Electronic Supplementary Material (ESI) for Green Chemistry.

SUPPORTING INFORMATION

Concise synthesis of *α*-amino cyclic boronates *via* multicomponent coupling of salicylaldehydes, amines, and $B_2(OH)_4$

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I. General Information

All reagents were purchased from Alfa-Aesar, Aldrich, TCI, ABCR, VWR, or Fluorochem, and were checked for purity by GC-MS and/or ^{1}H NMR spectroscopy and used as received. D_2O was purchased from Deutero GmbH, and CD_3OD was purchased from Sigma-Aldrich. Diboronic acid was purified by washing with dioxane following a reported method.[1]

The removal of solvent was performed on a rotary evaporator *in vacuo* at a maximum temperature of 40 °C. GC-MS analyses were performed using an Agilent 7890A gas chromatograph (column: HP-5MS 5% phenyl methyl siloxane, 30 m, ∅ 0.25 mm, film 0.25 *µ*m; injector: 250 °C; oven: 40 °C (2 min), 40 °C to 280 °C (20 °C·min^{-1}); carrier gas: He (1.2 mL·min^{-1})) equipped with an Agilent 5975C inert MSD with triple-axis detector operating in EI mode and an Agilent 7693A series auto sampler/injector. Elemental analyses were performed on a Leco CHNS-932 Elemental Analyzer. High-resolution mass spectra were recorded using a Thermo Fischer Scientific Exactive Plus Orbitrap MS system (ASAP, ESI or HESI probe). All NMR spectra were recorded at ambient temperature using Bruker DRX-300 (^{1}H, 300 MHz; ^{13}C{^{1}H}, 75 MHz; ^{11}B, 96 MHz) or Bruker Avance 500 NMR (^{1}H, 500 MHz; ^{13}C{^{1}H}, 125 MHz; ^{11}B, 160 MHz; ^{19}F{^{1}H}, 471 MHz) spectrometers. ^{1}H NMR chemical shifts are reported relative to TMS and were referenced *via* residual proton resonances of the corresponding deuterated solvent (D_2O, 4.79 ppm; CD_3OD, 3.31 ppm; $CDCl_3$, 7.26 ppm), whereas ^{13}C{^{1}H} NMR spectra are reported relative to TMS *via* the carbon signals of the deuterated solvent (CD_3OD, 49.00 ppm; $CDCl_3$, 77.16 ppm). ^{11}B NMR chemical shifts are quoted relative to $BF_3{\cdot}Et_2O$ as external standard. ^{19}F{^{1}H} NMR chemical shifts are quoted relative to $CFCl_3$ as the external standard.

II. Experimental Procedures

General procedures for the preparation of boroxines (Table 1 and Scheme 3).

In a 10 mL reaction tube equipped with a magnetic stirring bar, MeCN (2 mL), salicylaldehyde **1** (0.5 mmol), amine **2** (0.5 mmol, 1.0 equiv) and $B_2(OH)_4$ (0.75 mmol, 1.5 equiv) were added in this order. The reaction mixture was stirred at room temperature overnight, then filtred through filtre paper and washed with MeCN (10 mL). The product was dried under vacuum.

Preparation of 4f (Scheme 3).

In a 10 mL reaction tube equipped with a magnetic stirring bar, dimethylamine hydrochloride **2f** (0.5 mmol) and $NaHCO_3$ (0.5 mmol, 1.0 equiv) were dissolved in 2 mL of MeCN. Then, salicylaldehyde **1a** (0.5 mmol, 1.0 equiv) was added and the reaction was stirred for 30 min. After filtration using filtre paper, a clear yellow solution was obtained. To this filtrate, $B_2(OH)_4$ (0.75 mmol, 1.5 equiv) was added and the reaction mixture was stirred at room temperature overnight, then filtred through filtre paper and washed with MeCN (10 mL). The product was dried under vacuum.

Experimental procedure for the synthesis of 4a on a gram scale (10 mmol).

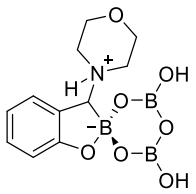
In a 25 mL reaction tube equipped with a magnetic stirring bar, MeCN (10 mL), salicylaldehyde **1a** (10 mmol, 1.221 g), morpholine **2a** (1.0 equiv, 10 mmol, 0.871 g) and $B_2(OH)_4$ (1.5 equiv, 15 mmol, 1.345 g) were added in this order. The reaction mixture was stirred at room temperature overnight, then filtered through filter paper and washed with MeCN (30 mL). The product **4a** was obtained as a white solid (2.791 g, 91%).

General procedures for the preparation of benzoxaborole-derived *α*-amino cyclic boronates.

In a 10 mL reaction tube equipped with a magnetic stirring bar, EtOH (2 mL), salicylaldehyde **1** (0.5 mmol), amine **2** (0.5 mmol, 1.0 equiv) and $B_2(OH)_4$ (0.75 mmol, 1.5 equiv) were added in this order. The reaction mixture was stirred at room temperature for 1 h. 1N HCl_{aq} (2 mL) was added to the reaction mixture, and the resulting solution was stirred for 15 min. The reaction mixture was extracted with Et_2O (2 x 5 mL) to remove impurities. The aqueous solution was evaporated to dryness to obtain a white residue, which was then dissolved in CH_2Cl_2 (5 mL). Removal of CH_2Cl_2 under vacuum gave the product.

III. Compound Characterization

4',6'-dihydroxy-3-(morpholino-4-ium)-3H-spiro[benzo[*d*][1,2]oxaborole-2,2'-[1,3,5,2,4,6]trioxatriborinan]-2-uide



4a, was isolated as a white solid (143 mg, 93%), m.p. = 223 °C.

^{1}H NMR (300 MHz, D_2O): δ = 7.42 (d, J = 8 Hz, 1H), 7.31 (dd, J = 8, 8 Hz, 1H), 6.88 (dd, J = 8, 8 Hz, 1H), 6.79 (d, J = 8 Hz, 1H), 4.08 (d, J = 14 Hz, 1H), 4.03 (d, J = 15 Hz, 1H), 3.90-3.69 (m, 2H), 3.54-3.29 (m, 3H), 3.20 (s, 1H), 3.17-3.03 (m, 1H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with D_2O.

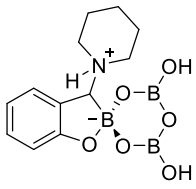
^{13}C{^{1}H} NMR (75 MHz, D_2O): δ = 162.8, 131.1, 130.4, 123.5, 118.6, 112.4, 64.4, 64.2, 60.7 (v br), 50.8, 48.9 ppm.

^{11}B NMR (96 MHz, D_2O): δ = 19.4, 6.9 ppm.

HRMS (ESI neg) *m/z*: $[M–H]^-$ Calcd for $C_{11}H_{15}B_3NO_7^-$ 306.1133; found: 306.1144.

Elem. Anal. Calcd (%) for $C_{11}H_{16}B_3NO_7$: C 43.08, H 5.26, N 4.57; found: C 43.02, H 5.56, N 4.57.

4',6'-dihydroxy-3-(piperidin-1-ium-1-yl)-3H-spiro[benzo[*d*][1,2]oxaborole-2,2'-[1,3,5,2,4,6]trioxatriborinan]-2-uide



4b was isolated as a white solid (134 mg, 88%), m.p. = 209 °C.

^{1}H NMR (300 MHz, D_2O): δ = 7.41 (d, J = 8 Hz, 1H), 7.29 (ddd, J = 8, 8, 1 Hz, 1H), 6.87 (ddd, J = 8, 8, 1 Hz, 1H), 6.77 (d, J = 8 Hz, 1H), 3.47-3.28 (m, 2H), 3.21 (ddd, J = 13, 13, 3 Hz, 1H), 3.12 (s, 1H), 2.79-2.59 (m, 1H), 2.02-1.55 (m, 5H), 1.47-1.23 (m, 1H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with D_2O.

^{13}C{^{1}H} NMR (75 MHz, D_2O): δ = 162.7, 130.7, 130.3, 124.4, 118.5, 112.3, 60.1 (v br), 52.7, 50.0,

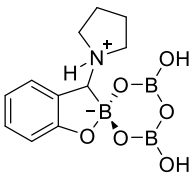
23.6, 23.3, 21.4 ppm.

^{11}B NMR (96 MHz, D_2O): δ = 19.4, 6.9 ppm.

HRMS (ESI neg) *m/z*: [*M*–H]$^-$ Calcd for $C_{12}H_{17}B_3NO_6^-$ 304.1341; found: 304.1351.

Elem. Anal. Calcd (%) for $C_{12}H_{18}B_3NO_6$: C 47.30, H 5.95, N 4.60; found: C 47.37, H 5.96, N 4.66.

4',6'-dihydroxy-3-(pyrrolidin-1-ium-1-yl)-3H-spiro[benzo[*d*][1,2]oxaborole-2,2'-[1,3,5,2,4,6]trioxatriborinan]-2-uide



4c was isolated as a white solid (119 mg, 82%), m.p. = 230 °C.

^{1}H NMR (300 MHz, D_2O): δ = 7.42 (dd, *J* = 8, 2 Hz, 1H), 7.27 (ddd, *J* = 8, 8, 2 Hz, 1H), 6.85 (ddd, *J* = 8, 8, 1 Hz, 1H), 6.77 (d, *J* = 8 Hz, 1H), 3.71-3.57 (m, 1H), 3.57-3.45 (m, 1H), 3.30 (s, 1H), 3.28-3.13 (m, 1H), 3.13-2.96 (m, 1H), 2.24-1.44 (m, 4H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with D_2O.

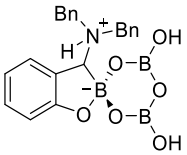
^{13}C{^{1}H} NMR (75 MHz, D_2O): δ = 162.3, 130.6, 129.7, 125.7, 118.4, 112.3, 57.2 (v br), 53.3, 51.8, 22.9, 22.6 ppm.

^{11}B NMR (96 MHz, D_2O): δ = 19.4, 7.0 ppm.

HRMS (ESI neg) *m/z*: [*M*–H]$^-$ Calcd for $C_{11}H_{15}B_3NO_6^-$ 290.1184; found: 290.1196.

Elem. Anal. Calcd (%) for $C_{11}H_{16}B_3NO_6$: C 45.45, H 5.55, N 4.82; found: C 45.25, H 5.36, N 4.49.

3-(dibenzylammonio)-4',6'-dihydroxy-3H-spiro[benzo[*d*][1,2]oxaborole-2,2'-[1,3,5,2,4,6]trioxatriborinan]-2-uide



4d was isolated as a white solid (148 mg, 71%), m.p. = 226 °C.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.56-7.31 (m, 9H), 7.29-7.16 (m, 3H), 6.85-6.72 (m, 2H), 4.40-4.13 (m, 3H), 3.77-3.47 (m, 2H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with CD_3OD.

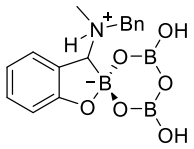
$^{13}C\{^1H\}$ NMR (75 MHz, CD_3OD): δ = 166.6, 133.2, 132.9, 132.1, 131.5 (2C), 131.3 (2C), 130.7(2C), 130.6, 130.4 (4C), 125.0, 119.2, 113.7, 57.3, 57.1 ppm. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, CD_3OD): δ = 18.4, 7.5 ppm.

HRMS (ESI neg) *m/z*: $[M–H]^-$ Calcd for $C_{21}H_{21}B_3NO_6^-$ 416.1654; found: 416.1668.

Elem. Anal. Calcd (%) for $C_{21}H_{22}B_3NO_6$: C 60.51, H 5.32, N 3.36; found: C 60.38, H 5.76, N 3.54.

3-(benzyl(methyl)ammonio)-4',6'-dihydroxy-3H-spiro[benzo[*d*][1,2]oxaborole-2,2'-[1,3,5,2,4,6]trioxatriborinan]-2-uide



4e was isolated as a white solid (111 mg, 65%), m.p. = 163 °C.

^1H NMR (300 MHz, D_2O) (mixture of diastereomers, *dr* = 55:45):

δ (major diastereomer) = 7.56–7.39 (m, 6H), 7.33 (dd, *J* = 8, 8 Hz, 1H), 6.96-6.87 (m, 1H), 6.82 (d, *J* = 8 Hz, 1H), 4.34 (d, *J* = 13 Hz, 1H), 4.18 (d, *J* = 13 Hz, 1H), 3.37 (s, 1H), 2.66 (s, 3H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with D_2O.

δ (minor diastereomer) = 7.56–7.39 (m, 6H), 7.32 (dd, *J* = 8, 8 Hz, 1H), 6.96-6.87 (m, 1H), 6.82 (d, *J* = 8 Hz, 1H), 4.48 (d, *J* = 13 Hz, 1H), 3.60 (d, *J* = 13 Hz, 1H), 3.35 (s, 1H), 2.71 (s, 3H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with D_2O.

$^{13}C\{^1H\}$ NMR (75 MHz, D_2O) (mixture of diastereomers, *dr* = 55:45):

δ (major diastereomer) = 162.8, 131.2, 131.0, 130.6 (2C), 130.0, 129.6, 129.1 (2C), 124.7, 118.7, 112.5, 59.6 (v br), 56.3, 37.5 ppm.

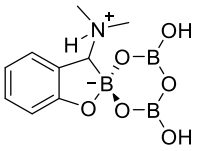
δ (minor diastereomer) = 162.9, 131.2, 131.0, 130.5 (2C), 130.0, 129.5, 129.0 (2C), 124.4, 118.6, 112.5, 59.6 (v br), 57.8, 38.6 ppm.

^{11}B NMR (96 MHz, D_2O) (mixture of diastereomers, *dr* = 55:45): δ = 19.4, 7.0 ppm.

HRMS (ESI neg) *m/z*: $[M–H]^-$ Calcd for $C_{15}H_{17}B_3NO_6^-$ 340.1341; found: 340.1353.

Elem. Anal. Calcd (%) for $C_{15}H_{18}B_3NO_6$: C 52.87, H 5.32, N 4.11; found: C 52.84, H 5.33, N 4.12.

3-(dimethylammonio)-4',6'-dihydroxy-3H-spiro[benzo[*d*][1,2]oxaborole-2,2'-[1,3,5,2,4,6]trioxatriborinan]-2-uide



4f was isolated as a white solid (104 mg, 79%), m.p. = 410 °C.

^{1}H NMR (500 MHz, D_2O): δ = 7.43 (d, J = 8 Hz, 1H), 7.31 (ddd, J = 8, 8, 1 Hz, 1H), 6.89 (ddd, J = 8, 8, 1 Hz, 1H), 6.79 (d, J = 8 Hz, 1H), 3.21 (s, 1H), 2.83 (s, 3H), 2.67 (s, 3H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with D_2O.

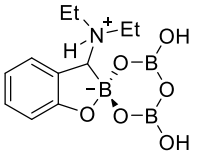
^{13}C{^{1}H} NMR (126 MHz, D_2O): δ = 162.7, 130.9, 130.0, 124.5, 118.6, 112.4, 60.4 (v br), 41.9, 39.9 ppm.

^{11}B NMR (160 MHz, D_2O): δ = 19.5, 7.0 ppm.

HRMS (ESI neg) *m/z*: [*M*–H]$^-$ Calcd for $C_9H_{13}B_3NO_6^-$ 264.1028; found: 264.1038.

Elem. Anal. Calcd (%) for $C_9H_{14}B_3NO_6$: C 40.85, H 5.33, N 5.29; found: C 40.71, H 5.39, N 5.17.

3-(diethylammonio)-4',6'-dihydroxy-3H-spiro[benzo[*d*][1,2]oxaborole-2,2'-[1,3,5,2,4,6]trioxatriborinan]-2-uide



4g was isolated as a white solid (123 mg, 84%), m.p. = 230 °C.

^{1}H NMR (300 MHz, D_2O): δ = 7.39 (d, J = 8 Hz, 1H), 7.28 (ddd, J = 8, 8, 1 Hz, 1H), 6.87 (ddd, J = 8, 8, 1 Hz, 1H), 6.78 (d, J = 8 Hz, 1H), 3.45 (s, 1H), 3.39-2.98 (m, 3H), 2.97–2.80 (m, 1H), 1.34-1.25 (m, 6H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with D_2O.

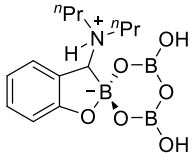
^{13}C{^{1}H} NMR (75 MHz, D_2O): δ = 162.7, 130.6, 129.6, 124.8, 118.6, 112.3, 54.5 (v br), 46.9, 46.9, 10.1, 9.7 ppm.

^{11}B NMR (96 MHz, D_2O): δ = 19.4, 7.0 ppm.

HRMS (ESI neg) *m/z*: [*M*–H]$^-$ Calcd for $C_{11}H_{17}B_3NO_6^-$ 292.1341; found: 292.1352.

Elem. Anal. Calcd (%) for $C_{11}H_{18}B_3NO_6$: C 45.14, H 6.20, N 4.79; found: C 45.15, H 6.33, N 4.48.

3-(dipropylammonio)-4',6'-dihydroxy-3H-spiro[benzo[*d*][1,2]oxaborole-2,2'-[1,3,5,2,4,6]trioxatriborinan]-2-uide



4h was isolated as a white solid (115 mg, 72%), m.p. = 130 °C.

^{1}H NMR (300 MHz, D_2O): δ = 7.39 (d, J = 8 Hz, 1H), 7.28 (dd, J = 8, 8 Hz, 1H), 6.86 (dd, J = 8, 8 Hz, 1H), 6.78 (d, J = 8 Hz, 1H), 3.44 (s, 1H), 3.31-2.92 (m, 3H), 2.87-2.66 (m, 1H), 1.89-1.59 (m, 4H), 0.98-0.81 (m, 6H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with D_2O.

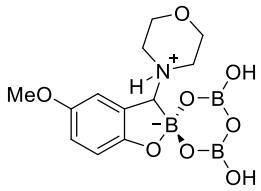
^{13}C{^{1}H} NMR (75 MHz, D_2O): δ = 162.7, 130.7, 129.6, 124.9, 118.6, 112.3, 56.2 (v br), 54.2, 53.9, 18.8.6, 18.2, 10.2, 10.2 ppm.

^{11}B NMR (96 MHz, D_2O): δ = 19.4, 7.0 ppm.

HRMS (ESI neg) *m/z*: [*M*–H]$^-$ Calcd for $C_{13}H_{21}B_3NO_6^-$ 320.1654; found: 320.1658.

Elem. Anal. Calcd (%) for $C_{13}H_{22}B_3NO_6$: C 48.68, H 6.91, N 4.37; found: C 48.45, H 6.94, N 4.28.

4',6'-dihydroxy-6-methoxy-3-(morpholino-4-ium)-3H-spiro[benzo[*d*][1,2]oxaborole-2,2'-[1,3,5,2,4,6]trioxatriborinan]-2-uide



4i was isolated as a white solid (150 mg, 89%), m.p. = 262 °C.

^{1}H NMR (300 MHz, D_2O): δ = 7.07 (d, J = 3 Hz, 1H), 6.95 (dd, J = 9, 3 Hz, 1H), 6.73 (d, J = 9 Hz, 1H), 4.08 (d, J = 14 Hz, 1H), 4.03 (d, J = 14 Hz, 1H), 3.81-3.79 (m, 5H), 3.50-3.31 (m, 3H), 3.18 (s, 1H), 3.16–3.03 (m, 1H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with D_2O.

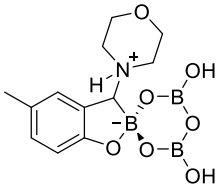
^{13}C{^{1}H} NMR (75 MHz, D_2O): δ = 157.3, 151.4, 124.0, 116.9, 116.2, 112.5, 64.4, 64.2, 60.4 (v br), 56.3, 50.7, 48.9 ppm.

^{11}B NMR (96 MHz, D_2O): δ = 19.3, 6.9 ppm.

HRMS (ESI neg) *m/z*: [*M*–H]$^-$ Calcd for $C_{12}H_{17}B_3NO_8^-$ 336.1239; found: 336.1240.

Elem. Anal. Calcd (%) for $C_{12}H_{18}B_3NO_8$: C 42.81, H 5.39, N 4.16; found: C 42.62, H 5.49., N 3.98.

4',6'-dihydroxy-5-methyl-3-(morpholino-4-ium)-3H-spiro[benzo[*d*][1,2]oxaborole-2,2'-[1,3,5,2,4,6]trioxatriborinan]-2-uide



4j was isolated as a white solid (135 mg, 84%), m.p. = 219 °C.

^{1}H NMR (500 MHz, D_2O): δ = 7.27 (s, 1H), 7.15 (d, J = 8 Hz, 1H), 6.71 (d, J = 8 Hz, 1H), 4.10 (d, J = 13 Hz, 1H), 4.04 (d, J = 13 Hz, 1H), 3.91-3.73 (m, 2H), 3.55-3.31 (m, 3H), 3.19 (s, 1H), 3.15-3.03 (m, 1H), 2.28 (s, 3H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with D_2O.

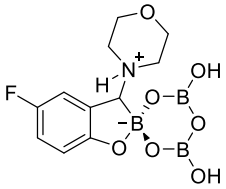
^{13}C{^{1}H} NMR (126 MHz, D_2O): δ = 160.5, 131.3, 130.7, 128.2, 123.4, 112.1, 64.4, 64.2, 60.9 (v br), 50.9, 48.9, 19.7 ppm.

^{11}B NMR (160 MHz, D_2O): δ = 19.4, 6.9 ppm.

HRMS (APCI neg) *m/z*: $[M–H]^-$ Calcd for $C_{12}H_{17}B_3NO_7^-$ 320.1290; found: 320.1271.

Elem. Anal. Calcd (%) for $C_{12}H_{18}B_3NO_7$: C 44.94, H 5.66, N 4.37; found: C 44.79, H 5.95., N 4.34.

5-fluoro-4',6'-dihydroxy-3-(morpholino-4-ium)-3H-spiro[benzo[*d*][1,2]oxaborole-2,2'-[1,3,5,2,4,6]trioxatriborinan]-2-uide



4k was isolated as a white solid (122 mg, 75%), m.p. = 295 °C.

^{1}H NMR (500 MHz, D_2O): δ = 7.20 (ddd, J = 9, 3, 1 Hz, 1H), 7.05 (ddd, J = 9, 9, 3 Hz, 1H), 6.73 (dd, J = 9, 5 Hz, 1H), 4.13-4.10 (m, 2H), 3.85–3.77 (m, 2H), 3.51–3.33 (m, 3H), 3.20 (s, 1H), 3.15 (m, 1H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with D_2O.

^{13}C{^{1}H} NMR (126 MHz, D_2O): δ = 158.9 (d, J = 2 Hz), 155.5 (d, J = 234 Hz), 124.0 (d, J = 8 Hz),

117.2 (d, *J* = 24 Hz), 116.5 (d, *J* = 23 Hz), 112.5 (d, *J* = 9 Hz), 64.4, 64.1, 60.1 (v br), 50.7, 49.0.

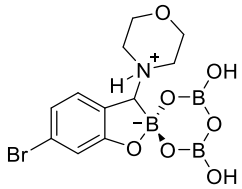
^{11}B NMR (160 MHz, D_2O): δ = 19.4, 7.1 ppm.

^{19}F{^{1}H} NMR (471 MHz, D_2O): δ = –126.3 ppm.

HRMS (ESI neg) *m/z*: [*M*–H]$^-$ Calcd for $C_{11}H_{14}B_3FNO_7^-$ 324.1039; found: 324.1038.

Elem. Anal. Calcd (%) for $C_{11}H_{15}B_3FNO_7$: C 40.69, H 4.66, N 4.31; found: C 40.58, H 4.67, N 4.30.

6-bromo-4',6'-dihydroxy-3-(morpholino-4-ium)-3H-spiro[benzo[*d*][1,2]oxaborole-2,2'-[1,3,5,2,4,6]trioxatriborinan]-2-uide



4l was isolated as a white solid (148 mg, 77%), m.p. = 272 °C.

^{1}H NMR (300 MHz, D_2O): δ = 7.57 (d, *J* = 2 Hz, 1H), 7.42 (dd, *J* = 9, 2 Hz, 1H), 6.70 (d, *J* = 9 Hz, 1H), 4.16-3.98 (m, 2H), 3.91-3.69 (m, 2H), 3.53-3.26 (m, 3H), 3.19 (s, 1H), 3.18-3.04 (m, 1H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with D_2O.

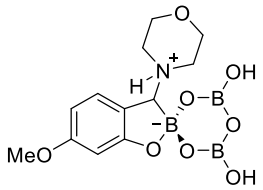
^{13}C{^{1}H} NMR (126 MHz, D_2O): δ = 162.0, 133.6, 132.7, 125.7, 114.2, 109.3, 64.3, 64.1, 60.3 (v br), 50.8, 49.0 ppm.

^{11}B NMR (96 MHz, D_2O): δ = 19.4, 7.0 ppm.

HRMS (ESI neg) *m/z*: [*M*–H]$^-$ Calcd for $C_{11}H_{14}B_3BrNO_7^-$ 384.0238; found: 384.0245.

Elem. Anal. Calcd (%) for $C_{11}H_{15}B_3BrNO_7$: C 34.27, H 3.92, N 3.63; found: C 34.19, H 3.94., N 3.59.

4',6'-dihydroxy-6-methoxy-3-(morpholino-4-ium)-3H-spiro[benzo[*d*][1,2]oxaborole-2,2'-[1,3,5,2,4,6]trioxatriborinan]-2-uide



4m was isolated as a white solid (140 mg, 83%), m.p. = 260 °C.

^{1}H NMR (300 MHz, D_2O): δ = 7.33 (d, *J* = 8 Hz, 1H), 6.48 (dd, *J* = 8, 3 Hz, 1H), 6.39 (d, *J* = 3 Hz, 1H), 4.17-3.95 (m, 2H), 3.86-3.72 (m, 5H), 3.49-3.26 (m, 3H), 3.14 (s, 1H), 3.06 (ddd, *J* = 13, 13, 4 Hz,

1H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with D_2O.

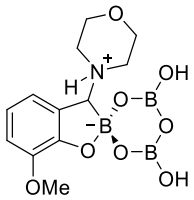
$^{13}C\{^1H\}$ NMR (126 MHz, D_2O): δ = 164.3, 161.5, 131.0, 116.2, 104.4, 98.2, 64.4, 64.2, 60.3 (v br), 55.3, 50.8, 48.7 ppm.

^{11}B NMR (160 MHz, D_2O): δ = 19.4, 7.2 ppm.

HRMS (ESI neg) *m/z*: $[M–H]^-$ Calcd for $C_{12}H_{17}B_3NO_8^-$ 336.1239; found: 336.1234.

Elem. Anal. Calcd (%) for $C_{12}H_{18}B_3NO_8$: C 42.81, H 5.39, N 4.16; found: C 42.62, H 5.45., N 4.11.

4',6'-dihydroxy-7-methoxy-3-(morpholino-4-ium)-3H-spiro[benzo[*d*][1,2]oxaborole-2,2'-[1,3,5,2,4,6]trioxatriborinan]-2-uide



4n was isolated as a white solid (121 mg, 72%), m.p. = 273 °C.

^1H NMR (300 MHz, D_2O): δ = 7.06 (d, *J* = 8 Hz, 1H), 7.02 (d, *J* = 8 Hz, 1H), 6.83 (dd, *J* = 8, 8 Hz, 1H), 4.07 (d, *J* = 14 Hz, 1H), 4.02 (d, *J* = 15 Hz, 1H), 3.92-3.72 (m, 5H), 3.52-3.31 (m, 3H), 3.20 (s, 1H), 3.08 (ddd, *J* = 13, 13, 4 Hz, 1H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with D_2O.

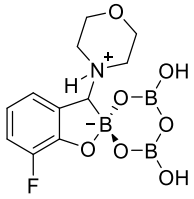
$^{13}C\{^1H\}$ NMR (75 MHz, D_2O): δ = 152.3, 145.9, 124.0, 122.6, 118.2, 113.6, 64.4, 64.1, 61.1 (v br), 55.7, 50.8, 48.9 ppm.

^{11}B NMR (96 MHz, D_2O): δ = 19.4, 7.1 ppm.

HRMS (ESI neg) *m/z*: $[M–H]^-$ Calcd for $C_{12}H_{17}B_3NO_8^-$ 336.1239; found: 336.1252.

Elem. Anal. Calcd (%) for $C_{12}H_{18}B_3NO_8$: C 42.81, H 5.39, N 4.16; found: C 42.71, H 5.36, N 4.09.

7-fluoro-4',6'-dihydroxy-3-(morpholino-4-ium)-3H-spiro[benzo[*d*][1,2]oxaborole-2,2'-[1,3,5,2,4,6]trioxatriborinan]-2-uide



4o was isolated as a white solid (133 mg, 82%), m.p. = 310 °C.

^{1}H NMR (500 MHz, D_2O): δ = 7.22 (d, J = 8 Hz, 1H), 7.14 (ddd, J = 11, 8, 1 Hz, 1H), 6.82 (ddd, J = 13, 8, 5 Hz, 1H), 4.12–4.00 (m, 2H), 3.86–3.75 (m, 2H), 3.50–3.35 (m, 3H), 3.24 (s, 1H), 3.12 (ddd, J = 12, 12, 4 Hz, 1H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with D_2O.

^{13}C{^{1}H} NMR (126 MHz, D_2O): δ = 150.0 (d, J = 11 Hz), 149.6 (d, J = 241 Hz), 126.5 (d, J = 5 Hz), 125.7 (d, J = 4 Hz), 118.2 (d, J = 6 Hz), 117.2 (d, J = 17 Hz), 64.4, 64.1, 60.2 (v br), 50.8, 49.0 ppm.

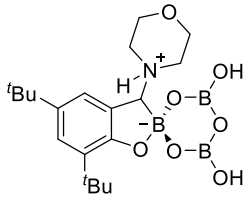
^{11}B NMR (160 MHz, D_2O): δ = 19.4, 7.4 ppm.

^{19}F{^{1}H} NMR (471 MHz, D_2O): δ = –139.1 ppm.

HRMS (ESI neg) *m/z*: [*M*–H]$^-$ Calcd for $C_{11}H_{14}B_3FNO_7^-$ 324.1039; found: 324.1040.

Elem. Anal. Calcd (%) for $C_{11}H_{15}B_3FNO_7$: C 40.69, H 4.66, N 4.31; found: C 40.58, H 4.73, N 4.32.

5,7-di-*tert*-butyl-4',6'-dihydroxy-3-(morpholino-4-ium)-3H-spiro[benzo[*d*][1,2]oxaborole-2,2'-[1,3,5,2,4,6]trioxatriborinan]-2-uide



4p was isolated as a white solid (142 mg, 68%), m.p. = 211 °C.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.20-7.14 (m, 2H), 4.02-3.89 (m, 2H), 3.75-3.62 (m, 2H), 3.38-3.22 (m, 3H), 3.13 (s, 1H), 3.12-3.02 (m, 1H), 1.40 (s, 9H), 1.28 (s, 9H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with CD_3OD.

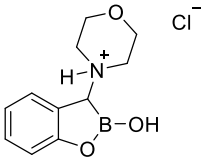
^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ = 162.9, 140.0, 134.4, 125.0, 124.9, 124.2, 65.8, 65.6, 62.9 (v br), 52.5, 51.0, 35.4, 35.1, 32.4 (3C), 29.9 (3C) ppm.

^{11}B NMR (96 MHz, CD_3OD): δ = 18.5, 7.5 ppm.

HRMS (ESI neg) *m/z*: [*M*–H]$^-$ Calcd for $C_{19}H_{31}B_3NO_7^-$ 418.2385; found: 418.2391.

Elem. Anal. Calcd (%) for $C_{19}H_{32}B_3NO_7$: C 54.48, H 7.70, N 3.34; found: C 54.33, H 7.69, N 3.31.

4-(2-hydroxy-2,3-dihydrobenzo[*d*][1,2]oxaborol-3-yl)morpholin-4-ium chloride



5a was isolated as a white solid (101 mg, 79%), **m.p. = 179 °C**.

^{1}H NMR (300 MHz, D_2O): δ = 7.40 (d, J = 8 Hz, 1H), 7.33 (dd, J = 8, 8 Hz, 1H), 6.93 (dd, J = 8, 8 Hz, 1H), 6.86 (d, J = 8 Hz, 1H), 4.14-3.90 (m, 2H), 3.88–3.66 (m, 2H), 3.53 (s, 1H), 3.49–3.22 (m, 3H), 3.04 (dd, J = 13, 13 Hz, 1H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with D_2O.

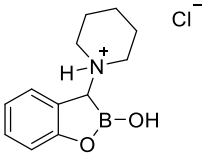
^{13}C{^{1}H} NMR (75 MHz, D_2O): δ = 160.2, 131.5 (2C), 121.3, 119.7, 113.7, 64.1, 64.0, 59.1 (v br), 51.3, 49.3 ppm.

^{11}B NMR (96 MHz, D_2O): δ = 14.3 ppm.

HRMS (ESI pos) *m/z*: [*M*–Cl]$^+$ Calcd for $C_{11}H_{15}BNO_3^+$ 220.1140; found: 220.1136.

Elem. Anal. Calcd (%) for $C_{11}H_{15}BClNO_3$: C 51.71, H 5.92, N 5.48; found: C 51.68, H 5.99, N 5.42.

1-(2-hydroxy-2,3-dihydrobenzo[*d*][1,2]oxaborol-3-yl)piperidin-1-ium chloride



5b was isolated as a white solid (95 mg, 75%), m.p. = 174 °C.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.35 (dd, J = 8, 2 Hz, 1H), 7.23 (ddd, J = 8, 8, 2 Hz, 1H), 6.91-6.76 (m, 2H), 3.60 (s, 1H), 3.42 (d, J = 13 Hz, 1H), 3.38 (d, J = 13 Hz, 1H), 3.22-3.02 (m, 1H), 2.86-2.54 (m, 1H), 1.95-1.62 (m, 5H), 1.54-1.24 (m, 1H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with CD_3OD.

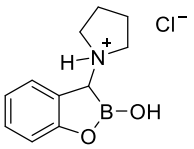
^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ = 162.5, 132.2, 132.1, 122.4, 120.3, 114.9, 58.8 (v br), 54.3, 51.9, 24.7, 24.5, 23.0 ppm.

^{11}B NMR (96 MHz, CD_3OD): δ = 16.3 ppm.

HRMS (ESI pos) *m/z*: [*M*–Cl]$^+$ Calcd for $C_{12}H_{17}BNO_2^+$ 218.1347; found: 218.1342.

