Regiocontrolled Allylic Functionalization of Internal Alkene via Selenium-π-Acid Catalysis Guided by Boron Substitution

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1. General information

Unless otherwise noted, all commercially available materials were used without further purification. Anhydrous CH_3CN, DMF and DMSO were purchased from Acros Organics and stored under argon.

NMR–spectra were recorded on Bruker AvanceIII-400M and Ascend^{TM} 500M in solvents as indicate. Chemical shifts (δ) are given in ppm relative to tetramethylsilane (δ = 0). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (Acetone-d6: δ_H = 2.05 ppm, δ_C = 29.84 ppm). The following abbreviations were used to describe peak splitting patterns: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets). Coupling constants (*J*) were reported in hertz unit (Hz).

High-resolution mass spectra (HRMS) were recorded on a Bruker VPEXII spectrometer with EI and ESI mode unless otherwise stated.

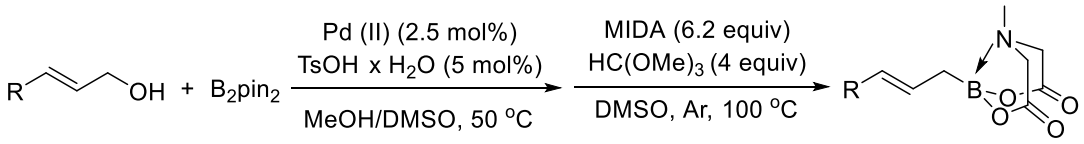
Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished by UV light (254 nm), or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh).

No attempts were made to optimize yields for substrate synthesis.

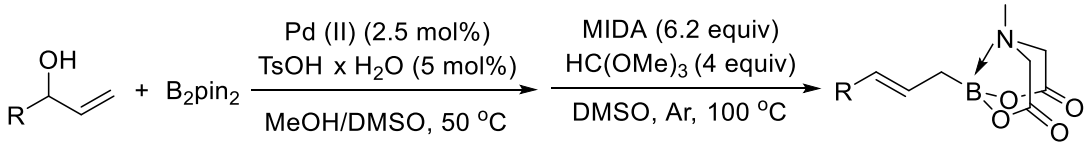
2. General procedure for preparation of the starting materials.

The allylic boronic esters were synthesized from allylic alcohols which were commercially available or reported before.[1] The allyl MIDA boronates were prepared according to the following procedure.[2]

General procedure A:

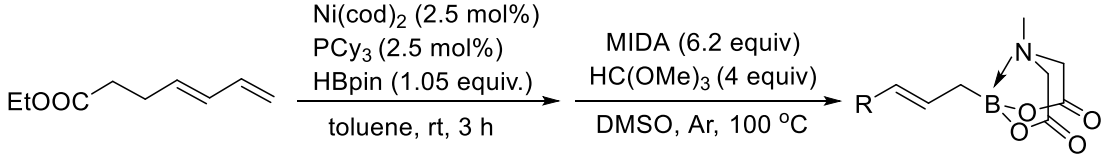


General procedure B:



An oven-dried round bottom flask was charged with di-μ-chlorobis{2-[(dimethylamino)methyl]phenyl-C, N}dipalladium (II) (0.025 equiv), bis(pinacolato) diboron (1.5 equiv) and $T_SOH \cdot H_2O$ (0.05 equiv). After being sealed with a septum, the flask was connected to an argon-vacuum line and was evacuated and backfilled with argon (x 3). DMSO (10 mL), MeOH (10 mL) and the allylic alcohol (10 mmol, 1 equiv) were added in turn by syringe under an argon atmosphere. The resulting reaction mixture was stirred vigorously at 50 ºC overnight then cooled to r.t. and H_2O was added. Ethyl acetate was then added and the layers were separated. The aqueous layer was extracted with ethyl acetate and the combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by flash chromatography. Then anhydrous DMSO (5 mL) was added to dissolve the product which was then added via syringe to a suspension of N-methyliminodiacetic acid (MIDA, 6.2 equiv) and $CH(OMe)_3$ (4.0 equiv) in DMSO (5 mL). The resulting mixture was stirred at 100 ºC until the allylic boronic esters was used up by GC-MS monitoring. After cooling to r.t., the reaction mixture was diluted with ethyl acetate (20 mL) and water (10 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 $MgSO_4$ 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.

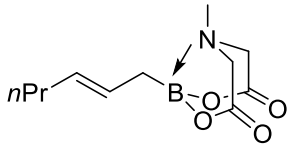
General procedure C[3]:



An oven-dried round bottom flask equipped with a magnetic stir bar was charged with bis(1,5-cyclooctadiene)nickel(0) (0.25 mmol), tricyclohexylphosphine (0.25 mmol), and toluene (20 mL) in the glovebox. The vial was capped and stirred for two minutes, then (*E*)-ethyl hepta-4,6-dienoate (10 mmol) was added, followed by pinacolborane

(10.5 mmol). The vial was capped with a teflon cap, sealed with electrical tape, removed from the glovebox, and allowed to stir at rt for 3 h. The reaction was concentrated in vacuo, and the crude reaction mixture was purified on silica gel. Then anhydrous DMSO (5 mL) was added to dissolve the product which was then added via syringe to a suspension of N-methyliminodiacetic acid (MIDA, 6.2 equiv) and $CH(OMe)_3$ (4.0 equiv) in DMSO (5 mL). The resulting mixture was stirred at 100 ºC until the allylic boronic esters was used up by GC-MS monitoring. After cooling to r.t., the reaction mixture was diluted with ethyl acetate (20 mL) and water (10 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 $MgSO_4$ 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.

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

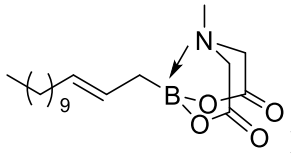


Following the general procedure A, the product **1a** was obtained in 84 % yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.30 (PE/EA = 1:3).

^{1}H NMR (400 MHz, Acetone-d_6) δ = 5.51-5.37 (m, 2H), 4.18 (d, J = 16.8 Hz, 2H), 3.94 (d, J = 16.9 Hz, 2H), 3.12 (s, 3H), 1.94 (q, J = 6.9 Hz, 2H), 1.56 (d, J = 6.8 Hz, 2H), 1.34 (sext, J = 7.4 Hz, 2H), 0.87 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ = 168.9, 129.9, 127.0, 61.8, 45.6, 34.5, 22.4, 13.6. ^{11}B NMR (128 MHz, DMSO-d_6) δ = 12.02.

HRMS: calculated for $C_{11}H_{18}BNO_4Na$ $[M+Na]^+$, 262.1223; Found, 262.1212.

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

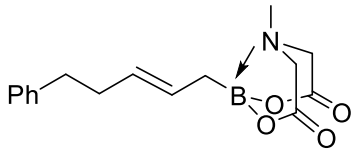


Following the general procedure B, the product **1c** was obtained in 60% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.31 (PE/EA = 1:4);

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 5.40 (d, J = 4.9 Hz, 2H), 3.92 (d, J = 16.9 Hz, 2H), 3.72 (d, J = 17.0 Hz, 2H), 2.87 (s, 3H), 1.98-1.94 (m, 1H), 1.50 (d, J = 4.8 Hz, 2H), 1.33-1.27 (m, 17H), 0.88 (t, J = 6.7 Hz, 3H). ^{11}B NMR (160 MHz, Acetonitrile-d_3) δ 12.3. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 169.0, 132.2, 127.3, 63.0, 46.5, 33.5, 32.6, 30.5, 30.4(2C), 30.2, 30.1, 30.0, 23.4, 14.4.

HRMS: calculated for $C_{18}H_{32}BNO_4Na$ $[M+Na]^+$, 360.2320; Found 360.2313.

(*E*)-6-methyl-2-(6-phenylhex-2-en-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (1e)

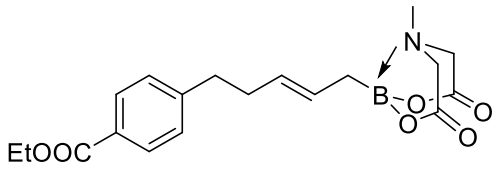


Following the general procedure B, the product **1e** was obtained in 37% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.29 (PE/EA = 1:4);

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.26 (t, J = 7.4 Hz, 2H), 7.22-7.11 (m, 3H), 5.68-5.00 (m, 2H), 4.14 (d, J = 17.1 Hz, 2H), 3.78 (d, J = 17.0 Hz, 2H), 2.77 (s, 3H), 2.61 (t, J = 7.6 Hz, 2H), 2.34 – 2.18 (m, 2H), 1.41 (d, J = 6.2 Hz, 2H). ^{11}B NMR (128 MHz, DMSO-d_6) δ 12.2. ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.8, 141.8, 129.5, 128.4, 128.2, 127.5, 125.7, 61.7, 45.5, 35.4, 34.1.

HRMS: calculated for $C_{16}H_{20}BNO_4Na$ $[M+Na]^+$, 324.1381; Found, 324.1369.

ethyl (*E*)-4-(5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-3-en-1-yl)benzoate (1f)

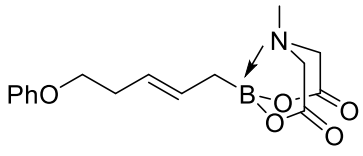


Following the general procedure B, the product **1f** was obtained in 54% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.15 (PE/EA = 1:4).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 5.44-5.28 (m, 2H), 4.30 (q, J = 7.1 Hz, 2H), 4.16 (d, J = 17.0 Hz, 2H), 3.83 (d, J = 17.0 Hz, 2H), 2.79 (s, 3H), 2.69 (t, J = 7.6 Hz, 2H), 2.28 (q, J = 7.1 Hz, 2H), 1.41 (d, J = 6.9 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{11}B NMR (128 MHz, DMSO-d_6) δ 11.2. ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.8, 165.7, 147.7, 129.1, 129.0, 128.7, 127.9, 127.5, 61.7, 60.5, 45.5, 35.3, 33.7, 14.2.

HRMS: calculated for $C_{19}H_{24}BNO_6Na$ $[M+Na]^+$, 396.1592; Found, 396.1580.

(*E*)-6-methyl-2-(5-phenoxypent-2-en-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione (1g)

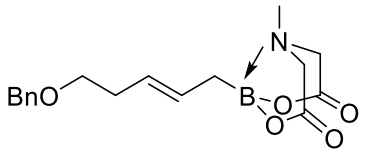


Following the general procedure B, the product **1g** was obtained in 16% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.23 (PE/EA = 1:4).

^{1}H NMR (500 MHz, DMSO-d_6) δ 7.29-7.25 (m, 2H), 6.93- 6.90 (m, 3H), 5.53 (dt, J = 15.1, 7.3 Hz, 1H), 5.40 (dt, J = 15.4, 6.7 Hz, 1H), 4.19 (d, J = 17.0 Hz, 2H), 4.05-3.81 (m, 4H), 2.86 (s, 3H), 2.39 (q, J = 6.7 Hz, 2H), 1.48 (d, J = 7.4 Hz,2H). ^{11}B NMR (160 MHz, Acetonitrile-d_3) δ 12.2. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 169.0, 159.9, 130.5, 130.5, 130.4, 127.9, 121.5, 115.4, 68.5, 63.0, 46.5, 33.5.

HRMS: calculated for $C_{16}H_{20}BNO_5Na$ $[M+Na]^+$, 340.1330; Found, 340.1321.

(*E*)-2-(5-(benzyloxy)pent-2-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1h)

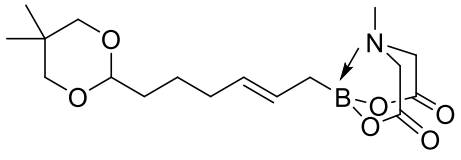


Following the general procedure B, the product **1h** was obtained in 34% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.29 (PE/EA = 1:4).

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 7.44-7.25 (m, 5H), 5.49 (dt, J = 14.8, 7.3 Hz, 1H), 5.41 (dt, J = 14.9, 6.6 Hz, 1H), 4.46 (s, 2H), 3.81 (d, J = 16.9 Hz, 2H), 3.69 (d, J = 16.9 Hz, 2H), 3.47 (t, J = 6.3 Hz, 2H), 2.83 (s, 3H), 2.25 (q, J = 6.4 Hz, 2H), 1.53 (d, J = 6.9 Hz, 2H). ^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.2. ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 169.0, 139.9, 129.5, 129.3, 128.8, 128.8, 128.4, 73.3, 70.9, 62.9, 46.3, 34.1.

HRMS: calculated for $C_{17}H_{22}BNO_5Na$ $[M+Na]^+$, 354.1486; Found, 354.1479.

(*E*)-2-(6-(5,5-dimethyl-1,3-dioxan-2-yl)hex-2-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1i)

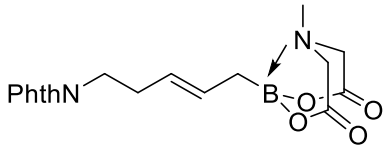


Following the general procedure B, the product **1i** was obtained in 37% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.28 (PE/EA = 1:4).

^{1}H NMR (400 MHz, DMSO-d_6) δ 5.73-4.98 (m, 2H), 4.39 (t, J = 4.9 Hz, 1H), 4.18 (d, J = 17.1 Hz, 2H), 3.91 (d, J = 17.0 Hz, 2H), 3.50 (d, J = 10.9 Hz, 2H), 3.36 (d, J = 10.7 Hz, 2H), 2.85 (s, 3H), 1.93 (q, J = 6.9 Hz, 2H), 1.51-1.34 (m, 6H), 1.07 (s, 3H), 0.66 (s, 3H). ^{11}B NMR (160 MHz, Acetone- d_6) δ 11.2. ^{13}C NMR (125 MHz, Acetone- d_6) δ 168.8, 129.8, 127.1, 101.1, 76.0, 61.8, 45.6, 33.8, 32.1, 29.7, 23.6, 22.8, 21.4.

HRMS: calculated for $C_{17}H_{28}BNO_6Na$ $[M+Na]^+$, 376.1905; Found, 376.1890.

(*E*)-2-(5-(1,3-dioxoisoindolin-2-yl)pent-2-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1j)

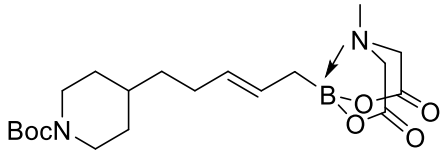


Following the general procedure B, the product **1j** was obtained in 65% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.14 (PE/EA = 1:4).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87-7.81 (m, 4H), 5.40 (dt, J = 14.9, 7.4 Hz, 1H), 5.28 (dt, J = 15.3, 6.8 Hz, 1H), 4.15 (d, J = 17.0 Hz, 1H), 3.87 (d, J = 17.0 Hz, 2H), 3.57 (t, J = 7.1 Hz, 2H), 2.80 (s, 3H), 2.27 (q, J = 7.0 Hz, 2H), 1.39 (d, J = 7.3 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.8, 167.8, 134.4, 131.5, 129.8, 126.0, 123.0, 61.7, 45.6, 37.5, 31.4.

HRMS: calculated for $C_{18}H_{19}BN_2O_6K$ $[M+K]^+$, 409.1082; Found, 409.1055.

tert-butyl (E)-4-(5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-3-en-1-yl)piperidine-1-carboxylate (1k)

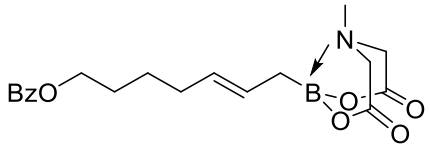


Following the general procedure A, the product **1k** was obtained in 15% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.11 (PE/EA = 1:4).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 5.50-5.32 (m, 2H), 3.99 (d, J = 13.4 Hz, 2H), 3.92 (d, J = 16.9 Hz, 2H), 3.72 (d, J = 16.9 Hz, 2H), 2.87 (s, 3H), 2.66 (s, 2H), 2.04-1.97 (m, 2H), 1.64 (d, J = 13.2 Hz, 2H), 1.51 (d, J = 6.1 Hz, 2H), 1.41 (s, 10H), 1.29-1.23 (m, 2H), 0.98 (qd, J = 12.4, 4.3 Hz, 2H). ^{11}B NMR (160 MHz, Acetonitrile-d_3) δ 12.3. ^{13}C NMR (125 MHz, Acetone-d_6) δ 169.0, 155.5, 132.0, 127.5, 79.5, 63.0, 46.6, 37.2, 36.1, 32.9, 30.5, 28.6.

HRMS: calculated for $C_{20}H_{33}BN_2O_6Na$ $[M+Na]^+$, 431.2328; Found, 431.2329.

(*E*)-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-5-en-1-yl benzoate (1l)

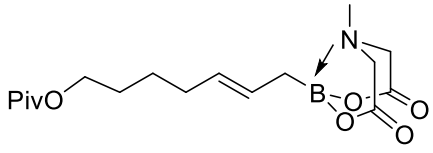


Following the general procedure B, the product **1l** was obtained in 30% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.22 (PE/EA = 1:4).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.51 (d, J = 7.5 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.08 (t, J = 7.6 Hz, 2H), 4.9-4.84 (m, 2H), 3.81 (t, J = 6.5 Hz, 2H), 3.74 (d, J = 17.0 Hz, 2H), 3.46 (d, J = 17.0 Hz, 2H), 2.40 (s, 3H), 1.56 (q, J = 7.0 Hz, 2H), 1.24 (p, J = 6.9 Hz, 2H), 0.98 (q, J = 5.9, 4.6 Hz, 4H). ^{11}B NMR (128 MHz, DMSO-d_6) δ 12.2. ^{13}C NMR (125 MHz, Acetone-d_6) δ 173.7, 168.7, 129.3, 127.8, 62.9, 60.4, 46.3, 34.1, 27.2, 25.6, 14.6.

HRMS: calculated for $C_{19}H_{25}BNO_6$ $[M+H]^+$, 374.1773; Found, 374.1789.

(*E*)-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-5-en-1-yl pivalate (1m)

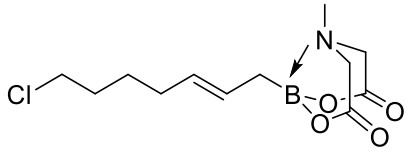


Following the general procedure A, the product **1m** was obtained in 46% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.23 (PE/EA = 1:4).

^{1}H NMR (400 MHz, DMSO-d_6) δ 5.47-5.18 (m, 2H), 4.18 (d, J = 17.0 Hz, 2H), 3.99 (t, J = 6.5 Hz, 2H), 3.90 (d, J = 17.0 Hz, 2H), 2.85 (s, 3H), 1.96 (q, J = 7.0 Hz, 3H), 1.60 -1.50 (m, 3H), 1.43 (d, J = 7.0 Hz, 3H), 1.37-1.29 (m, 3H), 1.13 (s, 9H). ^{11}B NMR (128 MHz, DMSO-d_6) δ 11.9. ^{13}C NMR (101 MHz, DMSO-d_6) δ 177.4, 168.8, 129.7, 127.3, 63.7, 61.8, 45.6, 38.2, 31.8, 27.6, 26.9, 25.5.

HRMS: calculated for $C_{17}H_{28}BNO_6Na$ $[M+Na]^+$, 376.1905; Found, 376.1893.

(*E*)-2-(7-chlorohept-2-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (1n)

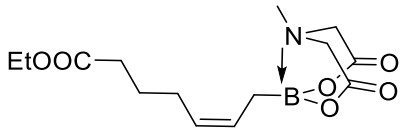


Following the general procedure A, the product **1n** was obtained in 32% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.26 (PE/EA = 1:4).

^{1}H NMR (500 MHz, DMSO-d_6) δ 5.43-5.35 (m, 1H), 5.32-5.27 (m, 1H), 4.18 (d, J = 17.0 Hz, 2H), 3.91 (d, J = 17.0 Hz, 2H), 3.62 (t, J = 6.6 Hz, 2H), 2.85 (s, 3H), 1.96 (q, J = 7.0 Hz, 2H), 1.76-1.61 (m, 2H), 1.46-1.38 (m, 4H). ^{11}B NMR (128 MHz, DMSO-d_6) δ 11.6. ^{13}C NMR (125 MHz, DMSO-d_6) δ 168.8, 129.5, 127.4, 61.8, 45.6, 45.3, 31.6, 31.4, 26.4.

HRMS: calculated for $C_{12}H_{19}BClNO_4Na$ $[M+Na]^+$, 310.0990; Found, 310.0996.

ethyl (*Z*)-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-5-enoate (1o)

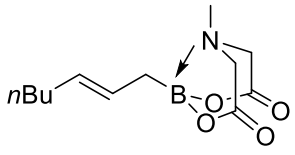


Following the general procedure C, the product **1o** was obtained in 18% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.13 (PE/EA = 1:4).

^{1}H NMR (500 MHz, Acetone-d_6) δ 5.55-5.49 (m, 1H), 5.35-5.29 (m,1H), 4.19 (d, J = 16.9 Hz, 2H), 4.08 (q, J = 7.1 Hz, 2H), 4.00 (d, J = 16.8 Hz, 2H), 3.12 (s, 3H), 2.30 (t, J = 7.4 Hz, 2H), 2.15-2.09 (m, 2H), 2.05 (p, J = 2.2 Hz, 2H), 1.65 (p, J = 7.5 Hz, 2H), 1.59 (d, J = 8.0 Hz, 2H), 1.21 (t, J = 7.1 Hz, 3H). ^{11}B NMR (128 MHz, DMSO-d_6) δ 12.0. ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 174.3, 169.0, 129.7, 127.5, 62.9, 60.8, 46.6, 34.3, 27.2, 25.6, 14.6.

HRMS: calculated for $C_{14}H_{22}BNO_6K$ $[M+K]^+$, 350.1174; Found, 350.1168.

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

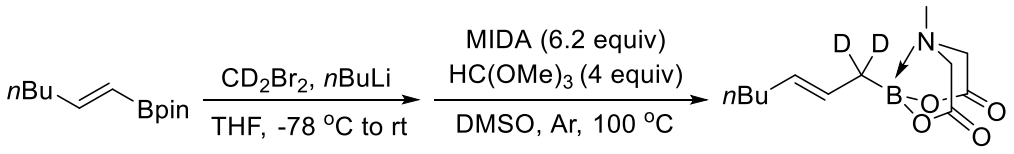


Following the general procedure A, the product **1p** was obtained in 65% yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.27 (PE/EA = 1:4).

^{1}H NMR (500 MHz, Acetone-d_6) δ 5.69-5.20 (m, 2H), 4.17 (d, J = 16.8 Hz, 2H), 3.93 (d, J = 16.9 Hz, 2H), 3.10 (s, 3H), 1.55 (d, J = 6.7 Hz, 2H), 1.97 (q, J = 6.6 Hz, 2H),1.41-1.24 (m, J = 4.1, 3.7 Hz, 4H), 1.13-0.77 (m, 3H). ^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.3. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 169.1, 132.2, 127.3, 63.0, 46.5, 33.2, 32.7, 23.0, 14.2.

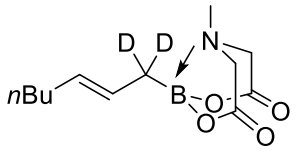
HRMS: calculated for $C_{12}H_{20}BNO_4Na$ $[M+Na]^+$, 276.1378; Found, 276.1379.

Synthesis of the deuterium allyl boronate 1p-D_2:[4]



A solution of vinylboronic acid pinacol ester and d_2-dibromomethane (1.5 equiv.) in THF was cooled to -78 °C. To this was added 2.5 M *n*BuLi in hexane (1.6 equiv.) dropwise from a syringe, and the reaction mixture was stirred at -78 °C for 0.5 h. It was then rapidly brought to room temperature and refluxed at 65 °C for 1.5 h. Then cooled to r.t. and H_2O was added. Ethyl acetate was then added and the layers were separated. The aqueous layer was extracted with ethyl acetate and the combined organic layers were dried ($MgSO_4$) and concentrated in vacuo. The crude product was purified by flash chromatography. Then anhydrous DMSO was added to dissolve the product which was then added via syringe to a suspension of N-methyliminodiacetic acid (MIDA, 6.2 equiv) and $CH(OMe)_3$ (4.0 equiv) in DMSO. The resulting mixture was stirred at 100 ºC until the allylic boronic esters was used up by GC-MS monitoring. After cooling to r.t., the reaction mixture was diluted with ethyl acetate and water. The organic phase was seperated and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layer was dried over anhydrous $MgSO_4$ 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.

(*E*)-2-(hept-2-en-1-yl-1,1-d_2)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione



^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 5.44-5.36 (m, 2H), 3.93 (d, *J* = 16.9 Hz, 2H), 3.72 (d, *J* = 16.9 Hz, 2H), 2.88 (s, 3H), 2.02-1.94 (m, 2H), 1.42-1.23 (m, 4H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 169.1, 132.2, 127.3, 63.0, 46.5, 33.2, 32.7, 23.0, 14.2.

HRMS: calculated for $C_{12}H_{18}D_2BNO_4Na$ $[M+Na]^+$, 278.1503; Found, 278.1500.

3. General procedure for the chlorination reaction

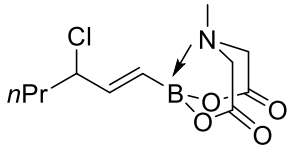
General procedure D:

The allyl MIDA boronates **1** (0.2 mmol, 1.0 equiv), phenyl selenium chloride (10 mol %, 0.02 mmol), *N*-chlorosuccinimide (NCS, 0.22 mmol, 1.1 equiv) and 4 Å MS (20 mg) were added in 3 mL CH_3CN producing the pale yellow solution. The reaction mixture was stirred at room temperature overnight. After completion of the reaction, the p-iodobenzole (0.2 mmol) was added and the NMR yield was determined by ^1H NMR. After that, the crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc from 2:1 to1:3, v/v) to afford the pure product as a white solid.

General procedure E:

The allyl MIDA boronates **1** (0.2 mmol, 1.0 equiv), phenyl selenium chloride (10 mol %, 0.02 mmol) and 4 Å MS (20 mg) were added in 1 mL CH_3CN. A solution of *N*-chlorosuccinimide (0.22 mmol, in 2 mL CH_3CN) was prepared then drawn into a 5 mL syringe equipped with a teflon needle. The solution of NCS was added via syringe pump at the rate of 0.4 mL/h. The reaction mixture was stirred at room temperature overnight. After completion of the reaction, the p-iodobenzole (0.2 mmol) was added and the NMR yield was determined by ^1H NMR. After that, the crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc from 2:1 to1:3, v/v) to afford the pure product as a white solid.

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

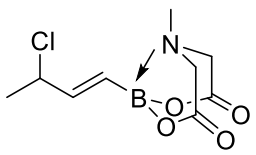


Following the general procedure **D**, the product **2a** was obtained in 84% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.25 (PE/EA = 1:4).

^1H NMR (400 MHz, Acetone-d_6) δ 6.12 (dd, *J* = 17.4, 7.9 Hz, 0H), 5.77 (dd, *J* = 17.5, 1.0 Hz, 0H), 4.50 (q, *J* = 7.1 Hz, 0H), 4.24 (d, *J* = 16.9 Hz, 1H), 4.05 (d, *J* = 17.0 Hz, 1H), 3.02 (s, 1H), 1.80 (dtd, *J* = 8.4, 6.6, 1.8 Hz, 1H), 1.56 – 1.33 (m, 1H), 0.92 (t, *J* = 7.4 Hz, 1H). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.4. ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.9, 144.9, 65.1, 62.4, 47.5, 41.0, 20.4, 13.7.

HRMS: calculated for $C_{11}H_{17}BClNO_4Na$ $[M+Na]^+$, 296.0833; Found, 296.0823.

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

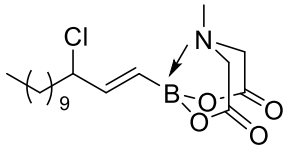


Following the general procedure **E**, the product **2b** was obtained in 64% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.26 (PE/EA = 1:4).

^{1}H NMR (400 MHz, Acetone-d_6) δ 6.17 (dd, J = 17.5, 7.1 Hz, 1H), 5.77 (d, J = 17.4 Hz, 1H), 4.66 (p, J = 6.7 Hz, 1H), 4.24 (d, J = 17.0 Hz, 2H), 4.05 (d, J = 17.0 Hz, 2H), 3.01 (s, 3H), 1.58 (d, J = 6.6 Hz, 3H). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.4. ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.9, 145.9, 62.4, 60.0, 47.5, 25.1.

HRMS: calculated for $C_9H_{13}BClNO_4Na$ [M+Na]$^+$, 268.0520; Found, 268.0525.

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

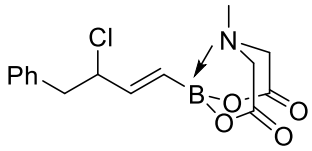


Following the general procedure **D**, the product **2c** was obtained in 84% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.30 (PE/EA = 1:4).

^{1}H NMR (400 MHz, Acetone-d_6) δ 6.12 (dd, J = 17.4, 7.9 Hz, 1H), 5.77 (dd, J = 17.5, 1.0 Hz, 1H), 4.49 (q, J = 6.8 Hz, 1H), 4.25 (d, J = 17.0 Hz, 2H), 4.05 (dd, J = 16.9, 1.7 Hz, 2H), 3.03 (s, 3H), 1.86-1.79 (m, 2H), 1.31-1.27 (m, 16H), 0.88 (t, J = 6.98 Hz, 3H). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.3. ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 169.2, 169.2, 145.5, 65.5, 62.5, 47.8, 38.8, 32.6, 30.3, 30.3, 30.2, 30.0, 29.7, 27.3, 23.4, 14.4.

HRMS: calculated for $C_{17}H_{30}BClNO_4$ [M+H]$^+$, 358.1954; Found, 358.1961.

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

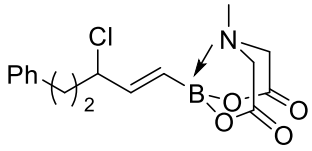


Following the general procedure **E**, the product **2d** was obtained in 51% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.27 (PE/EA = 1:4).

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.35 – 7.27 (m, 4H), 7.25 – 7.19 (m, 1H), 6.12 (dd, J = 17.4, 8.2 Hz, 1H), 5.64 (dd, J = 17.4, 0.9 Hz, 1H), 4.74 (q, J = 7.3 Hz, 1H), 4.18 (dd, J = 16.9, 1.5 Hz, 2H), 3.96 (d, J = 17.0 Hz, 1H), 3.83 (d, J = 16.9 Hz, 1H), 3.17 (dd, J = 7.3, 3.6 Hz, 1H), 2.68 (s, 3H). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.1. ^{13}C NMR (101 MHz, Acetone-d_6) δ 169.0, 168.7, 144.1, 138.8, 130.4, 129.2, 127.5, 65.3, 62.2, 47.2, 45.2.

HRMS: calculated for $C_{15}H_{17}BClNO_4Na$ [M+Na]$^+$, 344.0834; Found, 344.0819.

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



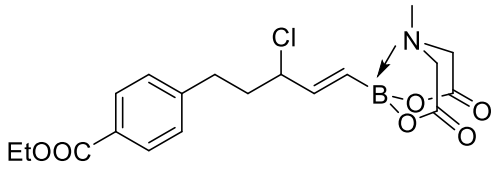
Following the general procedure **E**, the product **2e** was obtained in 71% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.30 (PE/EA = 1:4).

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.39 – 7.21 (m, 4H), 7.21 – 7.11 (m, 1H), 6.18 (dd, J = 17.4, 7.7 Hz, 1H), 5.79 (dd, J = 17.5, 1.0 Hz, 1H), 4.48 (q, J = 7.2 Hz, 1H), 4.24 (dd, J = 17.0, 1.0 Hz, 2H), 4.06 (d, J = 16.9 Hz, 2H), 3.03 (s, 3H), 2.87 – 2.66 (m, 2H),

2.23 – 2.08 (m, 2H). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.4.^{13}C NMR (101 MHz, Acetone-d_6) δ 168.9, 168.9, 144.5, 141.9, 129.3, 129.3, 126.8, 64.6, 62.4, 47.6, 40.7, 33.3.

HRMS: calculated for $C_{16}H_{19}BClNO_4Na$ $[M+Na]^+$, 358.0991; Found, 358.0978.

ethyl (*E*)-4-(3-chloro-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-4-en-1-yl)benzate (2f)

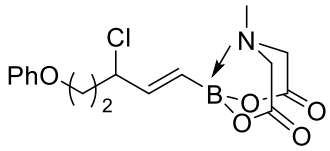


Following the general procedure **E**, the product **2f** was obtained in 66% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.16 (PE/EA = 1:4).

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.94 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 6.19 (dd, J = 17.4, 7.7 Hz, 1H), 5.81 (dd, J = 17.5, 0.9 Hz, 1H), 4.49 (q, J = 7.5 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 4.24 (d, J = 16.9 Hz, 2H), 4.06 (d, J = 16.9 Hz, 2H), 3.03 (s, 3H), 2.95 – 2.82 (m, 2H), 2.28-2.10 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.2. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 169.2, 169.2, 167.1, 147.8, 144.9, 130.4, 129.7, 129.5, 64.6, 62.6, 61.7, 47.9, 40.0, 33.3, 14.6.

HRMS: calculated for $C_{18}H_{21}BClNO_6Na$ $[M+Na]^+$, 430.1203; Found, 420.1213.

(*E*)-2-(3-chloro-5-phenoxypent-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2g)

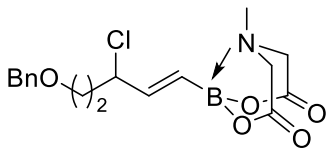


Following the general procedure **D**, the product **2g** was obtained in 58%NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.24 (PE/EA = 1:4).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.29 (dd, J = 8.6, 7.3 Hz, 2H), 6.99-6.90 (m, 3H), 6.18 (dd, J = 17.4, 7.9 Hz, 1H), 5.76 (d, J = 17.5 Hz, 1H), 4.76 (q, J = 7.8 Hz, 1H), 4.17-4.04 (m, 2H), 3.95 (d, J = 17.1 Hz, 2H), 3.77 (dd, J = 17.0, 6.4 Hz, 2H), 2.71 (s, 3H), 2.36-2.19 (m, 2H). ^{11}B NMR (160 MHz, Acetonitrile-d_3) δ 10.3. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 169.2, 169.2, 159.8, 144.7, 130.5, 121.8, 115.5, 65.5, 62.5, 62.5, 62.0, 47.8, 38.3.

HRMS: calculated for $C_{16}H_{19}BClNO_5Na$ $[M+Na]^+$, 374.0940; Found, 374.0943.

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

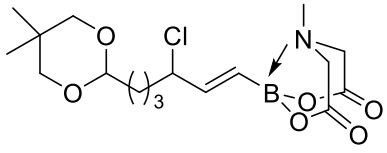


Following the general procedure **E**, the product **2h** was obtained in 64% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.27 (PE/EA = 1:4).

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 7.35 (d, J = 6.5 Hz, 4H), 7.30 (dt, J = 6.3, 2.9 Hz, 1H), 6.11 (dd, J = 17.4, 7.9 Hz, 1H), 5.70 (d, J = 17.5 Hz, 1H), 4.65 (q, J = 7.4 Hz, 1H), 4.48 (s, 2H), 3.95 (dd, J = 17.0, 2.6 Hz, 3H), 3.77 (dd, J = 17.3, 11.1 Hz, 3H), 3.61 (dtd, J = 11.0, 5.4, 2.7 Hz, 1H), 3.57-3.52 (m, 1H), 2.72 (s, 3H), 2.14-2.10 (m, 1H), 2.07-2.02 (m, 1H). ^{11}B NMR (160 MHz, Acetonitrile-d_3) δ 10.3. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 168.8, 168.8, 144.6, 139.4, 128.9, 128.2, 128.1, 73.1, 67.2, 62.1, 61.9, 47.4, 38.5.

HRMS: calculated for $C_{17}H_{21}BClNO_5Na$ [M+Na]$^+$, 388.1097; Found, 388.1081.

(*E*)-2-(3-chloro-6-(5,5-dimethyl-1,3-dioxan-2-yl)hex-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2i)

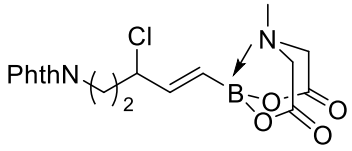


Following the general procedure **E**, the product **2i** was obtained in 79% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.28 (PE/EA = 1:4).

^{1}H NMR (500 MHz, Acetone-d_6) δ 6.11 (dd, J = 17.4, 7.9 Hz, 1H), 5.79 (d, J = 17.4 Hz, 1H), 4.50 (q, J = 7.2 Hz, 1H), 4.43 (t, J = 4.5 Hz, 1H), 4.24 (d, J = 17.0 Hz, 2H), 4.05 (dd, J = 17.0, 7.4 Hz, 2H), 3.54 (d, J = 10.7 Hz, 2H), 3.41 (d, J = 10.7 Hz, 2H), 3.02 (s, 3H), 1.85 (q, J = 6.1 Hz, 2H), 1.61-1.49 (m, 4H), 1.12 (s, 3H), 0.69 (s, 3H). ^{11}B NMR (160 MHz, Acetone-d_6) δ 10.3. ^{13}C NMR (125 MHz, Acetone-d_6) δ 168.9, 168.9, 144.8, 102.4, 77.4, 65.2, 62.4, 62.4, 47.6, 38.8, 34.9, 30.6, 23.3, 21.9, 21.7.

HRMS: calculated for $C_{17}H_{27}BClNO_6Na$ [M+Na]$^+$, 410.1515; Found, 410.1527.

(*E*)-2-(3-chloro-5-(1,3-dioxoisoindolin-2-yl)pent-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2j)

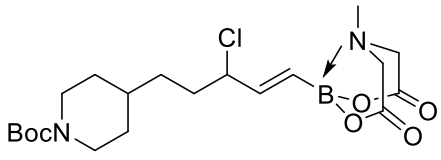


Following the general procedure **E**, the product **2j** was obtained in 63% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.15 (PE/EA = 1:4).

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.84 (d, J = 1.4 Hz, 4H), 6.18 (dd, J = 17.4, 7.5 Hz, 1H), 5.87 (dd, J = 17.5, 1.0 Hz, 1H), 4.65 (q, J = 7.0 Hz, 1H), 4.25 (dd, J = 17.0, 1.0 Hz, 2H), 4.07 (dd, J = 16.9, 2.1 Hz, 2H), 3.82 (td, J = 7.0, 2.5 Hz, 2H), 3.06 (s, 3H), 2.32 – 2.16 (m, 2H). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.3. ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.9, 168.9, 168.7, 143.9, 135.0, 133.2, 123.7, 62.4, 62.4, 62.3, 47.6, 37.4, 35.9.

HRMS: calculated for $C_{18}H_{18}BClN_2O_6Na$ [M+Na]$^+$, 427.0842; Found, 427.0851.

tert-butyl (*E*)-4-(3-chloro-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-4-en-1-yl)piperidine-1-carboxylate (2k)

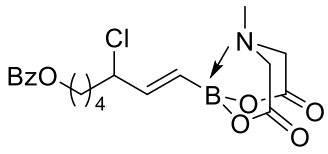


Following the general procedure **D**, the product **2k** was obtained in 78% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.11 (PE/EA = 1:4).

^{1}H NMR (400 MHz, Acetone-d_6) δ 6.13 (dd, J = 17.4, 7.9 Hz, 1H), 5.78 (dd, J = 17.4, 1.0 Hz, 1H), 4.49 (q, J = 6.8 Hz, 1H), 4.25 (d, J = 16.9 Hz, 2H), 4.05 (dd, J = 16.9, 1.8 Hz, 4H), 3.03 (s, 3H), 2.68 (bs, 2H), 1.93-1.81 (m, 2H), 1.67 (d, J = 12.6 Hz, 2H), 1.42 (s, 12H), 1.09-0.97 (m, 2H). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.4. ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.9, 155.0, 144.8, 79.1, 65.5, 62.4, 47.6, 36.4, 36.2, 34.1, 33.0, 32.9, 28.6.

HRMS: calculated for $C_{20}H_{32}BClN_2O_6Na$ $[M+Na]^+$, 465.1938; Found, 465.1921.

(*E*)-5-chloro-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-6-en-1-yl benzoate (2l)

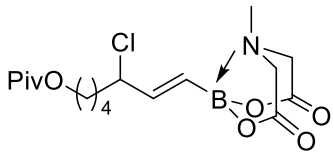


Following the general procedure **E**, the product **2l** was obtained in 79% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.23 (PE/EA = 1:4).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.05-7.98 (m, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 6.10 (dd, J = 17.5, 7.8 Hz, 1H), 5.71 (d, J = 17.5 Hz, 1H), 4.51 (q, J = 7.2 Hz, 1H), 4.30 (t, J = 6.4 Hz, 2H), 3.95 (d, J = 17.0 Hz, 2H), 3.78 (dd, J = 17.1, 6.2 Hz, 2H), 1.92-1.86 (m, 2H), 1.82-1.74 (m, 2H), 1.62-1.51 (m, 2H). ^{11}B NMR (160 MHz, Acetonitrile-d_3) δ 10.3. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 169.2, 167.2, 145.3, 134.0, 131.5, 130.2, 129.6, 65.5, 65.2, 62.5, 47.8, 38.4, 28.8, 23.9.

HRMS: calculated for $C_{19}H_{24}BClNO_6$ $[M+H]^+$, 408.1383; Found, 408.1390.

(*E*)-5-chloro-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-6-en-1-yl pivalate (2m)

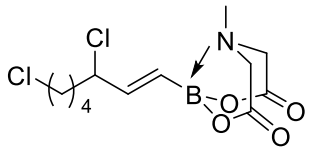


Following the general procedure **E**, the product **2m** was obtained in 80% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.23 (PE/EA = 1:4).

^{1}H NMR (400 MHz, Acetone-d_6) δ 6.13 (dd, J = 17.4, 7.8 Hz, 1H), 5.79 (dd, J = 17.4, 0.9 Hz, 1H), 4.52 (q, J = 7.1 Hz, 1H), 4.24 (d, J = 17.0 Hz, 2H), 4.14-3.90 (m, 4H), 3.02 (s, 3H), 1.92-1.84 (m, 2H), 1.74-1.62 (m, 2H), 1.60-1.44 (m, 0H), 1.17 (s, 9H). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.3. ^{13}C NMR (101 MHz, Acetone-d_6) δ 178.3, 168.9, 168.9, 144.7, 65.2, 64.5, 62.4, 47.6, 39.2, 38.5, 28.8, 27.5, 23.7.

HRMS: calculated for $C_{17}H_{27}BClNO_6Na$ $[M+Na]^+$, 410.1515; Found,410.1514.

(*E*)-2-(3,7-dichlorohept-1-en-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2n)

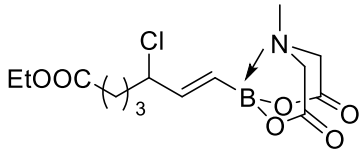


Following the general procedure **E**, the product **2n** was obtained in 79% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.27 (PE/EA = 1:4).

^{1}H NMR (500 MHz, Acetone-d_6) δ 6.13 (dd, J = 17.5, 7.8 Hz, 1H), 5.80 (d, J = 17.4 Hz, 1H), 4.52 (q, J = 7.2 Hz, 1H), 4.25 (d, J = 16.9 Hz, 2H), 4.05 (dd, J = 16.9, 3.8 Hz, 2H), 3.63 (t, J = 6.6 Hz, 2H), 3.03 (s, 3H), 1.91-1.78 (m, 4H), 1.67-1.53 (m, 2H). ^{11}B NMR (160 MHz, Acetone-d_6) δ 10.4. ^{13}C NMR (125 MHz, Acetone-d_6) δ 168.9, 168.9, 144.7, 65.0, 62.4, 47.6, 45.6, 38.2, 32.8, 24.7.

HRMS: calculated for $C_{12}H_{18}BCl_2NO_4Na$ [M+Na]$^+$, 344.0600; Found, 344.0608.

ethyl (*E*)-5-chloro-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-6-enoate (2o)

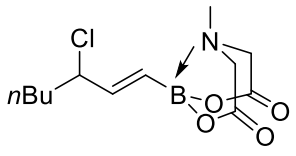


Following the general procedure **E**, the product **2o** was obtained in 73% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.14 (PE/EA = 1:4).

^{1}H NMR (400 MHz, Acetone-d_6) δ 6.12 (dd, J = 17.4, 7.8 Hz, 1H), 5.80 (dd, J = 17.4, 1.0 Hz, 1H), 4.53 (q, J = 6.8 Hz, 1H), 4.25 (d, J = 16.9 Hz, 2H), 4.13-4.01 (m, 4H), 3.03 (s, 3H), 2.34 (t, J = 7.3 Hz, 2H), 1.92-1.83 (m, 2H), 1.80-1.64 (m, 2H), 1.20 (t, J = 7.2 Hz, 3H). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.3. ^{13}C NMR (101 MHz, Acetone-d_6) δ 173.3, 169.0, 168.9, 144.6, 64.8, 62.4, 60.6, 47.5, 38.1, 33.8, 22.7, 14.5.

HRMS: calculated for $C_{14}H_{21}BClNO_6Na$ [M+Na]$^+$, 368.1045; Found, 368.1028.

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



R_F = 0.13 (PE/EA = 1:4).

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 6.09 (dd, J = 17.4, 7.9 Hz, 1H), 5.69 (dd, J = 17.5, 0.9 Hz, 1H), 4.48 (q, J = 7.2, 6.7 Hz, 1H), 3.97 (d, J = 17.0 Hz, 2H), 3.80 (dd, J = 17.1, 3.5 Hz, 2H), 2.77 (s, 3H), 1.85-1.80 (m, 2H), 1.48-1.24 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H). ^{11}B NMR (160 MHz, Acetonitrile-d_3) δ 10.2. ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 169.3, 169.2, 145.5, 65.5, 62.6, 47.9, 38.6, 29.4, 22.8, 14.2.

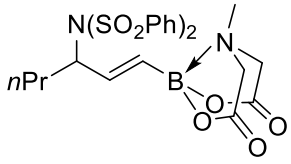
HRMS: calculated for $C_{12}H_{19}BClNO_4Na$ [M+Na]$^+$, 310.0988; Found, 310.0991.

4. General procedure for the imidation reaction

General procedure F:

Under an argon atmosphere the allyl MIDA boronates **1** (0.2 mmol, 1.0 equiv) and NFSI (0.3 mmol, 1.5 equiv) diphenyl diselenide (0.02 mmol, 10% mmol) and 4 Å molecular sieves (powder) were added to a 15 mL Schlenk tube. The dry DCE (2 mL) was added to the reaction mixture. After stirring at 35 ℃ for 12 h the solvent was evaporated. The *p*-iodobenzole (0.2 mmol) was added and the NMR yield was determined by ^{1}H NMR. After that, the crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc from 2:1 to1:3, v/v) to afford the pure product as a white solid.

(*E*)-*N*-(1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hex-1-en-3-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (3a)

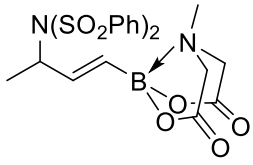


Following the general procedure **F**, the product **3a** was obtained in 68% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.27 (PE/EA = 1:4).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.90 (d, J = 7.9 Hz, 4H), 7.82-7.76 (m, 2H), 7.66 (t, J = 7.9 Hz, 4H), 6.15 (dd, J = 17.7, 7.1 Hz, 1H), 5.48 (dd, J = 17.7, 1.1 Hz, 1H), 4.52 (q, J = 7.2 Hz, 1H), 4.23 (d, J = 17.1 Hz, 2H), 3.91 (dd, J = 17.1, 13.0 Hz, 2H), 2.63 (s, 3H), 2.06-1.93 (m, 1H), 1.58 (t, J = 11.7 Hz, 1H), 1.30-0.92 (m, 2H), 0.73 (t, J = 7.3 Hz, 3H). ^{11}B NMR (160 MHz, Acetonitrile-d_3) δ 10.2. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 169.1, 169.1, 142.8, 135.2, 130.2, 129.2, 67.5, 62.4, 47.7, 36.4, 20.9, 13.8.

HRMS: calculated for $C_{23}H_{27}BN_2O_8S_2Na$ $[M+Na]^+$, 557.1198; Found, 557.1187.

(*E*)-*N*-(4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)but-3-en-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (3b)

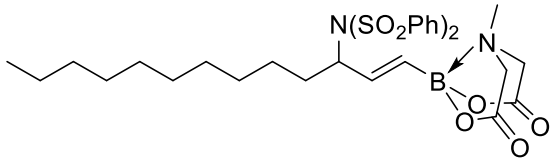


Following the general procedure **F**, the product **3b** was obtained in 56% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.26 (PE/EA = 1:4).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.95-7.89 (m, 4H), 7.77-7.72 (m, 2H), 7.65-7.59 (m, 4H), 6.15 (dd, J = 17.9, 5.4 Hz, 1H), 5.44 (dd, J = 17.9, 1.7 Hz, 1H), 4.81 (qdd, J = 7.0, 5.5, 1.7 Hz, 1H), 3.94 (d, J = 17.0 Hz, 2H), 3.70 (dd, J = 17.0, 5.2 Hz, 2H), 2.66 (s, 3H), 1.52 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 169.1, 143.9, 140.9, 135.2, 130.3, 129.1, 62.3, 62.3, 47.7, 19.6.

HRMS: calculated for $C_{21}H_{23}BN_2O_8S_2Na$ $[M+Na]^+$, 529.0885; Found, 529.0862.

(*E*)-*N*-(1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)tridec-1-en-3-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (3c)

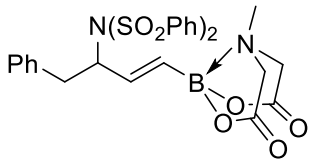


Following the general procedure **F**, the product **3c** was obtained in 64% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.32 (PE/EA = 1:4).

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.90 (d, J = 7.9 Hz, 4H), 7.81-7.75 (m, 2H), 7.66 (t, J = 7.8 Hz, 4H), 6.15 (dd, J = 17.8, 7.0 Hz, 1H), 5.49 (dd, J = 17.9, 1.2 Hz, 1H), 4.50 (q, J = 7.3 Hz, 1H), 4.23 (dd, J = 17.1, 2.2 Hz, 2H), 3.92 (dd, J = 17.1, 11.1 Hz, 2H), 2.63 (s, 3H), 2.01-1.90 (m, 1H), 1.67-1.60 (m, 1H), 1.28-1.06 (m, 16H), 0.86 (t, J = 6.8 Hz, 3H). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.2. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 169.1, 169.1, 142.9, 135.2, 130.2, 129.2, 67.8, 62.4, 47.7, 34.3, 32.6, 30.3, 30.2, 30.1, 30.0, 29.7, 27.6, 23.4, 14.4.

HRMS: calculated for $C_{30}H_{41}BN_2O_8S_2Na$ $[M+Na]^+$, 655.2295; Found, 655.2296.

(*E*)-*N*-(4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-1-phenylbut-3-en-2-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (3d)

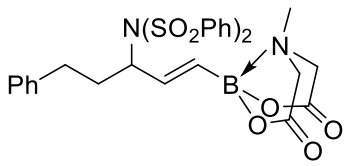


Following the general procedure **F**, the product **3d** was obtained in 30% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.27 (PE/EA = 1:4).

^{1}H NMR (500 MHz, Acetone-d_6) δ 8.04 (d, J = 7.8 Hz, 4H), 7.81-7.75 (m, 2H), 7.68 (t, J = 7.4 Hz, 4H), 7.25 (t, J = 7.4 Hz, 2H), 7.18 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 7.5 Hz, 2H), 6.41 (dd, J = 17.7, 7.7 Hz, 1H), 5.31 (d, J = 17.7 Hz, 1H), 4.80 (ddd, J = 11.3, 7.6, 3.9 Hz, 1H), 4.15 (d, J = 16.9 Hz, 2H), 3.85 (d, J = 16.9 Hz, 1H), 3.73 (d, J = 16.9 Hz, 1H), 3.51 (dd, J = 13.0, 11.1 Hz, 1H), 2.96 (dd, J = 13.1, 4.0 Hz, 1H), 2.51 (s, 3H). ^{11}B NMR (160 MHz, Acetone-d_6) δ 10.1. ^{13}C NMR (125 MHz, Acetone-d_6) δ 168.8, 168.7, 140.7, 138.8, 135.0, 130.2, 130.2, 129.4, 129.3, 127.5, 68.8, 62.2, 62.1, 47.1, 41.3.

HRMS: calculated for $C_{27}H_{27}BN_2O_8S_2Na$ $[M+Na]^+$, 605.1199; Found, 605.1198.

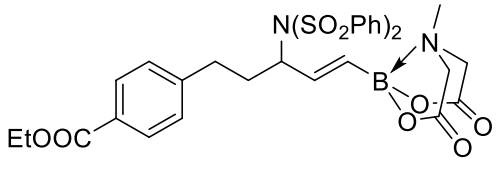
(*E*)-*N*-(1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-5-phenylpent-1-en-3-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (3e)



Following the general procedure **F**, the product **3e** was obtained in 74% NMR yield as a white solid after column chromatography (eluent =

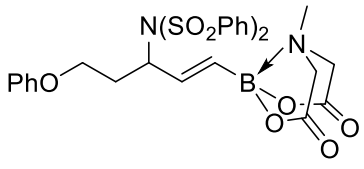
Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.30 (PE/EA = 1:4).
^{1}H NMR (500 MHz, Acetone-d_6) δ 7.93 (d, J = 7.7 Hz, 4H), 7.77 (t, J = 7.4 Hz, 2H), 7.65 (t, J = 7.7 Hz, 4H), 7.28 (t, J = 7.5 Hz, 2H), 7.20 (t, J = 7.4 Hz, 1H), 7.08 (d, J = 7.5 Hz, 2H), 6.42 (dd, J = 17.8, 7.0 Hz, 1H), 5.62 (d, J = 17.8 Hz, 1H), 4.67 (q, J = 7.5, 6.9 Hz, 1H), 4.25 (d, J = 16.9 Hz, 2H), 3.99 (dd, J = 19.5, 17.0 Hz, 2H), 2.95 (s, 3H), 2.62-2.54 (m, 1H), 2.52-2.39 (m, 2H), 2.02-1.98 (m, 1H). ^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 9.9. ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 169.2, 169.1, 142.3, 141.8, 135.2, 130.3, 129.4, 129.4, 129.1, 127.1, 66.7, 62.5, 47.8, 36.1, 33.5.
HRMS: calculated for $C_{28}H_{29}BN_2O_8S_2Na$ $[M+Na]^+$, 619.1356; Found, 619.1351.

ethyl (*E*)-4-(5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-3-(*N*-(phenylsulfonyl)phenylsulfonamido)pent-4-en-1-yl)benzoate (3f)



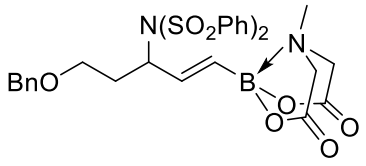
Following the general procedure **F**, the product **3f** was obtained in 66% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.16 (PE/EA = 1:4).
^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.91 (d, J = 8.2 Hz, 2H), 7.85 (d, J = 7.7 Hz, 4H), 7.73 (t, J = 7.4 Hz, 2H), 7.58 (t, J = 7.7 Hz, 4H), 7.16 (d, J = 8.1 Hz, 2H), 6.30 (dd, J = 17.8, 7.1 Hz, 1H), 5.44 (dd, J = 17.7, 1.1 Hz, 1H), 4.53 (q, J = 7.9, 7.1 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 3.96 (d, J = 17.1 Hz, 2H), 3.74 (dd, J = 17.0, 15.4 Hz, 2H), 2.67 (s, 3H), 2.63 (dd, J = 13.3, 4.5 Hz, 1H), 2.53-2.40 (m, 2H), 2.00 (dd, J = 16.1, 6.0 Hz, 1H), 1.36 (t, J = 7.1 Hz, 3H). ^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 10.1. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 168.7, 168.7, 166.7, 146.9, 141.7, 134.9, 130.0, 129.9, 129.2, 129.1, 128.7, 66.2, 62.1, 61.3, 47.4, 35.3, 33.1, 14.2.
HRMS: calculated for $C_{31}H_{34}BN_2O_{10}S_2$ $[M+H]^+$, 669.1748; Found, 669.1733.

(*E*)-*N*-(1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-5-phenoxypent-1-en-3-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (3g)



Following the general procedure **F**, the product **3g** was obtained in 57% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.24 (PE/EA = 1:4).
^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 7.93 (d, J = 7.7 Hz, 4H), 7.72 (t, J = 7.5 Hz, 2H), 7.60 (q, J = 7.9, 6.0 Hz, 4H), 7.27 (t, J = 7.7 Hz, 2H), 6.94 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 7.9 Hz, 2H), 6.30 (dd, J = 17.8, 7.4 Hz, 1H), 5.45 (d, J = 17.8 Hz, 1H), 4.90 (dt, J = 13.7, 6.5 Hz, 1H), 3.98-3.87 (m, 3H), 3.79 (td, J = 9.4, 4.3 Hz, 1H), 3.68 (ddd, J = 17.2, 9.7, 3.8 Hz, 2H), 2.59-2.48 (m, 4H), 2.30-2.19 (m, 1H). ^{11}B NMR (160 MHz, Acetonitrile-d_3) δ 10.1. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 169.1, 169.1, 159.7, 141.5, 135.3, 130.5, 130.3, 129.2, 121.8, 115.4, 65.2, 64.3, 62.4, 47.6, 34.2.
HRMS: calculated for $C_{28}H_{29}BN_2O_9S_2Na$ $[M+Na]^+$, 635.1305; Found, 635.1302.

(*E*)-*N*-(5-(benzyloxy)-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-1-en-3-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (3h)

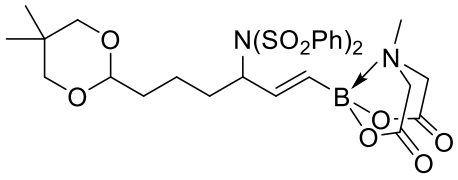


Following the general procedure **F**, the product **3h** was obtained in 54% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.30 (PE/EA = 1:4).

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.90 (d, J = 7.9 Hz, 4H), 7.72 (t, J = 7.5 Hz, 2H), 7.57 (t, J = 7.8 Hz, 4H), 7.412-7.35 (m, 2H), 7.32 (d, J = 7.2 Hz, 3H), 6.24 (dd, J = 17.8, 7.3 Hz, 1H), 5.38 (dd, J = 17.8, 1.2 Hz, 1H), 4.82 (td, J = 8.3, 5.1 Hz, 1H), 4.42 (d, J = 11.9 Hz, 1H), 4.32 (d, J = 11.9 Hz, 1H), 3.93 (dd, J = 17.0, 2.4 Hz, 2H), 3.68 (dd, J = 17.0, 12.3 Hz, 2H), 3.39 (dt, J = 10.1, 5.2 Hz, 1H), 3.29 (td, J = 9.4, 4.4 Hz, 1H), 2.57 (s, 3H), 2.41-2.33 (m,1H), 2.06-2.03 (m, 1H). ^{11}B NMR (160 MHz, Acetone-d_6) δ 10.3. ^{13}C NMR (125 MHz, Acetone-d_6) δ 168.9, 168.8, 141.5, 139.7, 134.9, 130.0, 129.2, 129.1, 128.4, 128.3, 73.2, 67.3, 64.2, 62.4, 47.5, 35.0.

HRMS: calculated for $C_{29}H_{31}BN_2O_9S_2Na$ $[M+Na]^+$, 649.1462; Found, 649.1435.

(*E*)-*N*-(6-(5,5-dimethyl-1,3-dioxan-2-yl)-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hex-1-en-3-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (3i)

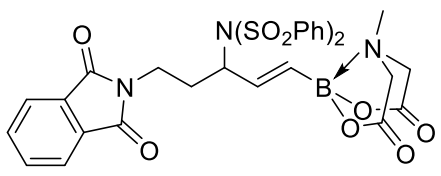


Following the general procedure **F**, the product **3i** was obtained in 65% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.29 (PE/EA = 1:4).

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 7.92 (d, J = 7.8 Hz, 4H), 7.74 (t, J = 7.5 Hz, 2H), 7.61 (t, J = 7.7 Hz, 4H), 6.19 (dd, J = 17.8, 7.0 Hz, 1H), 5.39 (d, J = 17.8 Hz, 1H), 4.53 (q, J = 7.3 Hz, 1H), 4.29 (t, J = 5.1 Hz, 1H), 3.93 (d, J = 17.0 Hz, 2H), 3.69 (dd, J = 16.9, 13.7 Hz, 2H), 3.51 (d, J = 11.2 Hz, 2H), 3.36 (d, J = 11.1 Hz, 2H), 2.62 (s, 3H), 2.08-2.03 (m, 1H), 1.86-1.77 (m, 1H), 1.46 (td, J = 7.9, 5.2 Hz, 2H), 1.28-1.19 (m, 2H), 1.10 (s, 3H), 0.69 (s, 3H). ^{11}B NMR (160 MHz, Acetonitrile-d_3) δ 10.1. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 169.1, 169.1, 142.7, 135.2, 130.3, 129.2, 102.4, 77.5, 67.6, 62.3, 47.7, 34.9, 34.1, 30.7, 23.2, 22.2, 21.8.

HRMS: calculated for $C_{29}H_{37}BN_2O_{10}S_2Na$ $[M+Na]^+$, 671.1880; Found, 671.1892.

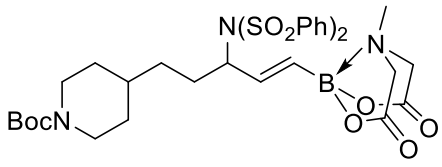
(*E*)-*N*-(5-(1,3-dioxoisoindolin-2-yl)-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-1-en-3-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (3j)



Following the general procedure **F**, the product **3j** was obtained in 56% NMR yield as a white solid after column chromatography (eluent

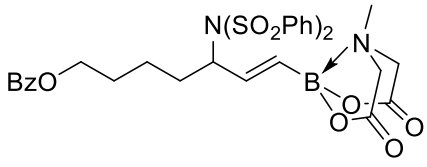
= Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.15 (PE/EA = 1:4).
^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.89-7.84 (m, 8H), 7.70 (t, J = 7.5 Hz, 2H), 7.55 (t, J = 7.8 Hz, 4H), 6.26 (dd, J = 17.8, 6.9 Hz, 1H), 5.55 (d, J = 17.8 Hz, 1H), 4.54-4.45 (m, 1H), 3.99 (d, J = 17.0 Hz, 2H), 3.77 (t, J = 16.5 Hz, 2H), 3.56 (dd, J = 8.1, 5.7 Hz, 2H), 2.75 (s, 3H), 2.58 (dt, J = 14.0, 4.8 Hz, 1H), 2.09 (d, J = 3.7 Hz, 1H). ^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 10.0. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 169.2, 141.2, 135.3, 135.3, 133.1, 130.3, 129.1, 124.0, 64.3, 62.4, 62.4, 47.8, 36.2, 33.8.
HRMS: calculated for $C_{30}H_{28}BN_3O_{10}S_2Na$ $[M+Na]^+$, 688.1207; Found, 688.1189.

tert-butyl (*E*)-4-(5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-3-(*N*-(phenylsulfonyl)phenylsulfonamido)pent-4-en-1-yl)piperidine-1-carboxylate (3k)



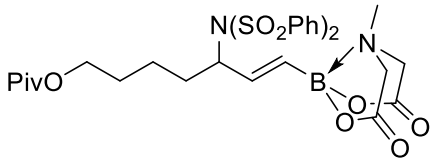
Following the general procedure **F**, the product **3k** was obtained in 58% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.11 (PE/EA = 1:4).
^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 7.93 (d, J = 7.9 Hz, 4H), 7.74 (t, J = 7.5 Hz, 2H), 7.61 (t, J = 7.7 Hz, 4H), 6.22 (dd, J = 17.8, 6.9 Hz, 1H), 5.44 (d, J = 17.8 Hz, 1H), 4.50 (q, J = 7.3 Hz, 1H), 3.95 (d, J = 16.9 Hz, 4H), 3.77-3.66 (m, 2H), 2.64 (s, 5H), 2.04 (td, J = 12.5, 11.4, 5.4 Hz, 1H), 1.77 (tt, J = 12.2, 5.8 Hz, 1H), 1.50 (d, J = 13.5 Hz, 1H), 1.41 (d, J = 1.7 Hz, 10H), 1.26 (q, J = 9.5, 7.8 Hz, 1H), 1.01 (ddt, J = 33.3, 12.1, 6.6 Hz, 2H), 0.85 (pd, J = 11.8, 4.0 Hz, 2H). ^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 10.2. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 169.1, 169.1, 155.4, 142.8, 135.3, 130.3, 129.2, 79.5, 67.9, 62.4, 47.7, 36.2, 34.4, 32.9, 32.7, 31.5, 28.6.
HRMS: calculated for $C_{32}H_{42}BN_3O_{10}S_2Na$ $[M+Na]^+$, 726.2303; Found, 726.2292.

(*E*)-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-5-(*N*-(phenylsulfonyl)phenylsulfonamido)hept-6-en-1-yl benzoate (3l)



Following the general procedure **F**, the product **3l** was obtained in 70% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.23 (PE/EA = 1:4).
^{1}H NMR (500 MHz, Acetone-d_6) δ 8.02 (d, J = 7.7 Hz, 6H), 7.74 (t, J = 7.4 Hz, 2H), 7.64 (t, J = 7.6 Hz, 5H), 7.54 (t, J = 7.6 Hz, 2H), 6.36 (dd, J = 17.8, 7.0 Hz, 1H), 5.59 (d, J = 17.7 Hz, 1H), 4.65 (q, J = 7.2 Hz, 1H), 4.27-4.17 (m, 4H), 3.93 (dd, J = 16.9, 8.1 Hz, 2H), 2.87 (s, 3H), 2.19 (ddt, J = 14.0, 9.2, 4.8 Hz, 1H), 1.89 (ddt, J = 16.4, 12.0, 5.9 Hz, 1H), 1.69 (p, J = 7.1 Hz, 2H), 1.42-1.28 (m, 2H). ^{11}B NMR (160 MHz, CD_3CN-d_6) δ 10.2. ^{13}C NMR (125 MHz, Acetone-d_6) δ 168.9, 168.8, 166.7, 142.3, 134.9, 133.8, 131.4, 130.2, 130.1, 129.4, 129.3, 67.5, 65.3, 62.3, 47.5, 34.2, 29.0, 24.4.
HRMS: calculated for $C_{31}H_{33}BN_2O_{10}S_2$ $[M+Na]^+$, 691.1568; Found, 691.1559.

(*E*)-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-5-(*N*-(phenylsulfonyl)phenylsulfonamido)hept-6-en-1-yl pivalate (3m)

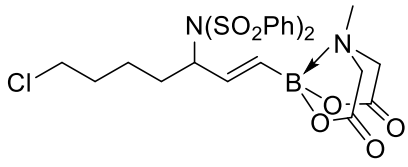


Following the general procedure **F**, the product **3m** was obtained in 64% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.24 (PE/EA = 1:4).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.93 (d, J = 7.9 Hz, 4H), 7.74 (t, J = 7.4 Hz, 2H), 7.61 (t, J = 7.8 Hz, 4H), 6.21 (dd, J = 17.8, 7.0 Hz, 1H), 5.40 (d, J = 17.8 Hz, 1H), 4.54 (q, J = 7.2 Hz, 1H), 3.98-3.87 (m, 4H), 3.69 (dd, J = 17.0, 13.4 Hz, 2H), 2.62 (s, 3H), 2.10-2.05(m, 1H), 1.86-1.77 (m, 1H), 1.51 (p, J = 7.0 Hz, 2H), 1.32-1.18 (m, 2H), 1.15 (s, 9H). ^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 10.0. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 178.9, 169.1, 169.0, 142.7 (2C), 135.2, 130.3, 129.2, 67.5, 64.7, 62.4, 47.7, 39.3, 34.0, 28.8, 27.5, 24.3.

HRMS: calculated for $C_{29}H_{37}BN_2O_{10}S_2Na$ $[M+Na]^+$, 671.1880; Found,671.1879.

(*E*)-*N*-(7-chloro-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-1-en-3-yl)-*N*-(phenylsulfonyl)benzenesulfonamide (3n)

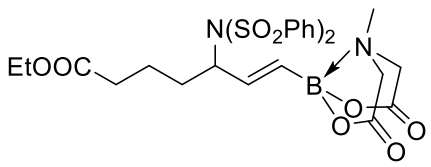


Following the general procedure **F**, the product **3n** was obtained in 52% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.26 (PE/EA = 1:4).

^{1}H NMR (500 MHz, Acetone-d_6) δ 8.02 (d, J = 7.8 Hz, 4H), 7.78 (t, J = 7.4 Hz, 2H), 7.67 (t, J = 7.7 Hz, 4H), 6.33 (dd, J = 17.8, 7.0 Hz, 1H), 5.55 (d, J = 17.8 Hz, 1H), 4.62 (q, J = 7.2 Hz, 1H), 4.23 (d, J = 16.9 Hz, 2H), 3.94 (dd, J = 16.9, 10.6 Hz, 2H), 3.50 (t, J = 6.6 Hz, 2H), 2.88 (s, 3H), 2.17-2.10 (m, 1H), 1.86-1.79 (m 1H), 1.69 (td, J = 8.9, 4.3 Hz, 2H), 1.41-1.29 (m, 2H). ^{11}B NMR (160 MHz, Acetone-d_6) δ 10.4. ^{13}C NMR (125 MHz, Acetone-d_6) δ 168.8, 168.8, 142.2, 135.0, 130.1, 129.3, 67.4, 62.3, 47.5, 45.4, 33.7, 32.8, 25.1.

HRMS: calculated for $C_{24}H_{28}BClN_2O_8S_2Na$ $[M+Na]^+$, 605.0965; Found, 605.0991.

ethyl (*E*)-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-5-(*N*-(phenylsulfonyl)phenylsulfonamido)hept-6-enoate (3o)



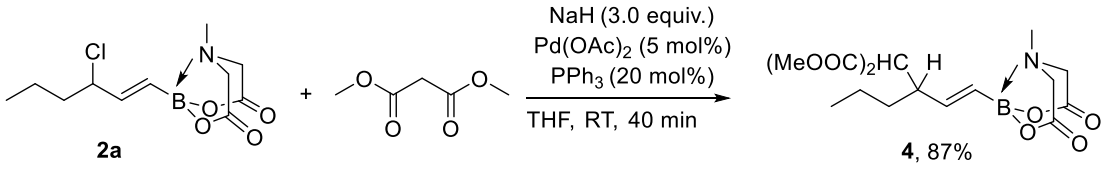
Following the general procedure **F**, the product **3o** was obtained in 16% NMR yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v). R_F = 0.13 (PE/EA = 1:4).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.93 (d, J = 7.7 Hz, 4H), 7.77-7.71 (m, 2H), 7.61

(t, J = 7.8 Hz, 4H), 6.19 (dd, J = 17.8, 7.0 Hz, 1H), 5.39 (dd, J = 17.8, 1.3 Hz, 1H), 4.55 (q, J = 7.2 Hz, 1H), 4.06 (q, J = 7.1 Hz, 2H), 3.94 (d, J = 17.0 Hz, 2H), 3.69 (dd, J = 17.0, 15.4 Hz, 2H), 2.62 (s, 3H), 2.12-2.01 (m, 2H), 1.85 (ddt, J = 13.1, 10.4, 6.2 Hz, 2H), 1.42 (dtd, J = 17.2, 13.8, 7.2 Hz, 2H), 1.20 (t, J = 7.1 Hz, 3H). ^{11}B NMR (160 MHz, Acetonitrile-d_3) δ 10.2. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 173.8, 169.1, 169.1, 142.5, 135.3, 130.3, 129.2, 67.3, 62.4, 61.0, 47.7, 34.1, 33.7, 23.1, 14.6.
HRMS: calculated for $C_{26}H_{31}BN_2O_{10}S_2Na$ $[M+Na]^+$, 629.1410; Found, 629.1399.

