**Supporting Information for:**

# Borylated Oximes: Versatile Building Blocks for Organic Synthesis

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**General Information**

The following reagents were used directly from commercial suppliers: dimethylforamide (DMF) and dimethylsulfoxide (DMSO) from Fischer; trifluoroacetic acid (TFA), N,N-diisopropylethylamine (DIPEA) from Sigma Aldrich; 4-methylpiperidine from Alfa Aesar; HATU (1-[Bis(dimethylamino)methylene]-1H-1,2,3-triazolo[4,5-b]pyridinium 3-oxid hexafluorophosphate) from Chem-Impex Int'l.; HCTU (o-(1- benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate) from Peptides International; Fmoc-protected amino acids from Bachem, and Rink Amide resin (200-400 mesh, 0.68 mmol/gram) from Novabiochem. Water was purified using a Millipore Milli-Q water purification system.

DCM, Methanol (MeOH) and triethylamine were distilled from $CaH_2$ under nitrogen. Acetonitrile (MeCN) was distilled from activated 4Å MS under nitrogen. Toluene was purified via solvent purification system. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl. All other solvents were of reagent grade quality and dried over 4Å MS prior to use. All other reagents were purchased from commercial sources and used as received.

Buffer A: $H_2O$ (0.05% TFA)

Buffer B: MeCN/$H_2O$ (9:1) (0.05% TFA)

**Chromatography**

Flash column chromatography was carried out using Silicycle 230-400 mesh silica gel, or ISCO Teledyne Combiflash $R_f$ 200 Flash system. Thin-layer chromatography (TLC) was performed on Macherey Nagel pre-coated glass backed TLC plates (SIL G/UV254, 0.25 mm) and visualized using a UV lamp (254 nm), $KMnO_4$ or curcumin stain. Reverse-phase chromatography was carried out using Redi*Sep* Rf Gold C18 Columns.

Peptides were purified by reversed-phase HPLC (RP-HPLC). Analytical RP-HPLC was carried out on an Agilent 1100 Series HPLC on a Phenomenex Jupiter Proteo column (4 µm, 90 2 Å, 150 × 4.6 mm) at a flow rate of 1 mL/min. Analytical injections were monitored at 214 nm. Preparative RP-HPLC was performed on a Waters Delta Prep 4000 equipped with a Waters UV detector model 486 and a Phenomenex Jupiter Proteo column (10 µm, 90 Å, 250 × 21.20 mm) at a flow rate of 15 mL/min. Preparative injections were monitored at 220 nm.

**Nuclear Magnetic Resonance Spectroscopy**

$^{1}$H NMR, $^{13}$C, and 2D NMR spectra were recorded on Varian Mercury 300 MHz, 400 MHz, 500 MHz, 600 MHz or 700 MHz spectrometers. $^{11}$B NMR were recorded using Bruker 400/500 MHz spectrometer at 128/160 MHz and referenced to an external standard of $BF_3 \cdot Et_2O$ ($\delta$ = 0 ppm). $^{1}$H NMR spectra chemical shifts ($\delta$) are reported in parts per million (ppm) referenced to residual protonated solvent peak ($CD_3CN$ $\delta$ = 1.94, DMSO-$d_6$, $\delta$ = 2.49, $CD_3OD$ $\delta$ = 3.31 center line). Spectral data is reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, ddt = doublet of doublet of triplets, dtd = doublet of triplet of doublets, m = multiplet, br = broad), coupling constant (*J*) in Hertz (Hz), and integration. $^{13}$C NMR spectra chemical shifts ($\delta$) are reported in parts per million (ppm) were referenced to carbon resonances in the NMR solvent ($CD_3CN$ $\delta$ = 118.3, DMSO-$d_6$, $\delta$ = 39.5, $CD_3OD$ $\delta$ = 49.0; center line). Carbons exhibiting significant line broadening brought about by boron substituents were not reported (quadrupolar relaxation). Carbons that were observed are noted (**C**-B).

**Mass Spectroscopy** 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.

Peptides were characterized using electrospray ionization MS on a LC-MS API 2000 Plus triple quadrupole mass spectrometer (Sciex). Peptides masses were calculated from the experimental mass to charge (m/z) ratios from all of the observed protonation states of a peptide by using the onboard analyst software package (Sciex). High resolution mass spectrometry (for **2d**) was performed Agilent ESI-TOF mass spectrometer using electrospray ionization. Samples were electrosprayed into the TOF reflectron analyzer at an ESI voltage of 4000V and a flow rate of 200 microliters/minute.

**RP-HPLC/MS**

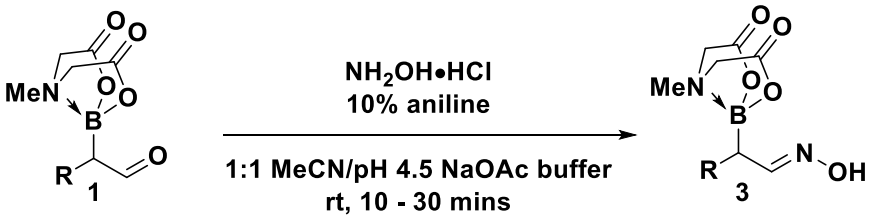
Low-resolution mass spectra (ESI) were collected on an Agilent Technologies 1200 series HPLC paired to a 6130 Mass Spectrometer. Compounds were resolved on Phenomenex's Kinetex 2.6u C18 50x4.6mm column at room temperature with a flow of 1 mL/min. The gradient consisted of

eluents A (0.1% formic acid in double distilled water) and B (0.1% formic acid in HPLC-grade acetonitrile).

*Method*: A linear gradient starting from 5% of B to 95% over 4 min at a flow rate of 1.0 mL/min. Stays constant at 95% for 1 min and then returns to 5% over 0.5 min.

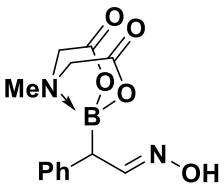
**Experimental Data**

**General Procedure for the Synthesis of α-boryl aldoximes**

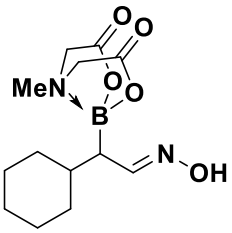



Boryl aldehyde (1 equiv.) and hydroxylamine hydrochloride (3 equiv.) were dissolved in a 1:1 acetonitrile:0.1 M pH 4.5 sodium acetate buffer to yield a final concentration of 0.1 M. Aniline (0.1 equiv.) was immediately added and the solution was stirred for 10 to 30 minutes. When the reaction was complete by TLC, brine was added and the product was extracted into 10% acetonitrile in EtOAc, dried over sodium sulfate, concentrated, and purified by column chromatography.

**(*E*)-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-phenylacetaldehyde oxime (3a).**

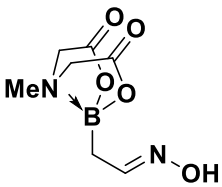



Synthesized according to general procedure. Scale: 1.82 mmol. Yield: 0.444 g, 84%, white solid. $R_f$ (EtOAc): 0.28. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 8.43 (s, 1H), 7.49 (dd, $J$ = 5.8, 0.8 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.26 – 7.18 (m, 3H), 4.01 – 3.92 (m, 3H), 3.77 (dd, $J$ = 17.2, 0.6 Hz, 1H), 3.21 (d, $J$ = 5.9 Hz, 1H), 3.00 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 169.0, 168.8, 153.9, 141.5, 130.0, 129.3, 126.8, 118.3, 64.2, 64.1, 47.0. $^{11}$B NMR (96 MHz, $CD_3CN$) $\delta$ 12.0. IR (neat) $\tilde{\nu}$ ($cm^{-1}$): 3233, 1767, 1747, 1305, 1097, 1026, 1005, 947, 878, 702. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{16}BN_2O_5$ 291.1152, found 291.1162.

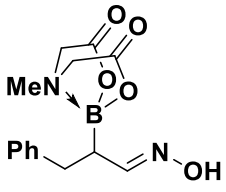
**(*E*)-2-cyclohexyl-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)acetaldehyde oxime (3b).** 

Synthesized according to general procedure. Scale: 0.20 mmol. Yield: 0.045 g, 75%, white powder. $R_f$ (EtOAc): 0.15. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 8.32 – 8.16 (m, 1H), 7.36 (d, $J$ = 8.3 Hz, 1H), 3.93 (d, $J$ = 17.2 Hz, 1H), 3.89 (d, $J$ = 16.6 Hz, 1H), 3.81 (d, $J$ = 17.2 Hz, 1H), 3.65 (d, $J$ = 16.6 Hz, 1H), 2.92 (s, 3H), 1.89 – 1.77 (m, 2H), 1.78 – 1.66 (m, 2H), 1.67 – 1.54 (m, 1H), 1.38 – 1.01 (m, 6H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 169.3, 168.7, 154.0, 63.4, 63.2, 46.7, 39.3, 34.4, 30.9, 27.7, 27.6, 27.0. $^{11}$B NMR (128 MHz, $CD_3CN$) $\delta$ 7.5. IR (neat) $\tilde{\nu}$ (cm$^{-1}$): 3333, 2928, 2855, 1748, 1727, 1452, 1284, 1026, 977, 856. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{22}BN_2O_5$ 297.1622, found 297.1624.

**(*E*)-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)acetaldehyde oxime (3c).** This product is unstable to long-term storage. Modified procedure: Boryl aldehyde (0.050 g, 0.25 mmol) and hydroxylamine hydrochloride (0.035 g, 0.50 mmol) were dissolved in acetonitrile (2.5 mL) and Amberlite IRA67 resin (1 scoop) was added and stirred until the starting materials dissolved. The reaction was monitored by TLC to assess reaction completion. Once complete, Amberlite IRA743 resin (1 scoop) was added to sequester the boric acid from decomposition. The solution was filtered, and resin washed with acetonitrile, and evaporated to yield pure product, which was used directly for the next reaction. Yield: 0.040 g, 74%, white hygroscopic powder, mixture of *E* and *Z* isomers. $R_f$ (1:4 MeCN:EtOAc): 0.2. $^1$H NMR (500 MHz, $CD_3CN$) Minor: $\delta$ 7.38 (t, $J$ = 6.1 Hz, 1H), 3.96 (d, $J$ = 16.9 Hz, 2H), 3.84 (d, $J$ = 16.9 Hz, 2H), 2.93 (s, 3H), 1.68 (d, $J$ = 6.1 Hz, 2H). Major: $\delta$ 6.70 (t, $J$ = 6.7 Hz, 1H), 3.95 (d, $J$ = 16.9 Hz, 2H), 3.81 (d, $J$ = 16.9 Hz, 2H), 2.93 (s, 3H), 1.91 (d, $J$ = 6.7 Hz, 2H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 168.9, 168.8, 150.6, 150.2, 63.3, 62.8, 47.0, 46.7. $^{11}$B NMR (128 MHz, $CD_3CN$) $\delta$ 11.8. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_7H_{12}BN_2O_5$ 215.0839, found 215.0839.

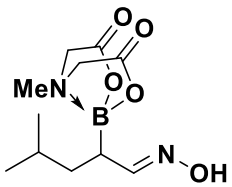


**(*E*)-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-3-phenylpropanal oxime (3d).**



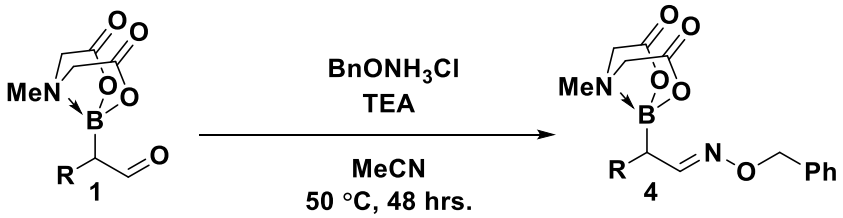
Synthesized according to general procedure. Scale: 0.85 mmol. Yield: 0.24 g, 94%, white powder. $R_f$ (1:9 MeCN:EtOAc): 0.32. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 8.13 (s, 1H), 7.32 – 7.24 (m, 2H), 7.24 – 7.11 (m, 4H), 4.01 (d, $J$ = 17.2 Hz, 1H), 3.97 (d, $J$ = 16.8 Hz, 1H), 3.89 (d, $J$ = 17.2 Hz, 1H), 3.72 (d, $J$ = 16.8 Hz, 1H), 3.04 (dd, $J$ = 14.2, 3.4 Hz, 1H), 3.00 (s, 3H), 2.72 (dd, $J$ = 14.2, 11.5 Hz, 1H), 2.23 (ddd, $J$ = 11.5, 7.7, 3.4 Hz, 1H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 169.1, 168.6, 154.7, 142.7, 129.9, 129.3, 126.9, 63.8, 63.5, 46.7, 35.3. $^{11}$B NMR (128 MHz, $CD_3CN$) $\delta$ 11.7. IR (neat) $\tilde{\nu}$ (cm$^{-1}$): 3182, 3034, 1778, 1741, 1630, 1343, 1300, 1032, 899, 697. HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{18}BN_2O_5$ 304.1340, found 304.1336.

**(*E*)-4-methyl-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pentanal oxime (3e).**



Synthesized according to general procedure. Scale: 1.96 mmol. Yield: 0.505 g, 95%, white powder. $R_f$ (EtOAc): 0.24. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 8.18 (br. s, 1H), 7.21 (d, $J$ = 8.5 Hz, 1H), 3.95 (d, $J$ = 17.1 Hz, 1H), 3.94 (d, $J$ = 16.8 Hz, 1H), 3.84 (d, $J$ = 17.1 Hz, 1H), 3.67 (d, $J$ = 16.8 Hz, 1H), 2.96 (s, 3H), 2.03 – 1.95 (m, 1H), 1.58 – 1.46 (m, 2H), 1.28 (ddd, $J$ = 14.1, 10.8, 2.9 Hz, 1H), 0.91 (d, $J$ = 6.5 Hz, 3H), 0.86 (d, $J$ = 6.5 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 168.9, 168.4, 155.2, 63.5, 63.2, 46.4, 37.8, 27.3, 23.9, 20.9. $^{11}$B NMR (160 MHz, $CD_3CN$) $\delta$ 11.9. IR (neat) $\tilde{\nu}$ (cm$^{-1}$): 3209, 2967, 1694, 1416, 1400, 1378, 1190, 882, 694. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{11}H_{20}BN_2O_5$ 271.1465, found 271.1477.

**General Procedure for the Synthesis of *O*-benzylaldoximes**



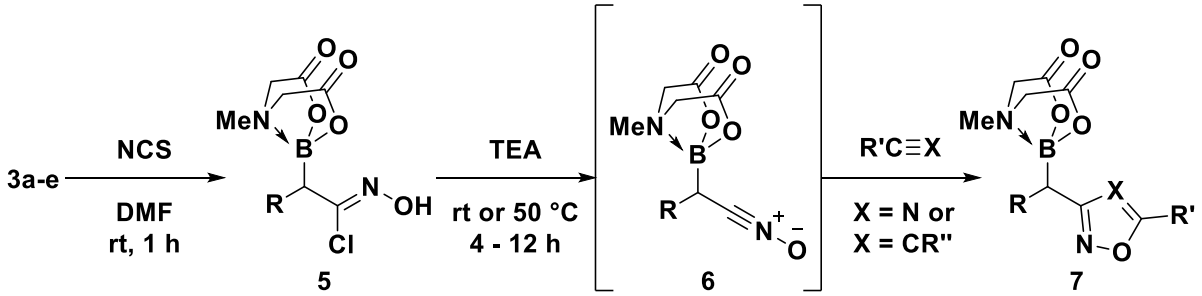

Boryl aldehyde (1 equiv.) and *O*-benzylhydroxylamine hydrochloride (1.5 equiv.) were dissolved in freshly distilled acetonitrile (0.2 M). Triethylamine (1.5 equiv.) was added and the solution stirred at 50 ºC for 48 hours. The solution was filtered, washed with EtOAc, concentrated, then purified using column chromatography.

**(*E*)-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-phenylacetaldehyde *O*-benzyl oxime (4a).** Synthesized according to general procedure. Scale: 1.82 mmol. Yield: 0.663 g, 96%, white solid. $R_f$ (EtOAc): 0.6. *E* (major) and *Z* (minor) isomers integrated relative to *E* isomer. $^1$H NMR (399 MHz, $CD_3CN$) $\delta$ 7.62 (d, $J$ = 6.3, 1H), 7.45 – 7.18 (m, 14 H), 7.04 (d, $J$ = 9.2 Hz, 0.3H), 5.09 (d, $J$ = 3.2 Hz, 0.7H), 5.03 (d, $J$ = 2.7 Hz, 2H), 4.13 (br. d, $J$ = 9.3 Hz, 0.3H), 4.02 (d, $J$ = 16.0 Hz, 0.3H), 3.94 (d, $J$ = 16.0 Hz, 0.3H), 3.91 (d, $J$ = 16.7 Hz, 1H), 3.76 (d, $J$ = 16.7 Hz, 1H), 3.74 (d, $J$ = 16.0 Hz, 0.3H), 3.72 (d, $J$ = 16.7 Hz, 1H), 3.68 (d, $J$ = 16.0 Hz, 0.3H), 3.41 (d, $J$ = 16.7 Hz, 1H), 3.21 (br. d, $J$ = 6.3 Hz, 1H), 2.88 (s, 1H), 2.83 (s, 3H). $^{13}$C NMR (100 MHz, $CD_3CN$): major isomer only $\delta$ 168.9, 168.6, 154.7, 141.0, 139.7, 130.0, 129.5, 129.4, 129.2, 128.8, 126.9, 75.9, 64.2, 63.8, 46.8. $^{11}$B NMR (96 MHz, $CD_3CN$) $\delta$ 11.2. IR (neat) $\tilde{\nu}$ ($cm^{-1}$): 2963, 1755, 1454, 1338, 1285, 1021, 700. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{22}BN_2O_5$ 381.1622, found 381.1625.

**(*E*)-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-3-phenylpropanal *O*-benzyl oxime (4b).** Synthesized according to general procedure. Scale: 2.00 mmol. Yield: 0.732 g, 93%, white solid. $R_f$ (EtOAc): 0.65. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 7.39 – 7.16 (m, 11H), 4.88 (d, $J$ = 12.9 Hz, 1H), 4.84 (d, $J$ = 12.9 Hz, 1H), 3.91 (d, $J$ = 17.3 Hz, 1H), 3.77 (d, $J$ = 17.3 Hz, 1H), 3.71 (d, $J$ = 16.9 Hz, 1H), 3.07 (d, $J$ = 16.9 Hz, 1H), 3.03 (dd, $J$ = 14.1, 3.3 Hz, 1H), 2.77 (s, 3H), 2.72 (dd, $J$ = 14.1, 12.1 Hz, 1H), 2.19 (ddd, $J$ = 12.1, 8.3, 3.3 Hz, 1H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 169.0, 168.3, 155.9, 142.5, 140.0, 129.8, 129.4, 129.3, 129.1, 128.7, 126.9, 75.6, 63.8, 63.0, 46.4, 35.2. $^{11}$B NMR (128 MHz, $CD_3CN$) $\delta$ 11.5. IR (neat) $\tilde{\nu}$ ($cm^{-1}$): 3021, 1775, 1740, 1454, 1342, 1296, 1034, 993, 897, 858, 694. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{24}BN_2O_5$ 395.1778, found 395.1783.

**(*E*)-4-methyl-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pentanal *O*-benzyl oxime (4c).** Synthesized according to general procedure. Scale: 1.57 mmol. Yield: 0.496 g, 88%, white powder. $R_f$ (EtOAc): 0.57. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 7.53 – 7.22 (m, 6H), 5.00 – 4.92 (m, 2H), 3.85 (d, $J$ = 17.2 Hz, 1H), 3.72 (d, $J$ = 17.2 Hz, 1H), 3.71 (d, $J$ = 16.9 Hz, 1H), 3.12 (d, $J$ = 16.9 Hz, 1H), 2.75 (s, 3H), 1.98 – 1.95 (m, 1H), 1.56 – 1.42 (m, 2H), 1.28 (ddd, $J$ = 13.0, 9.8, 3.0 Hz, 1H), 0.89 (d, $J$ = 6.5 Hz, 3H), 0.82 (d, $J$ = 6.5 Hz, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 169.0, 168.4, 156.6, 140.0, 129.4, 129.3, 128.7, 75.7, 63.6, 62.9, 46.3, 37.8, 27.6, 24.0, 21.0. $^{11}$B NMR (128 MHz, $CD_3CN$) $\delta$ 11.6. IR (neat) $\tilde{\nu}$ (cm$^{-1}$): 2964, 2876, 1750, 1624, 1452, 1339, 1301, 1023, 1004, 697. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{26}BN_2O_5$ 361.1935, found 361.1947.

**General Procedure for Cycloaddition of *in situ* Generated α-boryl nitrile oxides**




Aldoxime (1 equiv.) was dissolved in anhydrous DMF (0.4 M) and NCS (1.1 equiv.) was dissolved in a separate vial in an equal amount of DMF. The NCS solution was added in five portions to the aldoxime mixture every ten minutes. When the reaction was complete by TLC:

(A) Two volume equivalents (relative to final solvent volume) of dipolarophile was added followed by the addition of triethylamine (1.5 equiv.) the reaction was heated to 60 ºC for 4 – 12 hours until complete by TLC. After reaction completion, the product was extracted into EtOAc and washed with water, saturated sodium thiosulfate, water, brine, then dried over sodium sulfate. The product was purified by column chromatography.

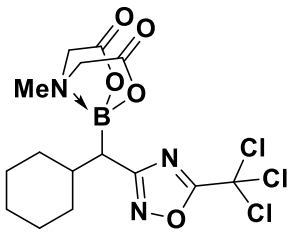
(B) The DMF was evaporated under high vacuum at room temperature and the residue was extracted into EtOAc and washed with water, saturated sodium thiosulfate, water, brine, then dried over sodium sulfate. The residue after evaporation was dissolved in THF (1 M) and dipolarophile

(10 equiv.) was added followed by triethylamine (1.5 equiv.) and stirred at room temperature or at 50 ºC. The product was purified by column chromatography.

(C) The DMF was evaporated under high vacuum at room temperature and the residue was extracted into EtOAc and washed with water, saturated sodium thiosulfate, water, brine, then dried over sodium sulfate. The residue after evaporation was dissolved in THF (0.1 M) and dipolarophile (1.2 equiv.) was added followed by the addition of triethylamine (1.3 equiv.) dissolved in one half of the starting volume of THF over 15 minutes. Stirred at room temperature. The product was purified by column chromatography.

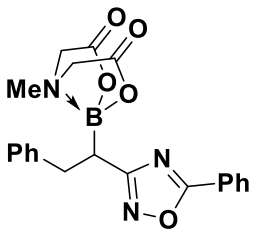
**6-methyl-2-(1-(5-methyl-1,2,4-oxadiazol-3-yl)-2-phenylethyl)-1,3,6,2-dioxazaborocane-4,8-dione (7a).** Synthesized according to general procedure A. Scale: 0.050 mmol. Yield: 8.9 mg, 52%, white solid. $R_f$ (1:9 MeCN:EtOAc): 0.5. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 7.25 – 7.16 (m, 2H), 7.15 – 7.06 (m, 3H), 4.00 (d, $J$ = 17.2 Hz, 1H), 3.89 (d, $J$ = 16.8 Hz, 1H), 3.88 (d, $J$ = 17.2 Hz, 1H), 3.50 (d, $J$ = 16.8 Hz, 1H), 3.16 (dd, $J$ = 14.1, 3.3 Hz, 1H), 3.04 (dd, $J$ = 14.1, 11.9 Hz, 1H), 3.00 (s, 3H), 2.77 (dd, $J$ = 11.9, 3.3 Hz, 1H), 2.45 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 177.6, 172.9, 169.0, 168.3, 142.4, 129.6, 129.1, 126.9, 63.8, 63.3, 46.5, 35.7, 12.6. $^{11}$B NMR (128 MHz, $CD_3CN$) $\delta$ 11.6. IR (neat) $\tilde{\nu}$ (cm$^{-1}$): 3031, 2973, 1771, 1739, 1591, 1449, 1293, 1213, 1032, 871, 696. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{19}BN_3O_5$ 344.1418, found 344.1425.

**6-methyl-2-(3-methyl-1-(5-(trichloromethyl)-1,2,4-oxadiazol-3-yl)butyl)-1,3,6,2-dioxazaborocane-4,8-dione (7b).** Synthesized according to general procedure B at room temperature. Scale: 0.15 mmol. Yield: 0.045 g, 73%, white solid. $R_f$ (EtOAc): 0.85. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 4.01 (d, $J$ = 17.2 Hz, 1H), 3.94 (d, $J$ = 17.0 Hz, 1H), 3.89 (d, $J$ = 17.2 Hz, 1H), 3.63 (d, $J$ = 17.0 Hz, 1H), 2.98 (s, 3H), 2.72 (dd, $J$ = 11.8, 3.1 Hz, 1H), 1.88 (ddd, $J$ = 13.8, 11.8, 3.8 Hz, 1H), 1.50 (ddd, $J$ = 13.8, 10.1, 3.1 Hz, 1H), 1.45 – 1.32 (m, 1H), 0.90 (d, $J$ = 6.5 Hz, 3H), 0.88 (d, $J$ = 6.6 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 175.5, 174.8, 168.8, 168.2, 63.9, 63.6, 46.9, 38.4, 27.5, 23.8, 21.1. $^{11}$B NMR (96 MHz, $CD_3CN$) $\delta$ 11.5. IR (neat) $\tilde{\nu}$ (cm$^{-1}$): 2958, 1779, 1746, 1567, 1337, 1286, 1067, 1037, 814, 801. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{18}BCl_3N_3O_5$ 412.0405, found 412.0406.

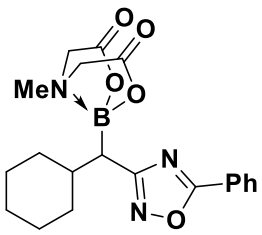


**2-(cyclohexyl(5-(trichloromethyl)-1,2,4-oxadiazol-3-yl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (7c).** Synthesized according to general procedure B at room temperature. Scale: 0.10 mmol. Yield: 0.023 g, 53% yield, white solid. $R_f$ (EtOAc): 0.86. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 3.99 (d, $J$ = 17.3 Hz, 1H), 3.89 (d, $J$ = 16.9 Hz, 1H), 3.87 (d, $J$ = 17.3 Hz, 1H), 3.54 (d, $J$ = 16.9 Hz, 1H), 2.83 (s, 3H), 2.52 (d, $J$ = 4.3 Hz, 1H), 1.99 – 1.95 (m, 1H), 1.86 – 1.66 (m, 4H), 1.66 – 1.55 (m, 1H), 1.45 – 0.99 (m, 5H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 174.5, 174.2, 169.1, 168.3, 63.9, 63.4, 46.9, 39.9, 34.1, 31.5, 27.6, 27.5, 26.9. $^{11}$B NMR (128 MHz, $CD_3CN$) $\delta$ 11.7. IR (neat) $\tilde{\nu}$ (cm$^{-1}$): 2931, 2861, 1778, 1752, 1573, 1337, 1290, 1042, 1030, 855, 798. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{20}BCl_3N_3O_5$ 438.0562, found 438.0563.

**6-methyl-2-(2-phenyl-1-(5-phenyl-1,2,4-oxadiazol-3-yl)ethyl)-1,3,6,2-dioxazaborocane-4,8-dione (7d).** Synthesized according to general procedure B but without THF as cosolvent in the cycloaddition. Instead neat benzonitrile (40 equiv) was used and heated to 50 ºC. Scale: 0.10 mmol. Yield: 0.037 g, 91%, white solid. $R_f$ (EtOAc): 0.31. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 8.10 – 8.01 (m, 2H), 7.68 – 7.62 (m, 1H), 7.60 – 7.54 (m, 2H), 7.23 – 7.15 (m, 2H), 7.15 – 7.08 (m, 3H), 4.03 (d, $J$ = 17.2 Hz, 1H), 3.90 (d, $J$ = 17.0 Hz, 1H), 3.90 (d, $J$ = 17.2 Hz, 1H), 3.52 (d, $J$ = 16.9 Hz, 1H), 3.25 (dd, $J$ = 14.1, 3.3 Hz, 1H), 3.12 (dd, $J$ = 14.0, 11.9 Hz, 1H), 3.01 (s, 3H), 2.88 (dd, $J$ = 11.8, 3.2 Hz, 1H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 176.2, 173.5, 169.1, 168.4, 142.3, 133.8, 130.3, 129.7, $^{11}$B NMR (160 MHz, $CD_3CN$) $\delta$ 11.4. IR (neat) $\tilde{\nu}$ (cm$^{-1}$): 3035, 2977, 1765, 1742, 1590, 1563, 1452, 1286, 1209, 1032, 872. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{21}BN_3O_5$ 406.1574, found 406.1570.

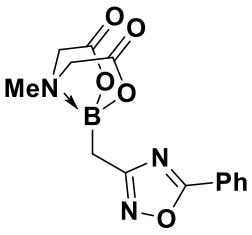


**2-(cyclohexyl(5-phenyl-1,2,4-oxadiazol-3-yl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (7e).** Synthesized according to general procedure B but without THF as cosolvent in the cycloaddition. Instead neat benzonitrile (40 equiv) was used and heated to 50 ºC. Scale: 0.10 mmol. Yield: 0.016 g, 41%, white solid. $R_f$ (EtOAc): 0.47. $^1$H NMR (400 MHz, $CD_3CN$) $\delta$ 8.13 – 8.03 (m, 2H), 7.68 – 7.62 (m, 1H), 7.62 – 7.55 (m, 2H), 3.96 (d, $J$ = 17.3 Hz, 1H), 3.88 – 3.78 (m, 2H), 3.46 (d, $J$ = 16.7 Hz, 1H), 2.81 (s, 3H), 2.44 (d, $J$ = 4.8 Hz, 1H), 1.88 – 1.53 (m,



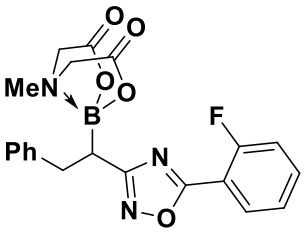
6H), 1.38 – 1.17 (m, 4H), 1.06 (m, 2H). $^{13}$C NMR (101 MHz, $CD_3CN$) $\delta$ 175.9, 173.2, 169.4, 168.6, 133.8, 130.3, 128.8, 125.5, 63.9, 63.5, 46.6, 40.0, 34.3, 31.8, 27.7, 27.5, 27.0. $^{11}$B NMR (128 MHz, $CD_3CN$) $\delta$ 12.0. IR (neat) $\tilde{\nu}$ ($cm^{-1}$): 2931, 2858, 1756, 1748, 1563, 1450, 1342, 1286, 1025, 965, 892, 689. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{25}BN_3O_5$ 398.1887, found 398.1895.