Elem. Anal. Calcd (%) for $C_{12}H_{17}BClNO_2$: C 56.85, H 6.76, N 5.52; found: C 56.68, H 6.88, N 5.37.

1-(2-hydroxy-2,3-dihydrobenzo[*d*][1,2]oxaborol-3-yl)pyrrolidin-1-ium chloride



5c was isolated as a white solid (99 mg, 83%), m.p. = 172 °C.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.32 (ddd, J = 8, 2, 1 Hz, 1H), 7.23 (ddd, J = 8, 7, 2 Hz, 1H), 6.90–6.79 (m, 2H), 3.83 (s, 1H), 3.69 (ddd, J = 12, 8, 5 Hz, 1H), 3.29–3.16 (m, 2H), 3.01 (ddd, J = 11, 8, 8 Hz, 1H), 2.24–1.73 (m, 4H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with CD_3OD.

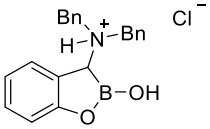
^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ = 161.3, 131.9, 131.9, 123.4, 120.4, 115.2, 55.4, 53.4, 24.0 (2C) ppm. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, CD_3OD): δ = 18.5 ppm.

HRMS (ESI pos) *m/z*: [*M*–Cl]$^+$ Calcd for $C_{11}H_{15}BNO_2^+$ 204.1190; found: 204.1187.

Elem. Anal. Calcd (%) for $C_{11}H_{15}BClNO_2$: C 55.16, H 6.31, N 5.85; found: C 54.97, H 6.29, N 5.73.

***N*,*N*-dibenzyl-2-hydroxy-2,3-dihydrobenzo[*d*][1,2]oxaborol-3-aminium chloride**



5d was isolated as a white solid (155 mg, 85%), m.p. = 177 °C.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.49–7.42 (m, 6H), 7.39-7.38 (m, 3H), 7.23 (ddd, J = 8, 8, 3 Hz, 3H), 6.90–6.78 (m, 2H), 4.39 (d, J = 13 Hz, 1H), 4.35 (d, J = 13 Hz, 1H), 4.25 (d, J = 13 Hz, 1H), 3.77 (d, J = 13 Hz, 1H), 3.70 (s, 1H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with CD_3OD.

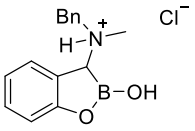
^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ = 165.5, 132.9, 132.7, 132.3, 131.6 (2C), 131.4 (2C), 131.1, 130.8, 130.6, 130.4 (4C), 124.2, 119.8, 114.1, 57.6, 57.2 ppm. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, CD_3OD): δ = 10.8 ppm.

HRMS (ESI pos) *m/z*: [*M*–Cl]$^+$ Calcd for $C_{21}H_{21}BNO_2^+$ 330.1660; found: 330.1648.

Elem. Anal. Calcd (%) for $C_{21}H_{21}BClNO_2$: C 68.98, H 5.79, N 3.83; found: C 68.74, H 5.88, N 3.85.

***N*-benzyl-2-hydroxy-*N*-methyl-2,3-dihydrobenzo[*d*][1,2]oxaborol-3-aminium chloride**



5e was isolated as a white solid (104 mg, 72%), m.p. = 183 °C.

^{1}H NMR (300 MHz, CD_3OD) (mixture of diastereomers, *dr* = 55:45):

δ (major diastereomer) = 7.51–7.36 (m, 6H), 7.34–7.20 (m, 1H), 6.94–6.81 (m, 2H), 4.44 (d, *J* = 13 Hz, 1H), 4.16 (d, *J* = 13 Hz, 1H), 3.71 (s, 1H), 2.70 (s, 3H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with CD_3OD.

δ (minor diastereomer) = 7.51–7.36 (m, 6H), 7.34–7.20 (m, 1H), 6.94–6.81 (m, 2H), 4.61 (d, *J* = 13 Hz, 1H), 3.78 (s, 1H), 3.49 (d, *J* = 13 Hz, 1H), 2.59 (s, 1H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with CD_3OD.

^{13}C{^{1}H} NMR (75 MHz, CD_3OD) (mixture of diastereomers, *dr* = 55:45):

δ (major diastereomer) = 163.1, 132.6, 132.5, 131.8 (2C), 130.8, 130.3, 130.2 (2C), 122.2, 120.6, 114.9, 58.1, 53.6 (v br), 38.8 ppm.

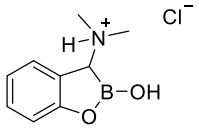
δ (minor diastereomer) = 163.1, 132.3, 132.3, 131.9 (2C), 130.9, 130.7, 130.2 (2C), 123.0, 120.4, 114.9, 60.6, 53.6 (v br), 39.9 ppm.

^{11}B NMR (96 MHz, CD_3OD) (mixture of diastereomers, *dr* = 55:45): δ = 15.7 ppm.

HRMS (ESI pos) *m/z*: [*M*–Cl]$^+$ Calcd for $C_{15}H_{17}BNO_2^+$ 254.1347; found: 254.1346.

Elem. Anal. Calcd (%) for $C_{15}H_{17}BClNO_2$: C 62.22, H 5.92, N 4.84; found: C 62.01, H 5.68, N 4.81.

2-hydroxy-N,N-dimethyl-2,3-dihydrobenzo[*d*][1,2]oxaborol-3-aminium chloride



5f was isolated as a white solid (59 mg, 55%), m.p. = 131 °C.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.39–7.32 (m, 1H), 7.31–7.22 (m, 1H), 6.91–6.81 (m, 2H), 3.67 (s, 1H), 2.85 (s, 3H), 2.65 (s, 3H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with CD_3OD.

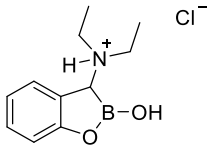
^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ = 162.4, 132.2, 132.1, 122.6, 120.3, 114.9, 59.3 (v br), 43.5, 41.4 ppm.

^{11}B NMR (96 MHz, CD_3OD): δ = 16.6 ppm.

HRMS (ESI pos) *m/z*: $[M–Cl]^+$ Calcd for $C_9H_{13}BNO_2^+$ 178.1034; found: 178.1031.

Elem. Anal. Calcd (%) for $C_9H_{13}BClNO_2$: C 50.64, H 6.14, N 6.56; found: C 50.52, H 6.08, N 6.47.

***N*,*N*-diethyl-2-hydroxy-2,3-dihydrobenzo[*d*][1,2]oxaborol-3-aminium chloride**



5g was isolated as a white solid (91 mg, 75%), m.p. = 136 °C.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.38–7.29 (m, 1H), 7.23 (ddd, 8, 8, 2 Hz, 1H), 6.87–6.82 (m, 2H), 3.83 (s, 1H), 3.28–3.05 (m, 3H), 2.76 (dq, *J* = 14, 7 Hz, 1H), 1.33 (t, *J* = 7 Hz, 3H), 1.25 (t, *J* = 7 Hz, 3H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with CD_3OD.

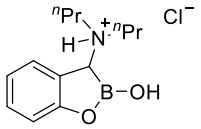
^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ = 162.5, 132.0, 131.5, 122.7, 120.4, 114.9, 54.0 (v br), 48.5, 47.5, 10.8, 9.8 ppm.

^{11}B NMR (96 MHz, CD_3OD): δ = 16.0 ppm.

HRMS (ESI pos) *m/z*: $[M–Cl]^+$ Calcd for $C_{11}H_{17}BNO_2^+$ 206.1347; found: 206.1344.

Elem. Anal. Calcd (%) for $C_{11}H_{17}BClNO_2$: C 54.70, H 7.10, N 5.80; found: C 54.55, H 7.23, N 5.78.

2-hydroxy-N,N-dipropyl-2,3-dihydrobenzo[*d*][1,2]oxaborol-3-aminium chloride



5h was isolated as a white solid (93 mg, 69%), m.p. = 138 °C.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.32 (ddd, *J* = 8, 2, 1 Hz, 1H), 7.25 (ddd, *J* = 8, 8, 2 Hz, 1H), 6.87–6.82 (m, 2H), 3.83 (s, 1H), 3.20–2.92 (m, 3H), 2.77–2.51 (m, 1H), 1.96–1.50 (m, 4H), 0.98 (t, *J* = 7 Hz, 3H), 0.87 (t, *J* = 7 Hz, 3H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with CD_3OD.

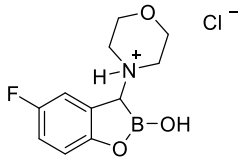
^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ = 162.9, 132.2, 131.5, 122.8, 120.4, 114.8, 56.1,54.9, 19.8, 18.8, 11.3, 11.3 ppm. The carbon atom directly attached to boron was not detected, likely due to quadrupolar broadening.

^{11}B NMR (96 MHz, CD_3OD): δ = 15.3 ppm.

HRMS (ESI pos) *m/z*: [*M*–Cl]$^+$ Calcd for $C_{13}H_{21}BNO_2^+$ 234.1660; found: 234.1656.

Elem. Anal. Calcd (%) for $C_{13}H_{21}BClNO_2$: C 57.92, H 7.85, N 5.20; found: C 57.85, H 7.81, N 5.11.

4-(5-fluoro-2-hydroxy-2,3-dihydrobenzo[*d*][1,2]oxaborol-3-yl)morpholin-4-ium chloride



5i was isolated as a white solid (101 mg, 74%), m.p. = 183 °C.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.20 (dd, *J* = 9, 3 Hz, 1H), 7.02 (ddd, *J* = 9, 9, 3 Hz, 1H), 6.81 (dd, *J* = 9, 5 Hz, 1H), 4.06–3.93 (m, 2H), 3.84–3.69 (m, 2H), 3.67 (s, 1H), 3.48–3.33 (m, 2H), 3.27–3.22 (m, 1H), 3.16 (ddd, *J* = 12, 12, 4 Hz, 1H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with CD_3OD.

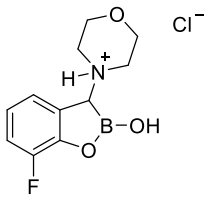
^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ = 158.1, 155.9 (d, *J* = 236 Hz), 121.7 (d, *J* = 8 Hz), 117.2 (d, *J* = 23 Hz), 116.7 (d, *J* = 23 Hz), 113.8 (d, *J* = 8 Hz), 63.9, 63.8, 57.1 (v br), 51.3, 49.9 ppm.

^{11}B NMR (96 MHz, CD_3OD): δ = 14.8 ppm.

HRMS (ESI pos) *m/z*: [*M*–Cl]$^+$ Calcd for $C_{11}H_{14}BFNO_3^+$ 238.1045; found: 238.1041.

Elem. Anal. Calcd (%) for $C_{11}H_{14}BClFNO_3$: C 48.31, H 5.16, N 5.12; found: C 48.22, H 5.29, N 5.07.

4-(7-fluoro-2-hydroxy-2,3-dihydrobenzo[*d*][1,2]oxaborol-3-yl)morpholin-4-ium chloride



5j was isolated as a white solid (111 mg, 81%), m.p. = 191 °C.

^{1}H NMR (300 MHz, CD_3OD): δ = 7.19 (ddd, *J* = 8, 1, 1 Hz, 1H), 7.10 (ddd, *J* = 11, 8, 1 Hz, 1H), 6.81 (ddd, *J* = 8, 8, 5 Hz, 1H), 4.04–3.90 (m, 2H), 3.84–3.70 (m, 2H), 3.68 (s, 1H), 3.46–3.34 (m, 2H), 3.29–3.26 (m, 1H), 3.08 (ddd, *J* = 12, 12, 4 Hz, 1H) ppm. Protons directly attached to nitrogen and oxygen were not detected due to exchange with CD_3OD.

^{13}C{^{1}H} NMR (75 MHz, CD_3OD): δ = 150.4 (d, *J* = 243 Hz), 149.4 (d, *J* = 12 Hz), 125.9 (d, *J* = 3 Hz), 124.1 (d, *J* = 4 Hz), 118.5 (d, *J* = 7 Hz), 117.1 (d, *J* = 18 Hz), 63.9, 63.8, 57.2 (v br), 51.5, 49.8 ppm.

^{11}B NMR (96 MHz, CD_3OD): δ = 14.6 ppm.

HRMS (ESI pos) *m/z*: [*M*–Cl]$^{+}$ Calcd for $C_{11}H_{14}BFNO_3^{+}$ 238.1045; found: 238.1041.

Elem. Anal. Calcd (%) for $C_{11}H_{14}BClFNO_3$: C 48.31, H 5.16, N 5.12; found: C 48.12, H 5.25, N 5.26.

IV. Mechanistic Studies

1. Stepwise reaction

Experimental procedures

(1) In a 10 mL reaction tube equipped with a magnetic stirring bar, MeCN (2 mL), salicylaldehyde **1a** (0.5 mmol), and morpholine **2a** (0.5 mmol, 1.0 equiv) were added in this order, and 1,3,5-trimethoxybenzene (0.25 mmol, 0.5 equiv) was then added as an internal calibration standard. The resulting mixture was analysed by ^{1}H NMR spectroscopy in $CDCl_3$ solution. The ^{1}H NMR spectrum is shown below (Figure S1). The aminal **4a'** was obtained in 26% NMR yield.

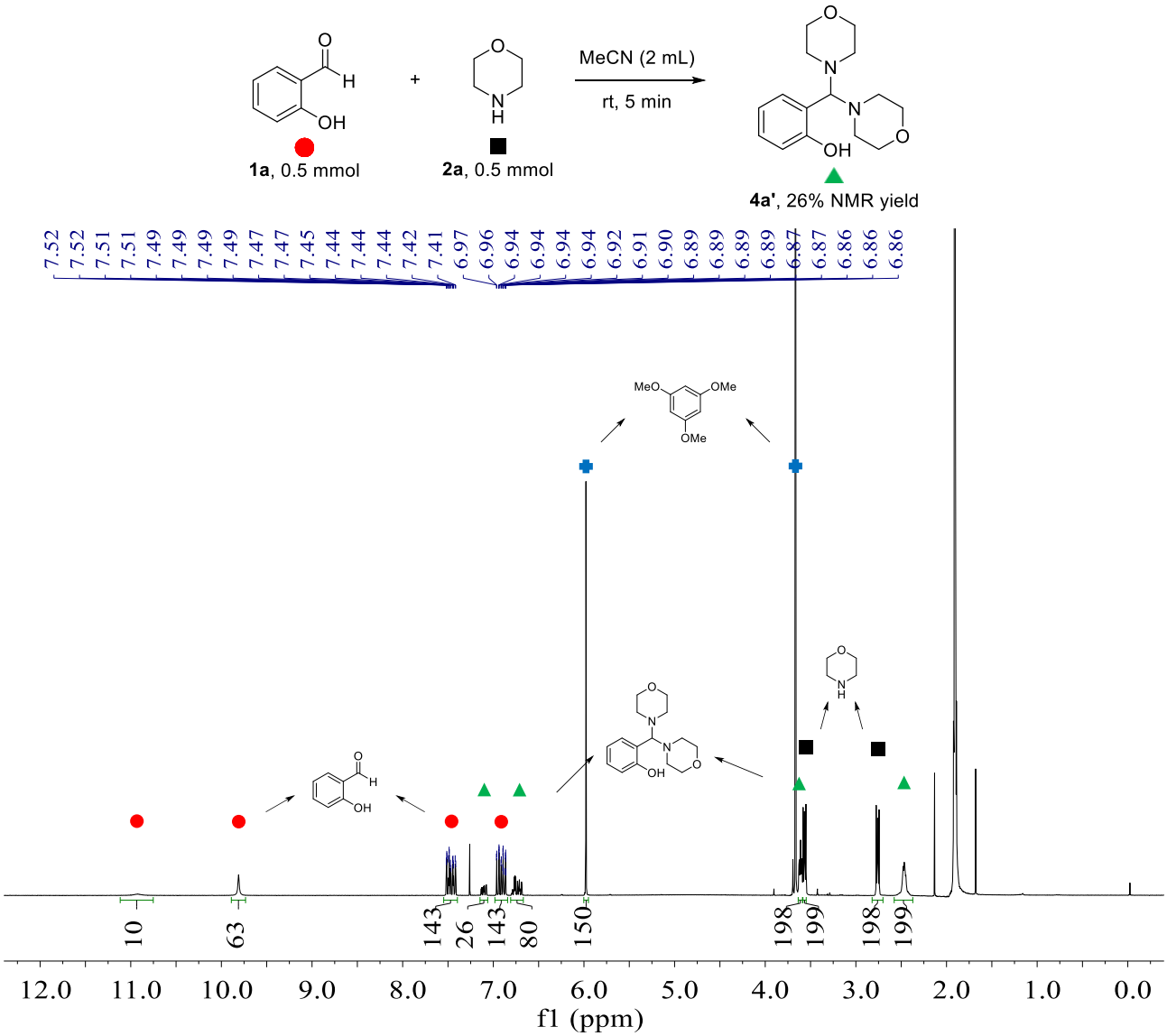


Figure S1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, rt) of the reaction mixture of **1a** and **2a** in MeCN; the product yield was determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene (blue + sign) as the internal calibration standard.

(2) To the above filtrate, $B_2(OH)_4$ (0.75 mmol, 1.5 equiv) was added and the reaction mixture was stirred at room temperature overnight, then filtered through filter paper and washed with MeCN (10 mL). The product was dried under vacuum to give **4a** as a white solid (141 mg, 92% isolated yield).

(3) To a 10 mL reaction tube equipped with a magnetic stirring bar, **4a** (141 mg, 0.46 mmol) and 1N HCl_{aq} (2 mL) were added. The resulting solution was stirred for 15 min, and then extracted with Et_2O (2 x 5 mL) to remove impurities. The aqueous solution was evaporated to dryness under vacuum to obtain a white residue, which was then dissolved in CH_2Cl_2 (5 mL). Removal of CH_2Cl_2 under vacuum gave the product **5a** as white solid (94% isolated yield).

2. Reaction of salicylaldehyde 1a with different rations of morpholine 2a.

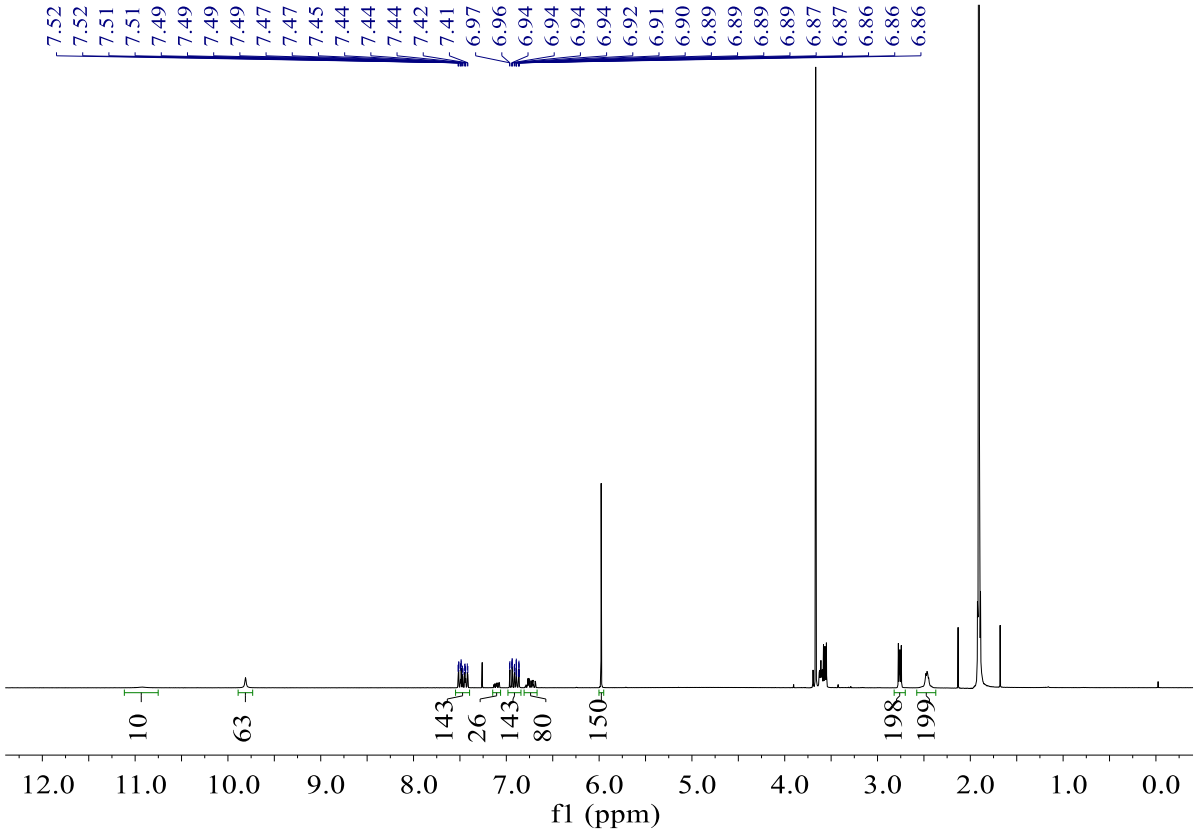


Figure S2. ^1H NMR spectrum of the reaction of salicylaldehyde **1a** with 1 equivalent of morpholine **2a** (300 MHz, $CDCl_3$, rt); 1,3,5-trimethoxybenzene was used as an internal standard.

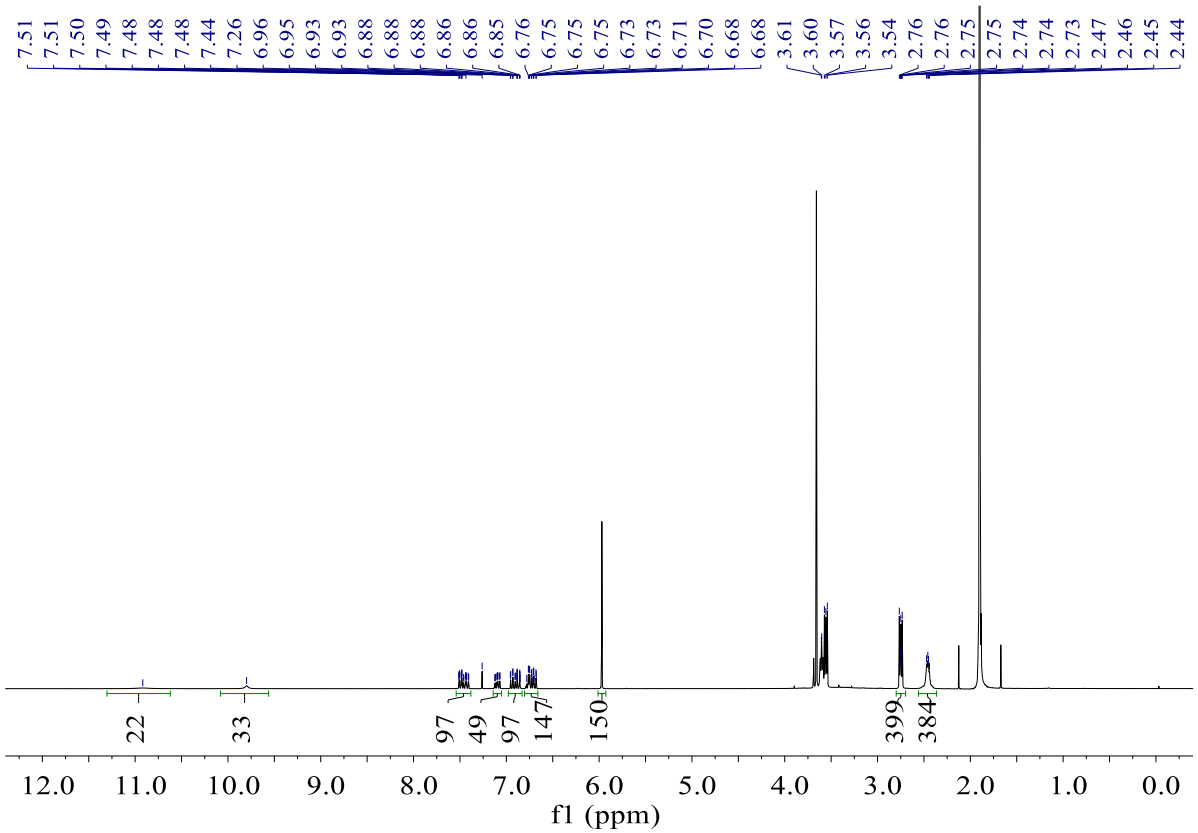


Figure S3. ^{1}H NMR spectrum of the reaction of salicylaldehyde **1a** with 2 equivalents of morpholine **2a** (300 MHz, $CDCl_3$, rt); 1,3,5-trimethoxybenzene was used as an internal standard.

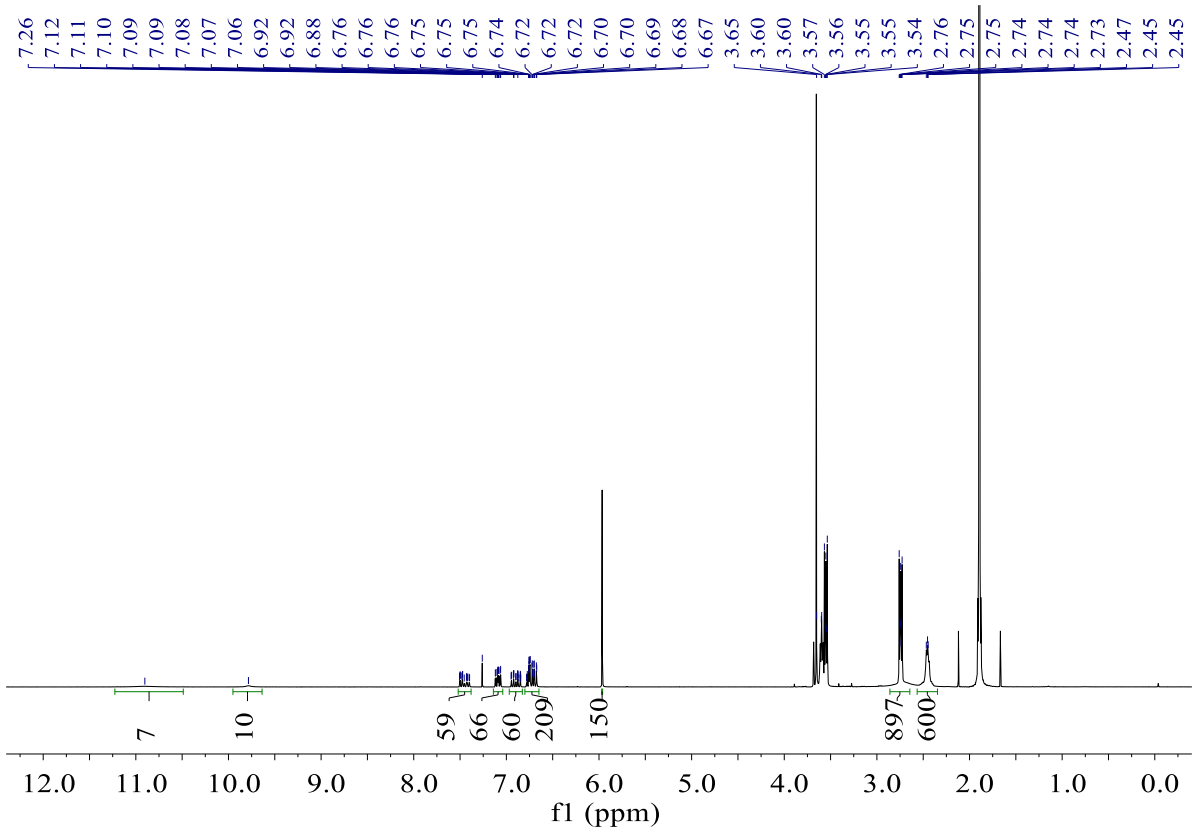


Figure S4. ^{1}H NMR spectrum of the reaction of salicylaldehyde **1a** with 3 equivalents of morpholine **2a** (300 MHz, $CDCl_3$, rt); 1,3,5-trimethoxybenzene was used as an internal standard.

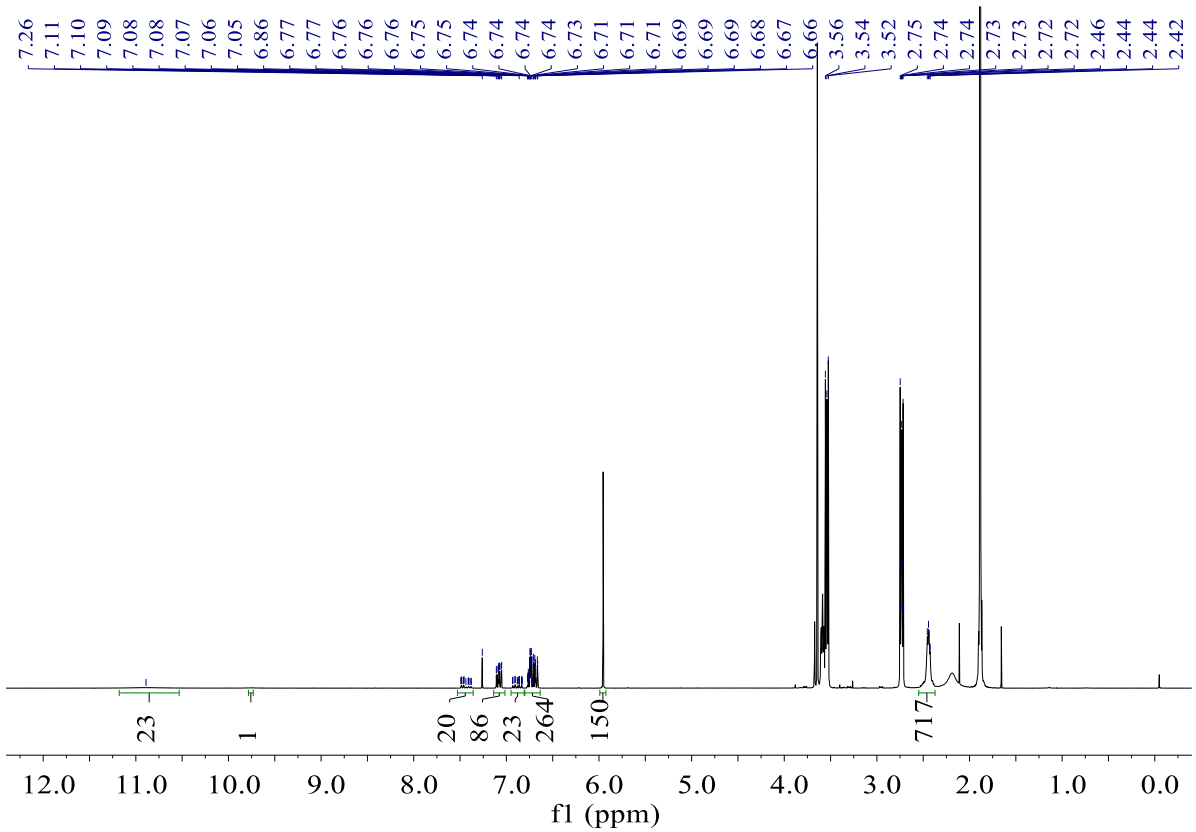


Figure S5. ^{1}H NMR spectrum of the reaction of salicylaldehyde **1a** with 5 equivalents of morpholine **2a** (300 MHz, $CDCl_3$, rt); 1,3,5-trimethoxybenzene was used as an internal standard.

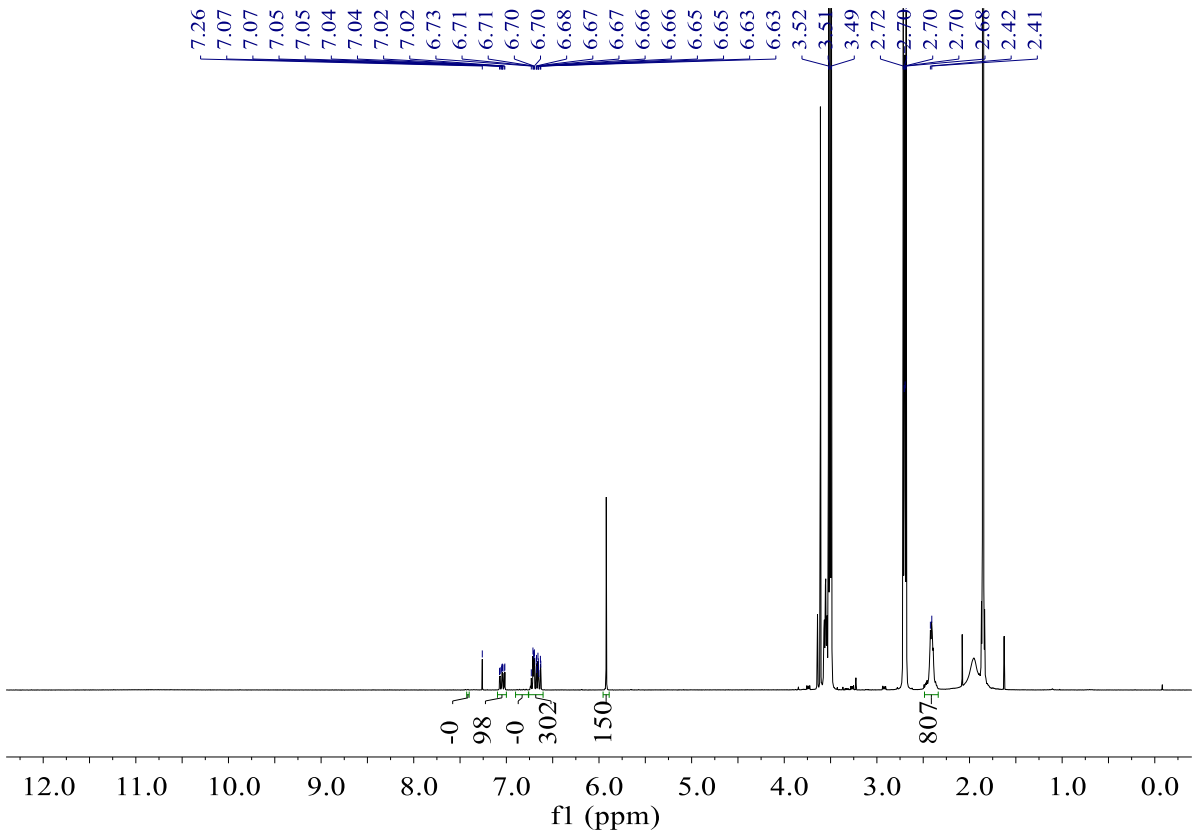
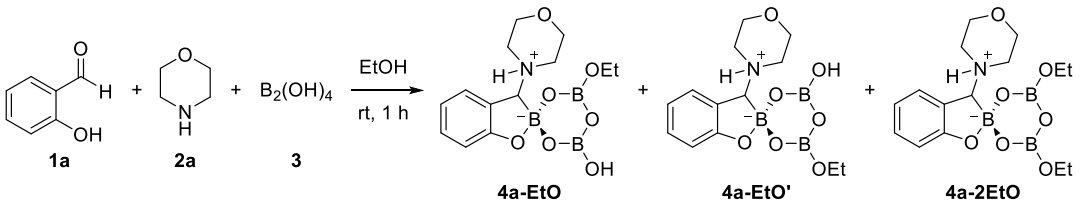


Figure S6. ^{1}H NMR spectrum of the reaction of salicylaldehyde **1a** with 10 equivalents of morpholine **2a** (300 MHz, $CDCl_3$, rt); 1,3,5-trimethoxybenzene was used as an internal standard.

