Supporting Information for

Facile synthesis of borofragments and their evaluation in activity-based protein profiling

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Table of Contents:

General experimental information

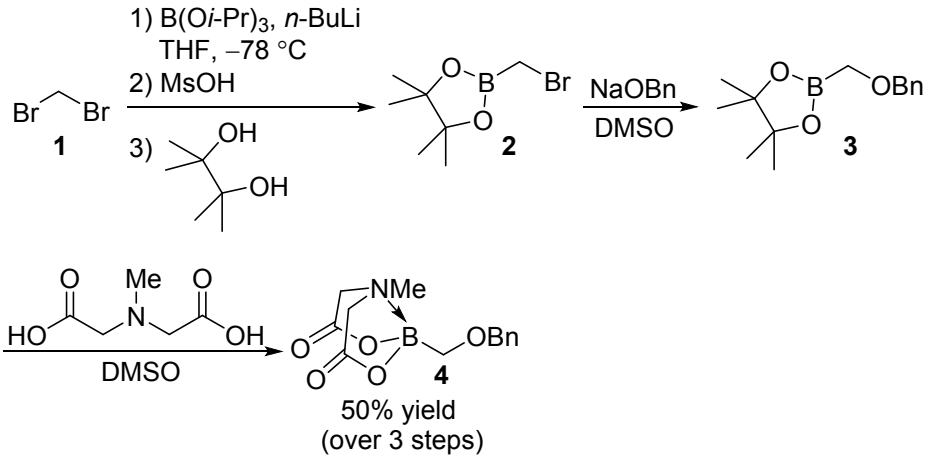
General: THF was distilled from sodium benzophenone ketyl. DMSO was dried and distilled over CaH_2.

Chromatography: Flash column chromatography was carried out using Silicycle 230-400 mesh silica gel. Thin-layer chromatography (TLC) was performed on Macherey Nagel precoated glass-backed TLC plates (SIL G/UV254, 0.25 mm) and visualized using a UV lamp (254 nm) or $KMnO_4$ stain in case of no UV activity.

Nuclear Magnetic Resonance Spectroscopy: NMR spectra were recorded at 25°C on Varian Mercury 400, Agilent DD2-500, or Agilent DD2 600 instrument. Recorded shifts for protons are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvents (DMSO-d_6: 2.50 or CD_3CN: δ 1.94, centre line). Chemical shifts for carbon resonances are reported in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (DMSO-d_6: 39.52 or CD_3CN: δ 1.32, centre line). **Carbons exhibiting significant line broadening brought about by boron substituents were not reported (quadrupolar relaxation)**.^{11}B NMR was recorded at 25°C on a Bruker Advance III 400 MHz spectrometer or on an Agilent DD2 600 MHz spectrometer with an Agilent OneNMR probe and referenced to an external standard of $BF_3 \cdot Et_2O$. Data are represented as follows: chemical shift δ in ppm, multiplicity (s singlet, d doublet, t triplet, q quartet, m multiplet, br broad), coupling constant *J* in Hz and integration.

Mass Spectrometry: High resolution mass spectra were obtained on a VG 70- 250S (double focusing) mass spectrometer at 70 eV or on an ABI/Sciex Qstar mass spectrometer with ESI source, MS/MS and accurate mass capabilities or on JEOL AccuTOF-DART instrument.

RP-HPLC/MS: Low resolution mass spectra (ESI) were collected on an Agilent Technologies 1200 series HPLC paired to a 6130 Mass Spectrometer. Compound **7j** was resolved on an Agilent Poroshell 120 EC-C_{18}, 2.7 μm, 4.6 x 50 mm^2 column at room temperature with a flow of 1 mL/min.



BenzyloxymethylMIDAboronate (**4**)**.** To a THF (300 mL) solution of triisopropyl borate (50.0 g, 266 mmol) and dibromomethane (48.5 g, 279 mmol) was added *n*-butyllithium (2.5 M *n*-hexane solution, 106 ml, 266 mmol) at –78 ºC over 2 h, and stirring was continued for 1 h. The resulting mixture was allowed to warm to 23°C and was stirred for 1 h. The mixture was cooled to 0 ºC, and MsOH (25.5 g, 266 mmol) was added. The resulting mixture was allowed to warm to 23°C. After 1 h of stirring, pinacol (31.4 g, 266 mmol) was added. The reaction mixture was stirred for an additional 3 h at 23°C and then filtered. The filtrate was concentrated under reduced pressure to afford the crude 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**)[1] as an oil which was carried over to the next step without distillation. A 60% dispersion of NaH in mineral oil (11.7 g, 292 mmol) was added to a DMSO (500 mL) solution of BnOH (27.5 mL, 266 mmol) at 23°C.[2] The resulting mixture was stirred at 23°C under nitrogen overnight. The mixture was cooled to 0 ºC, and the crude 2-(bromomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**) was added. The resulting mixture was allowed to warm to 23°C followed by stirring overnight and subsequent addition of MIDA (58.7g, 399 mmol). The reaction mixture was stirred at 100 ºC for 4 h. The solvent was removed under reduced pressure, and the crude residue was dissolved in ethyl acetate (1L) and washed with saturated $NH_4Cl_{(aq.)}$ (500 mL), saturated $NaHCO_{3(aq.)}$ (500 mL), and brine (500 mL). The solvent was removed under reduced pressure, and the resulting solid was washed with diethyl ether to give the title ~~compound **4** in 50% overall y~~ield (36.9 g) as an amorphous solid; ^{1}H NMR (400 MHz,

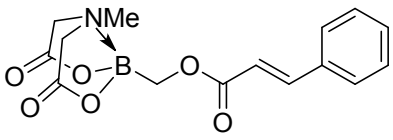
1) N. Murai, M. Yonaga and K. Tanaka, *Org. Lett.,* 2012, **14**, 1278–1281.
2) R. P. Singh and D. S. Matteson, *J. Org. Chem.,* 2000, **65**, 6650–6653.

CD_3CN) δ 2.97 (3H, s), 3.17 (2H, s), 3.78 (2H, d, *J* = 16.8 Hz), 3.95 (2H, d, *J* = 16.8 Hz), 4.47 (2H, s), 7.27–7.37 (5H, m); ^{13}C NMR (100 MHz, CD_3CN) δ 46.5, 62.9, 76.6, 128.4, 128.6, 129.2, 139.9, 169.2; ^{11}B NMR (128 MHz, CD_3CN) δ 11.0; HRMS (DART-TOF) calcd for $[C_{13}H_{16}BNO_5+NH_4]^+$ 295.14653, found 295.14677.

HydroxymethylMIDAboronate (5). A suspension of MIDA 2-((benzyloxy)methyl)boronate (**4**) (20.0 g, 72.2 mmol) and Pd/C (10%) (3.6 g) in ethyl acetate (1200 mL) was vigorously stirred under hydrogen atmosphere at 23°C for 16 h. The reaction mixture was filtered through a pad of celite, and the filtrate was concentrated in vacuo to yield the title compound in 98% yield (13.2 g) as an amorphous solid; ^1H NMR (400 MHz, CD_3CN) δ 2.34 (1H, br s), 3.02 (3H, s), 3.23 (2H, s), 3.80 (2H, d, *J* = 16.8 Hz), 3.94 (2H, d, *J* = 16.8 Hz); ^{13}C NMR (100 MHz, CD_3CN) δ 46.4, 63.0, 169.4; ^{11}B NMR (128 MHz, CD_3CN) δ 11.3; HRMS (DART-TOF) calcd for $[C_6H_{10}BNO_5+H]^+$ 188.07303, found 188.07335.

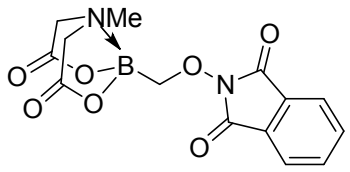
MIDA boryl methylbenzoate (7a). DIAD (81.1 mg, 0.401 mmol) was added to a THF solution (4.5 mL, 0.059 M) of the alcohol **5** (50.0 mg, 0.267 mmol), PPh_3 (105.2 mg, 0.401 mmol), and benzoic acid (**6a**) (49.0 mg, 0.401 mmol) in a 2 dram vial at 23°C. The resulting mixture was stirred for 30 min. The solvent was then removed, and the residue was suspended in 6.0 mL of Et_2O. The resulting suspension was centrifuged at 1600 rpm for 10 min. The supernatant was removed, and the pellet was resuspended in 6.0 mL of Et_2O and centrifuged at 1600 rpm for 10 min. This operation was repeated three times. After removing the supernatant, the pellet was dried in vacuo to afford **7a** (77.1 mg, 99% yield) as a white amorphous solid. ^1H NMR (400 MHz, CD_3CN) δ 3.04 (3H, s), 3.93 (2H, d, *J* = 17.2 Hz), 3.99 (2H, s), 4.09 (2H, d, *J* = 17.2 Hz), 7.48 (2H, m), 7.57 (1H, m), 7.95 (2H, m); ^{13}C NMR (100 MHz, CD_3CN) δ 47.3, 63.2, 129.6, 130.2, 131.3, 133.9, 167.6, 168.9; ^{11}B NMR (192 MHz, CD_3CN) δ 11.0; HRMS (DART-TOF) calcd for $[C_{13}H_{14}BNO_6+H]^+$ 292.09924, found 292.09971.

MIDA boryl methyl cinnamate (7b). DIAD (81.1 mg, 0.401 mmol) was added to a



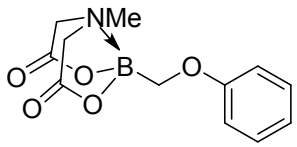
THF solution (4.5 mL, 0.059 M) of the alcohol **5** (50.0 mg, 0.267 mmol), PPh_3 (105.2 mg, 0.401 mmol), and cinnamic acid (**6b**) (59.4 mg, 0.401 mmol) in a 2 dram vial at 23°C. The resulting mixture was stirred for 30 min. The solvent was then removed, and the residue was suspended in 6.0 mL of Et_2O. The resulting suspension was centrifuged at 1600 rpm for 10 min. The supernatant was removed, and the pellet was resuspended in 6.0 mL of Et_2O and centrifuged at 1600 rpm for 10 min. This operation was repeated three times. After removing the supernatant, the pellet was dried in vacuo to afford **7b** (79.8 mg, 94% yield) as a white amorphous solid; ^{1}H NMR (500 MHz, CD_3CN) δ 3.02 (3H, s), 3.86 (2H, s), 3.93 (2H, d, J = 17.0 Hz), 4.06 (2H, d, J = 17.0 Hz), 6.57 (1H, d, J = 16.0 Hz), 7.41–7.42 (3H, m), 7.61–7.65 (3H, m); ^{13}C NMR (125 MHz, CD_3CN) δ 47.1, 63.2, 119.2, 129.1, 129.9, 131.3, 135.4, 145.1, 168.0, 168.9; ^{11}B NMR (192 MHz, DMSO-d_6) δ 10.8; HRMS (DART-TOF) calcd for $[C_{15}H_{16}BNO_6+H]^+$ 318.11489, found 318.11543.

((1,3-Dioxoisoindolin-2-yl)oxy)methyl(MIDA)boronate (7c). DIAD (64.9 mg, 0.321 mmol) was added to a THF solution (4.5 mL, 0.059 M) of the alcohol **5** (50.0 mg, 0.267



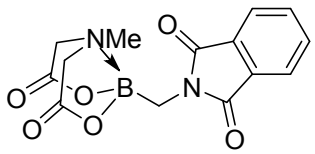
mmol), PPh_3 (84.2 mg, 0.321 mmol), and hydroxyphthalimide (**6c**) (43.6 mg, 0.267 mmol) in a 2 dram vial at 23°C. The resulting mixture was stirred for 30 min. The solvent was then removed, and the residue was suspended in 6.0 mL of Et_2O. The resulting suspension was centrifuged at 1600 rpm for 10 min. The supernatant was removed, and the pellet was resuspended in 6.0 mL of Et_2O and centrifuged at 1600 rpm for 10 min. This operation was repeated three times. After removing the supernatant, the pellet was dried in vacuo to afford **7c** (86.4 mg, 97% yield) as a white amorphous solid; ^{1}H NMR (400 MHz, CD_3CN) δ 3.33 (3H, s), 3.92 (2H, d, J = 17.2 Hz), 4.056 (2H, s), 4.064 (2H, d, J = 17.2 Hz), 7.81 (4H, m); ^{13}C NMR (100 MHz, CD_3CN) δ 47.3, 63.1, 124.0, 130.1, 135.6, 164.3, 168.9; ^{11}B NMR (128 MHz, CD_3CN) δ 10.1; HRMS (DART-TOF) calcd for $[C_{14}H_{13}BN_2O_7+H]^+$ 333.08941, found 333.08903.

MIDA phenoxymethylboronate (7d). DIAD (81.1 mg, 0.401 mmol) was added to a



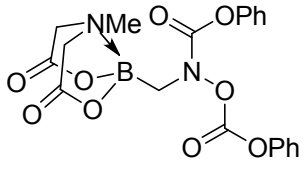
THF solution (4.5 mL, 0.059 M) of the alcohol **5** (50.0 mg, 0.267 mmol), PPh_3 (105.2 mg, 0.401 mmol), and phenol (**6d**) (50.3 mg, 0.535 mmol) in a 2 dram vial at 23°C. The resulting mixture was stirred for 12 h. The solvent was then removed, and the residue was suspended in 6.0 mL of Et_2O. The resulting suspension was centrifuged at 1600 rpm for 10 min. The supernatant was removed, and the pellet was resuspended in 6.0 mL of Et_2O and centrifuged at 1600 rpm for 10 min. This operation was repeated three times. After removing the supernatant, the pellet was dried in vacuo to afford **7d** (63.9 mg, 91% yield) as a white amorphous solid; ^{1}H NMR (500 MHz, CD_3CN) δ 2.99 (3H, s), 3.65 (2H, s), 3.94 (2H, d, J = 17.0 Hz), 4.05 (2H, d, J = 17.0 Hz), 6.95 (1H, m), 6.99 (2H, m), 7.29 (2H, m); ^{13}C NMR (125 MHz, CD_3CN) δ 46.8, 63.1, 115.1, 121.5, 130.3, 161.3, 169.1; ^{11}B NMR (128 MHz, CD_3CN) δ 11.0; HRMS (DART-TOF) calcd for $[C_{12}H_{14}BNO_5+NH_4]^+$ 281.13088, found 281.13149.

(1,3-Dioxoisoindolin-2-yl)methyl(MIDA)boronate (7e). DIAD (64.9 mg, 0.321



mmol) was added to a THF solution (4.5 mL, 0.059 M) of the alcohol **5** (50.0 mg, 0.267 mmol), PPh_3 (84.2 mg, 0.321 mmol), and phthalimide (**6e**) (39.3 mg, 0.267 mmol) in a 2 dram vial at 23°C. The resulting mixture was stirred for 30 min. The solvent was then removed, and the residue was suspended in 6.0 mL of Et_2O. The resulting suspension was centrifuged at 1600 rpm for 10 min. The supernatant was removed, and the pellet was resuspended in 6.0 mL of Et_2O and centrifuged at 1600 rpm for 10 min. This operation was repeated three times. After removing the supernatant, the pellet was dried in vacuo to afford **7e** (83.7 mg, 99% yield) as a white amorphous solid;^{1}H NMR (600 MHz, CD_3CN) δ 3.20 (3H, s), 3.24 (2H, s), 3.90 (2H, d, J = 17.4 Hz), 3.99 (2H, d, J = 17.4 Hz), 7.76–7.77 (2H, m), 7.79–7.80 (2H, m); ^{13}C NMR (125 MHz, CD_3CN) δ 47.5, 63.4, 123.6, 133.2, 135.0, 168.8, 169.9; ^{11}B NMR (192 MHz, DMSO-d_6) δ 10.6; HRMS (DART-TOF) calcd for $[C_{14}H_{13}BN_2O_6+H]^+$ 317.09449, found 317.09495.

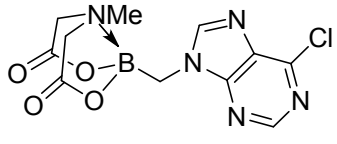
Phenyl (MIDA boryl methyl)((phenoxycarbonyl)oxy)carbamate (7f). DIAD (64.9



mg, 0.321 mmol) was added to a THF solution (4.5 mL, 0.059

M) of the alcohol **5** (50.0 mg, 0.267 mmol), PPh_3 (84.2 mg, 0.321 mmol), and *N*,*O*-bis(phenoxycarbonyl)hydroxylamine[3] (**6f**) (73.1 mg, 0.267 mmol) in a 2 dram vial at 23°C. The resulting mixture was stirred for 30 min. The solvent was then removed. The crude residue was purified by silica gel flash column chromatography (20–50% ethyl acetate/hexane, TLC; 100% ethyl acetate Rf = 0.50) to yield the title compound **7f** with a small amount of triphenylphosphine oxide. It was suspended in 4.0 mL of 50% Hexane/Et_2O. The resulting suspension was centrifuged at 1600 rpm for 10 min. The supernatant was removed and the pellet was resuspended in 1 mL of Et_2O and centrifuged at 1600 rpm for 10 min. This operation was repeated three times. After removing the supernatant, the pellet was dried in vacuo to afford **7f** (92.0 mg, 78% yield) as a white amorphous solid; ^{1}H NMR (500 MHz, CD_3CN) δ 3.10 (3H, s), 3.55 (2H, s), 3.95 (2H, d, *J* = 17.0 Hz), 4.07 (2H, d, *J* = 17.0 Hz), 7.16–7.19 (2H, m), 7.28–7.36 (4H, m), 7.41–7.48 (4H, m); ^{13}C NMR (125 MHz, CD_3CN) δ 47.4, 63.4, 122.0, 122.5, 127.1, 127.8, 130.5, 130.8, 151.8, 151.9, 154.3, 156.3, 168.8; ^{11}B NMR (192 MHz, CD_3CN) δ 10.7; HRMS (DART-TOF) calcd for $[C_{20}H_{19}BN_2O_9+H]^+$ 443.12618, found 443.12694.

(6-Chloro-9*H*-purin-9-yl)methyl(MIDA)boronate (7g). DIAD (64.9 mg, 0.321 mmol) was added to a THF solution (4.5 mL, 0.059 M) of the alcohol **5** (50.0 mg, 0.267 mmol), PPh_3 (84.2 mg, 0.321 mmol), and 6-chloropurine (**6g**) (41.3 mg, 0.267 mmol) in a 2 dram vial at 23°C. The resulting mixture was stirred for 30 min. The solvent was then removed, and the residue was suspended in 6.0 mL of Et_2O. The resulting suspension was centrifuged at 1600 rpm for 10 min. The supernatant was removed, and the pellet was resuspended in 6.0 mL of Et_2O and centrifuged at 1600 rpm for 10 min. This operation was repeated three times. After removing the supernatant, the pellet was dried in vacuo to afford **7g** (84.9 mg, 98% yield) as a white amorphous solid; ^{1}H NMR (500 MHz, CD_3CN) δ 3.03 (3H, s), 3.88 (2H, d, *J* = 17.0 Hz), 3.94 (2H, s), 4.03 (2H, d, *J* = 17.5 Hz), 8.30 (1H, s), 8.68 (1H, s); ^{13}C NMR (125 MHz, CD_3CN) δ 47.4, 63.5, 132.1,



3) A. O. Stewart and D. W. Brooks, *J. Org. Chem.,* 1992, **57**, 5020–5023.

148.2, 150.6, 152.2, 153.4, 168.4; ^{11}B NMR (192 MHz, DMSO-d_6) δ 10.6; HRMS (DART-TOF) calcd for $[C_{11}H_{11}BClN_5O_4+H]^+$ 324.06709, found 324.06705.

(Bis-Boc-9*H*-adenin-9-yl)methyl(MIDA)boronate (7h). DIAD (64.9 mg, 0.321 mmol) was added to a THF solution (4.5 mL, 0.059 M) of the alcohol **5** (50.0 mg, 0.267 mmol), PPh_3 (84.2 mg, 0.321 mmol), and Bis-Boc$_2$-adenine[4] (**6h**) (89.7 mg, 0.267 mmol) in a 2 dram vial at 23°C. The resulting mixture was stirred for 30 min. The solvent was then removed. The crude residue was purified by silica gel flash column chromatography (20–100% ethyl acetate/hexane, 20% acetonitrile/ethyl acetate, TLC; 30% acetonitrile/ethyl acetate Rf = 0.40) to yield the title compound **7h** (129.6 mg, 96% yield); ^{1}H NMR (500 MHz, CD_3CN) δ 1.39 (18H, s), 3.09 (3H, s), 3.91 (2H, d, *J* = 17.5 Hz), 3.94 (2H, s), 4.04 (2H, d, *J* = 17.5 Hz), 8.25 (1H, s), 8.76 (1H, s); ^{13}C NMR (125 MHz, CD_3CN) δ 27.9, 47.4, 63.5, 84.4, 129.0, 147.9, 150.5, 151.5, 152.2, 154.8, 168.4; ^{11}B NMR (192 MHz, CD_3CN) δ 10.8; HRMS (DART-TOF) calcd for $[C_{21}H_{29}BN_6O_8+H]^+$ 505.22182, found 505.22086.

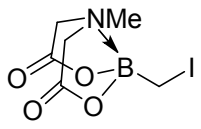
Benzo[d]thiazol-2-ylthio)methyl(MIDA)boronate (7i). DIAD (64.9 mg, 0.321 mmol) was added to a THF solution (4.5 mL, 0.059 M) of the alcohol **5** (50.0 mg, 0.267 mmol), PPh_3 (84.2 mg, 0.321 mmol), and 2-mercaptobenzothiazole (**6i**) (44.7 mg, 0.267 mmol) in a 2 dram vial at 23°C. The resulting mixture was stirred for 30 min. The solvent was then removed. The crude residue was purified by silica gel flash column chromatography (20–100% ethyl acetate/hexane, TLC; 30% acetonitrile/ethyl acetate Rf = 0.70) to yield the title compound **7i** (76.5 mg, 85% yield); amorphous solid; ^{1}H NMR (600 MHz, CD_3CN) δ 2.82 (2H, s), 3.05 (3H, s), 3.91 (2H, d, *J* = 16.8 Hz), 4.04 (2H, d, *J* = 16.8 Hz), 7.33 (1H, m), 7.45 (1H, m), 7.81 (1H, m), 7.88 (1H, m); ^{13}C NMR (125 MHz, CD_3CN) δ 47.3, 63.3, 122.0, 122.3, 125.1, 127.2, 136.1, 154.4, 168.5, 170.3; ^{11}B NMR (192 MHz, DMSO-d_6) δ 11.0; HRMS (DART-TOF) calcd for $[C_{13}H_{13}BN_2O_4S_2+H]^+$ 337.04880, found 337.04941.

4) S. Dey and P. Garner, *J. Org. Chem.,* 2000, **65**, 7697–7699.

MIDA (((1-phenyl-1*H*-tetrazol-5-yl)thio)methyl)boronate (7j). DIAD (64.9 mg, 0.321 mmol) was added to a THF solution (4.5 mL, 0.059 M) of the alcohol **5** (50.0 mg, 0.267 mmol), PPh_3 (84.2 mg, 0.321 mmol), and 1-phenyl-1*H*-tetrazole-5-thiol (**6j**) (47.7 mg, 0.267 mmol) in a 2 dram vial at 23°C. The resulting mixture was stirred for 30 min. The solvent was then removed, and the residue was suspended in 6.0 mL of Et_2O. The resulting suspension was centrifuged at 1600 rpm for 10 min. The supernatant was removed, and the pellet was resuspended in 6.0 mL of Et_2O and centrifuged at 1600 rpm for 10 min. This operation was repeated three times. After removing the supernatant, the pellet was dried in vacuo to afford **7j** (85.6 mg, 92% yield) as a white amorphous solid; ^{1}H NMR (400 MHz, CD_3CN) δ 2.84 (2H, s), 3.01 (3H, s), 3.91 (2H, d, J = 17.2 Hz), 4.04 (2H, d, J = 17.2 Hz), 7.63 (5H, s); ^{13}C NMR (100 MHz, CD_3CN) δ 47.3, 63.3, 125.2, 130.9, 131.3, 134.7, 156.9, 168.4; ^{11}B NMR (128 MHz, CD_3CN) δ 11.1; HRMS (DART-TOF) calcd for $[C_{13}H_{14}BN_5O_4S+H]^+$ 348.09378, found 348.09422.

