Halohydroxylation of Alkenyl MIDA Boronates: Switchable Stereoselectivity Induced by B(MIDA) Substituent

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Supporting Information

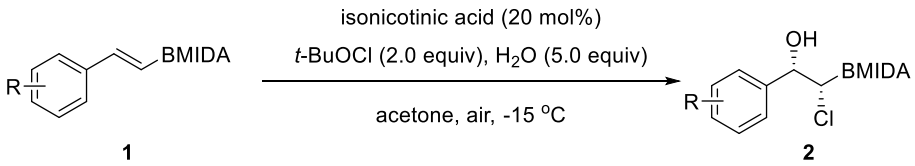
Contents

1. General information

The solvents were obtained from commercial suppliers and used without further purification unless otherwise stated. Proton (^{1}H) and Carbon NMR (^{13}C) were recorded at 400 MHz (500 MHz) and 101 MHz (126 MHz) NMR spectrometer, respectively. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

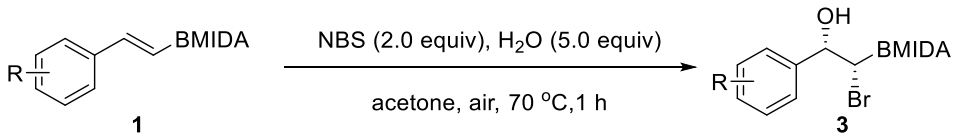
Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200‑300 mesh) with solvents distilled prior to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

2. General procedure for the synthesis of α–boryl chlorohydrins



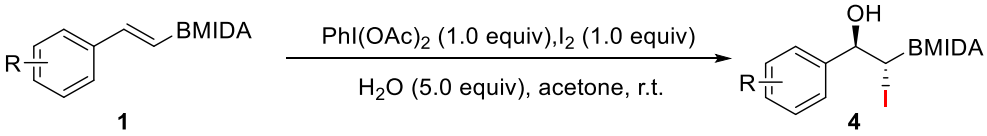
To a solution of alkenyl *N*-methyliminodiacetic (MIDA) boronate (0.3 mmol, 1.0 equiv) and isonicotinic acid (0.2 equiv) in acetone (2.5 mL) at -15 °C was added *t*-BuOCl (0.6 mmol, 2.0 equiv) and H_2O (1.5 mmol, 5.0 equiv). The reaction was stirred at -15 °C under air for 3 - 5 h and then 1 M HCl (5.0 mL) was added. The reaction mixture was extracted with EtOAc/acetone (10:1) for three times. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and acetone as eluent or recrystallized from EtOAc.

3. General procedure for the synthesis of α–boryl bromohydrins



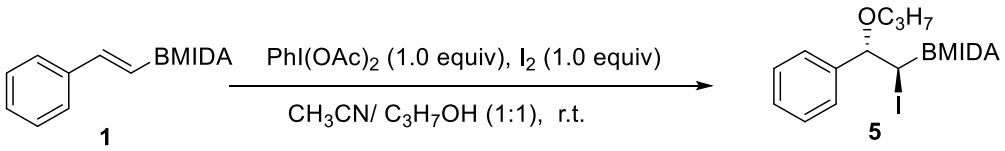
To a solution of alkenyl *N*-methyliminodiacetic (MIDA) boronate (0.3 mmol, 1.0 equiv) in acetone (2.5 mL) was added NBS (0.6 mmol, 2.0 equiv) and H_2O (1.5 mmol, 5.0 equiv). The reaction was stirred at 70 °C under air for 1 h and then concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and acetone as eluent or recrystallized from EtOAc.

4. General procedure for the synthesis of α–boryl iodohydrins

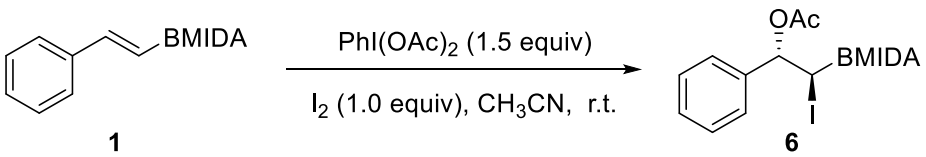


To a solution of alkenyl *N*-methyliminodiacetic (MIDA) boronate (0.3 mmol, 1.0 equiv) in acetone (2.5 mL) was added $PhI(OAc)_2$ (0.3 mmol, 1.0 equiv), I_2 (0.3 mmol, 1.0 equiv) and H_2O (1.5 mmol, 5.0 equiv). The reaction was stirred at room temperature under air until the alkenyl boronate was consumed as monitored by TLC analysis. The reaction mixture was diluted with saturated $NaHSO_3$ solution and extraceted wtih EtOAc for three times. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and acetone as eluent.

5. Synthesis of α–boryl iodoether and iodoester



To a solution of alkenyl *N*-methyliminodiacetic (MIDA) boronate (0.2 mmol, 1.0 equiv) in CH_3CN/C_3H_7OH (2.0 mL) was added $PhI(OAc)_2$ (0.2 mmol, 1.0 equiv), I_2 (0.2 mmol, 1.0 equiv). The reaction was stirred at room temperature under air until the alkenyl boronate was consumed as monitored by TLC analysis. The reaction mixture was diluted with saturated $NaHSO_3$ solution and extraceted wtih EtOAc for three times. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and acetone as eluent.

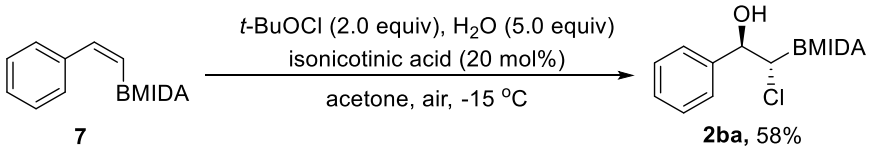


To a solution of alkenyl *N*-methyliminodiacetic (MIDA) boronate (0.2 mmol, 1.0 equiv) in anhydrous CH_3CN (2.0 mL) was added $PhI(OAc)_2$ (0.3 mmol, 1.5 equiv), I_2 (0.2 mmol, 1.0 equiv). The reaction was stirred at room temperature under air until the alkenyl boronate was consumed as monitored by TLC analysis. The reaction mixture was diluted with saturated $NaHSO_3$ solution and extraceted wtih EtOAc for three times. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under

reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and acetone as eluent.

6. Exploring the tolerance of the (*Z*)-alkenyl MIDA boronate

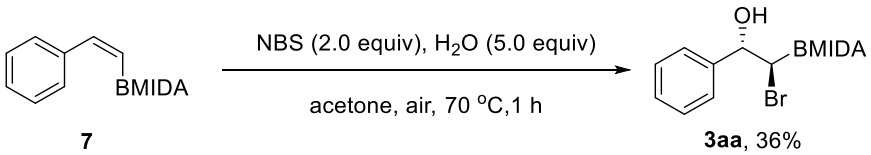
(a) Synthesis of compound **2ba**



7 **2ba,** 58%

To a solution of substrate **7** (0.3 mmol, 1.0 equiv) and isonicotinic acid (0.2 equiv) in acetone (2.5 mL) at -15 °C was added *t*-BuOCl (0.6 mmol, 2.0 equiv) and H_2O (1.5 mmol, 5.0 equiv). The reaction was stirred at -15 °C under air for 5 h and then 1 M HCl (5.0 mL) was added. The reaction mixture was extracted with EtOAc/acetone (10:1) for three times. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and acetone as eluent.

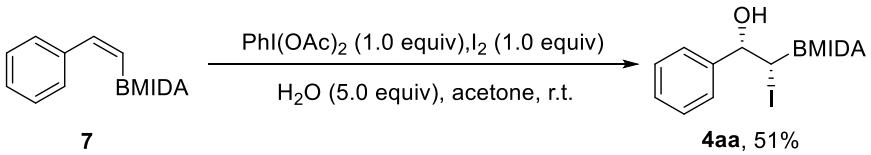
(b) Synthesis of compound **3aa**



7 **3aa**, 36%

To a solution of substrate **7** (0.3 mmol, 1.0 equiv) in acetone (2.5 mL) was added NBS (0.6 mmol, 2.0 equiv) and H_2O (1.5 mmol, 5.0 equiv). The reaction was stirred at 70 °C under air for 1 h and then concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and acetone as eluent.

(c) Synthesis of compound **4aa**



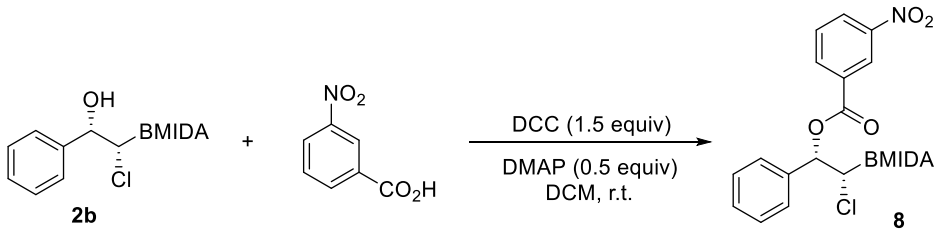
7 **4aa**, 51%

To a solution of substrate **7** (0.3 mmol, 1.0 equiv) in acetone (2.5 mL) was added $PhI(OAc)_2$ (0.3 mmol, 1.0 equiv), I_2 (0.3 mmol, 1.0 equiv) and H_2O (1.5 mmol, 5.0

equiv). The reaction was stirred at room temperature under air until the alkenyl boronate was consumed as monitored by TLC analysis. The reaction mixture was concentrated under reduced pressure and recrystallized from EtOAc.

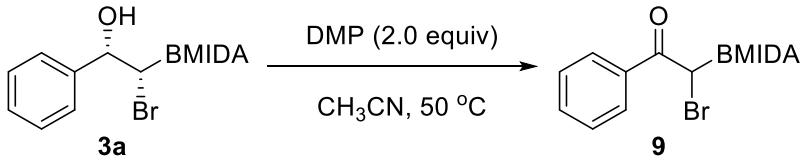
7. Derivatization of the products

(a) Synthesis of compound **8**



To a solution of **2b** (0.3 mmol, 1.0 equiv) in DCM (3.0 mL) was added DCC (0.45 mmol, 1.5 equiv), DMAP (0.15 mmol, 0.5 equiv). The reaction was stirred at room temperature overnight until the starting material was consumed as monitored by TLC analysis. The reaction mixture was diluted with 1M HCl solution and extraceted wtih EtOAc for three times. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and acetone as eluent.

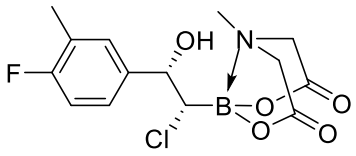
(b) Synthesis of compound **9**



To a solution of **3a** (0.2 mmol, 1.0 equiv) in CH_3CN (2.0 mL) was added DMP (0.4 mmol, 2.0 equiv). The reaction was stirred at 50 ^oC until the starting material was consumed as monitored by TLC analysis. The reaction mixture was then concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with a mixture of petroleum ether and acetone as eluent.

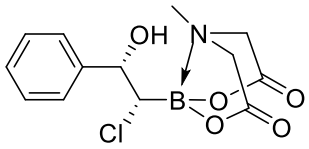
8. Characterization of the products

2-(1-chloro-2-(4-fluoro-3-methylphenyl)-2-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2a)



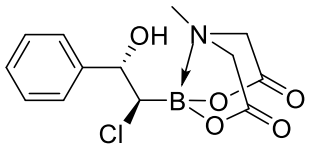
The compound **2a** was obtained in 78% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.45 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.27 (d, J = 6.8 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.05 (t, J = 9.1 Hz, 1H), 5.42 (d, J = 5.4 Hz, 1H), 5.01 (s, 1H), 4.41 (d, J = 17.4 Hz, 1H), 4.20 (d, J = 16.8 Hz, 1H), 4.06 (d, J = 17.3 Hz, 1H), 3.98 (d, J = 16.8 Hz, 1H), 3.75 (d, J = 2.6 Hz, 1H), 3.06 (s, 3H), 2.23 (d, J = 1.9 Hz, 3H); ^{19}F NMR (376 MHz, DMSO-d_6) δ -121.16; ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.1, 168.5, 159.6 (d, J = 240.5 Hz), 140.1 (d, J = 3.3 Hz), 129.3 (d, J = 4.9 Hz), 125.4 (d, J = 8.0 Hz), 122.9 (d, J = 17.3 Hz), 113.8 (d, J = 21.9 Hz), 71.5 , 62.6 , 62.3 , 46.2 , 14.4 (d, J = 3.1 Hz). **ESI-MS:** calcd for $C_{14}H_{16}BFClNO_5Na$ $[M + Na]^+$: 366.0689, found: 366.0696.

2-(1-chloro-2-hydroxy-2-phenylethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2b, major)



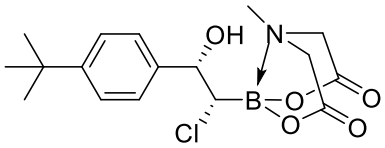
The compound **2b** was obtained in 85% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.4 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.39 (d, J = 7.0 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.21 (t, J = 7.2 Hz, 1H), 5.35 (s, 1H), 5.05 (d, J = 3.7 Hz, 1H), 4.40 (d, J = 17.4 Hz, 1H), 4.20 (d, J = 16.8 Hz, 1H), 4.05 (d, J = 17.4 Hz, 1H), 3.98 (d, J = 16.8 Hz, 1H), 3.77 (d, J = 2.5 Hz, 1H), 3.07 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.9, 168.3, 144.2, 127.4, 126.5, 126.2 , 71.9, 62.6, 62.3, 46.1. **ESI-MS:** calcd for $C_{13}H_{15}BClNO_5Na$ $[M + Na]^+$: 334.0626, found: 334.0630.

2-(1-chloro-2-hydroxy-2-phenylethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2ba, minor)



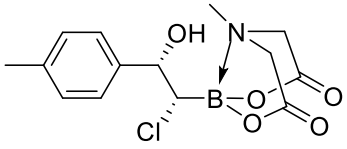
The diastereomer of compound **2b** was obtained in 6% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.32 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.37 (d, J = 6.9 Hz, 2H), 7.31 (t, J = 7.4 Hz, 2H), 7.24 (t, J = 7.0 Hz, 1H), 5.84 (d, J = 3.6 Hz, 1H), 4.66 (dd, J = 7.9, 3.6 Hz, 1H), 4.35 (d, J = 17.2 Hz, 1H), 4.21 (d, J = 16.7 Hz, 1H), 4.01 (d, J = 17.0 Hz, 2H), 3.76 (d, J = 7.8 Hz, 1H), 3.12 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.8, 168.7, 143.5, 127.5, 127.4, 127.2, 74.6, 63.3, 62.5, 46.3. **ESI-MS:** calcd for $C_{13}H_{15}BClNO_5$ Na [M + Na]$^+$: 334.0626, found: 334.0621.

2-(2-(4-(tert-butyl)phenyl)-1-chloro-2-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2c)



The compound **2c** was obtained in 66% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.63 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.35 – 7.29 (m, 4H), 5.30 (d, J = 5.2 Hz, 1H), 5.02 (dd, J = 5.3, 2.1 Hz, 1H), 4.41 (d, J = 17.4 Hz, 1H), 4.19 (d, J = 16.8 Hz, 1H), 4.05 (d, J = 17.4 Hz, 1H), 3.98 (d, J = 16.8 Hz, 1H), 3.73 (d, J = 2.1 Hz, 1H), 3.06 (s, 3H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.1, 168.5, 148.8, 141.3, 125.9, 124.2, 71.8, 62.6, 62.3, 46.2, 34.1, 31.2. **ESI-MS:** calcd for $C_{17}H_{23}BClNO_5Na$ [M + Na]$^+$: 390.1253, found: 390.1253.

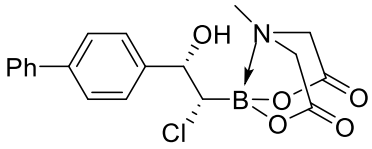
2-(1-chloro-2-hydroxy-2-(p-tolyl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2d)



The compound **2d** was obtained in 70% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.43 (PE:acetone = 1:1).

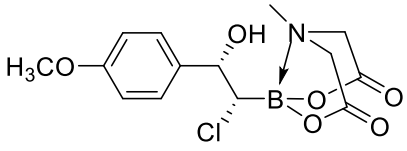
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.26 (d, J = 7.6 Hz, 2H), 7.11 (d, J = 7.7 Hz, 2H), 5.28 (s, 1H), 5.01 (s, 1H), 4.40 (d, J = 17.4 Hz, 1H), 4.19 (d, J = 16.8 Hz, 1H), 4.05 (d, J = 17.5 Hz, 1H), 3.98 (d, J = 16.8 Hz, 1H), 3.74 (s, 1H), 3.07 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.9, 168.4, 141.2, 135.4, 128.0, 126.1, 71.8, 62.6, 62.3, 46.1, 20.7. **ESI-MS:** calcd for $C_{14}H_{17}BClNO_5Na$ [M + Na]$^+$: 348.0783, found: 348.0785.

2-(2-([1,1'-biphenyl]-4-yl)-1-chloro-2-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2e)



The compound **2e** was obtained in 64% yield as a white solid after recrystallization from EtOAc. R_F = 0.42 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.68 – 7.61 (m, 4H), 7.50 – 7.44 (m, 4H), 7.35 (t, J = 7.4 Hz, 1H), 5.45 (d, J = 5.5 Hz, 1H), 5.11 (d, J = 5.1 Hz, 1H), 4.43 (d, J = 17.3 Hz, 1H), 4.22 (d, J = 16.7 Hz, 1H), 4.07 (d, J = 17.3 Hz, 1H), 4.00 (d, J = 16.8 Hz, 1H), 3.84 (s, 1H), 3.09 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.6, 168.9, 144.0, 140.6, 138.9, 129.4, 127.7, 127.3, 127.0, 126.3, 72.3, 63.1, 62.8, 46.7. **ESI-MS:** calcd for $C_{19}H_{19}BClNO_5Na$ [M + Na]$^+$: 410.0941, found: 410.0945.

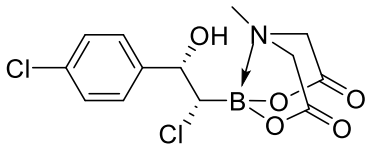
2-(1-chloro-2-hydroxy-2-(4-methoxyphenyl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2f)



The compound **2f** was obtained in 45% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.33 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.29 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 5.26 (d, J = 5.4 Hz, 1H), 5.00 (dd, J = 5.4, 2.5 Hz, 1H), 4.39 (d, J = 17.4 Hz, 1H), 4.19 (d, J = 16.8 Hz, 1H), 4.04 (d, J = 17.3 Hz, 1H), 3.98 (d, J = 16.8 Hz, 1H), 3.73 (s, 3H), 3.71 (d, J = 2.6 Hz, 1H), 3.06 (s, 3H); ^{13}C NMR (101 MHz, DMSO-

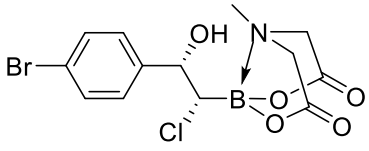
d_6) δ 169.1, 168.5, 158.0, 136.2, 127.3, 112.9, 71.7, 62.6, 62.3, 54.9, 46.1. **ESI-MS:** calcd for $C_{14}H_{17}BClNO_6Na$ $[M + Na]^+$: 364.0732, found: 364.0722.

2-(1-chloro-2-(4-chlorophenyl)-2-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2g)



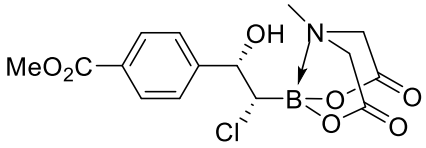
The compound **2g** was obtained in 68% yield as a white solid after recrystallization from EtOAc. R_F = 0.39 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.6 Hz, 2H), 5.48 (d, J = 5.5 Hz, 1H), 5.04 (dd, J = 5.7, 2.5 Hz, 1H), 4.40 (d, J = 17.4 Hz, 1H), 4.20 (d, J = 16.9 Hz, 1H), 4.05 (d, J = 17.4 Hz, 1H), 3.98 (d, J = 16.9 Hz, 1H), 3.78 (d, J = 2.6 Hz, 1H), 3.06 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.8, 168.3, 143.2, 131.0, 128.1, 127.4, 71.5, 62.6, 62.3, 46.1. **ESI-MS:** calcd for $C_{13}H_{14}BCl_2NO_5Na$ $[M + Na]^+$: 368.0237, found: 368.0240.

2-(2-(4-bromophenyl)-1-chloro-2-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2h)



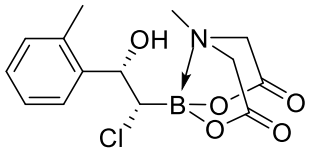
The compound **2h** was obtained in 63% yield as a white solid after recrystallization from EtOAc. R_F = 0.42 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.50 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.1 Hz, 2H), 5.52 (s, 1H), 5.03 (s, 1H), 4.41 (d, J = 17.3 Hz, 1H), 4.20 (d, J = 16.8 Hz, 1H), 4.06 (d, J = 17.4 Hz, 1H), 3.98 (d, J = 16.8 Hz, 1H), 3.79 (s, 1H), 3.06 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.0, 168.5, 143.7, 130.4, 128.5, 119.6, 71.5, 62.6, 62.3, 46.2. **ESI-MS:** calcd for $C_{13}H_{14}BClBrNO_5Na$ $[M + Na]^+$: 411.9732, found: 411.9732.

methyl 4-(2-chloro-1-hydroxy-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)ethyl) benzoate (2i)



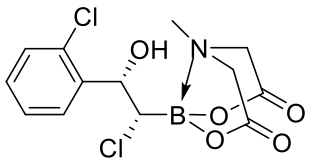
The compound **2i** was obtained in 51% yield as a white solid after recrystallization from EtOAc. R_F = 0.28 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 (d, J = 7.9 Hz, 2H), 7.55 (d, J = 8.0 Hz, 2H), 5.61 (s, 1H), 5.12 (s, 1H), 4.42 (d, J = 17.3 Hz, 1H), 4.21 (d, J = 16.8 Hz, 1H), 4.07 (d, J = 17.4 Hz, 1H), 3.98 (d, J = 16.8 Hz, 1H), 3.85 (s, 4H), 3.06 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.9, 168.5, 166.2, 149.9, 128.5, 127.9, 126.6, 71.9, 62.6, 62.3, 52.0, 46.2. **ESI-MS:** calcd for $C_{15}H_{17}BClNO_7Na$ [M + Na]$^+$: 392.0682, found: 392.0681.

2-(1-chloro-2-hydroxy-2-(o-tolyl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2j)



The compound **2j** was obtained in 74% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.42 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.51 (d, J = 7.4 Hz, 1H), 7.18 – 7.09 (m, 3H), 5.28 (d, J = 5.0 Hz, 1H), 5.22 (dd, J = 5.1, 2.5 Hz, 1H), 4.41 (d, J = 17.3 Hz, 1H), 4.20 (d, J = 16.8 Hz, 1H), 4.05 (d, J = 17.3 Hz, 1H), 3.99 (d, J = 16.8 Hz, 1H), 3.58 (s, 1H), 3.07 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.9, 168.5, 141.9, 133.2, 129.7, 127.6, 126.5, 124.9, 68.1, 62.6, 62.3, 46.1, 18.7. **ESI-MS:** calcd for $C_{14}H_{17}BClNO_5Na$ [M + Na]$^+$: 348.0783, found: 348.0766.

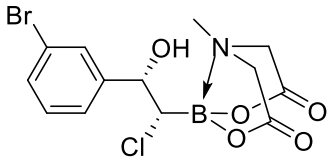
2-(1-chloro-2-(2-chlorophenyl)-2-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2k)



The compound **2k** was obtained in 58% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.42 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.64 (dd, J = 7.7, 1.7 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.28 (td, J = 7.6, 1.8 Hz, 1H), 5.54 (dd, J = 5.4, 2.2 Hz, 1H), 4.07 (d, J = 17.3 Hz, 1H),

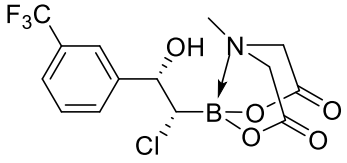
4.04 (d, *J* = 16.7 Hz, 1H), 3.96 (d, *J* = 16.8 Hz, 1H), 3.93 (d, *J* = 17.3 Hz, 1H), 3.89 (d, *J* = 2.2 Hz, 1H), 3.58 (d, *J* = 5.3 Hz, 1H), 3.08 (s, 3H); ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 169.0, 168.5, 141.0, 131.6, 130.4, 129.9, 129.7, 127.3, 70.6, 63.8, 63.4, 46.9. **ESI-MS:** calcd for $C_{13}H_{14}BCl_2NO_5Na$ $[M + Na]^+$: 368.0237, found: 368.0241.

2-(2-(3-bromophenyl)-1-chloro-2-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2l)



The compound **2l** was obtained in 70% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.41 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.59 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.9 Hz, 1H), 5.53 (s, 1H), 5.05 (s, 1H), 4.40 (d, *J* = 17.4 Hz, 1H), 4.21 (d, *J* = 16.7 Hz, 1H), 4.06 (d, *J* = 17.3 Hz, 1H), 3.98 (d, *J* = 16.8 Hz, 1H), 3.82 (s, 1H), 3.06 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.9, 168.4, 147.2, 129.7, 129.3, 129.0, 125.3, 121.0, 71.4, 62.6, 62.3, 46.2. **ESI-MS:** calcd for $C_{13}H_{14}BClBrNO_5Na$ $[M + Na]^+$: 411.9732, found: 411.9736.

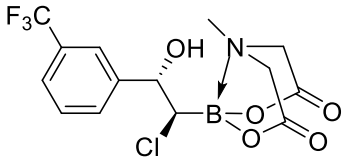
2-(1-chloro-2-hydroxy-2-(3-(trifluoromethyl)phenyl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane -4,8-dione (2m, major)



The compound **2m** was obtained in 48% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.46 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.84 (s, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.61 – 7.55 (m, 2H), 5.38 (dd, *J* = 5.2, 2.3 Hz, 1H), 4.42 (d, *J* = 5.1 Hz, 1H), 4.41 (d, *J* = 16.9 Hz, 1H), 4.30 (d, *J* = 16.6 Hz, 1H), 4.17 (d, *J* = 16.6 Hz, 1H), 4.16 (d, *J* = 17.2 Hz, 1H), 3.98 (d, *J* = 2.3 Hz, 1H), 3.35 (s, 3H); ^{19}F NMR (376 MHz, Acetone-d_6) δ -62.88; ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.8, 168.2, 146.1, 131.2, 120.3 (q, *J* = 31.6 Hz), 129.4,

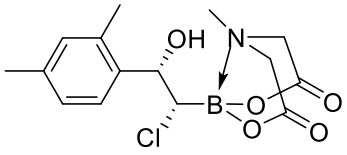
125.6 (q, *J* = 271.8 Hz), 124.5 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 4.1 Hz), 73.5, 64.0, 63.5, 46.9. **ESI-MS:** calcd for $C_{14}H_{14}BF_3ClNO_5Na$ $[M + Na]^+$: 402.0500, found: 402.0509.

2-(1-chloro-2-hydroxy-2-(3-(trifluoromethyl)phenyl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane -4,8-dione (minor)



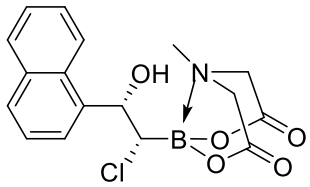
The diastereomer of compound **2m** was obtained in 40% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.41 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.81 (s, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 5.05 (dd, *J* = 7.1, 3.7 Hz, 1H), 4.94 (d, *J* = 3.7 Hz, 1H), 4.30 (d, *J* = 17.0 Hz, 2H), 4.20 (d, *J* = 16.9 Hz, 1H), 4.09 (d, *J* = 16.9 Hz, 1H), 3.92 (d, *J* = 7.0 Hz, 1H), 3.38 (s, 3H); ^{19}F NMR (376 MHz, Acetone-d_6) δ -62.88; ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.7, 168.2, 145.2, 132.6, 130.2 (q, *J* = 31.7 Hz), 129.2, 125.6 (q, *J* = 271.3 Hz), 125.2 (q, *J* = 4.0 Hz), 124.9 (q, *J* = 3.9 Hz), 75.5 , 64.3, 63.7, 46.9. **ESI-MS:** calcd for $C_{14}H_{14}BF_3ClNO_5Na$ $[M + Na]^+$: 402.0500, found: 402.0497.

2-(1-chloro-2-(2,4-dimethylphenyl)-2-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2n)



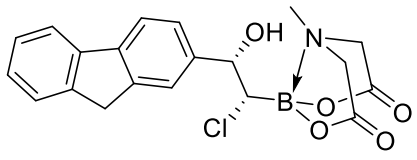
The compound **2n** was obtained in 53% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.48 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.38 (d, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.91 (s, 1H), 5.22 – 5.17 (m, 2H), 4.41 (d, *J* = 17.4 Hz, 1H), 4.20 (d, *J* = 16.8 Hz, 1H), 4.04 (d, *J* = 17.4 Hz, 1H), 3.99 (d, *J* = 16.7 Hz, 1H), 3.55 (d, *J* = 2.4 Hz, 1H), 3.06 (s, 3H), 2.24 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.5, 168.9, 139.5, 135.8, 133.4, 130.8, 128.0, 126.0, 68.5, 63.0, 62.8, 46.5, 21.1, 19.1. **ESI-MS:** calcd for $C_{15}H_{19}BClNO_5Na$ $[M + Na]^+$: 362.0940, found: 362.0940.

2-(1-chloro-2-hydroxy-2-(naphthalen-1-yl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2o)



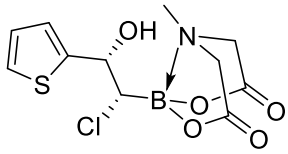
The compound **2o** was obtained in 61% yield as a white solid after recrystallization from EtOAc. R_F = 0.39 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97 – 7.93 (m, 2H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.74 (d, *J* = 7.1 Hz, 1H), 7.59 – 7.50 (m, 3H), 5.83 (d, *J* = 2.1 Hz, 1H), 5.58 (s, 1H), 4.48 (d, *J* = 17.4 Hz, 1H), 4.23 (d, *J* = 16.8 Hz, 1H), 4.09 (d, *J* = 17.4 Hz, 1H), 4.02 (d, *J* = 16.8 Hz, 1H), 3.80 (d, *J* = 2.2 Hz, 1H), 3.08 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.0, 168.3, 138.9, 133.1, 129.3, 128.8, 127.2, 126.1, 125.1, 125.0, 124.9, 122.2, 67.9, 62.7, 62.3, 46.1. **ESI-MS:** calcd for $C_{17}H_{17}BClNO_5Na$ $[M + Na]^+$: 384.0784, found: 384.0780.

2-(1-chloro-2-(9H-fluoren-2-yl)-2-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2p)



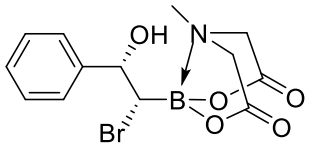
The compound **2p** was obtained in 50% yield as a white solid after recrystallization from EtOAc. R_F = 0.42 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86 (d, *J* = 7.5 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.61 (s, 1H), 7.57 (d, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 5.45 (d, *J* = 5.4 Hz, 1H), 5.14 (dd, *J* = 5.4, 2.4 Hz, 1H), 4.43 (d, *J* = 17.4 Hz, 1H), 4.21 (d, *J* = 16.8 Hz, 1H), 4.07 (d, *J* = 17.4 Hz, 1H), 4.00 (d, *J* = 16.8 Hz, 1H), 3.91 (s, 2H), 3.85 (d, *J* = 2.4 Hz, 1H), 3.09 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.1, 168.5, 143.3, 143.0, 142.3, 141.1, 139.7, 126.7, 126.4, 125.1, 124.9, 123.0, 119.8, 119.1, 72.2, 62.6, 62.3, 46.2, 36.4. **ESI-MS:** calcd for $C_{20}H_{19}BClNO_5Na$ $[M + Na]^+$: 422.0941, found: 422.0946.

2-(1-chloro-2-hydroxy-2-(thiophen-2-yl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (2q)



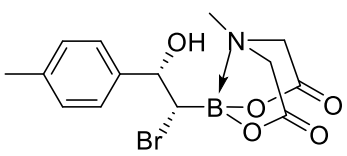
The compound **2q** was obtained in 28% yield as a yellow solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.38 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.34 (d, J = 5.3 Hz, 1H), 7.09 (d, J = 3.5 Hz, 1H), 6.95 (dd, J = 5.1, 3.6 Hz, 1H), 5.15 (dd, J = 7.9, 2.7 Hz, 1H), 5.06 (d, J = 3.6 Hz, 1H), 4.32 (d, J = 17.0 Hz, 1H), 4.25 (d, J = 16.8 Hz, 1H), 4.18 (d, J = 16.9 Hz, 1H), 4.13 (d, J = 16.9 Hz, 1H), 3.79 (d, J = 7.8 Hz, 1H), 3.36 (s, 3H); ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.7, 168.4, 147.9, 126.8, 126.3, 125.4, 72.5, 64.5, 63.7, 46.9. **ESI-MS:** calcd for $C_{11}H_{13}BClSNO_5Na$ $[M + Na]^+$: 340.0190, found: 340.0195.

2-(1-bromo-2-hydroxy-2-phenylethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3a)



The compound **3a** was obtained in 75% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.40 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.38 (d, J = 7.6 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.21 (t, J = 7.3 Hz, 1H), 5.40 (d, J = 5.3 Hz, 1H), 5.00 (d, J = 5.3 Hz, 1H), 4.42 (d, J = 17.3 Hz, 1H), 4.21 (d, J = 16.7 Hz, 1H), 4.07 (d, J = 17.4 Hz, 1H), 3.98 (d, J = 16.8 Hz, 1H), 3.80 (s, 1H), 3.09 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.0, 168.5, 145.0, 127.6, 126.6, 126.1, 71.5, 62.8, 62.6, 46.2. **ESI-MS:** calcd for $C_{13}H_{15}BBrNO_5Na$ $[M + Na]^+$: 378.0121, found: 378.0123.

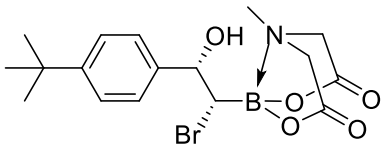
2-(1-bromo-2-hydroxy-2-(*p*-tolyl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione(3b)



The compound **3b** was obtained in 64% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.44 (PE:acetone = 1:1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.26 (d, J = 7.5 Hz, 2H), 7.11 (d, J = 7.3 Hz, 2H), 5.33 (s, 1H), 4.97 (s, 1H), 4.42 (d, J = 17.3 Hz, 1H), 4.21 (d, J = 16.8 Hz, 1H), 4.07 (d,

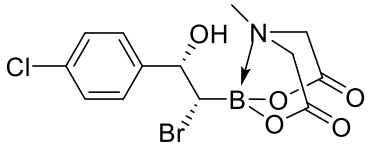
J = 17.4 Hz, 1H), 3.99 (d, *J* = 16.8 Hz, 1H), 3.78 (s, 1H), 3.09 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.9, 168.4, 142.0, 135.4, 128.1, 125.9, 71.3, 62.7, 62.5, 46.2, 20.7.

2-(1-bromo-2-(4-(tert-butyl)phenyl)-2-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3c)



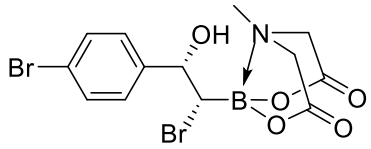
The compound **3c** was obtained in 57% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.51 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 5.12 (dd, *J* = 5.6, 1.9 Hz, 1H), 4.05 – 3.92 (m, 4H), 3.79 (d, *J* = 2.0 Hz, 1H), 3.29 (d, *J* = 5.6 Hz, 1H), 3.10 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.9, 168.5, 150.8, 142.1, 126.7, 125.6, 73.0, 63.9, 63.7, 46.9, 35.0, 31.6. **ESI-MS:** calcd for $C_{17}H_{23}BBrNO_5Na$ $[M + Na]^+$: 434.0748, found: 434.0744

2-(1-bromo-2-(4-chlorophenyl)-2-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3d)



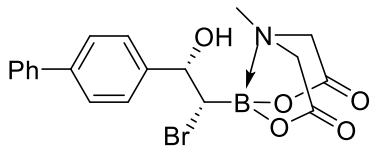
The compound **3d** was obtained in 69% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.46 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 5.53 (s, 1H), 5.00 (s, 1H), 4.42 (d, *J* = 17.4 Hz, 1H), 4.21 (d, *J* = 16.9 Hz, 1H), 4.07 (d, *J* = 17.4 Hz, 1H), 3.98 (d, *J* = 16.9 Hz, 1H), 3.81 (d, *J* = 2.1 Hz, 1H), 3.08 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.9, 168.4, 144.1, 131.0, 127.9, 127.4, 70.9, 62.7, 62.5, 46.2. **ESI-MS:** calcd for $C_{13}H_{14}BClBrNO_5Na$ $[M + Na]^+$: 411.9732, found: 411.9729.

2-(1-bromo-2-(4-bromophenyl)-2-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3e)



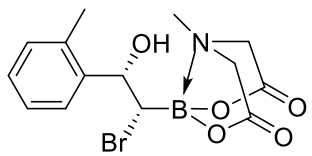
The compound **3e** was obtained in 54% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.46 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.50 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.2 Hz, 2H), 5.53 (d, *J* = 5.4 Hz, 1H), 4.98 (d, *J* = 4.6 Hz, 1H), 4.41 (d, *J* = 17.4 Hz, 1H), 4.21 (d, *J* = 16.9 Hz, 1H), 4.07 (d, *J* = 17.3 Hz, 1H), 3.98 (d, *J* = 16.8 Hz, 1H), 3.80 (d, *J* = 2.1 Hz, 1H), 3.08 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.9, 168.4, 144.5, 130.3, 128.3, 119.6, 70.9, 62.7, 62.5, 46.2. **ESI-MS:** calcd for $C_{13}H_{14}BBr_2NO_5Na$ $[M + Na]^+$: 455.9226, found: 455.9226.

2-(2-([1,1'-biphenyl]-4-yl)-1-bromo-2-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3f)



The compound **3f** was obtained in 59% yield as a white solid after recrystallization from EtOAc. R_F = 0.44 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.67 (d, *J* = 7.7 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.53 – 7.41 (m, 4H), 7.35 (t, *J* = 7.4 Hz, 1H), 5.06 (d, *J* = 1.9 Hz, 1H), 4.43 (d, *J* = 17.4 Hz, 1H), 4.22 (d, *J* = 16.9 Hz, 1H), 4.09 (d, *J* = 17.4 Hz, 1H), 4.00 (d, *J* = 16.8 Hz, 1H), 3.86 (d, *J* = 2.0 Hz, 1H), 3.11 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.9, 168.5, 144.4, 140.1, 138.4, 128.9, 127.2, 126.6, 126.6, 125.8, 71.3, 62.7, 62.6, 46.2. **ESI-MS:** calcd for $C_{19}H_{19}BBrNO_5Na$ $[M + Na]^+$: 454.0435, found: 454.0437.

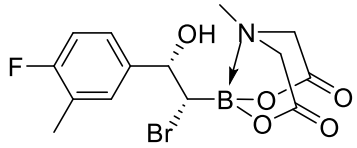
2-(1-bromo-2-hydroxy-2-(o-tolyl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3g)



The compound **3g** was obtained in 56% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.45 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.53 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.24 – 7.13 (m, 3H), 5.31 (dd, *J* = 4.9, 2.4 Hz, 1H), 4.05 (d, *J* = 17.3 Hz, 1H), 4.02 (s, 2H),

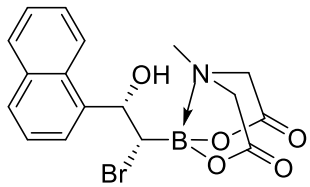
3.92 (d, *J* = 17.3 Hz, 1H), 3.70 (d, *J* = 2.4 Hz, 1H), 3.27 (d, *J* = 4.9 Hz, 1H), 3.10 (s, 3H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.9, 168.5, 142.6, 134.7, 130.9, 128.1, 127.9, 125.9, 69.7, 63.9, 63.7, 46.9, 19.1. **ESI-MS:** calcd for $C_{14}H_{17}BBrNO_5Na$ $[M + Na]^+$: 392.0278, found: 392.0274.

2-(1-bromo-2-(4-fluoro-3-methylphenyl)-2-hydroxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3h)



The compound **3h** was obtained in 77% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.44 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.26 (d, *J* = 7.9 Hz, 1H), 7.24 – 7.19 (m, 1H), 7.05 (t, *J* = 9.1 Hz, 1H), 5.42 (d, *J* = 5.3 Hz, 1H), 4.96 (d, *J* = 5.2 Hz, 1H), 4.41 (d, *J* = 17.4 Hz, 1H), 4.21 (d, *J* = 16.8 Hz, 1H), 4.07 (d, *J* = 17.4 Hz, 1H), 3.98 (d, *J* = 16.8 Hz, 1H), 3.77 (d, *J* = 2.1 Hz, 1H), 3.08 (s, 3H), 2.23 (s, 3H); ^{19}F NMR (376 MHz, DMSO-d_6) δ -121.22. ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.9, 168.4, 159.5 (d, *J* = 240.9 Hz), 140.8 (d, *J* = 3.3 Hz), 129.1 (d, *J* = 5.0 Hz), 125.2 (d, *J* = 7.8 Hz), 122.8 (d, *J* = 17.2 Hz), 113.8 (d, *J* = 21.9 Hz), 70.9, 62.7, 62.5, 46.2, 14.4 (d, *J* = 3.4 Hz). **ESI-MS:** calcd for $C_{14}H_{16}BFBrNO_5Na$ $[M + Na]^+$: 410.0184, found: 410.0183.

