Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Radical addition-polar termination cascade: efficient strategy for photoredox-neutral-catalyzed cyclopropanation and Giese-type reactions of alkenyl *N*-methyliminodiacetyl boronates

Yongjun Liu, Wenping Luo, Jiali Wu, Yewen Fang, Yan Li, Xiaoping Jin, Li Zhang, Zongyong Zhang, Fenfen Xu and Chan Du

Table of Contents

1 General Information

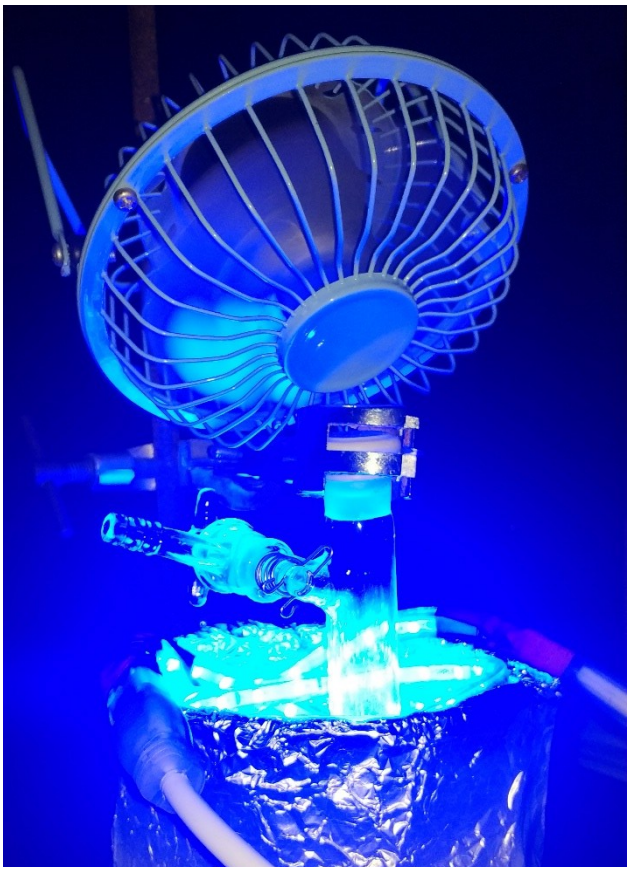
1.1 Solvents, Reagents, and Starting Materials

All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. Photocatalysts $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$[1a] and 4CzIPN[1b] were prepared according to published procedures. Alkenyl MIDA boronates were synthesized with reported procedures.[2] Halomethyl and alkyl silicates were reported in our previous literatures.[3] Dried solvents were obtained from commercial sources and used without further purification unless otherwise noted.

1.2 Instruments

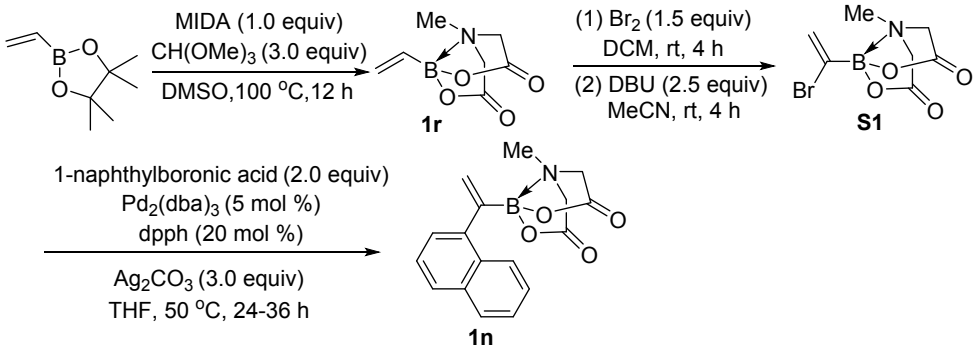
Hydrogen-1 and carbon-13 nuclear magnetic resonance spectra were recorded on a Bruker Avance 500 spectrometer (500 MHz). Fluorine-19 nuclear magnetic resonance spectra were recorded on a Bruker AVANCE III HD400 (400 MHz) spectrometer. Boron-11 nuclear magnetic resonance spectra were recorded on an ECZ600S (600 MHz) spectrometer. Chemical shifts were reported in ppm downfield from tetramethylsilane, and calibrated using residue undeuterated solvent (Aceton-d_6 at 2.05 ppm ^{1}H NMR; 206.68, 29.92 ppm ^{13}C NMR, DMSO-d_6 at 2.50 ppm ^{1}H NMR, 39.51 ppm ^{13}C NMR). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. High resolution mass spectra (HRMS) were recorded on Agilent 6210 ESI/TOF MS and Thermo Q Exactive Plus. Single Crystal X-ray Diffraction (SC-XRD) recorded on a Bruker D8 Quest. 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. Flash column chromatography was performed using silica gel (300-400 mesh) with solvents to use.

1.3 Picture of a Typical Reaction Setup



2 Synthesis of Alkenyl MIDA Boronates

2.1 General Procedure for the Preparation of Alkenyl MIDA Boronates

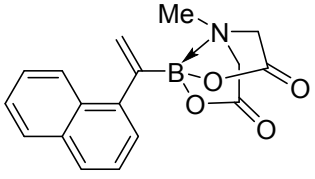


To an oven-dried Schlenk tube equipped with a stir bar was added pinacol vinylboronate (7.70 g, 50.0 mmol), anhydrous DMSO (42 mL), $CH(OMe)_3$ (15.92 g, 150 mmol) and *N*-methyliminodiacetic acid (MIDA, 8.83 g, 60.0 mmol). The resulting mixture was stirred at 100 °C

for 12 h. After cooling to room temperature, the reaction mixture was quenched by water (30 mL) and extracted by ethyl acetate (5 x 60 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The solid-liquid mixture was filtered and the filter cake was washed with ethyl acetate (3 x 5 mL). The product **1r** was collected by vacuum filtration in a yield of 60% (5.49 g) as a white solid.

To a stirred solution of **1r** (5.49 g, 30.0 mmol) in CH_2Cl_2 (50 mL) was added neat bromine (7.2 g, 45.0 mmol) dropwise over 5 min at 0 °C and the mixture turned out to be a cloudy orange solution. After 4 h at room temperature, the resulting orange solution was concentrated in vacuo to give a yellow solid. Residual bromine was removed by azeotroping with CH_2Cl_2 (50 mL). The resulting solid was suspended in MeCN (60 mL) and then 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 11.42 g 75.0 mmol) was added in one portion. After 4 h at room temperature, the solution was quenched by 1 M aq HCl (until the pH = 2-3) and extracted by ethyl acetate (4 x 50 mL). The combined organic layer was washed with brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated in vacuo. The resulting residue was passed through a plug of silica, eluting with acetone. The resulting solid was washed with ethyl acetate (3 x 5 mL). The product **S1** was collected by vacuum filtration in a yield of 70% (5.50 g) as a white solid.

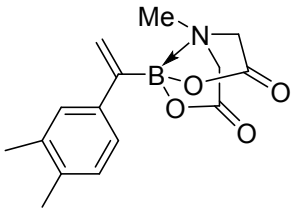
In a glovebox, to a 50 mL Schlenk tube charged with MIDA boronate **S1** (785.6 mg, 3.0 mmol), Ag_2CO_3 (2. 48 g, 9.0 mmol), 1-naphthylboronic acid (1.55 g, 9 mmol), 1,6-bis(diphenylphosphino)hexane (272.1 mg, 0.60 mmol), and $Pd_2(dba)_3$ (137. 4 mg, 0.15 mmol) was added dried THF (30 mL) via a syringe. The resulting mixture was stirred at 50 °C for 36 h. After cooling to room temperature, the reaction mixture was passed through a plug of silica, eluting with acetone, concentrated in vacuum. The resulting crude product was purified by flash chromatography on silica gel (eluent = petroleum ether /ethyl acetate 1:2 v/v) to afford the pure product **1n** (705.0 mg, 76%) as a white solid.



1n

6-methyl-2-(1-(naphthalen-1-yl)vinyl)-1,3,6,2-dioxazaborocane-4,8-dione (1n). ^{1}H NMR (500 MHz, Acetone-d_6) δ 8.20-8.18 (m, 1H), 7.90-7.88 (m, 1H), 7.79-7.77 (m, 1H), 7.50-7.45 (m, 2H),

7.44-7.42 (m, 2H), 6.14 (d, J = 3.4 Hz, 1H), 5.74 (s, 1H), 4.22 (d, J = 16.9 Hz, 2H), 3.92 (d, J = 16.9 Hz, 2H), 2.99 (s, 3H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 169.0, 143.2, 135.3, 132.7, 130.8, 129.2, 127.7, 126.6, 126.4, 126.2, 125.8, 63.0, 47.8; ^{11}B NMR (193 MHz, Acetone-d_6) δ 9.6; HRMS (ESI) $[M+Na]^+$: calculated for $C_{17}H_{16}BNNaO_4$: 332.1065, found 332.1064.



1e

2-(1-(3,4-dimethylphenyl)vinyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1e). Flash column chromatography to afford product **1e** as a white solid (198.8 mg, 23% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.19-7.17 (m, 1H), 7.13-7.11 (m, 1H), 7.05 (d, J = 7.8 Hz, 1H), 5.69-5.65 (m, 2H), 4.21 (d, J = 16.9 Hz, 2H), 3.81 (d, J = 16.9 Hz, 2H), 2.81 (s, 3H), 2.22 (s, 6H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 169.2, 143.2, 137.3, 135.7, 130.6, 129.9, 127.4, 126.1, 63.0, 47.9, 20.1, 19.6. ^{11}B NMR (193 MHz, Acetone-d_6) δ 9.7; HRMS (ESI) $[M+Na]^+$: calculated for $C_{15}H_{18}BNNaO_4$: 310.1221, found 310.1218.

2.2 List of Known Alkenyl MIDA Boronates

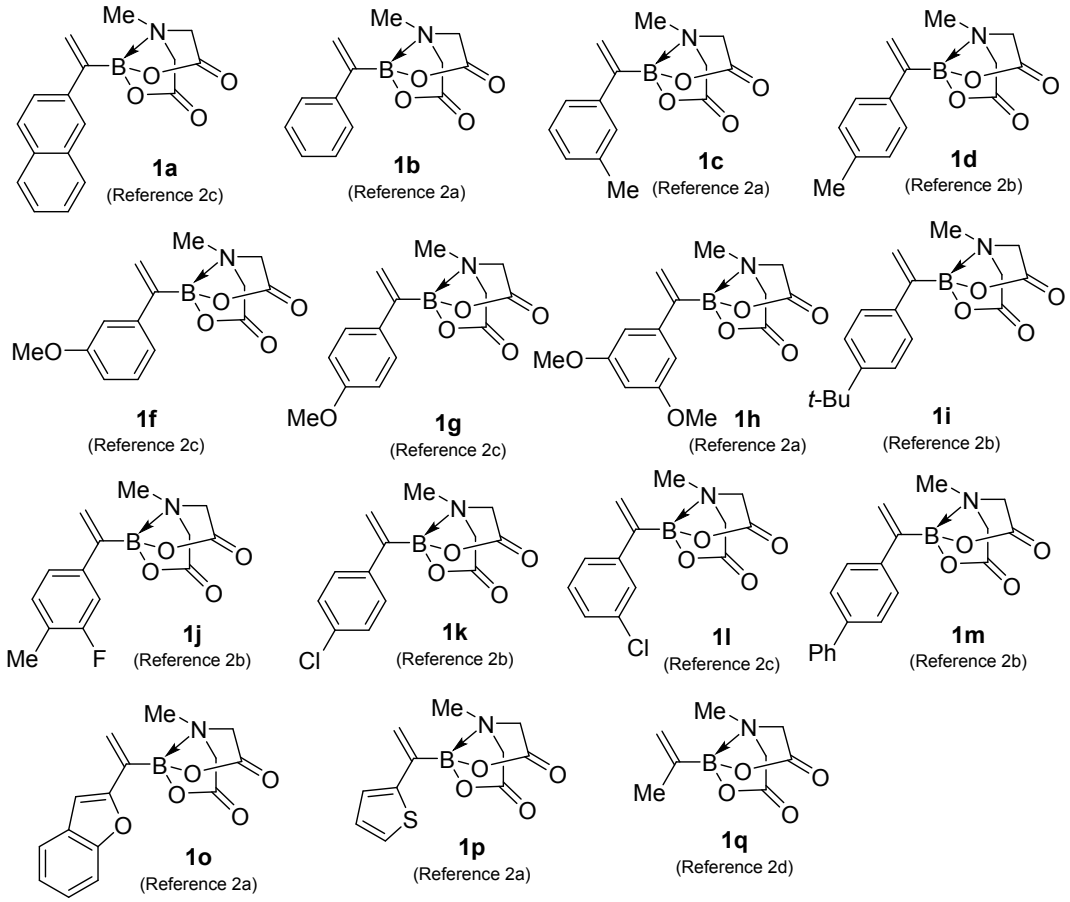
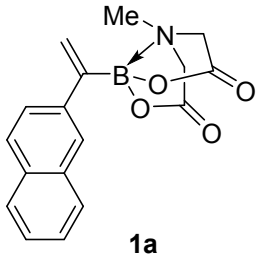
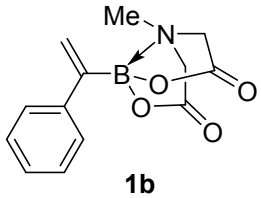


Figure S1: Alkenyl MIDA boronates synthesized according to literature precedents and corresponding references.



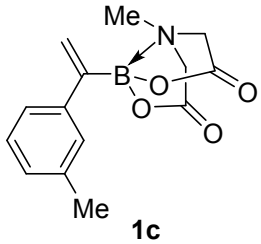
1a

6-methyl-2-(1-(naphthalen-2-yl)vinyl)-1,3,6,2-dioxazaborocane-4,8-dione (1a). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.90-7.84 (m, 4H), 7.60-7.58 (m, 1H), 7.50-7.45 (m, 2H), 5.85-5.83 (m, 2H), 4.24 (d, J = 17.0 Hz, 2H), 3.88 (d, J = 17.0 Hz, 2H), 2.87 (s, 3H).^{13}C NMR (126 MHz, Acetone-d_6) δ 169.0, 143.0, 134.5, 133.3, 128.9, 128.7, 128.6, 128.3, 127.3, 126.9, 126.7, 126.5, 62.8, 47.8.



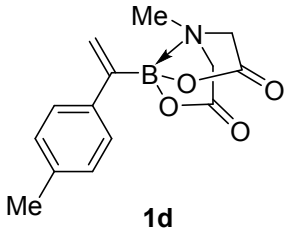
1b

6-methyl-2-(1-phenylvinyl)-1,3,6,2-dioxazaborocane-4,8-dione (1b). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.43-7.41 (m, 2H), 7.34-7.31 (m, 2H), 7.27-7.24 (m, 1H), 5.75-5.71 (m, 2H), 4.24 (d, J = 17.0 Hz, 2H), 3.86 (d, J = 17.0 Hz, 2H), 2.83 (s, 3H).^{13}C NMR (126 MHz, Acetone-d_6) δ 168.1, 144.6, 128.3, 127.6, 127.3, 126.6, 61.9, 46.8.



1c

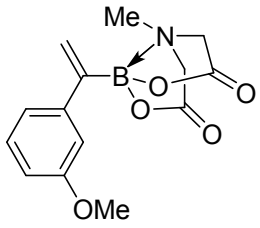
6-methyl-2-(1-(m-tolyl)vinyl)-1,3,6,2-dioxazaborocane-4,8-dione (1c). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.23 (s, 1H), 7.19-7.18 (m, 2H), 7.07-7.05 (m, 1H), 5.72-5.67 (m, 2H), 4.22 (d, J = 16.9 Hz, 2H), 3.82 (d, J=16.9 Hz, 2H), 2.82 (s, 3H), 2.30 (s, 3H).^{13}C NMR (126 MHz, Acetone-d_6) δ 169.1, 145.6, 138.7, 129.3(1), 129.2(5), 128.3, 128.0, 125.7, 63.0, 47.8, 21.8.



1d

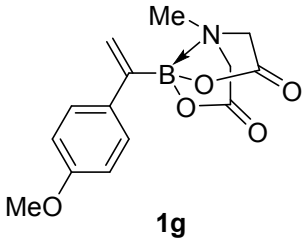
6-methyl-2-(1-(p-tolyl)vinyl)-1,3,6,2-dioxazaborocane-4,8-dione (1d). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.30 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 7.9 Hz, 2H), 5.71-5.68 (m, 2H), 4.23 (d, J =

16.9 Hz, 2H), 3.85 (d, J = 16.9 Hz, 2H), 2.82 (s, 3H), 2.31 (s, 3H).^{13}C NMR (126 MHz, Acetone-d_6) δ 169.2, 142.7, 137.1, 130.0, 128.5, 127.7, 63.0, 47.9, 21.3.



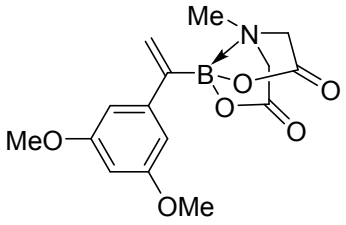
1f

2-(1-(3-methoxyphenyl)vinyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1f). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.25-7.22 (m, 1H), 7.00-6.97 (m, 2H), 6.83-6.81 (m, 1H), 5.76-5.73 (m, 2H), 4.25 (d, J = 17.0 Hz, 2H), 3.85 (d, J = 17.1 Hz, 2H), 3.79 (s, 3H), 2.84 (s, 3H).^{13}C NMR (126 MHz, DMSO-d_6) δ 169.3, 159.2, 145.7, 129.6, 127.8, 119.8, 113.0, 112.3, 62.0, 55.1, 47.3.



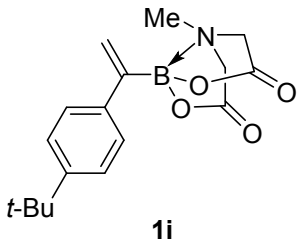
1g

2-(1-(4-methoxyphenyl)vinyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1g). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.37-7.34 (m, 2H), 6.90-6.87 (m, 2H), 5.67-5.66 (m, 2H), 4.23 (d, J = 16.9 Hz, 2H), 3.86 (d, J = 16.9 Hz, 2H), 3.80 (s, 3H), 2.82 (s, 3H).^{13}C NMR (126 MHz, Acetone-d_6) δ 169.2, 159.8, 137.7, 129.7, 127.1, 114.8, 62.9, 55.6, 47.8.



1h

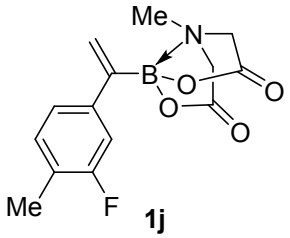
2-(1-(3,5-dimethoxyphenyl)vinyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1h). ^{1}H NMR (500 MHz, Acetone-d_6) δ 6.57 (d, J = 2.1 Hz, 2H), 6.37-6.36 (m, 1H), 5.74-5.73 (m, 2H), 4.24 (d, J = 17.0 Hz, 2H), 3.83 (d, J = 17.0 Hz, 2H), 3.76 (s, 6H), 2.85 (s, 3H).^{13}C NMR (126 MHz, Acetone-d_6) δ 169.2, 161.9, 147.6, 128.0, 106.5, 99.9, 63.1, 55.7, 47.8.



1i

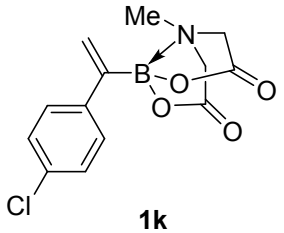
2-(1-(4-(tert-butyl)phenyl)vinyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1i). ^{1}H NMR

(500 MHz, Acetone-d_6) δ 7.38-7.35 (m, 4H), 5.71-5.70 (m, 2H), 4.24 (d, J = 16.9 Hz, 2H), 3.86 (d, J = 16.9 Hz, 2H), 2.83 (s, 3H), 1.32 (s, 9H).^{13}C NMR (126 MHz, Acetone-d_6) δ 169.2, 150.3, 142.6, 128.3, 127.8, 126.2, 63.0, 48.0, 35.2, 31.9.



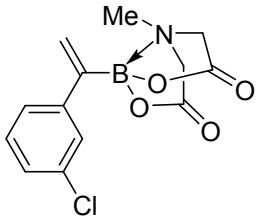
1j

2-(1-(3-fluoro-4-methylphenyl)vinyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1j). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.21-7.09 (m, 3H), 5.73 (s, 2H), 4.25 (d, J = 16.9 Hz, 2H), 3.90 (d, J = 16.9 Hz, 2H), 2.84 (s, 3H), 2.23 (d, J = 1.6 Hz, 3H).^{13}C NMR (126 MHz, Acetone-d_6) δ 169.1, 162.1 (d, J = 242.6 Hz), 145.4 (d, J = 7.6 Hz), δ132.5 (d, J = 5.5 Hz), 128.7, 124.3 (d, J = 3.1 Hz), 123.7 (d, J = 17.2 Hz), 115.0 (d, J = 22.5 Hz), 63.0, 48.0, 14.4 (d, J = 3.5 Hz).



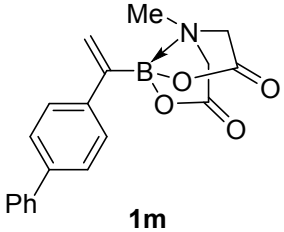
1k

2-(1-(4-chlorophenyl)vinyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1k). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.43-7.40 (m, 2H), 7.35-7.32 (m, 2H), 5.76-5.73 (m, 2H), 4.25 (d, J = 17.0 Hz, 2H), 3.92 (d, J = 17.0 Hz, 2H), 2.84 (s, 3H).^{13}C NMR (126 MHz, Acetone-d_6) δ 169.1, 144.4, 133.1, 130.4, 129.4, 129.1, 63.0, 48.0.



1l

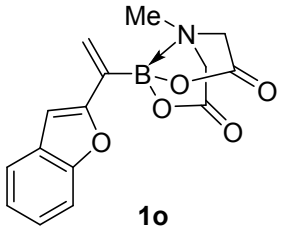
2-(1-(3-chlorophenyl)vinyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1l). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.43-7.26 (m, 4H), 5.78-5.75 (m, 2H), 4.26 (d, J = 16.9 Hz, 2H), 3.93 (d, J = 16.9 Hz, 2H), 2.86 (s, 3H).^{13}C NMR (126 MHz, Acetone-d_6) δ 169.1, 147.8, 134.7, 131.0, 129.7, 128.5, 127.6, 127.2, 62.9, 48.0.



1m

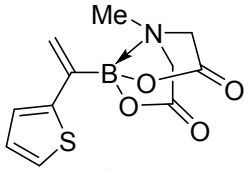
2-(1-([1,1'-biphenyl]-4-yl)vinyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1m). ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.70-7.68 (m, 2H), 7.65-7.64 (m, 2H), 7.54-7.52 (m, 2H), 7.49-7.46 (m, 2H), 7.38-7.35 (m, 1H), 5.78 (s, 2H), 4.27 (d, J = 17.0 Hz, 2H), 3.92 (d, J = 17.0 Hz, 2H), 2.88 (s,

3H).[13]C NMR (126 MHz, Acetone-d_6) δ 168.1, 143.6, 140.5, 139.1, 128.8, 128.1, 127.3, 127.2, 126.7, 126.6, 61.9, 46.9.



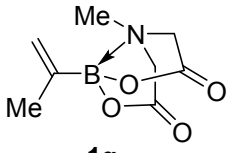
1o

2-(1-(benzofuran-2-yl)vinyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1o). [1]H NMR (500 MHz, Acetone-d_6) δ 7.60 (d, J = 7.5 Hz, 1H), 7.47-7.48 (m, 1H), 7.31-7.27 (m, 1H), 7.23-7.20 (m, 1H), 6.92 (s, 1H), 6.45 (s, 1H), 5.81 (d, J = 2.7 Hz, 1H), 4.41 (d, J = 17.1 Hz, 2H), 4.24 (d, J = 17.0 Hz, 2H), 3.04 (s, 3H).[13]C NMR (126 MHz, Acetone-d_6) δ 169.0, 158.6, 155.0, 130.0, 126.7, 125.2, 123.5, 121.8, 111.4, 104.7, 63.1, 47.9.



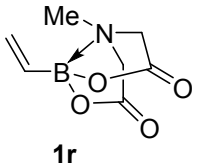
1p

6-methyl-2-(1-(thiophen-2-yl)vinyl)-1,3,6,2-dioxazaborocane-4,8-dione (1p). [1]H NMR (500 MHz, Acetone-d_6) δ 7.32 (d, J = 5.1 Hz, 1H), 7.15 (d, J = 3.5 Hz, 1H), 7.01-7.00 (m, 1H), 5.94 (s, 1H), 5.59-5.58 (m, 1H), 4.32 (d, J = 17.1 Hz, 2H), 4.02 (d, J = 17.1 Hz, 2H), 2.89 (s, 3H). [13]C NMR (126 MHz, Acetone-d_6) δ 169.2, 147.4, 128.8, 126.4, 125.9, 125.6, 63.2, 48.1.



1q

6-methyl-2-(prop-1-en-2-yl)-1,3,6,2-dioxazaborocane-4,8-dione (1q). [1]H NMR (500 MHz, Acetone-d_6) δ 5.47-5.33 (m, 2H), 4.24 (d, J = 17.0 Hz, 2H), 4.06 (d, J = 17.0 Hz, 2H), 3.02 (s, 3H), 1.80 (s, 3H).[13]C NMR (126 MHz, Acetone-d_6) δ 169.3, 124.7, 62.7, 47.2, 22.3.

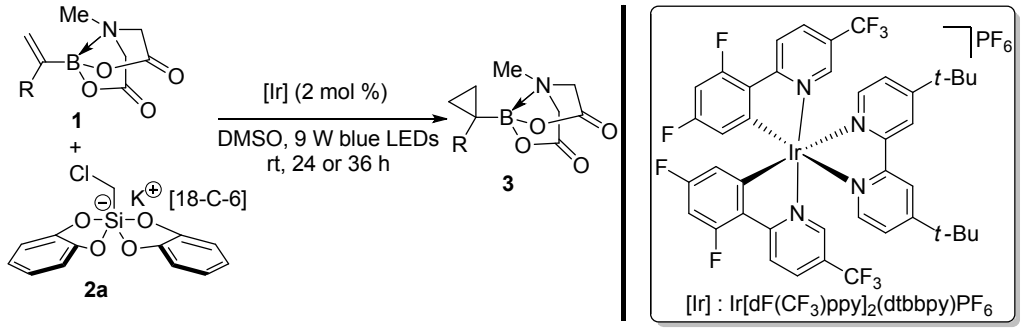


1r

6-methyl-2-vinyl-1,3,6,2-dioxazaborocane-4,8-dione (1r). [1]H NMR (500 MHz, Acetone-d_6) δ 6.02-5.95 (m, 1H), 5.75-5.67 (m, 2H), 4.23 (d, J = 16.9 Hz, 2H), 4.04 (d, J = 17.0 Hz, 2H), 3.02 (s, 3H).[13]C NMR (126 MHz, Acetone-d_6) δ 169.2, 129.6, 62.5, 47.5.

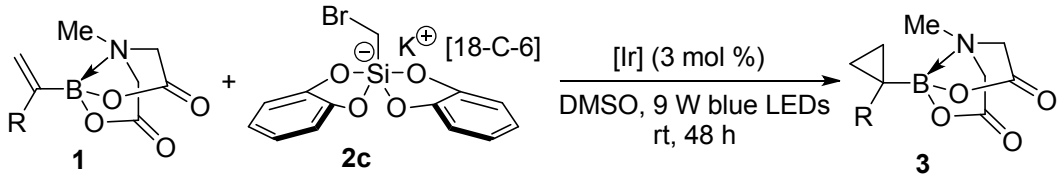
3 General Procedures of Photoredox-Catalyzed Reactions

3.1 General Procedure of Cyclopropanation of Alkenyl MIDA Boronates for Preparation of 3a-m and 3o-p



To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (4.5 mg, 0.004 mmol, 0.02 equiv), potassium [18-Crown-6] bis(catecholato)chloromethylsilicate **2a** (238.9 mg, 0.4 mmol, 2.0 equiv), the alkenyl MIDA boronate **1** (0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 24 or 36 h (cooling with a fan). After the reaction was complete, the reaction solution was diluted with saturated Na_2CO_3 aqueous solution, and was extracted with EtOAc (5 x 10 mL). The organic layer was washed with brine, dried over $MgSO_4$, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product **3** (eluent = petroleum ether /ethyl acetate 1:1-2 v/v).

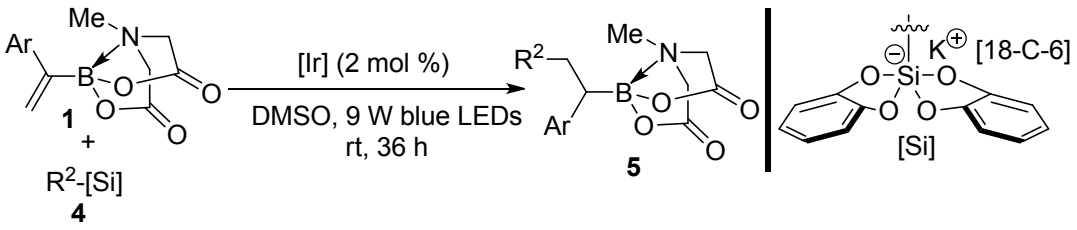
3.2 General Procedure of Cyclopropanation of Alkenyl MIDA Boronates for Preparation of 3n and 3q-r



To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (4.5 mg, 0.004 mmol, 0.02 equiv), potassium [18-Crown-6] bis(catecholato)bromomethylsilicate **2c** (256.6 mg, 0.4 mmol, 2.0 equiv), the alkenyl MIDA boronate **1** (0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LEDs strip spiraled within a bowel for 24 h (cooling with a

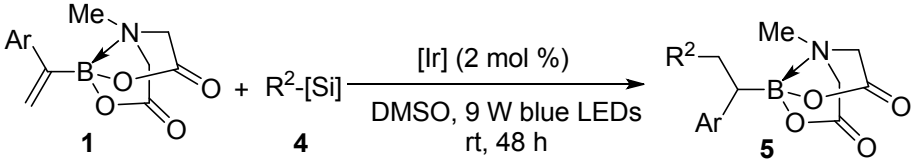
fan). After 24 h, an additional portion of $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (2.2 mg, 0.002 mmol, 0.01 equiv), potassium [18-Crown-6] bis(catecholato)bromomethylsilicate **2c** (64.1 mg, 0.1 mmol, 0.5 equiv), alkenyl MIDA boronate **1** (0.2 mmol, 1.0 equiv), and degassed DMSO (2.0 mL) was added under N_2, and the reaction was stirred for an additional 24 h under irradiation. After the reaction was complete, the reaction solution was diluted with saturated Na_2CO_3 aqueous solution, and was extracted with EtOAc (5 x 10 mL). The organic layer was washed with brine, dried over $MgSO_4$, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product **3** (eluent = petroleum ether /ethyl acetate 1:1-2 v/v).

3.3 General Procedure of Radical Addition of Alkenyl MIDA Boronates for Preparation of 5a-c, 5f-g, and 5i



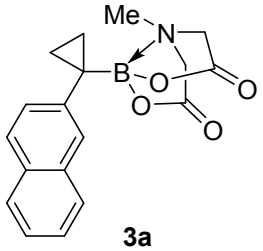
To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (4.5 mg, 0.004 mmol, 0.02 equiv), potassium [18-Crown-6] bis(catecholato)-alkylsilicate (0.5 mmol, 2.5 equiv), the alkenyl MIDA boronates (0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LED light strip spiraled within a bowel for 36 h (cooling with a fan). After the reaction was complete, the reaction solution was diluted with saturated Na_2CO_3 aqueous solution, and was extracted with EtOAc (5 x 10 mL). The organic layers were washed with brine, combined the organic layers and dried with $MgSO_4$, concentrated in vacuum. Flash chromatography over silica gel afforded the product **5** (eluent = petroleum ether /ethyl acetate 1: 2 v/v).

3.4 General Procedure of Radical Addition of Alkenyl MIDA Boronates for Preparation of 5d-e and 5h



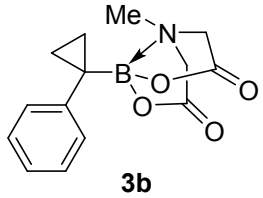
To an oven dried transparent 10 mL Schlenk tube equipped with stirring bar, $Ir[dF(CF_3)ppy)]_2(dtbbpy)PF_6$ (4.5 mg, 0.004 mmol, 0.02 equiv), potassium [18-Crown-6]

bis(catecholato)alkylsilicate **4** (0.5 mmol, 2.5 equiv), alkenyl MIDA boronate **1** (0.2 mmol, 1.0 equiv) were added. The tube was evacuated and filled with nitrogen for 3 times. The tube was then charged with degassed DMSO (6.0 mL, 0.033 M) via a syringe. The tube was irradiated with a 9 W blue LED light strip spiraled within a bowel for 24 h (cooling with a fan). After 24 h, an additional portion of potassium [18-Crown-6] bis(catecholato)alkylsilicate **4** (0.1 mmol, 0.5 equiv) and degassed DMSO (2.0 mL) were added under N_2, and the reaction was stirred for an additional 24 h under irradiation. After the reaction was complete, the reaction solution was diluted with saturated Na_2CO_3 aqueous solution, and was extracted with EtOAc (5 x 10 mL). The organic layer was washed with brine, dried over $MgSO_4$, filtered, and solvent was evaporated to obtain crude product. Flash chromatography over silica gel afforded the product **5** (eluent = petroleum ether /ethyl acetate 1:2 v/v).



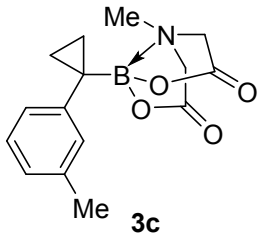
3a

6-methyl-2-(1-(naphthalen-2-yl)cyclopropyl)-1,3,6,2-dioxazaborocane-4,8-dione (3a). Flash column chromatography to afford product **3a** as a pale yellow solid (55.6 mg, 86% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.87 (s, 1H), 7.83-7.79 (m, 2H), 7.76 (d, J = 8.6 Hz, 1H), 7.68-7.64 (m, 1H), 7.46-7.40 (m, 2H), 4.08 (d, J = 16.9 Hz, 2H), 3.58 (d, J = 16.9 Hz, 2H), 3.19 (s, 3H), 1.01-0.99 (m, 2H), 0.87-0.85 (m, 2H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.5, 144.5, 134.5, 132.7, 130.6, 129.0, 128.4, 128.3, 126.6, 126.1, 63.4, 46.9, 10.7; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.2; HRMS (ESI) $[M+Na]^+$: calculated for $C_{18}H_{18}BNNaO_4$: 346.1221, found 346.1218.



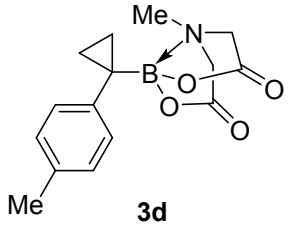
3b

6-methyl-2-(1-phenylcyclopropyl)-1,3,6,2-dioxazaborocane-4,8-dione (3b). Flash column chromatography to afford product **3b** as a white solid (38.8 mg, 71% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.33-7.28 (m, 2H), 7.13-7.06 (m, 2H), 7.01-6.96 (m, 1H), 3.94 (d, J = 16.8 Hz, 2H), 3.40 (d, J = 16.8 Hz, 2H), 2.99 (s, 3H), 0.79-0.77 (m, 2H), 0.61-0.60 (m, 2H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.7, 146.7, 131.6, 129.1, 126.4, 63.5, 46.9, 10.7; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.1; HRMS (ESI) $[M+Na]^+$: calculated for $C_{14}H_{16}BNNaO_4$: 296.1065, found 296.1071.



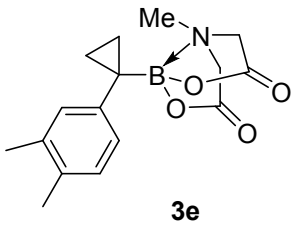
3c

methyl-2-(1-(m-tolyl)cyclopropyl)-1,3,6,2-dioxazaborocane-4,8-dione (3c). Flash column chromatography to afford product **3c** as a pale yellow solid (35.1 mg, 61% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.29 (s, 1H), 7.23 (d, J = 7.8 Hz, 1H), 7.13-7.10 (m, 1H), 6.95 (d, J = 7.4 Hz, 1H), 4.08 (d, J = 16.8 Hz, 2H), 3.51 (d, J = 16.8 Hz, 2H), 3.14 (s, 3H), 2.27 (s, 3H), 0.91-0.90 (m, 2H), 0.74-0.72 (m, 2H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.8, 146.6, 138.5, 132.5, 129.1, 128.6, 127.2, 63.5, 46.9, 21.7, 10.8; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.1; HRMS (ESI) [M+Na]$^{+}$: calculated for $C_{15}H_{18}BNNaO_4$: 310.1221, found 310.1226.



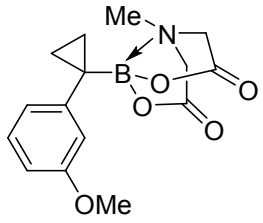
3d

methyl-2-(1-(p-tolyl)cyclopropyl)-1,3,6,2-dioxazaborocane-4,8-dione (3d). Flash column chromatography to afford product **3d** as a pale yellow solid (35.9 mg, 63% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.31 (d, J = 8.1 Hz, 2H), 7.04 (d, J = 7.9 Hz, 2H), 4.07 (d, J = 16.7 Hz, 2H), 3.52 (d, J = 16.7 Hz, 2H), 3.12 (s, 3H), 2.25 (s, 3H), 0.89-0.87 (m, 2H), 0.70-0.69 (m, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.8, 143.6, 135.7, 131.5, 129.8, 63.5, 46.9, 21.2, 10.8; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.0; HRMS (ESI) [M+Na]$^{+}$: calculated for $C_{15}H_{18}BNNaO_4$: 310.1221, found 310.1218.



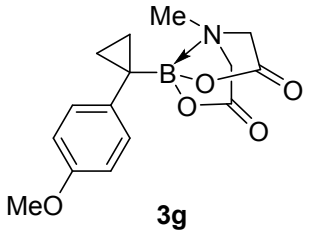
3e

2-(1-(3,4-dimethylphenyl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3e). Flash column chromatography to afford product **3e** as a pale yellow solid (48.3 mg, 80% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.22 (s, 1H), 7.13 (d, J = 7.7 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 4.05 (d, J = 16.8 Hz, 2H), 3.49 (d, J = 16.8 Hz, 2H), 3.12 (s, 3H), 2.18 (s, 3H), 2.17 (s, 3H), 0.87-0.86 (m, 2H), 0.70-0.68 (m, 2H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.6, 143.7, 136.7, 134.0, 132.7, 130.1, 128.7, 63.3, 46.6, 19.8, 19.3, 10.5; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.2; HRMS (ESI) [M+H]$^{+}$: calculated for $C_{16}H_{21}BNO_4$: 302.1558, found 302.1561.



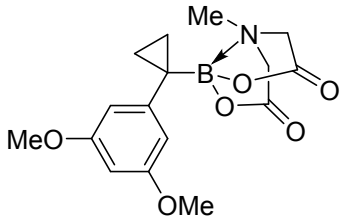
3f

2-(1-(3-methoxyphenyl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3f). Flash column chromatography to afford product **3f** as a pale yellow solid (40.1 mg, 66% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.16-7.11 (m, 1H), 7.04-7.03 (m, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.71-6.67 (m, 1H), 4.09 (d, J = 16.8 Hz, 2H), 3.75 (s, 3H), 3.54 (d, J = 16.8 Hz, 2H), 3.13 (s, 3H), 0.91-0.89 (m, 2H), 0.75-0.73 (m, 2H).; ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.8, 160.6, 148.3, 130.0, 123.4, 116.9, 112.6, 63.5, 55.5, 46.9, 10.9; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.0; HRMS (ESI) [M+Na]$^{+}$: calculated for $C_{15}H_{18}BNNaO_5$: 326.1170, found 326.1176.



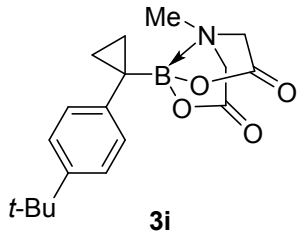
3g

2-(1-(4-methoxyphenyl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3g). Flash column chromatography to afford product **3g** as a pale yellow solid (42.3 mg, 70% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.36-7.34 (m, 2H), 6.82-6.79 (m, 2H), 4.08 (d, J = 16.8 Hz, 2H), 3.76 (s, 3H), 3.55 (d, J = 16.8 Hz, 2H), 3.14 (s, 3H), 0.89-0.87 (m, 2H), 0.70-0.68 (m, 2H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.8, 158.7, 138.4, 132.5, 114.5, 63.6, 55.6, 46.9, 10.8; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.1; HRMS (ESI) [M+Na]$^{+}$: calculated for $C_{15}H_{18}BNNaO_5$: 326.1170, found 326.1168.



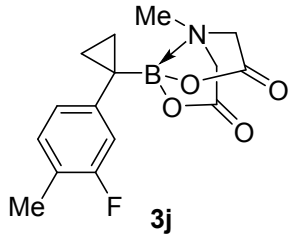
3h

2-(1-(3,5-dimethoxyphenyl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3h). Flash column chromatography to afford product **3h** as a pale yellow solid (50.4 mg, 76% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 6.62 (d, J = 2.2 Hz, 2H), 6.28-6.23 (m, 1H), 4.11 (d, J = 16.8 Hz, 2H), 3.75 (s, 6H), 3.57 (d, J = 16.8 Hz, 2H), 3.16 (s, 3H), 0.91-0.89 (m, 2H), 0.77-0.74 (m, 2H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.9, 161.7, 148.9, 109.1, 99.0, 63.5, 55.6, 46.8, 10.9; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.0; HRMS (ESI) [M+Na]$^{+}$: calculated for $C_{16}H_{20}BNNaO_6$: 356.1276, found 356.1281.