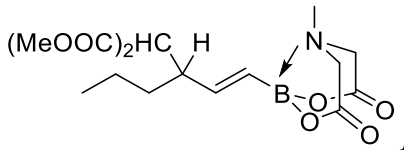
5. The synthesis of γ-functionalized benzyl MIDA boronates

Synthesis of compound 4: [5]



The dimethyl malonate (0.3 mmol, 3.0 equiv.) was added dropwise into the reaction flask filled with NaH (80% in oil) and THF (1 ml) under an atmosphere of nitrogen at 0 °C. Then the reaction mixture was stirred for 20 minutes at room temperature. In the glove box, **2a** (0.1 mmol, 1.0 equiv.), palladium acetate (5 mol%) and triphenylphosphine (20 mol%) were added into another 15 ml Schlenk reaction tube, sealed with rubber plug and removed out. The anhydrous THF (1 ml) was added with syringe. Under argon atmosphere, the reaction solution of dimethyl malonate was added into the Schlenk reaction tube by syringe. After the mixture was stirred for 40 minutes at room temperature. The solvents were removed on a rotary evaporator, and the crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc 1:3, v/v) to afford the pure product **4**（32.1 mg, 87%）as a white solid.

dimethyl (*E*)-2-(1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hex-1-en-3-yl)malonate

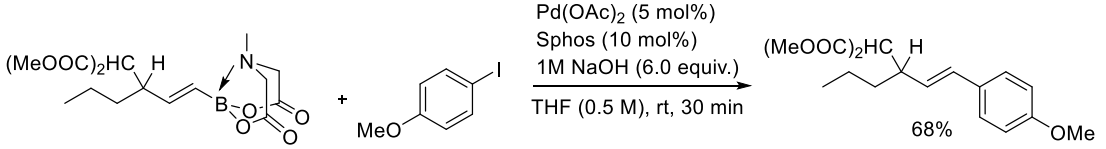


R_F = 0.16 (PE/EA = 1:3);

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 5.84 (dd, J = 17.7, 8.9 Hz, 1H), 5.50 (dd, J = 17.6, 0.8 Hz, 1H), 3.93 (dd, J = 17.0, 1.6 Hz, 2H), 3.73 (dd, J = 17.0, 15.8 Hz, 2H), 3.67 (s, 3H), 3.61 (s, 3H), 3.44 (d, J = 8.9 Hz, 1H), 2.82-2.75 (m, 1H), 2.73 (s, 3H), 1.40-1.31 (m, 3H), 1.25-1.16 (m, 1H), 0.88 (d, J = 7.0 Hz, 3H). ^{11}B NMR (160 MHz, Acetone-d_6) δ 10.4. ^{13}C NMR (125 MHz, Acetone-d_6) δ 169.2, 169.1, 168.9, 145.2, 62.2, 57.2, 52.5, 52.4, 47.4, 45.9, 35.0, 21.0, 14.1.

HRMS: calculated for $C_{16}H_{24}BNO_8Na$ $[M+Na]^+$, 392.1490; Found, 392.1482.

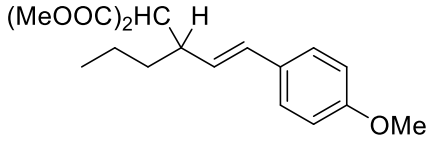
Synthesis of compound 5:



In the glove box, **4** (0.1 mmol, 1.0 equiv.), 4-iodoanisole (0.15 mmol, 1.5 equiv.) palladium(II) acetate (5 mol%) and 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (Sphos, 10 mol%) were added into 15 ml Schlenk reaction tube, sealed with rubber plug and removed out. Under argon atmosphere, the THF (0.2 mL) and 1M NaOH (6.0 equiv.)

were added with syringe then the reaction mixture was vigorously stirred at rt. After 30 mins, the reaction mixture was quenched with water (2 mL) and extracted with EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4, then concentrated in vacuo. The crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc 6/1, v/v) to afford the pure product **5** (21.8 mg, 68%).

dimethyl (*E*)-2-(1-(4-methoxyphenyl)hex-1-en-3-yl)malonate

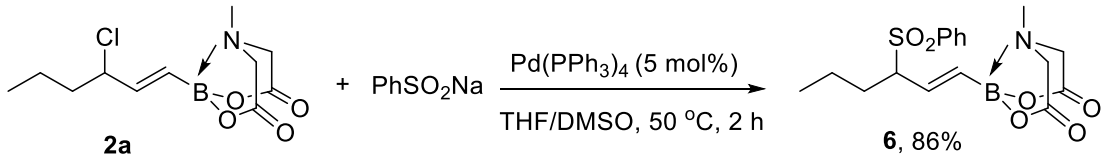


R_F = 0.30 (PE/EA = 6:1);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.38 (d, *J* = 15.7 Hz, 1H), 5.85 (dd, *J* = 15.7, 9.6 Hz, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 3.64 (s, 3H), 3.44 (d, *J* = 8.8 Hz, 1H), 2.91 (qd, *J* = 9.4, 3.5 Hz, 1H), 1.53-1.30 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 169.0, 168.8, 159.2, 132.0, 130.1, 127.6, 127.6, 114.1, 57.4, 55.5, 52.6, 52.4, 43.6, 35.2, 20.5, 14.0.

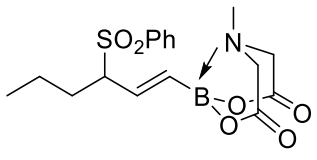
HRMS: calculated for $C_{18}H_{24}O_5Na$ [M+ Na]$^+$, 343.1516; Found, 343.1514.

Synthesis of compound 6:[5]



In the glove box, **2a** (0.1 mmol, 1.0 equiv.), Sodium benzenesulfinate (0.4 mmol, 4 equiv.) and tetrakis(triphenylphosphine)palladium (5 mol%) were added into 15 ml Schlenk reaction tube, sealed with rubber plug and removed out. Under argon atmosphere, the anhydrous THF (2 mL) and DMSO (0.3 mL) were added with syringe then the reaction mixture was vigorously stirred at 50 °C for 2 h. After cooling to the room temperature, the reaction mixture was quenched with water (5 mL) and extracted with EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4, then concentrated in vacuo. The crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc 1:3, v/v) to afford the pure product **6** (32.7 mg, 86%) as a white solid.

(*E*)-6-methyl-2-(3-(phenylsulfonyl)hex-1-en-1-yl)-1,3,6,2-dioxazaborocane-4,8-dione

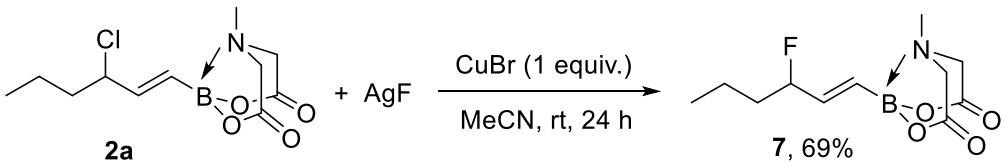


R_F = 0.23 (PE/EA = 1:4);

^{1}H NMR (400 MHz, Acetone-d_6) δ 8.35-8.29 (m, 2H), 8.20-8.15 (m, 1H), 8.13-8.06 (m, 2H), 6.28 (dd, *J* = 17.6, 9.0 Hz, 1H), 6.13 (d, *J* = 17.6 Hz, 1H), 4.65 (dd, *J* = 16.9, 0.9 Hz, 2H), 4.42 (d, *J* = 17.0 Hz, 1H), 4.33-4.21 (m, 2H), 3.20 (s, 3H), 2.46-2.37 (m, 1H), 2.17-2.08 (m, 1H), 1.95-1.86 (m, 1H), 1.78-1.71 (m, 1H), 1.35 (t, *J* = 7.3 Hz, 3H). ^{11}B NMR (128 MHz, Acetone-d_6) δ 9.9. ^{13}C NMR (125 MHz, CD_3CN) δ 169.1, 169.0, 139.1, 137.0, 134.7, 130.1, 129.7, 71.0, 62.4, 47.6, 29.4, 20.6, 13.8.

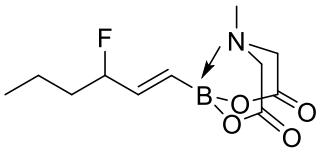
HRMS: calculated for $C_{17}H_{22}BNO_6SNa$ $[M+Na]^+$, 402.1156; Found, 402.1159.

Synthesis of compound 7:[6]



In the glove box, **2a** (0.1 mmol, 1.0 equiv.), AgF (0.5 mmol, 5.0 equiv.), CuBr (0.1 mmol) were added into 15 ml Schlenk reaction tube, sealed with rubber plug and removed out. Under argon atmosphere, the anhydrous MeCN (0.5 mL) was added with syringe then the reaction mixture was vigorously stirred at room temperature for 24 h. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc 1:3, v/v) to afford the pure product **7** (17.7 mg, 69%) as a white solid.

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

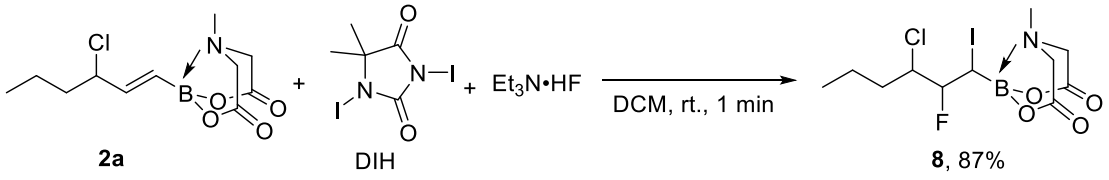


R_F = 0.24 (PE/EA = 1:3);

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 6.11 (ddd, J = 17.9, 15.3, 5.3 Hz, 1H), 5.72 (ddd, J = 17.9, 2.9, 1.4 Hz, 1H), 4.95 (ddtd, J = 49.2, 6.9, 5.4, 1.4 Hz, 1H), 3.96 (d, J = 17.0 Hz, 2H), 3.80 (dd, J = 17.0, 1.8 Hz, 2H), 2.15 (s, 3H), 1.73-1.52 (m, 2H), 1.48-1.32 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -178.4. ^{11}B NMR (160 MHz, Acetonitrile-d_3) δ 10.4. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 169.3, 143.9 (d, $^2J_{C\text{-}F}$ = 19.2 Hz), 95.1 (d, $^1J_{C\text{-}F}$ = 166.2 Hz), 62.5, 47.8, 37.9 (d, $^2J_{C\text{-}F}$ = 21.8 Hz), 18.8 (d, $^3J_{C\text{-}F}$ = 5.3 Hz), 14.1.

HRMS: calculated for $C_{11}H_{17}BFNO_4K$ $[M+K]^+$, 296.0868; Found, 296.0874.

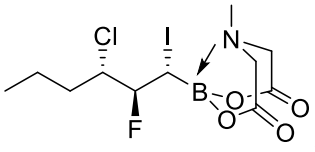
Synthesis of compound 8 and 12:[7]



2a (0.1 mmol, 1.0 equiv.) or **11** (0.1 mmol, 1.0 equiv.) 1,3-diiodo-5,5-dimethylhydantoin (DIH, 0.2 mmol, 1.0 equiv), DCM (0.5 mL) and $Et_3N{\cdot}HF$ (140 μL, 9.0 equiv) were added to a 15 mL screw cap vial equipped with a stirring bar. The solution was stirred at room temperature for 5 mins. The resulting mixture was quenched with 0.2 M $Na_2S_2O_3$ solution and then extracted with DCM. The organic phase was washed with 0.2 M HCl and brine. The combined organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The *p*-iodobenzole (0.1 mmol) was added and the NMR yield was determined by ^{1}H NMR.

After that, the crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc from 2:1 to1:3, v/v) to afford the pure product **8** (87% NMR yield) or **12** (72% NMR yield) as a white solid. Meanwhile, recrystallization (acetone/diethyl ether) was conducted to get pure product.

(±)-2-(3-chloro-2-fluoro-1-iodohexyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (8)

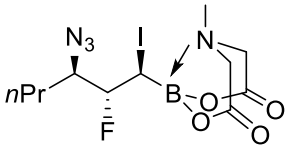


R_F = 0.31 (PE/EA = 1:3);

^{1}H NMR (400 MHz, DMSO-d_6) δ 4.84 (ddd, J = 46.9, 8.7, 3.2 Hz, 1H), 4.60 (dd, J = 22.6, 10.7 Hz, 1H), 4.43 (d, J = 17.4 Hz, 1H), 4.27 (dd, J = 17.2, 3.1 Hz, 1H), 4.12 (d, J = 17.4 Hz, 1H), 3.96 (dd, J = 17.2, 1.7 Hz, 1H), 3.86 (dd, J = 10.6, 8.6 Hz, 1H), 3.00 (s, 3H), 1.96 (dt, J = 15.4, 8.0 Hz, 1H), 1.62 (pd, J = 13.4, 12.6, 6.2 Hz, 2H), 1.50-1.35 (m, 1H), 0.92 (t, J = 7.3 Hz, 3H). ^{11}B NMR (160 MHz, Acetonitrile-d_3) δ 10.9. ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -171.9. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 168.2, 168.2, 100.2 (d, $^1J_{C\text{-}F}$ = 179.8 Hz), 65.3, 63.7, 63.6 (d, $^2J_{C\text{-}F}$ = 18.0 Hz), 47.5(2C), 34.2 (d, $^3J_{C\text{-}F}$ = 4.4 Hz), 20.3, 13.6.

HRMS: calculated for $C_{11}H_{17}BClFINO_4Na$ [M+Na]$^+$, 441.9862; Found, 441.9861.

(±)-2-(3-azido-2-fluoro-1-iodohexyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (12)



R_F = 0.28 (PE/EA = 1:2);

^{1}H NMR (400 MHz, Acetone-d_6) δ 4.71 (ddd, J = 47.0, 7.5, 4.4 Hz, 1H), 4.42 (d, J = 17.1 Hz, 1H), 4.32 (dd, J = 17.1, 2.7 Hz, 1H), 4.23 (d, J = 17.1 Hz, 1H), 4.11 (dd, J = 17.1, 1.2 Hz, 1H), 4.02-3.80 (m, 2H), 3.31 (s, 3H), 1.92-1.79 (m, 1H), 1.75-1.57 (m, 2H), 1.53-1.43 (m, 1H), 0.99 (t, J = 7.2 Hz, 3H). ^{11}B NMR (160 MHz, Acetone-d_6) δ10.8. ^{19}F NMR (376 MHz, Acetone-d_6) δ -173.0. ^{13}C NMR (101 MHz, Acetone-d_6) δ 167.9, 167.9, 98.1 (d, $^1J_{C\text{-}F}$ = 179.1 Hz), 65.1, 64.6 (d, $^2J_{C\text{-}F}$ = 23.1 Hz), 63.65 (d, $^3J_{C\text{-}F}$ = 4.6 Hz), 47.1 (2C), 31.1 (d, $^3J_{C\text{-}F}$ = 4.4 Hz), 20.0, 14.0.

HRMS: calculated for $C_{11}H_{17}BFIN_4O_4Na$ [M+ Na]$^+$, 449.0266; Found, 449,0274.

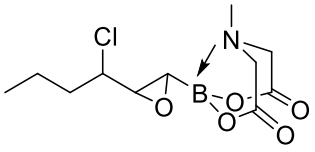
Synthesis of compound 9:

2a **9**, 94%

To the 15 mL tube were added **2a** (0.1 mmol, 1.0 equiv.), 3-Chloroperbenzoic acid (*m*CPBA, 0.25 mmol, 2.5 equiv.) and DCM (1.0 mL). The reaction mixture was vigorously stirred at 30 °C for 24 h. The solvent was then removed under reduced pressure, the crude product was purified by flash chromatography on silica with an

eluent (Petroleum ether/ EtOAc 1:3, v/v) to afford the pure product **9** (27.1 mg, 87%) as a white solid.

2-(3-(1-chlorobutyl)oxiran-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione

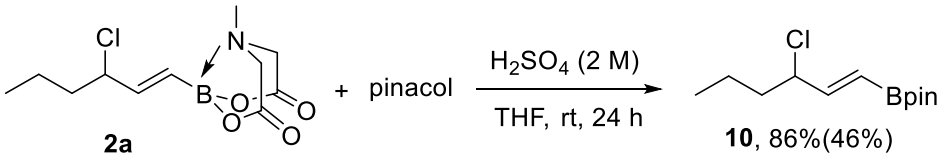


R_F = 0.24 (PE/EA = 1:3);

^{1}H NMR (400 MHz, Acetone-d_6) δ 4.33 (dd, J = 17.2, 3.1 Hz, 1H), 4.24 (dd, J = 16.8, 1.6 Hz, 1H), 4.15 (dd, J = 17.2, 2.3 Hz, 1H), 3.97 (dd, J = 16.8, 1.3 Hz, 1H), 3.67 (tdd, J = 7.4, 5.2, 3.2 Hz, 1H), 3.27 (d, J = 2.0 Hz, 3H), 3.08-2.99 (m, 1H), 2.39 (dd, J = 17.2, 2.9 Hz, 1H), 1.97-1.77 (m, 2H), 1.64-1.45 (m, 2H), 0.95 (td, J = 7.4, 1.5 Hz, 3H). ^{11}B NMR (160 MHz, Acetonitrile-d_3) δ 9.7. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 169.5, 169.4, 168.5, 168.4, 66.4, 64.3, 63.0, 62.9, 62.9, 60.3, 59.4, 47.4, 47.3, 38.6, 38.1, 20.3, 20.0, 13.8, 13.8.

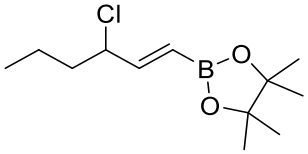
HRMS: calculated for $C_{11}H_{18}BClNO_5$ $[M+H]^+$, 290.0963; Found, 290.0964.

Synthesis of compound 10:



To the 15 mL tube were added **2a** (0.1 mmol, 1.0 equiv.), pinacol (0.5 mmol, 5.0 equiv.), H_2SO_4 (2 M, 4.0 equiv.) and THF (1.0 mL). The reaction mixture was vigorously stirred at room temperature for 24 h. The resulting mixture was quenched with water and then extracted with EA. The organic phase was washed with brine. The combined organic layer was dried over anhydrous Na_2SO_4. Then the p-iodobenzole (0.1 mmol) was added and the NMR yield was determined by ^{1}H NMR ($CDCl_3$, 86%). The crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc 1:3, v/v) to afford the pure product **10** (11.2 mg, 46%) as a colorless liquid.

(*E*)-2-(3-chlorohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

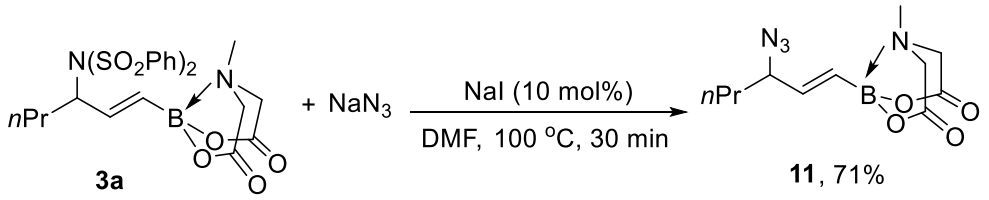


R_F = 0.24 (PE/EA = 100:1);

^{1}H NMR (400 MHz, Chloroform-d) δ 6.55 (dd, J = 17.7, 7.7 Hz, 1H), 5.62 (d, J = 17.7 Hz, 1H), 4.36 (q, J = 7.2 Hz, 1H), 1.76-1.82 (m, 2H), 1.46 (dq, J = 13.9, 6.7, 6.2 Hz, 2H), 1.27 (s, 12H), 0.92 (t, J = 7.4 Hz, 3H). ^{11}B NMR (128 MHz, Chloroform-d) δ 29.8. ^{13}C NMR (101 MHz, Chloroform-d) δ 151.5, 83.6, 63.7, 39.9, 24.9, 24.9, 19.7, 13.6.

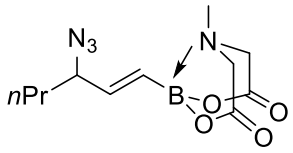
HRMS: calculated for $C_{12}H_{23}BClO_2$ $[M+H]^+$, 277.1197; Found, 277.1187.

Synthesis of compound 11:[8]



To the 15 mL tube were added **3a** (0.1 mmol, 1.0 equiv.), NaN_3 (0.2 mmol, 2.0 equiv.), NaI (10 mol%) and DMF (0.5 mL). The reaction mixture was vigorously stirred at 100 °C for 30 mins. After cooling to the room temperature, the reaction mixture was quenched with water (5 mL) and extracted with EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4. Then the p-iodobenzole (0.1 mmol) was added and the NMR yield was determined by ^{1}H NMR (71%). The crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc 1:3, v/v) to afford the pure product **11** as a white solid.

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

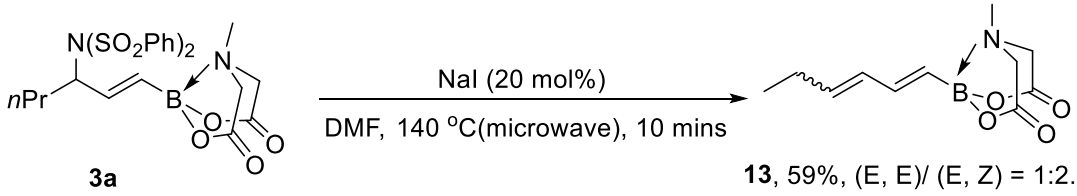


R_F = 0.28 (PE/EA = 1:3);

^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 5.99 (dd, J = 17.6, 7.0 Hz, 1H), 5.72 (d, J = 17.6 Hz, 1H), 3.98 (dd, J = 15.3, 8.2 Hz, 3H), 3.80 (d, J = 17.1 Hz, 2H), 2.80 (s, 3H), 1.52 (q, J = 7.3 Hz, 2H), 1.36 (dt, J = 15.4, 7.6 Hz, 2H), 0.91 (t, J = 7.3 Hz, 3H). ^{11}B NMR (160 MHz, Acetonitrile-d_3) δ 10.4. ^{13}C NMR (125 MHz, Acetonitrile-d_3) δ 169.2, 143.0, 66.7, 62.5, 62.5, 47.9, 36.8, 19.9, 14.0.

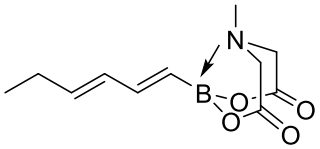
HRMS: calculated for $C_{11}H_{17}BN_4O_4Na$ $[M+Na]^+$, 303.1237; Found, 303.1227.

Synthesis of compound 13:



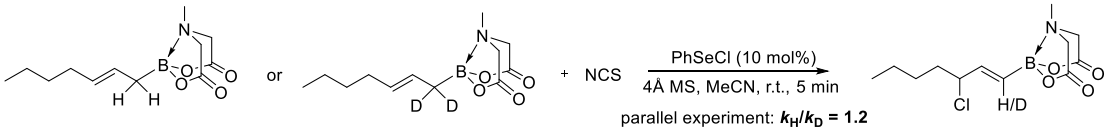
To the microwave tube were added **3a** (0.1 mmol, 1.0 equiv.), NaI (0.02 mmol, 20 mol%) and DMF (1 mL). The reaction mixture was vigorously stirred at 100 °C for 30 mins. After cooling to the room temperature, the reaction mixture was quenched with water (5 mL) and extracted with EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4. Then the p-iodobenzole (0.1 mmol) was added and the NMR yield was determined by ^{1}H NMR (59% for major). The crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc 1:3, v/v) to afford the pure product **13** as a white solid.

2-((1*E*)-hexa-1,3-dien-1-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (major)

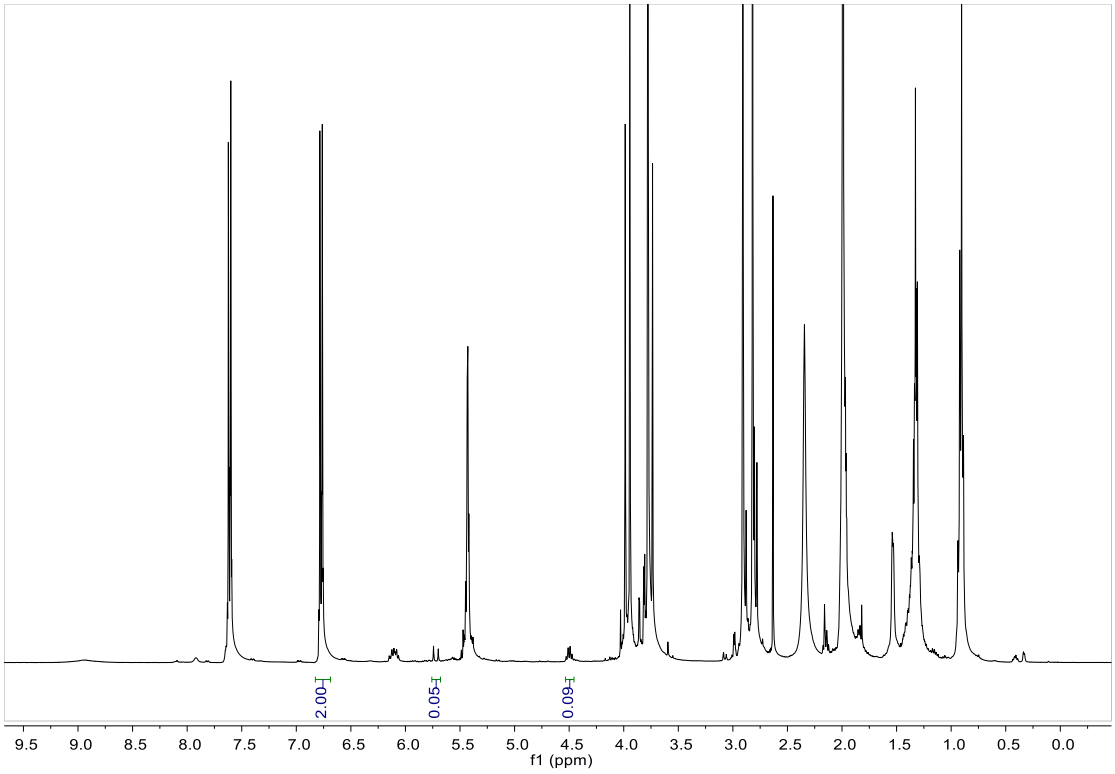


^{1}H NMR (400 MHz, Acetone-d_6) δ 6.53 (dd, J = 17.4, 10.2 Hz, 1H), 6.11 (ddt, J = 13.9, 10.1, 1.1 Hz, 1H), 5.79 (dt, J = 15.2, 6.6 Hz, 1H), 5.54 (d, J = 17.4 Hz, 1H), 4.20 (d, J = 16.9 Hz, 2H), 4.01 (d, J = 16.9 Hz, 2H), 2.98 (s, 3H), 2.15-2.06 (m, 3H), 0.99 (t, J = 7.5 Hz, 3H). ^{11}B NMR (128 MHz, Acetone-d_6) δ 10.7. ^{13}C NMR (101 MHz, Acetone-d_6) δ 169.1, 143.8, 137.9, 132.7, 62.3, 47.3, 26.2, 13.8. HRMS: calculated for $C_{11}H_{16}BNO_4Na$ $[M+Na]^+$, 260.1065; Found, 260.1065.

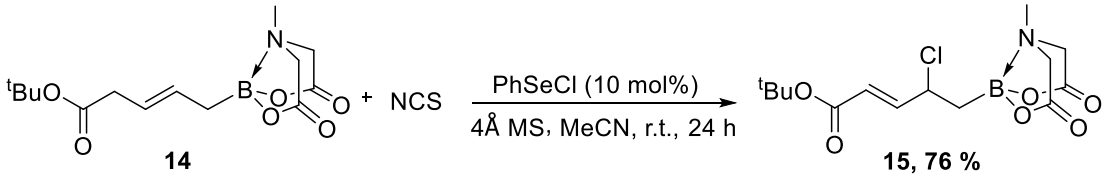
6. KIE experiments



The allyl MIDA boronates **1p** (0.1 mmol, 1.0 equiv), phenyl selenium chloride (10 mol %, 0.02 mmol), N-chlorosuccinimide (NCS, 0.11 mmol, 1.1 equiv), 4Å MS (10 mg) and 1.5 mL CH_3CN were added in a 5 mL round bottom flask. The deuterium allyl MIDA boronates **1p-D2** (0.1 mmol, 1.0 equiv), phenyl selenium chloride (10 mol %, 0.02 mmol), N-chlorosuccinimide (NCS, 0.11 mmol, 1.1 equiv), 4Å MS (10 mg) and 1.5 mL CH_3CN were added in another 5 mL round bottom flask. After the reaction mixture was stirred for 5 mins, the two reaction mixtures were mixed and *p*-iodoanisole (23.4 mg, 0.1 mmol) was then added as an internal standard. The mixture was diluted with acetonitrile (2 mL) and then evaporated under reduced pressure. Yields were determined by ^{1}H NMR. A kinetic isotope effect value k_H/k_D= 1.2 was obtained.

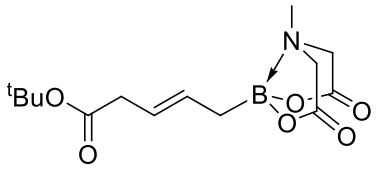


7. Intramolecular competition experiments and control experiment.



The allyl MIDA boronates **14** (0.2 mmol, 1.0 equiv), phenyl selenium chloride (10 mol %, 0.02 mmol), *N*-chlorosuccinimide (NCS, 0.22 mmol, 1.1 equiv) and 4 Å MS (20 mg) were added in 3 mL CH_3CN. The reaction mixture was stirred at room temperature for 24 h. After completion of the reaction, the crude product was purified by flash chromatography on silica with an eluent (Petroleum ether/ EtOAc from 2:1 to1:3, v/v) to afford the pure product **15** as a white solid (76% isolated yield).

***tert*-butyl (*E*)-5-(4-methyl-2,6-dioxotetrahydro-2*H*-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborol-8-yl)pent-3-enoate (14)**

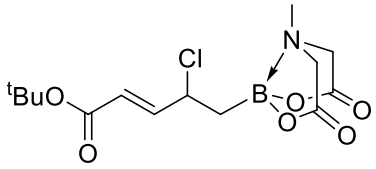


Following the general procedure B, the product **14** was obtained in 60 % yield as a white solid after column chromatography (eluent = Petroleum ether/ ethyl acetate 1:3 v/v).

^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 5.63-5.33 (m, 2H), 3.93 (dd, *J* = 16.9, 1.2 Hz, 2H), 3.77 (dd, *J* = 16.9, 1.2 Hz, 2H), 2.92-2.88 (m, 5H), 1.58 (d, *J* = 7.2 Hz, 2H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 172.5, 169.0, 131.8, 124.1, 80.9, 62.9, 62.9, 46.4, 39.9, 28.2. ^{11}B NMR (128 MHz, Acetonitrile-d_3) δ 12.1.

HRMS: calculated for $C_{14}H_{22}BNO_6Na$ $[M+Na]^+$, 334.1432; Found, 334.1429.

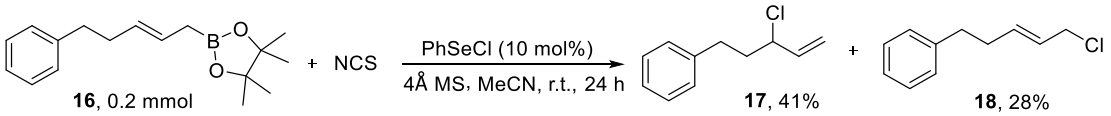
***tert*-butyl (*E*)-4-chloro-5-(4-methyl-2,6-dioxotetrahydro-2H-4l4,8l4-[1,3,2]oxazaborolo[2,3-b][1,3,2]oxazaborol-8-yl)pent-2-enoate (15)**



^{1}H NMR (500 MHz, Acetonitrile-d_3) δ 6.85 (dd, *J* = 15.4, 8.3 Hz, 1H), 5.91 (dd, *J* = 15.3, 1.1 Hz, 1H), 4.79 (tdd, *J* = 8.4, 6.6, 1.0 Hz, 1H), 3.95 (dd, *J* = 17.0, 3.4 Hz, 2H), 3.81 (t, *J* = 16.9 Hz, 2H), 2.87 (s, 3H), 1.46 (s, 9H), 1.40-1.35 (m, 2H). ^{13}C NMR (126 MHz, Acetonitrile-d_3) δ 168.9, 168.8, 166.2, 148.0, 123.5, 81.4, 62.9, 62.8, 60.1, 46.9, 28.2. ^{11}B NMR (160 MHz, Acetonitrile-d_3) δ 11.5.

HRMS: calculated for $C_{14}H_{21}BClNO_6Na$ $[M+Na]^+$, 368.1043; Found, 368.1049.

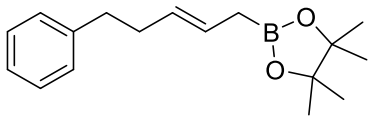
Control experiment



16, 0.2 mmol **17**, 41% **18**, 28%

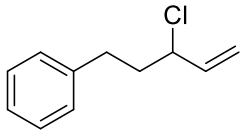
The allyl pinacol boronate **14** (0.2 mmol, 1.0 equiv), phenyl selenium chloride (10 mol %, 0.02 mmol), *N*-chlorosuccinimide (NCS, 0.22 mmol, 1.1 equiv) and 4 Å MS (20 mg) were added in 3 mL CH_3CN. The reaction mixture was stirred at room temperature for 24 h. After completion of the reaction, the crude product was purified by flash chromatography on silica to afford the pure product **17** (41%) and **18** (28%) as known compounds**.**

(*E*)-4,4,5,5-tetramethyl-2-(5-phenylpent-2-en-1-yl)-1,3,2-dioxaborolane (16)



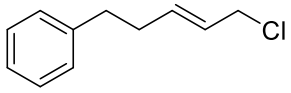
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29-7.23 (m, 2H), 7.22-7.12 (m, 3H), 5.58-5.37 (m, 3H), 2.65 (dd, *J* = 9.1, 6.6 Hz,3H), 2.37-2.17 (m, 3H), 1.64 (d, *J* = 6.3 Hz, 3H), 1.24 (s, 12H).

(3-chloropent-4-en-1-yl) benzene (17)



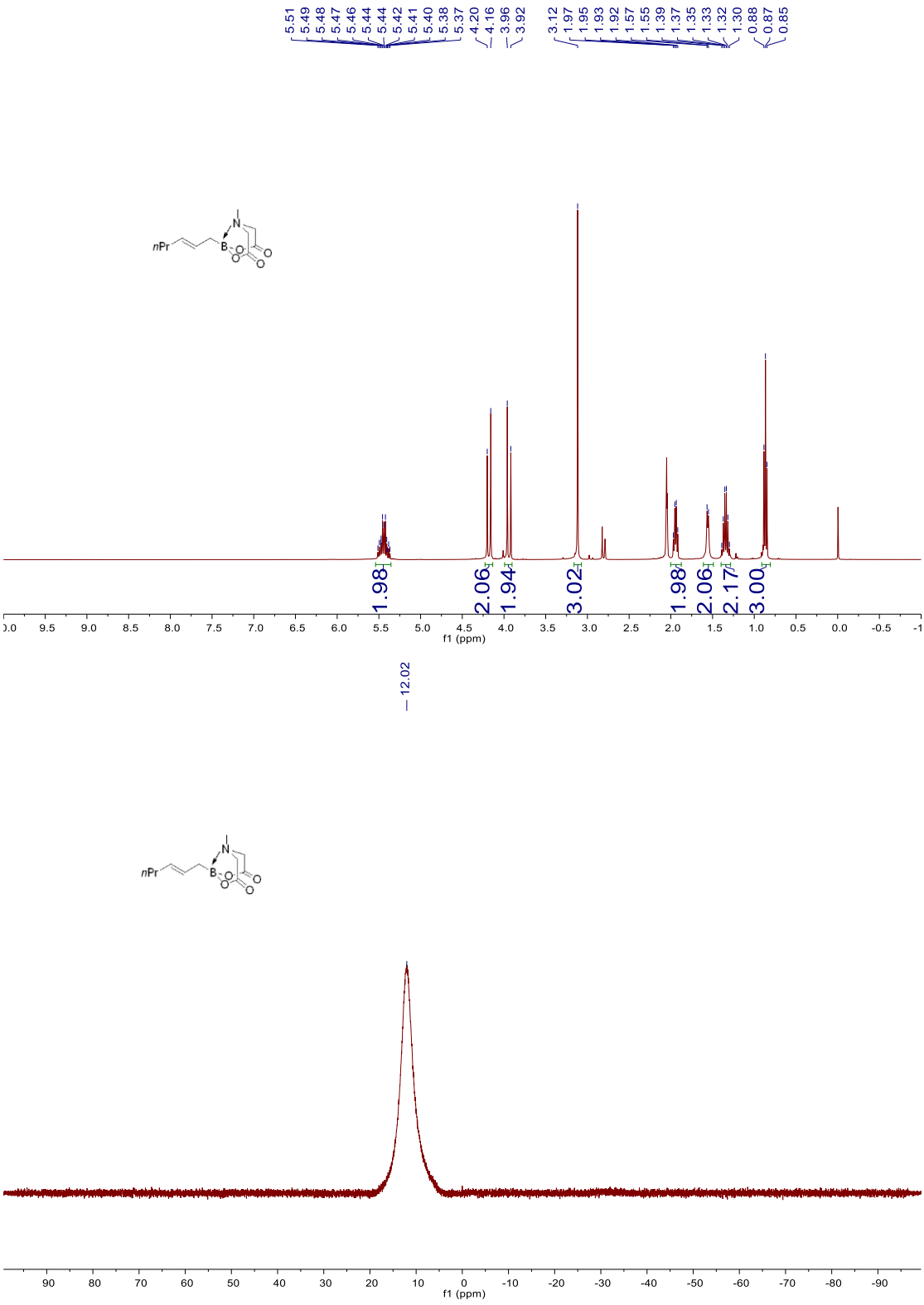
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32-7.28 (m, 2H), 7.23-7.19 (m, 3H), 5.92 (ddd, *J* = 16.9, 10.2, 8.1 Hz, 1H), 5.27 (dd, *J* = 16.9, 1.0 Hz,1H), 5.16 (dt, *J* = 10.1, 0.9 Hz, 1H), 4.32 (q, *J* = 7.4 Hz, 1H), 2.89-2.62 (m, 2H), 2.16-2.09 (m, 2H).

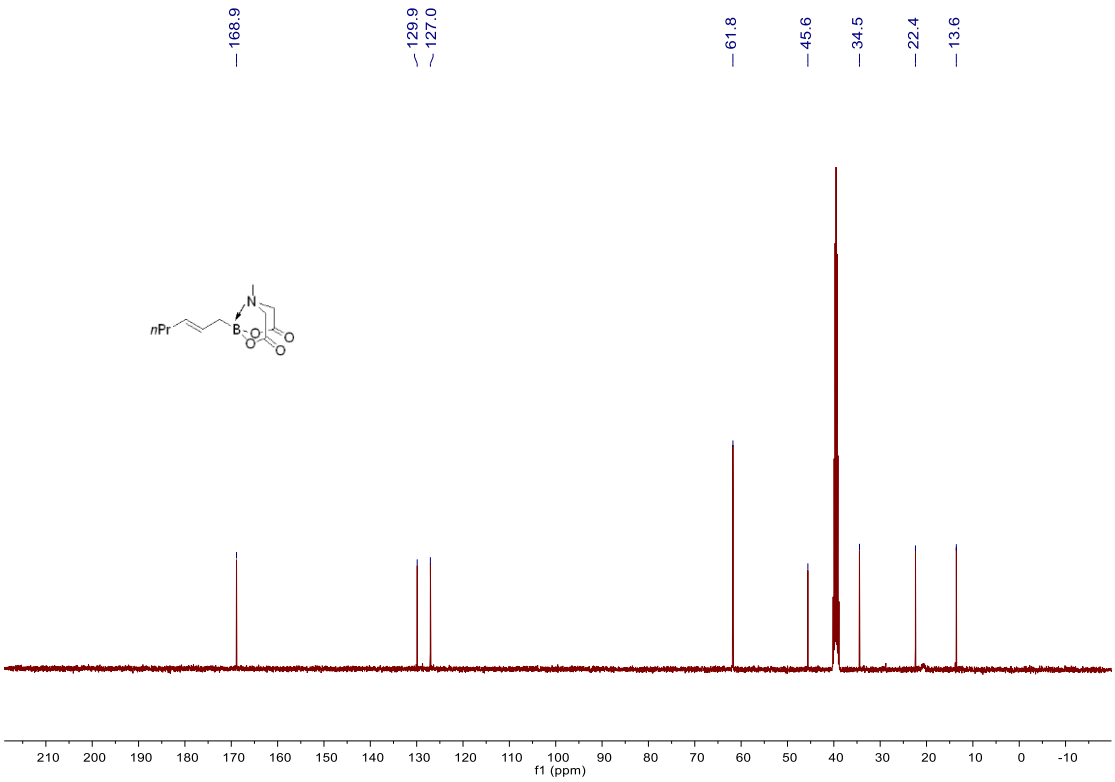
(*E*)-(5-chloropent-3-en-1-yl) benzene (18)

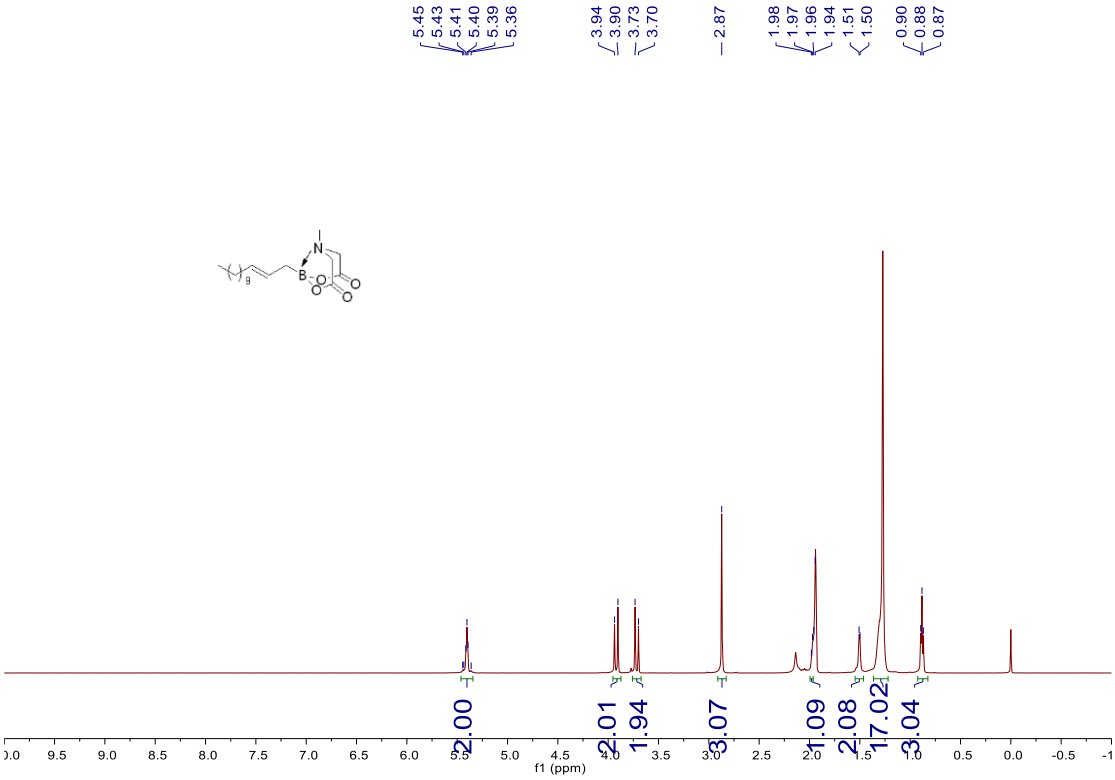


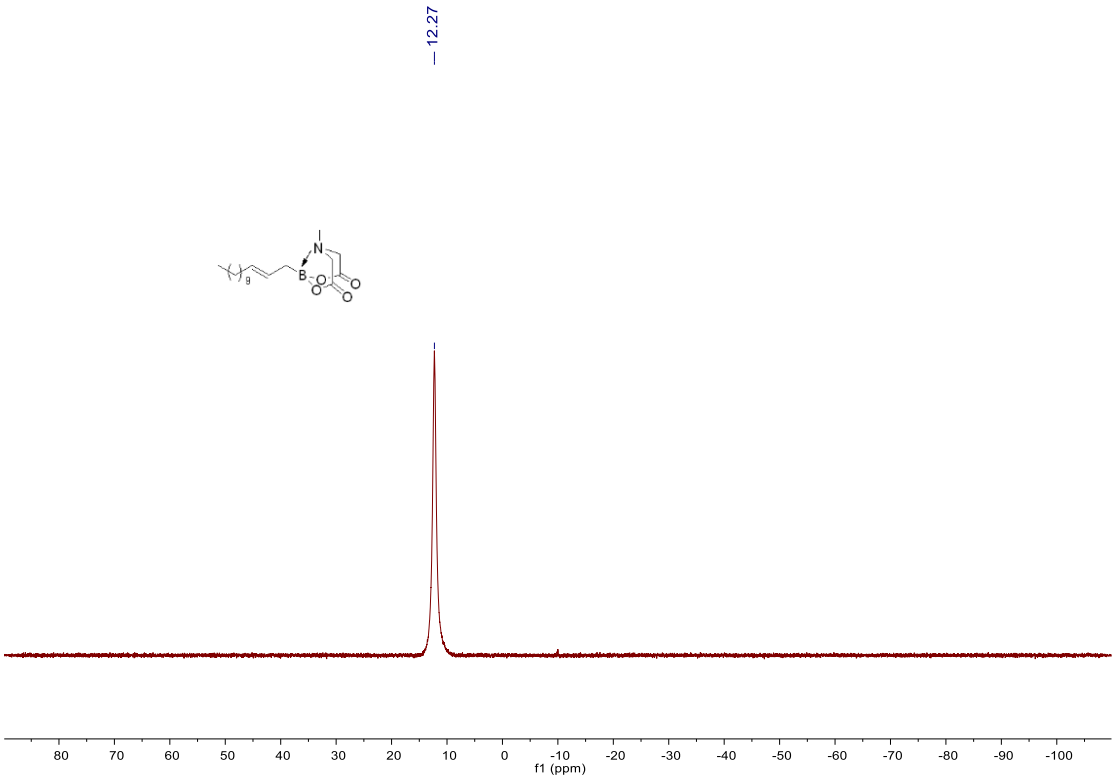
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (tt, *J* = 7.0, 1.0 Hz, 2H), 7.22-7.13 (m, 3H), 5.87-5.74 (m, 1H), 5.73-5.55 (m, 1H), 4.03 (dd, *J* = 7.0, 1.0 Hz, 2H), 2.71 (dd, *J* = 8.9, 6.7 Hz, 2H), 2.46-2.30 (m, 2H).

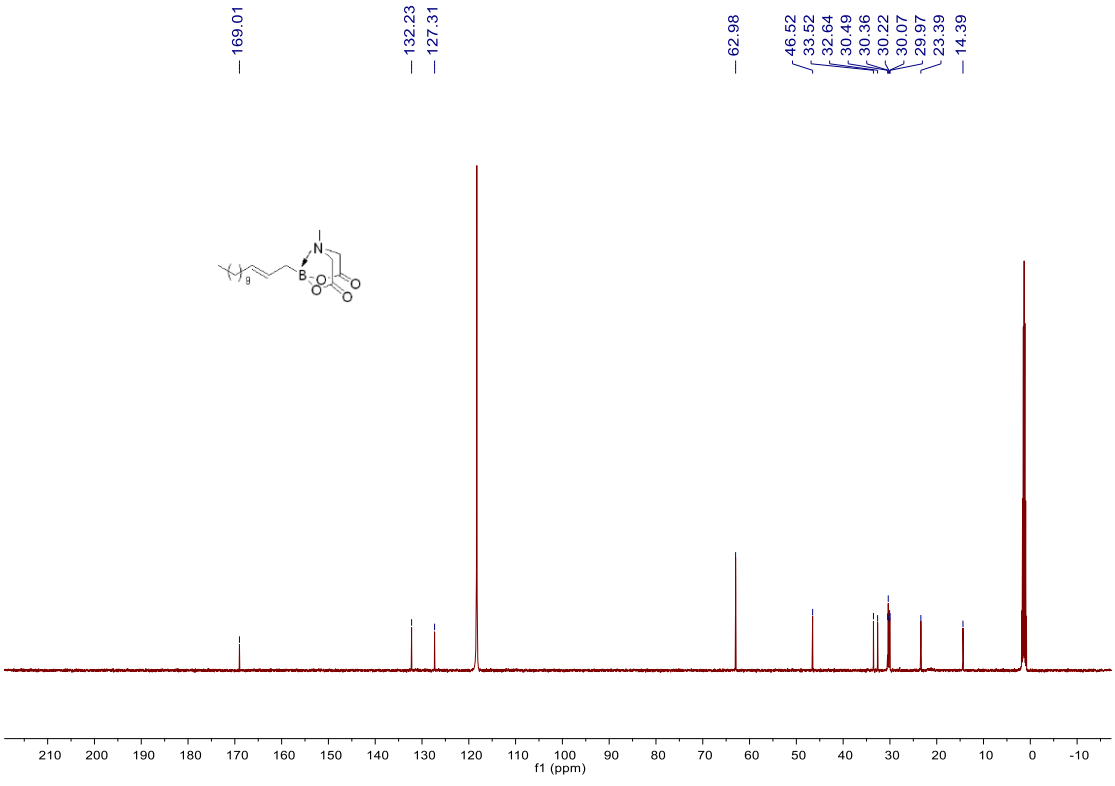
8. NMR spectrum of starting materials and products

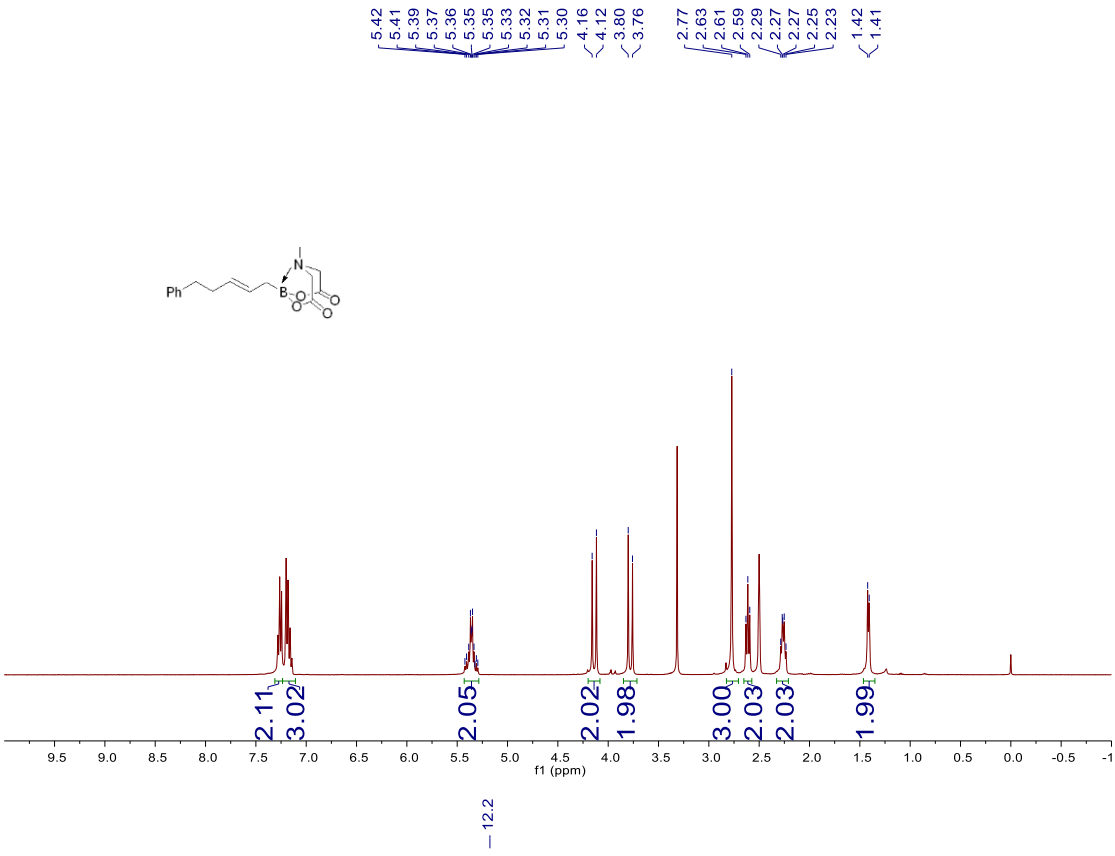



168.9
129.9
127.0
61.8
45.6
34.5
22.4
13.6
nPr
f1 (ppm)


5.45
5.43
5.41
5.40
5.39
5.36
3.94
3.90
3.73
3.70
2.87
1.98
1.97
1.96
1.94
1.51
1.50
0.90
0.88
0.87
2.00
2.01
1.94
3.07
1.09
2.08
17.02
3.04
f1 (ppm)


12.27
f1 (ppm)


169.01
132.23
127.31
62.98
46.52
33.52
32.64
30.49
30.36
30.22
30.07
29.97
23.39
14.39
f1 (ppm)


5.42
5.41
5.39
5.37
5.36
5.35
5.35
5.33
5.32
5.31
5.30
4.16
4.12
3.80
3.76
2.77
2.63
2.61
2.59
2.29
2.27
2.27
2.25
2.23
1.42
1.41
Ph
N
B
O
O
O
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3.02
2.05
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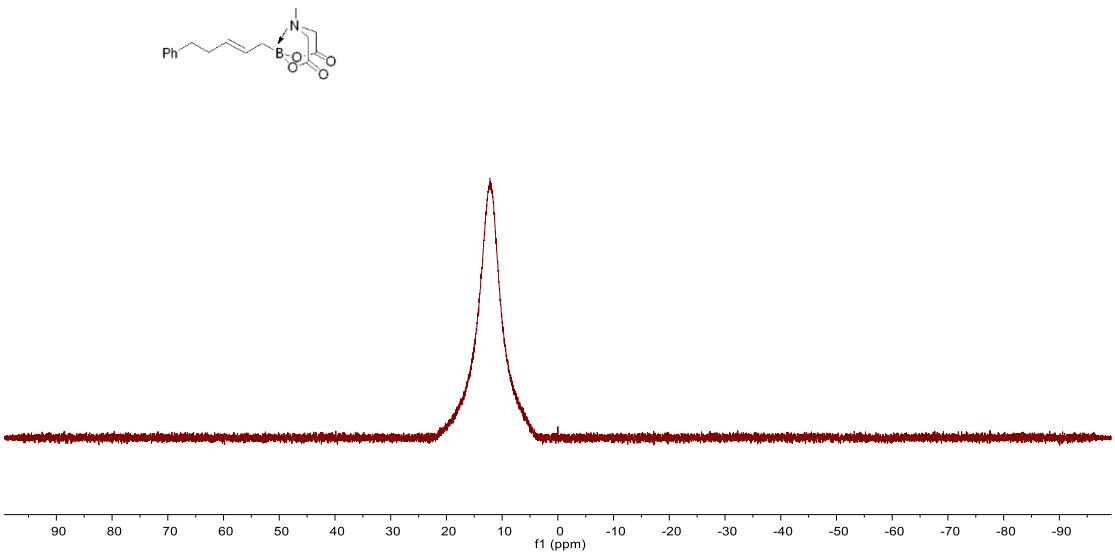
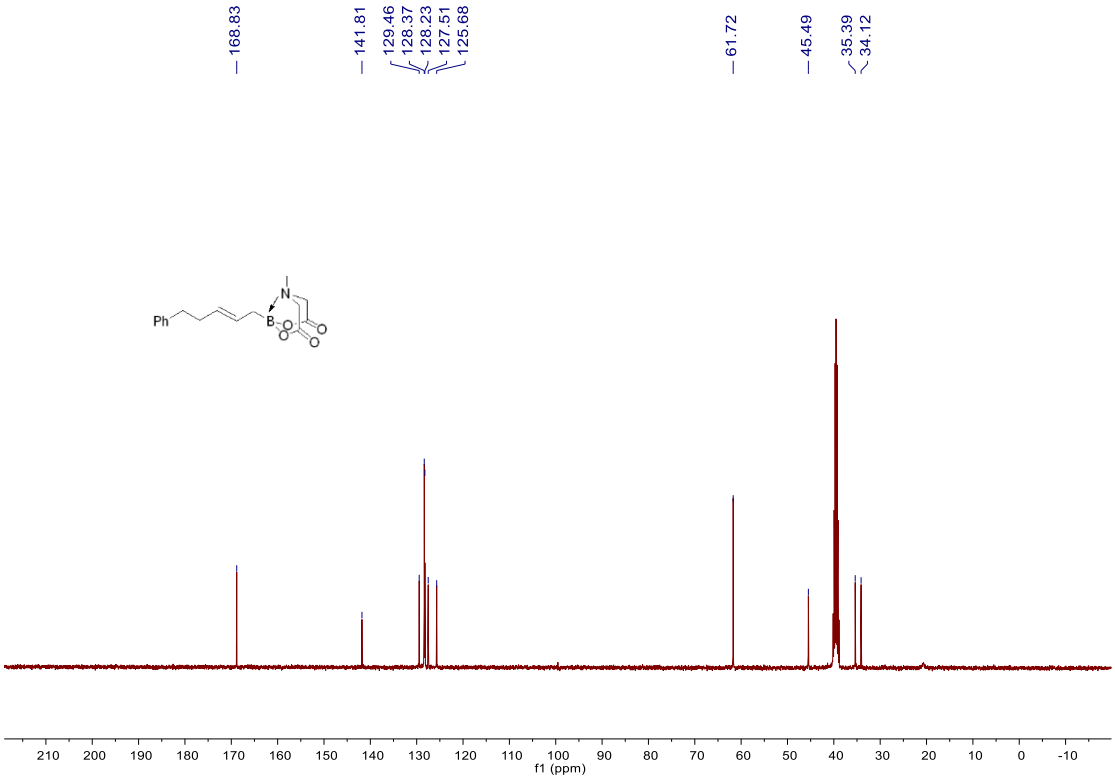
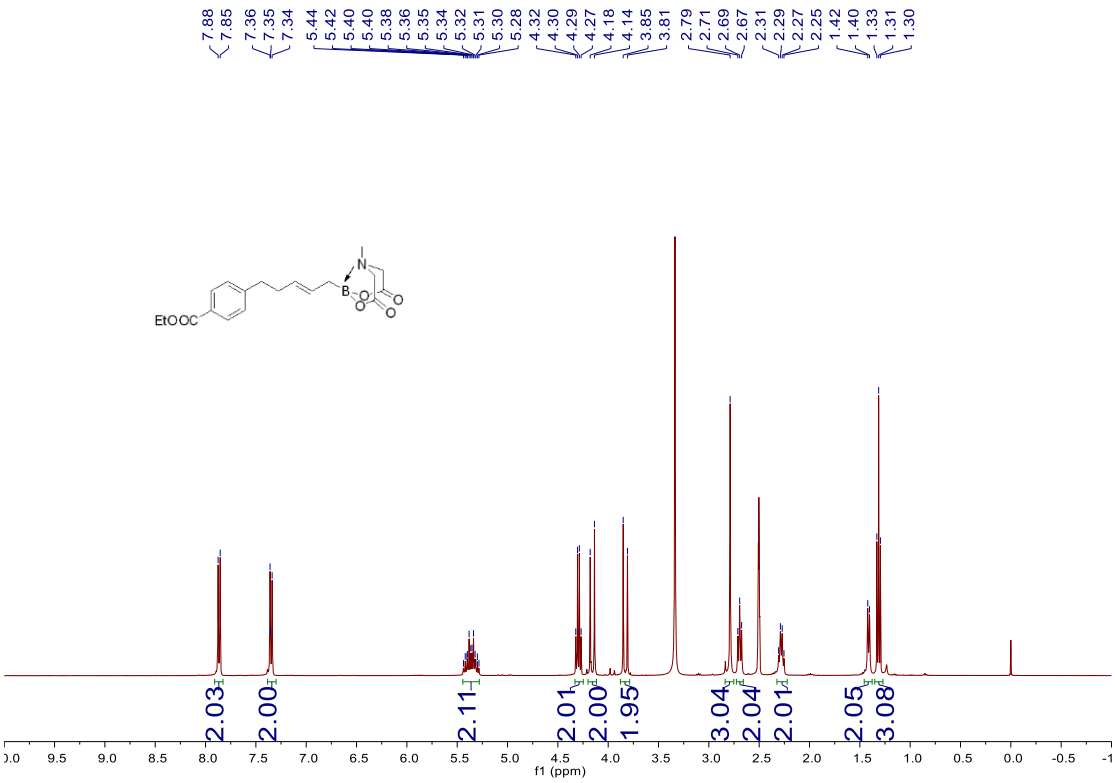
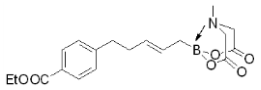
1.98
3.00
2.03
2.03
1.99
f1 (ppm)

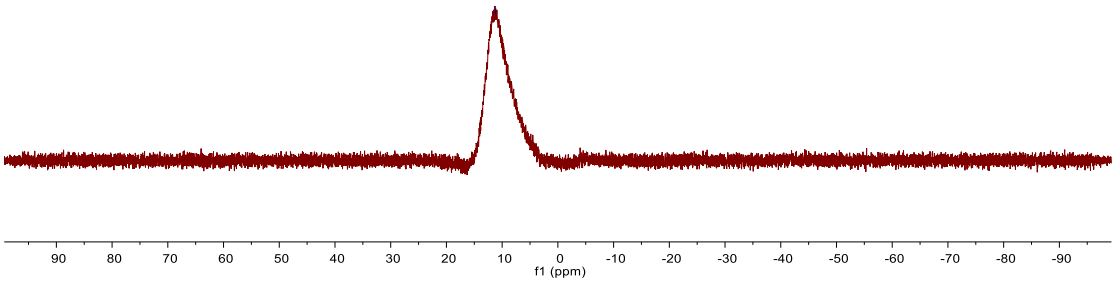

12.2
Ph
N
B
O
O
O
O
f1 (ppm)


168.83
141.81
129.46
128.37
128.23
127.51
125.68
61.72
45.49
35.39
34.12
Ph
f1 (ppm)

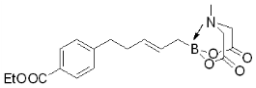

7.88
7.85
7.36
7.35
7.34
5.44
5.42
5.40
5.40
5.38
5.36
5.35
5.34
5.32
5.31
5.30
5.28
4.32
4.30
4.29
4.27
4.18
4.14
3.85
3.81
2.79
2.71
2.69
2.67
2.31
2.29
2.27
2.25
1.42
1.40
1.33
1.31
1.30
EtOOC
2.03
2.00
2.11
2.01
2.00
1.95
3.04
2.04
2.01
2.05
3.08
f1 (ppm)

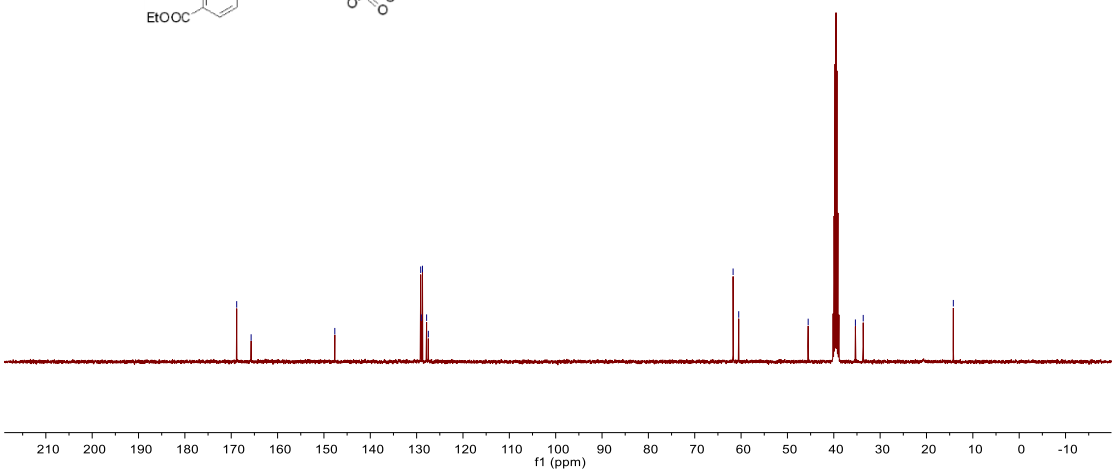


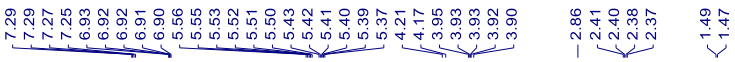
11.16

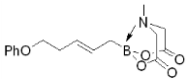


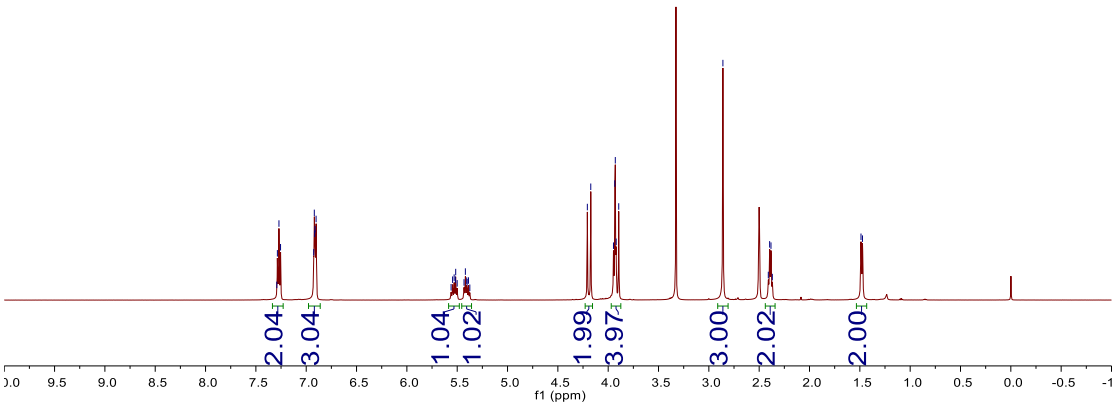
168.82
165.71
147.65
129.13
128.99
128.74
127.85
127.47
61.73
60.51
45.53
35.34
33.65
14.21

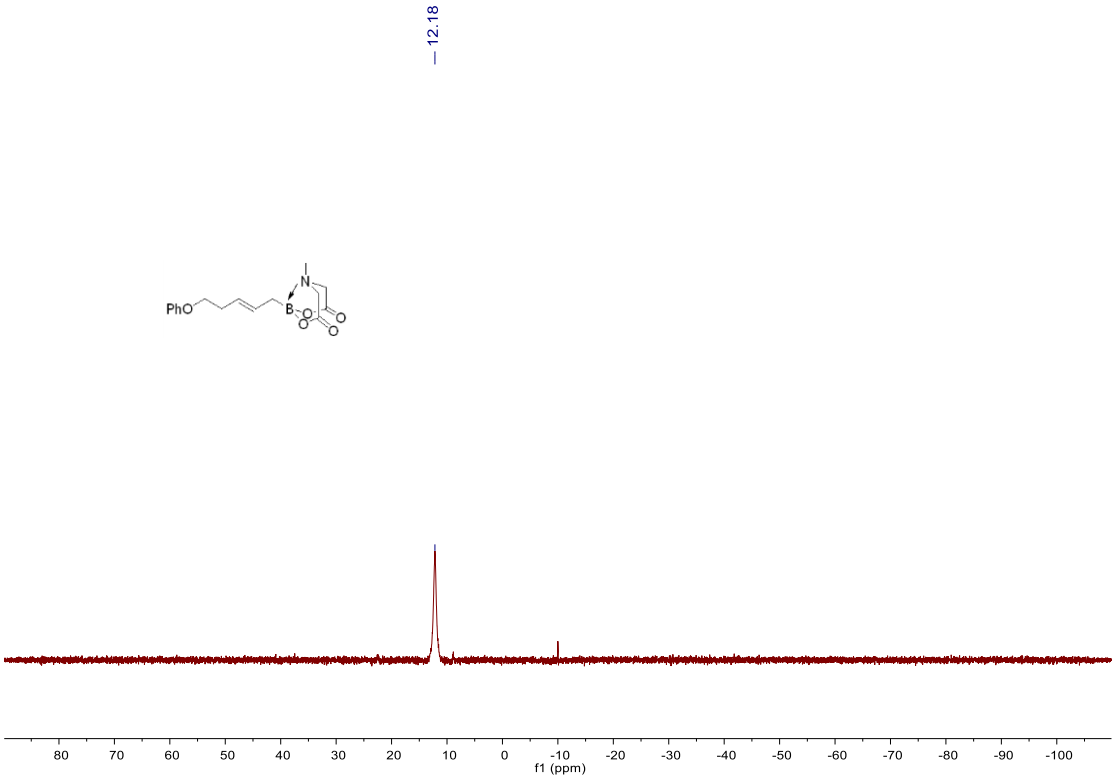


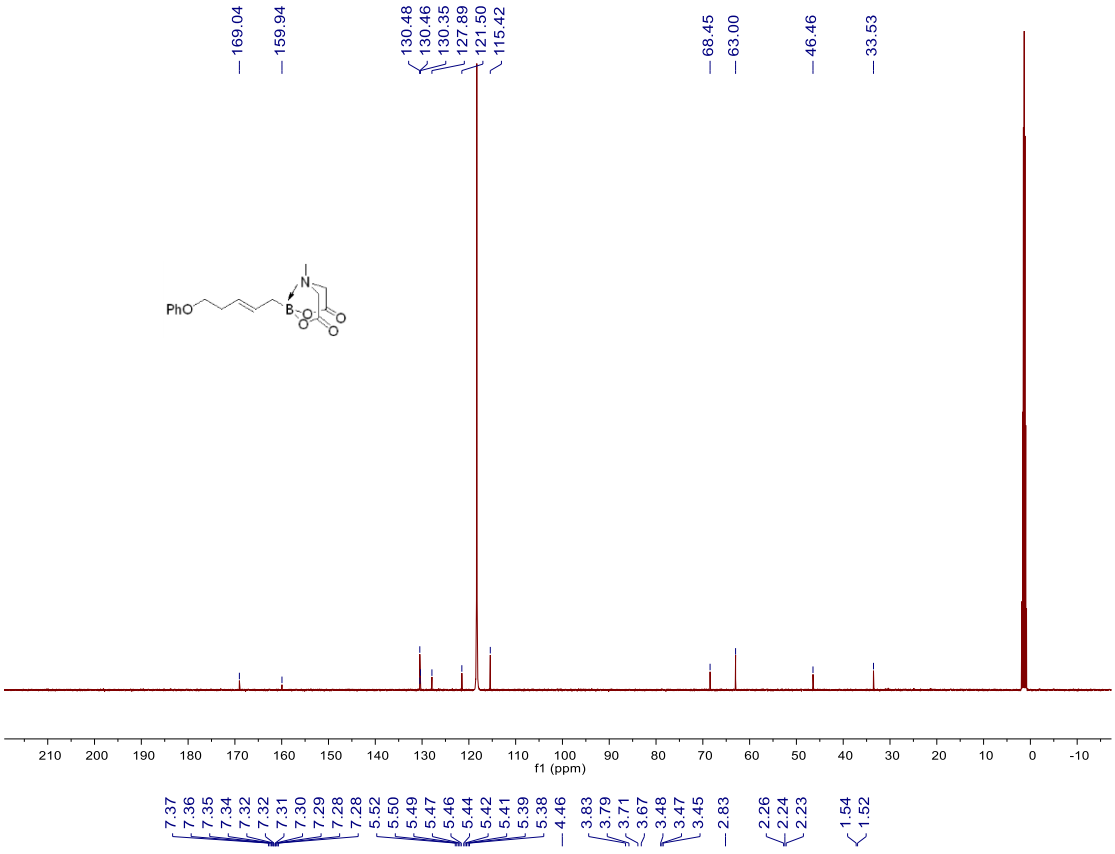


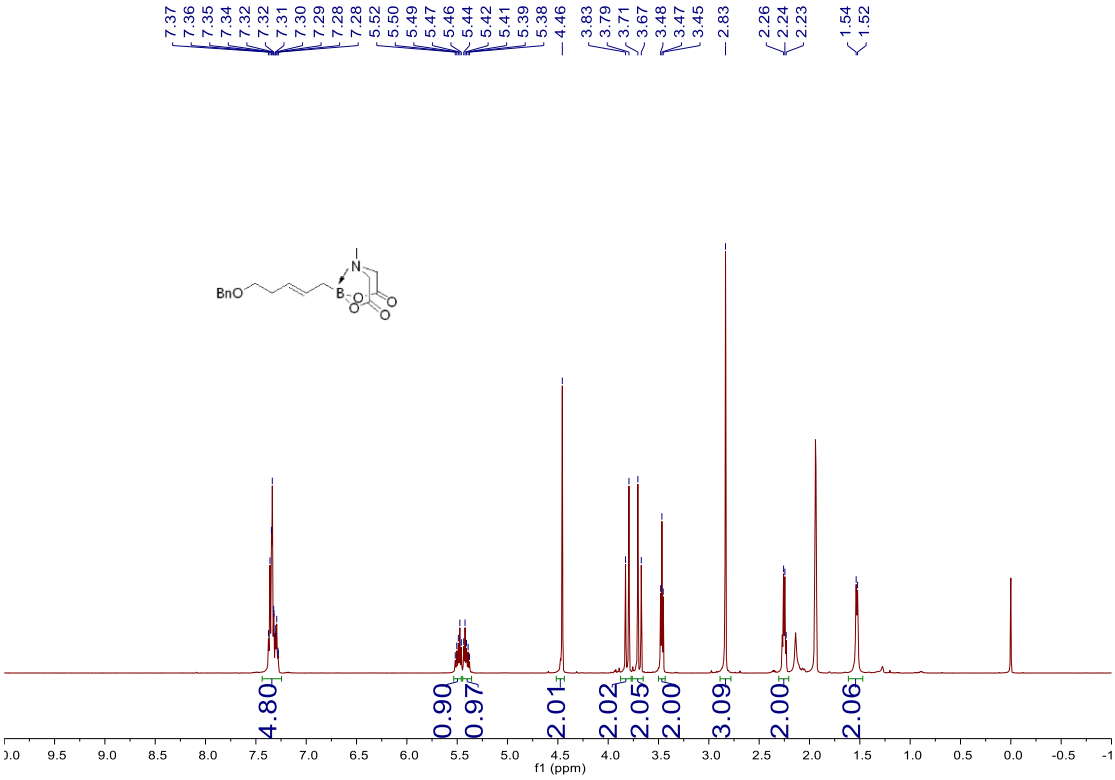

7.29
7.29
7.27
7.25
6.93
6.92
6.92
6.91
6.90
5.56
5.55
5.53
5.52
5.51
5.50
5.43
5.42
5.41
5.40
5.39
5.37
4.21
4.17
3.95
3.93
3.93
3.92
3.90
2.86
2.41
2.40
2.38
2.37
1.49
1.47

