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Catalytic undirected borylation of tertiary C–H bonds in bicyclo[1.1.1]pentanes and bicyclo[2.1.1]hexanes

In the format provided by the authors and unedited

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1. General Information

1.1 Reagents and Solvents

All catalytic reactions were assembled under inert atmosphere in a nitrogen-filled glovebox equipped with oxygen and water sensors (working levels ≤ 1.0 ppm and 0.5 ppm, respectively) and a low temperature refrigeration unit (–35 °C) unless otherwise noted. All other reactions were assembled under inert atmosphere with a Schlenk manifold or a nitrogen glovebox unless otherwise noted. All reagents and solvents were purchased from commercial sources and used as received, unless otherwise noted. All glassware was flame-dried or dried overnight at 120 °C, allowed to cool under vacuum, and stored in a N2-atomsphere drybox until use unless otherwise noted. Tetrahydrofuran, toluene, and diethyl ether were purified by passing the degassed solvents (N_2) through a column of activated alumina (solvent purification system purchased from Innovative Technologies, Newburyport, MA). Cyclooctane was degassed by three freeze-pump-thaw cycles and further dried for a week over activated 4 Å molecular sieves. Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. See section 2 for synthesis of reagents and substrates.

1.2 Chromatography and Data Analysis

Flash column chromatography was conducted on a Teledyne ISCO Combiflash Rf or Rf+ system, with prepacked RediSep Gold silica gel and C18 columns. All reactions were followed by thin-layer chromatography (TLC) when practical, using Merck Kieselgel 60 F_{254} fluorescent treated silica, which was visualized under UV light when practical, or by staining with a solution of anisaldehyde or phosphomolybdic acid followed by heating.

^{1}H, ^{11}B, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker AV-300, AVQ-400, AVB-400, AV-500, AV-600, NEO-500, and AV-700 spectrometers. Chemical shifts (δ) reported given in parts per million (ppm) relative to the residual solvent signal. Coupling constants (J) are given in Hertz (Hz), rounded to the nearest 0.1 Hz. The ^{1}H NMR spectra are reported as follows: ppm (multiplicity, coupling constants, number of protons). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). The carbon attached to boron is usually not observed.

High-resolution mass spectral (HRMS) data were obtained from the QB3/Chemistry Mass Spectrometry Facility at UC Berkeley.

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Gas Chromatography (GC) was performed on an HP 6890 GC system with an Agilent HP-5 column (25 m × 0.200 mm, 0.33 micron).

1.3 Naming of Compounds

Compound names were generated by ChemDraw 20.0 software (PerkinElmer), following the IUPAC nomenclature.

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2. Synthesis of reagents and substrates

As shown in Fig. S1, the bicyclic substrates were obtained from commercial vendors, prepared according to literature procedures, or independently synthesized (see below). A solution of [1.1.1]-propellane in diethyl ether was prepared from 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane and phenyllithium according to a known procedure.[1] Sodium bicyclo[1.1.1]pentanesulfinate was synthesized according to a literature procedure.[2] 2-methylphenanthroline,[3] 2,2'-((3-fluorophenyl)methylene)dipyridine,[4] 5-methyl-2-(thiophen-3-yl)pyridine,[5] 1-(4-(*tert*-butyl)phenyl)bicyclo[1.1.1]pentane,[6] bicyclo[1.1.1]pentan-1-yl(*tert*-butyl)sulfane,[7] bicyclo[1.1.1]pentan-1-yltributylstannane,[8] 1-(methylsulfonyl)bicyclo[1.1.1]pentane,[2] bicyclo[1.1.1]pentane-1-sulfonamide,[2] and *tert*-butyl bicyclo[1.1.0]butane-1-carboxylate[9] were synthesized according to literature precedent. The spectral data of the known compounds were identical to those reported in the literature. All other chemicals were purchased from commercial vendors and used as received unless otherwise noted.

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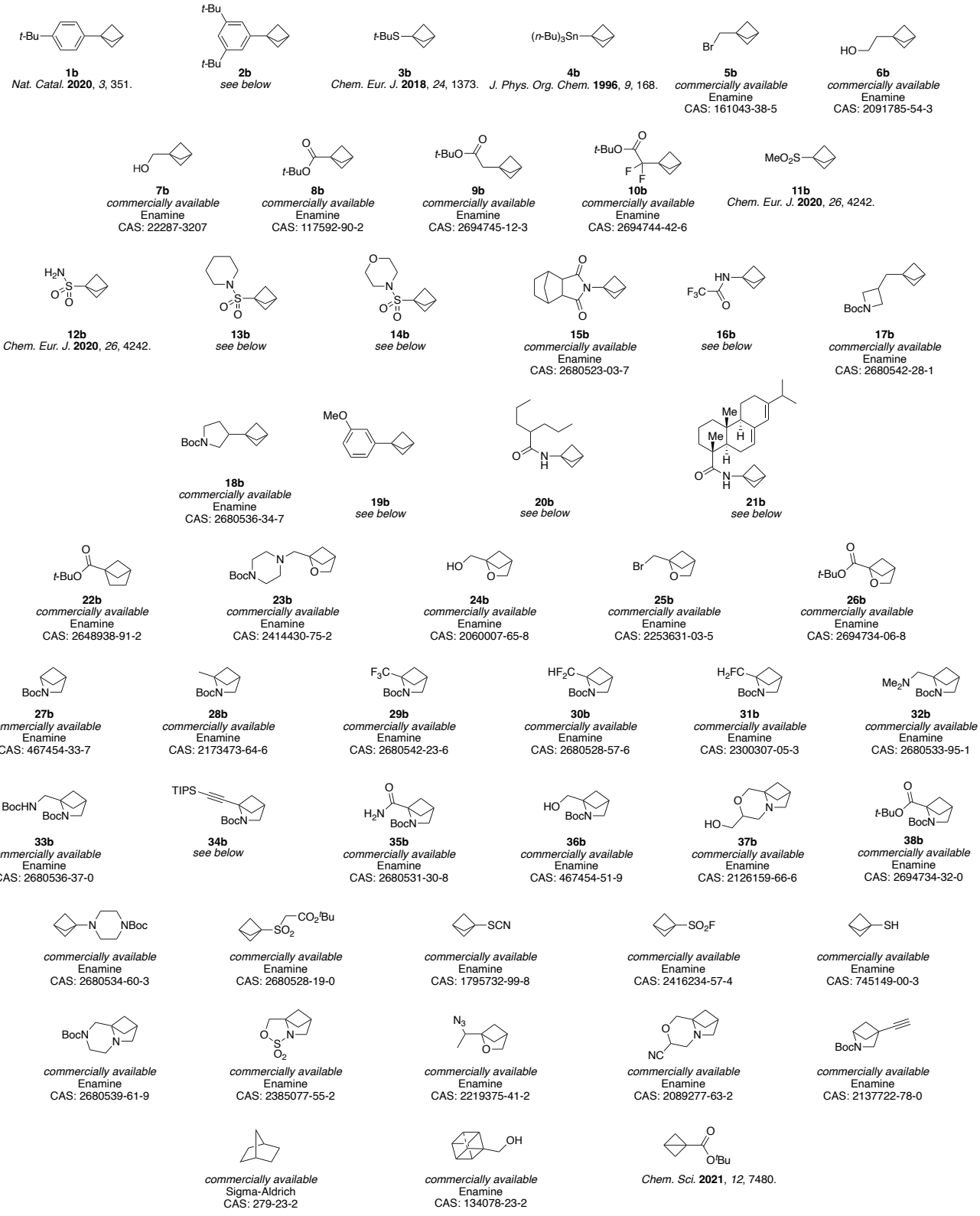

Fig. S1. Commercially availability and references for the synthesis of bicyclic substrates.

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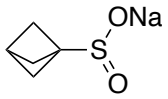
Sodium bicyclo-[1.1.1]-pentanesulfinate



Prepared according to literature procedures.[2]

^{1}H NMR (600 MHz, D_2O) δ 2.76 (s, 1H), 1.96 (s, 6H). [See spectrum]

^{13}C NMR (151 MHz, D_2O) δ 69.5, 57.4, 47.4, 37.6, 26.0. [See spectrum]

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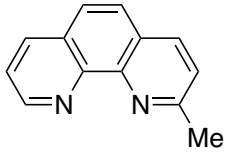
2-methyl-1,10-phenanthroline



Prepared according to literature procedures.[3]

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.37 (dd, *J* = 4.4, 1.8 Hz, 1H), 8.40 (dd, *J* = 8.1, 1.8 Hz, 1H), 8.30 (d, *J* = 8.2 Hz, 1H), 8.00 – 7.84 (m, 2H), 7.78 (dd, *J* = 8.1, 4.4 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 3.12 (s, 3H). [See spectrum]
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 150.2, 145.8, 145.6, 136.4, 128.9, 126.8, 126.6, 125.6, 123.9, 122.9, 25.9. [See spectrum]

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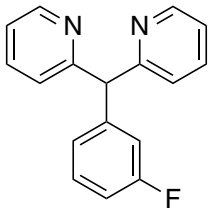
2,2'-((3-fluorophenyl)methylene)dipyridine (L3)



Prepared according to literature procedures.[4]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (dd, *J* = 4.9, 1.0 Hz, 2H), 7.77 (td, *J* = 7.7, 1.9 Hz, 2H), 7.44 – 7.37 (m, 3H), 7.29 (dd, *J* = 7.5, 4.8 Hz, 2H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.14 (dt, *J* = 10.2, 2.2 Hz, 1H), 7.06 (td, *J* = 8.8, 8.4, 2.4 Hz, 1H), 5.93 (s, 1H). [See spectrum]
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.1 (d, $J_{C–F}$ = 245.7 Hz), 161.6, 149.7, 144.4 (d, $J_{C–F}$ = 7.2 Hz), 136.8, 130.0 (d, $J_{C–H}$ = 8.3 Hz), 125.2 (d, $J_{C–F}$ = 3.0 Hz) , 124.1, 121.9, 116.4 (d, *J* = 22.1 Hz), 113.8 (d, *J* = 21.1 Hz), 61.5. [See spectrum]
^{19}F NMR (565 MHz, $CDCl_3$) δ -113.0 (q, *J* = 8.7 Hz). [See spectrum]

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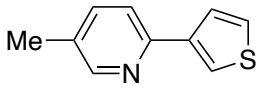
5-methyl-2-(thiophen-3-yl)pyridine (L4)



Prepared according to literature procedures.[5]

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.49 (s, 1H), 7.88 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.68 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.42 (dd, *J* = 5.0, 3.0 Hz, 1H), 2.39 (s, 3H). [See spectrum]
^{13}C NMR (151 MHz, $CDCl_3$) δ 151.2, 150.1, 142.3, 137.3, 131.4, 126.3, 126.3, 122.8, 119.9, 18.3. [See spectrum]

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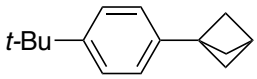
1-(4-(*tert*-butyl)phenyl)bicyclo[1.1.1]pentane (1b)



Prepared according to literature procedures.[6]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 2.68 (s, 1H), 2.21 (s, 6H), 1.45 (s, 9H). [See spectrum]
^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 138.9, 125.8, 125.1, 52.3, 47.0, 34.6, 31.5, 26.8. [See spectrum]

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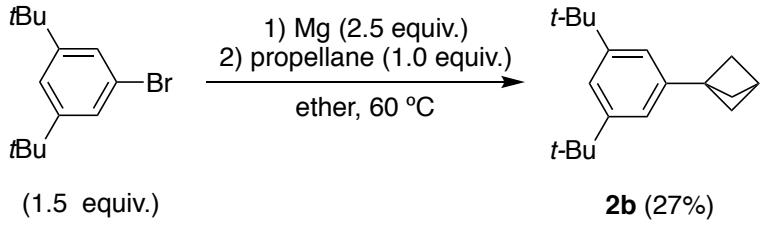
1-(3,5-di-*tert*-butylphenyl)bicyclo[1.1.1]pentane (2b)



(1.5 equiv.) **2b** (27%)

A flame-dried round bottom flask was charged with magnesium turnings (456 mg, 18.8 mmol, 2.50 equiv.), dry THF (1 mL), and a small crystal of iodine in an N_2 atmosphere. The mixture was stirred at room temperature until the solution became milky-white. Then, 1-bromo-3,5-di-*tert*-butylbenzene (3.03 g, 11.2 mmol, 1.50 equiv.) in 10 mL of ether was added dropwise, keeping the solution at a gentle reflux. The resulting solution was further stirred at room temperature for 3 h. Then, a 0.50 M solution of propellane in ether (15.0 mL, 7.50 mmol, 1.00 equiv.) was added. The mixture was heated at 60 ºC for 16 h. The reaction mixture was cooled to room temperature and carefully quenched with an aqueous solution of NH_4Cl (10 mL). The layers were separated, and the aqueous layer further extracted with diethyl ether (25 mL x 2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude material was purified by chromatography on silica gel, eluting with pentanes. The fractions were analyzed by GC-MS analysis, and the fractions containing the desired material were collected. The resulting white solid contained substantial amounts of biaryl, and was further purified by sublimation (200 mbar, 80 ºC). The title compound was obtained as a white solid (521 mg, 27%).

TLC: N/A

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, J = 1.9 Hz, 1H), 7.10 (d, J = 1.9 Hz, 2H), 2.58 (s, 1H), 2.12 (s, 6H), 1.36 (s, 18H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 150.6, 140.9, 120.8, 120.1, 52.4, 47.8, 35.0, 31.6, 26.7. [See spectrum]

HRMS (*m/z*): (EI+) calc'd for $C_{19}H_{28}$ $[M]^+$: 256.2191, found: 256.2194.

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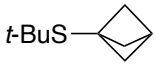
bicyclo[1.1.1]pentan-1-yl(*tert*-butyl)sulfane (3b)



Prepared according to literature procedures.[7]

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.75 (s, 1H), 2.13 (s, 6H), 1.41 (s, 9H). [See spectrum]
^{13}C NMR (126 MHz, $CDCl_3$) δ 56.0, 44.7, 44.1, 31.9, 30.6, 14.1. [See spectrum]

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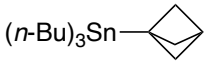
bicyclo[1.1.1]pentan-1-yltributylstannane (4b)



Prepared according to literature procedures.[8]

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.92 (s, 1H) tin satellites ($J_{H\text{-}119Sn}$ = 179.4 Hz, $J_{H\text{-}117Sn}$ = 171.4 Hz) , 2.01 (s, 6H), 1.60 – 1.42 (m, 6H), 1.38 – 1.27 (m, 6H), 0.93 (t, J = 7.3 Hz, 9H), 0.88 – 0.81 (m, 6H). [See spectrum]
^{13}C NMR (126 MHz, $CDCl_3$) δ 56.2, 39.2) tin satellites ($J_{C\text{-}Sn}$ = 117.0 Hz), 37.2, 29.4 tin satellites ($J_{C\text{-}Sn}$ = 20.2 Hz), 27.5 tin satellites ($J_{C\text{-}Sn}$ = 51.3 Hz), 13.9, 9.0 tin satellites ($J_{C\text{-}Sn}$ = 307.6). [See spectrum]

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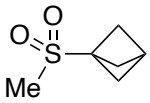
1-(methylsulfonyl)bicyclo[1.1.1]pentane (11b)



Prepared according to literature procedures.[2]

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.86 (s, 3H), 2.84 (s, 1H), 2.30 (s, 6H). [See spectrum]
^{13}C NMR (151 MHz, $CDCl_3$) δ 54.5, 50.7, 37.3, 26.4. [See spectrum]

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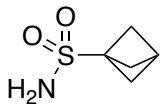
bicyclo[1.1.1]pentane-1-sulfonamide (12b)



Prepared according to literature procedures.[2]

^{1}H NMR (700 MHz, Acetone) δ 6.16 (bs, 2H), 2.80 (s, 1H), 2.25 (s, 6H). [See spectrum]
^{13}C NMR (176 MHz, Acetone) δ 54.8, 50.4, 25.5. [See spectrum]

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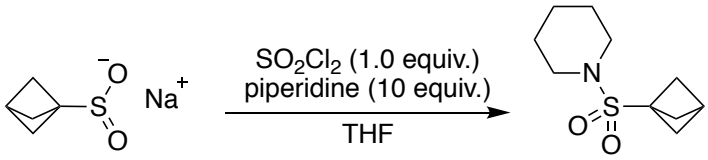
1-(bicyclo[1.1.1]pentan-1-ylsulfonyl)piperidine (13b)



13b (82%)

Sodium bicyclo[1.1.1]pentane-1-sulfinate (38.5 mg, 0.250 mmol, 1.00 equiv.) was suspended in THF (3 mL) and cooled to 0 ºC. SO_2Cl_2 (20 µL, 0.25 mmol, 1.0 equiv.) was added dropwise, and the mixture was allowed to warm to room temperature. The mixture was stirred until the complete dissolution of the starting material. Piperidine (247 µL, 2.50 mmol, 10.0 equiv.) was added dropwise, accompanied by the immediate formation of a cloudy white precipitate. The mixture was stirred at ambient temperature for 3 h and quenched carefully with water (5 mL). The biphasic mixture was extracted with ethyl acetate (30 mL x 3), dried over $MgSO_4$, filtered, and concentrated. The crude material was chromatographed on SiO_2, eluting with 33% ethyl acetate in hexanes to afford the title compound as a white powder (44.1 mg, 82%).

TLC: R_f = 0.50 (33% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.30 (t, J = 5.2 Hz, 4H), 2.69 (s, 1H), 2.23 (s, 6H), 1.70 – 1.48 (m, 6H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 53.6, 52.0, 47.2, 27.7, 26.2, 24.1. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{10}H_{18}NO_2S$ $[M+H]^+$: 216.1053, found: 216.1056.

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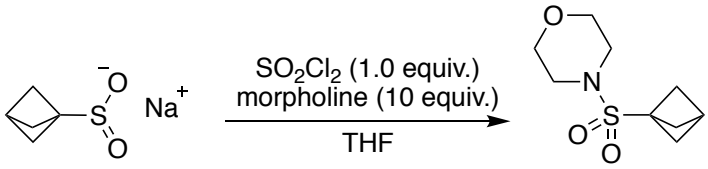
4-(bicyclo[1.1.1]pentan-1-ylsulfonyl)morpholine (14b)



14b (75%)

Sodium bicyclo[1.1.1]pentane-1-sulfinate (77.0 mg, 0.500 mmol, 1.00 equiv.) was suspended in THF (5 mL) and cooled to 0 ºC. SO_2Cl_2 (40 µL, 0.50 mmol, 1.0 equiv.) was added dropwise, and the mixture was allowed to warm to room temperature. The mixture was stirred until the starting material had fully dissolved. Morpholine (431 µL, 5.00 mmol, 10.0 equiv.) was added dropwise, accompanied by the immediate formation of a cloudy white precipitate. The mixture was stirred at ambient temperature for 3 h and quenched carefully with water (15 mL). The biphasic mixture was extracted with ethyl acetate (30 mL x 3), dried over $MgSO_4$, filtered, and concentrated. The crude material was chromatographed on SiO_2, eluting with 33% ethyl acetate in hexanes to afford the title compound as a white powder (81.1 mg, 75%).

TLC: R_f = 0.50 (33% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.75 – 3.69 (m, 4H), 3.38 – 3.32 (m, 4H), 2.73 (s, 1H), 2.26 (s, 6H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 67.1, 53.4, 52.2, 46.4, 28.0. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_9H_{15}NO_3SNa$ $[M+Na]^+$: 240.0665, found: 240.0665.

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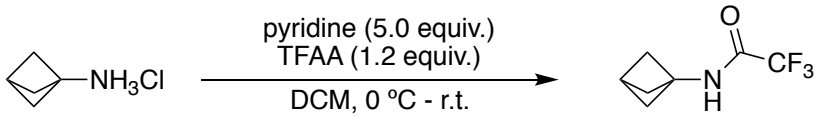
_N_-(bicyclo[1.1.1]pentan-1-yl)-2,2,2-trifluoroacetamide (16b)



16b (52%)

This is a known compound, and it was prepared in a similar manner to that reported in the patent literature.[10] Bicyclo[1.1.1]pentan-1-amine hydrochloride (120 mg, 1.00 mmol, 1.00 equiv.) and pyridine (400 µL, 5.00 mmol, 5.00 equiv.) were dissolved in dry DCM (10 mL). The cloudy mixture was cooled to 0 °C, and trifluoroacetic anhydride (167 µL, 1.20 mmol, 1.20 equiv.) was added dropwise via syringe. The mixture was allowed to warm to room temperature and stirred overnight. The crude mixture was concentrated and chromatographed over SiO_2 with 10% ethyl acetate in hexanes to afford the title compound as white flakes (94.0 mg, 52%).

TLC: R_f = 0.55 (10% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.63 (bs, 1H), 2.53 (s, 1H), 2.17 (s, 6H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8 (q, $J_{C–F}$ = 37.3 Hz), 115.5 (q, $J_{C–F}$ = 288.6 Hz), 52.7, 47.9, 24.8. [See spectrum]

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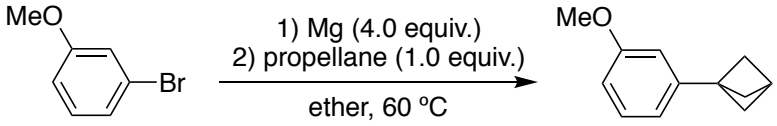
1-(3-methoxyphenyl)bicyclo[1.1.1]pentane (19b)



(2.5 equiv.) **19b** (15%)

A flame-dried round bottom flask was charged with magnesium turnings (292 mg, 12.0 mmol, 4.00 equiv.), dry THF (1 mL), and a small crystal of iodine. The mixture was stirred at room temperature until the solution became milky-white. Then, 1-bromo-3-methoxybenzene (1.40 g, 7.50 mmol, 2.50 equiv.) in 10 mL of ether was added dropwise, keeping the solution at a gentle reflux. The resulting solution was further stirred at room temperature for 3 h. Then, a 1.00 M solution of propellane in ether (3.00 mL, 3.00 mmol, 1.00 equiv.) was added. The mixture was heated at 60 ºC for 16 h. The reaction mixture was cooled to room temperature, and carefully quenched with an aqueous solution of NH_4Cl (5 mL). The layers were separated, and the aqueous layer further extracted with diethyl ether (10 mL x 2). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude material was chromatographed on silica gel and eluted with pentanes. The fractions were analyzed by GC-MS analysis, and the fractions containing the desired material were collected. The resulting oil was contaminated with anisole, which was removed by applying vacuum overnight. Some loss of the desired material occurred under vacuum, and the title compound was obtained as a colorless oil (78.0 mg, 15%).

TLC: N/A

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.17 (m, 1H), 6.85 – 6.79 (m, 1H), 6.79 – 6.72 (m, 2H), 3.81 (s, 3H), 2.54 (s, 1H), 2.07 (s, 6H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 143.5, 129.3, 118.5, 111.9, 111.8, 55.3, 52.3, 47.2, 26.7. [See spectrum]

HRMS (*m/z*): (EI+) calc'd for $C_{12}H_{14}O$ $[M]^+$: 174.1045, found: 174.1045.

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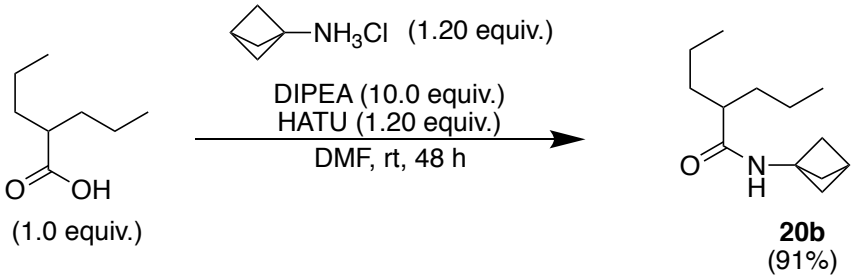
_N_-(bicyclo[1.1.1]pentan-1-yl)-2-propylpentanamide (20b)



DIPEA (1.78 mL, 10.4 mmol, 10.0 equiv.) was added to a stirred mixture of 2-propylpentanoic acid (150 mg, 1.04 mmol, 1.00 equiv.), bicyclo[1.1.1]pentan-1-amine hydrochloride (149 mg, 1.25 mmol, 1.20 equiv.) and HATU (478 mg, 1.26 mmol, 1.20 equiv.) in DMF (6 mL). The mixture was stirred at room temperature for 48 h. Water (10 mL) was added, and the reaction extracted with EtOAc (3x20 mL). The organic layers were separated, dried (Na_2SO_4), filtered, and the solvents evaporated in vacuo. The crude material was purified by flash column chromatography (silica, EtOAc in Heptane 0/100 to 30/70). The desired fractions were collected and concentrated in vacuo to give *N*-(bicyclo[1.1.1]pentan-1-yl)-2-propylpentanamide (198 mg, 0.95 mmol, 91%) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.85 (br s, 1 H), 2.44 (s, 1 H), 2.10 (s, 6 H), 1.90 (dq, J=9.22, 4.56 Hz, 1 H), 1.49 - 1.65 (m, 2 H), 1.22 - 1.40 (m, 6 H), 0.85 - 0.97 (m, 6 H). [See spectrum]

^{13}C NMR (101 MHz, $CDCl_3$) δ ppm 176.4 (s, 1 C), 52.7 (s, 4 C), 47.8 (s, 1 C), 35.2 (s, 2 C), 24.7 (s, 1 C), 20.8 (s, 2 C), 14.2 (s, 2 C). [See spectrum]

HRMS (ESI-TOF) Calculated for $C_{13}H_{24}NO$ $[M+H]^+$: 210.1780; Found: 210.1856.

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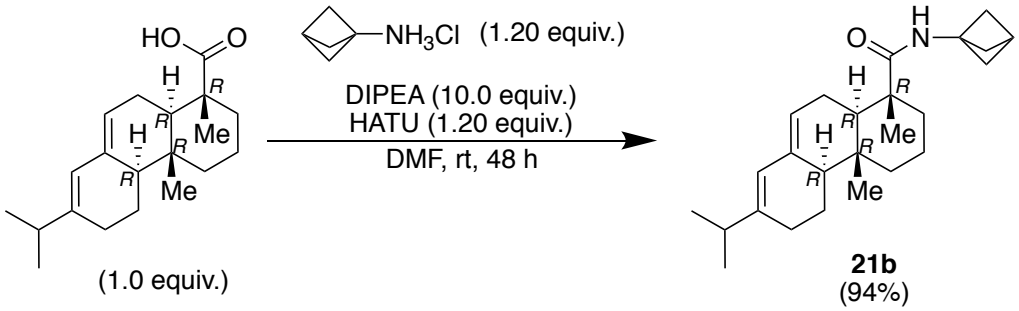
(1*R*,4a*R*,4b*R*,10a*R*)-*N*-(bicyclo[1.1.1]pentan-1-yl)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthrene-1-carboxamide (21b)



DIPEA (1.7 mL, 9.9 mmol, 10 equiv.) was added to a stirred mixture of abietic acid (300 mg, 0.99 mmol, 1.0 equiv.), bicyclo[1.1.1]pentan-1-amine hydrochloride (247 mg, 2.07 mmol, 1.20 equiv.) and HATU (456 mg, 1.2 mmol, 1.2 equiv.) in DMF (7.6 mL). The mixture was stirred at room temperature for 48 h. Water (10 mL) was added, and the reaction extracted with EtOAc (3x20 mL). The organic layers were separated, dried (Na_2SO_4), filtered and the solvents evaporated in vacuo. The crude material was purified by flash column chromatography (silica, EtOAc in Heptane 0/100 to 30/70). The desired fractions were collected and concentrated in vacuo to give (1*R*,4a*R*,4b*R*,10a*R*)-*N*-(bicyclo[1.1.1]pentan-1-yl)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthrene-1-carboxamide (342 mg, 0.93 mmol, 94 %) as white solid.

^{1}H NMR (500 MHz, DMSO-d_6) δ ppm 7.92 (s, 1 H) 5.70 (s, 1 H) 5.30 (br d, *J*=4.50 Hz, 1 H) 2.36 (s, 1 H) 2.18 (dt, *J*=13.54, 6.80 Hz, 1 H) 1.97 - 2.10 (m, 2 H) 1.93 (s, 6 H) 1.29 - 1.90 (m, 10 H) 1.05 - 1.16 (m, 5 H) 0.96 (d, *J*=6.75 Hz, 3 H) 0.95 (d, *J*=6.88 Hz, 3 H) 0.72 (s, 3 H). [See spectrum]

^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 178.0 (s, 1 C) 144.3 (s, 1 C) 134.9 (s, 1 C) 122.5 (s, 1 C) 120.8 (s, 1 C) 52.2 (s, 3 C) 50.4 (s, 1 C) 49.3 (s, 1 C) 45.6 (s, 1 C) 44.7 (s, 1 C) 37.6 (s, 1 C) 34.3 (s, 1 C) 34.2 (s, 1 C) 27.0 (s, 1 C) 24.8 (s, 1 C) 24.5 (s, 1 C) 22.0 (s, 1 C) 21.4 (s, 1 C) 20.8 (s, 1 C) 18.1 (s, 1 C) 16.8 (s, 1 C) 13.9 (s, 1 C). [See spectrum]

HRMS (ESI-TOF) Calculated for $C_{25}H_{38}NO$ $[M+H]^+$: 368.2875; Found: 368.2950.

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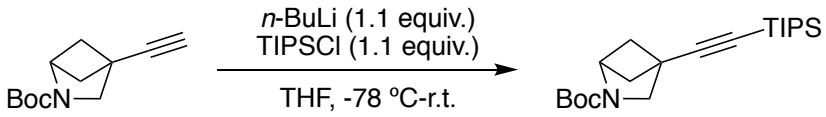
tert-butyl 4-((triisopropylsilyl)ethynyl)-2-azabicyclo[2.1.1]hexane-2-carboxylate (34b)



34b
75%

tert-butyl 4-ethynyl-2-azabicyclo[2.1.1]hexane-2-carboxylate (51.8 mg, 0.250 mmol, 1.00 equiv.) was dissolved in dry THF (1.0 mL) and cooled to -78 ºC. *n*-BuLi in hexanes (2.5 M, 0.110 mL, 0.275 mmol, 1.10 equiv.) was added dropwise, and the resultant mixture was stirred for 15 min. Then, TIPSCl (58.8 µL, 0.275 mmol, 1.10 equiv.) was added dropwise to the reaction mixture at -78 ºC. The mixture was warmed to ambient temperature and stirred for 1 h. Then, sat. $NaHCO_3$ was added (2 mL) and the mixture extracted with ethyl acetate (10 mL x 3). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude material was chromatographed on NEt_3-treated SiO_2 with 0→15% ethyl acetate in hexanes to afford the title compound as a clear oil (68.0 mg, 75%).

TLC: R_f = 0.65 (20% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.42 (s, 2H), 2.73 – 2.67 (m, 1H), 2.17 – 2.08 (m, 2H), 1.85 – 1.77 (m, 2H), 1.53 (s, 9H), 1.22 – 1.07 (m, 21H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 157.1, 104.4, 88.2, 80.2, 61.4, 52.0, 47.4, 35.4, 28.6, 18.8, 11.4. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{21}H_{37}NO_2SiNa$ $[M+Na]^+$:386.2491, found:386.2492.

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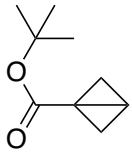
tert-butyl bicyclo-[1.1.0]-butane-1-carboxylate



Prepared according to literature procedures.[9]

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.33 (d, *J* = 3.5 Hz, 2H), 2.08 – 1.98 (m, 1H), 1.49 (s, 9H), 1.13 – 1.07 (m, 1H). [See spectrum]
^{13}C NMR (151 MHz, $CDCl_3$) δ 172.5, 80.4, 35.5, 28.2, 15.8, 10.2. [See spectrum]

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3. Evaluation of Conditions for the Borylation of Bridgehead C–H Bonds.

3.1 Evaluation of ligands and boron reagents.

In a nitrogen glovebox, a 4 mL vial was sequentially charged with the appropriate ligand (12.5 μmol, 5.00 mol%), [Ir] source (5.00 mol% iridium), adamantane (17.0 mg, 0.125 mmol, 0.500 equiv.), 4-*tert*butylphenylbicyclopentane (**1b**) (50.1 mg, 0.250 mmol, 1.00 equiv.), and boron reagent (0.375 mmol, 1.50 equiv.). A magnetic stir bar and 0.2 mL of cyclooctane were added to the vial, and the vial was tightly sealed with a Teflon lined cap. The vial was removed from the glovebox and heated at 100 ºC in a preheated aluminum heating block for the specified time. After cooling to ambient temperature, an aliquot was taken and subjected to GC analysis.

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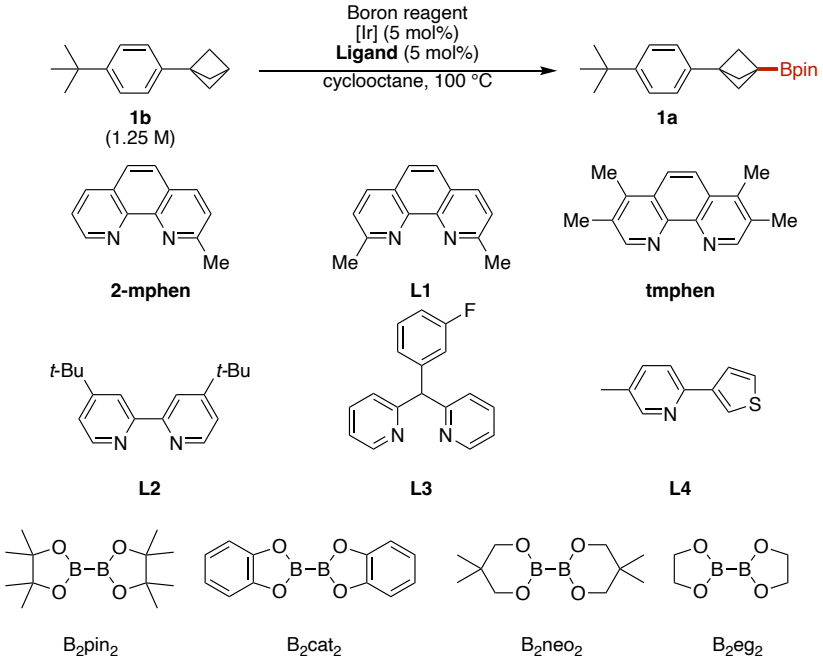

Entry	Ligand	Ir precatalyst	Boron reagent	Reaction time	GC yield (%)
1	**2-mphen**	(mesitylene)Ir(Bpin)$_3$	B_2pin_2 (3 equiv.)	24 h	89
2	**2-mphen**	(mesitylene)Ir(Bpin)$_3$	B_2pin_2 (3 equiv.)	2 h	92
3	**2-mphen**	(mesitylene)Ir(Bpin)$_3$	B_2pin_2 (1.5 equiv.)	2 h	89
4	**2-mphen**	[Ir(COD)(OMe)]$_2$	B_2pin_2 (1.5 equiv.)	2 h	90
5	**2-mphen**	[Ir(COD)(OMe)]$_2$	HBpin (1.5 equiv.)	2 h	19
6	**2-mphen**	[Ir(COD)(OMe)]$_2$	B_2cat_2 (1.5 equiv.)	2 h	0
7	**2-mphen**	[Ir(COD)(OMe)]$_2$	B_2neo_2 (1.5 equiv.)	2 h	0
8	**2-mphen**	[Ir(COD)(OMe)]$_2$	B_2eg_2 (1.5 equiv.)	2 h	0
9	**L1**	[Ir(COD)(OMe)]$_2$	B_2pin_2 (1.5 equiv.)	2 h	73
10	**tmphen**	[Ir(COD)(OMe)]$_2$	B_2pin_2 (1.5 equiv.)	2 h	4
11	**L2**	[Ir(COD)(OMe)]$_2$	B_2pin_2 (1.5 equiv.)	2 h	0
12	**L3**	[Ir(COD)(OMe)]$_2$	B_2pin_2 (1.5 equiv.)	2 h	20
13	**L4**	[Ir(COD)(OMe)]$_2$	B_2pin_2 (1.5 equiv.)	2 h	0
14	-	[Ir(COD)(OMe)]$_2$	B_2pin_2 (1.5 equiv.)	2 h	0
15	**2-mphen**	-	B_2pin_2 (1.5 equiv.)	2 h	0

Fig. S2. Evaluation of ligands and boron reagents for the borylation of tertiary C–H bonds.

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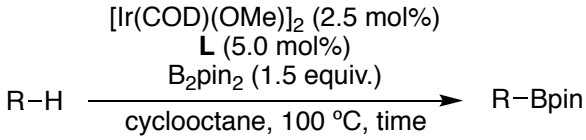
3.2 Evaluation of the effect of prolonged reaction times.

In a nitrogen glovebox, a 4 mL vial was sequentially charged with the appropriate ligand (12.5 μmol, 5.00 mol%), $[Ir(COD)(OMe)]_2$ (4.14 mg, 6.25 μmol, 2.50 mol%), substrate (0.250 mmol, 1.00 equiv.), and boron reagent (0.375 mmol, 1.50 equiv.). A magnetic stir bar and 0.2 mL of cyclooctane were added to the vial, and the vial was tightly sealed with a Teflon lined cap. The vial was removed from the glovebox and heated at 100 ºC in a preheated aluminum heating block for the specified time. After cooling to ambient temperature, $CDCl_3$ and CH_2Br_2 (internal standard) were added to the vial, and an aliquot was analyzed by ^1H NMR spectroscopy.



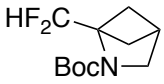
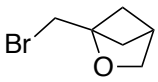
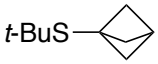
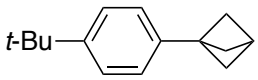
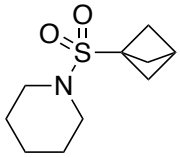
Entry	Substrate	**L** = 2-mphen, time = 2 h	**L** = tmphen, time = 24 h
1		quant.	quant.
2		50%	trace
3		80%	67%
4		86%	73%
5		90%	83%

Fig. S3. Comparison of yields obtained with tmphen, 24 h of heating versus those observed under the standard conditions.

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4. General procedures

4.1 General Conditions A: Catalytic borylation of bridgehead C–H bonds

In a nitrogen glovebox, a 4 mL vial was sequentially charged with 2-mphen (2.43 mg, 12.5 μmol, 5.00 mol%), $[Ir(COD)(OMe)]_2$ (6.25 μmol, 2.50 mol%), substrate (0.250 mmol, 1.00 equiv.), and B_2pin_2 (95.2 mg, 0.375 mmol, 1.50 equiv.) (If the substrate was a liquid, it was added last.). A magnetic stir bar and 0.2 mL of cyclooctane were added to the vial, and the vial was tightly sealed with a Teflon lined cap. The vial was removed from the glovebox and heated at 100 ºC in a preheated aluminum heating block for the specified time. After cooling to ambient temperature, $CDCl_3$ and CH_2Br_2 (internal standard) were added to the vial, and a sample was taken and analyzed by ^1H NMR spectroscopy to quantify the conversion. The mixture was then co-evaporated with MeOH (5 mL x 3) at 45 ºC (Caution: vigorous gas evolution upon addition of MeOH!). The crude residue was purified by flash column chromatography (silica or C18 reverse phase) to give the borylated product.

4.2 General Conditions B: In situ protection followed by catalytic borylation

In a nitrogen glovebox, a 4 mL vial was charged with substrate (0.250 mmol, 1.00 equiv.) and HBpin (0.325 mmol, 1.30 equiv.), and the vial was tightly sealed with a Teflon lined cap. The vial was removed from the glovebox and heated at 100 ºC in a preheated aluminum heating block for 45 min. The vial was then sent into the glovebox and sequentially charged with 2-mphen (2.43 mg, 12.5 μmol, 5.00 mol%), $[Ir(COD)(OMe)]_2$ (6.25 μmol, 2.50 mol%), and B_2pin_2 (95.2 mg, 0.375 mmol, 1.50 equiv.). A magnetic stir bar and 0.2 mL of cyclooctane were added to the vial, and the vial was again tightly sealed with a Teflon lined cap. The vial was removed from the glovebox and heated at 100 ºC in a preheated aluminum heating block for the specified time. After cooling to ambient temperature, $CDCl_3$ and CH_2Br_2 (internal standard) were added to the vial, and a sample was taken and analyzed by ^1H NMR spectroscopy to quantify conversion. The mixture was then co-evaporated with MeOH (5 mL x 3) at 45 ºC (Caution: vigorous gas evolution upon addition of MeOH!). The crude residue was purified by flash column chromatography (silica or C18 reverse phase) to give the borylated product.

4.3 General Conditions C: Catalytic borylation followed by treatment by KHF_2

In a nitrogen glovebox, a 4 mL vial was sequentially charged with 2-mphen (2.43 mg, 12.5 μmol, 5.00 mol%), $[Ir(COD)(OMe)]_2$ (6.25 μmol, 2.50 mol%), substrate (0.250 mmol, 1.00 equiv.), and B_2pin_2 (95.2 mg, 0.375 mmol, 1.50 equiv.) (If the substrate was a liquid, it was added last.). A magnetic stir bar and 0.2 mL of cyclooctane were added to the vial, and the vial was tightly sealed with a Teflon lined cap. The vial was removed from the glovebox and heated at 100 ºC in a preheated aluminum heating block for the specified time. After cooling to ambient temperature, the crude reaction mixture was passed through a thin pad of C18 reverse phase silica and eluted with acetonitrile. All volatile

materials were removed, and the crude residue was dissolved in a mixture of MeOH (0.4 mL) and THF (0.8 mL). Then, KHF_2 (97.6 mg, 1.25 mmol, 5.00 equiv.) in water (0.4 mL) was added, and the resulting biphasic mixture stirred overnight at room temperature. The resulting mixture was co-evaporated with a 1:1 mixture of MeOH and water (2 mL x 5) at 45 ºC to remove pinacol and boron byproducts. The residue was extracted with acetone, filtered, and the filtrate concentrated to dryness in vacuo. The resulting solids were washed with diethyl ether or pentane as appropriate to afford the desired trifluoroborate salt.

4.4 General tips for work up and purification of the bridgehead boronic esters

The progress of the reaction is most easily monitored by GC-MS analysis or ^{1}H NMR spectroscopy. One ion commonly seen for these compounds is the $[M-15]^+$ peak resulting from the loss of a methyl of the Bpin moiety.

In general, the bridgehead boronic esters are stable to ambient moisture and air. Prolonged manipulation or storage under ambient conditions is still not recommended because oxidation has been observed in select cases. We generally observed no decomposition when the product boronic esters were stored in a -20 ºC freezer under air.

The bridgehead boronic esters are stable towards water and methanol. Co-evaporation with methanol at 45 ºC is a convenient method to remove the HOBpin byproduct or to selectively protodeboronate more labile boronic esters.

Most of the BCP-Bpin compounds can be purified by column chromatography on silica, but protodeboronation occurs in select cases. In those cases, purification via column chromatography on C-18 reverse phase silica is recommended.

The BCP-Bpin compounds can generally be visualized on TLC plates with a *p*-anisaldehyde stain (Prepared by mixing 135 mL of absolute ethanol, 5 mL of concentrated sulfuric acid, 1.5 mL of glacial acetic acid, and 3.7 mL of *p*-anisaldehyde). Permanganate or phosphomolybdic acid stains are also occasionally useful, but less general, because the BCP-Bpin compounds do not always stain well with them. Note that pinacol, HOBpin, and B_2pin_2 tend to stain very strongly with all three stains, if present.

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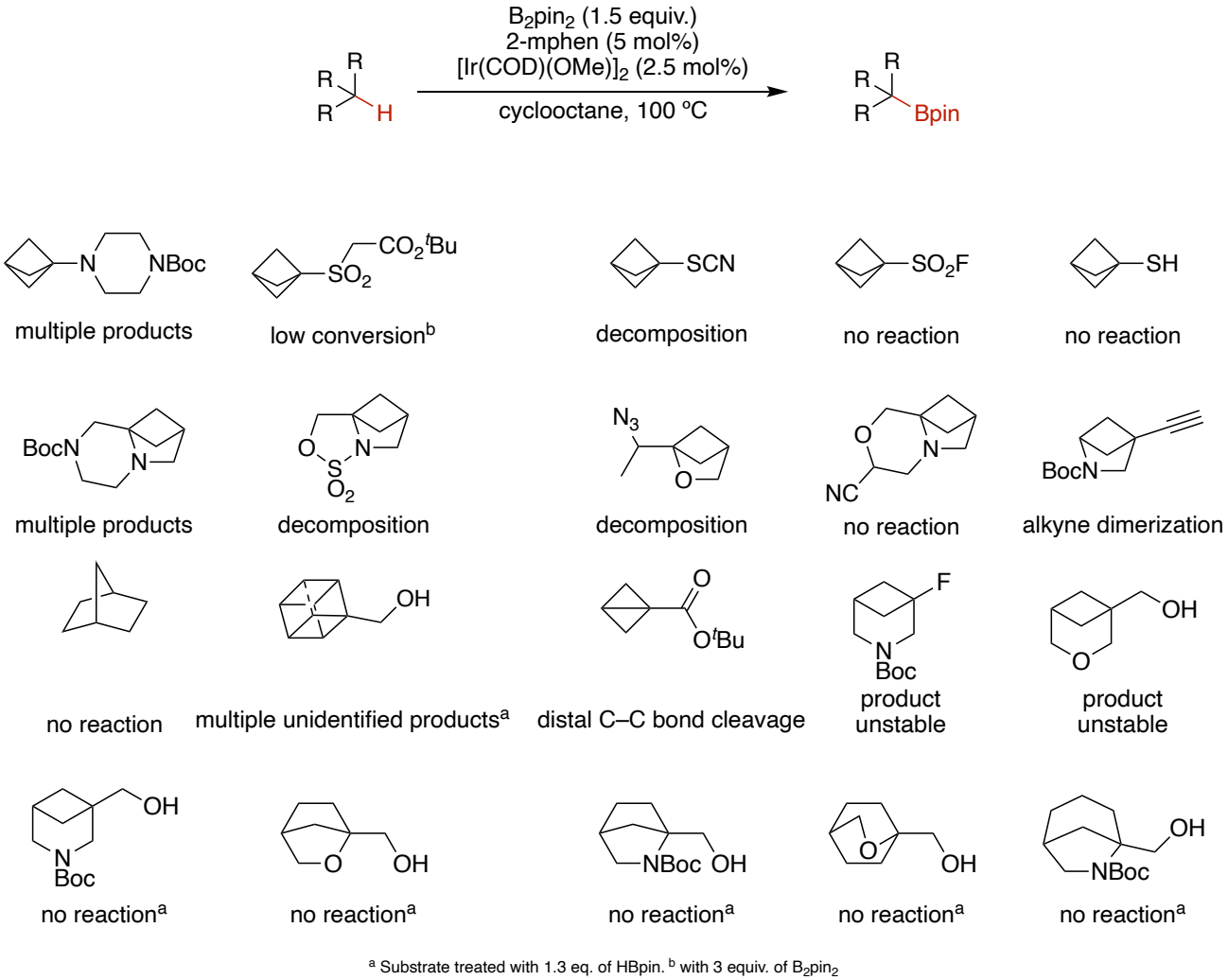
5. Scope of the catalytic borylation of bridgehead C–H bonds

5.1 Unsuccessful Substrates



[a] Substrate treated with 1.3 eq. of HBpin. [b] with 3 equiv. of B_2pin_2

Fig. S4. Substrates that did not undergo borylation of tertiary C–H bonds.

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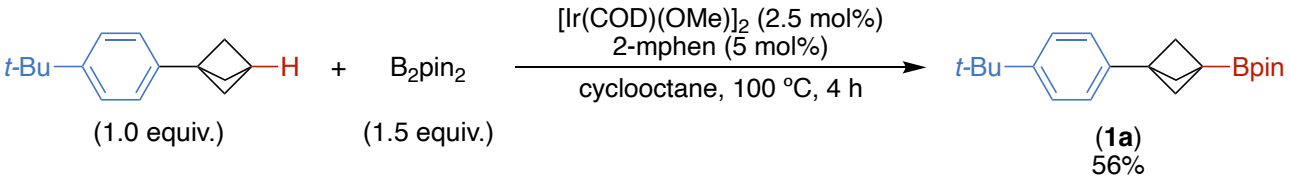
5.2 Bicyclo[1.1.1]pentane Substrates

2-(3-(4-(*tert*-butyl)phenyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a)



Prepared according to General Procedure A on a 0.25 mmol scale. The reaction mixture was heated for 4 h instead of the usual 2 h. The crude reaction mixture was eluted on SiO_2 with 10% ethyl acetate in hexanes as the eluent to afford 45.0 mg (56%) of the title compound as a white powder.

TLC: $R_f = 0.42$ (10% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.3 Hz, 2H), 2.17 (s, 6H), 1.31 (s, 9H), 1.28 (s, 12H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 139.4, 125.6, 125.1, 83.5, 53.2, 47.3, 34.6, 31.5, 24.9. [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.8. [See spectrum]

HRMS (*m/z*): (EI+) calc'd for $C_{21}H_{31}BO_2$ $[M]^+$: 326.2417, found: 326.2419.

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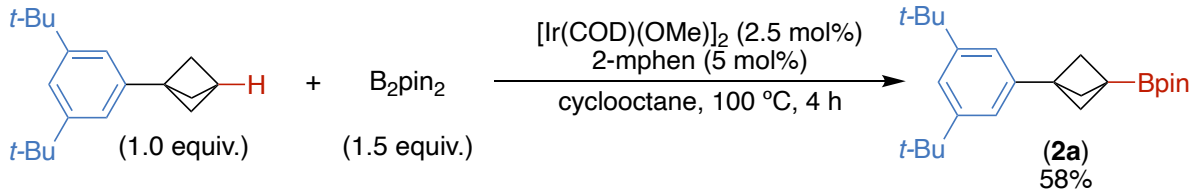
2-(3-(3,5-di-*tert*-butylphenyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a)



Prepared according to General Procedure A for borylation on a on a 0.40 mmol scale. The reaction mixture was heated for 4 h instead of the usual 2 h. The crude reaction mixture was eluted on SiO_2 with 10% ethyl acetate in hexanes as the eluent to afford 88.0 mg (58%) of the title compound as a white powder.

TLC: $R_f = 0.52$ (10% ethyl acetate in hexanes)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (t, $J = 1.9$ Hz, 1H), 7.05 (d, $J = 1.9$ Hz, 2H), 2.17 (s, 6H), 1.32 (s, 18H), 1.27 (s, 12H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 150.6, 141.4, 120.8, 119.8, 83.5, 53.3, 48.0, 35.0, 31.6, 24.9. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 30.8. [See spectrum]

HRMS (*m/z*): (EI+) calc'd for $C_{25}H_{39}BO_2$ $[M]^+$: 382.3043, found: 382.3047.

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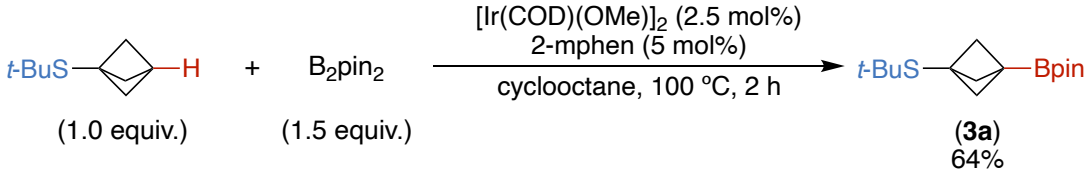
2-(3-(*tert*-butylthio)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3a)



Prepared according to General Procedure A on a 0.25 mmol scale. The crude reaction mixture was eluted on SiO_2 with 10% ethyl acetate in hexanes as the eluent to afford 45.0 mg (64%) of the title compound as a yellow oil that solidified upon standing.

TLC: R_f = 0.48 (10% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.18 (s, 6H), 1.36 (s, 9H), 1.23 (s, 12H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 83.5, 57.0, 44.8, 44.4, 31.9, 24.7. [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.7. [See spectrum]

HRMS (*m/z*): (EI+) calc'd for $C_{13}H_{17}NO_4$ $[M]^+$: 282.1825, found: 282.1824.

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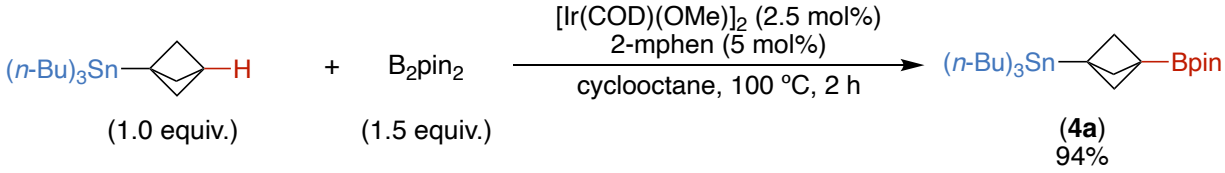
tributyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)stannane (4a)



Prepared according to General Procedure A on a 0.25 mmol scale. The crude reaction mixture was eluted on fully endcapped reverse phase silica with 10% dichloromethane in acetonitrile as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum. The residue was co-evaporated with methanol at 45 °C twice (5 mL each), diluted with pentane, and filtered through a glass fibre plug to afford 114 mg (94%) of the title compound as a viscous brown oil.

TLC: R_f = 0.70 (10% dichloromethane in acetonitrile)

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.11 (s, 6H), 1.51 – 1.41 (m, 6H), 1.33 – 1.23 (m, 6H), 1.21 (s, 12H), 0.88 (t, J = 7.3 Hz, 9H), 0.82 – 0.73 (m, with tin magnetic isotope satellites, $J(^{119}Sn^1H)$ = 24.7 Hz, $J(^{117}Sn^1H)$ = 23.8 Hz, 6H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 83.1, 57.0, 39.0, 29.3 (with tin magnetic isotope satellites, J_{Sn-C} = 10.2 Hz), 27.4 (with tin magnetic isotope satellites, J_{Sn-C} = 24.2 Hz), 24.7, 13.8, 8.8 (with tin magnetic isotope satellites, $J(^{119}Sn^{13}C)$ = 153.5 Hz, $J(^{117}Sn^{13}C)$ = 147.2 Hz). [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) δ 27.57. [See spectrum]

^{119}Sn NMR (224 MHz, $CDCl_3$) δ -71.27. [See spectrum]

HRMS (*m/z*): (EI+) calc'd for $C_{19}H_{36}BO_2Sn$ $[M\text{-}Bu]^+$ 427.1830 , found: 427.1830.

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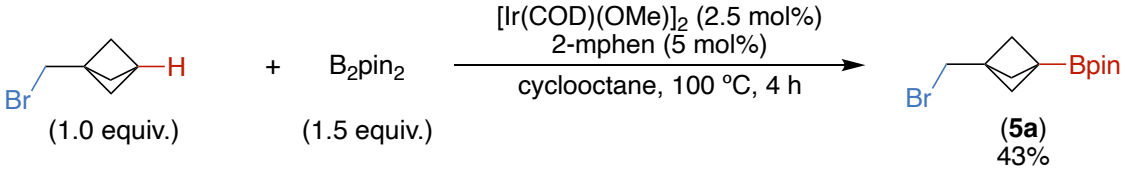
2-(3-(bromomethyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5a)



Prepared according to General Procedure A on a 0.25 mmol scale. The reaction mixture was heated for 4 h instead of the usual 2 h. The crude reaction mixture was eluted on SiO_2 with 0% → 20% ethyl acetate in hexanes as the eluent to afford 30.5 mg (43%) of the title compound as a white powder.

TLC: R_f = 0.45 (10% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.30 (s, 2H), 1.84 (s, 6H), 1.23 (s, 12H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 83.6, 50.9, 44.5, 35.1, 24.9. [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.4. [See spectrum]

HRMS (*m/z*): (EI+) calc'd for $C_{11}H_{17}BBrO_2$ $[M\text{-}Me]^+$: 271.0505, found: 271.0504.

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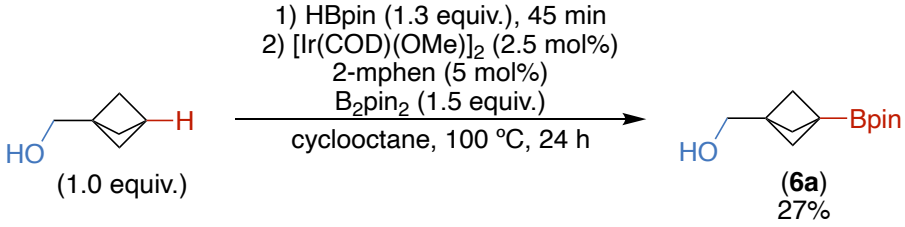
(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methanol (6a)



Prepared according to General Procedure B on a 0.10 mmol scale. The crude reaction mixture was eluted on SiO_2 with 20% → 30% ethyl acetate in hexanes as the eluent to afford 6.0 mg (27%) of the title compound as a white powder.

TLC: R_f = 0.70 (10% dichloromethane in acetonitrile)

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.46 (s, 2H), 1.82 (s, 6H), 1.24 (s, 12H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 83.5, 64.2, 49.9, 46.0, 24.9. [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.4. [See spectrum]

HRMS (*m/z*): (ESI-) calc'd for $C_{12}H_{20}BO_3$ $[M-H]^-$: 223.1511, found: 223.1512.

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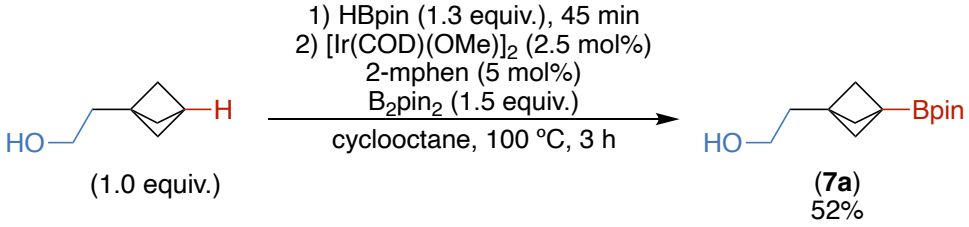
2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)ethan-1-ol) (7a)



Prepared according to General Procedure B on a 0.10 mmol scale. The crude reaction mixture was eluted on SiO_2 with 0% → 50% ethyl acetate in hexanes as the eluent to afford 12.3 mg (52%) of the title compound as a clear oil.

TLC: R_f = 0.48 (50% ethyl acetate in hexanes)

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.64 (t, J = 6.8 Hz, 2H), 1.81 (s, 6H), 1.63 (t, J = 6.8 Hz, 2H), 1.22 (s, 12H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 83.4, 61.2, 52.2, 43.9, 36.2, 24.9. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 30.4. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $[M+H]^+$: 239.1819, found: 239.1817.

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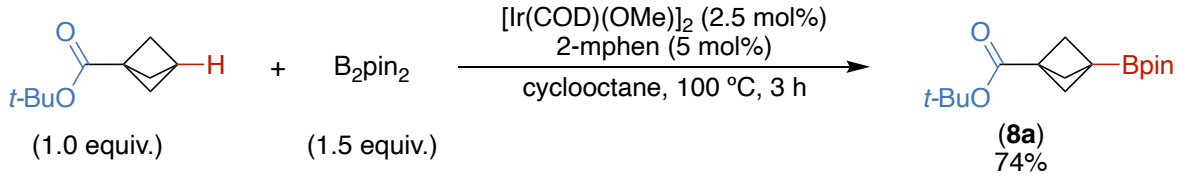
tert-butyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentane-1-carboxylate) (8a)



Prepared according to General Procedure A on a 0.25 mmol scale. The crude reaction mixture was eluted on SiO_2 with 10% → 35% ethyl acetate in hexanes as the eluent to afford 52.2 mg (71%) of the title compound as a white powder.

TLC: R_f = 0.32 (10 % ethyl acetate in hexanes)

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.05 (s, 6H), 1.40 (s, 9H), 1.21 (s, 12H) [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 83.6, 80.2, 52.3, 44.1, 28.1, 24.8. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 30.6 [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $[M+H]^+$: 295.2081, found: 295.2083.

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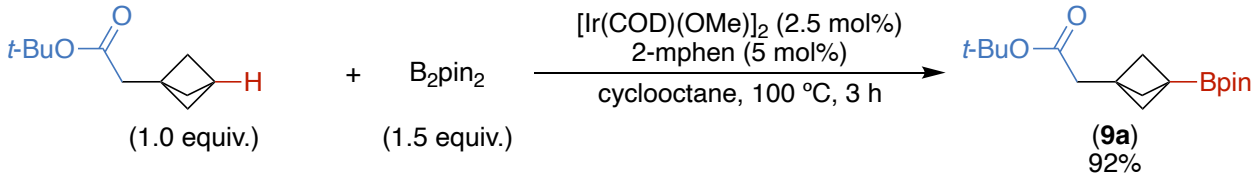
***tert*-butyl 2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)acetate (9a)**



Prepared according to General Procedure A on a 0.15 mmol scale. The reaction mixture was heated for 3 h instead of the usual 2 h. The crude reaction mixture was eluted on SiO_2 with 0% → 20% ethyl acetate in hexanes as the eluent to afford 42.9 mg (92%) of the title compound as a colorless oil.

TLC: R_f = 0.47 (10% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.28 (s, 2H), 1.85 (s, 6H), 1.42 (s, 9H), 1.22 (s, 12H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.8, 83.4, 80.2, 52.4, 41.9, 41.0, 28.3, 24.9. [See spectrum]

^{11}B NMR ^{11}B NMR (160 MHz, $CDCl_3$) δ 30.2. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{17}H_{29}BO_4$ $[M+H]^+$: 309.2232, found: 309.2231.

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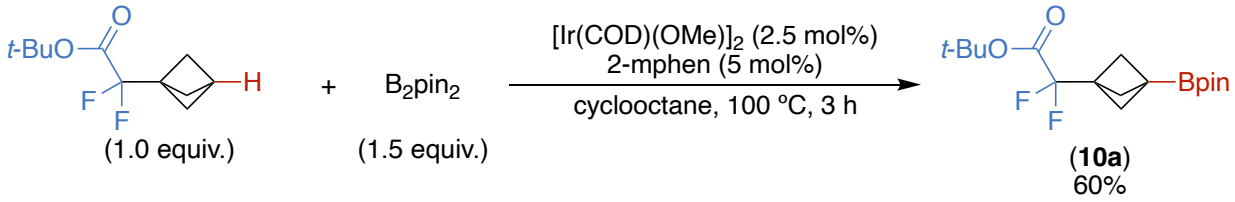
tert-butyl 2,2-difluoro-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)acetate (10a)



Prepared according to General Procedure A on a 0.15 mmol scale. The reaction mixture was heated for 3 h instead of the usual 2 h. The crude reaction mixture was eluted on SiO_2 with 0% → 20% ethyl acetate in hexanes as the eluent to afford 31.0 mg (60%) of the title compound as a white powder.

TLC: R_f = 0.41 (10% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.99 (s, 6H), 1.51 (s, 9H), 1.23 (s, 12H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 162.4 (t, J_{C-F} = 32.4 Hz) 112.9, 110.9 (t, J_{C-F} = 250.1 Hz), 109.0, 84.4, 83.8, 49.5, 43.6, 43.4 (t, J_{C-F} = 31.1 Hz), 43.2, 28.0, 24.9. [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.3. [See spectrum]

^{19}F NMR (470 MHz, $CDCl_3$) δ -113.4. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{17}H_{27}BF_2O_4Na$ $[M+Na]^+$: 367.1863, found: 367.1862.

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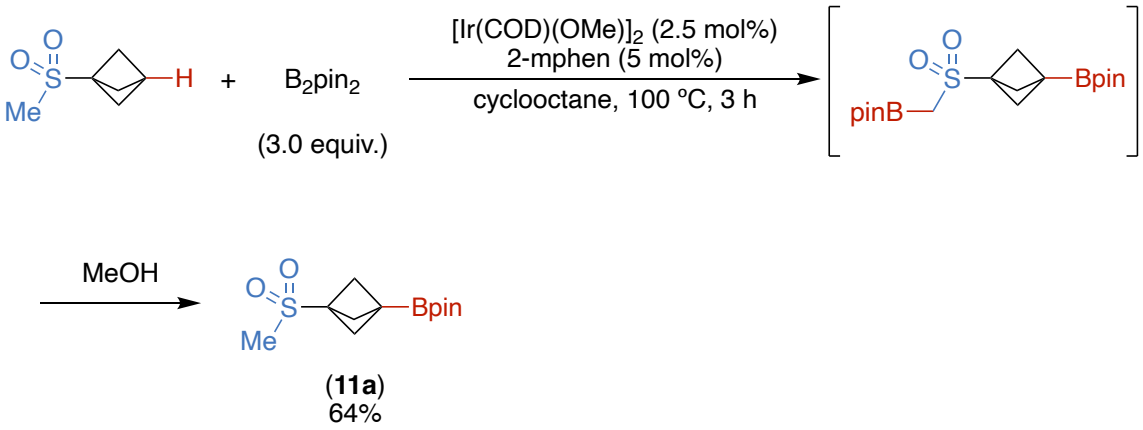
4,4,5,5-tetramethyl-2-(3-(methylsulfonyl)bicyclo[1.1.1]pentan-1-yl)-1,3,2-dioxaborolane (11a)



(**11a**)
64%

Prepared according to General Procedure A on a 0.25 mmol scale with 3 equiv. of B_2pin_2, instead of the usual 1.5 equiv. The reaction mixture was heated for 3 h, rather than the usual 2 h. The crude material was co-evaporated with methanol at 45 °C (10 mL x 4). The residue was dissolved in a minimal amount of CH_2Cl_2, layered with pentane, and stored at -20 ºC overnight. The resulting brown powder, which precipitated overnight, was collected and washed with pentane, affording 43.8 mg (64%) of the title compound as a brown solid.

TLC: N/A

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.76 (s, 3H), 2.26 (s, 6H), 1.23 (s, 12H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 84.3, 54.5, 51.4, 36.8, 25.0, 24.8. [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) δ 29.9. [See spectrum]

HRMS (*m/z*): (EI+) calc'd for $C_{12}H_{21}BO_4SNa$ $[M+Na]^+$: 295.1146, found: 295.1150.

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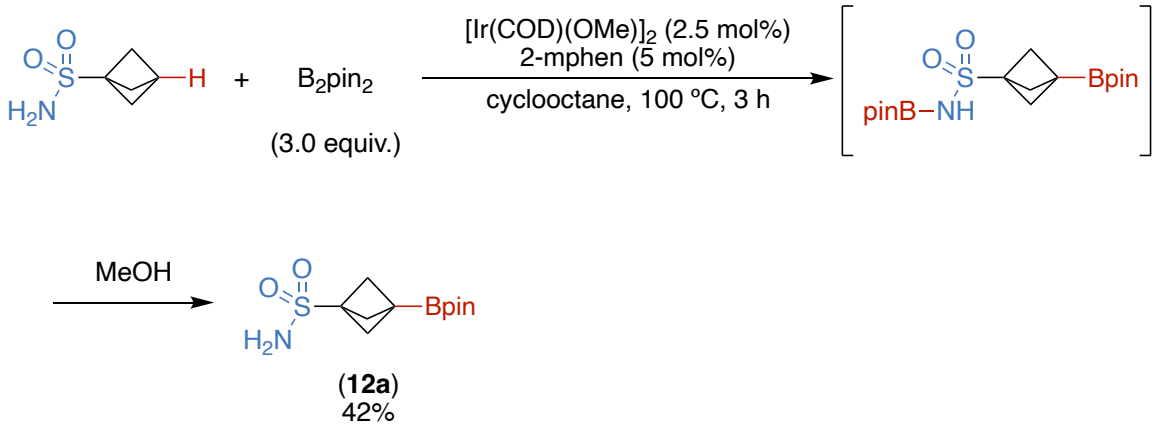
3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentane-1-sulfonamide (12a)



Prepared according to General Procedure A on a 0.25 mmol scale with 3 equiv. of B_2pin_2, instead of the usual 1.5 equiv. The reaction mixture was heated for 3 h, rather than the usual 2 h. The crude material was co-evaporated with methanol at 45 °C (30 mL x 2), then stirred with CH_2Cl_2 (30 mL) for 1 h. The suspension was filtered over a frit, and the solids were redissolved in methanol and concentrated to yield 28.7 mg (42%) of the title compound as a light brown solid.

TLC: N/A

^{1}H NMR (500 MHz, DMSO) δ 6.69 (s, 1H), 2.02 (s, 6H), 1.18 (s, 12H). [See spectrum]

^{13}C NMR (126 MHz, DMSO) δ 83.5, 54.3, 50.9, 39.4, 24.5. [See spectrum]

^{11}B NMR (160 MHz, DMSO) δ 29.5. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{11}H_{20}BNO_4SNa$ $[M+Na]^+$: 296.1098, found: 296.1100.

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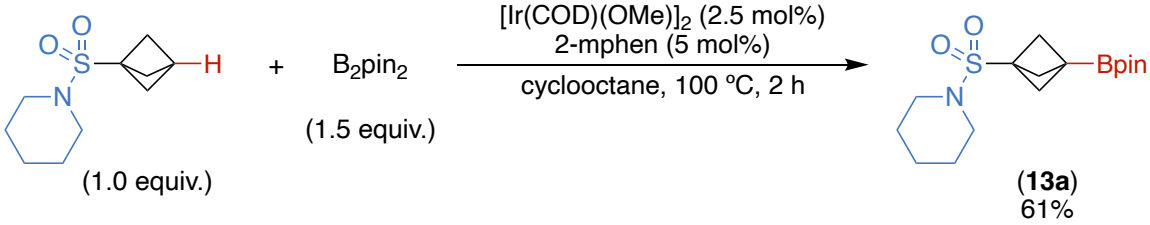
1-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)sulfonyl)piperidine (13a)



Prepared according to General Procedure A on a 0.10 mmol scale. The crude material was co-evaporated with methanol at 45 °C (10 mL x 3). The residue was dissolved in a minimal amount of CH_2Cl_2, layered with pentane, and stored at -20 ºC overnight. The resulting needles were collected and washed with pentane, affording 20.9 mg (61%) of the title compound as a beige solid.

TLC: N/A

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.29 (t, *J* = 5.2 Hz, 4H), 2.26 (s, 6H), 1.67 – 1.48 (m, 6H), 1.23 (s, 12H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 84.1, 53.8, 52.8, 47.1, 26.2, 24.9, 24.1. [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.0. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{16}H_{28}BNO_4SNa$ $[M+Na]^+$: 364.1724, found: 364.1729.

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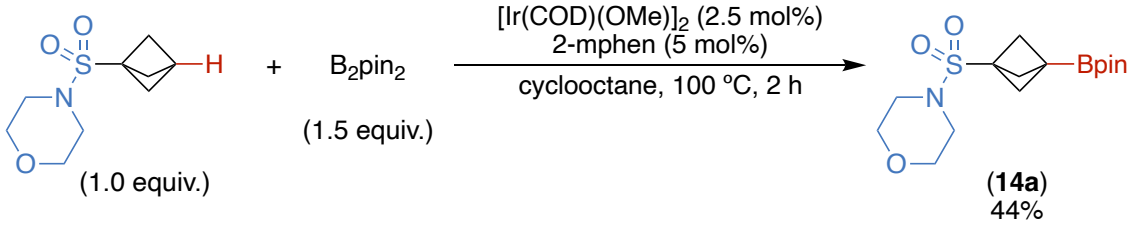
4-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)sulfonyl)morpholine (14a)



Prepared according to General Procedure A on a 0.10 mmol scale. The crude material was co-evaporated with methanol at 45 °C (10 mL x 3). The residue was dissolved in a minimal amount of CH_2Cl_2, layered with pentane, and stored at -20 ºC overnight. The resulting needles were collected and washed with pentane, affording 15.0 mg (44%) of the title compound as a brown solid.

TLC: N/A

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.73 – 3.66 (m, 4H), 3.36 – 3.31 (m, 4H), 2.29 (s, 6H), 1.24 (s, 12H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 84.2, 67.1, 53.6, 53.0, 46.4, 24.9. [See spectrum]

^{11}B NMR ^{11}B NMR (160 MHz, $CDCl_3$) δ 29.8. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{15}H_{26}BNO_5SNa$ $[M+Na]^+$: 366.1517, found: 366.1515.

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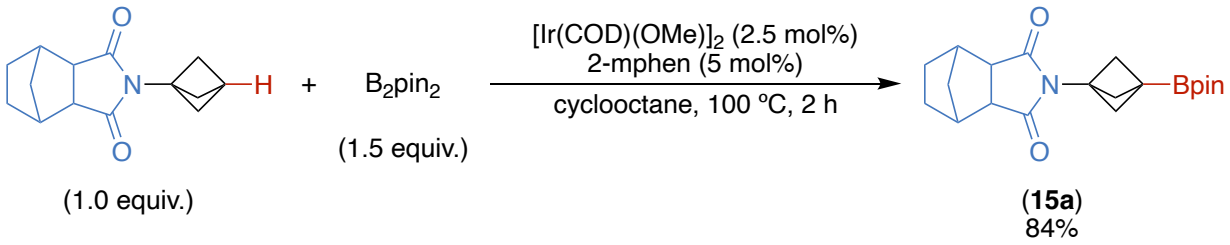
2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)hexahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione (15a)



Prepared according to General Procedure A on a 0.25 mmol scale. The crude reaction mixture was eluted on SiO_2 with 20% → 35% ethyl acetate in hexanes as the eluent to afford 75.2 mg (84%) of the title compound as a white powder.

TLC: R_f = 0.35 (25% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.94 (t, *J* = 2.7 Hz, 2H), 2.70 (p, *J* = 2.1 Hz, 2H), 2.39 (d, *J* = 2.0 Hz, 6H), 1.58 – 1.50 (m, 4H), 1.32 – 1.11 (m, 14H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 178.7, 83.7, 54.6, 48.8, 48.8, 47.6, 42.0, 39.5, 24.8. [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.7. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{20}H_{28}BNO_4$ $[M+Na]^+$: 380.2004, found: 380.2010.

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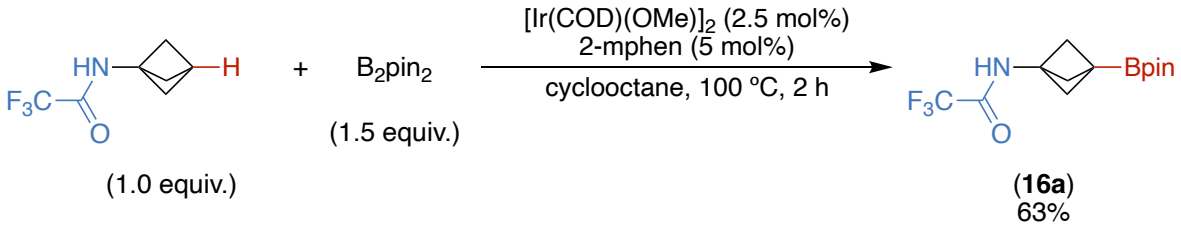
2,2,2-trifluoro-*N*-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)acetamide (16a)



Prepared according to General Procedure A on a 0.15 mmol scale. The crude reaction mixture was eluted on SiO_2 with 10% → 35% ethyl acetate in hexanes as the eluent to afford 28.9 mg (63%) of the title compound as a white powder.

TLC: R_f = 0.23 (20% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.53 (s, 1H), 2.23 (s, 6H), 1.25 (s, 12H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.7 (q, $J_{C\text{-}F}$ = 36.8 Hz), 115.5 (q, $J_{C\text{-}F}$ = 285.4 Hz), 83.8, 54.0, 47.5, 24.7. [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.7. [See spectrum]

^{19}F NMR (470 MHz, $CDCl_3$) δ -76.3. [See spectrum]

HRMS (*m/z*): (EI+) calc'd for $C_{13}H_{19}BF_3NO_3$ $[M]^+$: 305.1410, found: 305.1406.

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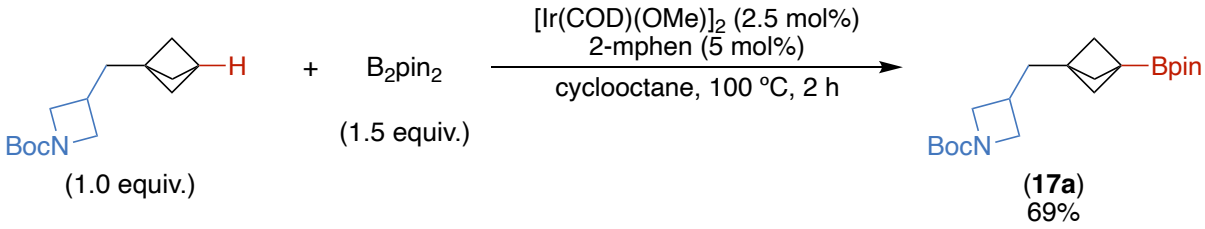
***tert*-butyl 3-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methyl)-azetidine-1-carboxylate (17a)**



Prepared according to General Procedure A on a 0.10 mmol scale. The crude reaction mixture was eluted on reverse phase silica with 40% → 100% acetonitrile in water as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford 25.0 mg (69%) of the title compound as a white solid.

TLC: R_f = 0.8 (50% acetonitrile in water)

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.97 (t, J = 8.4 Hz, 2H), 3.51 (dd, J = 8.5, 5.7 Hz, 2H), 2.50 (tt, J = 8.1, 5.7 Hz, 1H), 1.72 (s, 6H), 1.62 (d, J = 7.8 Hz, 2H), 1.42 (s, 9H), 1.22 (s, 12H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 83.4, 79.2, 55.0, 51.8, 50.0, 44.7, 37.9, 28.6, 26.8, 24.9. [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) δ 30.4. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{20}H_{35}BNO_4$ $[M+H]^+$: 364.2654, found: 364.2652.

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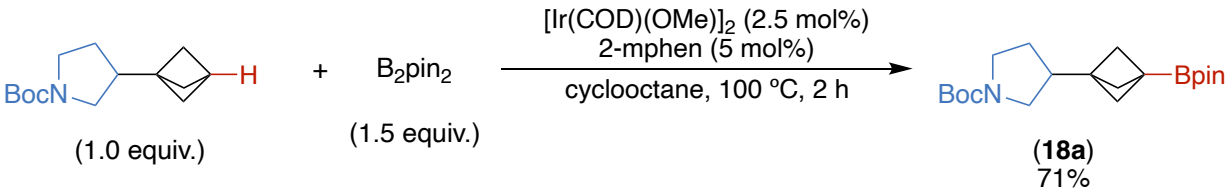
***tert*-butyl 3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)pyrrolidine-1-carboxylate (18a)**



Prepared according to General Procedure A on a 0.10 mmol scale. The crude reaction mixture was eluted on reverse phase silica with 40% → 100% acetonitrile in water as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford 25.8 mg (71%) of the title compound as a white powder.

TLC: R_f = 0.8 (50% acetonitrile in water)

^{1}H NMR (700 MHz, $CDCl_3$) δ 3.36 (br, 2H), 3.22 (br, 1H), 3.01 (br, 1H), 2.09 (p, *J* = 7.6 Hz, 1H), 1.79 (dt, *J* = 12.1, 6.1 Hz, 1H), 1.77 – 1.69 (m, 6H), 1.63 – 1.54 (m, 1H), 1.44 (s, 9H), 1.22 (s, 12H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.7, 83.4, 79.0, 50.0, 48.1, 46.5, 45.9, 40.8, 40.0, 28.7, 28.4, 27.7, 24.9. [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) (193 MHz, $CDCl_3$) δ 30.8. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{20}H_{34}BNO_4Na$ $[M+Na]^+$: 386.2473, found: 386.2472.

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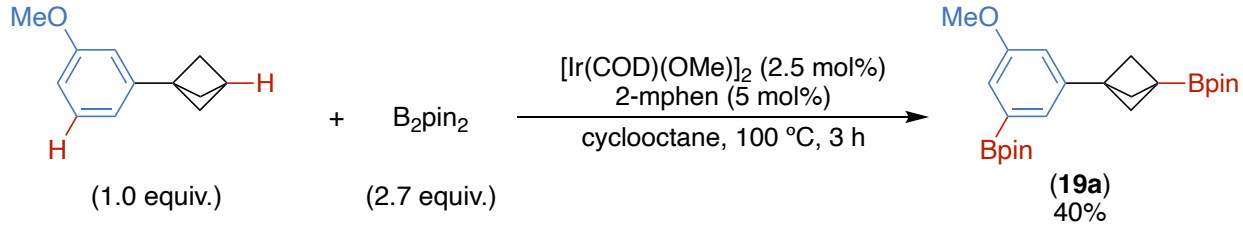
2-(3-methoxy-5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19a)



Prepared according to General Procedure A on a 0.1 mmol scale with 2.7 equiv. of B_2pin_2. The reaction mixture was heated for 3 h, rather than the usual 2 h. The crude reaction mixture was eluted on SiO_2 with 10% → 80% ethyl acetate in hexanes as the eluent to afford 17.1 mg (40%) of the title compound as a white powder.

TLC: R_f = 0.5 (10% ethyl acetate in hexanes)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (d, J = 1.4 Hz, 1H), 7.17 (d, J = 2.6 Hz, 1H), 6.83 (d, J = 1.2 Hz, 1H), 3.82 (s, 3H), 2.15 (s, 6H), 1.34 (s, 12H), 1.26 (s, 12H) [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 143.4, 124.6, 116.7, 115.8, 84.0, 83.5, 55.4, 53.2, 47.4, 25.0, 24.9, 24.9. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 31.5. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{24}H_{36}B_2O_5$ $[M+H]^+$: 427.2822, found: 427.2821.

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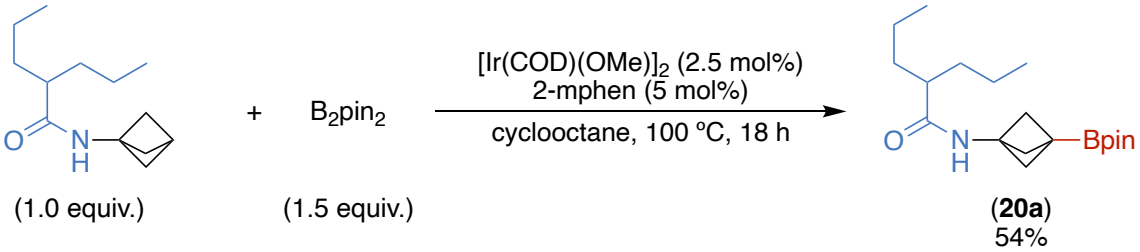
2-propyl-*N*-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)pentanamide (20a)



(1.0 equiv.) (1.5 equiv.) (**20a**) 54%

Prepared according to General Procedure A on a 0.48 mmol scale and a reaction time of 18 h. The crude reaction mixture was eluted on SiO_2 with 0% → 40% ethyl acetate in heptanes as the eluent to afford 87.0 mg (54%) of the title compound as a white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (br s, 1 H), 2.15 (s, 6 H), 1.81 - 1.93 (m, 1 H), 1.49 - 1.62 (m, 4 H), 1.28 - 1.32 (m, 4 H), 1.24 (s, 12 H), 0.88 (t, J=7.17 Hz, 6 H). [See spectrum]

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3 (s, 1 C), 83.4 (s, 2 C), 54.1 (s, 3 C), 48.3 (s, 1 C), 47.7 (s, 1 C), 35.1 (s, 2 C), 24.7 (s, 4 C), 21.3 (br s, 1 C), 20.8 (s, 2 C), 14.1 (s, 2 C). [See spectrum]

HRMS (ESI-TOF) Calculated for $C_{19}H_{35}BNO_3$ $[M+H]^+$: 336.2631; Found: 336.2713.

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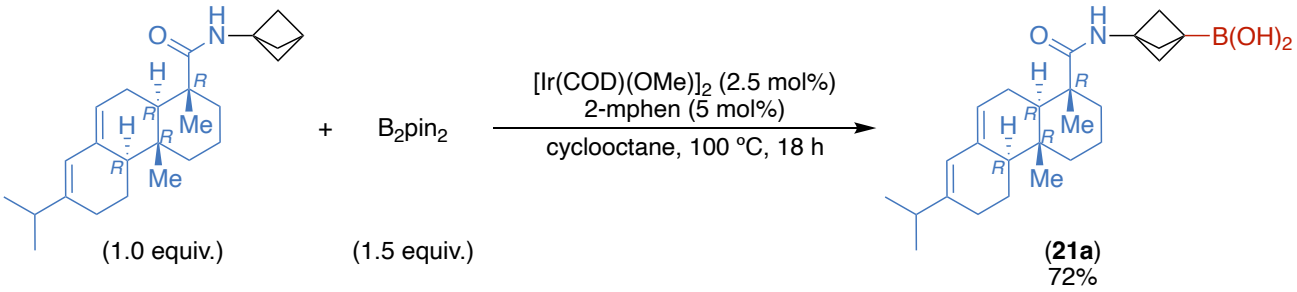
(3-((1*R*,4a*R*,4b*R*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthrene-1-carboxamido)bicyclo[1.1.1]pentan-1-yl)boronic acid (21a)



Prepared according to General Procedure A on a 0.27 mmol scale. The crude reaction mixture was eluted on SiO_2 with 0% → 10% methanol in dichloromethane as the eluent. The desired fractions were collected, and the solvents evaporated in vacuo. The crude material was further purified by RP HPLC (Stationary phase: C18 XBridge 30 x 100 mm 5 µm), Mobile phase: Gradient from 90% NH_4HCO_3 0.25% solution in Water, 10% CH_3CN to 10% NH_4HCO_3 0.25% solution in Water, 90% CH_3CN) to afford 81.0 mg (72%) of the title compound as a white powder.

^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 5.93 - 6.21 (m, 1 H) 5.76 (s, 1 H) 5.07 - 5.58 (m, 2 H) 2.18 - 2.26 (m, 1 H) 2.13 (s, 6 H) 1.65 - 2.10 (m, 9 H) 1.46 - 1.63 (m, 3 H) 1.09 - 1.25 (m, 5 H) 1.01 (br d, *J*=6.70 Hz, 3 H) 1.00 (d, *J*=6.90 Hz, 3 H) 0.81 (s, 3 H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 178.6 (s, 1 C), 145.4 (s, 1 C), 135.5 (s, 1 C), 122.3 (s, 1 C), 120.7 (s, 1 C), 54.0 (s, 1 C), 53.7 (s, 1 C), 51.0 (s, 1 C), 46.0 (s, 1 C), 41.0 (s, 1 C), 38.4 (s, 1 C), 37.4 (s, 1 C), 34.9 (s, 1 C), 34.7 (s, 1 C), 27.5 (s, 1 C), 25.3 (s, 1 C), 24.8 (s, 1 C), 22.5 (s, 1 C), 21.4 (s, 1 C), 20.9 (s, 1 C), 18.4 (s, 1 C), 16.9 (s, 1 C), 14.1 (s, 1 C). [See spectrum]

HRMS (ESI-TOF) Calculated for $C_{25}H_{38}BNO_3$ $[M+H]^+$: 412.2944; Found: 412.3024.

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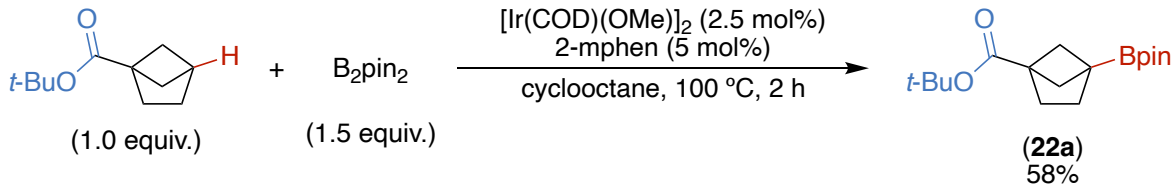
5.3 Bicyclo[2.1.1]hexane Substrates

tert-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[2.1.1]hexane-1-carboxylate (22a)



Prepared according to General Procedure A on a 0.10 mmol scale. The crude reaction mixture was eluted on reverse phase silica with 40% → 100% acetonitrile in water as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford 17.9 mg (58%) of the title compound as an off-white solid.

TLC: R_f = 0.68 (50% acetonitrile in water)

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.86 (ddd, J = 7.2, 4.0, 1.6 Hz, 4H), 1.83 – 1.77 (m, 2H), 1.43 (s, 9H), 1.34 (dd, J = 4.3, 2.0 Hz, 2H), 1.23 (s, 12H) [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 173.6, 83.3, 79.8, 54.7, 43.7, 30.2, 30.0, 28.2, 24.9. [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) δ 32.3. [See spectrum]

HRMS (*m/z*): (EI+) calc'd for $C_{16}H_{26}BO_4$ $[M\text{-}Me]^+$: 293.1924, found: 293.1921.