3. Reaction conducted in ethanol.



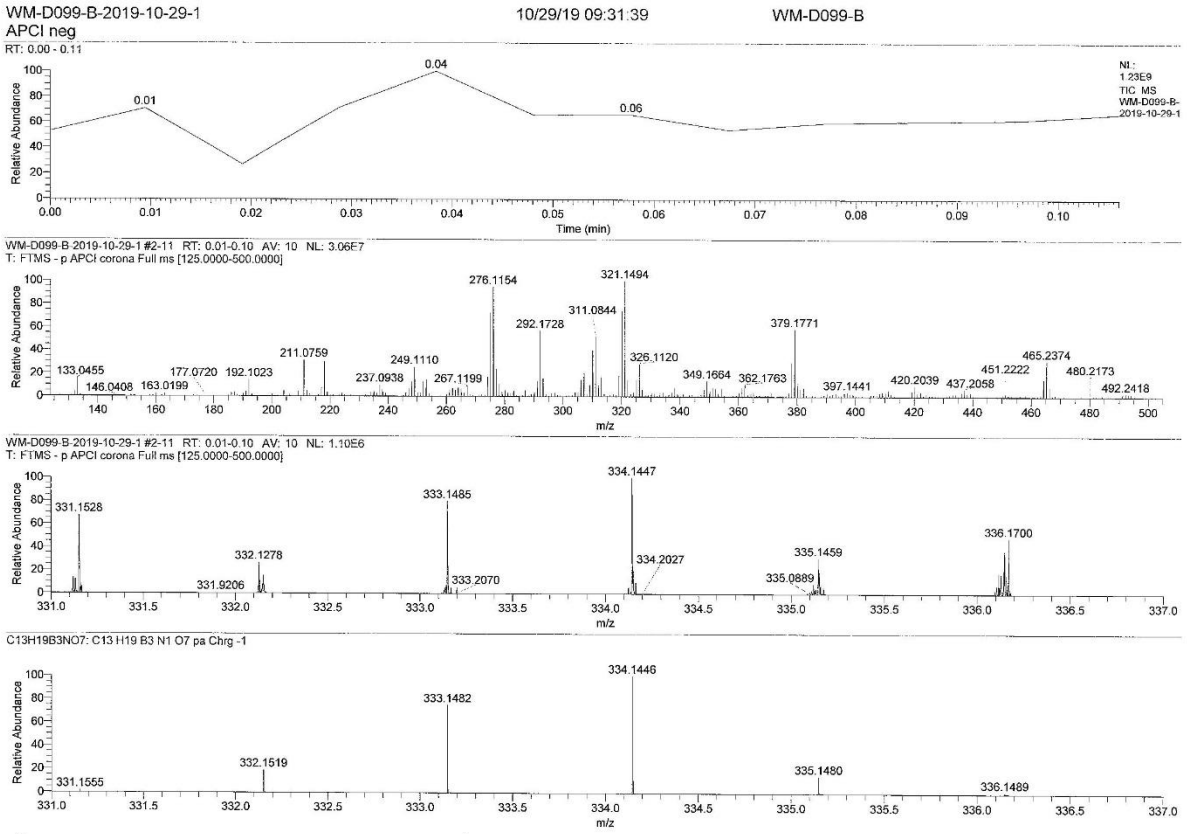


Figure S7. HRMS (APCI neg) of the reaction mixture; *m/z* of **4a-EtO** and/or **4a-EtO'**: [*M*–H]$^-$ calcd for $C_{13}H_{19}B_3NO_7^-$ 334.1446, found 334.1447.

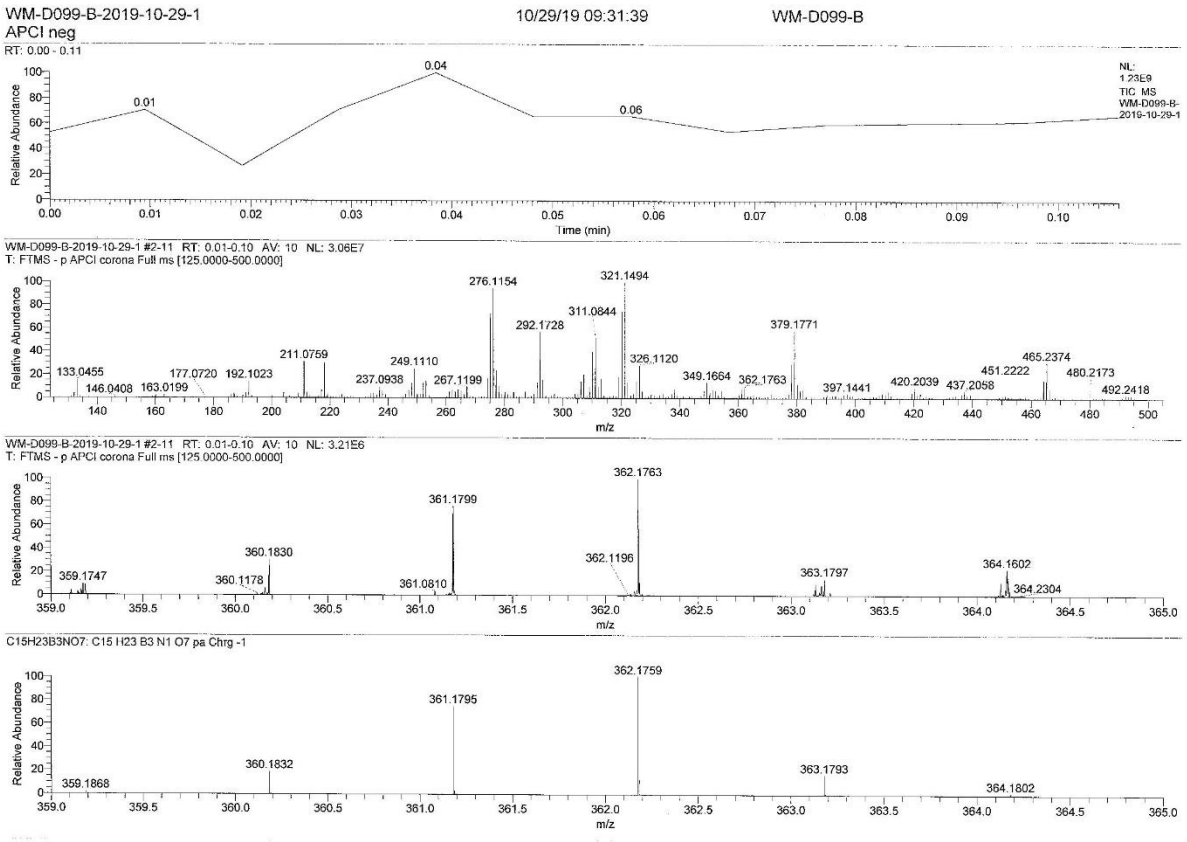


Figure S8. HRMS (APCI neg) of the reaction mixture; *m/z* of **4a-2EtO**: [*M*–H]$^-$ calcd for $C_{15}H_{23}B_3NO_7^-$ 362.1759, found 362.1763.

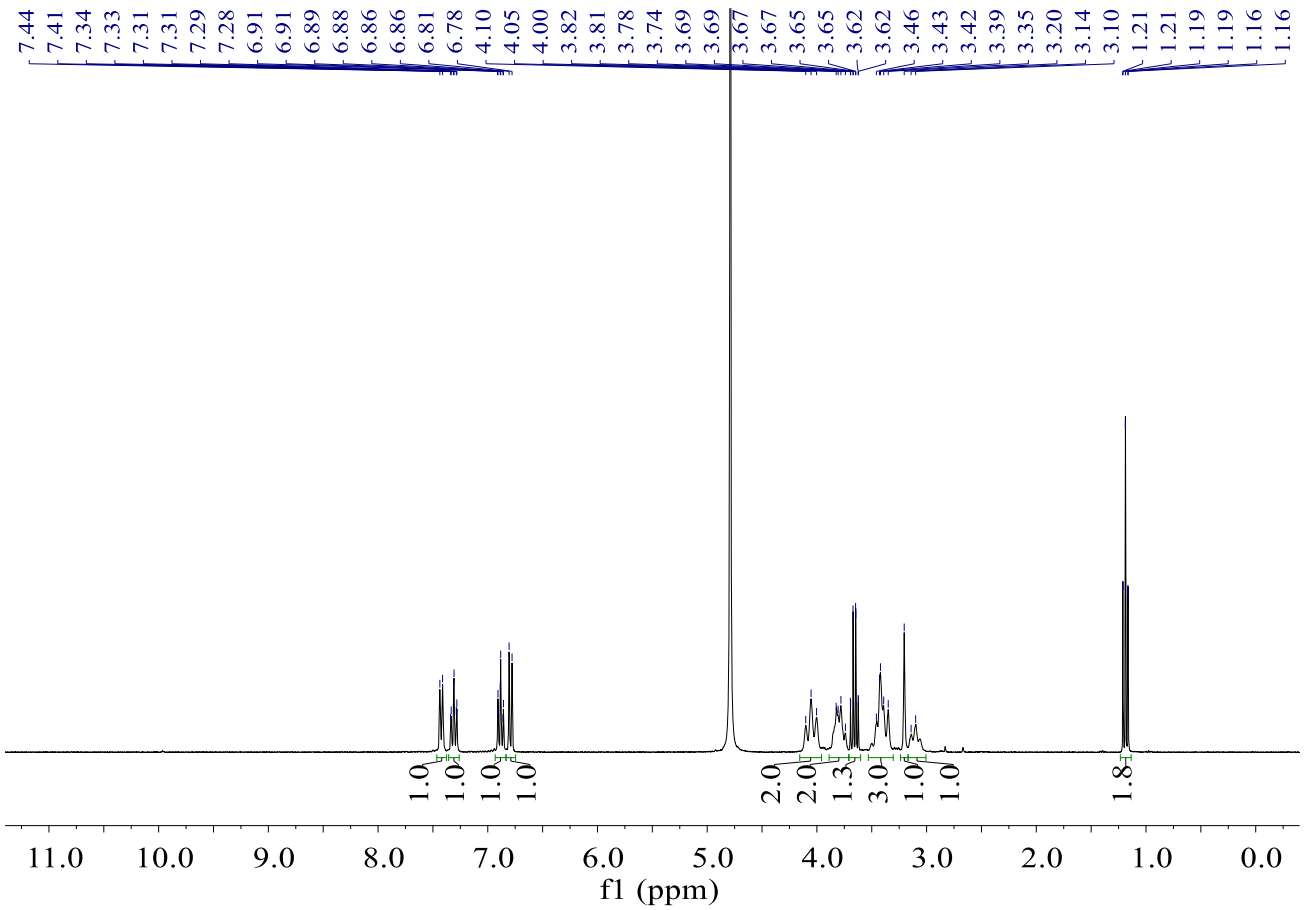


Figure S9. ^{1}H NMR spectrum of the reaction mixture (300 MHz, D_2O, rt).

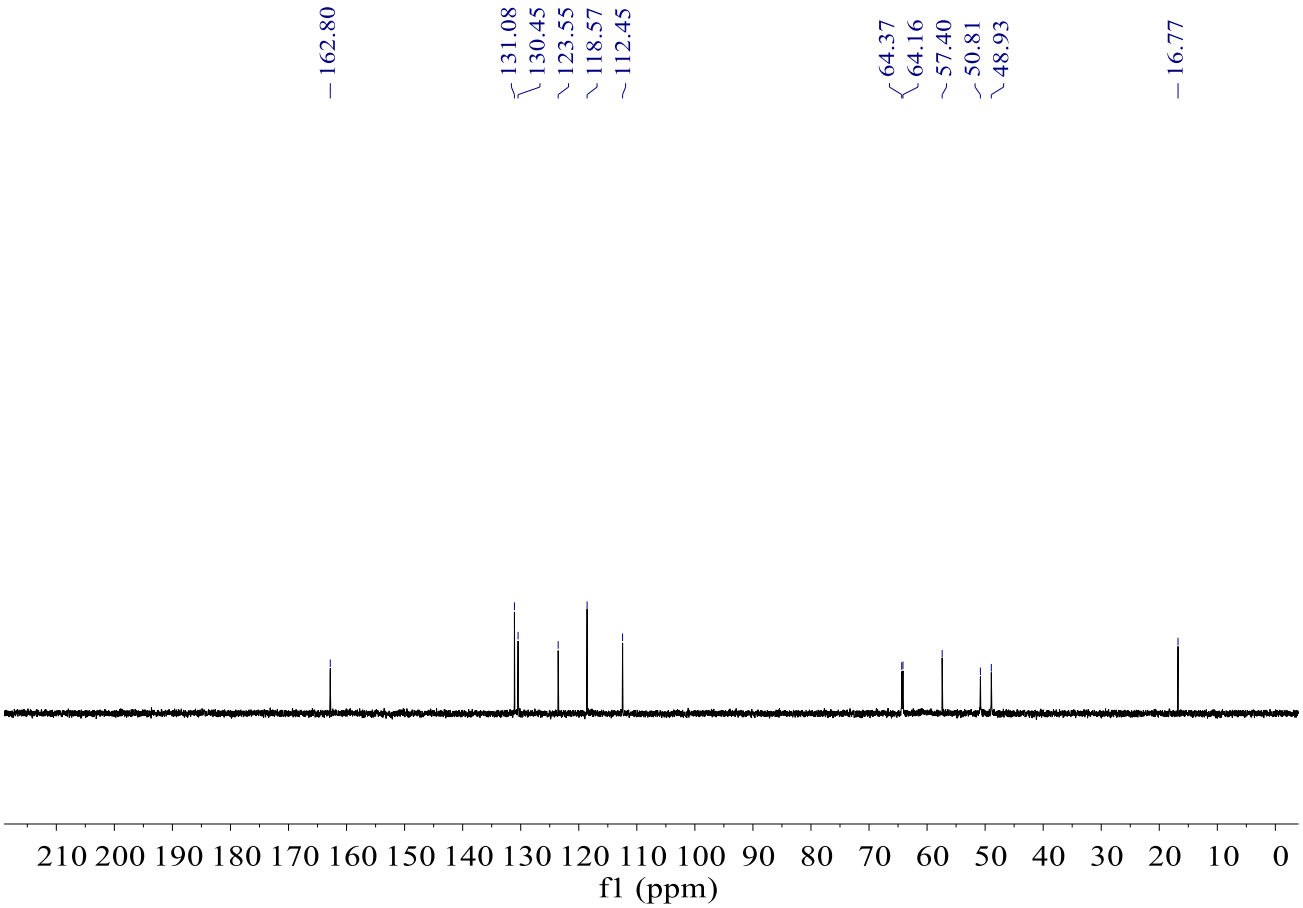


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of the reaction mixture (75 MHz, D_2O, rt).

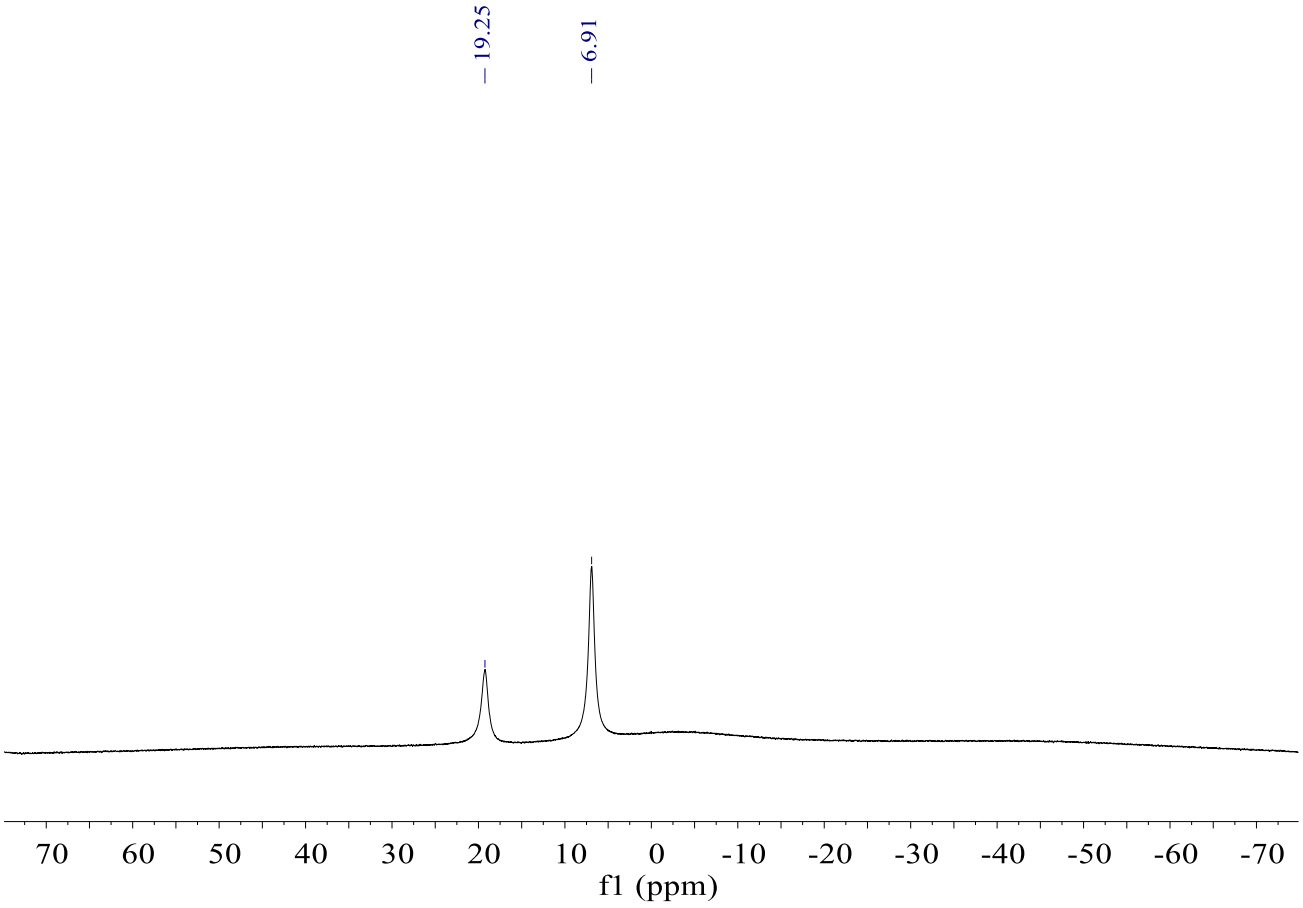
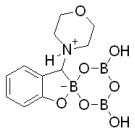


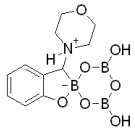
Figure S11. ^{11}B NMR spectrum of the reaction mixture (96 MHz, D_2O, rt).

V. NMR Spectra of Products

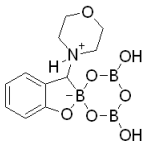
^{1}H NMR spectrum (300 MHz, D_2O) of **4a**



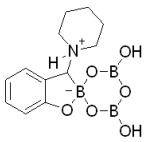
^{13}C{^{1}H} NMR spectrum (75 MHz, D_2O) of **4a**



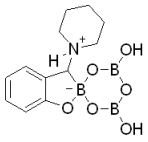
^{11}B NMR spectrum (96 MHz, D_2O) of **4a**



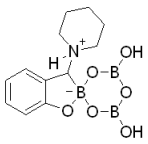
^{1}H NMR spectrum (300 MHz, D_2O) of **4b**



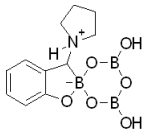
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, D_2O) of **4b**



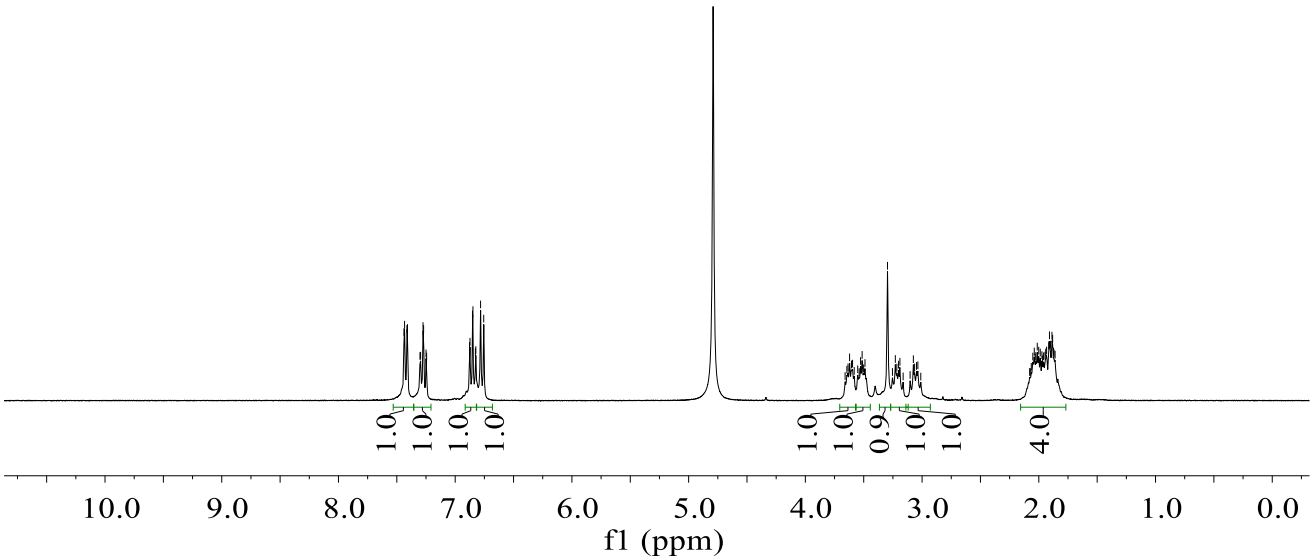
^{11}B NMR spectrum (96 MHz, D_2O) of **4b**



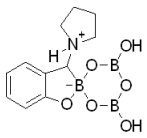
^{1}H NMR spectrum (300 MHz, D_2O) of **4c**



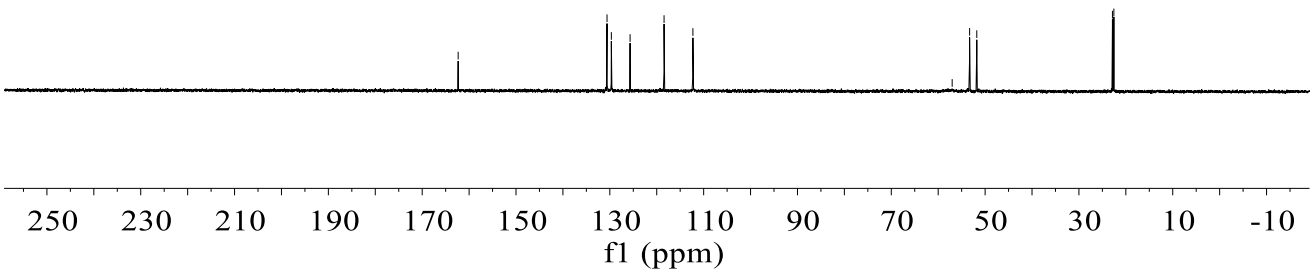
7.30 7.28 7.27 7.25 7.24 6.88 6.87 6.85 6.85 6.83 6.82 6.78 6.76 3.62 3.53 3.51 3.30 3.23 3.07 2.05 2.04 2.03 2.03 2.01 2.00 1.99 1.97 1.97 1.96 1.95 1.94 1.93 1.92 1.91 1.90 1.89 1.88 1.87 1.87 1.86



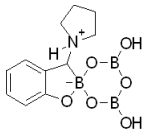
^{13}C{^{1}H} NMR spectrum (75 MHz, D_2O) of **4c**



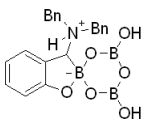
162.33 130.60 129.68 125.68 118.44 112.29 57.02 53.30 51.77 22.85 22.55



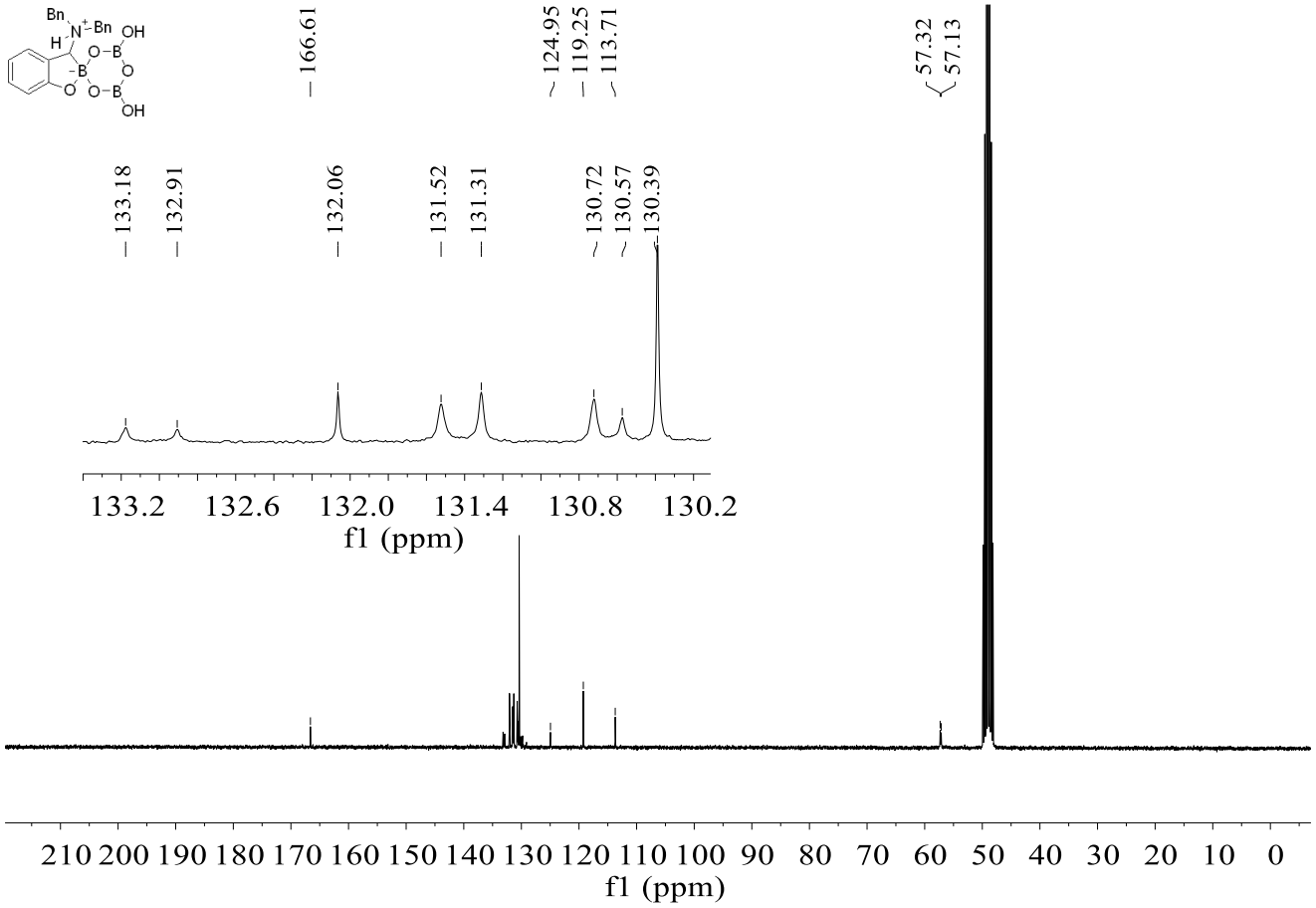
^{11}B NMR spectrum (96 MHz, D_2O) of **4c**



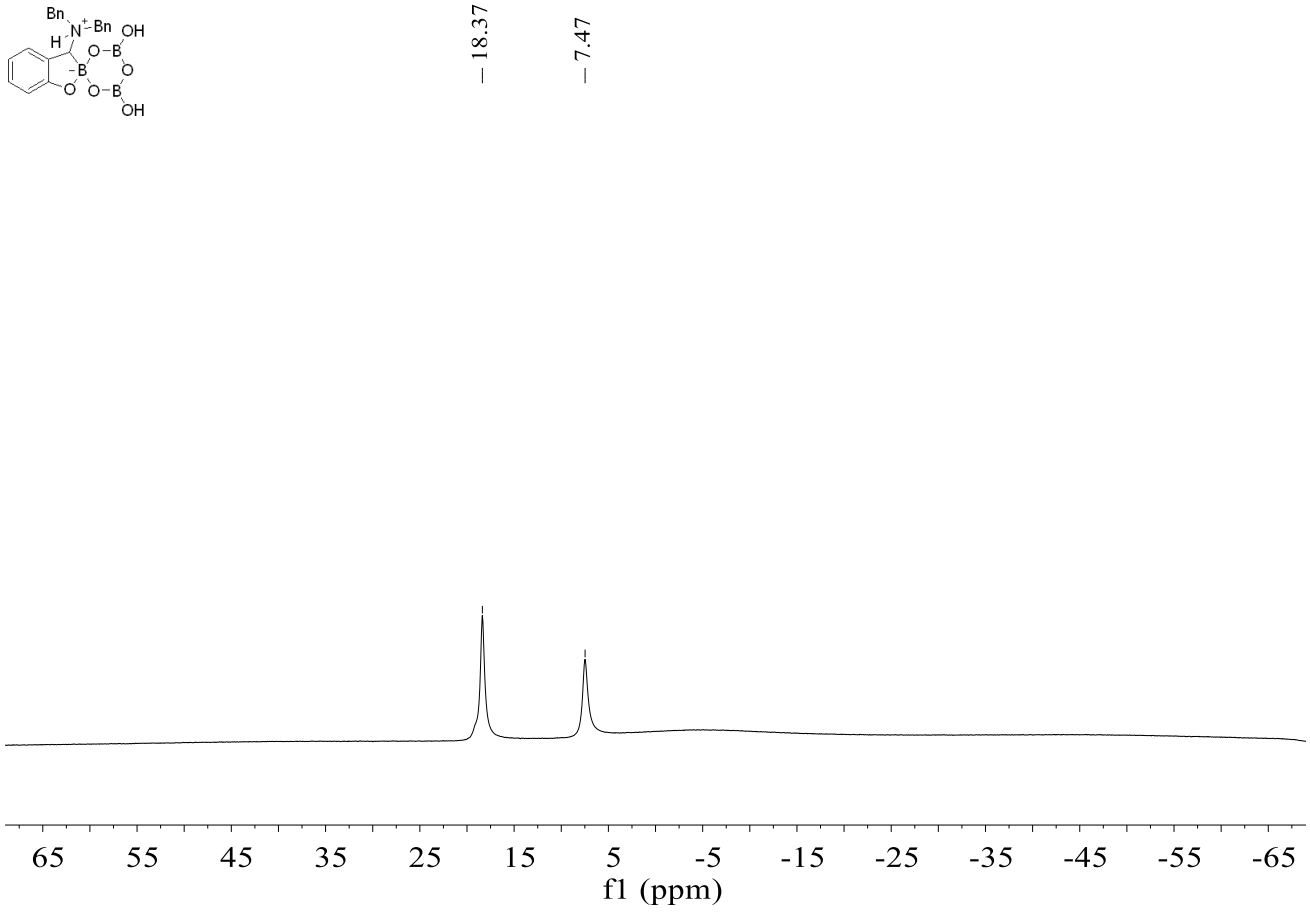
^{1}H NMR spectrum (300 MHz, CD_3OD) of **4d**



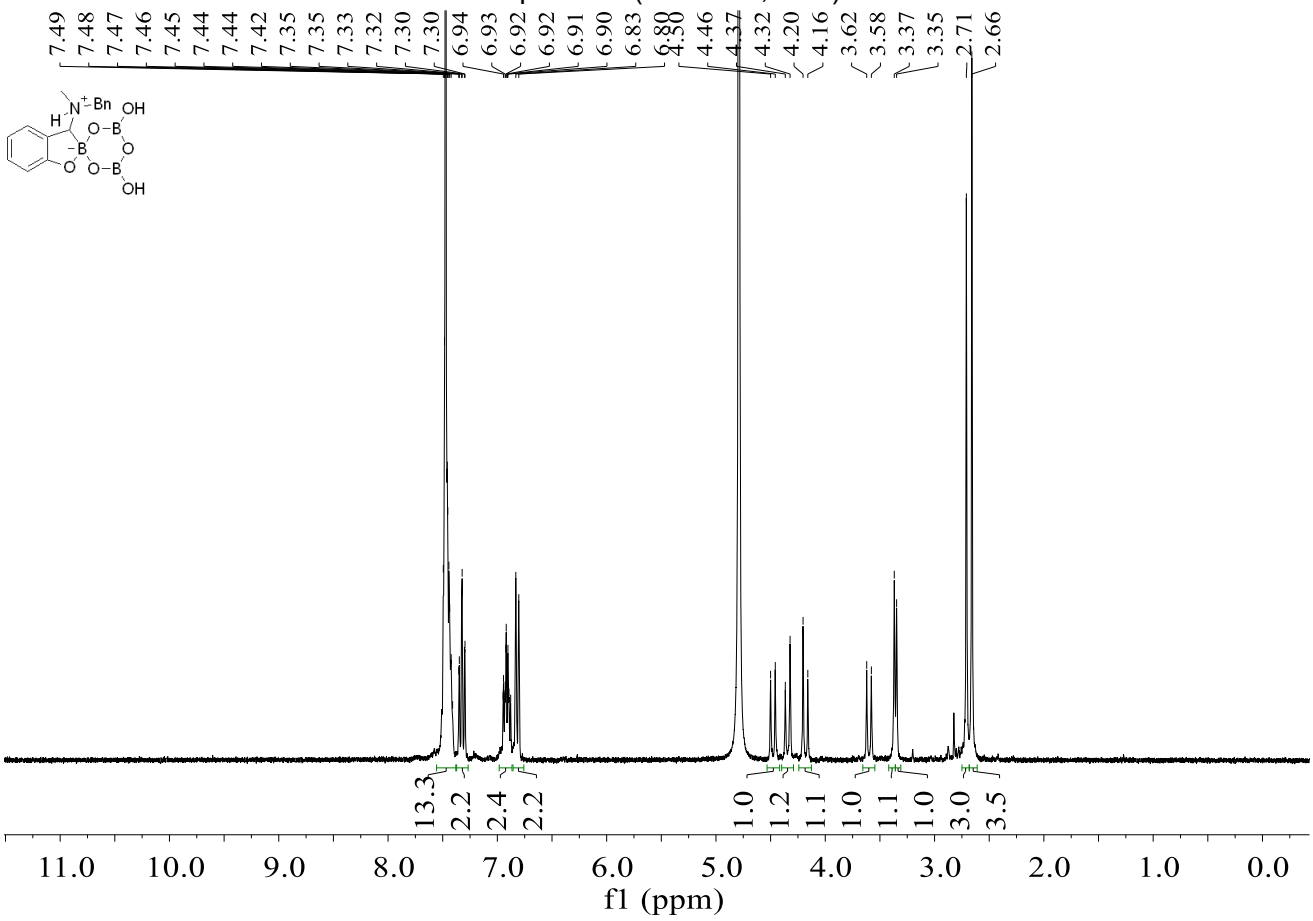
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, CD_3OD) of **4d**