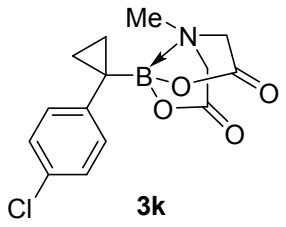
3i

2-(1-(4-(tert-butyl)phenyl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3i). Flash column chromatography to afford product **3i** as a pale yellow solid (43.1 mg, 66% yield); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.26-7.22 (m, 4H), 4.13 (d, J = 17.1 Hz, 2H), 3.56 (d, J = 17.1 Hz, 2H), 2.86 (s, 3H), 1.24 (s, 9H), 0.79-0.72 (m, 2H), 0.68-0.58 (m, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 169.1, 147.7, 142.7, 130.4, 125.0, 62.7, 46.8, 34.5, 31.7, 10.2; ^{11}B NMR (193 MHz, DMSO-d_6) δ 11.1; HRMS (ESI) [M+Na]$^{+}$: calculated for $C_{18}H_{24}BNNaO_4$: 352.1691, found 352.1696.



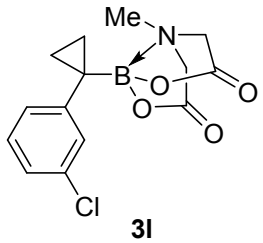
3j

2-(1-(3-fluoro-4-methylphenyl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione(3j). Flash column chromatography to afford product **3j** as a pale yellow solid (43.9 mg, 72% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.17-7.15 (m, 1H), 7.13 (s, 1H), 7.11-7.09 (m, 1H), 4.13 (d, J = 16.9 Hz, 2H), 3.64 (d, J = 16.9 Hz, 2H), 3.14 (s, 3H), 2.19 (d, J = 1.6 Hz, 3H), 0.92-0.91 (m, 2H), 0.75-0.74 (m, 2H); ^{13}C NMR (126 MHz, Acetone-d6) δ 168.8 , 161.9 (d, J = 242.7 Hz), 147.0 (d, J = 7.4 Hz), 132.2 (d, J = 5.6 Hz), 127.1 (d, J = 3.0 Hz), 122.4 (d, J = 17.1 Hz), 117.9 (d, J = 21.9 Hz), 63.6 , 47.2 , 14.3 (d, J = 3.4 Hz), 11.0; ^{19}F NMR (376 MHz, DMSO-d_6) δ -118.0; ^{11}B NMR (193 MHz, DMSO-d_6) δ 10.6; HRMS (ESI) [M+Na]$^{+}$: calculated for $C_{15}H_{17}BFNNaO_4$: 328.1127, found 328.1131.



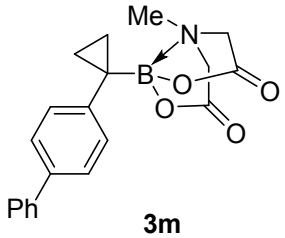
3k

2-(1-(4-chlorophenyl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3k). Flash column chromatography to afford product **3k** as a white solid (34.1 mg, 56% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.47−7.44 (m, 2H), 7.27-7.24 (m, 2H), 4.13 (d, J = 16.9 Hz, 2H), 3.67 (d, J = 16.9 Hz, 2H), 3.14 (s, 3H), 0.95-0.93 (m, 2H), 0.76-0.74 (m, 2H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.7, 145.9, 133.4, 131.6, 129.1, 63.6, 47.2, 11.0; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.0; HRMS (ESI) [M+Na]$^{+}$: calculated for $C_{14}H_{15}BClNNaO_4$: 330.0675, found 330.0679.



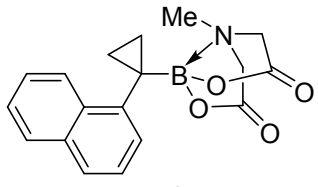
3l

2-(1-(3-chlorophenyl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3l). Flash column chromatography to afford product **3l** as a white solid (49.4 mg, 80% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.45-7.44 (m, 1H), 7.40 (d, J = 7.7 Hz, 1H), 7.27-7.22 (m, 1H), 7.18-7.12 (m, 1H), 4.14 (d, J = 17.0 Hz, 2H), 3.67 (d, J = 17.0 Hz, 2H), 3.13 (s, 3H), 0.95-0.93 (m, 2H), 0.78-0.76 (m, 2H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.4, 149.3, 134.2, 131.4, 130.5, 129.9, 126.3, 63.4, 47.0, 10.7; ^{11}B NMR (193 MHz, Acetone-d_6) δ 10.9; HRMS (ESI) $[M+Na]^+$: calculated for $C_{14}H_{15}BClNNaO_4$: 330.0675, found 330.0679.



3m

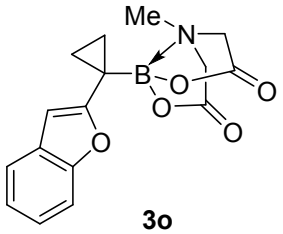
2-(1-([1,1'-biphenyl]-4-yl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3m). Flash column chromatography to afford product **3m** as a pale yellow solid (32.4 mg, 46% yield); ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.64 (d, J = 7.6 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H), 7.48-7.40 (m, 4H), 7.35-7.32 (m, 1H), 4.15 (d, J = 17.1 Hz, 2H), 3.63 (d, J = 17.1 Hz, 2H), 2.91 (s, 3H), 0.84-0.82 (m, 2H), 0.71-0.70 (m, 2H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 169.1, 145.3, 140.3, 137.3, 131.4, 129.3, 127.6, 126.8, 126.5, 62.8, 46.9, 10.4; ^{11}B NMR (193 MHz, DMSO-d_6) δ 10.2; HRMS (ESI) $[M+Na]^+$: calculated for $C_{20}H_{20}BNNaO_4$: 372.1378, found 372.1383.



3n

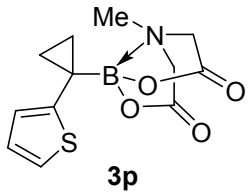
6-methyl-2-(1-(naphthalen-1-yl)cyclopropyl)-1,3,6,2-dioxazaborocane-4,8-dione (3n). Flash column chromatography to afford product **3n** as a pale yellow solid (38.5 mg, 60% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 8.58 (d, J = 8.5 Hz, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 8.2 Hz, 1H), 7.61 (d, J = 7.0 Hz, 1H), 7.51-7.48 (m, 1H), 7.45-7.42 (m, 1H), 7.37-7.34 (m, 1H), 4.14 (d, J = 17.1 Hz, 1H), 4.05 (d, J = 17.0 Hz, 1H), 3.91 (d, J = 16.6 Hz, 1H), 3.35 (s, 3H), 3.28 (d, J = 16.6 Hz, 1H), 1.40-1.36 (m, 1H), 1.17-1.13 (m, 1H), 1.07-1.04 (m, 1H), 0.57-0.53 (m, 1H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.9, 167.3, 143.7, 135.1, 134.6, 128.9, 128.7, 128.4, 127.4, 126.2, 125.8, 125.5, 63.6, 62.6, 47.2, 13.3, 11.3; ^{11}B NMR (193 MHz, DMSO-d_6) δ 10.9; HRMS

(ESI) $[M+Na]^+$: calculated for $C_{18}H_{18}BNNaO_4$: 346.1221, found 346.1227.



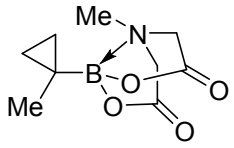
3o

2-(1-(benzofuran-2-yl)cyclopropyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3o). Flash column chromatography to afford product **3o** as a pale yellow solid (28.3 mg, 45% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.49-7.47 (m, 1H), 7.41-7.39 (m, 1H), 7.21-7.15 (m, 2H), 6.49-6.45 (m, 1H), 4.29 (d, J = 16.9 Hz, 2H), 4.06 (d, J = 16.9 Hz, 2H), 3.31 (s, 3H), 1.11-1.09 (m, 2H), 1.07-1.05 (m, 2H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.9, 164.9, 155.2, 130.3, 124.1, 123.7, 121.2, 111.5, 102.1, 64.1, 47.5, 12.8; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.0; HRMS (ESI) $[M+Na]^+$: calculated for $C_{16}H_{16}BNNaO_5$: 336.1014, found 336.1019.



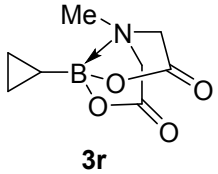
3p

6-methyl-2-(1-(thiophen-2-yl)cyclopropyl)-1,3,6,2-dioxazaborocane-4,8-dione (3p). Flash column chromatography to afford product **3p** as a pale yellow solid (28.4 mg, 51% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.17-7.16 (m, 1H), 6.92-6.91 (m, 1H), 6.88-6.87 (m, 1H), 4.17 (d, J = 16.8 Hz, 2H), 3.73 (d, J = 16.8 Hz, 2H), 3.14 (s, 3H), 0.99-0.98 (m, 2H), 0.86-0.84 (m, 2H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.6, 151.3, 127.4, 125.8, 124.0, 63.7, 47.0, 13.2; ^{11}B NMR (193 MHz, Acetone-d_6) δ 10.8; HRMS (ESI) $[M+Na]^+$: calculated for $C_{12}H_{14}BNNaO_4S$: 302.0629, found 302.0631.



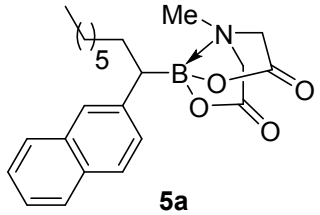
3q

6-methyl-2-(1-methylcyclopropyl)-1,3,6,2-dioxazaborocane-4,8-dione (3q). Flash column chromatography to afford product **3q** as a white solid (12.9 mg, 30% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 4.20 (d, J = 16.9 Hz, 2H), 4.05 (d, J = 17.0 Hz, 2H), 3.25 (s, 3H), 1.00 (s, 3H), 0.50-0.48 (m, 2H), 0.17-0.15 (m, 2H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 169.0, 63.6, 47.1, 22.3, 11.4; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.8; HRMS (ESI) $[M+Na]^+$: calculated for $C_9H_{14}BNNaO_4$: 234.0908, found 234.0910.



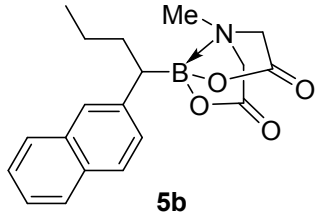
3r

2-cyclopropyl-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3r). Flash column chromatography to afford product **3r** as a pale yellow solid (7.1 mg, 18% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 4.18 (d, J = 16.8 Hz, 2H), 4.03 (d, J = 16.9 Hz, 2H), 3.21 (s, 3H), 0.45-0.43 (m, 2H), 0.16-0.15 (m, 2H), -0.23--0.29 (m, 1H). ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.1, 61.9, 46.0, 0.3. This spectral data is consistent with a previous literature report.[4]



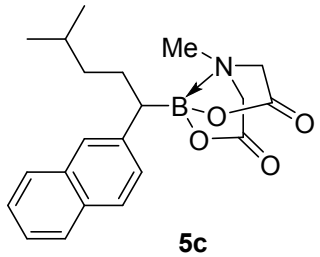
5a

6-methyl-2-(1-(naphthalen-2-yl)octyl)-1,3,6,2-dioxazaborocane-4,8-dione (5a). Flash column chromatography to afford product **5a** as a pale yellow solid (69.2 mg, 88% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.86-7.76 (m, 4H), 7.52-7.41 (m, 3H), 4.22 (d, J = 17.1 Hz, 1H), 4.06 (d, J = 17.1 Hz, 1H), 4.00 (d, J = 16.6 Hz, 1H), 3.15 (d, J = 16.6 Hz, 1H), 3.05 (s, 3H), 2.42-2.39 (m, 1H), 2.00-1.94 (m, 1H), 1.89-1.81 (m, 1H), 1.35-1.31 (m, 2H), 1.24-1.11 (m, 8H), 0.82 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 169.2, 168.6, 143.6, 134.9, 133.0, 128.9, 128.8, 128.6, 128.5, 128.4, 126.9, 126.0, 63.7, 63.4, 46.5, 33.3, 32.8, 30.4, 30.2, 29.7, 23.5, 14.5; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.7; HRMS (ESI) $[M+Na]^+$: calculated for $C_{23}H_{30}BNNaO_4$: 418.2160, found 418.2157.



5b

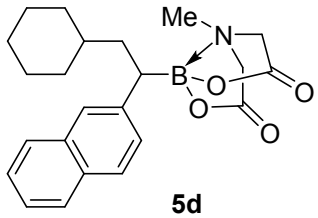
6-methyl-2-(1-(naphthalen-2-yl)butyl)-1,3,6,2-dioxazaborocane-4,8-dione(5b). Flash column chromatography to afford product **5b** as a pale yellow solid (43.5 mg, 64% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.86-7.76 (m, 4H), 7.51-7.41 (m, 3H), 4.22 (d, J = 17.1 Hz, 1H), 4.07 (d, J = 17.1 Hz, 1H), 4.01 (d, J = 16.6 Hz, 1H), 3.16 (d, J = 16.6 Hz, 1H), 3.06 (s, 3H), 2.46-2.39 (m, 1H), 1.96-1.80 (m, 2H), 1.17-1.09 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 169.2, 168.6, 143.5, 134.9, 132.9, 128.9, 128.8, 128.6, 128.4, 126.8, 125.9, 63.6, 63.4, 46.5, 35.5, 22.6, 14.4; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.6; HRMS (ESI) $[M+Na]^+$: calculated for $C_{19}H_{22}BNNaO_4$: 362.1534, found 362.1538.



5c

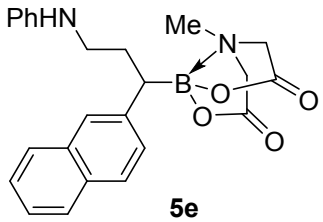
6-methyl-2-(4-methyl-1-(naphthalen-2-yl)pentyl)-1,3,6,2-dioxazaborocane-4,8-dione (5c).

Flash column chromatography to afford product **5c** as a pale yellow solid (44.6 mg, 61% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.85-7.74 (m, 4H), 7.50-7.40 (m, 3H), 4.21 (d, J = 17.1 Hz, 1H), 4.05 (d, J = 17.1 Hz, 1H), 3.99 (d, J = 16.6 Hz, 1H), 3.11 (d, J = 16.6 Hz, 1H), 3.04 (s, 3H), 2.35-2.33 (m, 1H), 2.00-1.97 (m, 1H), 1.86-1.78 (m, 1H), 1.52-1.46 (m, 1H), 1.11-1.04 (m, 1H), 0.98-0.91 (m, 1H), 0.80-0.75 (m, 6H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 169.0, 168.3, 143.4, 134.7, 132.7, 128.7, 128.6, 128.4, 128.3, 128.2, 126.6, 125.7, 63.5, 63.2, 46.3, 39.0, 30.9, 28.6, 23.3, 22.6; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.5; HRMS (ESI) $[M+Na]^+$: calculated for $C_{21}H_{26}BNNaO_4$: 390.1847, found 390.1851.



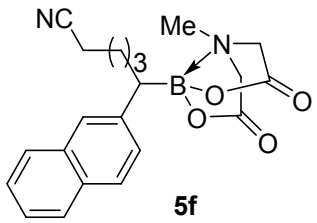
5d

(2-cyclohexyl-1-(naphthalen-2-yl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5d). Flash column chromatography to afford product **5d** as a pale yellow solid (65.9 mg, 84% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.86-7.78 (m, 4H), 7.52-7.41 (m, 3H), 4.22 (d, J = 17.1 Hz, 1H), 4.07 (d, J = 17.1 Hz, 1H), 4.00 (d, J = 16.6 Hz, 1H), 3.14 (d, J = 16.6 Hz, 1H), 3.09 (s, 3H), 2.63-2.60 (m, 1H), 1.92-1.87 (m, 1H), 1.73-1.47 (m, 6H), 1.12-0.82 (m, 6H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 169.0, 168.3, 143.4, 134.7, 132.7, 128.8, 128.5, 128.4, 128.2, 128.1, 126.6, 125.7, 63.5, 63.2, 46.2, 40.7, 35.9, 35.6, 32.4, 27.4, 27.0, 26.8; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.7; HRMS (ESI) $[M+Na]^+$: calculated for $C_{23}H_{28}BNNaO_4$: 416.2004, found 416.2007.



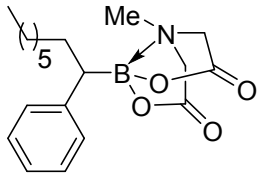
5e

6-methyl-2-(1-(naphthalen-2-yl)-3-(phenylamino)propyl)-1,3,6,2-dioxazaborocane-4,8-dione(5e). Flash column chromatography to afford product **5e** as a pale yellow solid (52.1 mg, 63% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.86-7.77 (m, 4H), 7.54 (d, J = 8.2 Hz, 1H), 7.46-7.42 (m, 2H), 7.00-6.97 (m, 2H), 6.49-6.44 (m, 3H), 4.75 (s, 1H), 4.22 (d, J = 17.1 Hz, 1H), 4.07-3.97 (m, 2H), 3.19 (d, J = 16.6 Hz, 1H), 3.05 (s, 3H), 2.94-2.91 (m, 2H), 2.61-2.58 (m, 1H), 2.30-2.25 (m, 1H), 2.15-2.09 (m, 1H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.9, 168.3, 150.0, 142.7, 134.7, 132.8, 129.7, 128.8, 128.6, 128.4, 128.3, 128.2, 126.7, 125.9, 116.7, 113.1, 63.5, 63.2, 46.3, 43.5, 32.8; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.6; HRMS (ESI) $[M+H]^+$: calculated for $C_{24}H_{26}BN_2O_4$: 417.1980, found 417.1982.



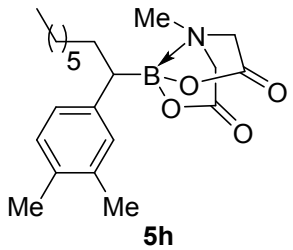
5f

6-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-6-(naphthalen-2-yl)hexanenitrile (5f). Flash column chromatography to afford product **5f** as a pale yellow solid (49.7 mg, 66% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.86-7.78 (m, 4H), 7.52-7.42 (m, 3H), 4.24 (d, J = 17.1 Hz, 1H), 4.08 (d, J = 17.1 Hz, 1H), 4.02 (d, J = 16.6 Hz, 1H), 3.16 (d, J = 16.6 Hz, 1H), 3.06 (s, 3H), 2.45-2.42 (m, 1H), 2.41-2.29 (m, 2H), 2.03-1.97 (m, 1H), 1.92-1.84 (m, 1H), 1.70-1.63 (m, 1H), 1.59-1.53 (m, 1H), 1.31-1.23 (m, 2H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.9, 168.3, 142.9, 134.7, 132.8, 128.7, 128.6, 128.4, 128.3, 126.7, 125.8, 120.7, 63.5, 63.2, 46.3, 32.3, 28.7, 26.2, 17.0; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.5; HRMS (ESI) $[M+Na]^+$: calculated for $C_{21}H_{23}BN_2NaO_4$: 401.1643, found 401.1641.



5g

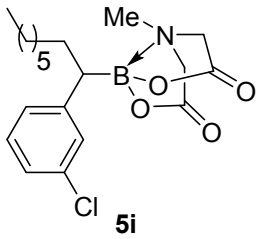
6-methyl-2-(1-phenyloctyl)-1,3,6,2-dioxazaborocane-4,8-dione (5g). Flash column chromatography to afford product **5g** as a pale yellow solid (44.5 mg, 65% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.28-7.22 (m, 4H), 7.14-7.11 (m, 1H), 4.17 (d, J = 17.1 Hz, 1H), 4.02 (d, J = 3.6 Hz, 1H), 3.99 (d, J = 3.1 Hz, 1H), 3.08 (d, J = 16.5 Hz, 1H), 2.98 (s, 3H), 2.20-2.16 (m, 1H), 1.91-1.87 (m, 1H), 1.74-1.66 (m, 1H), 1.29-1.18 (m, 8H), 1.12-1.08 (m, 2H), 0.83 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.9, 168.3, 145.6, 130.0, 129.1, 125.9, 63.4, 63.2, 46.2, 33.2, 32.6, 30.2, 30.0, 29.4, 23.3, 14.3; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.4; HRMS (ESI) $[M+Na]^+$: calculated for $C_{19}H_{28}BNNaO_4$: 368.2004, found 368.2009.



5h

2-(1-(3,4-dimethylphenyl)octyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5h). Flash column chromatography to afford product **5h** as a pale yellow solid (55.1 mg, 74% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.05 (s, 1H), 7.01-6.97 (m, 2H), 4.16 (d, J = 17.1 Hz, 1H), 3.99 (d, J = 7.7 Hz, 1H), 3.96 (d, J = 7.0 Hz, 1H), 3.01 (d, J = 16.5 Hz, 1H), 2.98 (s, 3H), 2.19 (s, 6H), 2.09 (s, 1H), 1.88-1.81 (m, 1H), 1.71-1.64 (m, 1H), 1.26-1.12 (m, 8H), 1.14-1.08 (m, 2H), 0.84 (t, J = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 167.7, 166.9, 141.2, 135.5, 132.2, 129.9,

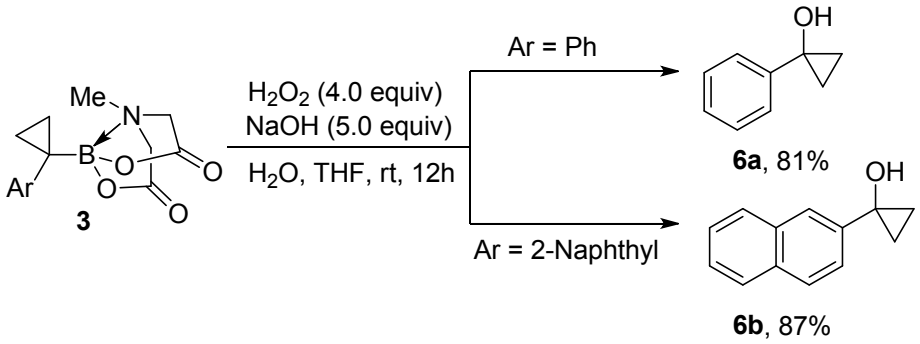
128.9, 126.0, 61.9, 61.7, 44.6, 31.7, 31.2, 28.8, 28.6, 28.0, 21.9, 18.5, 17.9, 12.9; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.4; HRMS (ESI) $[M+Na]^+$: calculated for $C_{21}H_{32}BNNaO_4$: 396.2317, found 396.2324.



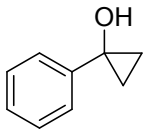
5i

2-(1-(3-chlorophenyl)octyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (5i). Flash column chromatography to afford product **5i** as a pale yellow solid (54.4 mg, 72% yield); ^{1}H NMR (500 MHz, Acetone-d_6) δ 7.32-7.31 (m, 1H), 7.29-7.23 (m, 2H), 7.18-7.16 (m, 1H), 4.24 (d, J = 17.0 Hz, 1H), 4.13 (d, J = 7.8 Hz, 1H), 4.10 (d, J = 8.0 Hz, 1H), 3.44 (d, J = 16.8 Hz, 1H), 3.06 (s, 3H), 2.27-2.25 (m, 1H), 1.90-1.84 (m, 1H), 1.74-1.66 (m, 1H), 1.31-1.17 (m, 8H), 1.14-1.00 (m, 2H), 0.85 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, Acetone-d_6) δ 168.7, 168.4, 148.5, 134.4, 130.6, 129.8, 128.4, 125.9, 63.3(4), 63.3(0), 46.5, 32.9, 32.6, 30.1, 29.9, 29.3, 23.3, 14.3; ^{11}B NMR (193 MHz, Acetone-d_6) δ 11.1; HRMS (ESI) $[M+H]^+$: calculated for $C_{19}H_{28}BClNO_4$: 380.1794, found 380.1792.

4 Oxidation of Cyclopropyl MIDA Boronates

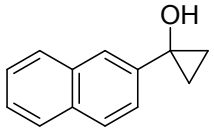


To the solution of MIDA boronate **3** (0.1 mmol) in THF (2 mL) was slowly added a premixed aqueous solution (including NaOH（20 mg, 5.0 equiv）, 30% H_2O_2 (45 mg, 4.0 equiv), H_2O (0.2 mL)) via a syringe at 0 °C. The reaction was then stirred at room temperature for 12 h and diluted with 5 mL water. The reaction mixture was extracted with EtOAc (5 mL × 3). The organic layers were combined, dried with anhydrous $MgSO_4$, filtered and concentrated in vacuum. The crude residue was purified using flash column chromatography on silica gel (PE/EtOAc 25 : 1) to afford the cyclopropanol **6** .



6a

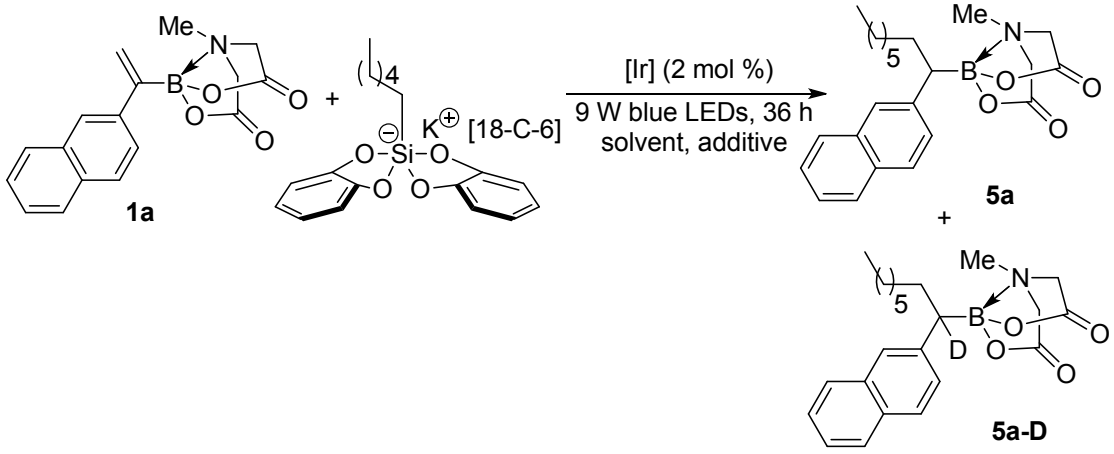
1-phenylcyclopropan-1-ol (6a). Flash column chromatography to afford product **6a** as a colorless oil (10.8 mg, 81% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.33 (m, 4H), 7.27-7.24 (m, 1H), 2.36 (s, 1H), 1.31-1.28 (m, 2H), 1.09-1.07 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.2, 128.4, 126.4, 124.4, 56.7, 17.8. This spectral data is consistent with a previous literature report.[5a]



6b

1-(naphthalen-2-yl)cyclopropan-1-ol (6b). Flash column chromatography to afford product **6b** as a white solid (16.1 mg, 87% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.85-7.82 (m, 3H), 7.52-7.46 (m, 2H), 7.34-7.32 (m, 1H), 2.47 (s, 1H), 1.39-1.36 (m, 2H), 1.22-1.18 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 133.3, 132.2, 128.2, 127.8, 127.6, 126.3, 125.6, 123.0 (2), 129.9 (7), 57.0, 17.9. This spectral data is consistent with a previous literature report.[5b]

5 Deuteration Studies

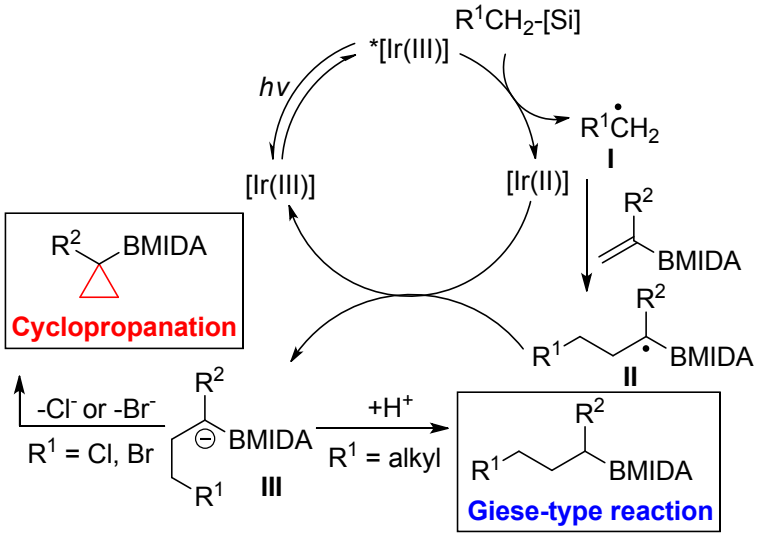


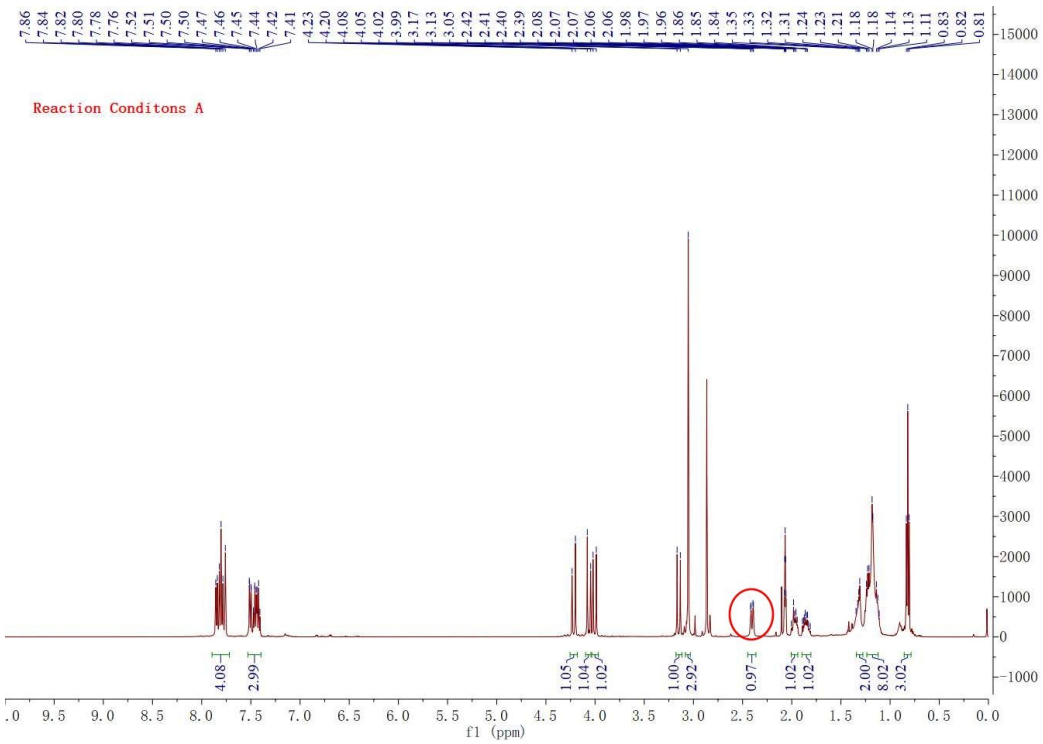
Entry	Solvent, Additive	Yield (5a+5a-D) (%)	D-Incorporation (%)
A	DMSO	88	0
B	DMSO-d_6	87	0

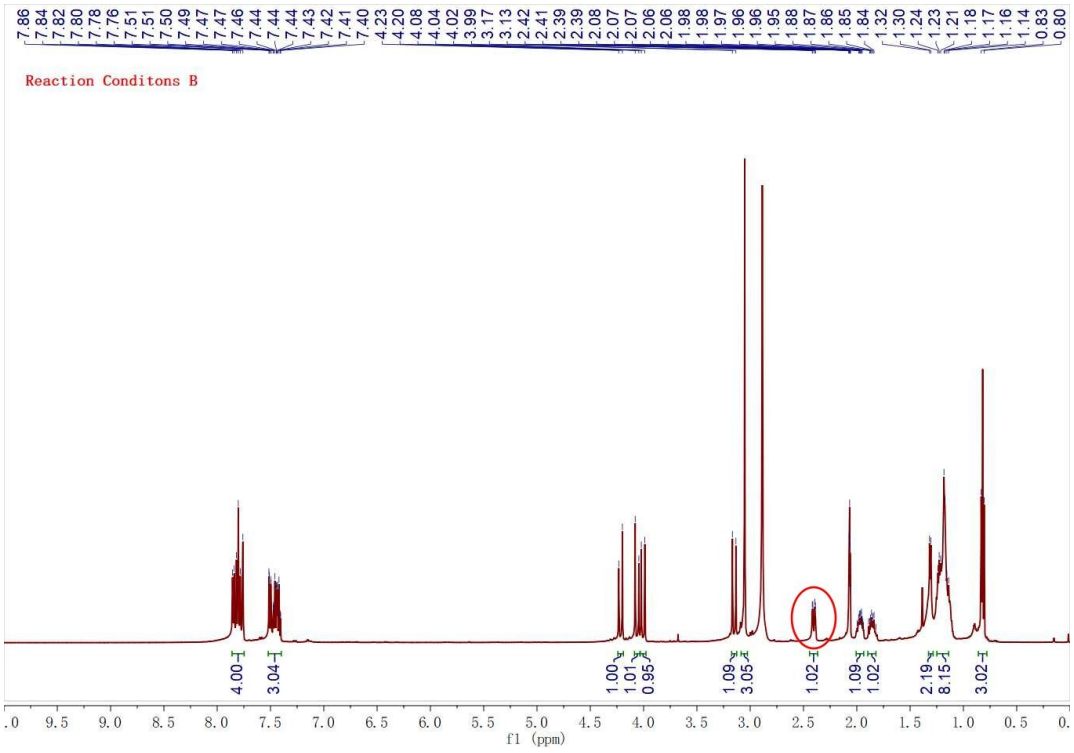
C	DMSO-d_6, 3 Å MS	91	0
D	DMSO-d_6, CD_3OD (65 equiv), 3 Å MS	79	60[a]

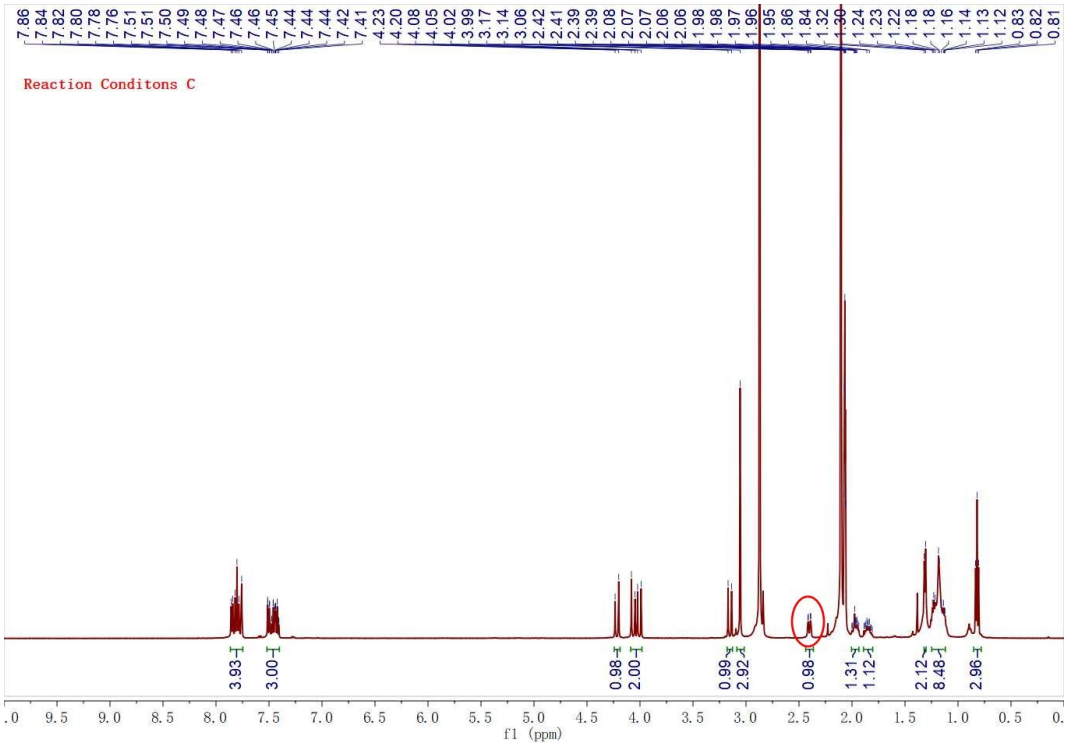
[a] The product **5a-D** with 60% D-incorporation was determined by ^1H NMR.

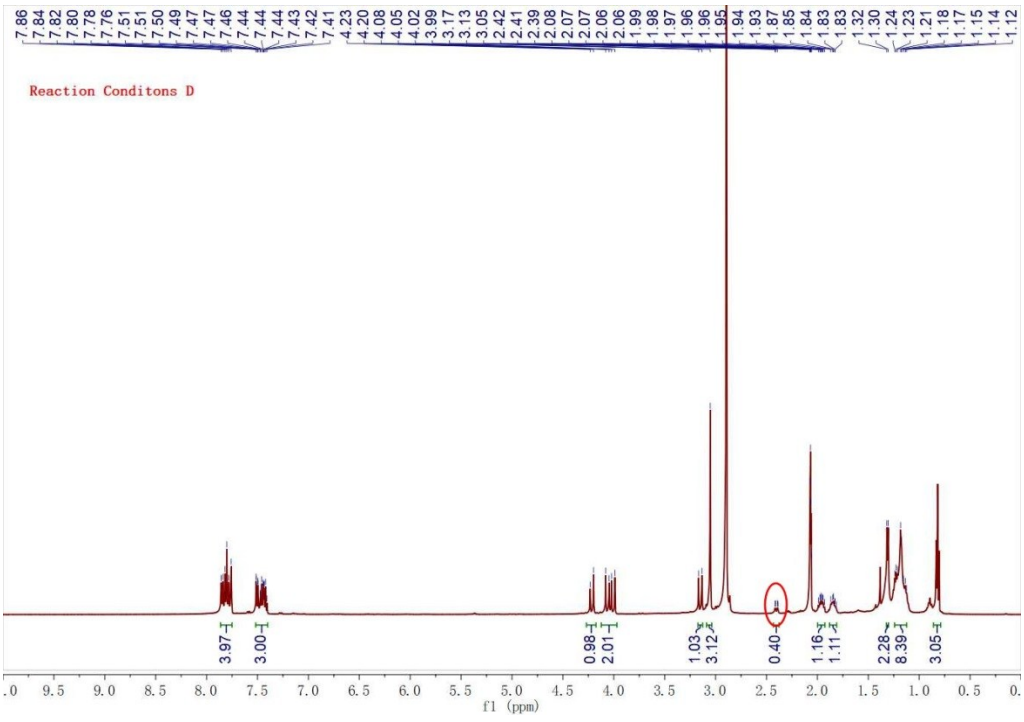
According to deuteration studies (entries B-C), when the reaction between **1a** and hexylsilicate was carried out in DMSO-d_6, the product **5a** was obtained without any observed deuterium incorporation, suggesting that the solvent DMSO is not the source of the proton for the termination step of carbanion **III**. Of note, the desired product **5a-D** with 60% D-incorporation was formed in the presence of CD_3OD (entry D), thus confirming the formation of α-boryl anion **III**. Based on these results, we propose that H_2O contaminants in the reaction mixture would be the source of the hydrogen atom in the product **5**.




Reaction Conditons A
f1 (ppm)


Reaction Conditons B
f1 (ppm)


Reaction Conditons C
f1 (ppm)


Reaction Conditons D
f1 (ppm)

6 References

[1] (*a*) M. S. Oderinde and J. W. Johannes, Practical Syntheses of [2,2'-bipyridine]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl]phenyl]Iridium(III) hexafluorophosphate, [Ir{dF(CF_3)ppy}$_2$(bpy)]PF_6 and [4,4'-bis(tert-butyl)-2,2'-bipyridine]bis[3,5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl]phenyl]iridium(III) hexafluorophosphate, [Ir{dF(CF_3)ppy}$_2$(dtbbpy)]PF_6, *Org. Synth.*, 2017, **94**, 77-92; (*b*) J. Luo and J. Zhang, Donor-Acceptor Fluorophores for Visible-Light-Promoted Organic Synthesis: Photoredox/Ni Dual Catalytic C(sp^3)-C(sp^2) Cross-Coupling, *ACS Catal.*, 2016, **6**, 873-877.

[2] (*a*) E. M. Woerly, J. E. Miller and M. D. Burke, (1-Bromovinyl)-MIDA boronate: a readily accessible and highly versatile building block for small molecule synthesis, *Tetrahedron,* 2013, **69***,* 7732-7740; (*b*) W.-X. Lv, Q. Li, J.-L. Li, Z. Li, E Lin, D.-H. Tan, Y.-H. Cai, W.-X. Fan and H. Wang, *gem*-Difluorination of Alkenyl *N*-methyliminodiacetyl Boronates: Synthesis of α- and β-Difluorinated Alkylborons, *Angew. Chem. Int. Ed.*, 2018, **57**, 16544-16548; (*c*) T. Ohtani, Y. Tsuchiya, D. Uraguchi and T. Ooi, Photocatalytic borylcyclopropanation of α-boryl styrenes, *Org. Chem. Front.*, 2019, **6**, 1734-1737; (*d*) Q. I. Churches, J. F. Hooper and C. A. Hutton, A General Method for Interconversion of Boronic Acid Protecting Groups: Trifluoroborates as Common Intermediates, *J. Org. Chem.*, 2015, **80**, 5428-5435.