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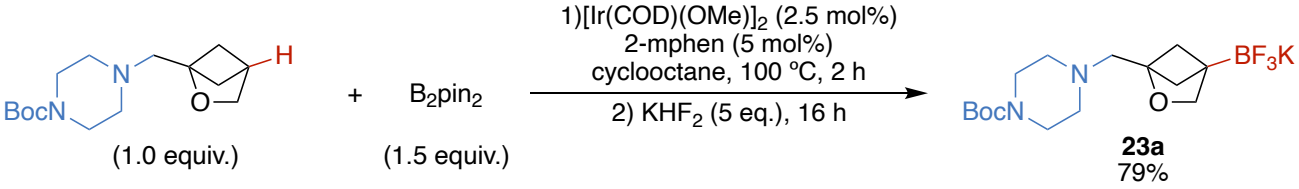
***tert*-butyl 4-((4-(trifluoro-λ4-boraneyl)-2-oxabicyclo[2.1.1]hexan-1-yl)methyl)piperazine-1-carboxylate, potassium salt (23a)**



Prepared according to General Procedure C on a 0.10 mmol scale. After washing with pentanes, 30.7 mg (79%) of the title compound was isolated as an off-white powder.

TLC: R_f = N/A

^{1}H NMR (600 MHz, Acetone) δ 3.57 (s, 2H), 3.37 – 3.29 (m, 4H), 2.55 (s, 2H), 2.46 – 2.41 (m, 4H), 1.50 – 1.46 (m, 2H), 1.42 (s, 9H), 1.20 – 1.16 (m, 2H). [See spectrum]

^{13}C NMR (151 MHz, Acetone) δ 155.1, 88.8, 79.4, 74.2, 60.9, 55.0, 43.8, 28.6. [See spectrum]

^{11}B NMR (193 MHz, Acetone) δ 2.6. [See spectrum]

^{19}F NMR (565 MHz, Acetone) δ -146.9. [See spectrum]

HRMS (*m/z*): (ESI-) calc'd for $C_{15}H_{25}BF_3N_2O_3$ $[M\text{-}K]^-$: 349.1916, found: 349.1915.

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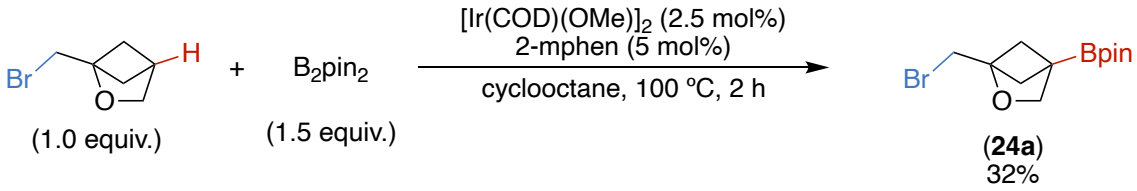
2-(1-(bromomethyl)-2-oxabicyclo[2.1.1]hexan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24a)



Prepared according to General Procedure A on a 0.10 mmol scale. The crude reaction mixture was eluted on reverse phase silica with 40% → 100% acetonitrile in water as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford 9.8 mg (32%) of the title compound as an off-white solid.

TLC: R_f = 0.56 (50% acetonitrile in water)

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.91 (s, 2H), 3.60 (s, 2H), 1.89 (dd, *J* = 4.7, 1.9 Hz, 2H), 1.63 – 1.59 (m, 2H), 1.25 (s, 12H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 88.0, 83.8, 72.8, 43.5, 31.5, 24.9. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 31.9. [See spectrum]

HRMS (*m/z*): (EI+) calc'd for $C_{11}H_{17}BBrO_3$ $[M\text{-}Me]^+$: 289.0434, found: 289.0436.

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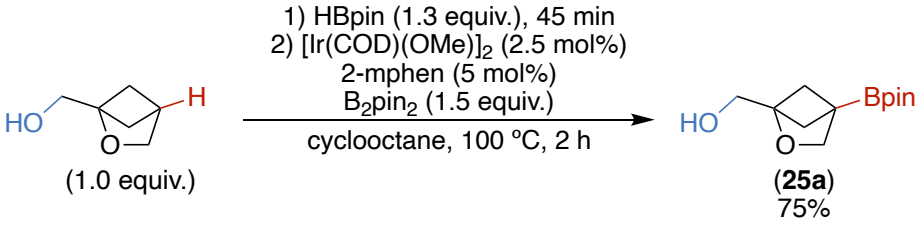
(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-oxabicyclo[2.1.1]hexan-1-yl)methanol (25a)



Prepared according to General Procedure B on a 0.10 mmol scale. The crude reaction mixture was eluted on reverse phase silica with 40% → 100% acetonitrile in water as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford 18.0 mg (75%) of the title compound as a clear oil.

TLC: R_f = 0.9 (50% acetonitrile in water)

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86 (s, 2H), 3.80 (d, J = 5.7 Hz, 2H), 1.92 (t, J = 6.1 Hz, 1H), 1.82 (dd, J = 4.7, 1.9 Hz, 2H), 1.57 (dd, J = 4.7, 1.9 Hz, 2H), 1.25 (s, 12H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 83.4, 79.2, 55.0, 51.8, 50.0, 44.7, 37.9, 28.6, 26.8, 24.9. [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) δ 31.6. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{12}H_{21}BO_4Na$ $[M+Na]^+$: 263.1425, found: 263.1425.

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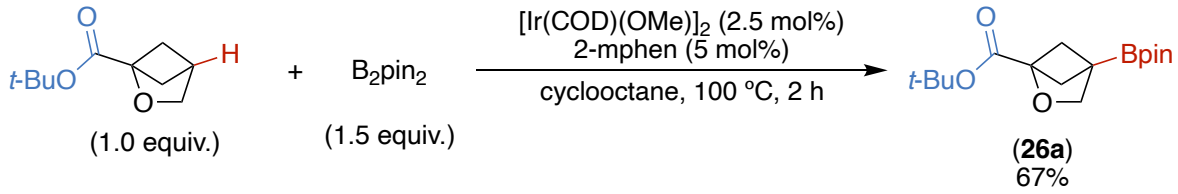
***tert*-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-oxabicyclo[2.1.1]hexane-1-carboxylate (26a)**



Prepared according to General Procedure A on a 0.10 mmol scale. The crude reaction mixture was eluted on reverse phase silica with 40% → 100% acetonitrile in water as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford 20.9 mg (67%) of the title compound as an off-white solid.

TLC: R_f = 0.56 (50% acetonitrile in water)

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.94 (s, 2H), 2.20 (dd, J = 4.6, 1.8 Hz, 2H), 1.76 (dd, J = 4.7, 1.8 Hz, 2H), 1.48 (s, 9H), 1.25 (s, 12H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.7, 87.2, 83.9, 81.9, 72.5, 44.5, 28.2, 28.0, 24.9. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 31.8. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{16}H_{27}BO_5Na$ $[M+Na]^+$: 333.1844, found: 333.1841.

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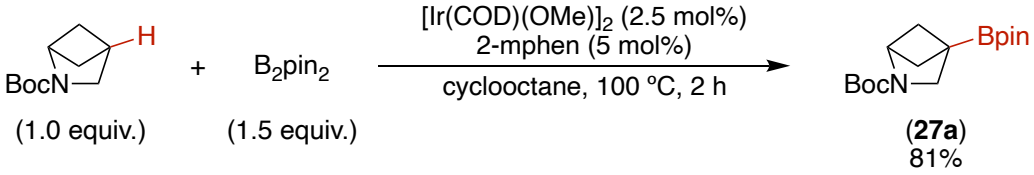
***tert*-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azabicyclo[2.1.1]hexane-2-carboxylate (27a)**



Prepared according to General Procedure A on a 0.10 mmol scale. The crude reaction mixture was eluted on reverse phase silica with 40% → 100% acetonitrile in water as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford 25.1 mg (87%) of the title compound as an off-white solid.

TLC: R_f = 0.52 (50% acetonitrile in water)

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.36 (s, 1H), 3.36 (s, 2H), 2.00 – 1.92 (m, 2H), 1.45 (s, 9H), 1.43 – 1.37 (m, 2H), 1.24 (s, 12H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.2, 82.6, 78.0, 60.8, 50.3, 41.3, 28.7, 27.5, 27.5, 23.7. [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) δ 31.5. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{16}H_{28}BNO_4$ $[M+Na]^+$: 332.2004, found: 332.1997.

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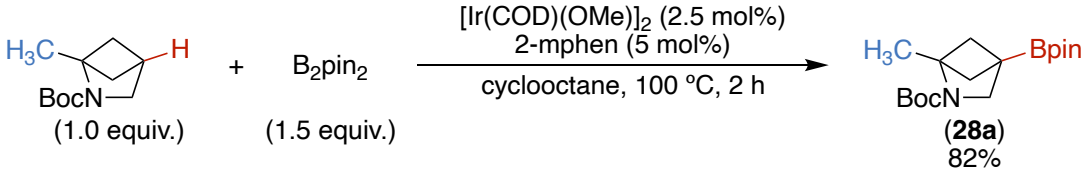
tert-butyl 1-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azabicyclo[2.1.1]hexane-2-carboxylate (28a)



Prepared according to General Procedure A on a 0.10 mmol scale. The crude reaction mixture was eluted on reverse phase silica with 40% → 100% acetonitrile in water as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford 26.6 mg (82%) of the title compound as a white powder.

TLC: R_f = 0.50 (50% acetonitrile in water)

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.42 (s, 2H), 1.79 – 1.72 (m, 2H), 1.66 (s, 3H), 1.55 – 1.48 (m, 2H), 1.44 (s, 9H), 1.24 (s, 12H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 83.4, 79.2, 55.0, 51.8, 50.0, 44.7, 37.9, 28.6, 26.8, 24.9. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 32.0. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{17}H_{31}BNO_4$ $[M+H]^+$: 324.2341, found: 324.2337.

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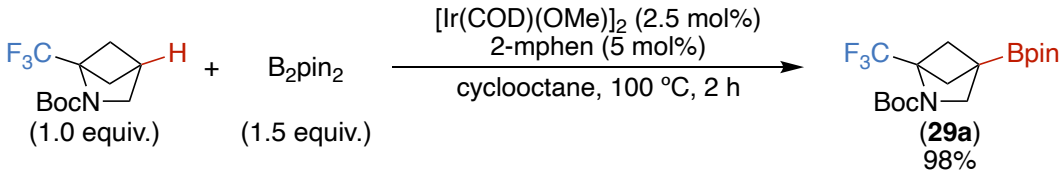
***tert*-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(trifluoromethyl)-2-azabicyclo[2.1.1]hexane-2-carboxylate (29a)**



Prepared according to General Procedure A on a 0.10 mmol scale. The crude reaction mixture was eluted on reverse phase silica with 40% → 100% acetonitrile in water as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford 37.0 mg (98%) of the title compound as an off-white solid.

TLC: R_f = 0.50 (50% acetonitrile in water)

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.54 (s, 2H), 2.26 – 2.19 (m, 2H), 1.73 – 1.69 (m, 2H), 1.46 (s, 9H), 1.25 (s, 12H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.5, 122.8 (q, J_{C-F} = 275.2 Hz), 84.2, 80.4, 70.8 (q, J_{C-F} = 36.9 Hz), 54.7, 42.5, 28.4, 24.9. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 31.4. [See spectrum]

^{19}F NMR (565 MHz, $CDCl_3$) δ -68.6. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{17}H_{27}BF_3NO_4Na$ $[M+Na]^+$: 400.1877, found:400.1876.

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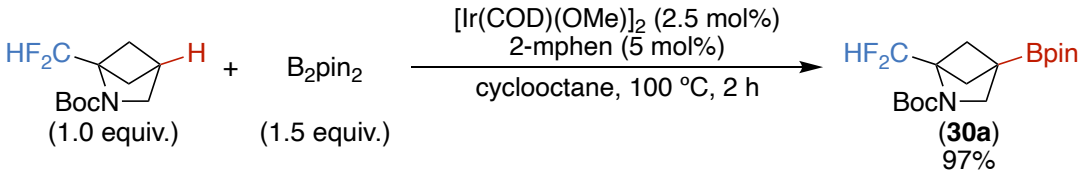
***tert*-butyl 1-(difluoromethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azabicyclo[2.1.1]hexane-2-carboxylate (30a)**



Prepared according to General Procedure A on a 0.10 mmol scale. The crude reaction mixture was eluted on reverse phase silica with 40% → 100% acetonitrile in water as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford 34.8 mg (97%) of the title compound as an off-white solid.

TLC: R_f = 0.4 (50% acetonitrile in water)

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.68 (t, $J_{F–H}$ = 56.1 Hz, 1H), 3.49 (s, 2H), 2.18 – 2.10 (m, 2H), 1.60 – 1.53 (m, 2H), 1.46 (s, 9H), 1.26 (s, 12H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.9, 112.48 (t, $J_{C–F}$ = 236.9 Hz), 84.0, 80.3, 72.6 (t, $J_{C–F}$ = 31.0 Hz), 54.7, 41.0, 28.6, 24.9. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 31.8. [See spectrum]

^{19}F NMR (565 MHz, $CDCl_3$) δ -124.8. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{17}H_{28}BF_2NO_4Na$ $[M+Na]^+$: 382.1972, found: 382.1970.

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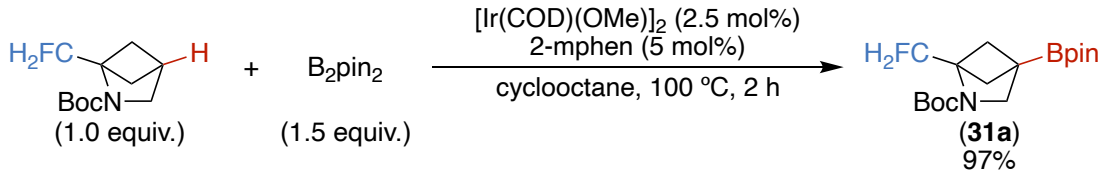
***tert*-butyl 1-(fluoromethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azabicyclo[2.1.1]hexane-2-carboxylate (31a)**



Prepared according to General Procedure A on a 0.10 mmol scale. The crude reaction mixture was eluted on reverse phase silica with 40% → 100% acetonitrile in water as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford 33.0 mg (97%) of the title compound as an off-white solid.

TLC: R_f = 0.45 (50% acetonitrile in water)

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.90 (d, $J_{F–H}$ = 47.9 Hz, 2H), 3.46 (s, 2H), 2.30 – 2.04 (m, 2H), 1.50 – 1.46 (m, 2H), 1.44 (s, 9H), 1.25 (s, 12H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.8, 83.8, 82.0 (d, $J_{C–F}$ = 161.0 Hz), 79.7, 72.5 (d, $J_{C–F}$ = 28.7 Hz), 54.5, 42.6, 28.6, 24.9. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 31.8. [See spectrum]

^{19}F NMR (565 MHz, $CDCl_3$) δ -220.1. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{17}H_{29}BFNO_4Na$ $[M+Na]^+$: 364.2066, found: 364.2058.

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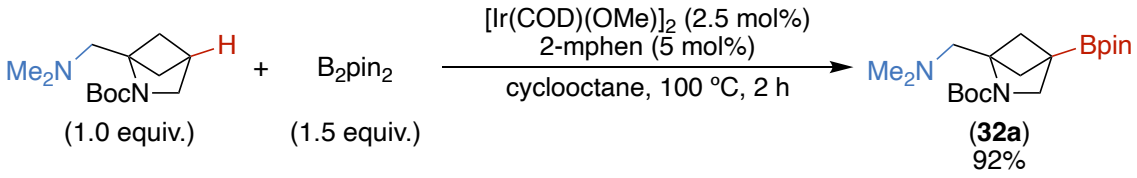
***tert*-butyl 1-((dimethylamino)methyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azabicyclo[2.1.1]hexane-2-carboxylate (32a)**



Prepared according to General Procedure A on a 0.10 mmol scale. The crude reaction mixture was eluted on reverse phase silica with 40% → 100% acetonitrile in water as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford 33.6 mg (92%) of the title compound as a brown solid.

TLC: R_f = 0.8 (50% acetonitrile in water)

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.43 (s, 2H), 3.01 (s, 2H), 2.28 (s, 6H), 2.07 – 2.03 (m, 2H), 1.56 – 1.45 (m, 2H), 1.44 (s, 9H), 1.23 (s, 12H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 156.4, 83.6, 79.0, 75.1, 60.1, 55.2, 47.6, 43.8, 28.8, 24.9. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 32.1. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{19}H_{36}BN_2O_4$ $[M+H]^+$: 367.2763, found: 367.2760.

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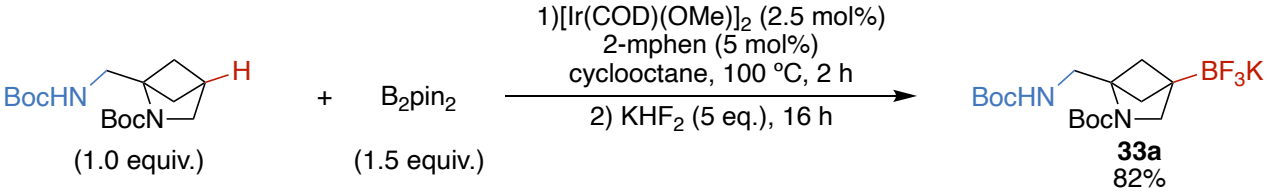
***tert*-butyl 1-(((*tert*-butoxycarbonyl)amino)methyl)-4-(trifluoro-λ4-boraneyl)-2-azabicyclo[2.1.1]hexane-2-carboxylate, potassium salt (33a)**



Prepared according to General Procedure C on a 0.10 mmol scale. After washing with pentanes, 34.5 mg (82%) of the title compound was obtained as an off-white solid.

TLC: R_f = N/A

^{1}H NMR (500 MHz, Acetone) δ 5.89 (s, 1H), 3.59 – 3.54 (m, 2H), 3.19 (s, 2H), 1.57 – 1.50 (m, 2H), 1.43 (s, 9H), 1.39 (s, 9H), 1.20 – 1.11 (m, 2H). [See spectrum]

^{13}C NMR (126 MHz, Acetone) δ 156.6, 156.1, 78.4, 78.3, 73.8, 56.9, 43.6, 42.6, 28.9, 28.6. [See spectrum]

^{11}B NMR (160 MHz, Acetone) δ 3.6. [See spectrum]

^{19}F NMR (470 MHz, Acetone) δ -147.7. [See spectrum]

HRMS (*m/z*): (ESI-) calc'd for $C_{16}H_{27}BF_3N_2O_4$ $[M\text{-}K]^-$: 379.2021, found: 379.2017.

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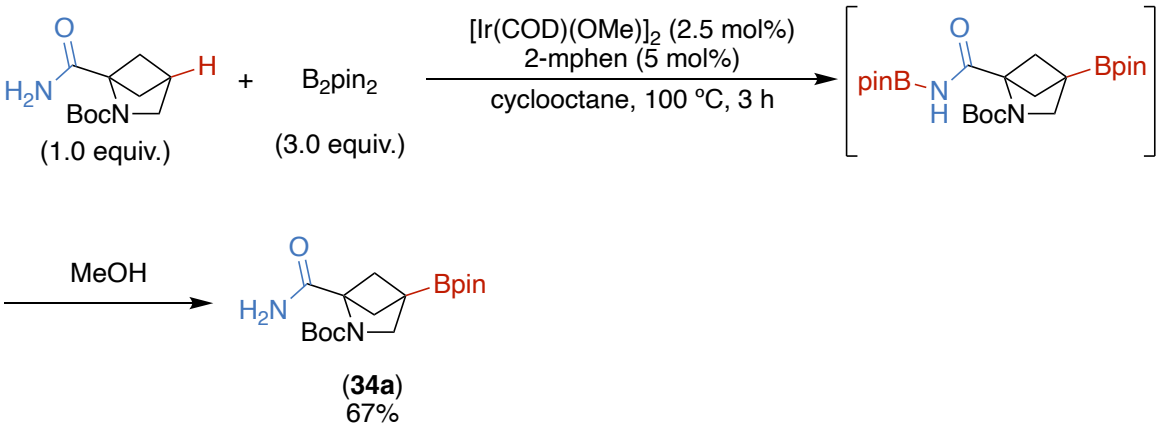
***tert*-butyl 1-carbamoyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azabicyclo[2.1.1]hexane-2-carboxylate (34a)**



Prepared according to General Procedure A on a 0.10 mmol scale with 3 equiv. of B_2pin_2 instead of the usual 1.5 equiv. The crude material was co-evaporated with methanol at 45 °C (30 mL x 2). The residue was washed repeatedly with pentane to afford 23.6 mg (67%) of the title compound as a brown solid.

TLC: R_f = N/A

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.85 (br s, 1H), 5.66 (br s, 1H), 3.53 (s, 2H), 2.24 – 2.17 (m, 2H), 1.69 – 1.65 (m, 2H), 1.43 (s, 9H), 1.24 (s, 12H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 158.3, 84.0, 81.1, 73.0, 55.6, 44.2, 28.4, 24.9. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 31.7. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{17}H_{30}BN_2O_5$ $[M+H]^+$: 353.2242, found: 353.2238.

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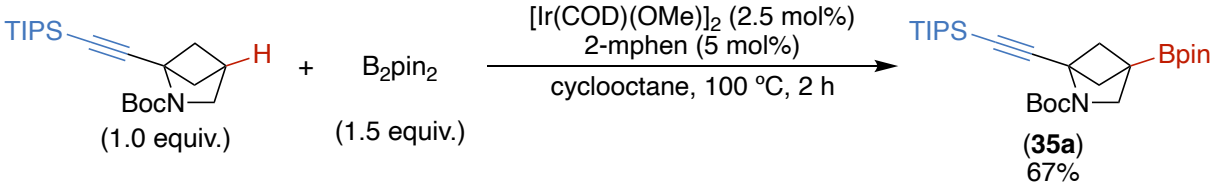
***tert*-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-((triisopropylsilyl)ethynyl)-2-azabicyclo[2.1.1]hexane-2-carboxylate (35a)**



Prepared according to General Procedure A on a 0.05 mmol scale. The crude reaction mixture was eluted on reverse phase silica with 50% → 100% acetonitrile in water as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford 16.3 mg (67%) of the title compound as an off-white solid.

TLC: R_f = 0.68 (50% acetonitrile in water)

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.44 (s, 2H), 2.14 (dd, *J* = 4.8, 1.8 Hz, 2H), 1.78 (dd, *J* = 4.6, 2.0 Hz, 2H), 1.47 (s, 9H), 1.24 (s, 12H), 1.07 (m, *J* = 3.9 Hz, 21H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.2, 104.6, 88.1, 83.9, 80.0, 62.3, 54.2, 48.8, 28.6, 24.9, 18.8, 11.4. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 32.1. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{27}H_{49}BNO_4Si$ $[M+H]^+$: 490.3518, found: 490.3517.

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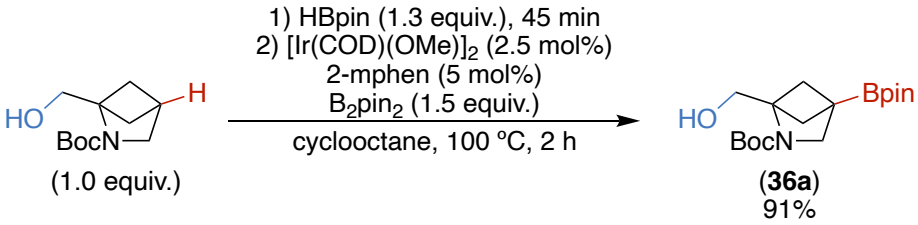
***tert*-butyl 1-(hydroxymethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azabicyclo[2.1.1]hexane-2-carboxylate (36a)**



Prepared according to General Procedure B on a 0.10 mmol scale. The crude reaction mixture was eluted on reverse phase silica with 40% → 100% acetonitrile in water as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford 30.8 mg (91%) of the title compound as an off-white solid.

TLC: R_f = 0.9 (50% acetonitrile in water)

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.92 (br s, 1H), 3.88 (d, J = 6.4 Hz, 2H), 3.43 (s, 2H), 1.86 – 1.78 (m, 2H), 1.60 – 1.56 (m, 2H), 1.46 (s, 9H), 1.25 (s, 12H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.8, 83.8, 79.9, 75.3, 61.9, 54.4, 43.5, 28.7, 24.9. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 32.0. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{17}H_{31}BNO_5$ $[M+H]^+$: 340.2290, found: 340.2290.

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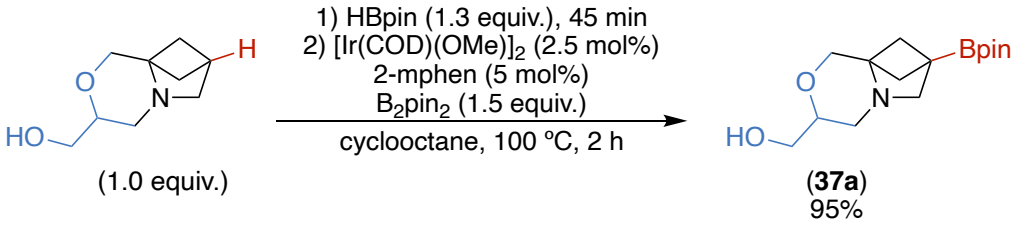
(7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetrahydro-1*H*,6*H*-7,8a-methanopyrrolo[2,1-*c*][1,4]oxazin-3-yl)methanol (37a)



Prepared according to General Procedure B on a 0.10 mmol scale. The crude reaction mixture was eluted on reverse phase silica with 40% → 100% acetonitrile in water as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford 28.0 mg (95%) of the title compound as an off-white solid.

TLC: R_f = 0.9 (50% acetonitrile in water)

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.94 (d, *J* = 11.8 Hz, 1H), 3.76 – 3.68 (m, 2H), 3.67 – 3.54 (m, 2H), 3.24 (d, *J* = 8.2 Hz, 1H), 2.90 (dd, *J* = 11.1, 2.3 Hz, 1H), 2.44 – 2.40 (m, 3H), 1.77 (dd, *J* = 10.2, 7.6 Hz, 1H), 1.72 (d, *J* = 6.9 Hz, 1H), 1.54 (d, *J* = 7.5 Hz, 1H), 1.42 (dd, *J* = 10.2, 7.0 Hz, 1H), 1.24 (s, 12H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 83.6, 69.4, 68.3, 64.3, 59.3, 52.8, 42.2, 37.3, 24.9. [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) δ 32.0. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{15}H_{27}BNO_4$ $[M+H]^+$: 296.2028, found: 296.2027.

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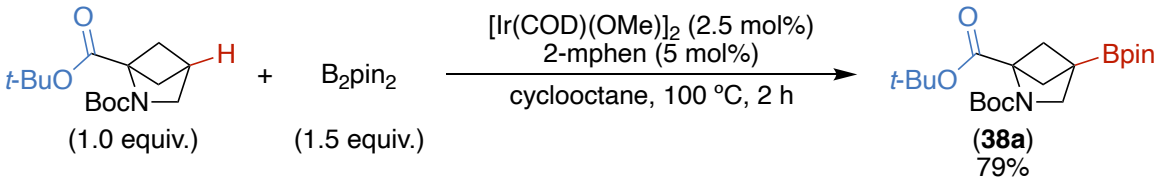
di-*tert*-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azabicyclo[2.1.1]hexane-1,2-dicarboxylate (38a)



Prepared according to General Procedure A on a 0.10 mmol scale. The crude reaction mixture was eluted on reverse phase silica with 40% → 100% acetonitrile in water as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford 32.5 mg (79%) of the title compound as a colorless oil.

TLC: R_f = 0.8 (50% acetonitrile in water)

^{1}H NMR (600 MHz, $CDCl_3$) δ 3.47 (s, 2H), 2.14 – 2.07 (m, 2H), 1.67 – 1.61 (m, 2H), 1.47 (s, 9H), 1.44 (s, 9H), 1.24 (s, 12H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0, 158.0, 83.9, 81.0, 80.3, 71.9, 55.1, 44.1, 28.5, 28.2, 24.9. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 31.9. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{21}H_{37}BNO_6$ $[M+H]^+$: 410.2708, found: 410.2703.

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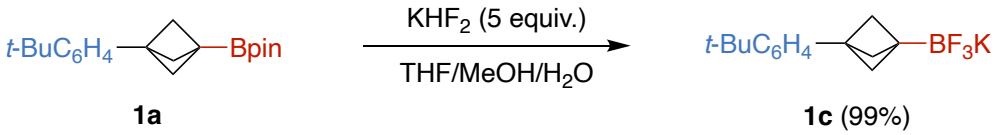
6. Transformations of bridgehead C–Bpin bonds

(3-(4-(*tert*-butyl)phenyl)bicyclo[1.1.1]pentan-1-yl)trifluoro-λ4-borane, potassium salt (1c)



1a **1c** (99%)

1a (70.0 mg, 0.215 mmol) was dissolved in a mixture of MeOH (0.6 mL) and THF (0.3 mL). Then, KHF_2 (84.0 mg, 1.08 mmol, 5.00 equiv.) in water (0.3 mL) was added with vigorous stirring. The resulting mixture was stirred at room temperature overnight. The reaction mixture was co-evaporated with 1:1 methanol:water repeatedly (2 mL x 5) to remove pinacol. The solid residue was extracted with acetone, filtered, and the filtrate concentrated. The resulting solids were washed with pentane to afford 66.2 mg (99%) of the title compound as an off-white powder.

TLC: N/A

^{1}H NMR (600 MHz, Acetone) δ 7.27 (d, *J* = 8.2 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 1.74 (s, 6H), 1.27 (s, 9H). [See spectrum]

^{13}C NMR (151 MHz, Acetone) δ 148.6, 142.7, 126.1, 125.4, 52.2, 52.1, 45.0, 34.8, 31.7. [See spectrum]

^{11}B NMR (193 MHz, Acetone) δ 1.6. [See spectrum]

^{19}F NMR (565 MHz, Acetone) δ -147.6. [See spectrum]

HRMS (*m/z*): (ESI-) calc'd for $C_{15}H_{19}BF_3$ $[M\text{-}K]^+$: 267.1537, found: 267.1537.

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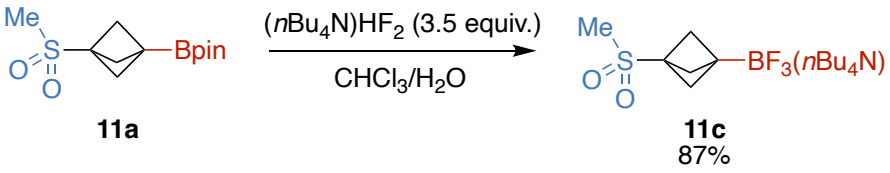
(3-(methylsulfonyl)bicyclo[1.1.1]pentan-1-yl)trifluoro-λ4-borane, tetrabutylammonium salt (11c)



11a (204 mg, 0.750 mmol) and (nBu$_4$N)HF$_2$ (739 mg, 2.62 mmol, 3.50 equiv.) were mixed and chloroform (5.0 mL) and water (10.0 mL) was added. The biphasic mixture with stirred vigorously for 16 h. The layers were separated, and the aqueous layer was further extracted with chloroform (10 mL x 2). The combined organic layers were dried with MgSO$_4$, filtered, and concentrated to afford 298 mg (87%) of the title compound as a colorless oil that solidified upon standing.

TLC: N/A

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.26 – 3.19 (m, 8H), 2.72 (s, 3H), 1.99 (s, 6H), 1.62 (p, J = 7.7 Hz, 8H), 1.43 (h, J = 7.4 Hz, 8H), 1.00 (t, J = 7.3 Hz, 12H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 58.9, 49.7, 49.7, 36.5, 25.0, 24.1, 19.8, 13.8. [See spectrum]

^{11}B NMR (160 MHz, $CDCl_3$) δ 2.3. [See spectrum]

^{19}F NMR (470 MHz, $CDCl_3$) δ -147.05. [See spectrum]

HRMS (*m/z*): (ESI-) calc'd for $C_6H_9BF_3O_2S$ [M-nBu$_4$N]$^+$: 213.0374, found: 213.0373.

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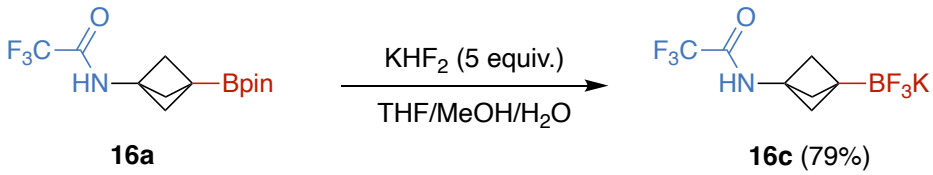
2,2,2-trifluoro-*N*-(3-(trifluoro-λ4-boraneyl)bicyclo[1.1.1]pentan-1-yl)acetamide, potassium salt (16c)



16a **16c** (79%)

16a (30.5 mg, 0.100 mmol) was dissolved in a mixture of MeOH (0.3 mL) and THF (0.15 mL). Then, KHF_2 (39.1 mg, 0.50 mmol, 5.00 equiv.) in water (0.15 mL) was added with vigorous stirring. The resulting mixture was stirred at room temperature overnight. The reaction mixture was co-evaporated with 1:1 methanol:water repeatedly (1 mL x 5) to remove pinacol. The solid residue was extracted with acetone, filtered, and the filtrate concentrated. The resulting solids were washed with pentane to afford the title compound as an off-white powder (22.6 mg, 79%)

TLC: N/A

^{1}H NMR (500 MHz, Acetone) δ 8.51 (bs, 1H), 1.78 (s, 6H). [See spectrum]

^{13}C NMR (151 MHz, Acetone) δ 156.90 (q, J_{C-F} = 35.5 Hz), 117.00 (q, J_{C-F} = 288.8 Hz), 54.3, 52.8, 47.2. [See spectrum]

^{11}B NMR (160 MHz, Acetone) δ 1.9. [See spectrum]

^{19}F NMR (470 MHz, Acetone) δ -77.7, -146.9. [See spectrum]

HRMS (*m/z*): (ESI-) calc'd for $C_7H_7BF_6KNO$ $[M-K]^+$: 246.0530, found: 246.0529.

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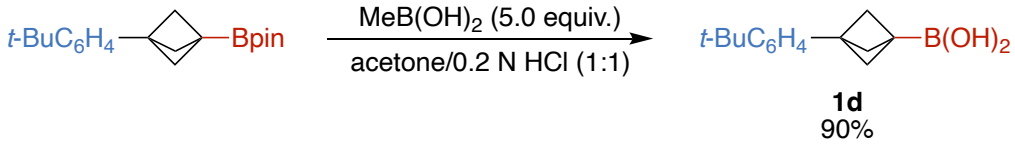
(3-(4-(*tert*-butyl)phenyl)bicyclo[1.1.1]pentan-1-yl)boronic acid (1d)



1d
90%

A 20 mL vial was charged with **1a** (42.4 mg, 0.130 mmol, 1.00 equiv.) and methyl boronic acid (38.9 mg, 0.650 mmol, 5.00 equiv.). Acetone (2 mL) and 0.2 N HCl (aq) (2 mL) were added in a 1:1 ratio. The vial was capped under ambient atmosphere and the reaction was stirred at room temperature for 16 h. The reaction mixture was concentrated to dryness, redissolved in acetone, and dried *in vacuo*. The residue was washed with pentanes and dried *in vacuo* to obtain the title compound as an off-white powder (28.5 mg, 90%).

TLC: N/A

^{1}H NMR (600 MHz, Acetone) δ 7.36 – 7.28 (m, 2H), 7.16 – 7.07 (m, 2H), 2.07 (s, 6H), 1.28 (s, 9H). [See spectrum]

^{13}C NMR (151 MHz, Acetone) δ 148.8, 139.6, 125.2, 124.8, 52.5, 45.8, 34.0, 30.8. [See spectrum]

^{11}B NMR (193 MHz, Acetone) δ 28.4. [See spectrum]

HRMS (*m/z*): (ESI-) calc'd for $C_{15}H_{20}BO_2$ $[M-H]^-$: 243.1562, found: 243.1560.

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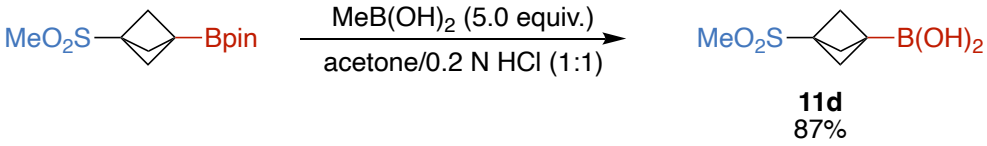
(3-(methylsulfonyl)bicyclo[1.1.1]pentan-1-yl)boronic acid (11d)



11d
87%

A 20 mL vial was charged with **11a** (81.6 mg, 0.300 mmol, 1.00 equiv.) and methyl boronic acid (89.8 mg, 1.50 mmol, 5.00 equiv.). Acetone (4 mL) and 0.2 N HCl (aq) (4 mL) were added in a 1:1 ratio. The vial was capped under ambient atmosphere, and the reaction was stirred at room temperature for 16 h. The reaction mixture was concentrated to dryness, redissolved in acetone, and dried *in vacuo*. The residue was washed with ether and dried *in vacuo* to obtain the title compound as an off-white powder (49.6 mg, 87%).

TLC: N/A

^{1}H NMR (500 MHz, Acetone) δ 2.77 (s, 3H), 2.17 (s, 6H). [See spectrum]

^{13}C NMR (151 MHz, Acetone) δ 54.5, 51.4, 36.9. [See spectrum]

^{11}B NMR (193 MHz, Acetone) δ 28.7. [See spectrum]

HRMS (*m/z*): (ESI-) calc'd for $C_6H_{10}BO_4S$ $[M-H]^-$: 189.0398, found: 189.0397.

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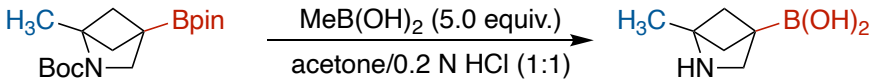
(1-methyl-2-azabicyclo[2.1.1]hexan-4-yl)boronic acid (28c)



A 20 mL vial was charged with **28a** (18 mg, 0.077 mmol, 1.0 equiv.) and methyl boronic acid (22 mg, 0.77 mmol, 10 equiv.). Acetone (1 mL) and 0.2 N HCl (aq) (1 mL) were added in a 1:1 ratio. The vial was capped under ambient atmosphere, and the reaction was stirred at room temperature for 22 h. The reaction mixture was concentrated to dryness, redissolved in acetone, and dried *in vacuo*. The residue was washed with pentane and dried *in vacuo* to obtain the title compound as a pale-yellow powder (9.6 mg, 88%).

TLC: N/A

^{1}H NMR (600 MHz, Acetone) δ 3.63 (s, 2H), 2.13 – 2.06 (m, 2H), 1.94 – 1.86 (m, 2H), 1.73 (s, 3H).

^{13}C NMR (151 MHz, Acetone) δ 71.5, 51.7, 43.2, 15.8.

^{11}B NMR (193 MHz, Acetone) δ 28.5, 19.2.

HRMS (*m/z*): (ESI+) calc'd for $C_{12}H_{24}B_2N_2O_4K$ $[2M+K]^+$: 321.1554, found: 321.1563.

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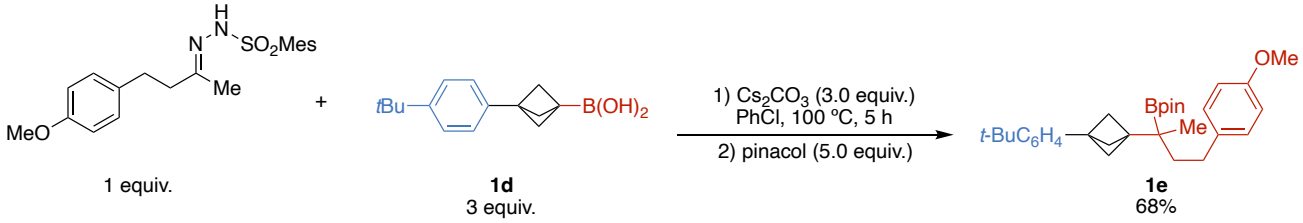
2-(2-(3-(4-(*tert*-butyl)phenyl)bicyclo[1.1.1]pentan-1-yl)-4-(4-methoxyphenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1e)



The reaction was conducted following Qin's procedure.[11] A 4 mL vial was charged with *N*'-(4-(4-methoxyphenyl)butan-2-ylidene)-2,4,6-trimethylbenzenesulfonohydrazide (mixture of isomers, 18.7 mg, 0.0500 mmol, 1.00 equiv.), **1d** (36.6 mg, 0.150 mmol, 3.00 equiv.), and cesium carbonate (48.9 mg, 0.150 mmol, 3.00 equiv.) and brought into the glovebox. Chlorobenzene (0.5 mL) and a stir bar were added, the vial was capped with a Teflon-lined cap, removed from the glovebox, and heated at 100 ºC in a preheated aluminum heating block for 5 h. The vial was cooled to room temperature, and pinacol (29.5 mg, 0.250 mmol, 5.00 equiv.) was added as a solid. The mixture was again heated at 100 ºC in an aluminum heating block for 1 h. The crude reaction mixture was chromatographed twice on silica gel (0 → 10% ethyl acetate in hexanes, then again with 2 → 3% ethyl acetate in hexanes) to afford the title compound as a white powder (15.5 mg, 63%).

TLC: R_f = 0.6 (10% ethyl acetate in hexanes)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.3 Hz, 2H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.56 (td, *J* = 13.0, 5.0 Hz, 1H), 2.45 (td, *J* = 13.0, 4.4 Hz, 1H), 1.91 – 1.82 (m, 6H), 1.30 (s, 9H), 1.28 (s, 12H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.8, 149.1, 139.0, 136.0, 129.4, 125.9, 125.1, 113.9, 83.4, 55.4, 50.0, 44.6, 40.4, 38.9, 34.6, 32.7, 31.5, 25.3, 25.1, 18.0. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 34.6. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{32}H_{46}BO_3$ $[M+H]^+$: 489.3535, found: 489.3529.

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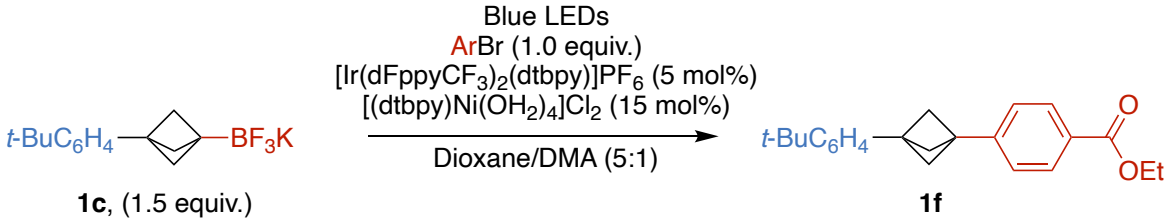
ethyl 4-(3-(4-(*tert*-butyl)phenyl)bicyclo[1.1.1]pentan-1-yl)benzoate (1f)



A slightly modified version of VanHeyst's procedure was followed.[12] A 4 mL vial was charged with **1c** (23.0 mg, 75.0 µmol, 1.5 equiv.) and Na_2CO_3 (10.6 mg, 0.100 mmol, 2.00 equiv.). The vial was then brought into a nitrogen glovebox. $[(dtbpy)Ni(OH_2)_4]Cl_2$ (3.53 mg, 7.50 µmol, 15.0 mol%), $[Ir(dFppyCF_3)(dtbpy)]PF_6$ (2.80 mg, 2.50 µmol, 5.00 mol%), ethyl 4-bromobenzoate (8.16 µL, 50.0 µmol, 1.00 equiv.), and a stir bar were added. Then, 0.5 mL of a 5:1 mixture of dioxane and DMA was added. The vial was tightly capped and removed from the glovebox. The vial was placed in a Merck Photoreactor (450 nm light source, 100% intensity, 1000 rpm stirring and 10000 rpm fan speed) for 16 h. The reaction mixture was diluted with water (5 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic extracts were washed with water (2 mL) and brine (2 mL), dried over $MgSO_4$, filtered, and concentrated. The crude material was chromatographed on silica with 0 → 20% ethyl acetate in hexanes) to afford the title compound as an off-white solid (4.3 mg, 25%).

TLC: R_f = 0.50 (5% ethyl acetate in hexanes)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 4.5 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 6H), 1.42 (t, *J* = 7.1 Hz, 3H), 1.35 (s, 9H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 149.7, 146.2, 137.8, 129.7, 128.8, 126.3, 126.0, 125.3, 61.0, 54.2, 41.0, 40.9, 34.6, 31.5, 14.5. [See spectrum]

HRMS (*m/z*): (EI+) calc'd for $C_{24}H_{28}O_2$ $[M]^+$: 348.2089, found: 348.2089.

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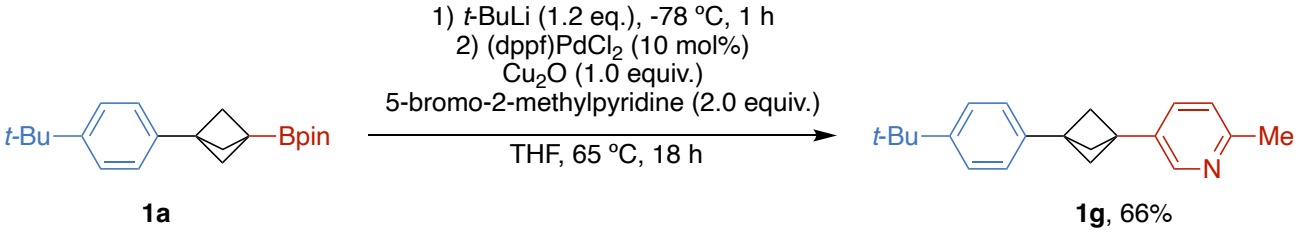
5-(3-(4-(*tert*-butyl)phenyl)bicyclo[1.1.1]pentan-1-yl)-2-methylpyridine (1g)



1a **1g**, 66%

The cross-coupling was performed by modifying a published procedure.[13] A flame-dried Schlenk flask was charged with **1a** (65.3 mg, 0.200 mmol, 1.00 equiv.) and dry THF (1.0 mL). The flask was cooled to -78 ºC, and 0.78 M *t*-BuLi in pentanes was added dropwise (0.316 mL, 0.240 mmol, 1.20 equiv.). The mixture was stirred at the same temperature for 1 h, and complete conversion to the corresponding borate was confirmed by ^{11}B NMR spectroscopy (~7 ppm). The septum on the Schlenk flask was firmly secured with electrical tape, and the flask brought into a nitrogen glovebox, where it was charged with (dppf)$PdCl_2$ (14.6 mg, 20.0 µmol, 0.100 equiv.), cuprous oxide (28.6 mg, 0.200 mmol, 1.00 equiv.), and 5-bromo-2-methylpyridine (68.8 mg, 0.400 mmol, 2.00 equiv.). The flask was stoppered with a glass stopper, a slight vacuum was applied to assist in maintaining the seal, and the mixture was heated in an oil bath at 65 ºC for 18 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (10 mL) and quenched with aqueous ammonium chloride (5 mL). The mixture was filtered through a bed of $MgSO_4$ and Celite, and the solids were washed with copious amounts of ethyl acetate. The combined organic washes were concentrated and chromatographed over silica with 0 → 30% ethyl acetate in hexanes) to afford the title compound as a yellow powder (38.2 mg, 66%)

TLC: R_f = 0.48 (25% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.35 (m, 2H), 7.28 – 7.21 (m, 2H), 7.10 (d, *J* = 7.9 Hz, 1H), 2.55 (s, 3H), 2.33 (s, 6H), 1.33 (s, 9H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.5, 149.7, 147.3, 137.7, 134.4, 133.3, 126.0, 125.3, 122.7, 54.2, 41.3, 38.8, 34.6, 31.5, 24.2. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{21}H_{26}N$ $[M+H]^+$: 292.2060, found: 292.2056.

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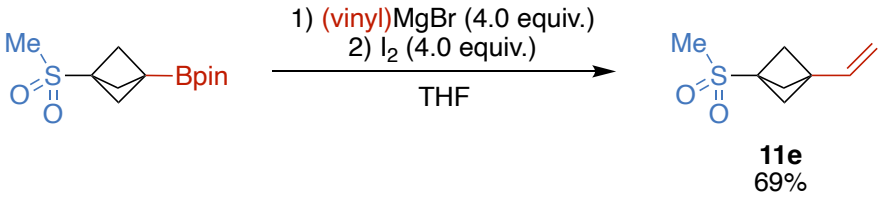
1-(methylsulfonyl)-3-vinylbicyclo[1.1.1]pentane (11e)



11e
69%

A flame-dried 25 mL round-bottom flask was charged with **11a** (68.0 mg, 0.250 mmol, 1.00 equiv.) and anhydrous THF (4 mL). The flask was cooled to -78 ºC. Vinylmagnesium bromide (1.0 M, 1.0 mmol, 1.0 mL, 4.0 equiv.) was added dropwise, and the resulting mixture was stirred at -78 ºC for 1 h. Then, I_2 (254 mg, 1.00 mmol, 4.00 equiv.) in MeOH (4.0 mL) was added dropwise, and the mixture stirred at -78 ºC for another hour. The flask was adjusted to 0 ºC, and sat. $Na_2S_2O_3$ (2 mL) was added. The mixture was diluted with water (10 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. The crude mixture was chromatographed on SiO_2 with 30% ethyl acetate in hexanes as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford the title compound as an off-white solid (29.6 mg, 69%).

TLC: R_f = 0.18 (33% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91 (dd, J = 17.1, 10.5 Hz, 1H), 5.17 (dd, J = 10.5, 1.5 Hz, 1H), 5.12 (dd, J = 17.2, 1.5 Hz, 1H), 2.83 (s, 3H), 2.23 (s, 6H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 134.2, 117.7, 52.0, 50.8, 39.8, 37.6. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_8H_{12}O_2NaS$ $[M+Na]^+$: 195.0450, found: 195.0449.

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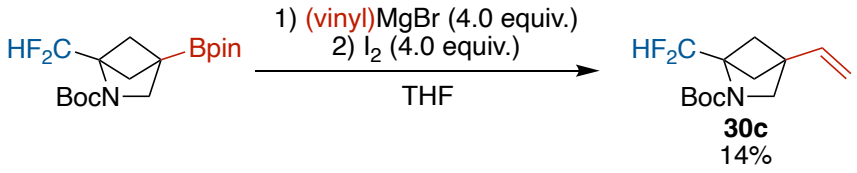
tert-butyl 1-(difluoromethyl)-4-vinyl-2-azabicyclo[2.1.1]hexane-2-carboxylate (30c)



A flame-dried 25 mL round-bottom flask was charged with **30a** (36 mg, 0.10 mmol, 1.0 equiv.) and anhydrous THF (2 mL). The flask was cooled to -78 ºC. Vinylmagnesium bromide (1.0 M, 0.40 mmol, 0.40 mL, 4.0 equiv.) was added dropwise, and the resulting mixture was stirred at -78 ºC for 1 h. Then, I_2 (0.10 g, 0.40 mmol, 4.0 equiv.) in MeOH (4.0 mL) was added dropwise, and the mixture stirred at -78 ºC for another hour. The flask was adjusted to 0 ºC, and sat. $Na_2S_2O_3$ (1 mL) was added. The mixture was diluted with water (5 mL) and extracted with ethyl acetate (15 mL x 3). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. The crude mixture was chromatographed on SiO_2 with 30% ethyl acetate in hexanes as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford the title compound as a colorless oil (3.6 mg, 14%). Note that the product is volatile.

TLC: N/A

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.84 (t, J_{H-F} = 56.3 Hz, 1H), 6.16 (dd, J = 17.3, 10.6 Hz, 1H), 5.34 (dd, J = 10.7, 1.3 Hz, 1H), 5.30 (dd, J = 17.4, 1.4 Hz, 1H), 3.52 (s, 2H), 2.25 – 2.09 (m, 2H), 1.99 – 1.83 (m, 2H), 1.70 (s, 2H), 1.62 (s, 9H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.3, 135.4, 116.7, 112.30 (t, J_{C-F} = 237.2 Hz), 80.7, 69.18 (t, J_{C-F} = 31.2 Hz), 55.4, 47.6, 43.3, 29.8, 28.5. [See spectrum]

^{19}F NMR (565 MHz, $CDCl_3$) δ -124.4. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{14}H_{24}F_2NO_3$ $[M+MeOH+H]^+$: 292.1719, found: 292.1722.

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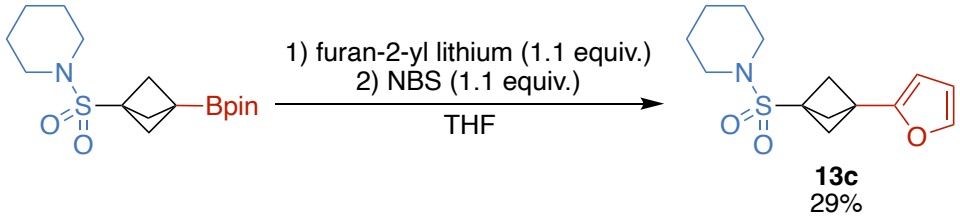
1-((3-(furan-2-yl)bicyclo[1.1.1]pentan-1-yl)sulfonyl)piperidine (13c)



A flame-dried 10 mL RBF was charged with furan (15.0 mg, 0.220 mmol, 1.10 equiv.) and anhydrous THF (3.0 mL). *n*-BuLi in hexanes (2.5 M, 88 µL, 0.22 mmol, 1.1 equiv.) was added dropwise at –78 ºC. The mixture was warmed to ambient temperature and stirred for 1 h. A separate flame-dried 25 mL RBF was charged with **13a** (68.3 mg, 0.200 mmol, 1.00 equiv.) and anhydrous THF (3.0 mL). The solution of furan-2-yl lithium was added dropwise at -78 ºC, and the mixture stirred at -78 ºC for 1 h. Then, *N*-bromosuccinimide (39.2 mg, 0.220 mmol, 1.10 equiv.) in anhydrous THF (3.0 mL) was added, and the mixture stirred at -78 ºC for another 1 h. The flask was adjusted to 0 ºC, and sat. $Na_2S_2O_3$ (2 mL) was added. The mixture was diluted with water (10 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. The crude mixture was chromatographed on SiO_2 with 20 → 30% ethyl acetate in hexanes as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford the title compound as an off-white solid (16.4 mg, 29%).

TLC: R_f = 0.35 (20% ethyl acetate in hexanes)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.31 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.10 (dd, *J* = 3.3, 0.9 Hz, 1H), 3.37 – 3.31 (m, 4H), 2.48 (s, 6H), 1.70 – 1.54 (m, 6H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 151.6, 142.3, 110.5, 106.6, 54.0, 50.5, 47.2, 35.6, 26.2, 24.1. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{14}H_{20}O_3NS$ $[M+H]^+$: 282.1158, found: 282.1160.

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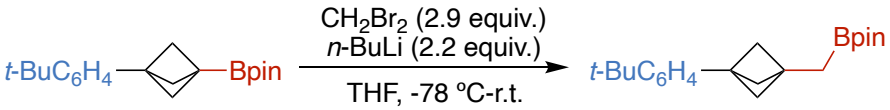
2-((3-(4-(*tert*-butyl)phenyl)bicyclo[1.1.1]pentan-1-yl)methyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1h)



A flame-dried 50 mL flask was charged with **1a** (33.0 mg, 0.100 mmol, 1.00 equiv.), dibromomethane (20.2 µL, 0.290 mmol, 2.90 equiv.) and 1.0 mL of anhydrous THF. The reaction mixture was cooled to -78 °C under an N_2 atmosphere. Then, *n*-BuLi (2.5 M in hexanes, 0.0880 mL, 0.220 mmol, 2.20 equiv.) was added dropwise. The reaction was stirred for 1 hour at -78 °C. The reaction mixture was then warmed to room temperature and was stirred at ambient temperature for 90 min. After this time, the reaction was quenched with sat. NH_4Cl (3 mL) and extracted with ethyl acetate (10 mL x 3). The organic layers were combined and washed with brine (15 mL), dried over Na_2SO_4, and concentrated. The crude reaction mixture was eluted on SiO_2 with 0% → 20% ethyl acetate in hexanes as the eluent. Fractions containing the desired compound were collected and concentrated under vacuum to afford the title compound as a white solid (19.1 mg, 56%).

TLC: R_f = 0.65 (10% ethyl acetate in hexanes)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.3 Hz, 2H), 1.96 (s, 6H), 1.31 (s, 10H), 1.27 (s, 13H), 1.16 (s, 2H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 148.9, 138.6, 125.8, 124.9, 83.0, 54.3, 41.5, 35.9, 34.4, 31.4, 24.9. [See spectrum]

^{11}B NMR (193 MHz, $CDCl_3$) δ 32.9. [See spectrum]

HRMS (*m/z*): (EI+) calc'd for $C_{22}H_{33}BO_2$ $[M]^+$: 340.2574, found: 340.2571.

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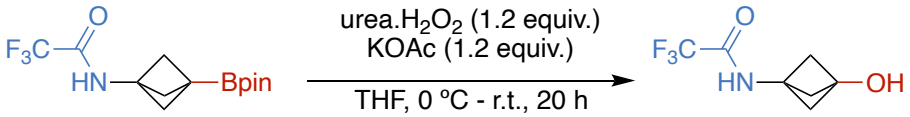
2,2,2-trifluoro-*N*-(3-hydroxybicyclo[1.1.1]pentan-1-yl)acetamide (16d)



16a **16e**, 73%

The reaction was performed by modifying a known procedure.[13] **16a** (30.5 mg, 0.100 mmol, 1.00 equiv.) was dissolved in THF (0.5 mL) in a 4 mL vial. To the solution was added urea•H_2O_2 (11.3 mg, 0.120 mmol, 1.20 equiv.) and potassium acetate (11.8 mg, 0.120 mmol, 1.20 equiv.) at 0 ºC. Then, water (0.3 mL) was also added at 0 ºC, and the mixture was stirred for 10 min. The cooling bath was removed, and the reaction mixture was stirred at room temperature for 20 h. The mixture was diluted with ethyl acetate (5 mL) and washed with saturated ammonium chloride (5 mL). The aqueous layer was extracted with ethyl acetate (5 mL x 2). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The crude material was chromatographed on silica with 30% ethyl acetate in hexanes to afford the title compound as a white powder (14.2 mg, 73%).

TLC: R_f = 0.3 (30% ethyl acetate in hexanes)

^{1}H NMR (600 MHz, Acetone) δ 8.93 (bs, 1H), 5.36 (bs, 1H), 2.18 (s, 6H). [See spectrum]

^{13}C NMR (151 MHz, Acetone) δ 205.2, 155.6 (q, $J_{C\text{-}F}$ = 36.5 Hz), 114.9 (q, $J_{C\text{-}F}$ = 287.9 Hz), 61.3, 54.4, 54.3, 40.0, 28.0. [See spectrum]

^{19}F NMR (565 MHz, Acetone) δ -77.6. [See spectrum]

HRMS (*m/z*): (ESI-) calc'd for $C_7H_7F_3NO_2$ [M-H]$^-$: 194.0434, found: 194.0436.

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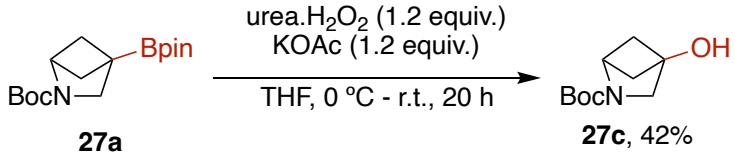
tert-butyl 4-hydroxy-2-azabicyclo[2.1.1]hexane-2-carboxylate (27c)



27a **27c**, 42%

The reaction was performed by modifying a known procedure.[13] Compound **27a** (18 mg, 0.057 mmol, 1.0 equiv.) was dissolved in THF (0.25 mL) in a 4 mL vial. To the solution was added urea•H_2O_2 (6.4 mg, 0.068 mmol, 1.2 equiv.) and potassium acetate (6.7 mg, 0.12 mmol, 1.2 equiv.) at 0 ºC. Then, water (0.15 mL) was also added at 0 ºC, and the mixture was stirred for 10 min. The cooling bath was removed, and the reaction mixture was stirred at room temperature for 20 h. The mixture was diluted with ethyl acetate (4 mL) and washed with saturated ammonium chloride (4 mL). The aqueous layer was extracted with ethyl acetate (4 mL x 2). The combined organic layers were washed with saturated aqueous sodium thiosulfate (2 mL), dried over Na_2SO_4, filtered, and concentrated. The crude material was chromatographed on silica with 30% ethyl acetate in hexanes to afford the title compound as a white powder (4.8 mg, 42%).

TLC: N/A

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.32 (s, 1H), 3.37 (s, 2H), 2.77 (s, 1H), 2.08 – 1.88 (m, 4H), 1.60 (s, 9H). [See spectrum]

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.4, 79.7, 76.0, 52.9, 50.9, 47.2, 28.6. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{13}H_{26}NO_4$ $[M+iPrOH+H]^+$: 260.1851, found: 260.1862.

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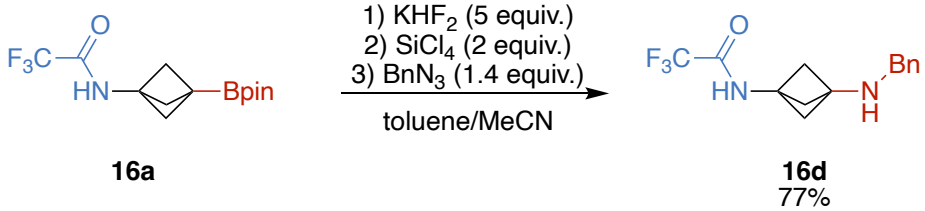
_N_-(3-(benzylamino)bicyclo[1.1.1]pentan-1-yl)-2,2,2-trifluoroacetamide (16e)



16a **16d** 77%

The reaction was performed by modifying a known procedure.[14] **16a** (45.8 mg, 0.150 mmol) was dissolved in a mixture of MeOH (0.4 mL) and THF (0.2 mL). Then, KHF_2 (58.6 mg, 0.750 mmol, 5.00 equiv.) in water (0.2 mL) was added with vigorous stirring. The resulting mixture was stirred at room temperature for 3 h. The reaction mixture was co-evaporated with 1:1 methanol:water repeatedly (1 mL x 5) to remove pinacol. The solid residue was extracted with acetone, filtered, and the filtrate concentrated. The residue was further co-evaporated with toluene (1 mL x 2) to remove residual water. The residue was dissolved in a mixture of toluene (1.5 mL) and acetonitrile (0.4 mL) in a 4 mL vial and sealed with a pressure-release septum cap. $SiCl_4$ (34.4 µL, 0.300 mmol, 2.00 equiv.) was added through the septum cap via a syringe, and the mixture was stirred for 20 min at room temperature. Then, a 0.5 M solution of benzyl azide in dichloromethane (0.42 mL, 0.21 mmol, 1.4 equiv.) was added through the septum cap. The vial was brought into a nitrogen glovebox, and the septum cap was replaced with a cap lined with a Teflon seal. The vial was heated in a 50 ºC aluminum heating block for 16 h. After the vial was cooled to room temperature, the contents were poured into water (5 mL), and the organic layer was extracted with aqueous 1 M HCl (10 mL x 5). The combined aqueous layers were basified with 2 M NaOH to pH = 9 and then extracted with ether (20 mL x 5). The ether extracts were combined, dried over $MgSO_4$, filtered, and concentrated. The crude material was chromatographed on silica gel with 100% ethyl acetate to afford the product as a white solid (33.0 mg, 77%).

TLC: R_f = 0.6 (100% ethyl acetate)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.20 (m, 5H), 6.69 (bs, 1H), 3.79 (s, 2H), 2.17 (s, 6H), 2.10 (bs, 1H). [See spectrum]

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.9 ($J_{C\text{-}F}$ = 37.3 Hz), 139.8, 128.5, 128.0, 127.2, 115.4 (q, $J_{C\text{-}F}$ = 288.7 Hz), 77.0, 53.5, 52.2, 50.4, 43.7. [See spectrum]

^{19}F NMR (470 MHz, $CDCl_3$) δ -76.0. [See spectrum]

HRMS (*m/z*): (ESI+) calc'd for $C_{14}H_{16}F_3N_2O$ $[M+H]^+$: 285.1210, found: 285.1209.

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7. Kinetic Studies

7.1 Measurement of $^{1}J_{C–H}$ coupling constants.

The $^{1}J_{C–H}$ coupling constants were measured by *J*-resolved 2D NMR spectroscopy. 5-10 mg of the compound of interest was dissolved in $CDCl_3$, and a *J*-resolved ^{13}C-^{1}H 2D-spectrum was obtained. The peaks were assigned by comparison to the known ^{13}C NMR spectrum and the desired $^{1}J_{C–H}$ coupling constant was directly read from the spectrum. The case of **1b** is shown as an example below in Fig. S5.

$^{1}J_{C–H}$ = 2783.10 – 2618.07 = 165.03 Hz.

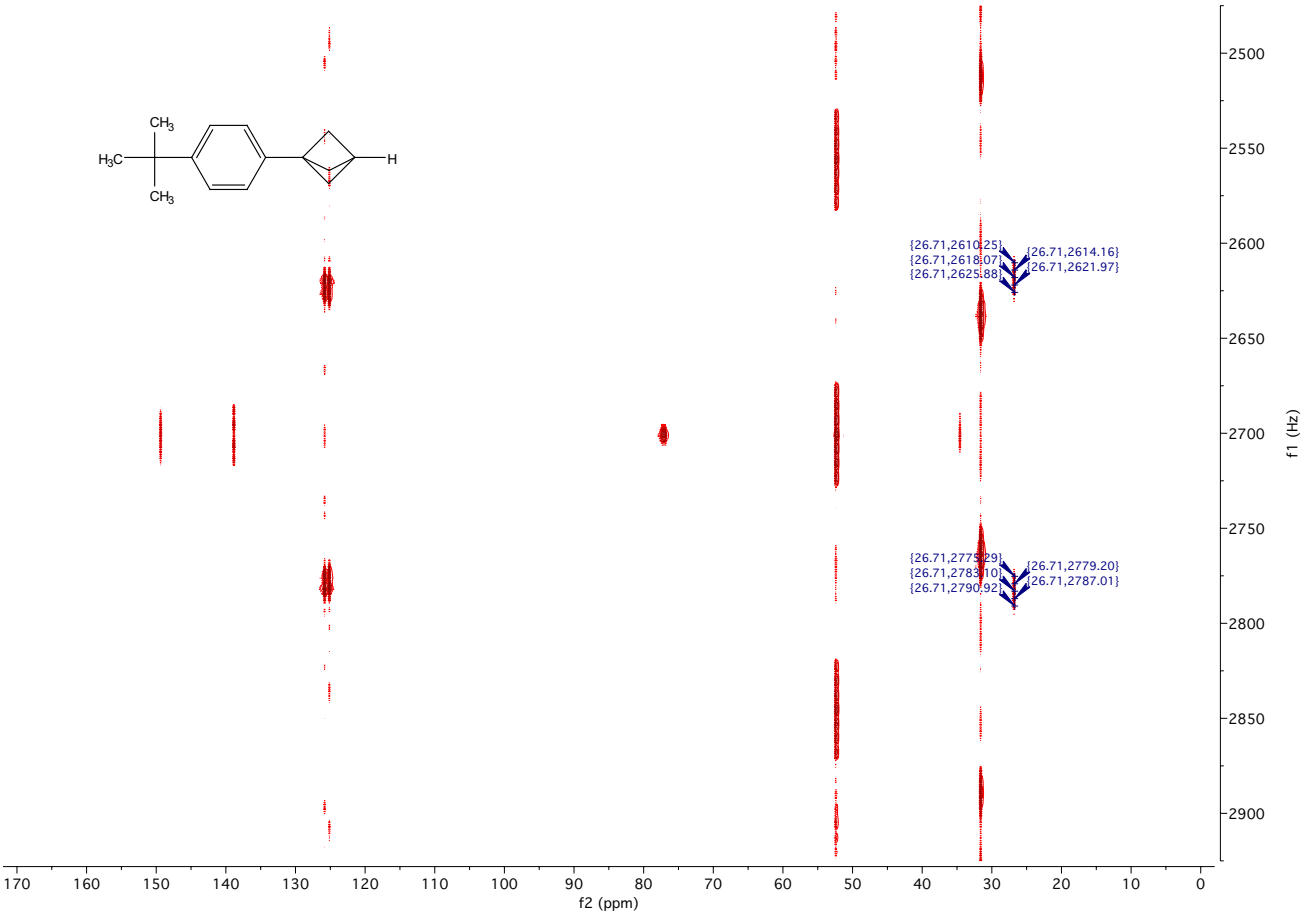

Fig. S5. Example for the measurement of $^{1}J_{C–H}$ coupling constants. The example given is a *J*-resolved ^{13}C-^{1}H 2D-spectrum of **1b**.

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7.2 Competition experiments.

The competition experiments with 2-mphen as ligand were run to low conversion to prevent H-D exchange from significantly affecting the ratios of products. (See Sec. 7.3) The competition experiments that were run to longer reaction times to achieve significant conversion are included for completeness.

Competition between different types of C–H bonds.

In a nitrogen glovebox, a 4 mL dram vial was charged with the appropriate ligand (25.0 µmol), $[Ir(COD)(OMe)]_2$ (8.29 mg, 12.5 µL), and B_2pin_2 (6.35 mg, 25.0 µmol). Anhydrous THF (2.5 mL) was added, after which the vial was tightly sealed with a Teflon-lined cap, removed from the glovebox, and heated in an aluminum heating block at 100 ºC for 5 min. The resultant solution was dispensed into fresh 4 mL vials (100 µL, 1.00 µmmol of catalyst), and the volatile materials were evaporated in vacuo. To the vials containing the catalyst were added B_2pin_2 (5.08 mg, 20.0 µmol), adamantane (6.81 mg, 50.0 µmol), 4-*tert*-butylphenylbicyclopentane (**1b**) (10.0 mg, 50.0 µmol), substrate (50.0 µL), cyclooctane (120 µL), and a flea stir bar. The vial was tightly sealed with a Teflon-lined cap, removed from the glovebox, and heated in an aluminum heating block at the specified temperature for the specified reaction time. After the appropriate amounts of time had elapsed, the vials were removed from the heating block, brought into the glovebox, and an aliquot removed for analysis by gas chromatography. The ratio of the products are shown in Fig. S6 and Fig. S7.

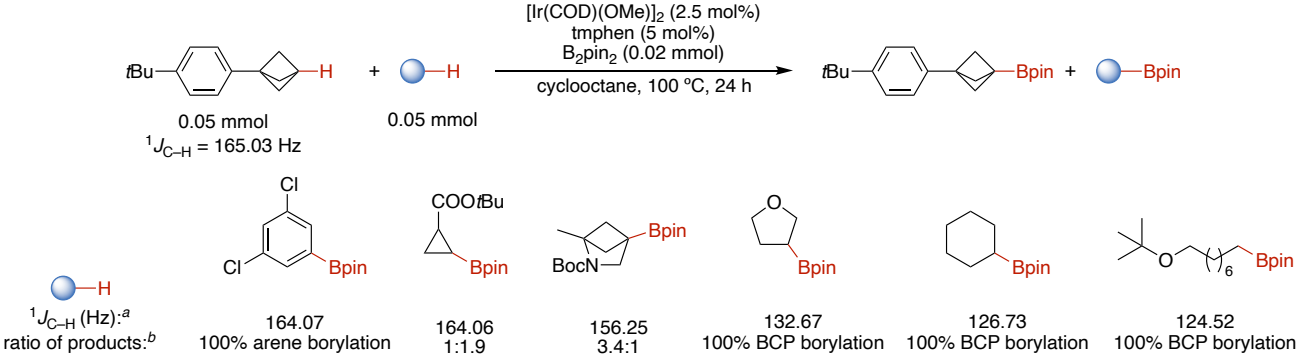

Fig. S6. Competition experiments with substrates containing different types of C–H bonds with tmphen. Ratios of products determined with tmphen as the ligand. Equivalent to Fig. 3a of the main text. [a] $^1J_{C–H}$ coupling constant of the C–H bond that underwent borylation. [b] Ratio of products determined by GC analysis.

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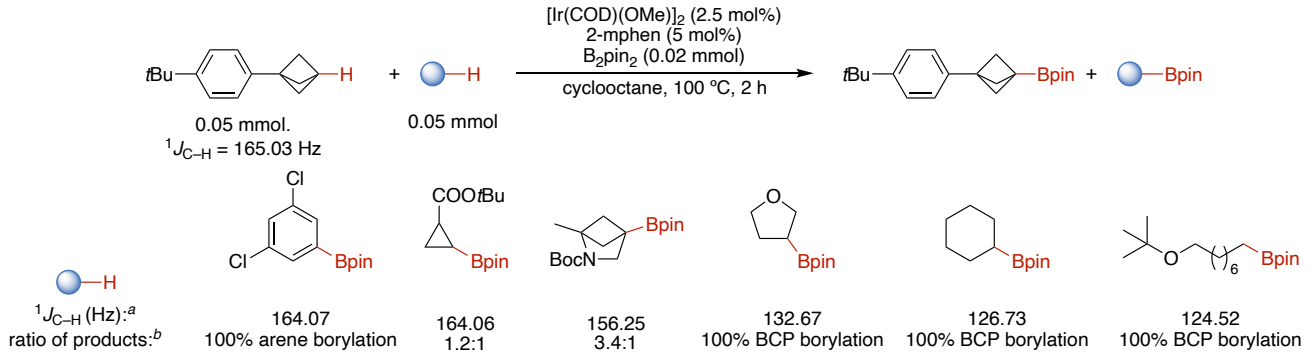

Fig. S7. Competition experiments with substrates containing different types of C–H bonds with 2-mphen. Ratio of products determined with 2-mphen as the ligand. [a] $^1J_{C–H}$ coupling constant of the C–H bond that underwent borylation. [b] Ratio of products determined by GC analysis.

Competition between BCP substrates.

In a nitrogen glovebox, a 4 mL dram vial was charged with the appropriate ligand (25.0 μmol), $[Ir(COD)(OMe)]_2$ (8.29 mg, 12.5 μL), and B_2pin_2 (6.35 mg, 25.0 μmol). Anhydrous THF (2.5 mL) was added, after which time the vial was tightly sealed with a Teflon-lined cap, removed from the glovebox, and heated in an aluminum heating block at 100 °C for 5 min. The resultant solution was dispensed into fresh 4 mL vials (100 μL, 1.00 μmmol of catalyst), and the volatile mateirals were evaporated in vacuo. To the vials containing the catalyst were added B_2pin_2 (5.08 mg, 20.0 μmol), bicyclo[1.1.1]pentan-1-yltributylstannane (**4b**) (17.9 mg, 50.0 μmol), substrate (50.0 μL), cyclooctane (120 μL), and a flea stir bar. The vial was tightly sealed with a Teflon-lined cap, removed from the glovebox, and heated in an aluminum heating block at the specified temperature for the specified reaction time. After the appropriate amounts of time had elapsed, the vials were removed from the heating block, cooled to room temperature, and CH_2Br_2 was added. An aliquot was taken and analyzed by ^{1}H NMR spectroscopy. The ratio of the products are shown in Fig. S8 and Fig. S9.

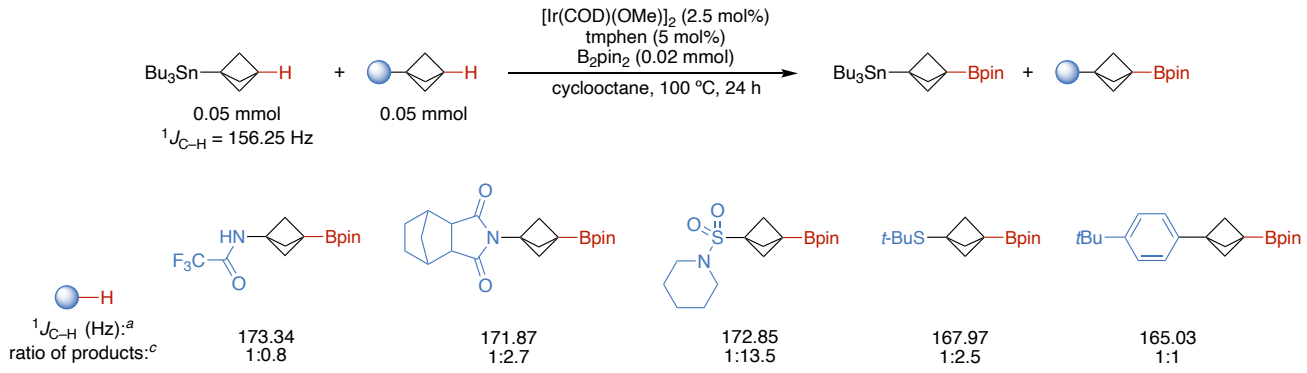

Fig. S8. Competition experiments with different BCP substrates with tmphen. Ratios of products determined with tmphen as the ligand. Equivalent to Fig. 3b of the main text. [a] $^1J_{C–H}$ coupling constant of the C–H bond that underwent borylation. [c] Ratio of products determined by NMR analysis.

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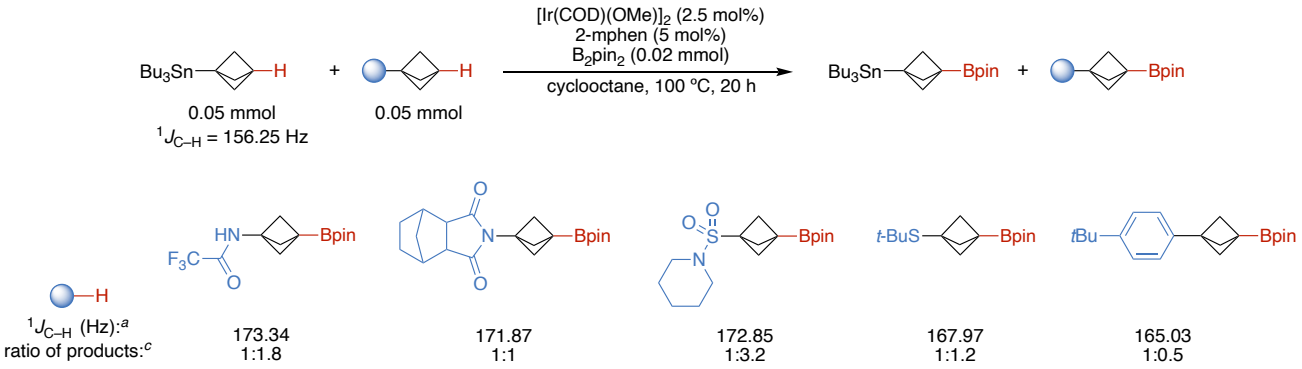

Fig. S9 Competition experiments with different BCP substrates with 2-mphen. Ratios of products determined with 2-mphen as the ligand. [a] $^1J_{C–H}$ coupling constant of the C–H bond that underwent borylation. [c] Ratio of products determined by NMR analysis.

7.3 Measurement of kinetic isotope effects

Initial attempts to measure KIE values by performing intermolecular competition reactions with **1b** and **1b**-d_1 were hampered by several factors. Because the bridgehead position was the only one that was labelled, both substrates would react to form identical product. Thus, determination of the KIE directly would require accurate determination of the ratio of isotopomers in the remaining starting material (ideally at high conversions of the material, as in a Singleton-type experiment).[15] Unfortunately, it was found that substantial H-D scrambling occurs through protodeboronation, especially at the longer reaction times required to reach high conversion. The source of the protons is presumably adventitious water or hydroxyl groups on the walls of the glass vial, although efforts to chemically modify the glass vials did not reduce the amount of protodeboronation. We thus resorted to the double competition experiment and independent initial rates measurements presented below, both of which were run to low conversion, where H-D scrambling is expected to introduce less error into the KIE value measured. An additional hurdle was the presence of substantial induction period during reactions catalyzed by complexes of both the 2-mphen and 2,9-dmphen systems, as shown below in Fig. S10. We observed no obvious induction period with tmphen as ligand.

Time courses showing the presence of induction periods for 2-mphen and 2,9-dmphen

In a nitrogen glovebox, a 4 mL vial was charged with 4-*tert*-butylphenylbicyclopentane (**1b**, 50.1 mg, 0.250 mmol), B_2pin_2 (95.2 mg, 0.375 mmol), (mesitylene)Ir(Bpin)$_3$ (8.67 mg, 0.0125 mmol), ligand, (2.95 mg, 0.0125 mmol), adamantane (17.0 mg, 0.125 mmol), and cyclooctane (200 µL). A stir bar was added to the mixture, and the vial tightly capped with a Teflon-lined cap. The vial was removed from the glovebox and heated in a preheated aluminum heating block at 100 ºC. Aliquots were removed at appropriate timepoints and analyzed by GC analysis.

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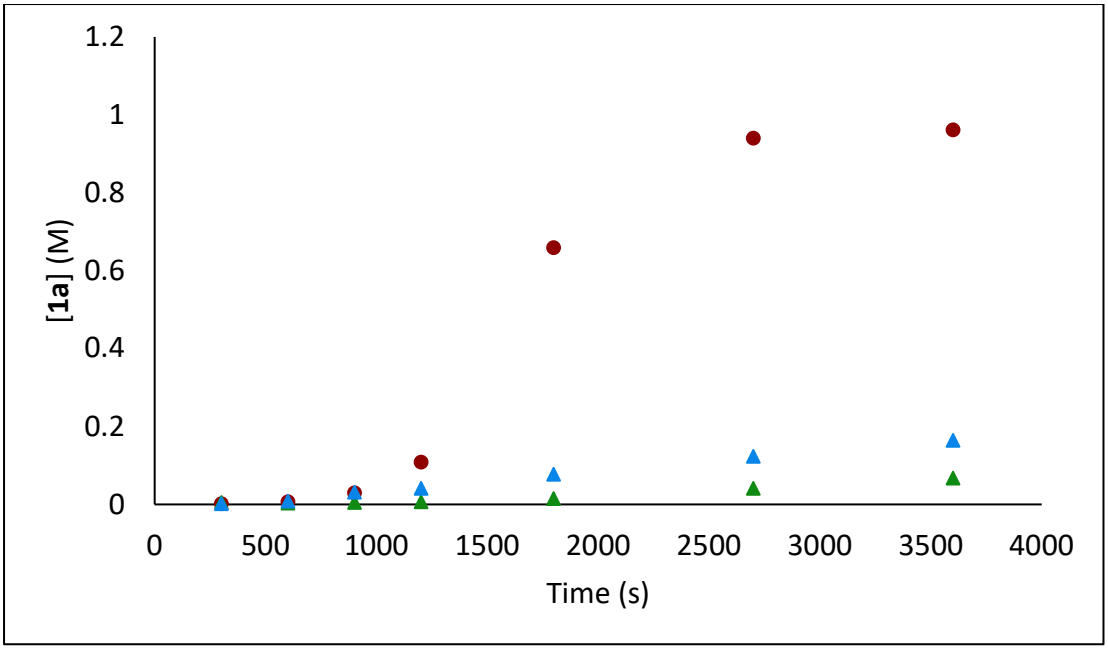
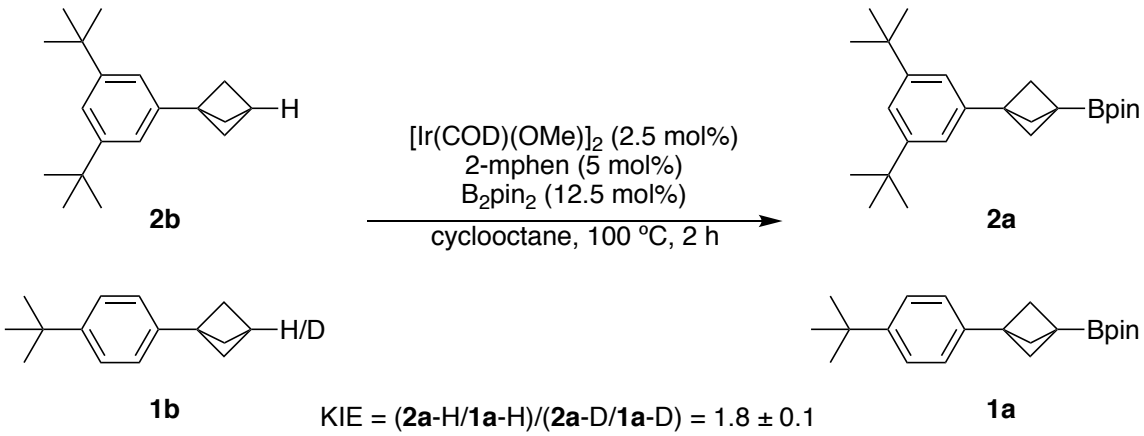


Fig. S10. Timecourses of the borylation of 1b. red circles: 2-mphen, green triangles: 2,9-dmphen, blue diamonds: tmphen.

Double competition experiment for the determination of the kinetic isotope effect

In a nitrogen glovebox, a 4 mL vial was charged with 3,5-di(*tert*-butyl)phenylbicyclopentane (**2b**, 32.1 mg, 0.125 mmol) and either 4-*tert*-butylphenylbicyclopentane (**1b**, 25.0 mg, 0.125 mmol) or 4-*tert*-butylphenylbicyclopentane-d_1 (**1b-*d*$_1$**, 25.0 mg, 0.125 mmol). Then, B_2pin_2 (7.94 mg, 0.0312 mmol), $[Ir(COD)OMe]_2$ (1.04 mg, 2.50 mol%), 2-mphen (0.61 mg, 5.0 mol%), and cyclooctane (100 µL) were added. A stir bar was added to the mixture, and the vial tightly capped with a Teflon-lined cap. The vial was removed from the glovebox and heated in a preheated aluminum heating block at 100 ºC for 2 h. Then, an aliquot was taken and analyzed by GC analysis. The relative integrations for the borylated products **1a** and **2a** were recorded, and the KIE value obtained by dividing the ratios obtained from reactions done with **1b** over those obtained with **1b-*d*$_1$**. The experiment was conducted in triplicate.



KIE = (**2a**-H/**1a**-H)/(**2a**-D/**1a**-D) = 1.8 ± 0.1

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Fig. S11. The setup for the double competition experiment. Equivalent to Fig. 5a of the main text.

Run 1: 1.90

Run 2: 1.90

Run 3: 1.68

KIE = 1.8 ± 0.1

An analogous reaction was initiated with only **1b-*d*$_1$** under the reaction conditions. The extent of H-D scrambling in the starting material was < 5% as judged by NMR analysis. Thus, we do not anticipate large errors arising from protodeboronation.

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Measurement of the KIE by the method of initial rates

In a nitrogen glovebox, a 4 mL vial was charged with either 4-*tert*-butylphenylbicyclopentane (**1b**, 50.1 mg, 0.250 mmol) or 4-*tert*-butylphenylbicyclopentane-d_1 (**1b-*d*$_1$**, 50.3 mg, 0.250 mmol). Then, B_2pin_2 (95.2 mg, 0.375 mmol), (mesitylene)Ir(Bpin)$_3$ (8.67 mg, 0.0125 mmol), tmphen (2.95 mg, 0.0125 mmol), adamantane (17.0 mg, 0.125 mmol), and cyclooctane (200 µL) were added. A stir bar was added to the mixture, and the vial tightly capped with a Teflon-lined cap. The vial was removed from the glovebox and heated in a preheated aluminum heating block at 100 ºC. Aliquots were removed at appropriate timepoints and analyzed by GC. The experiment was conducted in triplicate. The concentration of product **1a** was measured and plotted versus time to obtain the initial rates of the formation of **1a**.