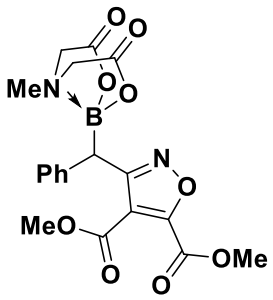
**6-methyl-2-((5-phenyl-1,2,4-oxadiazol-3-yl)methyl)-1,3,6,2-dioxazaborocane-4,8-dione (7f).**




Synthesized according to general procedure B but without THF as cosolvent in the cycloaddition. Instead neat benzonitrile (40 equiv) was used and heated to 50 ºC. Scale: 1.51 mmol. Yield: 0.104 g, 22%, white solid. $R_f$ (1:4 MeCN:EtOAc): 0.52. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 8.13 – 8.06 (m, 2H), 7.70 – 7.62 (m, 1H), 7.62 – 7.55 (m, 2H), 4.03 (d, $J$ = 16.9 Hz, 2H), 3.96 (d, $J$ = 16.9 Hz, 2H), 3.13 (s, 3H), 2.36 (s, 2H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 176.1, 171.0, 168.9, 133.9, 130.3, 128.8, 125.2, 63.7, 47.5. $^{11}$B NMR (128 MHz, $CD_3CN$) $\delta$ 12.0. IR (neat) $\tilde{\nu}$ ($cm^{-1}$): 3012, 2970, 1772, 1746, 1567, 1349, 1304, 1033, 998, 899. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{14}H_{15}BN_3O_5$ 316.1105, found 316.1101.

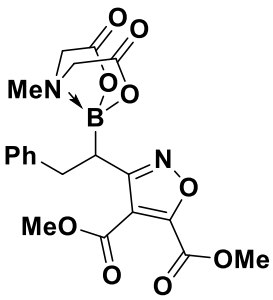
**2-(1-(5-(2-fluorophenyl)-1,2,4-oxadiazol-3-yl)-2-phenylethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (7g).** Synthesized according to general procedure B but 0.5 M in THF with 20 equivalents of dipolarophile heated to 50 ºC. Scale: 0.10 mmol. Yield: 0.019 g, 45%, white solid. $R_f$ (EtOAc): 0.50. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 8.06 (td, $J$ = 7.5, 1.8 Hz, 1H), 7.67 (dddd, $J$ = 8.4, 7.5, 5.1, 1.8 Hz, 1H), 7.43 – 7.29 (m, 2H), 7.24 – 7.16 (m, 2H), 7.15 – 7.11 (m, 3H), 4.04 (d, $J$ = 17.2 Hz, 1H), 3.91 (d, $J$ = 16.9 Hz, 1H), 3.91 (d, $J$ = 17.2 Hz, 1H), 3.56 (d, $J$ = 16.9 Hz, 1H), 3.25 (dd, $J$ = 14.0, 3.4 Hz, 1H), 3.12 (dd, $J$ = 14.0, 11.9 Hz, 1H), 3.03 (s, 3H), 2.91 (dd, $J$ = 11.9, 3.4 Hz, 1H). $^{13}$C NMR ($CD_3CN$) $\delta$ 172.3, 172.3, 172.2, 168.1, 167.4, 160.5 (d, $^1J_{CF}$ = 257.6 Hz), 141.2, 135.0 (d, $^2J_{CF}$ = 8.8 Hz), 130.8 (d, $^3J_{CF}$ = 1.3 Hz), 128.7, 128.1, 126.0, 125.1 (d, $^3J_{CF}$ = 3.7 Hz), 112.7 (d, $^2J_{CF}$ = 11.5 Hz), 63.0, 62.4, 45.7, 34.9. $^{11}$B NMR ($CD_3CN$) $\delta$ 11.6. $^{19}$F NMR ($CD_3CN$) $\delta$ -110.9. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{20}BFN_3O_5$ 423.1402, found 423.1405.





**dimethyl 3-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)(phenyl)methyl)isoxazole-4,5-dicarboxylate (7h).** Synthesized according to general procedure C. Scale: 0.10 mmol. Yield: 0.038 g, 88%, white solid. $R_f$ (1:9 MeCN:EtOAc): 0.7. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 7.31 – 7.17 (m, 5H), 4.02 (d, $J$ = 17.3 Hz, 1H), 3.99 (s, 1H), 3.98 (d, $J$ = 16.7 Hz, 1H), 3.94 (d, $J$ = 16.7 Hz, 1H), 3.90 (s, 3H), 3.82 (d, $J$ = 17.3 Hz, 1H), 3.66 (s, 3H), 2.87 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 168.9, 168.7, 165.4, 161.9, 160.5, 157.7, 140.2, 130.4, 129.1, 127.1, 117.0, 64.6, 64.5, 54.1, 53.3, 47.3. $^{11}$B NMR (128 MHz, $CD_3CN$) $\delta$ 11.6. IR (neat) $\tilde{\nu}$ (cm$^{-1}$): 3028, 2961, 1744, 1736, 1455, 1285, 1102, 1028, 955, 713. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{20}BN_2O_9$ 431.1262, found 431.1265.

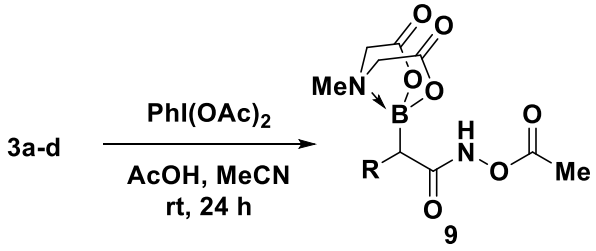
**dimethyl 3-(1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-phenylethyl)isoxazole-4,5-dicarboxylate (7i).** Synthesized according to general procedure C. Scale: 0.050 mmol. Yield: 0.018 g, 82%, white solid. $R_f$ (1:9 MeCN:EtOAc): 0.65. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 7.23 – 7.16 (m, 2H), 7.16 – 7.10 (m, 1H), 7.10 – 7.05 (m, 2H), 4.03 (d, $J$ = 17.2 Hz, 1H), 3.97 (d, $J$ = 16.9 Hz, 1H), 3.88 (s, 3H), 3.88 (d, $J$ = 17.2 Hz, 1H), 3.69 (d, $J$ = 16.9 Hz, 1H), 3.68 (s, 3H), 3.19 – 3.11 (m, 2H), 3.04 (dd, $J$ = 14.6, 13.1 Hz, 1H), 2.90 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 168.8, 168.4, 166.2, 162.3, 160.5, 157.9, 141.7, 129.7, 129.2, 127.0, 117.0, 63.8, 54.1, 53.2, 47.2, 37.1. $^{11}$B NMR (160 MHz, $CD_3CN$) $\delta$ 11.7. IR (neat) $\tilde{\nu}$ (cm$^{-1}$): 2970, 1784, 1739, 1452, 1338, 1277, 1200, 1103, 1033, 992, 701. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{23}BN_2O_9$ 445.1418, found 445.1417.



**ethyl 5-methyl-3-(3-methyl-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butyl)isoxazole-4-carboxylate (7j).** Synthesized according to general procedure C. Scale: 0.15 mmol. Yield: 0.026 g, 46%, white solid. $R_f$ (1:9 MeCN:EtOAc): 0.7. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 4.26 (q, $J$ = 7.1 Hz, 2H), 3.94 (d, $J$ = 17.1 Hz, 1H), 3.91 (d, $J$ = 16.8 Hz, 1H), 3.80 (d, $J$ = 17.1 Hz, 1H), 3.66 (d, $J$ = 16.8 Hz, 1H), 3.23 (dd, $J$ = 11.9, 3.0 Hz, 1H), 2.93 (s, 3H), 2.60 (s, 3H), 1.97 – 1.88 (m, 1H), 1.49 – 1.39 (m, 1H), 1.36 (ddd, $J$ = 13.4, 9.7, 3.0 Hz, 1H), 1.31 (t, $J$ = 7.1 Hz, 3H), 0.86 (d, $J$ = 5.9 Hz, 3H), 0.84 (d, $J$ = 5.9 Hz, 3H). $^{13}$C NMR (126 MHz,

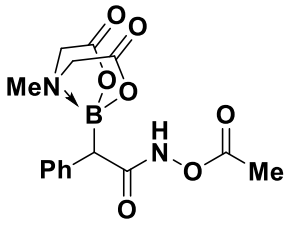
$CD_3CN$) $\delta$ 175.7, 169.0, 168.5, 167.0, 163.7, 110.2, 63.8, 63.5, 61.5, 46.9, 40.3, 27.6, 24.0, 21.6, 14.5, 13.9. $^{11}B$ NMR (96 MHz, $CD_3CN$) $\delta$ 12.0. IR (neat) $\tilde{\nu}$ ($cm^{-1}$): 2967, 2873, 1771, 1750, 1713, 1442, 1339, 1284, 1100, 1070, 1029, 992. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{17}H_{26}BN_2O_7$ 381.1833, found 381.1838.

**General Procedure for the Synthesis of α-boryl *N*-acetoxyamides**




Adapted from literature procedure.[1] Aldoxime (1 equiv.) and acetic acid (1 equiv.) were dissolved in acetonitrile (0.1 M). Diacetoxyiodobenzene (1.05 equiv.) dissolved in the same amount of acetonitrile (may require sonication to fully dissolve) was added dropwise with stirring over ten minutes. The reaction was stirred for 24 h, evaporated and purified by column chromatography.

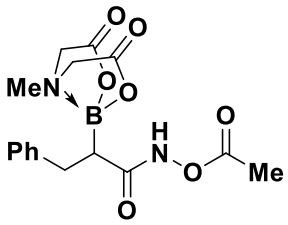
***N*-acetoxy-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-phenylacetamide (9a).**




Synthesized according to general procedure. Scale: 0.10 mmol. Yield: 0.020 g, 58%, white solid. $R_f$ (1:9 MeCN:EtOAc): 0.33. $^1H$ NMR (500 MHz, $CD_3CN$) $\delta$ 9.52 (s, 1H), 7.40 – 7.29 (m, 4H), 7.27 – 7.22 (m, 1H), 3.97 (d, $J$ = 17.2 Hz, 1H), 3.95 (d, $J$ = 16.4 Hz, 1H), 3.90 (d, $J$ = 16.4 Hz, 1H), 3.81 (d, $J$ = 17.2 Hz, 1H), 3.37 (s, 1H), 3.06 (s, 3H), 2.10 (s, 3H). $^{13}C$ NMR (126 MHz, $CD_3CN$) $\delta$ 172.6, 169.7, 169.0, 168.6, 138.4, 130.1, 129.3, 127.3, 64.1, 63.7, 46.9, 18.4. $^{11}B$ NMR (128 MHz, $CD_3CN$) $\delta$ 11.2. IR (neat) $\tilde{\nu}$ ($cm^{-1}$): 2964, 1757, 1751, 1668, 1288, 1183, 1025, 952, 705. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{18}BN_2O_7$ 348.1238, found 348.1239.

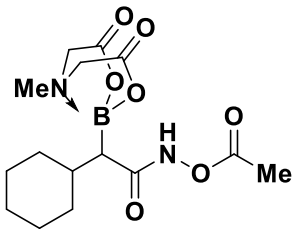
[1] Ghosh, H.; Patel, B. K. *Org. Biomol. Chem.* **2010**, *8*, 384–390.

***N*-acetoxy-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-3-phenylpropanamide (9b).**



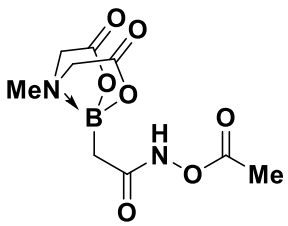
Synthesized according to general procedure. Scale: 0.15 mmol. Yield: 0.051 g, 94%, white solid. $R_f$ (1:9 MeCN:EtOAc): 0.35 (same $R_f$ as starting material). $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 9.32 (br. s, 1H), 7.31 – 7.25 (m, 2H), 7.23 – 7.17 (m, 3H), 3.99 (d, $J$ = 17.0 Hz, 1H), 3.95 (d, $J$ = 16.7 Hz, 1H), 3.87 (d, $J$ = 17.0 Hz, 1H), 3.84 (d, $J$ = 16.7 Hz, 1H), 3.13 (s, 3H), 3.04 – 2.93 (m, 2H), 2.31 – 2.22 (m, 1H), 2.05 (s, 3H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 173.3, 169.9, 168.9, 168.5, 142.2, 129.6, 129.3, 127.1, 63.7, 63.2, 46.4, 34.8, 18.3. $^{11}$B NMR (96 MHz, $CD_3CN$) $\delta$ 11.2. IR (neat) $\tilde{\nu}$ (cm$^{-1}$): 3191, 2964, 1757, 1748, 1654, 1458, 1290, 1186, 1030, 989, 700. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{20}BN_2O_7$ 362.1364, found 363.1373.

***N*-acetoxy-2-cyclohexyl-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)acetamide (9c).**

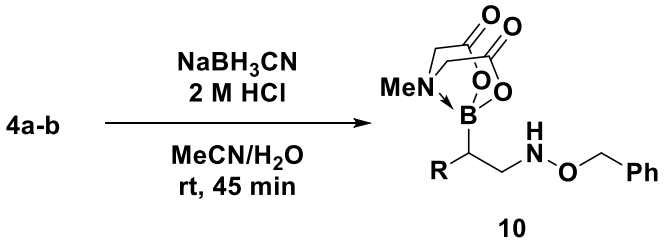


Synthesized according to general procedure. Scale: 0.10 mmol. Yield: 0.017 g, 49%, white solid. $R_f$ (1:9 MeCN:EtOAc): 0.56. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 9.59 (s, 1H), 3.91 (d, $J$ = 17.2 Hz, 1H), 3.85 (d, $J$ = 16.4 Hz, 1H), 3.78 (d, $J$ = 17.2 Hz, 1H), 3.71 (d, $J$ = 16.4 Hz, 1H), 3.05 (s, 3H), 2.13 (s, 3H), 1.89 – 1.80 (m, 2H), 1.76 – 1.68 (m, 3H), 1.65 – 1.58 (m, 1H), 1.36 – 1.02 (m, 6H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 173.9, 170.2, 169.4, 168.5, 63.6, 63.0, 46.1, 39.4, 34.4, 32.6, 27.6, 27.5, 27.0, 18.4. $^{11}$B NMR (96 MHz, $CD_3CN$) $\delta$ 11.3. IR (neat) $\tilde{\nu}$ (cm$^{-1}$): 2974, 2895, 1758, 1750, 1287, 1185, 1026, 954, 705. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{24}BN_2O_7$ 355.1677, found 355.1668.

***N*-acetoxy-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)acetamide (9d).** Synthesized according to general procedure. Scale: 0.40 mmol. Yield: 0.065 g, 49%, white solid. $R_f$ (1:4 MeCN:EtOAc): 0.15. $^1$H NMR (500 MHz, $CD_3CN$) $\delta$ 9.50 (s, 1H), 3.96 (d, $J$ = 16.8 Hz, 2H), 3.89 (d, $J$ = 16.8 Hz, 2H), 3.06 (s, 3H), 2.11 (s, 3H), 1.89 (s, 2H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 172.2, 169.7, 168.9, 63.4, 47.4, 18.4. $^{11}$B NMR (128 MHz, $CD_3CN$) $\delta$ 11.5. IR (neat) $\tilde{\nu}$ (cm$^{-1}$): 3303, 2964, 1802, 1755, 1683, 1279, 1173, 1028, 898. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_9H_{14}BN_2O_7$ 273.0894, found 273.0899.

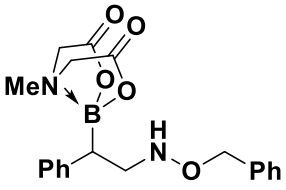


**General Procedure for the Synthesis of β-boryl hydroxylamines**



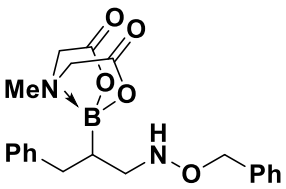

The aldoxime (1 equiv.) was dissolved in a 2:1 acetonitrile:water mixture (0.1 M final concentration) followed by the addition of sodium cyanoborohydride (2.5 equiv.). 3 M hydrochloric acid (6 equiv) was added dropwise to a stirred solution and was monitored by TLC from 30 minutes to 1 hour until complete. The crude was dry loaded onto Celite and purified by reverse phase column chromatography.

**2-(2-((benzyloxy)amino)-1-phenylethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (10a).**



Synthesized according to general procedure. Scale: 0.539 mmol. Yield: 0.175 g, 85%, white solid. $^{1}$H NMR (500 MHz, $CD_3CN$) $\delta$ 7.39 – 7.13 (m, 10H), 4.58 (s, 2H), 3.90 (d, $J$ = 17.1 Hz, 1H), 3.81 (d, $J$ = 17.1 Hz, 1H), 3.80 (d, $J$ = 16.8 Hz, 1H), 3.37 (dd, $J$ = 12.6, 4.3 Hz, 1H), 3.16 (d, $J$ = 16.8 Hz, 1H), 3.13 (dd, $J$ = 12.6, 10.6 Hz, 1H), 2.82 (s, 3H), 2.54 (dd, J = 10.6, 4.3 Hz, 1H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 169.1, 168.6, 143.6, 139.6, 130.1, 129.4, 129.2, 129.1, 128.5, 126.5, 76.0, 63.4, 63.3, 55.3, 46.6. $^{11}$B NMR (128 MHz, $CD_3CN$) $\delta$ 12.1. IR (neat) $\tilde{\nu}$ ($cm^{-1}$): 3273, 2928, 2852, 1758, 1621, 1393, 1290, 1025, 1007, 699. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{24}BN_2O_5$ 383.1778, found 383.1782.

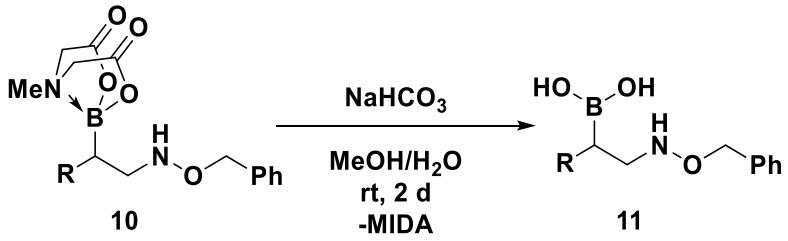
**2-(1-((benzyloxy)amino)-3-phenylpropan-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (10b).** Synthesized according to general procedure. Scale: 1.50 mmol. Yield: 0.416 g, 70%, white solid.



$^{1}$H NMR (500 MHz, $CD_3CN$) $\delta$ 7.46 – 7.08 (m, 10H), 4.52 (s, 2H), 3.92 (d, $J$ = 17.1 Hz, 1H), 3.83 (s, 2H), 3.77 (d, $J$ = 17.1 Hz, 1H), 2.89 (s, 3H), 2.92 – 2.85 (m, 1H), 2.82 (dd, $J$ = 11.6, 5.5 Hz, 1H), 2.78 (dd, $J$ = 11.6, 6.7 Hz, 1H), 2.46 (dd, $J$ = 14.0, 10.7 Hz, 1H), 1.40 – 1.31 (m, 1H). $^{13}$C NMR (126 MHz, $CD_3CN$) $\delta$ 169.3, 169.1, 143.6, 139.5, 130.0, 129.3, 129.2, 129.1, 128.5, 126.7, 75.5, 63.7, 63.2, 52.6, 46.7, 36.0. $^{11}$B NMR (128 MHz, $CD_3CN$) $\delta$ 12.9. IR (neat) $\tilde{\nu}$ ($cm^{-1}$):

3106, 3040, 1652, 1600, 1396, 1364, 916, 890, 729, 694. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{26}BN_2O_5$ 397.1935, found 397.1939.

**General Procedure for MIDA deprotection**

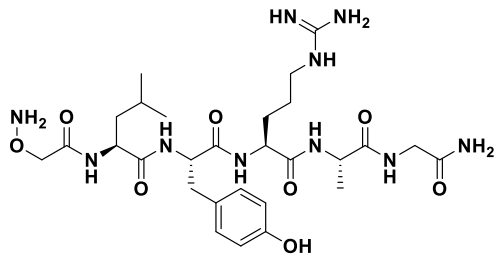



The MIDA boronate was dissolved in a 20:1 MeOH:$H_2O$ mixture (0.1 M final concentration) and sodium bicarbonate (10 equiv.) was added and stirred for 1 to 2 days. When complete by TLC, the product was dry loaded onto Celite and purified by reverse phase column chromatography ($H_2O$:MeCN 95:5 - 5:95, with 0.1% formic acid) and then lyophilized to obtain white solids.

**(2-((benzyloxy)amino)-1-phenylethyl)boronic acid (11a).** Synthesized according to general procedure. Scale: 0.039 mmol. Yield: 5.0 mg, 47%, white solid. $R_f$ (EtOAc): 0.5. $^1$H NMR (500 MHz, $CD_3OD$) $\delta$ 7.42 – 7.23 (m, 7H), 7.22 – 7.10 (m, 3H), 4.66 (s, 2H), 3.31 (dd, $J$ = 12.6, 7.9 Hz, 1H), 3.03 (dd, $J$ = 12.6, 7.5 Hz, 1H), 2.80 (br. t, $J$ = 7.9 Hz, 1H). $^{13}$C NMR (126 MHz, $CD_3OD$) $\delta$ 142.4, 139.1, 130.0, 129.7, 129.3, 129.3, 128.8, 126.8, 76.4, 56.0. $^{11}$B NMR (160 MHz, $CD_3OD$) $\delta$ 29.9. HRMS not taken as product decomposed. LC/MS retention time = 3.13 min.

**(1-((benzyloxy)amino)-3-phenylpropan-2-yl)boronic acid (11b).** Synthesized according to general procedure. Scale: 0.20 mmol. Yield: 0.048 g, 84%, white solid. $^1$H NMR (500 MHz, $CD_3OD$) $\delta$ 7.34 – 7.21 (m, 7H), 7.17 – 7.12 (m, 3H), 4.65 (s, 2H), 3.07 (dd, $J$ = 12.5, 9.1 Hz, 1H), 2.88 (dd, $J$ = 12.5, 5.5 Hz, 1H), 2.64 (dd, $J$ = 17.0, 8.1 Hz, 1H), 2.62 (dd, $J$ = 17.0, 8.4 Hz, 1H), 1.77 – 1.62 (m, 1H). $^{13}$C NMR (126 MHz, $CD_3OD$) $\delta$ 143.4, 139.1, 129.6, 129.3, 129.3, 129.2, 128.7, 126.8, 76.4, 54.8, 37.0. $^{11}$B NMR (128 MHz, $CD_3OD$) $\delta$ 31.4. IR (neat) $\tilde{\nu}$ ($cm^{-1}$): 3034, 2945, 1454, 1358, 1252, 1209, 738, 695. HRMS (DART) *m/z*: $[M + H]^+$ calcd for $C_{16}H_{21}BNO_3$ 286.1615, found 286.1617. LC/MS retention time = 3.33 min.

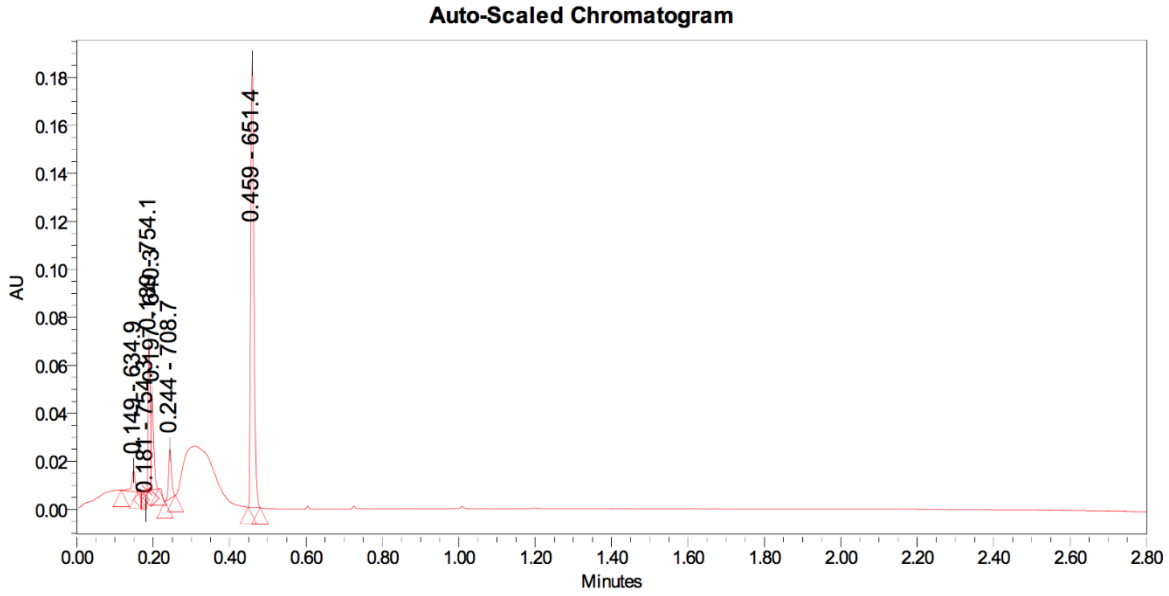
**Synthesis of Aminooxyacetyl Functionalized Peptide 12**



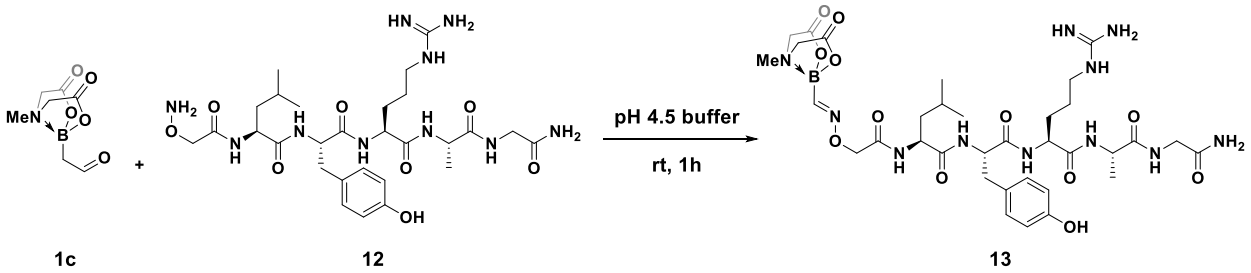
**12**

The peptide was chain assembled on Rink Amide resin (200-400 mesh, 0.68 mmol/gram). All amino acid couplings were carried out with the equivalent ratio of [5]:[5]:[7.5] of [amino acid]:[0.4 M HATU in DMF]:[DIPEA] for 20 minutes following standard SPPS protocol with N-terminal Fmoc-protection. Boc-aminooxyacetic acid was coupled in a base-free manner utilizing using the equivalent ratio of [5]:[5]:[5] of [amino acid]:[HOAt]:[DIC] in [1]:[1] of [DMF]:[DCM] by a 20 minute preactivation period followed by a 30 minute coupling. Following standard cleavage from resin using 125 μL TIPS, 125 μL $H_2O$, 4.75 mL conc. TFA, the TFA was blown off using $N_2$ and the resultant residue suspended in cold $Et_2O$. After this suspension was subjected to centrifugation for 15 minutes at 4000 rpm the organic supernatant was decanted into the waste and the remaining white solid was dissolved in 10% MeCN in $H_2O$ and lyophilized. The crude peptide thus obtained was purified via preparative reversed-phase HPLC (RP-HPLC) using a gradient of 100% buffer A to 80% buffer A / 20% buffer B over 40 minutes.

LC-MS trace of purified product; expected M=650.4, observed M+1=651.4.




**Oxime Ligation Reactions with Boryl Aldehyde 1c and Peptide 12**




**1c** **12** **13**

A stock solution of peptide **12** dissolved in 50mM $NaC_2H_3O_2$, pH 4.5 buffer at 1mg/mL concentration was prepared. A stock solution of boryl aldehyde **1c** dissolved in acetonitrile at 2 mg/mL was prepared. From these stock solutions, a set of 4 reactions varying the number of equivalents of boryl aldehyde were set up, with their final volumes brought up to a 1mL volume with 50mM $NaC_2H_3O_2$, pH 4.5 buffer:

PC-3-4: 250 μM peptide, 250 μM boryl aldehyde (1eq)

PC-3-5: 250 μM peptide, 500 μM boryl aldehyde (2eq)

PC-3-6: 250 μM peptide, 750 μM boryl aldehyde (3eq)

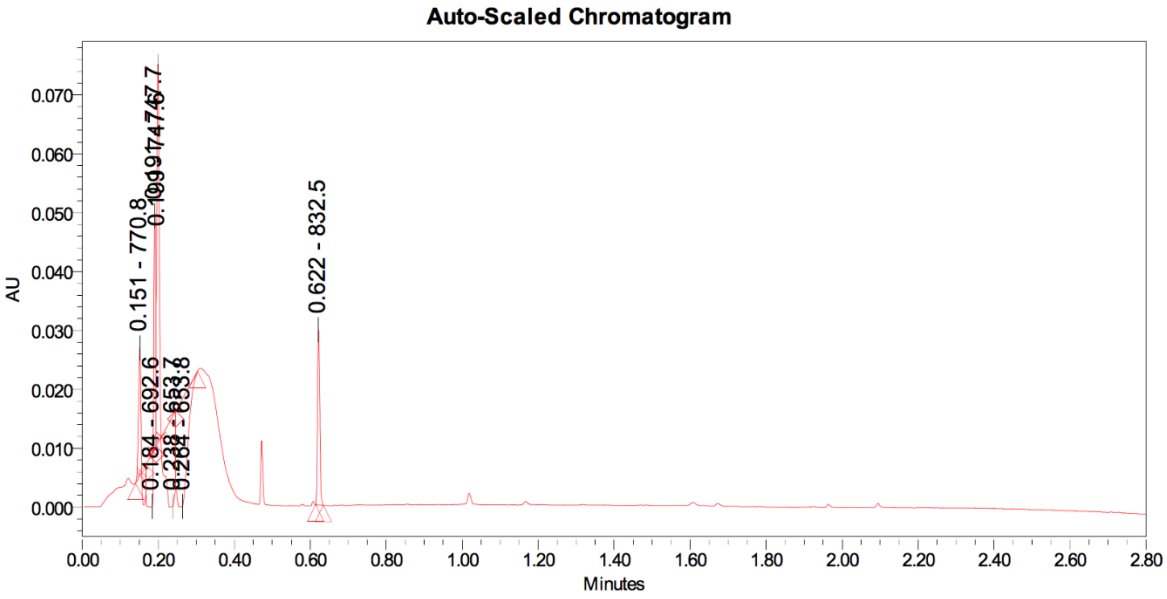
PC-3-7: 250 μM peptide, 1 mM boryl aldehyde (4eq)

Each reaction was placed in a 25°C heat block for 1 hour. Following filtration, each sample was run on LC-MS to determine turnover to product. 2eq is sufficient for a complete reaction.