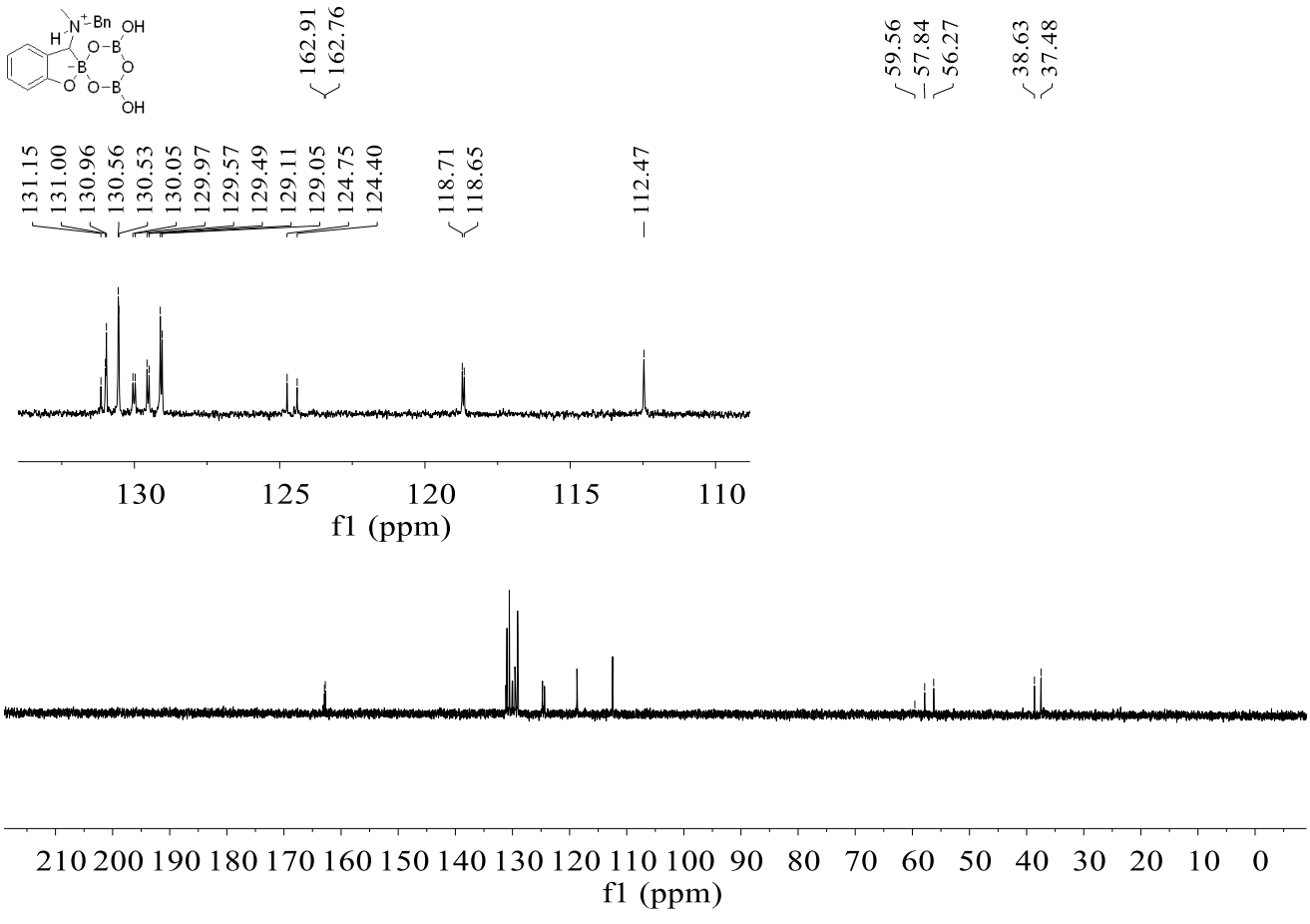
^{11}B NMR spectrum (96 MHz, CD_3OD) of **4d**



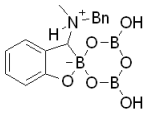
^{1}H NMR spectrum (300 MHz, D_2O) of **4e**



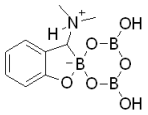
^{13}C{^{1}H} NMR spectrum (75 MHz, D_2O) of **4e**



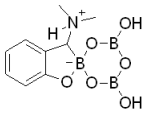
^{11}B NMR spectrum (96 MHz, D_2O) of **4e**



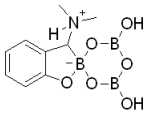
^{1}H NMR spectrum (300 MHz, D_2O) of **4f**



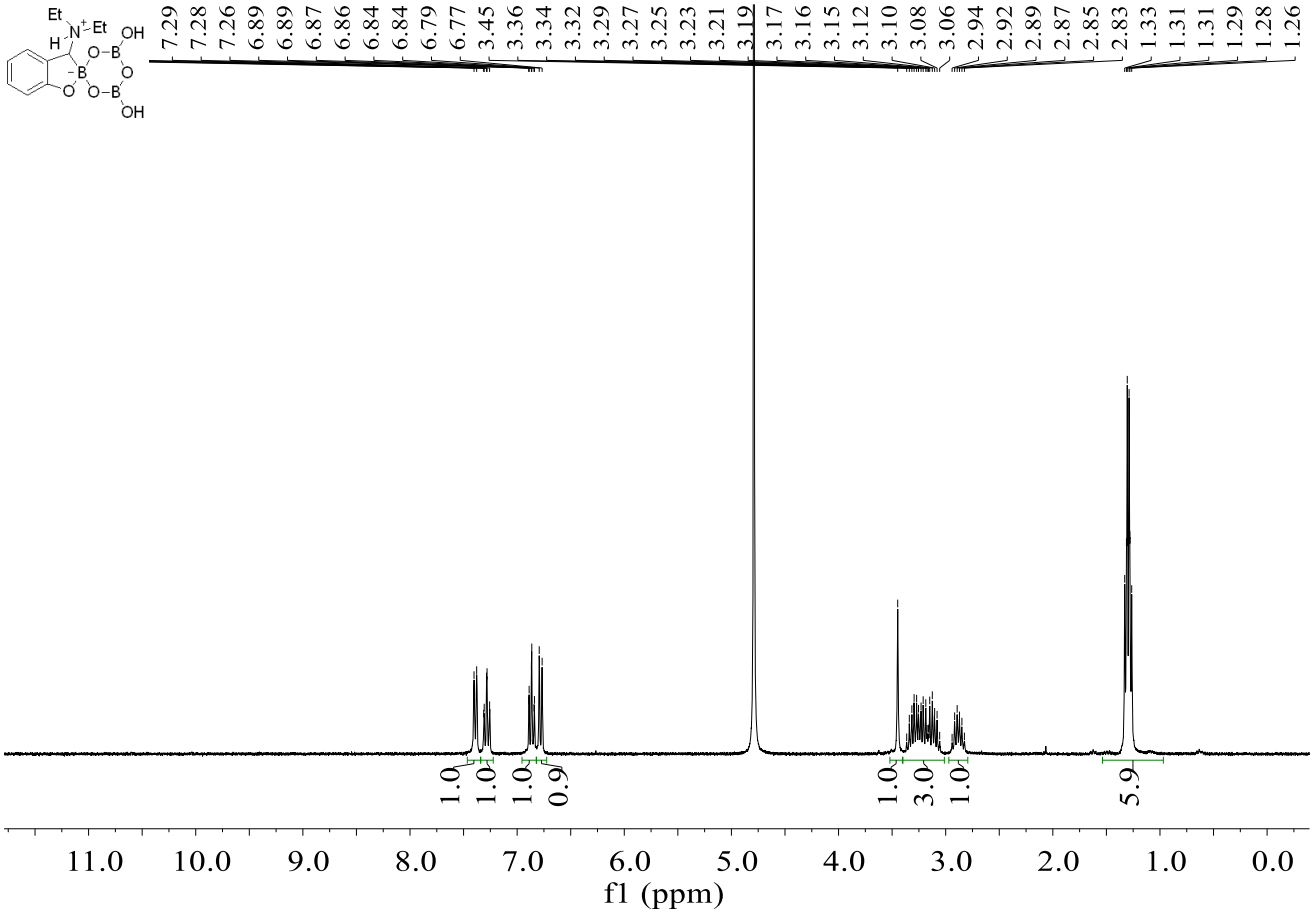
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, D_2O) of **4f**



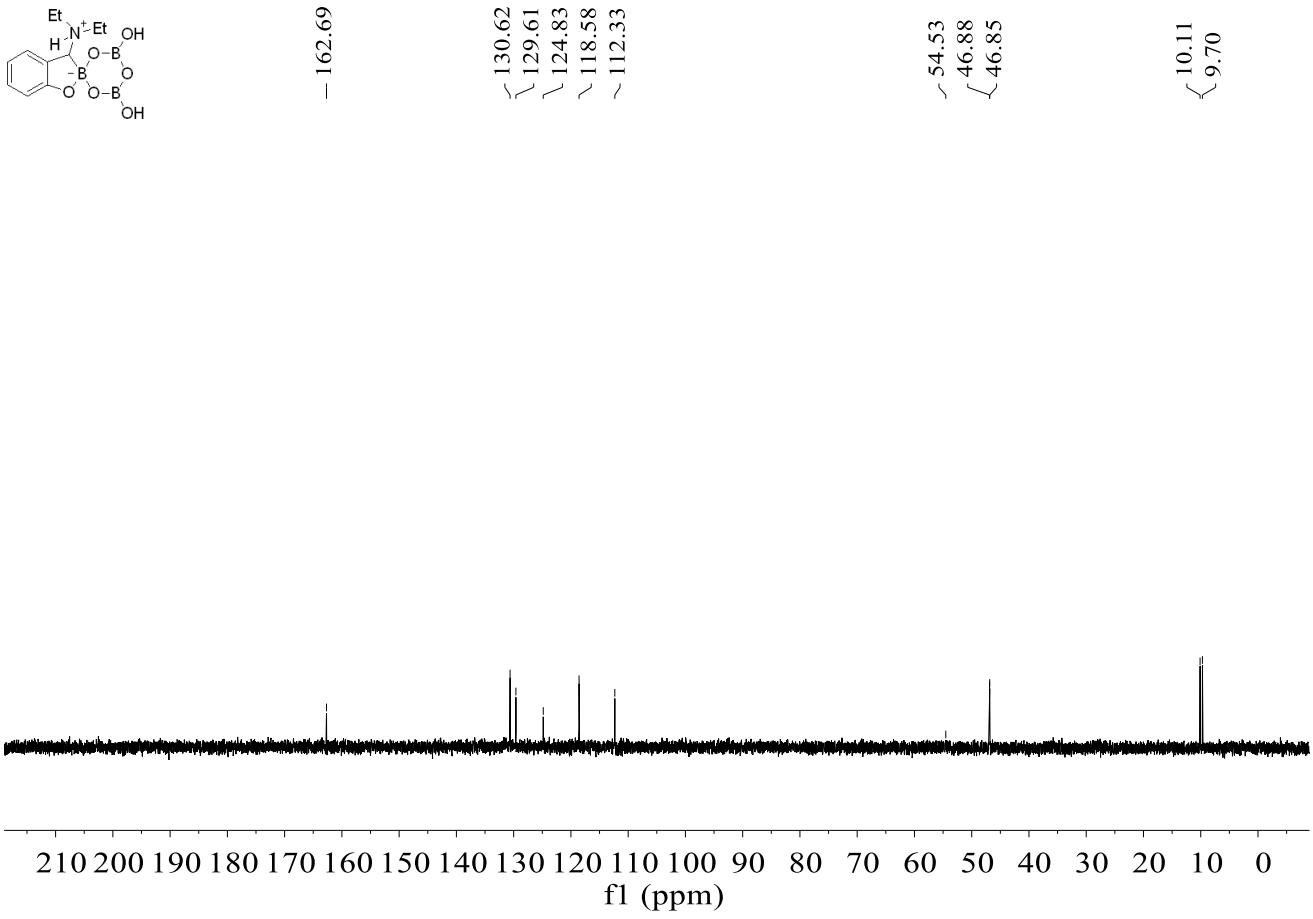
^{11}B NMR spectrum (96 MHz, D_2O) of **4f**



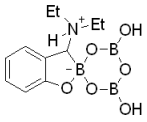
^{1}H NMR spectrum (300 MHz, D_2O) of **4g**



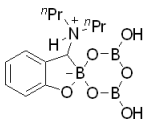
^{13}C{^{1}H} NMR spectrum (75 MHz, D_2O) of **4g**



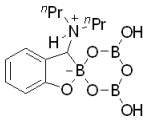
^{11}B NMR spectrum (96 MHz, D_2O) of **4g**



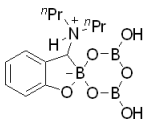
^{1}H NMR spectrum (300 MHz, D_2O) of **4h**



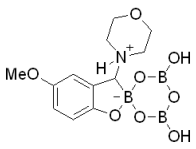
^{11}B NMR spectrum (96 MHz, D_2O) of **4h**



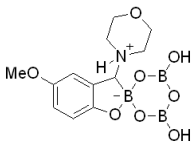
^{11}B NMR spectrum (96 MHz, D_2O) of **4h**



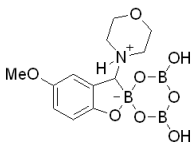
^{1}H NMR spectrum (300 MHz, D_2O) of **4i**



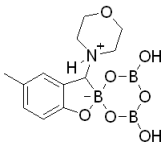
^{13}C{^{1}H} NMR spectrum (75 MHz, D_2O) of **4i**



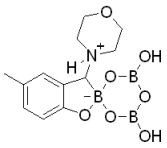
^{11}B NMR spectrum (96 MHz, D_2O) of **4i**



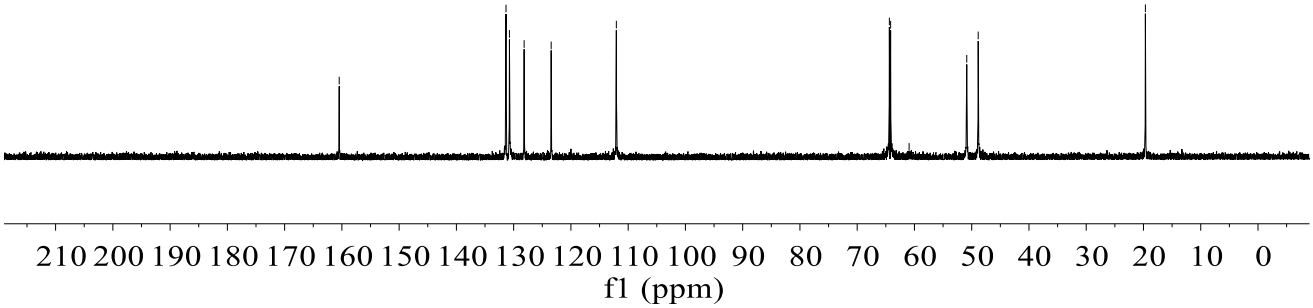
^{1}H NMR spectrum (300 MHz, D_2O) of **4j**



$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, D_2O) of **4j**

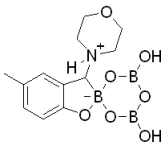


160.47
131.33
130.74
128.17
123.45
112.06
64.38
64.16
60.93
50.86
48.87
19.67

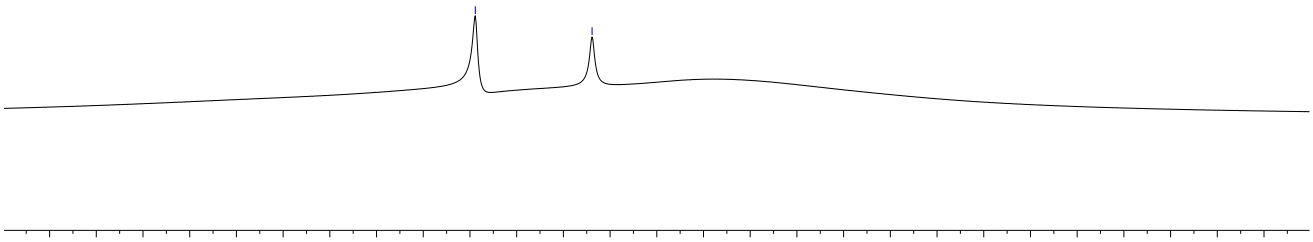


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{11}B NMR spectrum (96 MHz, D_2O) of **4j**

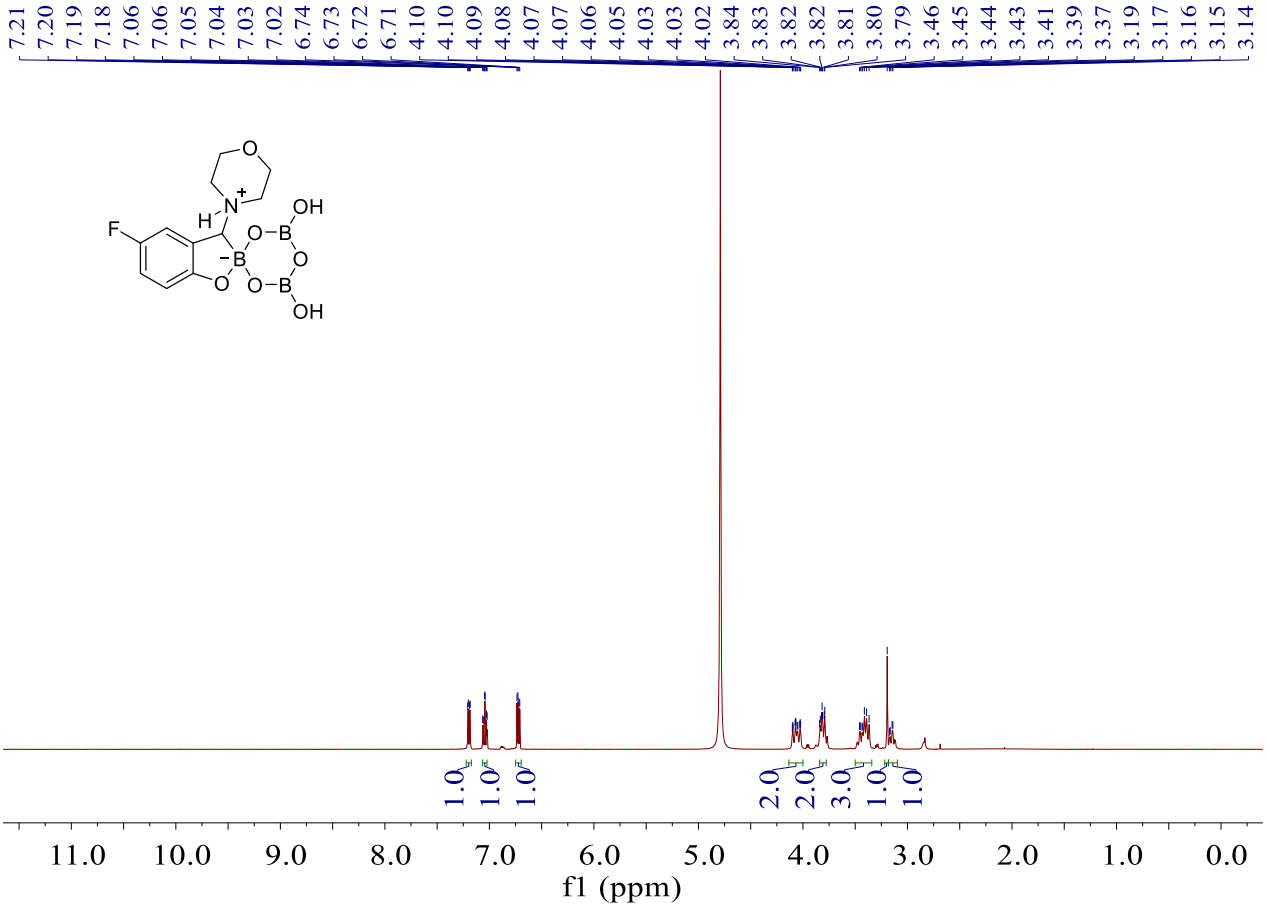


19.43
6.93

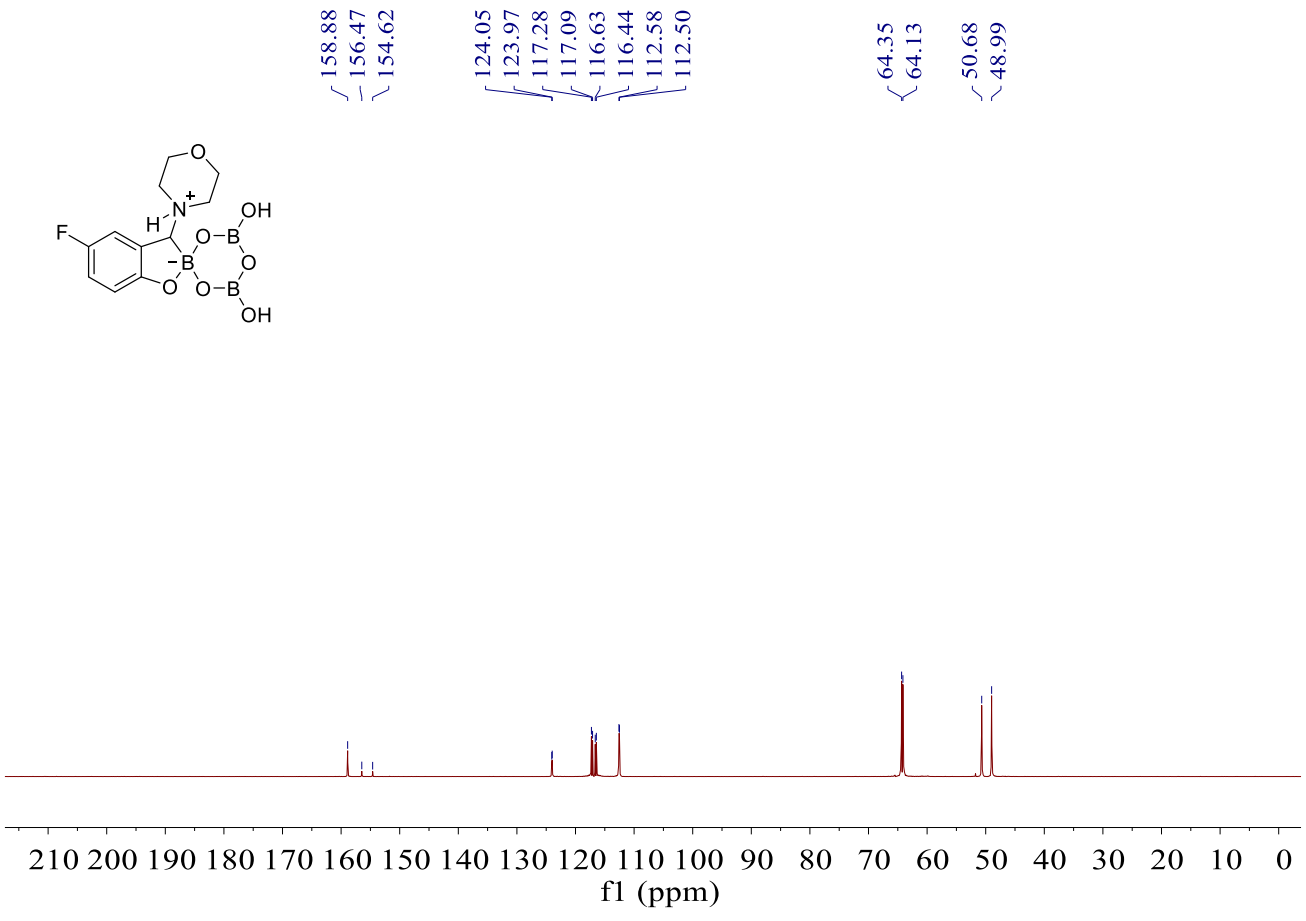


65 55 45 35 25 15 5 -5 -15 -25 -35 -45 -55 -65
f1 (ppm)

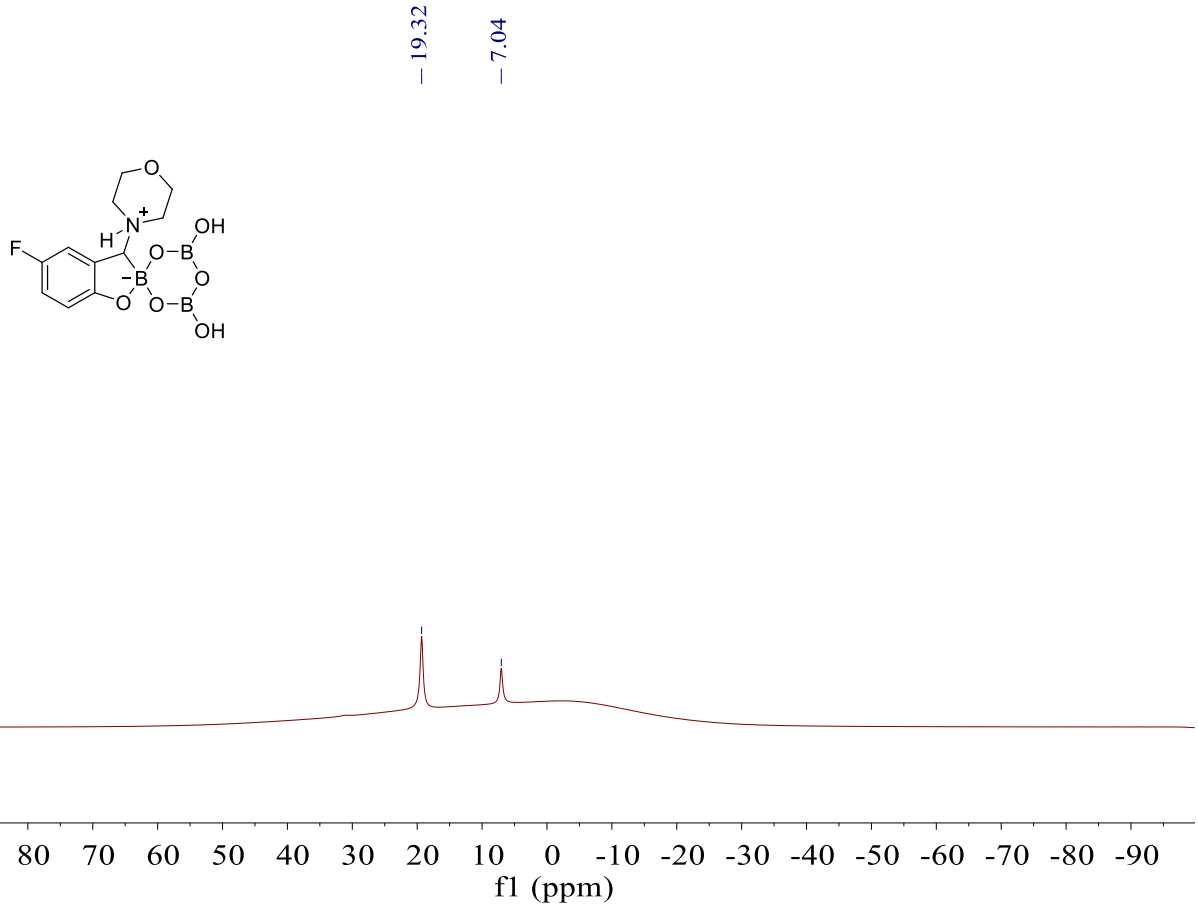
^{1}H NMR spectrum (500 MHz, D_2O) of **4k**



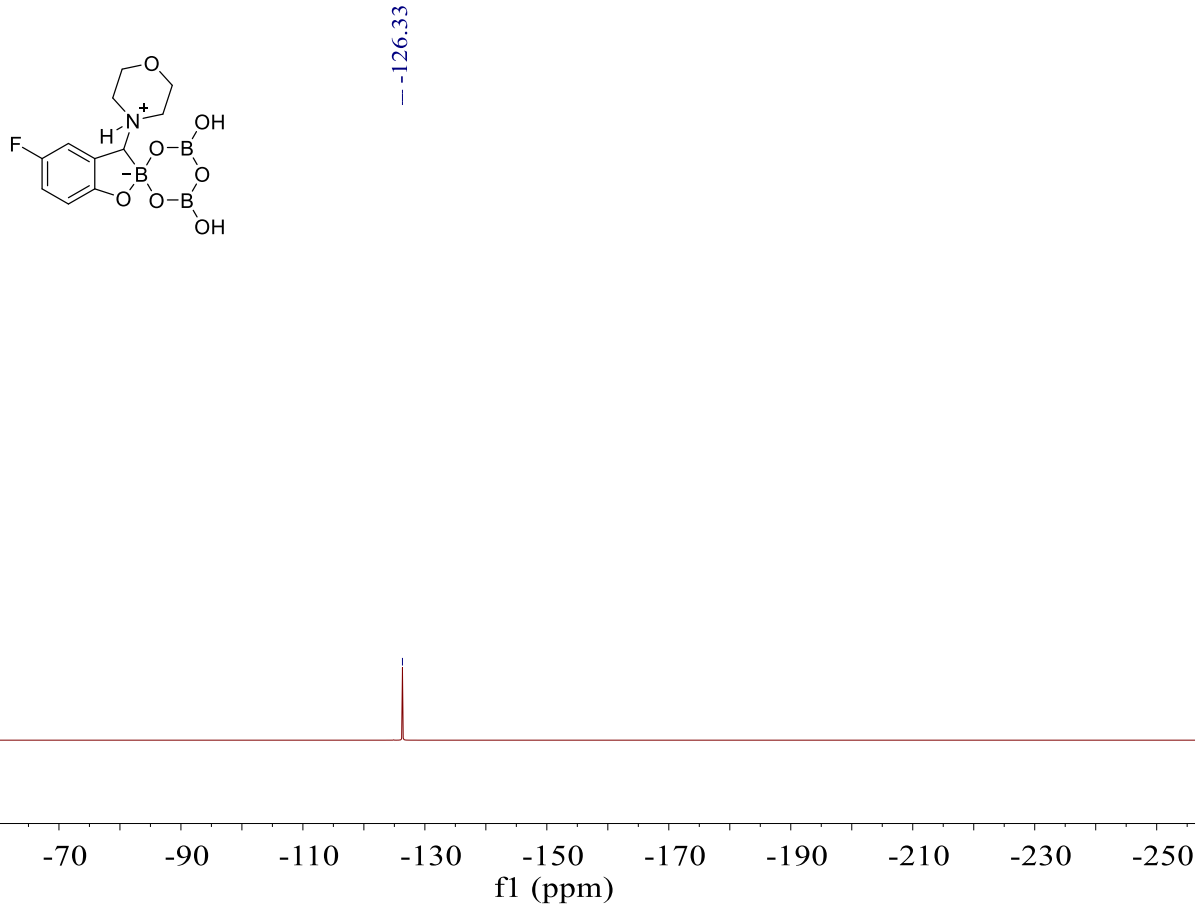
^{13}C{^{1}H} NMR spectrum (126 MHz, D_2O) of **4k**