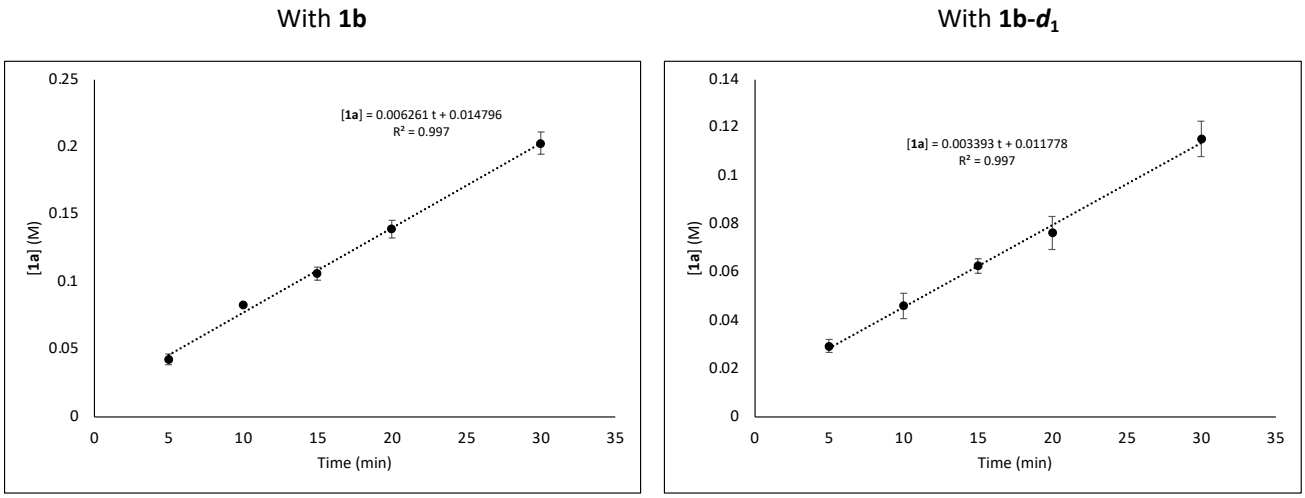

Fig. S12. Formation of borylated product 1a vs time with either 1b or 1b-*d*$_1$.

KIE = 0.0063/0.0034 = 1.8 ± 0.1

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7.4 Determination of the rate law of the catalytic reaction by the method of initial rates

Order in substrate.

In a nitrogen glovebox, adamantane (45.4 mg, 0.333 mmol) and B_2pin_2 (254 mg, 1.00 mmol) were dissolved in dry THF in a 2.0 mL volumetric flask. The resulting solution was dispensed into four 1-dram vials equipped with flea stir bars, (375 µL, 0.0625 mmol of adamantane, 0.188 mmol of B_2pin_2). In a 2.0 mL volumetric flask, 4-*tert*-butylphenylbicyclopentane (**1b**) (250 mg, 1.25 mmol) was dissolved in dry THF to make a 0.625 M solution. The solution was dispensed into the four 1-dram vials (100 µL, 0.0625 mmol; 200 µL, 0.125 mmol; 300 µL, 0.188 mmol; 400 µL, 0.250 mmol; respectively). In a 1-dram vial tmphen (11.8 mg, 0.0500 mmol), (mesitylene)Ir(Bpin)$_3$ (34.7 mg, 0.0500 mmol), and B_2pin_2 (12.7 mg, 0.0500 mmol) were dissolved in 1.00 mL dry THF. The vial was tightly sealed with a Teflon-lined cap and removed from the glovebox. The vial was heated in an aluminum heating block at 100 ºC for 5 min, resulting in a homogenous, deep red-brown solution. The vial was cooled to room temperature and returned to the glovebox. The solution was dispensed into the four 1-dram vials (125 µL, 6.25 µmmol of catalyst). All volatile materials were carefully evaporated from the four 1-dram vials in vacuo. Then, dry cyclooctane (400 µL) was added, the vials tightly sealed with Teflon-lined caps, and the vials removed from the glovebox. The vials were heated in an aluminum heating block at 100 ºC. At the appropriate timepoints, the vials were removed from the heating block, brought into the glovebox, and an aliquot removed for analysis by gas chromatography. The concentration of product **1a** was measured and plotted versus time to obtain the initial rates of the formation of **1a**.

Table S1. Initial concentrations of [**1b**], [catalyst], and [B_2pin_2] (varying [**1b**]), and the corresponding initial rates of formation of **1a**.

[**1b**] (M)	[catalyst] (mM)	[B_2pin_2] (M)	Initial Rate of Formation of **1a** ($mM.min^{-1}$)
0.156	15.6	0.469	0.101 ± 0.003
0.312	15.6	0.469	0.214 ± 0.004
0.469	15.6	0.469	0.359 ± 0.010
0.625	15.6	0.469	0.480 ± 0.014

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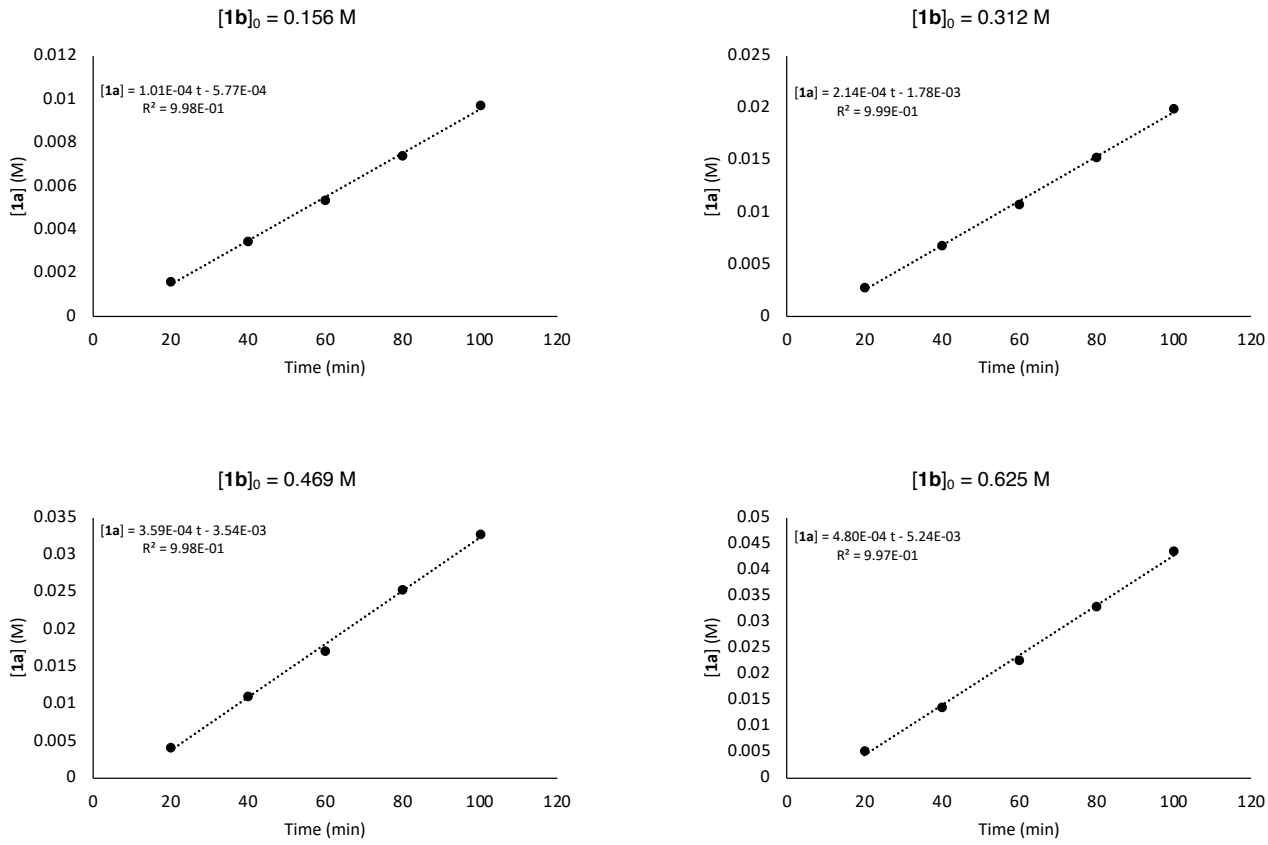

Fig. S13. Formation of borylated product **1a** *vs* time varying initial concentration of substrate **1b**.

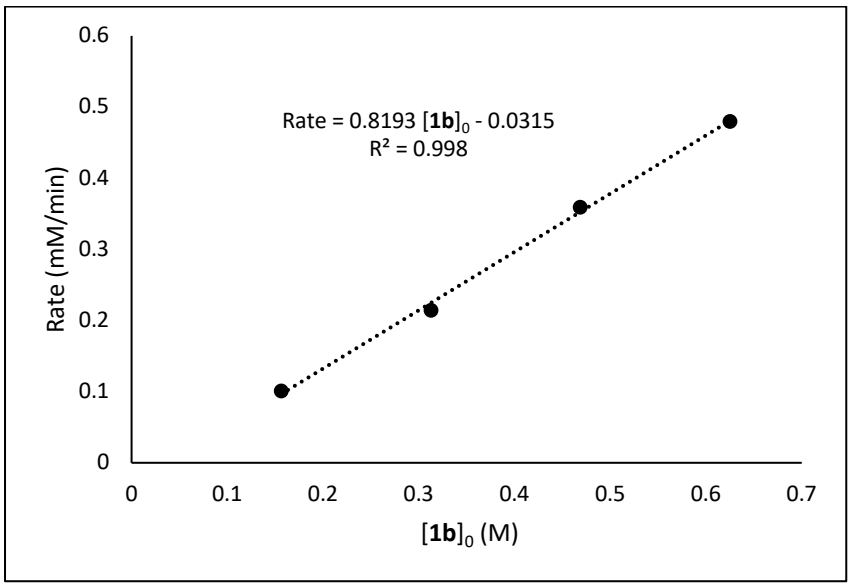

Fig. S14. Plot of the initial rate of the formation of **1a** varying the initial concentration of substrate **1b**. Reproduced in Fig. 4c of the main text.

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Order in catalyst.

In a nitrogen glovebox, B_2pin_2 (254 mg, 1.00 mmol) was dissolved in dry THF in a 2.0 mL volumetric flask. The resulting solution was dispensed into four 1-dram vials equipped with flea stir bars, (375 µL, 0.188 mmol of B_2pin_2). In a 1.0 mL volumetric flask, 4-*tert*-butylphenylbicyclopentane (**1b**) (125 mg, 0.625 mmol) and adamantane (42.6 mg, 0.313 mmol) were dissolved in dry THF. The solution was dispensed into the four 1-dram vials (200 µL, 0.125 mmol of **1b**, 0.0625 mmol of adamantane). In a 1-dram vial tmphen (11.8 mg, 0.0500 mmol), (mesitylene)Ir(Bpin)$_3$ (34.7 mg, 0.0500 mmol), and B_2pin_2 (12.7 mg, 0.0500 mmol) were dissolved in 1.00 mL dry THF. The vial was tightly sealed with a Teflon-lined cap and removed from the glovebox. The vial was heated in an aluminum heating block at 100 ºC for 5 min, resulting in a homogenous, deep red-brown solution. The vial was cooled to room temperature and returned to the glovebox. The solution was dispensed into the four 1-dram vials (62.5 µL, 3.13 µmol; 125 µL, 6.25 µmmol; 188 µL, 9.38 µmol; 250 µL, 12.5 µmol; respectively). All volatile materials were carefully removed from the four 1-dram vials in vacuo. Then, dry cyclooctane (400 µL) was added, the vials tightly sealed with Teflon-lined caps, and the vials removed from the glovebox. The vials were heated in an aluminum heating block at 100 ºC. At the appropriate timepoints, the vials were removed from the heating block, brought into the glovebox, and an aliquot taken for gas chromatography analysis. The concentration of product **1a** was measured and plotted versus time to obtain the initial rates of the formation of **1a**.

Table S2. Initial concentrations of [**1b**], [catalyst], and [B_2pin_2] (varying [catalyst]), and the corresponding initial rates of formation of **1a**.

[**1b**] (M)	[catalyst] (mM)	[B_2pin_2] (M)	Initial Rate of Formation of **1a** (mM.min^{-1})
0.312	7.81	0.469	0.172 ± 0.008
0.312	15.6	0.469	0.324 ± 0.006
0.312	23.4	0.469	0.564 ± 0.014
0.312	31.2	0.469	0.713 ± 0.006

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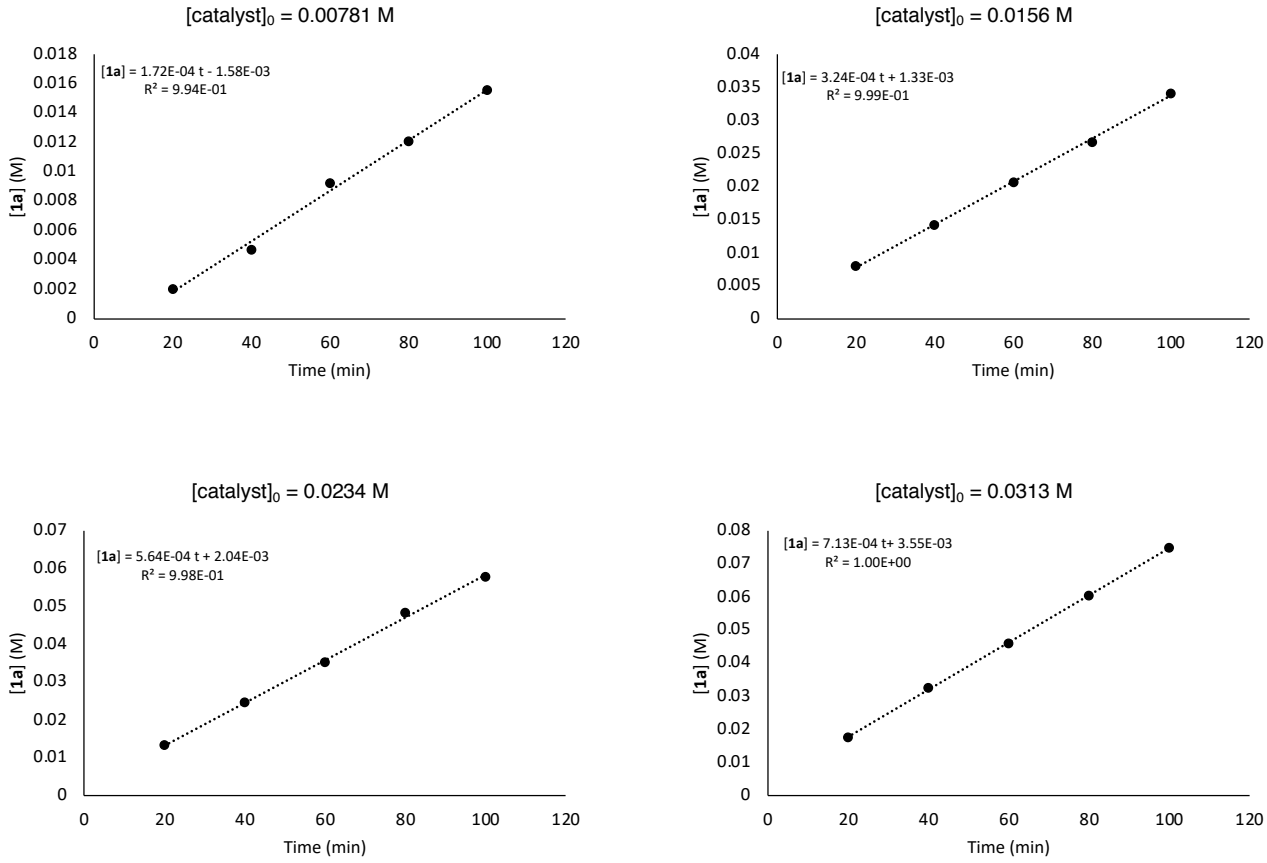

Fig. S15. Formation of borylated product **1a** *vs* time varying loading of catalyst.

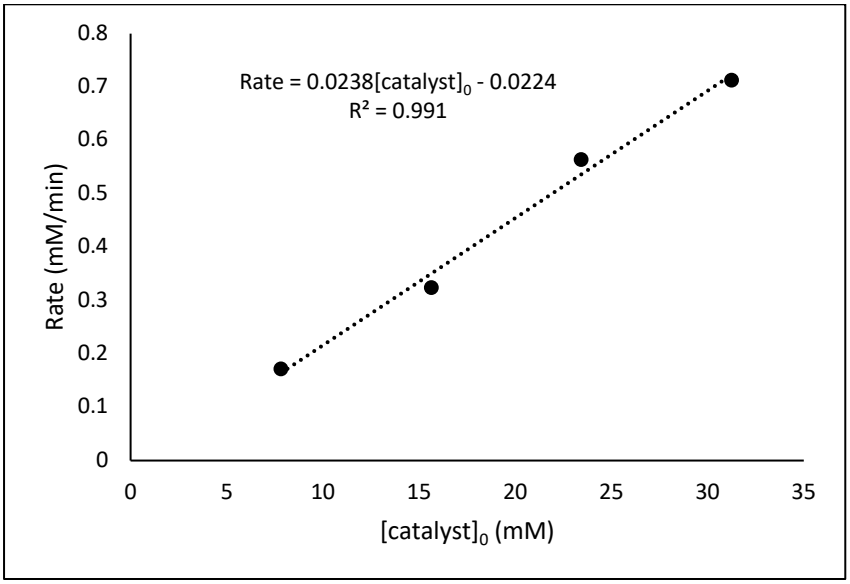

Fig. S16. Plot of the initial rate of the formation of **1a** varying the initial concentration of catalyst. Reproduced in Fig. 4c of the main text.

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Order in B_2pin_2.

In a nitrogen glovebox, B_2pin_2 (254 mg, 1.00 mmol) was dissolved in dry THF in a 2.0 mL volumetric flask. The resulting solution was dispensed into four 1-dram vials equipped with flea stir bars, (188 µL, 0.0938 mmol; 375 µL, 0.188 mmol; 563 µL, 0.281 mmol; 750 µL, 0.375 mmol; respectively). In a 1.0 mL volumetric flask, 4-*tert*-butylphenylbicyclopentane (**1b**) (125 mg, 0.625 mmol) and adamantane (42.6 mg, 0.313 mmol) were dissolved in dry THF. The solution was dispensed into the four 1-dram vials (200 µL, 0.125 mmol of **1b**, 0.0625 mmol of adamantane). In a 1-dram vial tmphen (11.8 mg, 0.0500 mmol), (mesitylene)Ir(Bpin)$_3$ (34.7 mg, 0.0500 mmol), and B_2pin_2 (12.7 mg, 0.0500 mmol) were dissolved in 1.00 mL dry THF. The vial was tightly sealed with a Teflon-lined cap and removed from the glovebox. The vial was heated in an aluminum heating block at 100 ºC for 5 min, resulting in a homogenous, deep red-brown solution. The vial was cooled to room temperature and returned to the glovebox. The solution was dispensed into the four 1-dram vials (125 µL, 6.25 µmmol of catalyst). All volatile materials were carefully removed from the four 1-dram vials in vacuo. Then, dry cyclooctane (400 µL) was added, the vials tightly sealed with Teflon-lined caps, and the vials removed from the glovebox. The vials were heated in an aluminum heating block at 100 ºC. At the appropriate timepoints, the vials were removed from the heating block, brought into the glovebox, and an aliquot taken for gas chromatography analysis. The concentration of product **1a** was measured and plotted versus time to obtain the initial rates of the formation of **1a**.

Table S3. Initial concentrations of [**1b**], [catalyst], and [B_2pin_2] (varying [B_2pin_2]), and the corresponding initial rates of formation of **1a**.

[**1b**] (M)	[(tmphen)Ir(Bpin)$_3$] (mM)	[B_2pin_2] (M)	Initial Rate of Formation of **1a** (mM.min^{-1})
0.312	15.6	0.234	0.238 ± 0.012
0.312	15.6	0.469	0.240 ± 0.008
0.312	15.6	0.703	0.240 ± 0.008
0.312	15.6	0.938	0.240 ± 0.010

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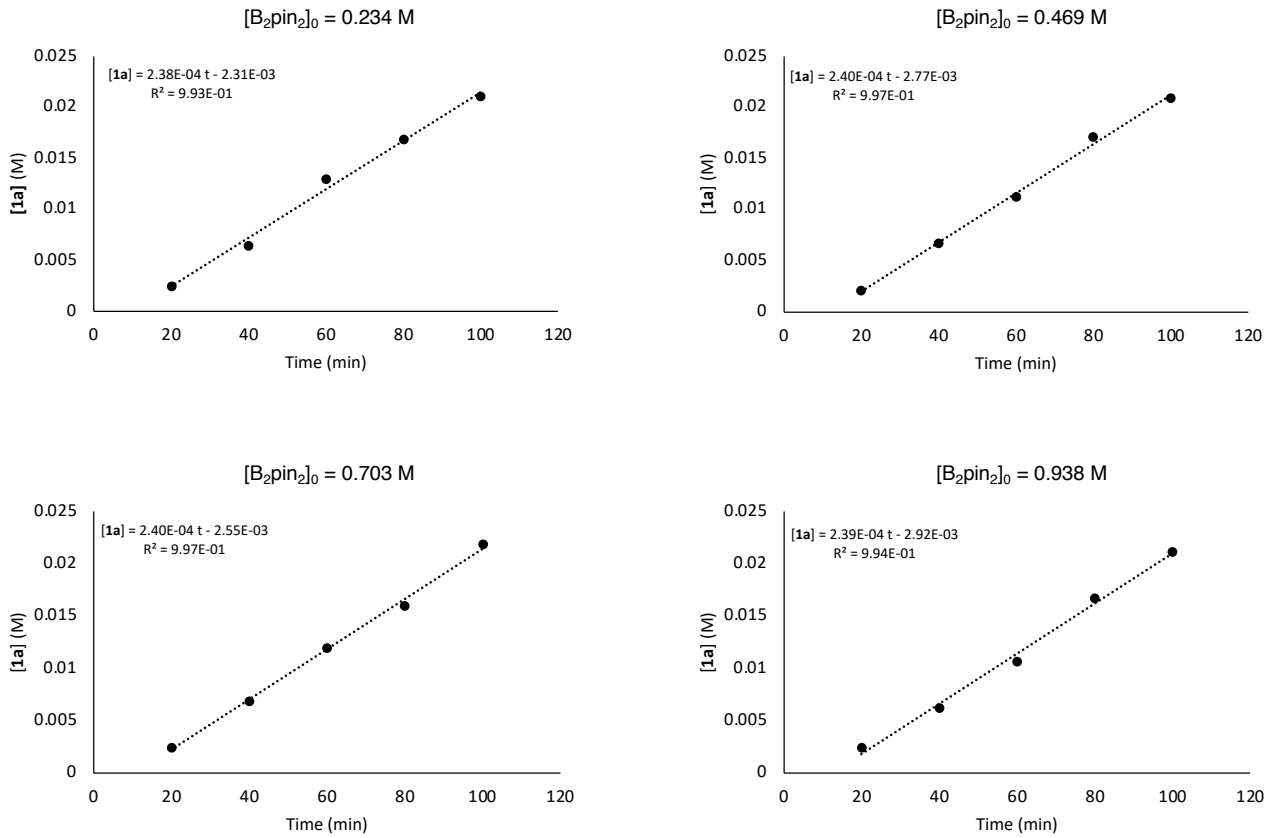

Fig. S17. Formation of borylated product **1a** *vs* time varying the initial concentration of B_2pin_2.

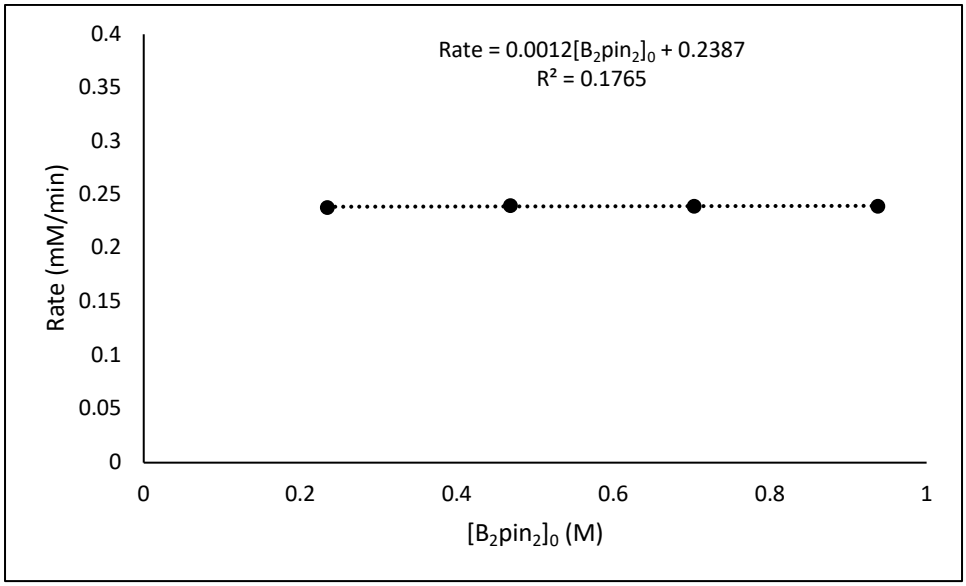

Fig. S18. Plot of the initial rate of the formation of **1a** varying the initial concentration of B_2pin_2. Reproduced in Fig. 4c of the main text.

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8. Computational Studies

8.1 General Considerations

DFT calculations were conducted at the Molecular Graphics and Computation Facility (MGCF) at the University of California, Berkeley using the Gaussian 16 software package.[16] Initial geometries were constructed in GaussView 6 and optimized to stationary points (either minima or first-order saddle points) using the PBE0 functional (the hybrid functional based on the Perdew-Burke-Ernzerhof functional [PBE][17,18] as described by Adamo[19]) with Grimme's D3 dispersion correction with Becke-Johnson damping (GD3-BJ)[20] and the basis sets def2-TZVP (with effective core potential) for Ir and def2-SVP for all light atoms (**BS1**). The nature of each stationary point was verified by accompanying frequency calculations (all positive eigenvalues for minima and exactly one negative eigenvalue for transition states). For each ground state and transition state, several isomeric geometries about the iridium center and conformers resulting from rotations of the boryl group about the Ir–B bond were considered. Their geometries and energies were optimized in Gaussian, and only those lowest in energy or relevant to the reaction coordinate are presented here. Connectivity of transition states to ground-state minima was established by following the intrinsic reaction coordinate (IRC). Frequencies were evaluated at 1 atm at 373.15 K (100 °C). Further single point energy (SPE) calculations were performed on the optimized geometries with the larger def2-QZVPD basis set[21] (with ECP)[22] on Ir and the def2-TZVPD basis set[21] on all light atoms (obtained through the Basis Set Exchange, accessed September 2021)[23-25] (**BS2**). The SPE calculations were performed in cyclohexane solvent using the SMD solvent continuum reported by Truhlar and co-workers.[26] In all cases, Gibbs free energies for calculations using **BS2** were approximated by summing the internal energy calculated with **BS2** and the thermal correction from the frequency calculation on the same structure with **BS1**. Coordinates for optimized geometries are given as a multi-structure XYZ file with titles matching the names of the structures given in Fig. 6 in the main text.

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8.2 Discussion of Alternate pathways

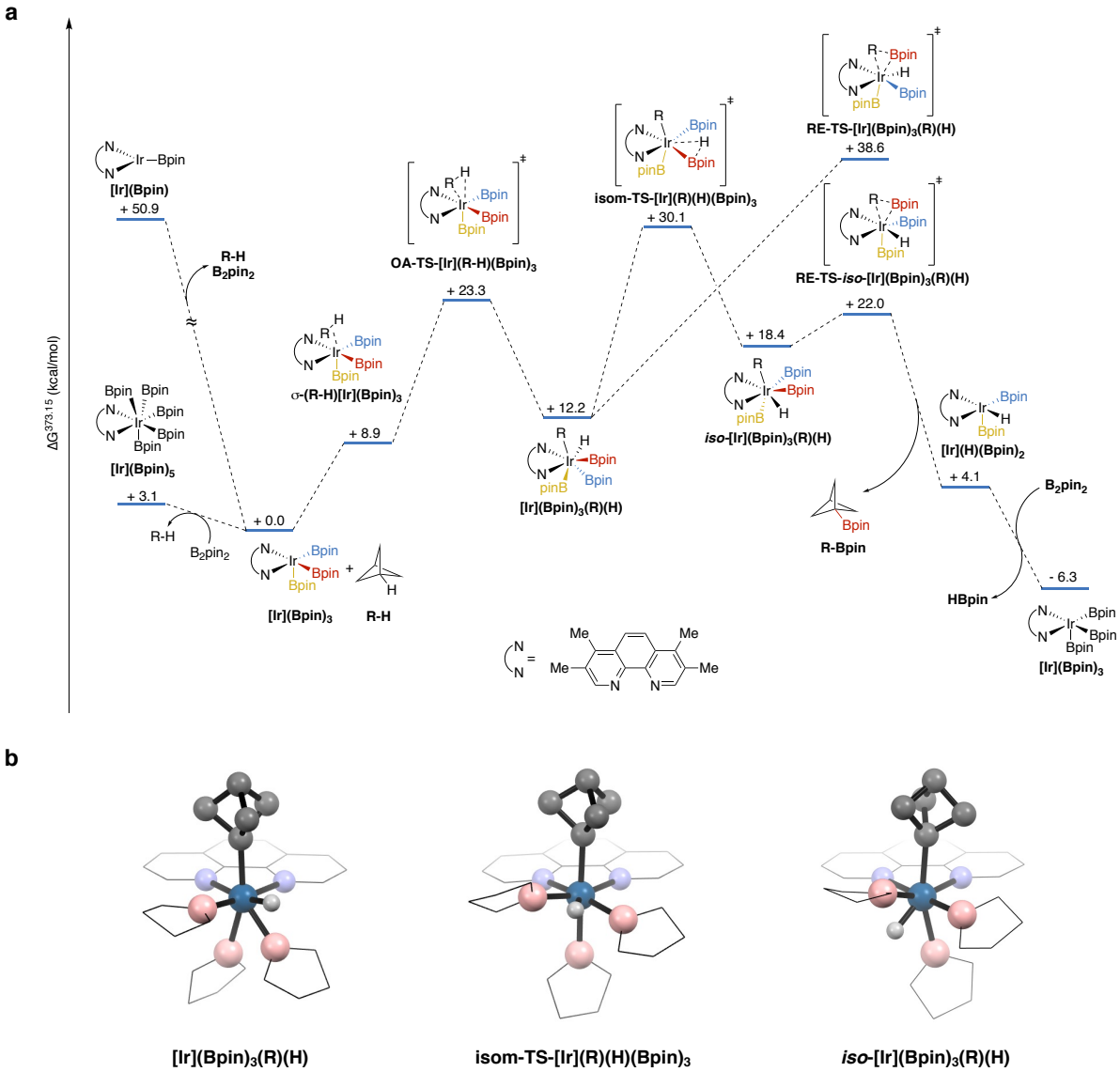

Fig. S19. Energy Diagram obtained via DFT calculations. Equivalent to Fig. 5 of the main text.

To investigate the possibility of a Ir(I)-Ir(III) cycle, the free energies of **[Ir](Bpin)**, B_2pin_2, and **[Ir](Bpin)$_3$** were calculated and compared. Formation of **[Ir](Bpin)$_3$** from **[Ir](Bpin)** and B_2pin_2 is exergonic by 50.9 kcal/mol. Thus, reactivity through Ir(I) species in the presence of large excesses of B_2pin_2 is unlikely. In contrast, the energy of **[Ir](Bpin)$_5$** is calculated to be only 3.1 kcal/mol above that of **[Ir](Bpin)$_3$** and B_2pin_2 Therefore, **[Ir](Bpin)$_5$** could be present in small quantities.

The isomerization process that we present here is analogous to that proposed for the borylation of chlorosilanes by Himo[27] and the borylation of benzylic C–H bonds by our own group.[28] The isomerization occurs through **isom-TS-[Ir](R)(H)(Bpin)$_3$,** which adopts a pentagonal-bipyramidal configuration in which the hydride is nearly coplanar with the phenanthroline ligand and two boryl groups.

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Sakaki has proposed an alternative isomerization pathway prior to the reductive elimination to form the C–B bond during the borylation of tetrahydrofuran.[29] This process involves the repositioning of the two boryl groups that are located below the phenanthroline plane. We were unable to find a transition state structure for such a potential isomerization mechanism for the Ir(V)-bicyclopentyl complex. When we performed IRC calculations and fully followed **RE-TS-[Ir](Bpin)$_3$(R)(H)** along its path to revert to the starting materials during an optimization calculation, we found that the structure of one of the steps resembled the transition state for isomerization reported by Sakaki. (See center structure in Fig. S20) Therefore, it appears that reductive elimination from the bicyclopentyl complex occurs in a continuous manner with no discrete transition state for isomerization during this process.

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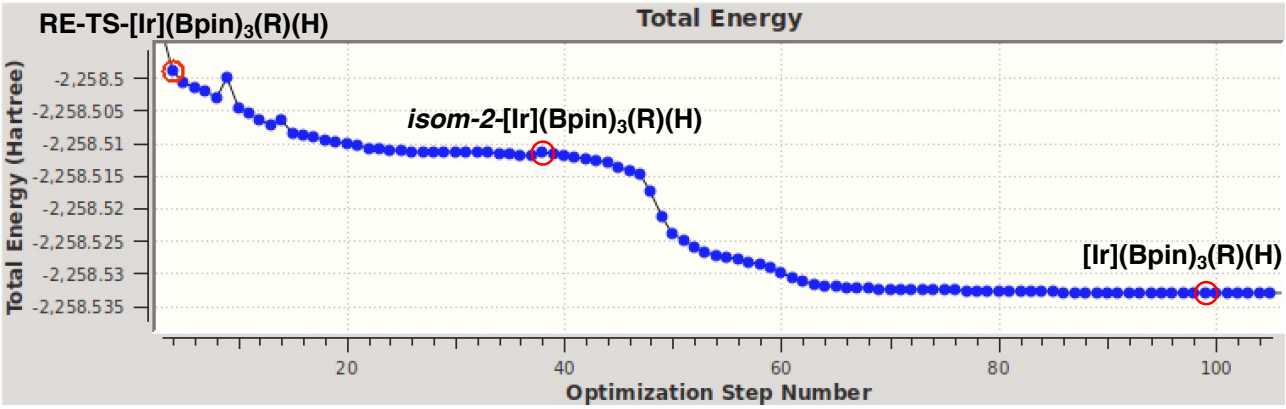

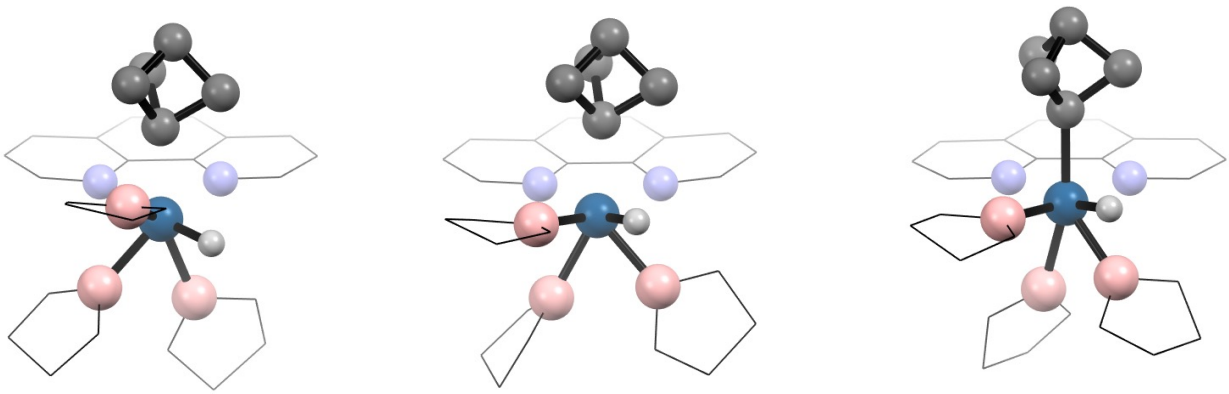

RE-TS-[Ir](Bpin)$_3$(R)(H) | *isom-2*-[Ir](Bpin)$_3$(R)(H) | [Ir](Bpin)$_3$(R)(H)

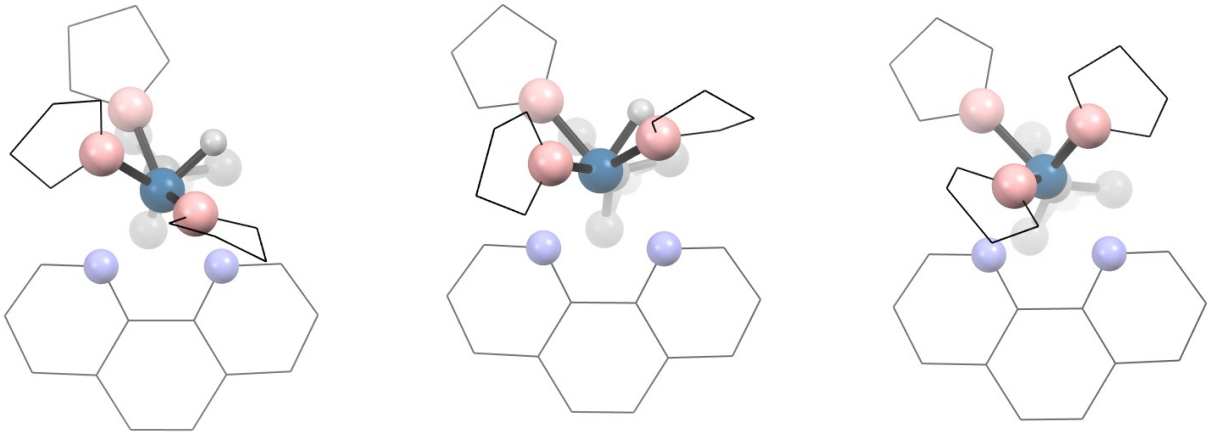

Fig. S20. Plot of energy *versus* step number for the structure changes along the reaction coordinate from RE-TS-[Ir](Bpin)$_3$(R)(H) to [Ir](Bpin)$_3$(R)(H) and selected structures.

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8.3 Calculated KIE value

Zero-point energies (ZPEs) were calculated assuming harmonic potentials for bicyclo-[1.1.1]-pentane, bicyclo-[1.1.1]-pentane-d_1, Isom-TS-[Ir](R)(H)(Bpin)$_3$, and Isom-TS-[Ir](R)(H)(Bpin)$_3$-d_1. The KIE value was obtained by applying the Eyring equation to the differences in ZPEs.

Species	ZPE-H (Hartree)	ZPE-D (Hartree)	ZPE-diff (Hartree)	ZPE-diff (kcal/mol)
bicyclopentane	0.117665	0.114414	0.003251	2.040
Isom-TS-[Ir](R)(H)(Bpin)$_3$	0.947681	0.945266	0.002415	1.515

KIE = exp((2.040-1.154)/0.741529) = 2.03

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9. NMR spectra

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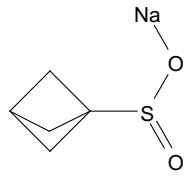
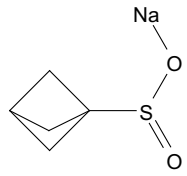
Sodium bicyclo[1.1.1]pentanesulfinate

[Experimental]

^{1}H NMR (600 MHz, D_2O)



^{13}C NMR (151 MHz, D_2O)



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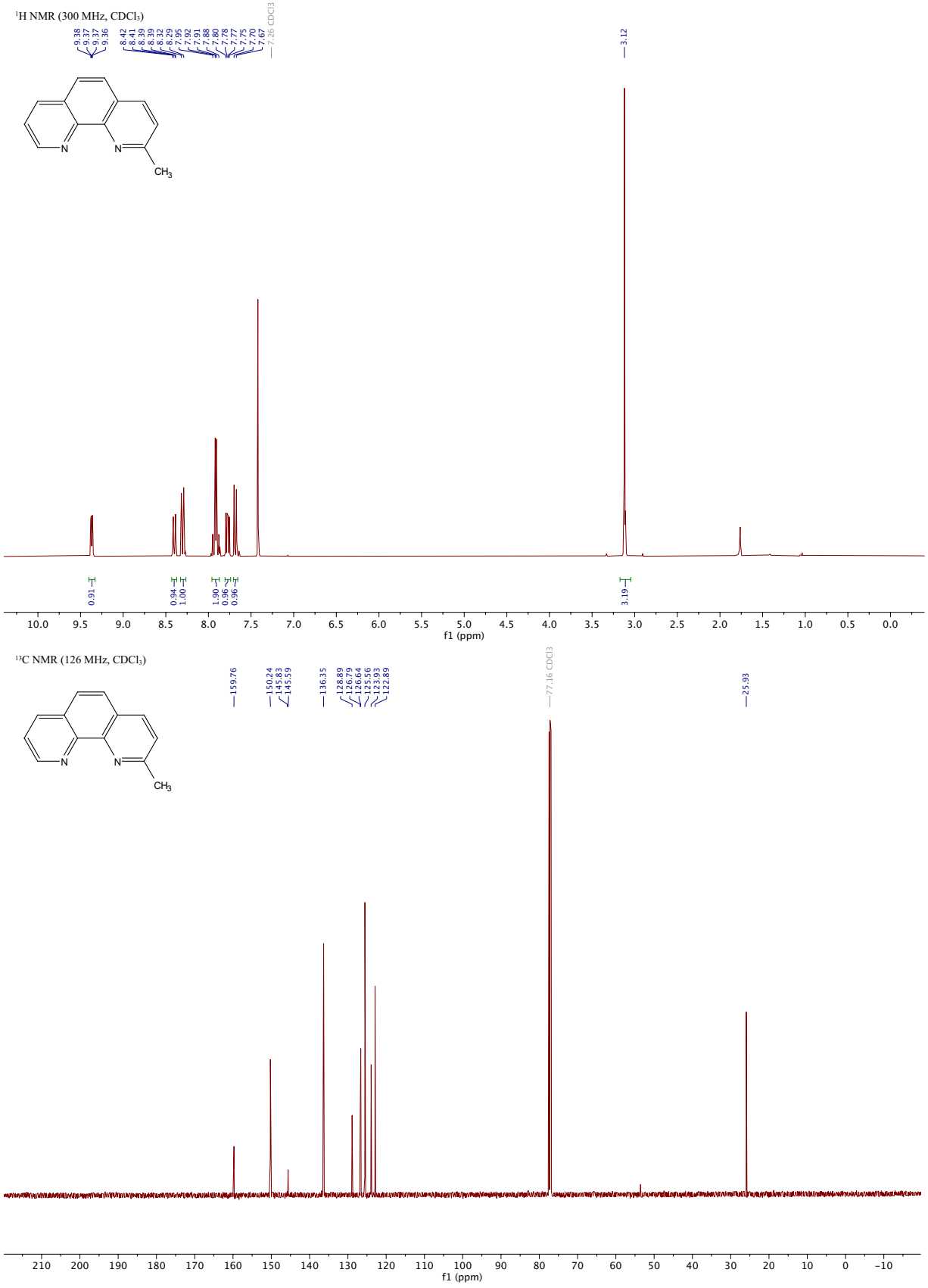
2-methylphenanthroline

[Experimental]



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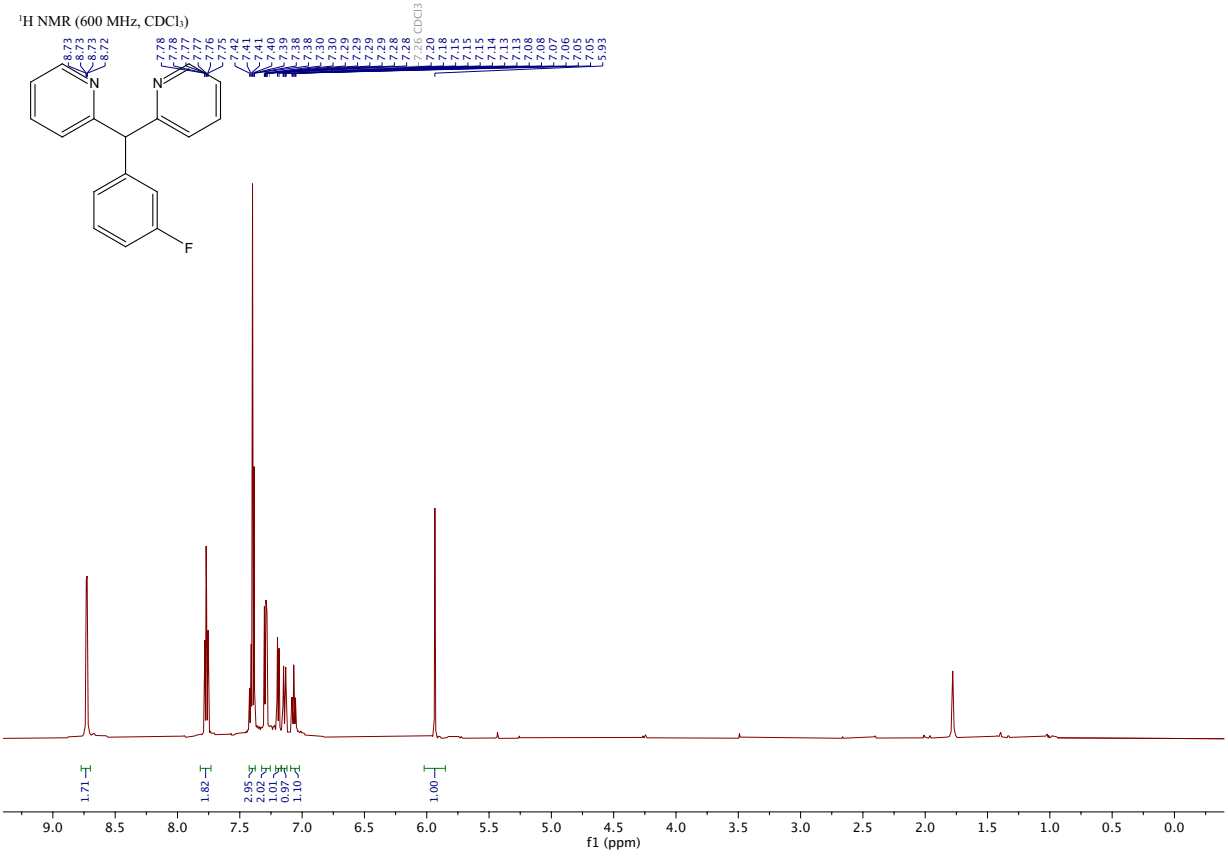
L3

2,2'-((3-fluorophenyl)methylene)dipyridine [Experimental]



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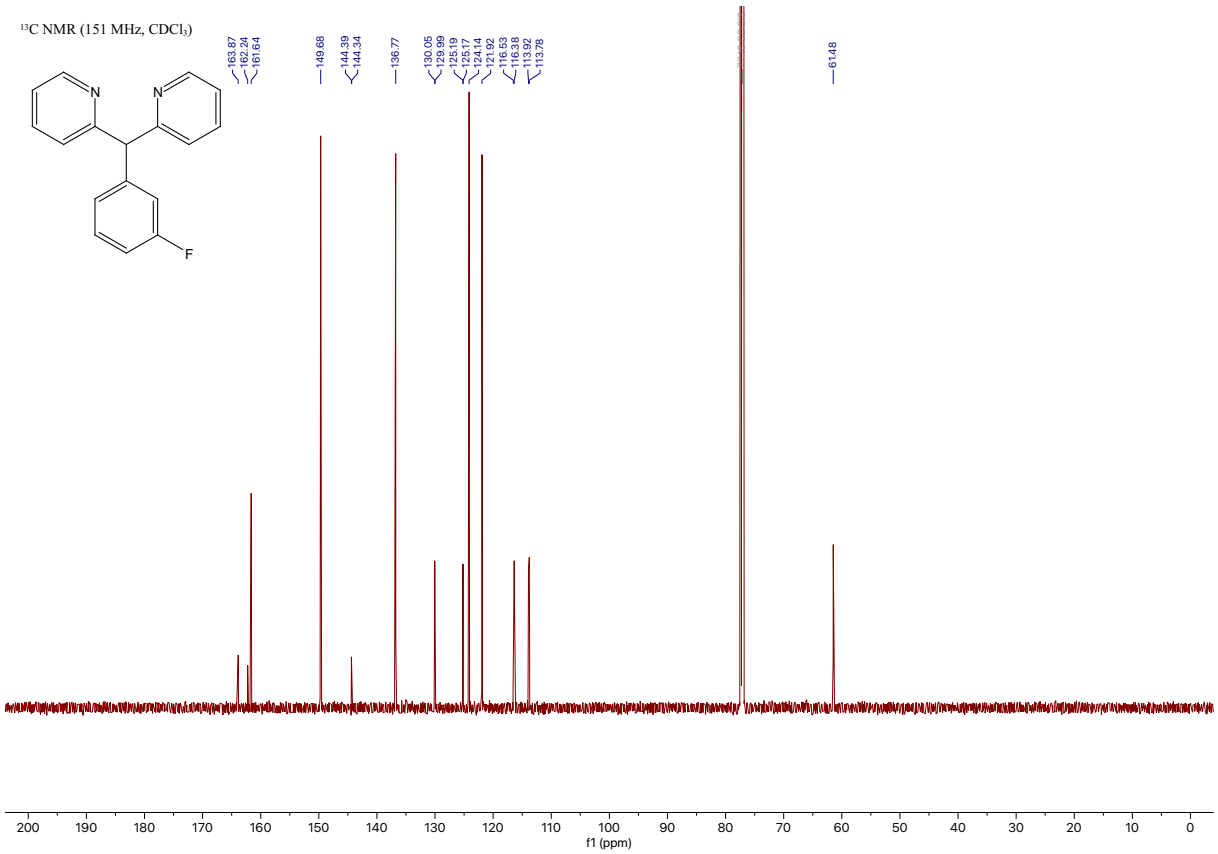
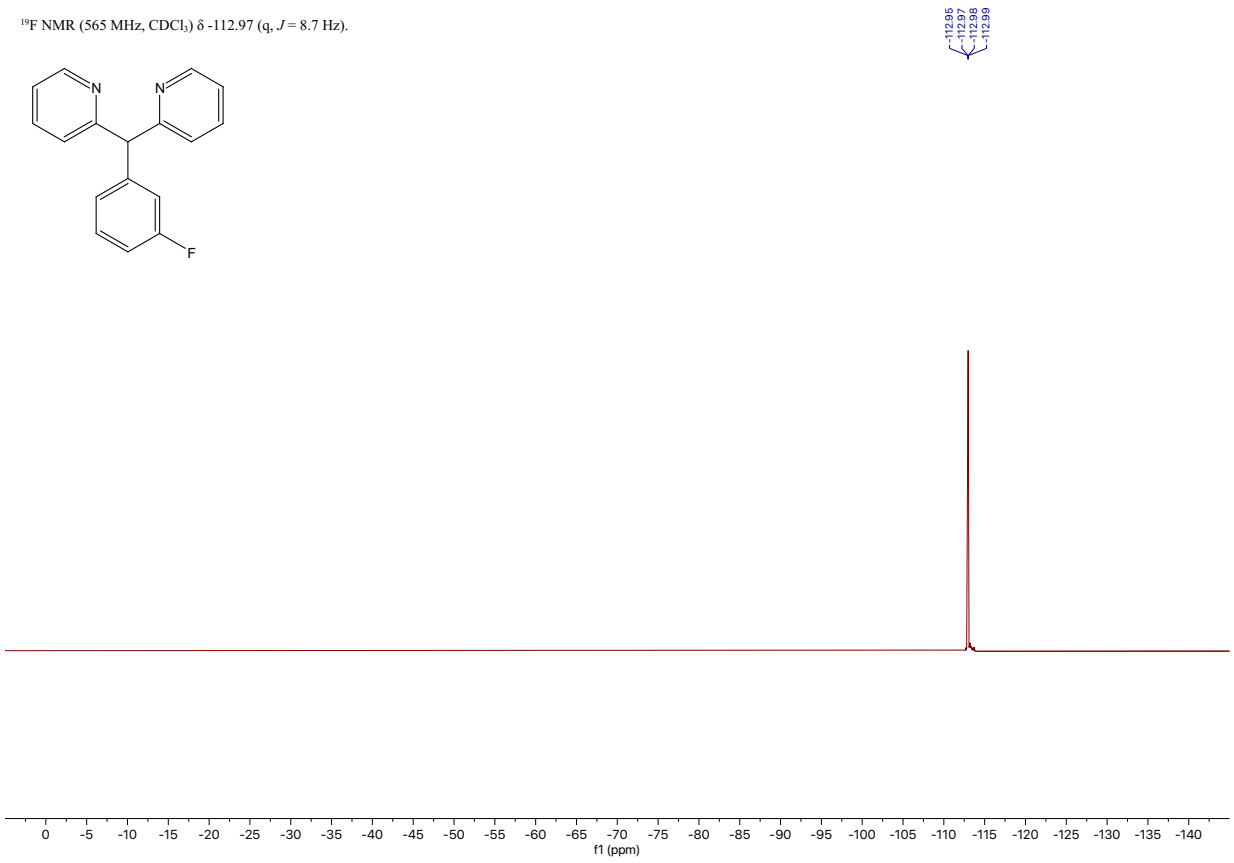
^{13}C NMR (151 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$) δ -112.97 (q, J = 8.7 Hz).



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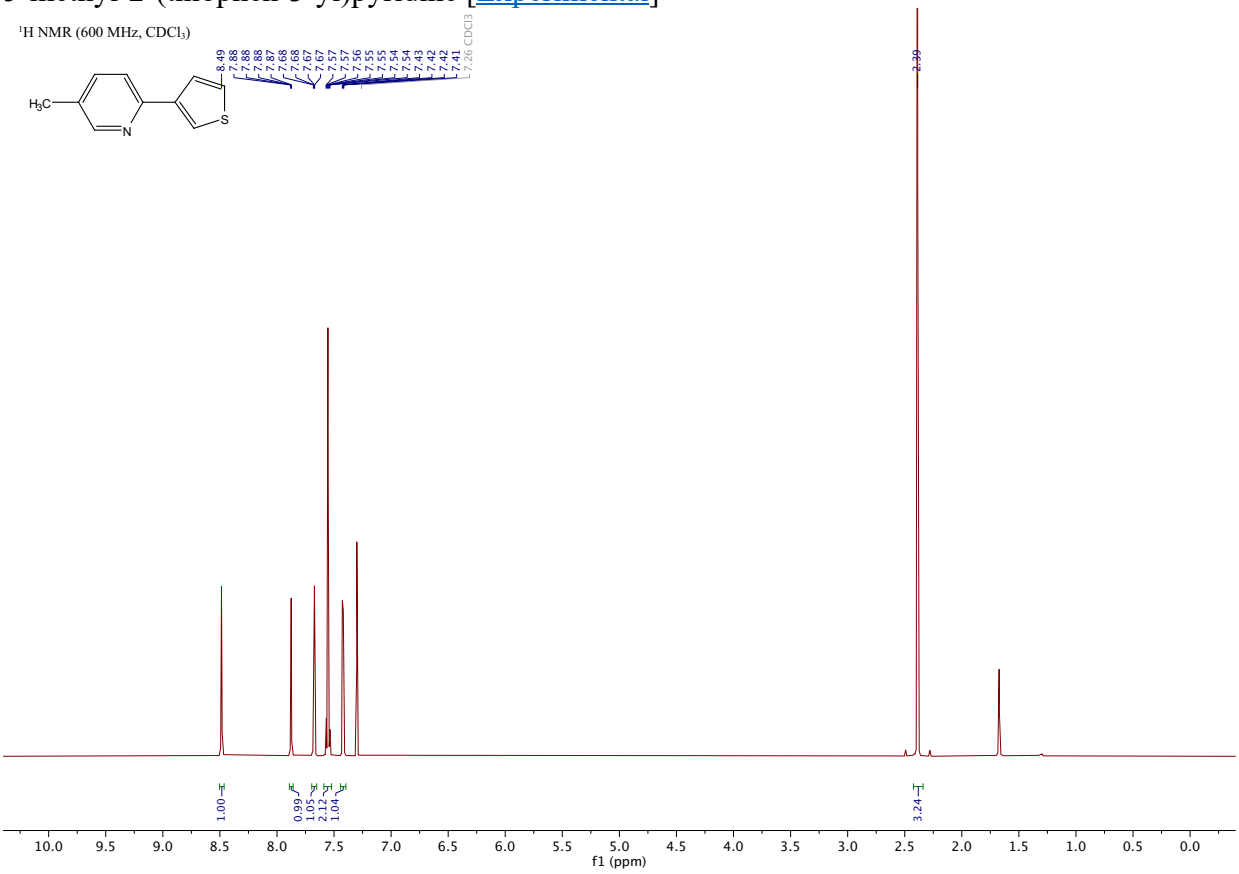
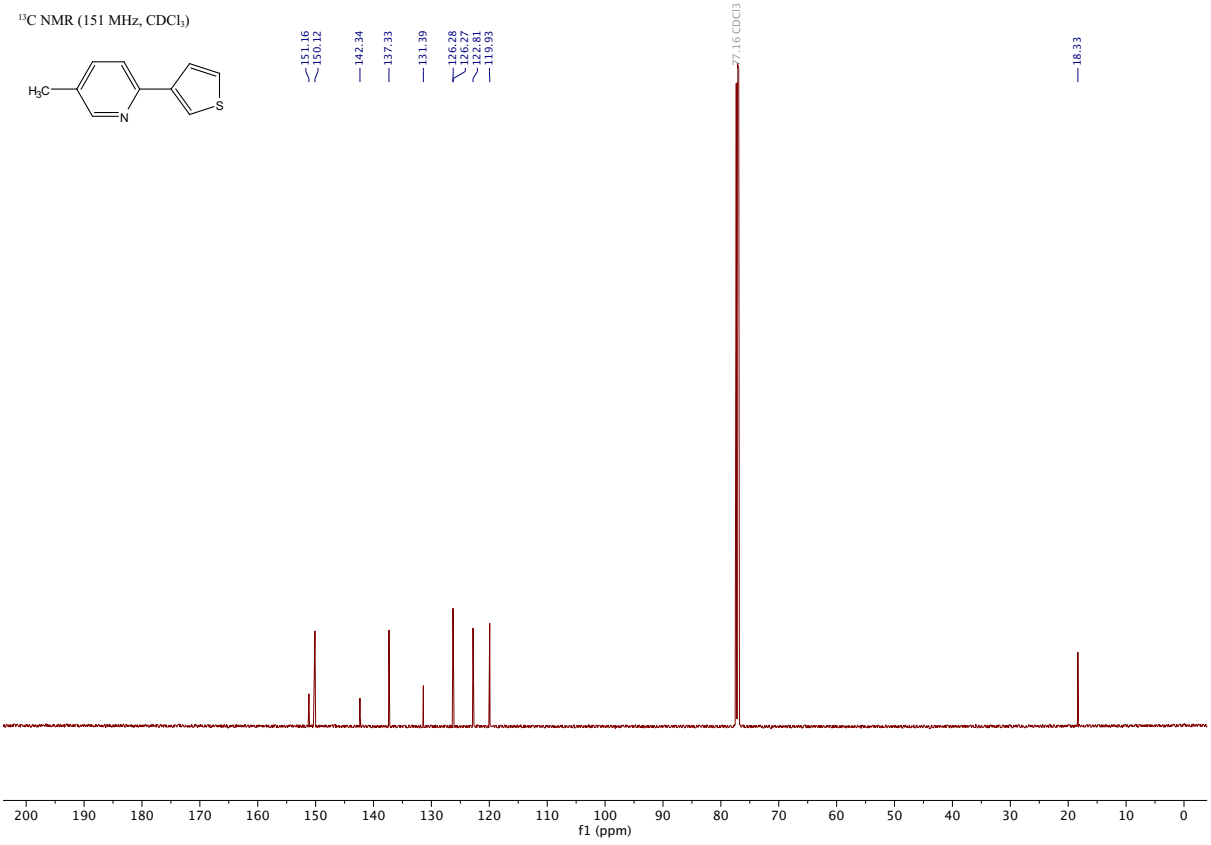
L4

5-methyl-2-(thiophen-3-yl)pyridine [Experimental]





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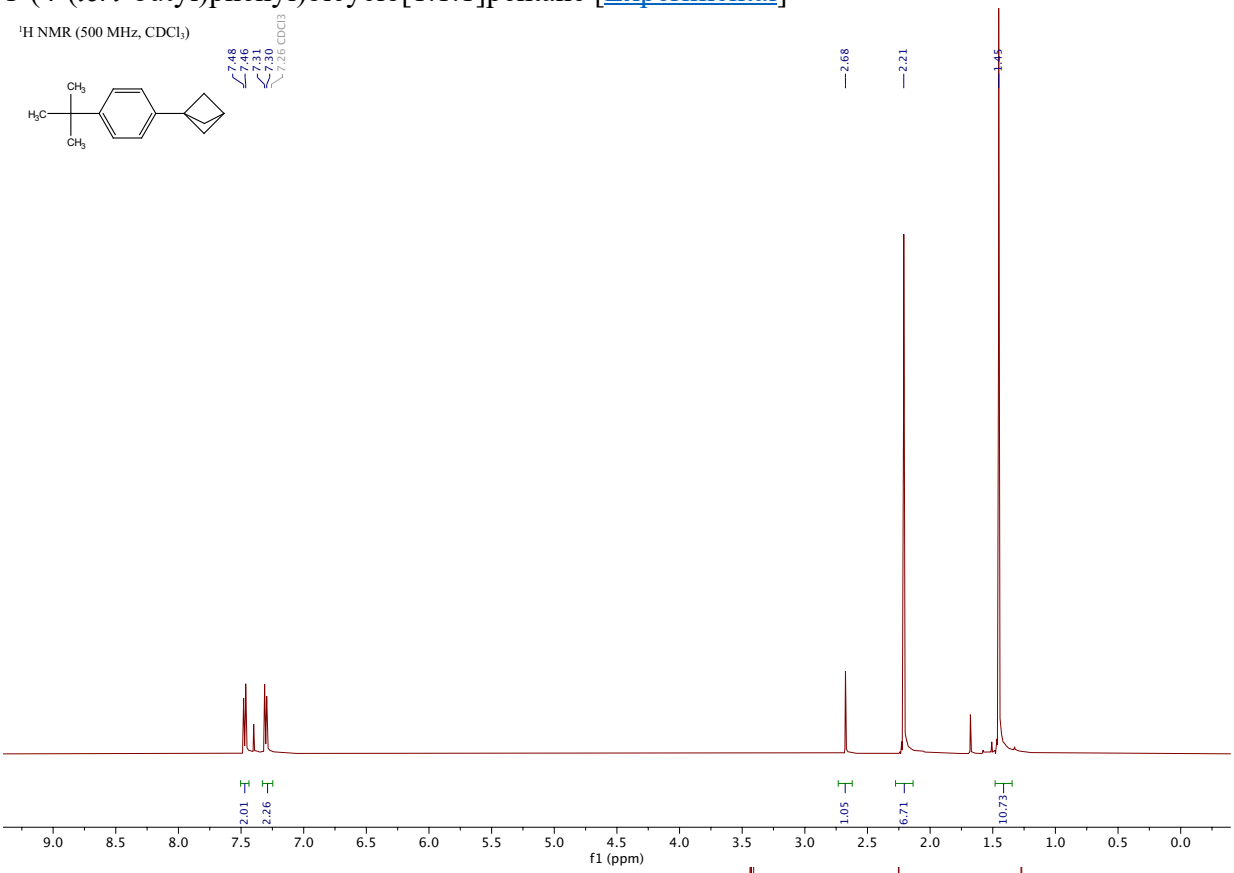
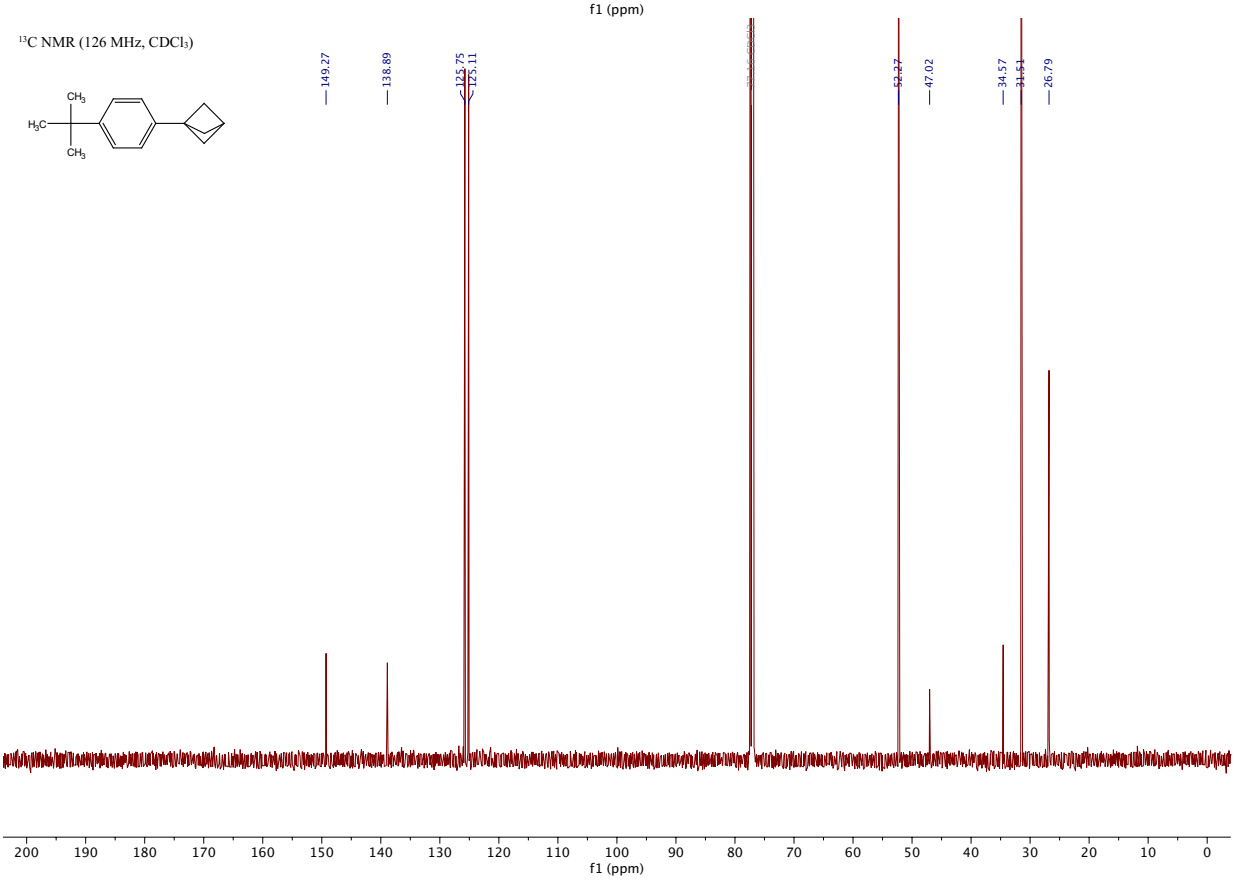
Compound 1b

1-(4-(*tert*-butyl)phenyl)bicyclo[1.1.1]pentane [Experimental]





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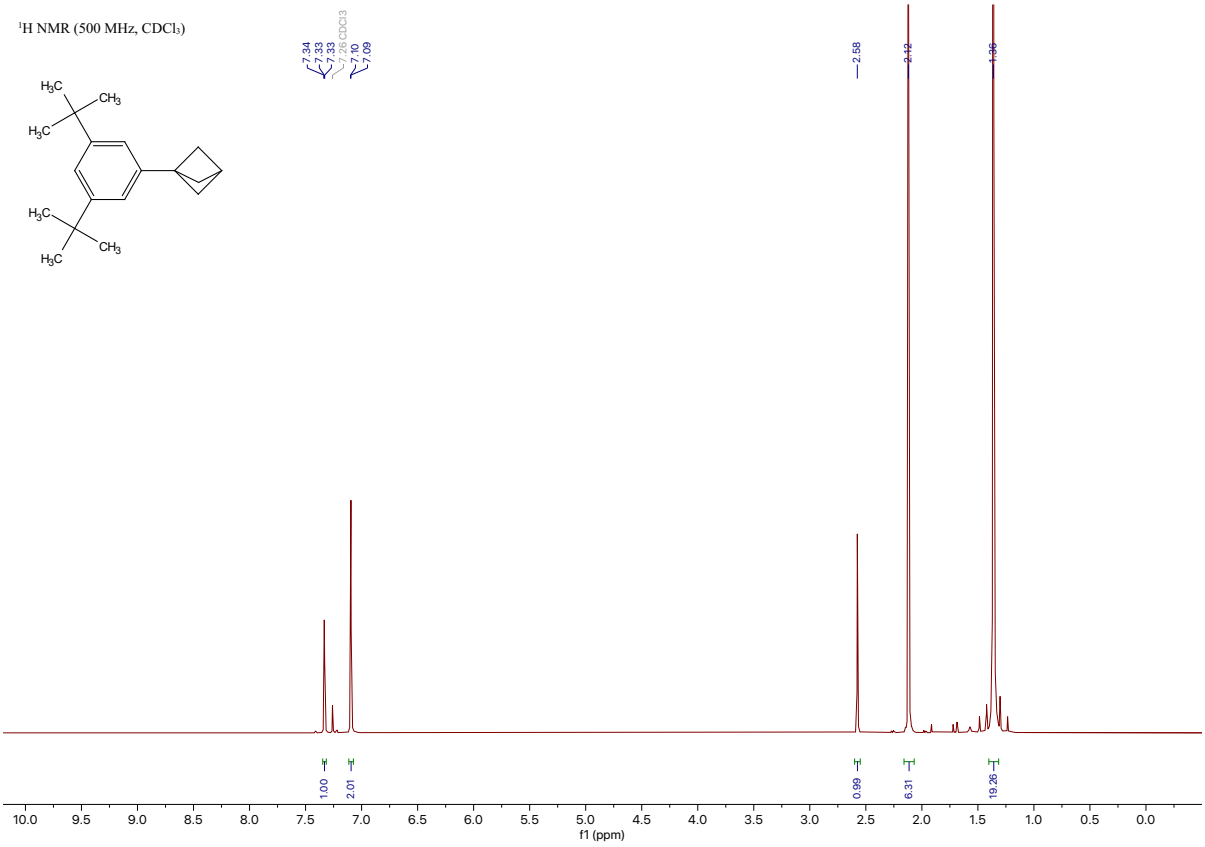
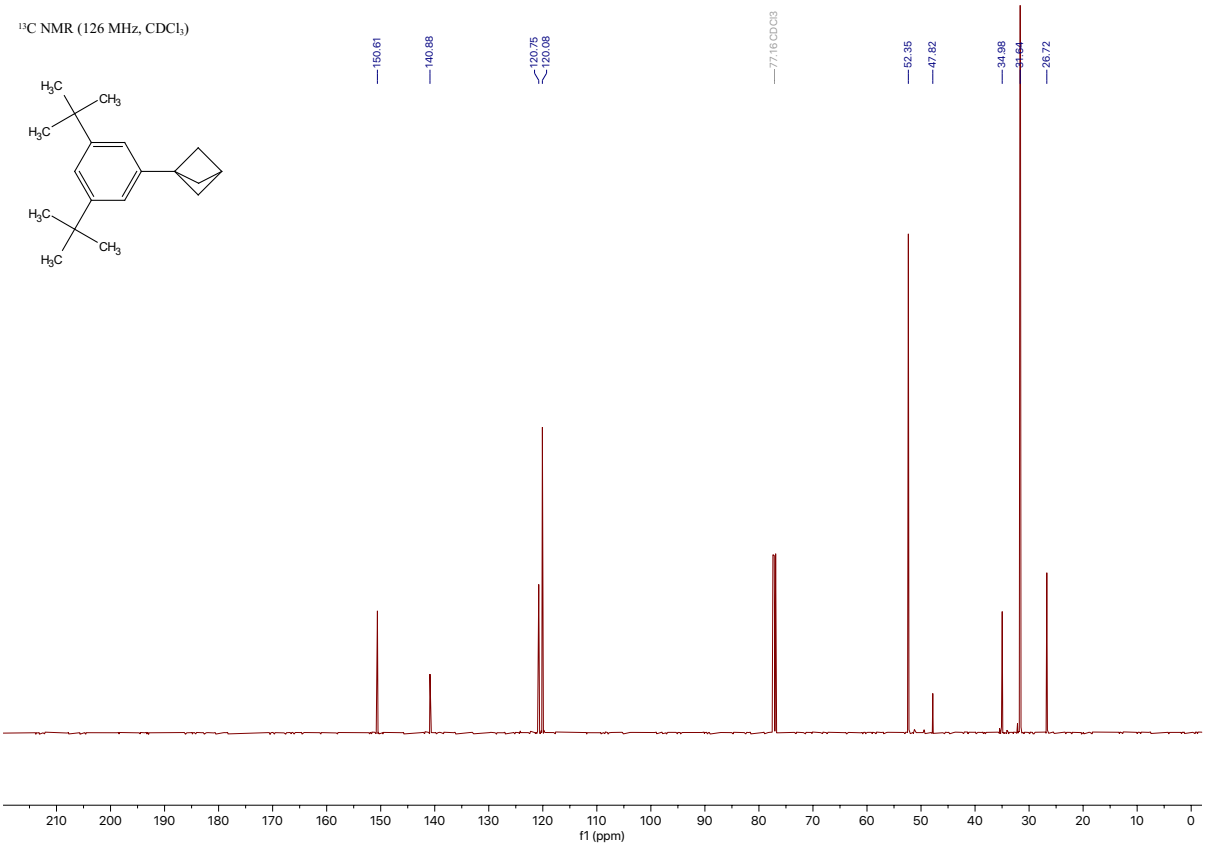
Compound 2b

1-(3,5-di-*tert*-butylphenyl)bicyclo[1.1.1]pentane [Experimental]





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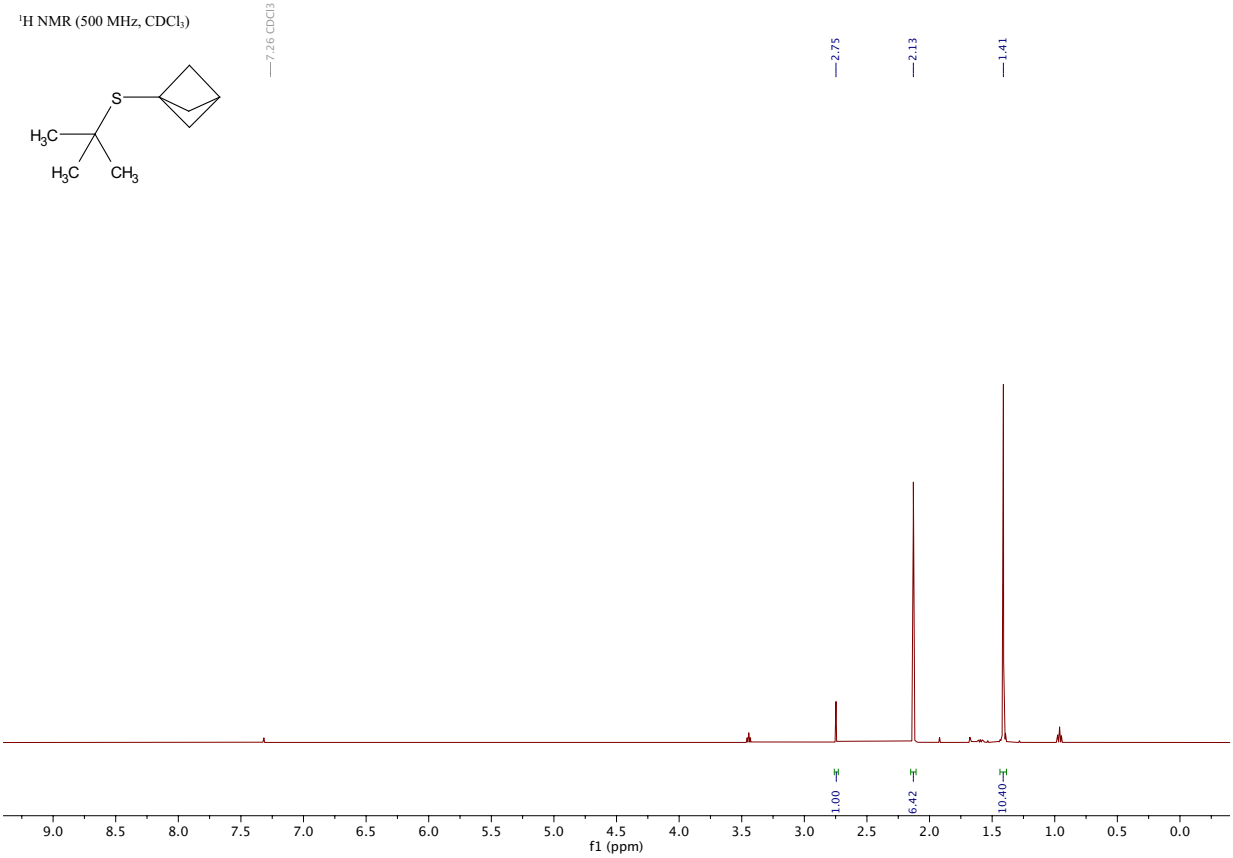
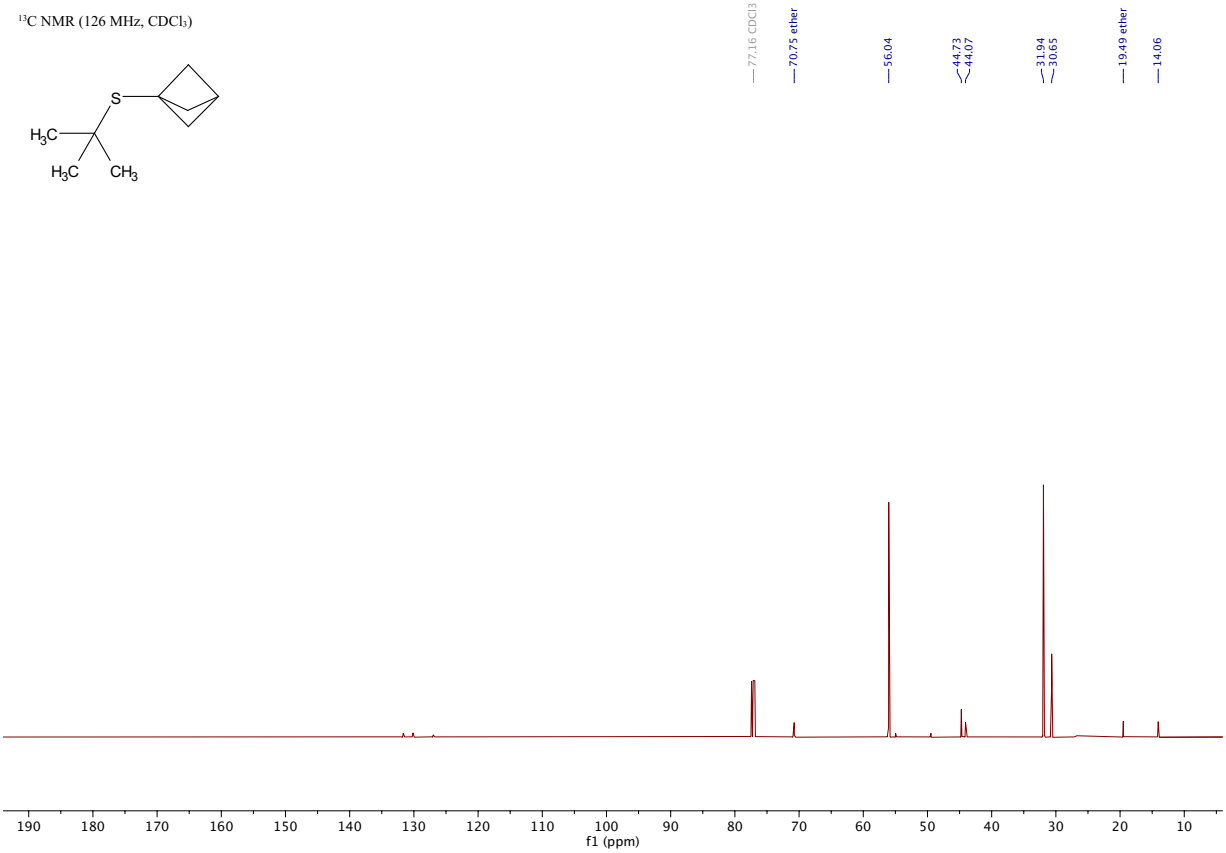
Compound 3b

bicyclo[1.1.1]pentan-1-yl(*tert*-butyl)sulfane [Experimental]

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



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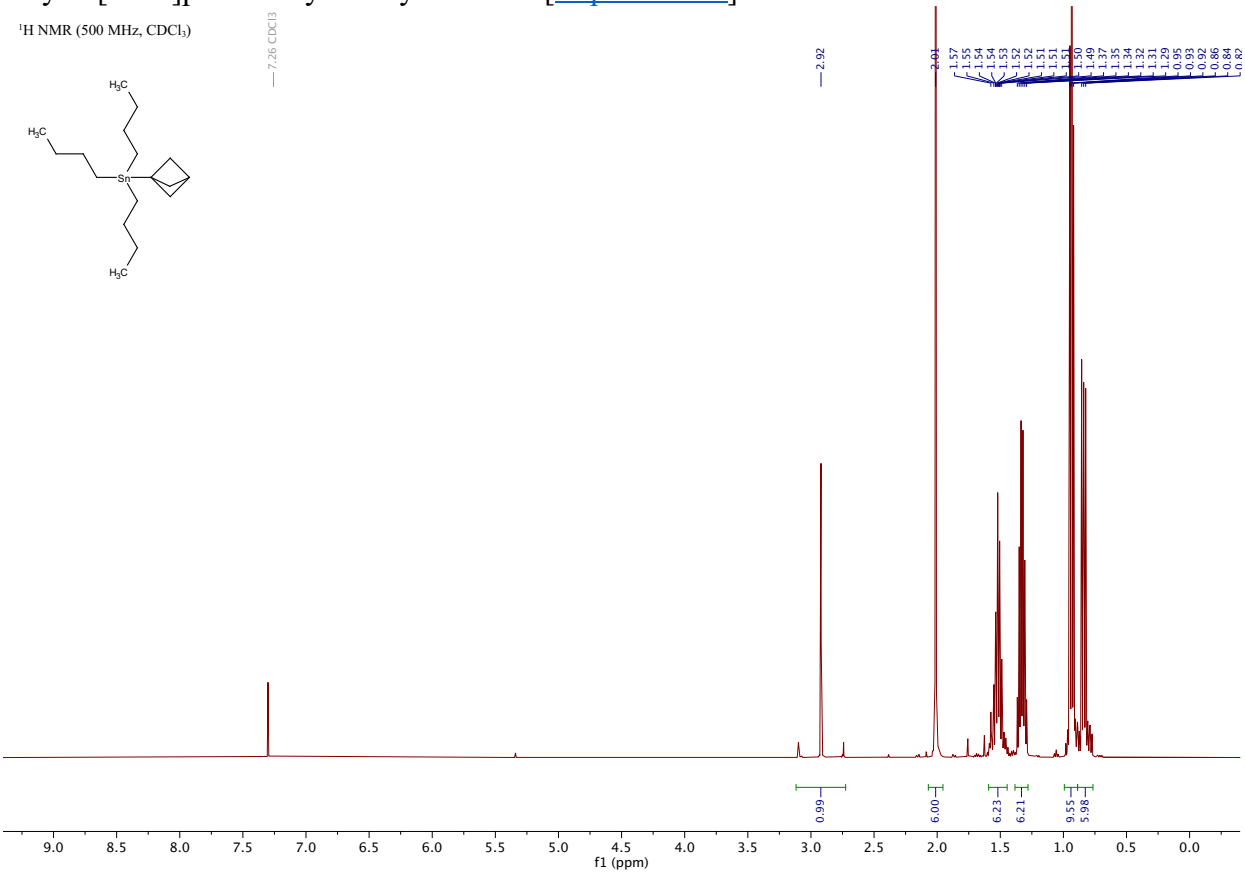
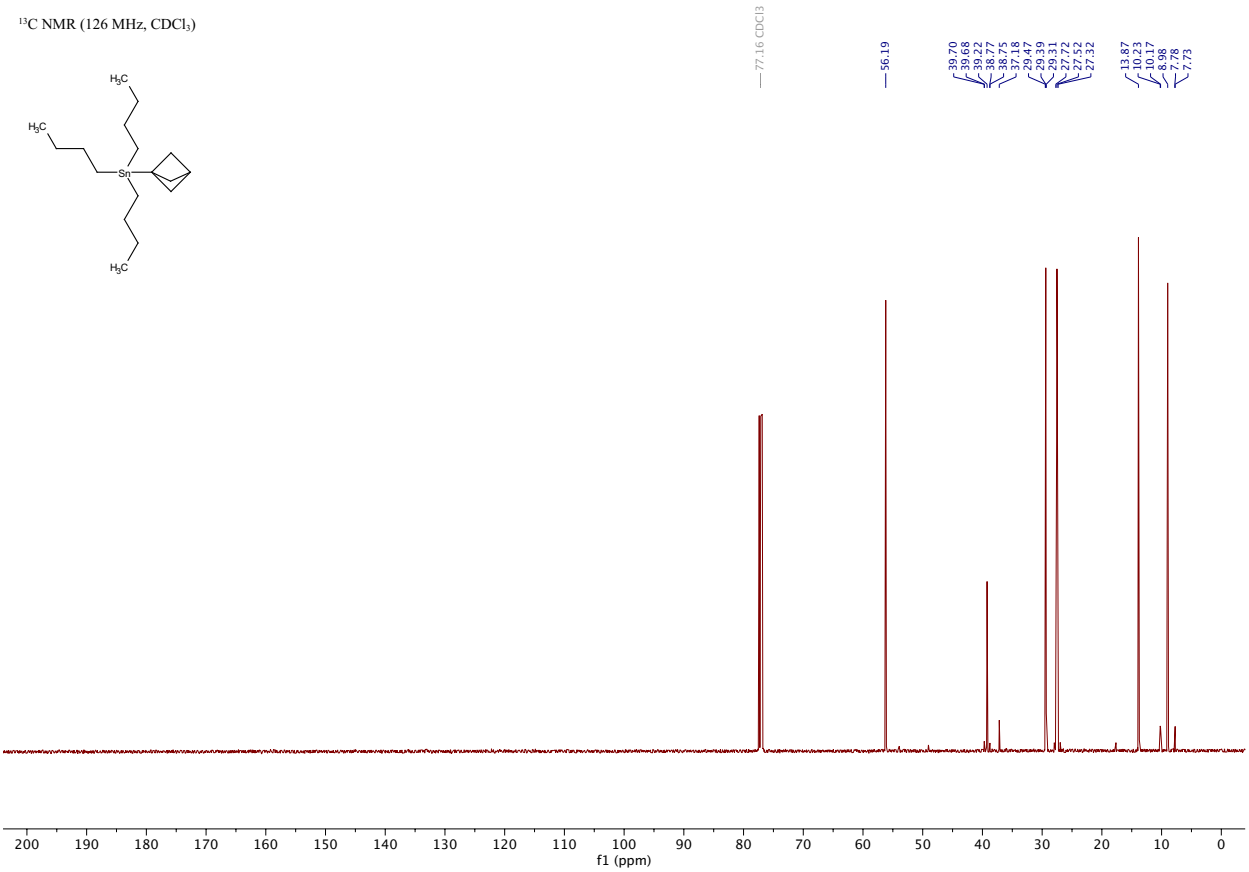
Compound 4b

bicyclo[1.1.1]pentan-1-yltributylstannane [Experimental]

