Supporting Information

Hypervalent Iodine-Mediated *β*-Difluoroalkylboron Synthesis via An Unusual 1,2-Hydrogen Shift Enabled by Boron Substitution

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content

1. General information

The solvents used were dried by distillation over the drying agents indicated in parentheses and were transferred under argon: toluene (Na-benzophenone), 1,2-dichloroethane (CaH_2). Anhydrous CH_3CN, DCM, THF and DMSO were purchased from Acros Organics and stored under argon. HF·Py (CAS: 32001-55-1) obtained from Tansoole was used unless otherwise stated. Other commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

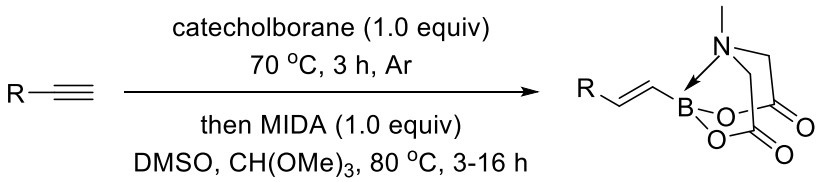
Proton (^1H), Fluorine (^{19}F), Carbon (^{13}C) were recorded at 400 MHz, 376 MHz, 101 MHz NMR spectrometer, respectively. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

No attempts were made to optimize yields for substrate synthesis.

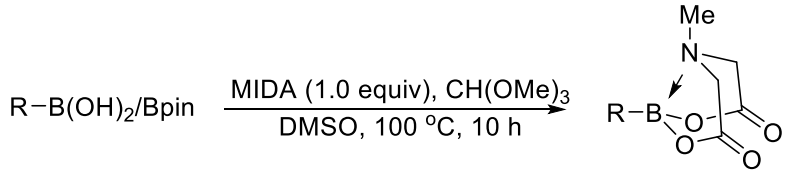
2. Synthesis of the starting materials

2.1 General procedure A:[1]



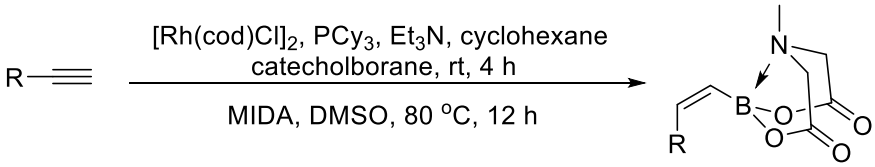
To a stirred solution of terminal alkynes (10.0 mmol) was added catecholborane (1.0 mL, 10.0 mmol) dropwise under Ar at 0 °C. The reaction was stirred at rt for 15 minutes and then heated to 70 °C for 3 h. After cooling to the room temperature, anhydrous DMSO (10 mL), $CH(OMe)_3$ (3.0 equiv) and *N*-methyliminodiacetic acid (MIDA, 10.0 mmol) were successively added under air condition. The resulting mixture was stirred at 80 °C for 3-16 h. After cooling to the room temperature, the reaction mixture was diluted with ethyl acetate (30 mL) and saturated sodium chloride solution (30 mL). The organic phase was seperated and the aqueous layer was extracted with ethyl acetate (30 mL) for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with an appropriate solvent as eluent to afford the pure product.

2.2 General procedure B:



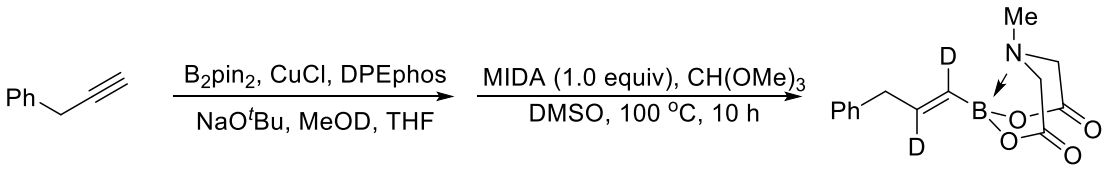
To a solution of alkenylboronic acid (10.0 mmol, 1 equiv) in anhydrous DMSO (10 mL) was successively added *N*-methyliminodiacetic acid (MIDA, 10.0 mmol), $CH(OMe)_3$ (3 equiv). The resulting mixture was stirred at 100 °C for 10 h. After cooling to the room temperature, the reaction mixture was diluted with ethyl acetate (30 mL) and saturated sodium chloride solution (30 mL). The organic phase was seperated and the aqueous layer was extracted with ethyl acetate (30 mL) for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and ethyl acetate (1:3) as eluent to afford products.

2.3 General procedure C:[2]



A flask was charged with $[Rh(cod)Cl]_2$ (0.15 mmol, 0.015 equiv) and PCy_3 (0.6 mmol, 0.06 equiv), then evacuated with Ar for three times. Cyclohexane (30.0 mL), Et_3N (10.0 mmol, 1.0 equiv) and catecholborane (10.0 mmol, 1.0 equiv) were successively added. After being stirred for 30 min, an alkyne (12.0 mmol, 1.2 equiv) was added in one portion and the mixture was stirred at rt for 4 h. Then a suspension of *N*-methyliminodiacetic acid (MIDA, 10.0 mmol) in DMSO (10 mL) was added. The resulting mixture was stirred at 80 °C for 12 h. After cooling to the room temperature, the reaction mixture was diluted with ethyl acetate (30 mL) and saturated sodium chloride solution (30 mL). The organic phase was seperated and the aqueous layer was extracted with ethyl acetate (20 mL) for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and ethyl acetate as eluent to afford products.

2.4 General procedure D:[3]

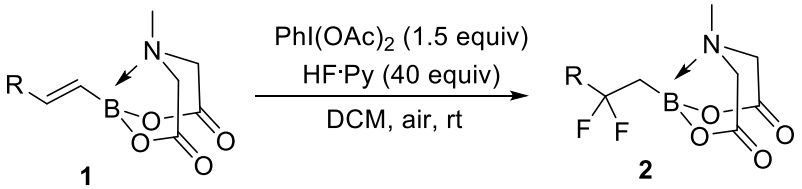


CuCl (30 mg, 0.3 mmol, 3 mol %), NaO^{t}Bu(60 mg, 0.3 mmol, 6 mol %) and DPEphos ligand (160 mg, 0.3 mmol, 3 mol %) were placed in an oven-dried Schlenkflask(100mL in volume) and THF (10 mL) were added under nitrogen. The reaction mixture was stirred for 30 min at room temperature and then, bis(pinacolato)diboron (2.79 g, 11.0 mmol,1.1 eq.) and THF (5 mL) were added. Thereaction mixture was stirred for another 10 min and the alkyne (10.0 mmol) was added, followed by MeOD (0.81 mL, 20.0 mmol, 2.0 eq.). The reaction tube was washed with THF (3 mL), sealed, and stirred until no starting material was detected by TLC. The reaction mixture was filtered through a pad of Celite and concentrated. The product was purified by silica gel chromatography.

To a solution of the resulting product (5.0 mmol, 1 equiv) in anhydrous DMSO (5 mL) was successively added *N*-methyliminodiacetic acid (MIDA, 5.0 mmol), $CH(OMe)_3$ (3 equiv). The resulting mixture was stirred at 100 °C for 10 h. After cooling to the room temperature, the reaction mixture was diluted with ethyl acetate (15 mL) and saturated sodium chloride solution (15 mL). The organic phase was seperated and the aqueous layer was extracted with ethyl acetate (15 mL) for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and ethyl acetate (1:3) as eluent to afford products.

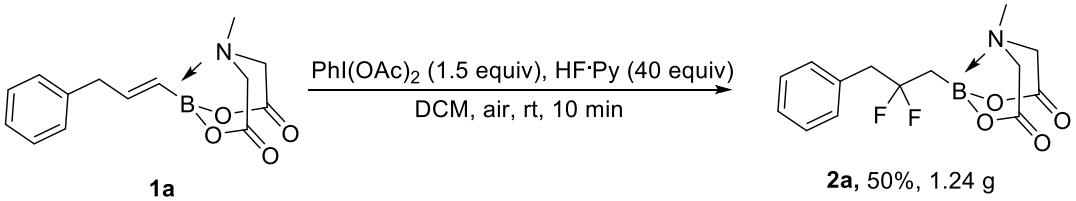
3. General procedure for the synthesis of *β*-difluorinated alkylborons

General procedure E:



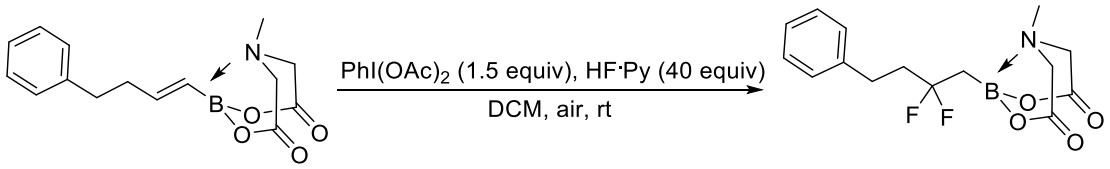
To a stirred solution of alkenyl MIDA boronates **1** (0.2 mmol, 1.0 equiv), $PhI(OAc)_2$ (0.3 mmol, 1.5 equiv) in DCM (2 mL) in a 10 mL of plastic tubing under ambient atmosphere was added HF·Py (40.0-100.0 equiv) in one portion. The reaction was allowed to stir at 25 °C until the complete consumption of boronates as monitored by TLC analysis. The reaction mixture was quenched by adding ethyl acetate (3 mL) and saturated sodium chloride solution (3 mL). The organic phase was seperated and the aqueous layer was extracted with ethyl acetate (2 mL) for two times. The combined organic layer (about 9 mL) was dried over anhydrous Na_2SO_4 and then directly purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **2**.

Gram-scale preparation



To a stirred solution of alkenyl MIDA boronates **1a** (8.0 mmol, 1.0 equiv), $PhI(OAc)_2$ (12.0 mmol, 1.5 equiv) in DCM (80 mL) in a 250 mL of plastic tubing under 0 °C was added HF·Py (40.0 equiv) in one portion. The reaction was allowed to stir at 25 °C until the complete consumption of boronates as monitored by TLC analysis. The reaction mixture was quenched under 0 °C by adding ethyl acetate (150

mL) and saturated sodium chloride solution (50 mL). The organic phase was seperated and the aqueous layer was extracted with ethyl acetate (50 mL) for two times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to 30 mL under reduced pressure and then directly purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **2a** (1.24 g, 50%).

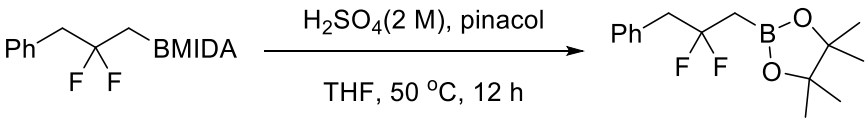


1g **2g,** 68%, 1.10 g

To a stirred solution of alkenyl MIDA boronates **1g** (5.0 mmol, 1.0 equiv), $PhI(OAc)_2$ (7.5 mmol, 1.5 equiv) in DCM (50 mL) in a 250 mL of plastic tubing under 0 °C was added HF·Py (40.0 equiv) in one portion. The reaction was allowed to stir at 25 °C until the complete consumption of boronates as monitored by TLC analysis. The reaction mixture was quenched under 0 °C by adding ethyl acetate (150 mL) and saturated sodium chloride solution (50 mL). The organic phase was seperated and the aqueous layer was extracted with ethyl acetate (50 mL) for two times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to 30 mL under reduced pressure and then directly purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **2g** (1.10 g, 68%).

4. Derivatization of the products

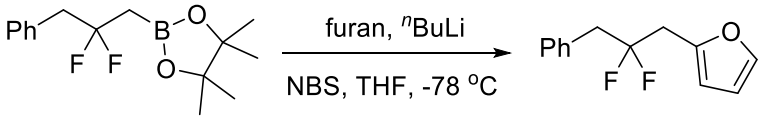
4.1 Synthesis of compound **4**:



2a **4**

To a stirred solution of **2a** (311 mg, 1.00 mmol) in THF (10 mL) was added 2 M H_2SO_4 (2.0 mmol) and pinacol (1.1 mmol) sequentially. The reaction mixture was stirred for 12 h at 50 °C before being quenched by the addition of water (10 mL). The mixture was then extracted by diethyl ether (10 mL × 3), dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude product was then purified by flash silica column chromatography (hexanes/EtOAc = 100:1) to give pure **4** (166 mg, 59%).

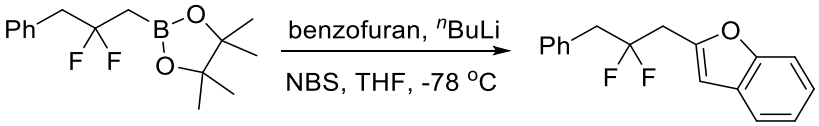
4.2 Synthesis of compound **5**:[4]



4 **5**

^{n}BuLi (2.5 M in hexanes, 0.24 mmol, 1.2 equiv) was added dropwise at –80 °C to a solution of furan (0.24 mmol, 1.2 equiv) in THF (1.0 mL).The cooling bath was removed and the mixture was stirred at room temperature for 1 h. The mixture was cooled to –80 °C and boronic ester **4** (0.2 mmol, 1.0 equiv.) was added dropwise as a solution in THF (1.0 mL). The mixture was stirred for 1 h at –80 °C and a solution of N-bromosuccinimide (0.24 mmol, 1.2 equiv.) in THF (1.0 mL) was added dropwise. After 12 h at –80 °C, a saturated aqueous solution of $Na_2S_2O_3$ was added and the reaction mixture was allowed to warm to room temperature. After addition of Et_2O and water, the layers were separated and the aqueous layer was extracted with Et_2O (3×5 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to give **5** as a colorless oil (24.4 mg, 0.11 mmol, 55%).

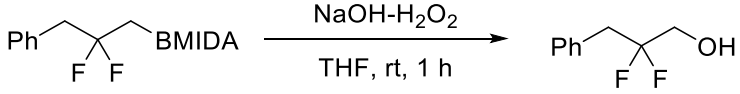
4.3 Synthesis of compound **6**:[4]



4 **6**

^{n}BuLi (2.5 M in hexanes, 0.24 mmol, 1.2 equiv) was added dropwise at –80 °C to a solution of benzofuran (0.24 mmol, 1.2 equiv) in THF (1.0 mL).The cooling bath was removed and the mixture was stirred at room temperature for 1 h. The mixture was cooled to –80 °C and boronic ester **4** (0.2 mmol, 1.0 equiv.) was added dropwise as a solution in THF (0.5 mL). The mixture was stirred for 1 h at –80 °C and a solution of N-bromosuccinimide (0.24 mmol, 1.2 equiv.) in THF (1.0 mL) was added dropwise. After 12 h at –80 °C, a saturated aqueous solution of $Na_2S_2O_3$ was added and the reaction mixture was allowed to warm to room temperature. After addition of Et_2O and water, the layers were separated and the aqueous layer was extracted with Et_2O (3×5 mL). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to give **6** as a colorless oil (19.0 mg, 0.07 mmol, 35%).

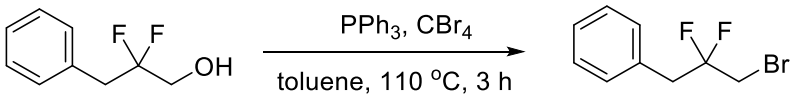
4.4 Synthesis of compound **7**:[5]



2a **7**, 87%

To a stirred solution of **2a** (0.2 mmol) in THF (2 mL) at 0 °C was successively added 0.5 mL of NaOH (3 M, 7.5 equiv) and 0.5 mL of 30% H_2O_2 dropwise. The reaction was stirred 10 minutes at 0 °C, followed by 1 hour at room temperature. Upon the completion of the reaction as determined by TLC, the mixture was cooled to 0 °C and saturated aqueous sodium thiosulfate solution (3 mL) was added dropwise. The aqueous layer was extracted with EtOAc(3×5 mL). The combined organic layers were dried over magnesium sulfate, filtered and concentrated. The crude product was purified by column chromatography on silica gel to provide **7** as a colorless oil (30 mg, 0.174 mmol, 87%).

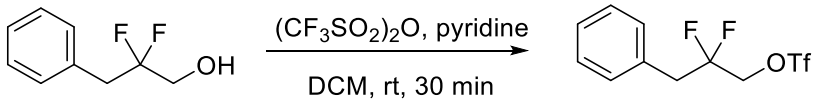
4.5 Synthesis of compound **8**:[6]



7 **8**, 77%

To a stirred solution of 2,2-difluoro-3-phenylpropan-1-ol **7** (0.67 mmol) in toluene (6.7 mL) was added triphenylphosphane (1.34 mmol) and carbon tetrabromide (1.34 mmol) at room temperature. The mixture was stirred for 3 h at 110 °C. Upon the completion of the reaction as determined by TLC, the mixture was cooled to rt before being quenched by the addition of water (20 mL). The mixture was then extracted by diethyl ether (20 mL × 3), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. After evaporation of the solvent the residue was purified by silica gel column chromatography with the solvent of petroleum ether as eluent to give bromide **8** (121 mg, 77%).

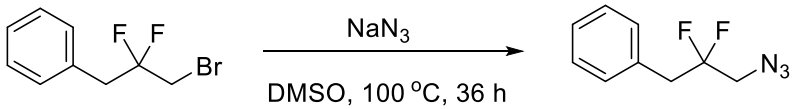
4.6 Synthesis of compound **9**:[7]



7 **9**, 54%

To a stirred solution of 2,2-difluoro-3-phenylpropan-1-ol **7** (0.6 mmol) in DCM (2 mL) at 0 °C, pyridine (0.9 mmol) and Trifluoromethanesulfonic anhydride (0.9 mmol) in DCM (2 mL) was added dropwise. Then the mixture was stirred for 30 min at room temperature. After the reaction was complete, the reaction mixture was quenched with water (5 mL). The aqueous layer was extracted three times with DCM (15 mL) and the combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent the residue was purified by neutral alumina column chromatography to give pure product **9** (99.4 mg, 54%).

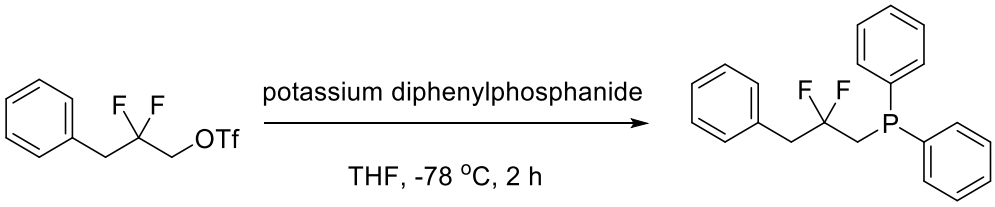
4.7 Synthesis of compound **10**:[8]



8 **10**, 43%

To a stirred solution of bromide **8** (0.11 mmol) in anhydrous DMSO (0.5 mL) in argon atmosphere was added NaN_3 (0.33 mmol). The reaction mixture was then stirred at 100 °C for 36 h. Upon the completion of the reaction as determined by TLC, the mixture was cooled to rt before being quenched by the addition of water (10 mL). The mixture was then extracted by ethyl acetate (10 mL × 3), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give azide **10** (9.2 mg, 43%).

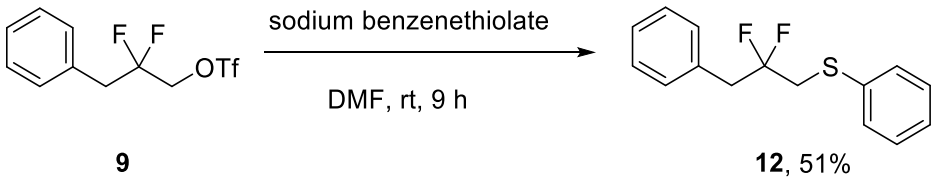
4.8 Synthesis of compound **11**:



9 **11**, 36%

To a stirred solution of sodium benzenethiolate (0.24 mmol) in anhydrous THF (2 mL) at -78 °C was added trifluoromethanesulfonate **9** (0.2 mmol) dropwise. The reaction mixture was then stirred at -78 °C for 2 h. Upon the completion of the reaction as determined by TLC, the mixture was quenched by the addition of water (10 mL). The mixture was then extracted by DCM (10 mL × 3), the combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by neutral alumina column chromatography to give the pure product **11** (24.2 mg, 36%).

4.9 Synthesis of compound **12**:

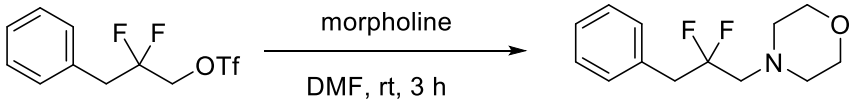


9 **12**, 51%

To a stirred solution of sodium benzenethiolate (1 mmol) in anhydrous DMF (2 mL) was added trifluoromethanesulfonate **9** (0.2 mmol) dropwise. The reaction mixture was then stirred at room temperature for 9 h. Upon the completion of the reaction as determined by TLC, the mixture was quenched by the addition of water (10 mL). The mixture was then extracted by diethyl ether (10 mL × 3), the

combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the pure product **12** (27.1 mg, 51%).

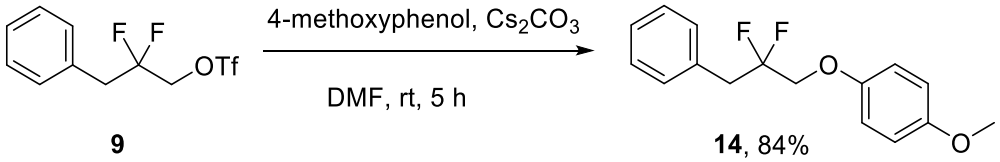
4.10 Synthesis of compound **13**:[9]



9 **13**, 84%

To a stirred solution of morpholine (0.8 mmol) in anhydrous DMF (1 mL) at 0 °C was added the trifluoromethanesulfonate **9** (0.2 mmol) dropwise. The reaction mixture was then stirred at 0 °C for 30 min, then 40 °C for 3 h. Upon the completion of the reaction as determined by TLC, the mixture was cooled to rt before being quenched by the addition of water (10 mL). The mixture was then extracted by diethyl ether (10 mL × 3), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. After evaporation of the solvent the residue was purified by flash chromatography on silica gel to give the pure product **13** (40.6 mg, 84%).

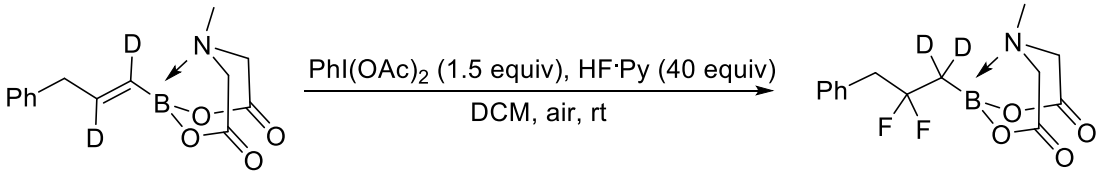
4.11 Synthesis of compound **14**:



9 **14**, 84%

To a stirred solution of benzyl 4-methoxyphenol (0.26 mmol) and Cs_2CO_3 (0.26 mmol) in anhydrous DMF (2 mL) was added trifluoromethanesulfonate **9** (0.2 mmol) dropwise. The reaction mixture was then stirred at room temperature for 5 h. Upon the completion of the reaction as determined by TLC, the mixture was quenched by the addition of water (10 mL). The mixture was then extracted by ethyl acetate (10 mL × 3), the combined organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel to give the pure product **14** (46.9 mg, 84%).

5. Deuterium labeling experiments

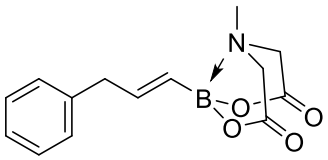


D-**1a** D-**2a**

To a stirred solution of alkenyl MIDA boronates D-**1a** (0.2 mmol, 1.0 equiv), $PhI(OAc)_2$ (0.3 mmol, 1.5 equiv) in DCM (2 mL) in a 10 mL of plastic tubing under ambient atmosphere was added HF·Py (100.0 equiv) in one portion. The reaction was allowed to stir at 25 °C 10 min. The reaction mixture was quenched by adding ethyl acetate (3 mL) and saturated sodium chloride solution (3 mL). The organic phase was seperated and the aqueous layer was extracted with ethyl acetate (2 mL) for two times. The combined organic layer (about 9 mL) was dried over anhydrous Na_2SO_4 and then directly purified by flash column chromatography on silica with the solvent of petroleum ether/EtOAc (1:2 v/v) as eluent to afford the pure product D-**2a** (45.0 mg, 72%).

6. Characterization of the starting materials and products

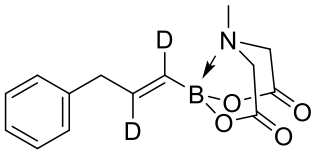
(E)-6-methyl-2-(3-phenylprop-1-en-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (1a)



1a

Following the general procedure A, the product **1a** was obtained in 68% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.27 (PE: ethyl acetate = 1:3). ^{1}H NMR (500 MHz, Acetonitrile-*d*$_3$) δ 7.30 (td, *J* = 7.8, 7.3, 2.5 Hz, 2H), 7.21 (d, *J* = 7.2 Hz, 3H), 6.30 – 6.10 (m, 1H), 5.47 (d, *J* = 17.5 Hz, 1H), 3.92 (d, *J* = 17.0 Hz, 2H), 3.75 (d, *J* = 17.0 Hz, 2H), 3.46 (d, *J* = 6.5 Hz, 2H), 2.75 (s, 3H). ^{13}C NMR (126 MHz, Acetonitrile-*d*$_3$) δ 168.94, 144.93, 140.89, 129.22, 129.02, 126.55, 61.93, 47.28, 42.00. **ESI-MS**: calcd for $C_{14}H_{16}BNO_4Na$ [M + Na]$^+$: 296.1067, found: 296.1058.

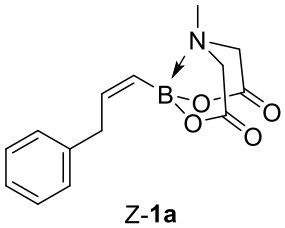
(E)-6-methyl-2-(3-phenylprop-1-en-1-yl-1,2-d2)-1,3,6,2-dioxazaborocane-4,8-dione (D-1a)



D-**1a**

Following the general procedure D, the product D-**1a** was obtained in 34% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.40 (PE: ethyl acetate = 1:3). ^{1}H NMR (500 MHz, Acetonitrile-*d*$_3$) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.24 – 7.16 (m, 3H), 3.92 (d, *J* = 17.0 Hz, 2H), 3.76 (d, *J* = 17.0 Hz, 2H), 3.45 (s, 2H), 2.75 (s, 3H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 169.66, 143.26, 140.46, 129.01, 128.87, 126.41, 61.77, 47.23, 41.54. **ESI-MS**: calcd for $C_{14}H_{14}D_2BNO_4Na$ [M + Na]$^+$: 298.1193, found: 298.1190.

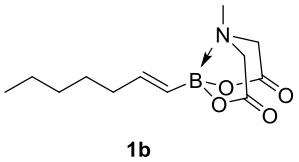
(Z)-6-methyl-2-(3-phenylprop-1-en-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (Z-1a)



Z-**1a**

Following the general procedure C, the product Z-**1a** was obtained in 50% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.32 (PE: ethyl acetate = 1:3). ^{1}H NMR (400 MHz, Acetonitrile-*d*$_3$) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.20 (dd, *J* = 17.6, 7.3 Hz, 3H), 6.42 – 6.21 (m, 1H), 5.38 (d, *J* = 13.9 Hz, 1H), 3.97 (d, *J* = 17.0 Hz, 2H), 3.81 (d, *J* = 17.1 Hz, 2H), 3.55 (d, *J* = 7.6 Hz, 2H), 2.84 (s, 3H). ^{13}C NMR (101 MHz, Acetonitrile-*d*$_3$) δ 168.88, 145.80, 141.69, 129.04, 128.96, 126.44, 62.07, 47.13, 37.33. **ESI-MS**: calcd for $C_{14}H_{16}BNO_4Na$ [M + Na]$^+$: 296.1067, found: 296.1074.

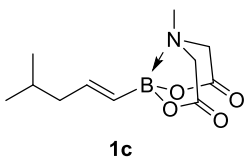
(E)-2-(hept-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1b)



1b

Following the general procedure A, the product **1b** was obtained in 56% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.34 (PE: ethyl acetate = 1:3). ^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 6.09 (dt, *J* = 17.5, 6.5 Hz, 1H), 5.47 (d, *J* = 17.6 Hz, 1H), 4.18 (d, *J* = 16.8 Hz, 2H), 3.98 (d, *J* = 16.8 Hz, 2H), 2.98 (s, 3H), 2.17 – 2.08 (m, 2H), 1.45-1.38 (m, 2H), 1.35 – 1.24 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 168.22, 145.16, 61.28, 46.43, 35.24, 31.31, 28.42, 22.30, 13.42. **ESI-MS**: calcd for $C_{12}H_{20}BNO_4Na$ [M + Na]$^+$: 276.1380, found: 276.1392.

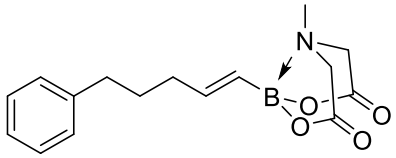
(E)-6-methyl-2-(4-methylpent-1-en-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (1c)



1c

Following the general procedure A, the product **1c** was obtained in 53% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.25 (PE: ethyl acetate = 1:3). ^{1}H NMR (500 MHz, Acetonitrile-*d*$_3$) δ 6.15 – 5.95 (m, 1H), 5.41 (d, *J* = 17.6 Hz, 1H), 3.93 (d, *J* = 17.0 Hz, 2H), 3.76 (d, *J* = 16.9 Hz, 2H), 2.76 (s, 3H), 2.02 (t, *J* = 7.2 Hz, 2H), 1.68 (dtt, *J* = 13.6, 6.8, 4.3 Hz, 1H), 0.89 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (126 MHz, Acetonitrile-*d*$_3$) δ 169.04, 145.34, 61.84, 47.25, 45.35, 28.39, 22.27. **ESI-MS**: calcd for $C_{11}H_{18}BNO_4Na$ [M + Na]$^+$: 262.1223, found: 262.1218.

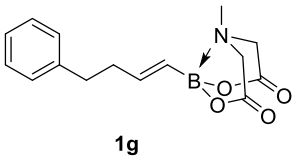
(E)-6-methyl-2-(5-phenylpent-1-en-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (1f)



1f

Following the general procedure A, the product **1f** was obtained in 57% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.33 (PE: ethyl acetate = 1:4). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.47 – 6.99 (m, 5H), 6.13 (dt, J = 17.6, 6.4 Hz, 1H), 5.50 (d, J = 17.6 Hz, 1H), 4.18 (d, J = 16.9 Hz, 2H), 3.99 (d, J = 16.9 Hz, 2H), 2.99 (s, 3H), 2.68 – 2.58 (m, 2H), 2.23 – 2.11 (m, 2H), 1.73 (p, J = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.25, 144.73, 142.48, 128.38, 128.22, 125.61, 61.29, 46.47, 35.17, 34.80, 30.68. **ESI-MS**: calcd for $C_{16}H_{20}BNO_4Na$ $[M + Na]^+$: 324.1381, found: 324.1369.

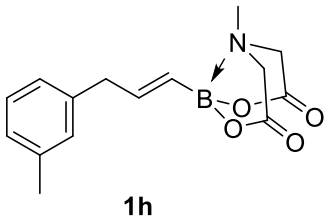
(E)-6-methyl-2-(4-phenylbut-1-en-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (1g)



1g

Following the general procedure A, the product **1g** was obtained in 61% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.28 (PE: ethyl acetate = 1:3). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.34 – 7.19 (m, 4H), 7.19 – 7.10 (m, 1H), 6.10 (dt, J = 17.6, 6.4 Hz, 1H), 5.45 (dt, J = 17.6, 1.5 Hz, 1H), 4.14 (d, J = 16.8 Hz, 2H), 3.89 (d, J = 16.8 Hz, 2H), 2.79 (s, 3H), 2.79 – 2.70 (m, 2H), 2.45 (tdd, J = 7.3, 6.4, 1.5 Hz, 2H). ^{13}C NMR (126 MHz, Acetonitril-$_{d3}$) δ 169.27, 145.72, 142.98, 129.38, 129.16, 126.59, 61.99, 47.24, 37.72, 35.47. **ESI-MS**: calcd for $C_{15}H_{18}BNO_4Na$ $[M + Na]^+$: 310.1224, found: 310.1219.

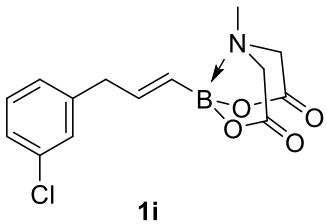
2-(2,2-difluoro-3-(m-tolyl)propyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1h)



1h

Following the general procedure A, the product **1h** was obtained in 59% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.30 (PE: ethyl acetate = 1:4). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.15 (t, J = 7.5 Hz, 1H), 7.04 – 6.94 (m, 3H), 6.21 (dt, J = 17.5, 6.5 Hz, 1H), 5.57 – 5.49 (m, 1H), 4.18 (d, J = 16.9 Hz, 2H), 3.99 (d, J = 16.9 Hz, 2H), 3.41 (dd, J = 6.6, 1.4 Hz, 2H), 2.99 (s, 3H), 2.28 (s, 3H).^{13}C NMR (126 MHz, Acetone-d_6) δ 168.18, 143.82, 140.17, 137.69, 129.34, 128.25, 126.57, 125.66, 61.39, 46.53, 41.65, 20.51. **ESI-MS**: calcd for $C_{15}H_{19}BNO_4$ $[M + H]^+$: 288.1404, found: 288.1399.

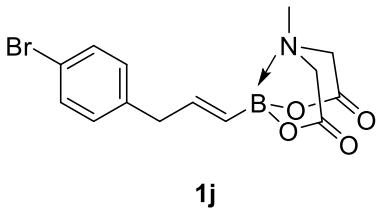
(E)-2-(3-(3-chlorophenyl)prop-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1i)



1i

Following the general procedure A, the product **1i** was obtained in 72% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.41 (PE: ethyl acetate = 1:4). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.36 – 7.13 (m, 1H), 6.20 (s, 0H), 5.57 (dt, J = 17.5, 1.6 Hz, 0H), 4.19 (d, J = 16.9 Hz, 0H), 4.00 (d, J = 16.9 Hz, 0H), 3.47 (dd, J = 6.4, 1.5 Hz, 2H), 3.00 (s, 3H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.93, 144.00, 143.31, 134.16, 130.61, 129.15, 127.80, 126.55, 61.94, 47.26, 41.43. **ESI-MS**: calcd for $C_{14}H_{16}BNO_4Cl$ $[M + H]^+$: 308.0858, found: 308.0845.

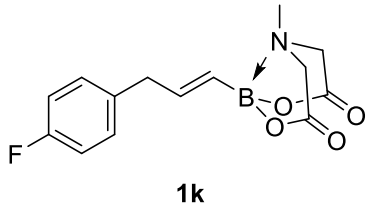
(E)-2-(3-(4-bromophenyl)prop-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1j)



1j

Following the general procedure A, the product **1j** was obtained in 59% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.40 (PE: ethyl acetate = 1:4). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.45 (d, J = 8.3 Hz, 2H), 7.18 (d, J = 8.3 Hz, 2H), 6.21 (dt, J = 17.5, 6.4 Hz, 1H), 5.54 (d, J = 17.5 Hz, 1H), 4.19 (d, J = 16.9 Hz, 2H), 4.00 (d, J = 16.9 Hz, 2H), 3.44 (d, J = 6.4 Hz, 2H) , 2.99 (s, 3H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.11 , 142.94 , 139.69 , 131.31 , 130.79 , 119.22 , 61.40 , 46.54 , 40.81 . **ESI-MS**: calcd for $C_{14}H_{15}BBrNO_4Na$ $[M + Na]^+$: 374.0172, found: 374.0160.

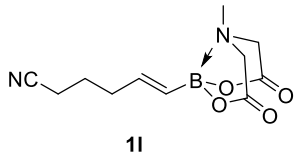
(E)-2-(3-(4-fluorophenyl)prop-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1k)



1k

Following the general procedure A, the product **1k** was obtained in 64% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.21 (PE: ethyl acetate = 1:4). ^{1}H NMR (500 MHz, Acetonitrile-*d*$_3$) δ 7.20 (dd, *J* = 8.5, 5.7 Hz, 2H), 7.08 – 6.97 (m, 2H), 6.19 (dt, *J* = 17.6, 6.4 Hz, 1H), 5.45 (d, *J* = 17.5 Hz, 1H), 3.93 (d, *J* = 16.9 Hz, 2H), 3.76 (d, *J* = 17.0 Hz, 2H), 3.46 – 3.41 (m, 2H), 2.75 (s, 3H). ^{13}C NMR (126 MHz, Acetonitrile-*d*$_3$) δ 168.95, 161.86 (d, *J* = 241.3 Hz), 144.73, 136.86 (d, *J* = 3.1 Hz), 130.89 (d, *J* = 8.1 Hz), 115.52 (d, *J* = 21.3 Hz), 61.92, 47.27, 41.02. **ESI-MS**: calcd for $C_{14}H_{15}BFNO_4Na$ [M + Na]$^+$: 314.0973, found: 314.0959.