Azidomethyl(MIDA)boronate (9). DPPA (574 mg, 2.09 mmol) was added to a THF solution (12 mL, 0.13 M) of the alcohol **5** (300 mg, 1.60 mmol), PPh_3 (505 mg, 1.93 mmol), and DIAD (389 mg, 1.93 mmol) in a 2 dram vial at 0 ºC. The resulting mixture was stirred for 30 min at 23°C. The solvent was then removed under reduced pressure. The crude residue was purified by silica gel flash column chromatography (30–100% ethyl acetate/hexane, TLC; ethyl acetate Rf = 0.60) to yield the title compound **9** (305 mg, 90% yield). **9** was also prepared from **10**: NaN_3 (13.6 mg, 0.209 mmol) was added to a DMF solution (5.0 mL) of **10** (56.4 mg, 0.190 mmol) at 23°C. The resulting mixture was stirred for 16 h at 60 ºC. The solvent was then removed. The crude residue was purified by silica gel flash column chromatography (30–100% ethyl acetate/hexane) to yield the title compound **9** in 75% yield (30.2 mg); amorphous solid; ^{1}H NMR (500 MHz, CD_3CN) δ 2.96 (3H, s), 2.98 (2H, s), 3.85 (2H, d, J = 17.0 Hz), 4.00 (2H, d, J = 17.0 Hz); ^{13}C NMR (125 MHz, CD_3CN) δ 46.9, 63.2, 168.8; ^{11}B NMR (128 MHz, CD_3CN) δ 10.8; HRMS (DART-TOF) calcd for $[C_6H_9BN_4O_4+NH_4]^+$ 230.10606, found 230.10546.

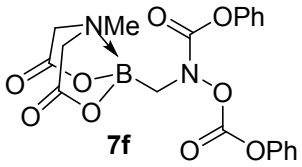
Iodomethyl(MIDA)boronate (10). Iodine (816 mg, 3.22 mmol) was added to a DCM



(40 mL) solution of the alcohol **5** (501 mg, 2.68 mmol), triphenylphosphine (844 mg, 3.22 mmol), and imidazole (275 mg, 4.05 mmol). The resulting mixture was stirred at 23°C for 1 hr. The mixture was then diluted with ethyl acetate and was washed with 5% $Na_2S_2O_{3(aq.)}$ Concentration of the mixture followed by purification using silica gel flash chromatography (50% ethyl acetate/hexane, EtOAc, 5–10% acetonitrile/ethyl acetate, TLC; 20% acetonitrile/ethyl acetate Rf 0.80) gave the title compound **10** (576 mg, 72% yield); amorphous solid; ^{1}H NMR (500 MHz, CD_3CN) δ 2.32 (2H, s), 2.98 (3H, s), 3.92 (2H, d, J = 17.4 Hz), 4.02 (2H, d, J = 17.4 Hz); ^{13}C NMR (125 MHz, CD_3CN) δ 46.7, 63.7, 168.4; ^{11}B NMR (128 MHz, CD_3CN) δ 10.9; HRMS (DART-TOF) calcd for $[C_6H_9BINO_4+NH_4]^+$ 315.00130, found 315.00164.

Detailed X-ray crystallographic information of Phenyl (MIDA boryl methyl)((phenoxycarbonyl)oxy)carbamate (7f)

Crystallization Conditions: (MIDA boryl methyl)((phenoxycarbonyl)oxy)carbamate (**7f**) was recrystallized from acetone and water to afford X-ray quality crystals. (mp 179 ºC)



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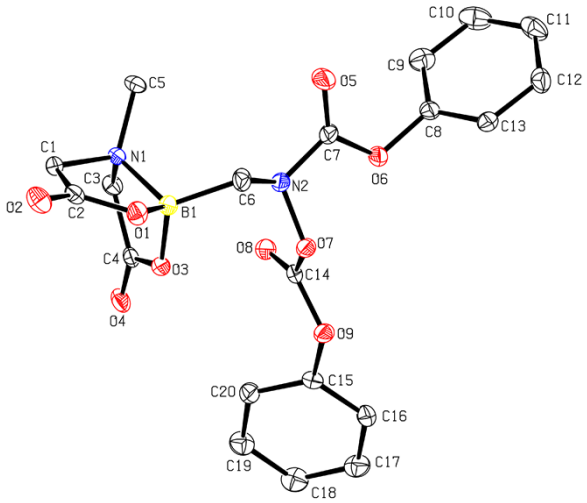


Table S1. Crystal data and structure refinement for Phenyl (MIDA boryl methyl)((phenoxycarbonyl)oxy)carbamate (**7f**)

Identification code	d13232twin	
Empirical formula	C20 H19 B N2 O9	
Formula weight	442.18	
Temperature	147(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 16.8086(4) Å	α= 90°.
	b = 10.0372(2) Å	β= 90.321(2)°.
	c = 24.1763(6) Å	γ = 90°.
Volume	4078.75(16) $Å^3$	
Z	8	
Density (calculated)	1.440 Mg/m^3	
Absorption coefficient	0.968 mm^{-1}	
F(000)	1840	
Crystal size	0.120 x 0.060 x 0.020 mm^3	
Theta range for data collection	3.656 to 66.589°.	
Index ranges	-19<=h<=19, -11<=k<=11, -28<=l<=28	
Reflections collected	13647	

Independent reflections	3520 [R(int) = ?]
Completeness to theta = 67.679°	95.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7529 and 0.6431
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3520 / 0 / 290
Goodness-of-fit on F^2	1.091
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR2 = 0.1156
R indices (all data)	R1 = 0.0520, wR2 = 0.1177
Extinction coefficient	n/a
Largest diff. peak and hole	0.192 and -0.235 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Phenyl (MIDA boryl methyl)((phenoxycarbonyl)oxy)carbamate (**7f**).

	x	y	z	U(eq)
O(1)	6695(1)	9766(2)	3262(1)	34(1)
O(2)	7430(1)	9873(2)	2496(1)	42(1)
O(3)	5404(1)	8725(2)	3372(1)	32(1)
O(4)	4528(1)	7263(2)	3033(1)	37(1)
O(5)	6696(1)	7682(3)	5199(1)	52(1)
O(6)	5399(1)	7793(2)	5444(1)	34(1)
O(7)	5024(1)	9009(2)	4578(1)	30(1)
O(8)	4397(1)	7070(2)	4340(1)	31(1)
O(9)	3773(1)	9050(2)	4511(1)	31(1)
N(1)	6576(1)	7370(2)	3354(1)	22(1)
N(2)	5762(1)	8304(2)	4568(1)	31(1)
C(1)	6928(2)	7756(2)	2805(1)	24(1)
C(2)	7060(2)	9245(3)	2828(1)	28(1)
C(3)	5851(2)	6538(3)	3285(1)	27(1)
C(4)	5179(2)	7525(3)	3210(1)	28(1)
C(5)	7196(2)	6719(3)	3711(1)	30(1)
C(6)	6323(2)	9079(3)	4223(1)	33(1)
C(7)	6021(2)	7935(3)	5093(1)	34(1)
C(8)	5614(2)	7437(3)	5991(1)	29(1)
C(9)	5806(2)	6143(3)	6116(1)	41(1)
C(10)	5968(2)	5833(4)	6664(2)	52(1)
C(11)	5925(2)	6793(4)	7069(1)	47(1)
C(12)	5721(2)	8080(3)	6932(1)	40(1)
C(13)	5570(2)	8417(3)	6385(1)	32(1)
C(14)	4393(2)	8219(3)	4459(1)	26(1)
C(15)	3015(2)	8640(3)	4324(1)	27(1)
C(16)	2383(2)	8969(3)	4653(1)	33(1)
C(17)	1621(2)	8684(3)	4469(1)	41(1)
C(18)	1505(2)	8087(3)	3959(1)	41(1)
C(19)	2148(2)	7776(3)	3636(1)	39(1)
C(20)	2916(2)	8052(3)	3809(1)	32(1)

B(1)	6237(2)	8803(3)	3579(1)	28(1)

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

Table S3. Bond lengths [Å] and angles [°] for Phenyl (MIDA boryl methyl)((phenoxycarbonyl)oxy)carbamate (**7f**)

O(1)-C(2)	1.325(3)
O(1)-B(1)	1.455(4)
O(2)-C(2)	1.198(3)
O(3)-C(4)	1.321(3)
O(3)-B(1)	1.487(3)
O(4)-C(4)	1.203(3)
O(5)-C(7)	1.190(3)
O(6)-C(7)	1.357(3)
O(6)-C(8)	1.416(3)
O(7)-C(14)	1.355(3)
O(7)-N(2)	1.428(3)
O(8)-C(14)	1.189(3)
O(9)-C(14)	1.340(3)
O(9)-C(15)	1.411(3)
N(1)-C(3)	1.485(3)
N(1)-C(5)	1.501(3)
N(1)-C(1)	1.505(3)
N(1)-B(1)	1.641(3)
N(2)-C(7)	1.390(4)
N(2)-C(6)	1.483(4)
C(1)-C(2)	1.511(4)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(3)-C(4)	1.513(4)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-B(1)	1.587(4)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(8)-C(9)	1.371(4)

C(8)-C(13)	1.371(4)
C(9)-C(10)	1.388(5)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.375(5)
C(10)-H(10A)	0.9500
C(11)-C(12)	1.376(5)
C(11)-H(11A)	0.9500
C(12)-C(13)	1.388(4)
C(12)-H(12A)	0.9500
C(13)-H(13A)	0.9500
C(15)-C(16)	1.372(4)
C(15)-C(20)	1.386(4)
C(16)-C(17)	1.384(4)
C(16)-H(16A)	0.9500
C(17)-C(18)	1.383(5)
C(17)-H(17A)	0.9500
C(18)-C(19)	1.373(4)
C(18)-H(18A)	0.9500
C(19)-C(20)	1.383(4)
C(19)-H(19A)	0.9500
C(20)-H(20A)	0.9500

C(2)-O(1)-B(1)	113.7(2)
C(4)-O(3)-B(1)	114.5(2)
C(7)-O(6)-C(8)	114.7(2)
C(14)-O(7)-N(2)	112.69(19)
C(14)-O(9)-C(15)	119.3(2)
C(3)-N(1)-C(5)	112.7(2)
C(3)-N(1)-C(1)	111.86(19)
C(5)-N(1)-C(1)	110.13(19)
C(3)-N(1)-B(1)	104.13(19)
C(5)-N(1)-B(1)	115.59(19)
C(1)-N(1)-B(1)	101.83(18)
C(7)-N(2)-O(7)	112.67(19)
C(7)-N(2)-C(6)	117.2(2)
O(7)-N(2)-C(6)	107.7(2)

N(1)-C(1)-C(2)	106.3(2)
N(1)-C(1)-H(1A)	110.5
C(2)-C(1)-H(1A)	110.5
N(1)-C(1)-H(1B)	110.5
C(2)-C(1)-H(1B)	110.5
H(1A)-C(1)-H(1B)	108.7
O(2)-C(2)-O(1)	124.5(3)
O(2)-C(2)-C(1)	124.9(2)
O(1)-C(2)-C(1)	110.6(2)
N(1)-C(3)-C(4)	104.9(2)
N(1)-C(3)-H(3A)	110.8
C(4)-C(3)-H(3A)	110.8
N(1)-C(3)-H(3B)	110.8
C(4)-C(3)-H(3B)	110.8
H(3A)-C(3)-H(3B)	108.8
O(4)-C(4)-O(3)	124.3(3)
O(4)-C(4)-C(3)	125.3(3)
O(3)-C(4)-C(3)	110.4(2)
N(1)-C(5)-H(5A)	109.5
N(1)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
N(1)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
N(2)-C(6)-B(1)	114.0(2)
N(2)-C(6)-H(6A)	108.8
B(1)-C(6)-H(6A)	108.8
N(2)-C(6)-H(6B)	108.8
B(1)-C(6)-H(6B)	108.8
H(6A)-C(6)-H(6B)	107.7
O(5)-C(7)-O(6)	125.4(3)
O(5)-C(7)-N(2)	123.3(2)
O(6)-C(7)-N(2)	111.0(2)
C(9)-C(8)-C(13)	122.7(3)
C(9)-C(8)-O(6)	120.2(3)
C(13)-C(8)-O(6)	117.0(2)

C(8)-C(9)-C(10)	117.8(3)
C(8)-C(9)-H(9A)	121.1
C(10)-C(9)-H(9A)	121.1
C(11)-C(10)-C(9)	120.8(3)
C(11)-C(10)-H(10A)	119.6
C(9)-C(10)-H(10A)	119.6
C(10)-C(11)-C(12)	120.1(3)
C(10)-C(11)-H(11A)	120.0
C(12)-C(11)-H(11A)	120.0
C(11)-C(12)-C(13)	120.1(3)
C(11)-C(12)-H(12A)	120.0
C(13)-C(12)-H(12A)	120.0
C(8)-C(13)-C(12)	118.5(3)
C(8)-C(13)-H(13A)	120.8
C(12)-C(13)-H(13A)	120.8
O(8)-C(14)-O(9)	129.2(2)
O(8)-C(14)-O(7)	127.8(2)
O(9)-C(14)-O(7)	103.0(2)
C(16)-C(15)-C(20)	122.3(2)
C(16)-C(15)-O(9)	116.3(2)
C(20)-C(15)-O(9)	121.1(2)
C(15)-C(16)-C(17)	118.8(3)
C(15)-C(16)-H(16A)	120.6
C(17)-C(16)-H(16A)	120.6
C(18)-C(17)-C(16)	120.2(3)
C(18)-C(17)-H(17A)	119.9
C(16)-C(17)-H(17A)	119.9
C(19)-C(18)-C(17)	119.8(3)
C(19)-C(18)-H(18A)	120.1
C(17)-C(18)-H(18A)	120.1
C(18)-C(19)-C(20)	121.3(3)
C(18)-C(19)-H(19A)	119.4
C(20)-C(19)-H(19A)	119.4
C(19)-C(20)-C(15)	117.7(3)
C(19)-C(20)-H(20A)	121.2
C(15)-C(20)-H(20A)	121.2

O(1)-B(1)-O(3)	111.0(2)
O(1)-B(1)-C(6)	110.8(2)
O(3)-B(1)-C(6)	114.7(2)
O(1)-B(1)-N(1)	102.8(2)
O(3)-B(1)-N(1)	99.8(2)
C(6)-B(1)-N(1)	116.7(2)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for Phenyl (MIDA boryl methyl)((phenoxycarbonyl)oxy)carbamate (**7f**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	46(1)	23(1)	32(1)	-4(1)	-1(1)	-1(1)
O(2)	54(1)	36(1)	35(1)	12(1)	-2(1)	-9(1)
O(3)	31(1)	38(1)	26(1)	-8(1)	-6(1)	9(1)
O(4)	26(1)	64(1)	22(1)	-3(1)	-3(1)	-5(1)
O(5)	25(1)	96(2)	34(1)	5(1)	-2(1)	12(1)
O(6)	24(1)	52(1)	25(1)	-2(1)	-1(1)	4(1)
O(7)	25(1)	36(1)	30(1)	-9(1)	-4(1)	4(1)
O(8)	32(1)	30(1)	31(1)	-3(1)	-3(1)	2(1)
O(9)	26(1)	33(1)	32(1)	-8(1)	-5(1)	4(1)
N(1)	22(1)	24(1)	20(1)	2(1)	-2(1)	1(1)
N(2)	22(1)	45(1)	27(1)	-8(1)	-3(1)	6(1)
C(1)	26(1)	27(1)	21(1)	1(1)	1(1)	1(1)
C(2)	34(1)	28(1)	23(1)	3(1)	-6(1)	0(1)
C(3)	26(1)	29(1)	26(1)	1(1)	-3(1)	-5(1)
C(4)	25(1)	43(2)	16(1)	-1(1)	0(1)	0(1)
C(5)	28(1)	34(2)	27(1)	6(1)	-8(1)	3(1)
C(6)	29(1)	43(2)	28(1)	-11(1)	-2(1)	-3(1)
C(7)	23(1)	50(2)	28(1)	-7(1)	1(1)	7(1)
C(8)	19(1)	41(2)	27(1)	2(1)	-1(1)	0(1)
C(9)	35(2)	36(2)	50(2)	-4(1)	-6(1)	-2(1)
C(10)	46(2)	42(2)	67(2)	22(2)	-8(2)	-3(2)
C(11)	37(2)	68(2)	36(2)	23(2)	-2(1)	-6(2)
C(12)	34(2)	59(2)	28(1)	-3(1)	4(1)	-4(1)
C(13)	26(1)	37(2)	32(1)	1(1)	2(1)	4(1)
C(14)	27(1)	33(2)	17(1)	-2(1)	-2(1)	4(1)
C(15)	24(1)	27(1)	29(1)	4(1)	-4(1)	0(1)
C(16)	34(1)	41(2)	24(1)	4(1)	2(1)	3(1)
C(17)	30(1)	48(2)	46(2)	14(1)	9(1)	1(1)
C(18)	29(2)	44(2)	50(2)	6(1)	0(1)	-11(1)
C(19)	37(2)	37(2)	43(2)	-5(1)	-9(1)	-7(1)

C(20)	29(1)	36(2)	30(1)	-4(1)	-1(1)	1(1)
B(1)	32(2)	26(2)	27(2)	-5(1)	-3(1)	4(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Phenyl (MIDA boryl methyl)((phenoxycarbonyl)oxy)carbamate (**7f**)

	x	y	z	U(eq)
H(1A)	6559	7526	2499	29
H(1B)	7438	7286	2746	29
H(3A)	5764	5978	3616	33
H(3B)	5898	5953	2957	33
H(5A)	7362	5877	3542	45
H(5B)	6975	6544	4078	45
H(5C)	7657	7311	3747	45
H(6A)	6873	8865	4340	40
H(6B)	6235	10041	4291	40
H(9A)	5827	5480	5836	49
H(10A)	6111	4947	6762	62
H(11A)	6037	6568	7443	57
H(12A)	5683	8738	7213	48
H(13A)	5439	9306	6285	38
H(16A)	2467	9385	5002	40
H(17A)	1177	8898	4693	49
H(18A)	981	7894	3833	49
H(19A)	2063	7364	3287	47
H(20A)	3360	7844	3584	38

Table S6. Torsion angles [°] for Phenyl (MIDA boryl methyl)((phenoxycarbonyl)oxy)carbamate (**7f**)

C(14)-O(7)-N(2)-C(7)	-98.8(3)
C(14)-O(7)-N(2)-C(6)	130.5(2)
C(3)-N(1)-C(1)-C(2)	130.2(2)
C(5)-N(1)-C(1)-C(2)	-103.6(2)
B(1)-N(1)-C(1)-C(2)	19.6(2)
B(1)-O(1)-C(2)-O(2)	175.7(3)
B(1)-O(1)-C(2)-C(1)	-3.1(3)
N(1)-C(1)-C(2)-O(2)	169.2(2)
N(1)-C(1)-C(2)-O(1)	-11.9(3)
C(5)-N(1)-C(3)-C(4)	149.9(2)
C(1)-N(1)-C(3)-C(4)	-85.3(2)
B(1)-N(1)-C(3)-C(4)	23.9(2)
B(1)-O(3)-C(4)-O(4)	179.7(2)
B(1)-O(3)-C(4)-C(3)	0.3(3)
N(1)-C(3)-C(4)-O(4)	164.2(2)
N(1)-C(3)-C(4)-O(3)	-16.5(3)
C(7)-N(2)-C(6)-B(1)	148.0(2)
O(7)-N(2)-C(6)-B(1)	-83.8(3)
C(8)-O(6)-C(7)-O(5)	6.5(4)
C(8)-O(6)-C(7)-N(2)	-179.1(2)
O(7)-N(2)-C(7)-O(5)	-158.6(3)
C(6)-N(2)-C(7)-O(5)	-32.8(4)
O(7)-N(2)-C(7)-O(6)	26.8(3)
C(6)-N(2)-C(7)-O(6)	152.6(2)
C(7)-O(6)-C(8)-C(9)	-78.7(3)
C(7)-O(6)-C(8)-C(13)	105.3(3)
C(13)-C(8)-C(9)-C(10)	-0.7(4)
O(6)-C(8)-C(9)-C(10)	-176.5(3)
C(8)-C(9)-C(10)-C(11)	1.0(5)
C(9)-C(10)-C(11)-C(12)	-0.1(5)
C(10)-C(11)-C(12)-C(13)	-1.0(5)
C(9)-C(8)-C(13)-C(12)	-0.5(4)
O(6)-C(8)-C(13)-C(12)	175.5(2)
C(11)-C(12)-C(13)-C(8)	1.3(4)

C(15)-O(9)-C(14)-O(8)	-11.4(4)
C(15)-O(9)-C(14)-O(7)	168.8(2)
N(2)-O(7)-C(14)-O(8)	-2.1(4)
N(2)-O(7)-C(14)-O(9)	177.69(18)
C(14)-O(9)-C(15)-C(16)	139.2(2)
C(14)-O(9)-C(15)-C(20)	-46.6(3)
C(20)-C(15)-C(16)-C(17)	1.0(4)
O(9)-C(15)-C(16)-C(17)	175.1(2)
C(15)-C(16)-C(17)-C(18)	-0.5(4)
C(16)-C(17)-C(18)-C(19)	0.1(5)
C(17)-C(18)-C(19)-C(20)	-0.2(5)
C(18)-C(19)-C(20)-C(15)	0.7(4)
C(16)-C(15)-C(20)-C(19)	-1.1(4)
O(9)-C(15)-C(20)-C(19)	-174.9(3)
C(2)-O(1)-B(1)-O(3)	-90.6(3)
C(2)-O(1)-B(1)-C(6)	140.7(2)
C(2)-O(1)-B(1)-N(1)	15.4(3)
C(4)-O(3)-B(1)-O(1)	122.1(2)
C(4)-O(3)-B(1)-C(6)	-111.4(3)
C(4)-O(3)-B(1)-N(1)	14.1(3)
N(2)-C(6)-B(1)-O(1)	169.4(2)
N(2)-C(6)-B(1)-O(3)	42.7(3)
N(2)-C(6)-B(1)-N(1)	-73.5(3)
C(3)-N(1)-B(1)-O(1)	-137.4(2)
C(5)-N(1)-B(1)-O(1)	98.4(2)
C(1)-N(1)-B(1)-O(1)	-20.9(2)
C(3)-N(1)-B(1)-O(3)	-23.0(2)
C(5)-N(1)-B(1)-O(3)	-147.2(2)
C(1)-N(1)-B(1)-O(3)	93.4(2)
C(3)-N(1)-B(1)-C(6)	101.2(3)
C(5)-N(1)-B(1)-C(6)	-23.0(3)
C(1)-N(1)-B(1)-C(6)	-142.4(2)

Symmetry transformations used to generate equivalent atoms:

Detailed X-ray crystallographic information of (6-Chloro-9*H*-purin-9-yl)methyl(MIDA)boronate (7g)

Crystallization Conditions: (6-Chloro-9*H*-purin-9-yl)methyl(MIDA)boronate (**7g**) was recrystallized from acetone and water to afford X-ray quality crystals. (mp 237 ºC)

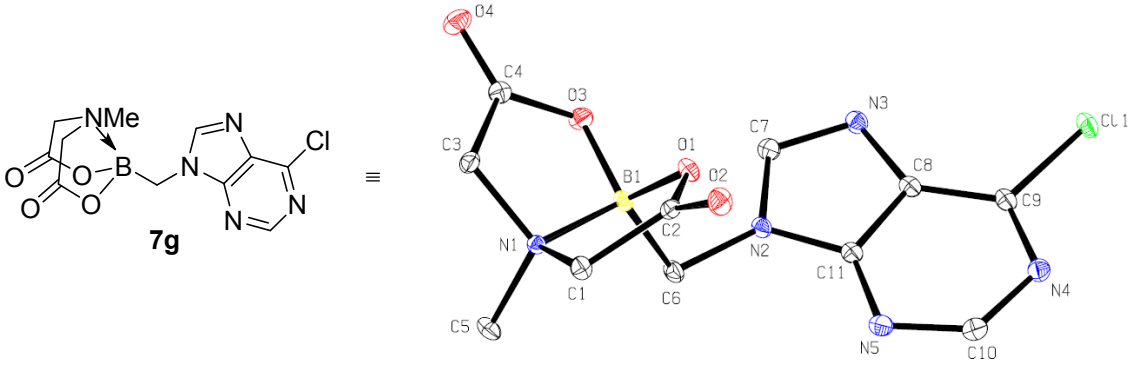


Table S7. Crystal data and structure refinement for (6-Chloro-9*H*-purin-9-yl)methyl(MIDA)boronate (**7g**)