PC-3-4: 250 μM peptide, 250 μM boryl aldehyde (1eq)

Starting material peptide – 0.46 min

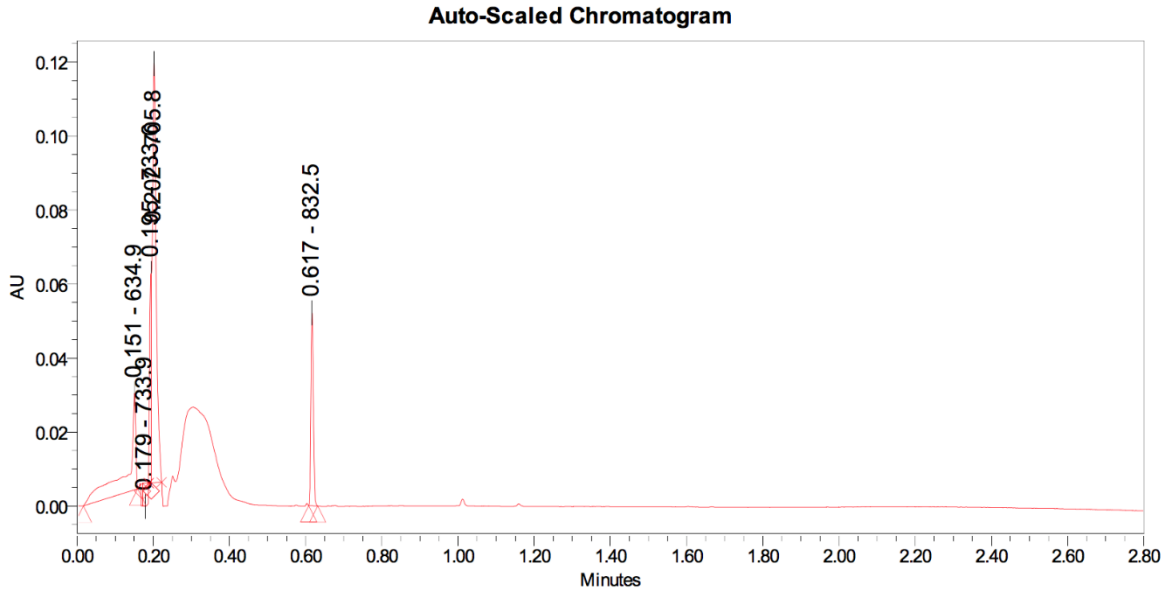
Product - 0.62 min




PC-3-5: 250 μM peptide, 500 μM boryl aldehyde (2eq)

Starting material peptide – 0.46 min

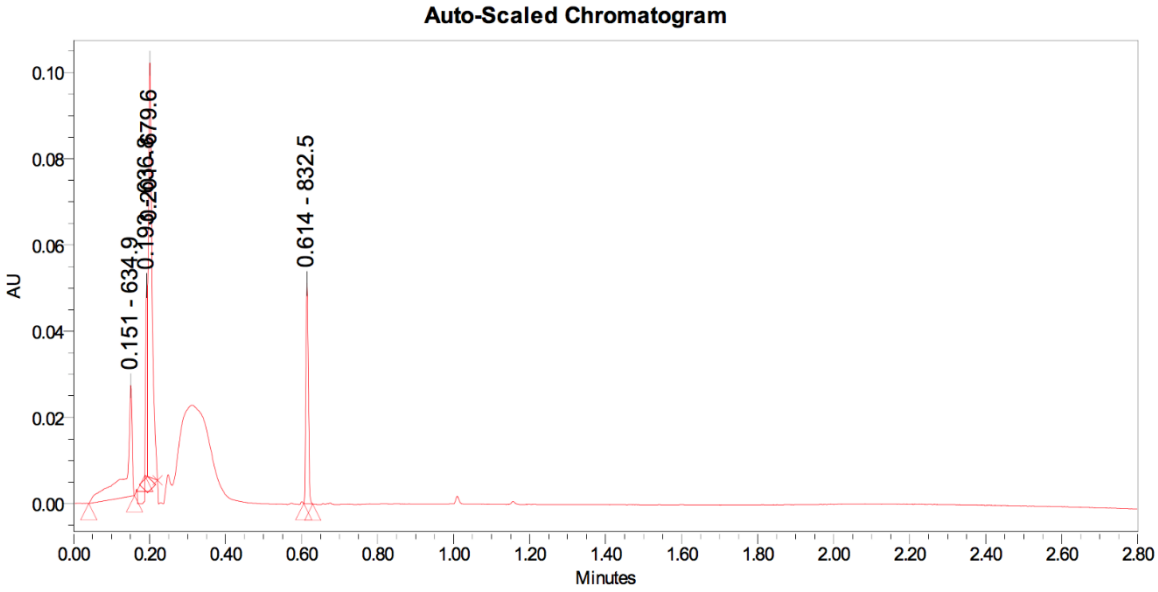
Product - 0.62 min



PC-3-6: 250 μM peptide, 750 μM boryl aldehyde (3eq)

Starting material peptide – 0.46 min

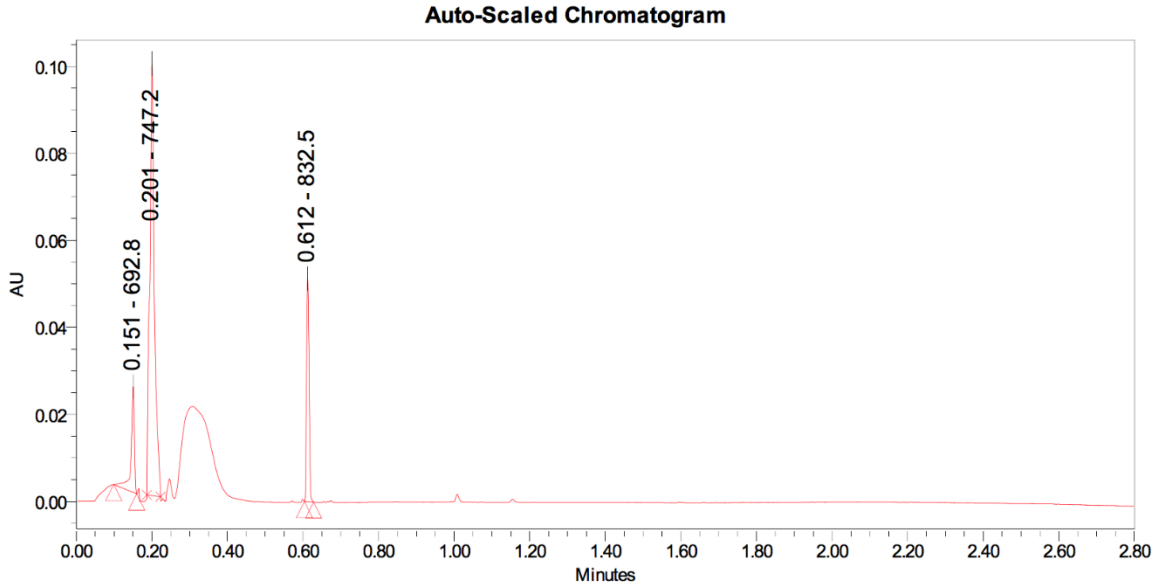
Product - 0.62 min




PC-3-7: 250 μM peptide, 1 mM boryl aldehyde (4eq)

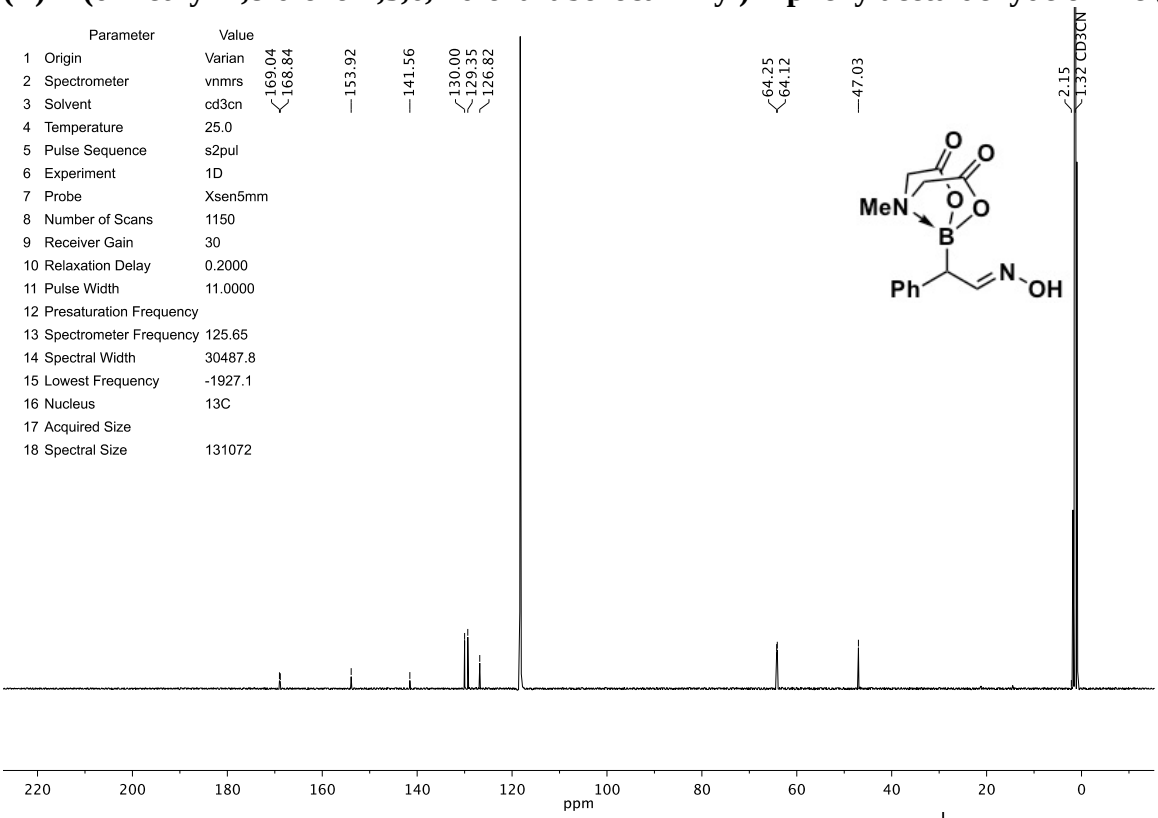
Starting material peptide – 0.46 min

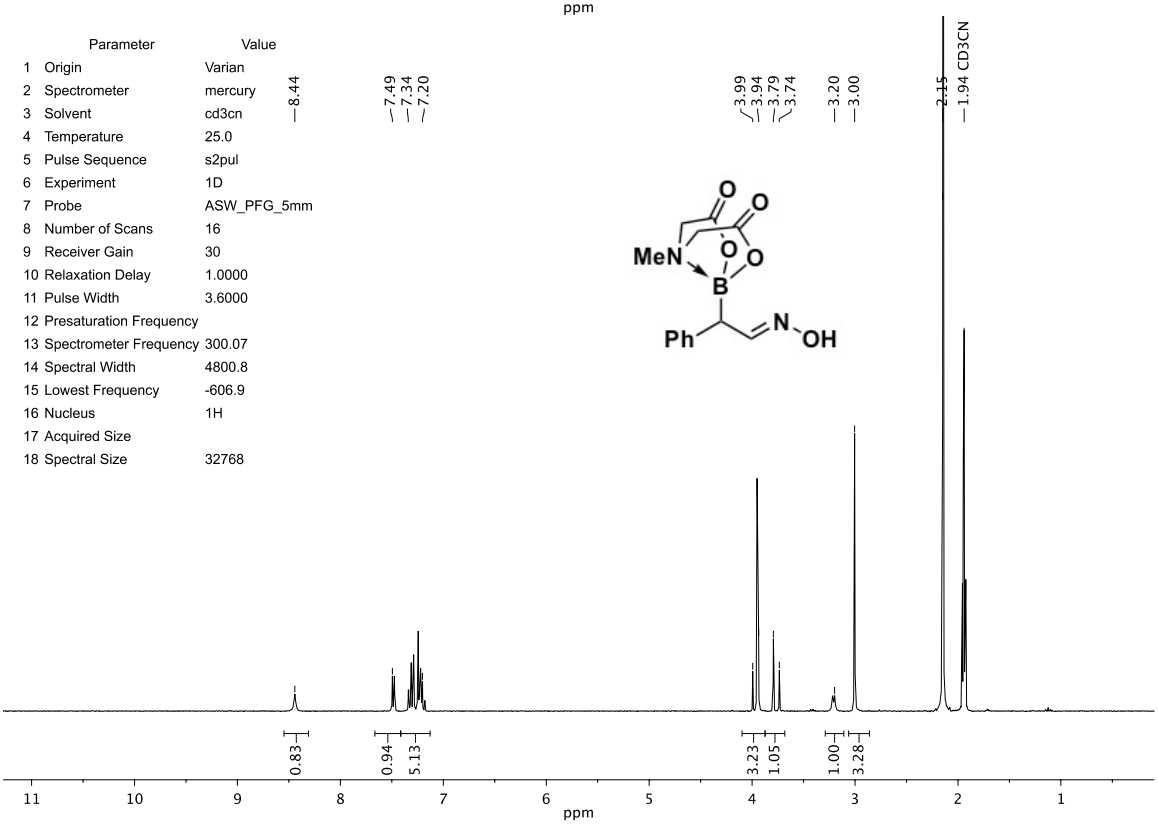
Product - 0.62 min



## $^{1}$H and $^{13}$C NMR Spectra

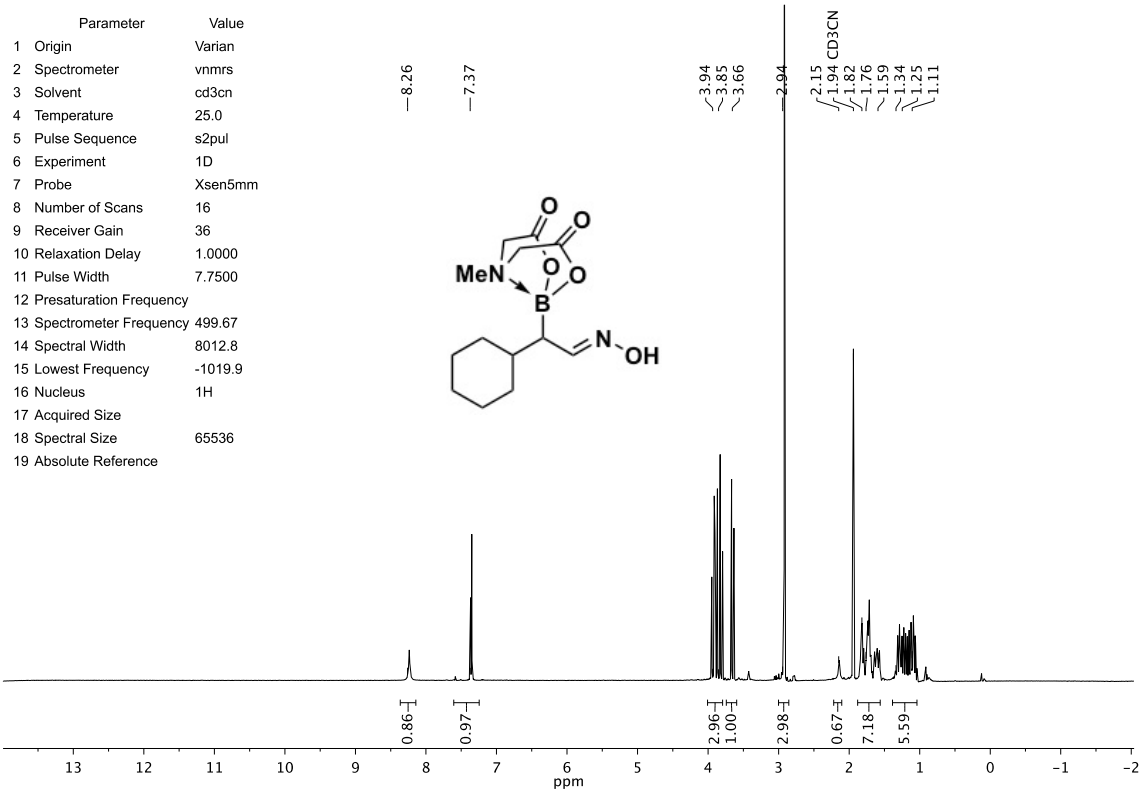
### (*E*)-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-phenylacetaldehyde oxime (3a).



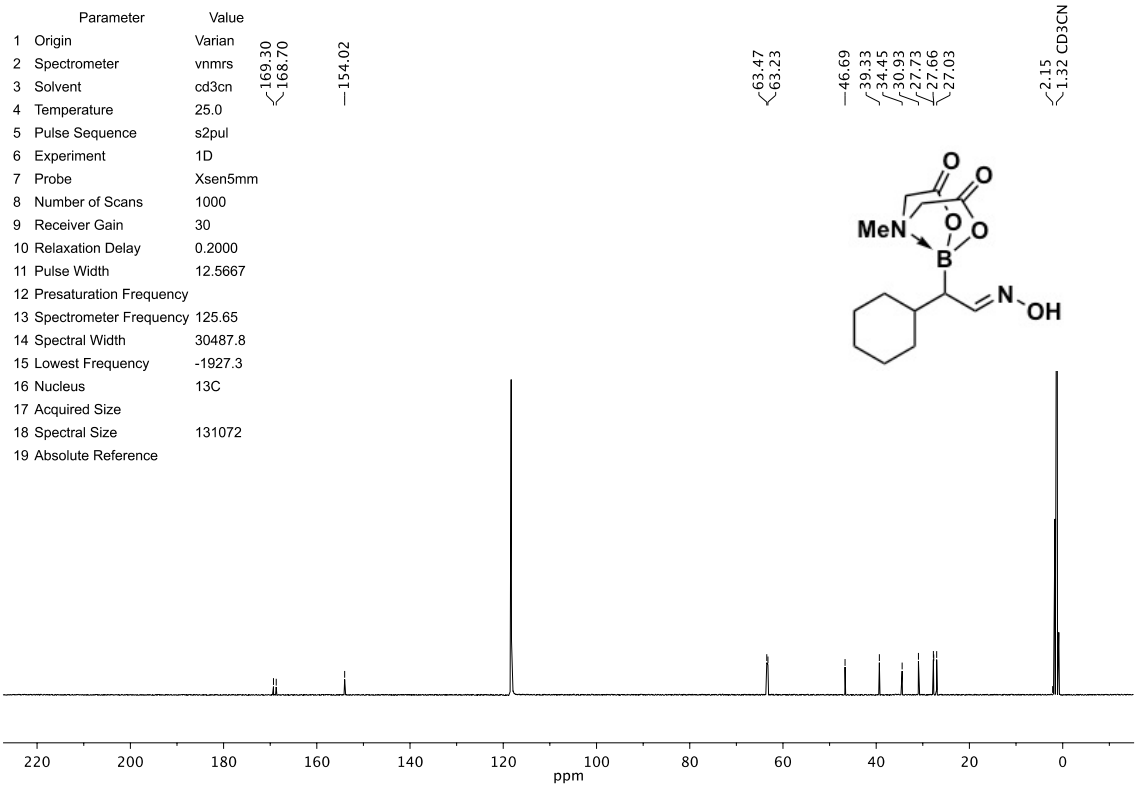



**(*E*)-2-cyclohexyl-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)acetaldehyde oxime (3b).**

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 16 |
| 9 | Receiver Gain | 36 |
| 10 | Relaxation Delay | 1.0000 |
| 11 | Pulse Width | 7.7500 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 499.67 |
| 14 | Spectral Width | 8012.8 |
| 15 | Lowest Frequency | -1019.9 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | |
| 18 | Spectral Size | 65536 |
| 19 | Absolute Reference | |

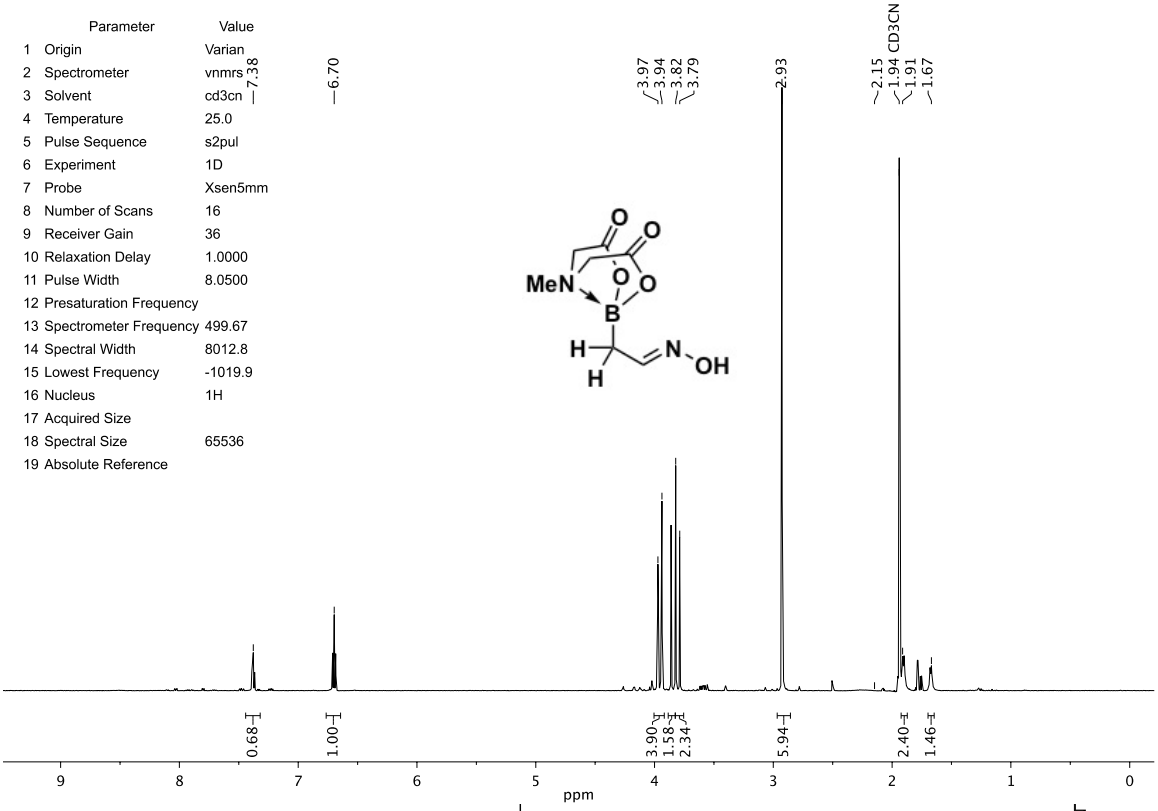



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 1000 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 12.5667 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 125.65 |
| 14 | Spectral Width | 30487.8 |
| 15 | Lowest Frequency | -1927.3 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |
| 19 | Absolute Reference | |

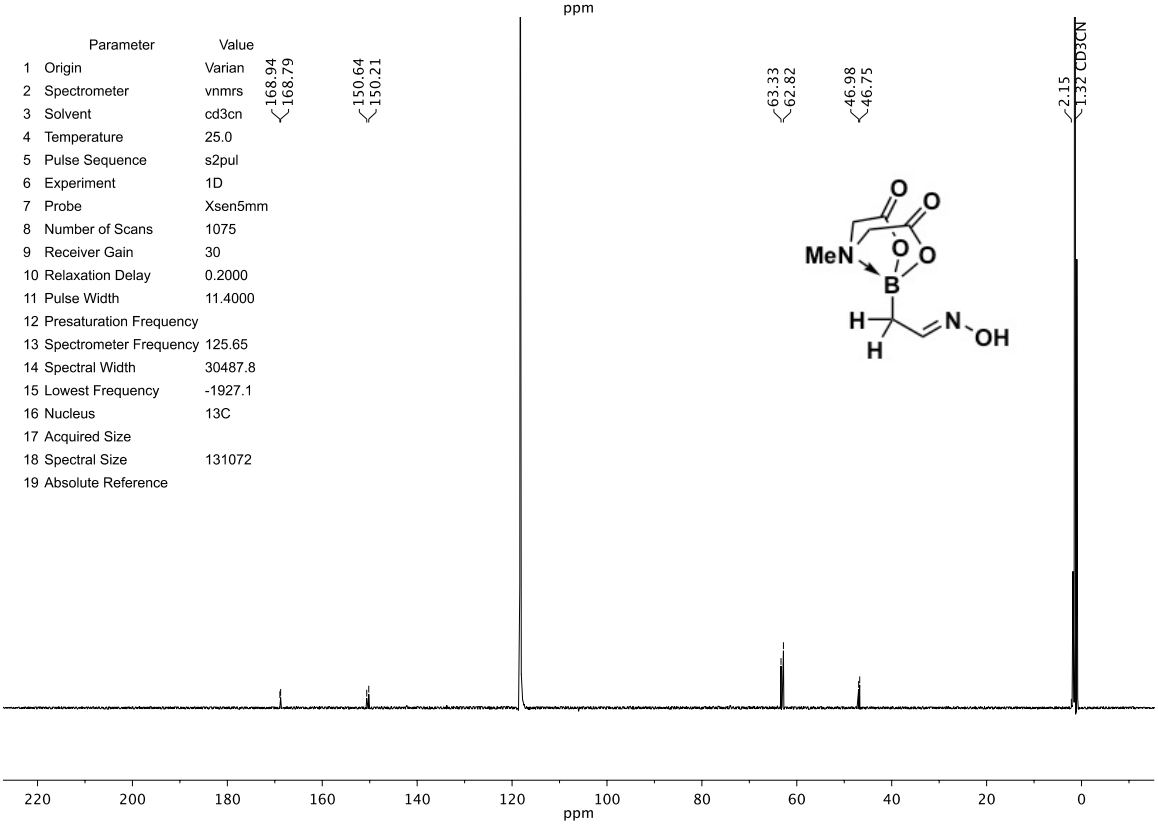


**(*E*)-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)acetaldehyde oxime (3c).**

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 16 |
| 9 | Receiver Gain | 36 |
| 10 | Relaxation Delay | 1.0000 |
| 11 | Pulse Width | 8.0500 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 499.67 |
| 14 | Spectral Width | 8012.8 |
| 15 | Lowest Frequency | -1019.9 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | |
| 18 | Spectral Size | 65536 |
| 19 | Absolute Reference | |

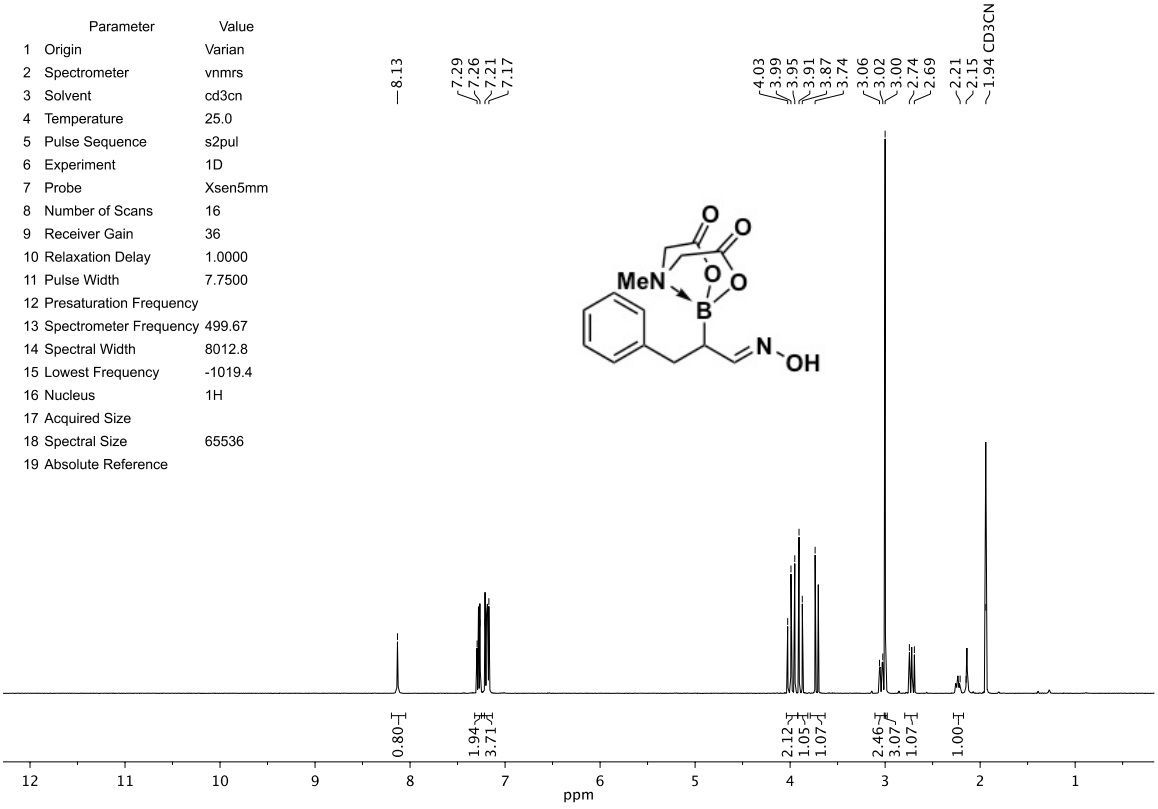



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 1075 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 11.4000 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 125.65 |
| 14 | Spectral Width | 30487.8 |
| 15 | Lowest Frequency | -1927.1 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |
| 19 | Absolute Reference | |

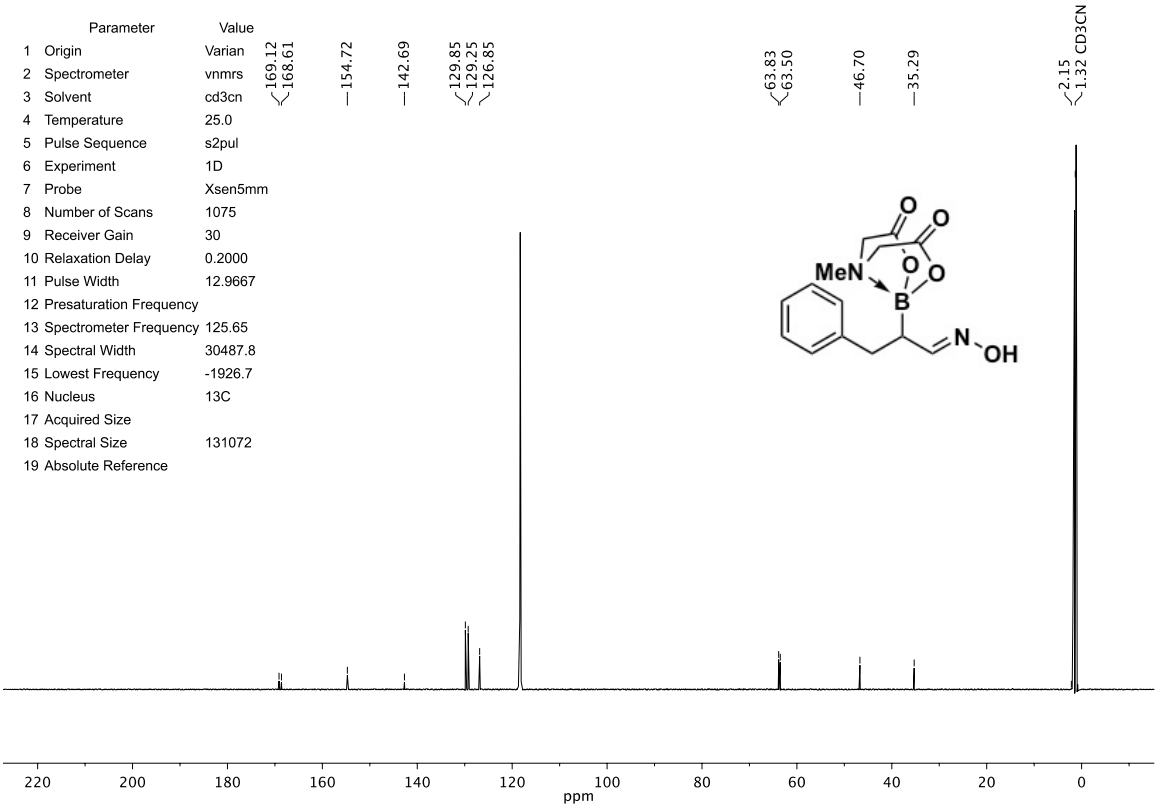


**(*E*)-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-3-phenylpropanal oxime (3d).**

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 16 |
| 9 | Receiver Gain | 36 |
| 10 | Relaxation Delay | 1.0000 |
| 11 | Pulse Width | 7.7500 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 499.67 |
| 14 | Spectral Width | 8012.8 |
| 15 | Lowest Frequency | -1019.4 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | |
| 18 | Spectral Size | 65536 |
| 19 | Absolute Reference | |