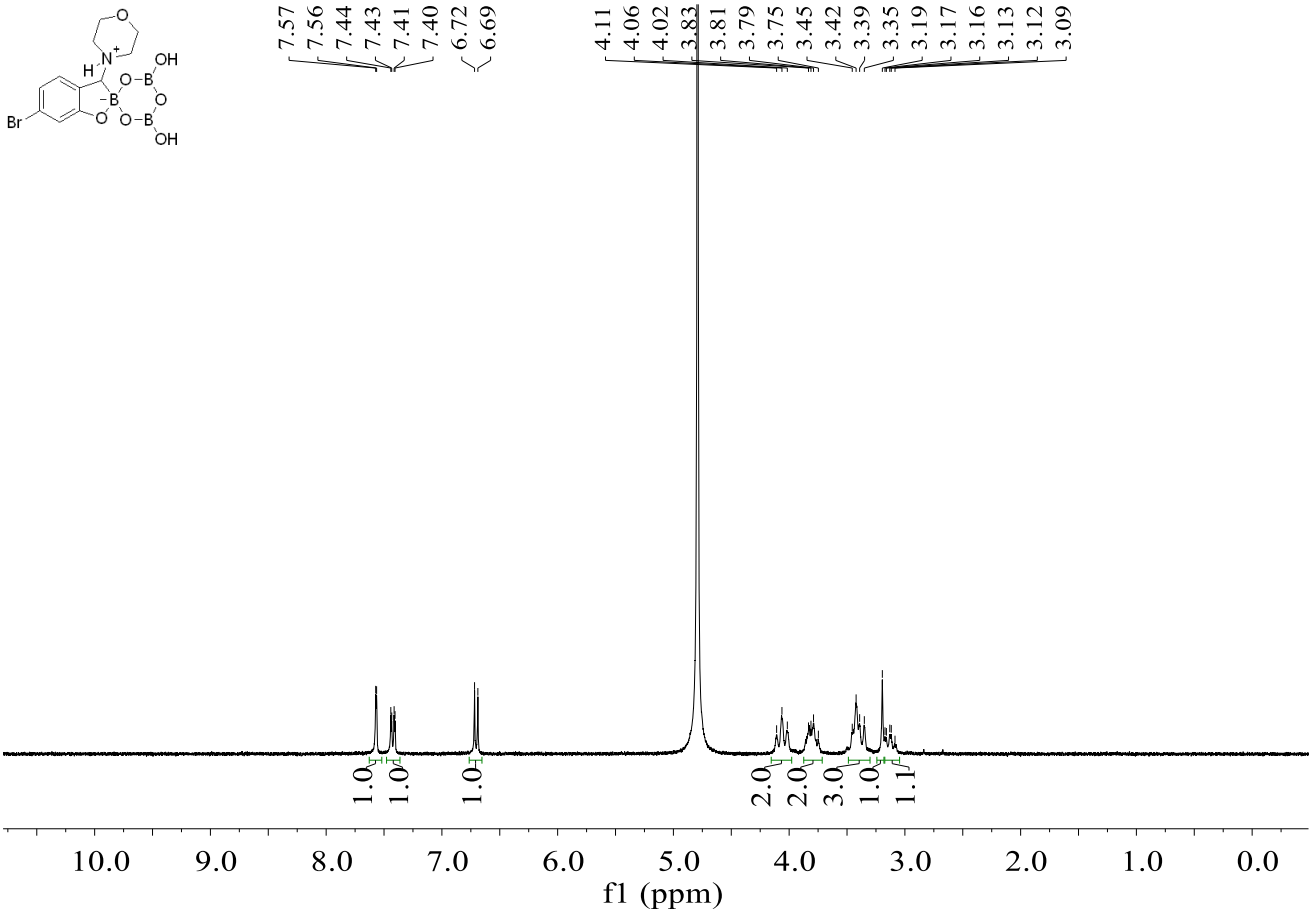
^{11}B NMR spectrum (160 MHz, D_2O) of **4k**



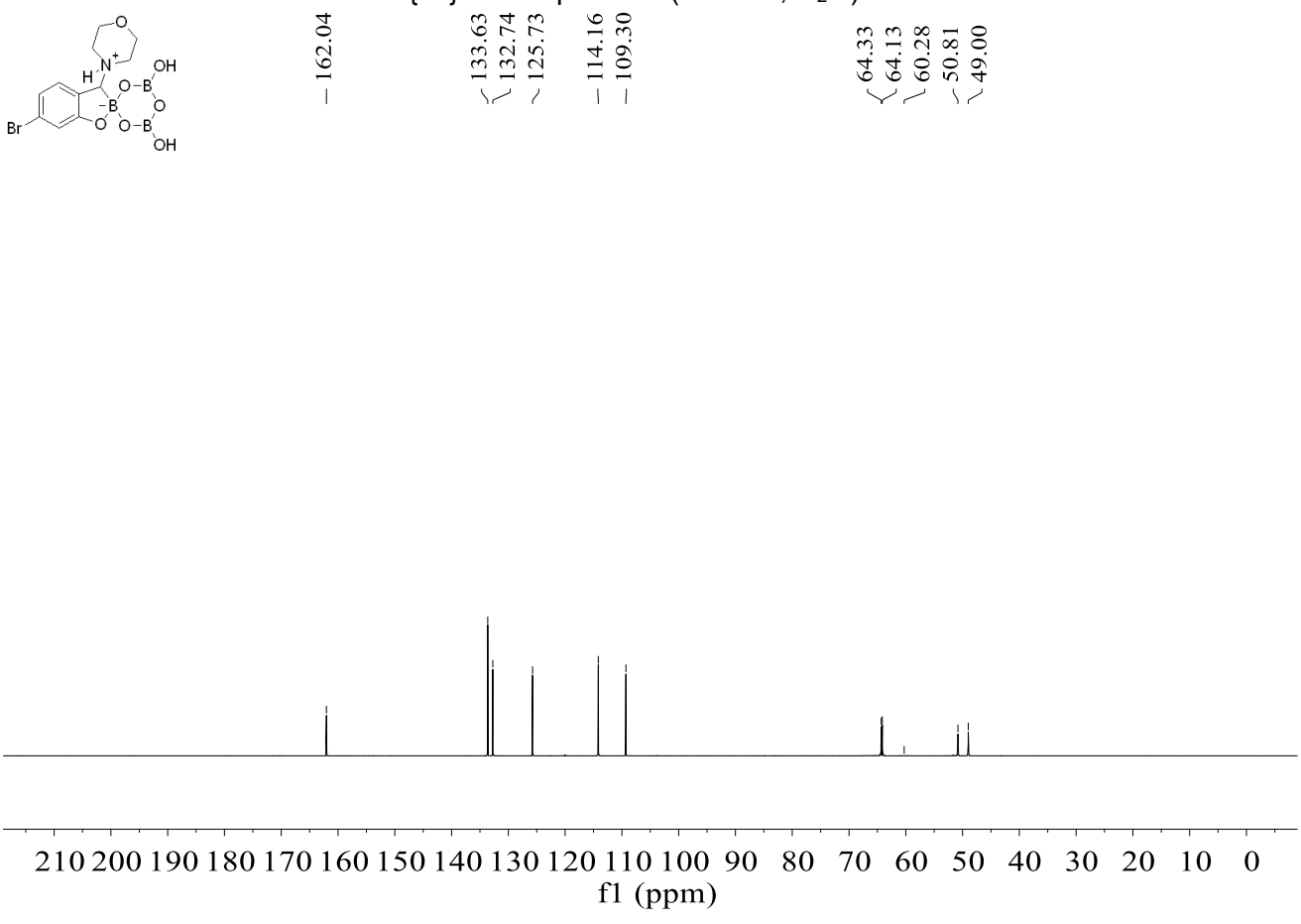
^{11}B NMR spectrum (160 MHz, D_2O) of **4k**



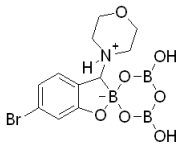
^{1}H NMR spectrum (300 MHz, D_2O) of **4l**



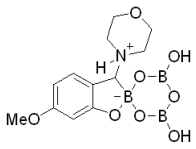
^{13}C{^{1}H} NMR spectrum (75 MHz, D_2O) of **4l**



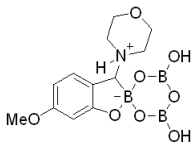
^{11}B NMR spectrum (96 MHz, D_2O) of **4l**



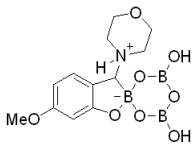
^{1}H NMR spectrum (300 MHz, D_2O) of **4m**

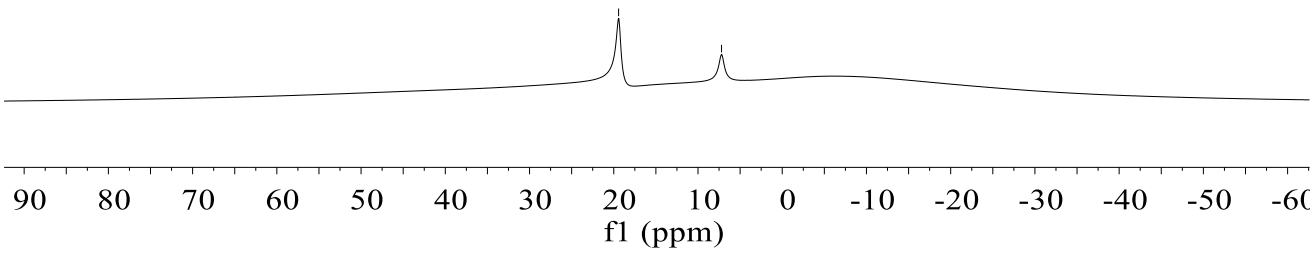


$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, D_2O) of **4m**

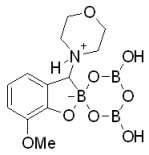


^{11}B NMR spectrum (96 MHz, D_2O) of **4m**

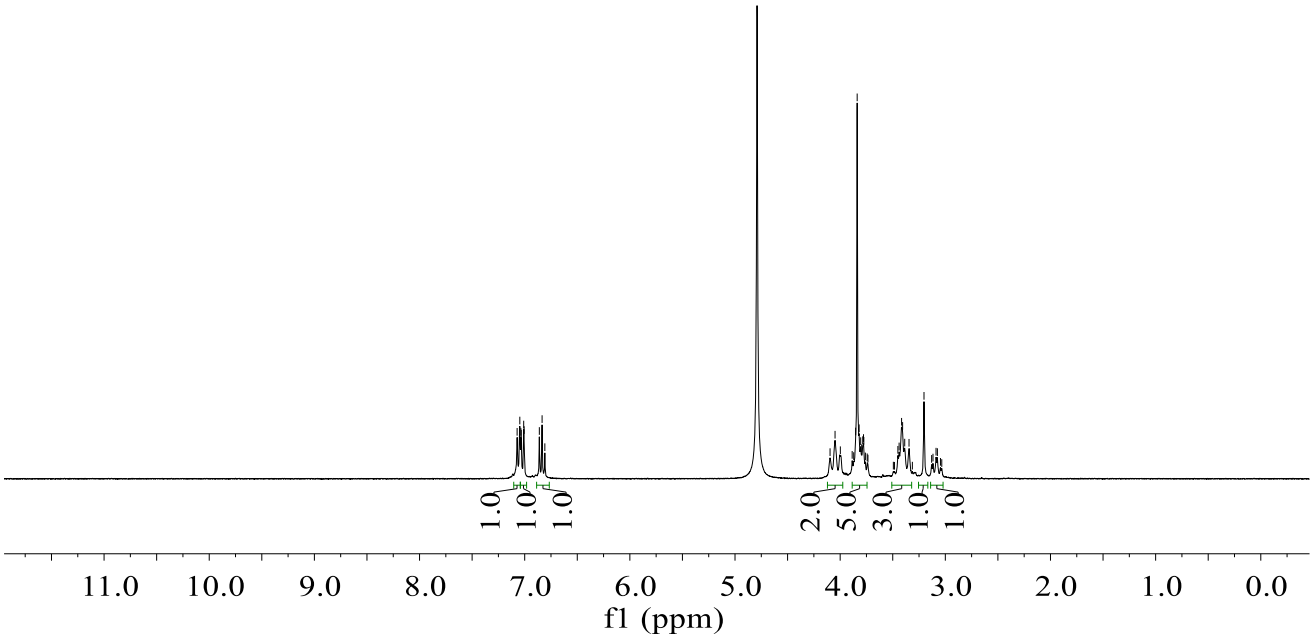




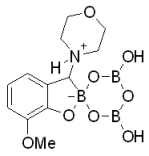
^{1}H NMR spectrum (300 MHz, D_2O) of **4n**



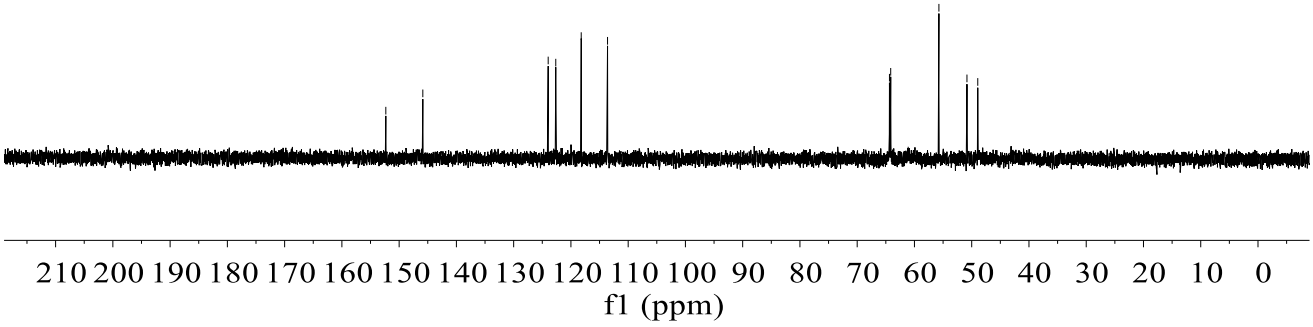
7.05 7.04 7.03 7.01 7.01 6.86 6.83 6.81 4.10 4.05 4.00 3.89 3.87 3.85 3.84 3.82 3.80 3.80 3.79 3.78 3.77 3.76 3.74 3.74 3.49 3.48 3.45 3.44 3.42 3.41 3.39 3.35 3.31 3.20 3.13 3.12 3.09 3.08 3.05 3.03



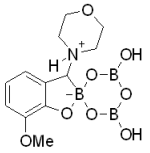
^{13}C{^{1}H} NMR spectrum (75 MHz, D_2O) of **4n**



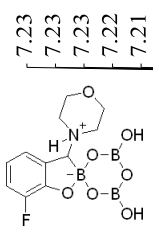
152.33 145.86 123.97 122.65 118.20 113.60 64.36 64.15 61.09 55.73 50.83 48.94



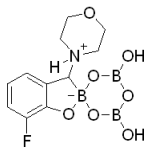
^{11}B NMR spectrum (96 MHz, D_2O) of **4n**



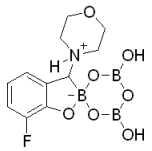
^{1}H NMR spectrum (500 MHz, D_2O) of **4o**



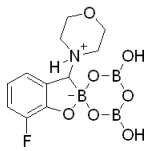
$^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, D_2O) of **4o**



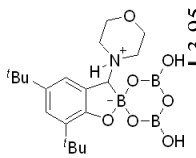
^{11}B NMR spectrum (160 MHz, D_2O) of **4o**



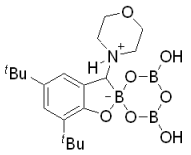
^{19}F NMR spectrum (471 MHz, D_2O) of **4o**



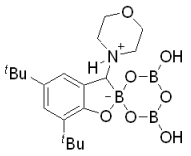
^{1}H NMR spectrum (300 MHz, CD_3OD) of **4p**



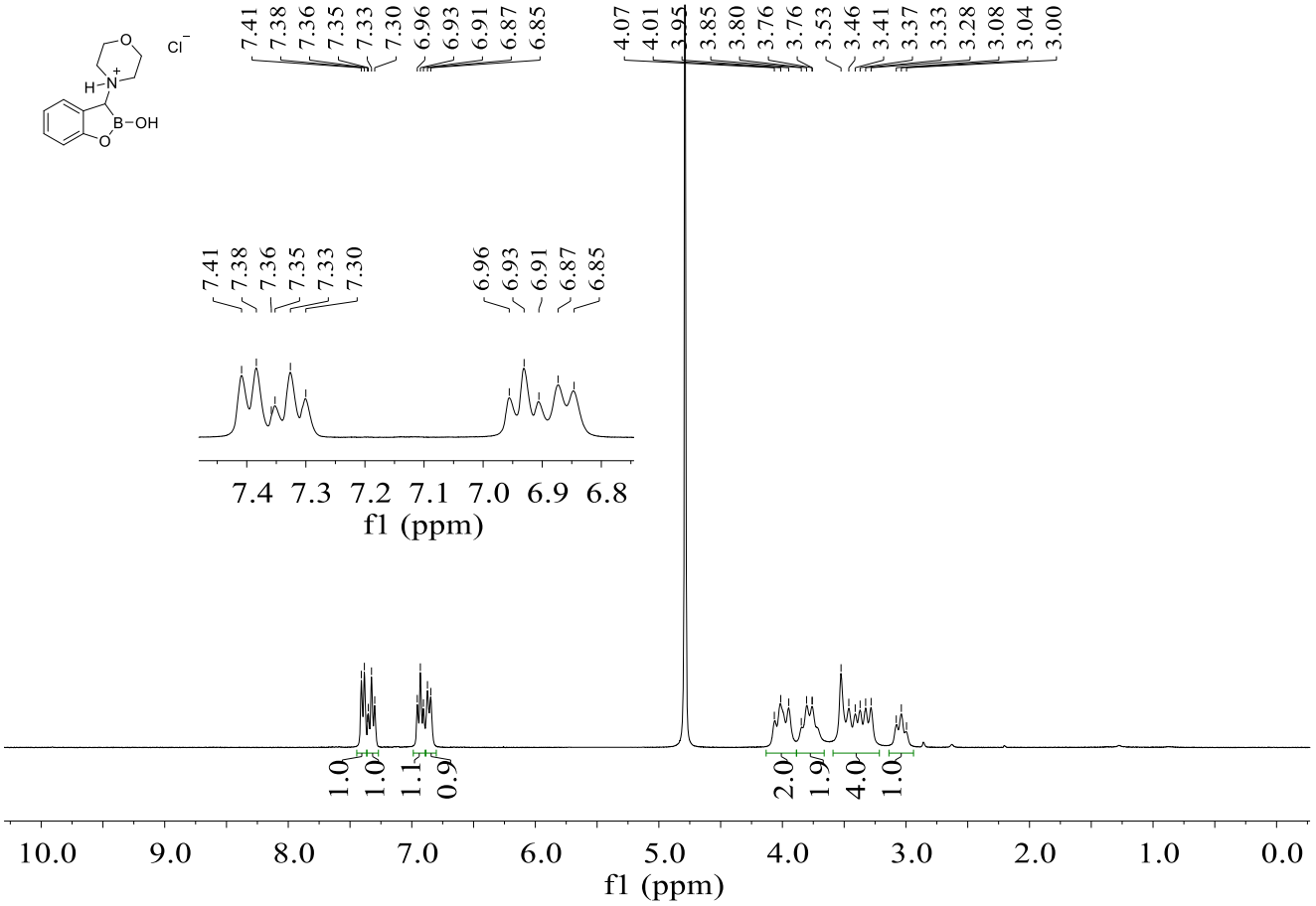
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, CD_3OD) of **4p**



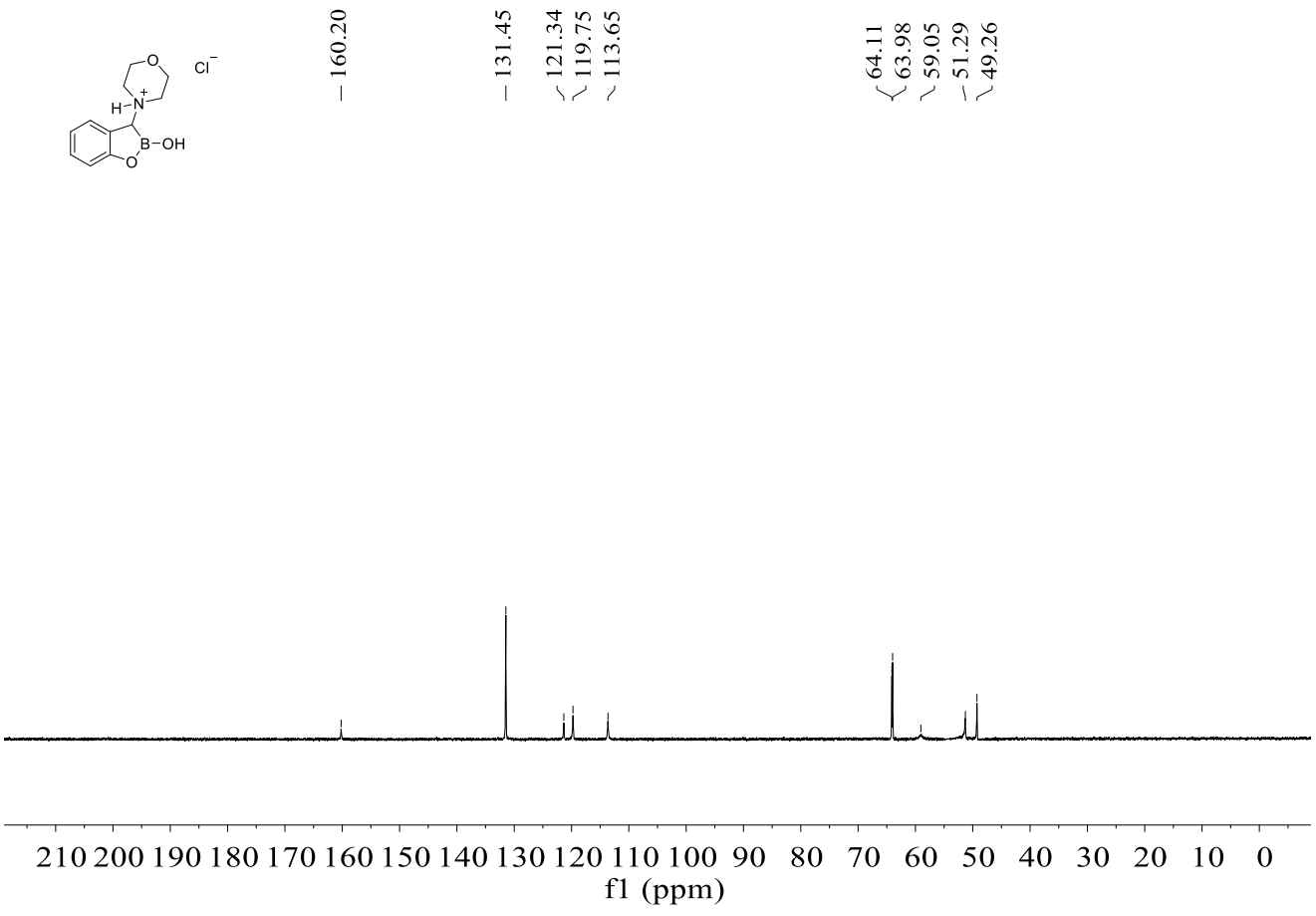
^{11}B NMR spectrum (96 MHz, CD_3OD) of **4p**



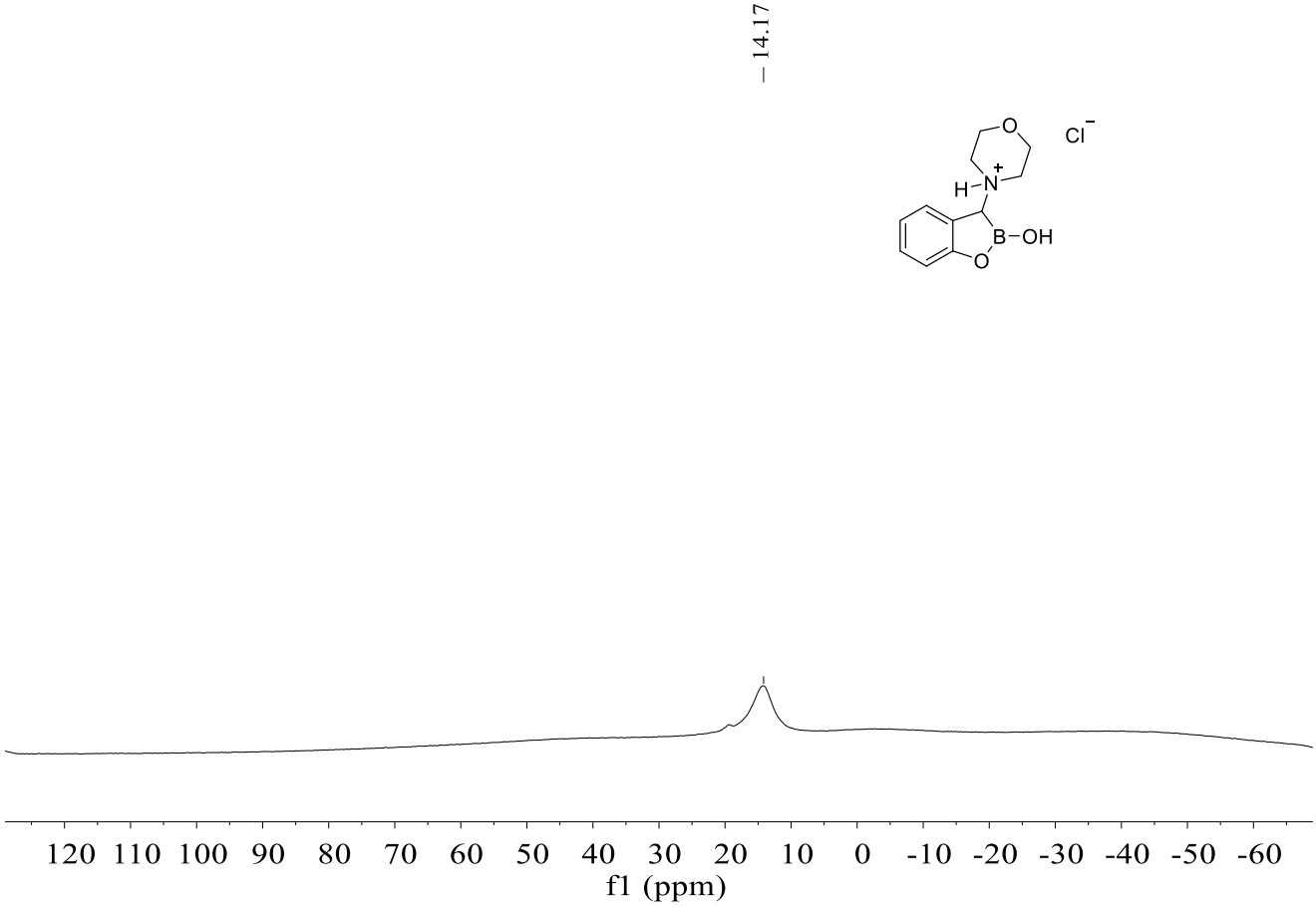
^{1}H NMR spectrum (300 MHz, D_2O) of **5a**



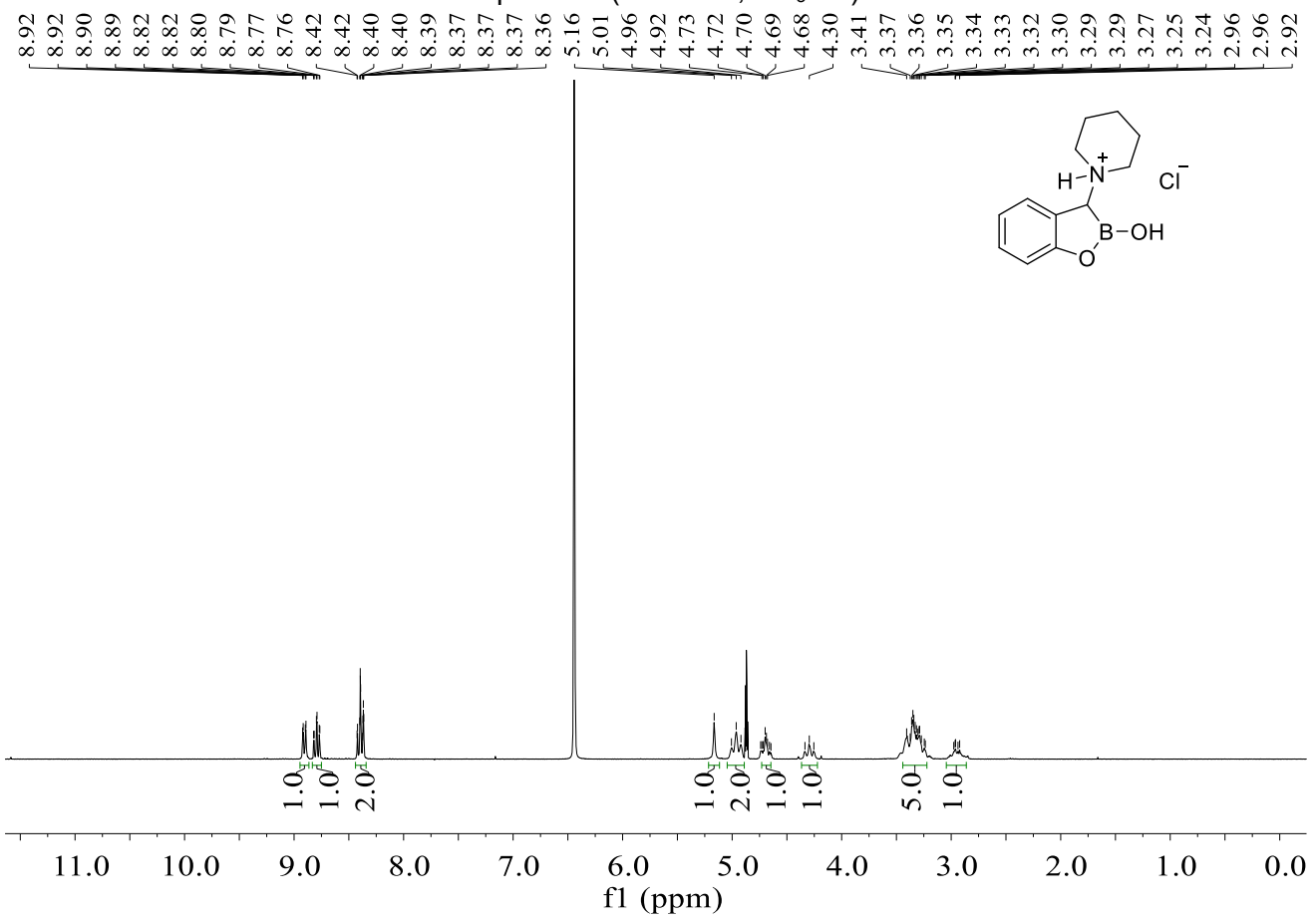
^{13}C{^{1}H} NMR spectrum (75 MHz, D_2O) of **5a**



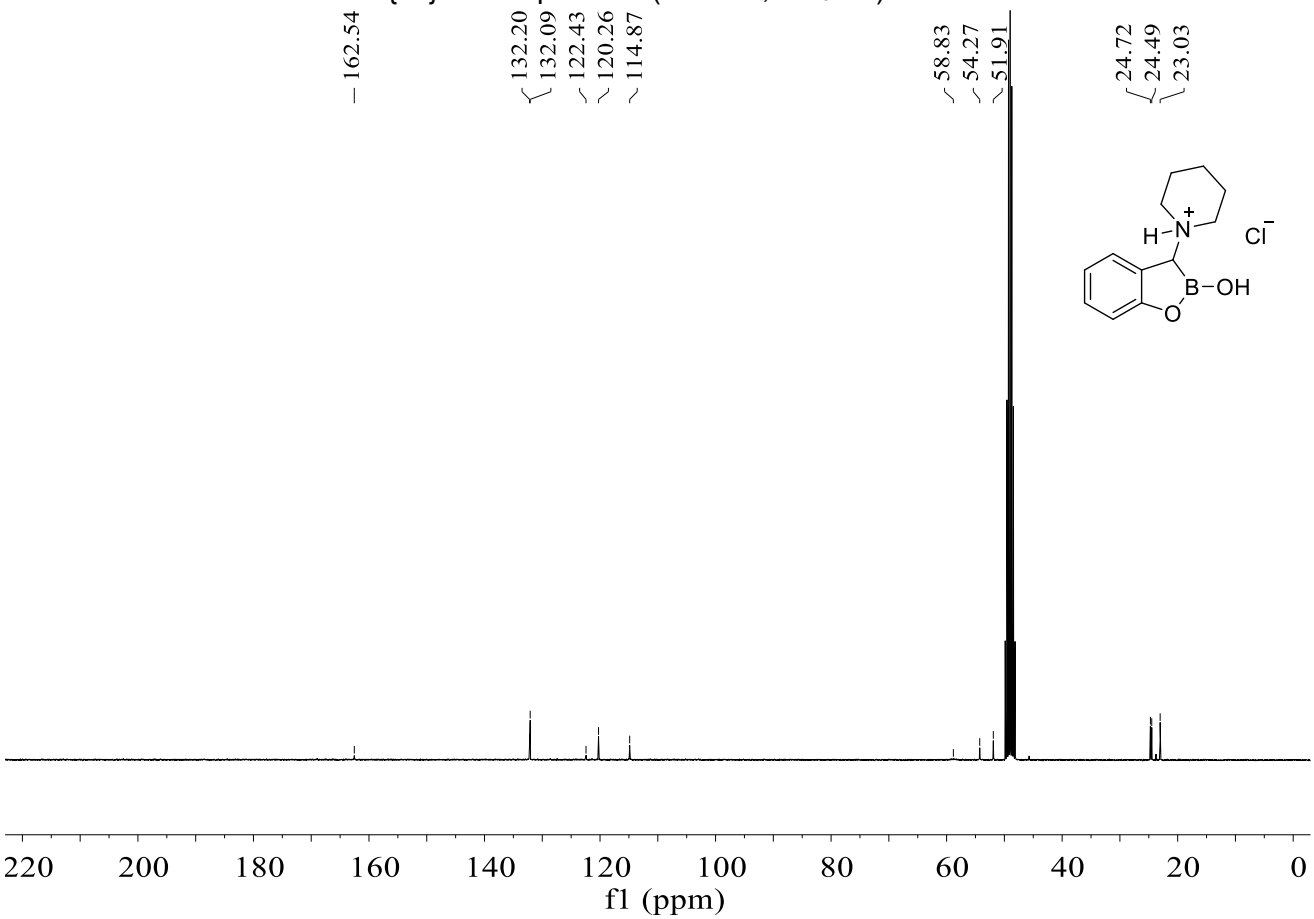
^{11}B NMR spectrum (96 MHz, D_2O) of **5a**