Identification code	d1360	
Empirical formula	C11 H19 B Cl N5 O8	
Formula weight	395.57	
Temperature	147(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 14.3477(18) Å	α= 90°.
	b = 6.9395(7) Å	β= 94.140(3)°.
	c = 17.098(2) Å	γ = 90°.
Volume	1698.0(3) Å^3	
Z	4	
Density (calculated)	1.547 Mg/m^3	
Absorption coefficient	0.278 mm^{-1}	
F(000)	824	
Crystal size	0.35 x 0.22 x 0.12 mm^3	
Theta range for data collection	1.79 to 27.51°.	
Index ranges	-18<=h<=18, -8<=k<=9, -22<=l<=22	
Reflections collected	15259	
Independent reflections	3886 [R(int) = 0.0392]	
Completeness to theta = 27.51°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6856	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3886 / 0 / 268
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R1 = 0.0330, wR2 = 0.0792
R indices (all data)	R1 = 0.0422, wR2 = 0.0854
Largest diff. peak and hole	0.357 and -0.223 e.Å^{-3}

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for (6-Chloro-9*H*-purin-9-yl)methyl(MIDA)boronate (**7g**).

	x	y	z	U(eq)
Cl(1)	4044(1)	3282(1)	5813(1)	19(1)
O(1)	7990(1)	4195(2)	4025(1)	17(1)
O(2)	7832(1)	6429(2)	3081(1)	24(1)
O(3)	8966(1)	2178(2)	4902(1)	18(1)
O(4)	10434(1)	2815(2)	5361(1)	25(1)
N(1)	9166(1)	2189(2)	3501(1)	12(1)
N(2)	6867(1)	1104(2)	4607(1)	15(1)
N(3)	6186(1)	1729(2)	5729(1)	17(1)
N(4)	4218(1)	2989(2)	4304(1)	19(1)
N(5)	5574(1)	1917(2)	3667(1)	18(1)
C(1)	8818(1)	3669(2)	2913(1)	17(1)
C(2)	8168(1)	4953(2)	3340(1)	16(1)
C(3)	10044(1)	2817(2)	3964(1)	18(1)
C(4)	9857(1)	2607(2)	4821(1)	17(1)
C(5)	9292(1)	267(2)	3127(1)	19(1)
C(6)	7607(1)	614(2)	4084(1)	17(1)
C(7)	6944(1)	1133(2)	5411(1)	17(1)
C(8)	5570(1)	2119(2)	5092(1)	15(1)
C(9)	4657(1)	2758(2)	5005(1)	16(1)
C(10)	4698(1)	2552(2)	3674(1)	21(1)
C(11)	5984(1)	1734(2)	4387(1)	15(1)
B(1)	8397(1)	2240(2)	4156(1)	14(1)
O(2W)	2226(1)	3934(2)	4365(1)	30(1)
O(4W)	8080(1)	166(2)	7118(1)	34(1)

O(1W)	5849(1)	2136(2)	7322(1)	24(1)
O(3W)	6565(1)	-1015(2)	8098(1)	36(1)

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table S9. Bond lengths [Å] and angles [°] for (6-Chloro-9*H*-purin-9-yl)methyl(MIDA)boronate (**7g**)

Cl(1)-C(9)	1.7297(14)
O(1)-C(2)	1.3261(17)
O(1)-B(1)	1.4879(19)
O(2)-C(2)	1.2031(18)
O(3)-C(4)	1.3304(17)
O(3)-B(1)	1.4650(18)
O(4)-C(4)	1.2030(17)
N(1)-C(5)	1.4960(18)
N(1)-C(1)	1.4974(18)
N(1)-C(3)	1.5032(17)
N(1)-B(1)	1.6286(18)
N(2)-C(11)	1.3668(18)
N(2)-C(7)	1.3706(18)
N(2)-C(6)	1.4768(17)
N(3)-C(7)	1.3180(18)
N(3)-C(8)	1.3792(18)
N(4)-C(9)	1.3226(19)
N(4)-C(10)	1.3547(19)
N(5)-C(10)	1.3325(19)
N(5)-C(11)	1.3326(18)
C(1)-C(2)	1.5148(19)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(3)-C(4)	1.5158(19)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800

C(6)-B(1)	1.597(2)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-H(7A)	0.9500
C(8)-C(9)	1.381(2)
C(8)-C(11)	1.4081(18)
C(10)-H(10A)	0.9500
O(2W)-H(2WA)	0.83(3)
O(2W)-H(2WB)	0.84(3)
O(4W)-H(4WA)	0.83(3)
O(4W)-H(4WB)	0.84(3)
O(1W)-H(1WA)	0.83(2)
O(1W)-H(1WB)	0.86(2)
O(3W)-H(3WA)	0.81(3)
O(3W)-H(3WB)	0.85(3)

C(2)-O(1)-B(1)	113.32(11)
C(4)-O(3)-B(1)	112.43(11)
C(5)-N(1)-C(1)	111.67(11)
C(5)-N(1)-C(3)	111.14(11)
C(1)-N(1)-C(3)	112.40(11)
C(5)-N(1)-B(1)	114.99(11)
C(1)-N(1)-B(1)	103.77(10)
C(3)-N(1)-B(1)	102.40(10)
C(11)-N(2)-C(7)	106.14(11)
C(11)-N(2)-C(6)	126.81(12)
C(7)-N(2)-C(6)	126.93(12)
C(7)-N(3)-C(8)	103.69(12)
C(9)-N(4)-C(10)	117.22(13)
C(10)-N(5)-C(11)	112.16(12)
N(1)-C(1)-C(2)	105.46(11)
N(1)-C(1)-H(1A)	110.7
C(2)-C(1)-H(1A)	110.7
N(1)-C(1)-H(1B)	110.7
C(2)-C(1)-H(1B)	110.7
H(1A)-C(1)-H(1B)	108.8

O(2)-C(2)-O(1)	124.39(13)
O(2)-C(2)-C(1)	124.61(13)
O(1)-C(2)-C(1)	110.95(12)
N(1)-C(3)-C(4)	106.37(11)
N(1)-C(3)-H(3A)	110.5
C(4)-C(3)-H(3A)	110.5
N(1)-C(3)-H(3B)	110.5
C(4)-C(3)-H(3B)	110.5
H(3A)-C(3)-H(3B)	108.6
O(4)-C(4)-O(3)	124.05(13)
O(4)-C(4)-C(3)	124.79(13)
O(3)-C(4)-C(3)	111.15(11)
N(1)-C(5)-H(5A)	109.5
N(1)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
N(1)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
N(2)-C(6)-B(1)	109.16(11)
N(2)-C(6)-H(6A)	109.8
B(1)-C(6)-H(6A)	109.8
N(2)-C(6)-H(6B)	109.8
B(1)-C(6)-H(6B)	109.8
H(6A)-C(6)-H(6B)	108.3
N(3)-C(7)-N(2)	114.15(13)
N(3)-C(7)-H(7A)	122.9
N(2)-C(7)-H(7A)	122.9
N(3)-C(8)-C(9)	134.26(13)
N(3)-C(8)-C(11)	110.66(12)
C(9)-C(8)-C(11)	115.07(13)
N(4)-C(9)-C(8)	121.55(13)
N(4)-C(9)-Cl(1)	117.53(11)
C(8)-C(9)-Cl(1)	120.93(11)
N(5)-C(10)-N(4)	127.97(14)
N(5)-C(10)-H(10A)	116.0
N(4)-C(10)-H(10A)	116.0

N(5)-C(11)-N(2)	128.60(13)
N(5)-C(11)-C(8)	126.02(13)
N(2)-C(11)-C(8)	105.36(12)
O(3)-B(1)-O(1)	110.25(12)
O(3)-B(1)-C(6)	113.20(12)
O(1)-B(1)-C(6)	111.32(11)
O(3)-B(1)-N(1)	103.67(10)
O(1)-B(1)-N(1)	101.19(11)
C(6)-B(1)-N(1)	116.35(11)
H(2WA)-O(2W)-H(2WB)	107(2)
H(4WA)-O(4W)-H(4WB)	103(2)
H(1WA)-O(1W)-H(1WB)	107(2)
H(3WA)-O(3W)-H(3WB)	111(2)

Symmetry transformations used to generate equivalent atoms:

Table S10. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (6-Chloro-9*H*-purin-9-yl)methyl(MIDA)boronate (**7g**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cl(1)	19(1)	18(1)	22(1)	-2(1)	9(1)	0(1)
O(1)	18(1)	14(1)	20(1)	-2(1)	7(1)	1(1)
O(2)	24(1)	18(1)	28(1)	2(1)	0(1)	5(1)
O(3)	18(1)	24(1)	14(1)	0(1)	2(1)	-4(1)
O(4)	24(1)	32(1)	19(1)	2(1)	-5(1)	-2(1)
N(1)	12(1)	12(1)	12(1)	0(1)	2(1)	0(1)
N(2)	14(1)	16(1)	17(1)	-2(1)	5(1)	-2(1)
N(3)	18(1)	18(1)	17(1)	0(1)	4(1)	-1(1)
N(4)	17(1)	17(1)	22(1)	-2(1)	2(1)	-1(1)
N(5)	20(1)	18(1)	17(1)	-2(1)	3(1)	-3(1)
C(1)	18(1)	17(1)	15(1)	3(1)	2(1)	3(1)
C(2)	13(1)	16(1)	18(1)	-2(1)	-1(1)	-1(1)
C(3)	12(1)	24(1)	16(1)	-1(1)	1(1)	-2(1)
C(4)	18(1)	14(1)	18(1)	1(1)	1(1)	0(1)

C(5)	23(1)	14(1)	21(1)	-4(1)	8(1)	0(1)
C(6)	15(1)	18(1)	20(1)	-4(1)	8(1)	-2(1)
C(7)	17(1)	17(1)	17(1)	0(1)	3(1)	-2(1)
C(8)	17(1)	10(1)	17(1)	0(1)	5(1)	-3(1)
C(9)	17(1)	11(1)	21(1)	-1(1)	7(1)	-3(1)
C(10)	21(1)	21(1)	19(1)	-1(1)	0(1)	-2(1)
C(11)	16(1)	10(1)	18(1)	-1(1)	4(1)	-4(1)
B(1)	14(1)	16(1)	12(1)	-1(1)	4(1)	0(1)
O(2W)	21(1)	45(1)	24(1)	-2(1)	3(1)	5(1)
O(4W)	35(1)	30(1)	37(1)	8(1)	5(1)	5(1)
O(1W)	28(1)	29(1)	17(1)	-2(1)	6(1)	3(1)
O(3W)	52(1)	28(1)	27(1)	0(1)	-8(1)	7(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for (6-Chloro-9*H*-purin-9-yl)methyl(MIDA)boronate (**7g**)

	x	y	z	U(eq)
H(1A)	8479	3047	2455	20
H(1B)	9345	4425	2728	20
H(3A)	10192	4173	3843	21
H(3B)	10577	1996	3837	21
H(5A)	9763	370	2741	28
H(5B)	8697	-154	2864	28
H(5C)	9499	-674	3530	28
H(6A)	7338	532	3535	21
H(6B)	7882	-653	4233	21
H(7A)	7497	757	5712	20
H(10A)	4370	2718	3175	25
H(1WA)	5910(16)	2030(30)	6844(14)	46(6)
H(1WB)	6087(15)	1120(30)	7546(12)	37(6)
H(2WA)	2792(18)	3690(30)	4334(13)	51(7)
H(2WB)	2146(18)	4160(40)	4839(16)	66(8)
H(3WA)	6644(18)	-2170(40)	8063(15)	56(8)

H(3WB)	6791(16)	-600(30)	8540(14)	49(7)
H(4WA)	8440(18)	-710(40)	7277(14)	53(7)
H(4WB)	7610(20)	0(40)	7376(16)	69(9)

Table S12. Torsion angles [°] for (6-Chloro-9*H*-purin-9-yl)methyl(MIDA)boronate (**7g**)

C(5)-N(1)-C(1)-C(2)	144.56(11)
C(3)-N(1)-C(1)-C(2)	-89.75(13)
B(1)-N(1)-C(1)-C(2)	20.13(13)
B(1)-O(1)-C(2)-O(2)	172.39(14)
B(1)-O(1)-C(2)-C(1)	-5.25(16)
N(1)-C(1)-C(2)-O(2)	171.69(13)
N(1)-C(1)-C(2)-O(1)	-10.68(15)
C(5)-N(1)-C(3)-C(4)	-107.00(13)
C(1)-N(1)-C(3)-C(4)	127.02(12)
B(1)-N(1)-C(3)-C(4)	16.28(14)
B(1)-O(3)-C(4)-O(4)	173.08(14)
B(1)-O(3)-C(4)-C(3)	-6.39(17)
N(1)-C(3)-C(4)-O(4)	172.96(14)
N(1)-C(3)-C(4)-O(3)	-7.58(16)
C(11)-N(2)-C(6)-B(1)	108.22(15)
C(7)-N(2)-C(6)-B(1)	-67.33(18)
C(8)-N(3)-C(7)-N(2)	-0.07(17)
C(11)-N(2)-C(7)-N(3)	0.04(17)
C(6)-N(2)-C(7)-N(3)	176.34(13)
C(7)-N(3)-C(8)-C(9)	178.92(16)
C(7)-N(3)-C(8)-C(11)	0.08(16)
C(10)-N(4)-C(9)-C(8)	0.7(2)
C(10)-N(4)-C(9)-Cl(1)	-179.16(11)
N(3)-C(8)-C(9)-N(4)	-179.02(15)
C(11)-C(8)-C(9)-N(4)	-0.2(2)
N(3)-C(8)-C(9)-Cl(1)	0.8(2)
C(11)-C(8)-C(9)-Cl(1)	179.62(10)
C(11)-N(5)-C(10)-N(4)	-0.3(2)
C(9)-N(4)-C(10)-N(5)	-0.4(2)

C(10)-N(5)-C(11)-N(2)	179.03(14)
C(10)-N(5)-C(11)-C(8)	0.9(2)
C(7)-N(2)-C(11)-N(5)	-178.45(14)
C(6)-N(2)-C(11)-N(5)	5.2(2)
C(7)-N(2)-C(11)-C(8)	0.01(15)
C(6)-N(2)-C(11)-C(8)	-176.29(13)
N(3)-C(8)-C(11)-N(5)	178.46(13)
C(9)-C(8)-C(11)-N(5)	-0.6(2)
N(3)-C(8)-C(11)-N(2)	-0.06(16)
C(9)-C(8)-C(11)-N(2)	-179.14(12)
C(4)-O(3)-B(1)-O(1)	-91.18(13)
C(4)-O(3)-B(1)-C(6)	143.39(12)
C(4)-O(3)-B(1)-N(1)	16.44(15)
C(2)-O(1)-B(1)-O(3)	126.61(12)
C(2)-O(1)-B(1)-C(6)	-106.90(13)
C(2)-O(1)-B(1)-N(1)	17.35(14)
N(2)-C(6)-B(1)-O(3)	71.84(15)
N(2)-C(6)-B(1)-O(1)	-53.01(15)
N(2)-C(6)-B(1)-N(1)	-168.21(11)
C(5)-N(1)-B(1)-O(3)	101.08(13)
C(1)-N(1)-B(1)-O(3)	-136.67(11)
C(3)-N(1)-B(1)-O(3)	-19.57(14)
C(5)-N(1)-B(1)-O(1)	-144.64(11)
C(1)-N(1)-B(1)-O(1)	-22.40(13)
C(3)-N(1)-B(1)-O(1)	94.70(12)
C(5)-N(1)-B(1)-C(6)	-23.87(17)
C(1)-N(1)-B(1)-C(6)	98.37(14)
C(3)-N(1)-B(1)-C(6)	-144.53(13)

Symmetry transformations used to generate equivalent atoms.

Table S13. Hydrogen bonds for (6-Chloro-9*H*-purin-9-yl)methyl(MIDA)boronate (**7g**) [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1WA)...N(3)	0.83(2)	1.98(2)	2.8144(17)	174(2)

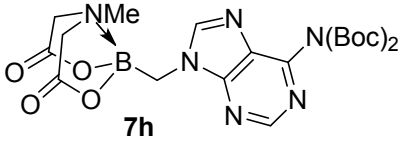
O(1W)-H(1WB)...O(3W)	0.86(2)	1.86(2)	2.7201(19)	176(2)
O(2W)-H(2WA)...N(4)	0.83(3)	2.11(3)	2.9406(18)	177(2)
O(2W)-H(2WB)...O(1)#1	0.84(3)	2.27(3)	3.0800(16)	161(3)
O(3W)-H(3WA)...O(4W)#2	0.81(3)	1.92(3)	2.729(2)	173(3)
O(3W)-H(3WB)...O(2W)#3	0.85(3)	1.89(3)	2.717(2)	162(2)
O(4W)-H(4WA)...O(1W)#2	0.83(3)	1.91(3)	2.7357(19)	174(2)
O(4W)-H(4WB)...O(3W)	0.84(3)	2.13(3)	2.955(2)	167(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1 #2 -x+3/2,y-1/2,-z+3/2 #3 x+1/2,-y+1/2,z+1/2

Detailed X-ray crystallographic information of of (Bis-Boc-9H-adenin-9-yl)methyl(MIDA)boronate (7h)

Crystallization Conditions: (Bis-Boc-9*H*-adenin-9-yl)methyl(MIDA)boronate (**7h**) was recrystallized from acetone and water to afford X-ray quality crystals. (mp 220 ºC)



7h

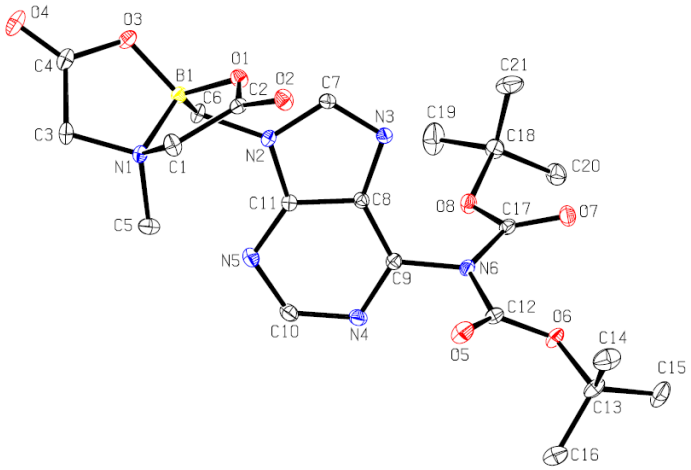


Table S14. Crystal data and structure refinement for (Bis-Boc-9*H*-adenin-9-yl)methyl(MIDA)boronate (**7h**)

Identification code	d1357	
Empirical formula	C21 H31 B N6 O9	
Formula weight	522.33	
Temperature	147(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 19.2489(7) Å	α= 90°.
	b = 7.1031(2) Å	β= 115.222(1)°.
	c = 20.6727(6) Å	γ = 90°.
Volume	2557.04(14) $Å^3$	
Z	4	
Density (calculated)	1.357 Mg/m^3	
Absorption coefficient	0.895 mm^{-1}	
F(000)	1104	
Crystal size	0.11 x 0.08 x 0.01 mm^3	
Theta range for data collection	2.54 to 66.47°.	
Index ranges	-22<=h<=21, -8<=k<=8, -20<=l<=24	
Reflections collected	17278	

Independent reflections	4414 [R(int) = 0.0362]
Completeness to theta = 66.47°	97.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.6999
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4414 / 0 / 349
Goodness-of-fit on F^2	1.063
Final R indices [I>2sigma(I)]	R1 = 0.0342, wR2 = 0.0869
R indices (all data)	R1 = 0.0383, wR2 = 0.0900
Largest diff. peak and hole	0.297 and -0.233 e.$Å^{-3}$

Table S15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for (Bis-Boc-9*H*-adenin-9-yl)methyl(MIDA)boronate (**7h**).

	x	y	z	U(eq)
O(1)	4912(1)	5399(1)	11085(1)	20(1)
O(2)	5640(1)	6467(1)	10562(1)	25(1)
O(3)	5188(1)	4114(1)	12263(1)	22(1)
O(4)	6011(1)	2809(2)	13285(1)	32(1)
O(5)	2824(1)	3157(2)	7638(1)	29(1)
O(6)	1619(1)	3978(1)	6855(1)	22(1)
O(7)	1045(1)	6254(1)	7538(1)	25(1)
O(8)	1037(1)	4465(1)	8442(1)	21(1)
N(1)	5460(1)	2269(2)	11419(1)	17(1)
N(2)	3450(1)	3617(2)	10484(1)	17(1)
N(3)	2782(1)	5511(2)	9547(1)	19(1)
N(4)	2348(1)	934(2)	8615(1)	21(1)
N(5)	3145(1)	594(2)	9877(1)	21(1)
N(6)	1907(1)	3830(2)	8028(1)	18(1)
C(1)	5950(1)	3512(2)	11197(1)	24(1)
C(2)	5495(1)	5290(2)	10906(1)	18(1)
C(3)	5883(1)	1513(2)	12161(1)	24(1)
C(4)	5717(1)	2863(2)	12641(1)	22(1)
C(5)	5123(1)	718(2)	10890(1)	28(1)
C(6)	3966(1)	3087(2)	11223(1)	19(1)

C(7)	3238(1)	5407(2)	10234(1)	20(1)
C(8)	2694(1)	3658(2)	9329(1)	16(1)
C(9)	2320(1)	2790(2)	8673(1)	17(1)
C(10)	2750(1)	-59(2)	9214(1)	23(1)
C(11)	3103(1)	2458(2)	9905(1)	16(1)
C(12)	2176(1)	3634(2)	7490(1)	20(1)
C(13)	1765(1)	3885(2)	6201(1)	26(1)
C(14)	2400(1)	5233(2)	6268(1)	37(1)
C(15)	995(1)	4498(3)	5626(1)	37(1)
C(16)	1945(1)	1862(2)	6092(1)	32(1)
C(17)	1289(1)	4995(2)	7964(1)	18(1)
C(18)	483(1)	5669(2)	8585(1)	25(1)
C(19)	378(1)	4533(3)	9158(1)	47(1)
C(20)	-271(1)	5806(2)	7924(1)	28(1)
C(21)	848(1)	7564(2)	8858(1)	38(1)
B(1)	4840(1)	3771(2)	11483(1)	17(1)
O(1W)	2284(1)	8411(2)	7489(1)	38(1)

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Table S16. Bond lengths [Å] and angles [°] for (Bis-Boc-9*H*-adenin-9-yl)methyl(MIDA)boronate (**7h**)

O(1)-C(2)	1.3247(15)
O(1)-B(1)	1.4597(17)
O(2)-C(2)	1.2044(16)
O(3)-C(4)	1.3268(17)
O(3)-B(1)	1.4784(16)
O(4)-C(4)	1.2041(16)
O(5)-C(12)	1.2001(16)
O(6)-C(12)	1.3172(15)
O(6)-C(13)	1.4943(14)
O(7)-C(17)	1.2019(16)
O(8)-C(17)	1.3257(15)
O(8)-C(18)	1.4927(15)
N(1)-C(5)	1.4918(17)
N(1)-C(3)	1.4971(15)

N(1)-C(1)	1.4990(16)
N(1)-B(1)	1.6473(17)
N(2)-C(7)	1.3683(17)
N(2)-C(11)	1.3688(16)
N(2)-C(6)	1.4722(15)
N(3)-C(7)	1.3142(17)
N(3)-C(8)	1.3788(17)
N(4)-C(9)	1.3268(17)
N(4)-C(10)	1.3472(17)
N(5)-C(11)	1.3293(17)
N(5)-C(10)	1.3349(17)
N(6)-C(17)	1.4078(16)
N(6)-C(12)	1.4192(16)
N(6)-C(9)	1.4322(15)
C(1)-C(2)	1.5080(18)
C(1)-H(1A)	0.9900
C(1)-H(1B)	0.9900
C(3)-C(4)	1.509(2)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-B(1)	1.6074(19)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-H(7A)	0.9500
C(8)-C(9)	1.3806(17)
C(8)-C(11)	1.4025(17)
C(10)-H(10A)	0.9500
C(13)-C(14)	1.512(2)
C(13)-C(15)	1.516(2)
C(13)-C(16)	1.517(2)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800