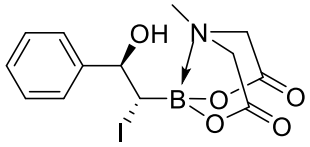
2-(1-bromo-2-hydroxy-2-(naphthalen-1-yl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3i)



The compound **3i** was obtained in 50% yield as a white solid after recrystallization from EtOAc. R_F = 0.44 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.95 (t, *J* = 9.5 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.61 – 7.48 (m, 3H), 5.74 (s, 1H), 5.62 (s, 1H), 4.49 (d, *J* = 17.4 Hz, 1H), 4.25 (d, *J* = 16.8 Hz, 1H), 4.11 (d, *J* = 17.5 Hz, 1H), 4.03 (d, *J* = 16.8 Hz, 1H), 3.83 (d, *J* = 2.0 Hz, 1H), 3.11 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 169.1, 168.4, 139.6, 133.2, 129.2, 128.9,

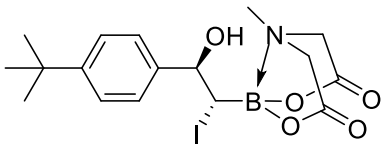
127.3, 126.3, 125.3, 125.0, 124.9, 122.1, 67.4, 62.9, 62.6, 46.2. **ESI-MS:** calcd for $C_{17}H_{17}BBrNO_5Na$ $[M + Na]^+$: 428.0278, found: 428.0285.

2-(2-hydroxy-1-iodo-2-phenylethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione（4a）



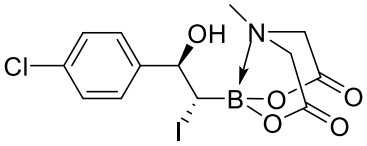
The compound **4a** was obtained in 69% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.37 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.43 (d, J = 7.0 Hz, 2H), 7.31 (t, J = 7.4 Hz, 2H), 7.24 (t, J = 7.1 Hz, 1H), 4.97 (d, J = 2.8 Hz, 1H), 4.82 (dd, J = 9.9, 3.0 Hz, 1H), 4.40 (d, J = 17.3 Hz, 1H), 4.31 (d, J = 16.3 Hz, 1H), 4.21 (d, J = 17.3 Hz, 1H), 4.16 (d, J = 16.3 Hz, 1H), 3.86 (d, J = 9.9 Hz, 1H), 3.46 (s, 3H); ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.6, 168.3, 145.6, 128.6, 128.4, 128.3, 78.0, 65.6, 63.8, 47.2. **ESI-MS:** calcd for $C_{13}H_{15}BINO_5Na$ $[M + Na]^+$: 425.9983, found: 425.9988.

2-(2-(4-(tert-butyl)phenyl)-2-hydroxy-1-iodoethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4b)



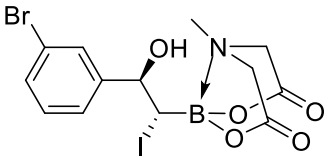
The compound **4b** was obtained in 86% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.57 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.36 (s, 4H), 4.86 (d, J = 2.8 Hz, 1H), 4.81 (dd, J = 10.1, 2.8 Hz, 1H), 4.41 (d, J = 17.3 Hz, 1H), 4.32 (d, J = 16.2 Hz, 1H), 4.22 (d, J = 17.2 Hz, 1H), 4.15 (d, J = 16.3 Hz, 1H), 3.86 (d, J = 10.1 Hz, 1H), 3.46 (s, 3H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.7, 168.4, 151.1, 142.7, 128.1, 125.5, 77.9, 65.7, 63.9, 47.2, 35.0, 31.7. **ESI-MS:** calcd for $C_{17}H_{23}BINO_5Na$ $[M + Na]^+$: 482.0609, found: 482.0607.

2-(2-(4-chlorophenyl)-2-hydroxy-1-iodoethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4c)



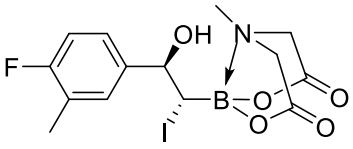
The compound **4c** was obtained in 54% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.46 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.47 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 5.08 (d, J = 3.0 Hz, 1H), 4.81 (dd, J = 9.3, 3.0 Hz, 1H), 4.39 (d, J = 17.2 Hz, 1H), 4.29 (d, J = 16.5 Hz, 1H), 4.20 (d, J = 17.2 Hz, 1H), 4.18 (d, J = 16.5 Hz, 1H), 3.85 (d, J = 9.4 Hz, 1H), 3.45 (s, 3H); ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.6, 168.3, 144.5, 133.5, 130.1, 128.6, 76.9, 65.5, 63.8, 47.2. **ESI-MS:** calcd for $C_{13}H_{14}BClINO_5Na$ [M + Na]$^+$: 459.9593, found: 459.9594.

2-(2-(3-bromophenyl)-2-hydroxy-1-iodoethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4d)



The compound **4d** was obtained in 56% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.46 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.64 (s, 1H), 7.47 – 7.40 (m, 2H), 7.28 (t, J = 7.8 Hz, 1H), 5.15 (d, J = 3.0 Hz, 1H), 4.80 (dd, J = 9.4, 3.1 Hz, 1H), 4.40 (d, J = 17.2 Hz, 1H), 4.29 (d, J = 16.5 Hz, 1H), 4.21 (d, J = 17.3 Hz, 1H), 4.19 (d, J = 16.5 Hz, 1H), 3.87 (d, J = 9.4 Hz, 1H), 3.45 (s, 3H); ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.6, 168.2, 148.2, 131.4, 131.1, 130.5, 127.6, 122.2, 76.9, 65.5, 63.8, 47.2. **ESI-MS:** calcd for $C_{13}H_{14}BBrINO_5Na$ [M + Na]$^+$: 503.9088, found: 503.9085.

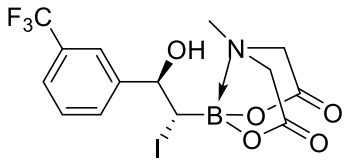
2-(2-(4-fluoro-3-methylphenyl)-2-hydroxy-1-iodoethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4e)



The compound **4e** was obtained in 57% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.46 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.31 – 7.28 (m, 1H), 7.24 –

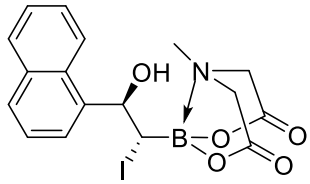
7.20 (m, 1H), 7.00 (t, *J* = 9.1 Hz, 1H), 4.70 (dd, *J* = 9.6, 3.0 Hz, 1H), 4.11 (d, *J* = 16.6 Hz, 1H), 4.09 (d, *J* = 17.2 Hz, 1H), 4.01 (d, *J* = 17.5 Hz, 1H), 3.92 (d, *J* = 16.6 Hz, 1H), 3.84 (d, *J* = 3.1 Hz, 1H), 3.75 (d, *J* = 9.6 Hz, 1H), 3.18 (s, 3H), 2.27 (s, 3H); ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -120.75; ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.9, 168.6, 161.6 (d, *J* = 242.6 Hz), 141.0 (d, *J* = 3.5 Hz), 131.5 (d, *J* = 5.2 Hz), 127.6 (d, *J* = 8.1 Hz), 124.9 (d, *J* = 17.4 Hz), 114.9 (d, *J* = 22.4 Hz), 76.9, 65.6, 63.8, 47.4, 14.6 (d, *J* = 3.7 Hz). **ESI-MS:** calcd for $C_{14}H_{16}BFINO_5Na$ $[M + Na]^+$: 458.0045, found: 458.0046.

2-(2-hydroxy-1-iodo-2-(3-(trifluoromethyl)phenyl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4f)



The compound **4f** was obtained in 87% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.46 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.74 (s, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 1H), 4.83 (dd, *J* = 8.9, 3.3 Hz, 1H), 4.13 – 4.06 (m, 3H), 4.00 (d, *J* = 17.3 Hz, 1H), 3.94 (d, *J* = 16.8 Hz, 1H), 3.80 (d, *J* = 8.9 Hz, 1H), 3.18 (s, 3H); ^{19}F NMR (376 MHz, Acetonitrile-d_3) δ -62.94; ^{13}C NMR (101 MHz, Acetonitrile-d_3) δ 168.8, 168.5, 146.3, 132.4, 130.2 (q, *J* = 31.8 Hz), 129.5, 125.5 (q, *J* = 271.4 Hz), 125.4 (q, *J* = 3.8 Hz), 125.1 (q, *J* = 3.9 Hz), 76.3, 65.4, 63.8, 47.4. **ESI-MS:** calcd for $C_{14}H_{14}BF_3INO_5Na$ $[M + Na]^+$: 493.9857, found: 493.9852.

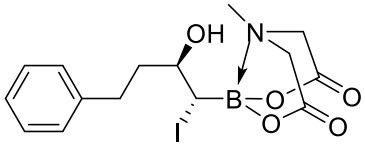
2-(2-hydroxy-1-iodo-2-(naphthalen-1-yl)ethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4g)



The compound **4g** was obtained in 66% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.43 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.25 (d, *J* = 8.5 Hz, 1H), 7.93 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.66 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.59 – 7.49

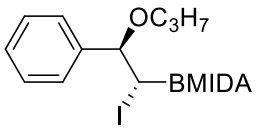
(m, 3H), 6.17 (d, *J* = 3.7 Hz, 1H), 5.46 (dd, *J* = 10.7, 3.4 Hz, 1H), 4.54 (d, *J* = 17.6 Hz, 1H), 4.21 – 4.07 (m, 4H), 3.31 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.6, 168.5, 140.5, 133.3, 130.9, 128.5, 127.8, 125.7, 125.3, 125.2, 124.9, 123.7, 72.7, 64.5, 62.7, 46.8. **ESI-MS:** calcd for $C_{17}H_{17}BINO_5Na$ [M + Na]$^+$: 476.0140, found: 476.0134.

2-(2-hydroxy-1-iodo-4-phenylbutyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4h)



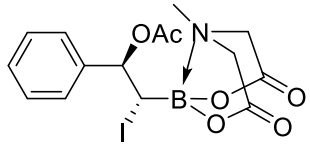
The compound **4h** was obtained in 64% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.30 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.27 – 7.22 (m, 4H), 7.17 – 7.13 (m, 1H), 4.30 – 4.24 (m, 2H), 4.19 – 4.11 (m, 2H), 4.04 (d, *J* = 5.2 Hz, 1H), 3.79 (d, *J* = 4.6 Hz, 1H), 3.42 – 3.39 (m, 1H), 3.29 (s, 3H), 2.94 – 2.86 (m, 1H), 2.74 – 2.65 (m, 1H), 2.14 – 2.05 (m, 1H), 1.90 – 1.80 (m, 1H); ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.3, 168.1, 143.5, 129.3, 129.1, 126.5, 72.1, 64.6, 63.8, 46.5, 39.9, 32.6. **ESI-MS:** calcd for $C_{15}H_{19}BINO_5Na$ [M + Na]$^+$: 454.0296, found: 454.0300.

2-(1-iodo-2-phenyl-2-propoxyethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione（5）



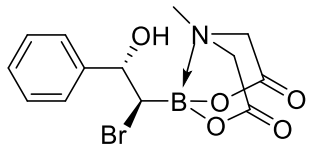
The compound **5** was obtained in 74% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.61 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.43 (d, *J* = 7.1 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.29 (t, *J* = 7.1 Hz, 1H), 4.47 – 4.40 (m, 2H), 4.26 (d, *J* = 16.7 Hz, 1H), 4.23 (d, *J* = 17.3 Hz, 1H), 4.15 (d, *J* = 16.7 Hz, 1H), 3.84 (d, *J* = 9.7 Hz, 1H), 3.46 (s, 3H), 3.26 (dt, *J* = 9.3, 6.5 Hz, 1H), 3.04 (dt, *J* = 9.3, 7.5 Hz, 1H), 1.46 (h, *J* = 7.3 Hz, 2H), 0.75 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.6, 168.3, 142.5, 129.2, 128.8, 128.7, 85.5, 71.5, 65.9, 64.3, 47.8, 23.5, 10.8. **ESI-MS:** calcd for $C_{16}H_{21}BINO_5Na$ [M + Na]$^+$: 468.0453, found: 468.0447.

2-iodo-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-1-phenylethyl acetate (6)



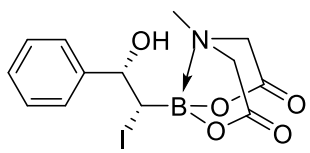
The compound **6** was obtained in 69% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.43 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.47 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.34 – 7.26 (m, 3H), 5.89 (d, *J* = 5.8 Hz, 1H), 4.35 (d, *J* = 17.3 Hz, 1H), 4.27 (d, *J* = 16.9 Hz, 1H), 4.18 (d, *J* = 17.3 Hz, 1H), 4.12 (d, *J* = 16.9 Hz, 1H), 4.09 (d, *J* = 5.9 Hz, 1H), 3.37 (s, 3H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, Acetone-d_6) δ 169.7, 168.1, 167.9, 140.7, 128.8, 128.6, 128.4, 76.1, 64.5, 64.0, 46.6, 21.3. **ESI-MS:** calcd for $C_{15}H_{17}BINO_6Na$ $[M + Na]^+$: 468.0089, found: 468.0095.

2-(1-bromo-2-hydroxy-2-phenylethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (3aa)



The compound **3aa** was obtained in 36% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.25 (t, *J* = 7.1 Hz, 1H), 5.92 (d, *J* = 3.5 Hz, 1H), 4.67 (dd, *J* = 8.4, 3.5 Hz, 1H), 4.39 (d, *J* = 17.4 Hz, 1H), 4.18 (d, *J* = 16.6 Hz, 1H), 4.04 (d, *J* = 17.3 Hz, 1H), 4.02 (d, *J* = 16.6 Hz, 1H), 3.79 (d, *J* = 8.3 Hz, 1H), 3.16 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 168.6, 143.9, 127.5, 127.4, 127.2, 74.7, 63.7, 62.6, 46.4.

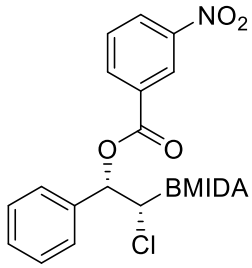
2-(2-hydroxy-1-iodo-2-phenylethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (4aa)



The compound **4aa** was obtained in 51% yield as a yellow solid after recrystallized from EtOAc. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.34 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 5.45 (s, 1H), 4.48 (s, 1H), 4.40 (d, *J* = 17.3 Hz, 1H), 4.24

(d, *J* = 16.9 Hz, 1H), 4.09 (d, *J* = 17.3 Hz, 1H), 4.00 (d, *J* = 16.9 Hz, 1H), 3.69 (s, 1H), 3.12 (s, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 168.7, 168.4, 146.6, 127.5, 126.5, 125.7, 70.8, 62.9, 62.8, 46.3.

2-chloro-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-1-phenylethyl 3-nitrobenzoate (8)



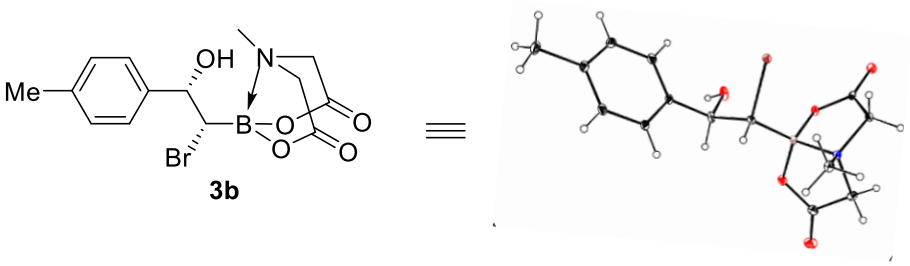
The compound **8** was obtained in 87% yield as a white solid after column chromatography (eluent = Petroleum ether/ acetone 3:1 v/v). R_F = 0.57 (PE:acetone = 1:1). ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.94 (t, *J* = 2.0 Hz, 1H), 8.64 (dt, *J* = 7.8, 1.3 Hz, 1H), 8.53 (ddd, *J* = 8.3, 2.4, 1.1 Hz, 1H), 7.89 (t, *J* = 8.0 Hz, 1H), 7.48 – 7.46 (m, 2H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.33 – 7.29 (m, 1H), 6.62 (d, *J* = 3.0 Hz, 1H), 4.37 (d, *J* = 17.3 Hz, 1H), 4.29 (d, *J* = 16.7 Hz, 1H), 4.20 (d, *J* = 3.0 Hz, 1H), 4.17 (d, *J* = 17.2 Hz, 1H), 4.16 (d, *J* = 16.6 Hz, 1H), 3.35 (s, 3H); ^{13}C NMR (101 MHz, Acetone-d_6) δ 168.6, 168.0, 164.1, 149.5, 139.9, 136.7, 132.9, 131.2, 129.1, 128.8, 128.6, 127.3, 125.4, 77.5, 63.9, 63.6 46.6. **ESI-MS:** calcd for $C_{20}H_{18}BClN_2O_8Na$ $[M + Na]^+$: 483.0741, found: 483.0740.

9. X-ray crystal structure data of compounds 3b and 4e

X-ray crystallographic data of compound 3b (CCDC: 1956104)

Crystal data for **3b**: chemical formula weight$_{370.02}$, *M* = 370.02, colourless needle, 0.4 × 0.05 × 0.05 mm^3, space group *C* 1 2/*c* 1 (No. 15), *V* = 3041.05(13) Å^3, *Z* = 8, D_c = 1.6162 g/cm^3, F_{000} = 1503.0215, Xcalibur, Onyx, Nova, Cu Kα radiation, λ = 1.54184 Å, *T* = 100K, $2\theta_{max}$ = 134.1º, 6092 reflections collected, 2719 unique (R_{int} = 0.0243). The structure was solved and refined using the programs XS (Sheldrick, 2008) and olex2.refine (Bourhis et al., 2015) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and to prepare the figures. Final *GooF* = 1.0609, *R1* = 0.0276, *wR2* = 0.0740, *R* indices based on 2563 reflections with

I I>=2u(I) (refinement on F^2), 202 parameters, 0 restraints. Lp and absorption corrections applied, μ = 3.894 mm^{-1}.



3b

Table 1 Crystal data and structure refinement for compound 3b.

Identification code	compound **3b**
Empirical formula	$C_{17.88}H_{16.25}N_{1.63}O_{1.63}Br_{1.63}B_{1.63}$
Formula weight	370.02
Temperature/K	100
Crystal system	monoclinic
Space group	C2/c
a/Å	21.4754(5)
b/Å	6.47129(11)
c/Å	24.0236(6)
α/°	90
β/°	114.374(3)
γ/°	90
Volume/Å^3	3041.05(13)
Z	8
ρ_{calc}g/cm^3	1.6162
μ/mm^{-1}	3.894
F(000)	1503.0
Crystal size/mm^3	0.4 × 0.05 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.08 to 134.14
Index ranges	-25 ≤ h ≤ 24, -7 ≤ k ≤ 7, -18 ≤ l ≤ 28
Reflections collected	6092
Independent reflections	2719 [R_{int} = 0.0243, R_{sigma} = 0.0255]
Data/restraints/parameters	2719/0/202
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0276, wR_2 = 0.0740
Final R indexes [all data]	R_1 = 0.0292, wR_2 = 0.0753
Largest diff. peak/hole / e Å^{-3}	0.45/-0.57

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for compound 3b. Ueq is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Br1	528.97(10)	7350.8(3)	381.88(9)	16.41(10)
O1	2135.6(8)	7175(2)	1210.0(6)	17.2(3)
O2	2427.1(7)	4623(2)	611.0(6)	20.6(3)
O3	2086.3(8)	8248(3)	2076.3(7)	24.7(3)
O5	1683.4(8)	9163(3)	-2.8(7)	27.9(4)
O6	3244.2(9)	2210(3)	939.6(9)	34.5(4)
N7	1785.6(8)	3648(3)	1199.9(7)	14.3(3)
C8	2762.5(11)	3055(4)	971.1(10)	21.6(4)
C9	1215.5(10)	5983(3)	151.7(9)	16.4(4)
C10	1993.7(10)	6926(3)	1691.0(9)	17.0(4)
C11	439.7(12)	9676(4)	-1049.2(10)	24.1(5)
C12	1219.9(11)	2142(3)	900.6(10)	19.0(4)
C13	1360.8(12)	7315(3)	-308(1)	20.0(5)
C14	-430.1(11)	8384(4)	-2003.2(9)	23.9(5)
C15	-130.2(12)	9988(4)	-1596.3(10)	26.7(5)
C16	434.6(10)	6100(3)	-1300.5(9)	18.8(4)
C17	-134.4(11)	6426(4)	-1842.4(9)	21.4(5)
C18	1698.3(10)	4818(3)	1697.3(9)	17.1(4)
C19	727.6(12)	7722(3)	-896.2(10)	18.8(5)
C20	-1046.8(12)	8738(5)	-2596.6(10)	33.6(6)
C21	2462.6(12)	2538(3)	1421.4(11)	20.4(5)
B22	1879.7(11)	5461(4)	761.4(10)	15.6(4)

Table 3 Anisotropic Displacement Parameters (Å2×10^3) for 3b. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Br1	15.71(15)	18.59(15)	14.37(15)	-0.64(7)	5.64(11)	-0.59(7)
O1	18.9(8)	18.4(7)	12.4(7)	-3.5(6)	4.7(6)	-0.8(5)
O2	18.3(7)	28.4(8)	17.7(7)	0.9(6)	10.0(6)	0.7(6)
O3	31.1(8)	22.1(8)	16.4(7)	0.3(7)	5.3(7)	-5.5(6)
O5	35.6(9)	31.5(9)	17.7(7)	-16.3(7)	11.9(7)	-0.5(6)
O6	24.1(9)	43.5(11)	39.7(11)	8.9(8)	17.0(9)	-1.6(8)
N7	14.0(8)	14.3(8)	13.8(8)	-0.9(7)	4.9(7)	-0.6(6)
C8	16.2(10)	25.1(11)	21.0(11)	-0.9(9)	5.2(9)	-4.5(9)
C9	18(1)	18(1)	14.3(9)	0.6(8)	7.6(8)	-0.7(8)
C10	15.1(10)	20.2(10)	11.5(10)	3.3(8)	1.3(8)	2.5(8)
C11	32.9(12)	23.6(11)	19.7(11)	1.8(10)	14.7(10)	1.9(9)
C12	16.7(11)	19.1(10)	17.5(11)	-5.9(9)	3.5(9)	-1.0(8)
C13	21.0(11)	26.3(12)	12.8(10)	-3.7(8)	7.0(9)	-0.7(8)
C14	19.4(11)	39.4(14)	17.1(10)	6.7(10)	11.7(9)	7.3(10)
C15	33.4(12)	28.2(12)	23.4(11)	11.7(10)	16.7(10)	10.3(9)
C16	20.4(10)	23.1(11)	14.9(10)	2.4(9)	9.4(8)	2.4(8)
C17	20.5(10)	32.1(13)	13.9(10)	0.4(9)	9.5(9)	0.9(9)
C18	18.8(10)	20.5(10)	12.1(9)	1.0(8)	6.5(8)	-0.2(8)
C19	21.1(11)	25.1(11)	13.3(10)	1.9(8)	10.2(9)	4.5(8)
C20	25.4(12)	57.1(17)	19.1(11)	14.5(12)	9.9(10)	13.7(11)
C21	17.2(11)	19.8(11)	21.7(12)	2.3(8)	5.6(10)	1.9(8)
B22	15(1)	18.5(11)	14(1)	-2.1(9)	6.8(9)	-0.3(9)

Table 4 Bond Lengths for 3b.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Br1	C9	1.9841(19)	C8	C21	1.507(3)
O1	C10	1.321(3)	C9	C13	1.531(3)
O1	B22	1.485(3)	C9	B22	1.603(3)
O2	C8	1.335(3)	C10	C18	1.508(3)
O2	B22	1.469(2)	C11	C15	1.392(3)
O3	C10	1.215(3)	C11	C19	1.389(3)
O5	C13	1.424(3)	C13	C19	1.526(3)
O6	C8	1.200(3)	C14	C15	1.389(4)
N7	C12	1.490(3)	C14	C17	1.398(4)
N7	C18	1.490(2)	C14	C20	1.510(3)
N7	C21	1.508(3)	C16	C17	1.385(3)
N7	B22	1.644(3)	C16	C19	1.391(3)

Table 5 Bond Angles for 3b.

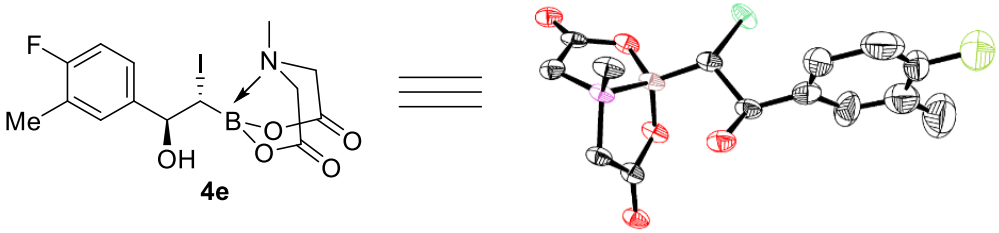
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
B22	O1	C10	113.21(16)	C19	C13	O5	112.96(18)
B22	O2	C8	113.19(16)	C19	C13	C9	113.33(18)
C18	N7	C12	111.81(15)	C17	C14	C15	117.2(2)
C21	N7	C12	109.52(16)	C20	C14	C15	121.5(2)
C21	N7	C18	112.39(15)	C20	C14	C17	121.3(2)
B22	N7	C12	116.66(15)	C14	C15	C11	121.9(2)
B22	N7	C18	103.93(14)	C19	C16	C17	120.7(2)
B22	N7	C21	102.15(14)	C16	C17	C14	121.4(2)
O6	C8	O2	123.7(2)	C10	C18	N7	105.01(15)
C21	C8	O2	110.95(17)	C13	C19	C11	122.1(2)
C21	C8	O6	125.4(2)	C16	C19	C11	118.6(2)
C13	C9	Br1	110.23(14)	C16	C19	C13	119.31(19)
B22	C9	Br1	108.82(12)	C8	C21	N7	106.05(17)
B22	C9	C13	114.09(17)	O2	B22	O1	111.11(16)
O3	C10	O1	123.8(2)	N7	B22	O1	100.05(14)
C18	C10	O1	111.65(17)	N7	B22	O2	102.51(16)
C18	C10	O3	124.54(19)	C9	B22	O1	115.42(17)
C19	C11	C15	120.2(2)	C9	B22	O2	110.71(15)
C9	C13	O5	107.57(16)	C9	B22	N7	115.94(16)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3b.

Atom	*x*	*y*	*z*	U(eq)
H16	626.9(10)	4755(3)	-1203.9(9)	22.5(5)
H17	-328.0(11)	5294(4)	-2110.4(9)	25.7(6)
H15	-319.2(12)	11336(4)	-1693.9(10)	32.0(6)
H11	632.4(12)	10804(4)	-779.6(10)	29.0(6)
H5	1882(13)	9730(20)	-198(7)	41.9(6)
H9	1016(1)	4646(3)	-52.9(9)	19.7(5)
H12a	1221(5)	1116(14)	1201.2(19)	28.4(7)
H12b	781.6(13)	2876(5)	737(6)	28.4(7)
H12c	1285(4)	1444(17)	566(5)	28.4(7)
H13	1697.2(12)	6552(3)	-420.6(10)	24.1(6)
H18a	1208.8(10)	4921(3)	1617.5(9)	20.5(5)
H18b	1946.9(10)	4133(3)	2096.9(9)	20.5(5)
H20c	-1416(4)	9350(30)	-2511.1(12)	50.5(9)
H20b	-925(3)	9680(20)	-2856(4)	50.5(9)
H20a	-1200(6)	7416(6)	-2808(4)	50.5(9)
H21a	2769.0(12)	3014(3)	1836.4(11)	24.4(6)
H21b	2396.1(12)	1028(3)	1433.9(11)	24.4(6)

X-ray crystallographic data of compound 4e (CCDC: 1526446)

Crystal data for **4e**: chemical formula weight$_{493.09}$, M = 0.4 × 0.3 × 0.2 mm^3, space group P 1 2$_1$/c 1 (No. 14), V = 1992.86(7) Å^3, Z = 4, D_c = 1.6433 g/cm^3, F_{000} = 986.6074, Xcalibur, Onyx, Nova, Cu Kα radiation, λ = 1.54184 Å, T =103 K, 2θ_{max} = 134.2º, 7761 reflections collected, 3447 unique (R_{int} = 0.0629). The structure was solved and refined using the programs SIR2008 (Burla et al., 2007) and olex2.refine (Bourhis et al., 2015) respectively. The program X-Seed (Barbour, 1999) was used as an interface to the SHELX programs, and to prepare the figures. Final *GooF* = 1.0517, *R1* = 0.0806, *wR2* = 0.2272, *R* indices based on 3147 reflections with I I>=2u(I) (refinement on F^2), 248 parameters, 0 restraints. Lp and absorption corrections applied, μ = 13.004 mm^{-1}.



4e

Table 1 Crystal data and structure refinement for compound 4e.

Identification code	Compound **4e**
Empirical formula	$C_{17}H_{22}NO_6IFB$
Formula weight	493.09
Temperature/K	N/A
Crystal system	monoclinic
Space group	P21/c
a/Å	17.3516(3)
b/Å	11.2310(2)
c/Å	10.6444(2)
α/°	90
β/°	106.1114(19)
γ/°	90
Volume/Å3	1992.86(7)
Z	4
ρcalcg/cm3	1.6433
μ/mm‑1	13.004
F(000)	986.6
Crystal size/mm3	0.4 × 0.3 × 0.2
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.3 to 134.16
Index ranges	-18 ≤ h ≤ 20, -10 ≤ k ≤ 13, -12 ≤ l ≤ 11
Reflections collected	7761
Independent reflections	3447 [Rint = 0.0629, Rsigma = 0.0540]
Data/restraints/parameters	3447/0/248
Goodness-of-fit on F2	1.052
Final R indexes [I>=2σ (I)]	R1 = 0.0806, wR2 = 0.2272
Final R indexes [all data]	R1 = 0.0844, wR2 = 0.2355
Largest diff. peak/hole / e Å-3	3.60/-1.75

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for compound 4e. Ueq is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
I1	6798.7(3)	7161.2(4)	10111.0(5)	46.3(3)
O1	3938(3)	5537(5)	8394(5)	41.0(12)
O2	5238(3)	5806(4)	8555(4)	35.5(10)
O3	5885(3)	5642(4)	6832(4)	35.6(11)
O4	7384(3)	4182(5)	8005(5)	42.4(12)
C5	5692(5)	3573(6)	6570(6)	32.6(14)
O6	5915(3)	4863(4)	4901(4)	39.4(11)
N7	5576(3)	3856(4)	7884(5)	28.7(11)
C8	9460(9)	6853(15)	9945(13)	83(3)
C9	6762(4)	5427(6)	9195(6)	32.6(14)
C10	4561(4)	5165(6)	8286(6)	32.9(15)
C11	5991(5)	2945(6)	8890(7)	36.8(16)
O12	7822(5)	11458(8)	10812(7)	80(2)
C13	5842(4)	4744(6)	5993(6)	32.3(14)
C14	4709(4)	3929(6)	7836(7)	34.0(14)
F15	10501(5)	6349(10)	11830(8)	113(3)
C16	7457(5)	5343(7)	8576(7)	39.7(16)
C17	8270(6)	5537(10)	9474(10)	60(2)
C18	7891(7)	11170(20)	8643(11)	107(6)
C19	8709(7)	6550(12)	9227(15)	84(4)
C20	8009(5)	10845(10)	10002(8)	54(2)
C21	8551(6)	4795(14)	10480(10)	75(4)
C22	9714(5)	6128(10)	10994(10)	60(2)
C23	9365(9)	5106(15)	11335(12)	92(4)
B24	5902(5)	5243(6)	8161(7)	31.7(16)
C25	8419(18)	9722(13)	10440(20)	148(10)
C2	9914(12)	7851(19)	9680(20)	128(8)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 4e. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^*2U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
I1	50.7(5)	38.1(4)	41.4(4)	7.89(17)	-1.5(3)	-17.31(17)
O1	56(3)	35(3)	37(3)	9(2)	20(2)	-1(2)
O2	51(3)	24(2)	30(2)	8.4(19)	8(2)	-3.5(18)
O3	60(3)	17(2)	26(2)	4.5(19)	6(2)	2.1(17)
O4	54(3)	38(3)	40(3)	4(2)	21(2)	-6(2)
C5	50(4)	24(3)	25(3)	2(3)	12(3)	-3(2)
O6	65(3)	31(2)	22(2)	-5(2)	12(2)	2.8(19)
N7	46(3)	19(2)	19(2)	5(2)	5(2)	0.9(19)
C8	82(8)	100(9)	69(7)	8(7)	25(6)	-6(7)
C9	49(4)	21(3)	28(3)	4(3)	12(3)	-2(2)
C10	57(4)	25(3)	18(3)	7(3)	12(3)	3(2)
C11	64(5)	22(3)	24(3)	8(3)	12(3)	6(2)
O12	100(6)	94(6)	63(4)	40(5)	48(4)	31(4)
C13	45(4)	22(3)	28(3)	1(3)	7(3)	1(2)
C14	51(4)	23(3)	32(3)	0(3)	19(3)	3(3)
F15	72(5)	158(9)	108(6)	-11(5)	23(4)	-36(6)
C16	55(4)	34(4)	32(3)	-2(3)	17(3)	-10(3)
C17	57(5)	76(6)	56(5)	-3(4)	30(4)	-30(5)
C18	62(7)	210(19)	48(6)	52(9)	15(5)	31(8)
C19	59(6)	82(8)	120(10)	-28(6)	39(7)	-50(8)
C20	36(4)	76(6)	49(5)	-15(4)	12(3)	-1(4)
C21	43(5)	129(11)	52(5)	9(6)	11(4)	-14(6)
C22	44(5)	71(6)	64(6)	-10(4)	13(4)	-14(5)
C23	101(9)	124(12)	55(6)	23(9)	30(6)	-6(7)
B24	56(5)	16(3)	23(3)	4(3)	11(3)	-1(3)
C25	300(30)	46(7)	156(16)	1(11)	150(20)	4(9)
C2	87(12)	160(20)	132(17)	-28(11)	22(11)	22(12)

Table 4 Bond Lengths for 4e.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	C9	2.171(6)	C8	C22	1.353(19)
O1	C10	1.193(9)	C8	C2	1.44(2)
O2	C10	1.339(9)	C9	C16	1.530(10)
O2	B24	1.475(9)	C9	B24	1.602(11)
O3	C13	1.335(8)	C10	C14	1.514(9)
O3	B24	1.476(8)	O12	C20	1.215(12)
O4	C16	1.429(9)	F15	C22	1.430(12)
C5	N7	1.501(8)	C16	C17	1.485(13)
C5	C13	1.505(9)	C17	C19	1.433(16)
O6	C13	1.211(8)	C17	C21	1.338(17)
N7	C11	1.510(8)	C18	C20	1.450(14)
N7	C14	1.494(9)	C20	C25	1.46(2)
N7	B24	1.656(9)	C21	C23	1.494(18)
C8	C19	1.358(19)	C22	C23	1.391(19)

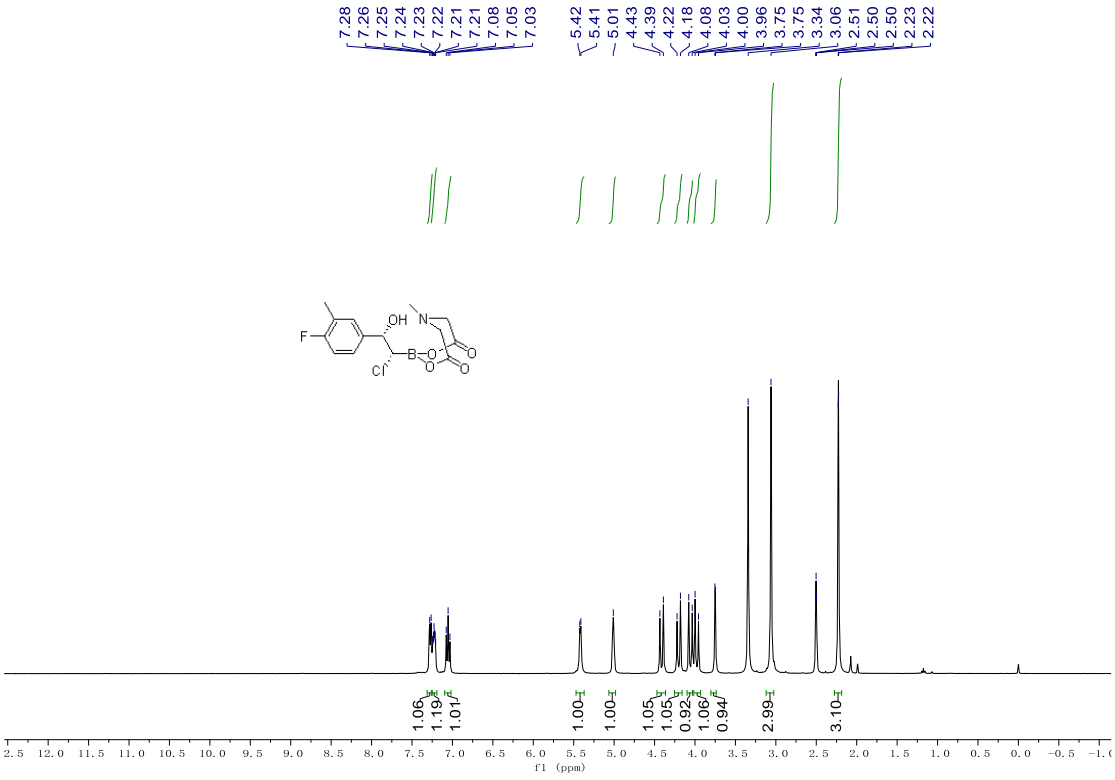
Table 5 Bond Angles for 4e.

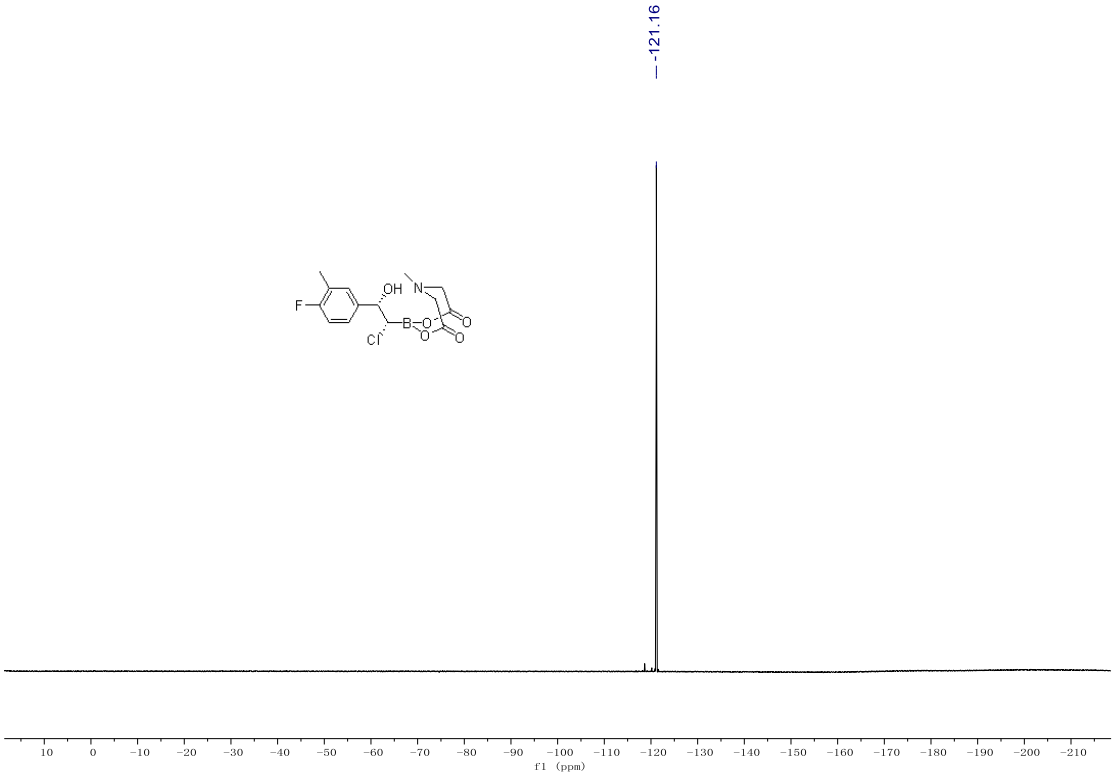
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
B24	O2	C10	114.7(5)	C9	C16	O4	104.5(6)
B24	O3	C13	113.2(5)	C17	C16	O4	111.4(7)
C13	C5	N7	106.2(5)	C17	C16	C9	115.9(6)
C11	N7	C5	110.9(5)	C19	C17	C16	117.2(11)
C14	N7	C5	111.9(5)	C21	C17	C16	119.6(10)
C14	N7	C11	109.9(5)	C21	C17	C19	123.2(11)
B24	N7	C5	103.7(5)	C17	C19	C8	124.8(15)
B24	N7	C11	116.0(5)	C18	C20	O12	124.9(11)
B24	N7	C14	104.2(5)	C25	C20	O12	117.8(11)
C22	C8	C19	110.8(14)	C25	C20	C18	117.2(12)
C2	C8	C19	125.1(16)	C23	C21	C17	114.5(13)
C2	C8	C22	124.0(15)	F15	C22	C8	116.4(11)
C16	C9	I1	108.7(5)	C23	C22	C8	130.2(11)
B24	C9	I1	109.3(4)	C23	C22	F15	113.0(11)
B24	C9	C16	113.0(5)	C22	C23	C21	116.1(12)
O2	C10	O1	123.8(6)	O3	B24	O2	109.5(5)
C14	C10	O1	126.1(7)	N7	B24	O2	101.5(5)
C14	C10	O2	110.2(6)	N7	B24	O3	101.5(5)
C5	C13	O3	111.8(5)	C9	B24	O2	113.7(5)
O6	C13	O3	123.8(6)	C9	B24	O3	112.7(6)
O6	C13	C5	124.4(6)	C9	B24	N7	116.8(5)
C10	C14	N7	107.3(6)				

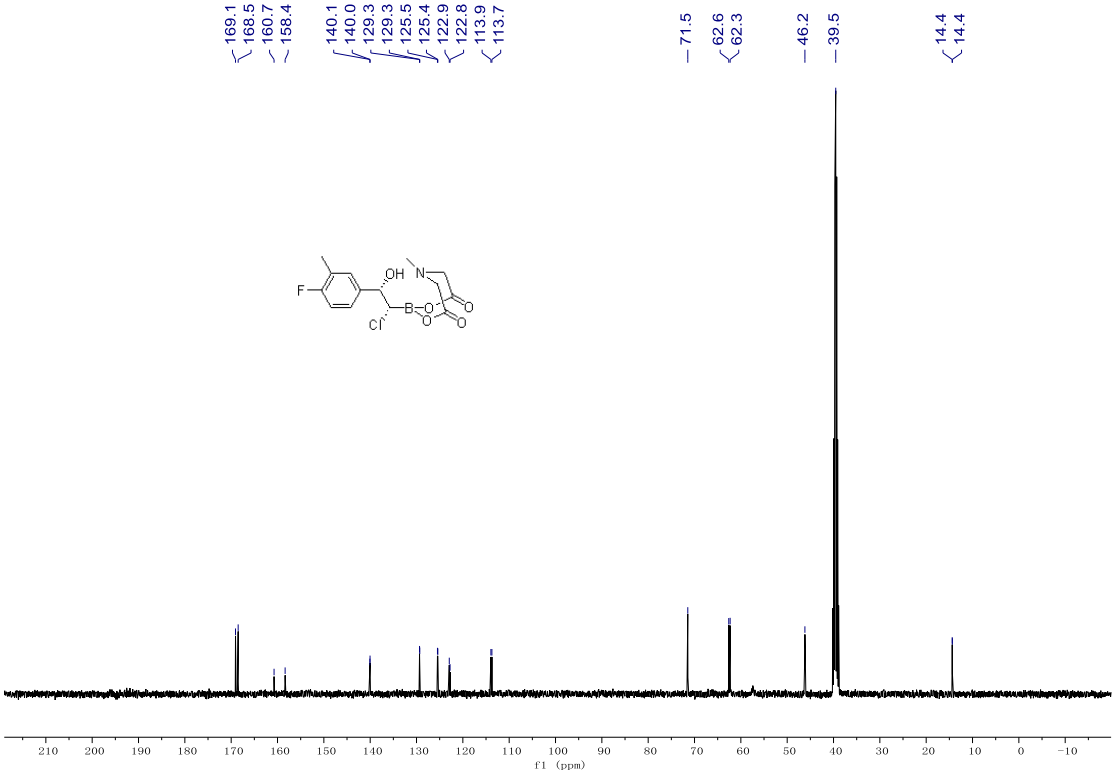
Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 4e.