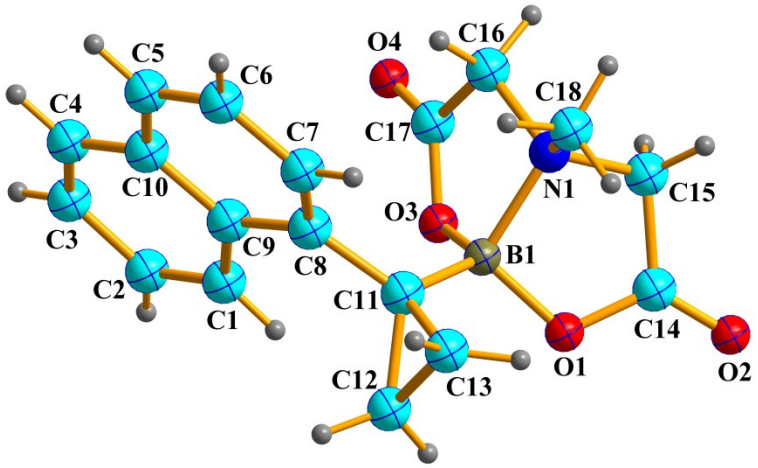
[3] (*a*) T. Guo, L. Zhang, X. Liu, Y. Fang, X. Jin, Y. Yang, Y. Li, B. Chen and M. Ouyang, Visible-Light-Promoted Redox-Neutral Cyclopropanation Reactions of α-Substituted Vinylphosphonates and Other Michael Acceptors with Chloromethyl Silicate as Methylene Transfer Reagent, *Adv. Synth. Catal.*, 2018, **360**, 4459-4463; (*b*) W. Luo, Y. Yang, Y. Fang, X. Zhang, X. Jin, G. Zhao, L. Zhang, Y. Li, W. Zhou, T. Xia and B. Chen, Photoredox-Catalyzed Cyclopropanation of 1,1-Disubstituted Alkenes via Radical-Polar Crossover Process, *Adv. Synth. Catal.*, 2019, **361**, 4215-4221; (*c*) W. Luo, Y. Fang, L, Zhang, T. Xu, Y. Liu, Y. Li, X. Jin, J. Bao, X. Wu and Z. Zhang,

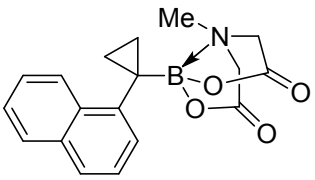
Bromomethyl Silicate: A Robust Methylene Transfer Reagent for Radical-Polar Crossover Cyclopropanation of Alkenes, *Eur. J. Org. Chem.*, 2020, 1778-1781.

[4] B. E. Uno, E. P. Gillis and M. D. Burke, Vinyl MIDA boronate: a readily accessible and highly versatile building block for small molecule synthesis, *Tetrahedron,* 2019, **65***,* 3130-3138.

[5] (*a*) L. R. Mills, C. Zhou, E. Fung and S. A. L. Rousseaux, Ni-Catalyzed β-Alkylation of Cyclopropanol-Derived Homoenolates, *Org. Lett.*, 2019, **21**, 8805-8809; (*b*) X.-P. He, Y.-J. Shu, J.-J. Dai, W.-M. Zhang, Y.-S. Feng and H.-J. Xu, Copper-catalysed ring-opening trifluoromethylation of cyclopropanols, *Org. Biomol. Chem.*, 2015, **13**, 7159-7163.

7 X-Ray Crystal Data for Compound 3n

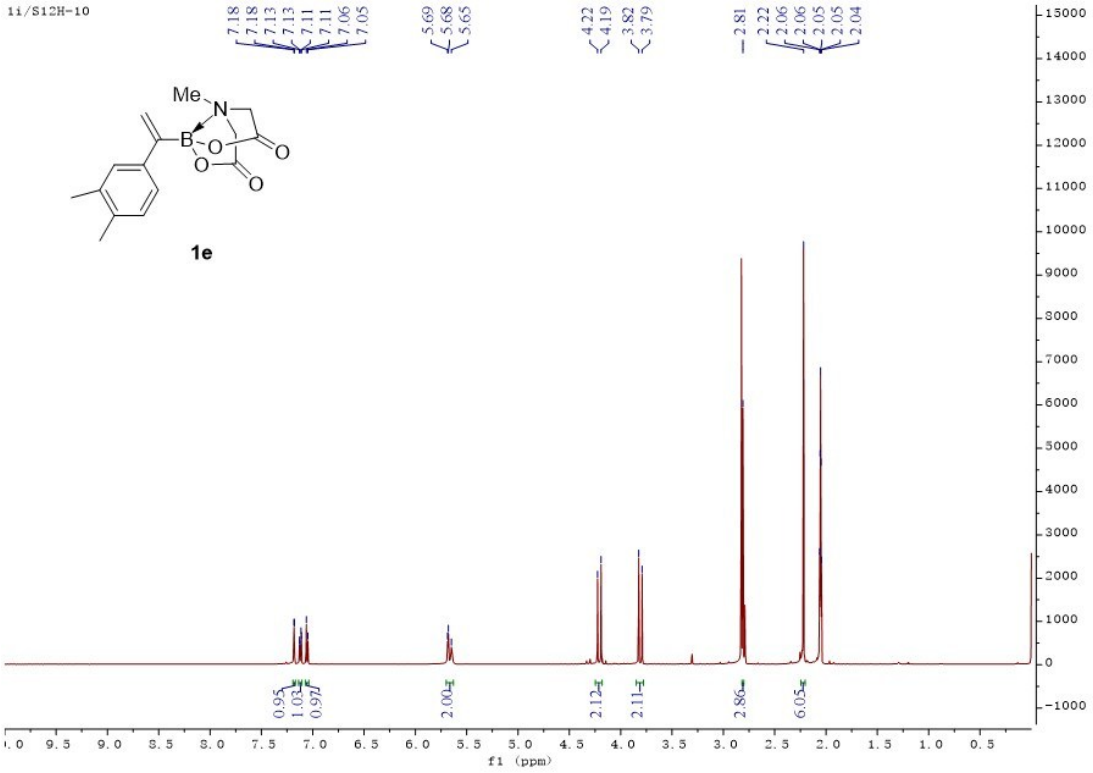


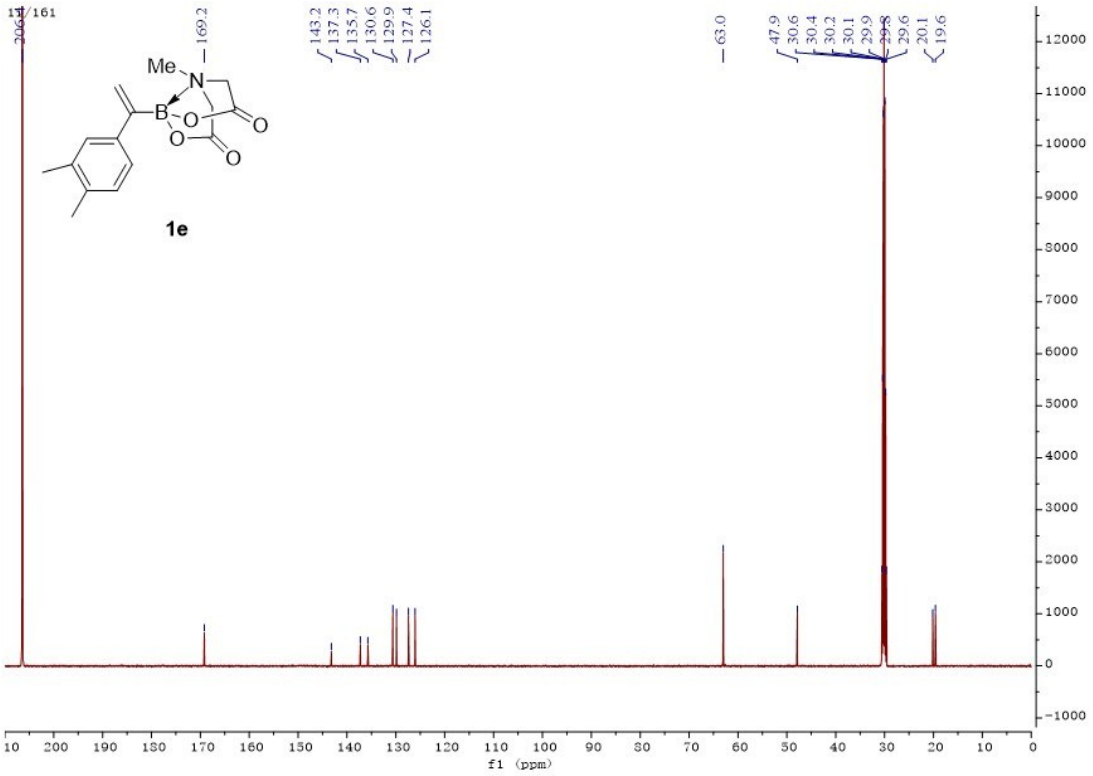


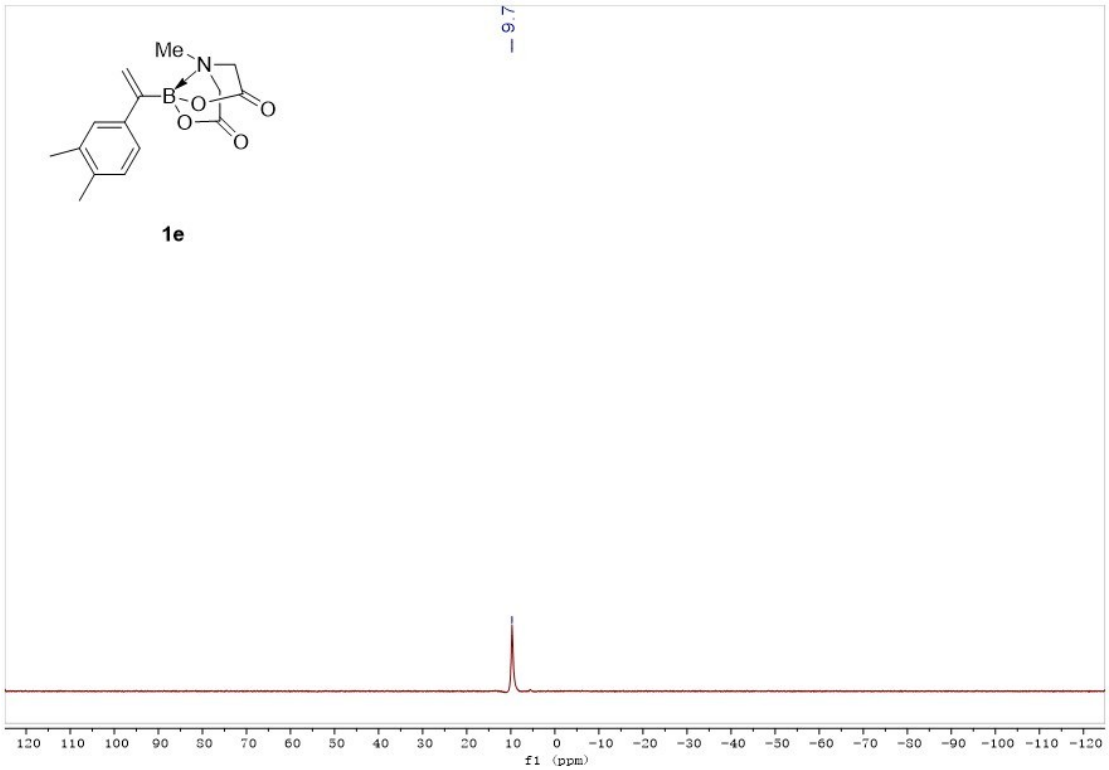
3n (CCDC 1976108)

Compound	**3n**
Identification code	a
Empirical formula	$C_{18}H_{18}BNO_4$
Formula weight	323.14
Temperature	295(2) K
Description	block
Crystal size (mm)	0.45 × 0.36 × 0.29
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	7.2859(7)
b (Å)	8.4515(8)
c (Å)	25.879(2)
Volume (Å^3)	1593.6(3)
Z,	4
D_{cald} (g cm^{-3})	1.347
μ (mm^{-1})	0.094
F(000)	680
θ range (°)	2.5–27.4
Limiting indices	$-9 \le h \le 8$, $-10 \le k \le 10$, $-27 \le l \le 33$
Reflections collected / unique	8560 / 3610
R_{int}	0.0741
Absorption correction	Empirical
Data / restraints / parameters	3610 / 0 / 218
Goodness-of-fit on F^2	1.048
R_1, wR_2 [$I \ge 2(I)$]	0.0654, 0.0831
$\delta\rho_{max}$, $\delta\rho_{min}$ (e·Å^{-3})	0.157, –0.185

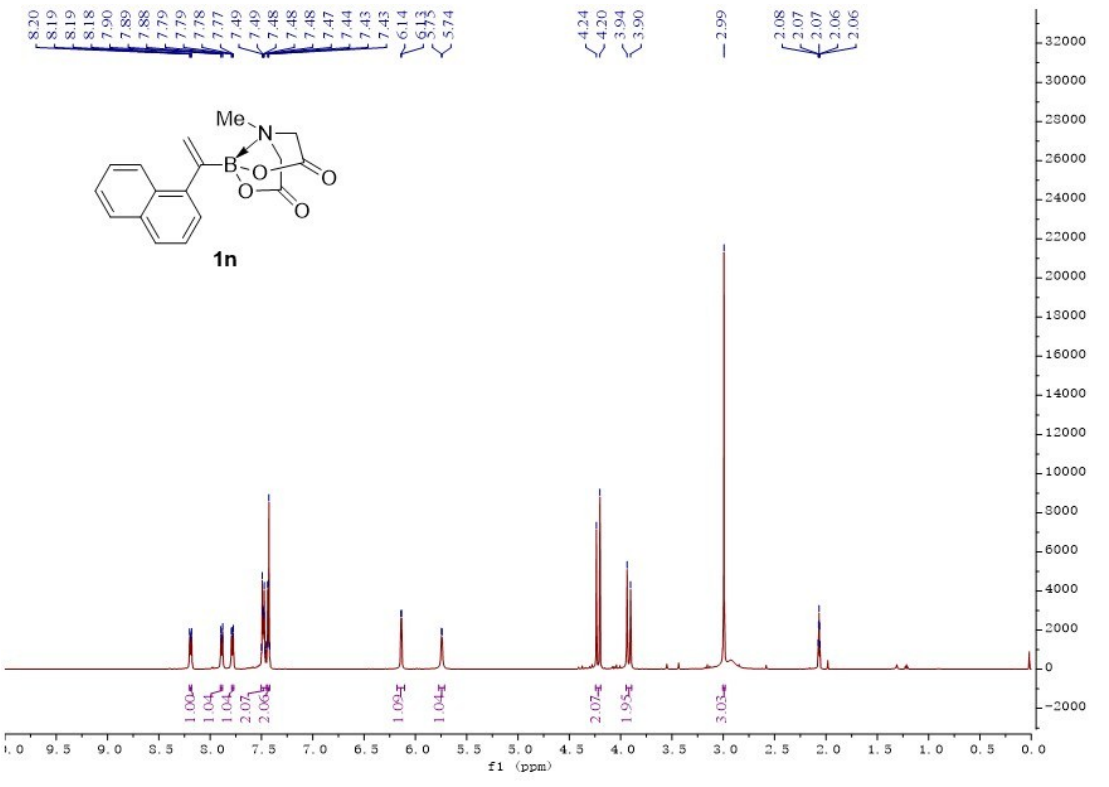
8 NMR Spectra of New Compounds



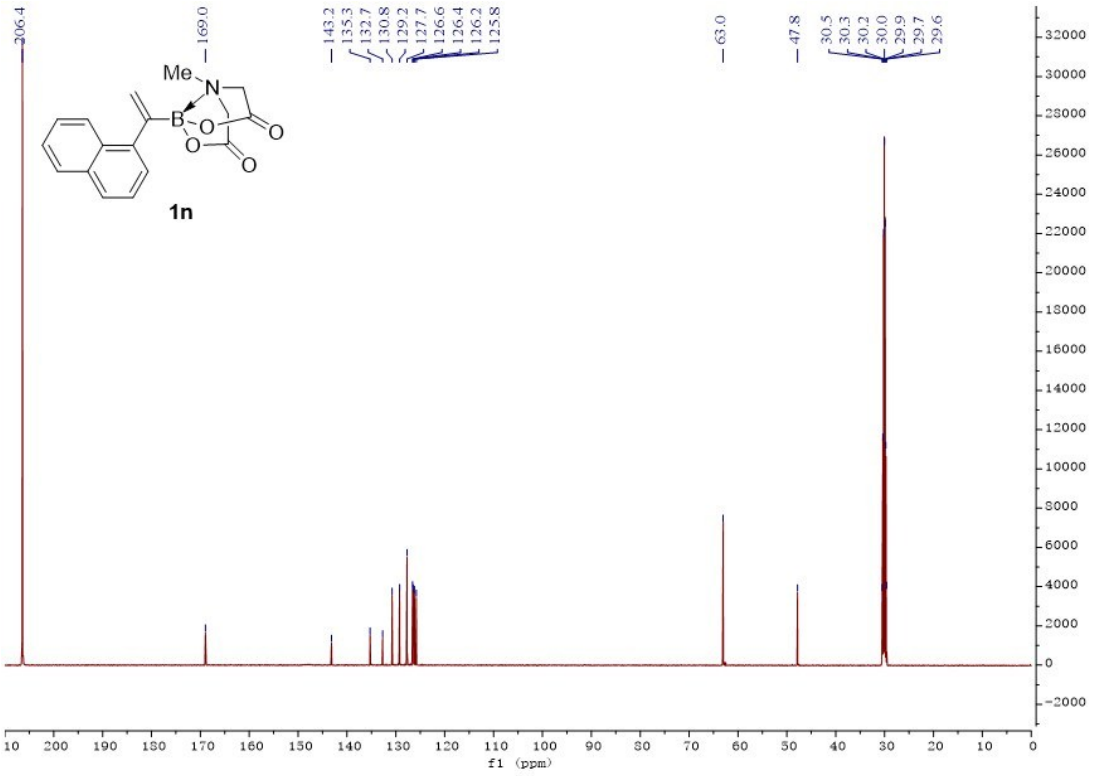


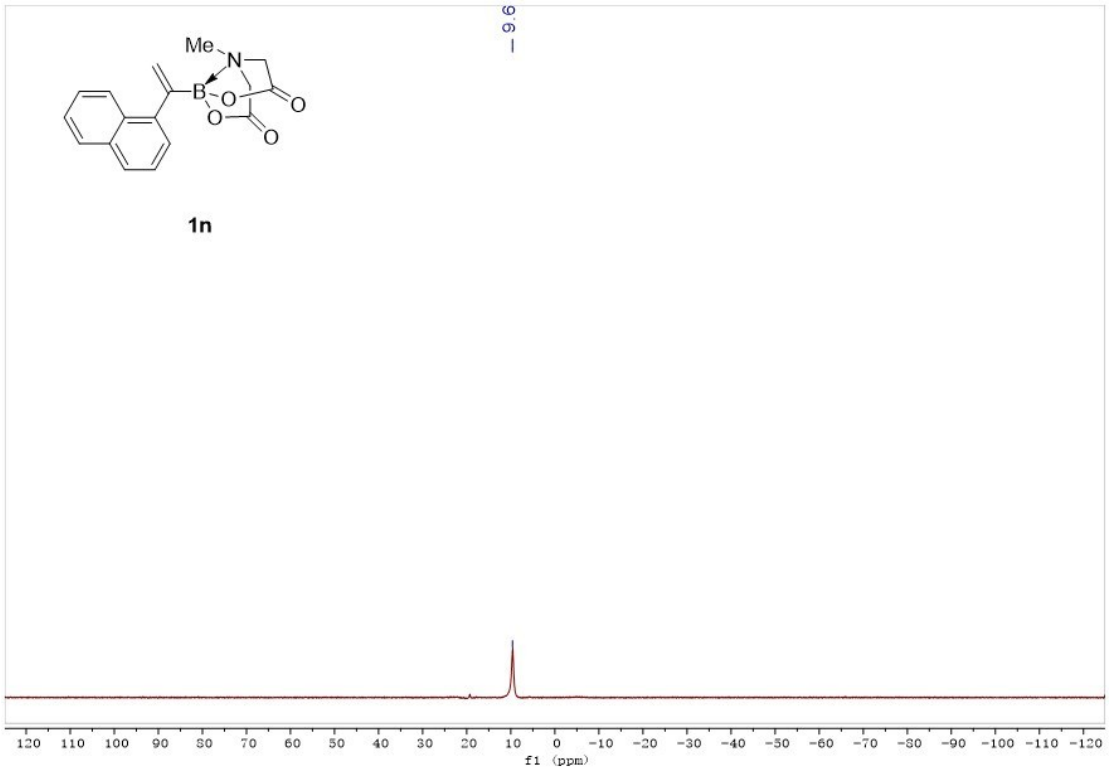

Me
N
B
O
O
O
O
9.7
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

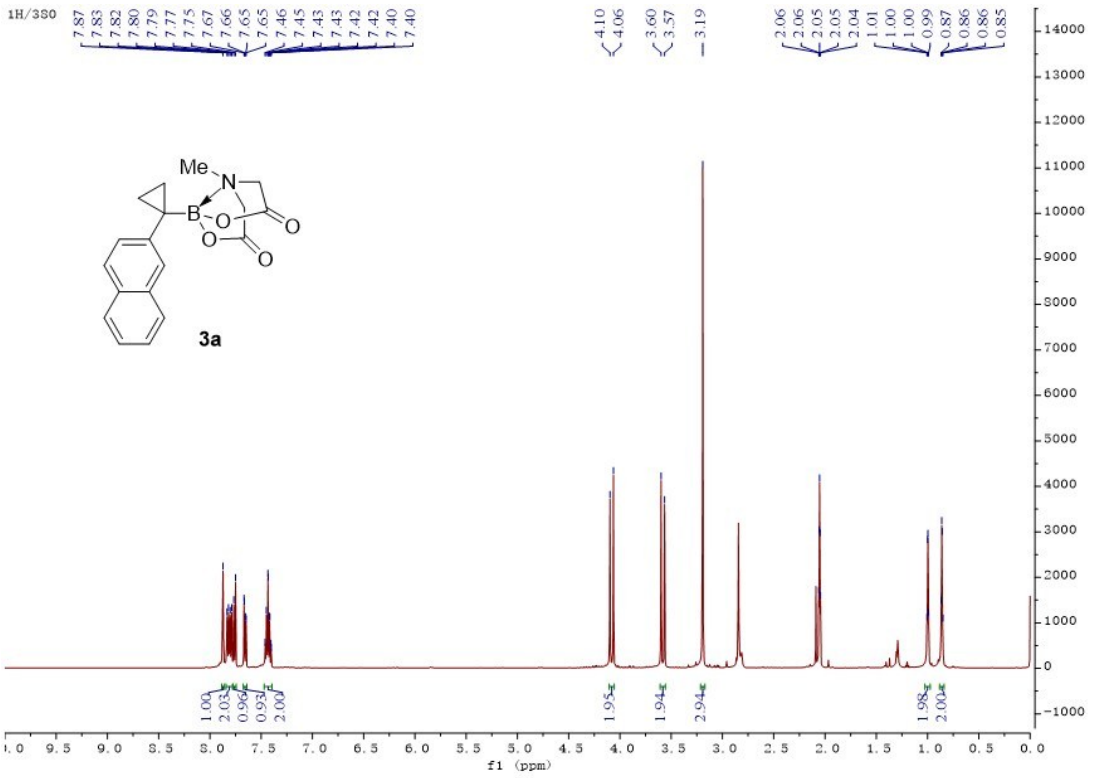
1e

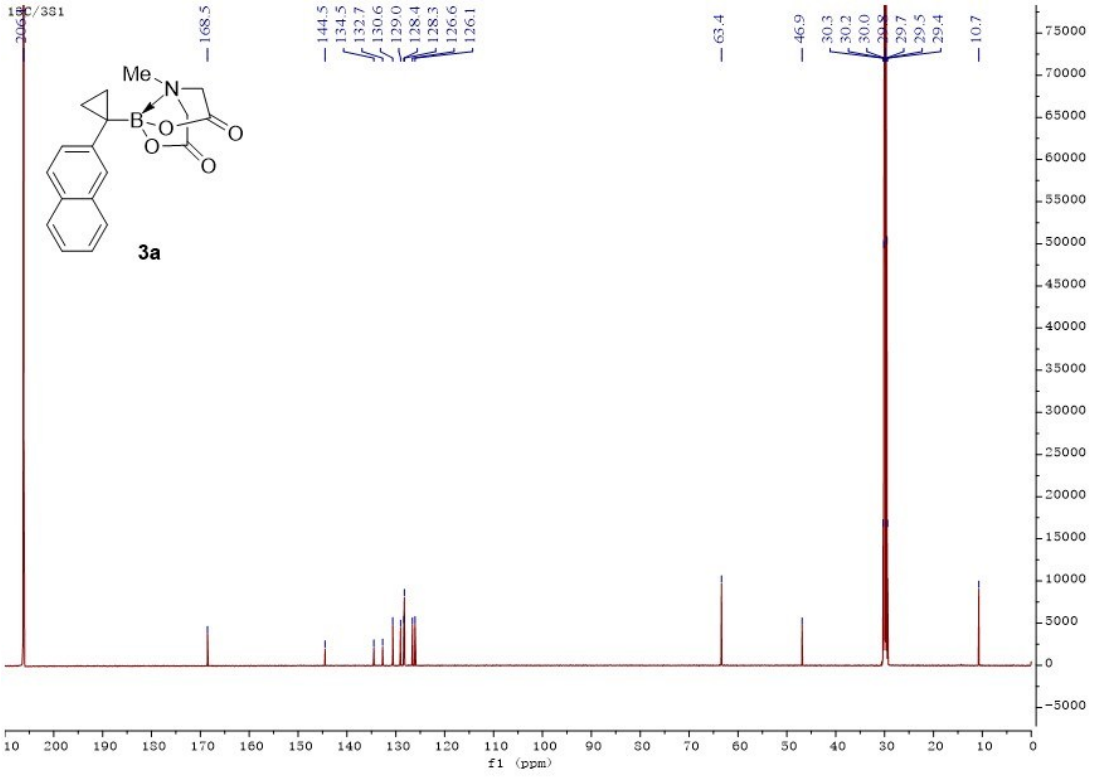

8.20
8.19
8.19
8.18
7.90
7.89
7.88
7.79
7.79
7.78
7.77
7.49
7.49
7.48
7.48
7.48
7.47
7.44
7.43
7.43
6.14
6.13
5.75
5.74
4.24
4.20
3.94
3.90
2.99
2.08
2.07
2.07
2.06
2.06
Me
N
B
O
O
O
O
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
1.00
1.04
1.04
2.07
2.06
1.09
1.04
2.07
1.95
3.03
f1 (ppm)

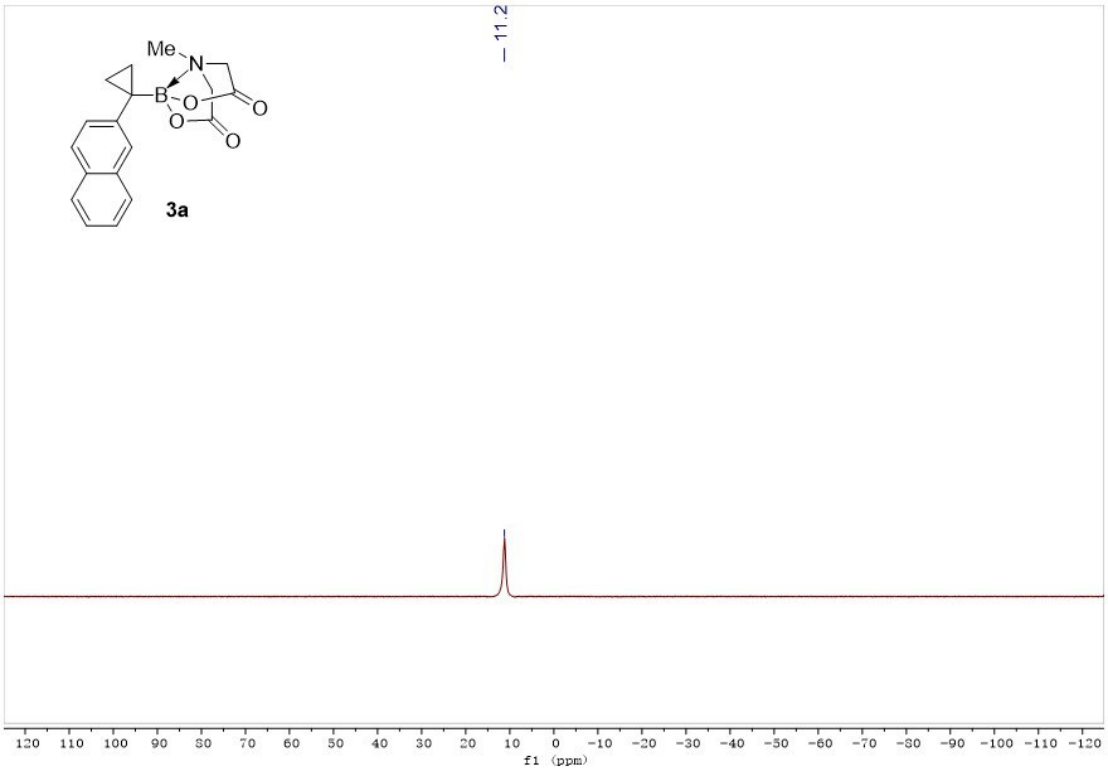
1n

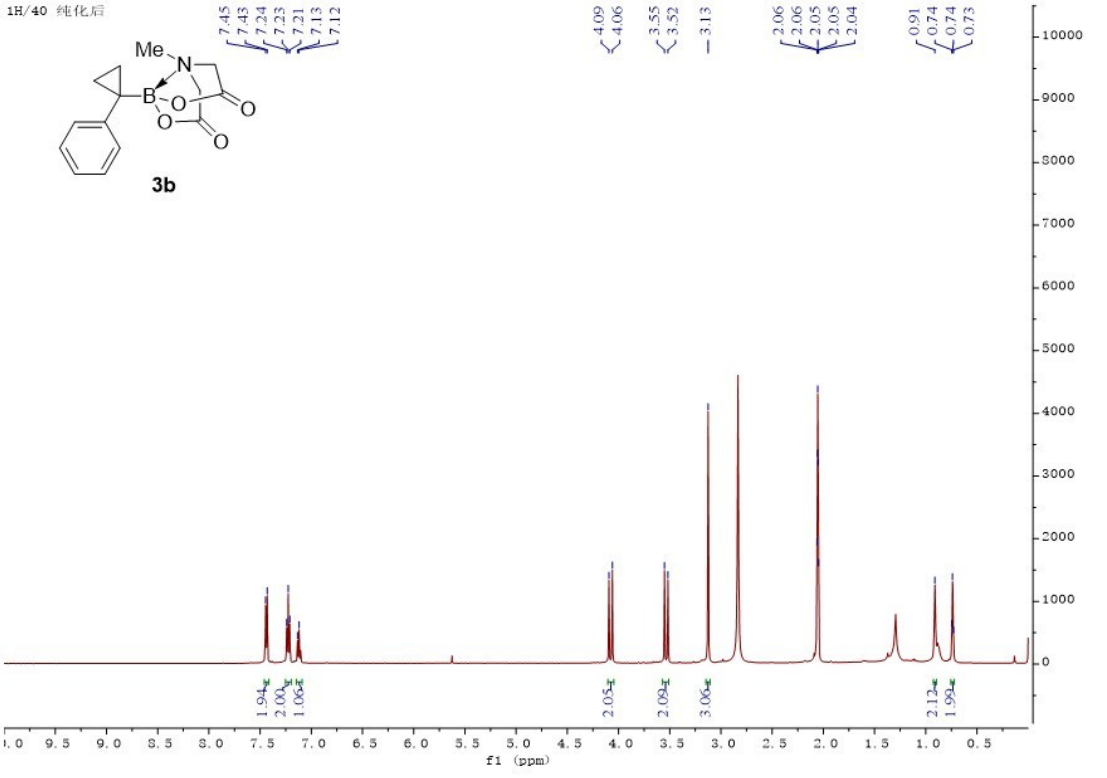

206.4
169.0
143.2
135.3
132.7
130.8
129.2
127.7
126.6
126.4
126.2
125.8
63.0
47.8
30.5
30.3
30.2
30.0
29.9
29.7
29.6
Me
N
B
O
O
O
O
1n
f1 (ppm)

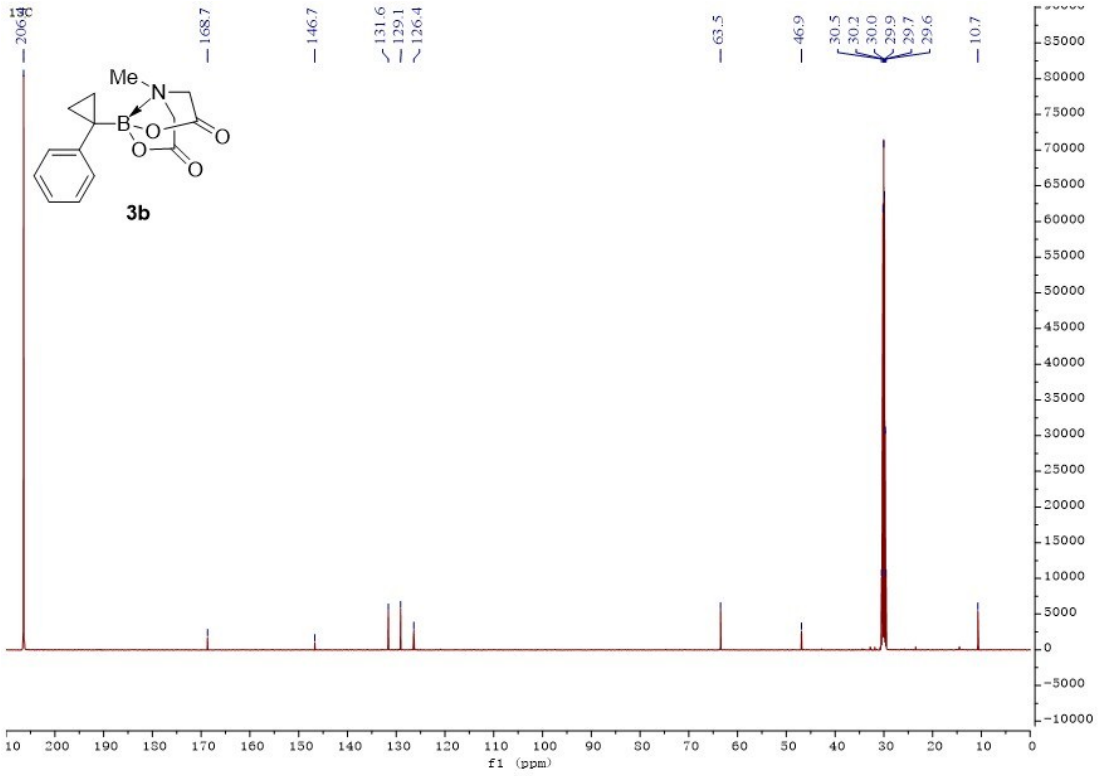

9.6
Me
N
B
O
O
O
O
1n
f1 (ppm)

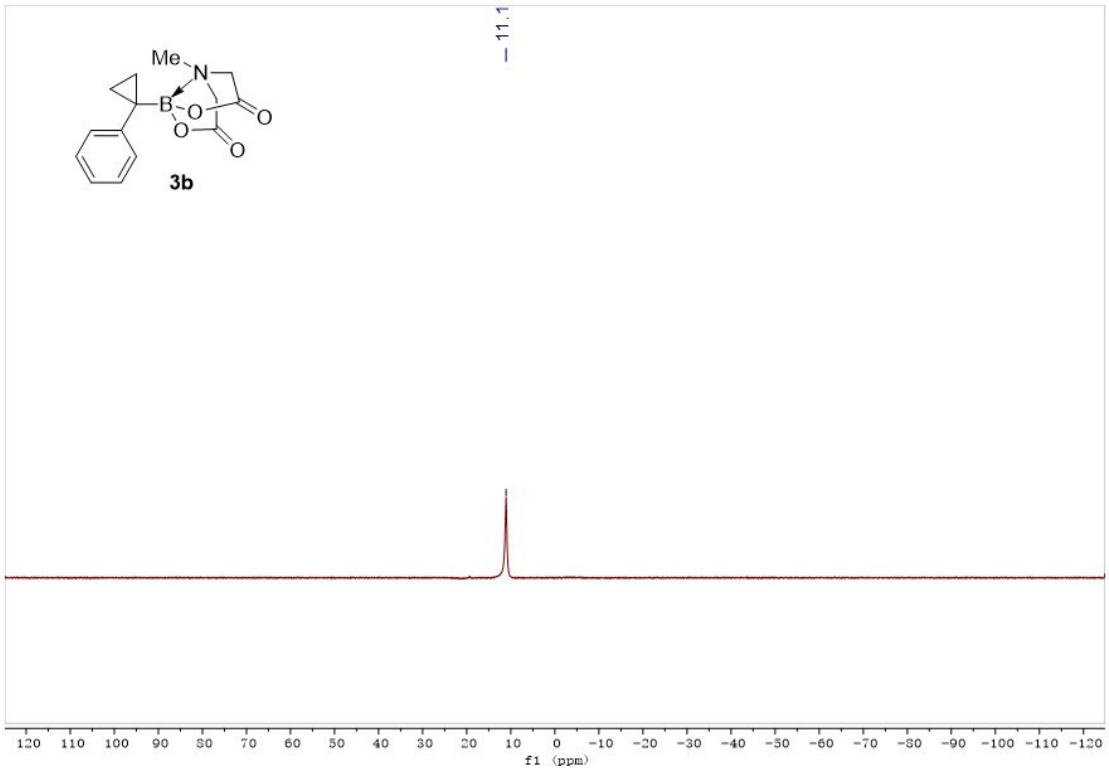

1H/3S0
7.87
7.83
7.82
7.80
7.79
7.77
7.75
7.67
7.66
7.65
7.65
7.46
7.45
7.43
7.43
7.42
7.42
7.40
7.40
4.10
4.06
3.60
3.57
3.19
2.06
2.06
2.05
2.05
2.04
1.01
1.00
1.00
0.99
0.87
0.86
0.86
0.85
Me
N
B
O
O
O
O
3a
1.00
2.03
0.96
0.93
2.00
1.95
1.94
2.94
1.98
2.00
f1 (ppm)

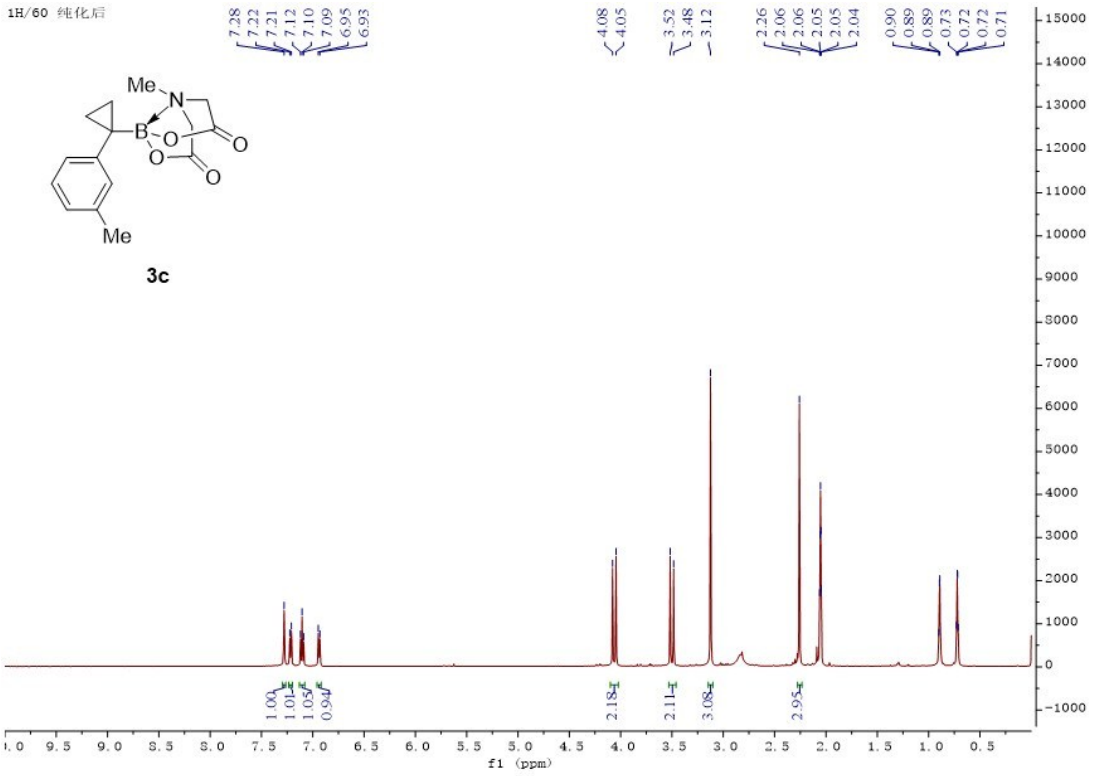

13C/3S1
206.4
168.5
144.5
134.5
132.7
130.6
129.0
128.4
128.3
126.6
126.1
63.4
46.9
30.3
30.2
30.0
29.8
29.7
29.5
29.4
10.7
Me
N
B
O
O
O
O
3a
f1 (ppm)