C(15)-H(15A)	0.9800
C(15)-H(15B)	0.9800
C(15)-H(15C)	0.9800
C(16)-H(16A)	0.9800
C(16)-H(16B)	0.9800
C(16)-H(16C)	0.9800
C(18)-C(21)	1.512(2)
C(18)-C(20)	1.5141(19)
C(18)-C(19)	1.517(2)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
O(1W)-H(1WA)	1.01(3)
O(1W)-H(1WB)	0.98(2)

C(2)-O(1)-B(1)	113.99(10)
C(4)-O(3)-B(1)	114.18(10)
C(12)-O(6)-C(13)	120.50(10)
C(17)-O(8)-C(18)	120.24(10)
C(5)-N(1)-C(3)	111.24(11)
C(5)-N(1)-C(1)	110.13(10)
C(3)-N(1)-C(1)	112.77(10)
C(5)-N(1)-B(1)	115.70(10)
C(3)-N(1)-B(1)	104.28(9)
C(1)-N(1)-B(1)	102.41(9)
C(7)-N(2)-C(11)	105.83(10)
C(7)-N(2)-C(6)	126.18(10)
C(11)-N(2)-C(6)	127.96(11)
C(7)-N(3)-C(8)	103.43(10)
C(9)-N(4)-C(10)	117.81(11)

C(11)-N(5)-C(10)	111.90(11)
C(17)-N(6)-C(12)	124.05(10)
C(17)-N(6)-C(9)	120.19(10)
C(12)-N(6)-C(9)	115.73(10)
N(1)-C(1)-C(2)	106.36(10)
N(1)-C(1)-H(1A)	110.5
C(2)-C(1)-H(1A)	110.5
N(1)-C(1)-H(1B)	110.5
C(2)-C(1)-H(1B)	110.5
H(1A)-C(1)-H(1B)	108.6
O(2)-C(2)-O(1)	124.13(12)
O(2)-C(2)-C(1)	125.13(12)
O(1)-C(2)-C(1)	110.73(10)
N(1)-C(3)-C(4)	105.68(10)
N(1)-C(3)-H(3A)	110.6
C(4)-C(3)-H(3A)	110.6
N(1)-C(3)-H(3B)	110.6
C(4)-C(3)-H(3B)	110.6
H(3A)-C(3)-H(3B)	108.7
O(4)-C(4)-O(3)	123.67(13)
O(4)-C(4)-C(3)	125.05(13)
O(3)-C(4)-C(3)	111.26(10)
N(1)-C(5)-H(5A)	109.5
N(1)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
N(1)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
N(2)-C(6)-B(1)	114.66(10)
N(2)-C(6)-H(6A)	108.6
B(1)-C(6)-H(6A)	108.6
N(2)-C(6)-H(6B)	108.6
B(1)-C(6)-H(6B)	108.6
H(6A)-C(6)-H(6B)	107.6
N(3)-C(7)-N(2)	114.51(11)
N(3)-C(7)-H(7A)	122.7

N(2)-C(7)-H(7A)	122.7
N(3)-C(8)-C(9)	133.48(11)
N(3)-C(8)-C(11)	110.85(11)
C(9)-C(8)-C(11)	115.61(11)
N(4)-C(9)-C(8)	120.55(11)
N(4)-C(9)-N(6)	117.14(11)
C(8)-C(9)-N(6)	122.29(11)
N(5)-C(10)-N(4)	127.93(12)
N(5)-C(10)-H(10A)	116.0
N(4)-C(10)-H(10A)	116.0
N(5)-C(11)-N(2)	128.43(11)
N(5)-C(11)-C(8)	126.17(11)
N(2)-C(11)-C(8)	105.38(11)
O(5)-C(12)-O(6)	128.45(11)
O(5)-C(12)-N(6)	121.06(11)
O(6)-C(12)-N(6)	110.45(11)
O(6)-C(13)-C(14)	110.16(11)
O(6)-C(13)-C(15)	101.48(10)
C(14)-C(13)-C(15)	111.84(13)
O(6)-C(13)-C(16)	108.59(11)
C(14)-C(13)-C(16)	112.75(13)
C(15)-C(13)-C(16)	111.40(12)
C(13)-C(14)-H(14A)	109.5
C(13)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(13)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(13)-C(15)-H(15A)	109.5
C(13)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	109.5
C(13)-C(15)-H(15C)	109.5
H(15A)-C(15)-H(15C)	109.5
H(15B)-C(15)-H(15C)	109.5
C(13)-C(16)-H(16A)	109.5
C(13)-C(16)-H(16B)	109.5

H(16A)-C(16)-H(16B)	109.5
C(13)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
O(7)-C(17)-O(8)	127.25(12)
O(7)-C(17)-N(6)	123.79(11)
O(8)-C(17)-N(6)	108.97(10)
O(8)-C(18)-C(21)	109.07(11)
O(8)-C(18)-C(20)	110.45(10)
C(21)-C(18)-C(20)	113.18(12)
O(8)-C(18)-C(19)	101.23(11)
C(21)-C(18)-C(19)	112.13(13)
C(20)-C(18)-C(19)	110.12(13)
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(18)-C(21)-H(21A)	109.5
C(18)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(18)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
O(1)-B(1)-O(3)	112.08(11)
O(1)-B(1)-C(6)	112.84(10)
O(3)-B(1)-C(6)	109.75(10)
O(1)-B(1)-N(1)	102.80(9)
O(3)-B(1)-N(1)	100.79(9)

C(6)-B(1)-N(1)	117.92(11)
H(1WA)-O(1W)-H(1WB)	98.3(18)

Symmetry transformations used to generate equivalent atoms:

Table S17. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for (Bis-Boc-9*H*-adenin-9-yl)methyl(MIDA)boronate (**7h**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	20(1)	19(1)	23(1)	2(1)	12(1)	2(1)
O(2)	29(1)	22(1)	28(1)	6(1)	16(1)	-1(1)
O(3)	19(1)	30(1)	15(1)	-2(1)	6(1)	1(1)
O(4)	29(1)	45(1)	15(1)	4(1)	4(1)	-10(1)
O(5)	17(1)	46(1)	24(1)	-4(1)	8(1)	3(1)
O(6)	18(1)	34(1)	14(1)	0(1)	7(1)	0(1)
O(7)	29(1)	25(1)	23(1)	7(1)	12(1)	8(1)
O(8)	20(1)	26(1)	20(1)	5(1)	10(1)	6(1)
N(1)	18(1)	18(1)	15(1)	2(1)	7(1)	0(1)
N(2)	16(1)	19(1)	14(1)	0(1)	4(1)	0(1)
N(3)	20(1)	16(1)	17(1)	-2(1)	4(1)	1(1)
N(4)	21(1)	18(1)	22(1)	-3(1)	6(1)	0(1)
N(5)	20(1)	18(1)	23(1)	3(1)	8(1)	0(1)
N(6)	18(1)	21(1)	14(1)	0(1)	5(1)	3(1)
C(1)	22(1)	25(1)	30(1)	8(1)	16(1)	3(1)
C(2)	19(1)	20(1)	16(1)	-2(1)	8(1)	-3(1)
C(3)	23(1)	26(1)	20(1)	9(1)	7(1)	4(1)
C(4)	17(1)	30(1)	17(1)	3(1)	5(1)	-6(1)
C(5)	33(1)	22(1)	27(1)	-6(1)	11(1)	1(1)
C(6)	17(1)	26(1)	12(1)	4(1)	5(1)	1(1)
C(7)	21(1)	16(1)	18(1)	-2(1)	6(1)	1(1)
C(8)	15(1)	16(1)	17(1)	0(1)	6(1)	1(1)
C(9)	14(1)	19(1)	17(1)	0(1)	6(1)	1(1)
C(10)	22(1)	16(1)	27(1)	-1(1)	7(1)	1(1)
C(11)	13(1)	17(1)	17(1)	1(1)	7(1)	-1(1)

C(12)	18(1)	22(1)	17(1)	-4(1)	7(1)	-3(1)
C(13)	27(1)	38(1)	16(1)	-3(1)	13(1)	-4(1)
C(14)	46(1)	42(1)	35(1)	-7(1)	28(1)	-13(1)
C(15)	37(1)	56(1)	18(1)	6(1)	10(1)	7(1)
C(16)	31(1)	39(1)	26(1)	-9(1)	14(1)	-4(1)
C(17)	16(1)	21(1)	14(1)	-2(1)	4(1)	0(1)
C(18)	22(1)	33(1)	23(1)	2(1)	12(1)	10(1)
C(19)	45(1)	70(1)	41(1)	23(1)	32(1)	25(1)
C(20)	21(1)	30(1)	32(1)	1(1)	10(1)	5(1)
C(21)	33(1)	45(1)	34(1)	-17(1)	14(1)	4(1)
B(1)	18(1)	20(1)	15(1)	0(1)	7(1)	1(1)
O(1W)	38(1)	36(1)	46(1)	-15(1)	24(1)	-6(1)

Table S18. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for (Bis-Boc-9*H*-adenin-9-yl)methyl(MIDA)boronate (**7h**)

	x	y	z	U(eq)
H(1A)	6064	2886	10825	28
H(1B)	6441	3800	11612	28
H(3A)	6441	1456	12295	28
H(3B)	5700	232	12198	28
H(5A)	5536	-83	10887	42
H(5B)	4834	1254	10413	42
H(5C)	4778	-37	11024	42
H(6A)	3961	1700	11265	23
H(6B)	3761	3625	11548	23
H(7A)	3406	6487	10532	23
H(10A)	2753	-1386	9158	27
H(14A)	2277	6494	6382	56
H(14B)	2449	5273	5816	56
H(14C)	2885	4806	6651	56
H(15A)	875	5770	5732	56
H(15B)	595	3625	5613	56

H(15C)	1016	4498	5161	56
H(16A)	1522	1045	6064	48
H(16B)	2421	1469	6495	48
H(16C)	2008	1764	5647	48
H(19A)	875	4392	9573	71
H(19B)	173	3288	8969	71
H(19C)	19	5188	9303	71
H(20A)	-194	6514	7552	43
H(20B)	-650	6455	8043	43
H(20C)	-457	4538	7748	43
H(21A)	930	8222	8479	56
H(21B)	1342	7384	9272	56
H(21C)	508	8316	8999	56
H(1WA)	1790(15)	7700(40)	7378(13)	83(8)
H(1WB)	2240(12)	9350(30)	7815(11)	59(6)

Table S19. Torsion angles [°] for (Bis-Boc-9*H*-adenin-9-yl)methyl(MIDA)boronate (**7h**)

C(5)-N(1)-C(1)-C(2)	104.97(12)
C(3)-N(1)-C(1)-C(2)	-130.12(11)
B(1)-N(1)-C(1)-C(2)	-18.64(12)
B(1)-O(1)-C(2)-O(2)	178.12(12)
B(1)-O(1)-C(2)-C(1)	-2.41(14)
N(1)-C(1)-C(2)-O(2)	-166.01(12)
N(1)-C(1)-C(2)-O(1)	14.53(14)
C(5)-N(1)-C(3)-C(4)	-141.86(11)
C(1)-N(1)-C(3)-C(4)	93.84(12)
B(1)-N(1)-C(3)-C(4)	-16.48(13)
B(1)-O(3)-C(4)-O(4)	-172.86(12)
B(1)-O(3)-C(4)-C(3)	5.84(15)
N(1)-C(3)-C(4)-O(4)	-173.35(12)
N(1)-C(3)-C(4)-O(3)	7.97(14)
C(7)-N(2)-C(6)-B(1)	-65.94(16)
C(11)-N(2)-C(6)-B(1)	112.09(14)
C(8)-N(3)-C(7)-N(2)	-0.62(14)

C(11)-N(2)-C(7)-N(3)	0.35(15)
C(6)-N(2)-C(7)-N(3)	178.73(11)
C(7)-N(3)-C(8)-C(9)	-176.41(14)
C(7)-N(3)-C(8)-C(11)	0.65(14)
C(10)-N(4)-C(9)-C(8)	0.02(18)
C(10)-N(4)-C(9)-N(6)	178.52(11)
N(3)-C(8)-C(9)-N(4)	178.16(13)
C(11)-C(8)-C(9)-N(4)	1.20(17)
N(3)-C(8)-C(9)-N(6)	-0.3(2)
C(11)-C(8)-C(9)-N(6)	-177.22(11)
C(17)-N(6)-C(9)-N(4)	122.31(13)
C(12)-N(6)-C(9)-N(4)	-59.38(15)
C(17)-N(6)-C(9)-C(8)	-59.22(16)
C(12)-N(6)-C(9)-C(8)	119.09(13)
C(11)-N(5)-C(10)-N(4)	0.65(19)
C(9)-N(4)-C(10)-N(5)	-1.1(2)
C(10)-N(5)-C(11)-N(2)	-177.81(12)
C(10)-N(5)-C(11)-C(8)	0.82(18)
C(7)-N(2)-C(11)-N(5)	178.95(12)
C(6)-N(2)-C(11)-N(5)	0.6(2)
C(7)-N(2)-C(11)-C(8)	0.09(13)
C(6)-N(2)-C(11)-C(8)	-178.26(11)
N(3)-C(8)-C(11)-N(5)	-179.36(11)
C(9)-C(8)-C(11)-N(5)	-1.72(18)
N(3)-C(8)-C(11)-N(2)	-0.47(13)
C(9)-C(8)-C(11)-N(2)	177.17(10)
C(13)-O(6)-C(12)-O(5)	-3.1(2)
C(13)-O(6)-C(12)-N(6)	179.24(11)
C(17)-N(6)-C(12)-O(5)	155.50(13)
C(9)-N(6)-C(12)-O(5)	-22.73(18)
C(17)-N(6)-C(12)-O(6)	-26.65(17)
C(9)-N(6)-C(12)-O(6)	155.12(11)
C(12)-O(6)-C(13)-C(14)	-57.76(17)
C(12)-O(6)-C(13)-C(15)	-176.37(12)
C(12)-O(6)-C(13)-C(16)	66.18(15)
C(18)-O(8)-C(17)-O(7)	-11.31(19)

C(18)-O(8)-C(17)-N(6)	168.76(10)
C(12)-N(6)-C(17)-O(7)	-18.15(19)
C(9)-N(6)-C(17)-O(7)	160.01(12)
C(12)-N(6)-C(17)-O(8)	161.78(11)
C(9)-N(6)-C(17)-O(8)	-20.06(15)
C(17)-O(8)-C(18)-C(21)	-60.79(15)
C(17)-O(8)-C(18)-C(20)	64.20(16)
C(17)-O(8)-C(18)-C(19)	-179.15(13)
C(2)-O(1)-B(1)-O(3)	97.96(12)
C(2)-O(1)-B(1)-C(6)	-137.53(11)
C(2)-O(1)-B(1)-N(1)	-9.45(13)
C(4)-O(3)-B(1)-O(1)	-124.22(11)
C(4)-O(3)-B(1)-C(6)	109.58(12)
C(4)-O(3)-B(1)-N(1)	-15.51(13)
N(2)-C(6)-B(1)-O(1)	24.08(15)
N(2)-C(6)-B(1)-O(3)	149.85(11)
N(2)-C(6)-B(1)-N(1)	-95.61(13)
C(5)-N(1)-B(1)-O(1)	-102.65(12)
C(3)-N(1)-B(1)-O(1)	134.85(10)
C(1)-N(1)-B(1)-O(1)	17.15(11)
C(5)-N(1)-B(1)-O(3)	141.52(10)
C(3)-N(1)-B(1)-O(3)	19.01(12)
C(1)-N(1)-B(1)-O(3)	-98.69(10)
C(5)-N(1)-B(1)-C(6)	22.16(15)
C(3)-N(1)-B(1)-C(6)	-100.34(12)
C(1)-N(1)-B(1)-C(6)	141.96(11)

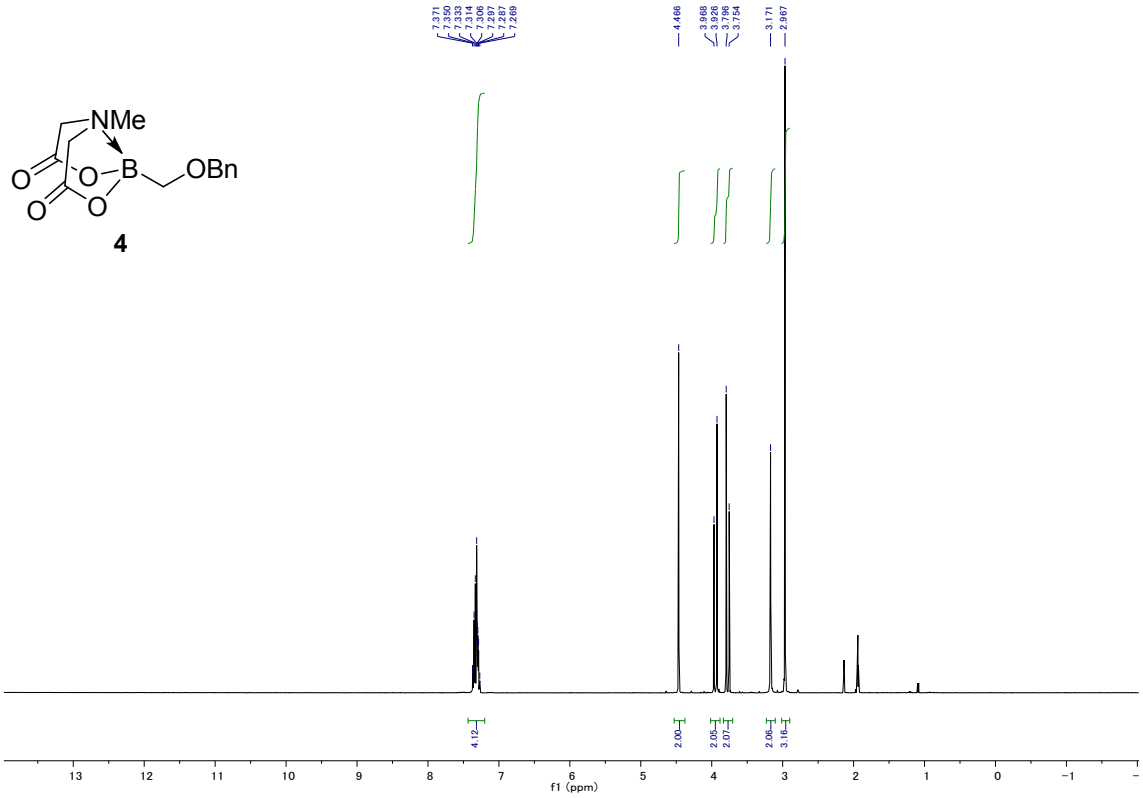
Symmetry transformations used to generate equivalent atoms:

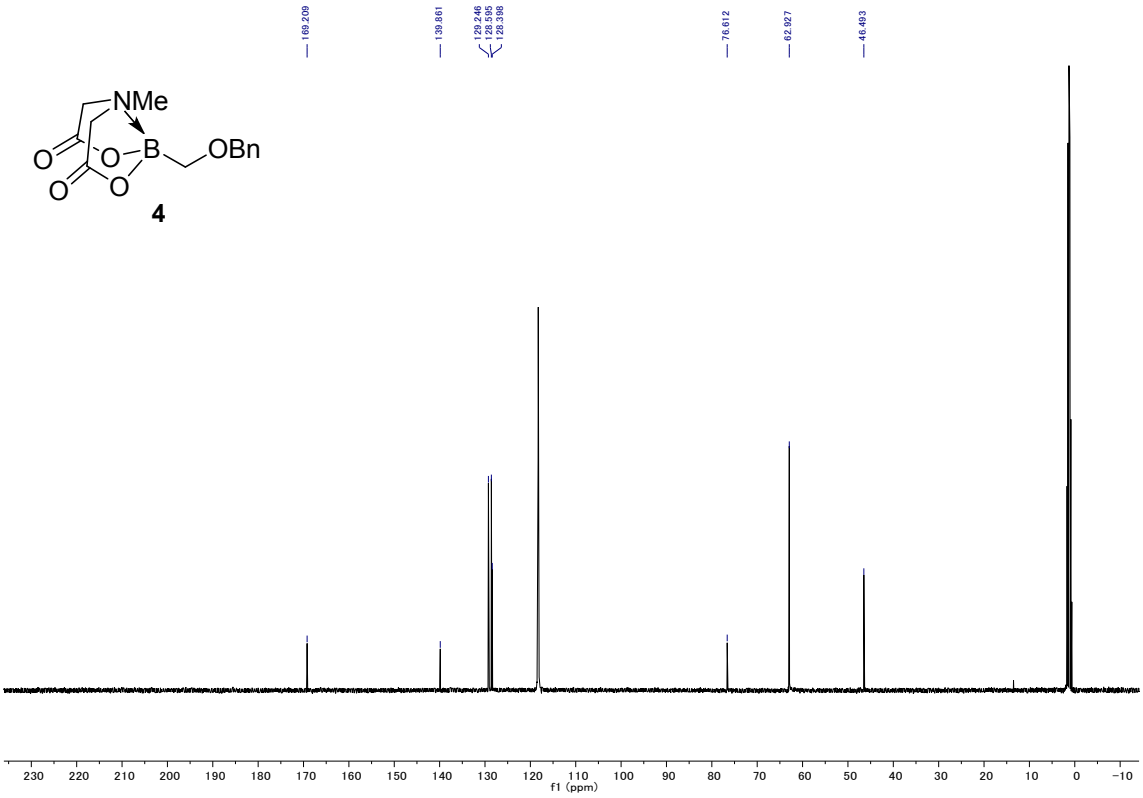
Table S20. Hydrogen bonds for (Bis-Boc-9*H*-adenin-9-yl)methyl(MIDA)boronate (**7h**) [Å and °]

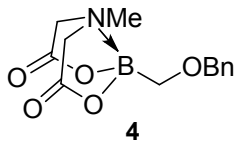
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1WA)...O(7)	1.01(3)	1.90(3)	2.8729(15)	159(2)
O(1W)-H(1WB)...N(4)#1	0.98(2)	1.94(2)	2.8981(15)	167.5(19)

Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z

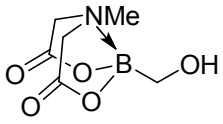

NMe
B
OBn
O
O
O
O
4
7.371
7.350
7.333
7.314
7.306
7.297
7.287
7.269
4.466
3.968
3.956
3.796
3.754
3.171
2.967
4.12
2.00
2.05
2.07
2.06
3.16
f1 (ppm)


NMe
B
OBn
O
O
O
O
4
169.209
139.861
129.246
128.595
128.398
76.612
62.927
46.493
f1 (ppm)