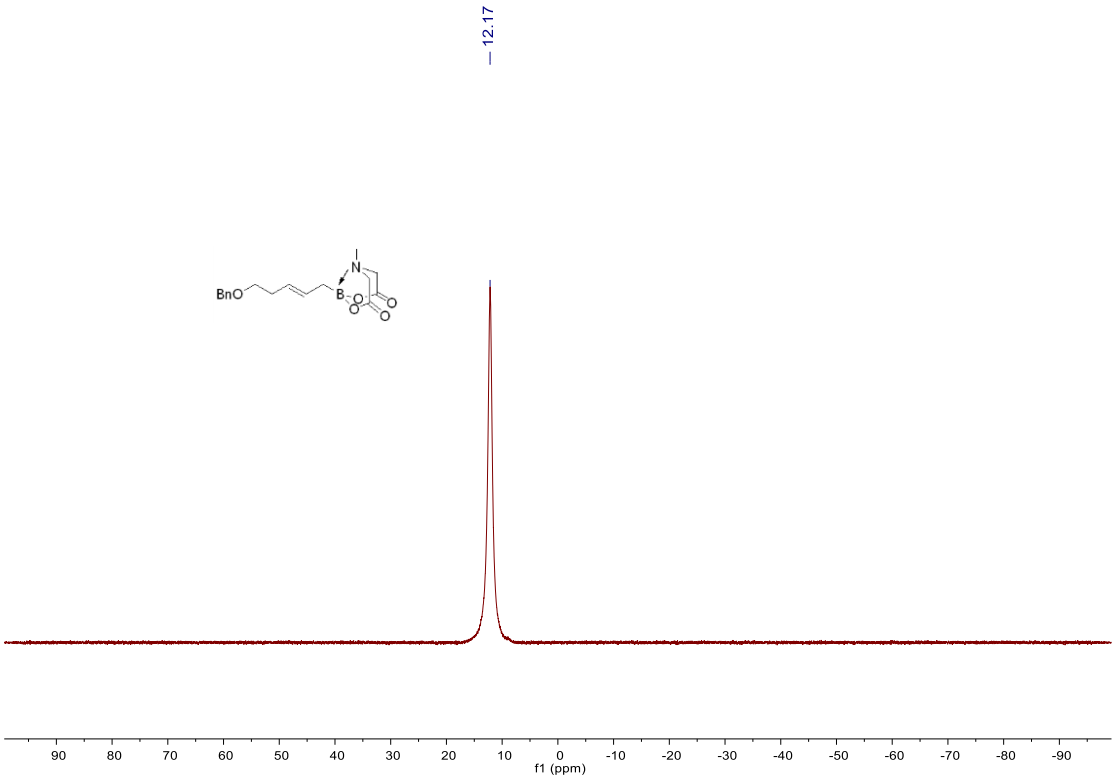

PhO
N
B
O
O
O
O

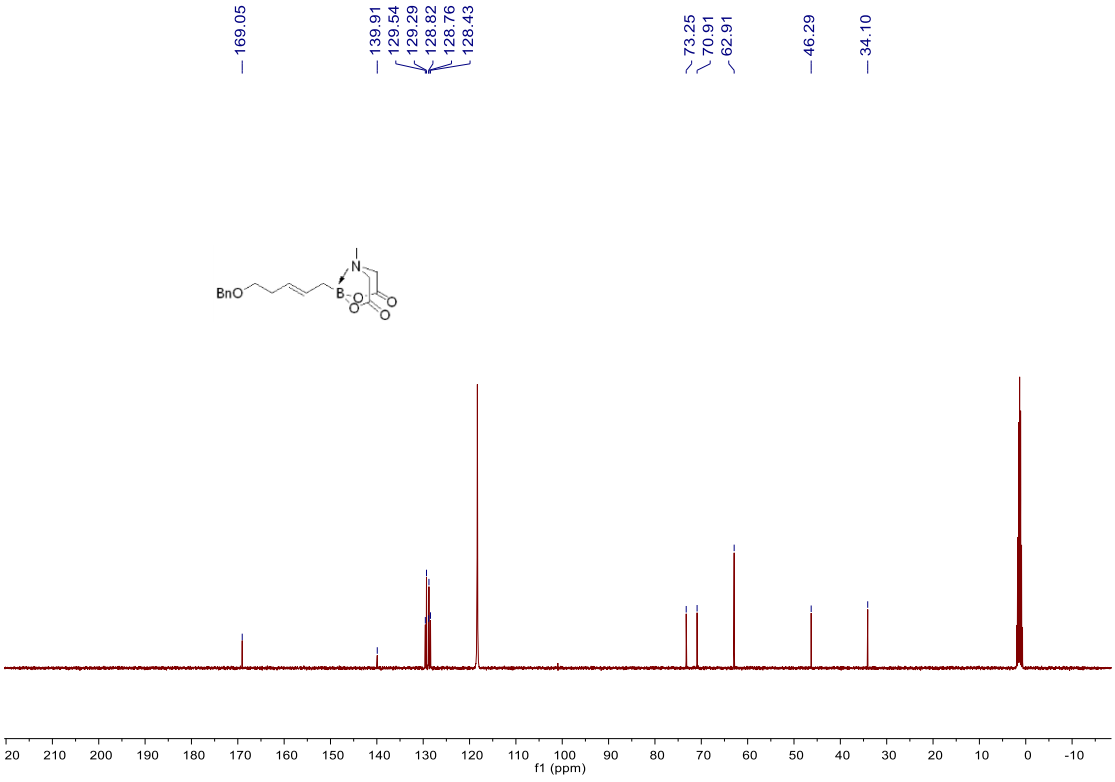

2.04
3.04
1.04
1.02
1.99
3.97
3.00
2.02
2.00
f1 (ppm)

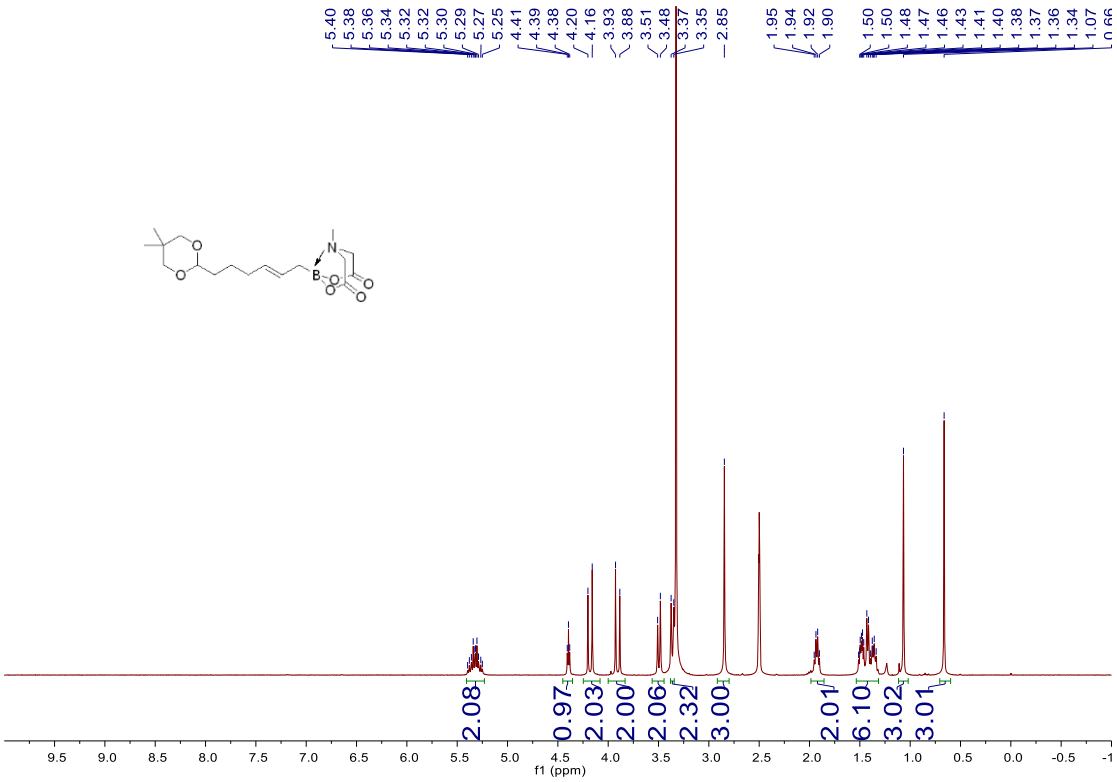

12.18
f1 (ppm)

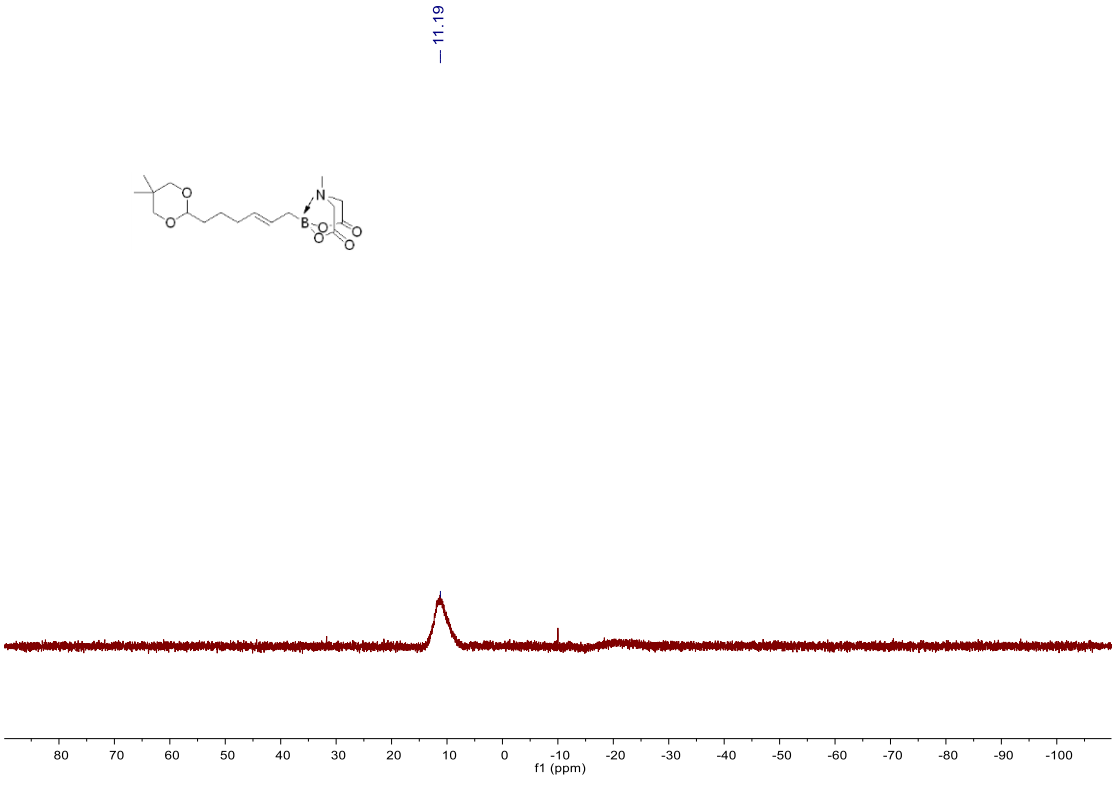

169.04
159.94
130.48
130.46
130.35
127.89
121.50
115.42
68.45
63.00
46.46
33.53
PhO
f1 (ppm)

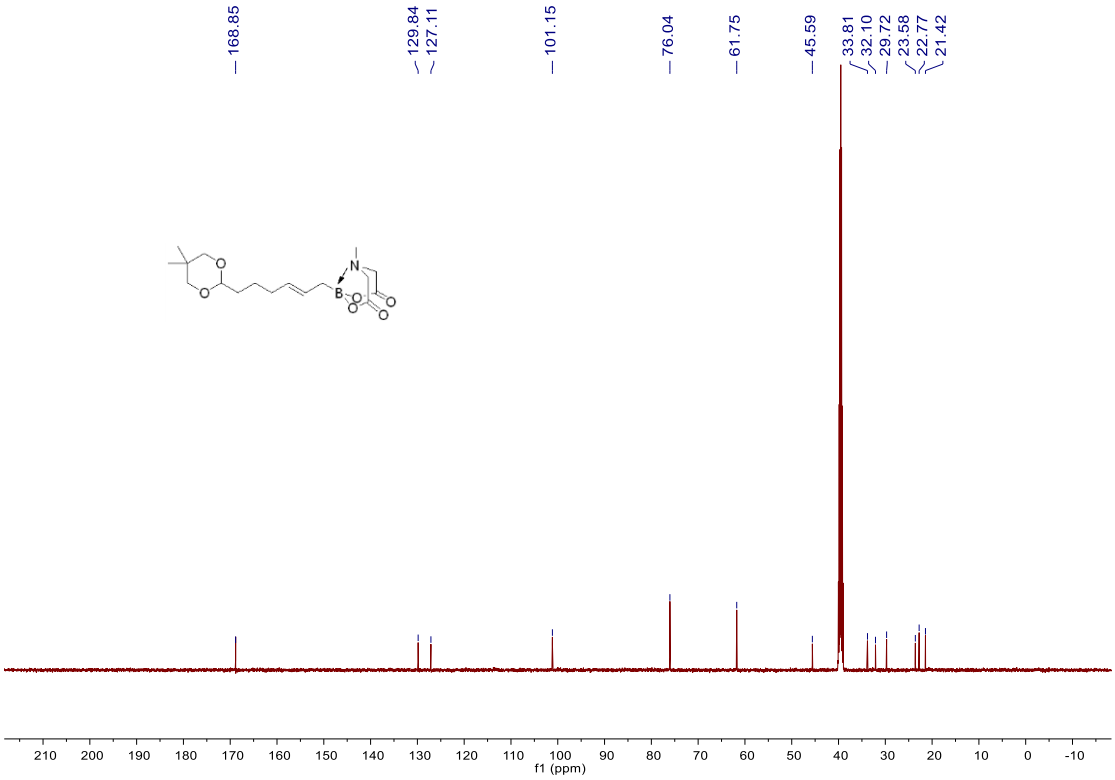

7.37
7.36
7.35
7.34
7.32
7.32
7.31
7.30
7.29
7.28
7.28
5.52
5.50
5.49
5.47
5.46
5.44
5.42
5.41
5.39
5.38
4.46
3.83
3.79
3.71
3.67
3.48
3.47
3.45
2.83
2.26
2.24
2.23
1.54
1.52
BnO
4.80
0.90
0.97
2.01
2.02
2.05
2.00
3.09
2.00
2.06
f1 (ppm)


12.17
BnO
f1 (ppm)


169.05
139.91
129.54
129.29
128.82
128.76
128.43
73.25
70.91
62.91
46.29
34.10
BnO
f1 (ppm)


5.40
5.38
5.36
5.34
5.32
5.32
5.30
5.29
5.27
5.25
4.41
4.39
4.38
4.20
4.16
3.93
3.88
3.51
3.48
3.37
3.35
2.85
1.95
1.94
1.92
1.90
1.50
1.50
1.48
1.47
1.46
1.43
1.41
1.40
1.38
1.37
1.36
1.34
1.07
2.08
0.97
2.03
2.00
2.06
2.32
3.00
2.01
6.10
3.02
3.01
f1 (ppm)


11.19
f1 (ppm)


168.85
129.84
127.11
101.15
76.04
61.75
45.59
33.81
32.10
29.72
23.58
22.77
21.42
f1 (ppm)


7.88
7.87
7.87
7.86
7.86
7.85
7.84
7.83
7.83
7.83
7.82
5.45
5.43
5.41
5.39
5.37
5.32
5.30
5.28
5.28
5.26
5.25
4.18
4.13
3.90
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3.58
3.56
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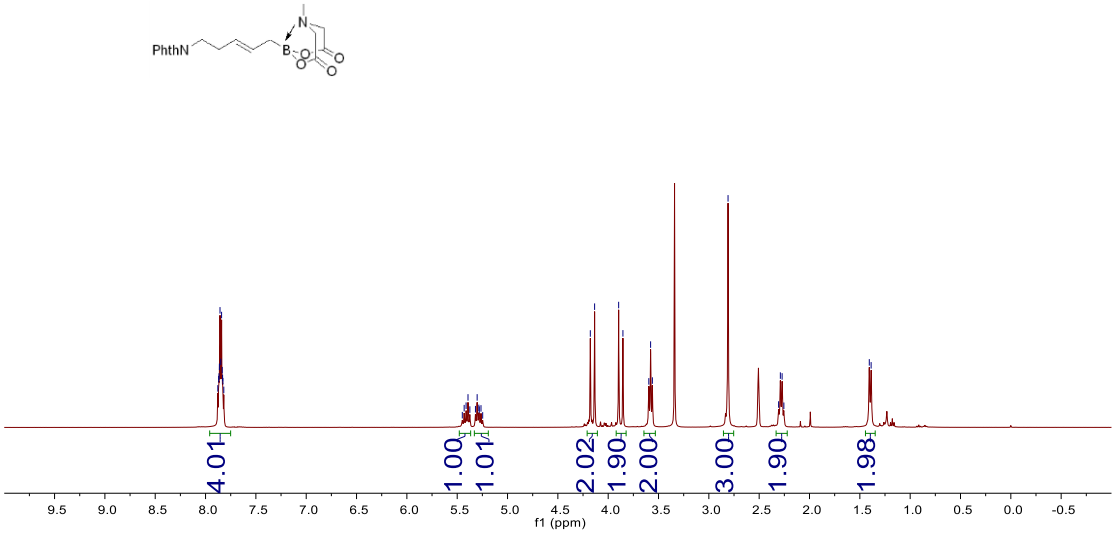
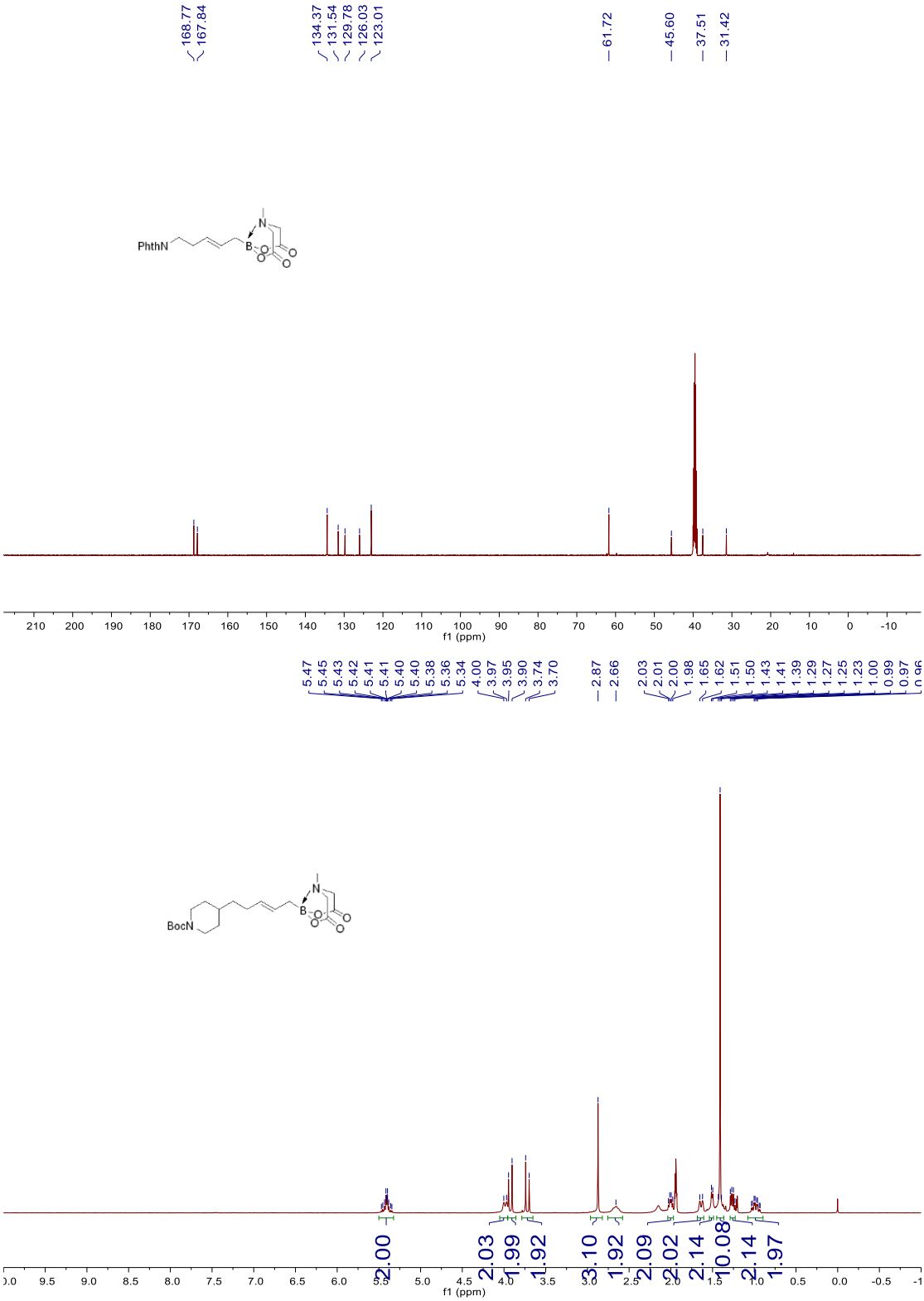
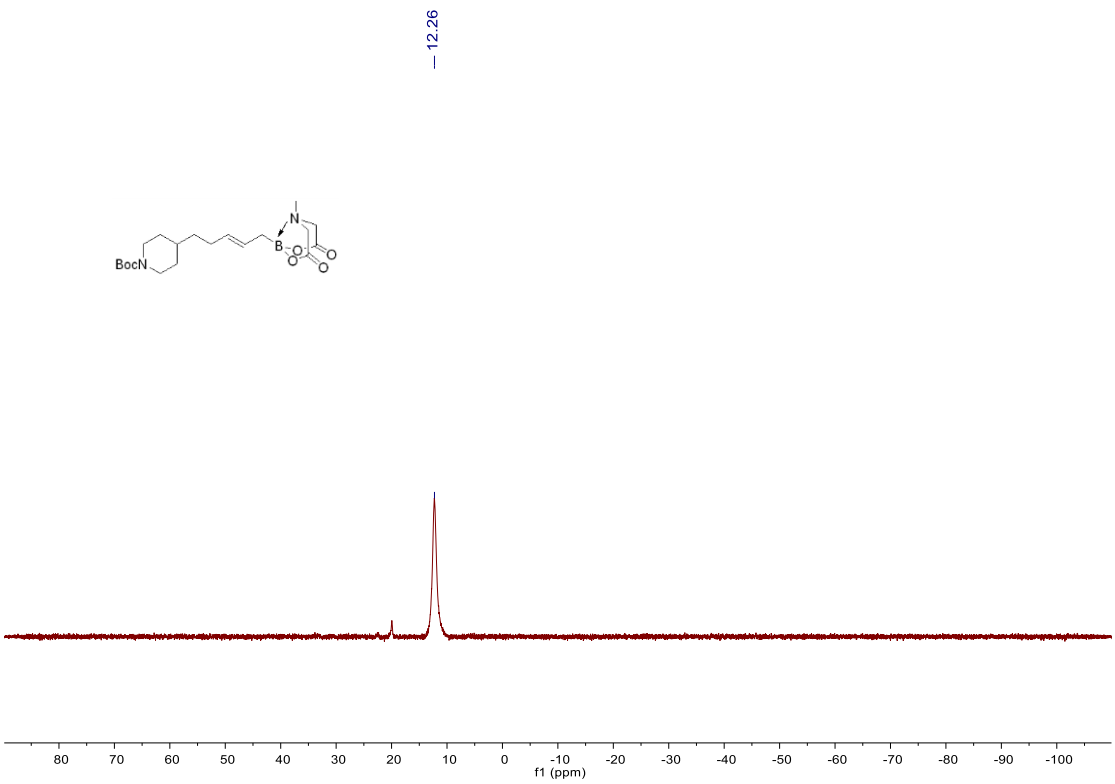
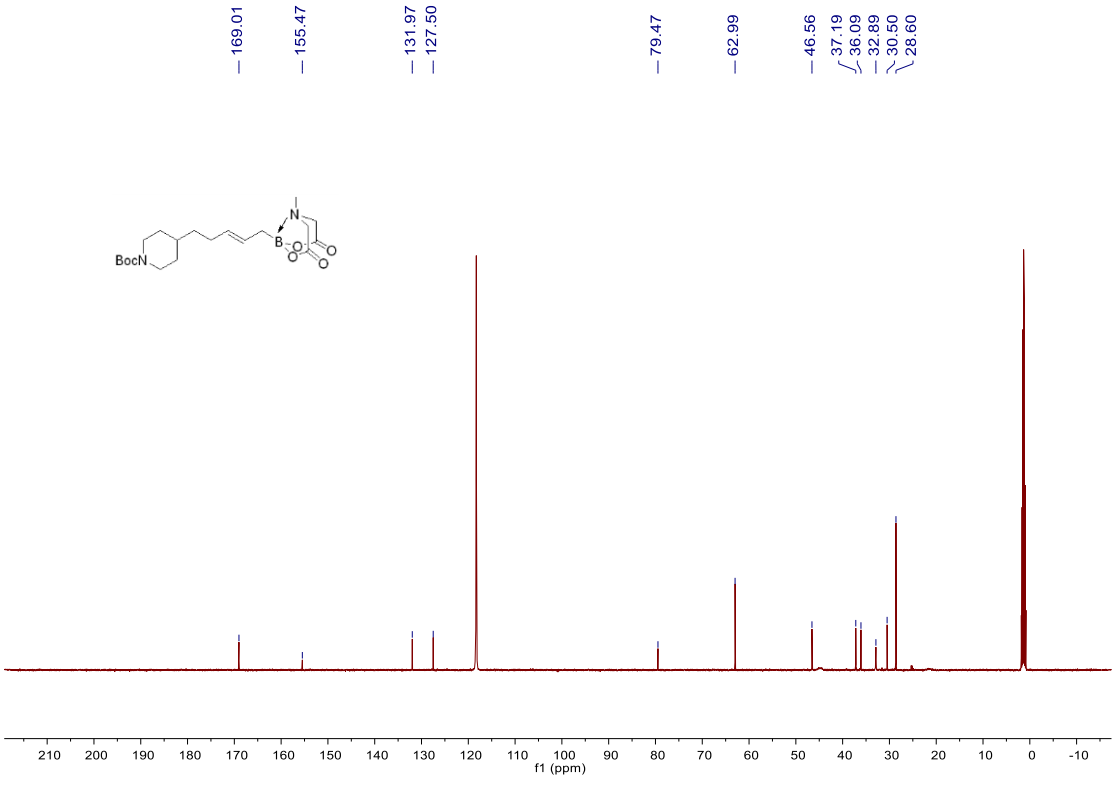
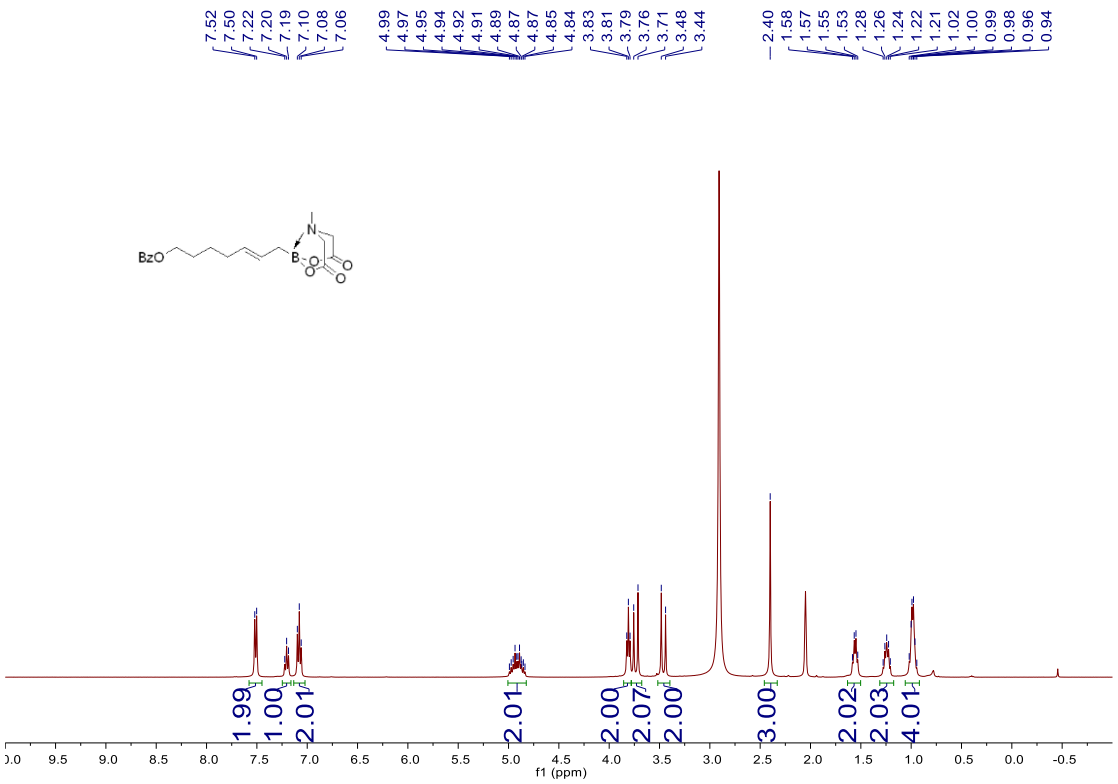
2.31
2.29
2.27
2.25
1.41
1.39

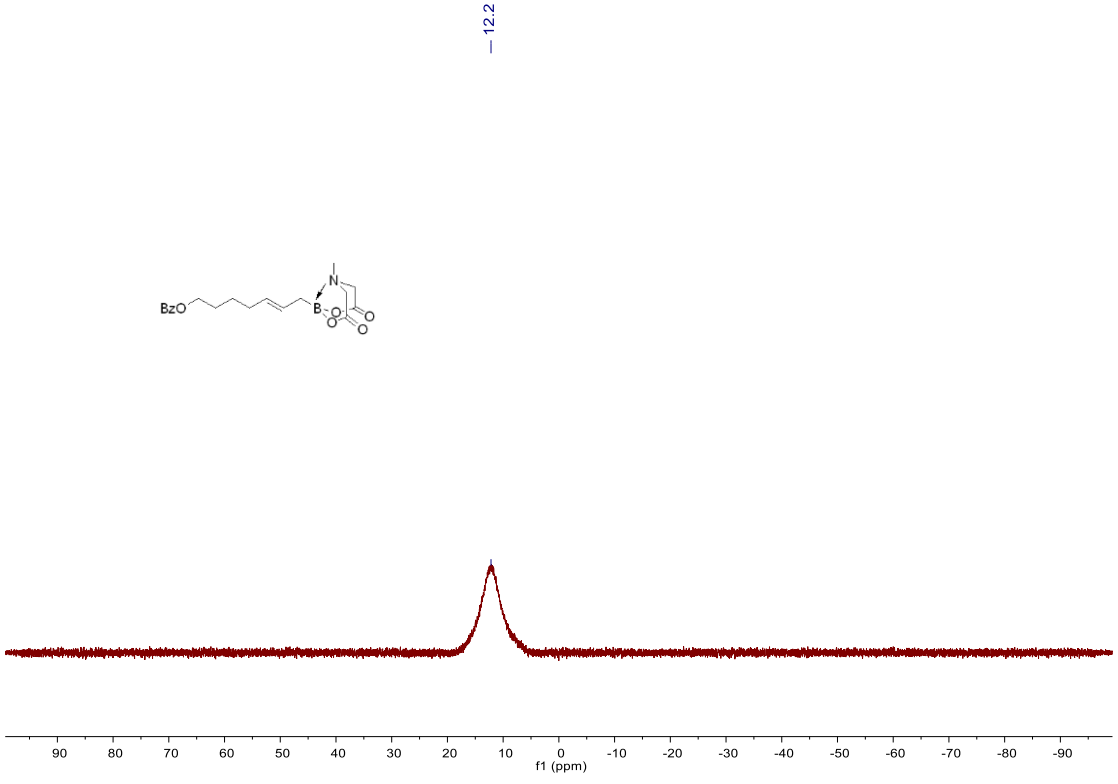

PhthN
4.01
1.00
1.01
2.02
1.90
2.00
3.00
1.90
1.98
f1 (ppm)

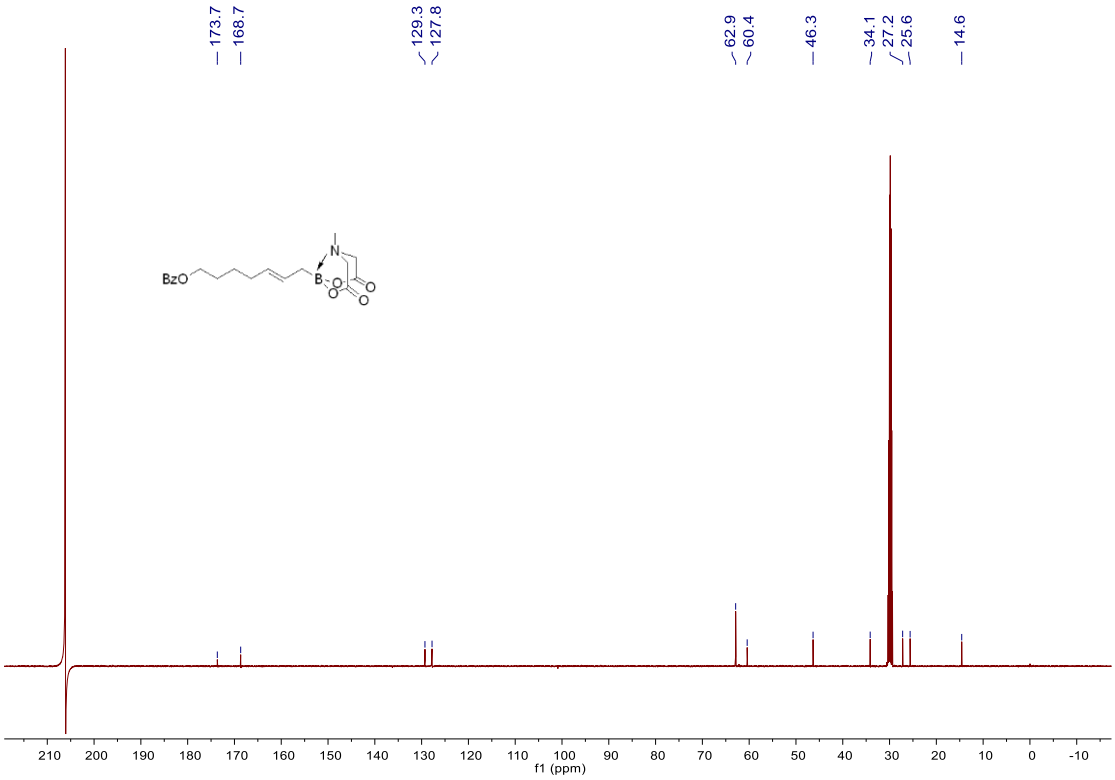

168.77
167.84
134.37
131.54
129.78
126.03
123.01
61.72
45.60
37.51
31.42
PhthN
f1 (ppm)
5.47
5.45
5.43
5.42
5.41
5.41
5.40
5.40
5.38
5.36
5.34
4.00
3.97
3.95
3.90
3.74
3.70
2.87
2.66
2.03
2.01
2.00
1.98
1.65
1.62
1.51
1.50
1.43
1.41
1.39
1.29
1.27
1.25
1.23
1.00
0.99
0.97
BocN
2.00
2.03
1.99
1.92
3.10
1.92
2.09
2.02
2.14
10.08
2.14
1.97
f1 (ppm)

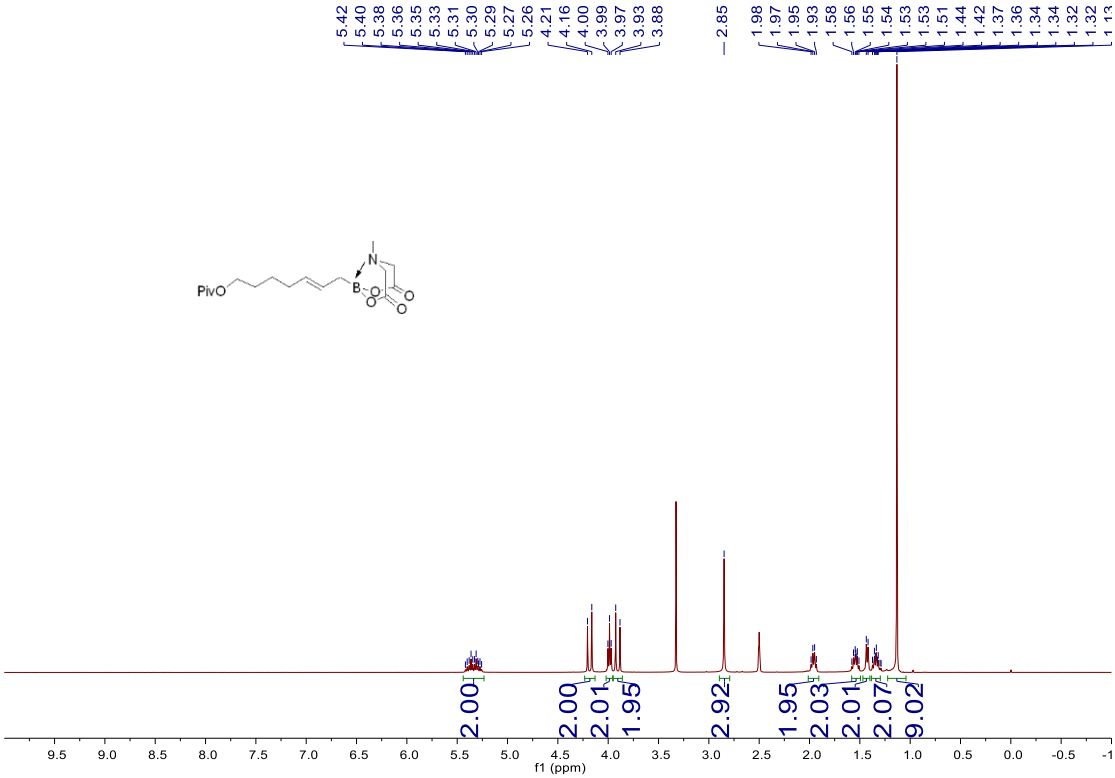

12.26
BocN
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)

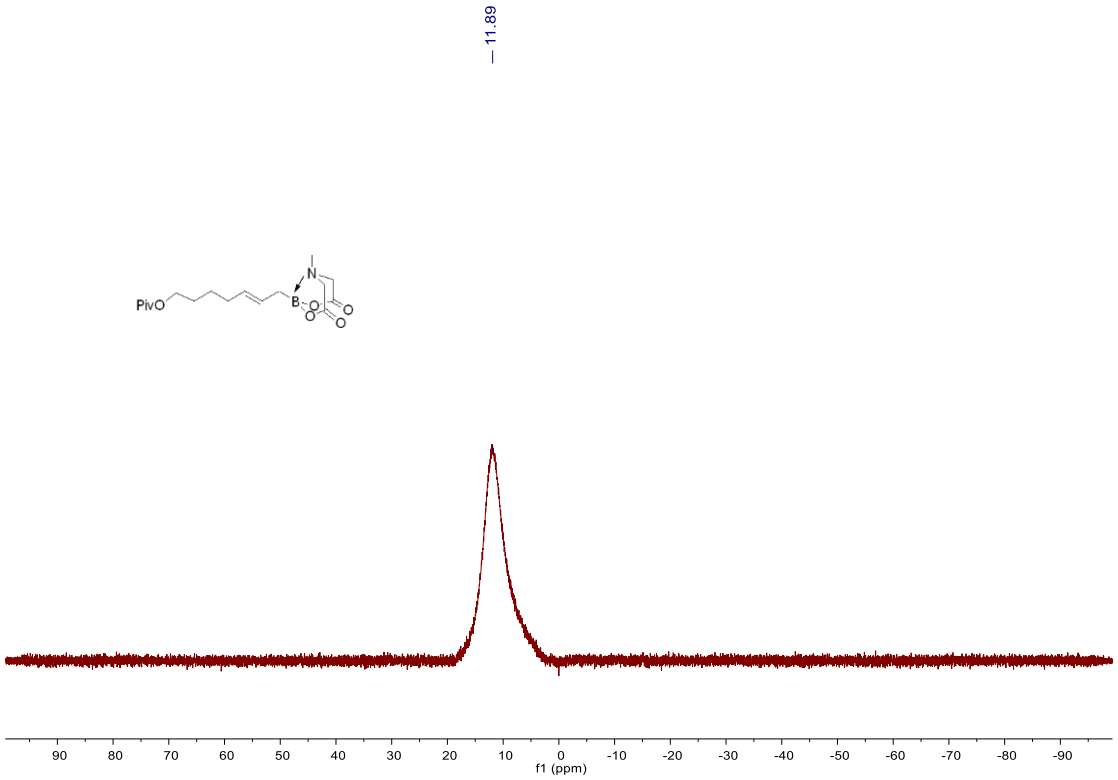

169.01
155.47
131.97
127.50
79.47
62.99
46.56
37.19
36.09
32.89
30.50
28.60
BocN
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

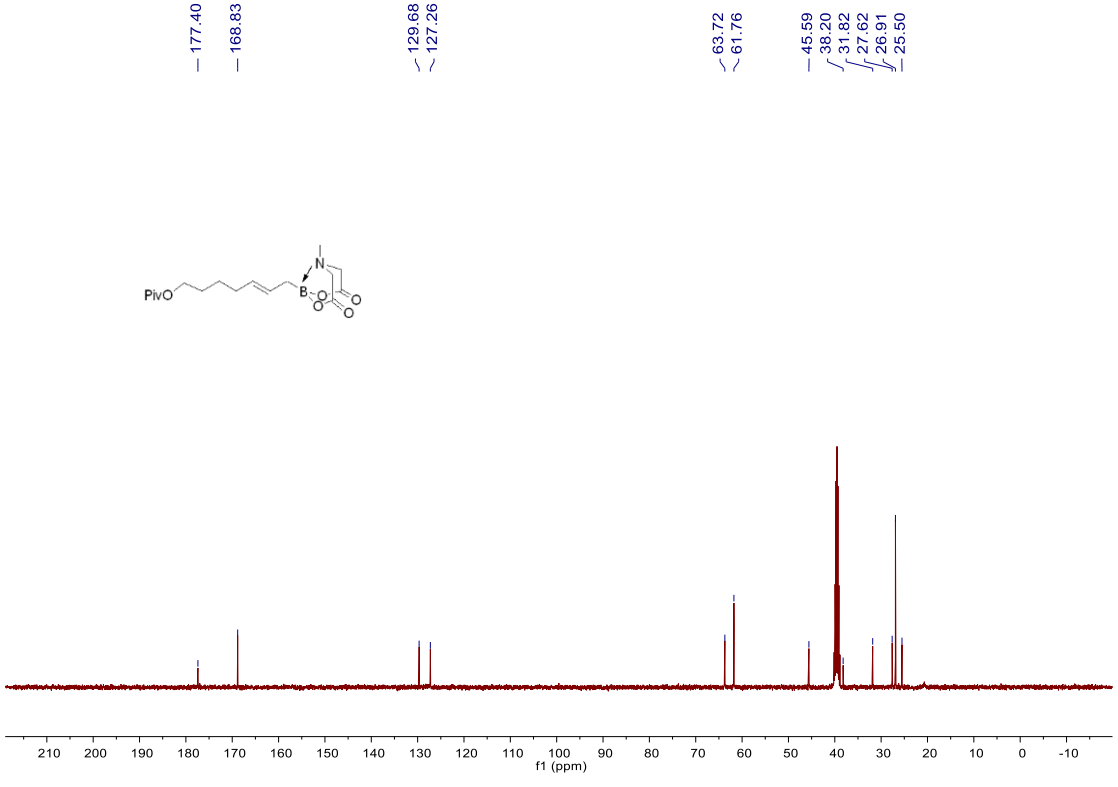

7.52
7.50
7.22
7.20
7.19
7.10
7.08
7.06
4.99
4.97
4.95
4.94
4.92
4.91
4.89
4.87
4.87
4.85
4.84
3.83
3.81
3.79
3.76
3.71
3.48
3.44
2.40
1.58
1.57
1.55
1.53
1.28
1.26
1.24
1.22
1.21
1.02
1.00
0.99
0.98
0.96
0.94
BzO
N
B
O
O
O
1.99
1.00
2.01
2.01
2.00
2.07
2.00
3.00
2.02
2.03
4.01
f1 (ppm)

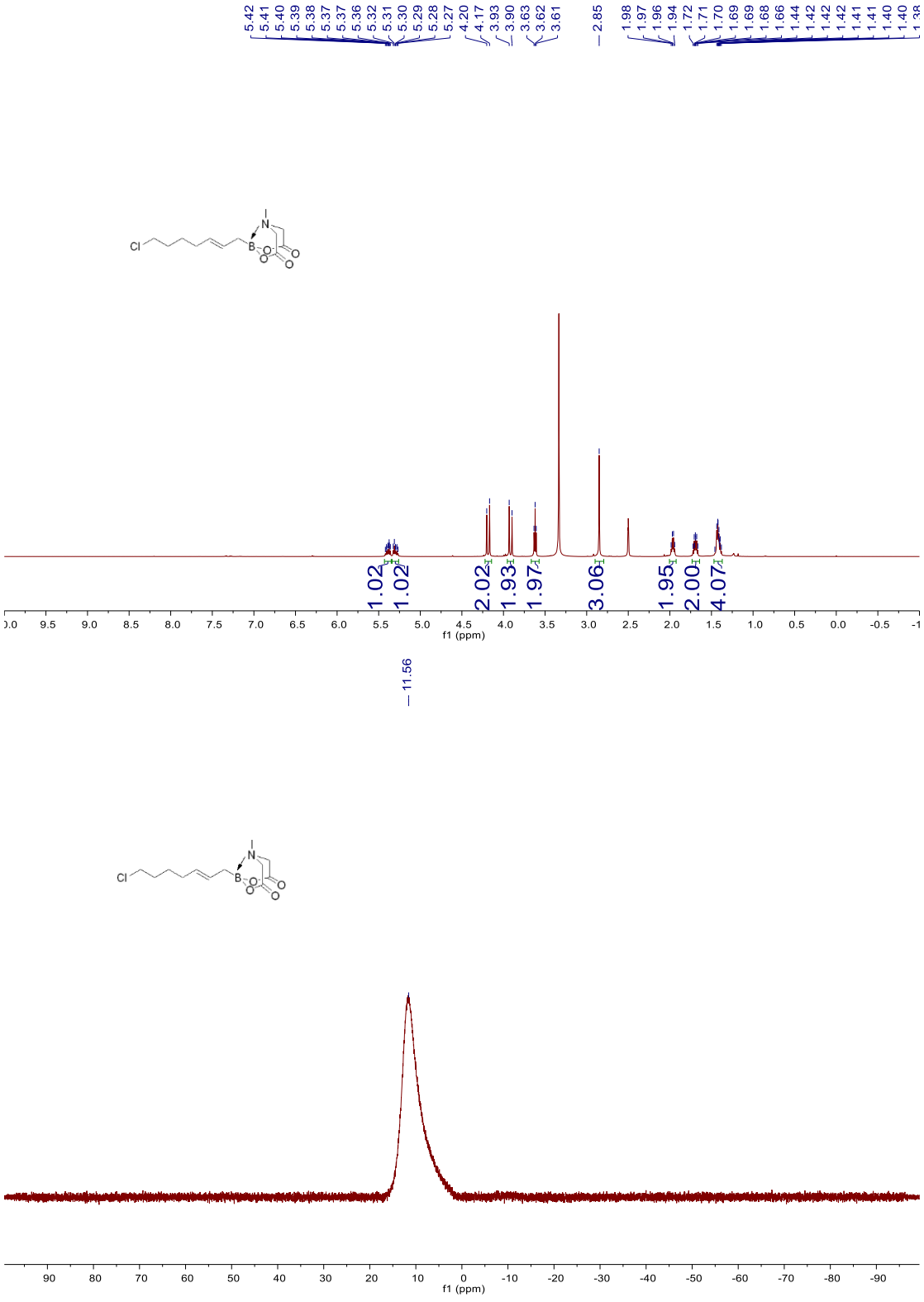

12.2
BzO
N
B
O
O
O
f1 (ppm)

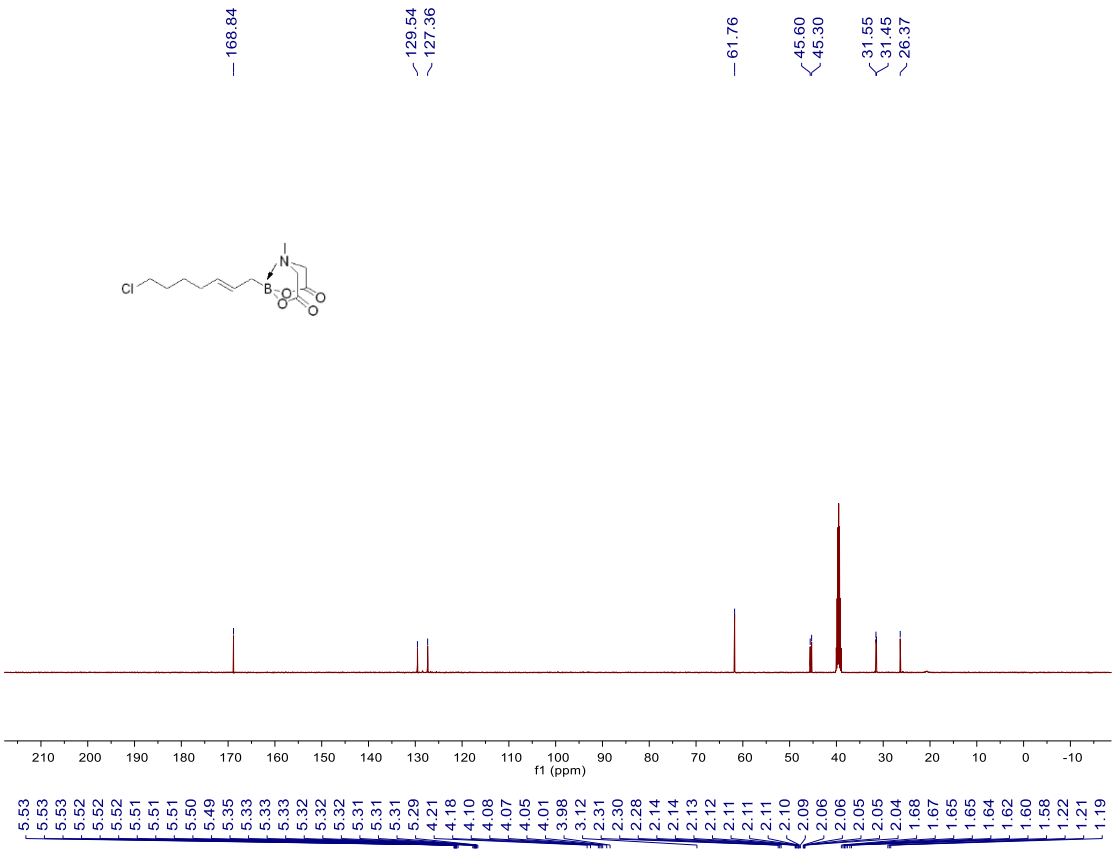

173.7
168.7
129.3
127.8
62.9
60.4
46.3
34.1
27.2
25.6
14.6
BzO
N
B
O
f1 (ppm)

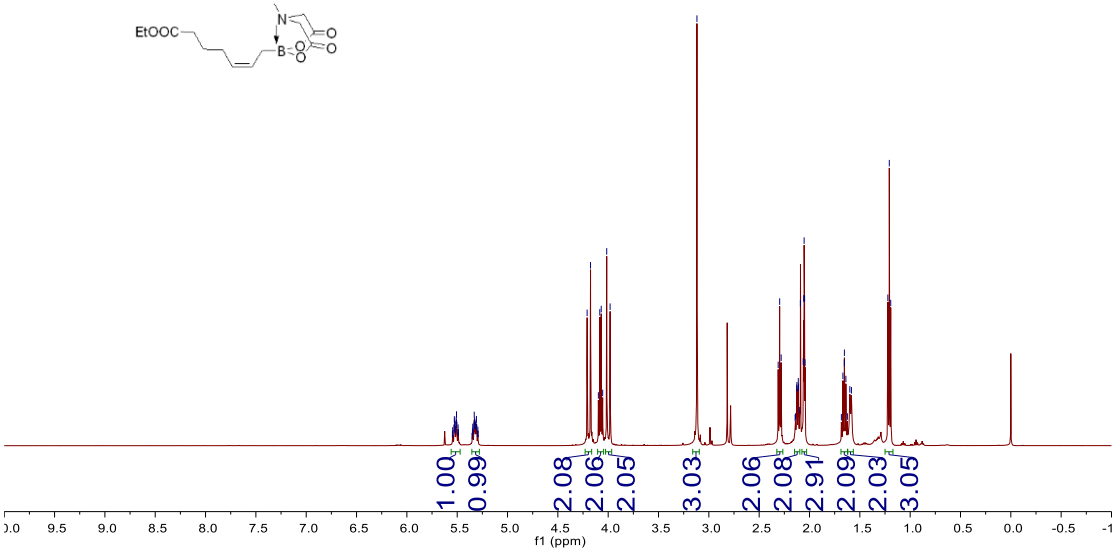

5.42
5.40
5.38
5.36
5.35
5.33
5.31
5.30
5.29
5.27
5.26
4.21
4.16
4.00
3.99
3.97
3.93
3.88
2.85
1.98
1.97
1.95
1.93
1.58
1.56
1.55
1.54
1.53
1.53
1.51
1.44
1.42
1.37
1.36
1.34
1.32
1.32
PivO
N
B
O
2.00
2.00
2.01
1.95
2.92
1.95
2.03
2.01
2.07
9.02
f1 (ppm)

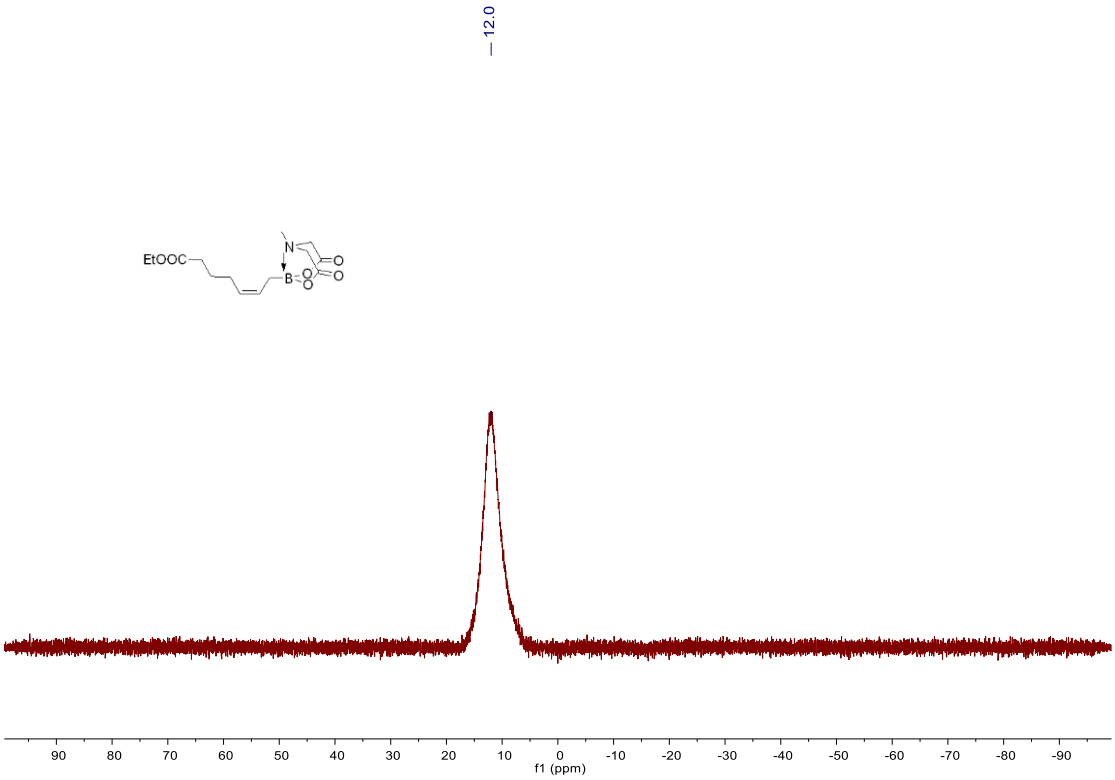

11.89
PivO
B
O
N
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

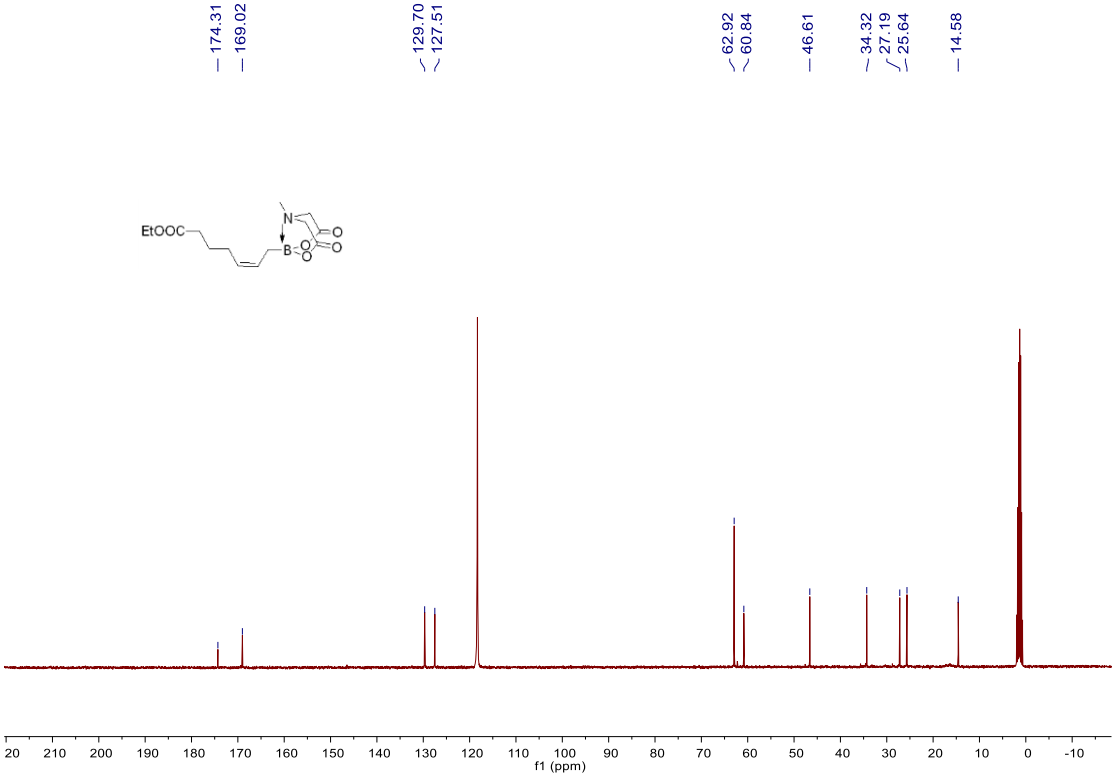

177.40
168.83
129.68
127.26
63.72
61.76
45.59
38.20
31.82
27.62
26.91
25.50
PivO
B
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

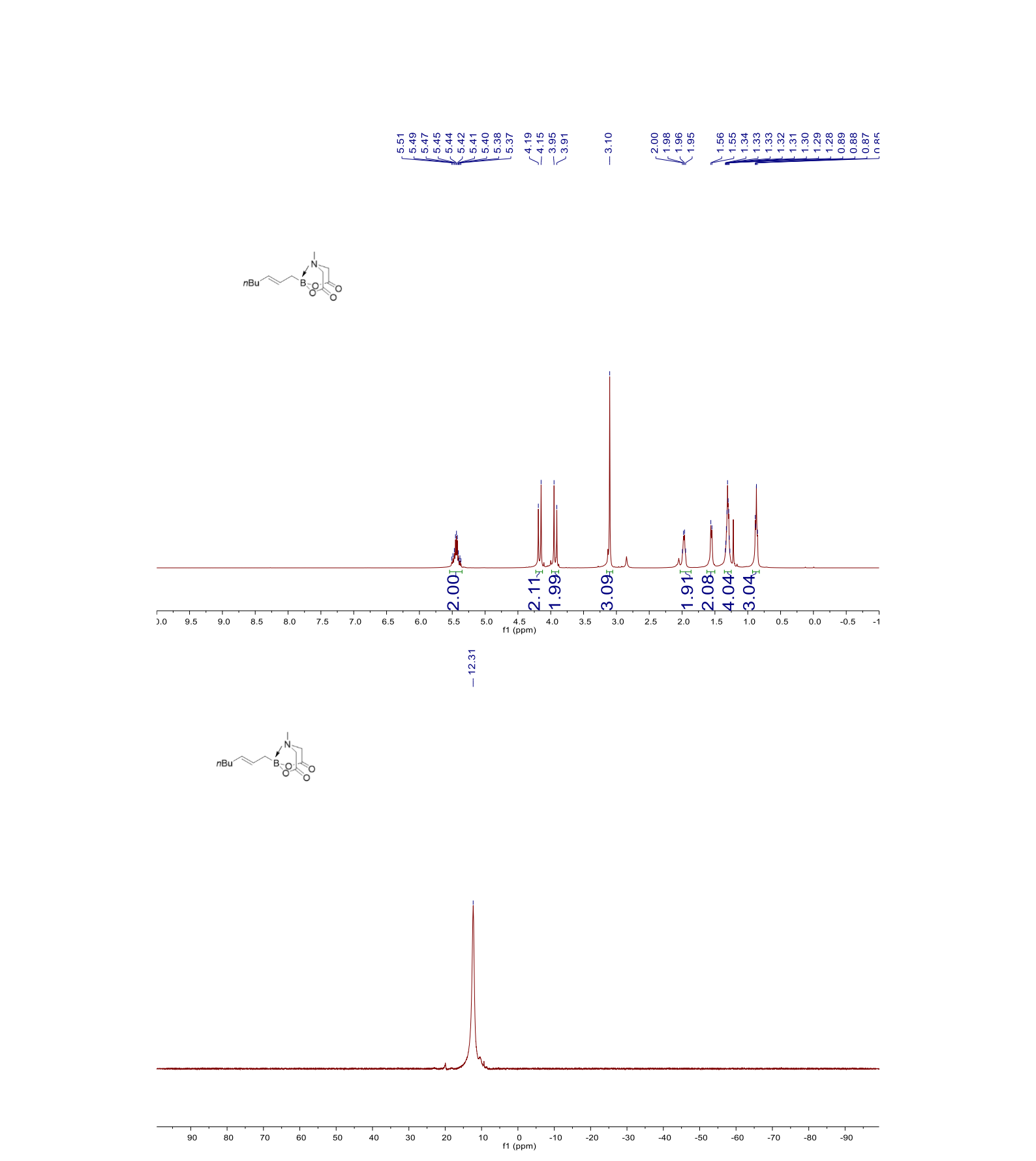

5.42
5.41
5.40
5.39
5.38
5.37
5.37
5.36
5.32
5.31
5.30
5.29
5.28
5.27
4.20
4.17
3.93
3.90
3.63
3.62
3.61
2.85
1.98
1.97
1.96
1.94
1.72
1.71
1.70
1.69
1.69
1.68
1.66
1.44
1.42
1.42
1.42
1.41
1.41
1.40
1.40
Cl
N
B
O
O
O
O
1.02
1.02
2.02
1.93
1.97
3.06
1.95
2.00
4.07
f1 (ppm)
11.56
Cl
N
B
O
O
O
O
f1 (ppm)

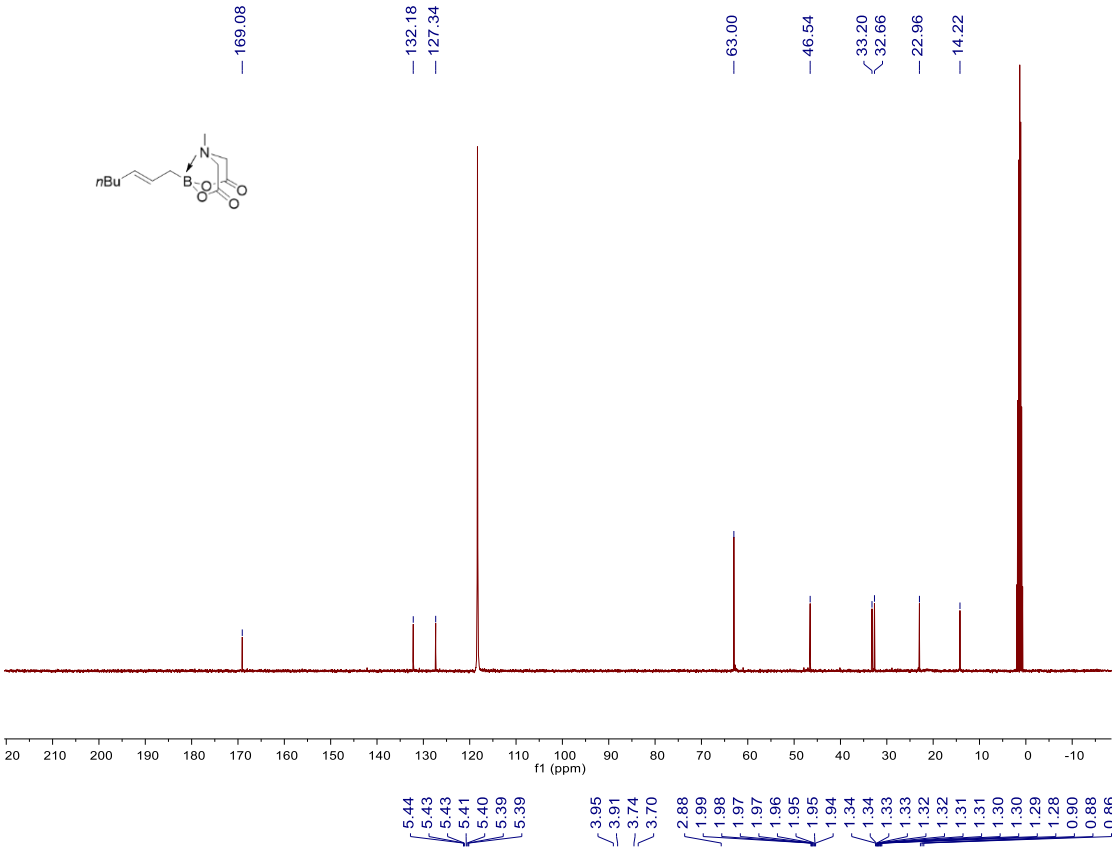

168.84
129.54
127.36
61.76
45.60
45.30
31.55
31.45
26.37
Cl
N
B
O
O
O
f1 (ppm)

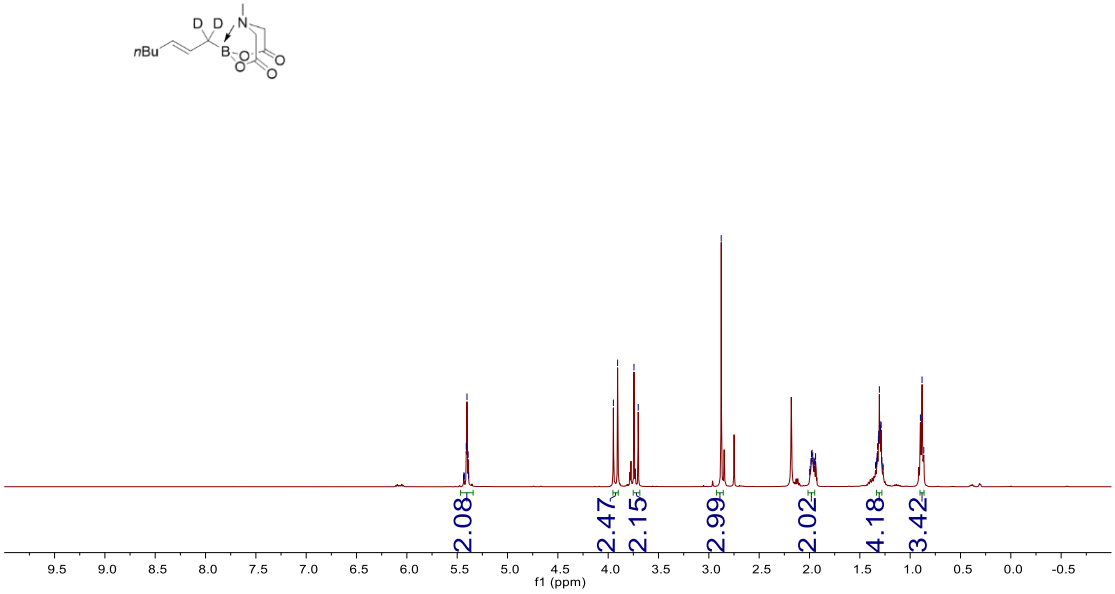

EtOOC
N
B
O
O
O
1.00
0.99
2.08
2.06
2.05
3.03
2.06
2.08
2.91
2.09
2.03
3.05
f1 (ppm)