Atom	*x*	*y*	*z*	U(eq)
H21	8264(6)	4139(14)	10636(10)	90(4)
H23	9624(9)	4644(15)	12052(12)	110(5)
H19	8461(7)	7036(12)	8523(15)	101(5)
H4	7410(60)	4230(12)	7250(30)	63.7(18)
H5a	6146(5)	3042(6)	6663(6)	39.2(17)
H5b	5217(5)	3192(6)	6015(6)	39.2(17)
H9	6834(4)	4813(6)	9872(6)	39.1(17)
H11b	5760(30)	2175(11)	8640(30)	55(2)
H11a	6552(8)	2920(40)	8940(40)	55(2)
H11c	5930(30)	3160(30)	9728(14)	55(2)
H14a	4377(4)	3792(6)	6951(7)	40.8(17)
H14b	4579(4)	3333(6)	8404(7)	40.8(17)
H16	7369(5)	5931(7)	7871(7)	47.7(19)
H18a	7460(60)	10710(90)	8100(16)	160(9)
H18b	7760(90)	12000(30)	8530(30)	160(9)
H18c	8380(30)	11030(130)	8400(40)	160(9)
H25a	8830(90)	9600(100)	10000(170)	222(15)
H25b	8660(120)	9750(80)	11360(40)	222(15)
H25c	8040(30)	9080(30)	10200(200)	222(15)
H2a	10420(40)	7580(30)	9610(170)	193(11)
H2b	9620(50)	8220(100)	8870(90)	193(11)
H2c	10000(90)	8420(80)	10380(90)	193(11)

