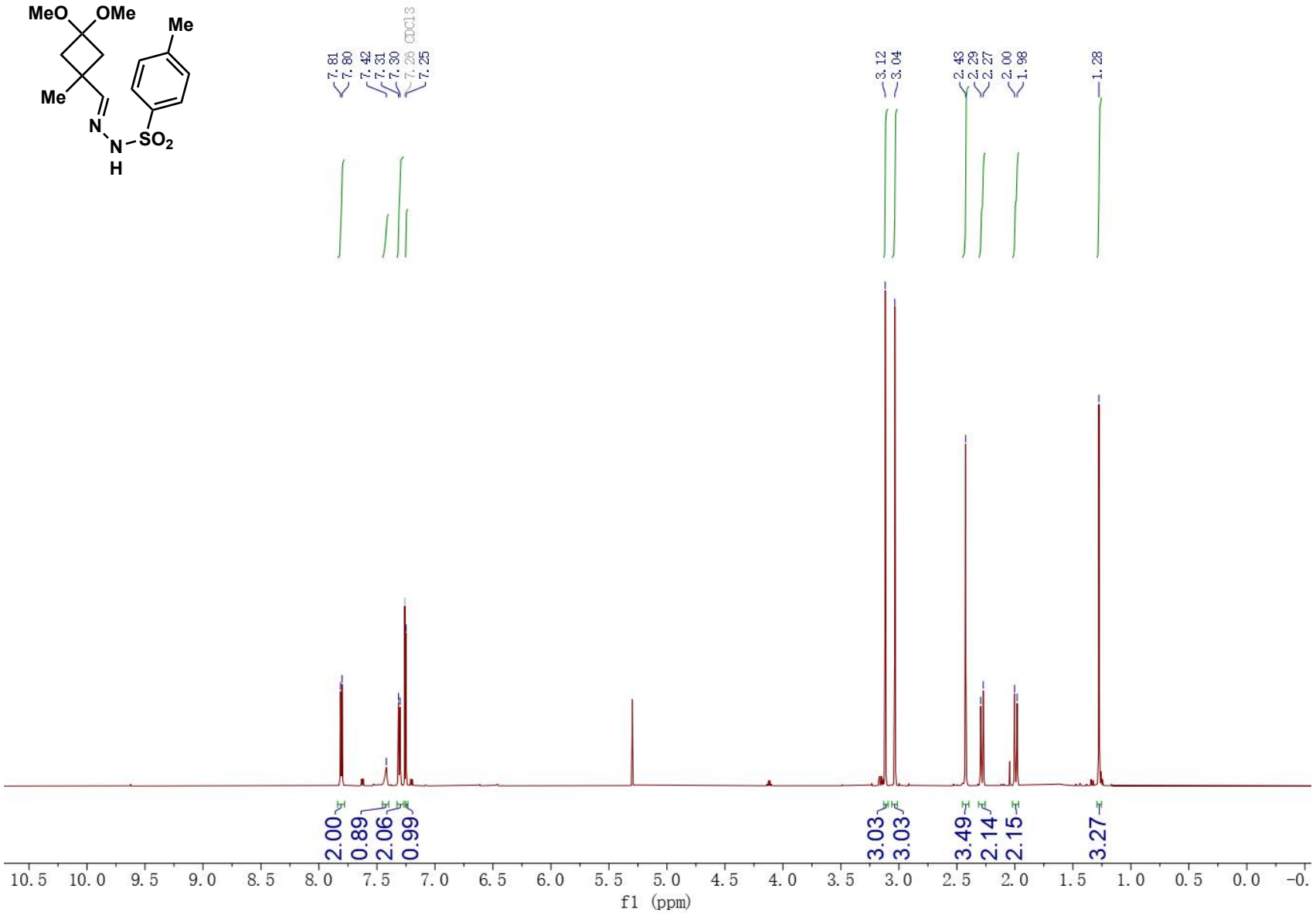
Compound 25 ^{13}C NMR



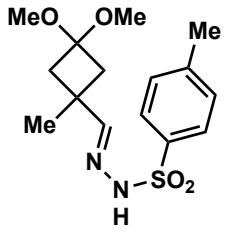
Compound 25 ^{11}B NMR



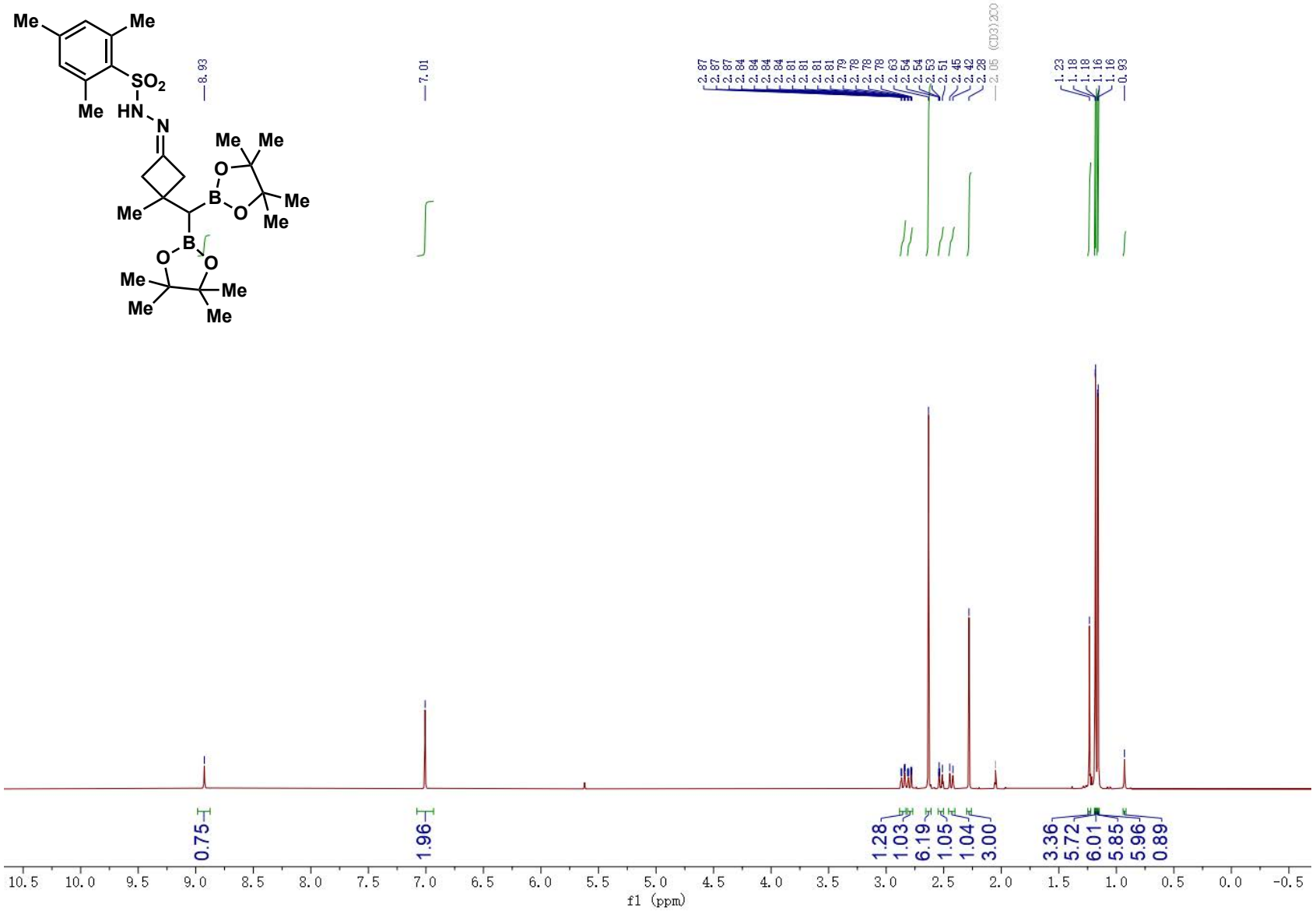
Compound SI-9 ^{1}H NMR



Compound SI-9 ^{13}C NMR



Compound SI-10 ^{1}H NMR



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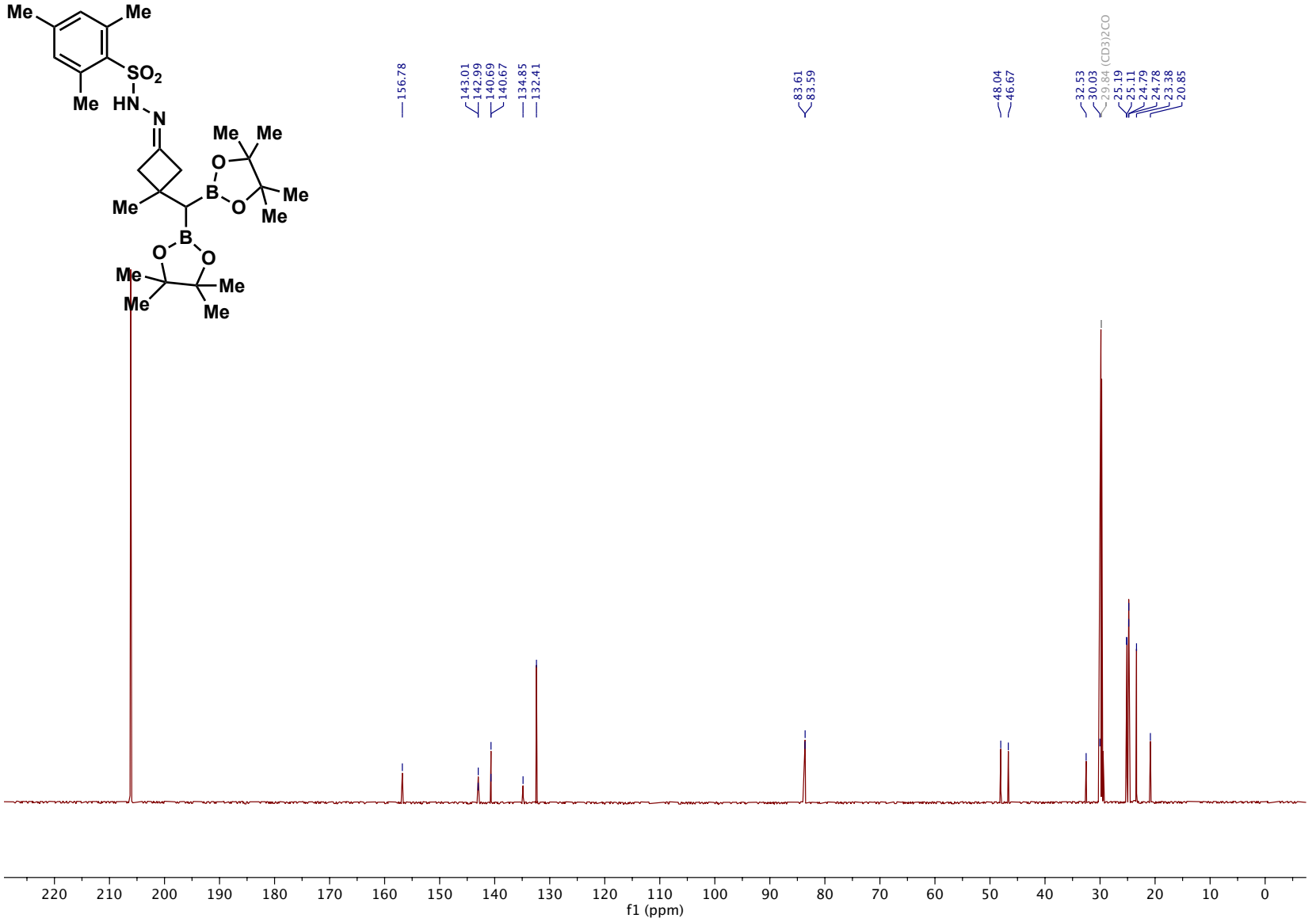

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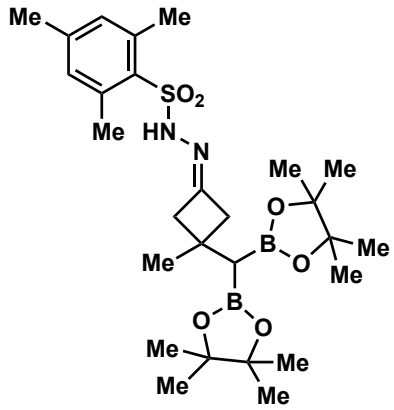
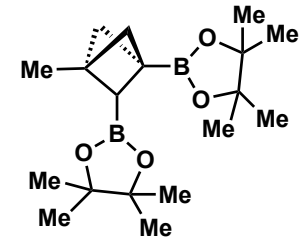
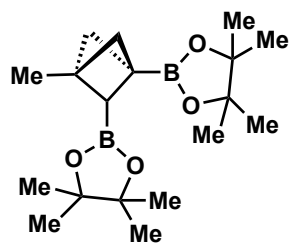