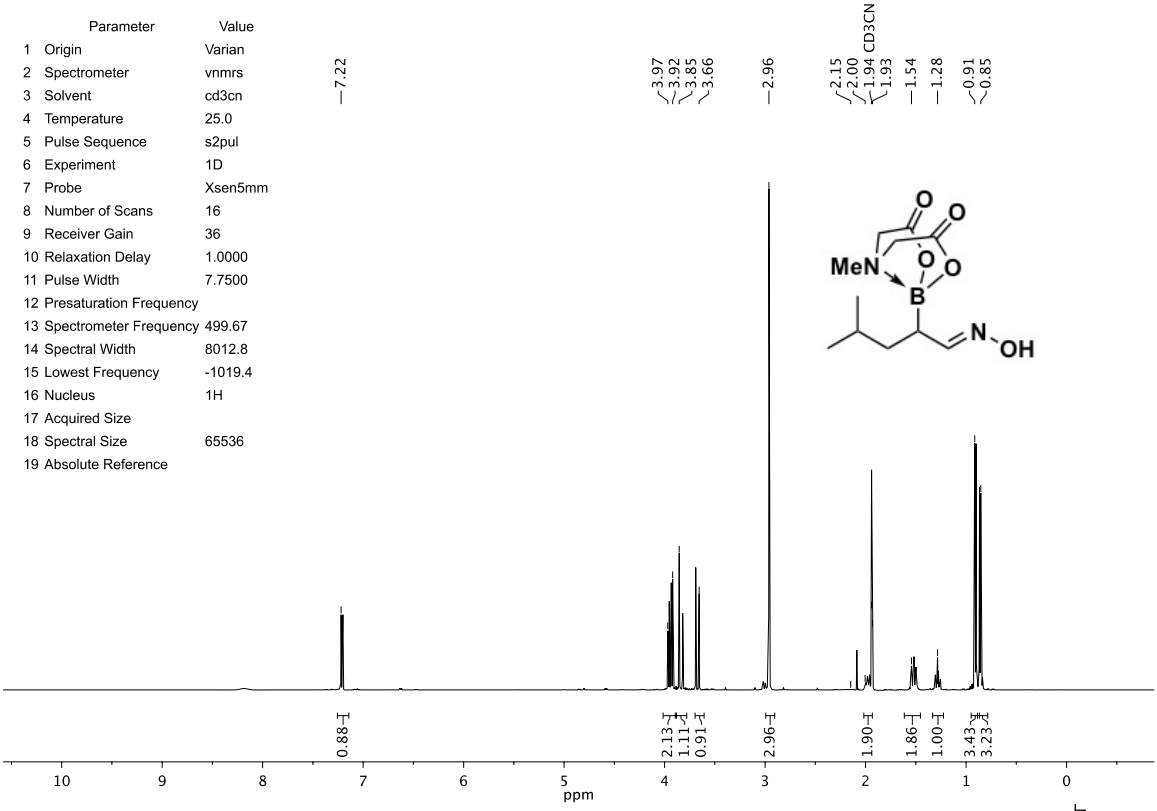



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 1075 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 12.9667 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 125.65 |
| 14 | Spectral Width | 30487.8 |
| 15 | Lowest Frequency | -1926.7 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |
| 19 | Absolute Reference | |

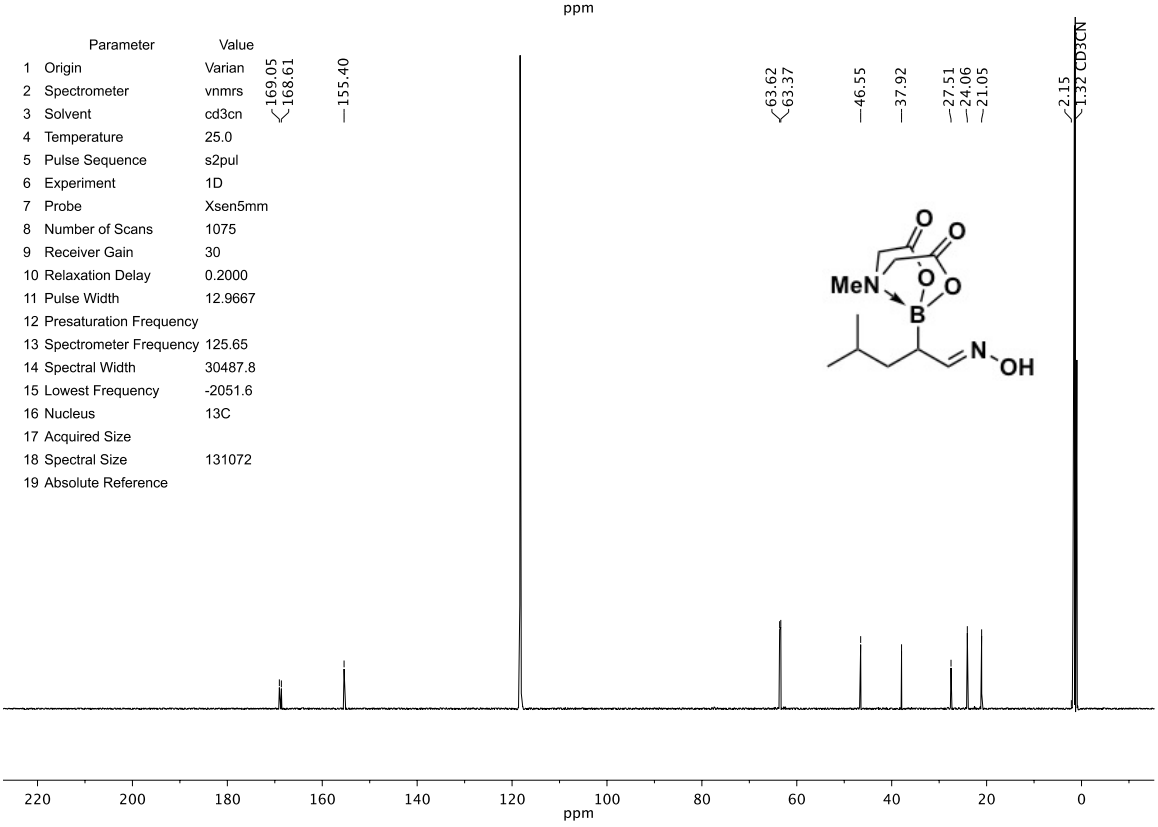


**(*E*)-4-methyl-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pentanal oxime (3e).**

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 16 |
| 9 | Receiver Gain | 36 |
| 10 | Relaxation Delay | 1.0000 |
| 11 | Pulse Width | 7.7500 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 499.67 |
| 14 | Spectral Width | 8012.8 |
| 15 | Lowest Frequency | -1019.4 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | |
| 18 | Spectral Size | 65536 |
| 19 | Absolute Reference | |

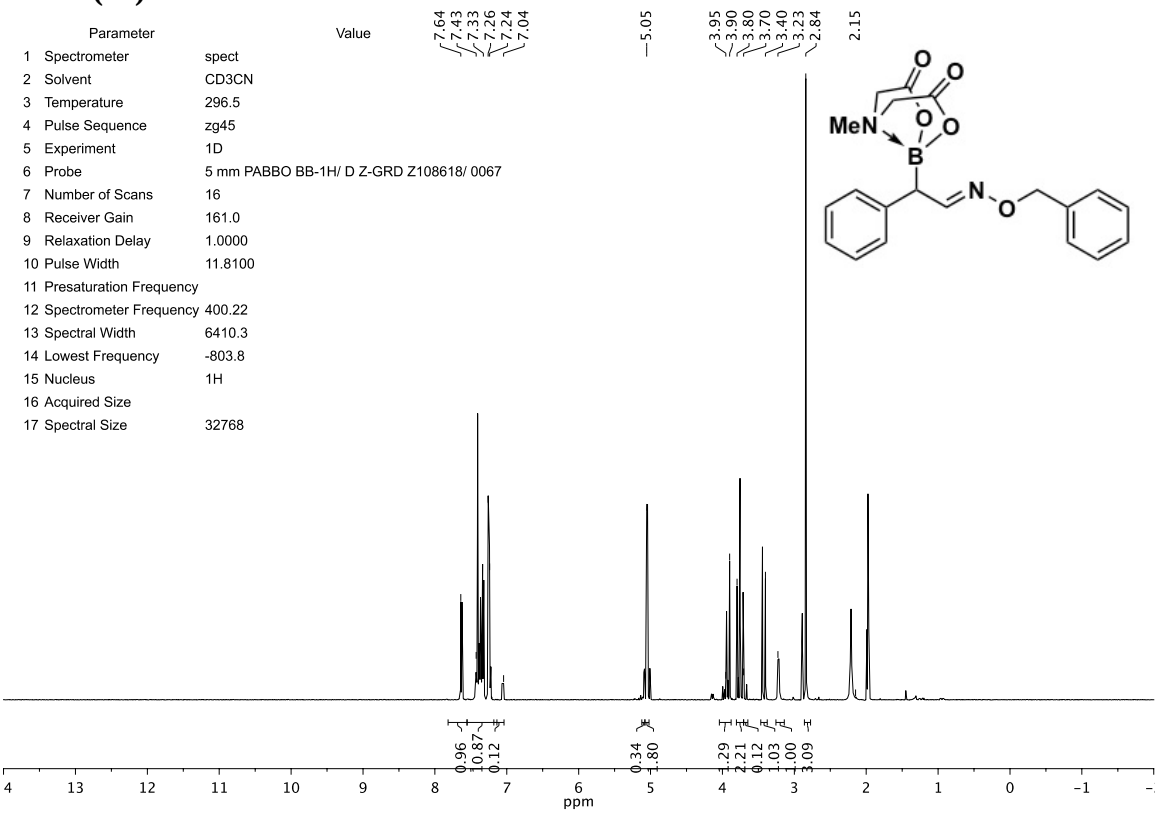



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 1075 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 12.9667 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 125.65 |
| 14 | Spectral Width | 30487.8 |
| 15 | Lowest Frequency | -2051.6 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |
| 19 | Absolute Reference | |

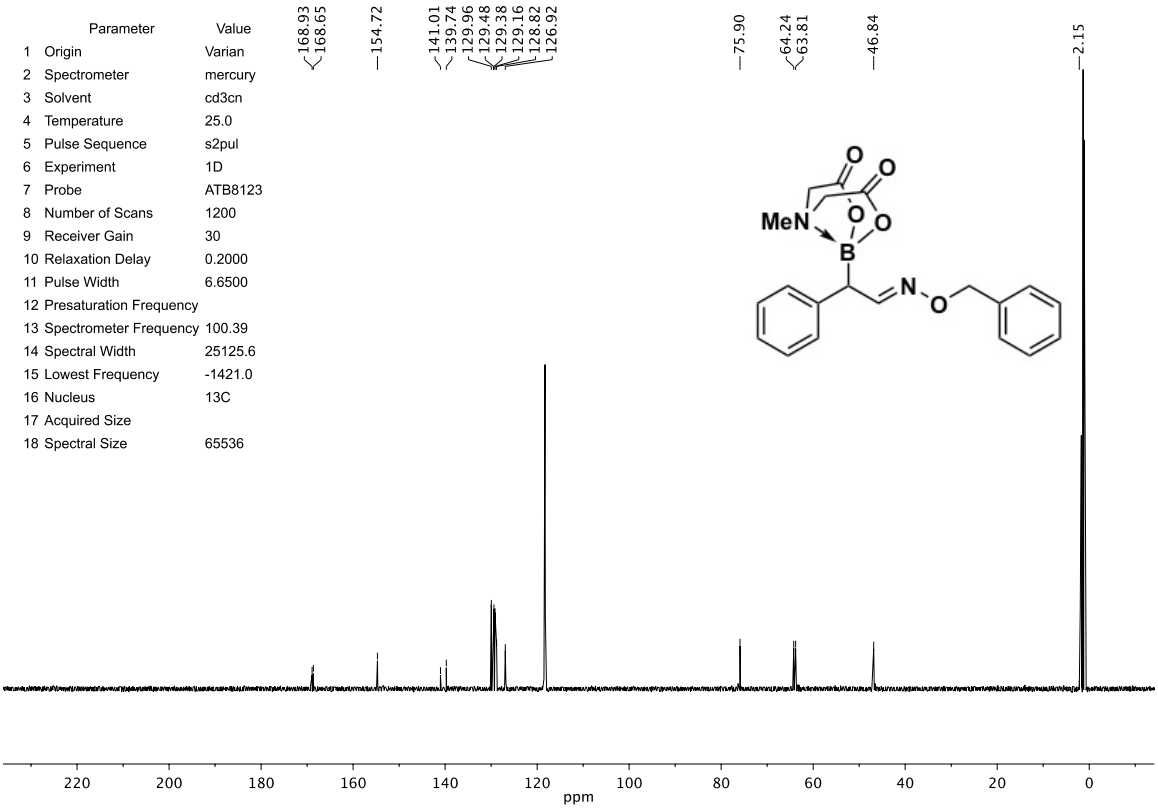


**(*E*)-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-phenylacetaldehyde *O*-benzyl oxime (4a).**

| | Parameter | Value |
|---|---|---|
| 1 | Spectrometer | spect |
| 2 | Solvent | CD3CN |
| 3 | Temperature | 296.5 |
| 4 | Pulse Sequence | zg45 |
| 5 | Experiment | 1D |
| 6 | Probe | 5 mm PABBO BB-1H/ D Z-GRD Z108618/ 0067 |
| 7 | Number of Scans | 16 |
| 8 | Receiver Gain | 161.0 |
| 9 | Relaxation Delay | 1.0000 |
| 10 | Pulse Width | 11.8100 |
| 11 | Presaturation Frequency | |
| 12 | Spectrometer Frequency | 400.22 |
| 13 | Spectral Width | 6410.3 |
| 14 | Lowest Frequency | -803.8 |
| 15 | Nucleus | 1H |
| 16 | Acquired Size | |
| 17 | Spectral Size | 32768 |

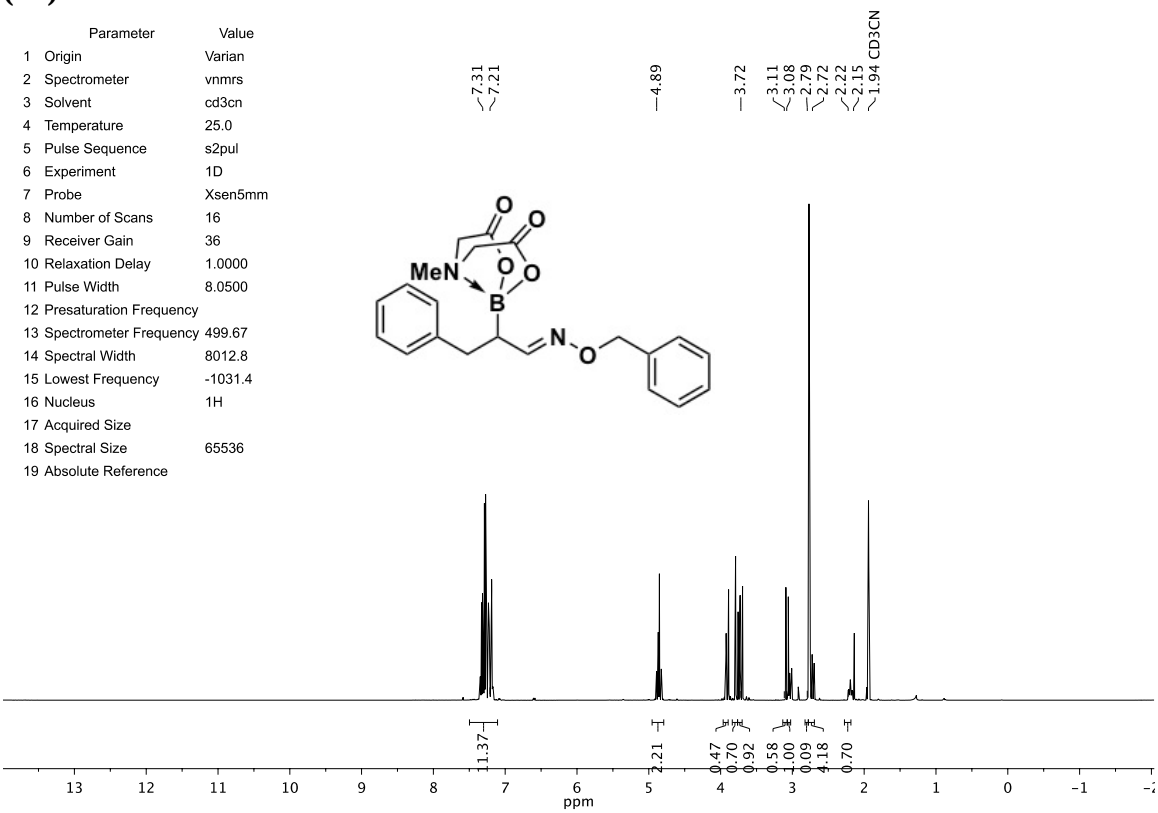



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | mercury |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | ATB8123 |
| 8 | Number of Scans | 1200 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 6.6500 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 100.39 |
| 14 | Spectral Width | 25125.6 |
| 15 | Lowest Frequency | -1421.0 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 65536 |

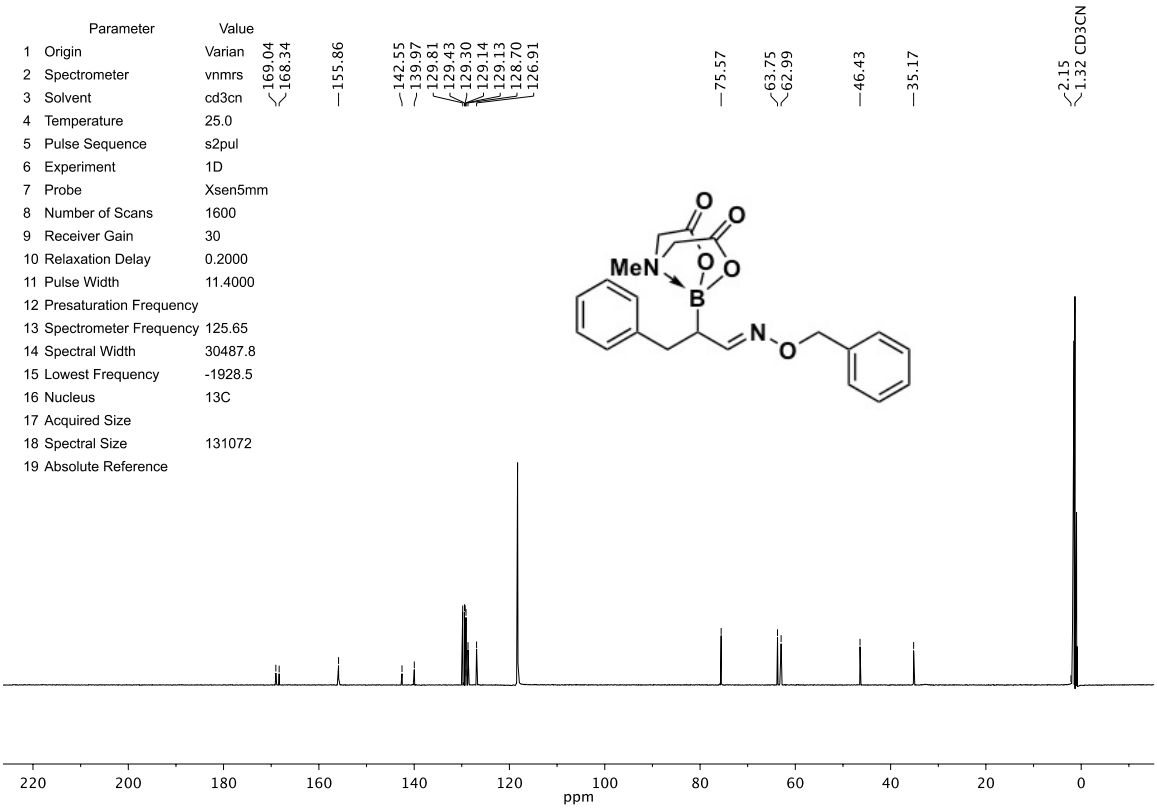


**(*E*)-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-3-phenylpropanal *O*-benzyl oxime (4b).**

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 16 |
| 9 | Receiver Gain | 36 |
| 10 | Relaxation Delay | 1.0000 |
| 11 | Pulse Width | 8.0500 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 499.67 |
| 14 | Spectral Width | 8012.8 |
| 15 | Lowest Frequency | -1031.4 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | |
| 18 | Spectral Size | 65536 |
| 19 | Absolute Reference | |

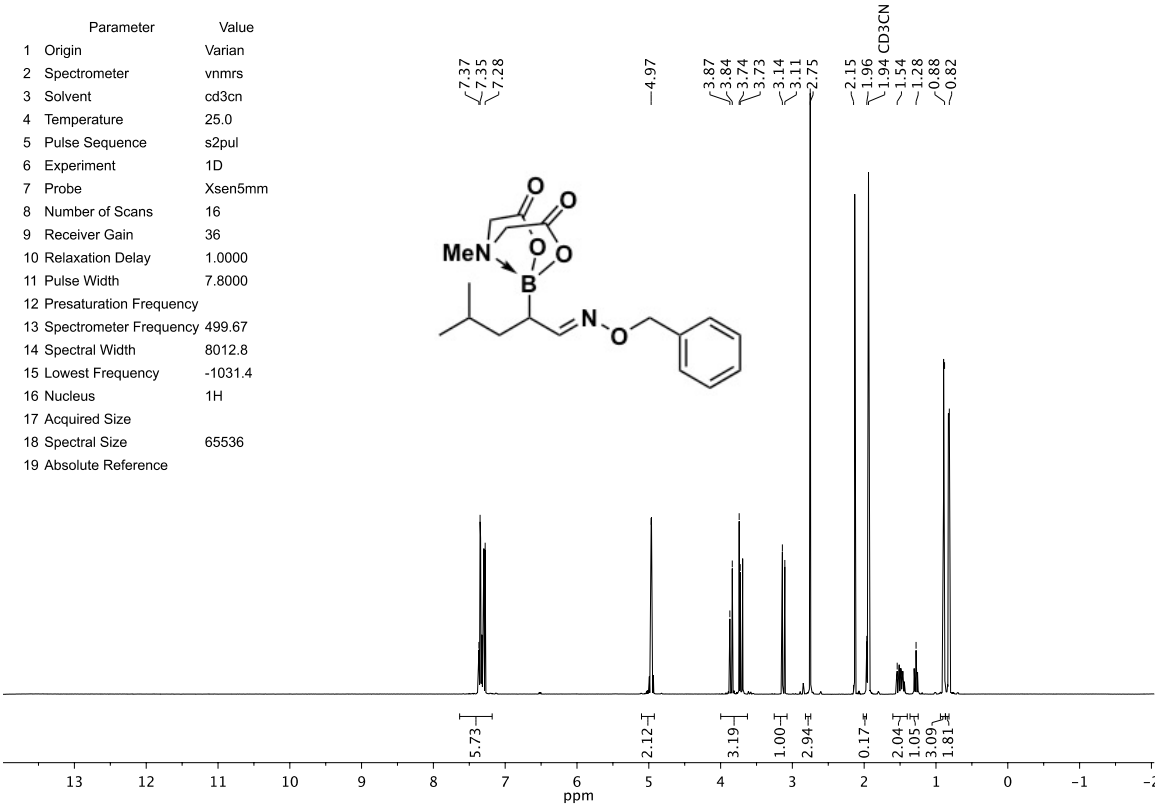



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 1600 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 11.4000 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 125.65 |
| 14 | Spectral Width | 30487.8 |
| 15 | Lowest Frequency | -1928.5 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |
| 19 | Absolute Reference | |

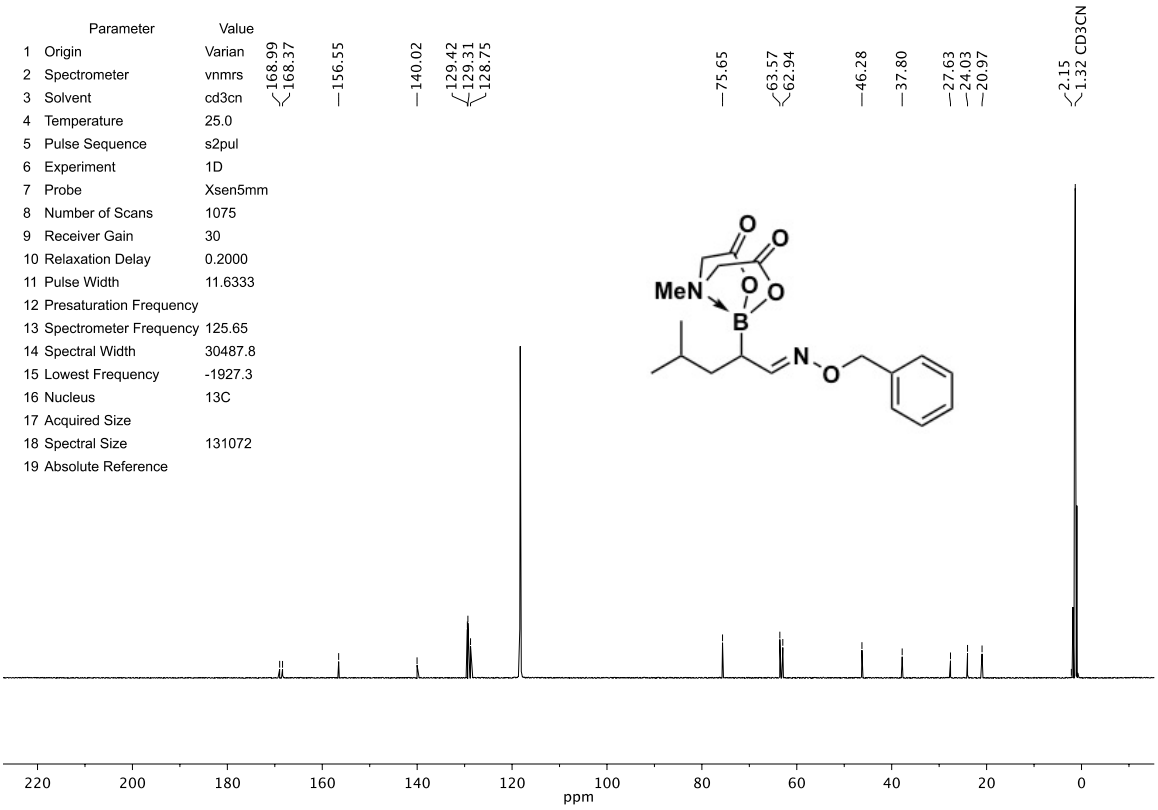


**(*E*)-4-methyl-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pentanal *O*-benzyl oxime (4c).**

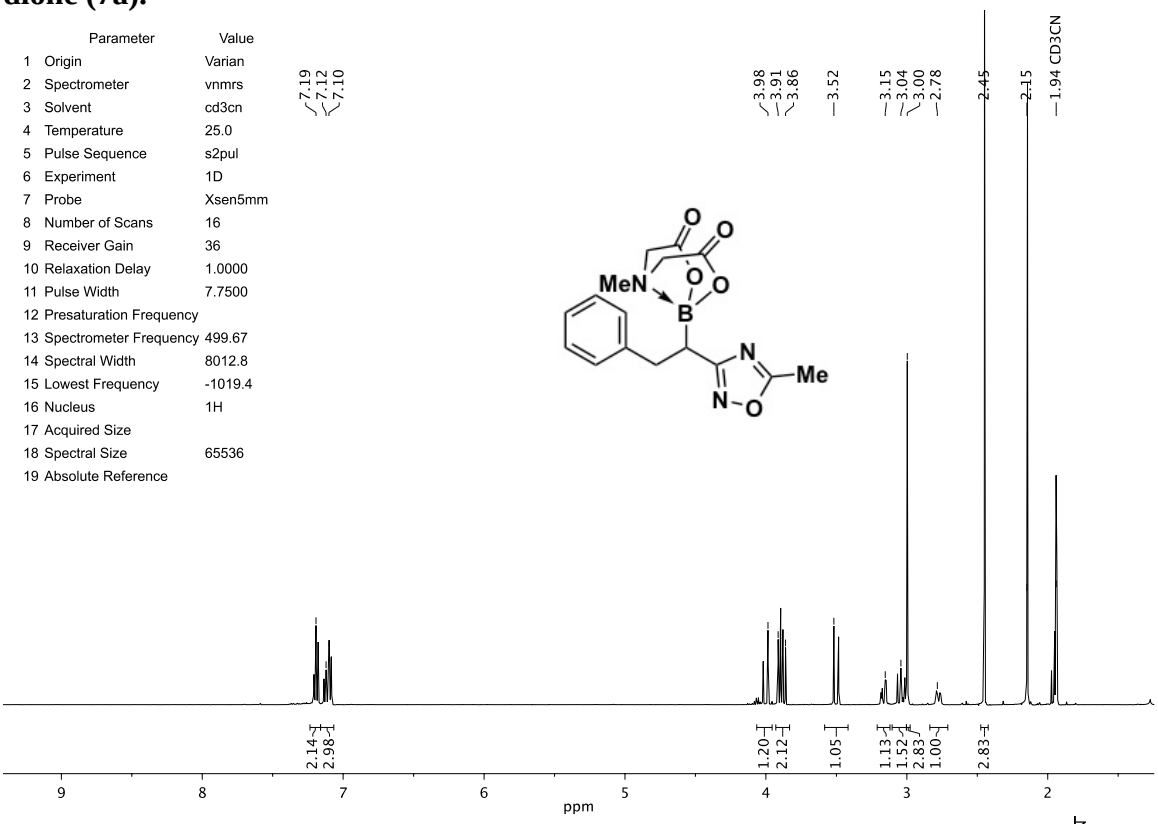
| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 16 |
| 9 | Receiver Gain | 36 |
| 10 | Relaxation Delay | 1.0000 |
| 11 | Pulse Width | 7.8000 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 499.67 |
| 14 | Spectral Width | 8012.8 |
| 15 | Lowest Frequency | -1031.4 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | |
| 18 | Spectral Size | 65536 |
| 19 | Absolute Reference | |