(E)-6-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hex-5-enenitrile (1l)

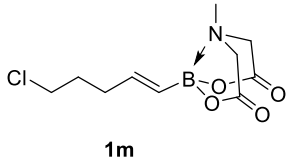


1l

Following the general procedure A, the product **1l** was obtained in 48% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.26 (ethyl acetate). ^{1}H NMR (500 MHz, Acetonitrile-*d*$_3$) δ 6.04 (dt, *J* = 17.7, 6.4 Hz, 1H), 5.50 (d, *J* = 17.7 Hz, 1H), 3.94 (d, *J* = 17.0 Hz, 2H), 3.78 (d, *J* = 17.0 Hz, 2H), 2.77 (s, 3H), 2.37 (t, *J* = 7.2 Hz, 2H), 2.24 (q, *J* = 7.1 Hz, 2H), 1.74 (p, *J* = 7.2 Hz, 2H). ^{13}C NMR (126 MHz, CD_3CN) δ 169.5, 144.5, 121.3, 62.3, 47.6, 34.9, 25.1, 16.9. **ESI-MS**: calcd for $C_{11}H_{15}BN_2O_4Na$ [M + Na]$^+$: 273.1019, found: 273.1013.

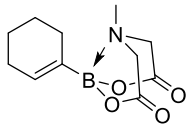
(E)-2-(5-chloropent-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1m)

Following the general procedure A, the product **1m** was obtained in 51% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.27 (PE: ethyl acetate = 1:3). ^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 6.08 (dt, *J* = 17.6, 6.5 Hz, 1H), 5.55 (dt, *J* = 17.6, 1.5 Hz, 1H), 4.19 (d, *J* = 16.9 Hz, 2H), 4.01 (d, *J* = 16.8 Hz, 2H), 3.62 (t, *J* = 6.6 Hz, 2H), 3.00 (s, 3H), 2.40 – 2.18 (m, 2H), 1.89 (p, *J* = 6.7 Hz, 2H). ^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 168.19, 143.20, 61.33, 46.45, 44.39, 32.26, 31.56. **ESI-MS**: calcd for $C_{10}H_{15}BClNO_4Na$ [M + Na]$^+$: 282.0677, found: 282.0675.



1m

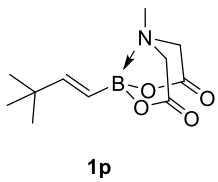
2-(cyclohex-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1n)



1n

Following the general procedure B, the product **1n** was obtained in 87% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.23 (PE: ethyl acetate = 1:3). ^{1}H NMR (400 MHz, Acetone-*d*$_6$) δ 6.06 (s, 1H), 4.17 (d, *J* = 16.9 Hz, 2H), 4.00 (d, *J* = 16.9 Hz, 2H), 2.98 (s, 3H), 2.07-2.04 (m, 4H), 1.60 (td, *J* = 3.8, 1.8 Hz, 4H). ^{13}C NMR (101 MHz, Acetone-*d*$_6$) δ 168.37, 134.80, 61.60, 46.11, 26.35, 25.99, 22.73, 22.31. **ESI-MS**: calcd for $C_{11}H_{16}BNO_4Na$ [M + Na]$^+$: 260.1067, found: 260.1064.

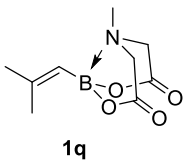
(E)-2-(3,3-dimethylbut-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1p)



1p

Following the general procedure A, the product **1p** was obtained in 47% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). *R*$_F$ = 0.29 (PE: ethyl acetate = 1:3). ^{1}H NMR (400 MHz, Acetonitrile-*d*$_3$) δ 6.10 (d, *J* = 18.0 Hz, 1H), 5.34 (d, *J* = 18.1 Hz, 1H), 3.93 (d, *J* = 17.0 Hz, 2H), 3.76 (d, *J* = 17.0 Hz, 2H), 2.74 (s, 3H), 1.02 (s, 9H). ^{13}C NMR (126 MHz, DMSO-*d*$_6$) δ 169.68, 154.96, 61.72, 47.18, 40.88, 34.43, 29.62. **ESI-MS:** calcd for $C_{11}H_{18}BNO_4Na$ [M + Na]$^+$: 262.1223, found: 262.1217.

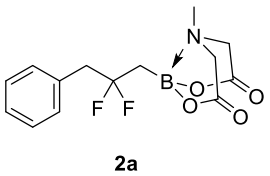
6-methyl-2-(2-methylprop-1-en-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (1q)



1q

Following the general procedure B, the product **1q** was obtained in 84% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.21 (PE: ethyl acetate = 1:3). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 5.02 (t, J = 1.3 Hz, 1H), 3.91 (d, J = 17.0 Hz, 2H), 3.75 (d, J = 16.9 Hz, 2H), 2.78 (s, 3H), 1.84 (d, J = 1.4 Hz, 3H), 1.78 (d, J = 1.2 Hz, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 169.4, 150.9, 62.4, 47.3, 29.8, 21.2. **ESI-MS**: calcd for $C_9H_{14}BNO_4Na$ $[M + Na]^+$: 220.0753, found: 220.0757.

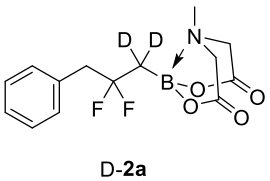
2-(2,2-difluoro-3-phenylpropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2a)



2a

Following the general procedure E, the product **2a** (**1a** as substrate, HF·Py 100.0 equiv was used, 10 min) was obtained in 61% yield (38.0 mg) and the product **2a** (Z-**1a** as substrate, HF·Py 40.0 equiv was used, 5 min) was obtained in 52% yield (32.3 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.33 (PE: ethyl acetate = 1:3). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.42 – 7.12 (m, 5H), 4.27 (d, J = 16.9 Hz, 2H), 4.03 (d, J = 16.9 Hz, 2H), 3.27 (t, J = 16.8 Hz, 2H), 3.12 (s, 3H), 1.50 (t, J = 19.1 Hz, 2H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 167.63, 134.43 (t, J = 4.2 Hz), 130.62, 128.12, 126.91, 126.03 (t, J = 239.9 Hz), 62.03, 45.97, 43.92 (t, J = 26.6 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -84.41. **ESI-MS:** calcd for $C_{14}H_{16}BF_2NO_4Na$ $[M + Na]^+$: 334.1035, found: 334.1024.

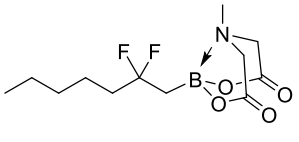
2-(2,2-difluoro-3-phenylpropyl-1,1-d2)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (D-**2a)**



D-2a

The product D-**2a** (HF·Py 100.0 equiv was used, 10 min) was obtained in 72% yield (45.0 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.29 (PE: ethyl acetate = 1:3). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.98 – 7.05 (m, 5H), 4.27 (d, J = 16.9 Hz, 2H), 4.03 (d, J = 16.9 Hz, 2H), 3.27 (t, J = 16.8 Hz, 2H), 3.11 (s, 3H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 167.66, 134.43 (t, J = 4.3 Hz), 130.62, 128.12, 126.91, 126.02 (t, J = 239.6 Hz), 62.03, 45.97, 43.91 (td, J = 26.4, 1.8 Hz). **ESI-MS:** calcd for $C_{14}H_{14}D_2BF_2NO_4Na$ $[M + Na]^+$: 336.1161, found: 336.1156.

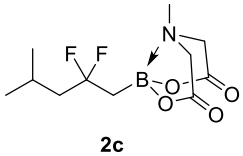
2-(2,2-difluoroheptyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2b)



2b

Following the general procedure E, the product **2b** (HF·Py 100.0 equiv was used, 10 min) was obtained in 56% yield (32.6 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.33 (PE: ethyl acetate = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.21 (d, J = 17.0 Hz, 2H), 3.97 (d, J = 17.0 Hz, 2H), 2.86 (s, 3H), 1.94 – 1.76 (m, 2H), 1.49 – 1.34 (m, 4H), 1.29 (dt, J = 7.7, 4.1 Hz, 4H), 0.93 – 0.83 (m, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 167.78, 127.12 (t, J = 238.3 Hz), 61.88, 45.85, 37.94 (t, J = 25.9 Hz), 31.41, 22.23 (t, J = 4.4 Hz), 13.37. ^{19}F NMR (376 MHz, Acetone-d_6) δ -84.91. **ESI-MS:** calcd for $C_{12}H_{20}BF_2NO_4Na$ $[M + Na]^+$: 314.1348, found: 314.1350.

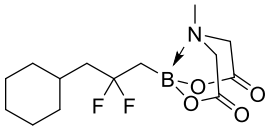
2-(2,2-difluoro-4-methylpentyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2c)



2c

Following the general procedure E, the product **2c** (HF·Py 100.0 equiv was used, 10 min) was obtained in 53% yield (29.4 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.35 (PE: ethyl acetate = 1:3). ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.21 (d, J = 17.0 Hz, 0H), 3.97 (d, J = 17.0 Hz, 0H), 2.87 (s, 1H), 1.89 (dt, J = 13.0, 6.5 Hz, 0H), 1.78 (td, J = 17.8, 6.3 Hz, 0H), 1.41 (t, J = 19.2 Hz, 0H), 0.93 (d, J = 6.5 Hz, 1H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 167.69, 127.34 (t, J = 239.1 Hz), 61.89, 46.12 (t, J = 25.1 Hz), 45.86, 23.32 (t, J = 3.7 Hz), 22.93. ^{19}F NMR (376 MHz, Acetone-d_6) δ -82.57. **ESI-MS:** calcd for $C_{11}H_{18}BF_2NO_4Na$ $[M + Na]^+$: 300.1191, found: 300.1183.

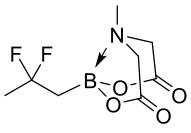
2-(3-cyclohexyl-2,2-difluoropropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2d)



2d

Following the general procedure E, the product **2d** (PIFA, HF·Py CAS: 62778-11-4 40.0 equiv was used, 1 min) was obtained in 33% yield (20.9 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.33 (PE: ethyl acetate = 1:3). ^{1}H NMR (500 MHz, Acetonitrile-*d3*) δ 3.95 (d, *J* = 17.0 Hz, 2H), 3.79 (d, *J* = 17.0 Hz, 2H), 2.88 (s, 3H), 1.87 – 1.74 (m, 4H), 1.65 (dd, *J* = 25.6, 13.3 Hz, 4H), 1.46 (t, *J* = 19.6 Hz, 2H), 1.35 – 1.11 (m, 3H), 0.99 (q, *J* = 13.5, 12.4 Hz, 2H).^{13}C NMR (126 MHz, Acetone-*d6*) δ 167.57, 127.45 (t, *J* = 239.1 Hz), 62.34(t, *J* = 4.3 Hz), 61.91, 45.87, 45.07 (t, *J* = 24.5 Hz), 33.76, 32.63 (t, *J* = 3.0 Hz), 26.01. ^{19}F NMR (376 MHz, Acetone-*d6*) δ -82.02. **ESI-MS:** calcd for $C_{14}H_{22}BF_2NO_4Na$ [M + Na]$^+$: 340.1505, found: 340.1501.

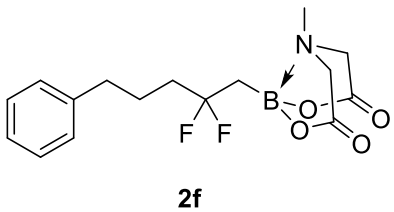
2-(2,2-difluoropropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2e)



2e

Following the general procedure E, the product **2e** (HF·Py 40.0 equiv was used, 5 min) was obtained in 80% yield (37.6 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.18 (PE: ethyl acetate = 1:3). ^{1}H NMR (500 MHz, Acetonitrile-*d3*) δ 3.97 (d, *J* = 17.0 Hz, 2H), 3.80 (d, *J* = 17.0 Hz, 2H), 2.89 (s, 3H), 1.68 (d, *J* = 18.8 Hz, 2H), 1.49 (t, *J* = 18.6 Hz, 2H). ^{13}C NMR (126 MHz, Acetone-*d6*) δ 167.59, 126.02 (t, *J* = 235.7 Hz), 61.89, 45.86, 24.62 (t, *J* = 28.5 Hz). ^{19}F NMR (376 MHz, Acetone-*d6*) δ -76.97. **ESI-MS:** calcd for $C_8H_{12}BF_2NO_4Na$ [M + Na]$^+$: 258.0721, found: 258.0724.

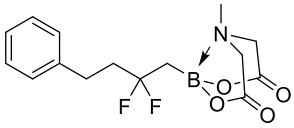
2-(2,2-difluoro-5-phenylpentyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2f)



2f

Following the general procedure E, the product **2f** (HF·Py 40.0 equiv was used, 30 min) was obtained in 62% yield (42.0 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.38 (PE: ethyl acetate = 1:4). ^{1}H NMR (400 MHz, Acetone-*d6*) δ 7.45 – 7.00 (m, 5H), 4.21 (d, *J* = 17.0 Hz, 2H), 3.97 (d, *J* = 17.0 Hz, 2H), 2.85 (s, 3H), 2.60 (t, *J* = 7.7 Hz, 2H), 1.88 (td, *J* = 16.3, 8.7 Hz, 2H), 1.71 (q, *J* = 8.3 Hz, 2H), 1.41 (t, *J* = 19.2 Hz, 2H). ^{13}C NMR (101 MHz, Acetone-*d6*) δ 167.66, 142.04, 128.36, 128.29, 127.01 (t, *J* = 238.6 Hz),125.76, 61.87, 45.81, 37.65 (t, *J* = 26.1 Hz), 35.23, 24.75 (t, *J* = 4.7 Hz). ^{19}F NMR (376 MHz, Acetone-*d6*) δ -83.25. **ESI-MS:** calcd for $C_{16}H_{20}BF_2NO_4Na$ [M + Na]$^+$: 362.1349, found: 362.1338.

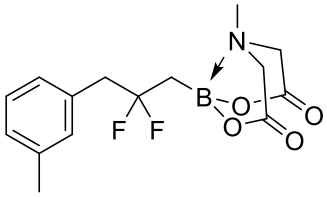
2-(2,2-difluoro-4-phenylbutyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2g)



2g

Following the general procedure E, the product **2g** (HF·Py 100.0 equiv was used, 10 min) was obtained in 76% yield (49.4 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.35 (PE: ethyl acetate = 1:3). ^{1}H NMR (400 MHz, Acetone-*d6*) δ 7.22 – 7.01 (m, 5H), 4.13 (d, *J* = 16.9 Hz, 2H), 3.93 (d, *J* = 16.9 Hz, 2H), 3.05 (s, 3H), 2.66 – 2.61 (m, 2H), 2.20 – 2.04 (m, 2H), 1.47 (t, *J* = 18.9 Hz, 2H). ^{13}C NMR (101 MHz, Acetonitrile-*d3*) δ 168.43, 141.82, 129.06, 128.90, 127.30 (t, *J* = 238.83 Hz), 126.61, 62.41, 46.61, 40.58 (t, *J* = 26.0 Hz), 29.26 (t, *J* = 5.3 Hz). ^{19}F NMR (471 MHz, Acetone-*d6*) δ -84.92. **ESI-MS:** calcd for $C_{15}H_{18}BF_2NO_4Na$ [M + Na]$^+$: 348.1192, found: 348.1191.

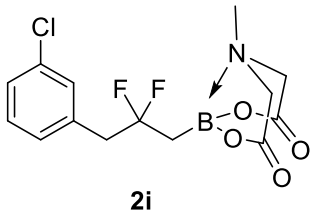
2-(2,2-difluoro-3-(m-tolyl)propyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2h)



2h

Following the general procedure E, the product **2h** (HF·Py 40.0 equiv was used, 10 min) was obtained in 60% yield (39.1 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.30 (PE: ethyl acetate = 1:4). ^{1}H NMR (400 MHz, Acetonitrile-*d3*) δ 7.21 (t, *J* = 7.5 Hz, 1H), 7.14 – 6.95 (m, 3H), 3.98 (d, *J* = 17.2 Hz, 2H), 3.79 (d, *J* = 17.0 Hz, 2H), 3.20 (t, *J* = 17.0 Hz, 2H), 2.84 (s, 3H), 2.32 (s, 3H), 1.43 (t, *J* = 19.6 Hz, 2H). ^{13}C NMR (101 MHz, Acetonitrile-*d3*) δ 168.43, 138.45, 134.73 (t, *J* = 4.0 Hz), 131.89, 128.70, 128.27, 128.20, 126.64 (t, *J* = 239.7 Hz), 62.51, 46.66, 44.54 (t, *J* = 26.5 Hz), 20.96. ^{19}F NMR (376 MHz, Acetonitrile-*d3*) δ -85.24. **ESI-MS:** calcd for $C_{15}H_{18}BF_2NO_4Na$ [M + Na]$^+$: 348.1192, found: 348.1196.

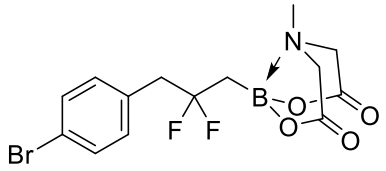
2-(3-(3-chlorophenyl)-2,2-difluoropropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2i)



2i

Following the general procedure E, the product **2i** (HF·Py CAS: 62778-11-4 100.0 equiv was used, 1 min) was obtained in 57% yield (39.3 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.38 (PE: ethyl acetate = 1:4). ^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 7.28 –7.16 (m, 4H), 3.91 (d, J = 17.1 Hz, 2H), 3.72 (d, J = 17.0 Hz, 2H), 3.17 (t, J = 16.9 Hz, 2H), 2.77 (s, 3H), 1.37 (t, J = 19.6 Hz, 2H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.42, 137.08 (t, J = 4.0 Hz), 133.98, 131.00, 130.40, 129.74, 127.68, 126.25(t, J = 239.9 Hz), 62.49, 46.68, 44.10 (t, J = 26.7 Hz). ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -85.46. **ESI-MS:** calcd for $C_{14}H_{15}BF_2NO_4ClNa$[M + Na]$^+$: 368.0646, found: 368.0647.

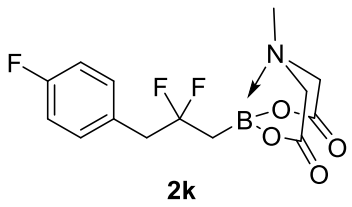
2-(3-(4-bromophenyl)-2,2-difluoropropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2j)



2j

Following the general procedure E, the product **2j** (HF·Py 100.0 equiv was used, 1 min) was obtained in 53% yield (41.2 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.31 (PE: ethyl acetate = 1:4). The compound was synthesized according to a procedure by K. J. Szabó et al[10]. ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.49 (dd, J = 9.0, 2.6 Hz, 2H), 7.23 (dd, J = 8.2, 5.7 Hz, 2H), 3.98 (d, J = 17.0 Hz, 2H), 3.79 (d, J = 17.1 Hz, 2H), 3.22 (t, J = 16.9 Hz, 2H), 2.84 (s, 3H), 1.43 (t, J = 19.5 Hz, 2H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.38, 134.16 (t, J = 4.2 Hz), 133.19, 131.79, 126.27 (t, J = 240.0 Hz), 121.20, 62.49, 46.67, 43.90 (t, J = 26.6 Hz). ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -85.53. **ESI-MS:** calcd for $C_{14}H_{15}BF_2NO_4BrNa$ [M + Na]$^+$: 412.0140, found: 412.0133.

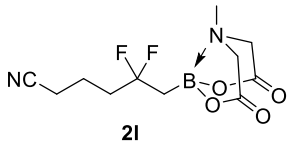
2-(2,2-difluoro-3-(4-fluorophenyl)propyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2k)



2k

Following the general procedure E, the product **2k** (HF·Py 40.0 equiv was used, 5 min) was obtained in 76% yield (50.0 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.25 (PE: ethyl acetate = 1:4). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.26 – 7.18 (m, 2H), 7.07 – 6.82 (m, 2H), 3.90 (d, J = 17.1 Hz, 2H), 3.72 (d, J = 17.0 Hz, 2H), 3.16 (t, J = 17.0 Hz, 2H), 2.77 (s, 3H), 1.35 (t, J = 19.4 Hz, 2H). ^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 168.43, 162.62 (d, J = 242.9 Hz), 132.96 (d, J = 8.2 Hz), 130.90 (d, J = 3.7 Hz), 126.46 (t, J = 239.7 Hz), 115.44 (d, J = 21.4 Hz), 62.52, 46.69, 43.70 (t, J = 26.6 Hz). ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -85.77, -117.64. **ESI-MS:** calcd for $C_{14}H_{16}BF_3NO_4$ [M + H]$^+$: 330.1122, found: 330.1111.

5,5-difluoro-6-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hexanenitrile (2l)

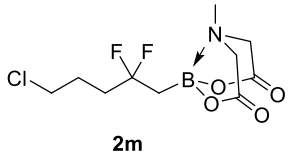


2l

Following the general procedure E, the product **2l** (HF·Py 40.0 equiv was used, 15 min) was obtained in 63% yield (36.3 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.52 (ethyl acetate: acetone = 3:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 4.22 (d, J = 17.0 Hz, 1H), 3.98 (d, J = 17.0 Hz, 1H), 2.56 (t, J = 7.2 Hz, 1H), 1.99 (dq, J = 15.4, 8.1 Hz, 1H), 1.77 – 1.67 (m, 1H), 1.44 (t, J = 19.2 Hz, 1H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 167.64, 126.47 (t, J = 238.9 Hz), 119.44, 61.88, 45.86, 36.77 (t, J = 26.4 Hz), 19.08 (t, J = 5.1 Hz), 16.03. ^{19}F NMR (471 MHz, Acetone-d_6) δ -85.49. **ESI-MS:** calcd for $C_{11}H_{15}BF_2N_2O_4Na$ [M + Na]$^+$: 311.0987, found: 311.0998.

2-(5-chloro-2,2-difluoropentyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2m)

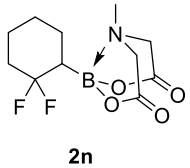
Following the general procedure E, the product **2m** (**1m** as substrate, HF·Py 40.0 equiv was used, 4 h) was obtained in 71% yield (42.2 mg) as a white solid after column chromatography (eluent = Petroleum



2m

ether/ ethyl acetate 1:2 v/v). R_F = 0.22 (PE: ethyl acetate = 1:3). ^{1}H NMR (500 MHz, Acetone-d_6) δ 4.25 (d, J = 16.9 Hz, 2H), 4.04 (d, J = 16.9 Hz, 2H), 3.64 (t, J = 6.6 Hz, 2H), 3.17 (s, 3H), 1.98 (dq, J = 17.2, 8.5 Hz, 2H), 1.83 (p, J = 7.1 Hz, 2H), 1.63 (p, J = 8.4, 7.5 Hz, 2H), 1.54 (t, J = 19.0 Hz, 2H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.42, 127.38 (t, J = 238.5 Hz), 62.42, 46.64, 45.28, 36.00 (t, J = 26.3 Hz), 26.38 (t, J = 4.8 Hz). ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -86.03. **ESI-MS:** calcd for $C_{10}H_{15}BClF_2NO_4Na$ [M + Na]$^+$: 320.0645, found: 320.0636.

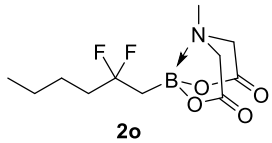
2-(2,2-difluorocyclohexyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2n)



2n

Following the general procedure E, the product **2n** (HF·Py 100.0 equiv was used, 1 min) was obtained in 31% yield (17.1 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.36 (PE: ethyl acetate = 1:3). ^{1}H NMR (400 MHz, Acetone-d_6) δ 4.27 (d, J = 17.2 Hz, 1H), 4.16 (dt, J = 16.5, 1.5 Hz, 1H), 4.06 (d, J = 17.2 Hz, 1H), 3.88 (d, J = 16.6 Hz, 1H), 3.17 (s, 3H), 1.87 – 1.49 (m, 8H), 1.37 (ddd, J = 16.4, 8.8, 4.1 Hz, 1H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.11, 167.02, 127.26(t, J = 241.1 Hz), 62.99, 61.77 (t, J = 2.9 Hz), 45.89 (t, J = 3.3 Hz), 33.91 (t, J = 24.8 Hz), 25.95 (t, J = 5.2 Hz), 23.75, 23.28 (t, J = 5.1 Hz). ^{19}F NMR (471 MHz, Acetone-d_6) δ -83.56, -84.07. **ESI-MS:** calcd for $C_{11}H_{16}BF_2NO_4Na$ [M + Na]$^+$: 298.1035, found: 298.1033.

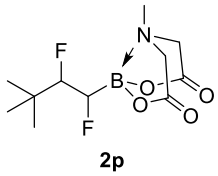
2-(2,2-difluorohexyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2o)



2o

Following the general procedure E, the product **2o** (*Z*-**1o** as substrate, HF·Py 40.0 equiv was used, 1 h) was obtained in 57% yield (31.5 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.37 (PE: ethyl acetate = 1:3). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 3.96 (d, J = 17.0 Hz, 2H), 3.80 (d, J = 17.0 Hz, 2H), 2.89 (s, 3H), 1.97 (t, J = 14.7 Hz, 2H), 1.56 – 1.31 (m, 6H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, Acetonitril-d_3) δ 168.48, 127.90 (t, J = 238.0 Hz), 62.40, 46.60, 38.31 (t, J = 25.9 Hz), 25.16, 22.73, 13.75. ^{19}F NMR (471 MHz, Acetonitril-d_3) δ -85.45. **ESI-MS:** calcd for $C_{11}H_{18}BF_2NO_4Na$ [M + Na]$^+$: 300.1191, found: 300.1188.

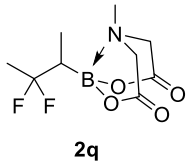
2-(1,2-difluoro-3,3-dimethylbutyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2p)



2p

Following the general procedure E, the product **2p** (PIFA, HF·Py CAS: 62778-11-4 40.0 equiv was used, 5 min) was obtained in 51% yield (28.2 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.37 (PE: ethyl acetate = 1:3). ^{1}H NMR (400 MHz, Acetone-d_6) δ 4.27 (d, J = 17.3 Hz, 1H), 4.14 (dd, J = 16.5, 4.4 Hz, 1H), 4.04 (d, J = 17.3 Hz, 1H), 3.87 (dd, J = 16.6, 1.8 Hz, 1H), 3.11 (s, 3H), 1.61 (d, J = 15.6 Hz, 1H), 1.42 (t, J = 22.0 Hz, 9H), 1.04 (dd, J = 44.3, 15.6 Hz, 1H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.32, 167.37, 103.03 – 97.07 (m), 62.66, 62.00 (d, J = 7.3 Hz), 46.17 (d, J = 4.0 Hz), 22.09 (dd, J = 24.7, 5.4 Hz), 21.33 (ddd, J = 30.1, 25.4, 5.4 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -150.34 (d, J = 12.9 Hz), -153.69 (d, J = 12.8 Hz). **ESI-MS:** calcd for $C_{11}H_{18}BF_2NO_4Na$ [M + Na]$^+$: 300.1191, found: 300.1186.

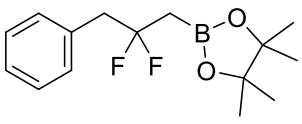
2-(3,3-difluorobutan-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2q)



2q

Following the general procedure E, the product **2q** (HF·Py 20.0 equiv was used, 30 min) was obtained in 73% yield (36.4 mg) as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:2 v/v). R_F = 0.43 (PE: ethyl acetate = 3:1). ^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 3.99 (d, J = 17.4 Hz, 1H), 3.94 (d, J = 16.8 Hz, 1H), 3.85 (dd, J = 17.2, 1.4 Hz, 1H), 3.78 (d, J = 16.9 Hz, 1H), 2.94 (s, 3H), 1.71 – 1.57 (m, 4H), 1.04 (d, J = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.00, 167.36, 128.54 (dd, J = 239.2, 236.9 Hz), 62.95, 62.18 (d, J = 3.3 Hz), 45.95 (d, J = 3.2 Hz), 21.26 (t, J = 28.6 Hz), 10.88 (dd, J = 9.6, 4.4 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -81.31 (d, J = 239.7 Hz), -83.85 (d, J = 239.6 Hz). **ESI-MS:** calcd for $C_9H_{14}BF_2NO_4Na$ [M + Na]$^+$: 272.0878, found: 272.0880.

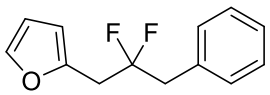
2-(2,2-difluoro-3-phenylpropyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4)



4

The product **4** was obtained in 59% yield (166 mg) as a colorless oil after column chromatography (eluent = Petroleum ether/ ethyl acetate 100:1 v/v). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.29 (m, 5H), 3.29 (t, *J* = 15.8 Hz, 2H), 1.52 (t, *J* = 18.6 Hz, 2H), 1.32 (s, 12H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 134.18 (t, *J* = 4.9 Hz), 130.45, 128.34, 127.16, 124.80 (t, *J* = 241.0 Hz), 83.86, 44.07 (t, *J* = 26.5 Hz), 24.77. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -84.51. **ESI-MS:** calcd for $C_{15}H_{21}BF_2O_2Na$ $[M + Na]^+$: 305.1498. found: 305.1504.

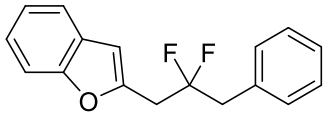
2-(2,2-difluoro-3-phenylpropyl)furan (5)



5

The product **5** was obtained in 55% yield (24.4 mg) as a colorless oil after column chromatography (eluent = Petroleum ether/ ethyl acetate 100:1 v/v). R_F = 0.28 (PE). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.40 (m, 1H), 7.41-7.28 (m, 5H), 6.37 (dd, *J* = 3.5, 1.8 Hz, 1H), 6.25 (d, *J* = 3.2 Hz, 1H), 3.16 (t, *J* = 15.0 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.51 (t, *J* = 6.3 Hz), 141.19, 131.95 (t, *J* = 4.3 Hz), 129.49, 127.40, 126.36, 121.16 (t, *J* = 244.1 Hz), 109.61, 108.24, 41.11 (t, *J* = 25.3 Hz), 34.05 (t, *J* = 28.3 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -94.55. **ESI-MS:** calcd for $C_{13}H_{13}F_2O$ $[M + H]^+$: 223.0929. found: 223.0928.

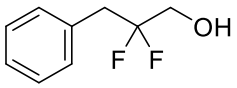
2-(2,2-difluoro-3-phenylpropyl)benzofuran (6)



6

The product **6** was obtained in 35% yield (19.0 mg) as a colorless oil after column chromatography (eluent = Petroleum ether/ ethyl acetate 100:1 v/v). R_F = 0.21 (PE). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.65 – 7.55 (m, 1H), 7.51– 7.48 (m, 1H), 7.40 – 7.20 (m, 7H), 6.73 (s, 1H), 3.39 (t, *J* = 15.8 Hz, 2H), 3.30 (t, *J* = 17.0 Hz, 2H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 154.97, 150.96, 133.21 (t, *J* = 4.1 Hz), 130.60, 128.64, 128.33, 127.29, 124.14, 124.03, 122.20 (t, *J* = 243.7 Hz), 120.26, 110.82, 106.26, 42.10 (t, *J* = 24.9 Hz), 35.35 (t, *J* = 27.6 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -95.66. **EI-MS:** calcd for $C_{17}H_{14}F_2O$: 272.1007, found: 272.1010.

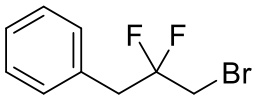
2,2-difluoro-3-phenylpropan-1-ol (7)



7

The product **7** was obtained in 87% yield (30.0 mg) as a colorless oil after column chromatography (eluent = Petroleum ether/ ethyl acetate 50:1 v/v). R_F = 0.57 (PE: ethyl acetate = 6:1). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 – 7.28 (m, 5H), 3.67 (td, *J* = 12.5, 6.9 Hz, 2H), 3.26 (t, *J* = 16.4 Hz, 2H), 1.91 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 132.67 (t, *J* = 4.8 Hz), 130.39, 128.56, 127.48, 122.40 (t, *J* = 243.5 Hz), 63.15 (t, *J* = 31.7 Hz), 39.72 (t, *J* = 24.7 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -106.92. **EI-MS:** calcd for $C_9H_{10}F_2O$: 172.0694, found: 172.0693.

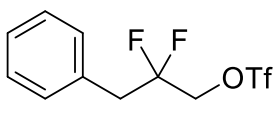
(3-bromo-2,2-difluoropropyl)benzene (8)



8

The product **8** was obtained in 77% yield (121 mg) as a colourless solid after column chromatography (eluent = Petroleum ether). R_F = 0.52 (PE). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.42 – 7.24 (m, 5H), 3.62 (t, *J* = 14.0 Hz, 2H), 3.37 (t, *J* = 16.6 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 132.24 (t, *J* = 5.0 Hz), 130.27, 128.71, 127.80, 120.76 (t, *J* = 244.3 Hz), 40.72 (t, *J* = 25.0 Hz), 30.56 (t, *J* = 33.4 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -98.94 . **EI-MS:** calcd for $C_9H_9BrF_2$: 233.9850, 235.9830. found: 233.9852, 235.9831.

2,2-difluoro-3-phenylpropyl trifluoromethanesulfonate (9)

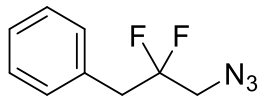


9

The product **9** was obtained in 54% yield (99.4 mg) as a brown liquid after column chromatography (eluent = Petroleum ether/ ethyl acetate 20:1 v/v). R_F = 0.61 (PE: ethyl acetate = 15:1). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.46 – 7.03 (m, 5H), 4.95 (t, *J* = 12.8 Hz, 2H), 3.45 (t, *J* = 17.3 Hz, 2H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 131.33 (t, *J* = 3.9 Hz), 130.50, 128.59, 127.77, 119.13 (t, *J* = 244.6 Hz), 118.51

(q, J = 318.6 Hz) , 73.60 (t, J = 29.5 Hz), 39.21 (t, J = 23.2 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -75.74 – -75.82 (m), -107.29 – -107.32 (m). **EI-MS:** calcd for $C_{10}H_9F_5O_3S$: 304.0187, found: 304.0188.

(3-azido-2,2-difluoropropyl)benzene (10)

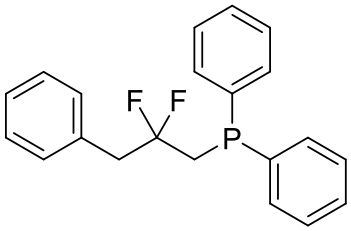


10

The product **10** was obtained in 43% yield (9.2 mg) as a colourless liquid after column chromatography (eluent = Petroleum ether). R_F = 0.45 (PE). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.26 (m, 5H), 3.37 (t, J = 12.7 Hz, 2H), 3.25 (t, J = 16.1 Hz, 2H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 133.40 (t, J = 4.4 Hz), 131.32 , 129.31 , 128.32 , 123.19 (t, J = 243.9 Hz), 53.82 (t, J = 29.2 Hz), 40.97 (t, J = 24.2 Hz). ^{19}F NMR (376 MHz, Acetone-d_6) δ -102.77. **EI-MS:** calcd for $C_9H_8NF_2$[M - N_2H]: 168.0619, found: 168.0620.

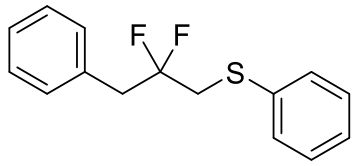
(2,2-difluoro-3-phenylpropyl)diphenylphosphane (11)

The product **11** was obtained in 36% yield (24.2 mg) as a colourless liquid after column chromatography (eluent = Petroleum ether). R_F = 0.28 (PE). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.47 – 7.26 (m, 15H), 3.35 (t, J = 16.7 Hz, 2H), 2.74 (td, J = 17.6, 1.9 Hz, 2H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 138.41 (d, J = 11.6 Hz), 134.05 (t, J = 4.2 Hz), 133.15 (d, J = 20.5 Hz), 131.12 , 129.59 , 129.18 (d, J = 7.3 Hz), 128.92 , 127.89 , 124.97 (td, J = 241.5, 13.4 Hz), 43.75 (td, J = 25.5, 4.9 Hz), 36.60 (td, J = 25.2, 19.0 Hz). ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -88.50 (d, J = 21.1 Hz). ^{31}P NMR (162 MHz, Acetonitrile-d_3) δ -27.42 (tt, J = 21.5, 8.2 Hz). **ESI-MS:** calcd for $C_{21}H_{20}F_2P$ $[M + H]^+$: 341.1265, found: 341.1252.



11

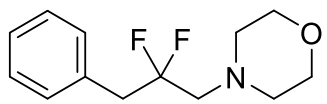
(2,2-difluoro-3-phenylpropyl)(phenyl)sulfane (12)



12

The product **12** was obtained in 51% yield (27.1 mg) as a colourless liquid after column chromatography (eluent = Petroleum ether). R_F = 0.37 (PE). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.47 – 7.23 (m, 10H), 3.35 (t, J = 15.9 Hz, 2H), 3.23 (t, J = 13.9 Hz, 2H).^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 135.83 , 133.53 (t, J = 4.1 Hz), 131.06 , 130.42 , 129.69 , 128.97 , 127.96 , 127.44 , 123.69 (t, J = 242.9 Hz), 41.80 (t, J = 25.0 Hz), 39.49 (t, J = 28.2 Hz). ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -96.16. **EI-MS:** calcd for $C_{15}H_{14}F_2S$: 264.0779, found: 264.0782.