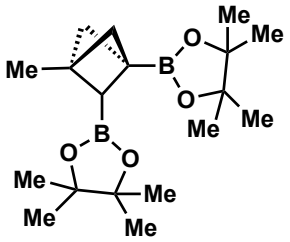
Compound 13 ^{1}H NMR



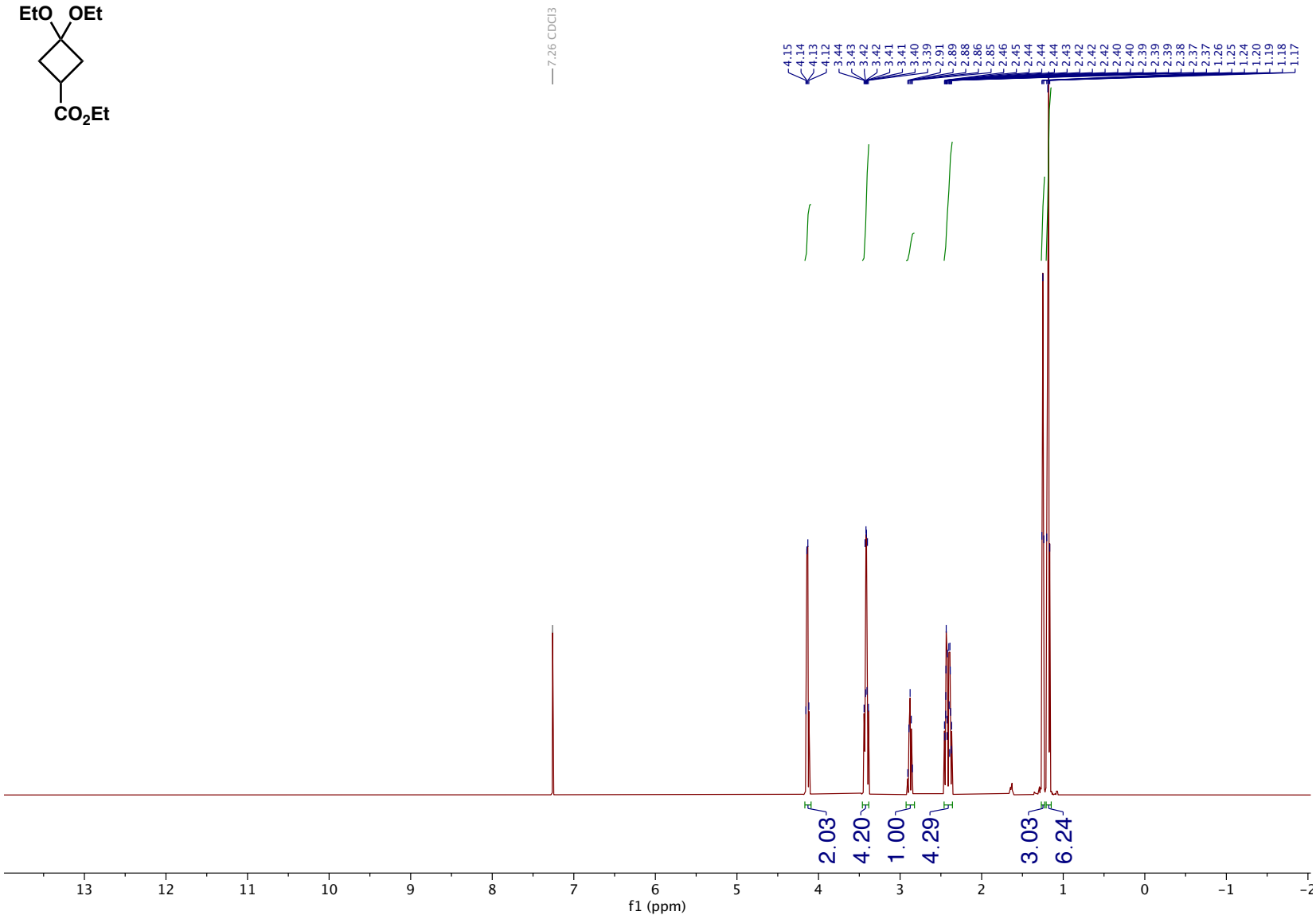
Compound 13 ^{13}C NMR



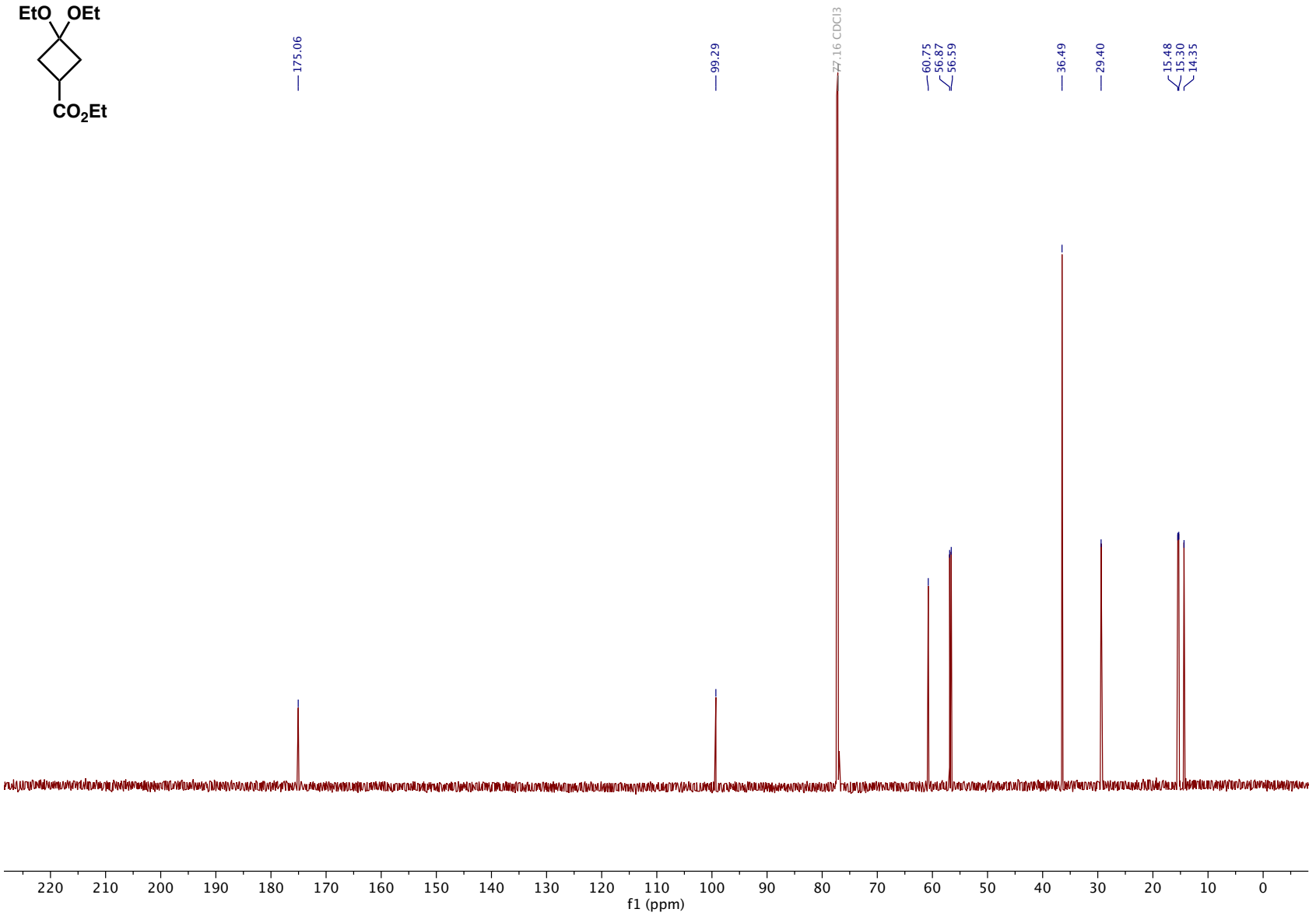
Compound 13 ^{11}B NMR



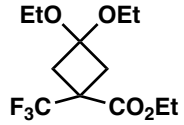
Compound SI-12 ^{1}H NMR



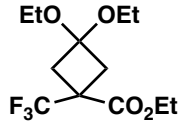
Compound SI-12 ^{13}C NMR



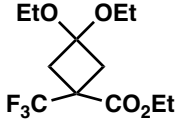
Compound SI-13 ^{1}H NMR



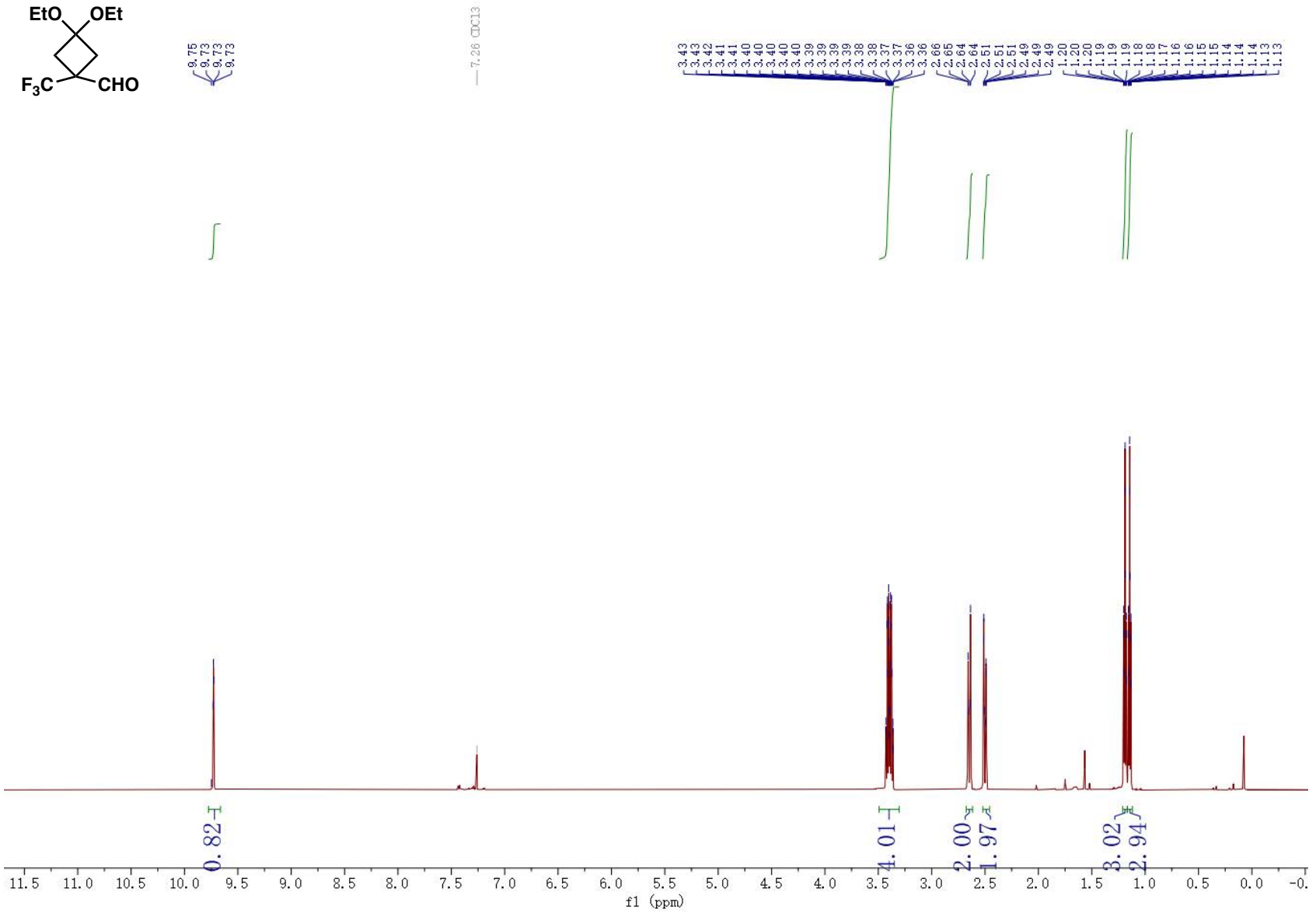
Compound SI-13 ^{13}C NMR



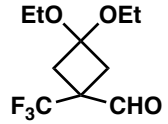
Compound SI-13 ^{19}F NMR



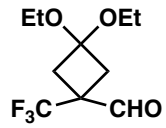
Compound SI-14 ^{1}H NMR



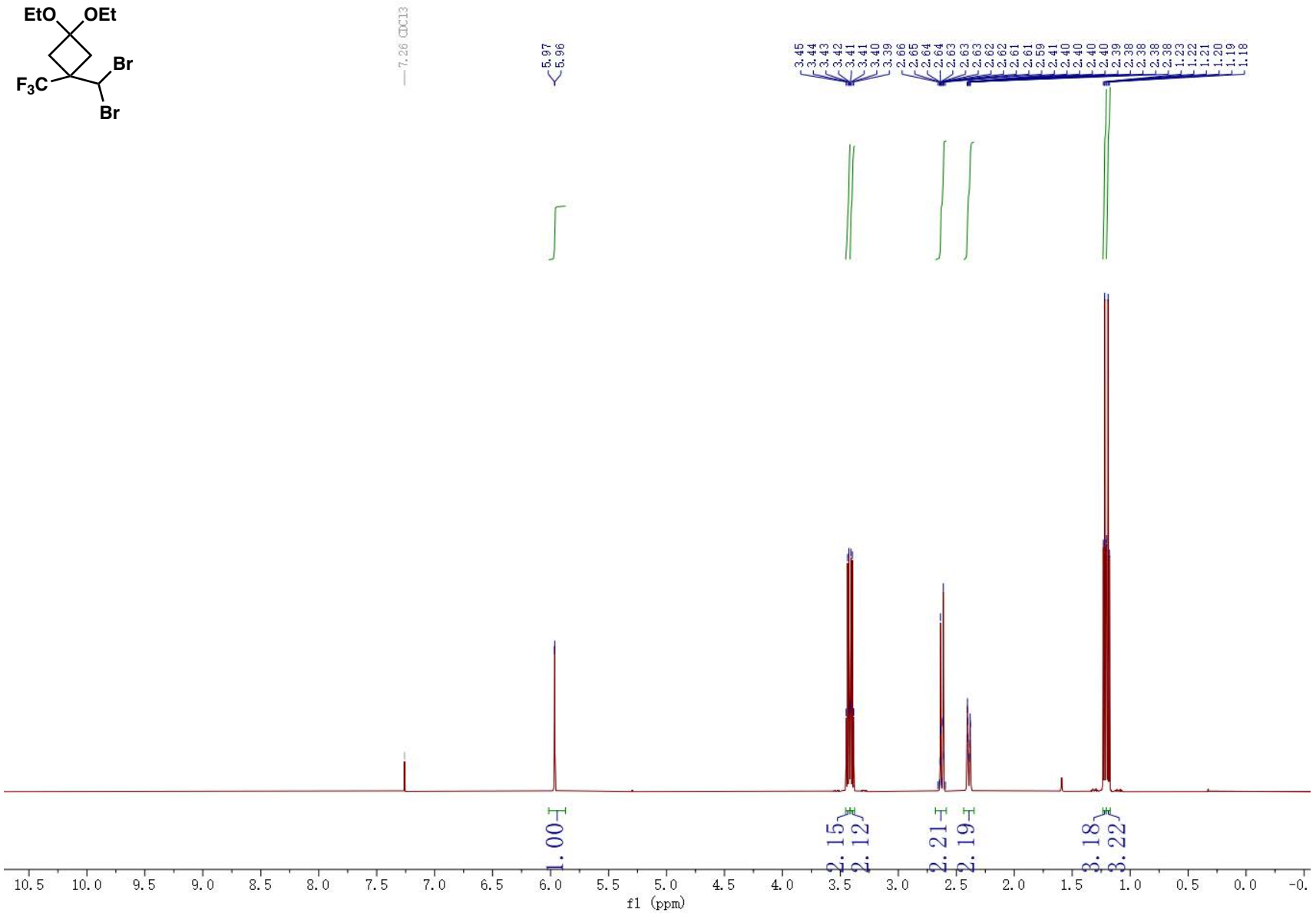
Compound SI-14 ^{13}C NMR



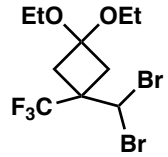
Compound SI-14 ^{19}F NMR



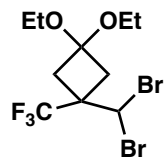
Compound SI-15 ^{1}H NMR



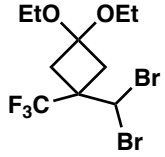
Compound SI-15 ^{13}C NMR



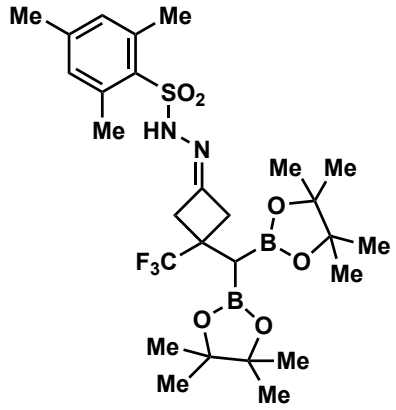
Compound SI-15 ^{19}F NMR

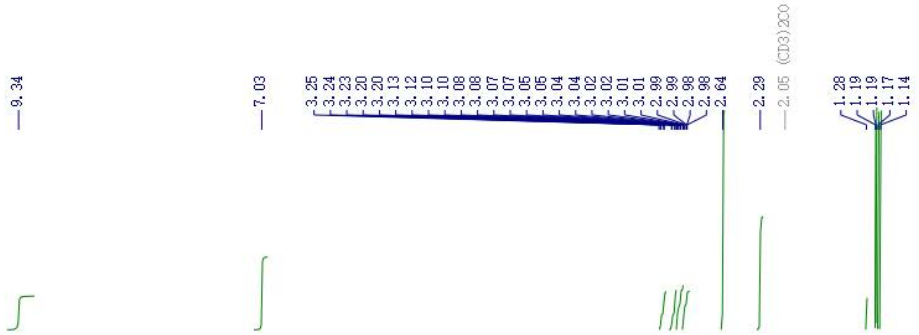


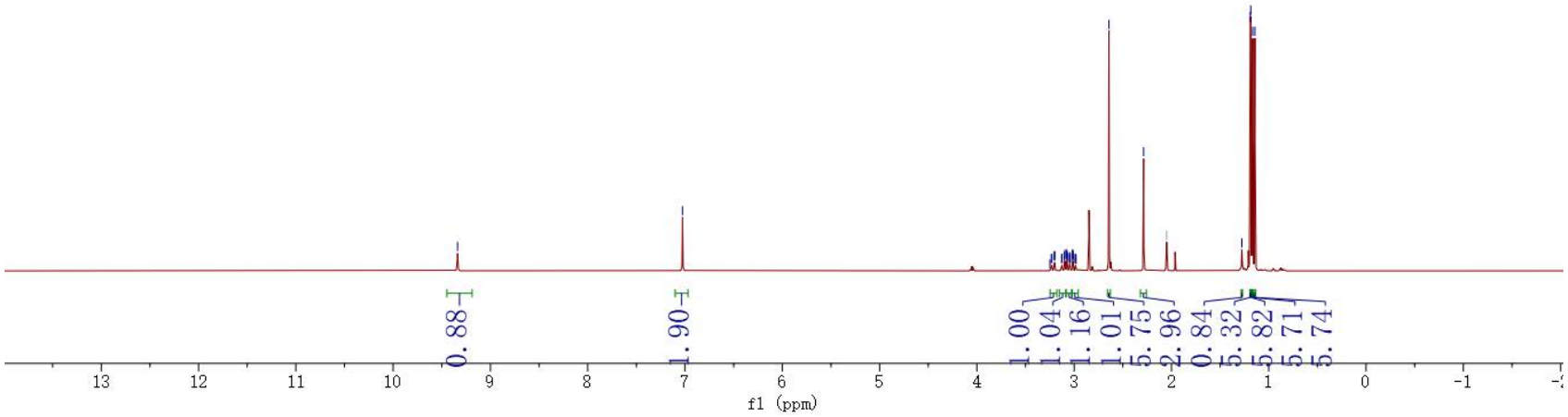
Compound SI-15 ^{11}B NMR



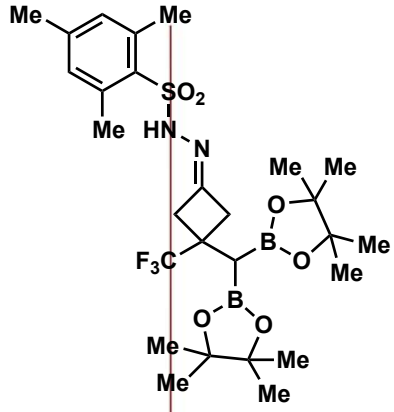
Compound SI-16 ^{1}H NMR



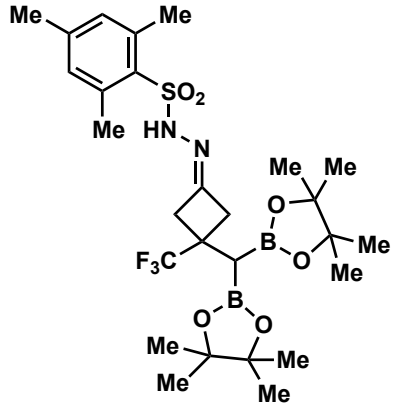




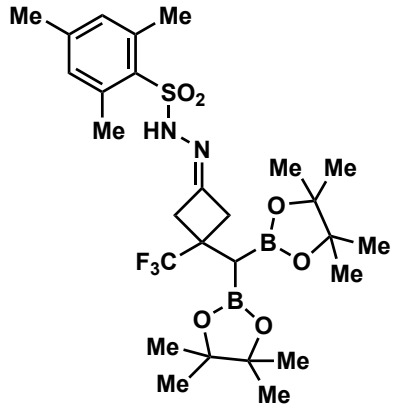
Compound SI-16 ^{13}C NMR



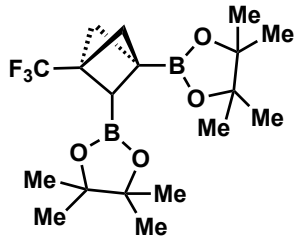
Compound SI-16 ^{11}B NMR



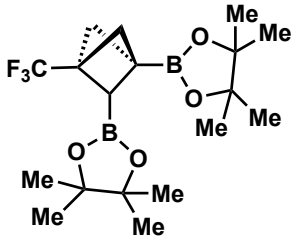
Compound SI-16 ^{19}F NMR



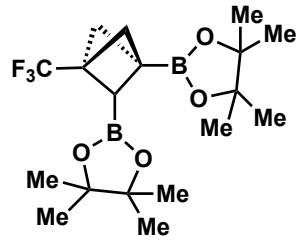
Compound 26 ^{1}H NMR



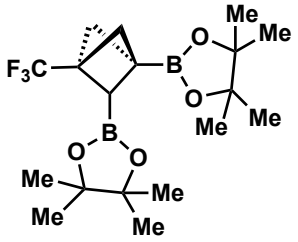
Compound 26 ^{13}C NMR



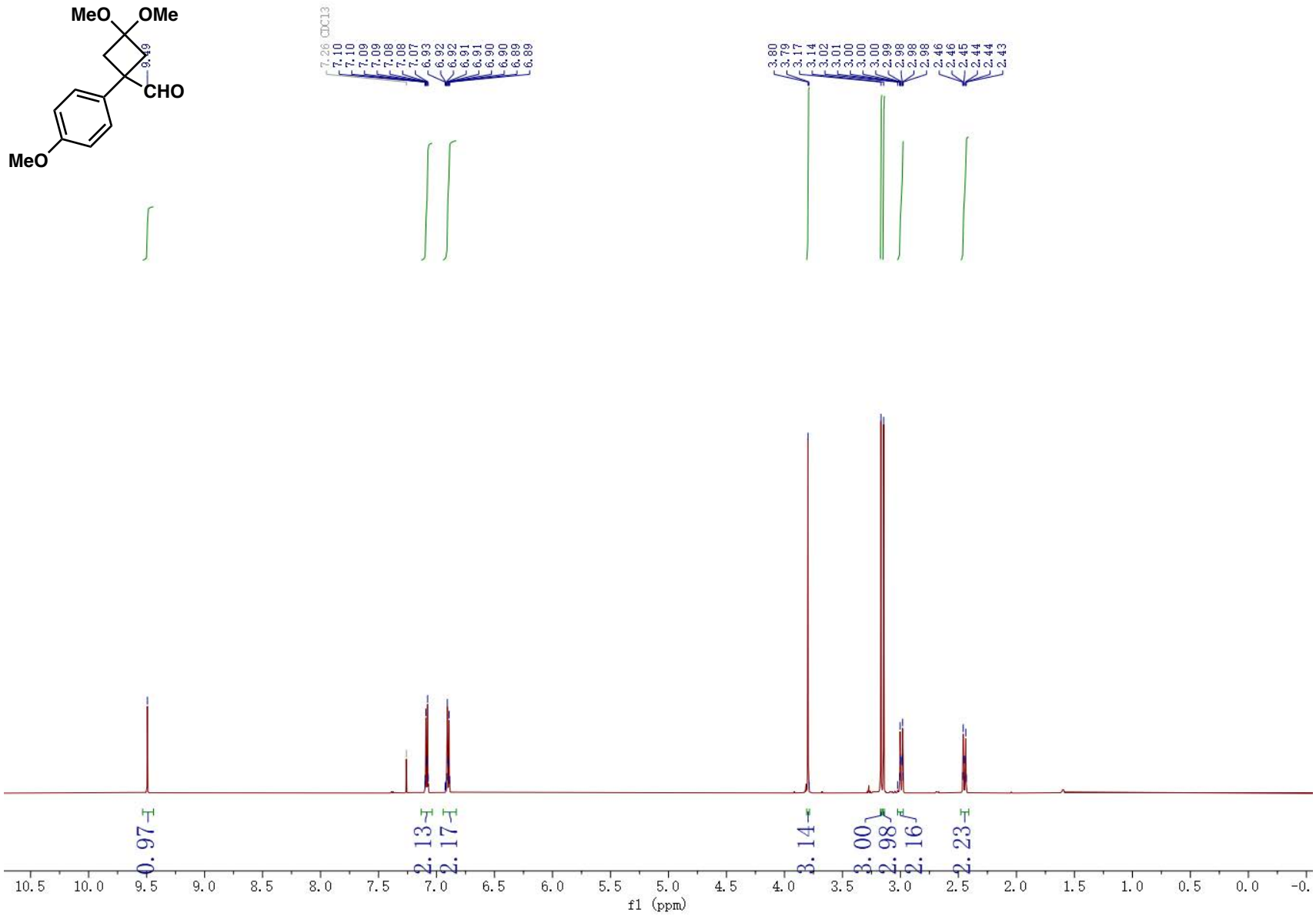
Compound 26 ^{11}B NMR



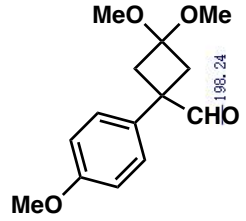
Compound 26 ^{19}F NMR



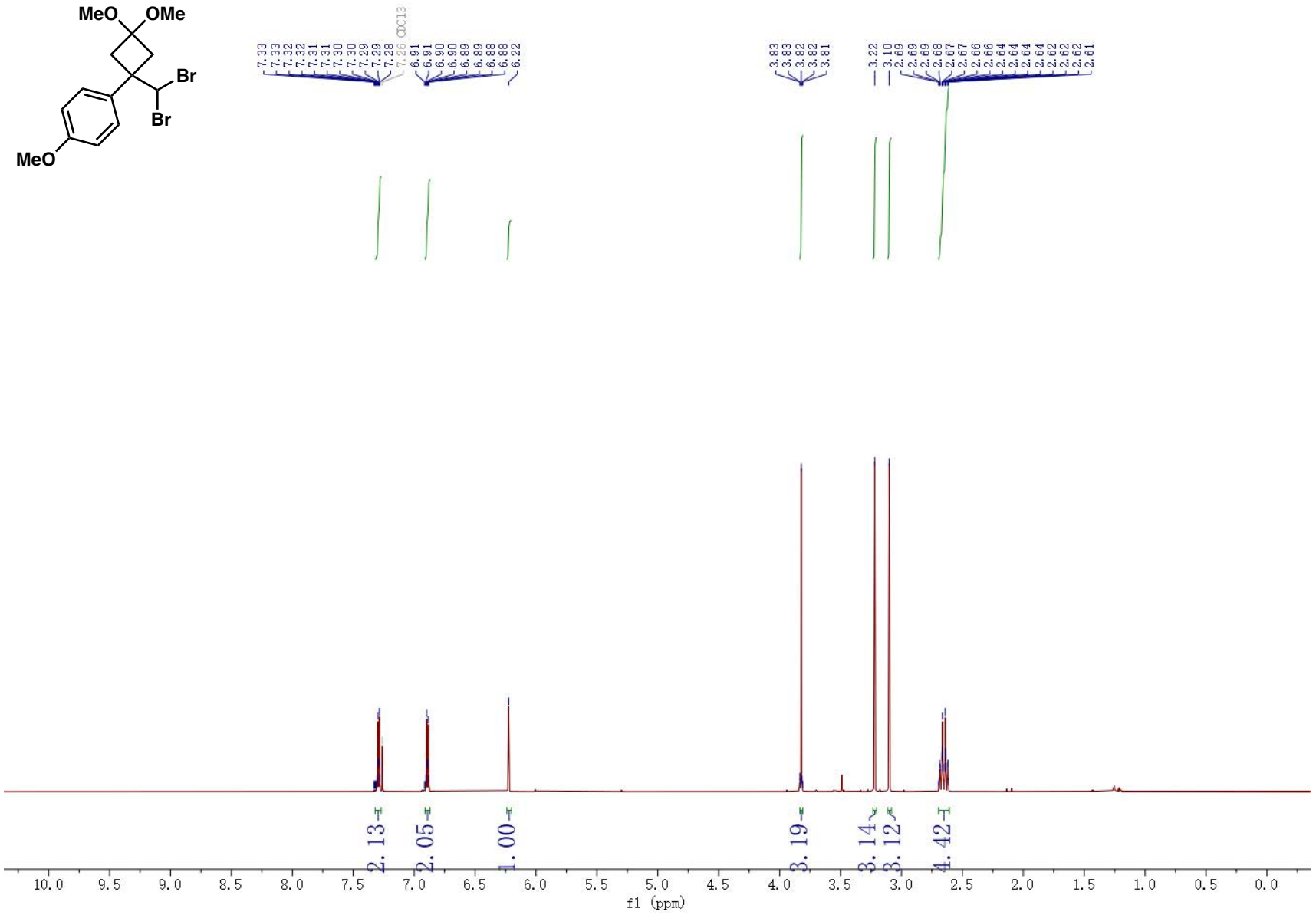
Compound SI-18 ^{1}H NMR



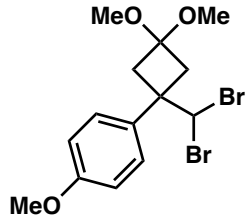
Compound SI-18 ^{13}C NMR



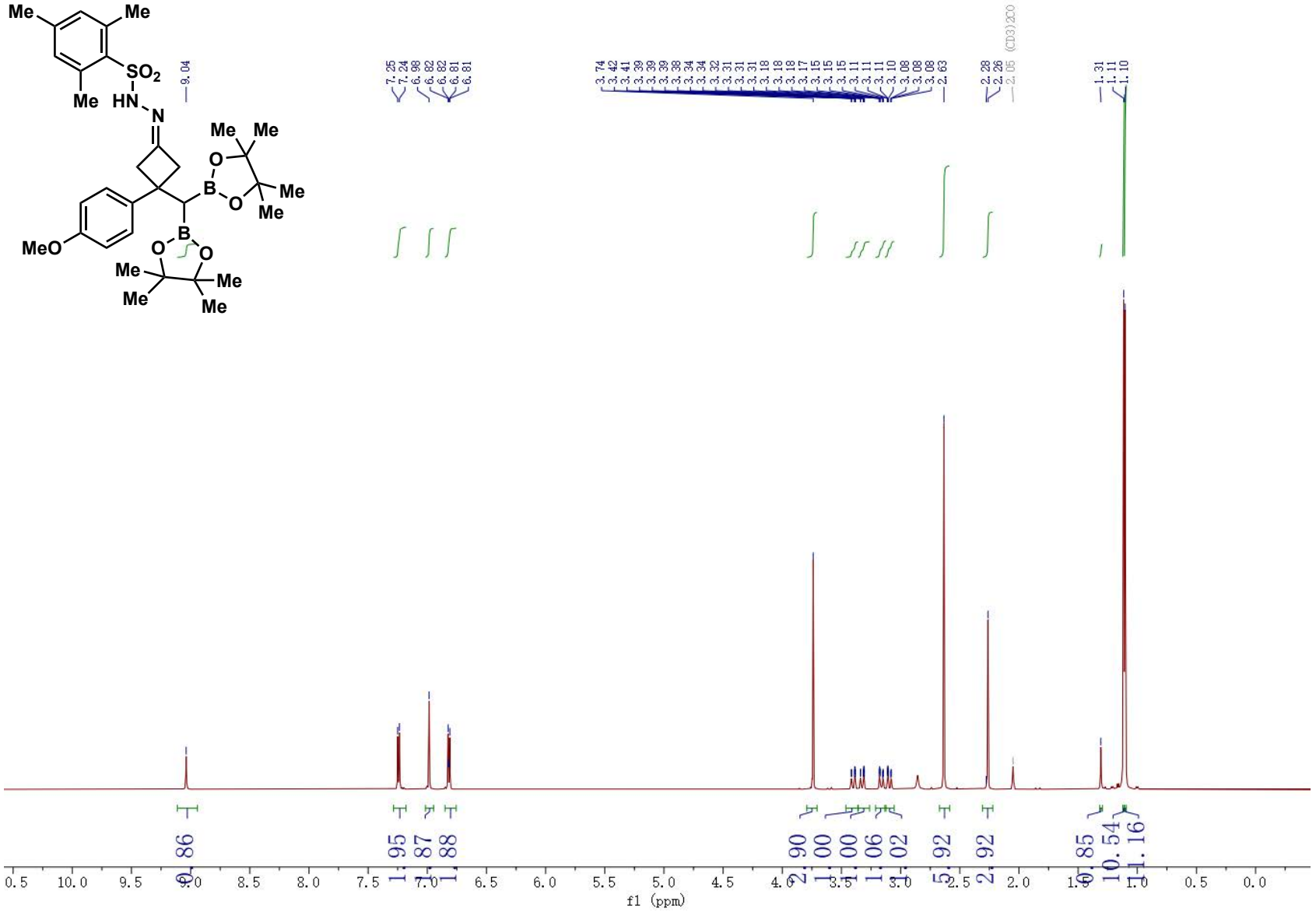
Compound SI-19 ^{1}H NMR



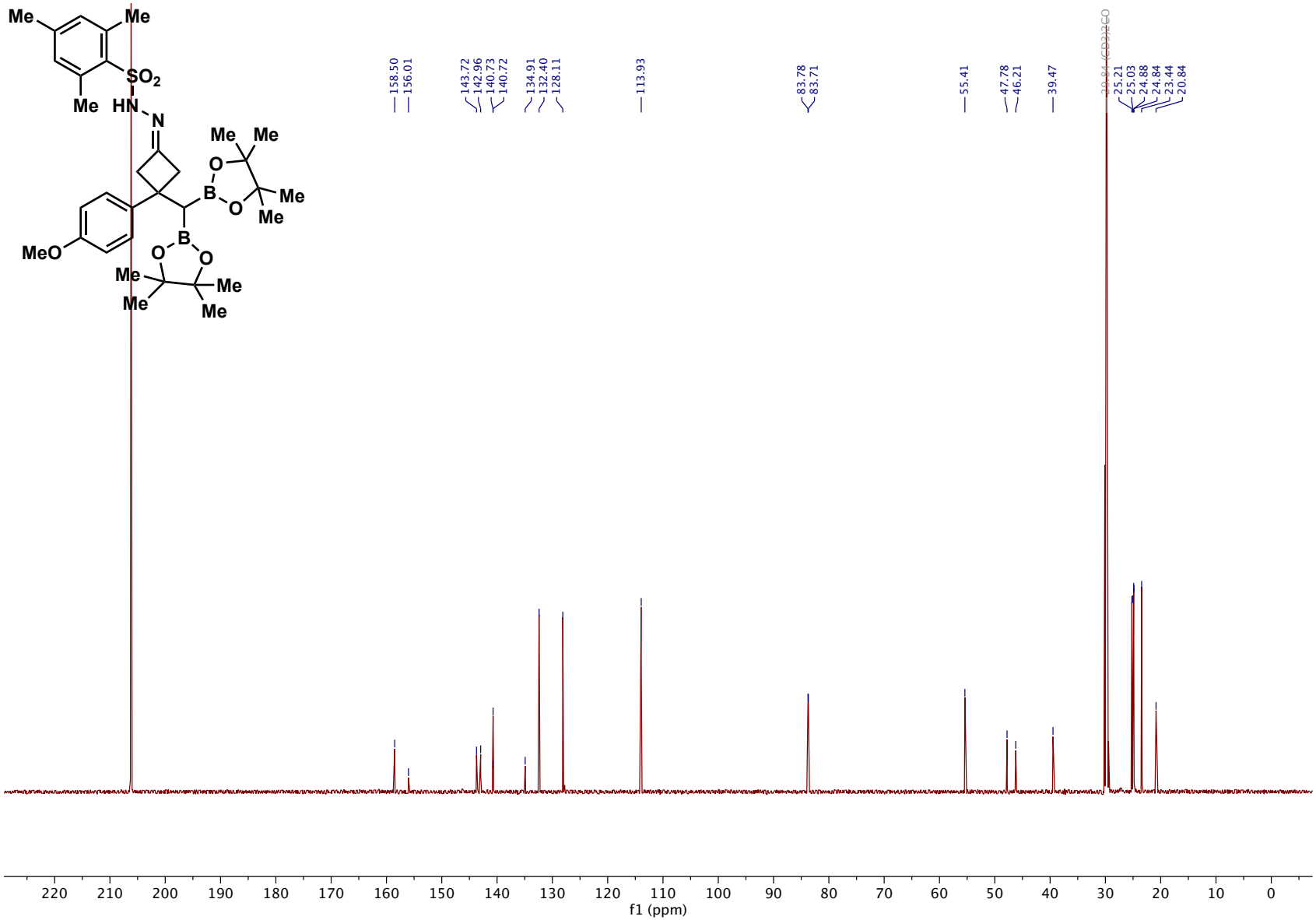
Compound SI-19 ^{13}C NMR



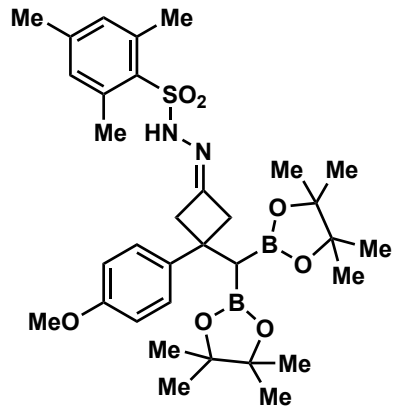
Compound SI-20 ^{1}H NMR



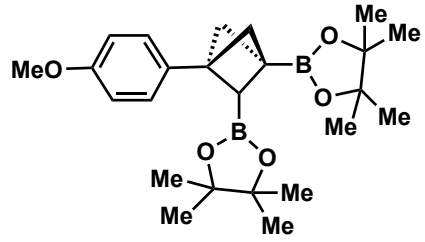
Compound SI-20 ^{13}C NMR



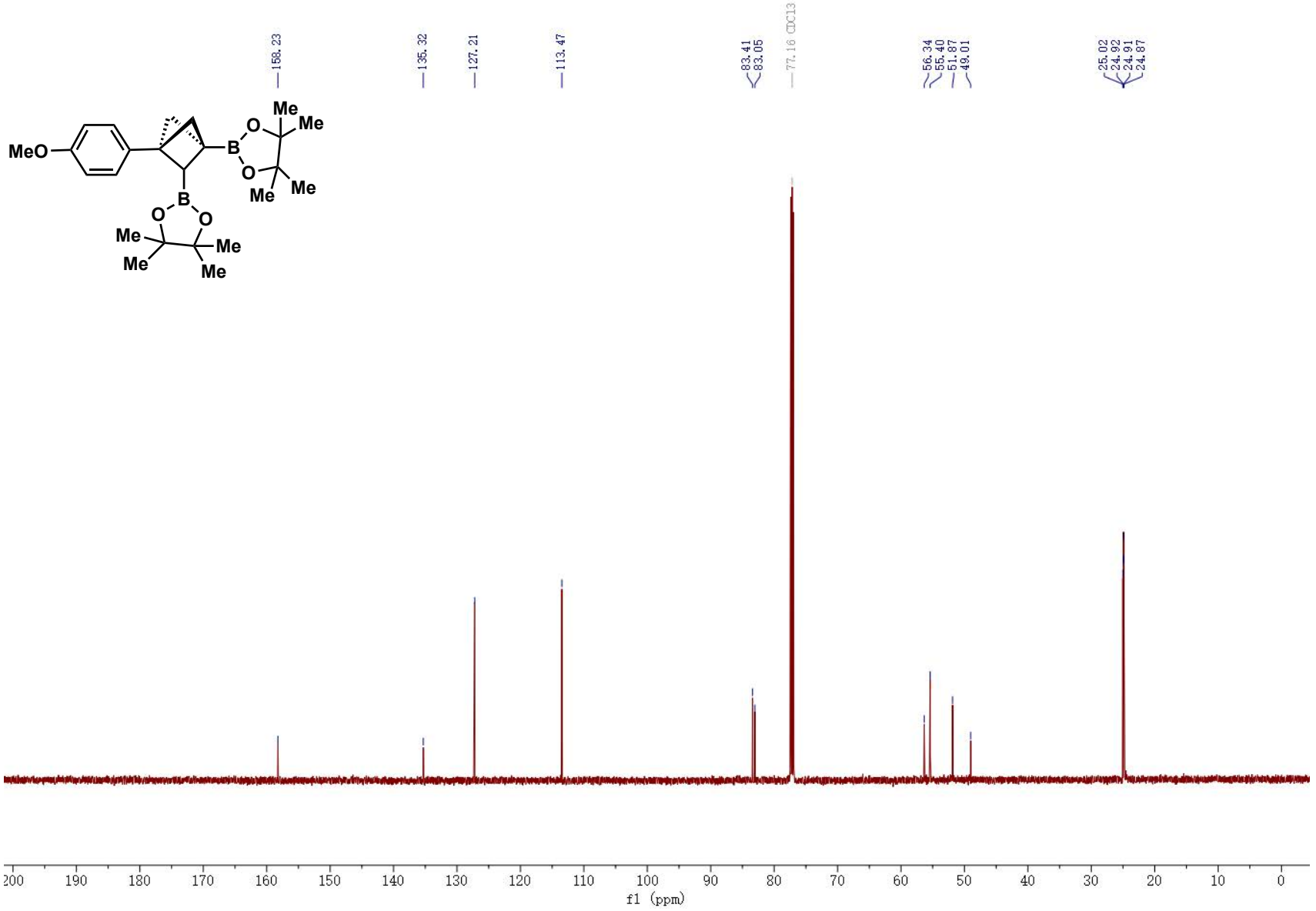
Compound SI-20 ^{11}B NMR



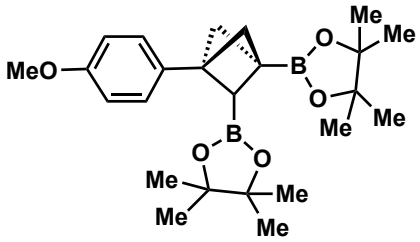
Compound 27 ^{1}H NMR



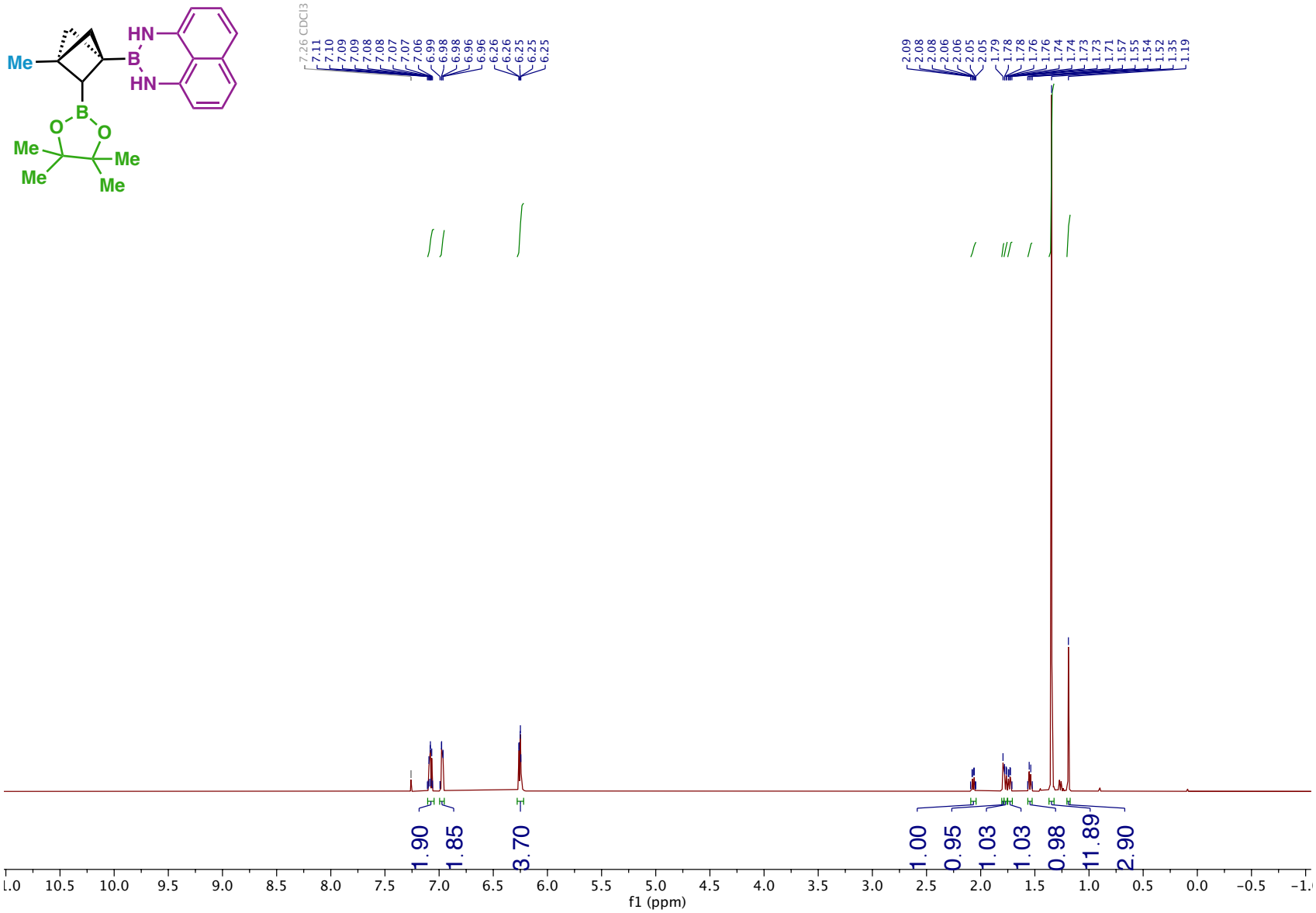
Compound 27 ^{13}C NMR



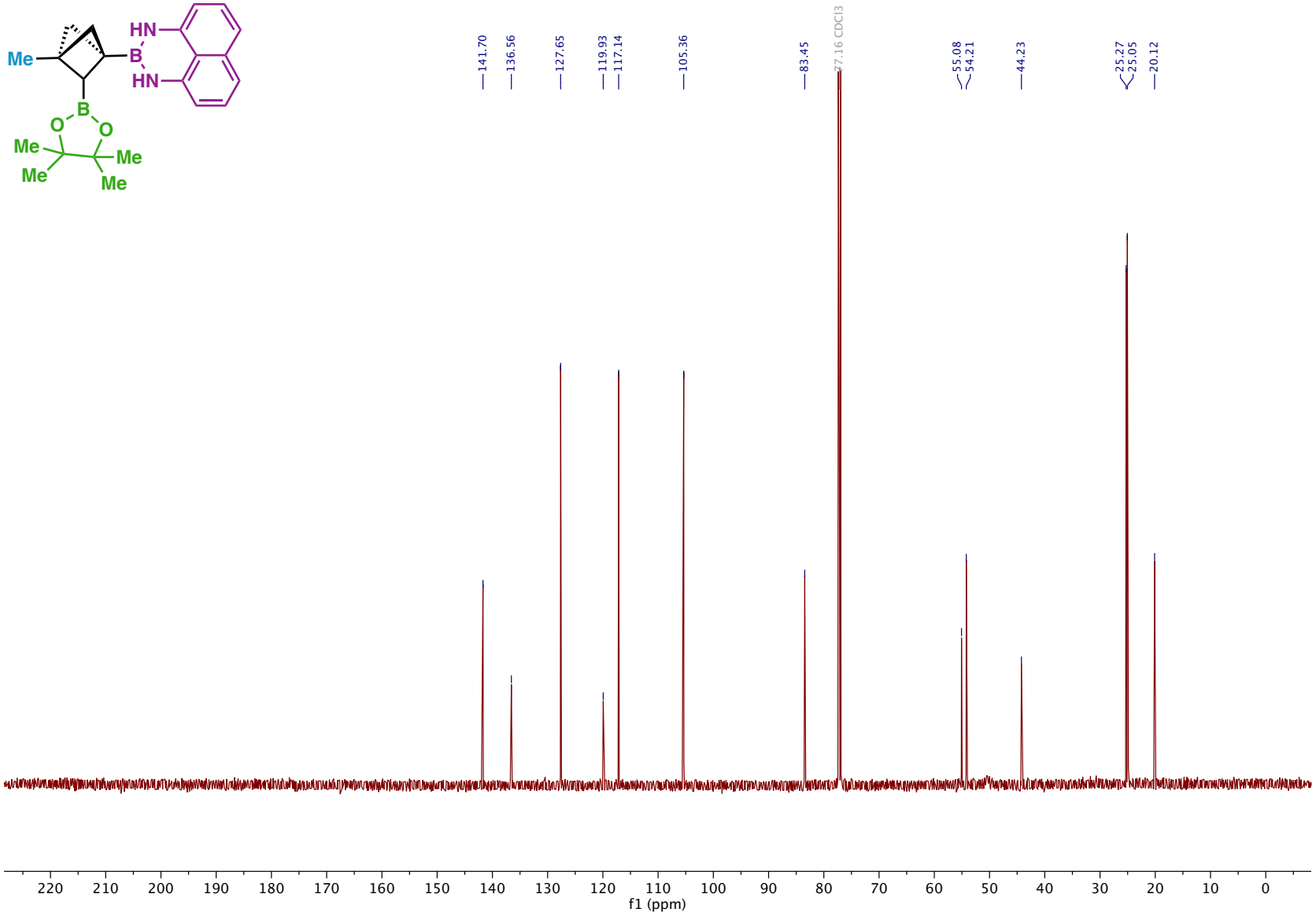
Compound 27 ^{11}B NMR



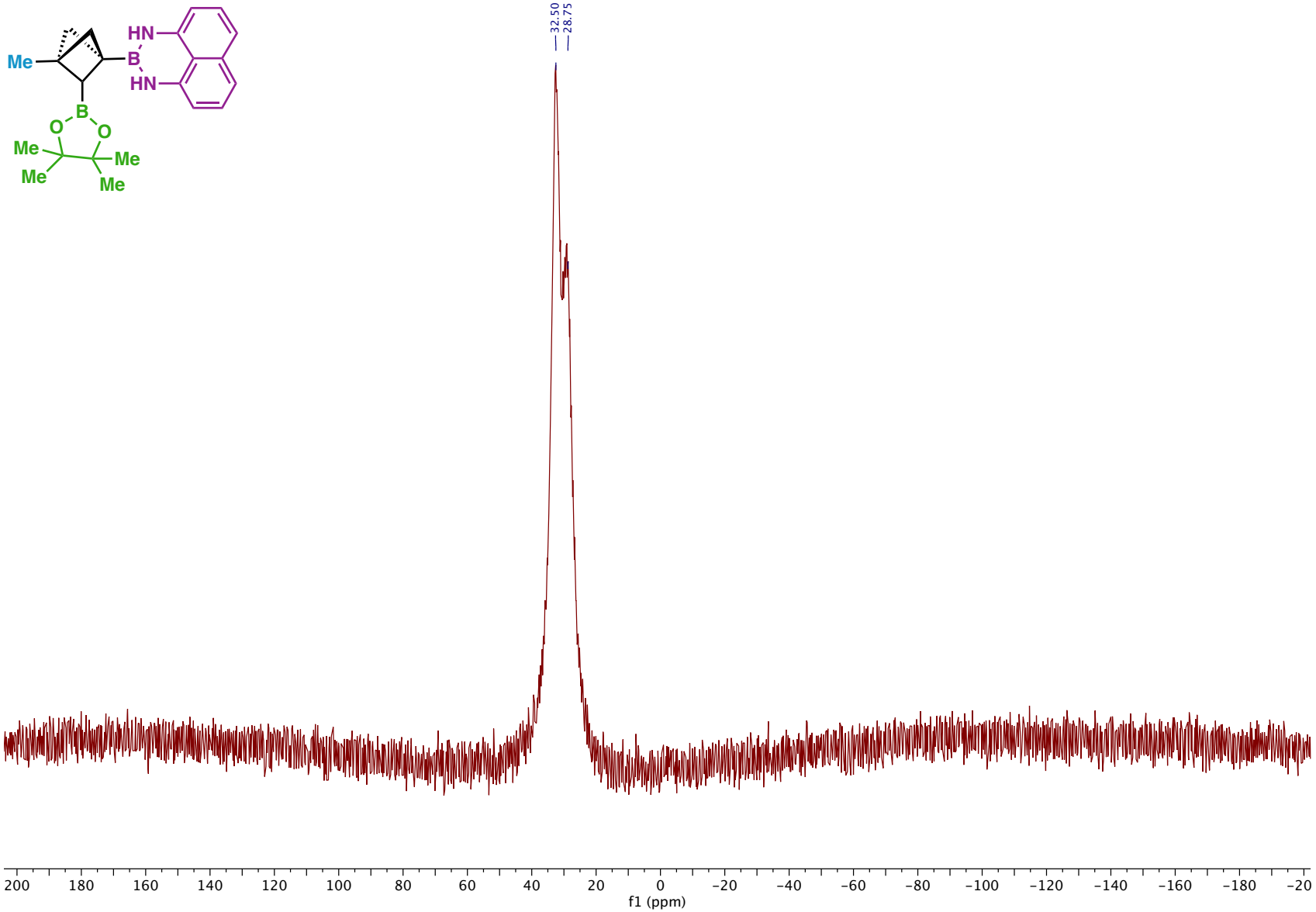
Compound 15 ^{1}H NMR



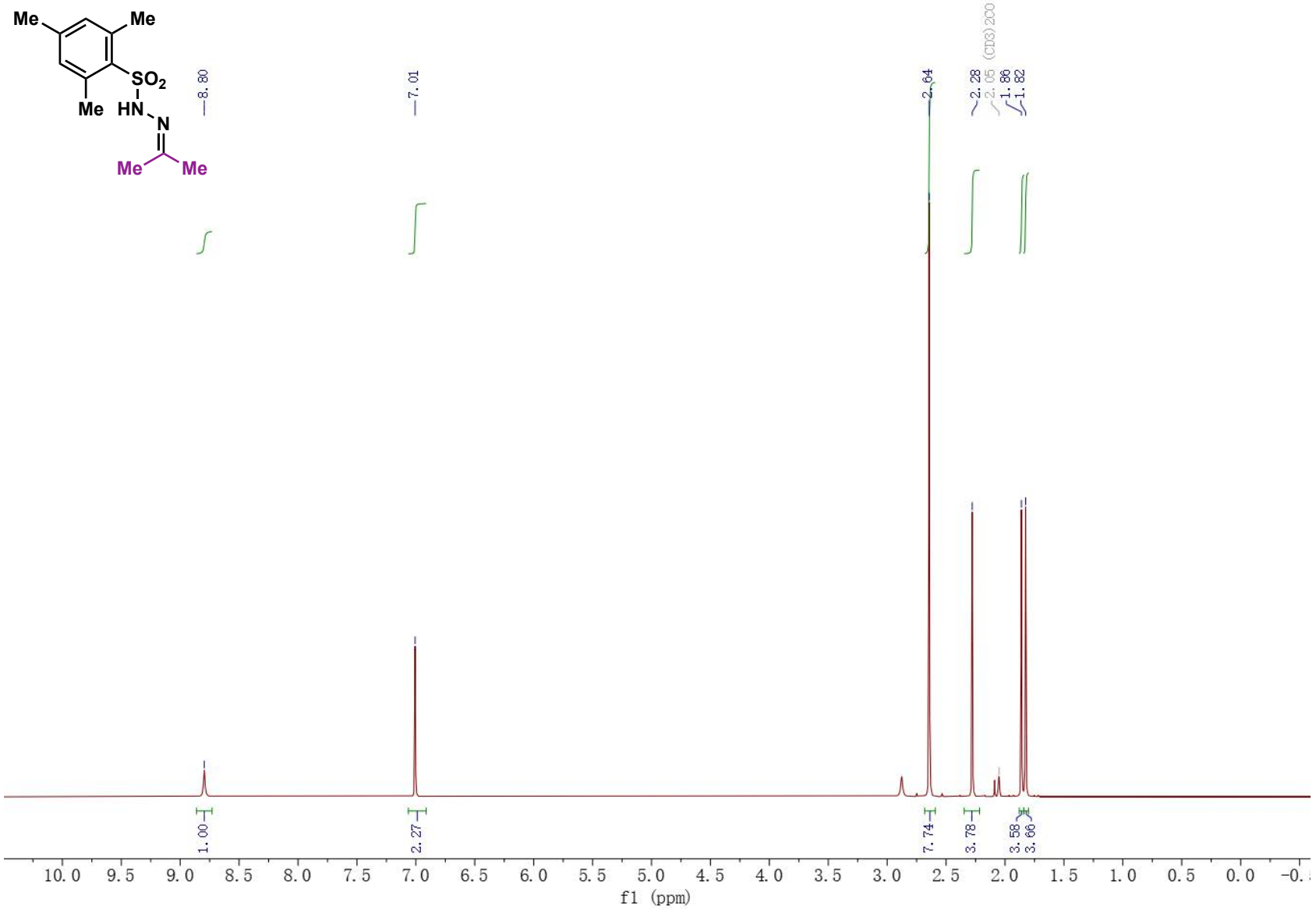
Compound 15 ^{13}C NMR



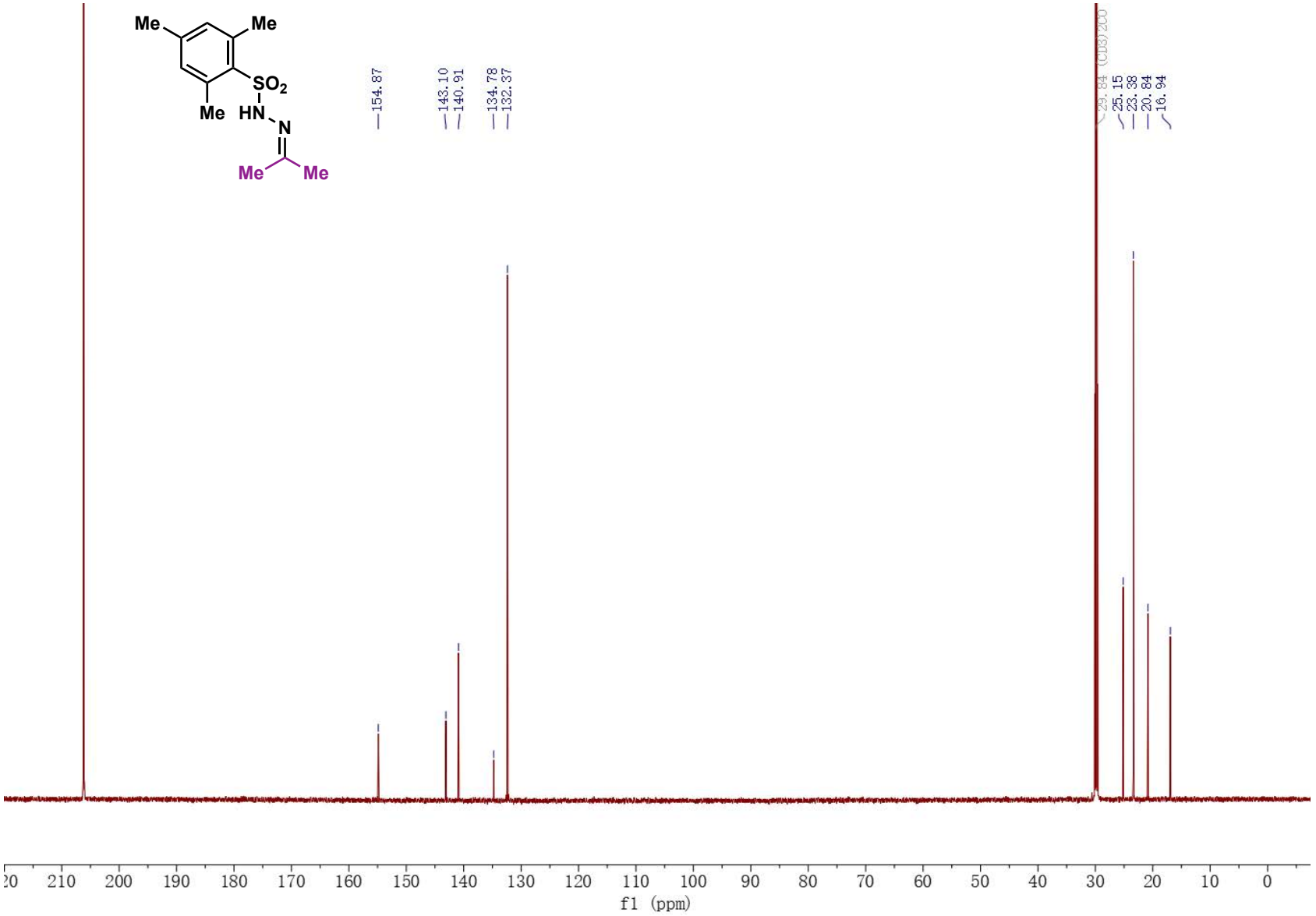
Compound 15 ^{11}B NMR



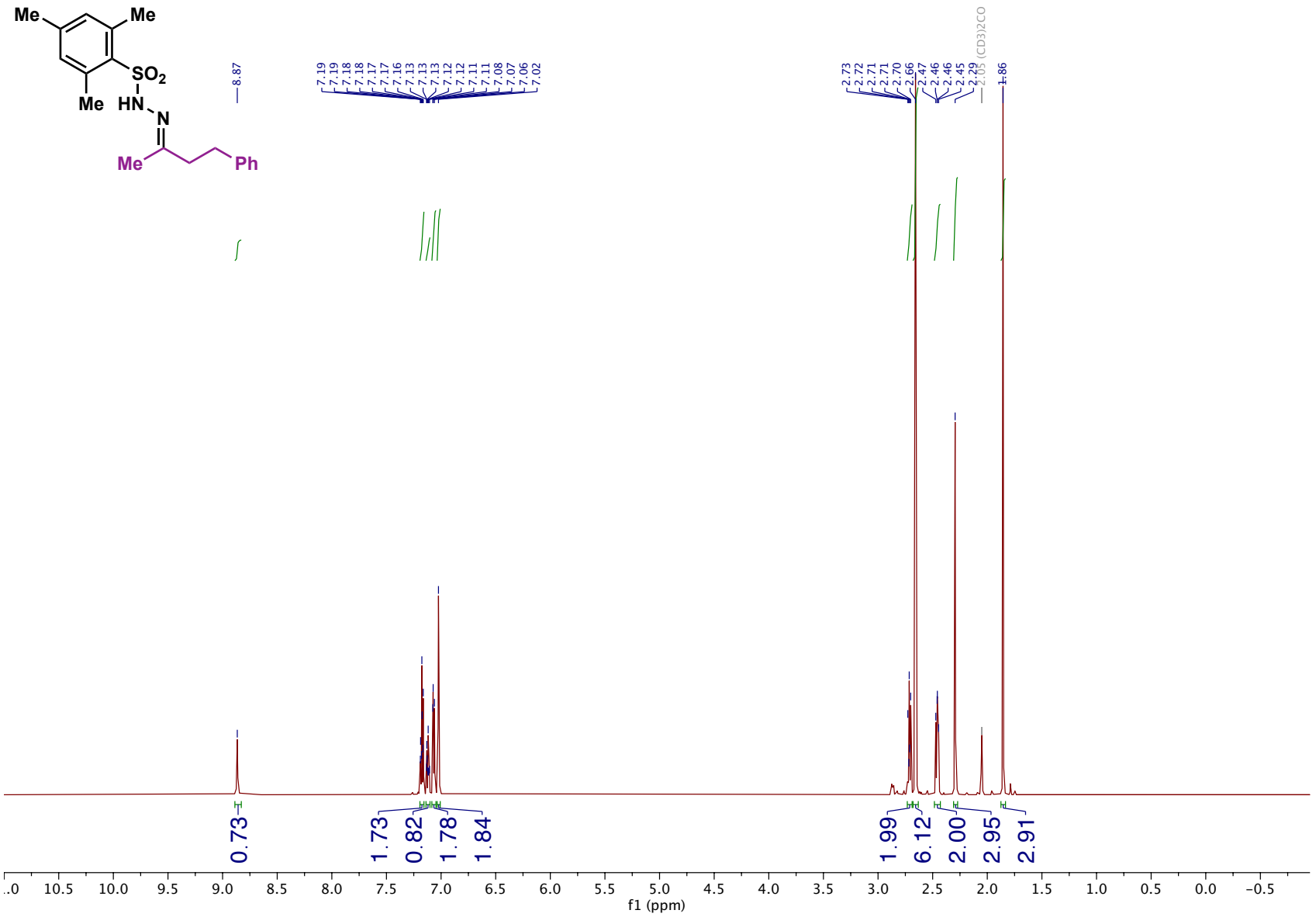
Compound 17 ^{1}H NMR



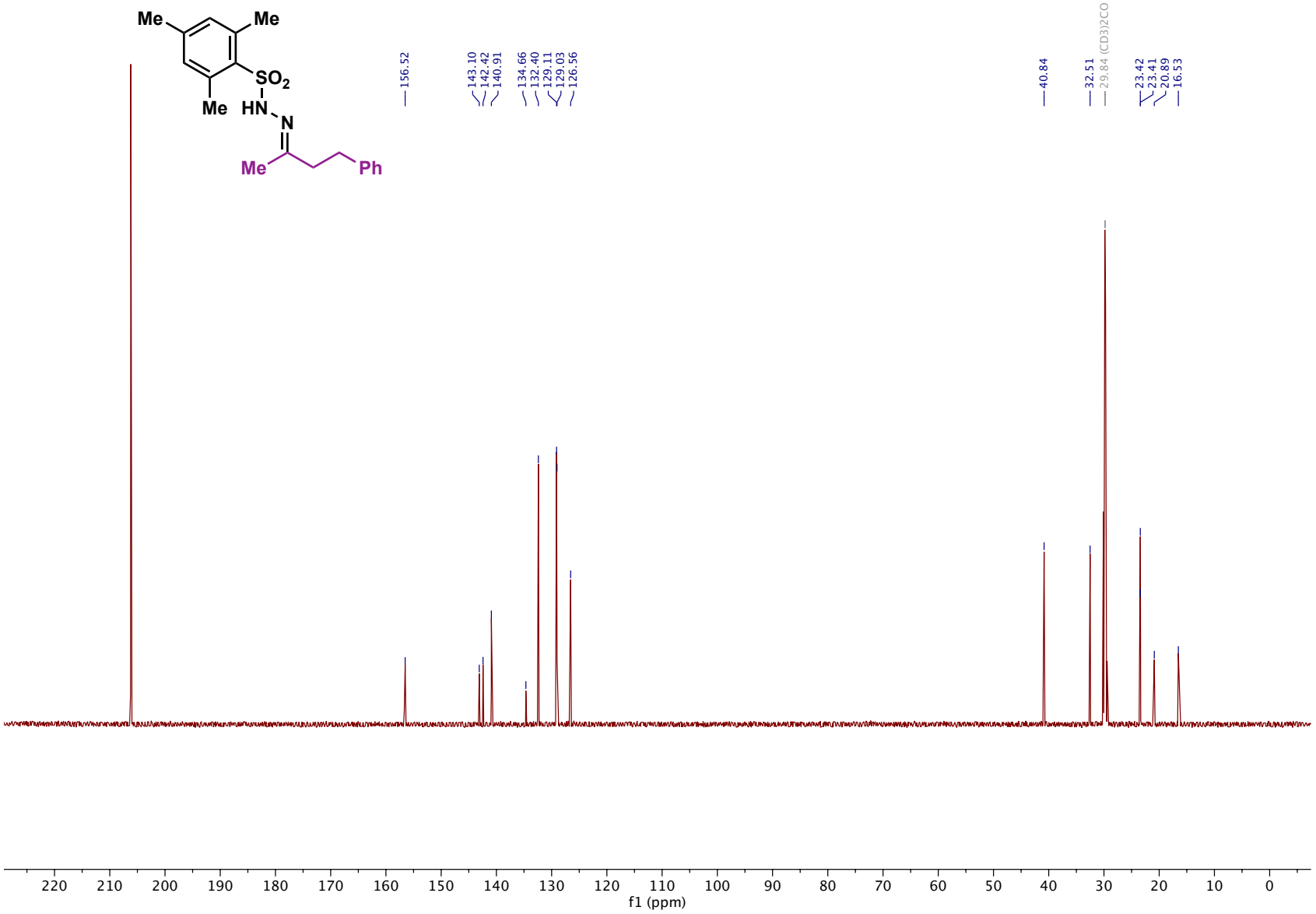
Compound 17 ^{13}C NMR



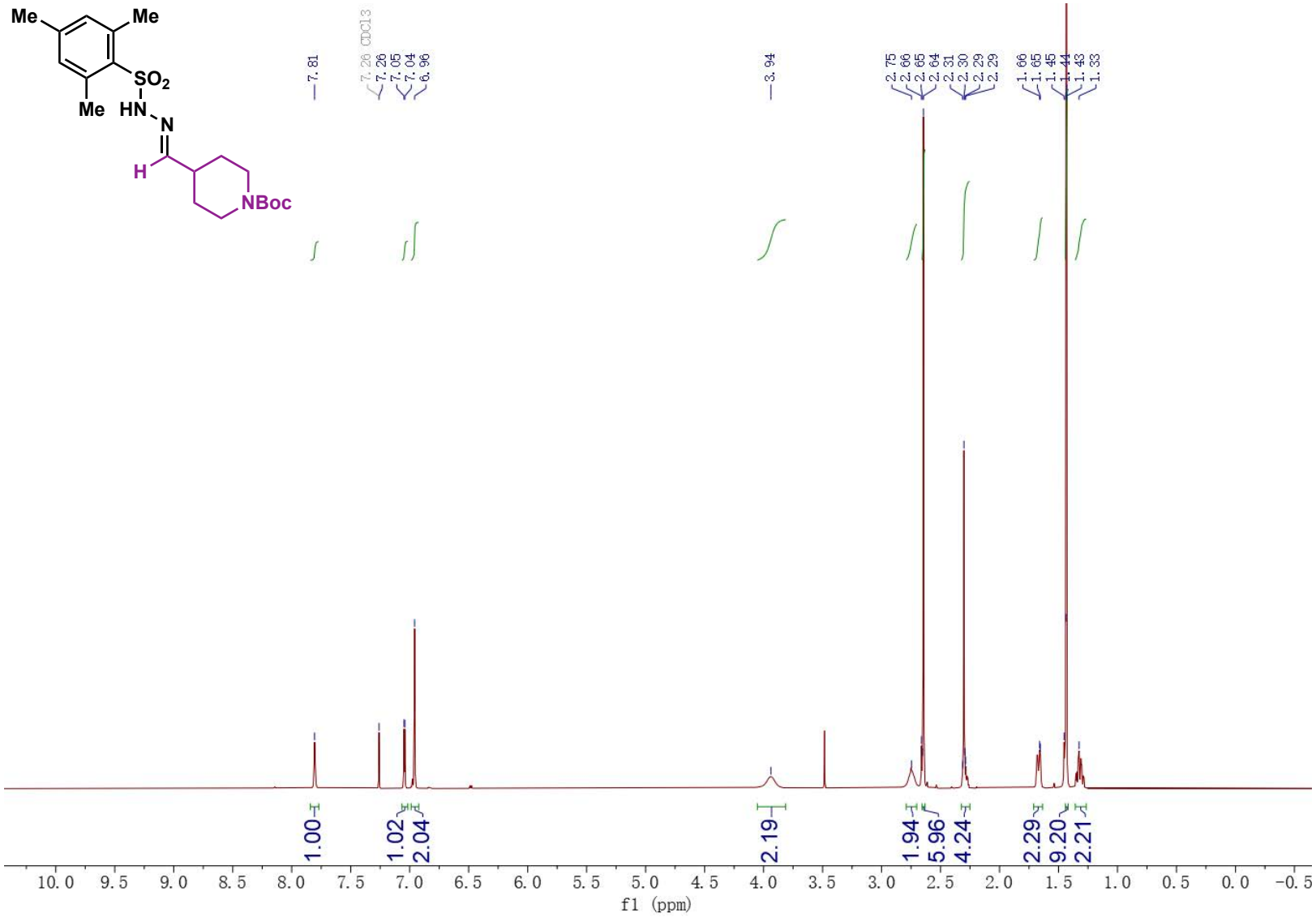
Compound SI-22 ^{1}H NMR



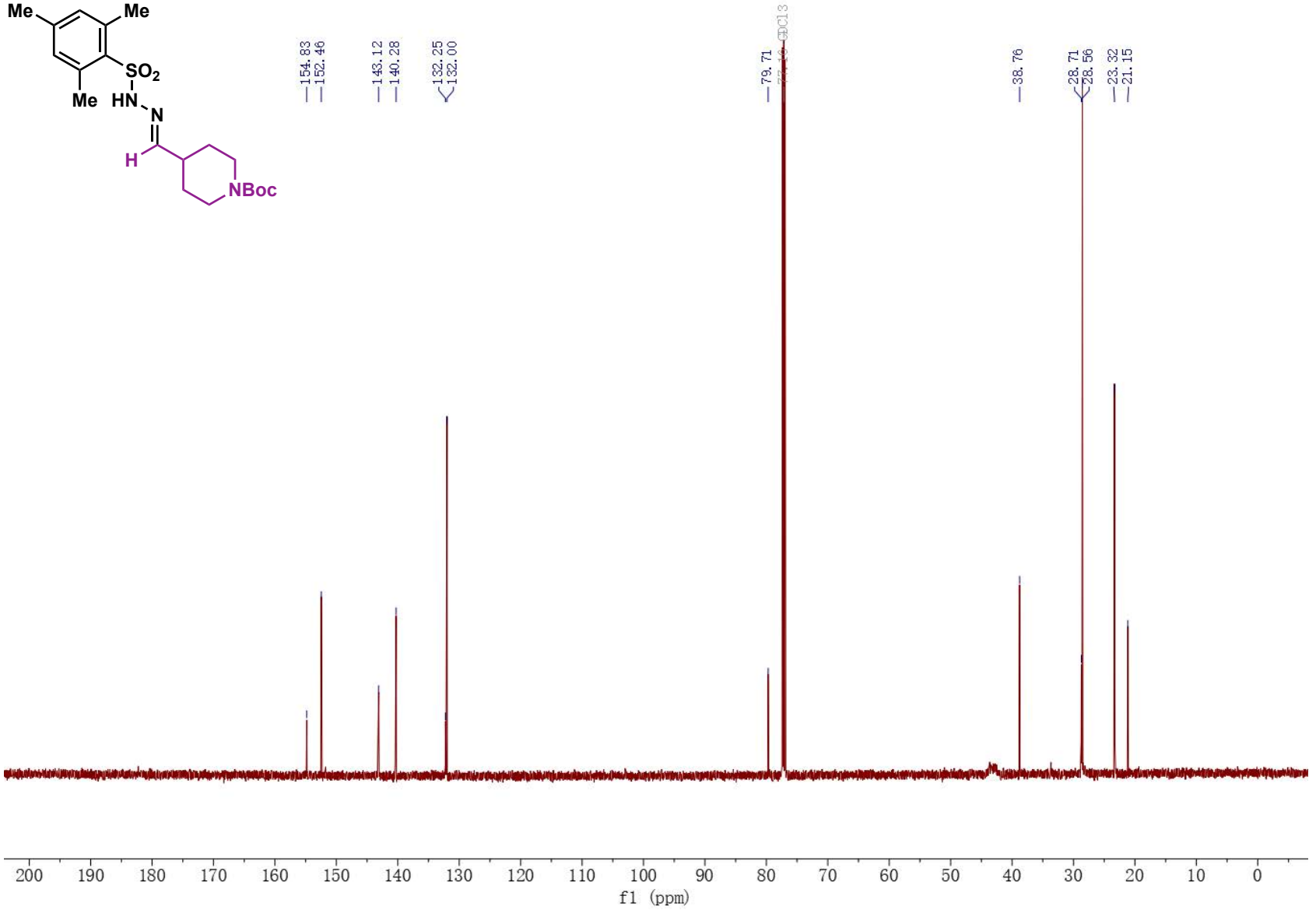
Compound SI-22 ^{13}C NMR



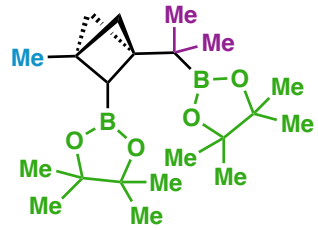
Compound SI-23 ^{1}H NMR



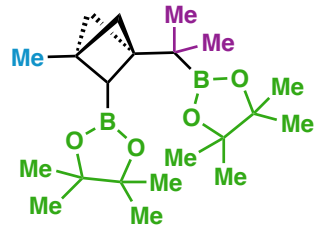
Compound SI-23 ^{13}C NMR



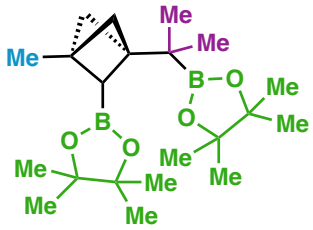
Compound 18 ^{1}H NMR



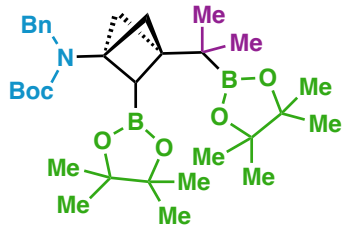
Compound 18 ^{13}C NMR



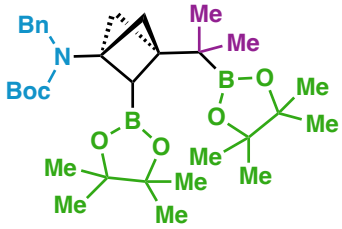
Compound 18 ^{11}B NMR



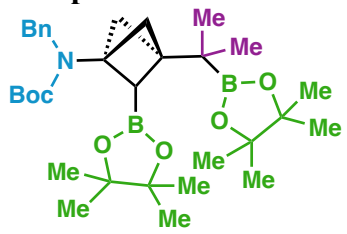
Compound 32 ^{1}H NMR



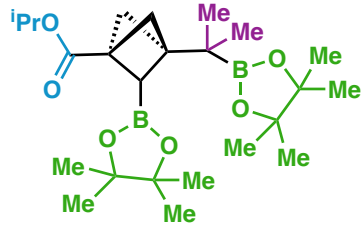
Compound 32 ^{13}C NMR



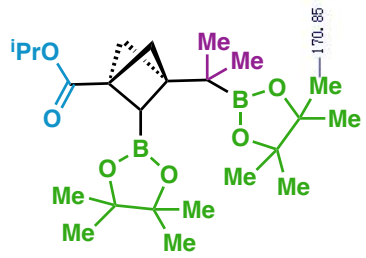
Compound 32 ^{11}B NMR



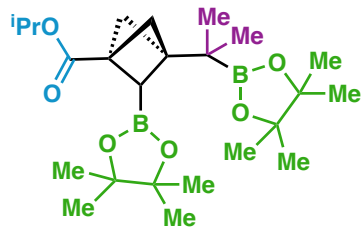
Compound 33 ^{1}H NMR



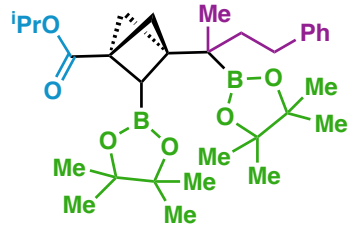
Compound 33 ^{13}C NMR



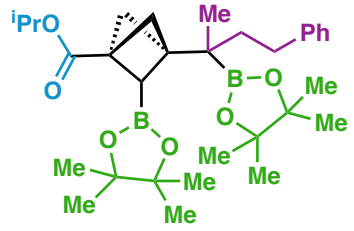
Compound 33 ^{11}B NMR



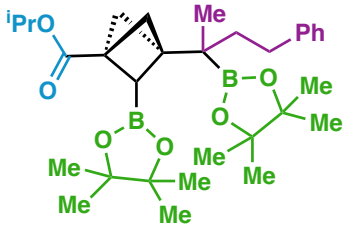
Compound 34 ^{1}H NMR



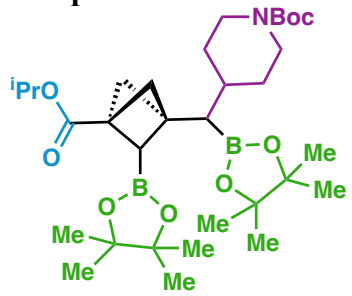
Compound 34 ^{13}C NMR



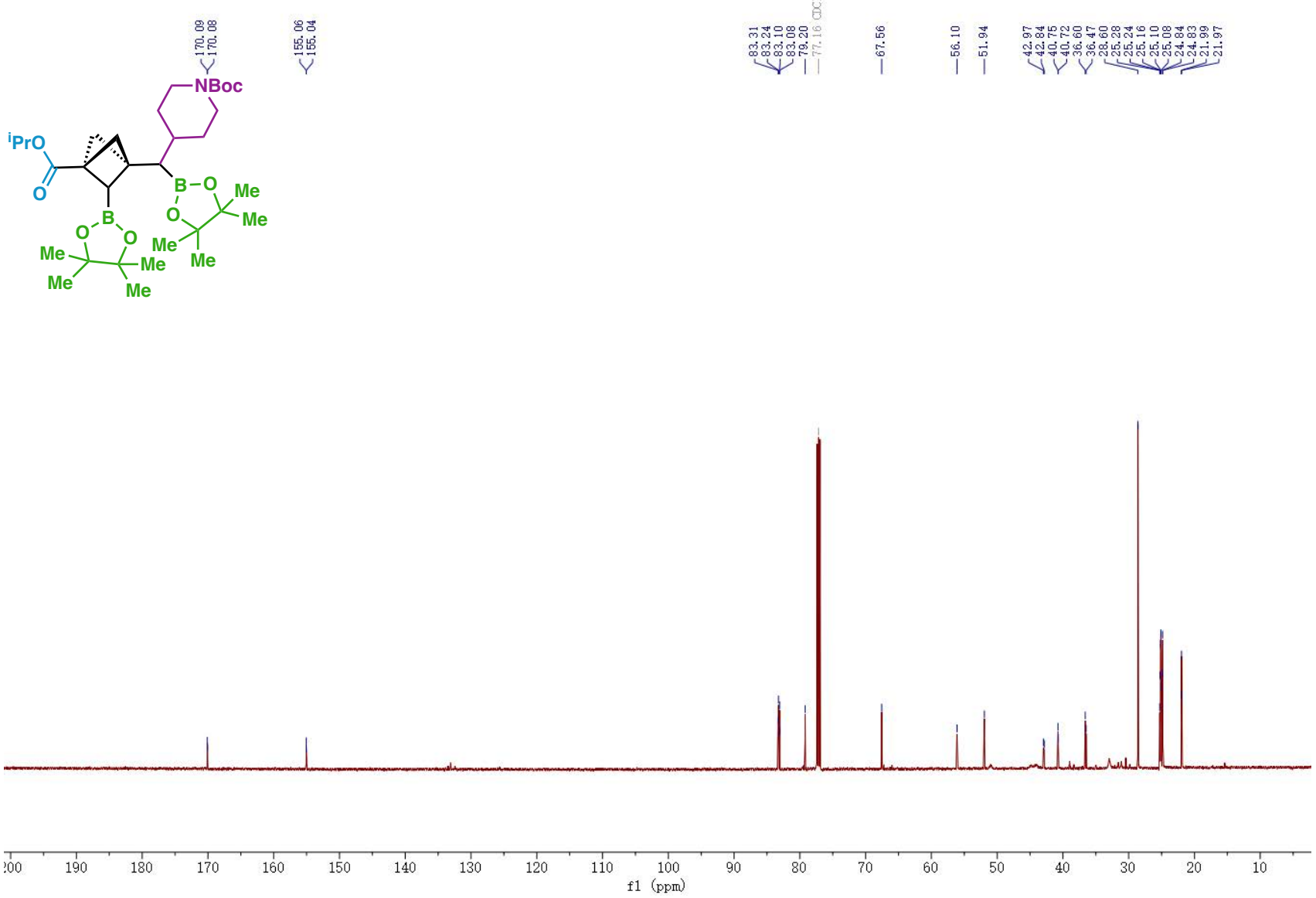
Compound 34 ^{11}B NMR



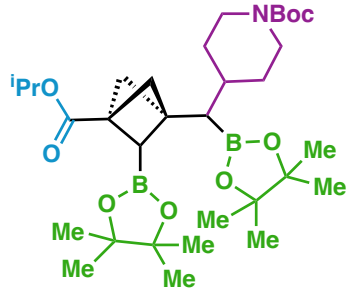
Compound 35 ^{1}H NMR



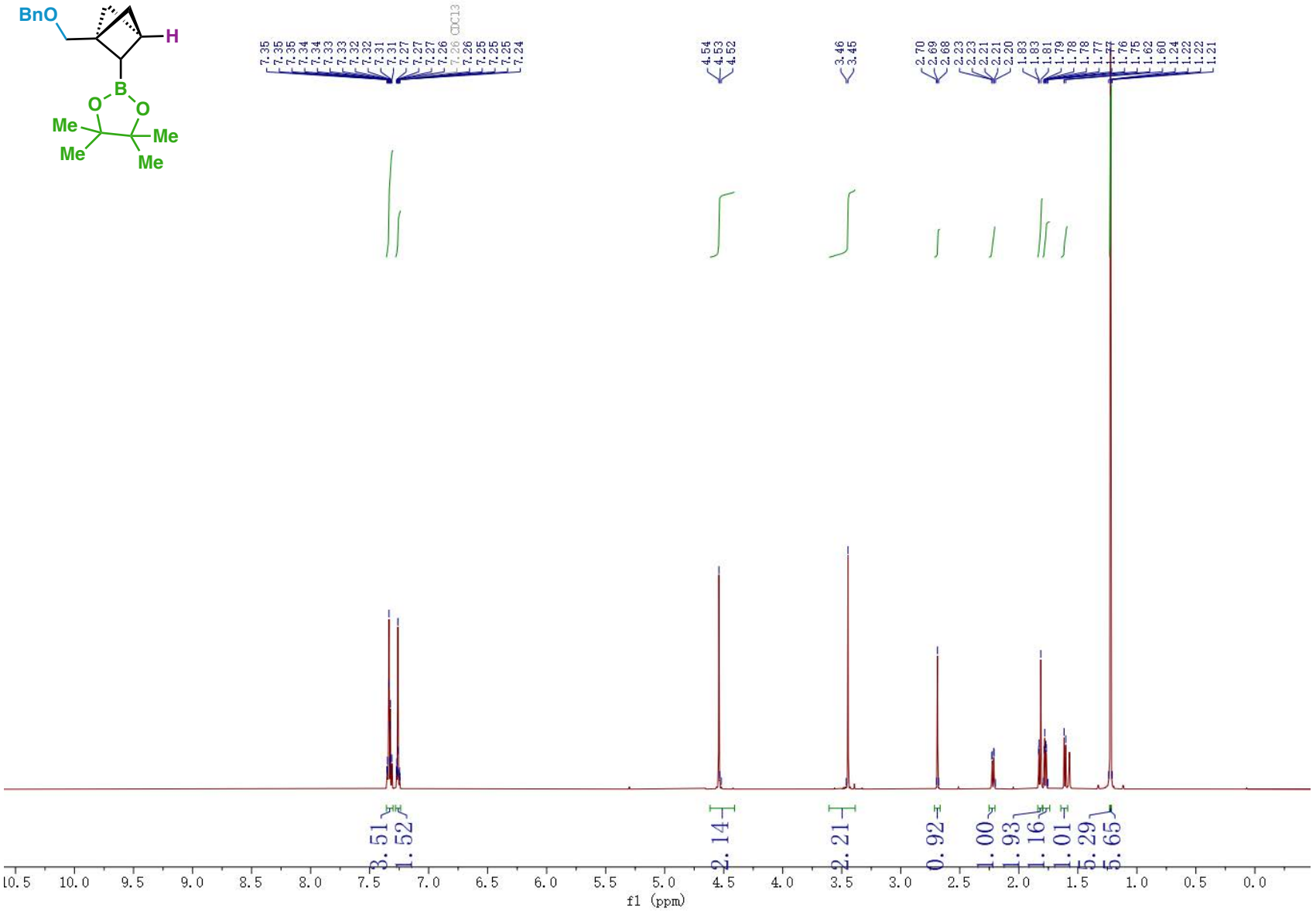
Compound 35 ^{13}C NMR



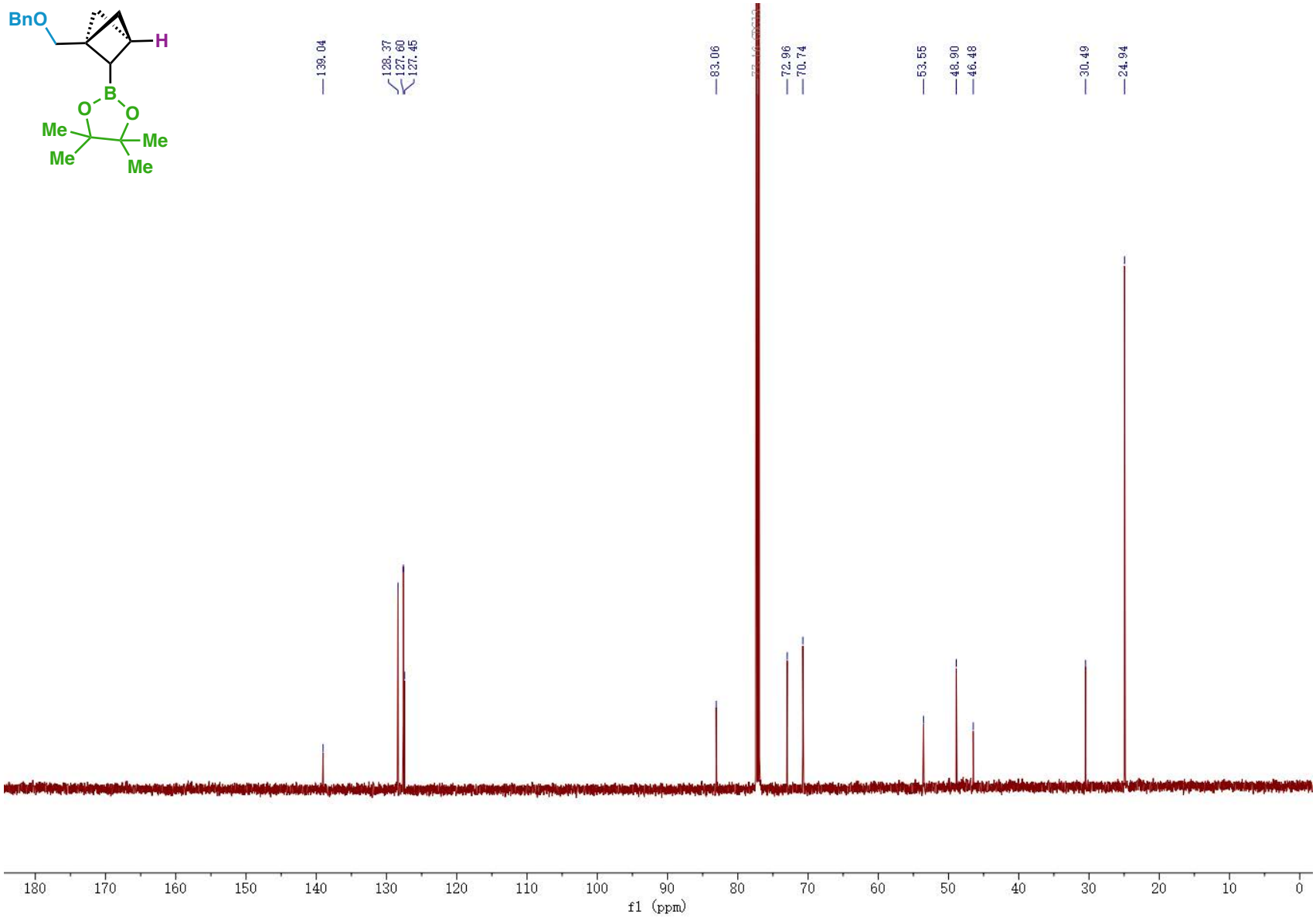
Compound 35 ^{11}B NMR



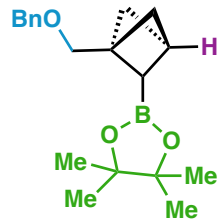
Compound 36 ^{1}H NMR



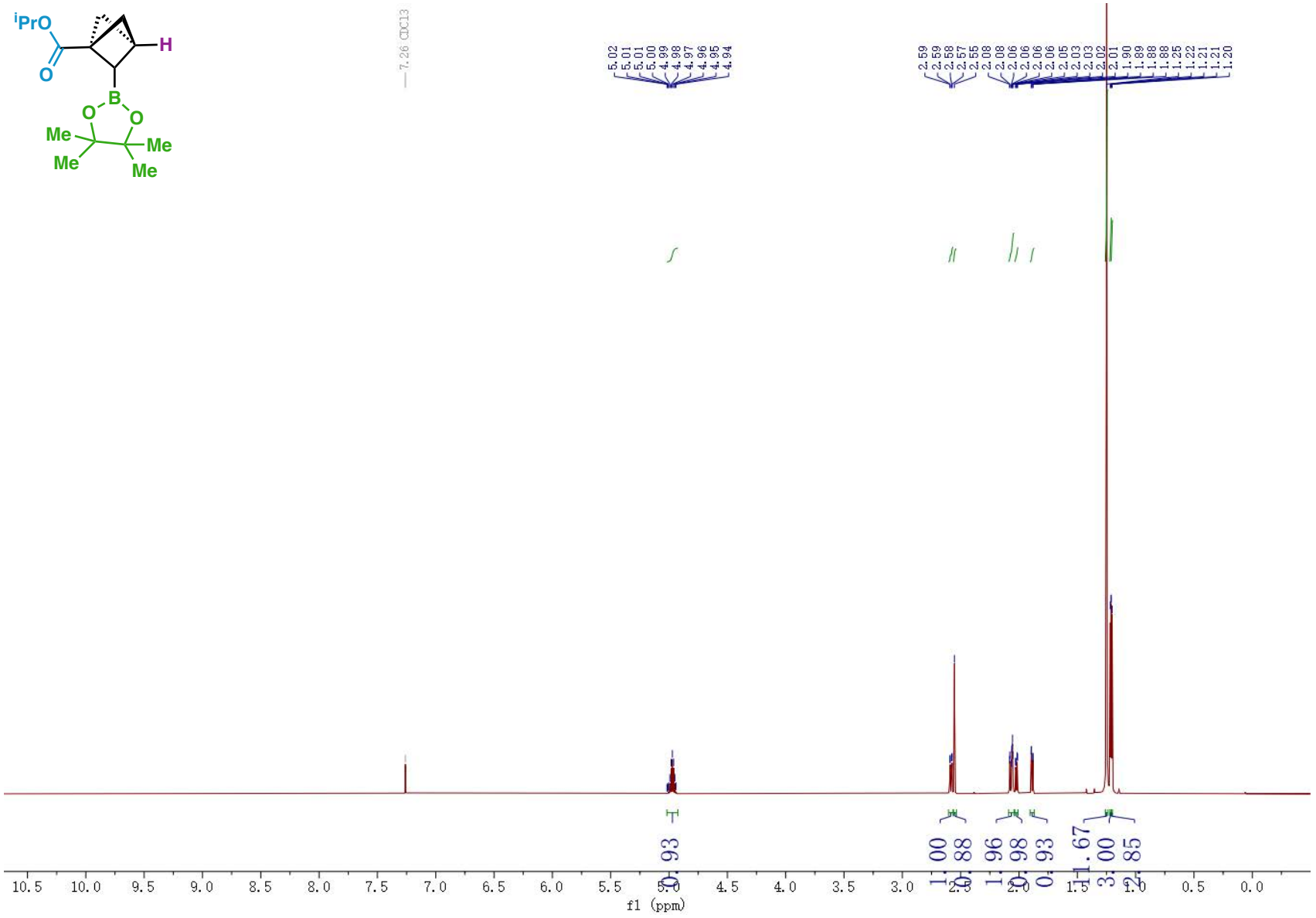
Compound 36 ^{13}C NMR



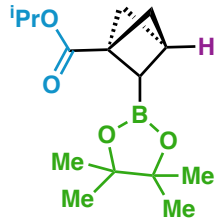
Compound 36 ^{11}B NMR



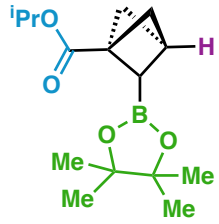
Compound 37 ^{1}H NMR



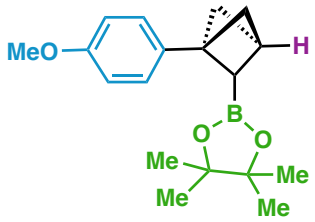
Compound 37 ^{13}C NMR



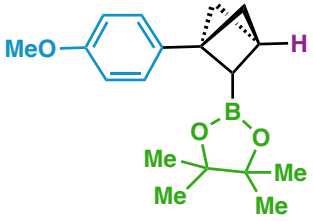
Compound 37 ^{11}B NMR



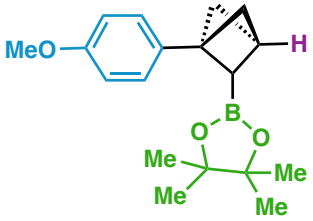
Compound 38 ^{1}H NMR



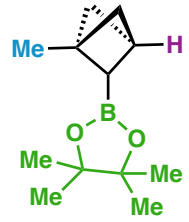