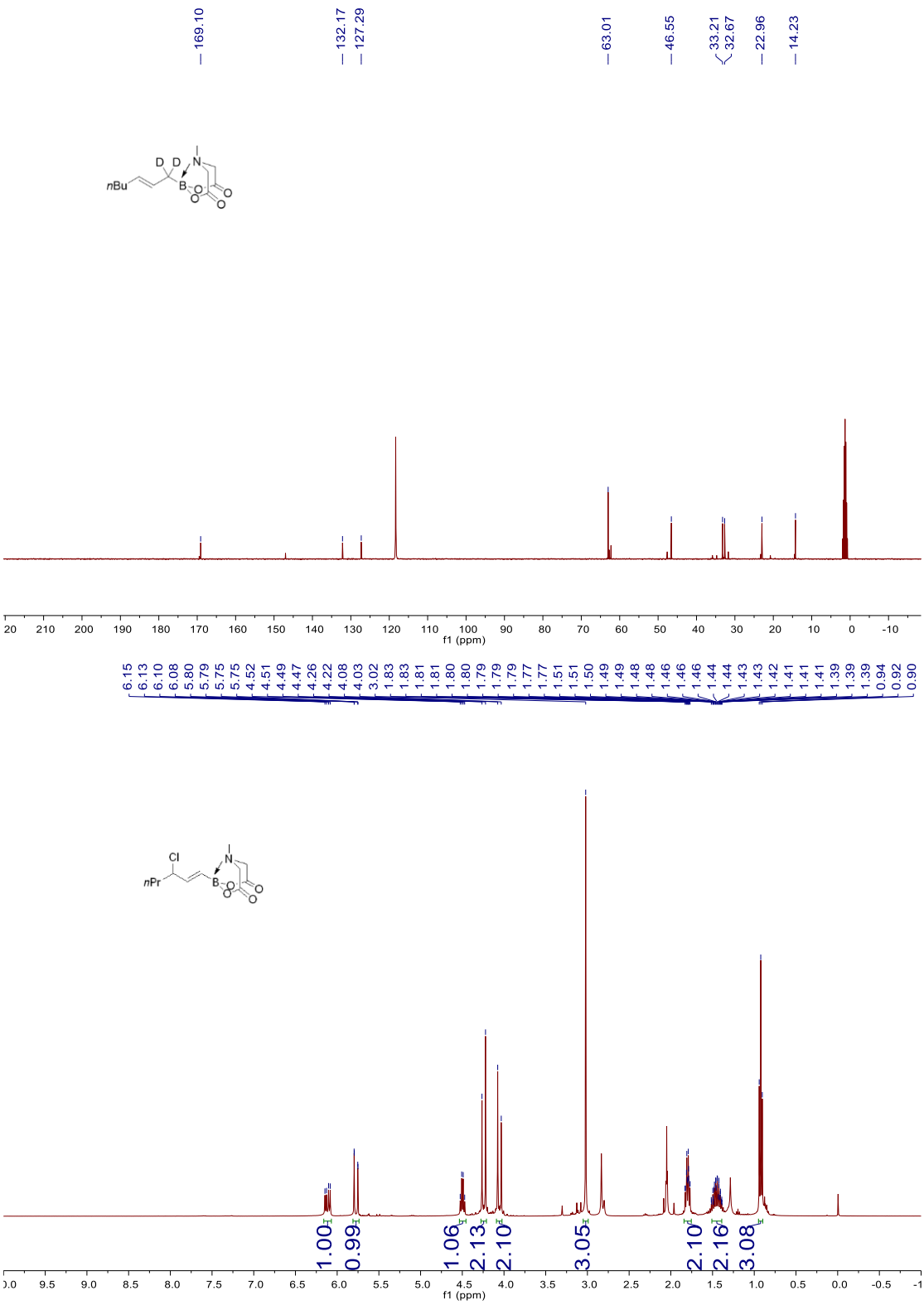

12.0
EtOOC
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

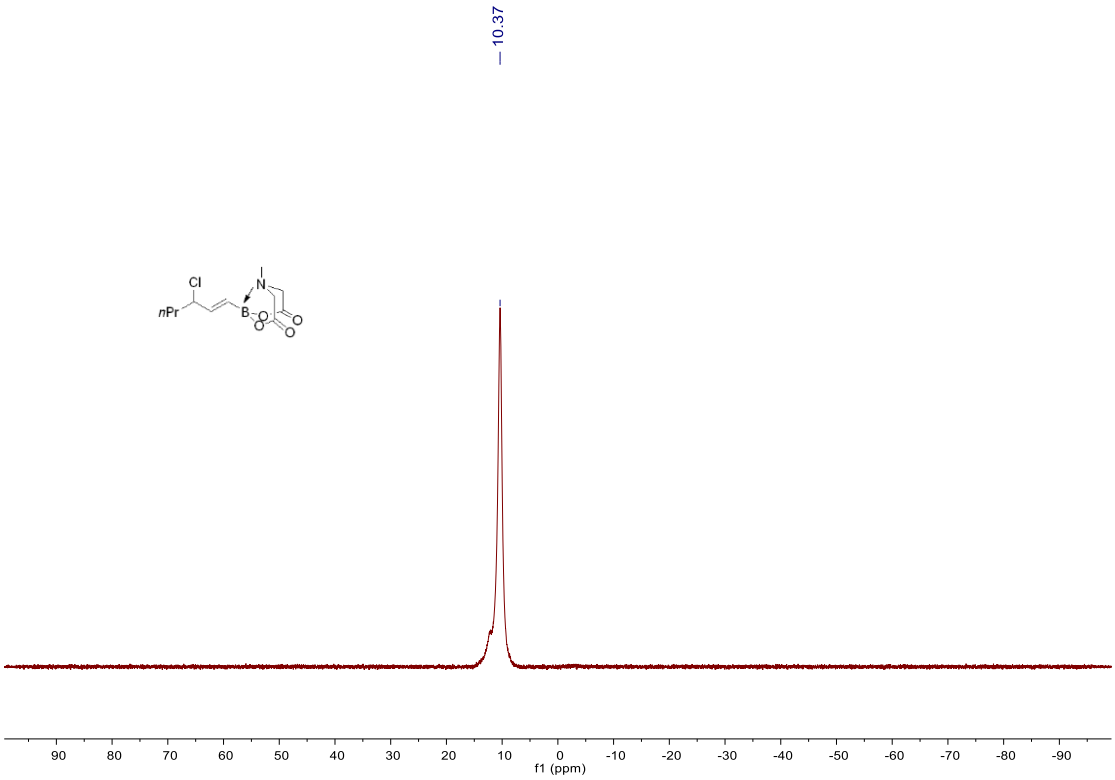

174.31
169.02
129.70
127.51
62.92
60.84
46.61
34.32
27.19
25.64
14.58
EtOOC
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

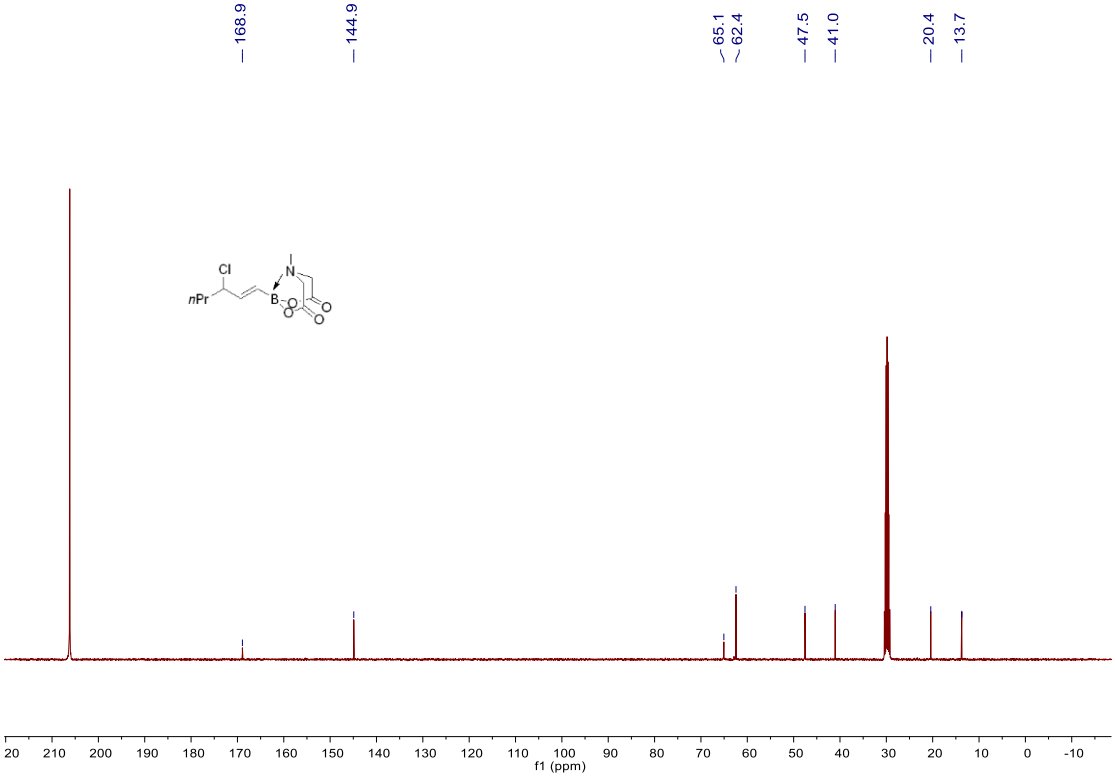

5.51
5.49
5.47
5.45
5.44
5.42
5.41
5.40
5.38
5.37
4.19
4.15
3.95
3.91
3.10
2.00
1.98
1.96
1.95
1.56
1.55
1.34
1.33
1.32
1.31
1.30
1.29
1.28
0.89
0.88
0.87
nBu
N
B
O
O
O
2.00
2.11
1.99
3.09
1.91
2.08
4.04
3.04
f1 (ppm)
12.31
nBu
N
B
O
O
O
f1 (ppm)

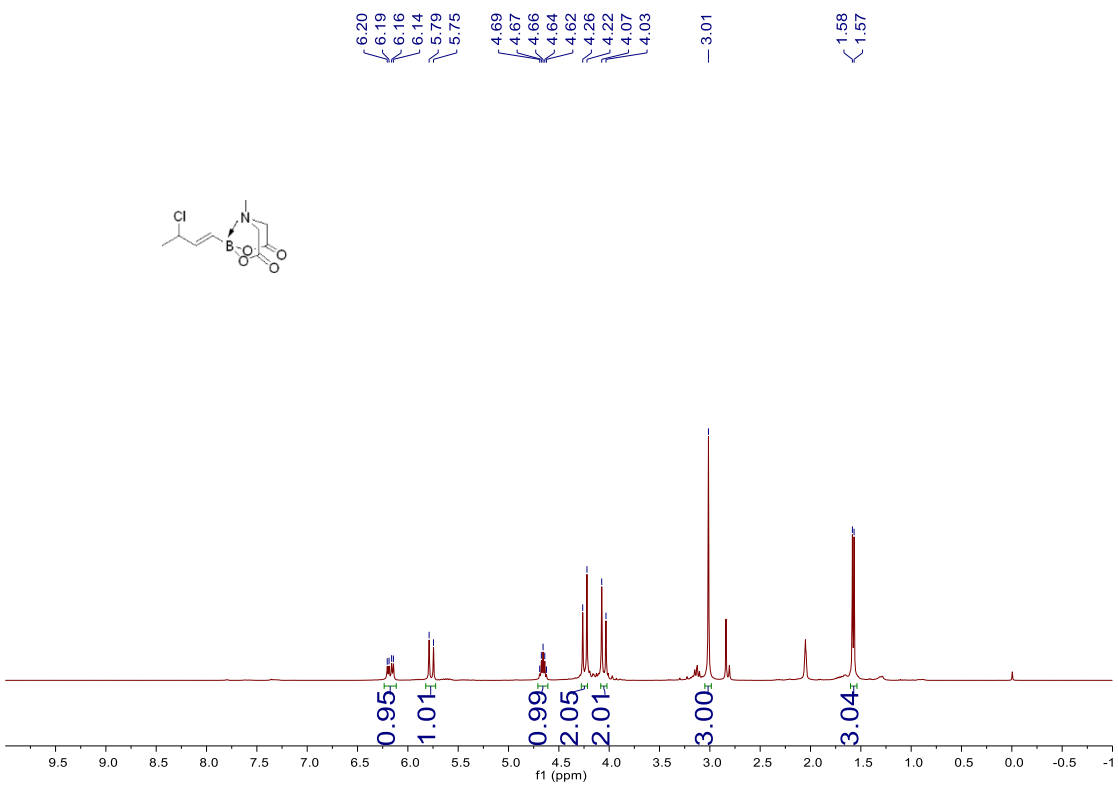

169.08
132.18
127.34
63.00
46.54
33.20
32.66
22.96
14.22
nBu
N
B
O
O
O
O
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
5.44 5.43 5.43 5.41 5.40 5.39 5.39
3.95 3.91 3.74 3.70
2.88 1.99 1.98 1.97 1.97 1.96 1.95 1.95 1.94
1.34 1.34 1.33 1.33 1.32 1.32 1.31 1.31 1.30 1.30 1.29 1.28 0.90 0.88

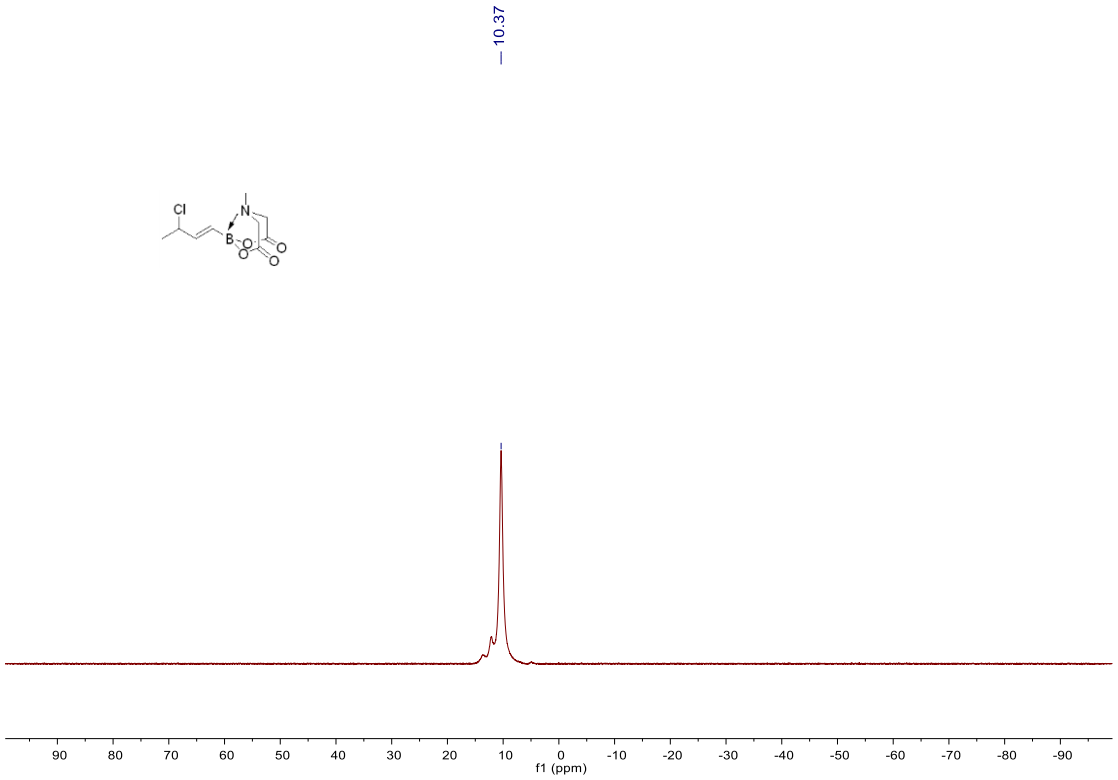

D
D
nBu
N
B
O
O
O
2.08
2.47
2.15
2.99
2.02
4.18
3.42
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

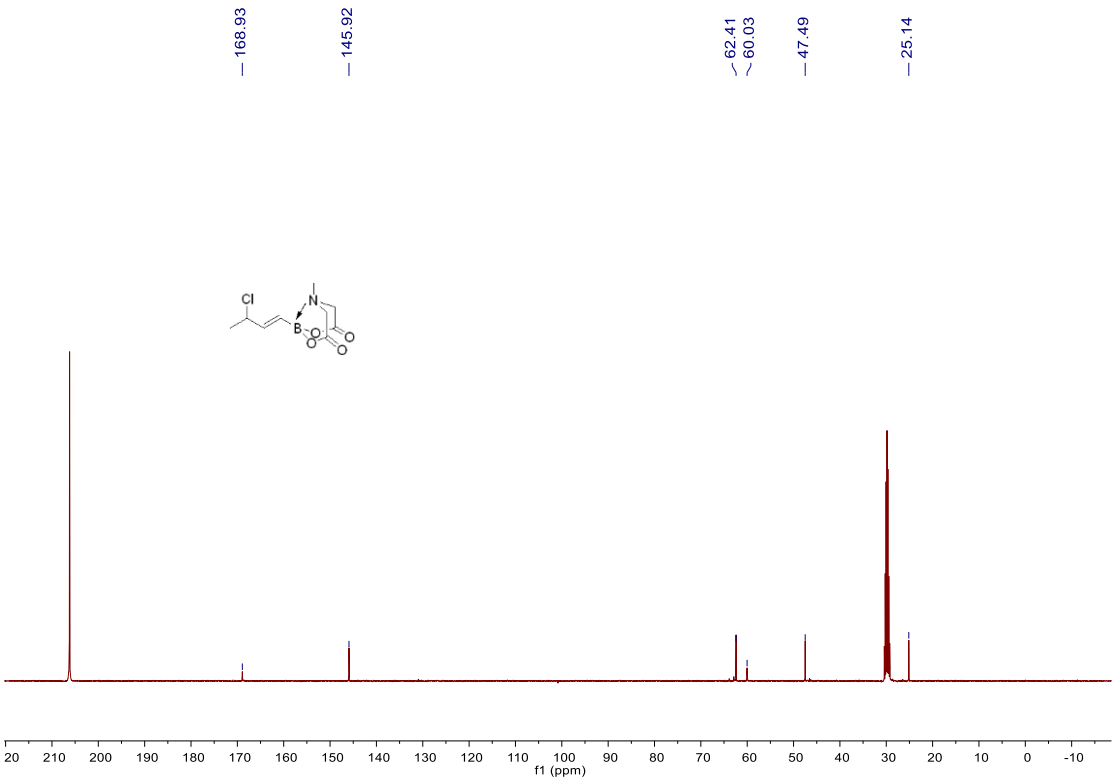

169.10
132.17
127.29
63.01
46.55
33.21
32.67
22.96
14.23
D
D
N
nBu
B
O
O
O
f1 (ppm)
6.15
6.13
6.10
6.08
5.80
5.79
5.75
5.75
4.52
4.51
4.49
4.47
4.26
4.22
4.08
4.03
3.02
1.83
1.81
1.80
1.80
1.79
1.79
1.79
1.77
1.77
1.51
1.51
1.50
1.49
1.49
1.48
1.48
1.46
1.46
1.46
1.44
1.44
1.43
1.42
1.41
1.41
1.41
1.39
1.39
0.94
0.92
0.90
Cl
nPr
1.00
0.99
1.06
2.13
2.10
3.05
2.10
2.16
3.08
f1 (ppm)

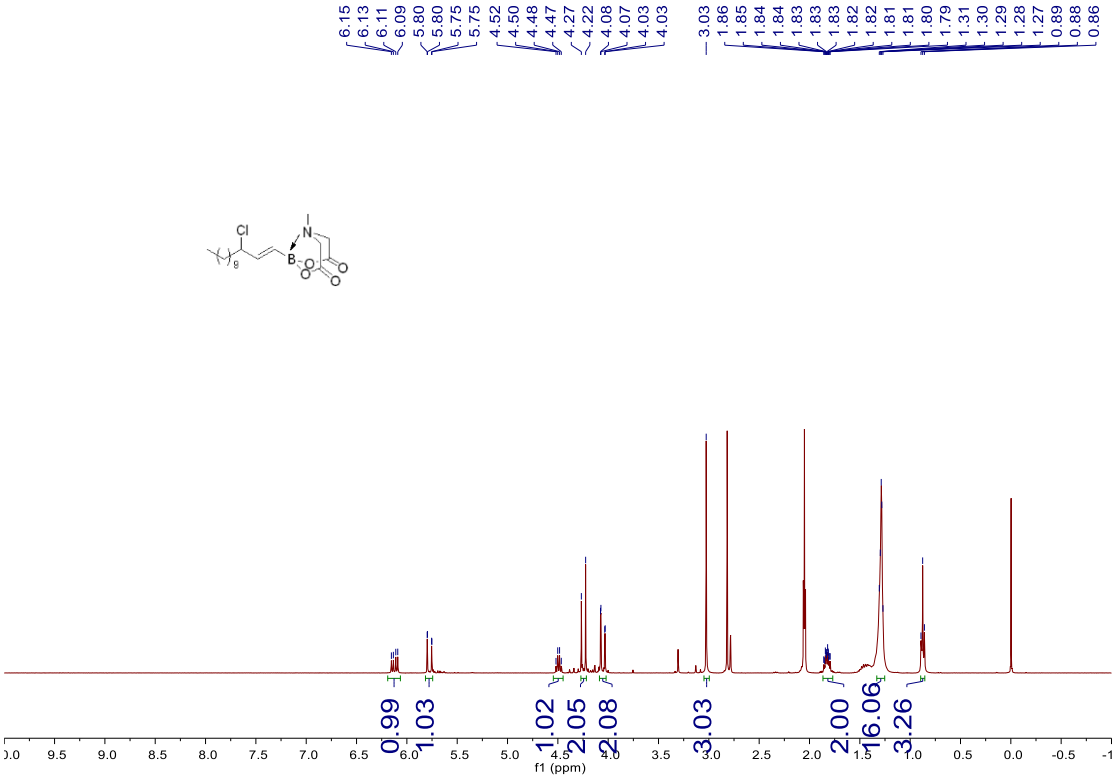

10.37
Cl
nPr
N
B
O
O
O
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

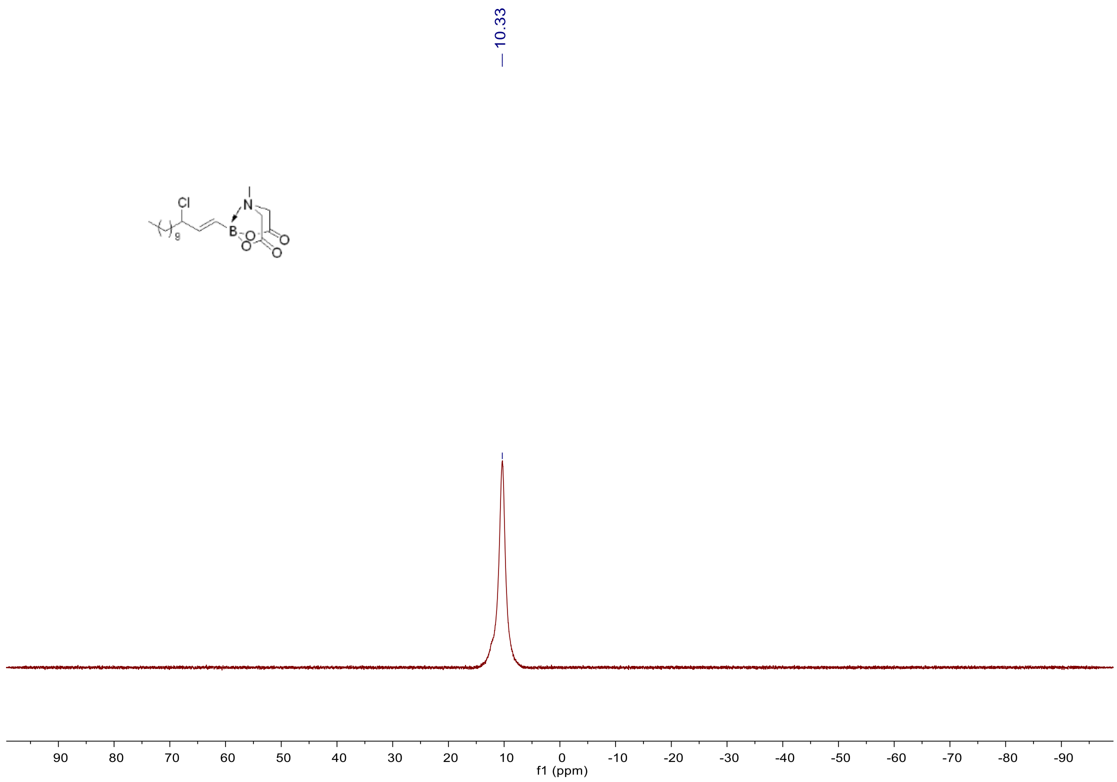

168.9
144.9
65.1
62.4
47.5
41.0
20.4
13.7
Cl
nPr
N
B
O
O
O
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


6.20
6.19
6.16
6.14
5.79
5.75
4.69
4.67
4.66
4.64
4.62
4.26
4.22
4.07
4.03
3.01
1.58
1.57
Cl
N
B
O
O
O
O
0.95
1.01
0.99
2.05
2.01
3.00
3.04
f1 (ppm)

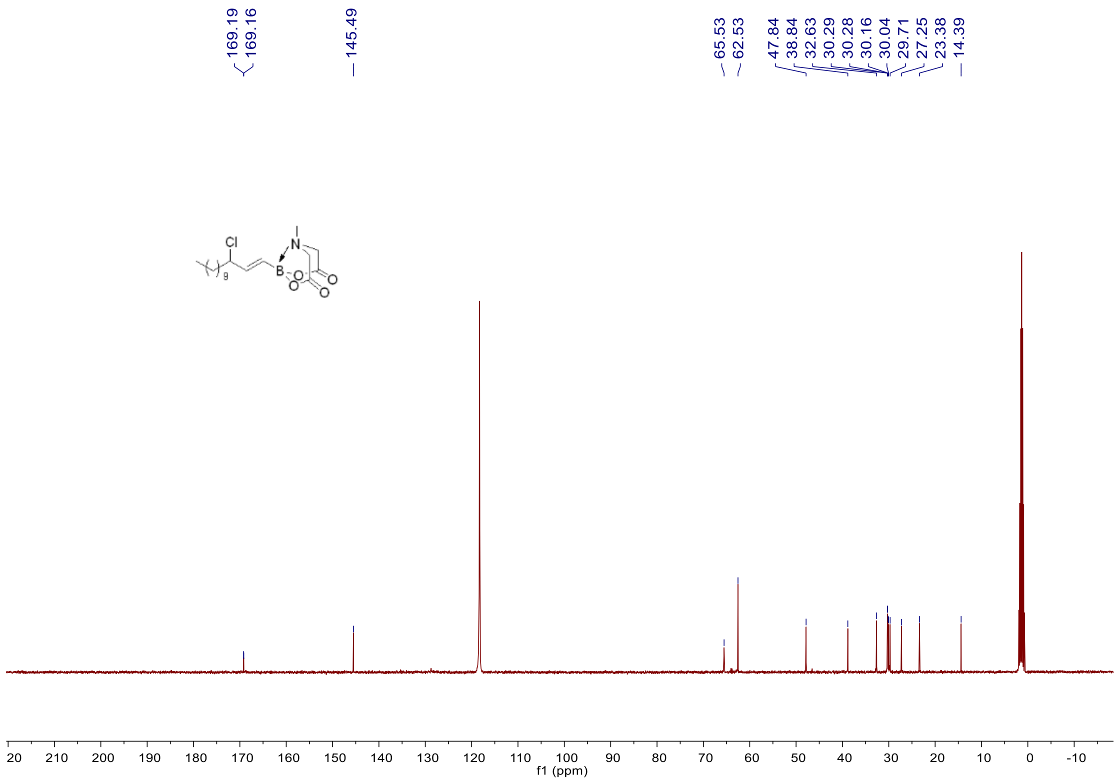

10.37
Cl
N
B
O
O
O
O
f1 (ppm)


168.93
145.92
62.41
60.03
47.49
25.14
Cl
N
B
O
O
O
O
f1 (ppm)

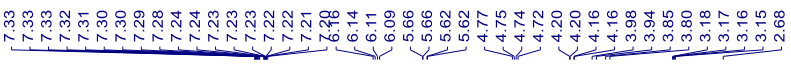

6.15
6.13
6.11
6.09
5.80
5.80
5.75
5.75
4.52
4.50
4.48
4.47
4.27
4.22
4.08
4.07
4.03
4.03
3.03
1.86
1.85
1.84
1.84
1.83
1.83
1.83
1.82
1.82
1.81
1.81
1.80
1.79
1.31
1.30
1.29
1.28
1.27
0.89
0.88
0.86
Cl
N
B
O
O
O
O
g
0.99
1.03
1.02
2.05
2.08
3.03
2.00
16.06
3.26
f1 (ppm)

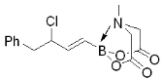


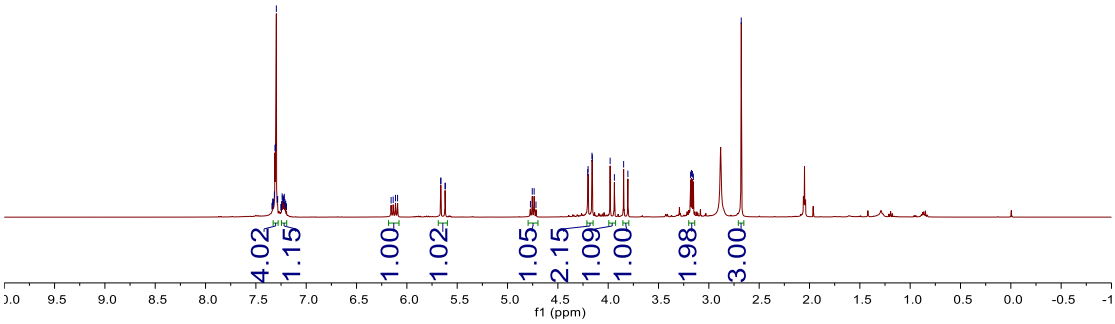
10.33
Cl
N
B
O
O
O
O
9
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

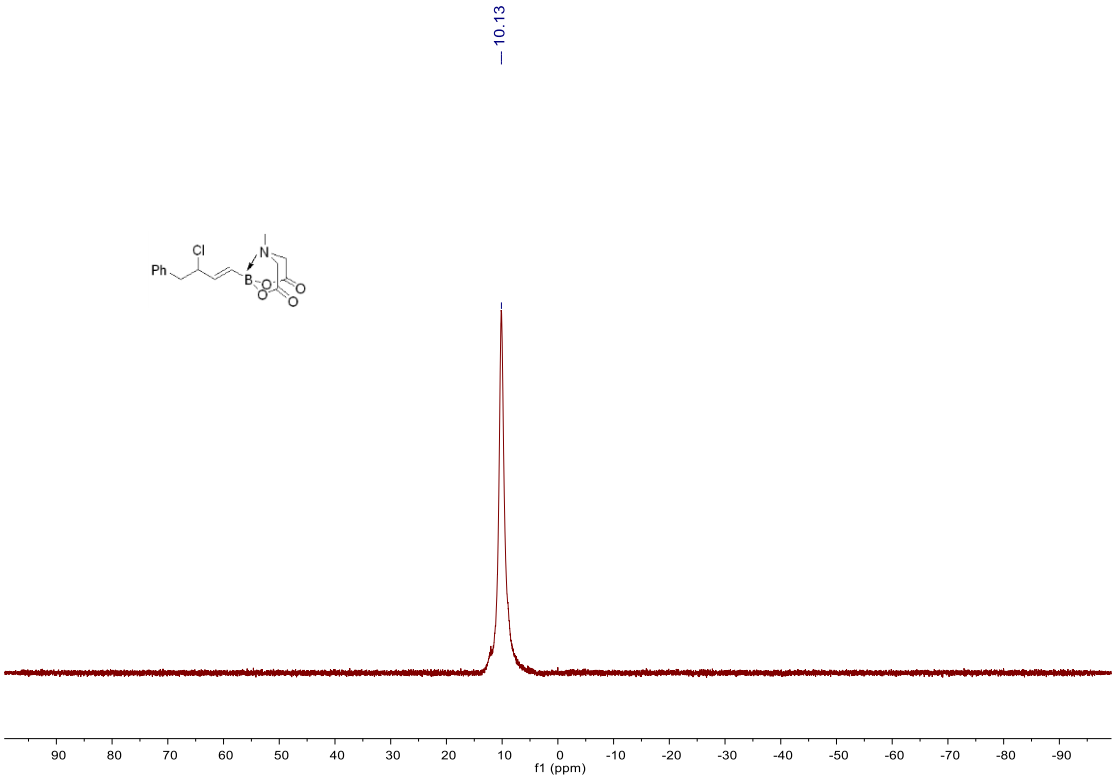


169.19
169.16
145.49
65.53
62.53
47.84
38.84
32.63
30.29
30.28
30.16
30.04
29.71
27.25
23.38
14.39
Cl
N
B
O
O
O
O
9
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

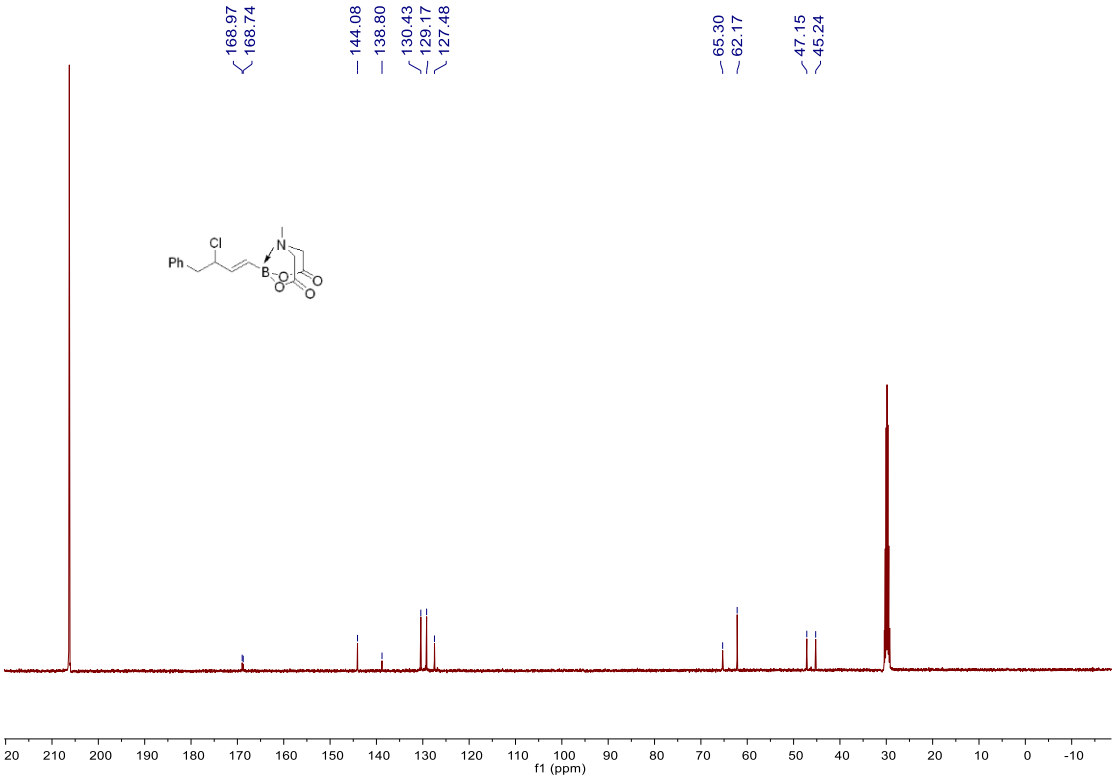

7.33
7.33
7.33
7.32
7.31
7.30
7.30
7.29
7.28
7.24
7.24
7.23
7.23
7.23
7.22
7.22
7.21
6.18
6.14
6.11
6.09
5.66
5.66
5.62
5.62
4.77
4.75
4.74
4.72
4.20
4.20
4.16
4.16
3.98
3.94
3.85
3.80
3.18
3.17
3.16
3.15
2.68

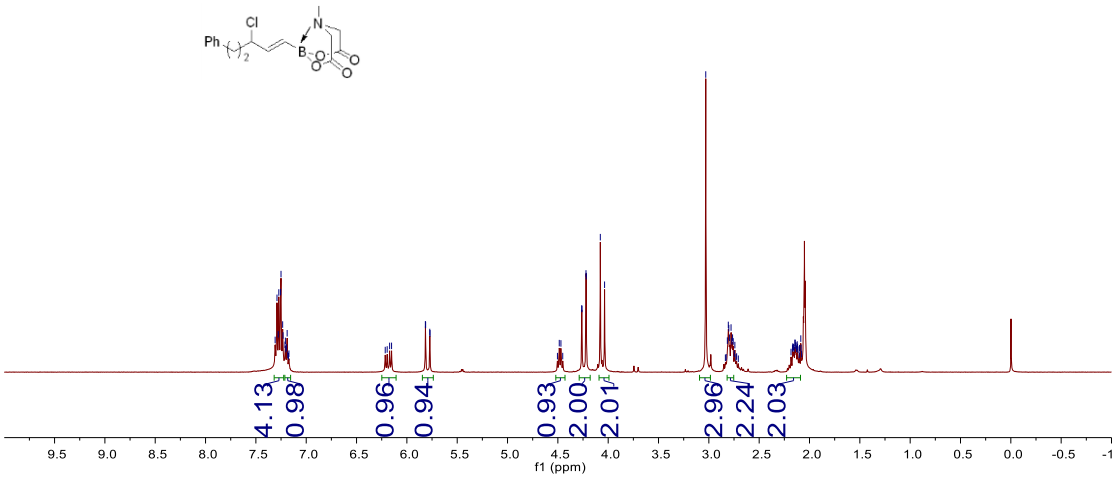

Ph
Cl
N
B
O
O
O

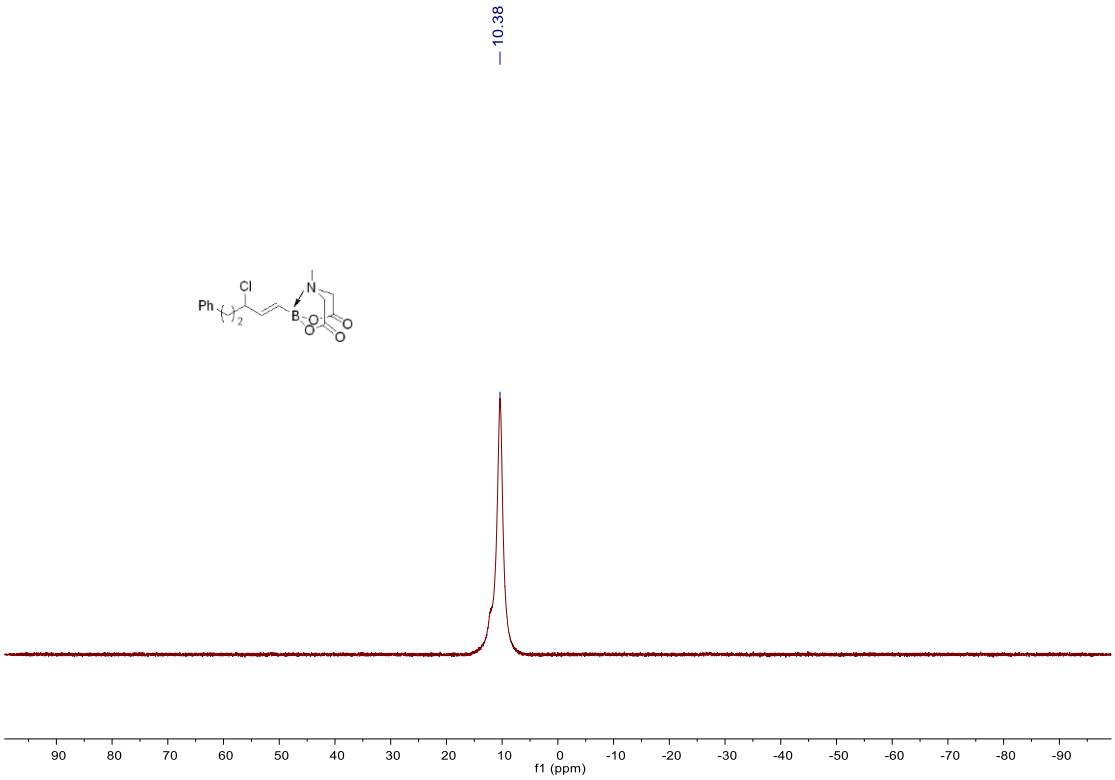

4.02
1.15
1.00
1.02
1.05
2.15
1.09
1.00
1.98
3.00
f1 (ppm)

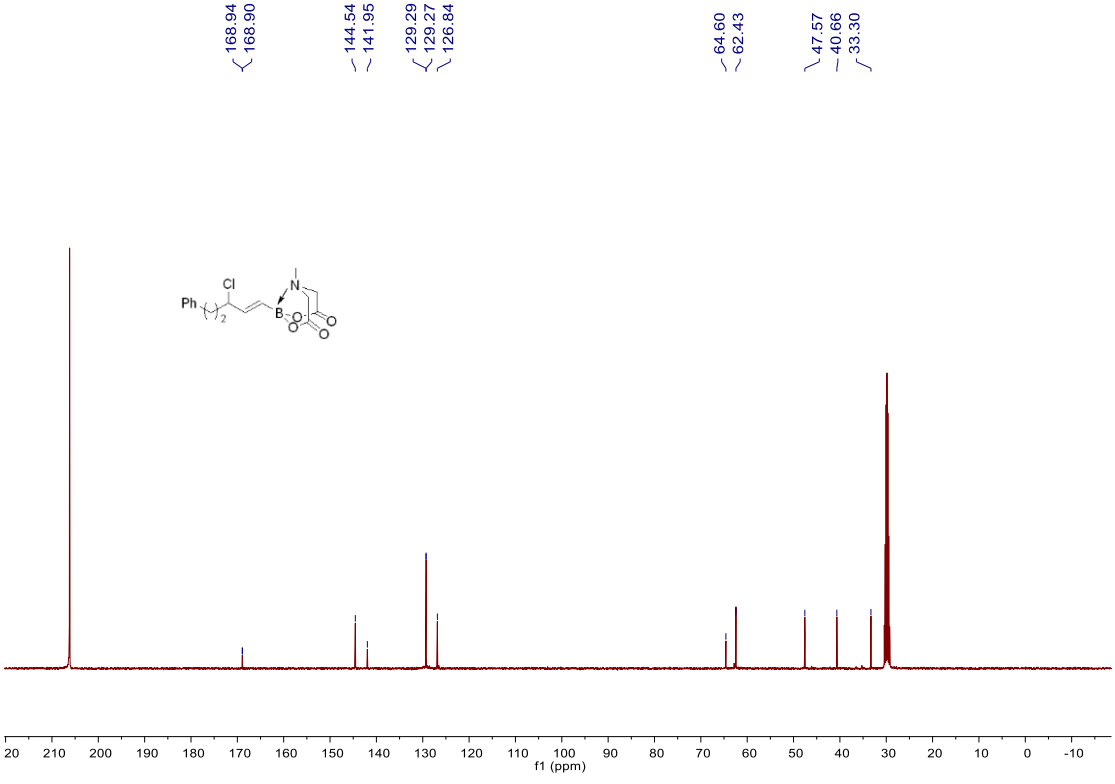

10.13
f1 (ppm)

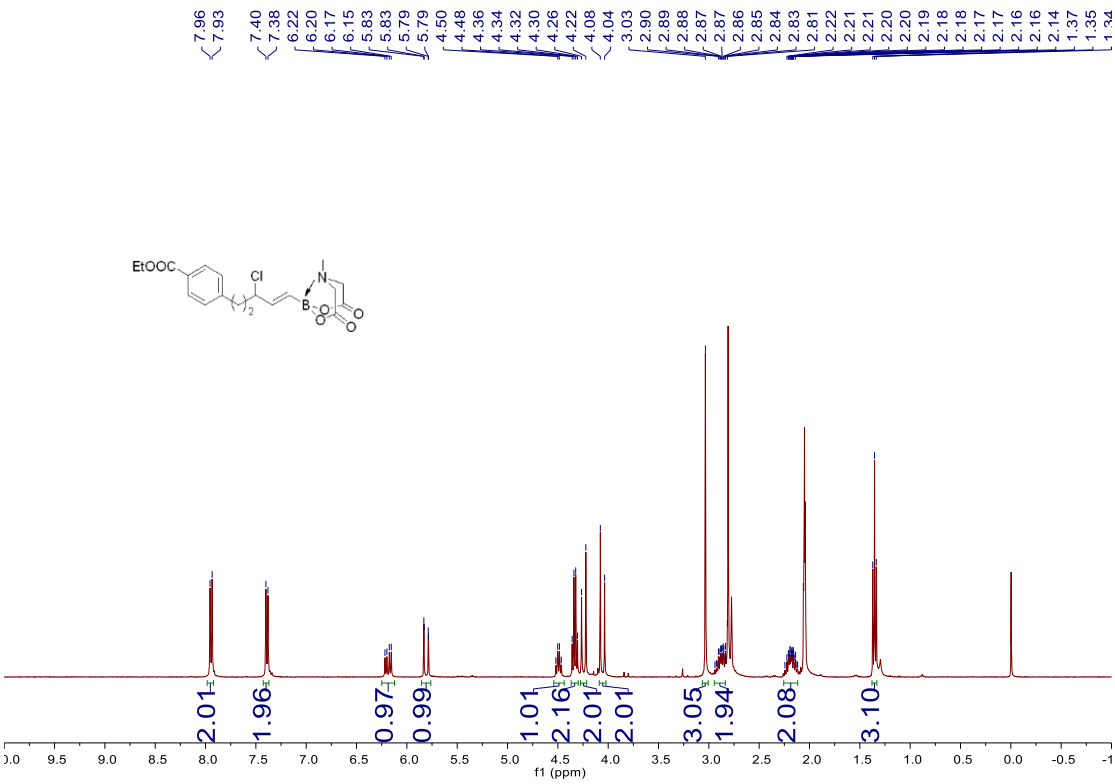
Ph
Cl
N
B
O
O
O

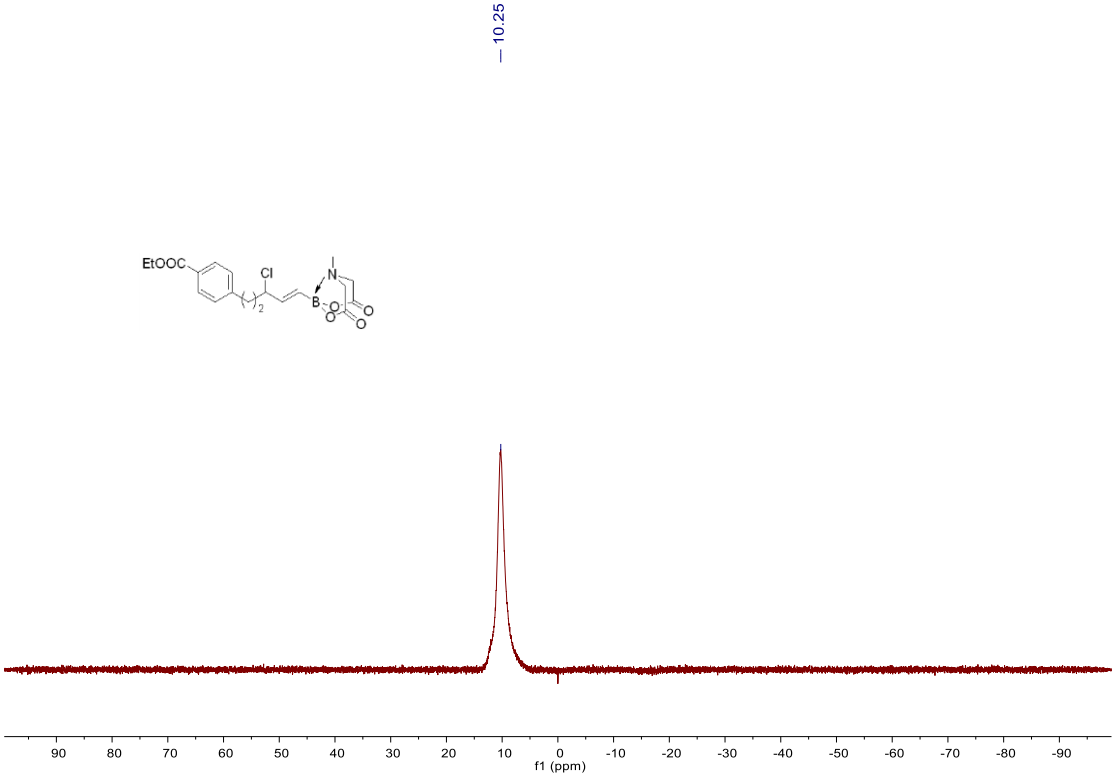

168.97
168.74
144.08
138.80
130.43
129.17
127.48
65.30
62.17
47.15
45.24
Cl
Ph
N
B
O
O
O
f1 (ppm)

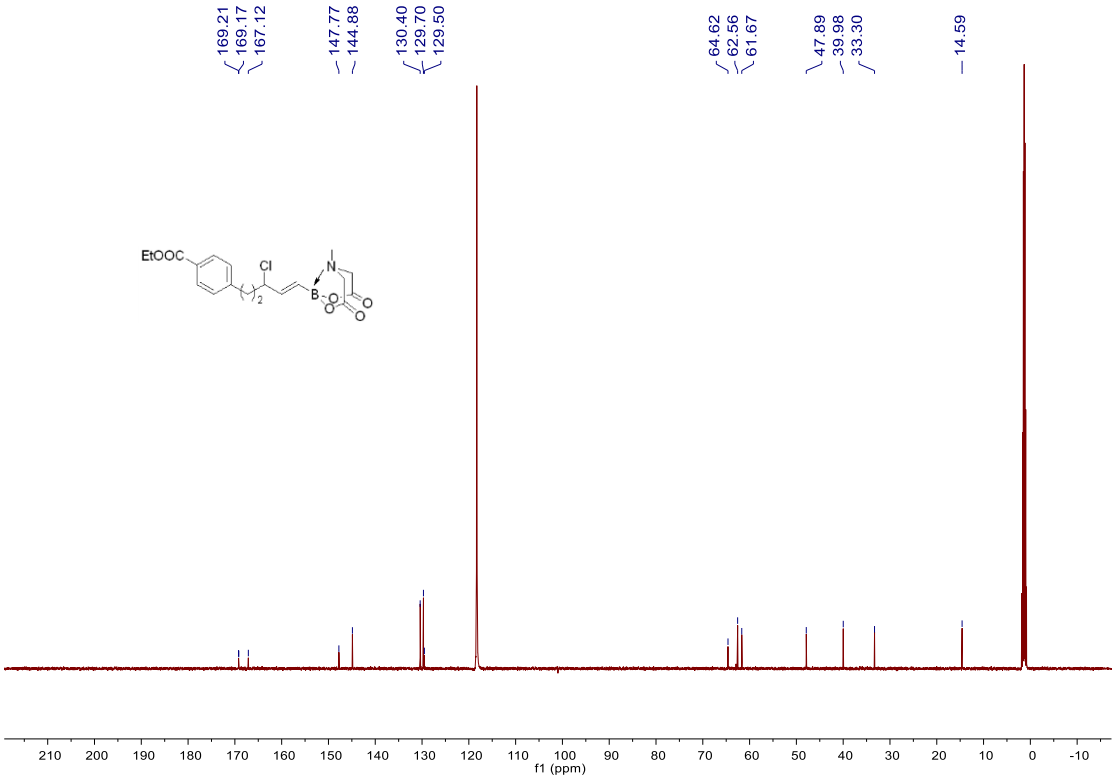

Cl
Ph
N
B
O
O
O
4.13
0.98
0.96
0.94
0.93
2.00
2.01
2.96
2.24
2.03
f1 (ppm)

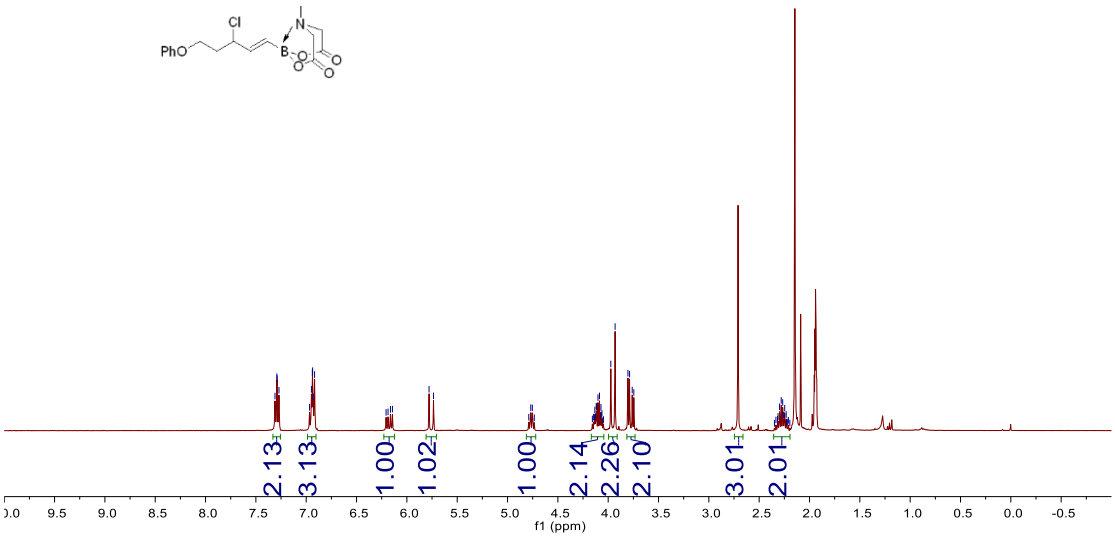

10.38
Cl
Ph
N
B
O
O
O
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

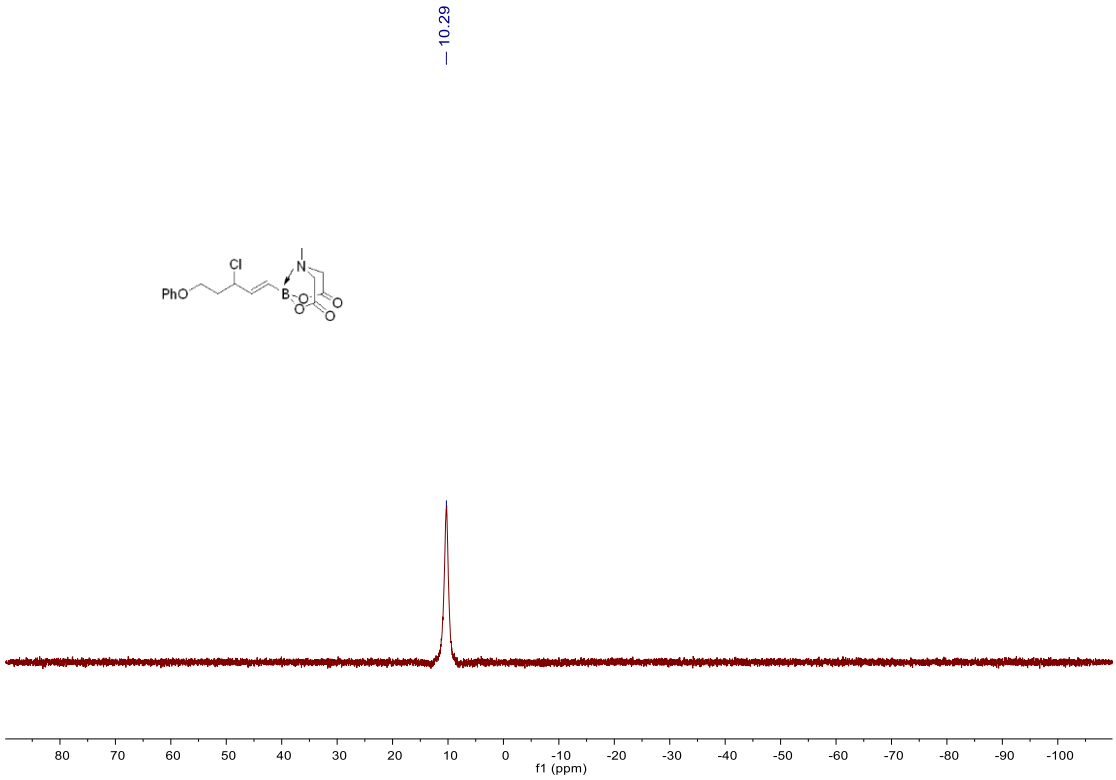

168.94
168.90
144.54
141.95
129.29
129.27
126.84
64.60
62.43
47.57
40.66
33.30
Cl
Ph
N
B
O
O
O
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

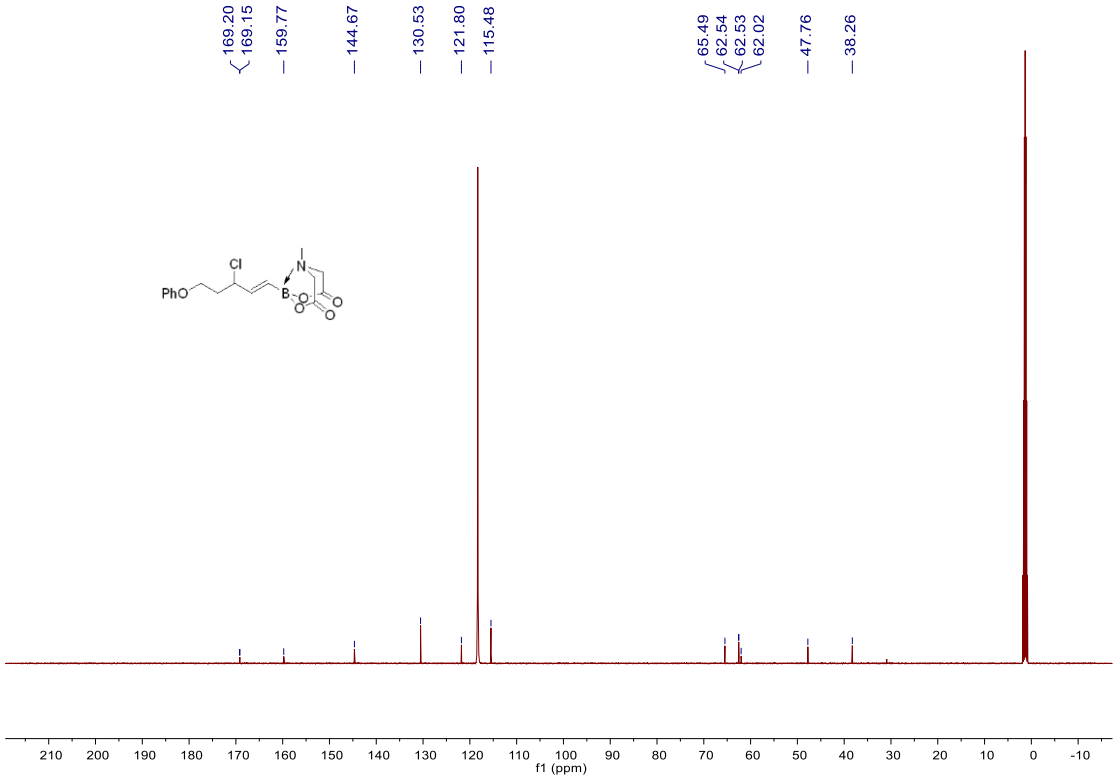

7.96
7.93
7.40
7.38
6.22
6.20
6.17
6.15
5.83
5.83
5.79
5.79
4.50
4.48
4.36
4.34
4.32
4.30
4.26
4.22
4.08
4.04
3.03
2.90
2.89
2.88
2.87
2.87
2.86
2.85
2.84
2.83
2.81
2.22
2.21
2.21
2.20
2.20
2.19
2.18
2.18
2.17
2.17
2.16
2.16
2.14
1.37
1.35
1.34
EtOOC
Cl
N
B
O
O
O
O
2.01
1.96
0.97
0.99
1.01
2.16
2.01
2.01
3.05
1.94
2.08
3.10
f1 (ppm)


10.25
EtOOC
Cl
N
B
O
O
O
f1 (ppm)


169.21
169.17
167.12
147.77
144.88
130.40
129.70
129.50
64.62
62.56
61.67
47.89
39.98
33.30
14.59
EtOOC
Cl
N
B
O
O
O
O
f1 (ppm)


Cl
N
PhO
B
O
O
O
2.13
3.13
1.00
1.02
1.00
2.14
2.26
2.10
3.01
2.01
f1 (ppm)


10.29
Cl
N
PhO
B
O
O
O
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)


169.20
169.15
159.77
144.67
130.53
121.80
115.48
65.49
62.54
62.53
62.02
47.76
38.26
Cl
N
PhO
B
O
O
O
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)


7.37
7.36
7.35
7.31
7.30
7.30
7.29
7.28
6.14
6.12
6.10
6.09
5.72
5.69
4.67
4.66
4.64
4.63
4.48
3.97
3.96
3.93
3.93
3.80
3.77
3.76
3.74
3.62
3.62
3.61
3.61
3.60
3.60
3.60
3.59
3.59
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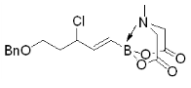
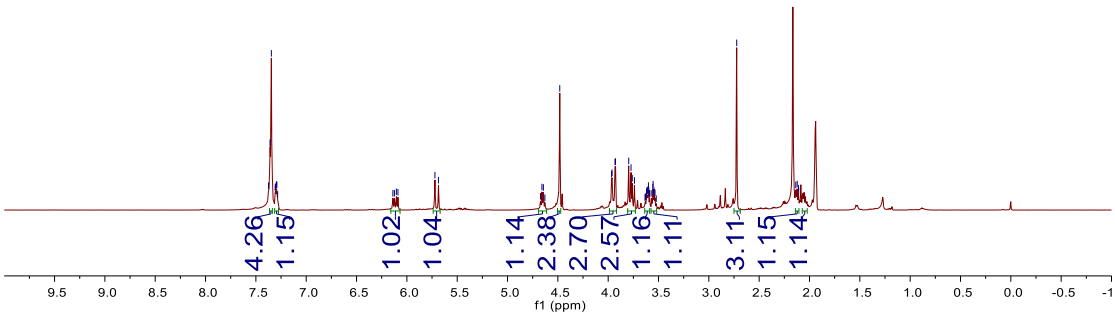
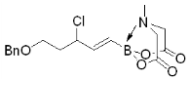
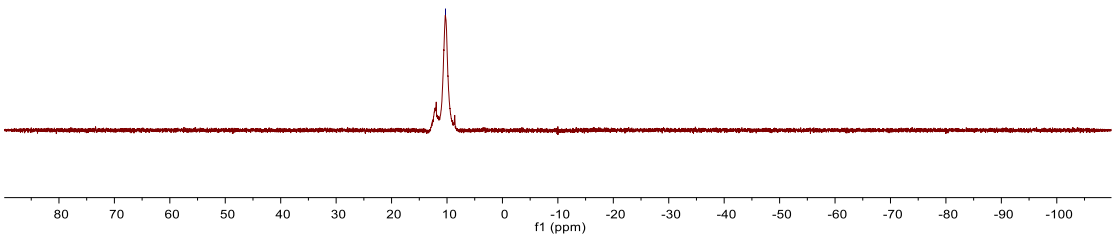
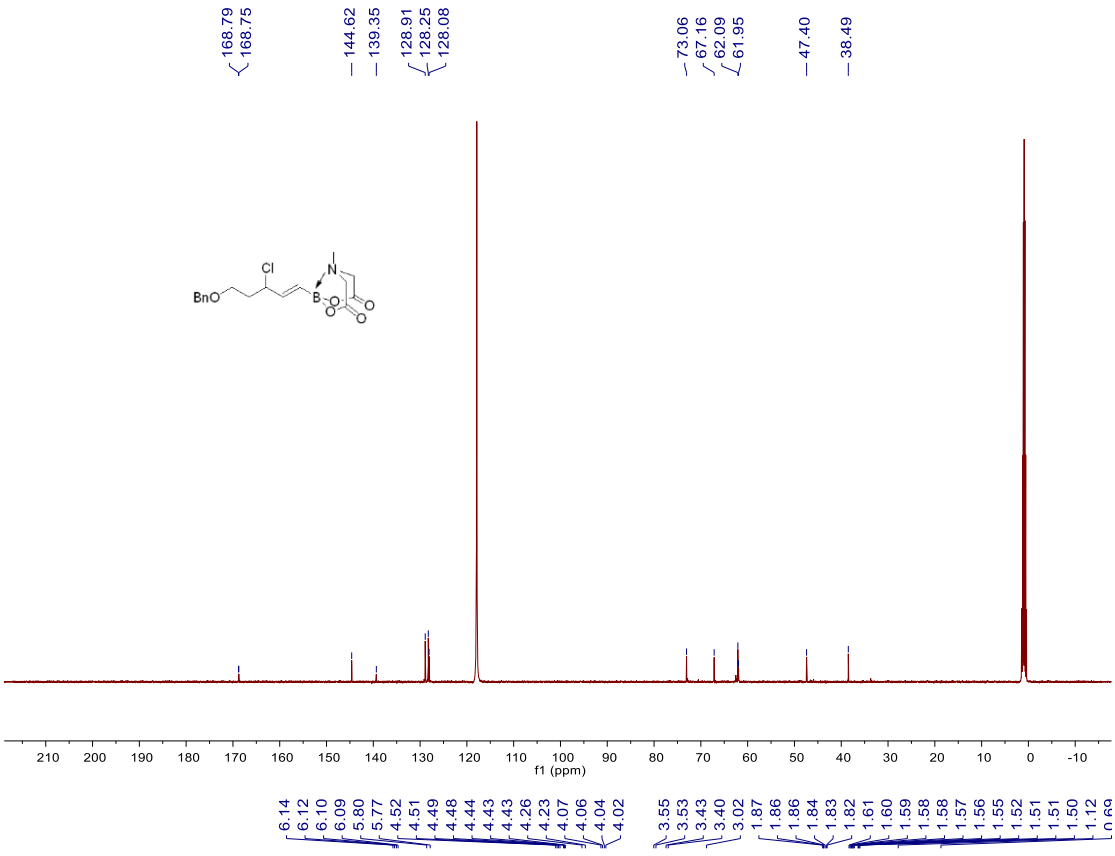
3.53
2.72
2.14
2.12
2.11
2.11

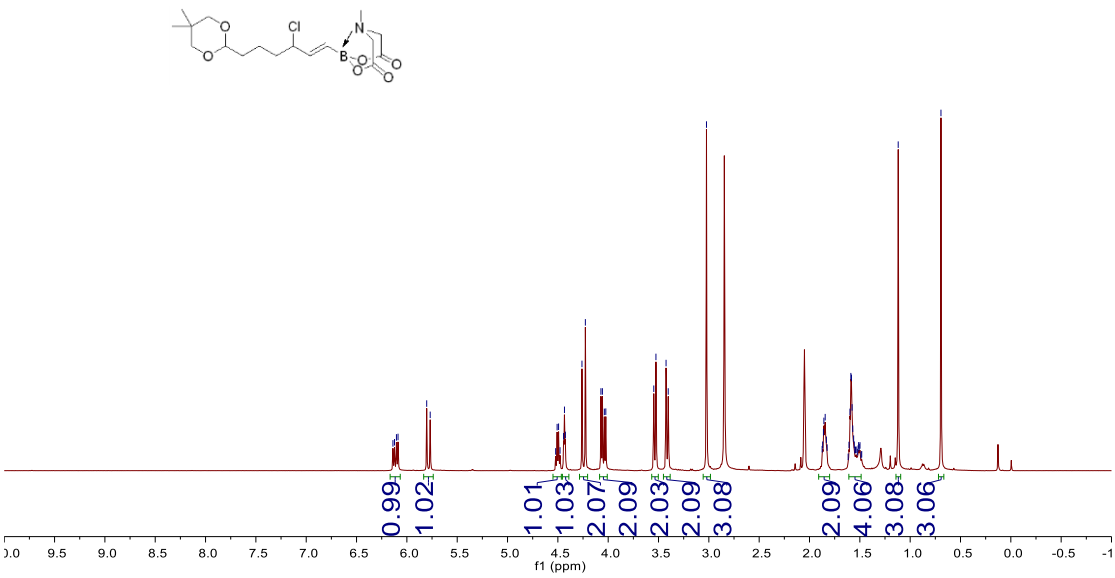

Cl
N
BnO
B
O
O
O
O

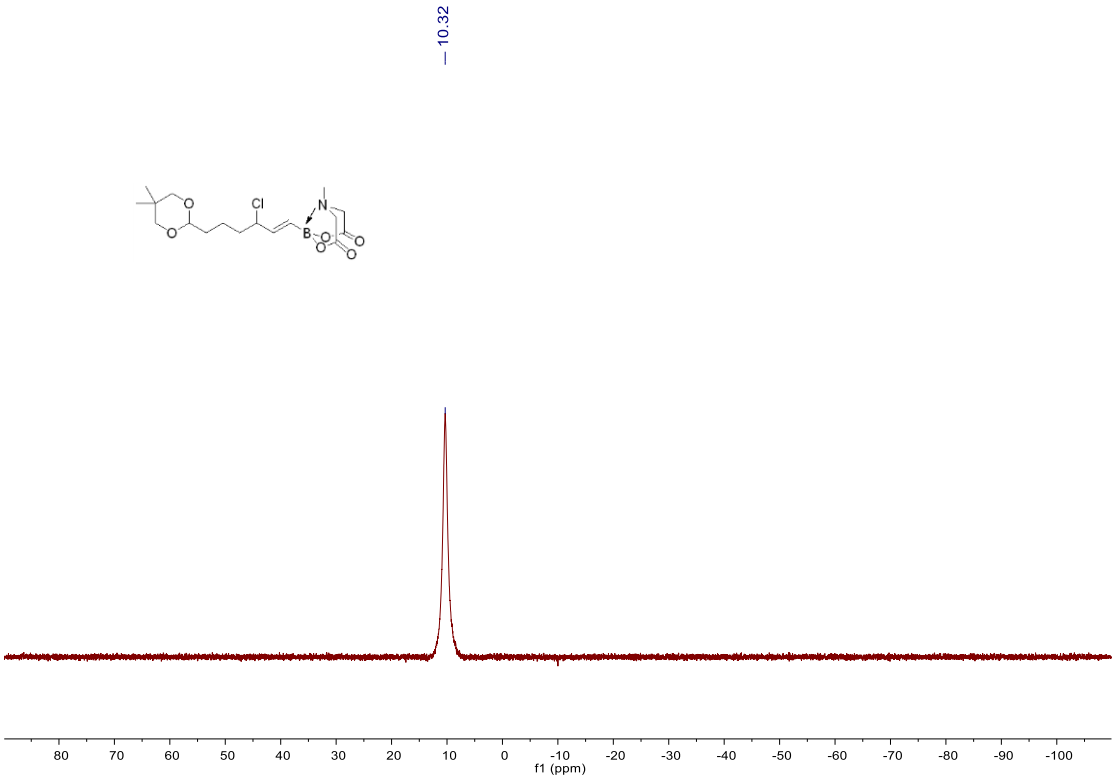

4.26
1.15
1.02
1.04
1.14
2.38
2.70
2.57
1.16
1.11
3.11
1.15
1.14
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