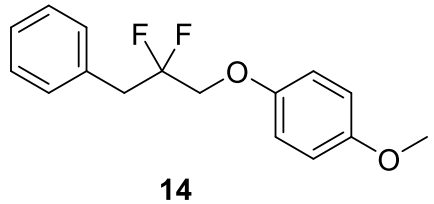
4-(2,2-difluoro-3-phenylpropyl)morpholine (13)



13

The product **13** was obtained in 84% yield (40.6 mg) as a yellow liquid after column chromatography (eluent = Petroleum ether/ ethyl acetate 20:1 v/v). R_F = 0.29 (PE: ethyl acetate = 15:1). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.44 – 7.19 (m, 5H), 3.80 – 3.50 (m, 4H), 3.29 (t, J = 17.1 Hz, 2H), 2.59 (t, J = 13.9 Hz, 2H), 2.52 – 2.49 (m, 4H). ^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 134.30 (t, J = 4.3 Hz), 131.17 , 128.82 , 127.69 , 125.15 (t, J = 242.2 Hz), 67.18 , 61.35 (t, J = 28.1 Hz), 54.80 , 40.90 (t, J = 24.5 Hz). ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -97.54. **ESI-MS:** calcd for $C_{13}H_{18}NOF_2$ $[M + H]^+$: 242.1351, found: 242.1348.

1-(2,2-difluoro-3-phenylpropoxy)-4-methoxybenzene (14)

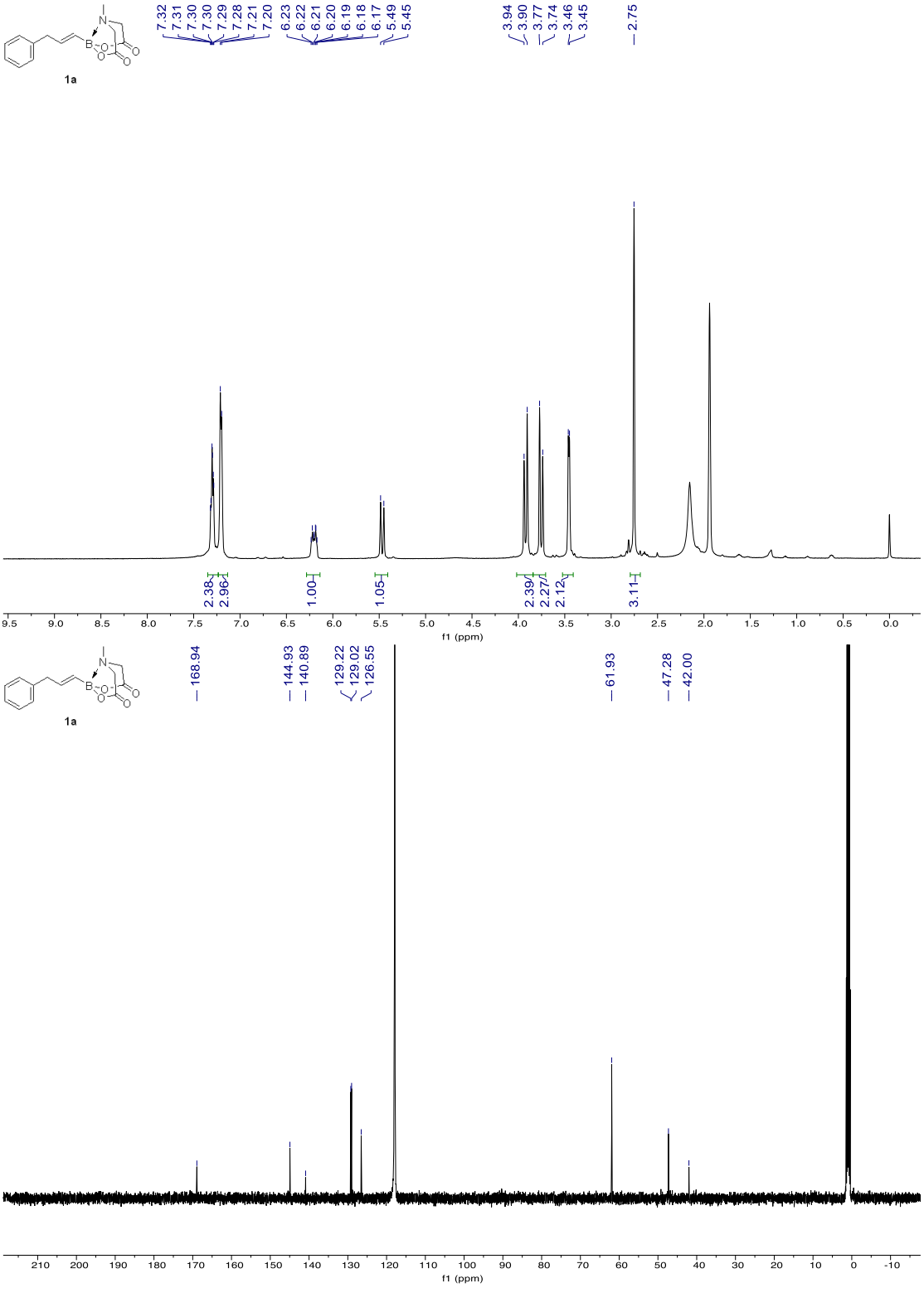


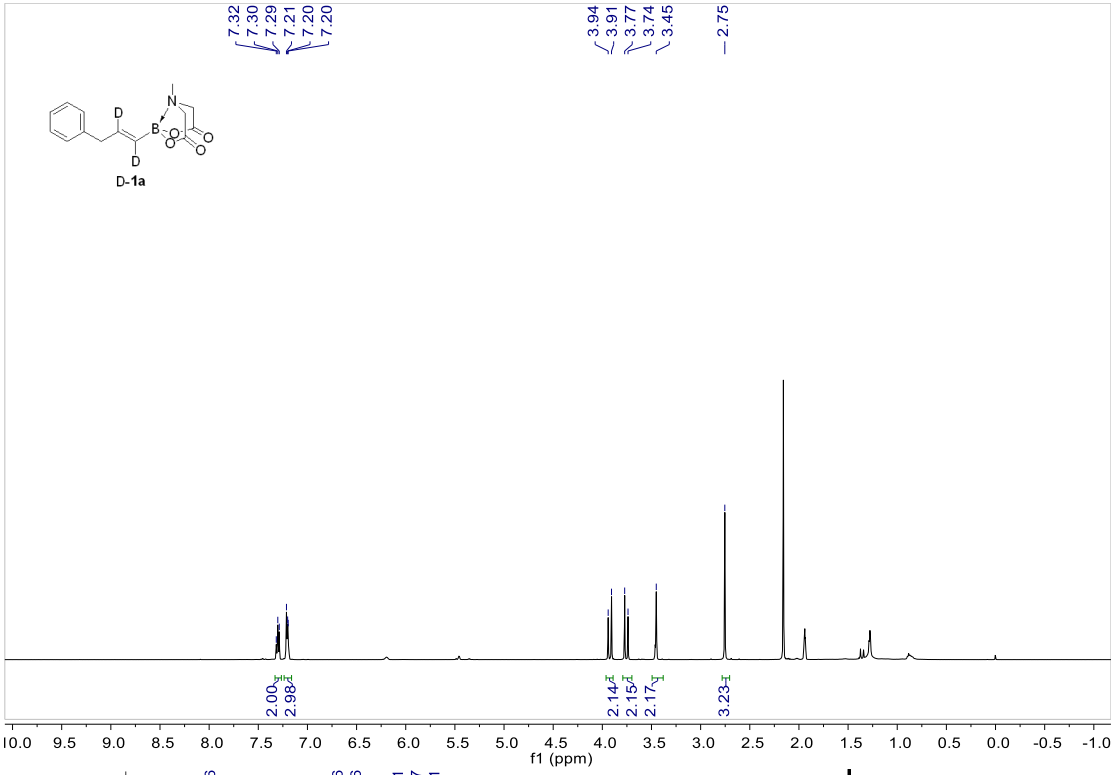
14

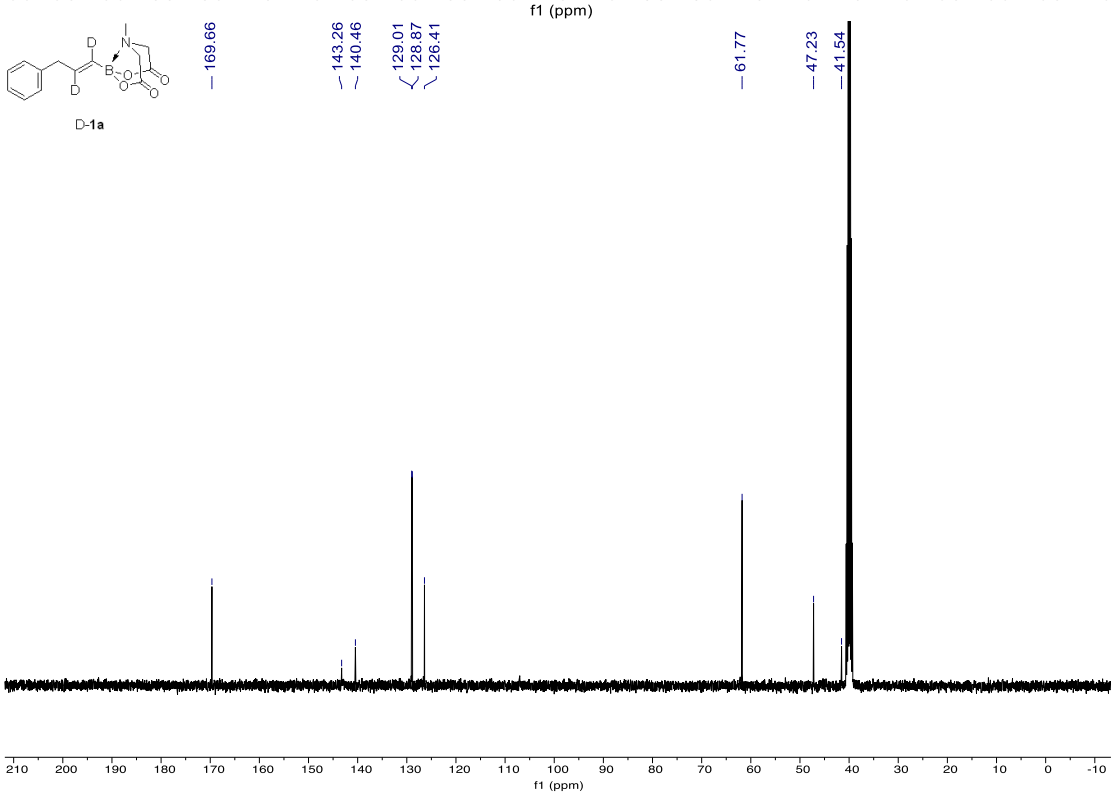
The product **14** was obtained in 84% yield (46.9 mg) as a yellow liquid after column chromatography (eluent = Petroleum ether). R_F = 0.44 (PE: ethyl acetate = 20:1). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.50 – 7.23 (m, 5H), 6.99 – 6.72 (m, 4H), 4.05 (t, J = 12.1 Hz, 2H), 3.74 (s, 3H), 3.38 (t, J = 17.3 Hz, 2H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 155.21 , 152.53 , 133.40 (t, J = 4.4 Hz), 131.09 , 128.99 , 127.97 , 122.52 (t, J = 242.8 Hz), 116.37, 115.25, 68.96 (t,

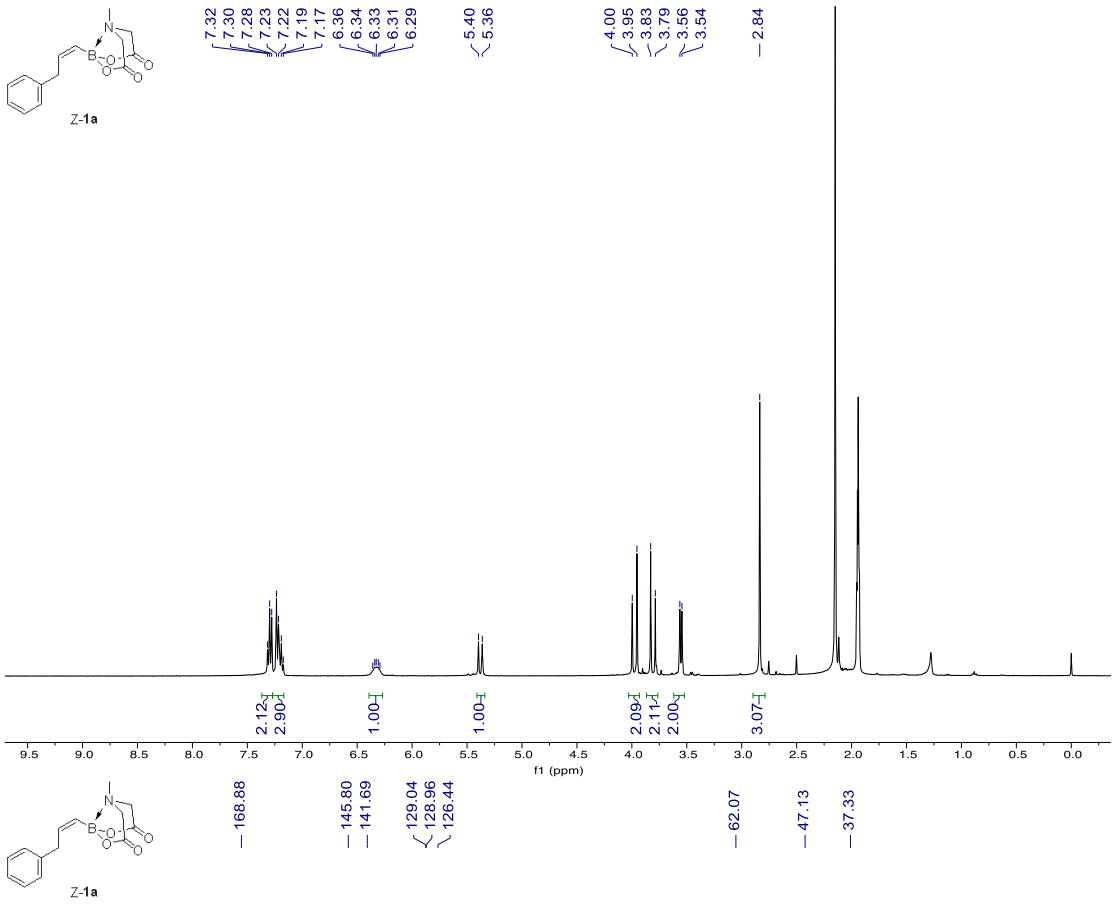
J = 32.8 Hz), 55.80 , 40.09 (t, J = 24.2 Hz). ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -105.10. **ESI-MS:** calcd for $C_{16}H_{17}O_2F_2$ [M + H]$^+$: 279.1191, found: 279.1193.

7. NMR spectrum of the starting materials and products




7.32
7.30
7.29
7.21
7.20
7.20
3.94
3.91
3.77
3.74
3.45
2.75
D-1a
2.00
2.98
2.14
2.15
2.17
3.23
f1 (ppm)


169.66
143.26
140.46
129.01
128.87
126.41
61.77
47.23
41.54
D-1a
f1 (ppm)


Z-1a
7.32
7.30
7.28
7.23
7.22
7.19
7.17
6.36
6.34
6.33
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6.29
5.40
5.36
4.00
3.95
3.83
3.79
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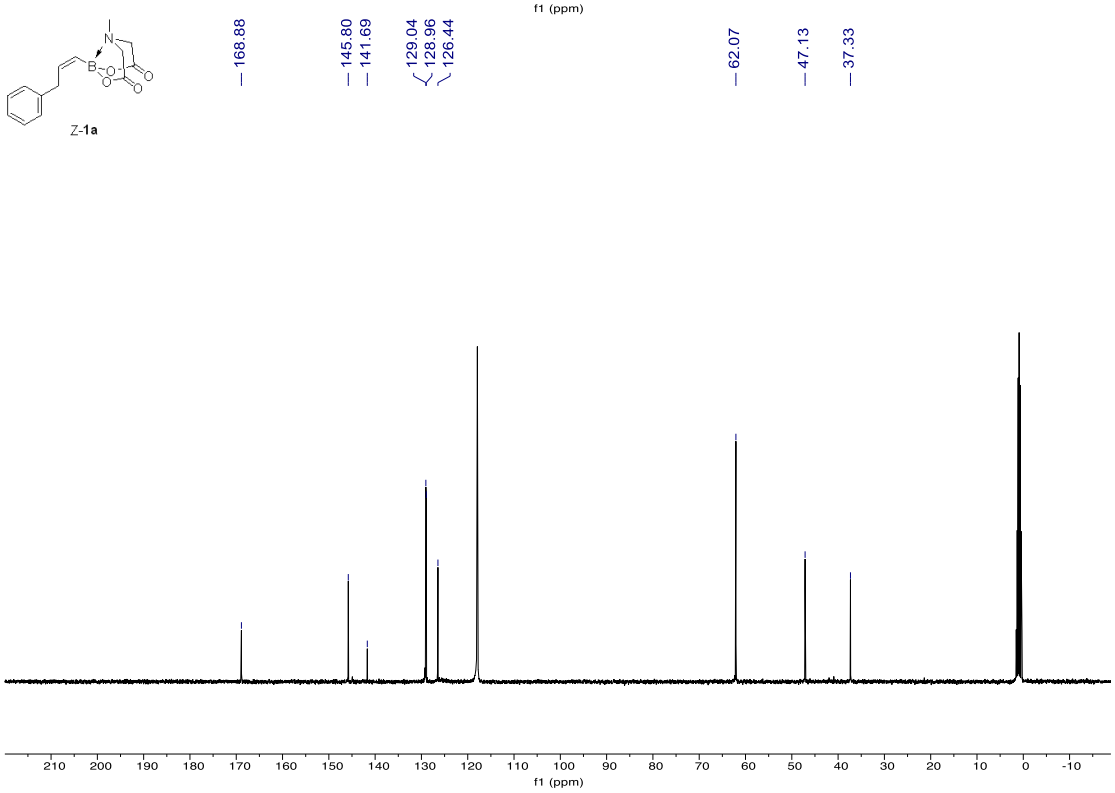
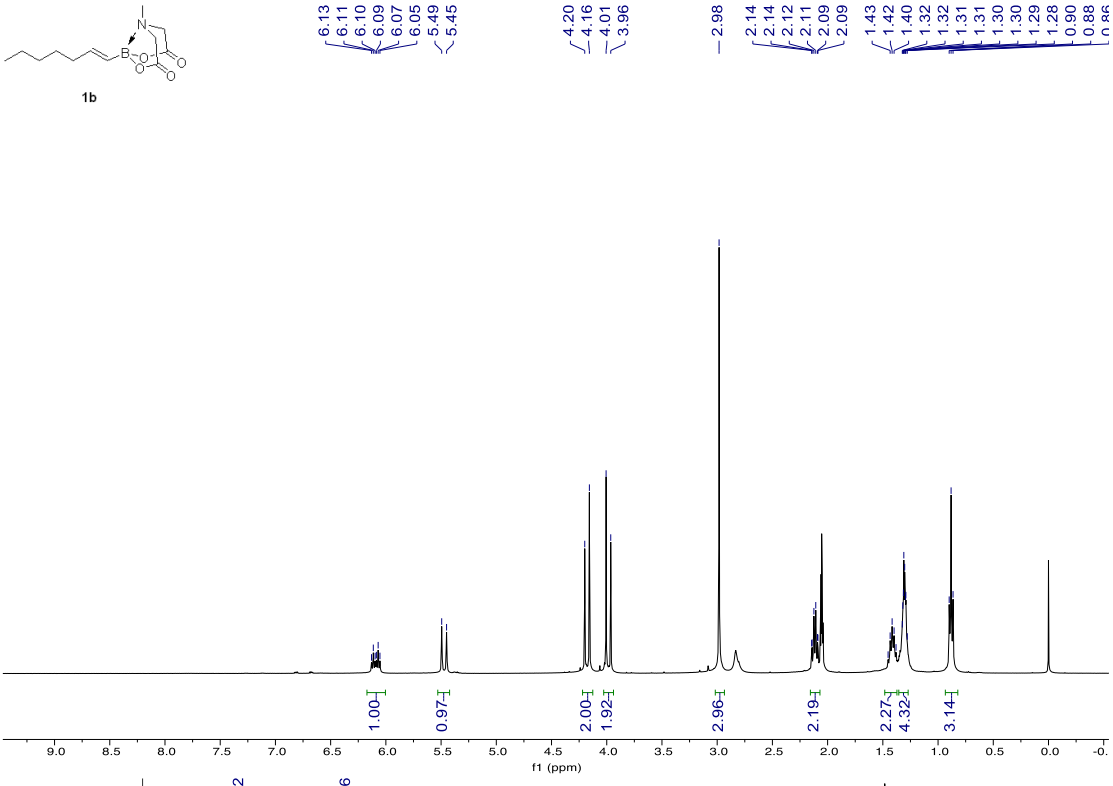
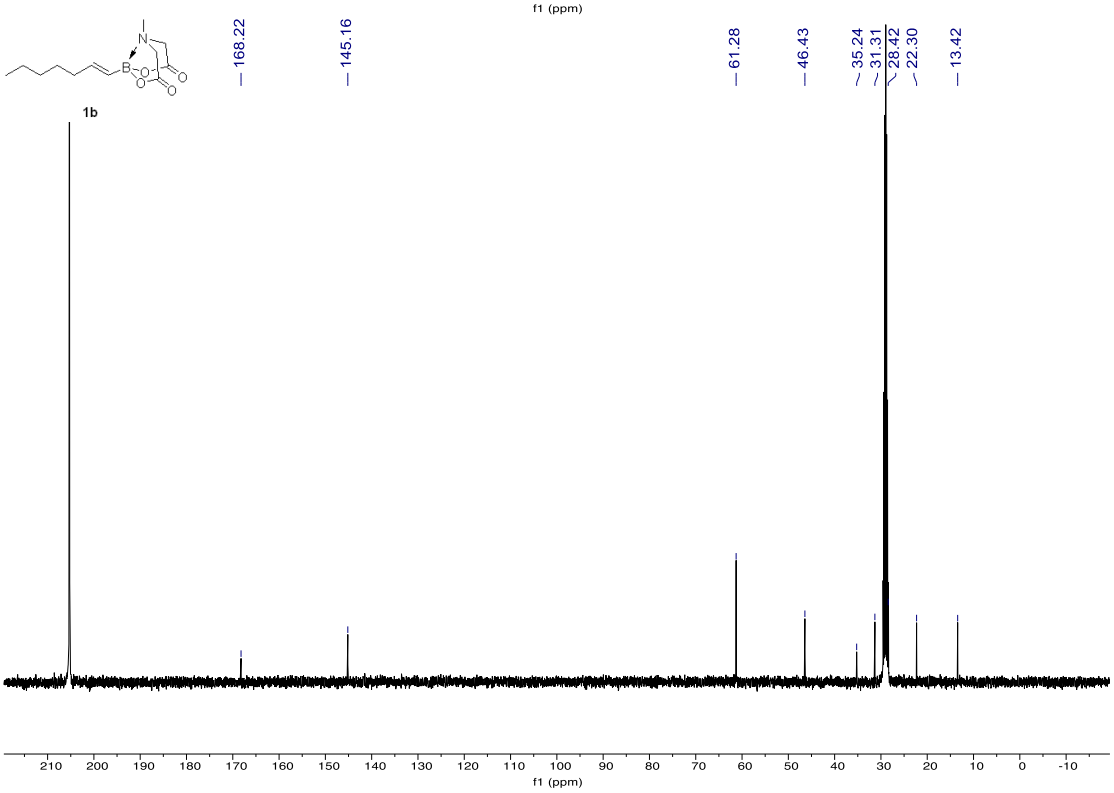
1.00
2.09
2.11
2.00
3.07
f1 (ppm)


Z-1a
168.88
145.80
141.69
129.04
128.96
126.44
62.07
47.13
37.33
f1 (ppm)


1b
6.13
6.11
6.10
6.09
6.07
6.05
5.49
5.45
4.20
4.16
4.01
3.96
2.98
2.14
2.14
2.12
2.11
2.09
2.09
1.43
1.42
1.40
1.32
1.32
1.31
1.31
1.30
1.30
1.29
1.28
0.90
0.88
1.00
0.97
2.00
1.92
2.96
2.19
2.27
4.32
3.14
f1 (ppm)


1b
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61.28
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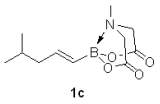
35.24
31.31
28.42
22.30
13.42
f1 (ppm)



1c


6.09
6.08
6.07
6.07
6.05
6.05
6.04
6.03
6.02
6.02
5.42
5.39
3.95
3.91
3.78
3.74
2.76
2.04
2.02
2.01
1.72
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1.70
1.69
1.68
1.68
1.67
1.67
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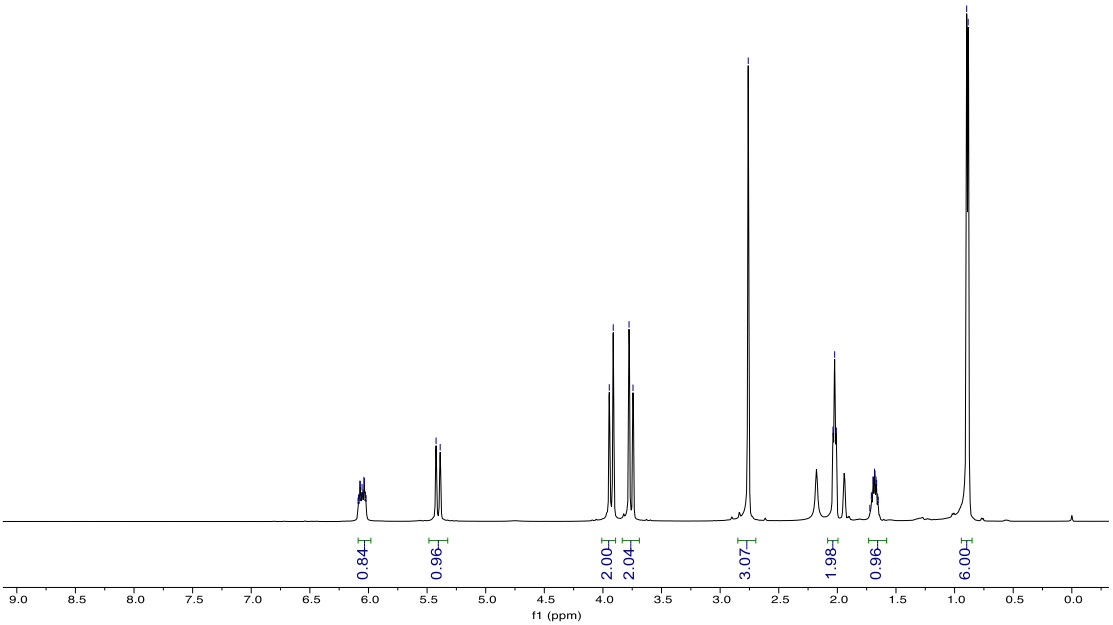
1.65
0.90
0.88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0.96
6.00
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8.5
8.0
7.5
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6.5
6.0
5.5
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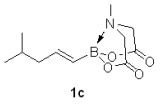
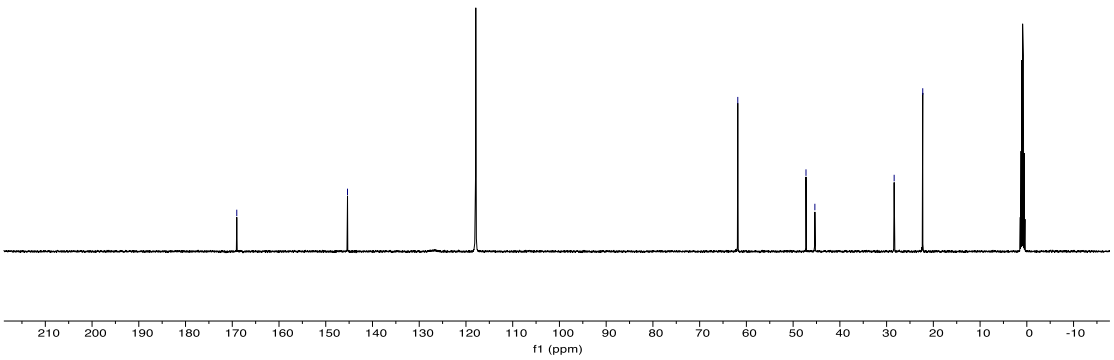
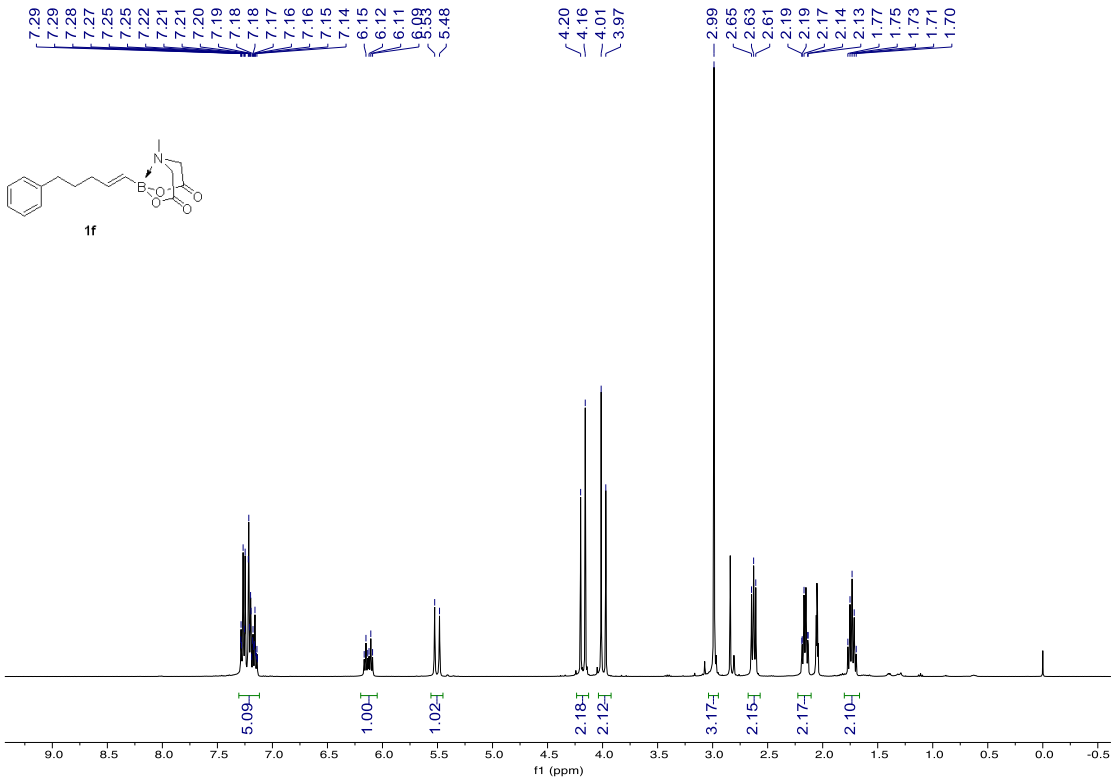
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



1c


169.04
145.34
61.84
47.25
45.35
28.39
22.27


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.29
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7.27
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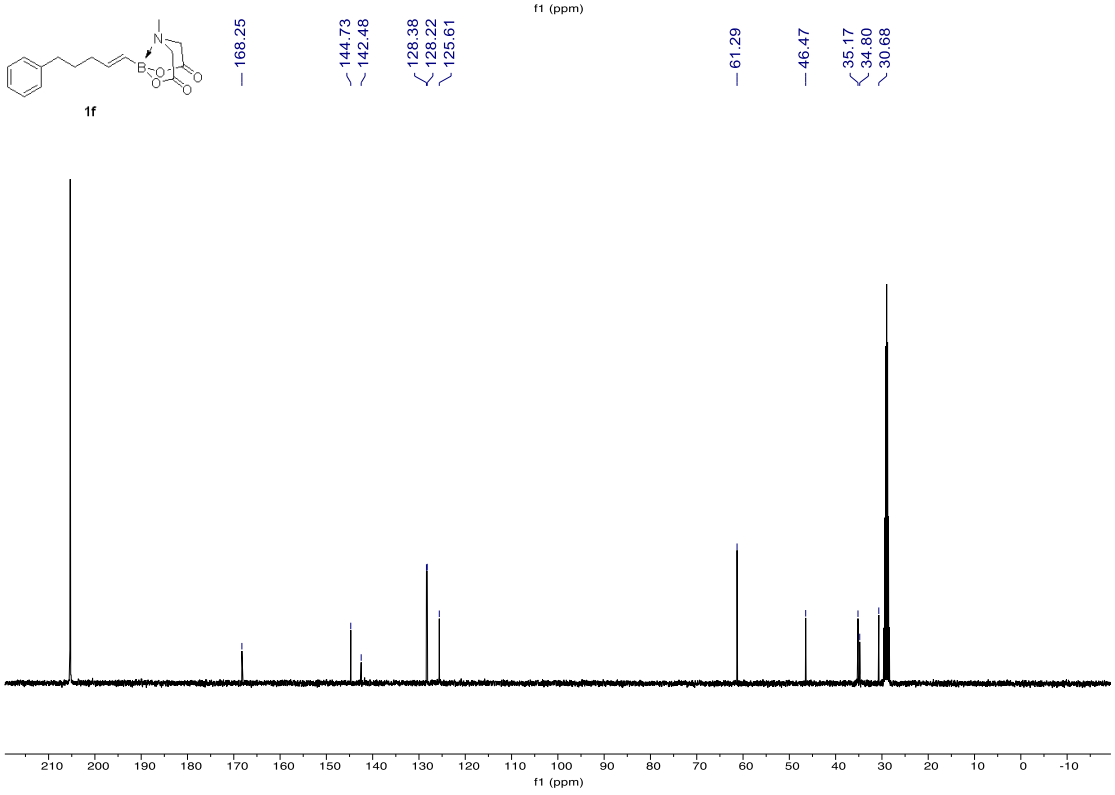
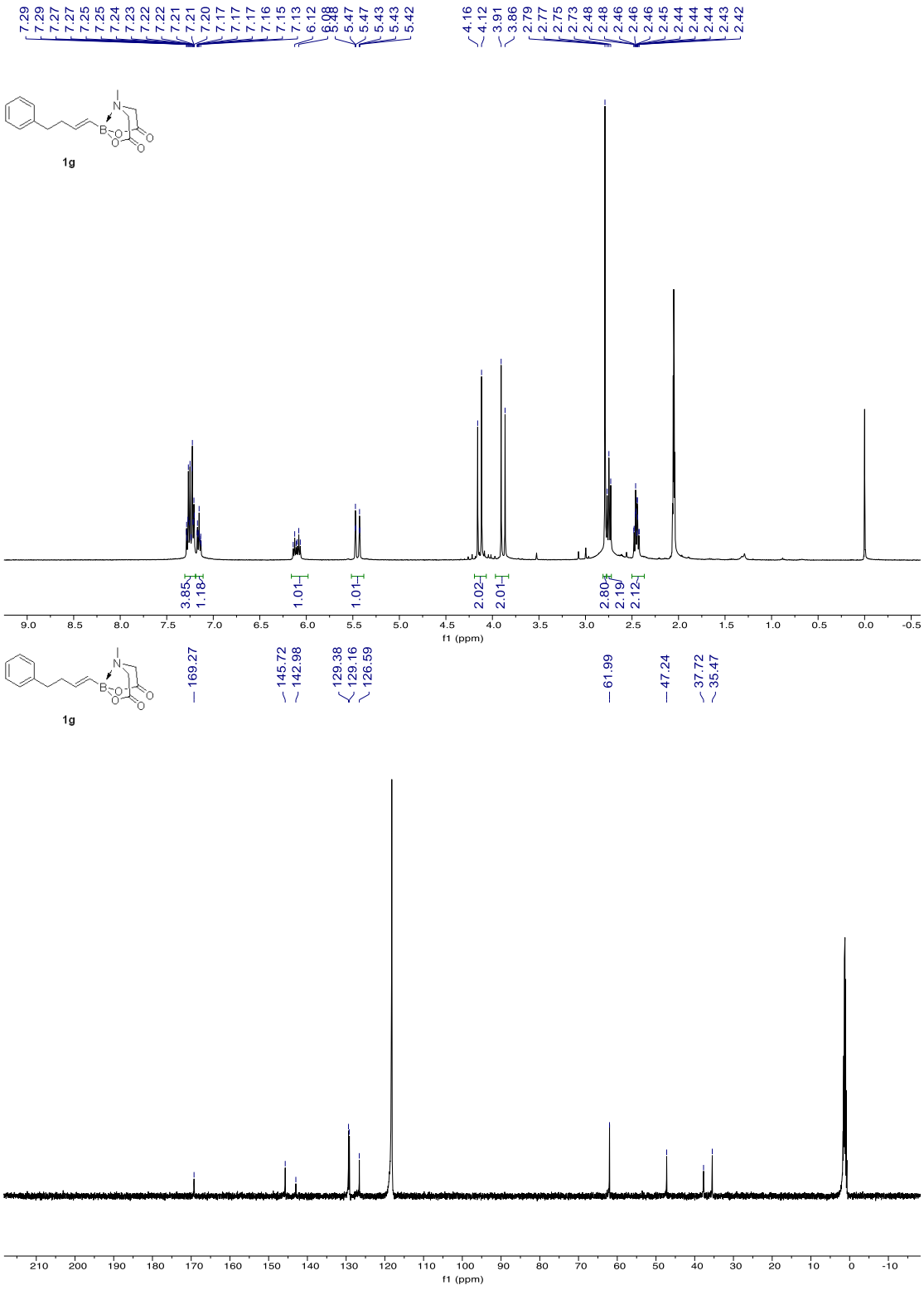
7.22
7.21
7.21
7.20
7.19
7.18
7.18
7.17
7.16
7.16
7.15
7.14
6.15
6.12
6.11
6.09
5.93
5.48
4.20
4.16
4.01
3.97
2.99
2.65
2.63
2.61
2.19
2.19
2.17
2.14
2.13
1.77
1.75
1.73
1.71
1.70
1f
5.09
1.00
1.02
2.18
2.12
3.17
2.15
2.17
2.10
f1 (ppm)