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

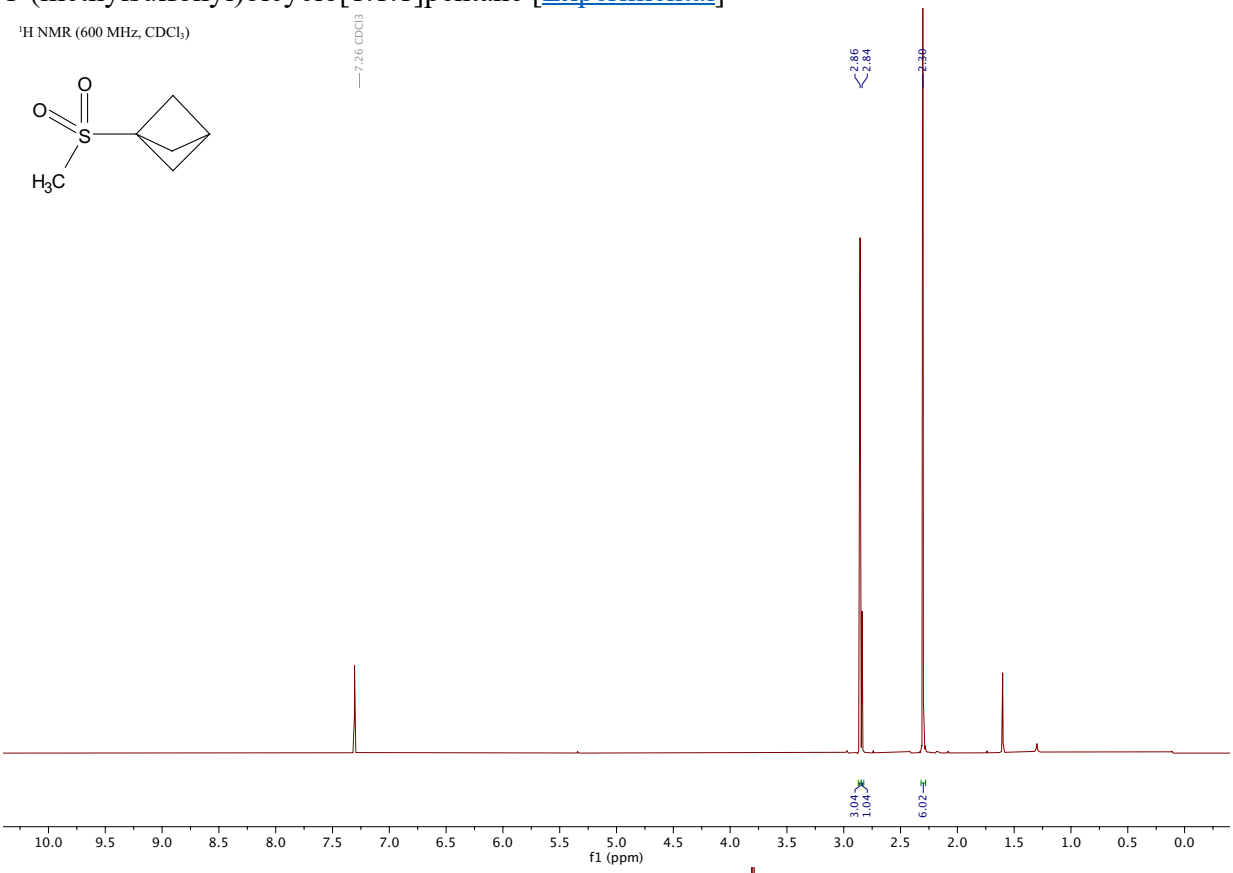


[*Return to table of contents*]

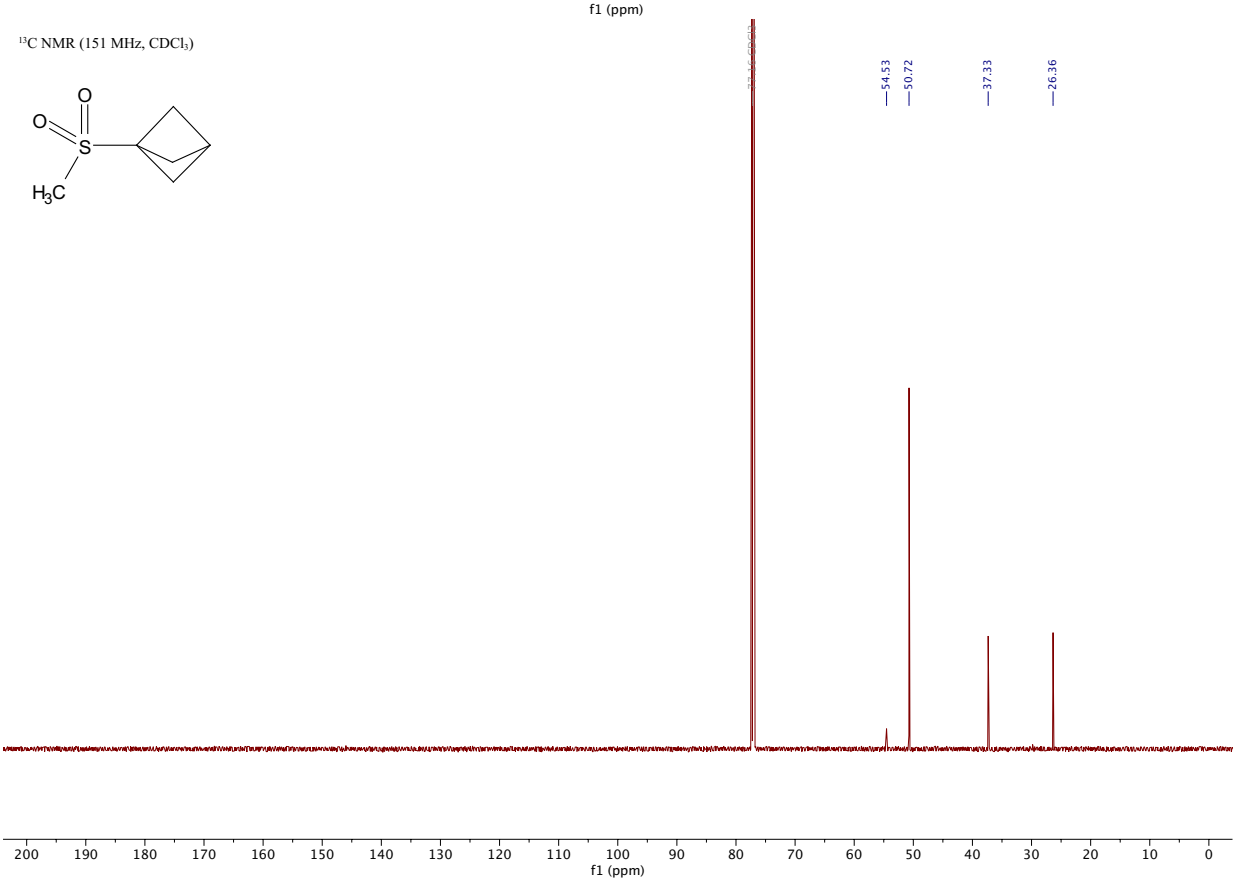
Compound 11b

1-(methylsulfonyl)bicyclo[1.1.1]pentane [Experimental]

^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

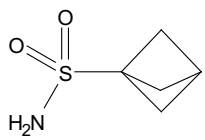


[*Return to table of contents*]

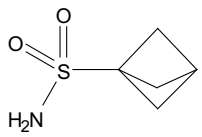
Compound 12b

bicyclo[1.1.1]pentane-1-sulfonamide [Experimental]

^{1}H NMR (700 MHz, Acetone)



^{13}C NMR (176 MHz, Acetone)

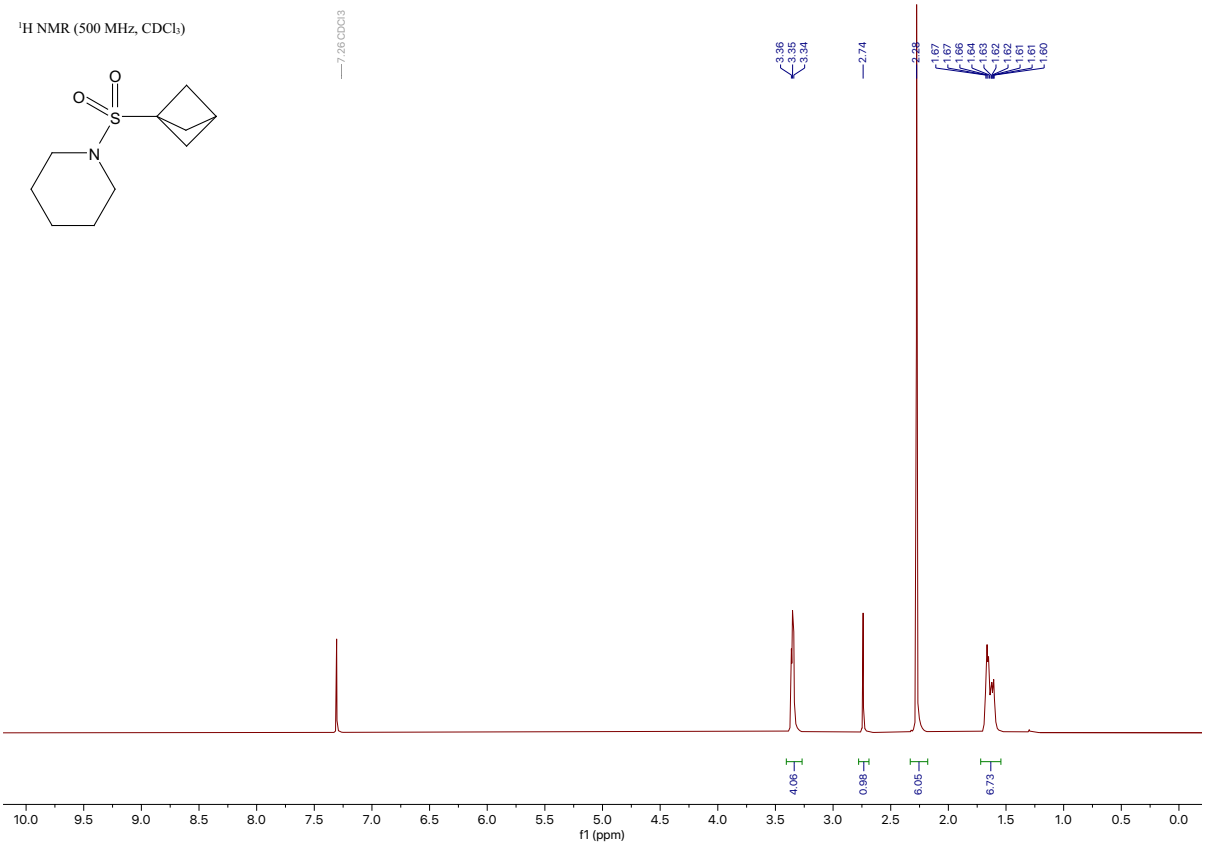


[*Return to table of contents*]

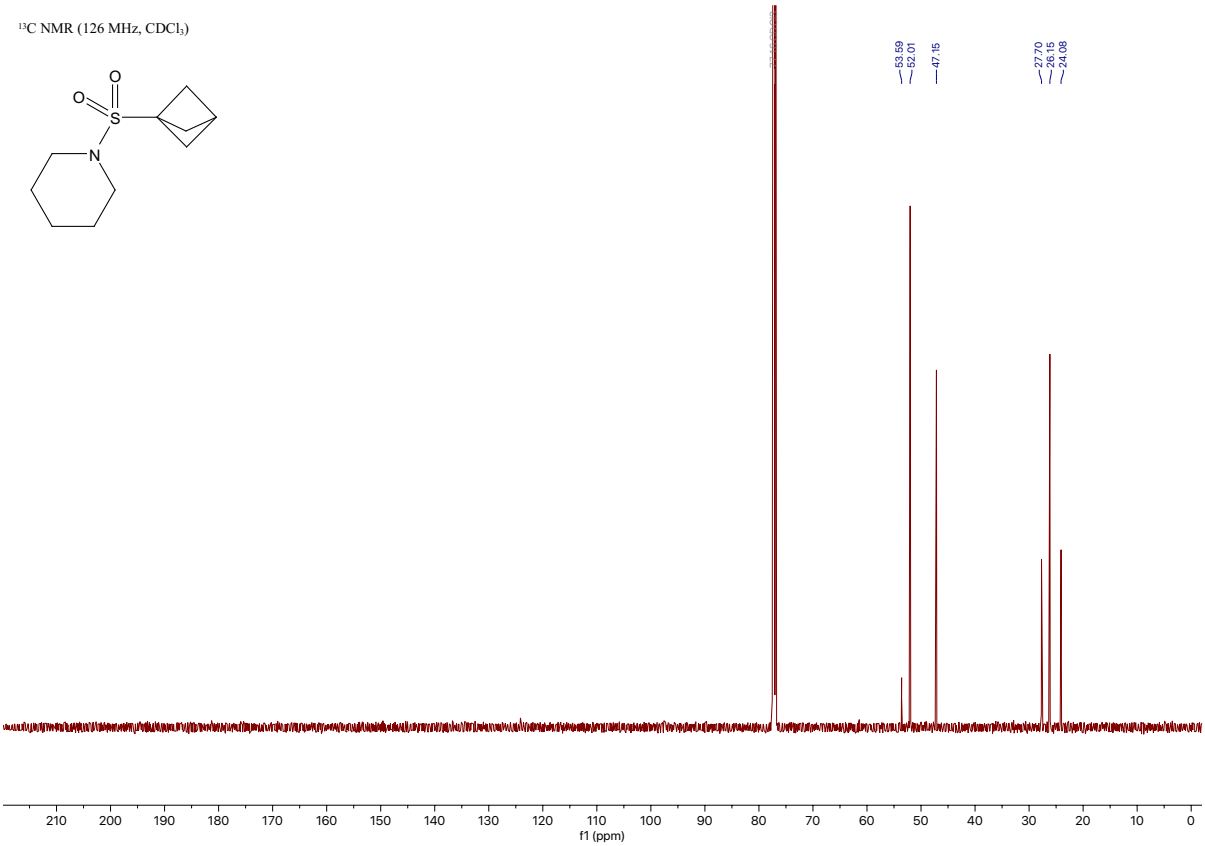
Compound 13b

1-(bicyclo[1.1.1]pentan-1-ylsulfonyl)piperidine [Experimental]

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



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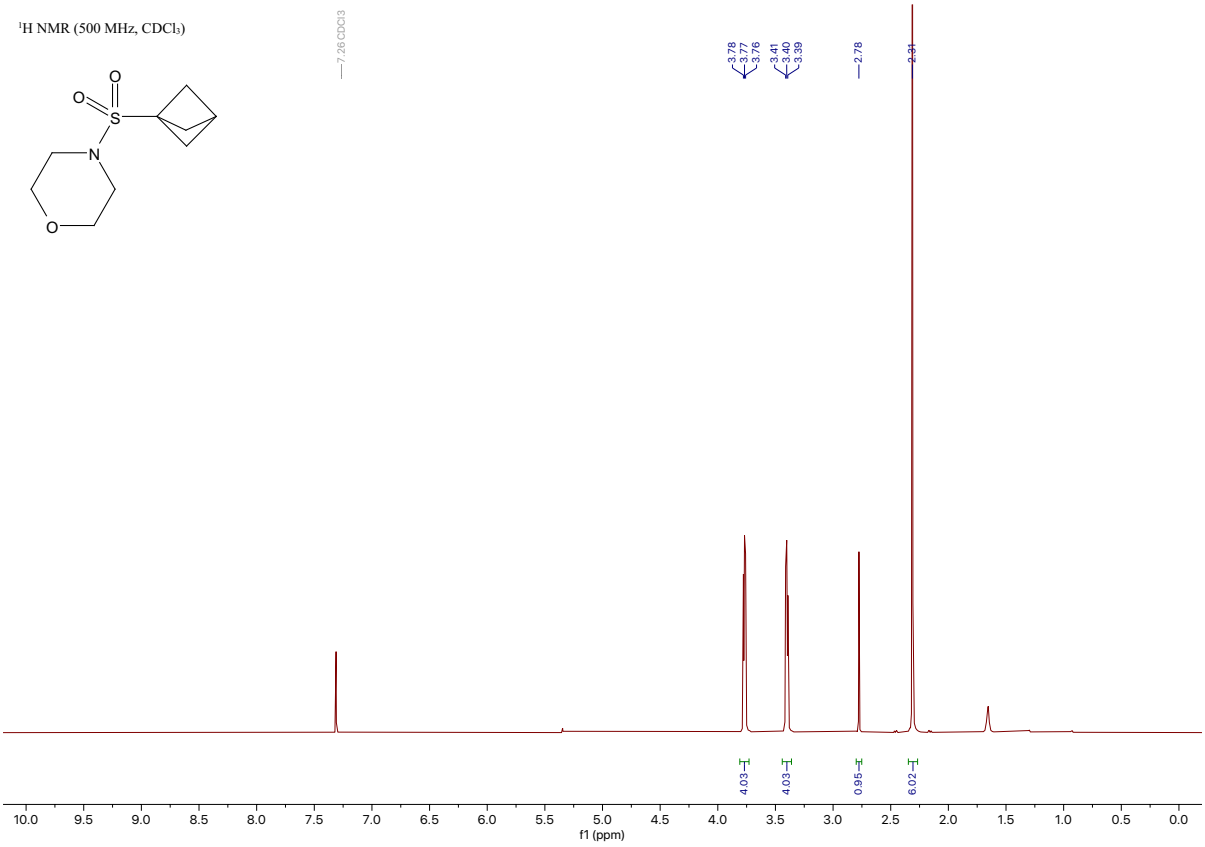
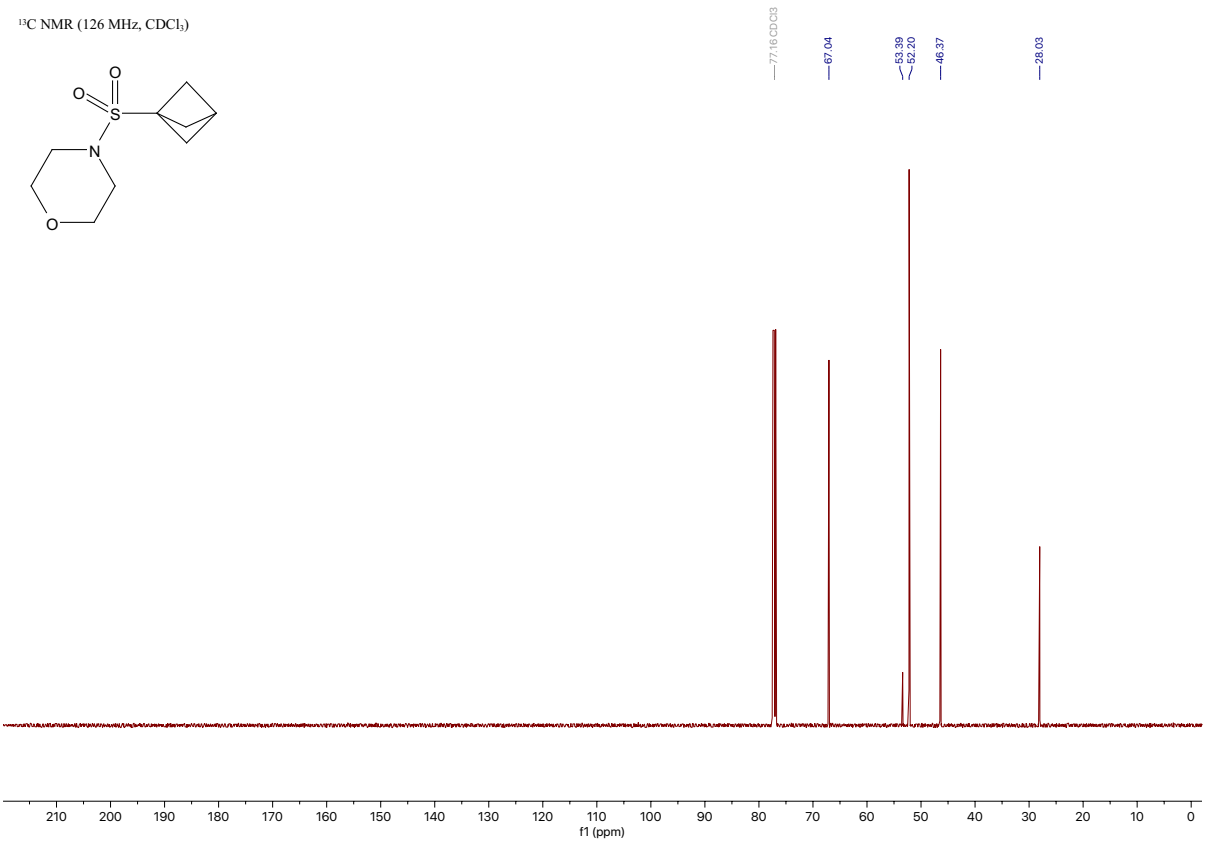
Compound 14b

4-(bicyclo[1.1.1]pentan-1-ylsulfonyl)morpholine [Experimental]

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



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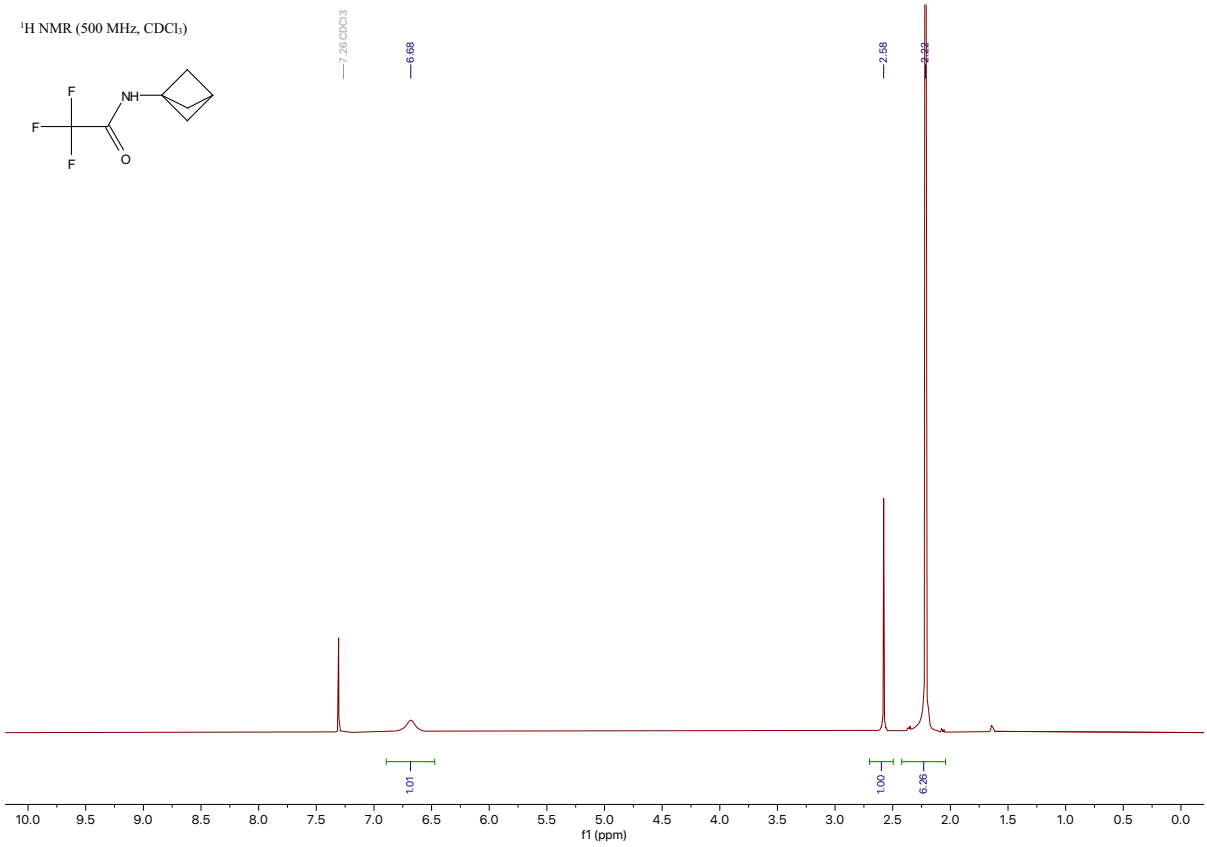
Compound 16b

N-(bicyclo[1.1.1]pentan-1-yl)-2,2,2-trifluoroacetamide

[Experimental]



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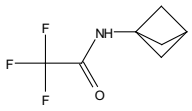
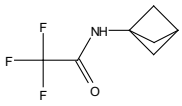
^{13}C NMR (126 MHz, $CDCl_3$)



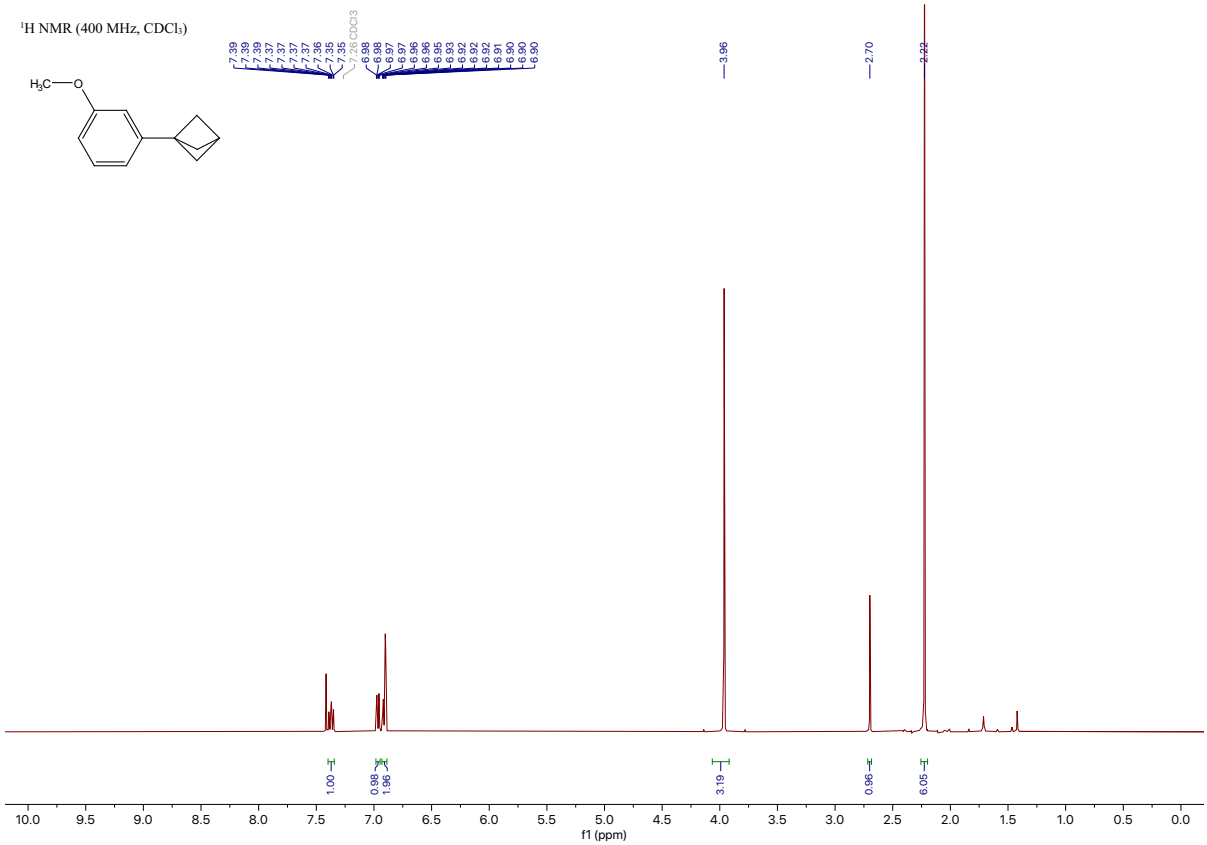
^{19}F NMR (470 MHz, $CDCl_3$)

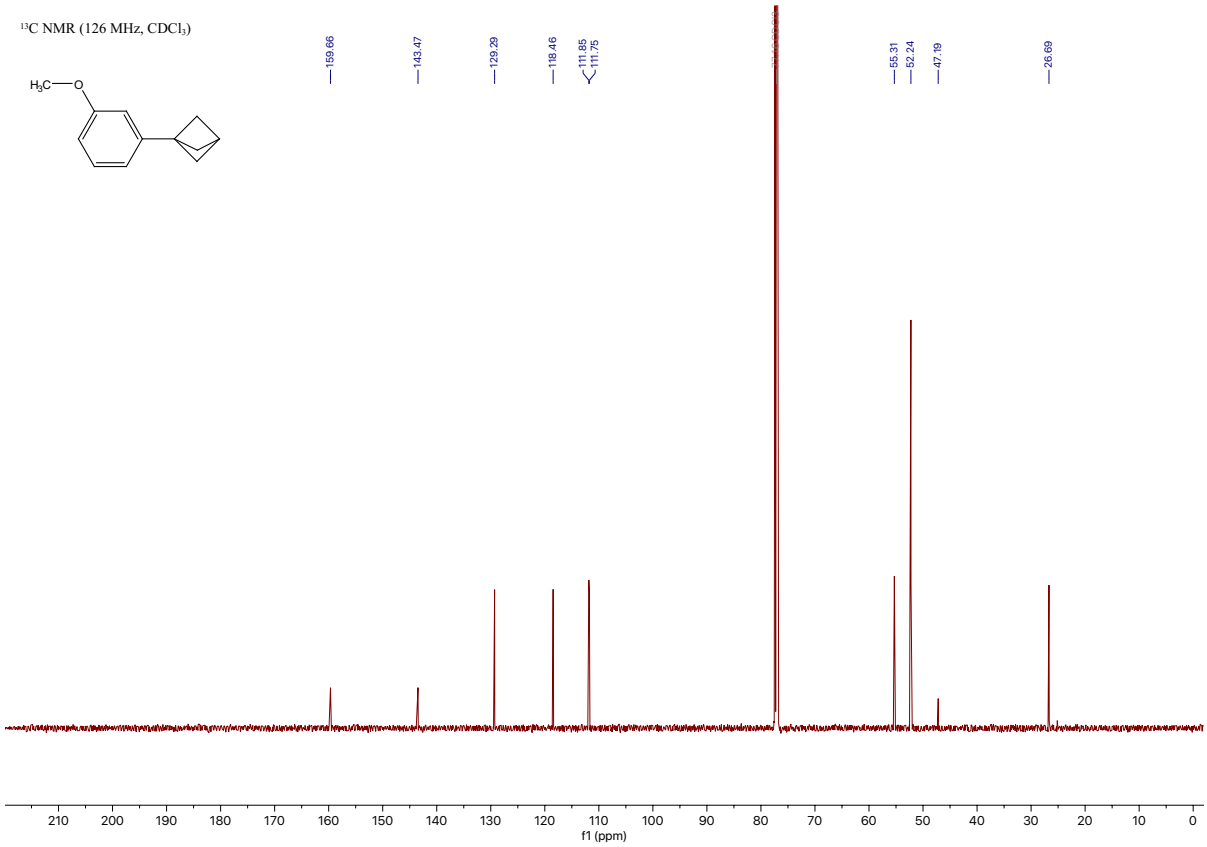


[*Return to table of contents*]

Compound 19b

1-(3-methoxyphenyl)bicyclo[1.1.1]pentane [Experimental]





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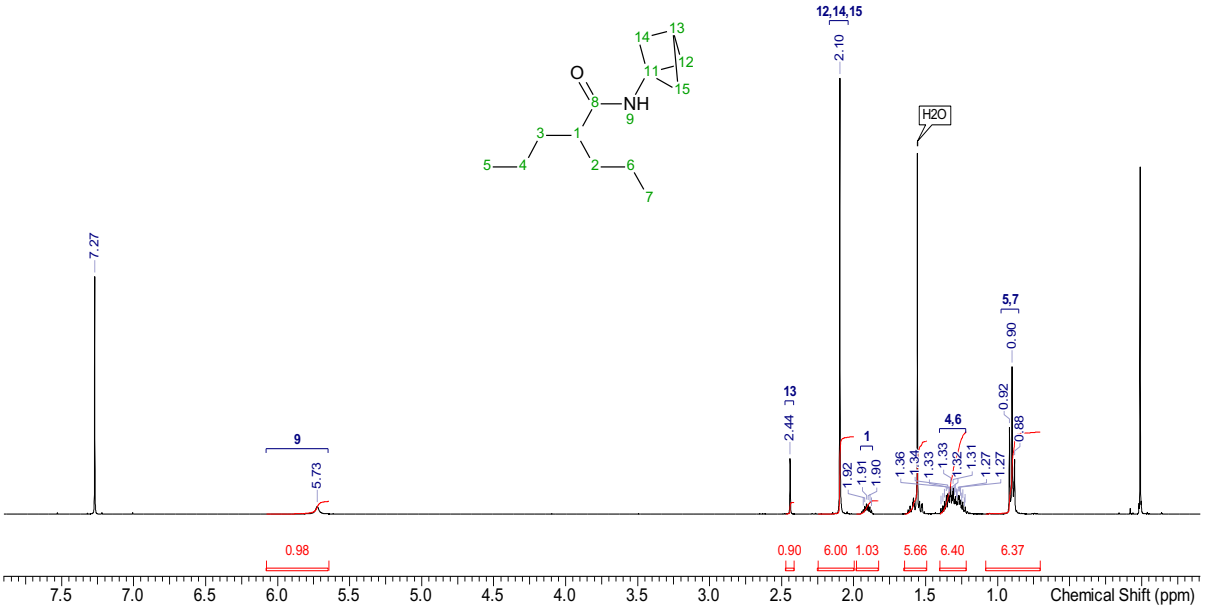
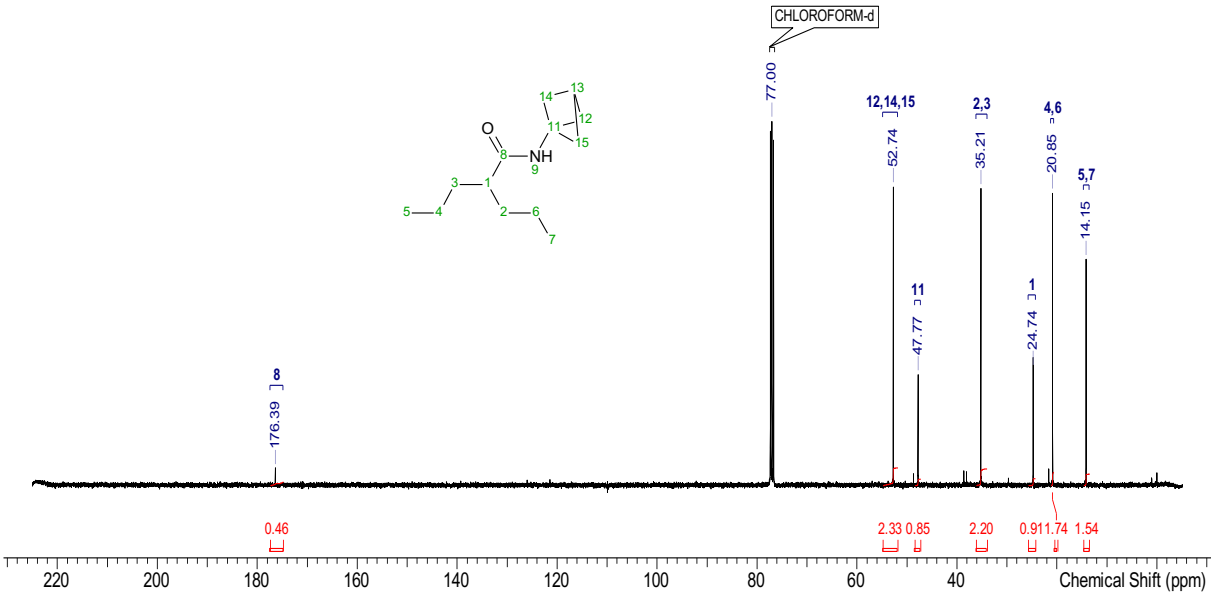
Compound 20b

***N*-(bicyclo[1.1.1]pentan-1-yl)-2-propylpentanamide** [Experimental]

[Return to table of contents]





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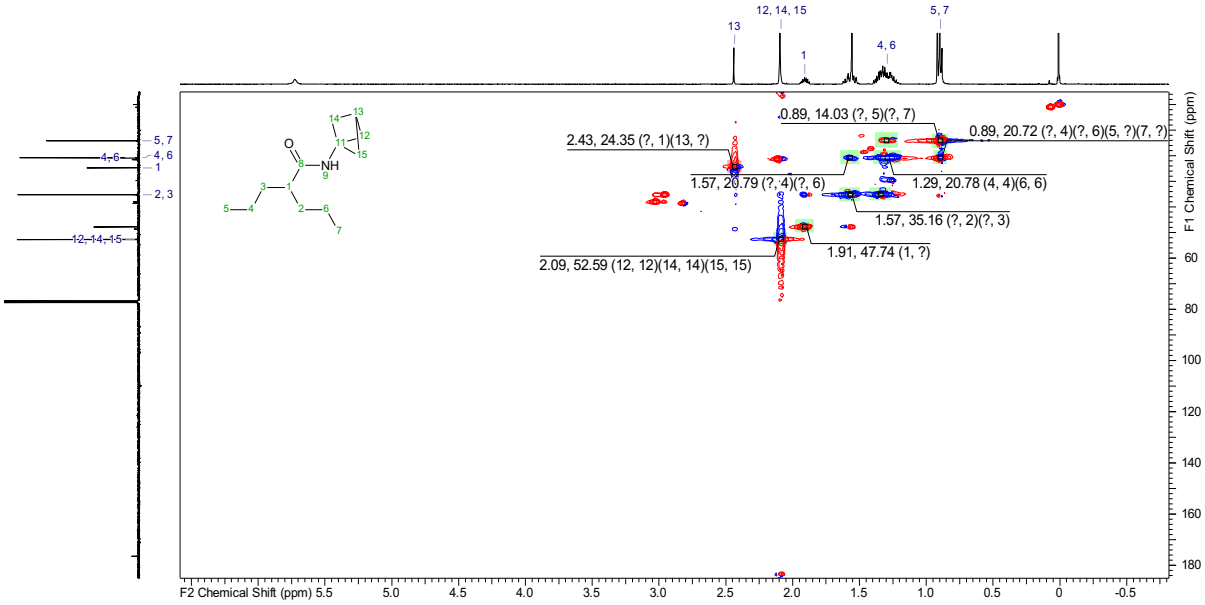

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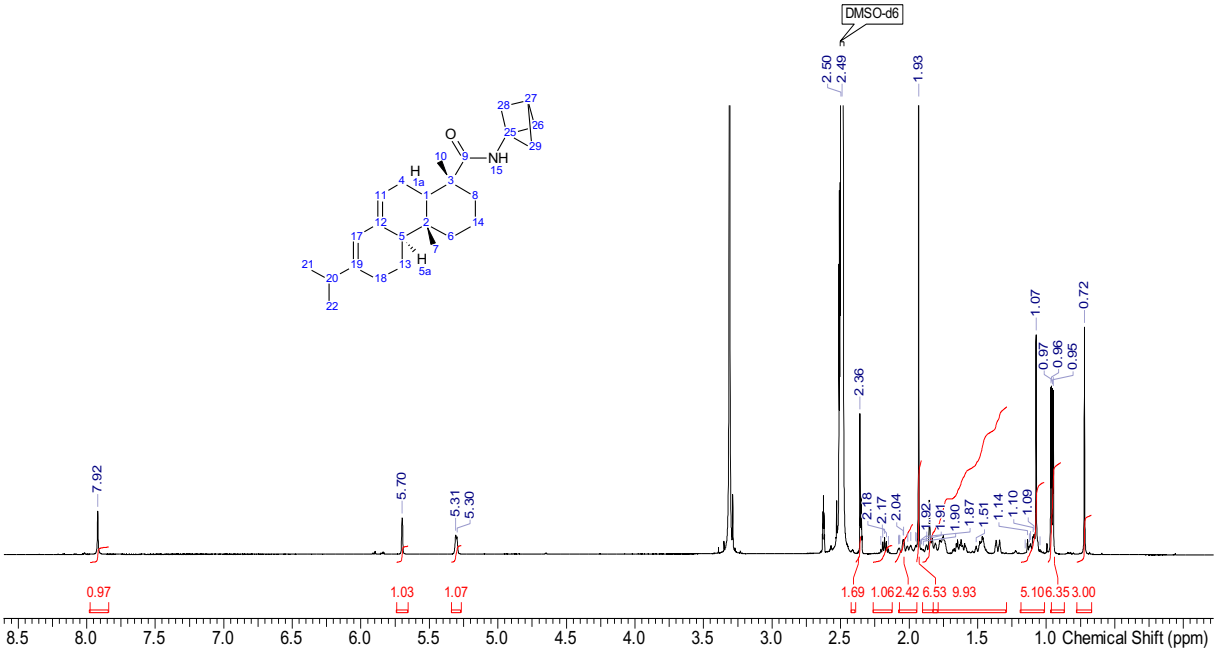
Compound 21b

(1*R*,4a*R*,4b*R*,10a*R*)-*N*-(bicyclo[1.1.1]pentan-1-yl)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthrene-1-carboxamide [Experimental]



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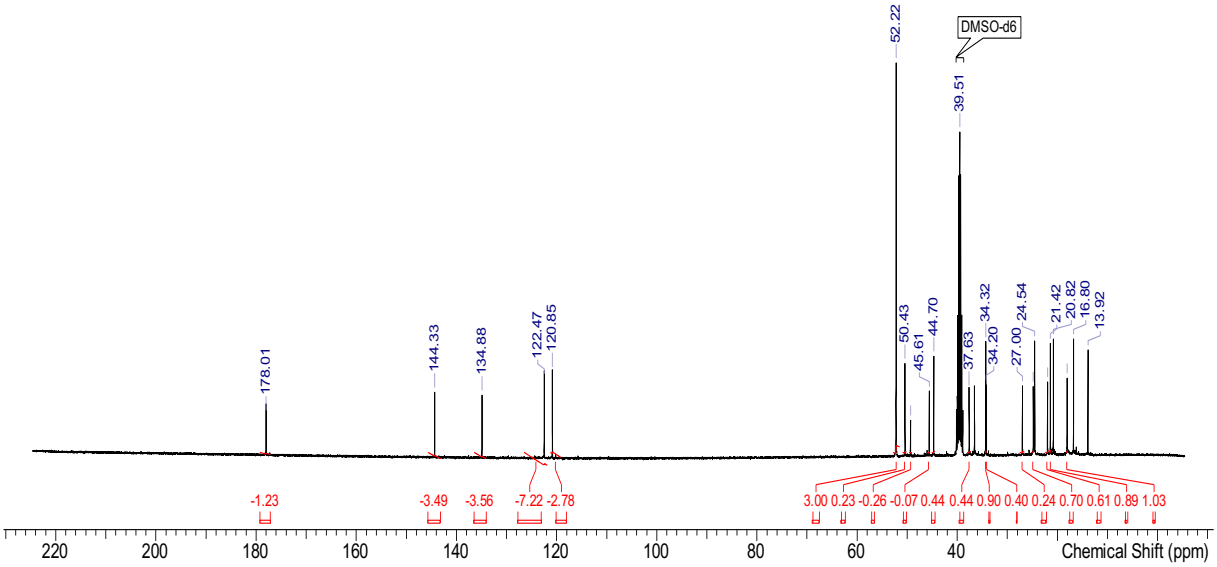

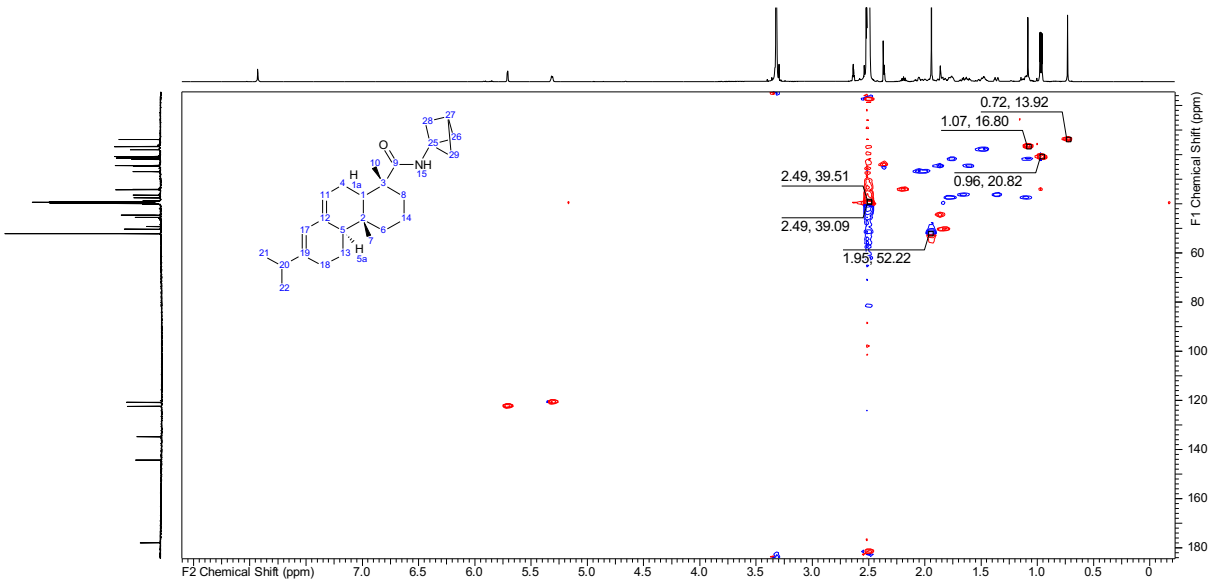

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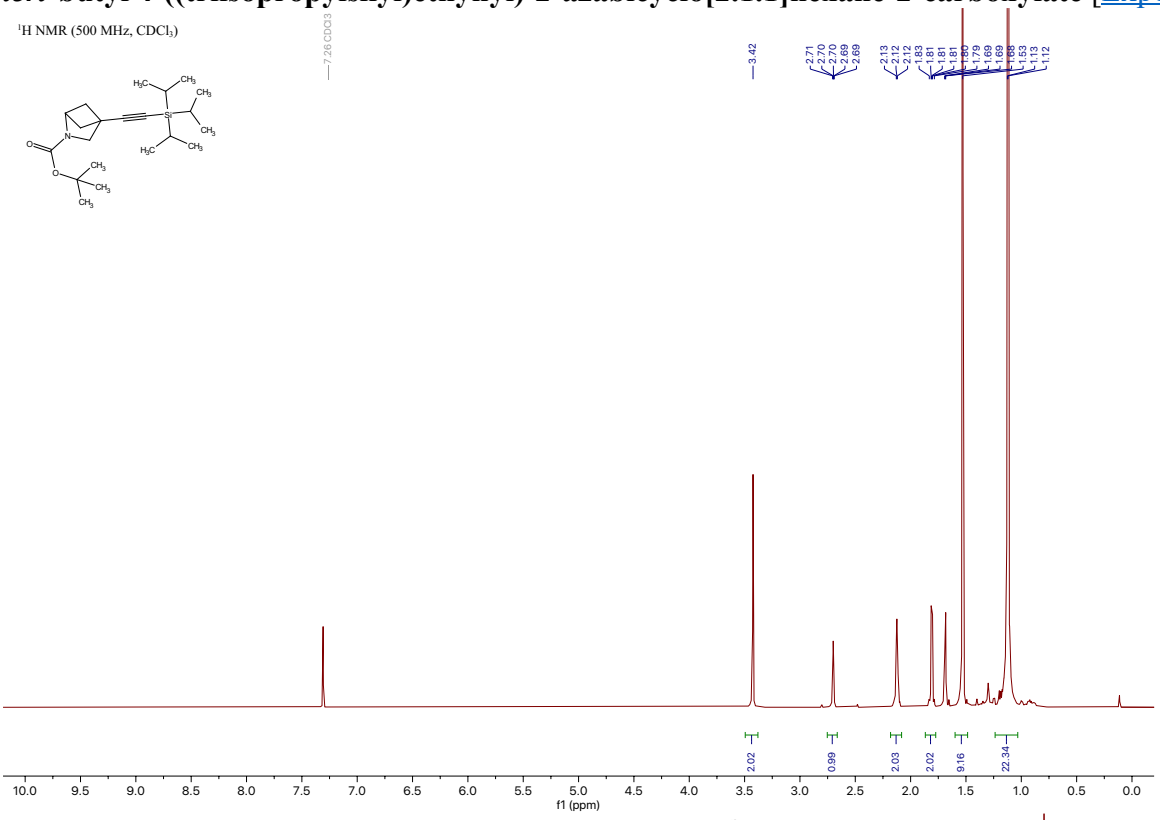
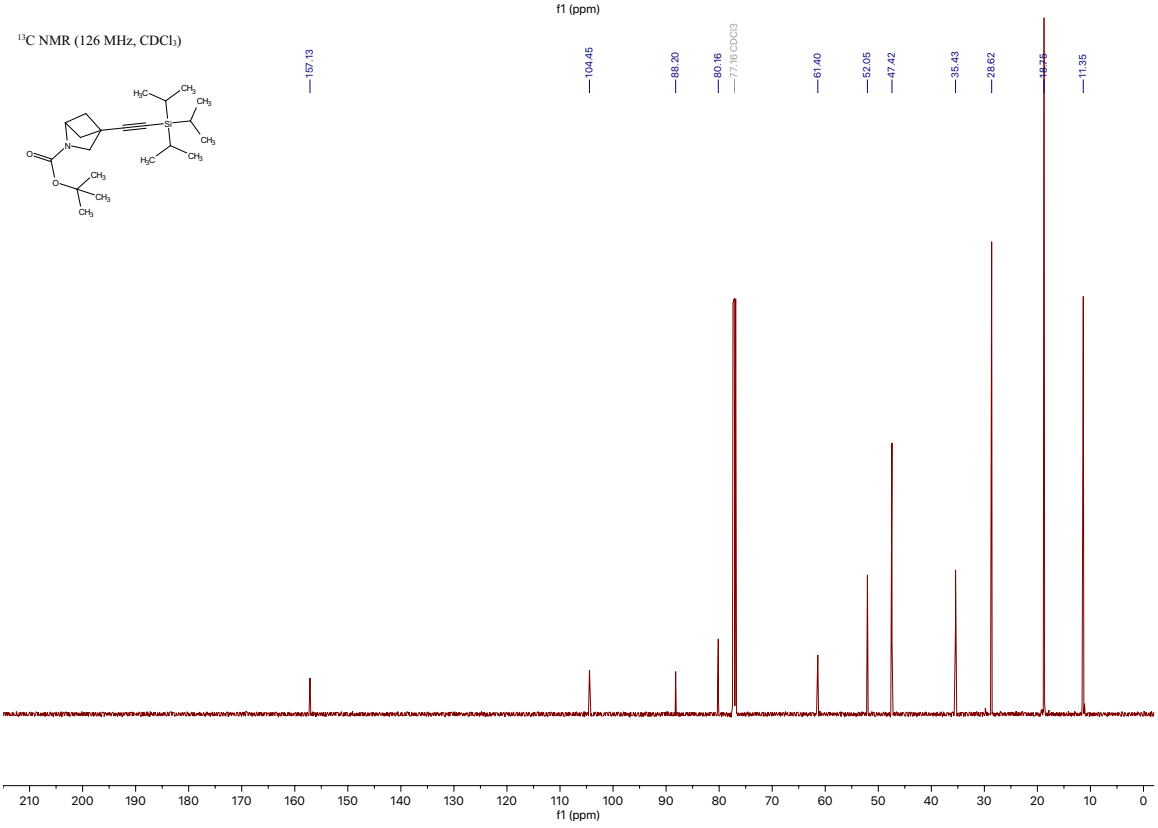
Compound 34b

tert-butyl 4-((triisopropylsilyl)ethynyl)-2-azabicyclo[2.1.1]hexane-2-carboxylate [Experimental]

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)



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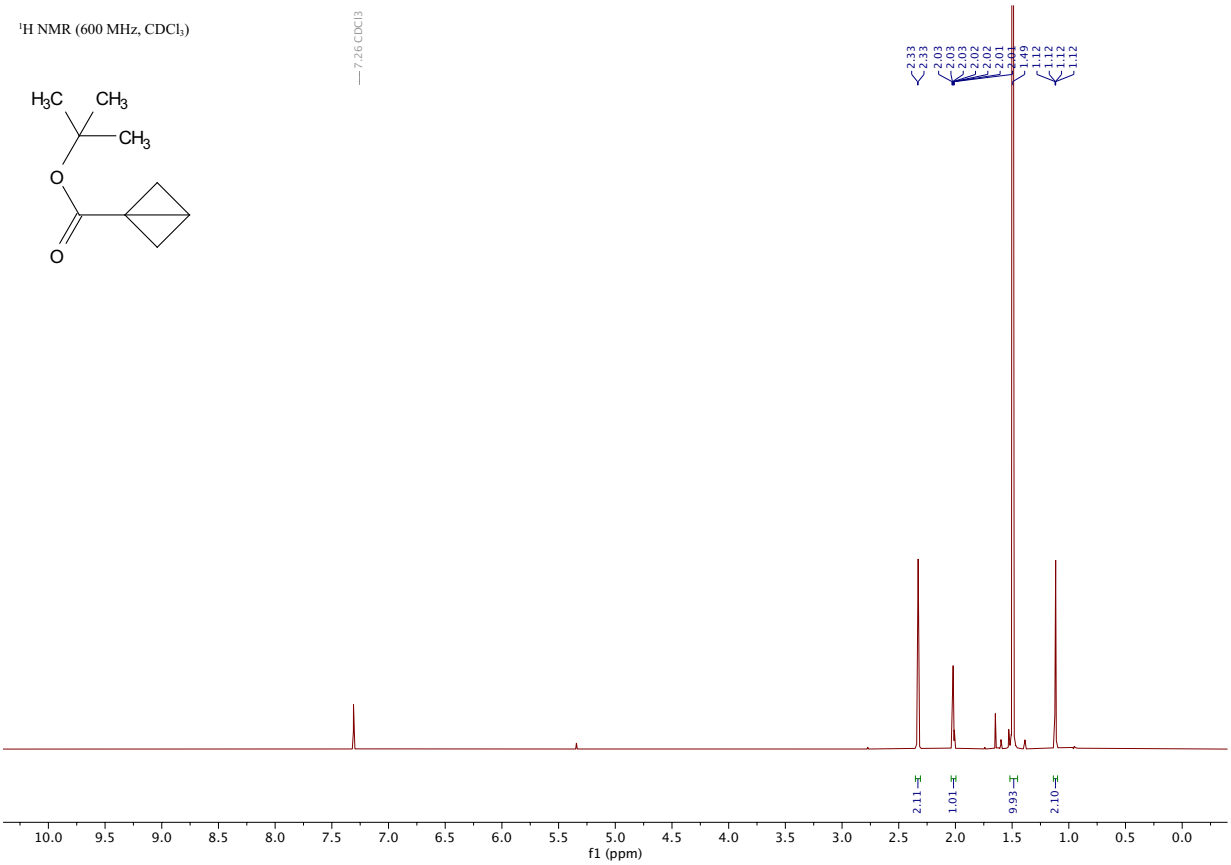
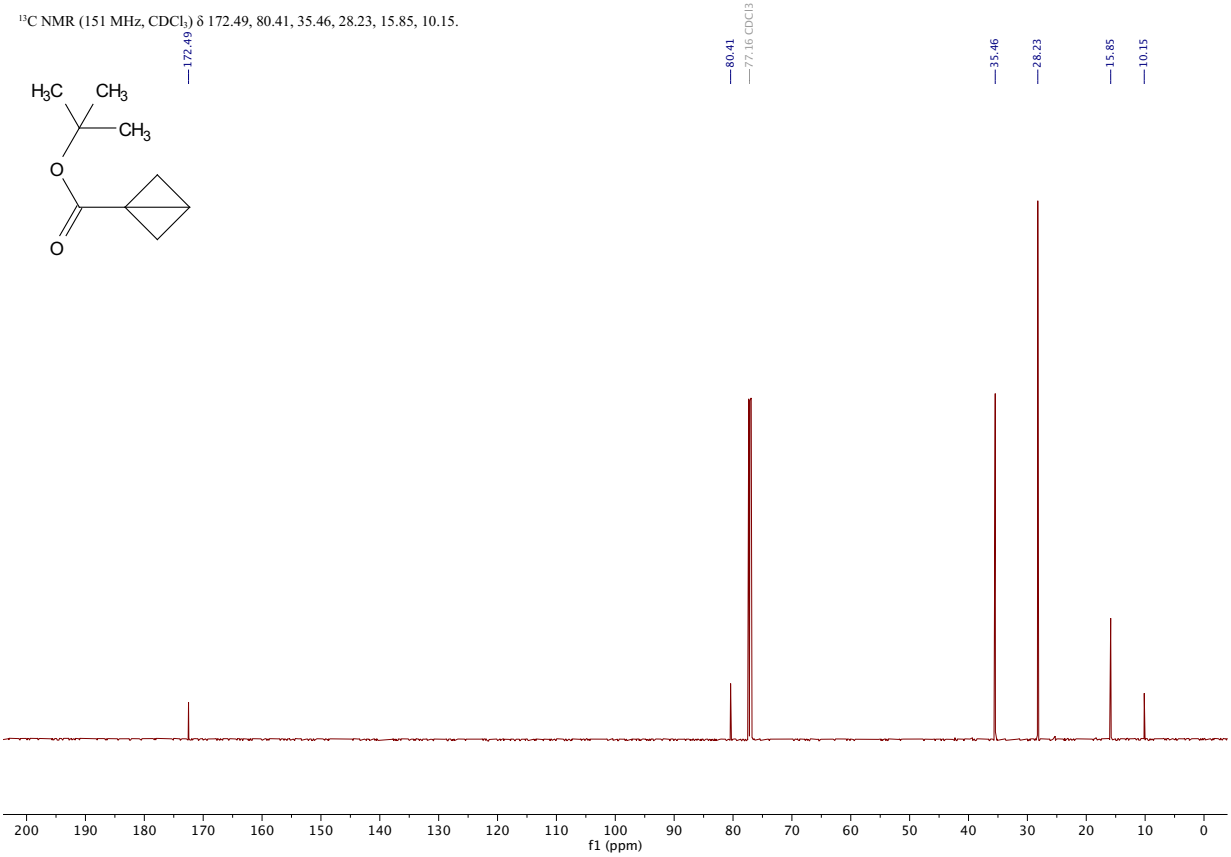
bicyclo[1.1.0]butane-1-carboxylic acid, *tert*-butyl ester

[Experimental]

^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$) δ 172.49, 80.41, 35.46, 28.23, 15.85, 10.15.



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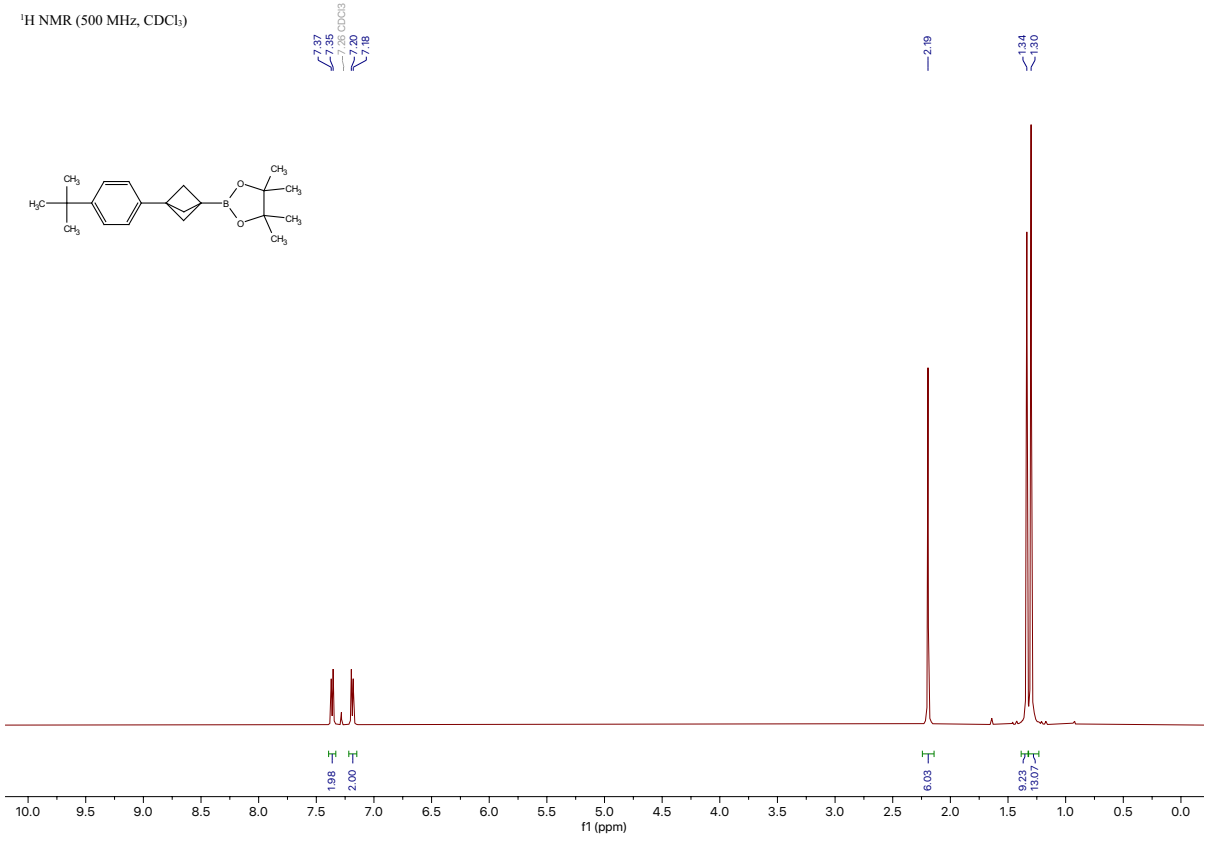
Compound 1a

2-(3-(4-(*tert*-butyl)phenyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

[Experimental]



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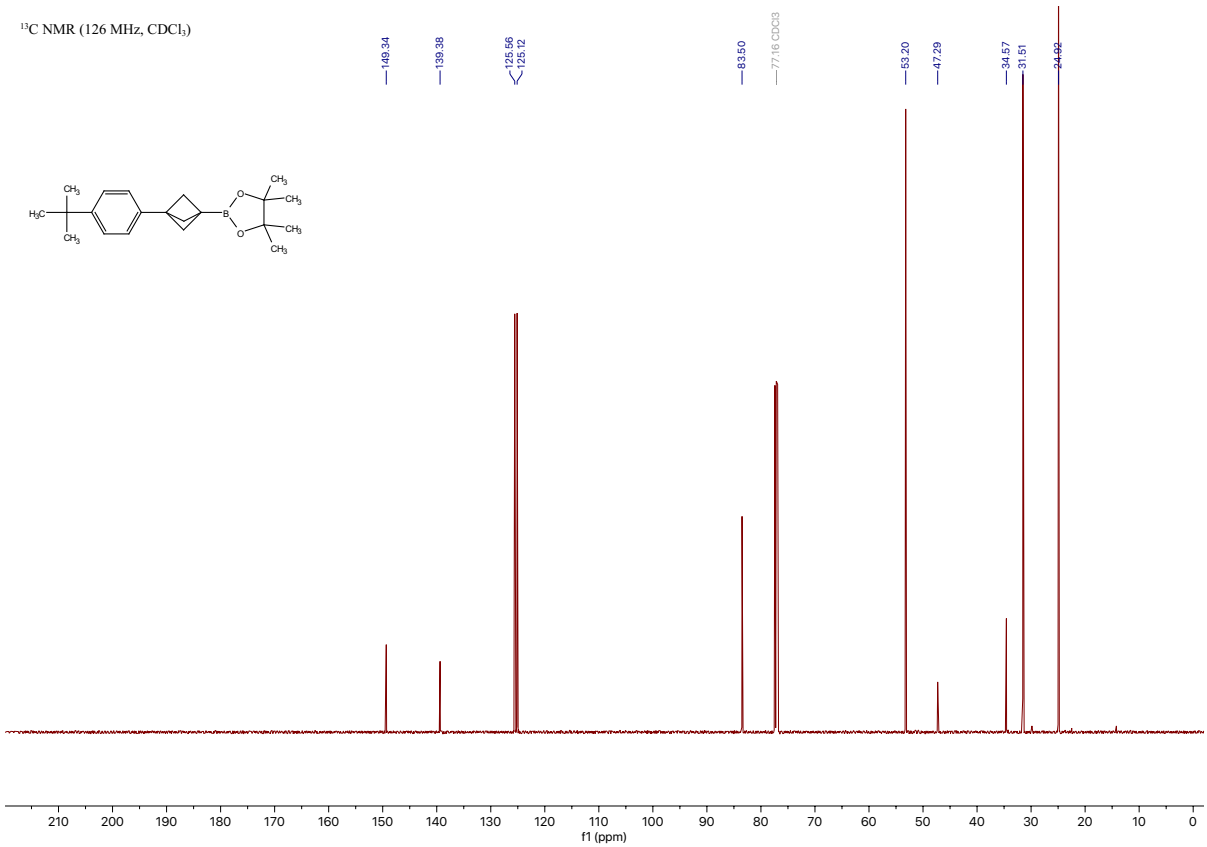
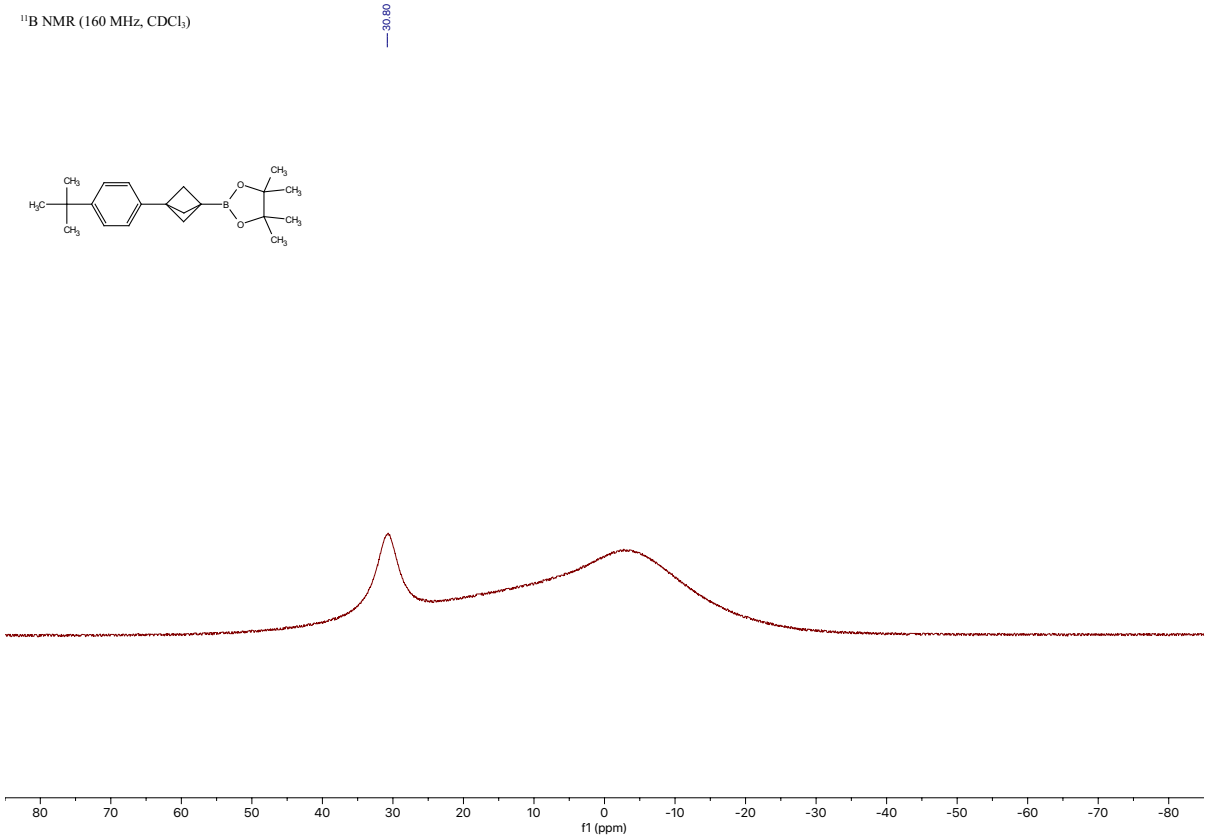
^{13}C NMR (126 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)



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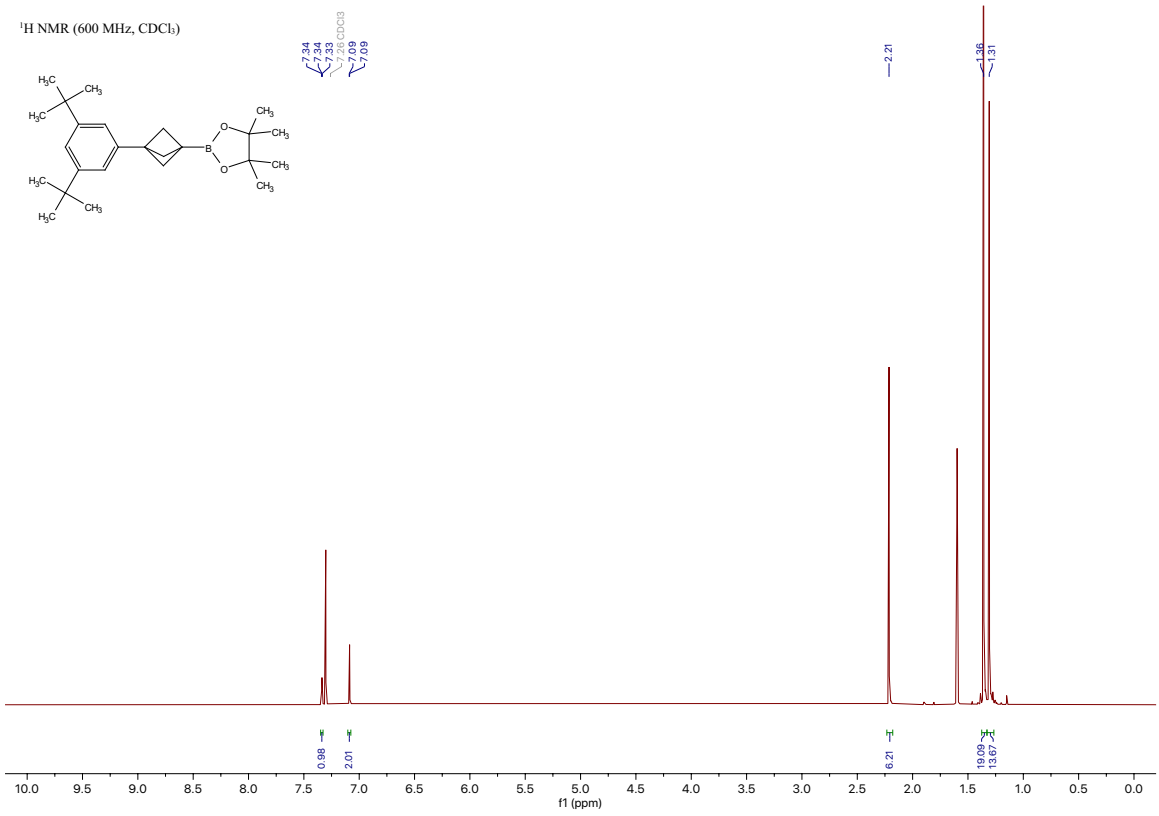
Compound 2a

2-(3-(3,5-di-*tert*-butylphenyl)bicyclo[1.1.1]pentan-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

[Experimental]



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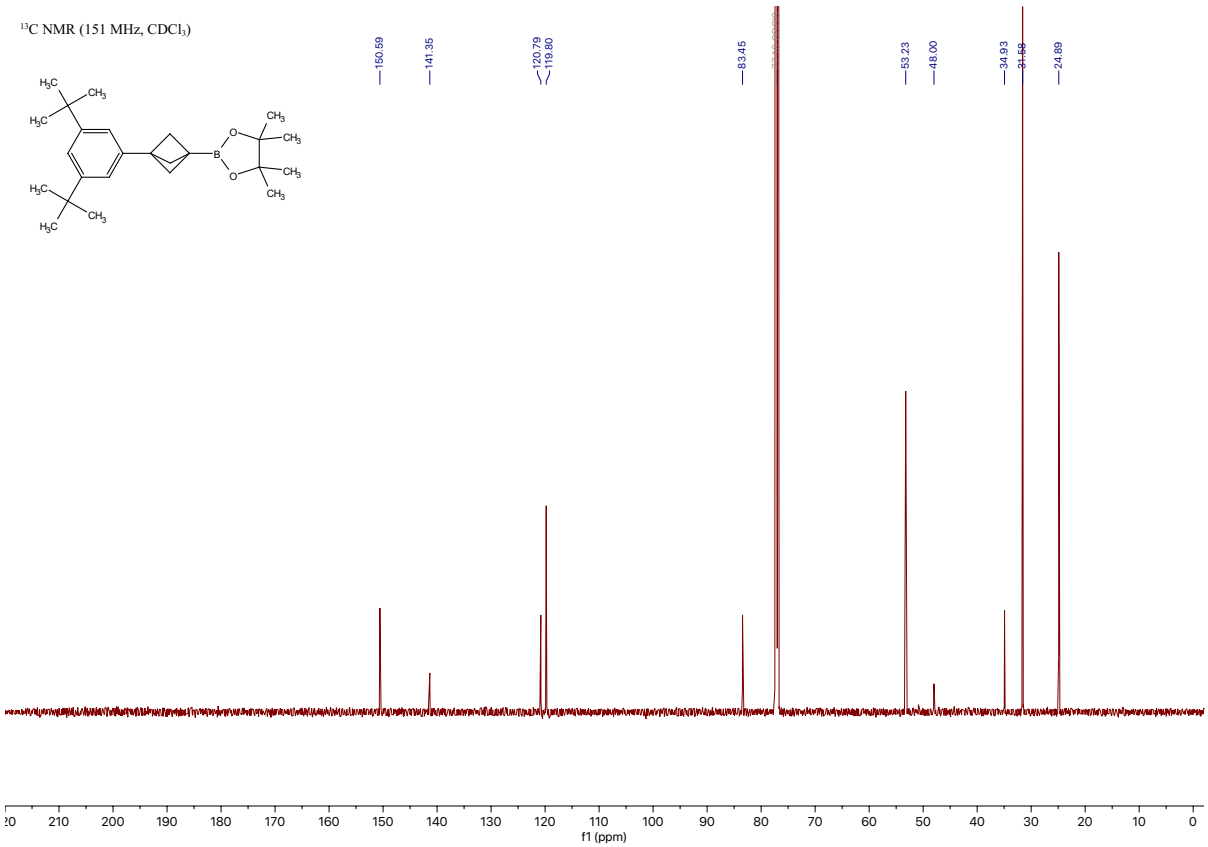
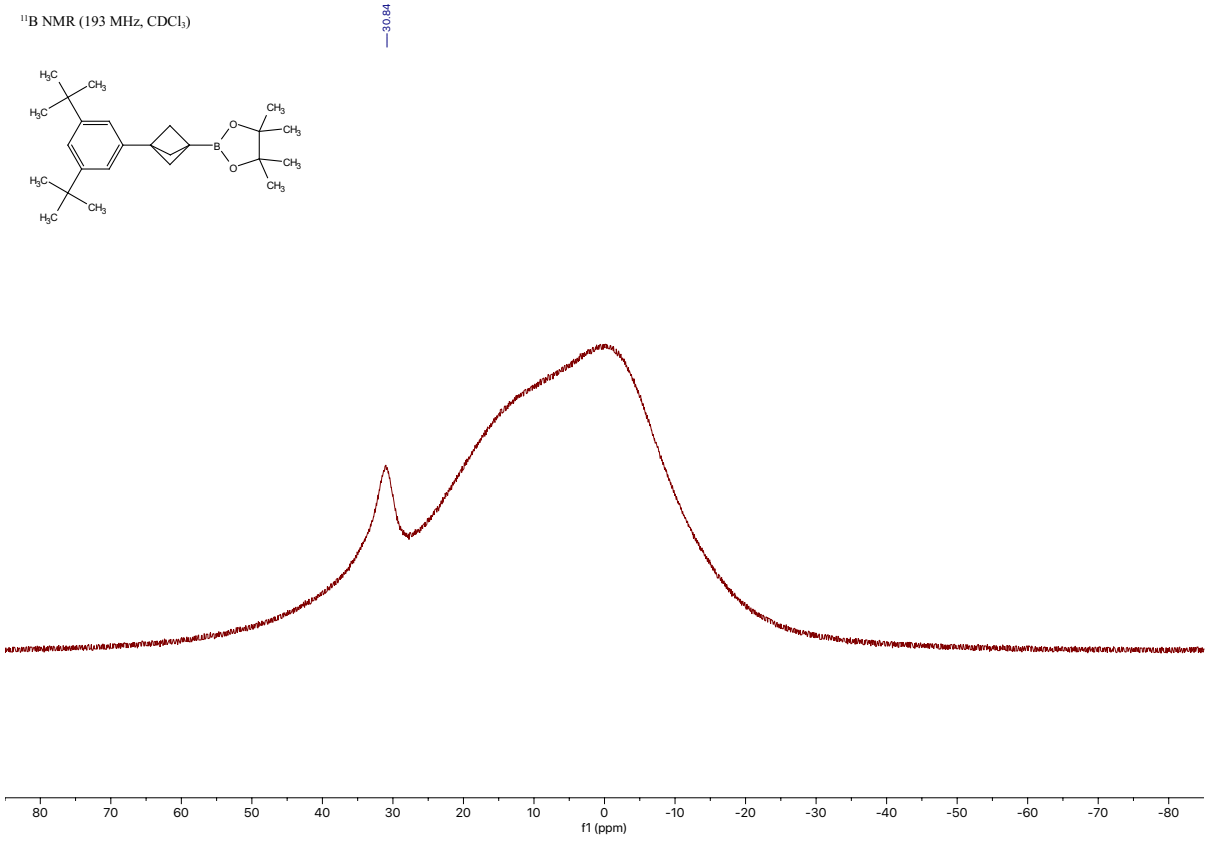
^{13}C NMR (151 MHz, $CDCl_3$)



^{11}B NMR (193 MHz, $CDCl_3$)



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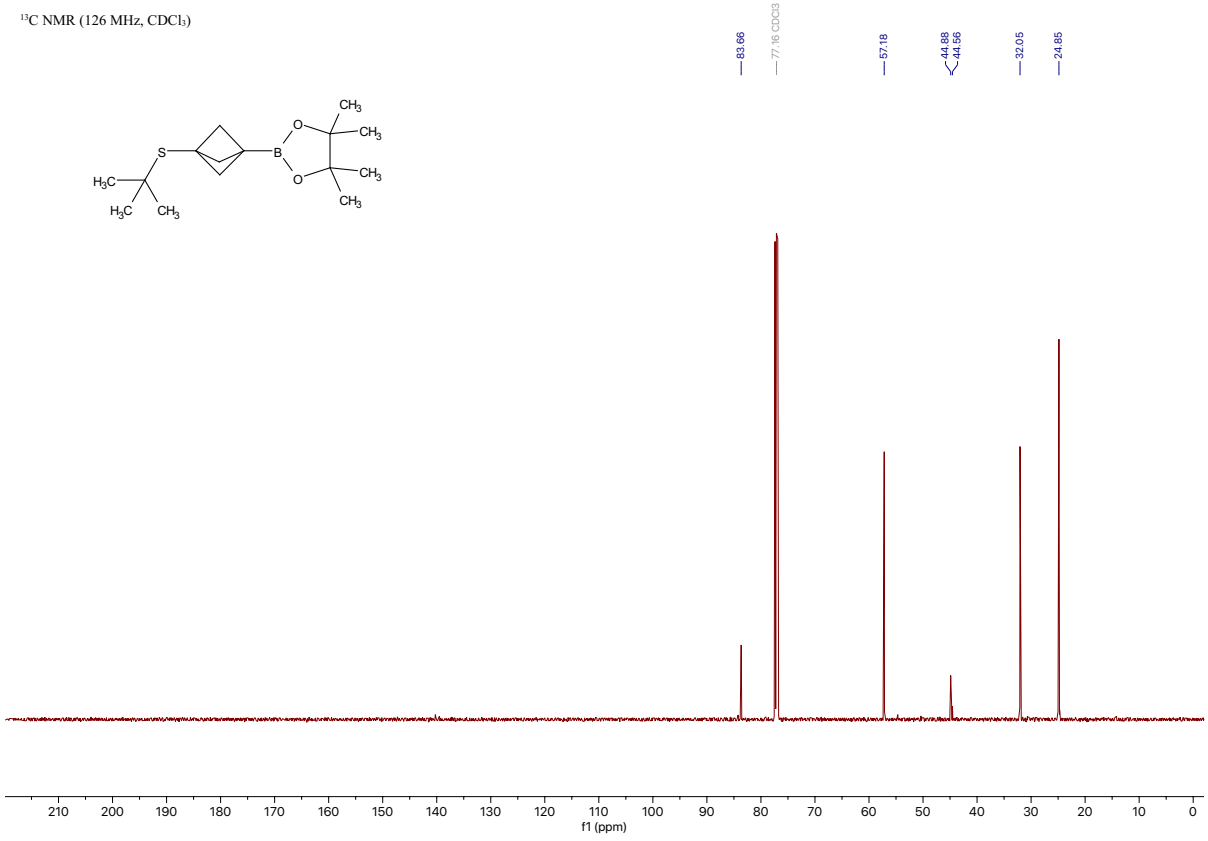
Compound 3a

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

[Experimental]



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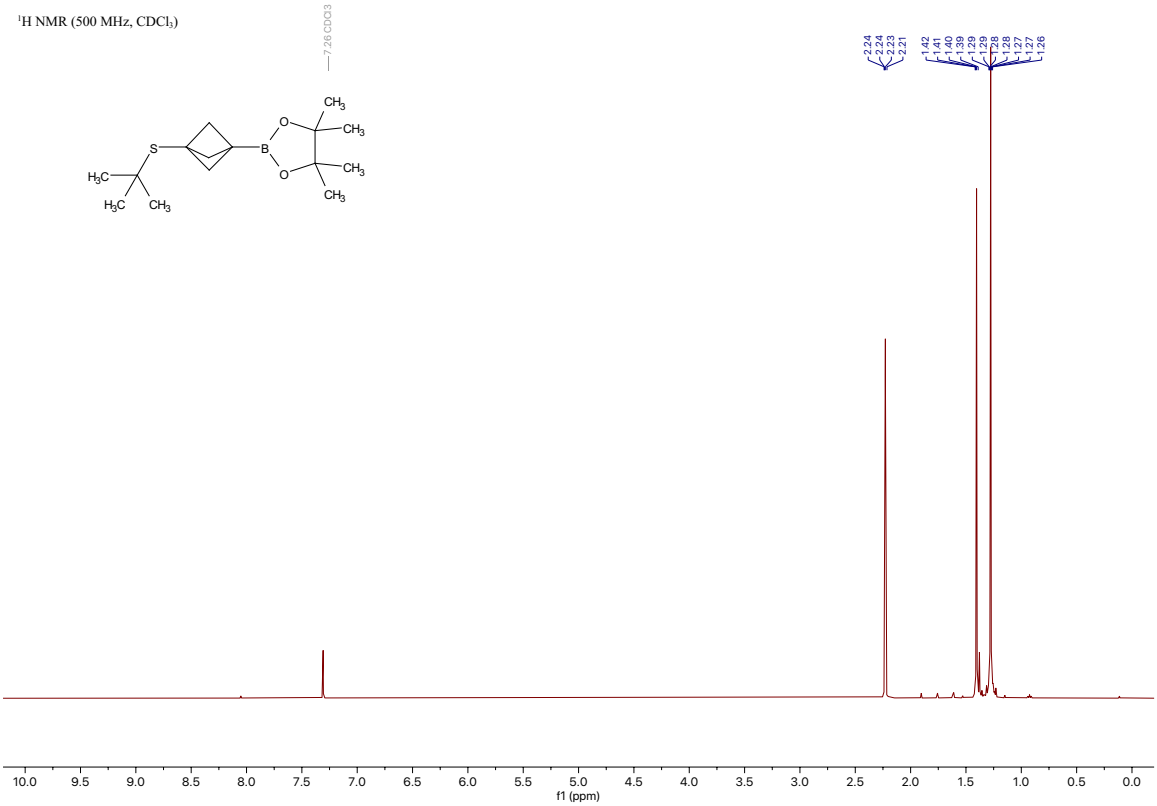
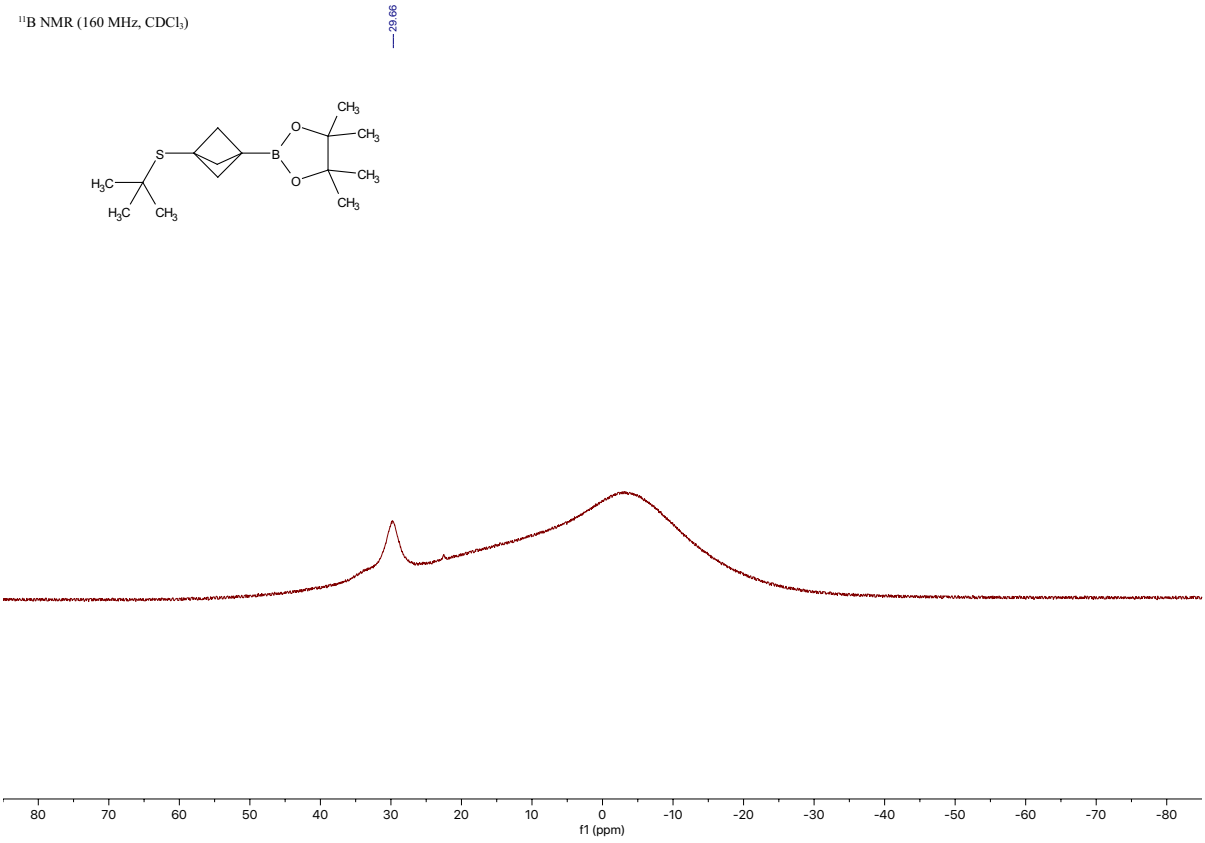
^{1}H NMR (500 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)