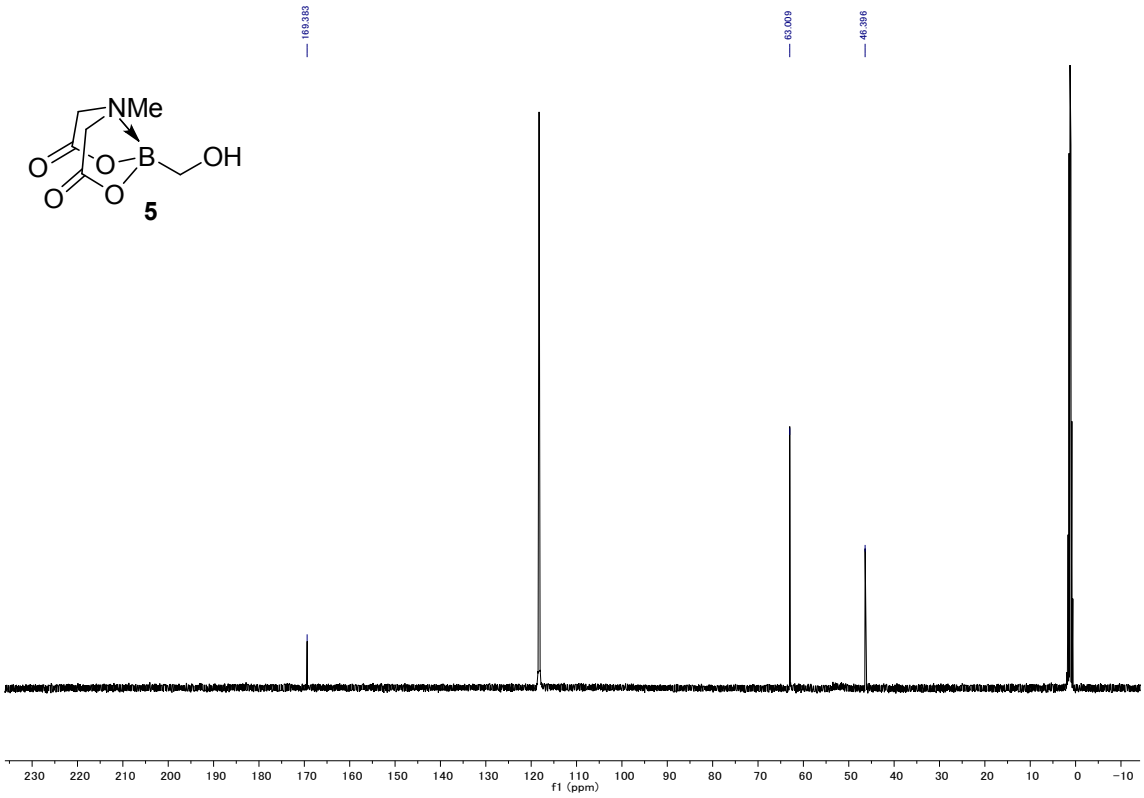


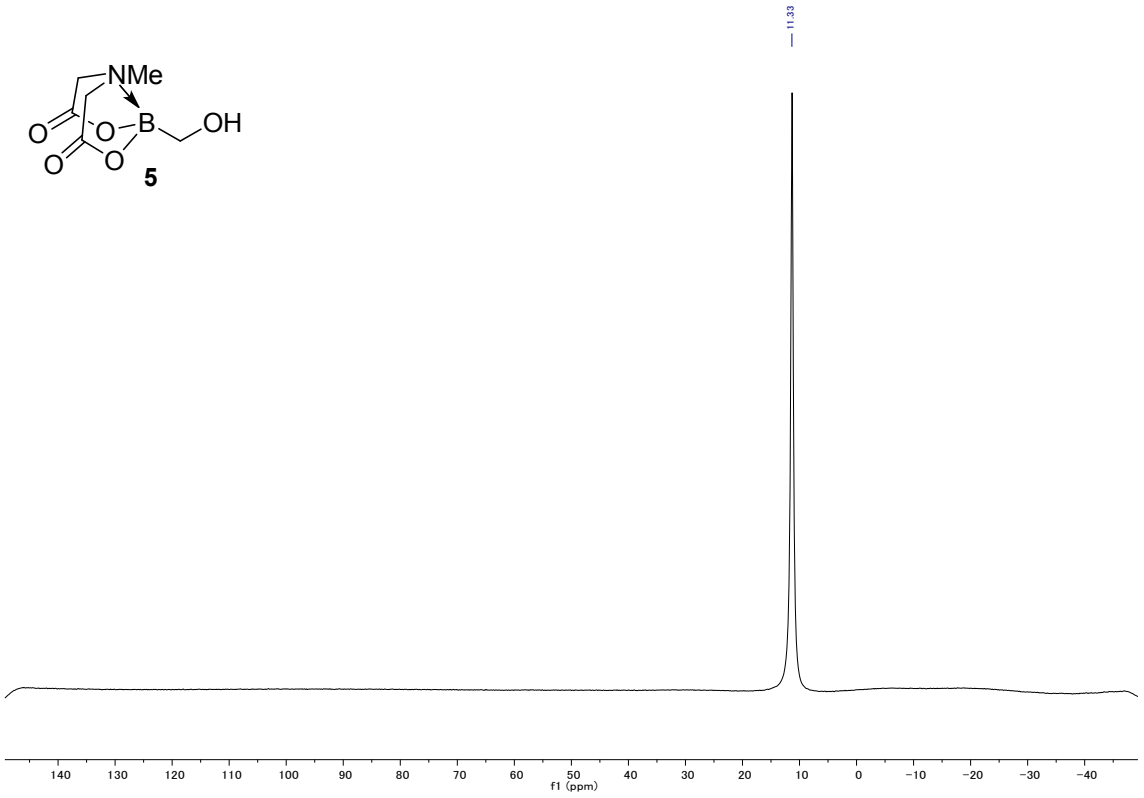
4

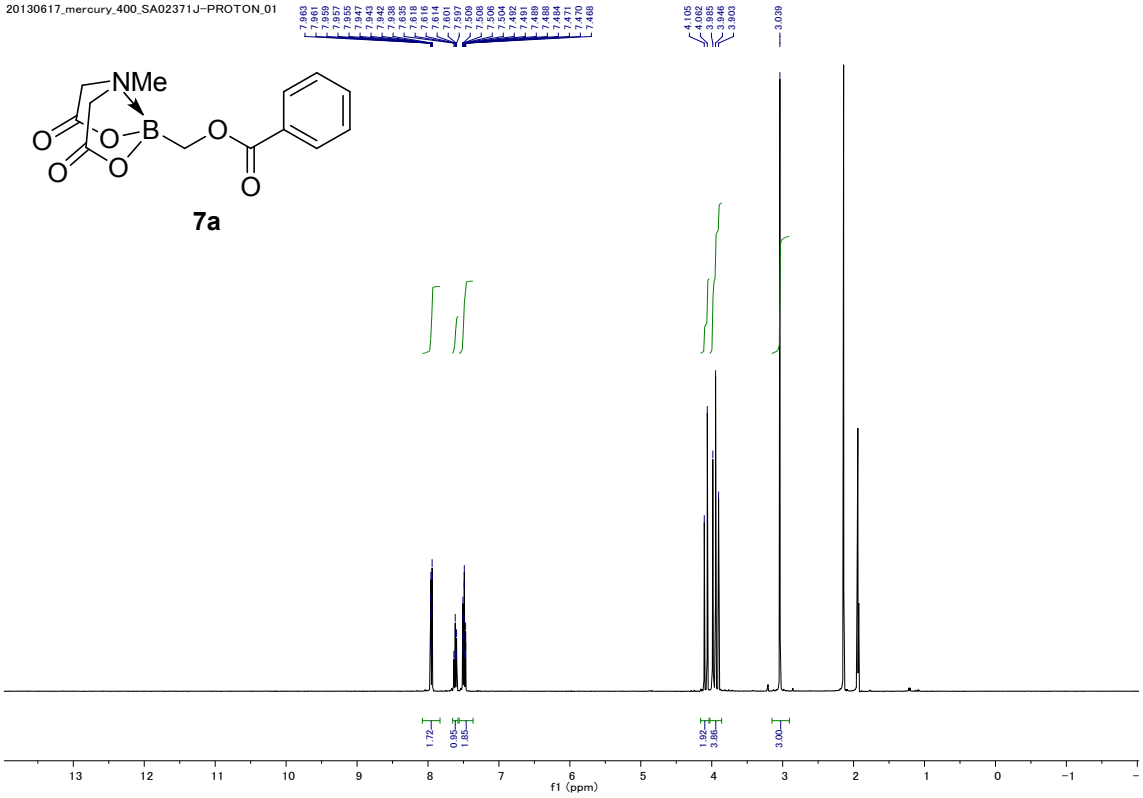
20130617_vnmrs_400_SAHOCH2BJ-PROTON_01
SAHOCH2BJ

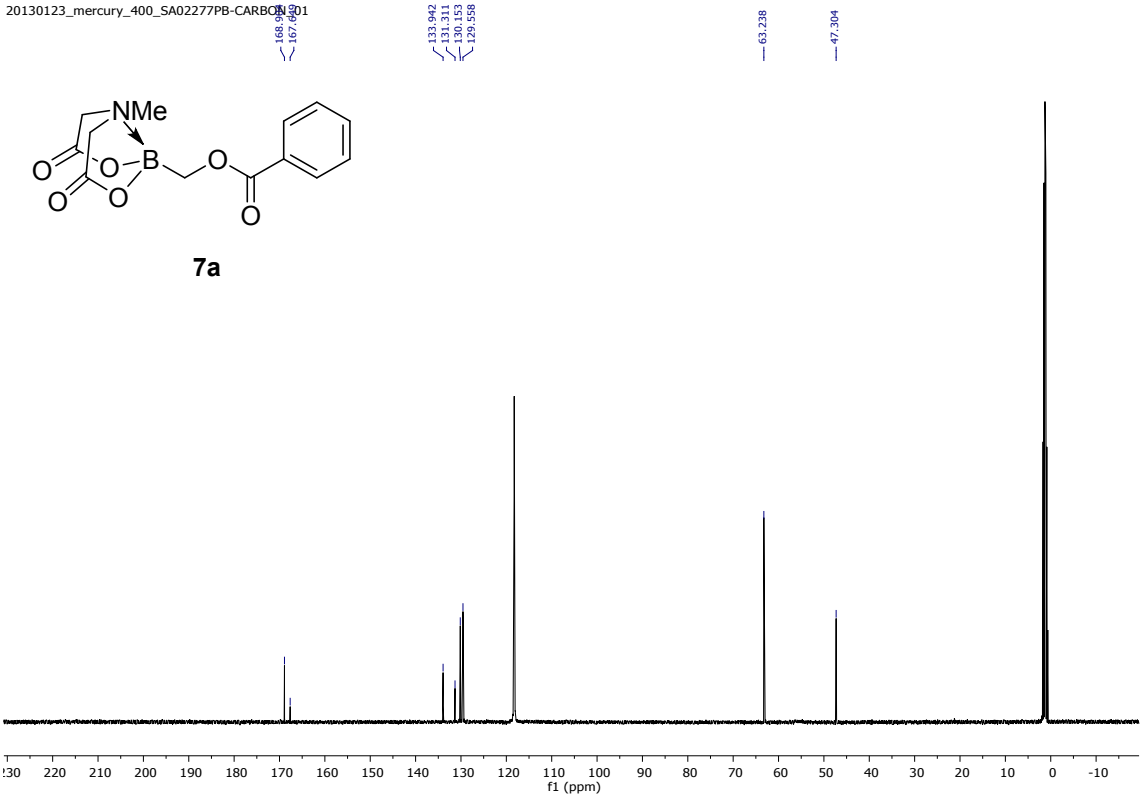


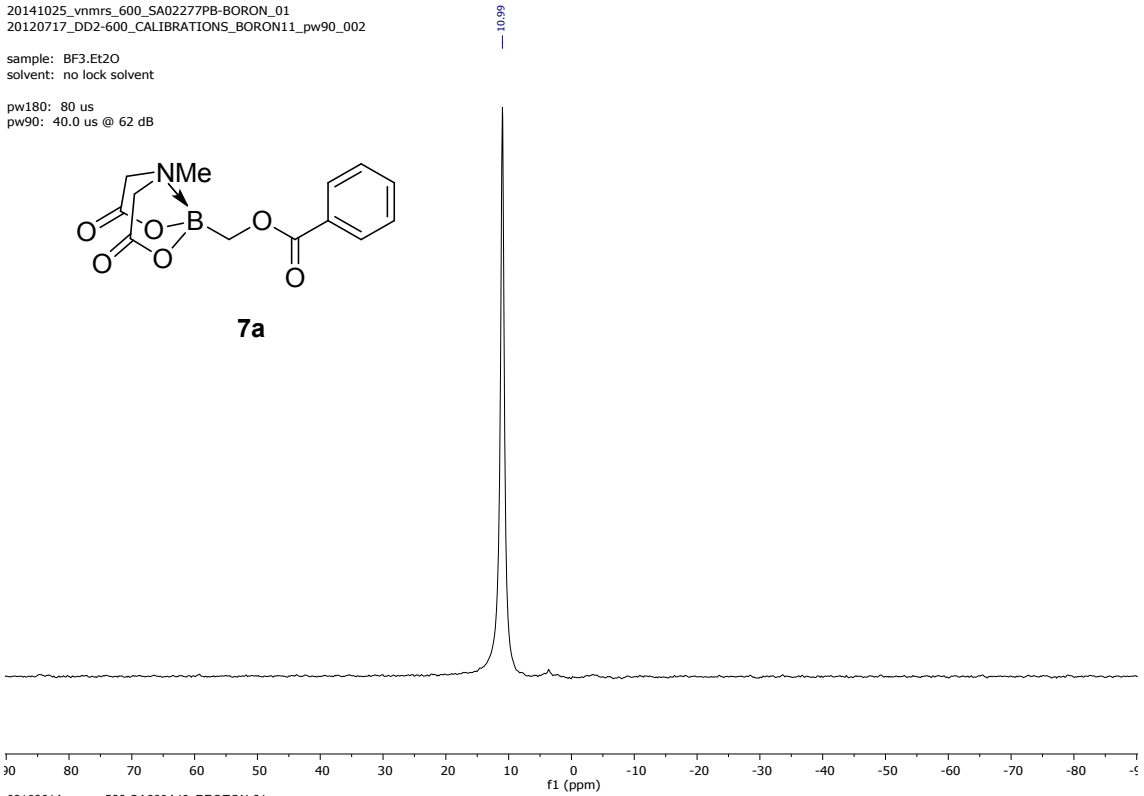
5


169.383
63.009
46.396
NMe
O
O
B
OH
O
O
5
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

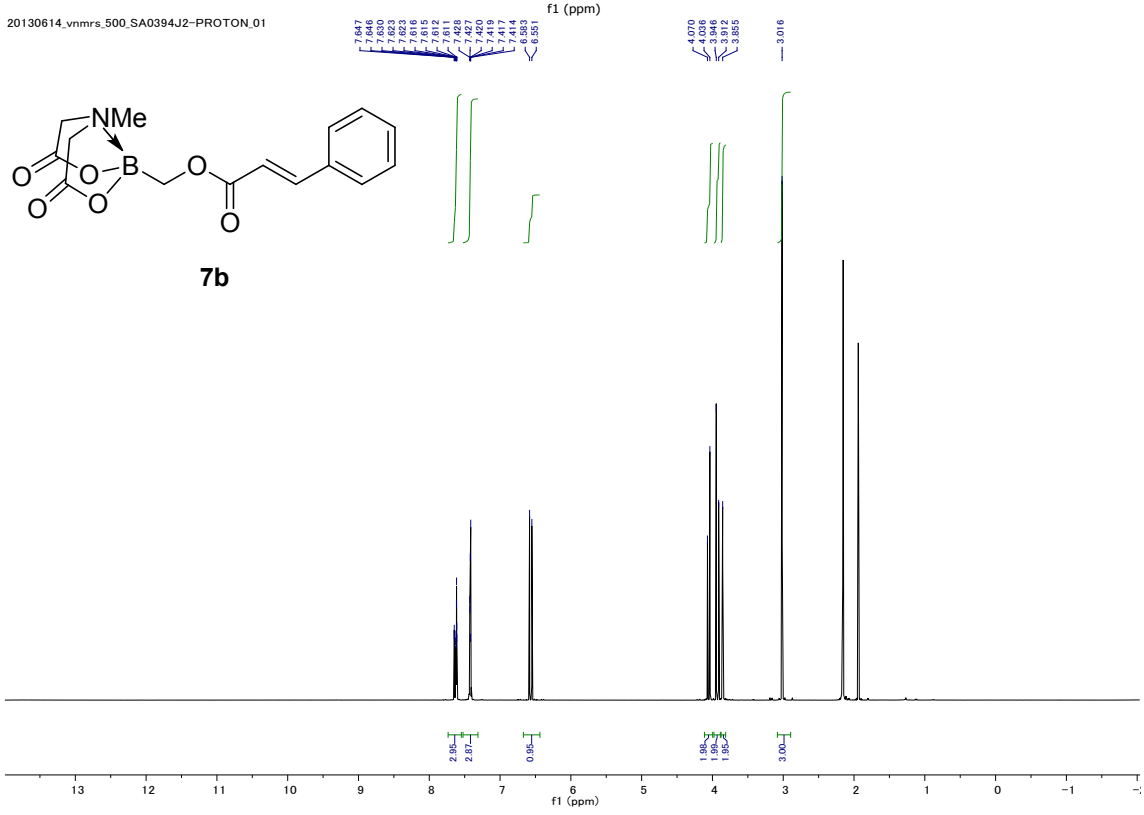

11.33
NMe
O
O
B
OH
O
O
5
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)


20130617_mercury_400_SA02371J-PROTON_01
NMe
B
O
7a
f1 (ppm)

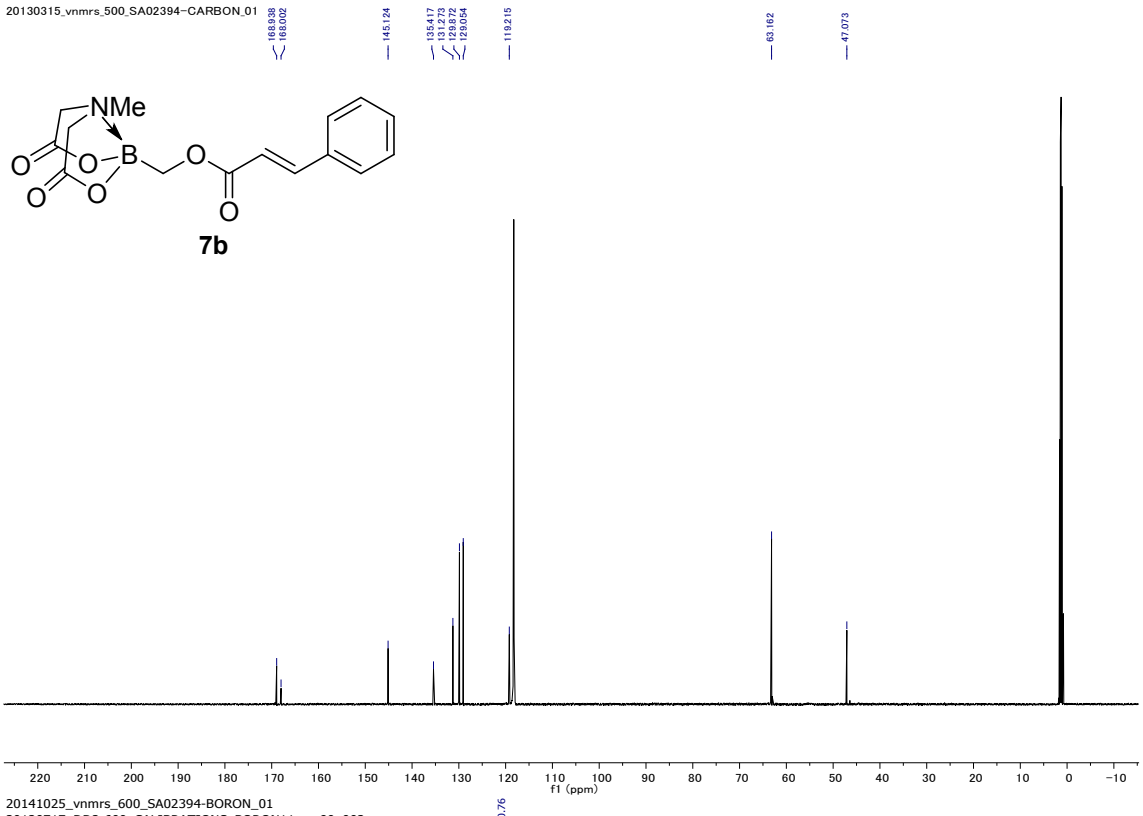

20130123_mercury_400_SA02277PB-CARBON_01
NMe
B
O
7a
f1 (ppm)

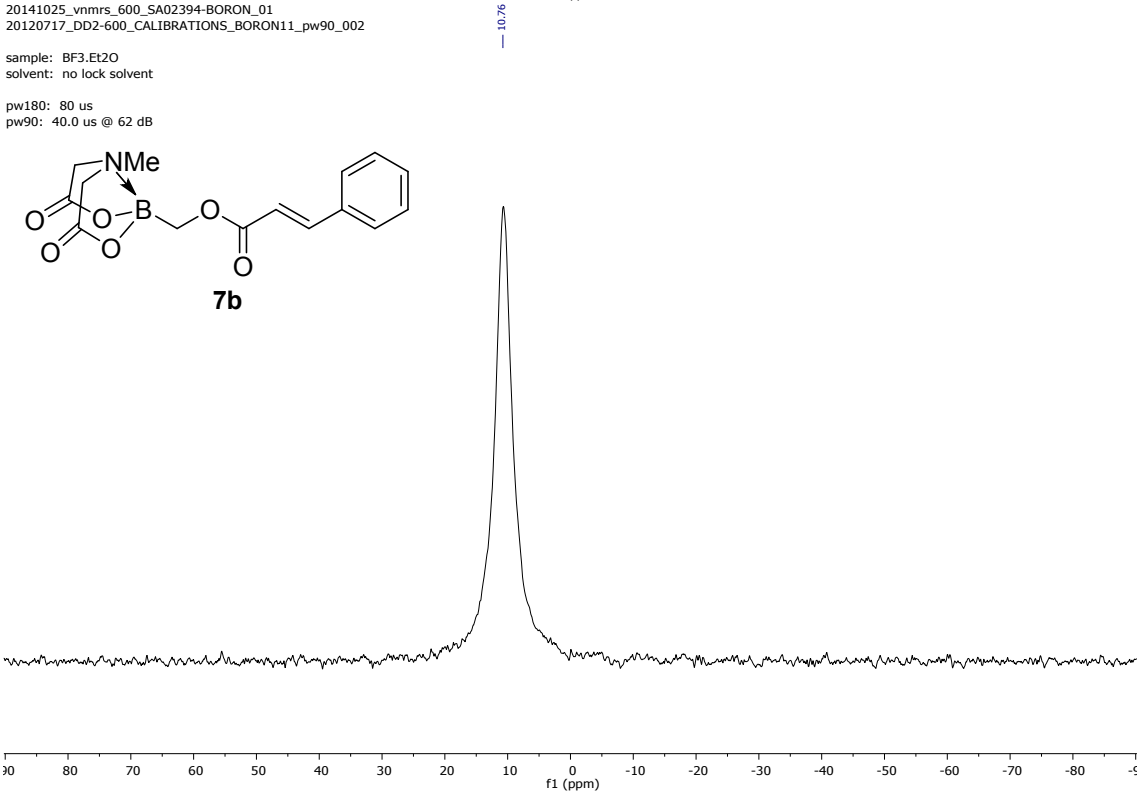

20141025_vnmrs_600_SA02277PB-BORON_01
20120717_DD2-600_CALIBRATIONS_BORON11_pw90_002
sample: BF3.Et2O
solvent: no lock solvent
pw180: 80 us
pw90: 40.0 us @ 62 dB
10.99
NMe
B
O
f1 (ppm)