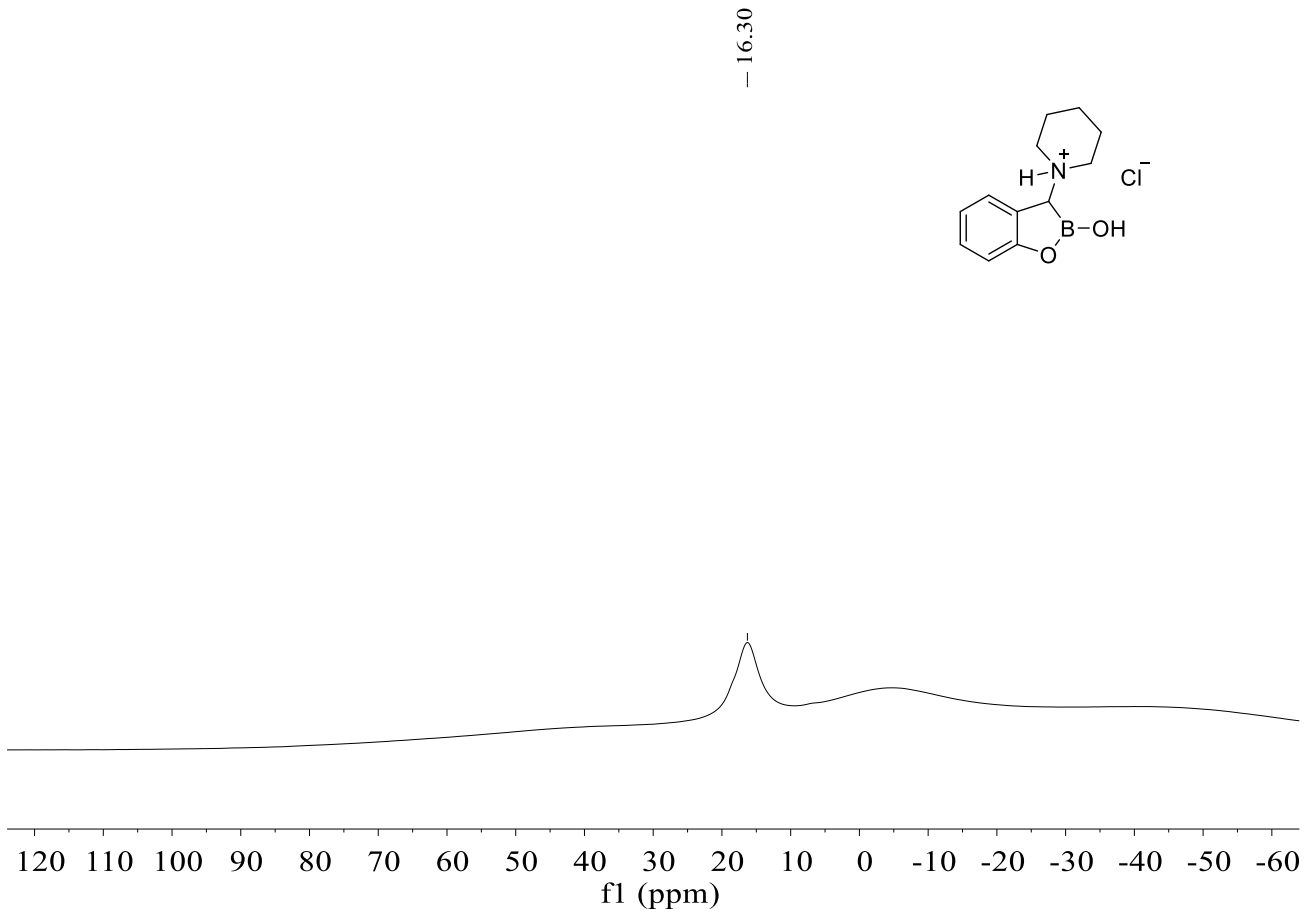
^{1}H NMR spectrum (300 MHz, CD_3OD) of **5b**



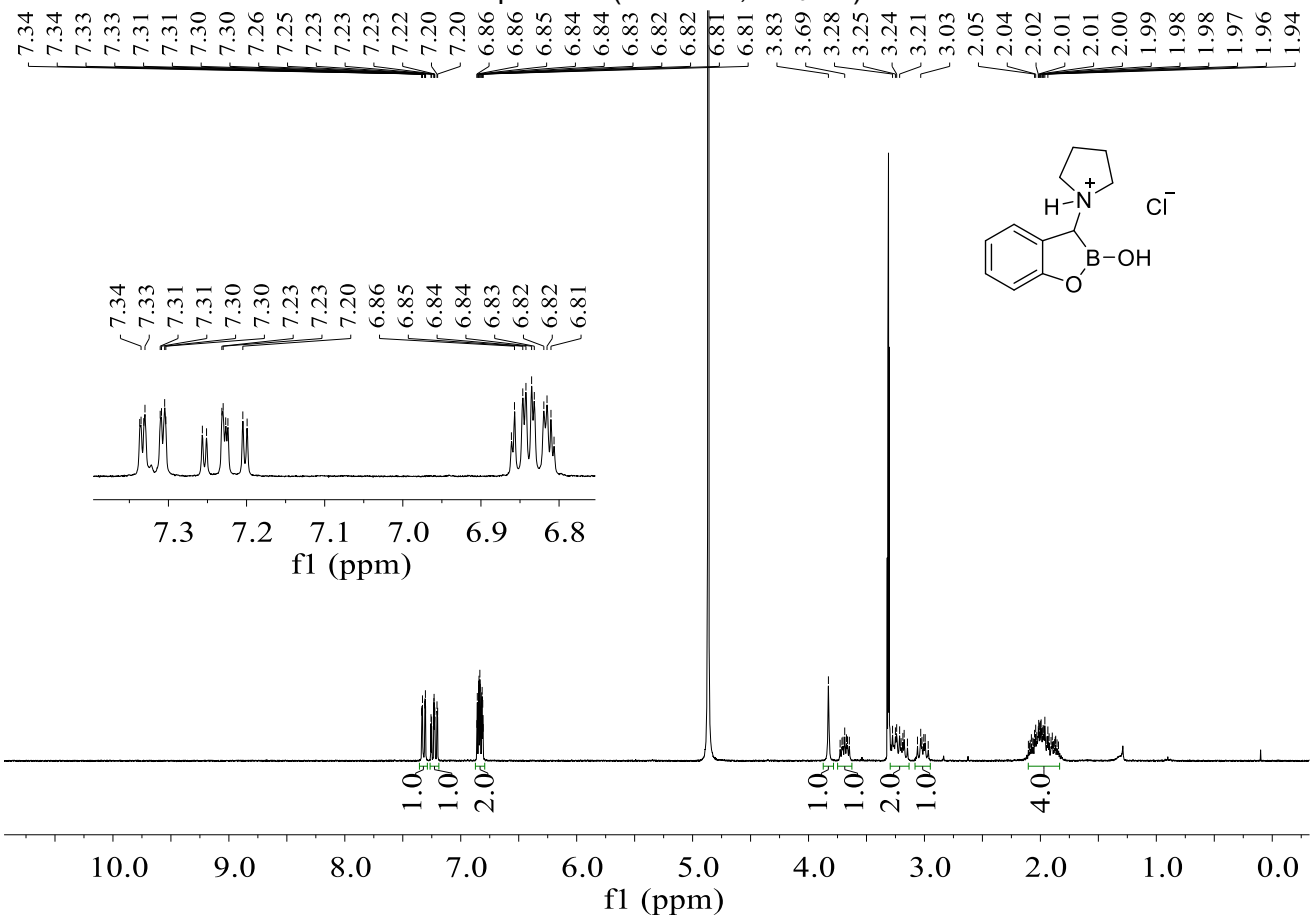
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, CD_3OD) of **5b**



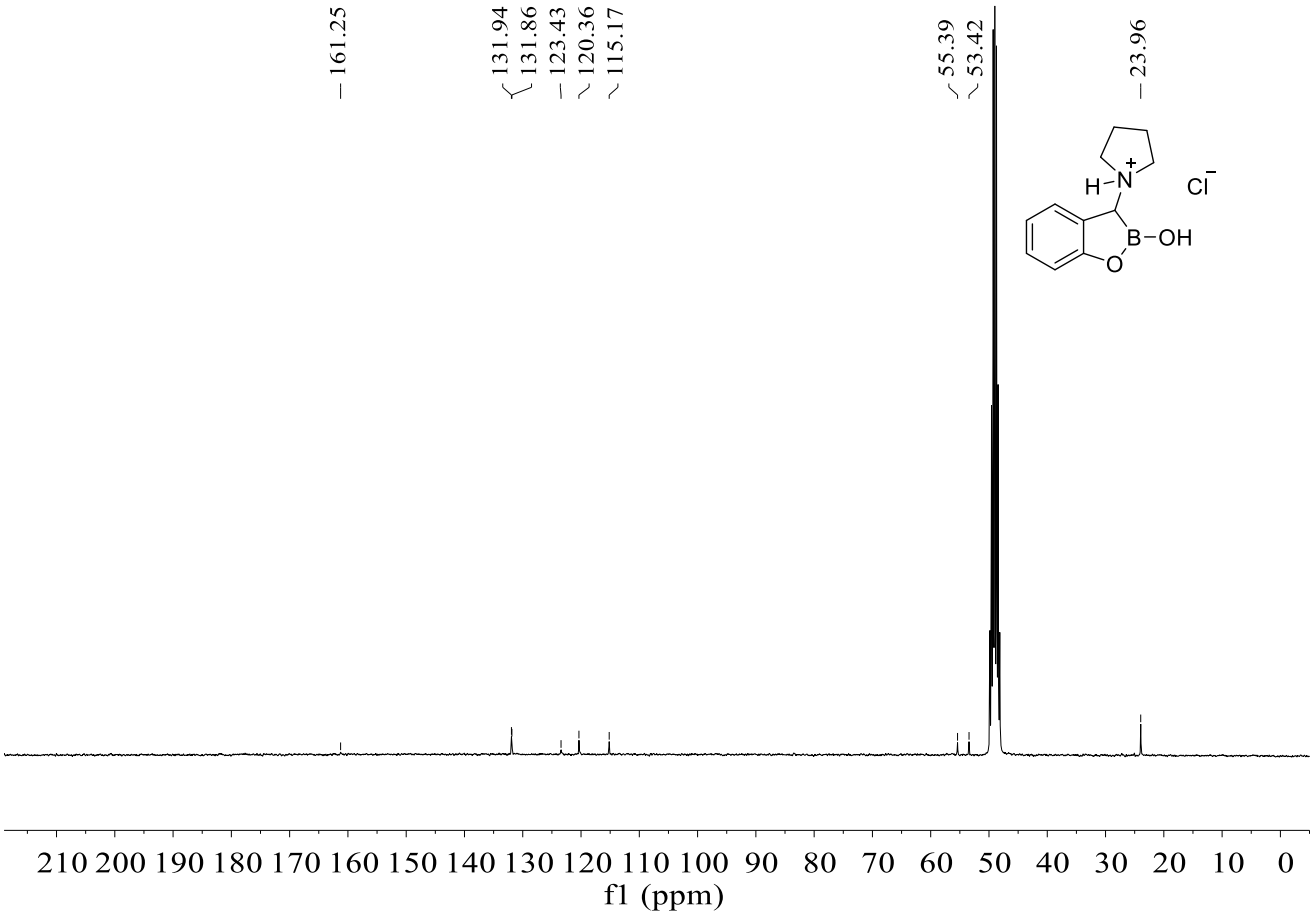
^{11}B NMR spectrum (96 MHz, CD_3OD) of **5b**



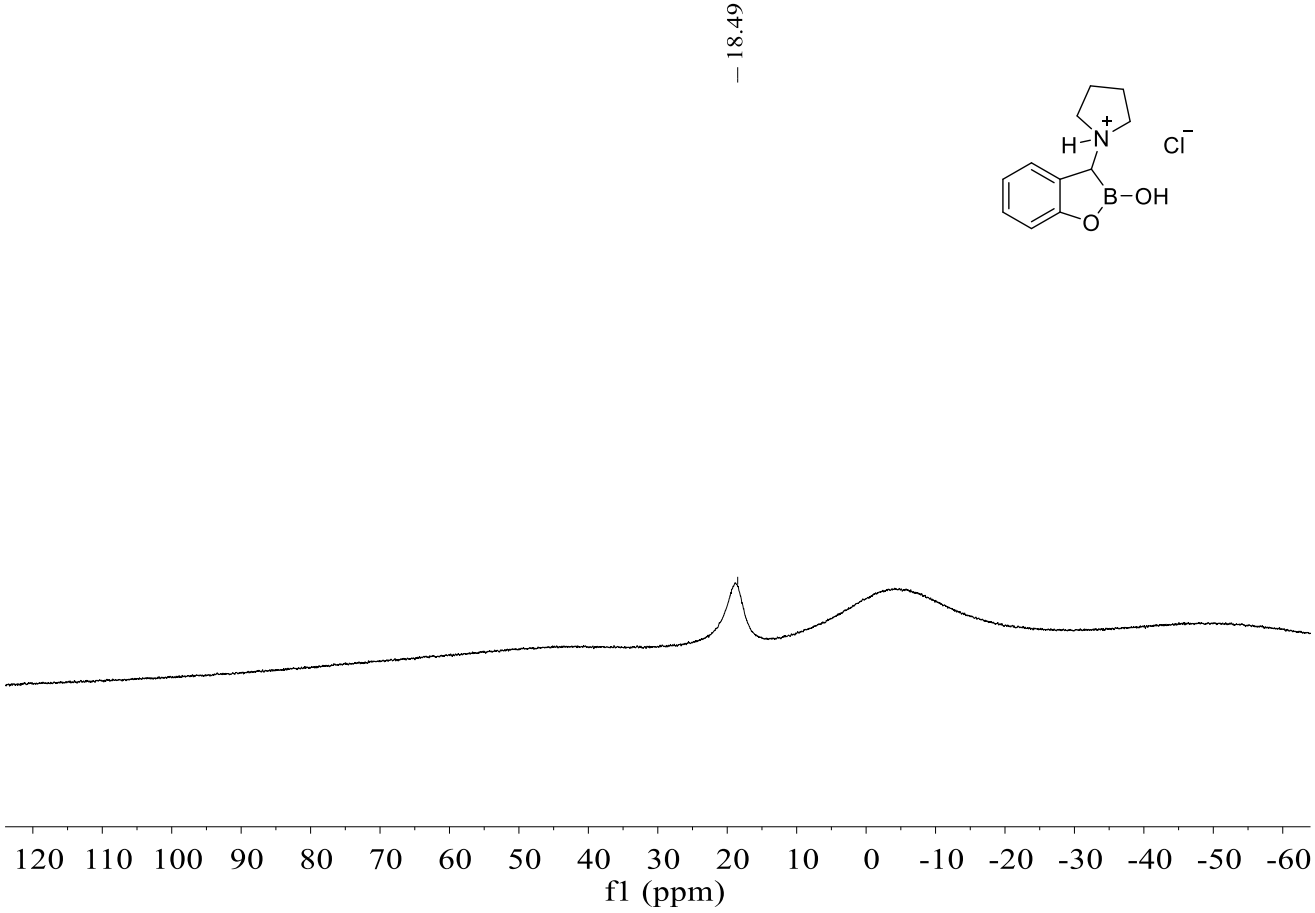
^{1}H NMR spectrum (300 MHz, CD_3OD) of **5c**



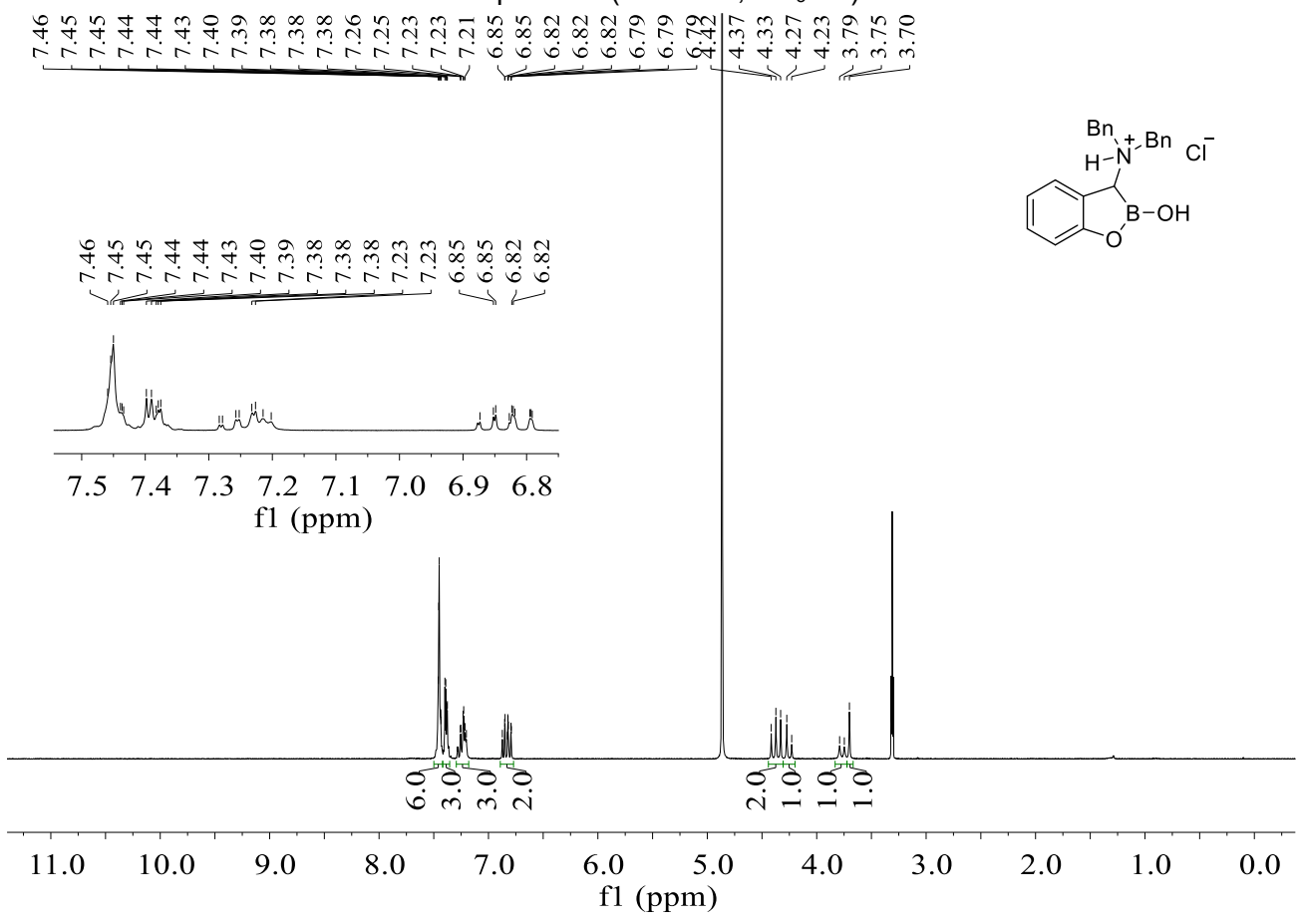
^{13}C{^{1}H} NMR spectrum (75 MHz, CD_3OD) of **5c**



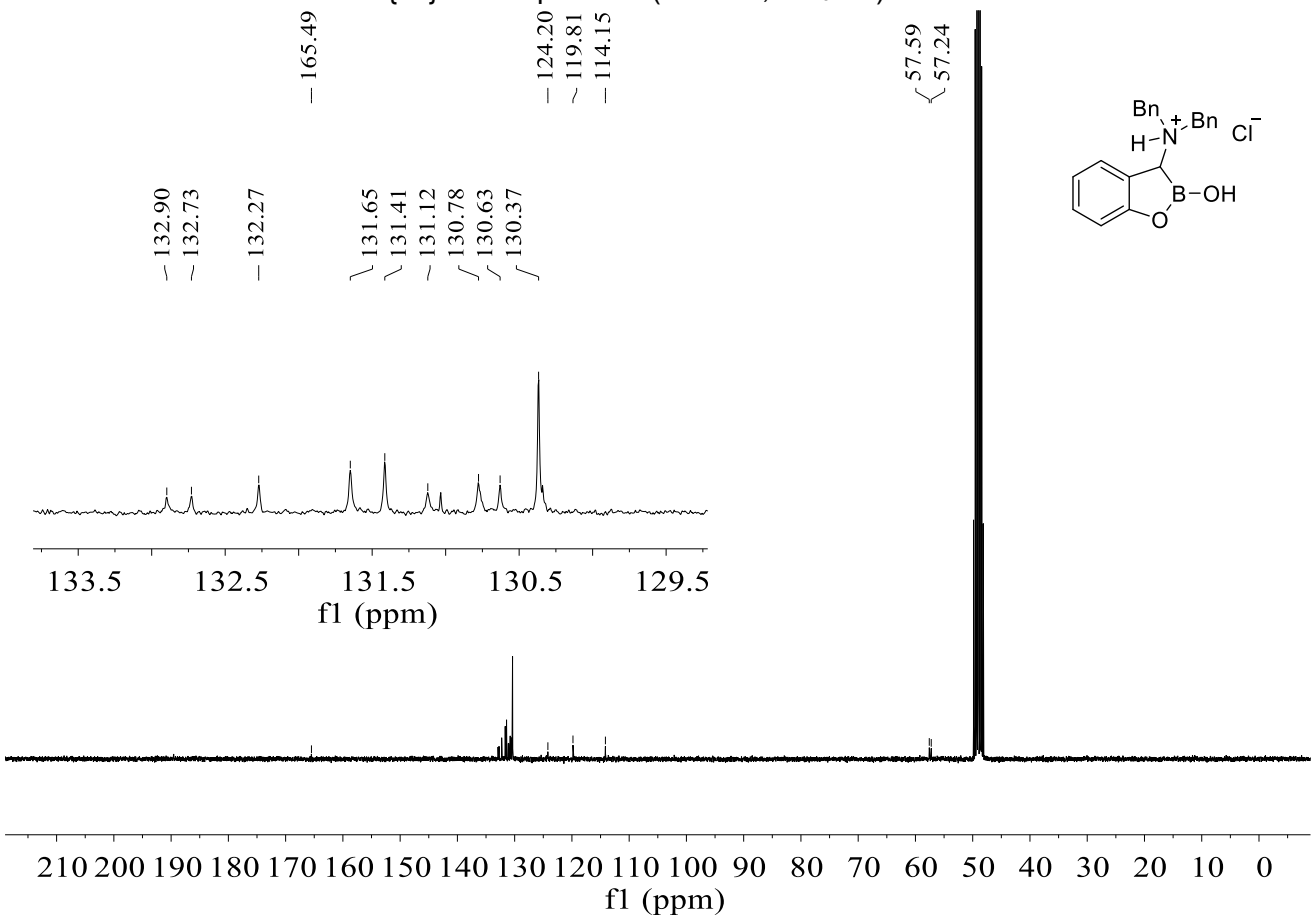
^{11}B NMR spectrum (96 MHz, CD_3OD) of **5c**



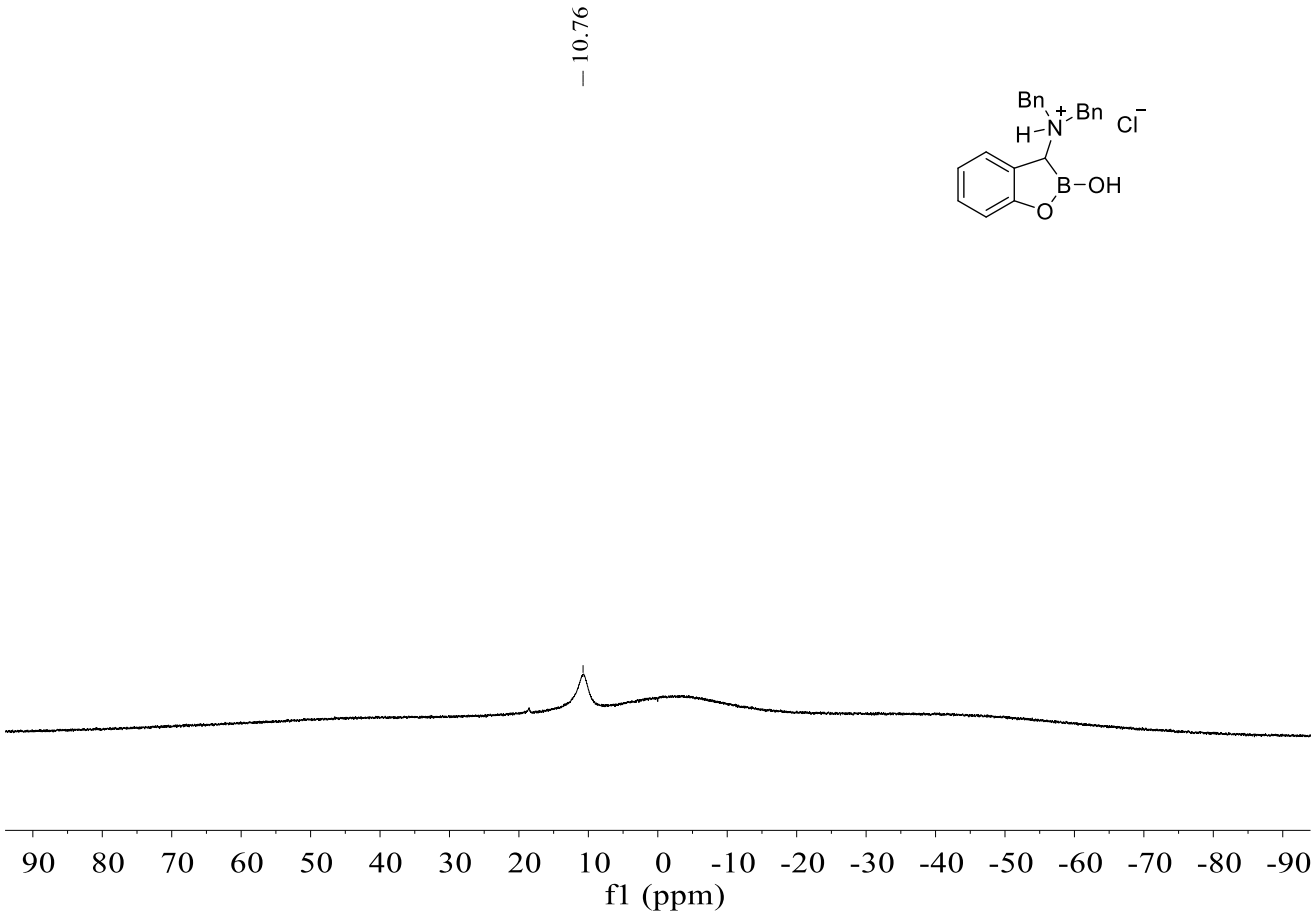
^{1}H NMR spectrum (300 MHz, CD_3OD) of **5d**



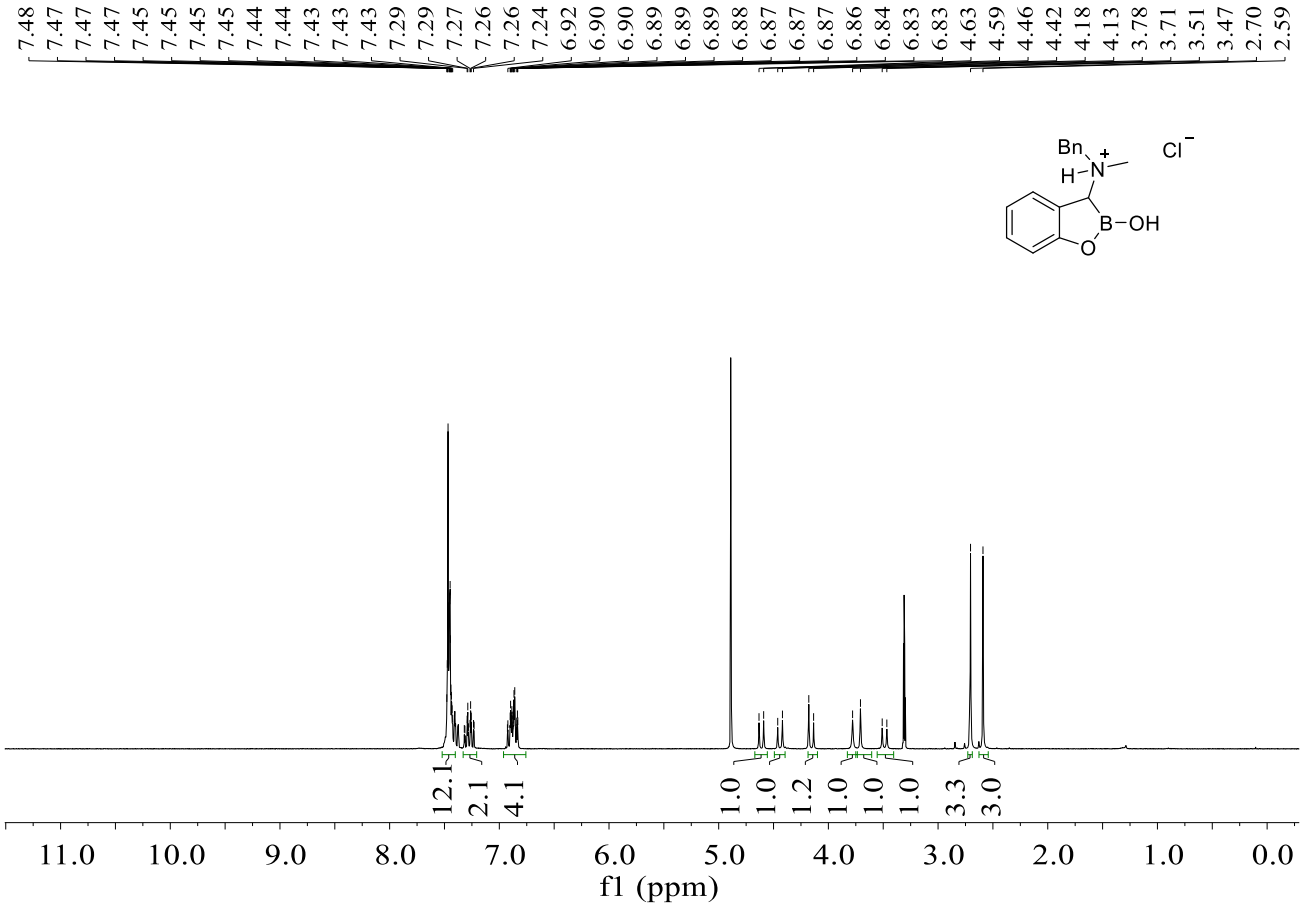
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, CD_3OD) of **5d**



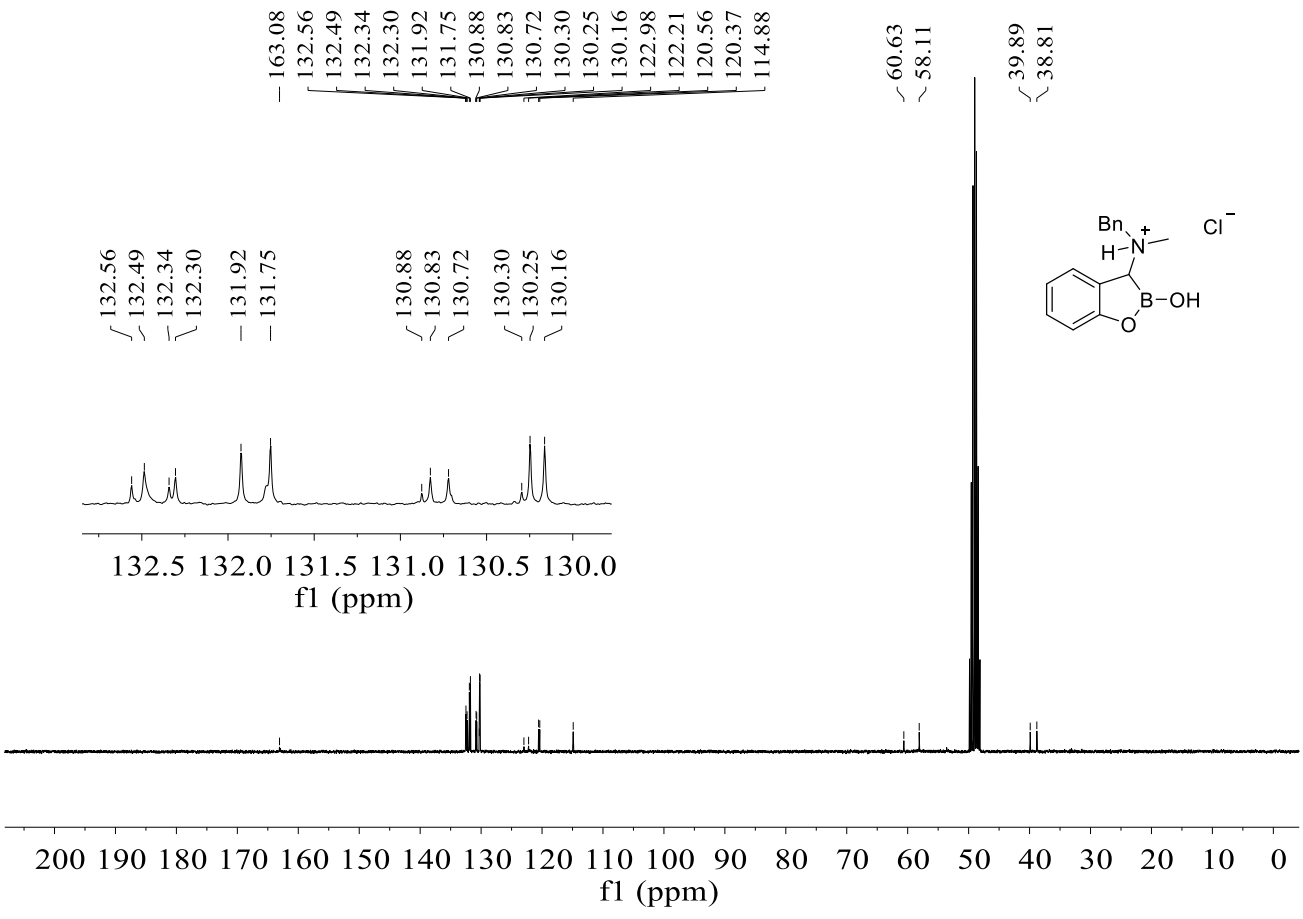
^{11}B NMR spectrum (96 MHz, CD_3OD) of **5d**