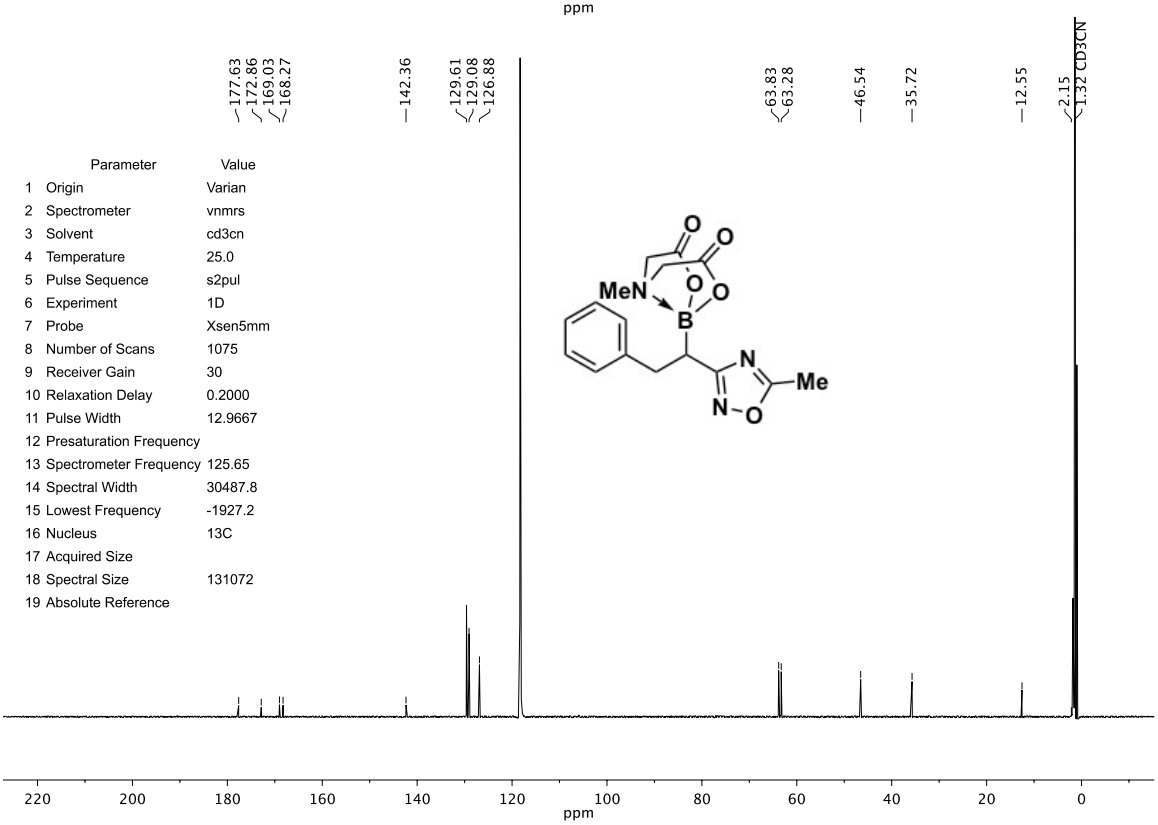



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 1075 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 11.6333 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 125.65 |
| 14 | Spectral Width | 30487.8 |
| 15 | Lowest Frequency | -1927.3 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |
| 19 | Absolute Reference | |



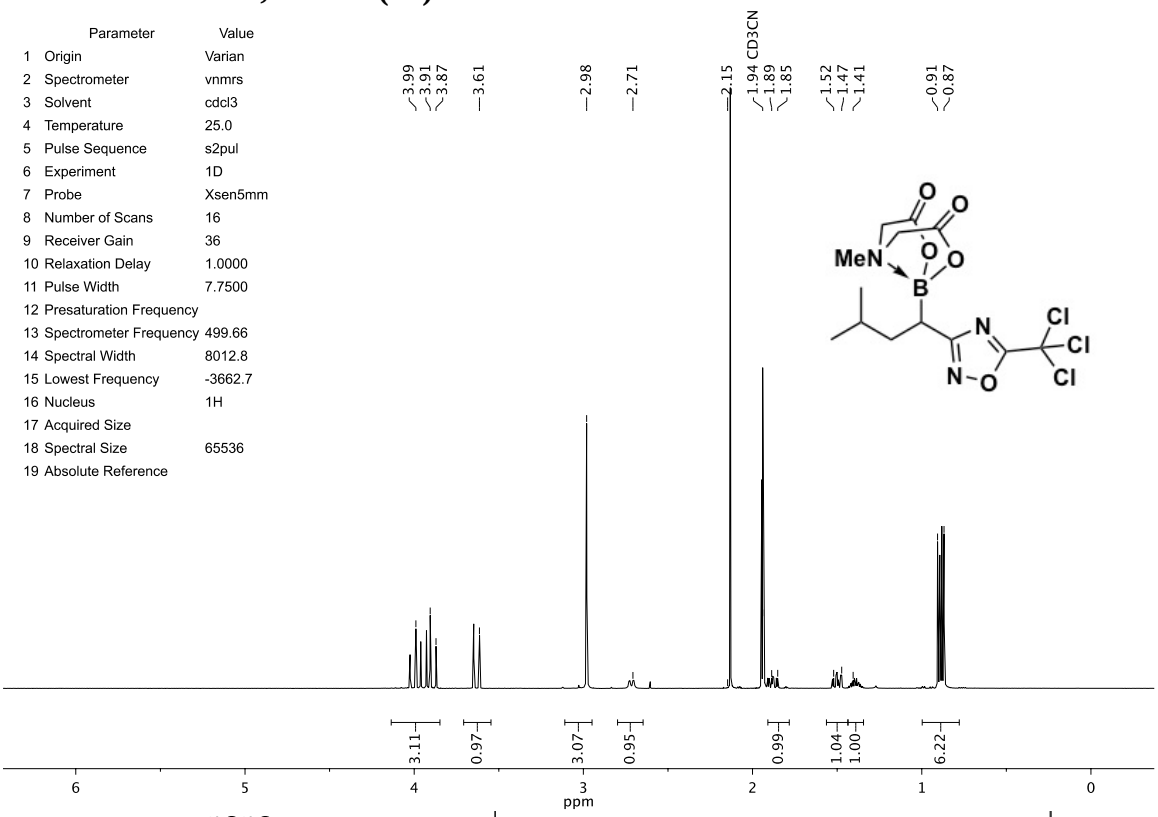
**6-methyl-2-(1-(5-methyl-1,2,4-oxadiazol-3-yl)-2-phenylethyl)-1,3,6,2-dioxazaborocane-4,8-dione (7a).**



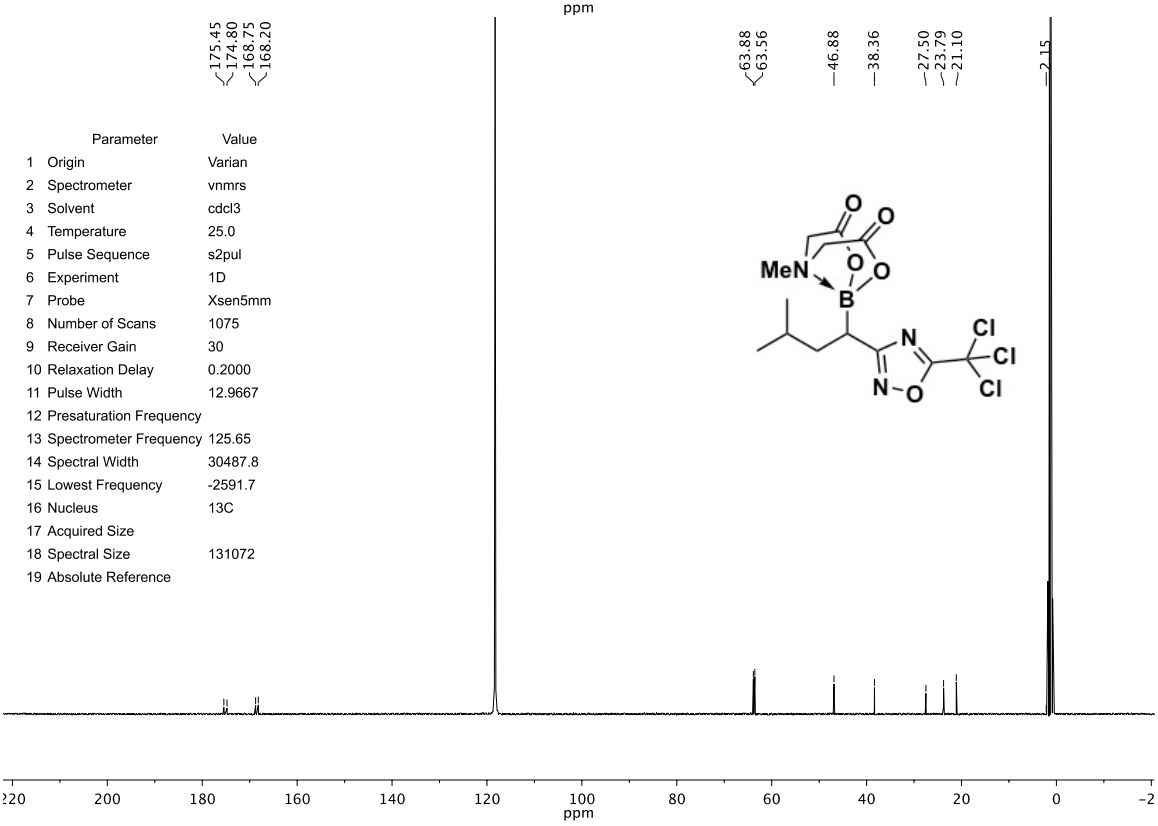



**6-methyl-2-(3-methyl-1-(5-(trichloromethyl)-1,2,4-oxadiazol-3-yl)butyl)-1,3,6,2-dioxazaborocane-4,8-dione (7b).**

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cdcl3 |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 16 |
| 9 | Receiver Gain | 36 |
| 10 | Relaxation Delay | 1.0000 |
| 11 | Pulse Width | 7.7500 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 499.66 |
| 14 | Spectral Width | 8012.8 |
| 15 | Lowest Frequency | -3662.7 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | |
| 18 | Spectral Size | 65536 |
| 19 | Absolute Reference | |

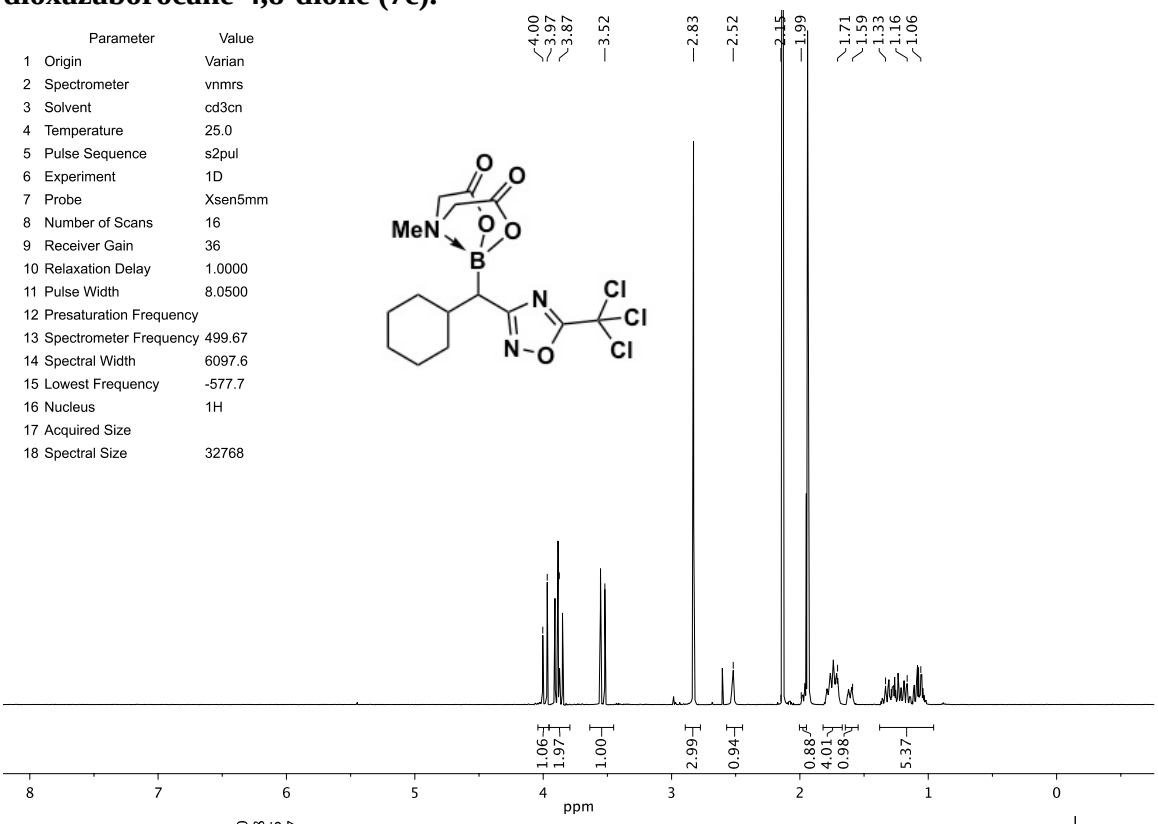



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cdcl3 |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 1075 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 12.9667 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 125.65 |
| 14 | Spectral Width | 30487.8 |
| 15 | Lowest Frequency | -2591.7 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |
| 19 | Absolute Reference | |

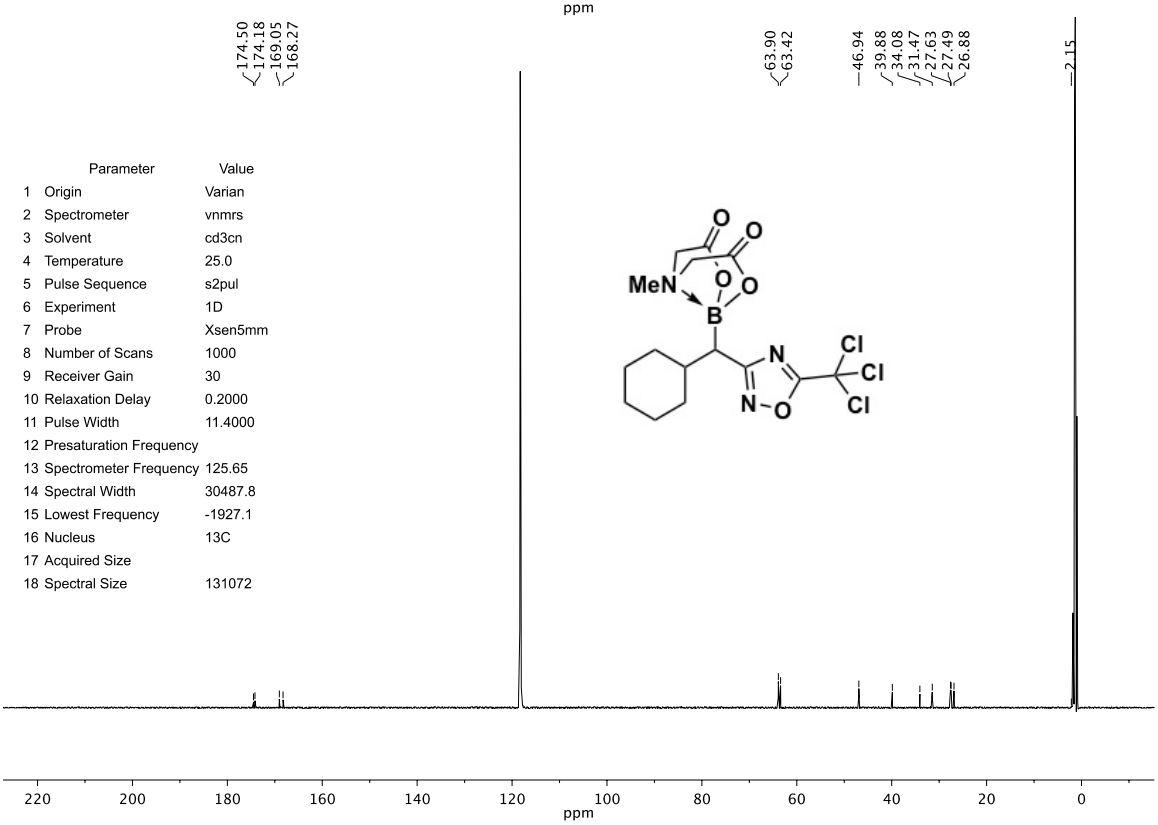


**2-(cyclohexyl(5-(trichloromethyl)-1,2,4-oxadiazol-3-yl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (7c).**

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 16 |
| 9 | Receiver Gain | 36 |
| 10 | Relaxation Delay | 1.0000 |
| 11 | Pulse Width | 8.0500 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 499.67 |
| 14 | Spectral Width | 6097.6 |
| 15 | Lowest Frequency | -577.7 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | |
| 18 | Spectral Size | 32768 |

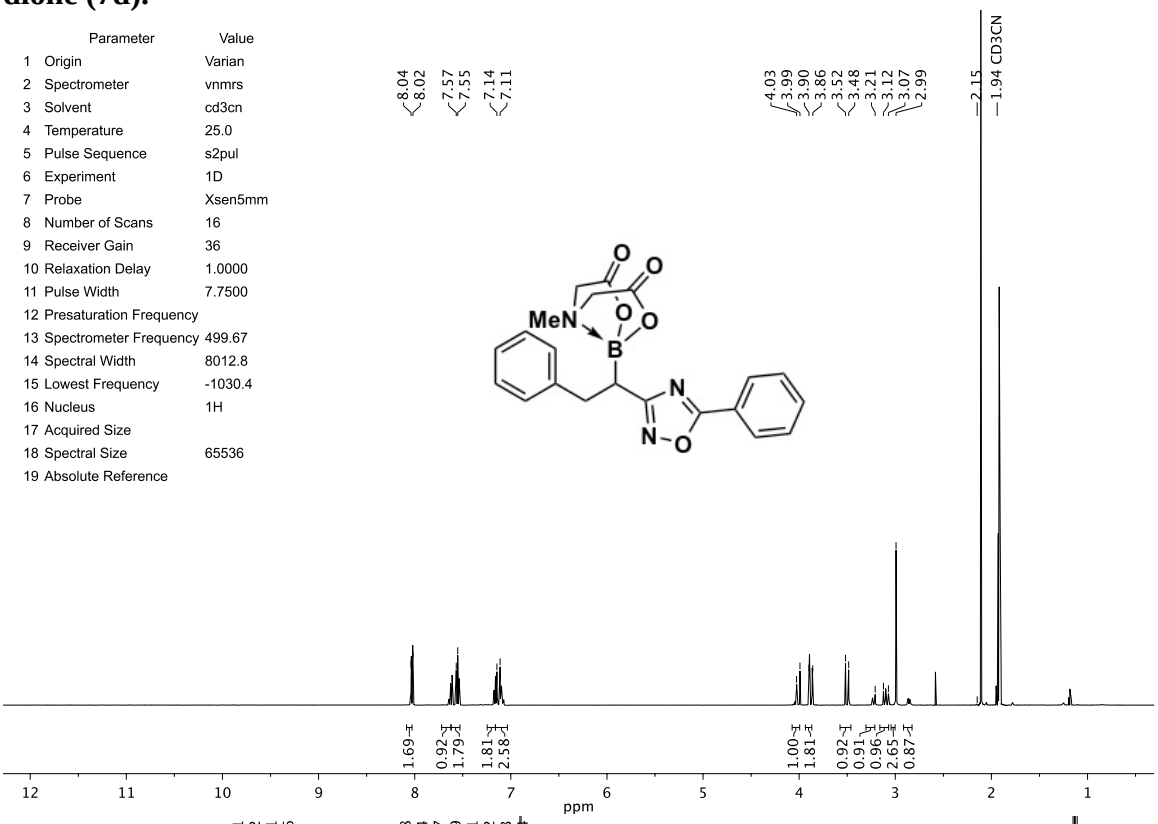



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 1000 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 11.4000 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 125.65 |
| 14 | Spectral Width | 30487.8 |
| 15 | Lowest Frequency | -1927.1 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |

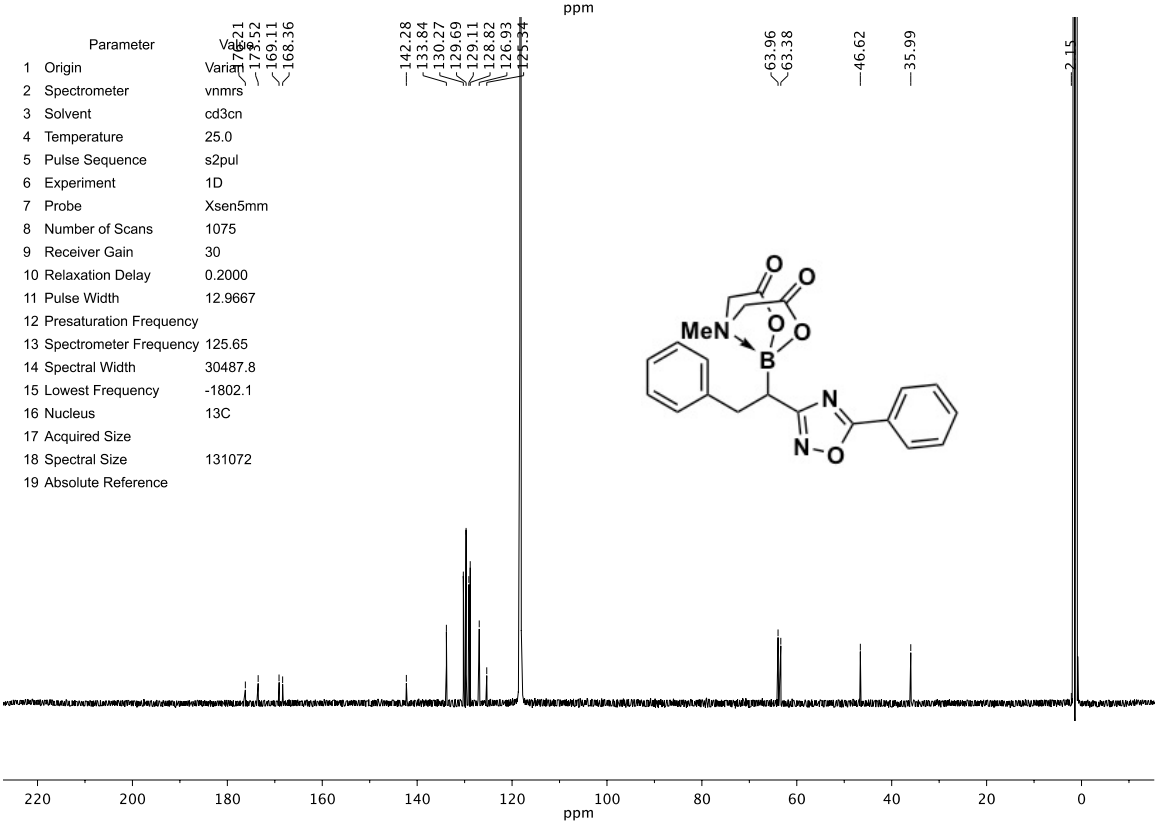


**6-methyl-2-(2-phenyl-1-(5-phenyl-1,2,4-oxadiazol-3-yl)ethyl)-1,3,6,2-dioxazaborocane-4,8-dione (7d).**

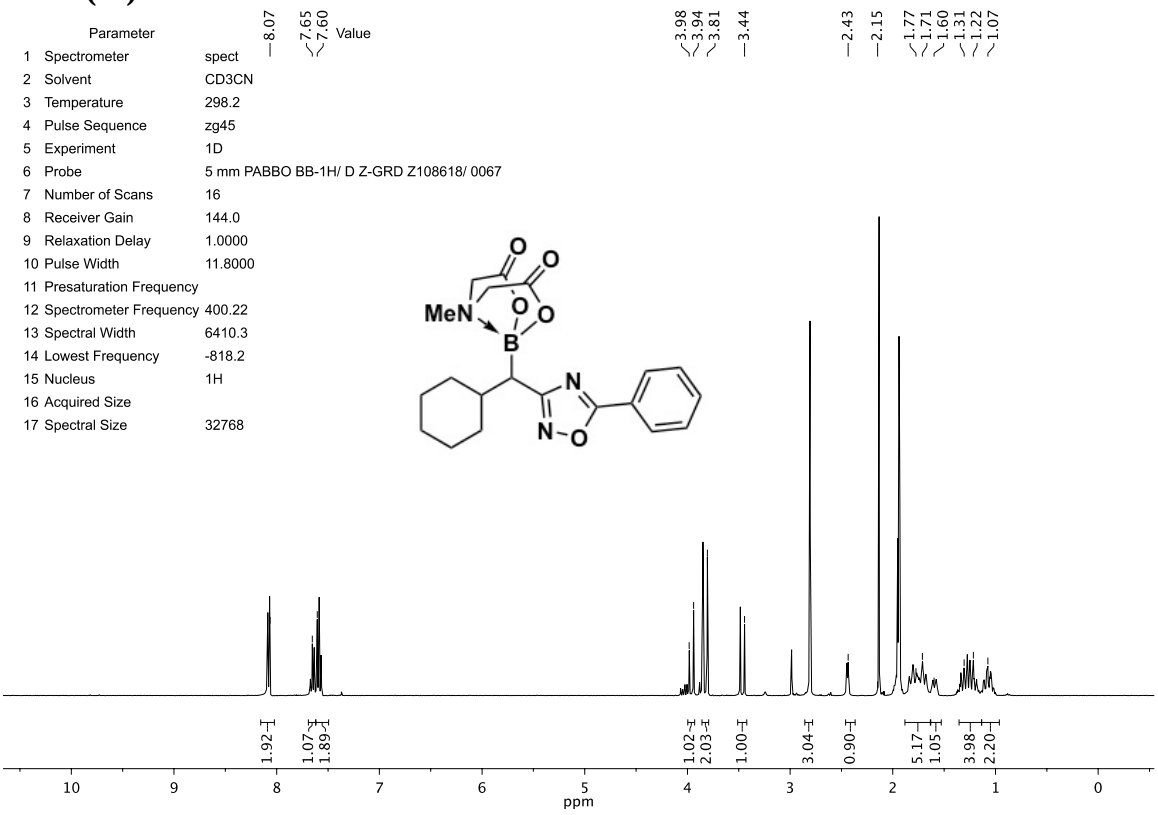
| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 16 |
| 9 | Receiver Gain | 36 |
| 10 | Relaxation Delay | 1.0000 |
| 11 | Pulse Width | 7.7500 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 499.67 |
| 14 | Spectral Width | 8012.8 |
| 15 | Lowest Frequency | -1030.4 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | |
| 18 | Spectral Size | 65536 |
| 19 | Absolute Reference | |



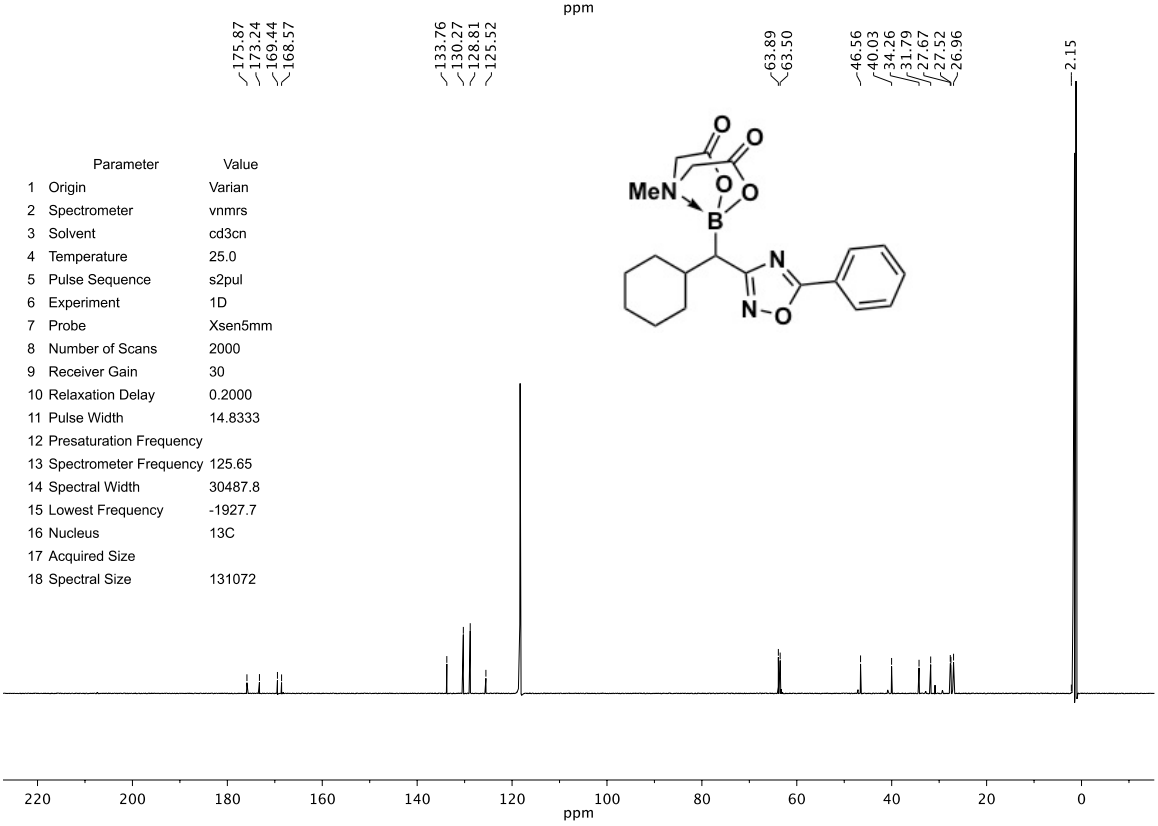

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 1075 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 12.9667 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 125.65 |
| 14 | Spectral Width | 30487.8 |
| 15 | Lowest Frequency | -1802.1 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |
| 19 | Absolute Reference | |



## 2-(cyclohexyl(5-phenyl-1,2,4-oxadiazol-3-yl)methyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (7e).

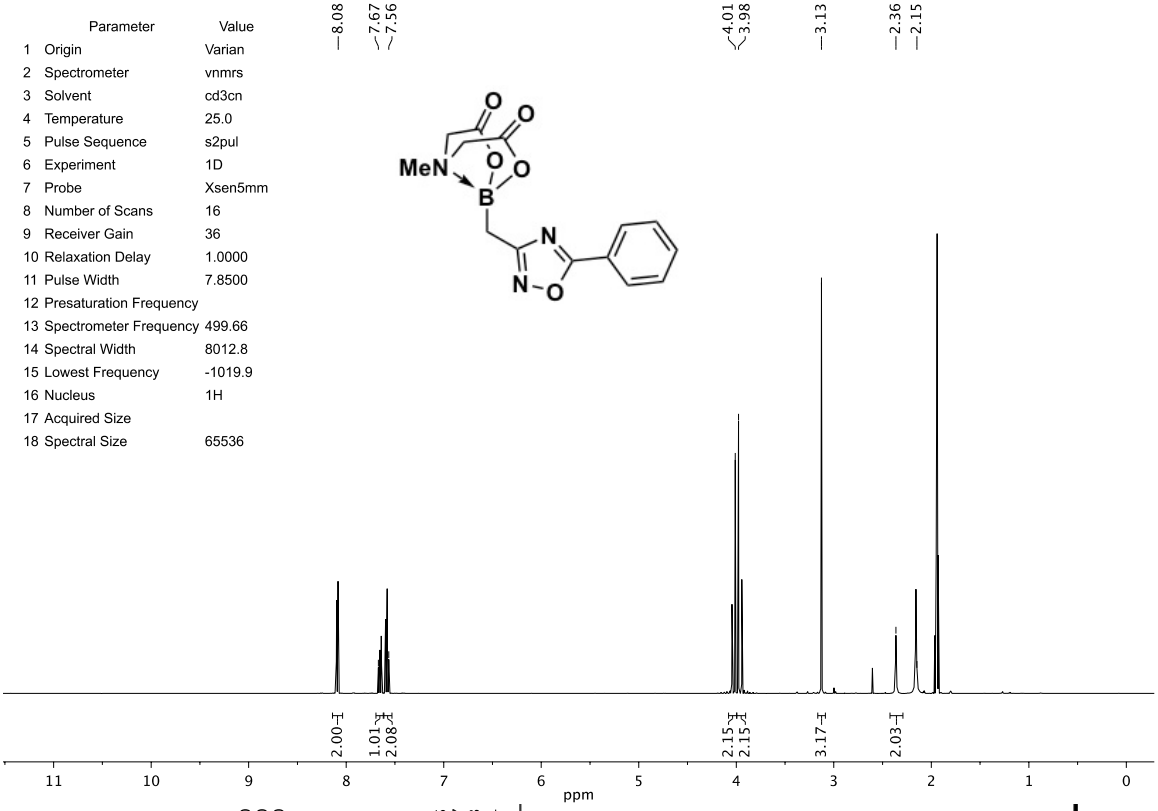



| Parameter | Value |
|---|---|
| 1 Spectrometer | spect |
| 2 Solvent | CD3CN |
| 3 Temperature | 298.2 |
| 4 Pulse Sequence | zg45 |
| 5 Experiment | 1D |
| 6 Probe | 5 mm PABBO BB-1H/ D Z-GRD Z108618/ 0067 |
| 7 Number of Scans | 16 |
| 8 Receiver Gain | 144.0 |
| 9 Relaxation Delay | 1.0000 |
| 10 Pulse Width | 11.8000 |
| 11 Presaturation Frequency | |
| 12 Spectrometer Frequency | 400.22 |
| 13 Spectral Width | 6410.3 |
| 14 Lowest Frequency | -818.2 |
| 15 Nucleus | 1H |
| 16 Acquired Size | |
| 17 Spectral Size | 32768 |