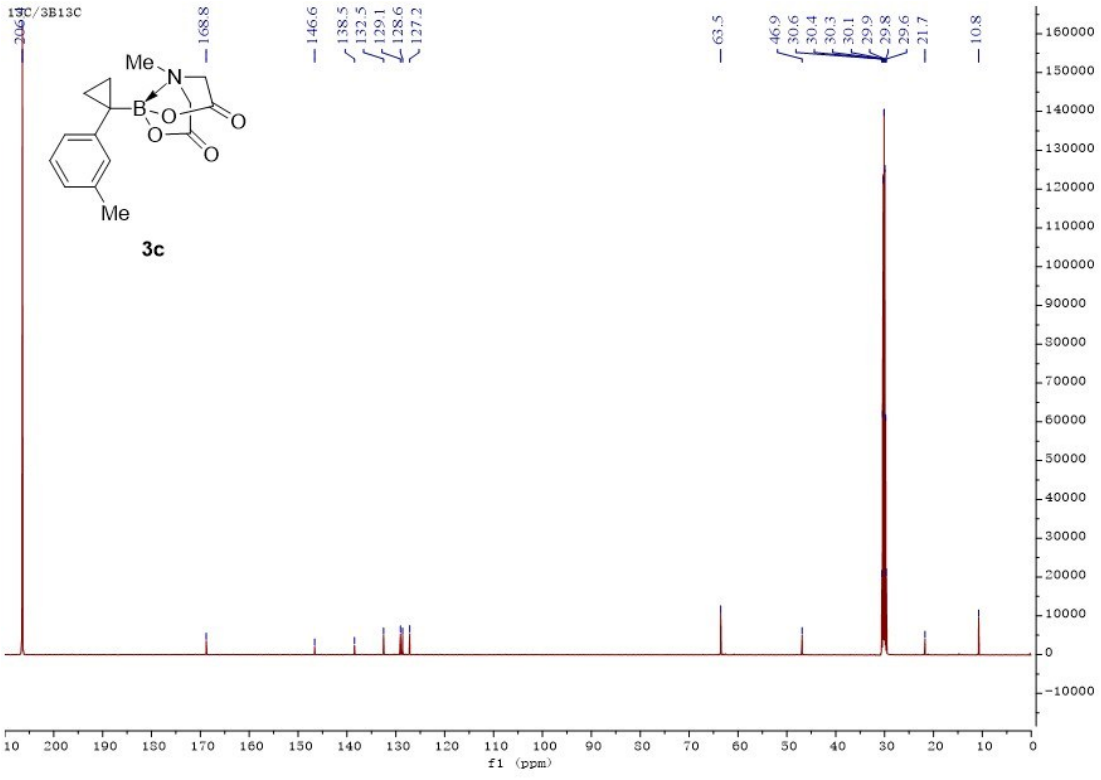

11.2
Me
N
B
O
O
O
O
3a
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

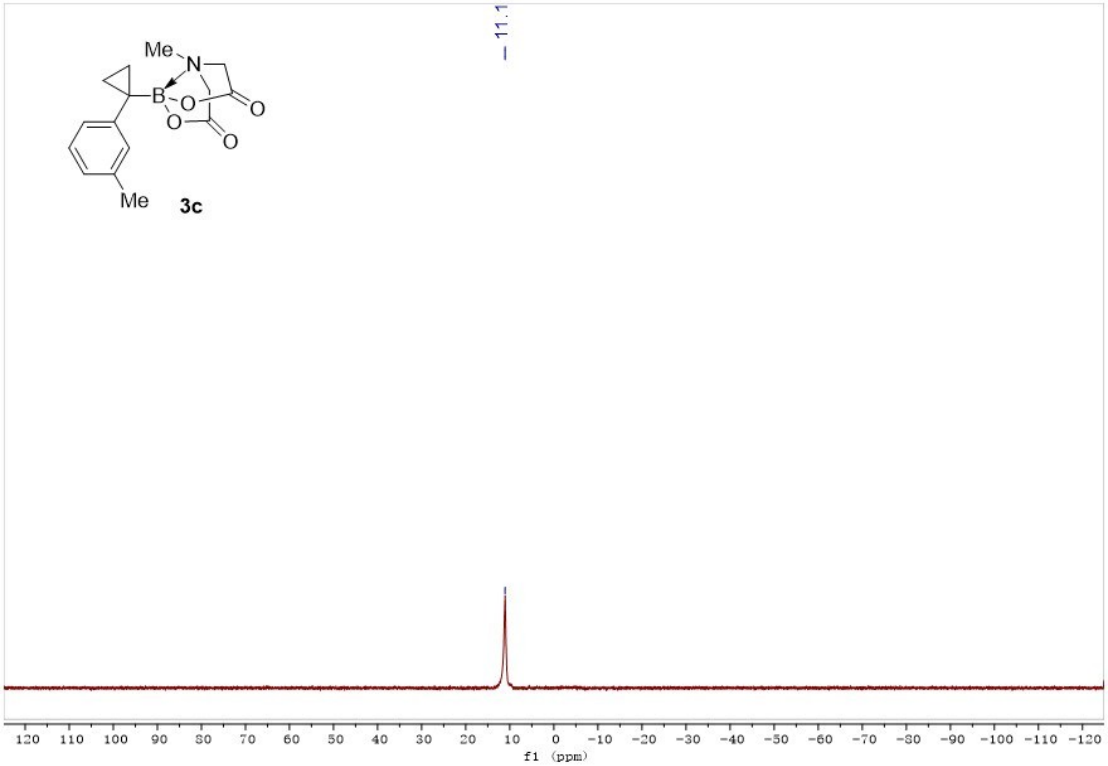

1H/40 纯化后
7.45
7.43
7.24
7.23
7.21
7.13
7.12
4.09
4.06
3.55
3.52
3.13
2.06
2.06
2.05
2.05
2.04
0.91
0.74
0.74
0.73
Me
N
B
O
O
O
O
3b
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
1.94
2.00
1.06
2.05
2.09
3.06
2.12
1.94
f1 (ppm)

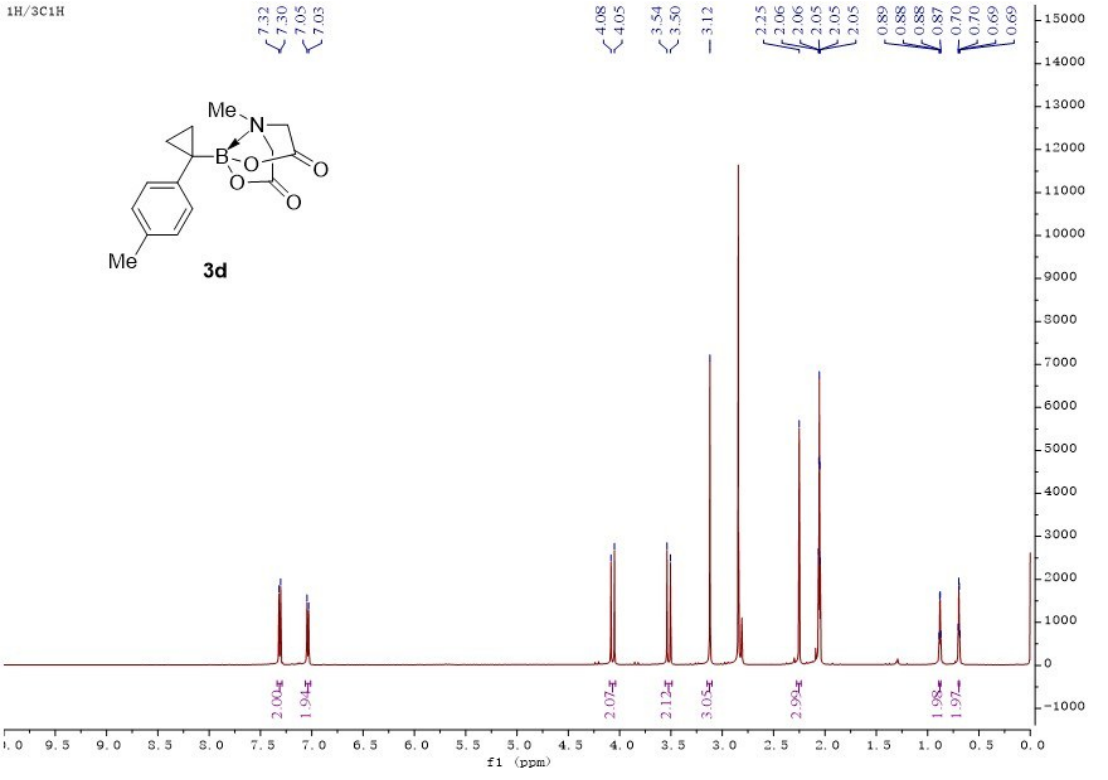

206.4
168.7
146.7
131.6
129.1
126.4
63.5
46.9
30.5
30.2
30.0
29.9
29.7
29.6
10.7
Me
N
B
O
O
O
O
3b
f1 (ppm)

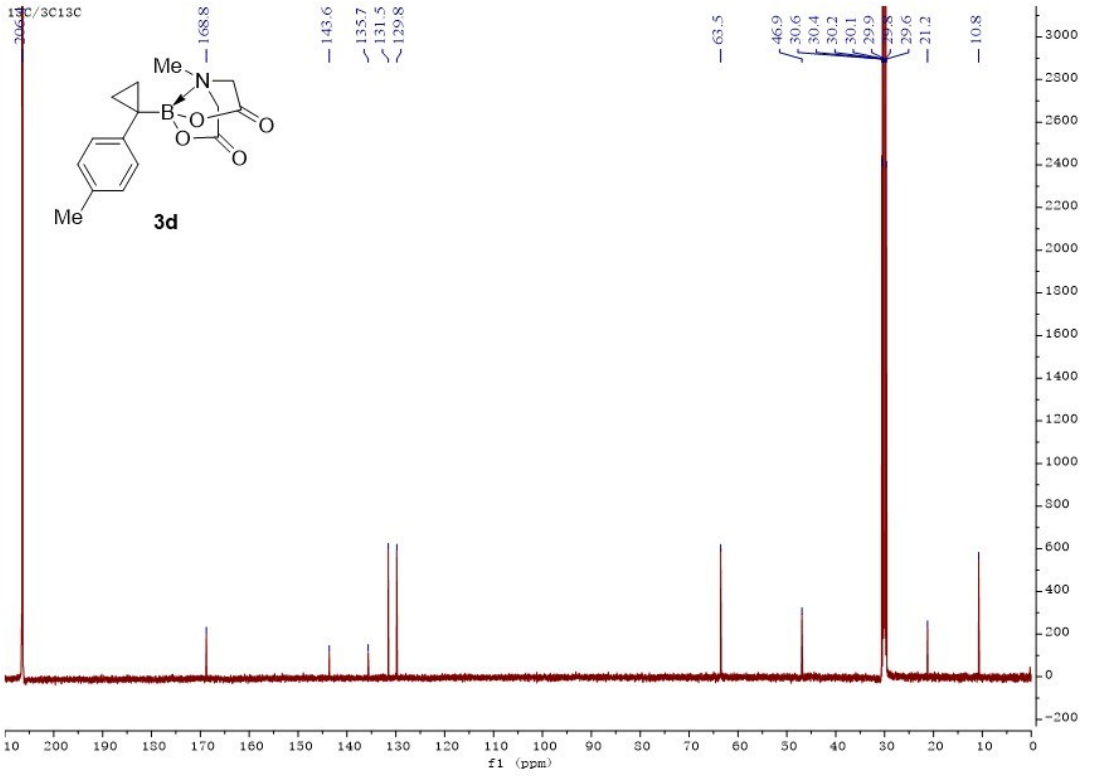

11.1
Me
N
B
O
O
O
O
3b
f1 (ppm)

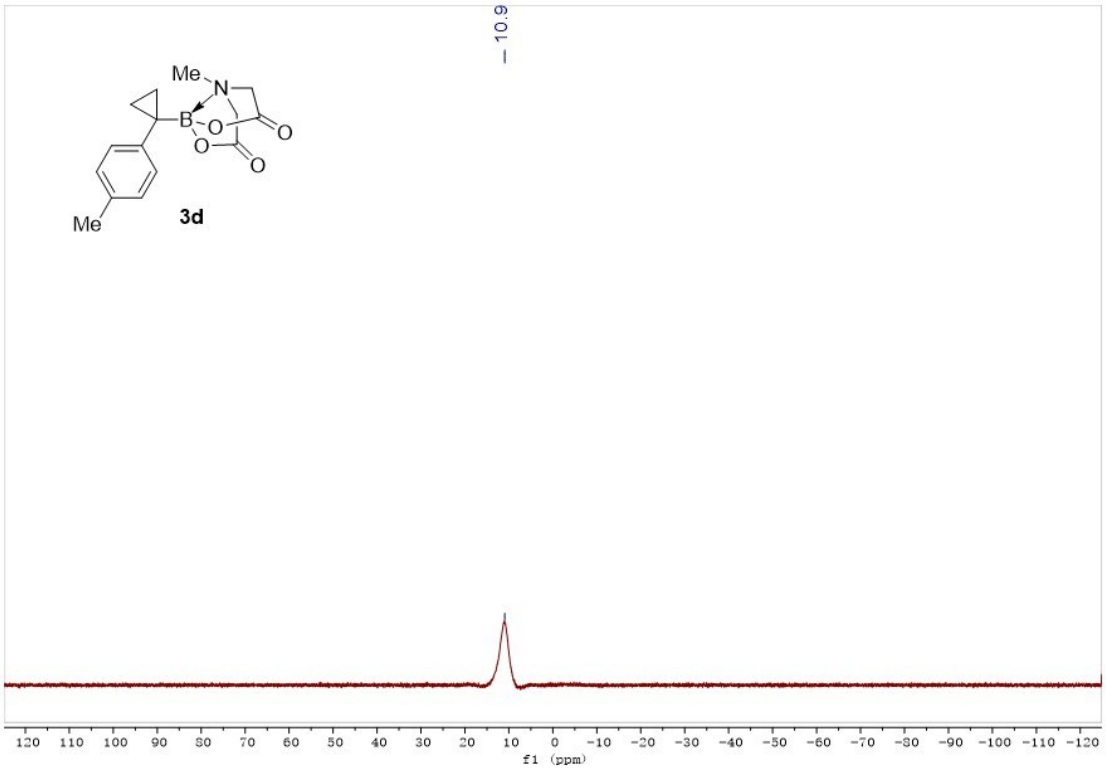

1H/60 纯化后
7.28
7.22
7.21
7.12
7.10
7.09
6.95
6.93
4.08
4.05
3.52
3.48
3.12
2.26
2.06
2.06
2.05
2.05
2.04
0.90
0.89
0.89
0.73
0.72
0.72
0.71
Me
N
B
O
O
O
O
Me
3c
1.00
1.01
1.05
0.94
2.18
2.11
3.08
2.95
f1 (ppm)

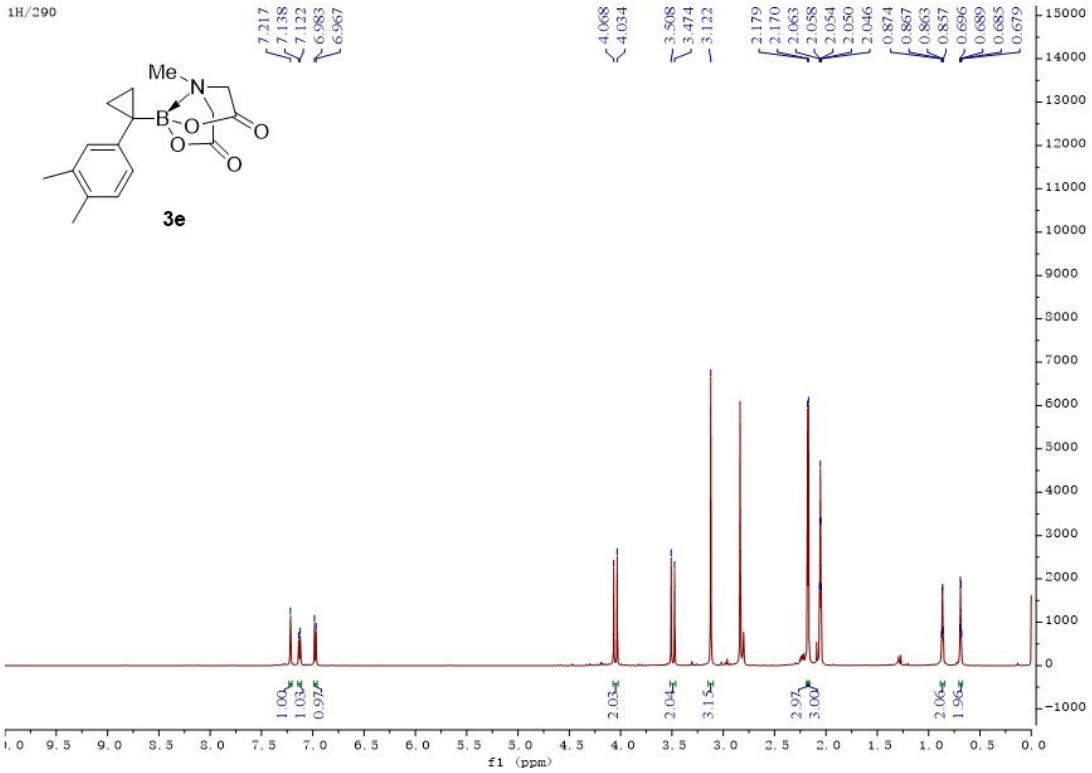

13C/3B13C
206.7
168.8
146.6
138.5
132.5
129.1
128.6
127.2
63.5
46.9
30.6
30.4
30.3
30.1
29.9
29.8
29.6
21.7
10.8
Me
N
B
O
O
O
O
Me
3c
f1 (ppm)

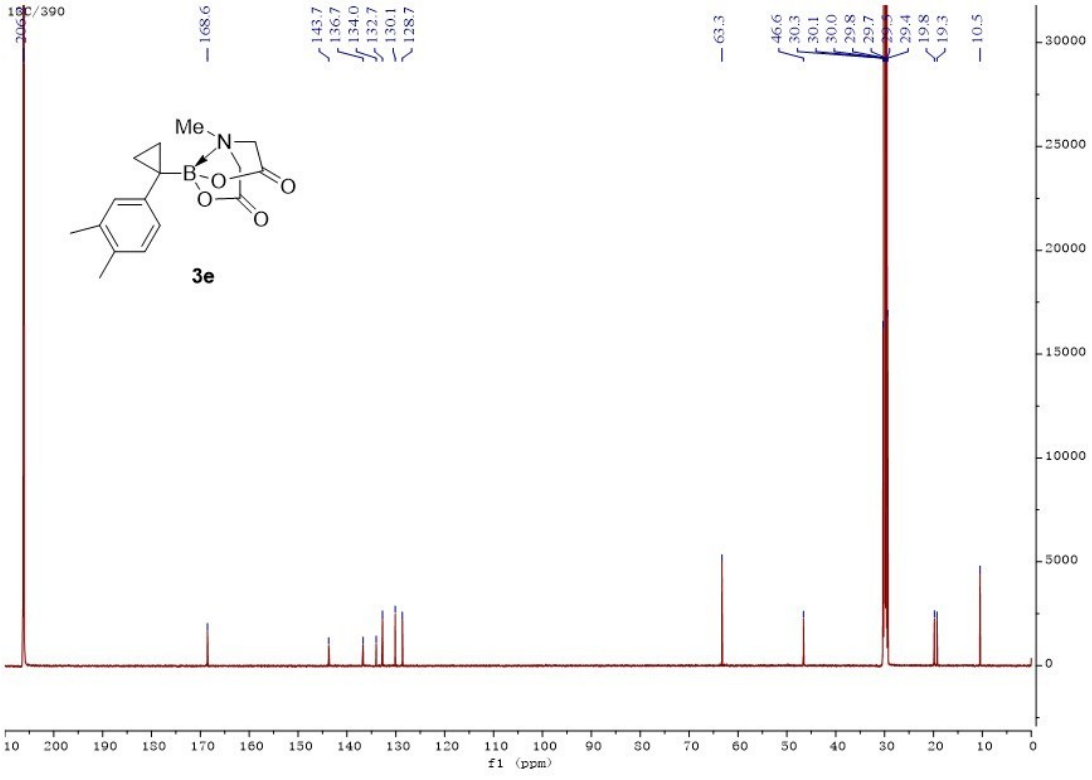

Me
N
B
O
O
O
O
Me
3c
11.1
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

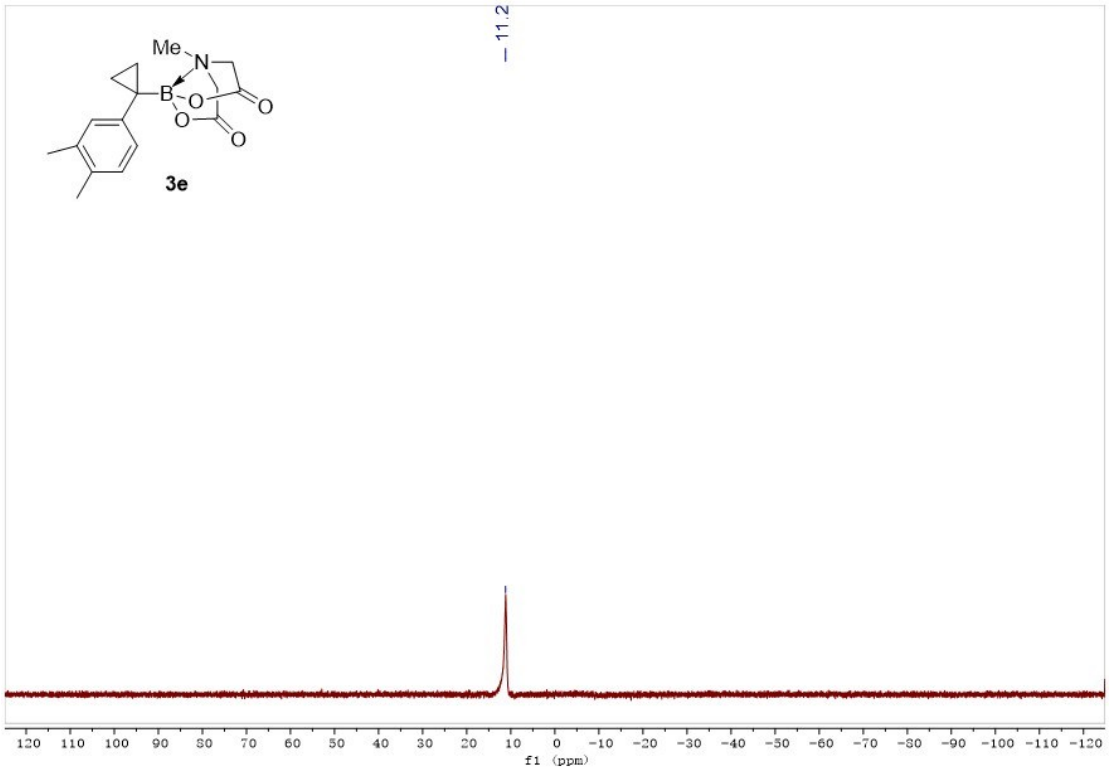

1H/3C1H
7.32
7.30
7.05
7.03
4.08
4.05
3.54
3.50
3.12
2.25
2.06
2.06
2.05
2.05
2.05
0.89
0.88
0.88
0.87
0.70
0.70
0.69
0.69
Me
N
B
O
O
O
O
Me
3d
2.00
1.94
2.07
2.12
3.05
2.99
1.98
1.97
f1 (ppm)

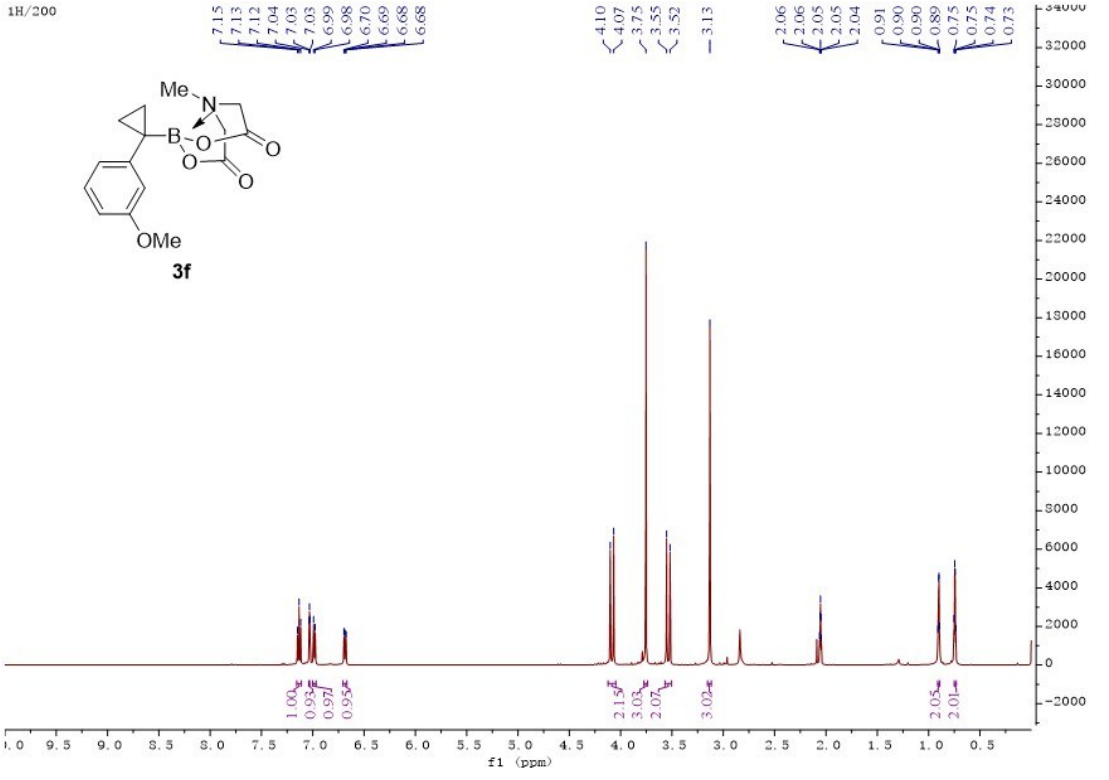

13C/3C13C
206.4
168.8
143.6
135.7
131.5
129.8
63.5
46.9
30.6
30.4
30.2
30.1
29.9
29.8
29.6
21.2
10.8
Me
N
B
O
O
O
O
Me
3d
f1 (ppm)

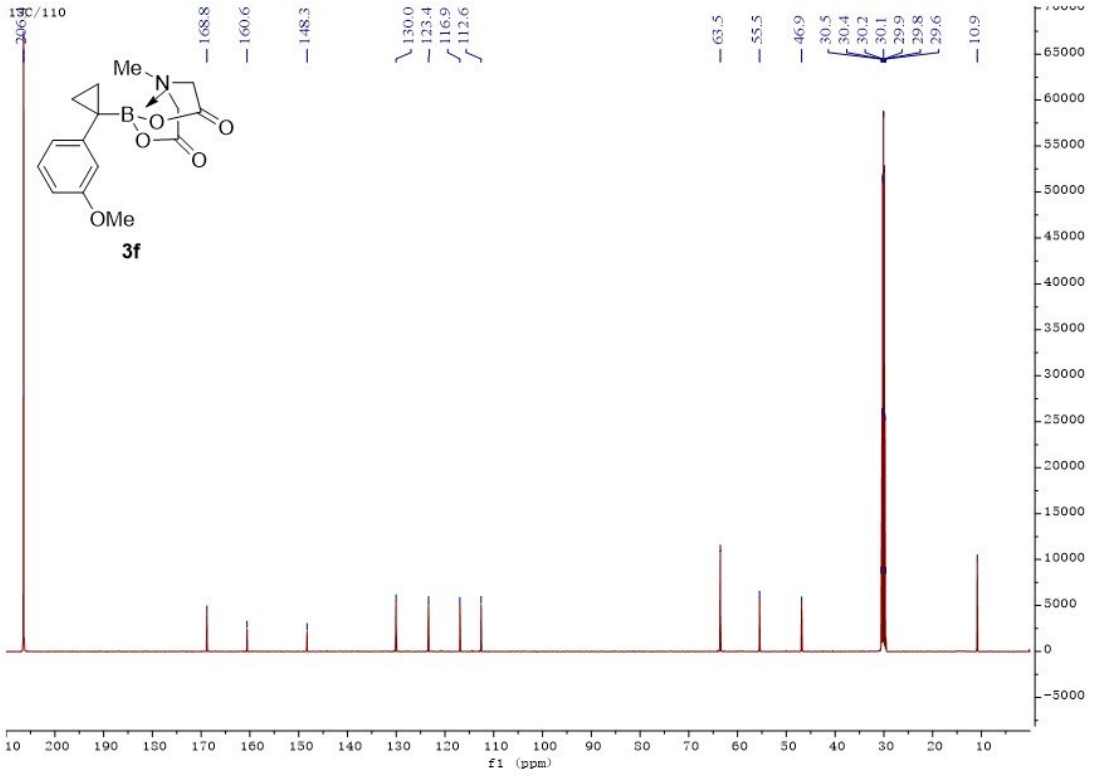

10.9
Me
N
B
O
O
O
O
Me
3d
f1 (ppm)

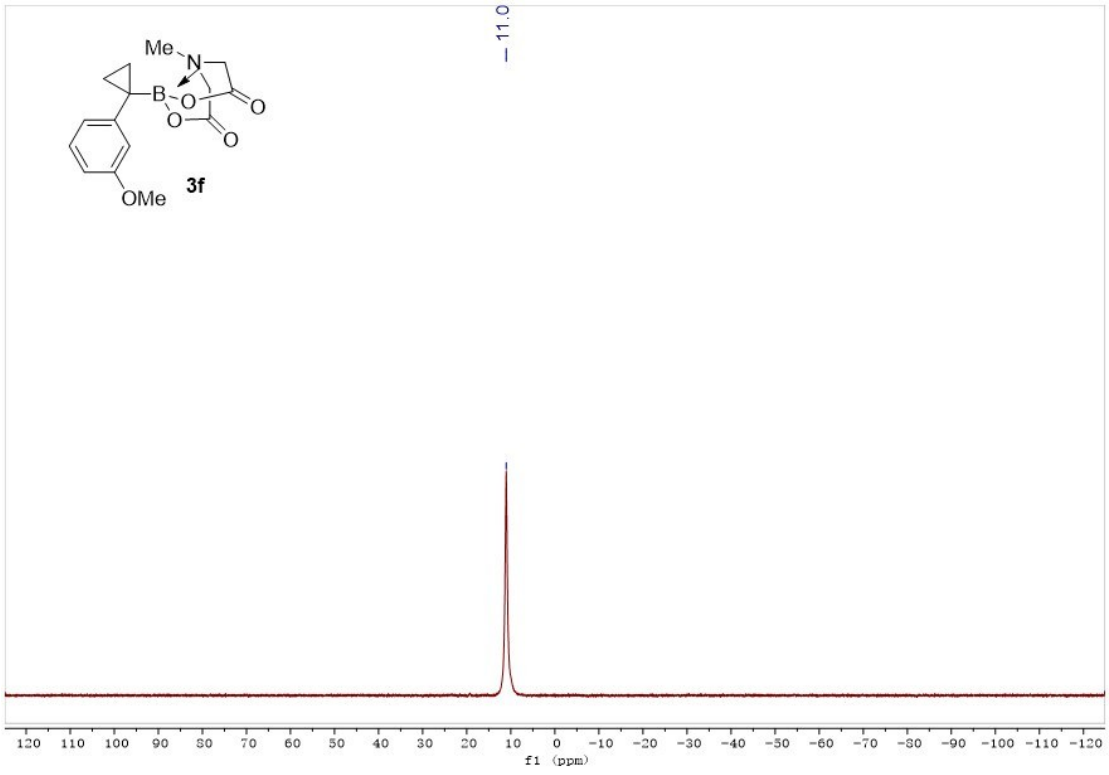

1H/290
7.217
7.138
7.122
6.983
6.967
4.068
4.034
3.508
3.474
3.122
2.179
2.170
2.063
2.058
2.054
2.050
2.046
0.874
0.867
0.863
0.857
0.696
0.689
0.685
0.679
Me
N
B
O
O
O
O
3e
1.00
1.03
0.97
2.03
2.04
3.15
2.97
3.00
2.06
1.96
f1 (ppm)

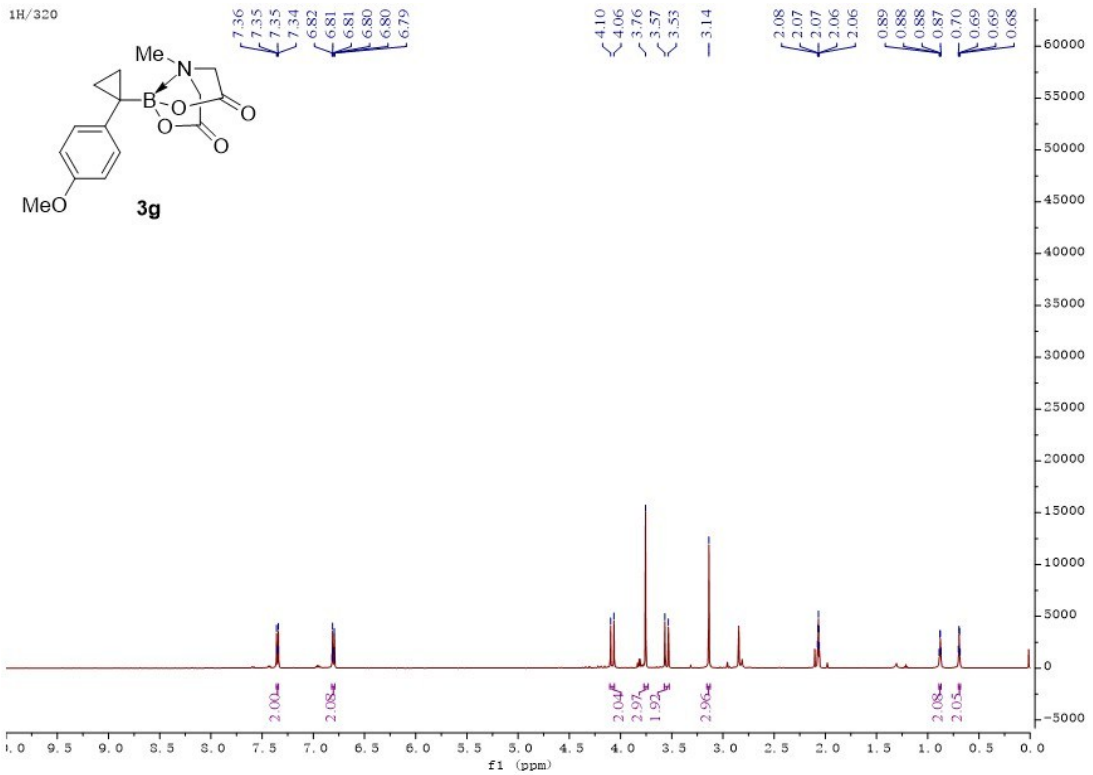

13C/390
206.8
168.6
143.7
136.7
134.0
132.7
130.1
128.7
63.3
46.6
30.3
30.1
30.0
29.8
29.7
29.4
19.8
19.3
10.5
Me
N
B
O
O
O
O
3e
f1 (ppm)

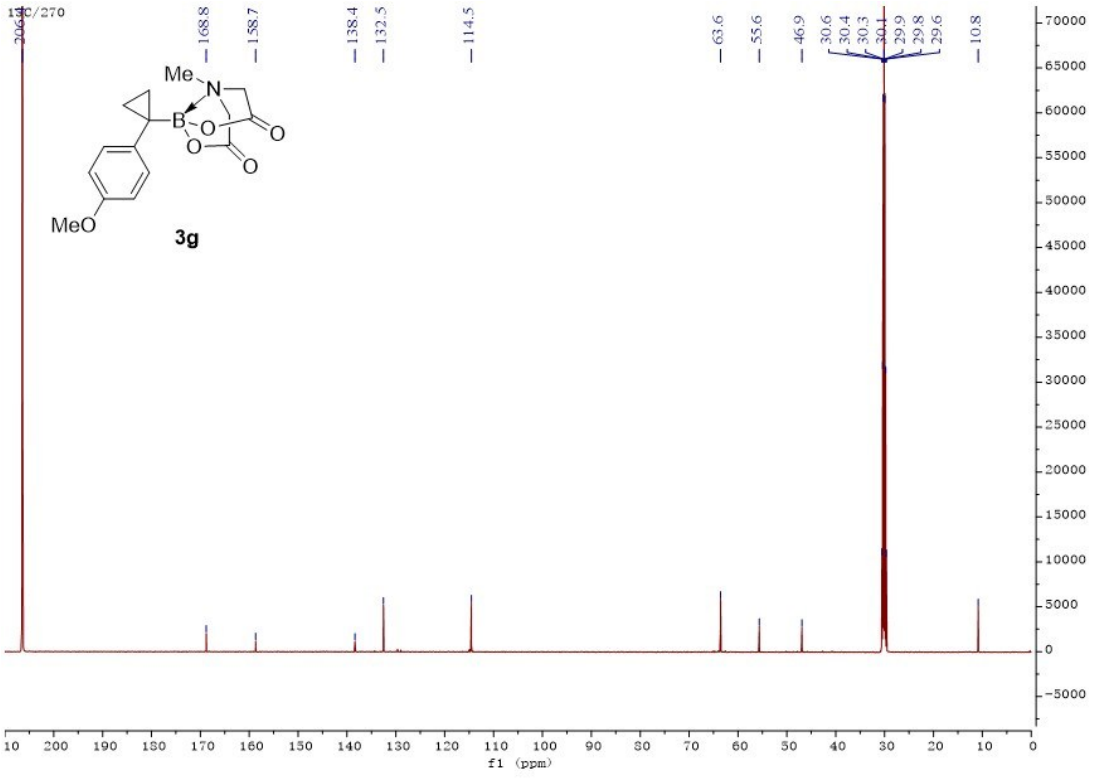

11.2
Me
N
B
O
O
O
O
3e
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

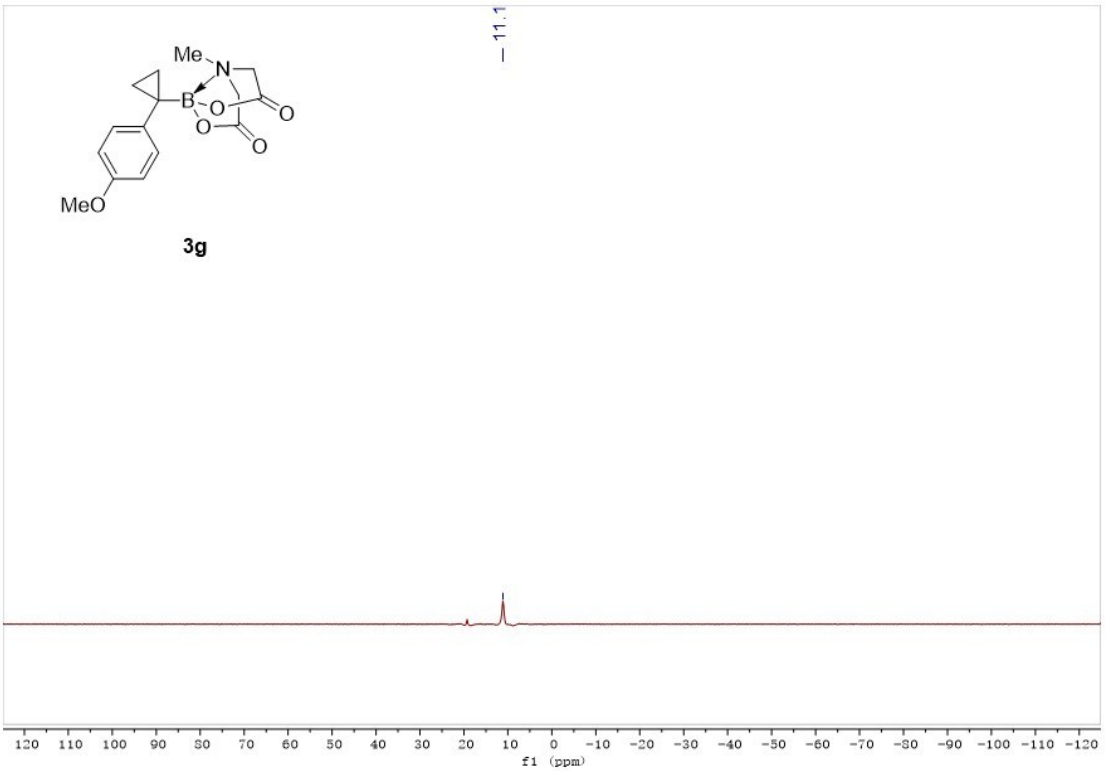

1H/200
7.15
7.13
7.12
7.04
7.03
7.03
6.99
6.98
6.70
6.69
6.68
6.68
4.10
4.07
3.75
3.55
3.52
3.13
2.06
2.06
2.05
2.05
2.04
0.91
0.90
0.90
0.89
0.75
0.75
0.74
0.73
Me
N
B
O
O
O
O
OMe
3f
1.00
0.93
0.97
0.95
2.15
3.03
2.07
3.02
2.05
2.01
f1 (ppm)