Compound 38 ^{13}C NMR



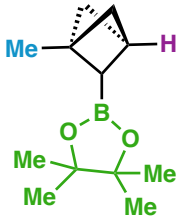
Compound 38 ^{11}B NMR



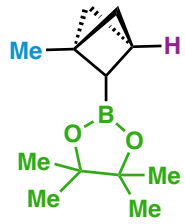
Compound 39 ^{1}H NMR



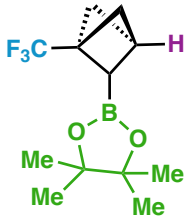
Compound 39 ^{13}C NMR



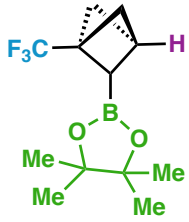
Compound 39 ^{11}B NMR



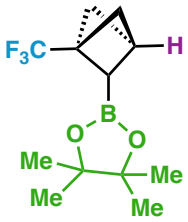
Compound 40 ^{1}H NMR



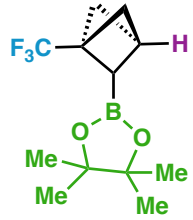
Compound 40 ^{13}C NMR



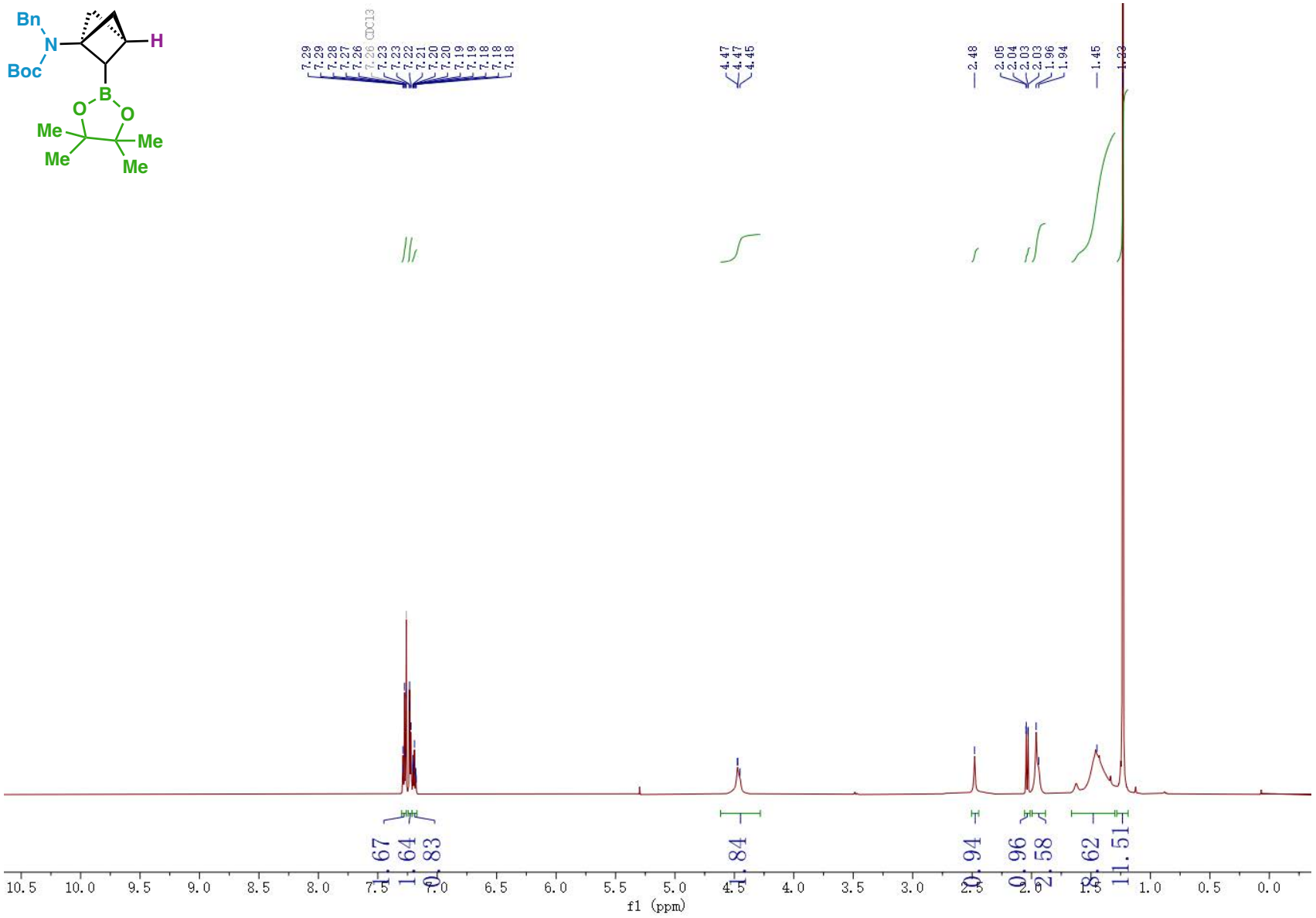
Compound 40 ^{11}B NMR



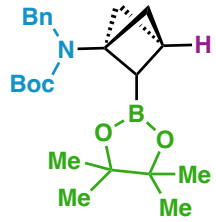
Compound 40 ^{19}F NMR



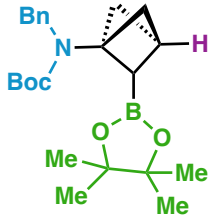
Compound 41 ^{1}H NMR



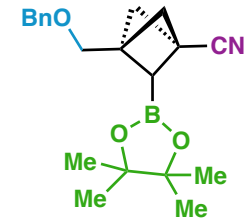
Compound 41 ^{13}C NMR



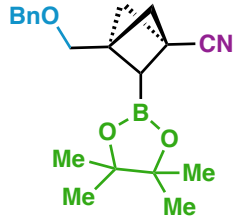
Compound 41 ^{11}B NMR



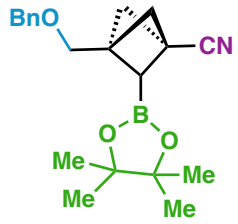
Compound 42 ^{1}H NMR



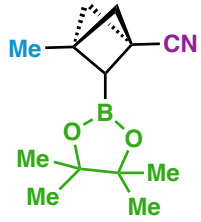
Compound 42 ^{13}C NMR



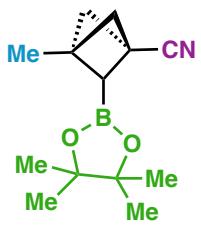
Compound 42 ^{11}B NMR



Compound 43 ^{1}H NMR

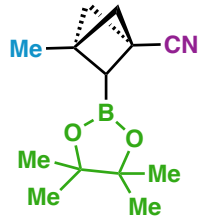


Compound 43 ^{13}C NMR

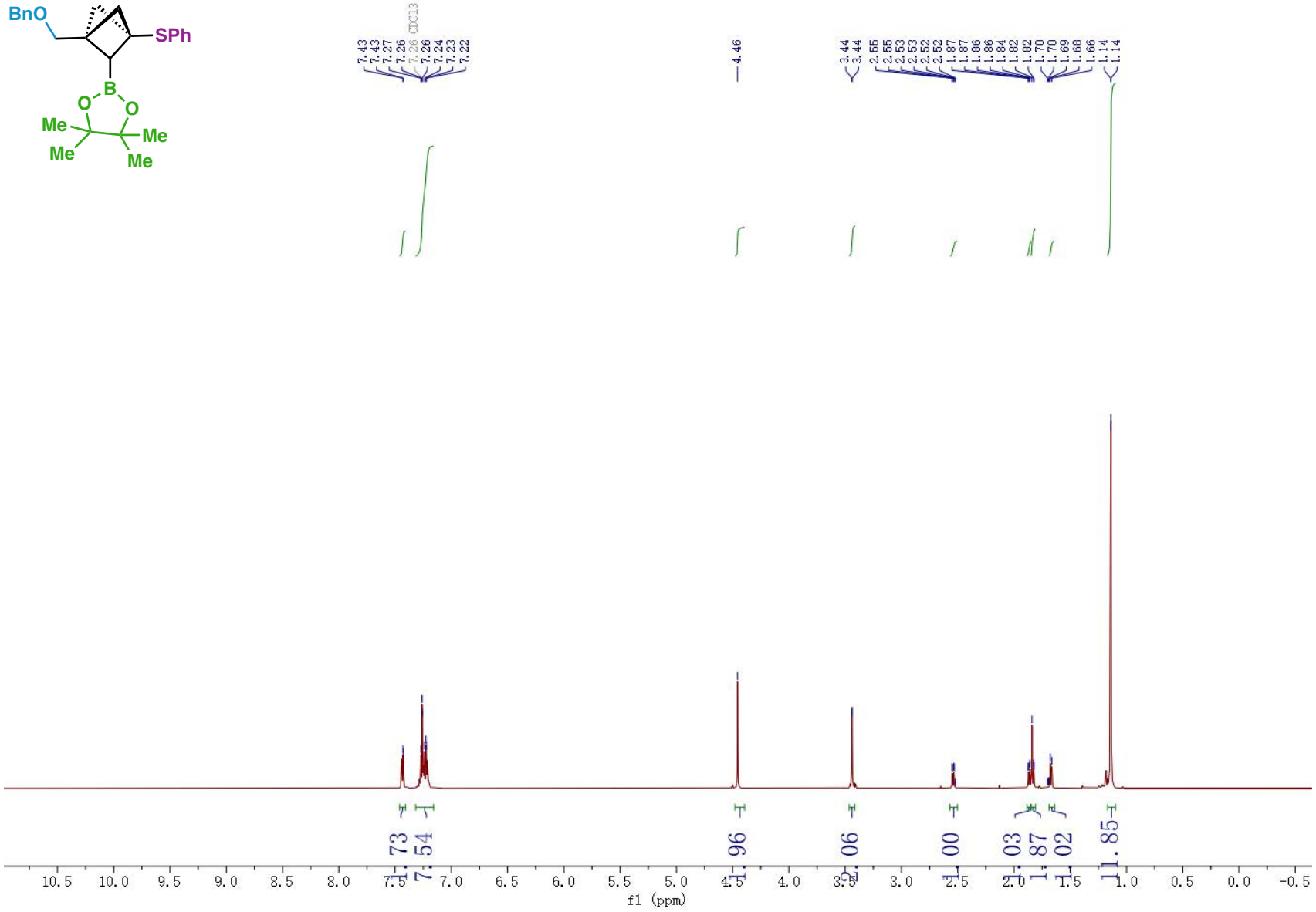


Compound 43 HSQC

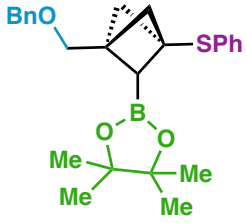
Compound 43 ^{11}B NMR



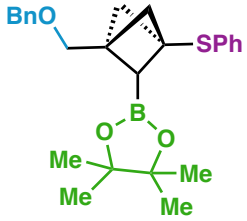
Compound 44 ^{1}H NMR



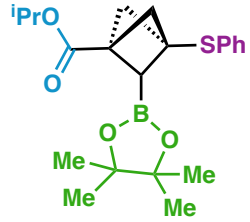
Compound 44 ^{13}C NMR



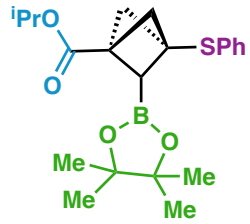
Compound 44 ^{11}B NMR



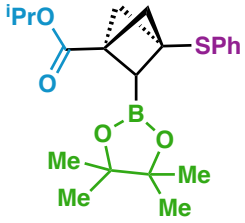
Compound 45 ^{1}H NMR



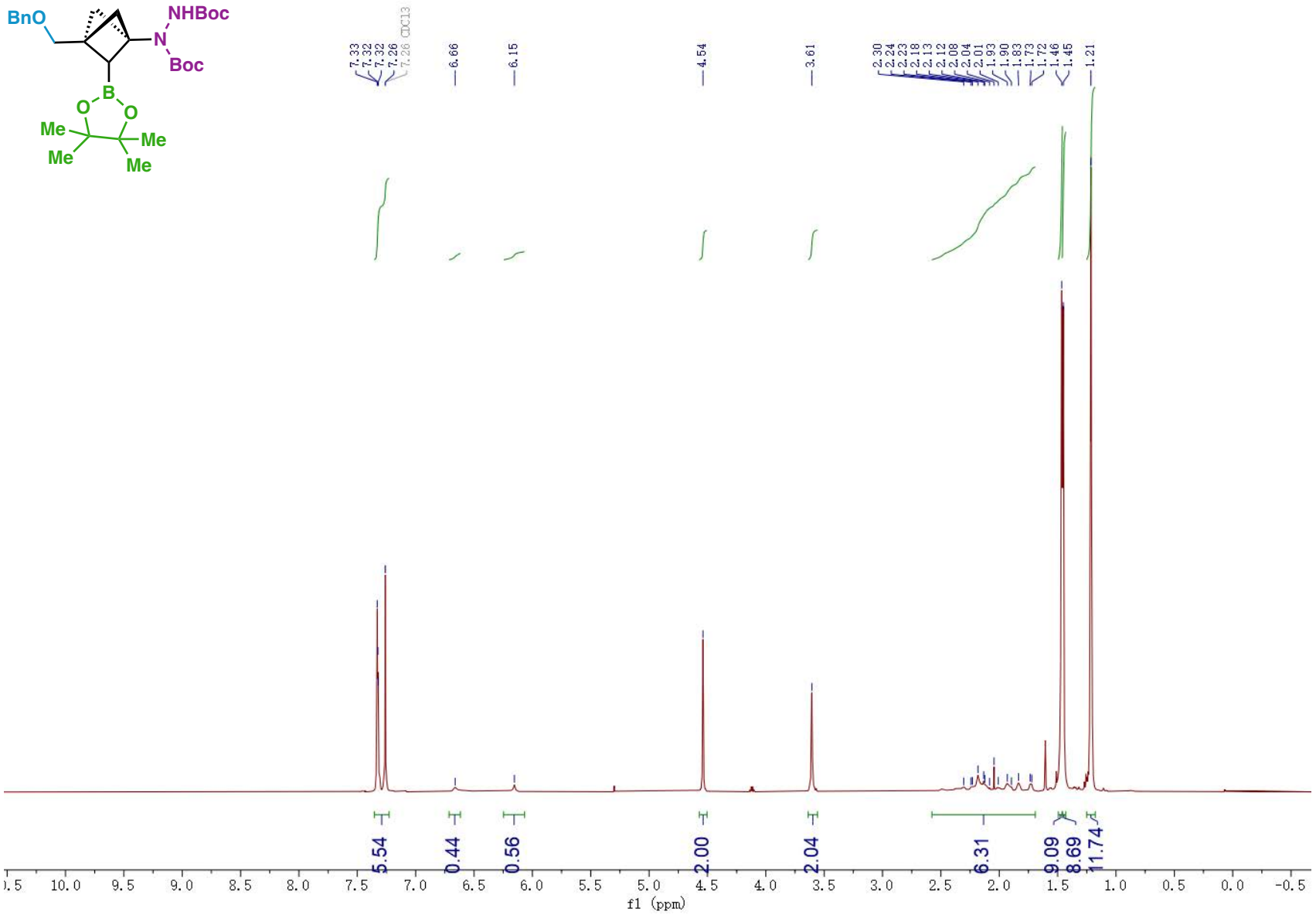
Compound 45 ^{13}C NMR



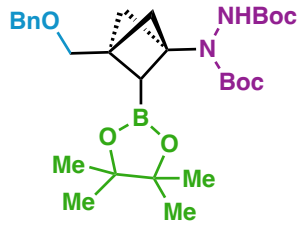
Compound 45 ^{11}B NMR



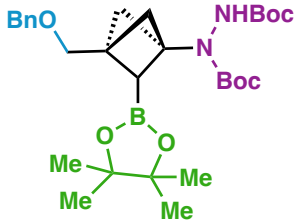
Compound 46 ^{1}H NMR



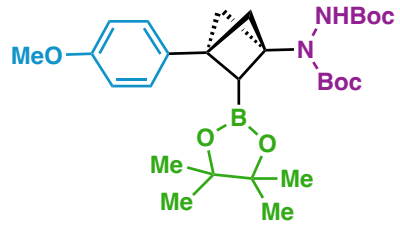
Compound 46 ^{13}C NMR



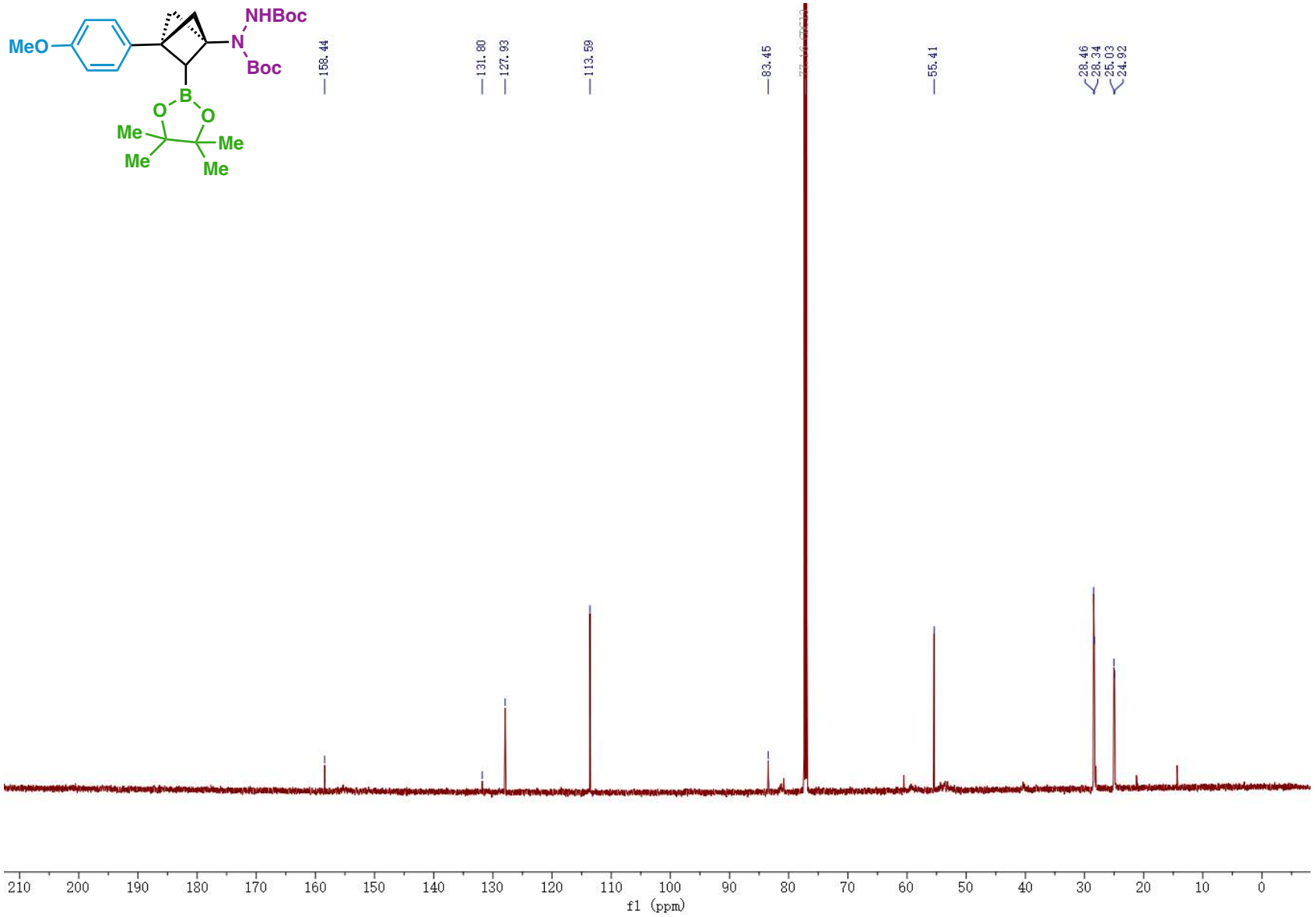
Compound 46 ^{11}B NMR



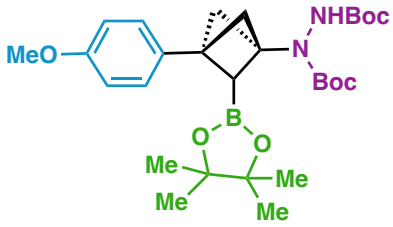
Compound 47 ^{1}H NMR



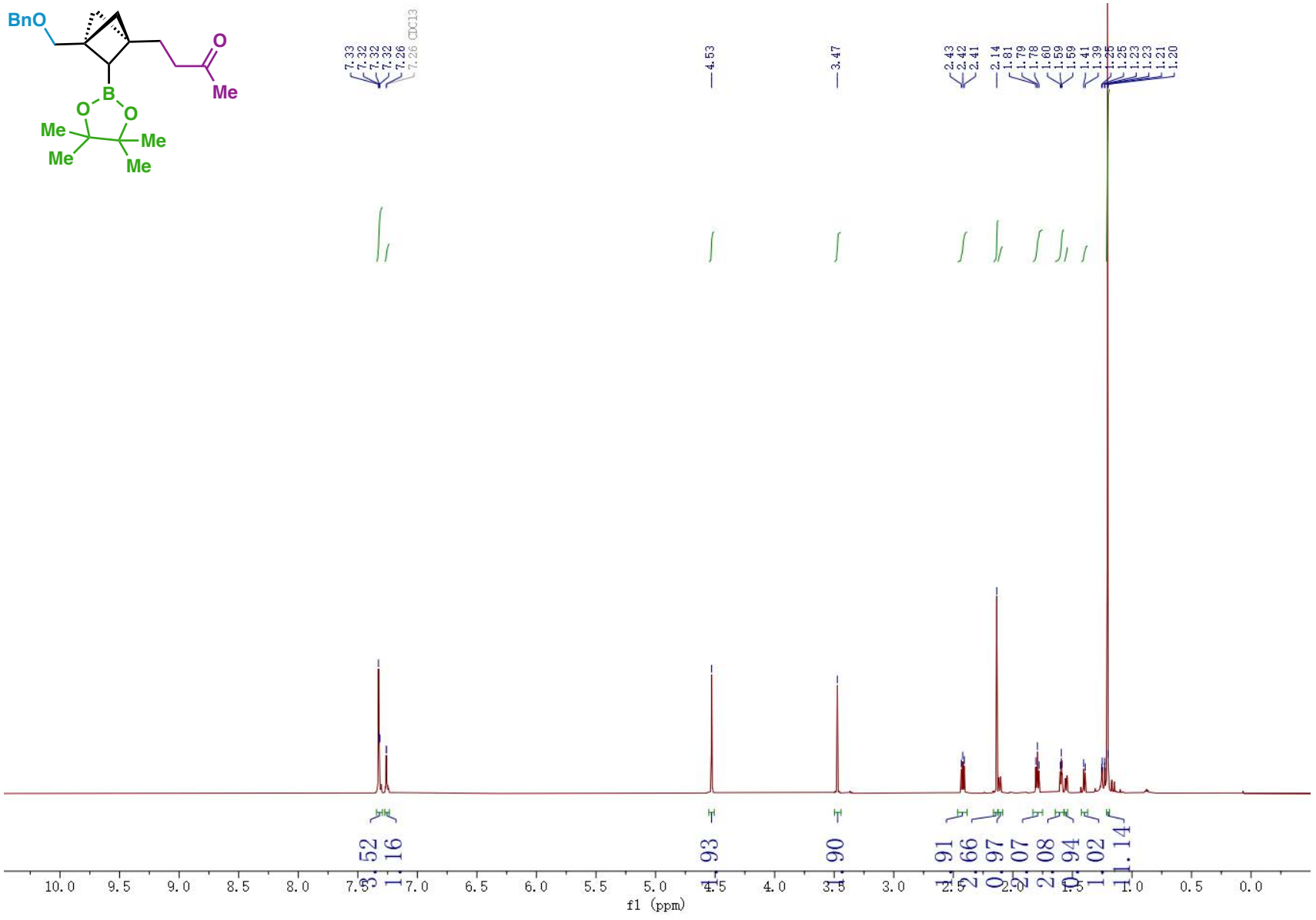
Compound 47 ^{13}C NMR



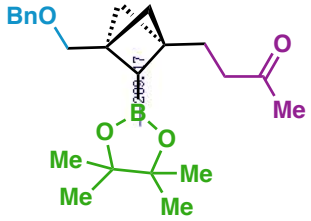
Compound 47 ^{11}B NMR



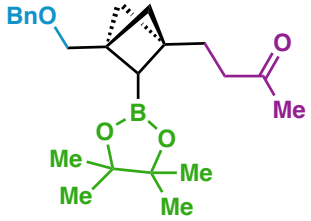
Compound 48 ^{1}H NMR



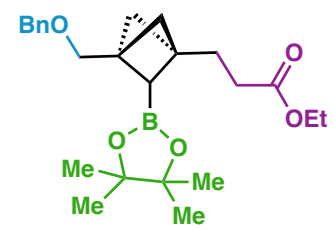
Compound 48 ^{13}C NMR



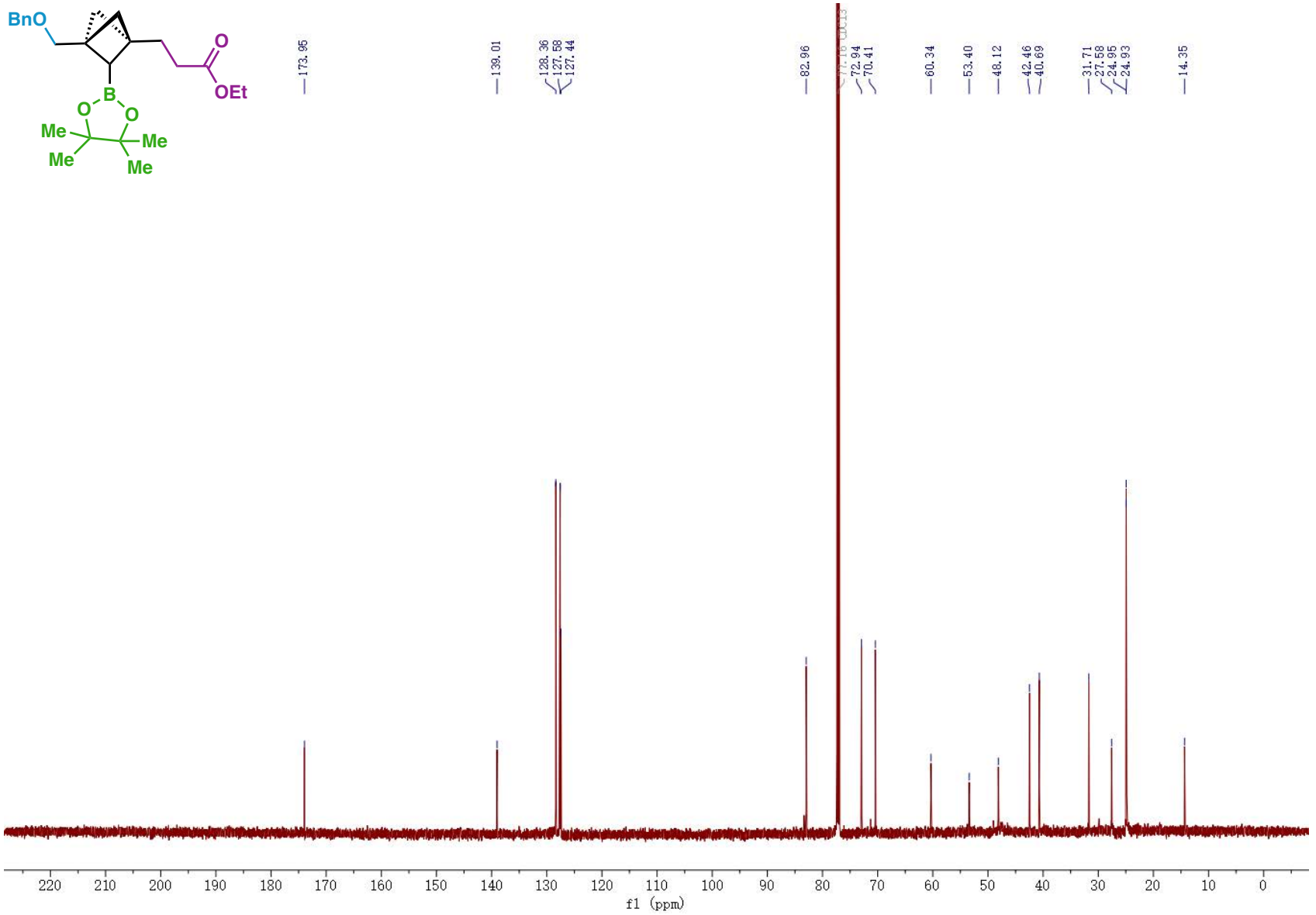
Compound 48 ^{11}B NMR



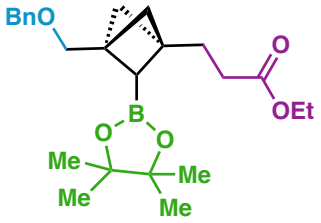
Compound 49 ^{1}H NMR



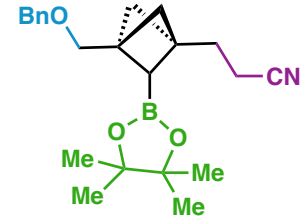
Compound 49 ^{13}C NMR



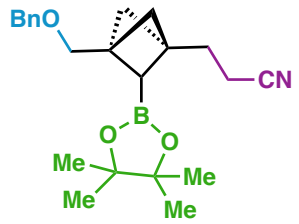
Compound 49 ^{11}B NMR



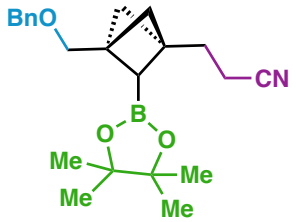
Compound 50 ^{1}H NMR



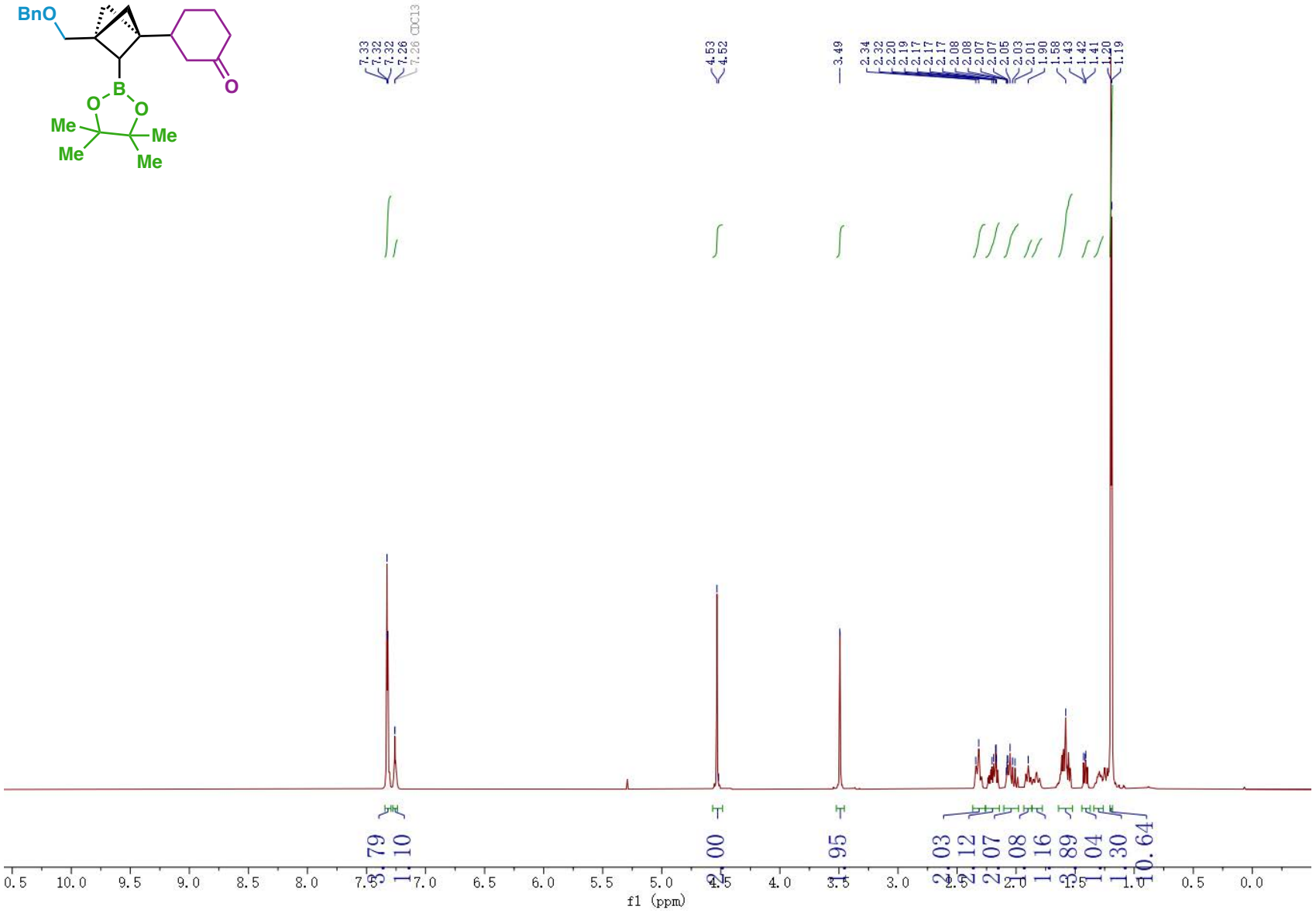
Compound 50 ^{13}C NMR



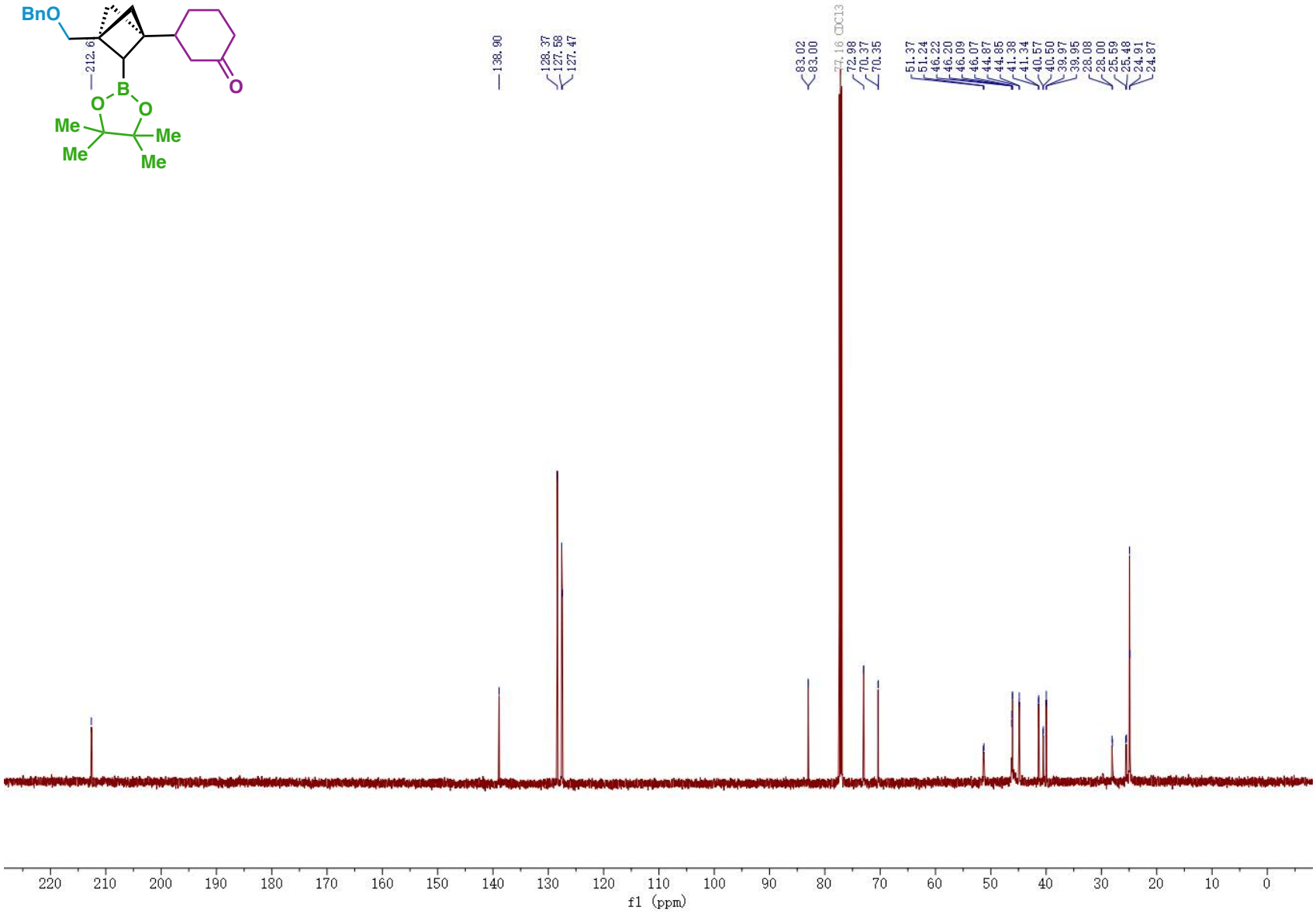
Compound 50 ^{11}B NMR



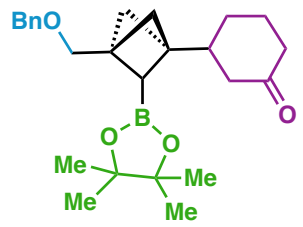
Compound 51 ^{1}H NMR



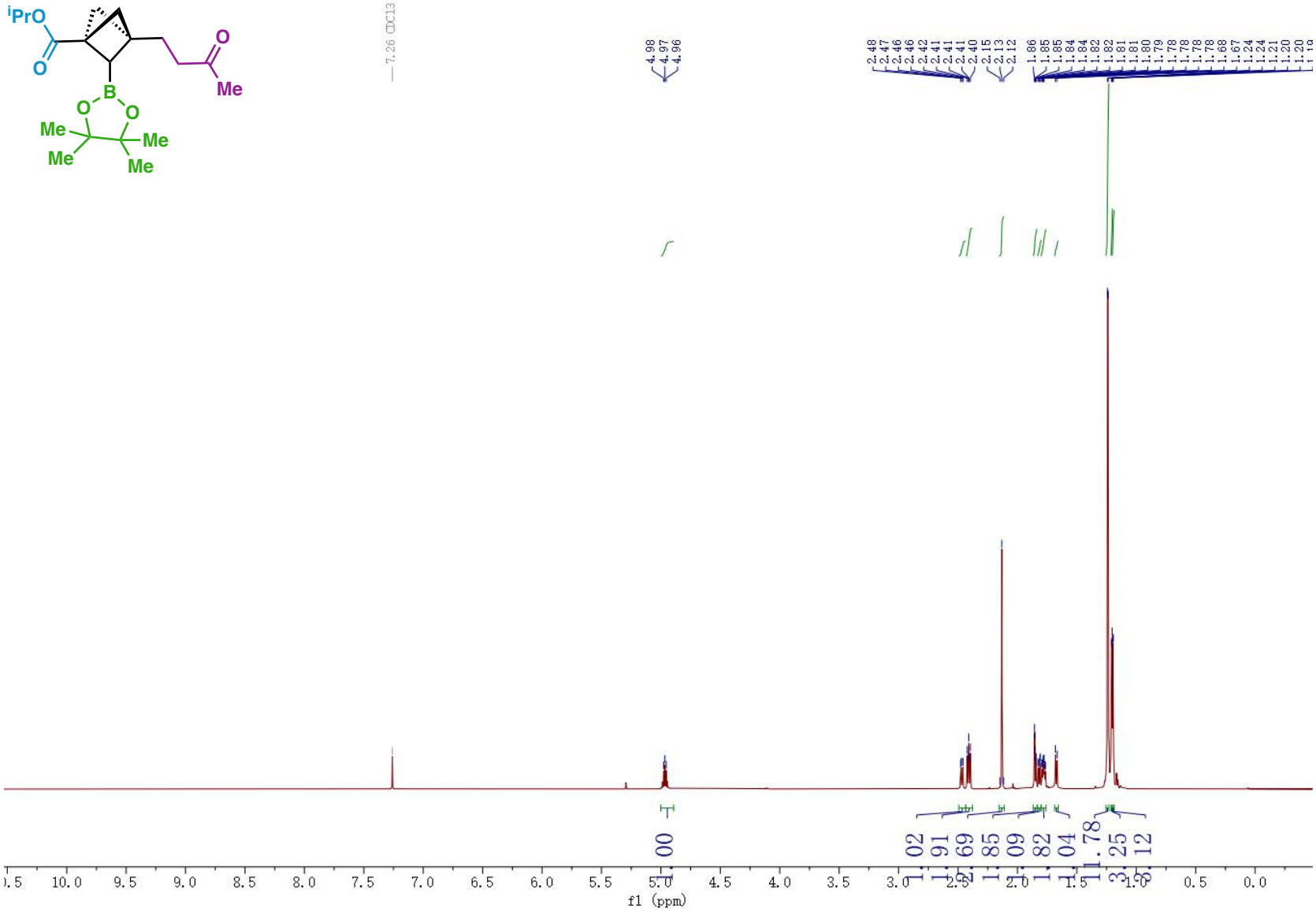
Compound 51 ^{13}C NMR



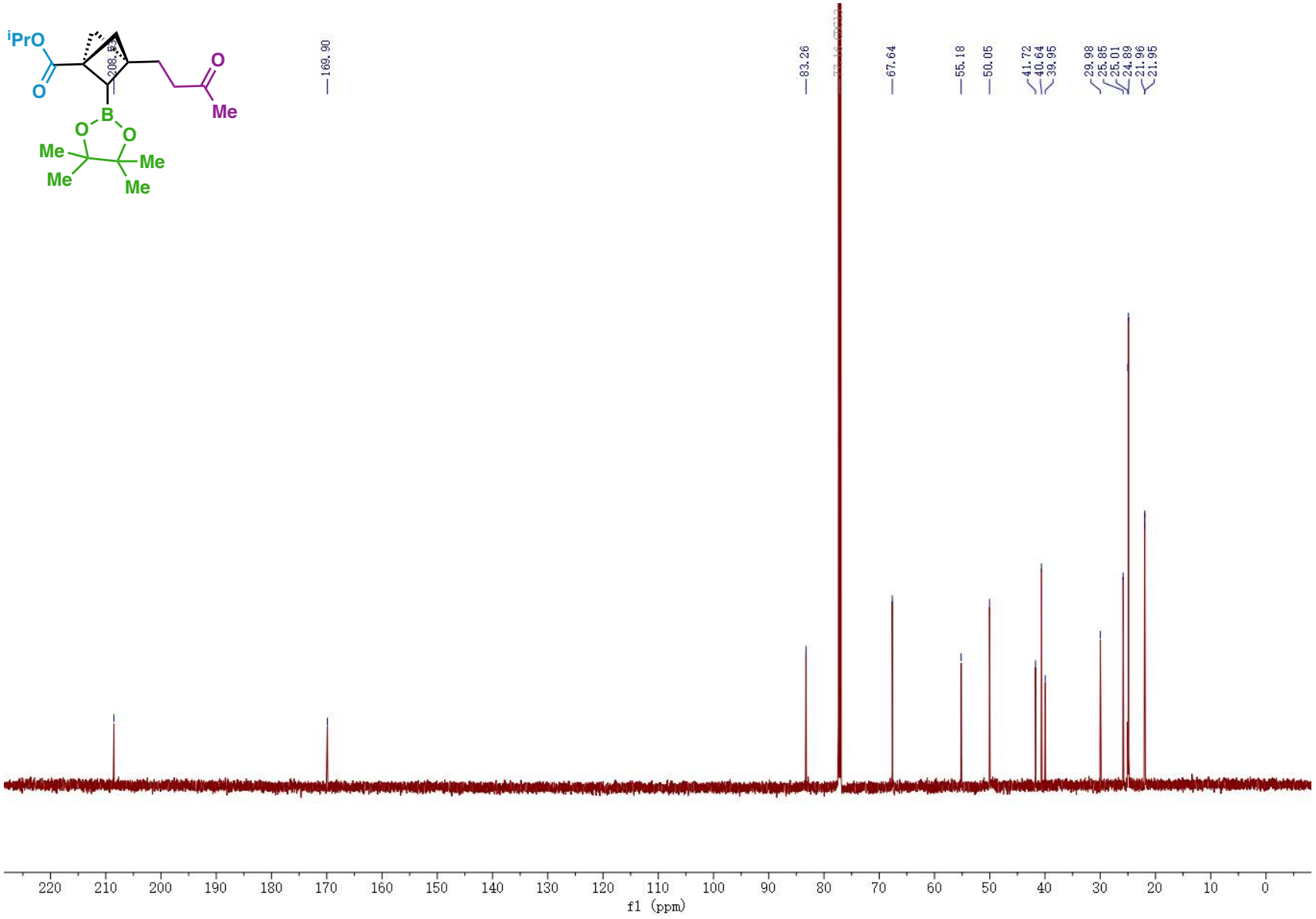
Compound 51 ^{11}B NMR



Compound 52 ^{1}H NMR



Compound 52 ^{13}C NMR



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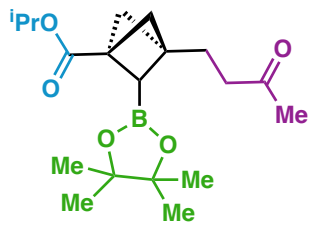
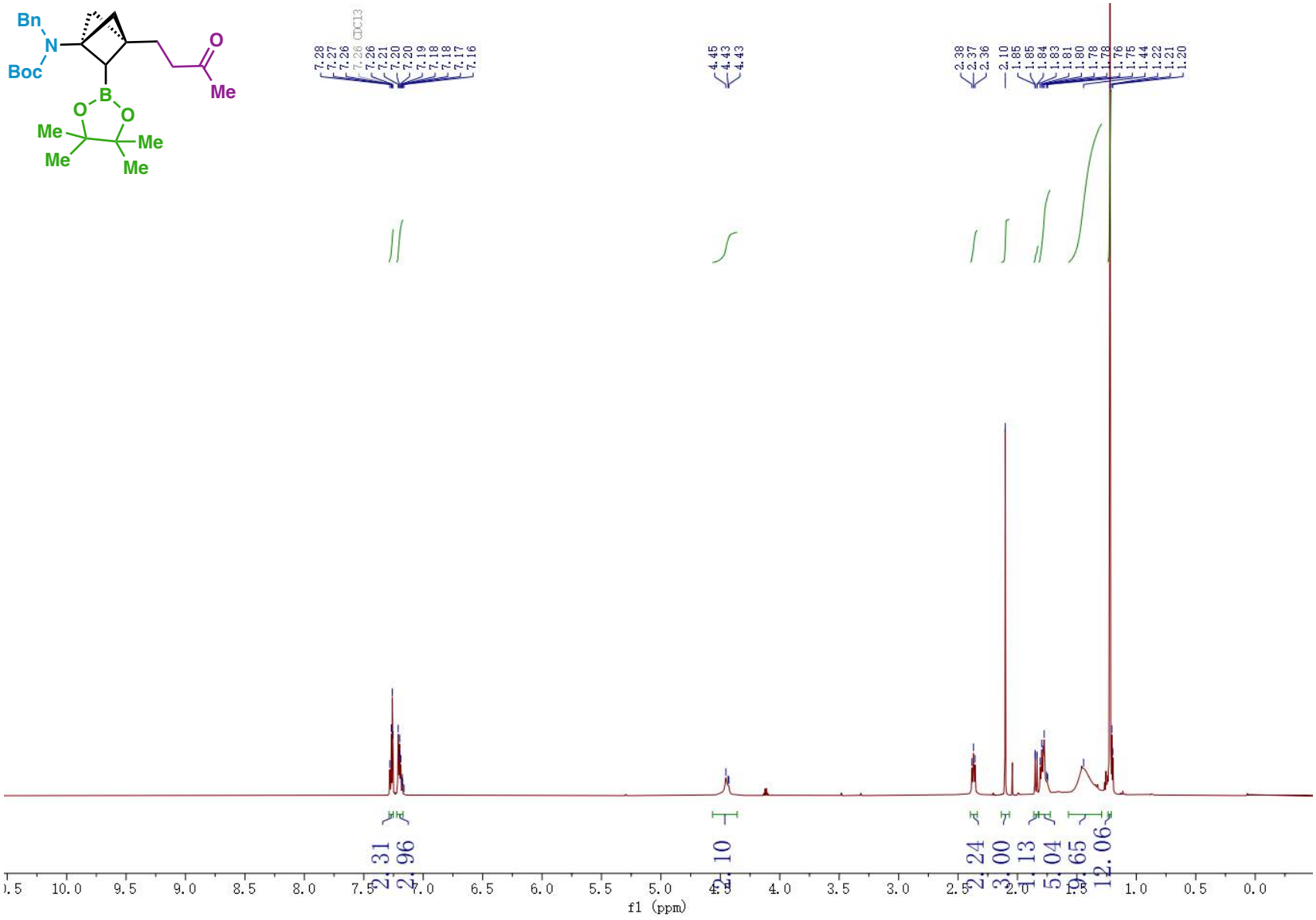
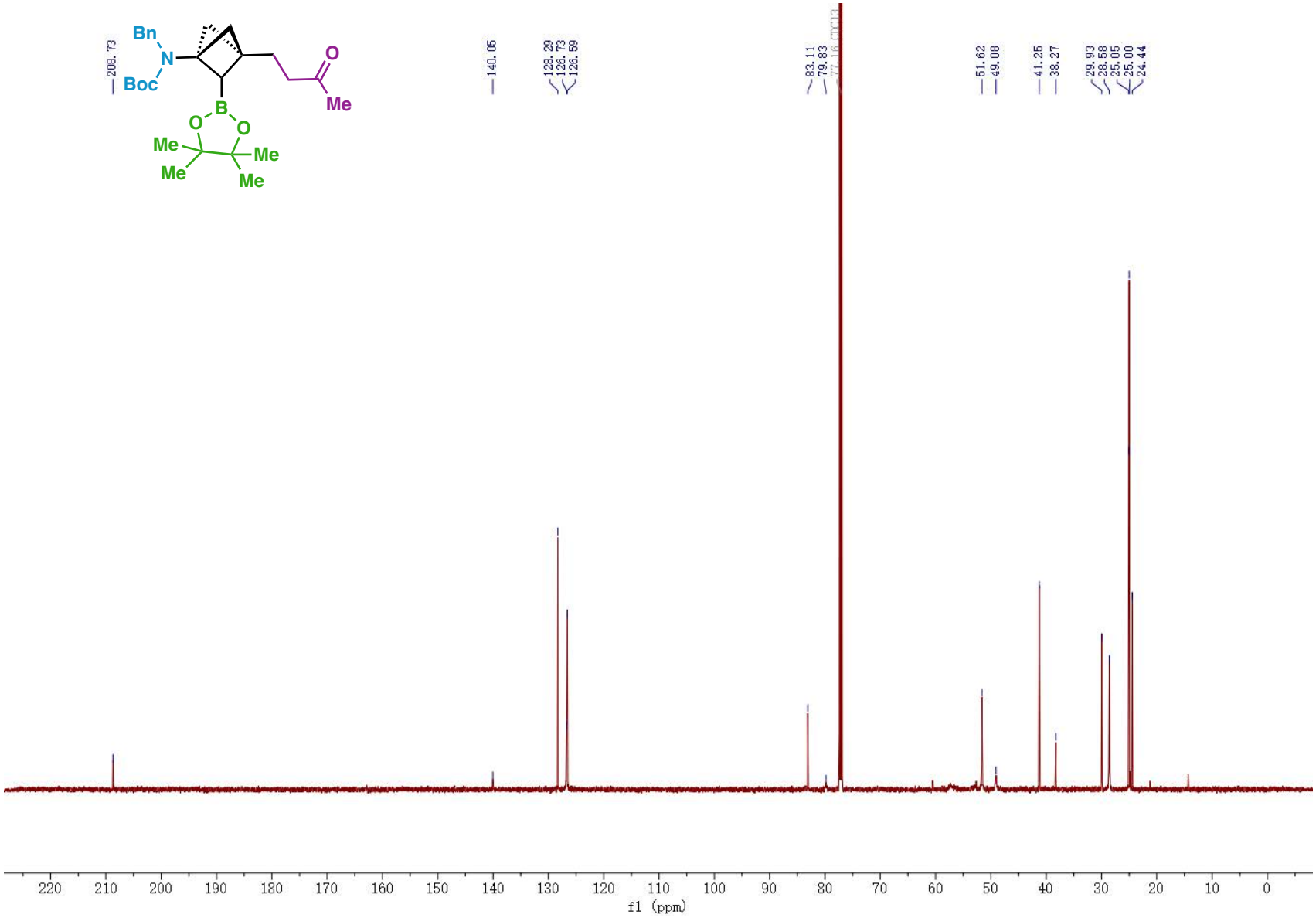


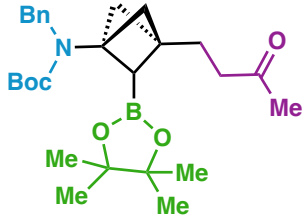
Compound 53 ^{1}H NMR



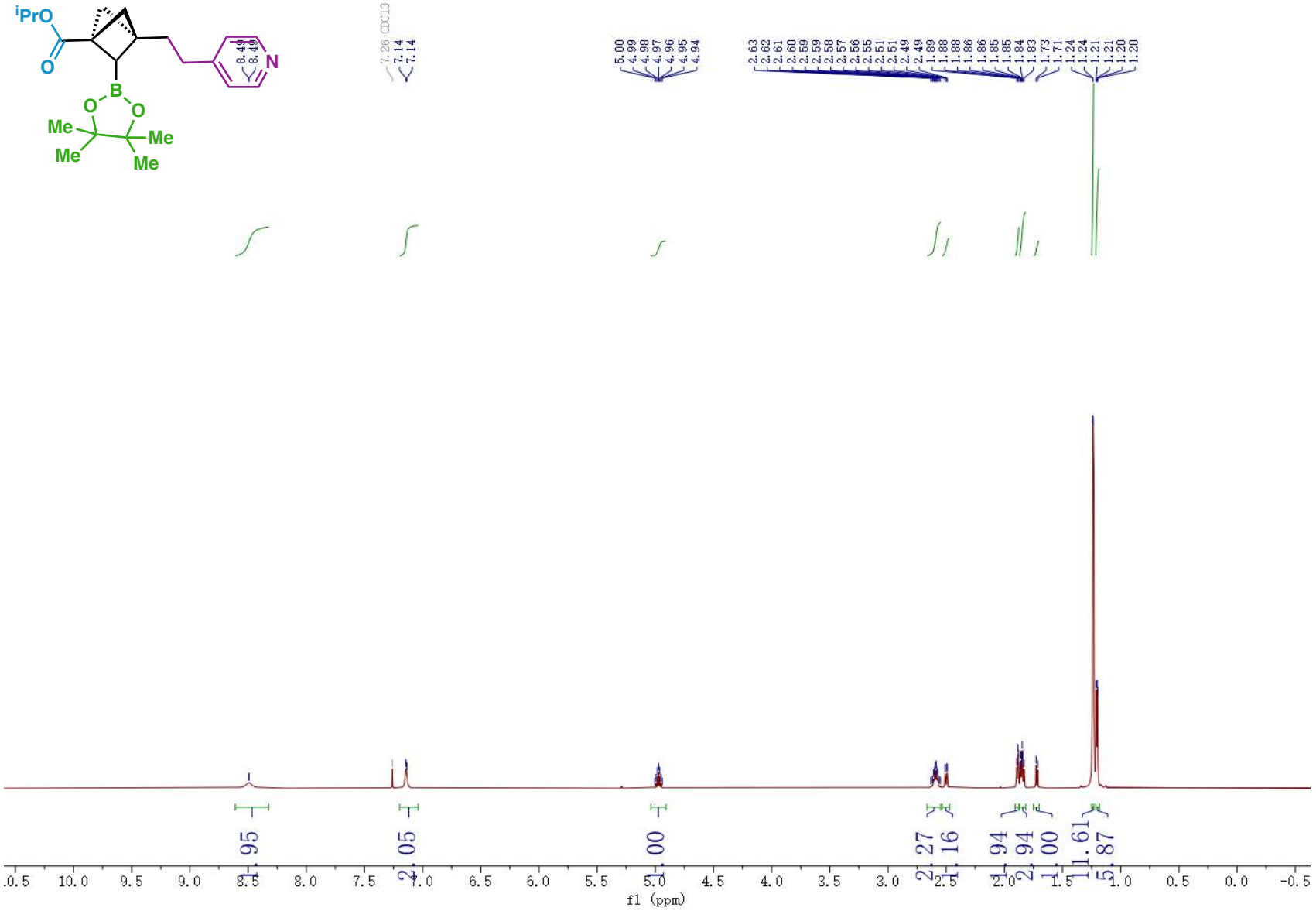
Compound 53 ^{13}C NMR



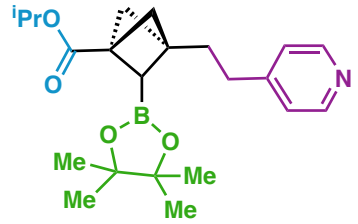
Compound 53 ^{11}B NMR



Compound 54 ^{1}H NMR



Compound 54 ^{13}C NMR



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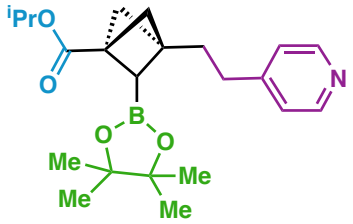
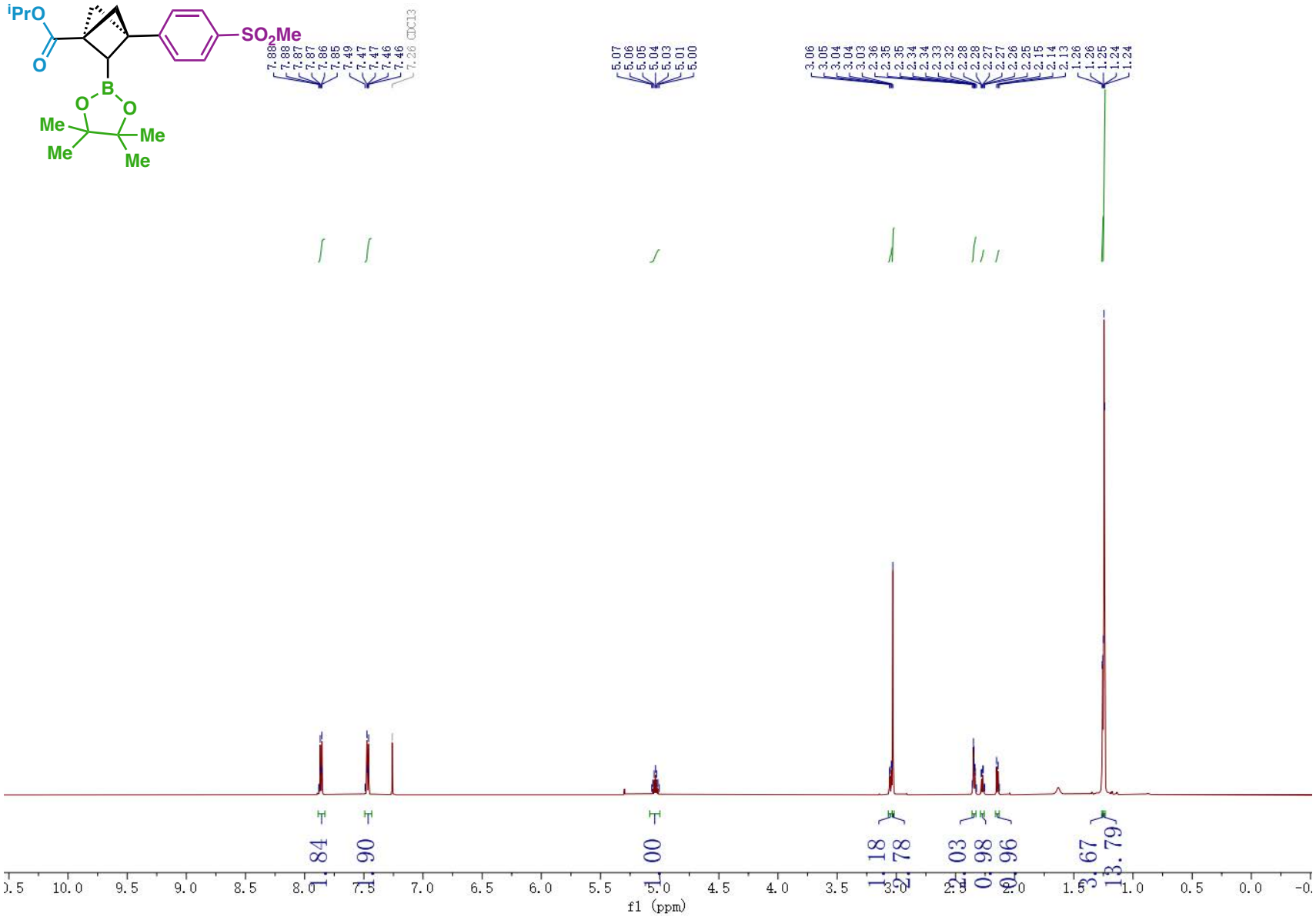


Compound 55 ^{1}H NMR



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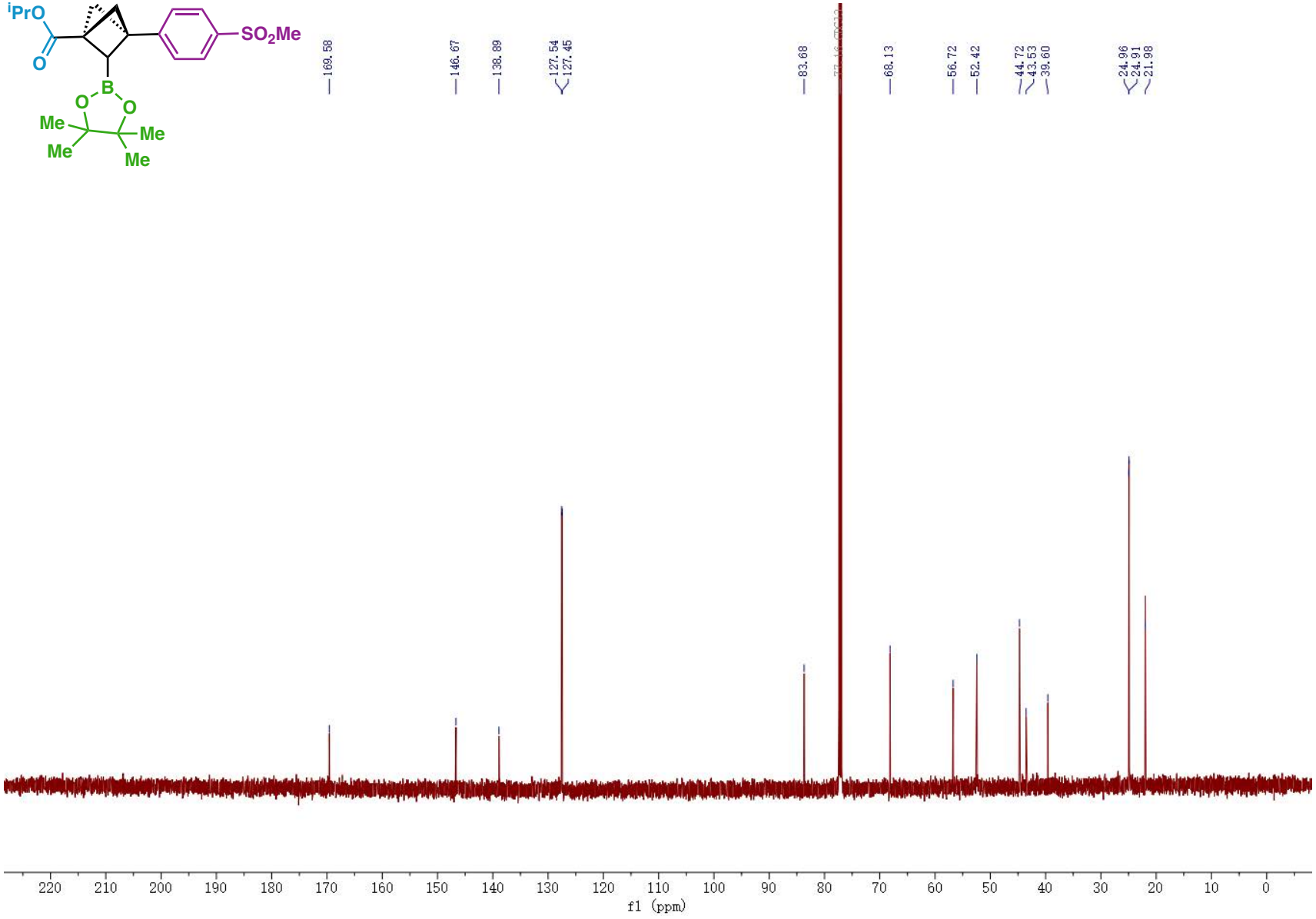
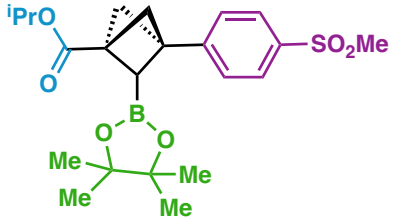
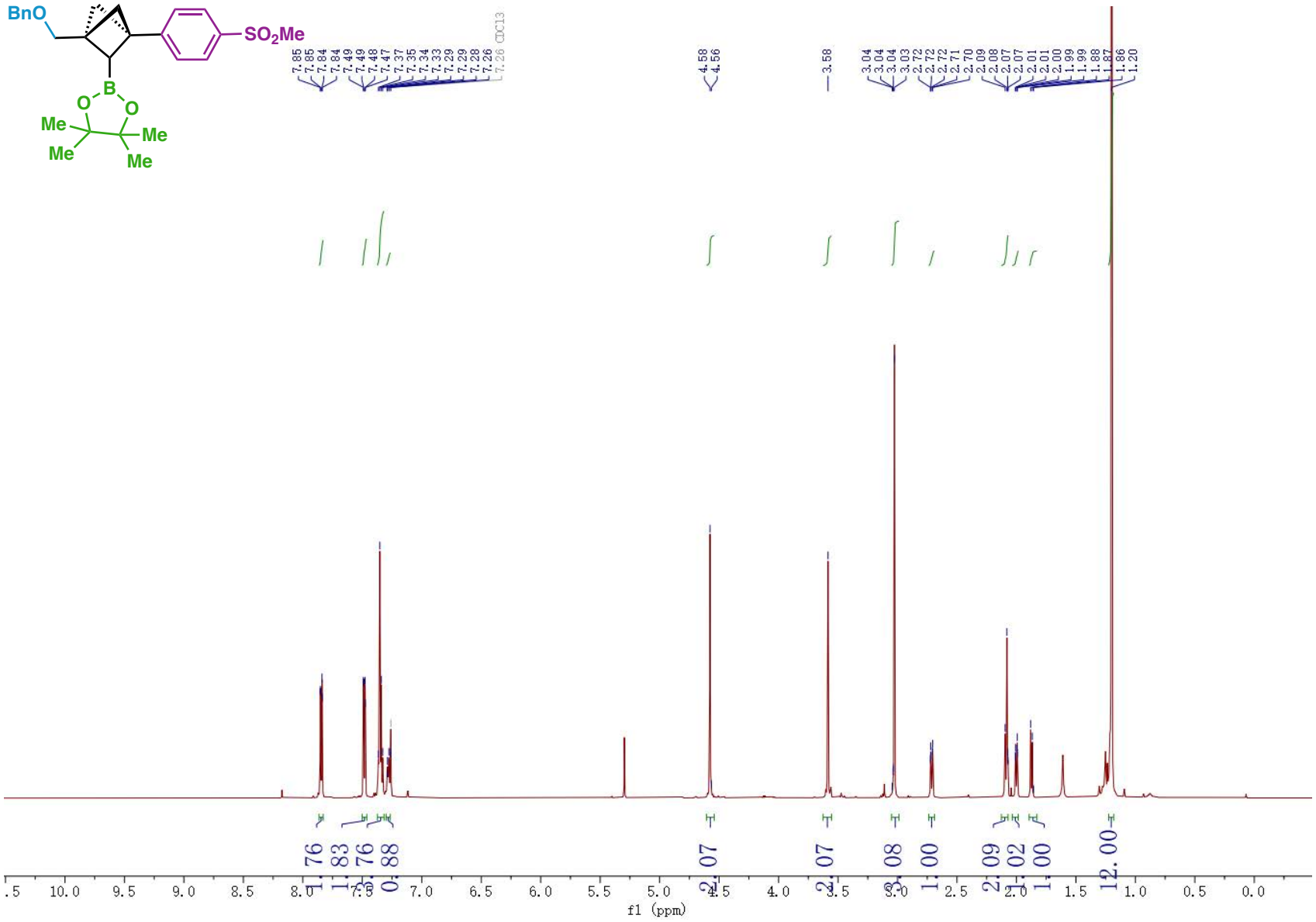


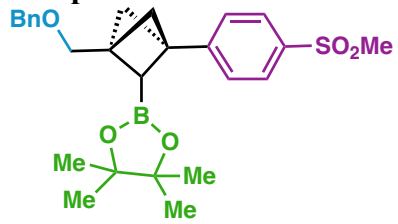
Compound 55 ^{11}B NMR



Compound 56 ^{1}H NMR



Compound 56 ^{13}C NMR



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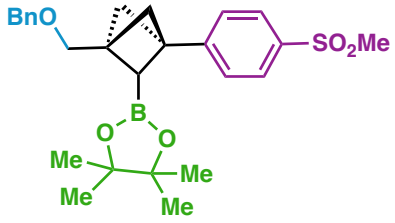
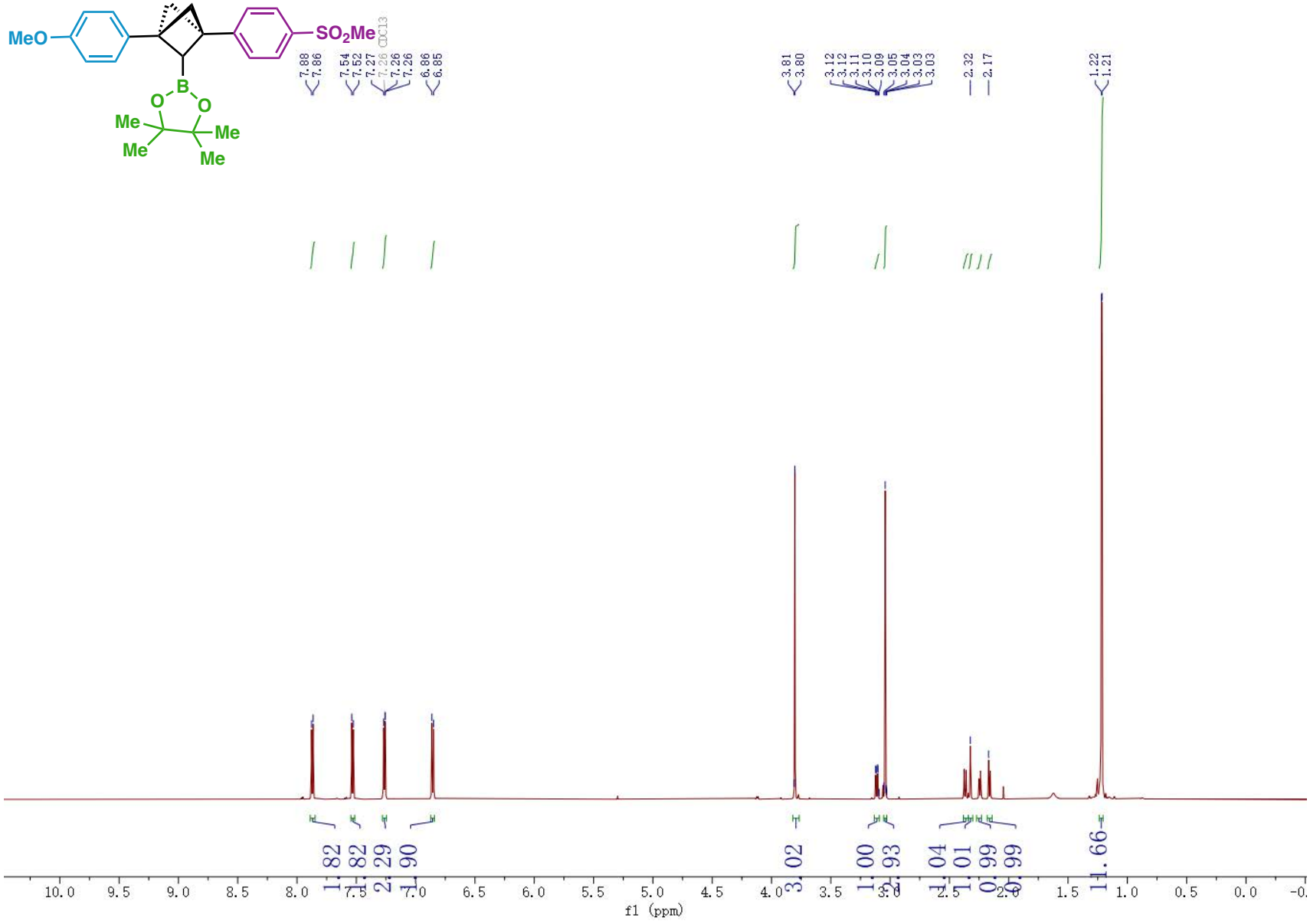


Compound 57 ^{1}H NMR



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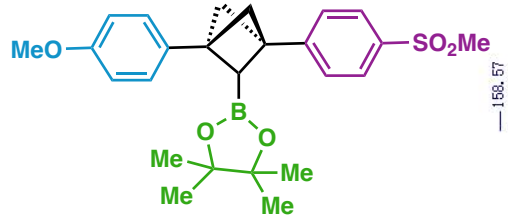

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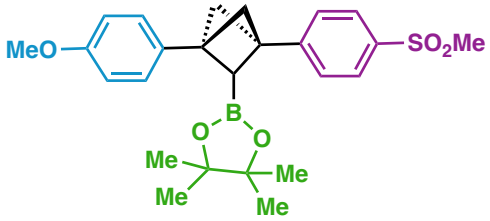
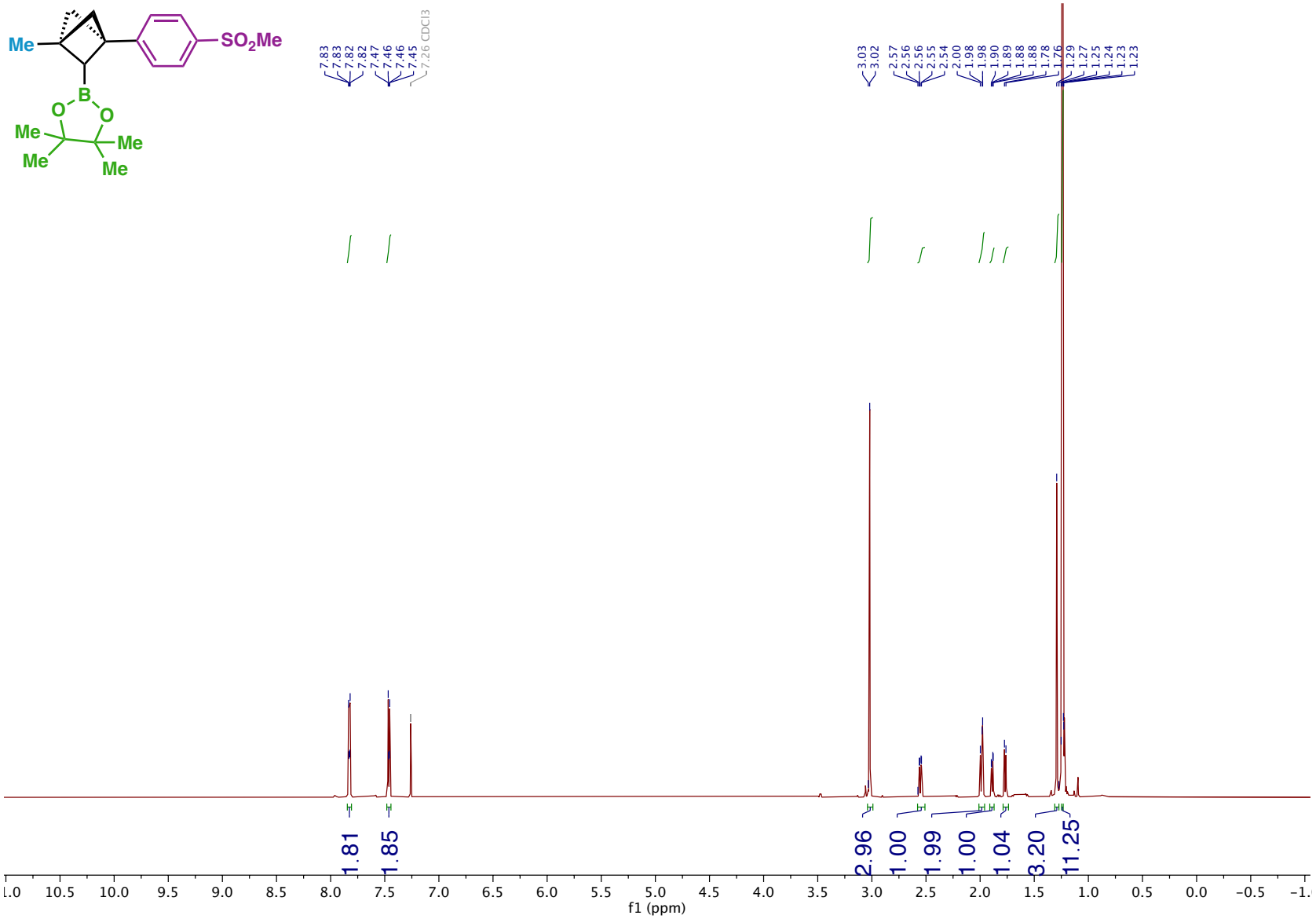
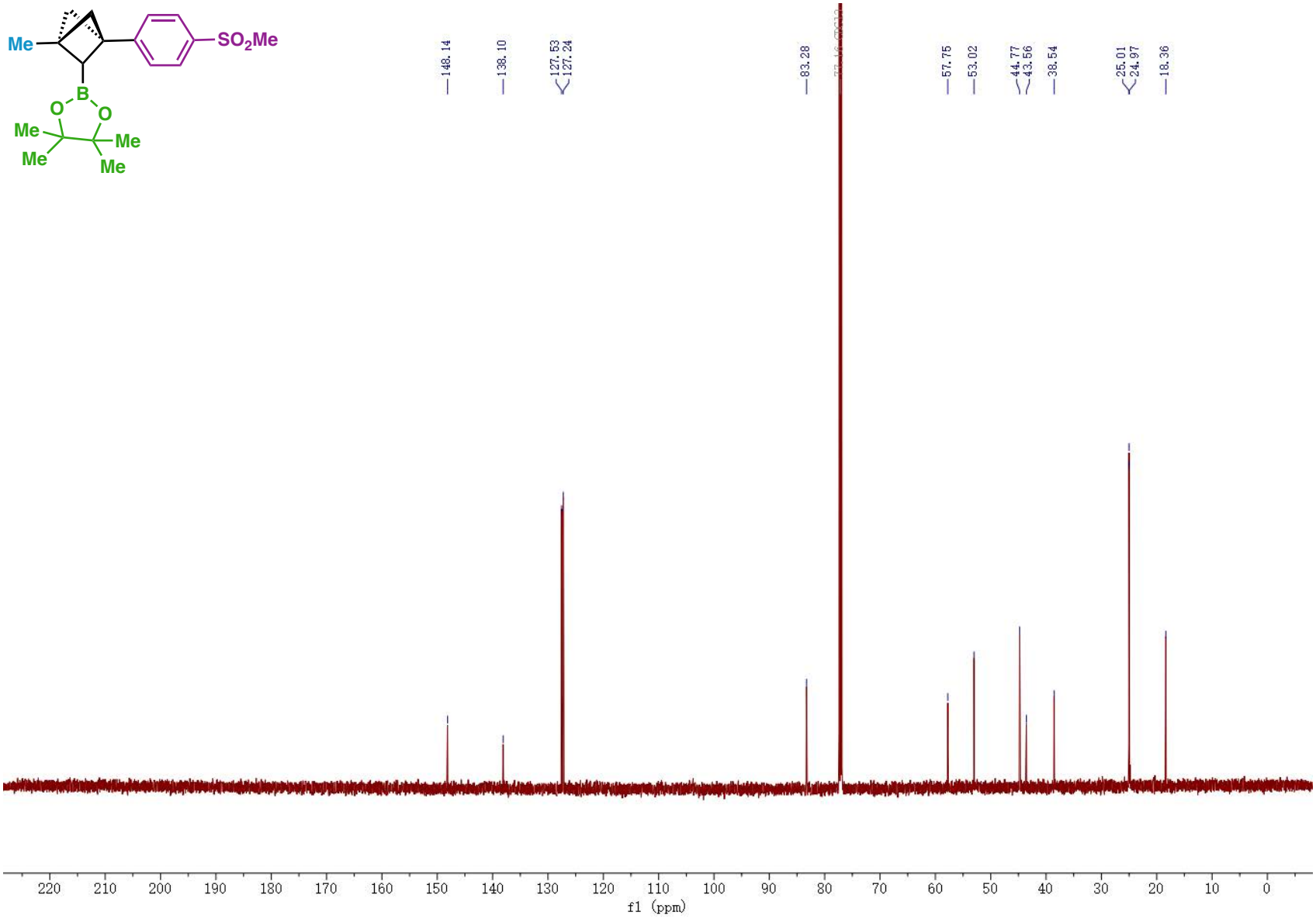


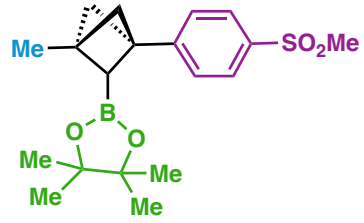
Compound 58 ^{1}H NMR



Compound 58 ^{13}C NMR



Compound 58 ^{11}B NMR



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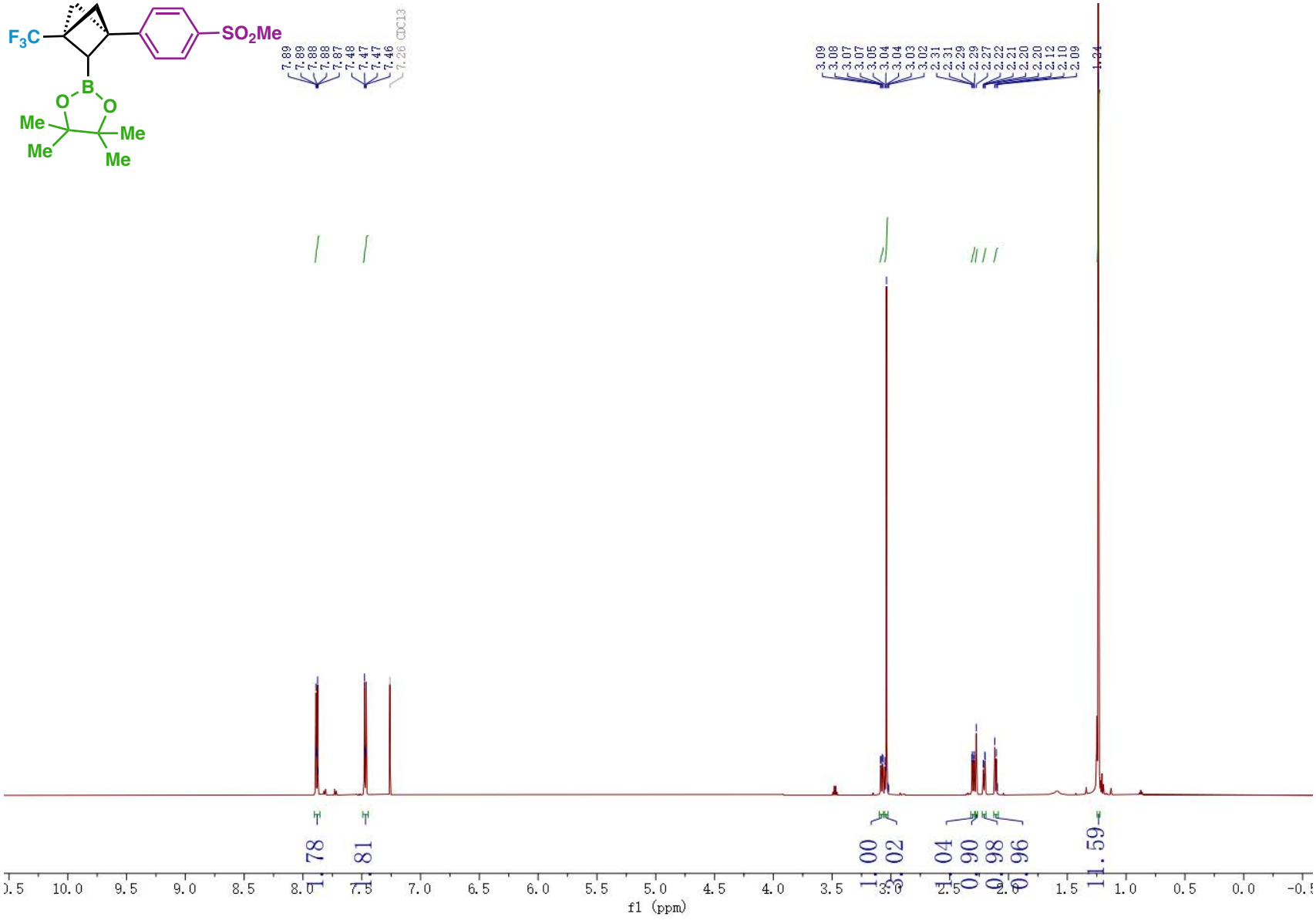
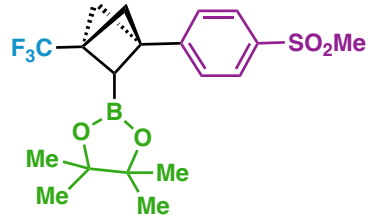
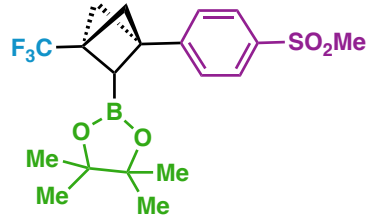