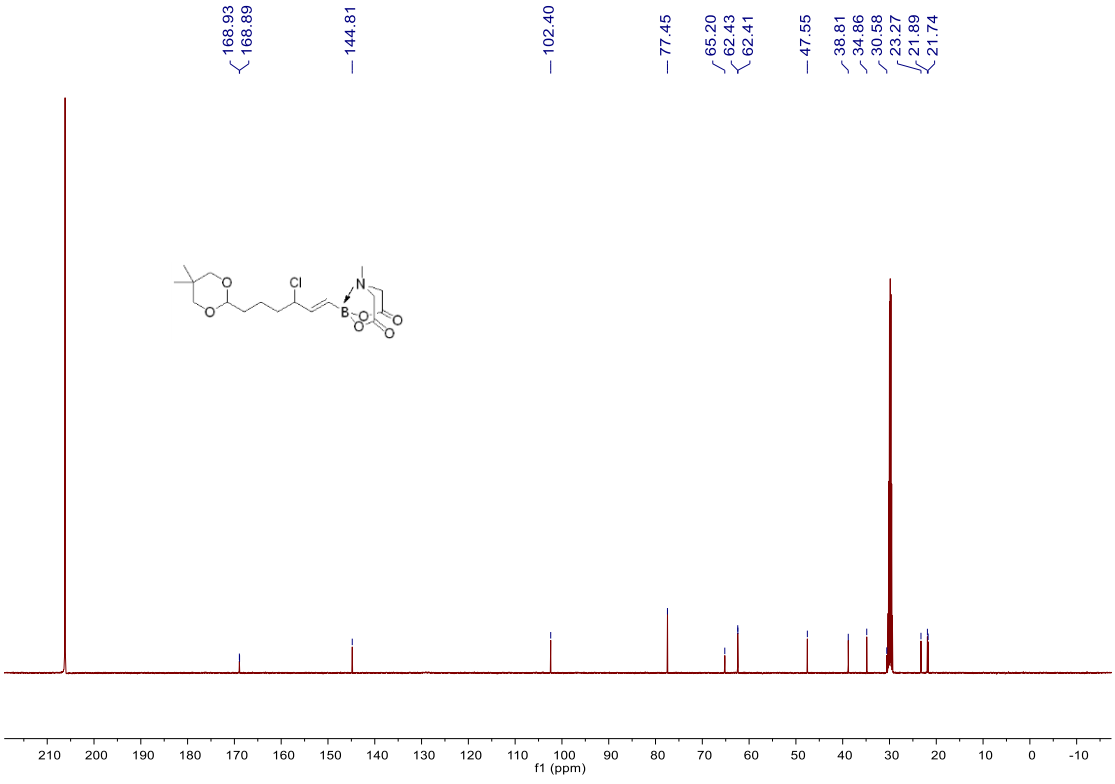

Cl
N
BnO
B
O
O
O
O

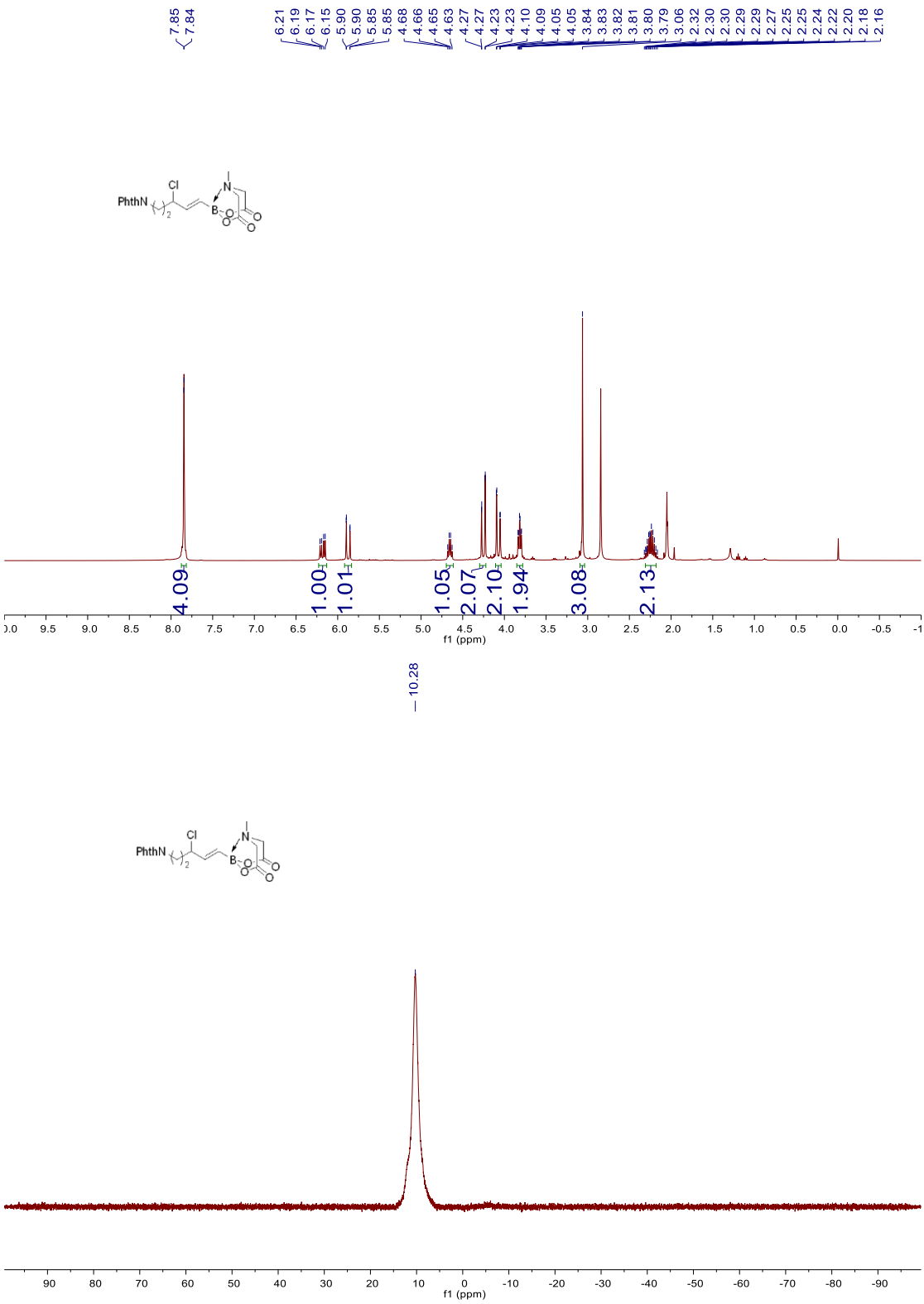

10.27
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)

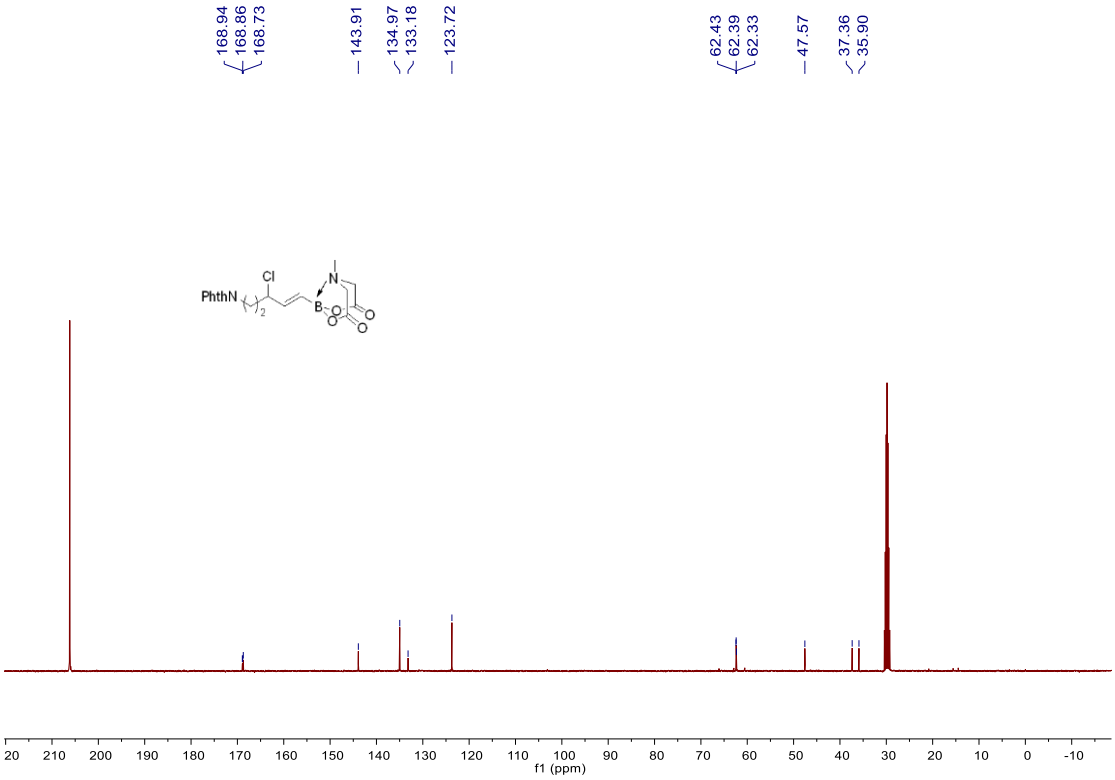

168.79
168.75
144.62
139.35
128.91
128.25
128.08
73.06
67.16
62.09
61.95
47.40
38.49
BnO
Cl
N
B
O
O
O
f1 (ppm)
6.14
6.12
6.10
6.09
5.80
5.77
4.52
4.51
4.49
4.48
4.44
4.43
4.43
4.26
4.23
4.07
4.06
4.04
4.02
3.55
3.53
3.43
3.40
3.02
1.87
1.86
1.86
1.84
1.83
1.82
1.61
1.60
1.59
1.58
1.58
1.57
1.56
1.55
1.52
1.51
1.51
1.50
1.12

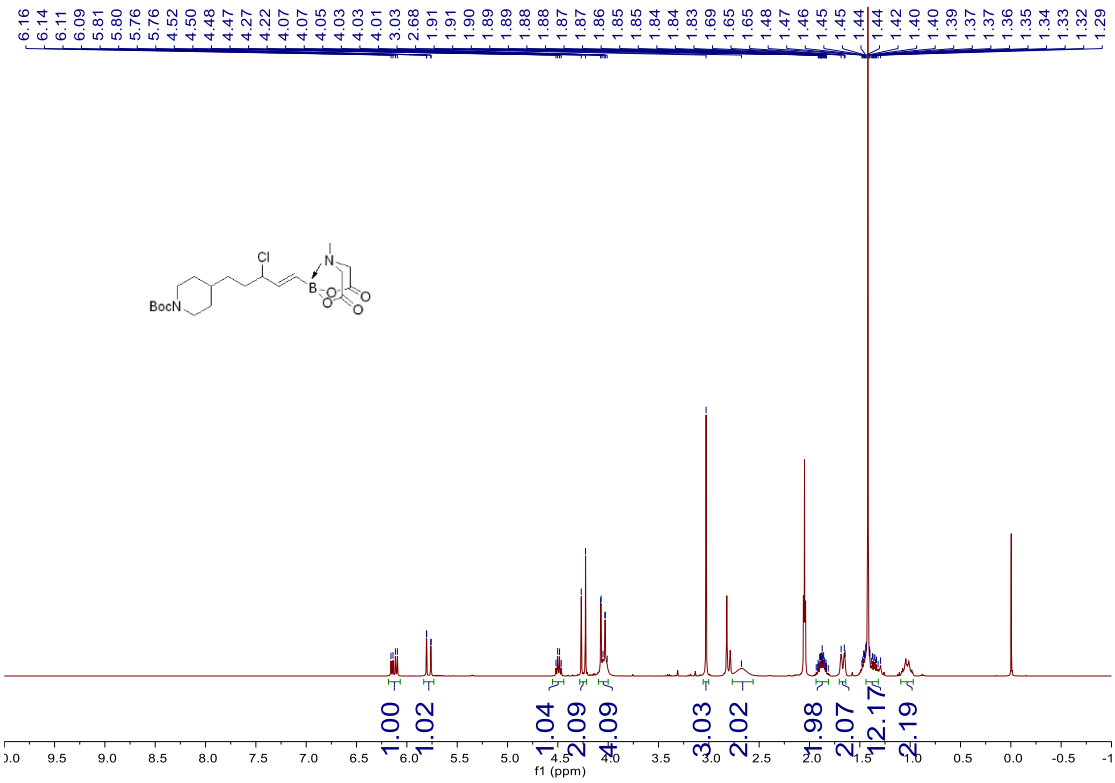

Cl
N
B
O
O
O
0.99
1.02
1.01
1.03
2.07
2.09
2.03
2.09
3.08
2.09
4.06
3.08
3.06
f1 (ppm)

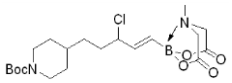

10.32
Cl
N
B
O
f1 (ppm)


168.93
168.89
144.81
102.40
77.45
65.20
62.43
62.41
47.55
38.81
34.86
30.58
23.27
21.89
21.74
Cl
N
B
O
f1 (ppm)

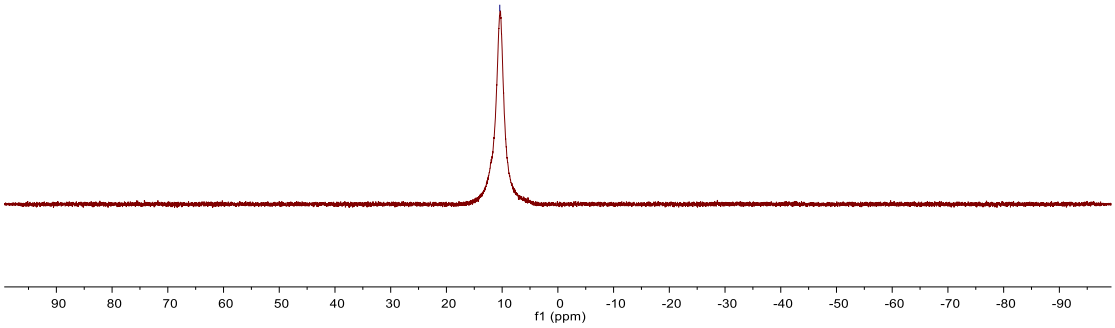

7.85
7.84
6.21
6.19
6.17
6.15
5.90
5.90
5.85
5.85
4.68
4.66
4.65
4.63
4.27
4.27
4.23
4.23
4.10
4.09
4.05
4.05
3.84
3.83
3.82
3.81
3.80
3.79
3.06
2.32
2.30
2.30
2.29
2.29
2.27
2.25
2.25
2.24
2.22
2.20
2.18
2.16
PhthN
Cl
N
B
O
O
O
4.09
1.00
1.01
1.05
2.07
2.10
1.94
3.08
2.13
f1 (ppm)
10.28
PhthN
Cl
N
B
O
O
O
f1 (ppm)


168.94
168.86
168.73
143.91
134.97
133.18
123.72
62.43
62.39
62.33
47.57
37.36
35.90
PhthN
Cl
N
B
O
O
O
f1 (ppm)

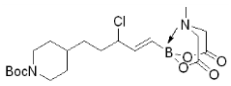

6.16
6.14
6.11
6.09
5.81
5.80
5.76
5.76
4.52
4.50
4.48
4.47
4.27
4.22
4.07
4.07
4.05
4.03
4.03
4.01
3.03
2.68
1.91
1.91
1.90
1.89
1.89
1.88
1.88
1.87
1.87
1.86
1.85
1.85
1.84
1.84
1.83
1.69
1.65
1.65
1.48
1.47
1.46
1.45
1.45
1.44
1.44
1.42
1.40
1.40
1.39
1.37
1.37
1.36
1.35
1.34
1.33
1.32
1.29
BocN
Cl
N
B
O
O
O
1.00
1.02
1.04
2.09
4.09
3.03
2.02
1.98
2.07
12.17
2.19
f1 (ppm)



10.43



168.90
154.99
144.83
79.11
65.51
62.44
47.58
36.37
36.17
34.08
32.99
32.87
28.58




8.02
8.00
7.64
7.62
7.60
7.52
7.50
7.48
6.13
6.11
6.09
6.07
5.73
5.69
4.54
4.52
4.50
4.49
4.31
4.30
4.28
3.98
3.93
3.81
3.79
3.76
3.75
1.92
1.91
1.91
1.91
1.90
1.89
1.88
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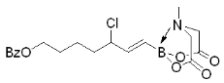
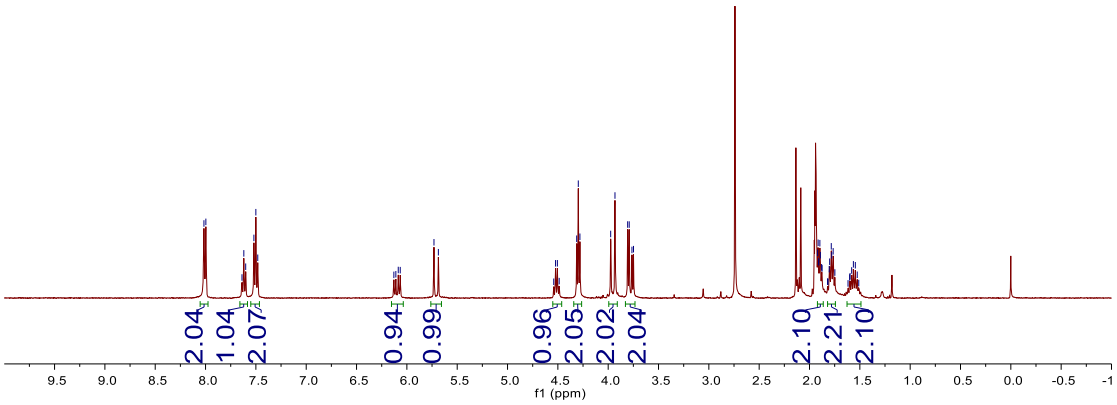
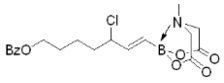
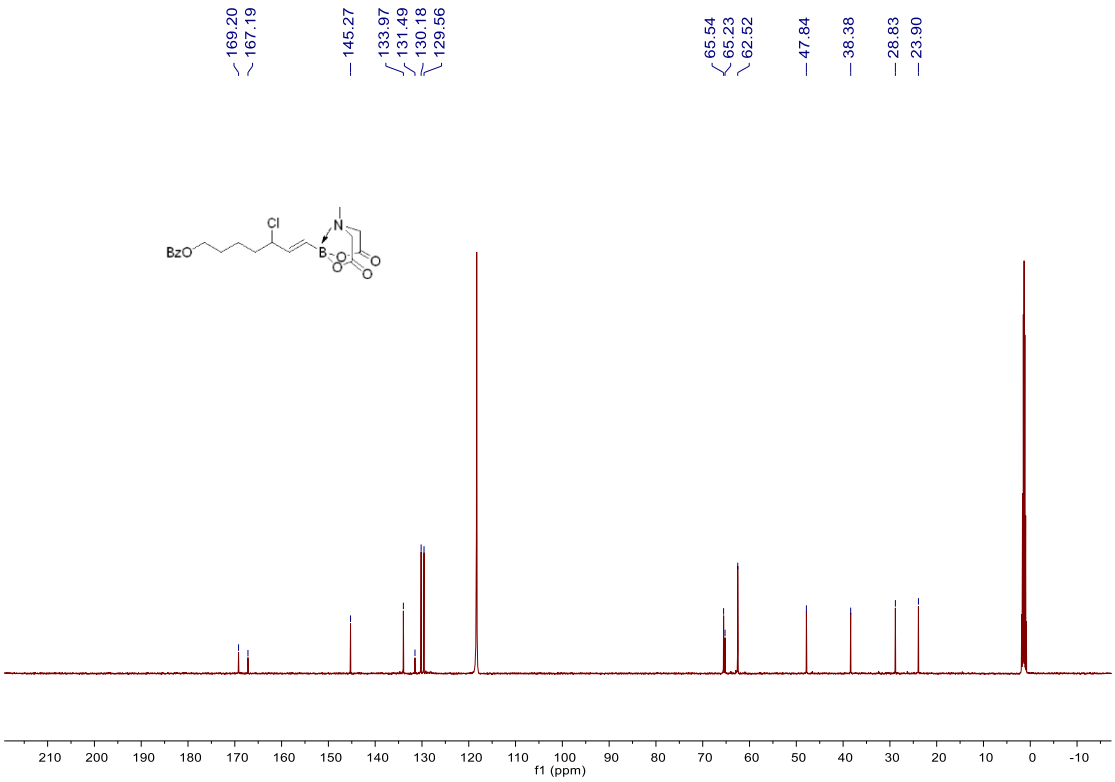
1.75
1.60
1.60
1.58
1.56
1.54

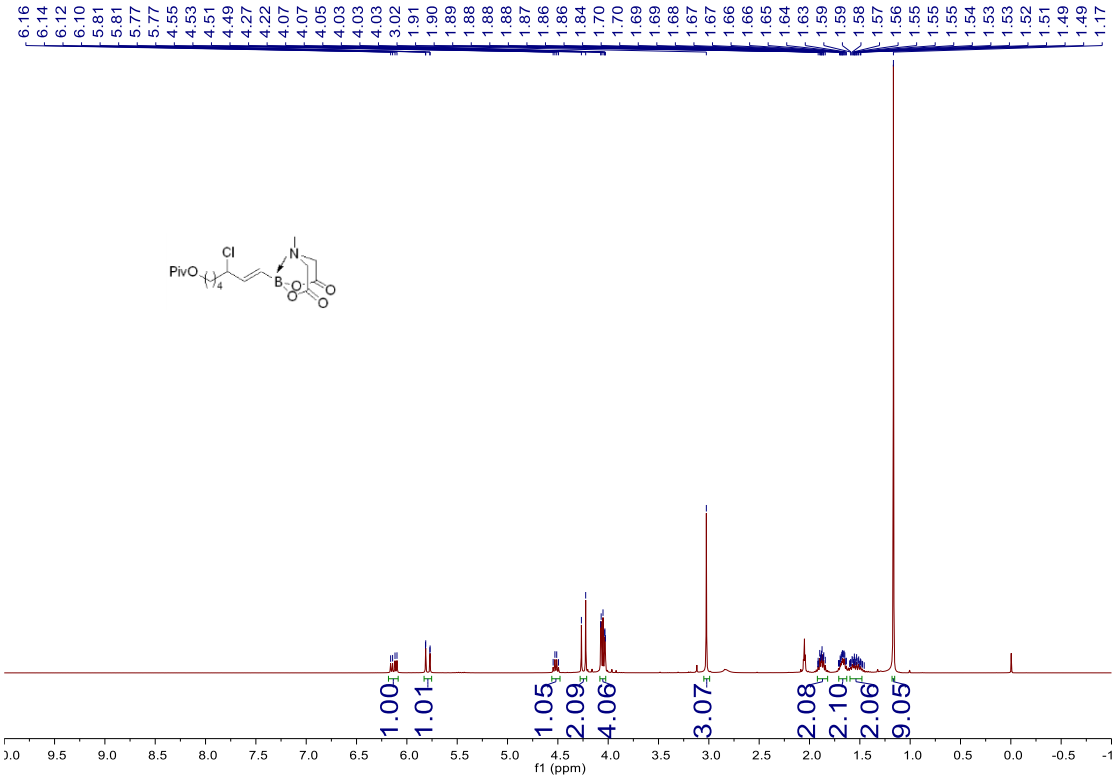

Cl
N
BzO
B
O
O
O

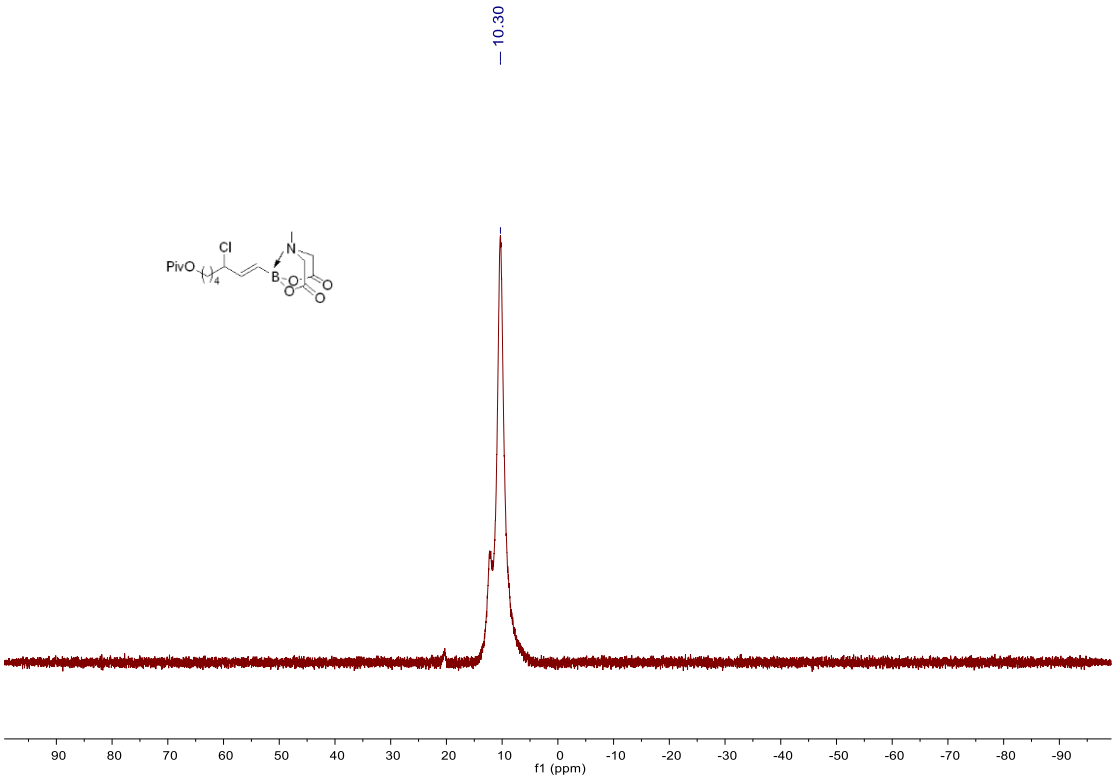

2.04
1.04
2.07
0.94
0.99
0.96
2.05
2.02
2.04
2.10
2.21
2.10
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

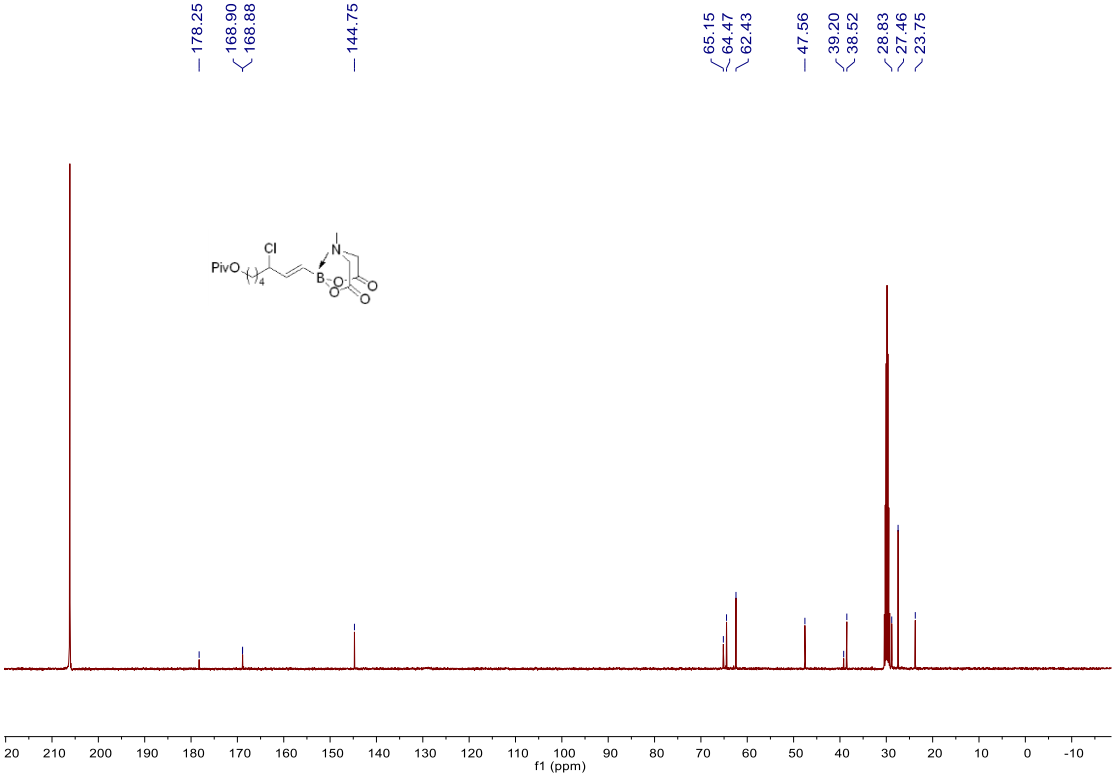

Cl
N
BzO
B
O
O
O

10.27
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)


169.20
167.19
145.27
133.97
131.49
130.18
129.56
65.54
65.23
62.52
47.84
38.38
28.83
23.90
BzO
Cl
N
B
O
O
O
O
f1 (ppm)


6.16
6.14
6.12
6.10
5.81
5.81
5.77
5.77
4.55
4.53
4.51
4.49
4.27
4.22
4.07
4.07
4.05
4.03
4.03
4.03
3.02
1.91
1.90
1.89
1.88
1.88
1.88
1.87
1.86
1.86
1.84
1.70
1.70
1.69
1.69
1.68
1.67
1.67
1.66
1.66
1.65
1.64
1.63
1.59
1.59
1.58
1.57
1.56
1.55
1.55
1.55
1.54
1.53
1.53
1.52
1.51
1.49
1.49
1.17
PivO
Cl
N
B
O
O
O
O
1.00
1.01
1.05
2.09
4.06
3.07
2.08
2.10
2.06
9.05
f1 (ppm)


10.30
Cl
PivO
N
B
O
O
O
O
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


178.25
168.90
168.88
144.75
65.15
64.47
62.43
47.56
39.20
38.52
28.83
27.46
23.75
Cl
PivO
N
B
O
O
O
O
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)


6.15
6.14
6.12
6.10
5.82
5.78
4.55
4.53
4.52
4.50
4.26
4.23
4.07
4.07
4.04
4.03
3.64
3.63
3.61
3.03
1.91
1.90
1.90
1.89
1.88
1.88
1.87
1.86
1.86
1.85
1.84
1.83
1.83
1.82
1.82
1.82
1.81
1.81
1.80
1.80
1.79
1.79
1.65
1.65
1.64
1.63
1.63
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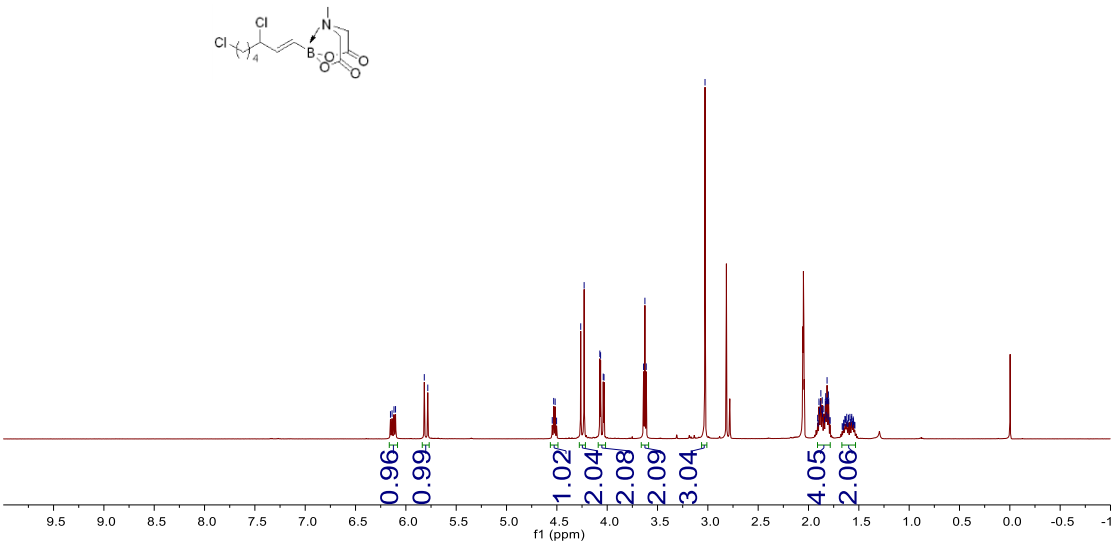
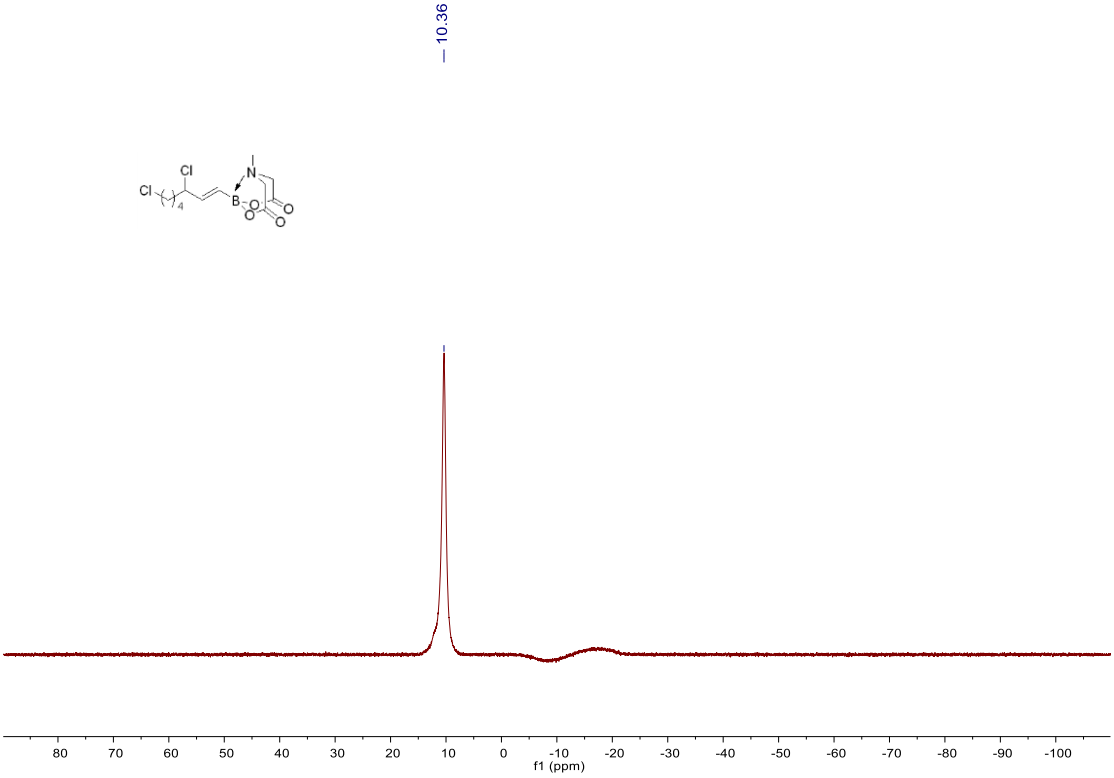
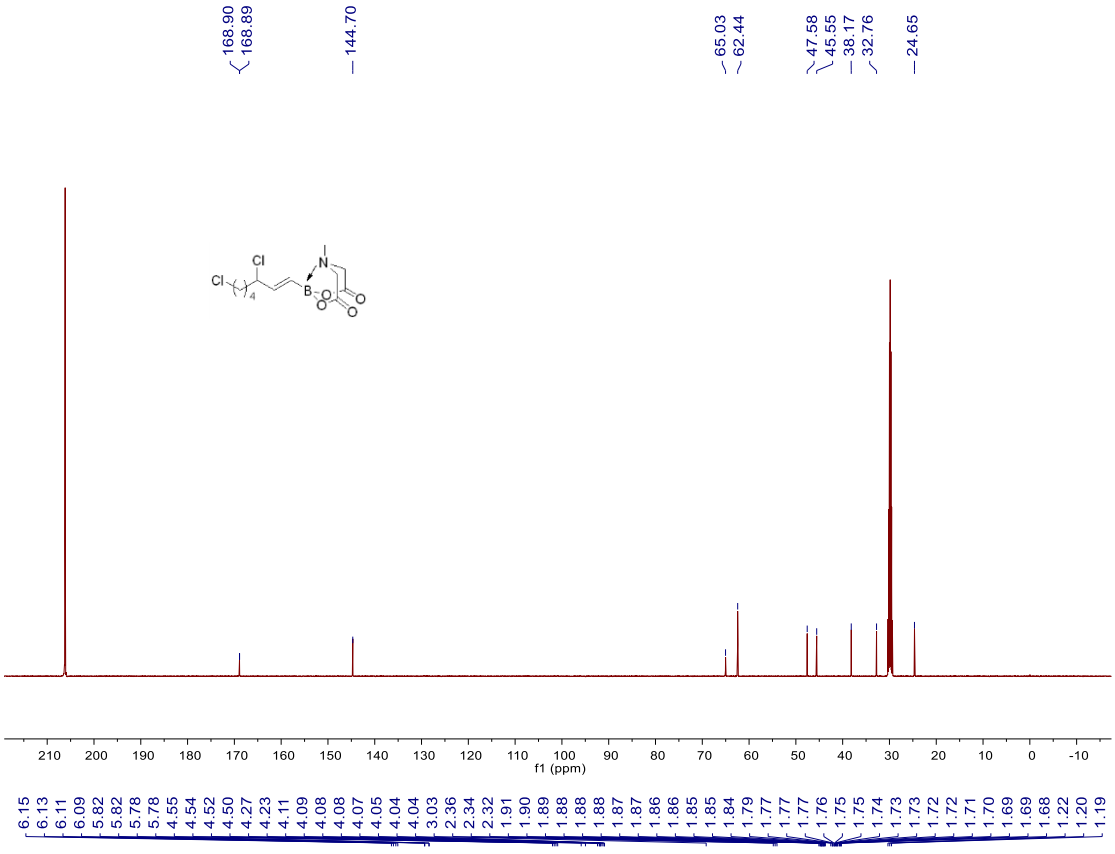
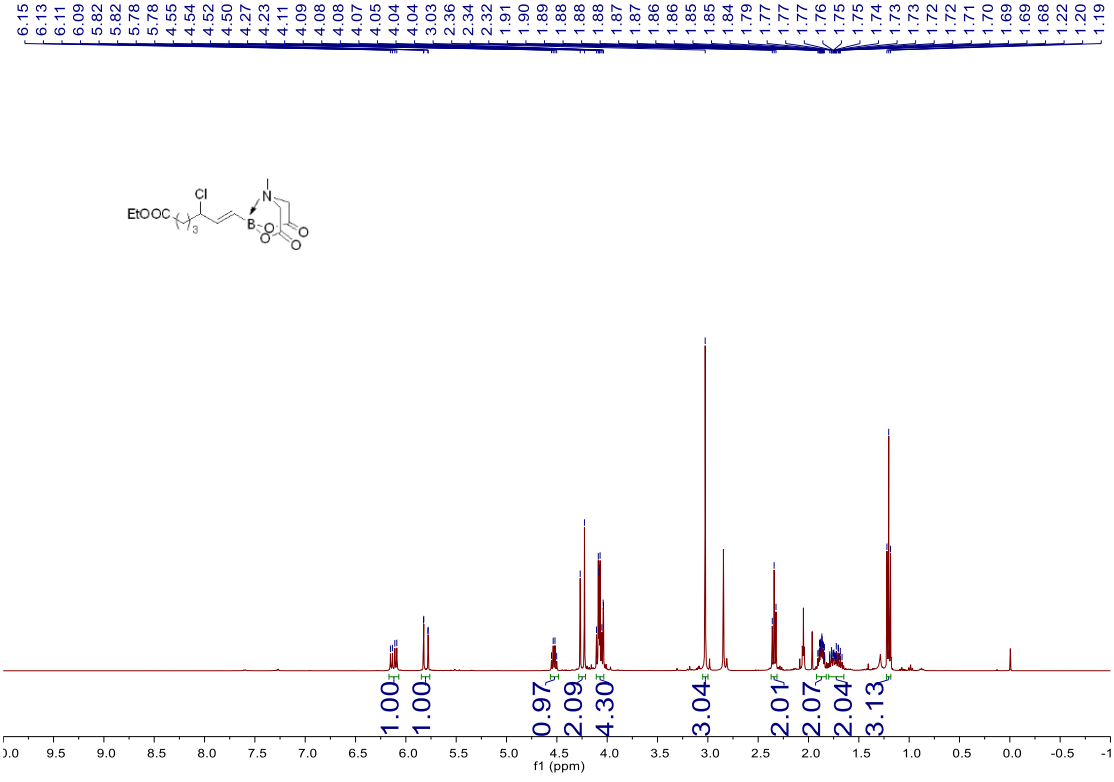
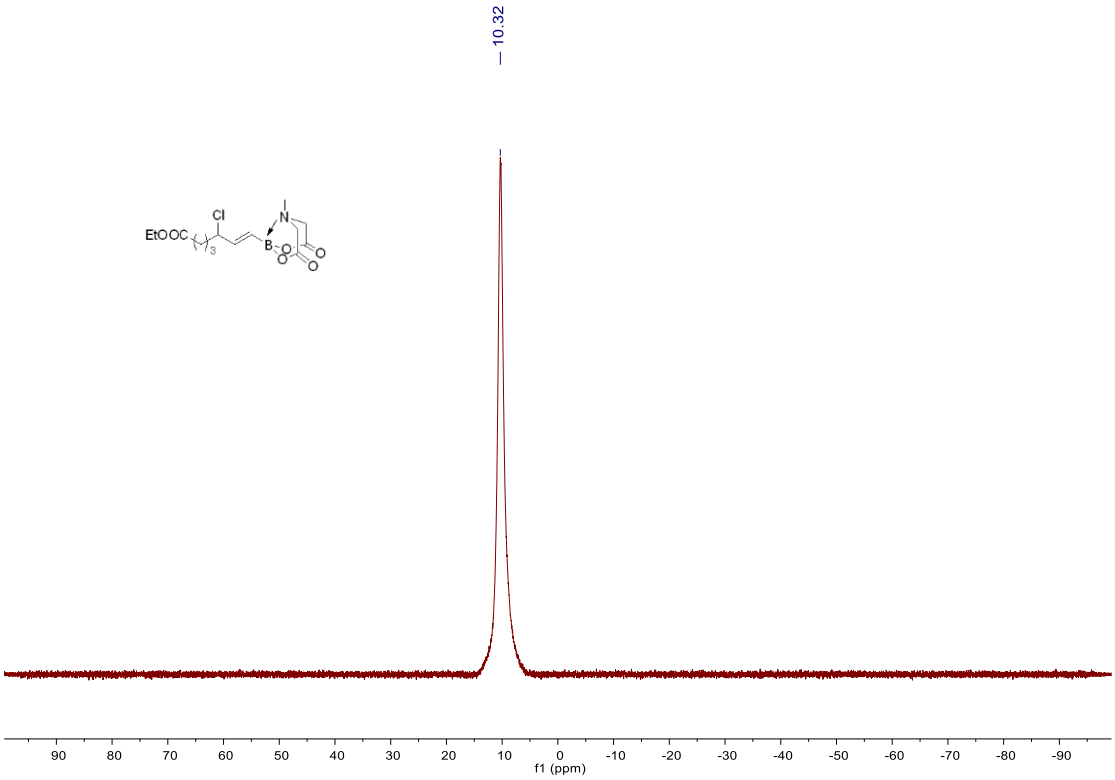
1.60
1.59
1.58
1.57
1.57
1.56
1.56
1.56
1.55


0.96
0.99
1.02
2.04
2.08
2.09
3.04
4.05
2.06
f1 (ppm)

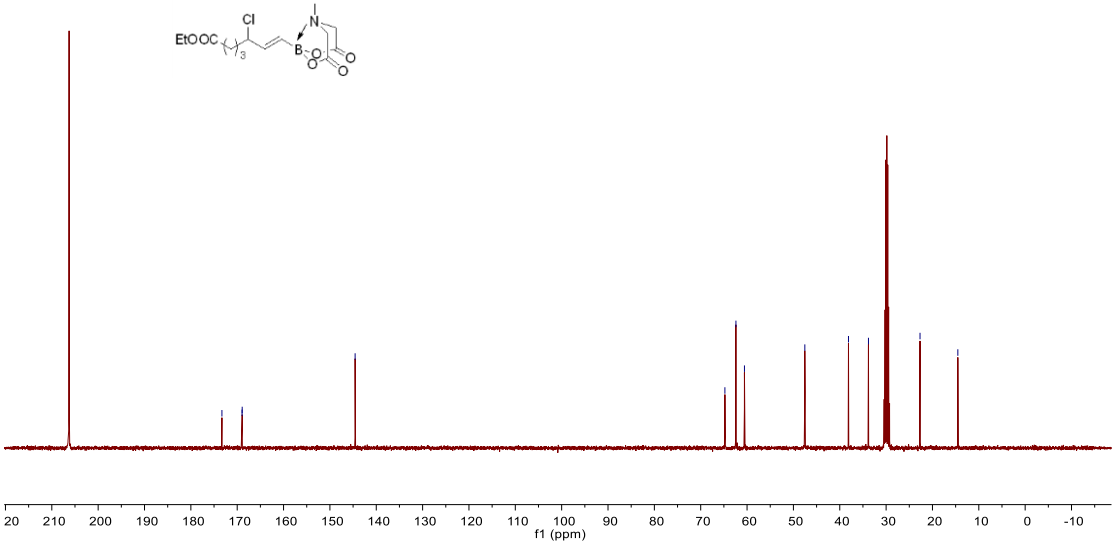

10.36
f1 (ppm)

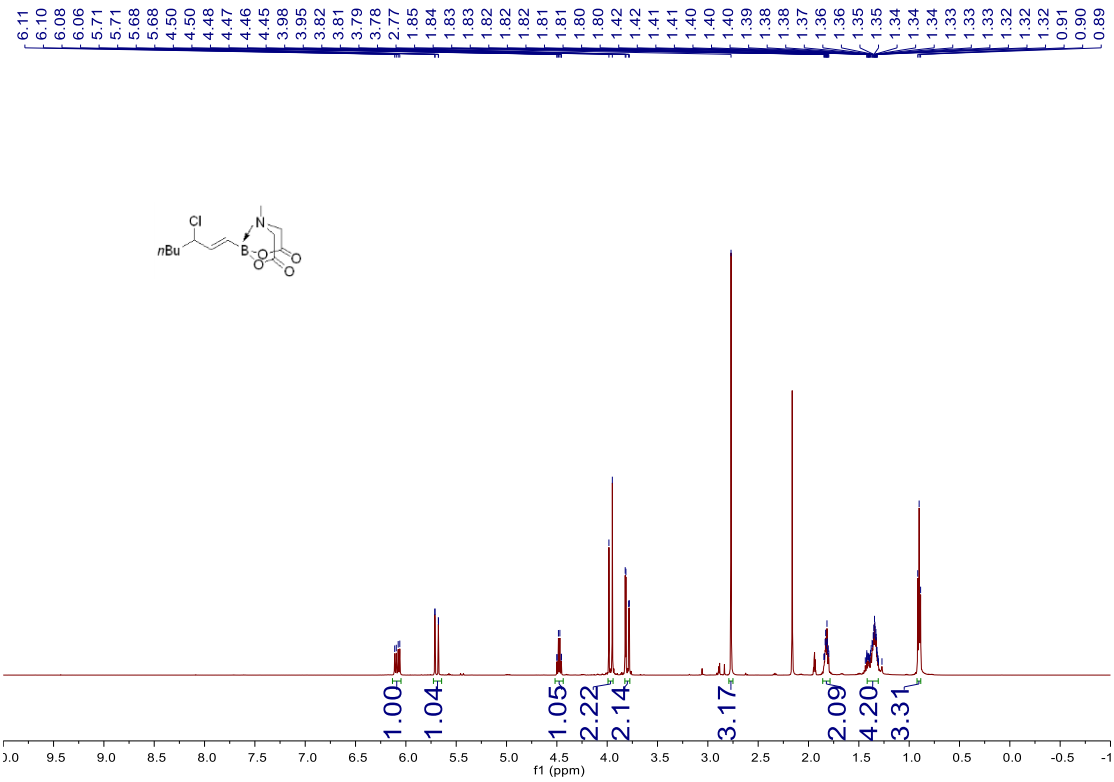

168.90
168.89
144.70
65.03
62.44
47.58
45.55
38.17
32.76
24.65
Cl
Cl
4
N
B
O
O
O
O
f1 (ppm)

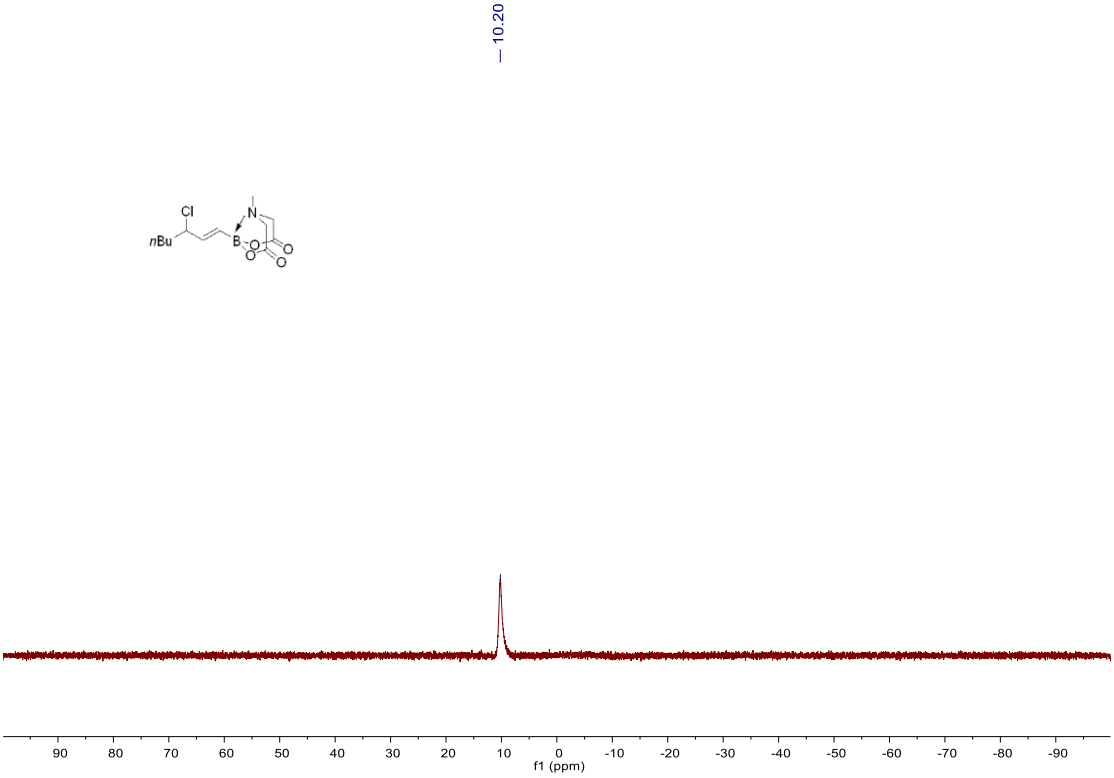

EtOOC
Cl
3
N
B
O
O
O
O
1.00
1.00
0.97
2.09
4.30
3.04
2.01
2.07
2.04
3.13
f1 (ppm)

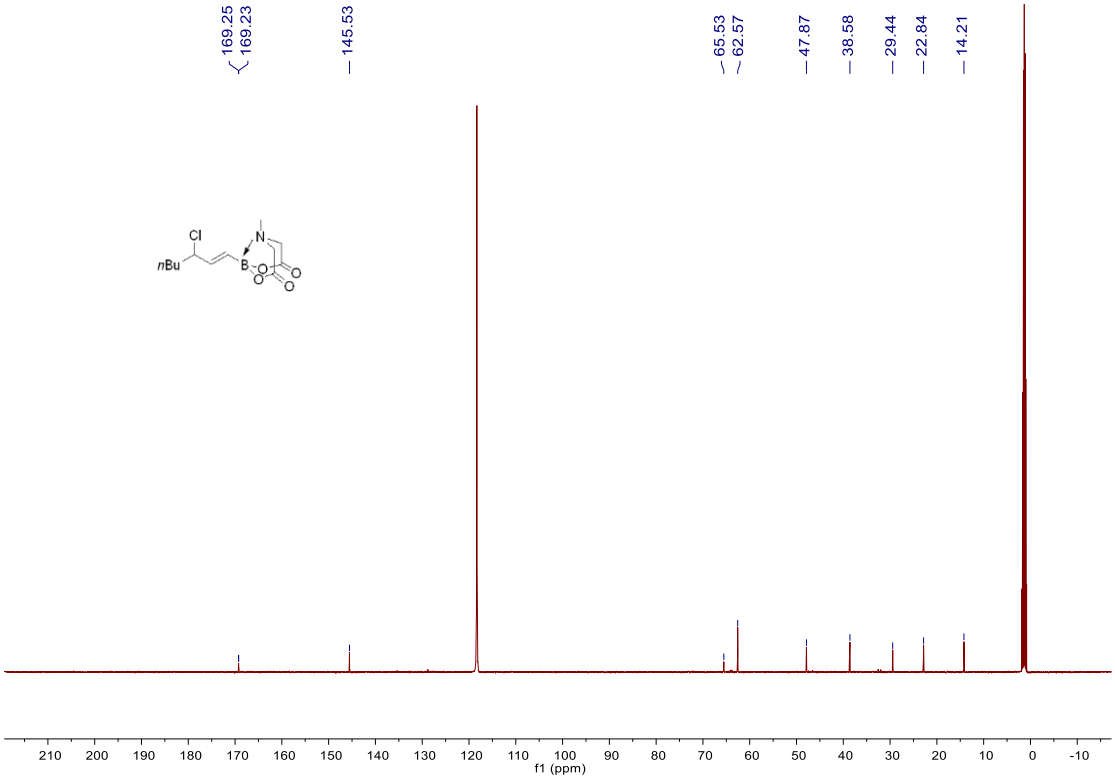


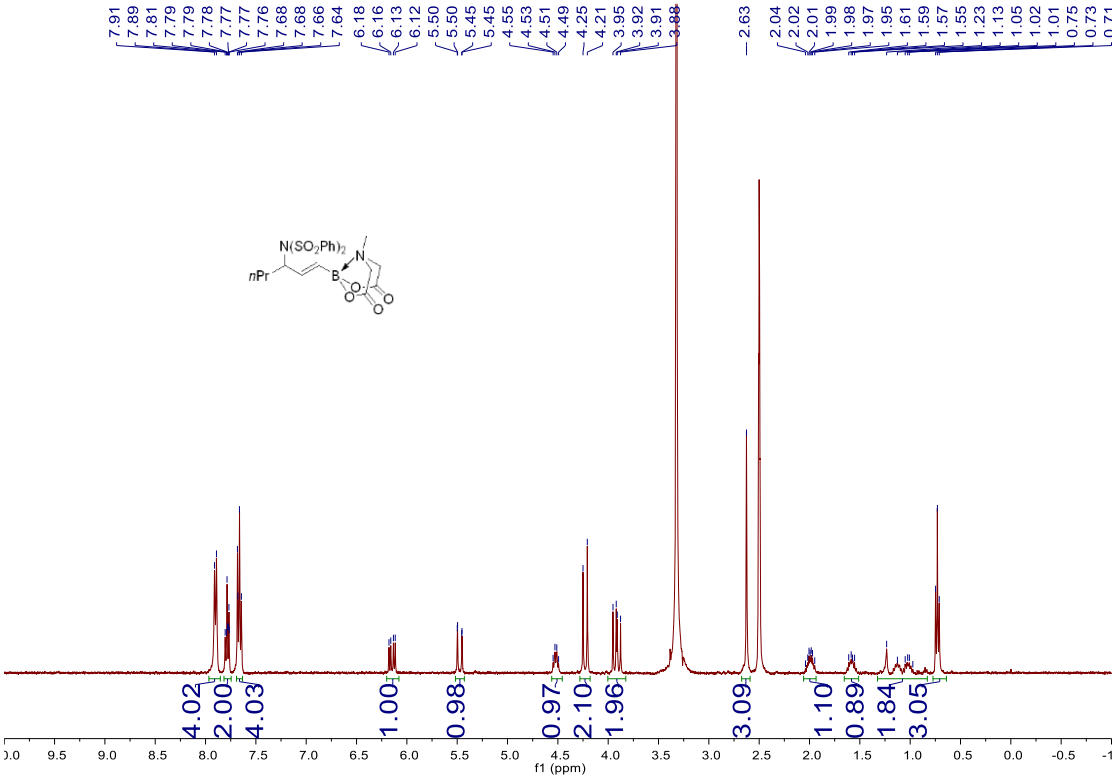
173.30
168.95
168.92
144.56
64.78
62.40
60.56
47.54
38.12
33.81
22.68
14.53

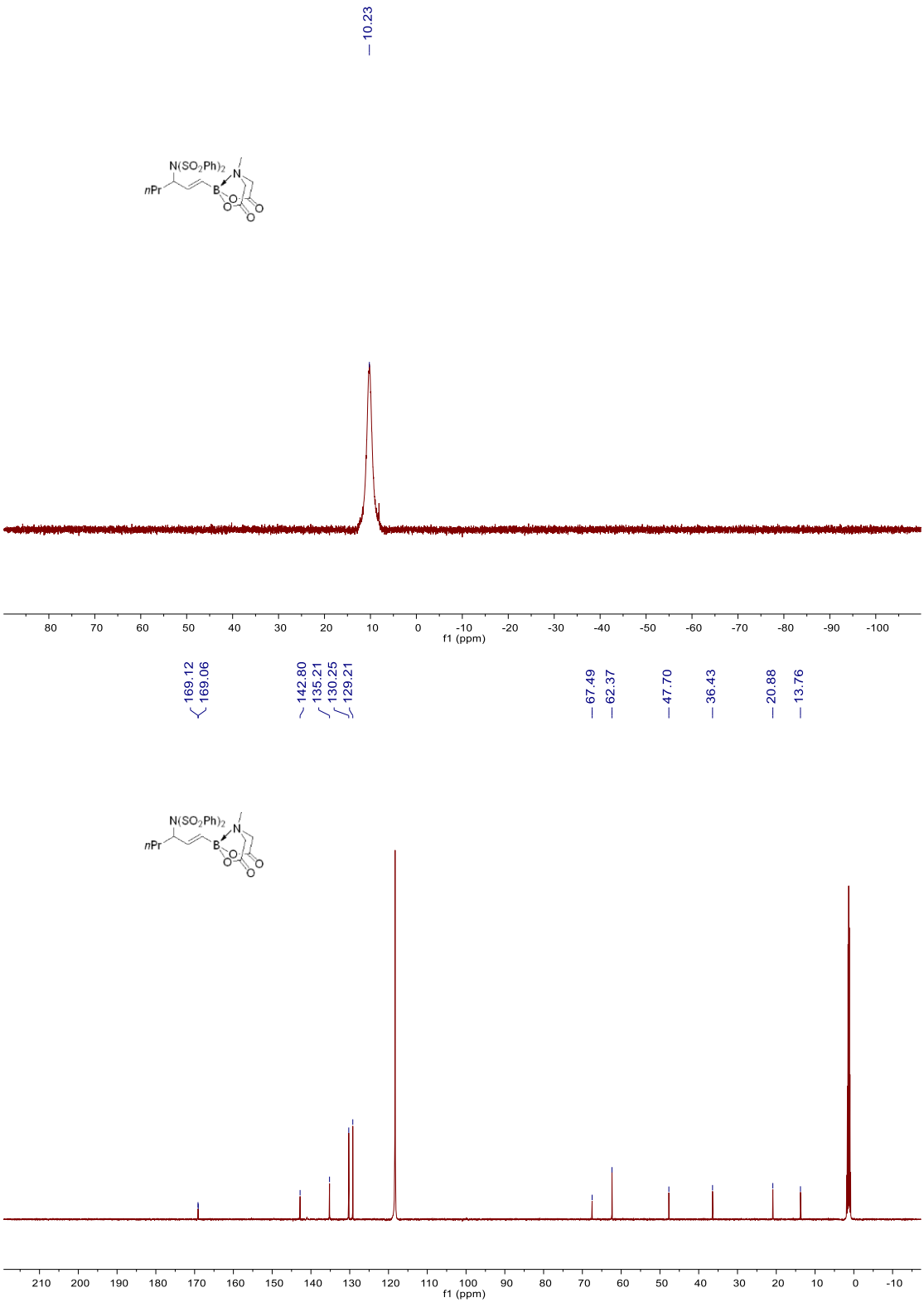



6.11 6.10 6.08 6.06 5.71 5.71 5.68 5.68 4.50 4.50 4.48 4.47 4.46 4.45 3.98 3.95 3.82 3.81 3.79 3.78 2.77 1.85 1.84 1.83 1.83 1.82 1.82 1.82 1.81 1.81 1.80 1.80 1.42 1.42 1.41 1.41 1.40 1.40 1.40 1.39 1.38 1.38 1.37 1.36 1.36 1.35 1.35 1.34 1.34 1.33 1.33 1.32 1.32 1.32 0.91 0.90 0.89
Cl
nBu
N
B
O
O
O
1.00 1.04 1.05 2.22 2.14 3.17 2.09 4.20 3.31
f1 (ppm)

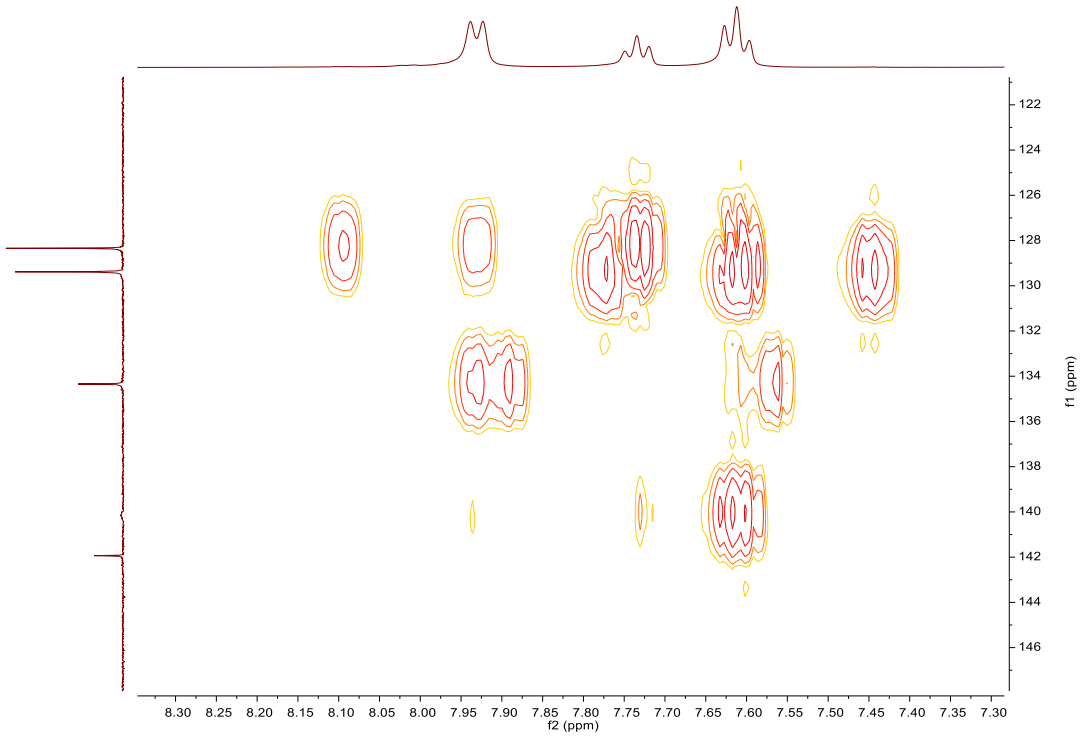

10.20
Cl
nBu
N
B
O
O
O
f1 (ppm)

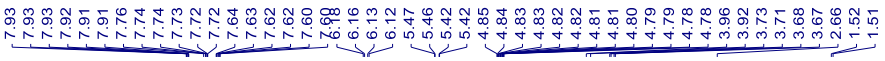

169.25
169.23
145.53
65.53
62.57
47.87
38.58
29.44
22.84
14.21
Cl
nBu
N
B
O
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

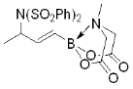

7.91
7.89
7.81
7.79
7.79
7.78
7.77
7.77
7.76
7.68
7.68
7.66
7.64
6.18
6.16
6.13
6.12
5.50
5.50
5.45
5.45
4.55
4.53
4.51
4.49
4.25
4.21
3.95
3.92
3.91
3.88
2.63
2.04
2.02
2.01
1.99
1.98
1.97
1.95
1.61
1.59
1.57
1.55
1.23
1.13
1.05
1.02
1.01
0.75
0.73
N(SO2Ph)2
nPr
N
B
O
O
O
O
4.02
2.00
4.03
1.00
0.98
0.97
2.10
1.96
3.09
1.10
0.89
1.84
3.05
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)

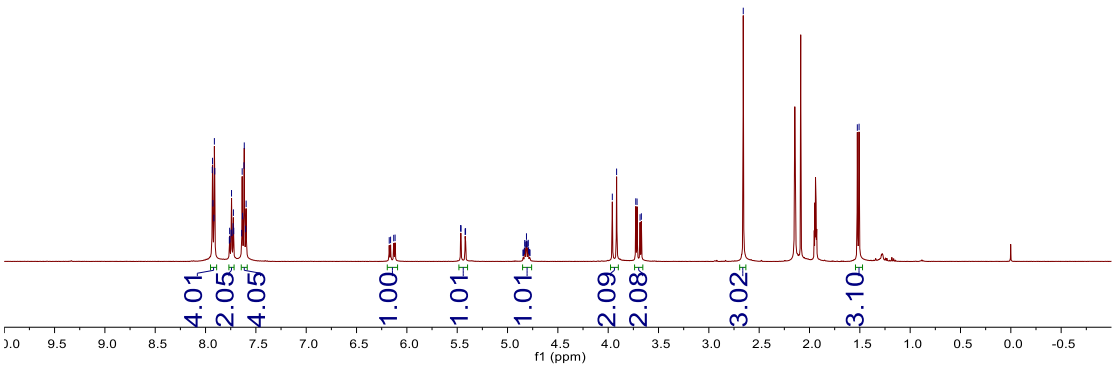


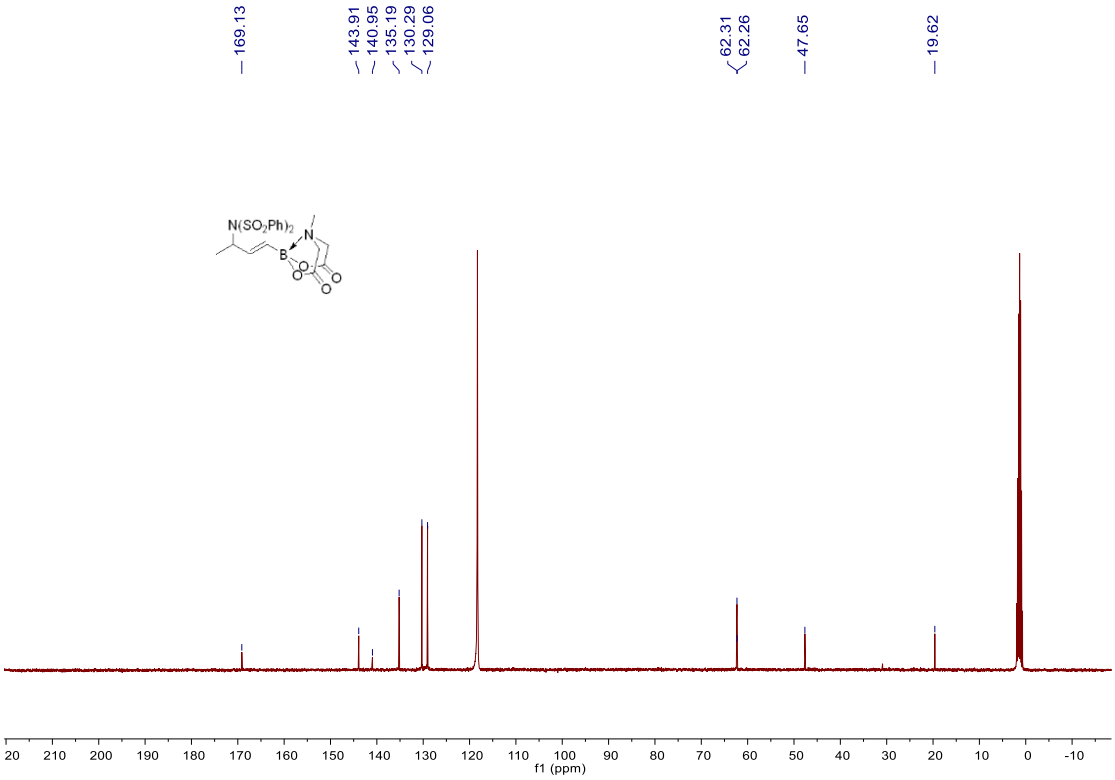
HMBC of **3a** (as below) shows a carbon signal peak at 140 ppm while there is no signal peak in ^{13}C NMR spectrum. Meanwhile there are lots of products showing the same phenomenon.