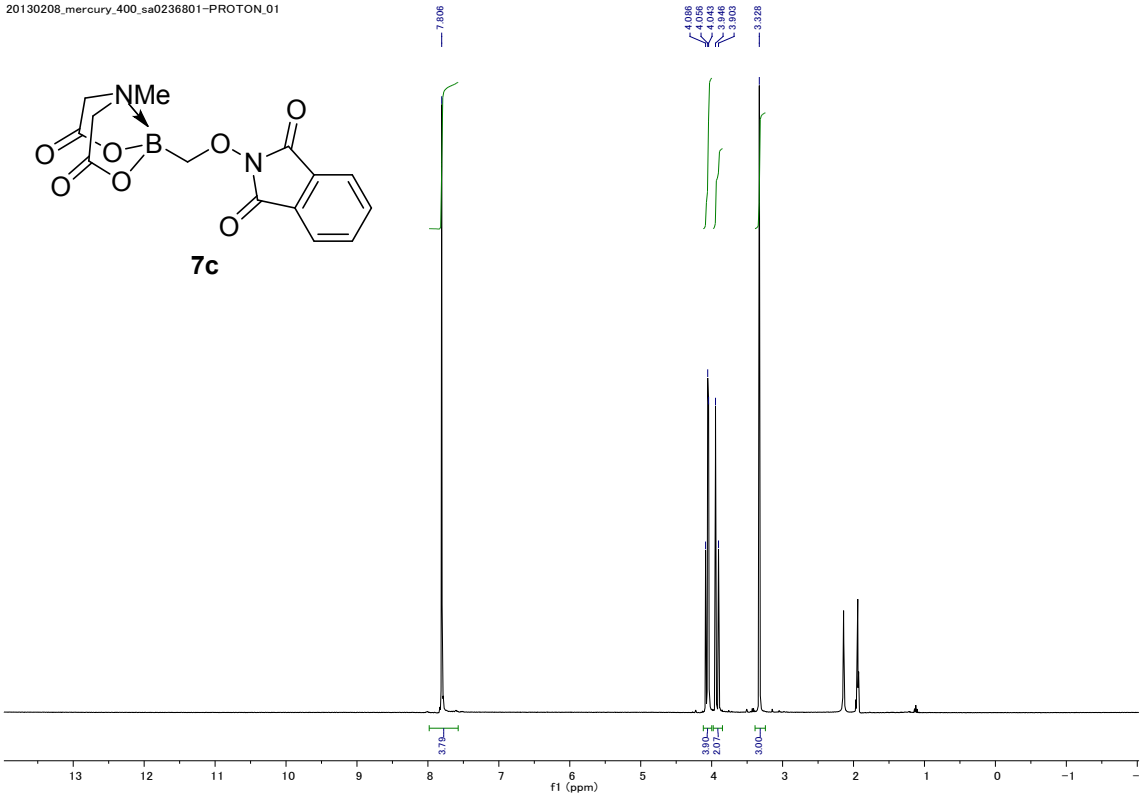
7a

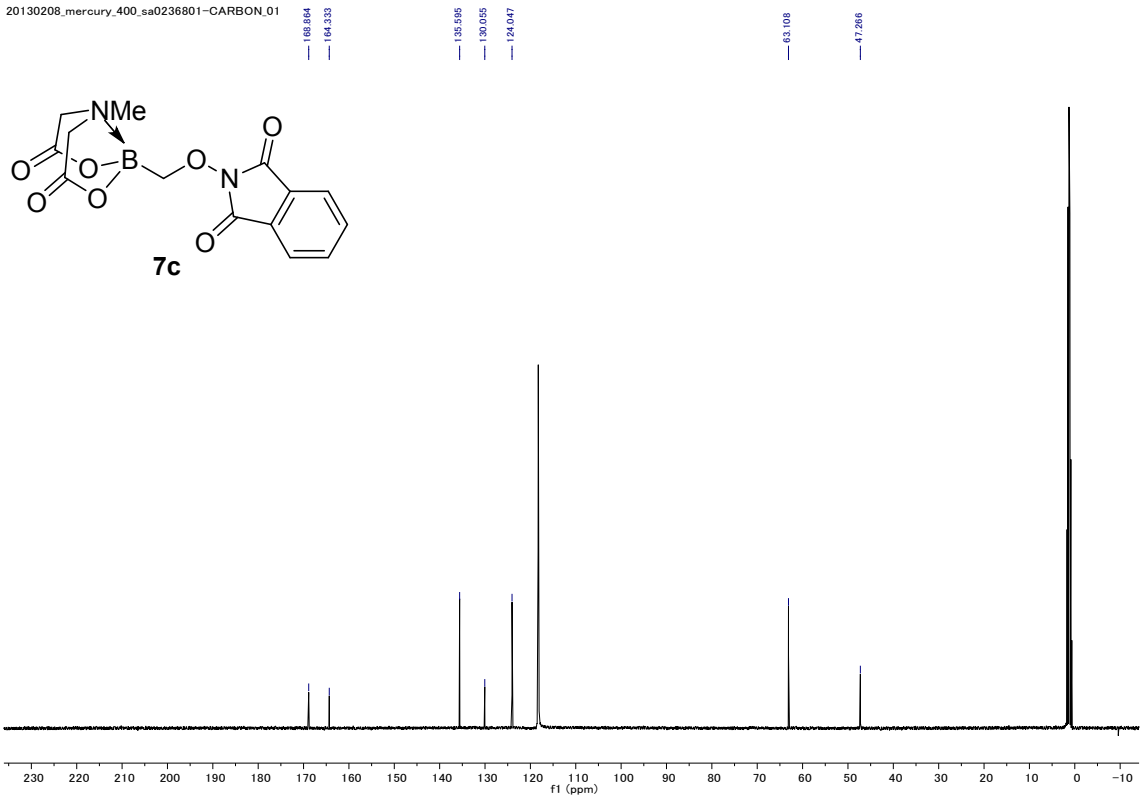

20130614_vnmrs_500_SA0394J2-PROTON_01
7.647
7.646
7.633
7.623
7.616
7.615
7.612
7.611
7.428
7.427
7.420
7.419
7.417
7.414
6.583
6.551
4.070
4.066
3.946
3.912
3.855
3.016
NMe
B
O
2.95
2.87
0.95
1.98
1.98
1.95
3.00
f1 (ppm)

7b

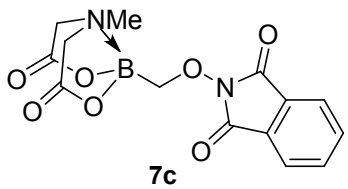

20130315_vnmrs_500_SA02394-CARBON_01
168.938
168.002
145.124
135.417
131.273
129.872
129.054
119.215
63.162
47.073
NMe
B
O
O
O
O
O
O
7b
f1 (ppm)


20141025_vnmrs_600_SA02394-BORON_01
20120717_DD2-600_CALIBRATIONS_BORON11_pw90_002
sample: BF3.Et2O
solvent: no lock solvent
pw180: 80 us
pw90: 40.0 us @ 62 dB
10.76
NMe
B
O
O
O
O
O
O
7b
f1 (ppm)


20130208_mercury_400_sa0236801-PROTON_01
7.806
4.086
4.066
4.043
3.946
3.903
3.328
NMe
O
O
B
O
N
O
O
O
O
7c
3.79
3.90
2.07
3.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

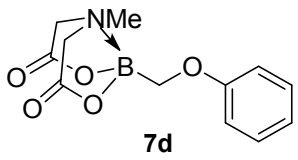

20130208_mercury_400_sa0236801-CARBON_01
168.864
164.333
135.595
130.055
124.047
63.108
47.266
NMe
O
O
B
O
N
O
O
O
O
7c
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

20130207-sadachi-SA0236801.2.fid
chem_Boron CD3CN /opt/data sadachi 50

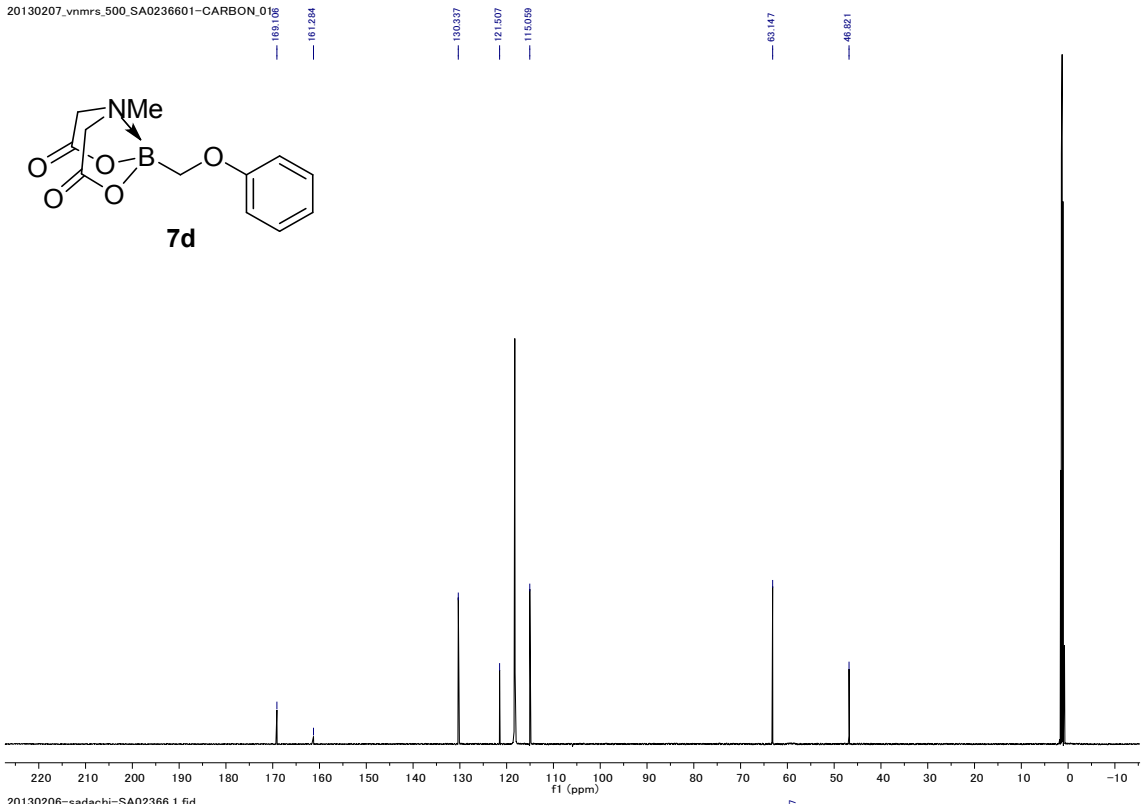


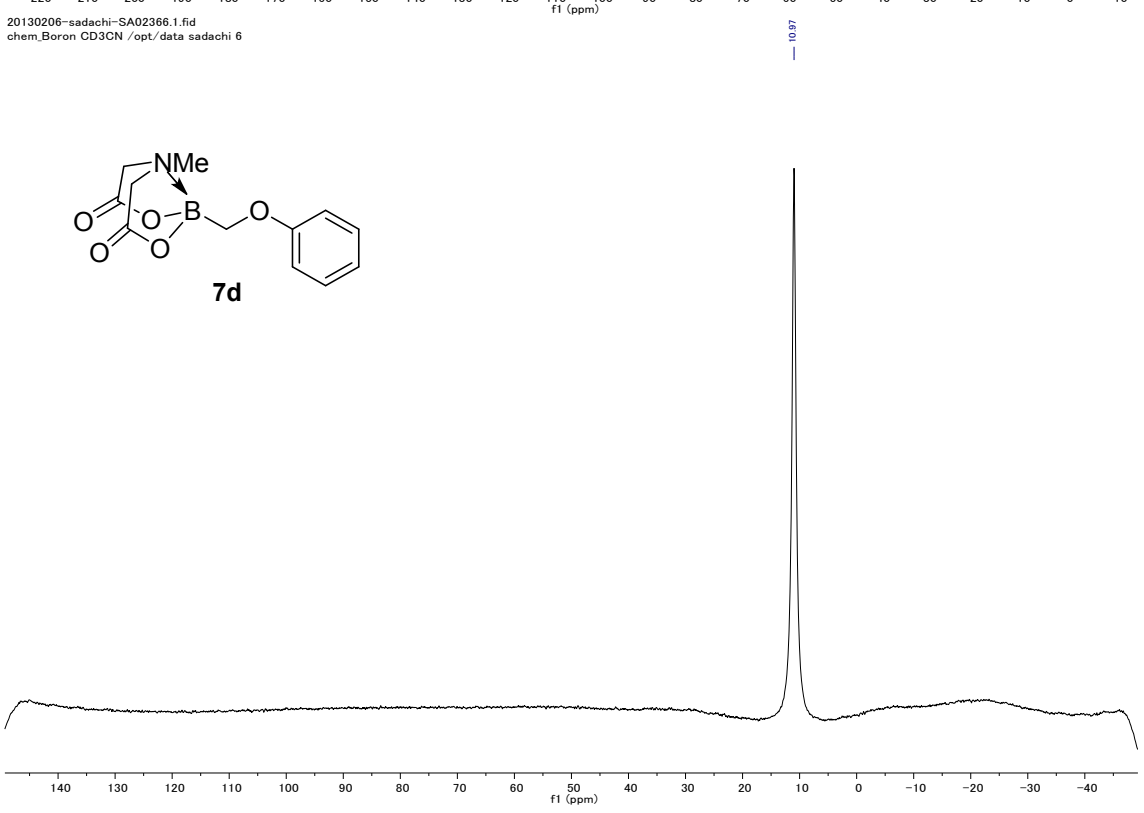
7c

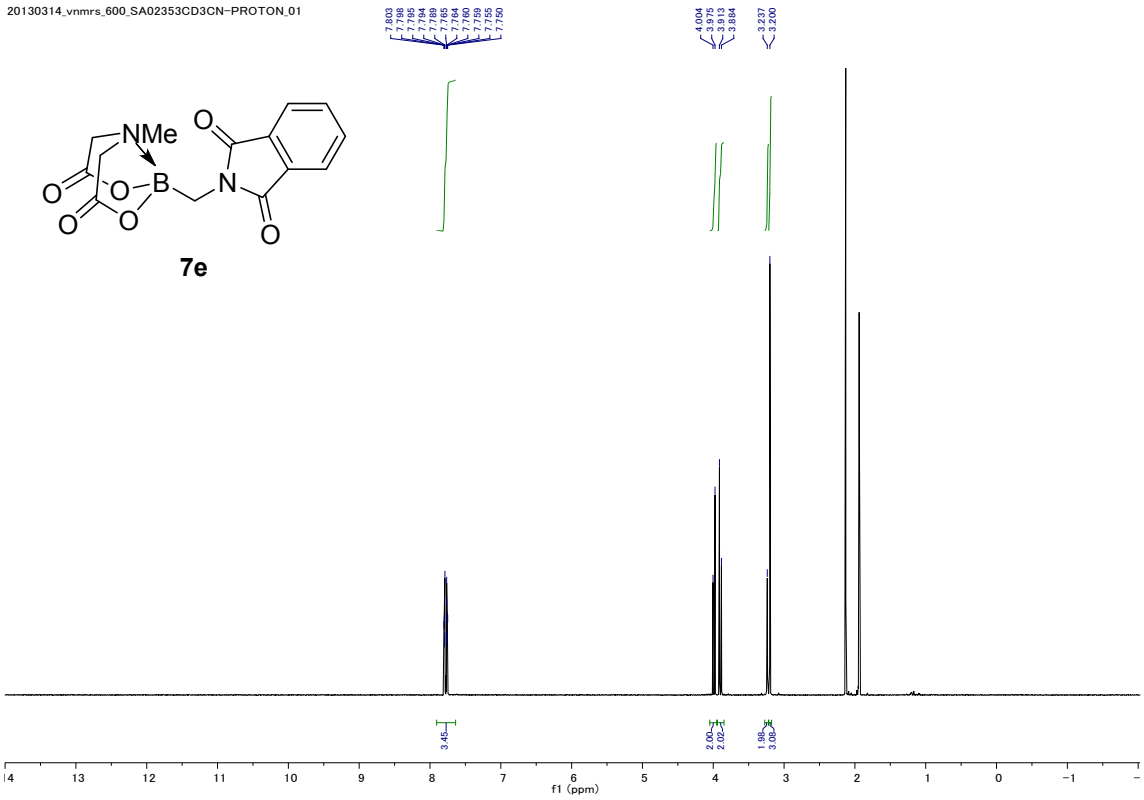
20130207_vnmrs_500_SA0236601-PROTON_02

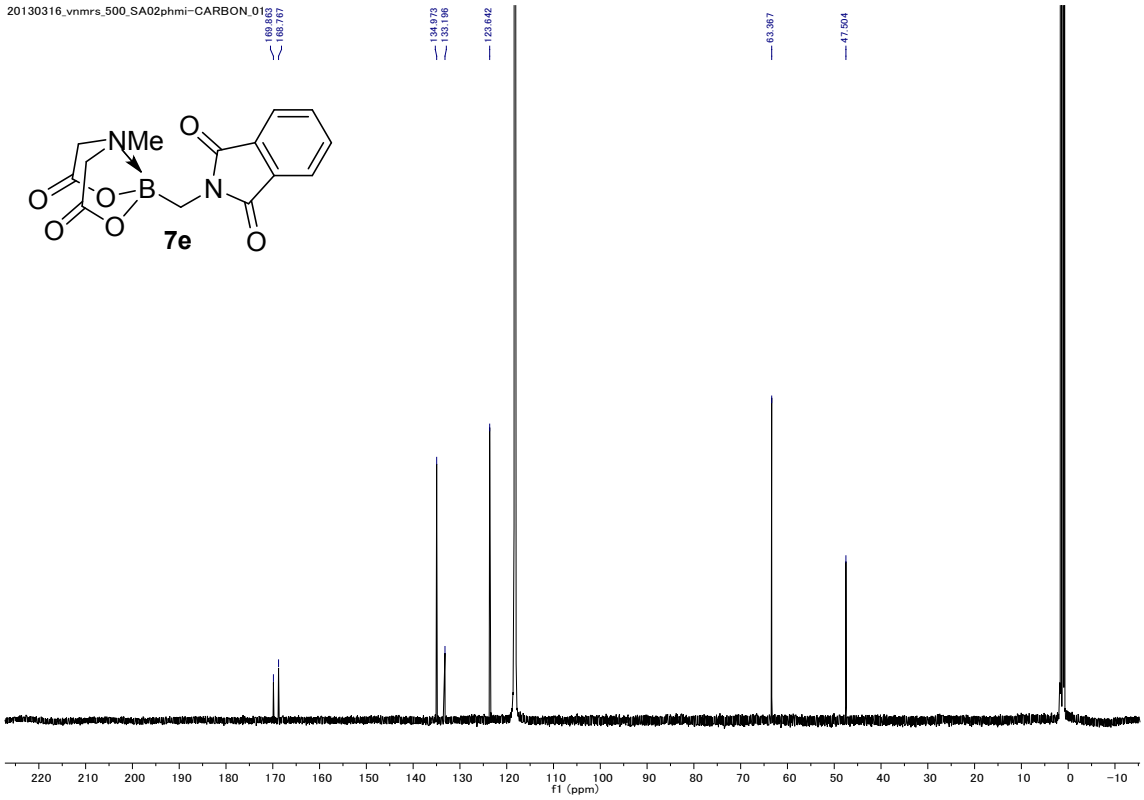


7d

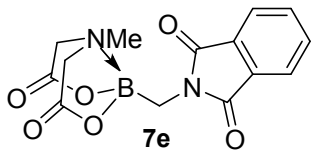

20130207_vnmrs_500_SA0236601-CARBON_01
169.106
161.284
130.337
121.507
115.059
63.147
46.821
NMe
O
O
B
O
O
O
7d
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


20130206-sadachi-SA02366.1.fid
chem_Boron CD3CN /opt/data sadachi 6
10.97
NMe
O
O
B
O
O
O
7d
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30 −40
f1 (ppm)


20130314_vnmrs_600_SA02353CD3CN-PROTON_01
7.803
7.798
7.795
7.794
7.789
7.765
7.764
7.760
7.756
7.755
7.750
4.004
3.975
3.913
3.884
3.237
3.200
NMe
B
N
O
7e
3.45
2.00
2.02
1.98
3.00
f1 (ppm)

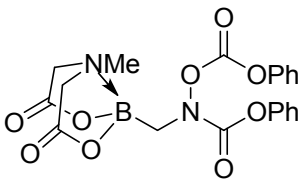

20130316_vnmrs_500_SA02phmi-CARBON_01
169.963
168.767
134.973
133.196
123.642
63.367
47.504
NMe
B
N
O
7e
f1 (ppm)