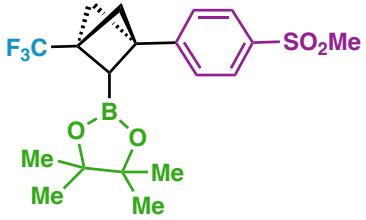
Compound 59 ^{13}C NMR



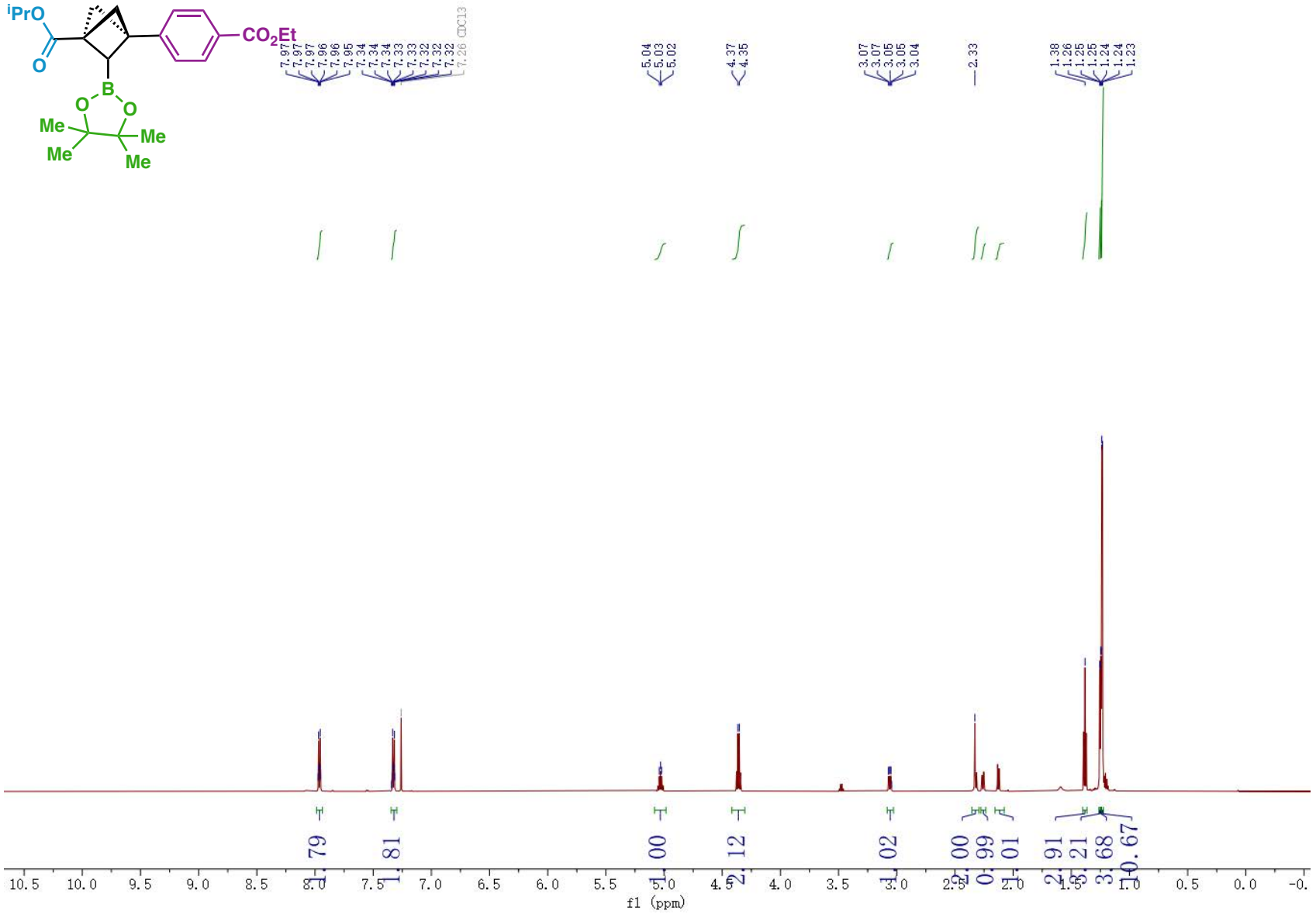
Compound 59 ^{11}B NMR



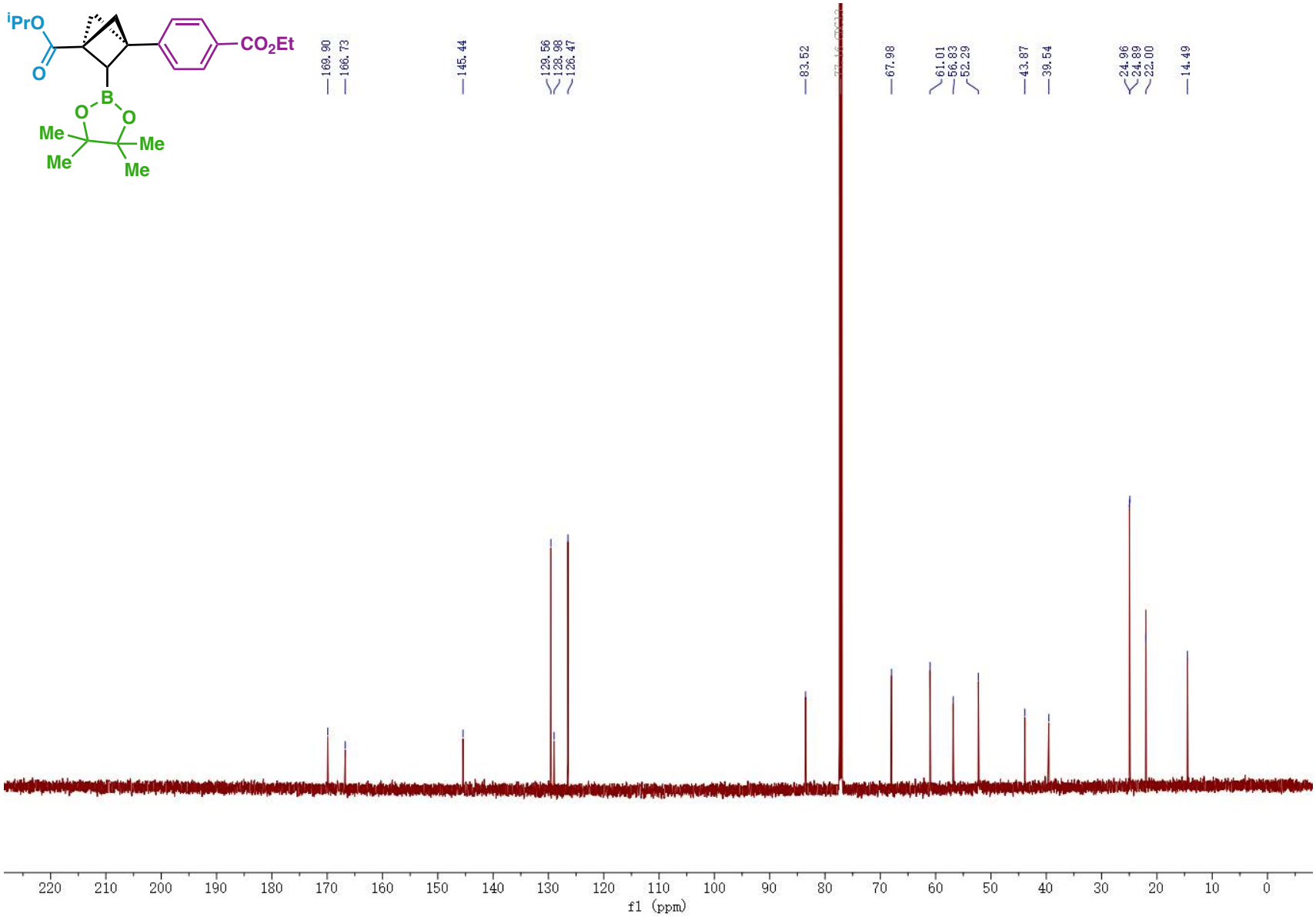
Compound 59 ^{19}F NMR



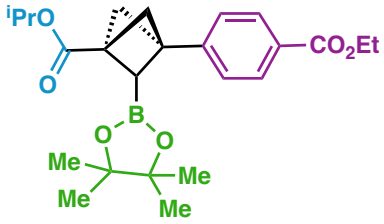
Compound 60 ^{1}H NMR



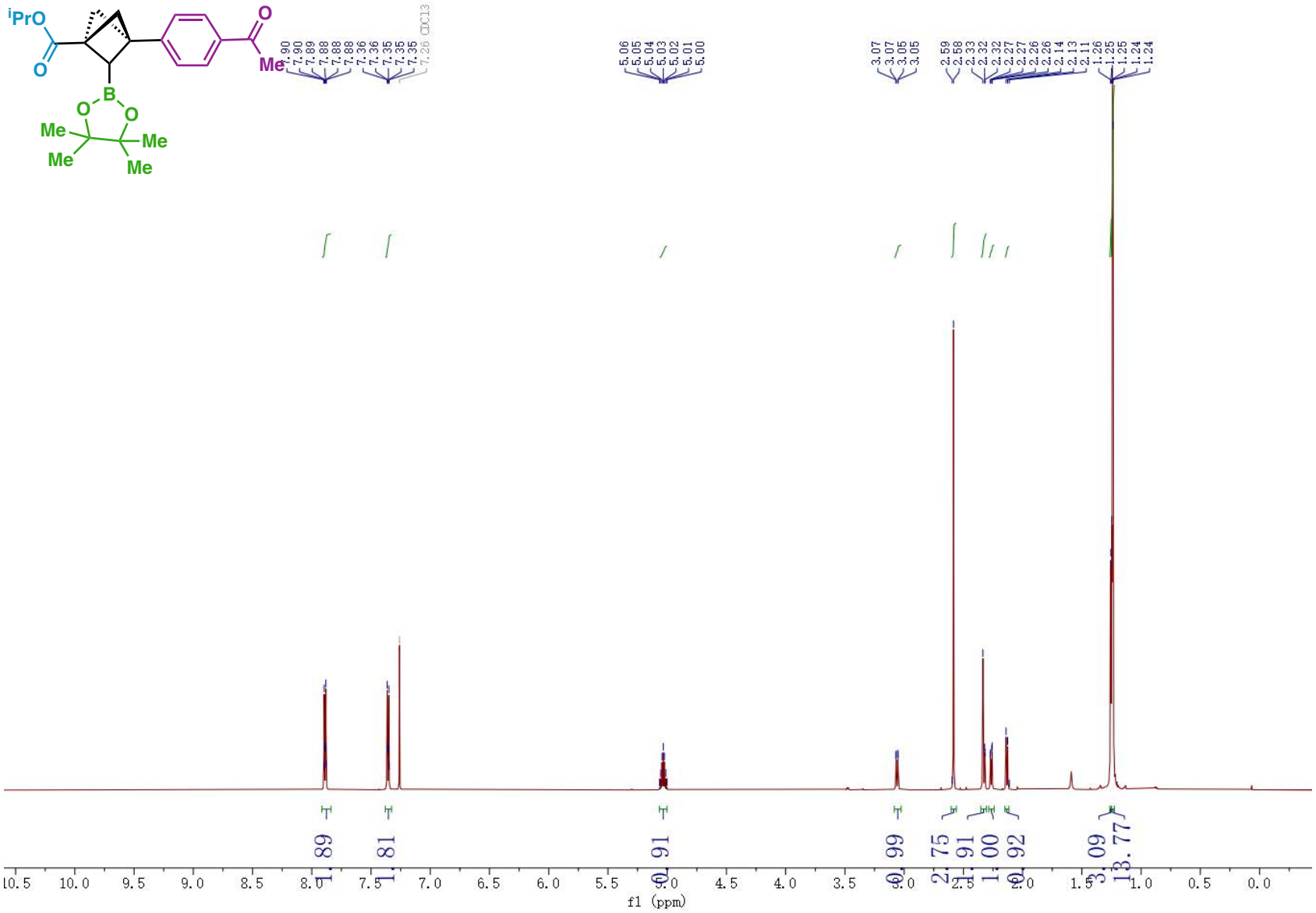
Compound 60 ^{13}C NMR



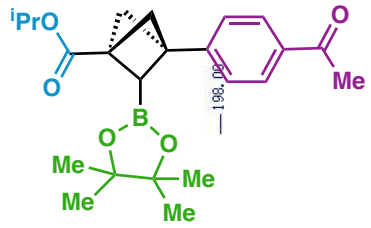
Compound 60 ^{11}B NMR



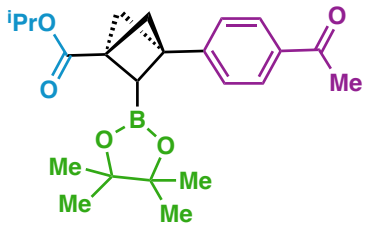
Compound 61 ^{1}H NMR



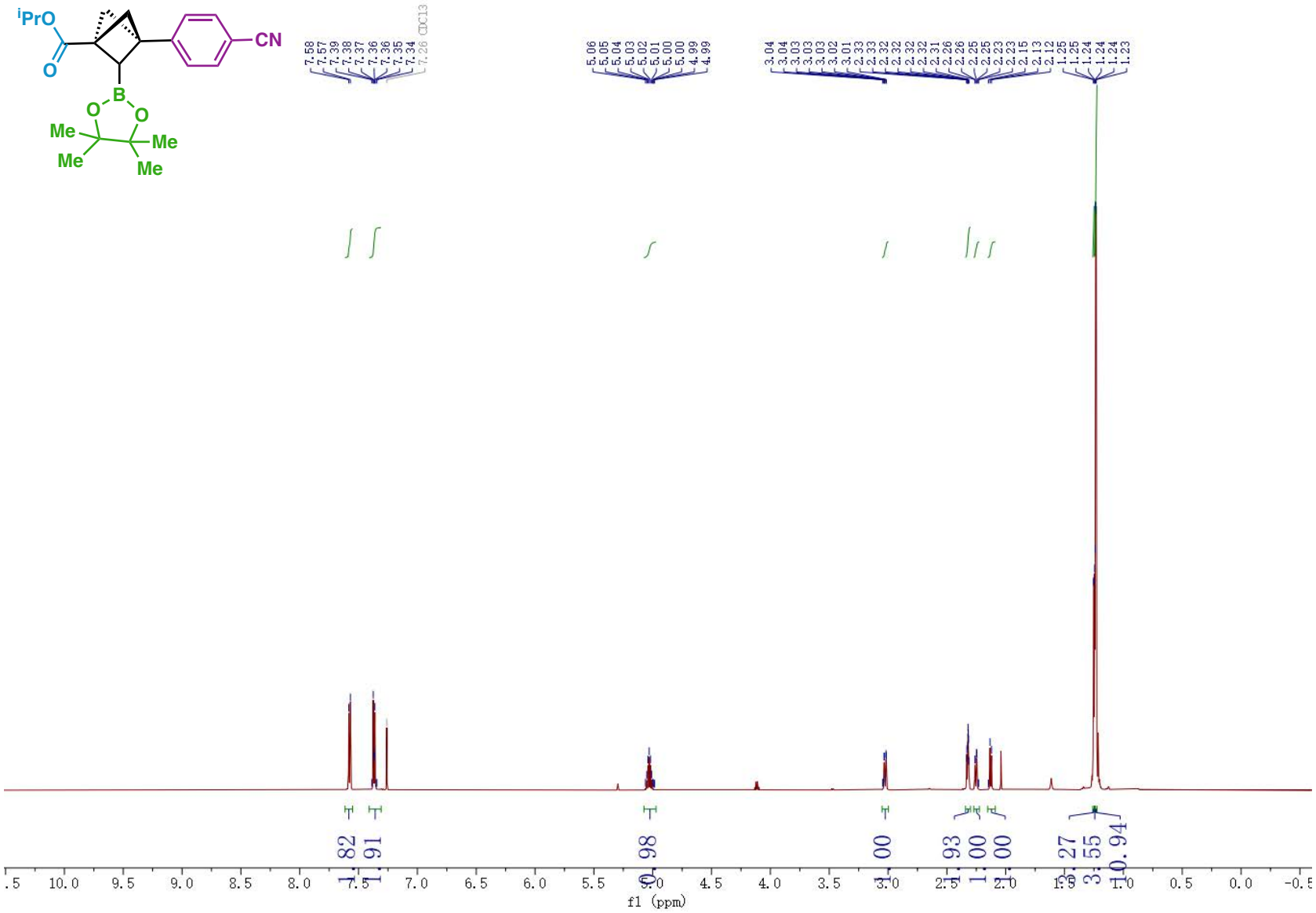
Compound 61 ^{13}C NMR



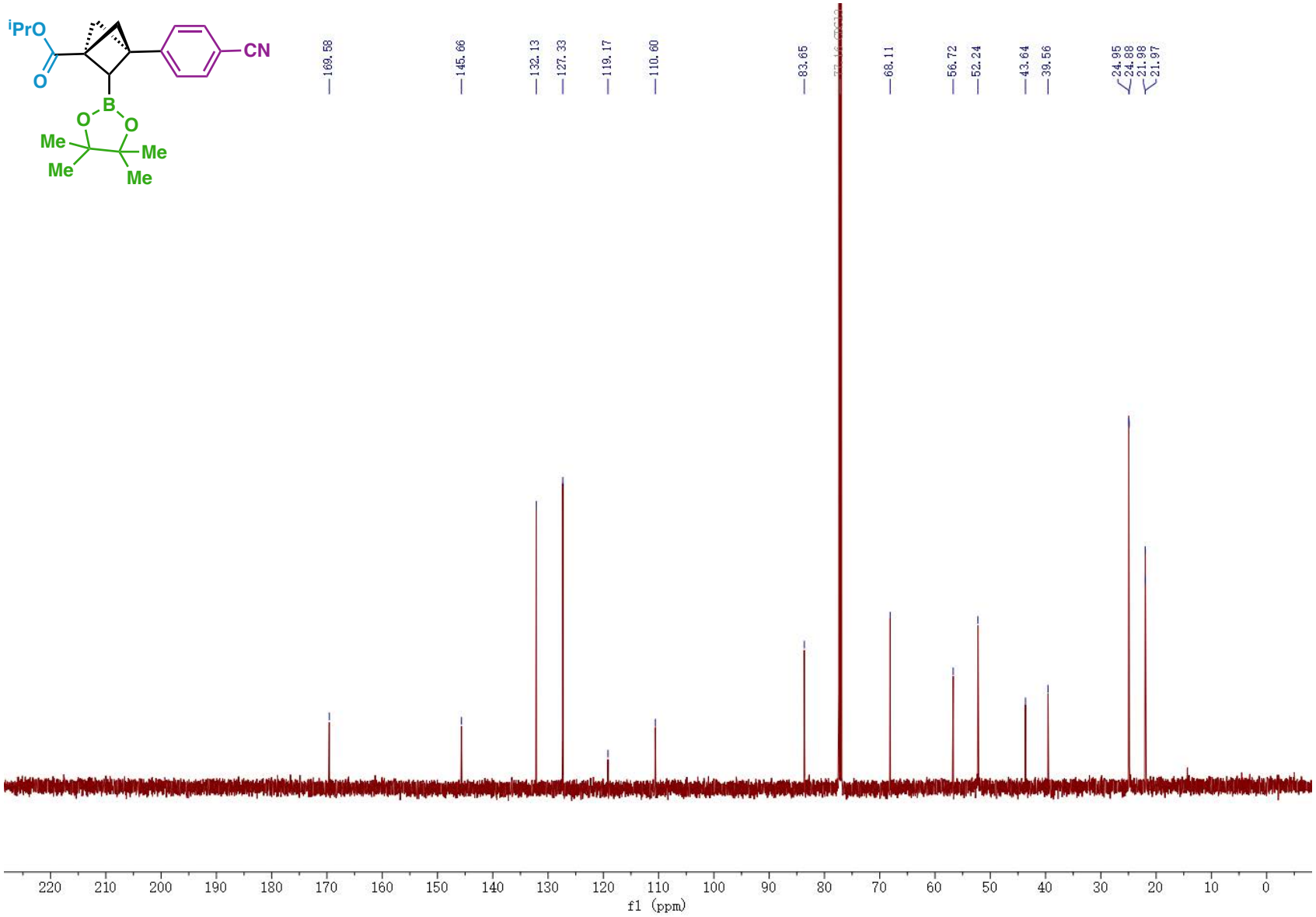
Compound 61 ^{11}B NMR



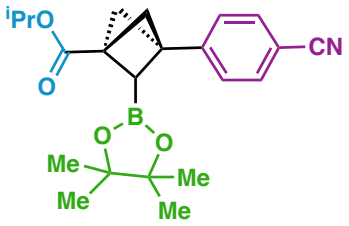
Compound 62 ^{1}H NMR



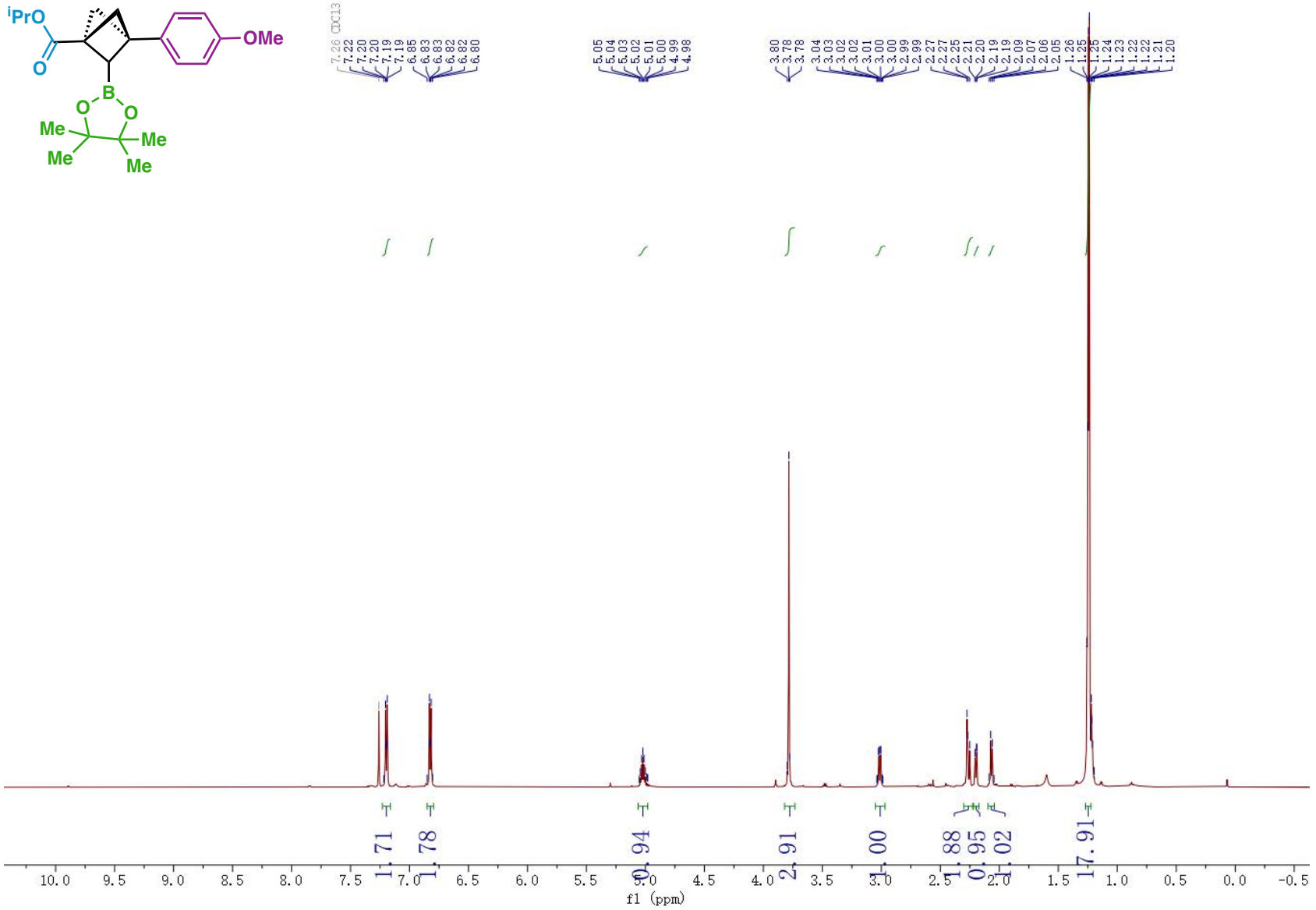
Compound 62 ^{13}C NMR



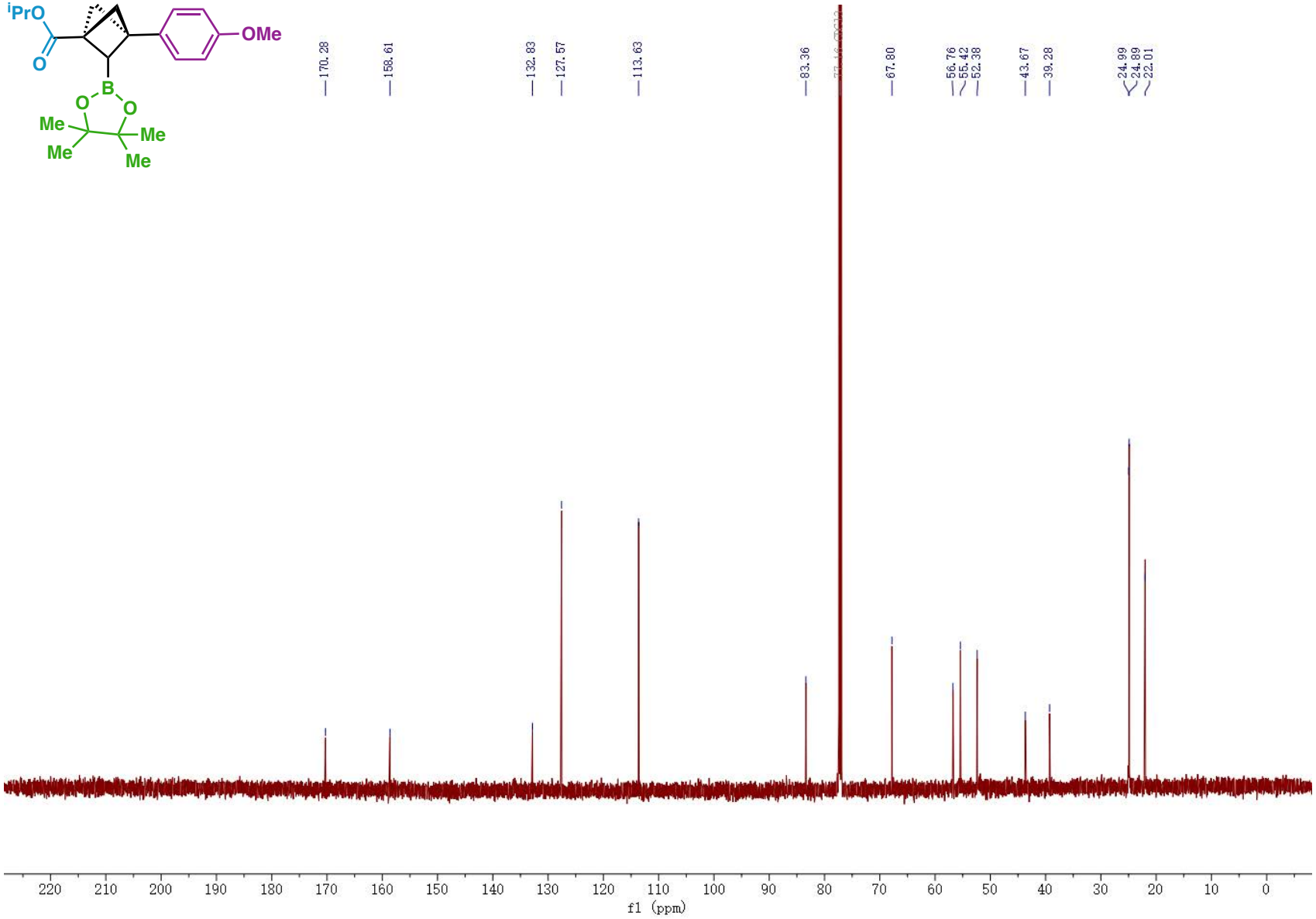
Compound 62 ^{11}B NMR



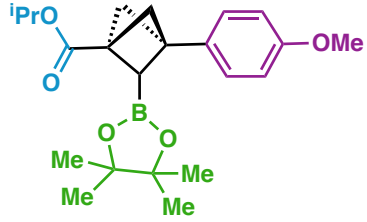
Compound 63 ^{1}H NMR



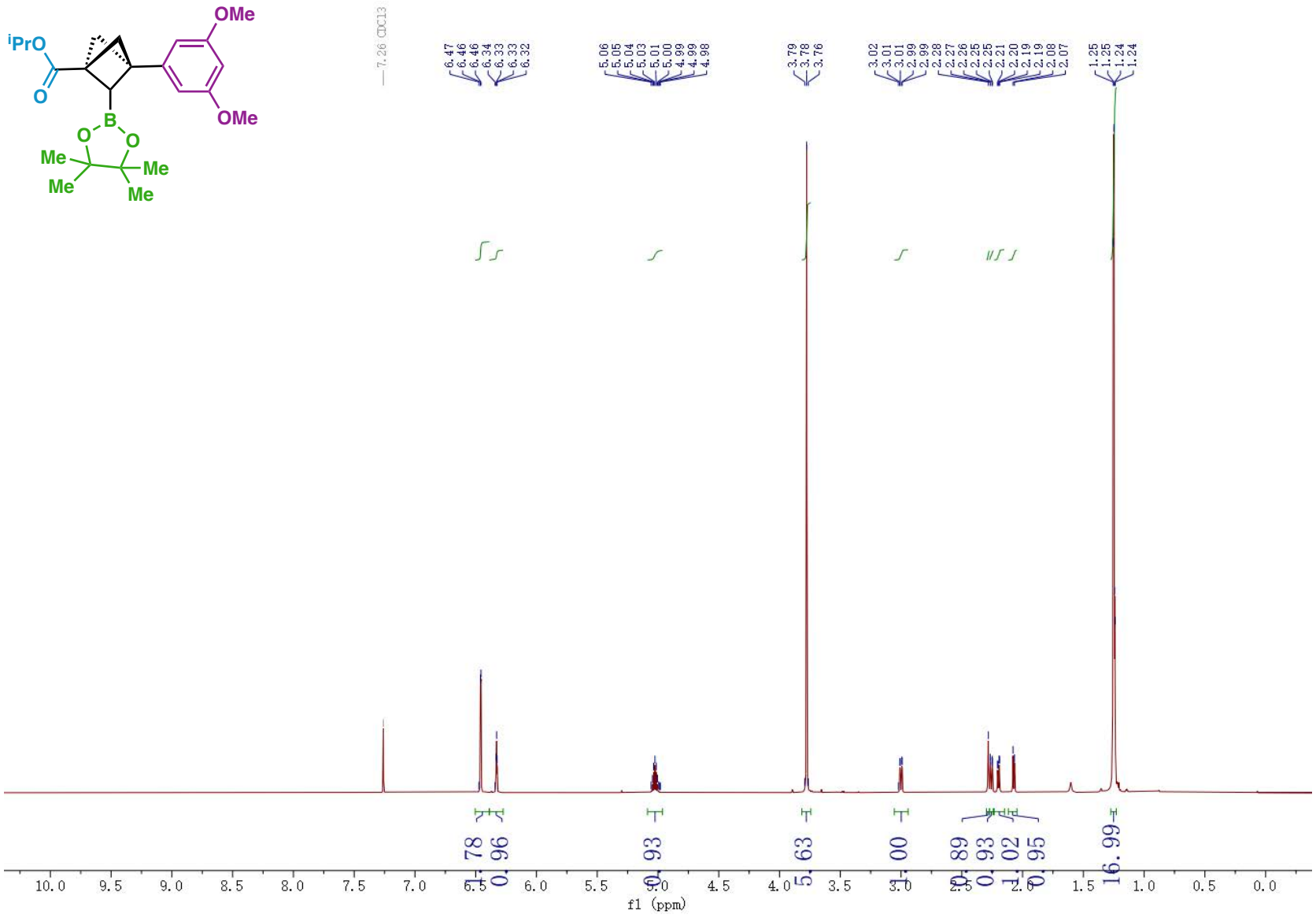
Compound 63 ^{13}C NMR



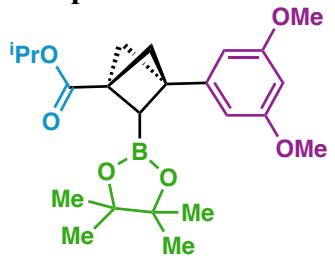
Compound 63 ^{11}B NMR



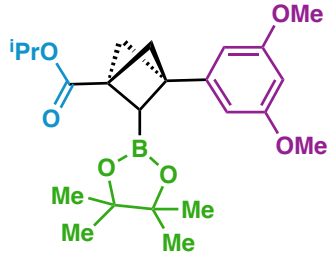
Compound 64 ^{1}H NMR



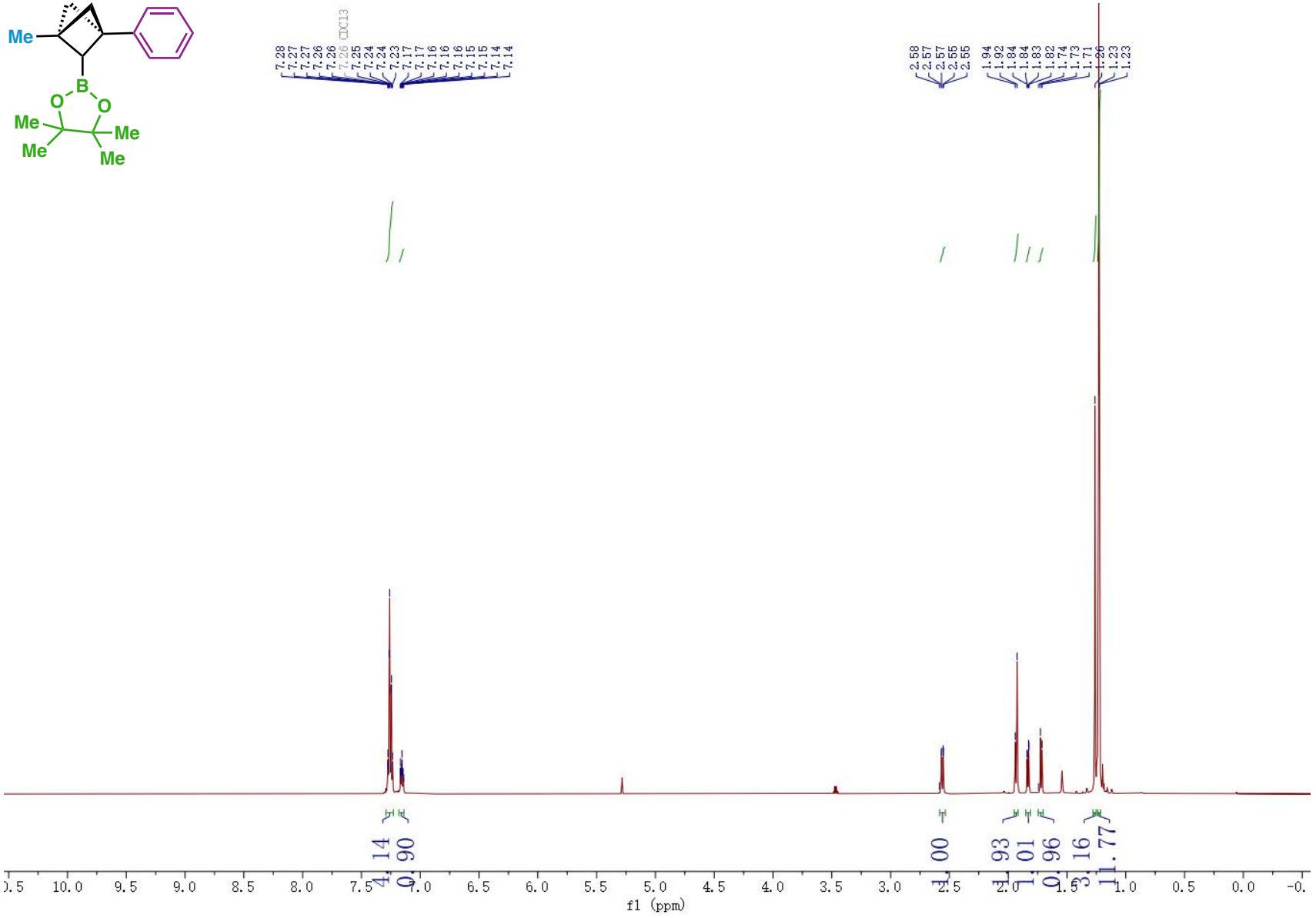
Compound 64 ^{13}C NMR



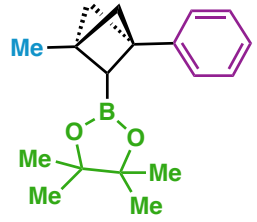
Compound 64 ^{11}B NMR



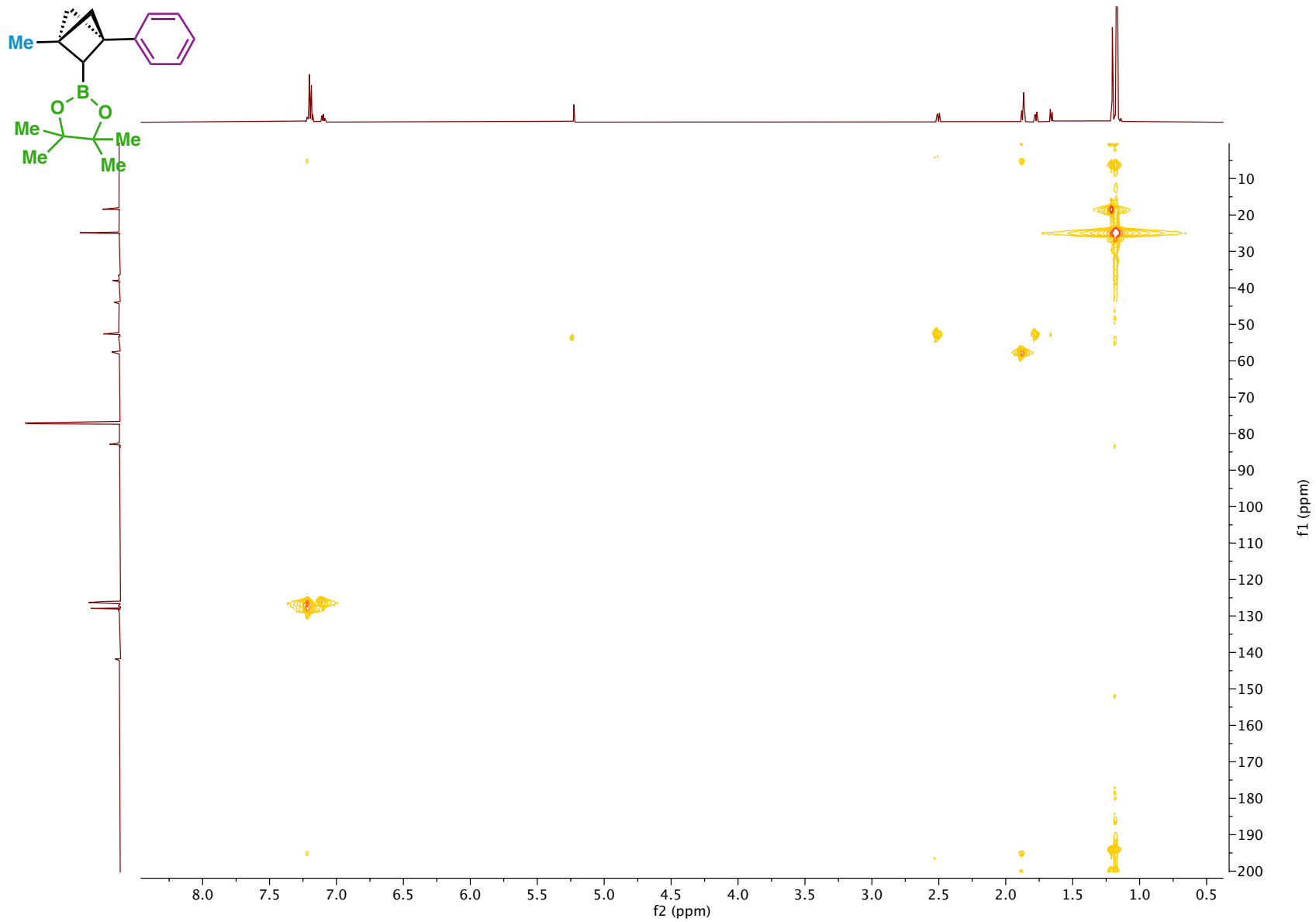
Compound 65 ^{1}H NMR



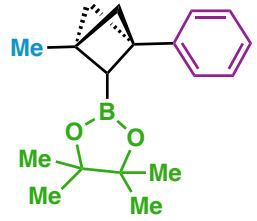
Compound 65 ^{13}C NMR



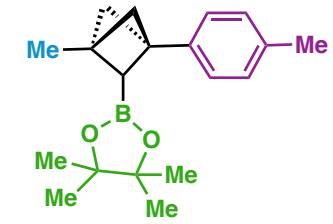
Compound 65 HSQC



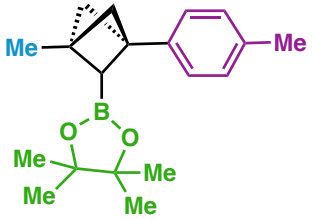
Compound 65 ^{11}B NMR



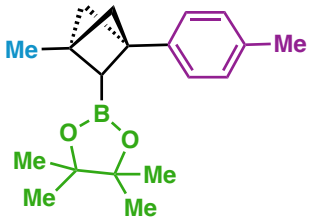
Compound 66 ^{1}H NMR



Compound 66 ^{13}C NMR



Compound 66 ^{11}B NMR



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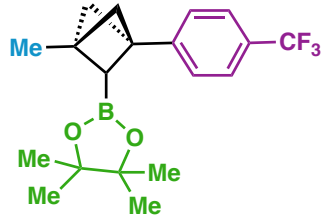
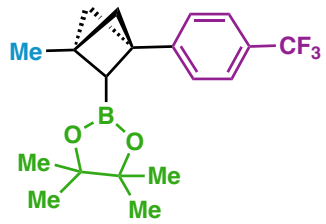
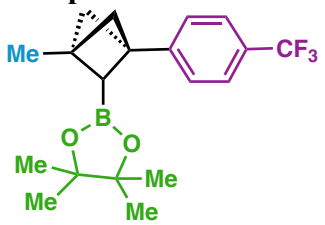


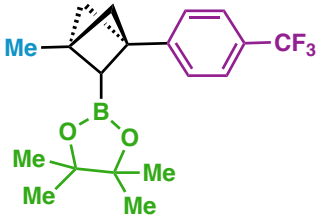
Compound 67 ^{13}C NMR



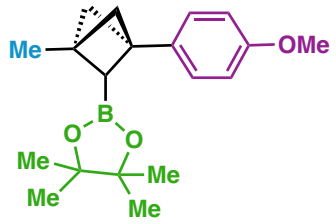
Compound 67 ^{11}B NMR



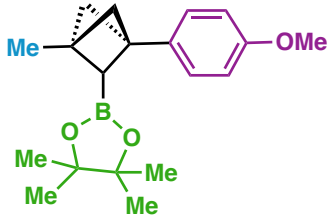
Compound 67 ^{19}F NMR



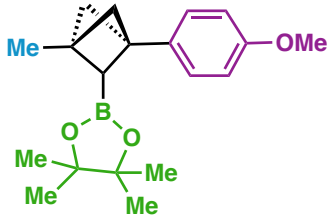
Compound 68 ^{1}H NMR



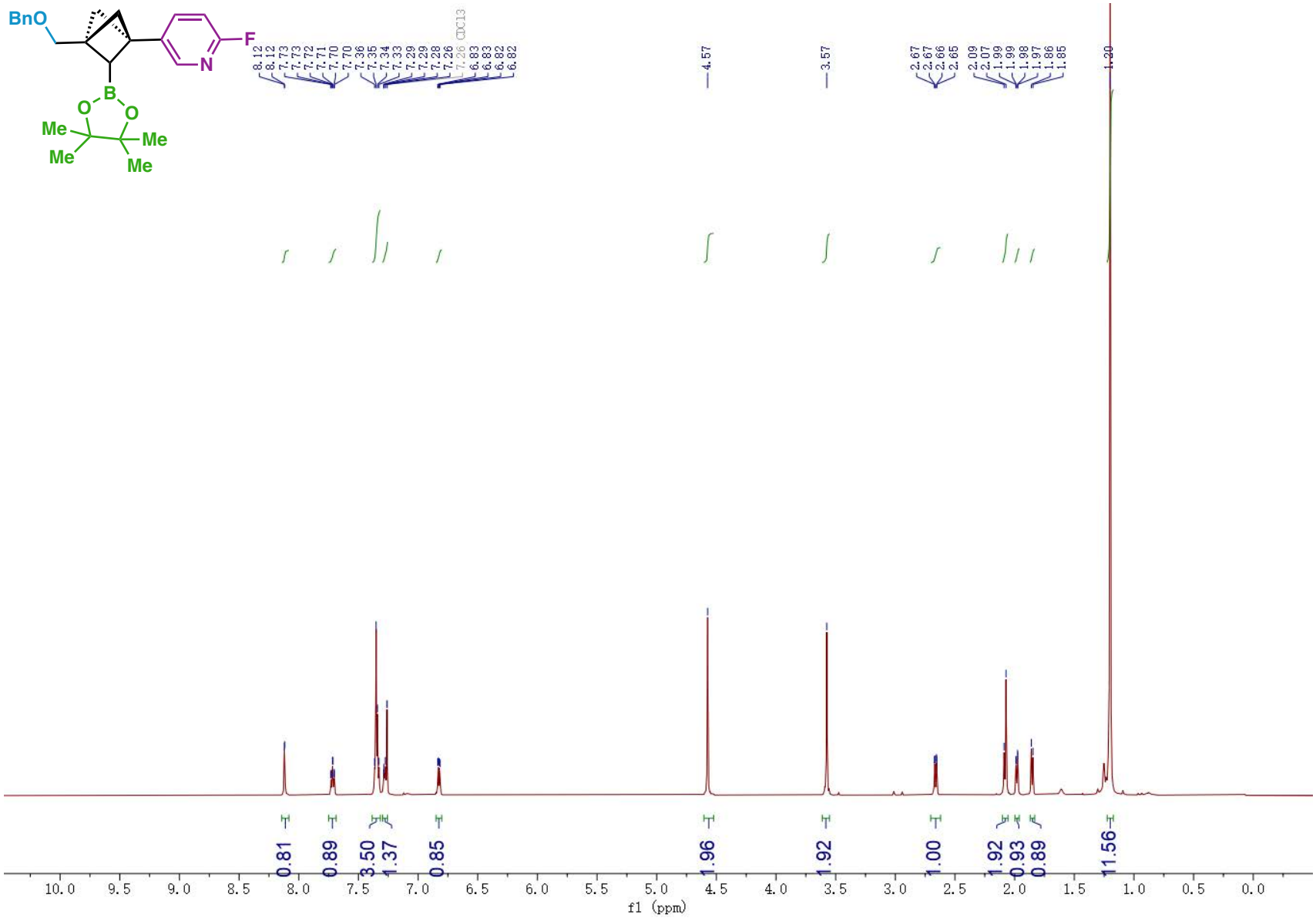
Compound 68 ^{13}C NMR



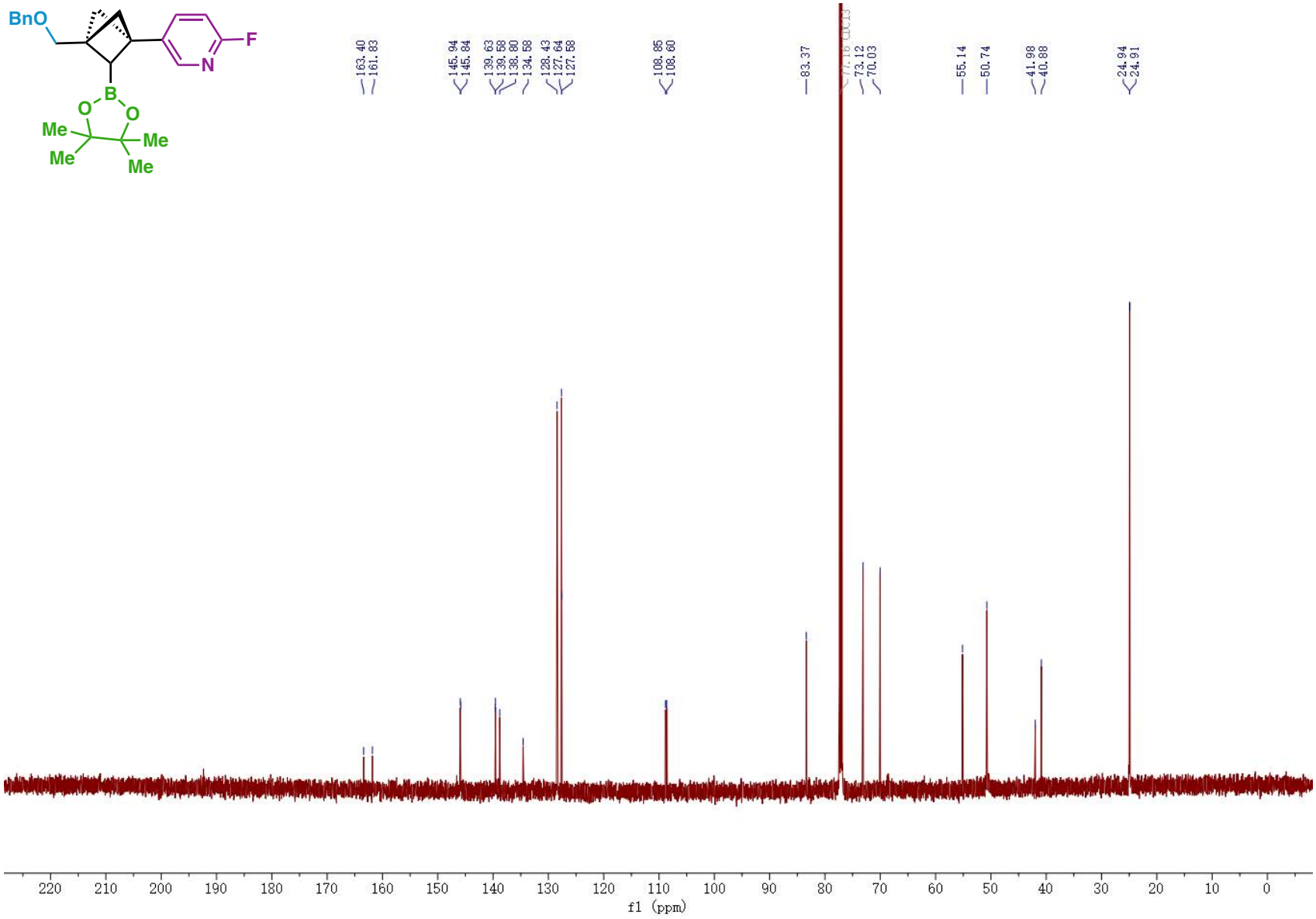
Compound 68 ^{11}B NMR



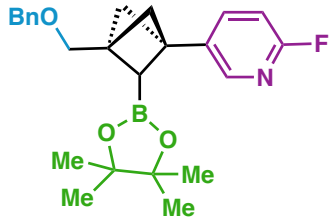
Compound 69 ^{1}H NMR



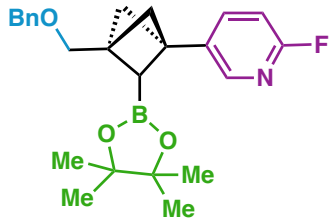
Compound 69 ^{13}C NMR



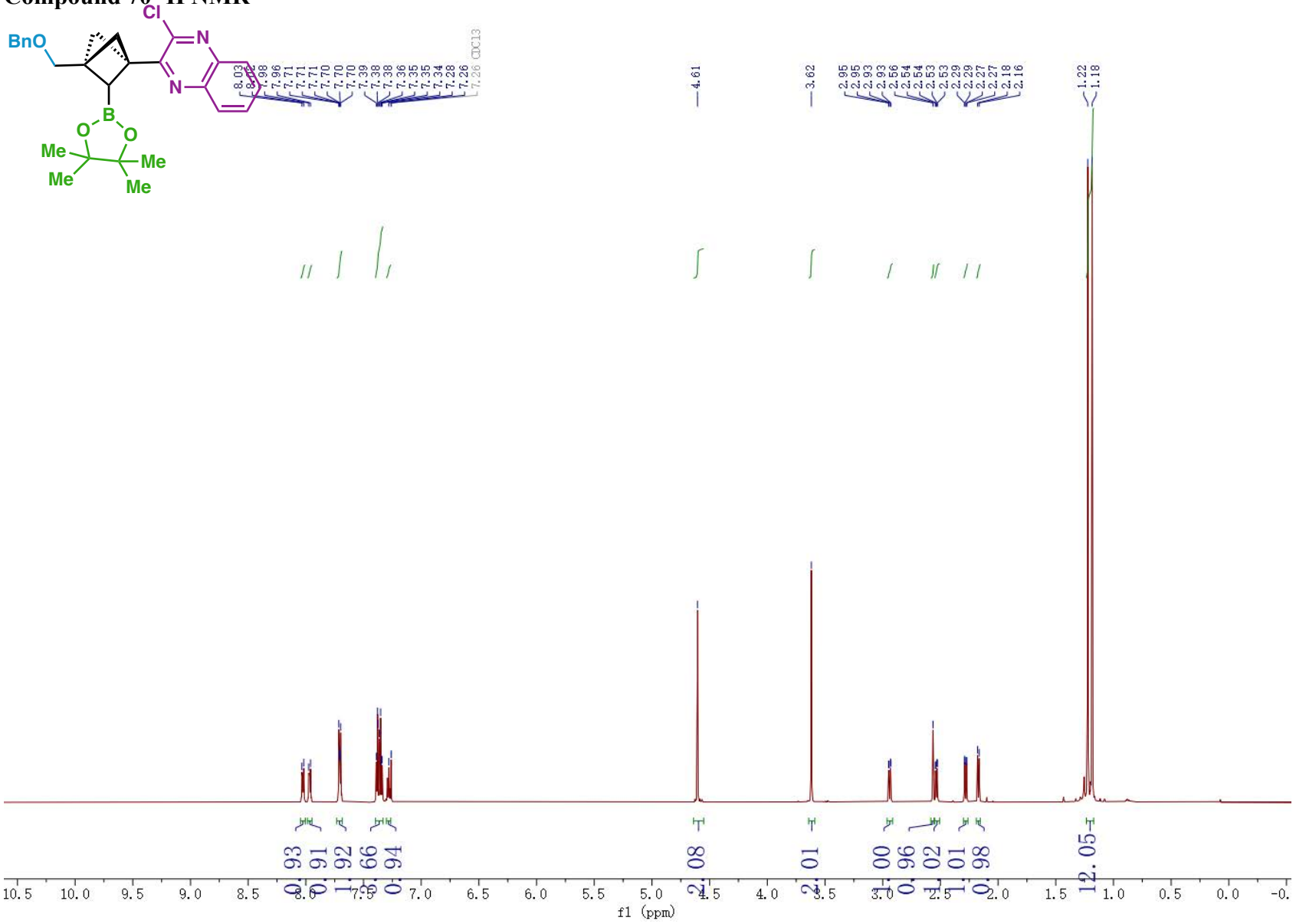
Compound 69 ^{11}B NMR



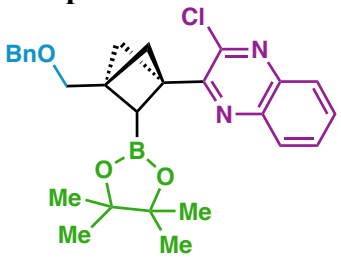
Compound 69 ^{19}F NMR



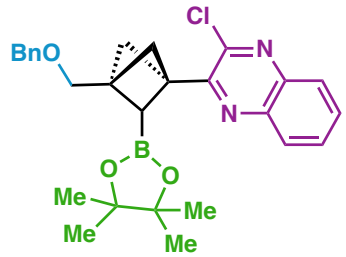
Compound 70 ^{1}H NMR



Compound 70 ^{13}C NMR



Compound 70 ^{11}B NMR



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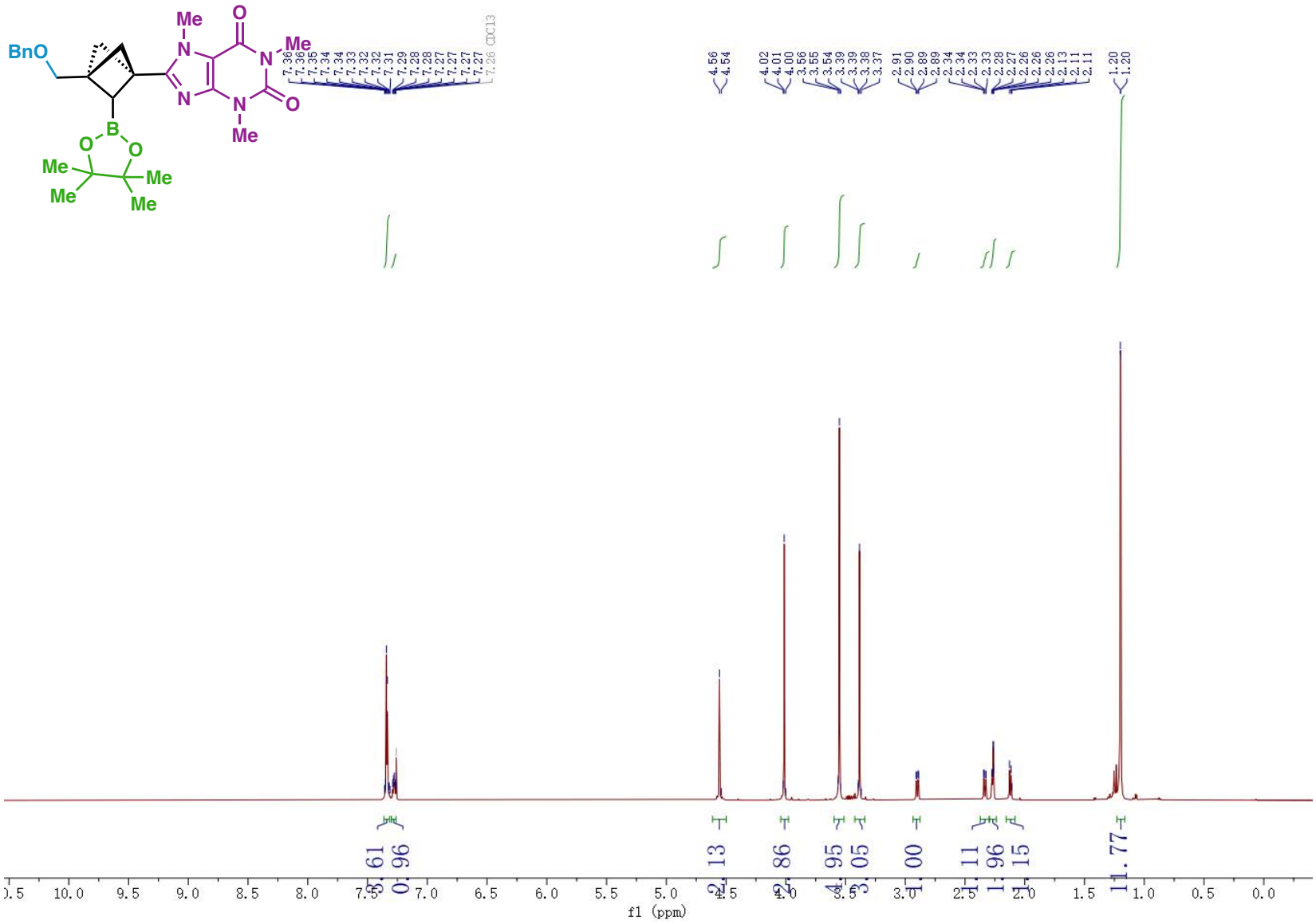
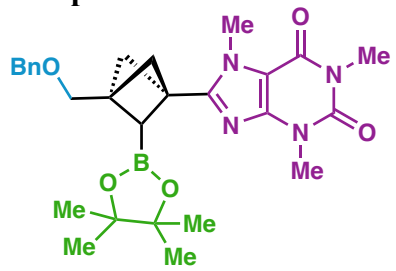


Compound 71 ^{13}C NMR



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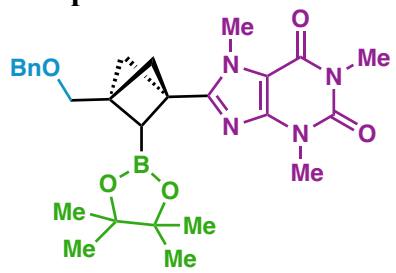
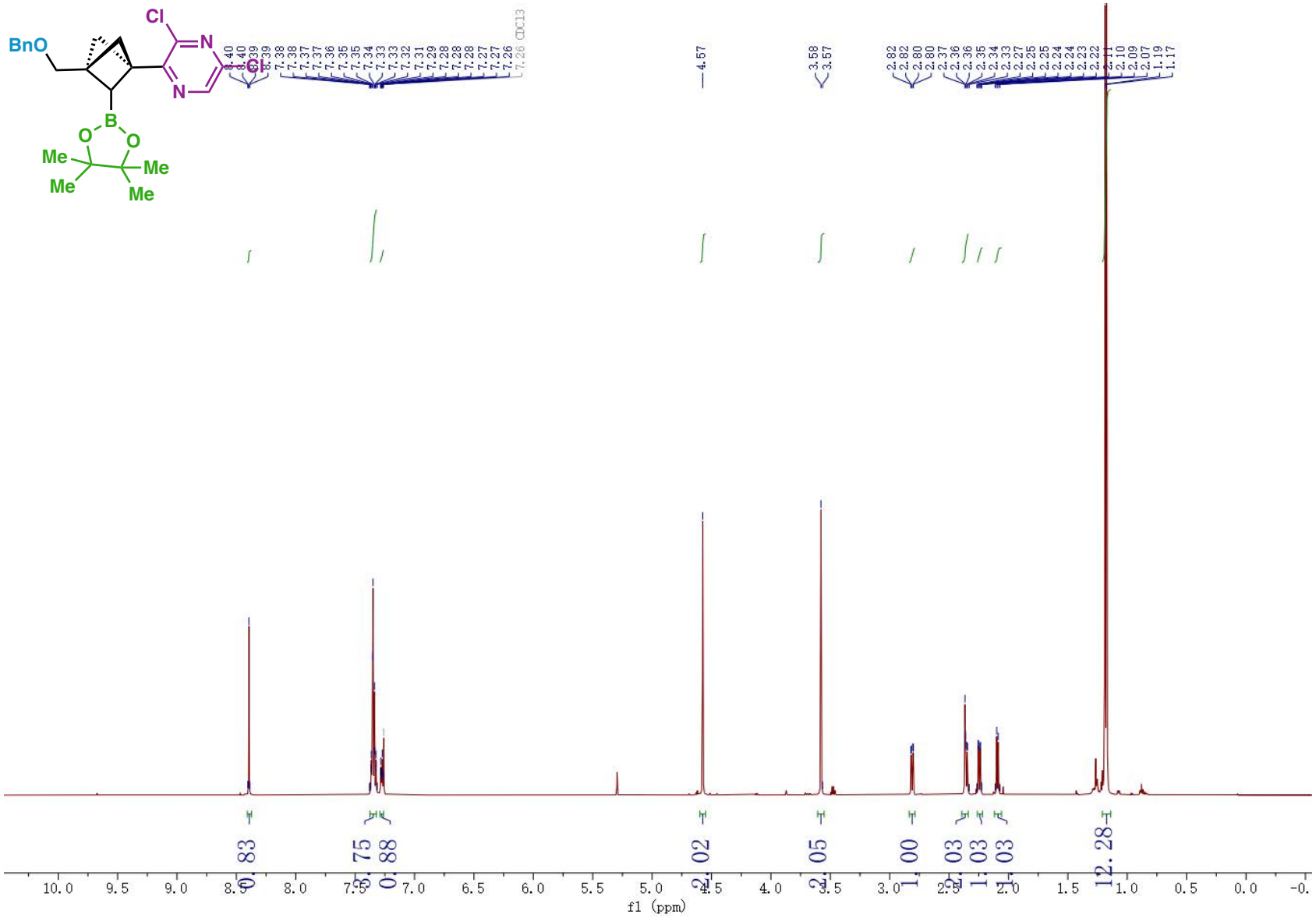
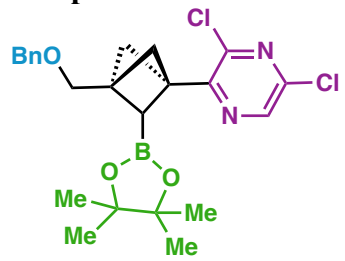


Compound 72 ^{1}H NMR



Compound 72 ^{13}C NMR



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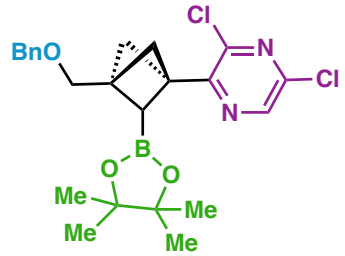
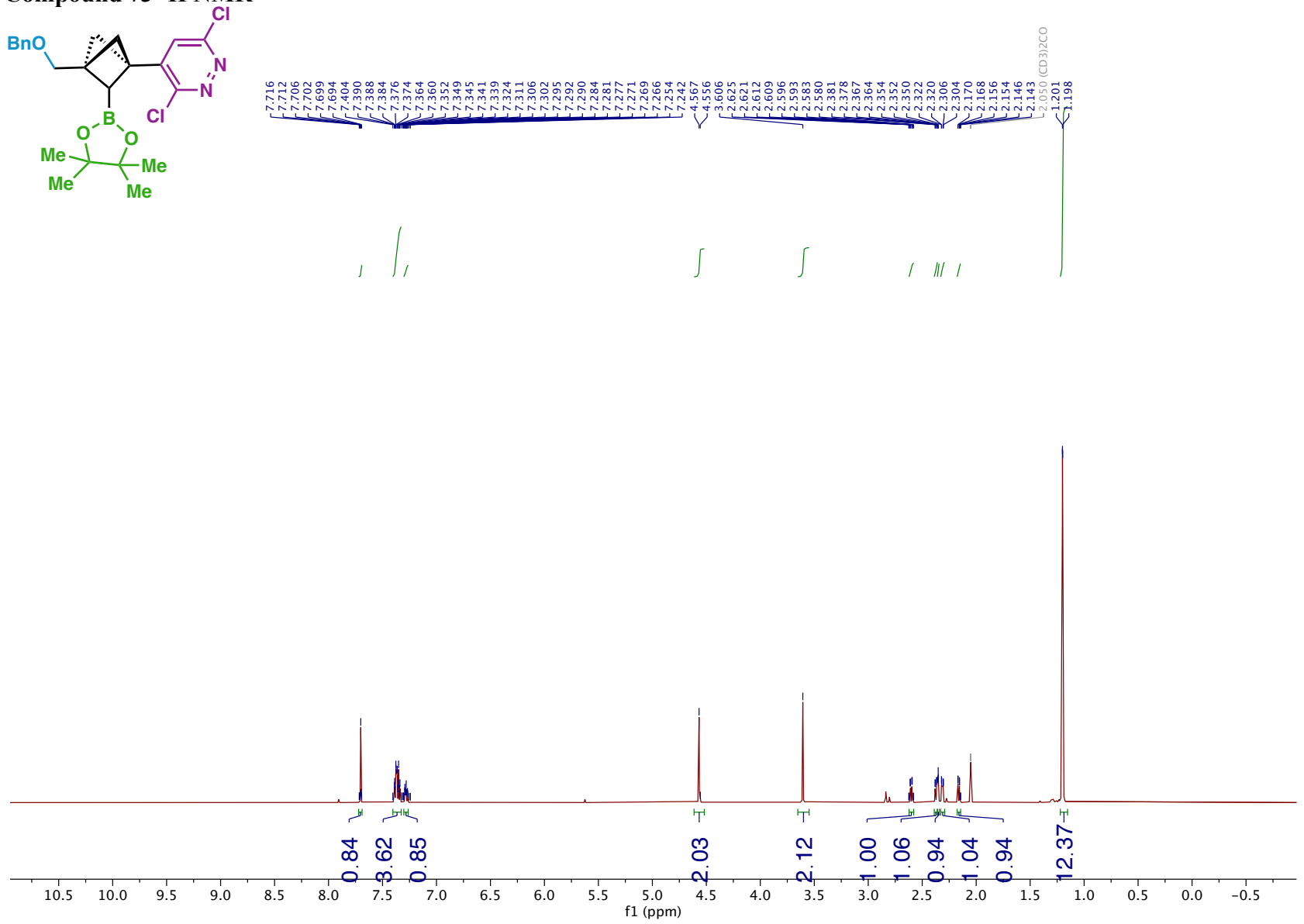


Compound 73 ^{1}H NMR



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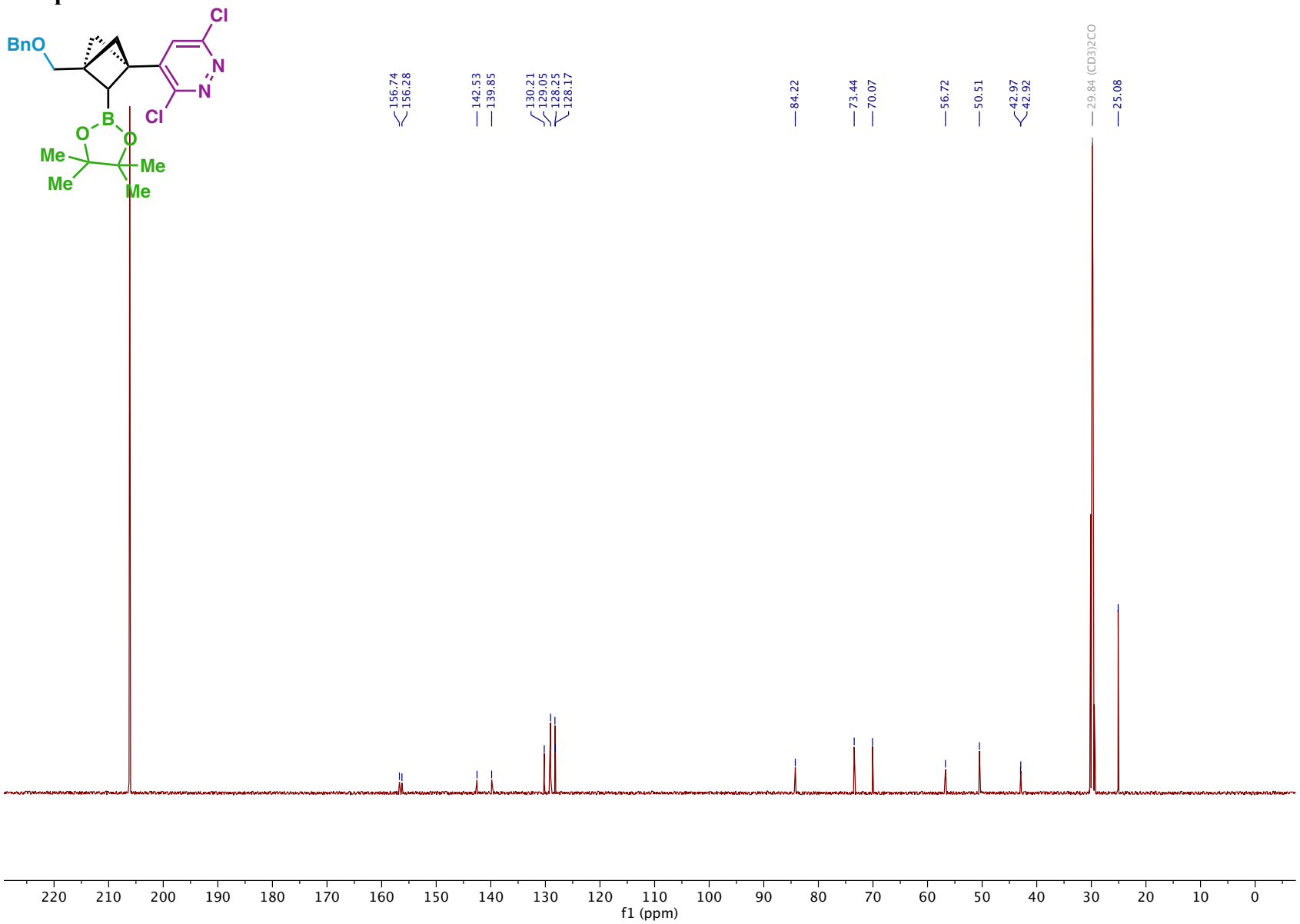
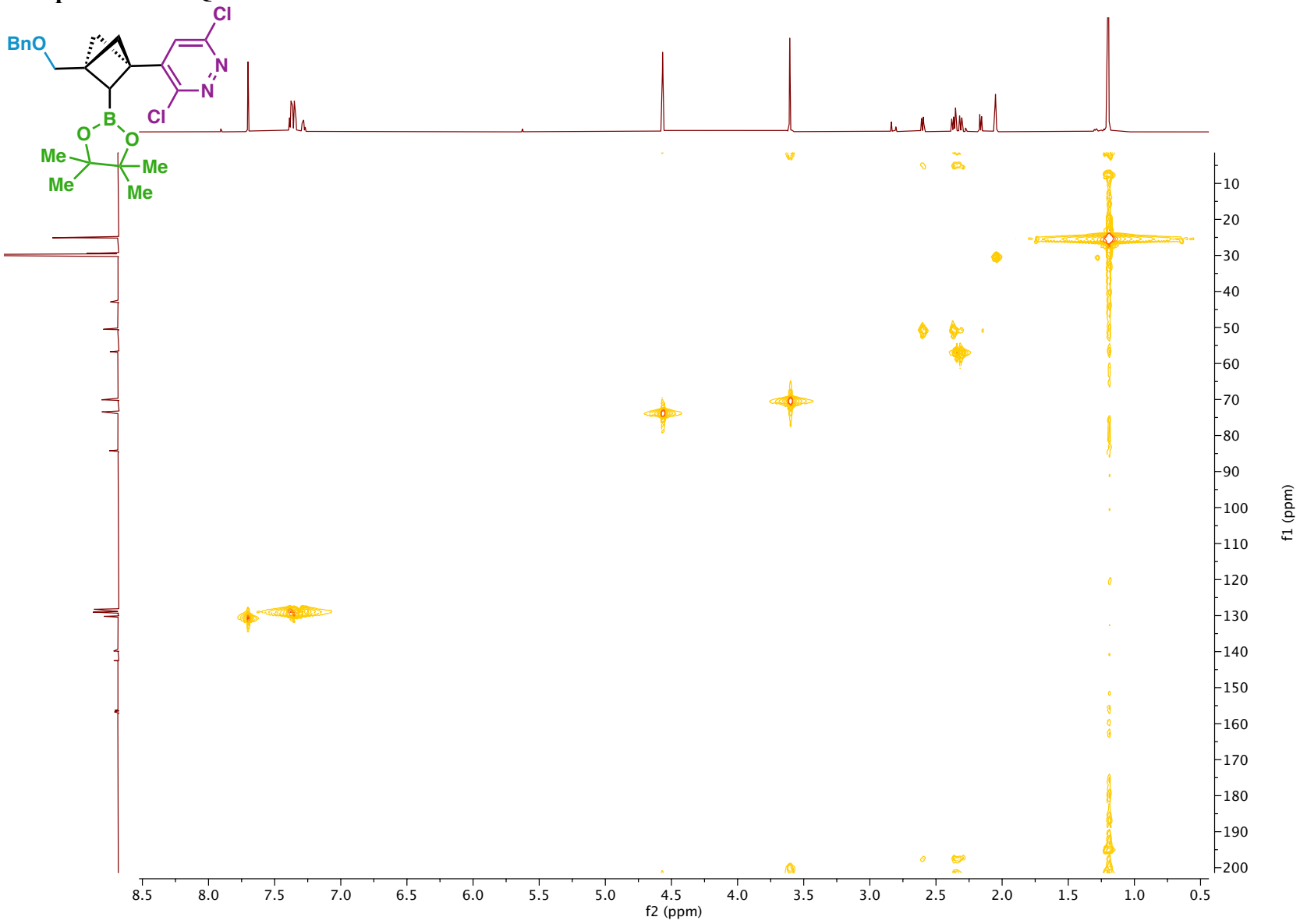


Compound 73 HSQC



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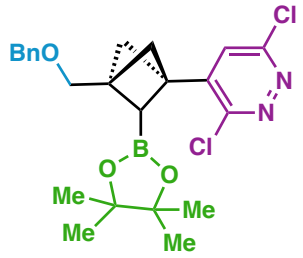
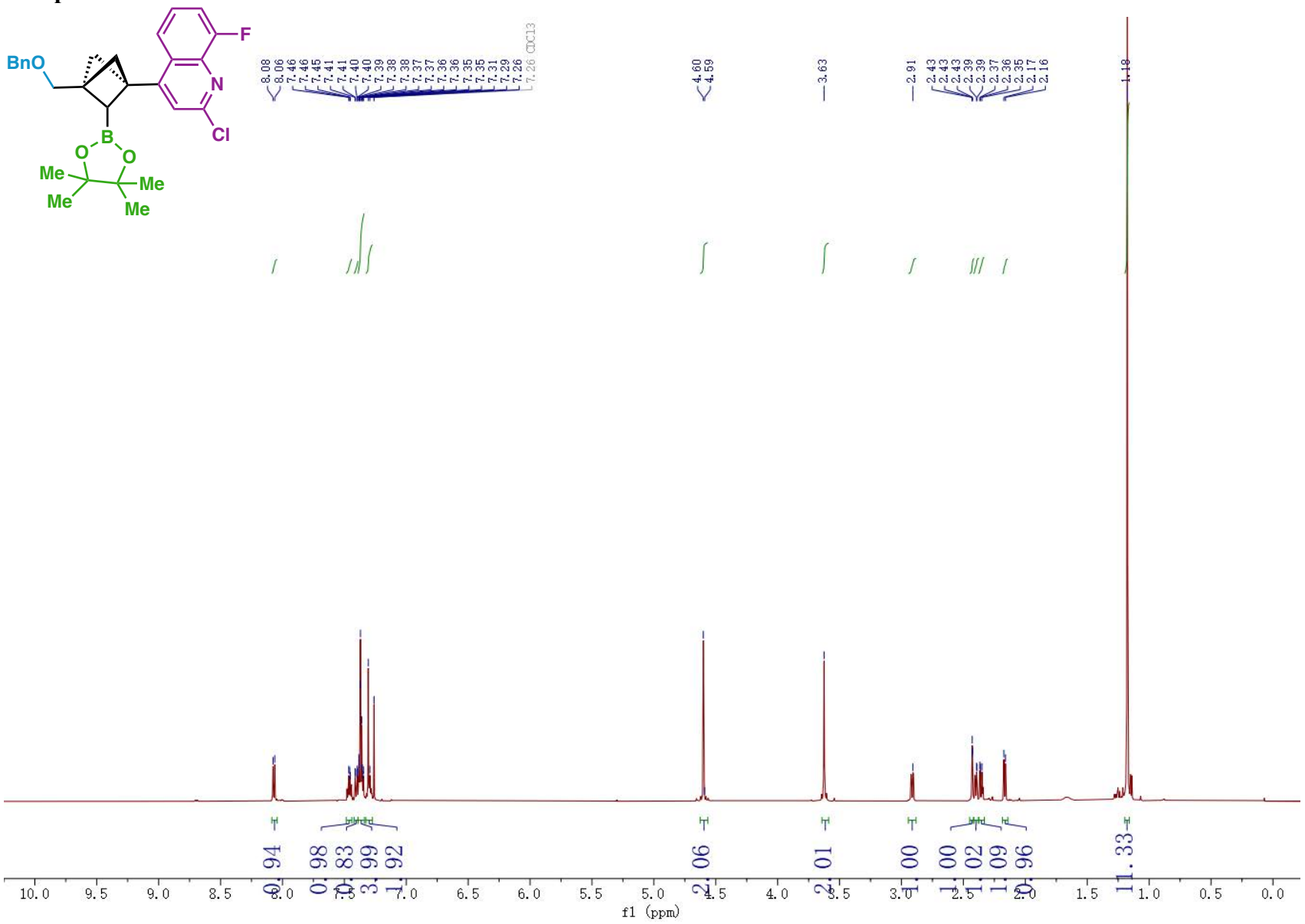
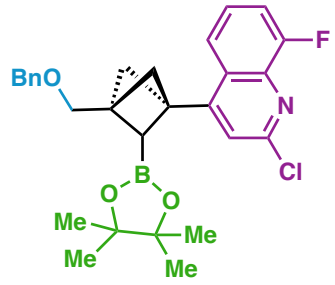