168.25
144.73
142.48
128.38
128.22
125.61
61.29
46.47
35.17
34.80
30.68
1f
f1 (ppm)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7.27
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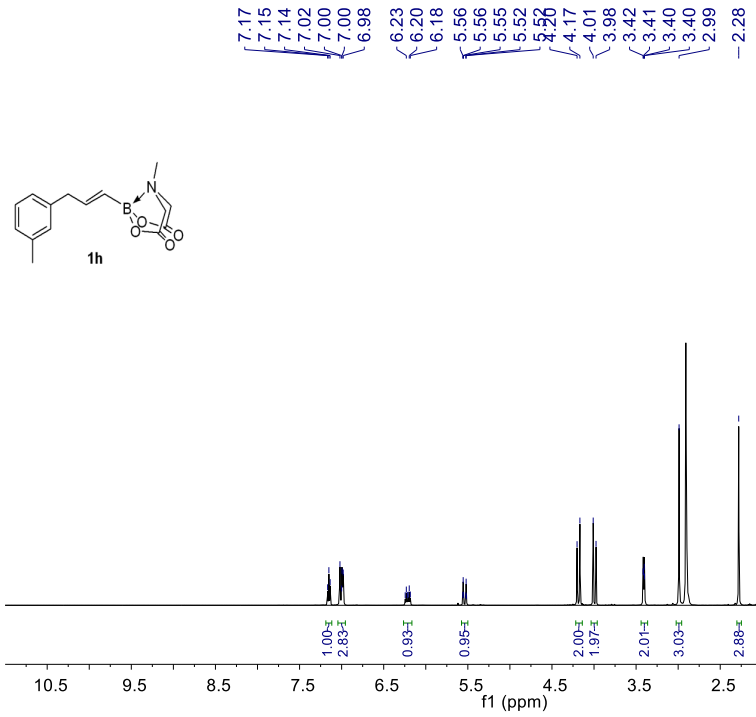
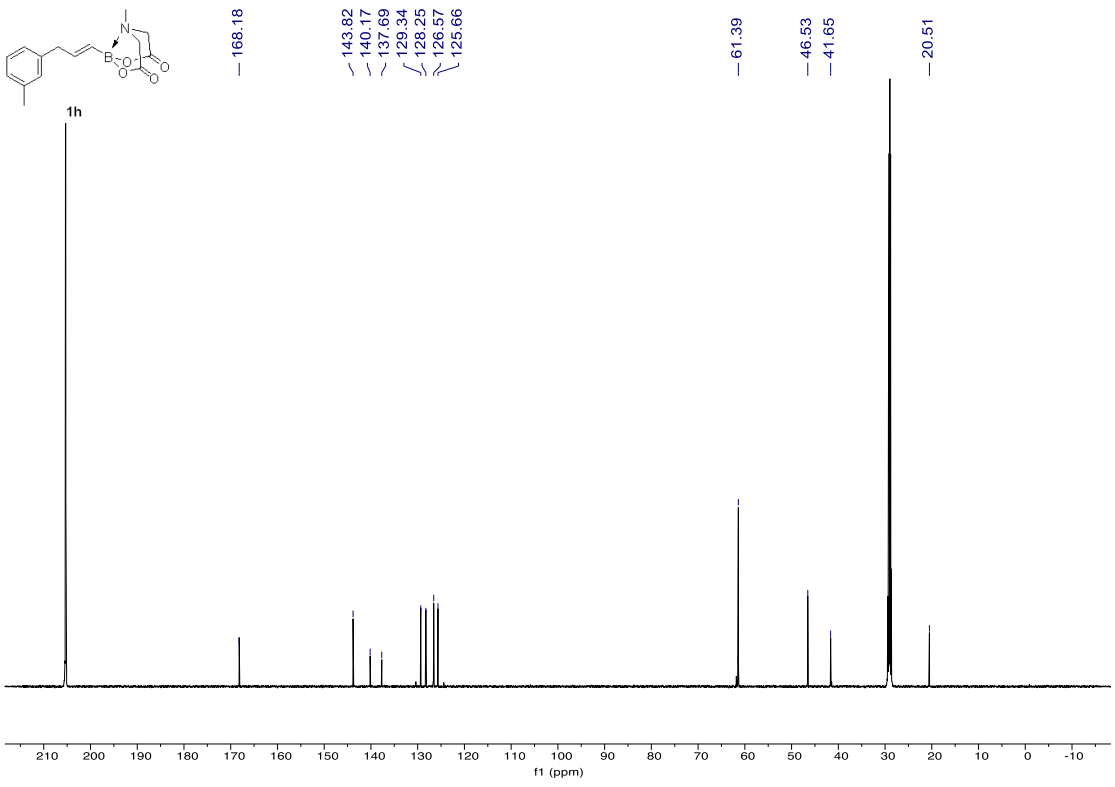
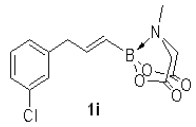
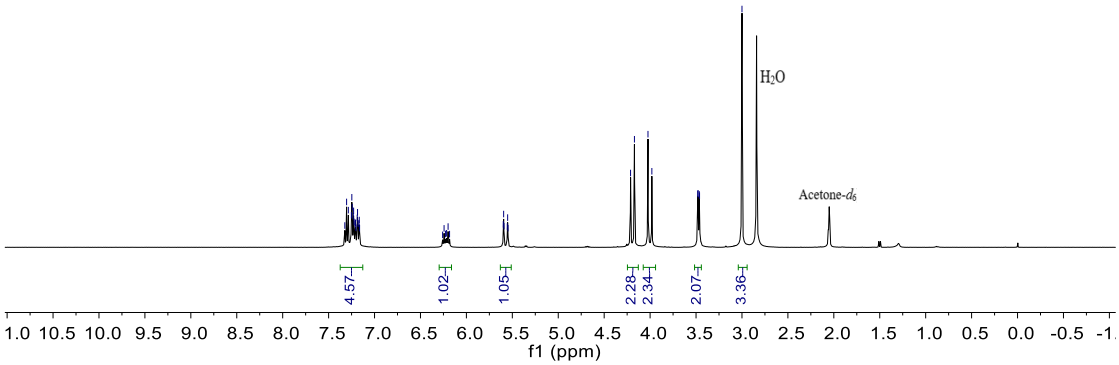
7.23
7.22
7.22
7.21
7.21
7.20
7.17
7.17
7.17
7.16
7.15
7.13
6.12
6.08
5.48
5.47
5.47
5.43
5.43
5.42
4.16
4.12
3.91
3.86
2.79
2.77
2.75
2.73
2.48
2.48
2.46
2.46
2.46
2.45
2.44
2.44
2.44
2.43
2.42
1g
3.85
1.18
1.01
1.01
2.02
2.01
2.80
2.19
2.12
f1 (ppm)
1g
169.27
145.72
142.98
129.38
129.16
126.59
61.99
47.24
37.72
35.47
f1 (ppm)

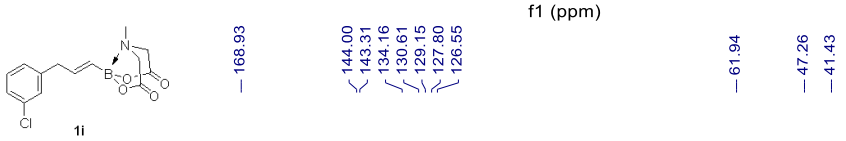

7.17
7.15
7.14
7.02
7.00
7.00
6.98
6.23
6.20
6.18
5.56
5.56
5.55
5.52
4.17
4.01
3.98
3.42
3.41
3.40
3.40
2.99
2.28
1h
1.00
2.83
0.93
0.95
2.00
1.97
2.01
3.03
2.88
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


168.18
143.82
140.17
137.69
129.34
128.25
126.57
125.66
61.39
46.53
41.65
20.51
1h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.32
7.30
7.29
7.25
7.25
7.24
7.23
7.23
7.22
7.21
7.21
7.20
7.19
7.19
7.18
7.17
7.17
7.16
6.26
6.24
6.23
6.22
6.20
6.18
5.60
5.59
5.59
5.55
5.55
5.55
4.21
4.17
4.02
3.98
3.48
3.48
3.47
3.46
3.00


Cl
1i


H2O
Acetone-d6
4.57
1.02
1.05
2.28
2.34
2.07
3.36
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


168.93
144.00
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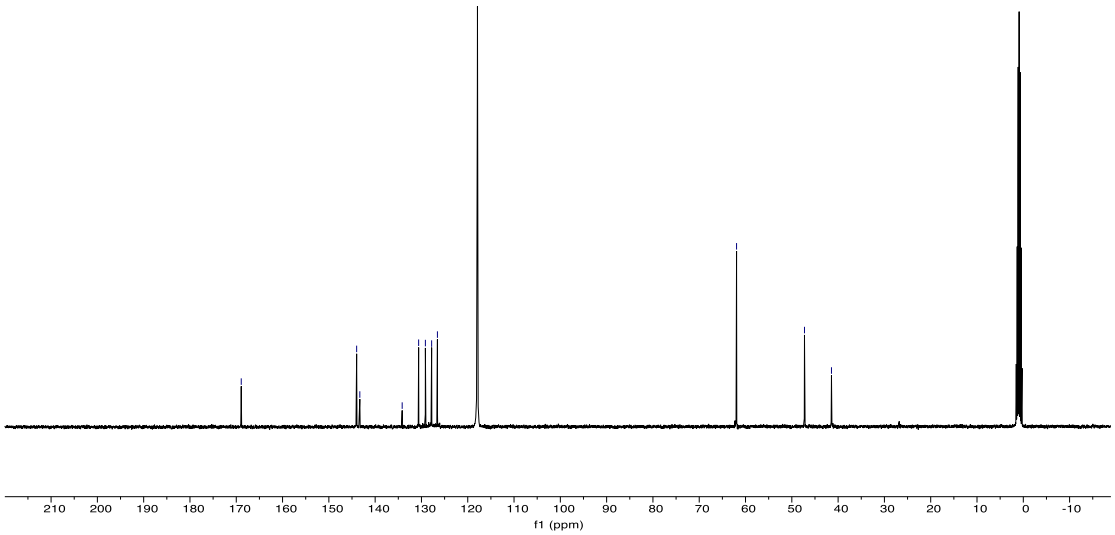
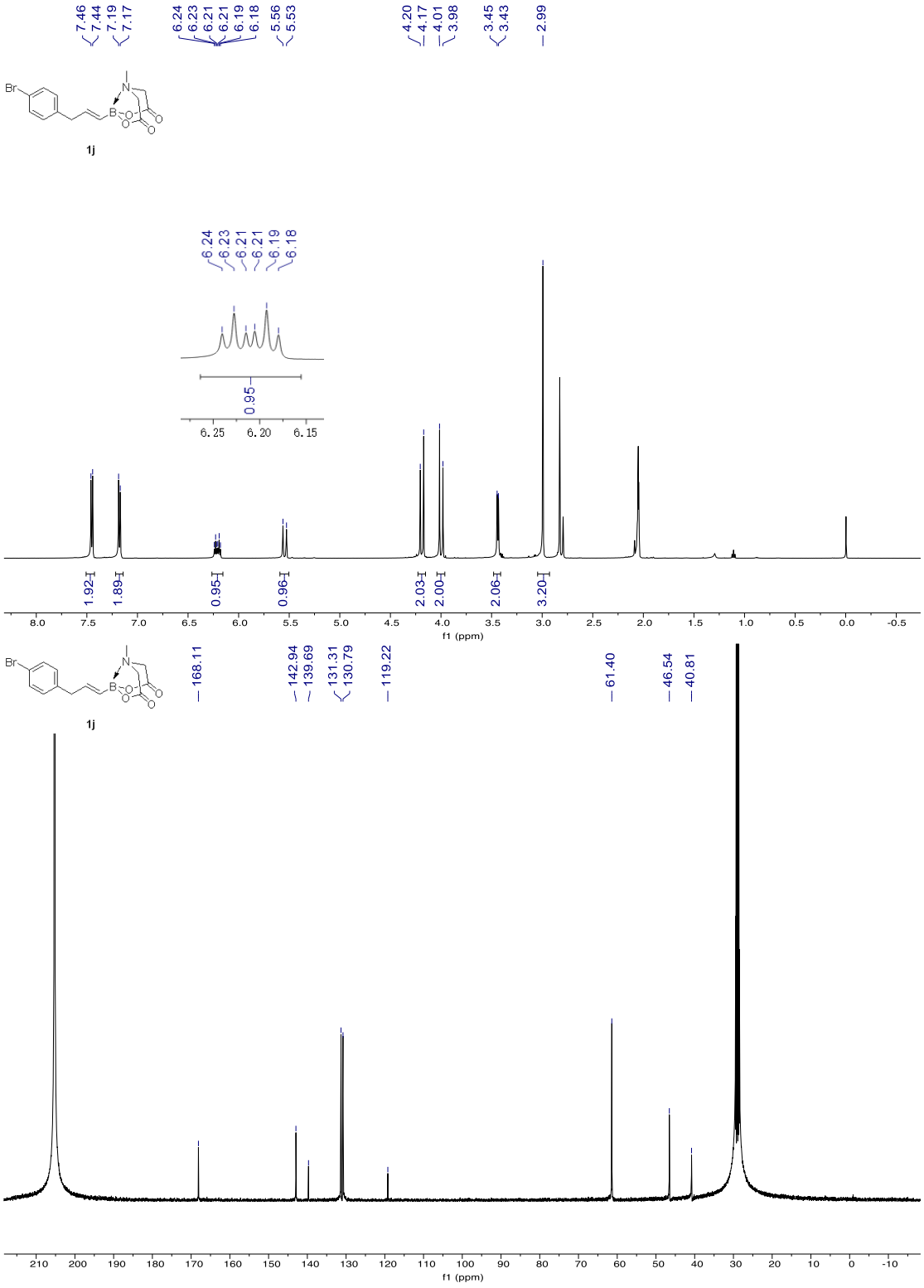
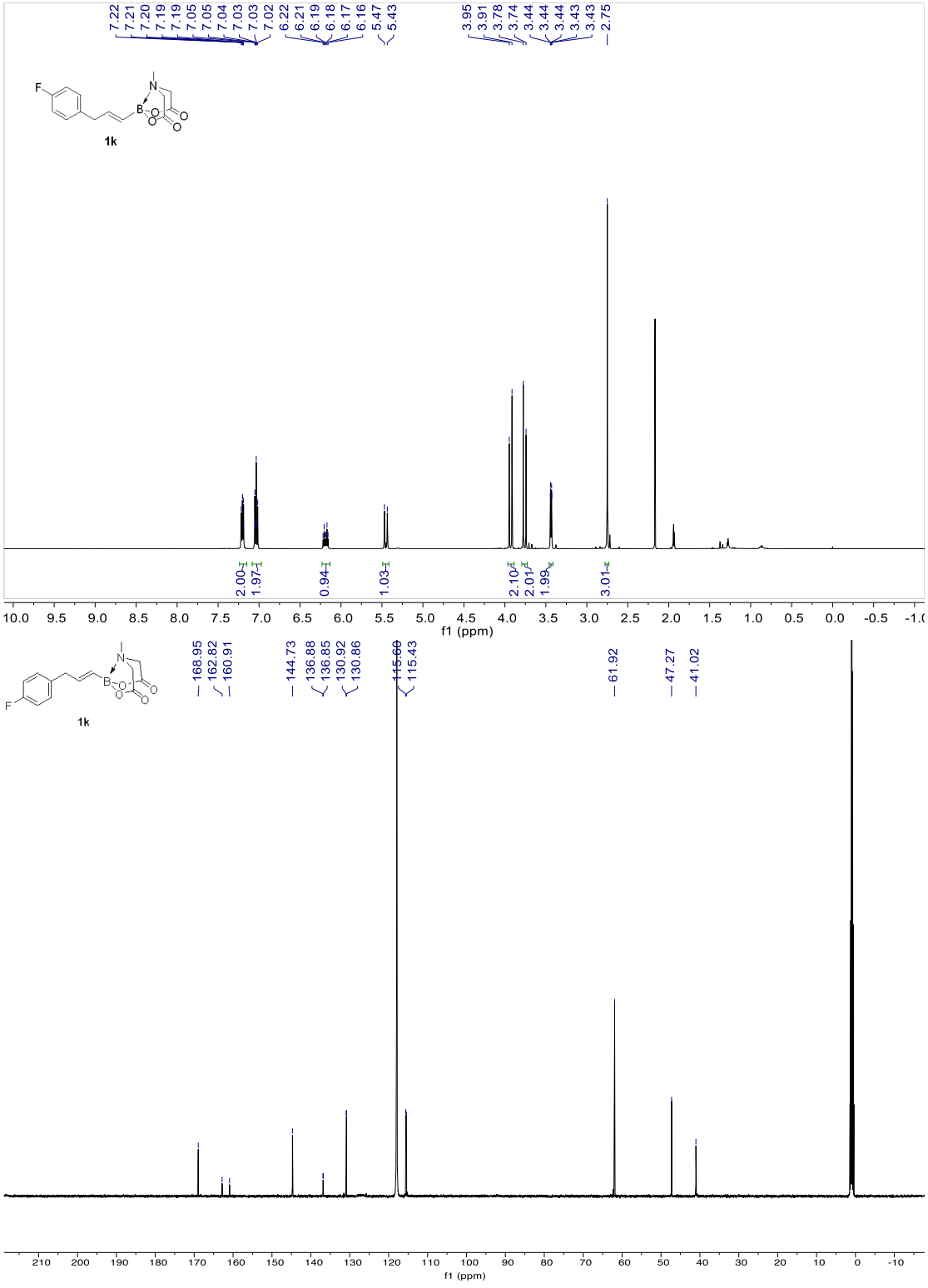
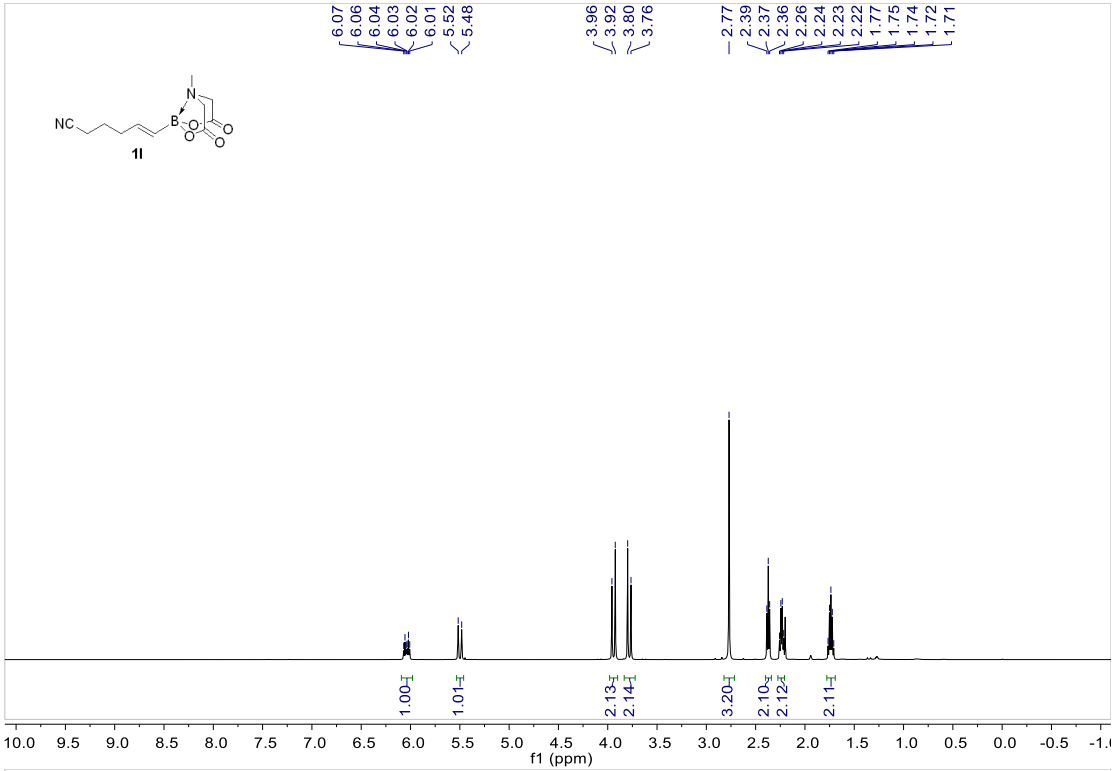
134.16
130.61
129.15
127.80
126.55
61.94
47.26
41.43
Cl
1i


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.46
7.44
7.19
7.17
6.24
6.23
6.21
6.21
6.19
6.18
5.56
5.53
4.20
4.17
4.01
3.98
3.45
3.43
2.99
Br
1j
0.95
1.92
1.89
0.95
0.96
2.03
2.00
2.06
3.20
f1 (ppm)
168.11
142.94
139.69
131.31
130.79
119.22
61.40
46.54
40.81


7.22
7.21
7.20
7.19
7.19
7.05
7.05
7.04
7.03
7.03
7.02
6.22
6.21
6.19
6.18
6.17
6.16
5.47
5.43
3.95
3.91
3.78
3.74
3.44
3.44
3.44
3.43
3.43
2.75
F
N
B
O
O
O
O
1k
2.00
1.97
0.94
1.03
2.10
2.01
1.99
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
168.95
162.82
160.91
144.73
136.88
136.85
130.92
130.86
115.60
115.43
61.92
47.27
41.02
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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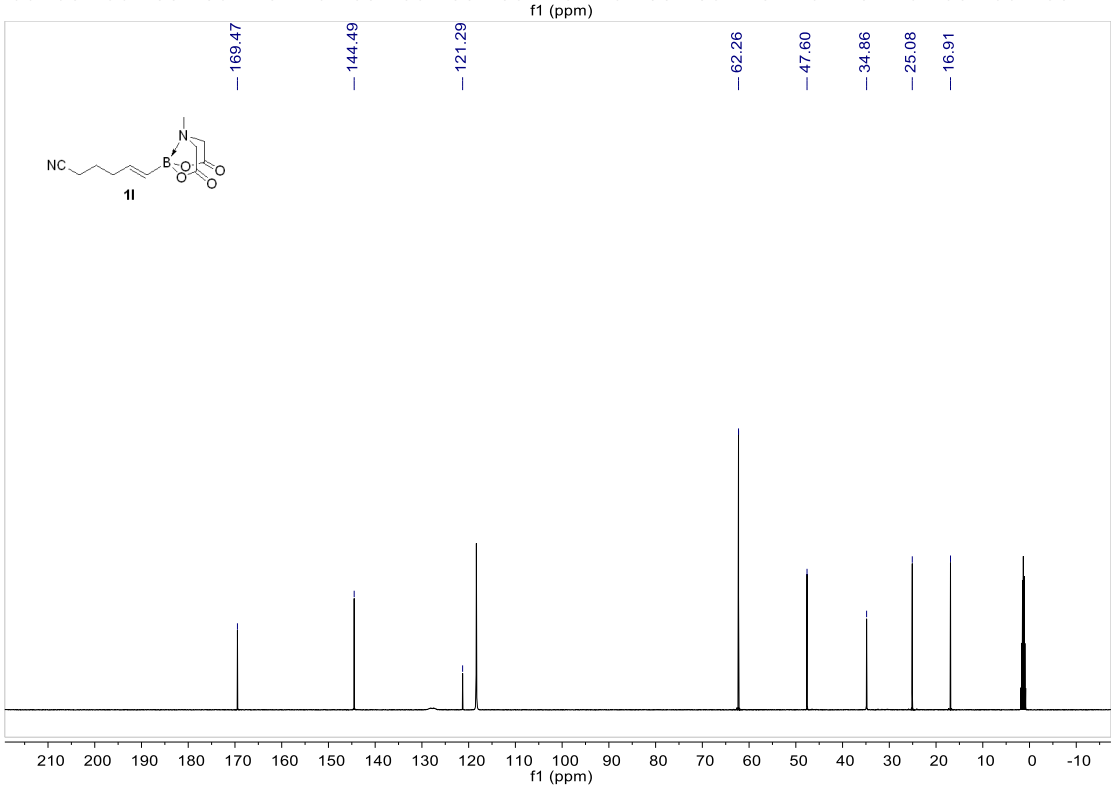
6.06
6.04
6.03
6.02
6.01
5.52
5.48
3.96
3.92
3.80
3.76
2.77
2.39
2.37
2.36
2.26
2.24
2.23
2.22
1.77
1.75
1.74
1.72
1.71
NC
1l
1.00
1.01
2.13
2.14
3.20
2.10
2.12
2.11
f1 (ppm)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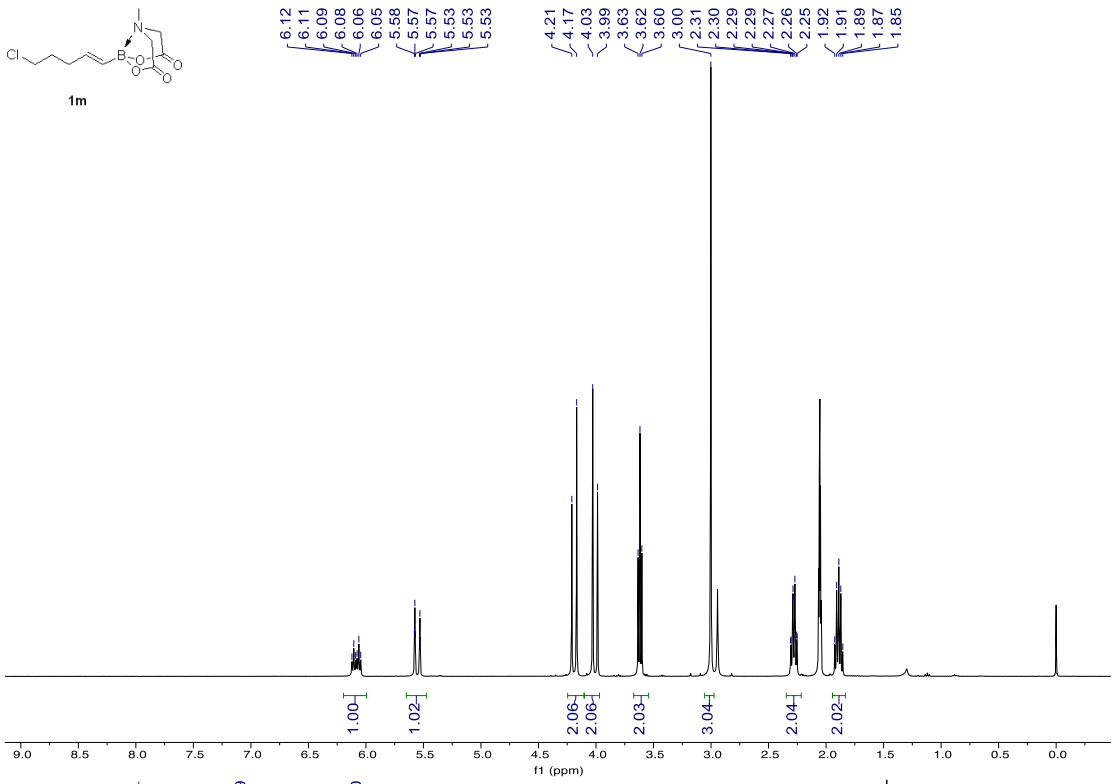
62.26
47.60
34.86
25.08
16.91
NC
1l
f1 (ppm)


1m
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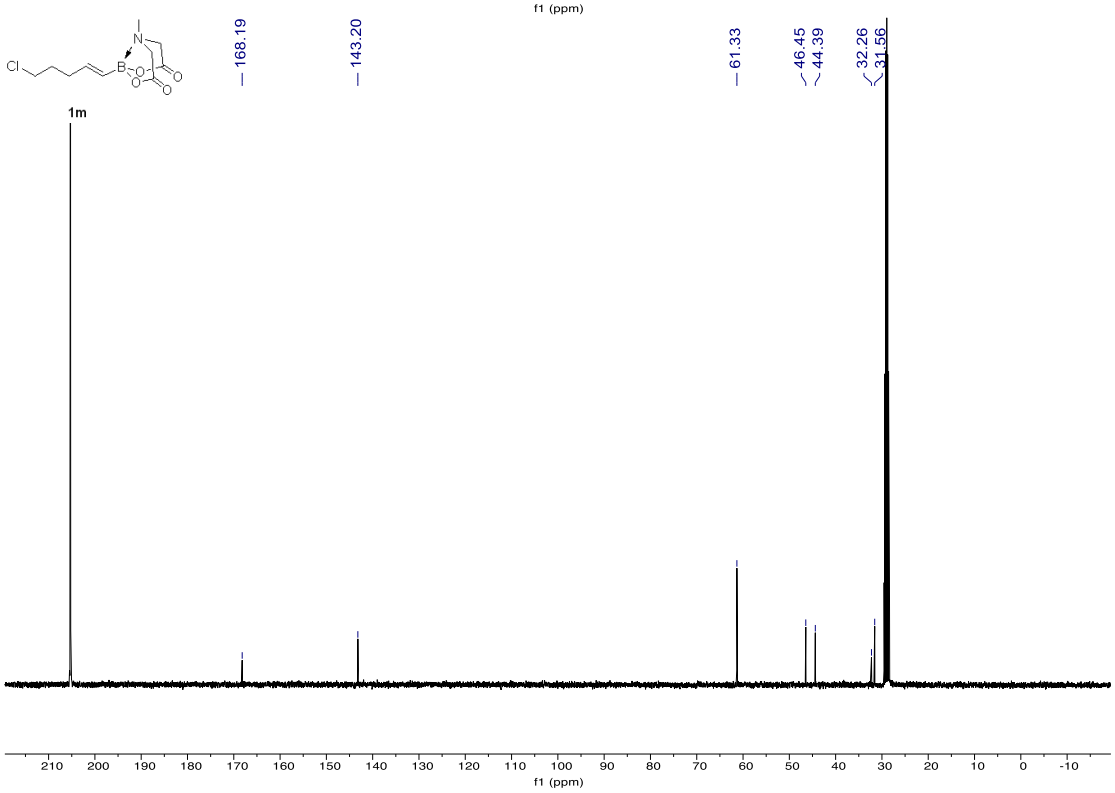
6.11
6.09
6.08
6.06
6.05
5.58
5.57
5.57
5.53
5.53
5.53
4.21
4.17
4.03
3.99
3.63
3.62
3.60
3.00
2.31
2.30
2.29
2.29
2.27
2.26
2.25
1.92
1.91
1.89
1.87
1.85
1.00
1.02
2.06
2.06
2.03
3.04
2.04
2.02
f1 (ppm)


1m
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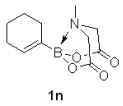
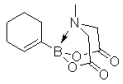
61.33
46.45
44.39
32.26
31.56
f1 (ppm)



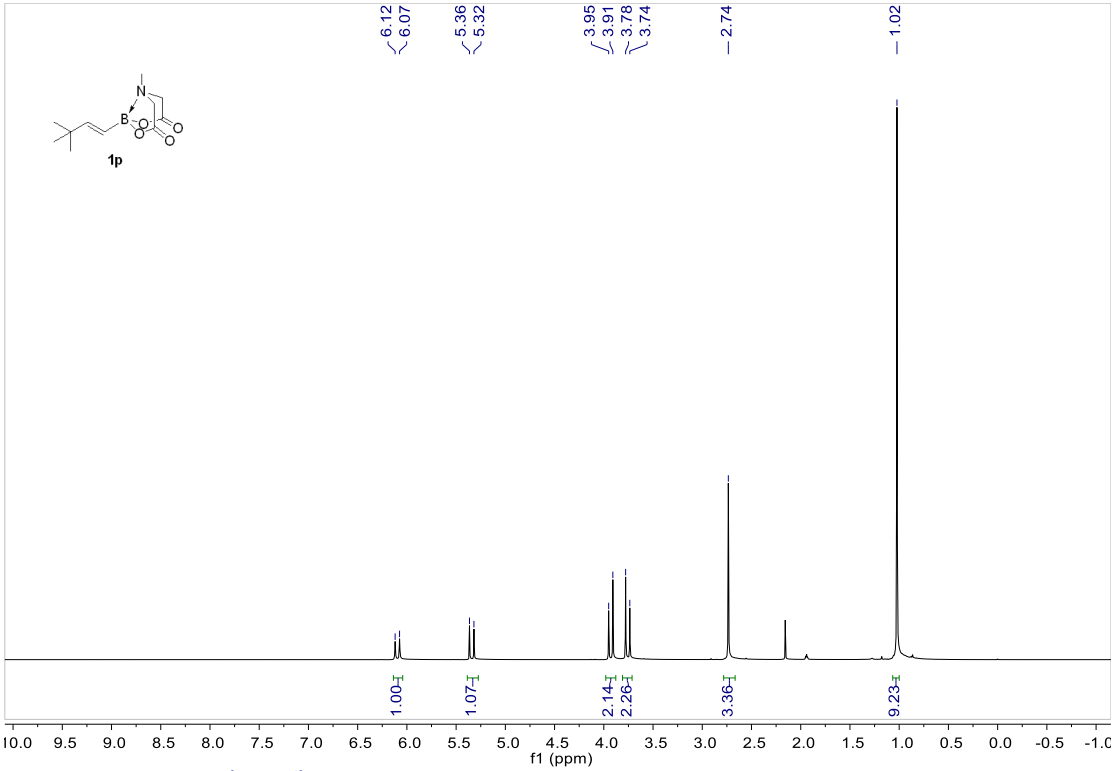
1n

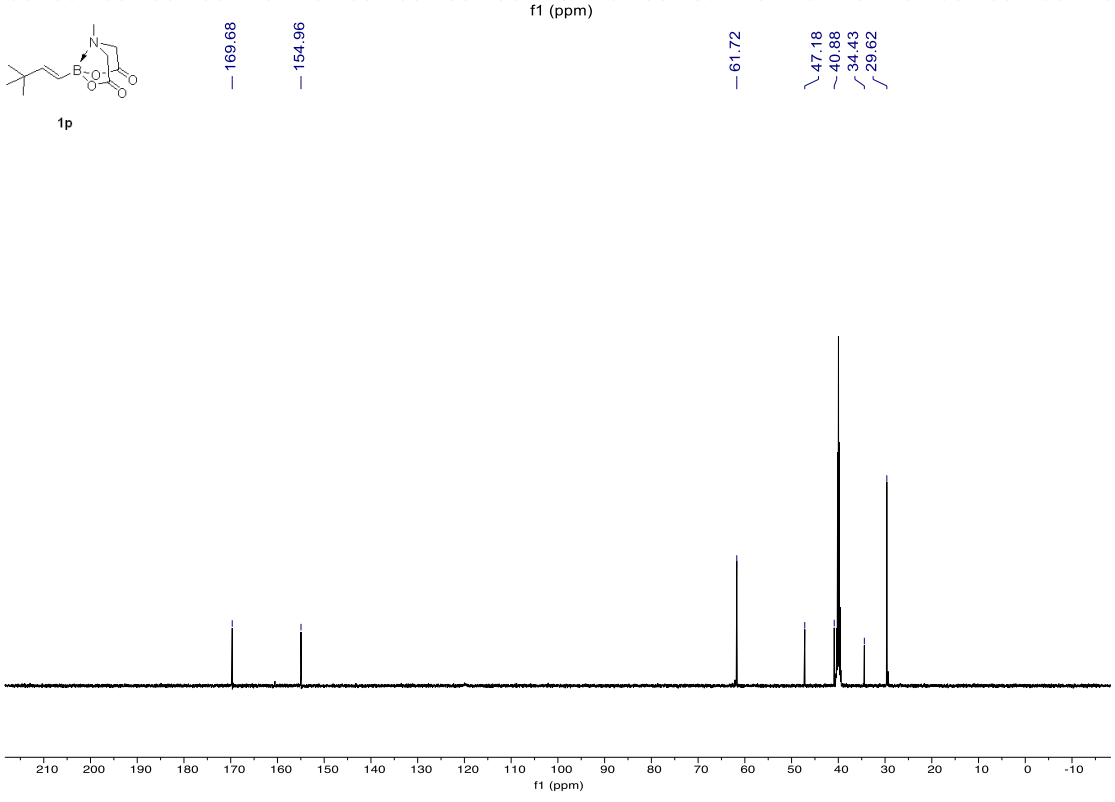
6.06
4.19
4.15
4.02
3.97
2.98
2.07
2.06
2.05
2.05
2.04
2.04
1.61
1.61
1.60
1.60
1.59
1.59
1.58
0.87
2.08
2.02
3.00
3.70
4.18
f1 (ppm)



1n

168.37
134.80
61.60
46.11
26.35
25.99
22.73
22.31
f1 (ppm)