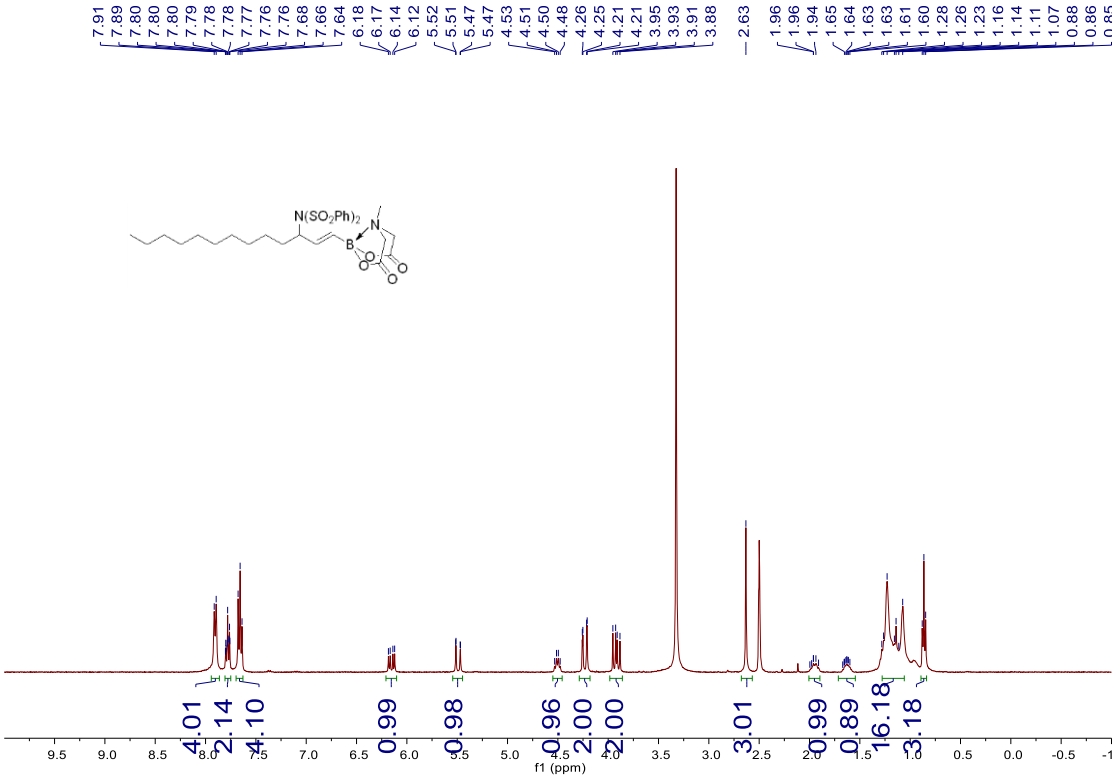

f1 (ppm)
f2 (ppm)

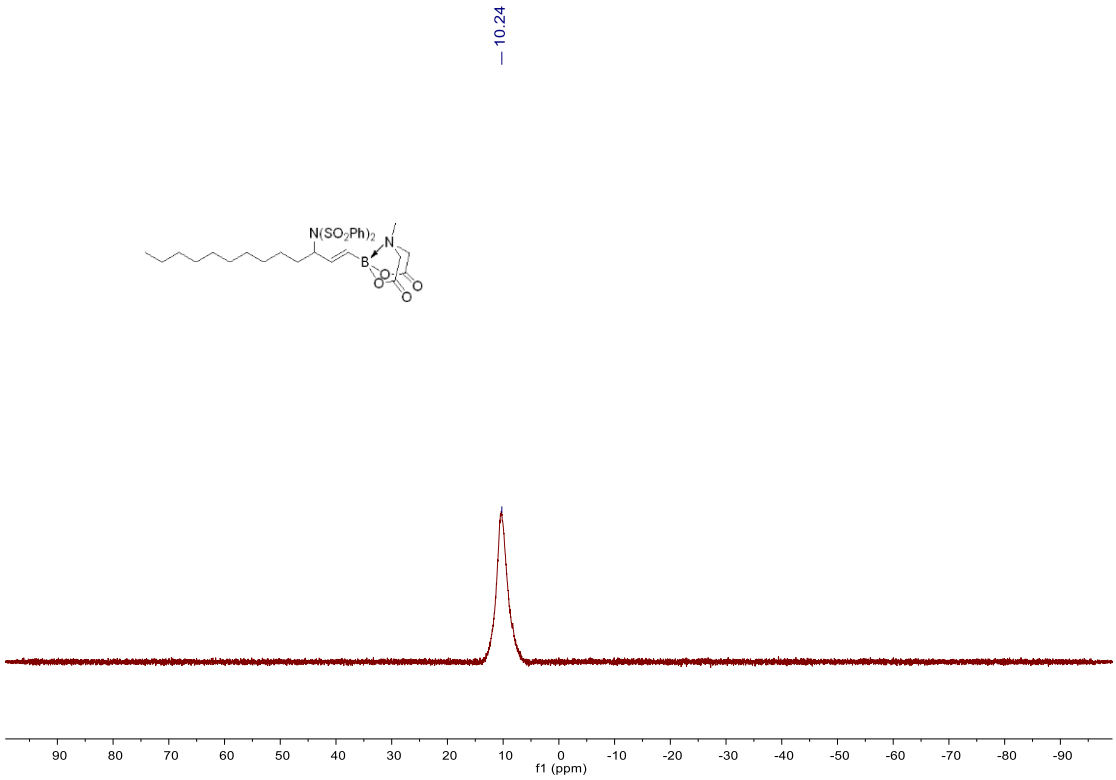

7.93
7.93
7.93
7.92
7.91
7.91
7.76
7.74
7.74
7.73
7.72
7.72
7.64
7.63
7.62
7.62
7.60
7.60
6.18
6.16
6.13
6.12
5.47
5.46
5.42
5.42
4.85
4.84
4.83
4.83
4.82
4.82
4.81
4.81
4.80
4.79
4.79
4.78
4.78
3.96
3.92
3.73
3.71
3.68
3.67
2.66
1.52
1.51

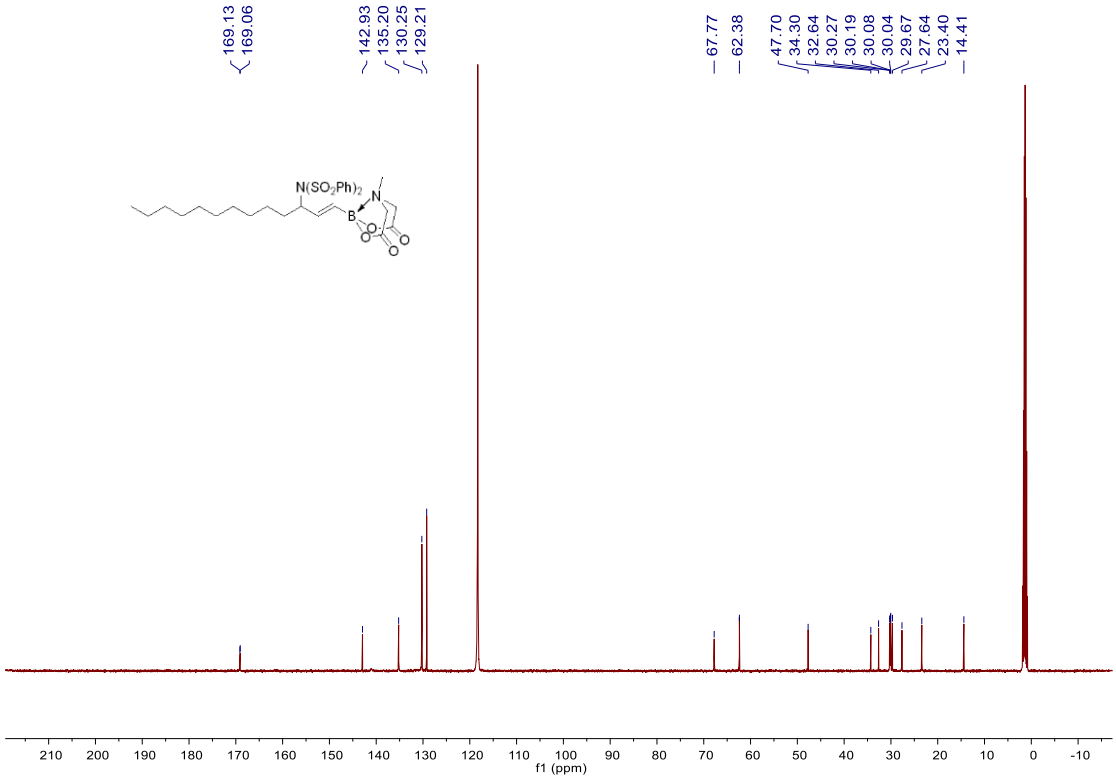

N(SO2Ph)2
N
B
O
O
O
O


4.01
2.05
4.05
1.00
1.01
1.01
2.09
2.08
3.02
3.10
f1 (ppm)

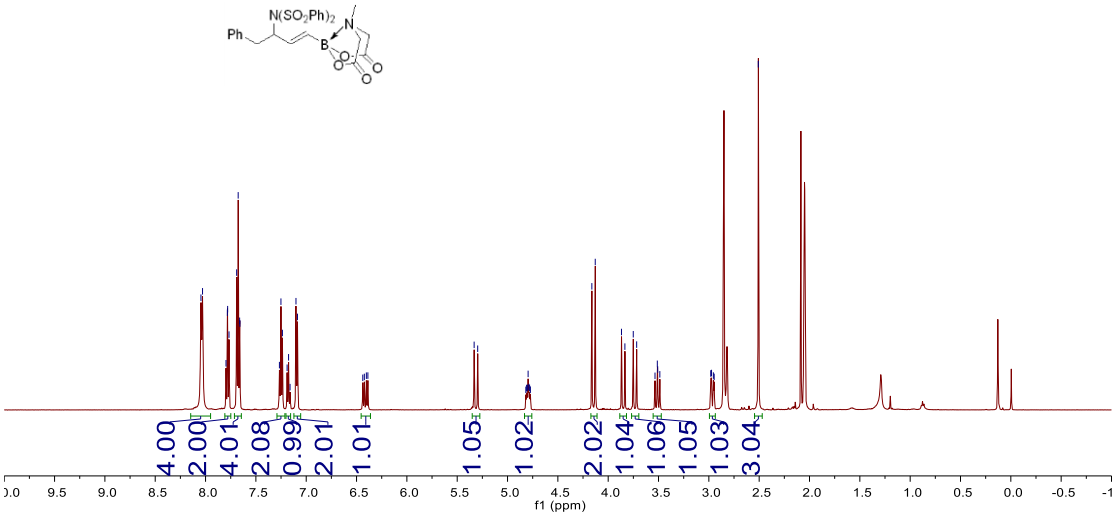

169.13
143.91
140.95
135.19
130.29
129.06
62.31
62.26
47.65
19.62
N(SO2Ph)2
f1 (ppm)

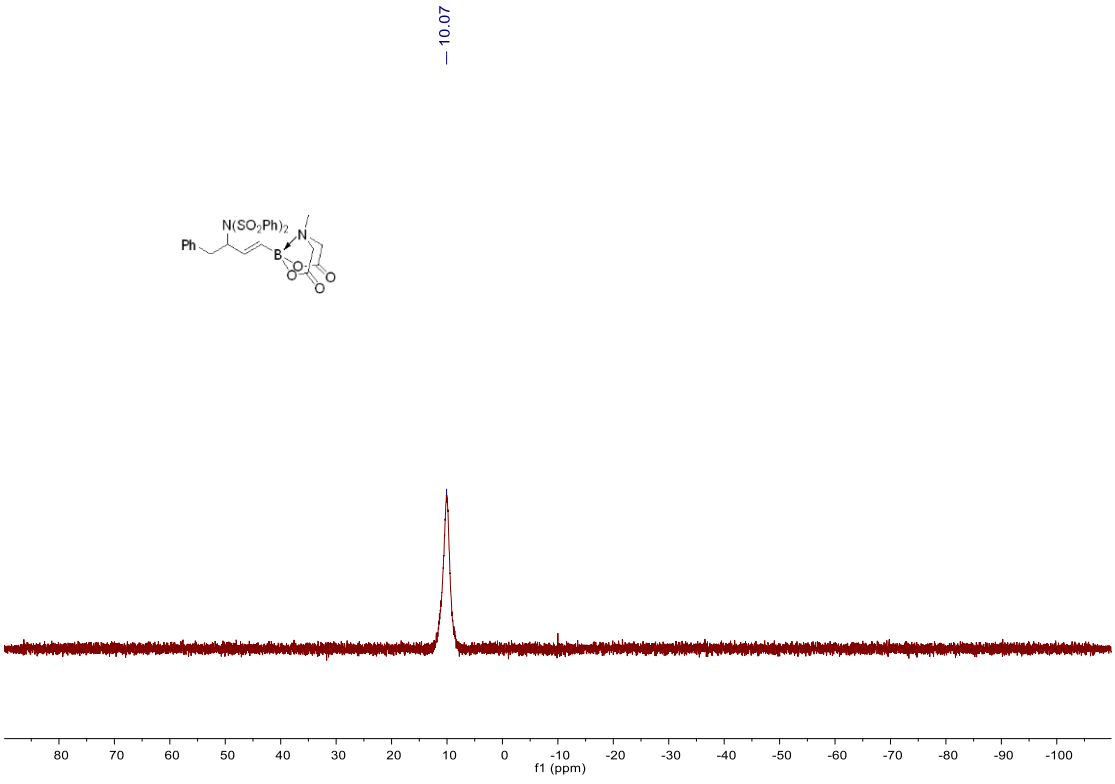

7.91
7.89
7.80
7.80
7.80
7.79
7.78
7.78
7.77
7.76
7.76
7.68
7.66
7.64
6.18
6.17
6.14
6.12
5.52
5.51
5.47
5.47
4.53
4.51
4.50
4.48
4.26
4.25
4.21
4.21
3.95
3.93
3.91
3.88
2.63
1.96
1.96
1.94
1.65
1.64
1.63
1.63
1.61
1.60
1.28
1.26
1.23
1.16
1.14
1.11
1.07
0.88
0.86
N(SO2Ph)2
4.01
2.14
4.10
0.99
0.98
0.96
2.00
2.00
3.01
0.99
0.89
16.18
3.18
f1 (ppm)

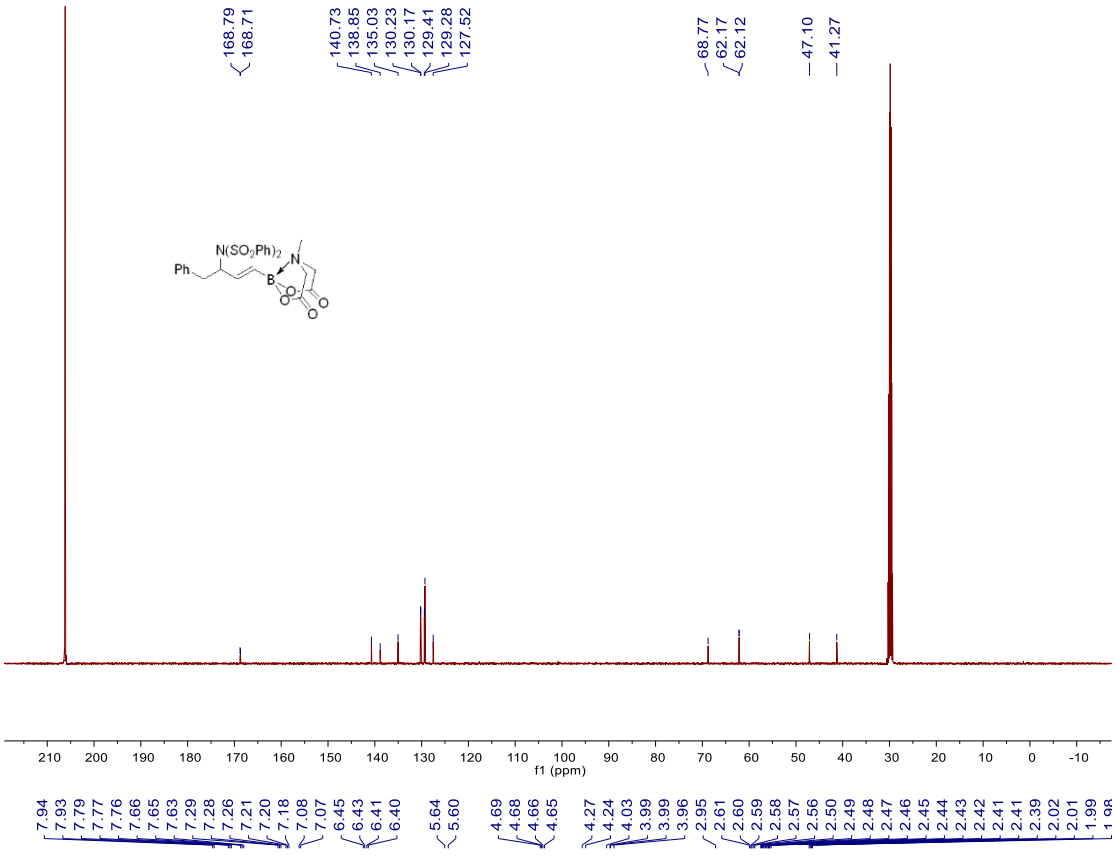

10.24
N(SO2Ph)2
B
f1 (ppm)

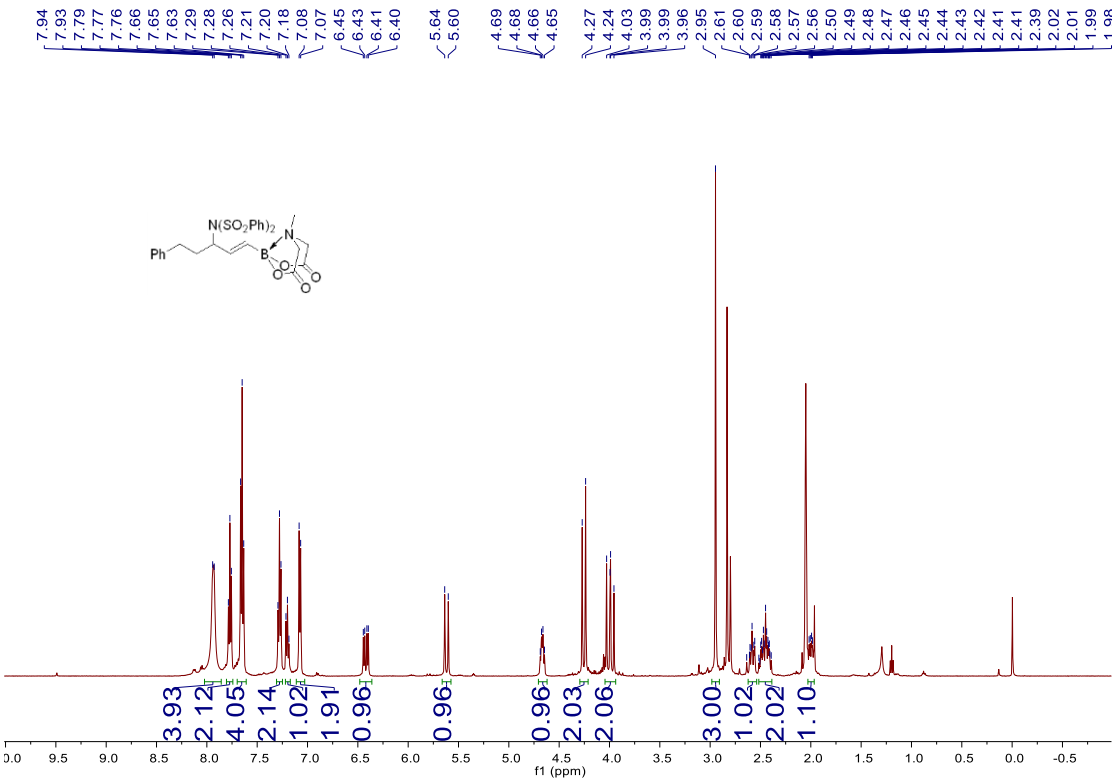

169.13
169.06
142.93
135.20
130.25
129.21
67.77
62.38
47.70
34.30
32.64
30.27
30.19
30.08
30.04
29.67
27.64
23.40
14.41
N(SO2Ph)2
B
f1 (ppm)

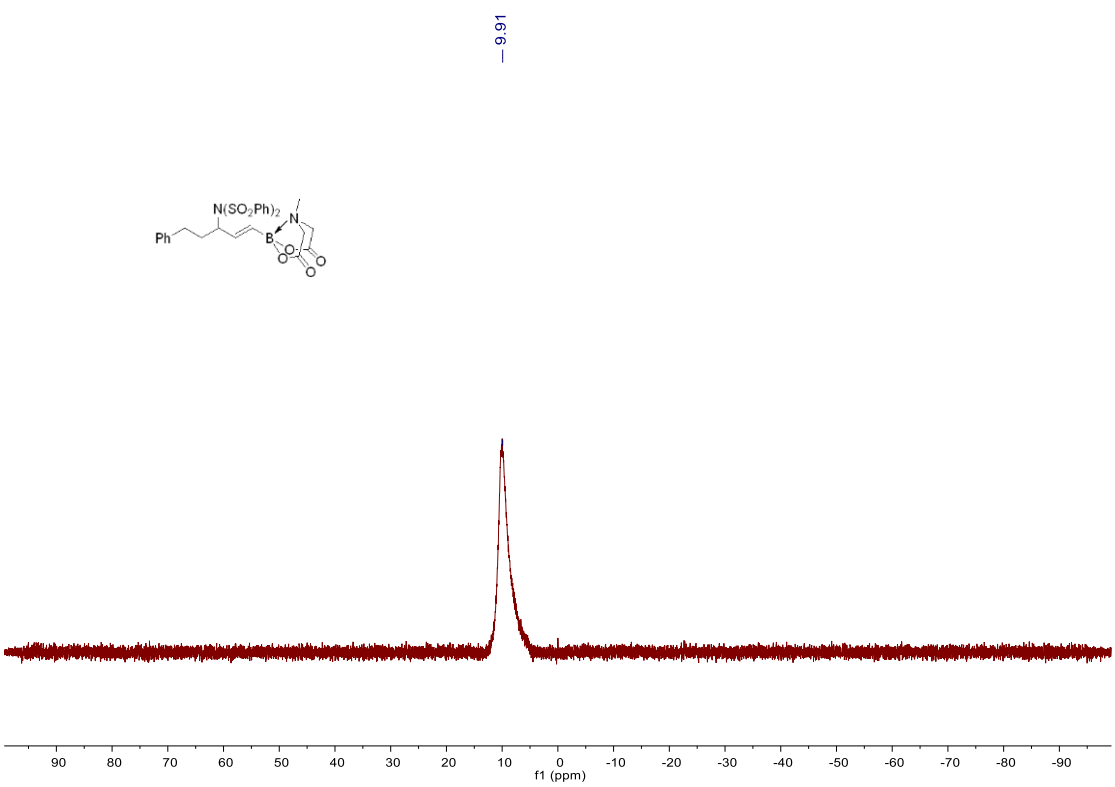

8.05
8.03
7.80
7.78
7.78
7.77
7.69
7.68
7.66
7.66
7.27
7.25
7.24
7.19
7.18
7.16
7.10
7.09
6.44
6.42
6.40
6.39
5.33
5.30
4.82
4.81
4.80
4.80
4.79
4.78
4.77
4.16
4.13
3.87
3.83
3.75
3.72
3.53
3.51
3.51
3.49
2.98
2.97
2.96
2.95
2.51

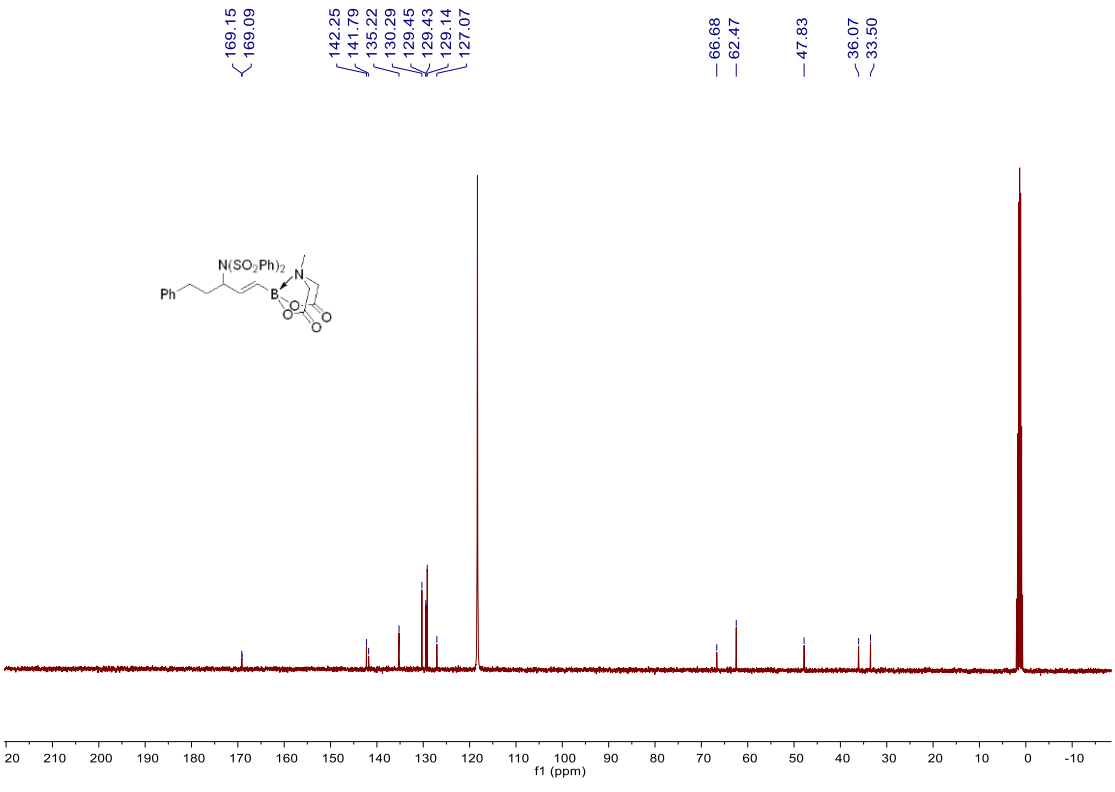

N(SO2Ph)2
Ph
B
O
O
O
4.00
2.00
4.01
2.08
0.99
2.01
1.01
1.05
1.02
2.02
1.04
1.06
1.05
1.03
3.04
f1 (ppm)


10.07
N(SO2Ph)2
Ph
B
O
O
O
f1 (ppm)

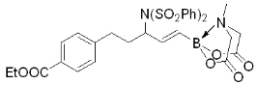

168.79
168.71
140.73
138.85
135.03
130.23
130.17
129.41
129.28
127.52
68.77
62.17
62.12
47.10
41.27
N(SO2Ph)2
Ph
B
O
O
O
O
O
N
f1 (ppm)

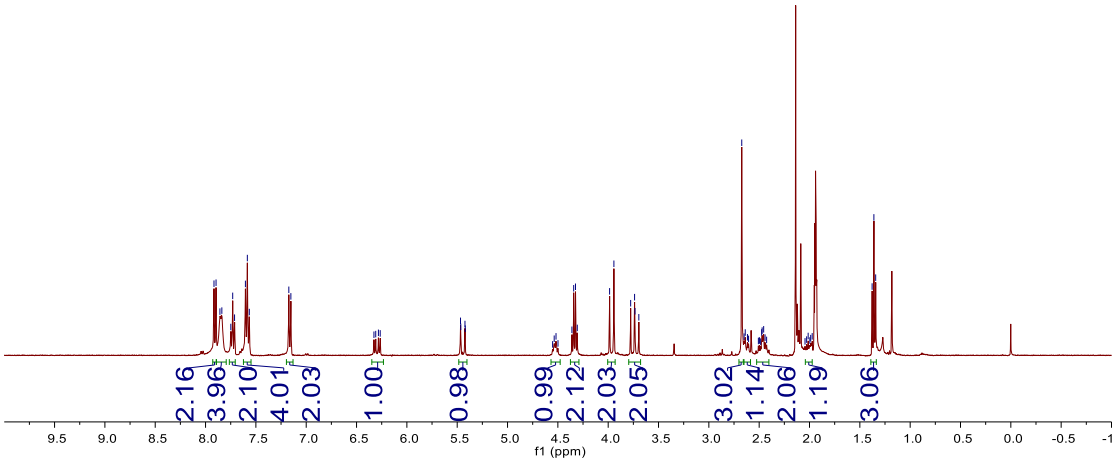

7.94
7.93
7.79
7.77
7.76
7.66
7.65
7.63
7.29
7.28
7.26
7.21
7.20
7.18
7.08
7.07
6.45
6.43
6.41
6.40
5.64
5.60
4.69
4.68
4.66
4.65
4.27
4.24
4.03
3.99
3.99
3.96
2.95
2.61
2.60
2.59
2.58
2.57
2.56
2.50
2.49
2.48
2.47
2.46
2.45
2.44
2.43
2.42
2.41
2.41
2.39
2.02
2.01
1.99
N(SO2Ph)2
Ph
B
O
O
O
O
O
N
3.93
2.12
4.05
2.14
1.02
1.91
0.96
0.96
0.96
2.03
2.06
3.00
1.02
2.02
1.10
f1 (ppm)


9.91
N(SO2Ph)2
Ph
B
O
O
O
O
N
f1 (ppm)

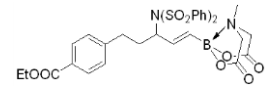

169.15
169.09
142.25
141.79
135.22
130.29
129.45
129.43
129.14
127.07
66.68
62.47
47.83
36.07
33.50
N(SO2Ph)2
Ph
B
O
O
O
O
N
f1 (ppm)

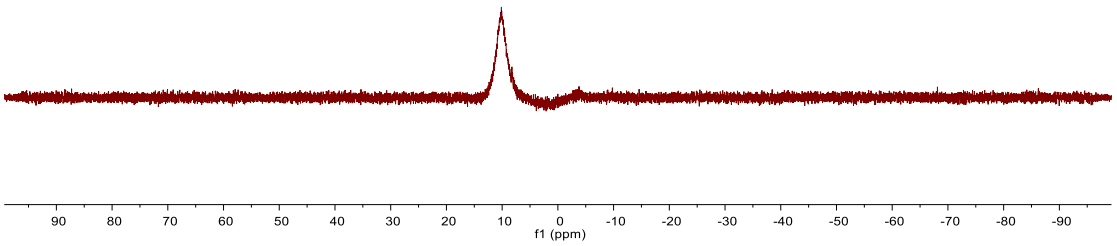

7.92
7.90
7.86
7.84
7.75
7.73
7.71
7.60
7.58
7.57
7.17
7.15
6.33
6.31
6.28
6.26
5.47
5.46
5.42
5.42
4.54
4.52
4.36
4.34
4.32
4.31
3.99
3.94
3.78
3.74
3.73
3.70
2.67
2.65
2.64
2.62
2.61
2.51
2.50
2.48
2.47
2.46
2.44
2.43
2.03
2.01
2.00
1.99
1.97
1.38
1.36
1.34

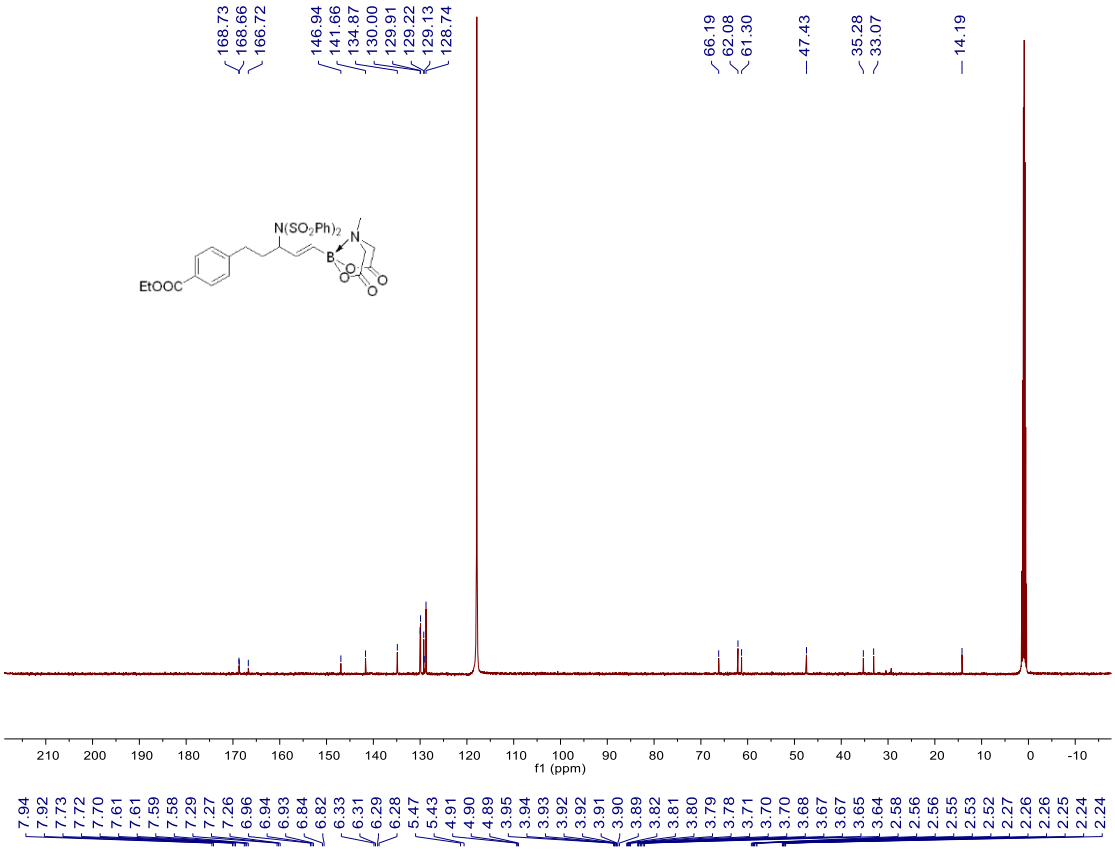

N(SO2Ph)2
N
B
O
O
O
O
EtOOC

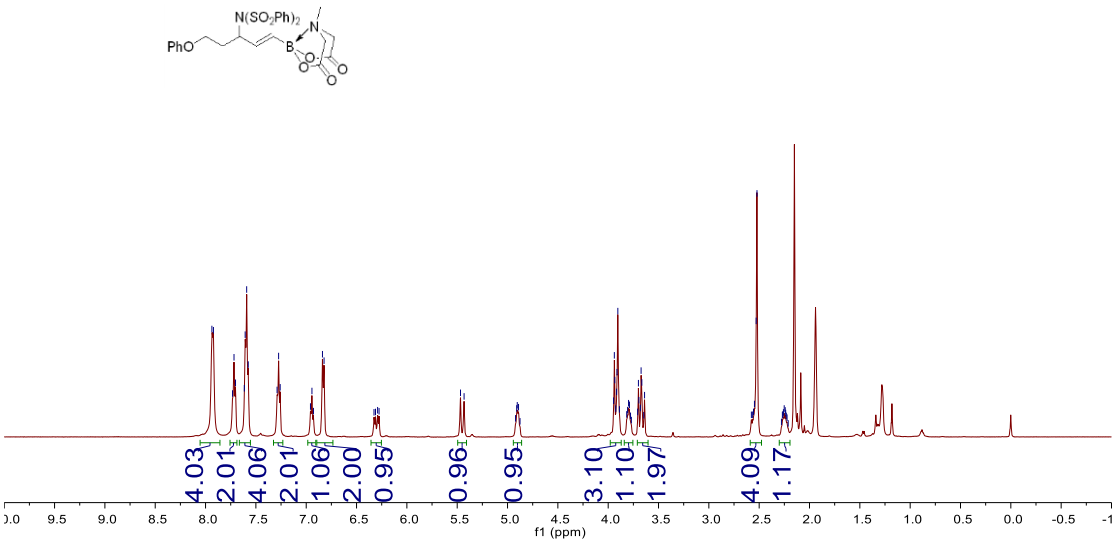

2.16
3.96
2.10
4.01
2.03
1.00
0.98
0.99
2.12
2.03
2.05
3.02
1.14
2.06
1.19
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

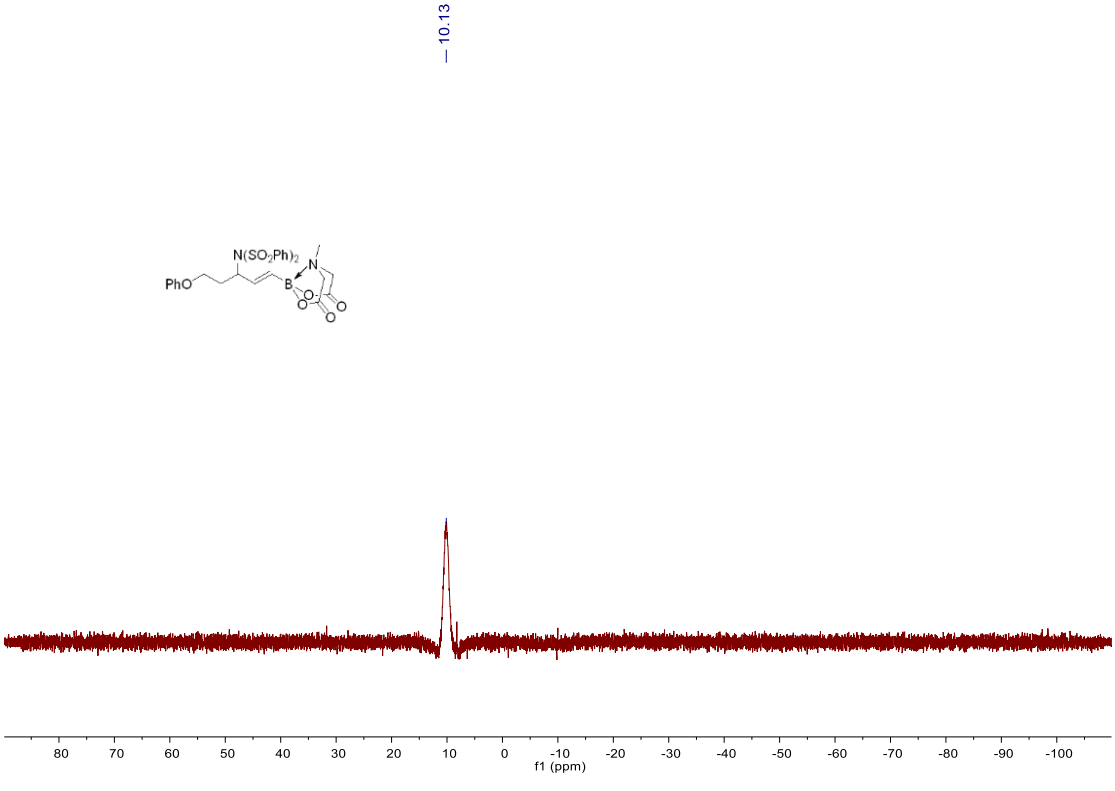

10.15

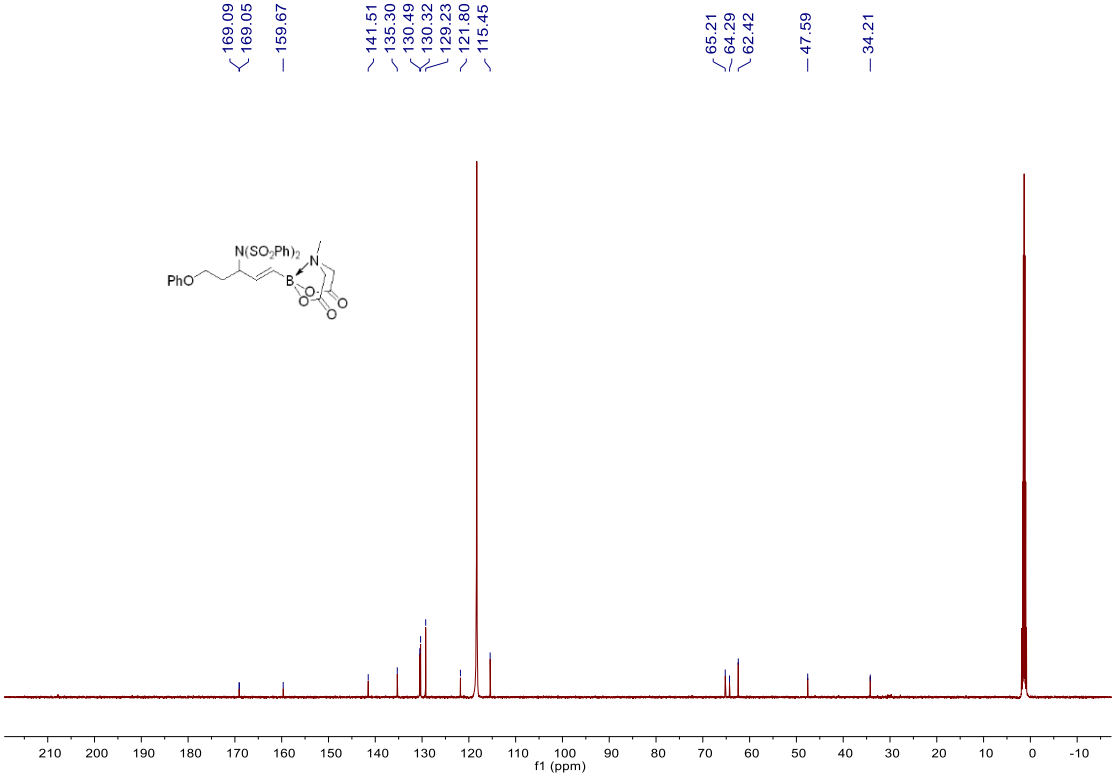

N(SO2Ph)2
N
B
O
O
O
O
EtOOC

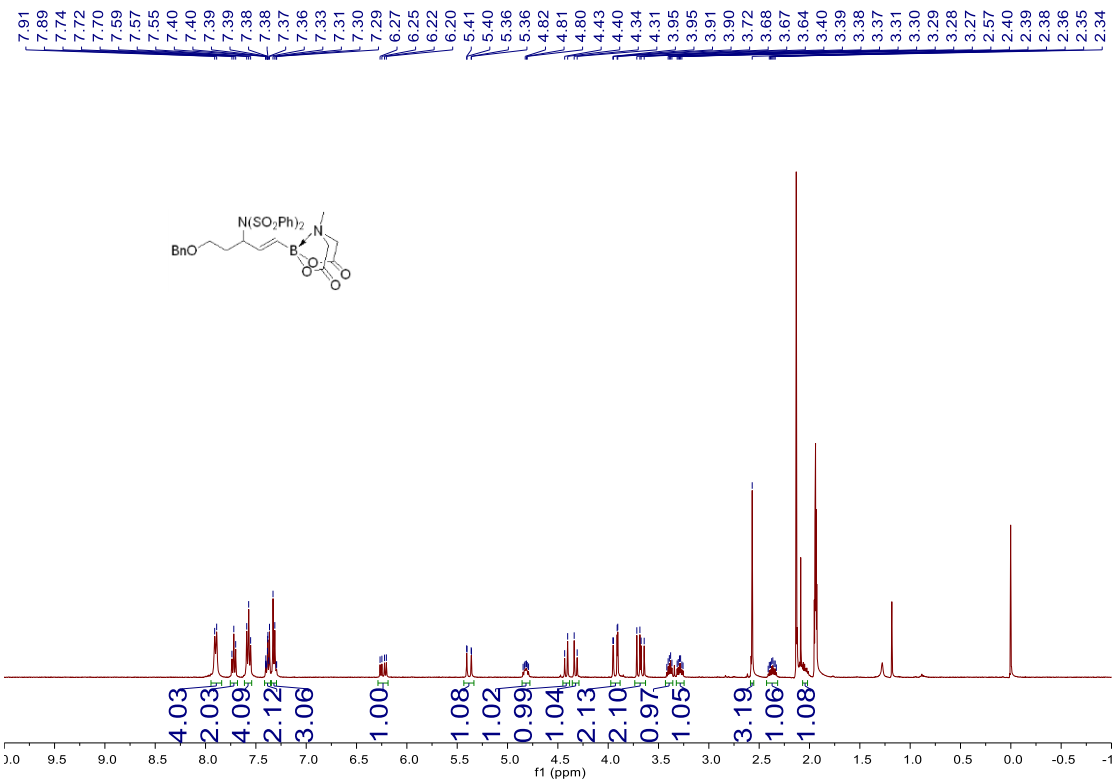

90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)

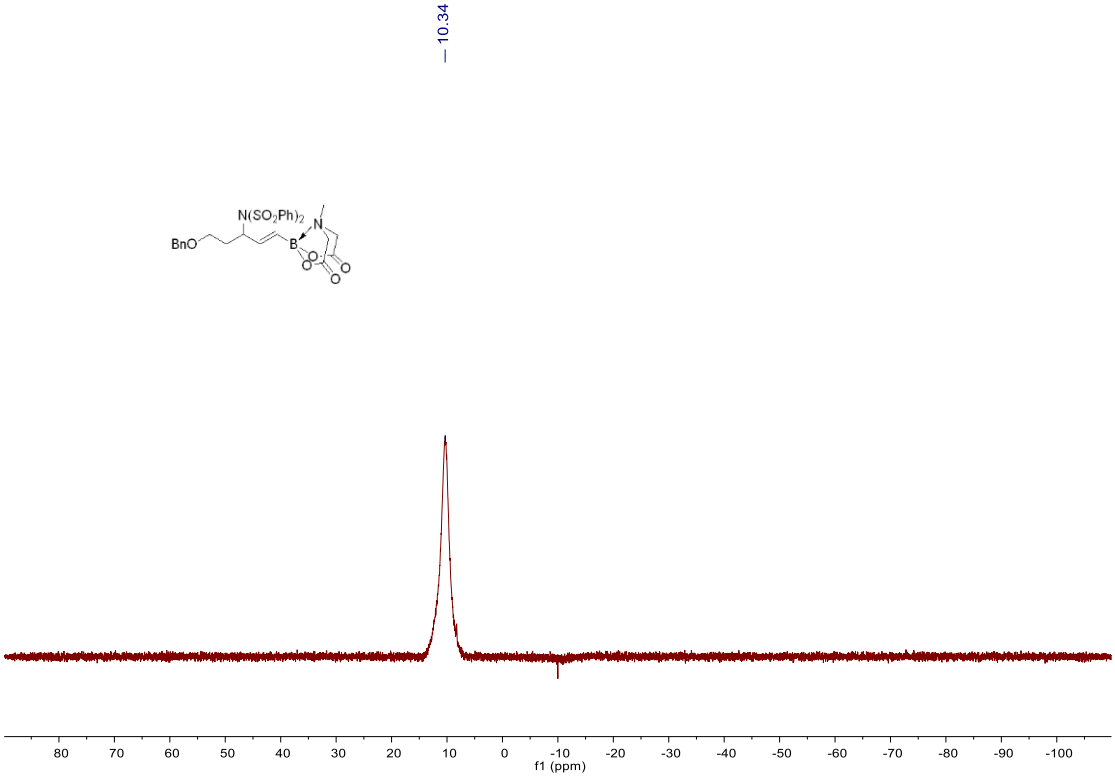

168.73
168.66
166.72
146.94
141.66
134.87
130.00
129.91
129.22
129.13
128.74
66.19
62.08
61.30
47.43
35.28
33.07
14.19
N(SO2Ph)2
N
B
O
O
O
O
EtOOC
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
7.94 7.92 7.73 7.72 7.70 7.61 7.59 7.58 7.29 7.27 7.26 6.96 6.94 6.93 6.84 6.82 6.33 6.31 6.29 6.28 5.47 5.43 4.91 4.90 4.89 3.95 3.94 3.93 3.92 3.91 3.90 3.89 3.82 3.81 3.80 3.79 3.78 3.71 3.70 3.70 3.68 3.67 3.67 3.65 3.64 2.58 2.56 2.56 2.55 2.53 2.52 2.27 2.26 2.26 2.25 2.24 2.24

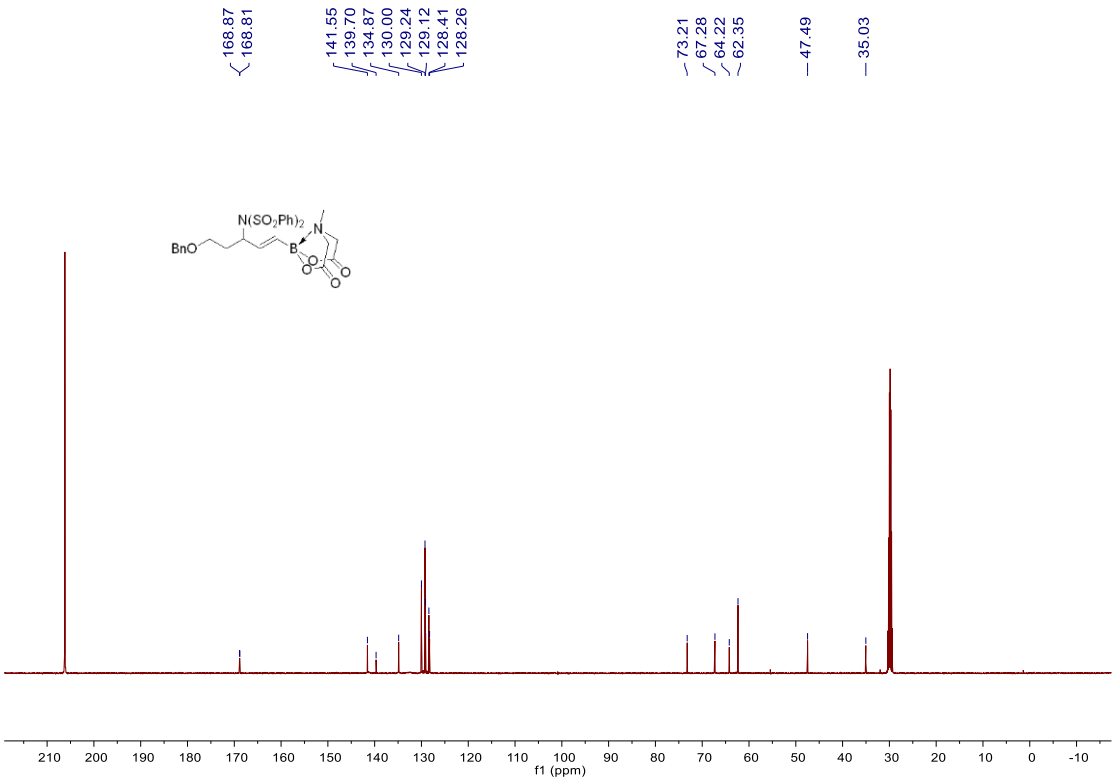

N(SO2Ph)2
N
B
O
O
O
O
PhO
4.03 2.01 4.06 2.01 1.06 2.00 0.95 0.96 0.95 3.10 1.10 1.97 4.09 1.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


10.13
N(SO2Ph)2
PhO
B
O
O
O
O
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

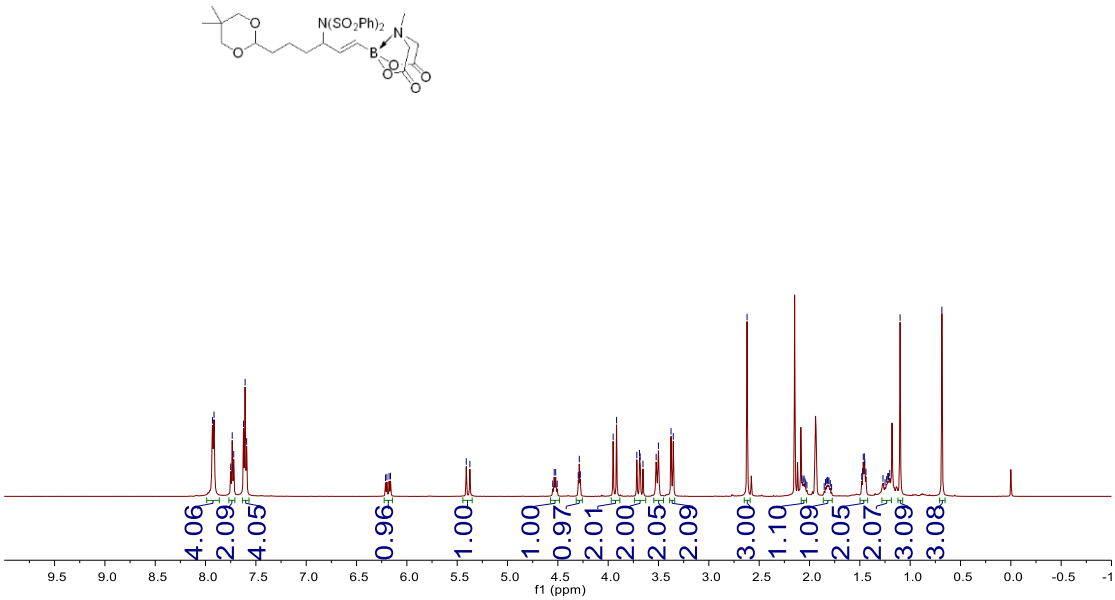

169.09
169.05
159.67
141.51
135.30
130.49
130.32
129.23
121.80
115.45
65.21
64.29
62.42
47.59
34.21
N(SO2Ph)2
PhO
B
O
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.91 7.89 7.74 7.72 7.70 7.59 7.57 7.55 7.40 7.40 7.39 7.39 7.38 7.38 7.37 7.36 7.33 7.31 7.30 7.29 6.27 6.25 6.22 6.20 5.41 5.40 5.36 5.36 4.82 4.81 4.80 4.43 4.40 4.34 4.31 3.95 3.95 3.91 3.90 3.72 3.68 3.67 3.64 3.40 3.39 3.38 3.37 3.31 3.30 3.29 3.28 3.27 2.57 2.40 2.39 2.38 2.36 2.35 2.34
N(SO2Ph)2
BnO
4.03 2.03 4.09 2.12 3.06 1.00 1.08 1.02 0.99 1.04 2.13 2.10 0.97 1.05 3.19 1.06 1.08
f1 (ppm)

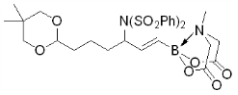

10.34
N(SO2Ph)2
BnO
f1 (ppm)

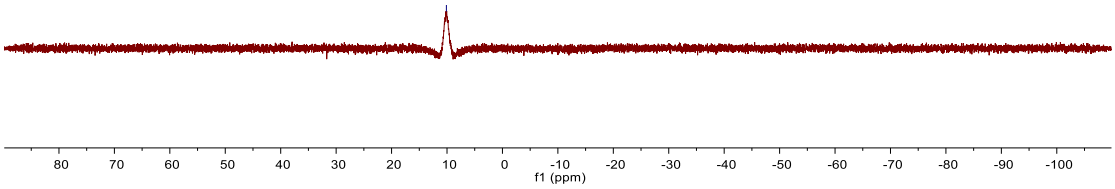

168.87
168.81
141.55
139.70
134.87
130.00
129.24
129.12
128.41
128.26
73.21
67.28
64.22
62.35
47.49
35.03
N(SO2Ph)2
BnO
f1 (ppm)


7.93
7.92
7.75
7.73
7.72
7.62
7.61
7.59
6.21
6.20
6.18
6.16
5.41
5.37
4.55
4.54
4.52
4.51
4.30
4.29
4.28
3.95
3.92
3.72
3.69
3.68
3.65
3.52
3.50
3.38
3.35
2.62
2.08
2.06
2.05
2.04
2.04
2.03
1.84
1.83
1.82
1.82
1.81
1.79
1.48
1.47
1.47
1.46
1.45
1.44
1.27
1.25
1.23
1.22
1.22
1.21
1.20
1.10
0.69

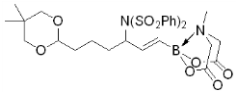

N(SO2Ph)2
4.06
2.09
4.05
0.96
1.00
1.00
0.97
2.01
2.00
2.05
2.09
3.00
1.10
1.09
2.05
2.07
3.09
3.08
f1 (ppm)

10.11





169.10
169.06
142.72
135.23
130.27
129.23
102.36
77.48
67.63
62.34
47.69
34.90
34.13
30.67
23.17
22.16
21.85




7.89
7.89
7.88
7.87
7.86
7.85
7.84
7.84
7.72
7.70
7.69
7.57
7.55
7.53
6.29
6.27
6.25
6.23
5.57
5.53
4.53
4.52
4.51
4.49
4.48
4.02
3.97
3.81
3.77
3.73
3.58
3.56
3.56
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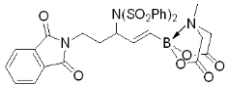
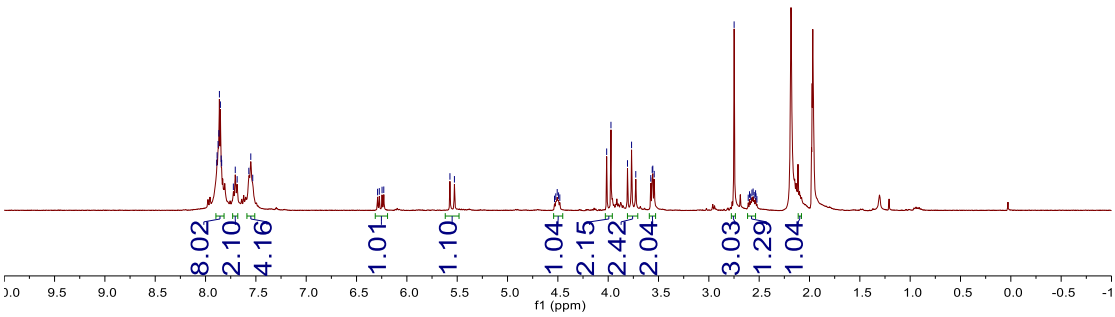
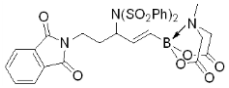
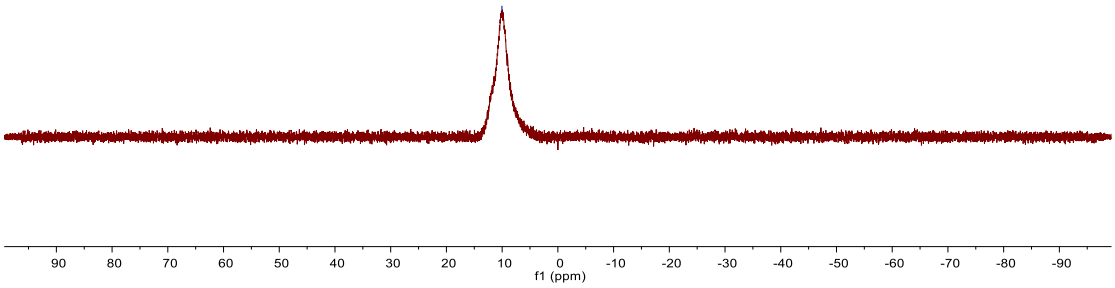
2.75
2.61
2.60
2.58
2.57
2.56
2.55
2.54
2.53
2.52

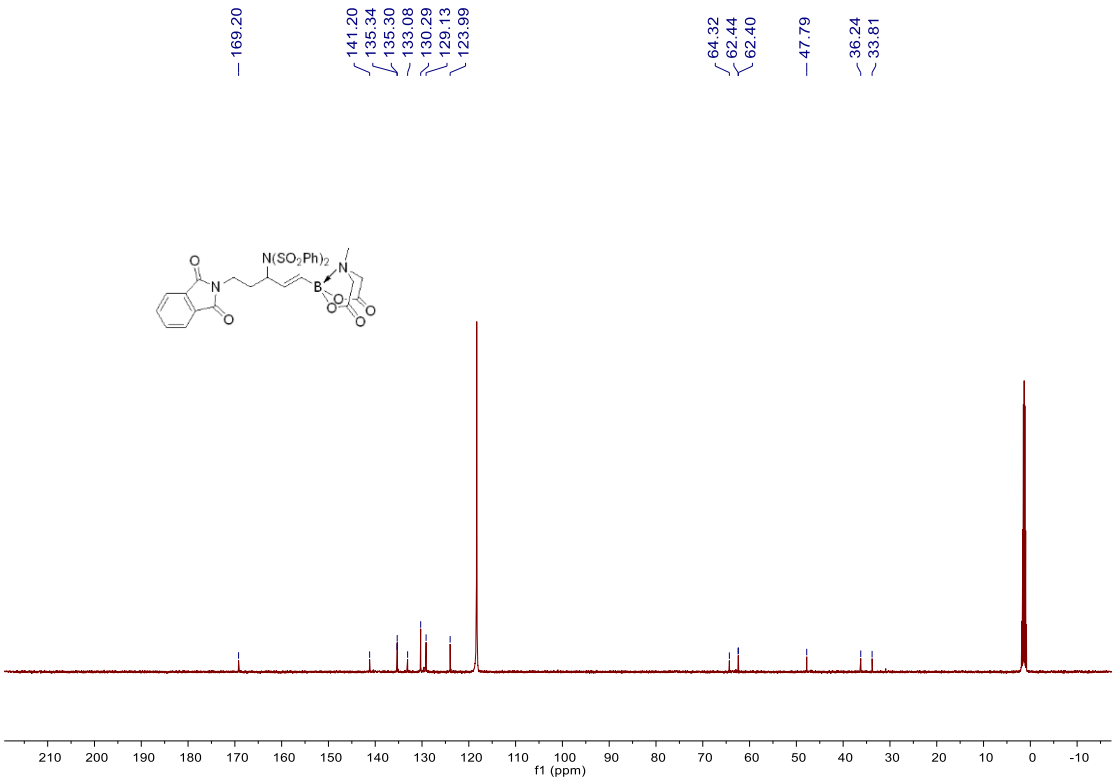

N(SO2Ph)2
N
B
O
O
O
O
O
O
O

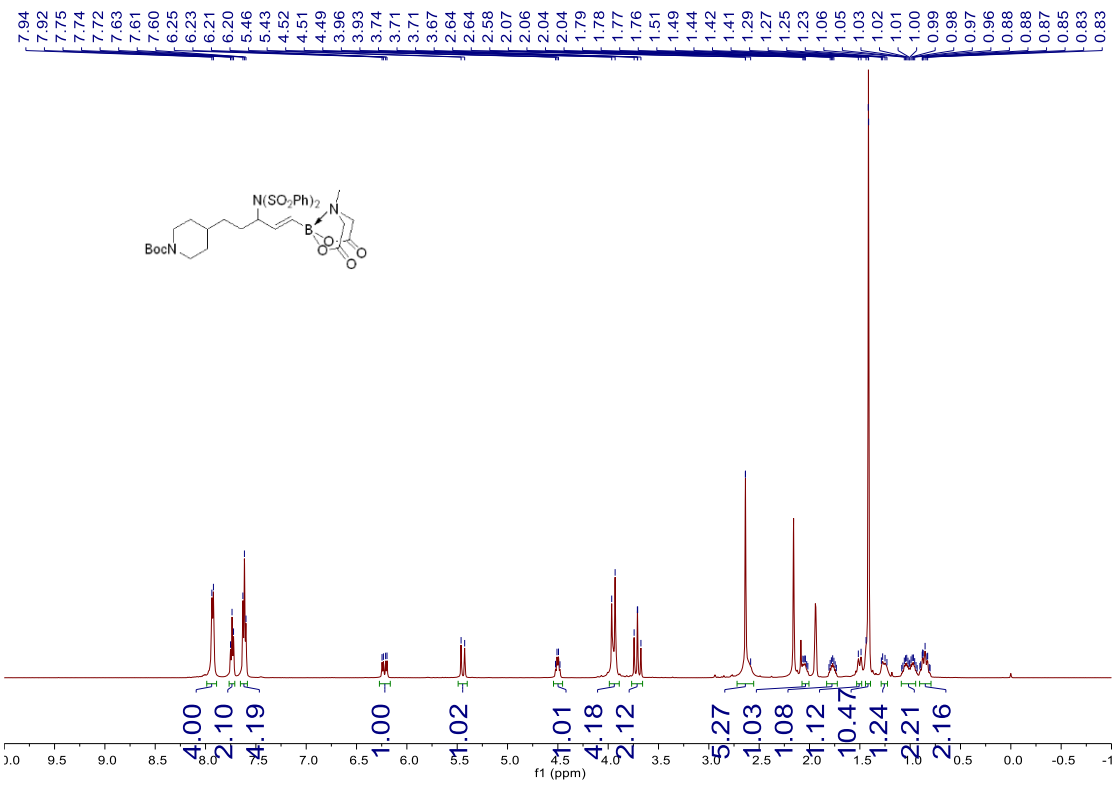

8.02
2.10
4.16
1.01
1.10
1.04
2.15
2.42
2.04
3.03
1.29
1.04
f1 (ppm)

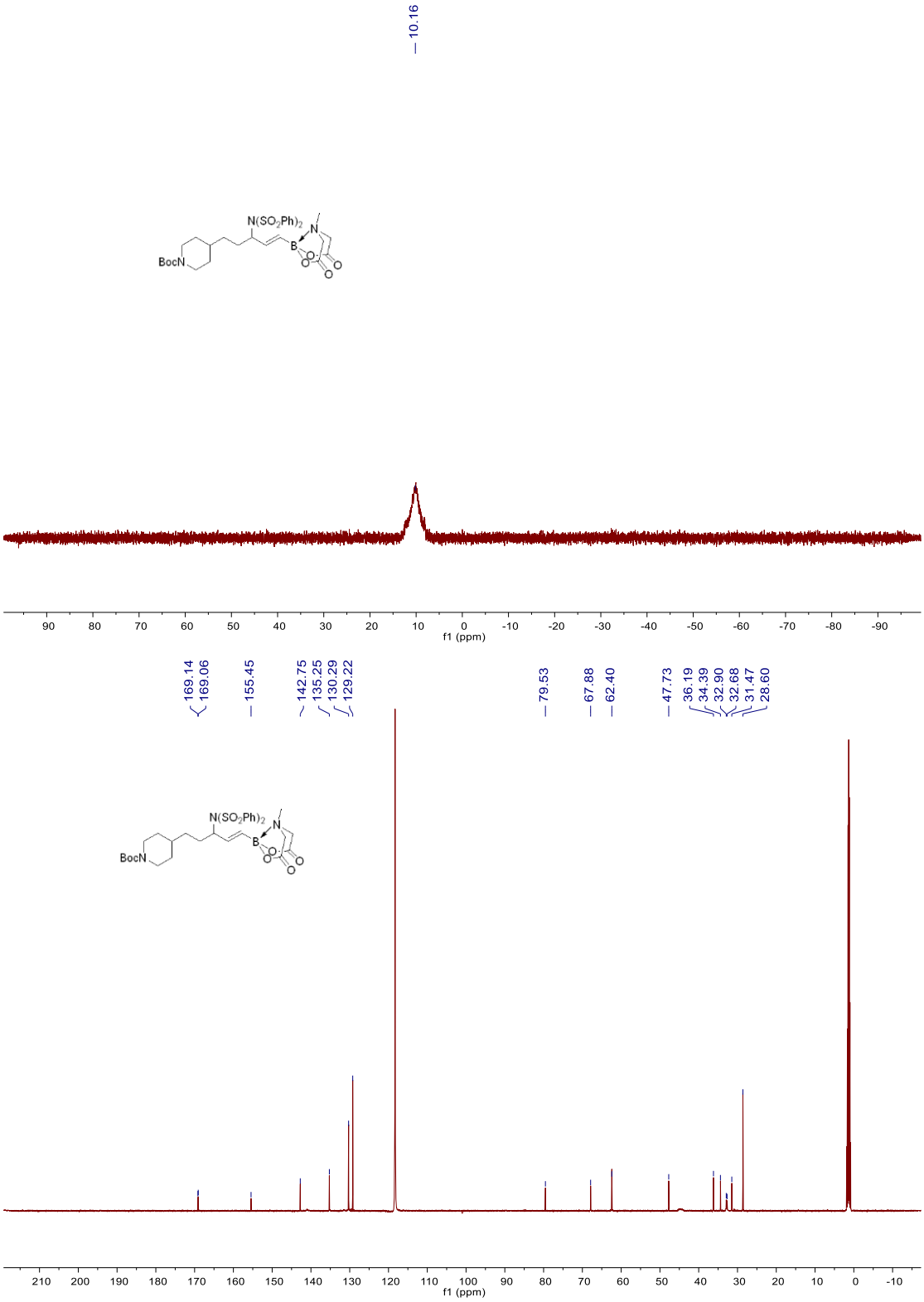

10.04


N(SO2Ph)2
N
B
O
O
O
O
O
O
O

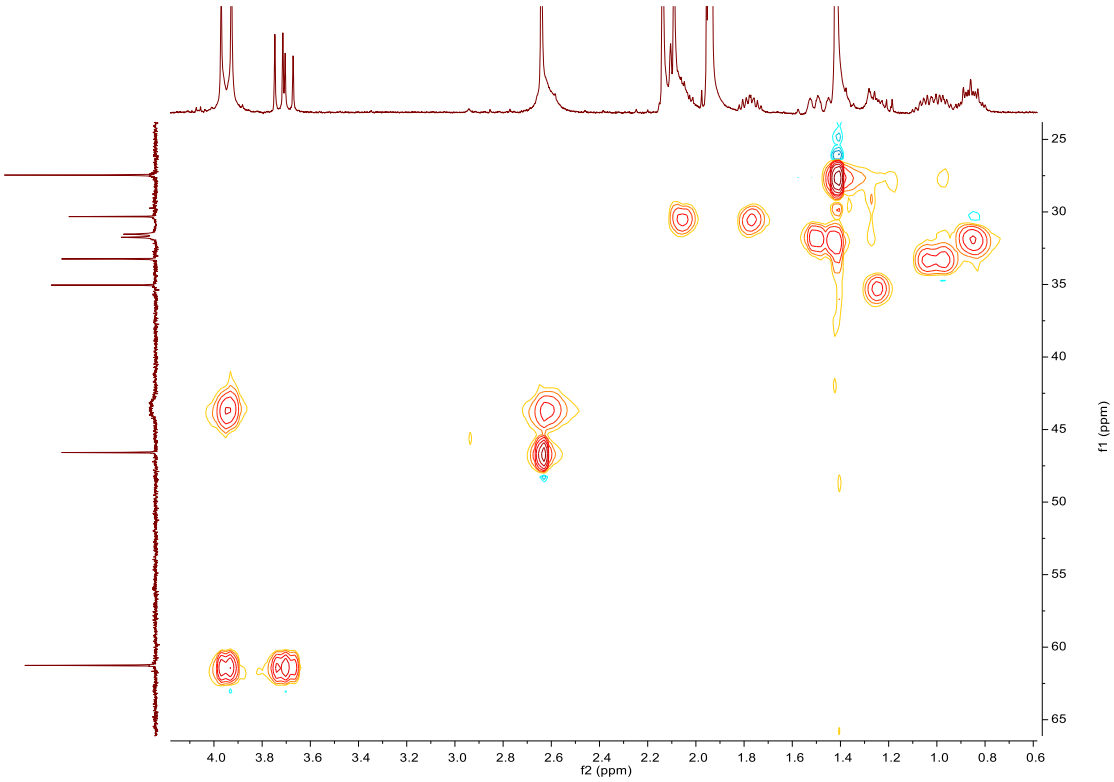

f1 (ppm)


169.20
141.20
135.34
135.30
133.08
130.29
129.13
123.99
64.32
62.44
62.40
47.79
36.24
33.81
N(SO2Ph)2
f1 (ppm)

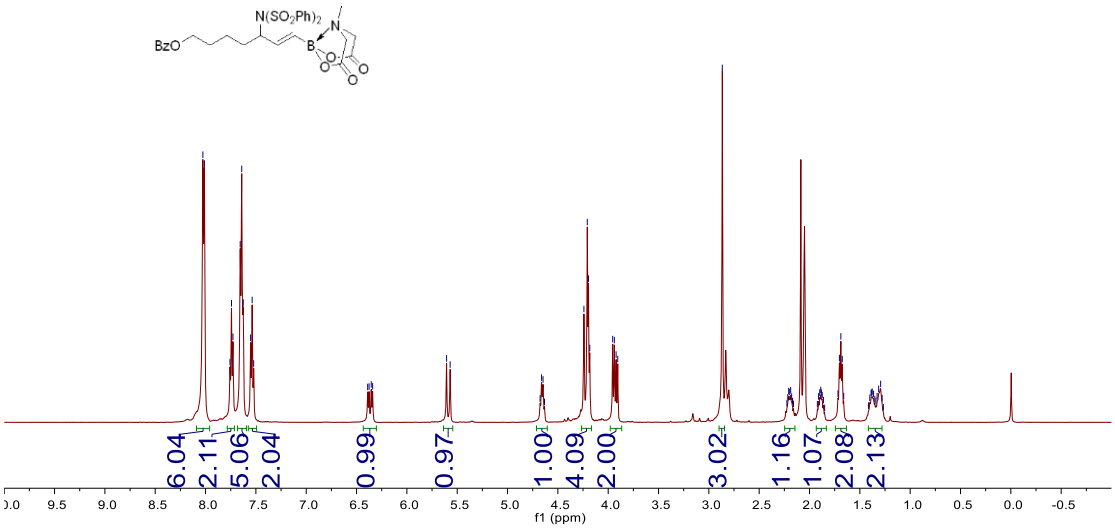

7.94
7.92
7.75
7.74
7.72
7.63
7.61
7.60
6.25
6.23
6.21
6.20
5.46
5.43
4.52
4.51
4.49
3.96
3.93
3.74
3.71
3.67
2.64
2.64
2.58
2.07
2.06
2.04
2.04
1.79
1.78
1.77
1.76
1.51
1.49
1.44
1.42
1.41
1.29
1.27
1.25
1.23
1.06
1.05
1.03
1.02
1.01
1.00
0.99
0.98
0.97
0.96
0.88
0.87
0.85
0.83
0.83
N(SO2Ph)2
BocN
4.00
2.10
4.19
1.00
1.02
1.01
4.18
2.12
5.27
1.03
1.08
1.12
10.47
1.24
2.21
2.16
f1 (ppm)

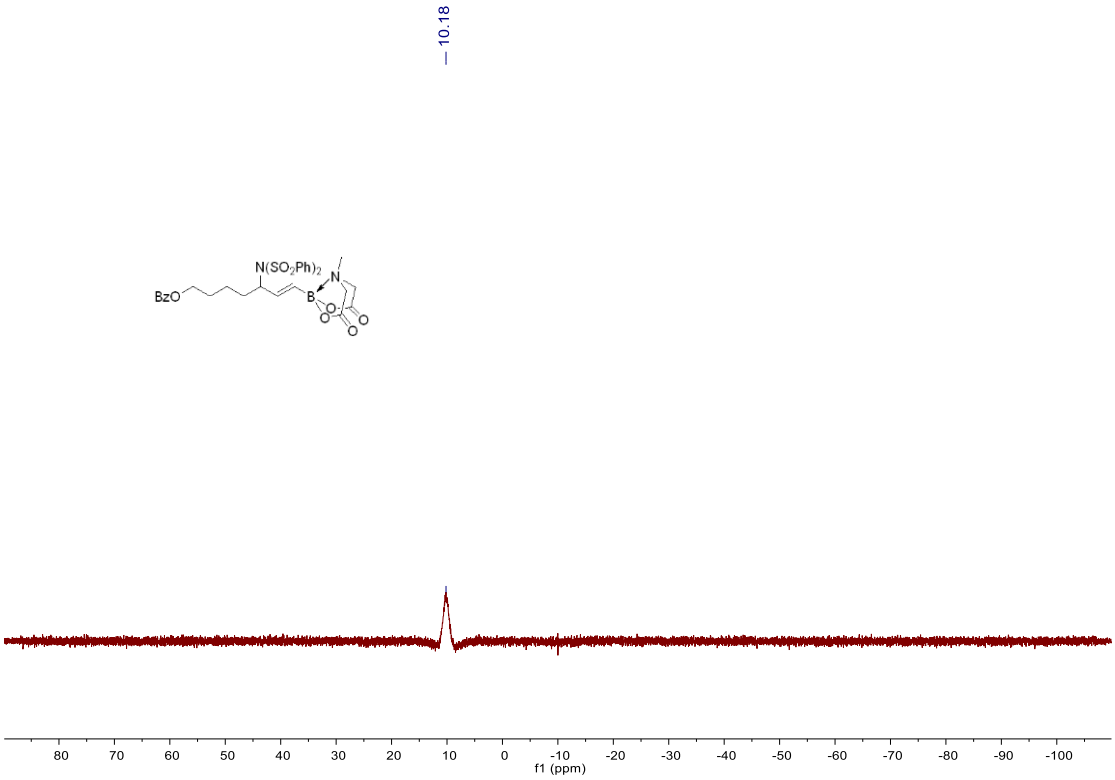


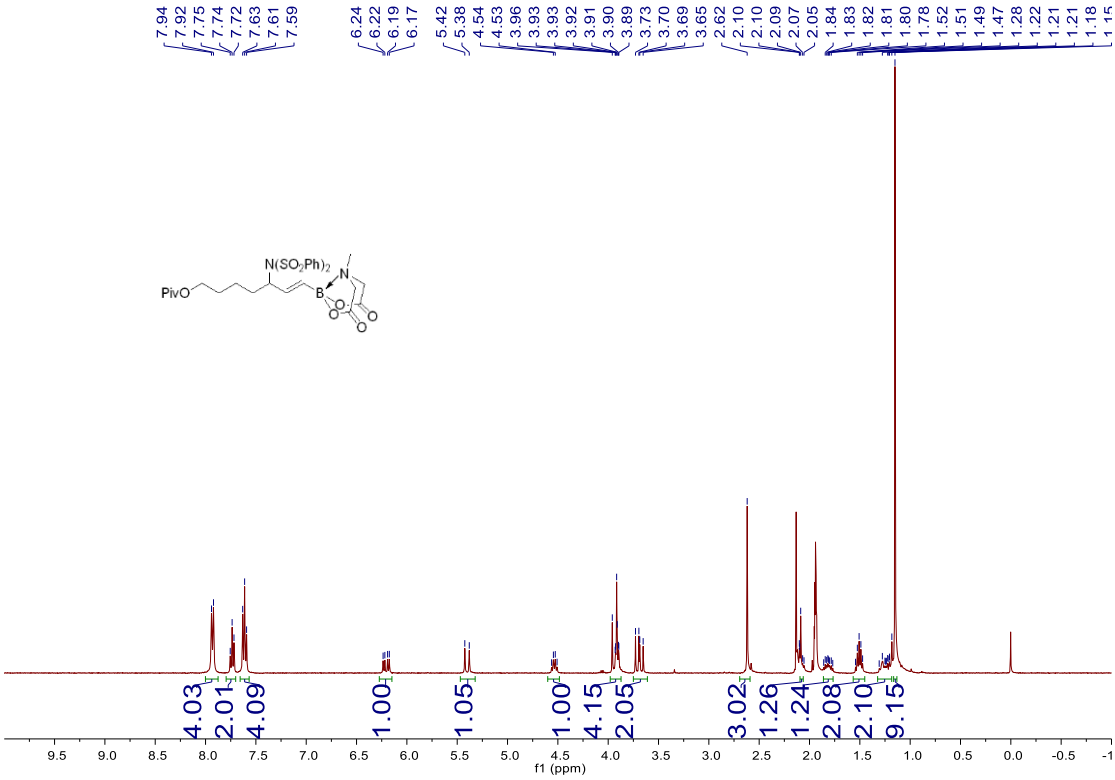
HMQC of **3k** (as below) shows carbon signal peak at 42 ppm while there is no signal peak in ^{13}C NMR spectrum.