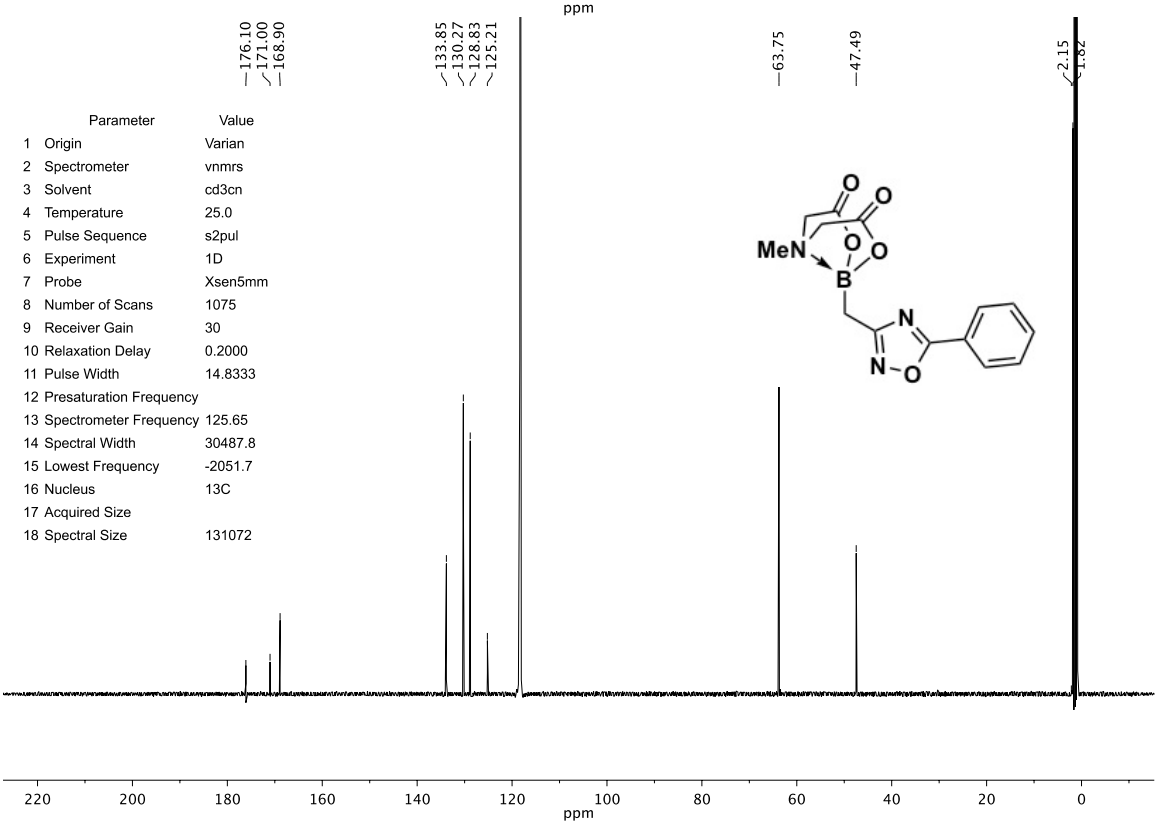



| Parameter | Value |
|---|---|
| 1 Origin | Varian |
| 2 Spectrometer | vnmrs |
| 3 Solvent | cd3cn |
| 4 Temperature | 25.0 |
| 5 Pulse Sequence | s2pul |
| 6 Experiment | 1D |
| 7 Probe | Xsen5mm |
| 8 Number of Scans | 2000 |
| 9 Receiver Gain | 30 |
| 10 Relaxation Delay | 0.2000 |
| 11 Pulse Width | 14.8333 |
| 12 Presaturation Frequency | |
| 13 Spectrometer Frequency | 125.65 |
| 14 Spectral Width | 30487.8 |
| 15 Lowest Frequency | -1927.7 |
| 16 Nucleus | 13C |
| 17 Acquired Size | |
| 18 Spectral Size | 131072 |

**6-methyl-2-((5-phenyl-1,2,4-oxadiazol-3-yl)methyl)-1,3,6,2-dioxazaborocane-4,8-dione (7f).**

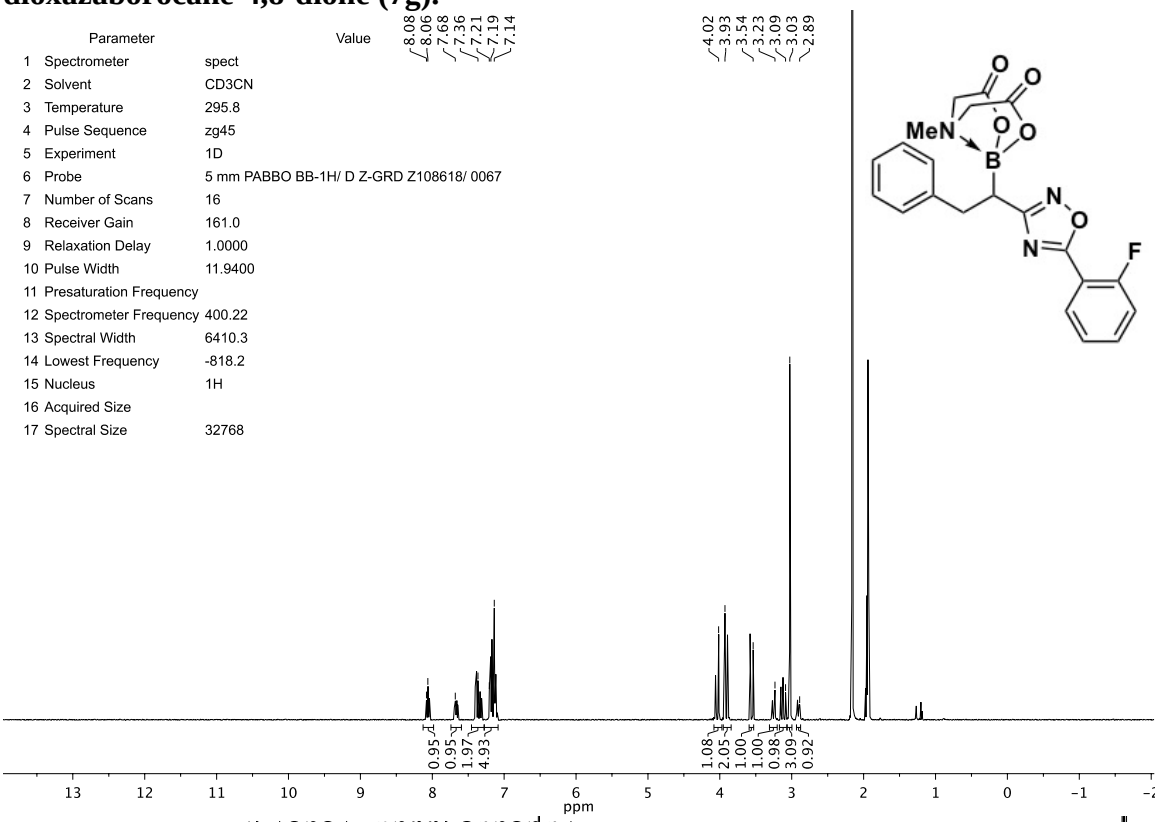



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 16 |
| 9 | Receiver Gain | 36 |
| 10 | Relaxation Delay | 1.0000 |
| 11 | Pulse Width | 7.8500 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 499.66 |
| 14 | Spectral Width | 8012.8 |
| 15 | Lowest Frequency | -1019.9 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | |
| 18 | Spectral Size | 65536 |

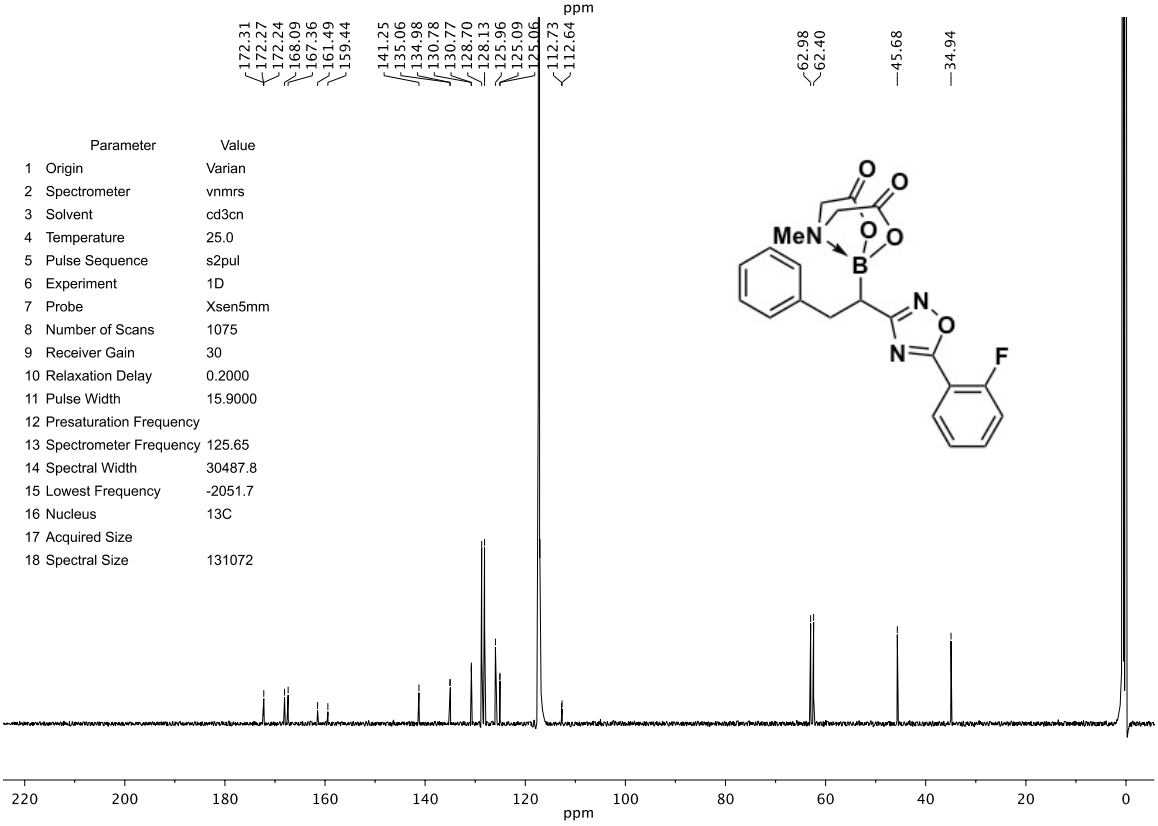



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 1075 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 14.8333 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 125.65 |
| 14 | Spectral Width | 30487.8 |
| 15 | Lowest Frequency | -2051.7 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |

**2-(1-(5-(2-fluorophenyl)-1,2,4-oxadiazol-3-yl)-2-phenylethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (7g).**

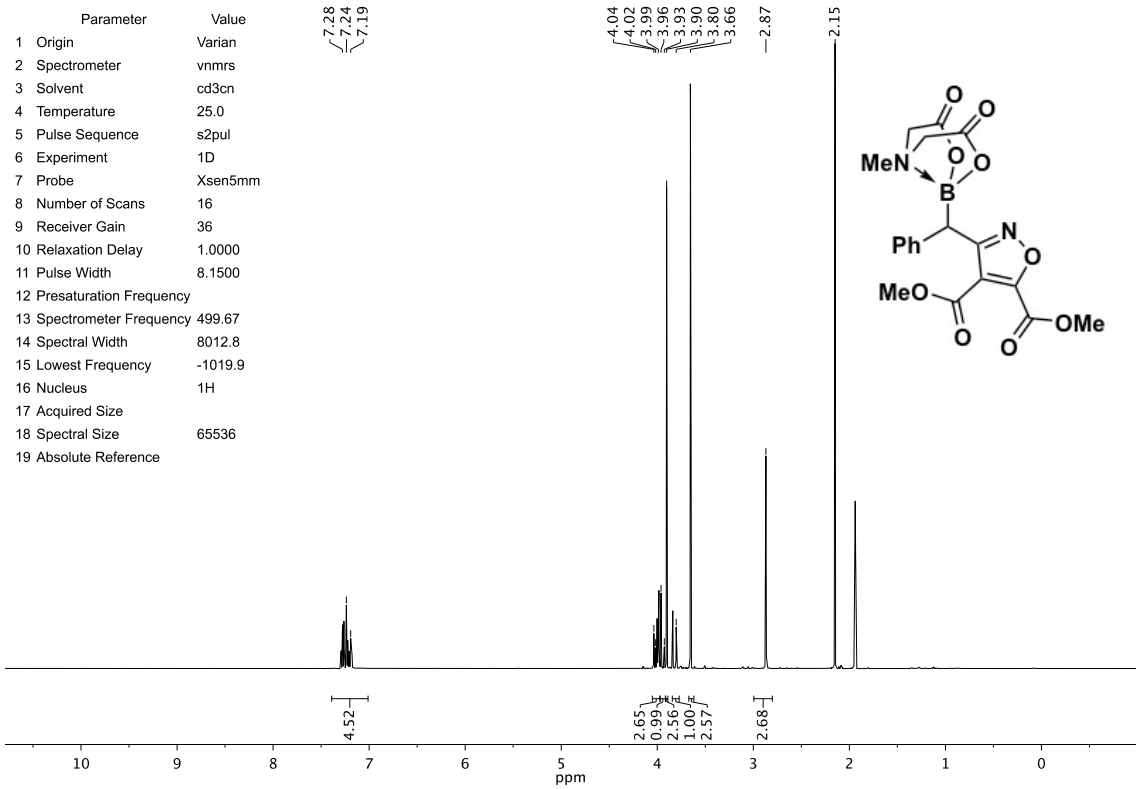


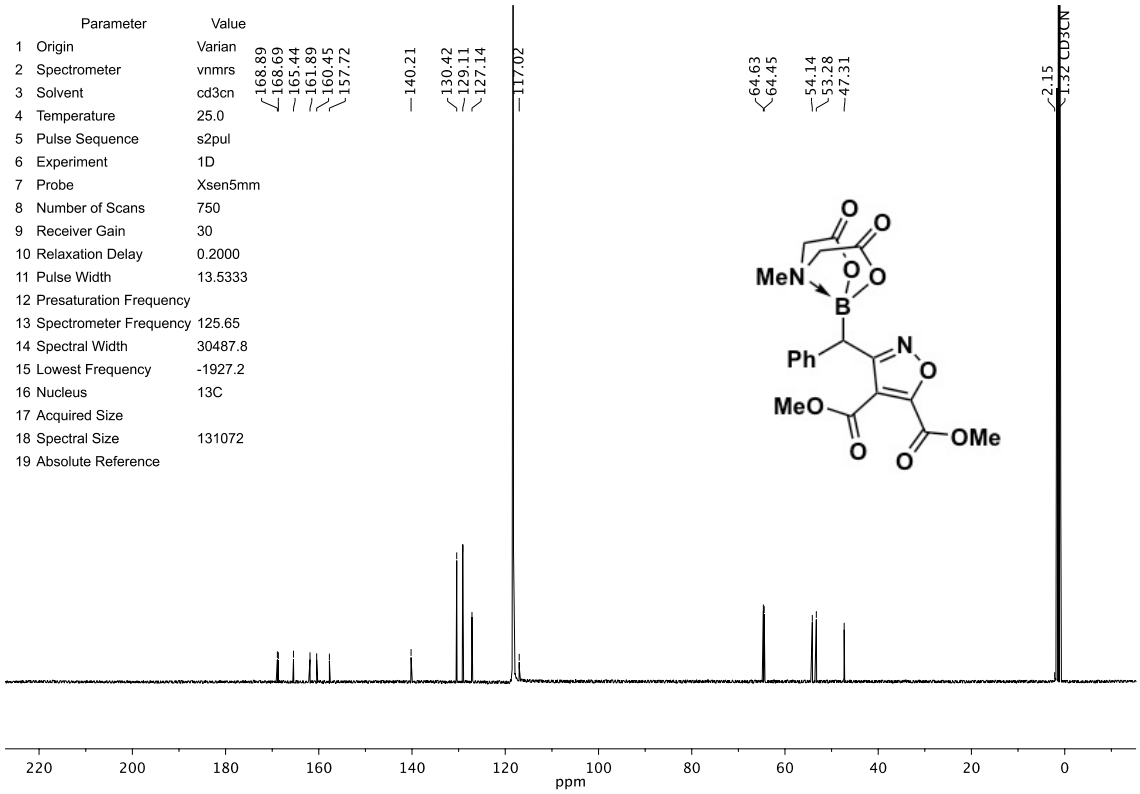

| Parameter | Value |
|---|---|
| 1 Spectrometer | spect |
| 2 Solvent | CD3CN |
| 3 Temperature | 295.8 |
| 4 Pulse Sequence | zg45 |
| 5 Experiment | 1D |
| 6 Probe | 5 mm PABBO BB-1H/ D Z-GRD Z108618/ 0067 |
| 7 Number of Scans | 16 |
| 8 Receiver Gain | 161.0 |
| 9 Relaxation Delay | 1.0000 |
| 10 Pulse Width | 11.9400 |
| 11 Presaturation Frequency | |
| 12 Spectrometer Frequency | 400.22 |
| 13 Spectral Width | 6410.3 |
| 14 Lowest Frequency | -818.2 |
| 15 Nucleus | 1H |
| 16 Acquired Size | |
| 17 Spectral Size | 32768 |




| Parameter | Value |
|---|---|
| 1 Origin | Varian |
| 2 Spectrometer | vnmrs |
| 3 Solvent | cd3cn |
| 4 Temperature | 25.0 |
| 5 Pulse Sequence | s2pul |
| 6 Experiment | 1D |
| 7 Probe | Xsen5mm |
| 8 Number of Scans | 1075 |
| 9 Receiver Gain | 30 |
| 10 Relaxation Delay | 0.2000 |
| 11 Pulse Width | 15.9000 |
| 12 Presaturation Frequency | |
| 13 Spectrometer Frequency | 125.65 |
| 14 Spectral Width | 30487.8 |
| 15 Lowest Frequency | -2051.7 |
| 16 Nucleus | 13C |
| 17 Acquired Size | |
| 18 Spectral Size | 131072 |

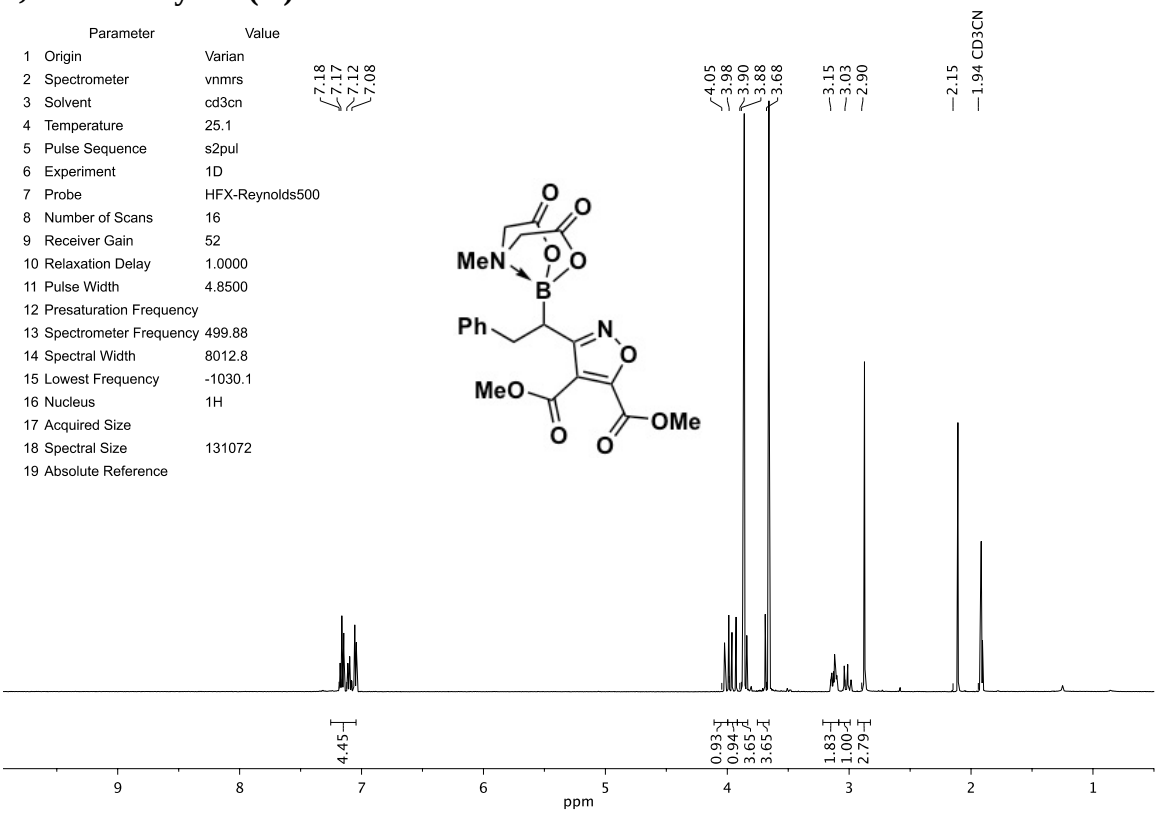
**dimethyl 3-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)(phenyl)methyl)isoxazole-4,5-dicarboxylate (7h).**



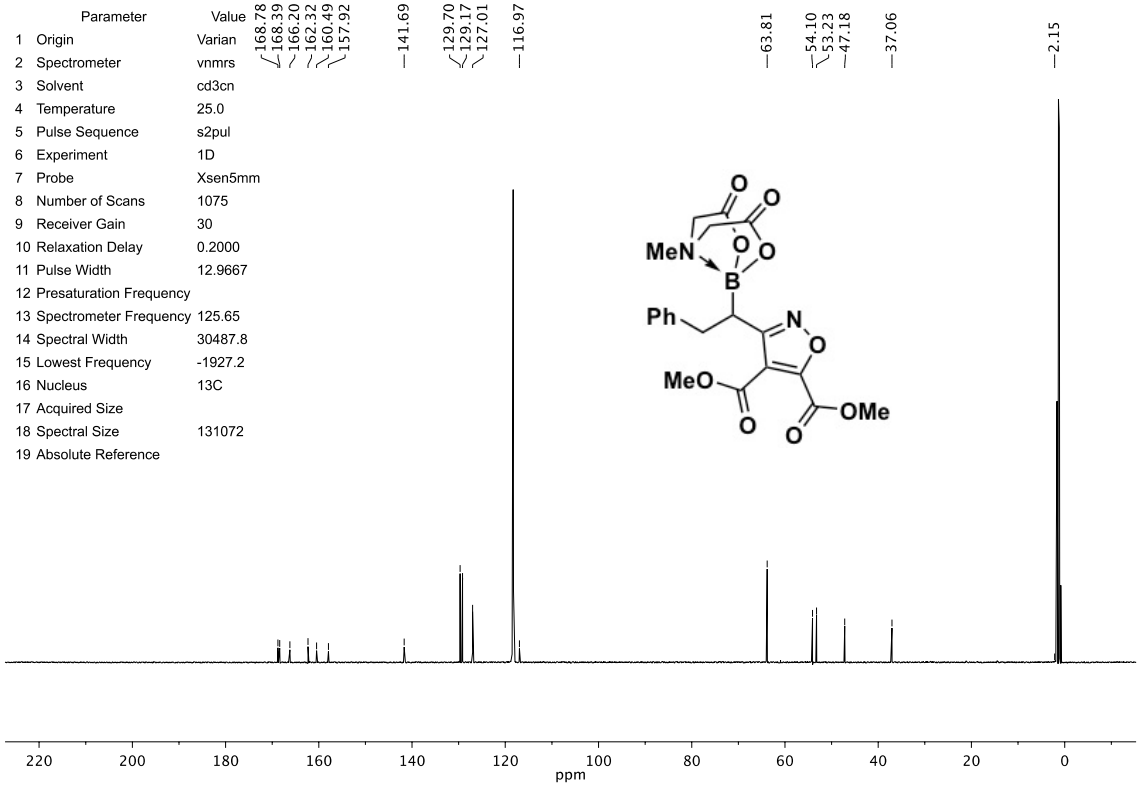



**dimethyl 3-(1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-phenylethyl)isoxazole-4,5-dicarboxylate (7i).**

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.1 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | HFX-Reynolds500 |
| 8 | Number of Scans | 16 |
| 9 | Receiver Gain | 52 |
| 10 | Relaxation Delay | 1.0000 |
| 11 | Pulse Width | 4.8500 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 499.88 |
| 14 | Spectral Width | 8012.8 |
| 15 | Lowest Frequency | -1030.1 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |
| 19 | Absolute Reference | |

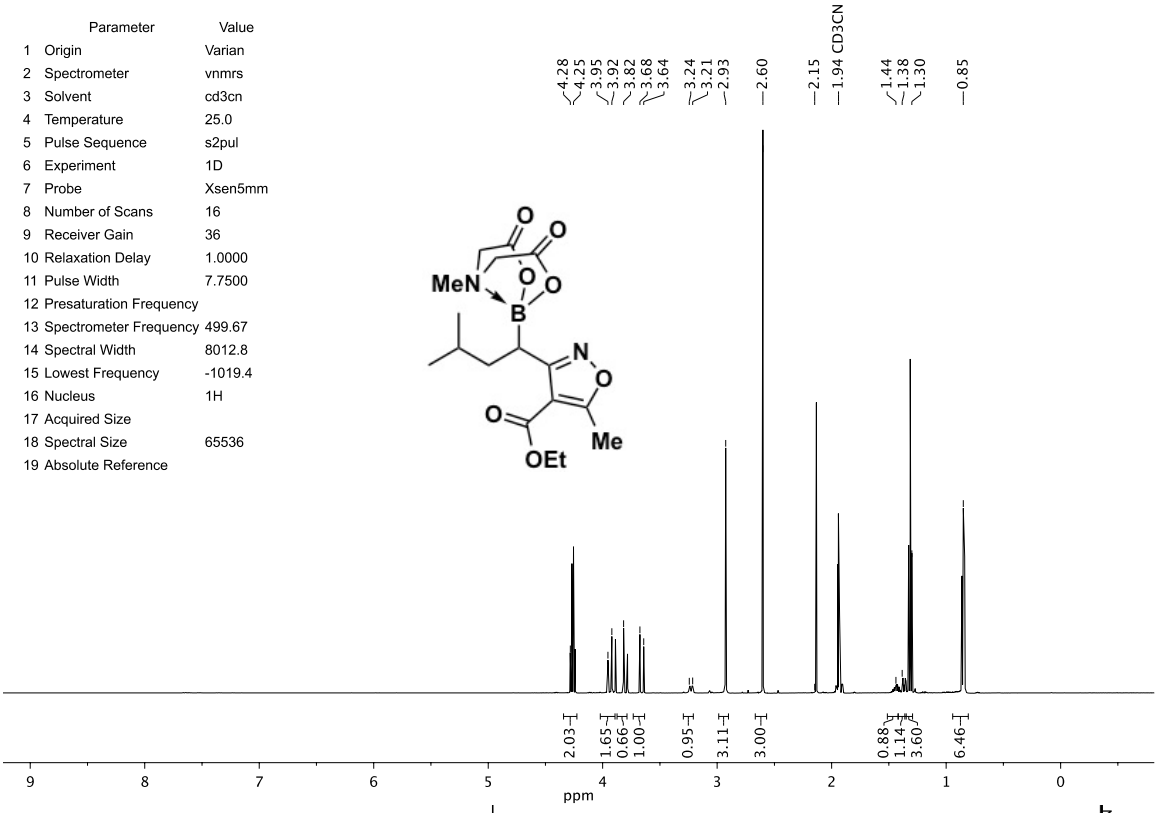



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 1075 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 12.9667 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 125.65 |
| 14 | Spectral Width | 30487.8 |
| 15 | Lowest Frequency | -1927.2 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |
| 19 | Absolute Reference | |

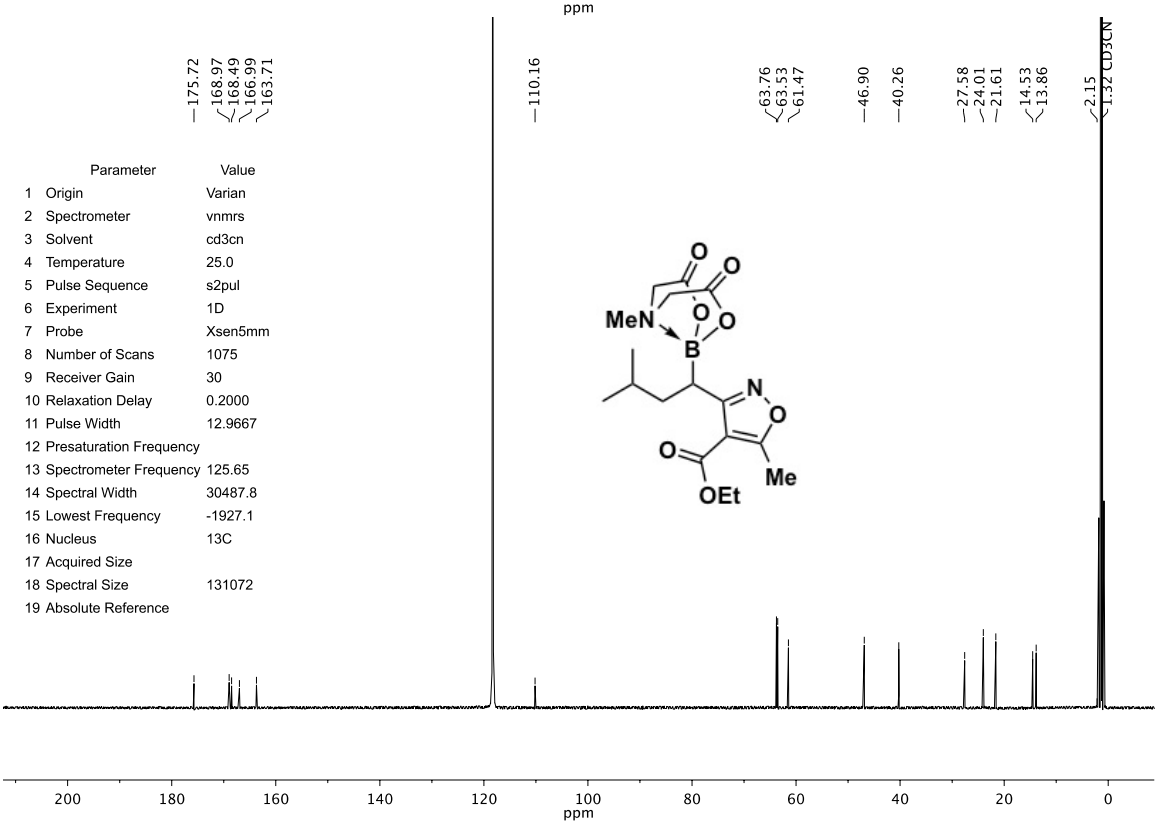


**ethyl 5-methyl-3-(3-methyl-1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)butyl)isoxazole-4-carboxylate (7j).**