6.12
6.07
5.36
5.32
3.95
3.91
3.78
3.74
2.74
1.02
1p
1.00
1.07
2.14
2.26
3.36
9.23
f1 (ppm)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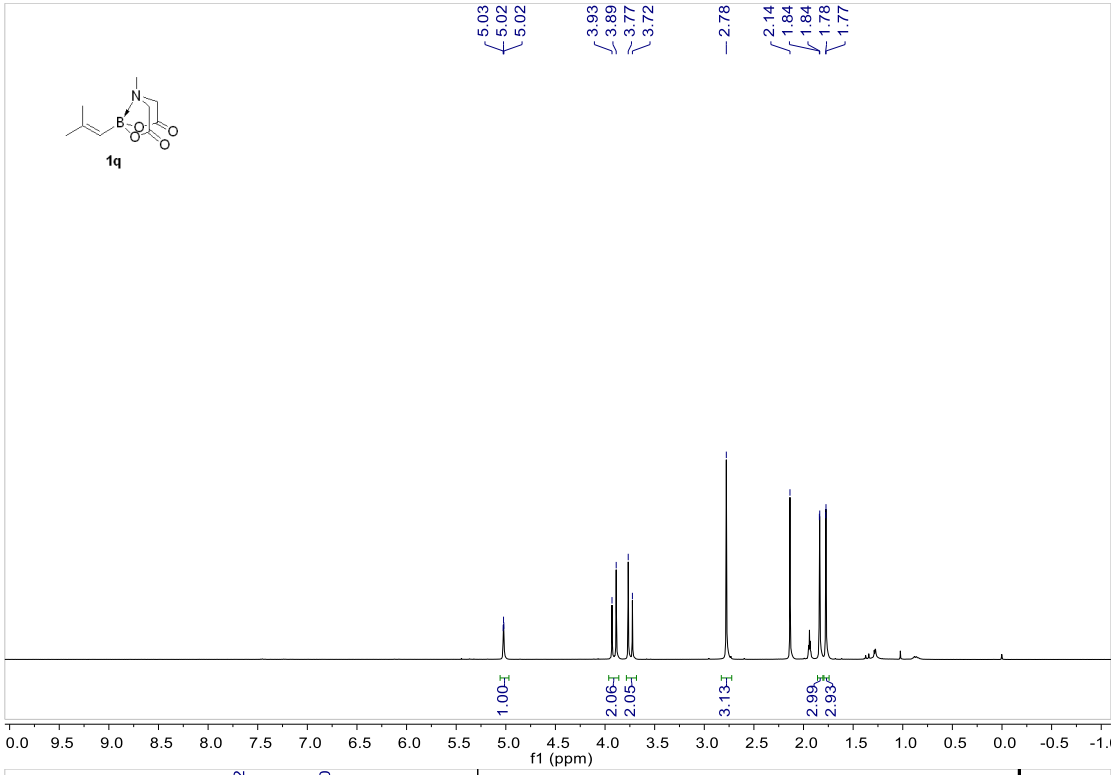
47.18
40.88
34.43
29.62
1p
f1 (ppm)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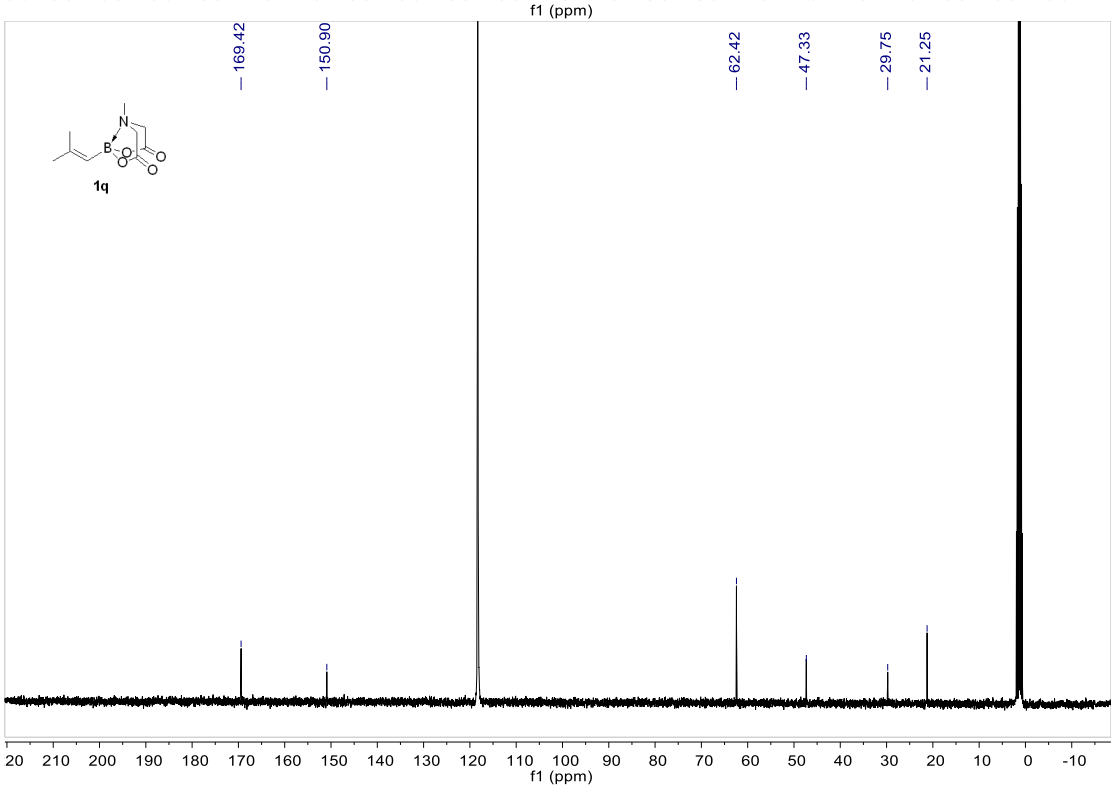
5.02
5.02
3.93
3.89
3.77
3.72
2.78
2.14
1.84
1.84
1.78
1.77
1q
1.00
2.06
2.05
3.13
2.99
2.93
f1 (ppm)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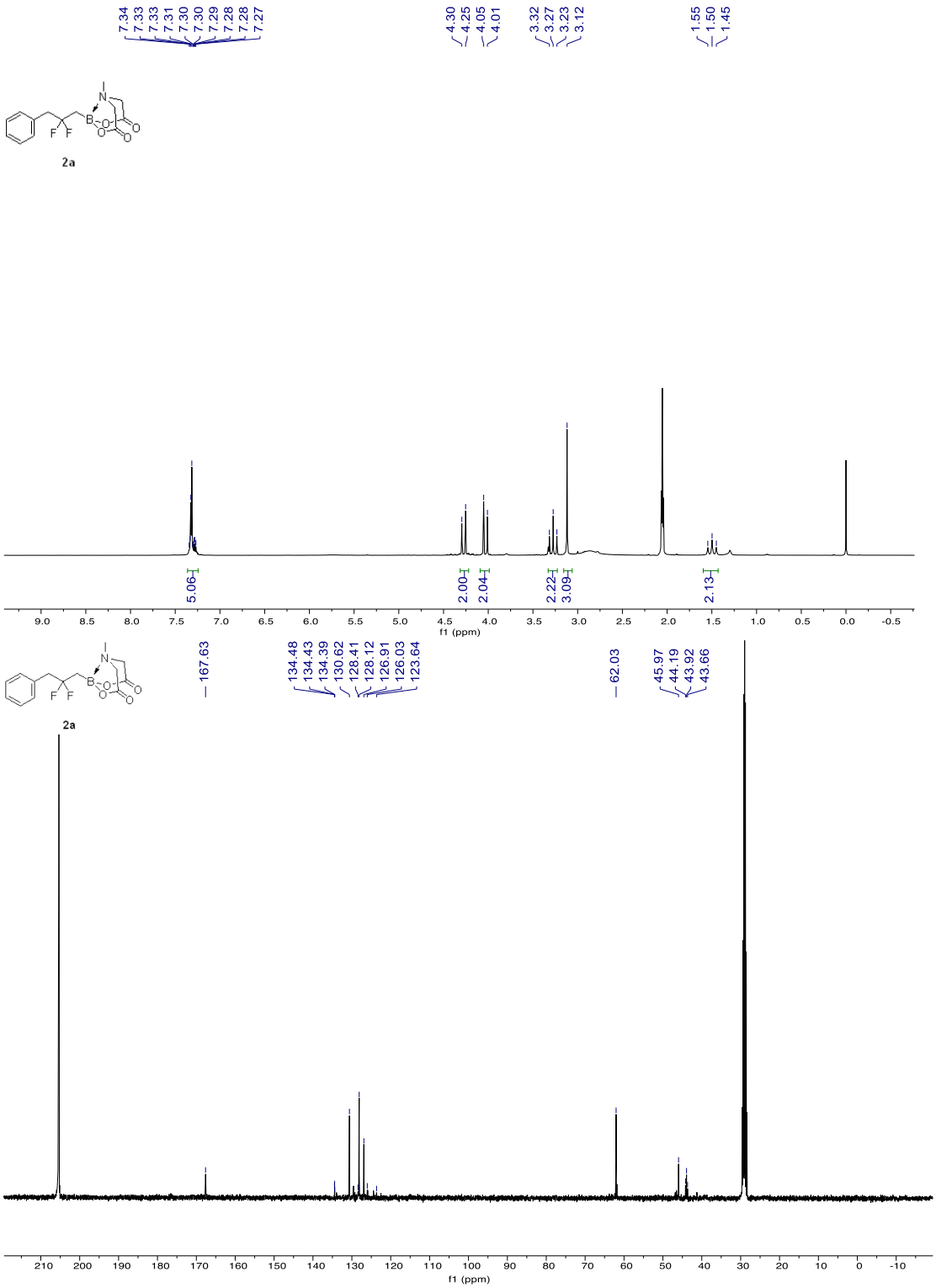
150.90
62.42
47.33
29.75
21.25
1q
f1 (ppm)


7.34
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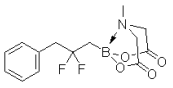
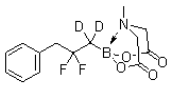
7.30
7.29
7.28
7.28
7.27
4.30
4.25
4.05
4.01
3.32
3.27
3.23
3.12
1.55
1.50
1.45
2a
5.06
2.00
2.04
2.22
3.09
2.13
f1 (ppm)
167.63
134.48
134.43
134.39
130.62
128.41
128.12
126.91
126.03
123.64
62.03
45.97
44.19
43.92
43.66
2a
f1 (ppm)



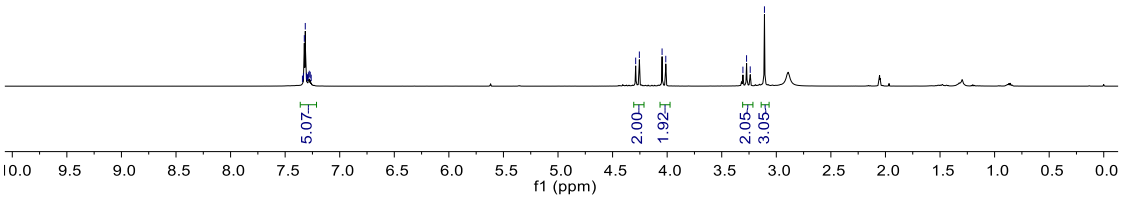
2a

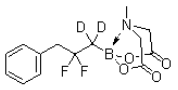
-84.41
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



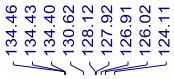
D-2a


7.34
7.33
7.32
7.32
7.30
7.30
7.29
7.29
7.28
7.27
7.26
4.29
4.25
4.05
4.01
3.31
3.27
3.24
3.11

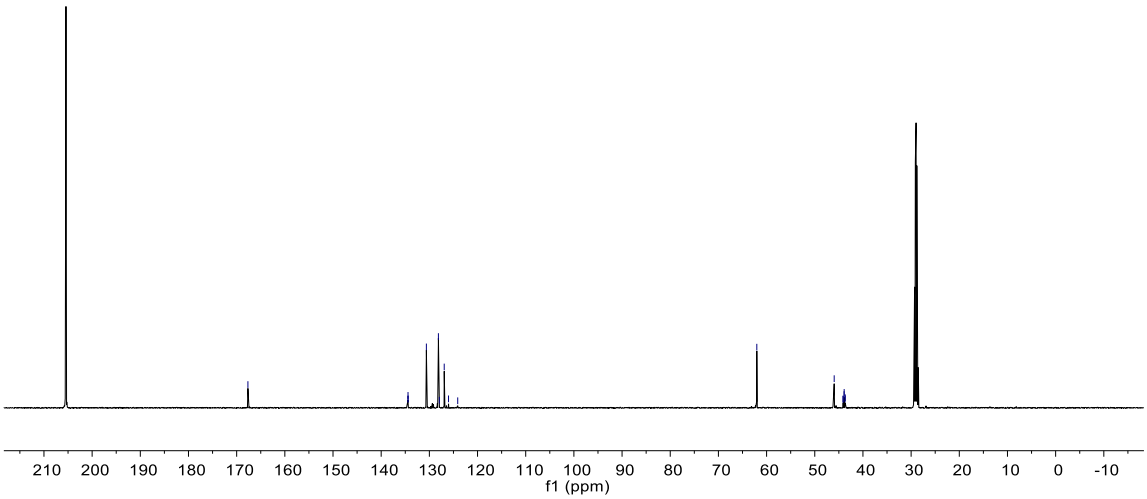

5.07
2.00
1.92
2.05
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

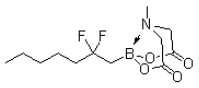


D-**2a**


167.66
134.46
134.43
134.40
130.62
128.12
127.92
126.91
126.02
124.11

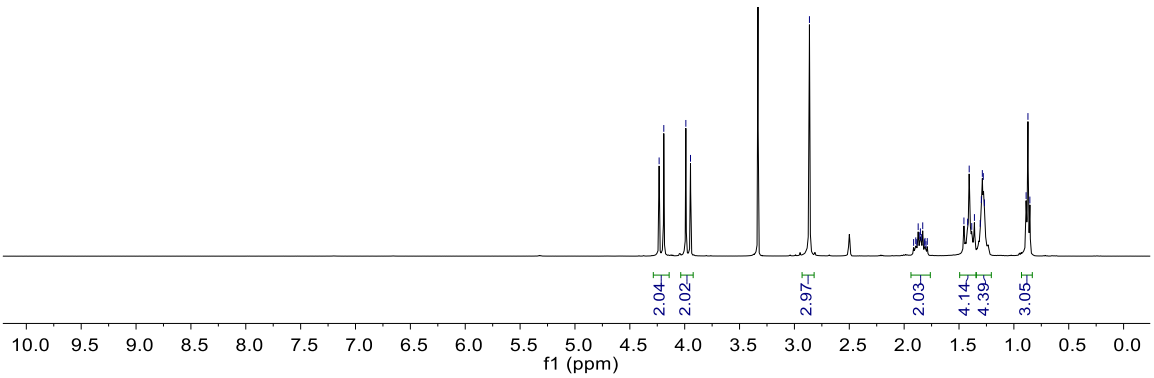

62.03
45.97
44.12
44.12
43.92
43.89
43.70
43.68

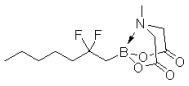

f1 (ppm)



2b

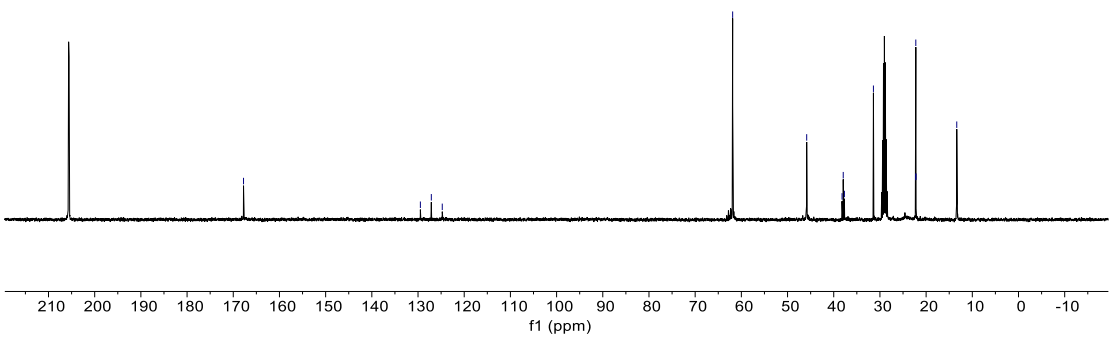

4.23
4.19
3.99
3.95
2.86
1.91
1.89
1.88
1.87
1.86
1.85
1.84
1.83
1.82
1.81
1.80
1.79
1.46
1.42
1.41
1.38
1.36
1.31
1.30
1.29
1.28
1.27
0.89
0.87
0.85

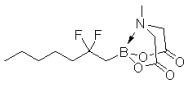

2.04
2.02
2.97
2.03
4.14
4.39
3.05
f1 (ppm)



2b

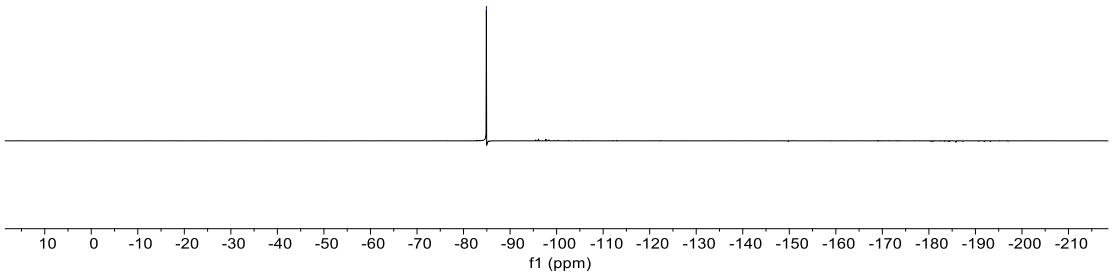

167.78
129.49
127.12
124.75
61.88
45.85
38.20
37.94
37.69
31.41
22.28
22.23
22.19
13.37

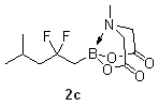

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



2b

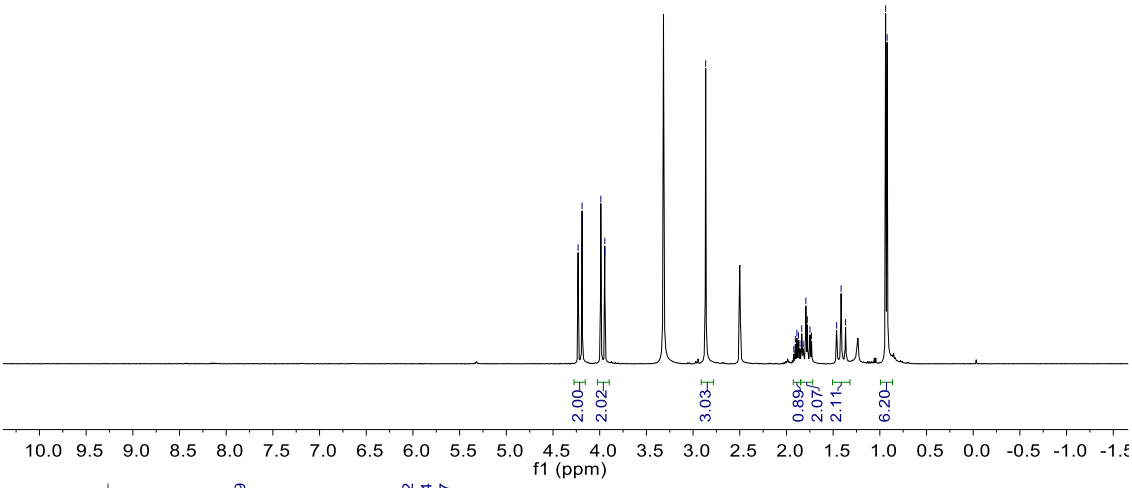

-84.91

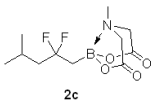

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



2c

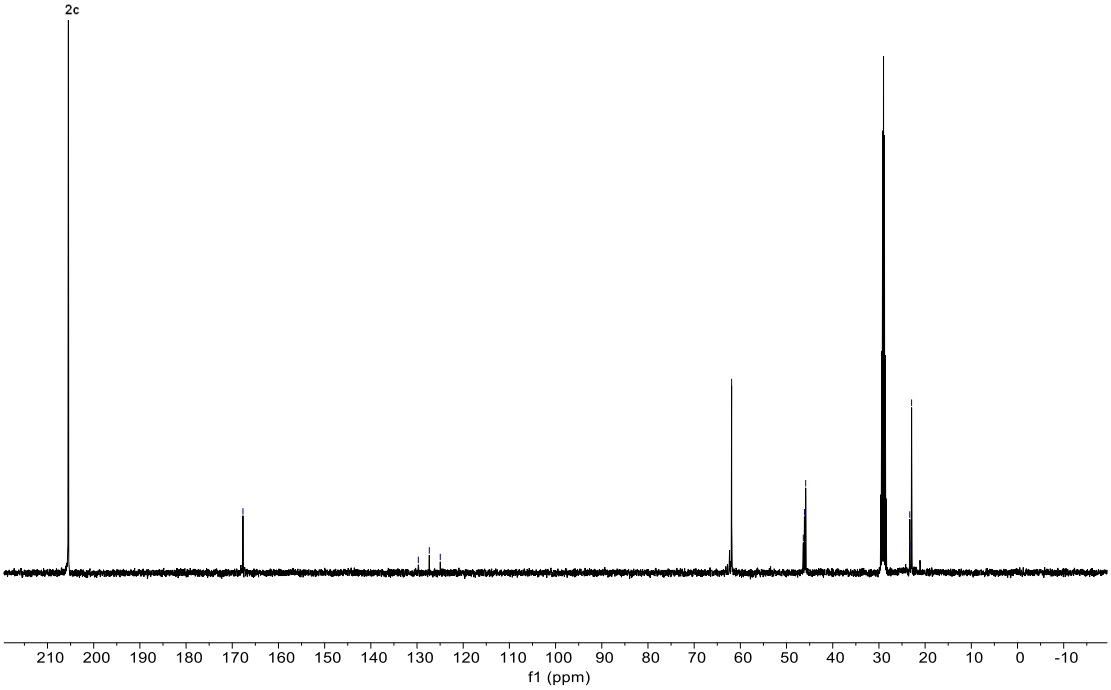
4.23
4.19
4.19
3.99
3.95
3.95
2.87
1.92
1.90
1.89
1.87
1.86
1.84
1.82
1.79
1.78
1.75
1.73
1.46
1.41
1.37
0.94
0.92

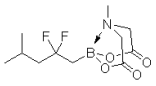




2c

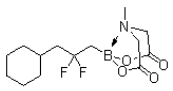
167.69
129.72
127.34
124.97
61.89
46.37
46.12
45.86
23.36
23.32
23.29
22.93



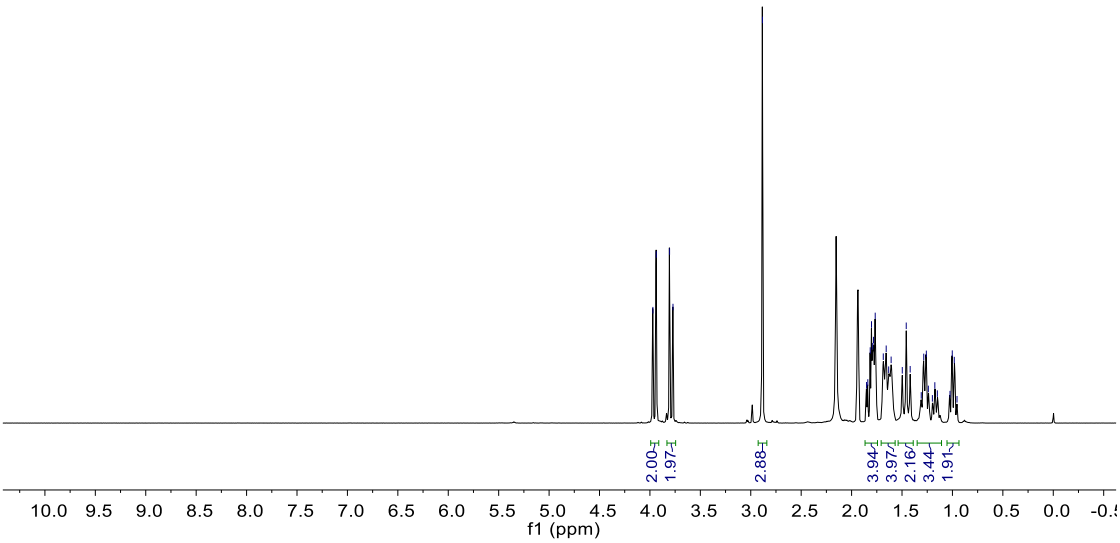


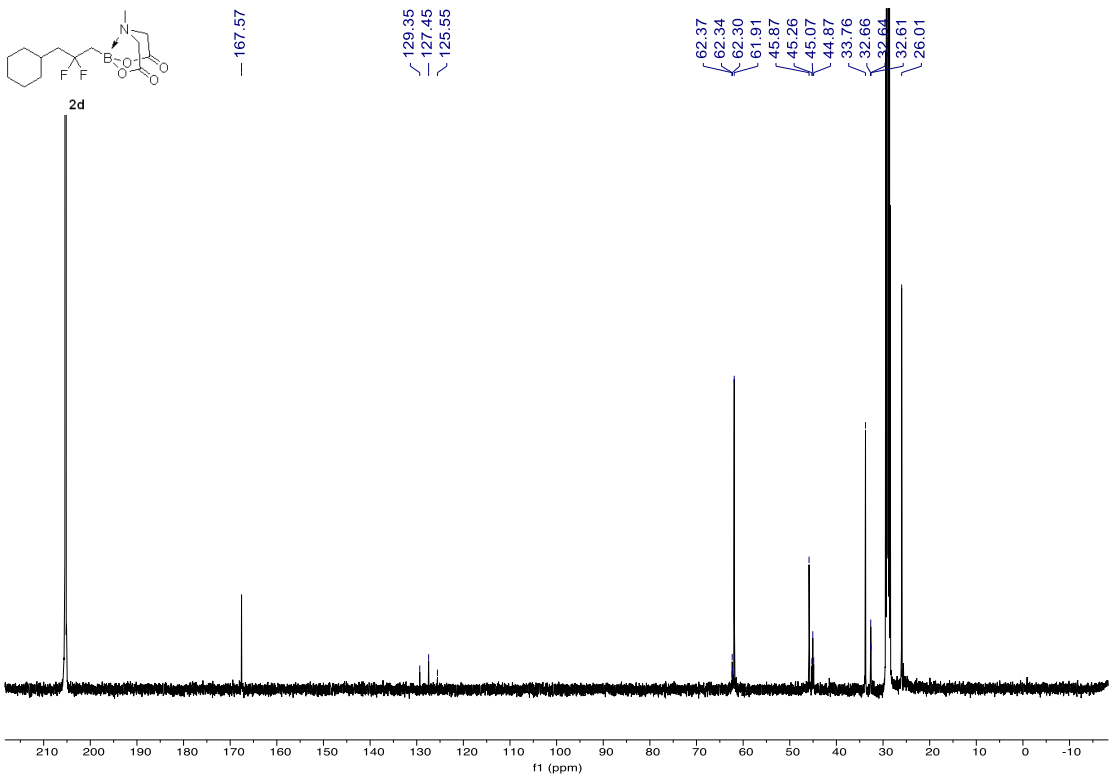
2c

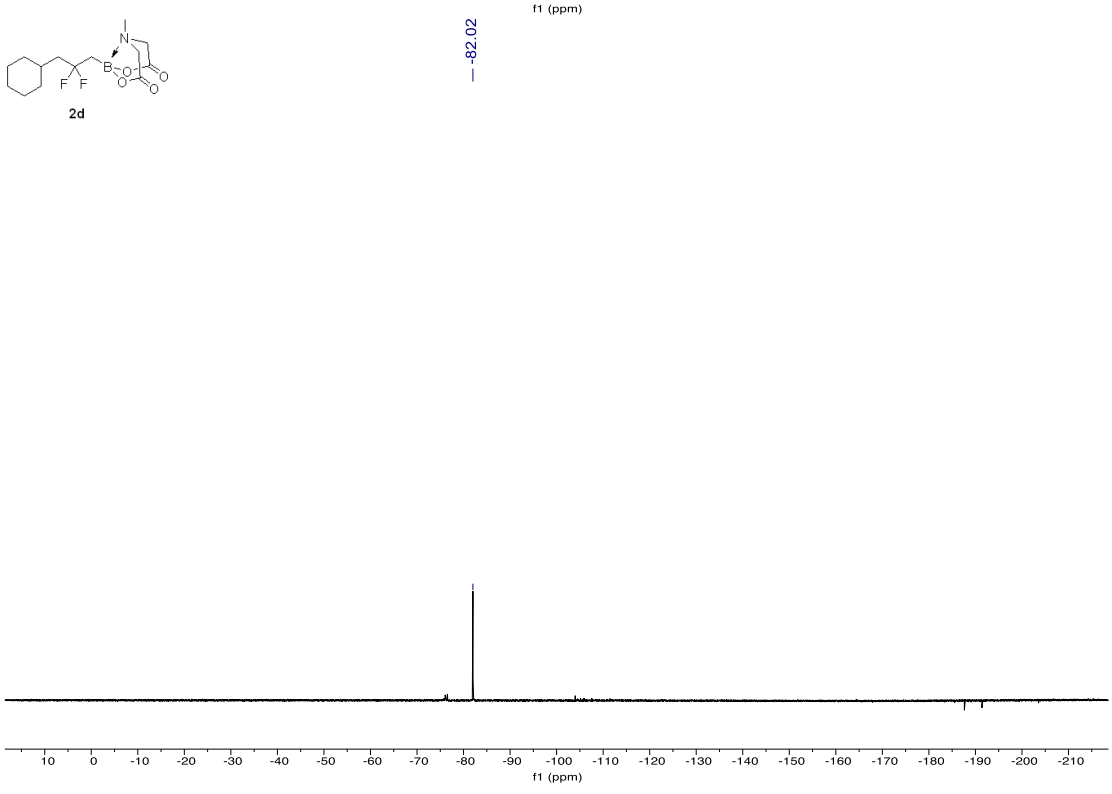
-82.57
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
3.97 3.94 3.81 3.77 2.88 1.85 1.84 1.82 1.80 1.79 1.78 1.77 1.69 1.66 1.63 1.61 1.50 1.46 1.42 1.31 1.28 1.26 1.24 1.20 1.17 1.15 1.02 1.00 0.98 0.95

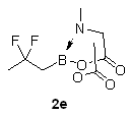


2d

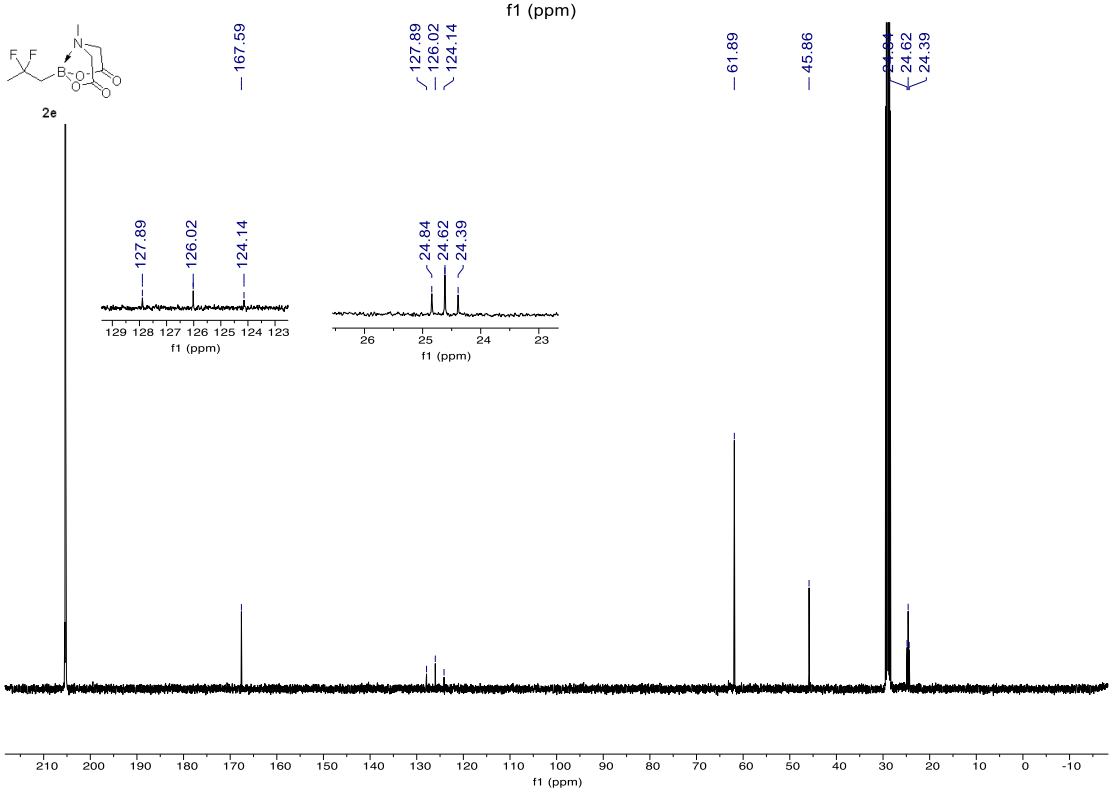

2.00 1.97 2.88 3.94 3.97 2.16 3.44 1.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

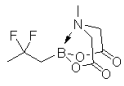

2d
167.57
129.35
127.45
125.55
62.37
62.34
62.30
61.91
45.87
45.26
45.07
44.87
33.76
32.66
32.64
32.61
26.01
f1 (ppm)


2d
-82.02
f1 (ppm)


2e

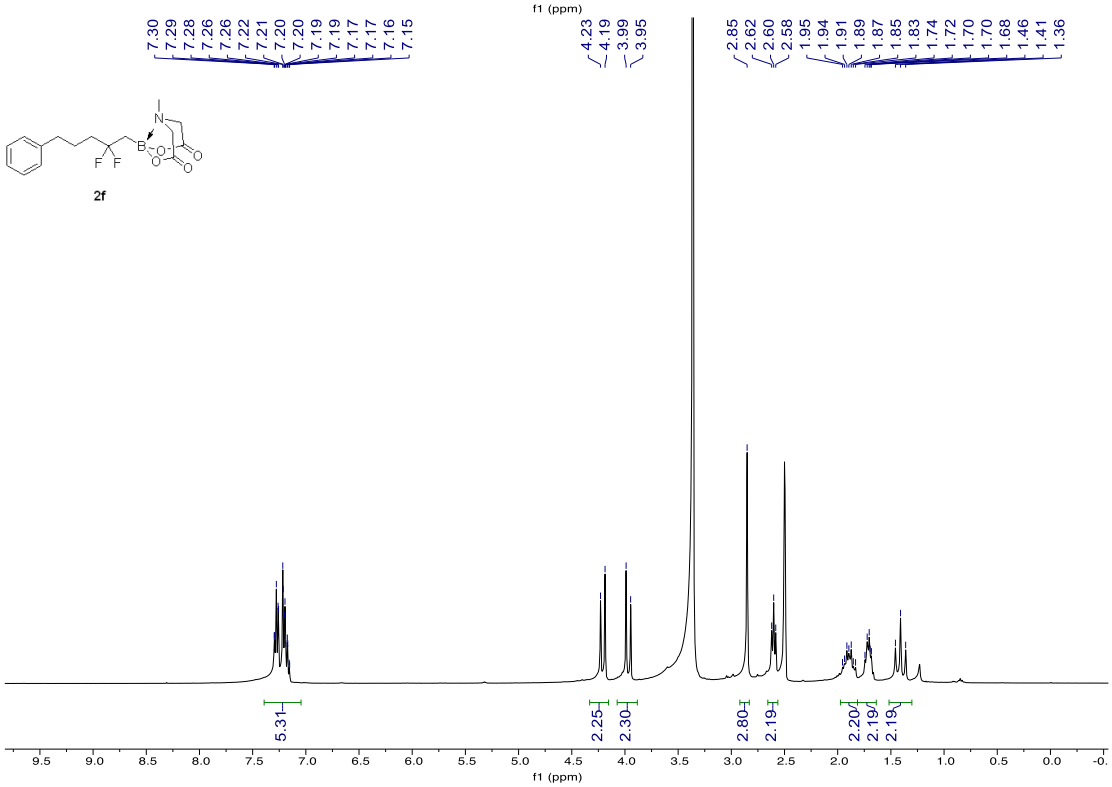
3.98
3.95
3.82
3.78
2.89
1.70
1.66
1.62
1.52
1.49
1.45
2.05
1.96
2.87
2.95
2.00
f1 (ppm)


2e
167.59
127.89
126.02
124.14
61.89
45.86
24.84
24.62
24.39
f1 (ppm)