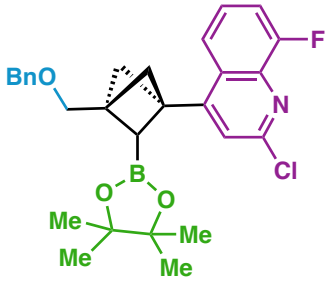
Compound 74 ^{1}H NMR



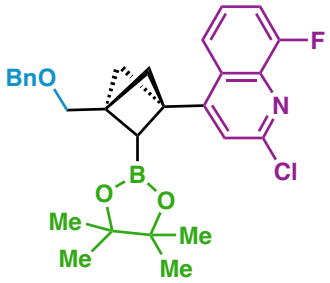
Compound 74 ^{13}C NMR



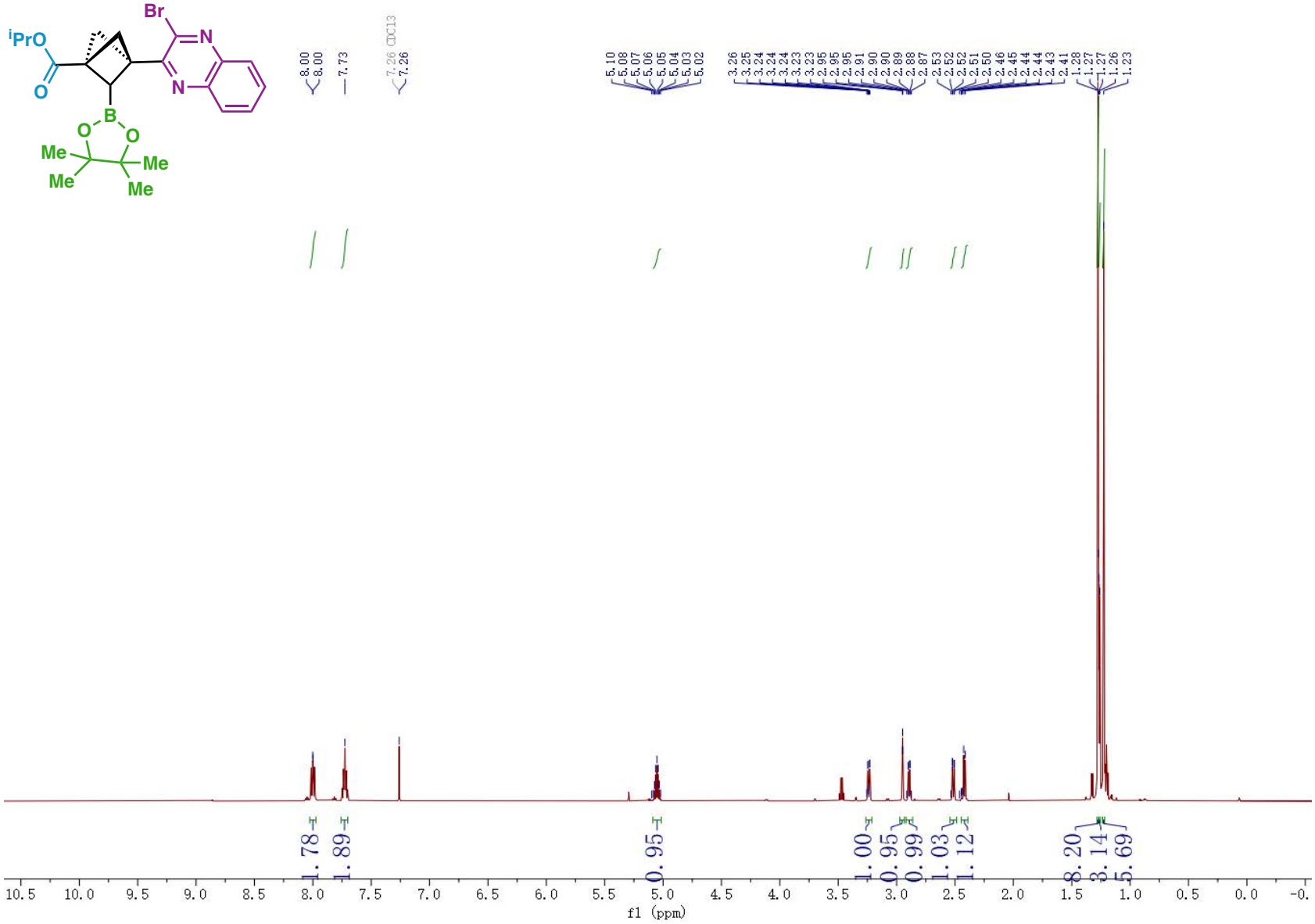
Compound 74 ^{11}B NMR



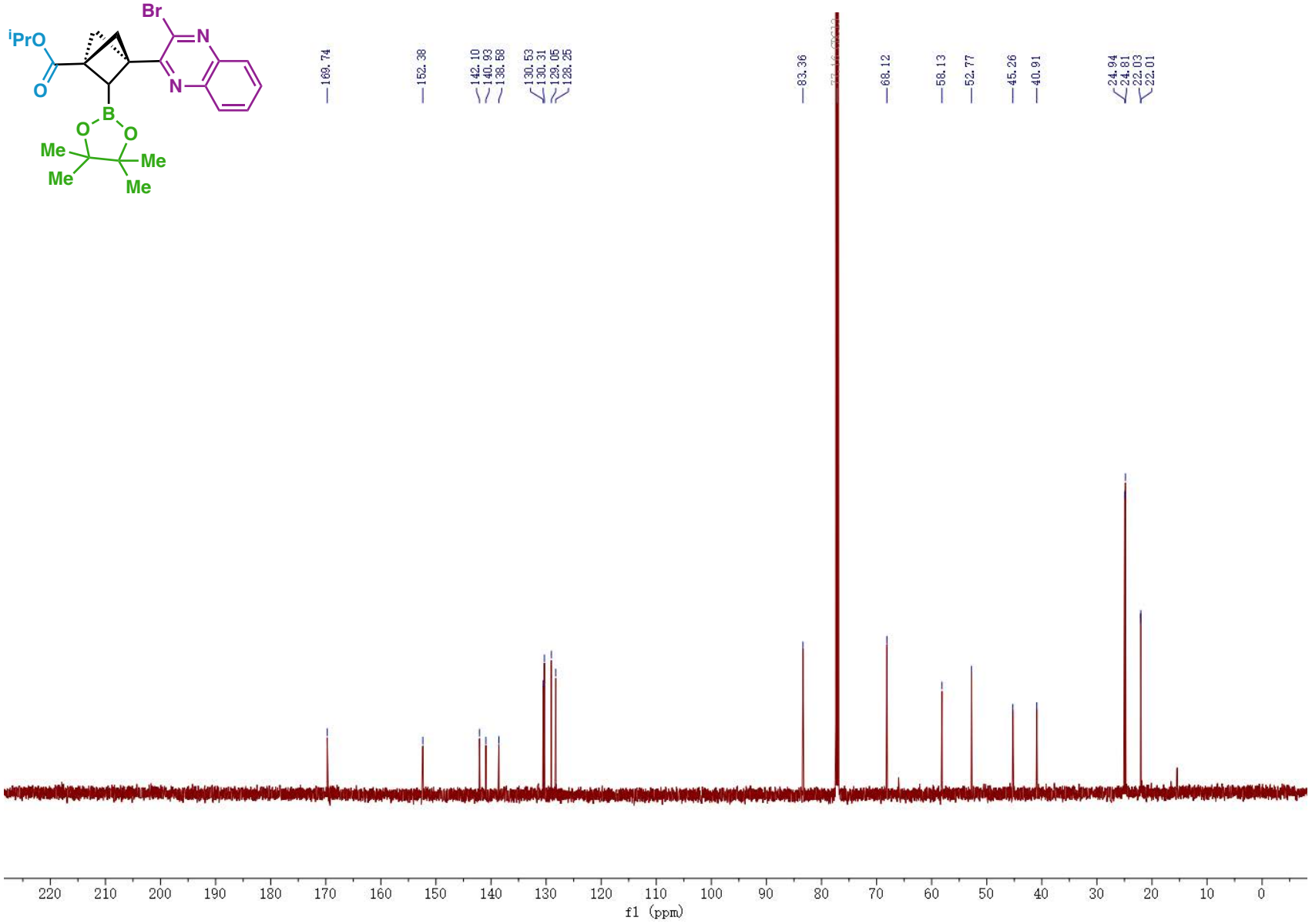
Compound 74 ^{19}F NMR



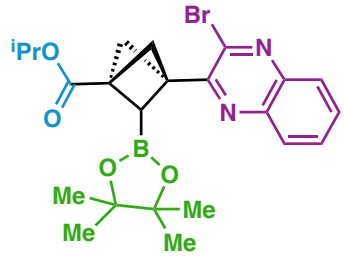
Compound 75 ^{1}H NMR



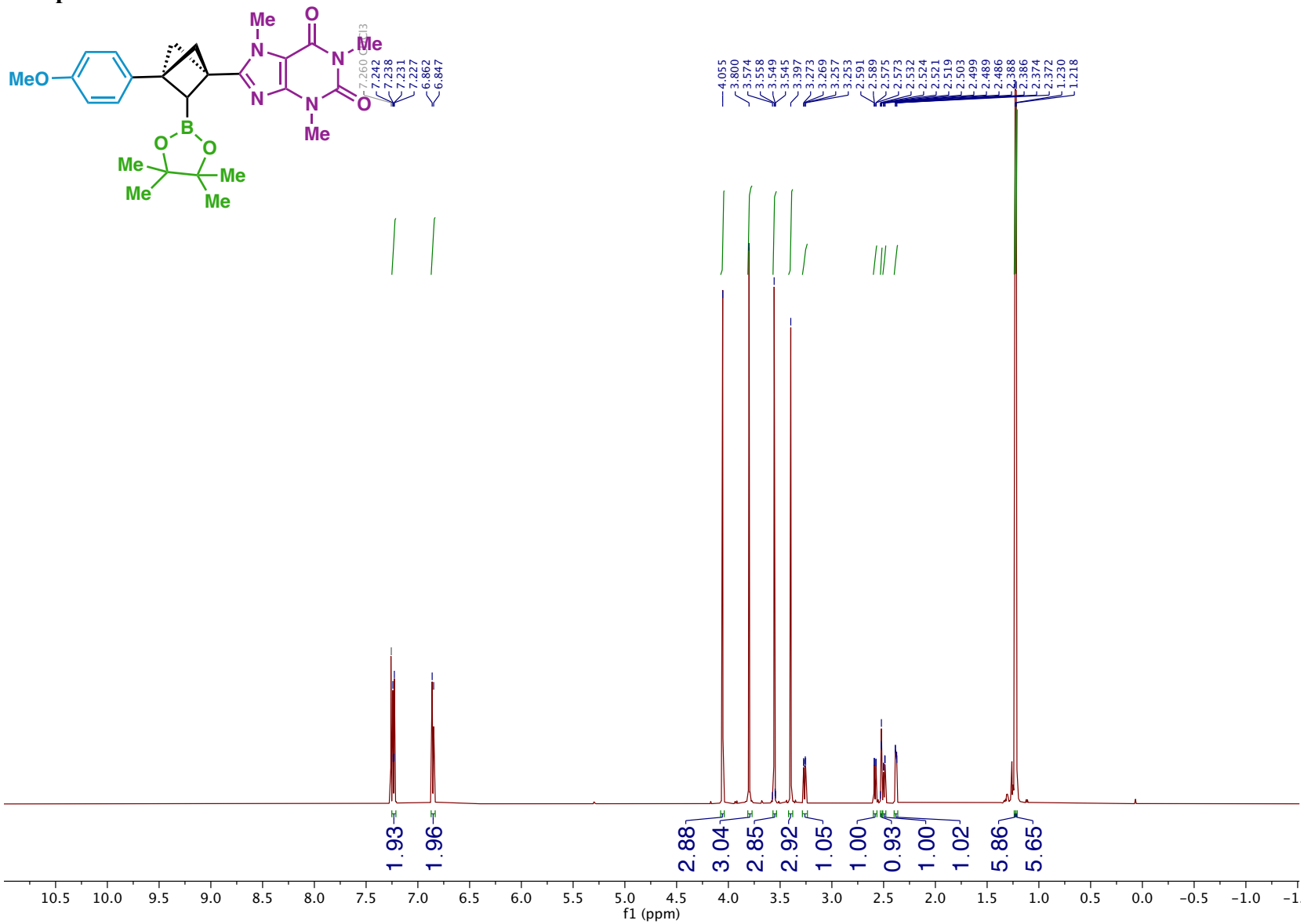
Compound 75 ^{13}C NMR



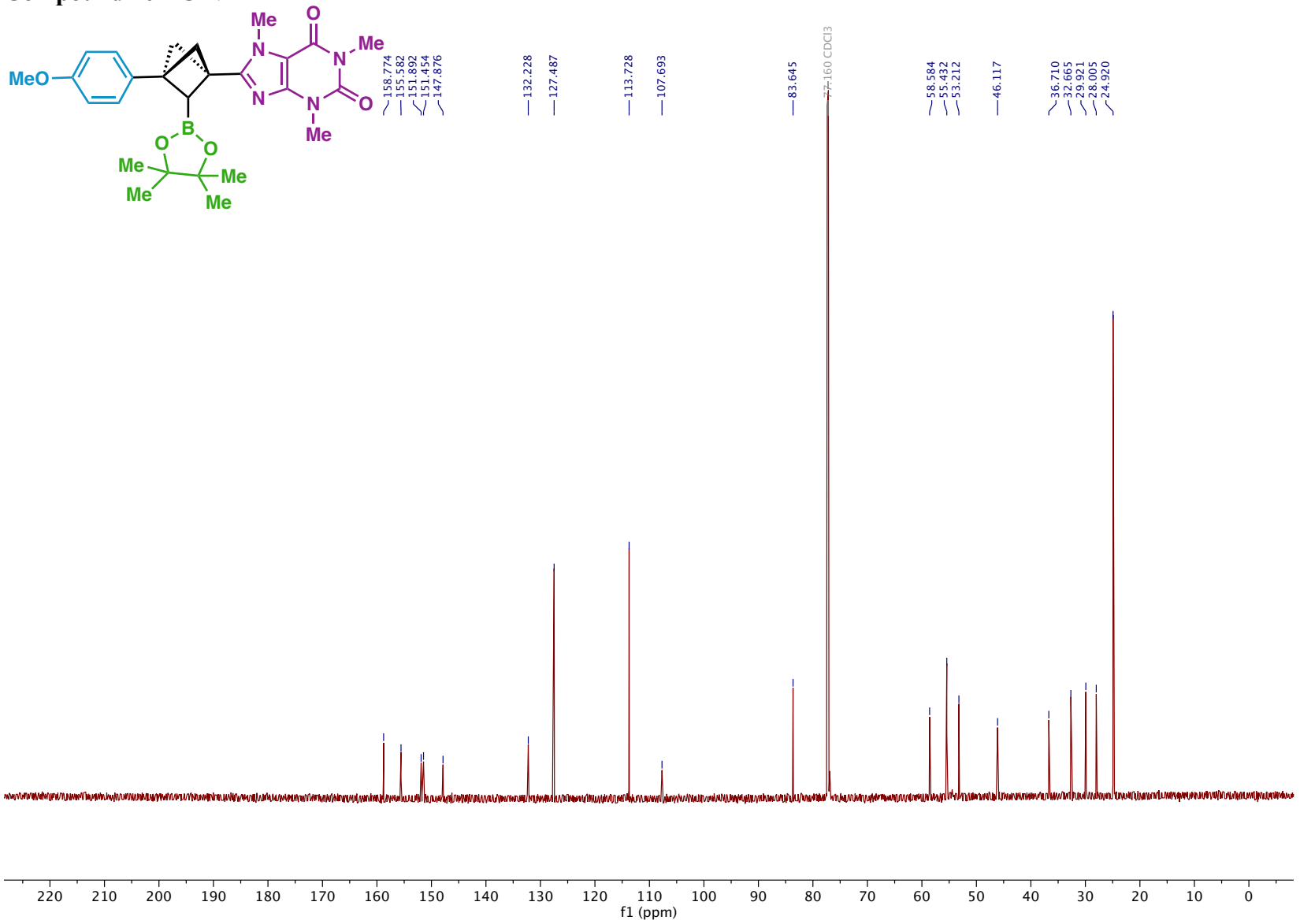
Compound 75 ^{11}B NMR



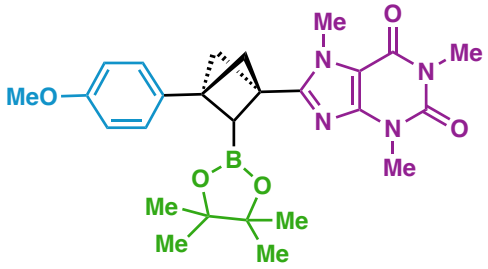
Compound 76 ^{1}H NMR



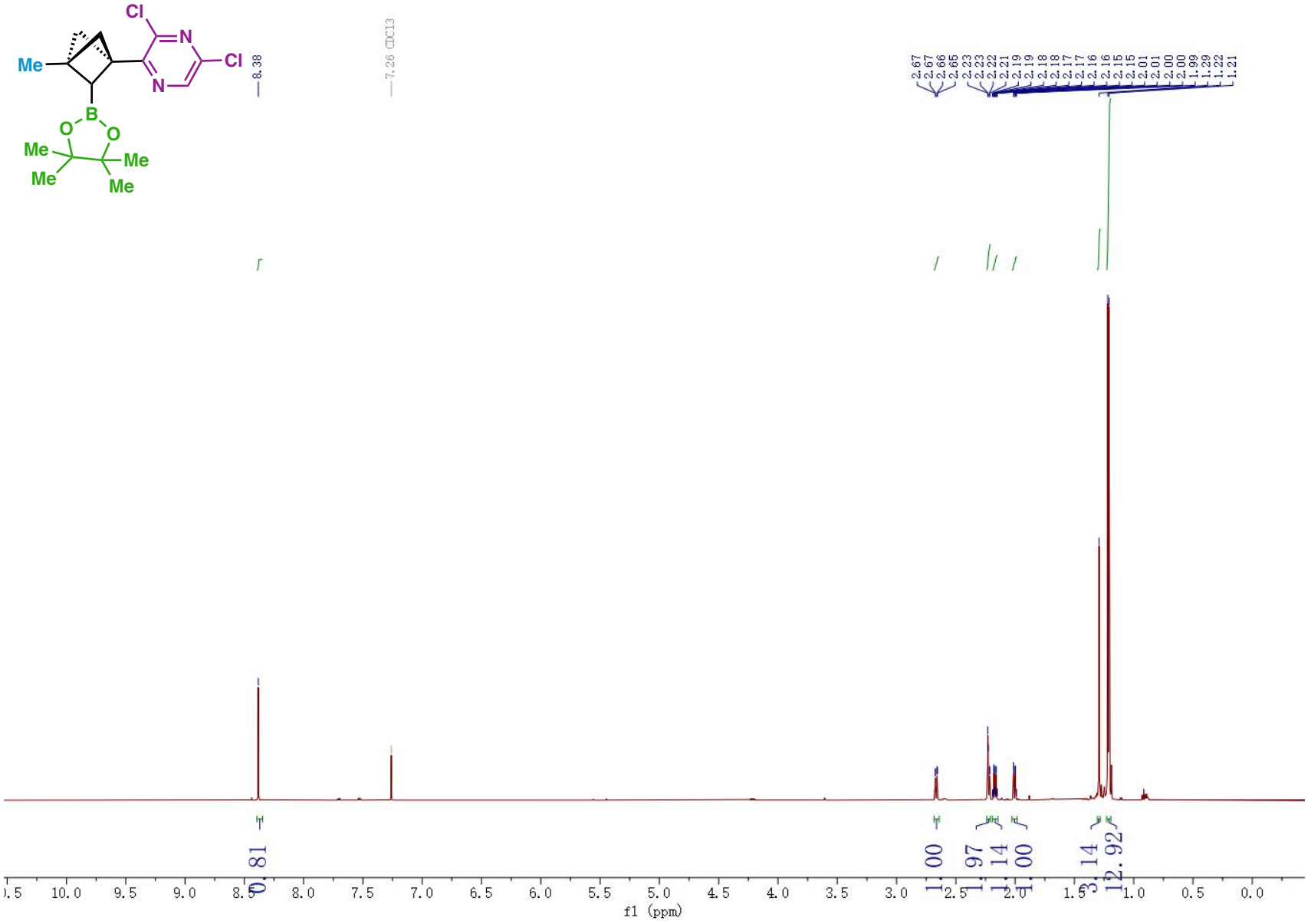
Compound 76 ^{13}C NMR



Compound 76 ^{11}B NMR



Compound 77 ^{1}H NMR



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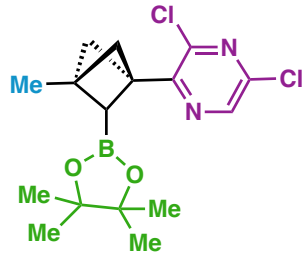
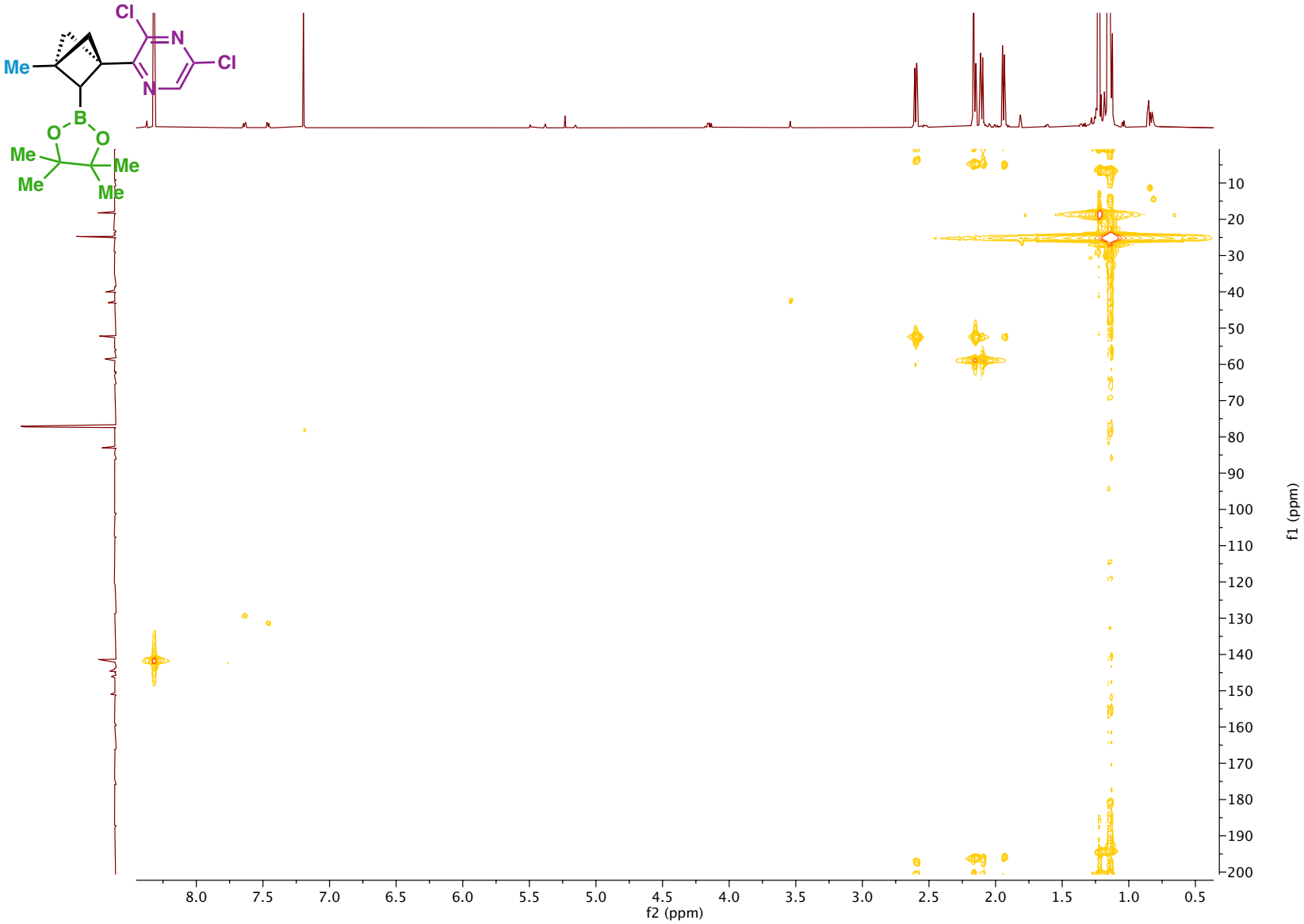
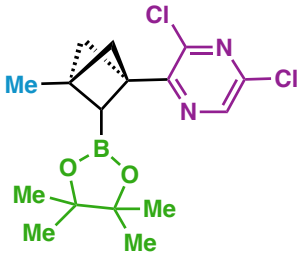


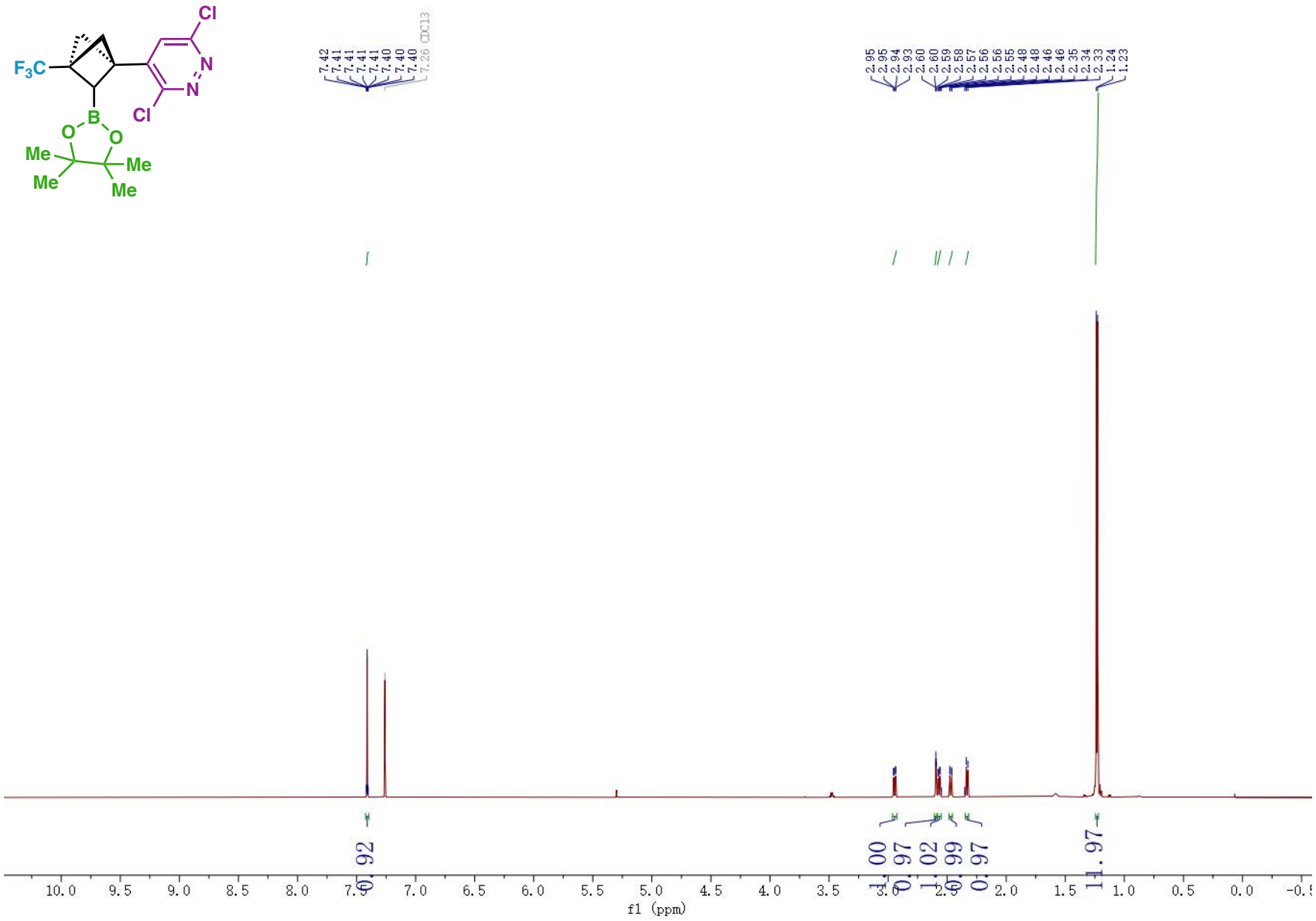
Compound 77 HSQC



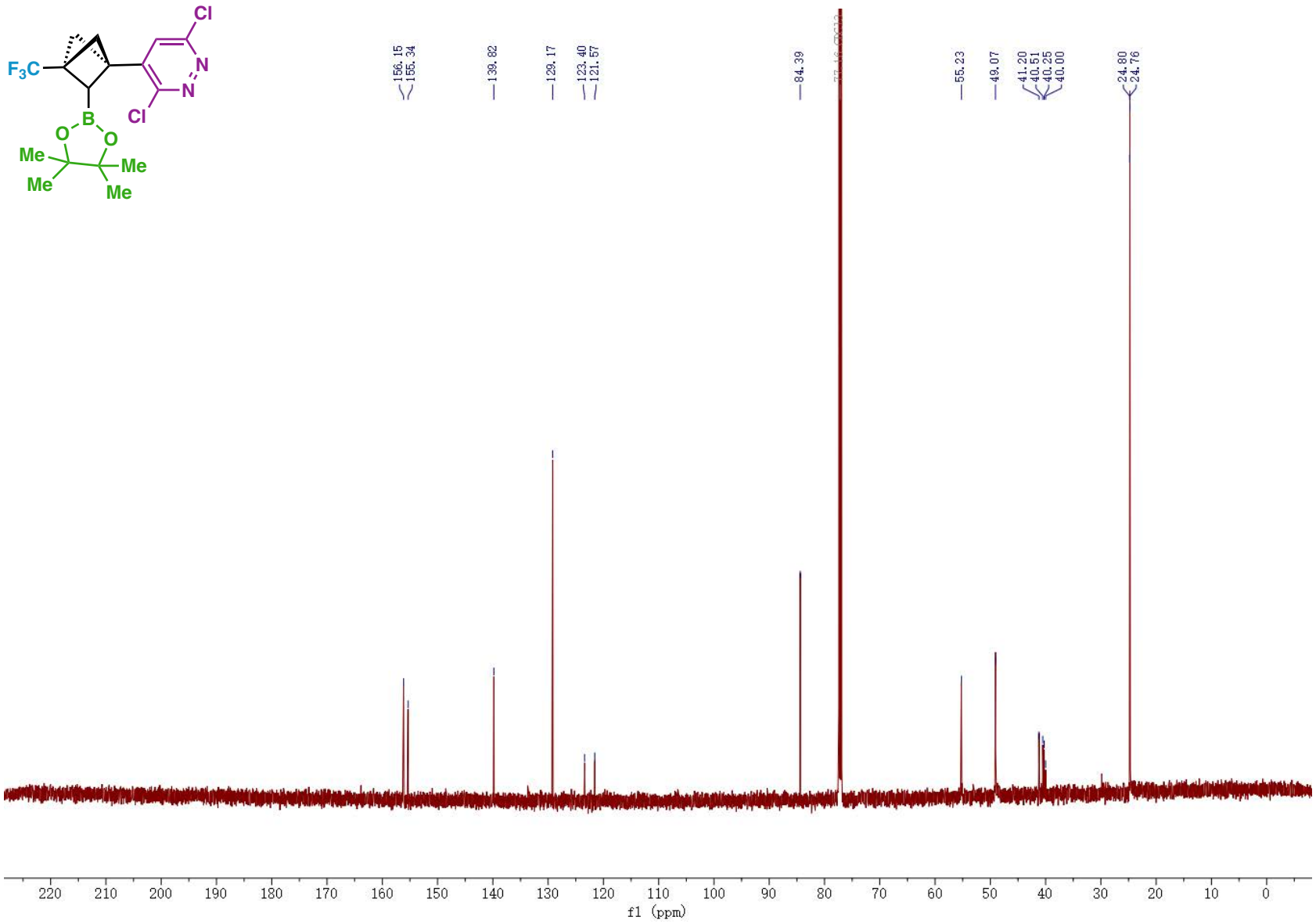
Compound 77 ^{11}B NMR



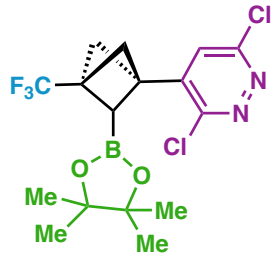
Compound 78 ^{1}H NMR



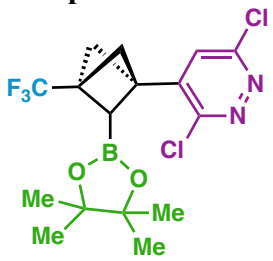
Compound 78 ^{13}C NMR



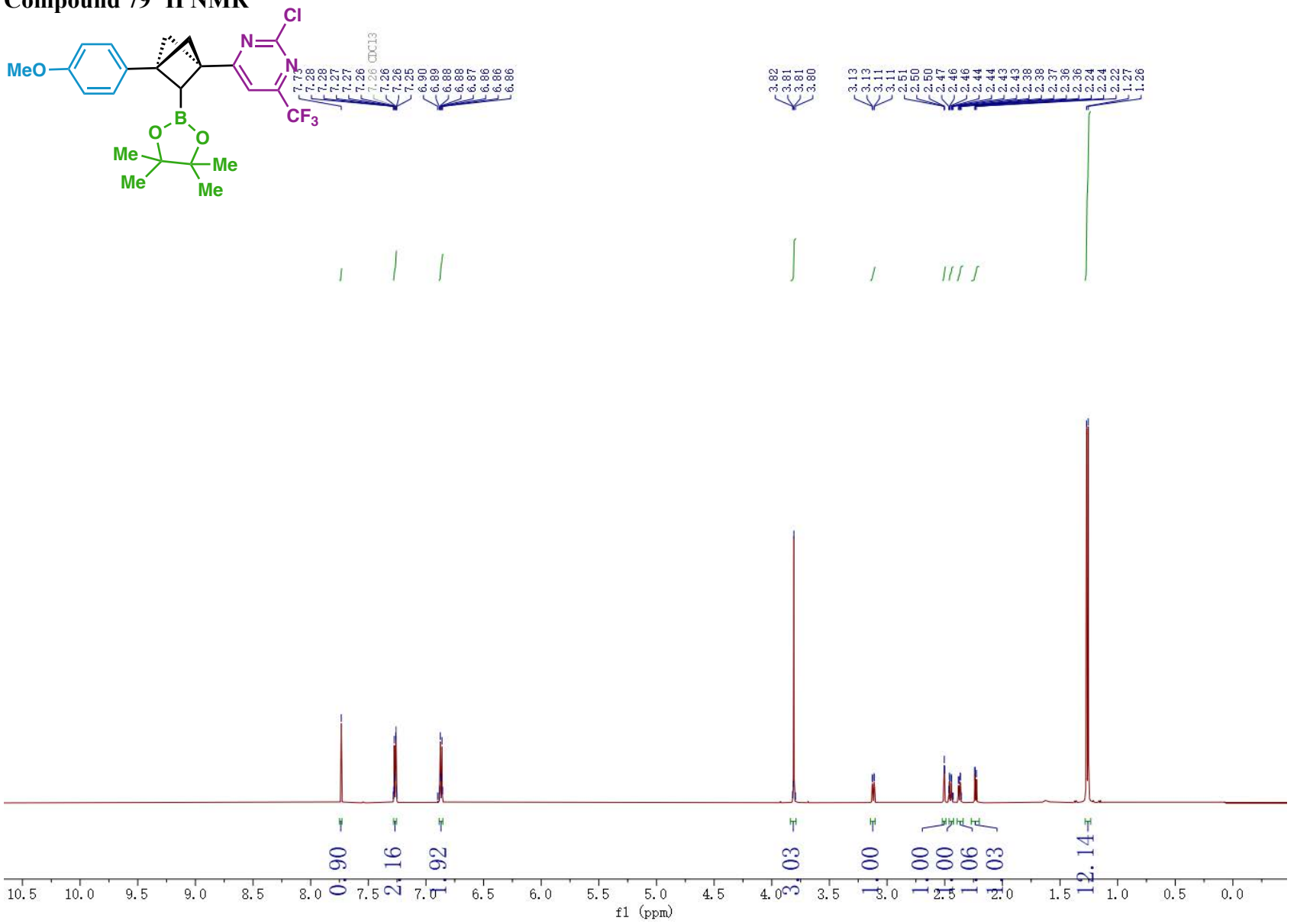
Compound 78 ^{11}B NMR



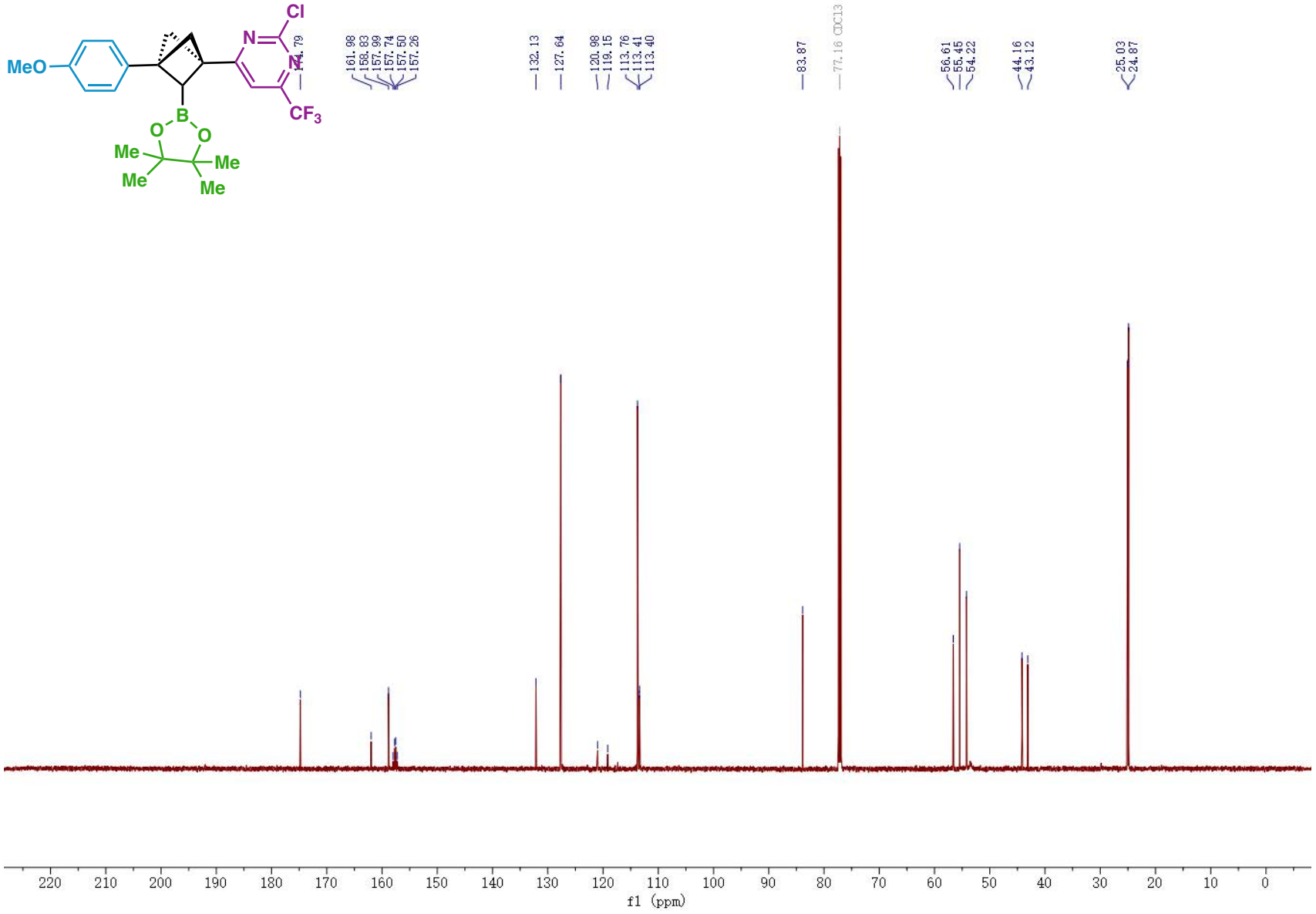
Compound 78 ^{19}F NMR



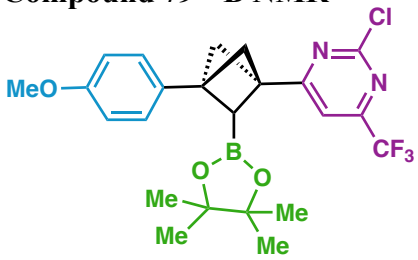
Compound 79 ^{1}H NMR



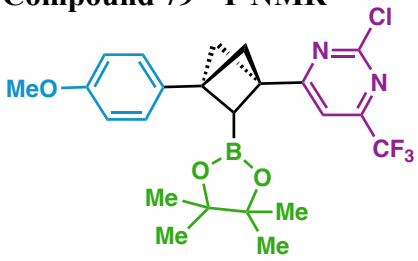
Compound 79 ^{13}C NMR



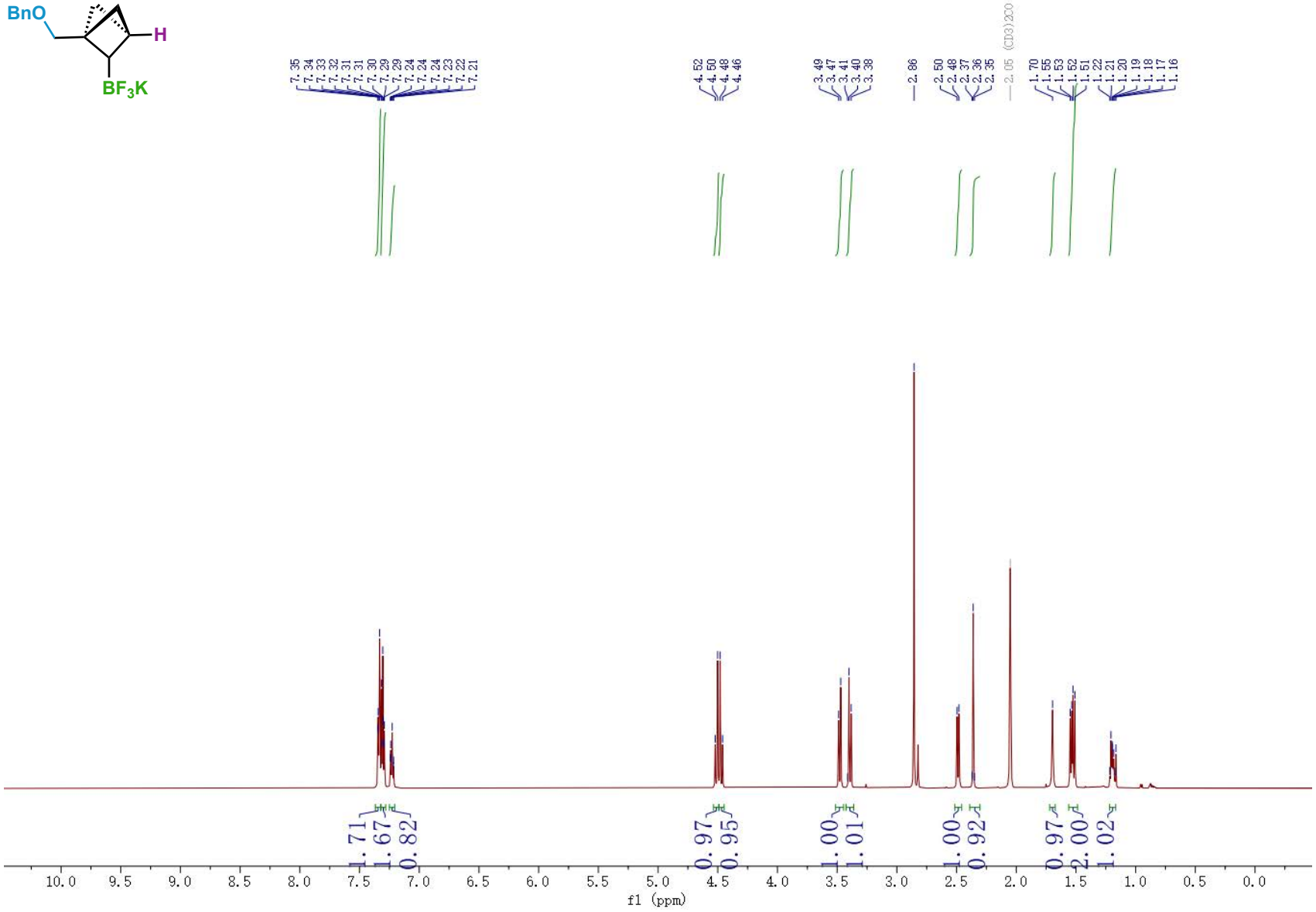
Compound 79 ^{11}B NMR



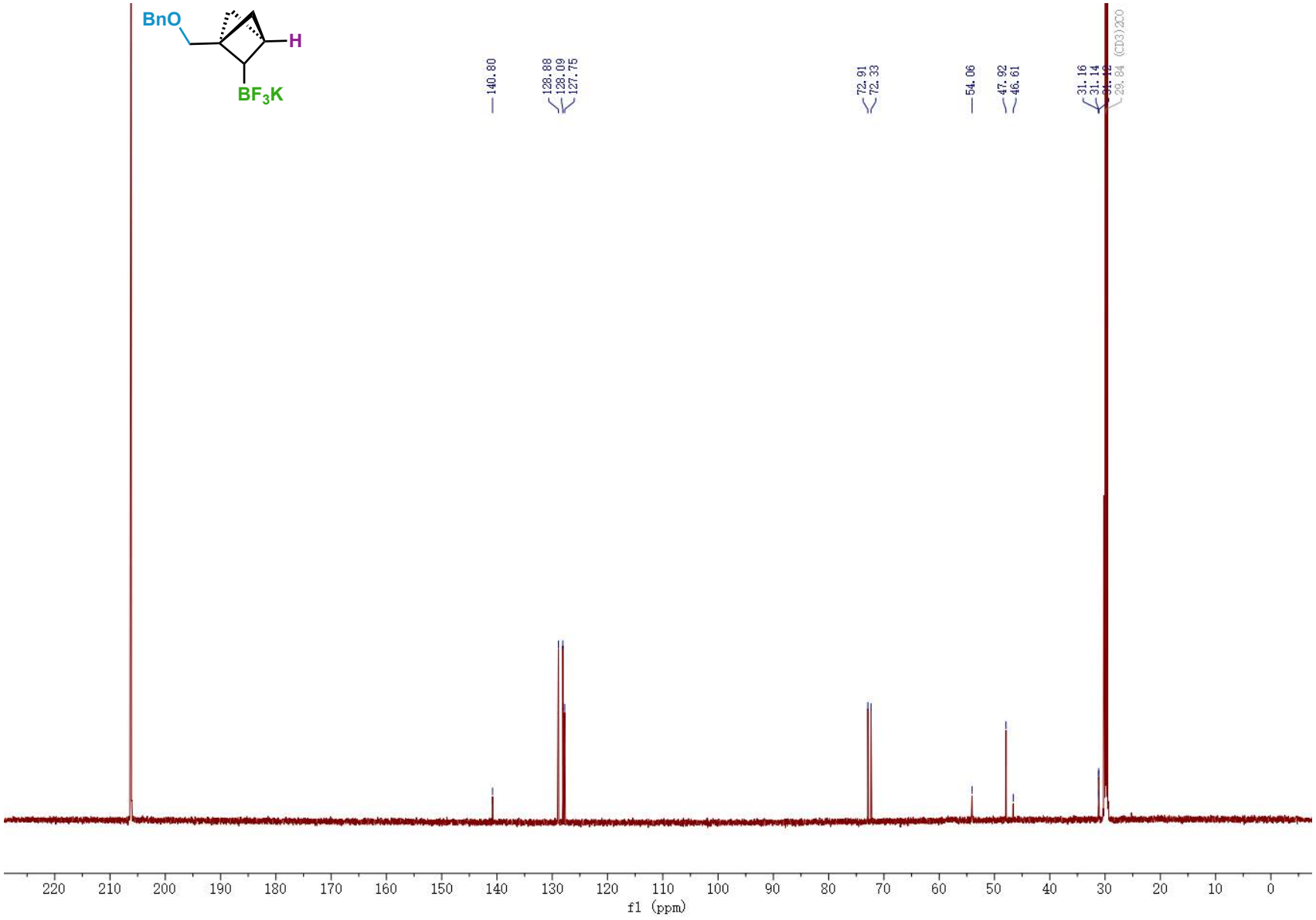
Compound 79 ^{19}F NMR



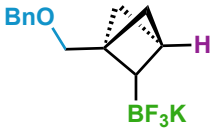
Compound 80 ^{1}H NMR

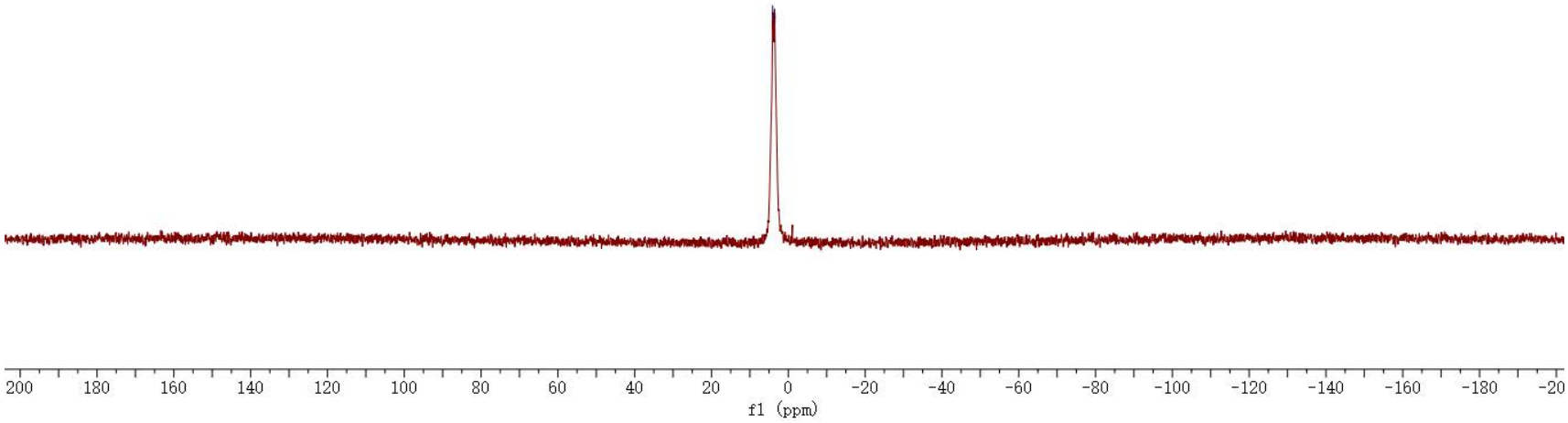


Compound 80 ^{13}C NMR

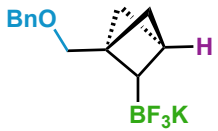


Compound 80 ^{11}B NMR





Compound 80 ^{19}F NMR



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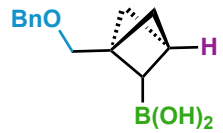
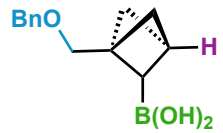
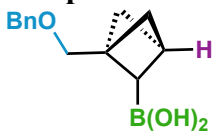


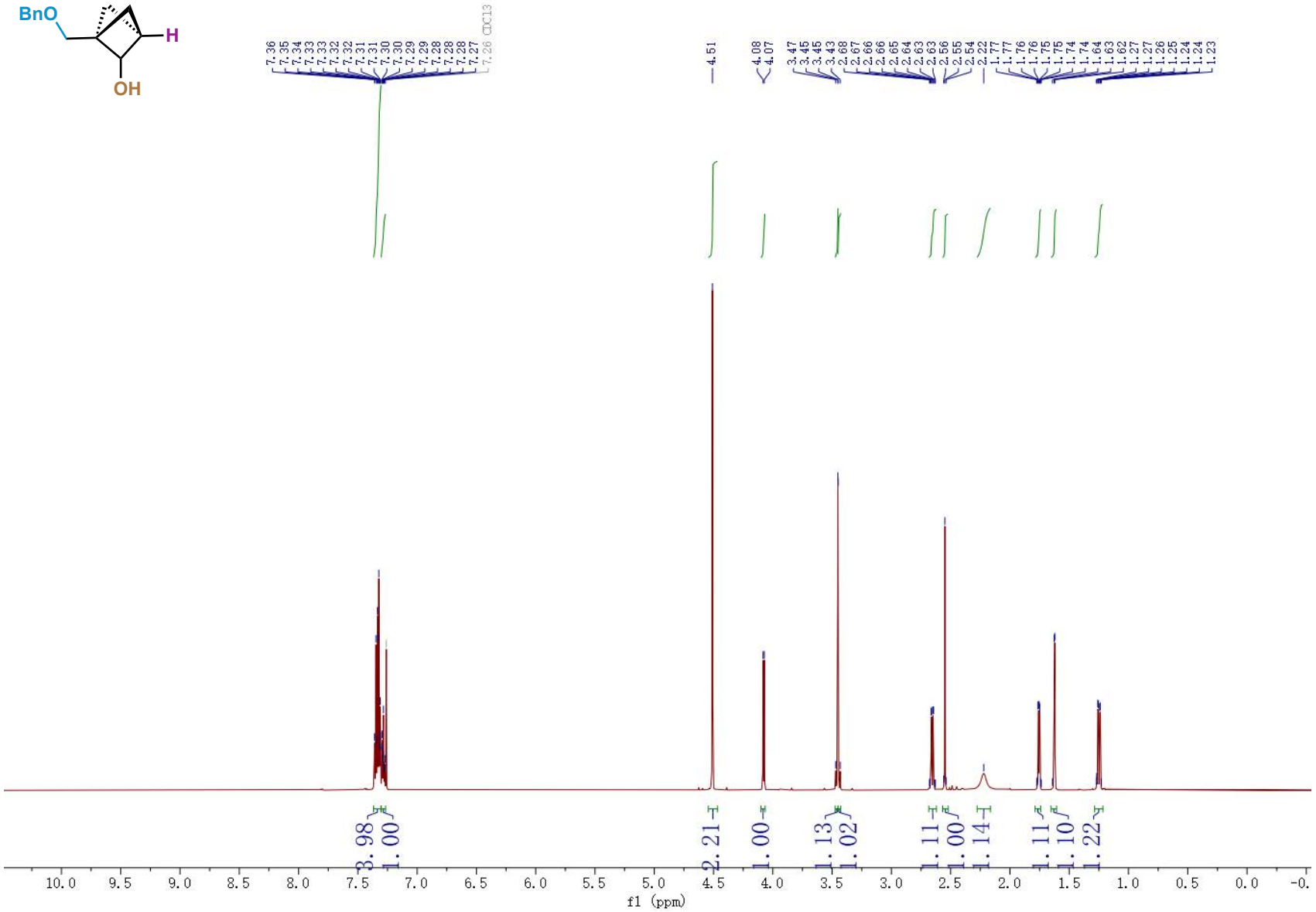
Compound 81 ^{13}C NMR



Compound 81 ^{11}B NMR



Compound 82 ^{1}H NMR



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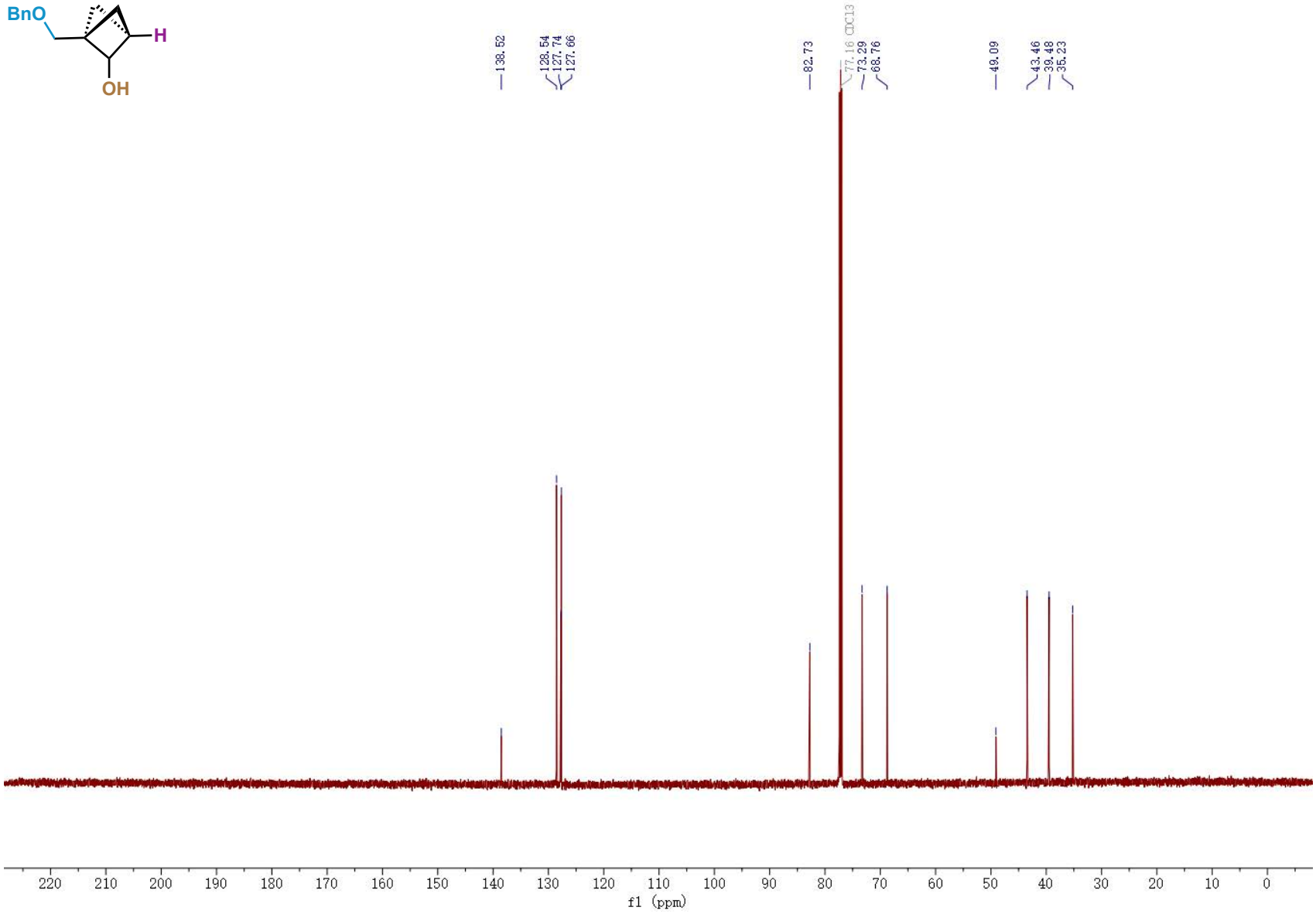
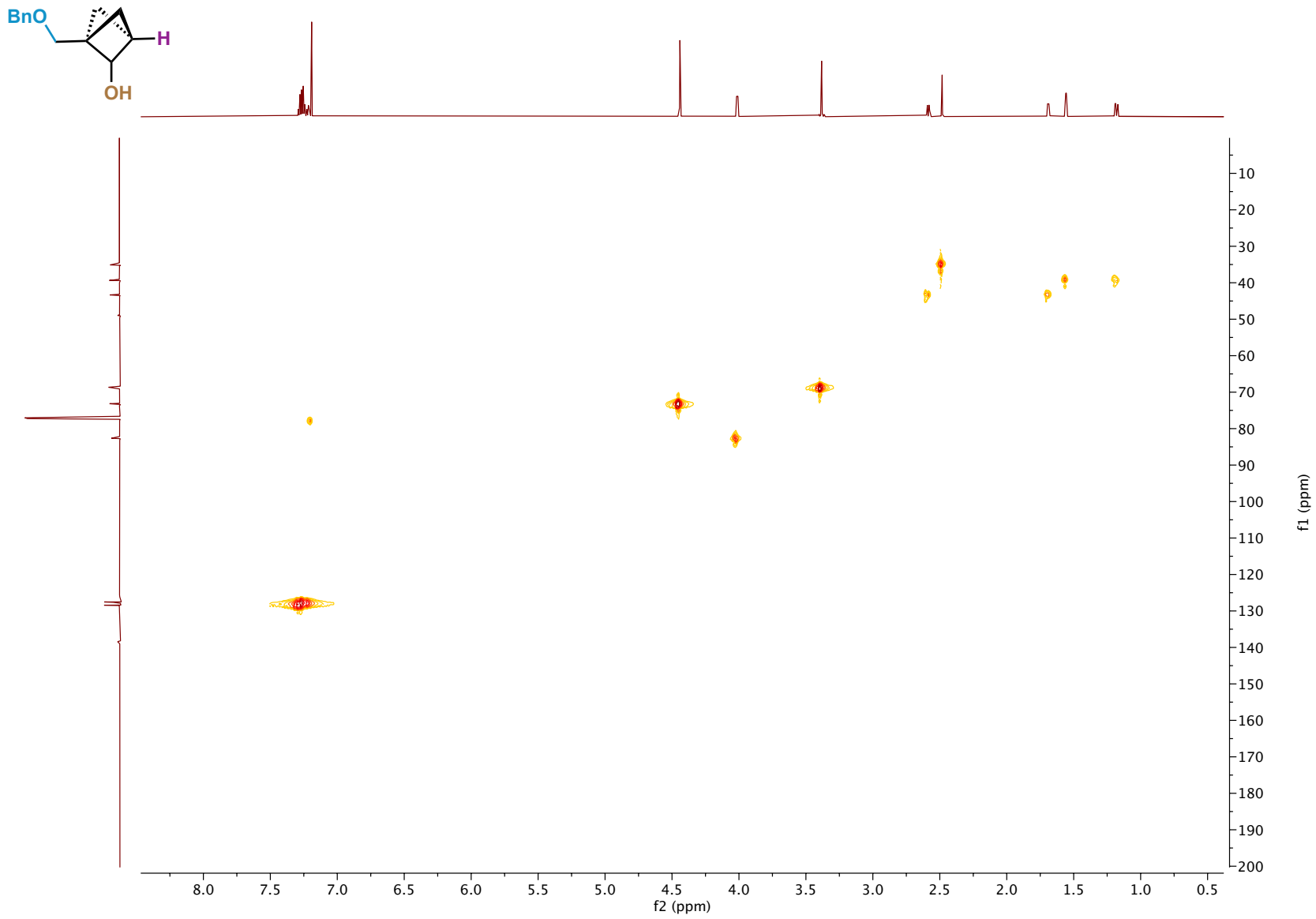
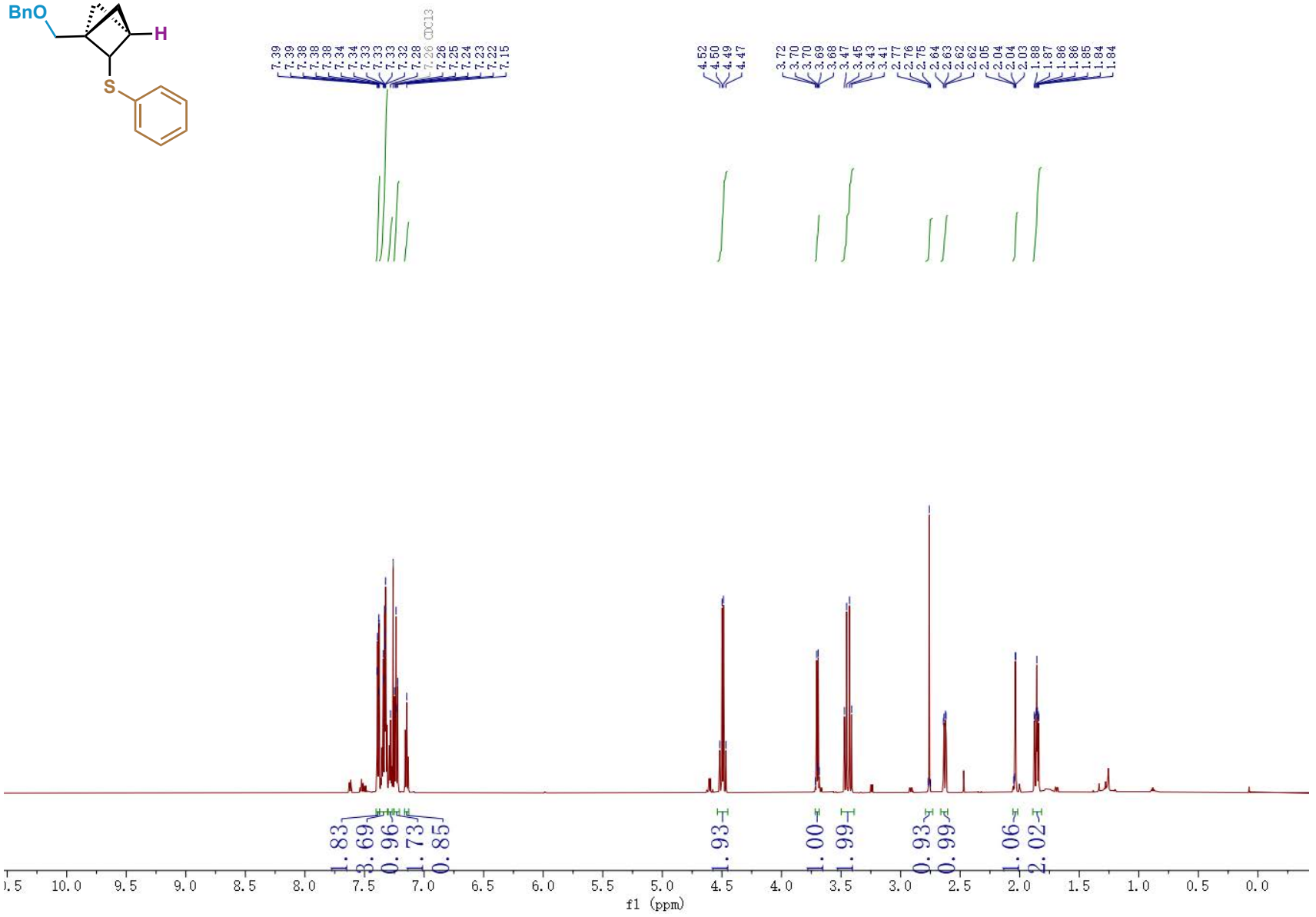


Compound 82 HSQC



Compound 83 ^{1}H NMR



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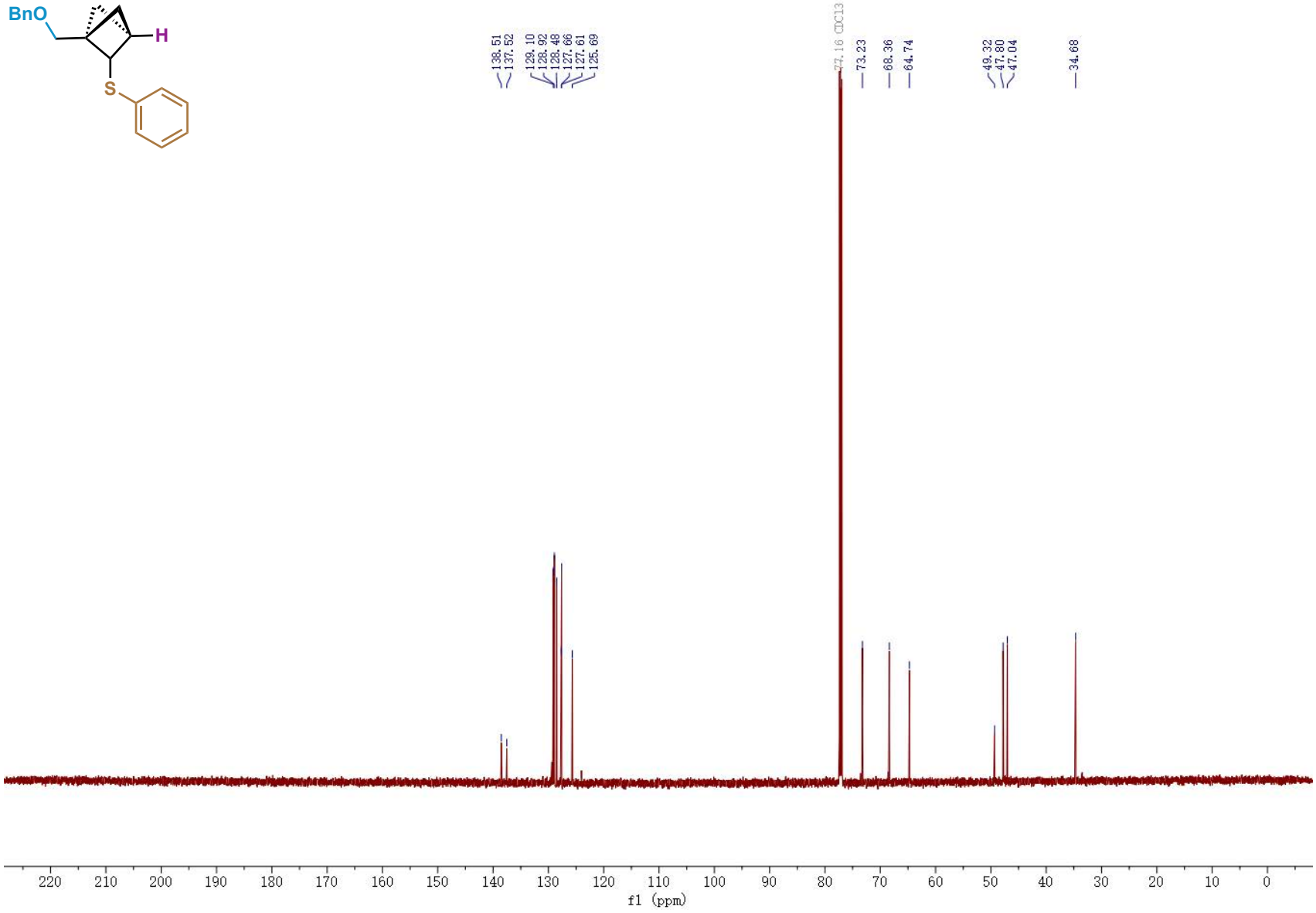

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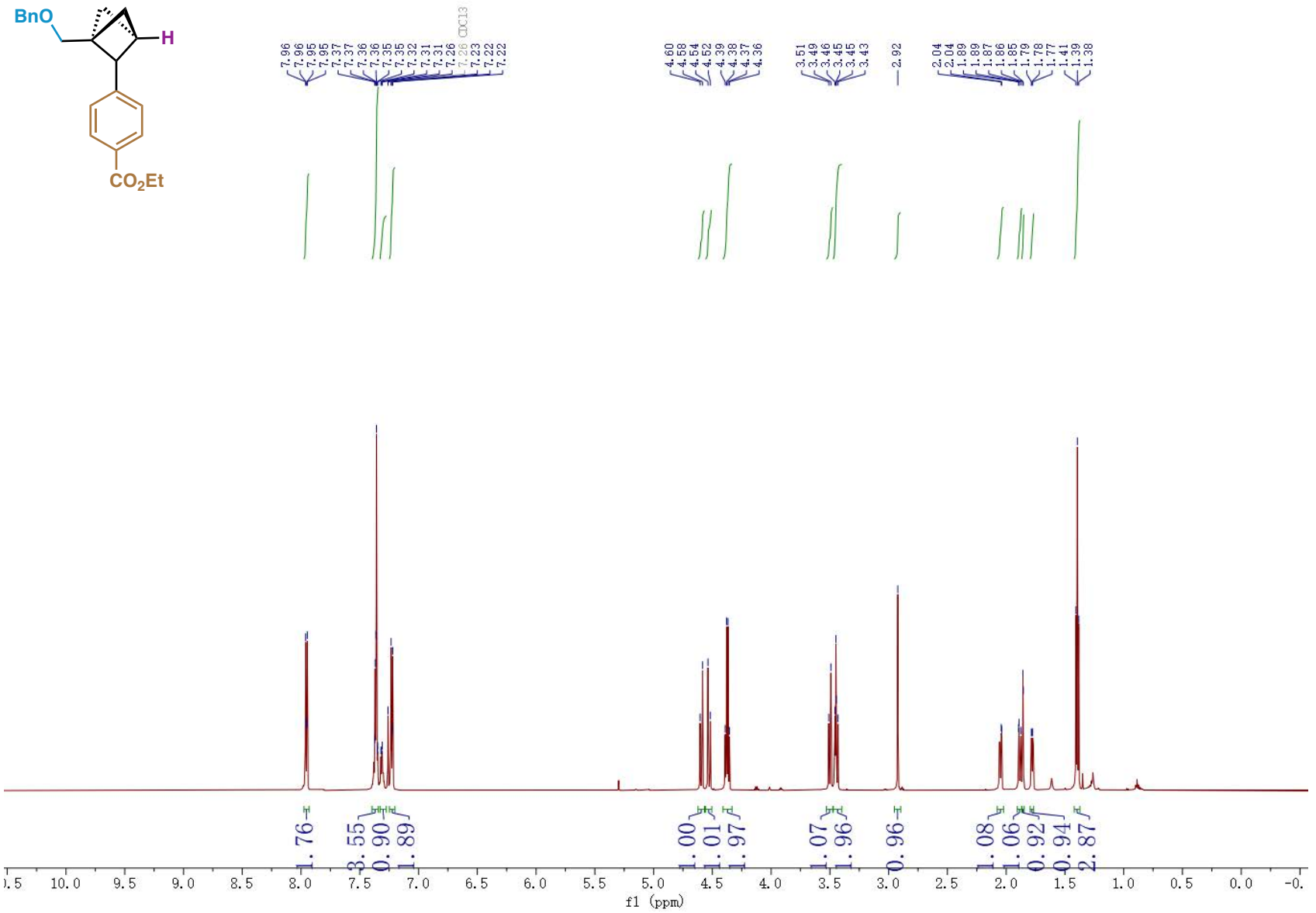