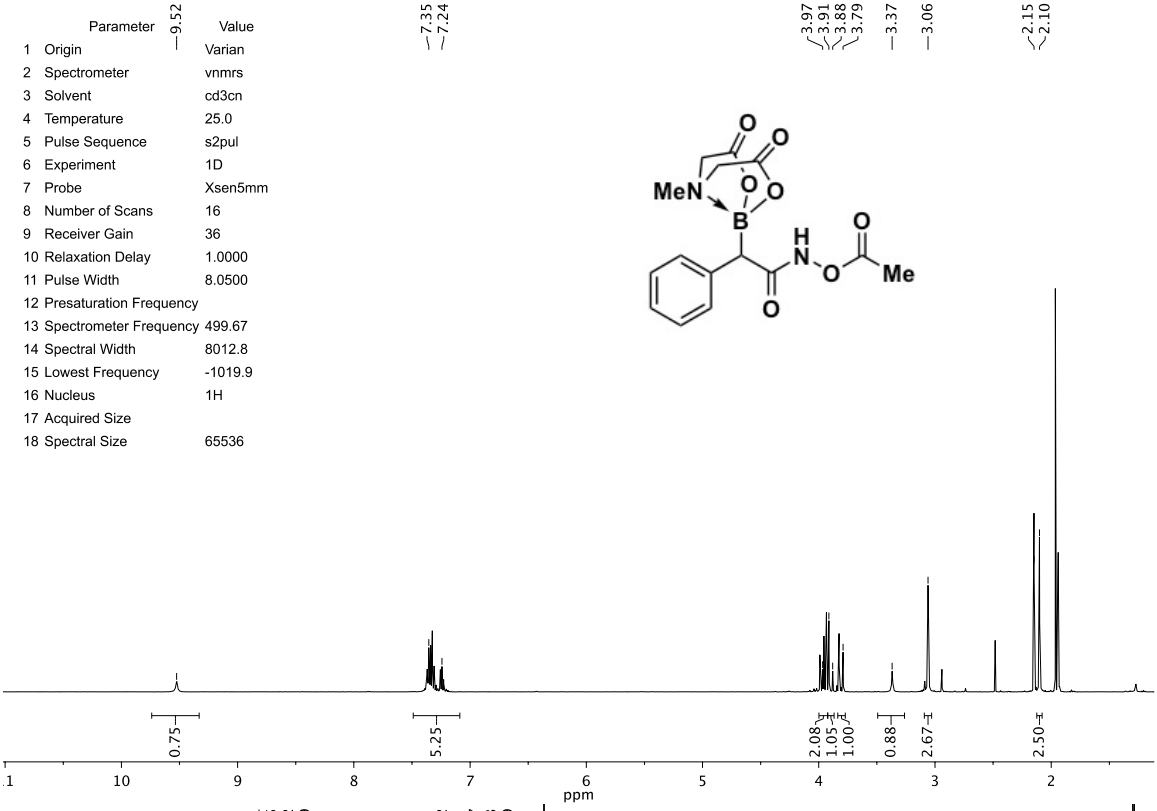
| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 16 |
| 9 | Receiver Gain | 36 |
| 10 | Relaxation Delay | 1.0000 |
| 11 | Pulse Width | 7.7500 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 499.67 |
| 14 | Spectral Width | 8012.8 |
| 15 | Lowest Frequency | -1019.4 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | |
| 18 | Spectral Size | 65536 |
| 19 | Absolute Reference | |



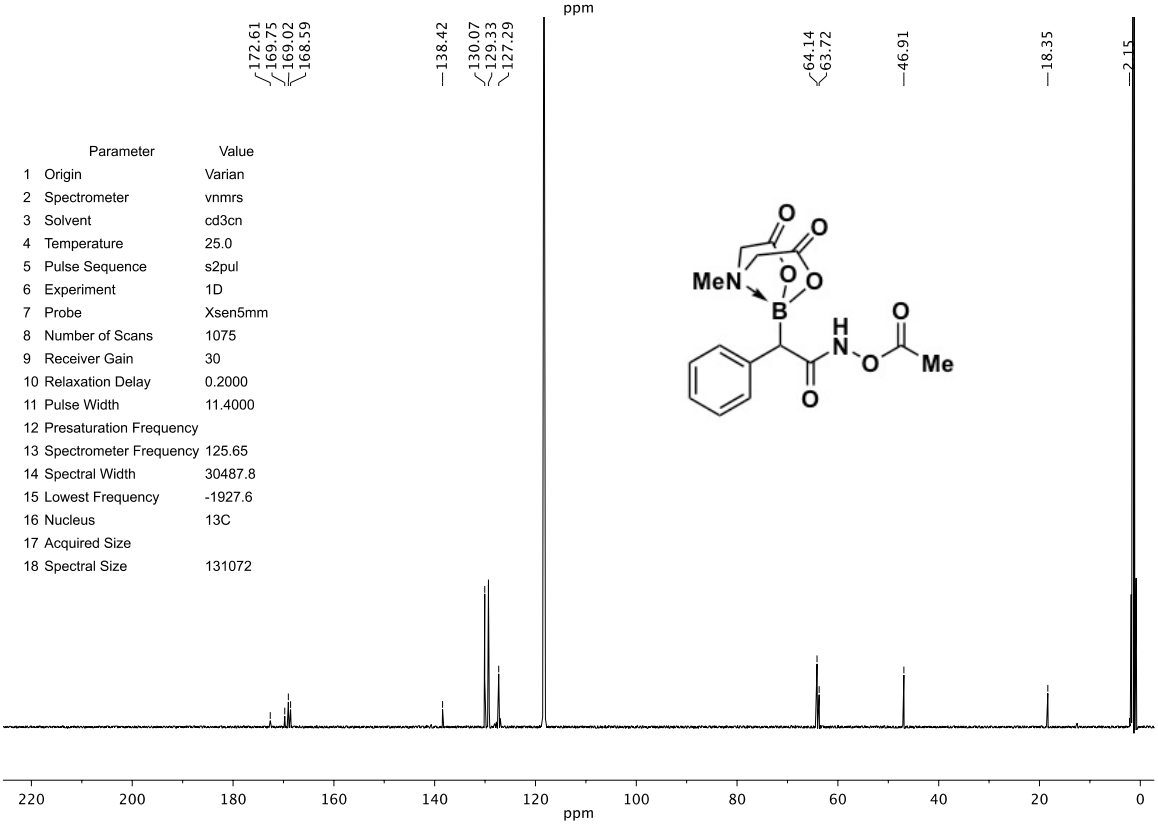

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 1075 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 12.9667 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 125.65 |
| 14 | Spectral Width | 30487.8 |
| 15 | Lowest Frequency | -1927.1 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |
| 19 | Absolute Reference | |



**_N_-acetoxy-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-phenylacetamide (9a).**

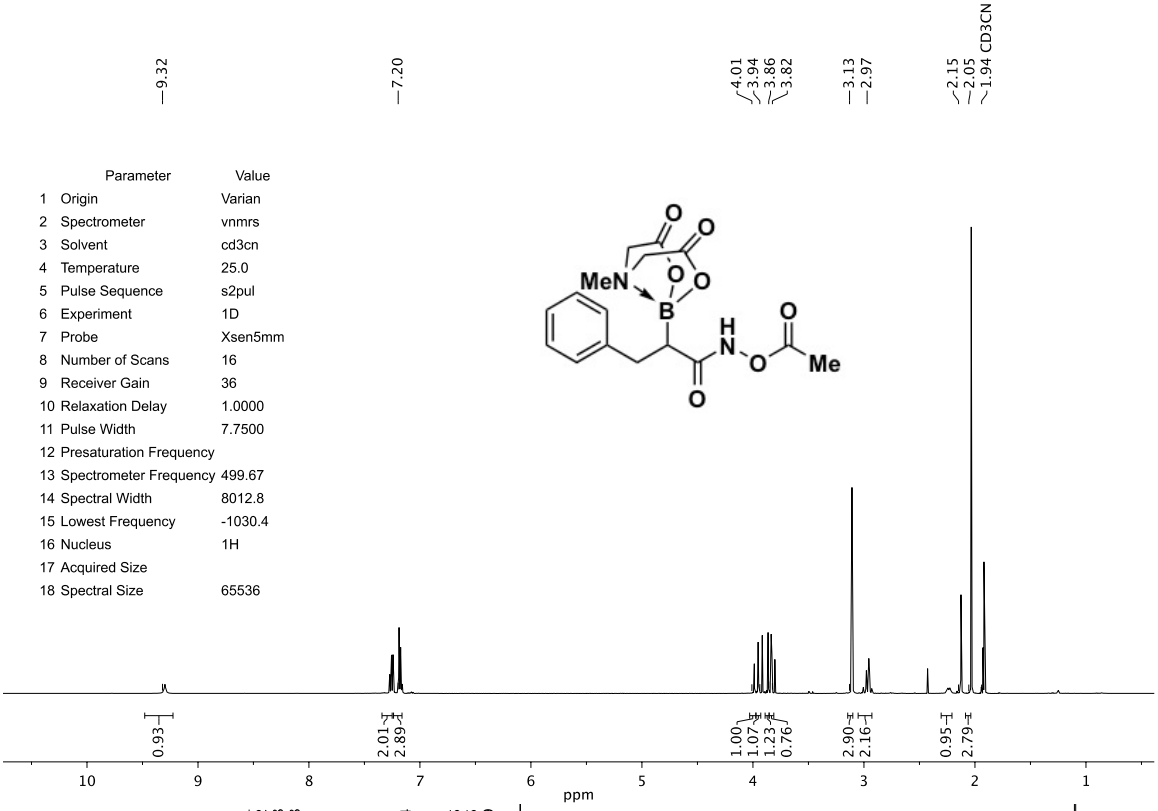


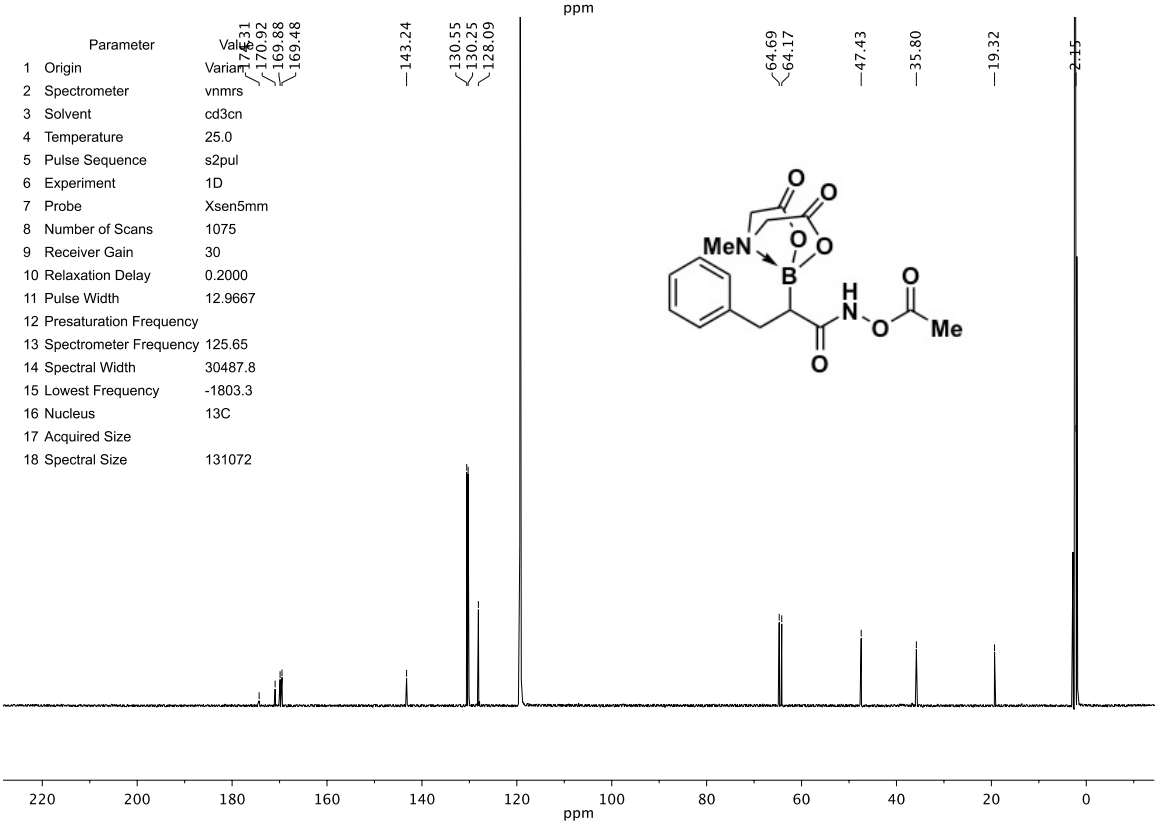

| Parameter | Value |
|---|---|
| 1 Origin | Varian |
| 2 Spectrometer | vnmrs |
| 3 Solvent | cd3cn |
| 4 Temperature | 25.0 |
| 5 Pulse Sequence | s2pul |
| 6 Experiment | 1D |
| 7 Probe | Xsen5mm |
| 8 Number of Scans | 16 |
| 9 Receiver Gain | 36 |
| 10 Relaxation Delay | 1.0000 |
| 11 Pulse Width | 8.0500 |
| 12 Presaturation Frequency | |
| 13 Spectrometer Frequency | 499.67 |
| 14 Spectral Width | 8012.8 |
| 15 Lowest Frequency | -1019.9 |
| 16 Nucleus | 1H |
| 17 Acquired Size | |
| 18 Spectral Size | 65536 |



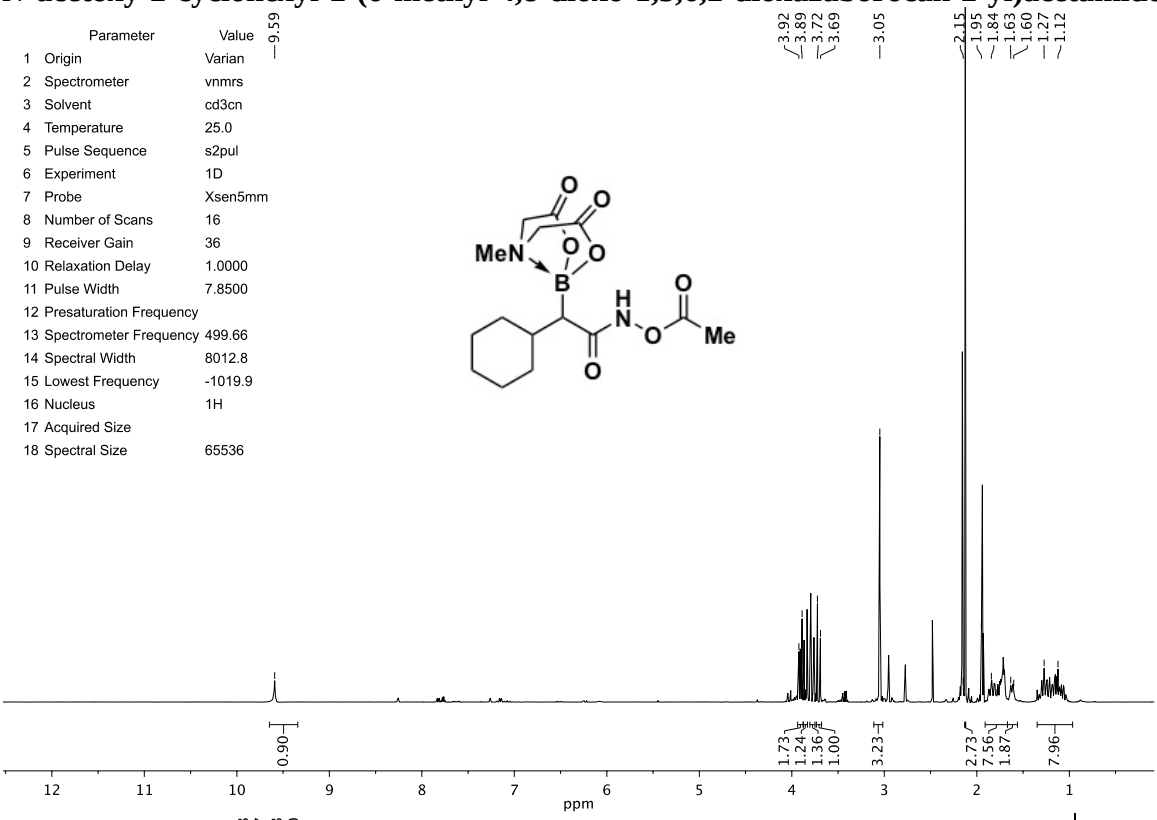

| Parameter | Value |
|---|---|
| 1 Origin | Varian |
| 2 Spectrometer | vnmrs |
| 3 Solvent | cd3cn |
| 4 Temperature | 25.0 |
| 5 Pulse Sequence | s2pul |
| 6 Experiment | 1D |
| 7 Probe | Xsen5mm |
| 8 Number of Scans | 1075 |
| 9 Receiver Gain | 30 |
| 10 Relaxation Delay | 0.2000 |
| 11 Pulse Width | 11.4000 |
| 12 Presaturation Frequency | |
| 13 Spectrometer Frequency | 125.65 |
| 14 Spectral Width | 30487.8 |
| 15 Lowest Frequency | -1927.6 |
| 16 Nucleus | 13C |
| 17 Acquired Size | |
| 18 Spectral Size | 131072 |

**_N_-acetoxy-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-3-phenylpropanamide (9b).**

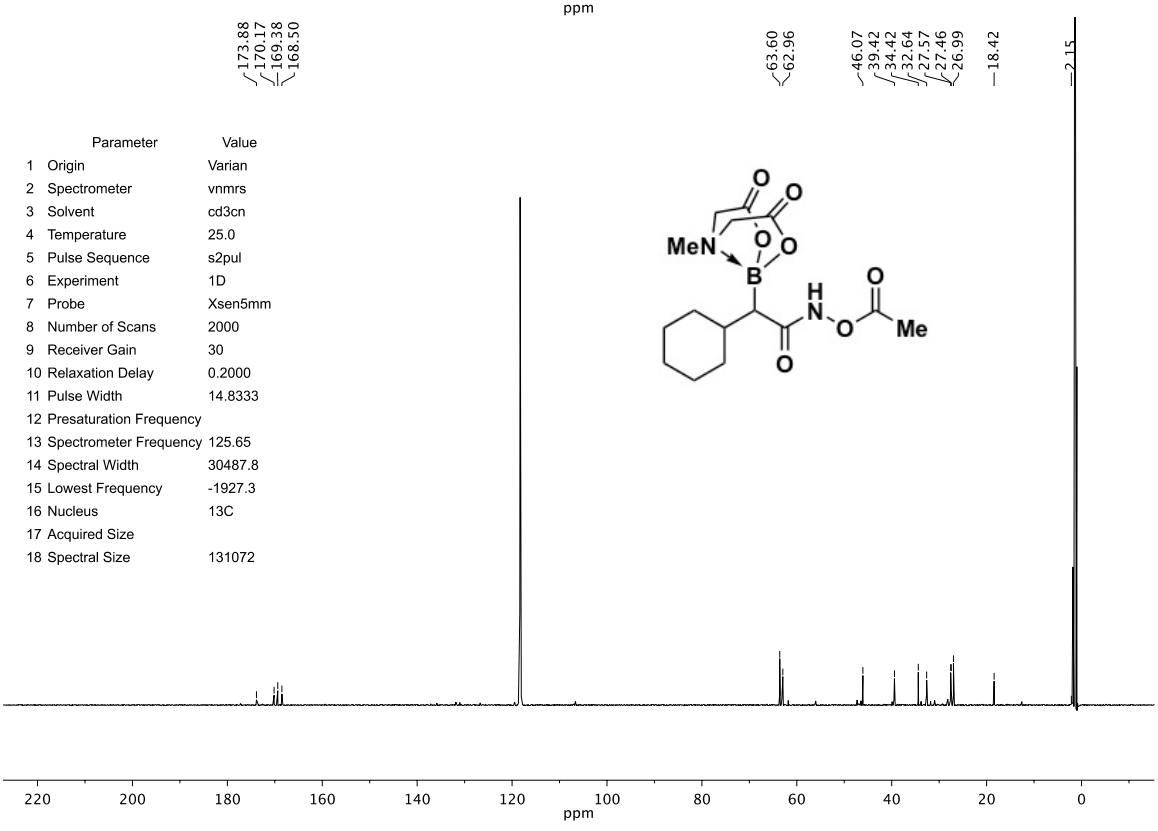


**_N_-acetoxy-2-cyclohexyl-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)acetamide (9c).**



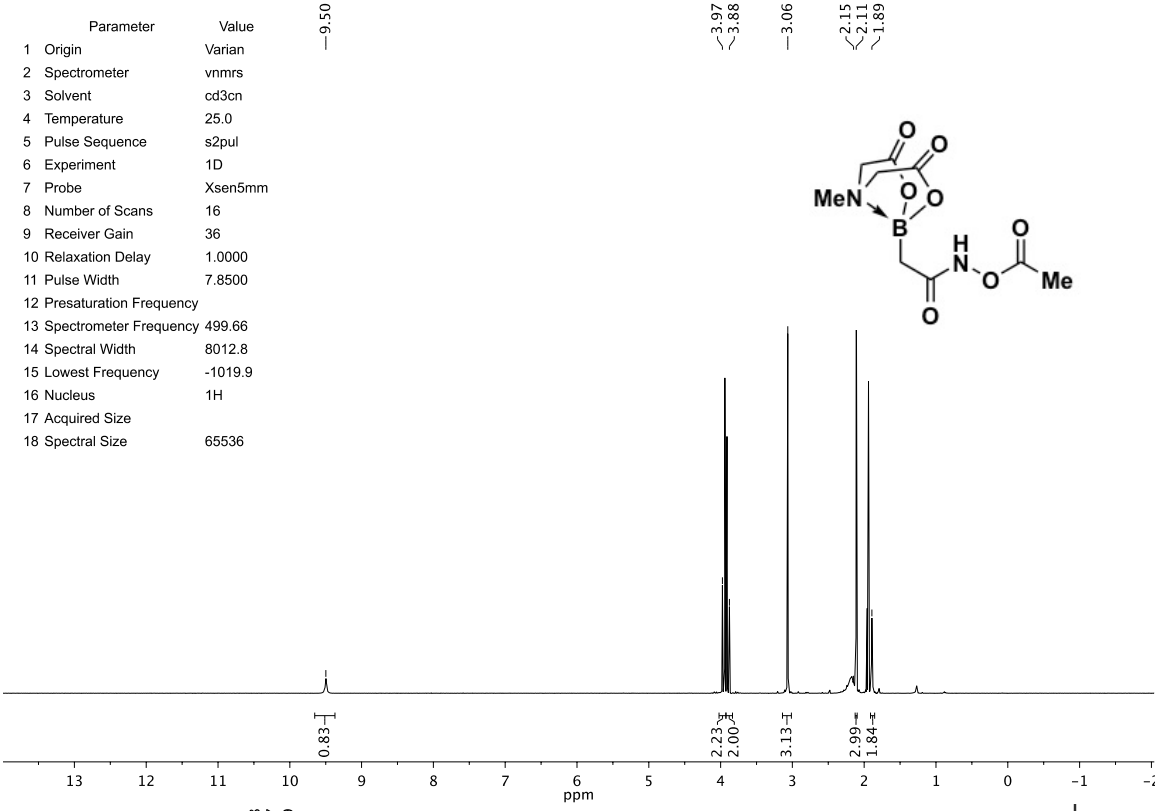

| Parameter | Value |
|---|---|
| 1 Origin | Varian |
| 2 Spectrometer | vnmrs |
| 3 Solvent | cd3cn |
| 4 Temperature | 25.0 |
| 5 Pulse Sequence | s2pul |
| 6 Experiment | 1D |
| 7 Probe | Xsen5mm |
| 8 Number of Scans | 16 |
| 9 Receiver Gain | 36 |
| 10 Relaxation Delay | 1.0000 |
| 11 Pulse Width | 7.8500 |
| 12 Presaturation Frequency | |
| 13 Spectrometer Frequency | 499.66 |
| 14 Spectral Width | 8012.8 |
| 15 Lowest Frequency | -1019.9 |
| 16 Nucleus | 1H |
| 17 Acquired Size | |
| 18 Spectral Size | 65536 |



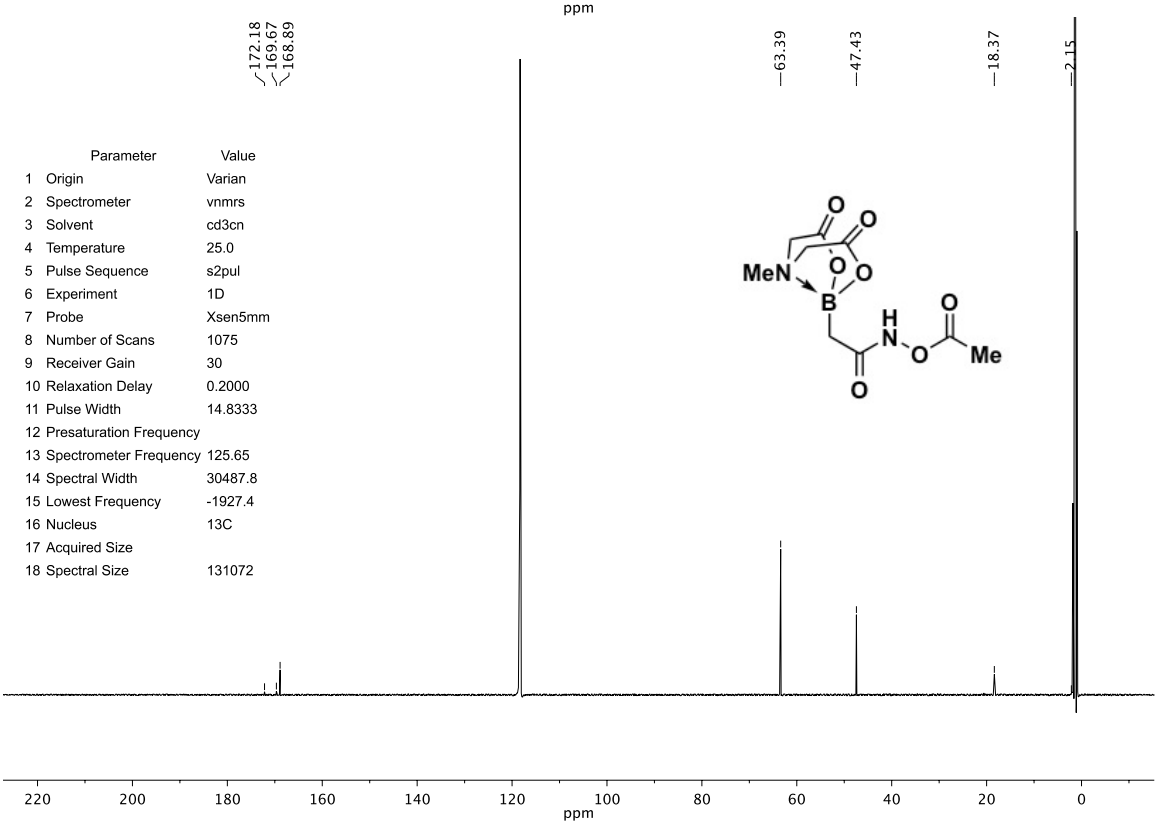

| Parameter | Value |
|---|---|
| 1 Origin | Varian |
| 2 Spectrometer | vnmrs |
| 3 Solvent | cd3cn |
| 4 Temperature | 25.0 |
| 5 Pulse Sequence | s2pul |
| 6 Experiment | 1D |
| 7 Probe | Xsen5mm |
| 8 Number of Scans | 2000 |
| 9 Receiver Gain | 30 |
| 10 Relaxation Delay | 0.2000 |
| 11 Pulse Width | 14.8333 |
| 12 Presaturation Frequency | |
| 13 Spectrometer Frequency | 125.65 |
| 14 Spectral Width | 30487.8 |
| 15 Lowest Frequency | -1927.3 |
| 16 Nucleus | 13C |
| 17 Acquired Size | |
| 18 Spectral Size | 131072 |

## *N*-acetoxy-2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)acetamide (9d).

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 16 |
| 9 | Receiver Gain | 36 |
| 10 | Relaxation Delay | 1.0000 |
| 11 | Pulse Width | 7.8500 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 499.66 |
| 14 | Spectral Width | 8012.8 |
| 15 | Lowest Frequency | -1019.9 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | |
| 18 | Spectral Size | 65536 |

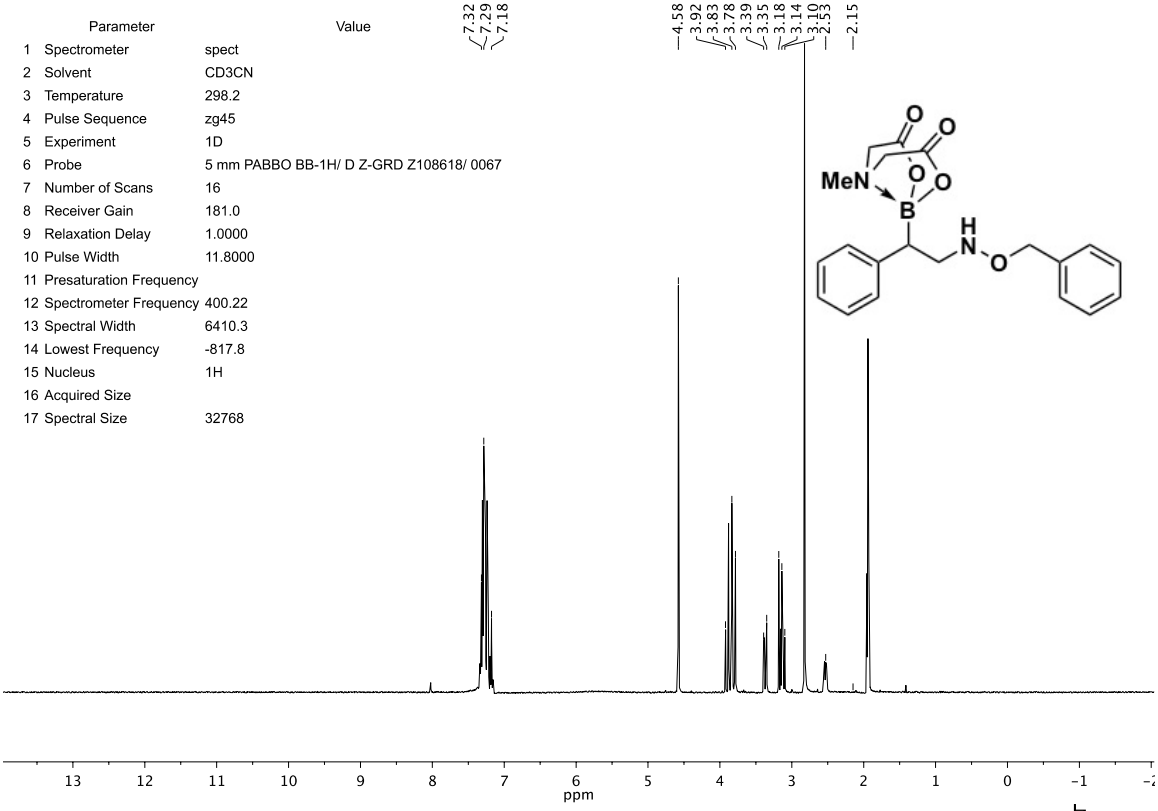



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 1075 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 14.8333 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 125.65 |
| 14 | Spectral Width | 30487.8 |
| 15 | Lowest Frequency | -1927.4 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |