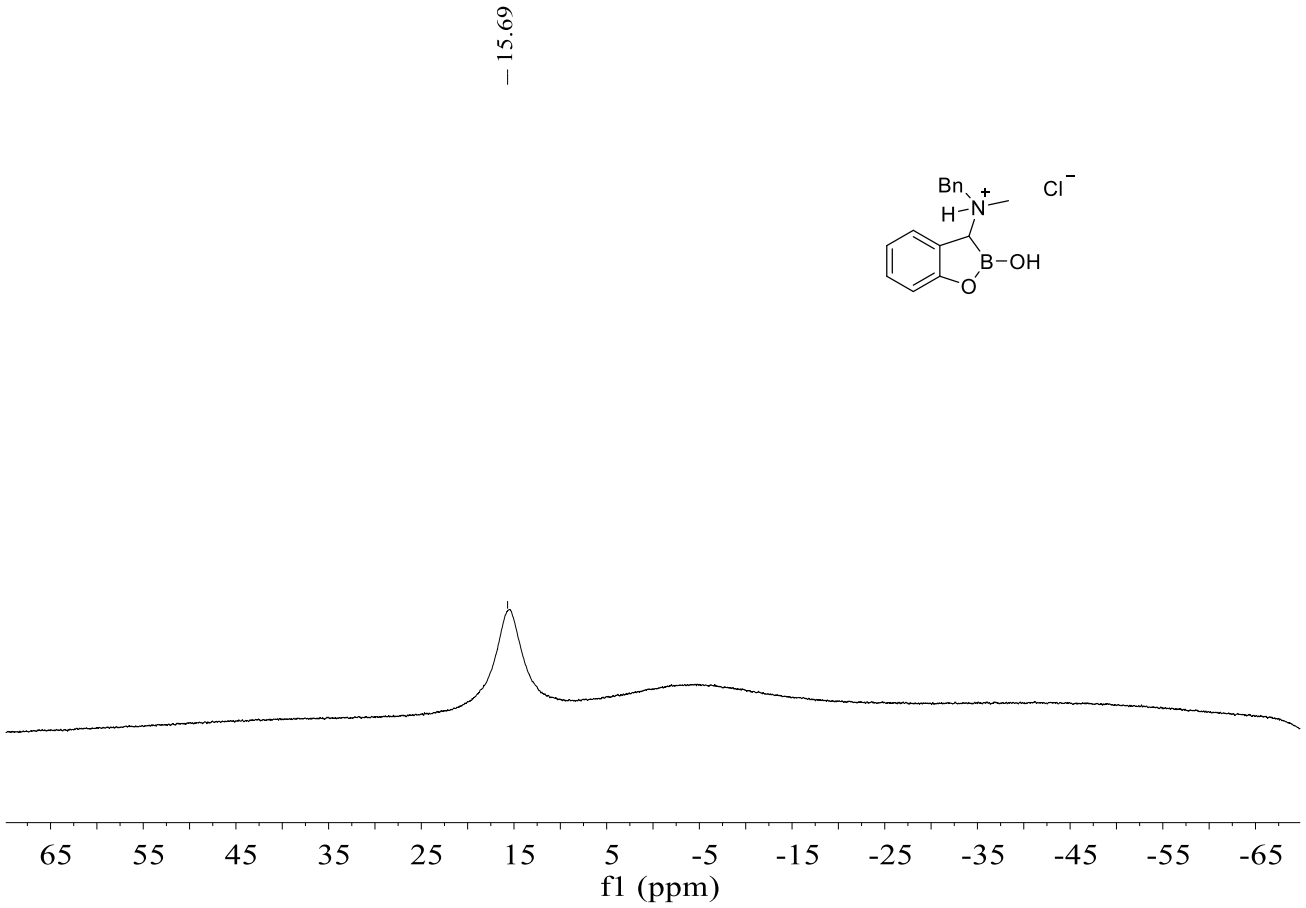
^{1}H NMR spectrum (300 MHz, CD_3OD) of **5e**



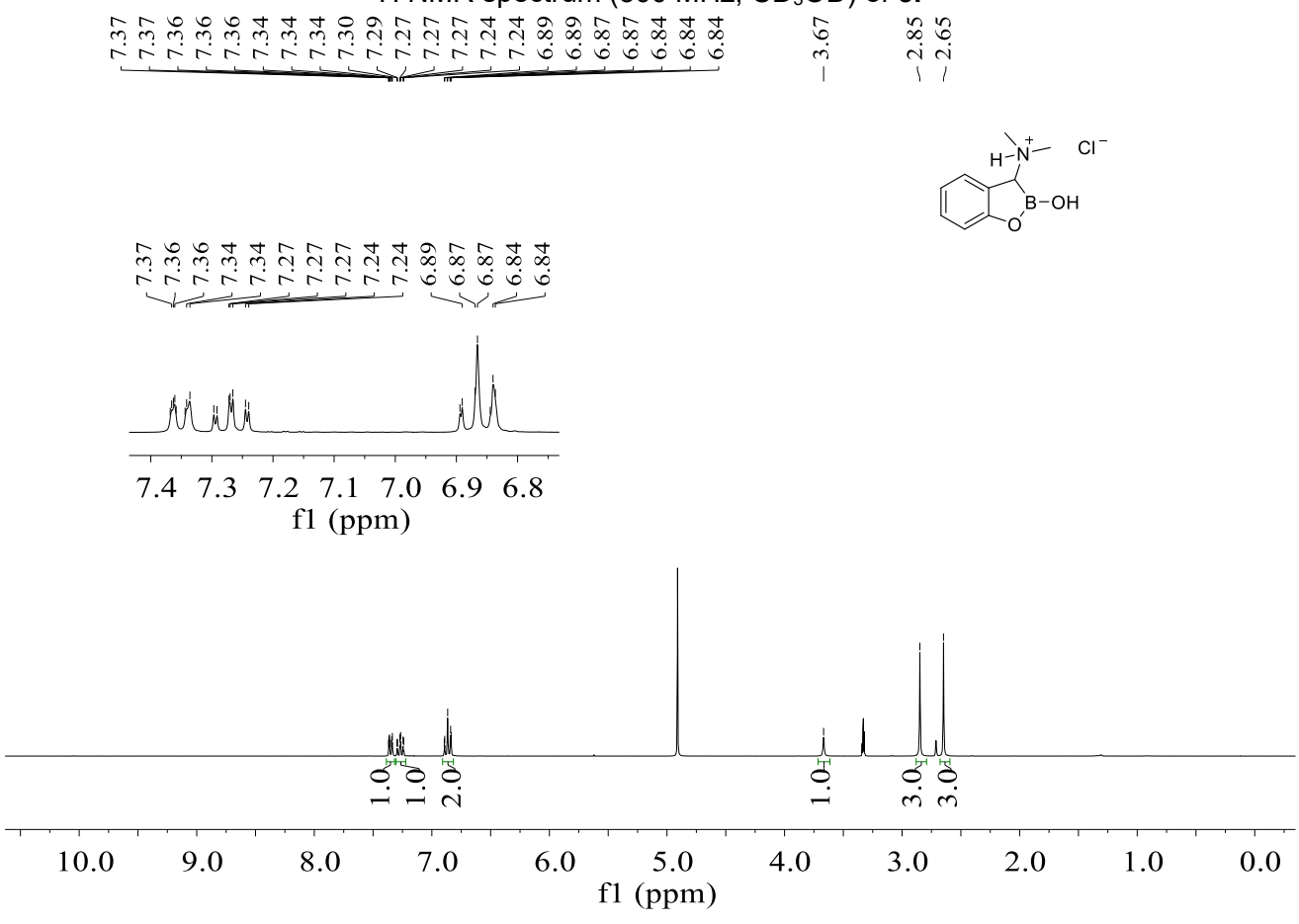
^{13}C{^{1}H} NMR spectrum (75 MHz, CD_3OD) of **5e**



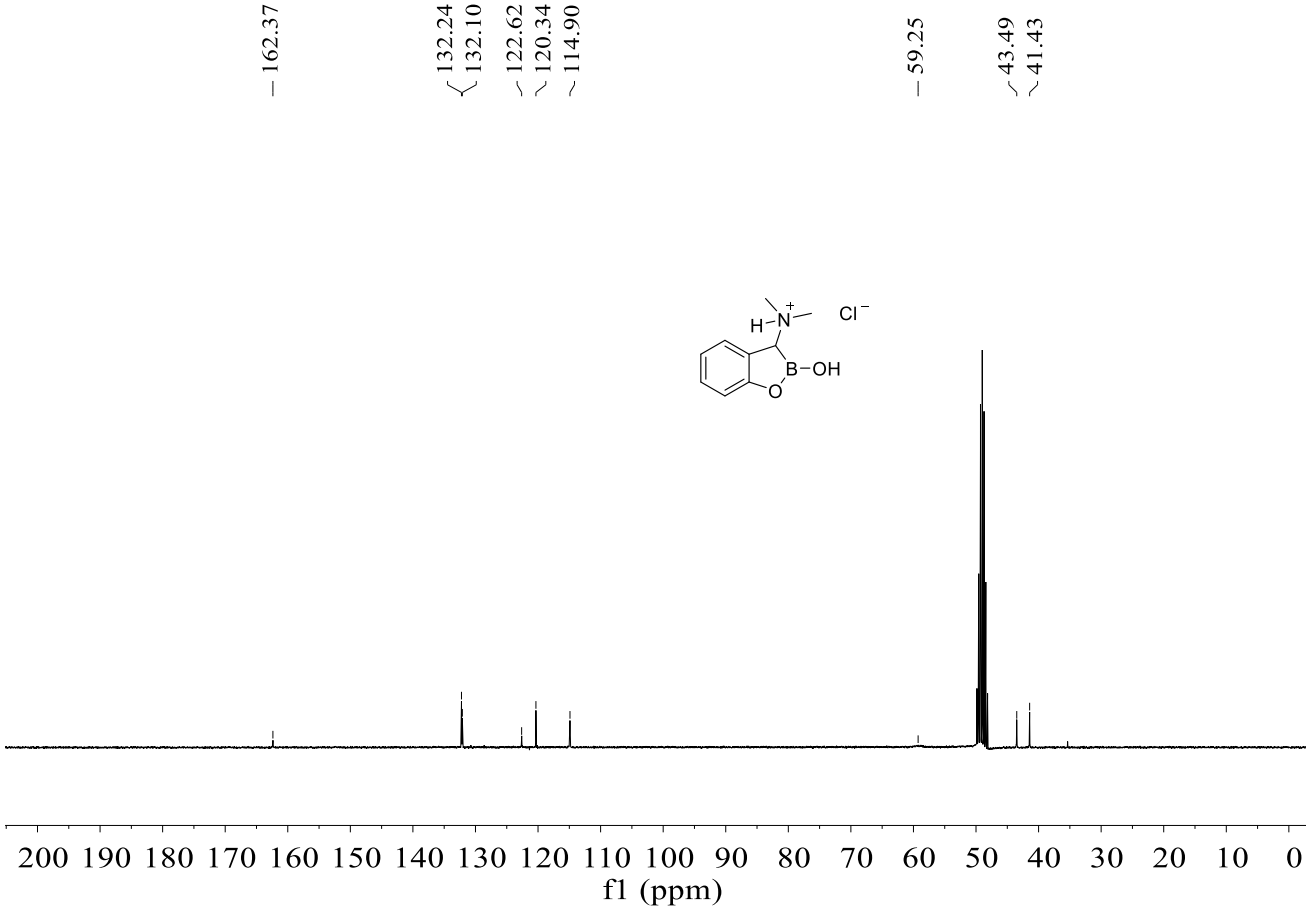
^{11}B NMR spectrum (96 MHz, CD_3OD) of **5e**



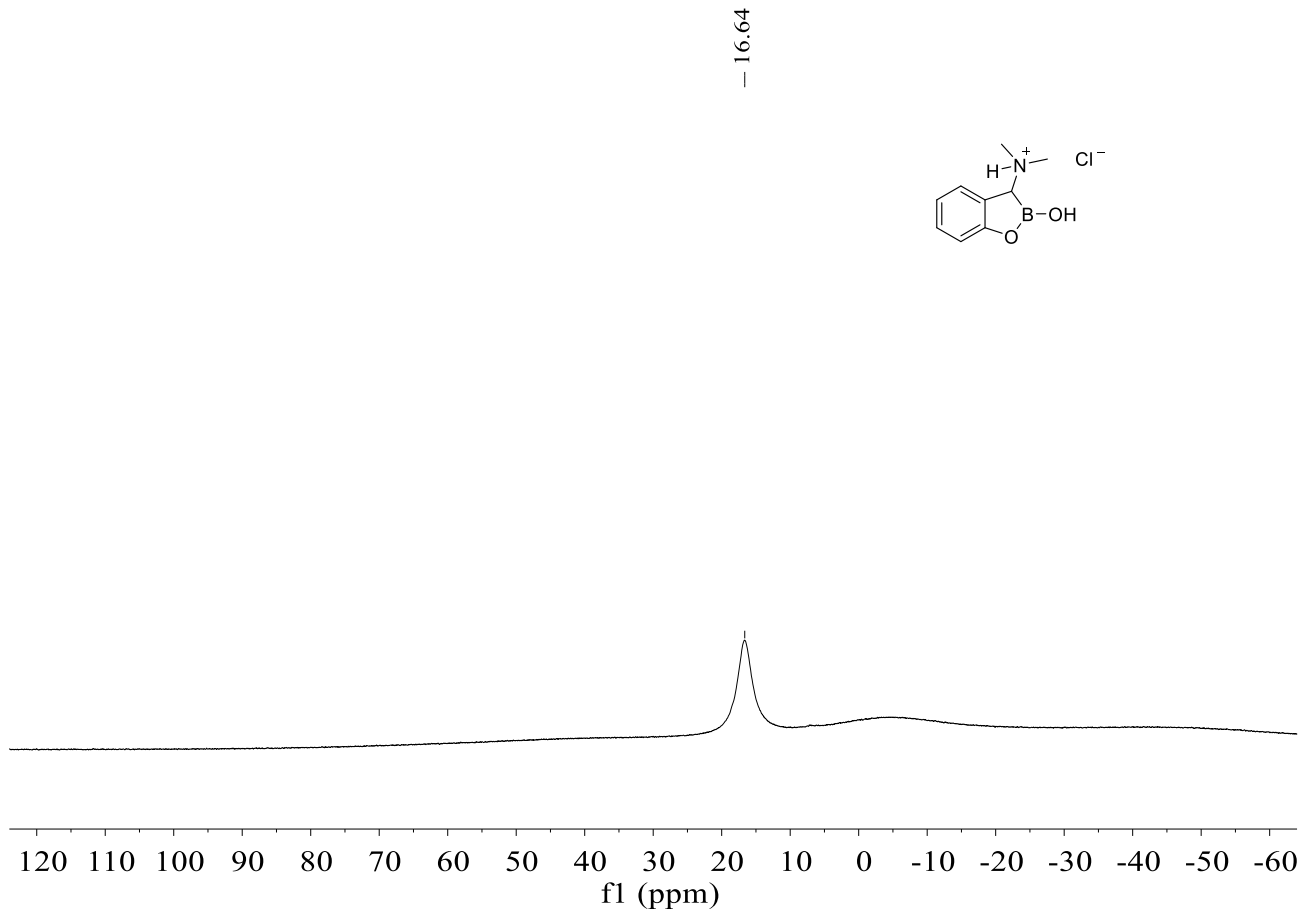
^{1}H NMR spectrum (300 MHz, CD_3OD) of **5f**



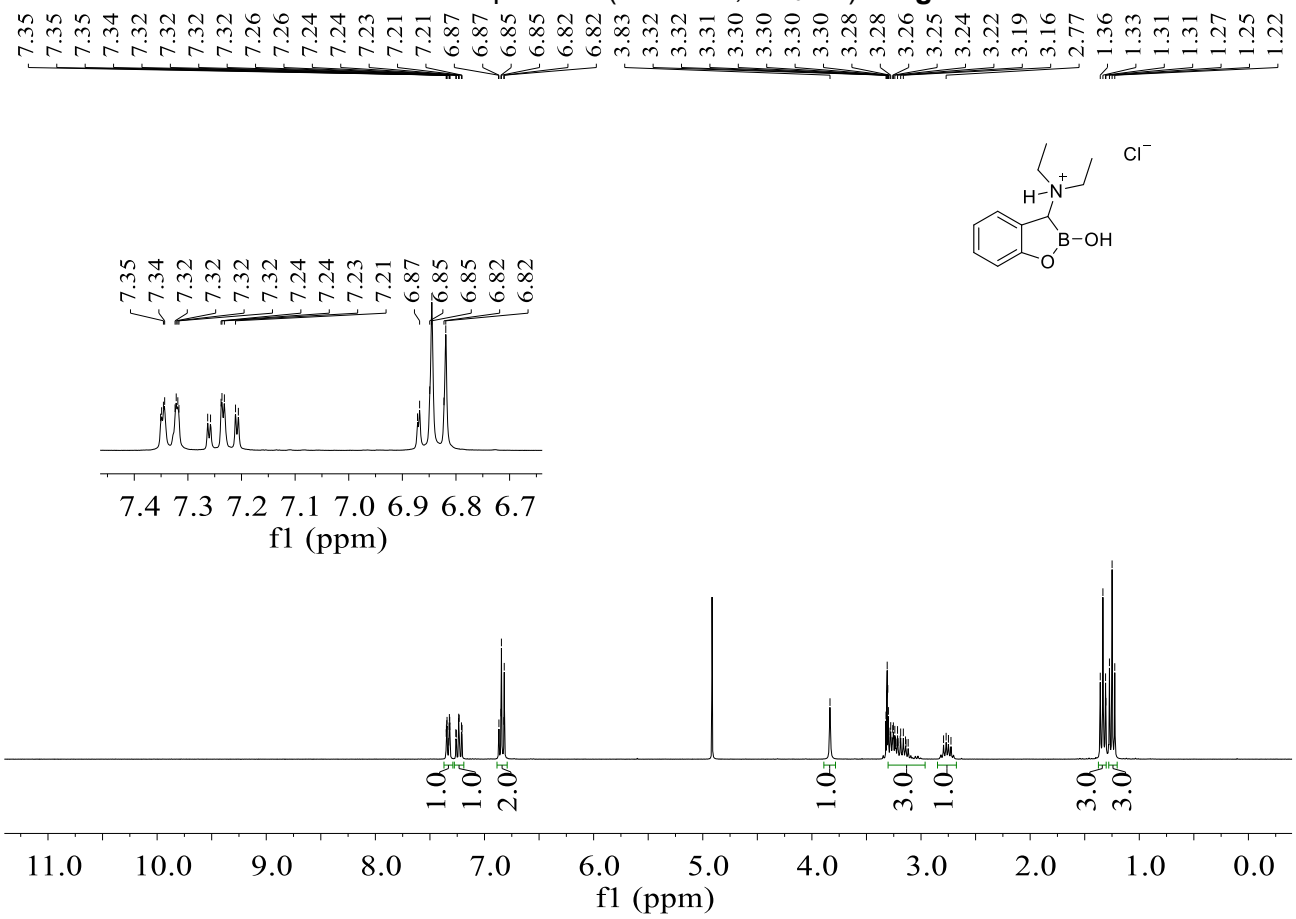
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, CD_3OD) of **5f**



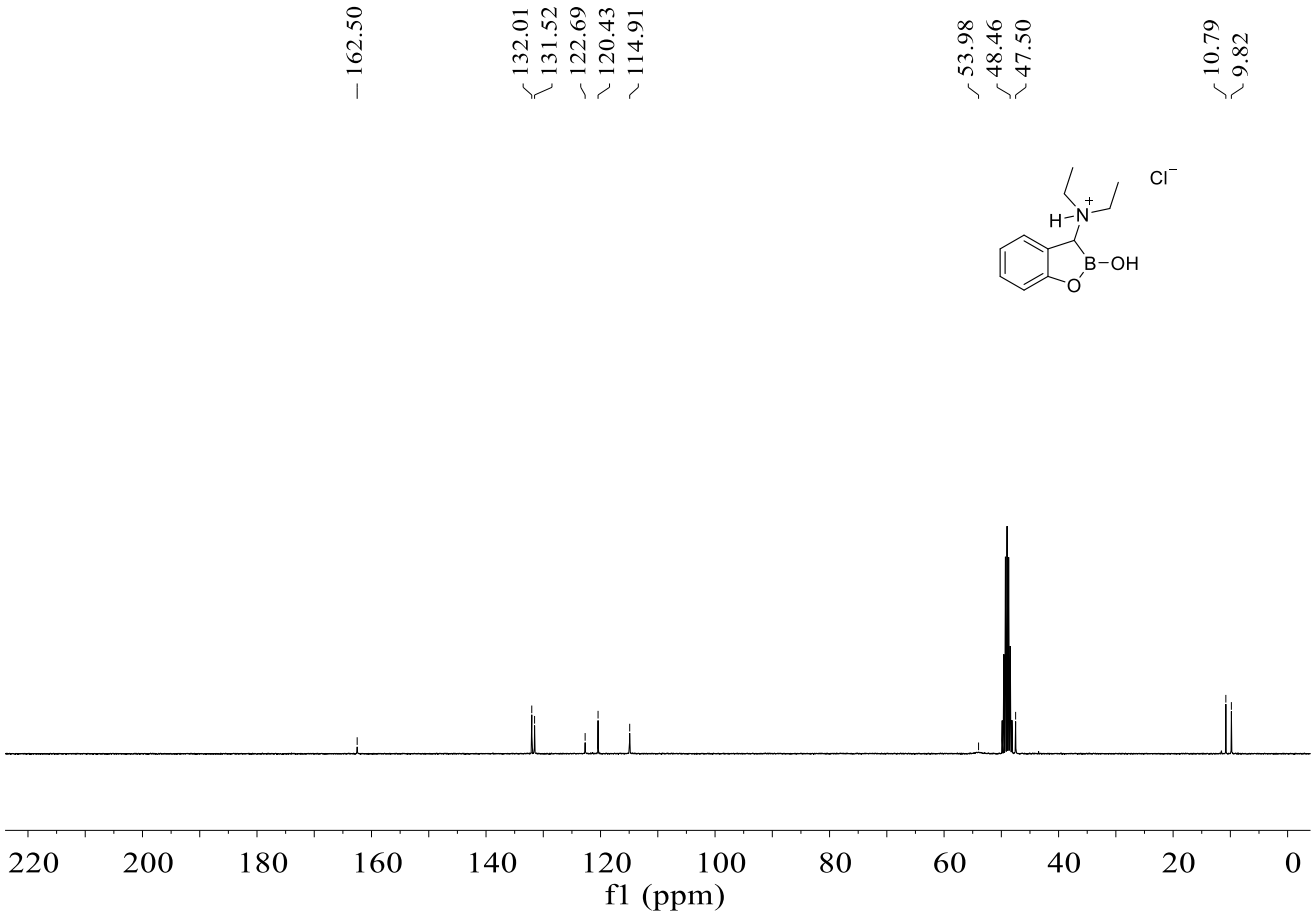
^{11}B NMR spectrum (96 MHz, CD_3OD) of **5f**



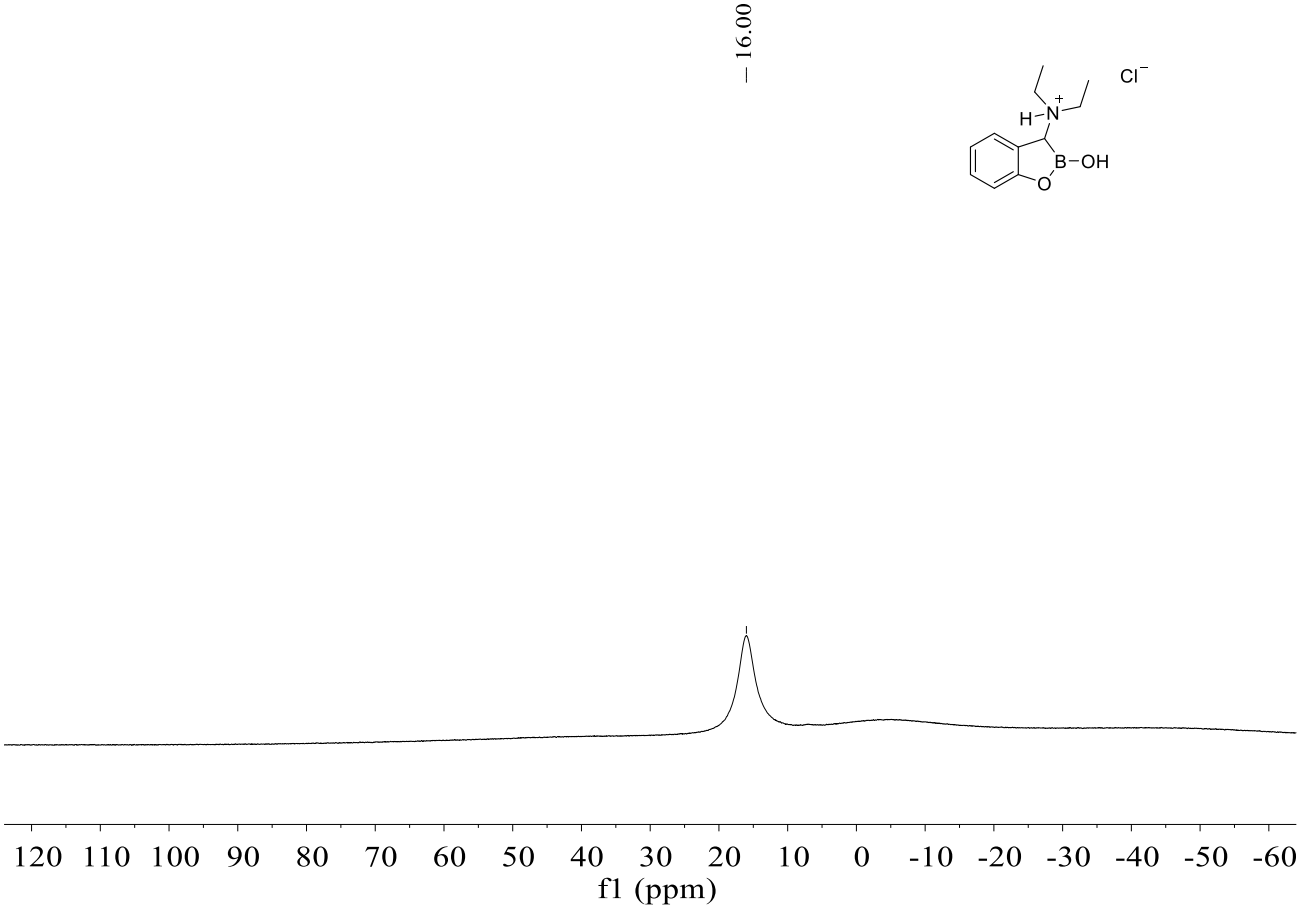
^{1}H NMR spectrum (300 MHz, CD_3OD) of **5g**



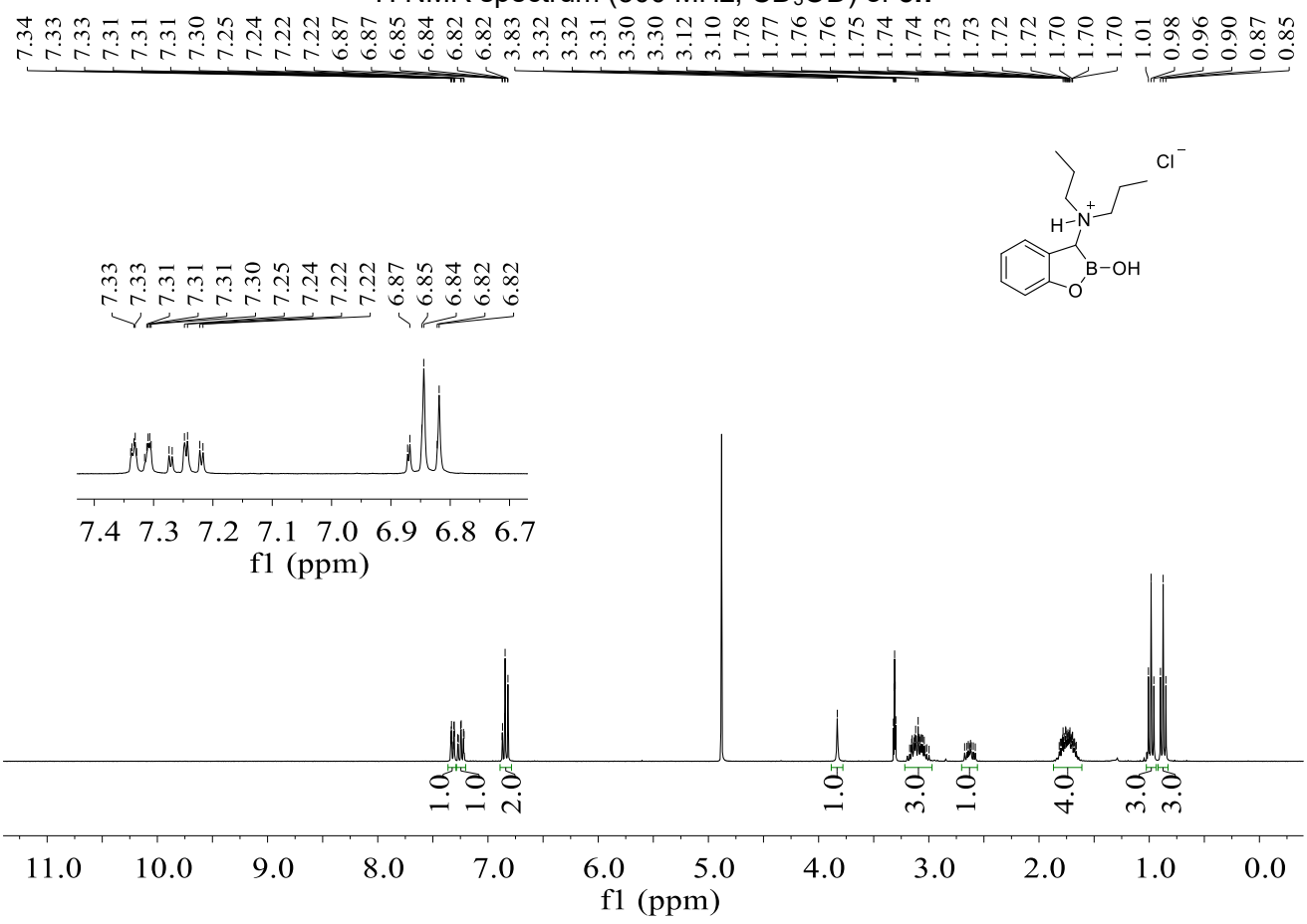
^{13}C{^{1}H} NMR spectrum (75 MHz, CD_3OD) of **5g**



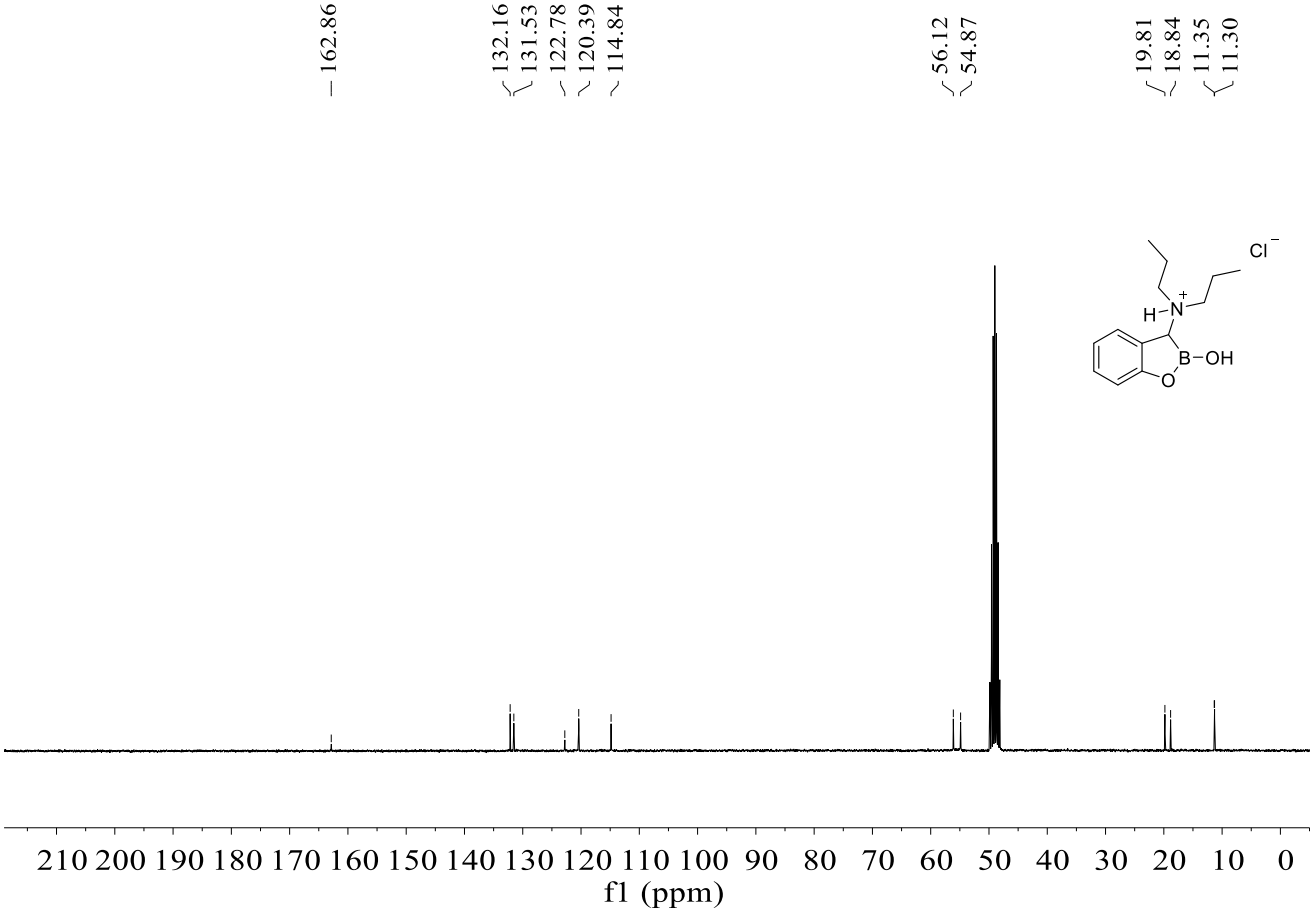
^{11}B NMR spectrum (96 MHz, CD_3OD) of **5g**