10.NMR spectrum of products



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O
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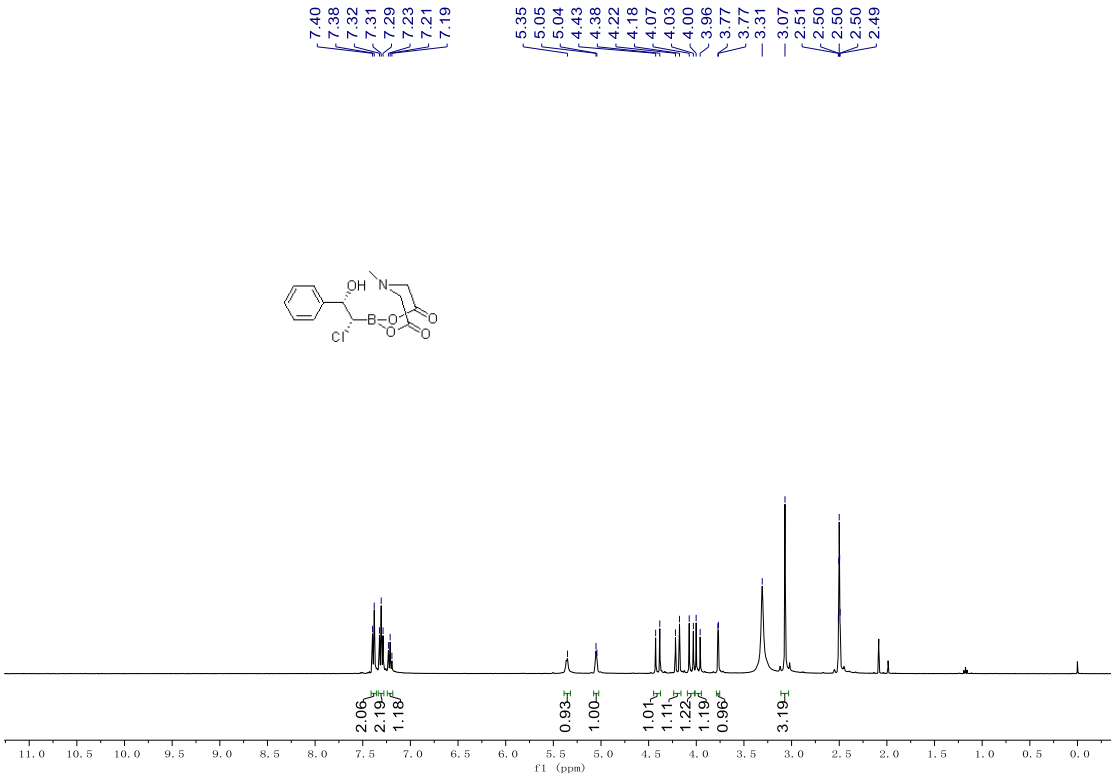
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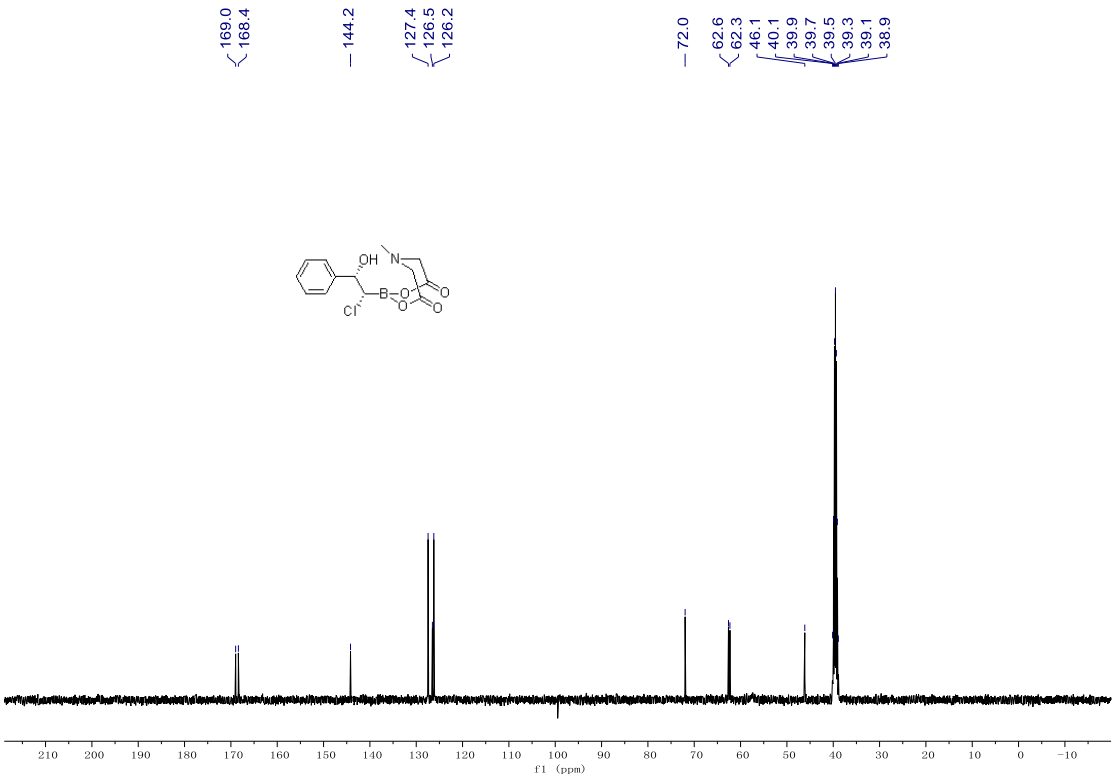
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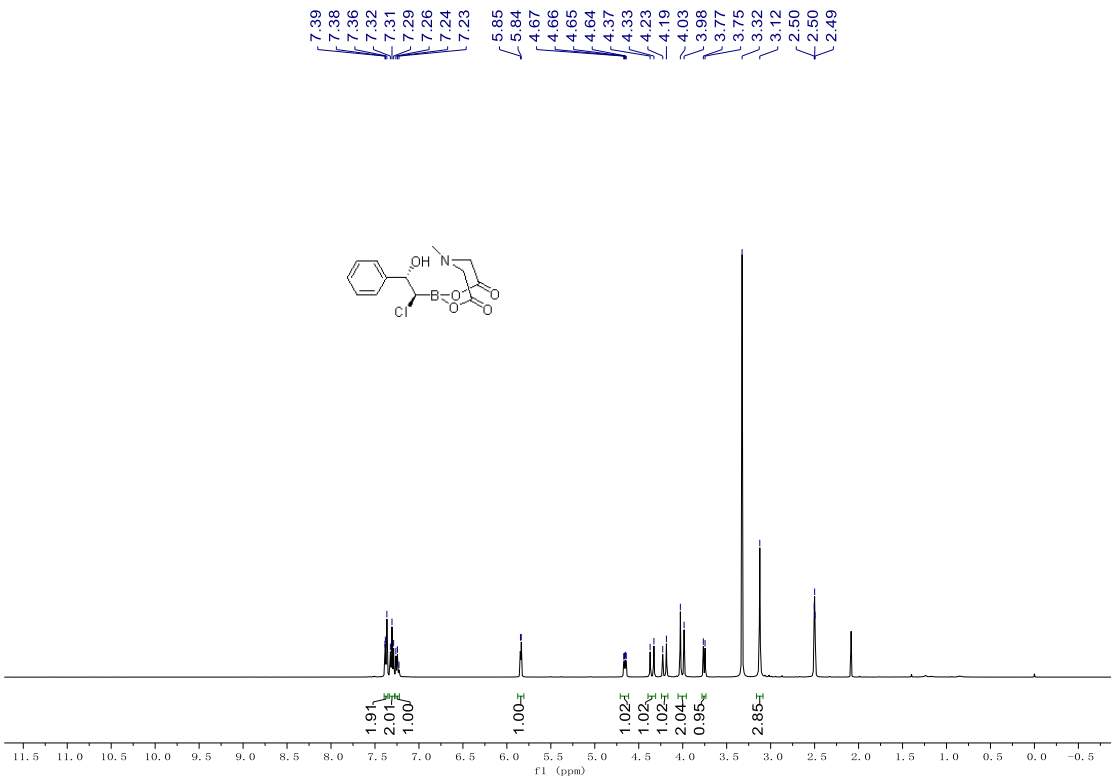
O
Cl
f1 (ppm)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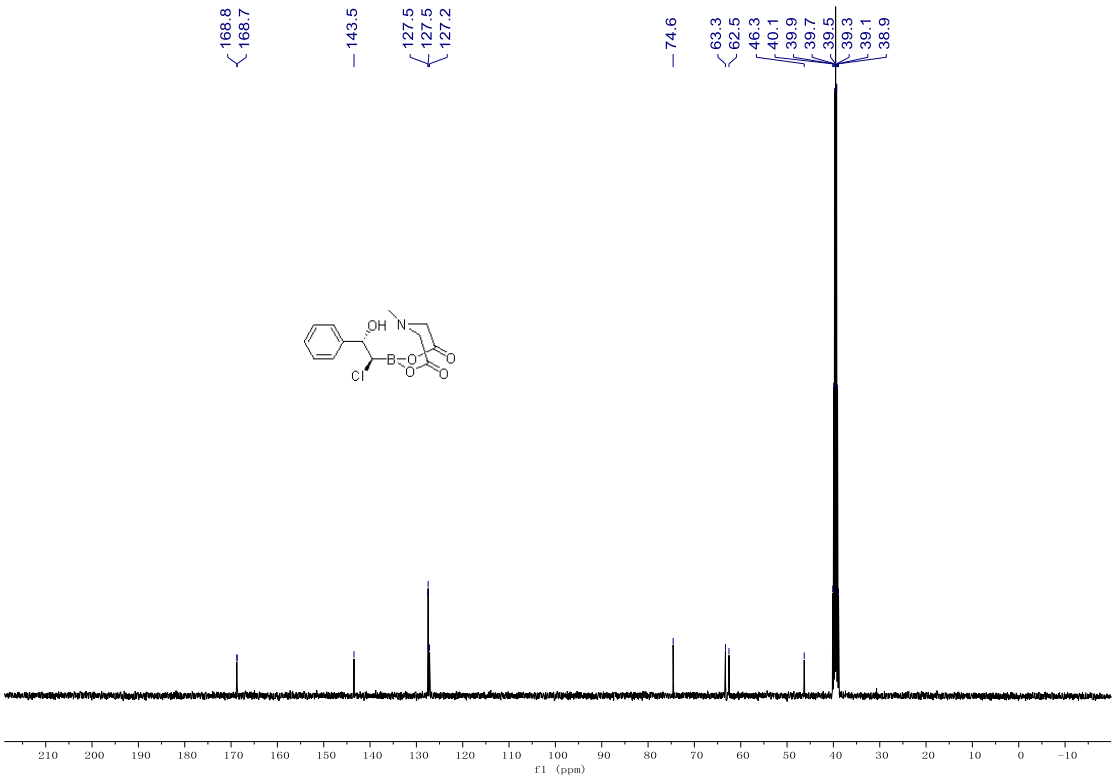
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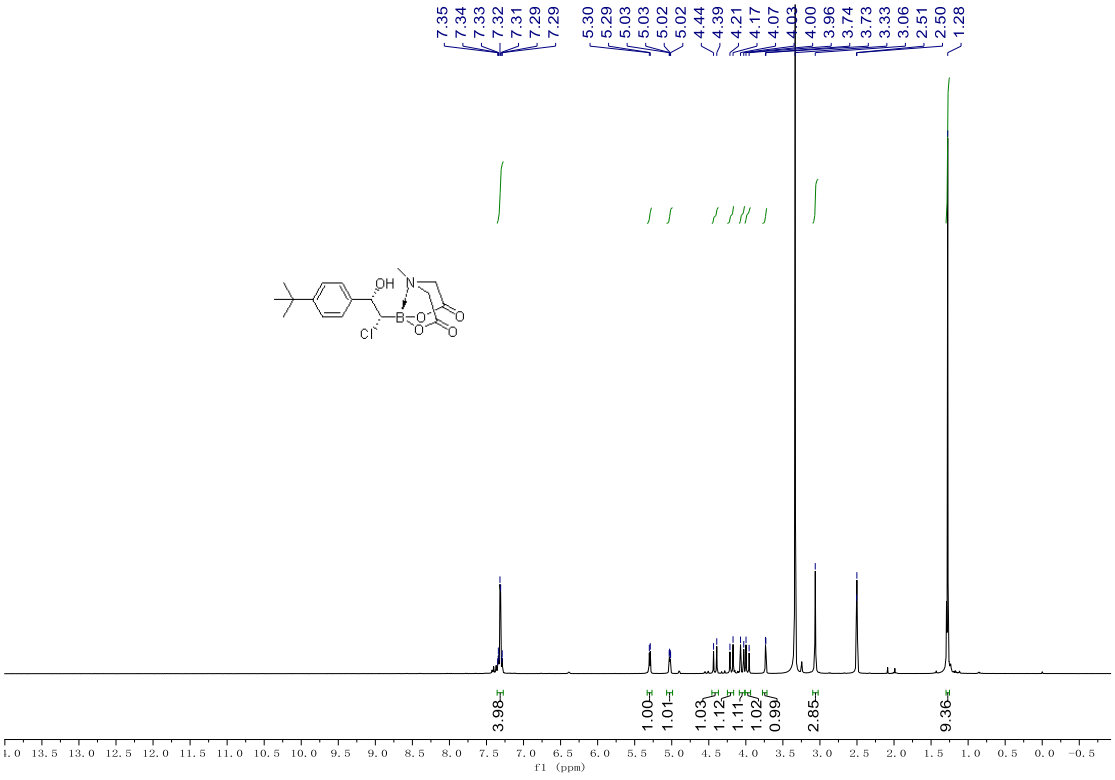
B
O
O
O
O
Cl
f1 (ppm)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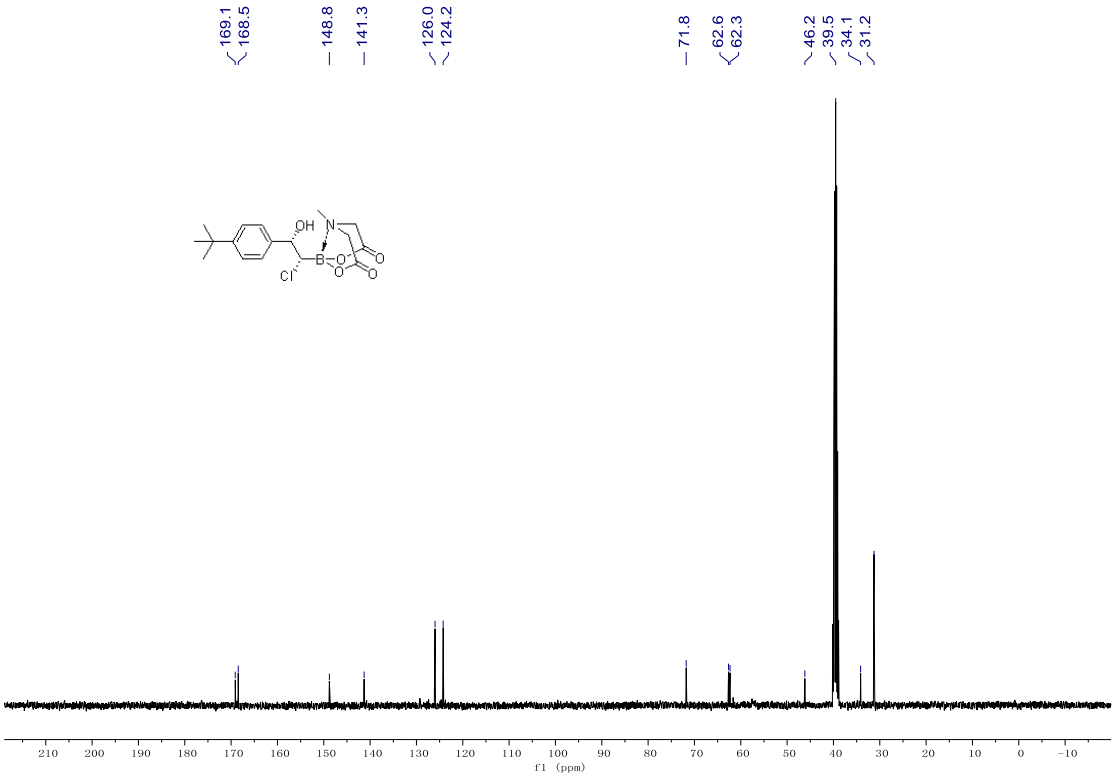
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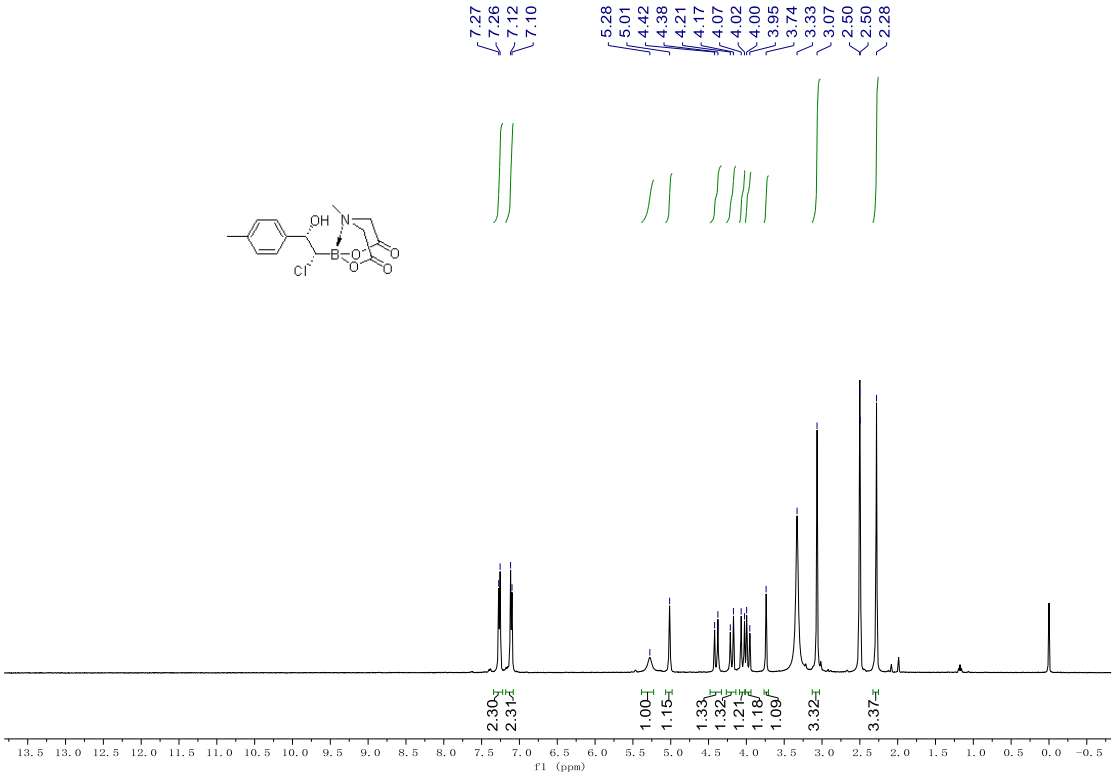
Cl
f1 (ppm)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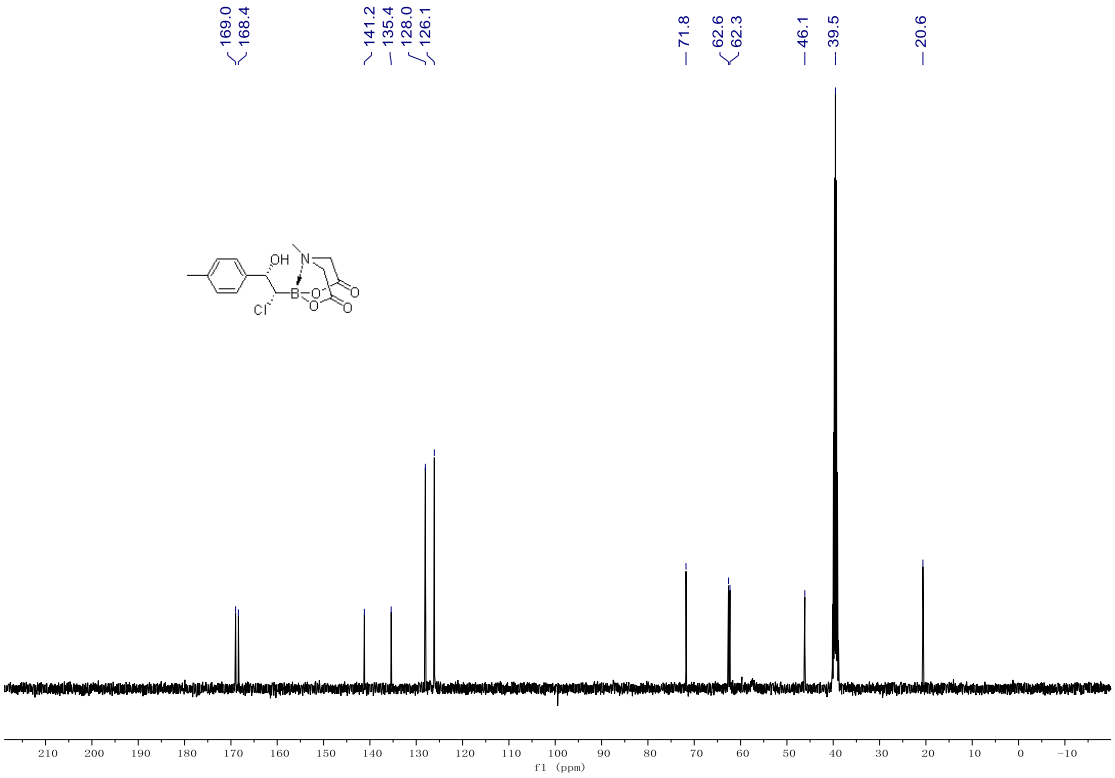
f1 (ppm)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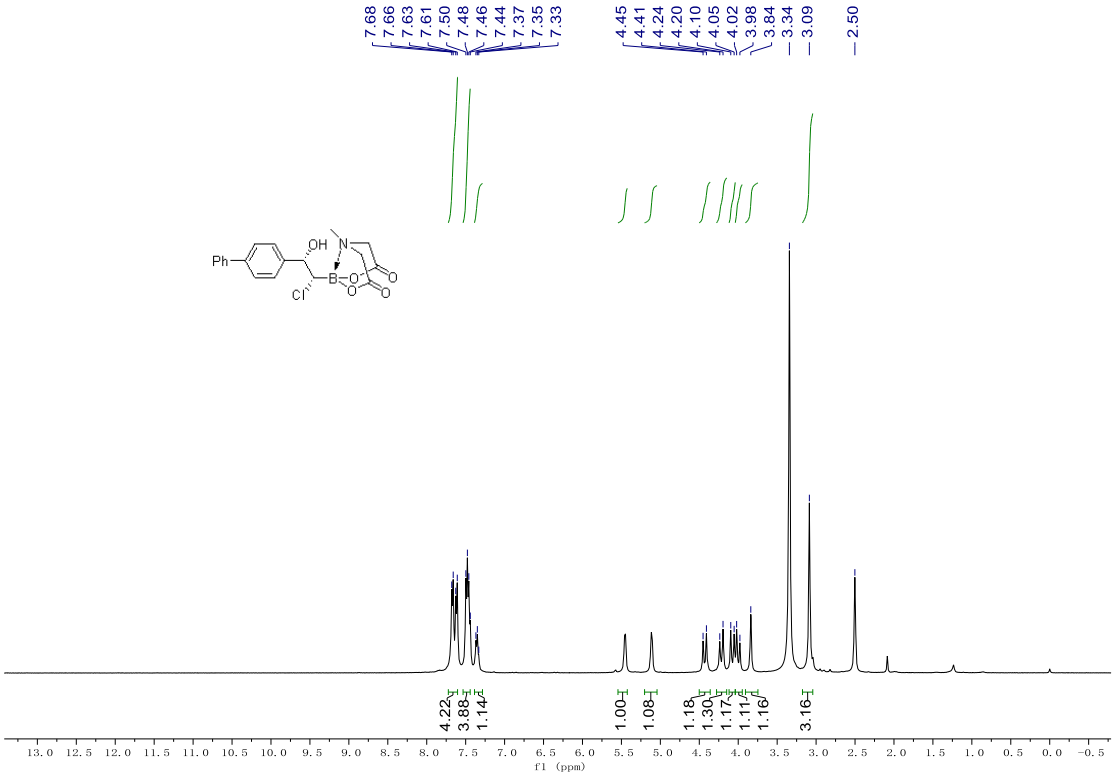
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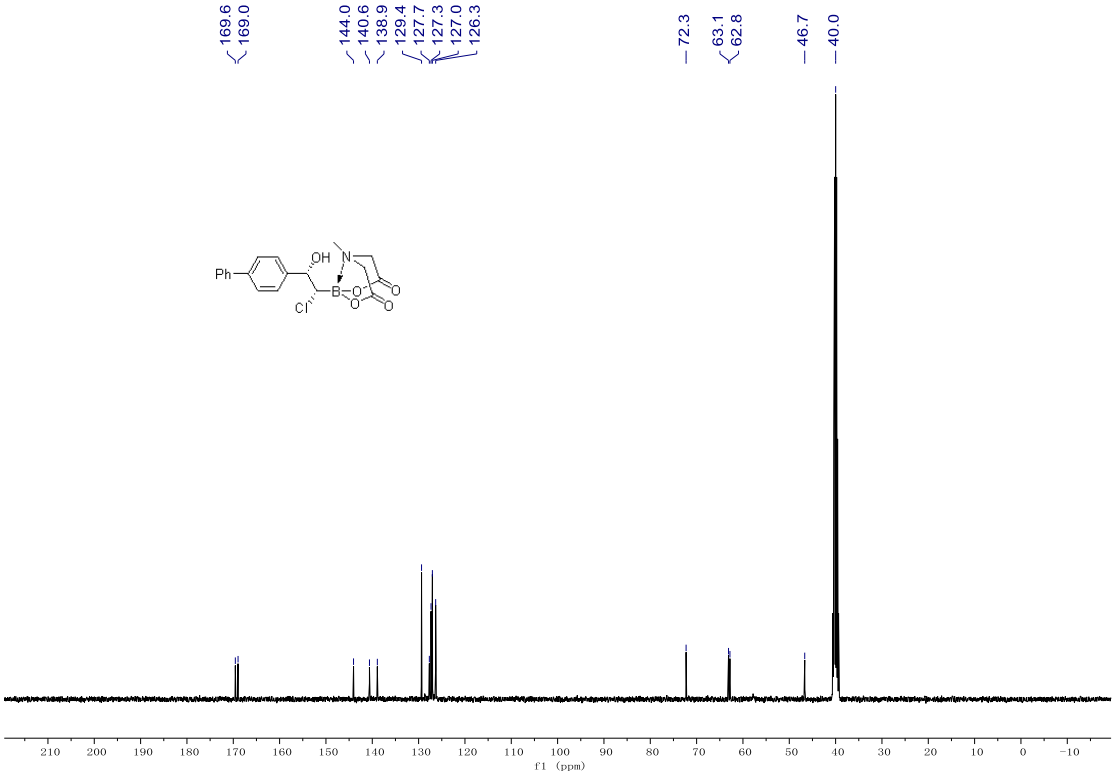
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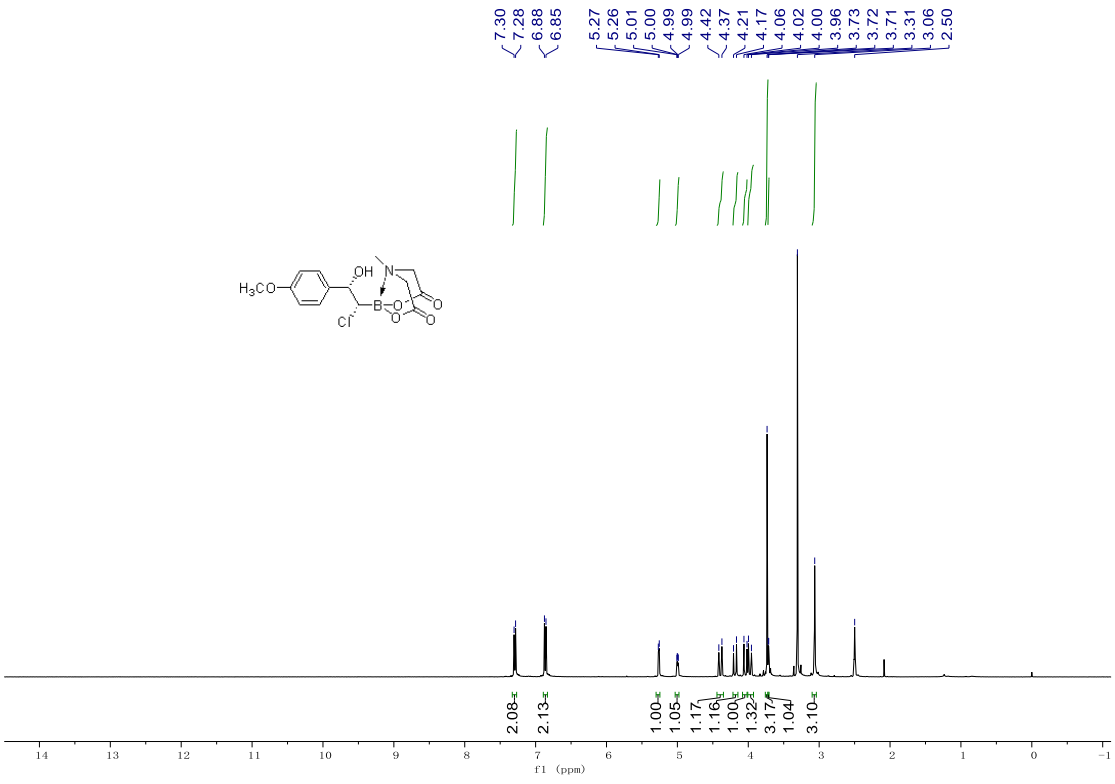
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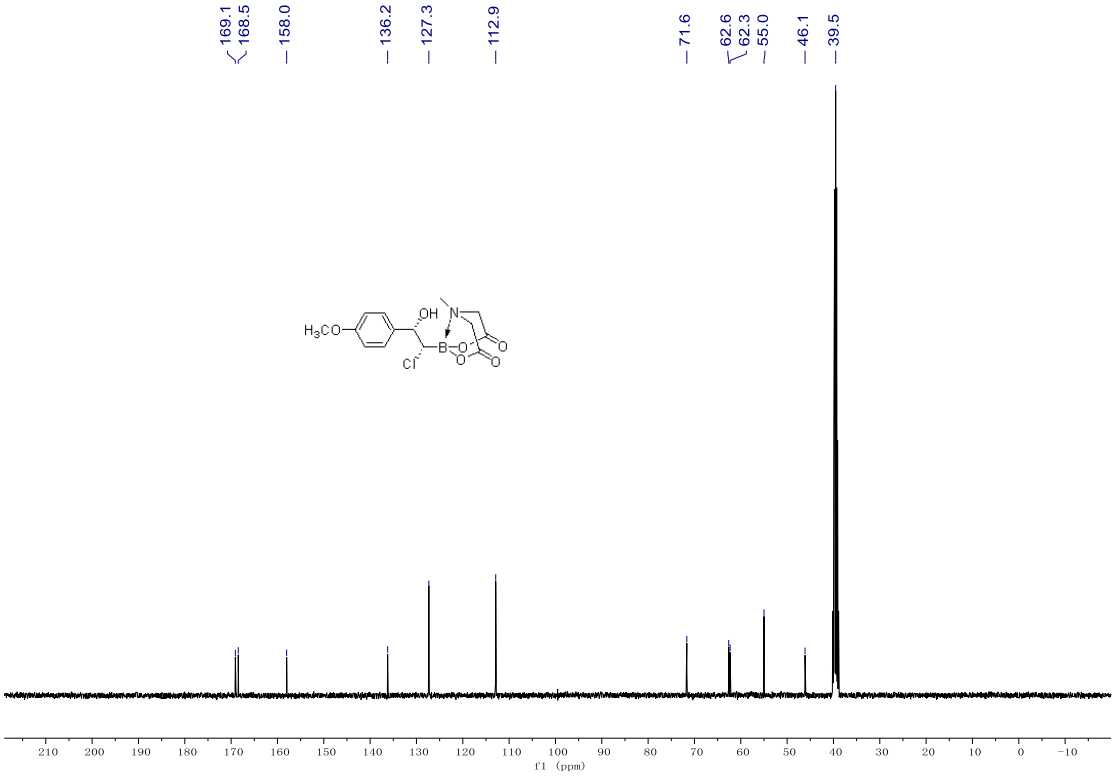
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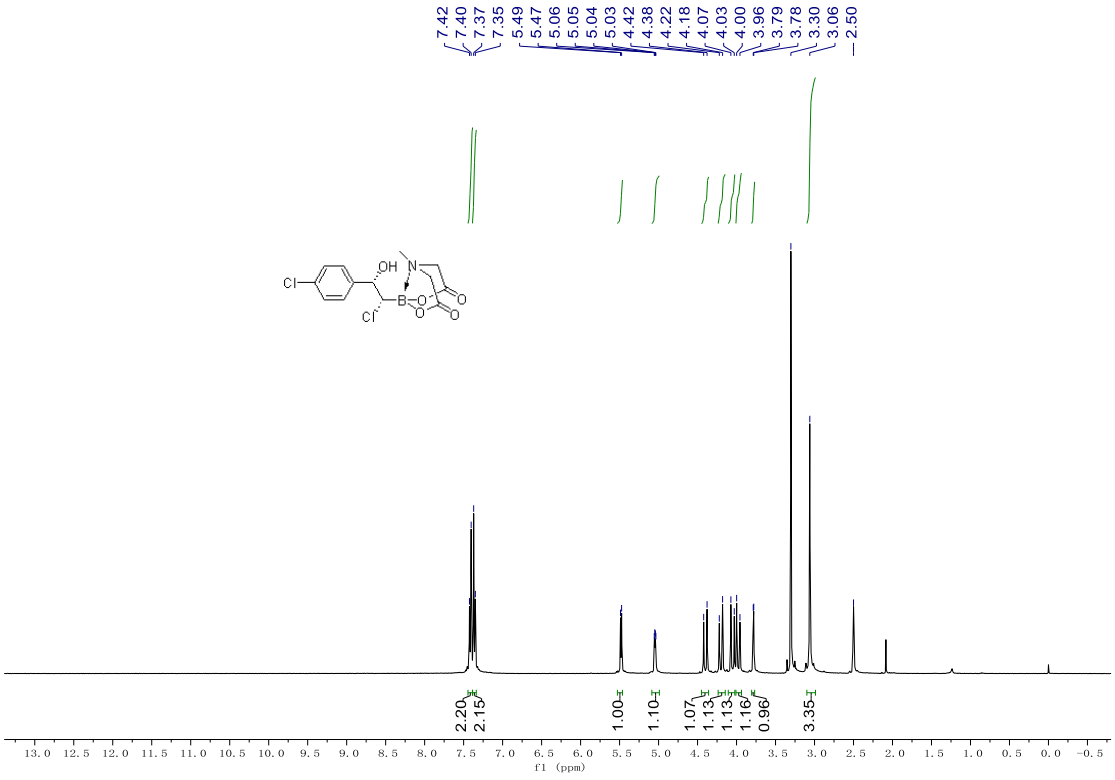
Cl
f1 (ppm)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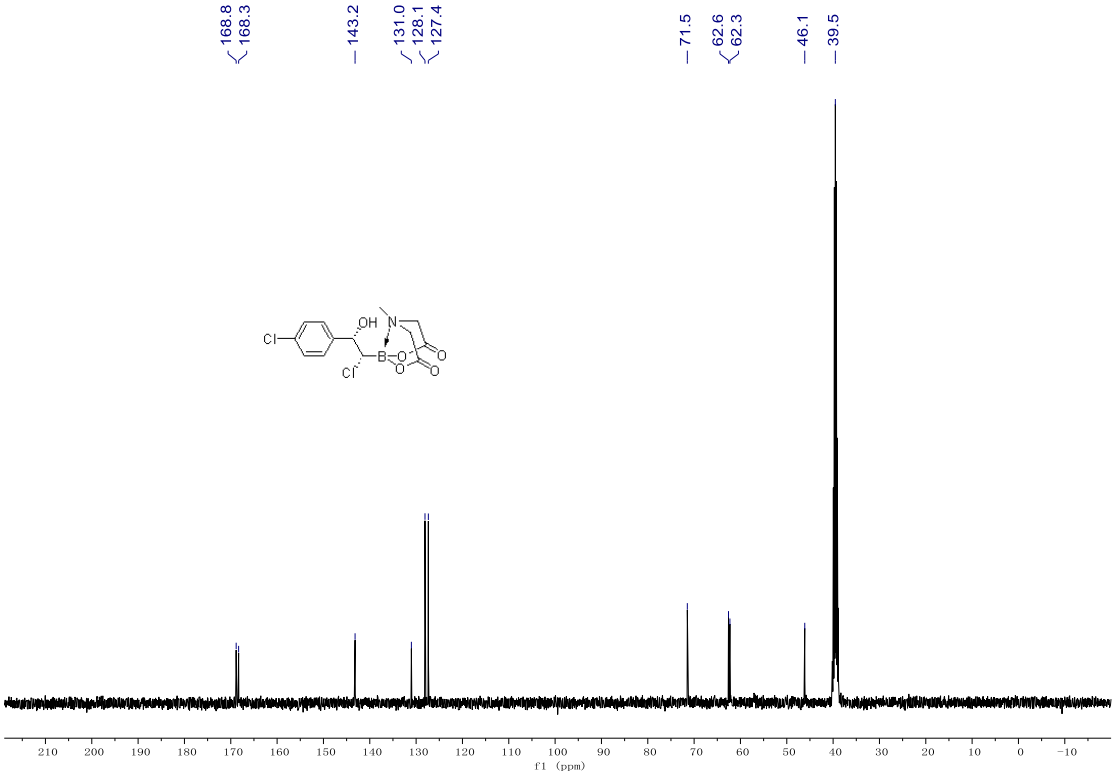
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B
O
O
O
O
Cl
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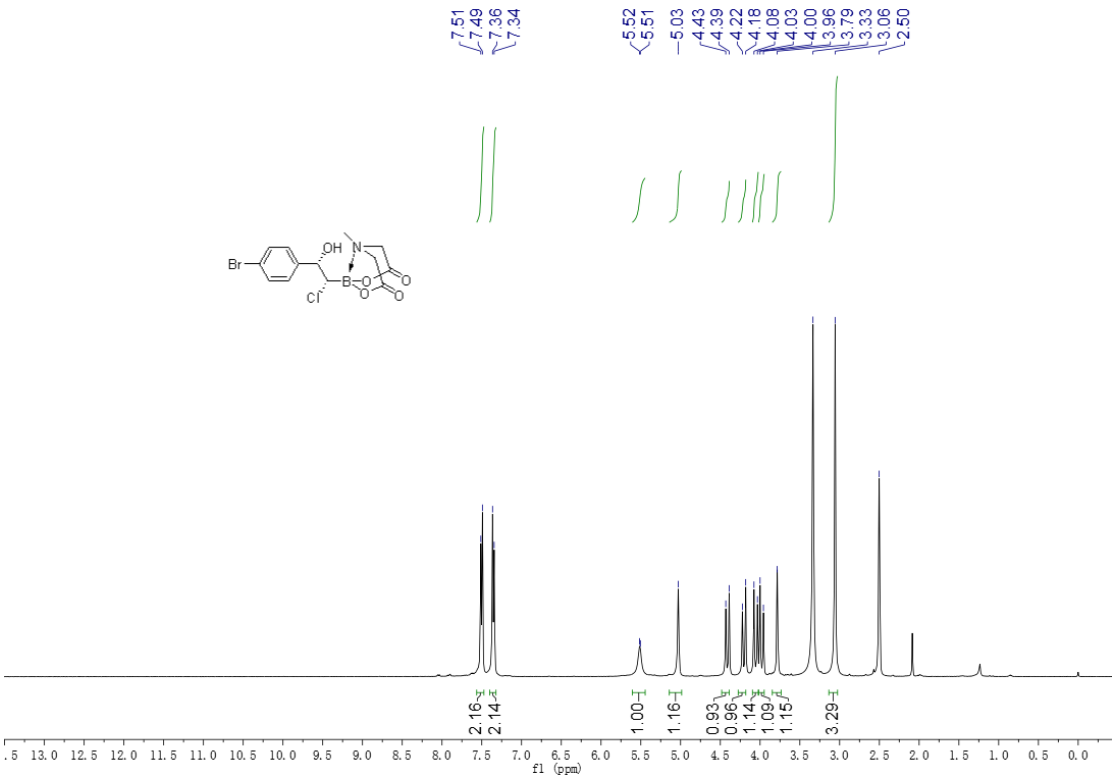
f1 (ppm)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5.51
5.03
4.43
4.39
4.22
4.18
4.08
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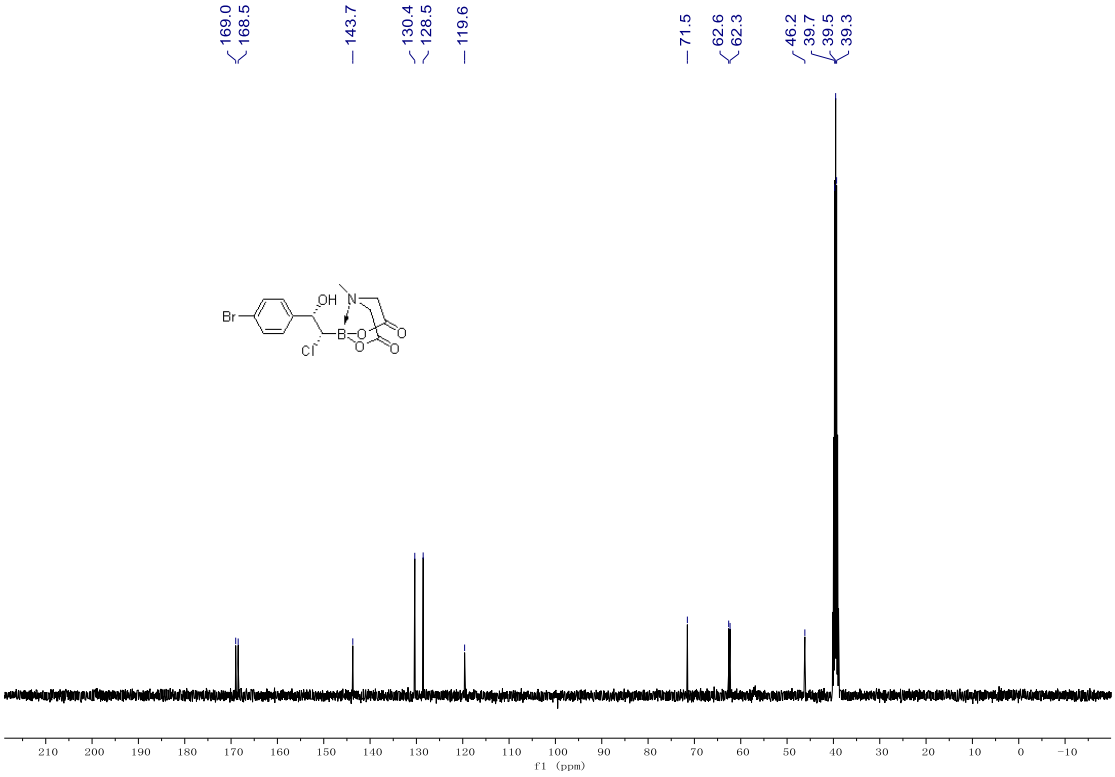
4.00
3.96
3.79
3.33
3.06
2.50
Br
OH
N
B
O
O
O
O
Cl
2.16
2.14
1.00
1.16
0.93
0.96
1.14
1.09
1.15
3.29
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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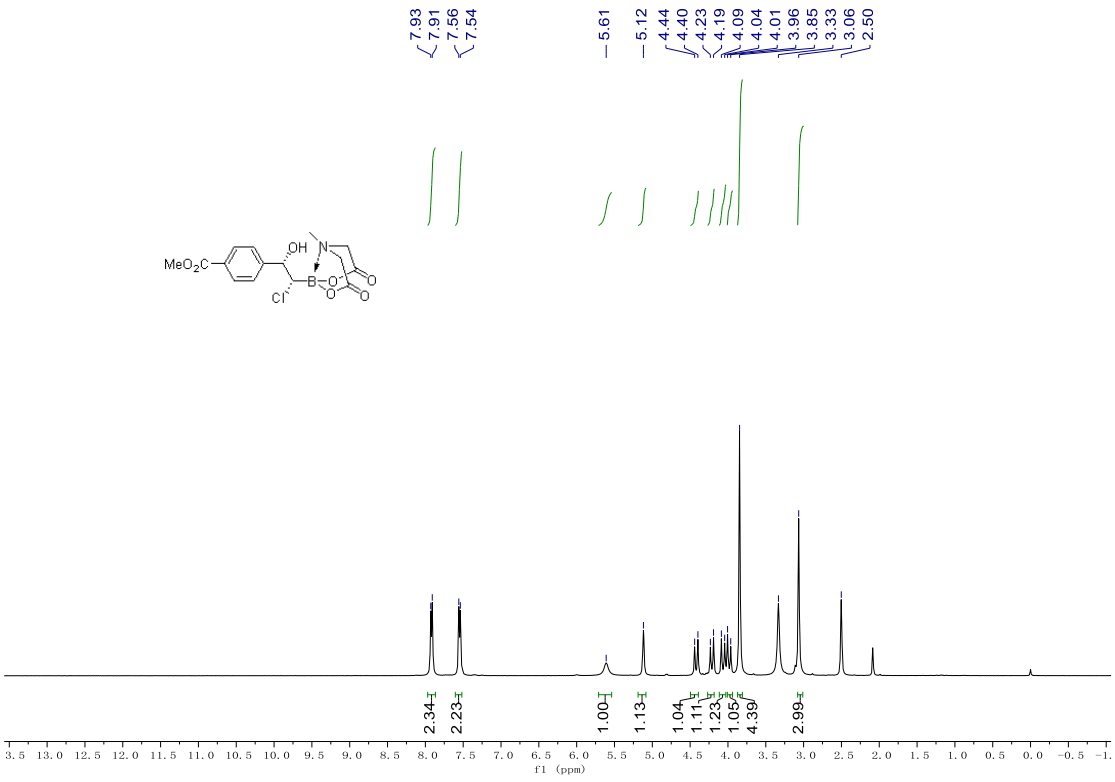
168.5
143.7
130.4
128.5
119.6
71.5
62.6
62.3
46.2
39.7
39.5
39.3
Br
OH
N
B
O
O
O
O
Cl
f1 (ppm)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7.91
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7.54
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5.12
4.44
4.40
4.23
4.19
4.09
4.04
4.01
3.96
3.85
3.33
3.06
2.50
MeO2C
OH
N
B
O
O
O
O
Cl
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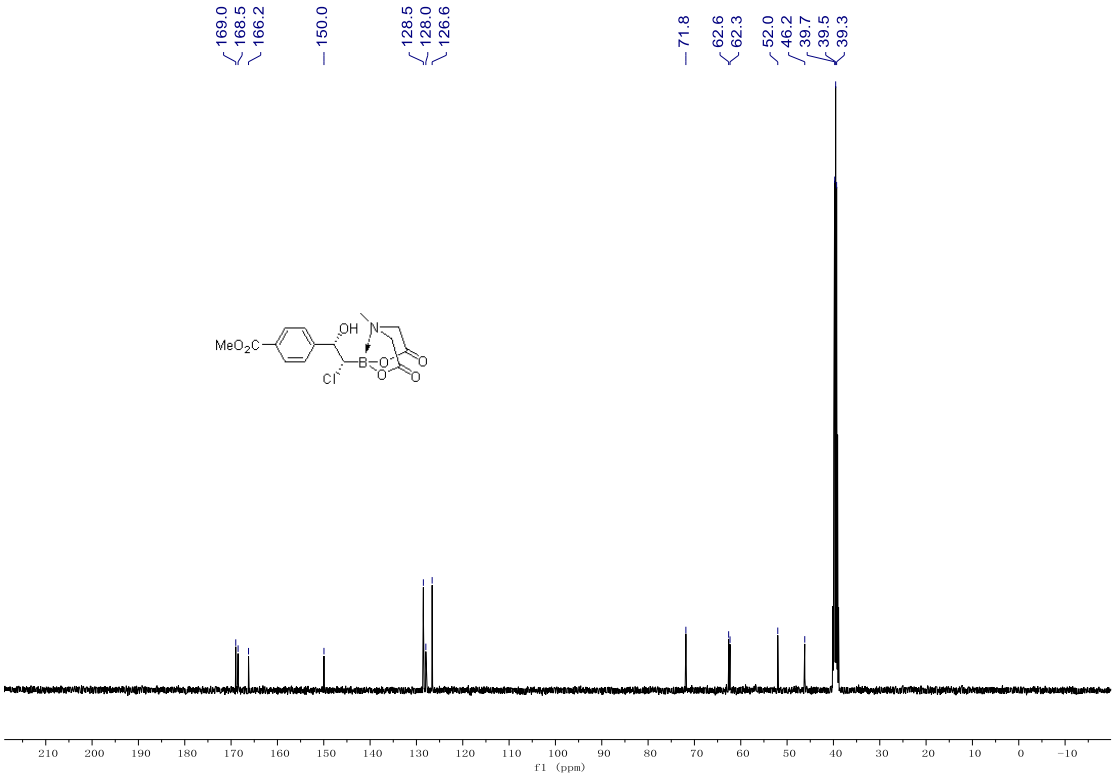
2.23
1.00
1.13
1.04
1.11
1.23
1.05
4.39
2.99
f1 (ppm)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128.5
128.0
126.6
71.8
62.6
62.3
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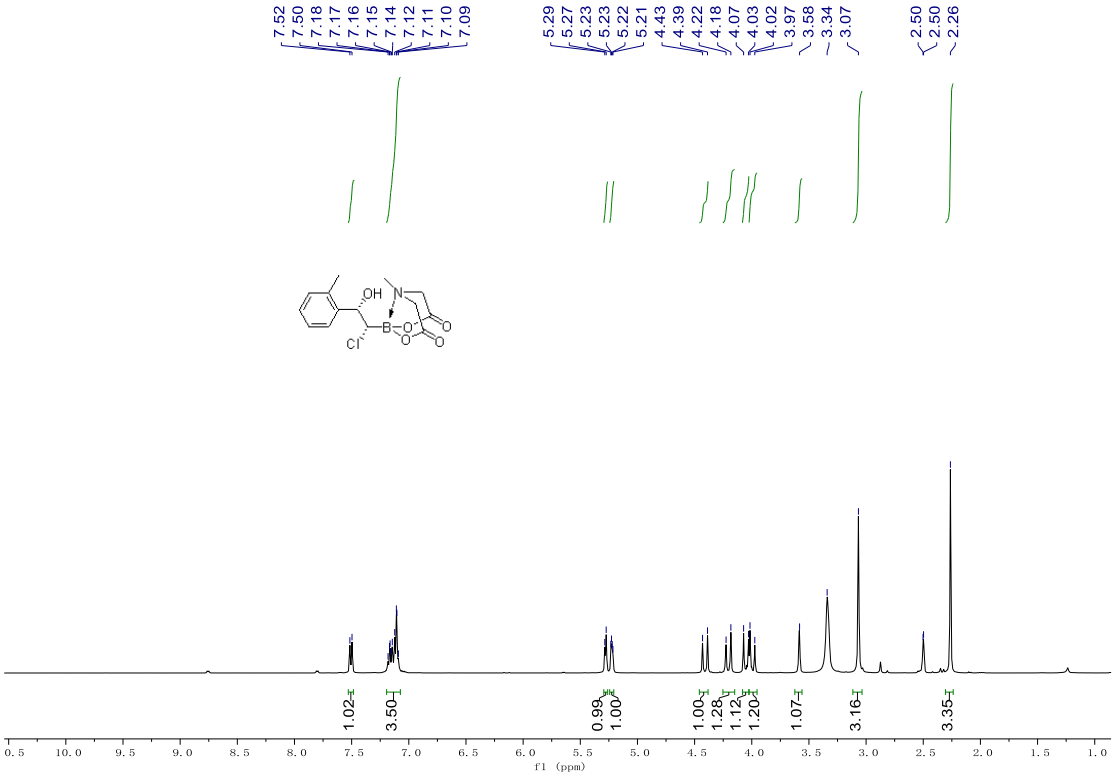
46.2
39.7
39.5
39.3
MeO2C
OH
N
B
O
Cl
f1 (ppm)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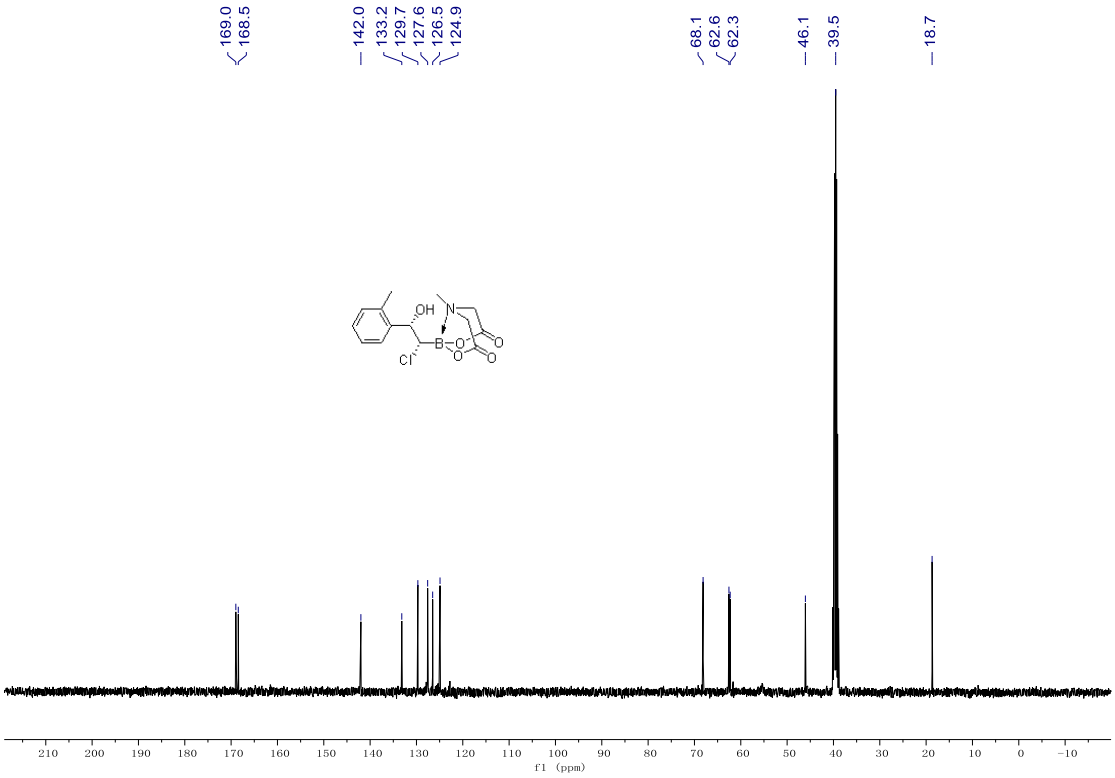
7.12
7.11
7.10
7.09
5.29
5.27
5.23
5.23
5.22
5.21
4.43
4.39
4.22
4.18
4.07
4.03
4.02
3.97
3.58
3.34
3.07
2.50
2.50
2.26
OH
N
B
O
Cl
1.02
3.50
0.99
1.00
1.00
1.28
1.12
1.20
1.07
3.16
3.35
f1 (ppm)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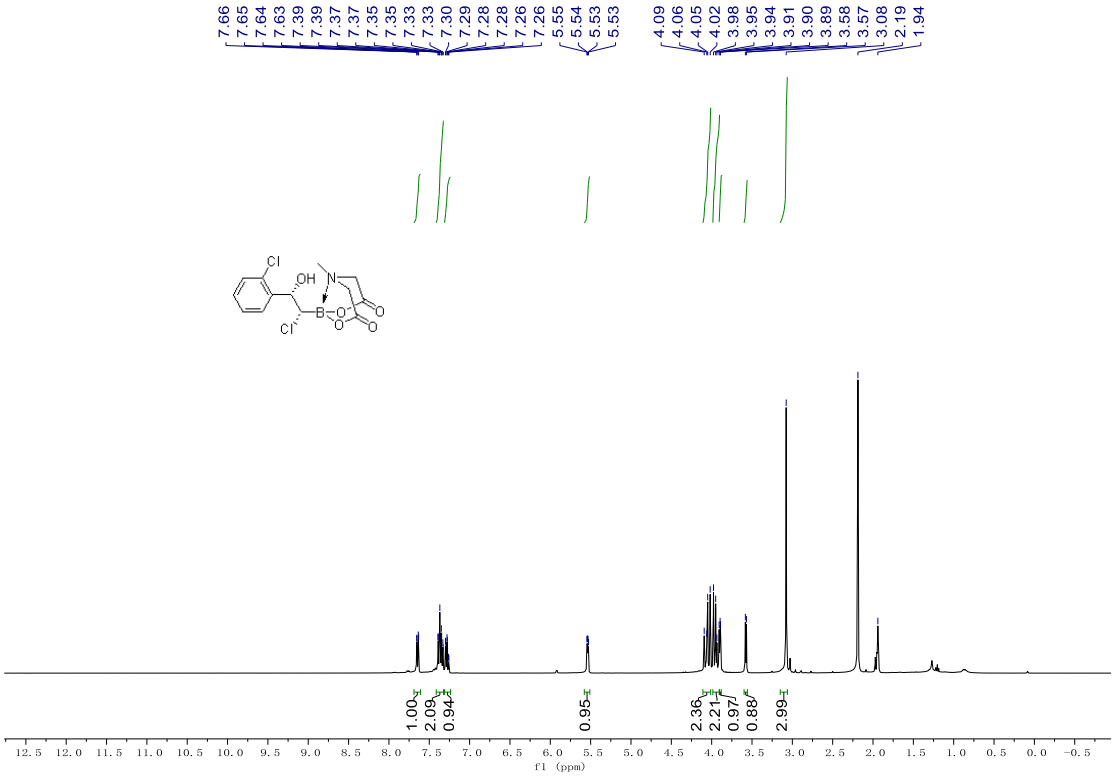
142.0
133.2
129.7
127.6
126.5
124.9
68.1
62.6
62.3
46.1
39.5
18.7
OH
N
B
O
O
O
O
Cl
f1 (ppm)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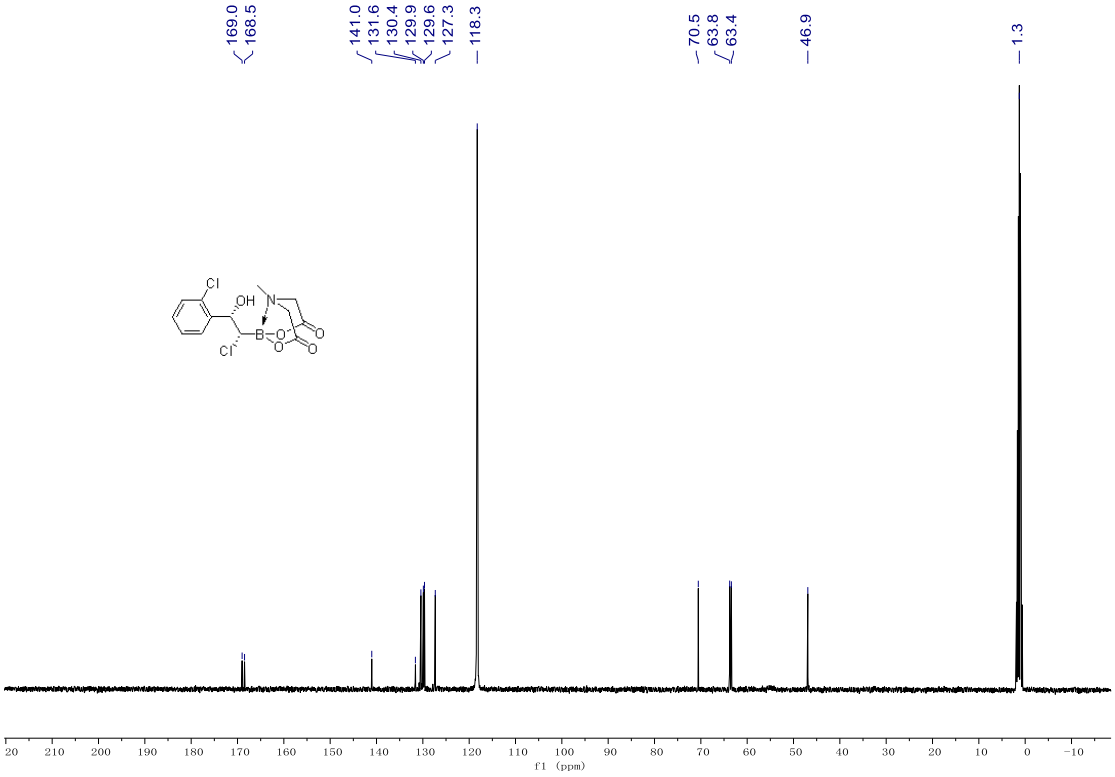
7.35
7.33
7.33
7.30
7.29
7.28
7.28
7.26
7.26
5.55
5.54
5.53
5.53
4.09
4.06
4.05
4.02
3.98
3.95
3.94
3.91
3.90
3.89
3.58
3.57
3.08
2.19
1.94
Cl
OH
N
B
O
O
O
O
Cl
1.00
2.09
0.94
0.95
2.36
2.21
0.97
0.88
2.99
f1 (ppm)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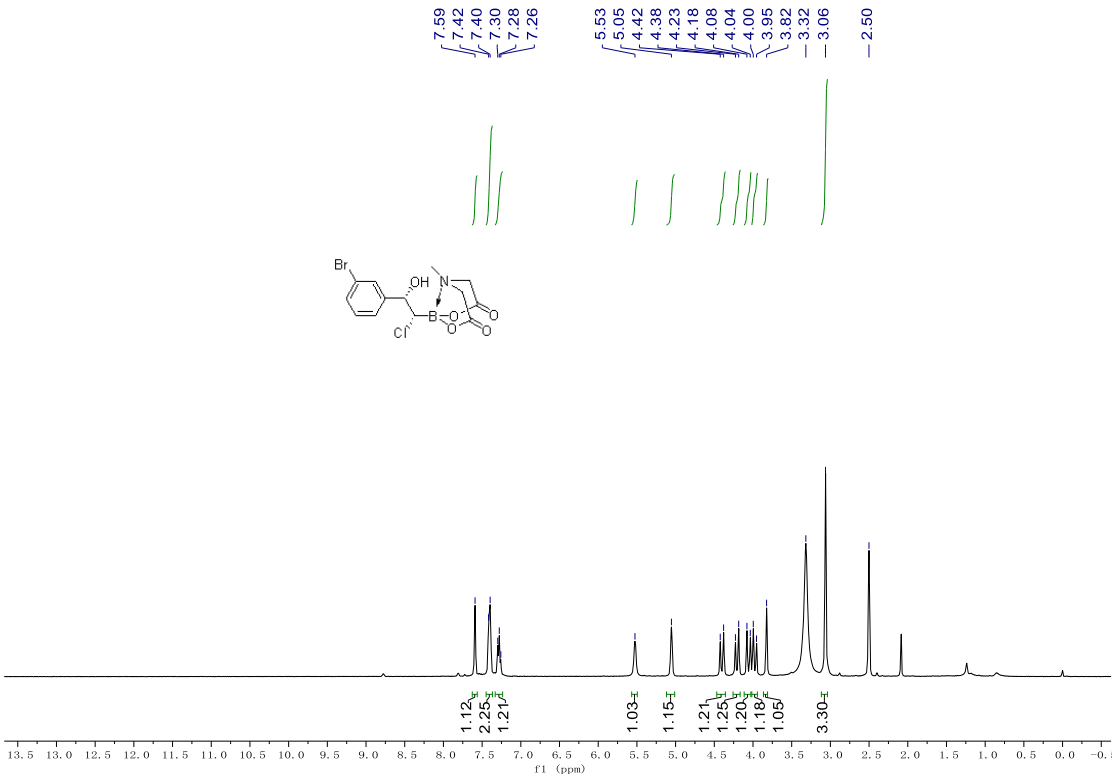
168.5
141.0
131.6
130.4
129.9
129.6
127.3
118.3
70.5
63.8
63.4
46.9
1.3
Cl
OH
N
B
O
O
O
O
Cl
f1 (ppm)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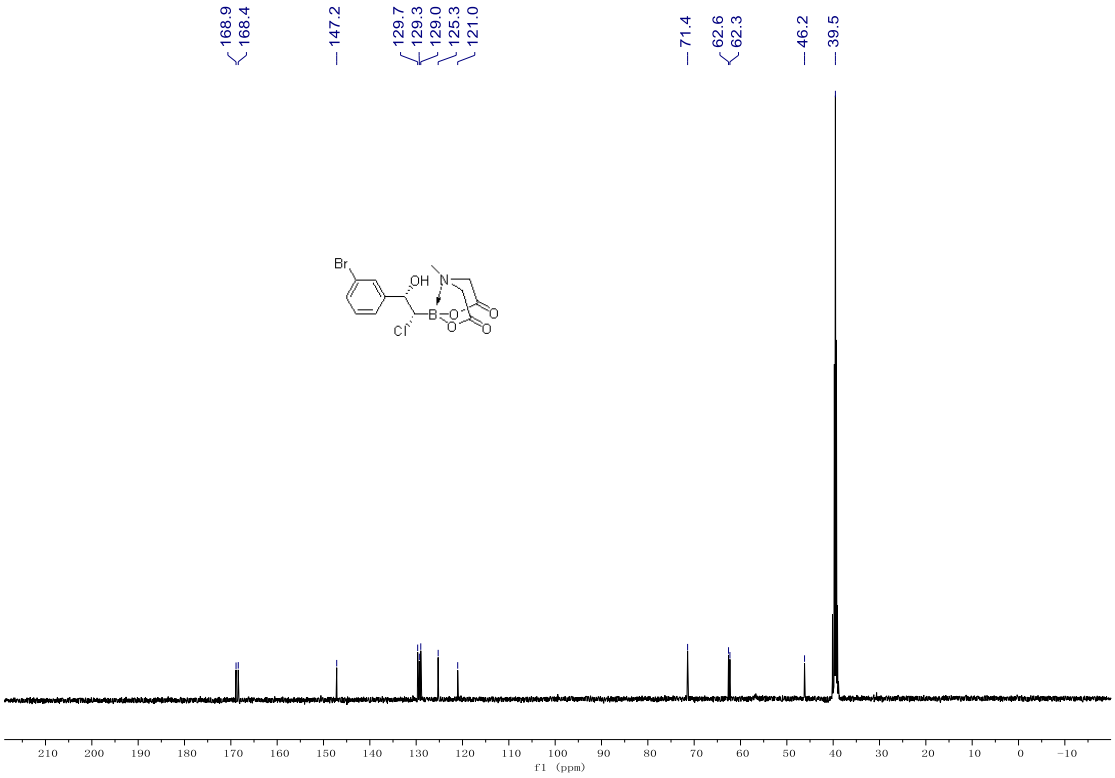
7.42
7.40
7.30
7.28
7.26
5.53
5.05
4.42
4.38
4.23
4.18
4.08
4.04
4.00
3.95
3.82
3.32
3.06
2.50
Br
OH
N
B
O
O
O
O
Cl
1.12
2.25
1.21
1.03
1.15
1.21
1.25
1.20
1.18
1.05
3.30
f1 (ppm)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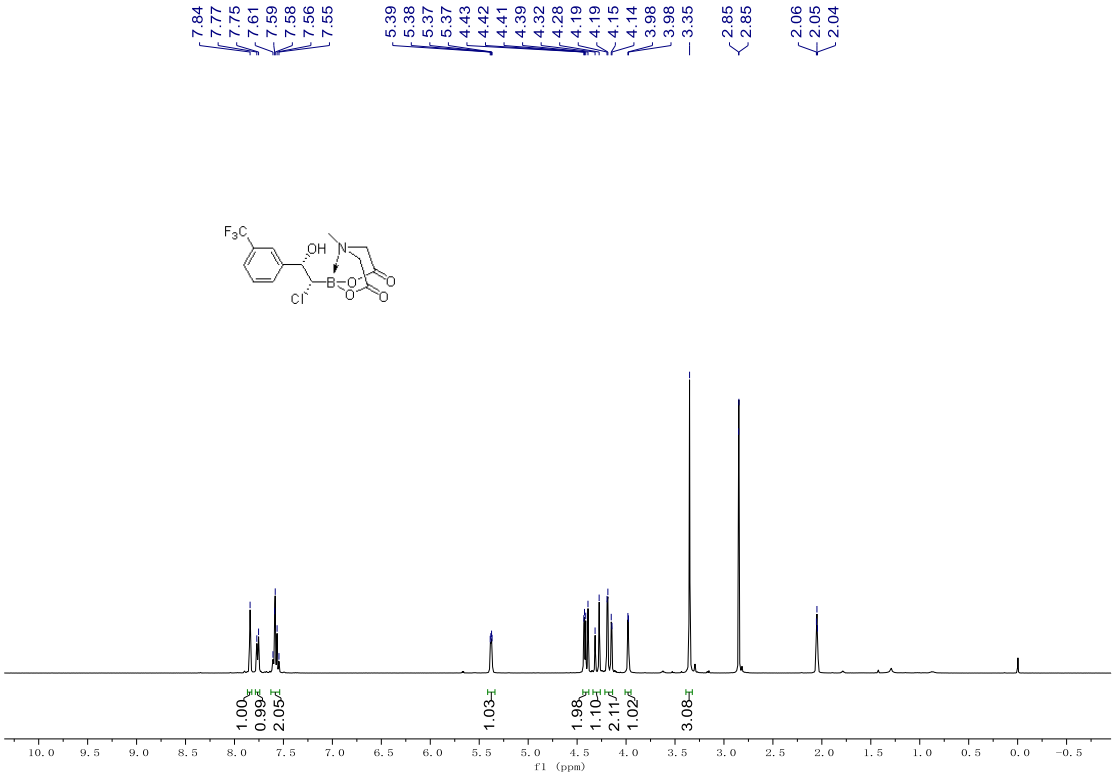
168.4
147.2
129.7
129.3
129.0
125.3
121.0
71.4
62.6
62.3
46.2
39.5
Br
OH
N
B
O
O
O
O
Cl
f1 (ppm)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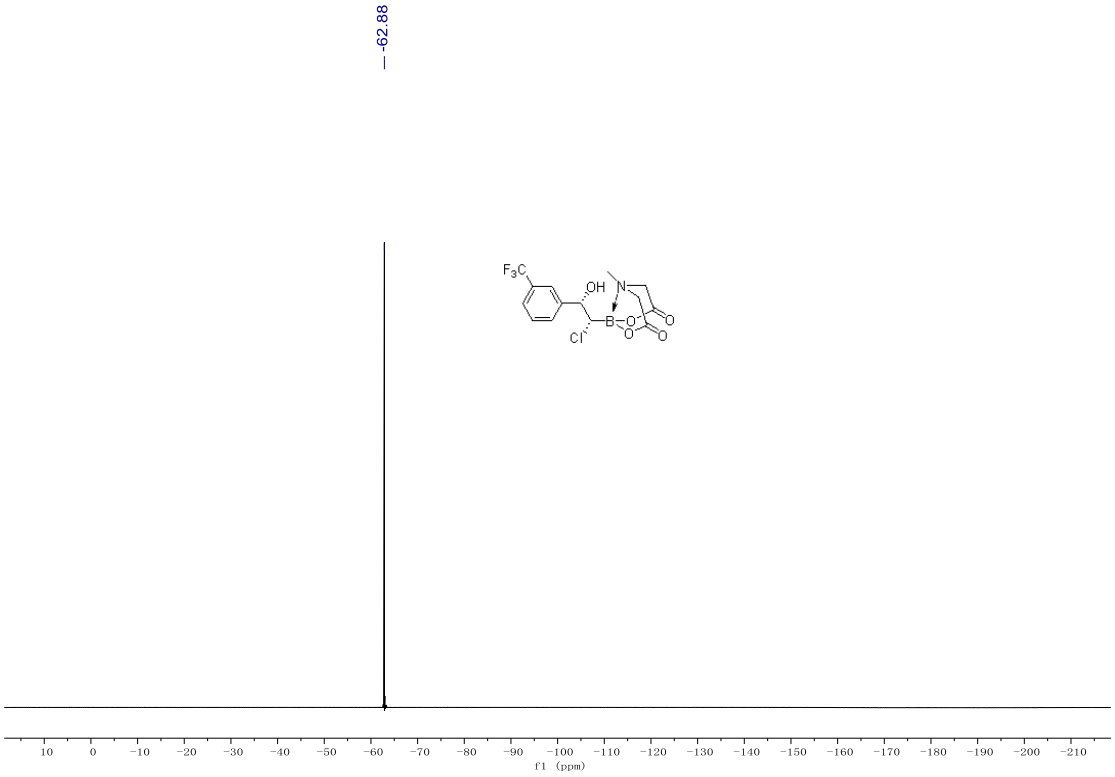
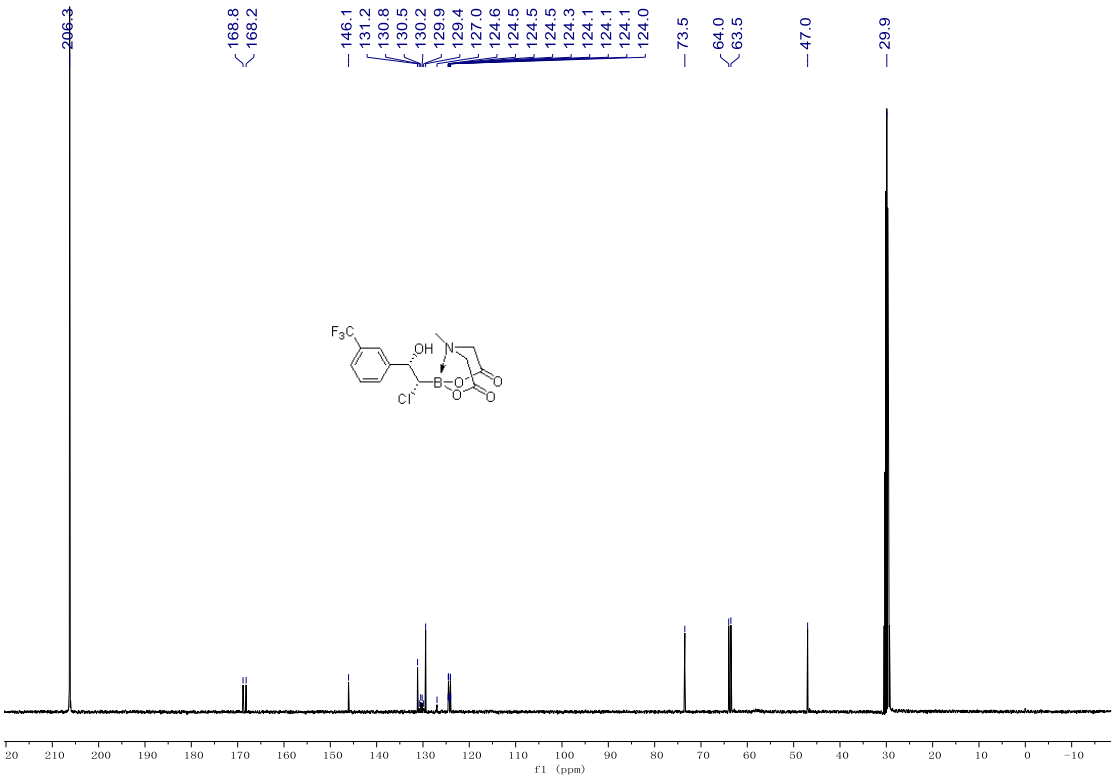
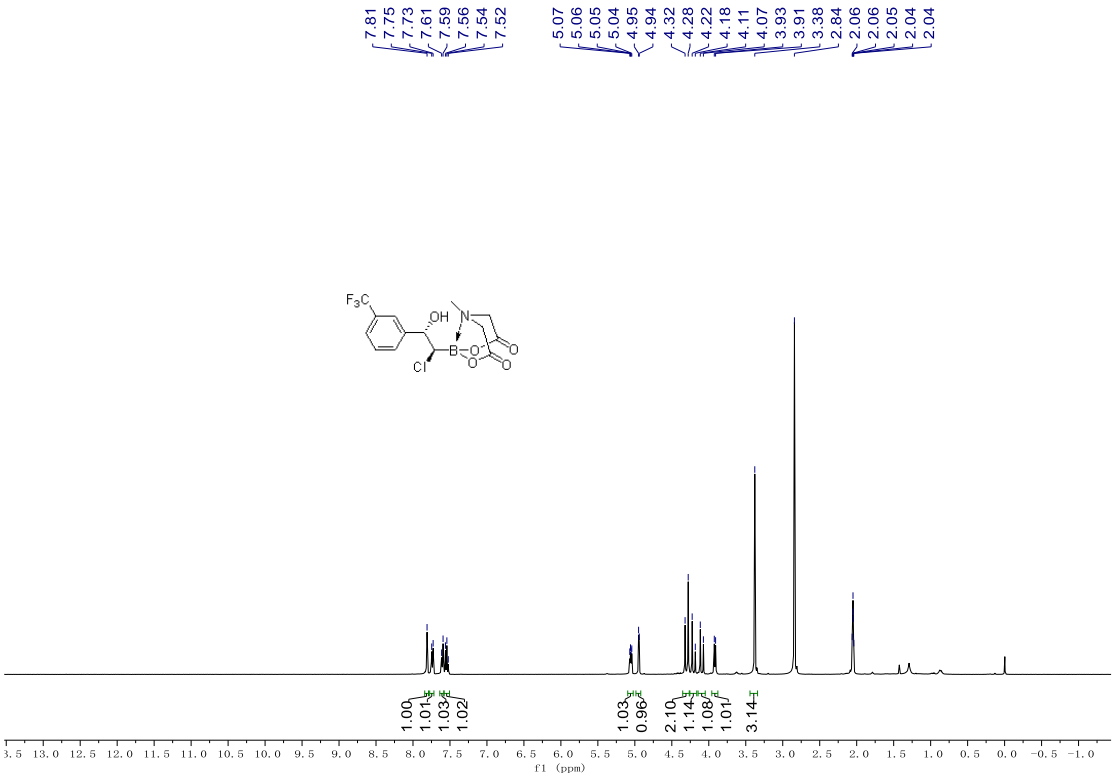
7.77
7.75
7.61
7.59
7.58
7.56
7.55
5.39
5.38
5.37
5.37
4.43
4.42
4.41
4.39
4.32
4.28
4.19
4.19
4.15
4.14
3.98
3.98
3.35
2.85
2.85
2.06
2.05
2.04
F3C
OH
N
B
O
O
O
O
Cl
1.00
0.99
2.05
1.03
1.98
1.10
2.11
1.02
3.08
f1 (ppm)


-62.88
F3C
OH
N
B
O
O
O
O
Cl
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)