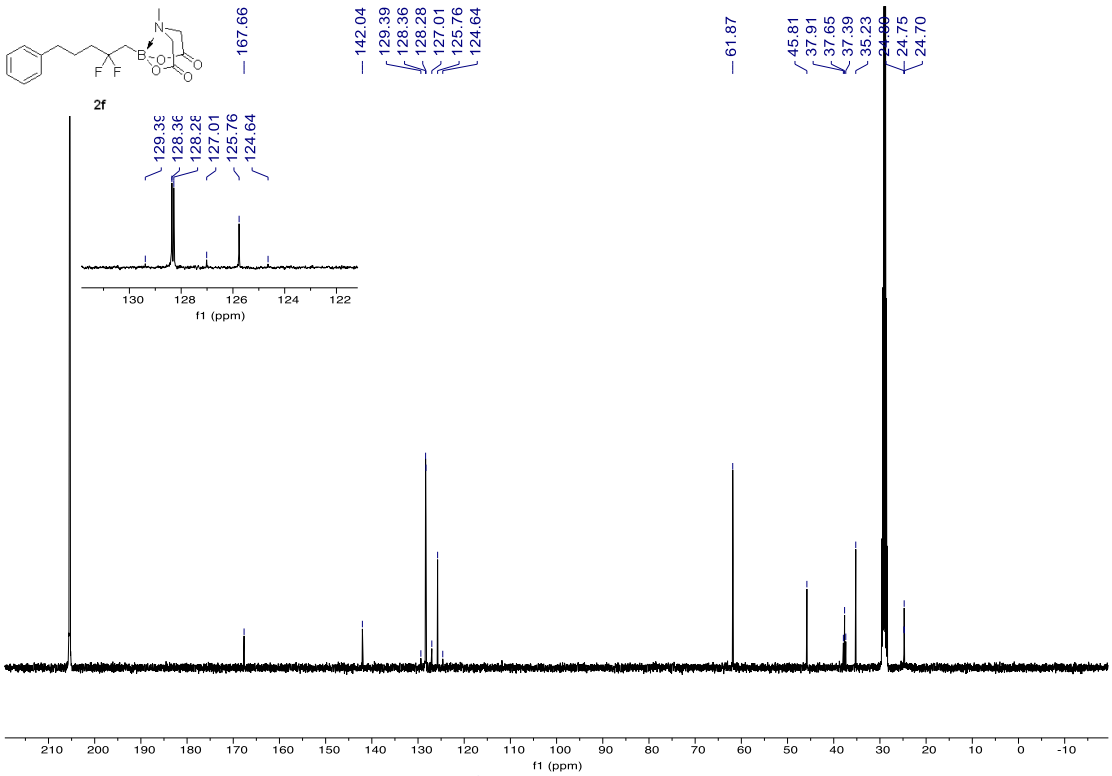


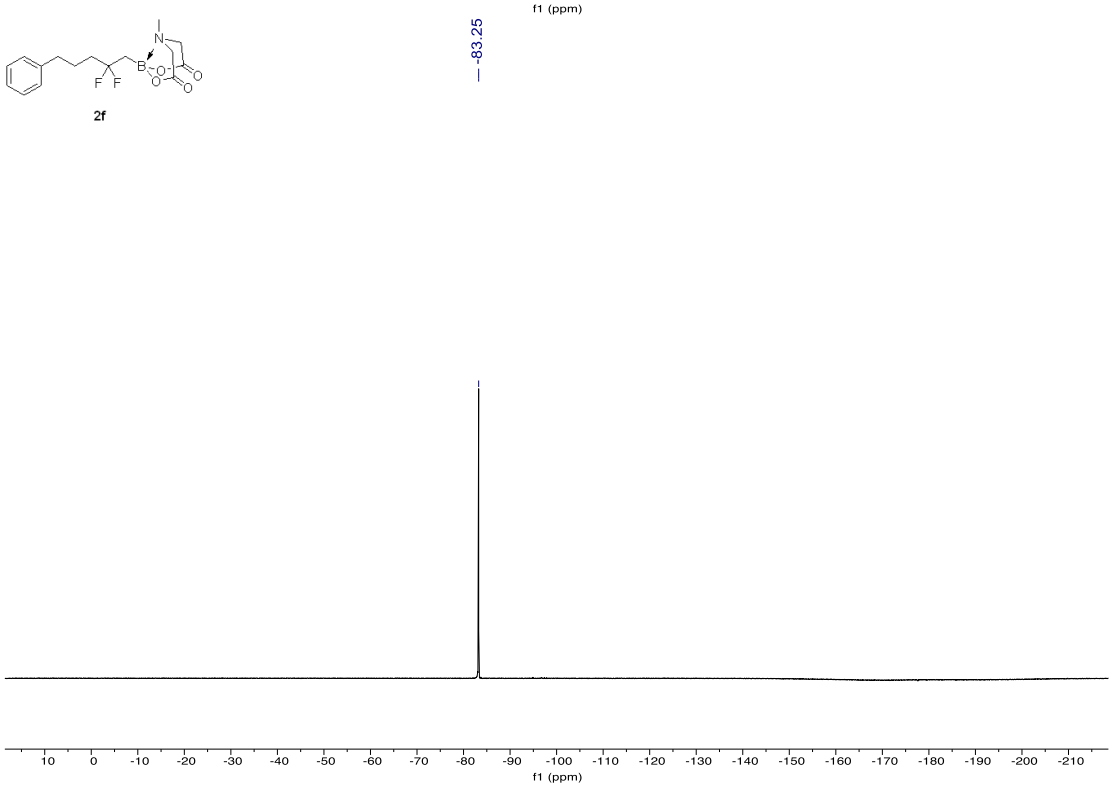
2e

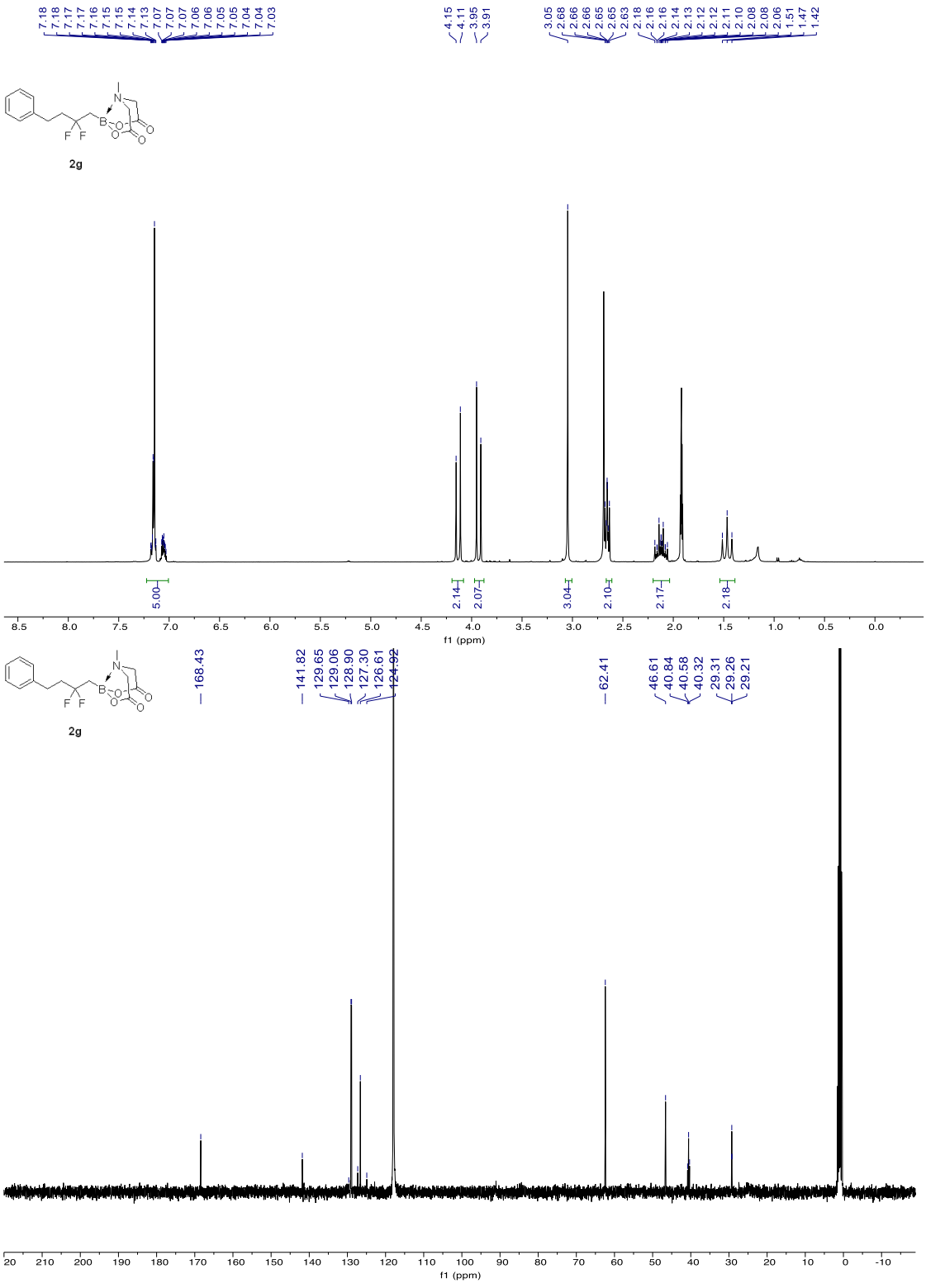
-76.97
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

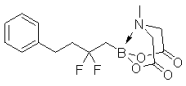

7.30 7.29 7.28 7.26 7.26 7.22 7.21 7.20 7.20 7.19 7.19 7.17 7.17 7.16 7.15
4.23 4.19 3.99 3.95
2.85 2.62 2.60 2.58 1.95 1.94 1.91 1.89 1.87 1.85 1.83 1.74 1.72 1.70 1.70 1.68 1.46 1.41 1.36
5.31 2.25 2.30 2.80 2.19 2.20 2.19 2.19
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

2f


2f
167.66
142.04
129.39
128.36
128.28
127.01
125.76
124.64
61.87
45.81
37.91
37.65
37.39
35.23
24.75
24.70
f1 (ppm)

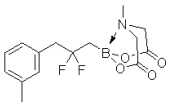

2f
-83.25
f1 (ppm)


7.18
7.18
7.17
7.17
7.16
7.15
7.15
7.14
7.13
7.07
7.07
7.07
7.06
7.06
7.05
7.05
7.04
7.04
7.03
4.15
4.11
3.95
3.91
3.05
2.68
2.66
2.66
2.65
2.65
2.63
2.18
2.16
2.16
2.14
2.13
2.12
2.12
2.11
2.10
2.08
2.08
2.06
1.51
1.47
1.42
2g
5.00
2.14
2.07
3.04
2.10
2.17
2.18
f1 (ppm)
2g
168.43
141.82
129.65
129.06
128.90
127.30
126.61
124.92
62.41
46.61
40.84
40.58
40.32
29.31
29.26
29.21
f1 (ppm)



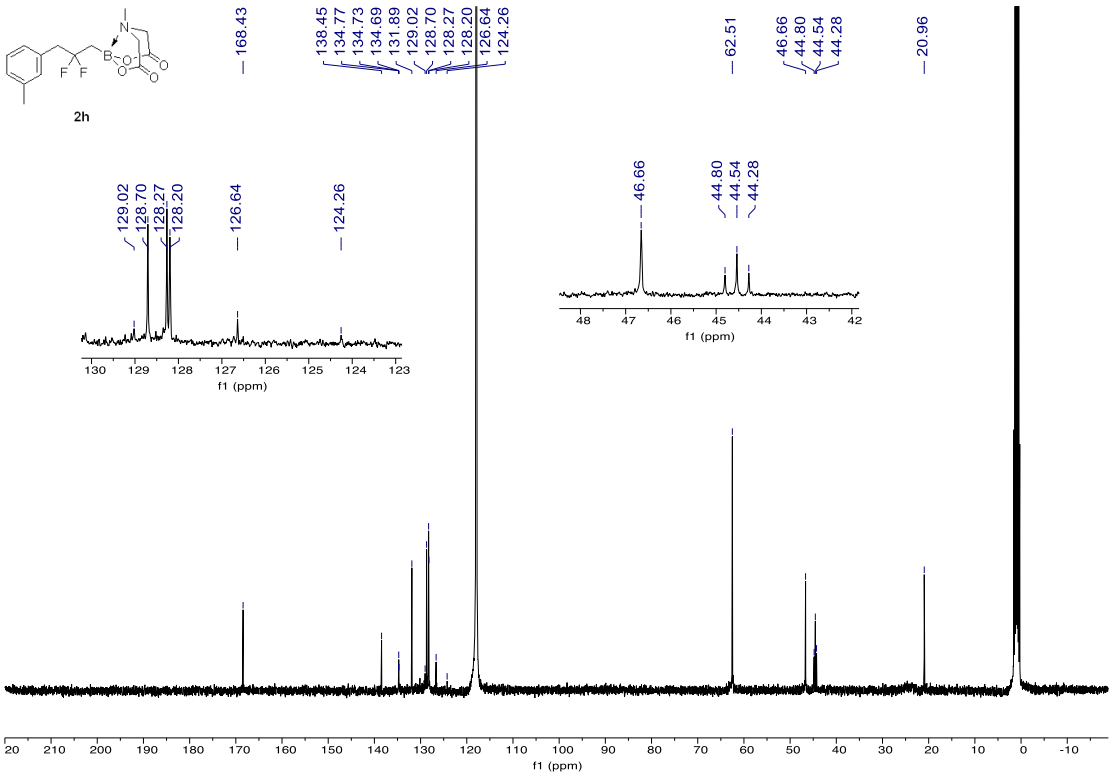
2g

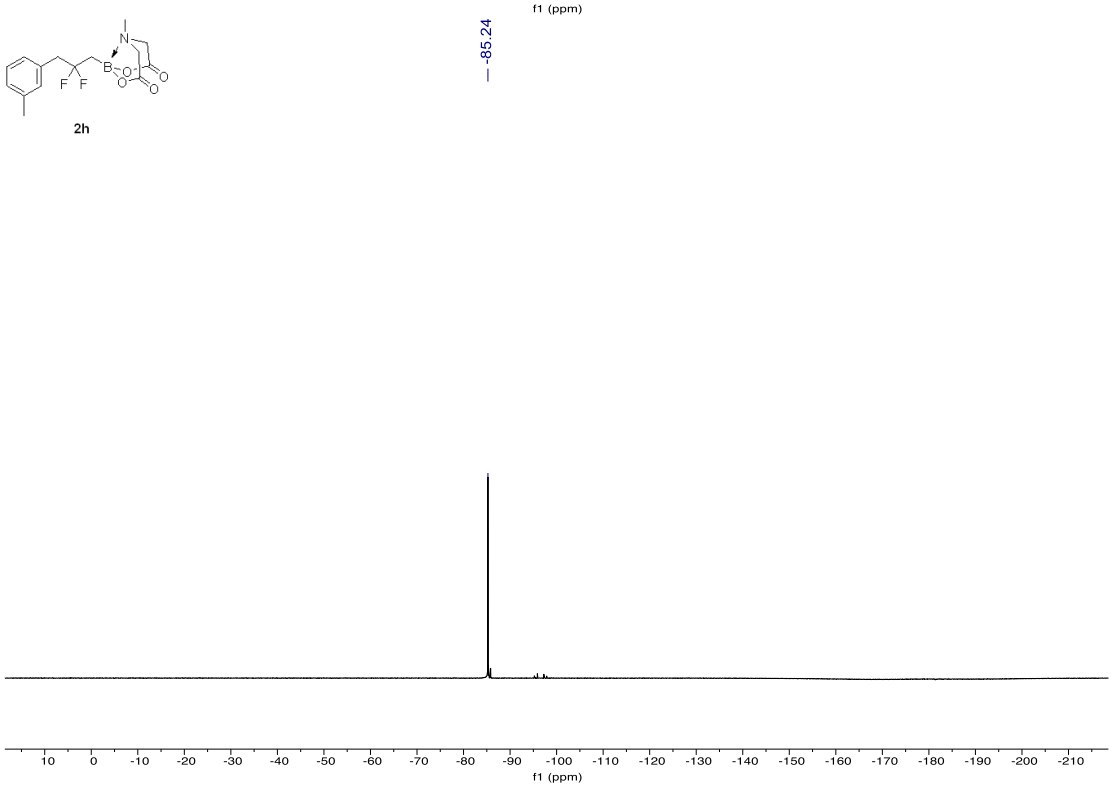
-84.92
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

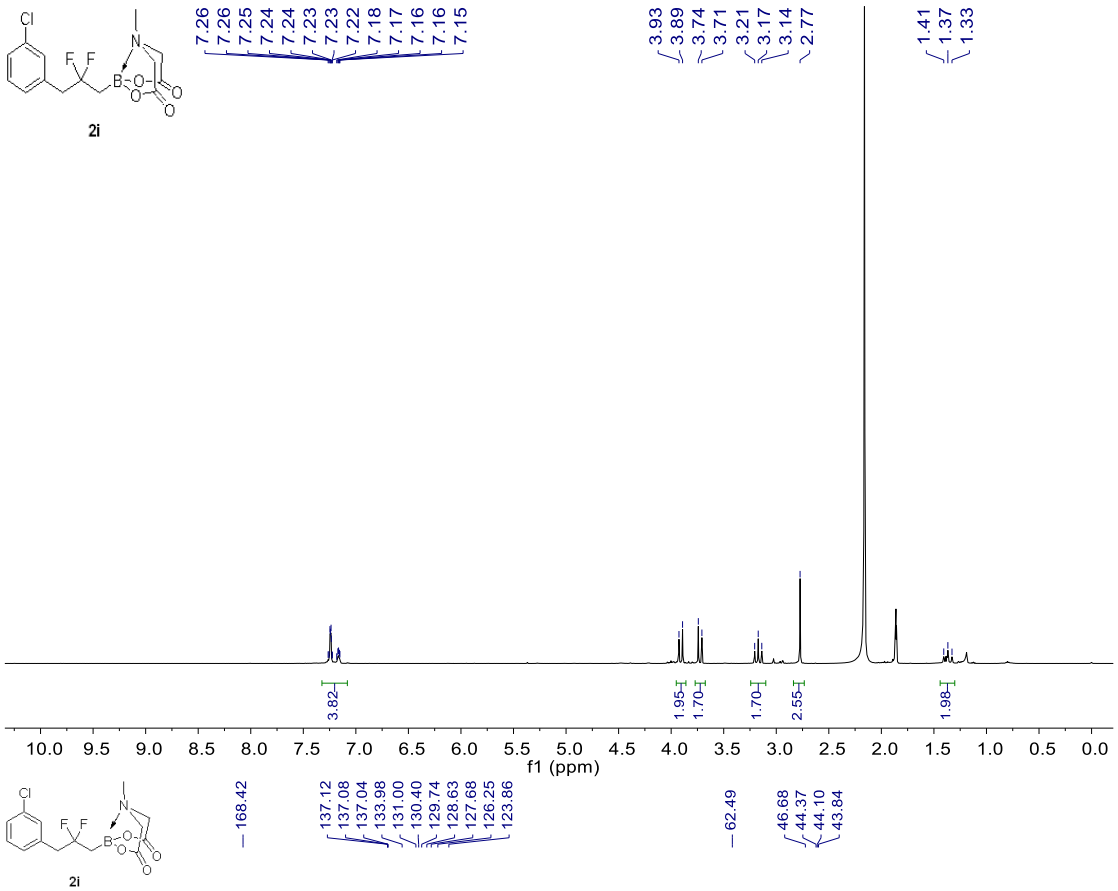


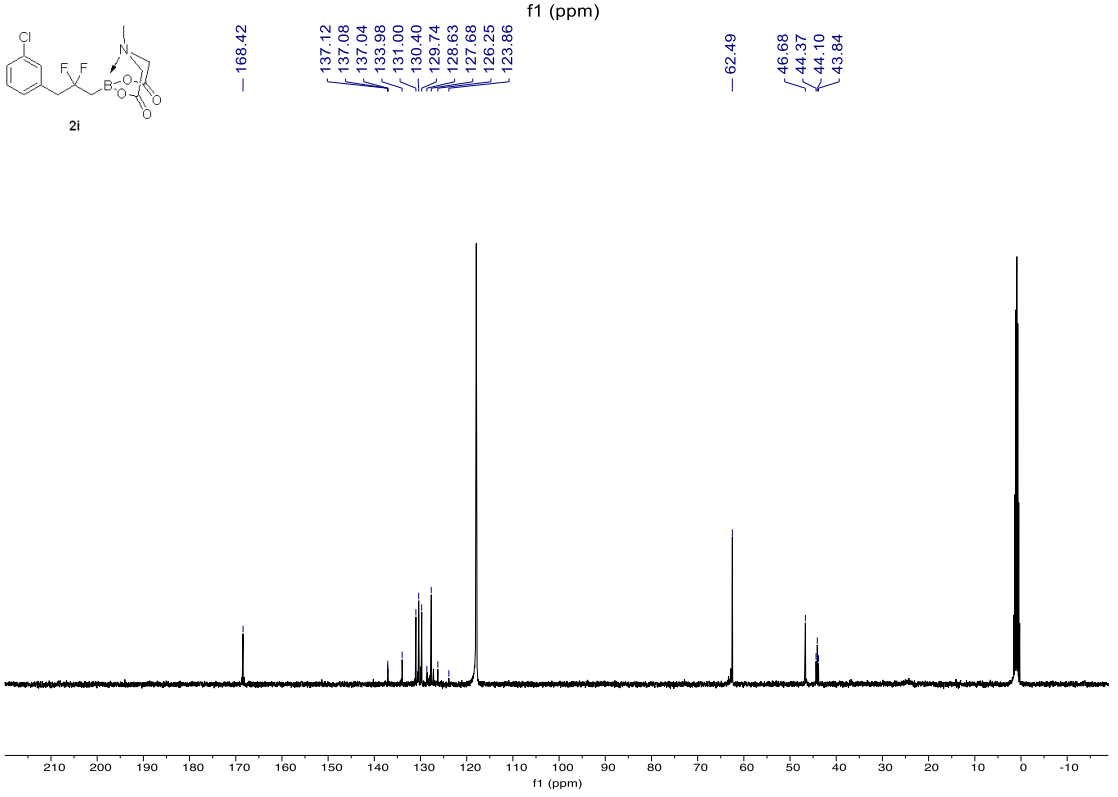
2h

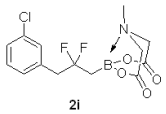
7.23
7.21
7.19
7.12
7.09
7.07
4.00
3.96
3.81
3.77
3.24
3.20
3.15
2.84
2.32
1.48
1.43
1.38
1.25
2.95
2.19
1.88
2.00
2.96
3.18
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


2h
168.43
138.45
134.77
134.73
134.69
131.89
129.02
128.70
128.27
128.20
126.64
124.26
62.51
46.66
44.80
44.54
44.28
20.96
f1 (ppm)

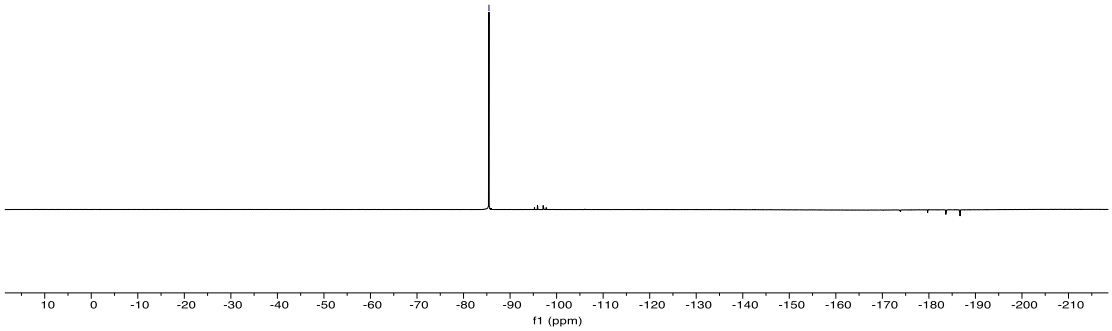

2h
-85.24
f1 (ppm)

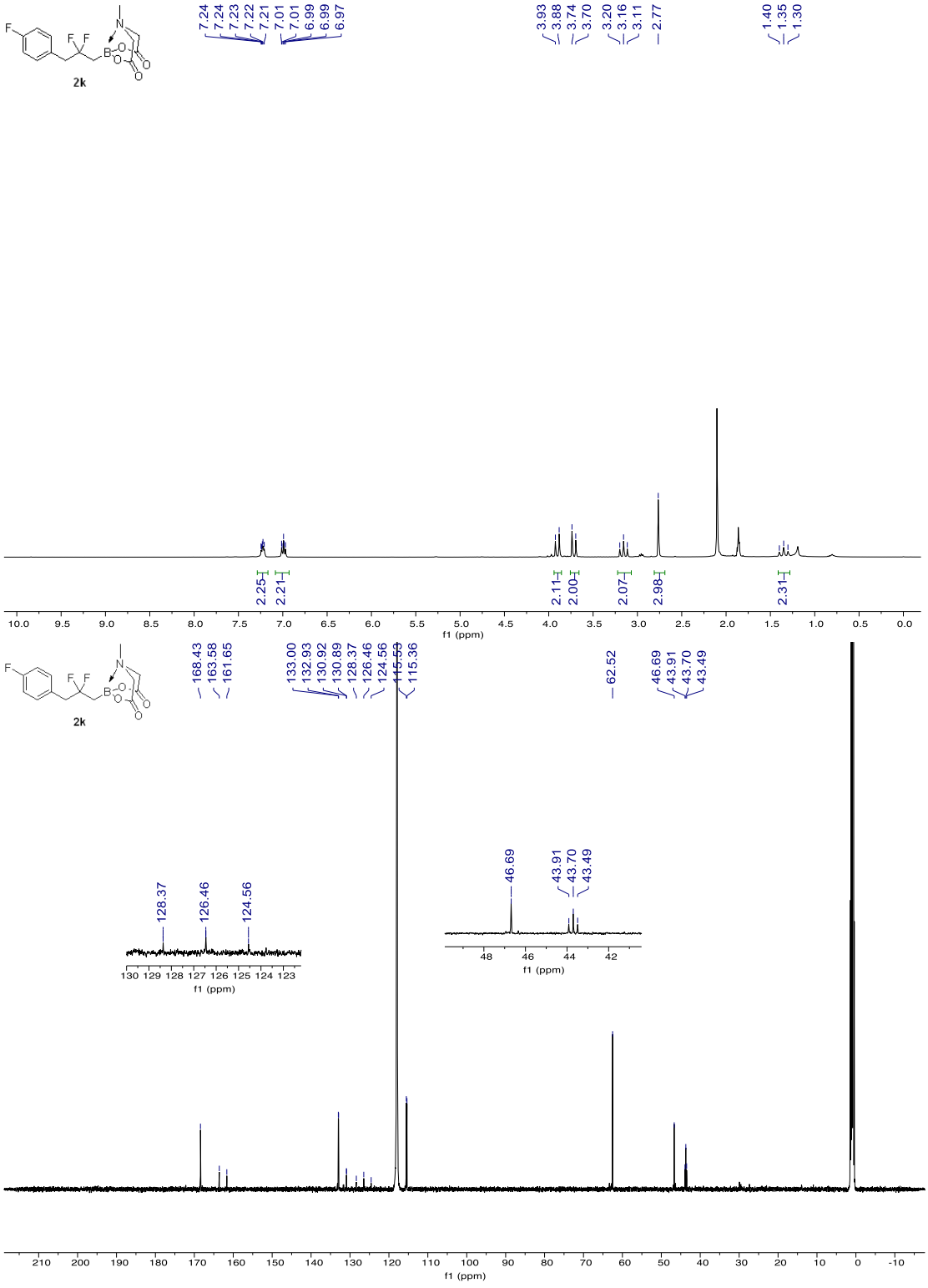

Cl
F F
B
O
O
O
O
N
2i
7.26
7.26
7.25
7.24
7.24
7.23
7.23
7.22
7.18
7.17
7.16
7.16
7.15
3.93
3.89
3.74
3.71
3.21
3.17
3.14
2.77
1.41
1.37
1.33
3.82
1.95
1.70
1.70
2.55
1.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

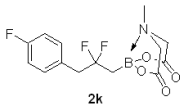

Cl
F F
B
O
O
O
O
N
2i
168.42
137.12
137.08
137.04
133.98
131.00
130.40
129.74
128.63
127.68
126.25
123.86
62.49
46.68
44.37
44.10
43.84
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Cl
F
F
N
B
O
O
O
O

2i


-85.46
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


2k
7.24
7.24
7.23
7.22
7.21
7.01
7.01
6.99
6.99
6.97
3.93
3.88
3.74
3.70
3.20
3.16
3.11
2.77
1.40
1.35
1.30
2.25
2.21
2.11
2.00
2.07
2.98
2.31
f1 (ppm)
168.43
163.58
161.65
133.00
132.93
130.92
130.89
128.37
126.46
124.56
115.53
115.36
62.52
46.69
43.91
43.70
43.49
128.37
126.46
124.56
f1 (ppm)
46.69
43.91
43.70
43.49
f1 (ppm)
f1 (ppm)

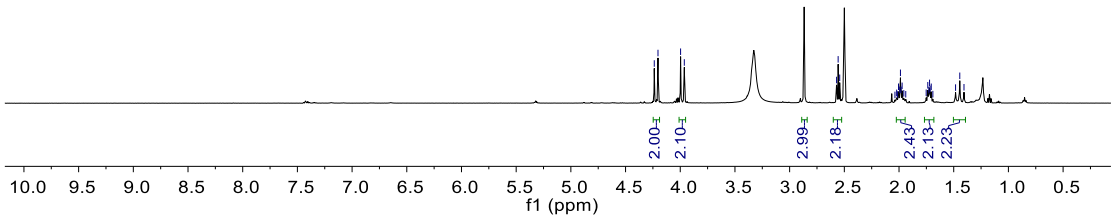


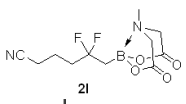
2k

-85.77
-117.64
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

2l

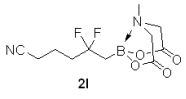
4.24
4.20
4.00
3.96
2.57
2.56
2.54
2.04
2.02
2.01
2.00
1.99
1.99
1.98
1.97
1.96
1.94
1.75
1.74
1.73
1.72
1.72
1.71
1.69
1.48
1.44
1.41


2.00
2.10
2.99
2.18
2.43
2.13
2.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



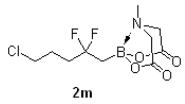
2l

167.64
128.37
126.47
124.57
119.44
61.88
45.86
36.98
36.77
36.56
19.12
19.08
19.04
16.03
f1 (ppm)

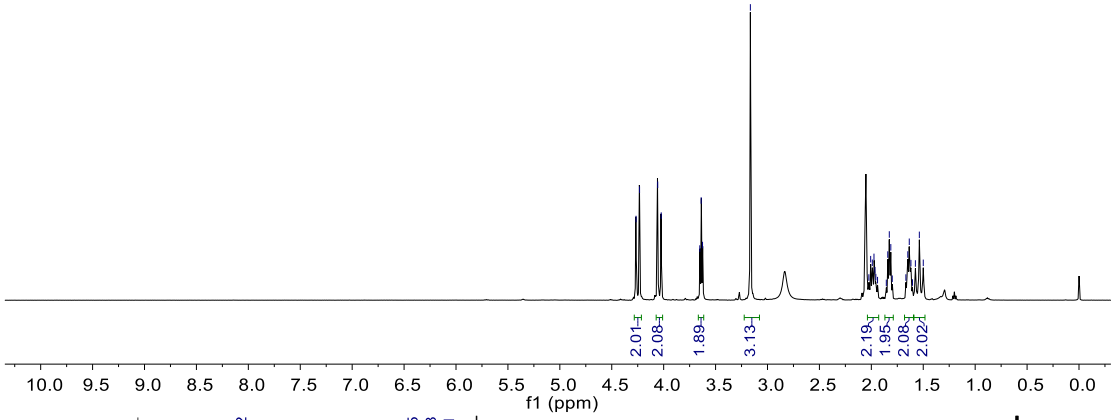


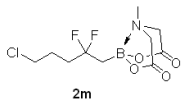
2l

-85.49
f1 (ppm)

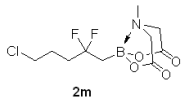

F
F
Cl
B
N
O
O
O
O
2m


4.27
4.23
4.06
4.02
3.65
3.64
3.63
3.17
2.02
2.01
1.99
1.97
1.97
1.96
1.84
1.83
1.81
1.67
1.65
1.63
1.62
1.58
1.54


2.01
2.08
1.89
3.13
2.19
1.95
2.08
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

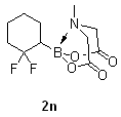

F
F
Cl
B
N
O
O
O
O
2m

168.42
129.75
127.38
125.01
62.42
46.64
45.28
36.26
36.00
35.74
26.42
26.38
26.33
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


F
F
N
Cl
B
O
O
O
O

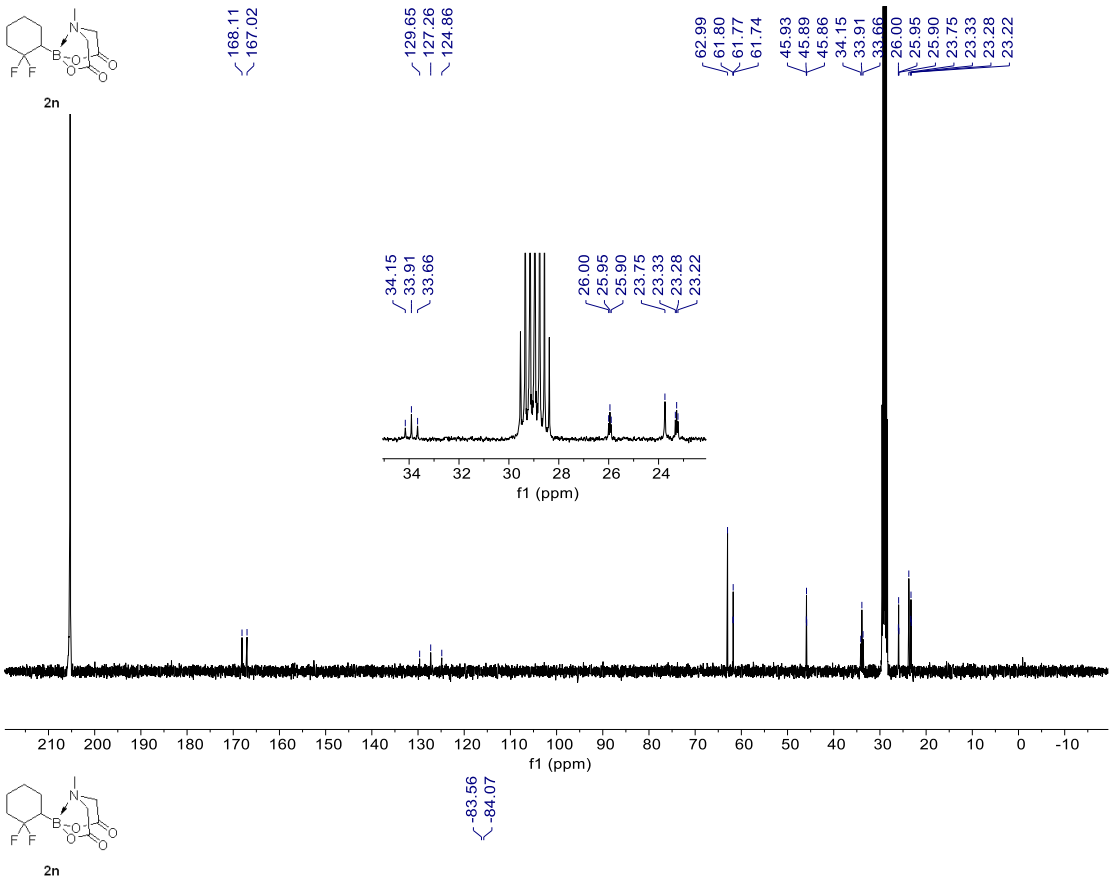
2m

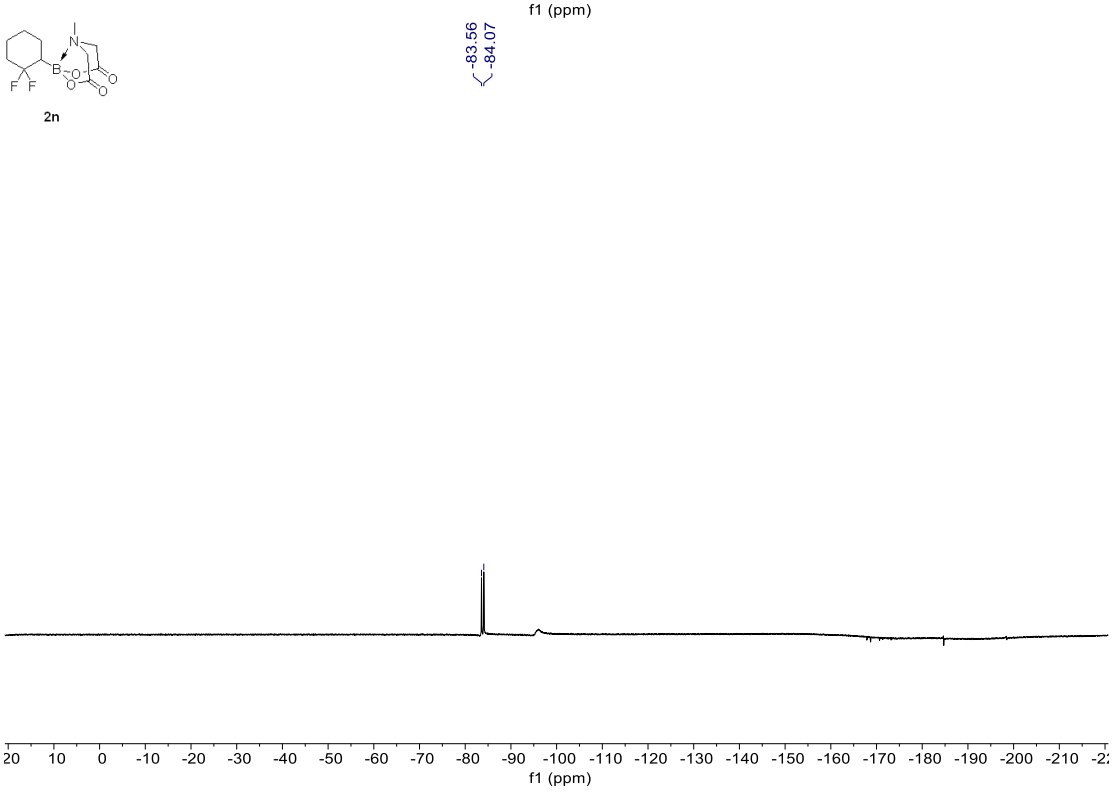
-86.03
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