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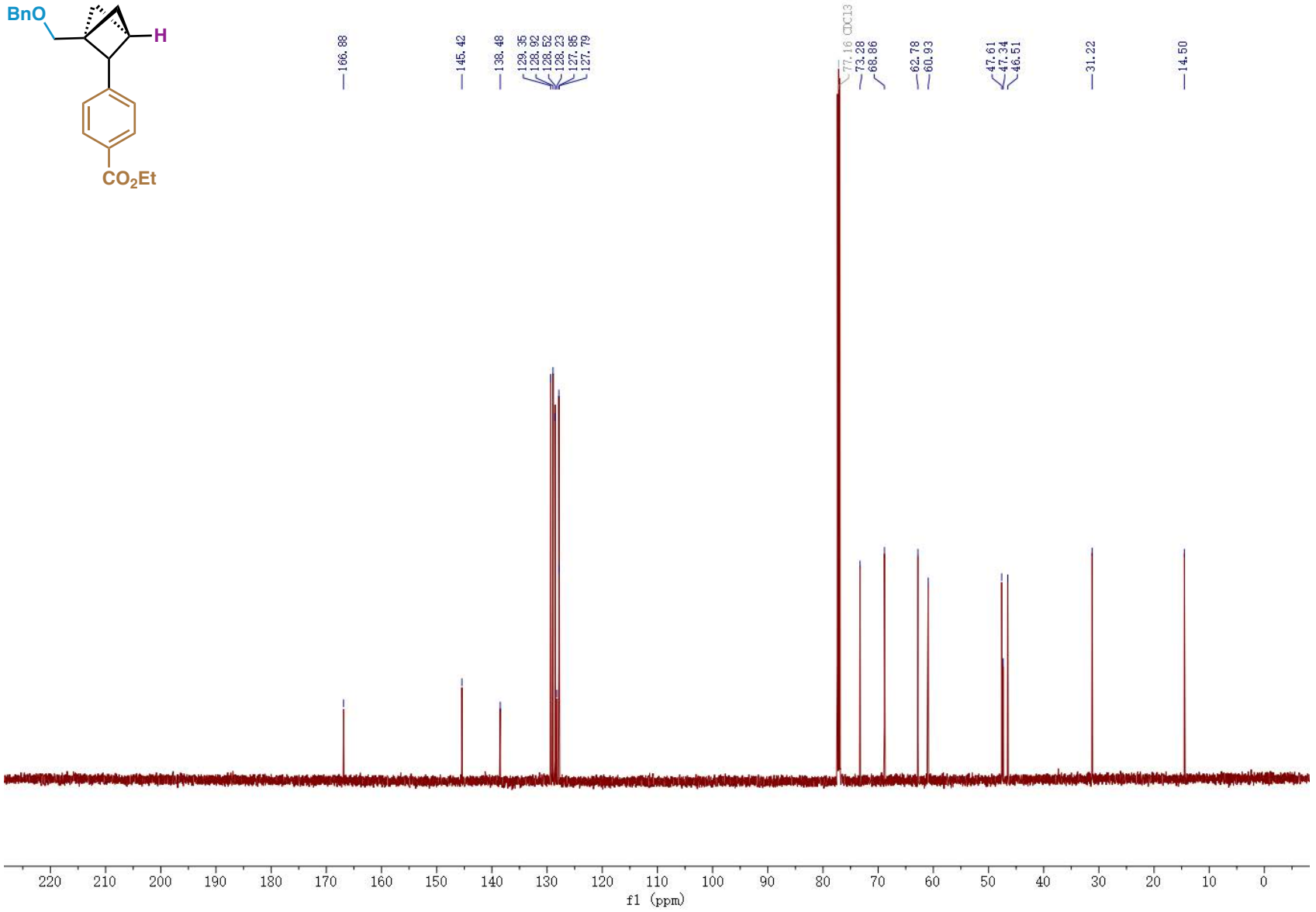

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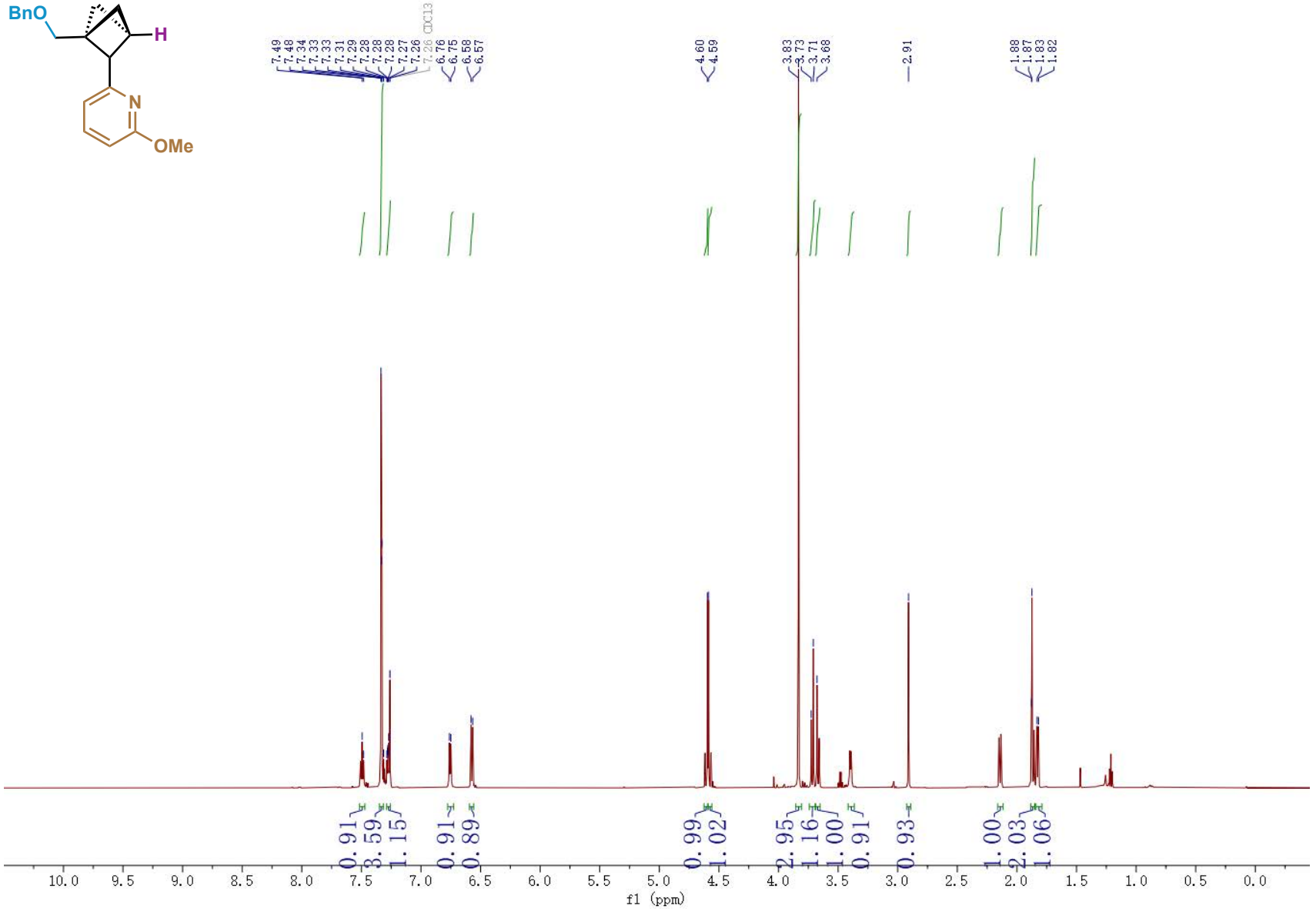

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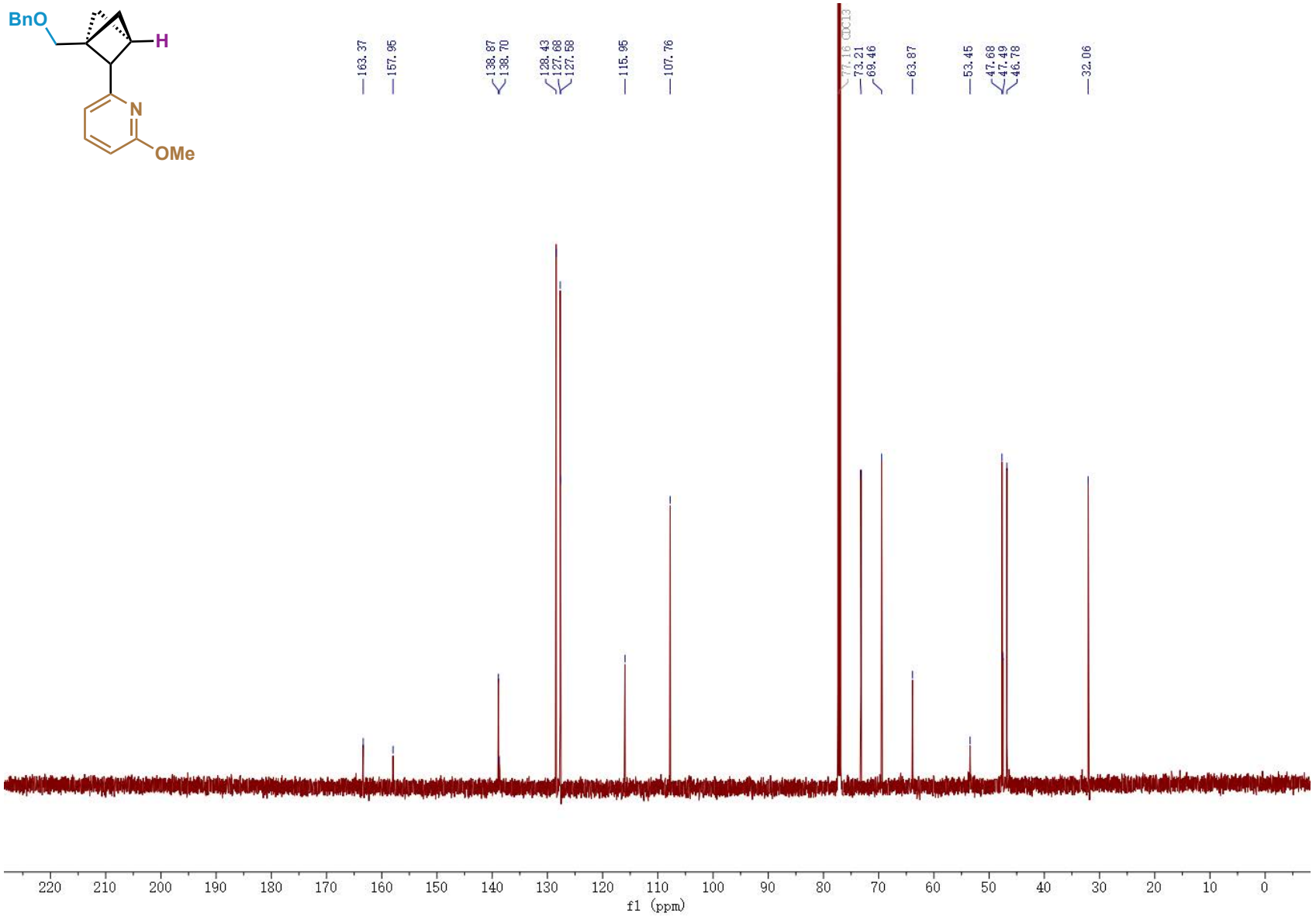

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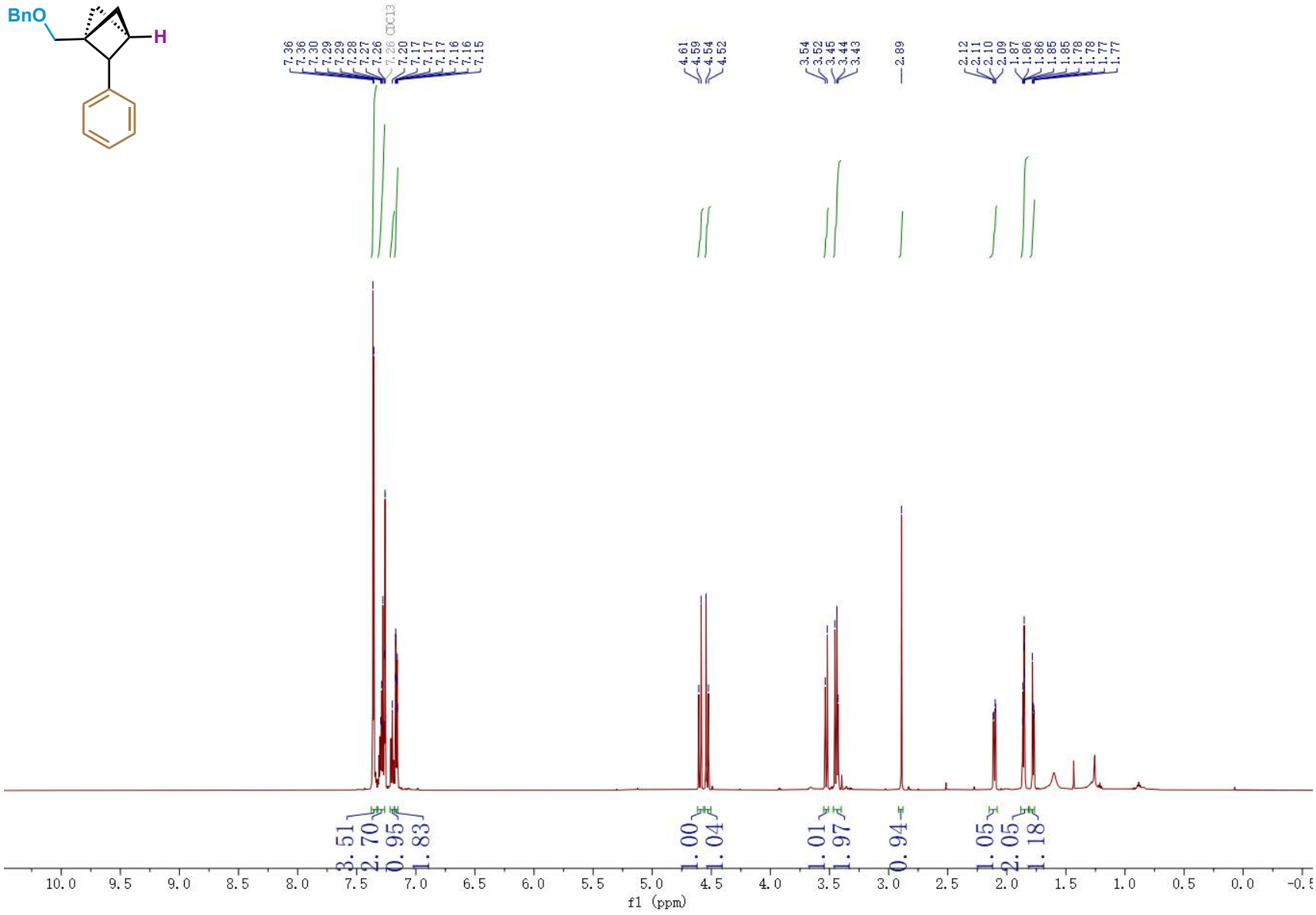

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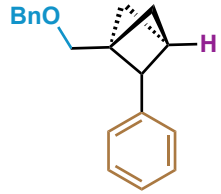
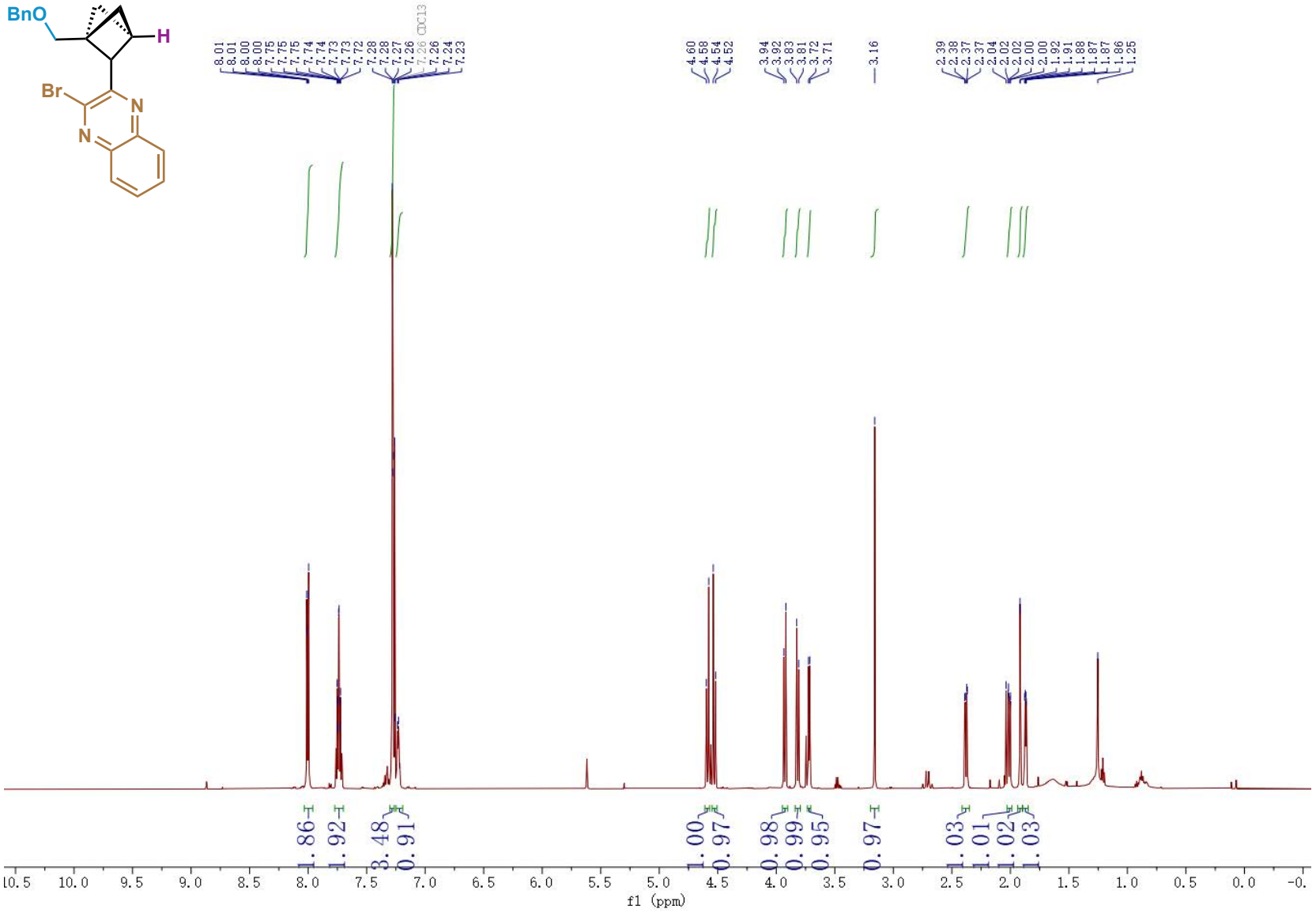


Compound 87 ^{1}H NMR



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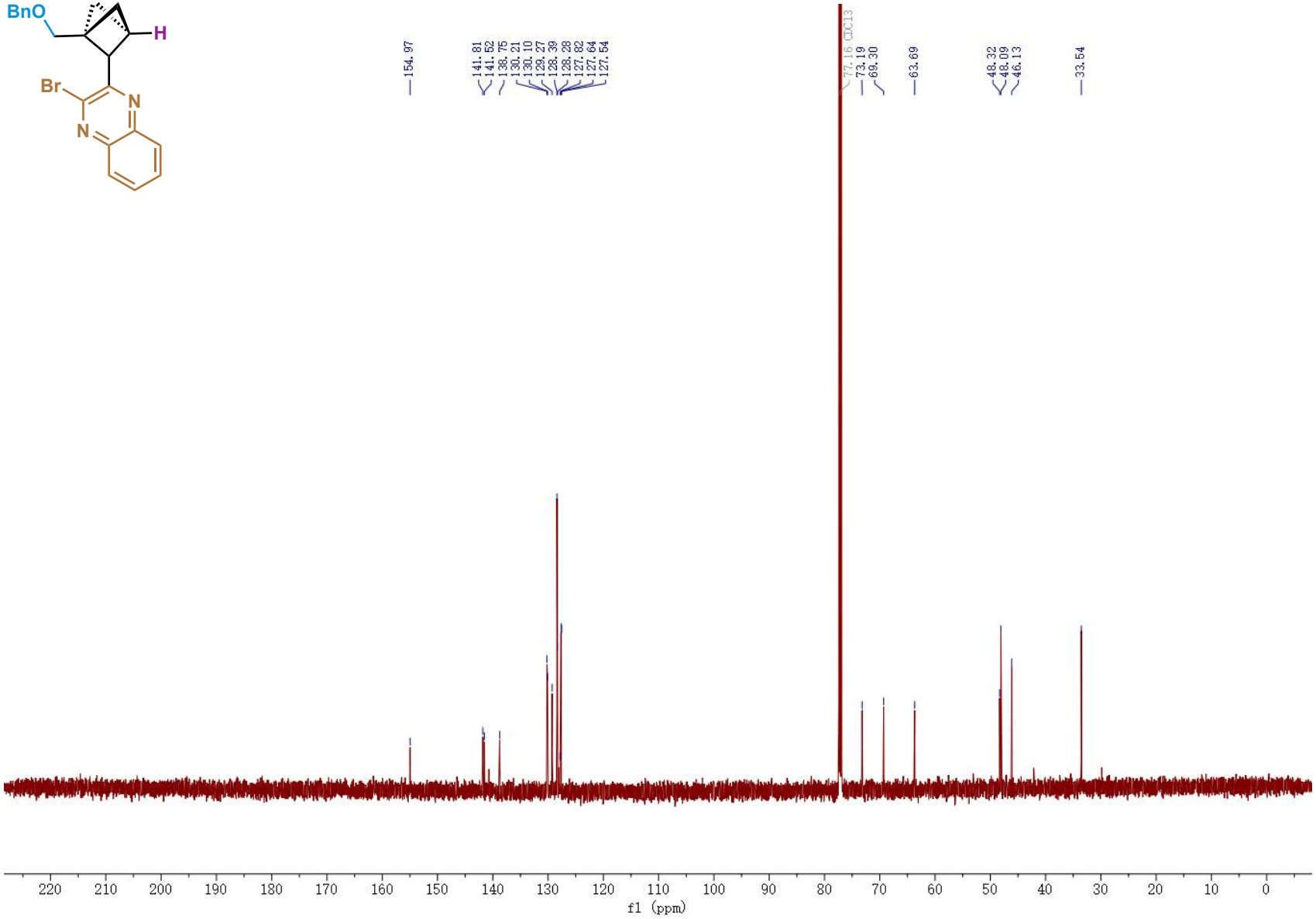

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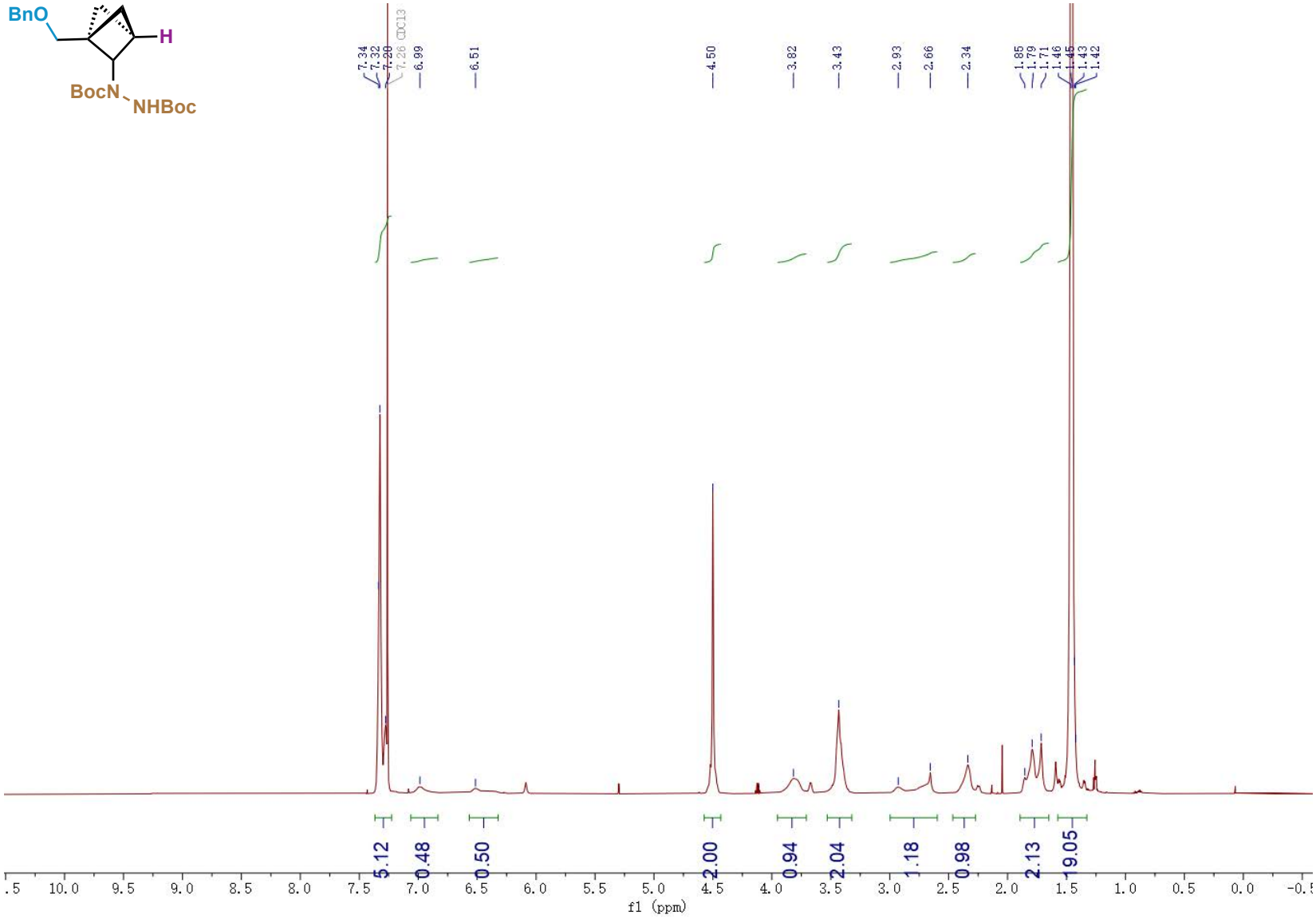

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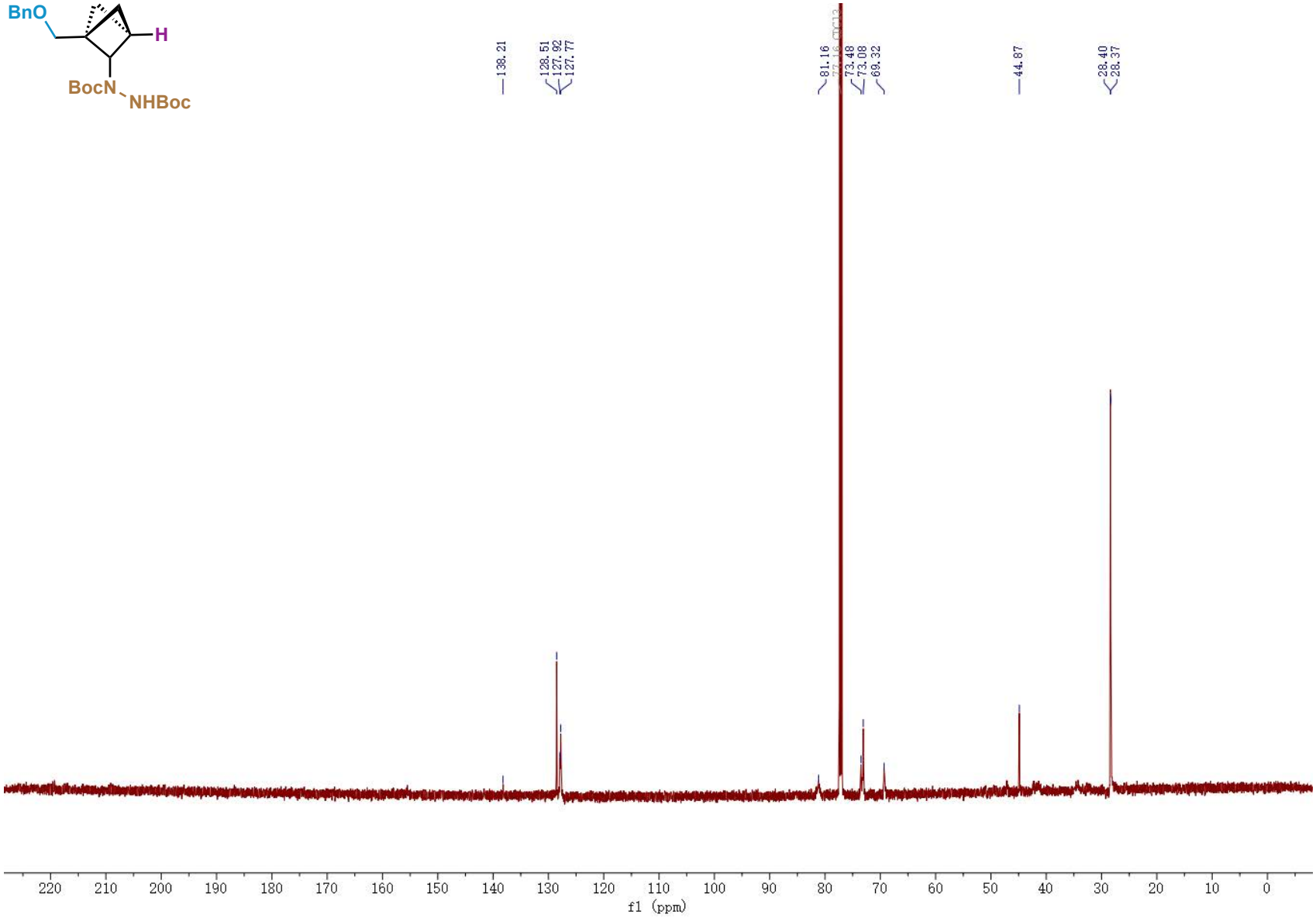

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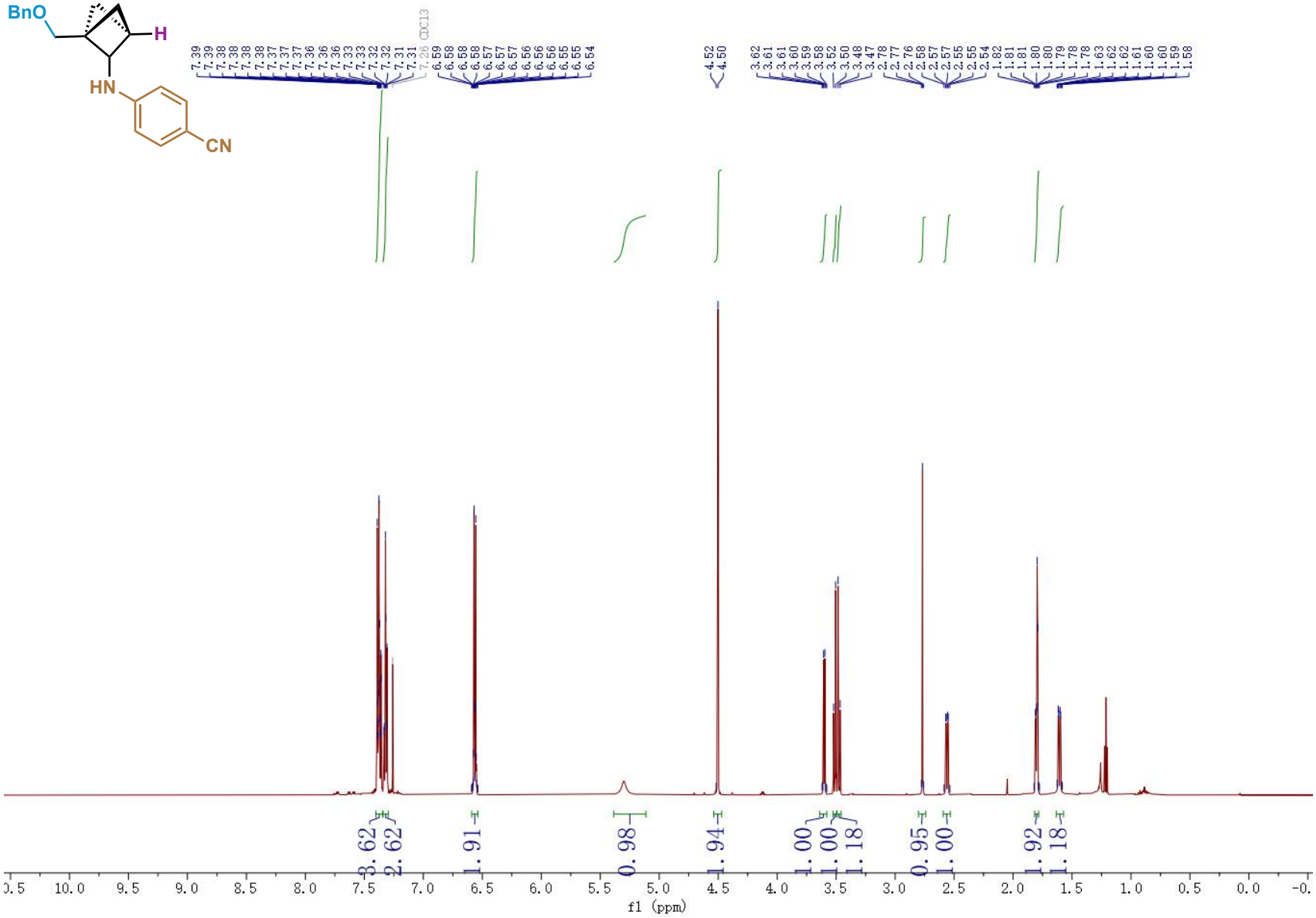

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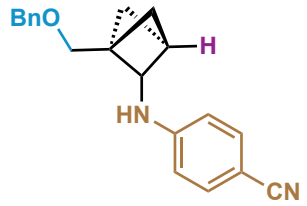

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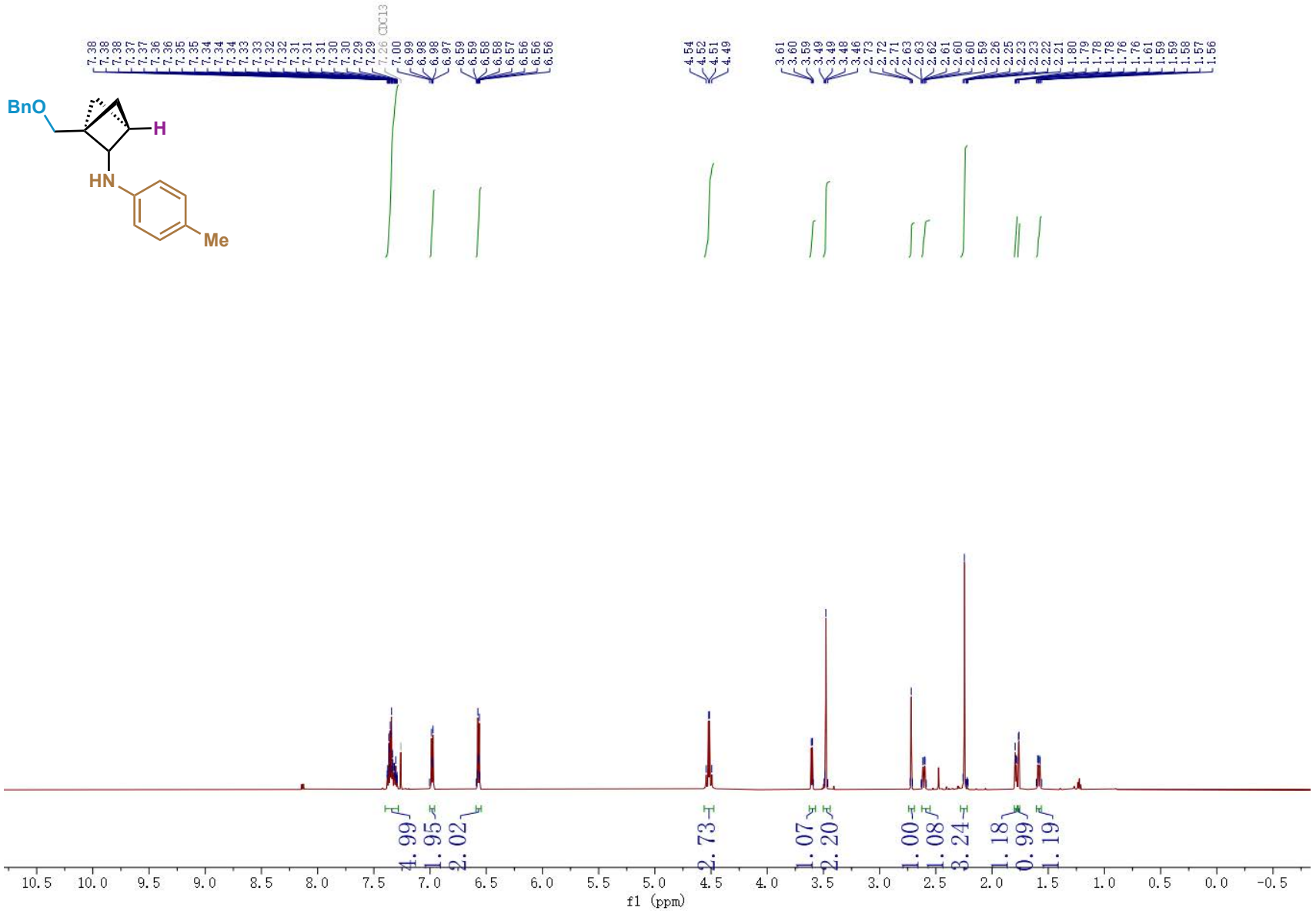

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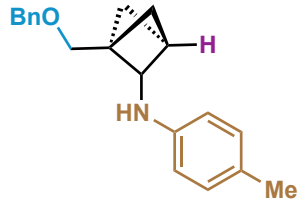

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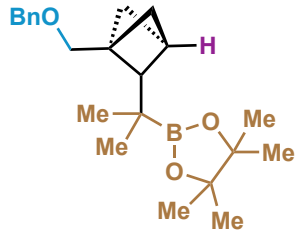
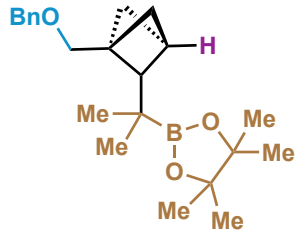
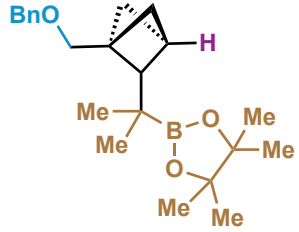