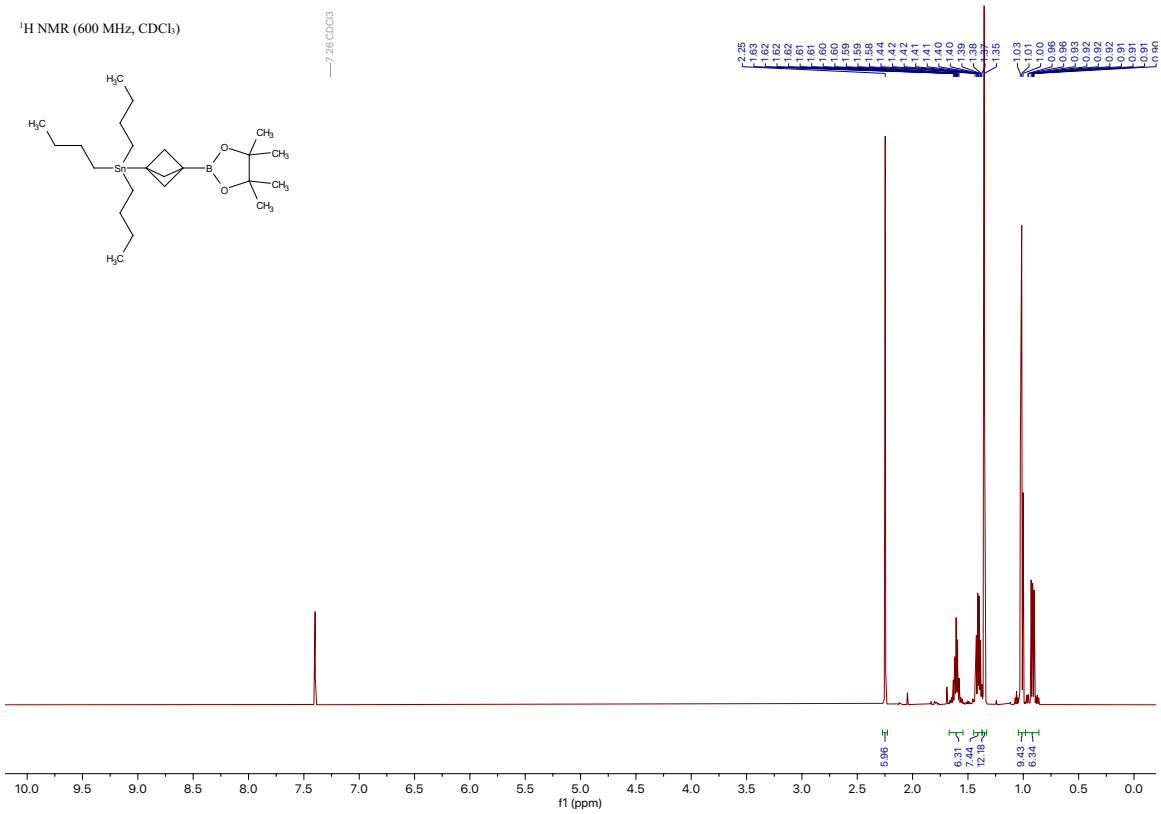


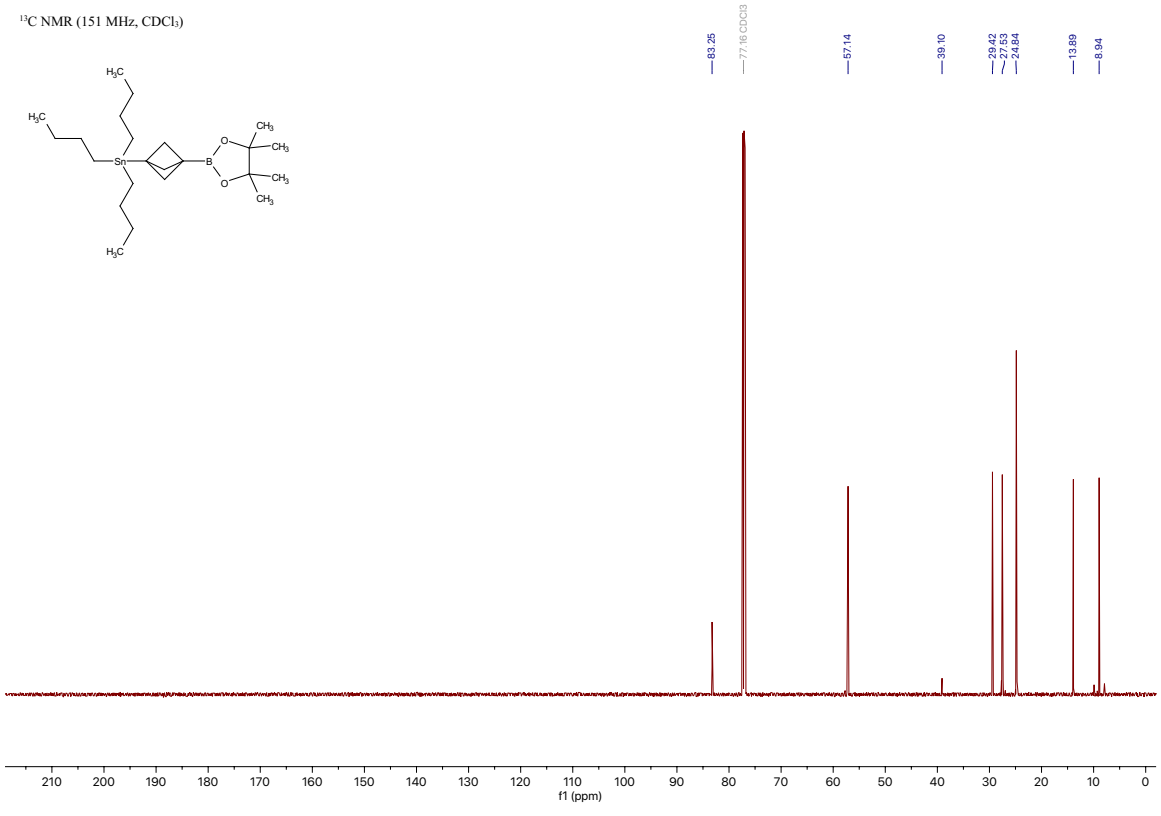
[*Return to table of contents*]

Compound 4a

tributyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)stannane

[Experimental]





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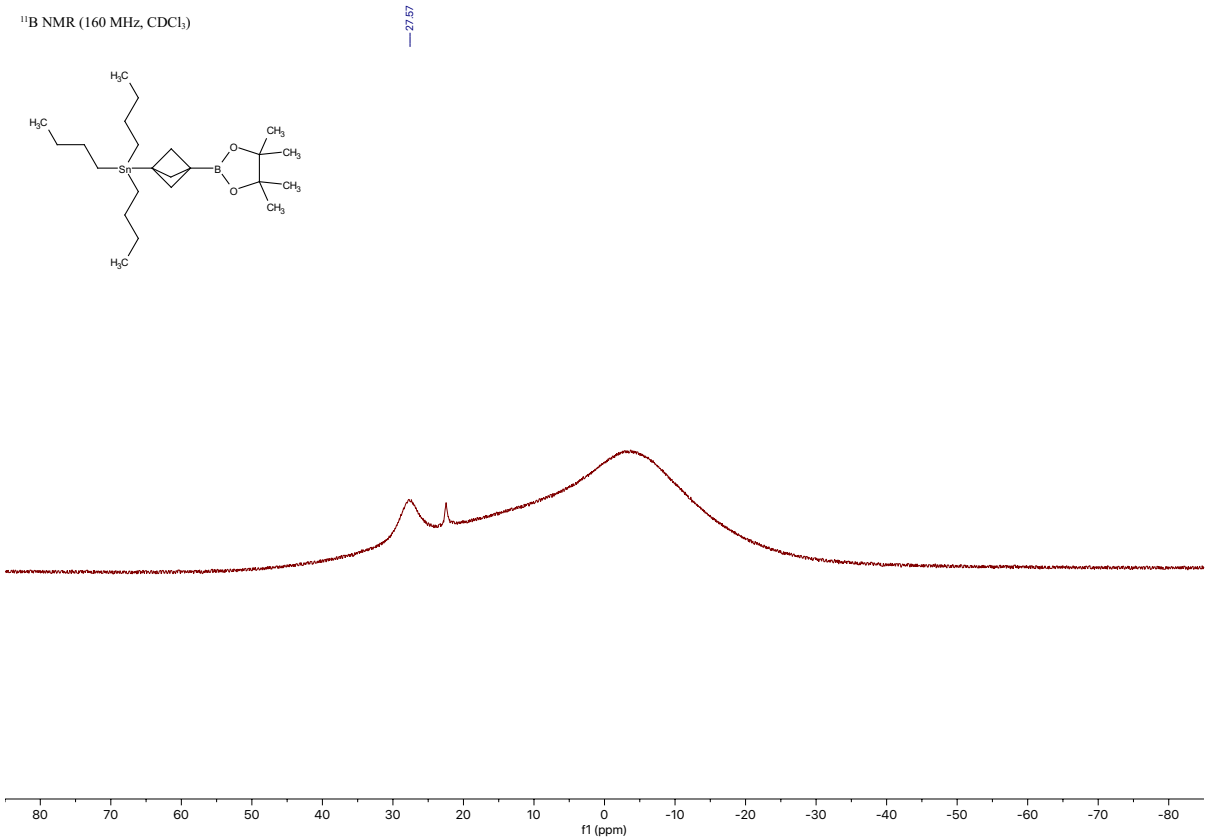
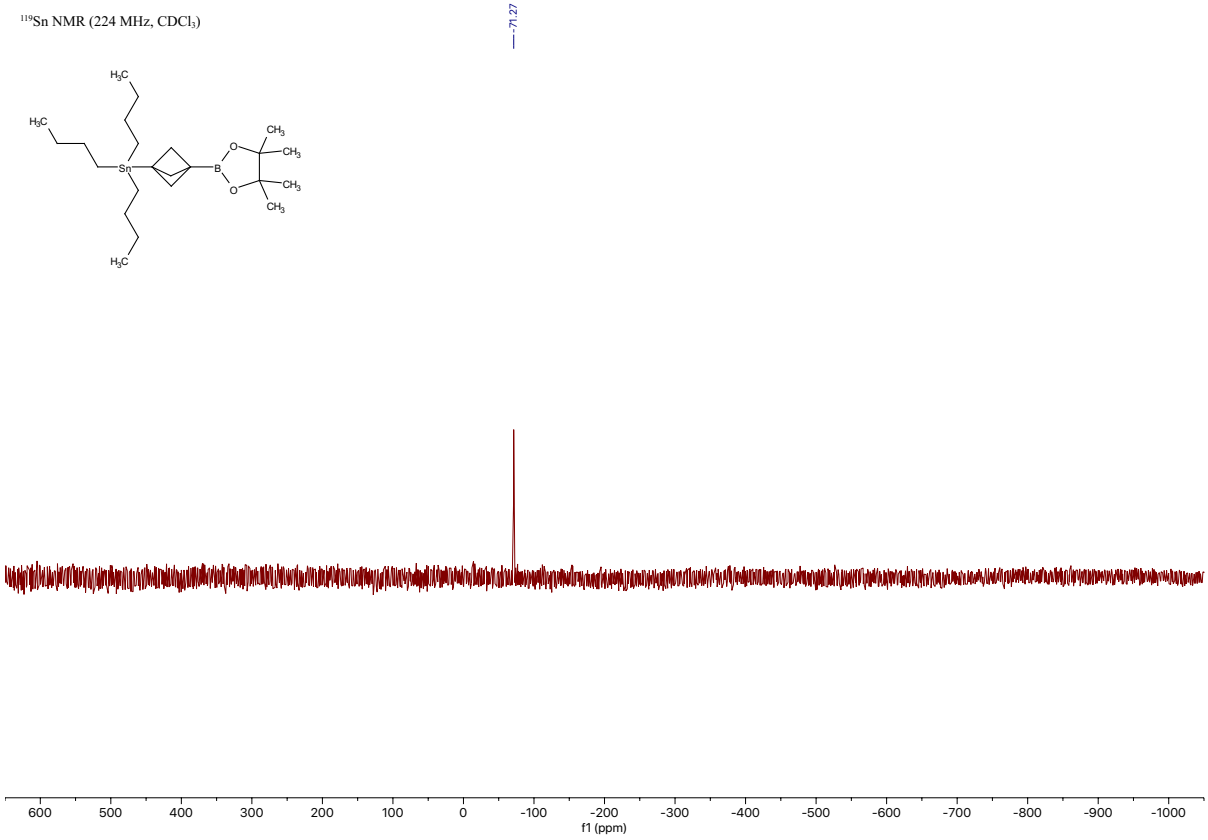
^{11}B NMR (160 MHz, $CDCl_3$)



^{119}Sn NMR (224 MHz, $CDCl_3$)



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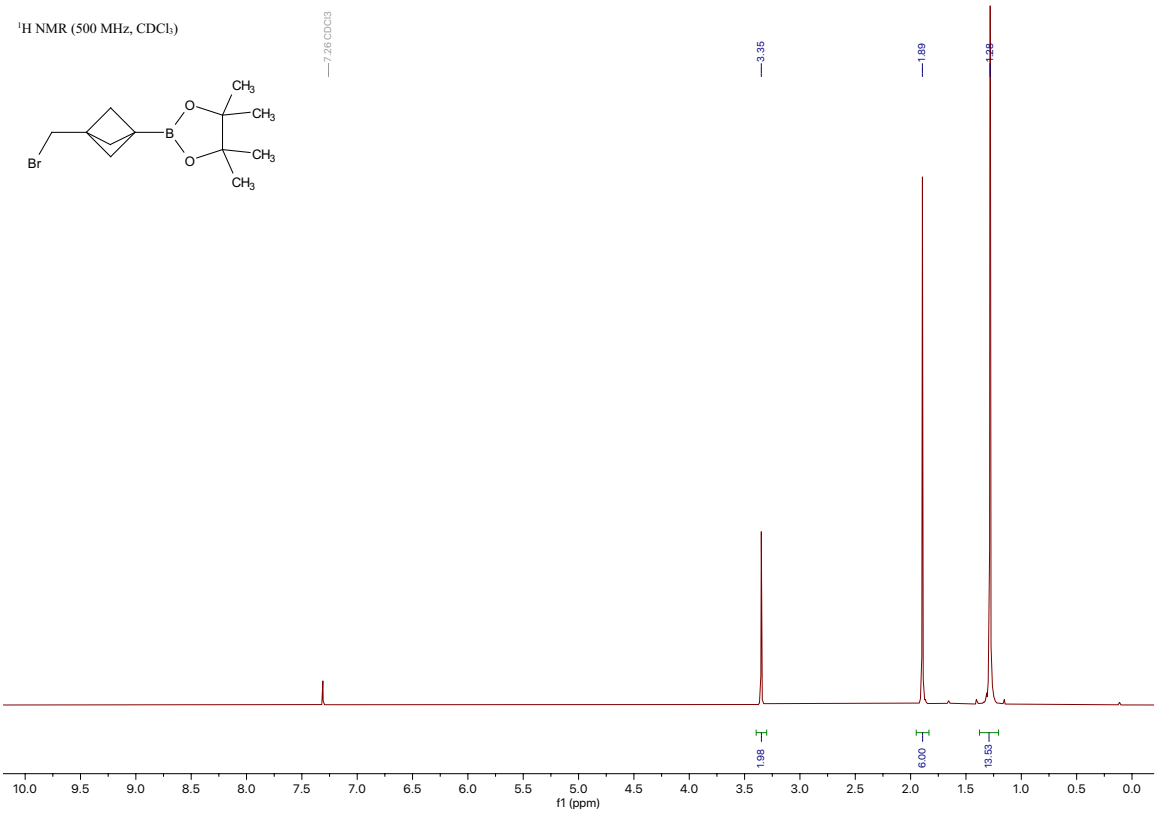
Compound 5a

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

[Experimental]



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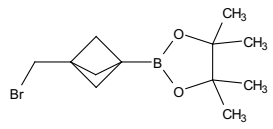
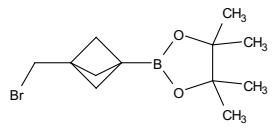
^{13}C NMR (126 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)



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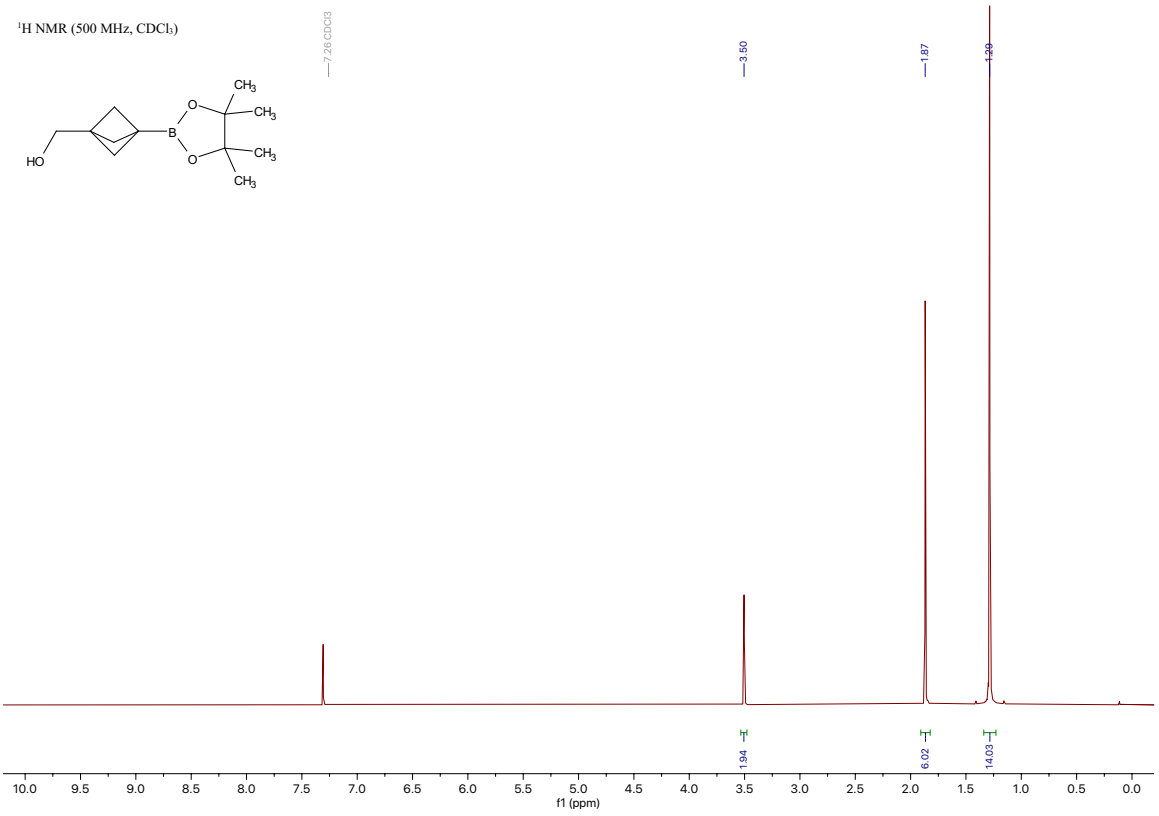
Compound 6a

(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)methanol

[Experimental]



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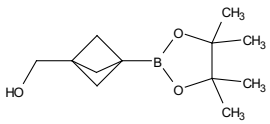
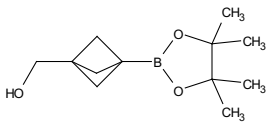
^{13}C NMR (126 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)



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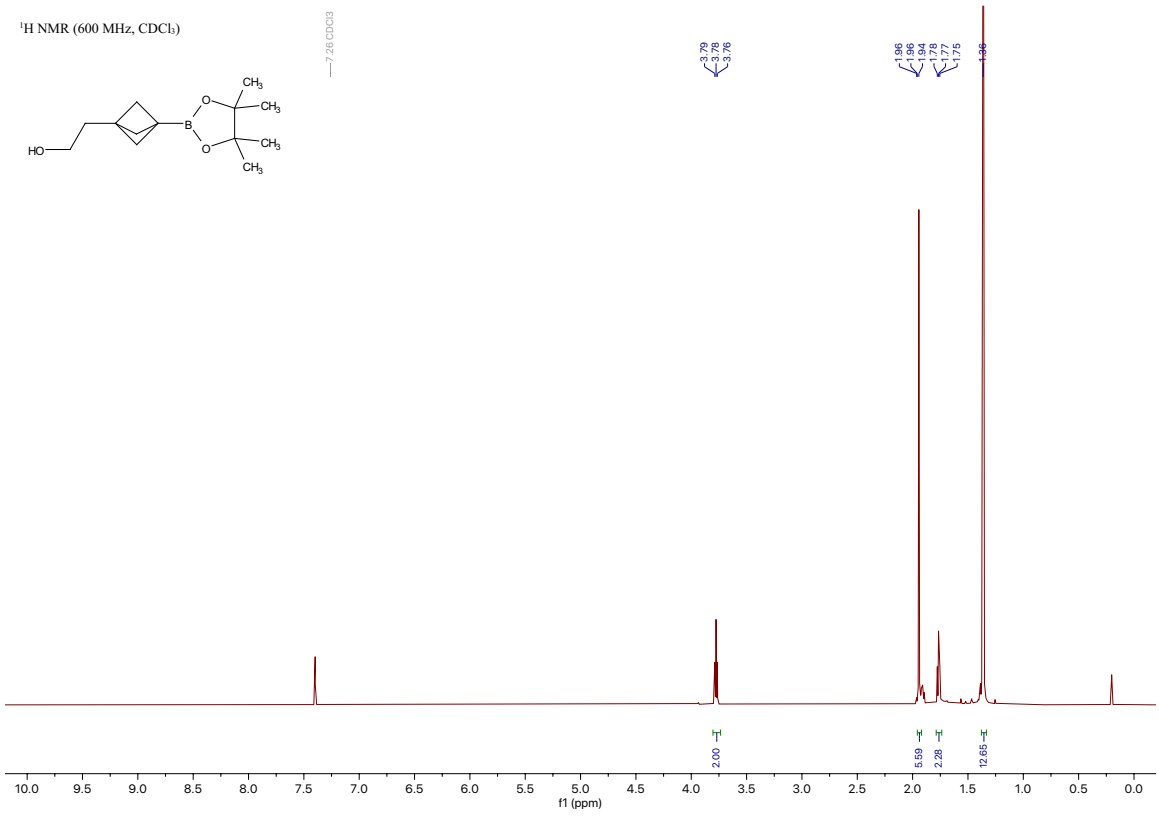
Compound 7a

2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)ethan-1-ol)

[Experimental]



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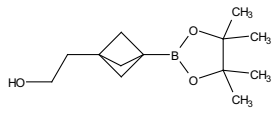
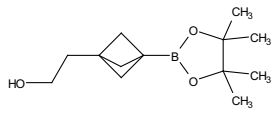
^{13}C NMR (151 MHz, $CDCl_3$)



^{11}B NMR (193 MHz, $CDCl_3$)

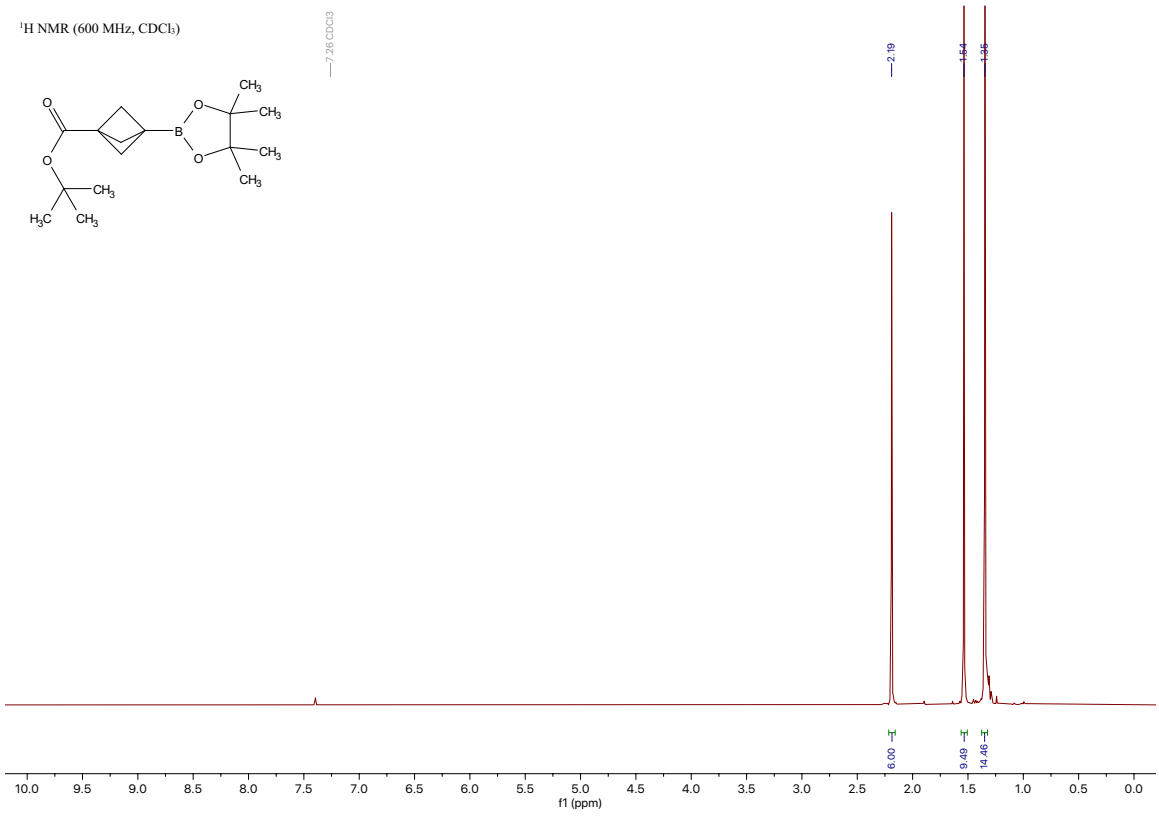


[*Return to table of contents*]

Compound 8a

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

[Experimental]



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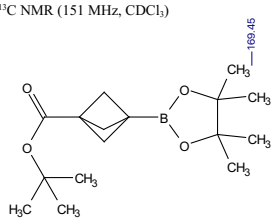
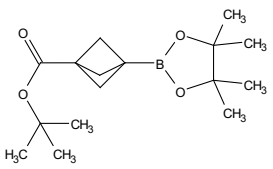
^{13}C NMR (151 MHz, $CDCl_3$)



^{11}B NMR (193 MHz, $CDCl_3$)

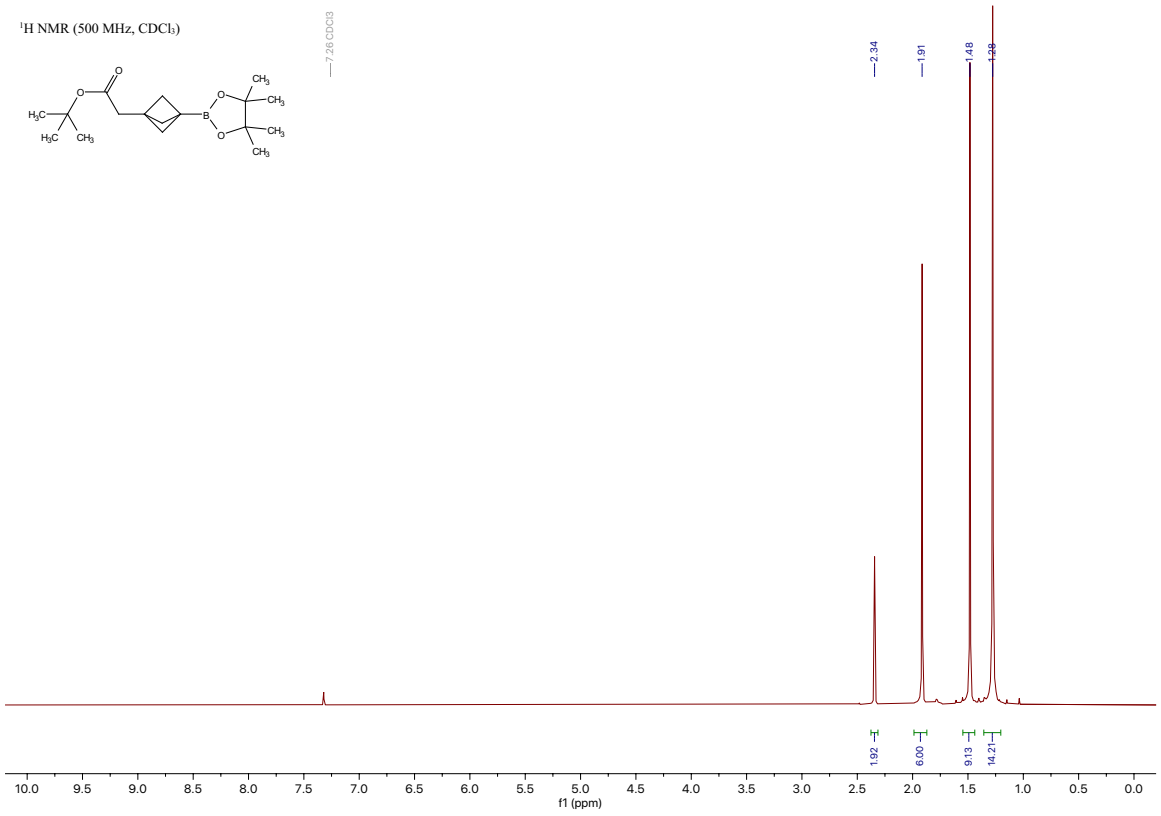


[*Return to table of contents*]

Compound 9a

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

[Experimental]



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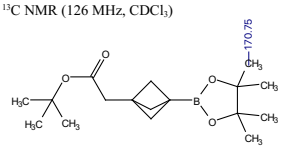
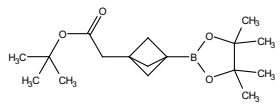
^{13}C NMR (126 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)



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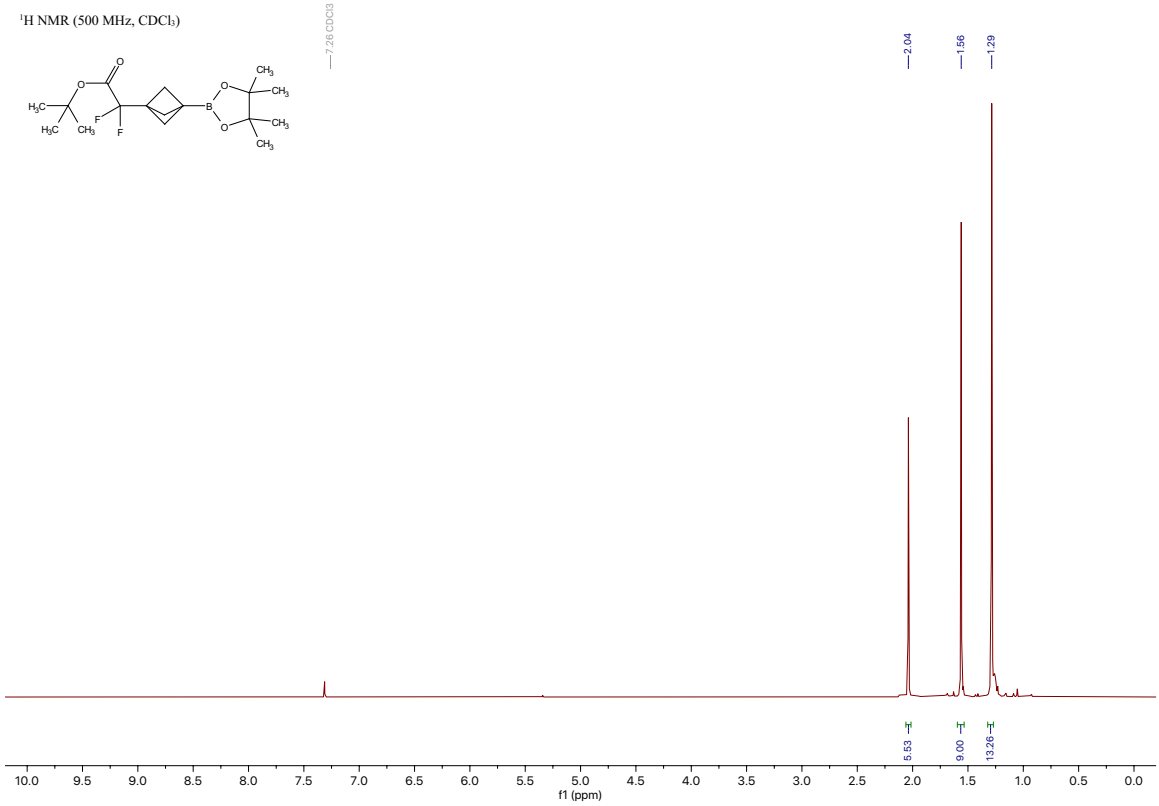
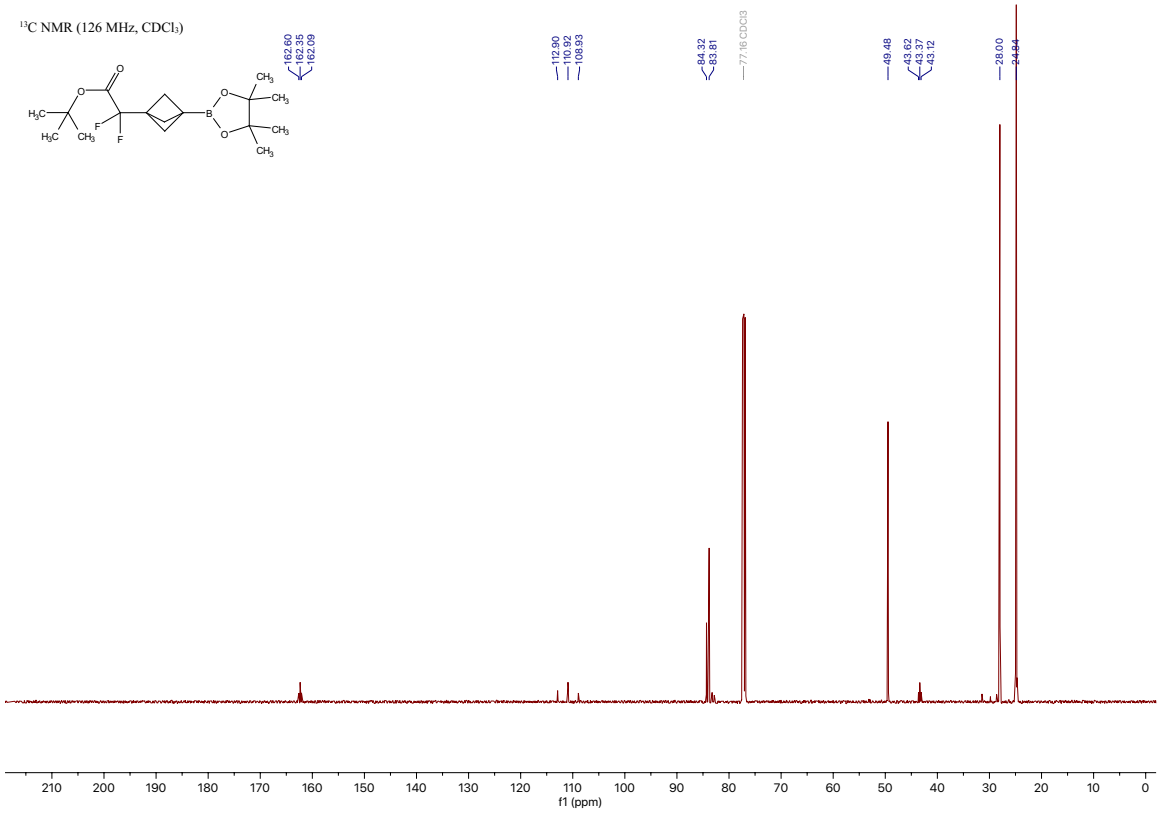
Compound 10a

***tert*-butyl 2,2-difluoro-2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)acetate** [Experimental]





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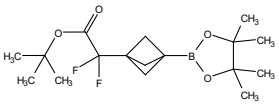
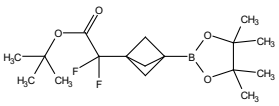
^{11}B NMR (160 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$)



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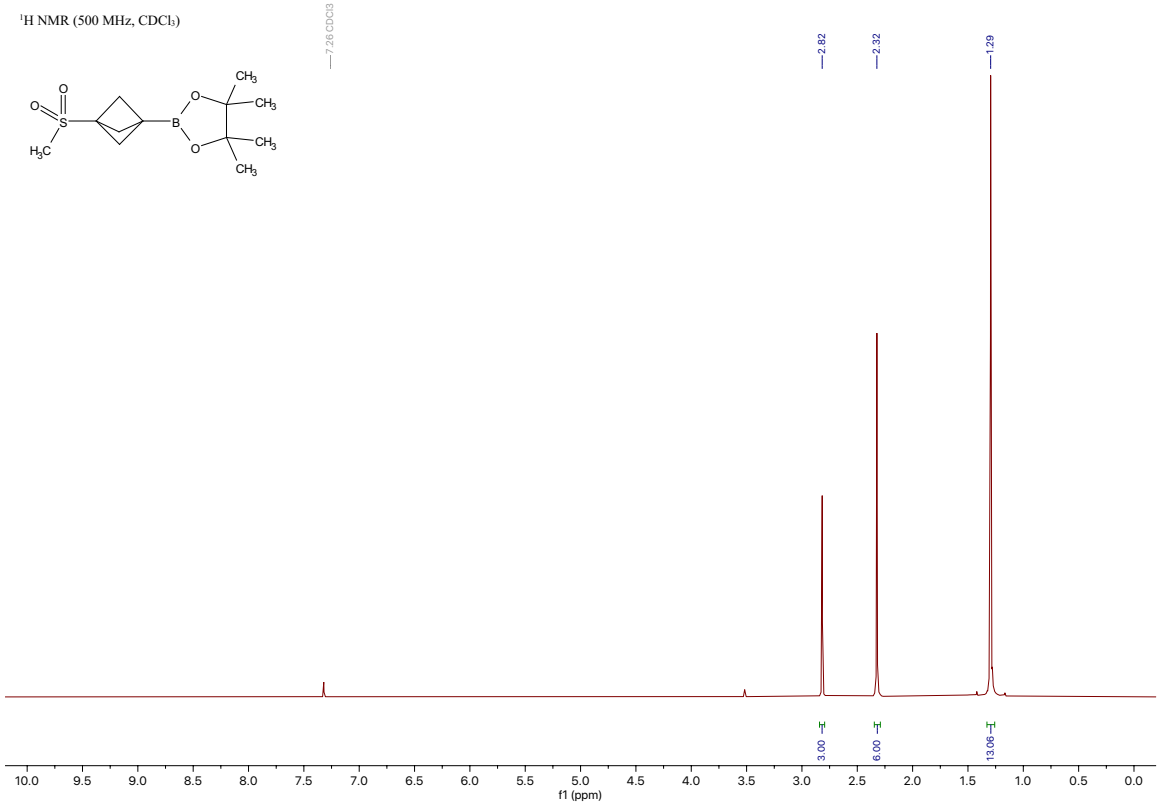
Compound 11a

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

[Experimental]



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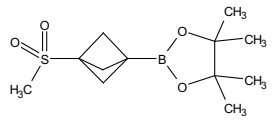
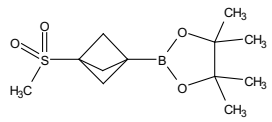
^{13}C NMR (126 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)



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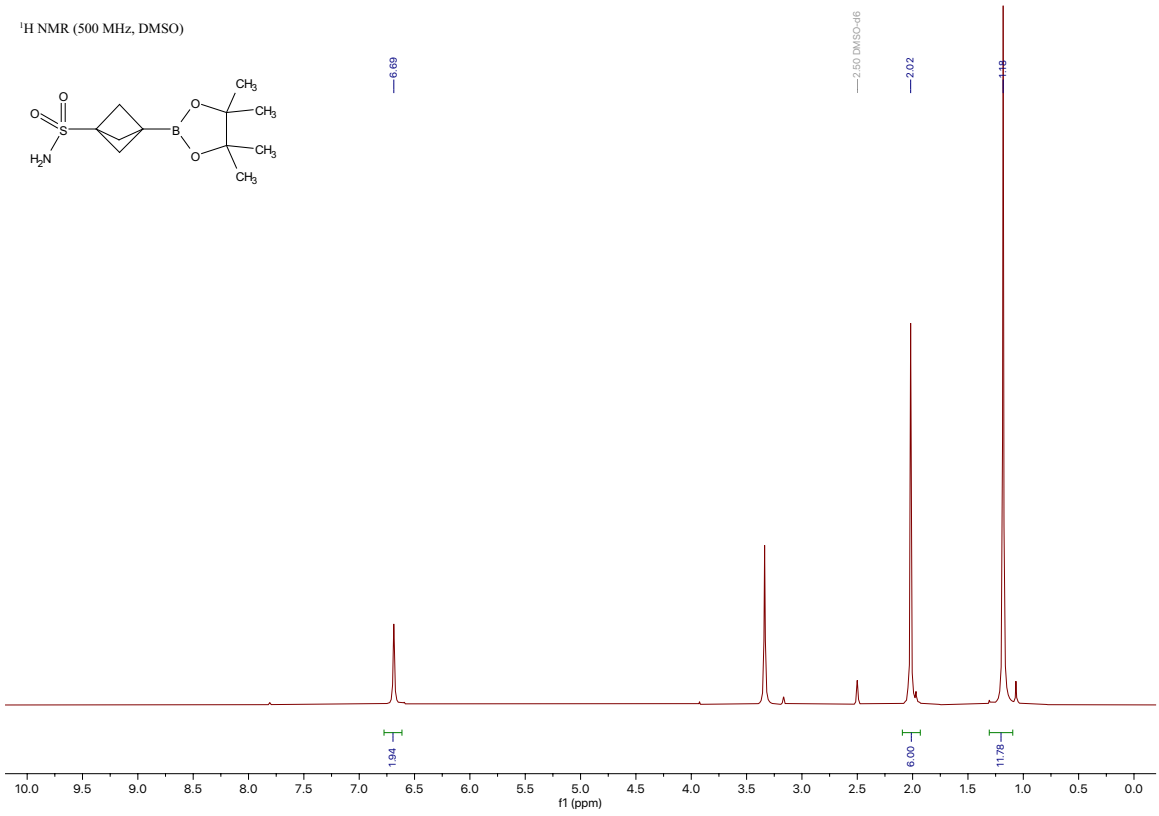
Compound 12a

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

[Experimental]



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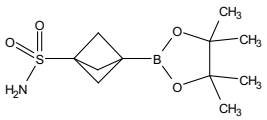
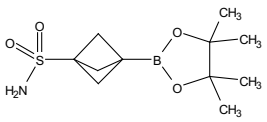
^{13}C NMR (126 MHz, DMSO)



^{11}B NMR (160 MHz, DMSO)

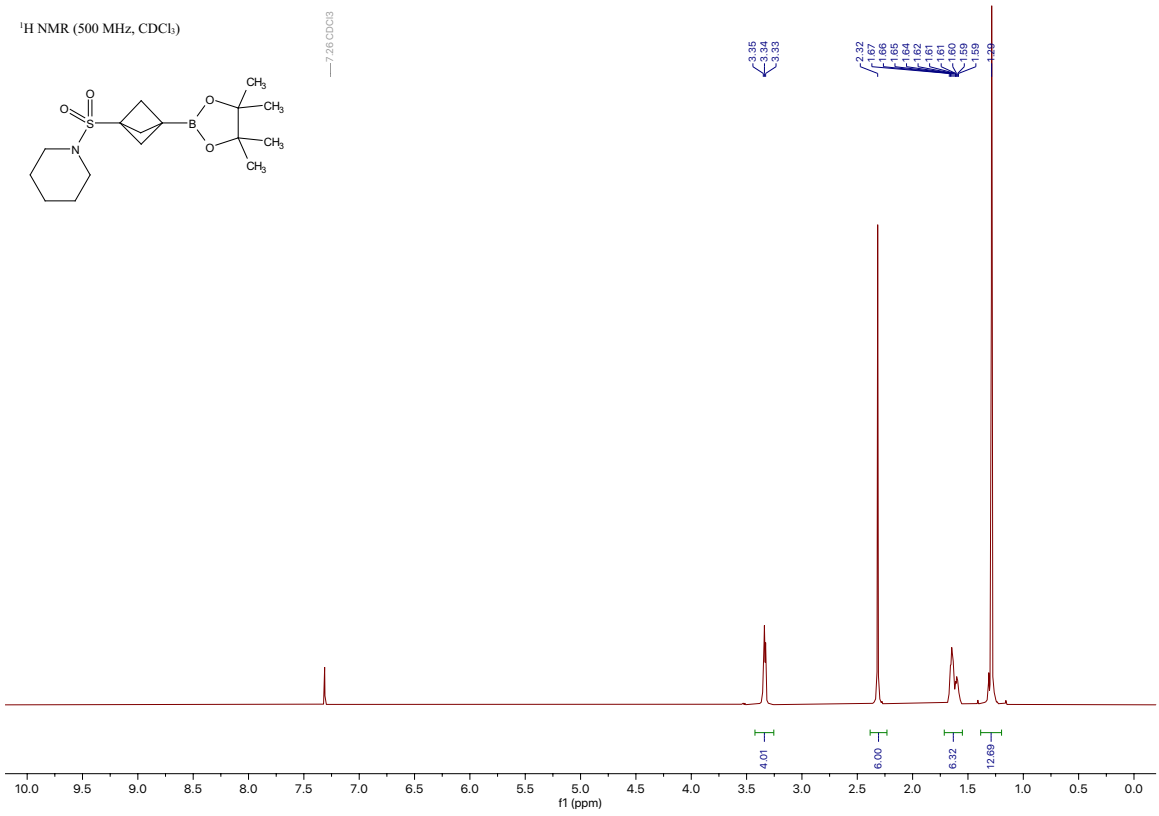


[*Return to table of contents*]

Compound 13a

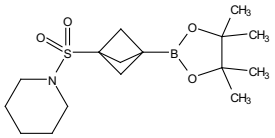
1-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)sulfonyl)piperidine

[Experimental]

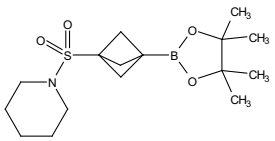


[*Return to table of contents*]

^{13}C NMR (126 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)



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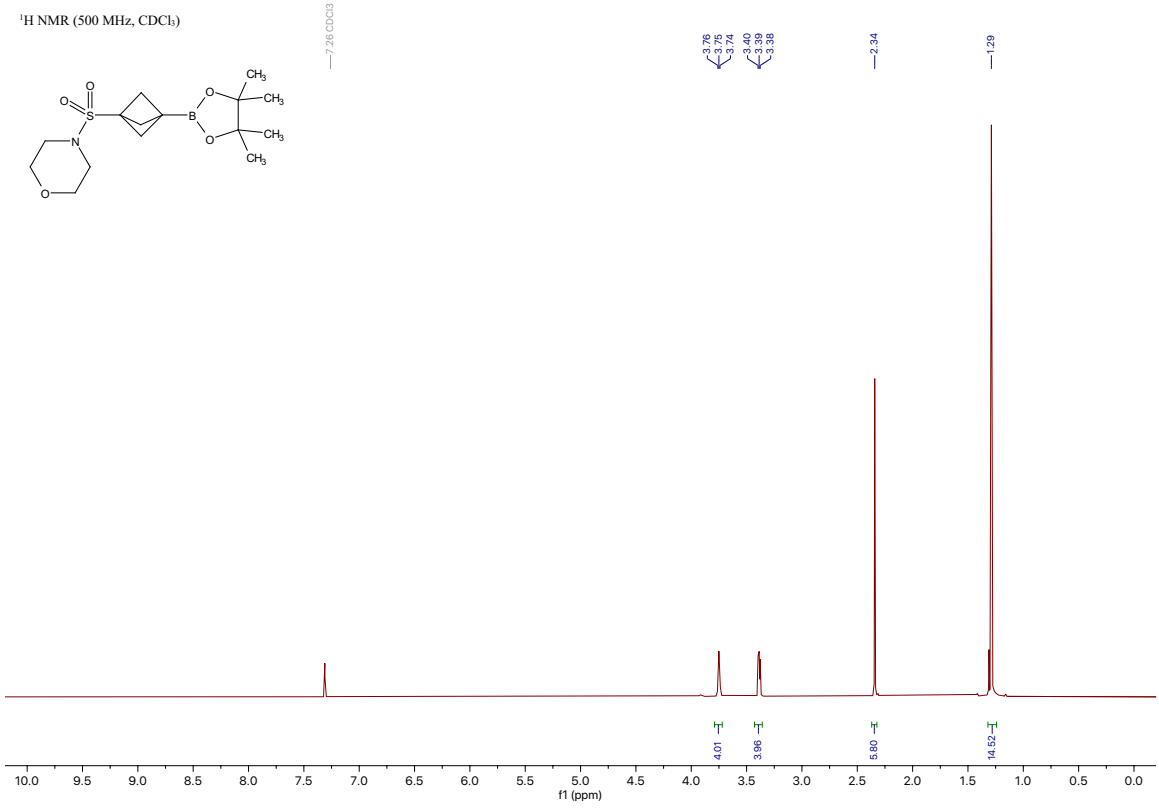
Compound 14a

4-((3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)sulfonyl)morpholine [Experimental]



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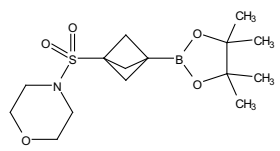
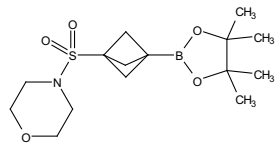
^{13}C NMR (126 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)



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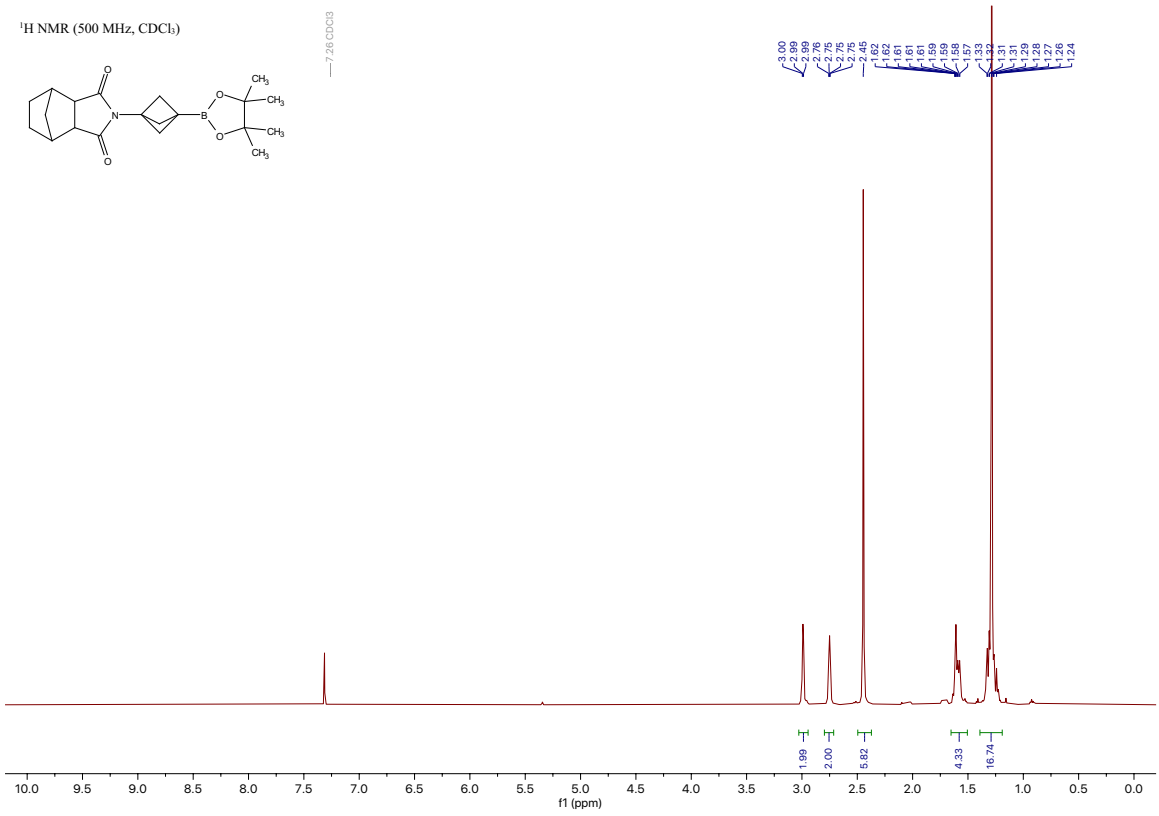
Compound 15a

2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)hexahydro-1*H*-4,7-methanoisoindole-1,3(2*H*)-dione [Experimental]



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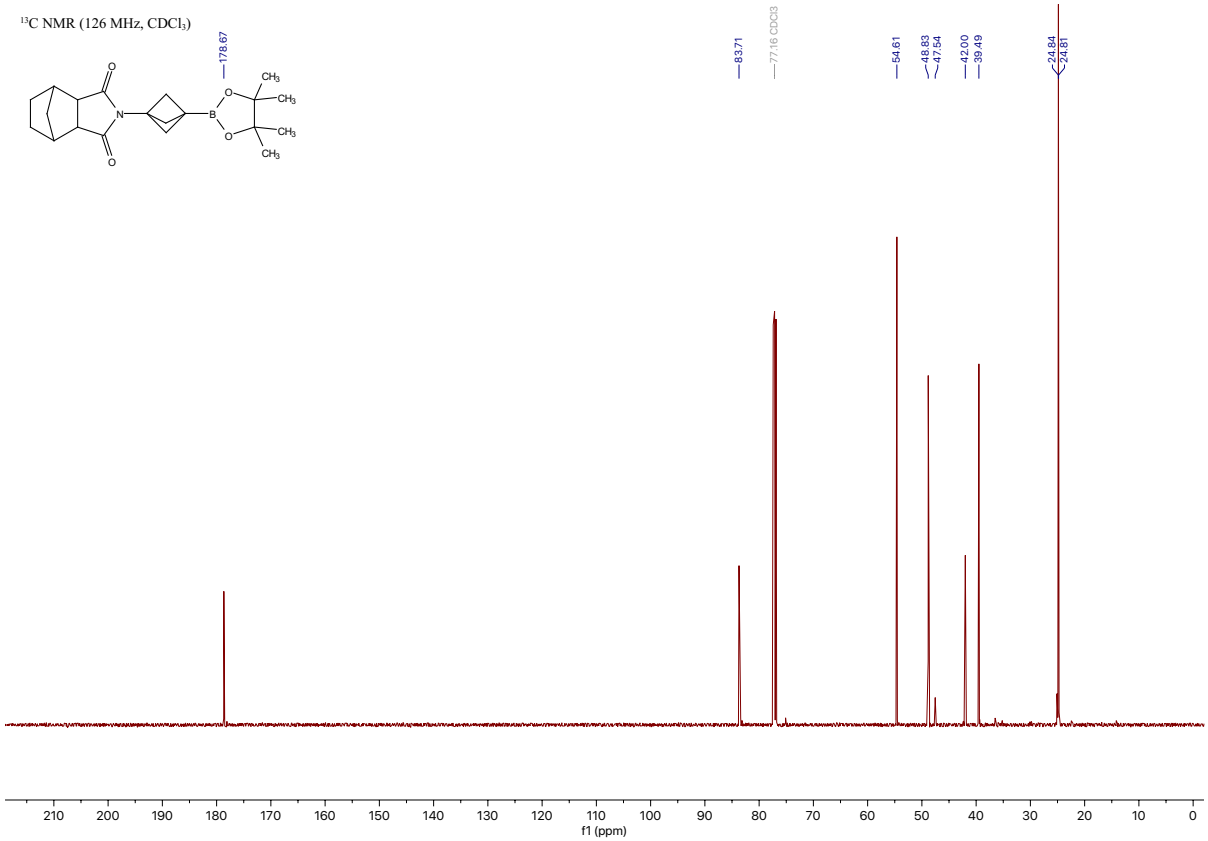
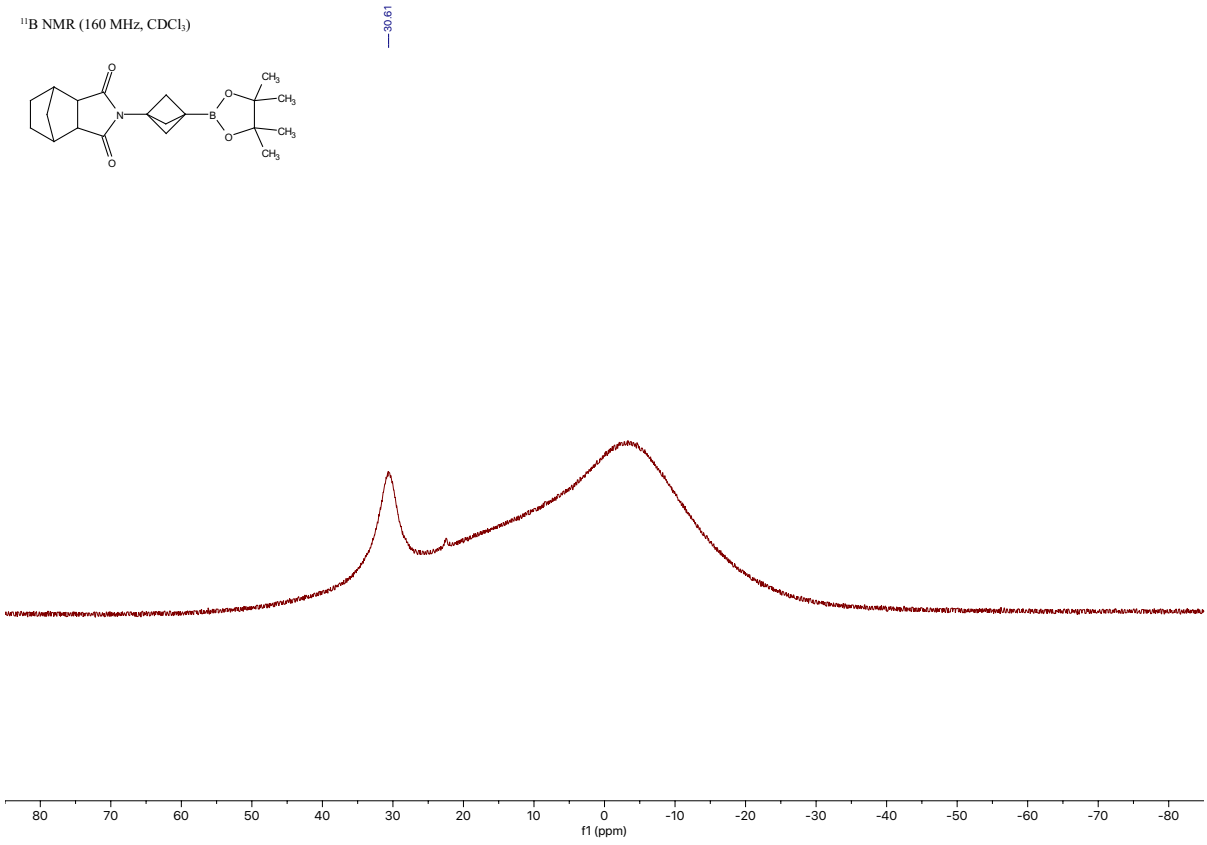
^{13}C NMR (126 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)



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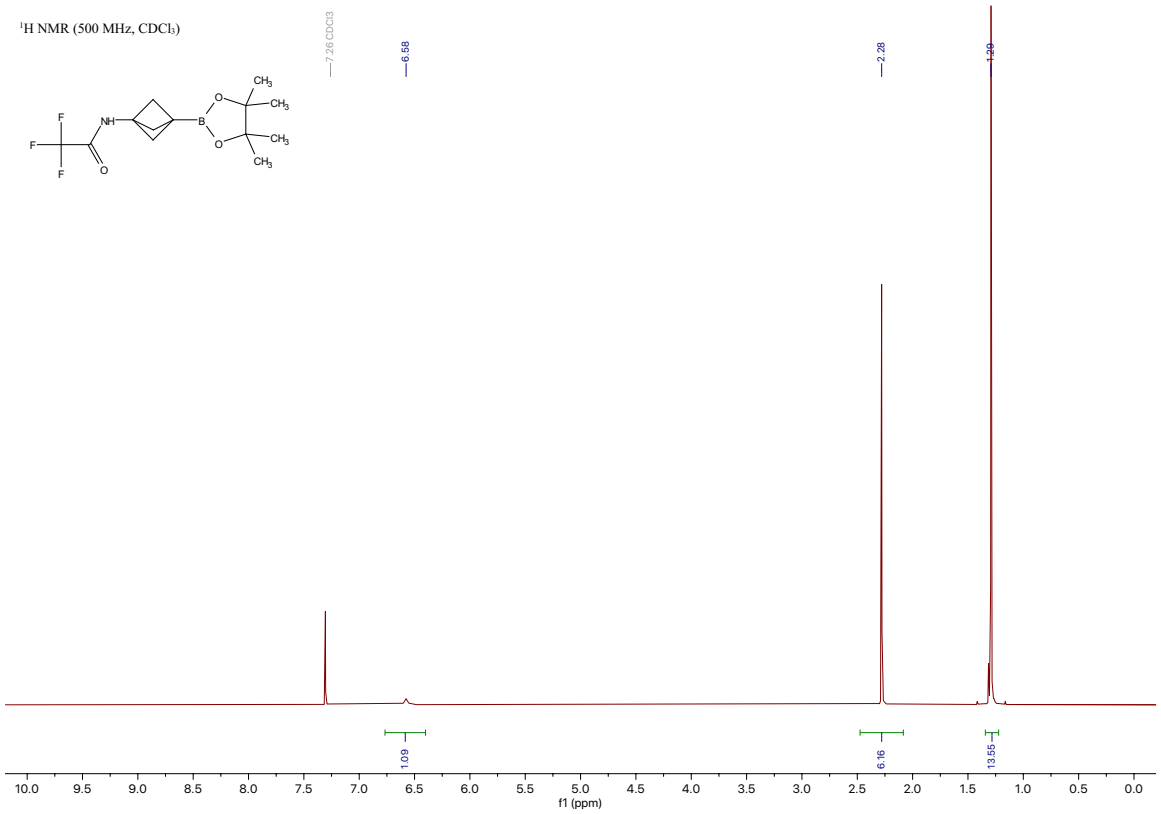
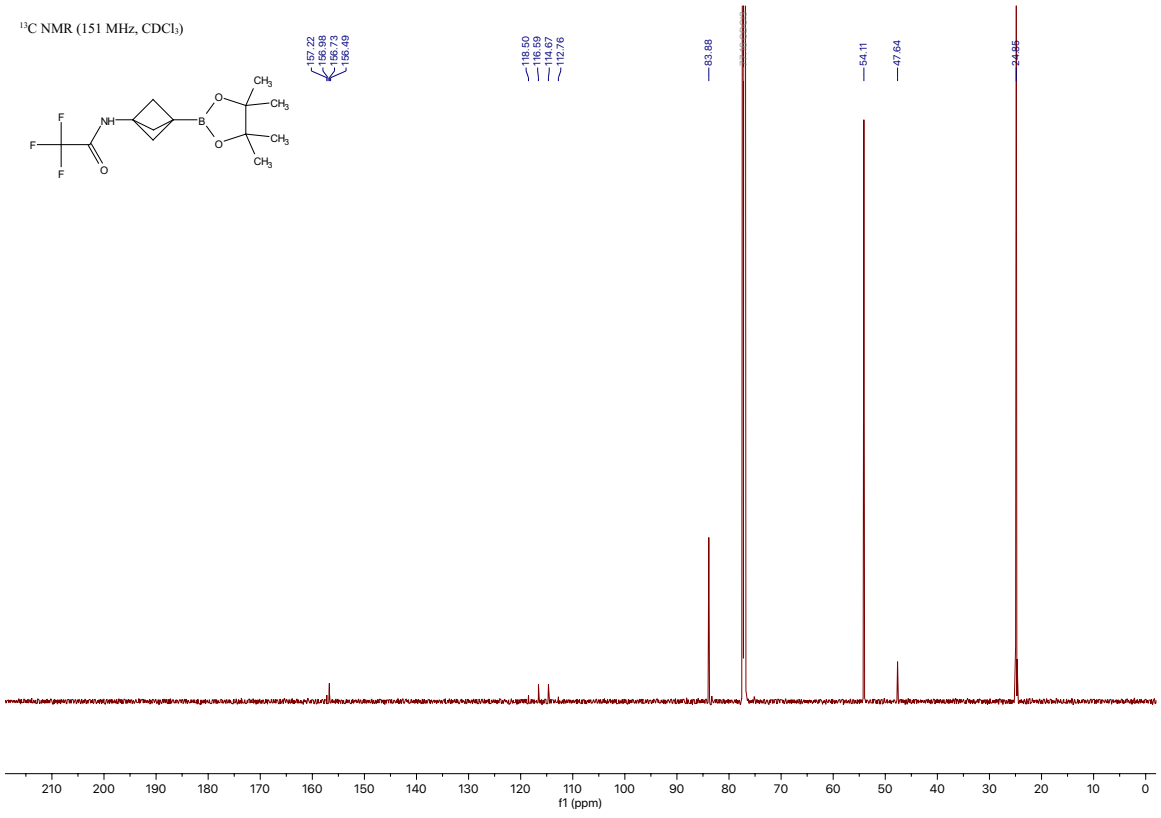
Compound 16a

2,2,2-trifluoro-*N*-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)acetamide [Experimental]





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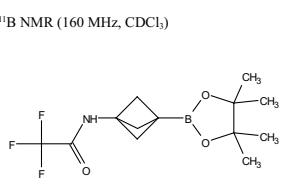
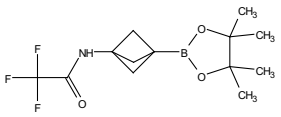
^{11}B NMR (160 MHz, $CDCl_3$)



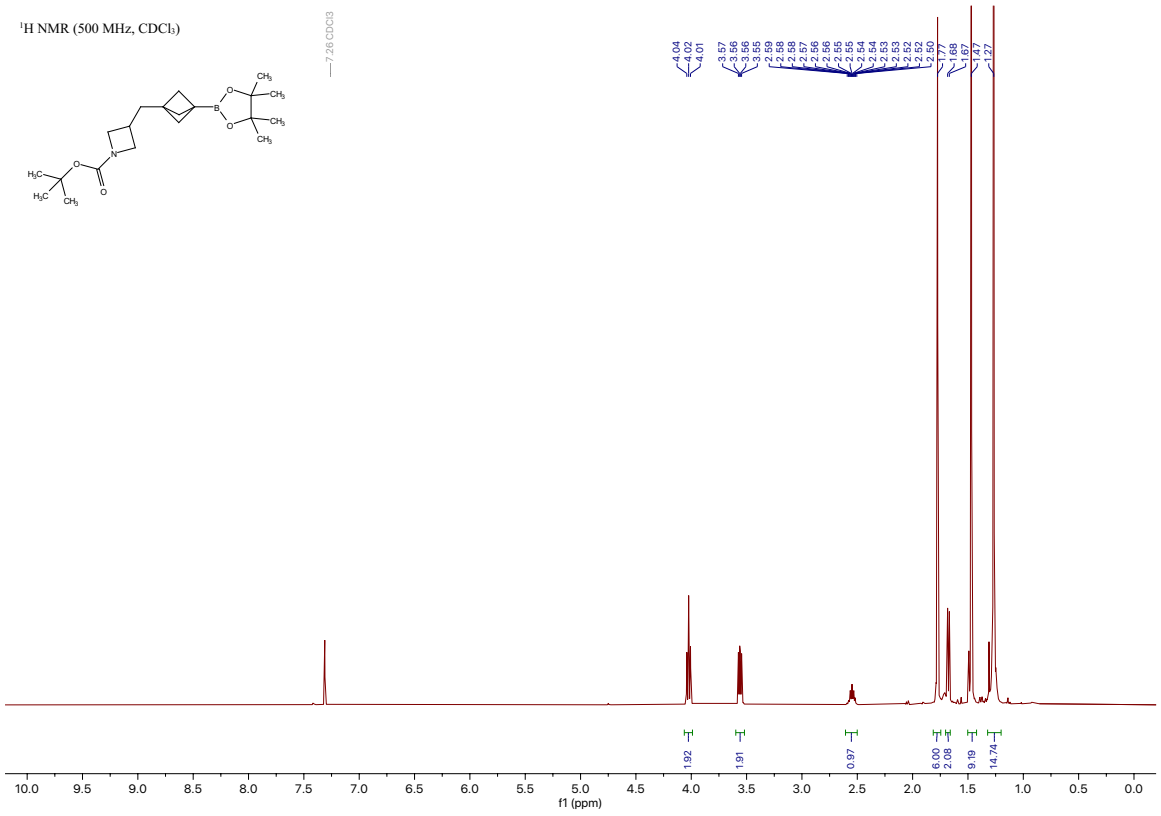
^{19}F NMR (470 MHz, $CDCl_3$)



[*Return to table of contents*]

Compound 17a

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



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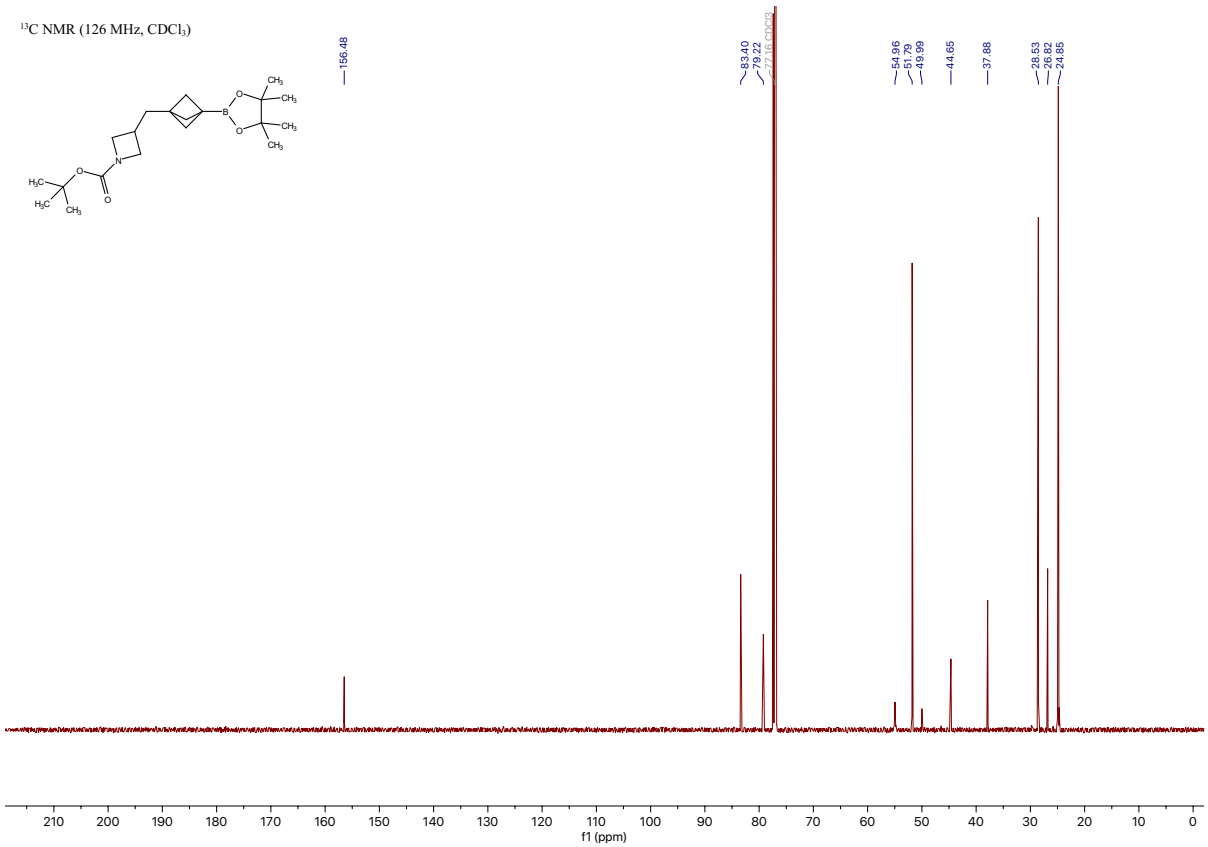
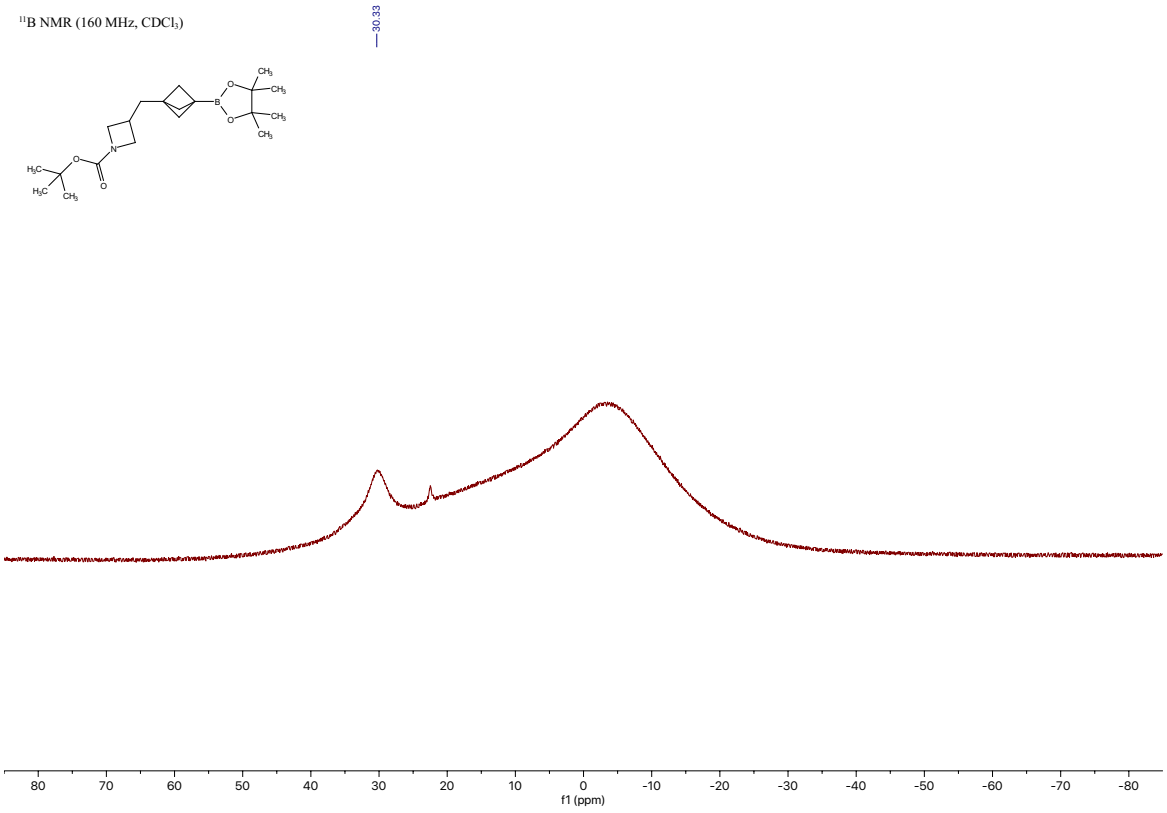
^{13}C NMR (126 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)



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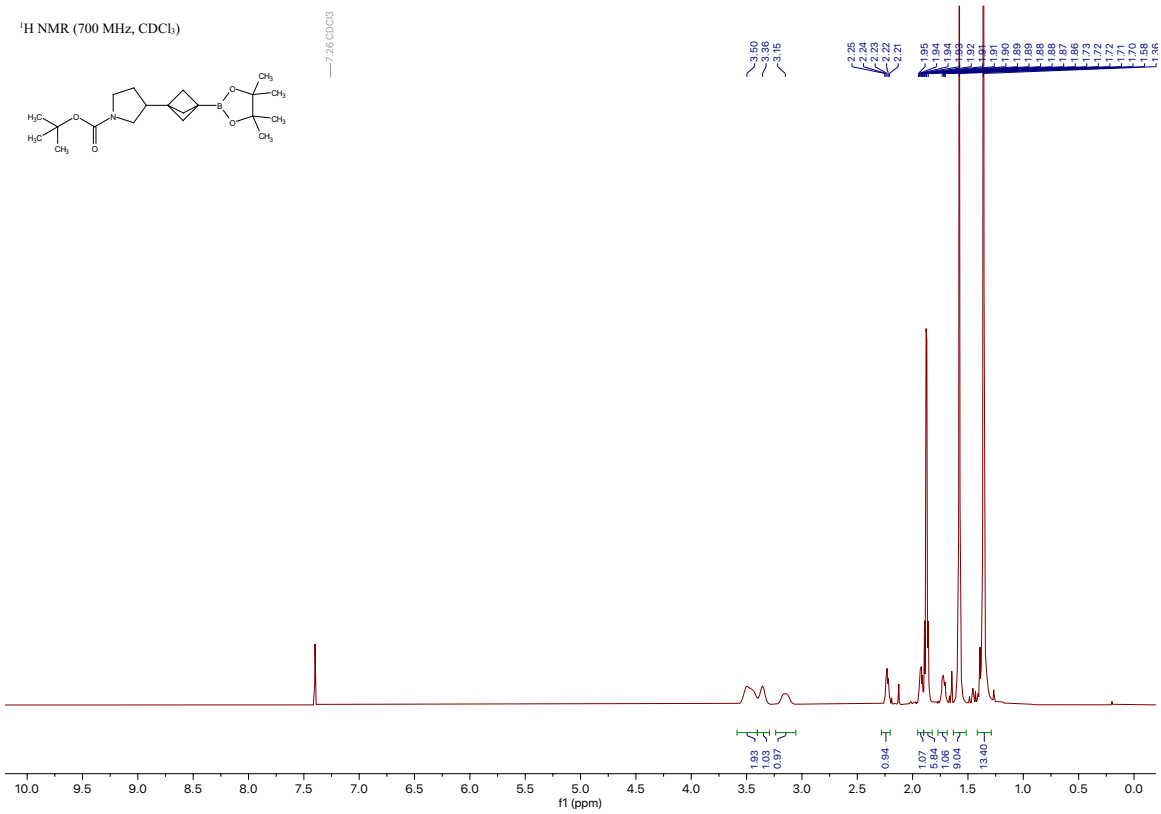
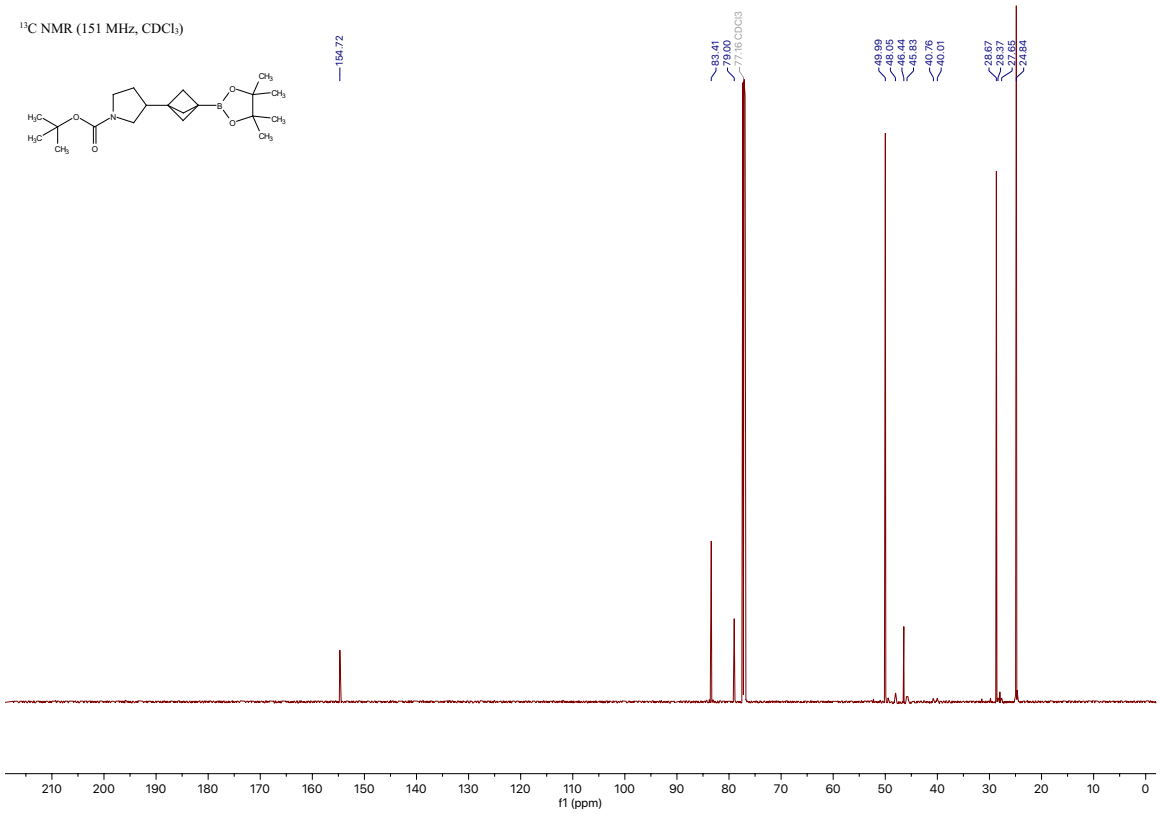
Compound 18a

***tert*-butyl 3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)pyrrolidine-1-carboxylate** [Experimental]





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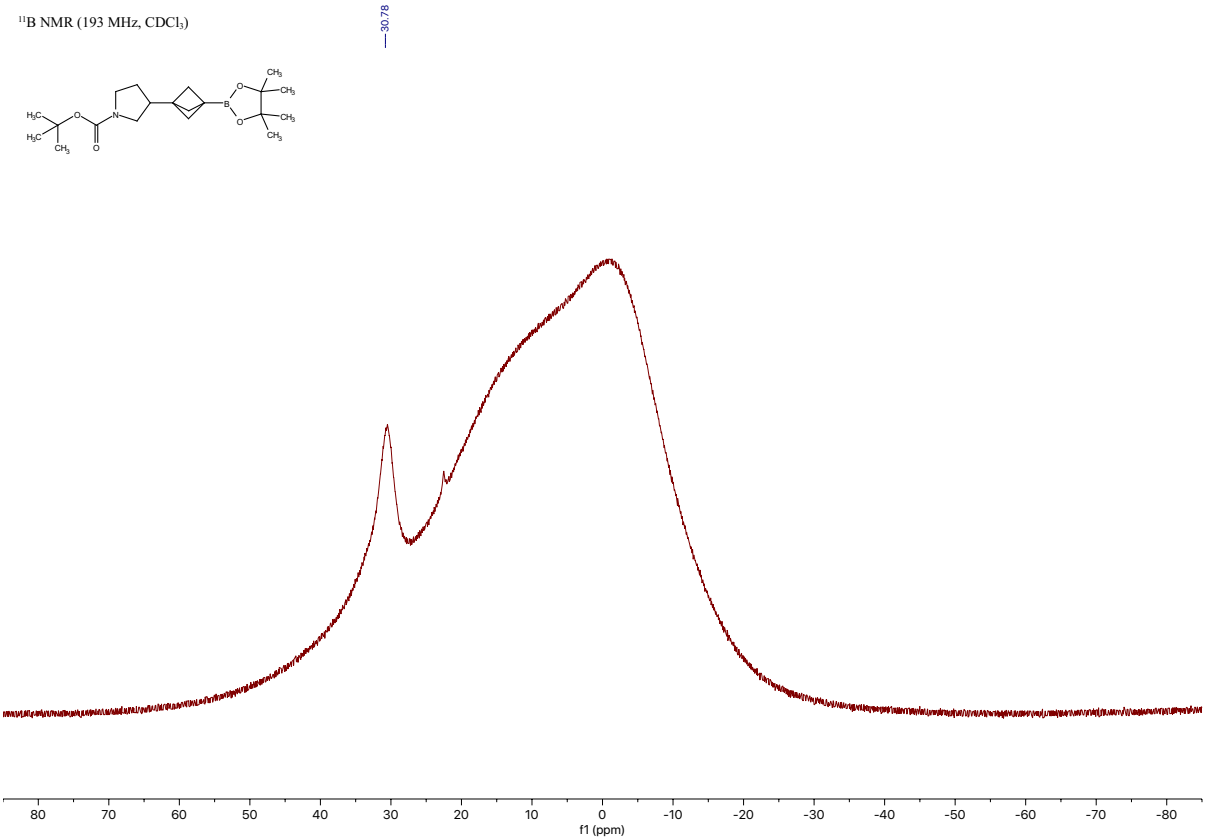
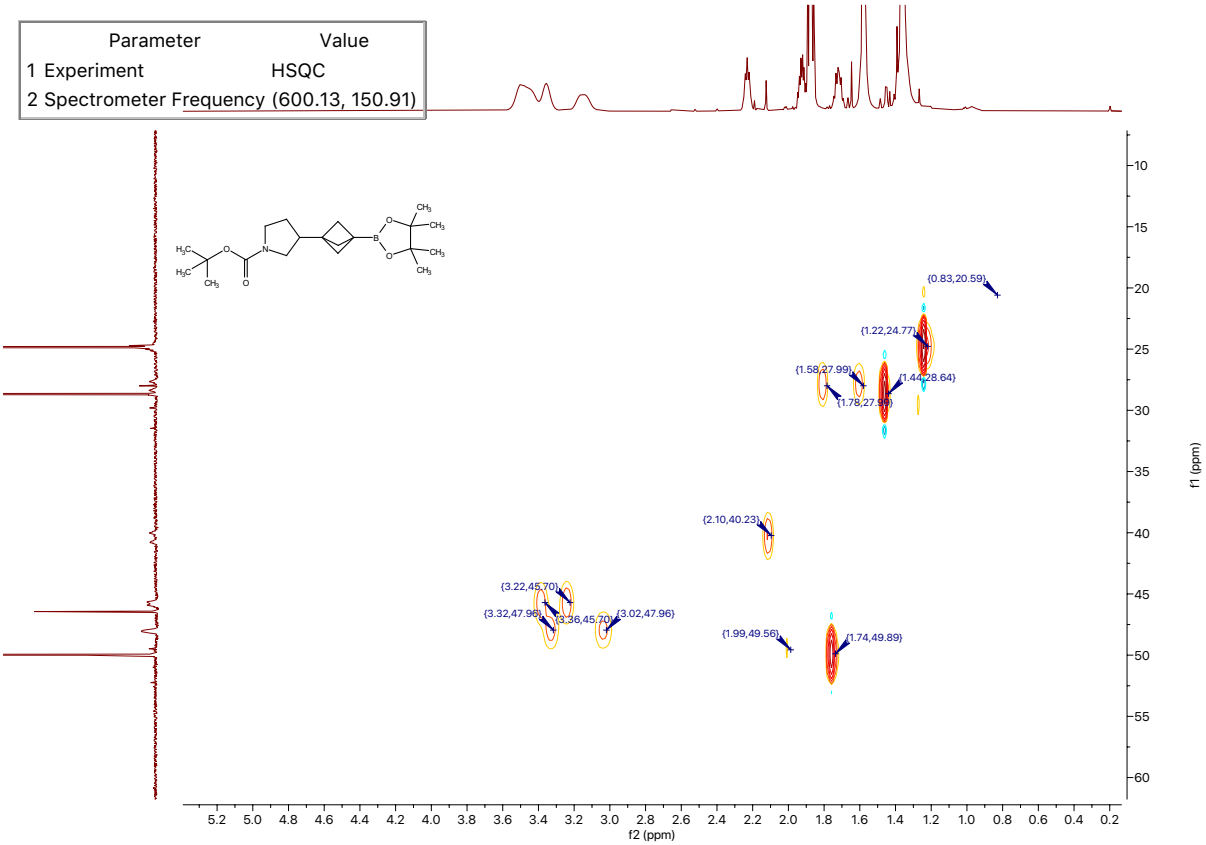
^{11}B NMR (193 MHz, $CDCl_3$)



Parameter	Value
1 Experiment	HSQC
2 Spectrometer Frequency	(600.13, 150.91)