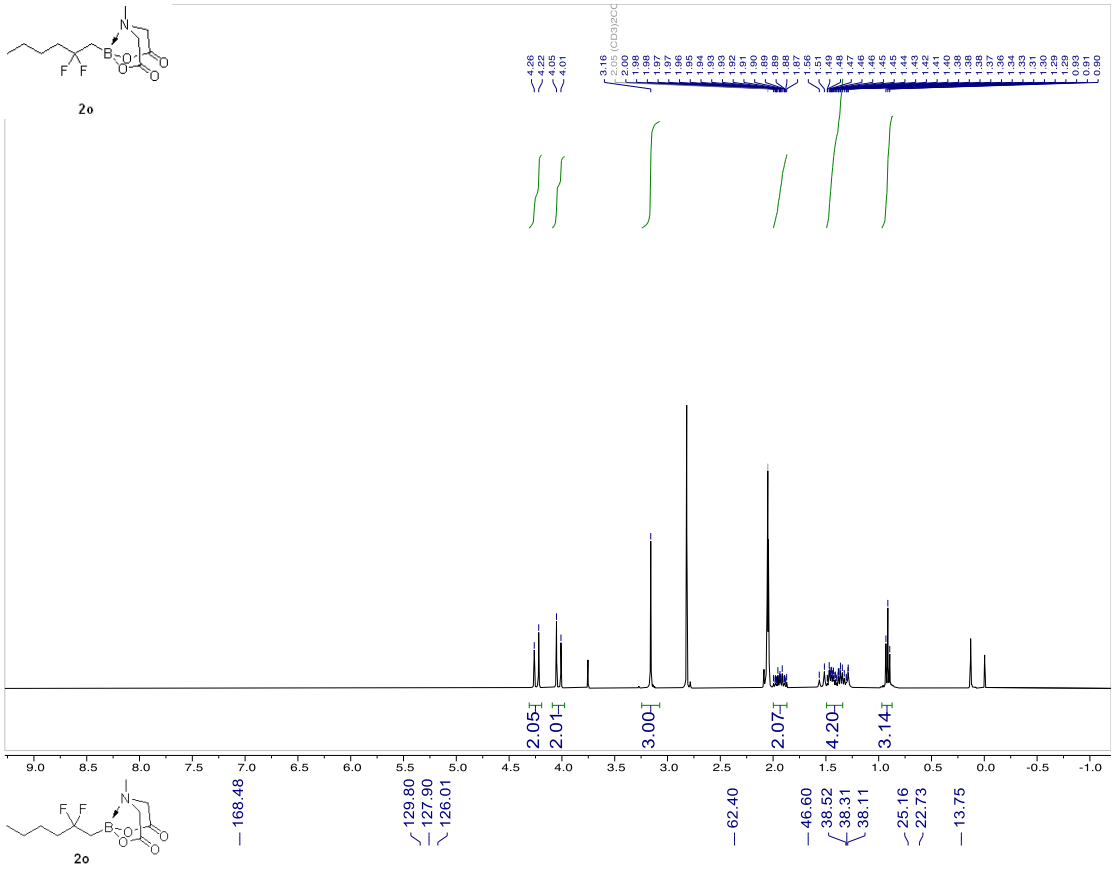

N
B
O
O
O
F
F

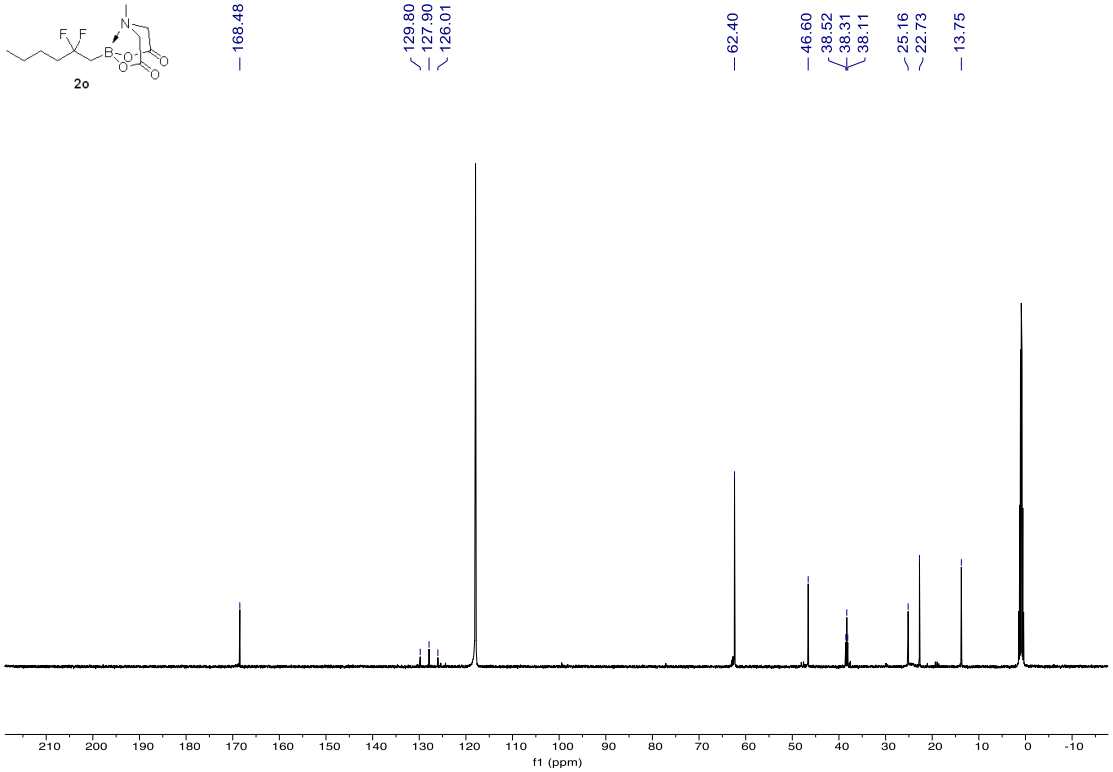
2n

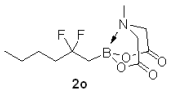
4.29
4.25
4.18
4.17
4.17
4.14
4.13
4.08
4.04
3.90
3.86
3.75
3.17
2.05 (CD3)2CO
1.81
1.80
1.78
1.76
1.75
1.74
1.73
1.72
1.71
1.69
1.68
1.66
1.65
1.63
1.62
1.60
1.59
1.58
1.56
1.40
1.38
1.37
1.36
1.34
1.19
1.04
1.05
1.36
3.00
7.94
1.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


2n
168.11
167.02
129.65
127.26
124.86
62.99
61.80
61.77
61.74
45.93
45.89
45.86
34.15
33.91
33.66
26.00
25.95
25.90
23.75
23.33
23.28
23.22
f1 (ppm)
f1 (ppm)


2n
-83.56
-84.07
f1 (ppm)

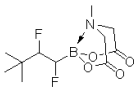

2o
4.26
4.22
4.05
4.01
3.16
2.05 (CD3)2CO
2.00
1.98
1.97
1.97
1.96
1.95
1.94
1.93
1.93
1.92
1.91
1.90
1.89
1.89
1.88
1.87
1.56
1.51
1.49
1.48
1.47
1.46
1.46
1.45
1.45
1.44
1.43
1.42
1.41
1.40
1.39
1.38
1.37
1.36
1.34
1.33
1.31
1.30
1.29
0.93
0.91
0.90
2.05
2.01
3.00
2.07
4.20
3.14
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0


2o
168.48
129.80
127.90
126.01
62.40
46.60
38.52
38.31
38.11
25.16
22.73
13.75
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



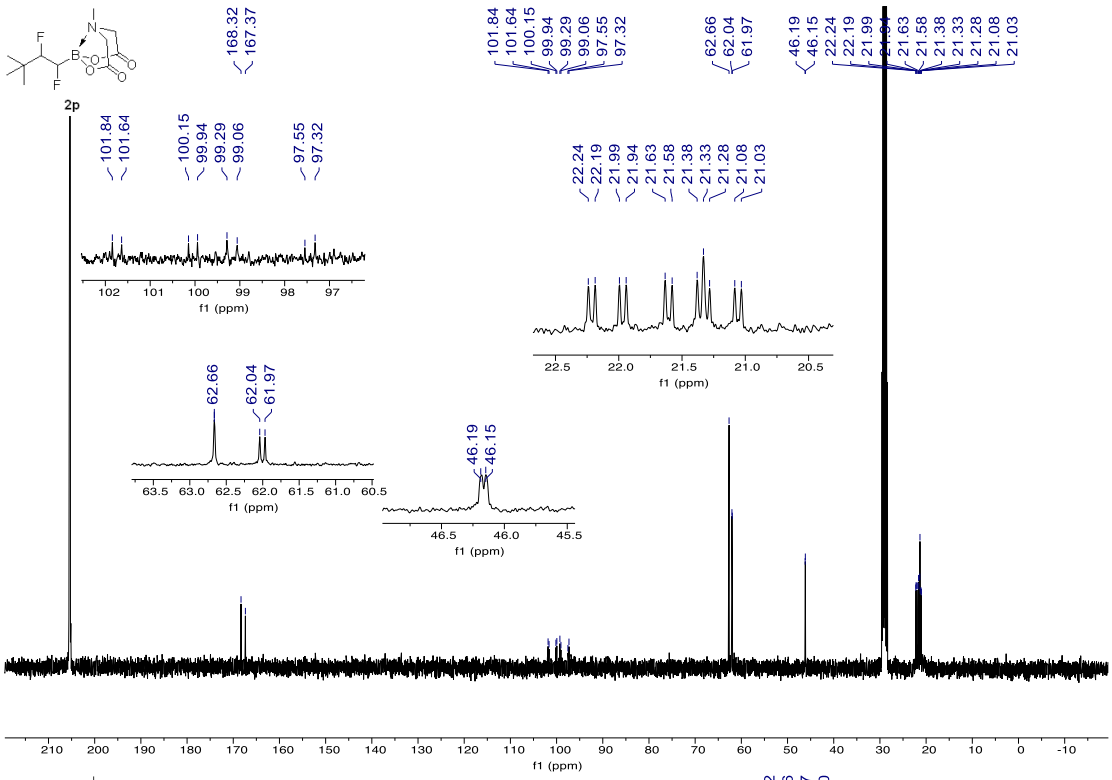
2o

-85.45
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

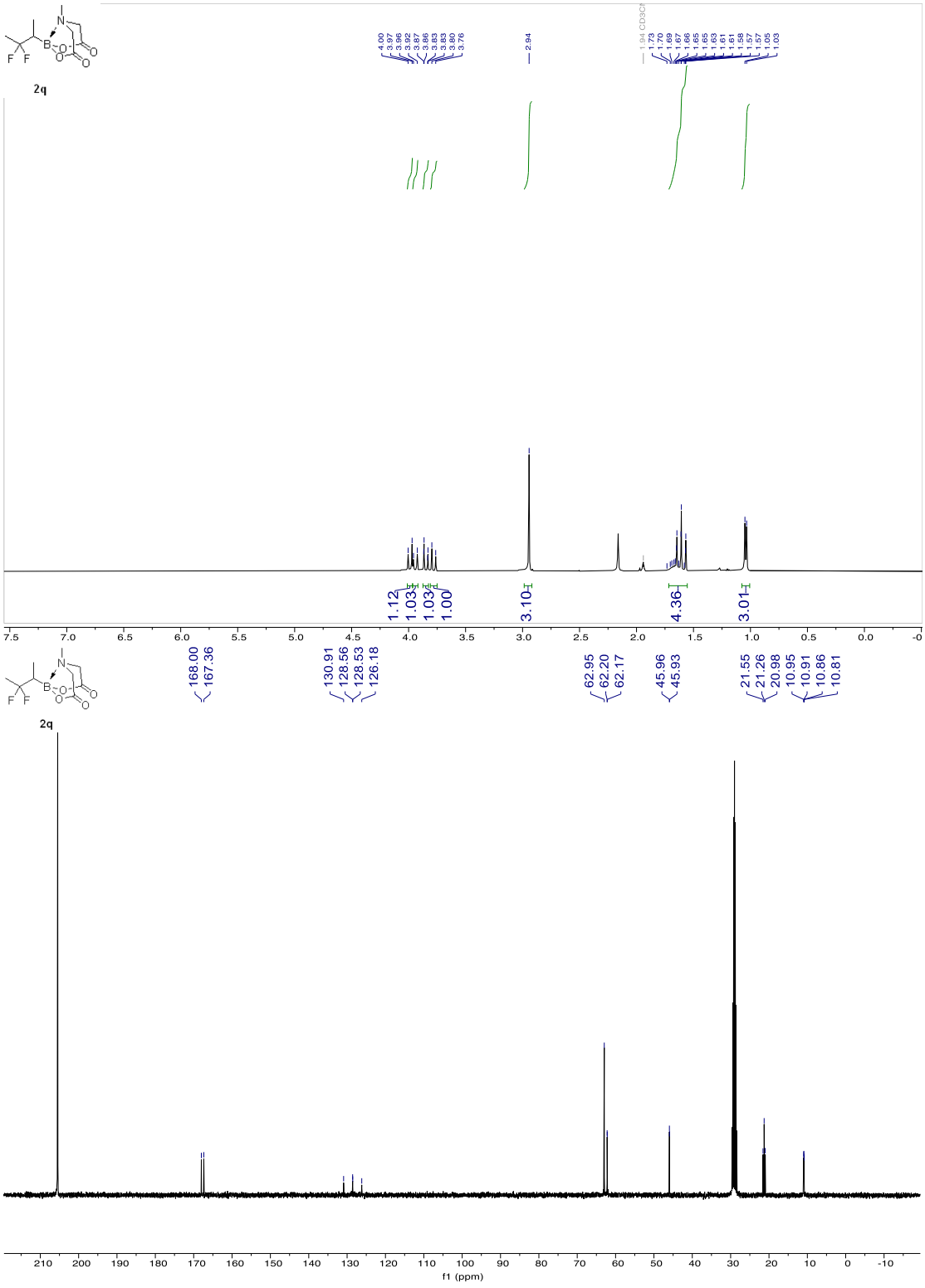


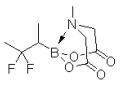
2p

4.29
4.25
4.16
4.15
4.12
4.11
4.06
4.02
3.90
3.89
3.85
3.85
3.11
1.63
1.59
1.47
1.42
1.36
1.11
1.07
1.00
0.96
1.08
1.11
1.14
1.00
3.09
1.22
9.22
1.08
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


2p
168.32
167.37
101.84
101.64
100.15
99.94
99.29
99.06
97.55
97.32
62.66
62.04
61.97
46.19
46.15
22.24
22.19
21.99
21.94
21.63
21.58
21.38
21.33
21.28
21.08
21.03
f1 (ppm)

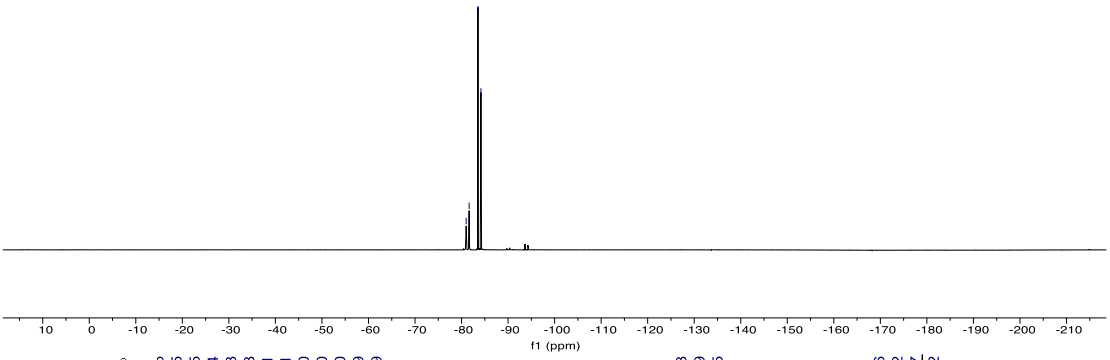

2p
-150.32
-150.36
-153.67
-153.70
f1 (ppm)


2q
4.00
3.97
3.96
3.92
3.87
3.86
3.83
3.83
3.80
3.76
2.94
1.94 CD3CN
1.73
1.70
1.69
1.67
1.66
1.65
1.65
1.63
1.61
1.61
1.58
1.57
1.57
1.05
1.03
1.12
1.03
1.03
1.00
3.10
4.36
3.01
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
168.00
167.36
130.91
128.56
128.53
126.18
62.95
62.20
62.17
45.96
45.93
21.55
21.26
20.98
10.95
10.91
10.86
10.81
2q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



2q

-81.00
-81.63
-83.53
-84.17

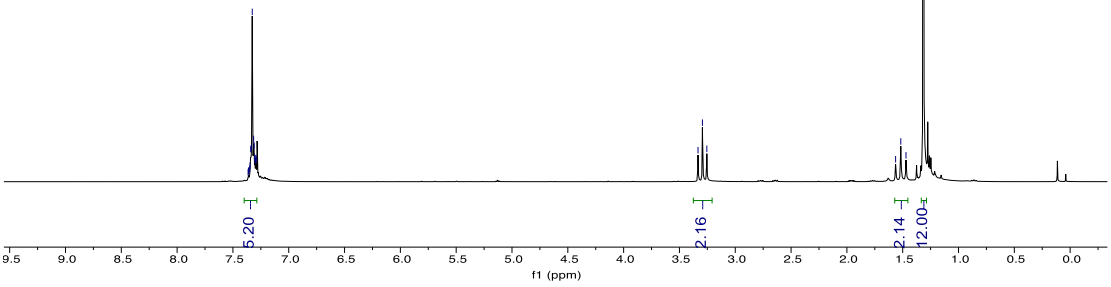


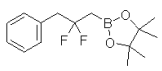
4

7.35
7.35
7.34
7.33
7.33
7.31
7.31
7.30
7.30
7.30
7.29
7.29

3.33
3.29
3.25

1.56
1.52
1.47
1.32





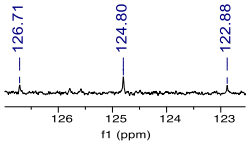
4

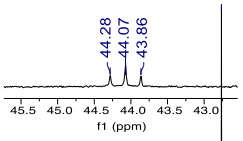

134.22
134.18
134.14
130.45
128.34
127.16
126.71
124.80
122.88

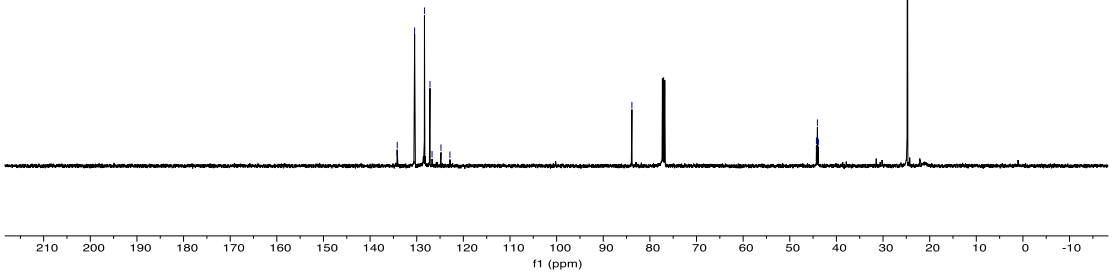

83.86

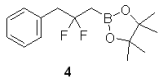

44.28
44.07
43.86


24.77


126.71
124.80
122.88
126
125
124
123
f1 (ppm)

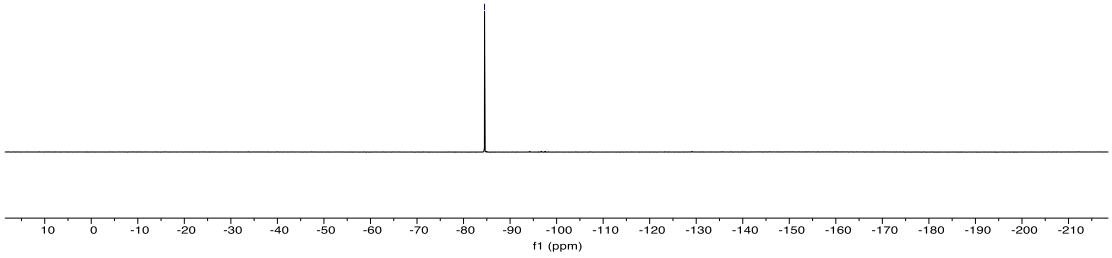

44.28
44.07
43.86
45.5
45.0
44.5
44.0
43.5
43.0
f1 (ppm)

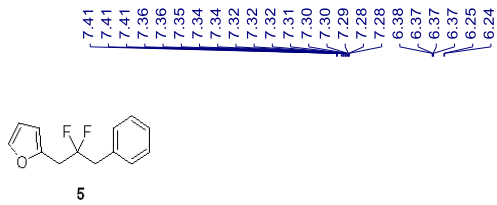

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

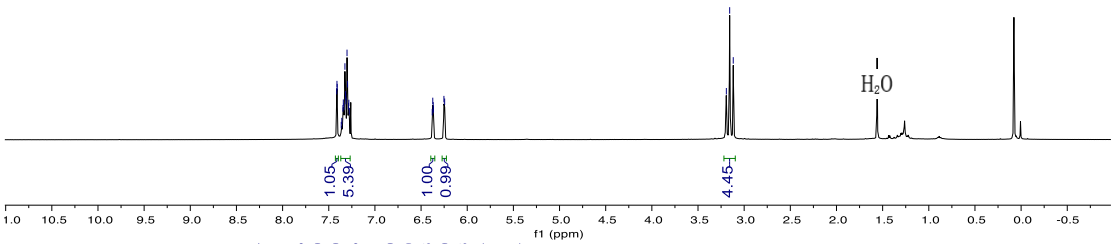


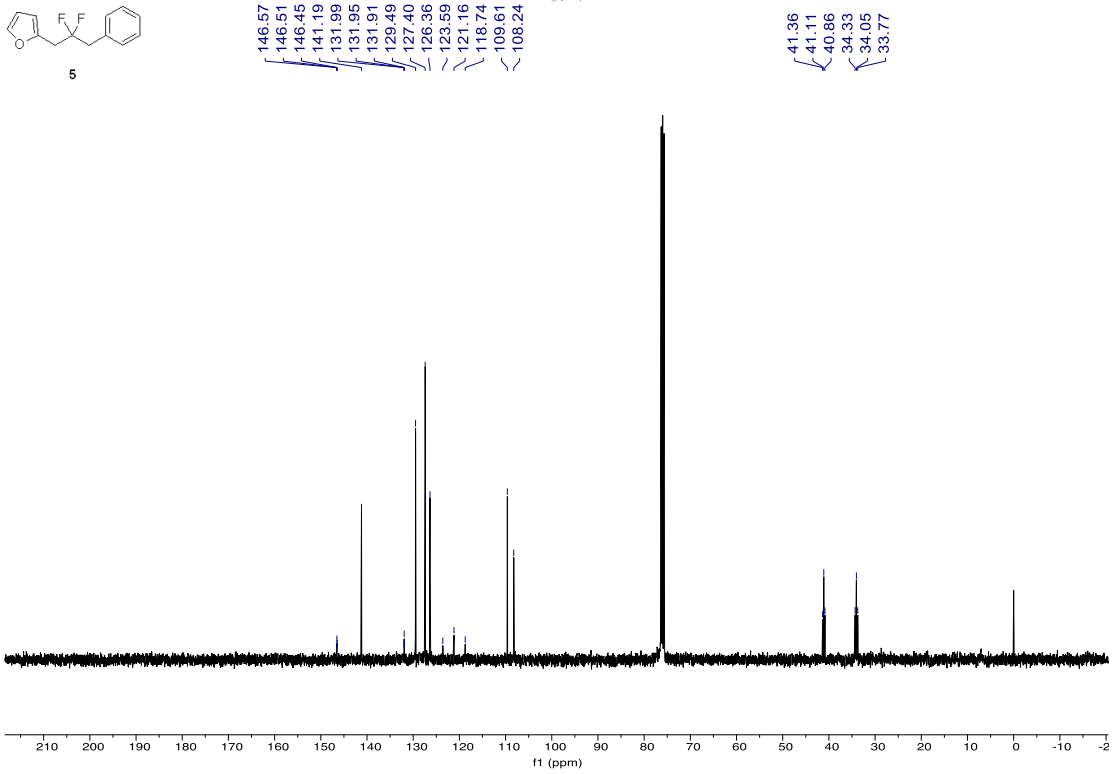
4

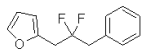

-84.51


10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.41
7.41
7.41
7.36
7.36
7.35
7.34
7.34
7.32
7.32
7.32
7.31
7.30
7.30
7.29
7.28
7.28
6.38
6.37
6.37
6.37
6.25
6.24
3.19
3.16
3.12
F F
O
5

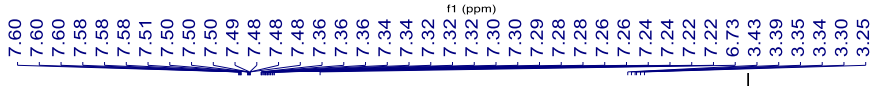

H2O
1.05
5.39
1.00
0.99
4.45
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

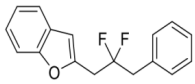

F F
O
5
146.57
146.51
146.45
141.19
131.99
131.95
131.91
129.49
127.40
126.36
123.59
121.16
118.74
109.61
108.24
41.36
41.11
40.86
34.33
34.05
33.77
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -2
f1 (ppm)


F
F
O

5

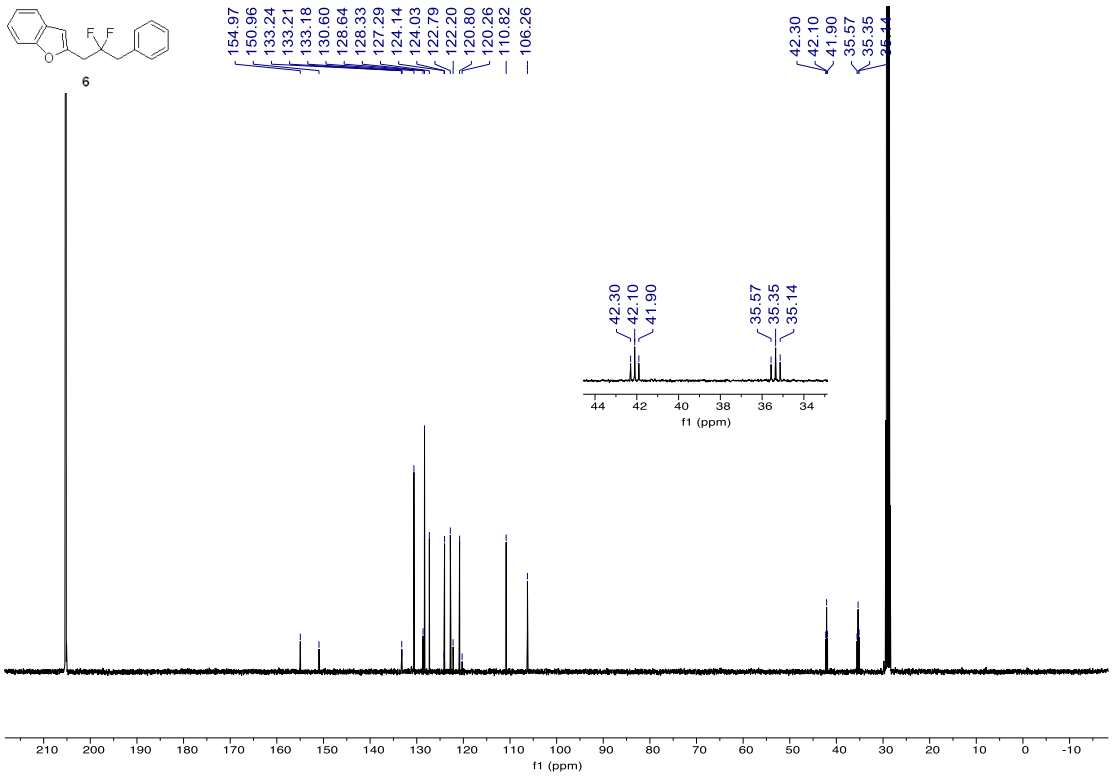
-94.55
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

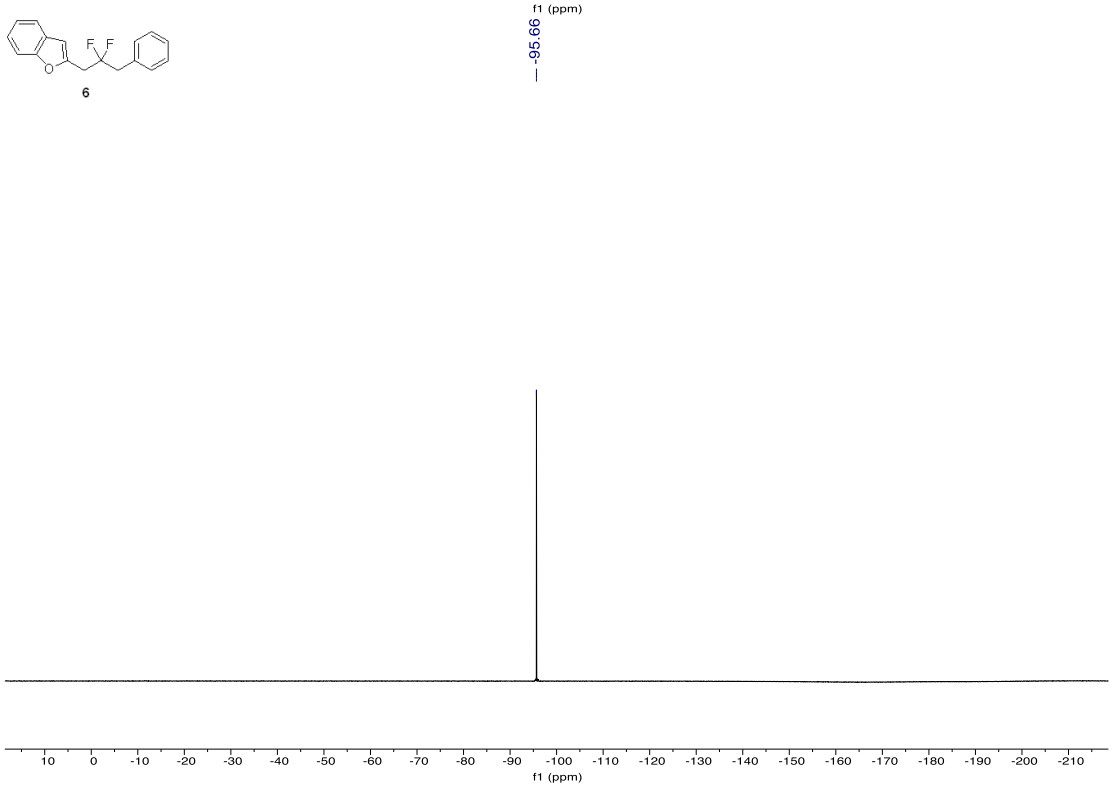

7.60 7.60 7.60 7.58 7.58 7.51 7.50 7.50 7.50 7.49 7.48 7.48 7.48 7.36 7.36 7.36 7.34 7.34 7.32 7.32 7.32 7.30 7.30 7.29 7.28 7.28 7.26 7.26 7.24 7.24 7.22 7.22 6.73 3.43 3.39 3.35 3.34 3.30 3.25


F
F
O

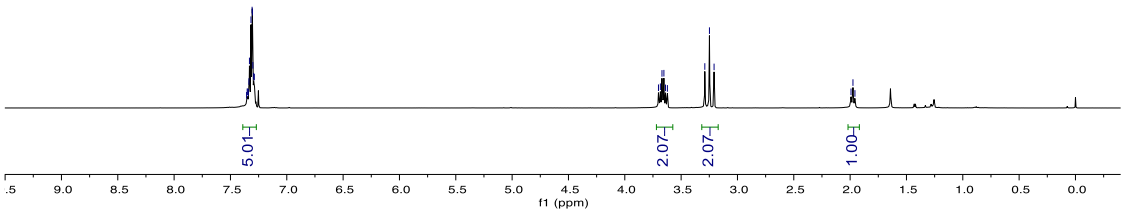
6

H2O
CD3CN
0.95
0.95
7.36
0.96
2.15
2.11
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

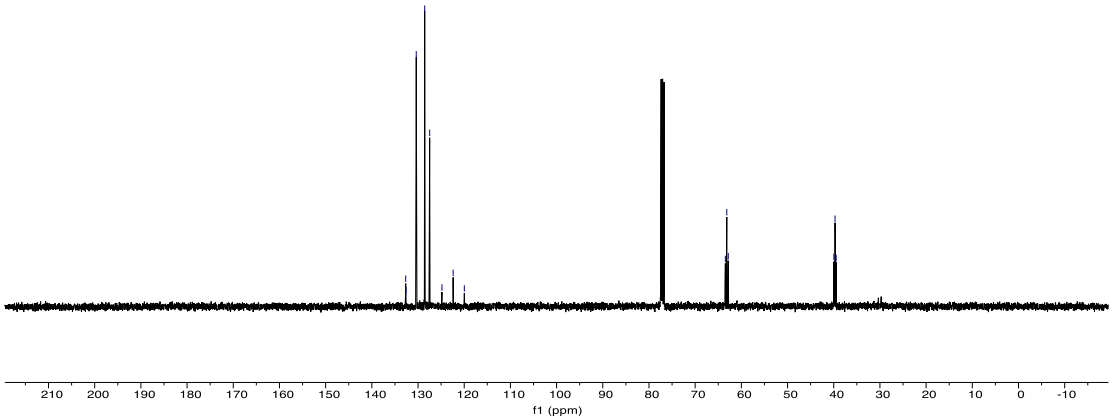

6
154.97
150.96
133.24
133.21
133.18
130.60
128.64
128.33
127.29
124.14
124.03
122.79
122.20
120.80
120.26
110.82
106.26
42.30
42.10
41.90
35.57
35.35
35.14
f1 (ppm)

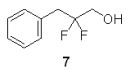

6
-95.66
f1 (ppm)


OH
F F
7
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.31
7.30
7.30
7.29
7.29
3.70
3.68
3.67
3.65
3.64
3.62
3.29
3.25
3.21
1.99
1.97
1.96


5.01
2.07
2.07
1.00
f1 (ppm)

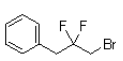

OH
F F
7
132.72
132.67
132.62
130.39
128.56
127.48
124.82
122.40
119.98
63.47
63.15
62.84
39.97
39.72
39.47


f1 (ppm)


OH
F F

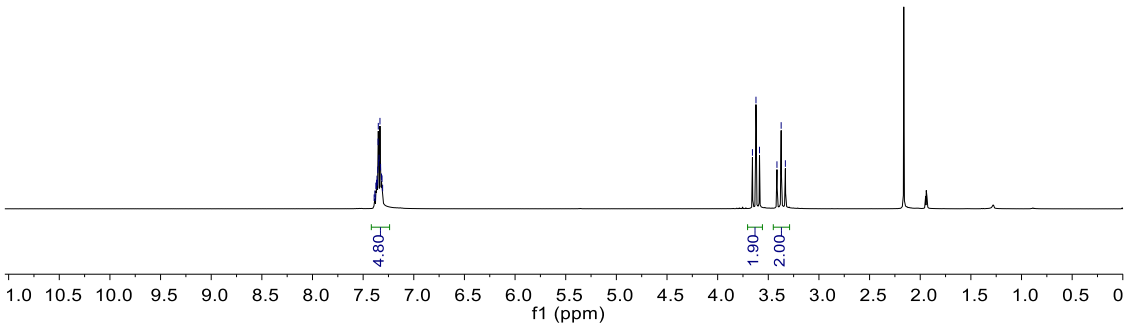
7

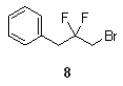
-106.92
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


F F
Br

8


7.39 7.38 7.38 7.37 7.37 7.37 7.36 7.36 7.36 7.35 7.35 7.35 7.34 7.33 7.32 7.31 7.31
3.66 3.62 3.59 3.41 3.37 3.33