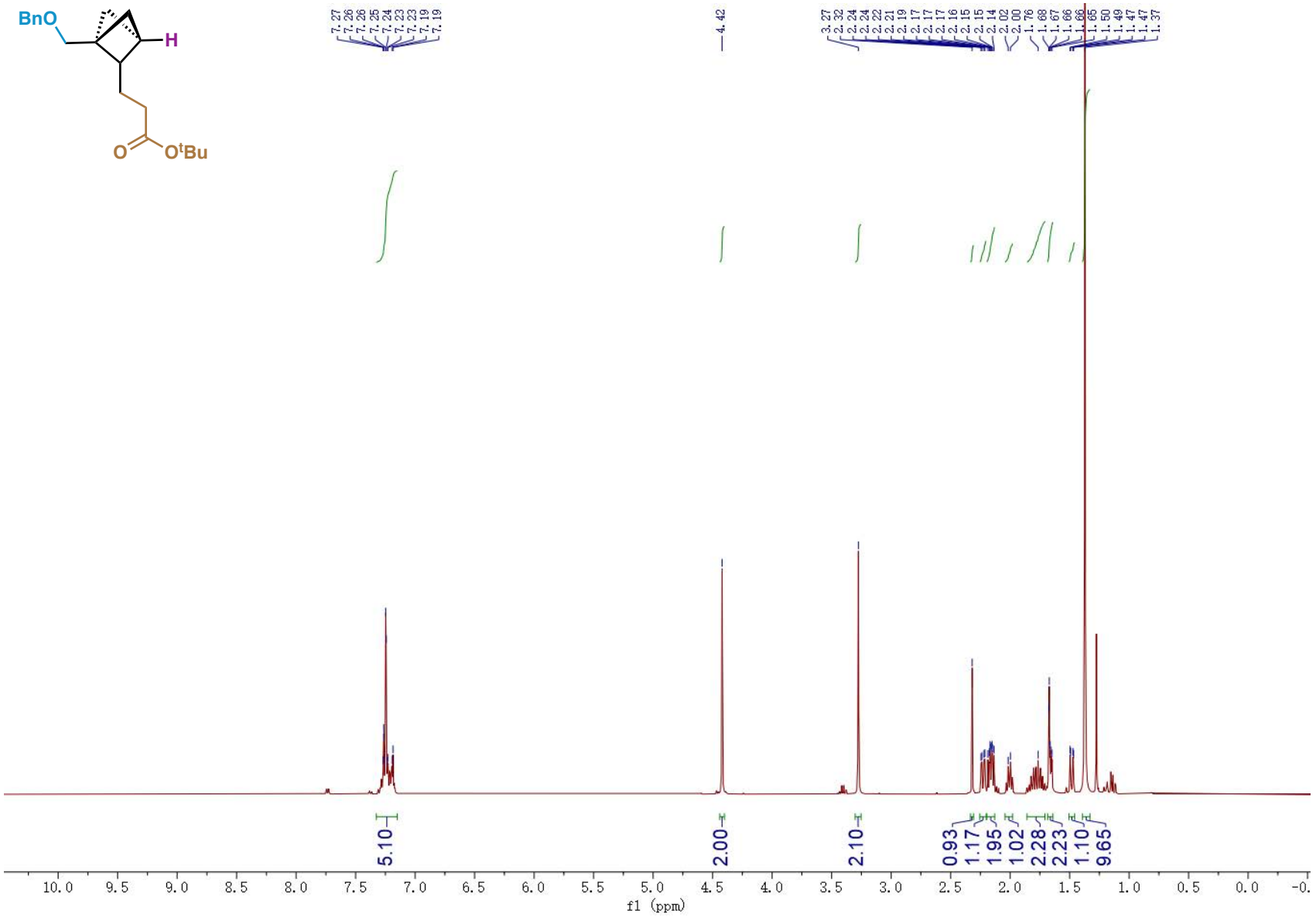
Compound 91 ^{13}C NMR



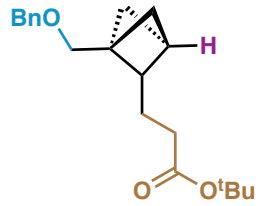
Compound 91 ^{11}B NMR



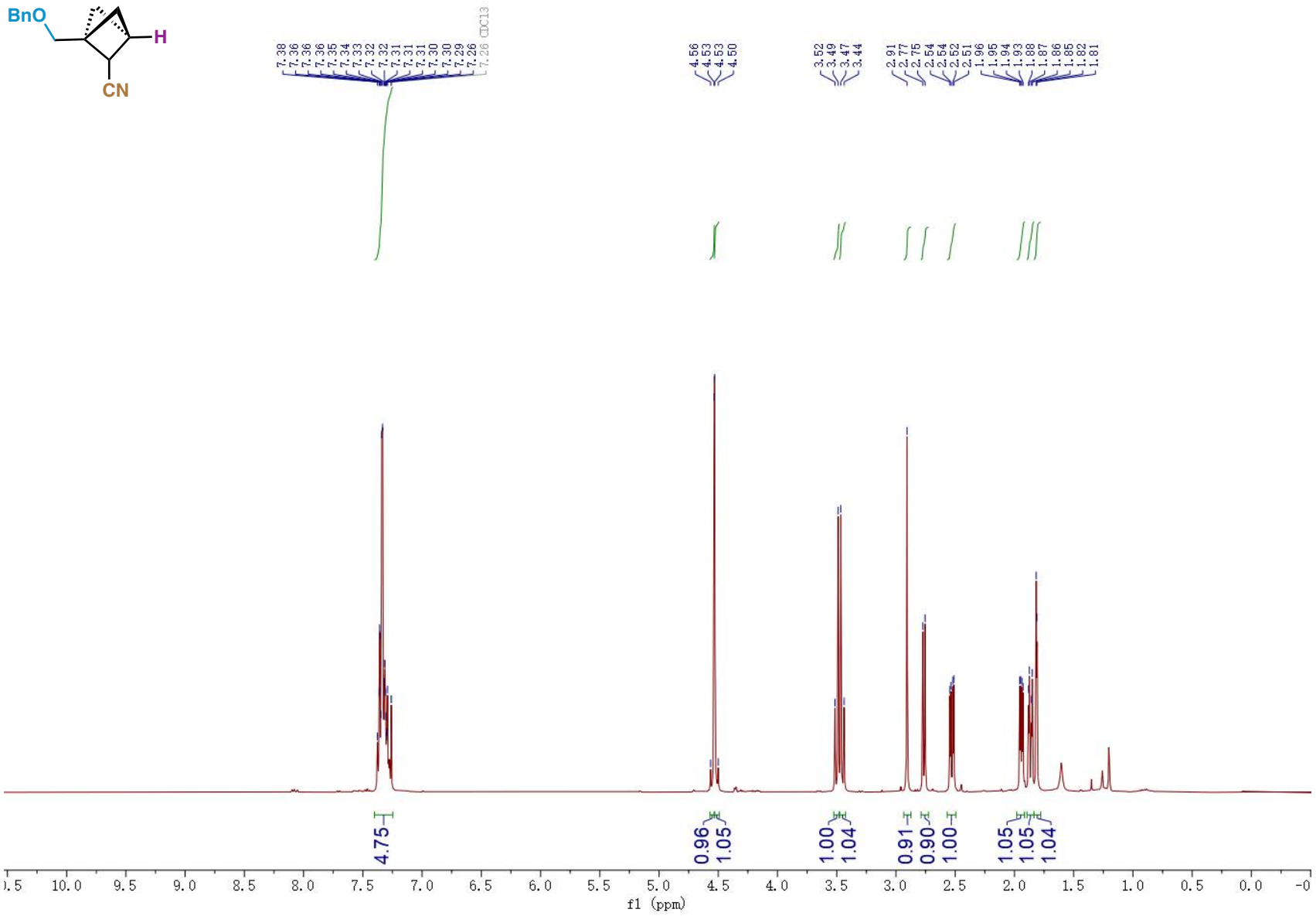
Compound 92 ^{1}H NMR



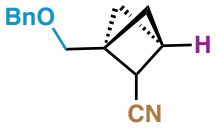
Compound 92 ^{13}C NMR



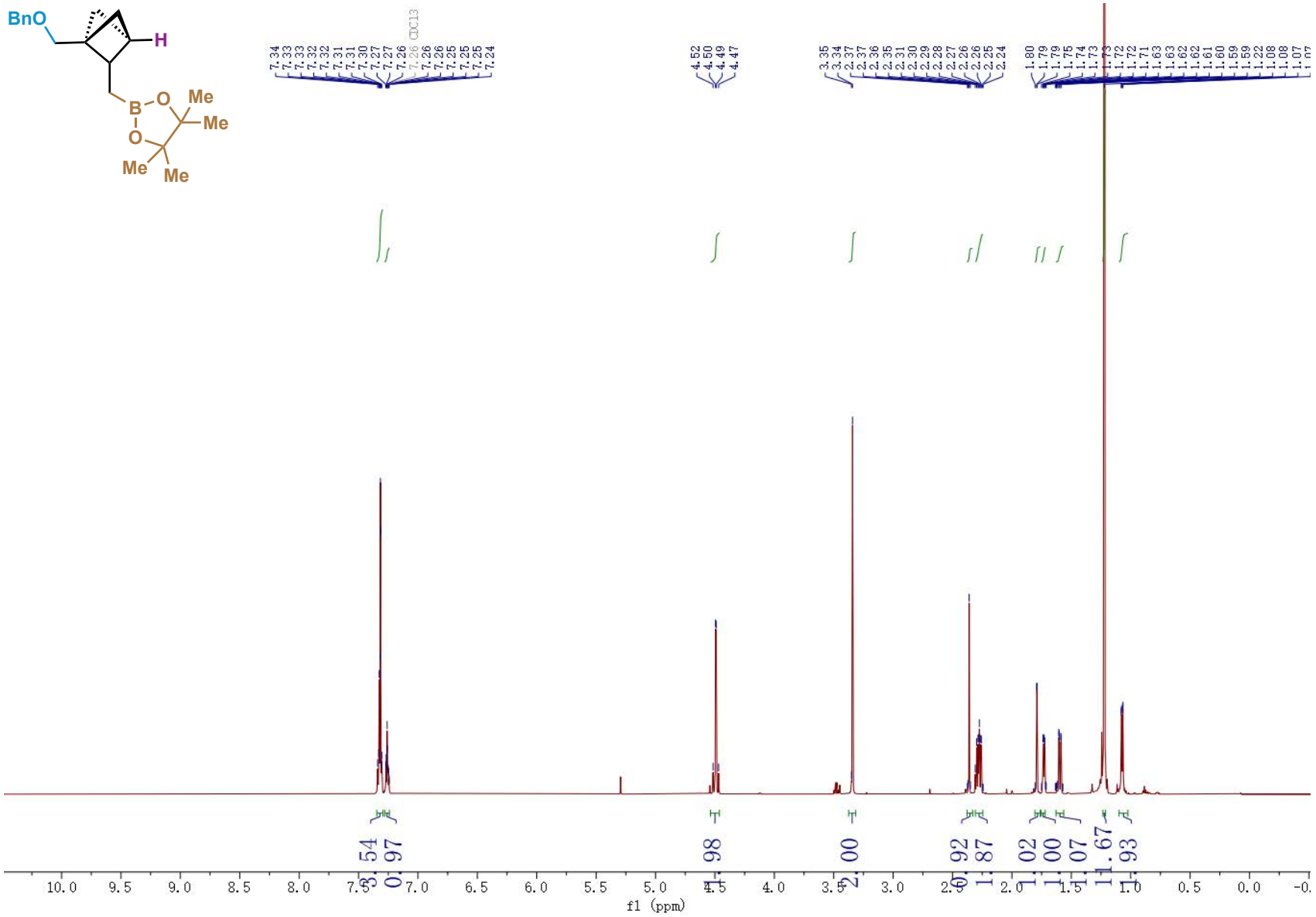
Compound 93 ^{1}H NMR



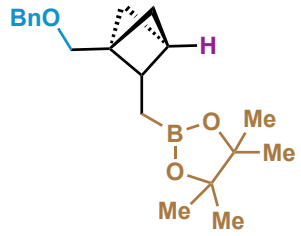
Compound 93 ^{13}C NMR



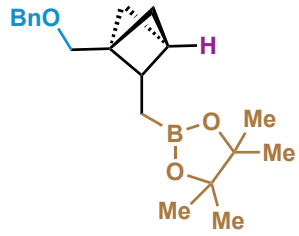
Compound 94 ^{1}H NMR



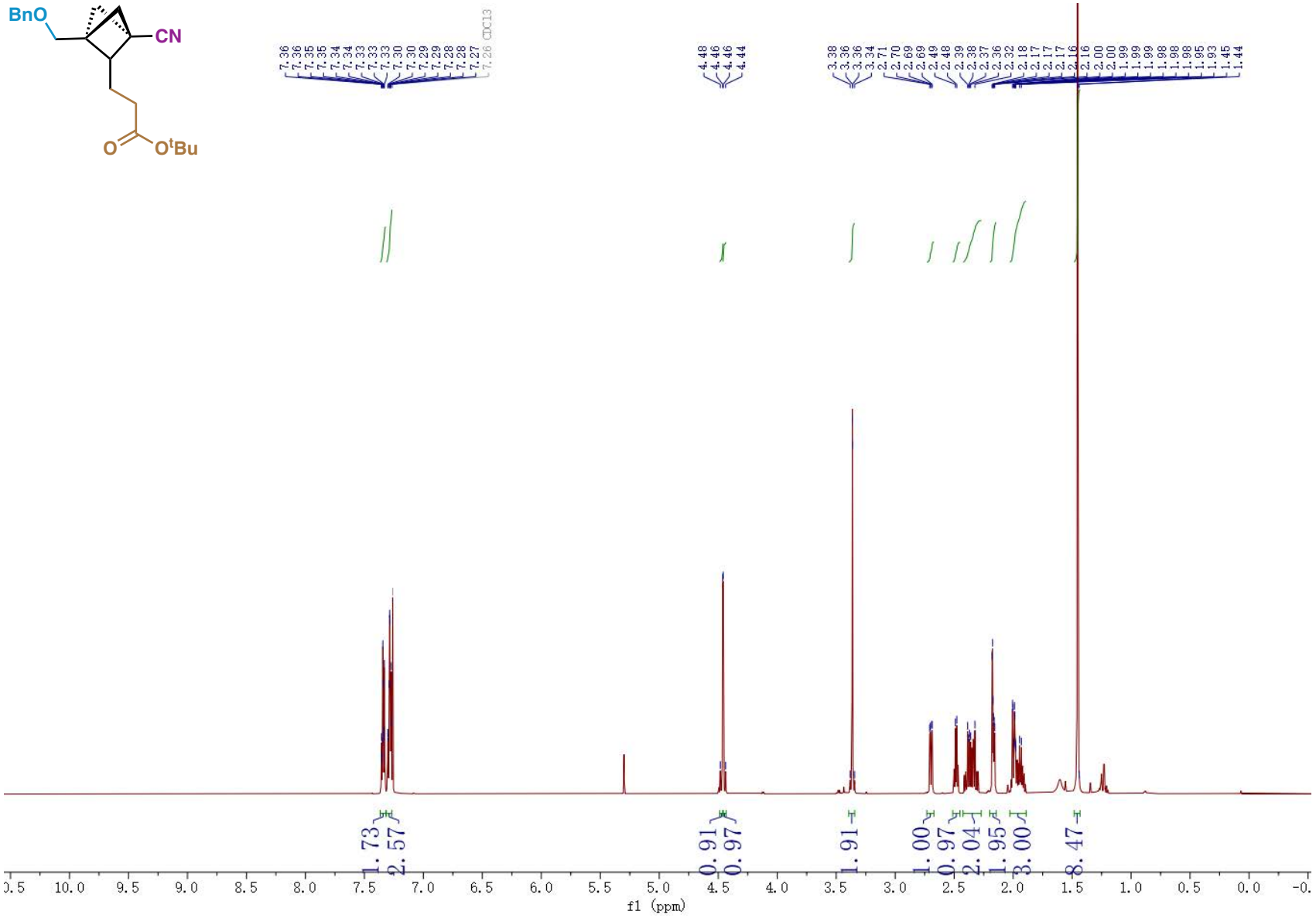
Compound 94 ^{13}C NMR



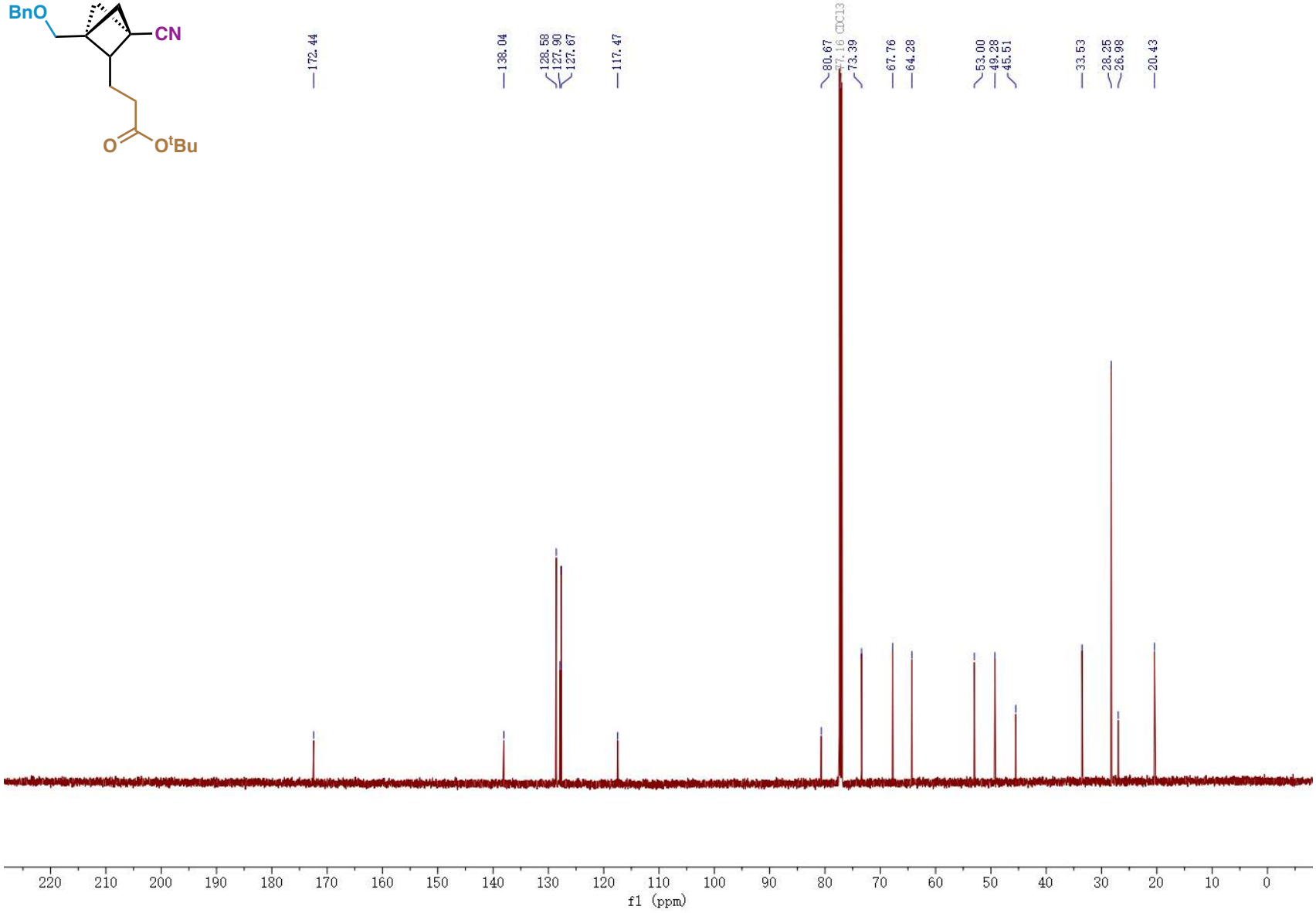
Compound 94 ^{11}B NMR



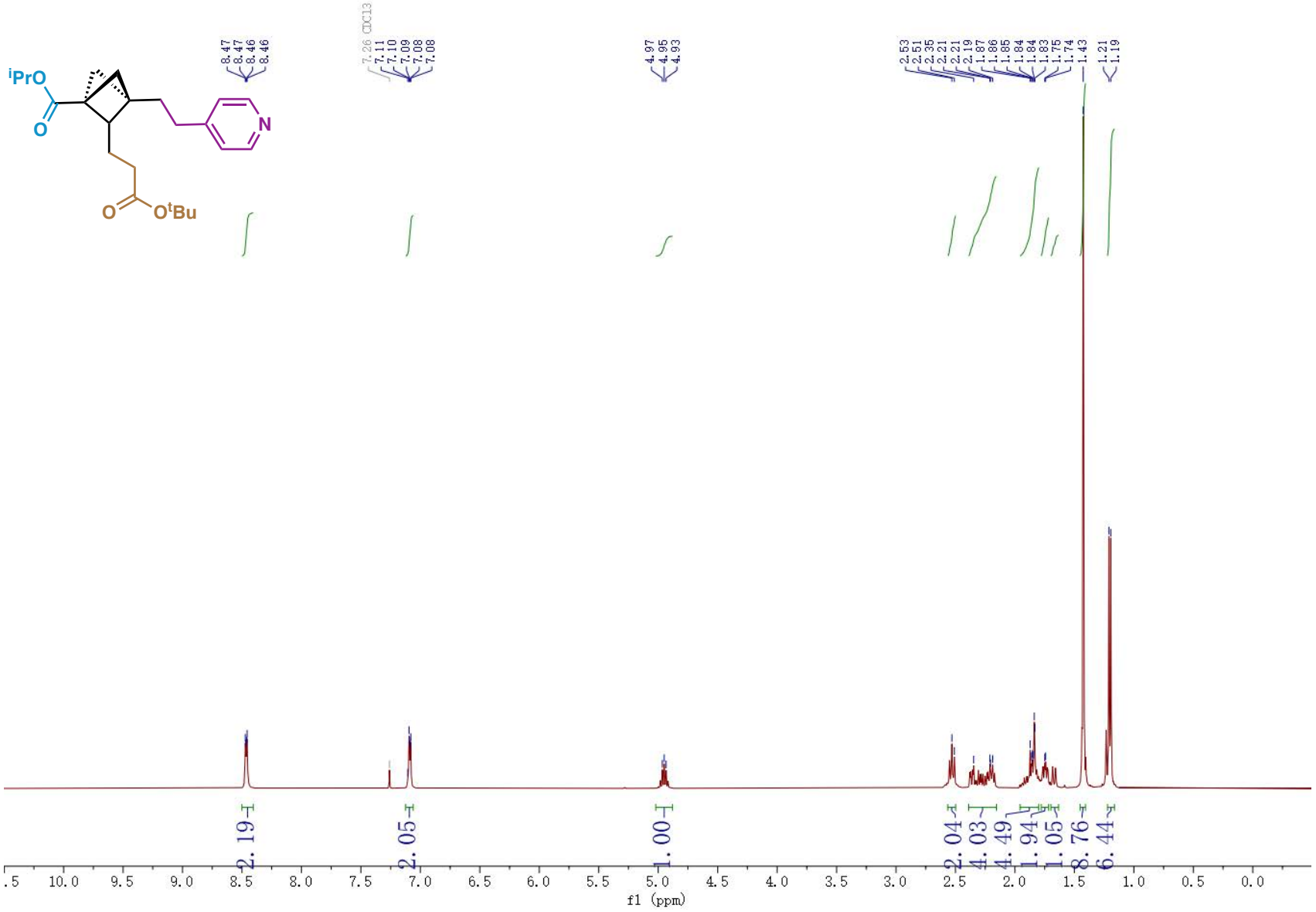
Compound 96 ^{1}H NMR



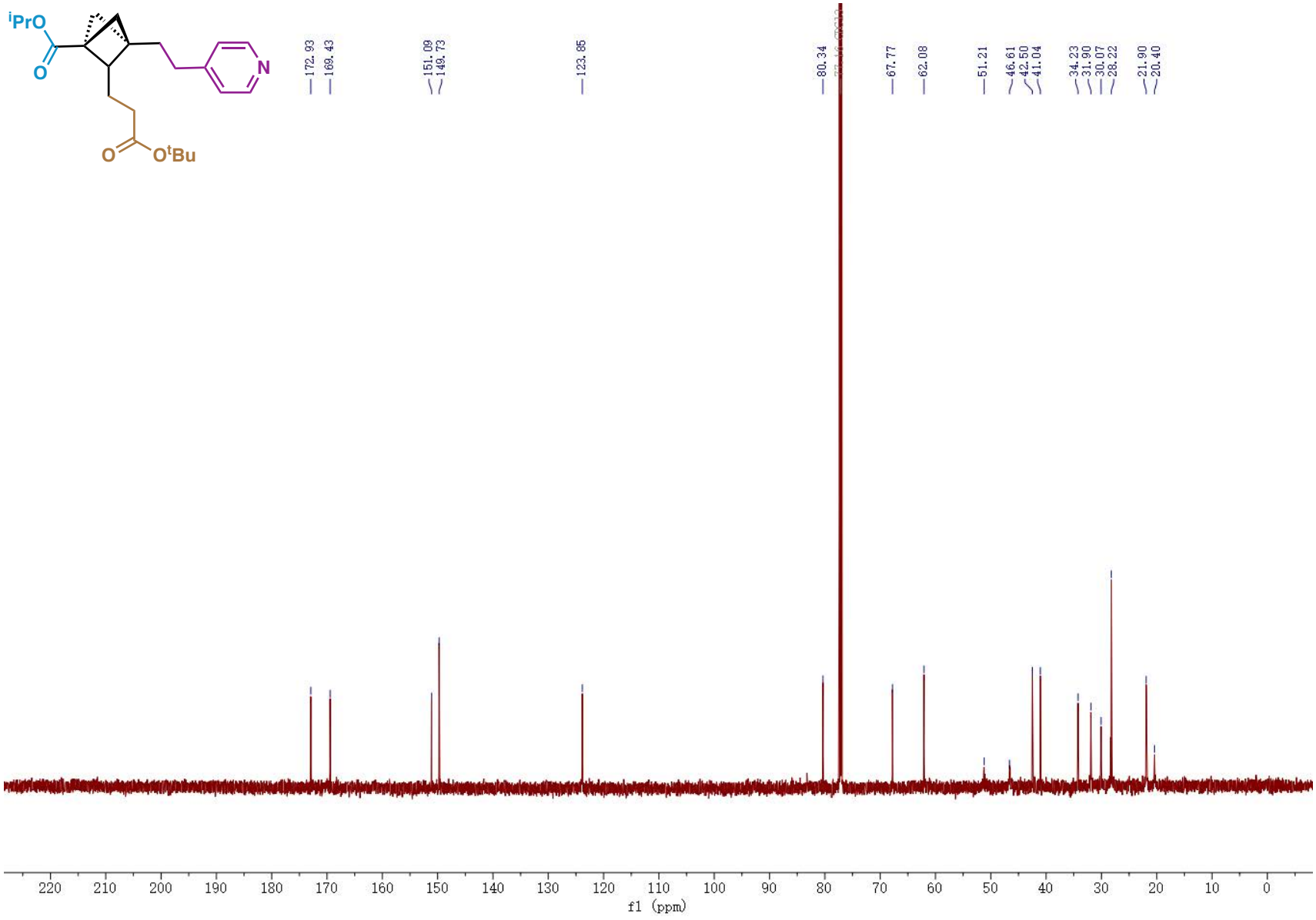
Compound 96 ^{13}C NMR



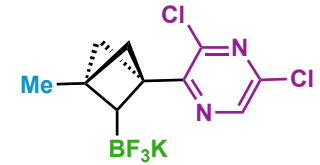
Compound 97 ^{1}H NMR



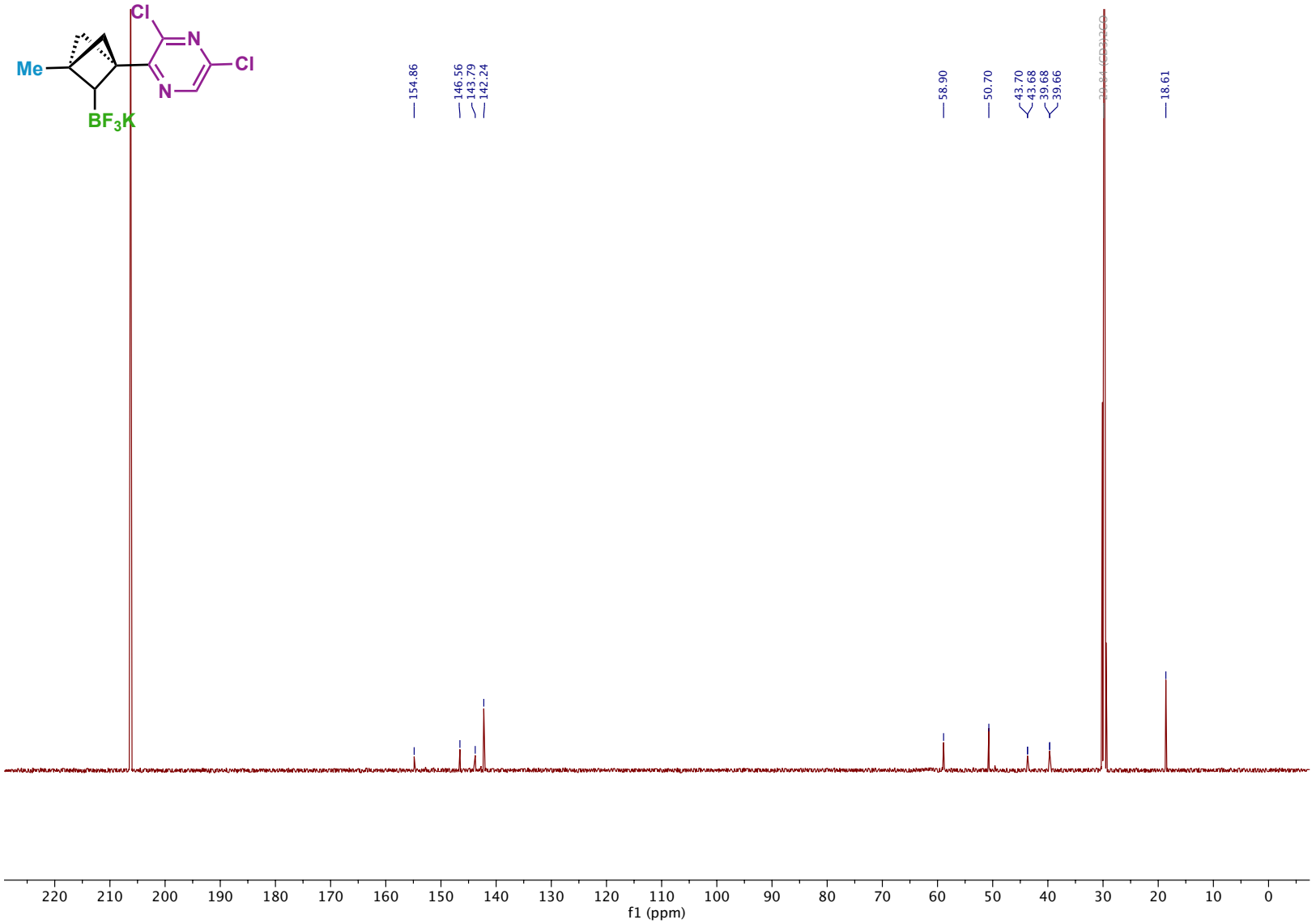
Compound 97 ^{13}C NMR



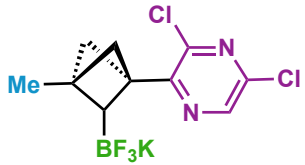
Compound SI-24 ^{1}H NMR



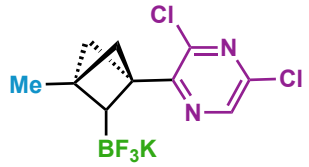
Compound SI-24 ^{13}C NMR



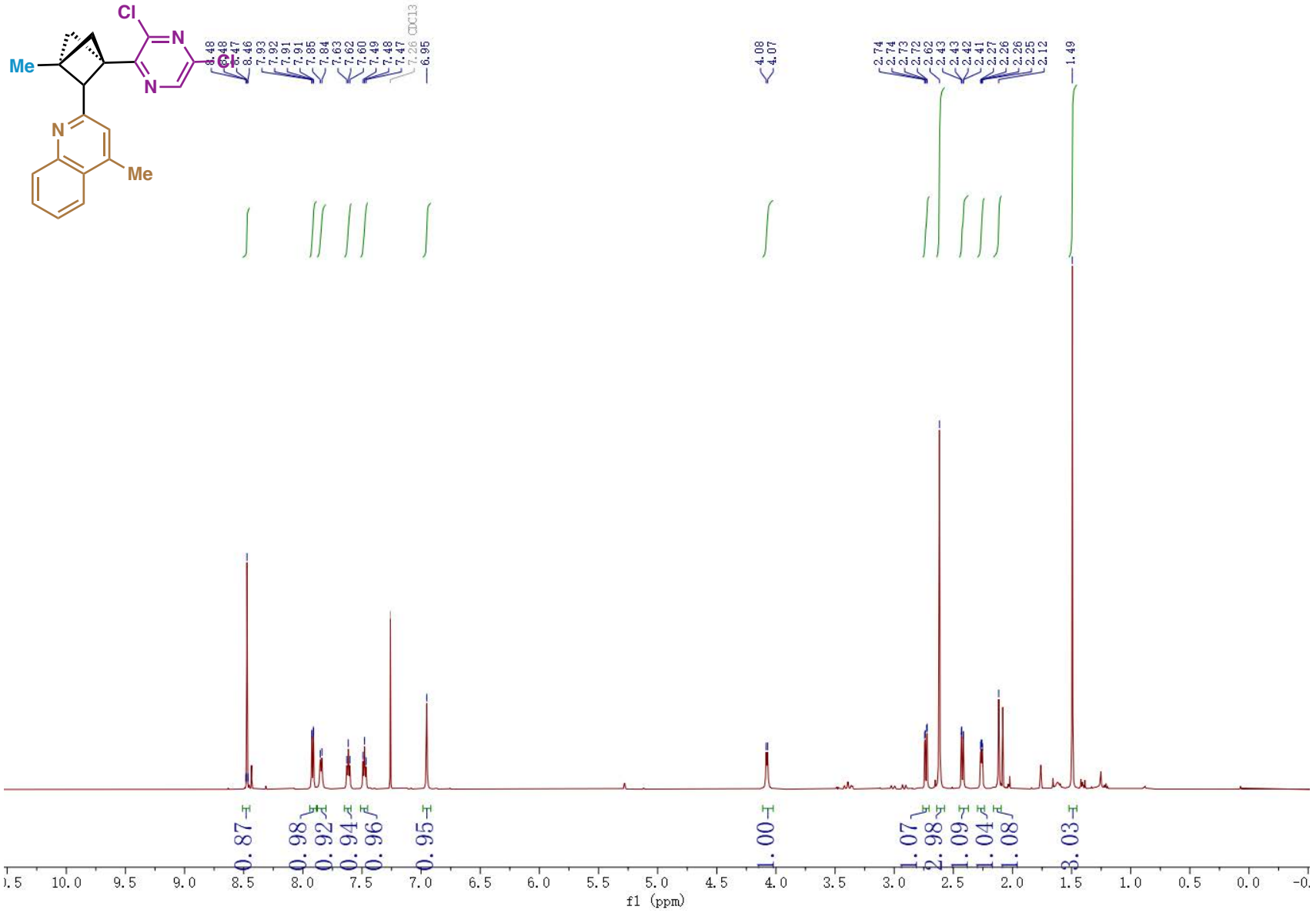
Compound SI-24 ^{19}F NMR



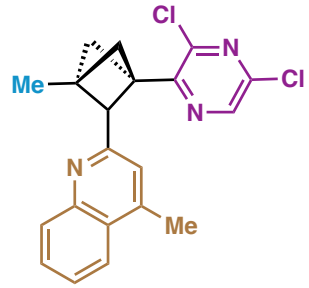
Compound SI-24 ^{11}B NMR



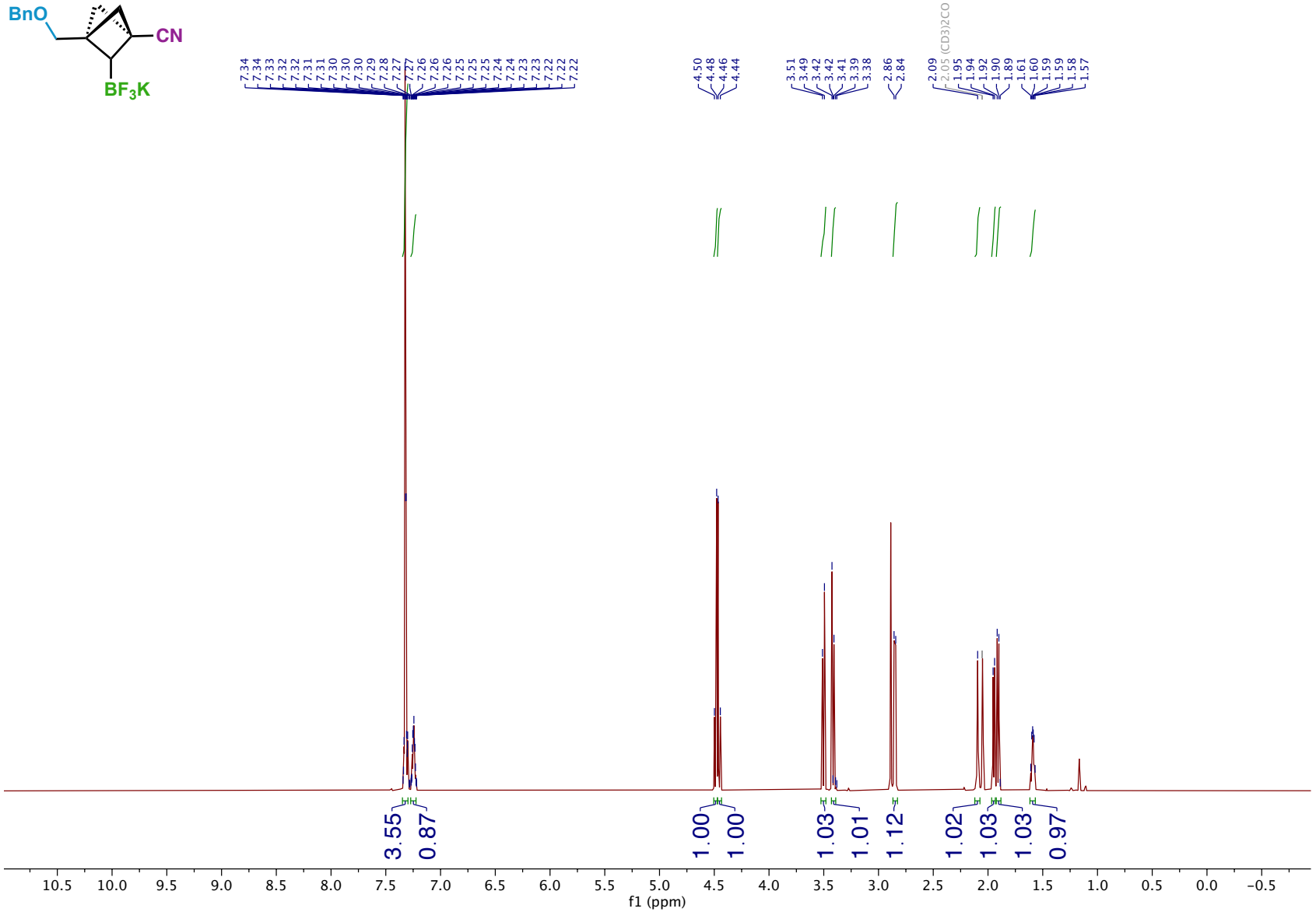
Compound 98 ^{1}H NMR



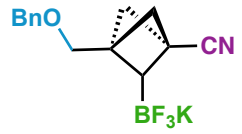
Compound 98 ^{13}C NMR



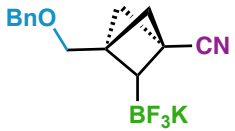
Compound SI-25 ^{1}H NMR



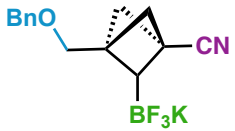
Compound SI-25 ^{13}C NMR



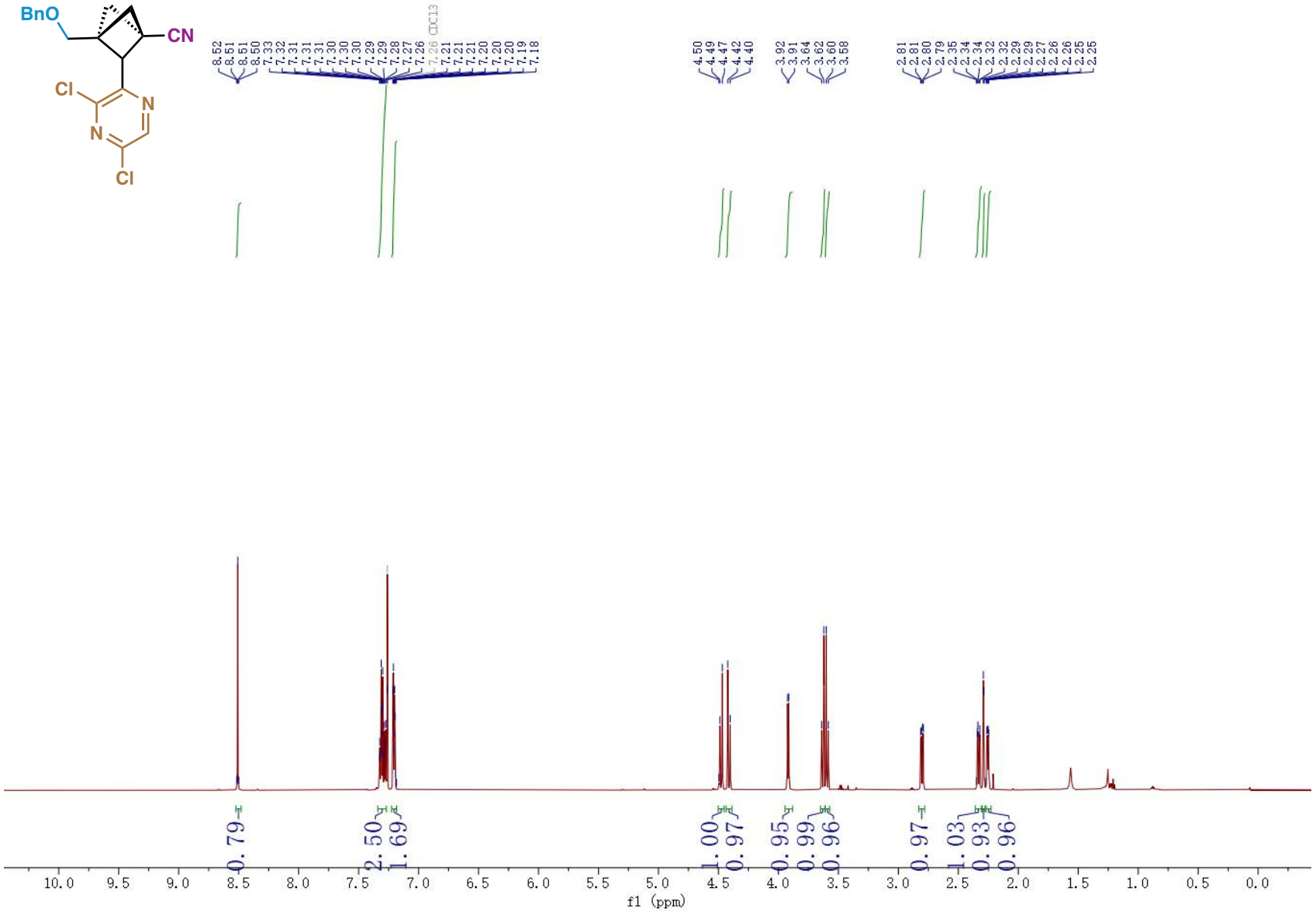
Compound SI-25 ^{19}F NMR



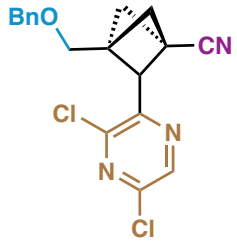
Compound SI-25 ^{11}B NMR



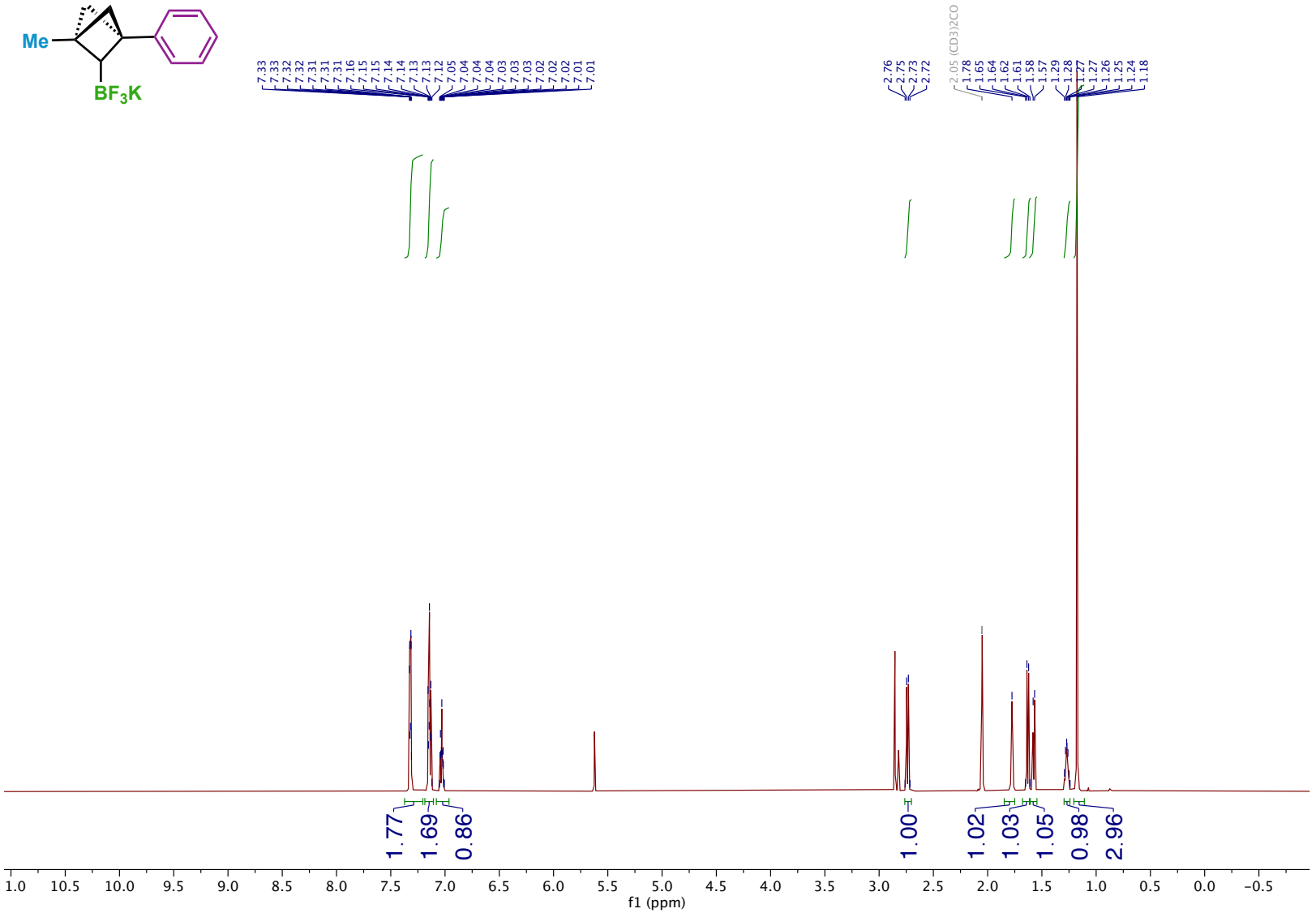
Compound 99 ^{1}H NMR



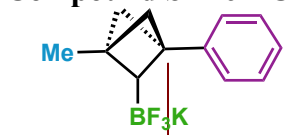
Compound 99 ^{13}C NMR



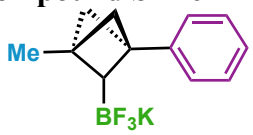
Compound SI-26 ^{1}H NMR



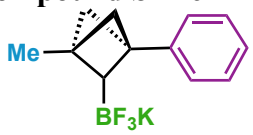
Compound SI-26 ^{13}C NMR



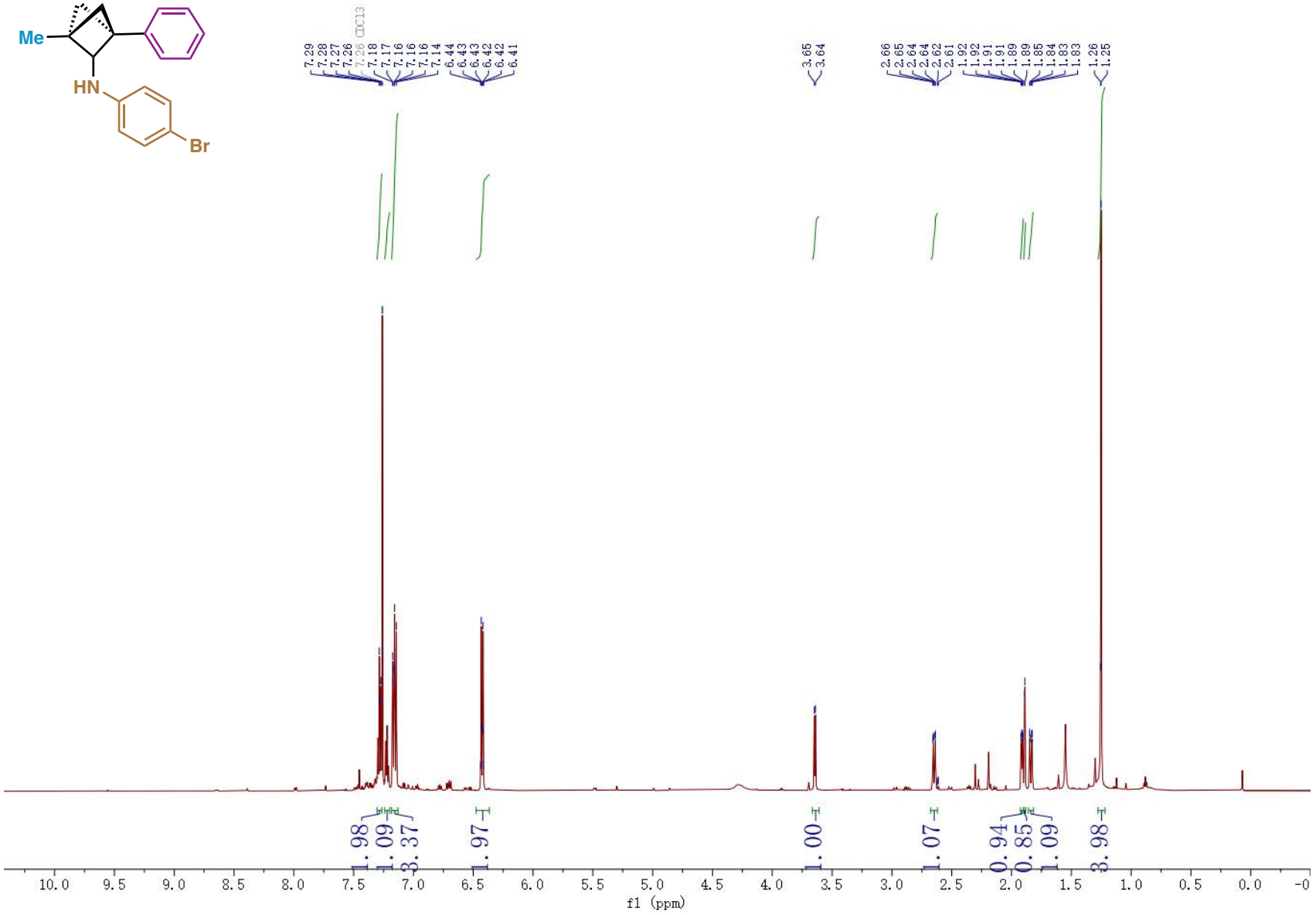
Compound SI-26 ^{19}F NMR



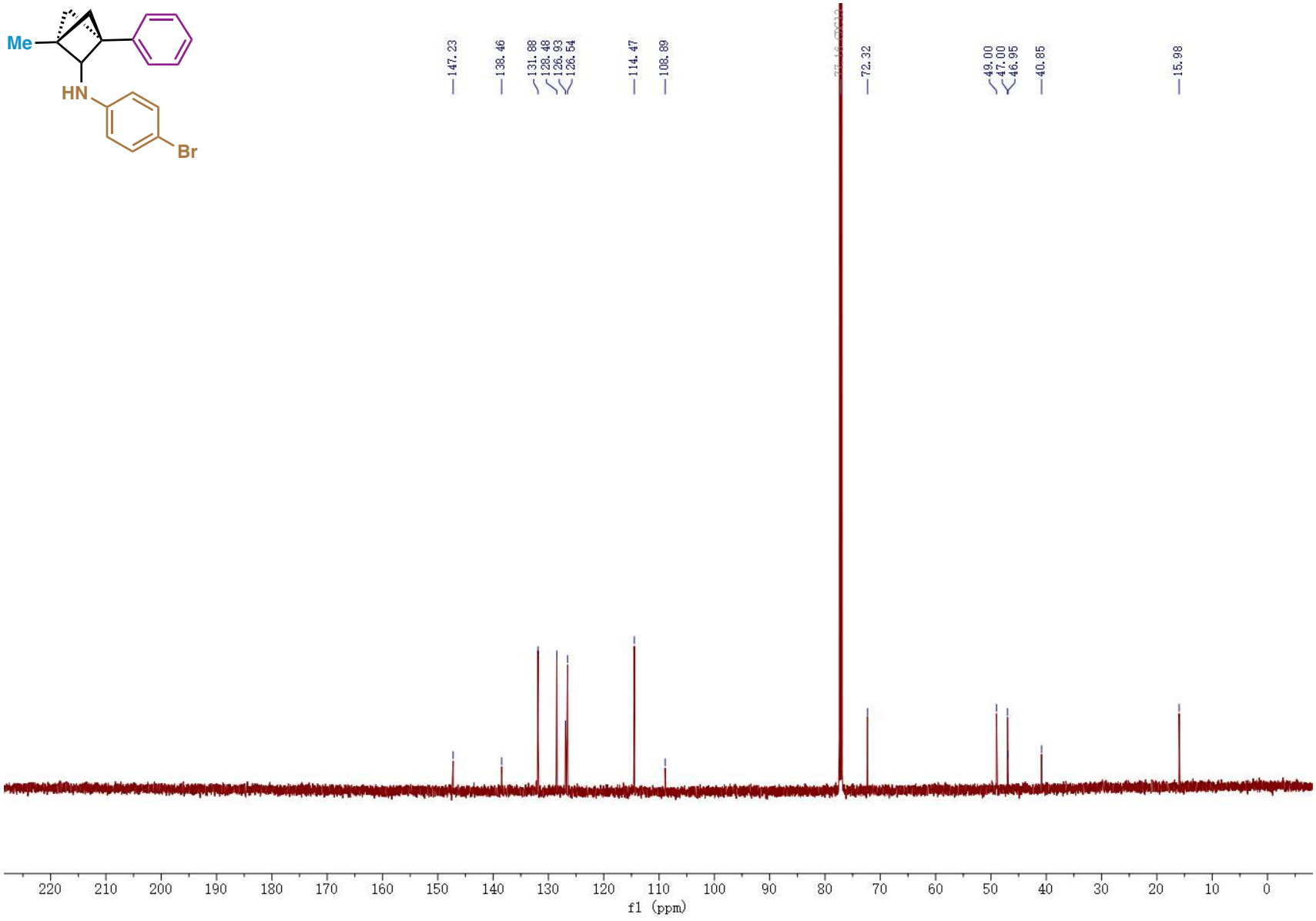
Compound SI-26 ^{11}B NMR



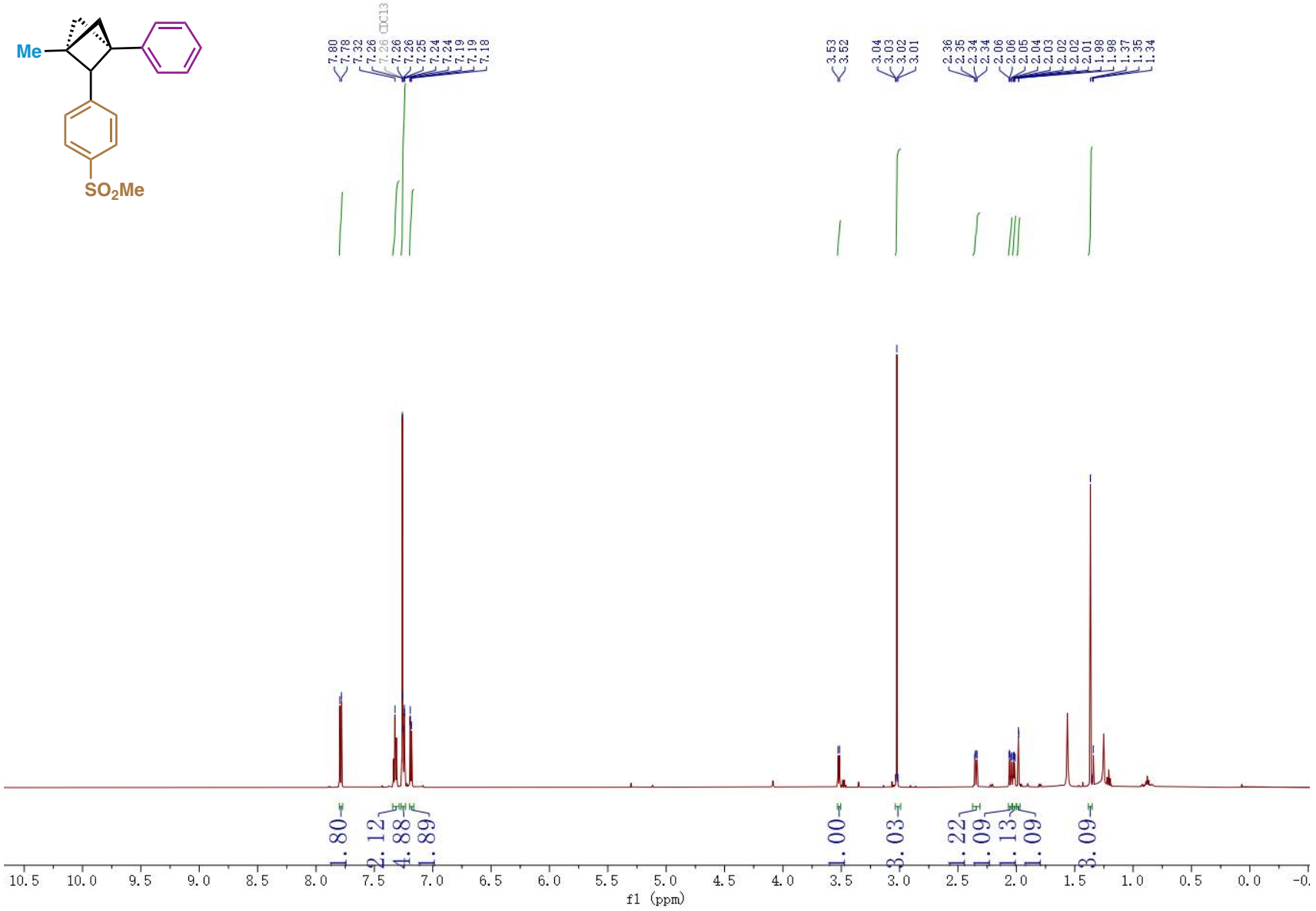
Compound 100 ^{1}H NMR



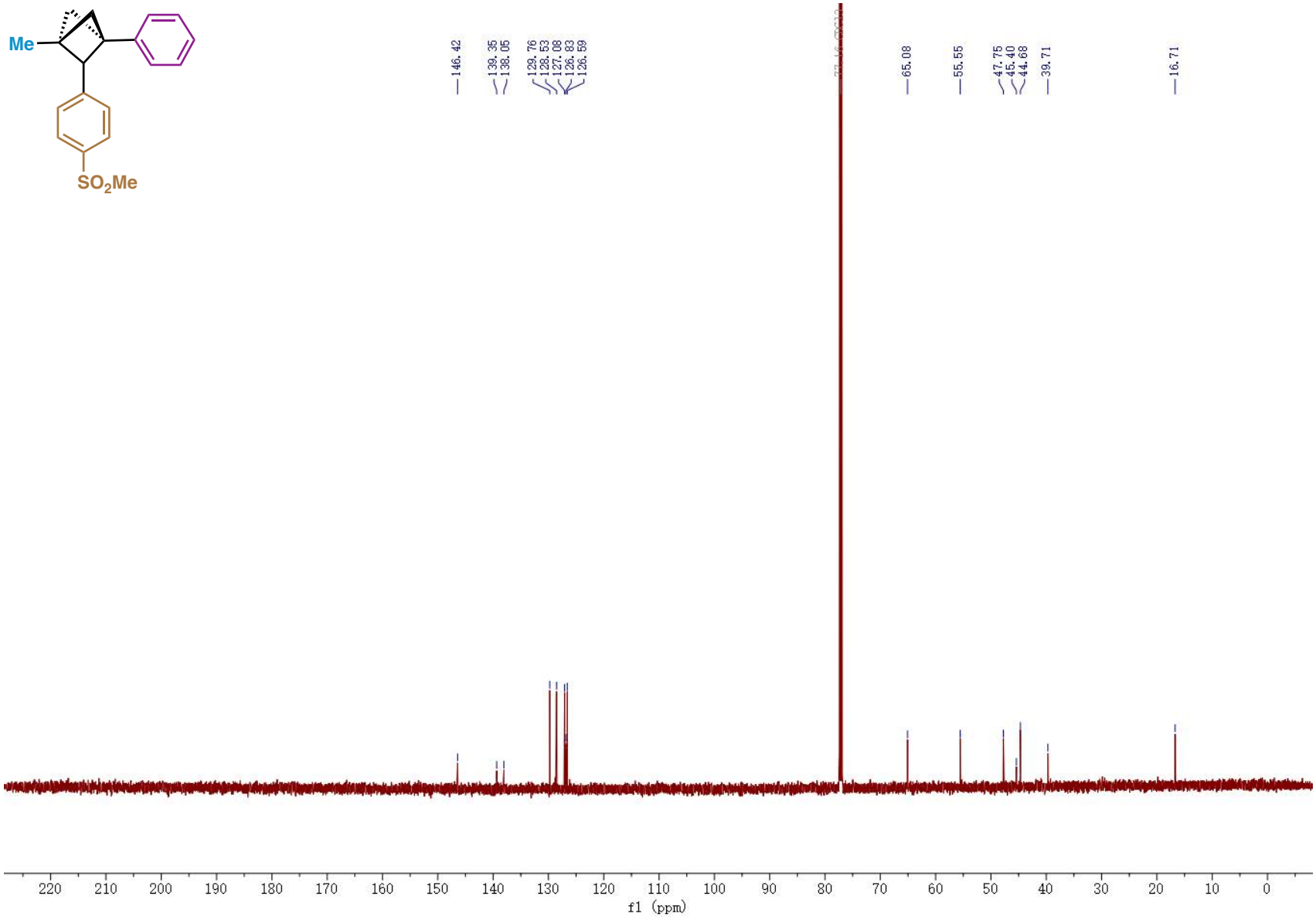
Compound 100 ^{13}C NMR



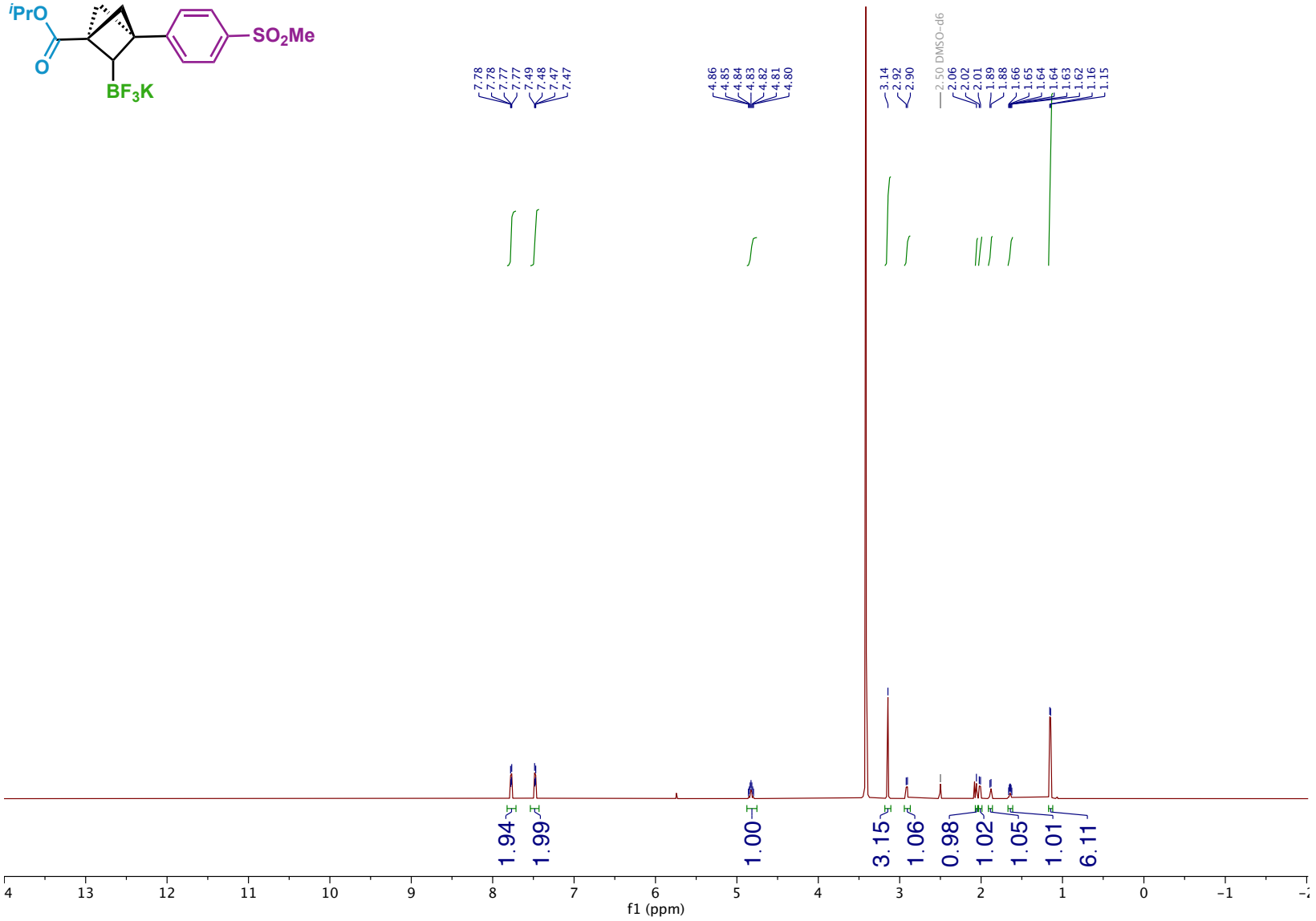
Compound 101 ^{1}H NMR



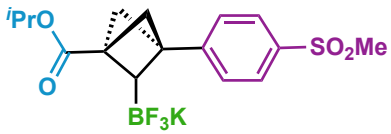
Compound 101 ^{13}C NMR



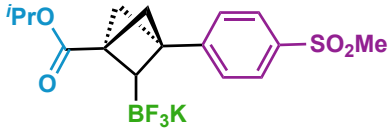
Compound SI-27 ^{1}H NMR



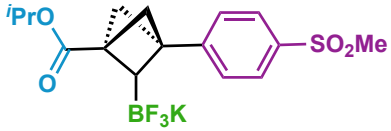
Compound SI-27 ^{13}C NMR



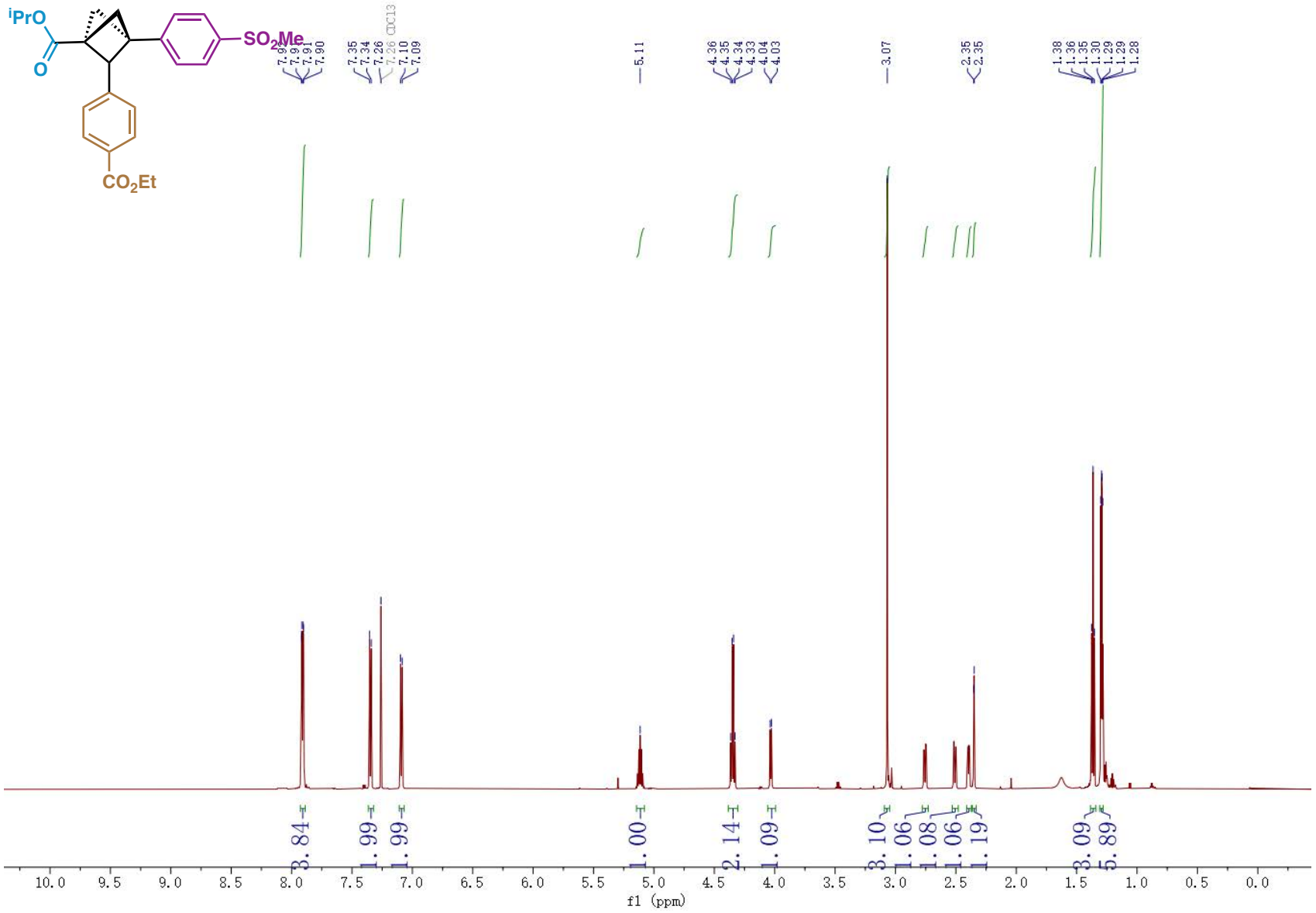
Compound SI-27 ^{19}F NMR



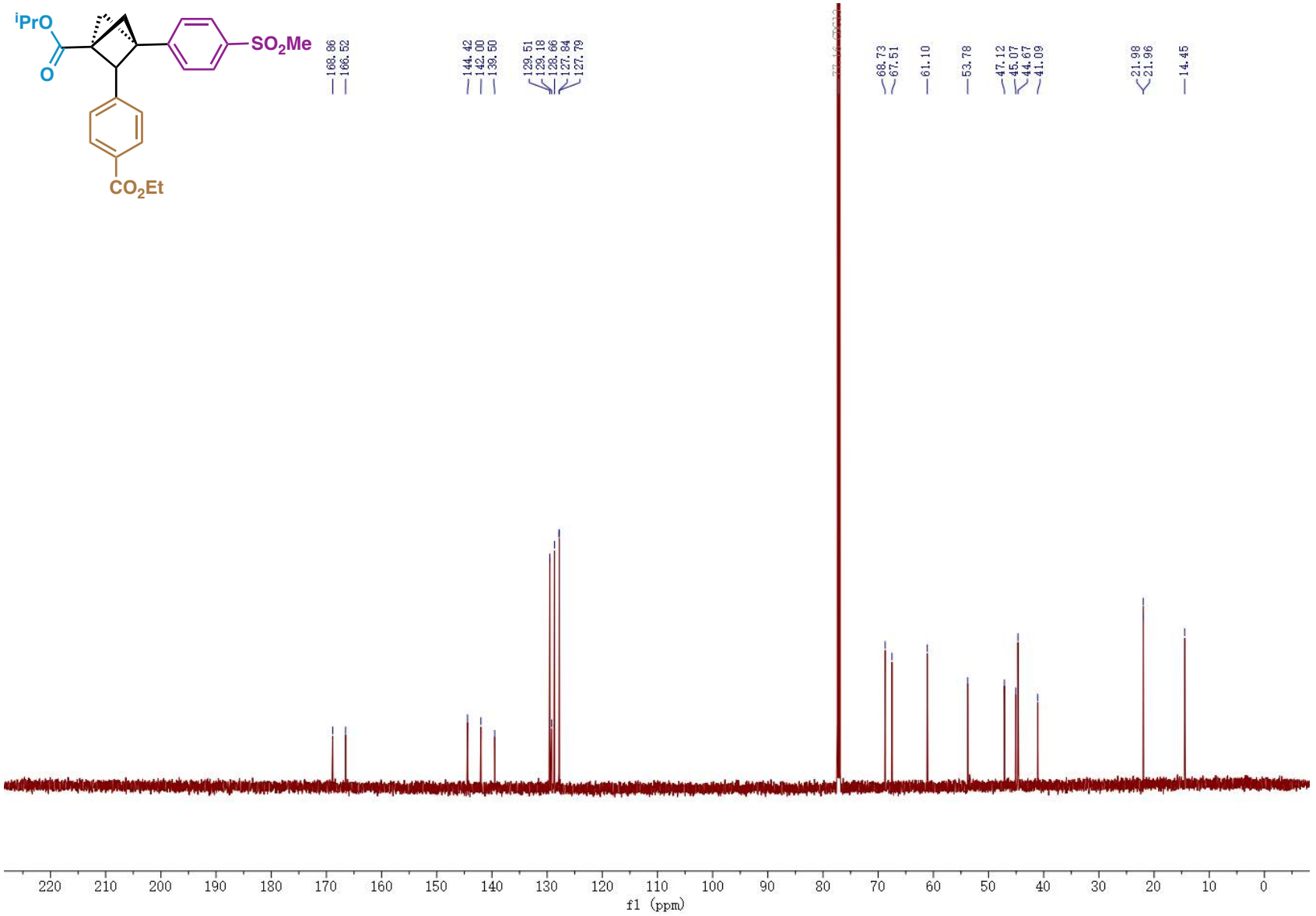
Compound SI-27 ^{11}B NMR



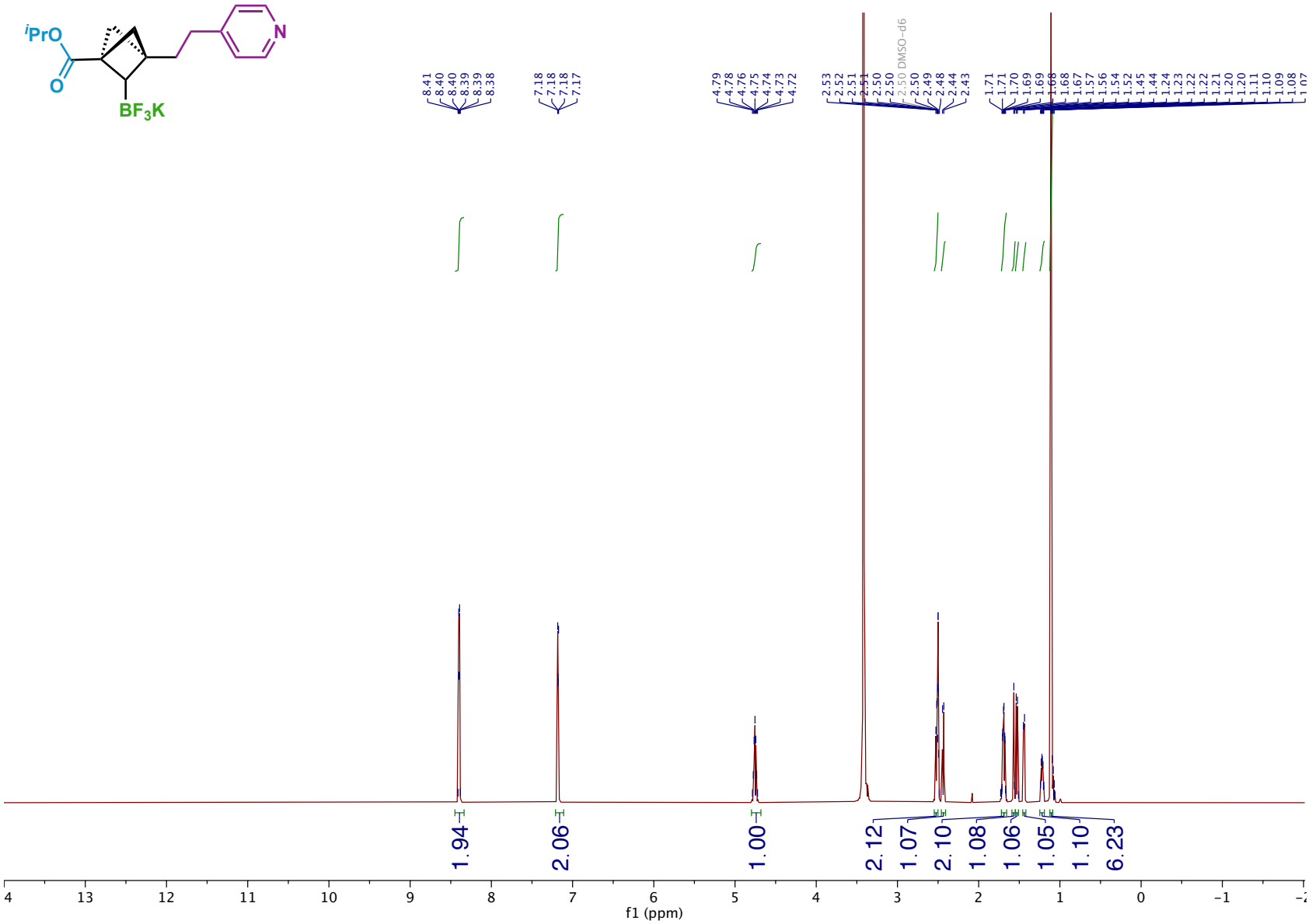
Compound 102 ^{1}H NMR



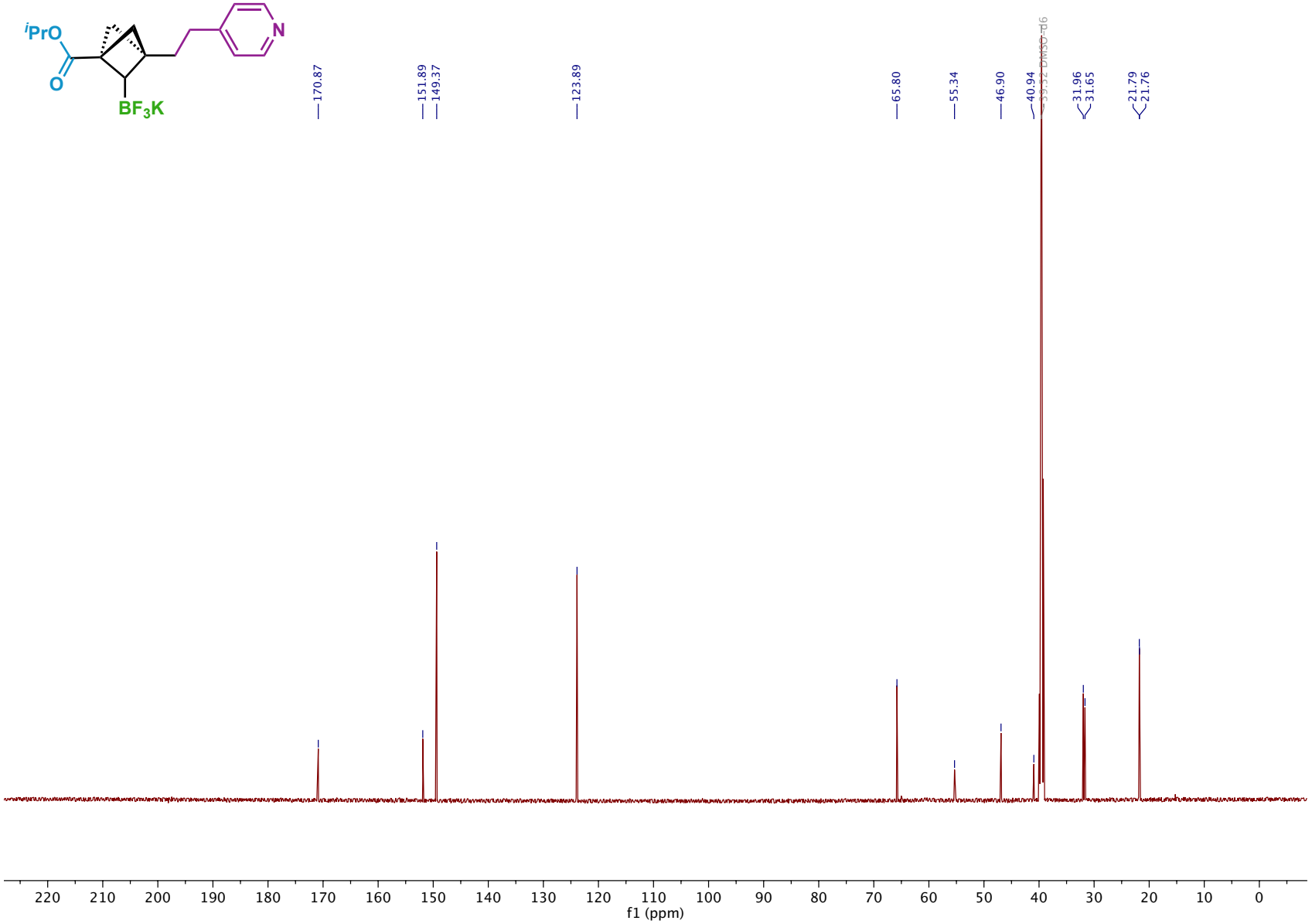
Compound 102 ^{13}C NMR