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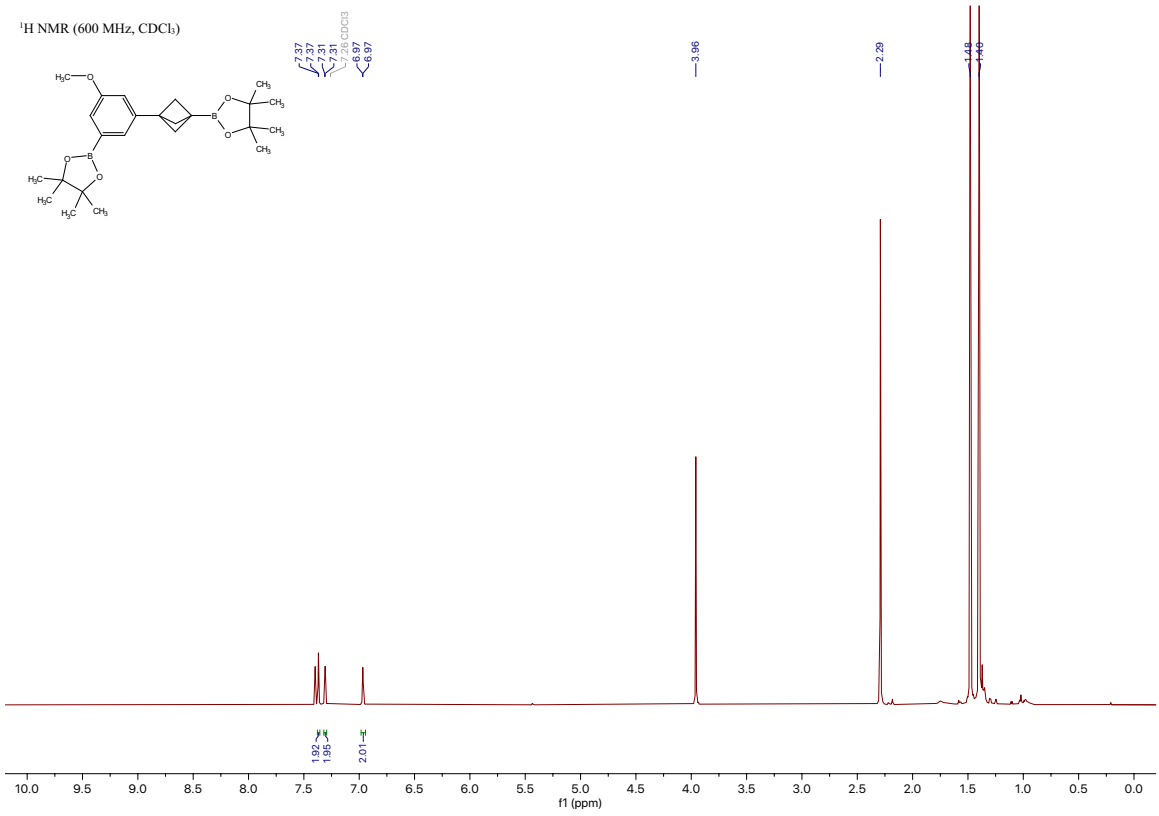
Compound 19a

2-(3-methoxy-5-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [Experimental]



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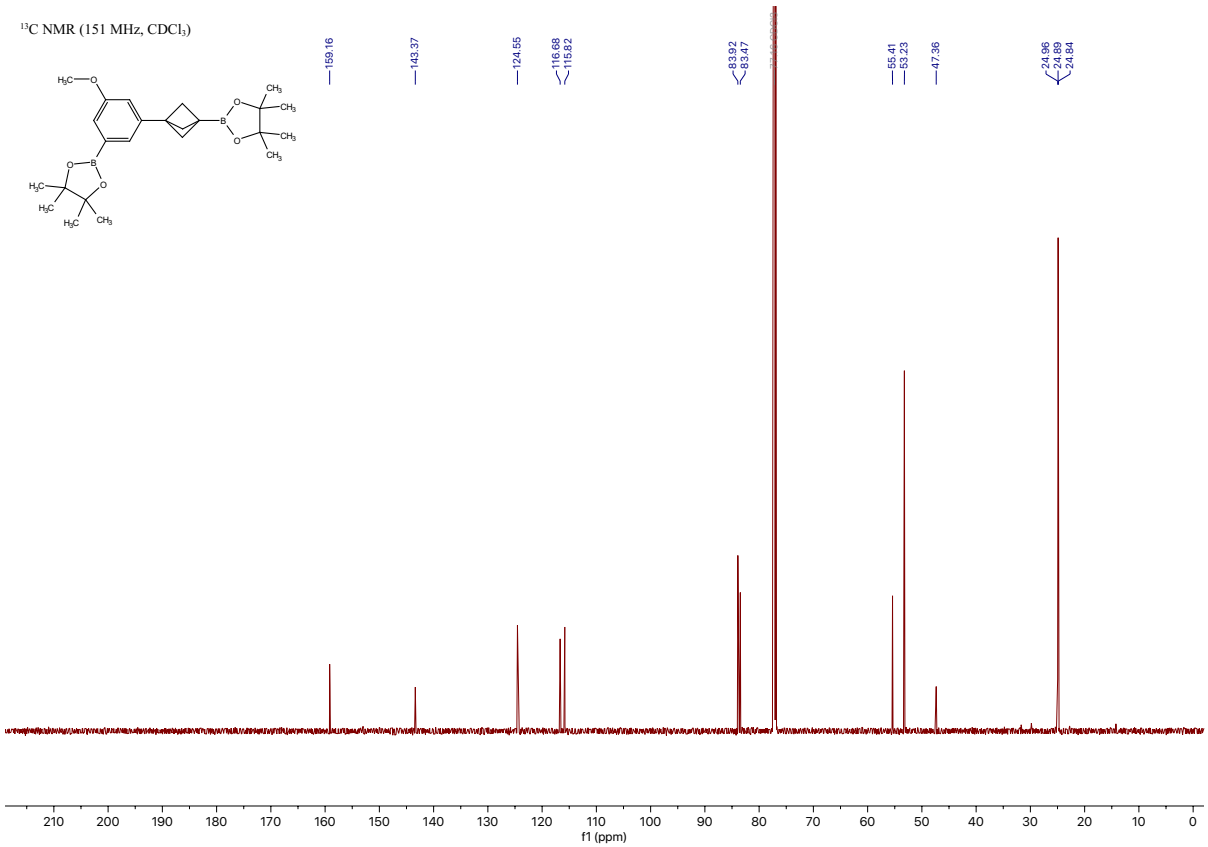
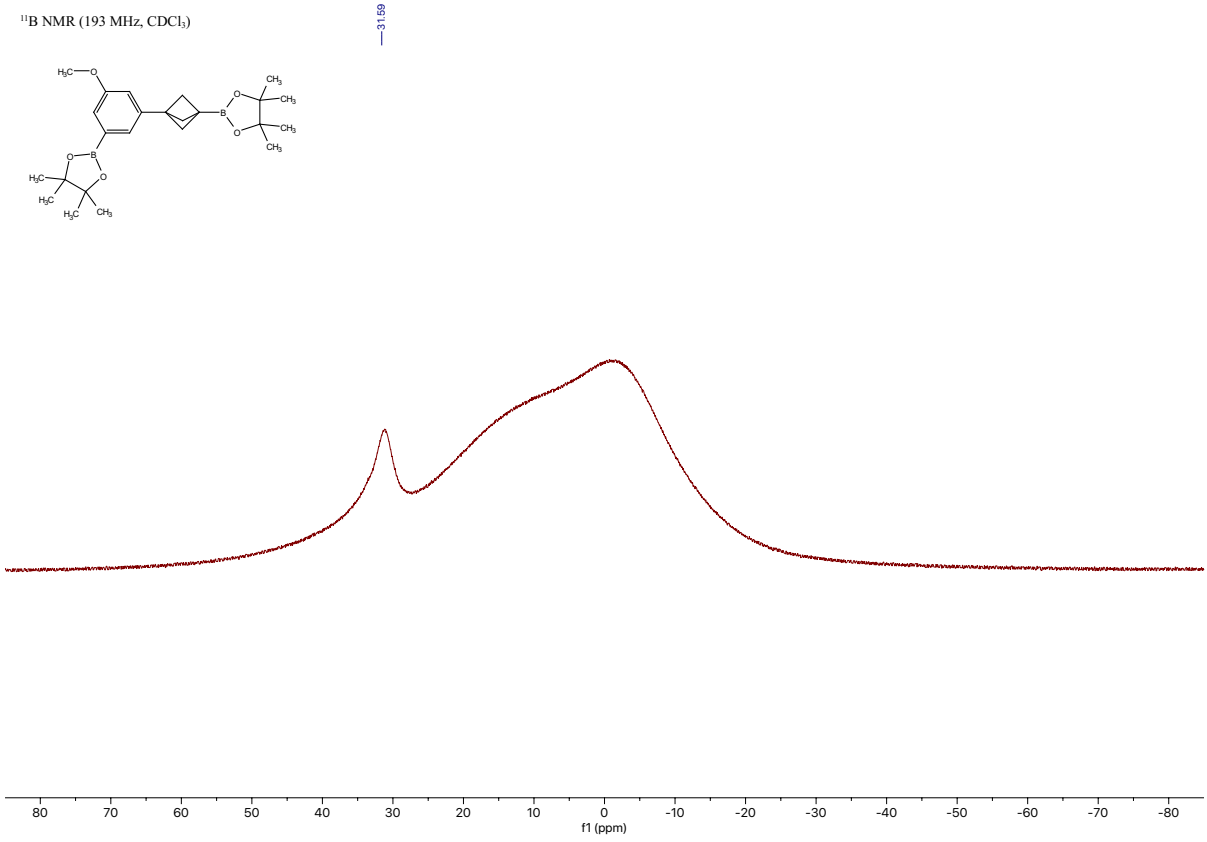
^{13}C NMR (151 MHz, $CDCl_3$)



^{11}B NMR (193 MHz, $CDCl_3$)



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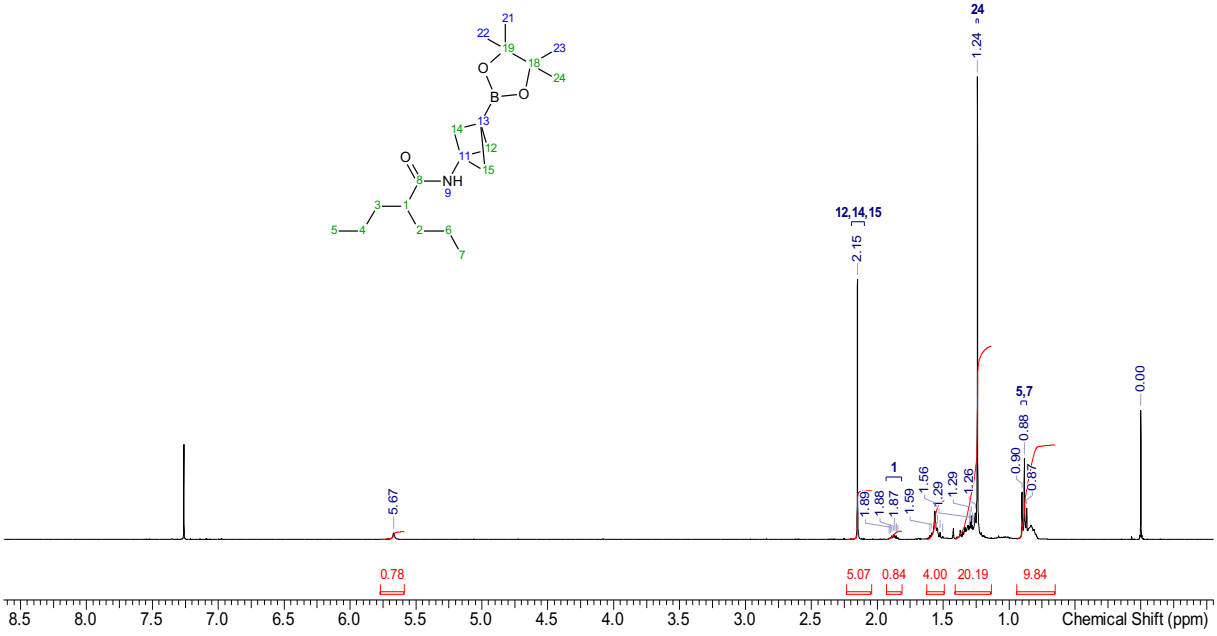
Compound 20a

2-propyl-*N*-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[1.1.1]pentan-1-yl)pentanamide [Experimental]



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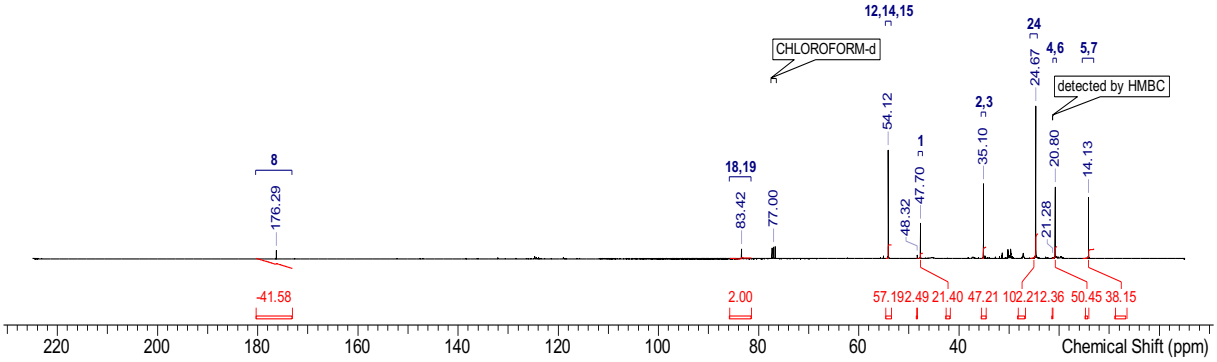

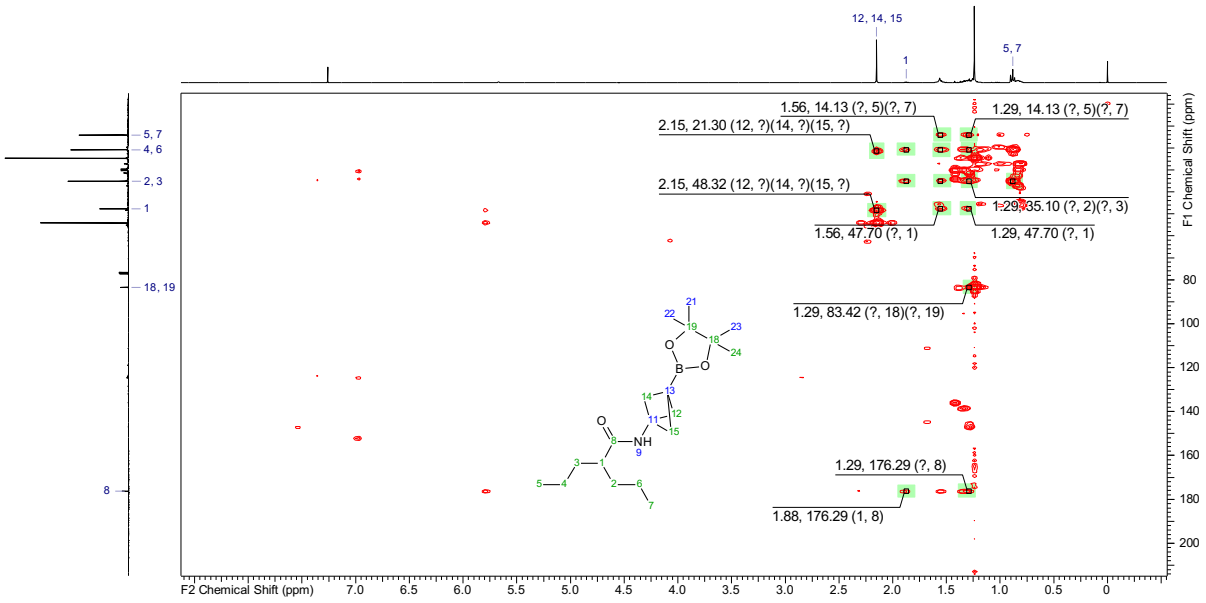

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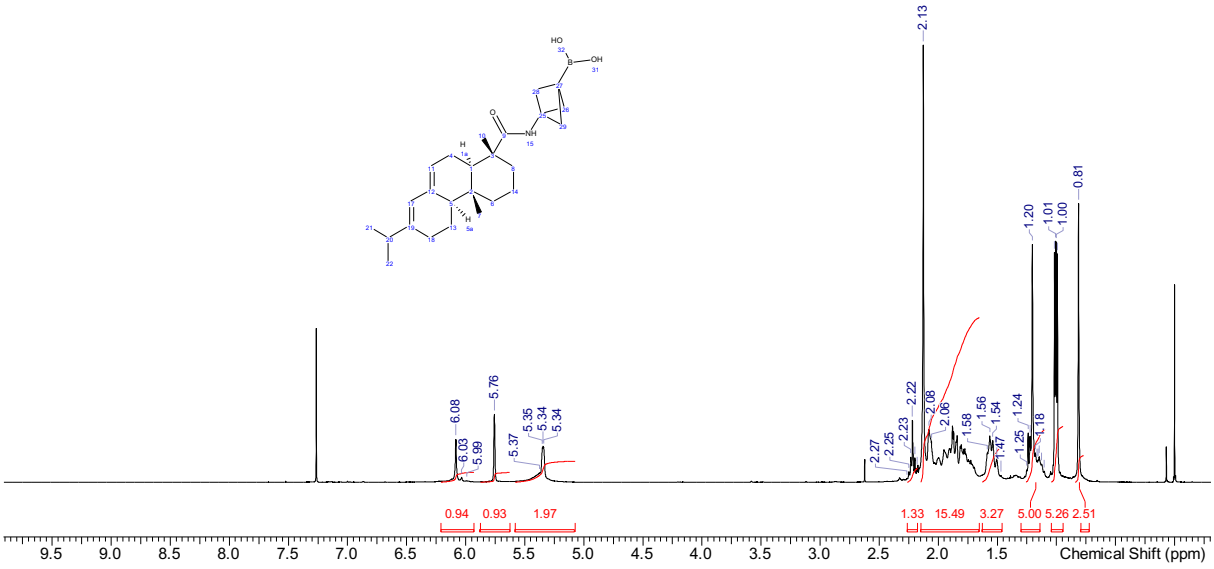
Compound 21a

(3-((1*R*,4a*R*,4b*R*,10a*R*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,4b,5,6,10,10a-decahydrophenanthrene-1-carboxamido)bicyclo[1.1.1]pentan-1-yl)boronic acid [Experimental]



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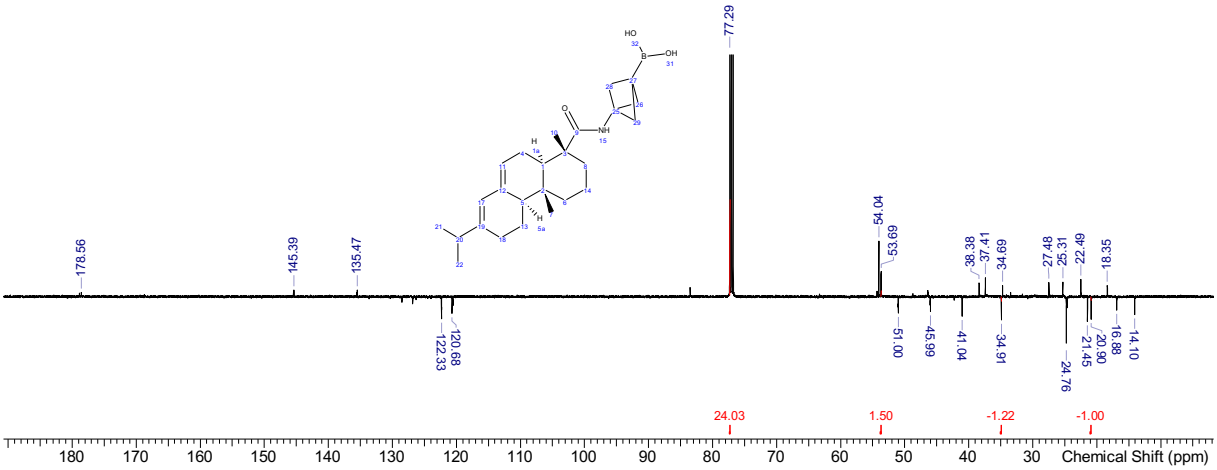

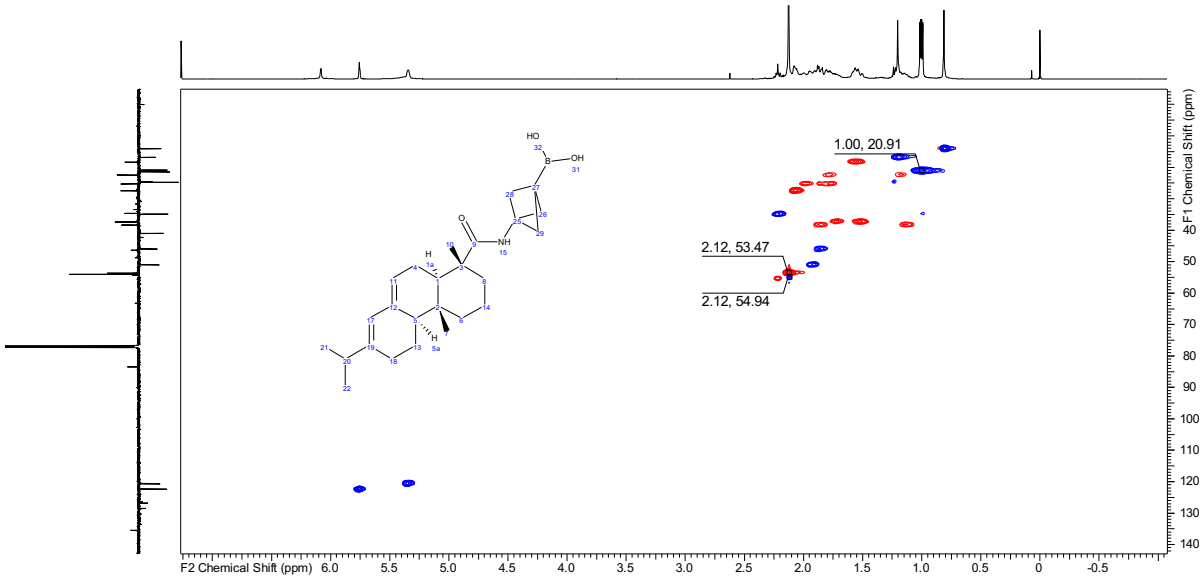

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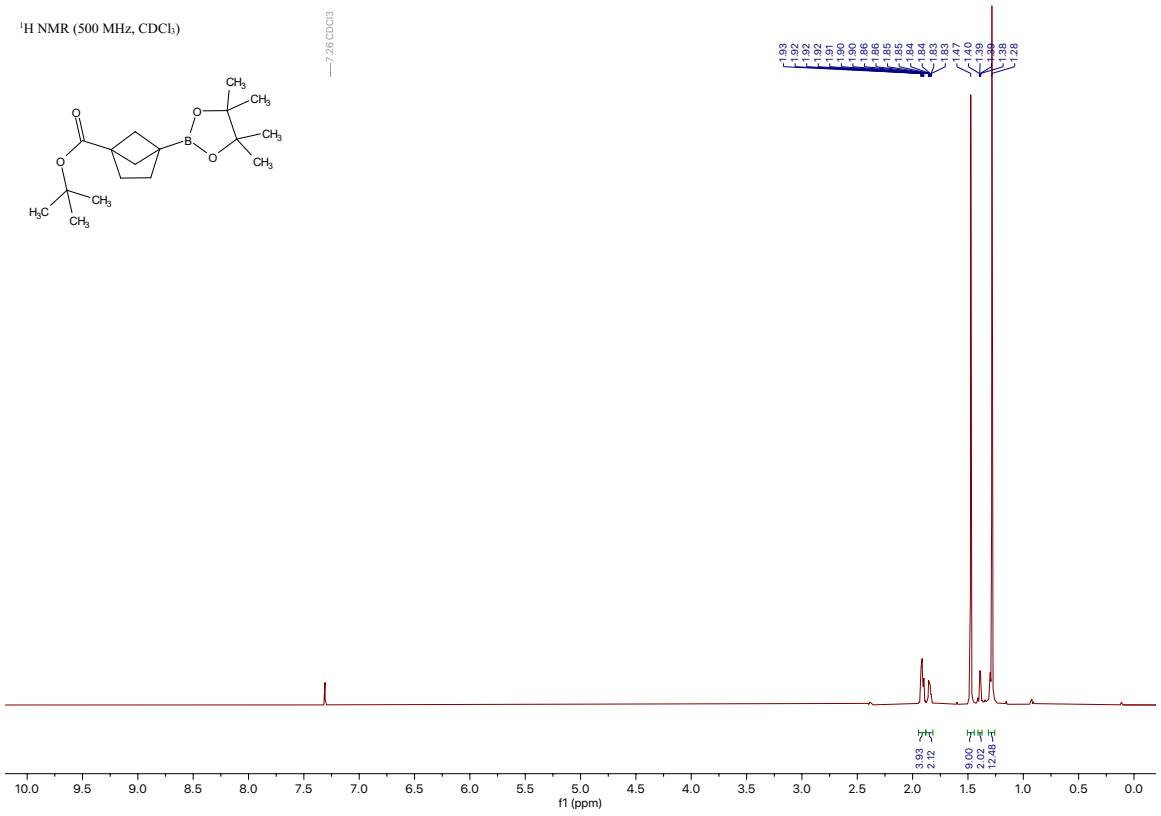
Compound 22a

***tert*-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)bicyclo[2.1.1]hexane-1-carboxylate**

[Experimental]



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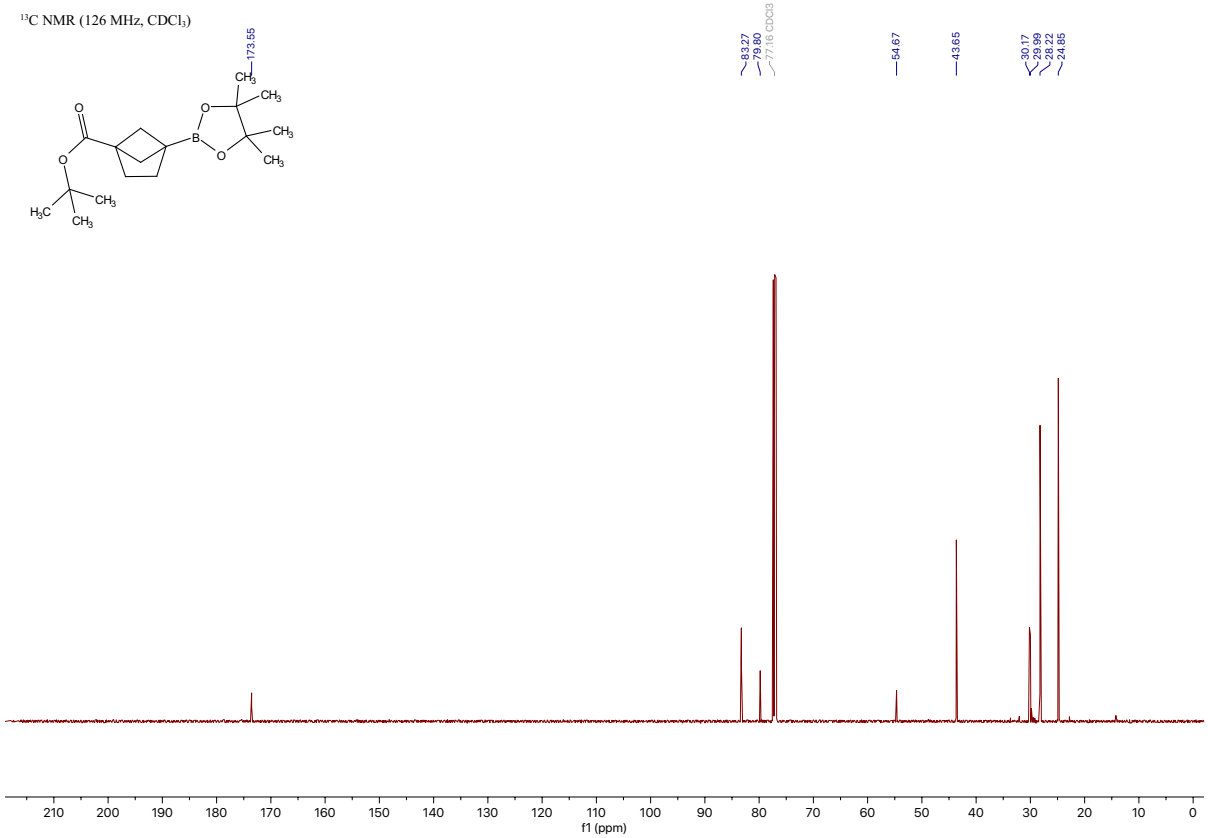
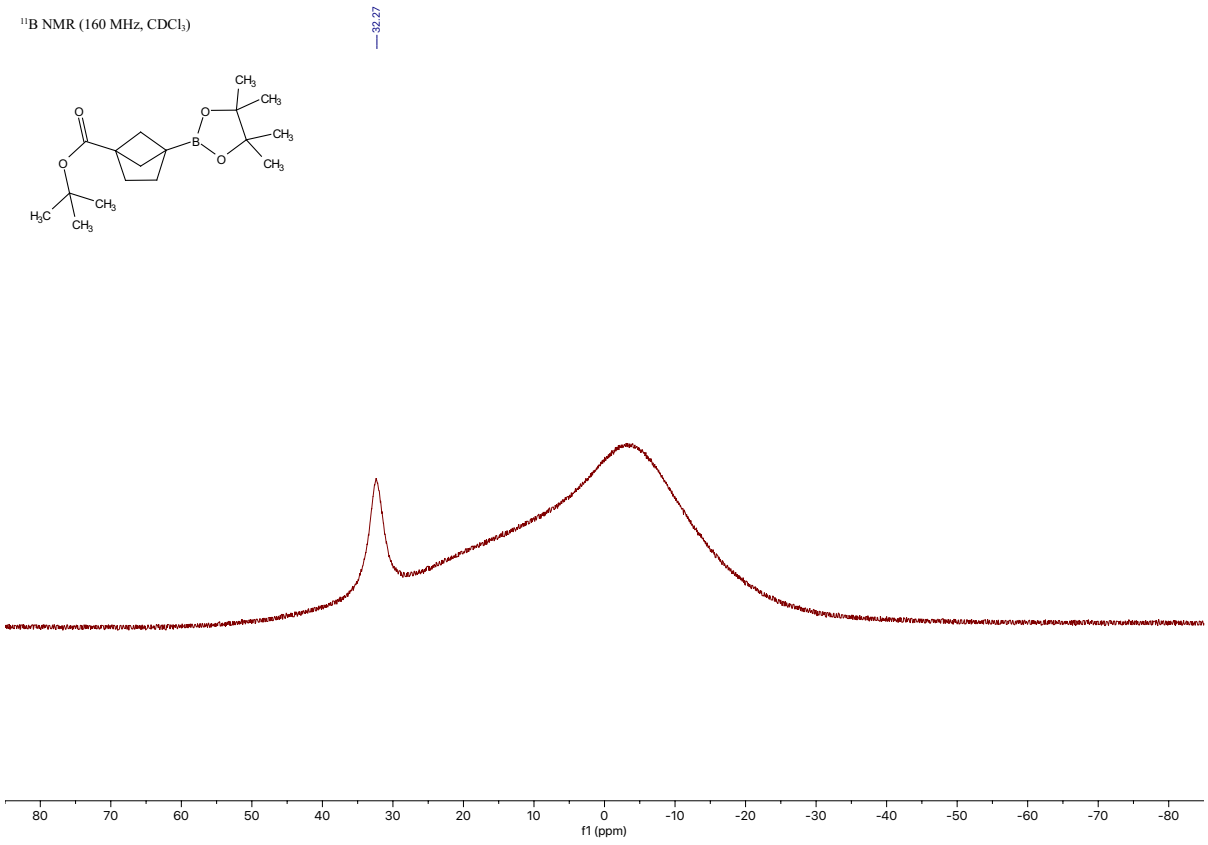
^{13}C NMR (126 MHz, $CDCl_3$)



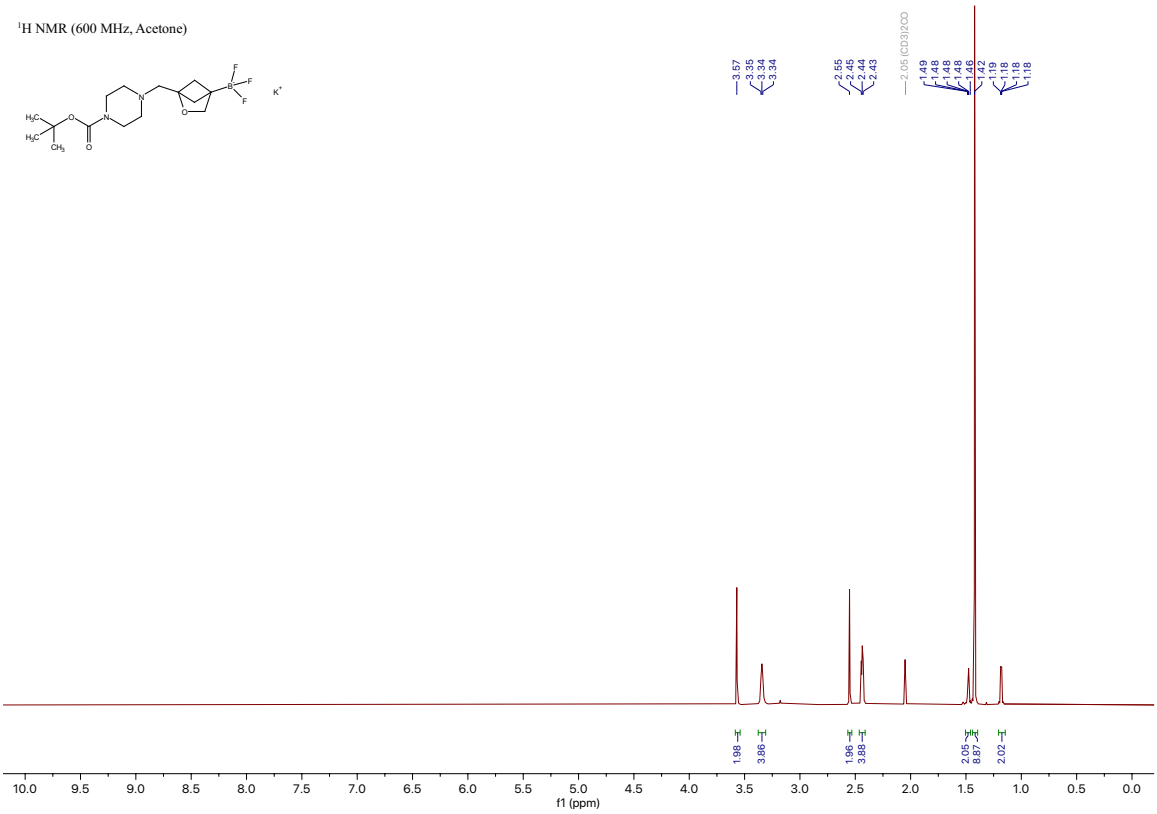
^{11}B NMR (160 MHz, $CDCl_3$)

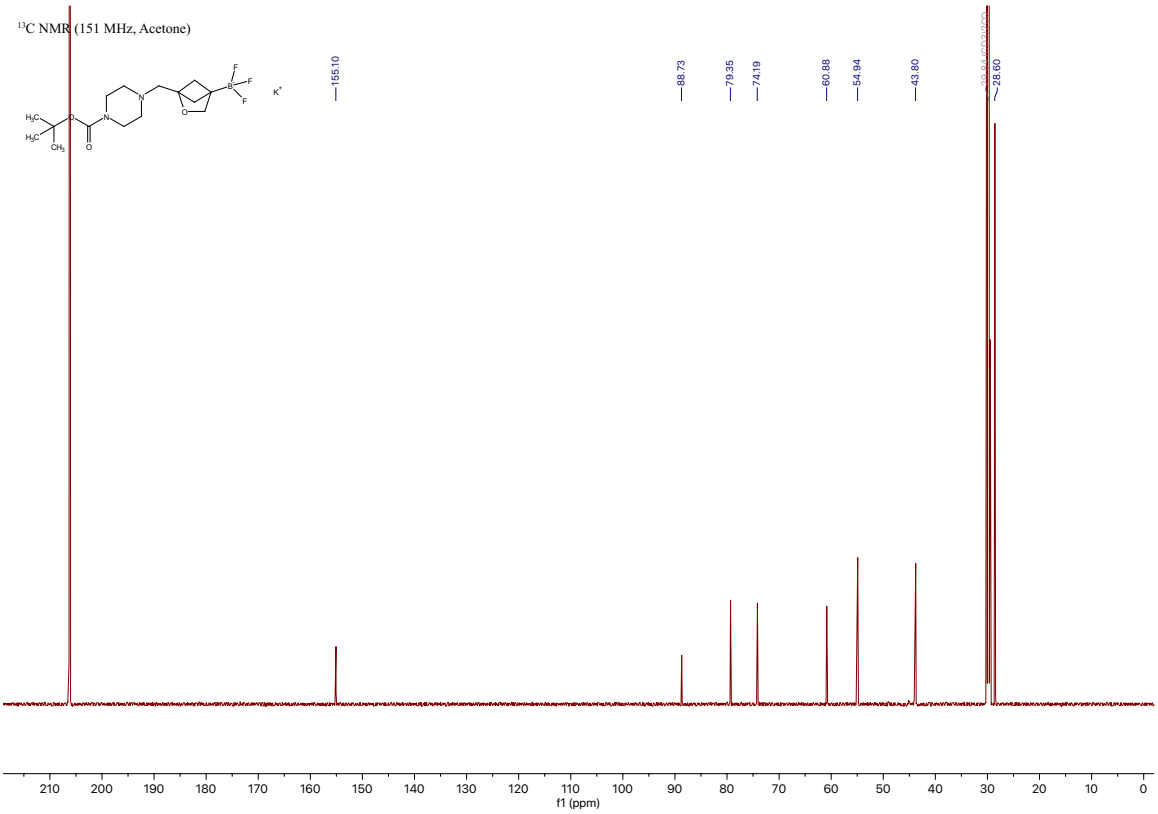


[*Return to table of contents*]

Compound 23a

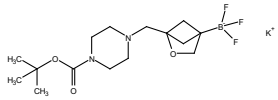
***tert*-butyl 4-((4-(trifluoro-λ4-boraneyl)-2-oxabicyclo[2.1.1]hexan-1-yl)methyl)piperazine-1-carboxylate, potassium salt** [Experimental]



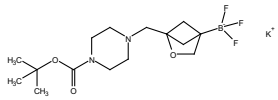


[*Return to table of contents*]

^{11}B NMR (193 MHz, Acetone)



^{19}F NMR (565 MHz, Acetone)



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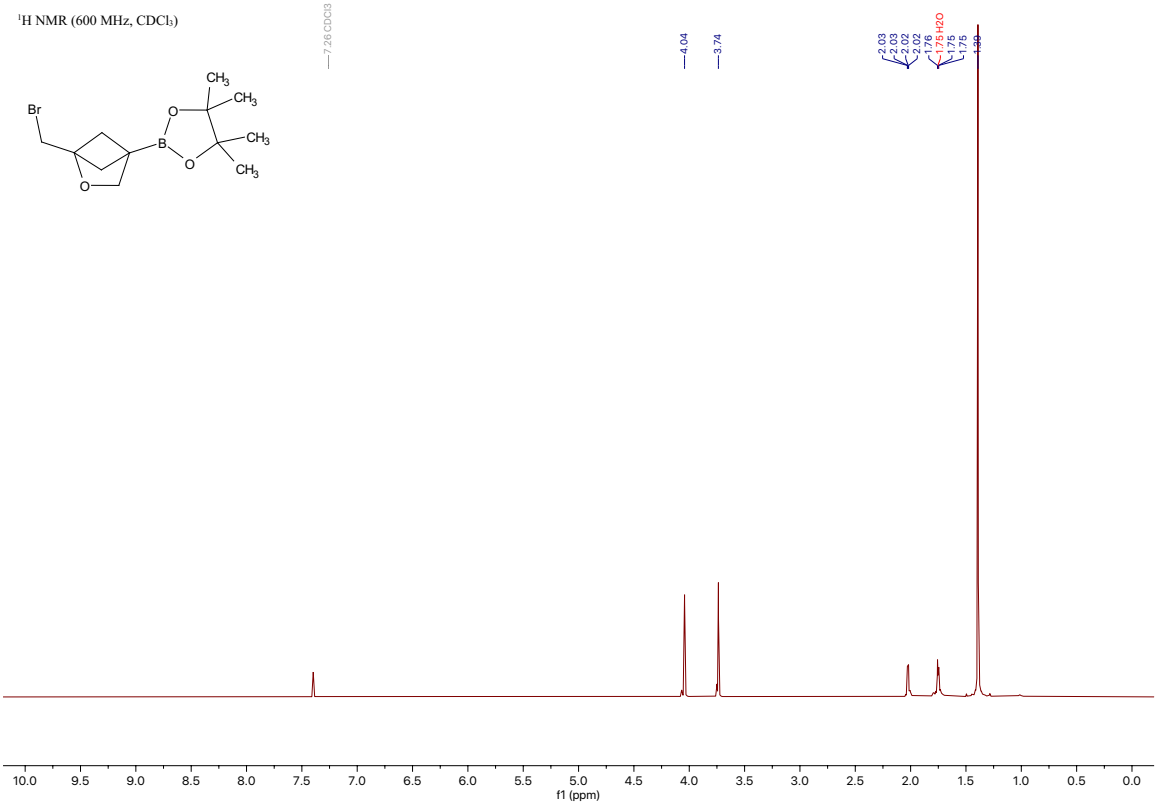
Compound 24a

2-(1-(bromomethyl)-2-oxabicyclo[2.1.1]hexan-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

[Experimental]



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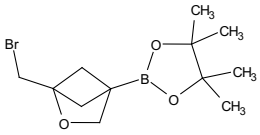
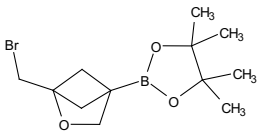
^{13}C NMR (151 MHz, $CDCl_3$)



^{11}B NMR (193 MHz, $CDCl_3$)



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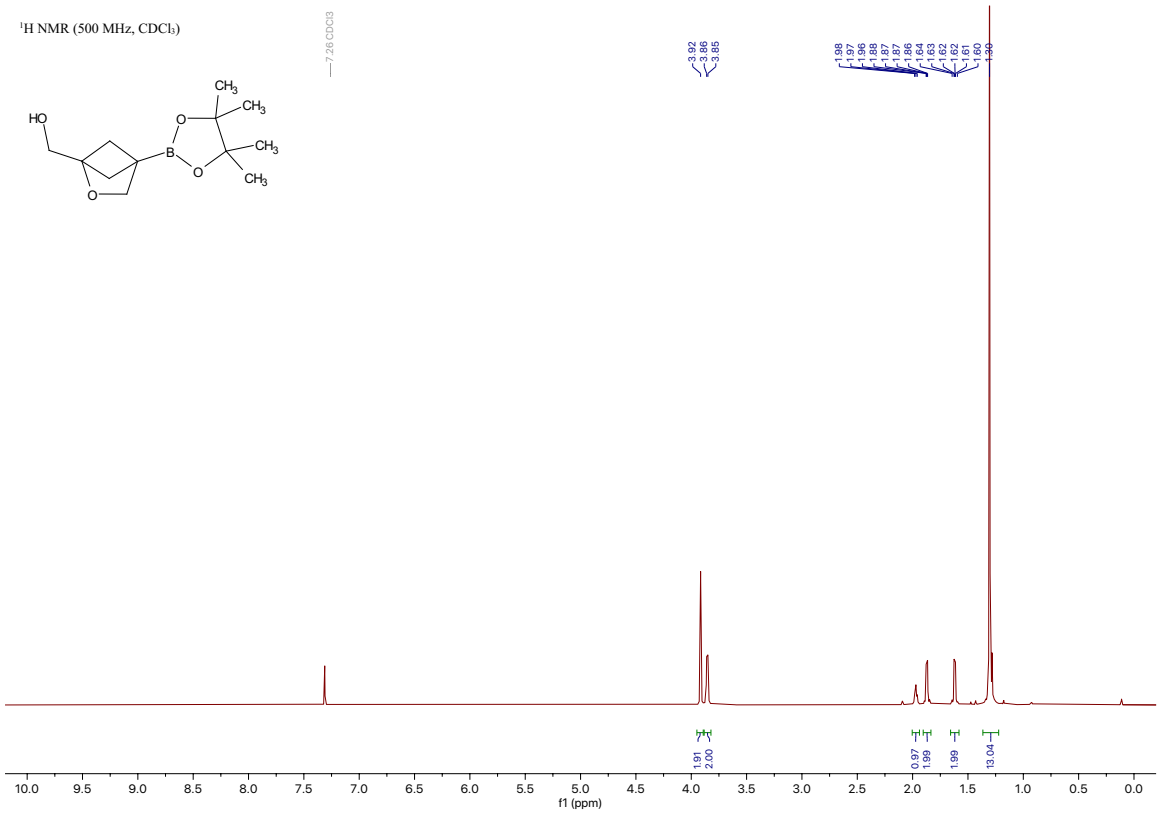
Compound 25a

(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-oxabicyclo[2.1.1]hexan-1-yl)methanol

[Experimental]



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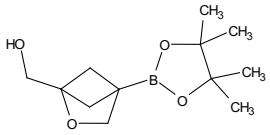
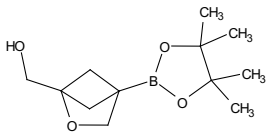
^{13}C NMR (126 MHz, $CDCl_3$)



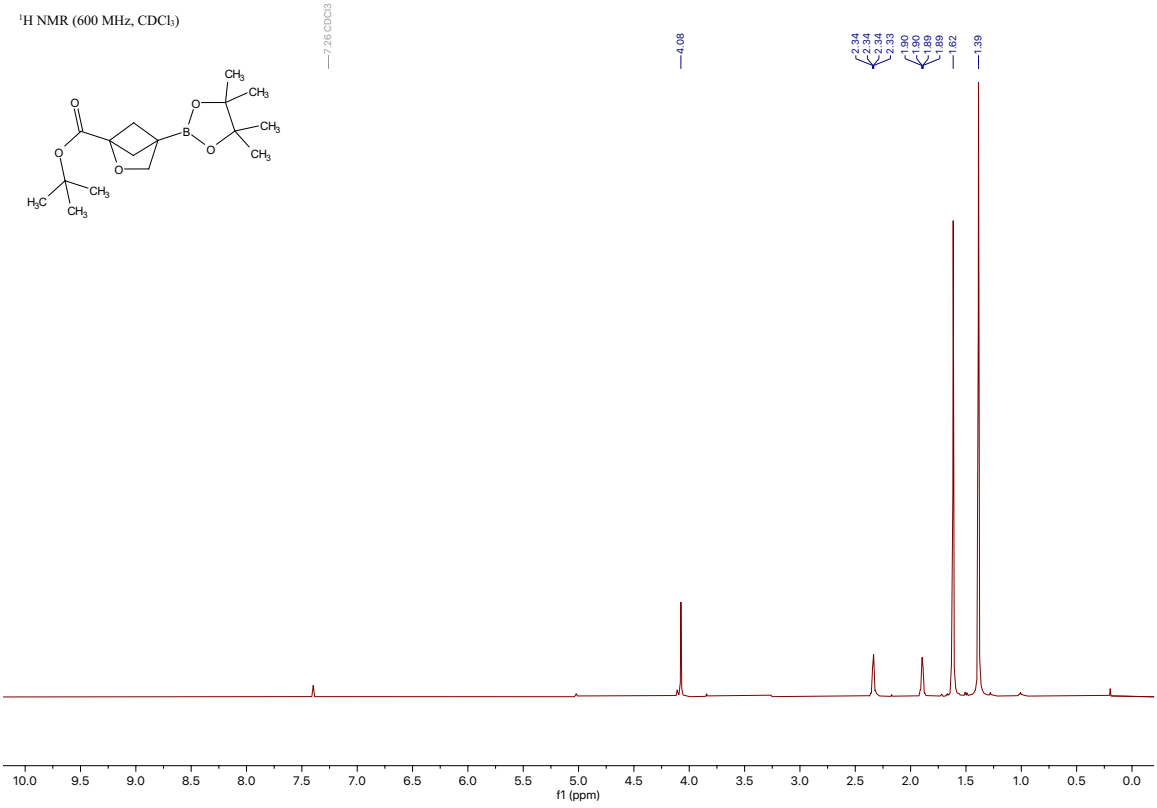
^{11}B NMR (160 MHz, $CDCl_3$) δ 31.64.



[*Return to table of contents*]

Compound 26a

***tert*-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-oxabicyclo[2.1.1]hexane-1-carboxylate** [Experimental]



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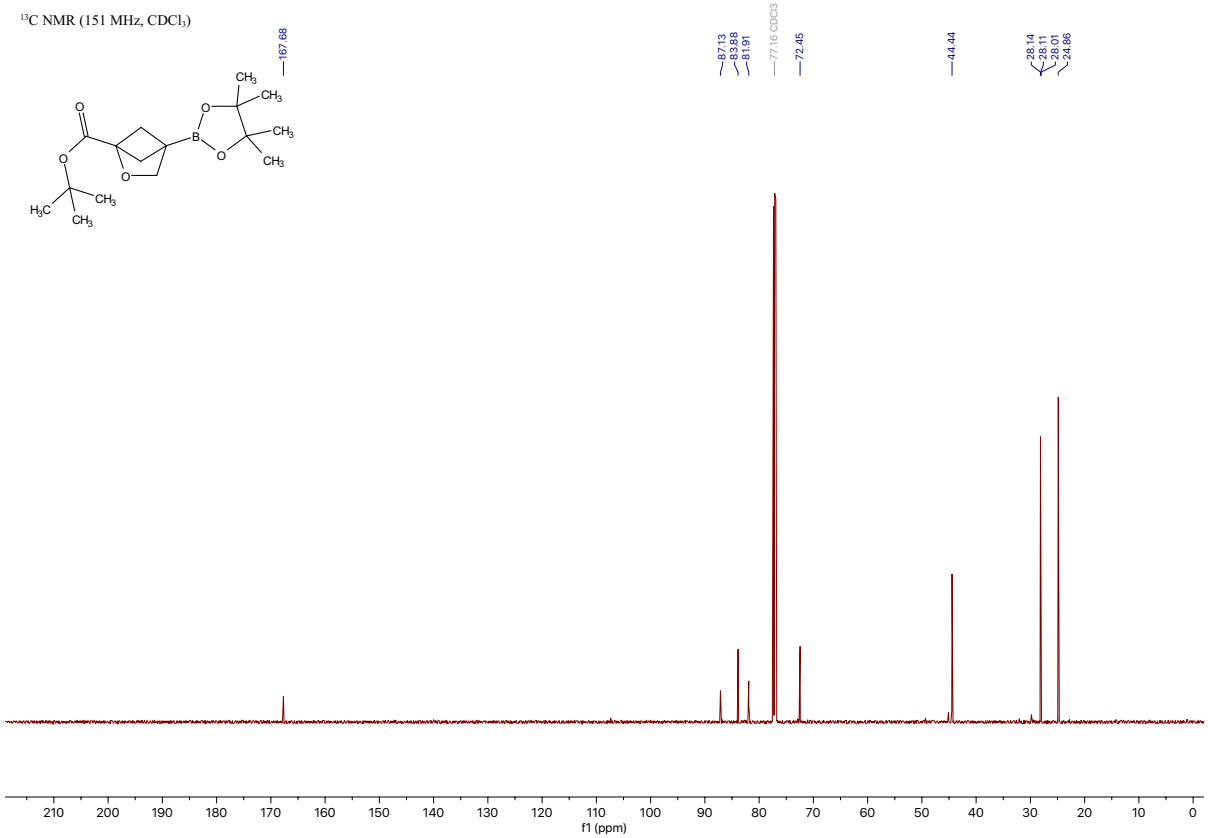
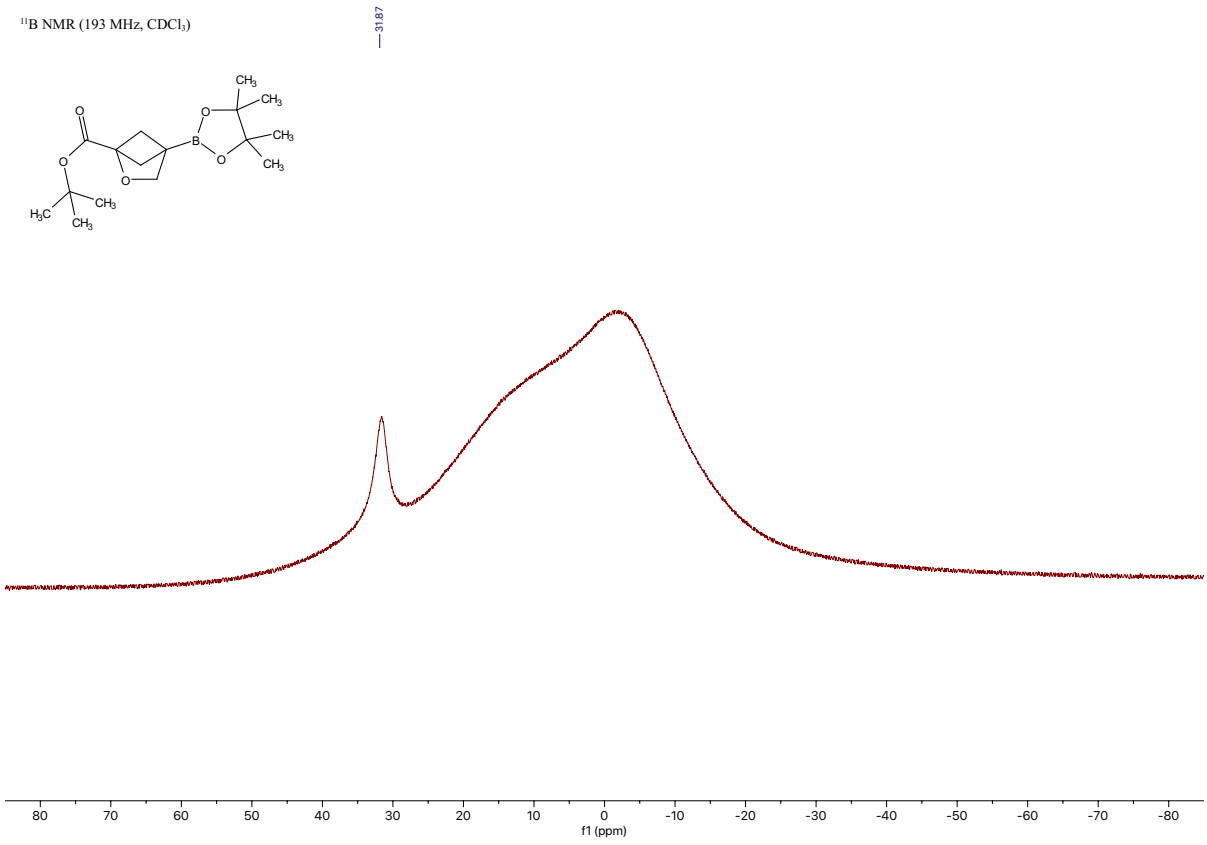
^{13}C NMR (151 MHz, $CDCl_3$)



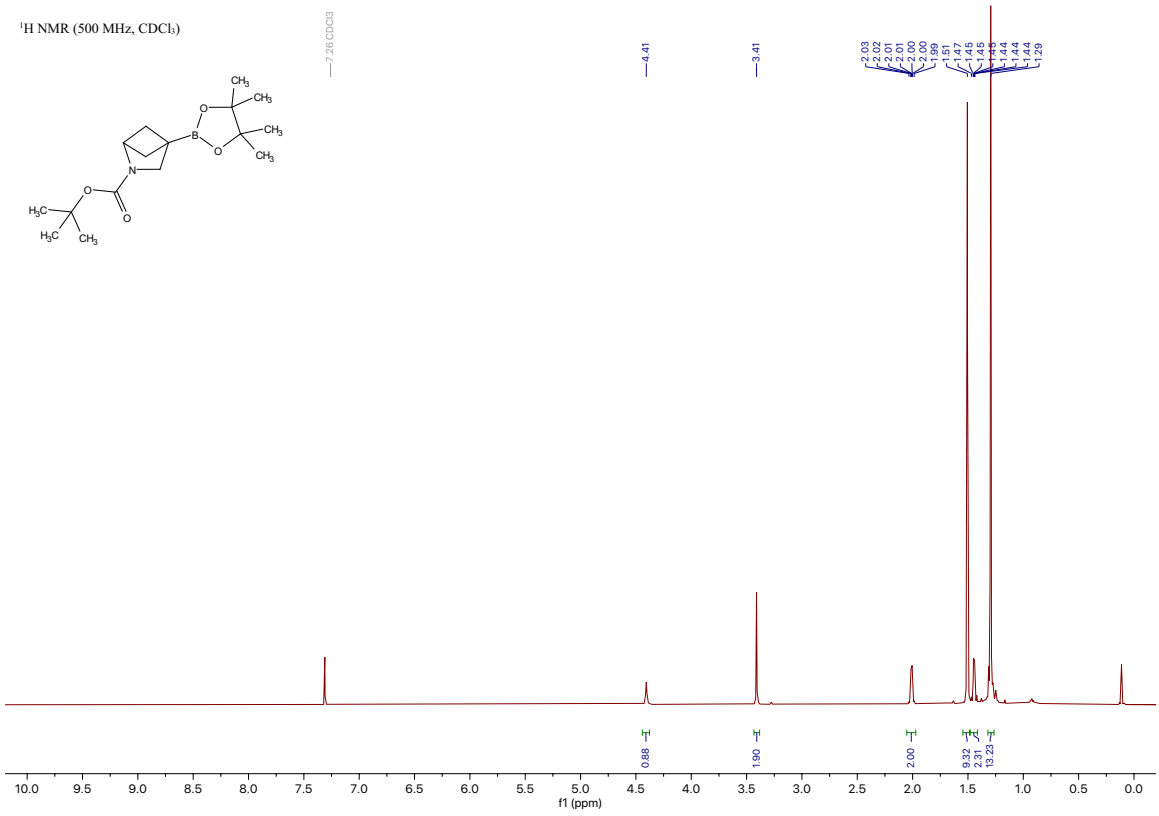
^{11}B NMR (193 MHz, $CDCl_3$)



[*Return to table of contents*]

Compound 27a

***tert*-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azabicyclo[2.1.1]hexane-2-carboxylate** [Experimental]



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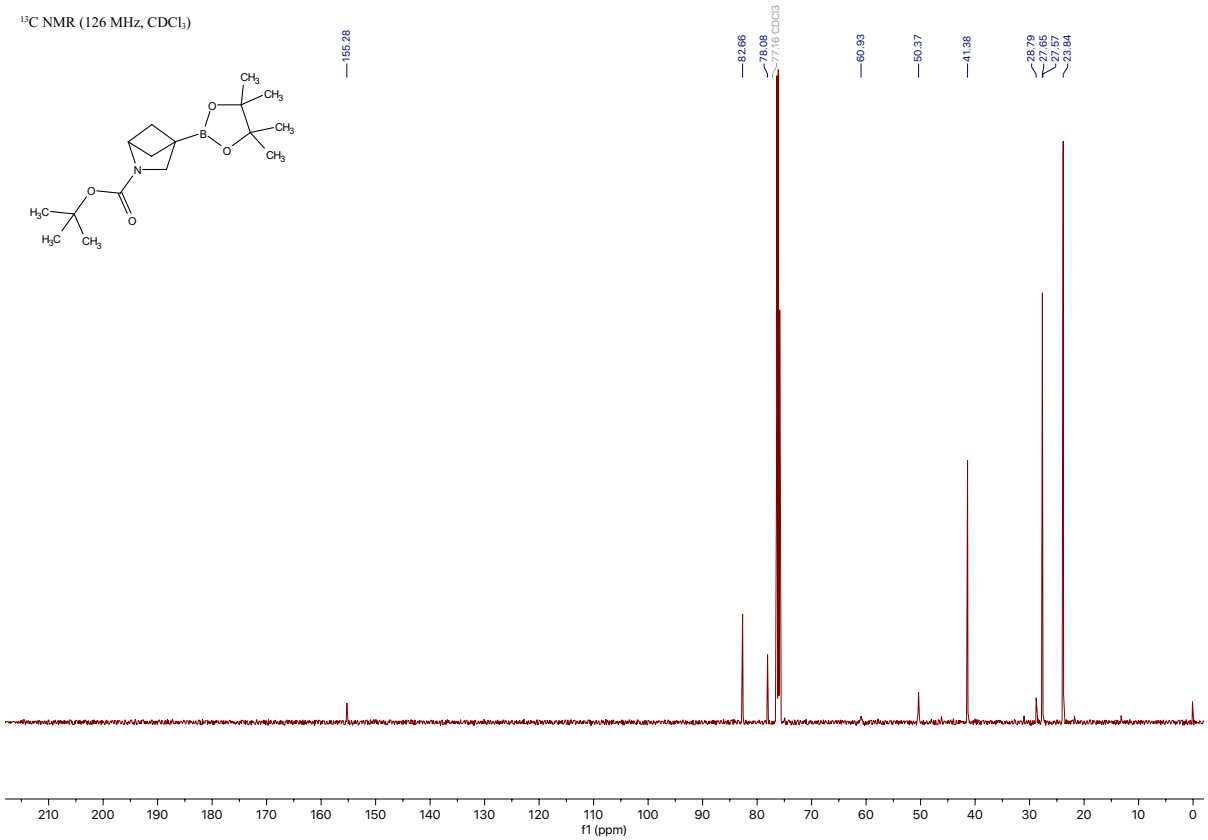
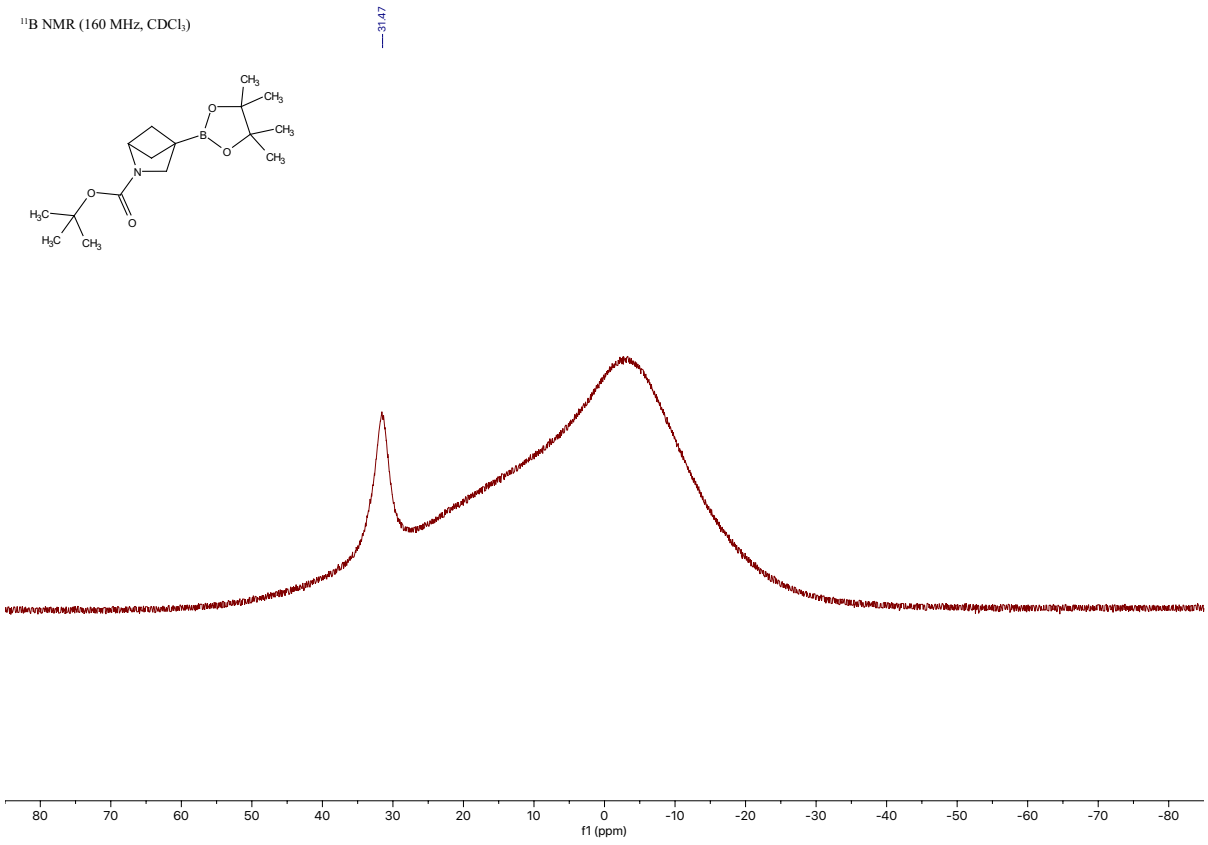
^{13}C NMR (126 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)



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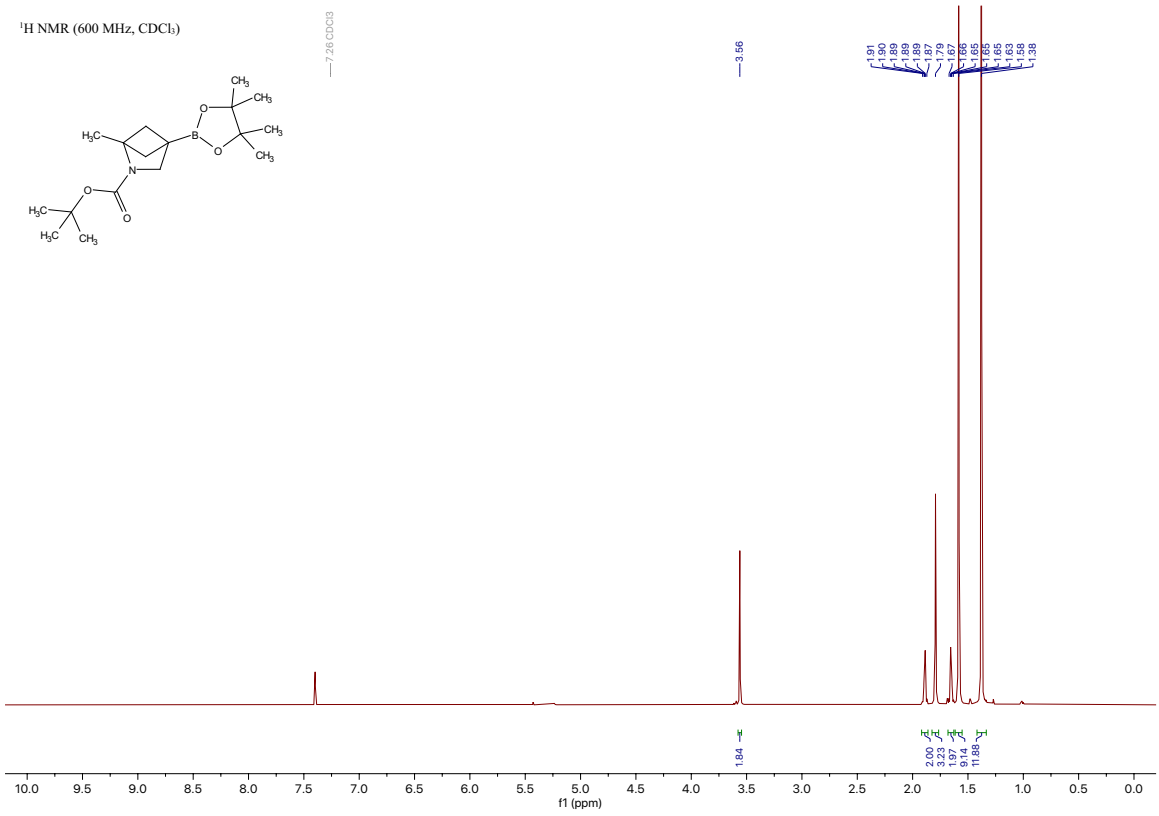
Compound 28a

***tert*-butyl 1-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azabicyclo[2.1.1]hexane-2-carboxylate**

[Experimental]



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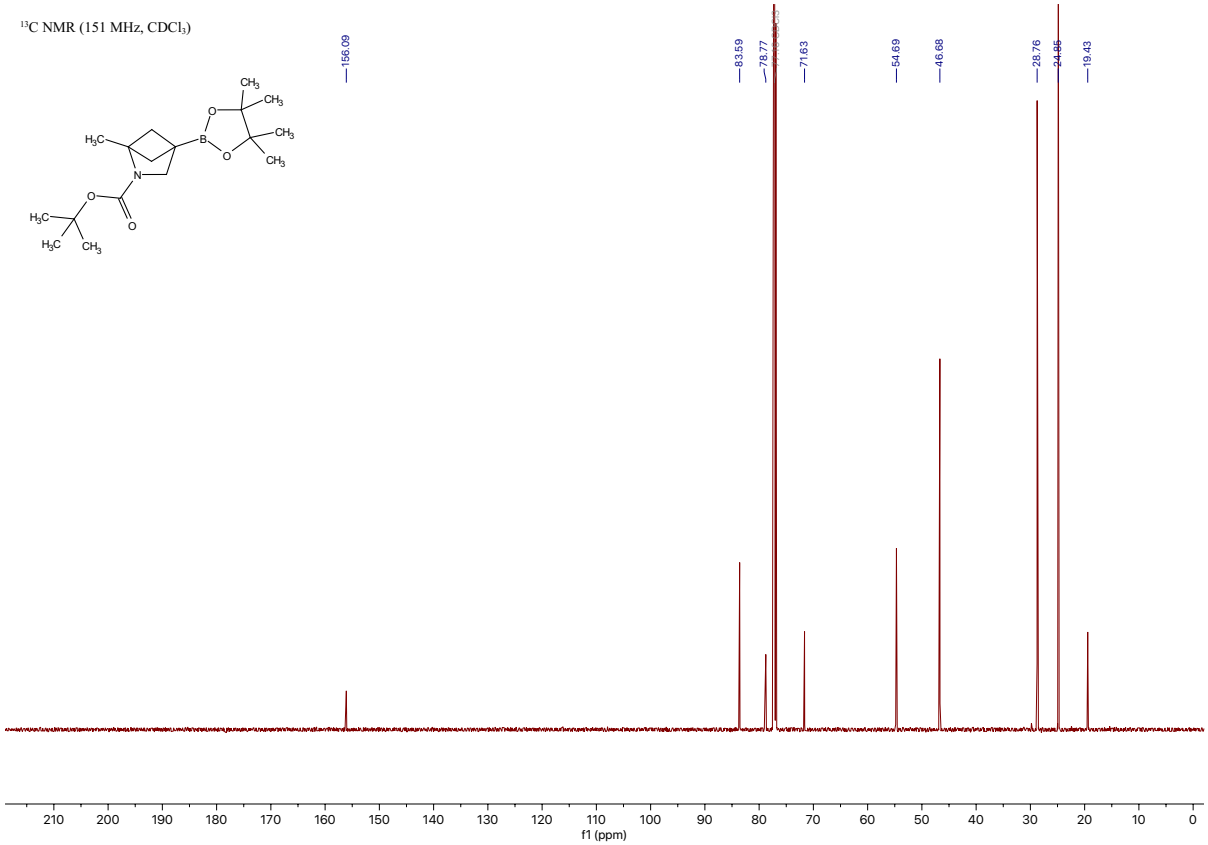
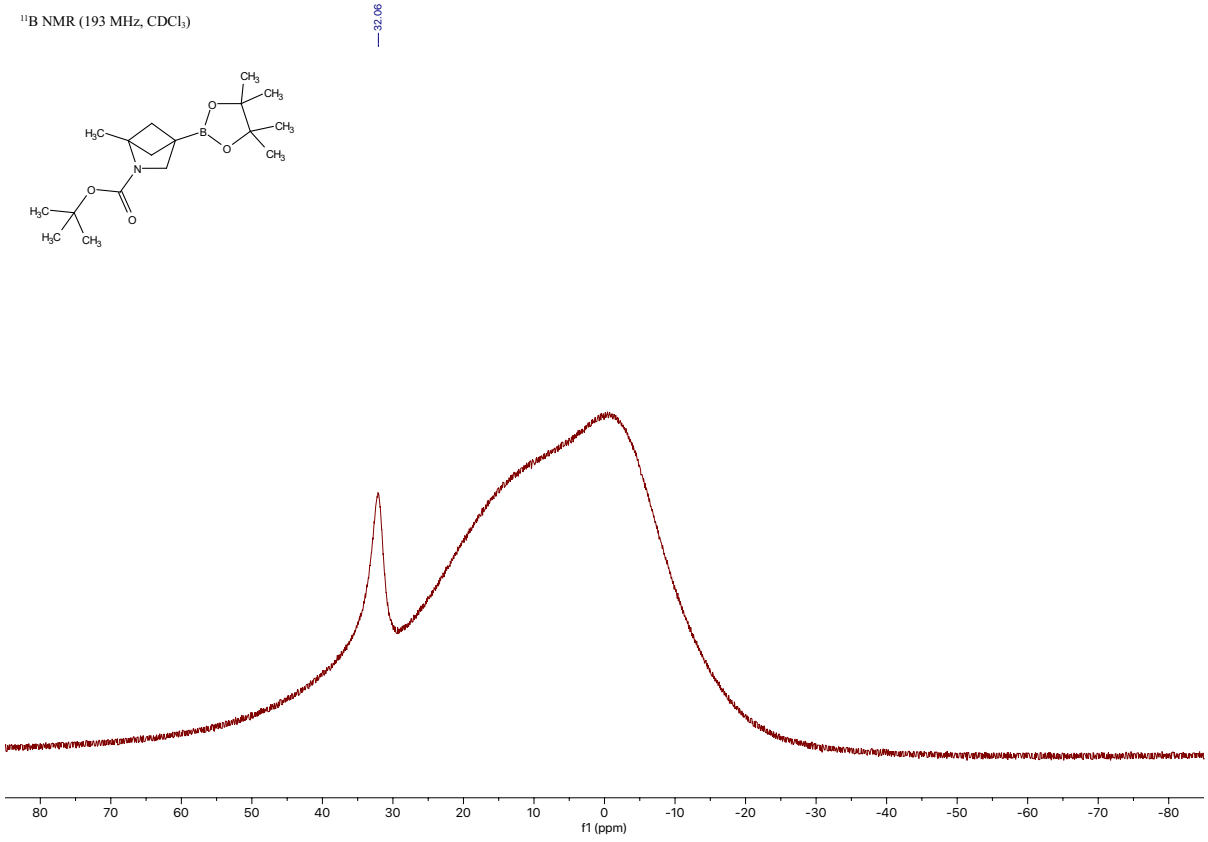
^{13}C NMR (151 MHz, $CDCl_3$)



^{11}B NMR (193 MHz, $CDCl_3$)



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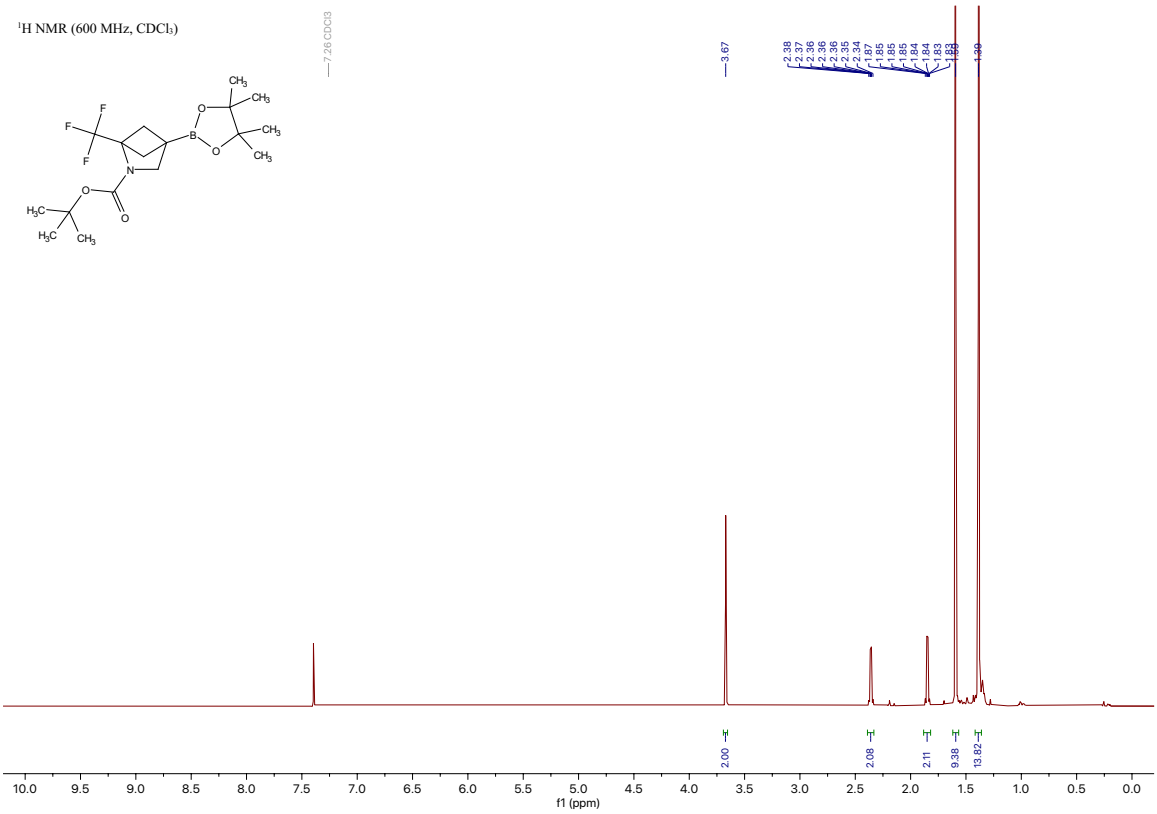
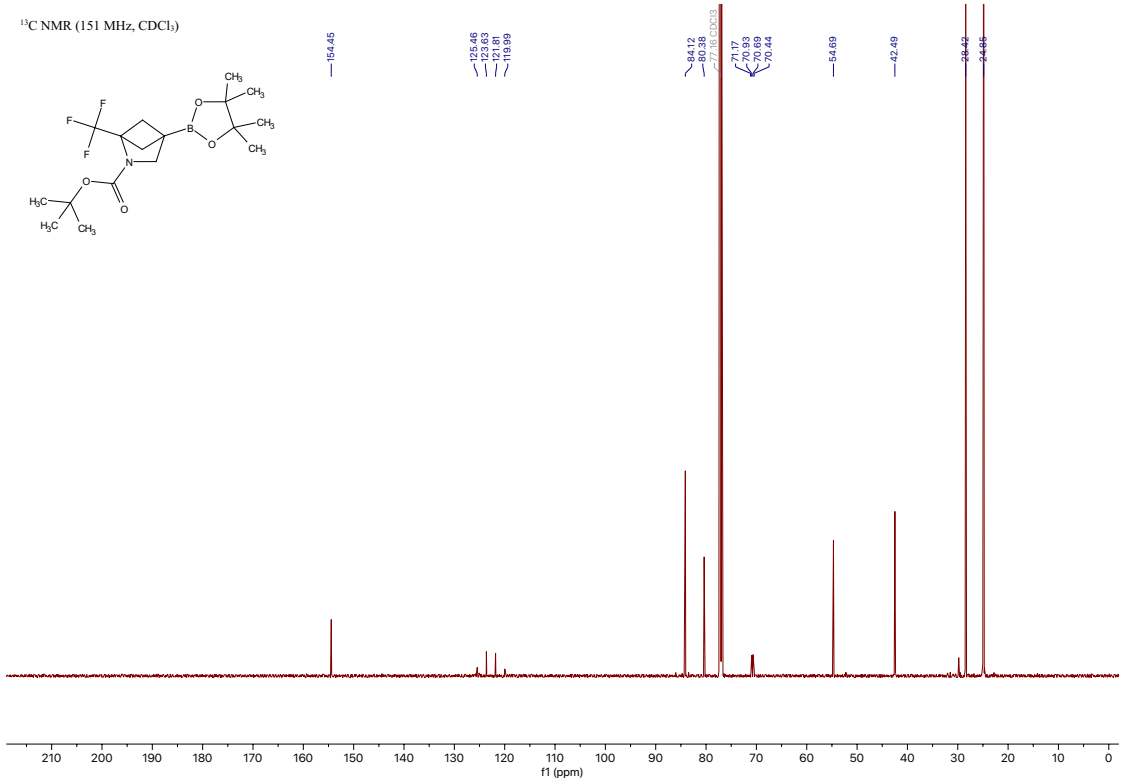
Compound 29a

***tert*-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(trifluoromethyl)-2-azabicyclo[2.1.1]hexane-2-carboxylate** [Experimental]

^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)



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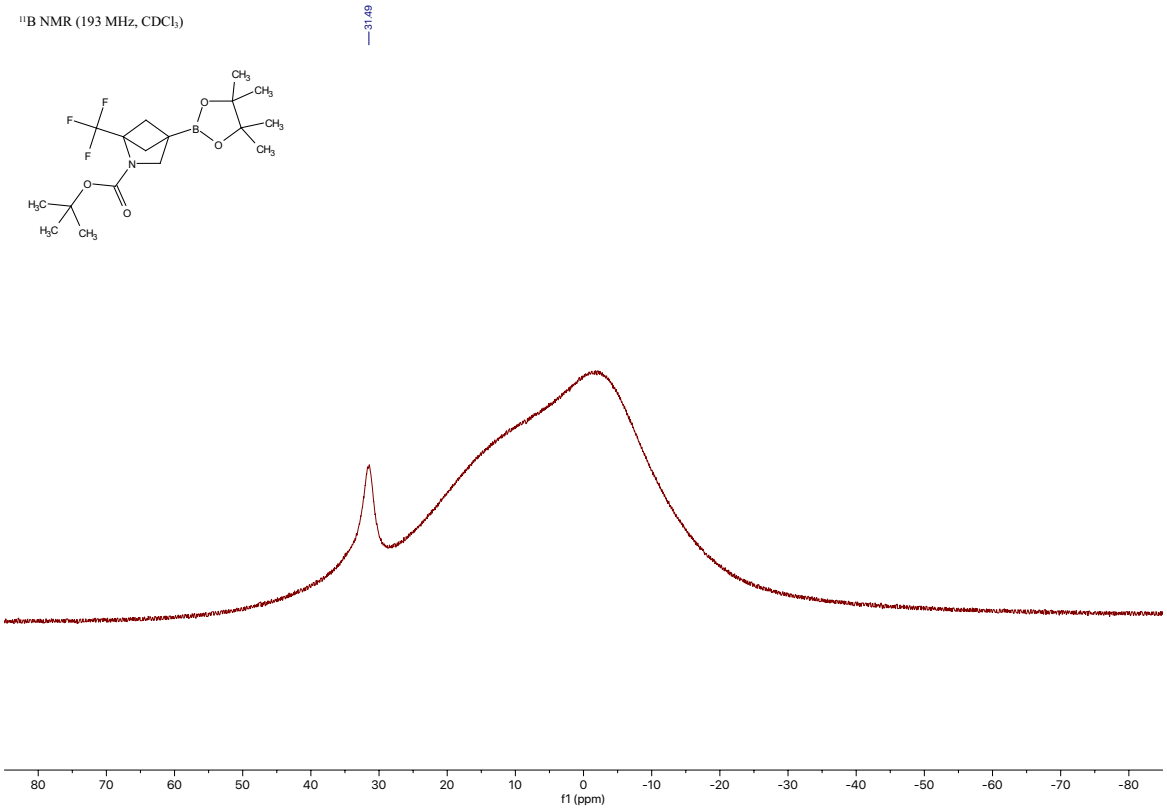
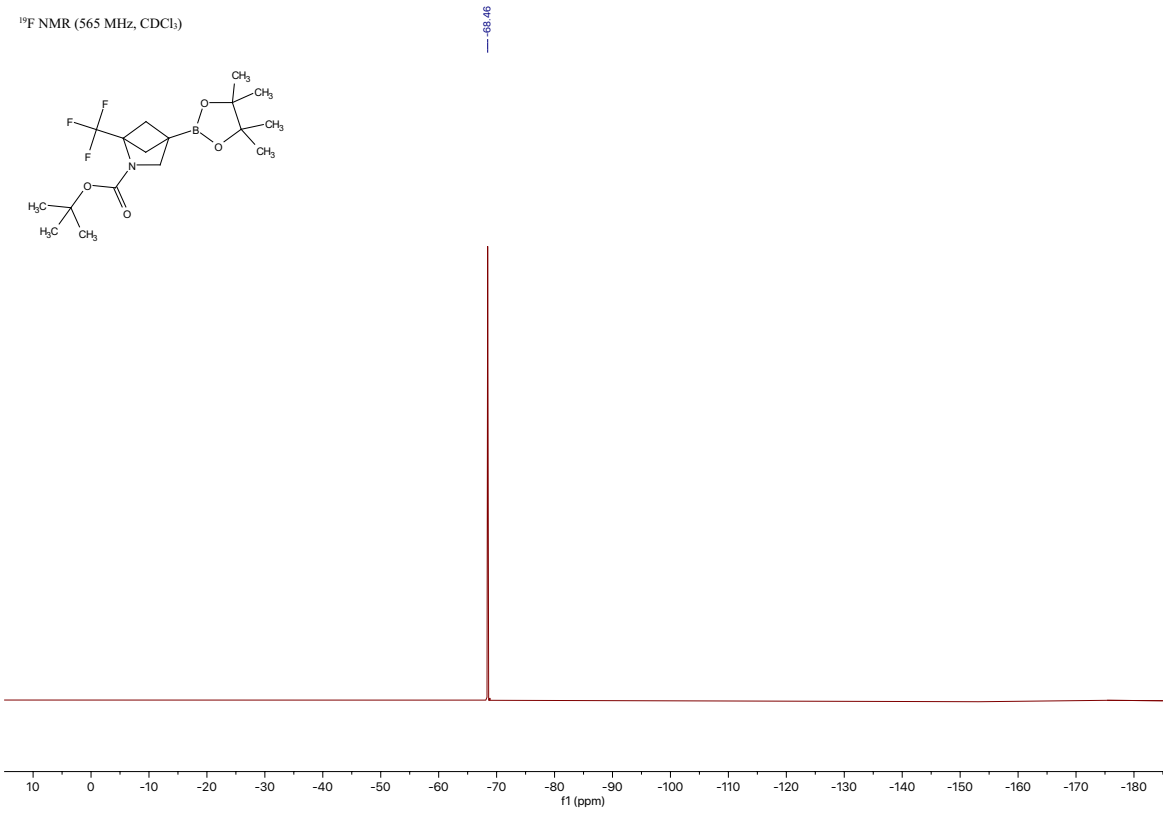
^{11}B NMR (193 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$)