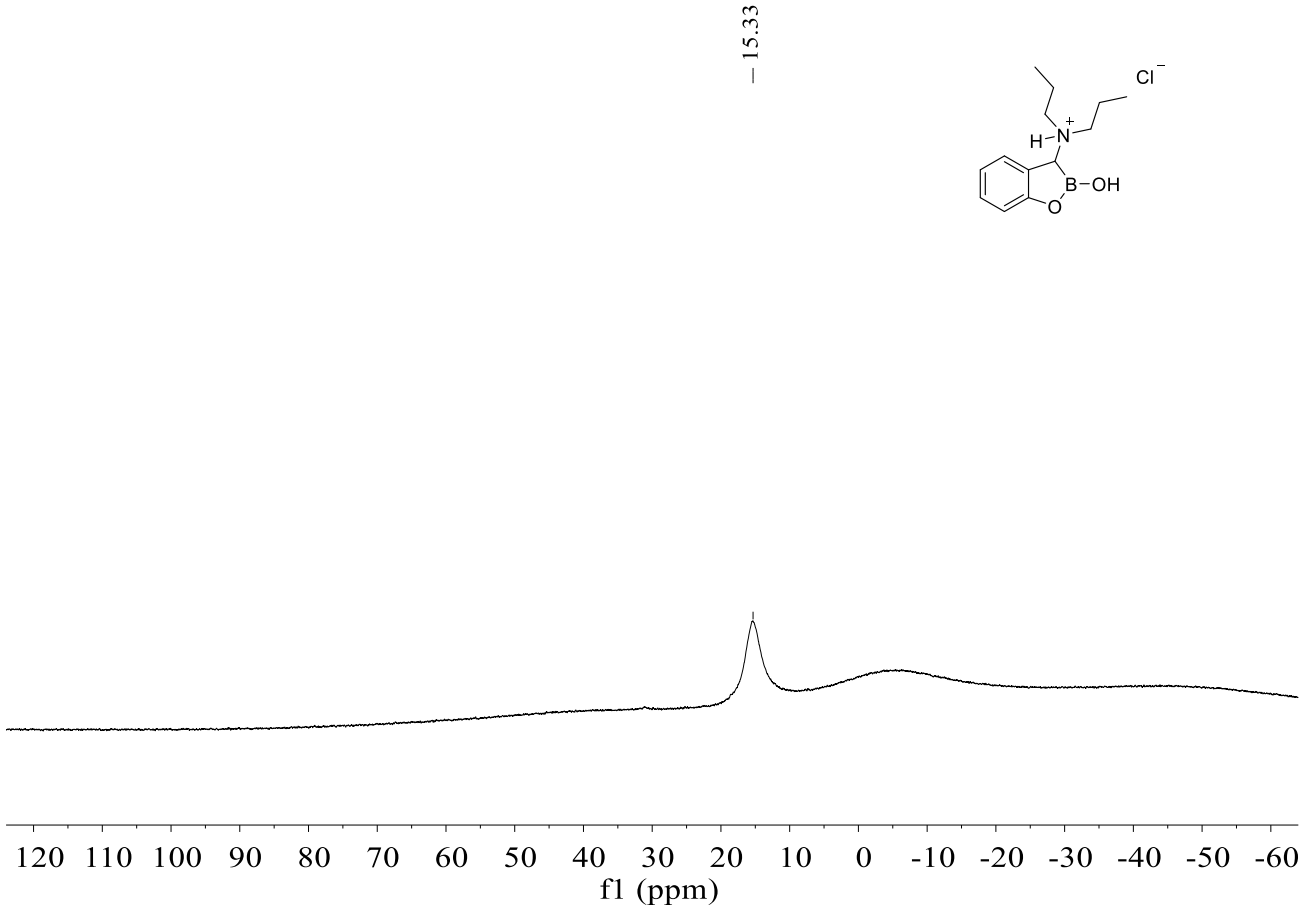
^{1}H NMR spectrum (300 MHz, CD_3OD) of **5h**



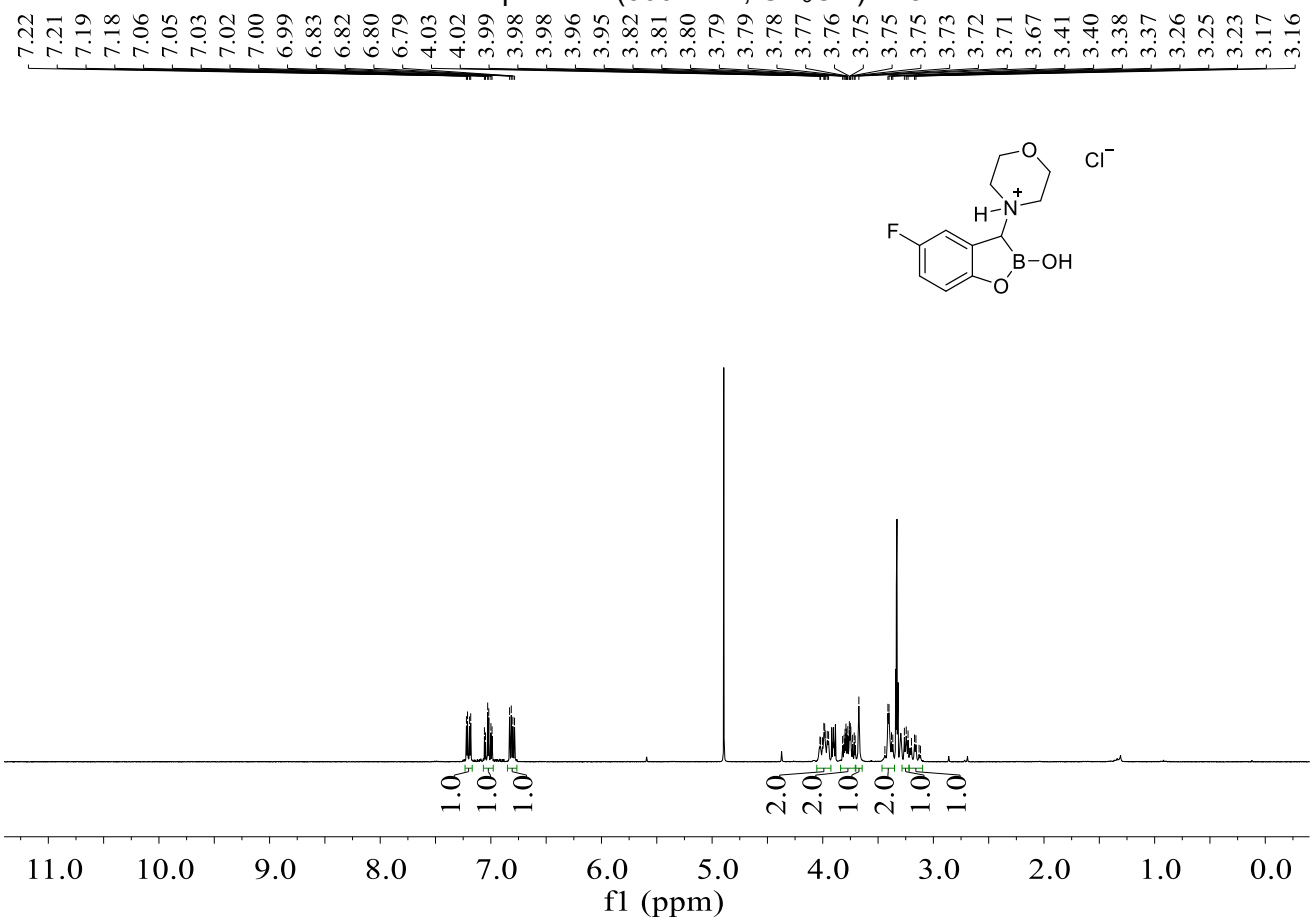
$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, CD_3OD) of **5h**



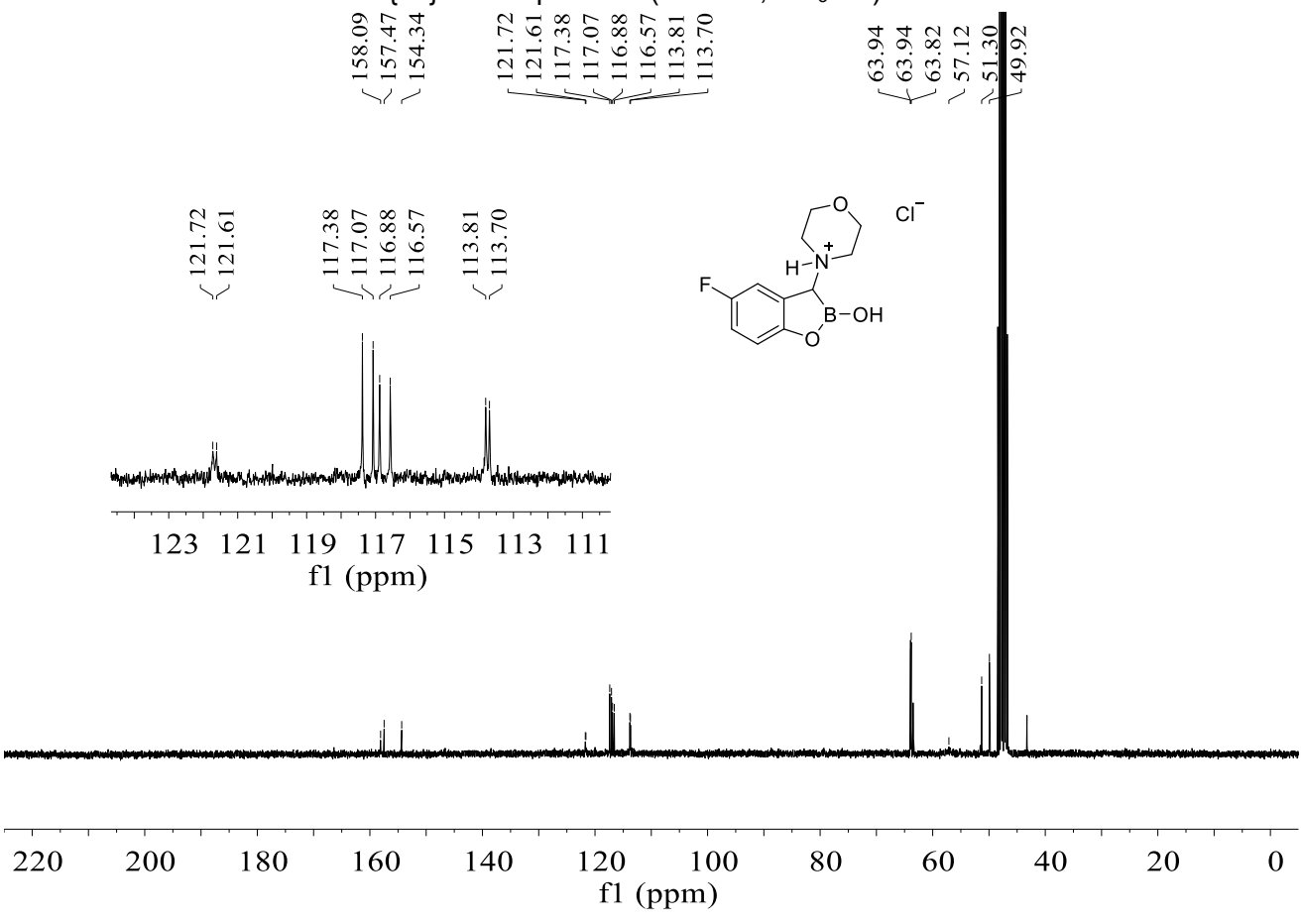
^{11}B NMR spectrum (96 MHz, CD_3OD) of **5h**



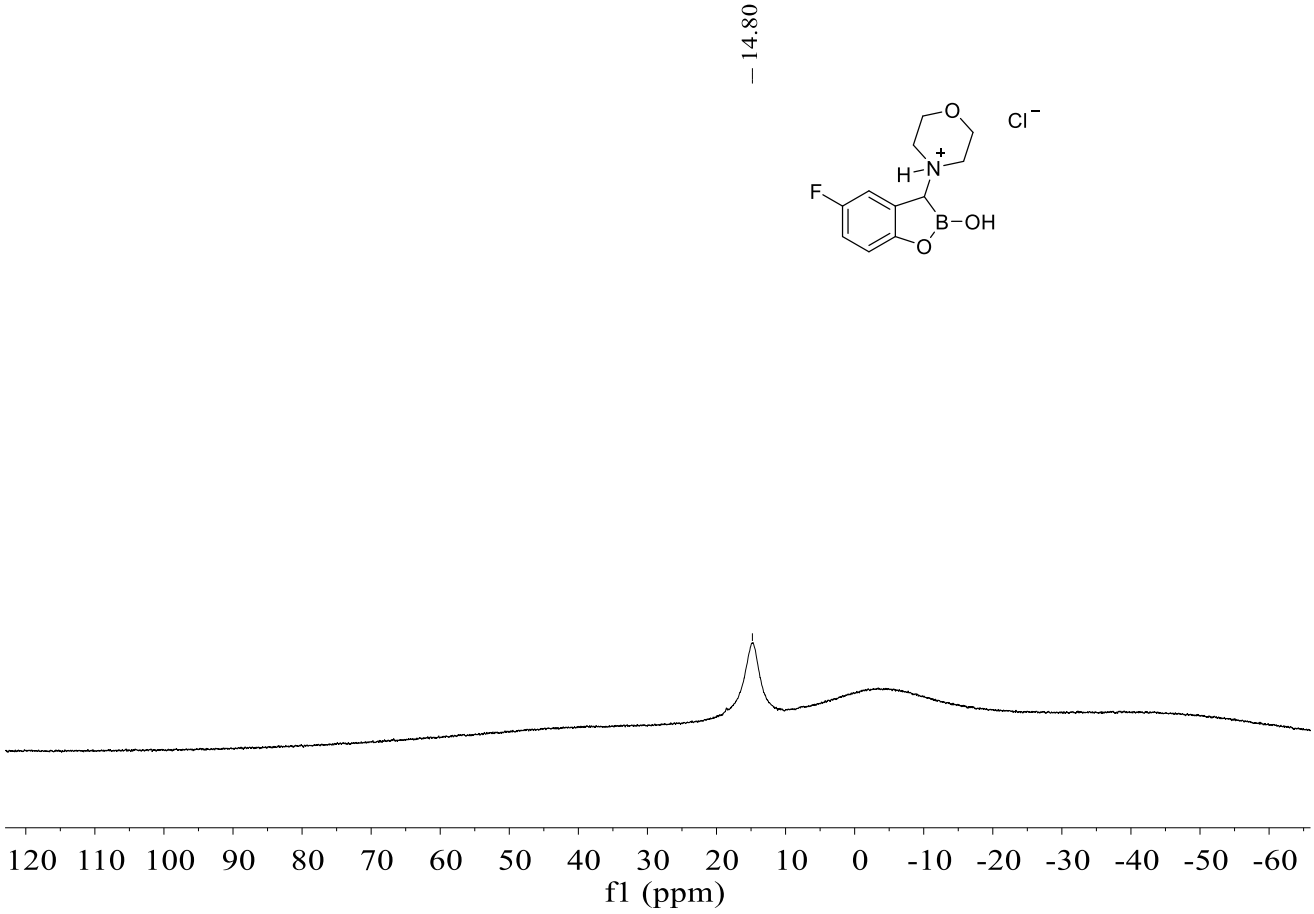
^{1}H NMR spectrum (300 MHz, CD_3OD) of **5i**



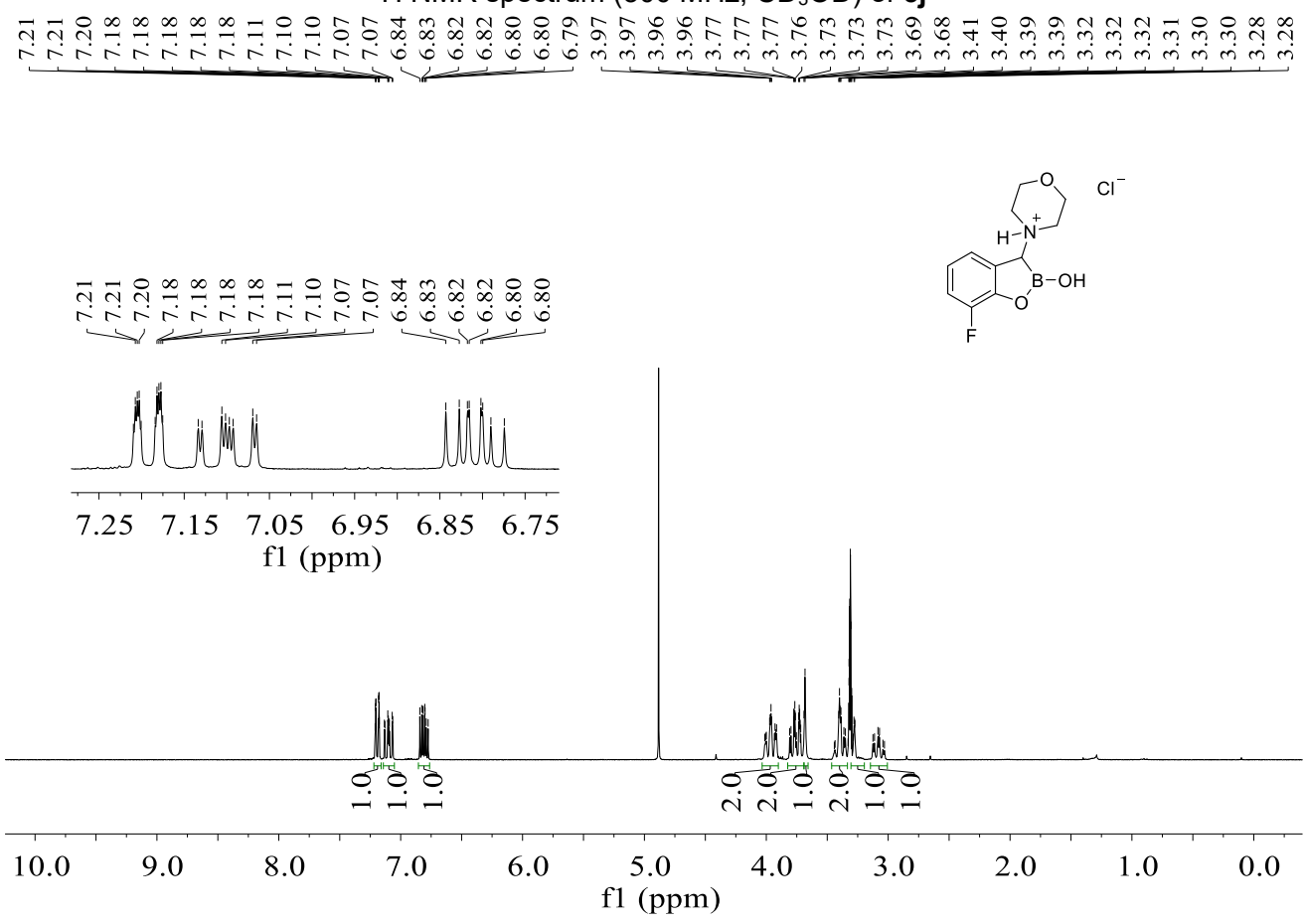
^{13}C{^{1}H} NMR spectrum (75 MHz, CD_3OD) of **5i**



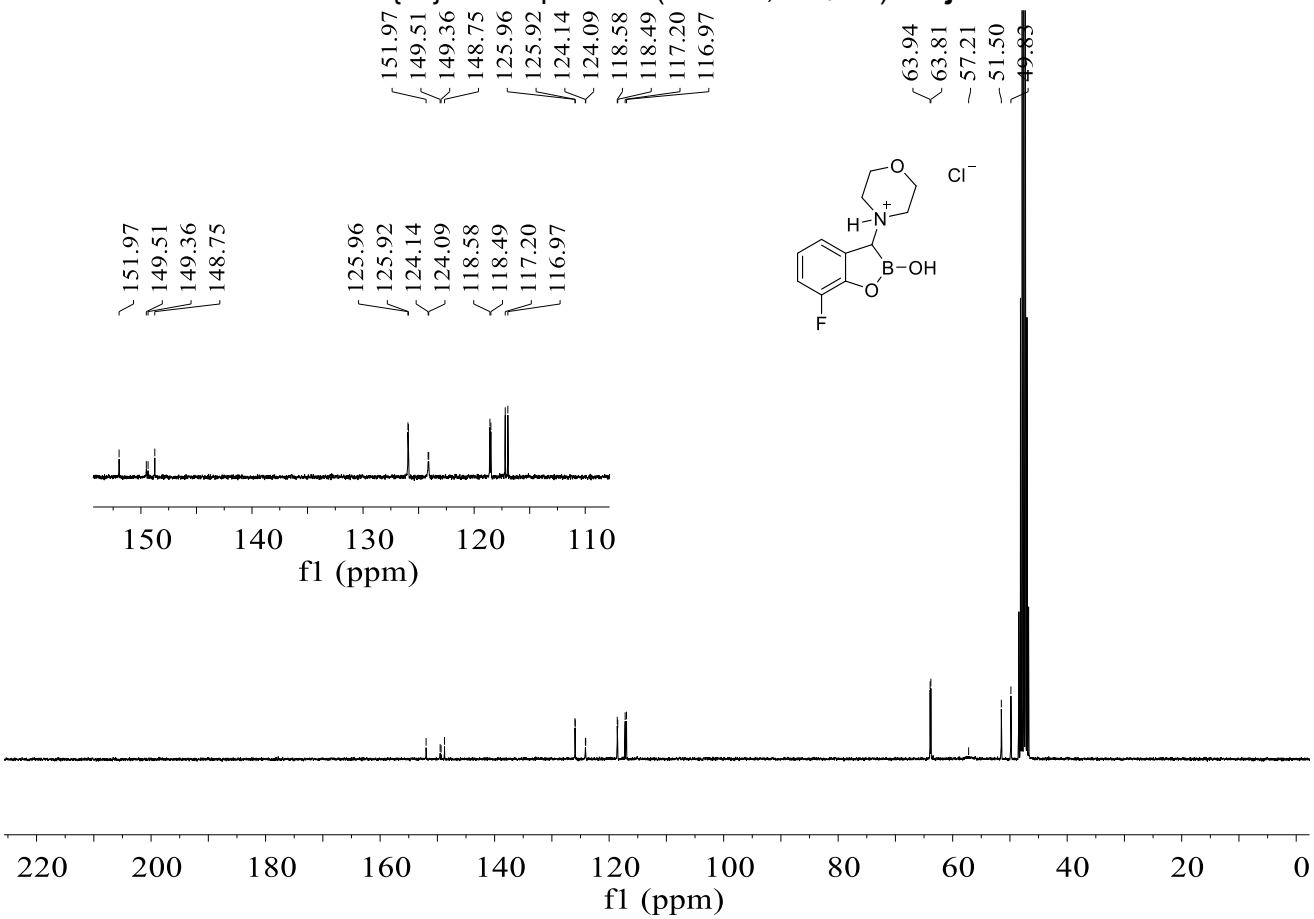
^{11}B NMR spectrum (96 MHz, CD_3OD) of **5i**



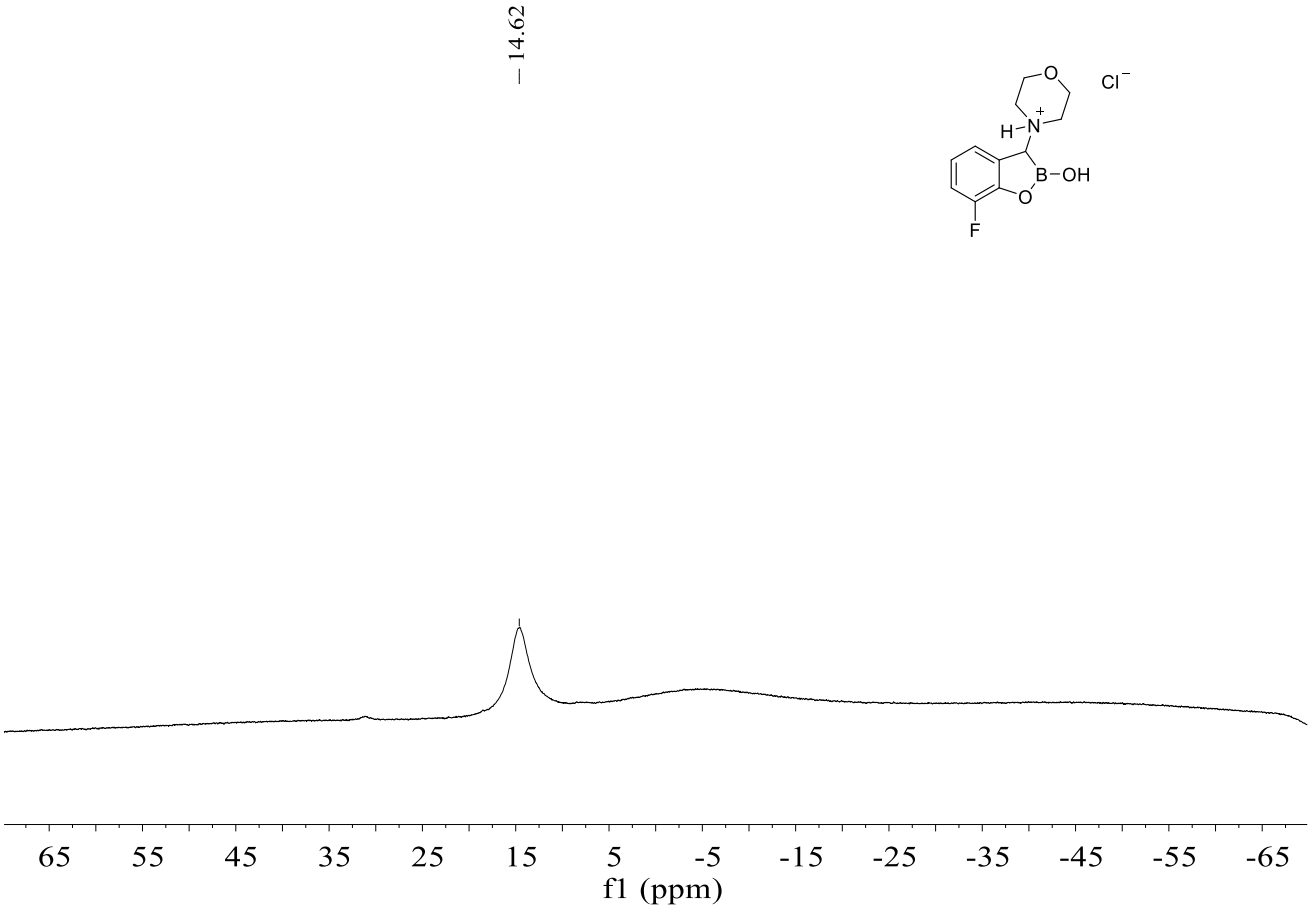
^{1}H NMR spectrum (300 MHz, CD_3OD) of **5j**



$^{13}C\{^{1}H\}$ NMR spectrum (75 MHz, CD_3OD) of **5j**



^{11}B NMR spectrum (96 MHz, CD_3OD) of **5j**



VI. Single-crystal X-ray Diffraction Studies

Crystal structure determination Crystals suitable for single-crystal X-ray diffraction were selected, coated in perfluoropolyether oil, and mounted on MiTeGen sample holders. Diffraction data were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector using Mo-K_α radiation monochromated by graphite (**4p**) or multi-layer mirror (**4a** and **4d**). The crystals were cooled using Oxford Cryostream low-temperature devices. Data were collected at 100 K. The images were processed and corrected for Lorentz-polarization effects and absorption as implemented in the Bruker software packages. The structures were solved using the intrinsic phasing method (SHELXT)[2] and Fourier expansion technique. All non-hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms 'riding' in idealised positions, by full-matrix least squares against F^2 of all data, using SHELXL[3] software and the SHELXLE[4] graphical user interface. Diamond[5] software was used for graphical representation. Crystal data and experimental details are listed in Table S1; full structural information has been deposited with the Cambridge Crystallographic Data Centre. CCDC-1964346 (**4a**), 1964347 (**4d**), and 1964348 (**4p**).

Table S1 Single-crystal X-ray diffraction data and structure refinements of compounds **4a**, **4d**, and **4p**.

Data	**4a**	**4d**	**4p**
CCDC number	1964346	1964347	1964348
Empirical formula	$C_{11}H_{16}B_3NO_7$	$C_{21}H_{22}B_3NO_6 \cdot 2(C_3H_6O)$	$C_{19}H_{32}B_3NO_7$
Formula weight / $g \cdot mol^{-1}$	306.68	532.98	418.88
T / K	100(2)	100(2)	100(2)
λ / Å, radiation	0.71073, MoKα	0.71073, MoKα	0.71073, MoKα
Crystal size / mm^3	0.40×0.15×0.07	0.54 ×0.27×0.16	0.53 ×0.27×0.20
Crystal color, habit	colourless plate	colourless block	colourless plate
μ / mm^{-1}	0.123	0.094	0.092
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a / Å	8.430(6)	9.549(5)	11.314(7)
b / Å	17.184(13)	11.307(2)	11.980(8)
c / Å	9.073(7)	13.260(3)	17.961(10)
α / °	90	100.88(3)	72.586(9)
β / °	93.26(4)	92.261(11)	79.494(13)
γ / °	90	105.79(3)	72.755(19)
Volume / $Å^3$	1312.2(17)	1346.6(8)	2207(2)
Z	4	2	4
ρ_{calc} / $g \cdot cm^{-3}$	1.552	1.314	1.261
F(000)	640	564	896
θ range / °	2.370 – 26.057	1.571 – 26.478	1.895–26.420
Reflections collected	10207	15073	40589
Unique reflections	2587	5534	9038
Parameters / restraints	203 / 0	399 / 162	557 / 1
GooF on F^2	1.032	1.048	1.016
R_1 [I>2σ(I)]	0.0472	0.0415	0.0718
wR^2 (all data)	0.1188	0.1076	0.1569
Max. / min. residual electron density / $e \cdot Å^{-3}$	0.321 / –0.220	0.295 / –0.266	0.426 / –0.291

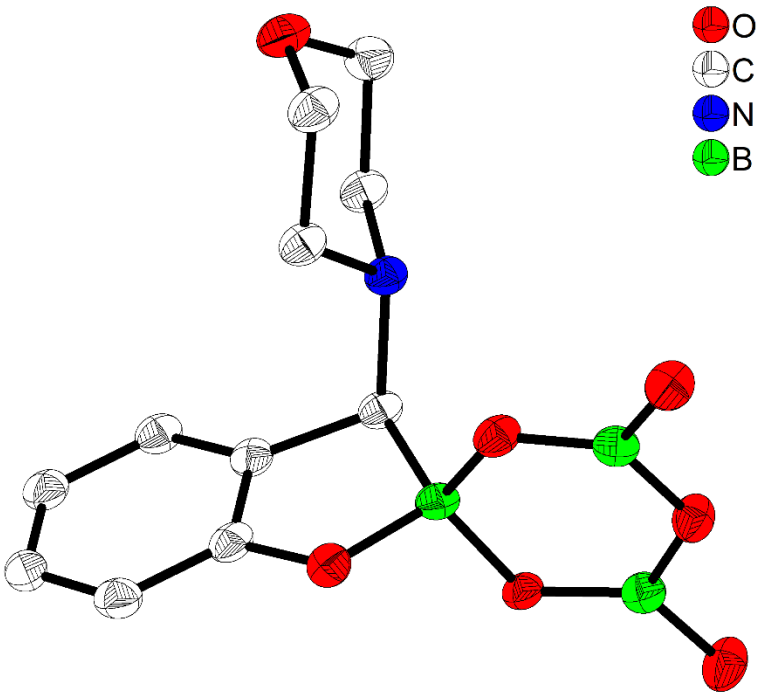


Figure S1. Molecular structure of **4a** in the solid state at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

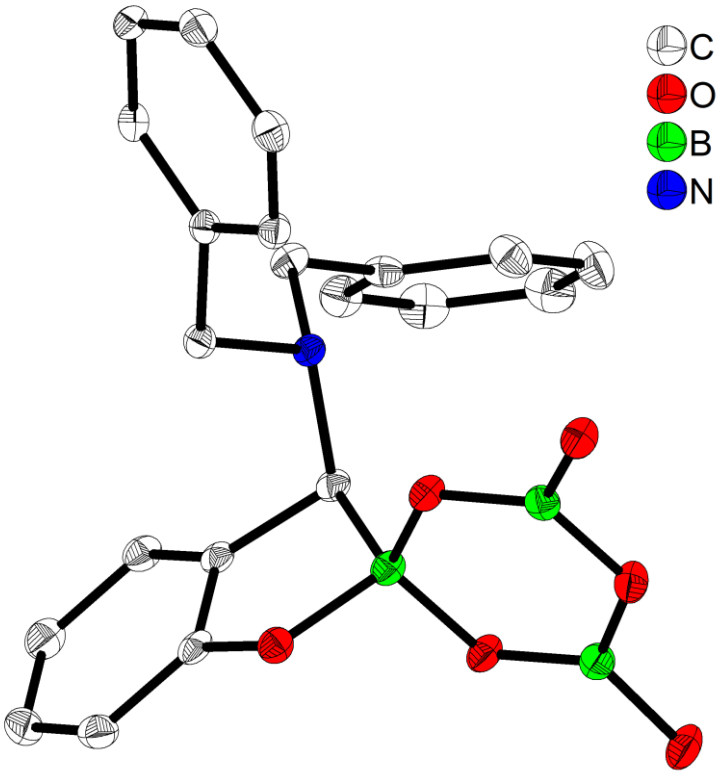


Figure S2. Molecular structure of **4d** in the solid state at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level. H atoms and solvent molecules are omitted for clarity.

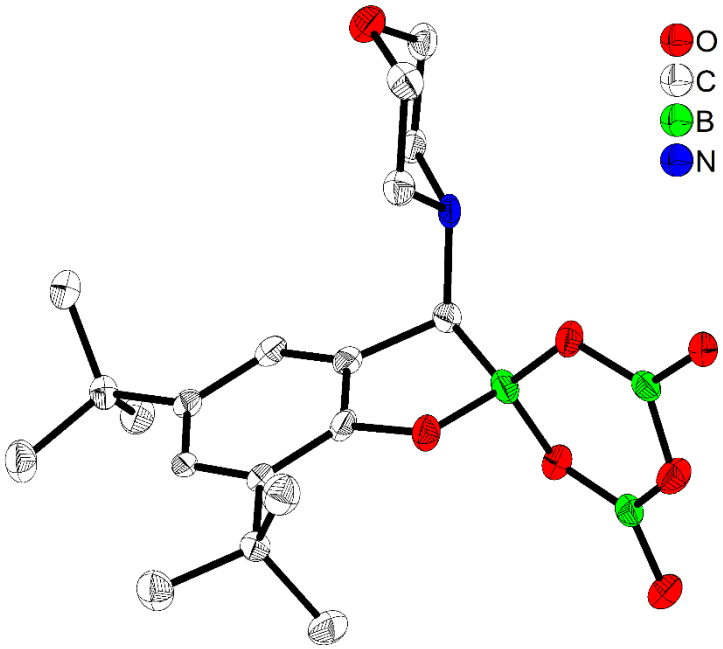


Figure S3. Molecular structure of **4p** in the solid state at 100 K. Atomic displacement ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity. Only one of two independent molecules is shown here.

VII. References

1. M. Raducan, R. Alam and K. J. Szabó, *Angew. Chem. Int. Ed.*, 2012, **51**, 13050-13053.
2. G. Sheldrick, *Acta Crystallogr.*, 2015, **A71**, 3-8.
3. G. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112-122.
4. C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.*, 2011, **44**, 1281-1284.
5. Brandenburg, K. Diamond (version 4.4.0), Crystal and Molecular Structure Visualization, Crystal Impact, H. Putz & K. Brandenburg GbR, Bonn (Germany), 2017.