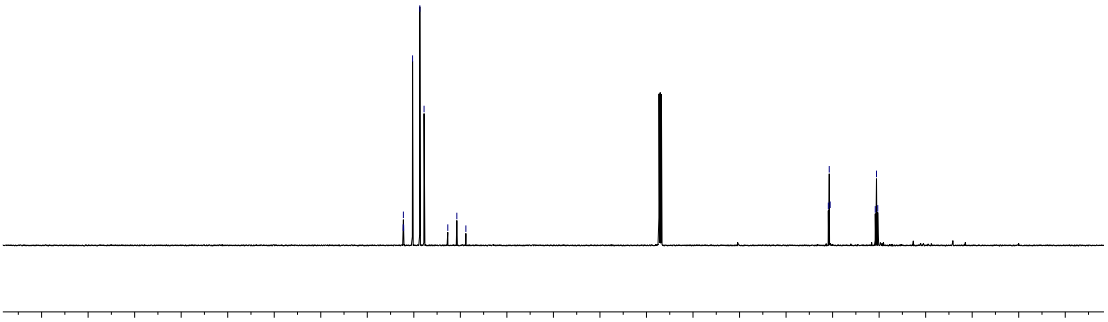

4.80
1.90
2.00
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)



8

132.28
132.24
132.20
130.27
128.71
127.80
122.70
120.76
118.81

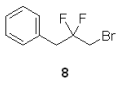
40.92
40.72
40.52
30.83
30.56
30.30



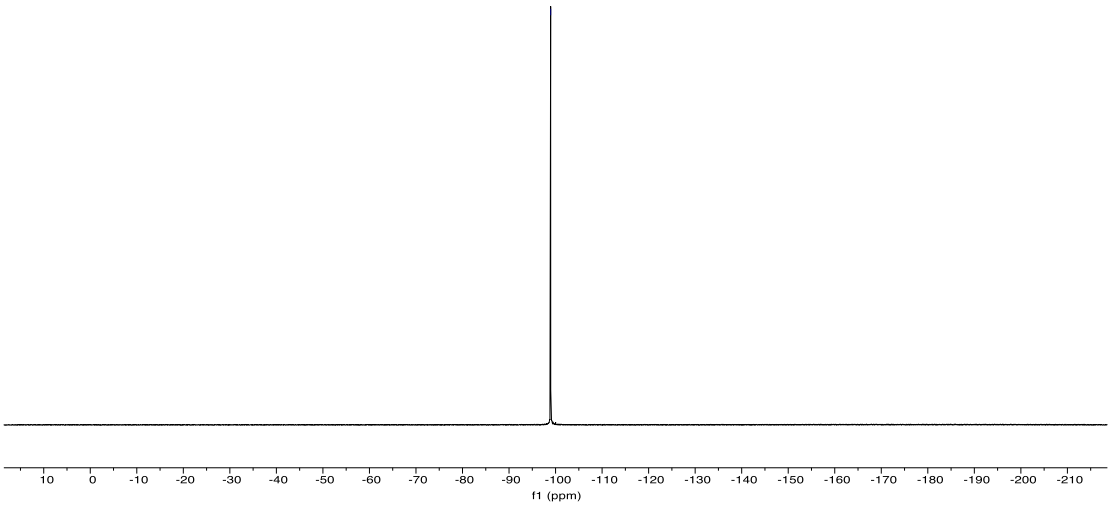
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

-98.94



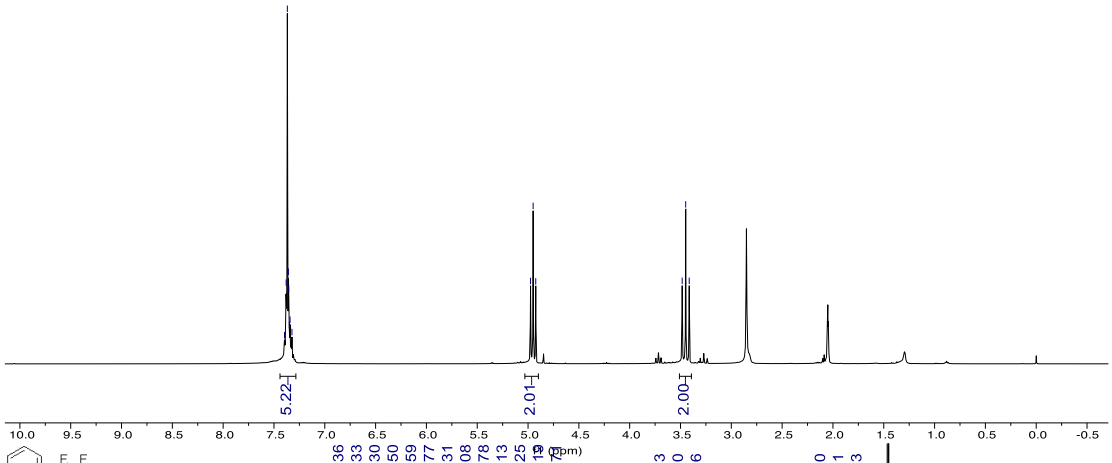
8

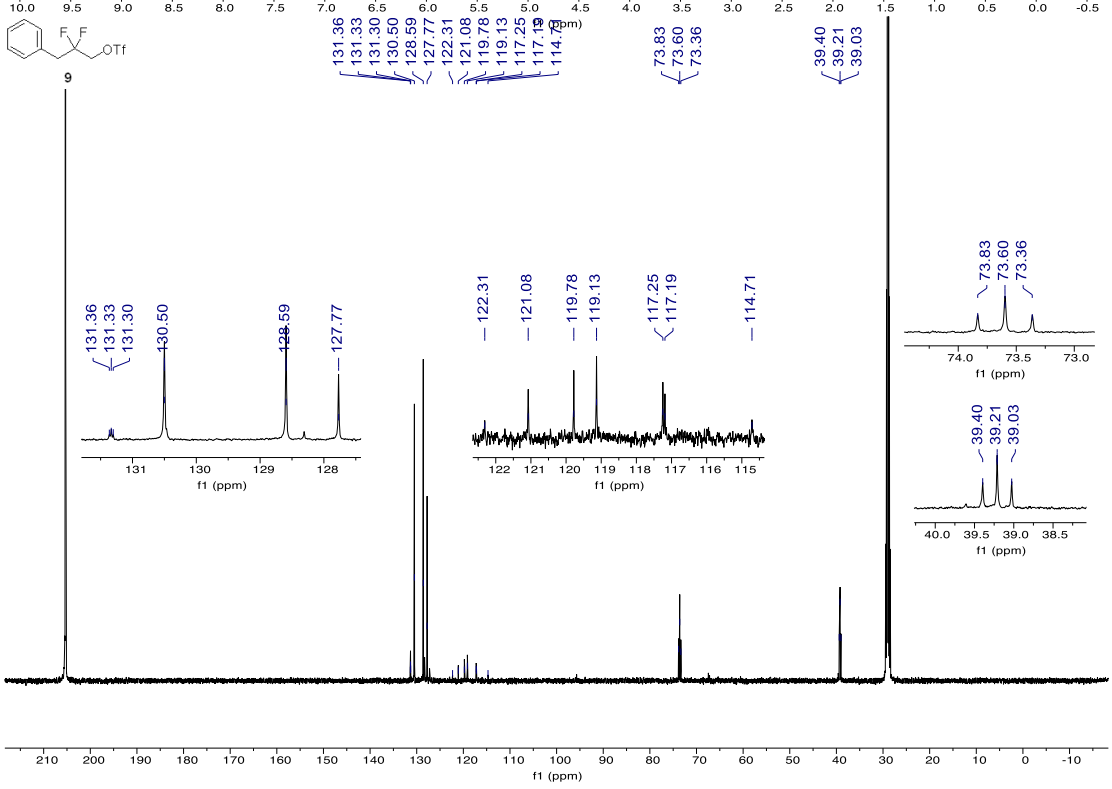


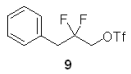
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

f1 (ppm)


F F
OTf
9
7.40
7.38
7.37
7.36
7.36
7.35
7.34
7.32
4.98
4.95
4.92
3.48
3.45
3.41

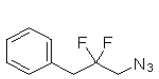

5.22
2.01
2.00
f1 (ppm)


F F
OTf
9
131.36
131.33
131.30
130.50
128.59
127.77
122.31
121.08
119.78
119.13
117.25
117.19
114.71
73.83
73.60
73.36
39.40
39.21
39.03
f1 (ppm)


F F
OTf

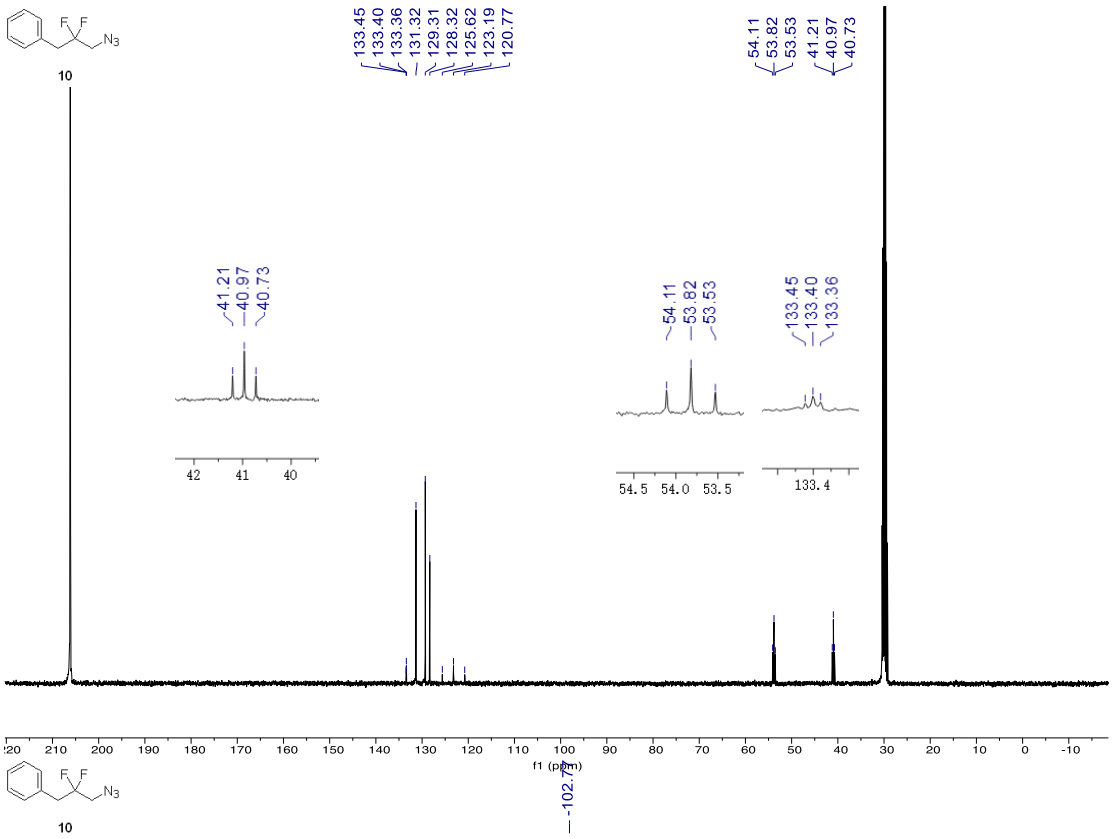
9

-75.78
-75.78
-107.30
-107.31
-107.31
-75.76 -75.78 -75.80
-107.25 -107.30 -107.35
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

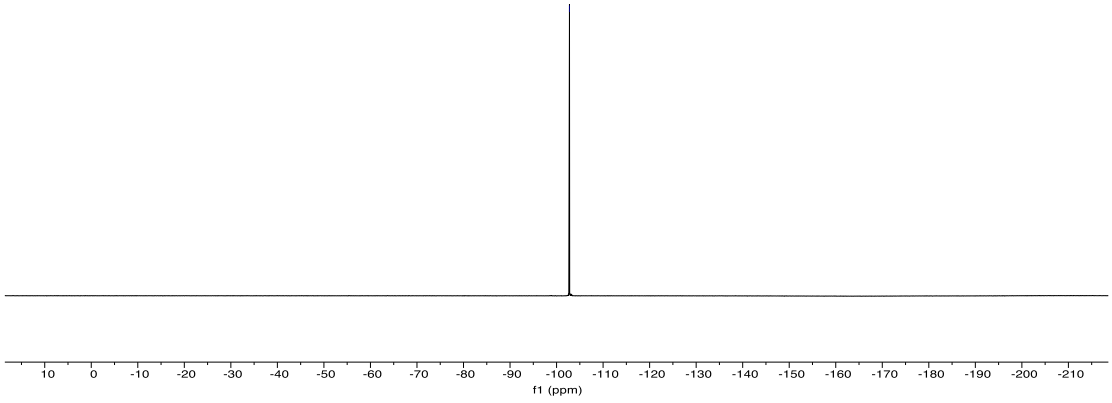

F F
N3

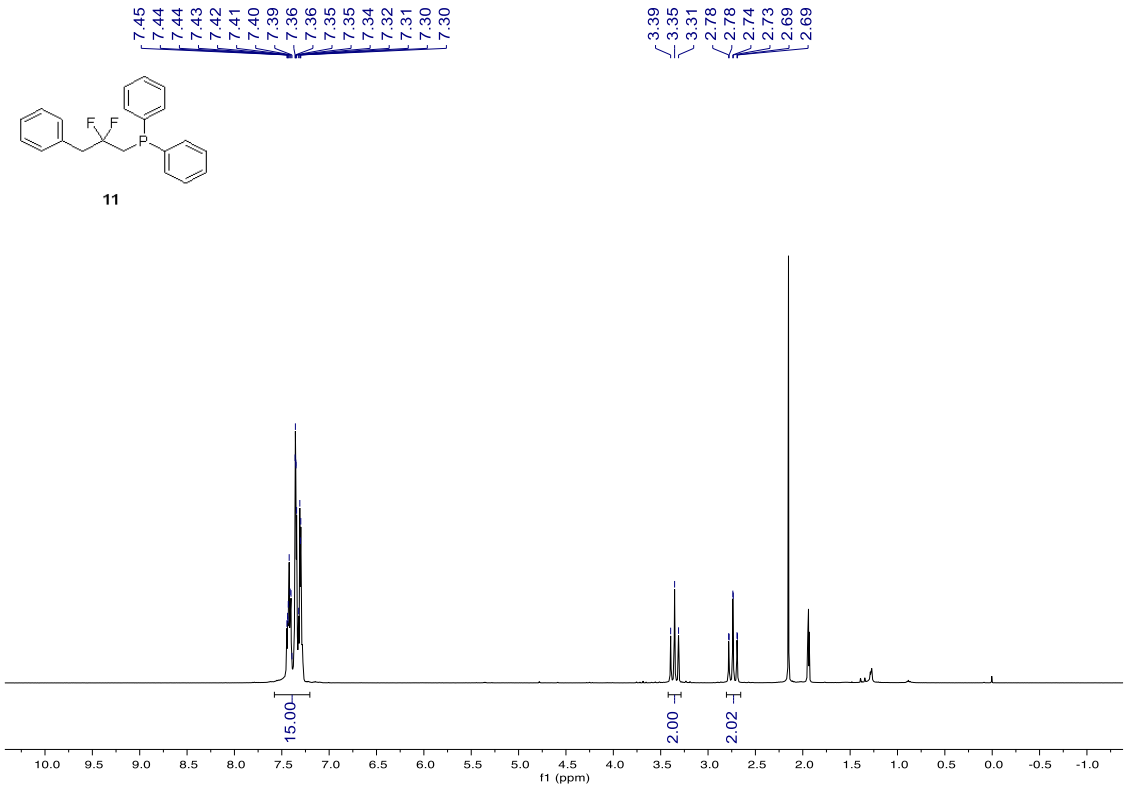
10

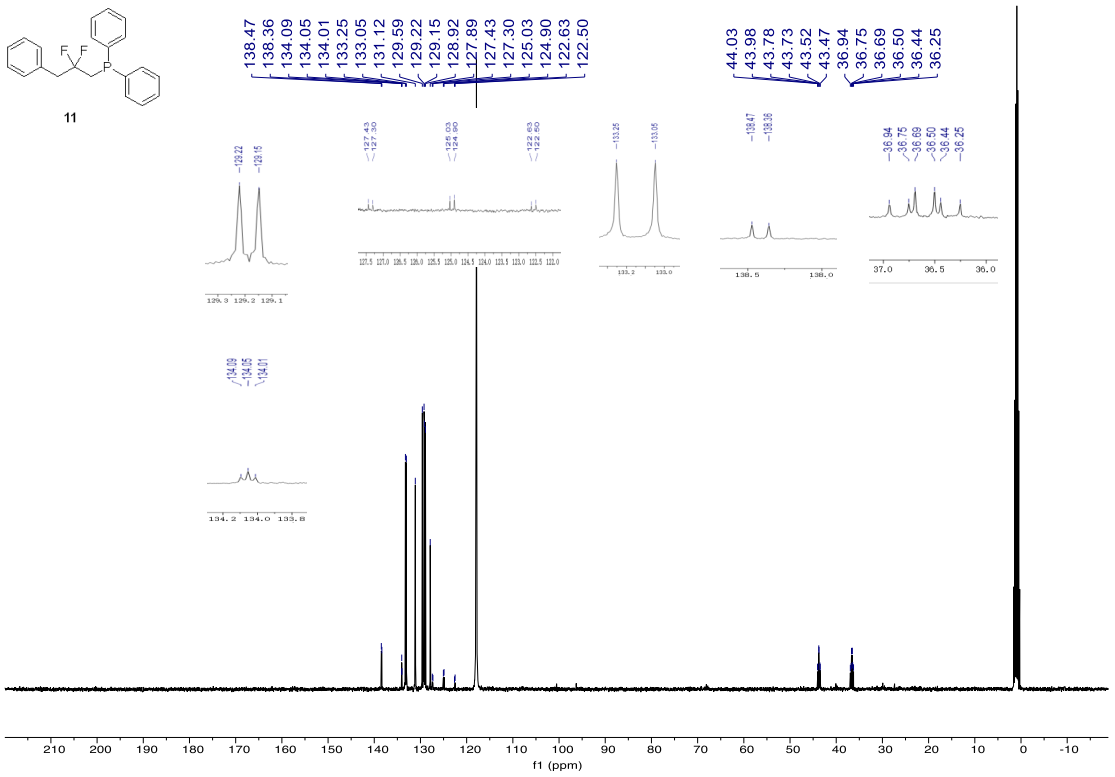
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.31
7.29
7.27
3.40
3.37
3.34
3.29
3.25
3.21
5.00
2.02
2.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

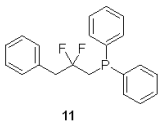

F F
N3
10
133.45
133.40
133.36
131.32
129.31
128.32
125.62
123.19
120.77
54.11
53.82
53.53
41.21
40.97
40.73
41.21
40.97
40.73
42
41
40
54.11
53.82
53.53
54.5
54.0
53.5
133.45
133.40
133.36
133.4
f1 (ppm)

F F
N3
10
-102.73


f1 (ppm)

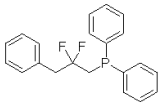

7.45
7.44
7.44
7.43
7.42
7.41
7.40
7.39
7.36
7.36
7.35
7.35
7.34
7.32
7.31
7.30
7.30
3.39
3.35
3.31
2.78
2.78
2.74
2.73
2.69
2.69
F
F
P
11
15.00
2.00
2.02
f1 (ppm)


138.47
138.36
134.09
134.05
134.01
133.25
133.05
131.12
129.59
129.22
129.15
128.92
127.89
127.43
127.30
125.03
124.90
122.63
122.50
44.03
43.98
43.78
43.73
43.52
43.47
36.94
36.75
36.69
36.50
36.44
36.25
F
F
P
11
f1 (ppm)



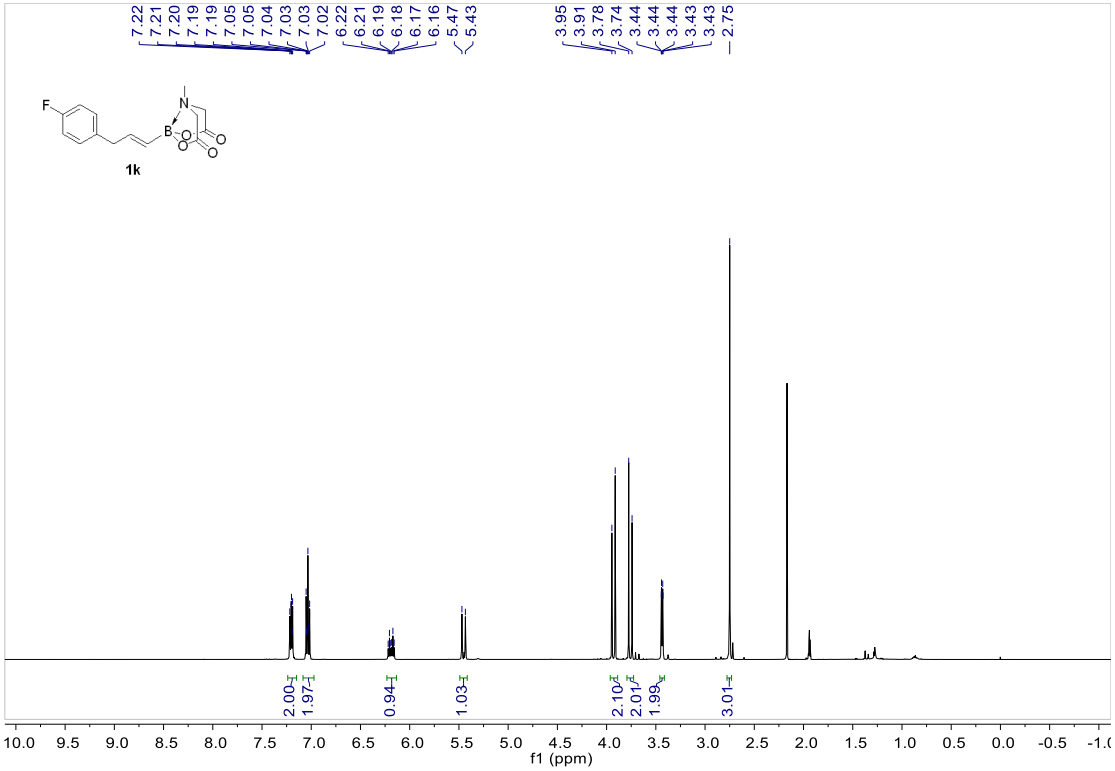
11

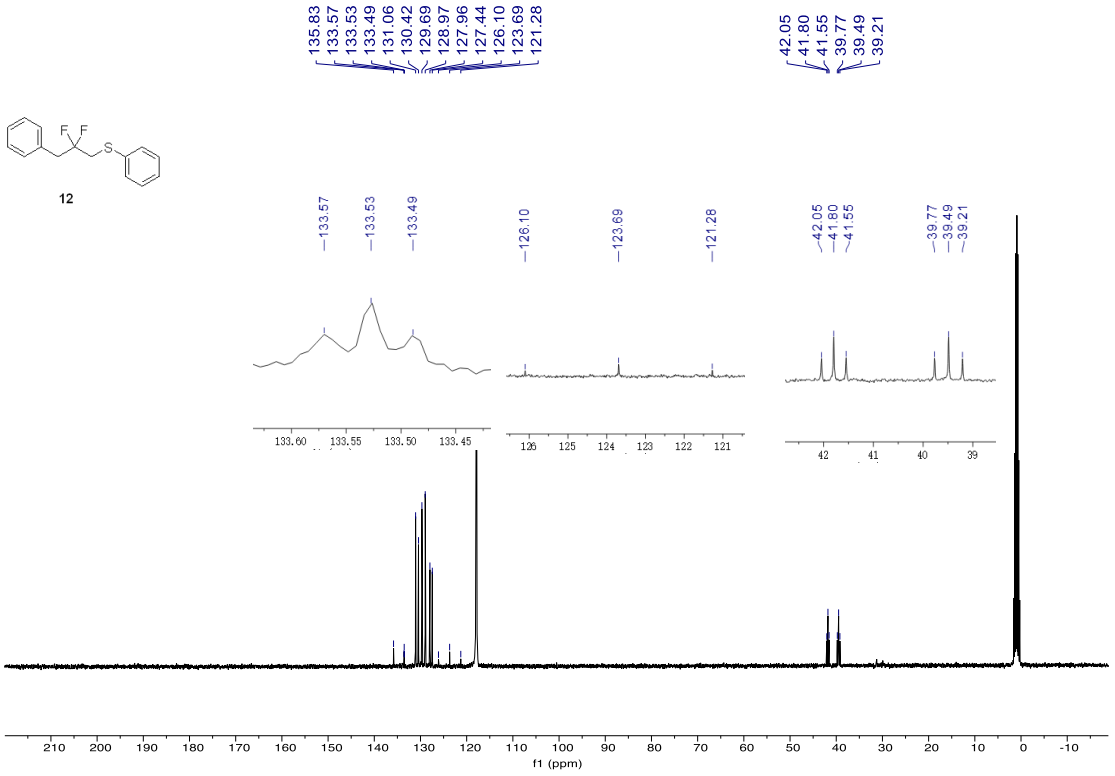
-88.48
-88.53
-88.48
-88.53
-88.45
-88.50
-88.55
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

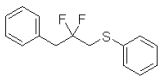


11

-27.24
-27.29
-27.33
-27.37
-27.42
-27.46
-27.50
-27.55
-27.60
-27.0
-27.5
-28.0
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

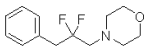

7.22
7.21
7.20
7.19
7.19
7.05
7.05
7.04
7.03
7.03
7.02
6.22
6.21
6.19
6.18
6.17
6.16
5.47
5.43
3.95
3.91
3.78
3.74
3.44
3.44
3.44
3.43
3.43
2.75
F
N
B
O
O
O
O
1k
2.00
1.97
0.94
1.03
2.10
2.01
1.99
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


135.83
133.57
133.53
133.49
131.06
130.42
129.69
128.97
127.96
127.44
126.10
123.69
121.28
42.05
41.80
41.55
39.77
39.49
39.21
F
F
S
12
133.57
133.53
133.49
126.10
123.69
121.28
42.05
41.80
41.55
39.77
39.49
39.21
133.60 133.55 133.50 133.45
126 125 124 123 122 121
42 41 40 39
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

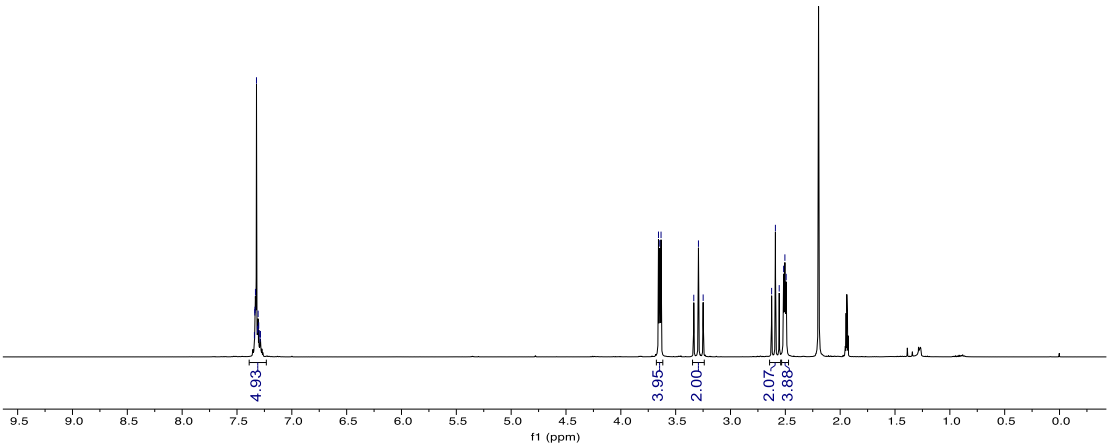

F
F
S

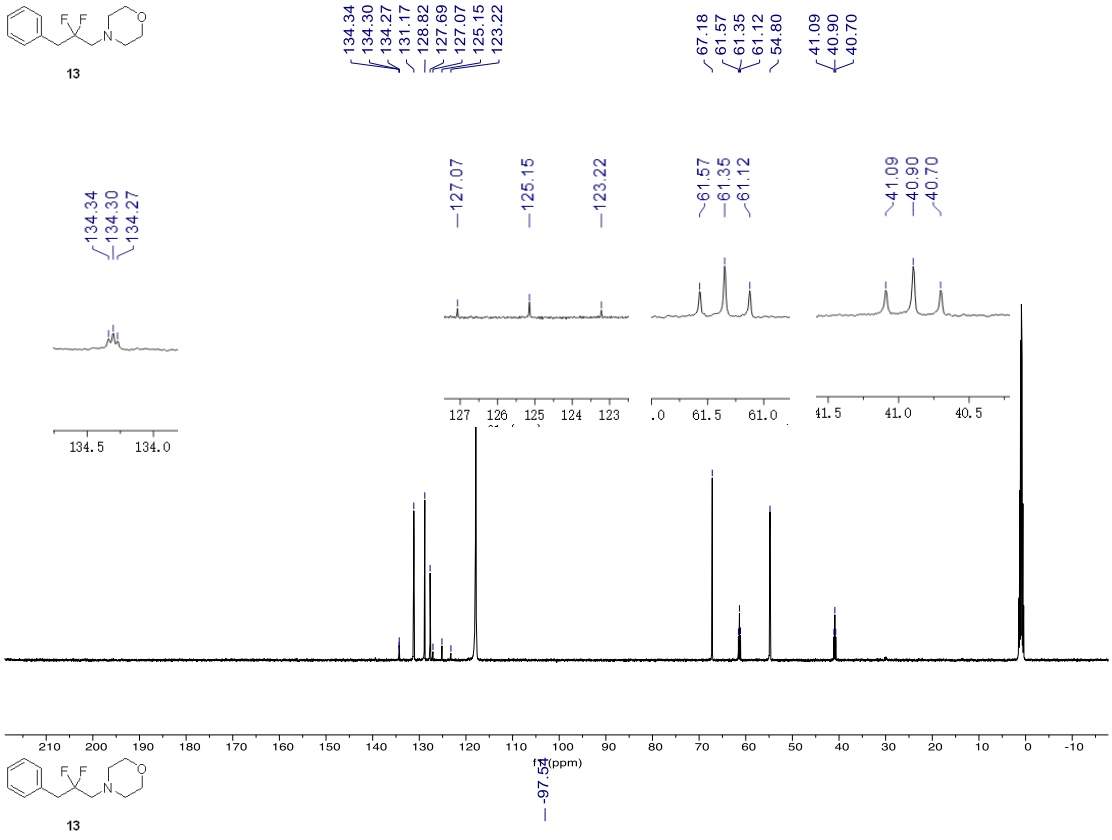
12

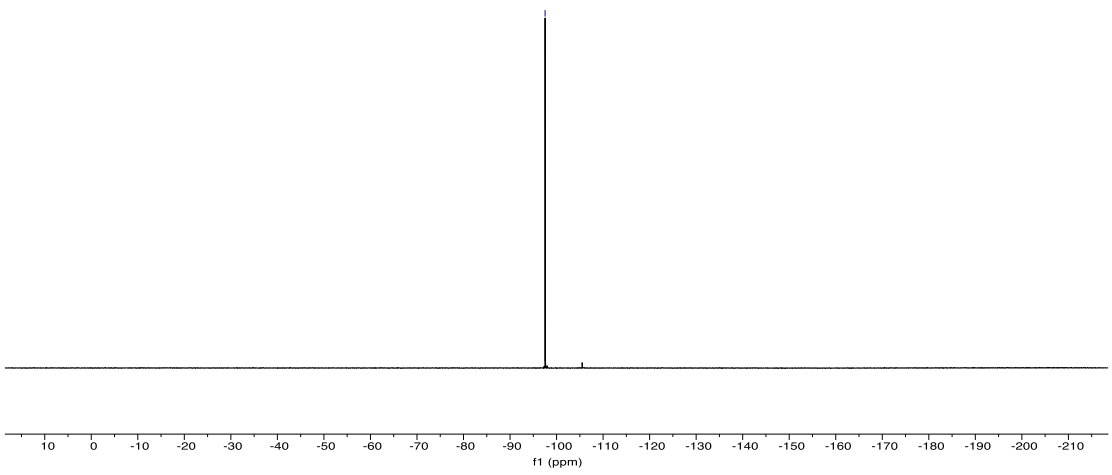
-96.16
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
7.34 7.34 7.34 7.33 7.32 7.31 7.31 7.31 7.30 7.30 7.29 7.29
3.66 3.65 3.63 3.33 3.29 3.25 2.63 2.59 2.56 2.52 2.50 2.49

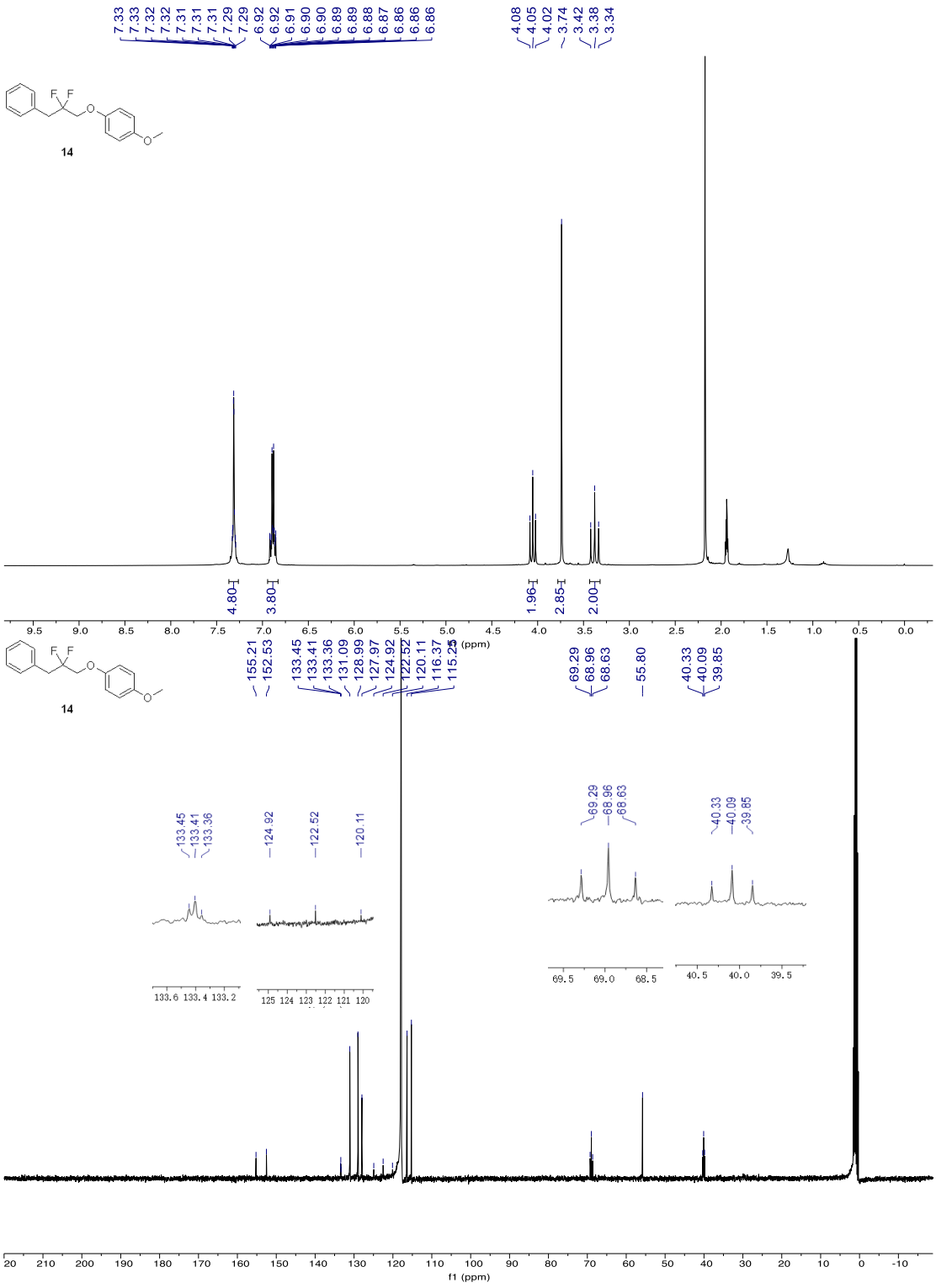

F
F
N
O

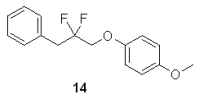
13


4.93
3.95
2.00
2.07
3.88
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


13
134.34
134.30
134.27
131.17
128.82
127.69
127.07
125.15
123.22
67.18
61.57
61.35
61.12
54.80
41.09
40.90
40.70
f1 (ppm)
13


-97.54
f1 (ppm)


7.33
7.33
7.32
7.32
7.31
7.31
7.31
7.29
7.29
6.92
6.92
6.91
6.90
6.90
6.89
6.89
6.88
6.87
6.86
6.86
6.86
4.08
4.05
4.02
3.74
3.42
3.38
3.34
F F
O
O
14
4.80
3.80
1.96
2.85
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
155.21
152.53
133.45
133.41
133.36
131.09
128.99
127.97
124.92
122.52
120.11
116.37
115.25
69.29
68.96
68.63
55.80
40.33
40.09
39.85
133.6 133.4 133.2
125 124 123 122 121 120
69.5 69.0 68.5
40.5 40.0 39.5
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


F
F
O
O

14

-105.10
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
f1 (ppm)

8. References

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