20130314_vnmrs_600_SA02353-BORON_01

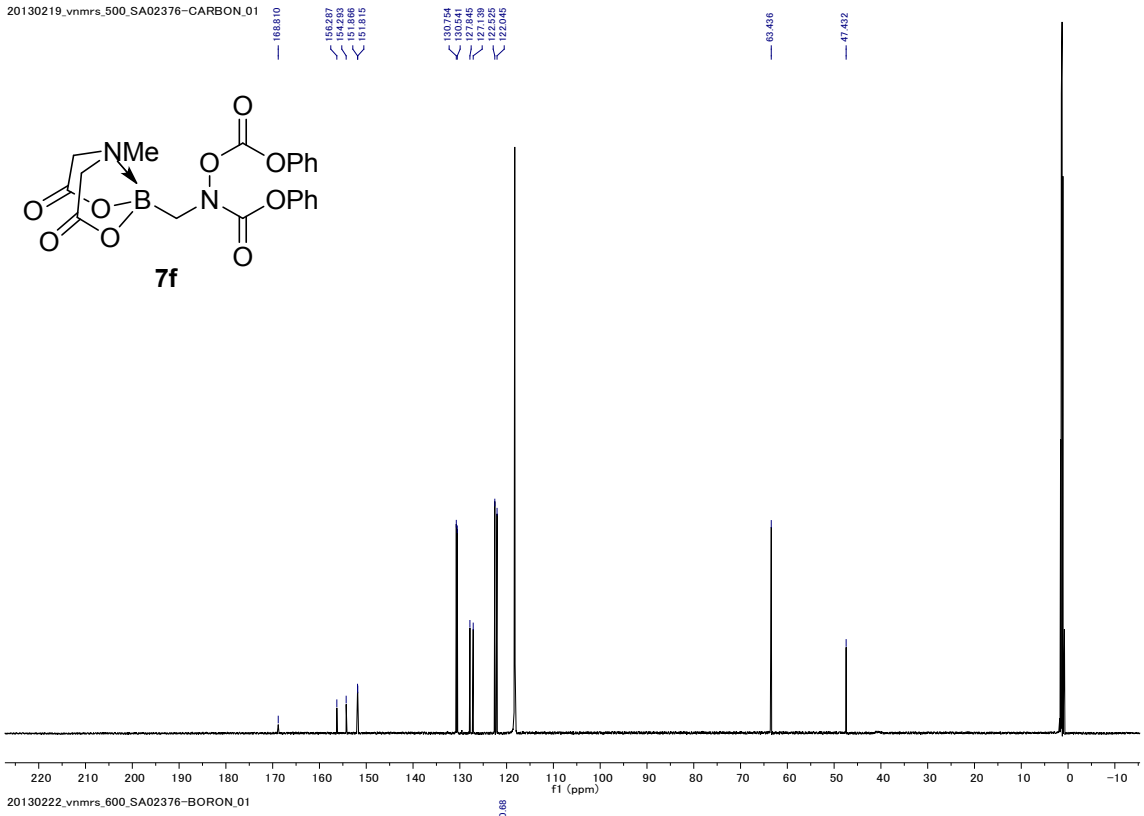


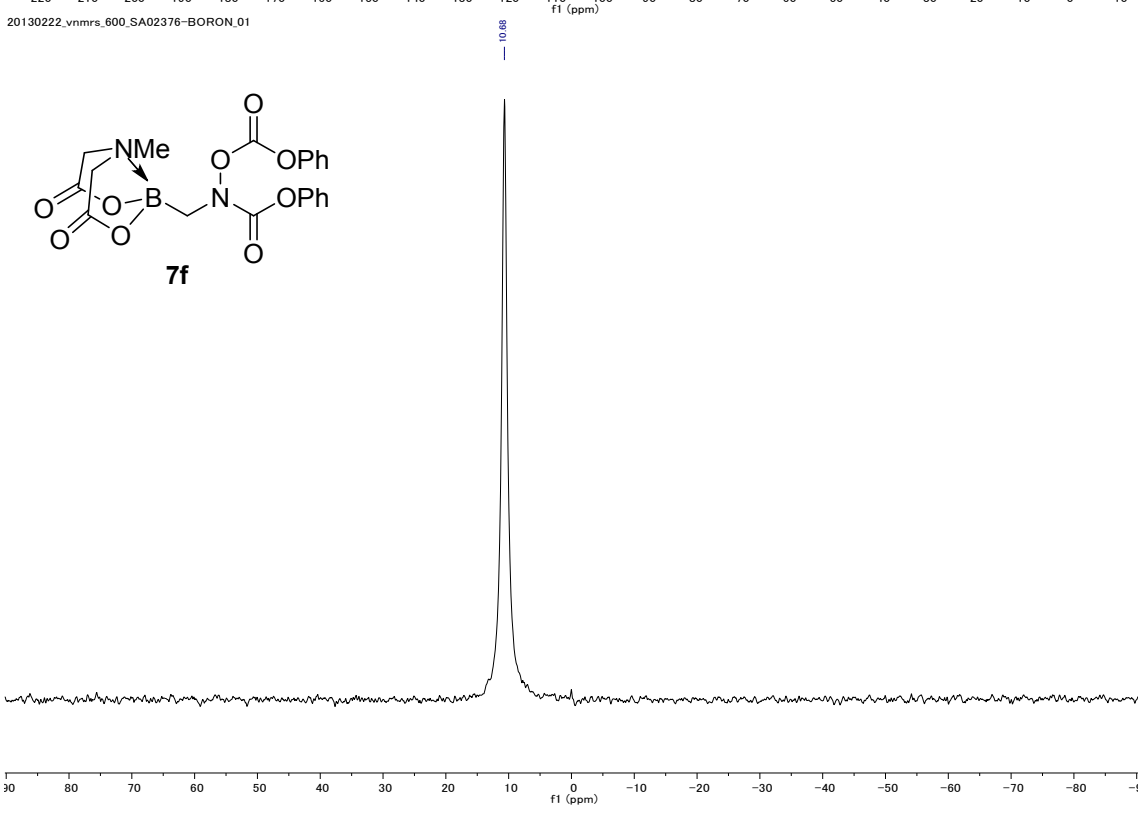
7e

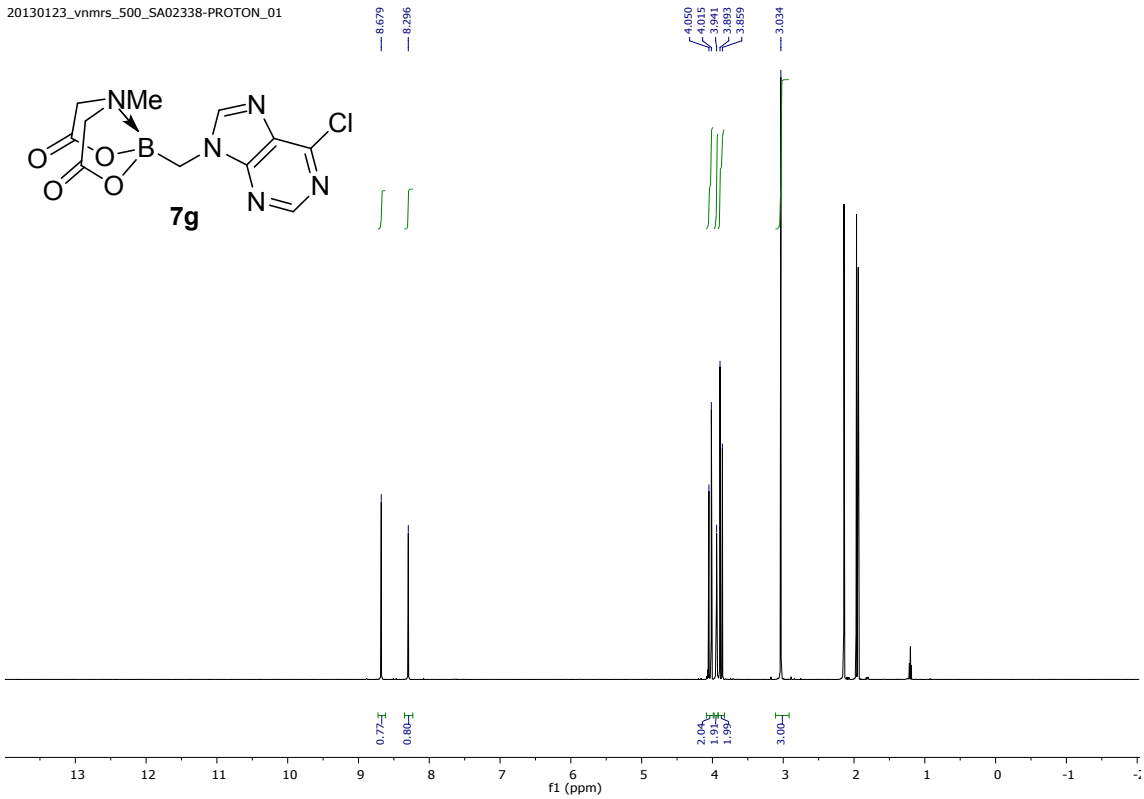
20130219_vnmrs_500_SA02376-PROTON_01

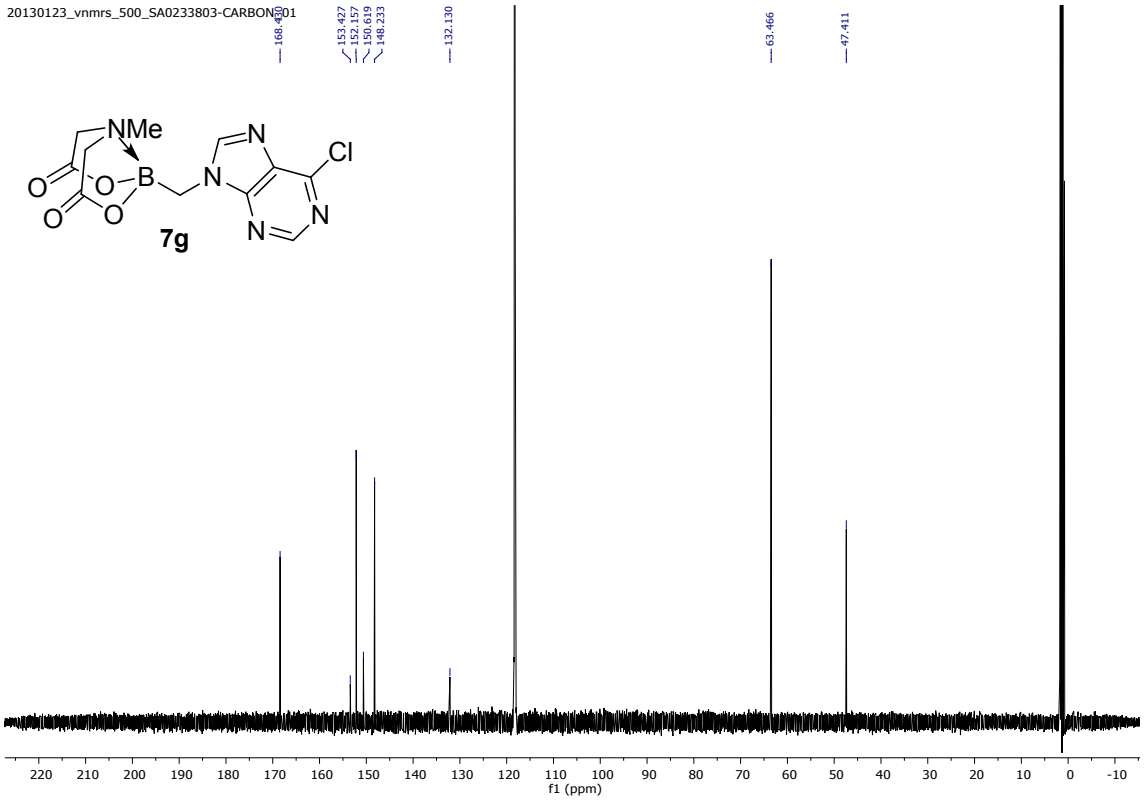


7f

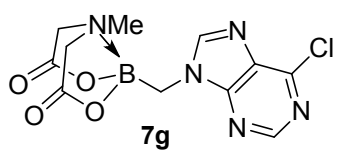

20130219_vnmrs_500_SA02376-CARBON_01
168.810
156.287
154.293
151.966
151.815
130.754
130.541
127.845
127.139
123.325
122.045
63.436
47.432
NMe
O
OPh
B
N
OPh
7f
f1 (ppm)


20130222_vnmrs_600_SA02376-BORON_01
10.68
NMe
O
OPh
B
N
OPh
7f
f1 (ppm)


20130123_vnmrs_500_SA02338-PROTON_01
8.679
8.296
4.050
4.015
3.941
3.893
3.859
3.034
NMe
B
O
N
Cl
7g
0.77
0.80
2.04
1.91
1.99
3.00
f1 (ppm)

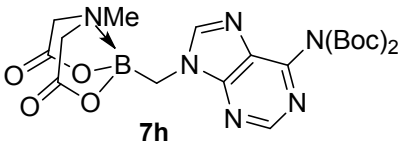

20130123_vnmrs_500_SA0233803-CARBON_01
168.460
153.427
152.157
150.619
148.233
132.130
63.466
47.411
NMe
B
O
N
Cl
7g
f1 (ppm)

20130125_vnmrs_600_SA0233802-s2pul_01

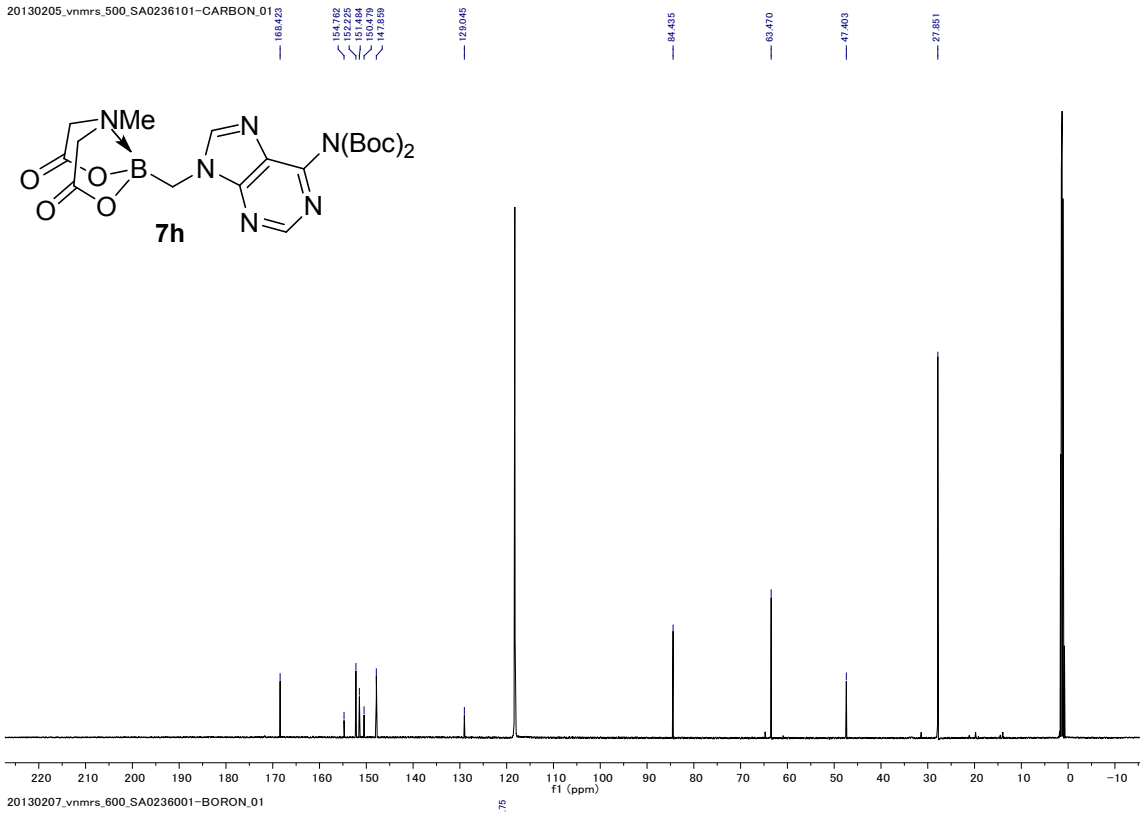


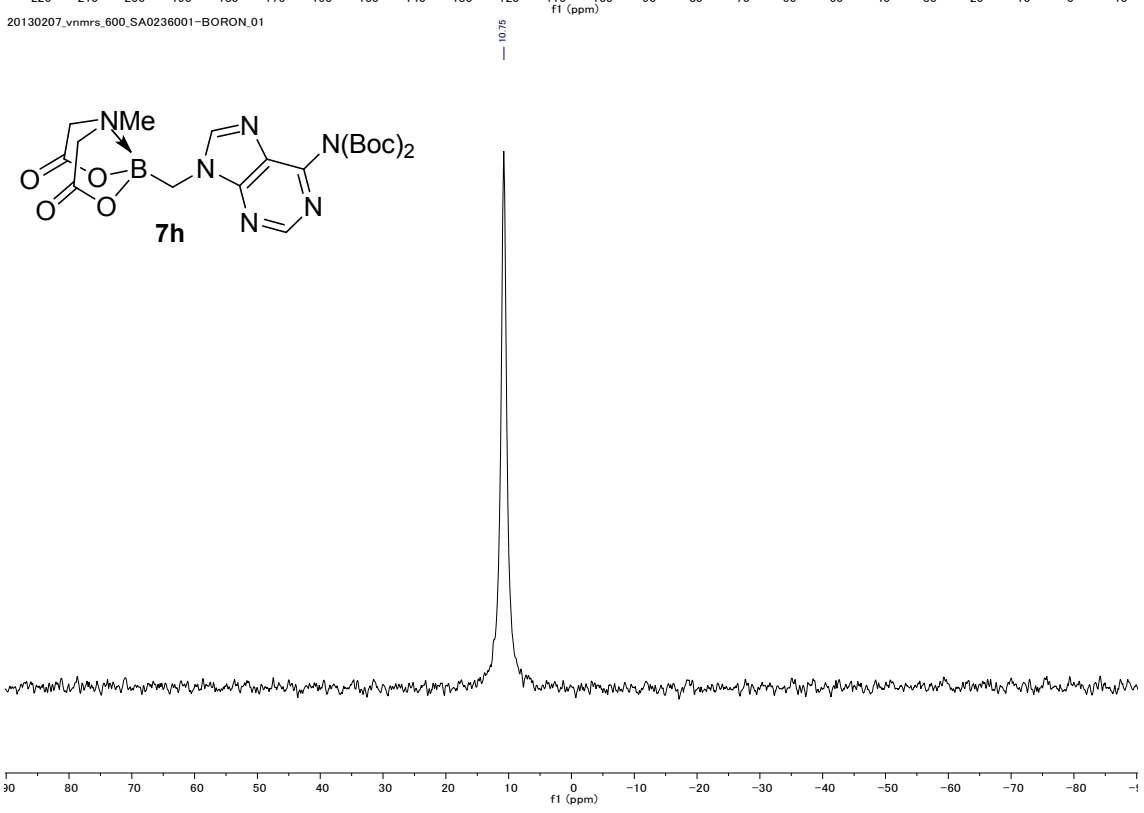
7g

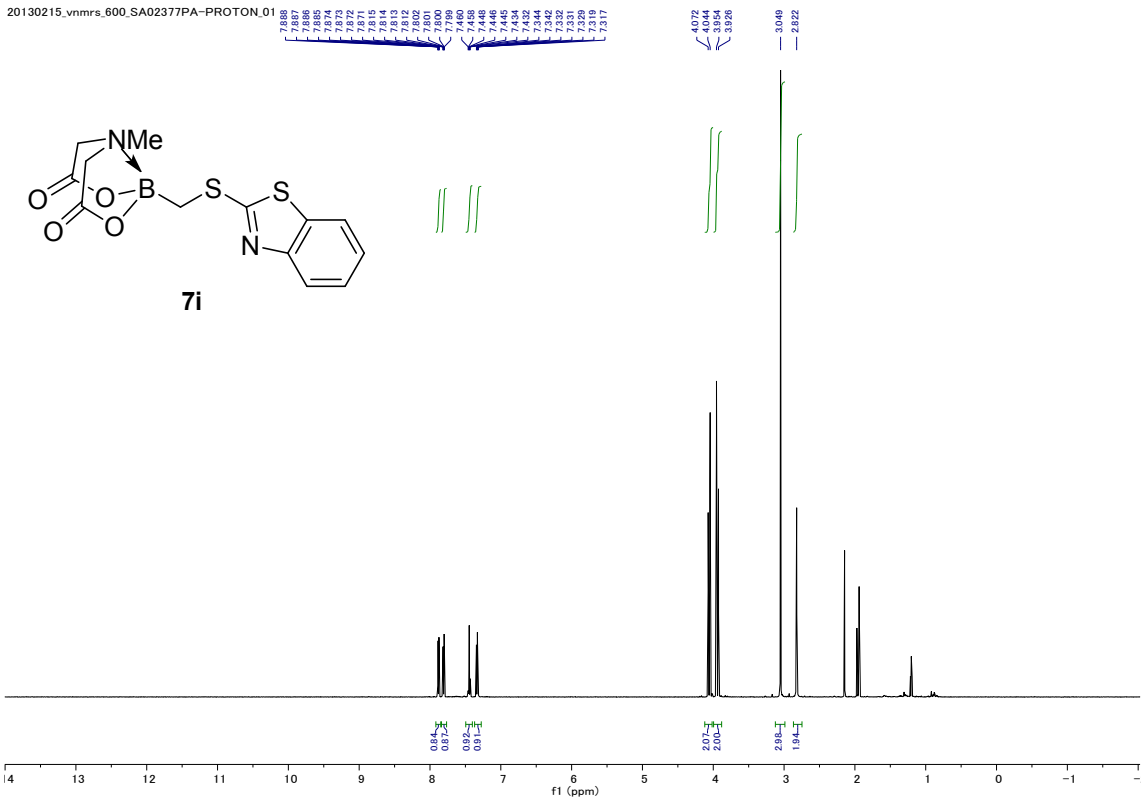
20130205_vnmrs_500_SA0236101-PROTON_03

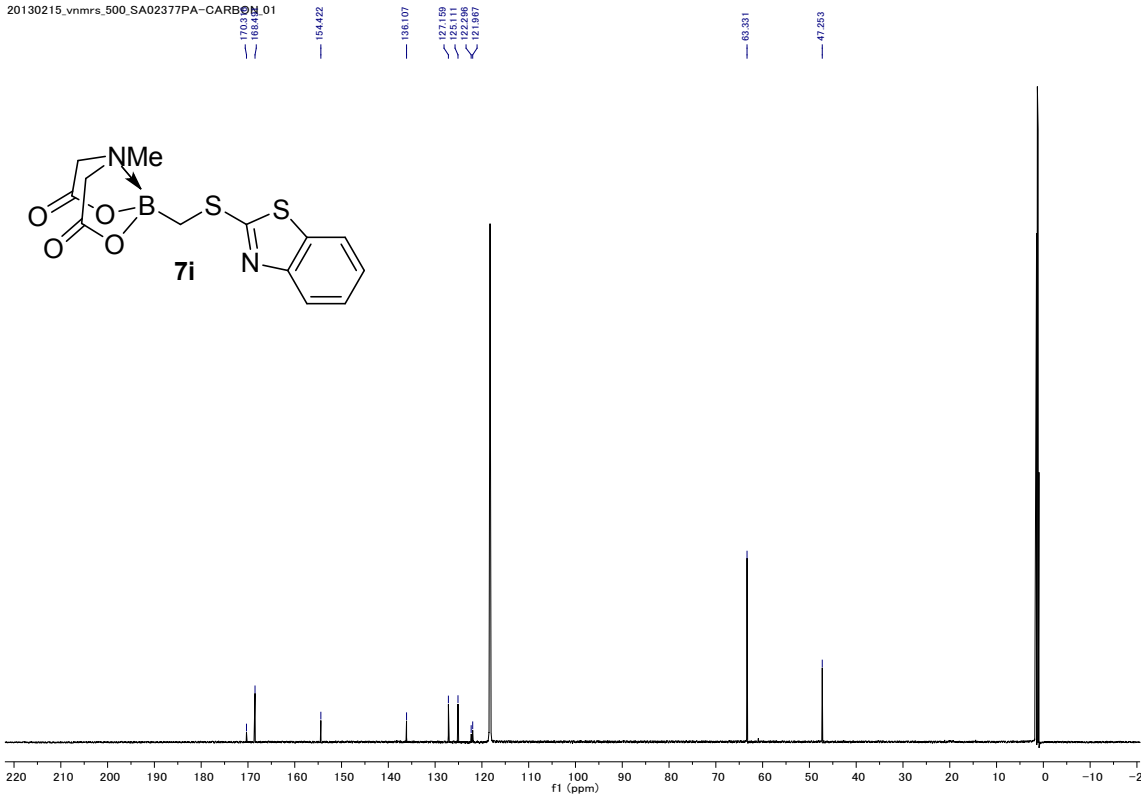


7h


20130205_vnmrs_500_SA0236101-CARBON_01
168.423
154.762
152.225
151.484
150.479
147.839
129.045
84.435
63.470
47.403
27.851
NMe
N(Boc)2
7h
f1 (ppm)


20130207_vnmrs_600_SA0236001-BORON_01
10.75
NMe
N(Boc)2
7h
f1 (ppm)

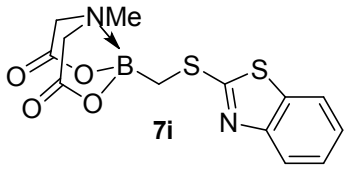

20130215_vnmrs_600_SA02377PA-PROTON_01
7.888
7.887
7.886
7.885
7.874
7.873
7.872
7.871
7.815
7.814
7.813
7.812
7.802
7.801
7.800
7.799
7.460
7.458
7.448
7.446
7.445
7.434
7.432
7.344
7.342
7.332
7.331
7.329
7.319
7.317
4.072
4.044
3.954
3.926
3.049
2.822
NMe
B
S
S
N
O
O
O
O
7i
0.84
0.87
0.92
0.91
2.07
2.00
2.98
1.94
f1 (ppm)


20130215_vnmrs_500_SA02377PA-CARBON_01
170.334
168.417
154.422
136.107
127.159
125.111
123.286
121.667
63.331
47.253
NMe
B
S
S
N
O
O
O
O
7i
f1 (ppm)

20141025_vnmrs_600_SA02377PA-BORON_01
20120717_DD2-600_CALIBRATIONS_BORON11_pw90_002

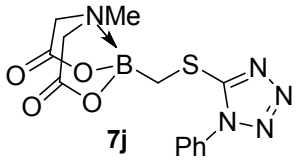
sample: BF3.Et2O
solvent: no lock solvent

pw180: 80 us
pw90: 40.0 us @ 62 dB

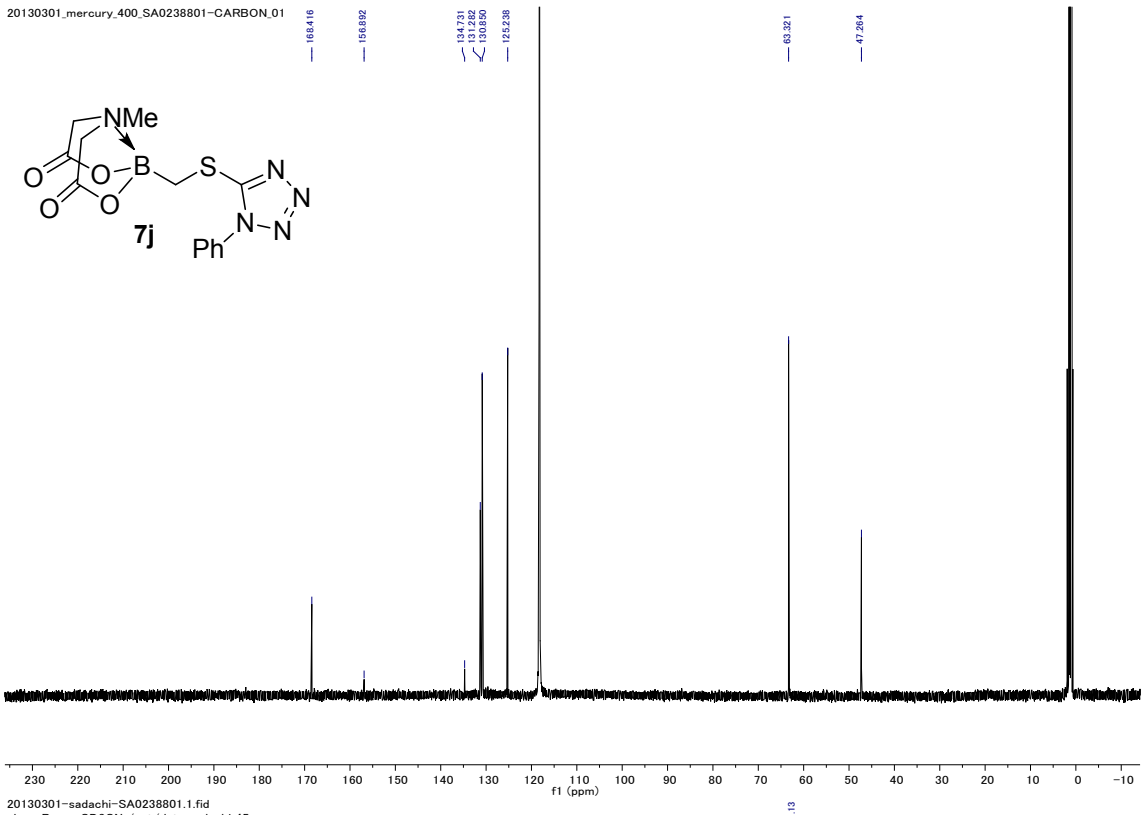


7i

20130301_vnmrs_400_SA0238801-PROTON_01
SA0238801



7j


20130301_mercury_400_SA0238801-CARBON_01
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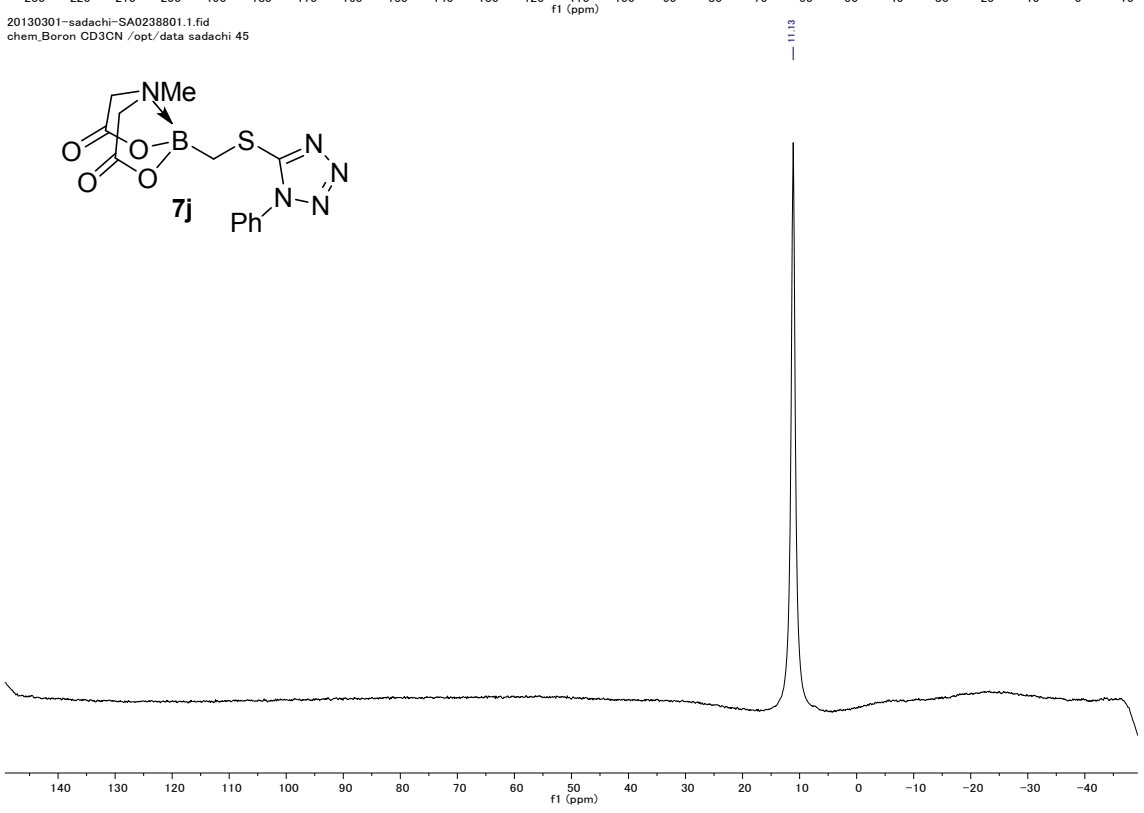
156.892
134.731
131.282
130.850
125.238
63.321
47.264
NMe
B
O
S
N
Ph
7j
f1 (ppm)