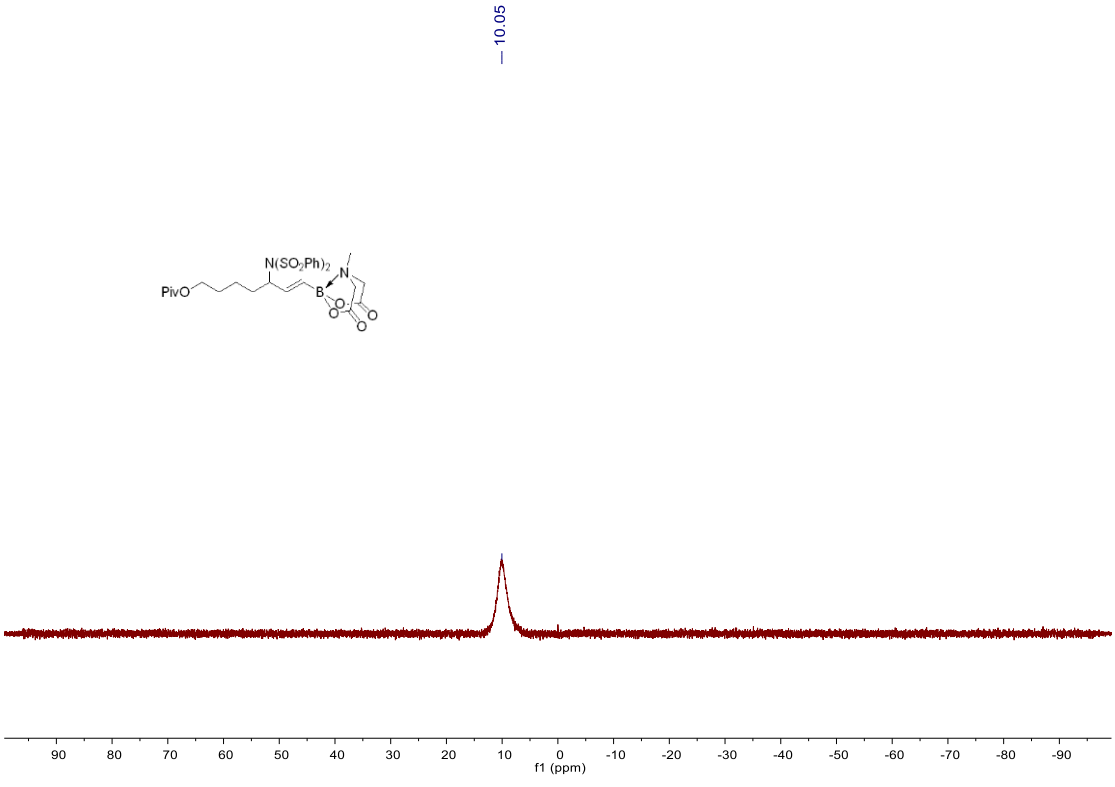


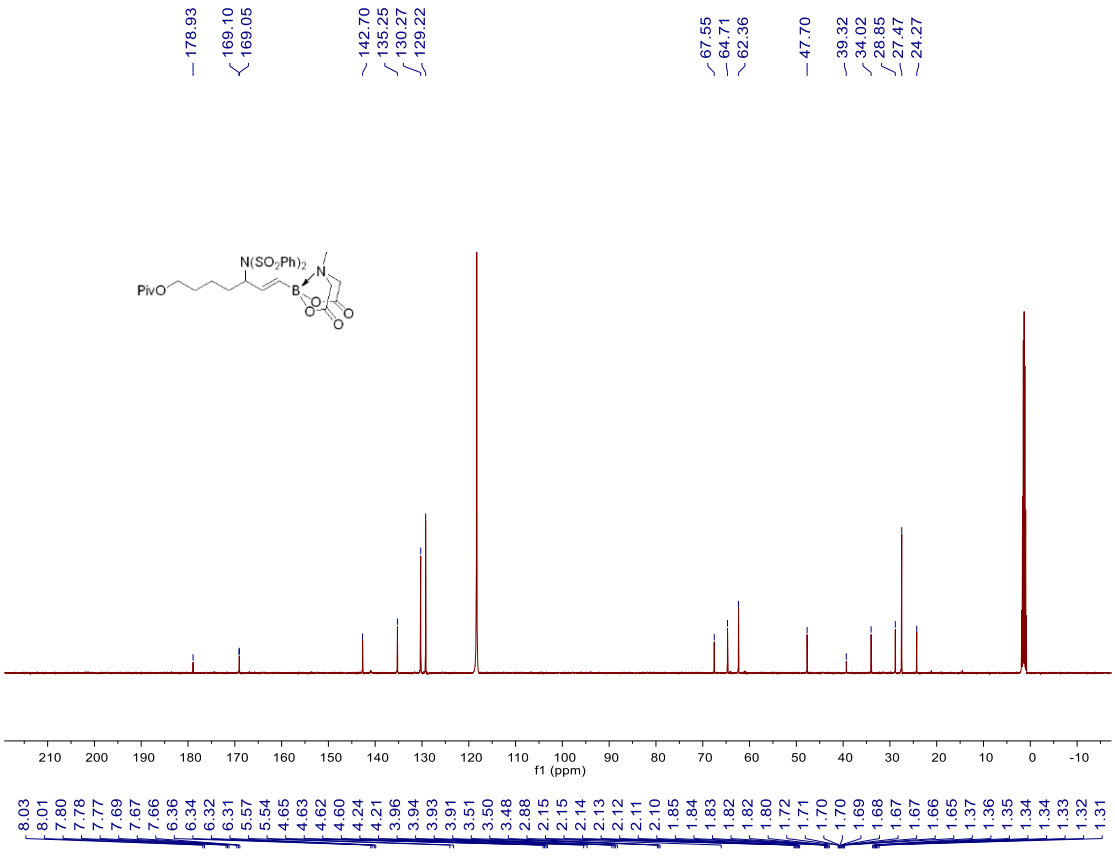
8.03 8.01 7.76 7.74 7.73 7.66 7.64 7.63 7.55 7.54 7.52 6.39 6.38 6.35 6.34 5.61 5.57 4.68 4.66 4.65 4.63 4.24 4.21 4.20 4.18 3.96 3.94 3.92 3.91 2.87 2.22 2.22 2.21 2.20 2.19 2.18 2.17 1.91 1.90 1.89 1.88 1.87 1.86 1.72 1.70 1.69 1.67 1.66 1.40 1.39 1.38 1.38 1.36 1.35 1.34 1.33 1.31 1.29 1.28

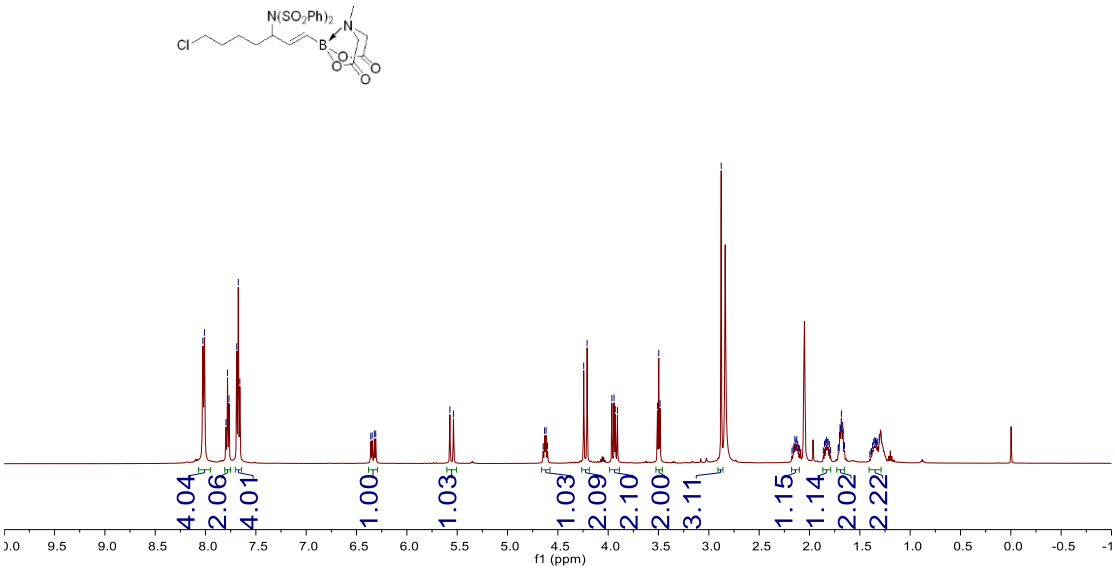


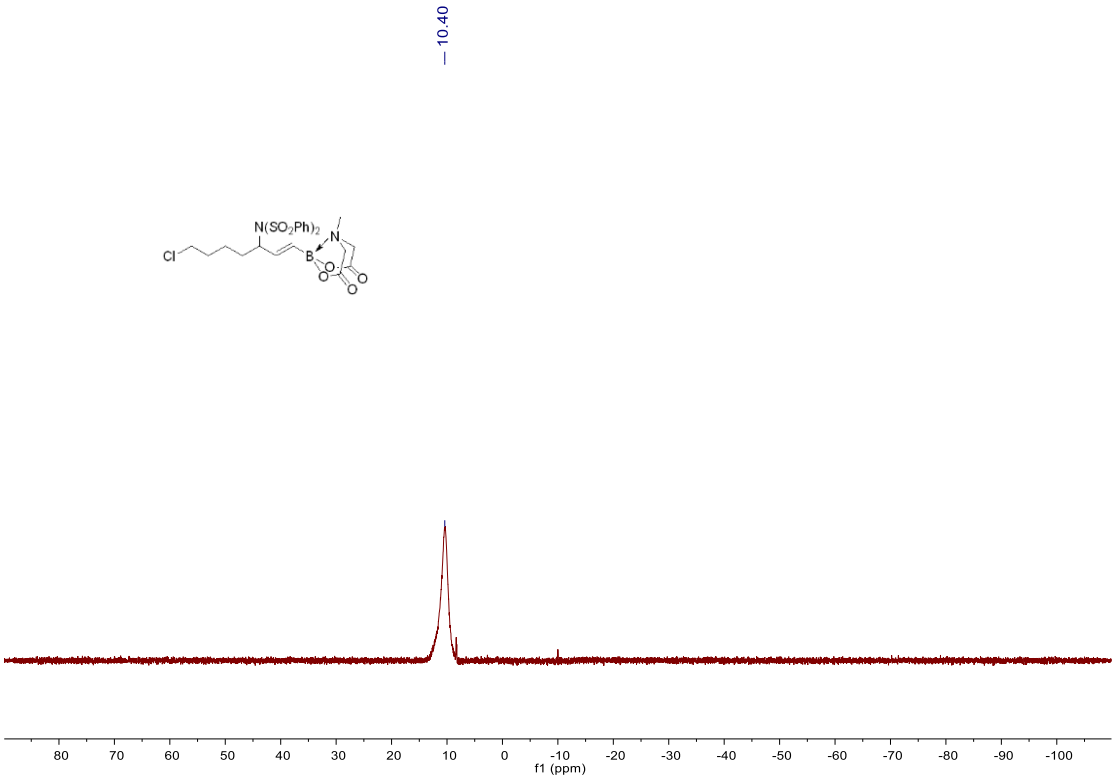

10.18
N(SO2Ph)2
BzO
B
N
O
O
O
O
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)
168.85
168.80
166.69
142.32
134.93
133.83
131.40
130.19
130.06
129.43
129.26
67.50
65.27
62.32
47.48
34.16
28.96
24.44
N(SO2Ph)2
BzO
B
N
O
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

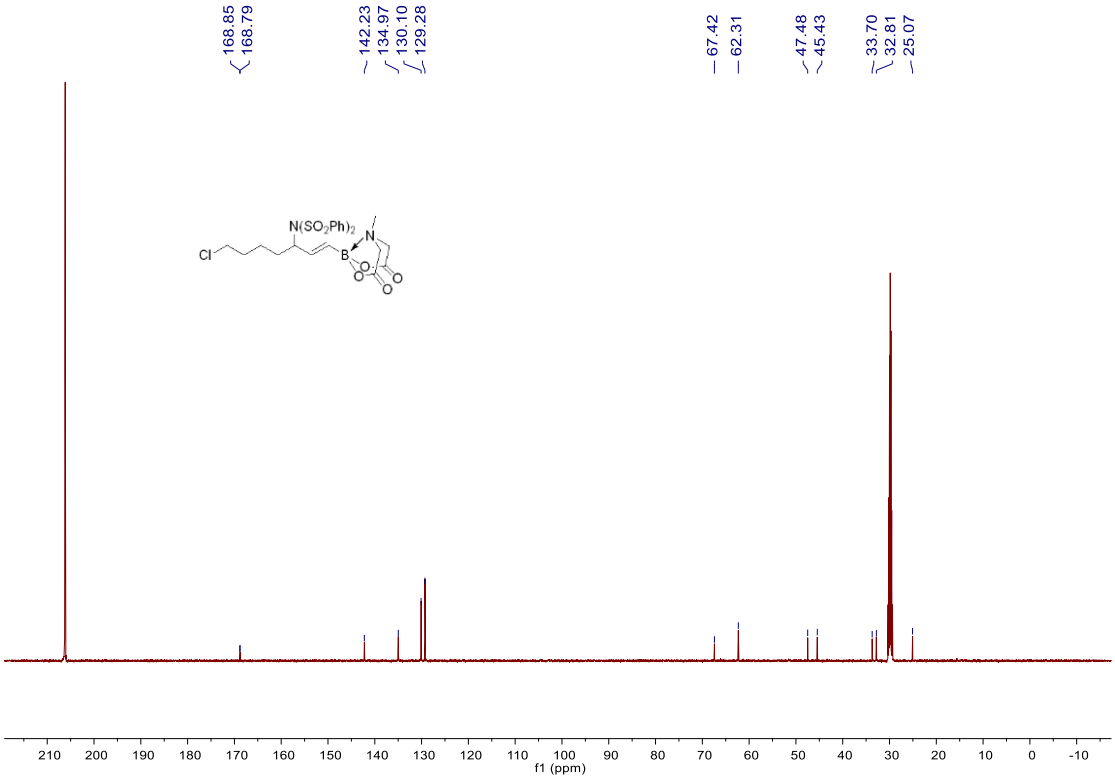

7.94
7.92
7.75
7.74
7.72
7.63
7.61
7.59
6.24
6.22
6.19
6.17
5.42
5.38
4.54
4.53
3.96
3.93
3.93
3.92
3.91
3.90
3.89
3.73
3.70
3.69
3.65
2.62
2.10
2.10
2.09
2.07
2.05
1.84
1.83
1.82
1.81
1.80
1.78
1.52
1.51
1.49
1.47
1.28
1.22
1.21
1.21
1.18
PivO
N(SO2Ph)2
B
4.03
2.01
4.09
1.00
1.05
1.00
4.15
2.05
3.02
1.26
1.24
2.08
2.10
9.15
f1 (ppm)

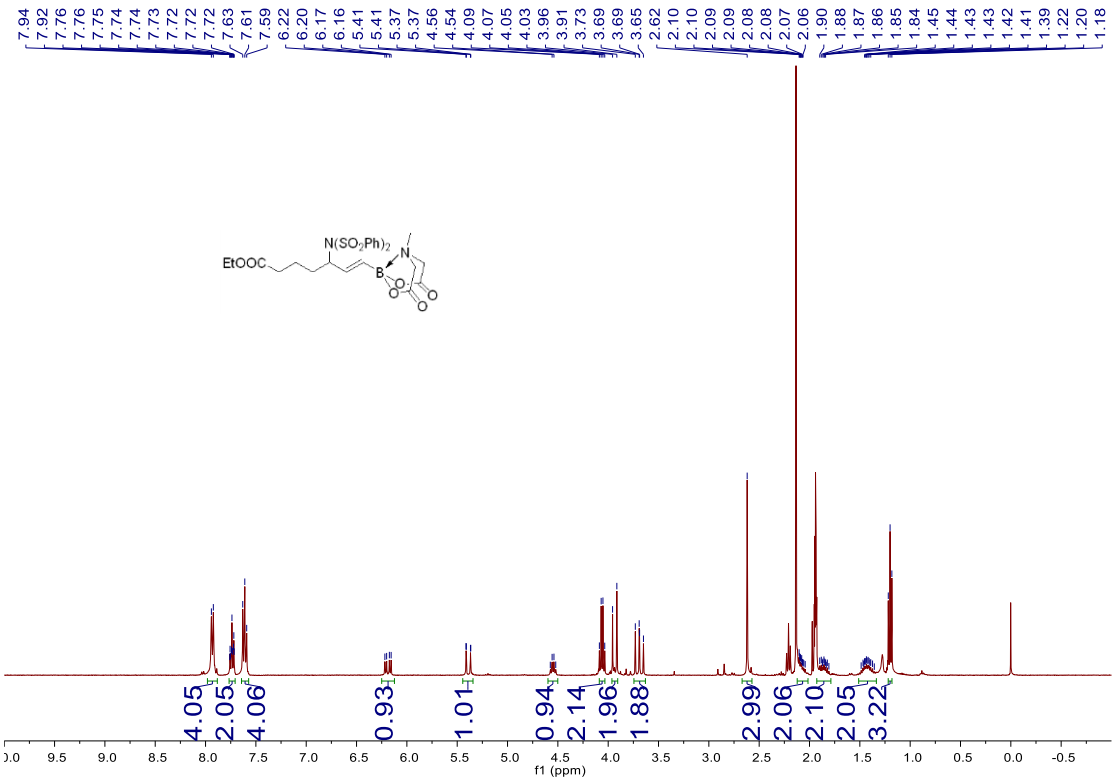

10.05
PivO
N(SO2Ph)2
B
f1 (ppm)

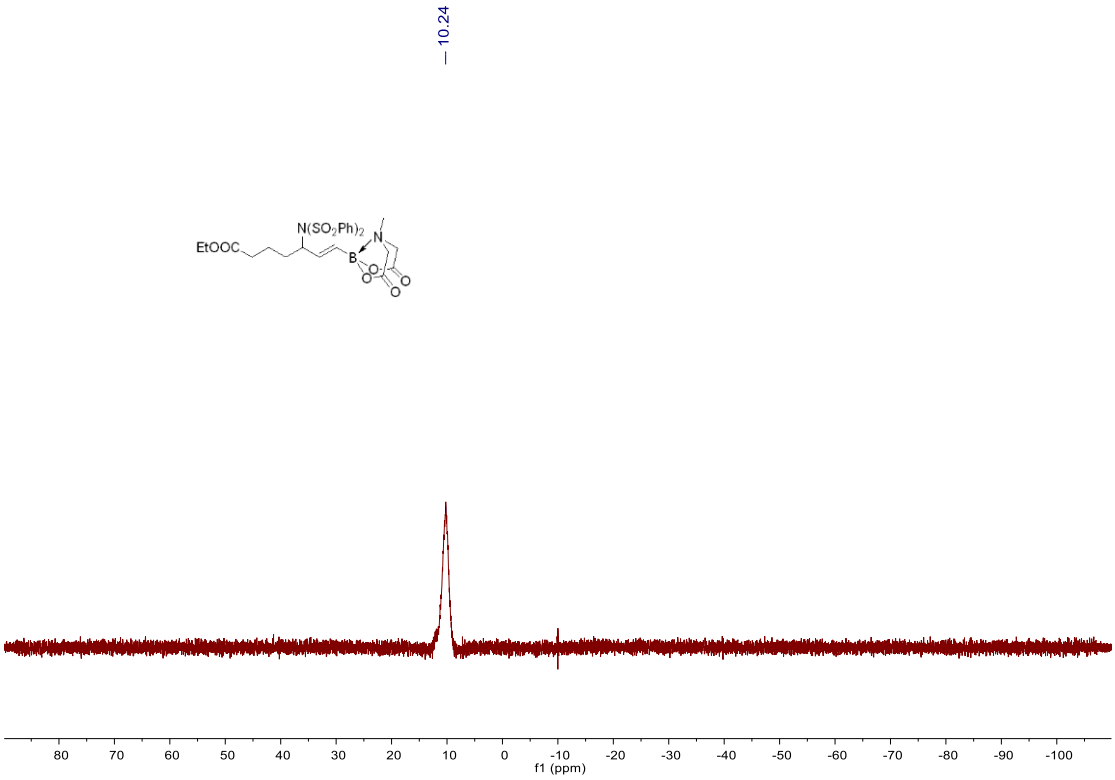

178.93
169.10
169.05
142.70
135.25
130.27
129.22
67.55
64.71
62.36
47.70
39.32
34.02
28.85
27.47
24.27
PivO
N(SO2Ph)2
B
f1 (ppm)

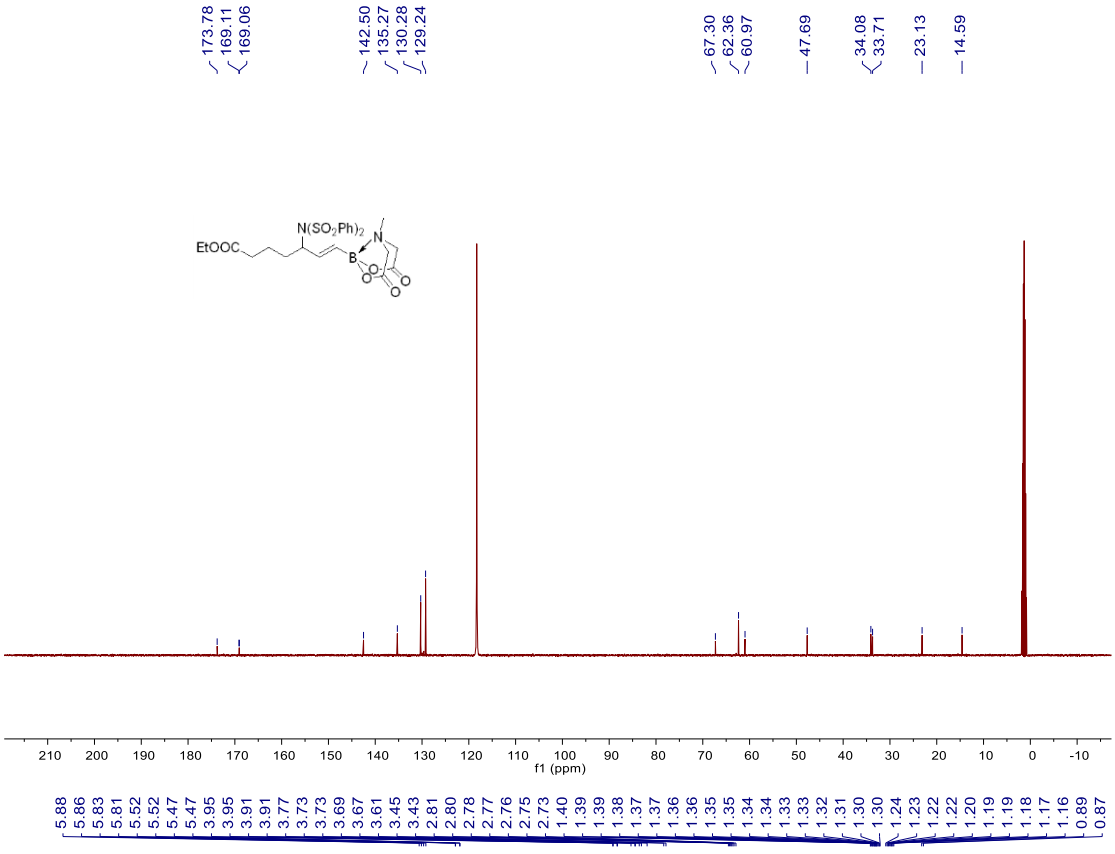

Cl
N(SO2Ph)2
B
4.04
2.06
4.01
1.00
1.03
1.03
2.09
2.10
2.00
3.11
1.15
1.14
2.02
2.22
f1 (ppm)

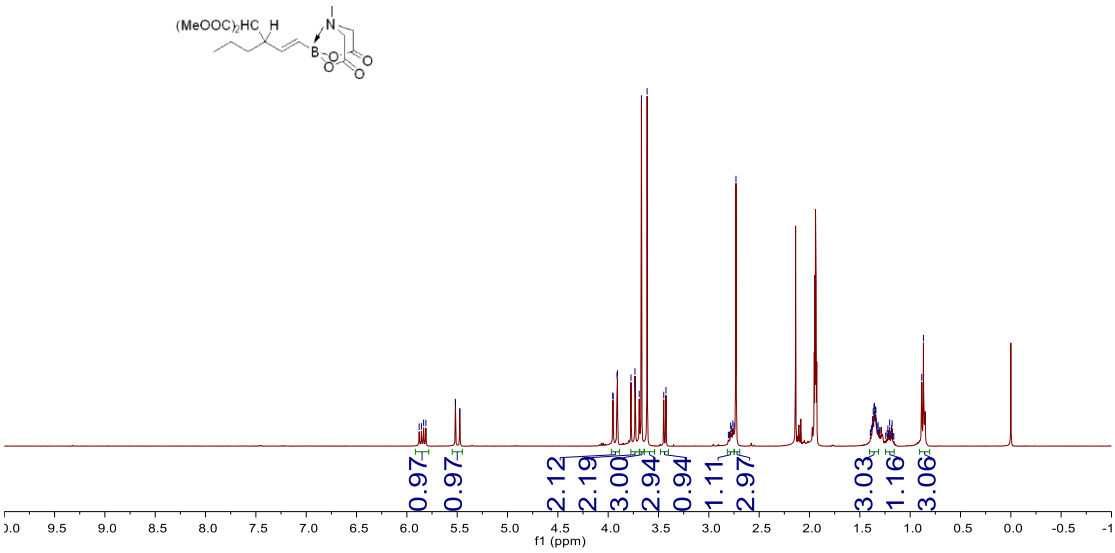

10.40
N(SO2Ph)2
Cl
B
O
O
O
N
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

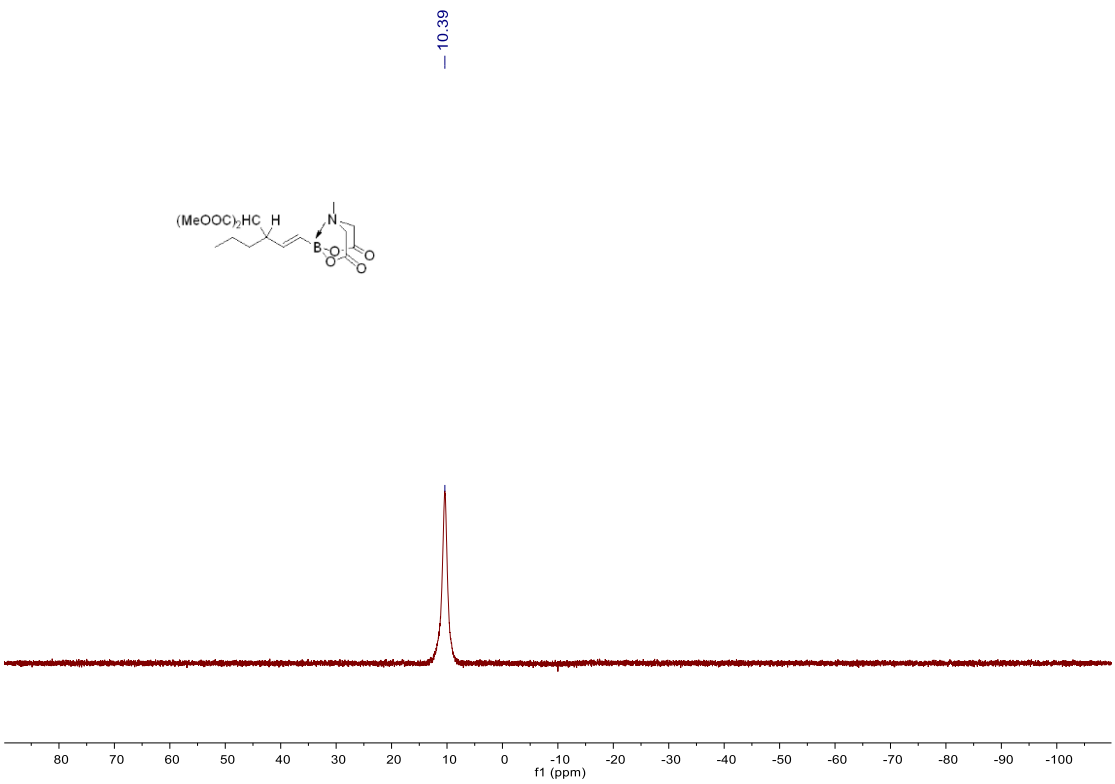

168.85
168.79
142.23
134.97
130.10
129.28
67.42
62.31
47.48
45.43
33.70
32.81
25.07
N(SO2Ph)2
Cl
B
O
O
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

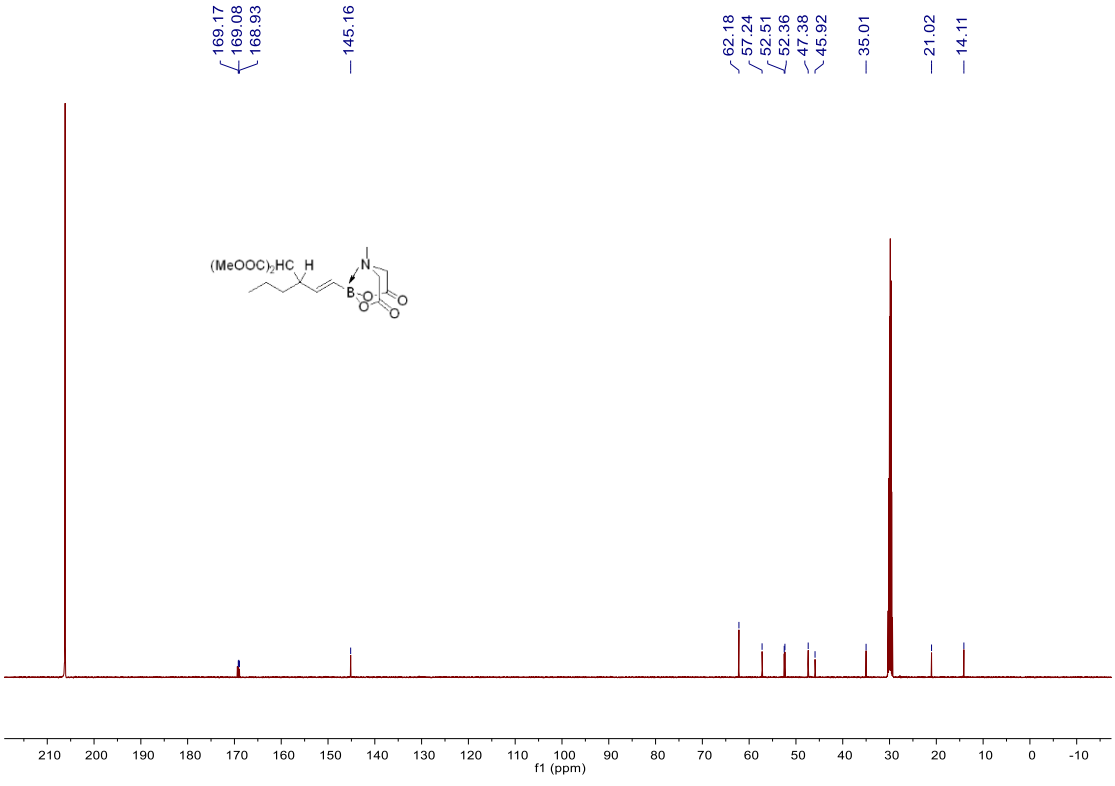

7.94 7.92 7.76 7.76 7.75 7.74 7.74 7.73 7.72 7.72 7.72 7.63 7.61 7.59
6.22 6.20 6.17 6.16 5.41 5.41 5.37 5.37 4.56 4.54 4.09 4.07 4.05 4.03 3.96 3.91 3.73 3.69 3.69 3.65
2.62 2.10 2.10 2.09 2.09 2.08 2.08 2.07 2.06 1.90 1.88 1.87 1.86 1.85 1.84 1.45 1.44 1.43 1.43 1.42 1.41 1.39 1.22 1.20 1.18
N(SO2Ph)2
EtOOC
B
O
O
O
4.05 2.05 4.06 0.93 1.01 0.94 2.14 1.96 1.88 2.99 2.06 2.10 2.05 3.22
f1 (ppm)

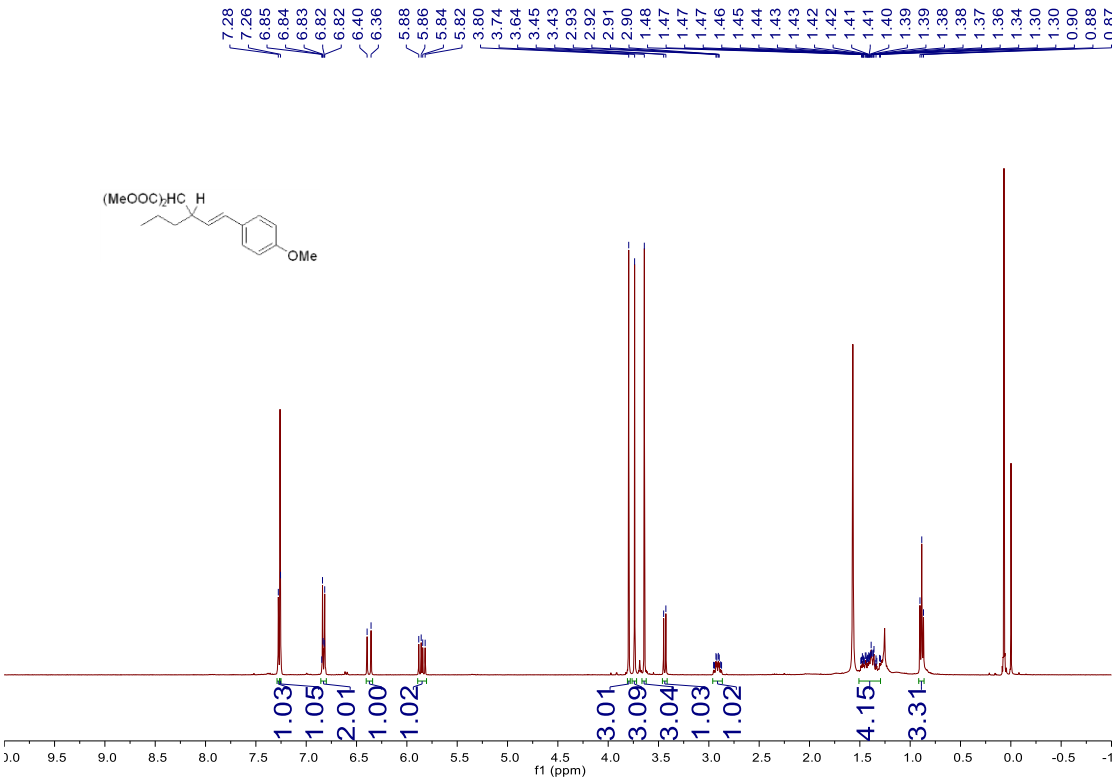

10.24
N(SO2Ph)2
EtOOC
B
O
O
O
f1 (ppm)

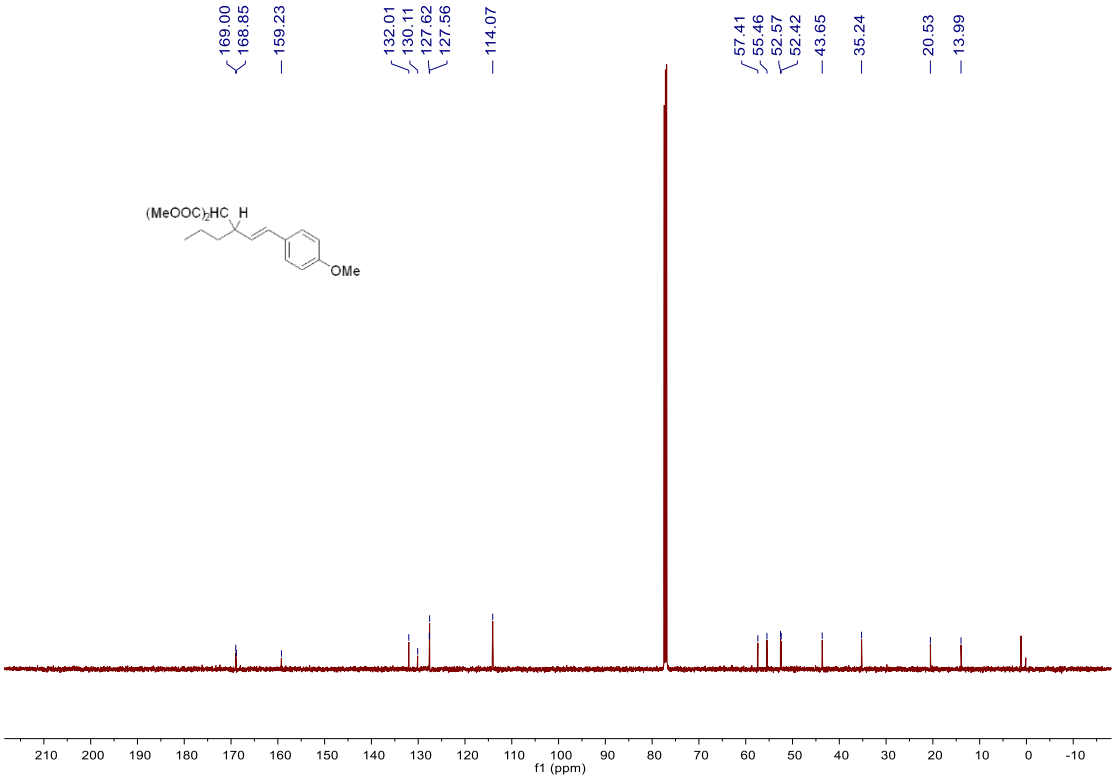

173.78
169.11
169.06
142.50
135.27
130.28
129.24
67.30
62.36
60.97
47.69
34.08
33.71
23.13
14.59
EtOOC
N(SO2Ph)2
f1 (ppm)


(MeOOC)2HC
H
0.97
0.97
2.12
2.19
3.00
2.94
0.94
1.11
2.97
3.03
1.16
3.06
f1 (ppm)


10.39
(MeOOC)2HC
H
N
B
O
O
O
O
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)


169.17
169.08
168.93
145.16
62.18
57.24
52.51
52.36
47.38
45.92
35.01
21.02
14.11
(MeOOC)2HC
H
N
B
O
O
O
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)


7.28 7.26 6.85 6.84 6.83 6.82 6.82 6.40 6.36 5.88 5.86 5.84 5.82 3.80 3.74 3.64 3.45 3.43 2.93 2.92 2.91 2.90 1.48 1.47 1.47 1.47 1.46 1.45 1.44 1.43 1.43 1.42 1.42 1.41 1.41 1.40 1.39 1.39 1.38 1.38 1.37 1.36 1.34 1.30 1.30 0.90 0.88
(MeOOC)2HC H
OMe
1.03 1.05 2.01 1.00 1.02 3.01 3.09 3.04 1.03 1.02 4.15 3.31
f1 (ppm)


169.00 168.85 159.23 132.01 130.11 127.62 127.56 114.07 57.41 55.46 52.57 52.42 43.65 35.24 20.53 13.99
(MeOOC)2HC H
OMe
f1 (ppm)


8.33
8.33
8.33
8.32
8.31
8.31
8.20
8.18
8.17
8.16
8.16
8.16
8.12
8.12
8.11
8.11
8.10
8.10
8.09
8.08
8.08
8.07
6.31
6.29
6.27
6.25
6.15
6.10
4.67
4.67
4.63
4.62
4.44
4.40
4.32
4.28
4.27
4.26
4.25
4.25
4.24
4.23
4.22
3.20
2.43
2.42
2.41
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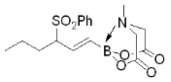
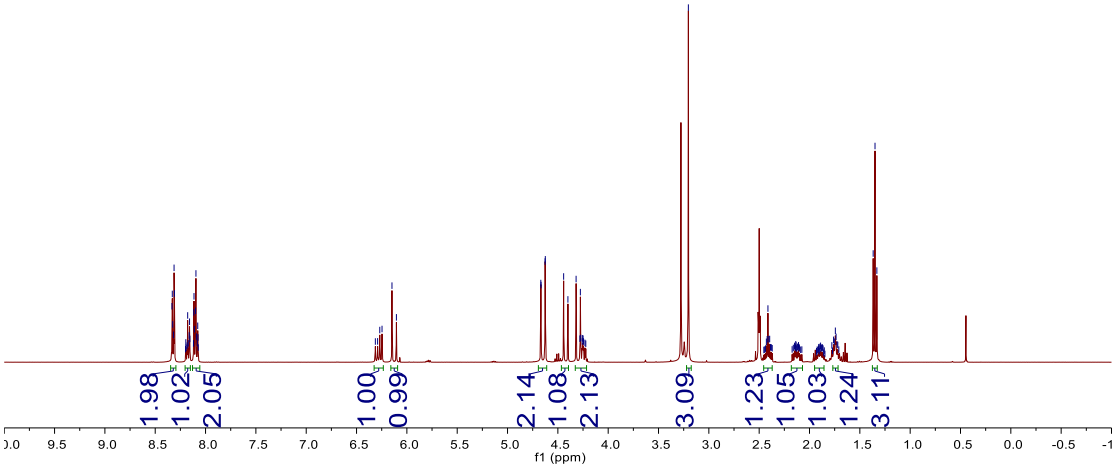
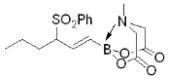
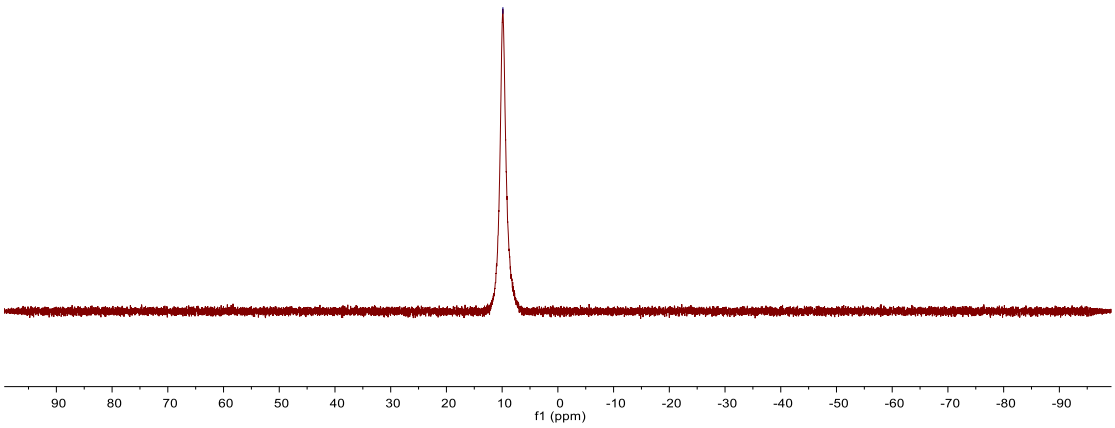
2.40
2.14
1.76
1.75
1.74
1.74
1.73
1.37
1.35
1.33

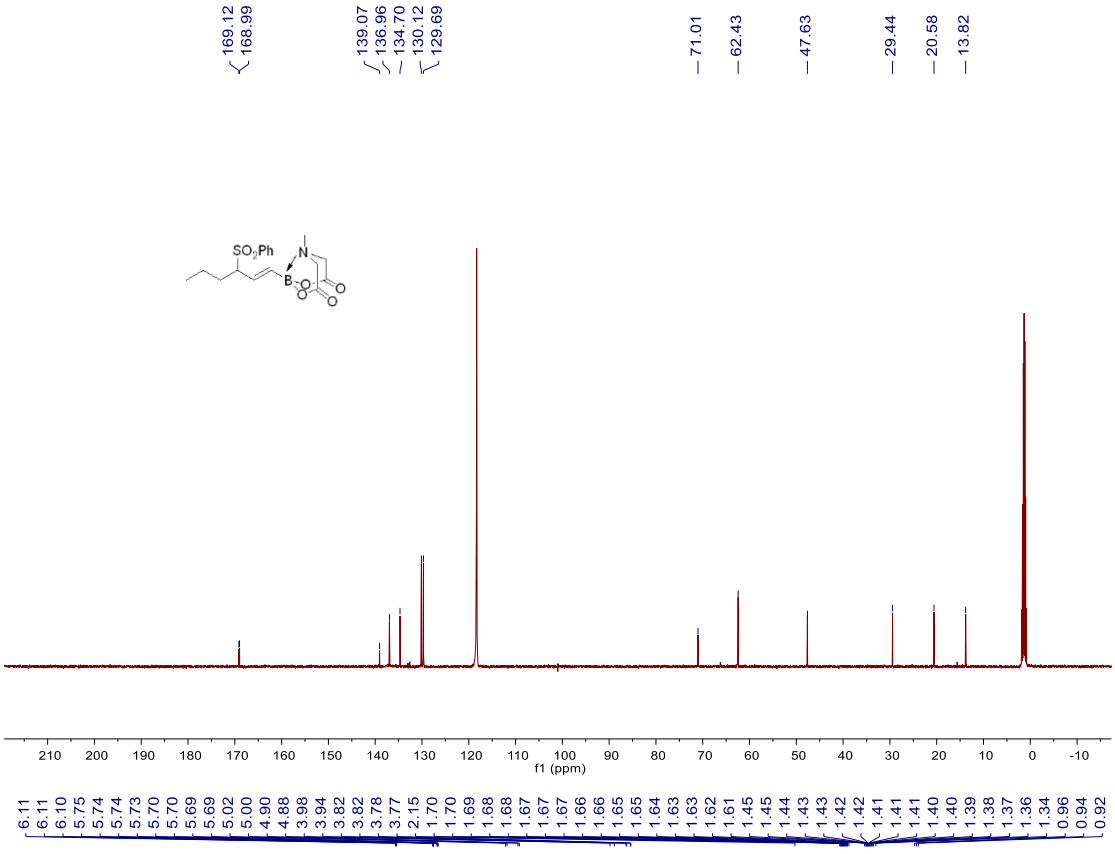

SO2Ph
N
B
O
O
O
O

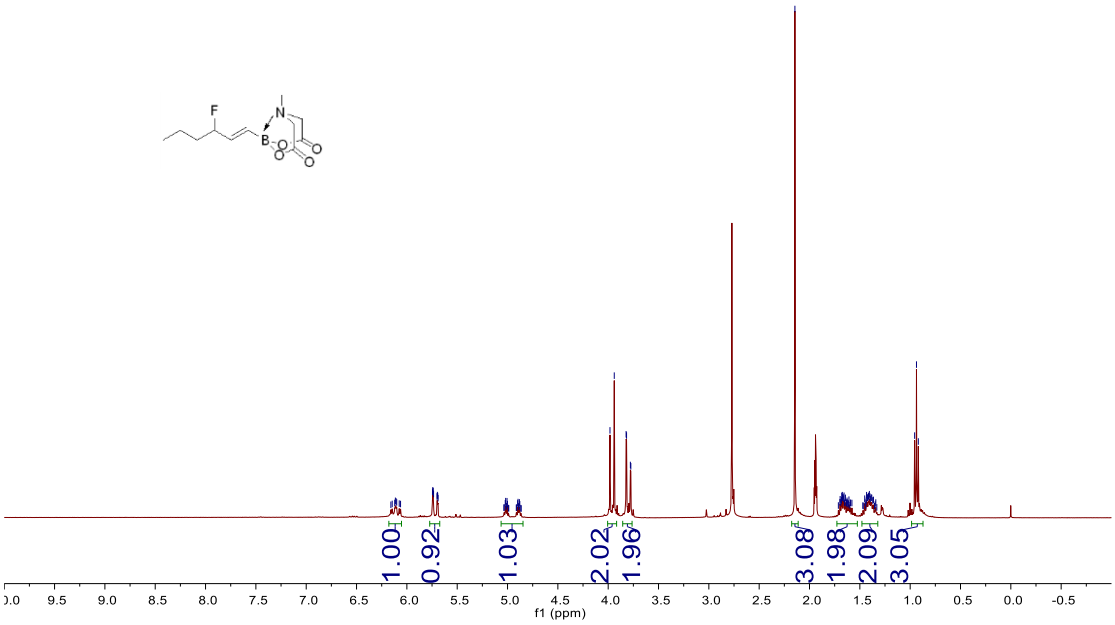

1.98
1.02
2.05
1.00
0.99
2.14
1.08
2.13
3.09
1.23
1.05
1.03
1.24
3.11
f1 (ppm)

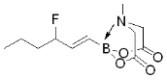

9.86

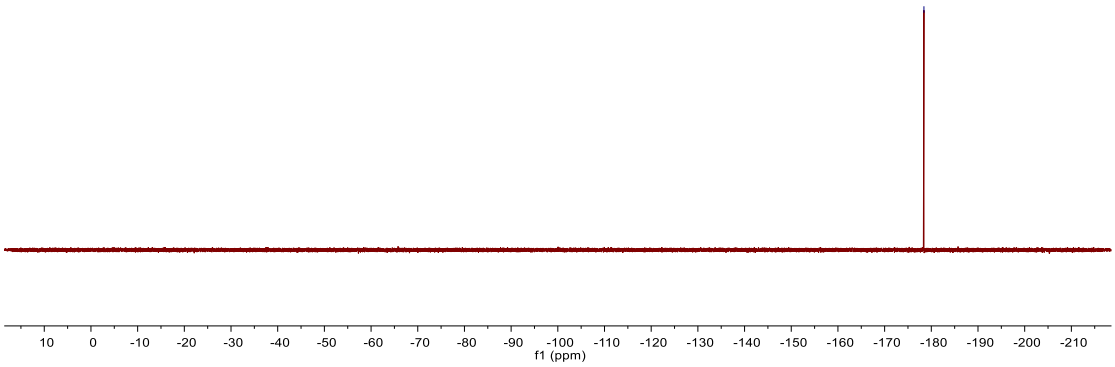

SO2Ph
N
B
O
O
O
O


f1 (ppm)


169.12
168.99
139.07
136.96
134.70
130.12
129.69
71.01
62.43
47.63
29.44
20.58
13.82
SO2Ph
N
B
O
O
O
O
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)
6.11 6.11 6.10 5.75 5.74 5.74 5.73 5.70 5.70 5.69 5.69 5.02 5.00 4.90 4.88 3.98 3.94 3.82 3.82 3.78 3.77 2.15 1.70 1.70 1.69 1.68 1.68 1.67 1.67 1.67 1.66 1.66 1.65 1.65 1.64 1.63 1.63 1.62 1.61 1.45 1.45 1.44 1.43 1.43 1.42 1.42 1.41 1.41 1.41 1.40 1.40 1.39 1.38 1.37 1.36 1.34 0.96 0.94 0.92


F
N
B
O
O
O
1.00
0.92
1.03
2.02
1.96
3.08
1.98
2.09
3.05
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
N
B
O
O
O


-178.42
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
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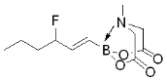
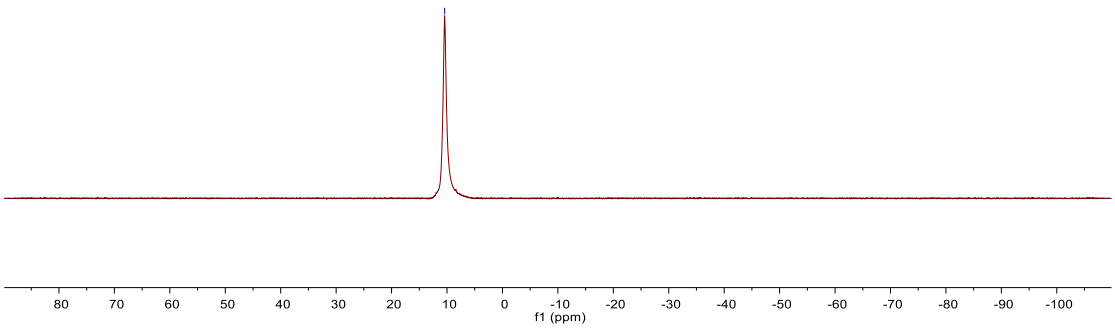
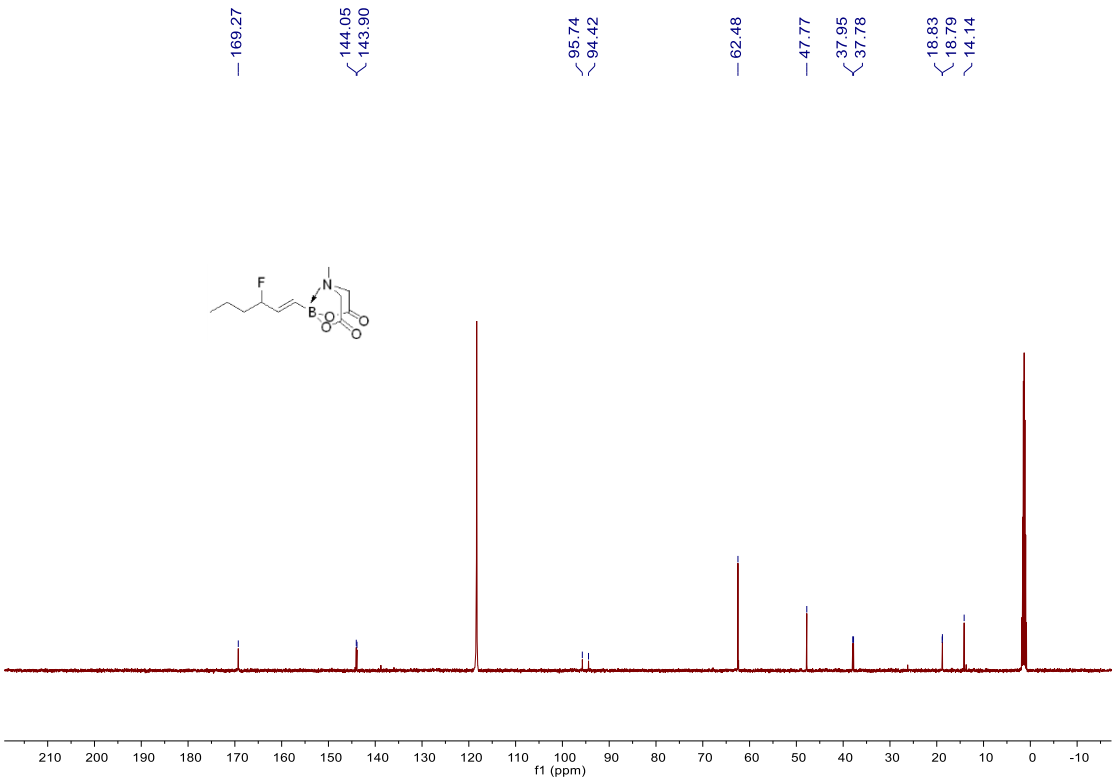
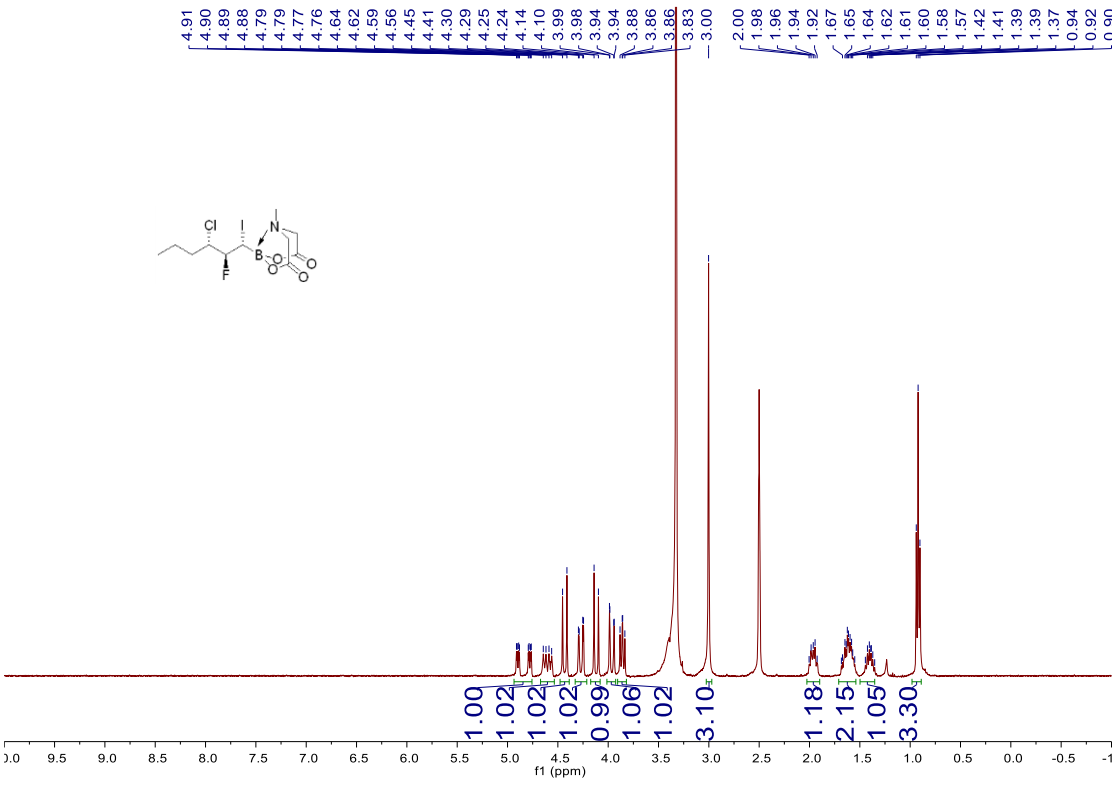
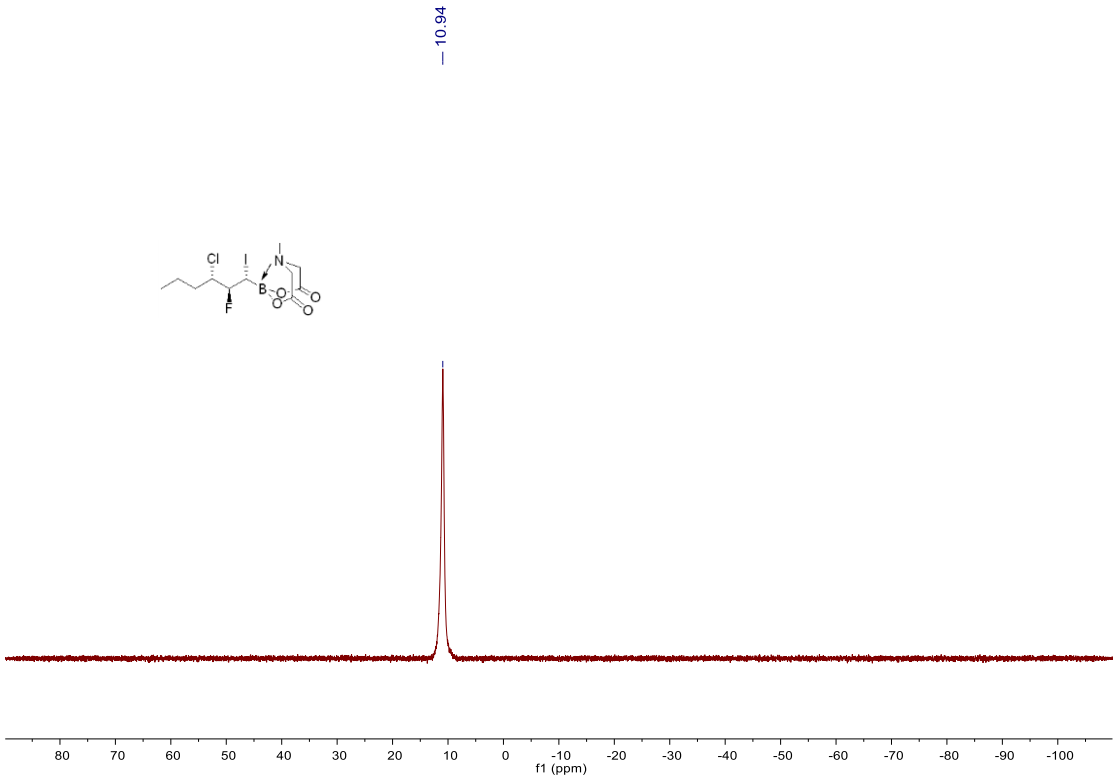
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

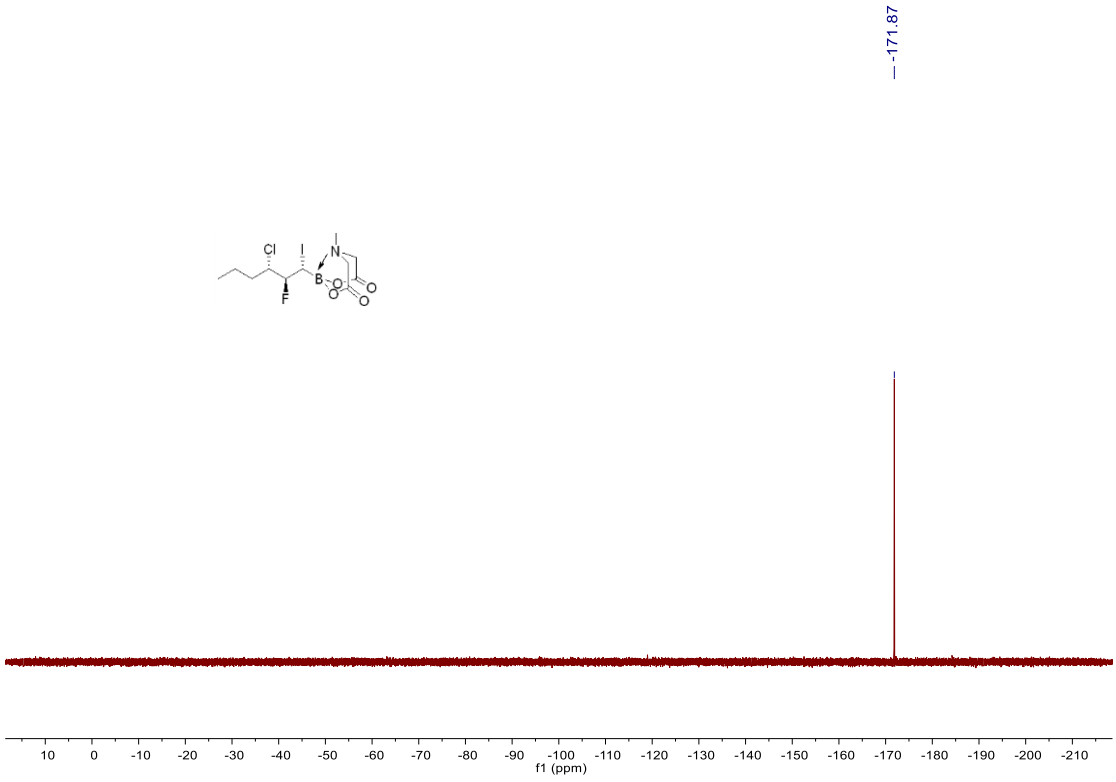

F
N
B
O
O
O

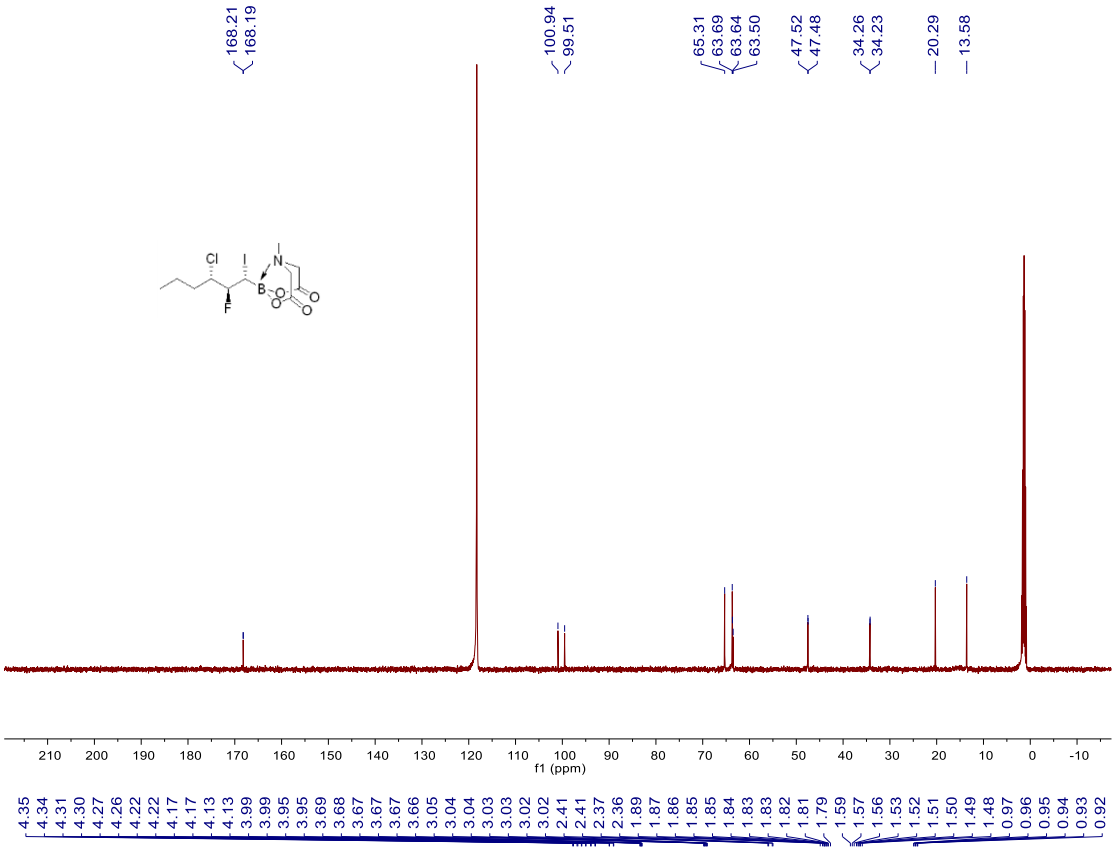

10.42
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)

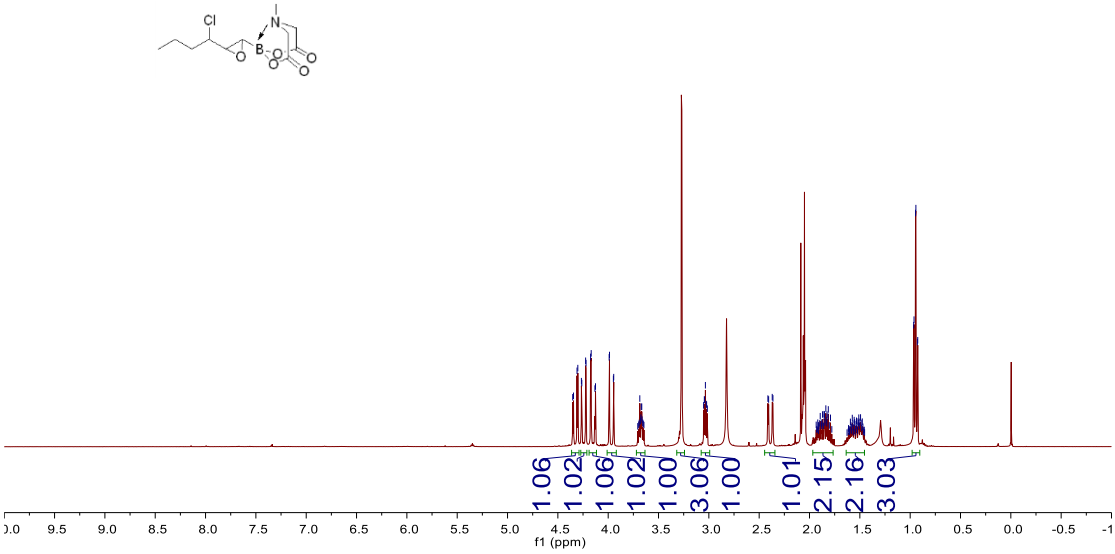

169.27
144.05
143.90
95.74
94.42
62.48
47.77
37.95
37.78
18.83
18.79
14.14
F
N
B
O
O
O
f1 (ppm)