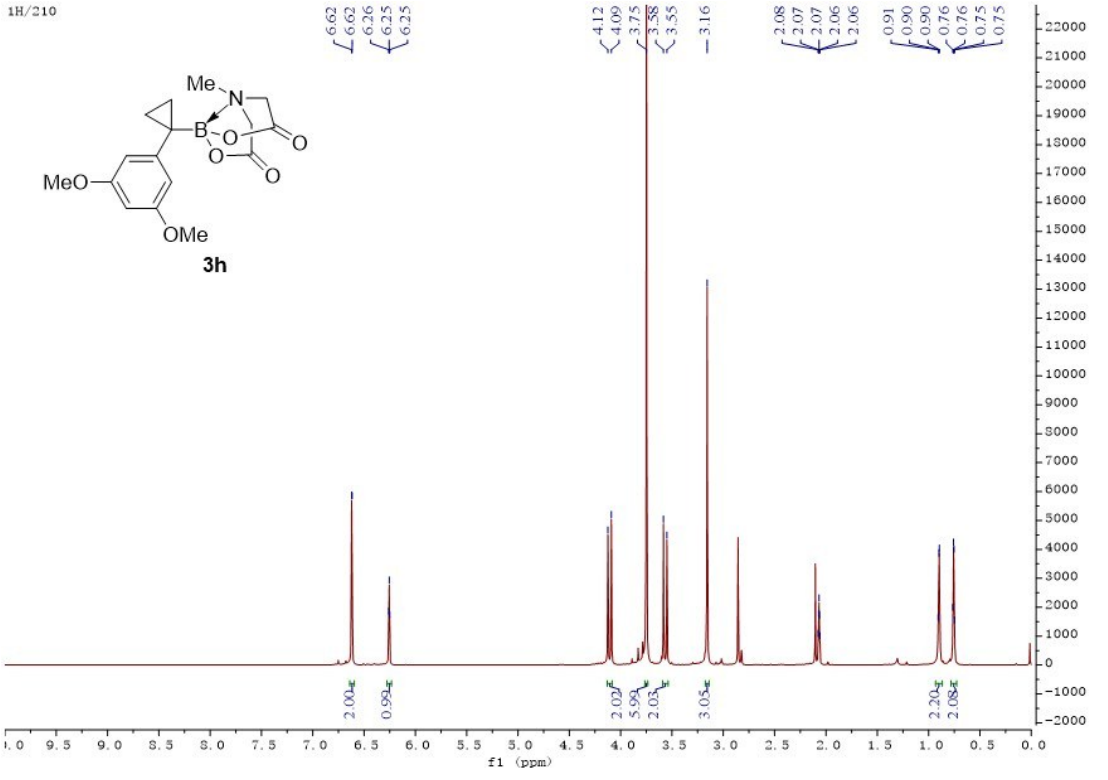

13C/110
206.4
168.8
160.6
148.3
130.0
123.4
116.9
112.6
63.5
55.5
46.9
30.5
30.4
30.2
30.1
29.9
29.8
29.6
10.9
Me
N
B
O
O
O
O
OMe
3f
f1 (ppm)

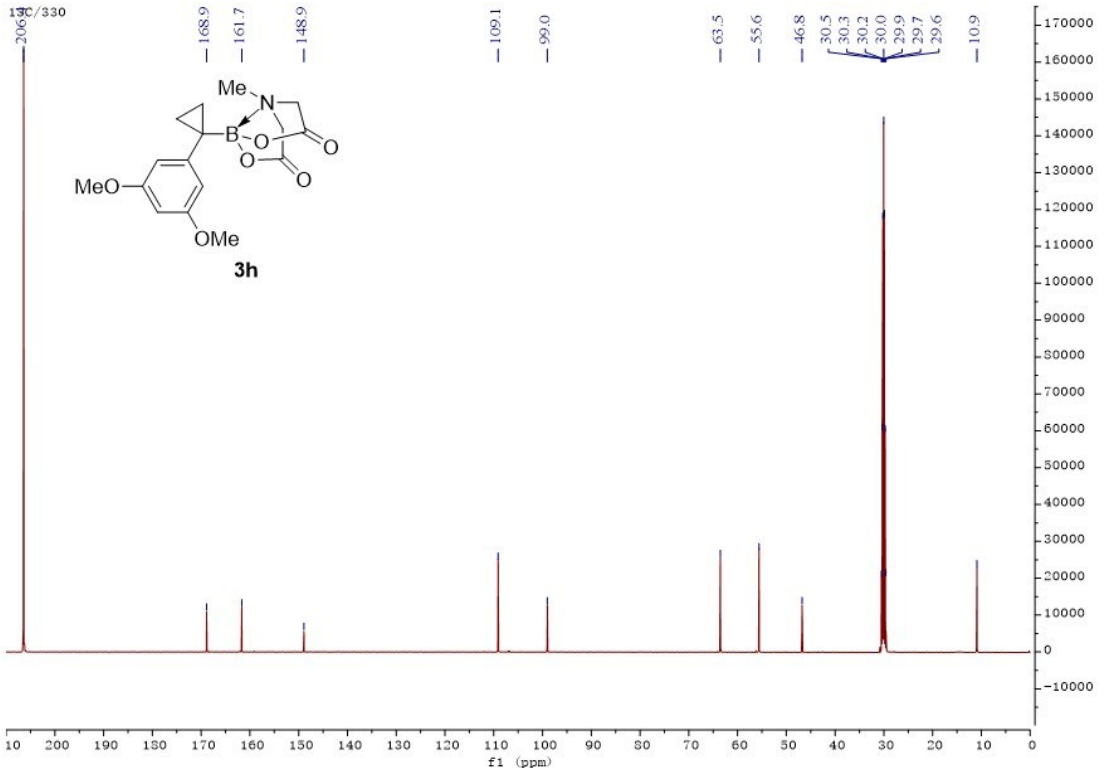

11.0
Me
N
B
O
O
O
O
OMe
3f
f1 (ppm)

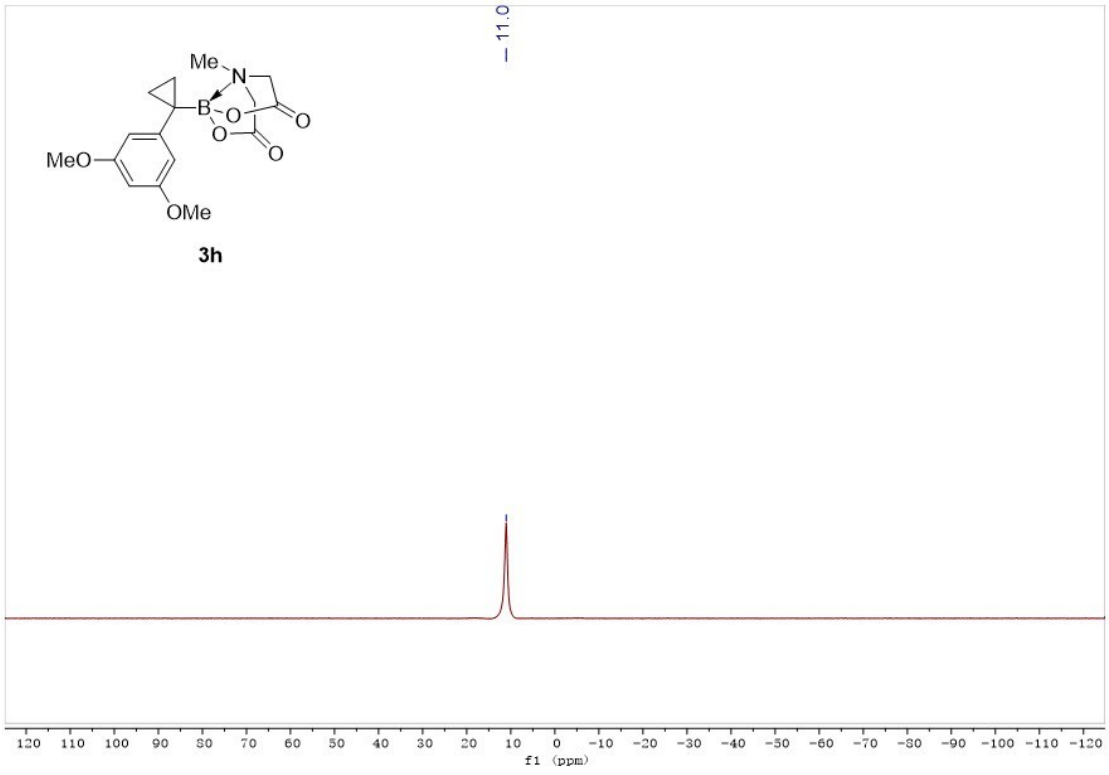

1H/320
Me
N
B
O
O
O
O
MeO
3g
7.36
7.35
7.35
7.34
6.82
6.81
6.81
6.80
6.80
6.79
4.10
4.06
3.76
3.57
3.53
3.14
2.08
2.07
2.07
2.06
2.06
0.89
0.88
0.88
0.87
0.70
0.69
0.69
0.68
2.00
2.08
2.04
2.97
1.92
2.96
2.08
2.05
f1 (ppm)

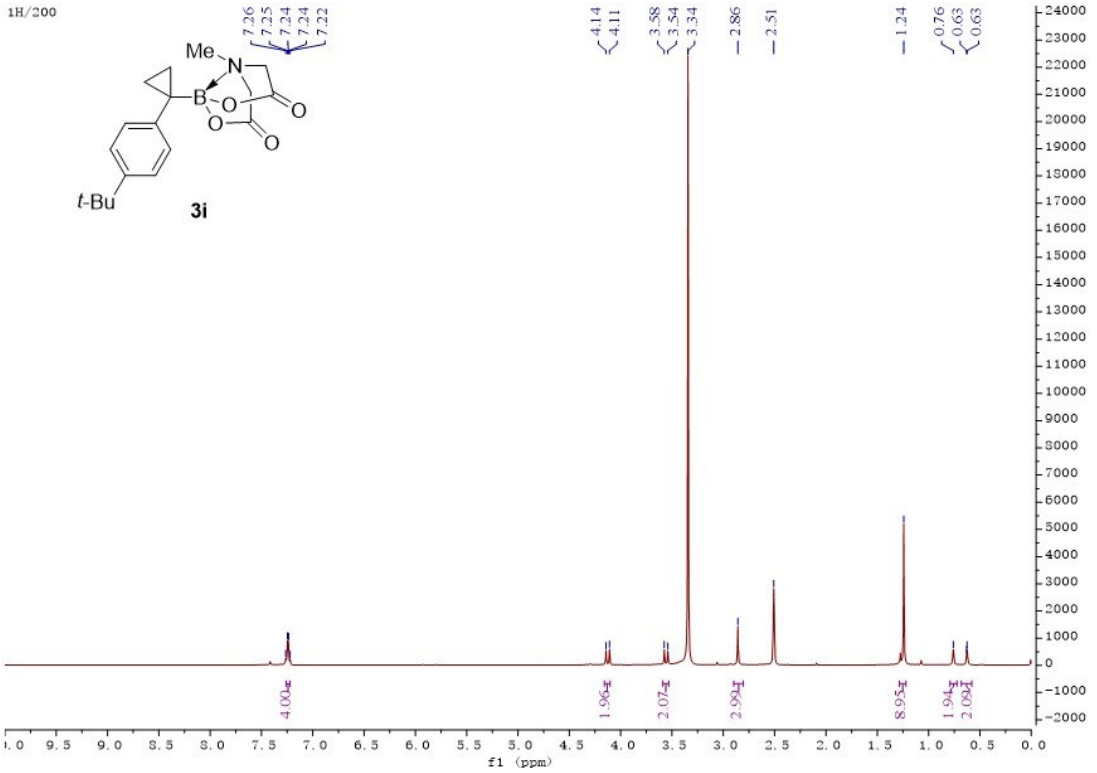

13C/270
Me
N
B
O
O
O
O
MeO
3g
168.8
158.7
138.4
132.5
114.5
63.6
55.6
46.9
30.6
30.4
30.3
30.1
29.9
29.8
29.6
10.8
f1 (ppm)

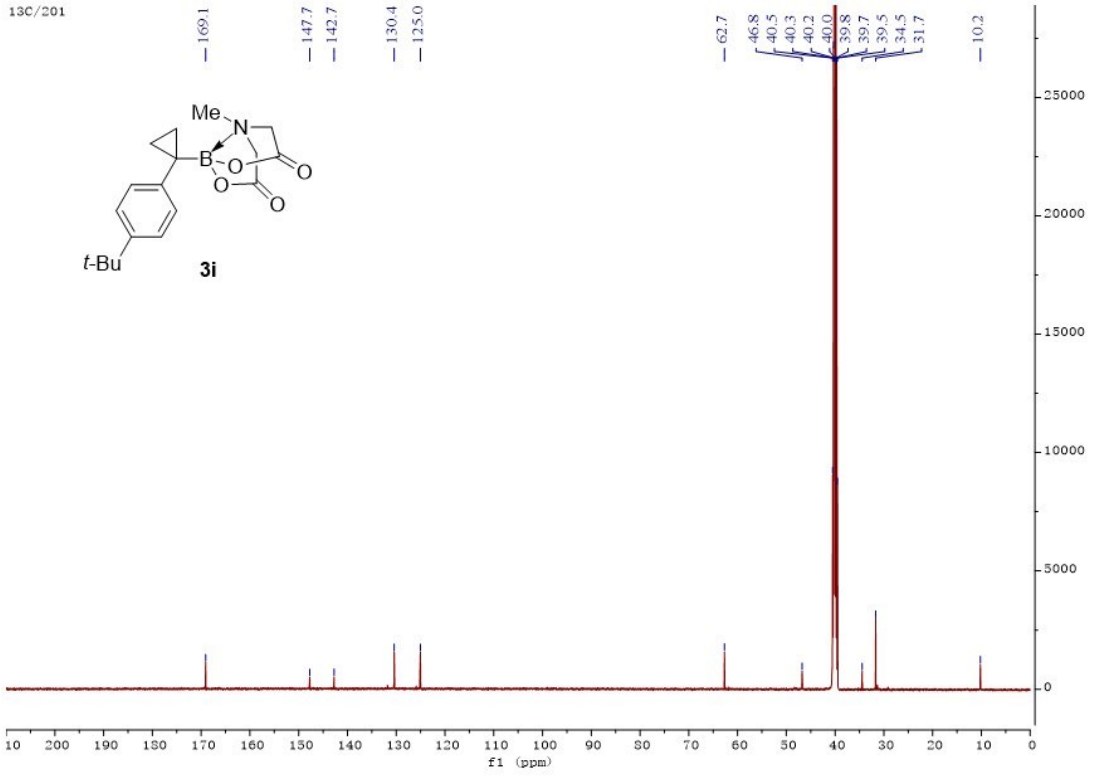

Me
N
B
O
O
O
O
MeO
3g
11.1
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

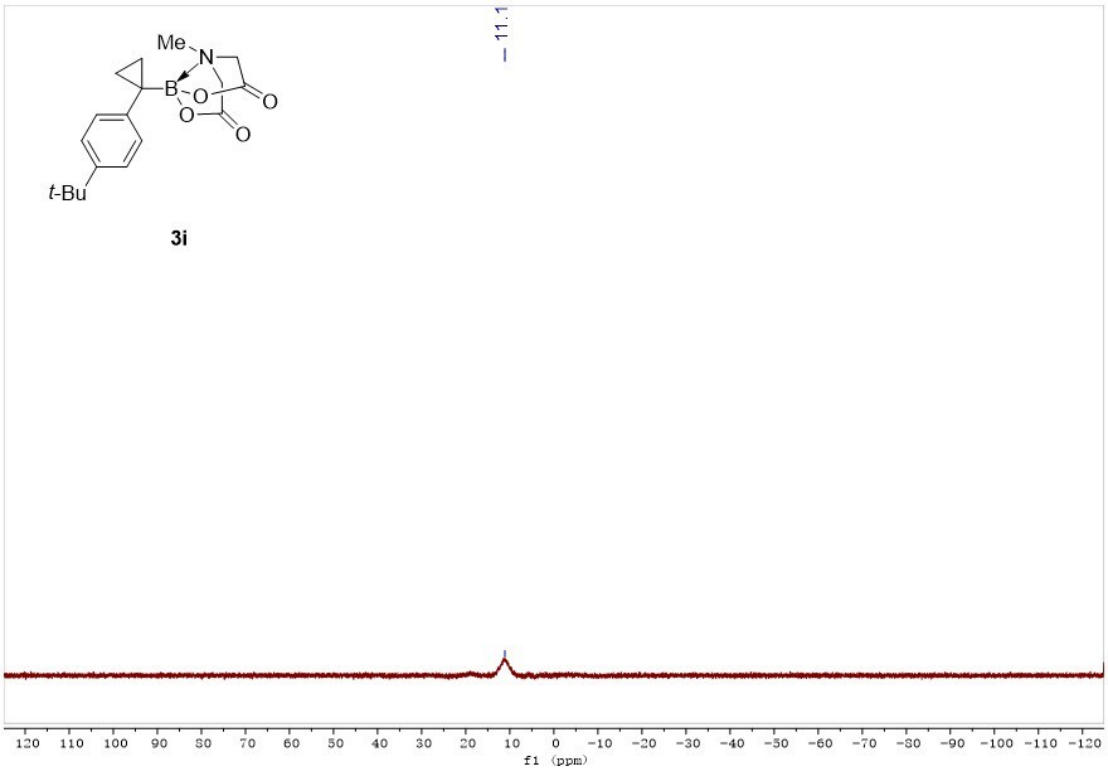

1H/210
6.62
6.62
6.26
6.25
6.25
4.12
4.09
3.75
3.58
3.55
3.16
2.08
2.07
2.07
2.06
2.06
0.91
0.90
0.90
0.76
0.76
0.75
0.75
Me
N
B
O
O
O
O
MeO
OMe
3h
2.00
0.99
2.02
5.99
2.03
3.05
2.20
2.08
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
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)


13C/330
206.4
168.9
161.7
148.9
109.1
99.0
63.5
55.6
46.8
30.5
30.3
30.2
30.0
29.9
29.7
29.6
10.9
Me
N
B
O
O
O
O
MeO
OMe
3h
f1 (ppm)

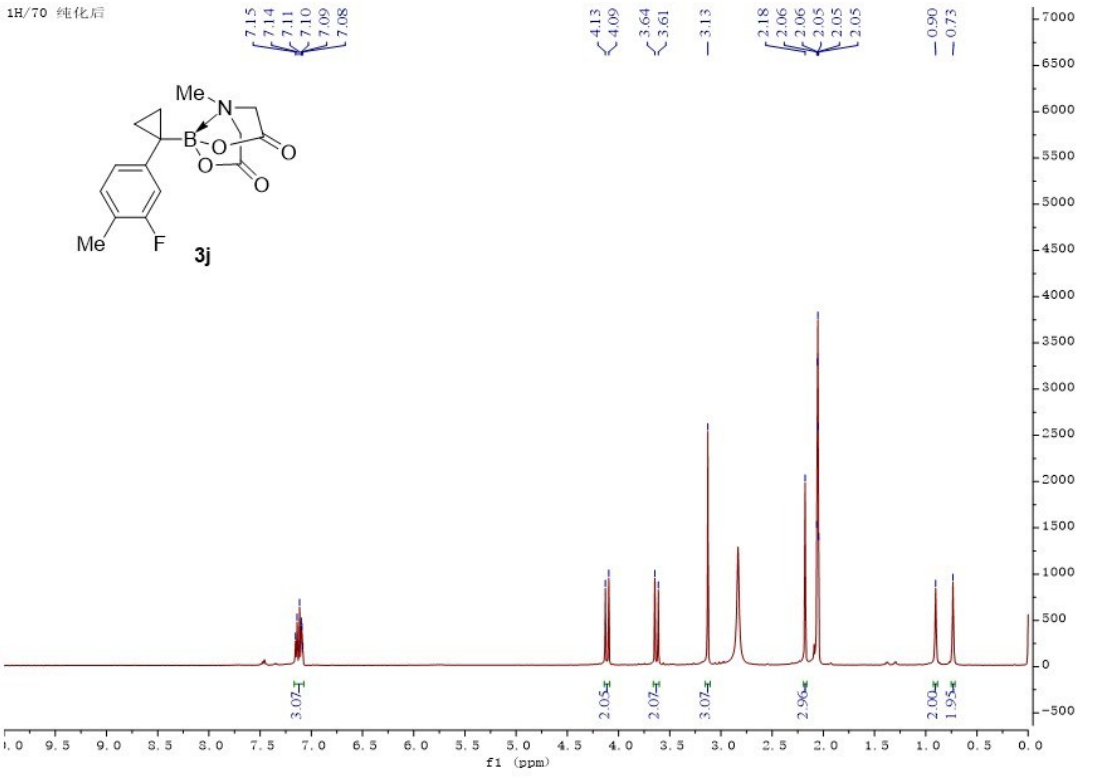

11.0
Me
N
B
O
O
O
O
MeO
OMe
3h
f1 (ppm)


1H/200
Me
N
B
O
O
O
O
t-Bu
3i
7.26
7.25
7.24
7.24
7.22
4.14
4.11
3.58
3.54
3.34
2.86
2.51
1.24
0.76
0.63
0.63
4.00
1.96
2.07
2.99
8.95
1.94
2.09
f1 (ppm)

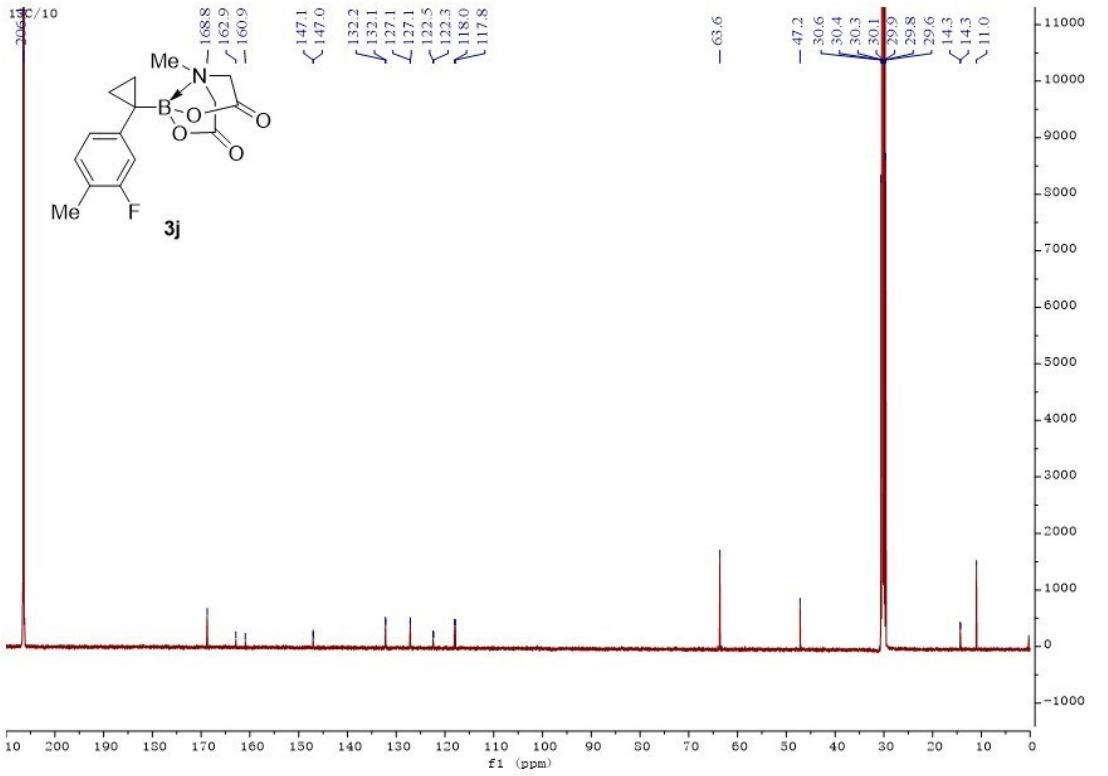

13C/201
Me
N
B
O
O
O
O
t-Bu
3i
169.1
147.7
142.7
130.4
125.0
62.7
46.8
40.5
40.3
40.2
40.0
39.8
39.7
39.5
34.5
31.7
10.2
f1 (ppm)

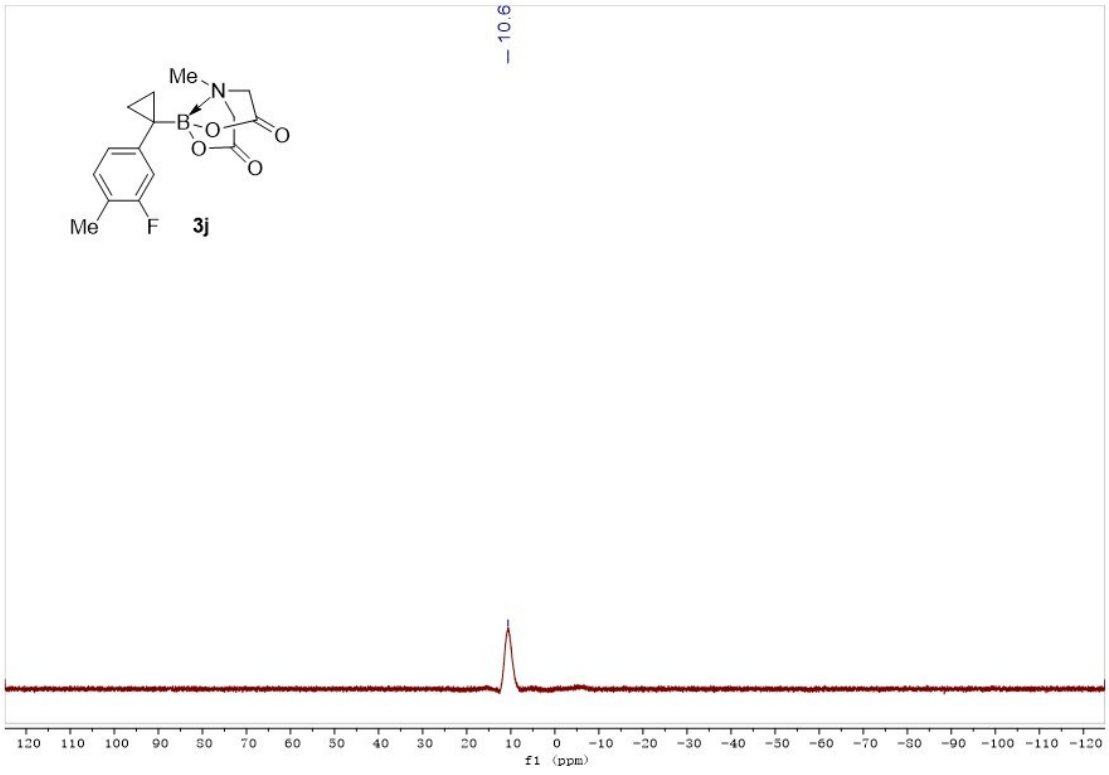

11.1
Me
N
B
O
O
O
O
t-Bu
f1 (ppm)

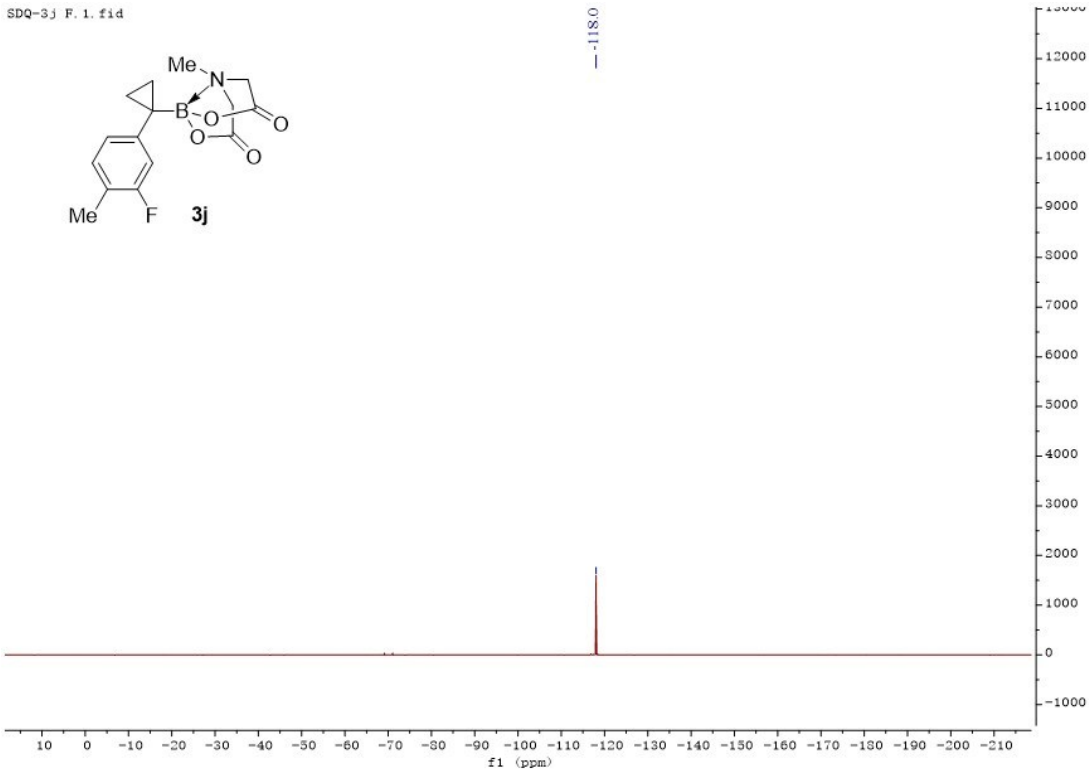
3i

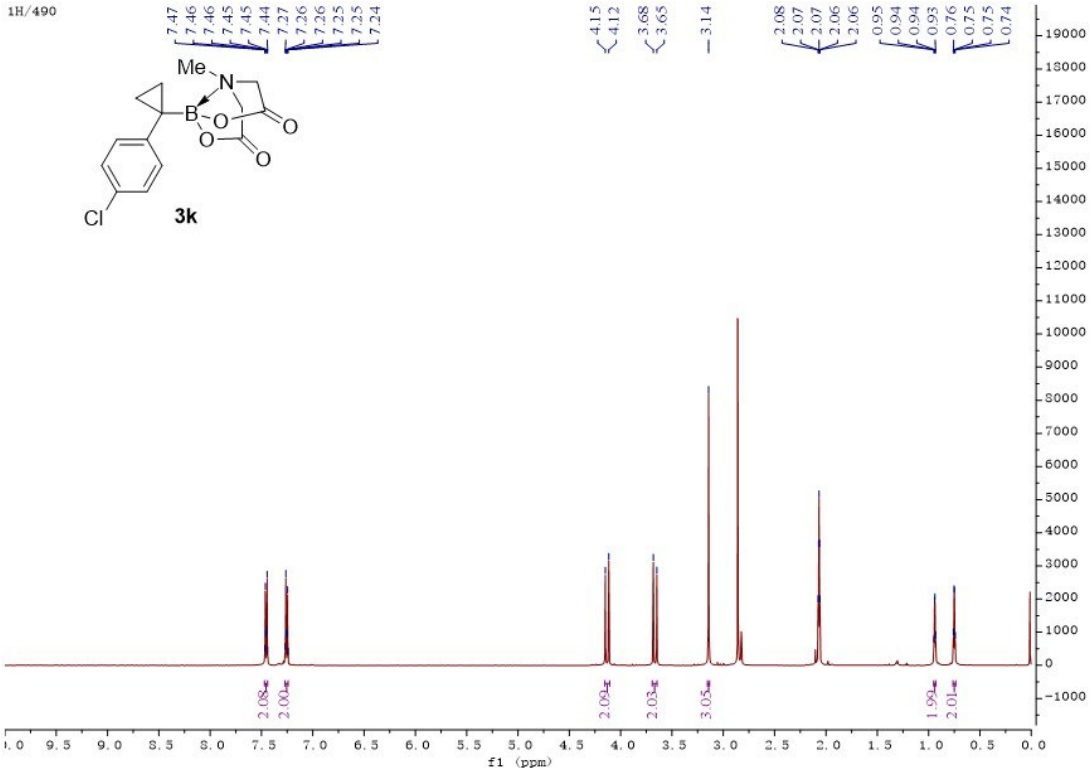

1H/70 纯化后
7.15
7.14
7.11
7.10
7.09
7.08
4.13
4.09
3.64
3.61
3.13
2.18
2.06
2.06
2.05
2.05
2.05
0.90
0.73
Me
N
B
O
O
O
O
Me
F
3.07
2.05
2.07
3.07
2.96
2.00
1.95
f1 (ppm)

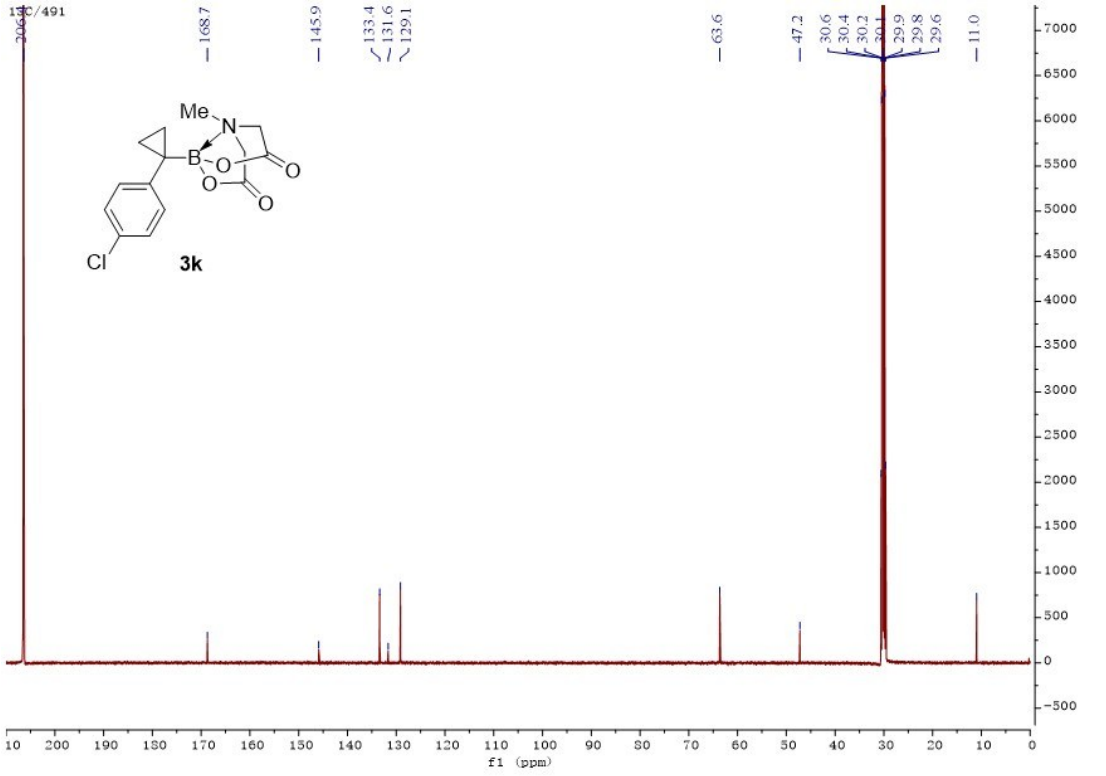
3j

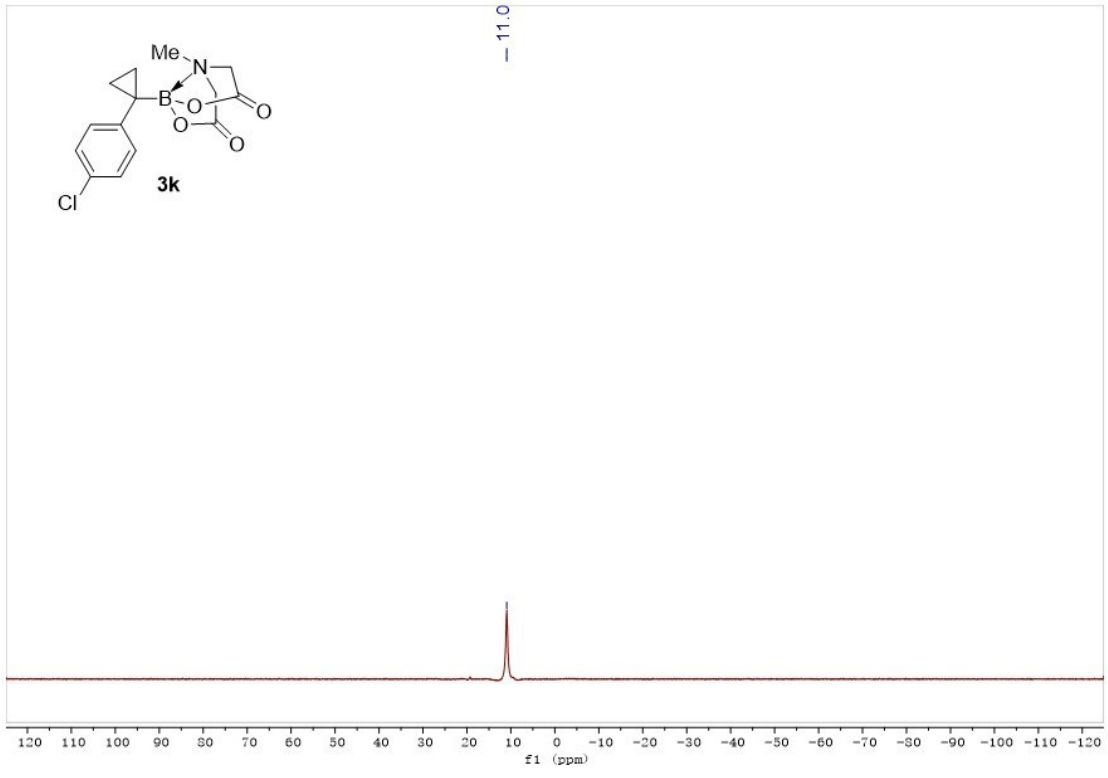

11C/10
206.4
168.8
162.9
160.9
147.1
147.0
132.2
132.1
127.1
127.1
122.5
122.3
118.0
117.8
63.6
47.2
30.6
30.4
30.3
30.1
29.9
29.8
29.6
14.3
14.3
11.0
Me
N
B
O
O
O
O
Me
F
3j
f1 (ppm)

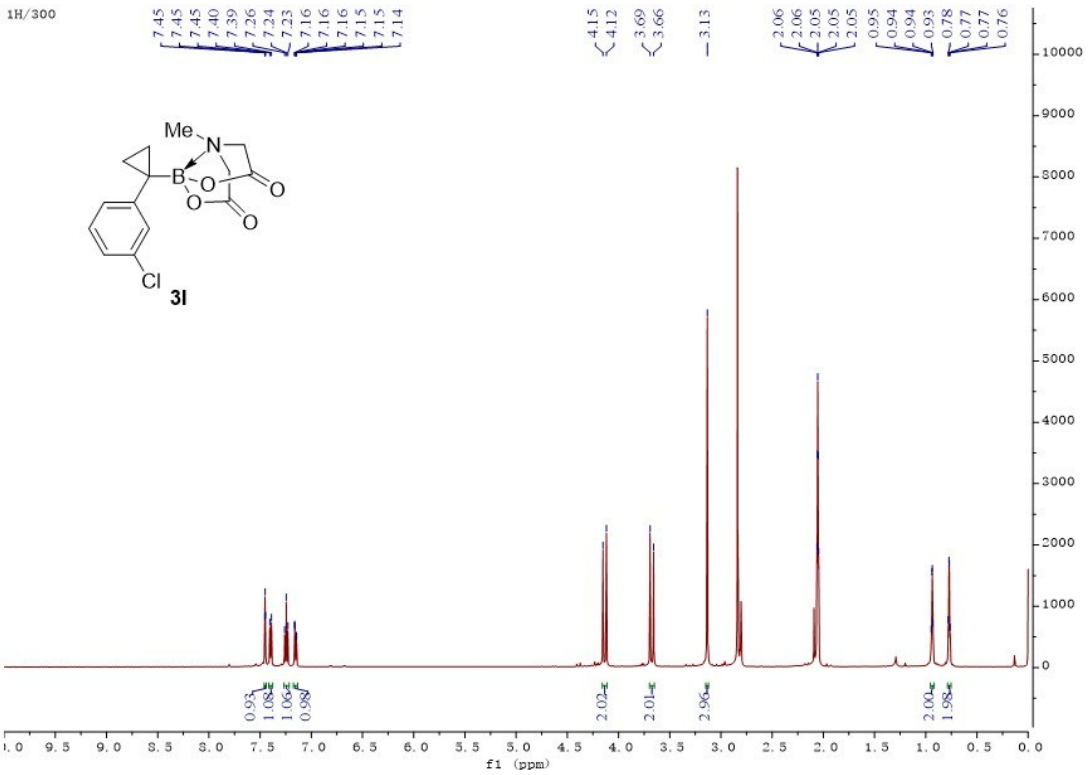

10.6
Me
N
B
O
O
O
O
Me
F
3j
f1 (ppm)

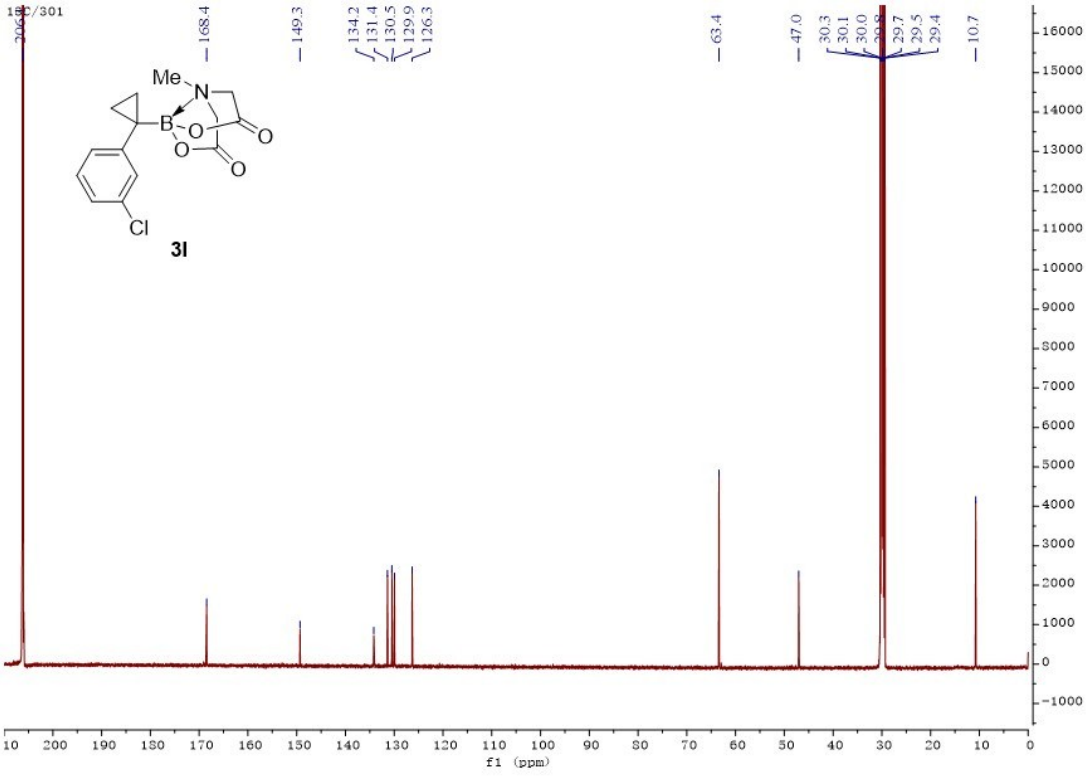

SDQ-3j F.1.fid
-118.0
Me
N
B
O
O
O
O
Me
F
3j
f1 (ppm)