206.3
168.8
168.2
146.1
131.2
130.8
130.5
130.2
129.9
129.4
127.0
124.6
124.5
124.5
124.5
124.3
124.1
124.1
124.1
124.0
73.5
64.0
63.5
47.0
29.9
F3C
OH
N
B
O
O
O
O
Cl
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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7.73
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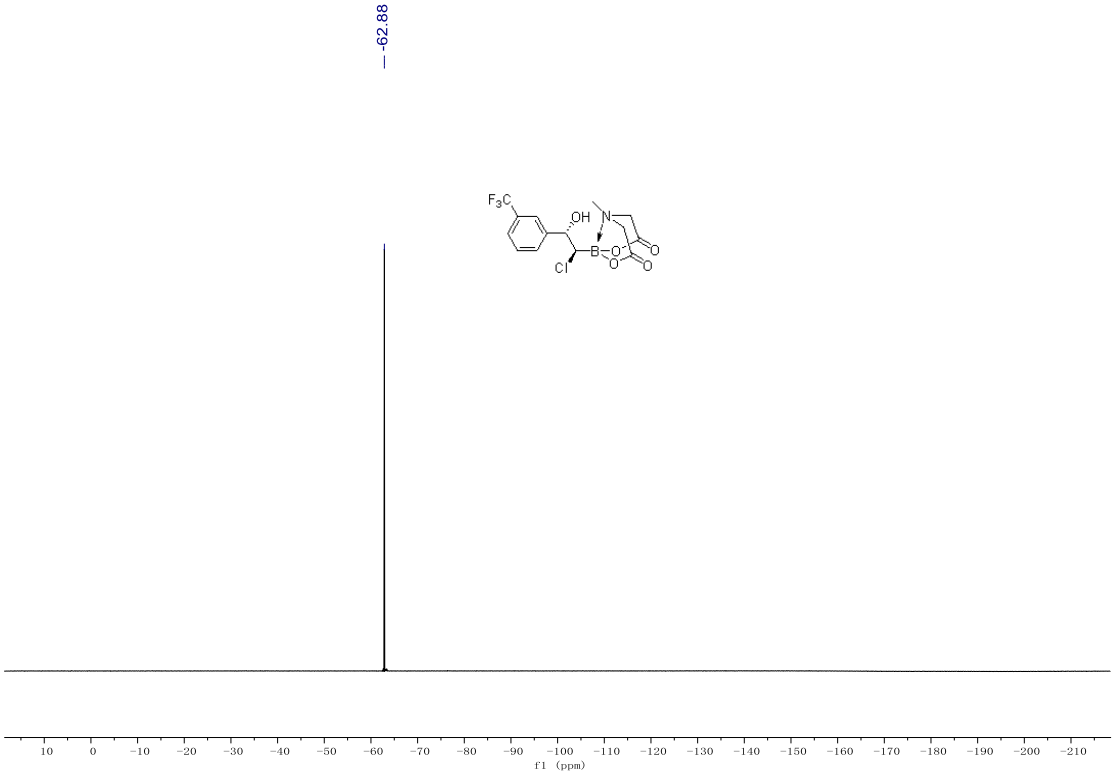
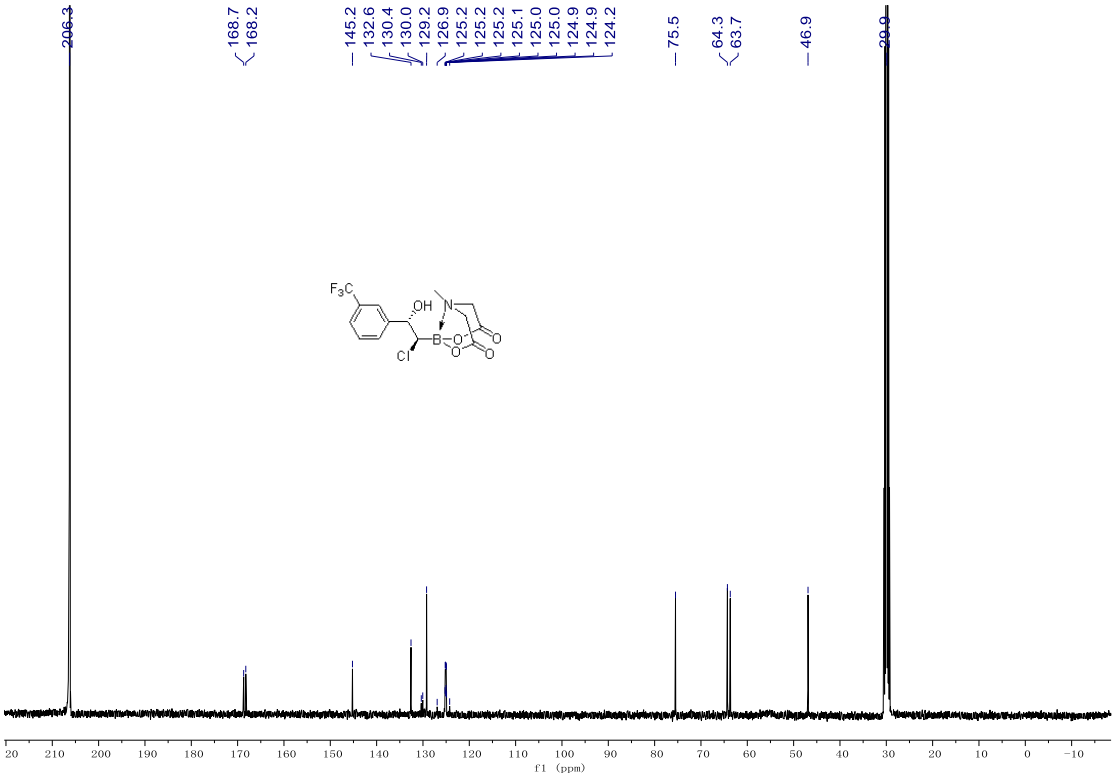
7.59
7.56
7.54
7.52
5.07
5.06
5.05
5.04
4.95
4.94
4.32
4.28
4.22
4.18
4.11
4.07
3.93
3.91
3.38
2.84
2.06
2.06
2.05
2.04
2.04
F3C
OH
N
B
O
O
O
O
Cl
1.00
1.01
1.03
1.02
1.03
0.96
2.10
1.14
1.08
1.01
3.14
f1 (ppm)


-62.88
F3C
OH
N
B
O
O
O
O
Cl
f1 (ppm)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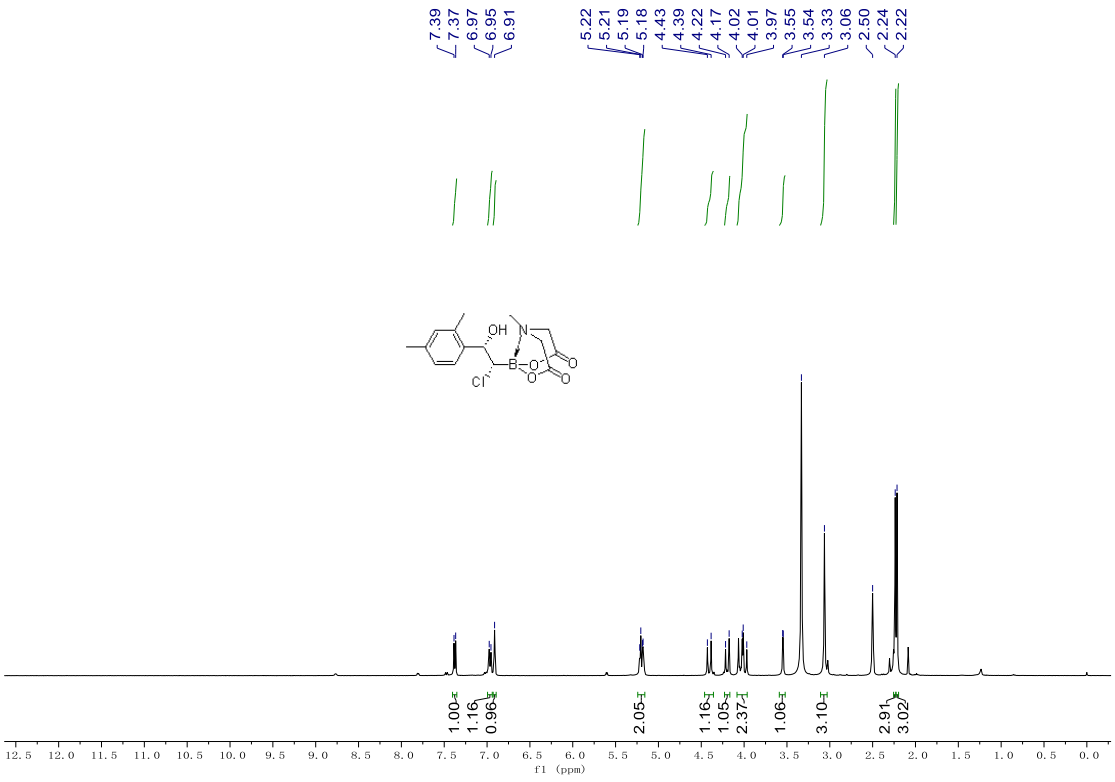
168.2
145.2
132.6
130.4
130.0
129.2
126.9
125.2
125.2
125.2
125.1
125.0
125.0
124.9
124.9
124.2
75.5
64.3
63.7
46.9
29.9
F3C
OH
N
B
O
O
O
O
Cl
f1 (ppm)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7.37
6.97
6.95
6.91
5.22
5.21
5.19
5.18
4.43
4.39
4.22
4.17
4.02
4.01
3.97
3.55
3.54
3.33
3.06
2.50
2.24
2.22
OH
N
B
O
O
O
O
Cl
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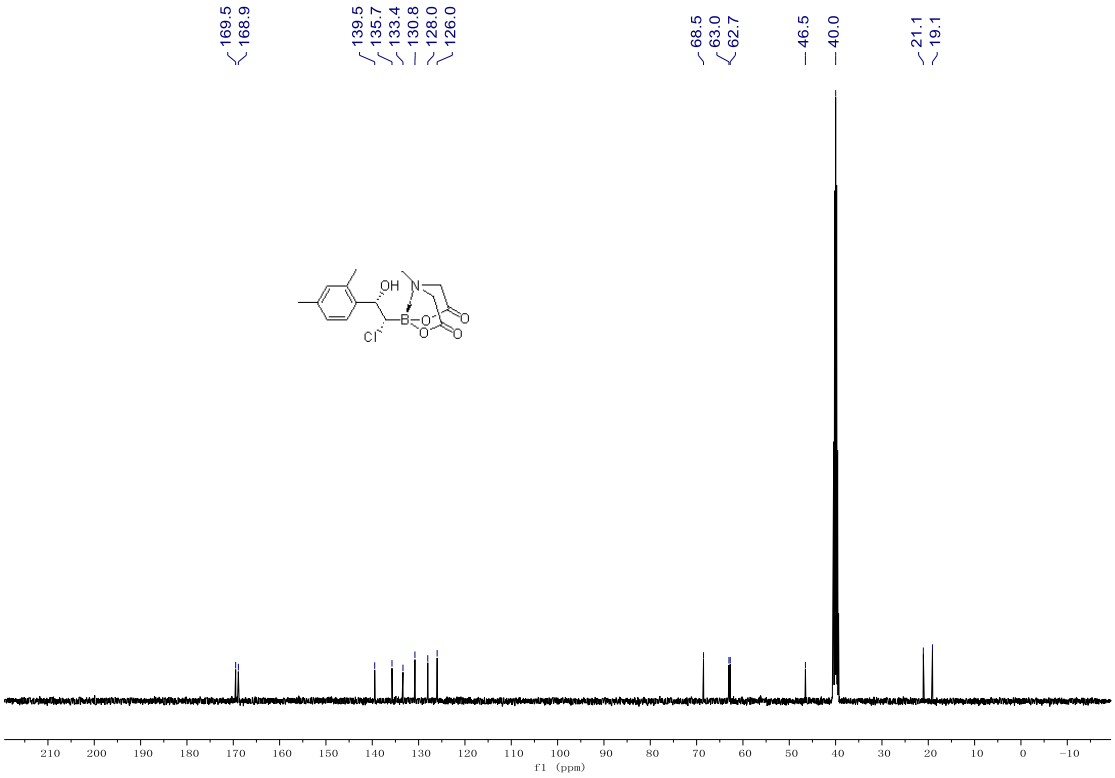
2.05
1.16
1.05
2.37
1.06
3.10
2.91
3.02
f1 (ppm)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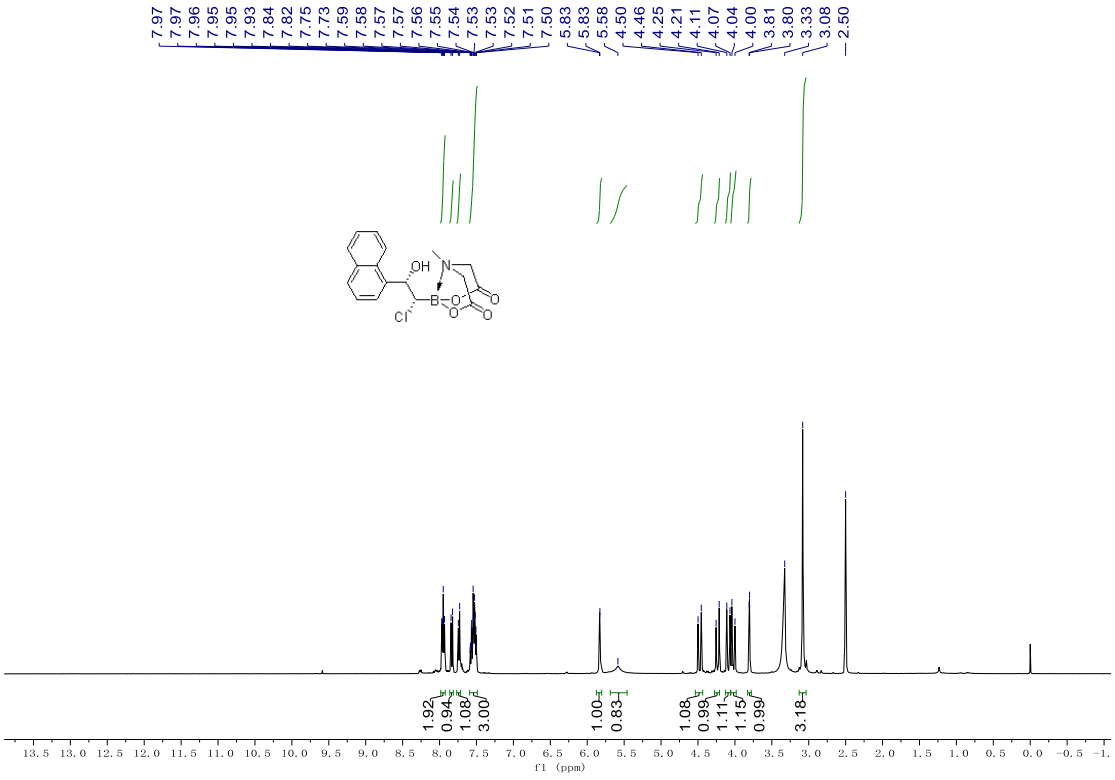
135.7
133.4
130.8
128.0
126.0
68.5
63.0
62.7
46.5
40.0
21.1
19.1
OH
N
B
O
O
O
O
Cl
f1 (ppm)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7.95
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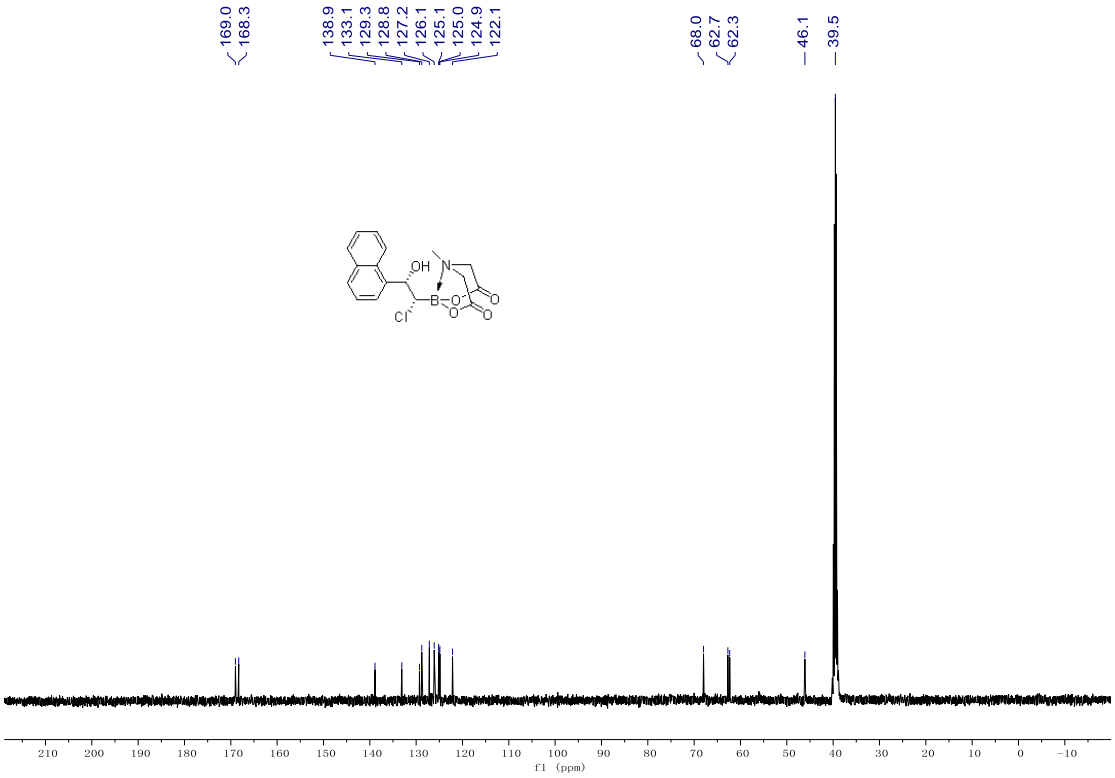
7.75
7.73
7.59
7.58
7.57
7.57
7.56
7.55
7.54
7.53
7.53
7.52
7.51
7.50
5.83
5.83
5.58
4.50
4.46
4.25
4.21
4.11
4.07
4.04
4.00
3.81
3.80
3.33
3.08
2.50
OH
N
B
O
O
O
O
Cl
1.92
0.94
1.08
3.00
1.00
0.83
1.08
0.99
1.11
1.15
0.99
3.18
f1 (ppm)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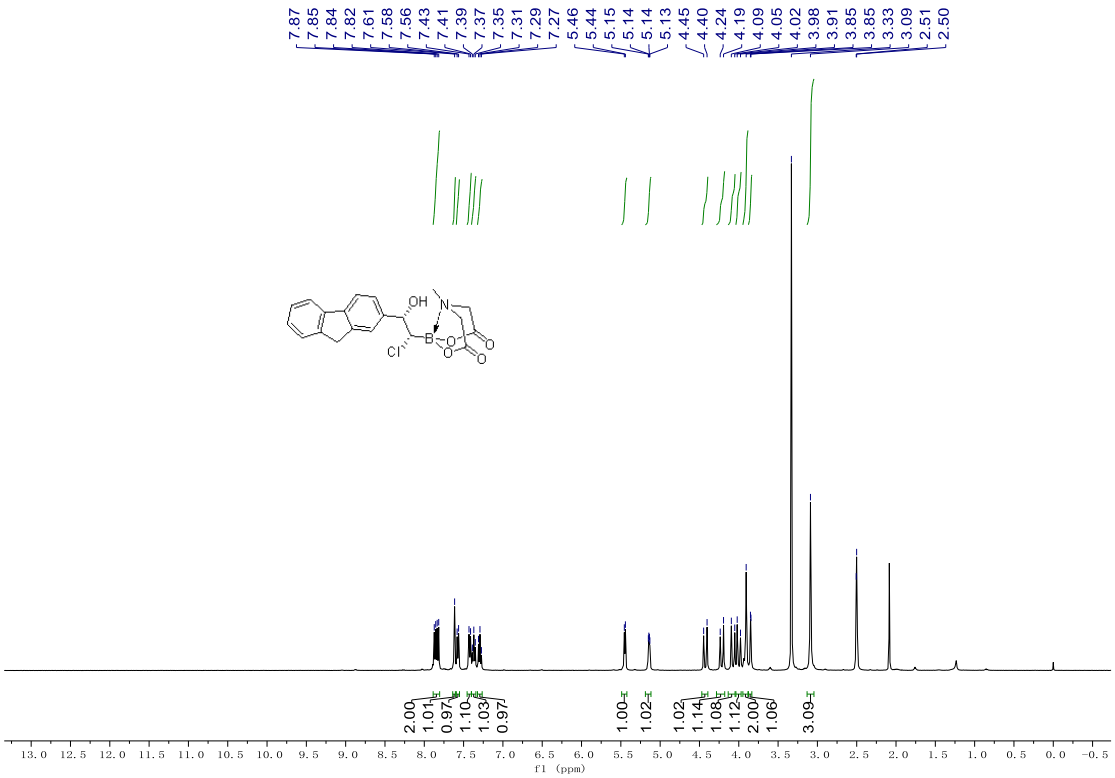
133.1
129.3
128.8
127.2
126.1
125.1
125.0
124.9
122.1
68.0
62.7
62.3
46.1
39.5
OH
N
B
O
O
O
O
Cl
f1 (ppm)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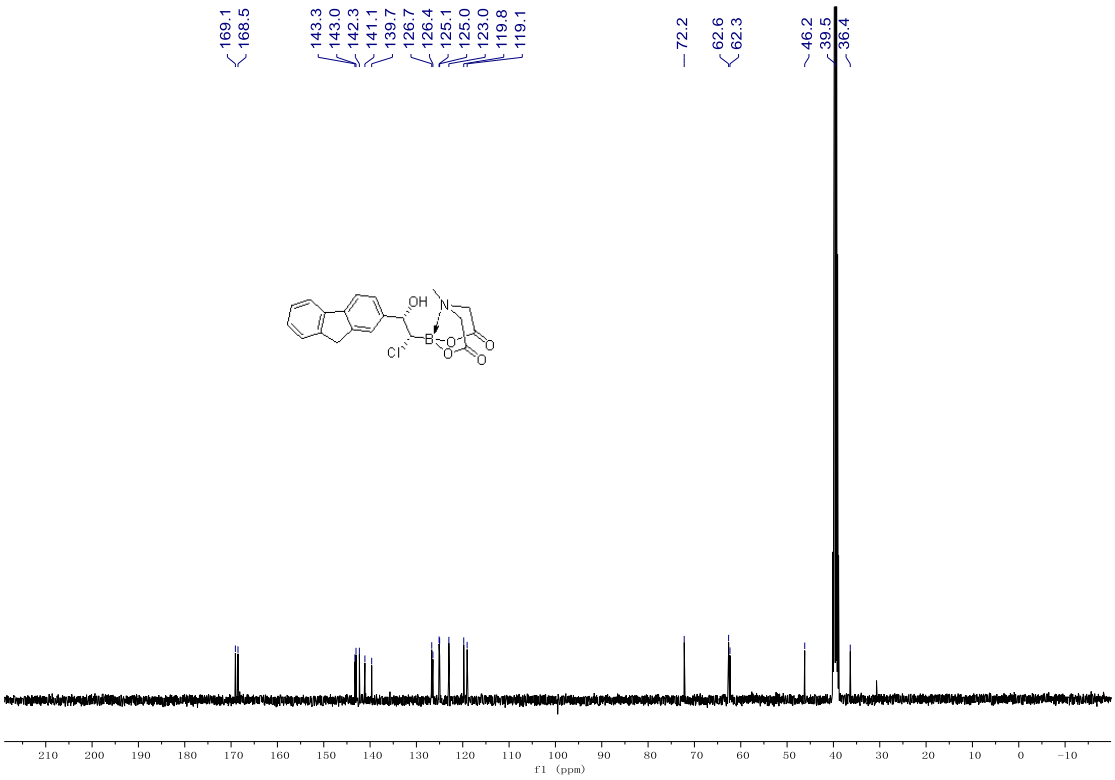
7.37
7.35
7.31
7.29
7.27
5.46
5.44
5.15
5.14
5.14
5.13
4.45
4.40
4.24
4.19
4.09
4.05
4.02
3.98
3.91
3.85
3.85
3.33
3.09
2.51
2.50
OH
N
B
O
O
O
O
Cl
2.00
1.01
0.97
1.10
1.03
0.97
1.00
1.02
1.02
1.14
1.05
1.12
2.00
1.06
3.09
f1 (ppm)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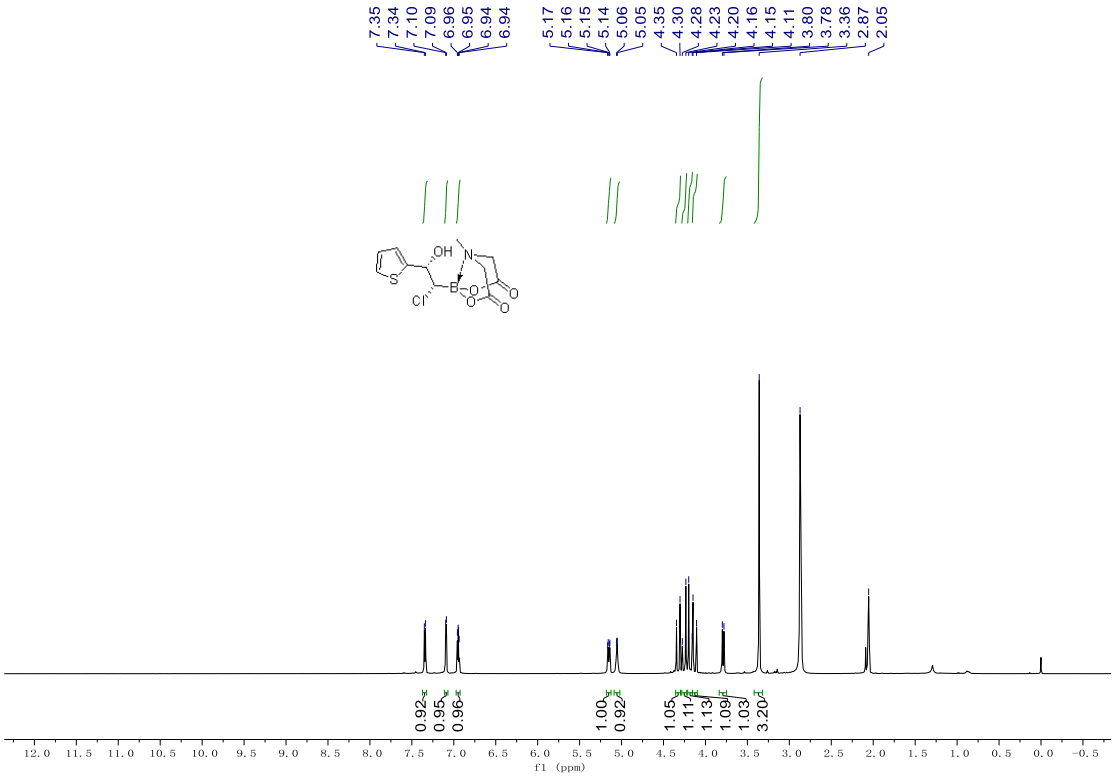
142.3
141.1
139.7
126.7
126.4
125.1
125.0
123.0
119.8
119.1
72.2
62.6
62.3
46.2
39.5
36.4
OH
N
B
Cl
O
f1 (ppm)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7.09
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6.95
6.94
6.94
5.17
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5.15
5.14
5.06
5.05
4.35
4.30
4.28
4.23
4.20
4.16
4.15
4.11
3.80
3.78
3.36
2.87
2.05
OH
N
B
Cl
O
S
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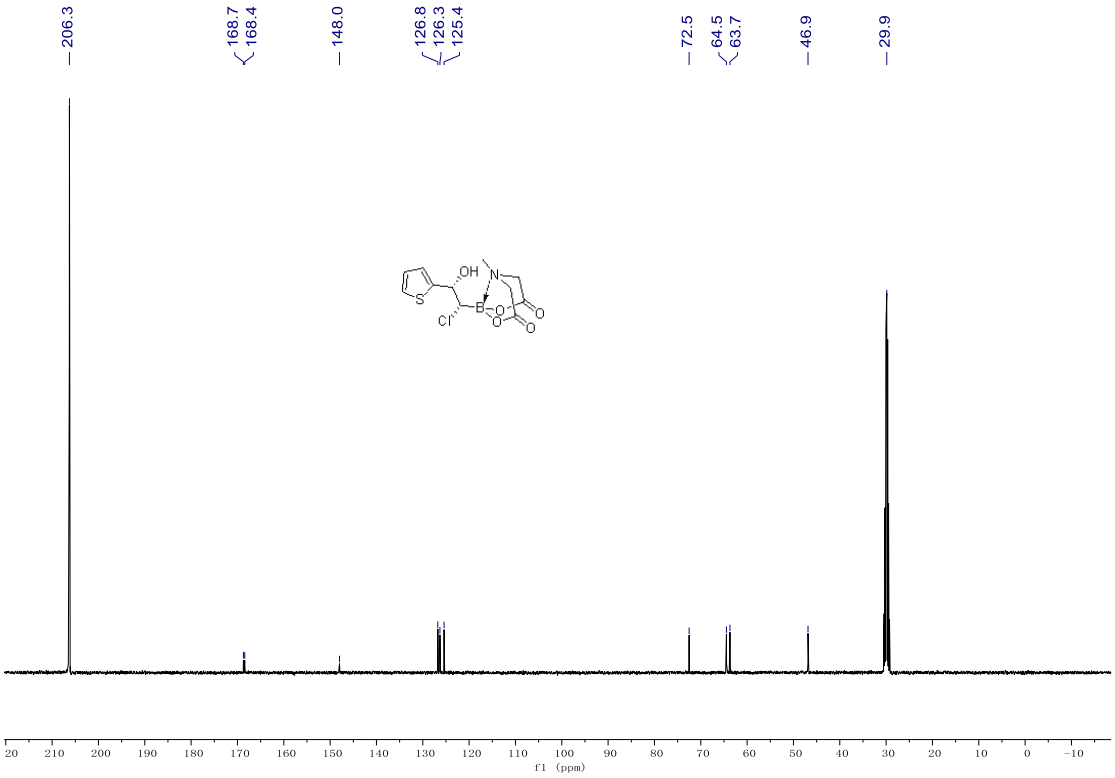
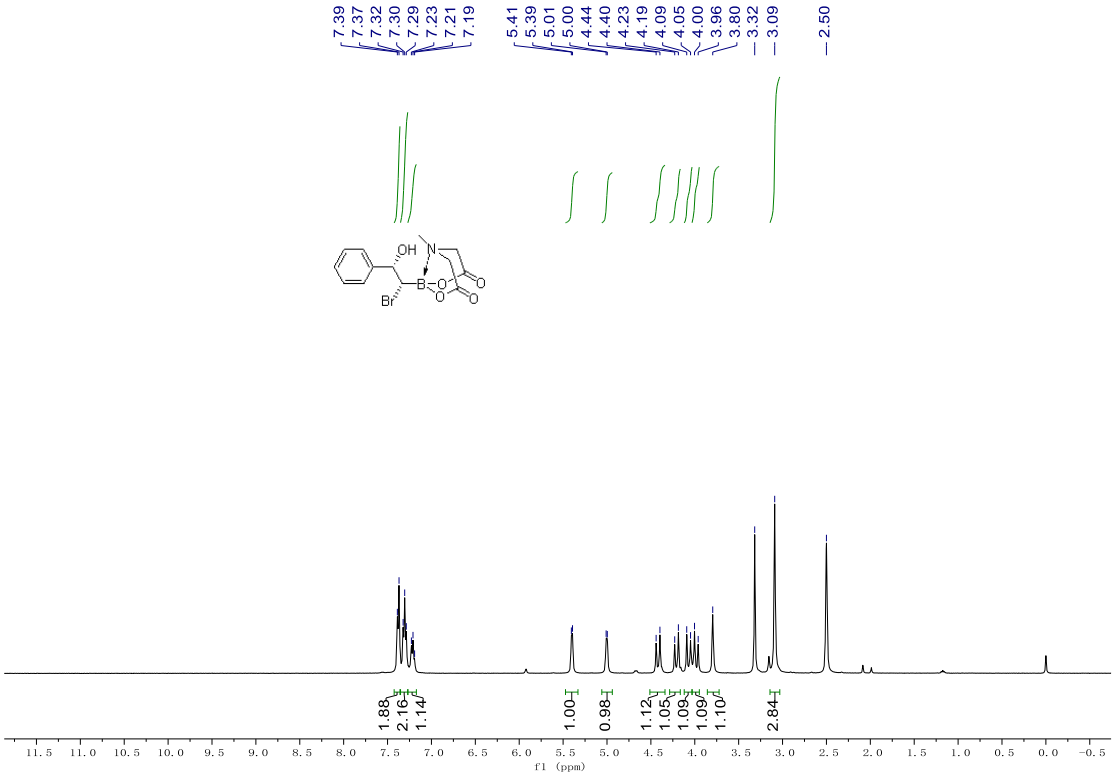
0.96
1.00
0.92
1.05
1.11
1.13
1.09
1.03
3.20
f1 (ppm)


206.3
168.7
168.4
148.0
126.8
126.3
125.4
72.5
64.5
63.7
46.9
29.9
OH
N
S
Cl
B
O
O
O
O
f1 (ppm)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7.37
7.32
7.30
7.29
7.23
7.21
7.19
5.41
5.39
5.01
5.00
4.44
4.40
4.23
4.19
4.09
4.05
4.00
3.96
3.80
3.32
3.09
2.50
OH
N
Br
B
O
O
O
O
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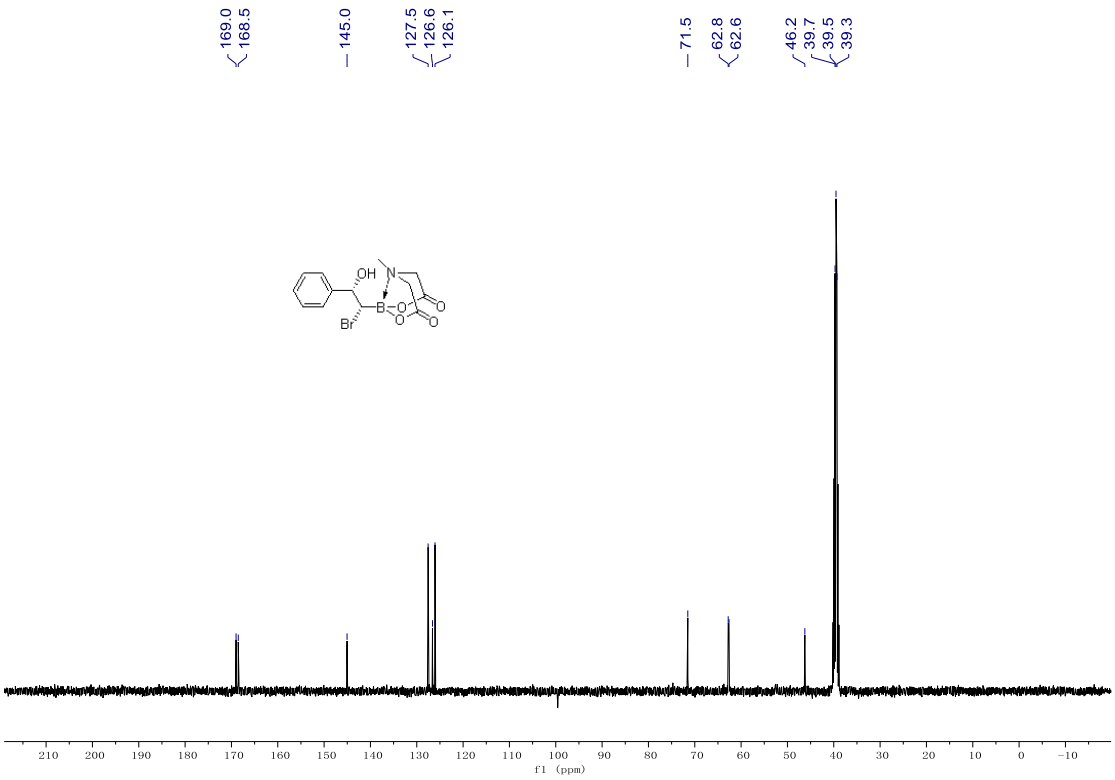
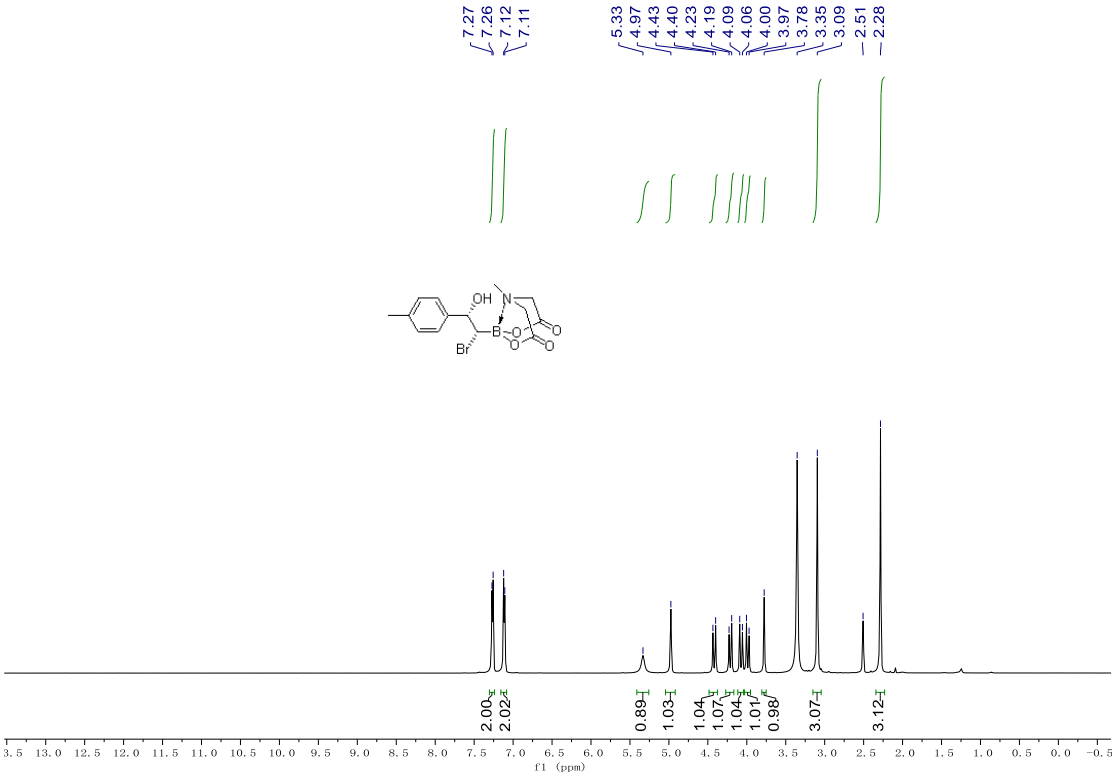
2.16
1.14
1.00
0.98
1.12
1.05
1.09
1.09
1.10
2.84
f1 (ppm)