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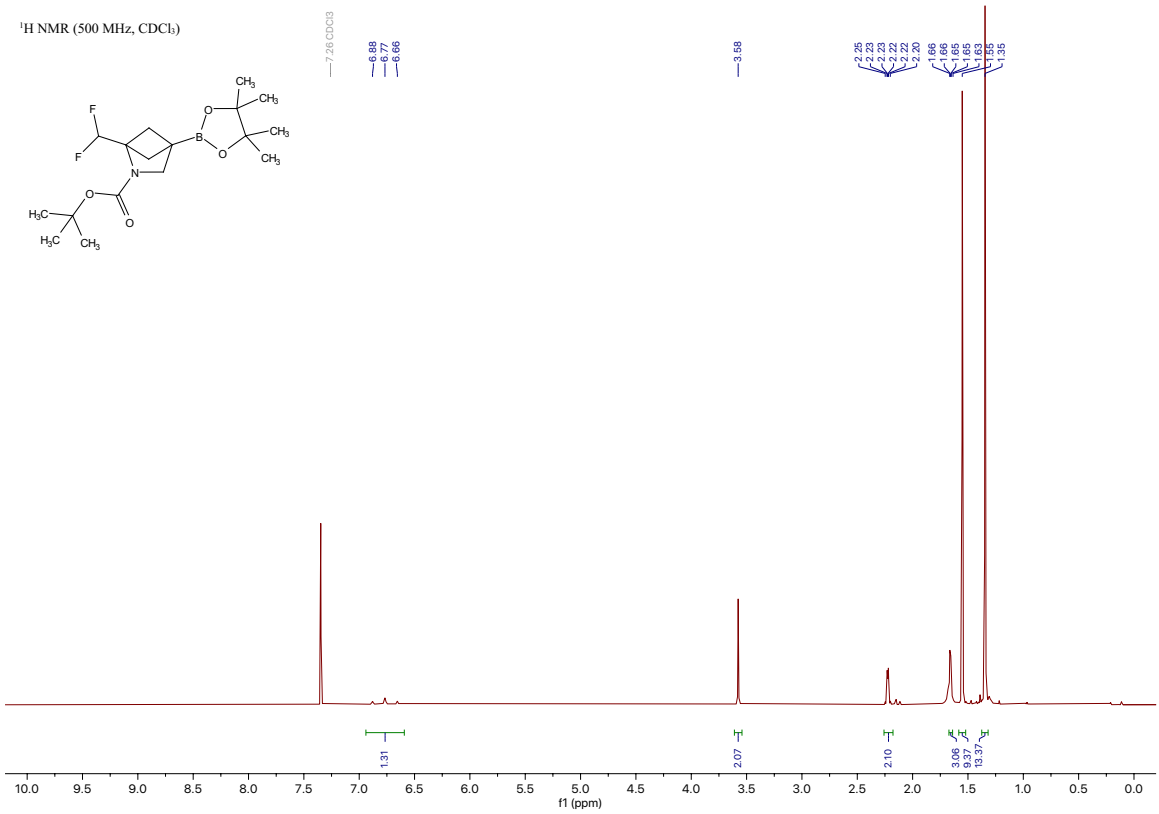
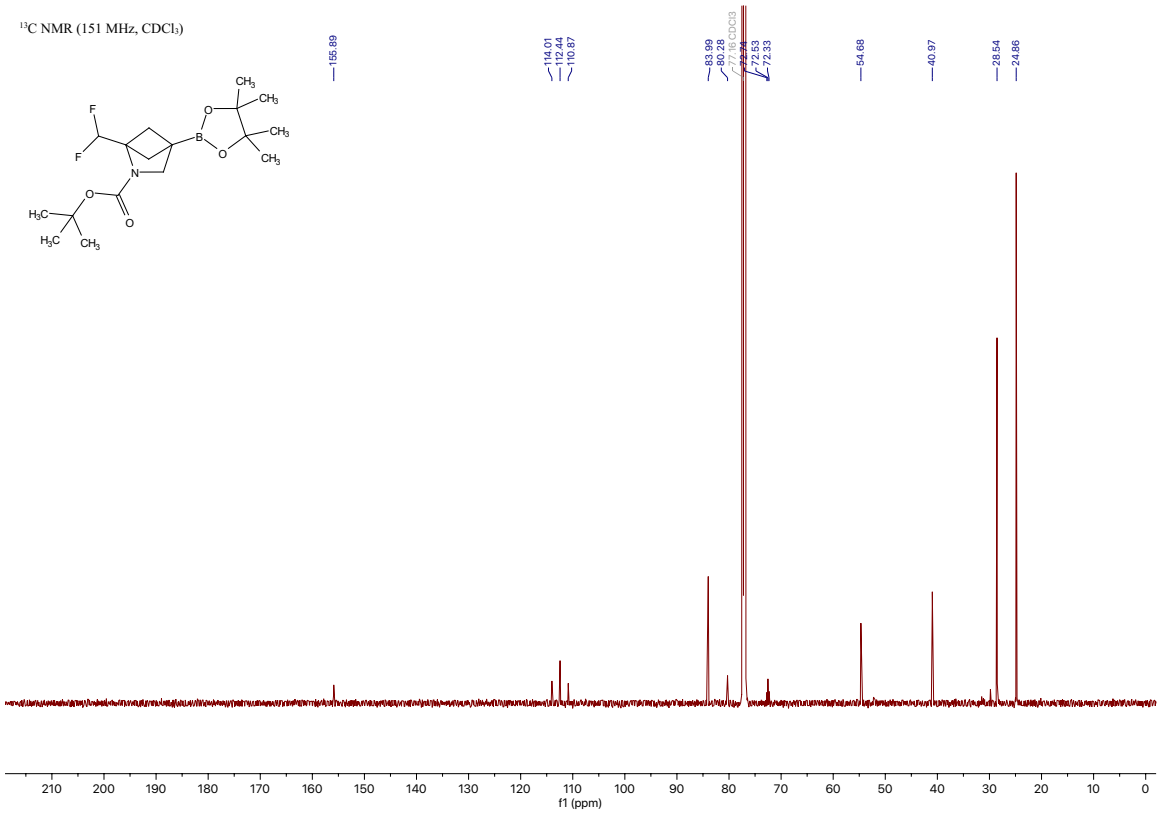
Compound 30a

***tert*-butyl 1-(difluoromethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azabicyclo[2.1.1]hexane-2-carboxylate** [Experimental]





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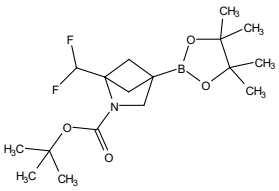
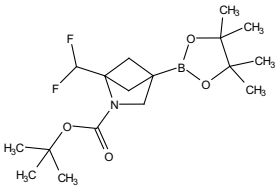
^{11}B NMR (193 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$)



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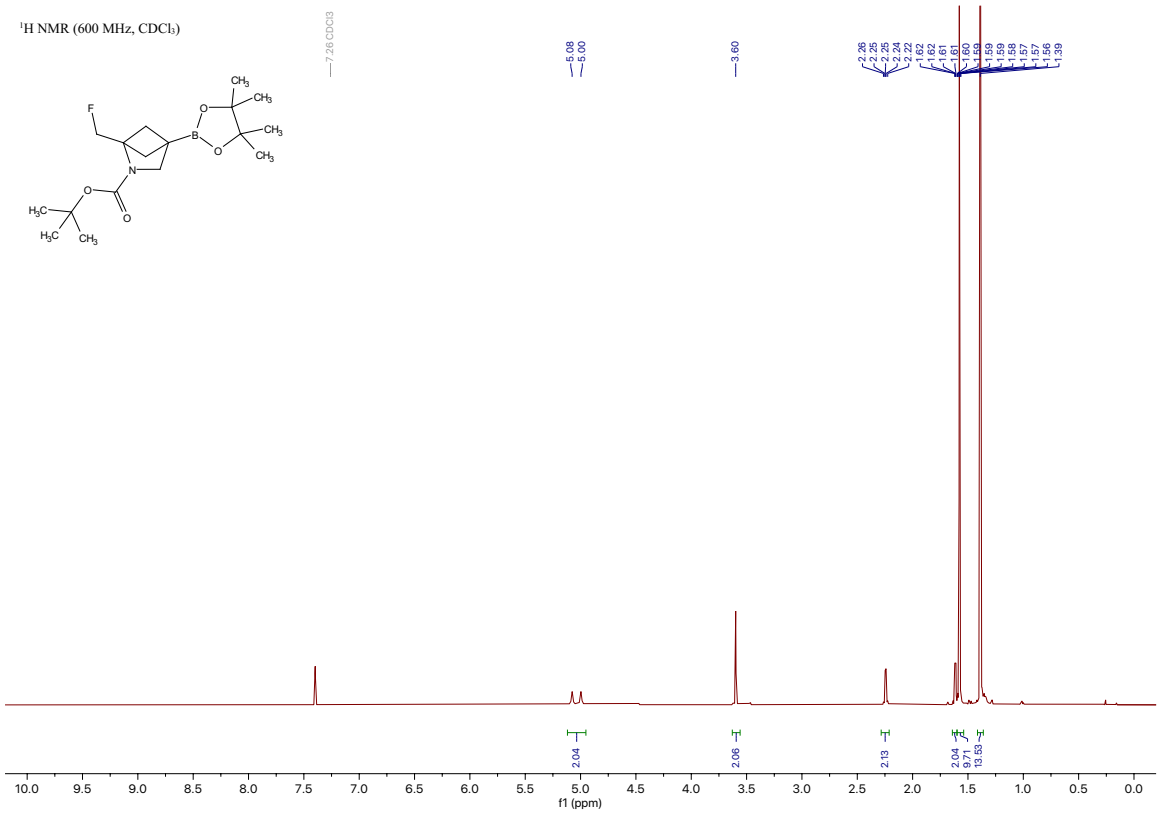
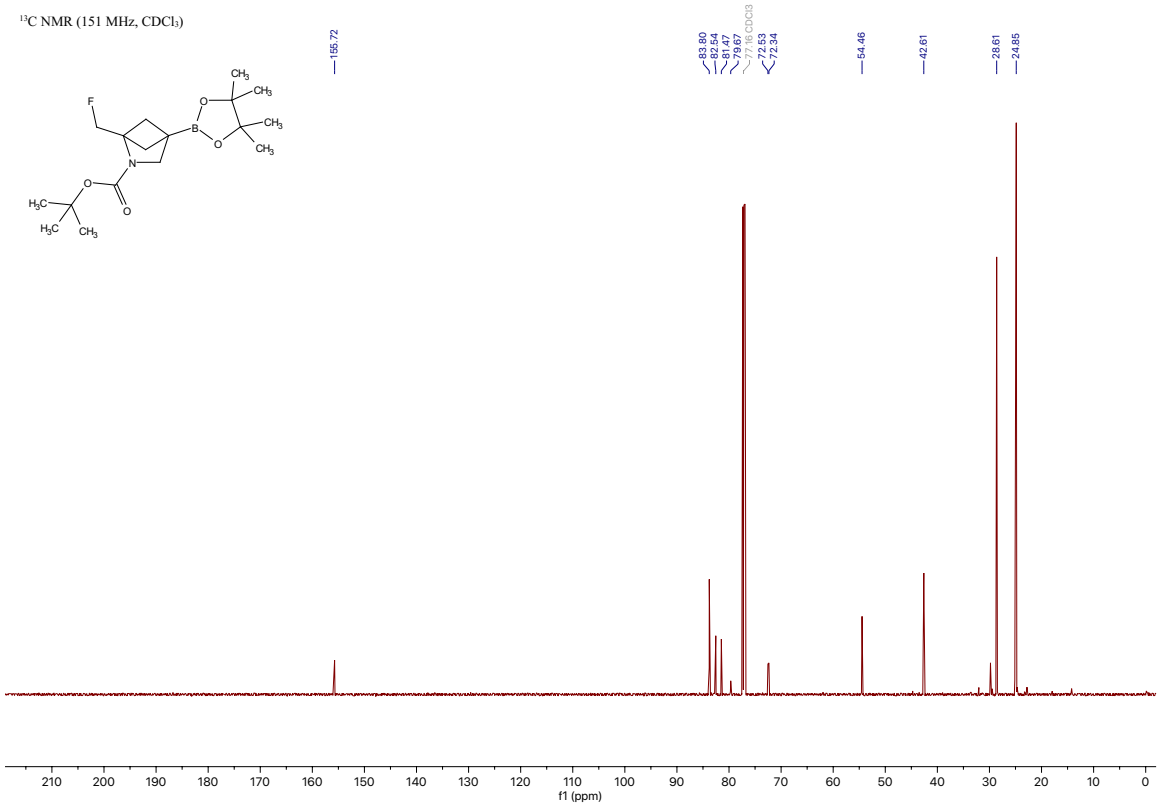
Compound 31a

***tert*-butyl 1-(fluoromethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azabicyclo[2.1.1]hexane-2-carboxylate** [Experimental]





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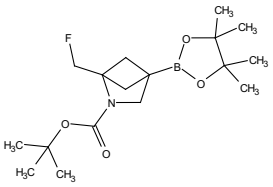
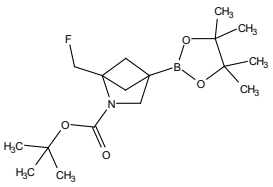
^{11}B NMR (193 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$)



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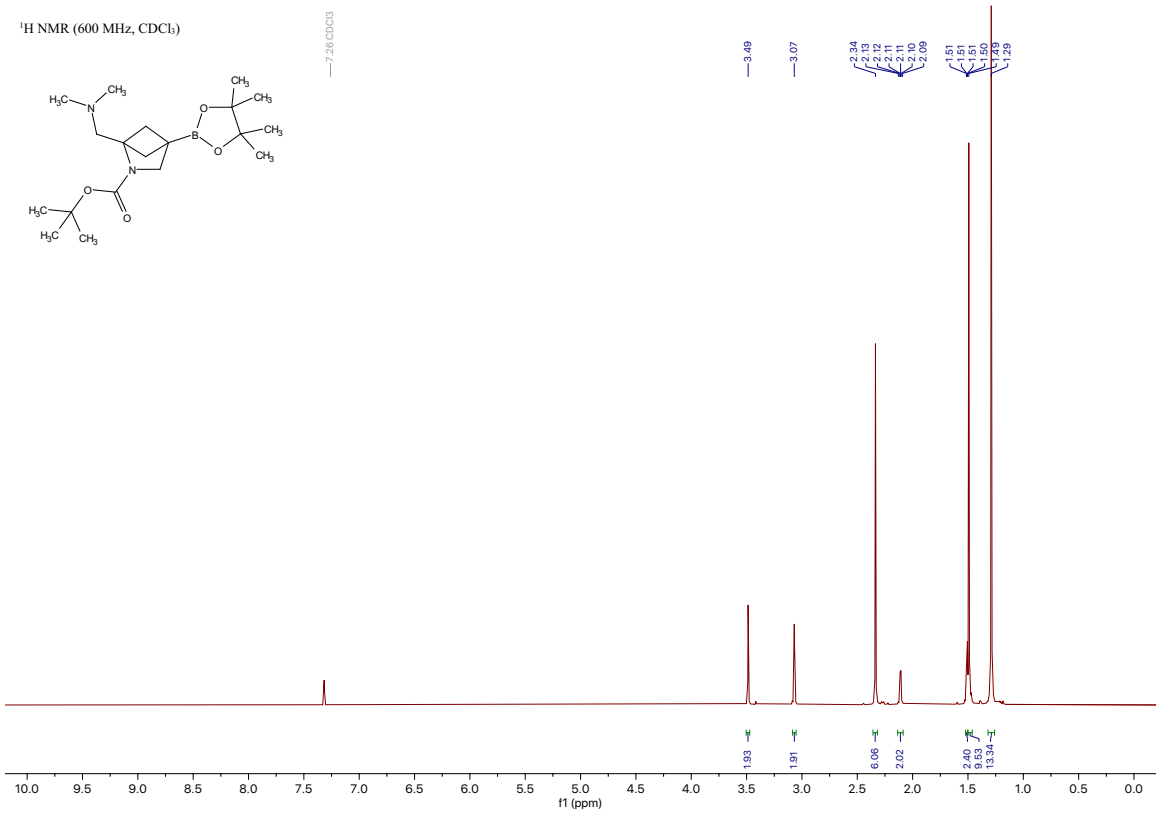
Compound 32a

***tert*-butyl 1-((dimethylamino)methyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azabicyclo[2.1.1]hexane-2-carboxylate** [Experimental]



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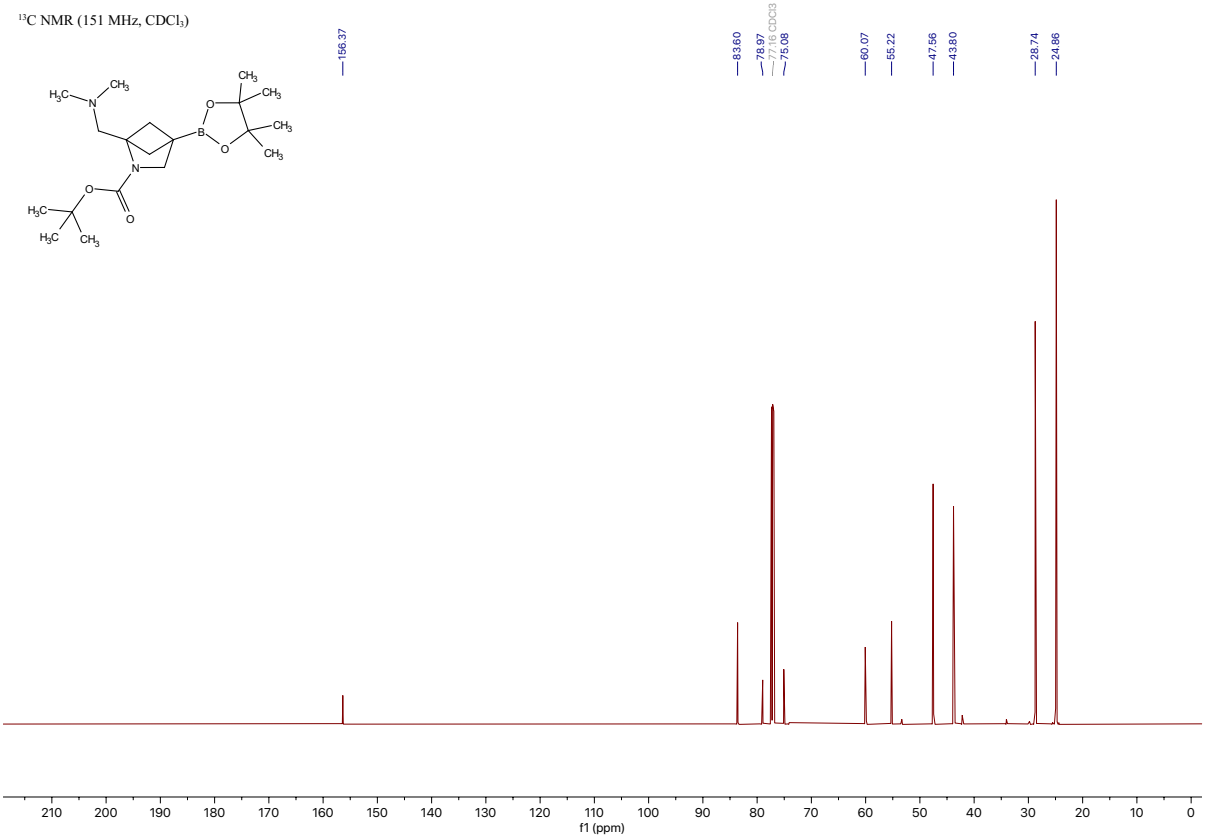
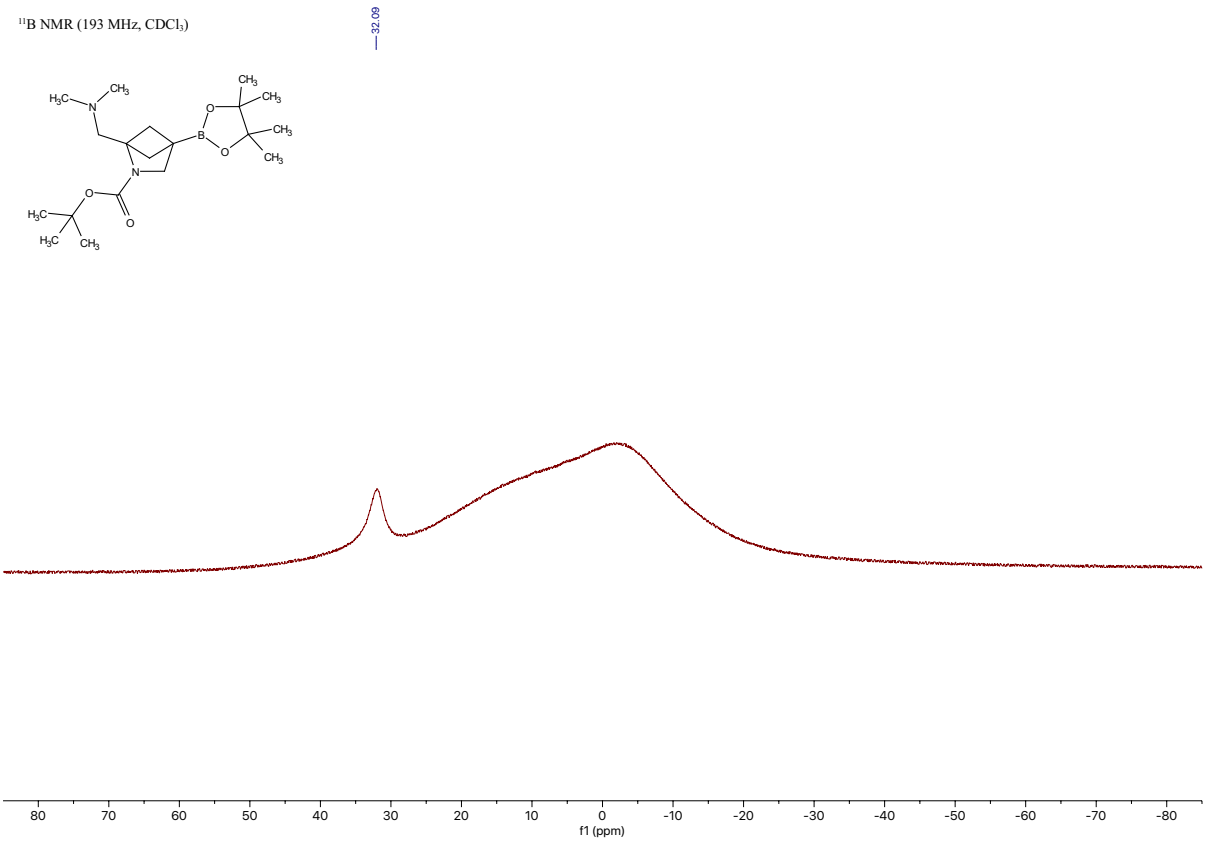
^{13}C NMR (151 MHz, $CDCl_3$)



^{11}B NMR (193 MHz, $CDCl_3$)



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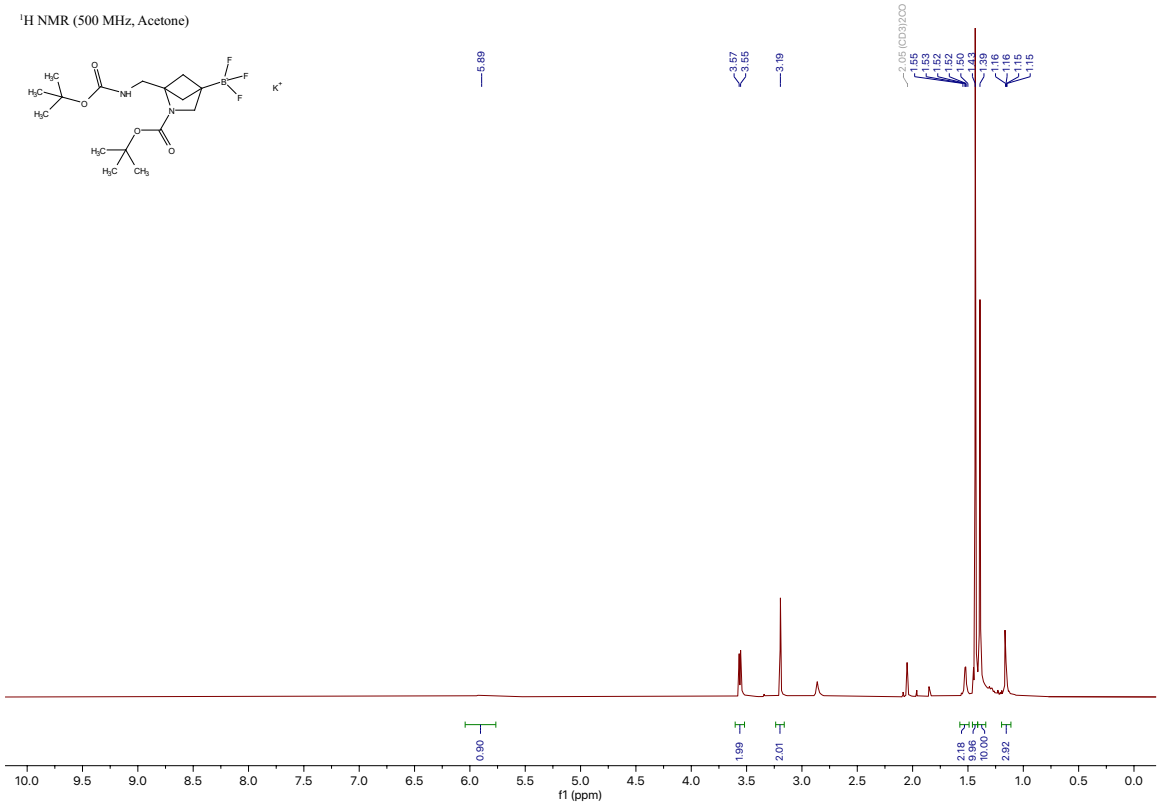
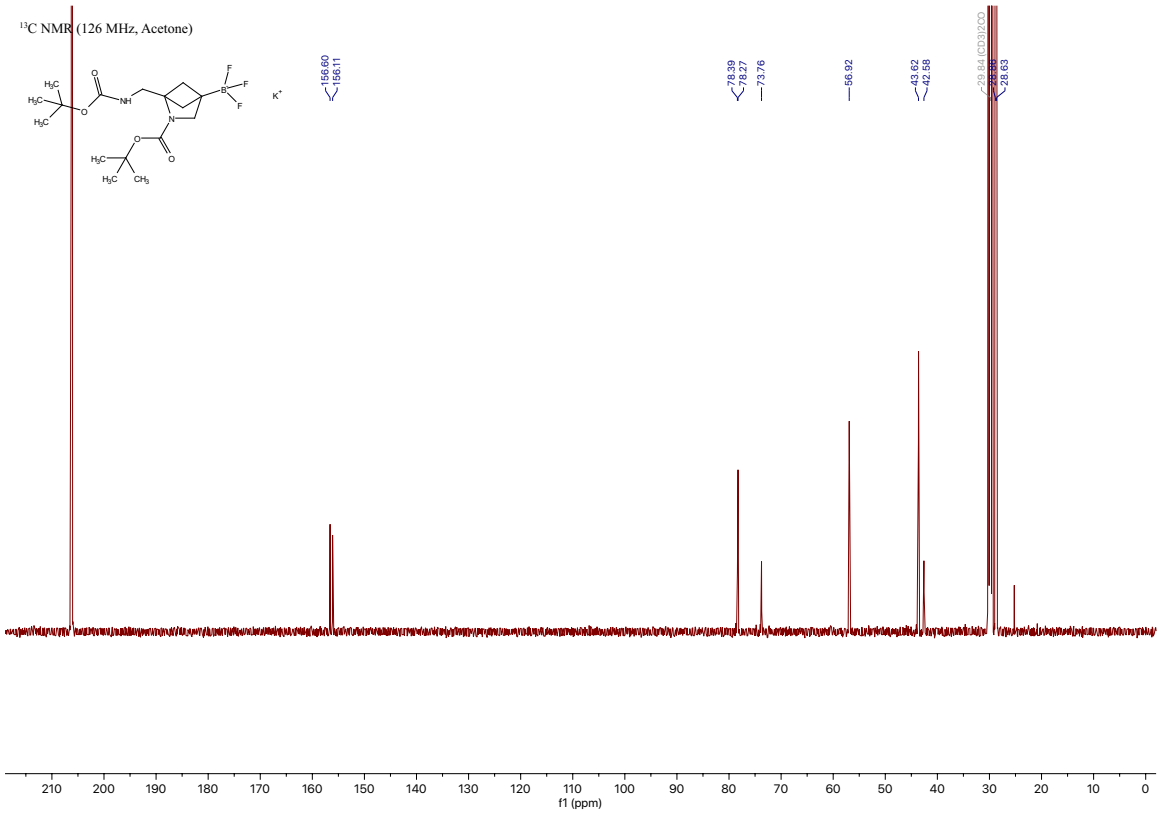
Compound 33a

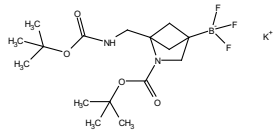
***tert*-butyl 1-(((*tert*-butoxycarbonyl)amino)methyl)-4-(trifluoro-λ4-boraneyl)-2-azabicyclo[2.1.1]hexane-2-carboxylate, potassium salt** [Experimental]



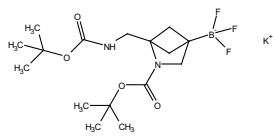


[*Return to table of contents*]

^{11}B NMR (160 MHz, Acetone)



^{19}F NMR (470 MHz, Acetone)



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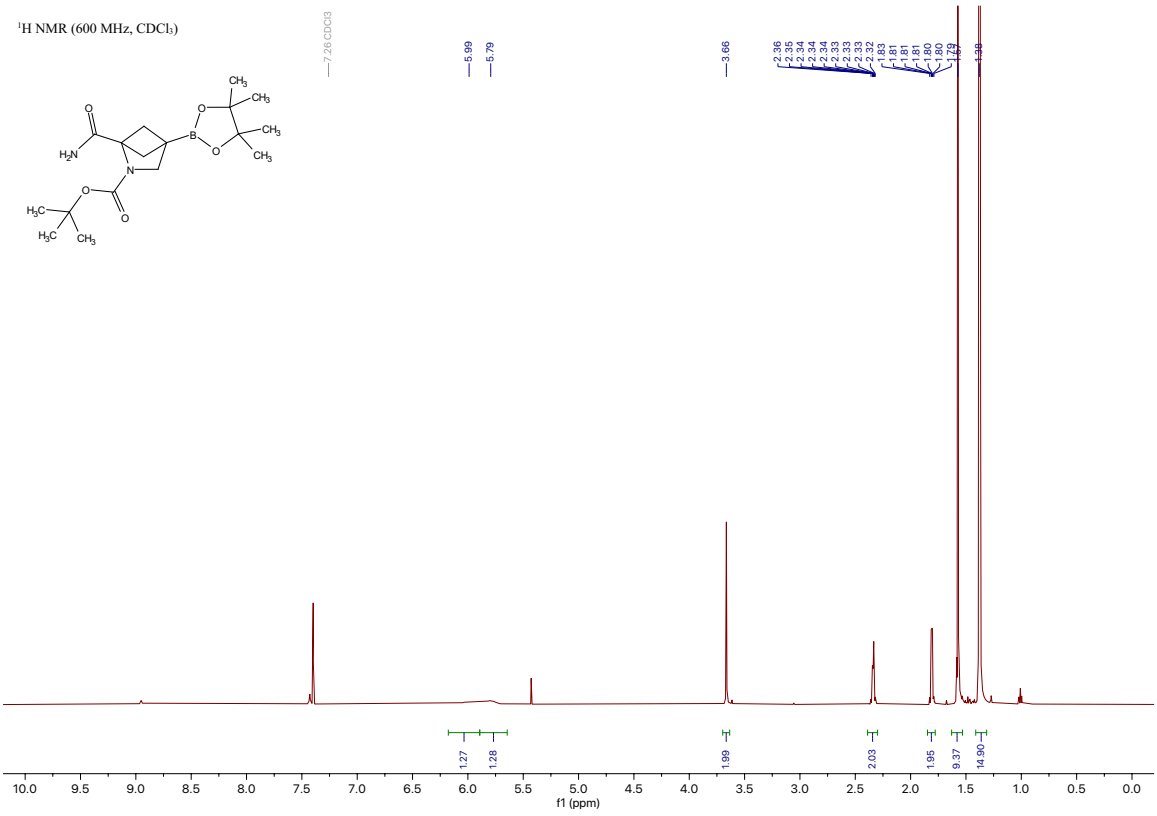
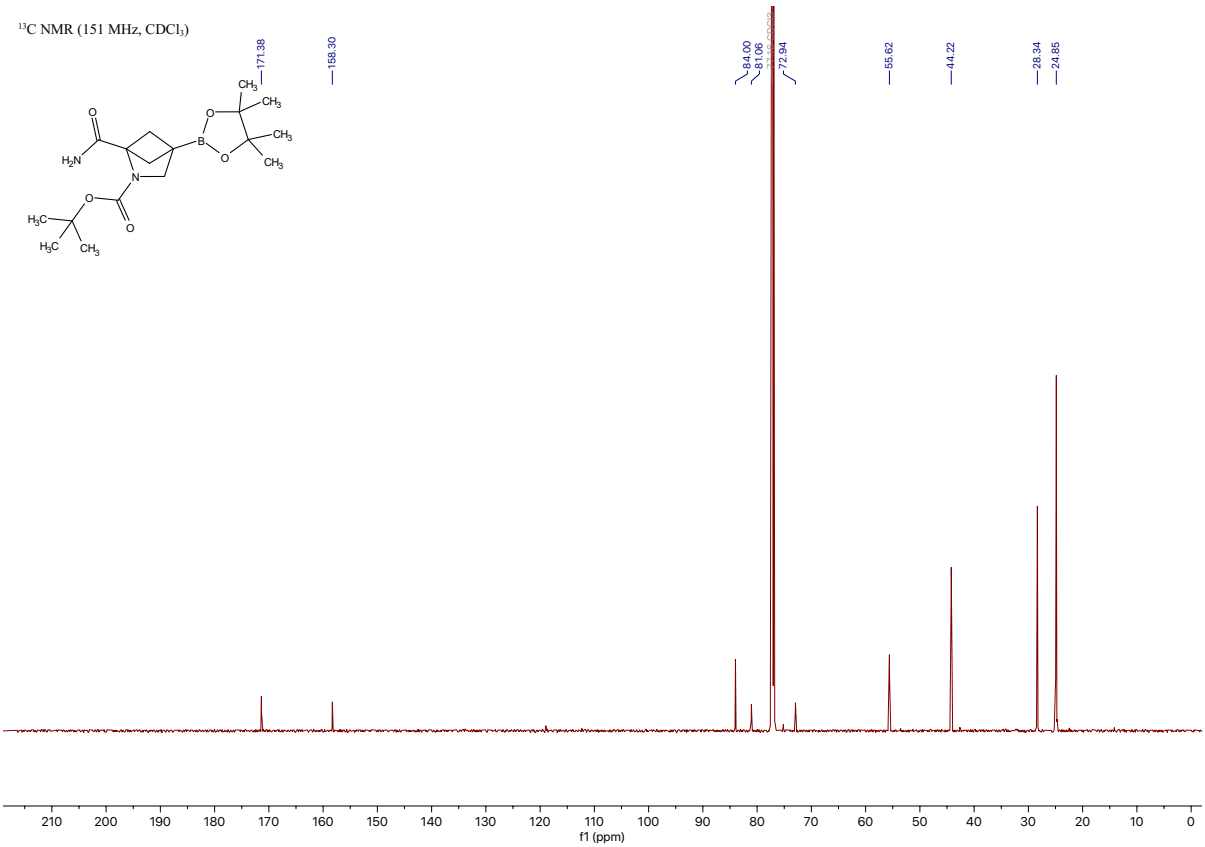
Compound 34a

***tert*-butyl 1-carbamoyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azabicyclo[2.1.1]hexane-2-carboxylate** [Experimental]

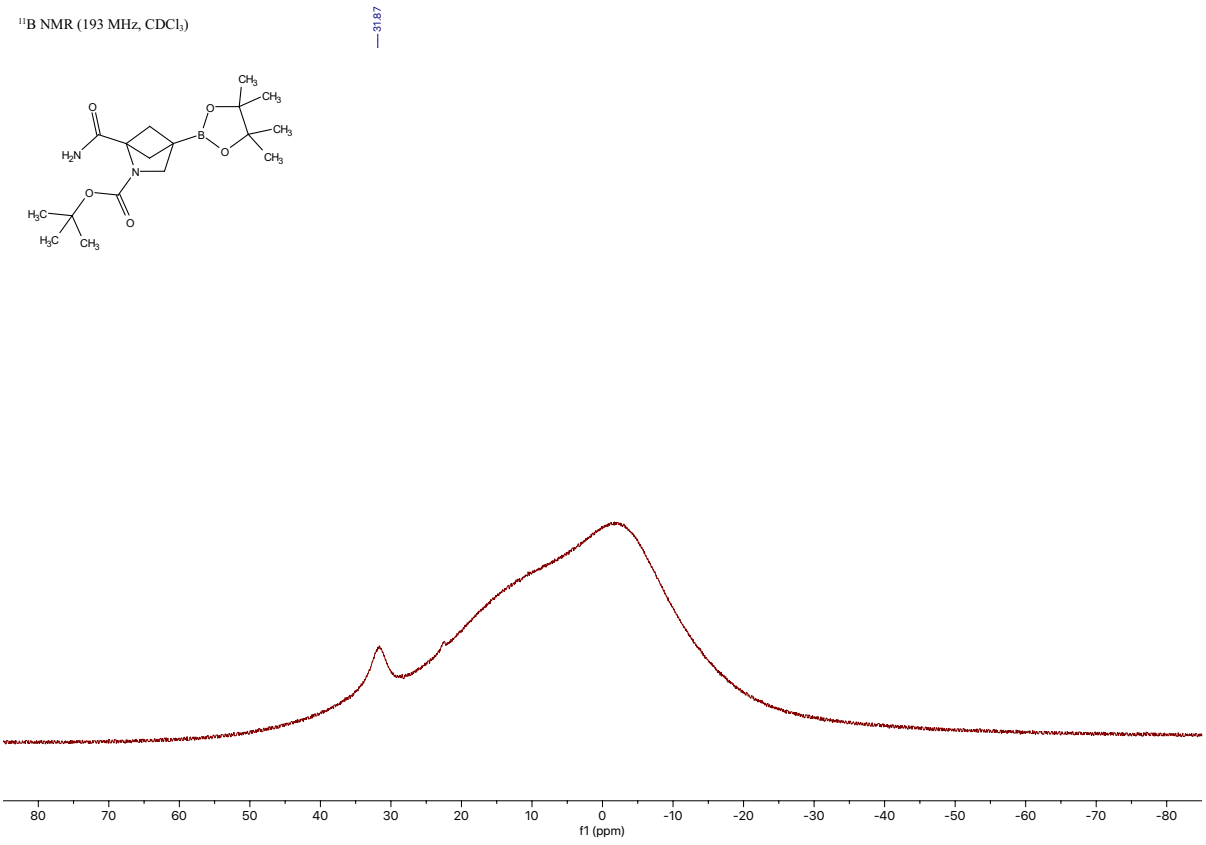


[*Return to table of contents*]

^{13}C NMR (151 MHz, $CDCl_3$)



^{11}B NMR (193 MHz, $CDCl_3$)



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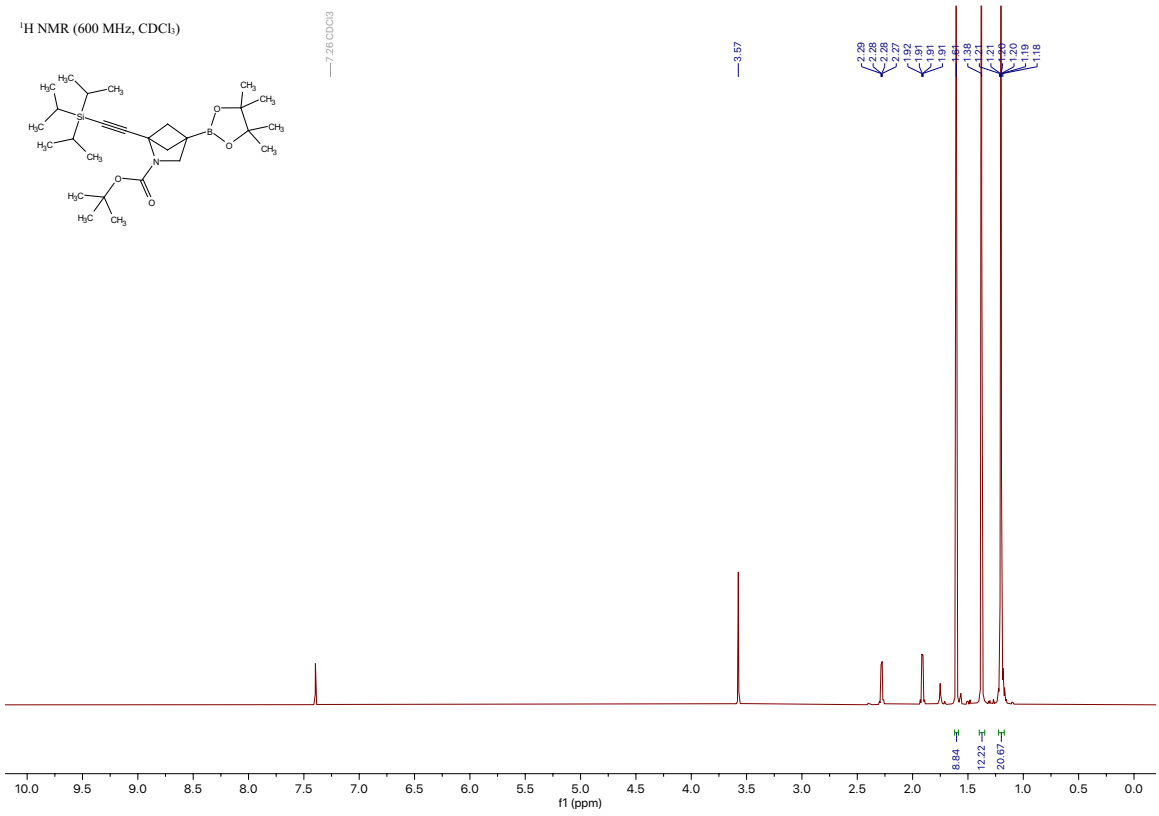
Compound 35a

***tert*-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-((triisopropylsilyl)ethynyl)-2-azabicyclo[2.1.1]hexane-2-carboxylate** [Experimental]



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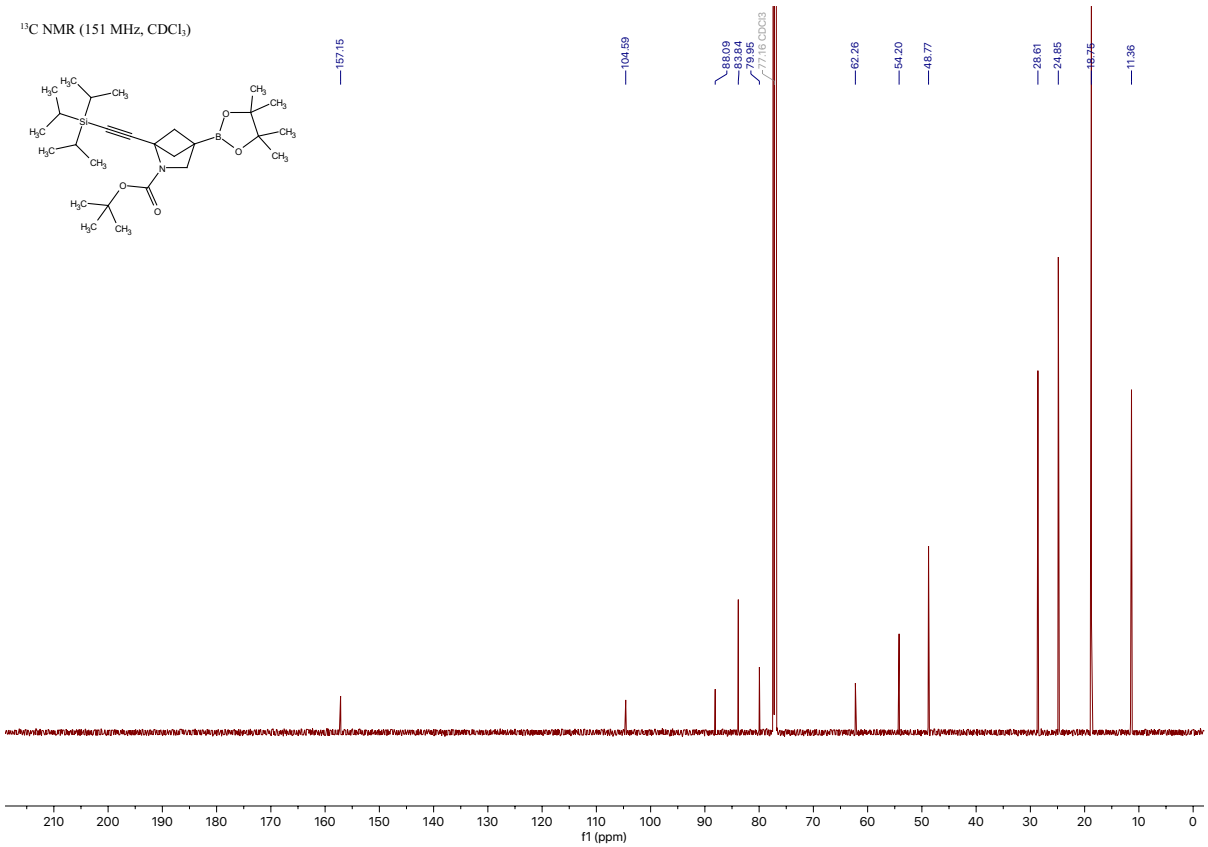
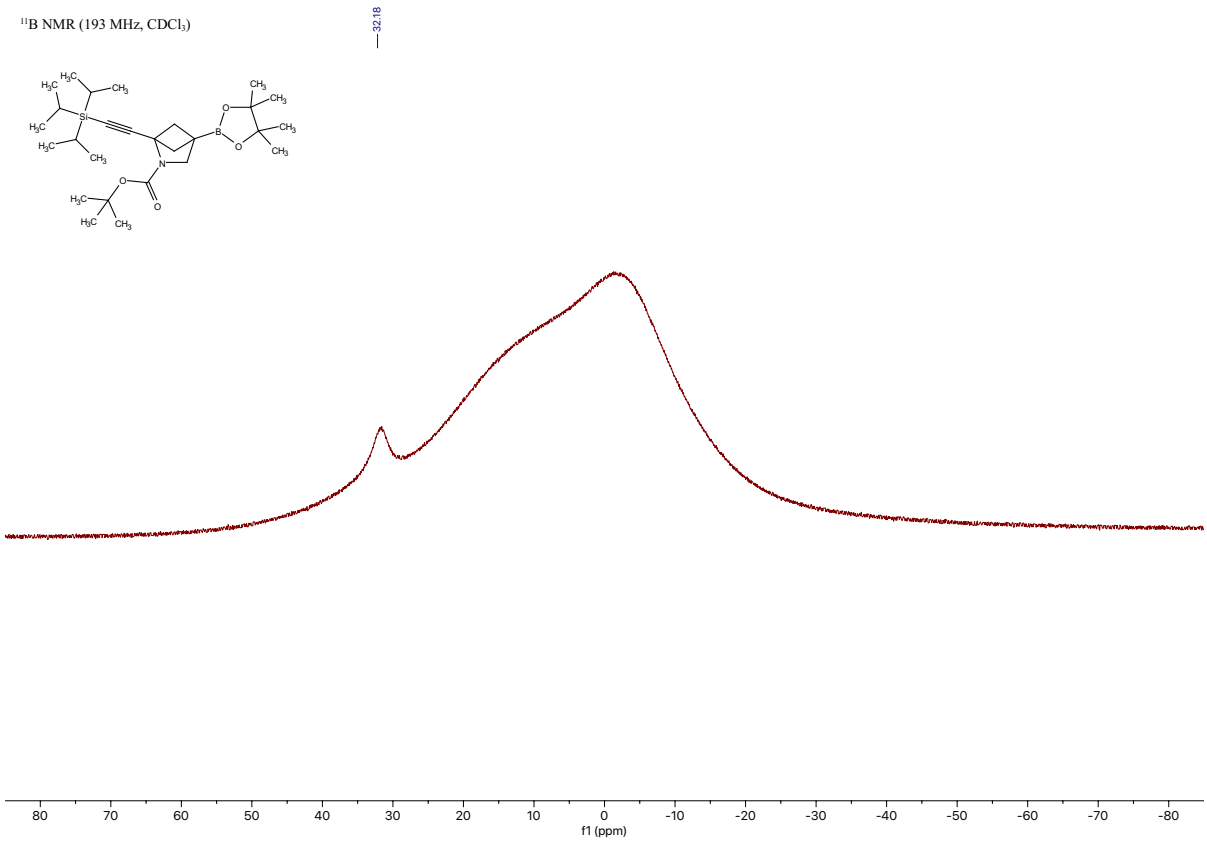
^{13}C NMR (151 MHz, $CDCl_3$)



^{11}B NMR (193 MHz, $CDCl_3$)



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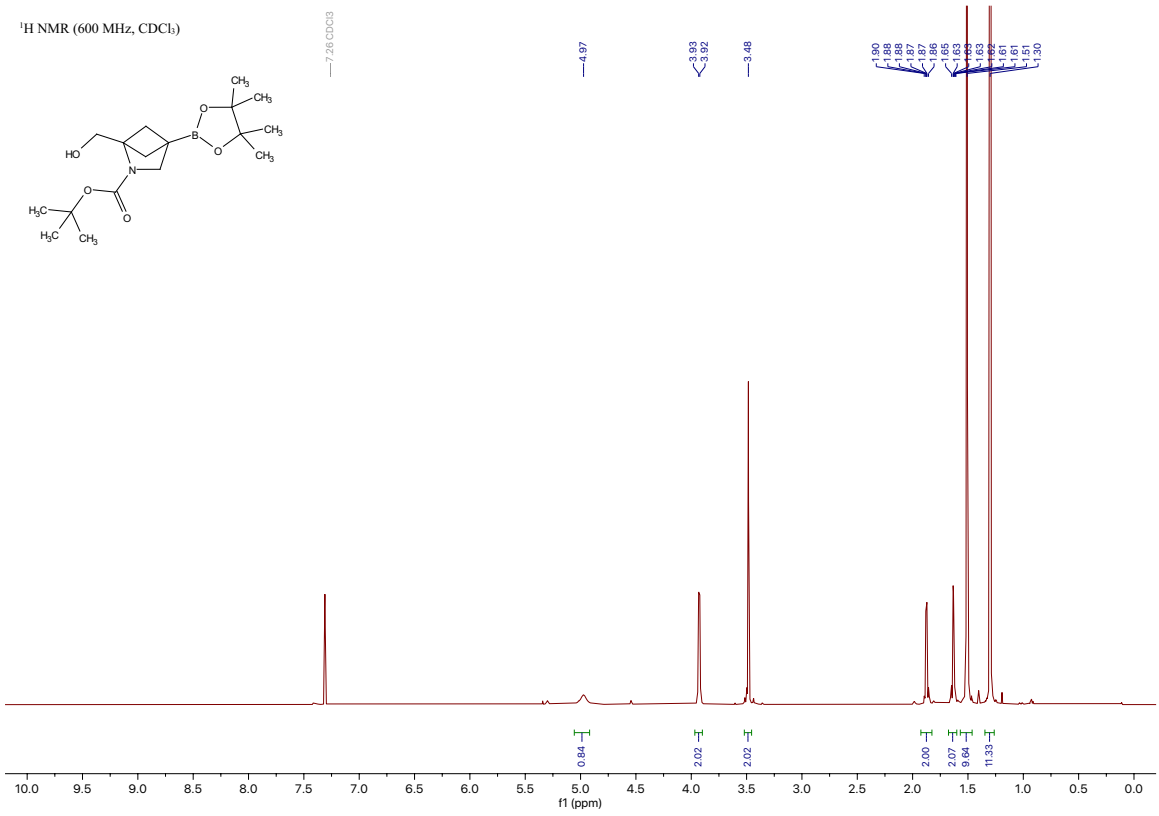
Compound 36a

***tert*-butyl 1-(hydroxymethyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azabicyclo[2.1.1]hexane-2-carboxylate** [Experimental]



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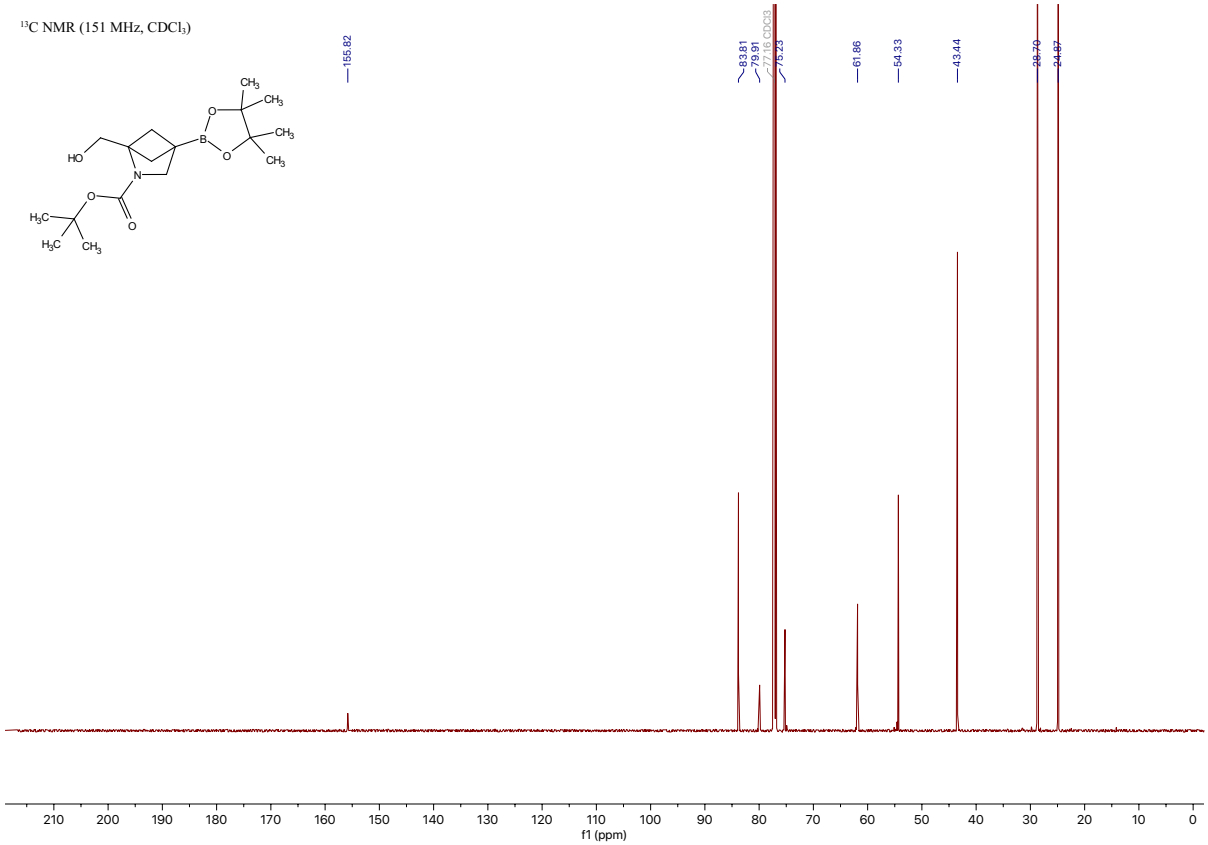
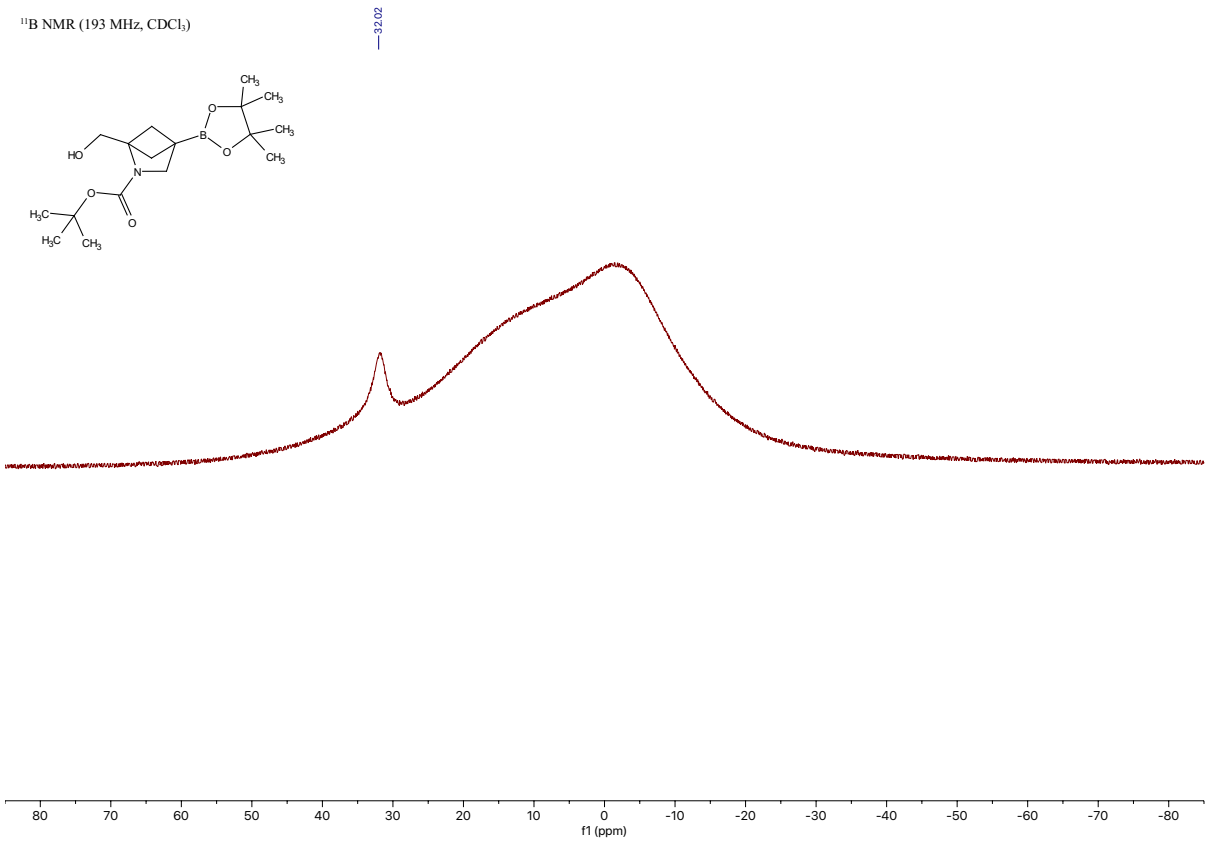
^{13}C NMR (151 MHz, $CDCl_3$)



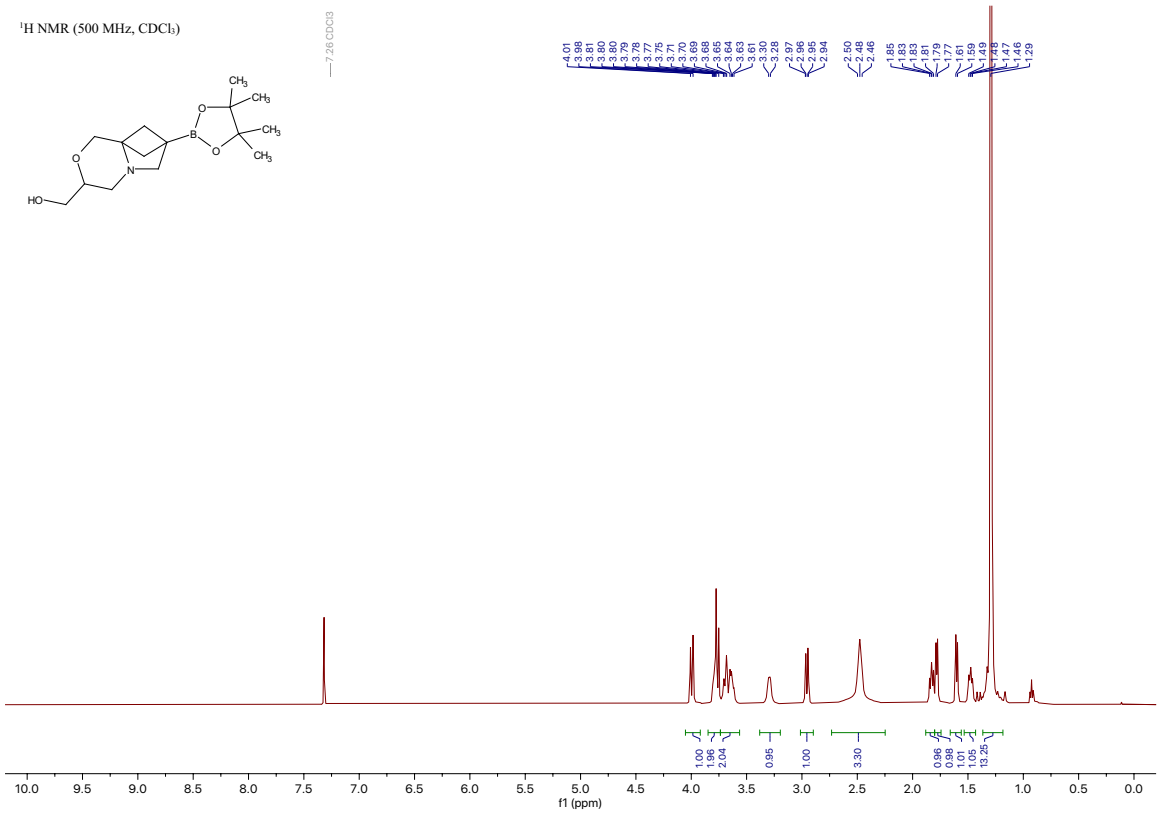
^{11}B NMR (193 MHz, $CDCl_3$)



[*Return to table of contents*]

Compound 37a

(7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)tetrahydro-1*H*,6*H*-7,8a-methanopyrrolo[2,1-*c*][1,4]oxazin-3-yl)methanol [Experimental]



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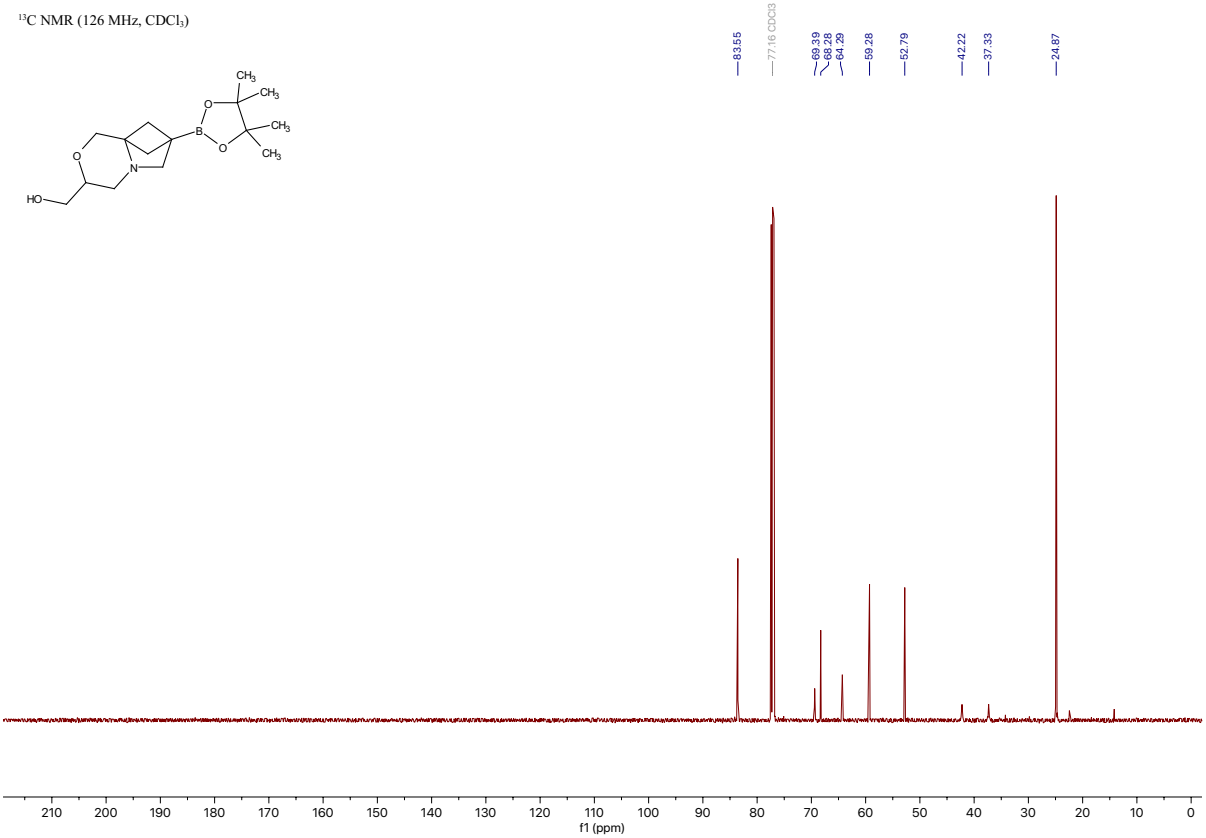
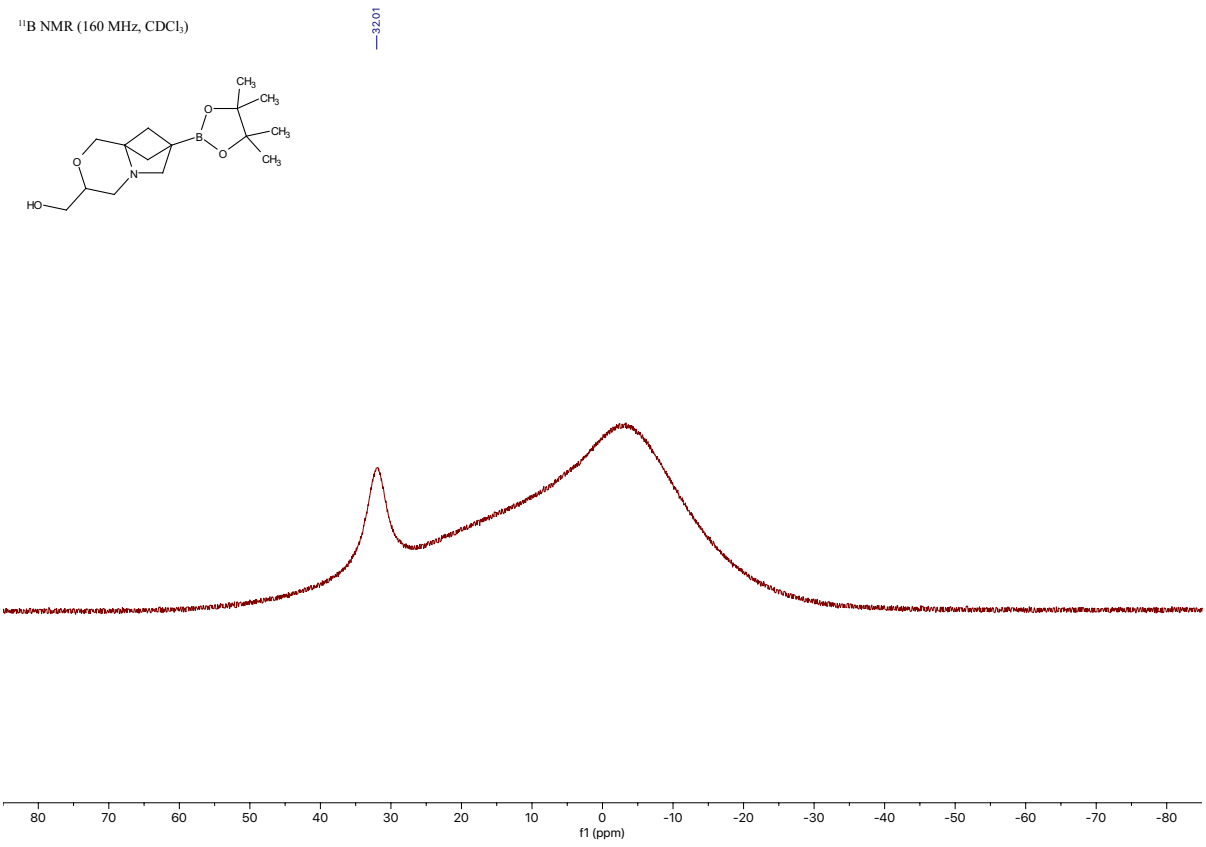
^{13}C NMR (126 MHz, $CDCl_3$)



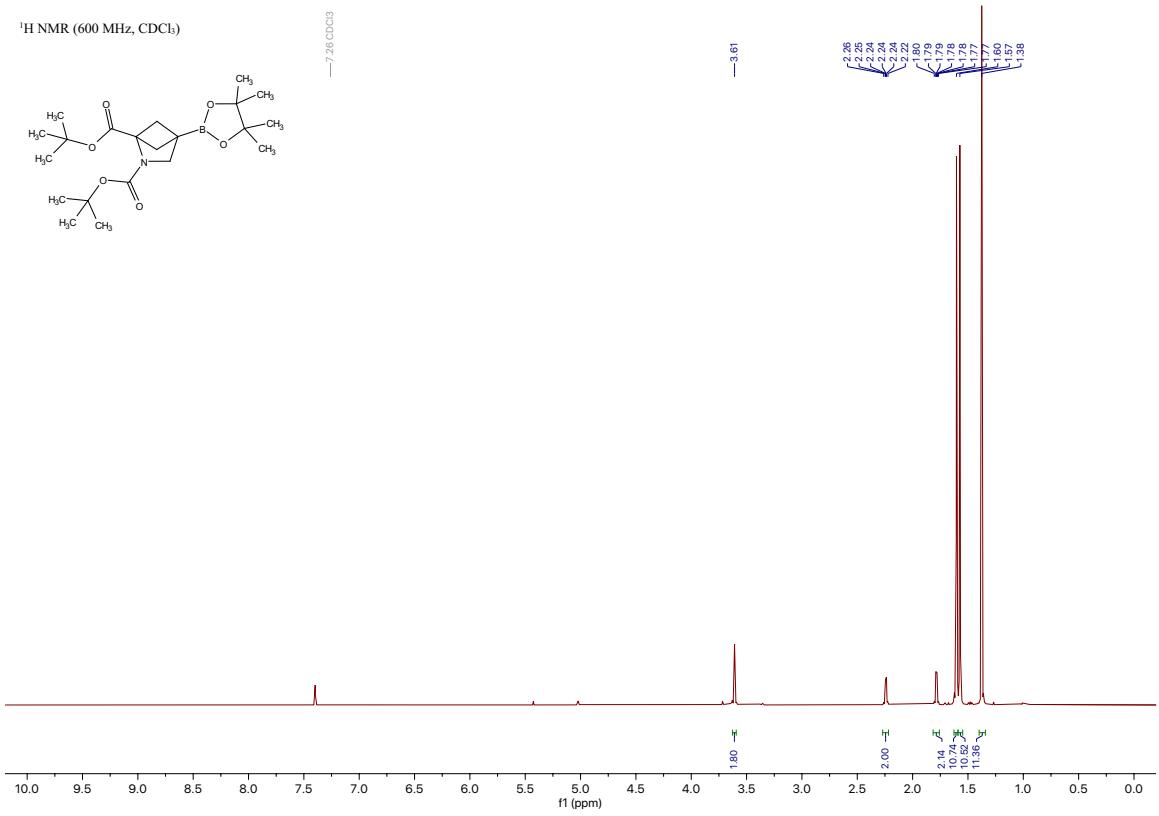
^{11}B NMR (160 MHz, $CDCl_3$)



[*Return to table of contents*]

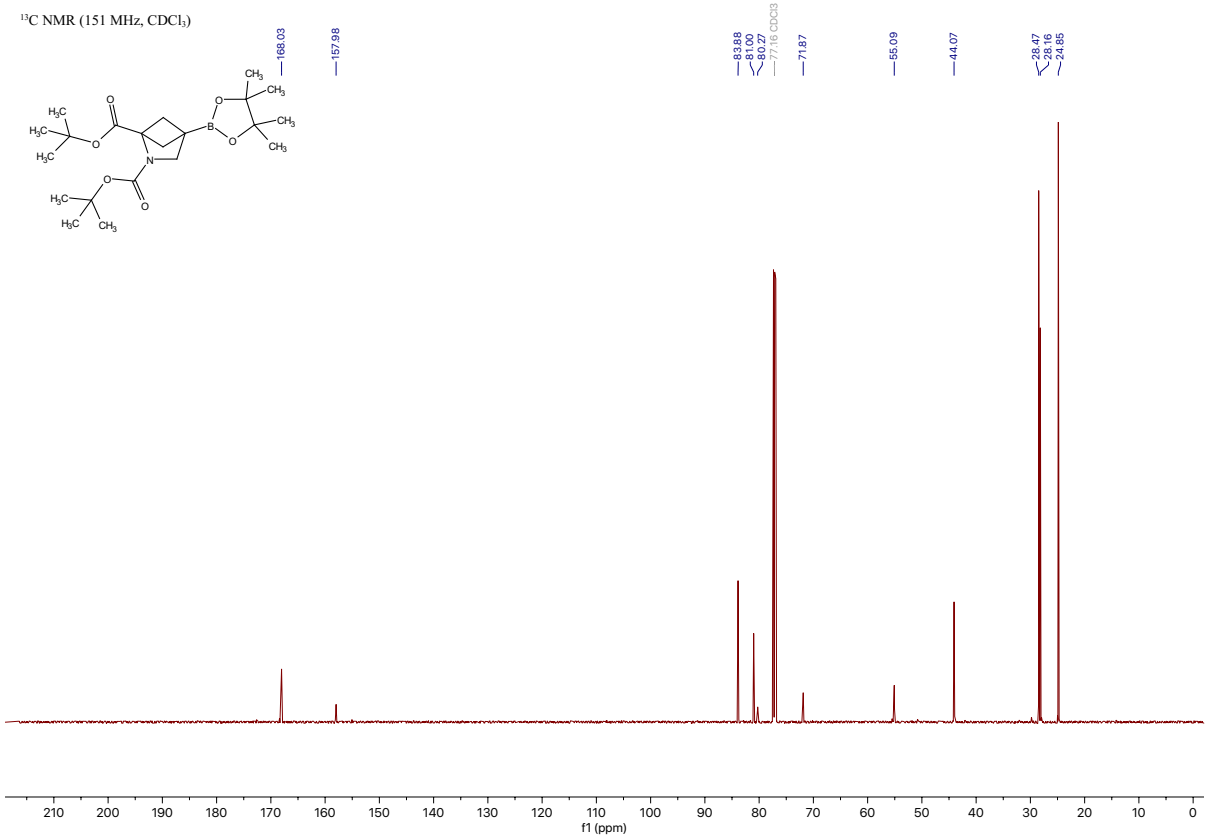
Compound 38a

di-*tert*-butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-azabicyclo[2.1.1]hexane-1,2-dicarboxylate [Experimental]

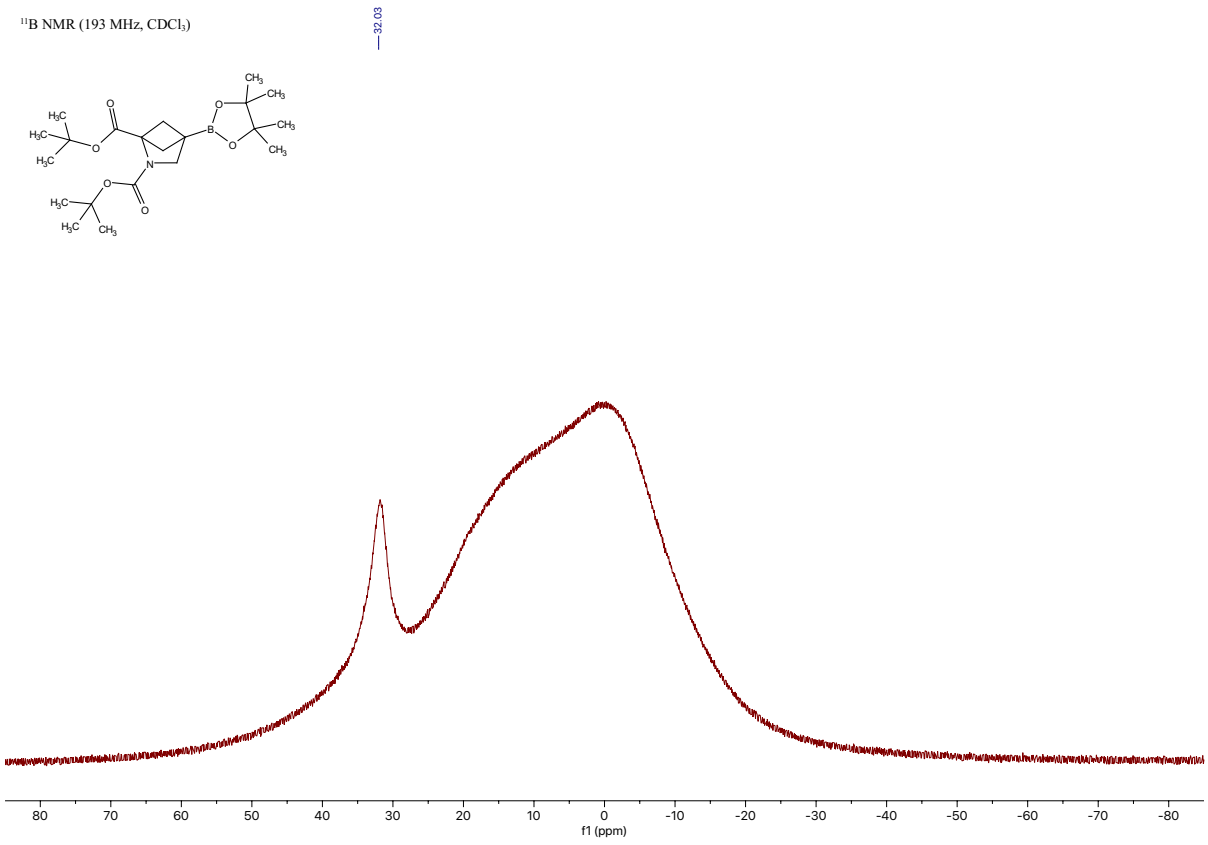


[*Return to table of contents*]

^{13}C NMR (151 MHz, $CDCl_3$)



^{11}B NMR (193 MHz, $CDCl_3$)

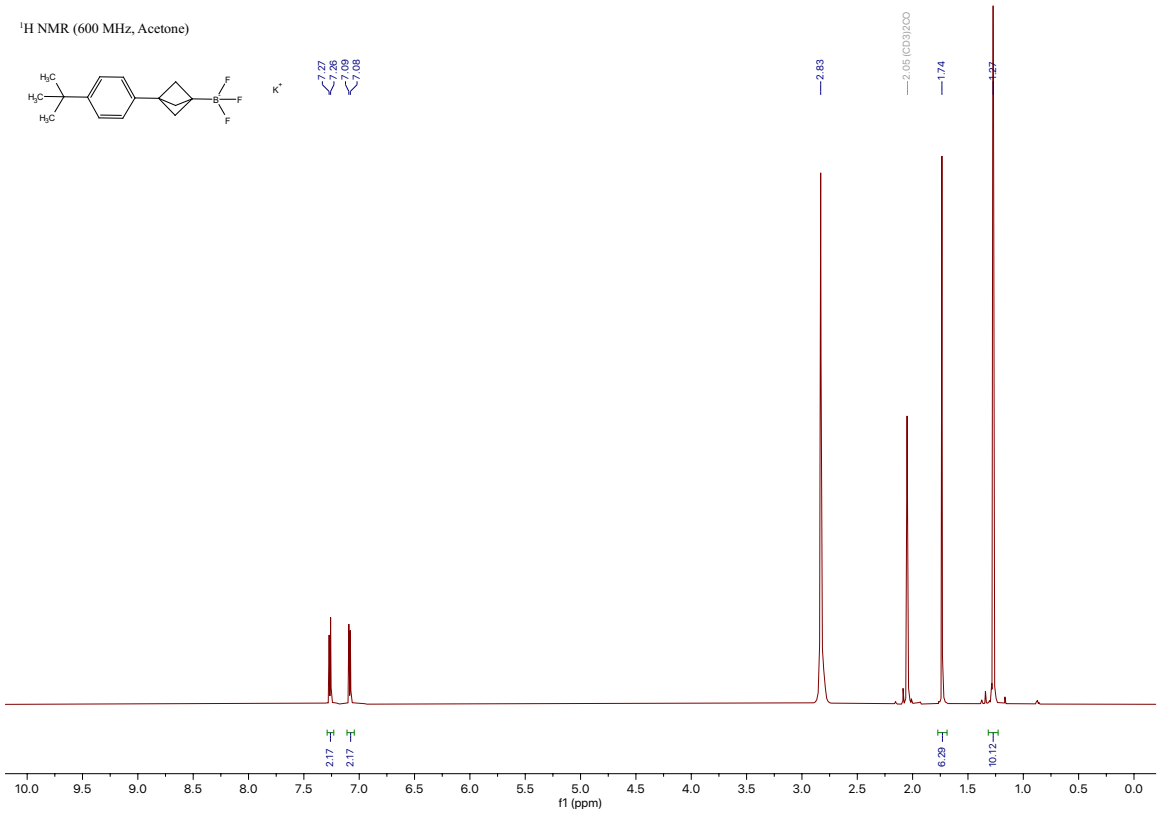


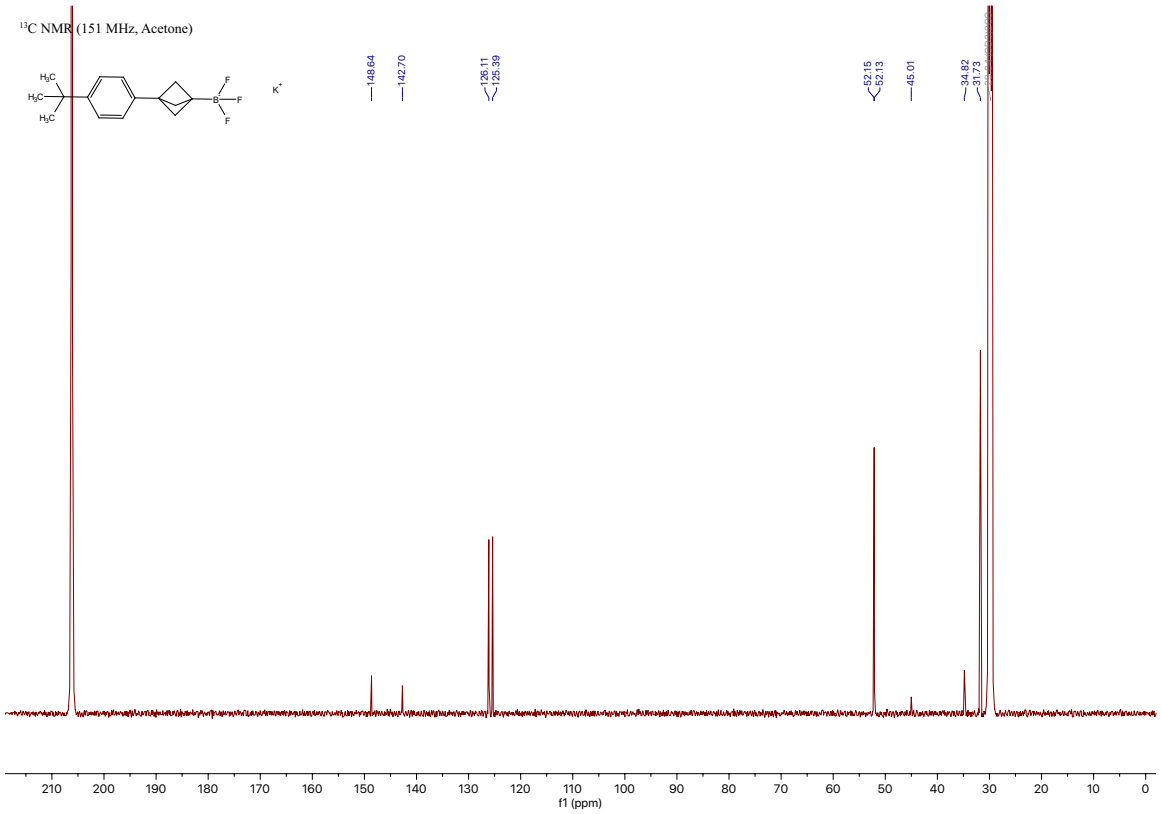
[*Return to table of contents*]

Compound 1c

(3-(4-(*tert*-butyl)phenyl)bicyclo[1.1.1]pentan-1-yl)trifluoro-λ4-borane, potassium salt

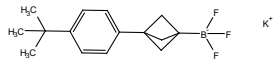
[Experimental]



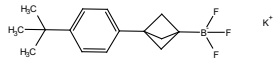


[*Return to table of contents*]

^{11}B NMR (193 MHz, Acetone)



^{19}F NMR (565 MHz, Acetone)

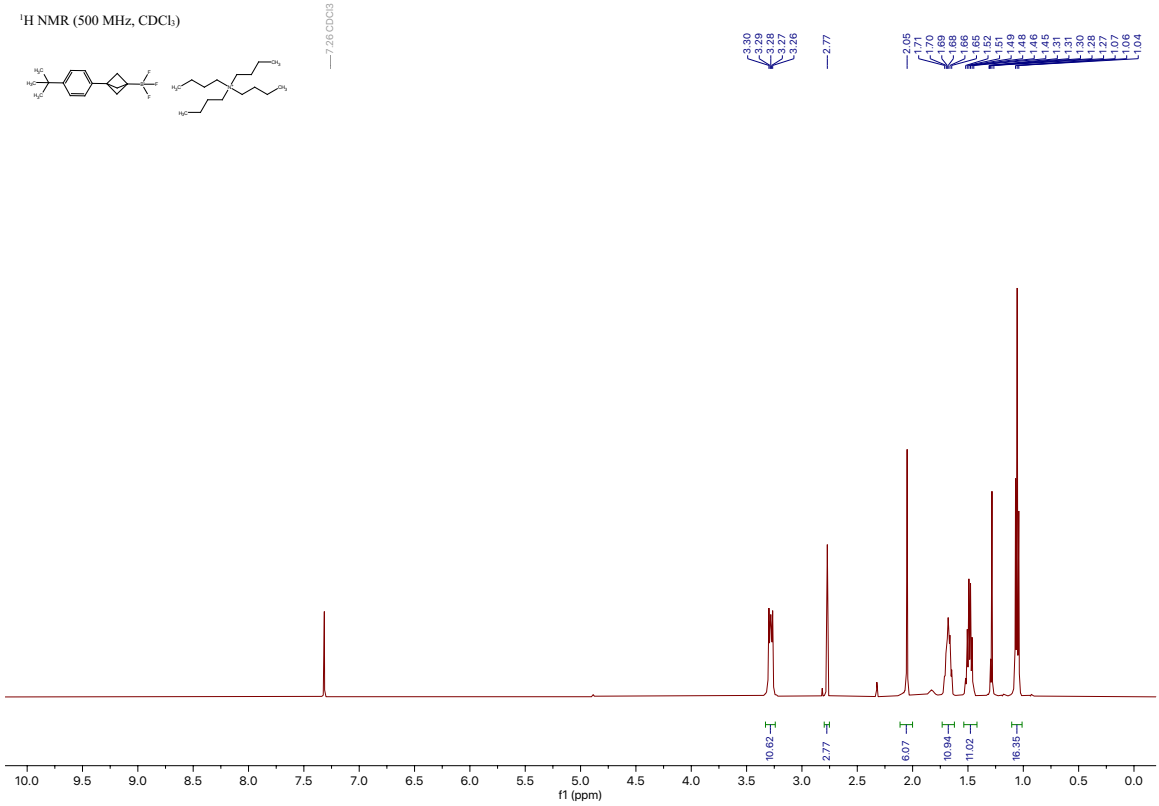


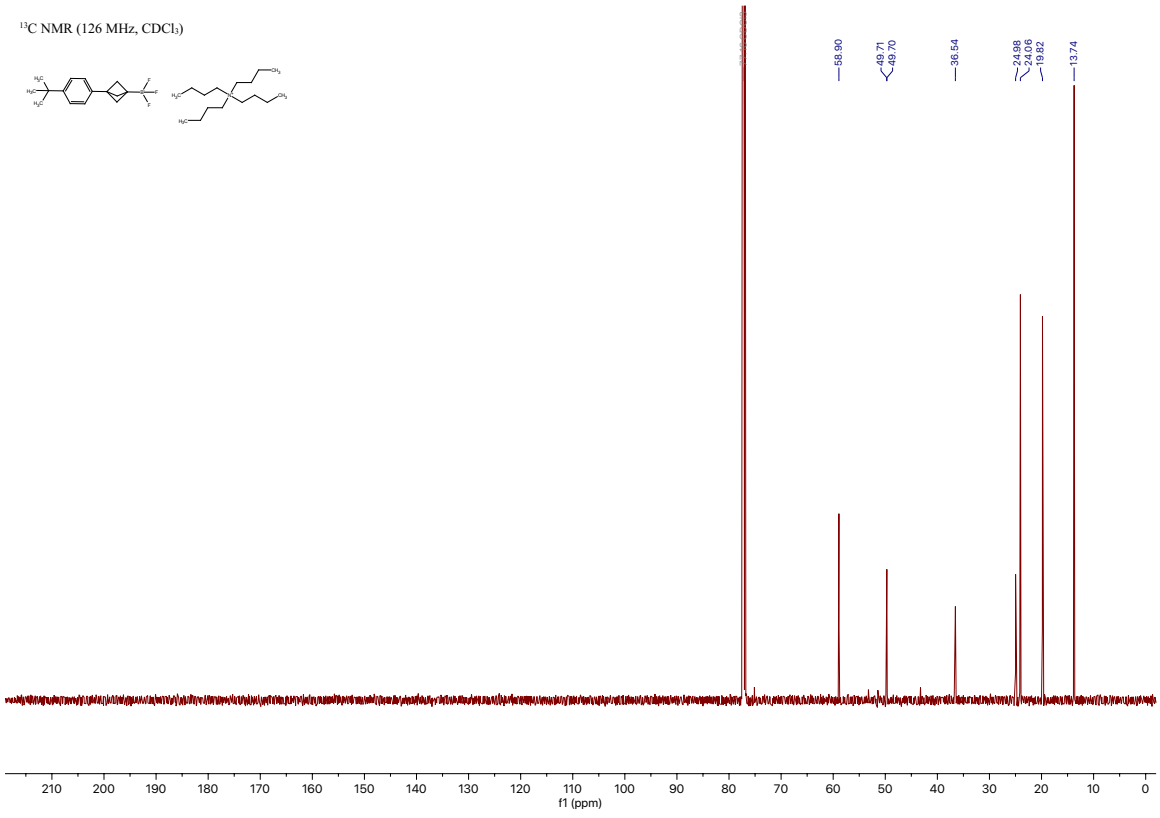
[*Return to table of contents*]

Compound 11c

(3-(methylsulfonyl)bicyclo[1.1.1]pentan-1-yl)trifluoro-λ4-borane, tetrabutylammonium salt

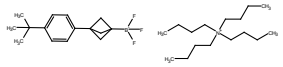
[Experimental]



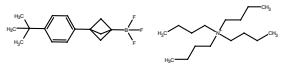


[*Return to table of contents*]

^{11}B NMR (160 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$)

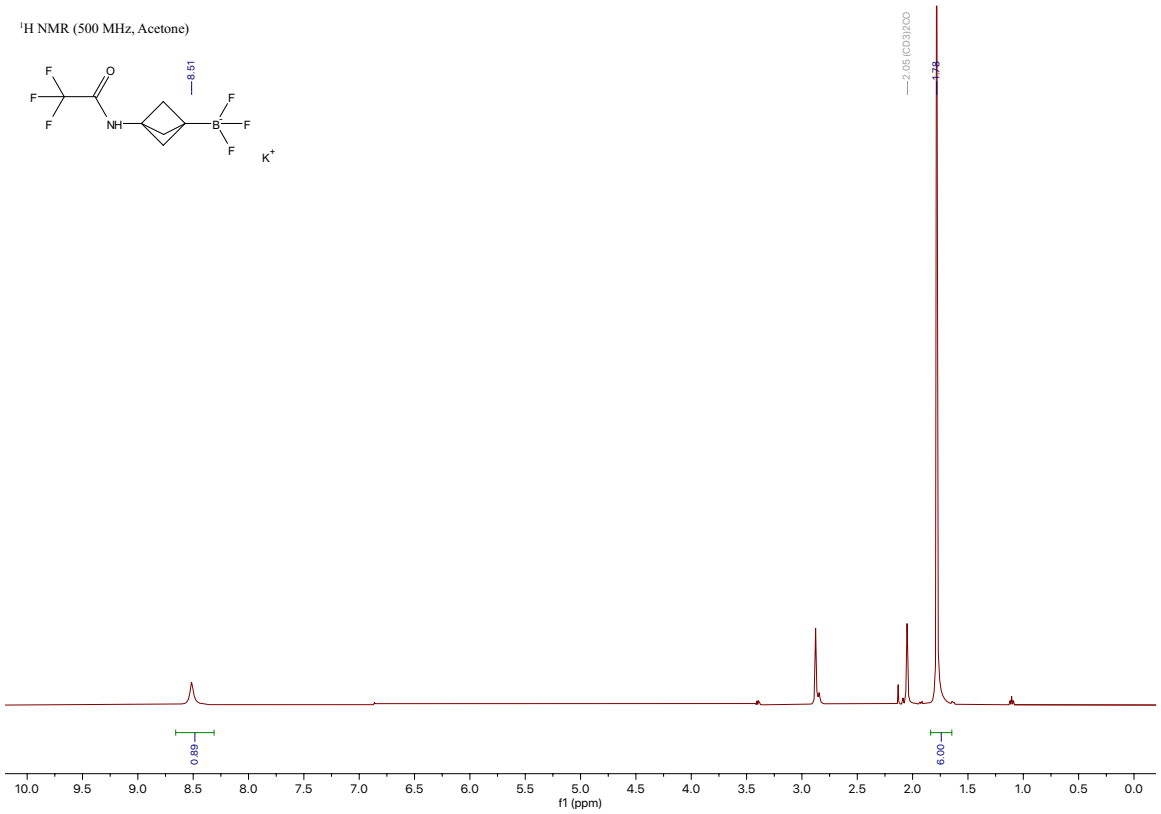


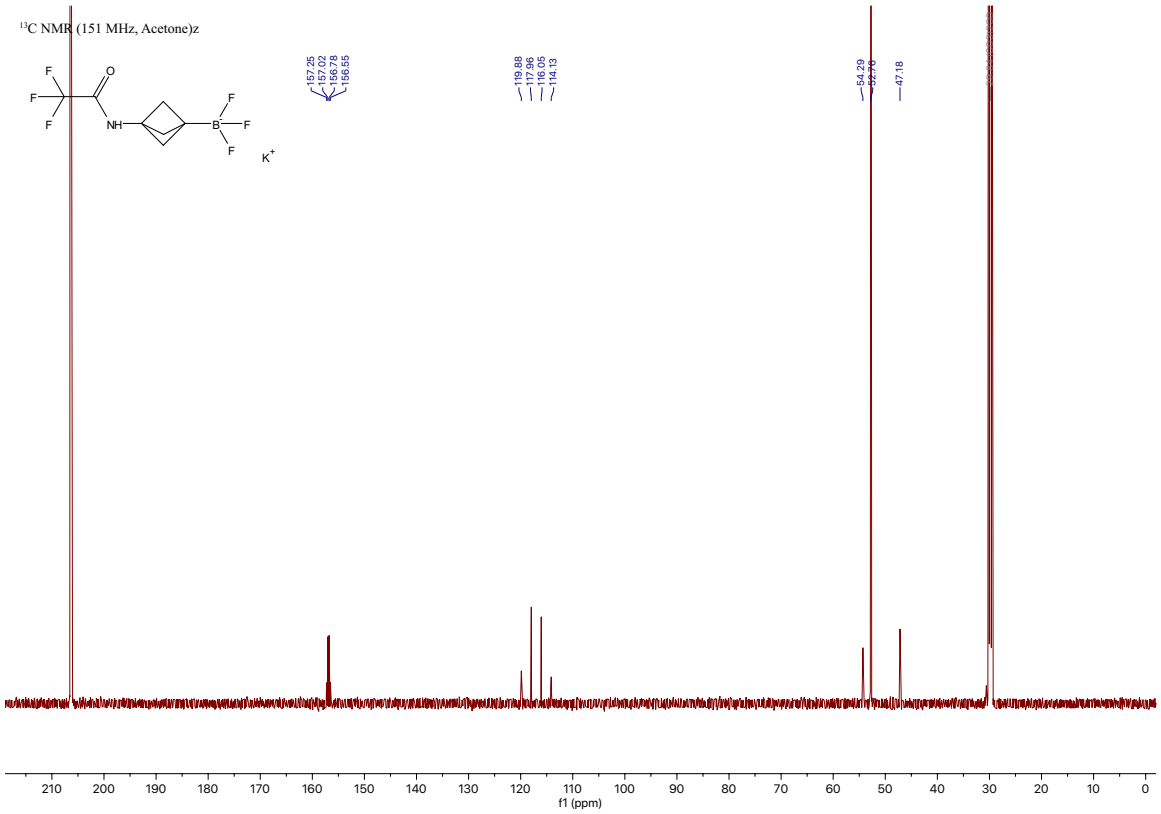
[*Return to table of contents*]

Compound 16c

2,2,2-trifluoro-*N*-(3-(trifluoro-λ4-boraneyl)bicyclo[1.1.1]pentan-1-yl)acetamide, potassium salt

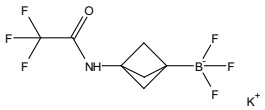
[Experimental]



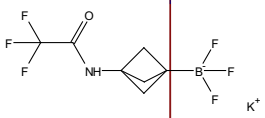


[*Return to table of contents*]

^{11}B NMR (160 MHz, Acetone) δ 2.87.