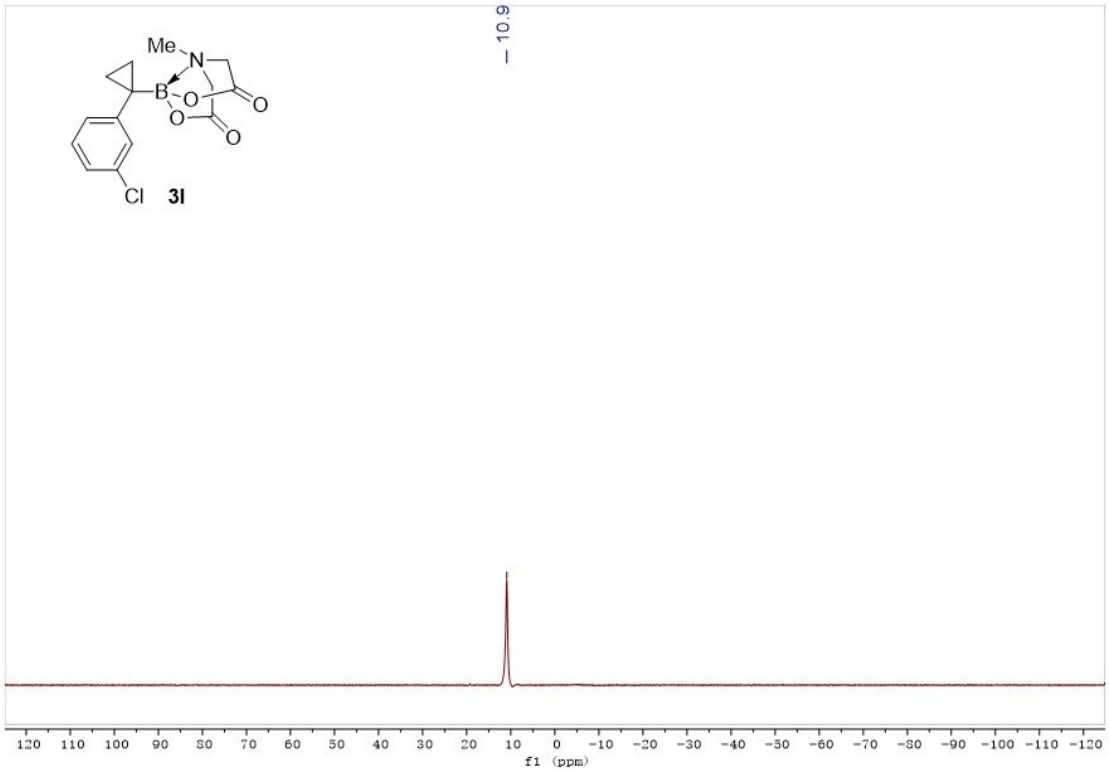

1H/490
7.47
7.46
7.46
7.45
7.45
7.44
7.27
7.26
7.26
7.25
7.25
7.24
4.15
4.12
3.68
3.65
3.14
2.08
2.07
2.07
2.06
2.06
0.95
0.94
0.94
0.93
0.76
0.75
0.75
0.74
Me
N
B
O
O
O
O
Cl
3k
2.08
2.00
2.09
2.03
3.05
1.99
2.01
f1 (ppm)

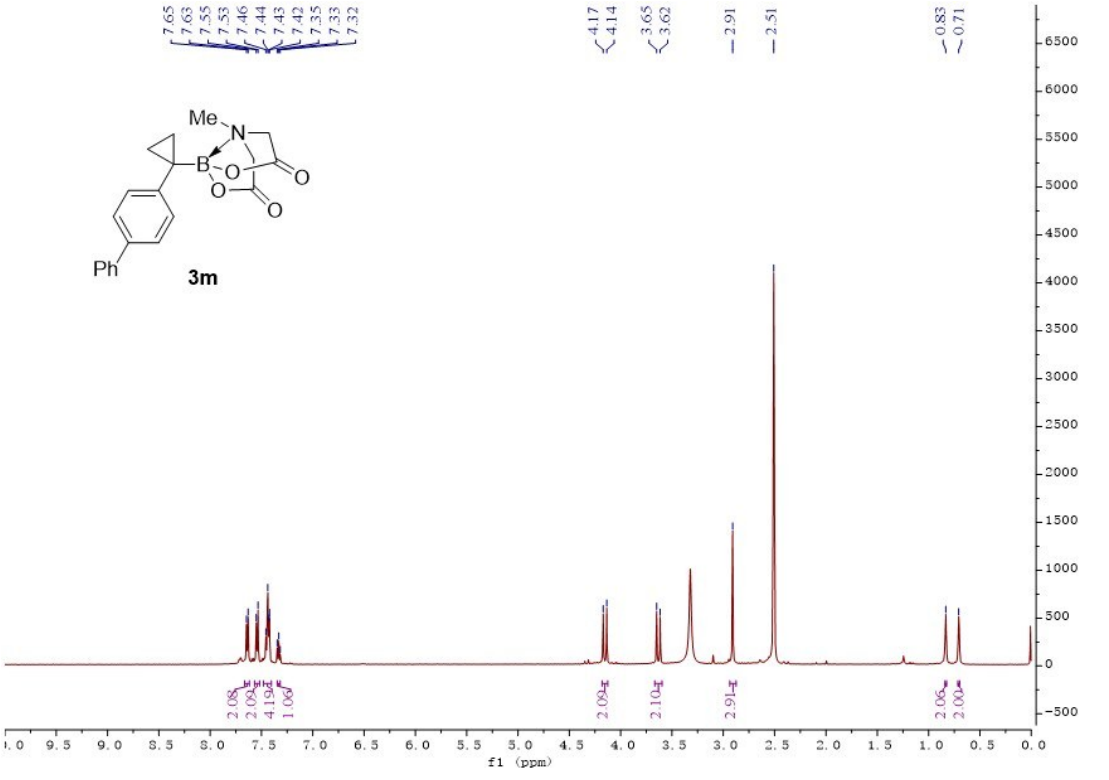

13C/491
168.7
145.9
133.4
131.6
129.1
63.6
47.2
30.6
30.4
30.2
30.1
29.9
29.8
29.6
11.0
Me
N
B
O
O
O
O
Cl
3k
f1 (ppm)

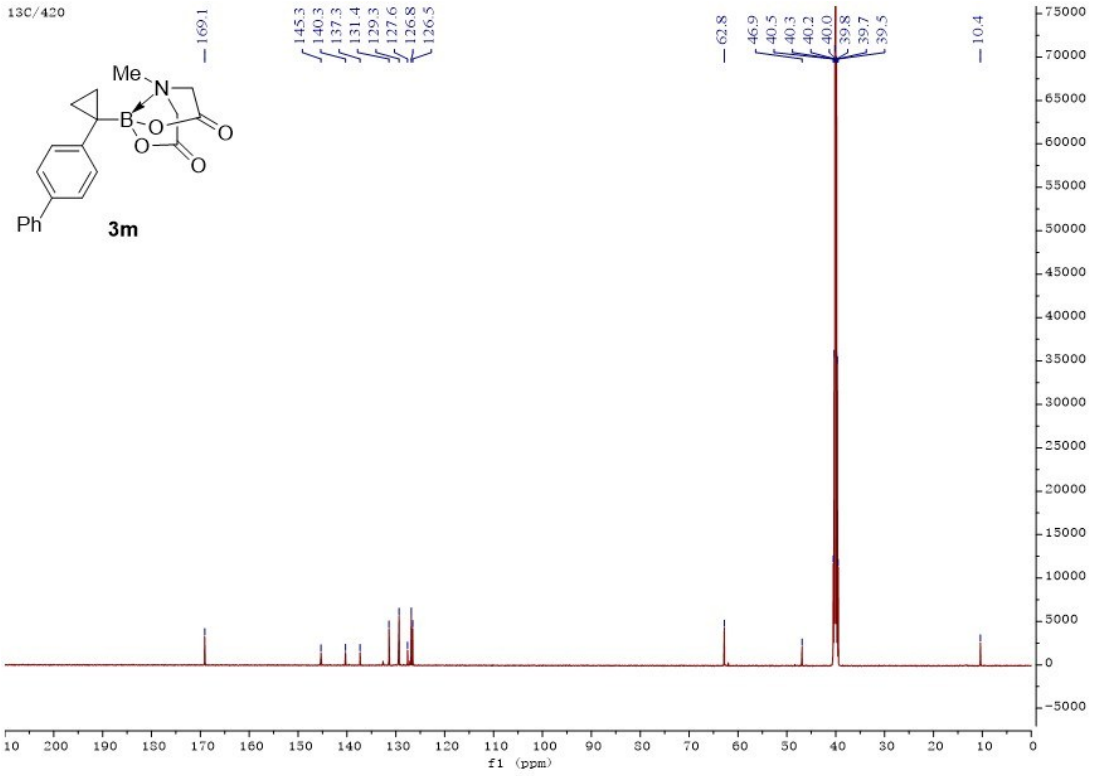

11.0
Me
N
B
O
O
O
O
Cl
3k
f1 (ppm)

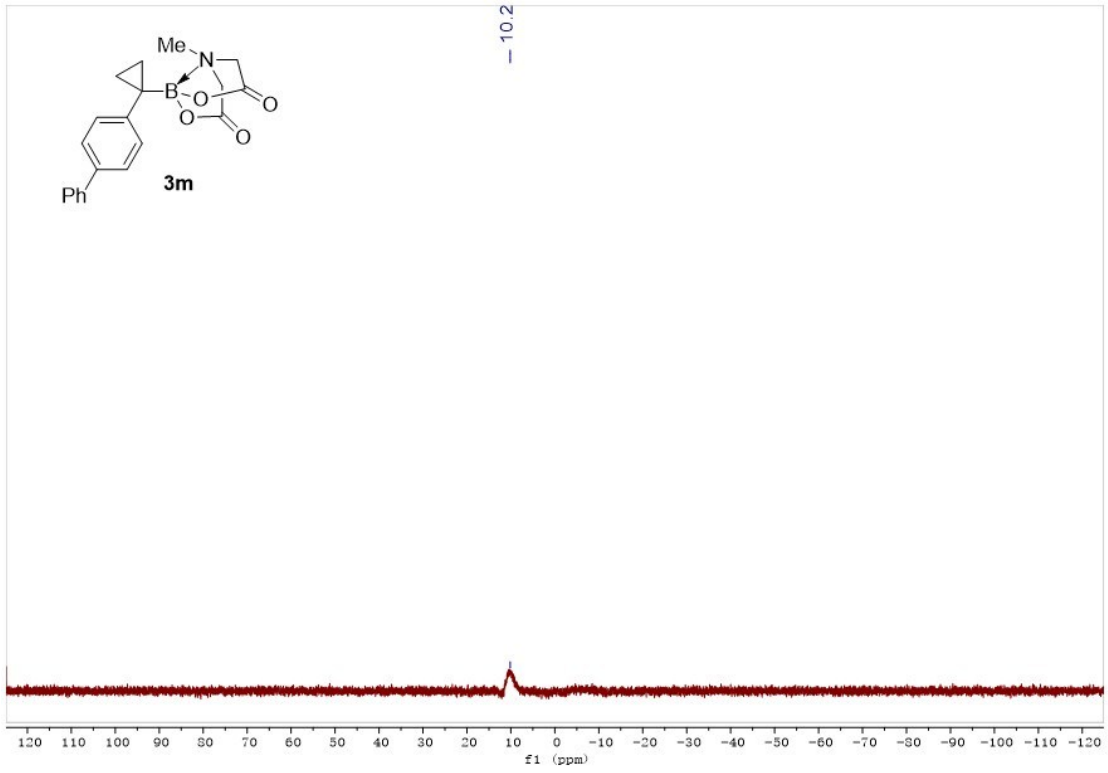

1H/300
7.45
7.45
7.45
7.40
7.39
7.26
7.24
7.23
7.16
7.16
7.16
7.15
7.15
7.14
4.15
4.12
3.69
3.66
3.13
2.06
2.06
2.05
2.05
2.05
0.95
0.94
0.94
0.93
0.78
0.77
0.77
0.76
Me
N
B
O
O
O
O
Cl
3l
0.93
1.08
1.06
0.98
2.02
2.01
2.96
2.00
1.98
f1 (ppm)

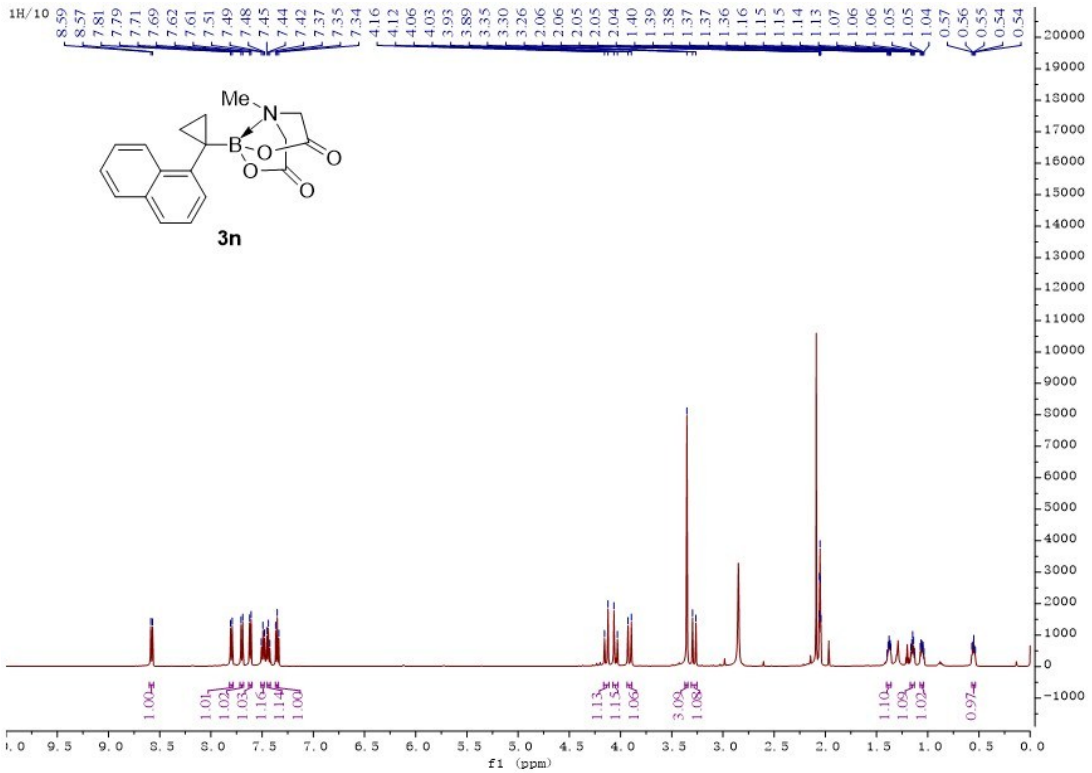

168.4
149.3
134.2
131.4
130.5
129.9
126.3
63.4
47.0
30.3
30.1
30.0
29.7
29.5
29.4
10.7
Me
N
B
O
O
O
O
Cl
3l
f1 (ppm)

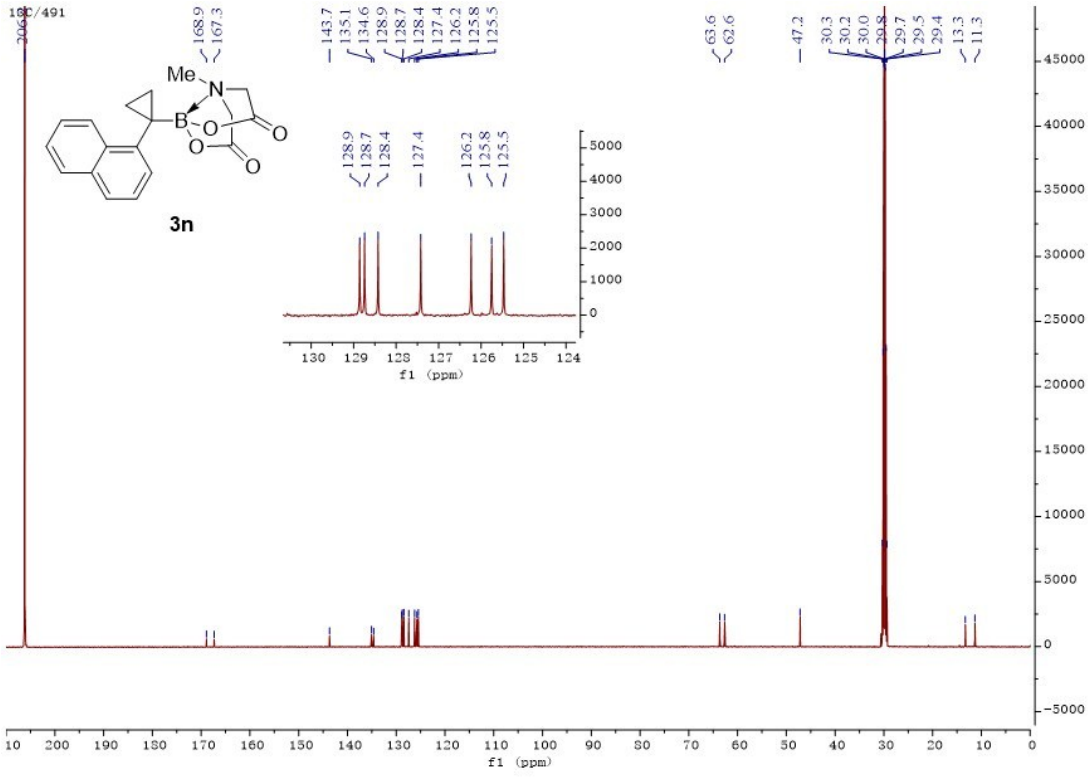

10.9
Me
N
B
O
O
O
O
Cl
3l
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

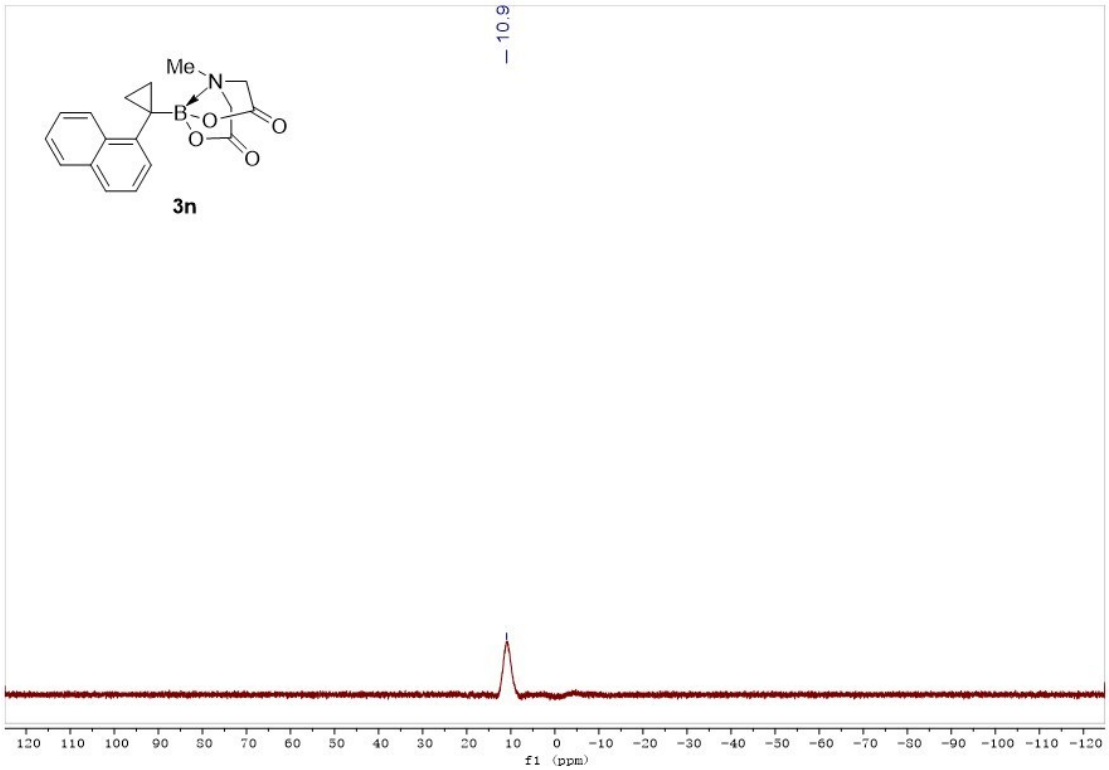

7.65
7.63
7.55
7.53
7.46
7.44
7.43
7.42
7.35
7.33
7.32
4.17
4.14
3.65
3.62
2.91
2.51
0.83
0.71
Me
N
B
O
O
O
O
Ph
3m
2.08
2.09
4.19
1.00
2.09
2.10
2.91
2.06
2.00
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
f1 (ppm)

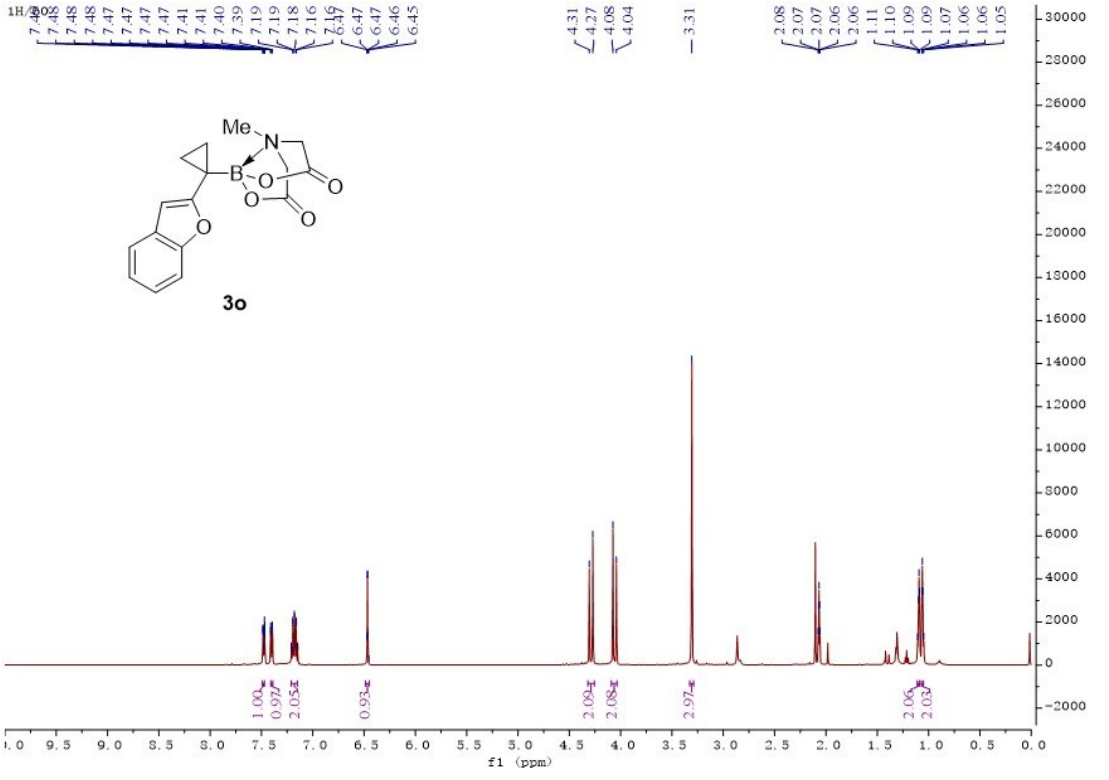

13C/420
169.1
145.3
140.3
137.3
131.4
129.3
127.6
126.8
126.5
62.8
46.9
40.5
40.3
40.2
40.0
39.8
39.7
39.5
10.4
Me
N
B
O
O
O
O
Ph
3m
f1 (ppm)

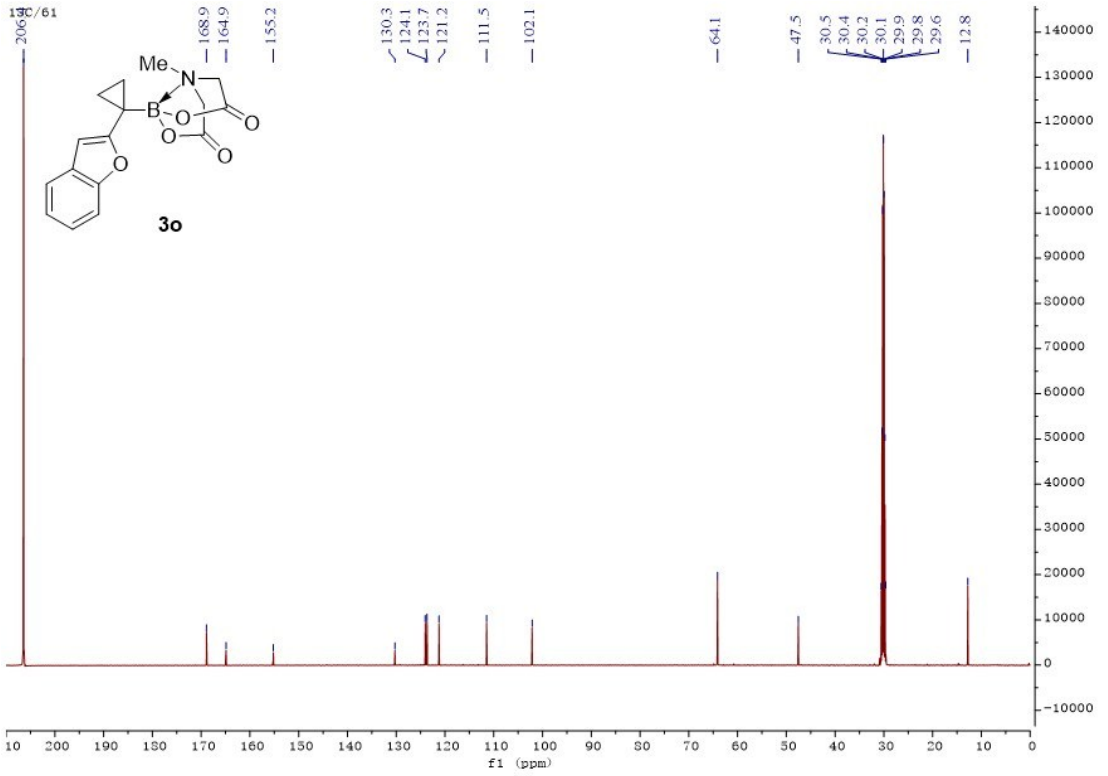

10.2
Me
N
B
O
O
O
O
Ph
3m
f1 (ppm)

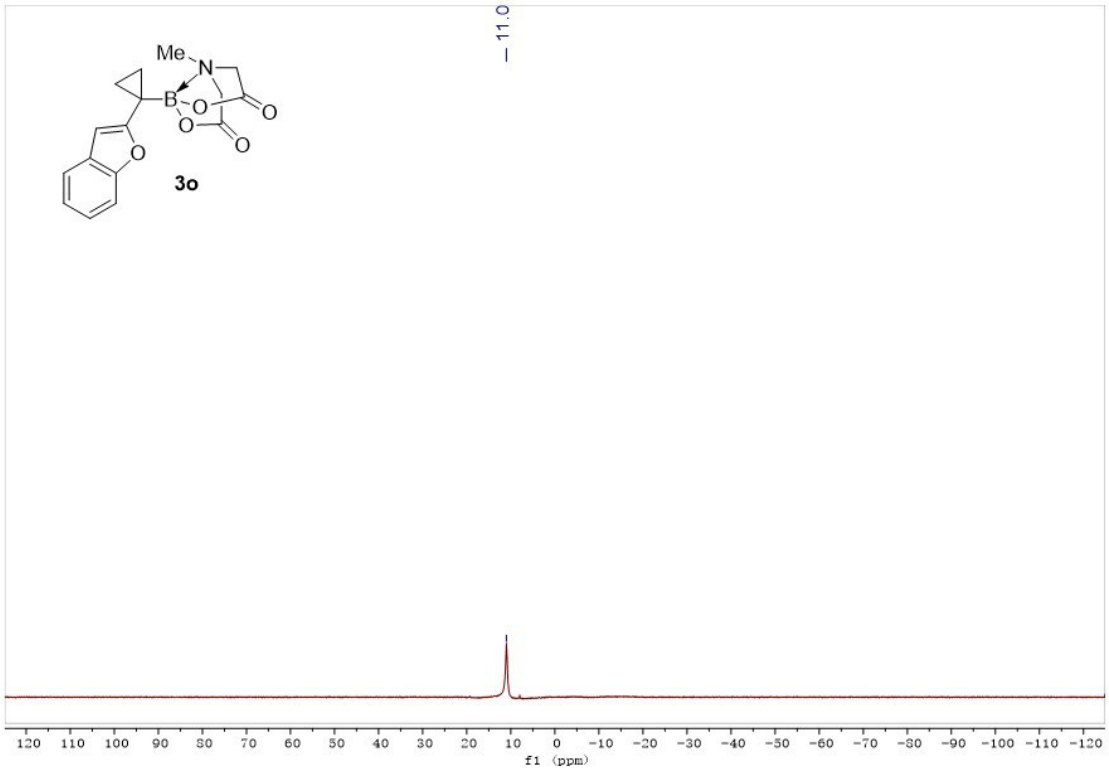

1H/10
Me
N
B
O
O
O
O
3n
f1 (ppm)

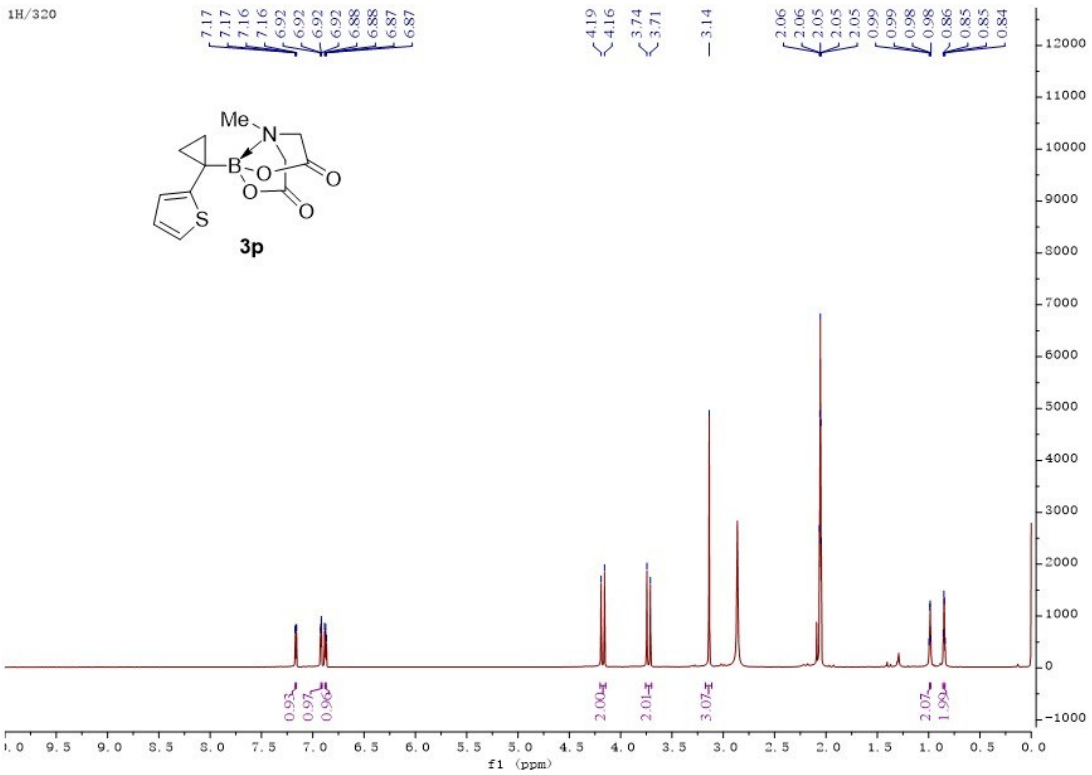

13C/491
Me
N
B
O
O
O
O
3n
f1 (ppm)
f1 (ppm)

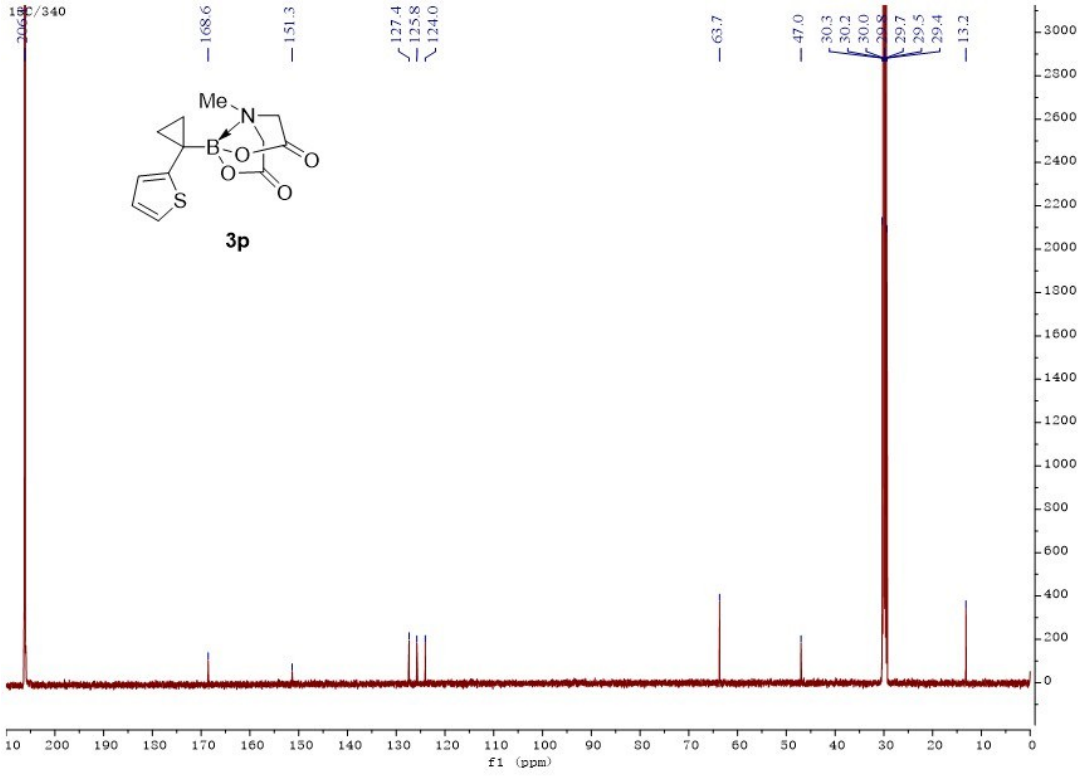

10.9
Me
N
B
O
O
O
O
3n
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

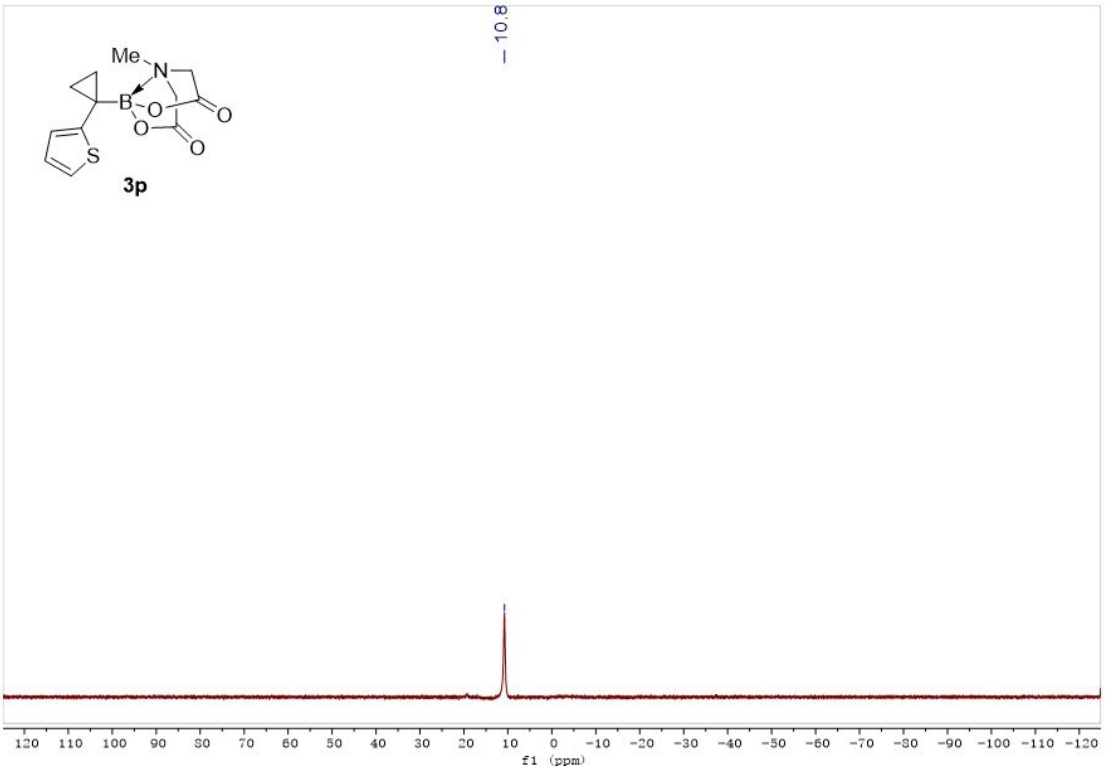

7.48
7.47
7.41
7.40
7.39
7.19
7.18
7.16
6.47
6.46
6.45
4.31
4.27
4.08
4.04
3.31
2.08
2.07
2.06
1.11
1.10
1.09
1.07
1.06
1.05
Me
N
B
O
O
O
O
O
3o
1.00
0.97
2.05
0.93
2.09
2.08
2.97
2.06
2.03
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
9.5 9.0 8.5 8.0 7.5 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)

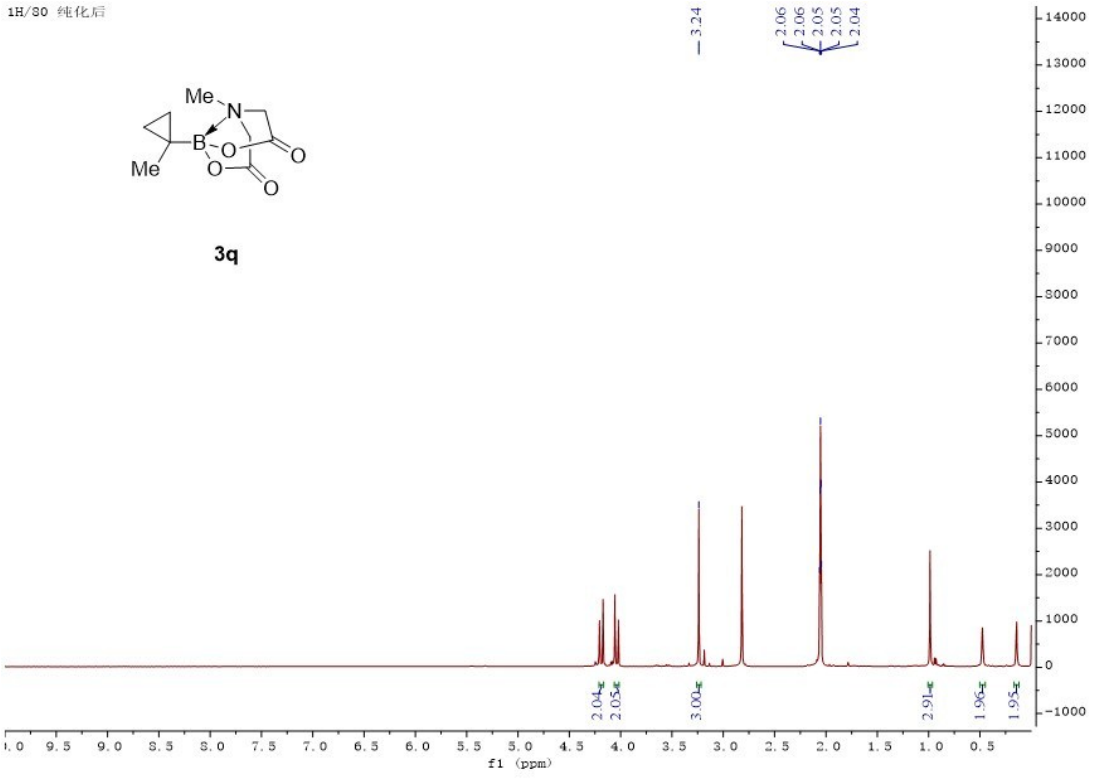

13C/61
206.4
168.9
164.9
155.2
130.3
124.1
123.7
121.2
111.5
102.1
64.1
47.5
30.5
30.4
30.2
30.1
29.9
29.8
29.6
12.8
Me
N
B
O
O
O
O
O
3o
f1 (ppm)