169.0
168.5
145.0
127.5
126.6
126.1
71.5
62.8
62.6
46.2
39.7
39.5
39.3
OH
N
B
O
O
O
O
Br
f1 (ppm)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7.26
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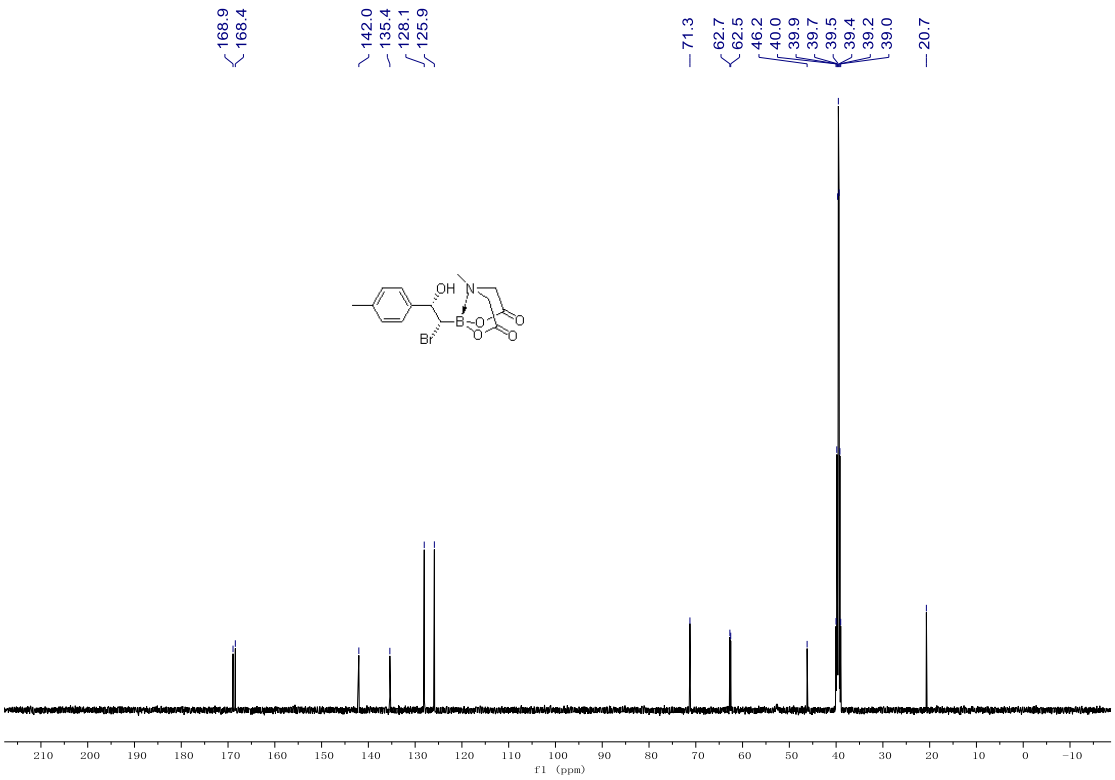
7.11
5.33
4.97
4.43
4.40
4.23
4.19
4.09
4.06
4.00
3.97
3.78
3.35
3.09
2.51
2.28
OH
N
B
O
O
O
O
Br
2.00
2.02
0.89
1.03
1.04
1.07
1.04
1.01
0.98
3.07
3.12
f1 (ppm)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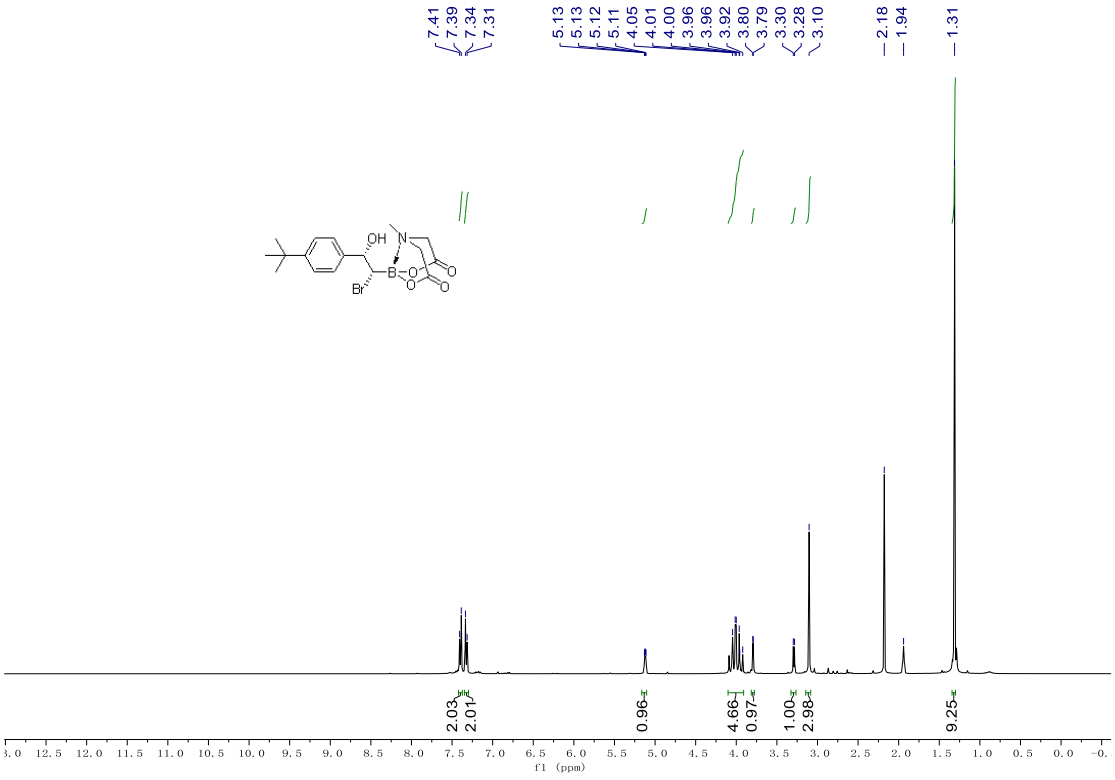
168.4
142.0
135.4
128.1
125.9
71.3
62.7
62.5
46.2
40.0
39.9
39.7
39.5
39.4
39.2
39.0
20.7
OH
N
B
O
O
O
O
Br
f1 (ppm)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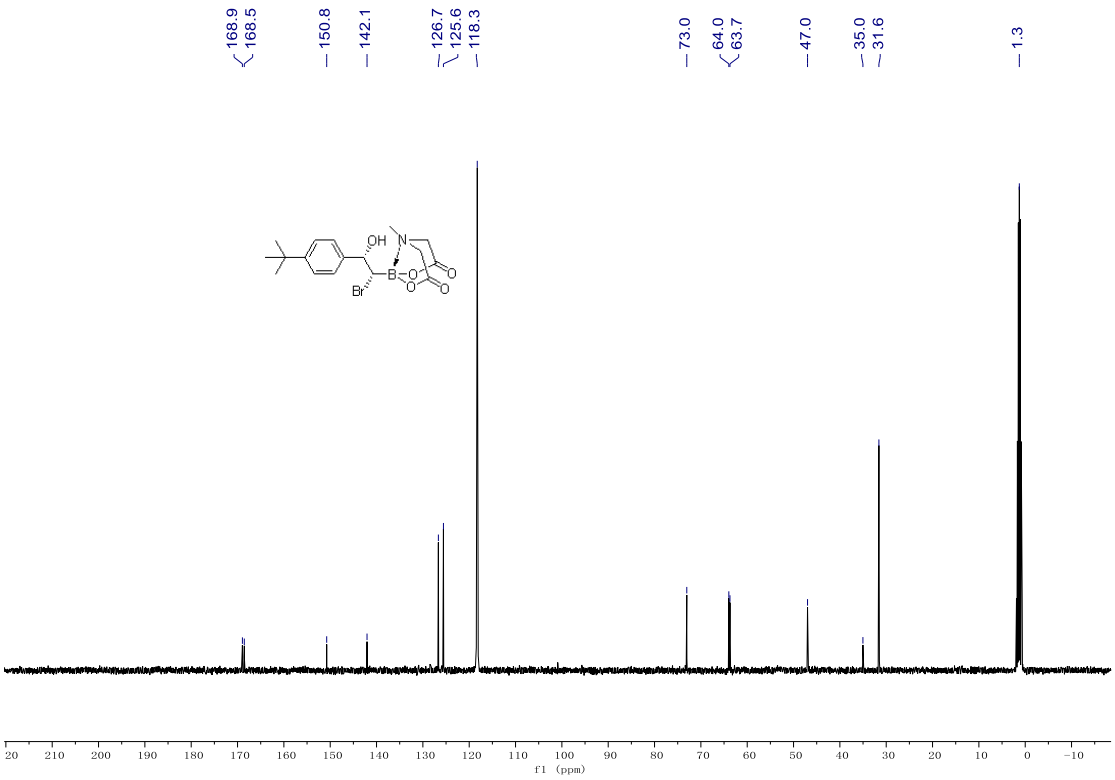
7.39
7.34
7.31
5.13
5.13
5.12
5.11
4.05
4.01
4.00
3.96
3.96
3.92
3.80
3.79
3.30
3.28
3.10
2.18
1.94
1.31
OH
N
B
O
O
O
O
Br
2.03
2.01
0.96
4.66
0.97
1.00
2.98
9.25
f1 (ppm)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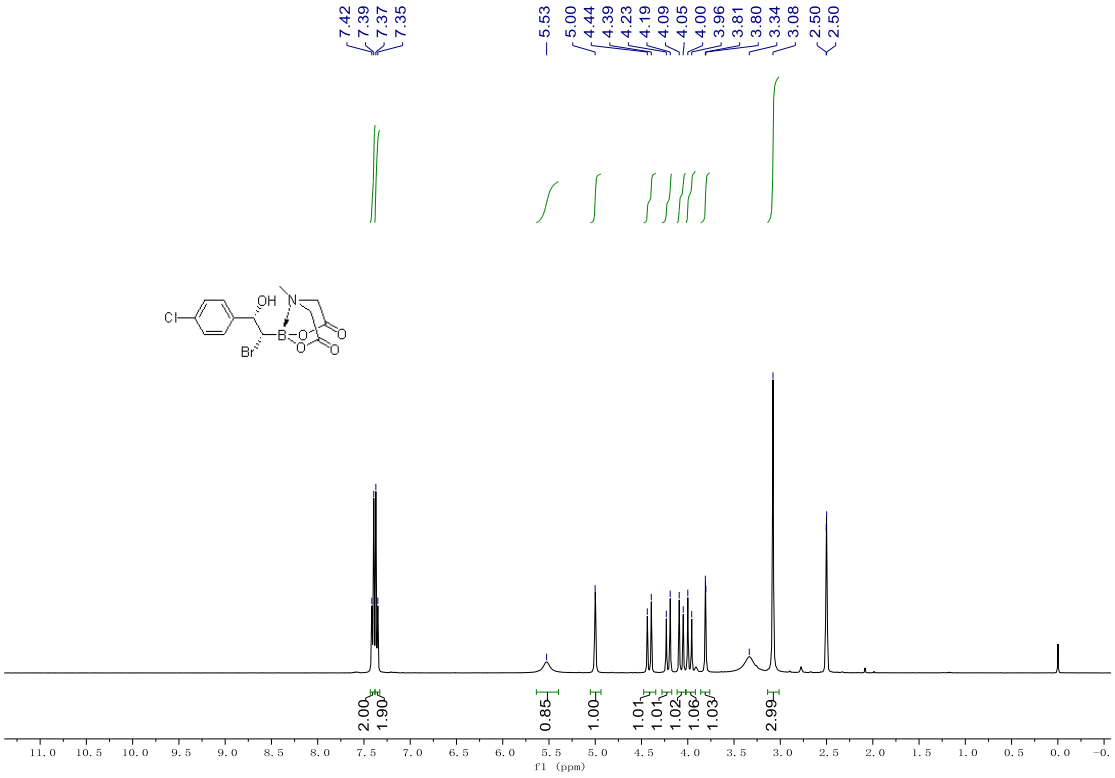
168.5
150.8
142.1
126.7
125.6
118.3
73.0
64.0
63.7
47.0
35.0
31.6
1.3
OH
N
B
O
O
O
O
Br
f1 (ppm)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7.39
7.37
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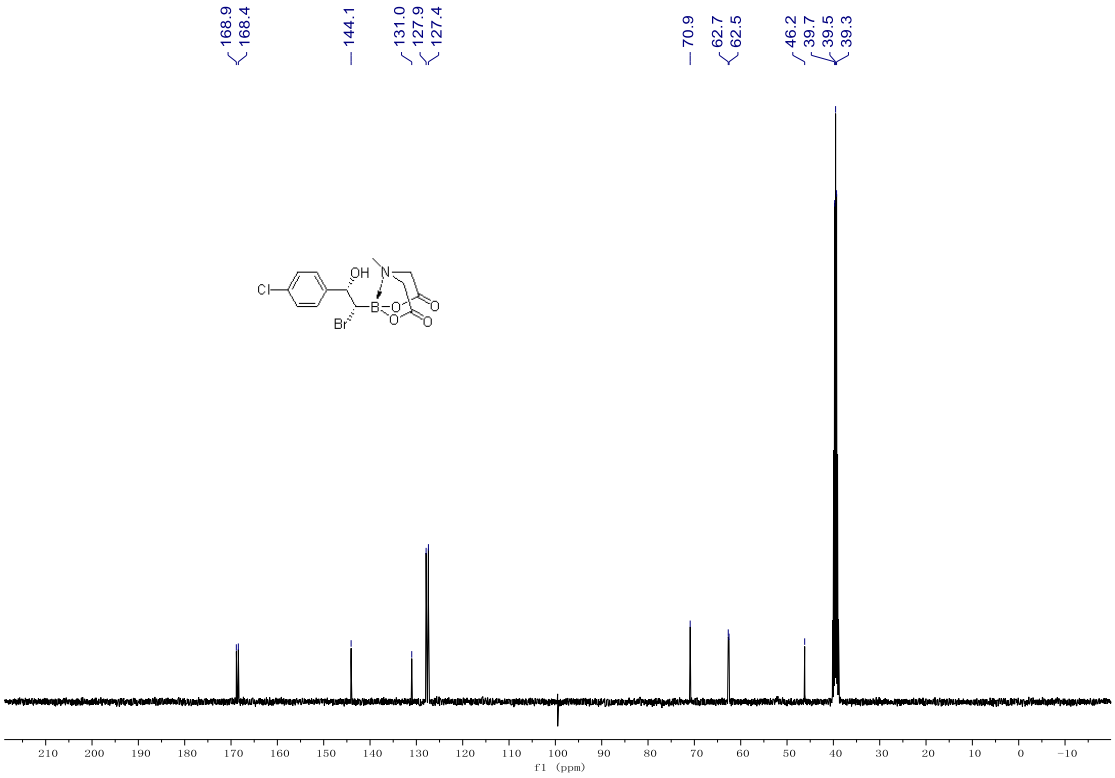
5.00
4.44
4.39
4.23
4.19
4.09
4.05
4.00
3.96
3.81
3.80
3.34
3.08
2.50
2.50
Cl
OH
N
B
O
O
O
O
Br
2.00
1.90
0.85
1.00
1.01
1.01
1.02
1.06
1.03
2.99
f1 (ppm)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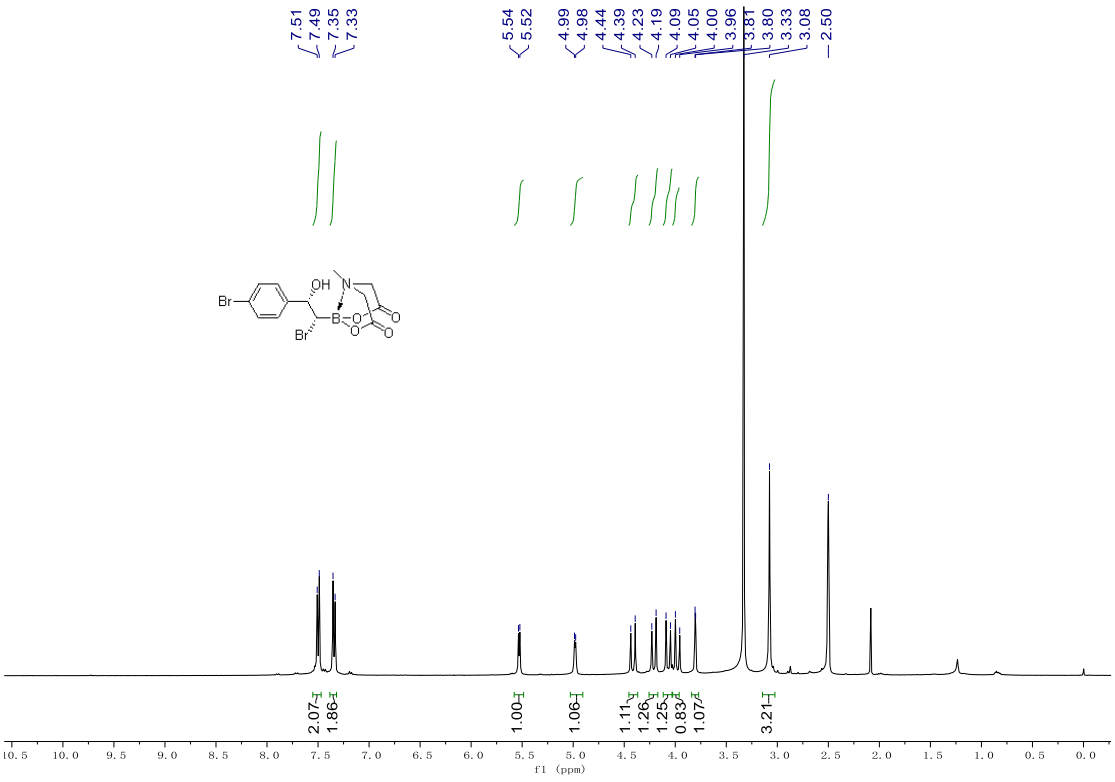
168.4
144.1
131.0
127.9
127.4
70.9
62.7
62.5
46.2
39.7
39.5
39.3
Cl
OH
N
B
O
O
O
O
Br
f1 (ppm)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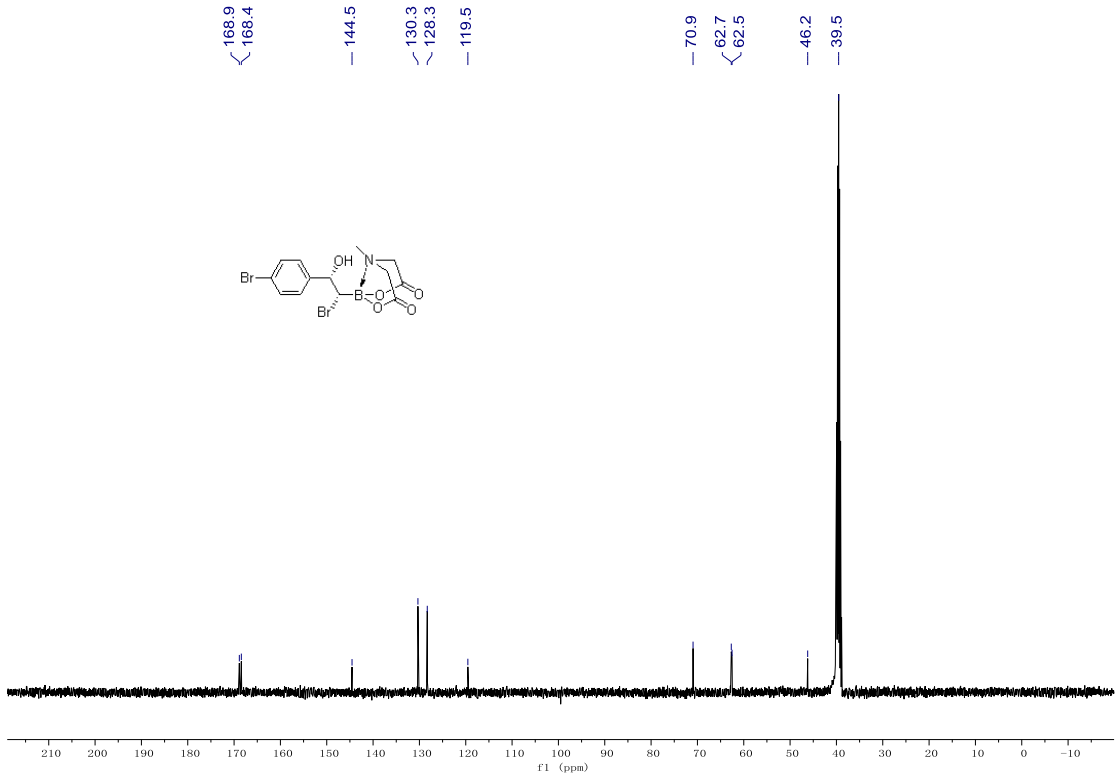
7.49
7.35
7.33
5.54
5.52
4.99
4.98
4.44
4.39
4.23
4.19
4.09
4.05
4.00
3.96
3.81
3.80
3.33
3.08
2.50
Br
OH
N
B
O
O
O
O
Br
2.07
1.86
1.00
1.06
1.11
1.26
1.25
0.83
1.07
3.21
f1 (ppm)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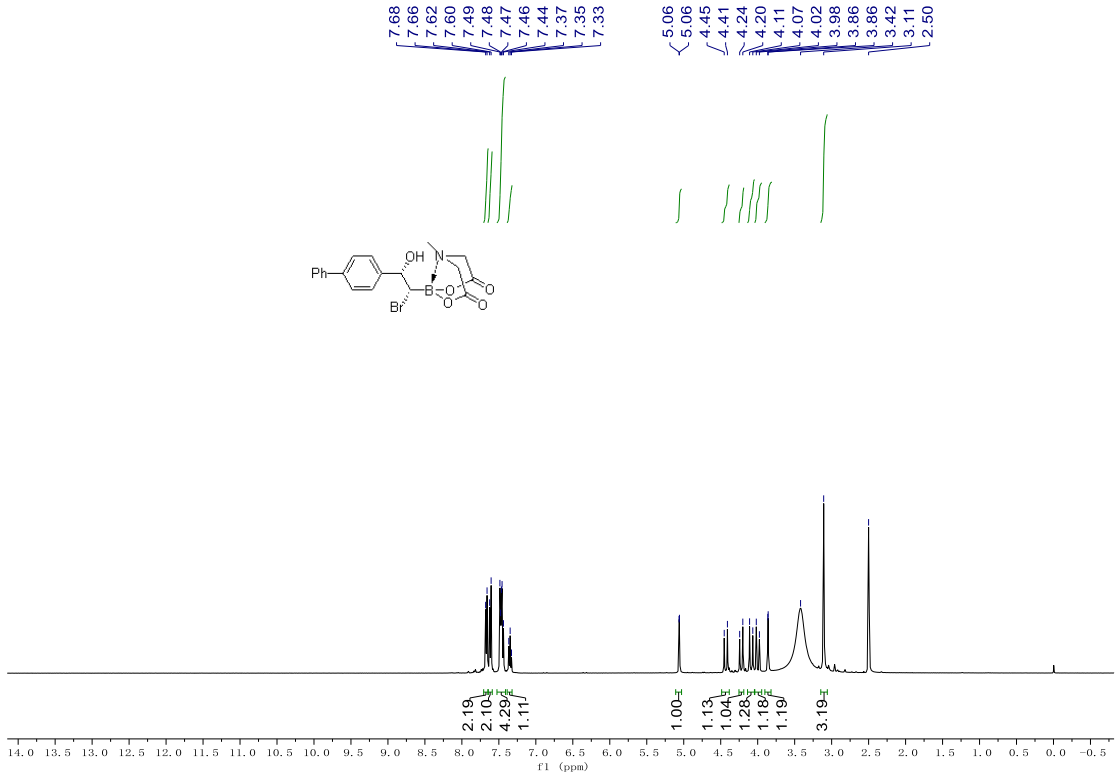
168.4
144.5
130.3
128.3
119.5
70.9
62.7
62.5
46.2
39.5
Br
OH
N
B
O
O
O
O
Br
f1 (ppm)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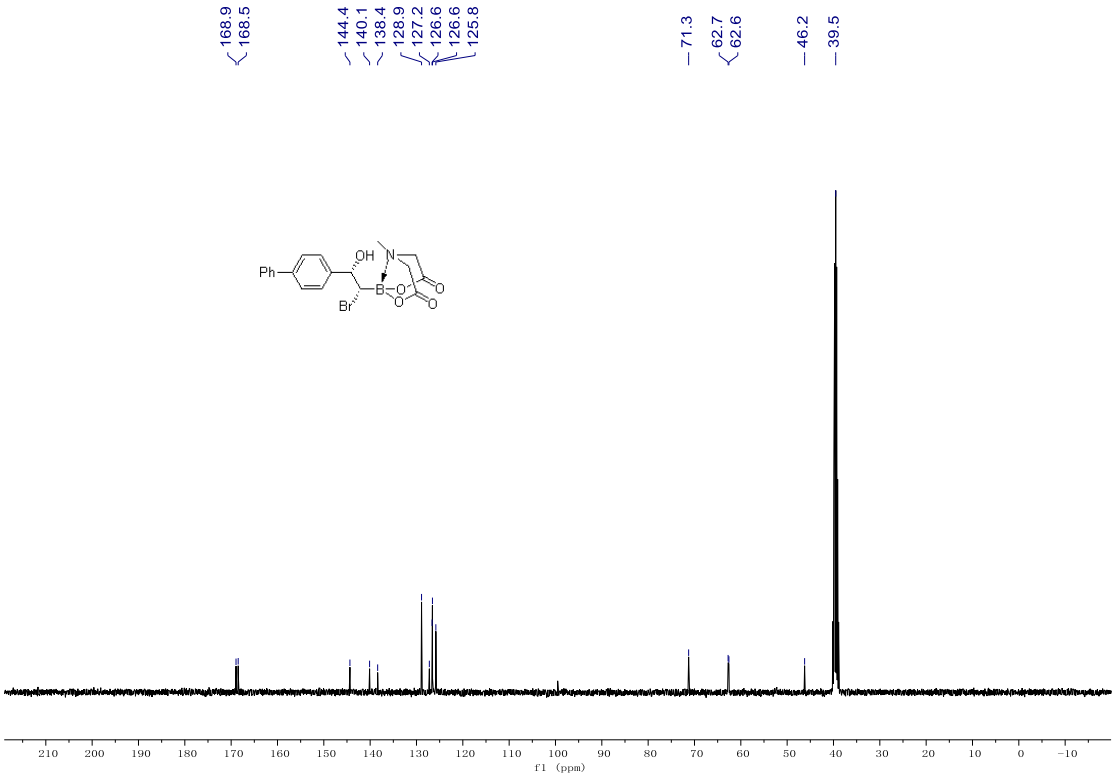
7.48
7.47
7.46
7.44
7.37
7.35
7.33
5.06
5.06
4.45
4.41
4.24
4.20
4.11
4.07
4.02
3.98
3.86
3.86
3.42
3.11
2.50
Ph
OH
N
B
O
O
O
O
Br
2.19
2.10
4.29
1.11
1.00
1.13
1.04
1.28
1.18
1.19
3.19
f1 (ppm)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168.5
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138.4
128.9
127.2
126.6
126.6
125.8
71.3
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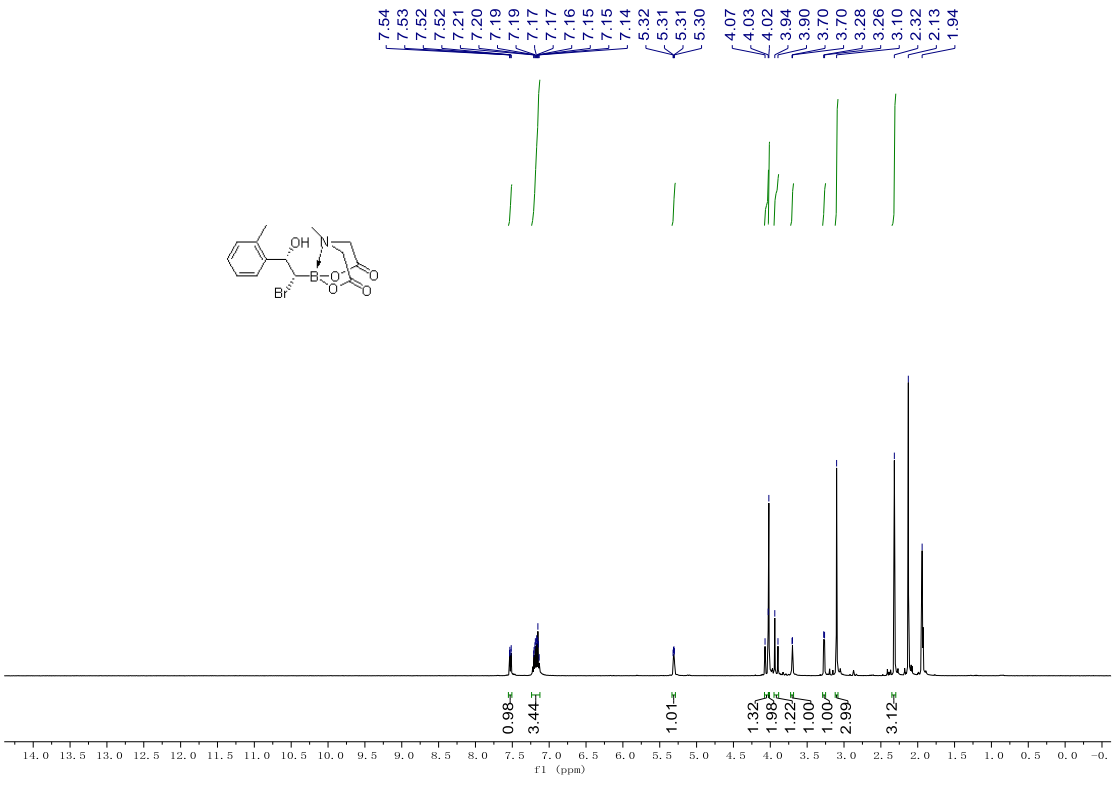
62.6
46.2
39.5
Ph
OH
N
B
O
O
O
O
Br
f1 (ppm)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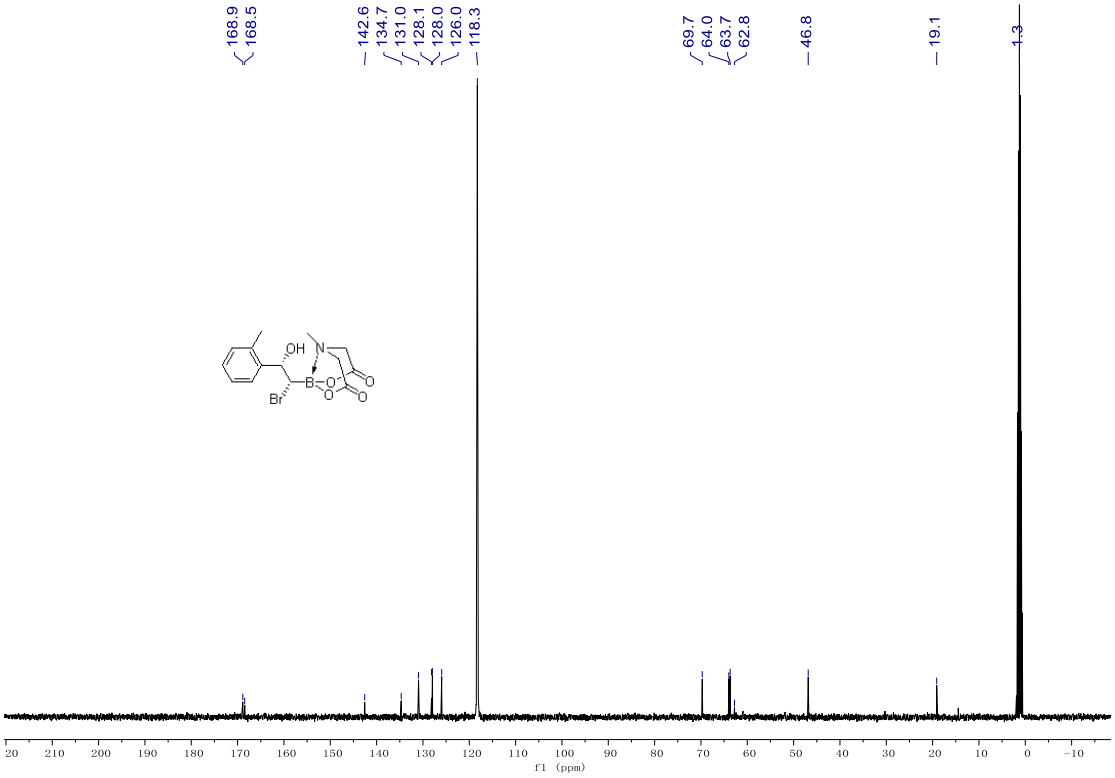
7.53
7.52
7.52
7.21
7.20
7.19
7.19
7.17
7.17
7.16
7.15
7.15
7.14
5.32
5.31
5.31
5.30
4.07
4.03
4.02
3.94
3.90
3.70
3.70
3.28
3.26
3.10
2.32
2.13
1.94
OH
N
B
O
O
O
O
Br
0.98
3.44
1.01
1.32
1.98
1.22
1.00
1.00
2.99
3.12
f1 (ppm)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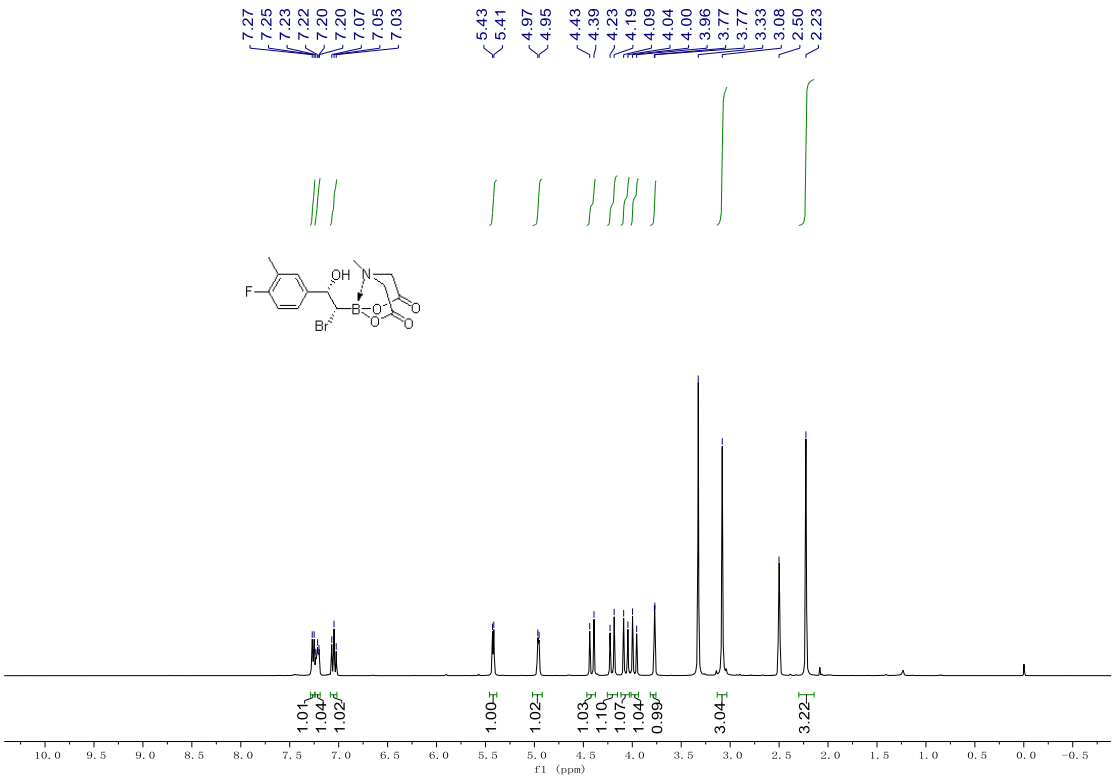
168.5
142.6
134.7
131.0
128.1
128.0
126.0
118.3
69.7
64.0
63.7
62.8
46.8
19.1
1.3
OH
N
B
O
O
O
O
Br
f1 (ppm)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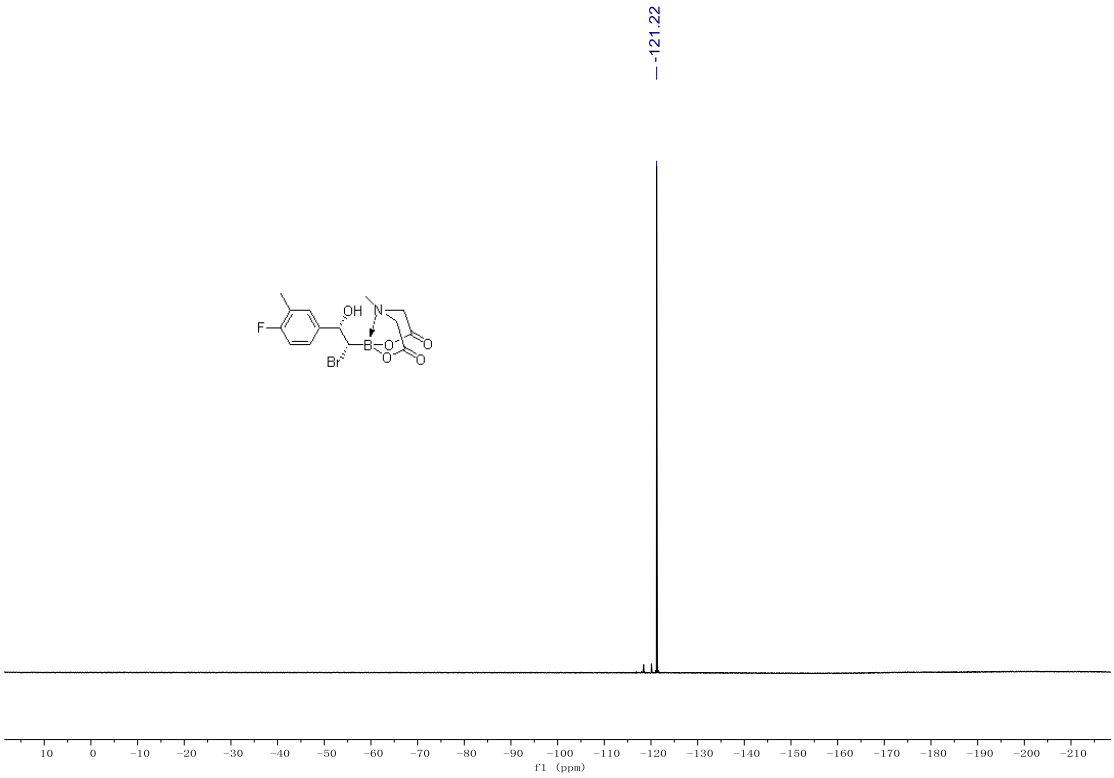
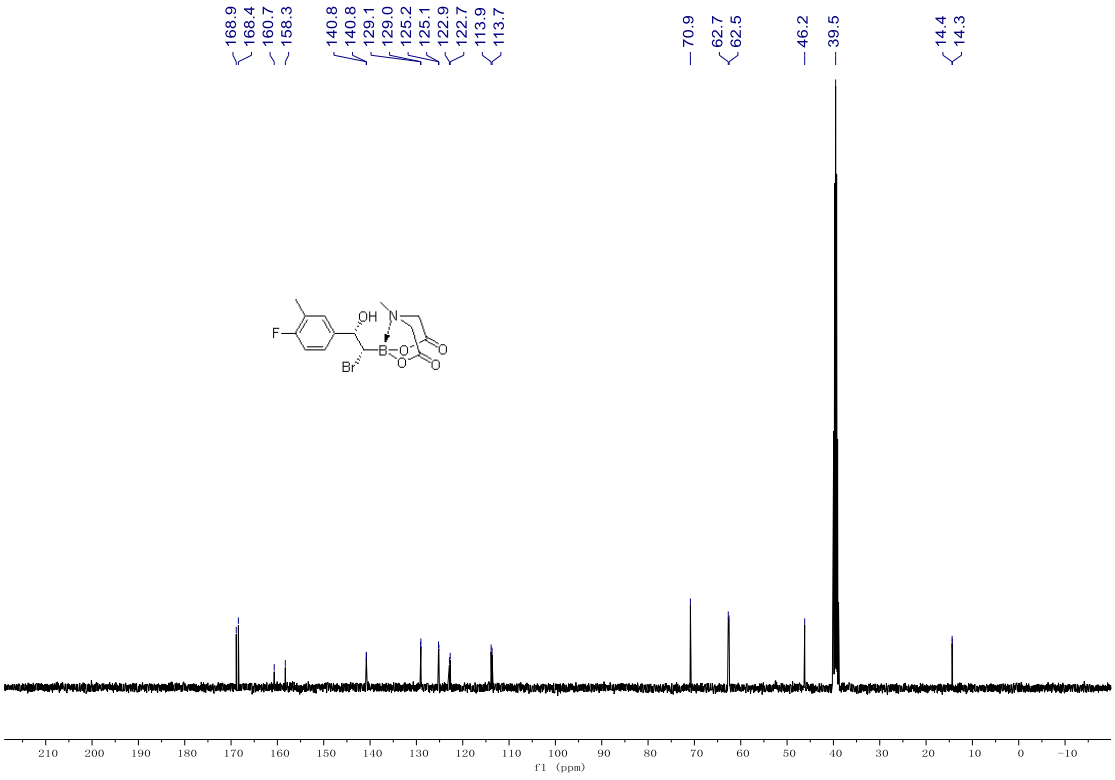
7.25
7.23
7.22
7.20
7.20
7.07
7.05
7.03
5.43
5.41
4.97
4.95
4.43
4.39
4.23
4.19
4.09
4.04
4.00
3.96
3.77
3.77
3.33
3.08
2.50
2.23
F
OH
N
B
O
O
O
O
Br
1.01
1.04
1.02
1.00
1.02
1.03
1.10
1.07
1.04
0.99
3.04
3.22
f1 (ppm)


-121.22
F
OH
N
Br
B
O
O
O
O
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)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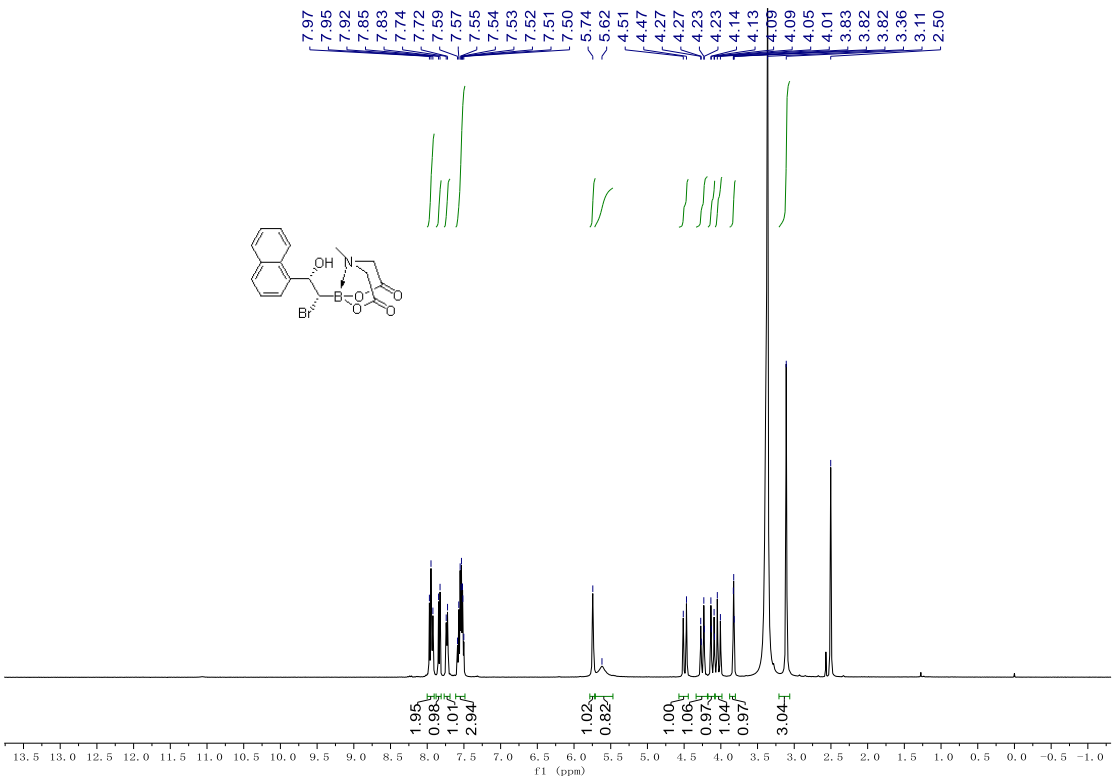
168.4
160.7
158.3
140.8
140.8
129.1
129.0
125.2
125.1
122.9
122.7
113.9
113.7
70.9
62.7
62.5
46.2
39.5
14.4
14.3
F
OH
N
Br
B
O
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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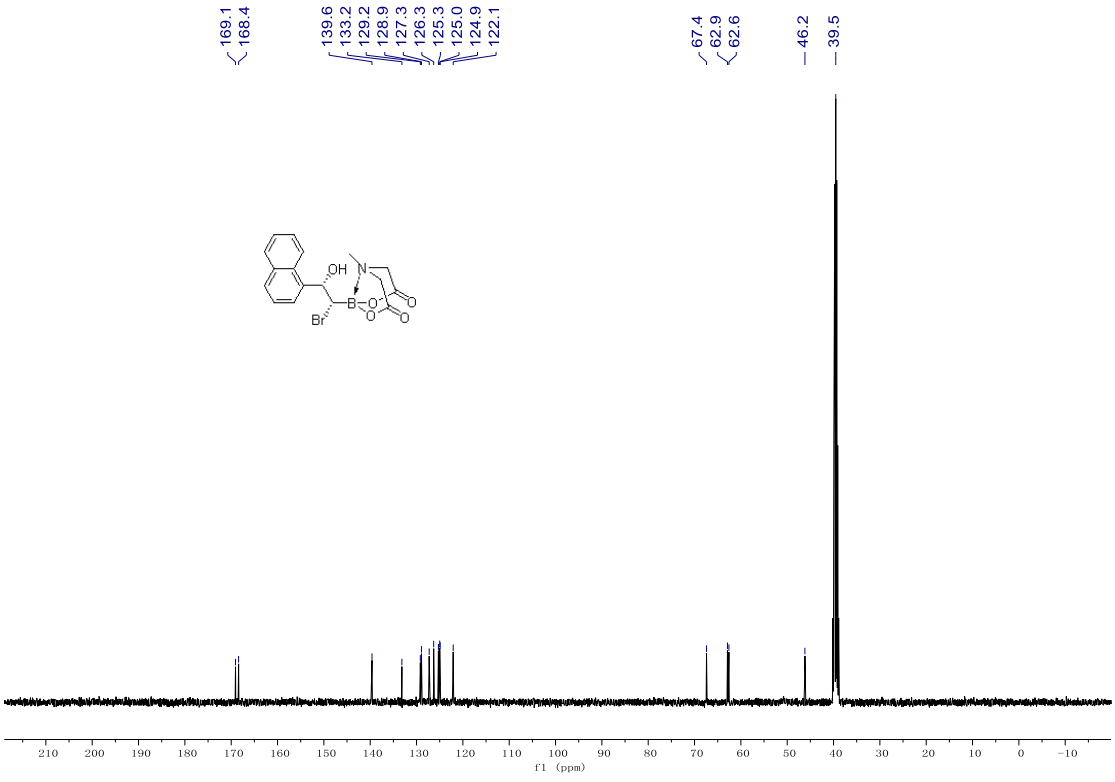
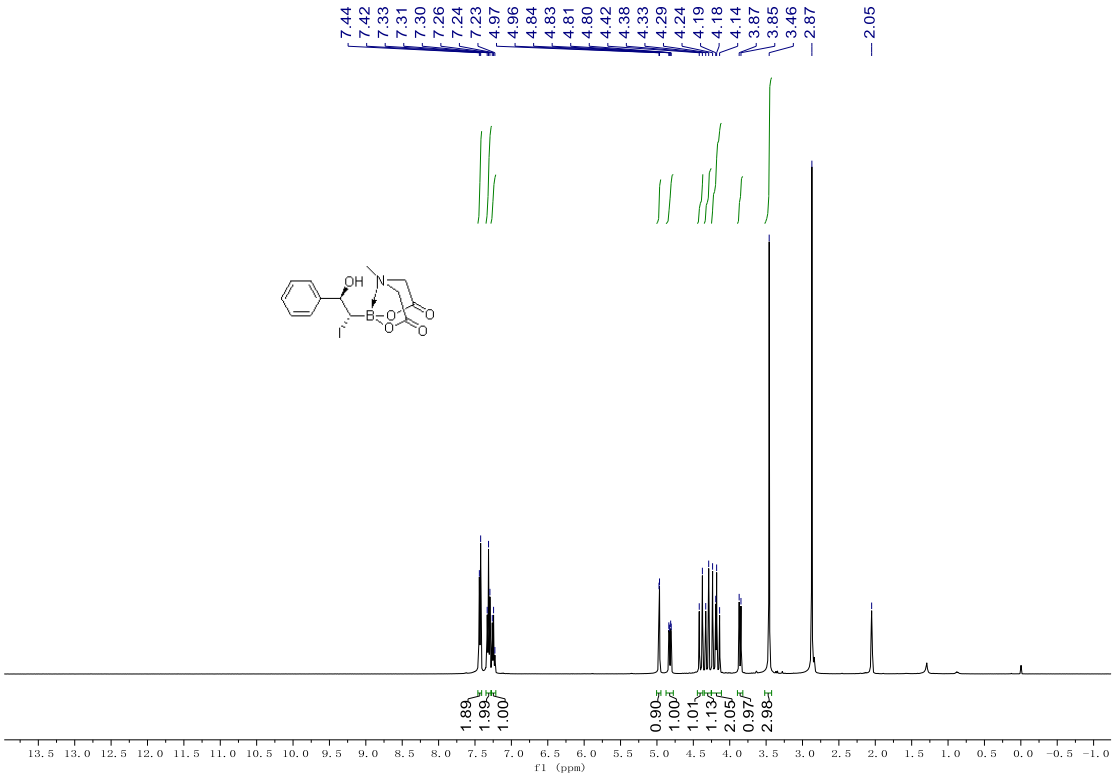
7.92
7.85
7.83
7.74
7.72
7.59
7.57
7.55
7.54
7.53
7.52
7.51
7.50
5.74
5.62
4.51
4.47
4.27
4.27
4.23
4.23
4.14
4.13
4.09
4.09
4.05
4.01
3.83
3.82
3.82
3.36
3.11
2.50
OH
N
B
O
O
O
O
Br
1.95
0.98
1.01
2.94
1.02
0.82
1.00
1.06
0.97
1.04
0.97
3.04
f1 (ppm)