20130301-sadachi-SA0238801.1.fid
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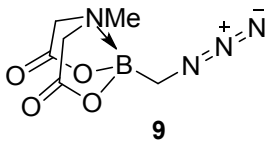
11.13
NMe
B
O
S
N
Ph
7j
f1 (ppm)

20130620_vnmrs_500_SA02316-PROTON_01



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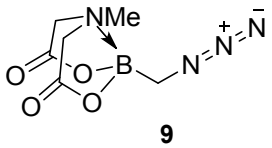

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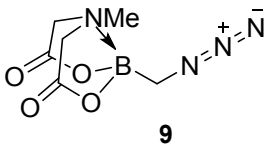

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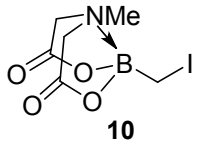

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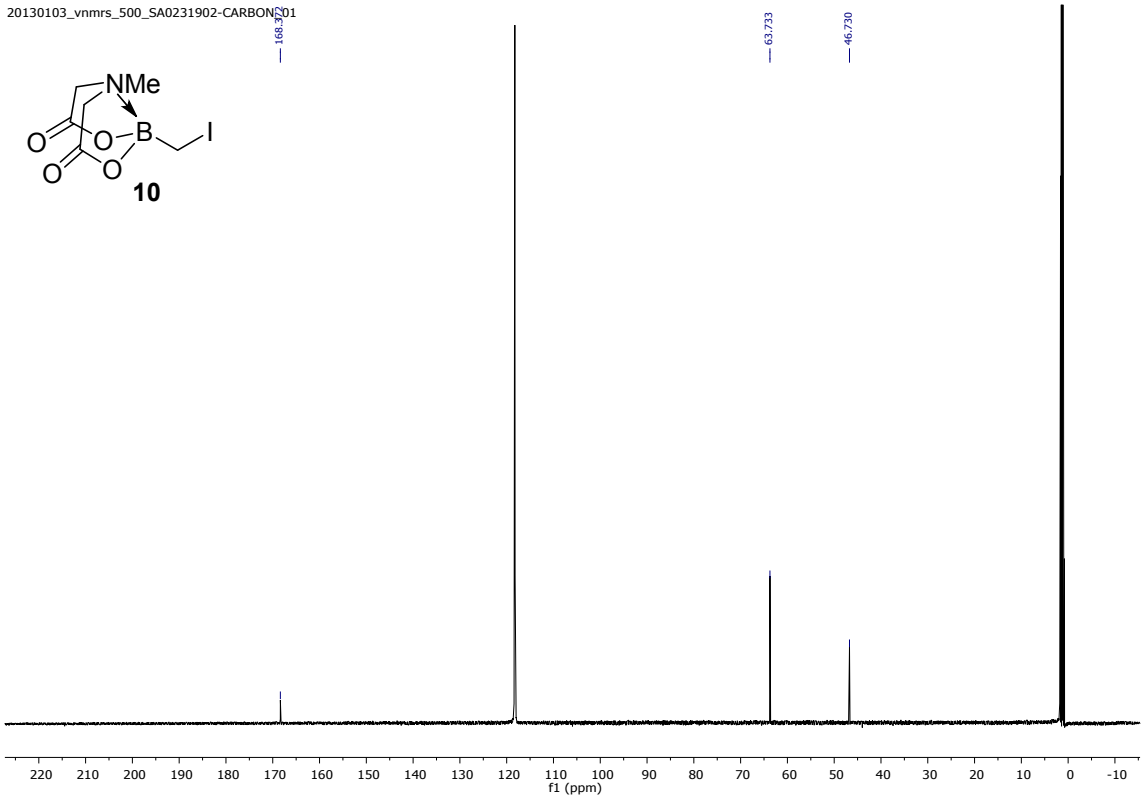
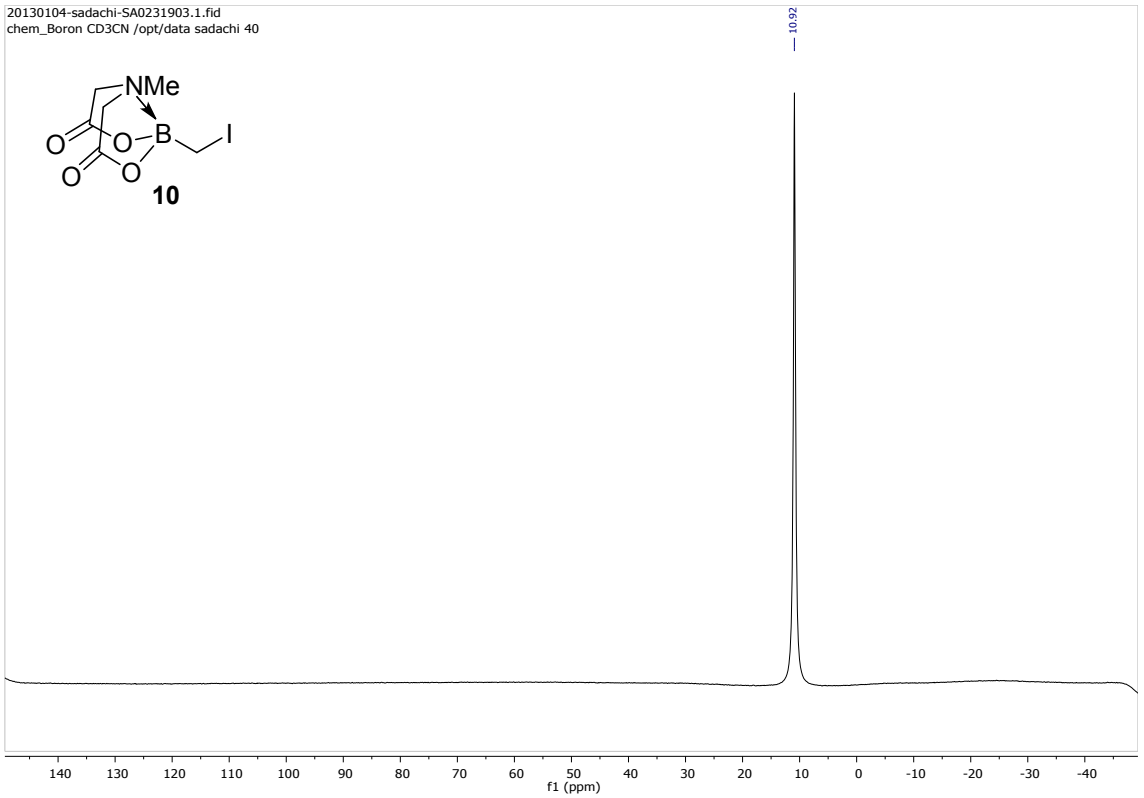
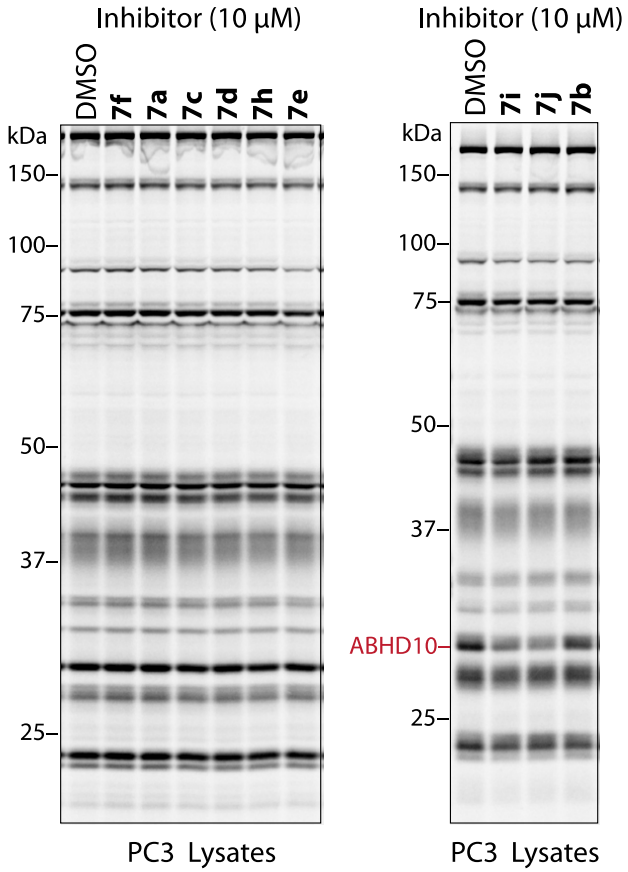

20130103_vnmrs_500_SA0231902-CARBON-01
168.377
63.733
46.730
NMe
B
I
O
O
O
O
10
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


20130104-sadachi-SA0231903.1.fid
chem_Boron CD3CN /opt/data sadachi 40
10.92
NMe
B
I
O
O
O
O
10
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

Activity-Based Protein Profiling (ABPP)



Supplementary Figure 1. *In vitro* gel-based competitive ABPP of (MIDA)boronates. The PC3 cell lysates were treated with DMSO or (MIDA)boronate **7** (10 µM) for 30 min followed by FP-Rh (30 min). Partial inhibition of a band corresponding to ABHD10 was observed for compounds **7i** and **7j**.

Cell Proteome Preparation. Cell proteomes were prepared from PC3 cells grown in RPMI-1640 media (Caisson Labs) with 10% FBS (Omega Scientific, Inc.). Cells were harvested with a cell scraper and washed 2x with Dulbeco's Phosphate Buffered Saline (DPBS) then lysed using probe sonication with the Branson Sonifier 250. Soluble cell fractions were prepared by ultracentrifugation (100,000 g, 45 min) of total cell lysates to remove membrane components (pellet). The DC Protein Assay from Bio-Rad was then used to measure proteome concentrations and proteomes were diluted in DPBS to 1.0 mg/mL total protein concentration for ABPP experiments.

***In Vitro* Competitive Activity-Based Protein Profiling.** Cell proteomes (50 μL, 1 mg/mL) were treated with inhibitors (1 μL in DMSO) or DMSO (1 μL) and incubated for either 30 or 120 minutes at 37 °C. Fluorophosphonate-Rhodamine (FP-Rh) (1 μL, 50 μM in DMSO) was then added to each proteome and incubated for another 30 minutes at room temperature. Samples were then quenched with 4X SDS Loading Buffer (17 μL) and proteins were resolved by SDS-PAGE (10% Acrylamide Gels made in-house). Serine hydrolase activity was determined after fluorescent gel imaging on a Hitachi FMBio II by quantifying the fluorescence intensity of target gel bands using ImageJ 1.45s.

***In Vitro* Competitive SILAC-ABPP.** SILAC (Stable Isotope Labeling by Amino Acids in Cell Culture)-ABPP experiments and analyses were performed as described before.[5,6,7] Briefly, cell pellets from 'heavy' and 'light' labeled cells were lysed in DPBS using probe sonication, and protein concentration was determined using the DC Assay. Heavy and light protein samples (500 μL, 2 mg/mL) were incubated separately at 37 °C for 2 h with inhibitor (1 μL in DMSO) or DMSO (1 μL), respectively. The samples were then incubated with FP-Biotin (500 μM, 1 μL) for 60 minutes at room temperature and then quenched by combining them into a methanol:chloroform mixture (4:1, 2.5 mL). The FP-labeled proteins were enriched, trypsin-digested and the tryptic peptides resolved by two-dimensional liquid chromatography using strong cation exchange and C18 resins and analyzed by tandem MS using an Agilent 1100-series quaternary pump and Thermo Scientific LTQ Orbitrap ion trap mass spectrometer. MS2 data were searched using the ProLuCID algorithm (http://fields.scripps.edu/downloads.php) against a UniProt human protein sequence database concatenated with a reverse decoy database for false positive assessment. Heavy and light peptides identified from the ProLuCID search were quantified by in-house software described previously.[8]

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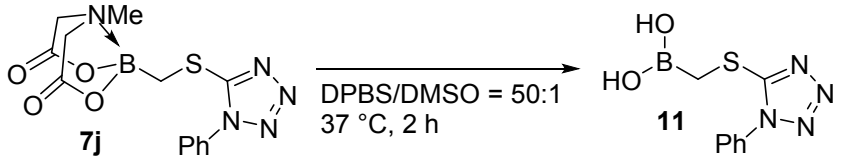
5) A. Adibekian, B. R. Martin, C. Wang, K.–L. Hsu, D. A. Bachovchin, S. Niessen, H. Hoover and B. F. Cravatt, *Nat. Chem. Biol.,* 2011, **7**, 469–478.
6) A. M. Zuhl, J. T. Mohr, D. A. Bachovchin, S. Niessen, K.–L. Hsu, J. M. Berlin, M. Dochnahl, M. P. López-Alberca, G. C. Fu and B. F. Cravatt, *J. Am. Chem. Soc.,* 2012, **134**, 5068–5071.
7) A. J. Link, J. Eng, D. M. Schieltz, E. Carmack, G. J. Mize, D. R. Morris, B. M. Garvik and J. R., III Yates, *Nat. Biotechnol.,* 1999, **17**, 676–682.
8) E. Weerapana, C. Wang, G. M. Simon, F. Richter, S. Khare, M. B. D. Dillon, D. A.

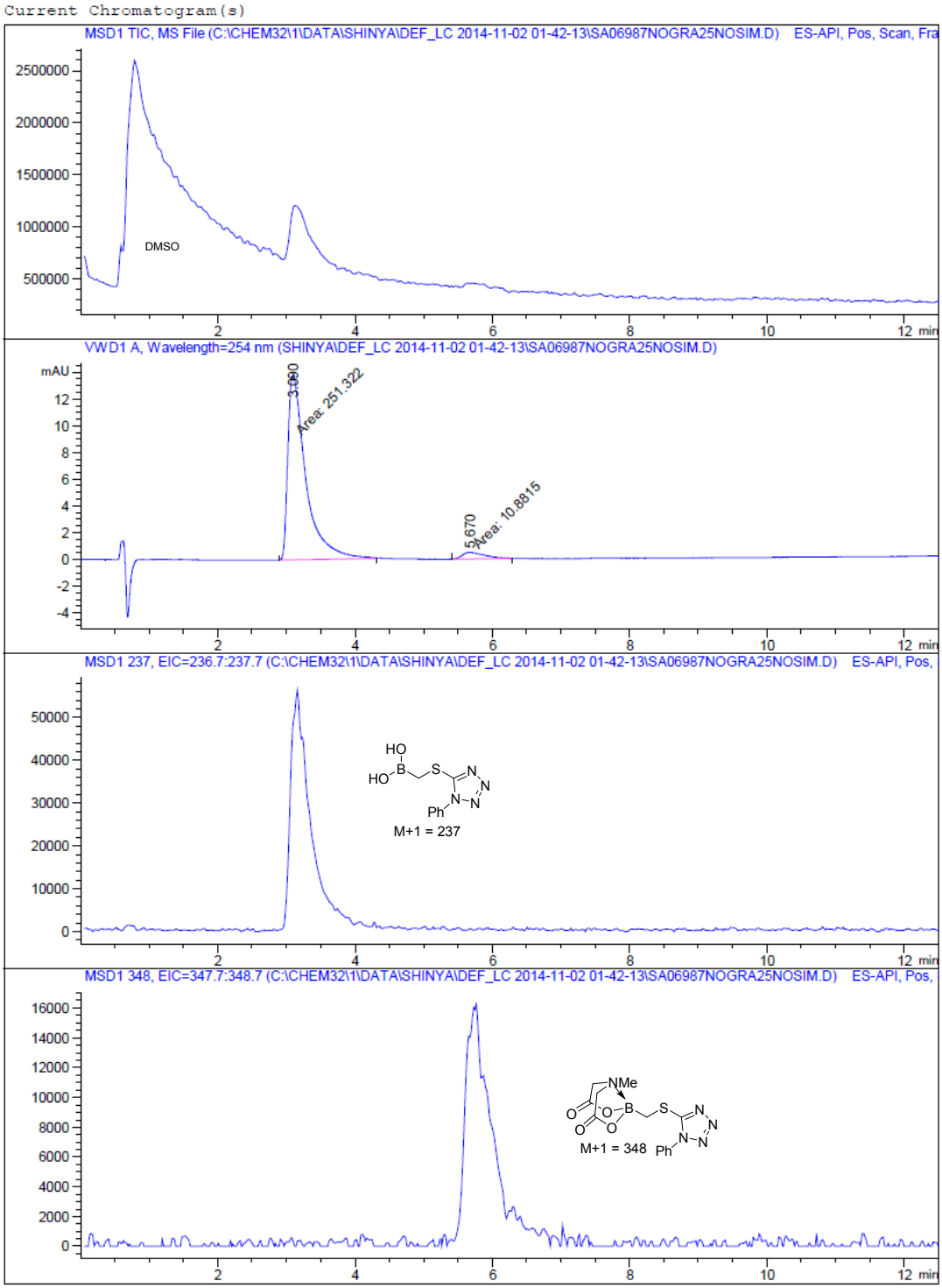
Stability of 7j in DPBS/DMSO



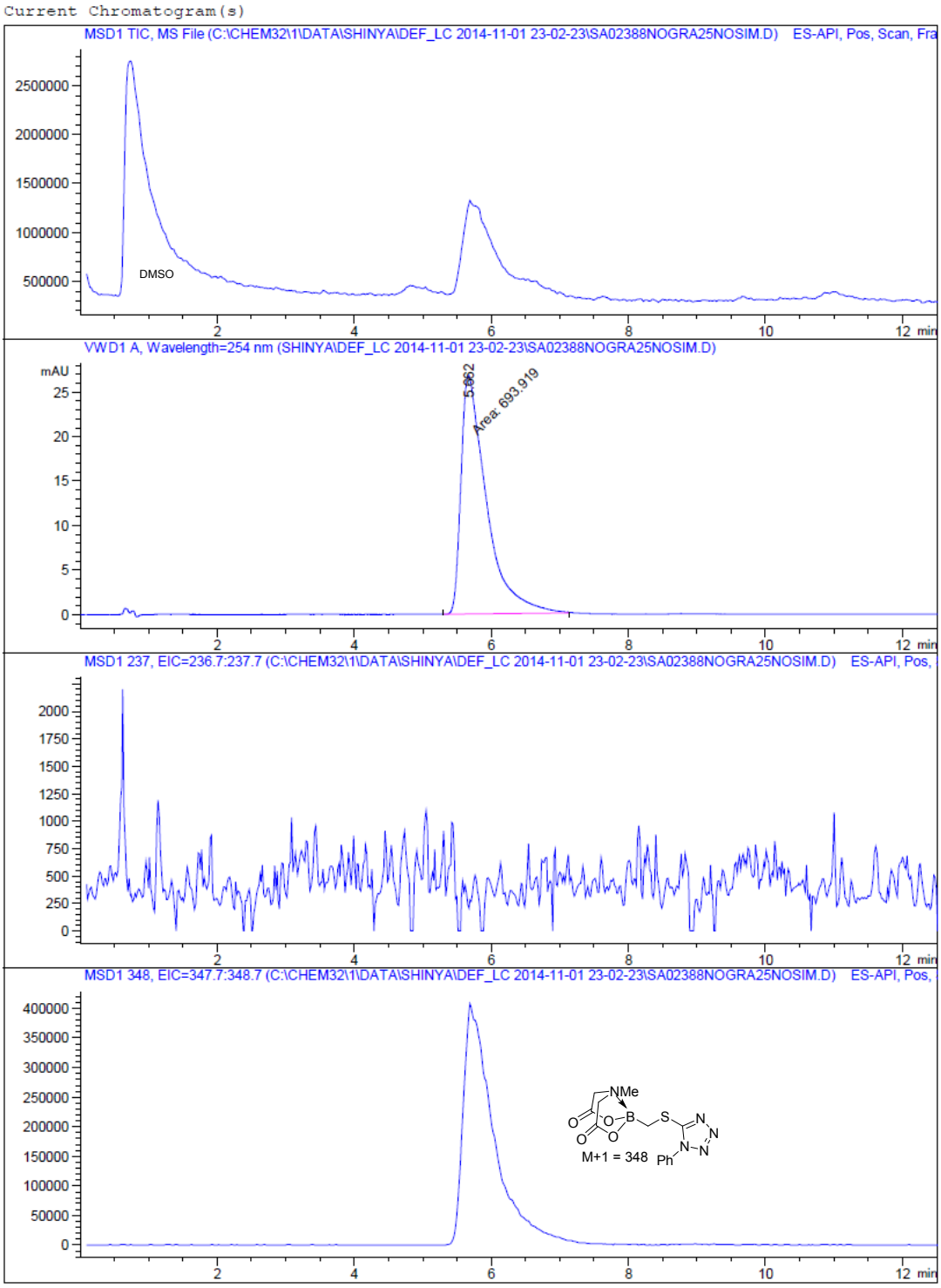
DPBS (980 μL) was added to a DMSO (20 μL) solution of compound **7j** (0.35 mg, 1 μmol) (pH 7.0). The resulting mixture was stirred at 37°C for 2 h. RP-HPLC/MS analysis showed the formation the corresponding boronic acid **11** (M+1 =237) (Flow: 1 mL/min, mobile phase: MeCN + formic acid 0.09% : Water + formic acid 0.1% = 25:75 (no gradient). retention times: 3.1 min (**11**), 5.7 min (**7j**) UV (254 nm) peak area ratio: **11**:**7j** = 251:11). RP-HPLC/MS analysis of **7j** in MeCN/DMSO (50/1) (1000 μM) under the same analytical condition did not show the presence of **11**.

Bachovchin, K. Mowen, D. Baker and B. F. Cravatt, *Nature,* 2010, **468**, 790−795.

7j in DPBS/DMSO (50/1) (after 2 h)



7j in MeCN/DMSO (50/1)



DPBS/DMSO (50/1) (Blank)