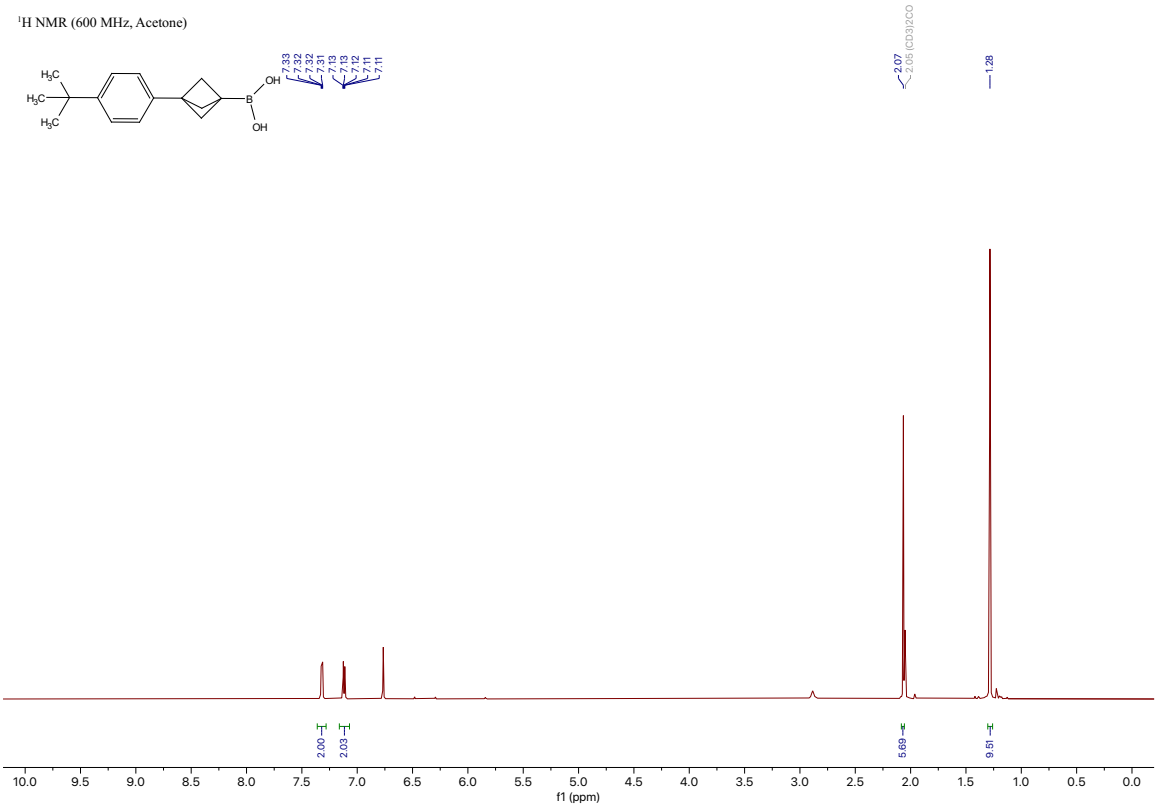
^{19}F NMR (470 MHz, Acetone)



[*Return to table of contents*]

Compound 1d

(3-(4-(*tert*-butyl)phenyl)bicyclo[1.1.1]pentan-1-yl)boronic acid [Experimental]



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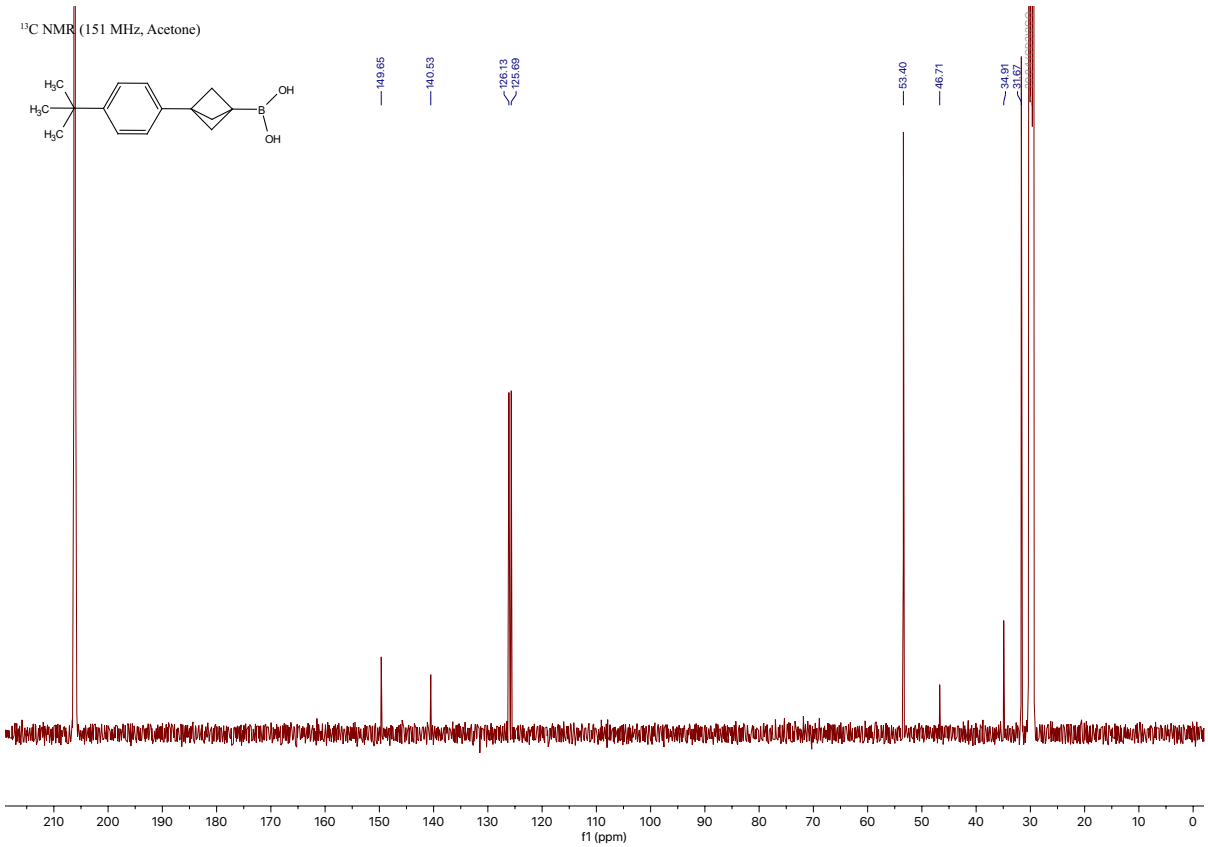
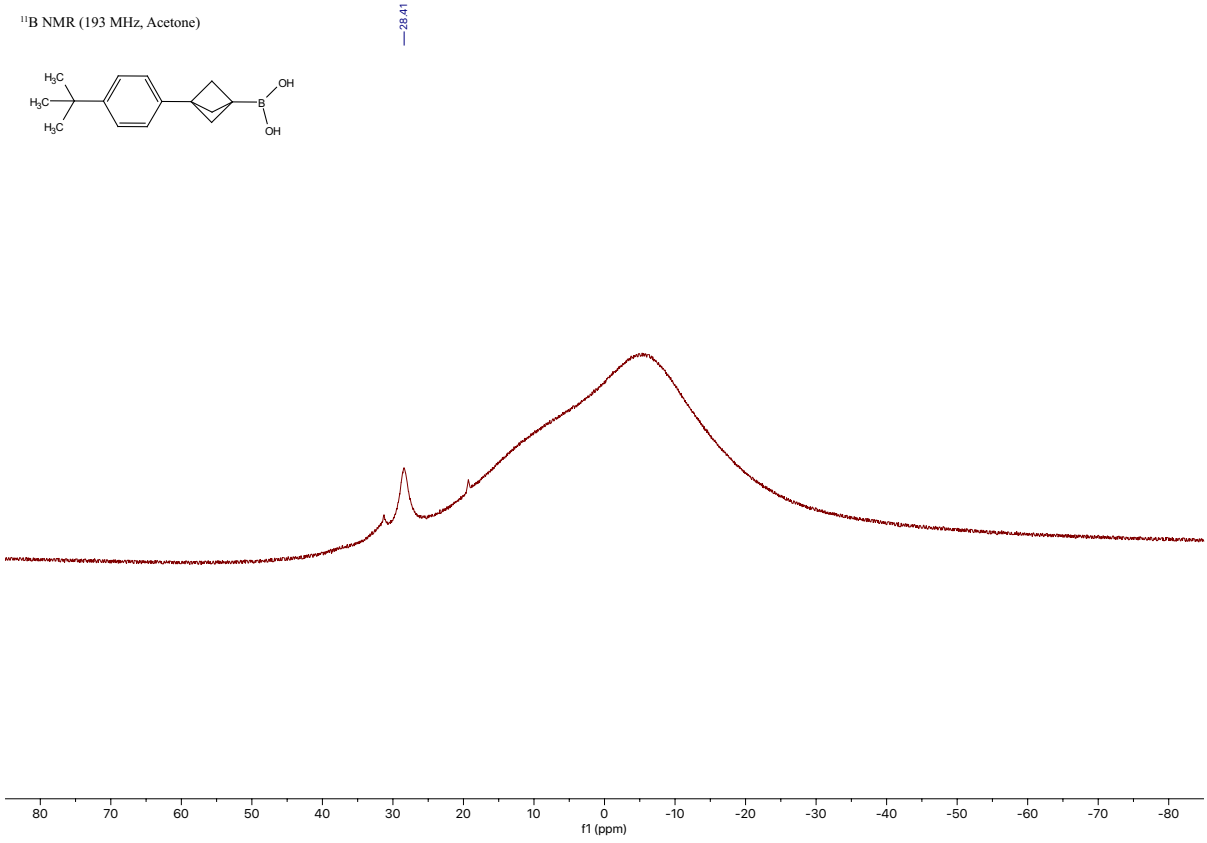
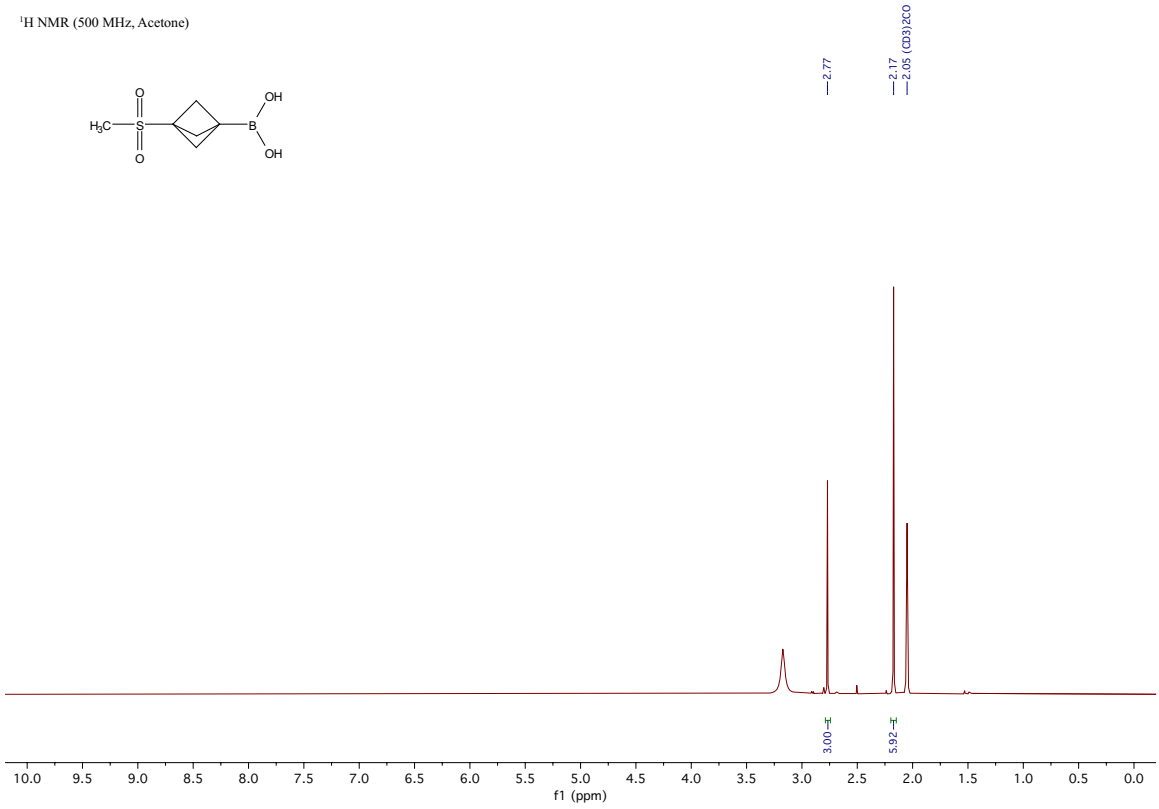




[*Return to table of contents*]

Compound 11d

(3-(methylsulfonyl)bicyclo[1.1.1]pentan-1-yl)boronic acid [Experimental]



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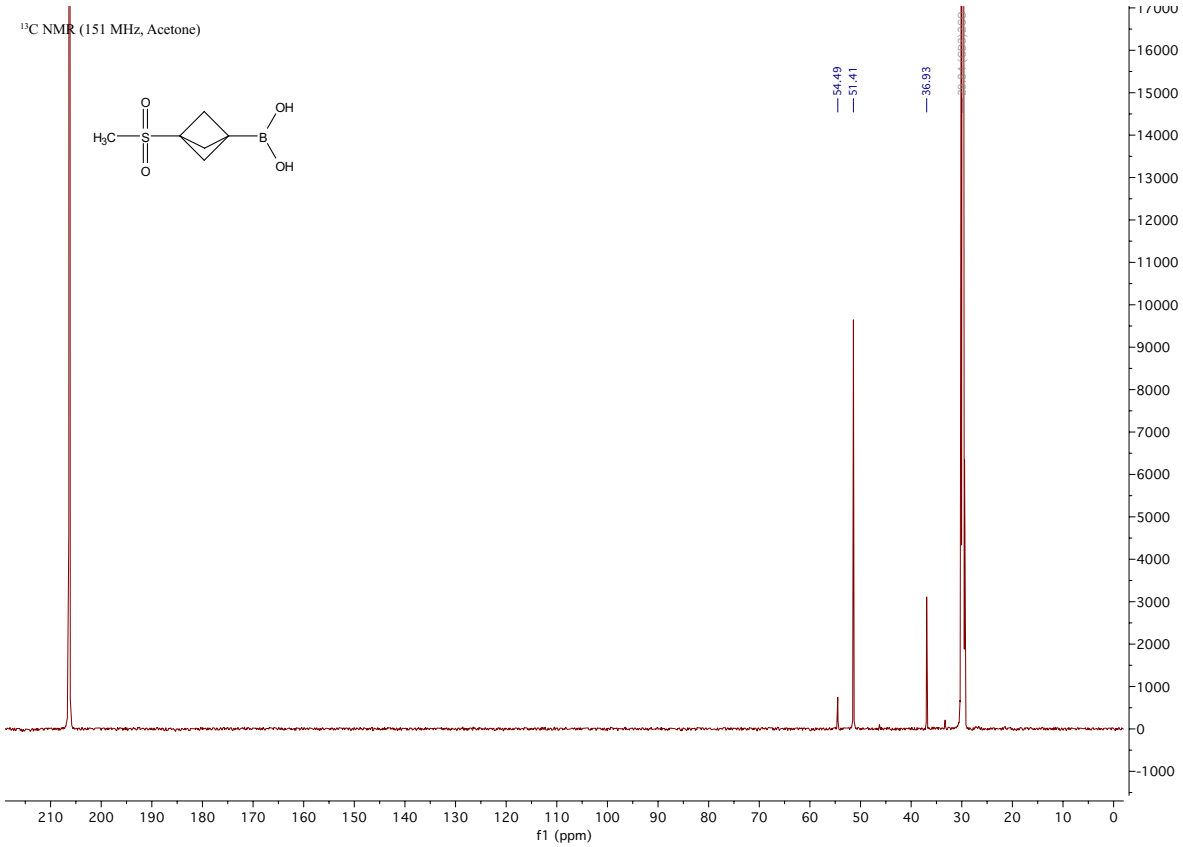
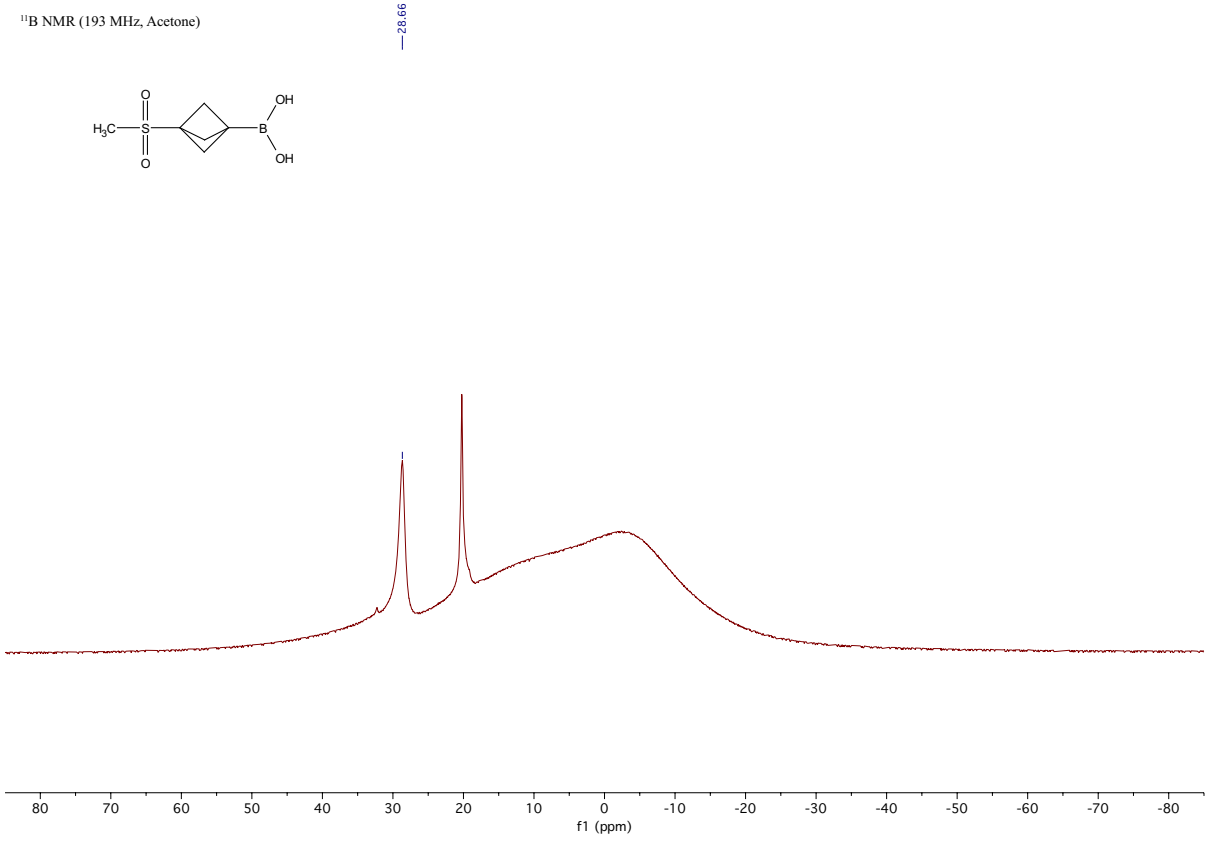


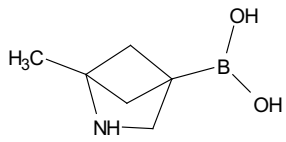


[*Return to table of contents*]

Compound 28c

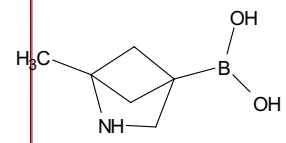
(1-methyl-2-azabicyclo[2.1.1]hexan-4-yl)boronic acid [Experimental]

^{1}H NMR (600 MHz, Acetone)

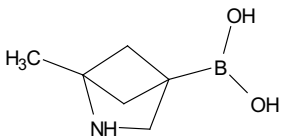


[Return to table of contents]

^{13}C NMR (151 MHz, Acetone)



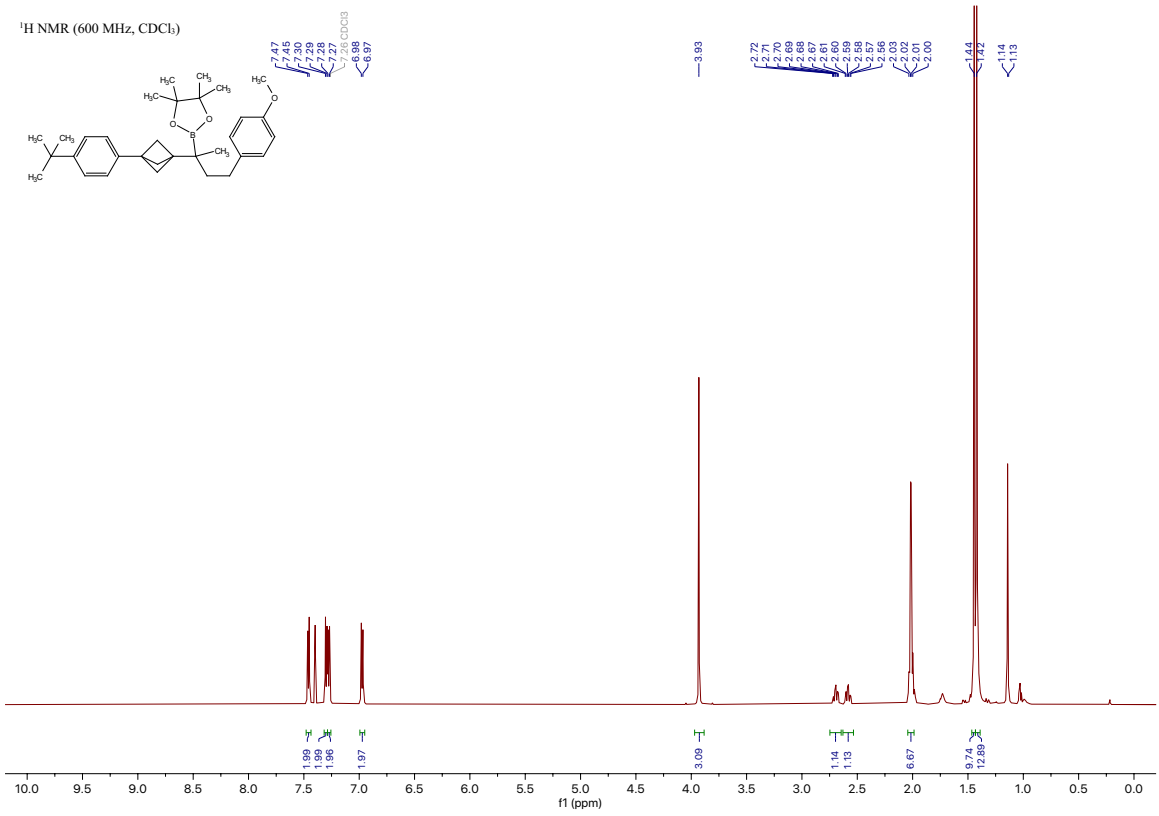
^{11}B NMR (193 MHz, Acetone)



[*Return to table of contents*]

Compound 1e

2-(2-(3-(4-(*tert*-butyl)phenyl)bicyclo[1.1.1]pentan-1-yl)-4-(4-methoxyphenyl)butan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [Experimental]



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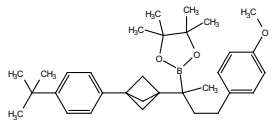
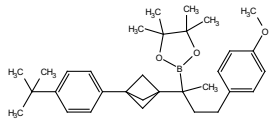
^{13}C NMR (151 MHz, $CDCl_3$)



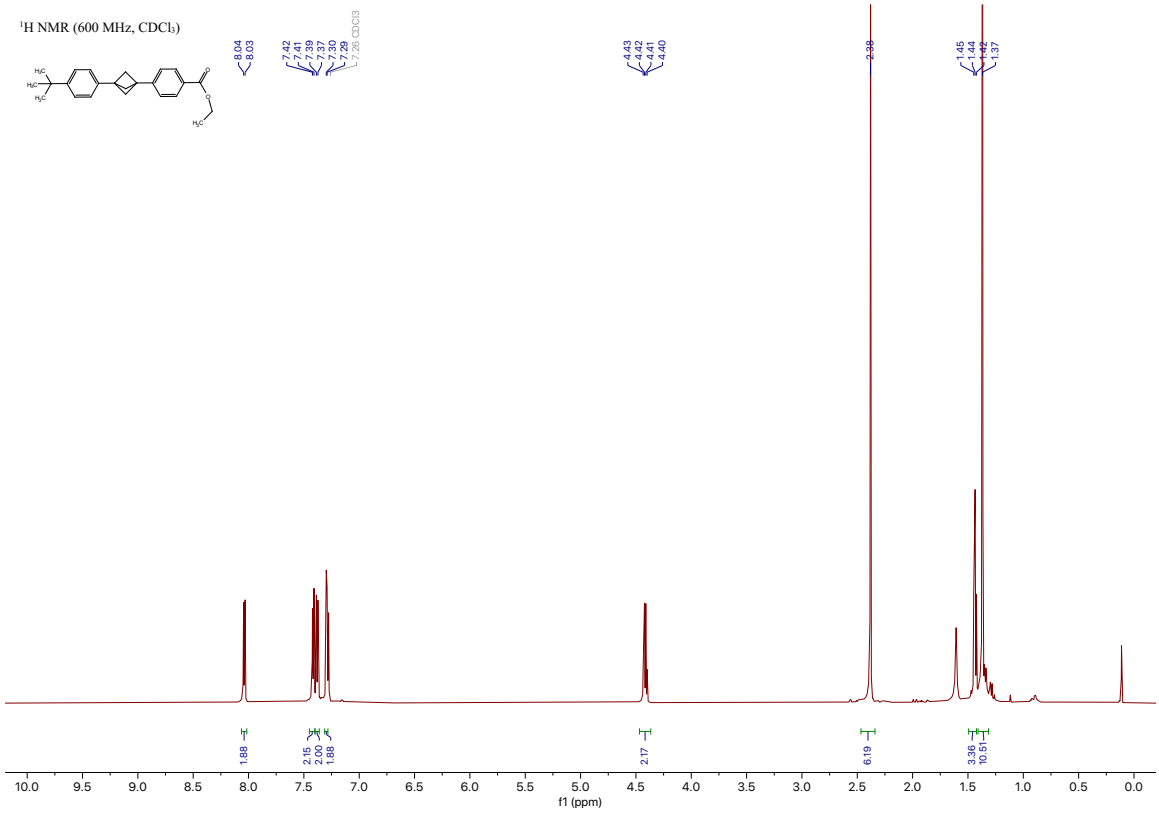
^{11}B NMR (193 MHz, $CDCl_3$)

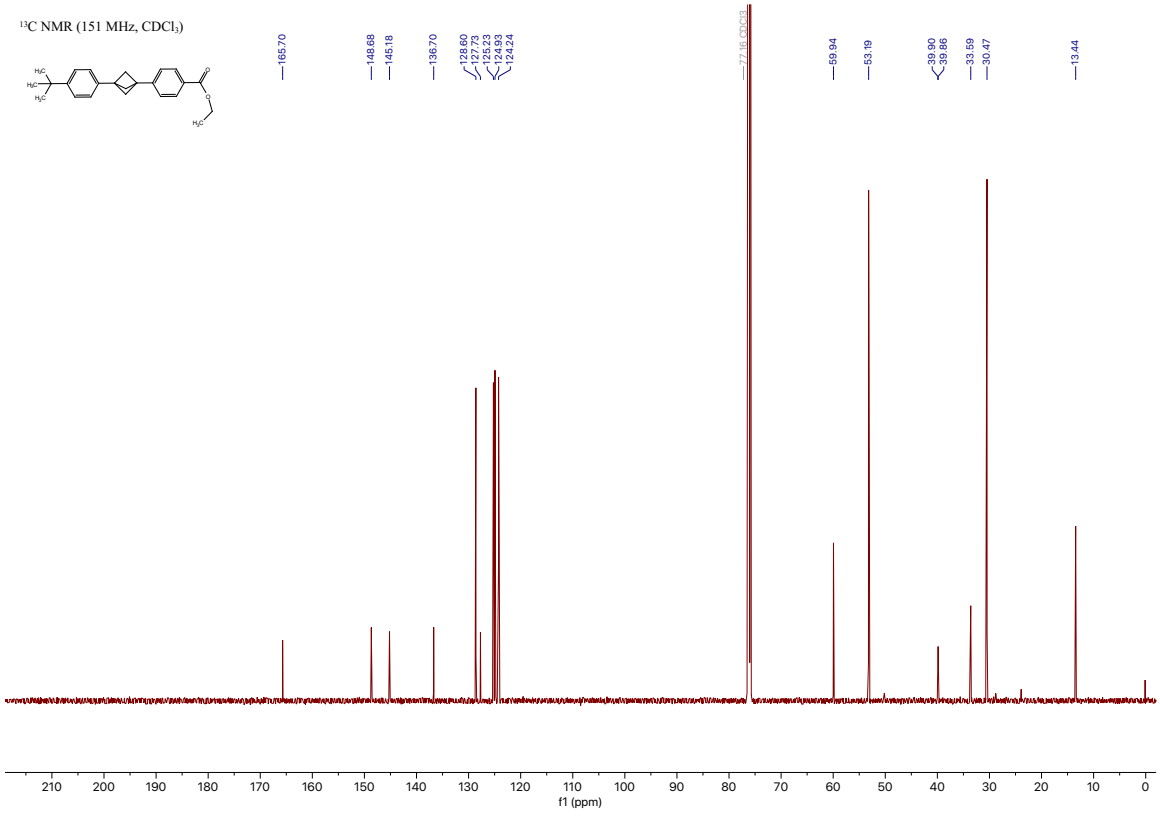


[*Return to table of contents*]

Compound 1f

ethyl 4-(3-(4-(*tert*-butyl)phenyl)bicyclo[1.1.1]pentan-1-yl)benzoate [Experimental]

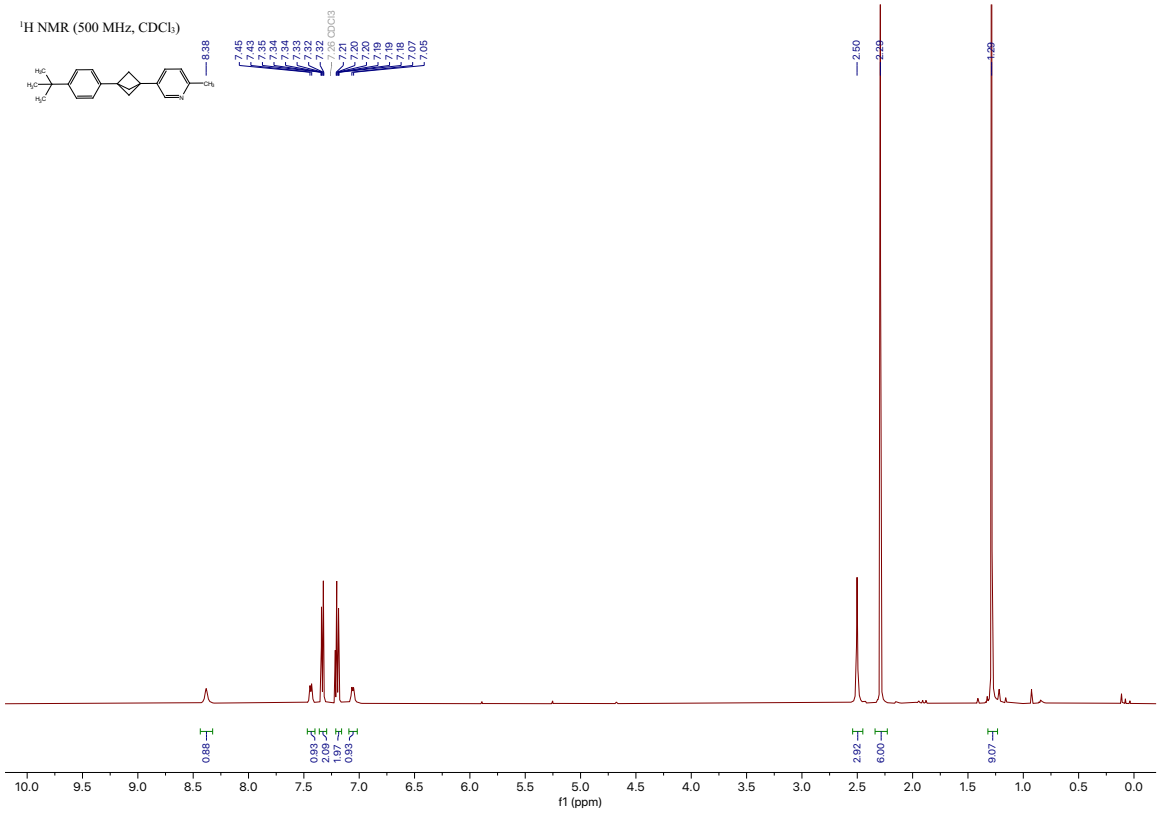


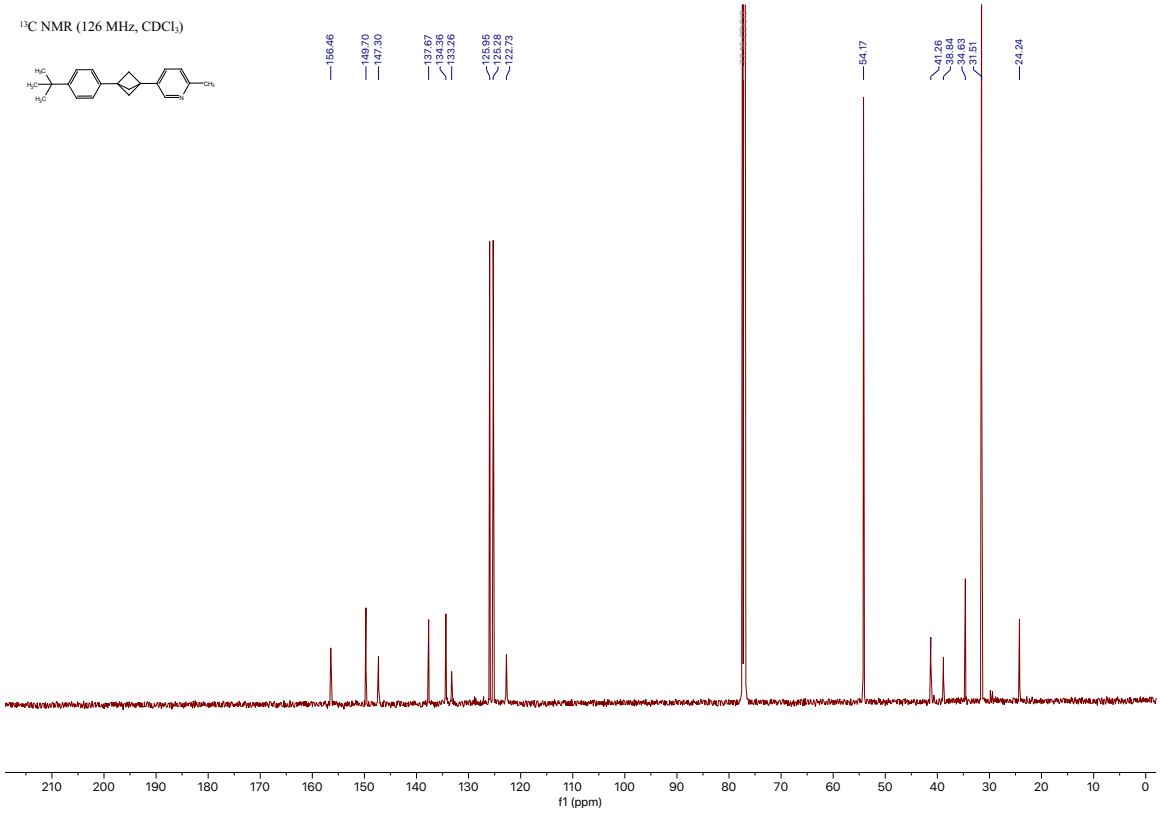


[*Return to table of contents*]

Compound 1g

5-(3-(4-(*tert*-butyl)phenyl)bicyclo[1.1.1]pentan-1-yl)-2-methylpyridine [Experimental]



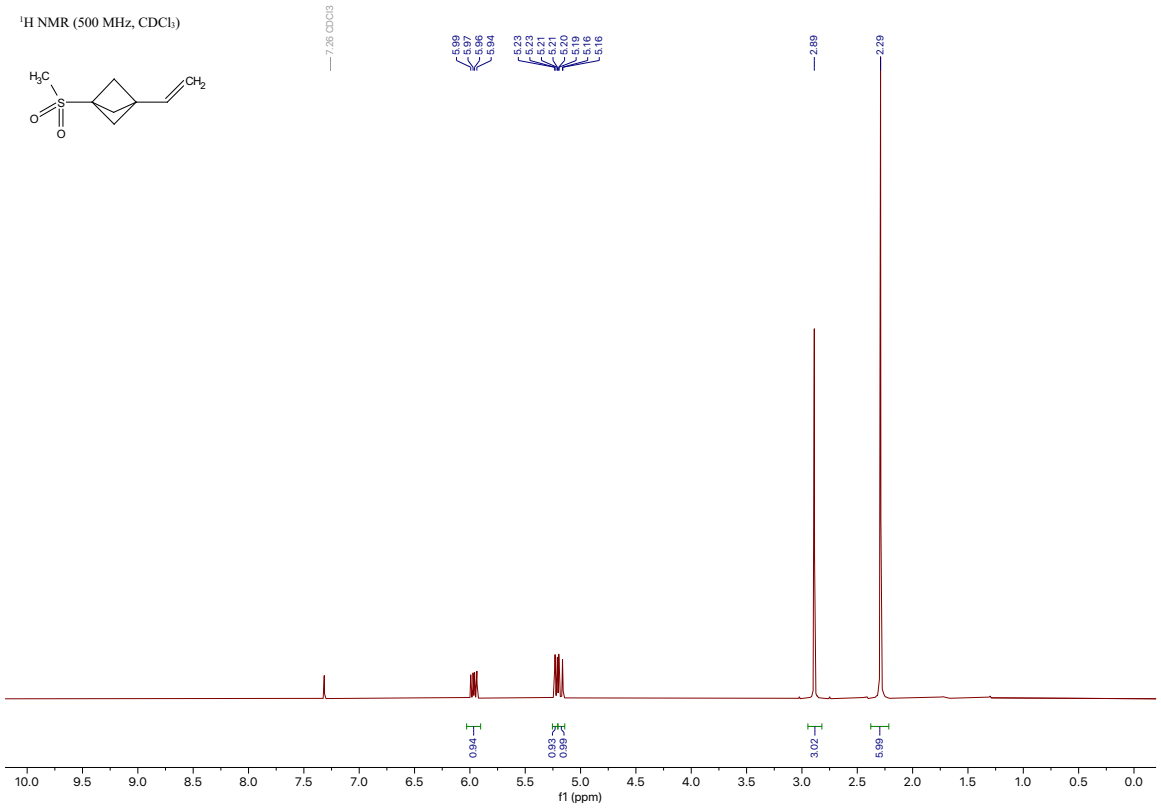


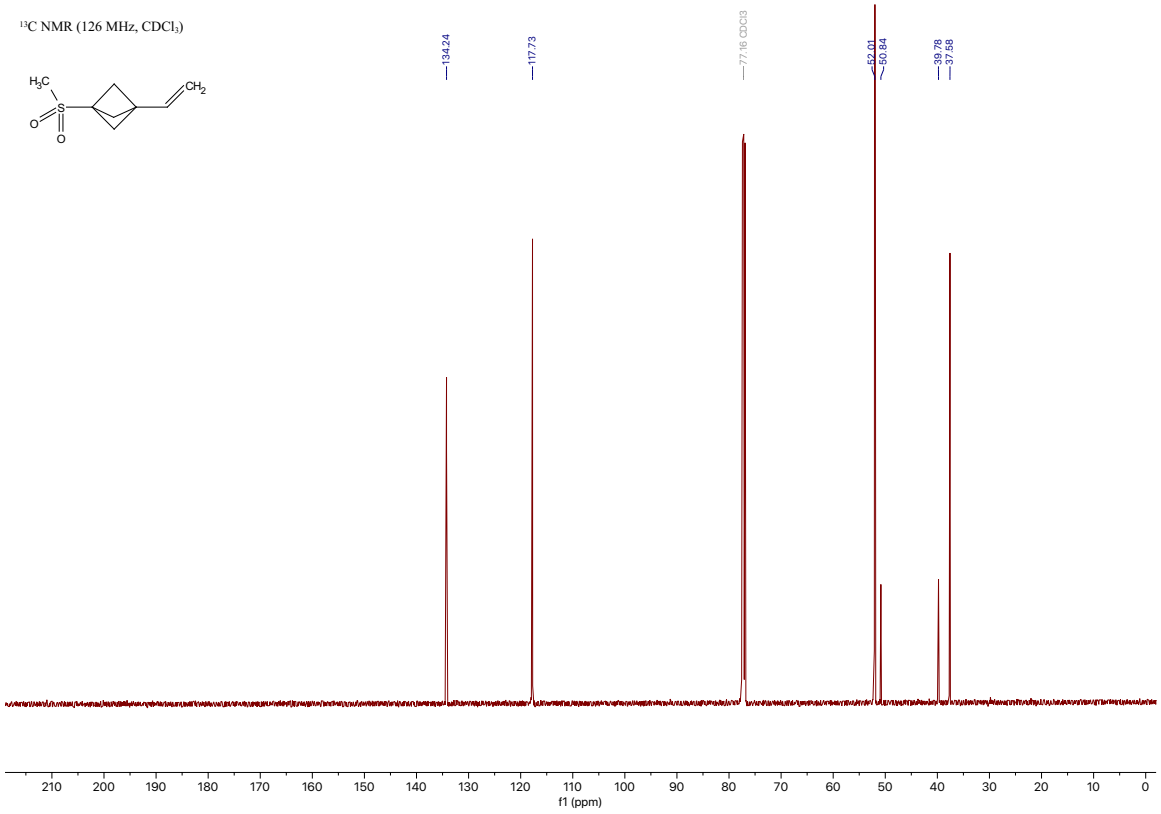
[*Return to table of contents*]

Compound 11e

1-(methylsulfonyl)-3-vinylbicyclo[1.1.1]pentane

[Experimental]

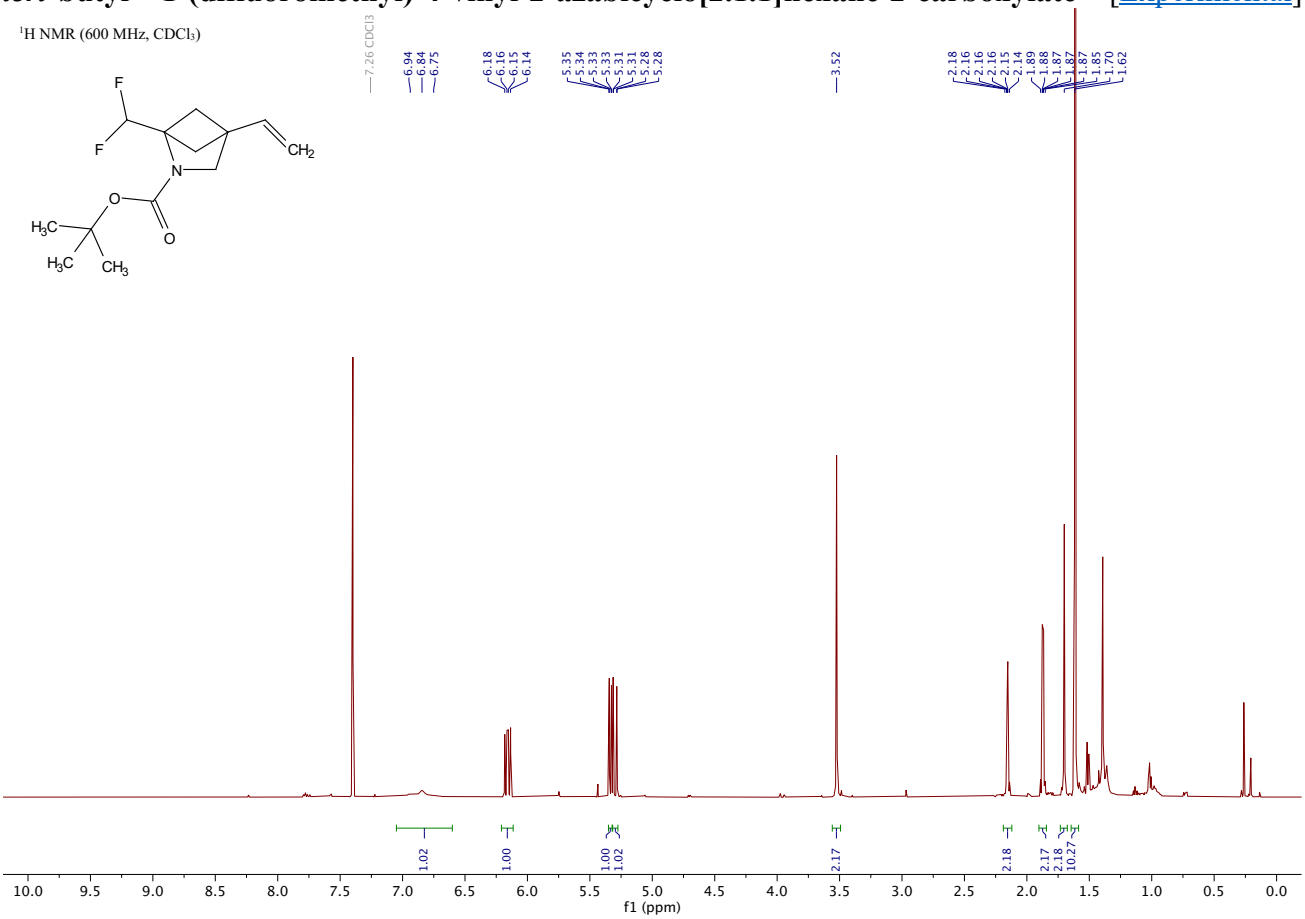




[*Return to table of contents*]

Compound 30c

tert-butyl 1-(difluoromethyl)-4-vinyl-2-azabicyclo[2.1.1]hexane-2-carboxylate [Experimental]



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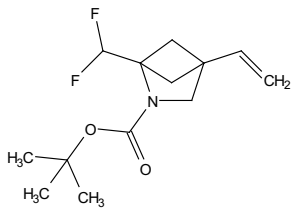
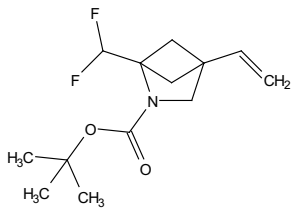
^{13}C NMR (151 MHz, $CDCl_3$)



^{19}F NMR (565 MHz, $CDCl_3$)

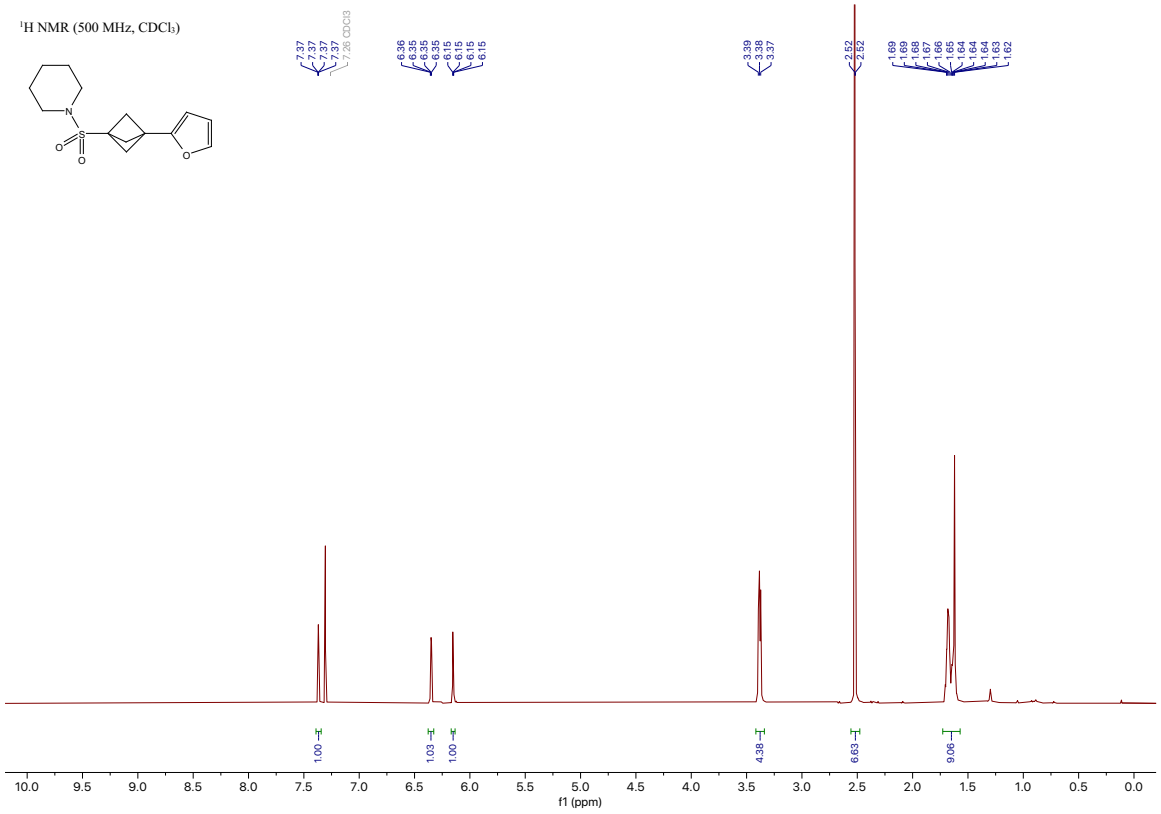


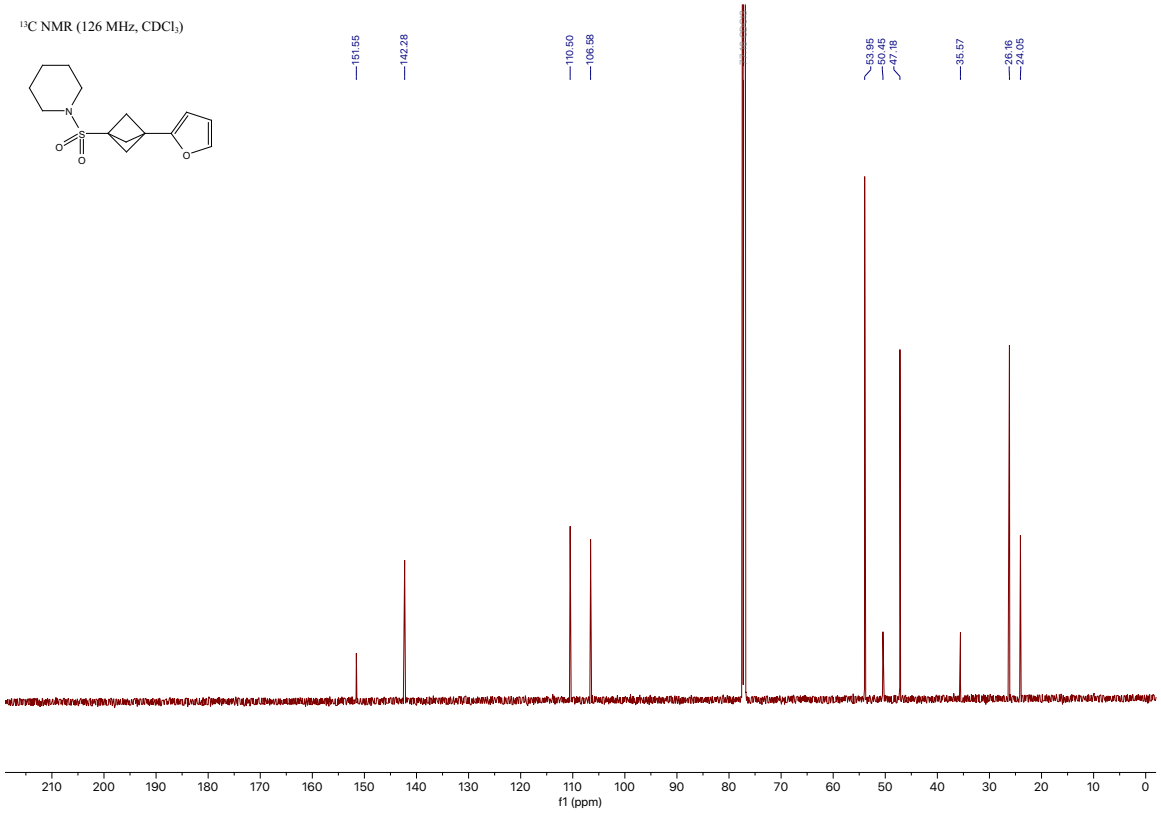
[*Return to table of contents*]

Compound 13c

1-((3-(furan-2-yl)bicyclo[1.1.1]pentan-1-yl)sulfonyl)piperidine

[Experimental]

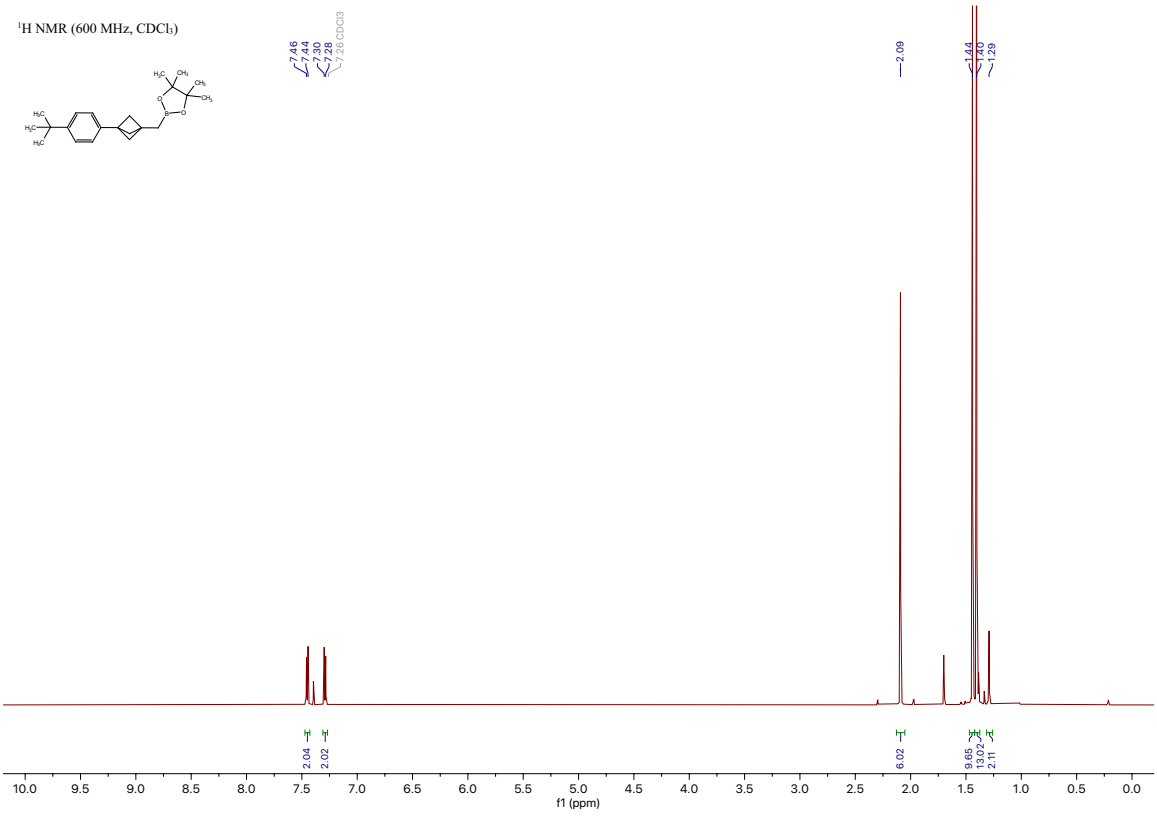




[*Return to table of contents*]

Compound 1h

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



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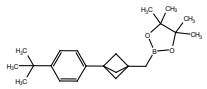
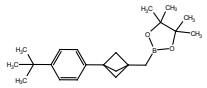
^{13}C NMR (151 MHz, $CDCl_3$)



^{11}B NMR (193 MHz, $CDCl_3$)

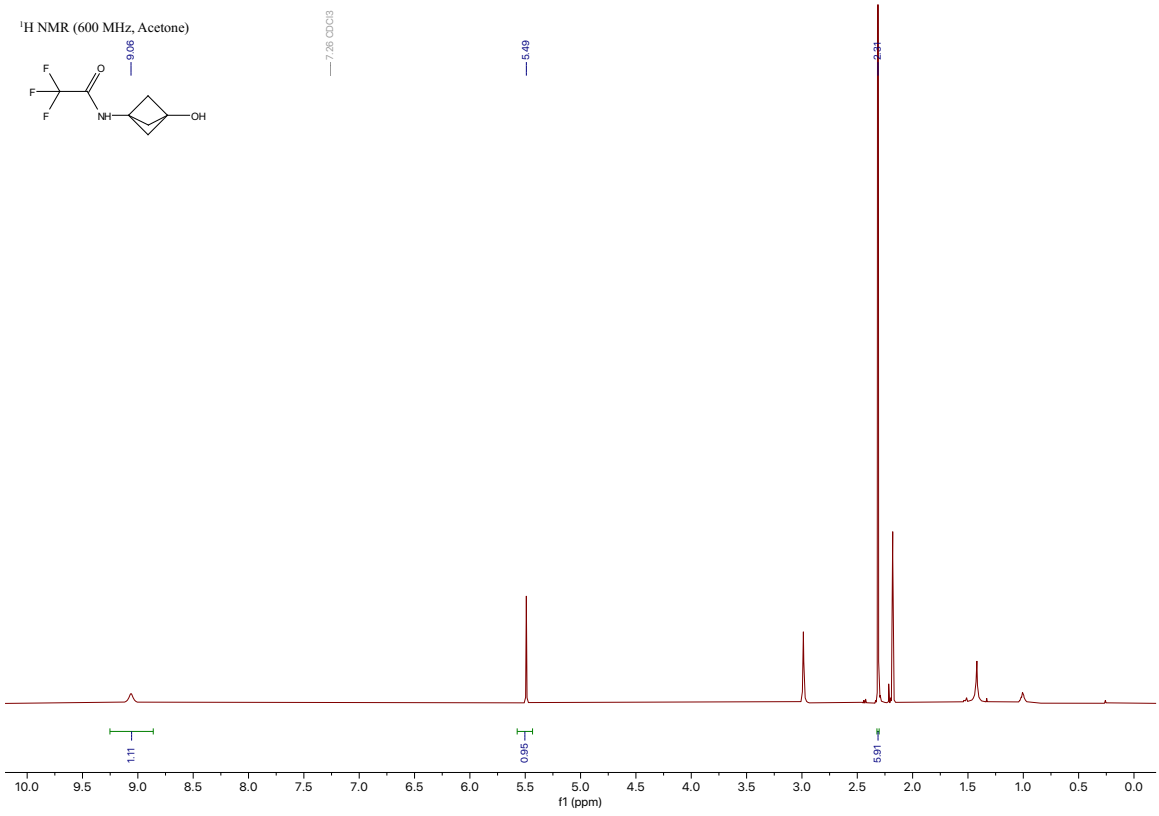


[*Return to table of contents*]

Compound 16d

2,2,2-trifluoro-*N*-(3-hydroxybicyclo[1.1.1]pentan-1-yl)acetamide

[Experimental]



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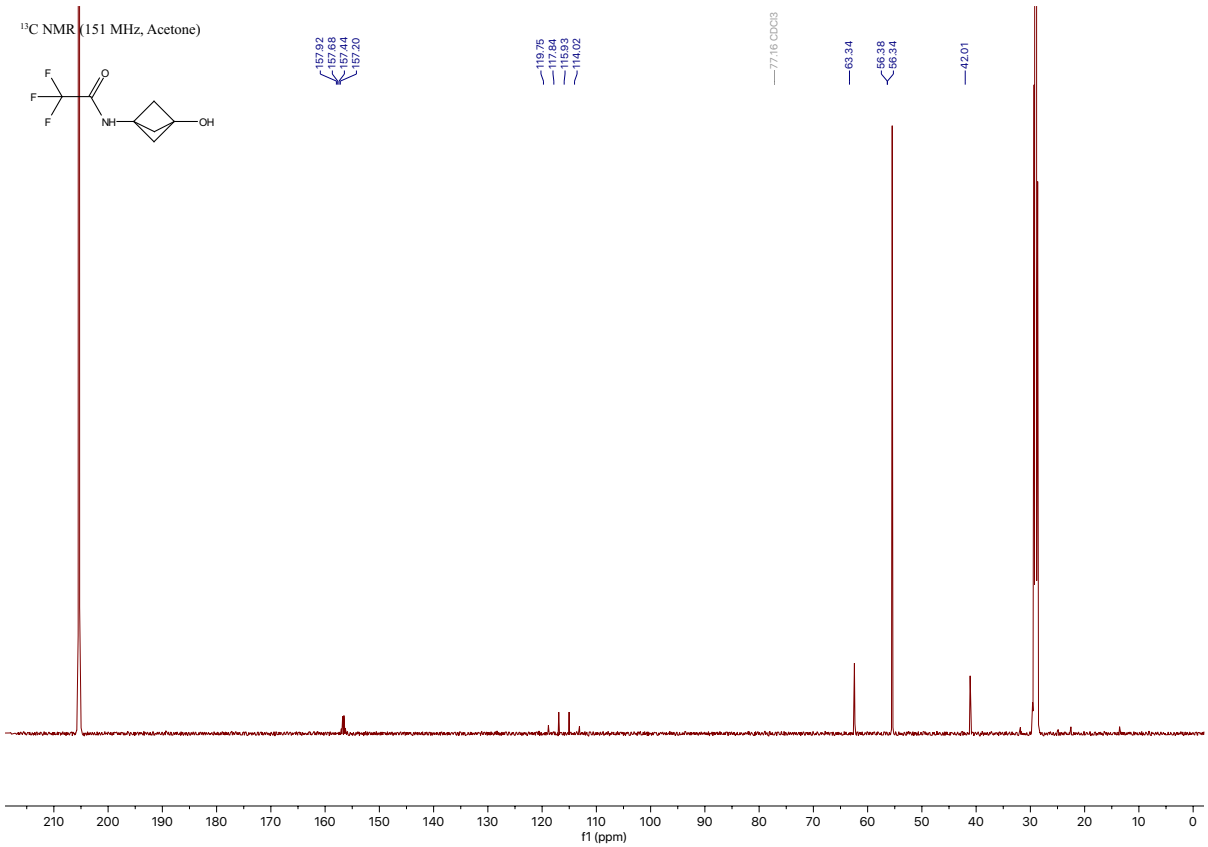

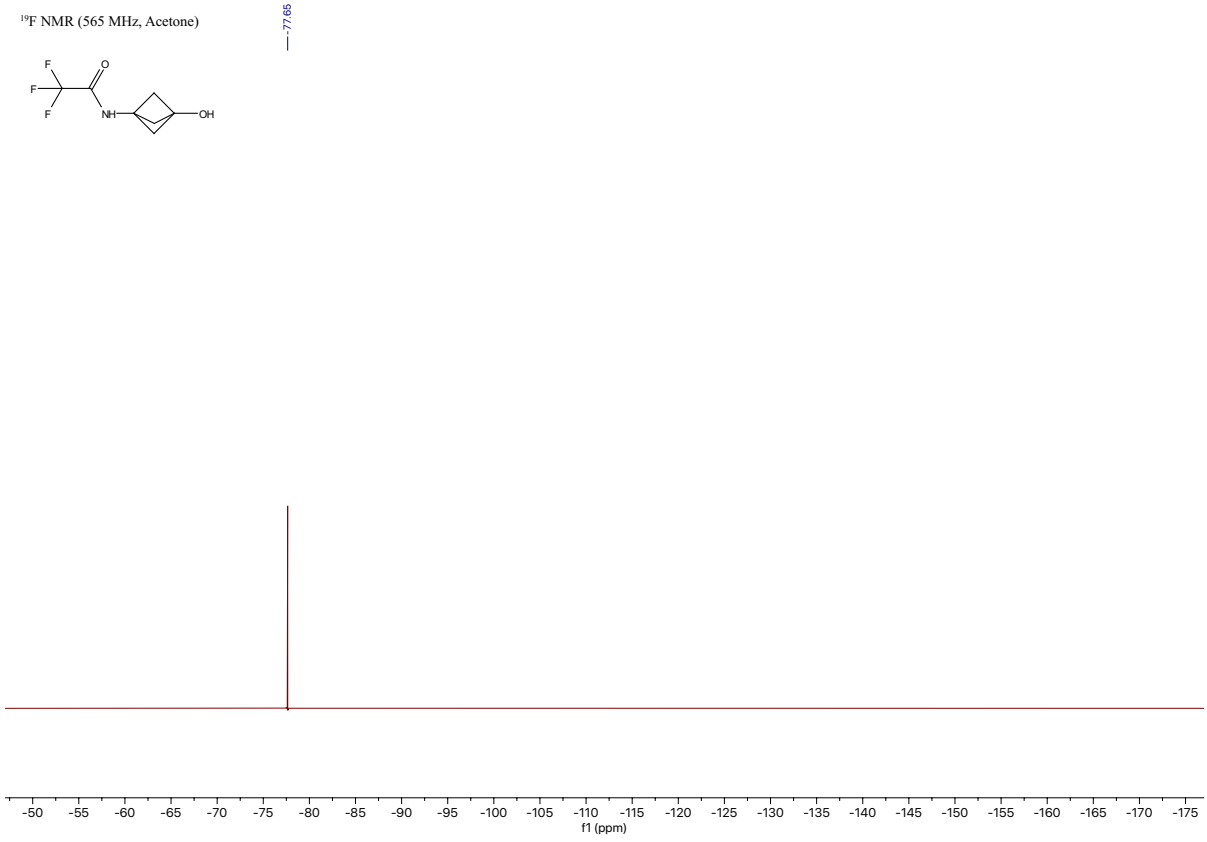

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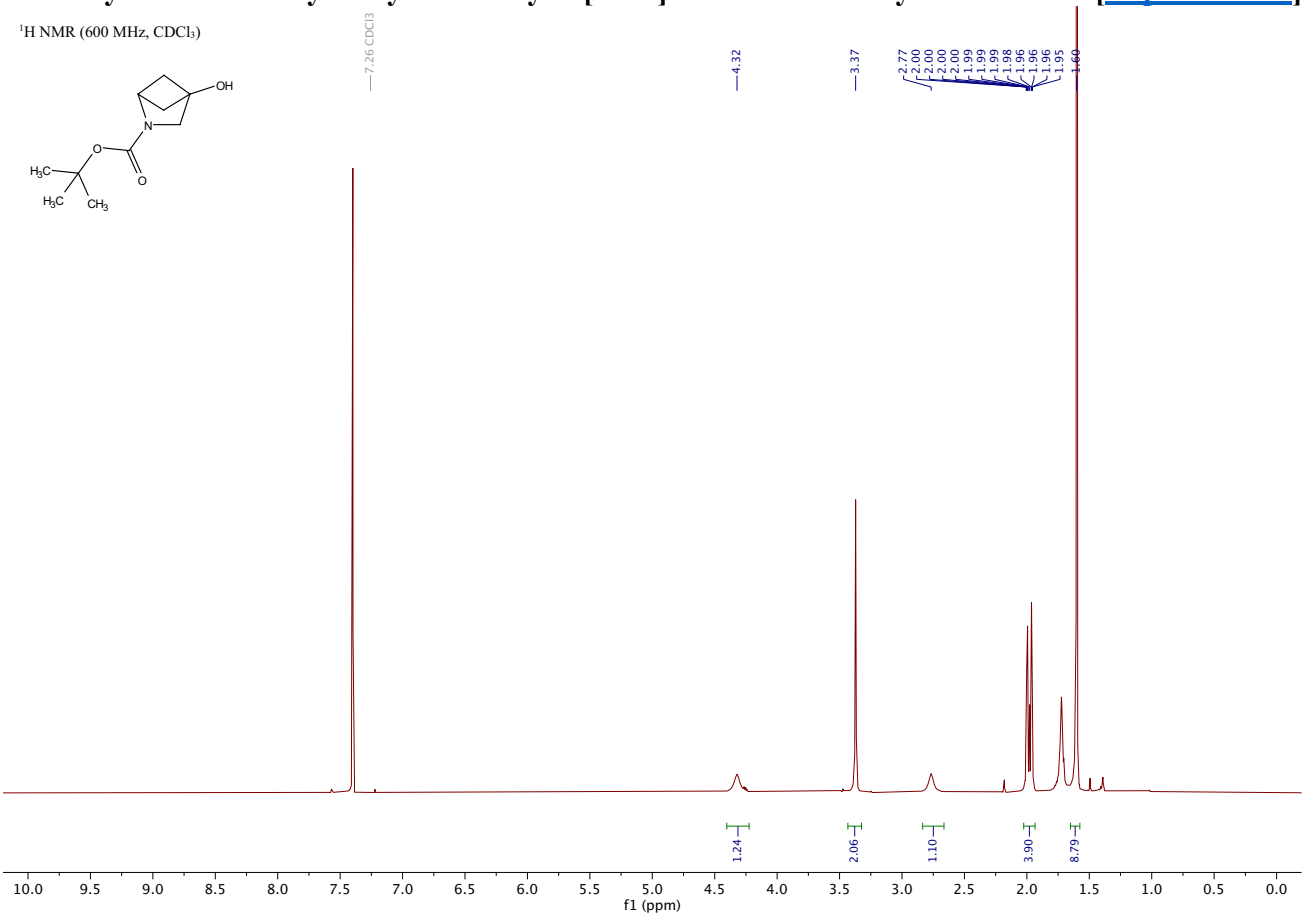
Compound 27c

***tert*-butyl 4-hydroxy-2-azabicyclo[2.1.1]hexane-2-carboxylate** [Experimental]



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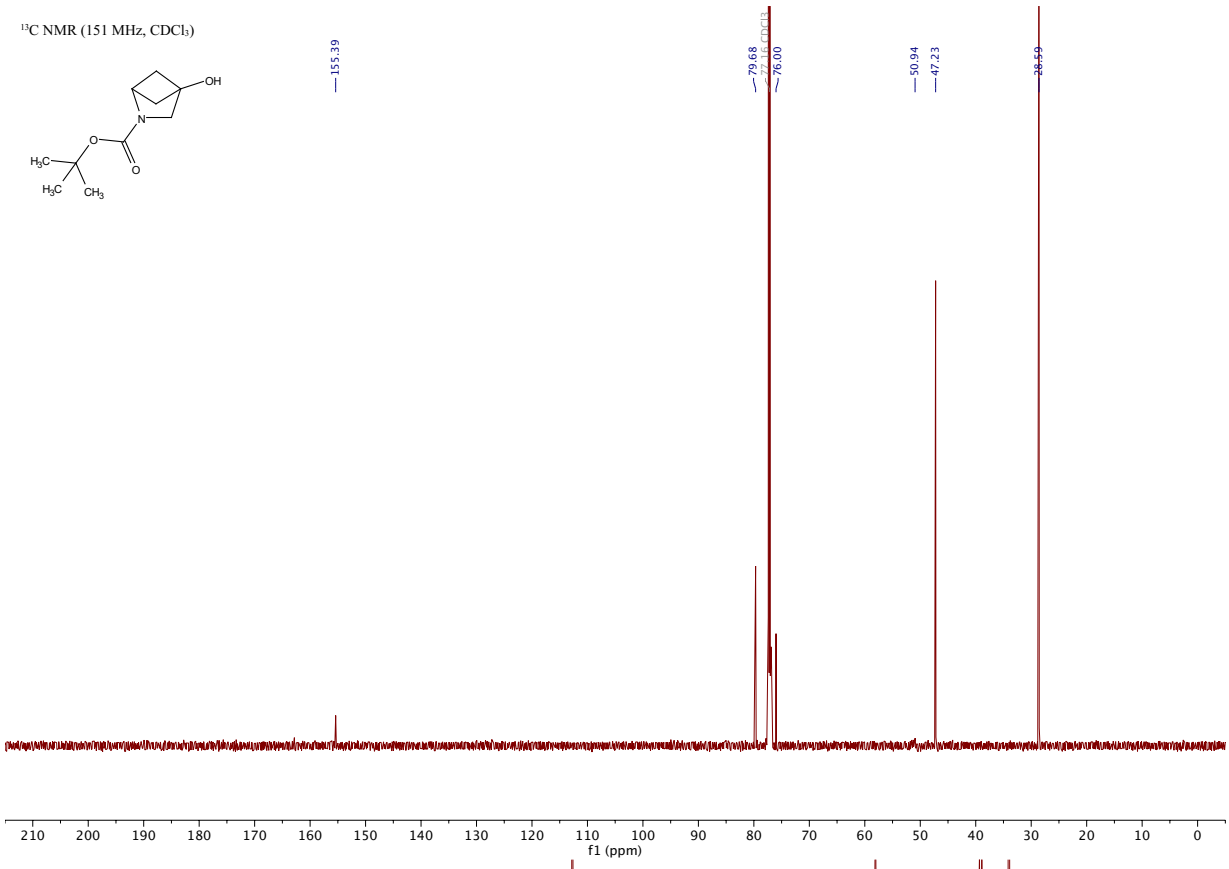

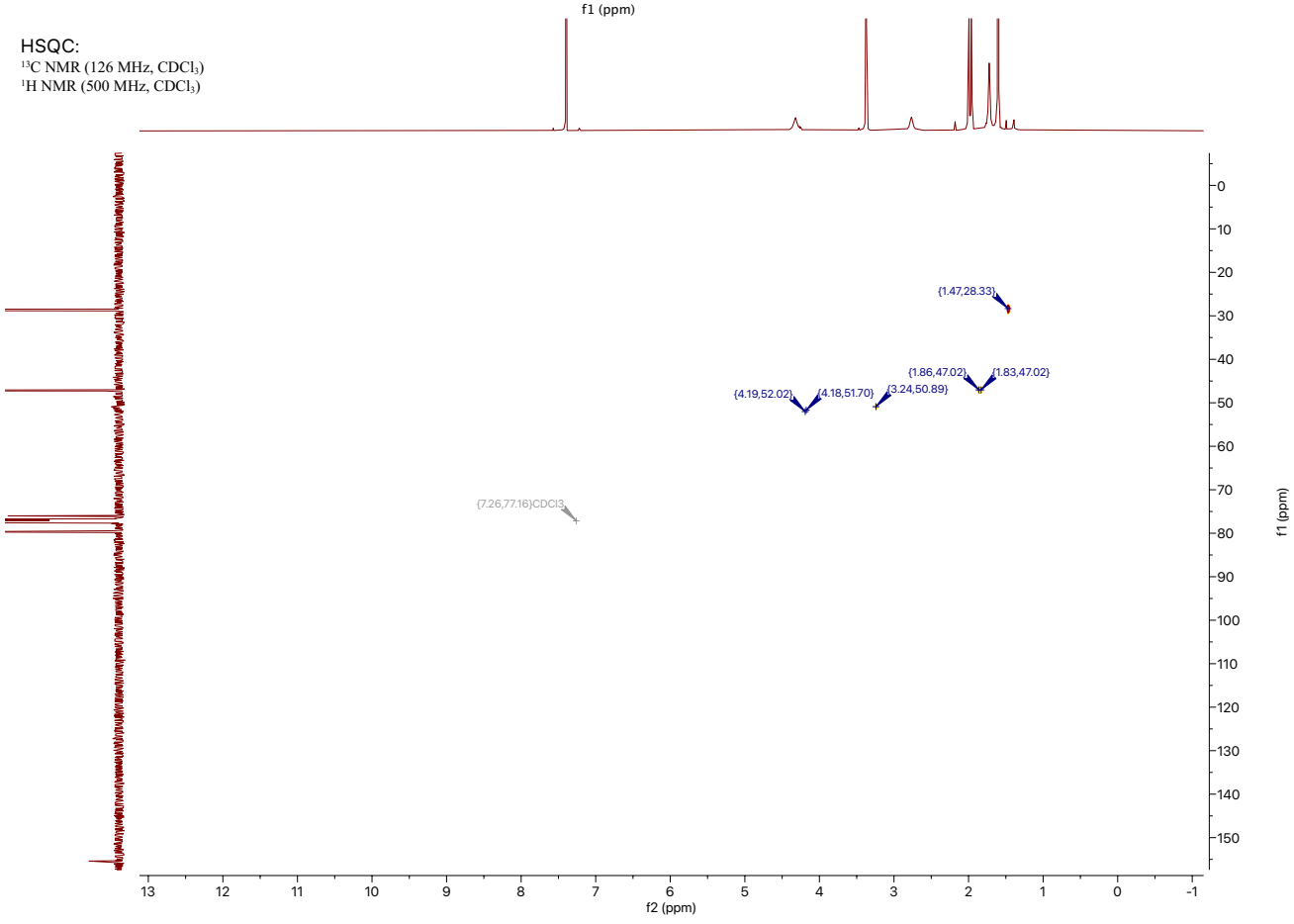

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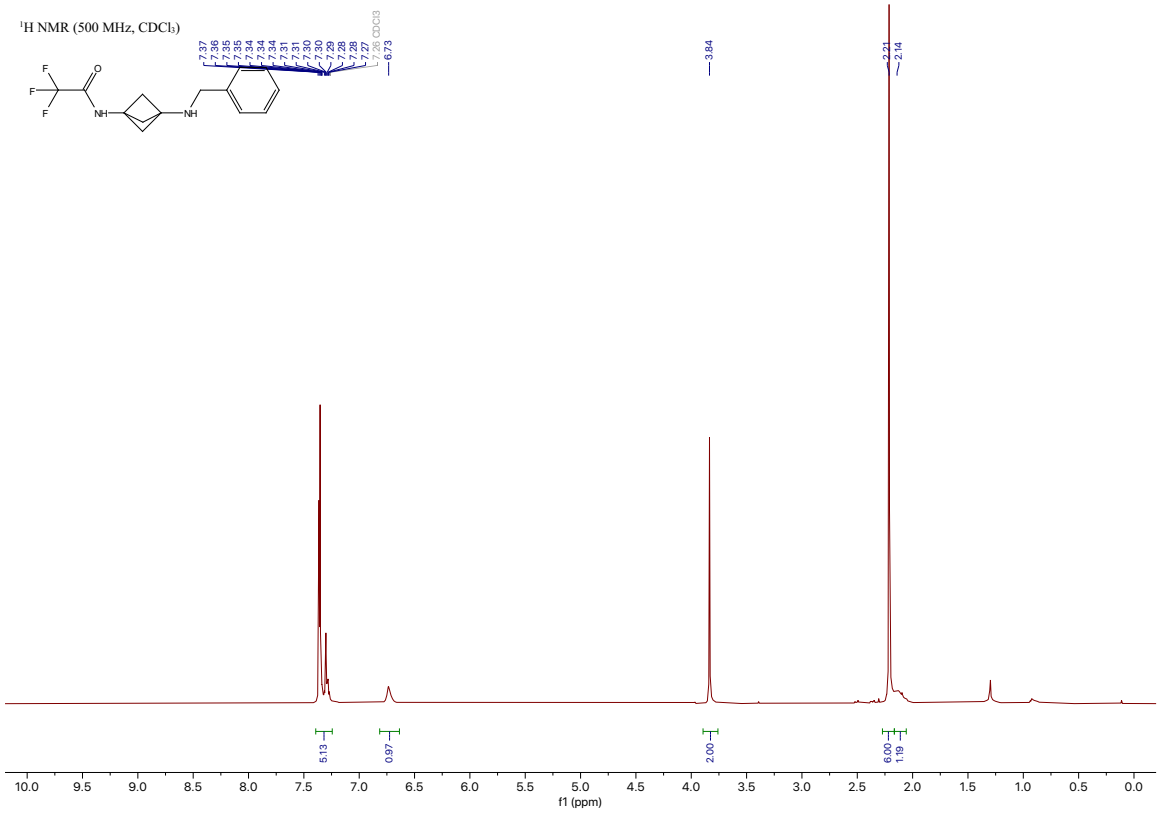
Compound 16e

N-(3-(benzylamino)bicyclo[1.1.1]pentan-1-yl)-2,2,2-trifluoroacetamide [Experimental]



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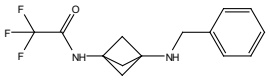
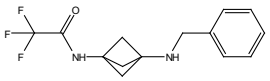
^{13}C NMR (126 MHz, $CDCl_3$)



^{19}F NMR (470 MHz, $CDCl_3$)



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