169.1
168.4
139.6
133.2
129.2
128.9
127.3
126.3
125.3
125.0
124.9
122.1
67.4
62.9
62.6
46.2
39.5
OH
N
B
O
O
O
O
Br
f1 (ppm)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7.26
7.24
7.23
4.97
4.96
4.84
4.83
4.81
4.80
4.42
4.38
4.33
4.29
4.24
4.19
4.18
4.14
3.87
3.85
3.46
2.87
2.05
OH
N
B
O
O
O
O
I
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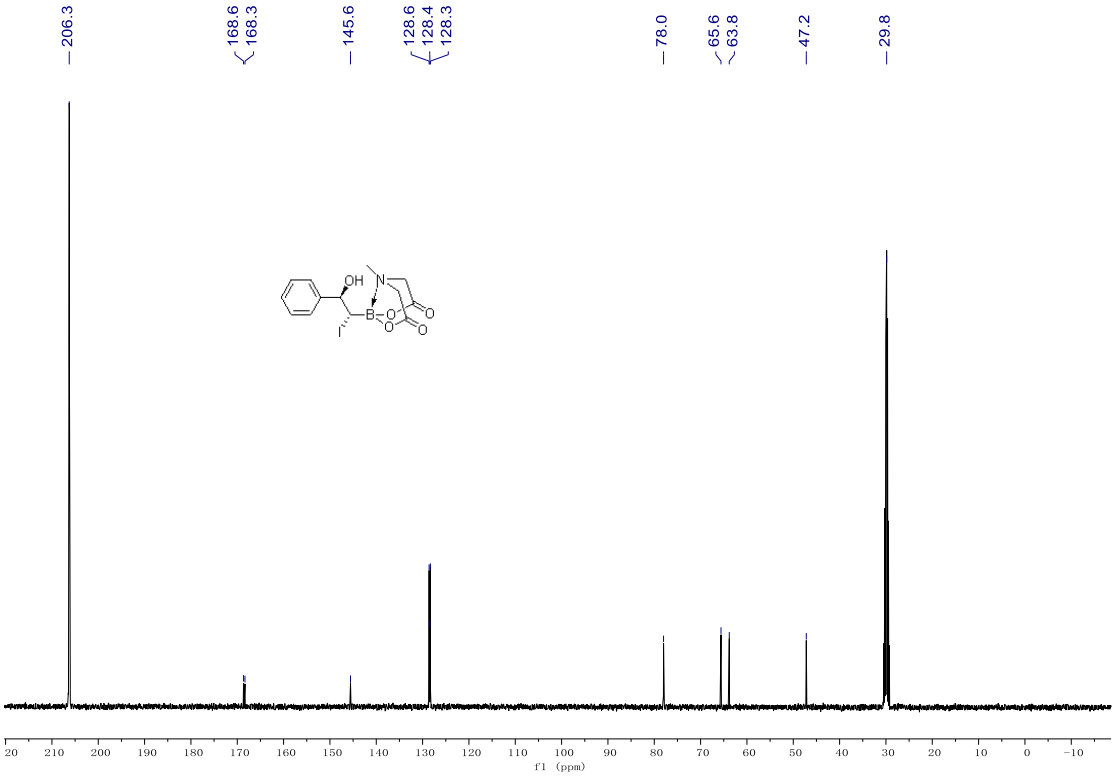
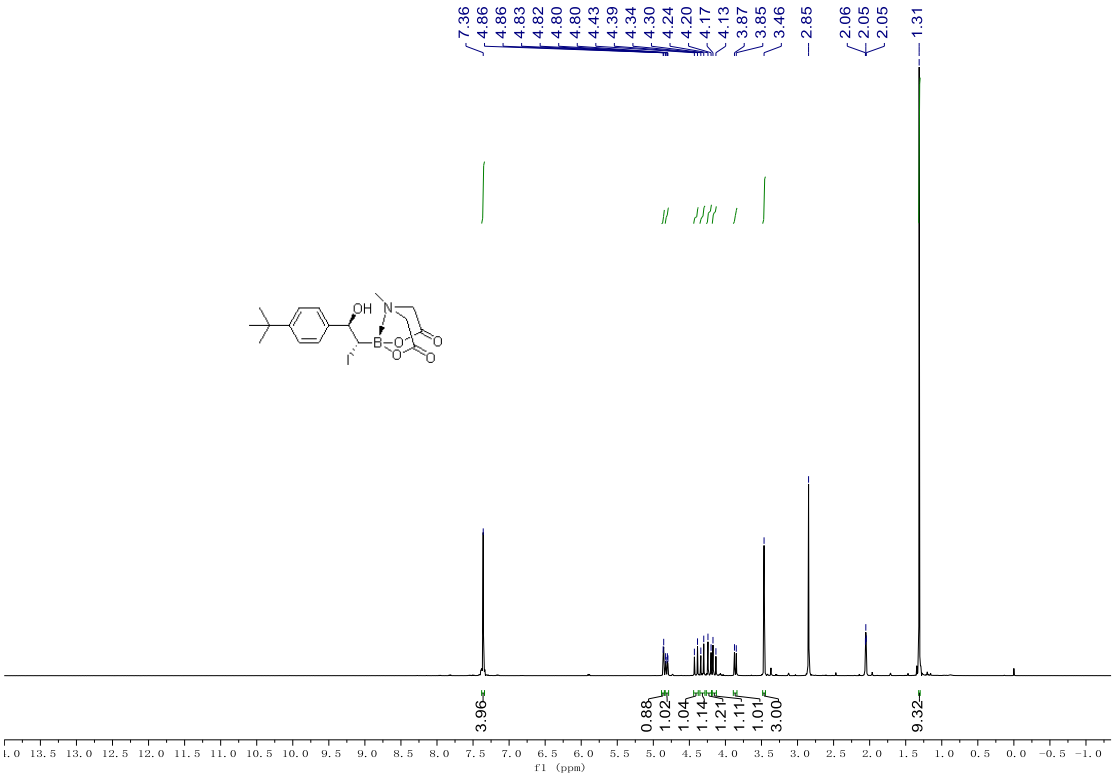
1.99
1.00
0.90
1.00
1.01
1.13
2.05
0.97
2.98
f1 (ppm)


206.3
168.6
168.3
145.6
128.6
128.4
128.3
78.0
65.6
63.8
47.2
29.8
OH
N
B
O
O
O
O
I
f1 (ppm)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4.86
4.86
4.83
4.82
4.80
4.80
4.43
4.39
4.34
4.30
4.24
4.20
4.17
4.13
3.87
3.85
3.46
2.85
2.06
2.05
2.05
1.31
3.96
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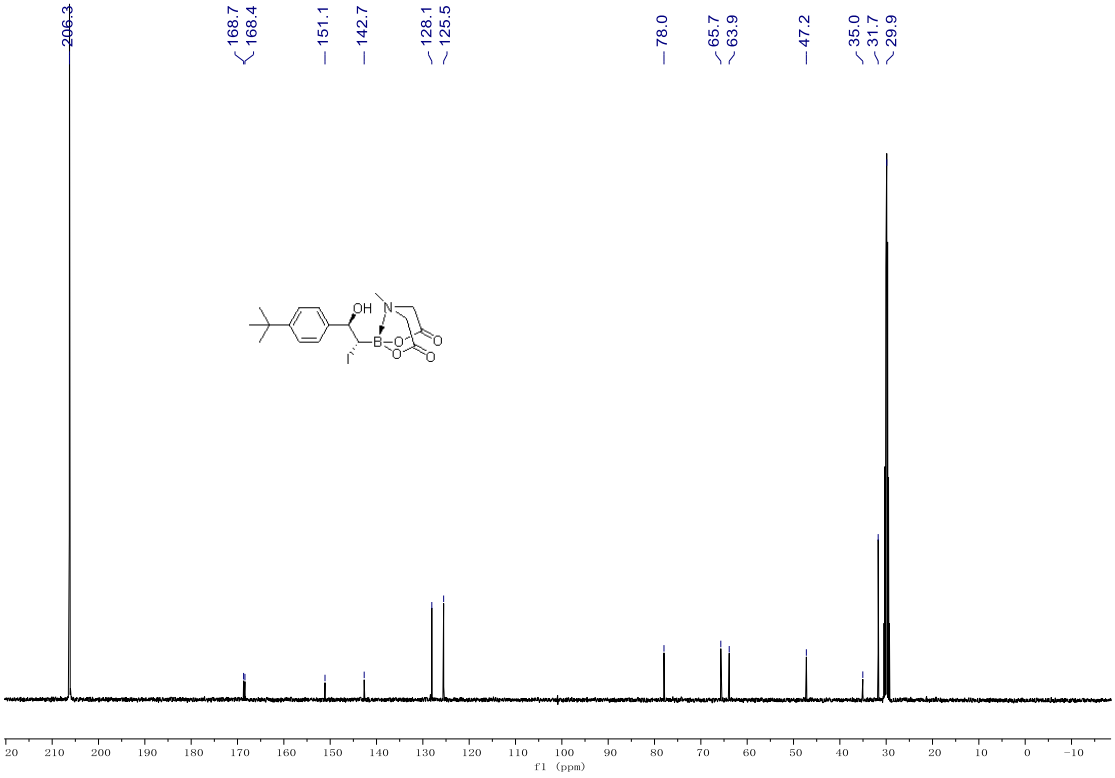
1.02
1.04
1.14
1.21
1.11
1.01
3.00
9.32
f1 (ppm)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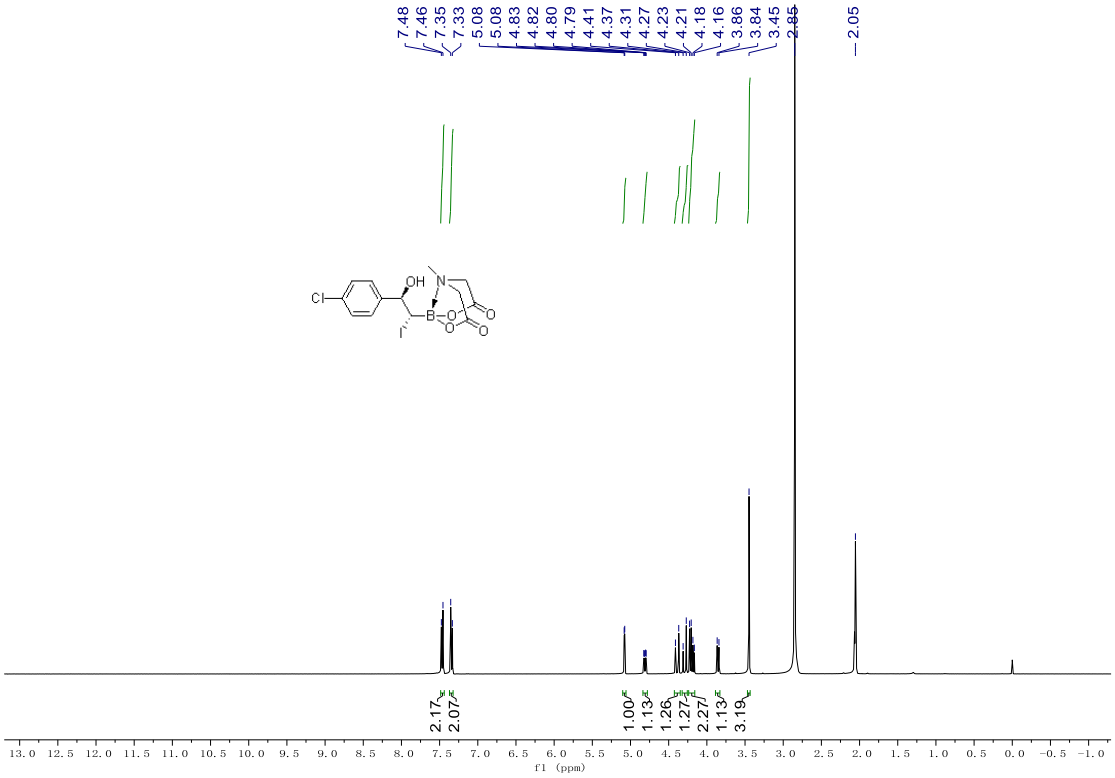
168.7
168.4
151.1
142.7
128.1
125.5
78.0
65.7
63.9
47.2
35.0
31.7
29.9
f1 (ppm)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7.35
7.33
5.08
5.08
4.83
4.82
4.80
4.79
4.41
4.37
4.31
4.27
4.23
4.21
4.18
4.16
3.86
3.84
3.45
2.85
2.05
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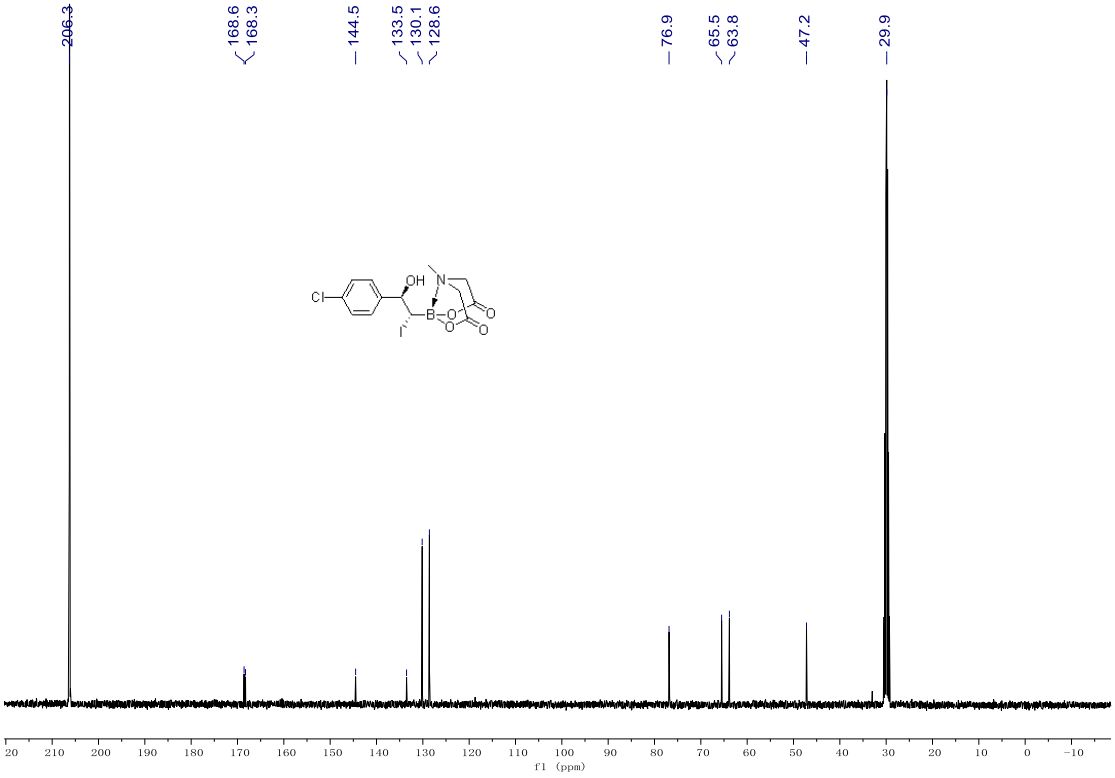
2.07
1.00
1.13
1.26
1.27
2.27
1.13
3.19
f1 (ppm)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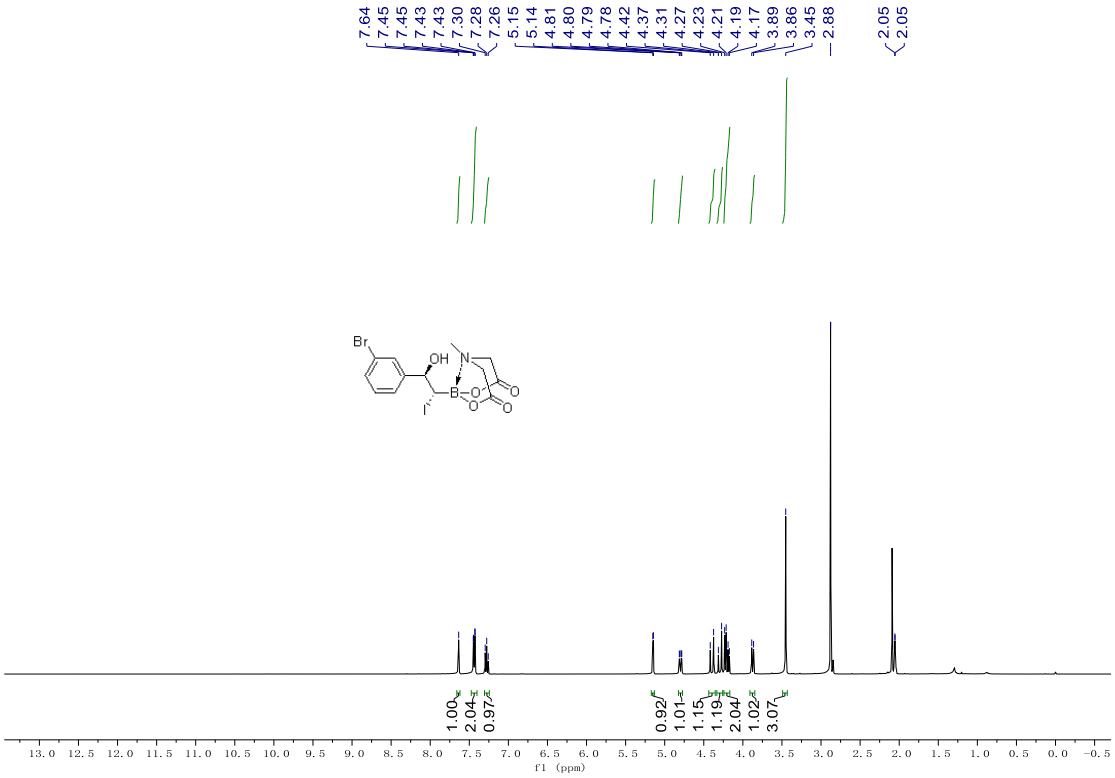
168.6
168.3
144.5
133.5
130.1
128.6
76.9
65.5
63.8
47.2
29.9
f1 (ppm)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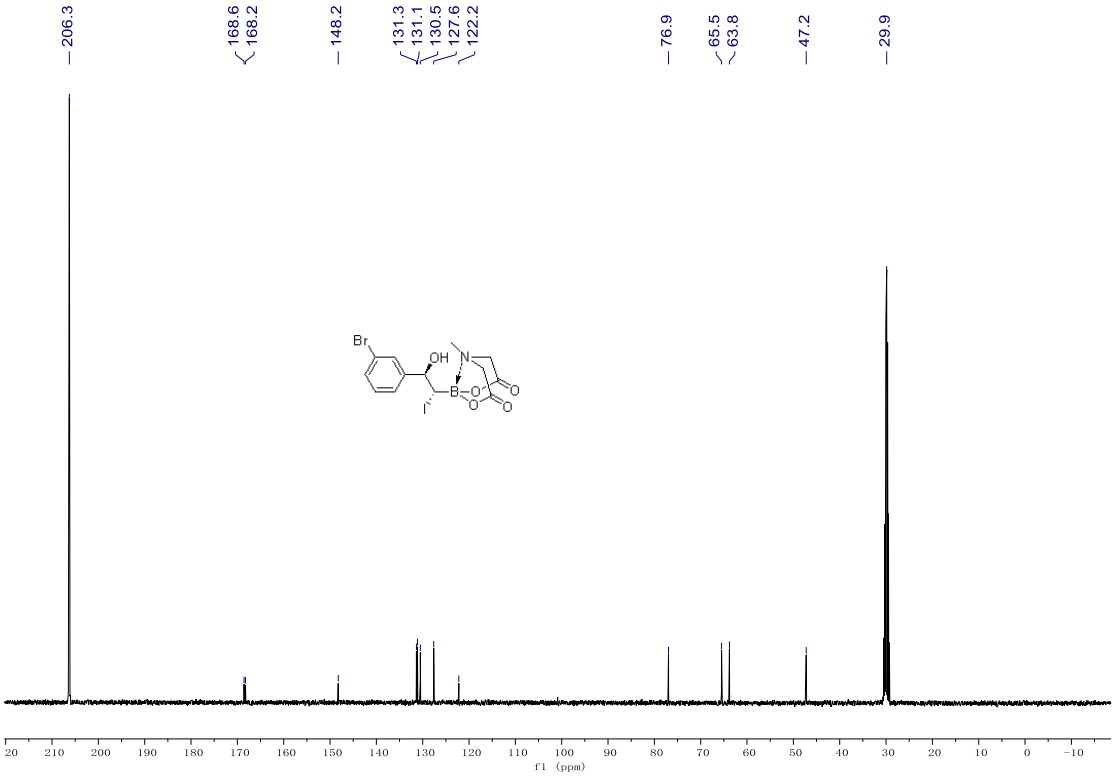
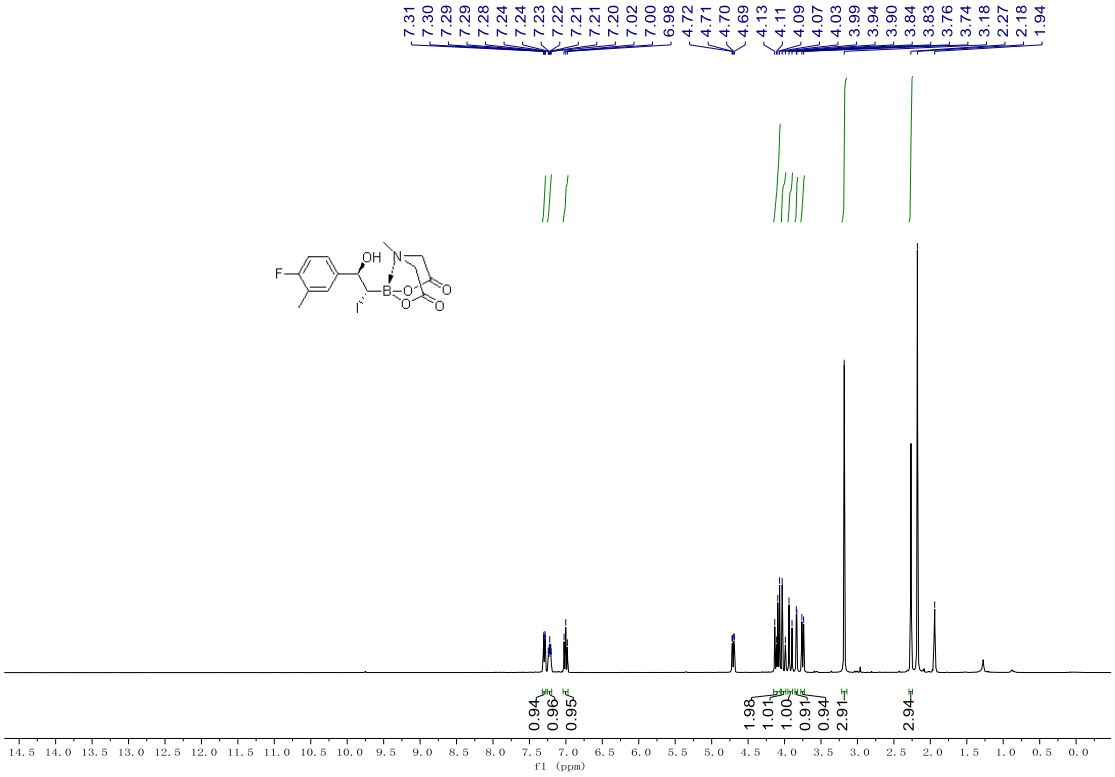
7.43
7.30
7.28
7.26
5.15
5.14
4.81
4.80
4.79
4.78
4.42
4.37
4.31
4.27
4.23
4.21
4.19
4.17
3.89
3.86
3.45
2.88
2.05
2.05
Br
OH
N
B
O
O
O
O
I
1.00
2.04
0.97
0.92
1.01
1.15
1.19
2.04
1.02
3.07
f1 (ppm)


206.3
168.6
168.2
148.2
131.3
131.1
130.5
127.6
122.2
76.9
65.5
63.8
47.2
29.9
Br
OH
N
B
O
O
O
O
I
f1 (ppm)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7.29
7.29
7.28
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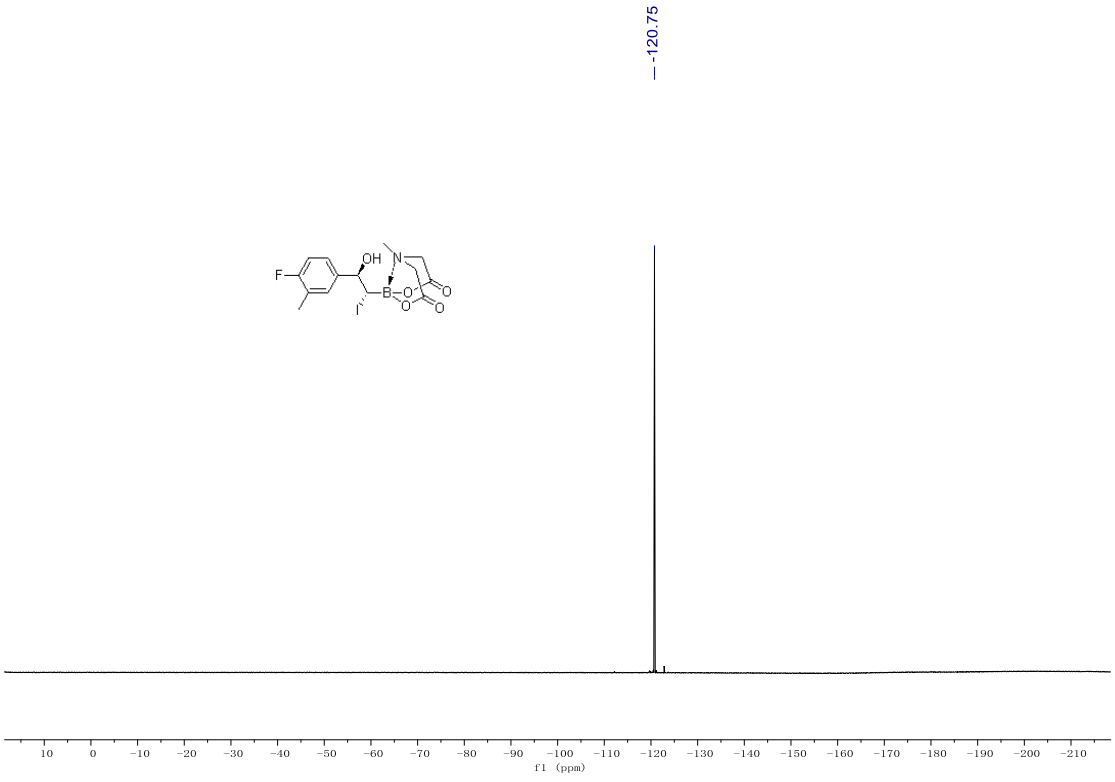
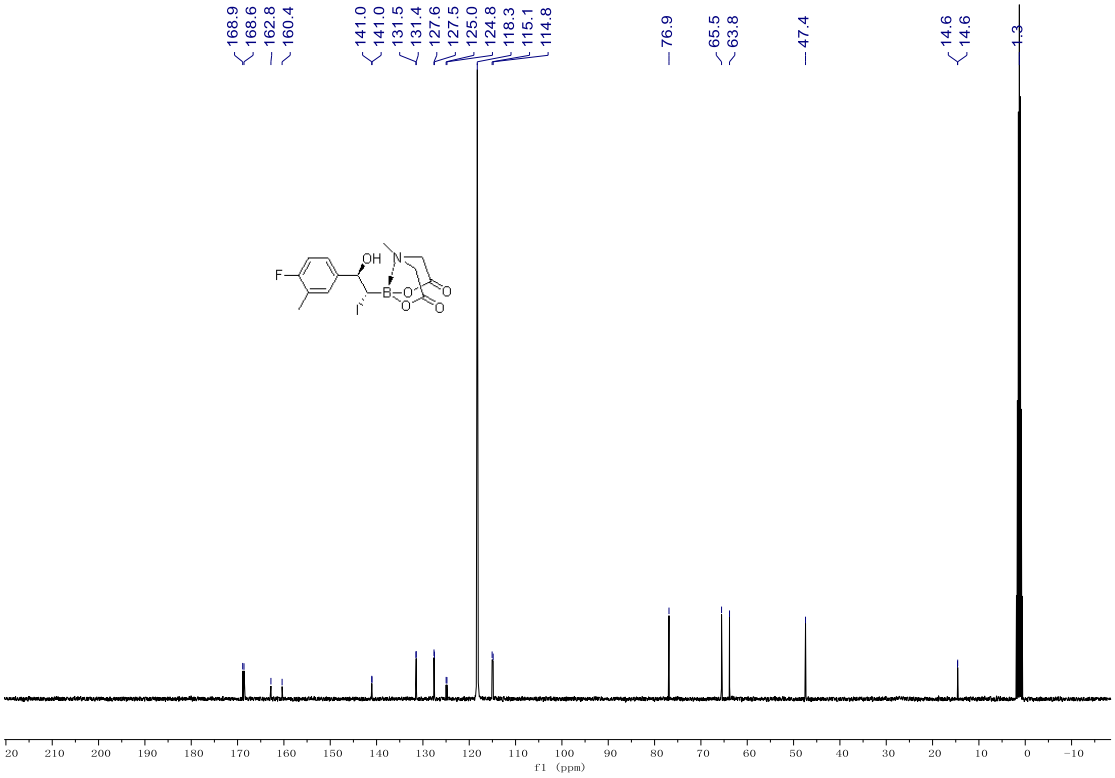
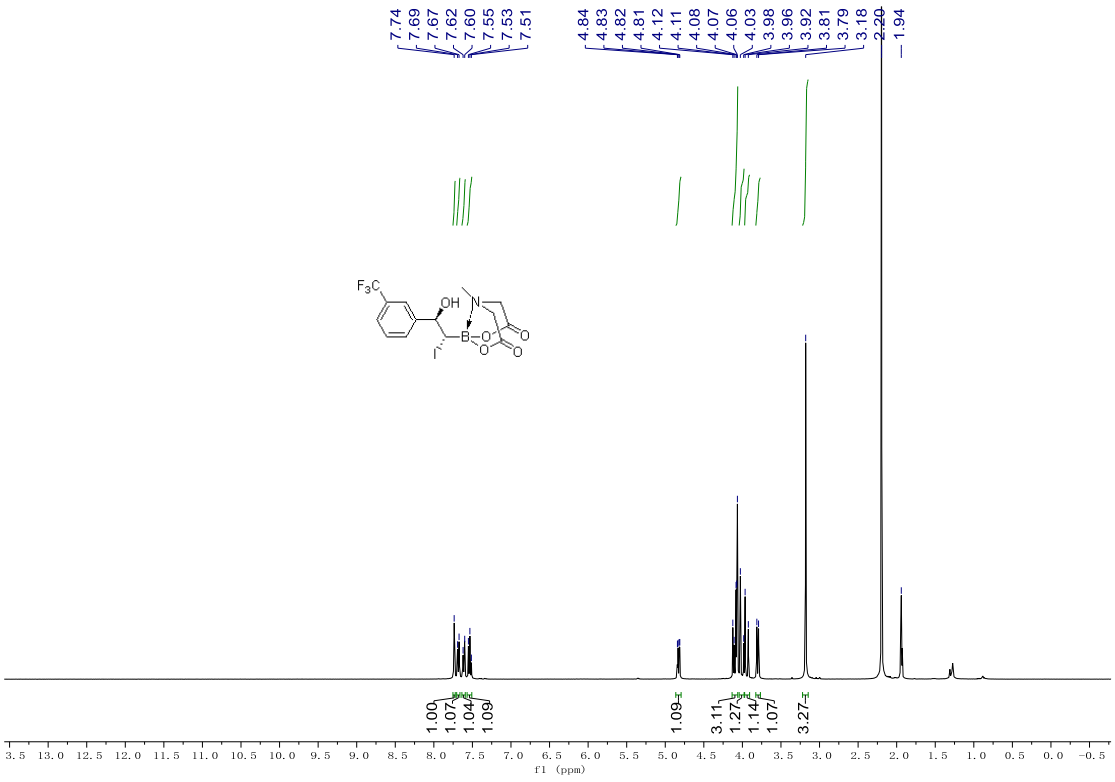
7.24
7.23
7.22
7.21
7.21
7.20
7.02
7.00
6.98
4.72
4.71
4.70
4.69
4.13
4.11
4.09
4.07
4.03
3.99
3.94
3.90
3.84
3.83
3.76
3.74
3.18
2.27
2.18
1.94
OH
N
F
B
O
O
O
O
I
0.94
0.96
0.95
1.98
1.01
1.00
0.91
0.94
2.91
2.94
f1 (ppm)


-120.75
OH
N
F
B
O
O
O
O
I
f1 (ppm)


168.9
168.6
162.8
160.4
141.0
141.0
131.5
131.4
127.6
127.5
125.0
124.8
118.3
115.1
114.8
76.9
65.5
63.8
47.4
14.6
14.6
1.3
F
OH
N
B
O
O
O
O
I
f1 (ppm)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7.60
7.55
7.53
7.51
4.84
4.83
4.82
4.81
4.12
4.11
4.08
4.07
4.06
4.03
3.98
3.96
3.92
3.81
3.79
3.18
2.20
1.94
F3C
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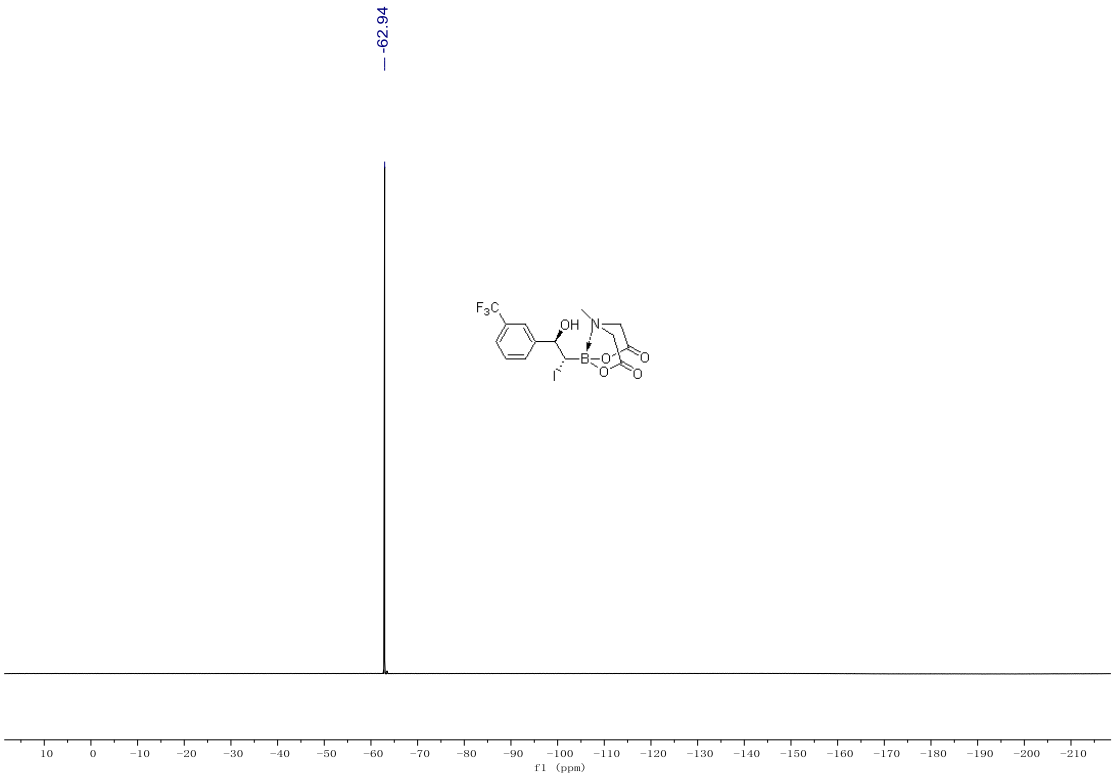
B
O
O
O
O
I
1.00
1.07
1.04
1.09
1.09
3.11
1.27
1.14
1.07
3.27
f1 (ppm)