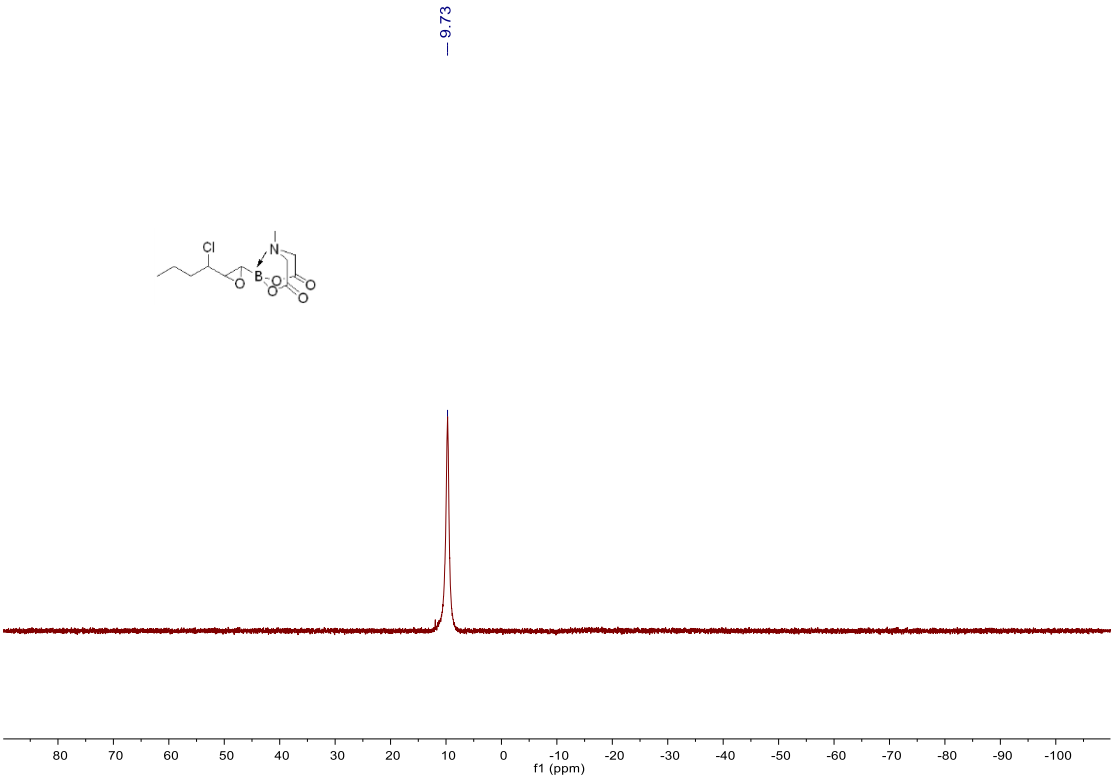

4.91
4.90
4.89
4.88
4.79
4.79
4.77
4.76
4.64
4.62
4.59
4.56
4.45
4.41
4.30
4.29
4.25
4.24
4.14
4.10
3.99
3.98
3.94
3.94
3.88
3.86
3.86
3.83
3.00
2.00
1.98
1.96
1.94
1.92
1.67
1.65
1.64
1.62
1.61
1.60
1.58
1.57
1.42
1.41
1.39
1.39
1.37
0.94
0.92
Cl
I
F
N
B
O
O
O
1.00
1.02
1.02
1.02
0.99
1.06
1.02
3.10
1.18
2.15
1.05
3.30
f1 (ppm)

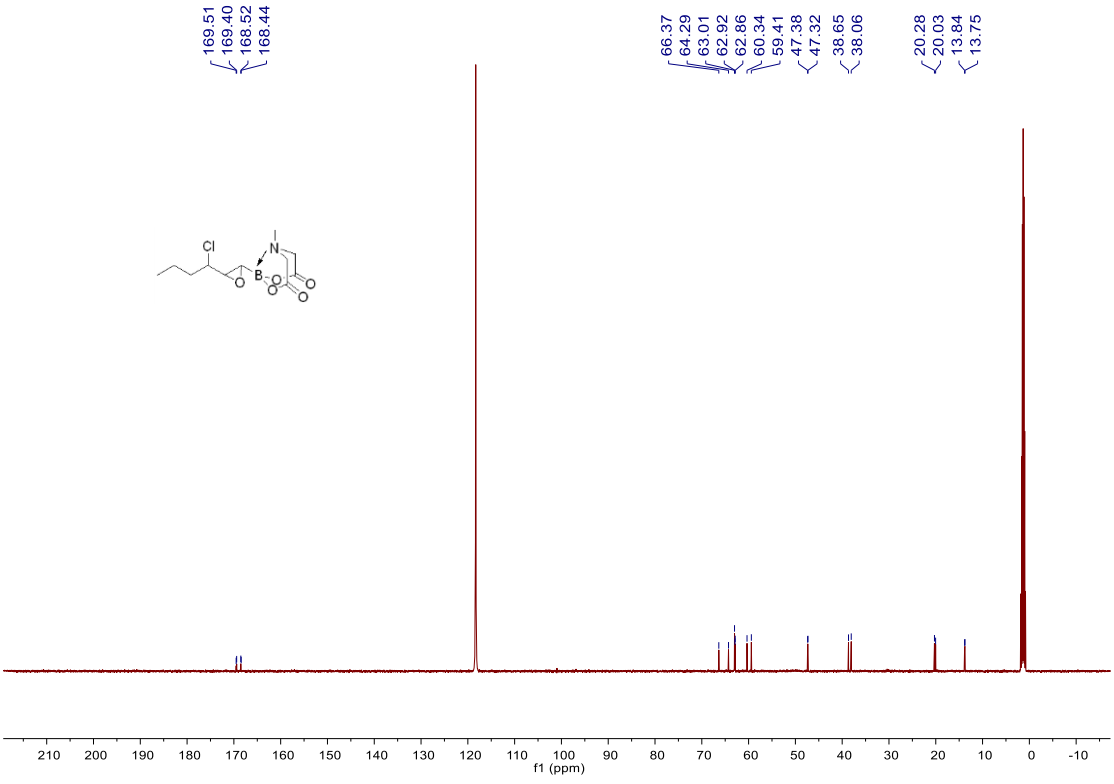

10.94
Cl
I
N
B
O
O
O
O
F
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)

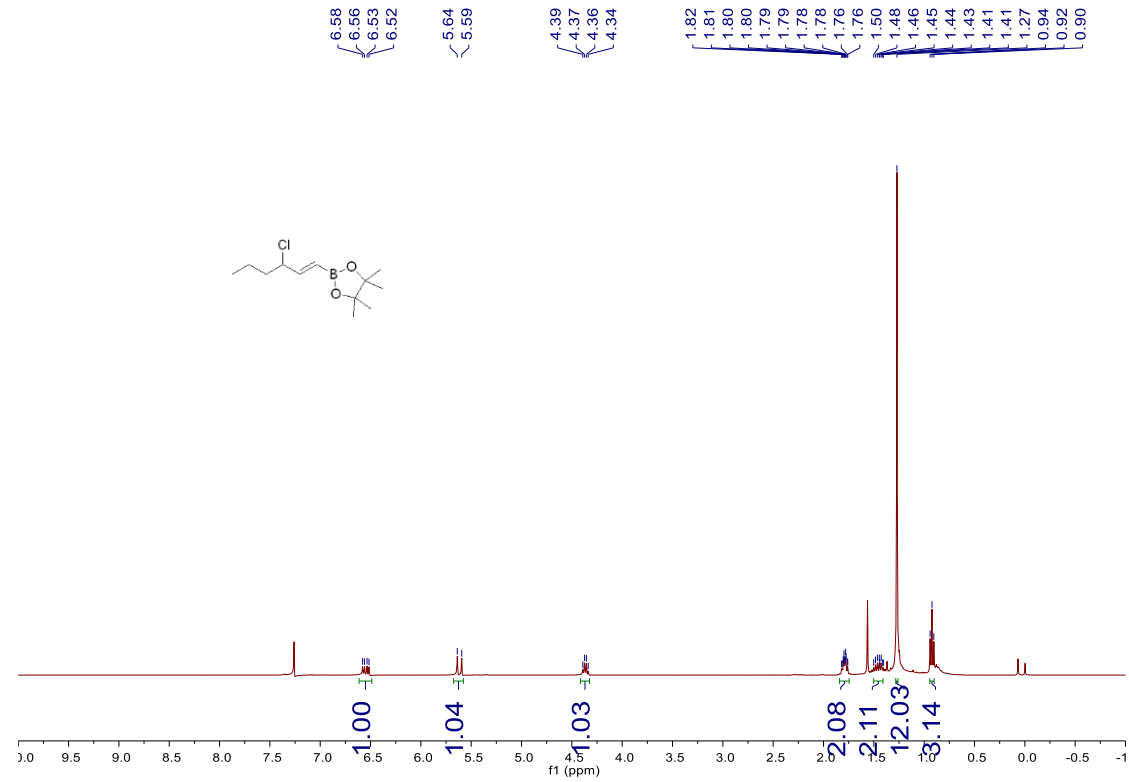

-171.87
Cl
I
N
B
O
O
O
O
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

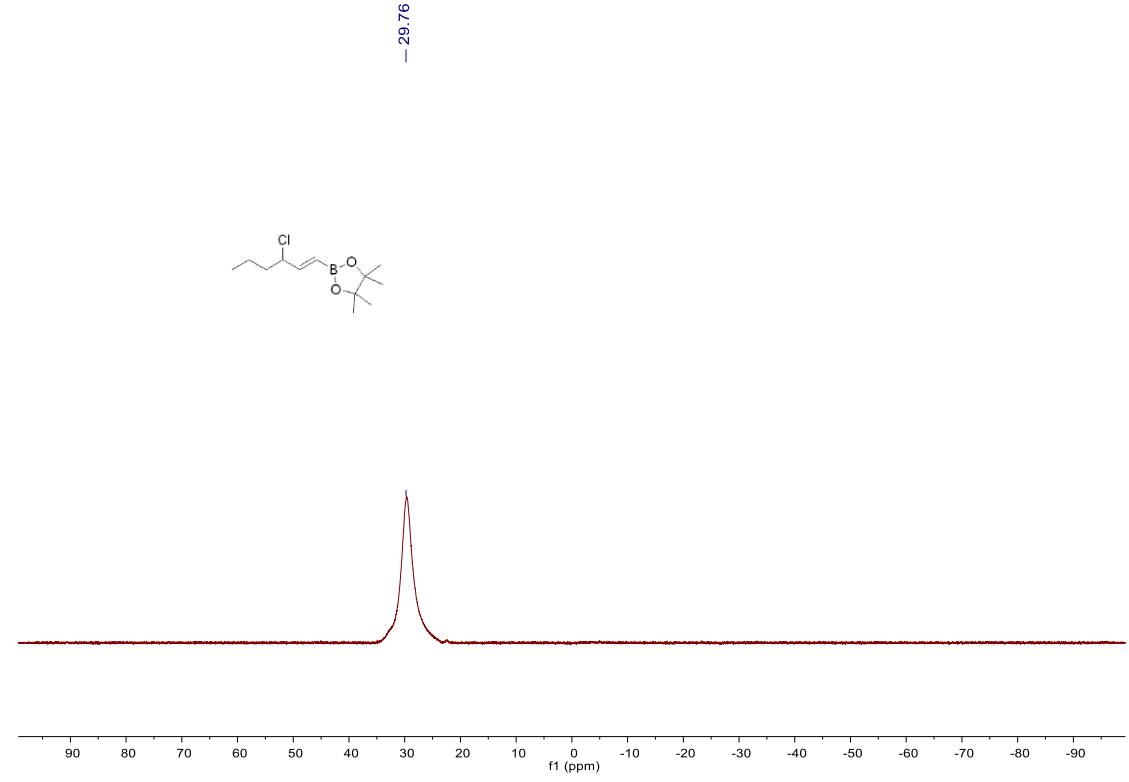

168.21
168.19
100.94
99.51
65.31
63.69
63.64
63.50
47.52
47.48
34.26
34.23
20.29
13.58
Cl
I
F
N
B
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
4.35 4.34 4.31 4.30 4.27 4.26 4.22 4.22 4.17 4.17 4.13 4.13 3.99 3.99 3.95 3.95 3.69 3.68 3.67 3.67 3.67 3.66 3.05 3.04 3.04 3.03 3.03 3.03 3.02 3.02 2.41 2.41 2.37 2.36 1.89 1.87 1.86 1.85 1.85 1.84 1.83 1.83 1.82 1.81 1.79 1.59 1.57 1.56 1.53 1.52 1.51 1.50 1.49 1.48 0.97 0.96 0.95 0.94 0.93 0.92

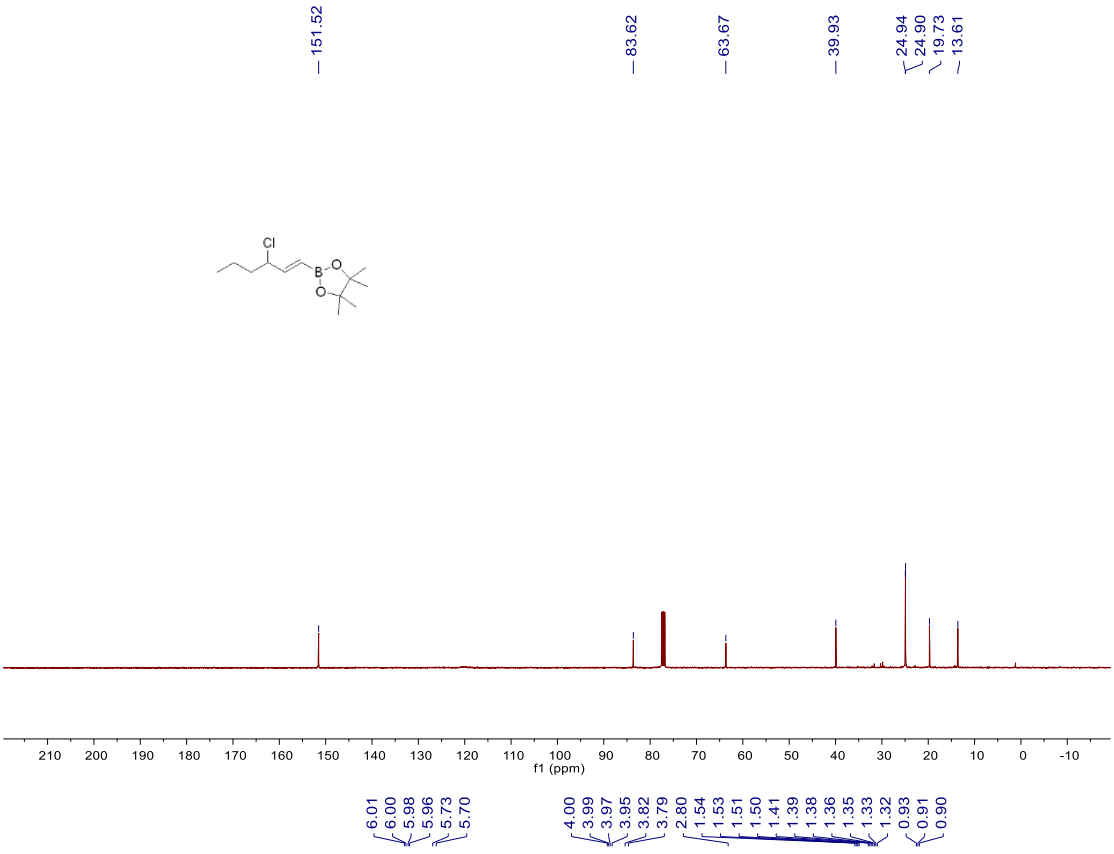

Cl
N
B
O
O
O
1.06 1.02 1.06 1.02 1.00 3.06 1.00 1.01 2.15 2.16 3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

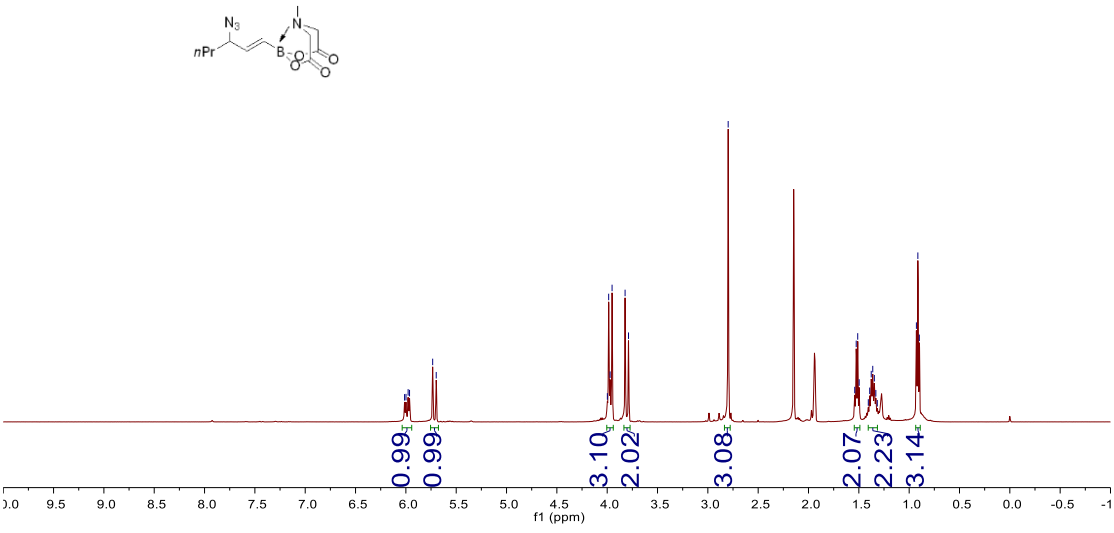

9.73
Cl
N
B
O
f1 (ppm)

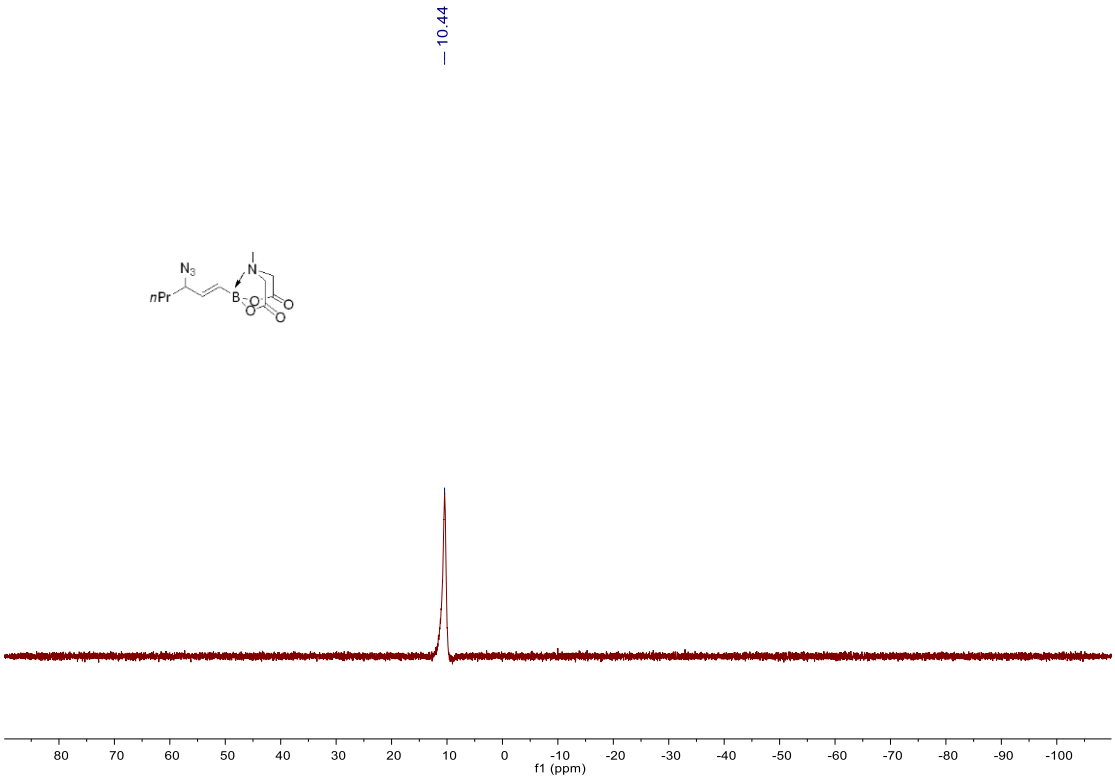

169.51
169.40
168.52
168.44
66.37
64.29
63.01
62.92
62.86
60.34
59.41
47.38
47.32
38.65
38.06
20.28
20.03
13.84
13.75
Cl
N
B
O
f1 (ppm)

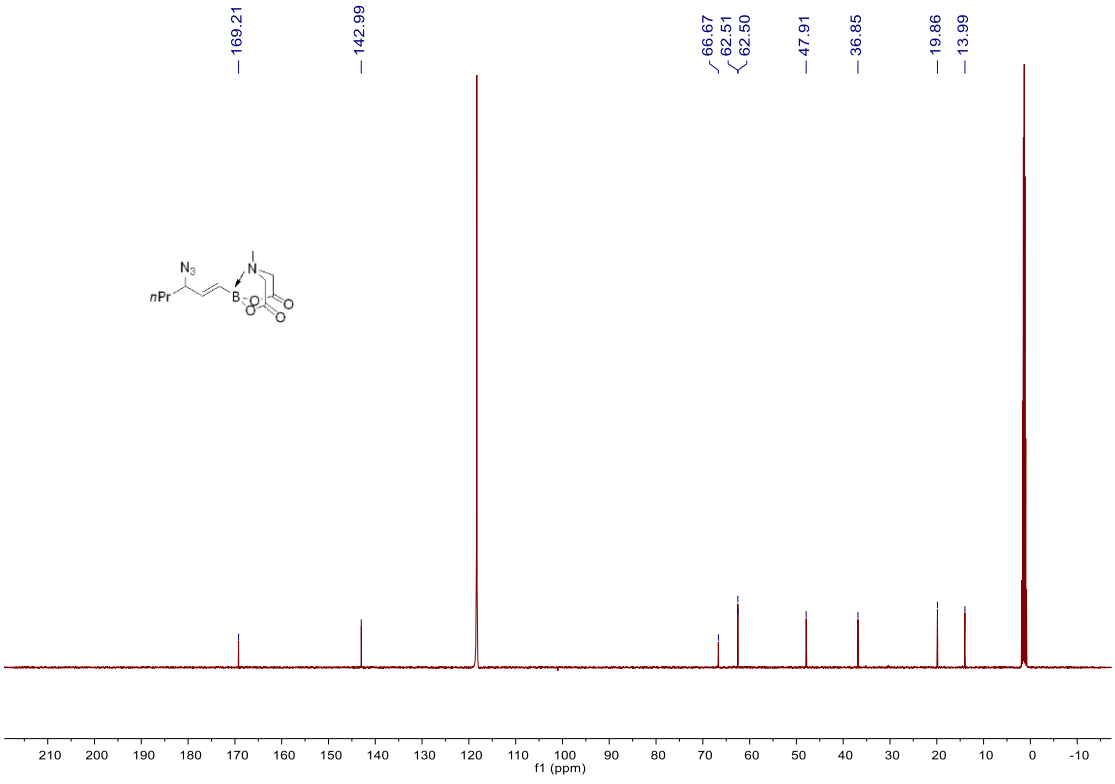

6.58
6.56
6.53
6.52
5.64
5.59
4.39
4.37
4.36
4.34
1.82
1.81
1.80
1.80
1.79
1.79
1.78
1.78
1.76
1.76
1.50
1.48
1.46
1.45
1.44
1.43
1.41
1.41
1.27
0.94
0.92
0.90
Cl
B
O
O
1.00
1.04
1.03
2.08
2.11
12.03
3.14
f1 (ppm)

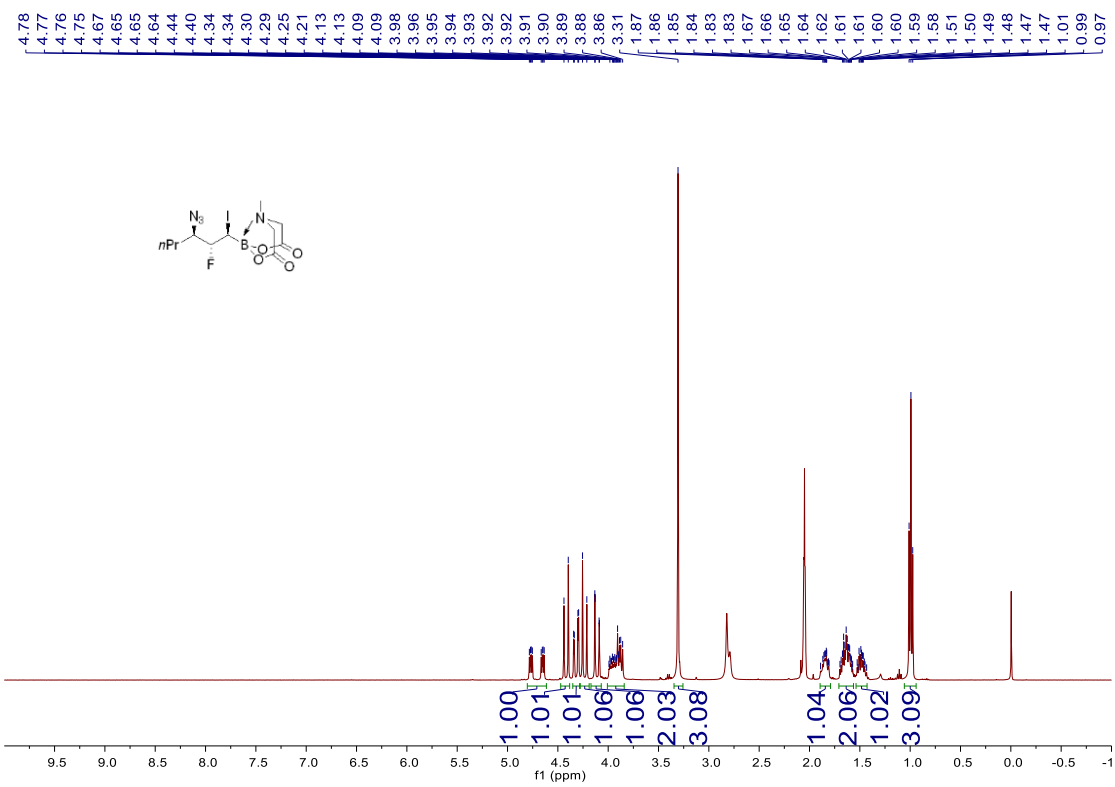

29.76
Cl
B
O
O
f1 (ppm)

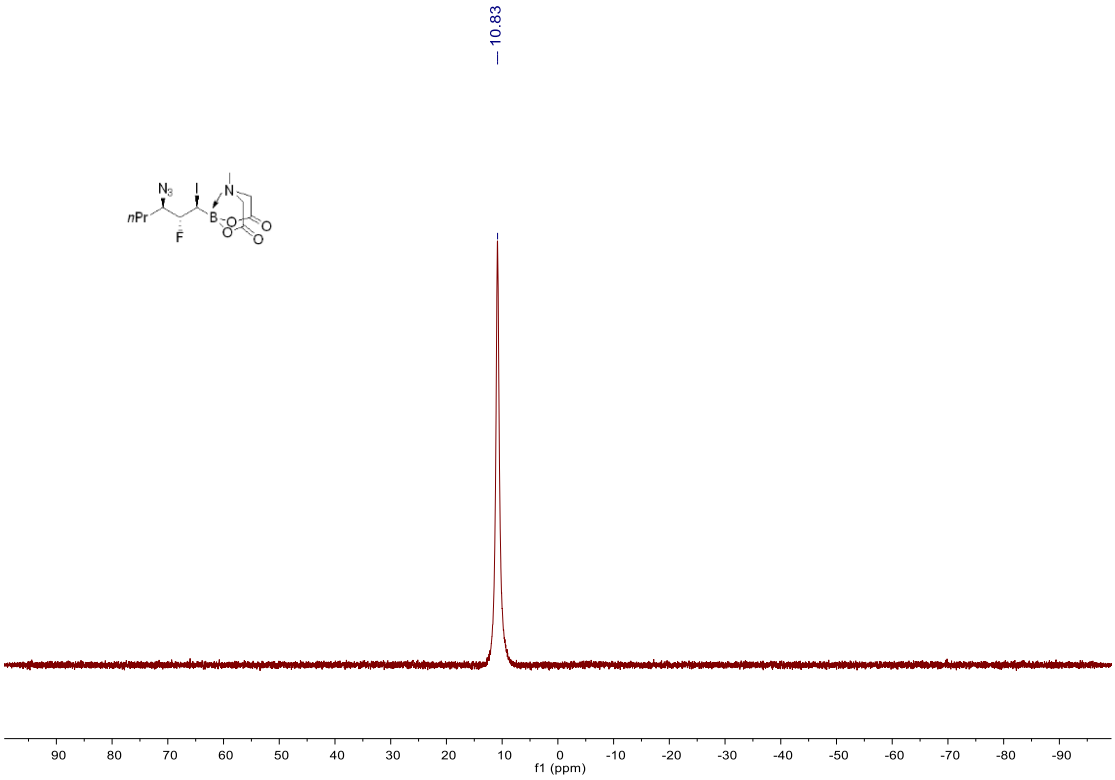

151.52
83.62
63.67
39.93
24.94
24.90
19.73
13.61
Cl
B
O
O
f1 (ppm)
6.01
6.00
5.98
5.96
5.73
5.70
4.00
3.99
3.97
3.95
3.82
3.79
2.80
1.54
1.53
1.51
1.50
1.41
1.39
1.38
1.36
1.35
1.33
1.32
0.93
0.91
0.90

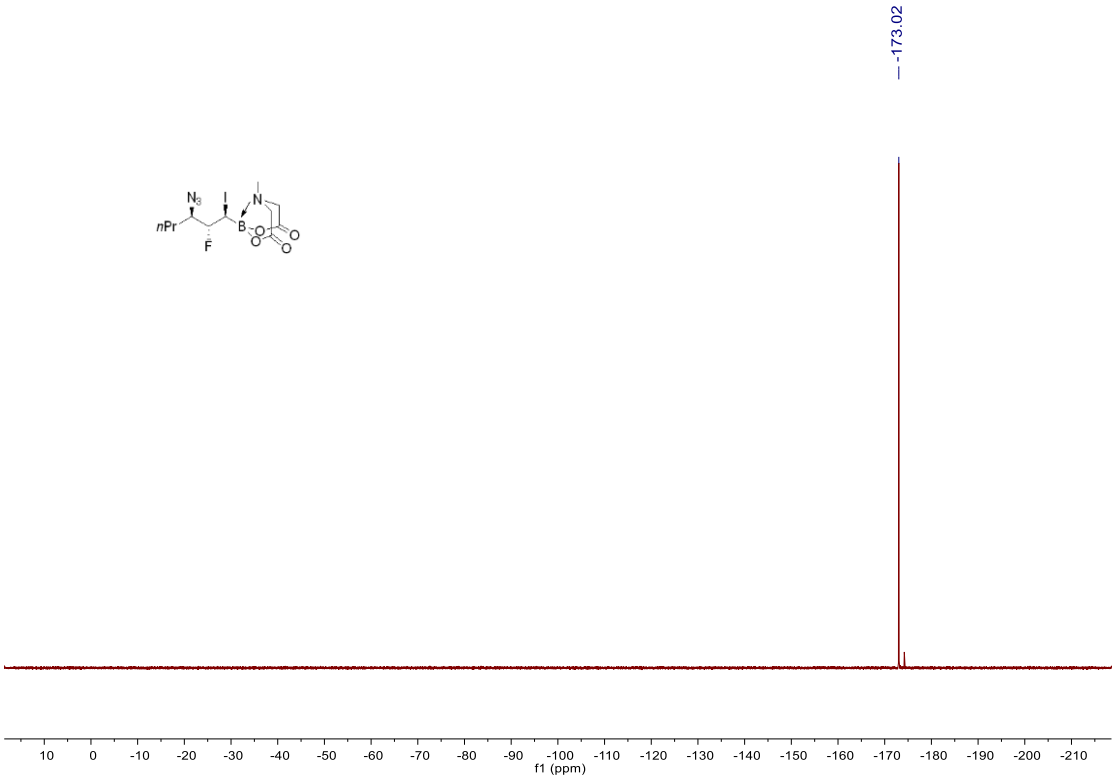

N3
nPr
B
N
O
O
O
f1 (ppm)
0.99
0.99
3.10
2.02
3.08
2.07
2.23
3.14

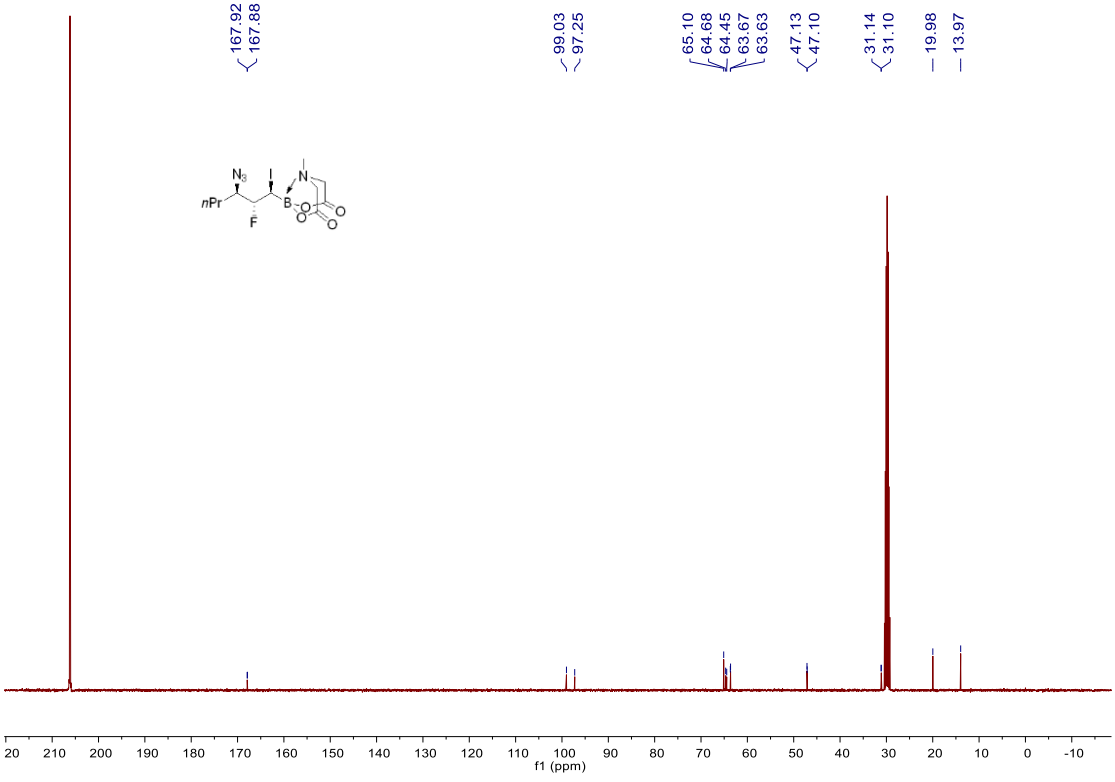

10.44
N3
nPr
B
O
O
O
N
80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100
f1 (ppm)

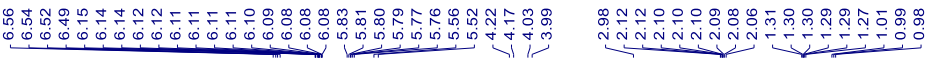

169.21
142.99
66.67
62.51
62.50
47.91
36.85
19.86
13.99
N3
nPr
B
O
O
O
N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


4.78 4.77 4.76 4.75 4.67 4.65 4.65 4.64 4.44 4.40 4.34 4.34 4.30 4.29 4.25 4.21 4.13 4.13 4.09 4.09 3.98 3.96 3.95 3.94 3.93 3.92 3.92 3.91 3.90 3.89 3.88 3.86 3.31 1.87 1.86 1.85 1.84 1.83 1.83 1.67 1.66 1.65 1.64 1.62 1.61 1.61 1.60 1.60 1.59 1.58 1.51 1.50 1.49 1.48 1.47 1.47 1.01 0.99 0.97
nPr
F
1.00 1.01 1.01 1.06 1.06 2.03 3.08 1.04 2.06 1.02 3.09
f1 (ppm)


10.83
nPr
F
f1 (ppm)


-173.02
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)


167.92
167.88
99.03
97.25
65.10
64.68
64.45
63.67
63.63
47.13
47.10
31.14
31.10
19.98
13.97
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)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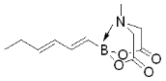
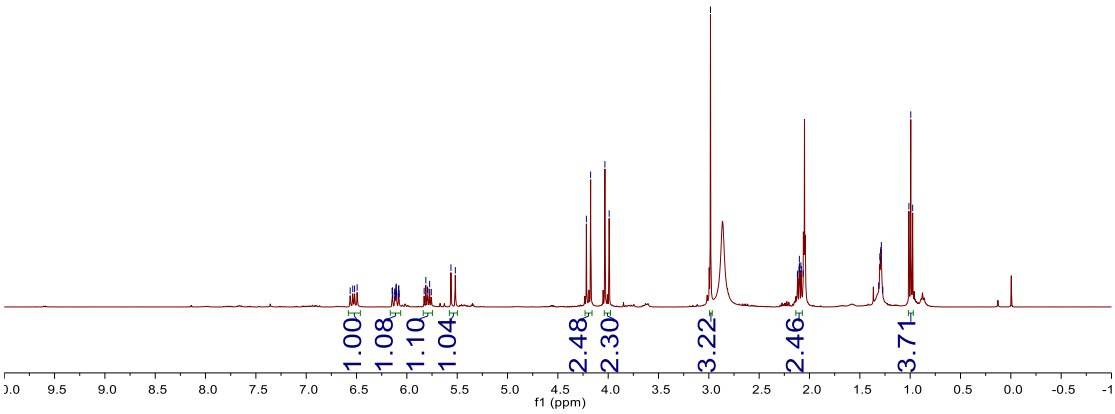
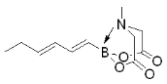
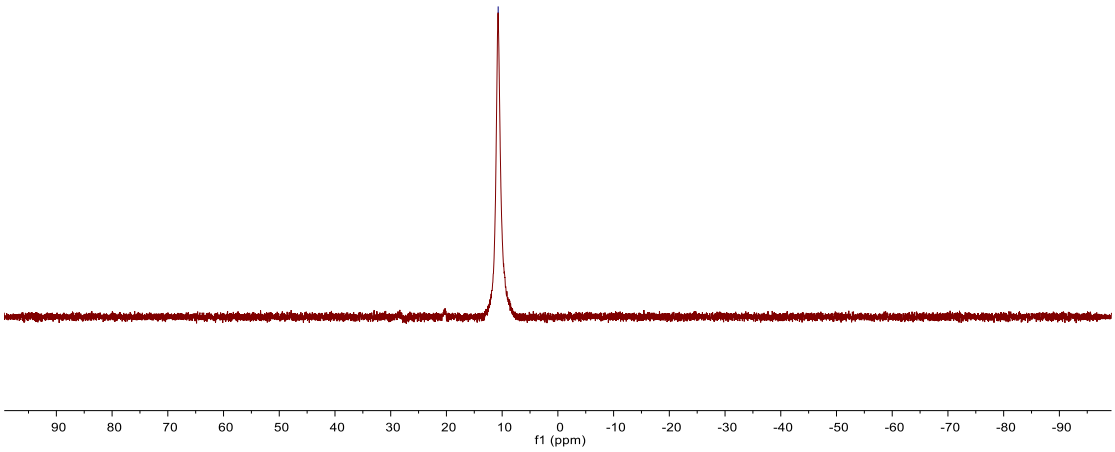
6.54
6.52
6.49
6.15
6.14
6.14
6.12
6.12
6.11
6.11
6.11
6.11
6.10
6.09
6.08
6.08
6.08
5.83
5.81
5.80
5.79
5.77
5.76
5.56
5.52
4.22
4.17
4.03
3.99
2.98
2.12
2.12
2.10
2.10
2.10
2.09
2.08
2.06
1.31
1.30
1.30
1.29
1.29
1.27
1.01
0.99
0.98

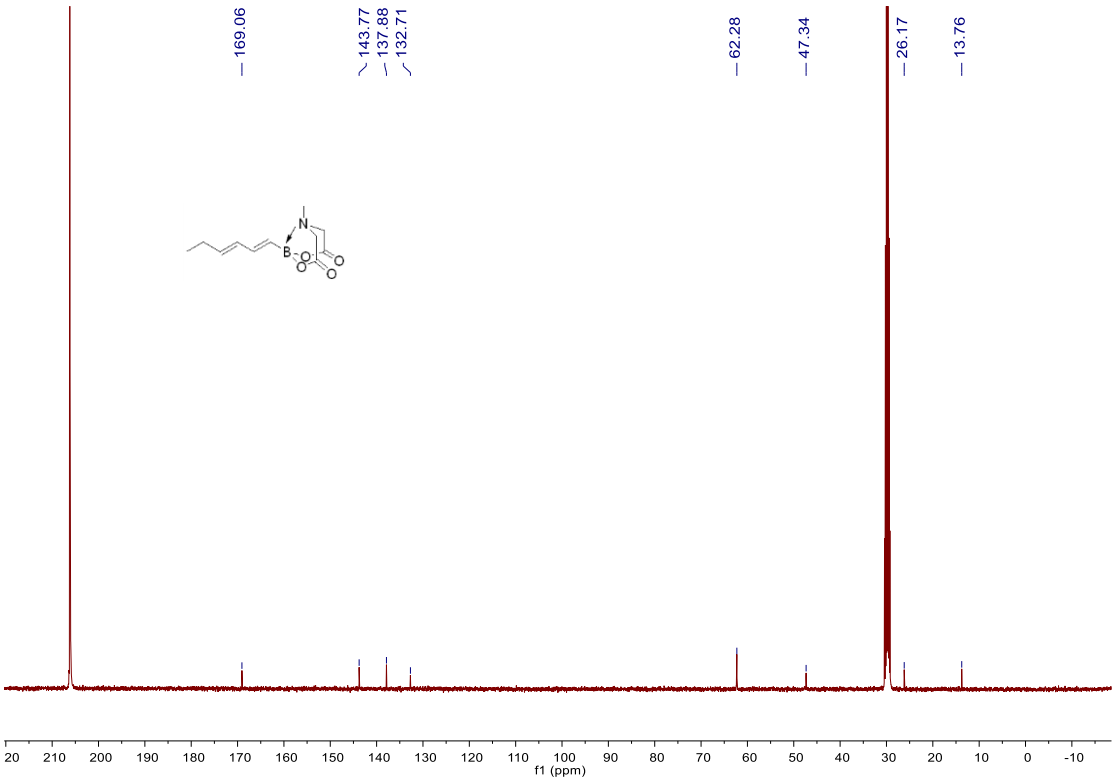



1.00
1.08
1.10
1.04
2.48
2.30
3.22
2.46
3.71
f1 (ppm)


10.72




f1 (ppm)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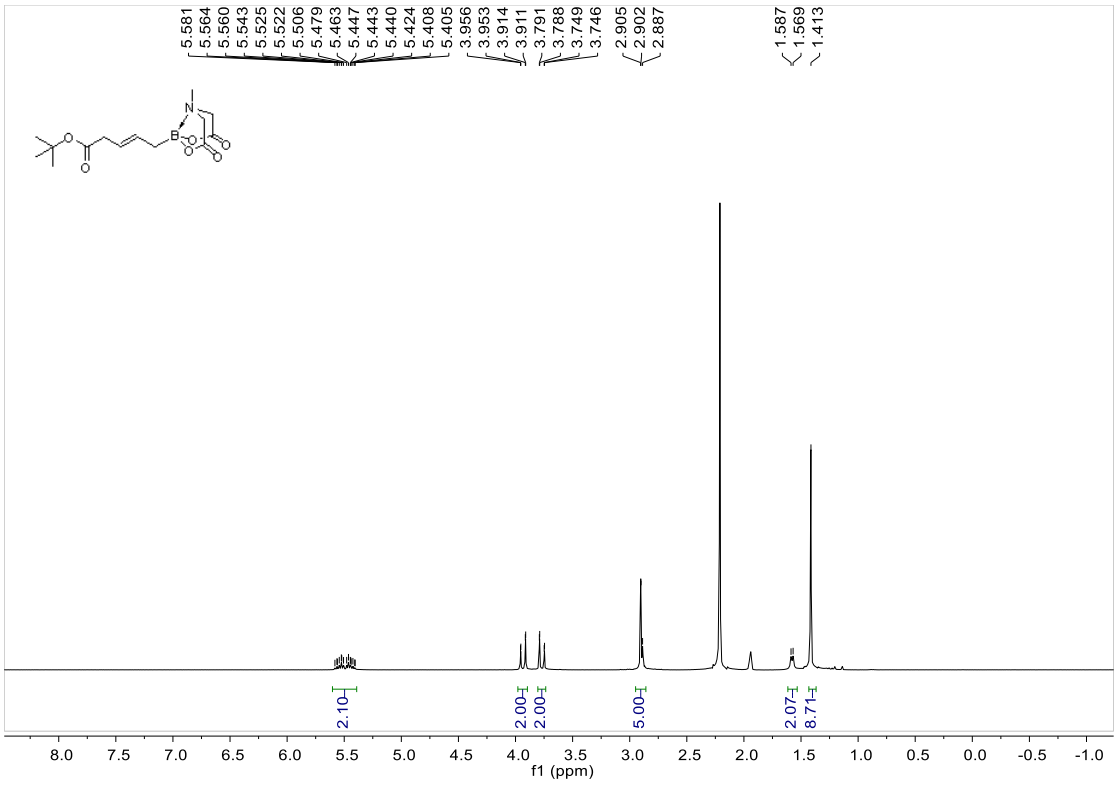
143.77
137.88
132.71
62.28
47.34
26.17
13.76
f1 (ppm)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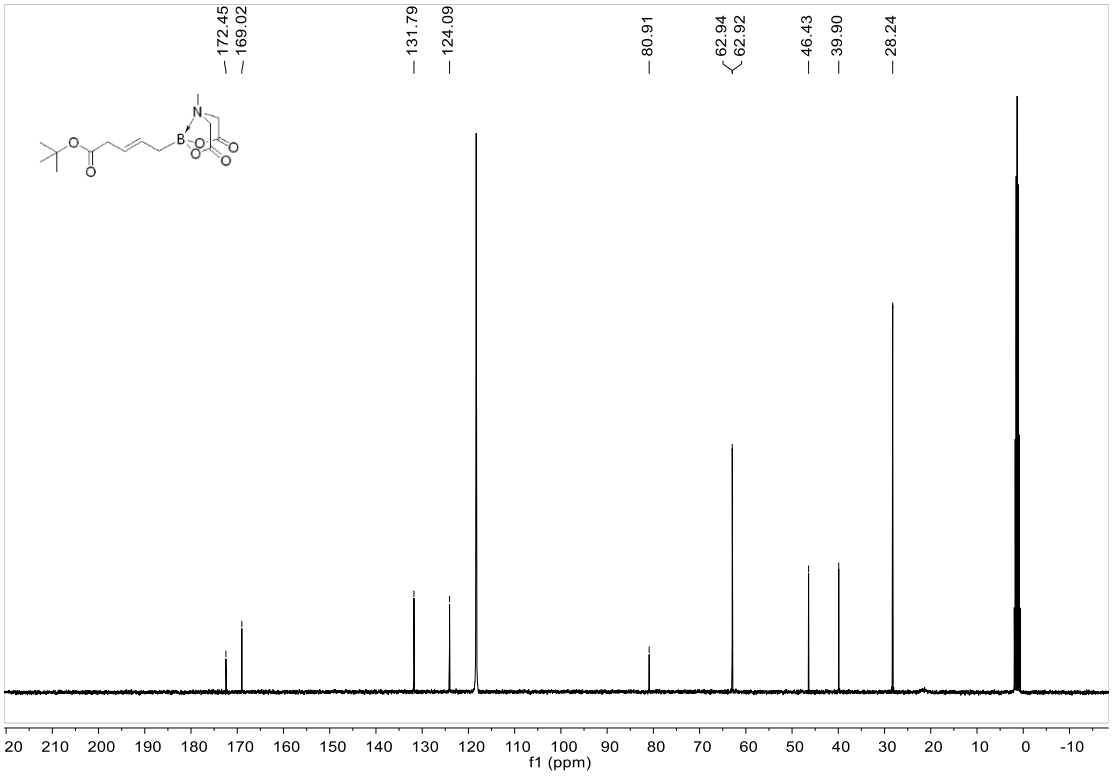
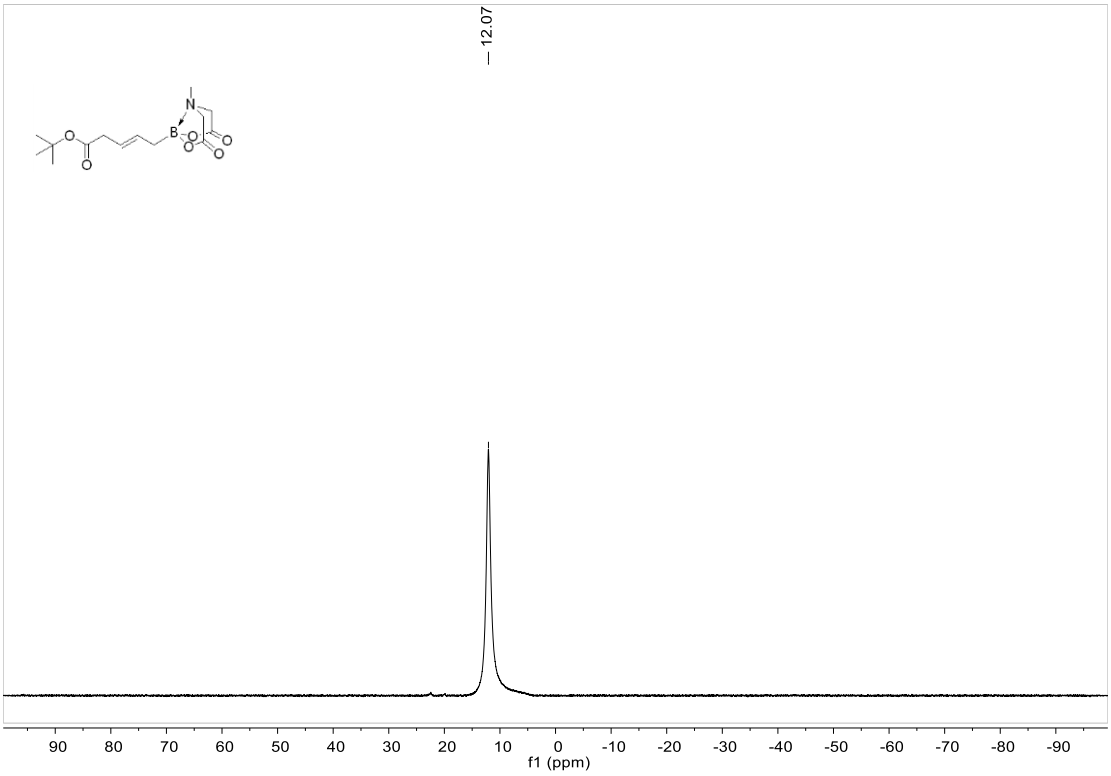
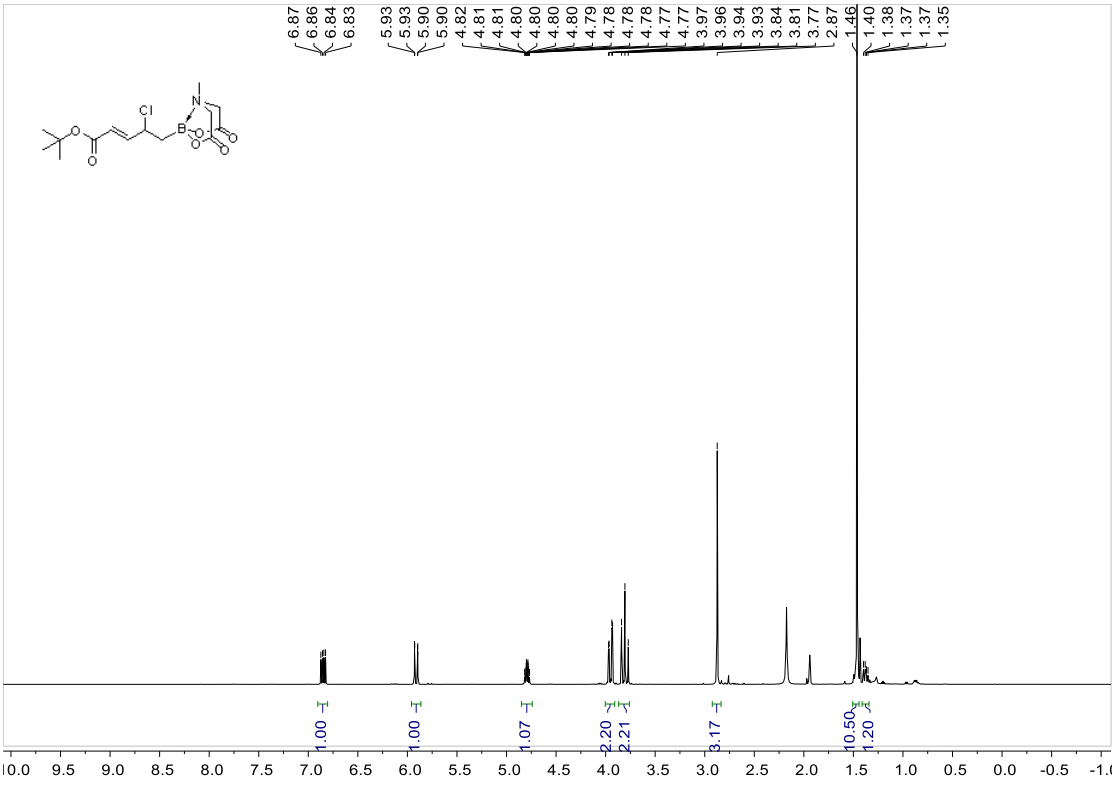
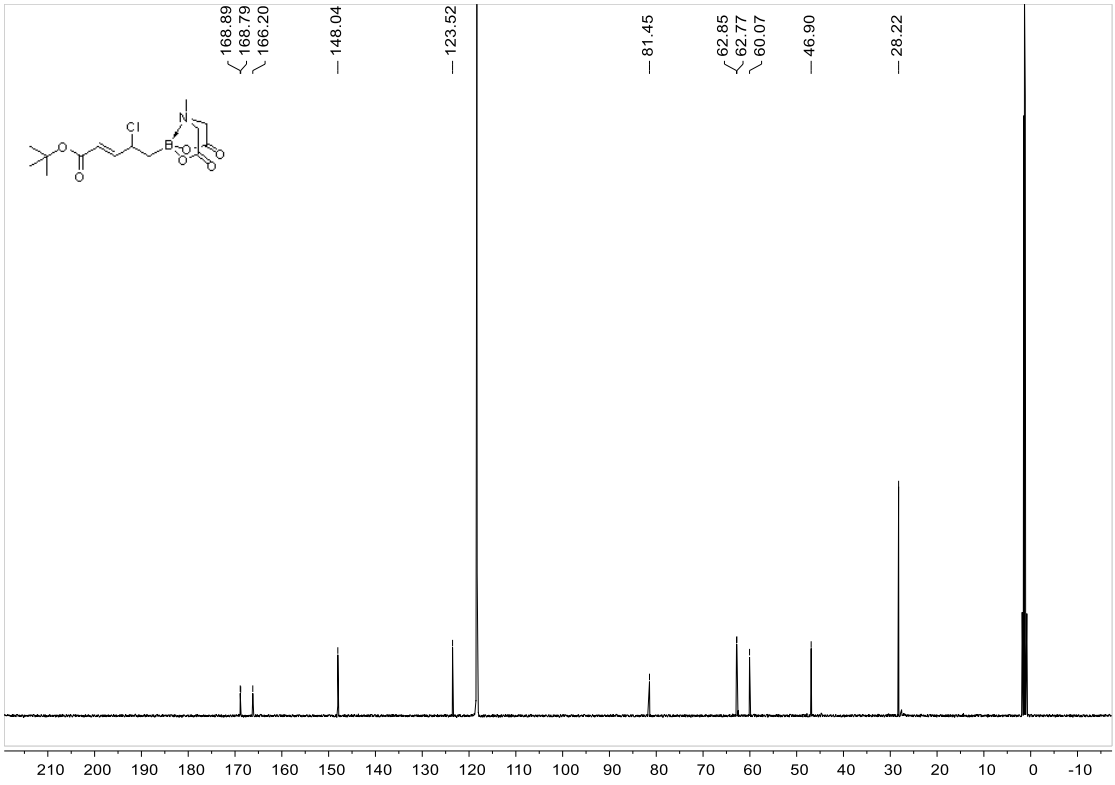
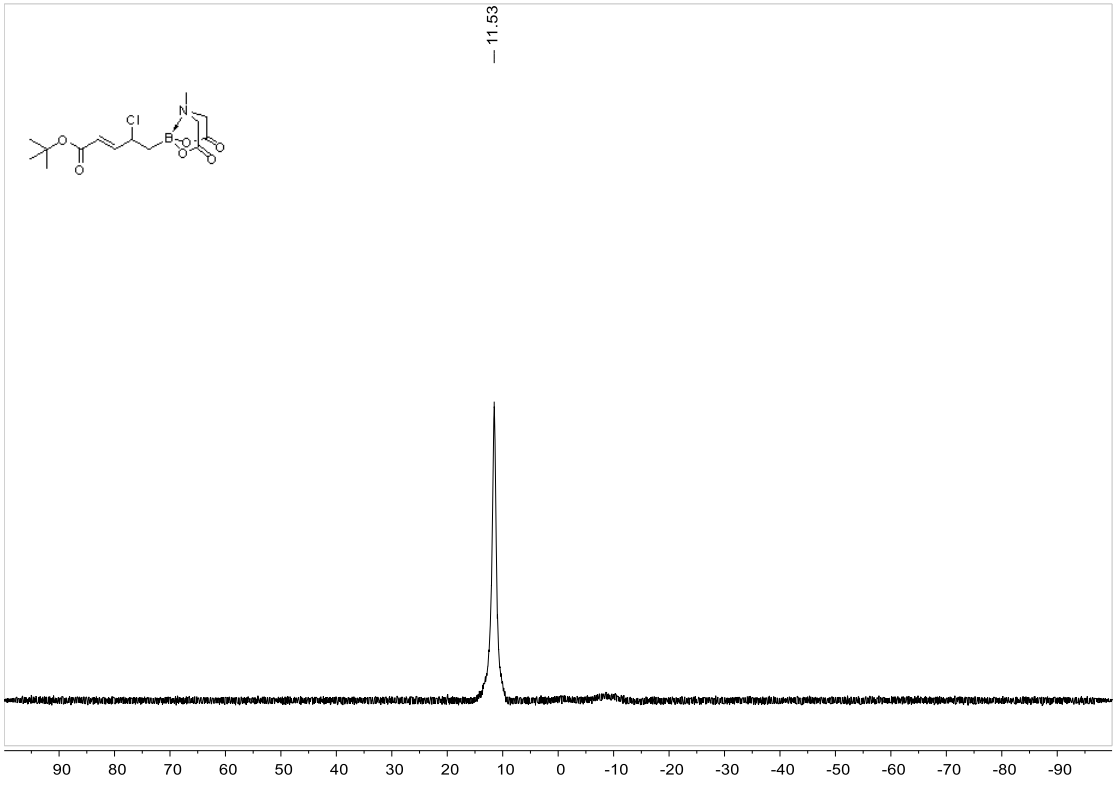
5.564
5.560
5.543
5.525
5.522
5.506
5.479
5.463
5.447
5.443
5.440
5.424
5.408
5.405
3.956
3.953
3.914
3.911
3.791
3.788
3.749
3.746
2.905
2.902
2.887
1.587
1.569
1.413
2.10
2.00
2.00
5.00
2.07
8.71
f1 (ppm)


172.45
169.02
131.79
124.09
80.91
62.94
62.92
46.43
39.90
28.24
f1 (ppm)


12.07
f1 (ppm)


6.87
6.86
6.84
6.83
5.93
5.93
5.90
5.90
4.82
4.81
4.81
4.80
4.80
4.80
4.80
4.79
4.78
4.78
4.78
4.77
4.77
3.97
3.96
3.94
3.93
3.84
3.81
3.77
2.87
1.46
1.40
1.38
1.37
1.37
1.35
1.00
1.00
1.07
2.20
2.21
3.17
10.50
1.20


168.89
168.79
166.20
148.04
123.52
81.45
62.85
62.77
60.07
46.90
28.22
Cl
N
B
O
O
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


11.53
Cl
N
B
O
O
O
O
O
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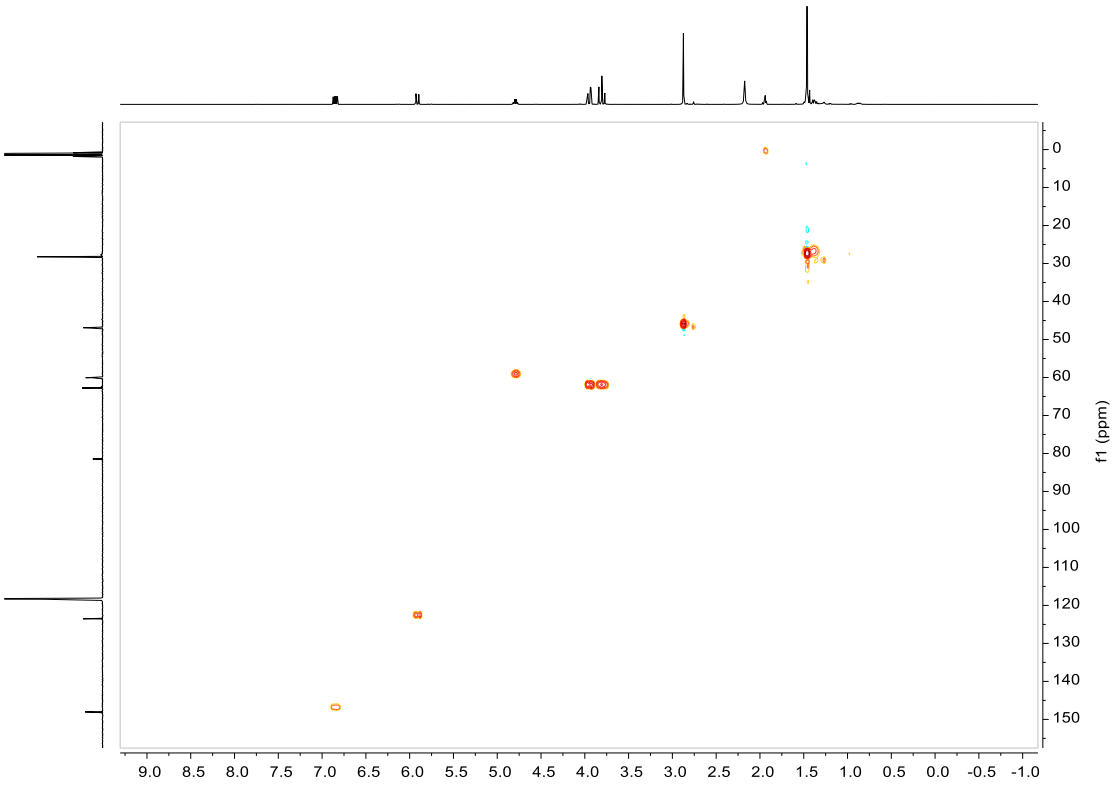
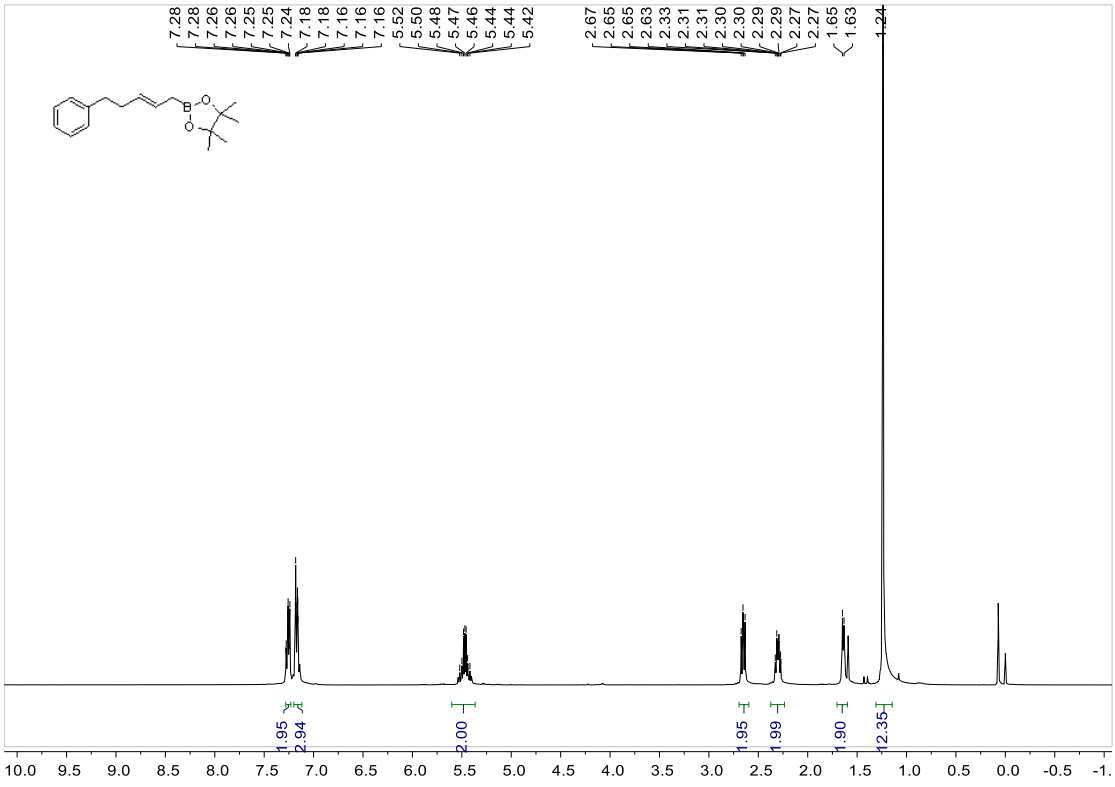

f1 (ppm)


7.28
7.28
7.26
7.26
7.25
7.25
7.24
7.18
7.16
7.16
7.16
5.52
5.50
5.48
5.47
5.46
5.44
5.44
5.42
2.67
2.65
2.65
2.63
2.33
2.31
2.31
2.30
2.30
2.29
2.29
2.27
2.27
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1.63
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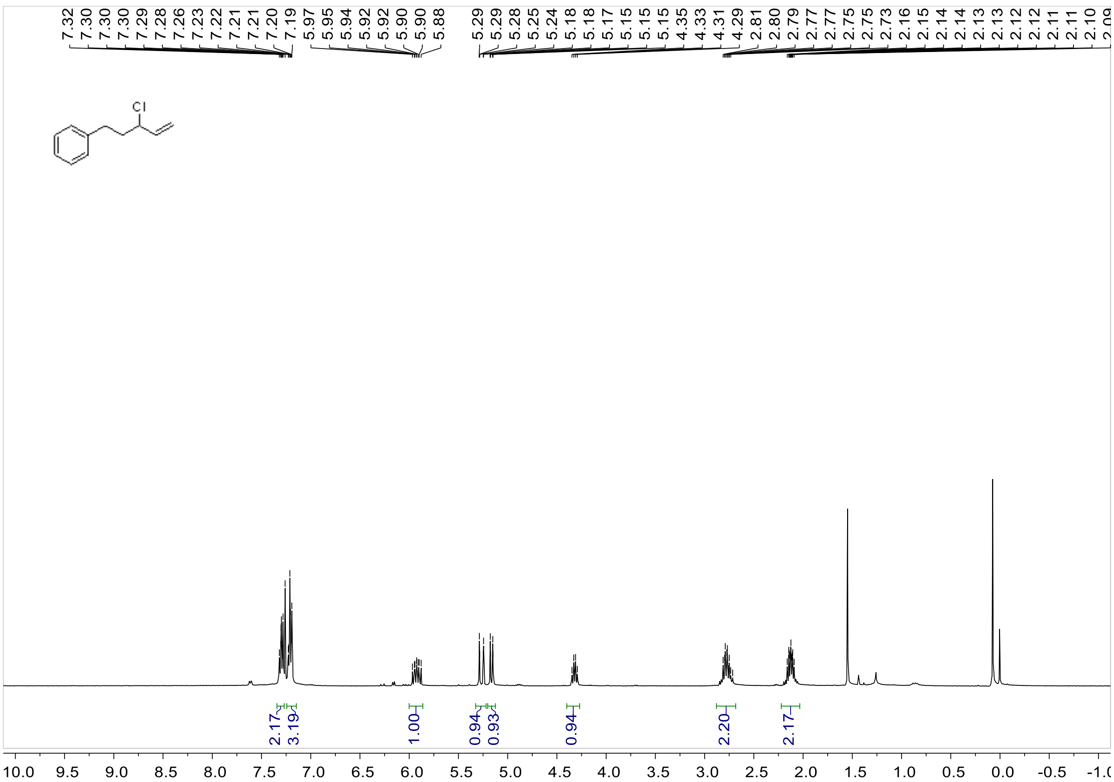
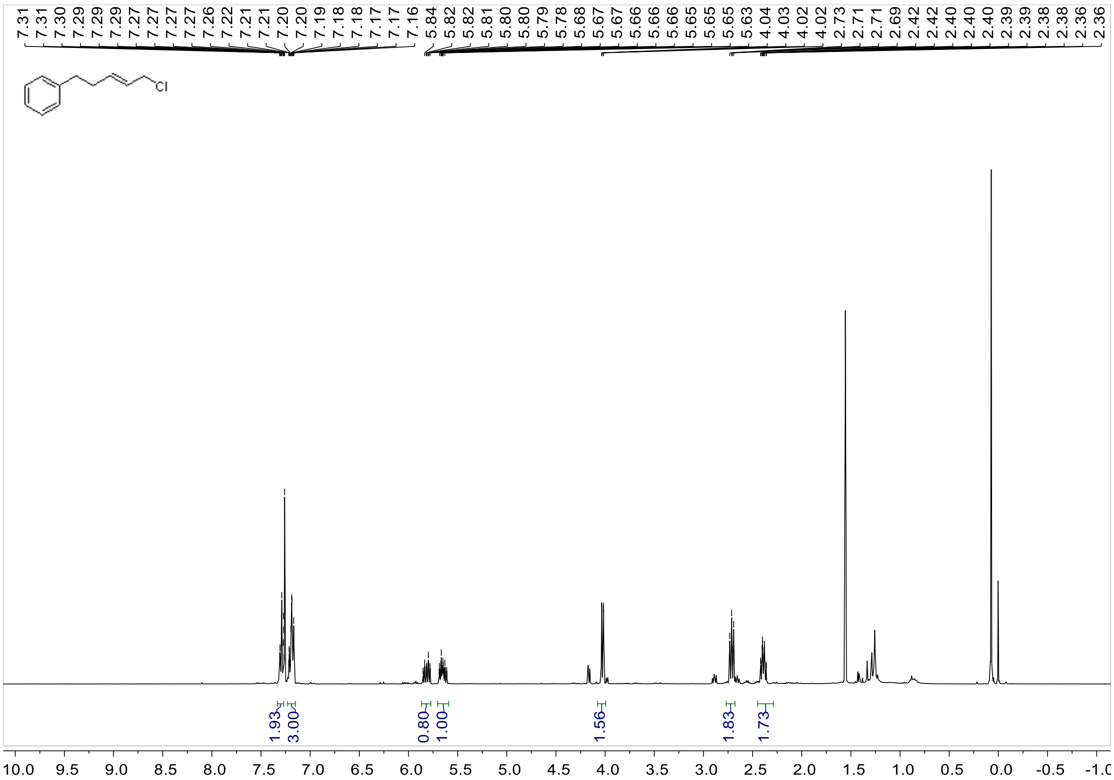
2.94
2.00
1.95
1.99
1.90
12.35


7.32 7.30 7.30 7.30 7.29 7.28 7.26 7.23 7.22 7.21 7.21 7.20 7.19 5.97 5.95 5.94 5.92 5.92 5.90 5.90 5.88 5.29 5.29 5.28 5.25 5.24 5.18 5.18 5.17 5.15 5.15 5.15 4.35 4.33 4.31 4.29 2.81 2.80 2.79 2.77 2.77 2.75 2.75 2.73 2.16 2.15 2.14 2.14 2.13 2.13 2.12 2.12 2.11 2.11 2.10
Cl
2.17 3.19 1.00 0.94 0.93 0.94 2.20 2.17
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


7.31 7.31 7.30 7.29 7.29 7.27 7.27 7.27 7.26 7.22 7.21 7.21 7.20 7.20 7.19 7.18 7.17 7.17 7.16 5.84 5.82 5.81 5.80 5.79 5.78 5.68 5.67 5.67 5.66 5.66 5.65 5.65 5.65 5.63 4.04 4.03 4.02 4.02 2.73 2.71 2.71 2.69 2.42 2.42 2.40 2.40 2.40 2.39 2.39 2.38 2.38 2.36 2.36
Cl
1.93 3.00 0.80 1.00 1.56 1.83 1.73
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

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