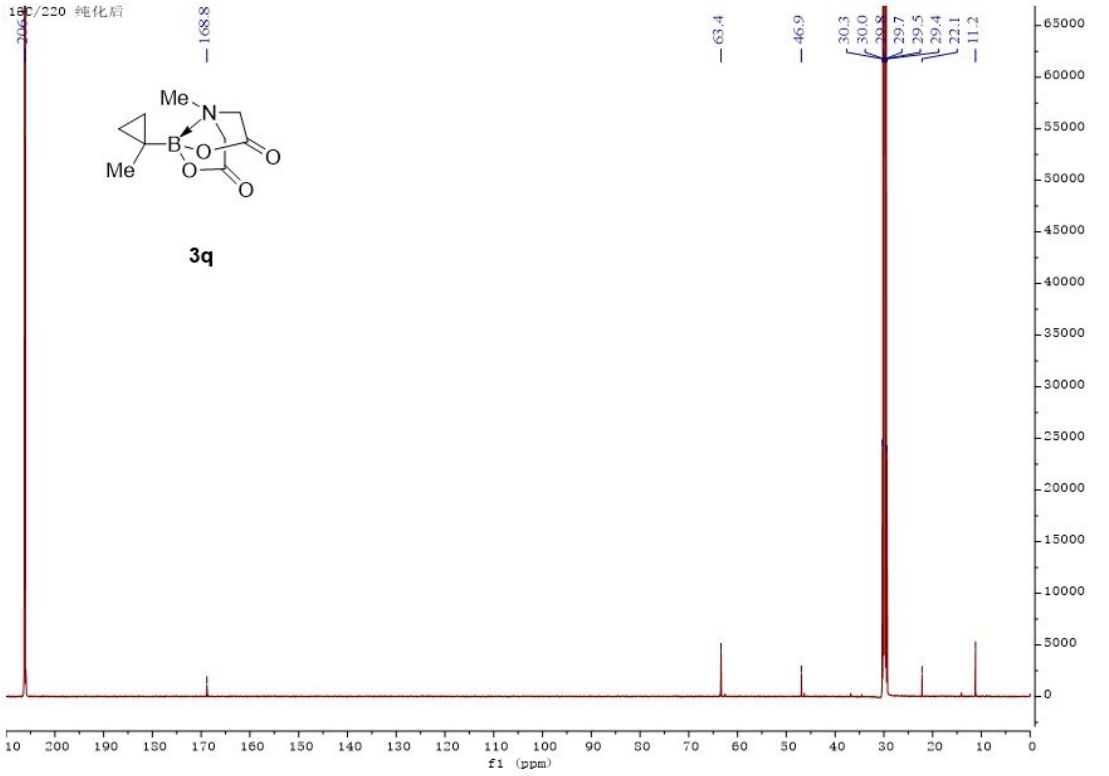

11.0
Me
N
B
O
O
O
O
O
3o
f1 (ppm)

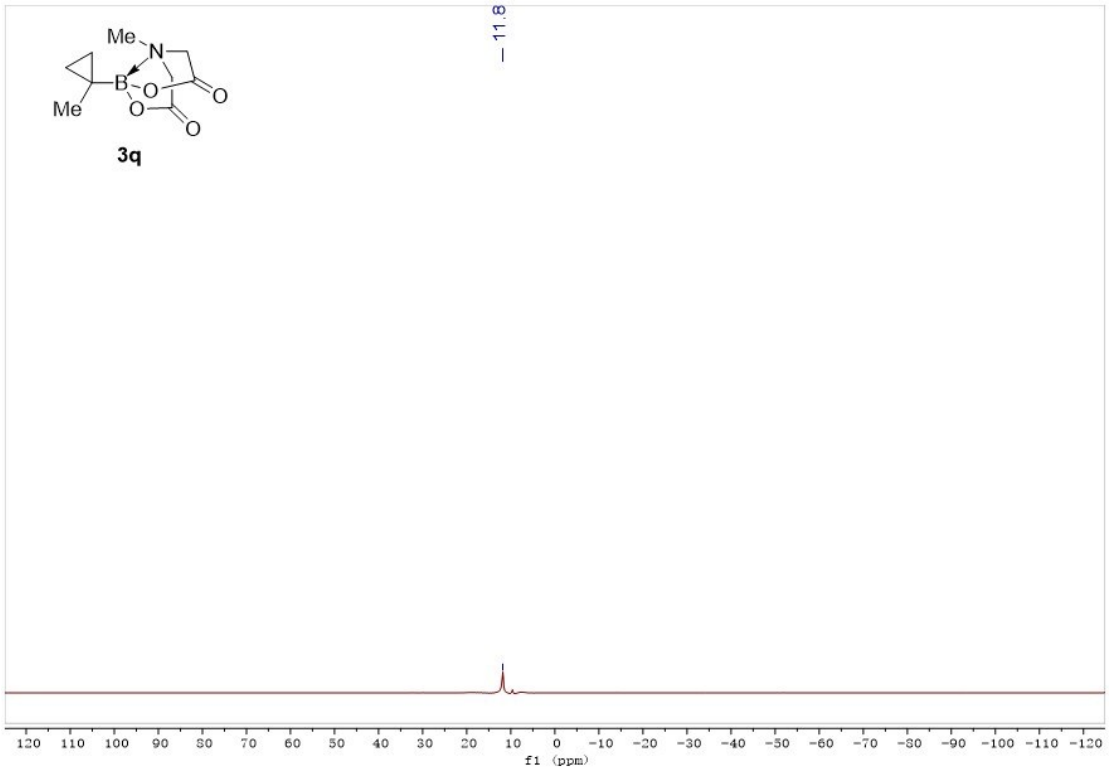

1H/320
7.17
7.17
7.16
7.16
6.92
6.92
6.92
6.88
6.88
6.87
6.87
4.19
4.16
3.74
3.71
3.14
2.06
2.06
2.05
2.05
2.05
0.99
0.99
0.98
0.98
0.86
0.85
0.85
0.84
Me
N
B
O
O
O
O
S
3p
0.93
0.97
0.96
2.00
2.01
3.07
2.07
1.99
f1 (ppm)

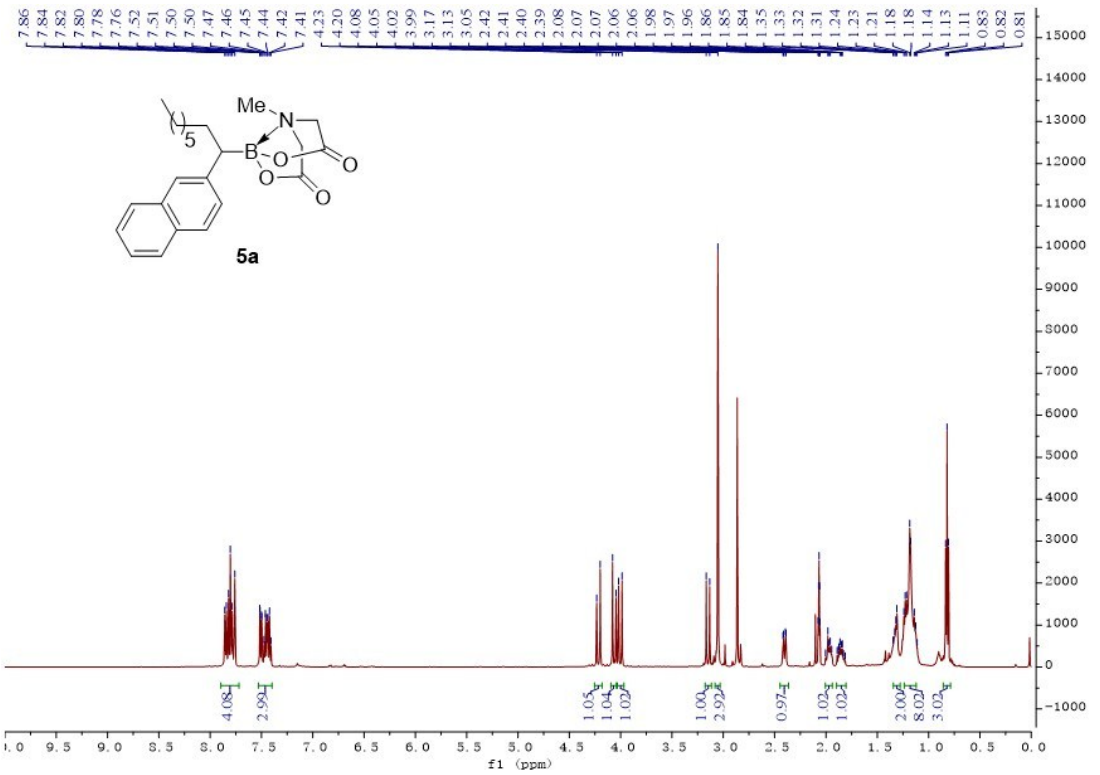

13C/340
206.4
168.6
151.3
127.4
125.8
124.0
63.7
47.0
30.3
30.2
30.0
29.8
29.7
29.5
29.4
13.2
Me
N
B
O
O
O
O
S
3p
f1 (ppm)

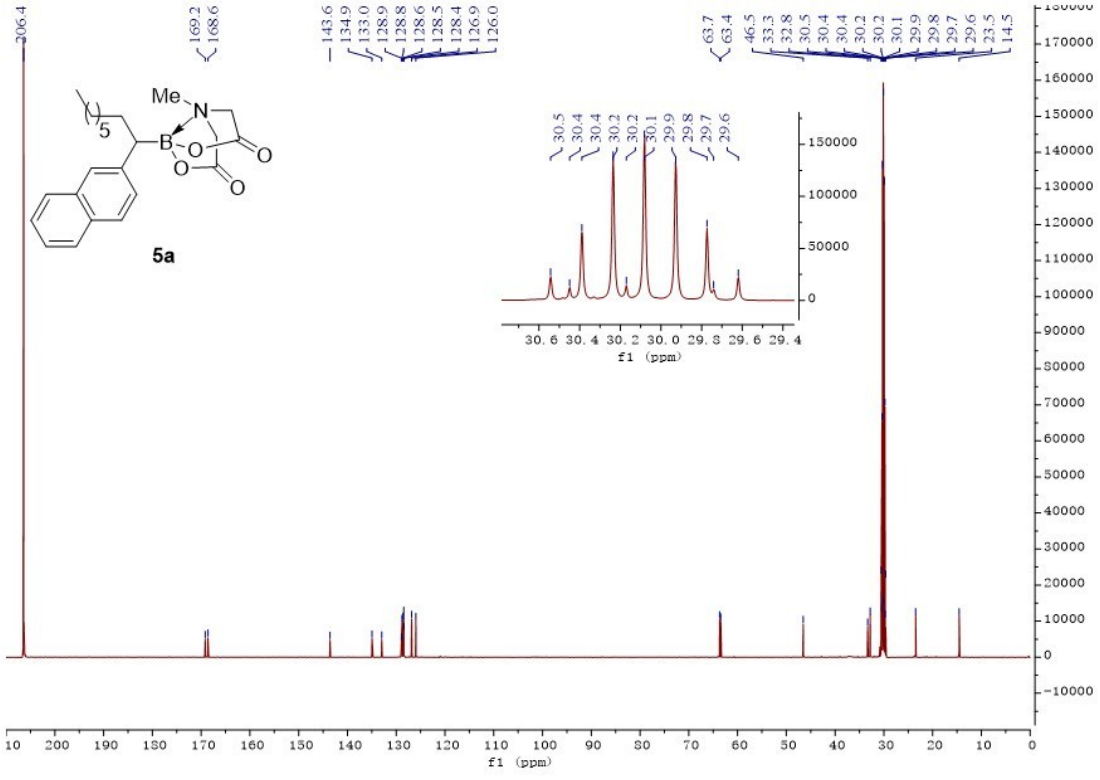

10.8
Me
N
B
O
O
O
O
S
3p
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

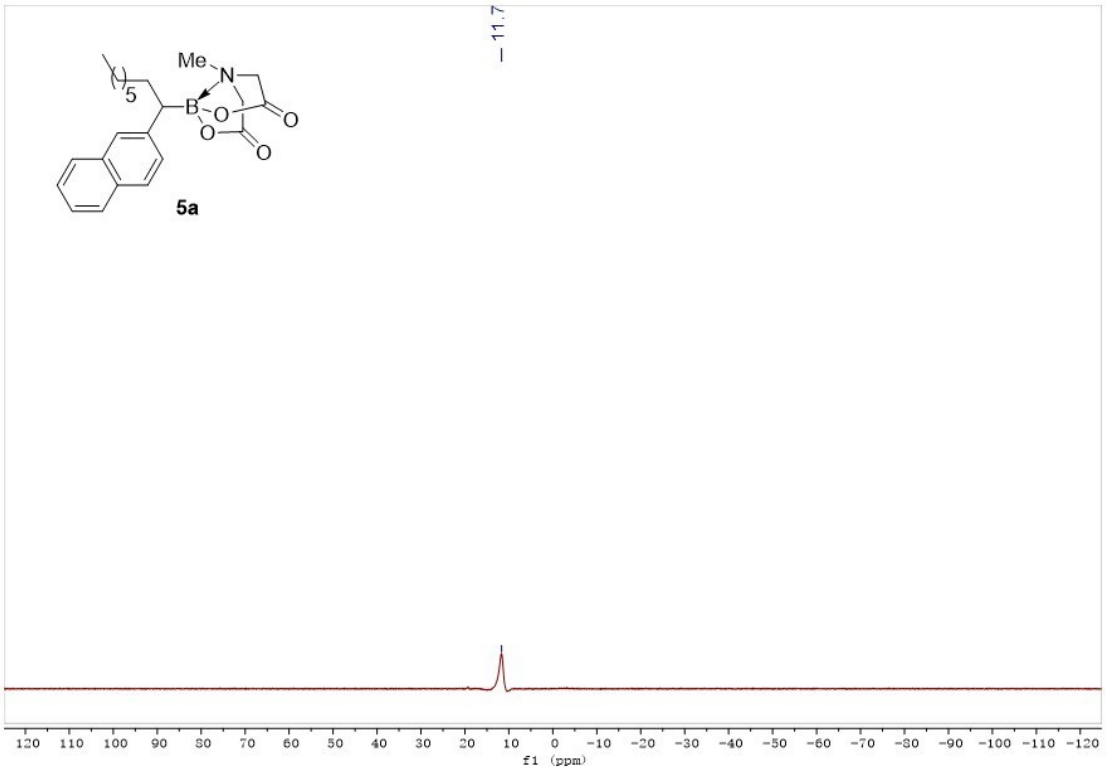

1H/80 纯化后
3.24
2.06
2.06
2.05
2.05
2.04
Me
N
B
O
O
O
O
Me
3q
2.04
2.05
3.00
2.91
1.96
1.95
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

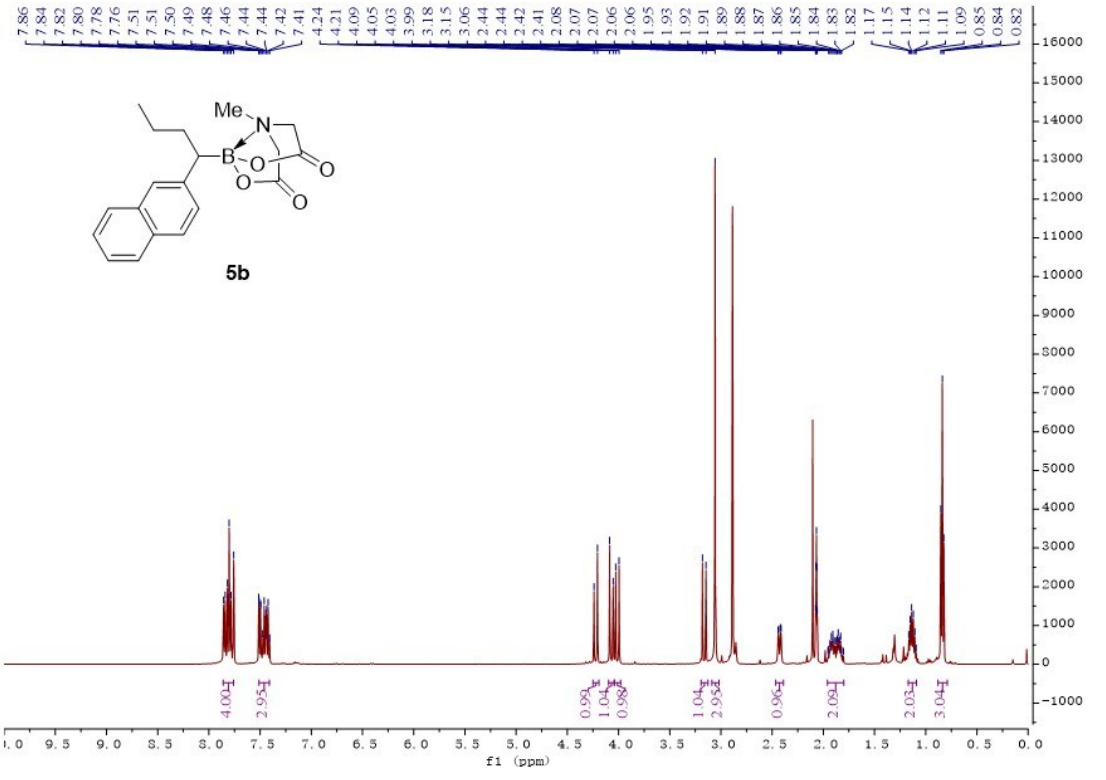

168.8
63.4
46.9
30.3
30.0
29.7
29.5
29.4
22.1
11.2
Me
N
B
O
Me
O
O
O
3q
f1 (ppm)

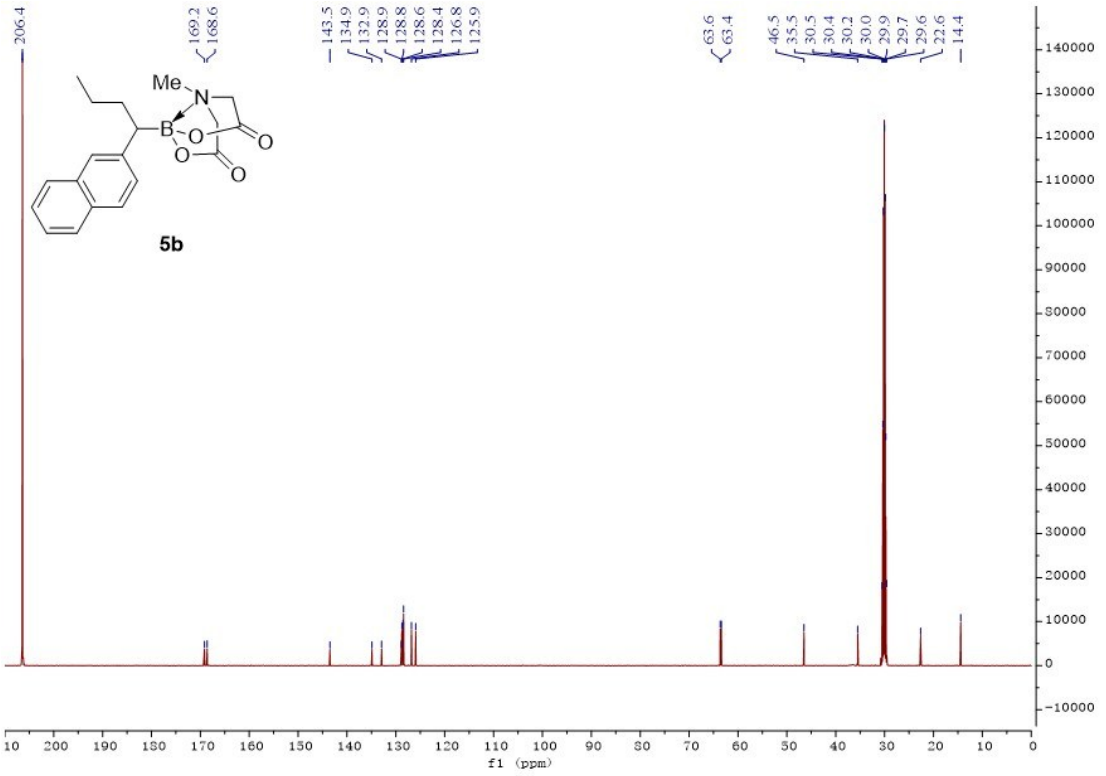

11.8
Me
N
B
O
Me
O
O
O
3q
f1 (ppm)

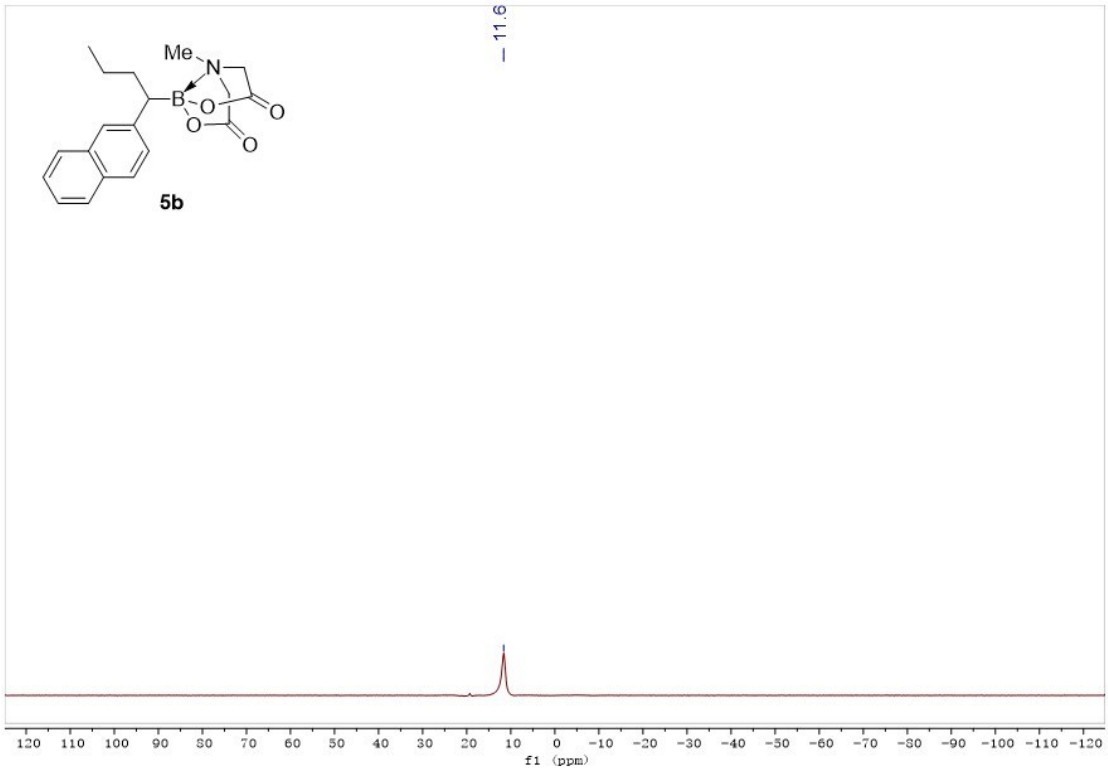

Me
N
B
O
O
O
O
5
5a
f1 (ppm)

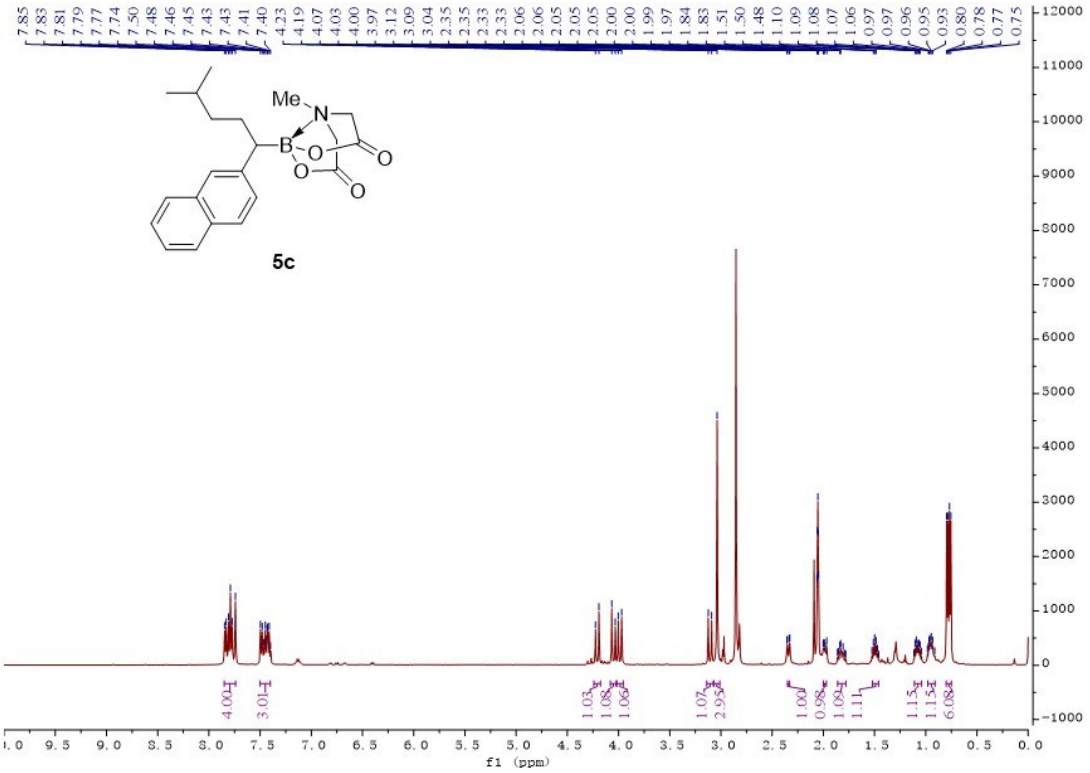

Me
N
B
O
O
O
O
5
5a
f1 (ppm)
f1 (ppm)

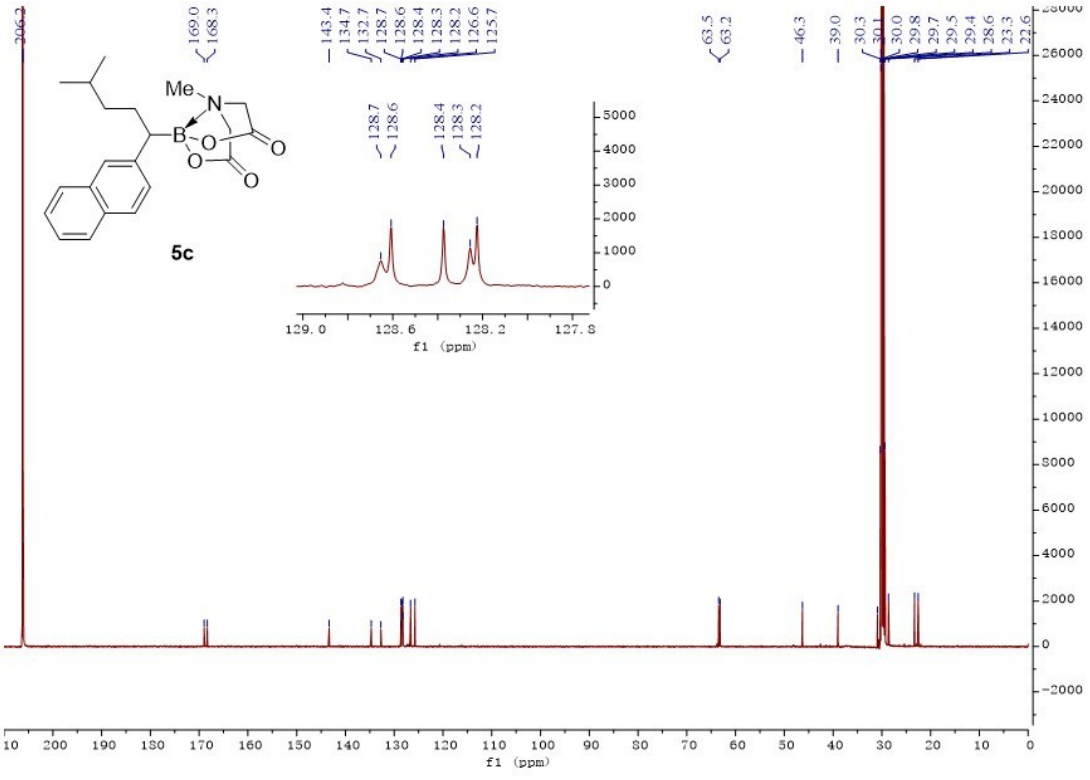

Me
N
B
O
O
O
O
5
5a
11.7
f1 (ppm)

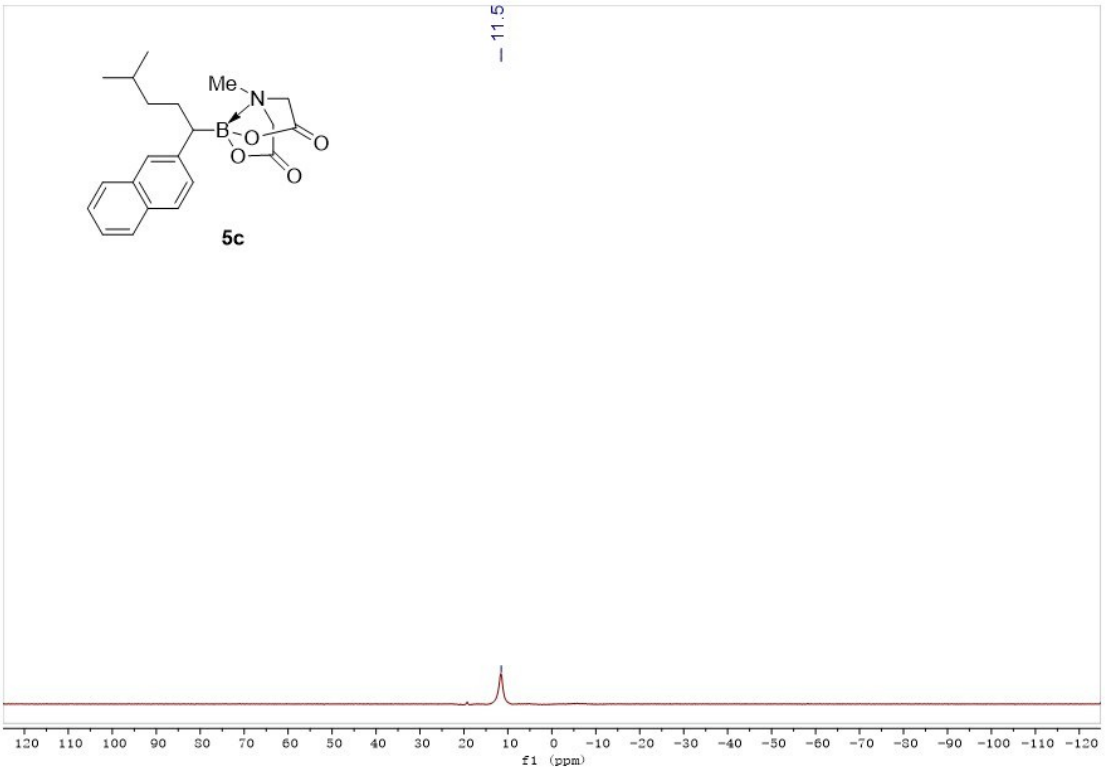

Me
N
B
O
O
O
O
5b
f1 (ppm)

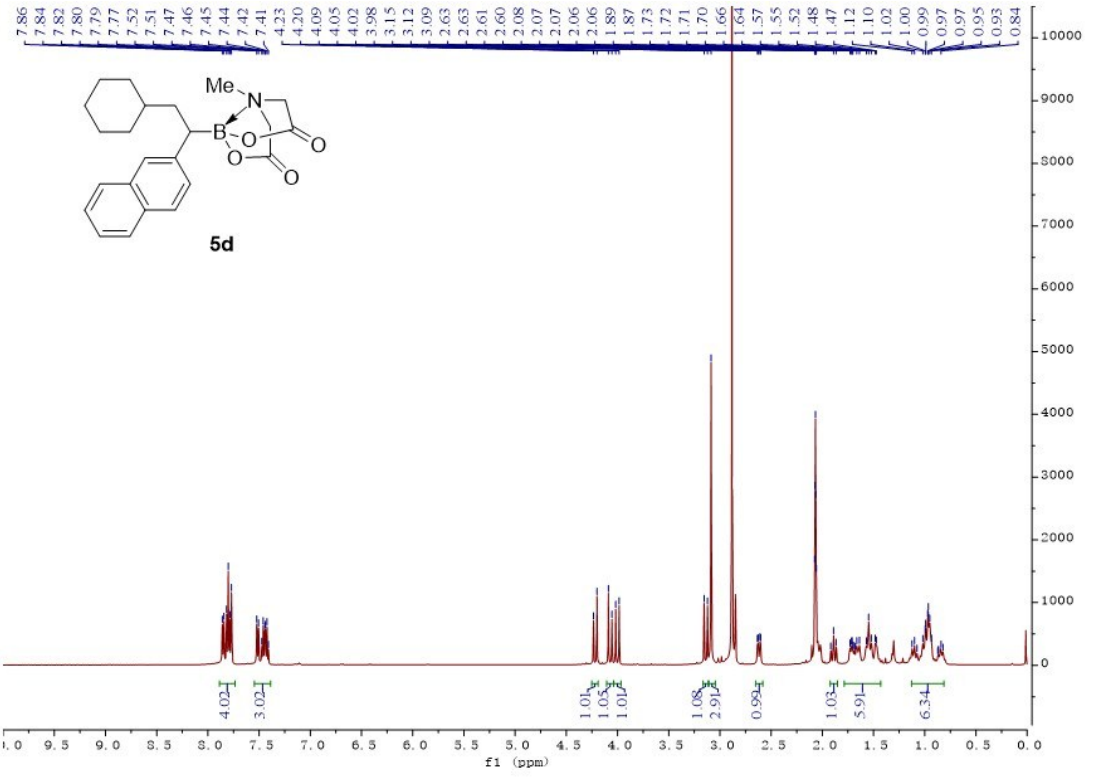

206.4
169.2
168.6
143.5
134.9
132.9
128.9
128.8
128.6
128.4
126.8
125.9
63.6
63.4
46.5
35.5
30.5
30.4
30.2
30.0
29.9
29.7
29.6
22.6
14.4
Me
N
B
O
O
O
O
5b
f1 (ppm)

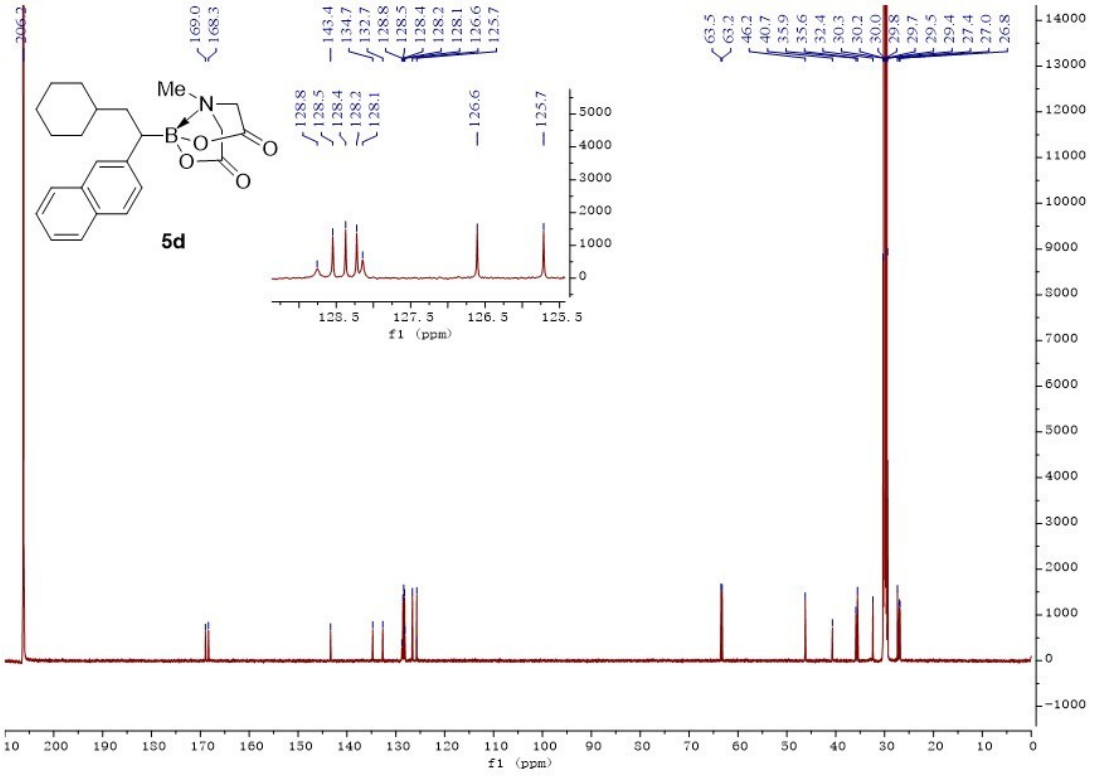

11.6
Me
N
B
O
O
O
O
5b
f1 (ppm)

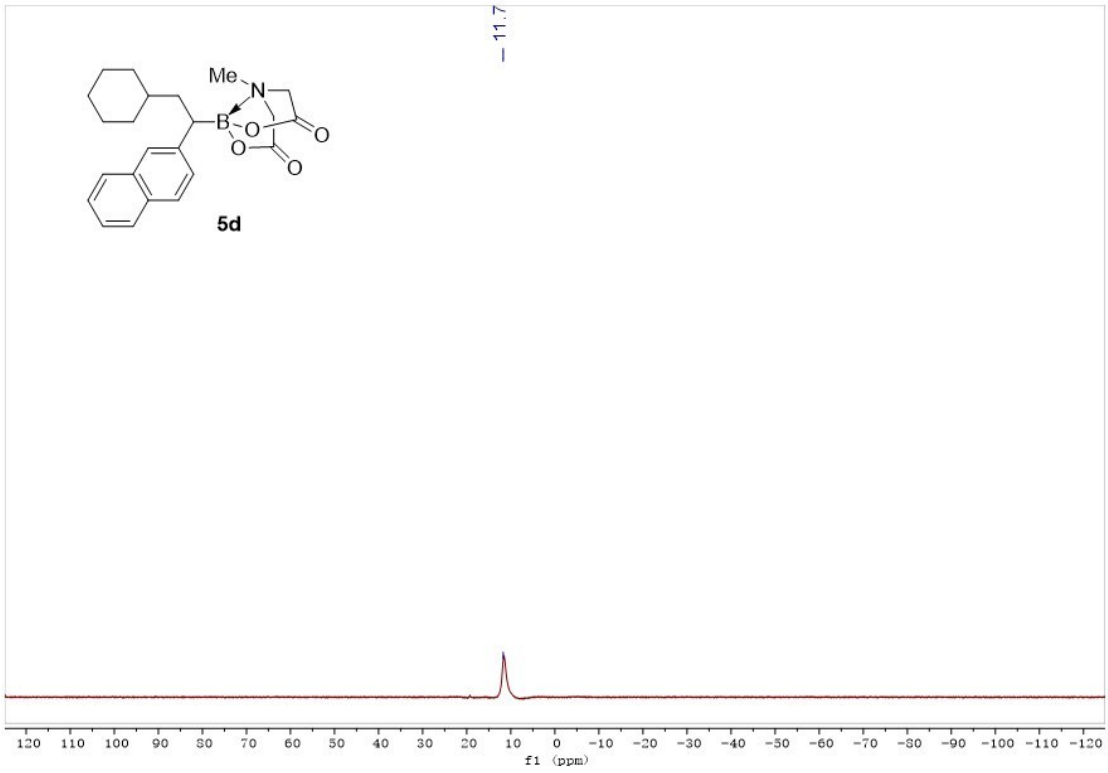

Me
N
B
O
O
O
O
5c
f1 (ppm)

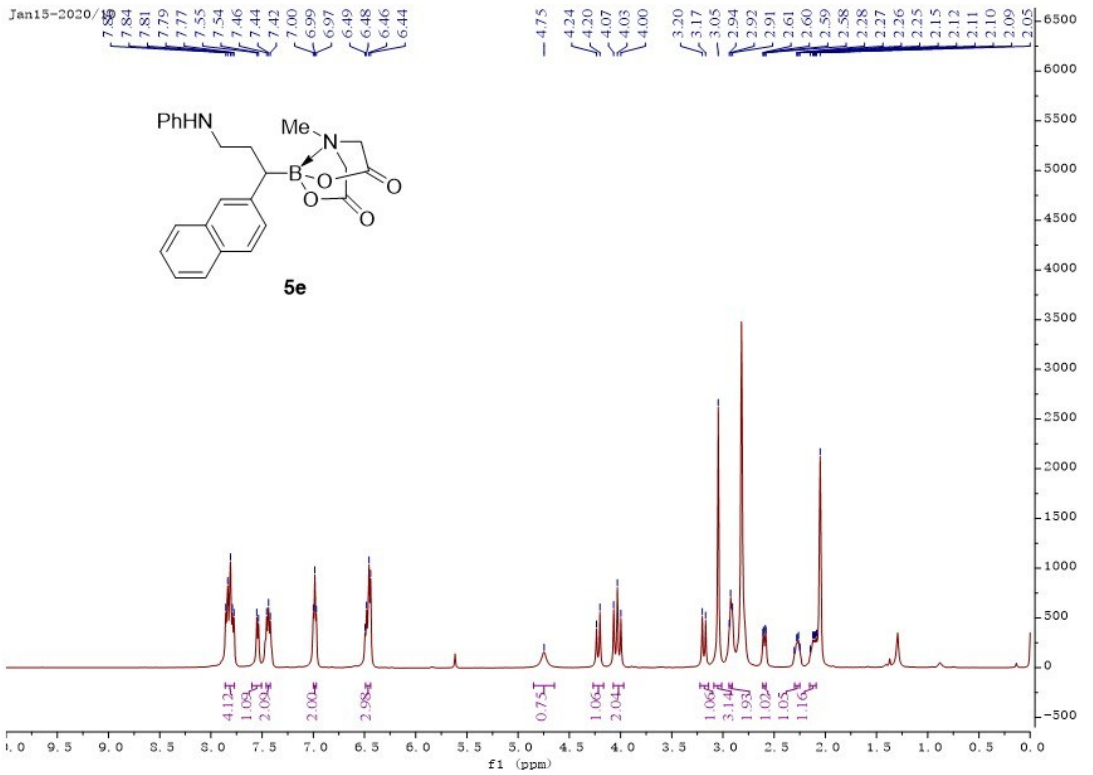

Me
N
B
O
O
O
O
5c
f1 (ppm)
f1 (ppm)