-62.94
F3C
OH
N
B
O
O
O
O
I
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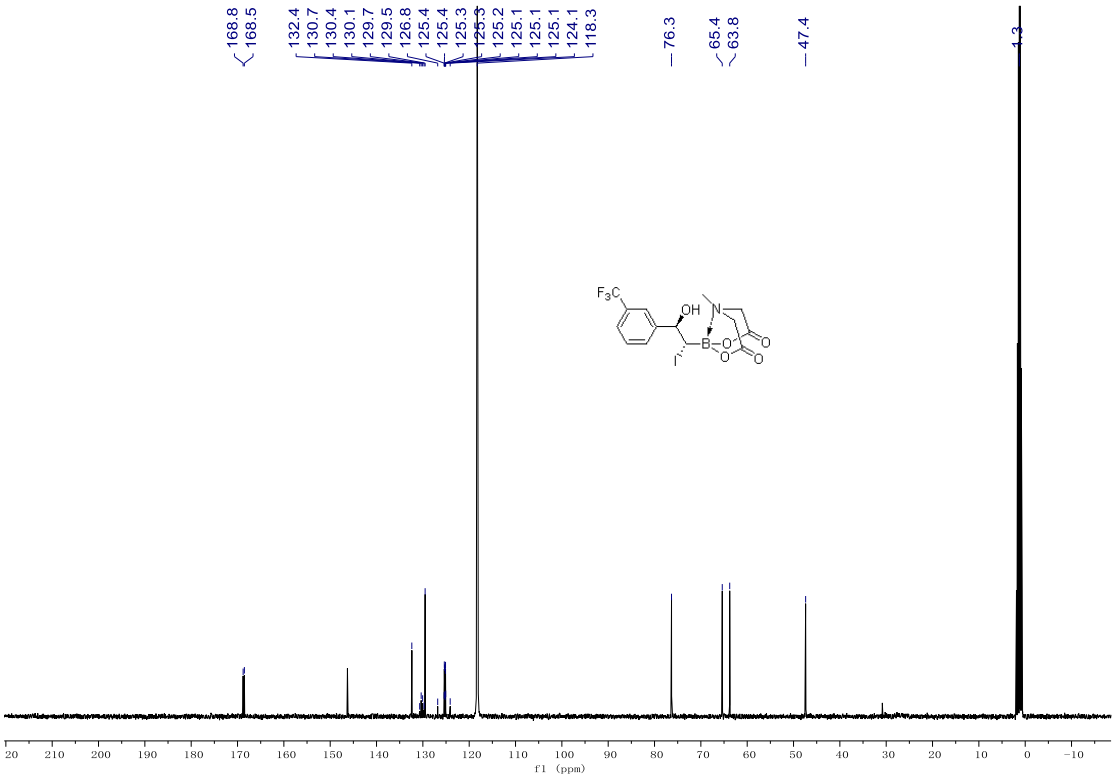
f1 (ppm)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129.5
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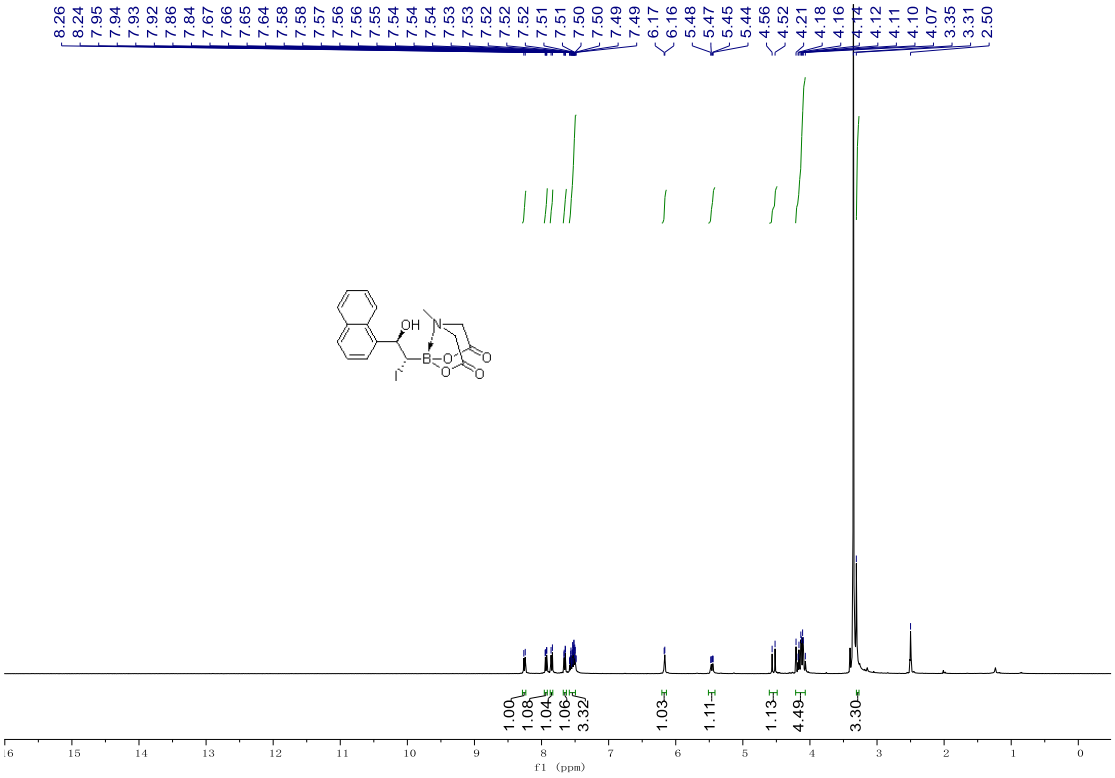
125.4
125.3
125.3
125.2
125.1
125.1
125.1
124.1
118.3
76.3
65.4
63.8
47.4
1.3
F3C
OH
N
B
O
O
O
O
I
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.64
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7.58
7.57
7.56
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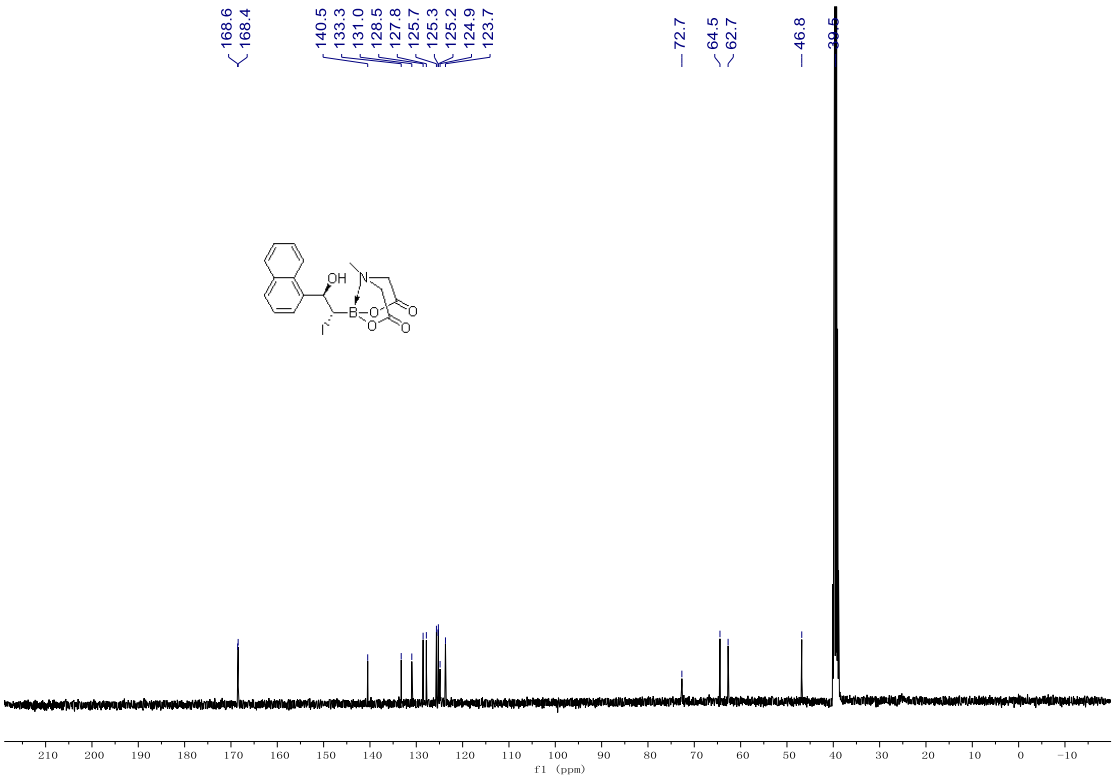
7.55
7.54
7.54
7.54
7.53
7.52
7.52
7.52
7.51
7.51
7.50
7.50
7.49
7.49
6.17
6.16
5.48
5.47
5.45
5.44
4.56
4.52
4.21
4.18
4.16
4.14
4.12
4.11
4.10
4.07
3.35
3.31
2.50
OH
N
B
O
O
O
O
1.00
1.08
1.04
1.06
3.32
1.03
1.11
1.13
4.49
3.30
f1 (ppm)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128.5
127.8
125.7
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125.2
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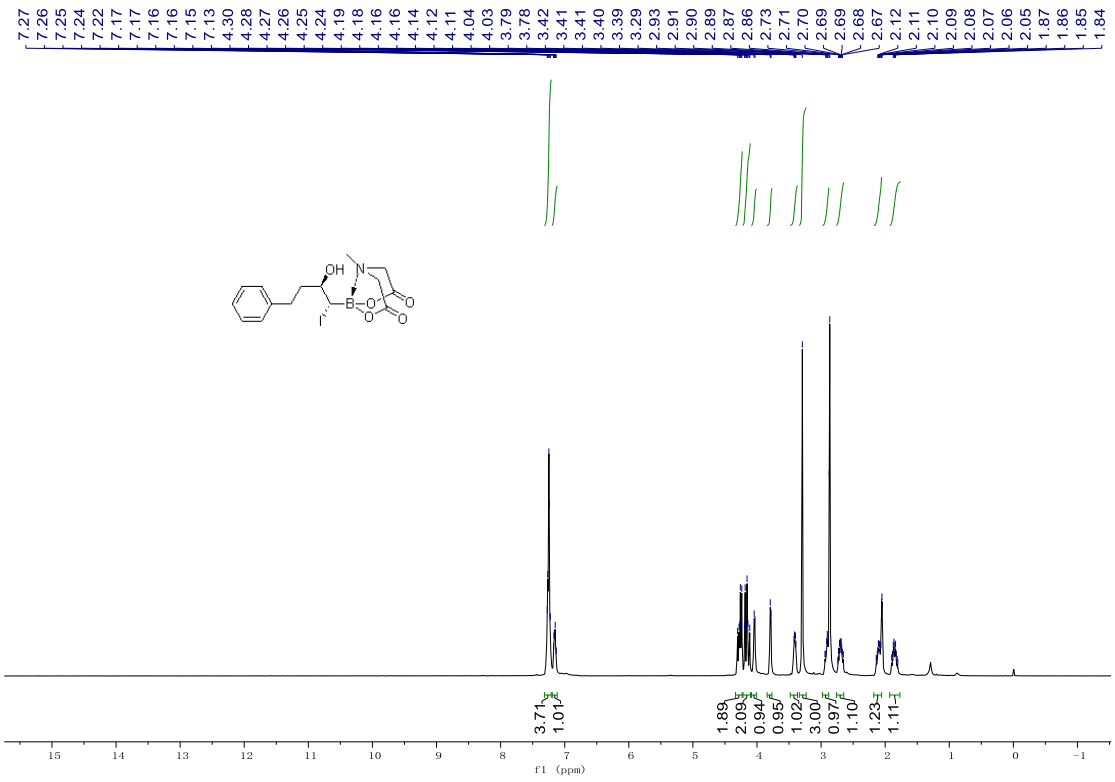
64.5
62.7
46.8
39.5
OH
N
B
O
O
O
O
f1 (ppm)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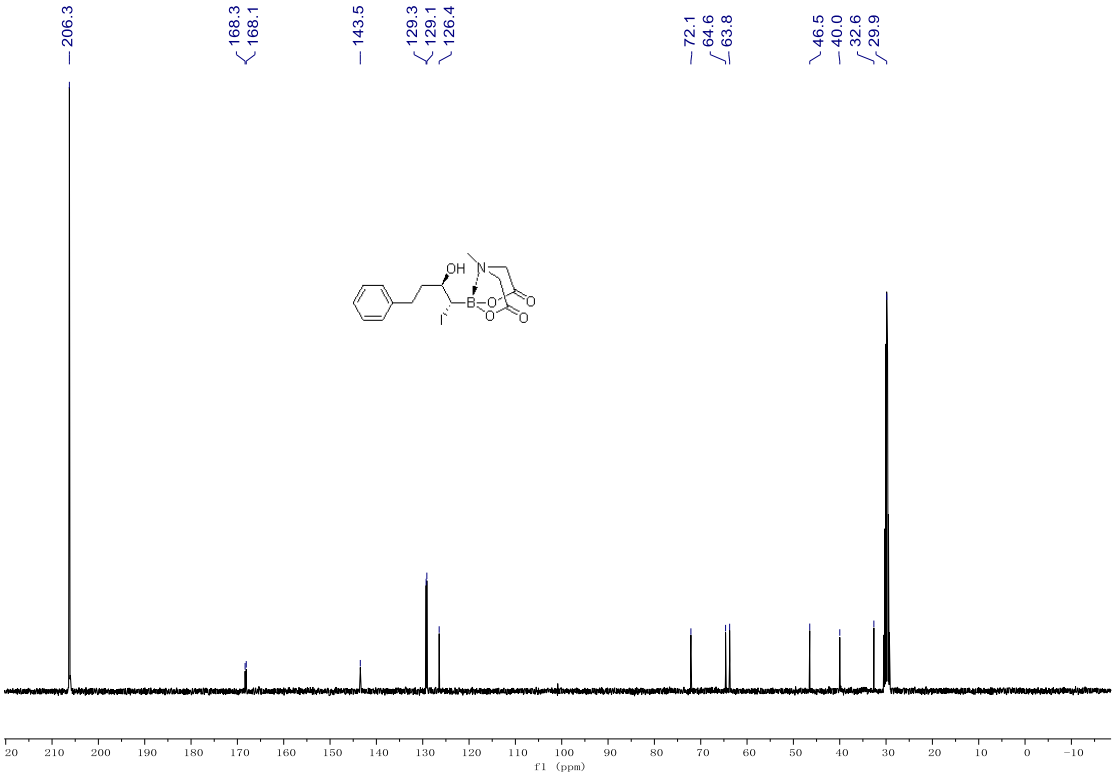
OH
N
B
O
O
O
O
3.71
1.01
1.89
2.09
0.94
0.95
1.02
3.00
0.97
1.10
1.23
1.11
f1 (ppm)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168.1
143.5
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129.1
126.4
72.1
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46.5
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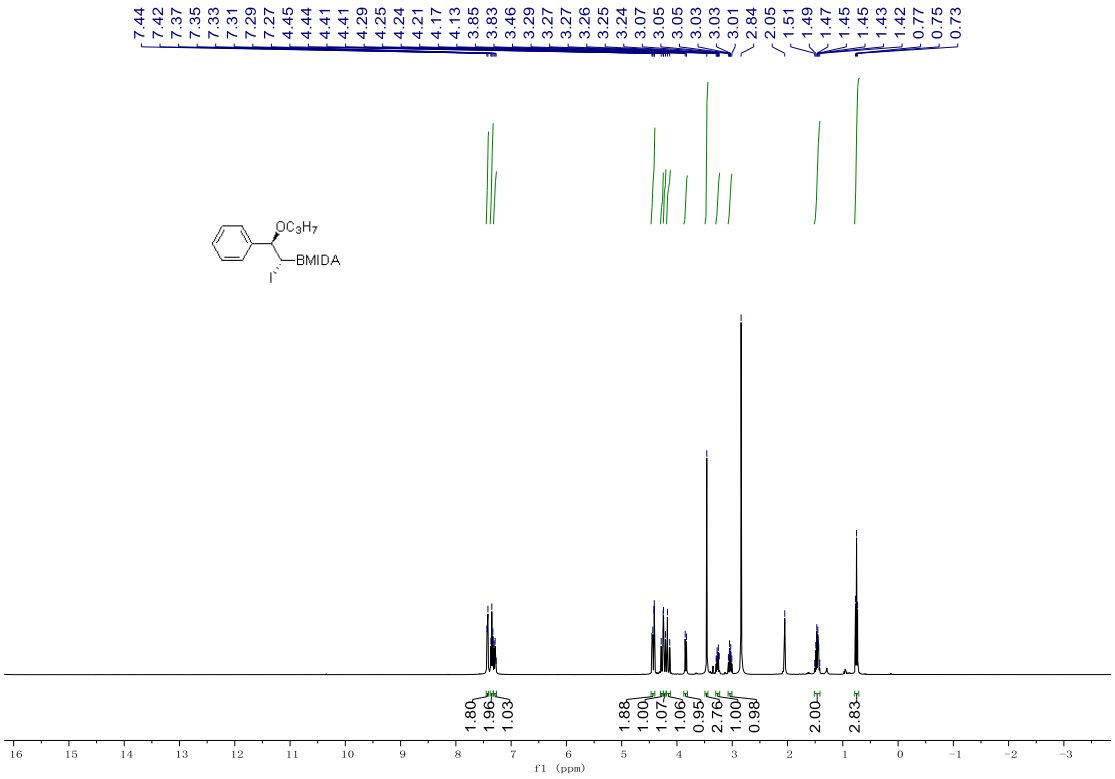
32.6
29.9
OH
N
B
O
O
O
O
f1 (ppm)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7.31
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7.27
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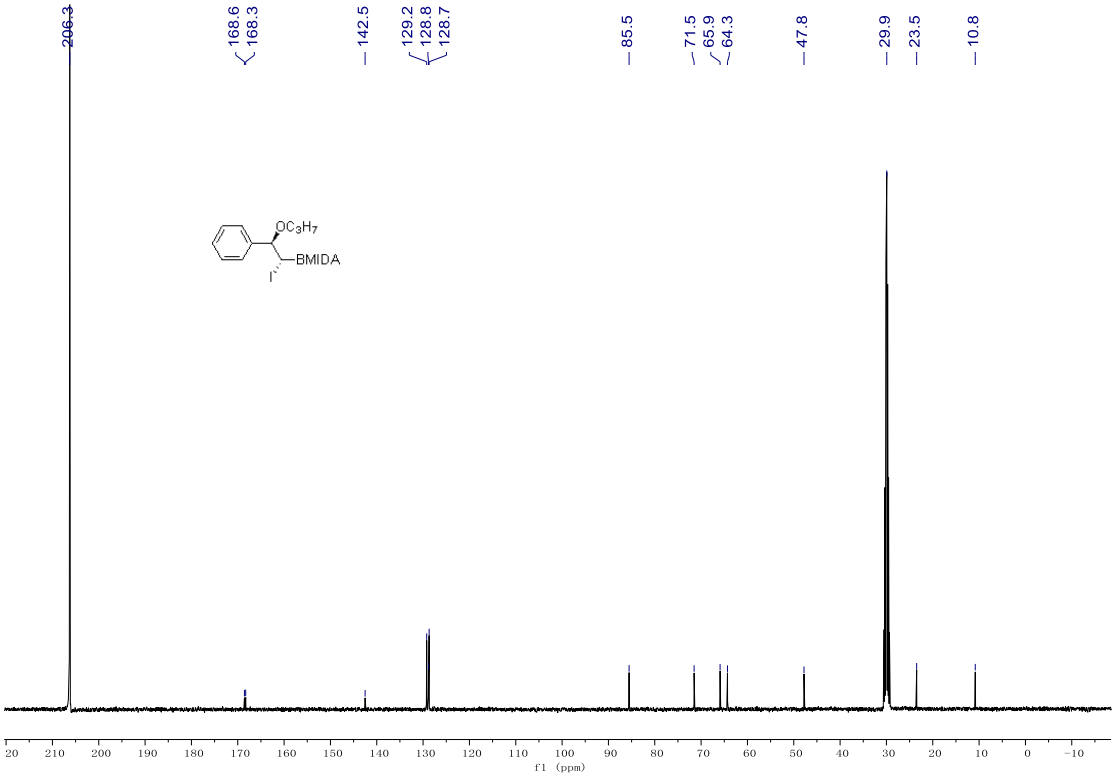
4.41
4.41
4.29
4.25
4.24
4.21
4.17
4.13
3.85
3.83
3.46
3.29
3.27
3.27
3.26
3.25
3.24
3.07
3.05
3.05
3.03
3.03
3.01
2.84
2.05
1.51
1.49
1.47
1.45
1.45
1.43
1.42
0.77
0.75
0.73
OC3H7
BMIDA
1.80
1.96
1.03
1.88
1.00
1.07
1.06
0.95
2.76
1.00
0.98
2.00
2.83
f1 (ppm)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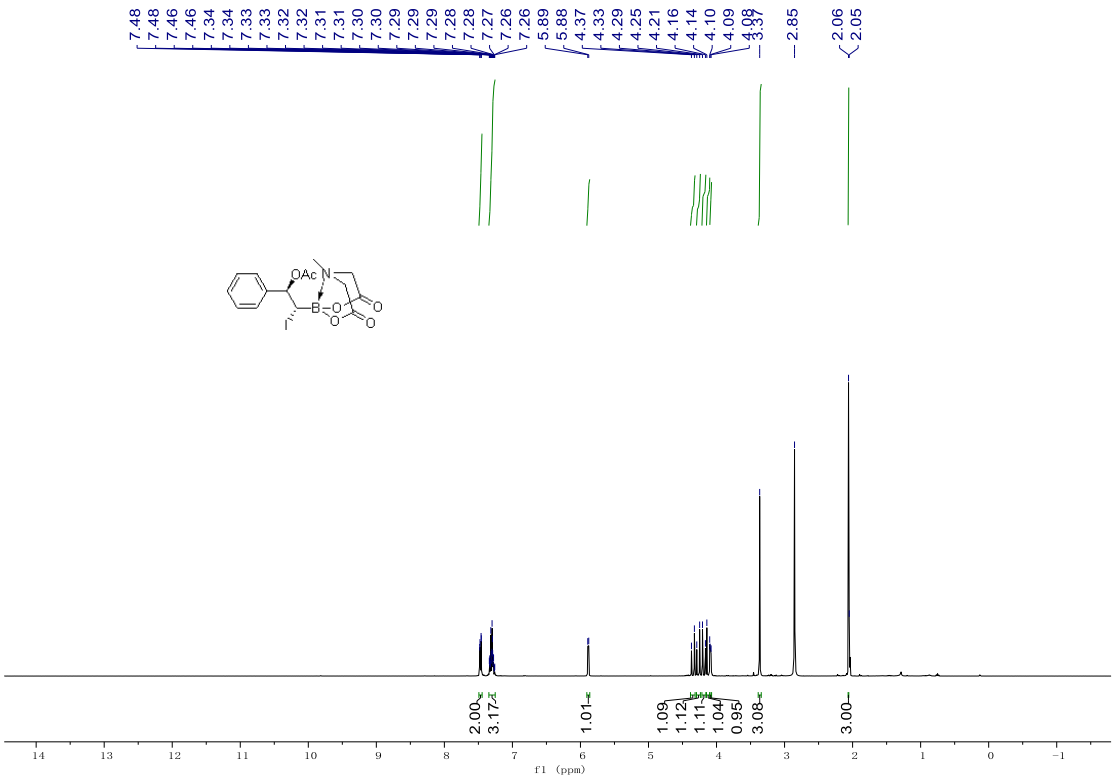
168.6
168.3
142.5
129.2
128.8
128.7
85.5
71.5
65.9
64.3
47.8
29.9
23.5
10.8
OC3H7
BMIDA
f1 (ppm)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7.33
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7.30
7.29
7.29
7.29
7.28
7.28
7.27
7.26
7.26
5.89
5.88
4.37
4.33
4.29
4.25
4.21
4.16
4.14
4.10
4.09
4.08
3.37
2.85
2.06
2.05
OAc
N
B
O
O
O
O
O
I
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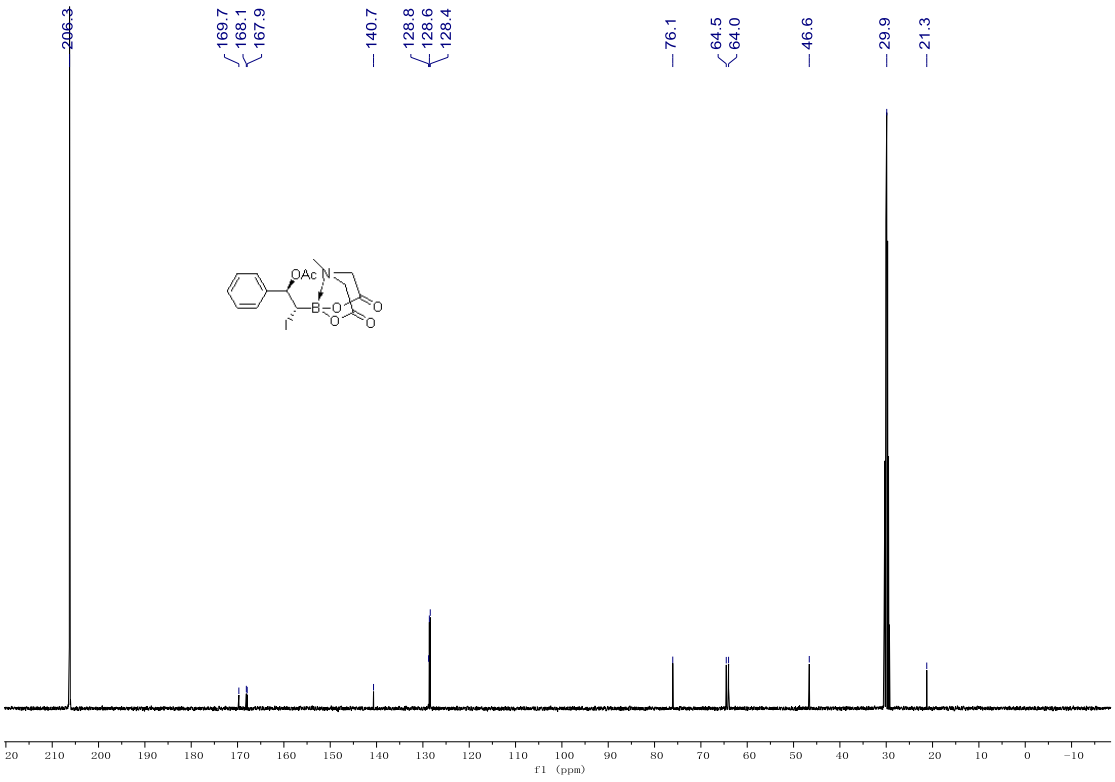
3.17
1.01
1.09
1.12
1.11
1.04
0.95
3.08
3.00
f1 (ppm)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167.9
140.7
128.8
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128.4
76.1
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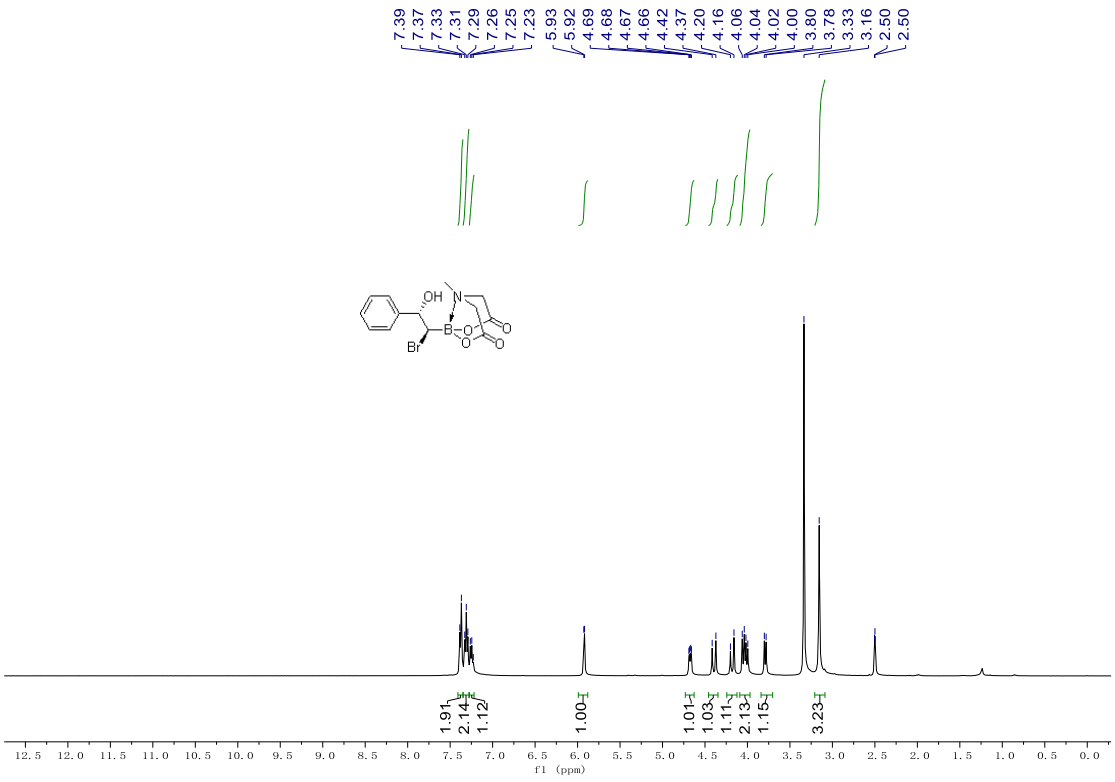
46.6
29.9
21.3
OAc
N
B
O
O
O
O
O
I
f1 (ppm)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7.37
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7.31
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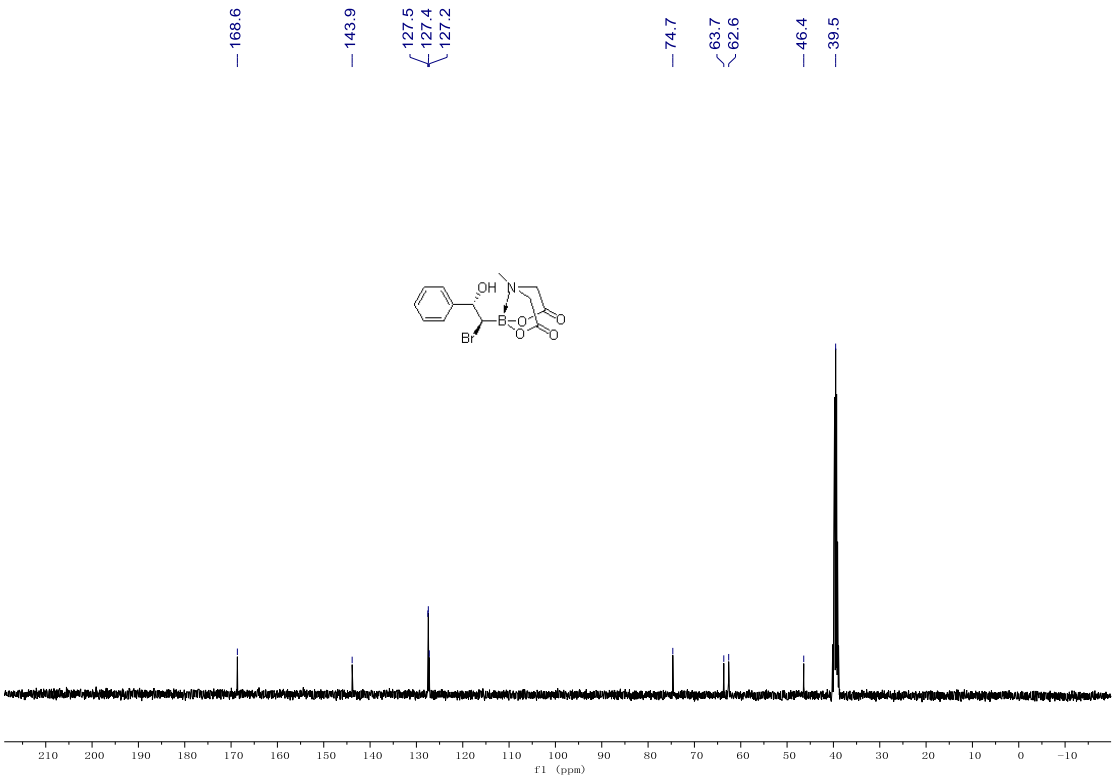
7.23
5.93
5.92
4.69
4.68
4.67
4.66
4.42
4.37
4.20
4.16
4.06
4.04
4.02
4.00
3.80
3.78
3.33
3.16
2.50
2.50
OH
N
B
O
O
O
O
Br
1.91
2.14
1.12
1.00
1.01
1.03
1.11
2.13
1.15
3.23
f1 (ppm)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143.9
127.5
127.4
127.2
74.7
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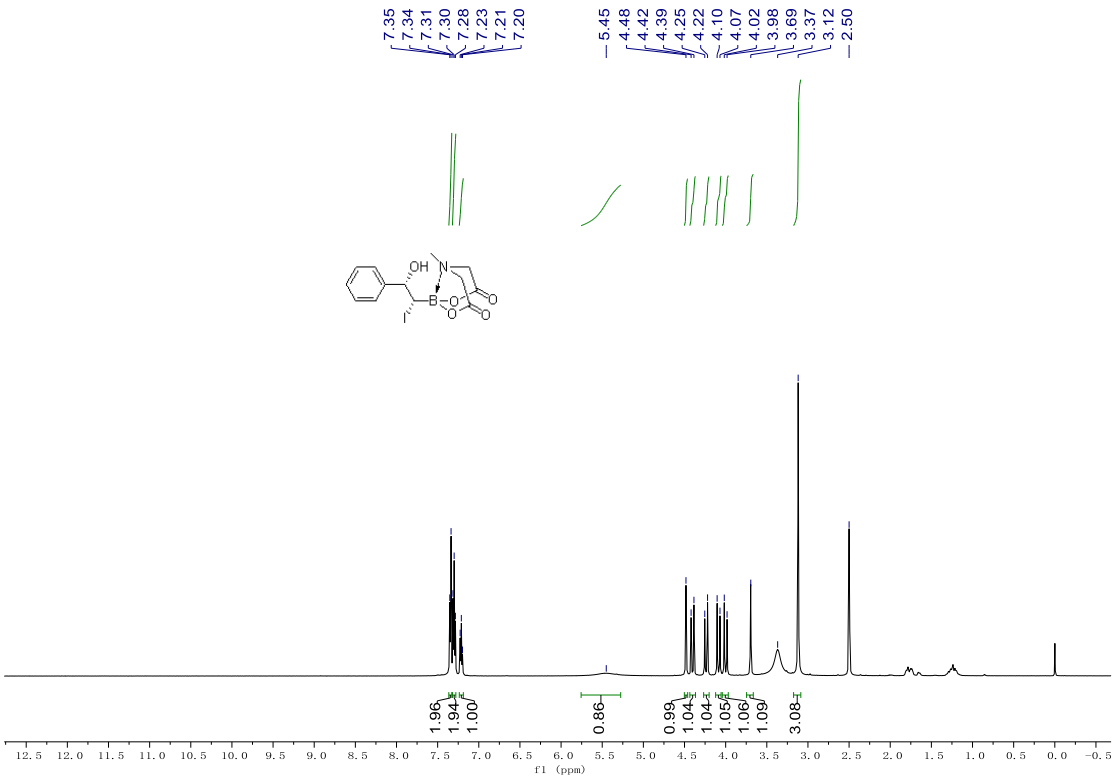
62.6
46.4
39.5
OH
N
B
O
O
O
O
Br
f1 (ppm)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7.34
7.31
7.30
7.28
7.23
7.21
7.20
5.45
4.48
4.42
4.39
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4.22
4.10
4.07
4.02
3.98
3.69
3.37
3.12
2.50
OH
N
B
O
O
O
O
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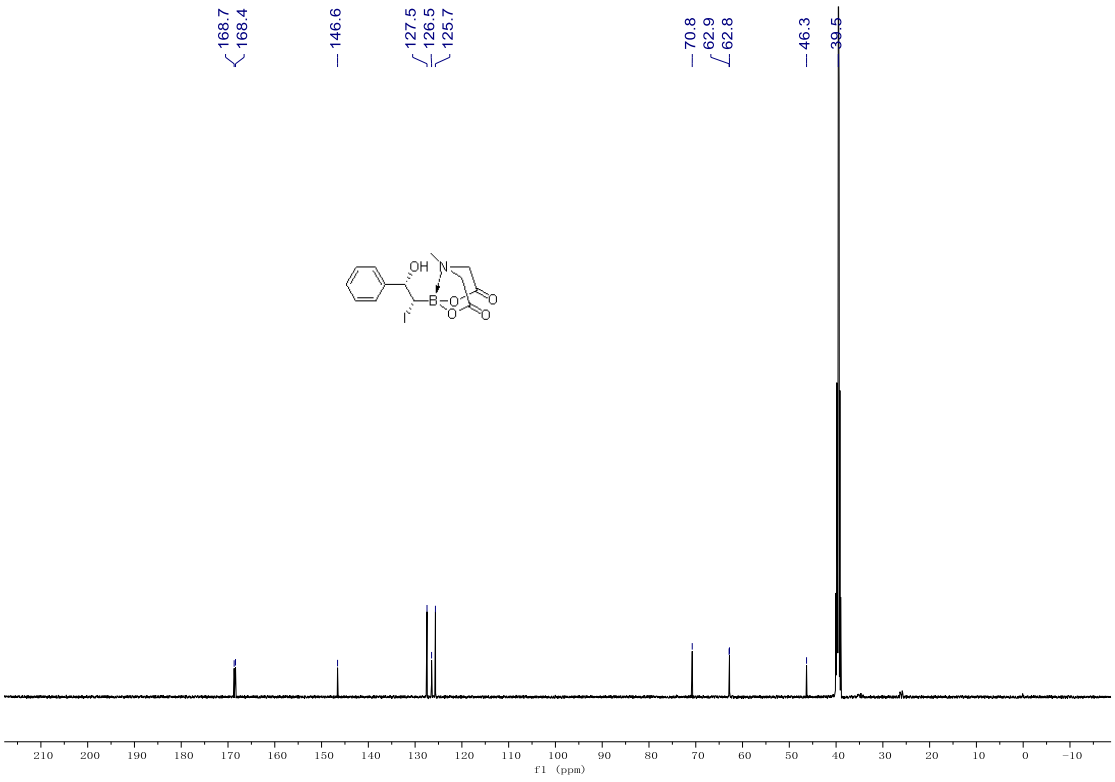
1.00
0.86
0.99
1.04
1.04
1.05
1.06
1.09
3.08
f1 (ppm)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168.4
146.6
127.5
126.5
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62.9
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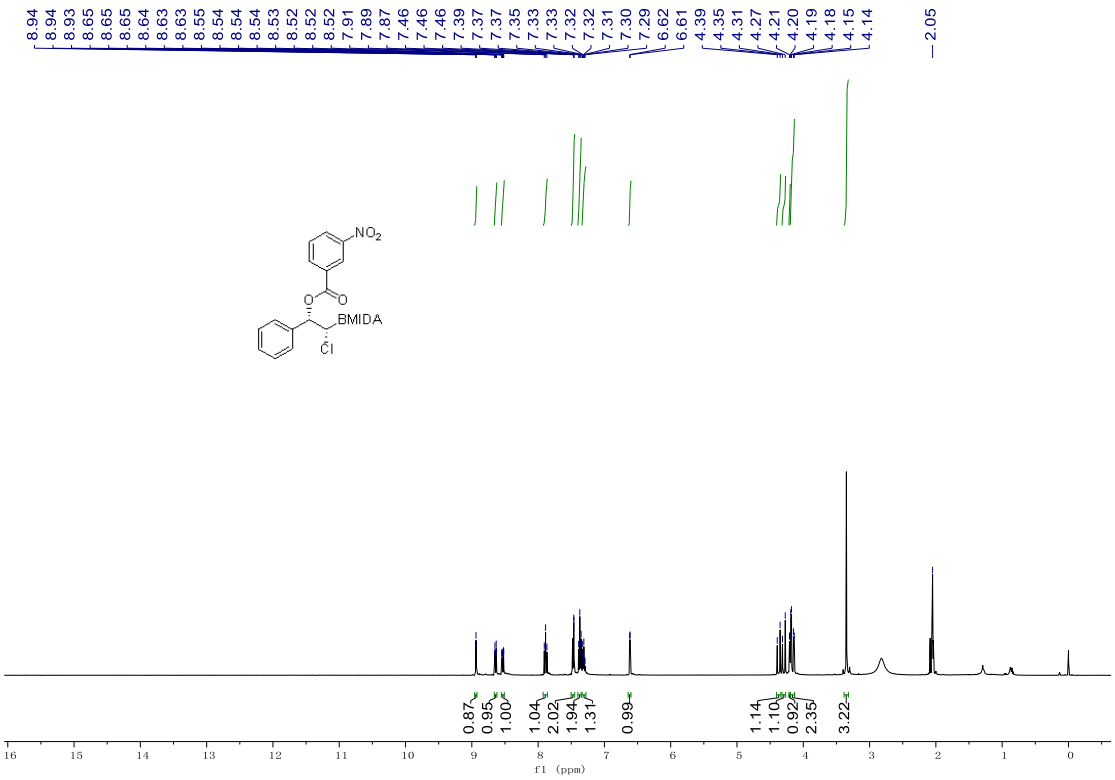
46.3
39.5
OH
N
B
O
O
O
O
f1 (ppm)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8.55
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8.53
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4.27
4.21
4.20
4.19
4.18
4.15
4.14
2.05
NO2
O
O
BMIDA
Cl
0.87
0.95
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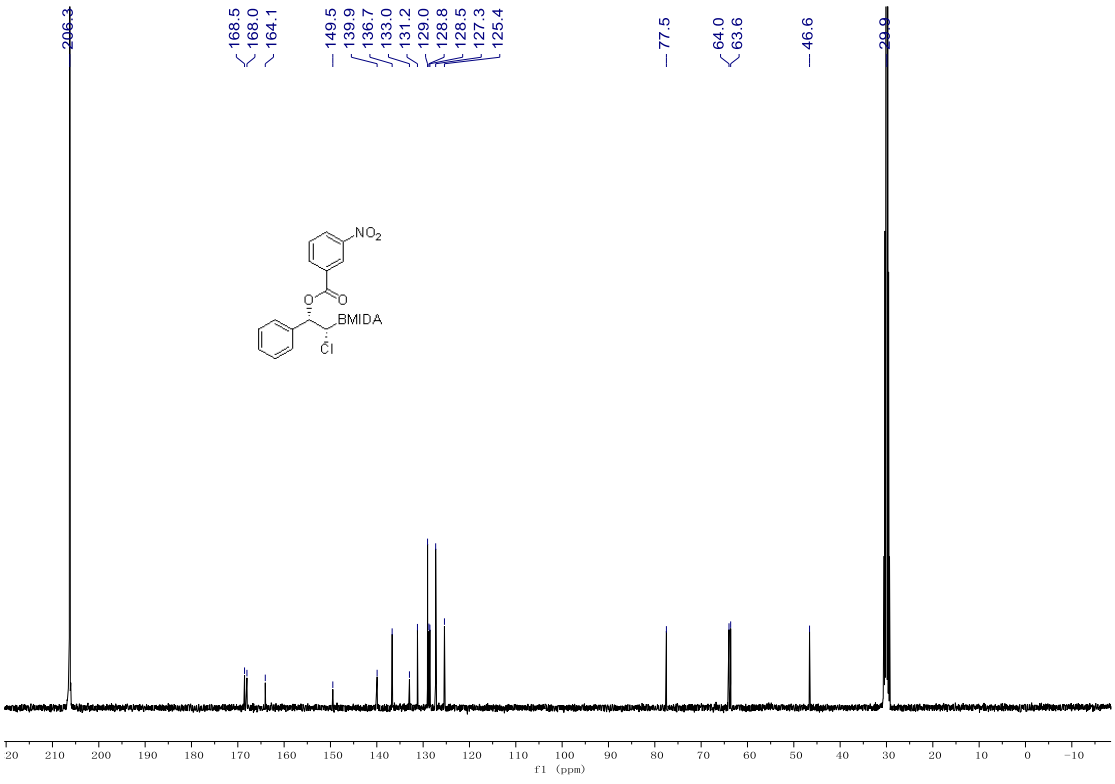
2.02
1.94
1.31
0.99
1.14
1.10
0.92
2.35
3.22
f1 (ppm)


206.3
168.5
168.0
164.1
149.5
139.9
136.7
133.0
131.2
129.0
128.8
128.5
127.3
125.4
77.5
64.0
63.6
46.6
29.9
NO2
O
O
BMIDA
Cl
f1 (ppm)