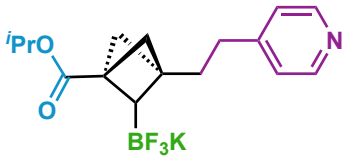
Compound SI-28 ^{1}H NMR



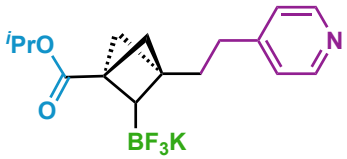
Compound SI-28 ^{13}C NMR



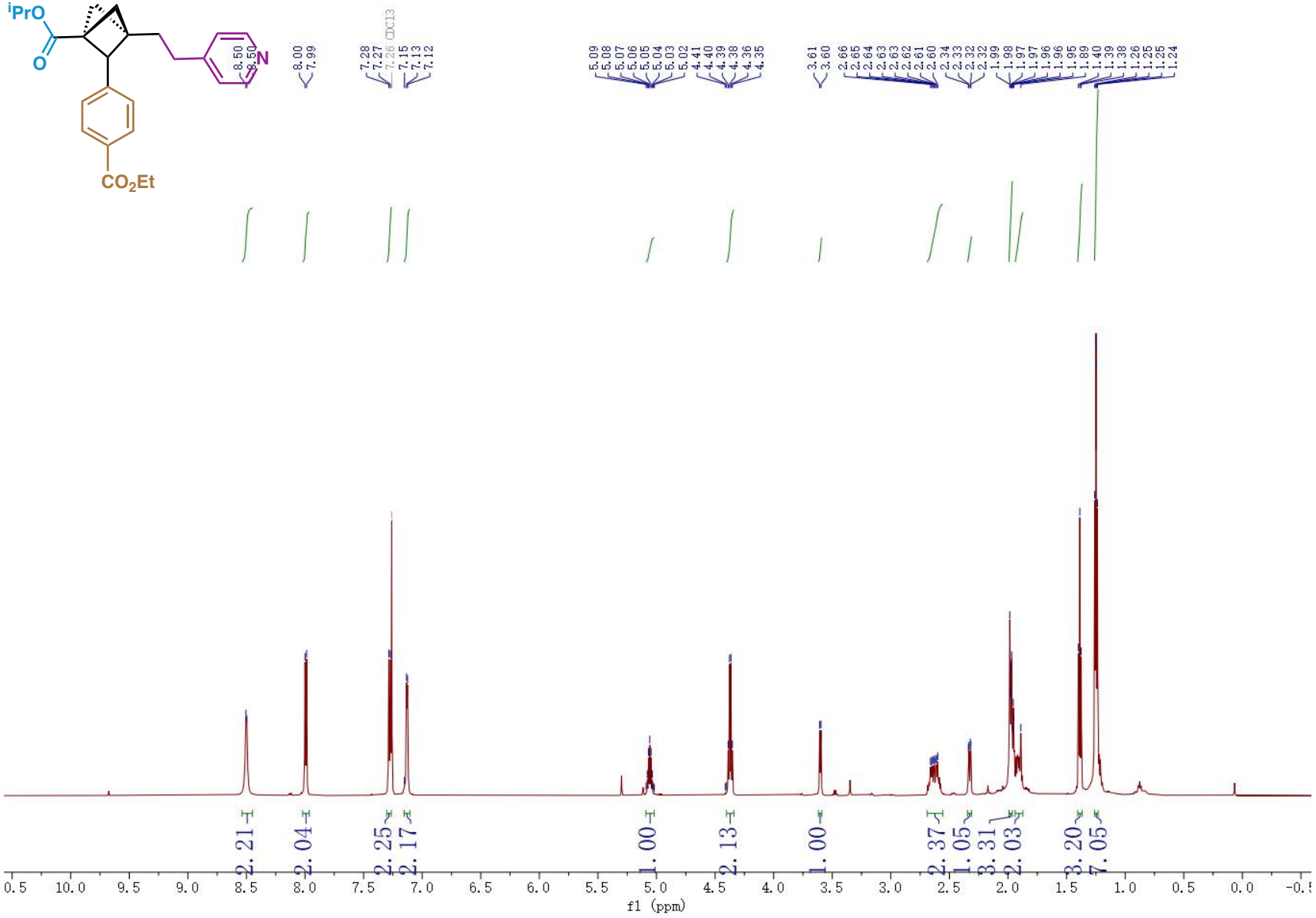
Compound SI-28 ^{19}F NMR



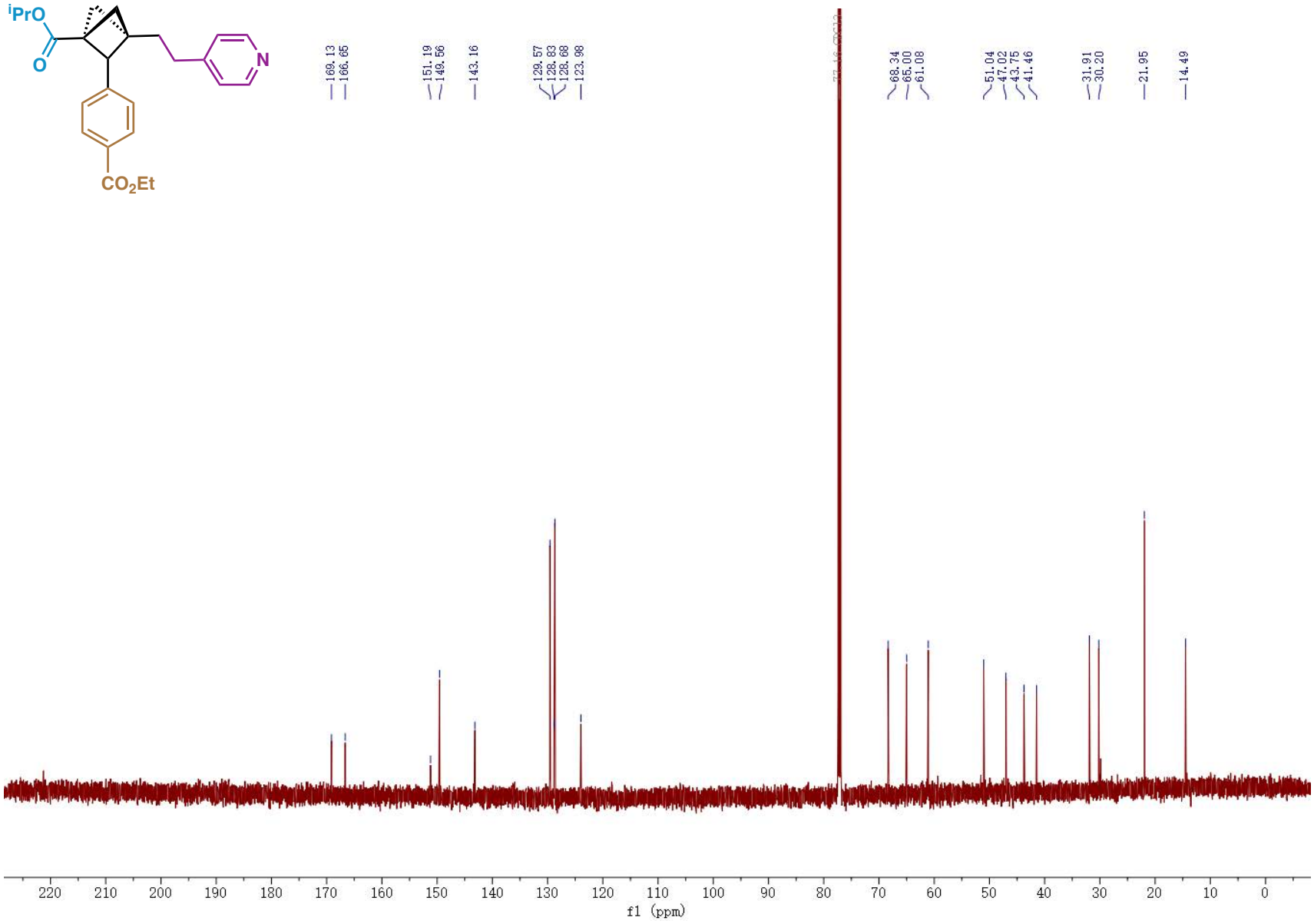
Compound SI-28 ^{11}B NMR



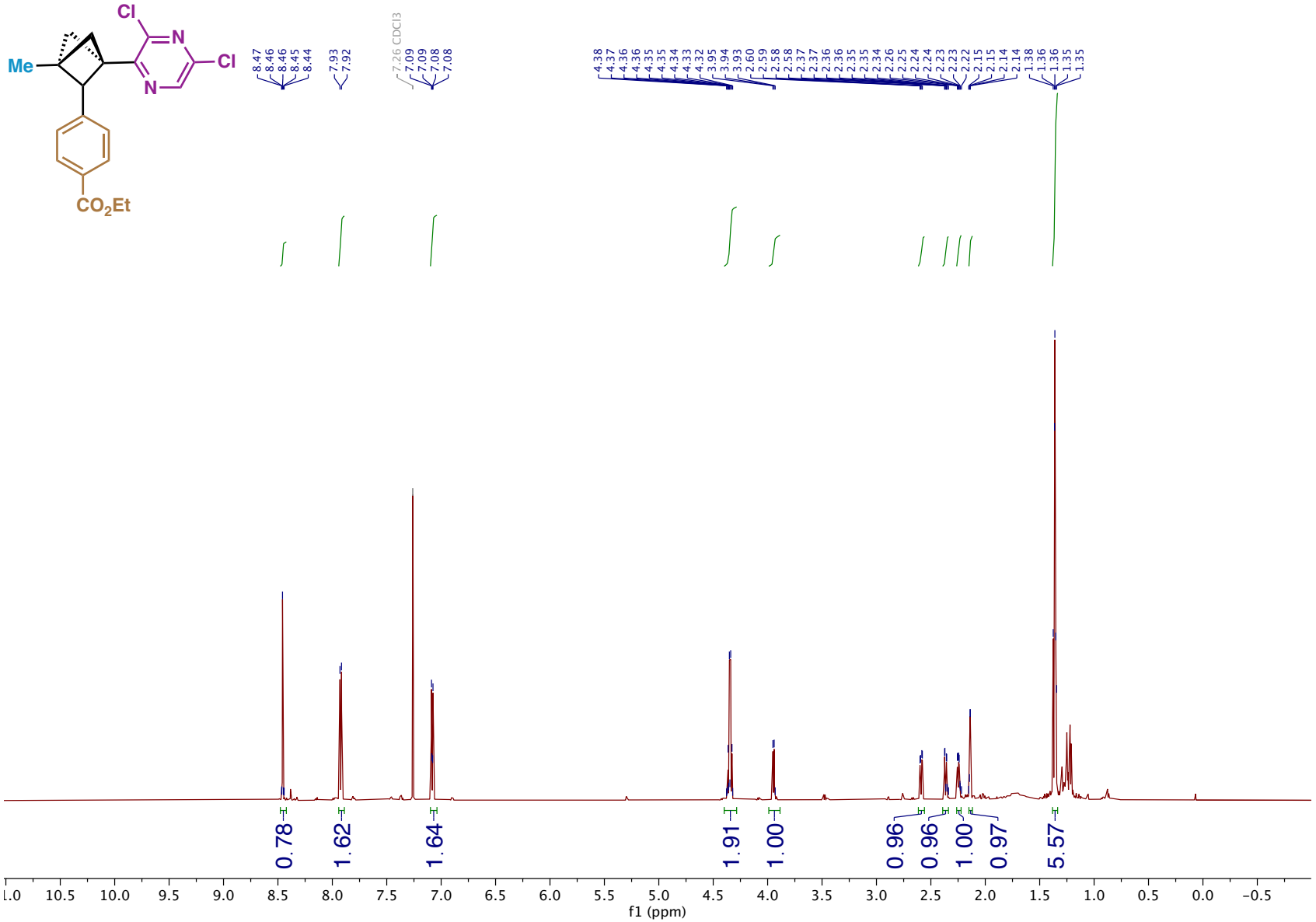
Compound 103 ^{1}H NMR



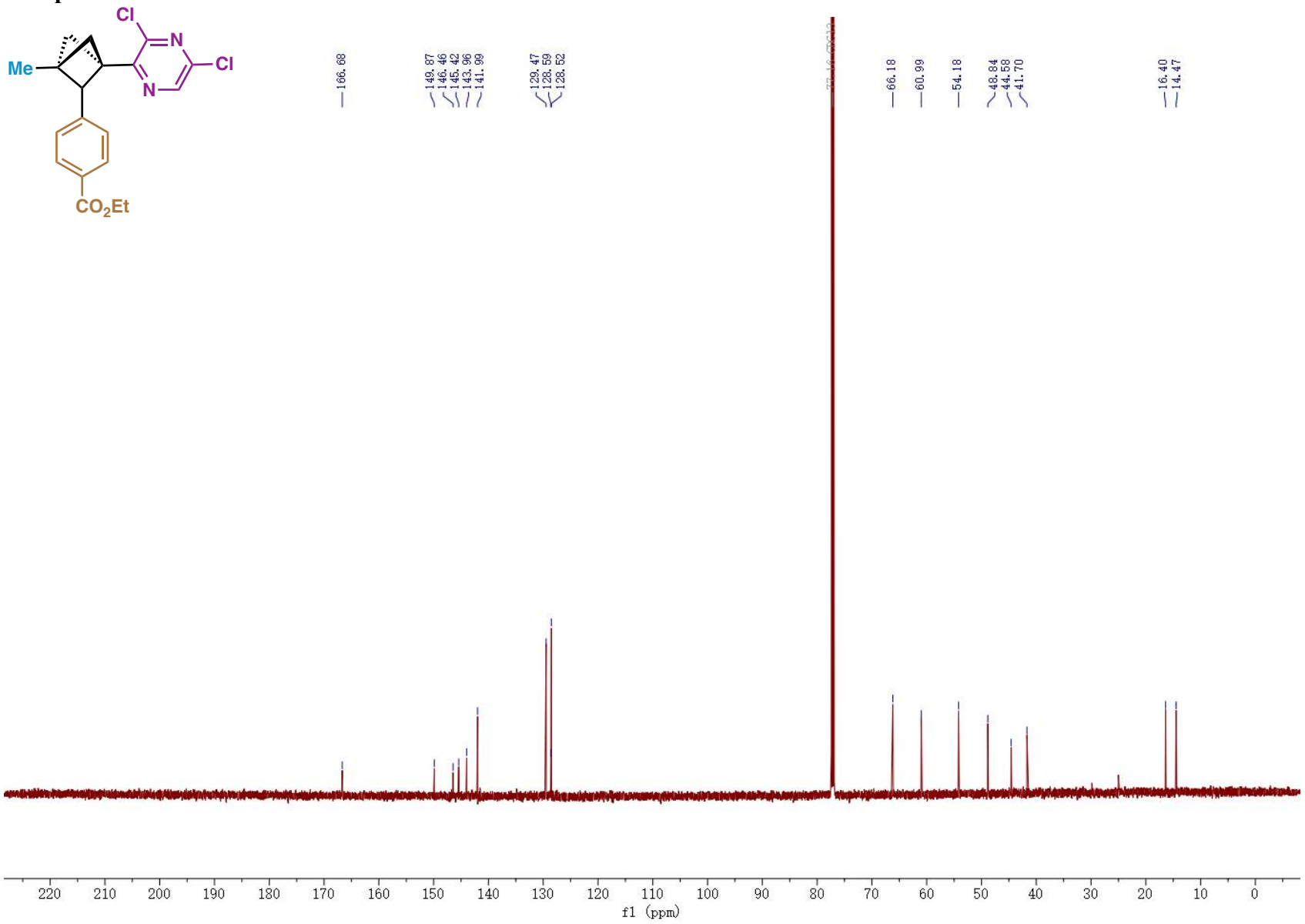
Compound 103 ^{13}C NMR



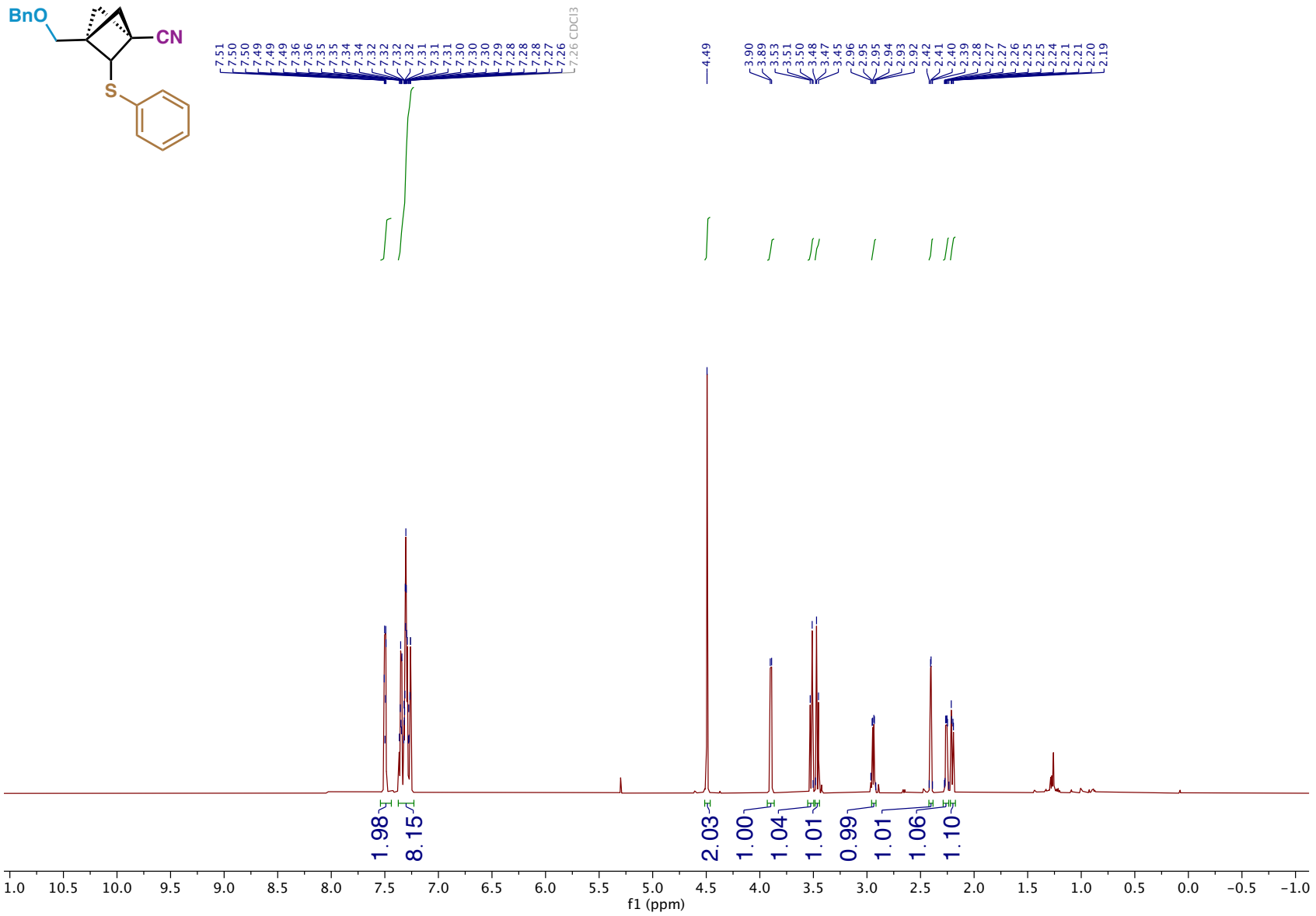
Compound 104 ^{1}H NMR



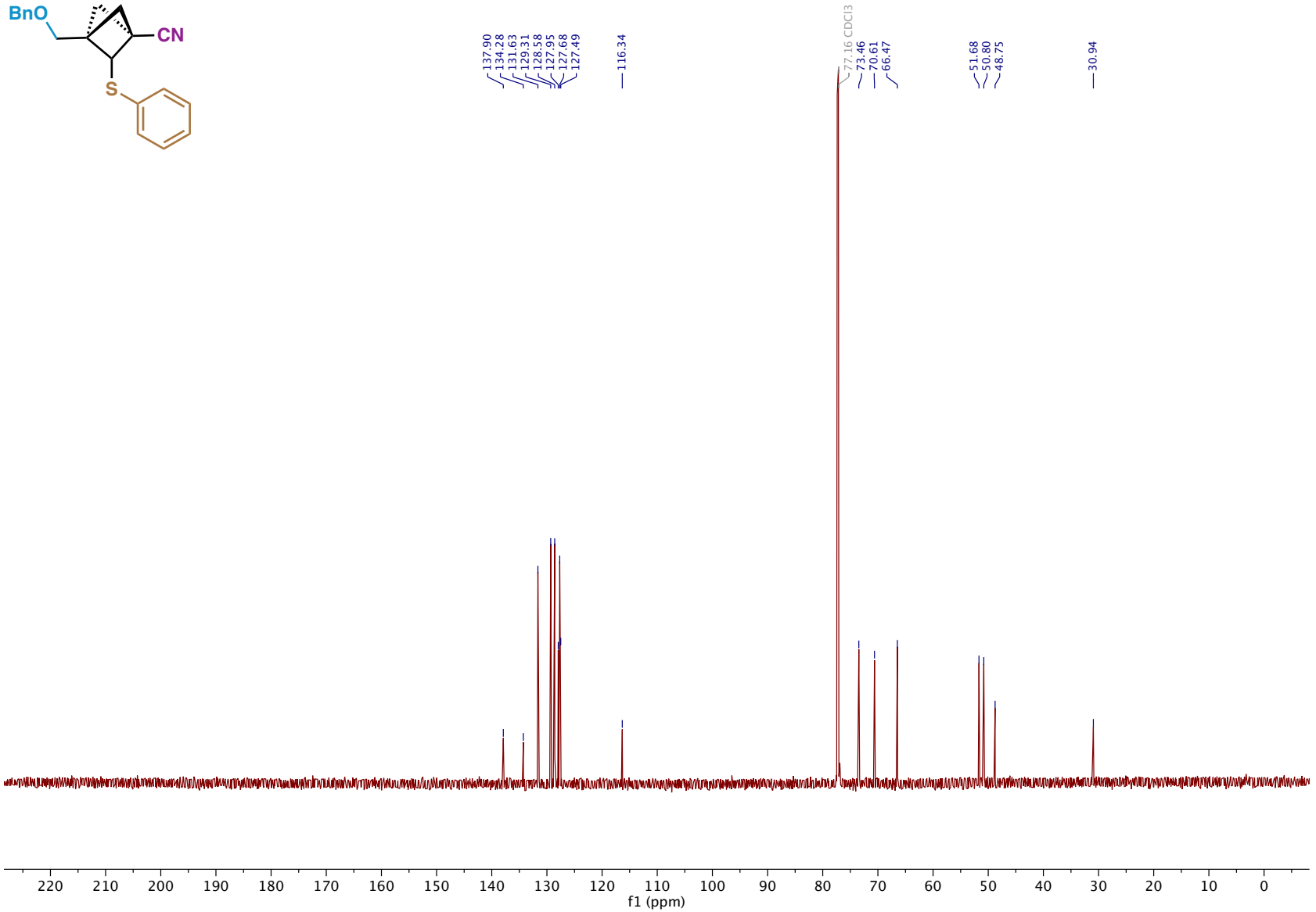
Compound 104 ^{13}C NMR



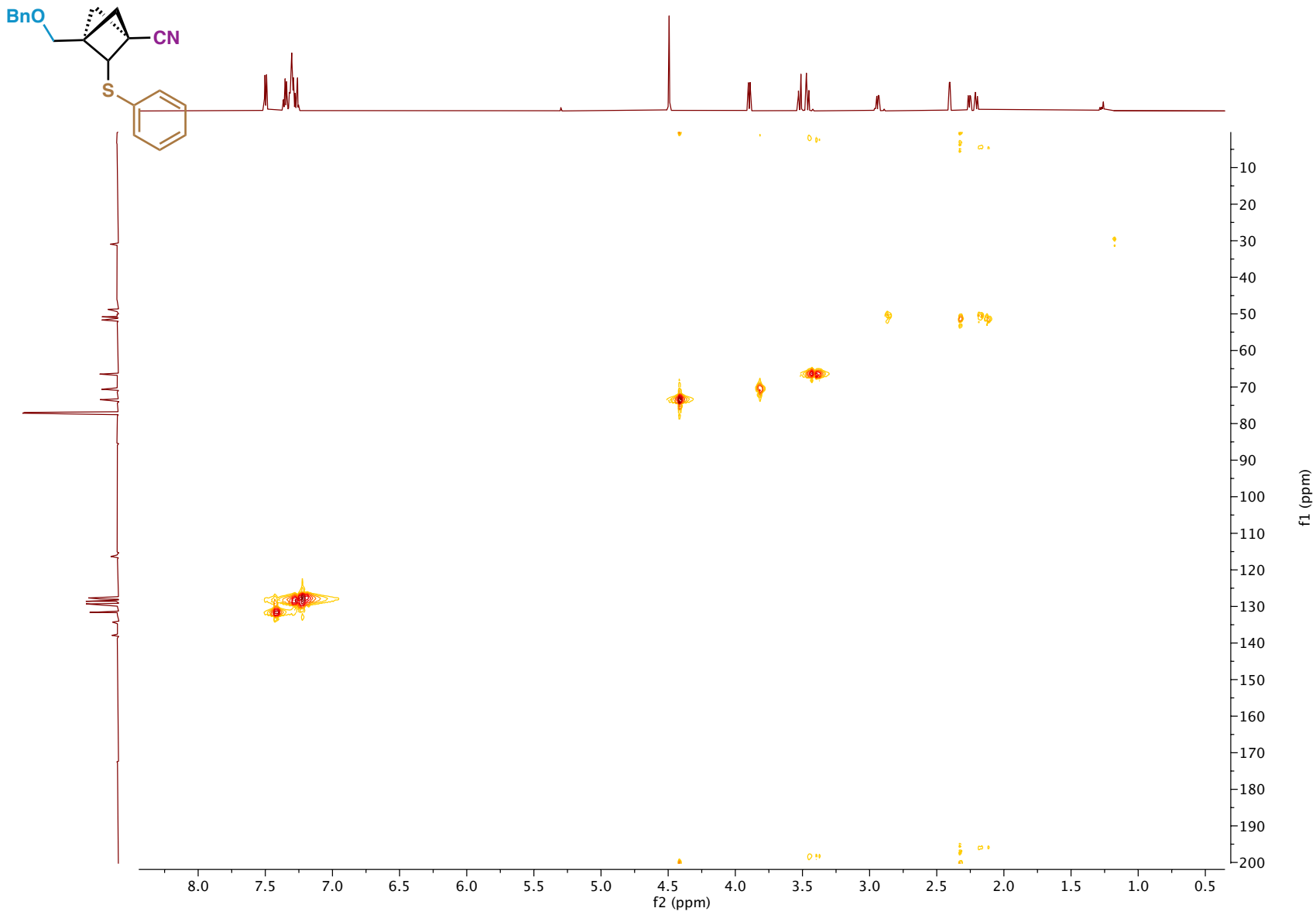
Compound 105 ^{1}H NMR



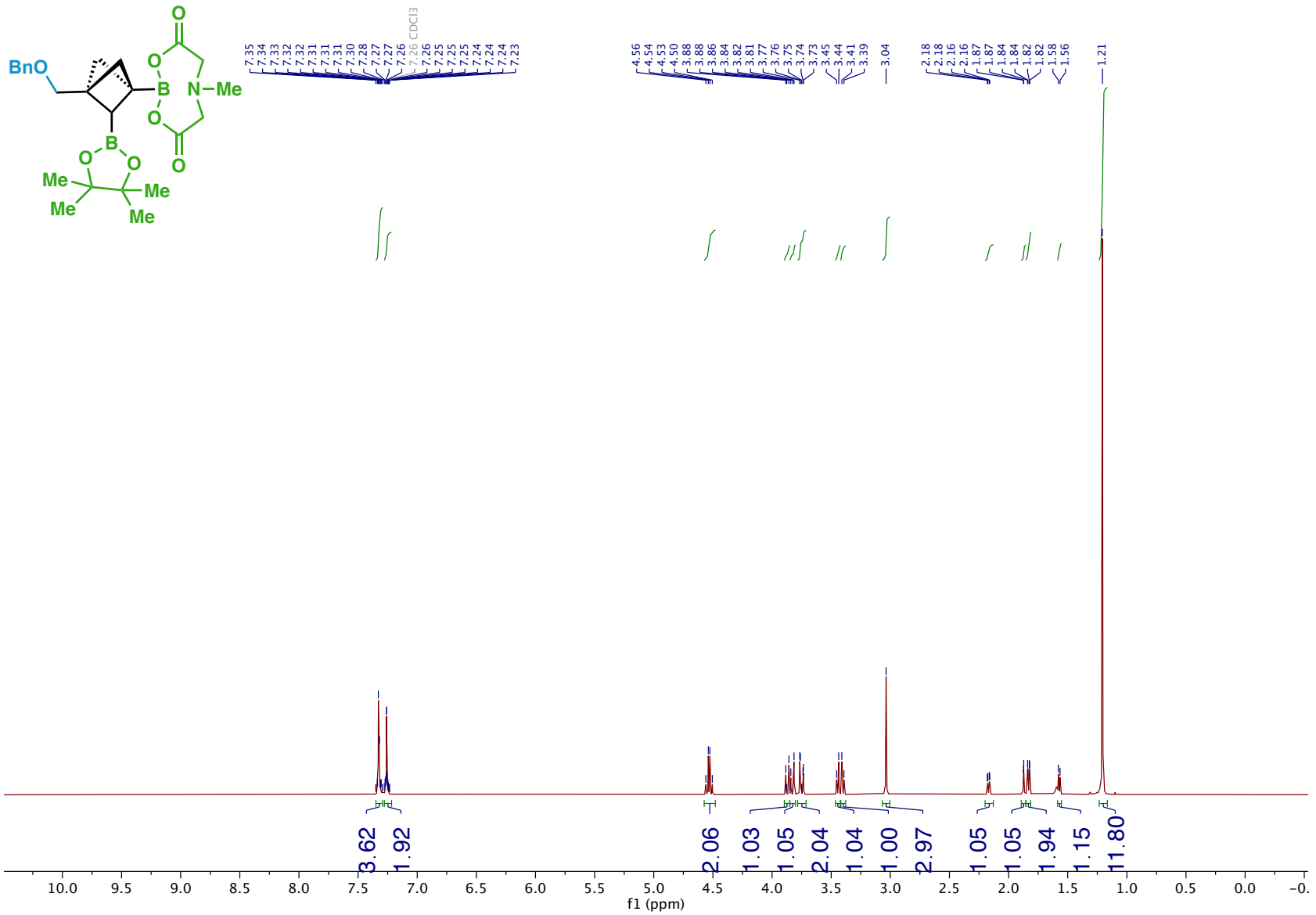
Compound 105 ^{13}C NMR



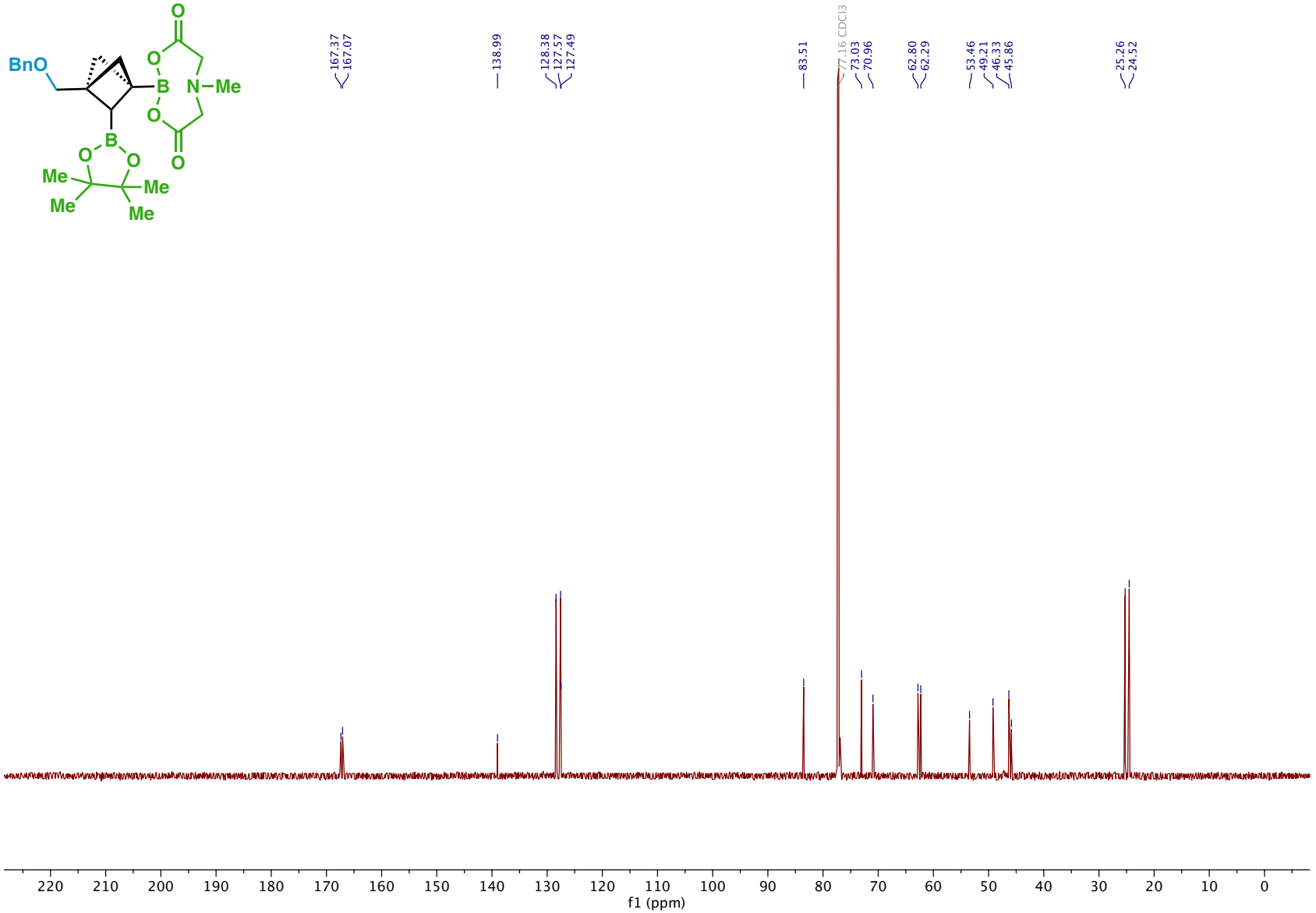
Compound 105 HSQC



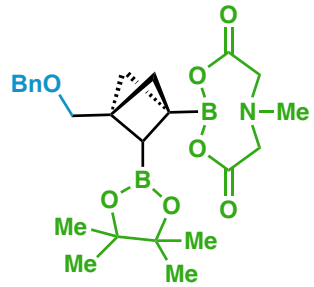
Compound 109 ^{1}H NMR



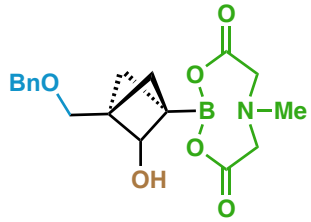
Compound 109 ^{13}C NMR



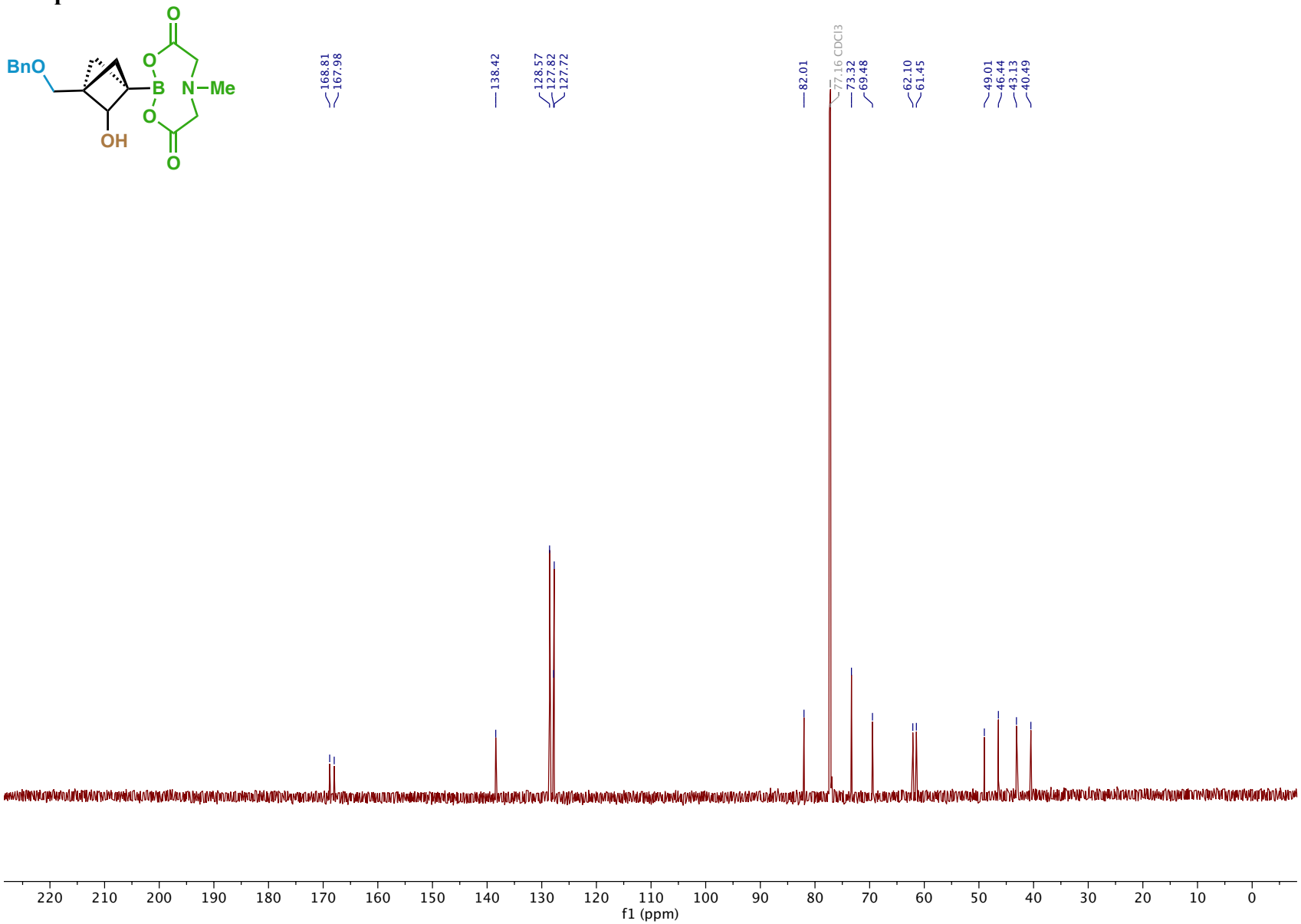
Compound 109 ^{11}B NMR



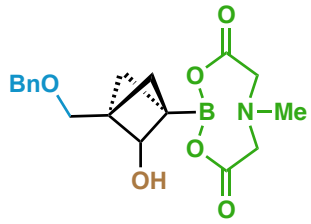
Compound 111 ^{1}H NMR



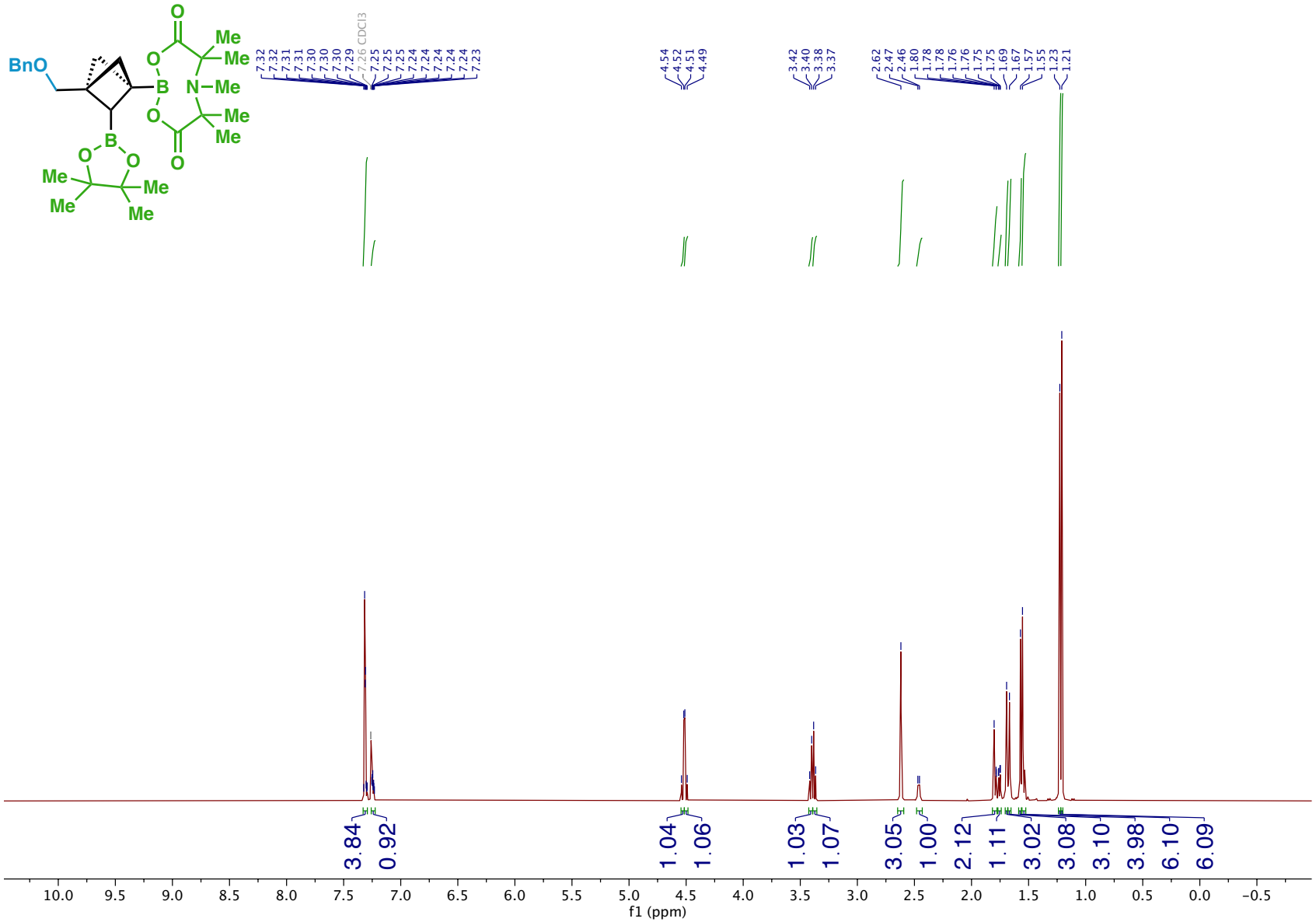
Compound 111 ^{13}C NMR



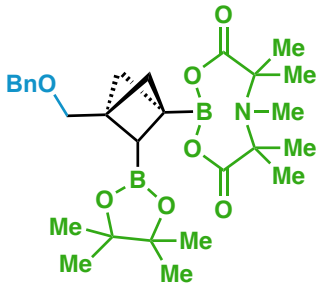
Compound 111 ^{11}B NMR



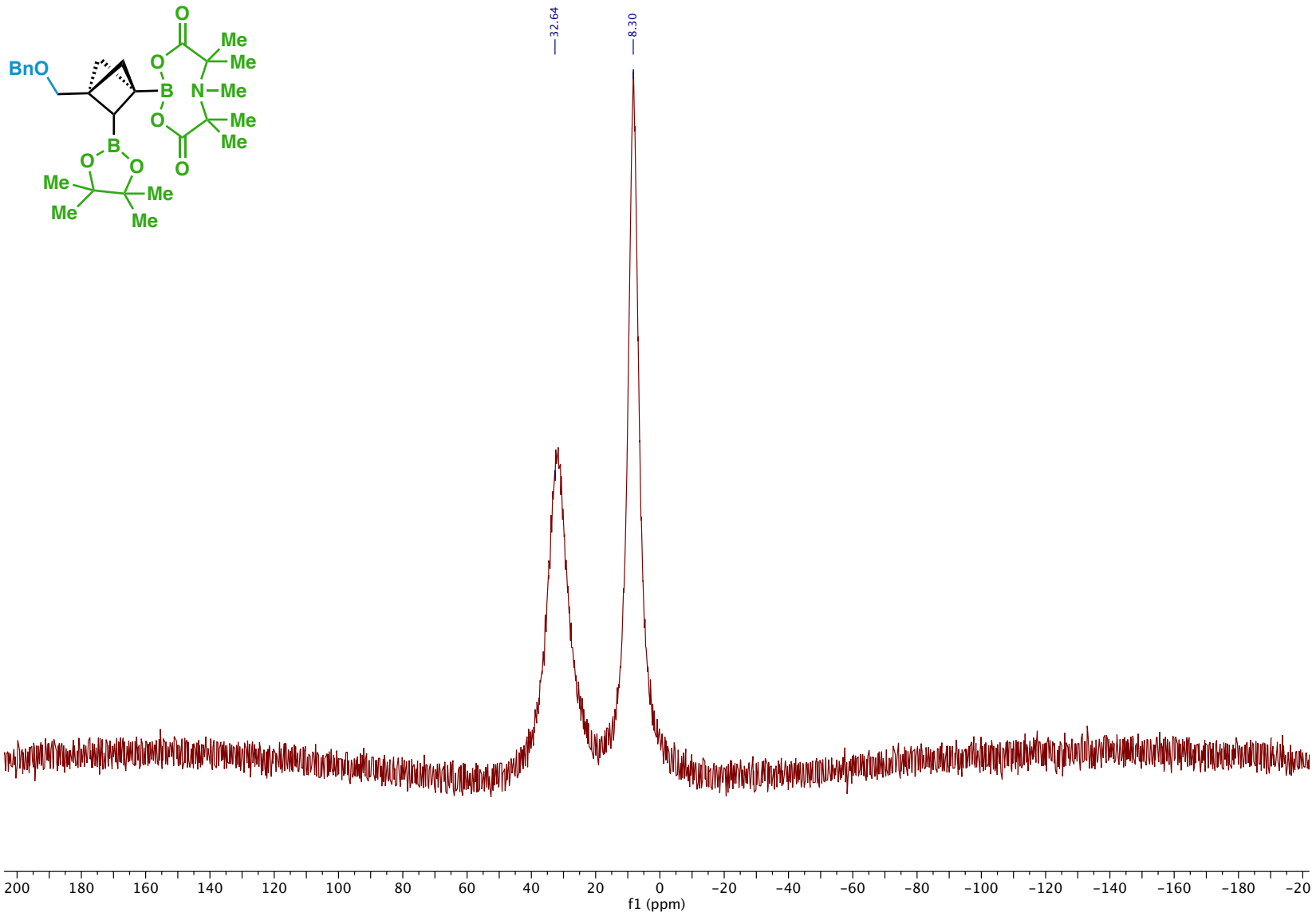
Compound 110 ^{1}H NMR



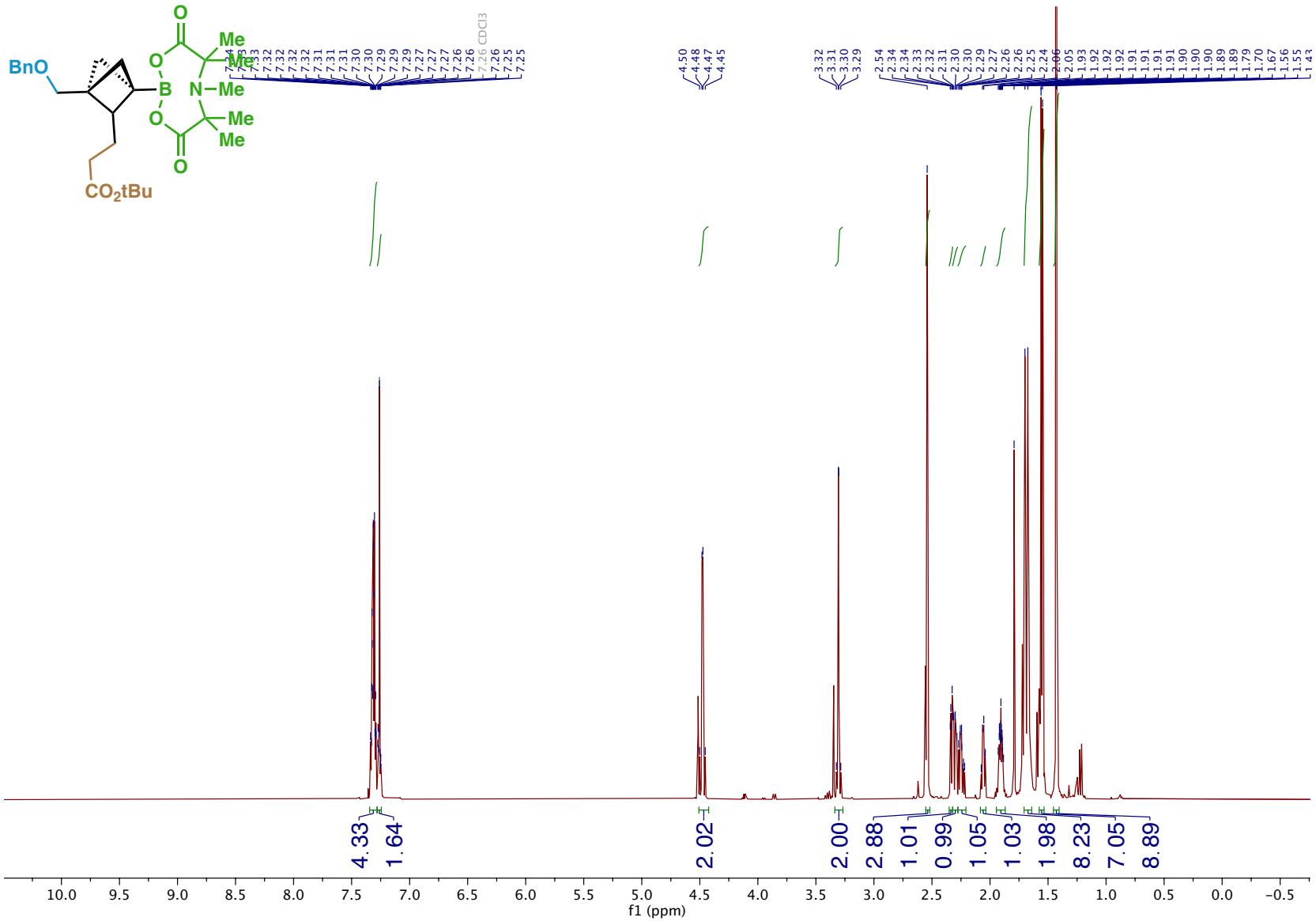
Compound 110 ^{13}C NMR



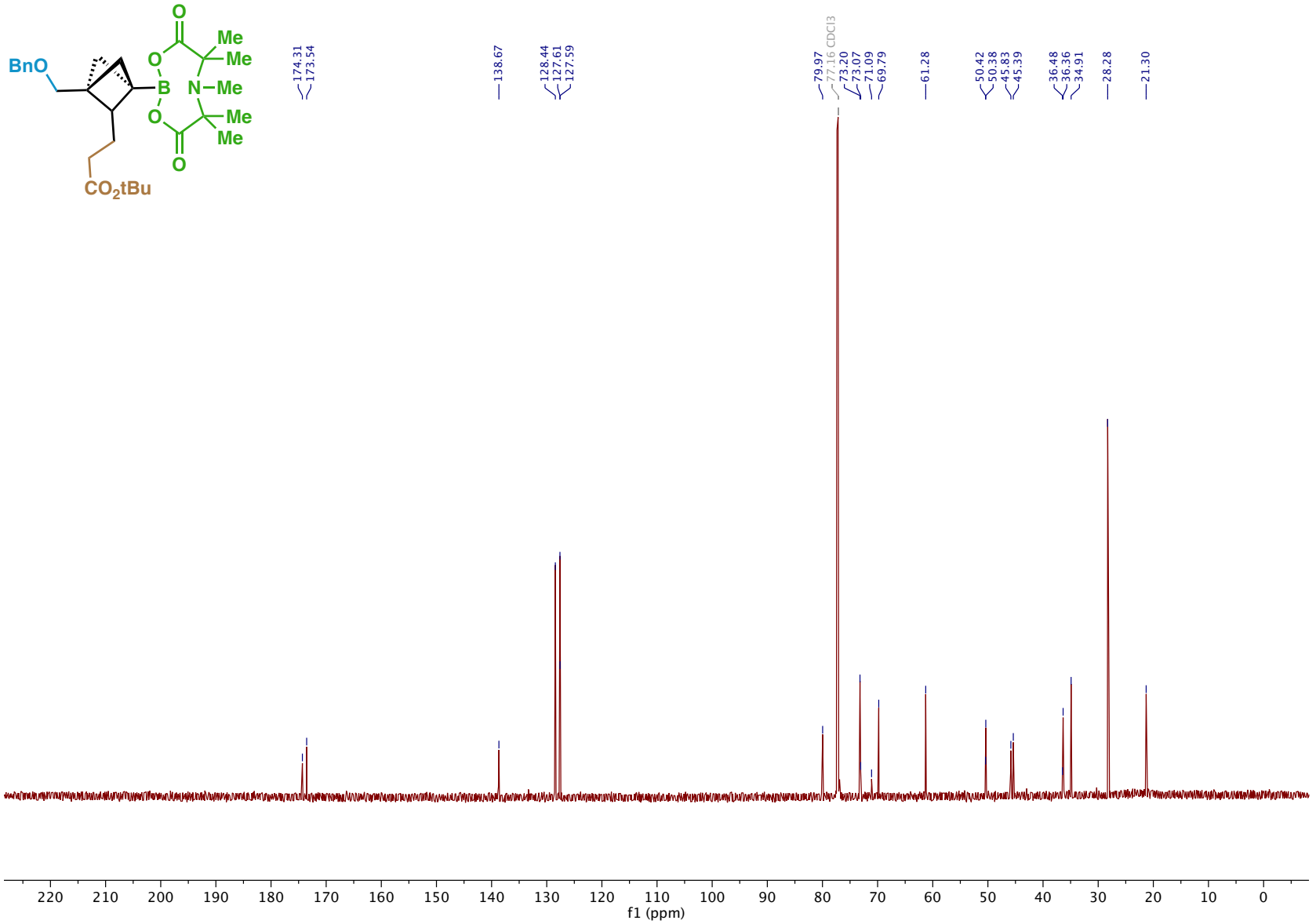
Compound 110 ^{11}B NMR



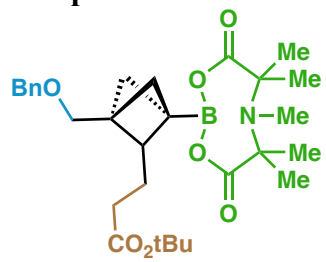
Compound 112 ^{1}H NMR



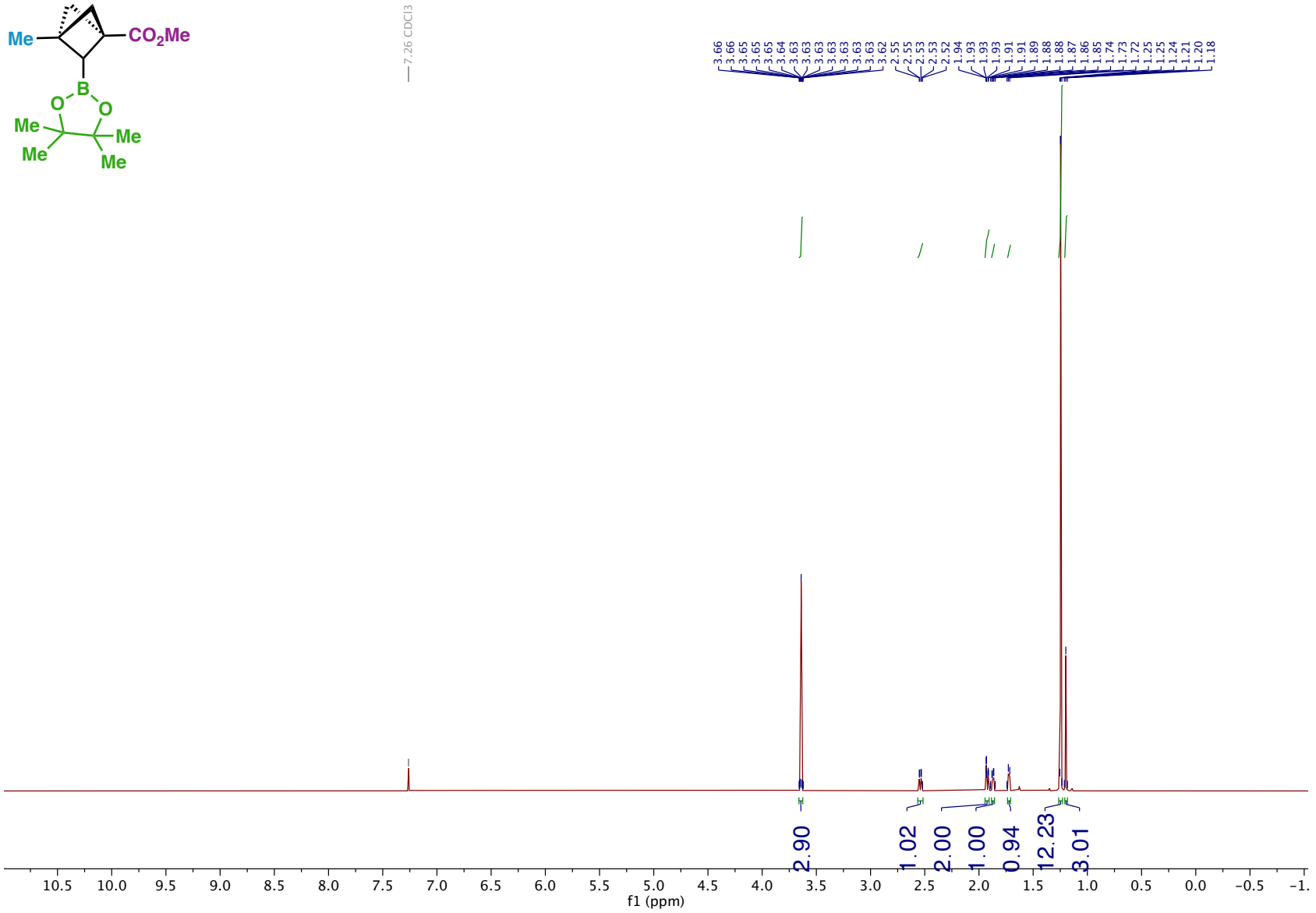
Compound 112 ^{13}C NMR



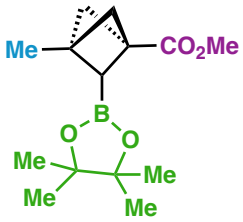
Compound 112 ^{11}B NMR



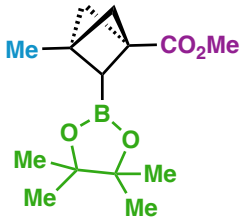
Compound 113 ^{1}H NMR



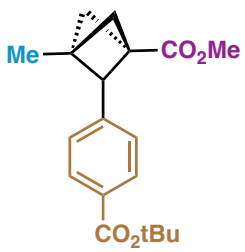
Compound 113 ^{13}C NMR



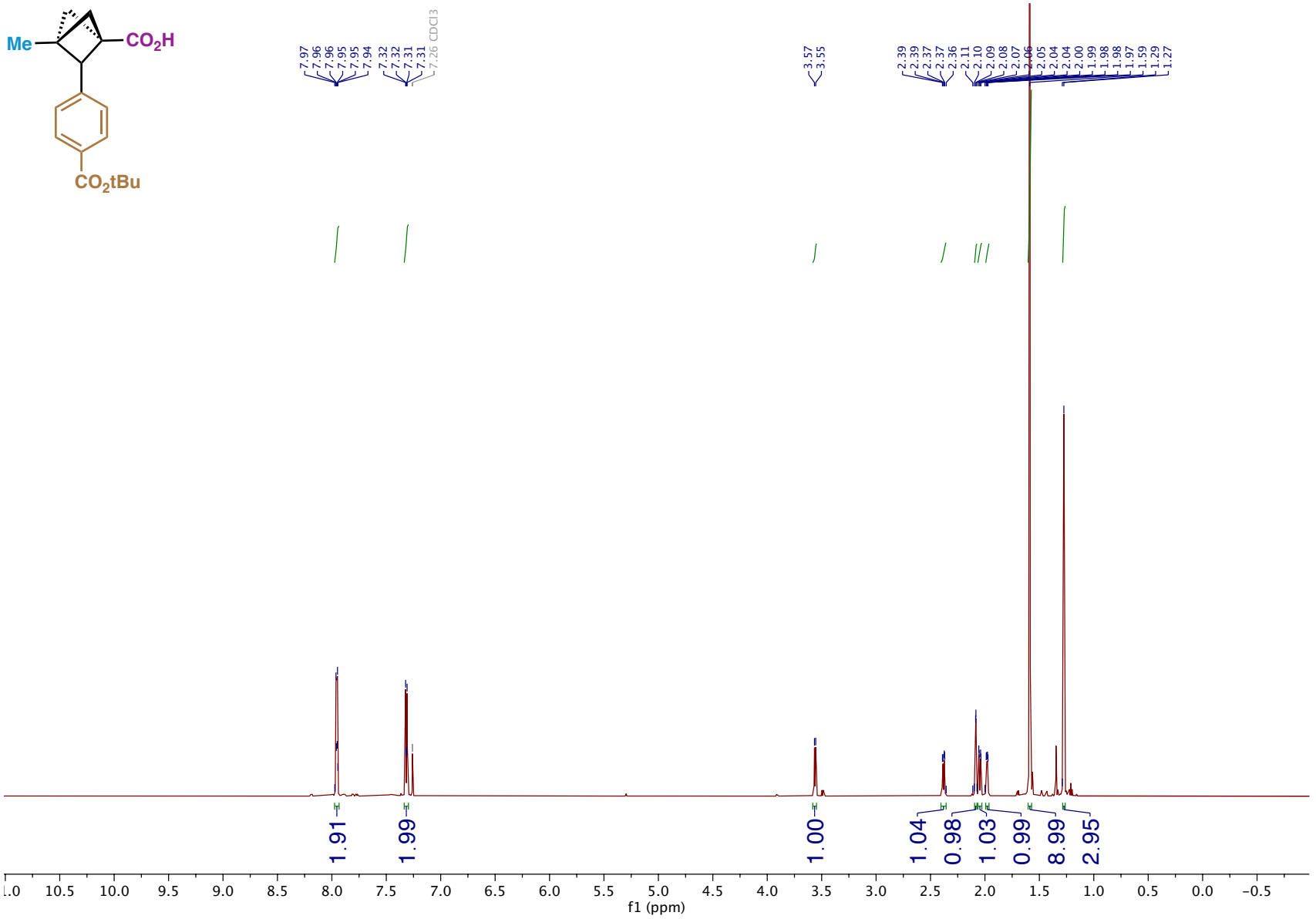
Compound 113 ^{11}B NMR



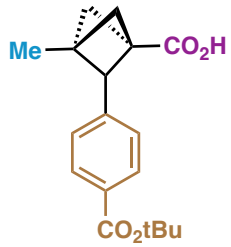
Compound SI-30 ^{1}H NMR (containing 20% **SI-29**)



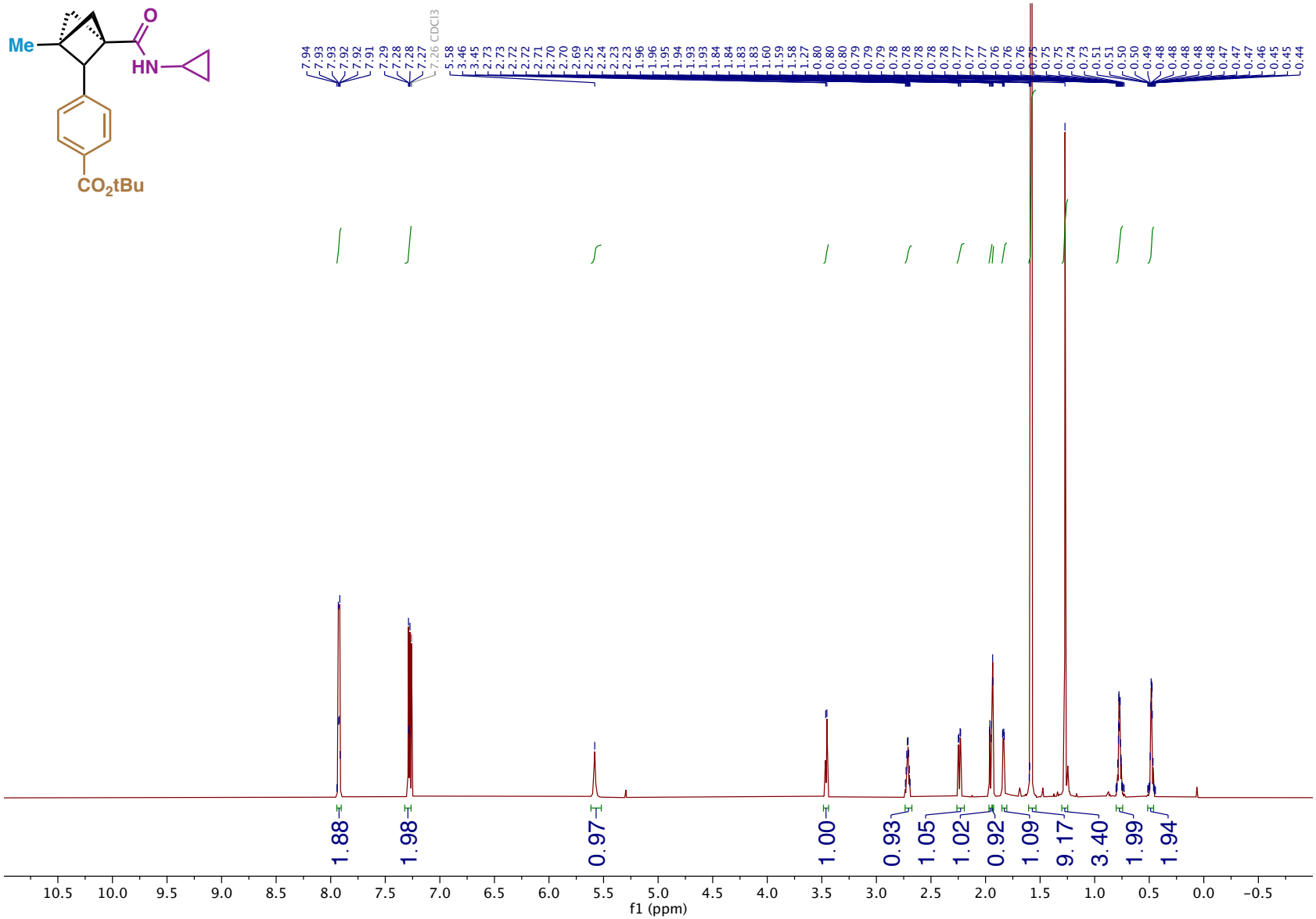
Compound 114 ^{1}H NMR



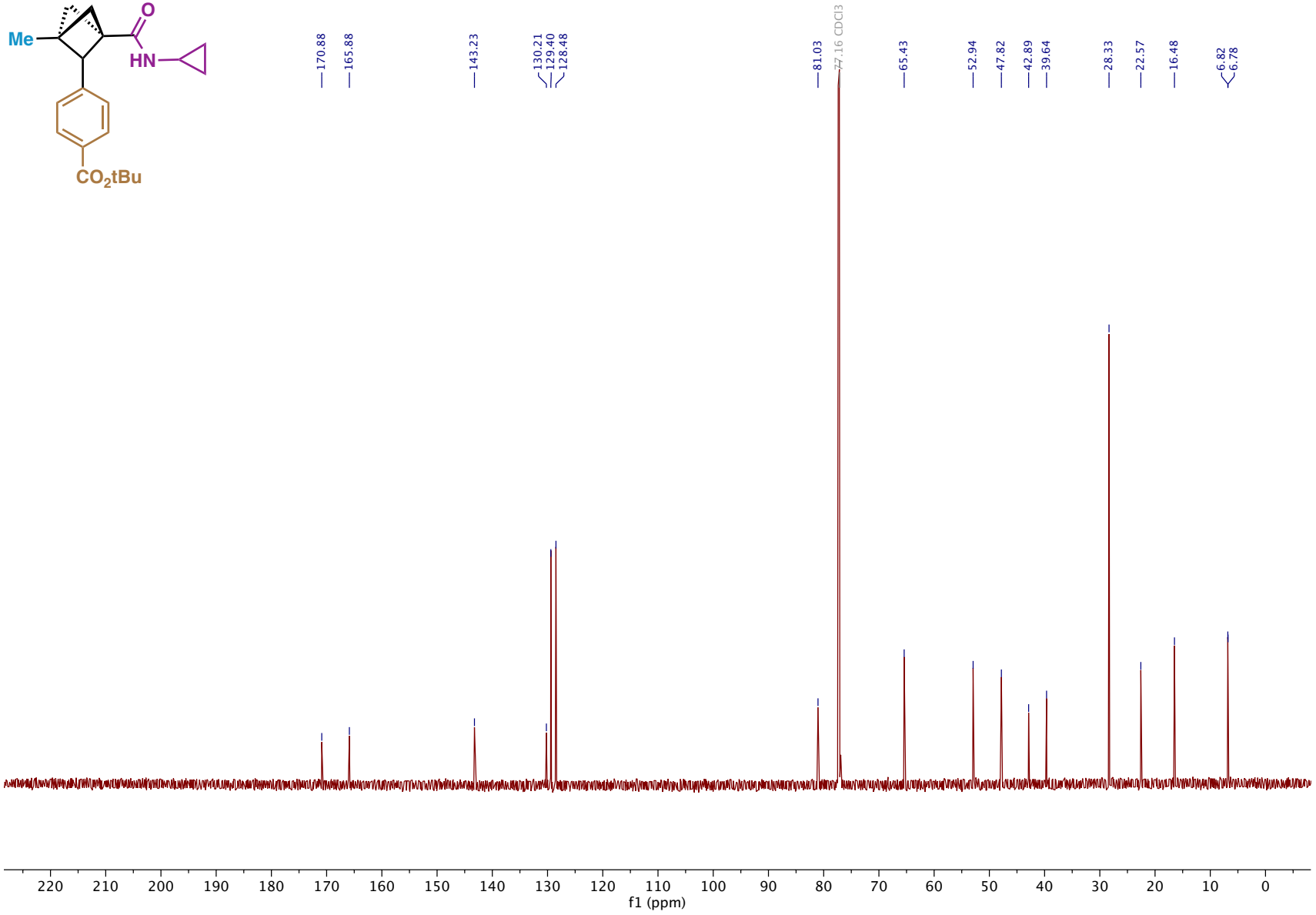
Compound 114 ^{13}C NMR



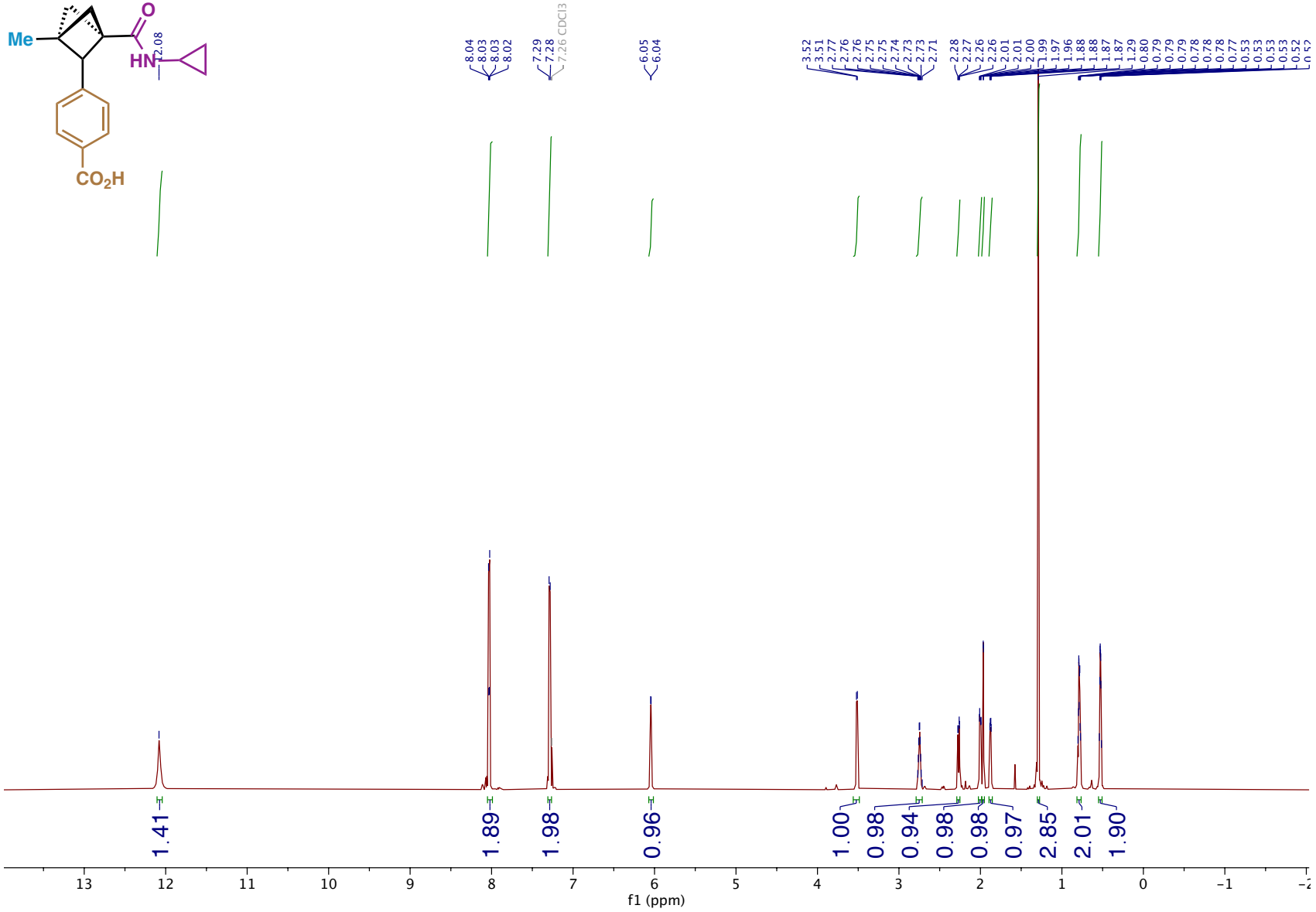
Compound SI-31 ^{1}H NMR



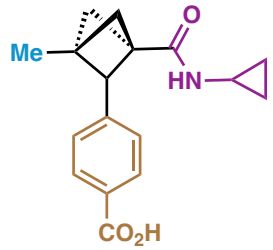
Compound SI-31 ^{13}C NMR



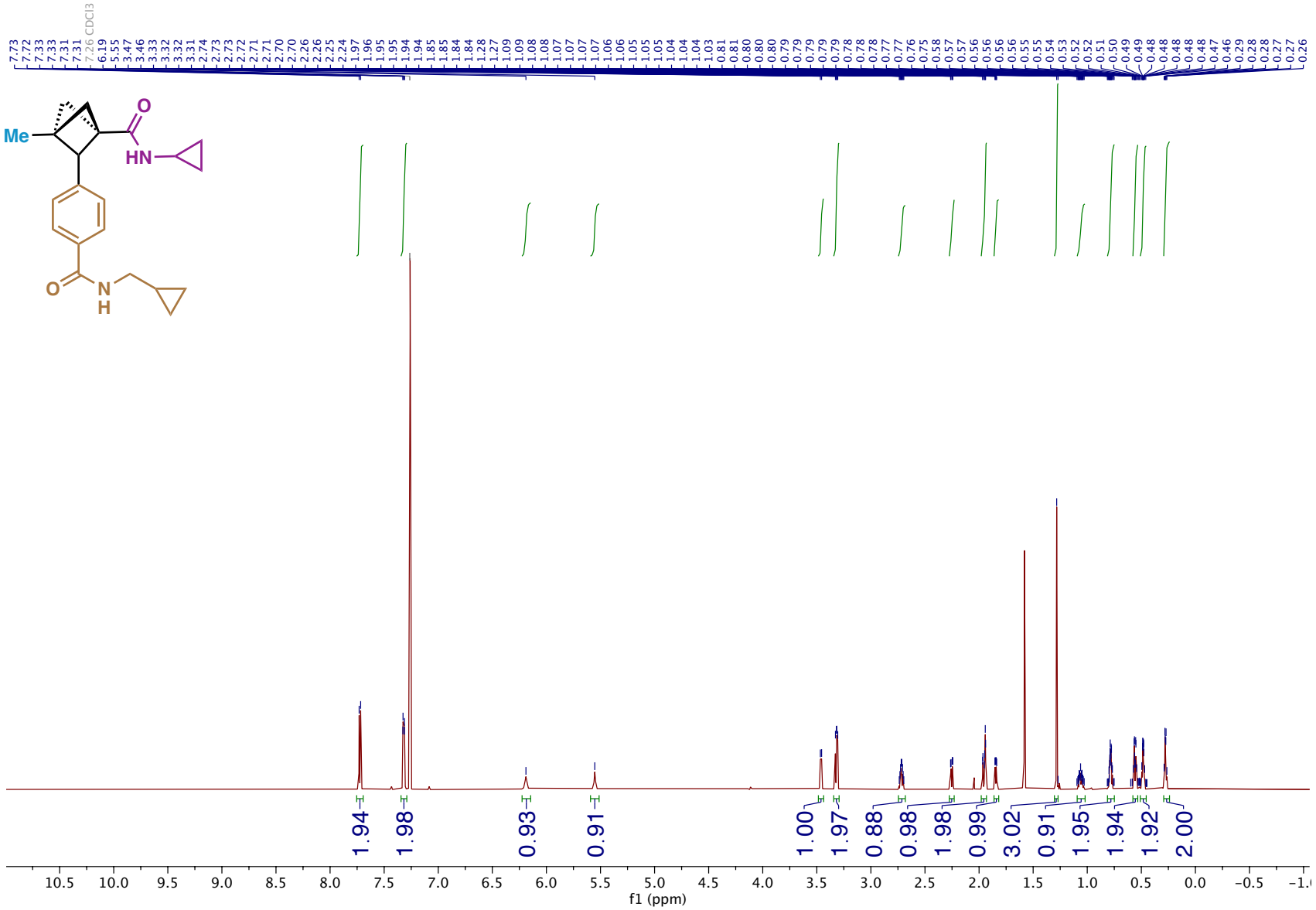
Compound SI-32 ^{1}H NMR



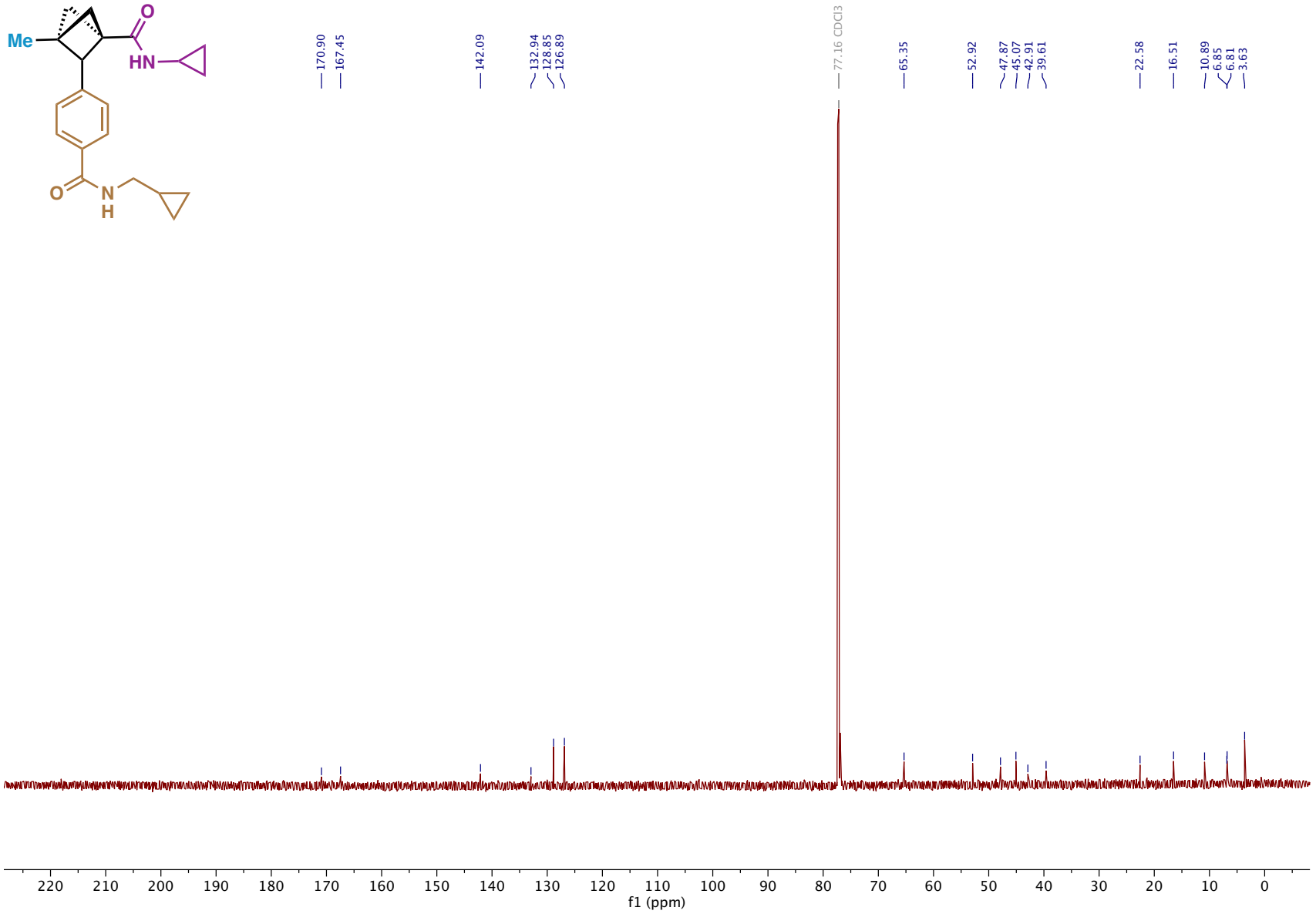
Compound SI-32 ^{13}C NMR



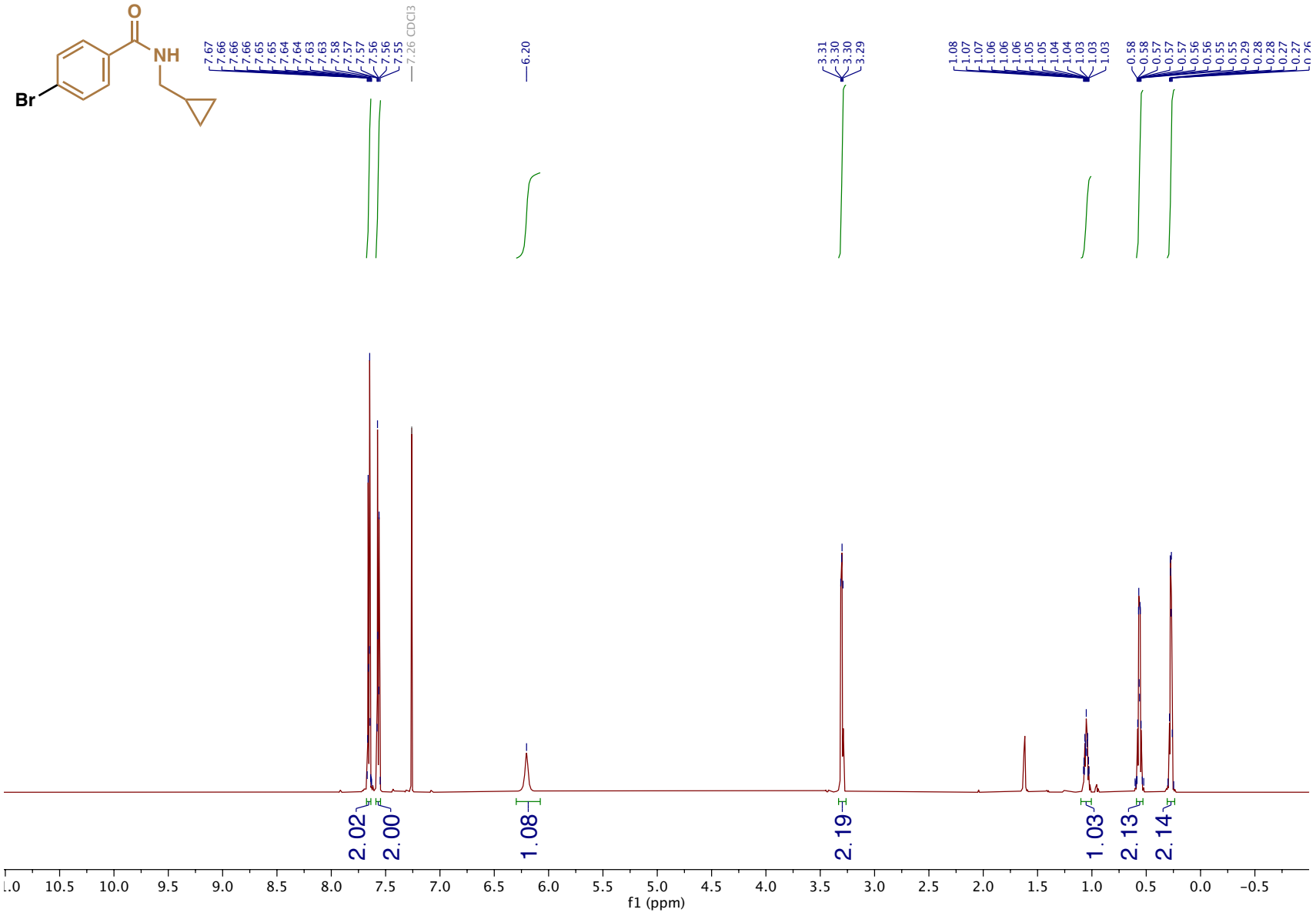
Compound 115 ^{1}H NMR



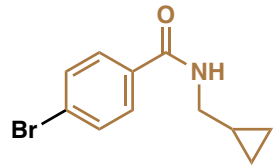
Compound 115 ^{13}C NMR



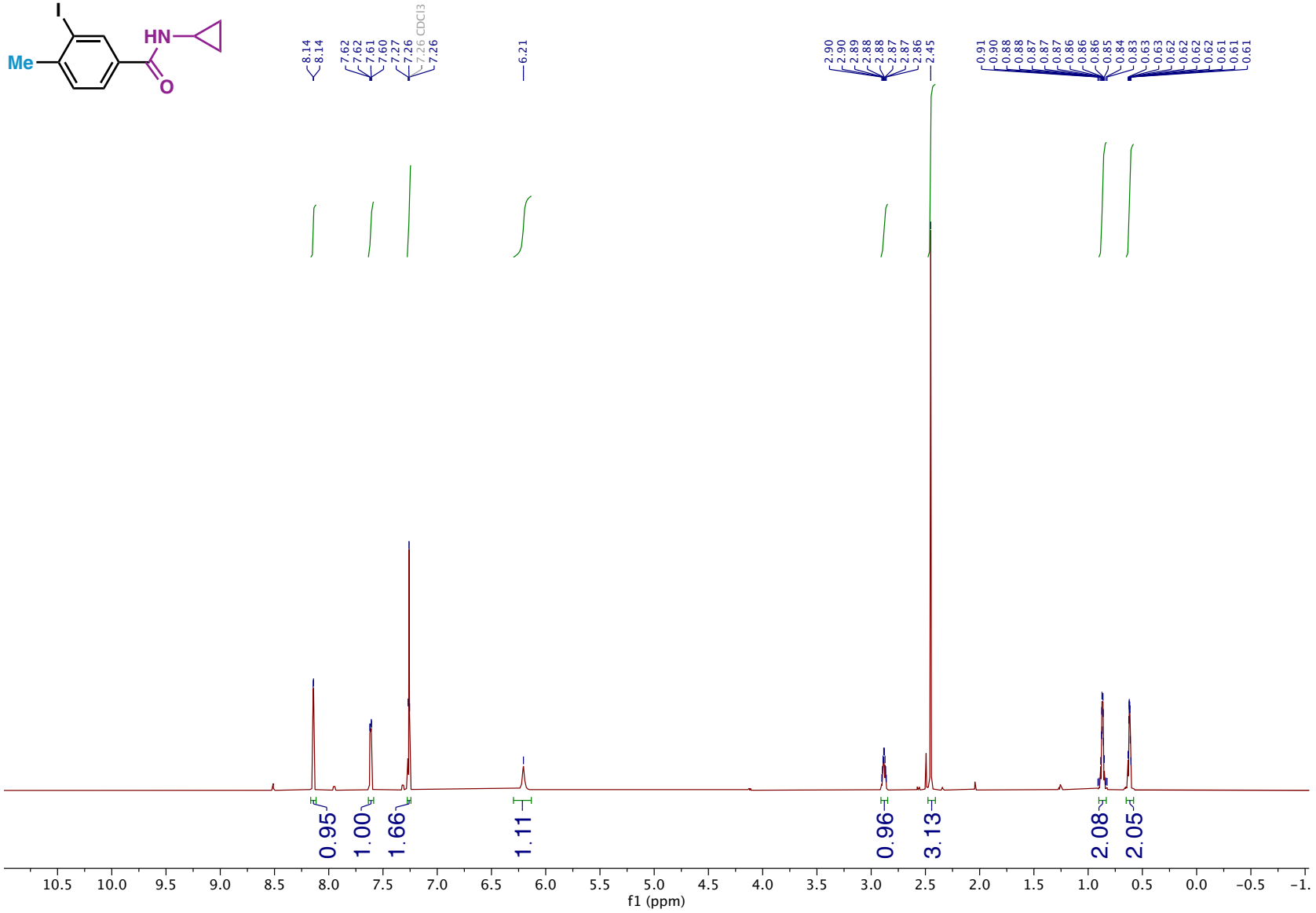
Compound SI-33 ^{1}H NMR



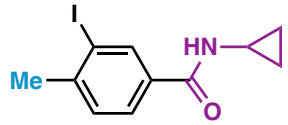
Compound SI-33 ^{13}C NMR



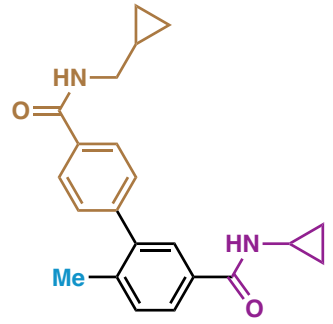
Compound SI-34 ^{1}H NMR



Compound SI-34 ^{13}C NMR



Compound 116 ^{1}H NMR



Compound 116 ^{13}C NMR