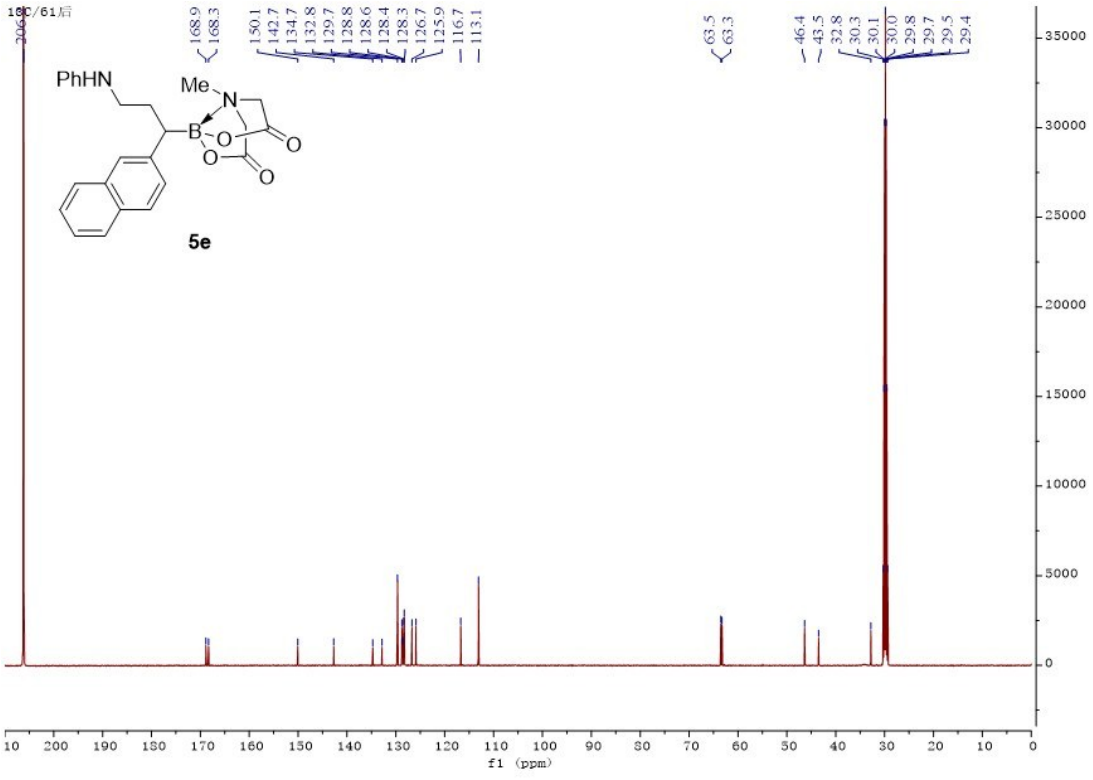

11.5
Me
N
B
O
O
O
O
5c
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

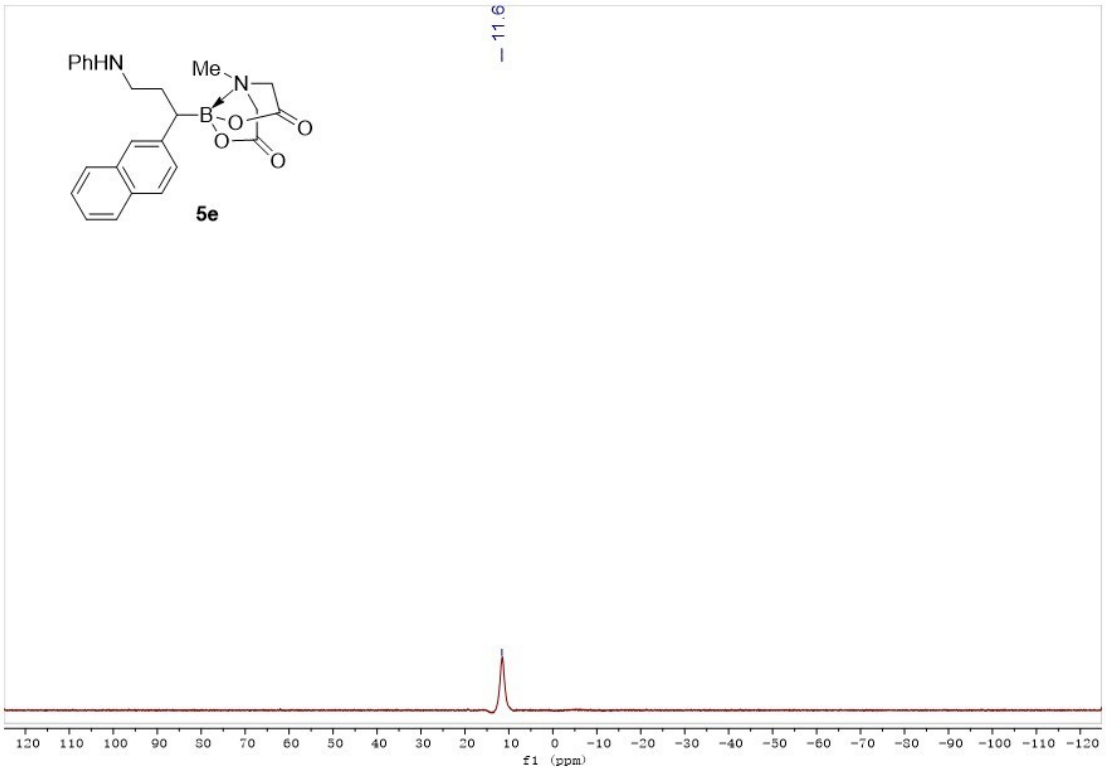

7.86 7.84 7.82 7.80 7.79 7.77 7.52 7.51 7.47 7.46 7.45 7.44 7.42 7.41 4.23 4.20 4.09 4.05 4.02 3.98 3.15 3.12 3.09 2.63 2.61 2.60 2.08 2.07 2.07 2.06 2.06 1.89 1.87 1.73 1.72 1.71 1.70 1.66 1.64 1.57 1.55 1.52 1.48 1.47 1.12 1.10 1.02 1.00 0.99 0.97 0.97 0.95 0.93 0.84
Me
N
B
O
O
O
O
5d
4.02 3.02 1.01 1.05 1.01 1.08 2.91 0.99 1.03 5.91 6.34
10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 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)

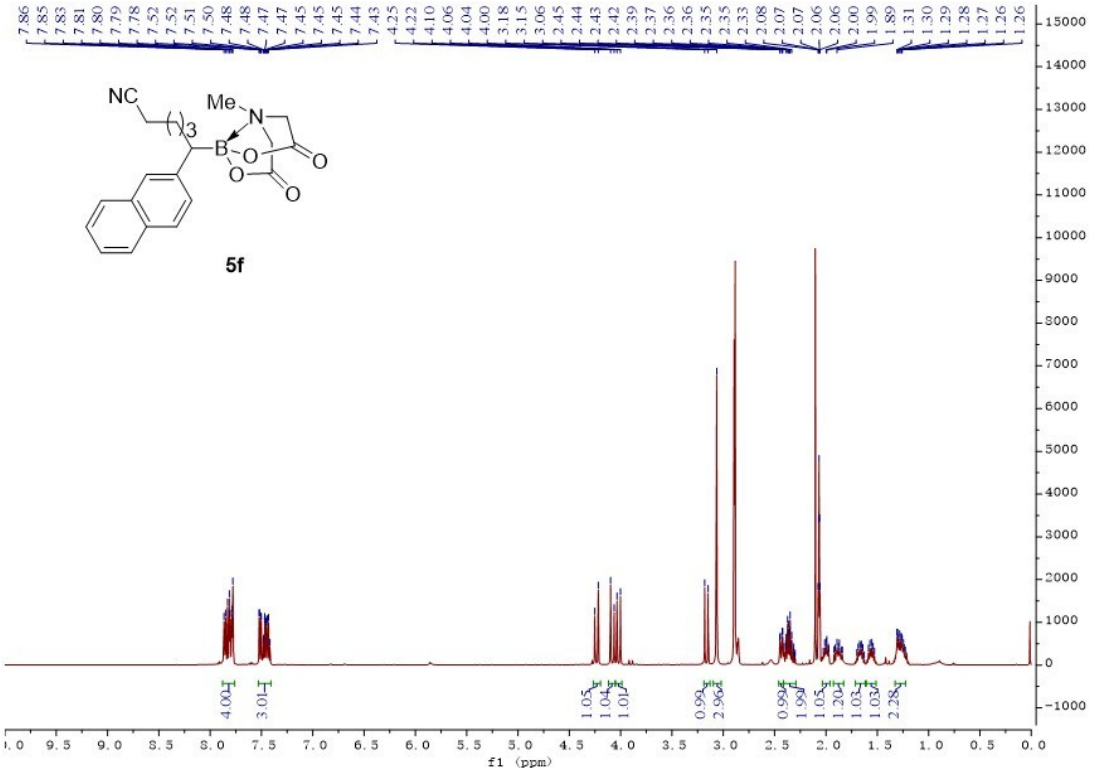

206.2
169.0
168.3
143.4
134.7
132.7
128.8
128.5
128.4
128.2
128.1
126.6
125.7
63.5
63.2
46.2
40.7
35.9
35.6
32.4
30.3
30.2
30.0
29.8
29.7
29.5
29.4
27.4
27.0
26.8
Me
N
B
O
O
O
O
5d
f1 (ppm)

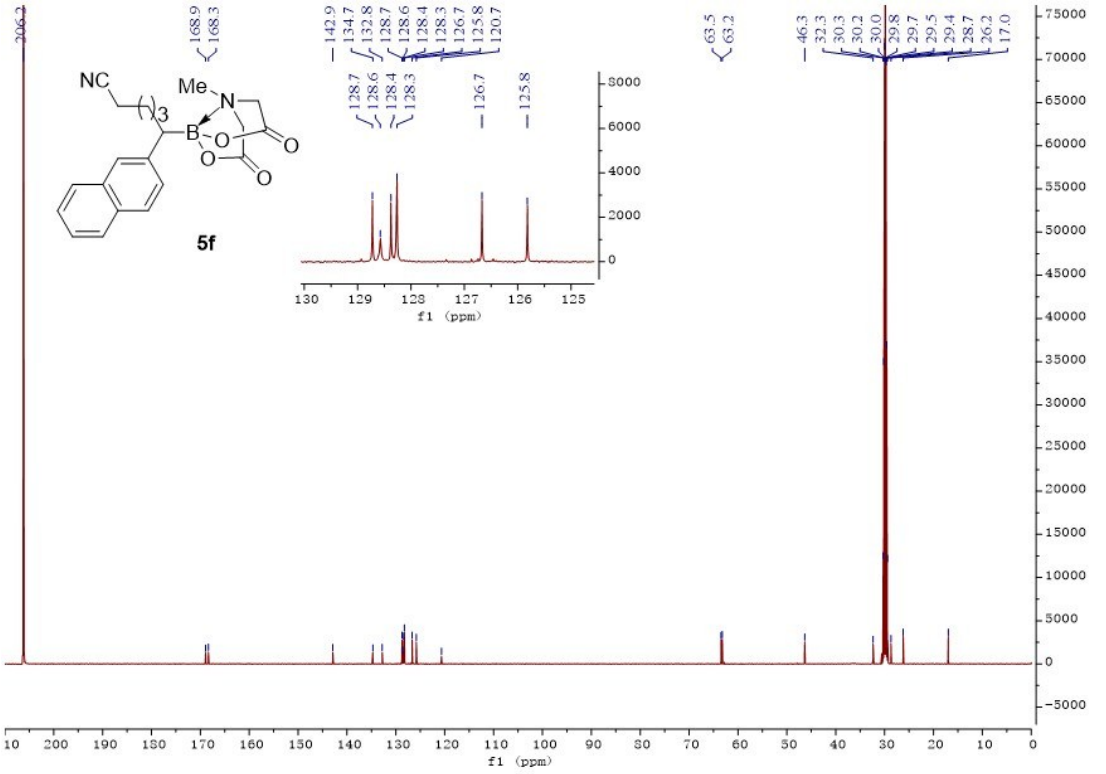

11.7
Me
N
B
O
O
O
O
5d
f1 (ppm)

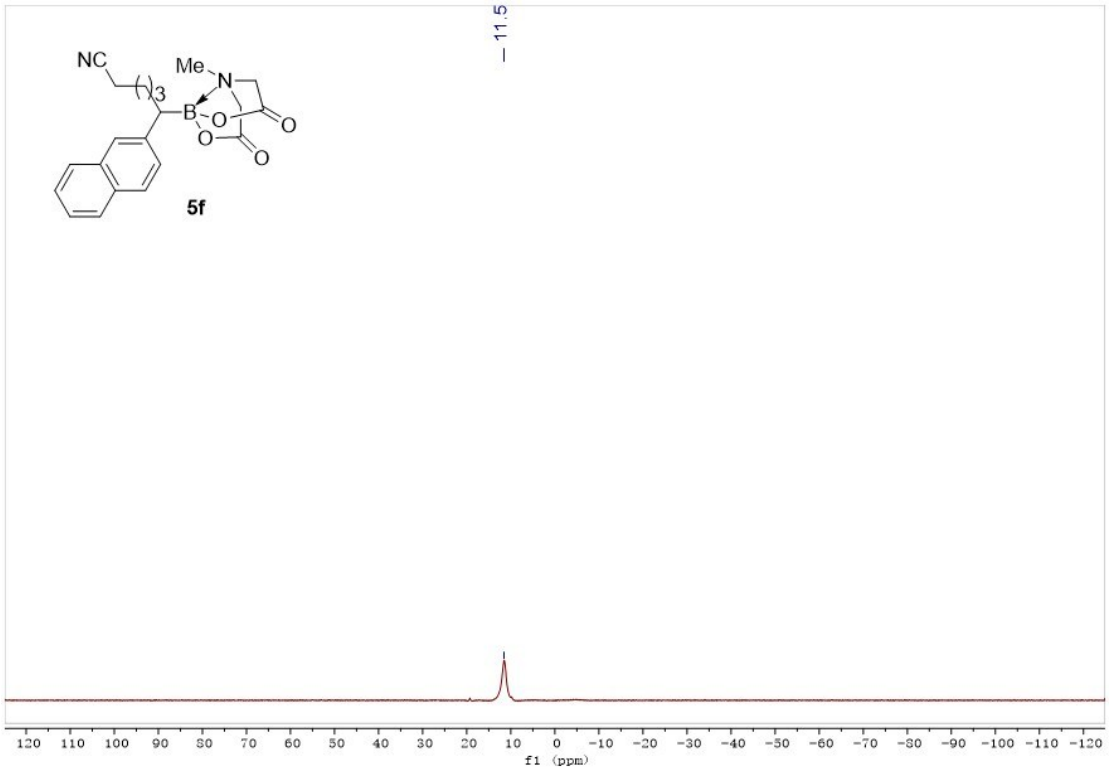

PhHN
Me
N
B
O
O
O
O
5e
f1 (ppm)

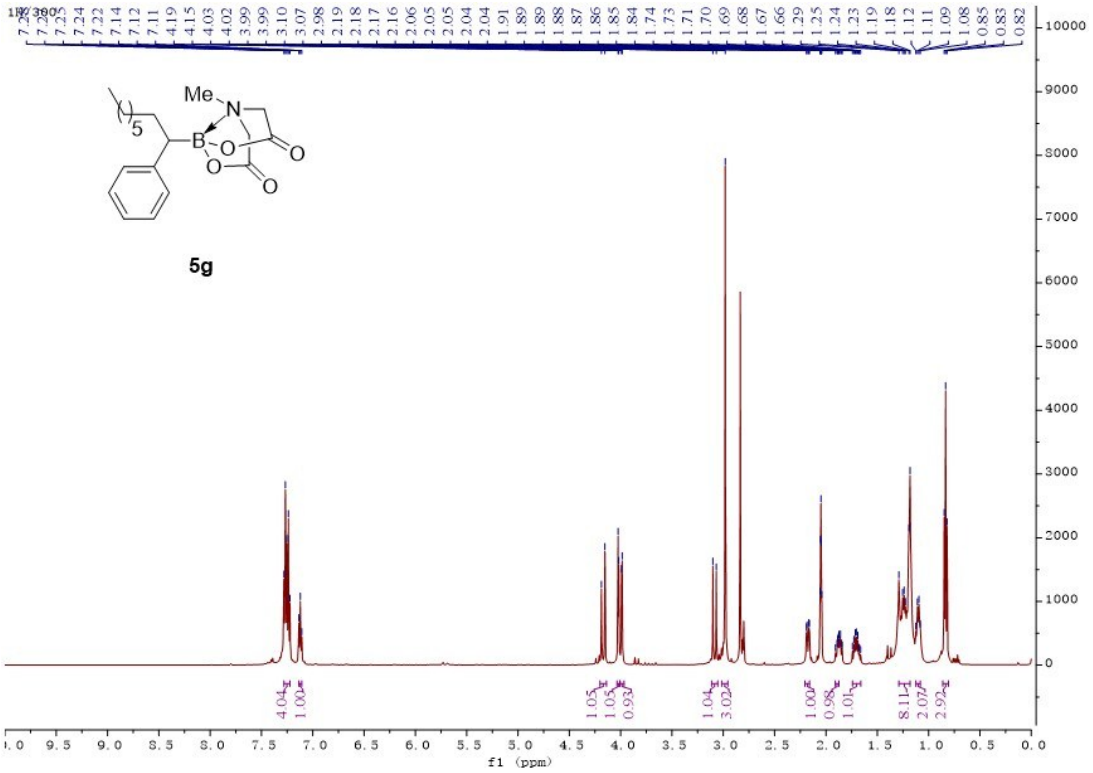

PhHN
Me
N
B
O
O
O
O
5e
f1 (ppm)

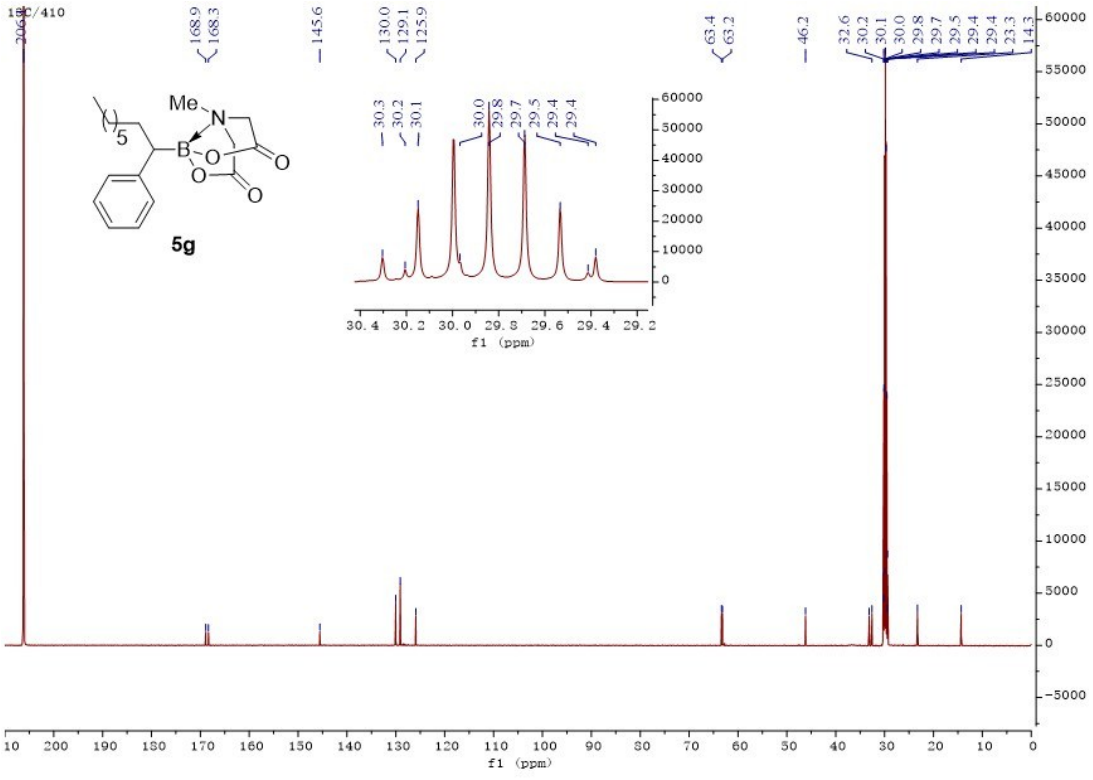

PhHN
Me
N
B
O
O
O
O
5e
11.6
f1 (ppm)

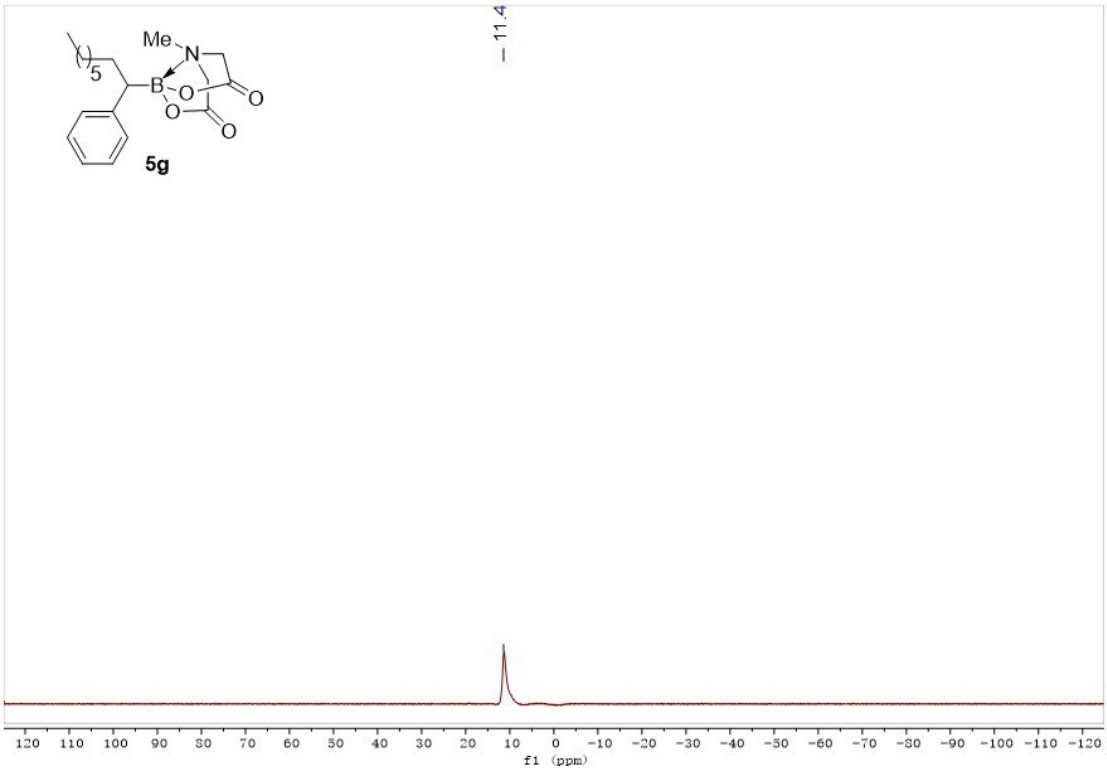

NC
3
Me
N
B
O
O
O
O
5f
4.00
3.01
1.05
1.04
1.01
0.99
2.96
0.99
1.99
1.05
1.20
1.03
1.03
2.28
f1 (ppm)

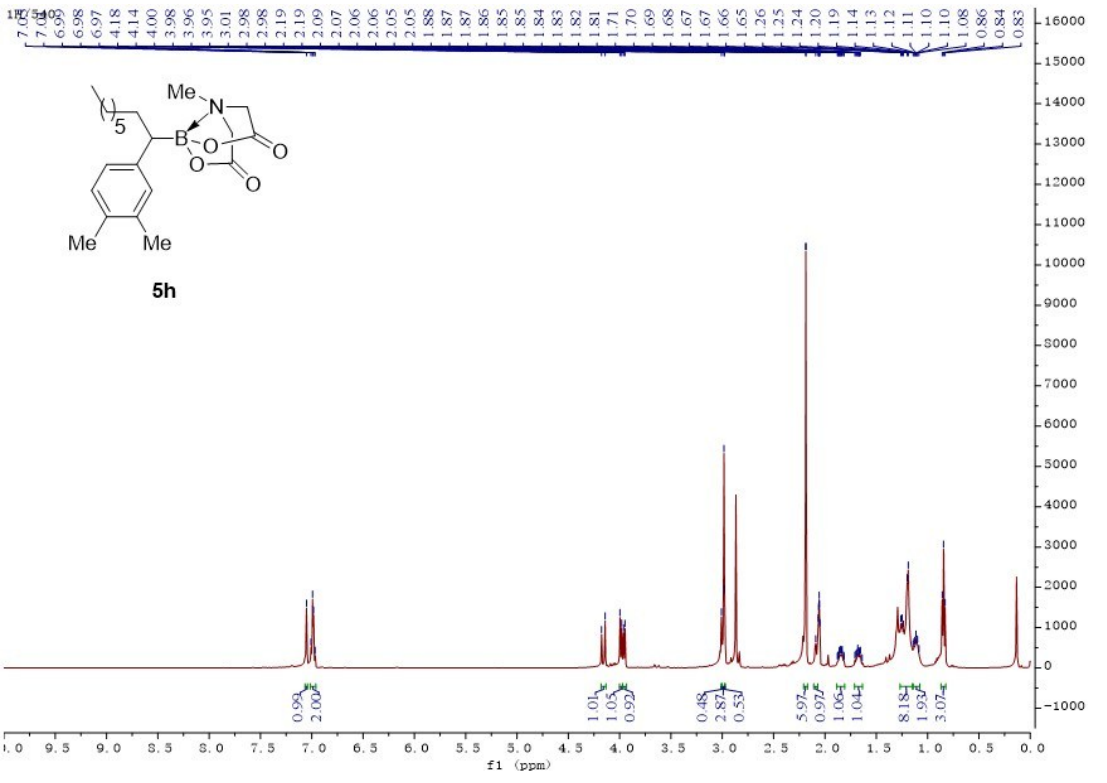

206.2
168.9
168.3
142.9
134.7
132.8
128.7
128.6
128.4
128.3
126.7
125.8
120.7
63.5
63.2
46.3
32.3
30.3
30.2
30.0
29.8
29.7
29.5
29.4
28.7
26.2
17.0
NC
Me
N
B
O
O
O
O
3
5f
f1 (ppm)

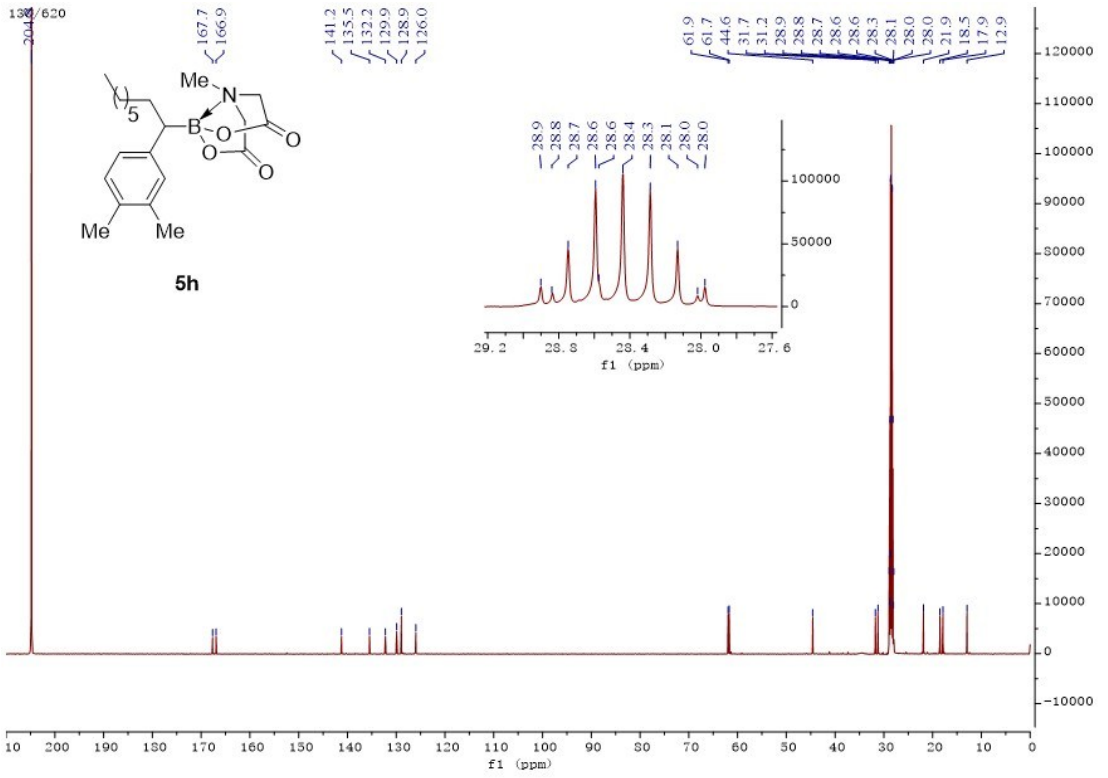

11.5
NC
Me
N
B
O
O
O
O
3
5f
f1 (ppm)

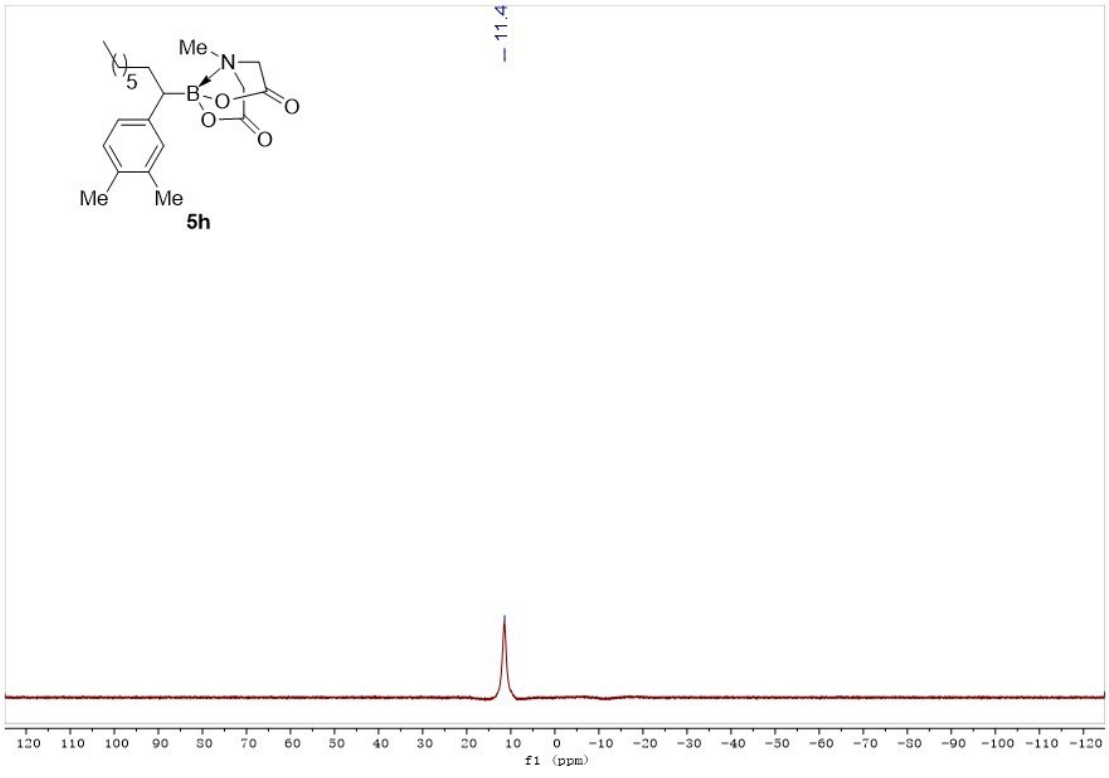

5g
f1 (ppm)

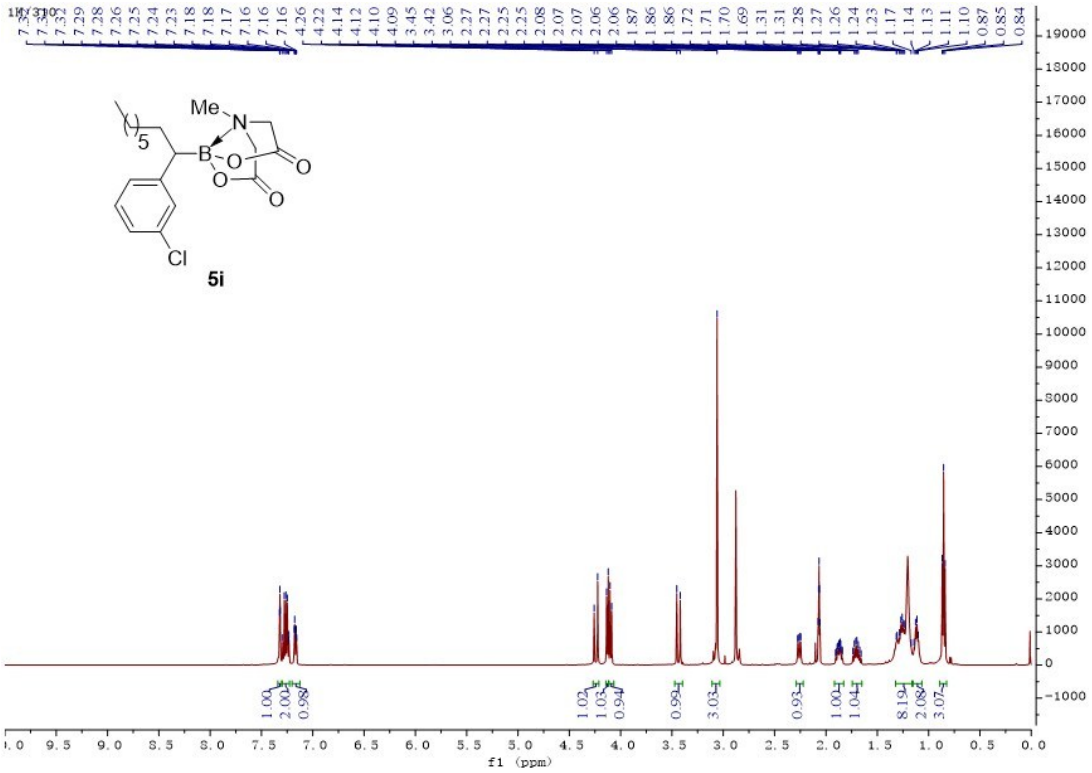

5g
f1 (ppm)

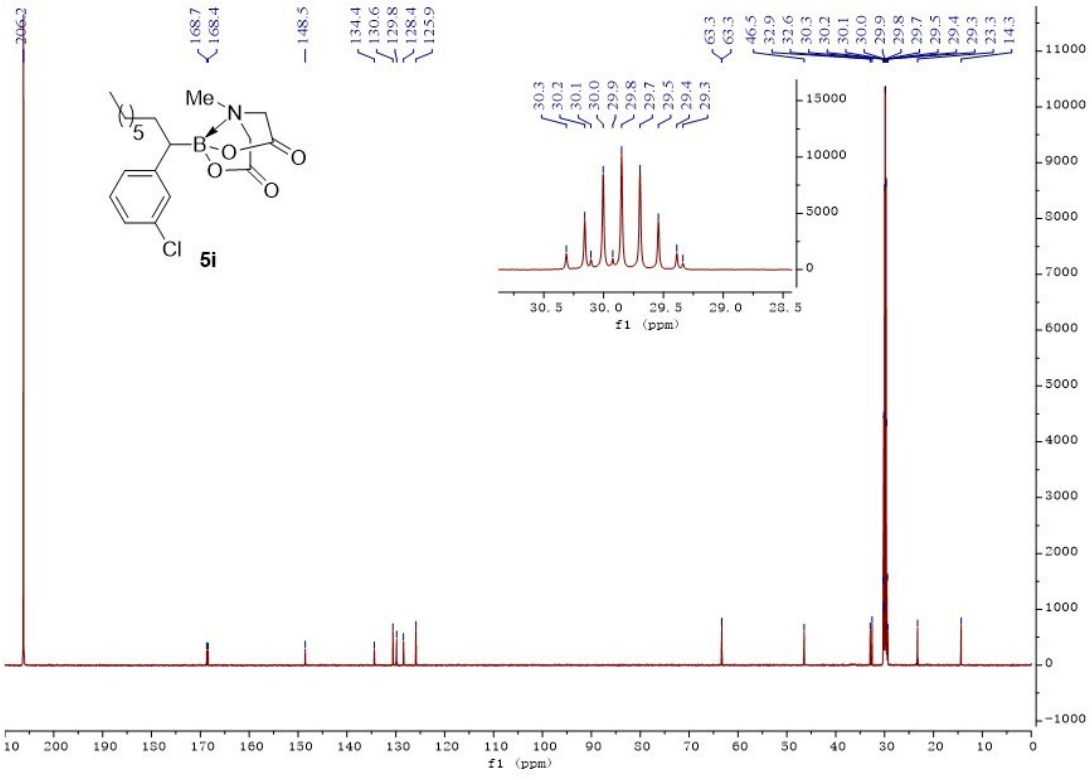

Me
N
B
O
O
O
O
5
5g
11.4
f1 (ppm)

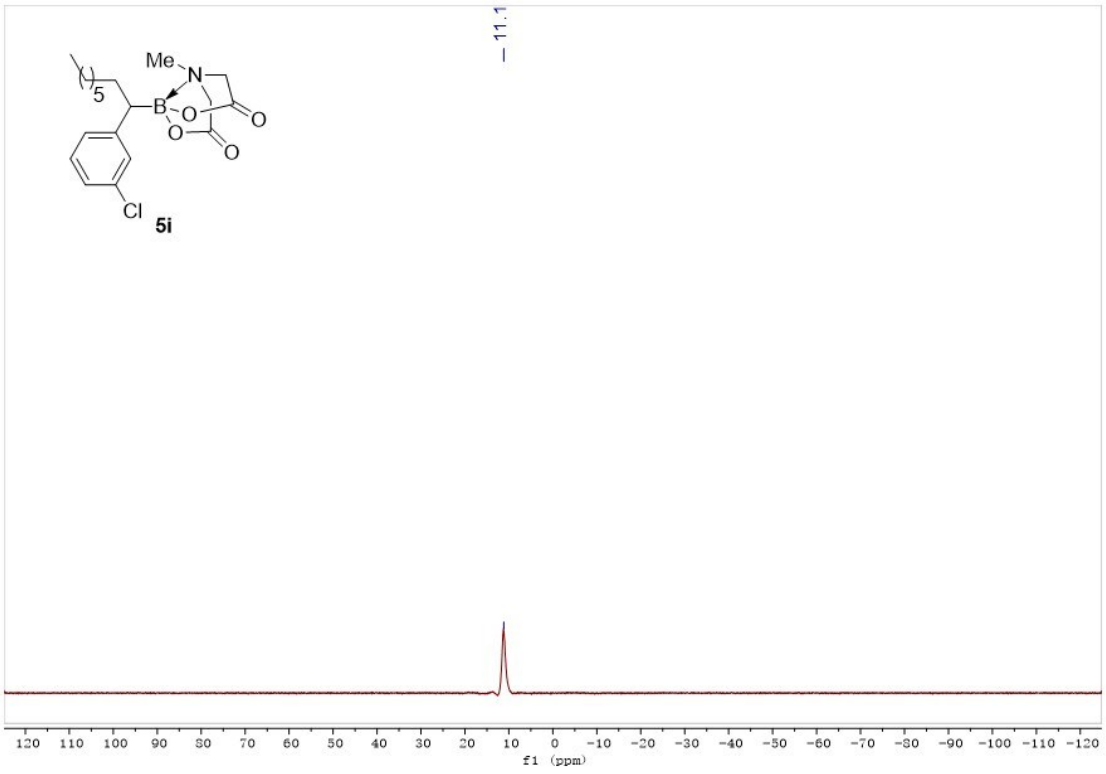

Me
N
B
O
O
O
O
5
Me
Me
5h
f1 (ppm)


5h
f1 (ppm)


5h
f1 (ppm)


Me
N
B
O
O
O
O
5
Cl
5i
f1 (ppm)


Me
N
B
O
O
O
O
5
Cl
5i
f1 (ppm)
f1 (ppm)


11.1
Me
N
B
O
O
O
O
5
Cl
5i
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)