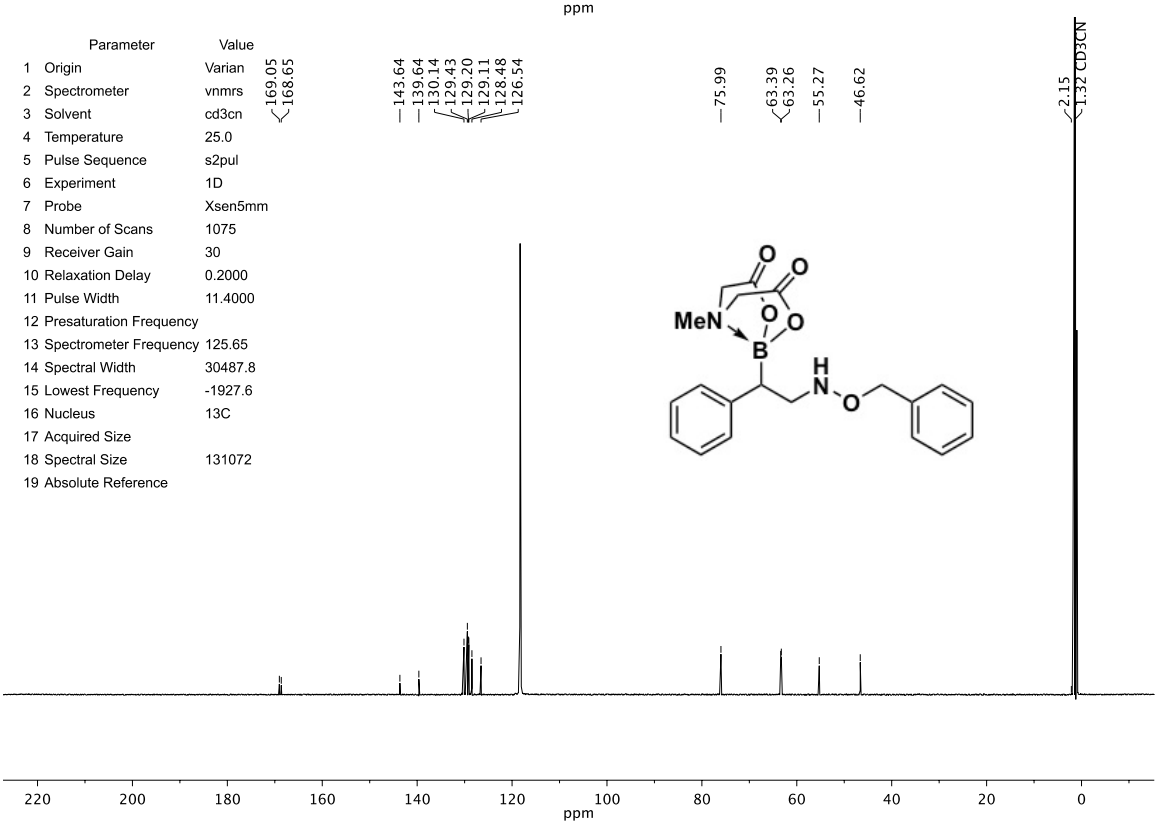


**2-(2-((benzyloxy)amino)-1-phenylethyl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (10a).**

| | Parameter | Value |
|---|---|---|
| 1 | Spectrometer | spect |
| 2 | Solvent | CD3CN |
| 3 | Temperature | 298.2 |
| 4 | Pulse Sequence | zg45 |
| 5 | Experiment | 1D |
| 6 | Probe | 5 mm PABBO BB-1H/ D Z-GRD Z108618/ 0067 |
| 7 | Number of Scans | 16 |
| 8 | Receiver Gain | 181.0 |
| 9 | Relaxation Delay | 1.0000 |
| 10 | Pulse Width | 11.8000 |
| 11 | Presaturation Frequency | |
| 12 | Spectrometer Frequency | 400.22 |
| 13 | Spectral Width | 6410.3 |
| 14 | Lowest Frequency | -817.8 |
| 15 | Nucleus | 1H |
| 16 | Acquired Size | |
| 17 | Spectral Size | 32768 |

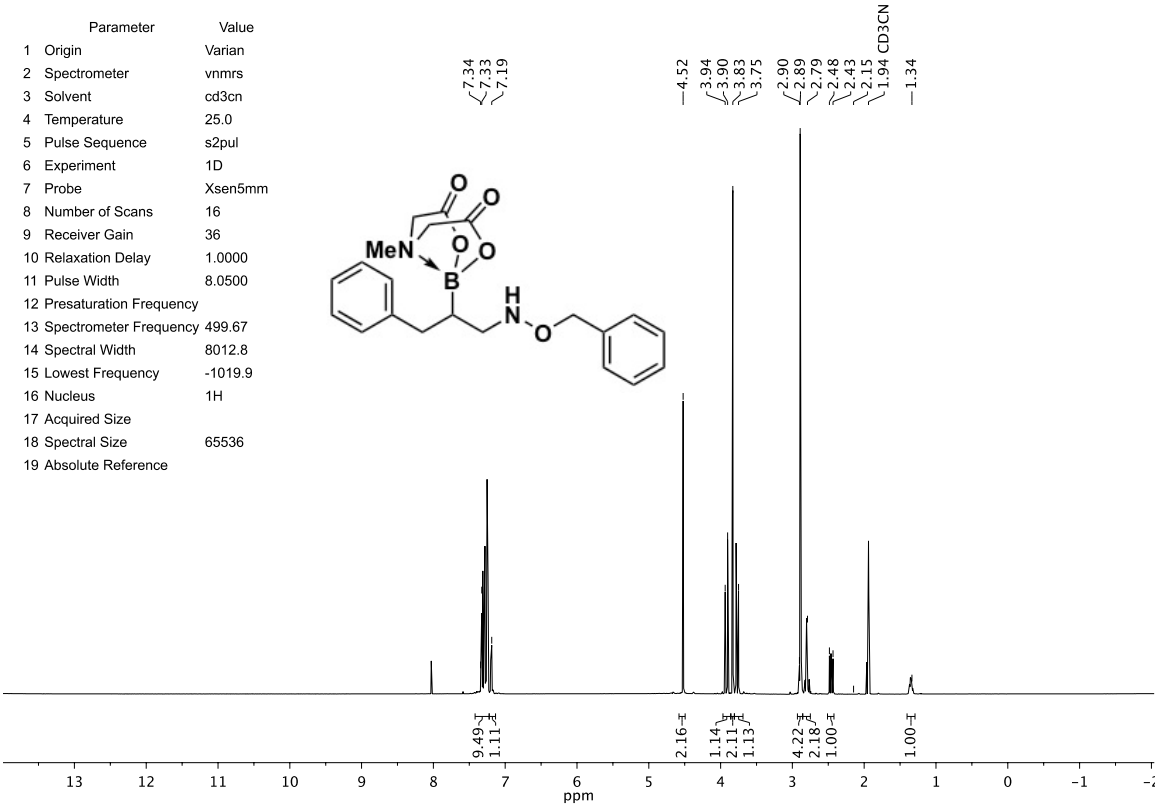



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 1075 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 11.4000 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 125.65 |
| 14 | Spectral Width | 30487.8 |
| 15 | Lowest Frequency | -1927.6 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |
| 19 | Absolute Reference | |

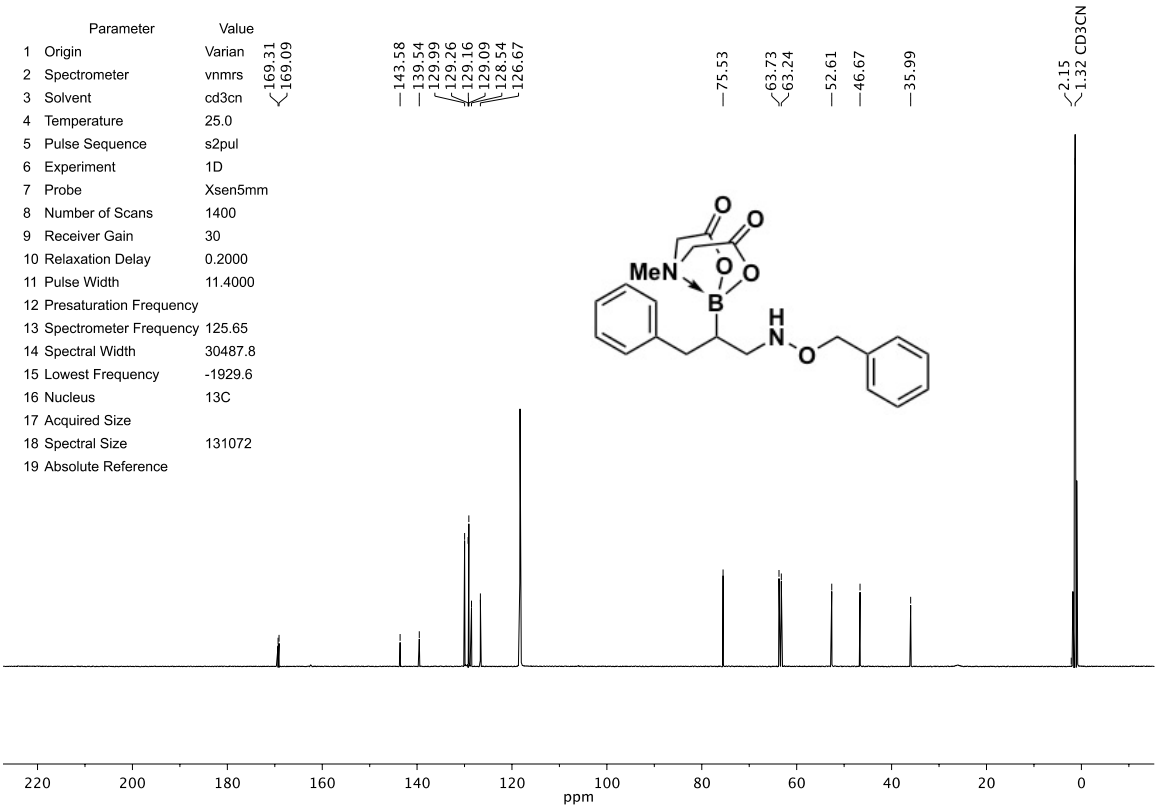


**2-(1-((benzyloxy)amino)-3-phenylpropan-2-yl)-6-methyl-1,3,6,2-dioxazaborocane-4,8-dione (10b).**

| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 16 |
| 9 | Receiver Gain | 36 |
| 10 | Relaxation Delay | 1.0000 |
| 11 | Pulse Width | 8.0500 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 499.67 |
| 14 | Spectral Width | 8012.8 |
| 15 | Lowest Frequency | -1019.9 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | |
| 18 | Spectral Size | 65536 |
| 19 | Absolute Reference | |

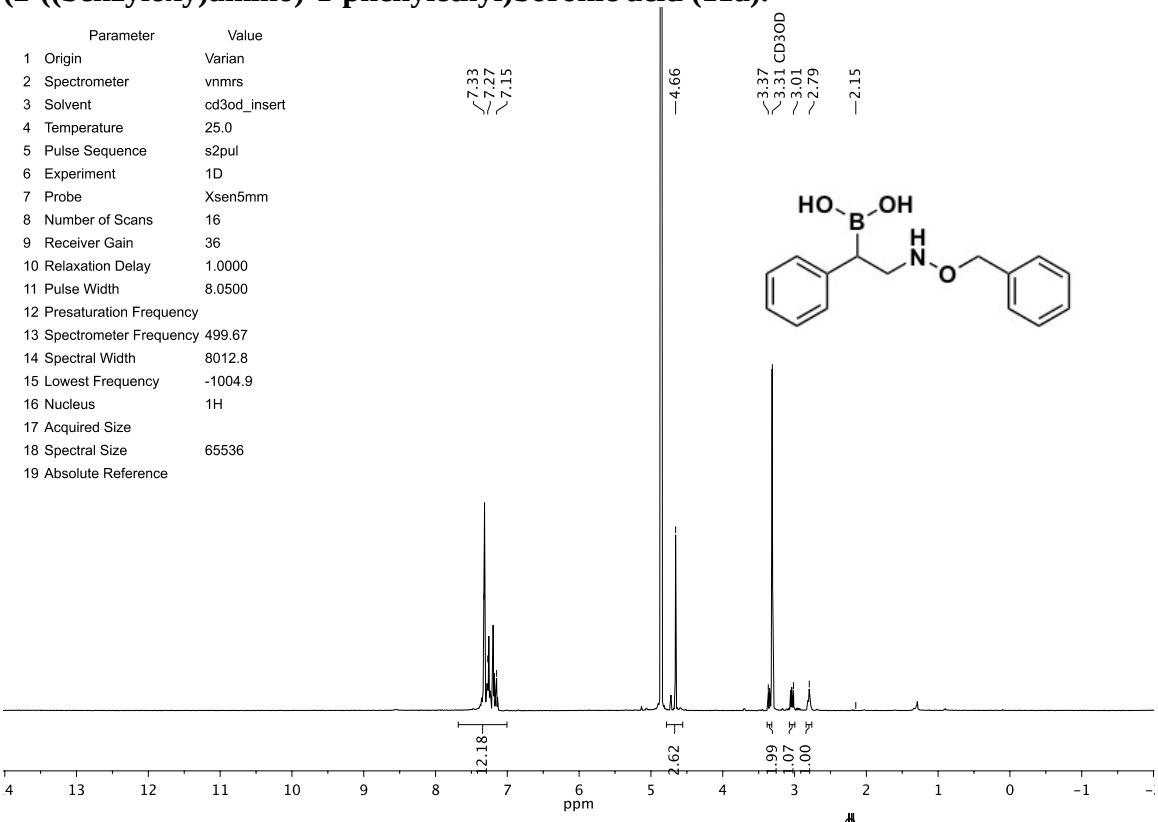



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3cn |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 1400 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 11.4000 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 125.65 |
| 14 | Spectral Width | 30487.8 |
| 15 | Lowest Frequency | -1929.6 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |
| 19 | Absolute Reference | |

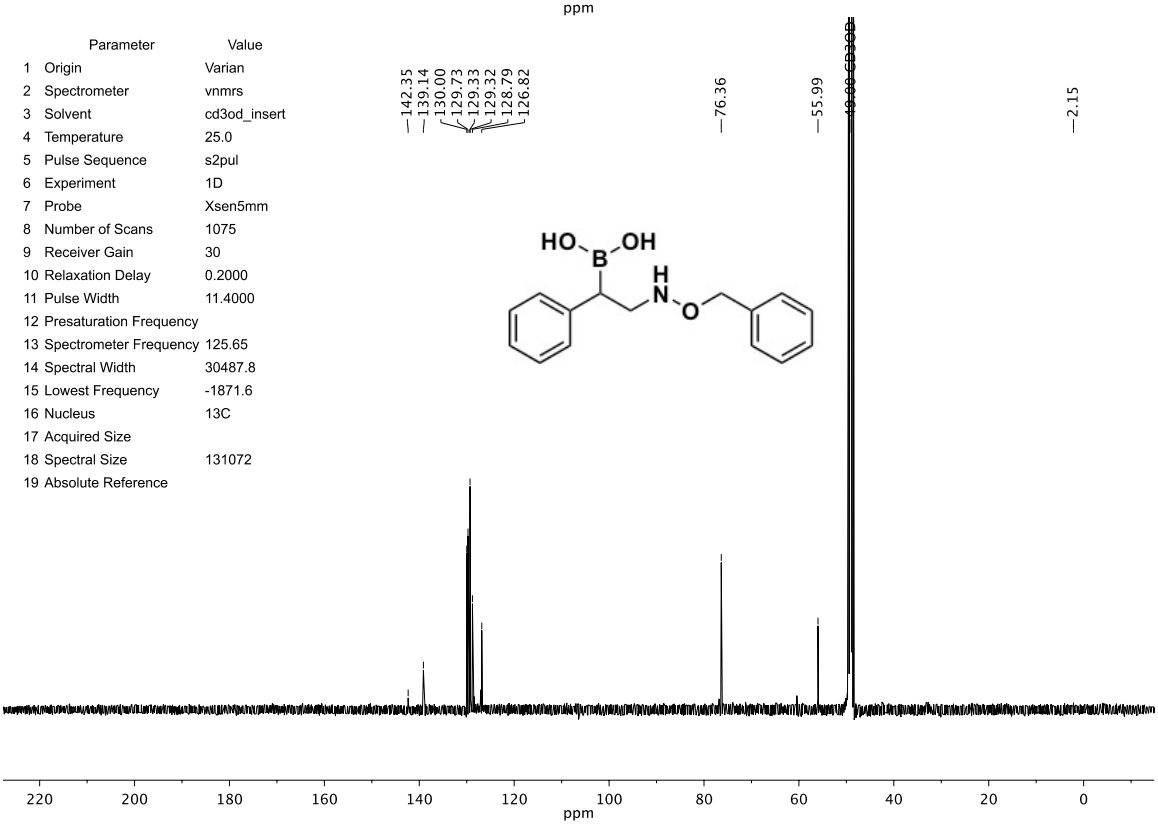


**(2-((benzyloxy)amino)-1-phenylethyl)boronic acid (11a).**

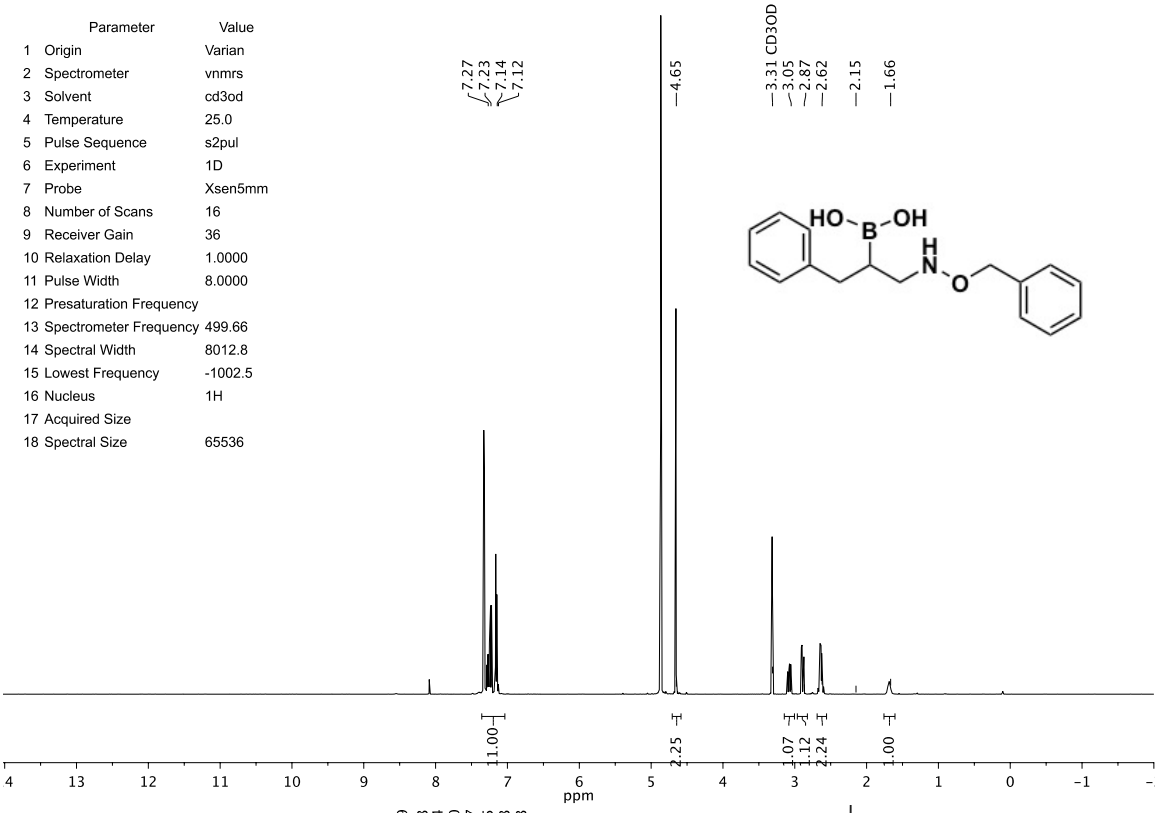
| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3od_insert |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 16 |
| 9 | Receiver Gain | 36 |
| 10 | Relaxation Delay | 1.0000 |
| 11 | Pulse Width | 8.0500 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 499.67 |
| 14 | Spectral Width | 8012.8 |
| 15 | Lowest Frequency | -1004.9 |
| 16 | Nucleus | 1H |
| 17 | Acquired Size | |
| 18 | Spectral Size | 65536 |
| 19 | Absolute Reference | |

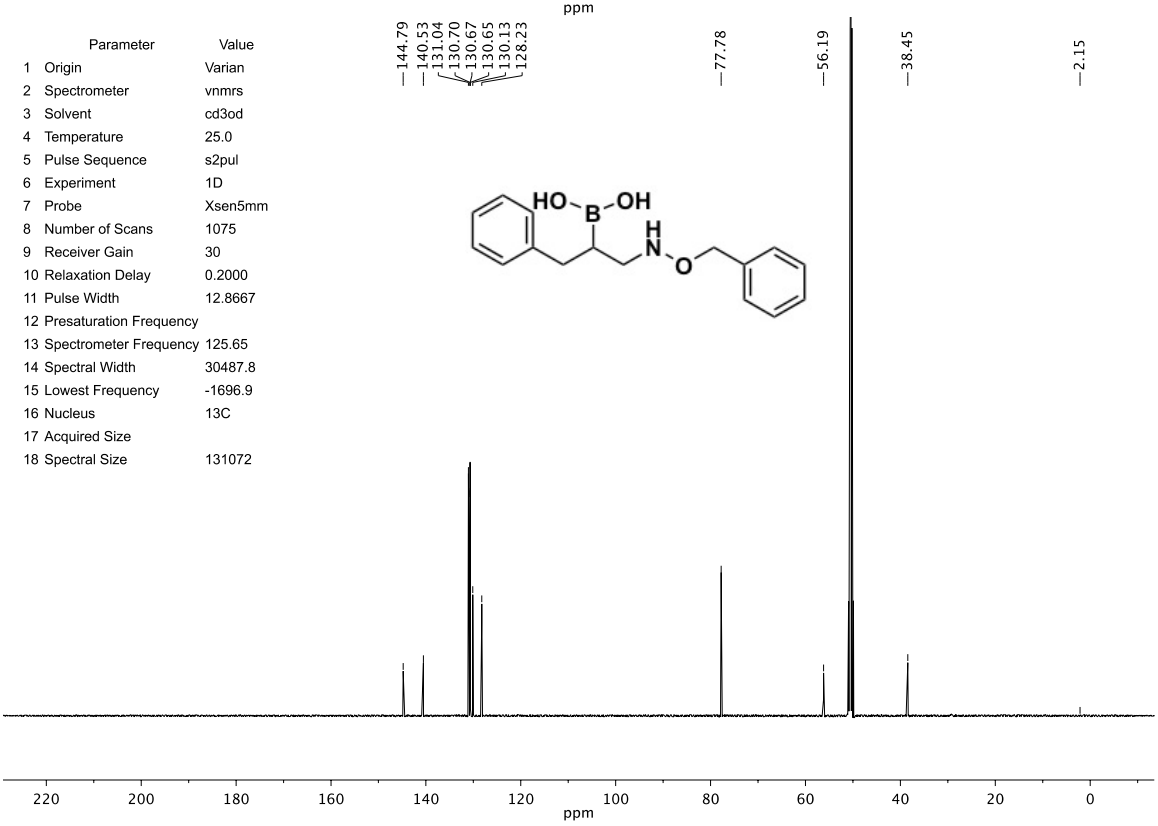



| | Parameter | Value |
|---|---|---|
| 1 | Origin | Varian |
| 2 | Spectrometer | vnmrs |
| 3 | Solvent | cd3od_insert |
| 4 | Temperature | 25.0 |
| 5 | Pulse Sequence | s2pul |
| 6 | Experiment | 1D |
| 7 | Probe | Xsen5mm |
| 8 | Number of Scans | 1075 |
| 9 | Receiver Gain | 30 |
| 10 | Relaxation Delay | 0.2000 |
| 11 | Pulse Width | 11.4000 |
| 12 | Presaturation Frequency | |
| 13 | Spectrometer Frequency | 125.65 |
| 14 | Spectral Width | 30487.8 |
| 15 | Lowest Frequency | -1871.6 |
| 16 | Nucleus | 13C |
| 17 | Acquired Size | |
| 18 | Spectral Size | 131072 |
| 19 | Absolute Reference | |



**(1-((benzyloxy)amino)-3-phenylpropan-2-yl)boronic acid (11b).**



**Crystallographic Data for 3b**

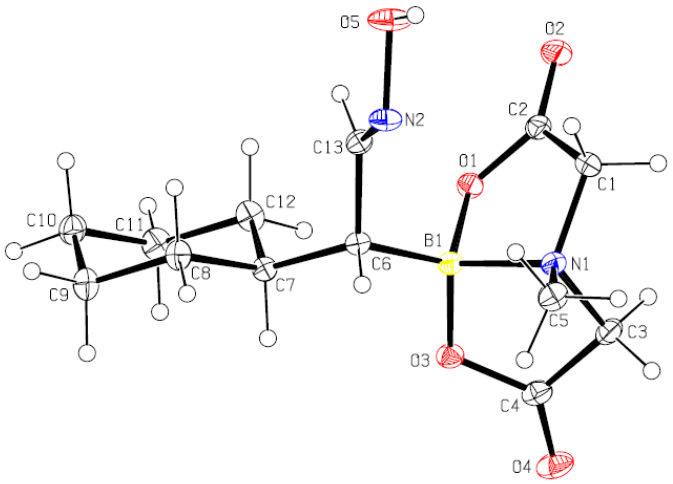



Table 1. Crystal data and structure refinement for d1574.

| | | |
|---|---|---|
| Identification code | d1574 | |
| Empirical formula | C15 H24 B N3 O5 | |
| Formula weight | 337.18 | |
| Temperature | 147(2) K | |
| Wavelength | 1.54178 Å | |
| Crystal system | Monoclinic | |
| Space group | $P2_1/c$ | |
| Unit cell dimensions | a = 9.8379(6) Å | a= 90°. |
| | b = 14.0414(8) Å | b= 98.623(3)°. |
| | c = 12.8082(7) Å | g = 90°. |
| Volume | 1749.30(18) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.280 $Mg/m^3$ | |
| Absorption coefficient | 0.788 $mm^{-1}$ | |
| F(000) | 720 | |
| Crystal size | 0.170 x 0.100 x 0.050 $mm^3$ | |
| Theta range for data collection | 4.546 to 67.265°. | |
| Index ranges | -11<=h<=11, -16<=k<=16, -15<=l<=15 | |
| Reflections collected | 33599 | |
| Independent reflections | 3091 [R(int) = 0.0361] | |
| Completeness to theta = 67.265° | 98.5 % | |
| Absorption correction | Semi-empirical from equivalents | |

| | |
|---|---|
| Max. and min. transmission | 0.7529 and 0.6911 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3091 / 0 / 223 |
| Goodness-of-fit on $F^2$ | 1.047 |
| Final R indices [I>2sigma(I)] | R1 = 0.0313, wR2 = 0.0805 |
| R indices (all data) | R1 = 0.0339, wR2 = 0.0824 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.236 and -0.164 e.Å$^{-3}$ |

Table 2. Atomic coordinates ( x $10^4$) and equivalent isotropic displacement parameters (Å$^2$x $10^3$) for d1574. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| O(1) | 7094(1) | 9911(1) | 3932(1) | 22(1) |
| O(2) | 5344(1) | 10857(1) | 4186(1) | 34(1) |
| O(3) | 8232(1) | 8371(1) | 3888(1) | 24(1) |
| O(4) | 7990(1) | 7173(1) | 5004(1) | 36(1) |
| O(5) | 5408(1) | 10948(1) | 661(1) | 37(1) |
| N(1) | 5841(1) | 8577(1) | 3122(1) | 22(1) |
| N(2) | 6152(1) | 10093(1) | 934(1) | 26(1) |
| C(1) | 4893(1) | 9389(1) | 3214(1) | 26(1) |
| C(2) | 5778(1) | 10137(1) | 3839(1) | 24(1) |
| C(3) | 5982(1) | 7946(1) | 4077(1) | 26(1) |
| C(4) | 7496(1) | 7768(1) | 4384(1) | 25(1) |
| C(5) | 5434(1) | 8001(1) | 2146(1) | 28(1) |
| C(6) | 7936(1) | 9387(1) | 2197(1) | 19(1) |
| C(7) | 9499(1) | 9613(1) | 2392(1) | 20(1) |
| C(8) | 10016(1) | 9843(1) | 1351(1) | 25(1) |
| C(9) | 11562(1) | 10024(1) | 1509(1) | 29(1) |
| C(10) | 11943(1) | 10820(1) | 2307(1) | 30(1) |
| C(11) | 11462(1) | 10591(1) | 3353(1) | 30(1) |
| C(12) | 9913(1) | 10403(1) | 3205(1) | 27(1) |
| C(13) | 7101(1) | 10210(1) | 1711(1) | 22(1) |

| | | | | |
|---|---|---|---|---|
| B(1) | 7376(1) | 9079(1) | 3263(1) | 19(1) |
| N(1S) | 2337(1) | 7726(1) | 3249(1) | 54(1) |
| C(1S) | 2011(1) | 7687(1) | 4063(1) | 41(1) |
| C(2S) | 1604(2) | 7641(1) | 5104(1) | 61(1) |

Table 3. Bond lengths [Å] and angles [°] for d1574.

| | |
|---|---|
| O(1)-C(2) | 1.3210(14) |
| O(1)-B(1) | 1.4997(14) |
| O(2)-C(2) | 1.2071(14) |
| O(3)-C(4) | 1.3347(14) |
| O(3)-B(1) | 1.4612(14) |
| O(4)-C(4) | 1.2041(14) |
| O(5)-N(2) | 1.4219(12) |
| O(5)-H(5O) | 0.96(2) |
| N(1)-C(1) | 1.4886(14) |
| N(1)-C(5) | 1.4935(14) |
| N(1)-C(3) | 1.4992(14) |
| N(1)-B(1) | 1.6514(15) |
| N(2)-C(13) | 1.2691(15) |
| C(1)-C(2) | 1.5142(16) |
| C(1)-H(1A) | 0.9900 |
| C(1)-H(1B) | 0.9900 |
| C(3)-C(4) | 1.5035(17) |
| 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)-C(13) | 1.4976(15) |
| C(6)-C(7) | 1.5532(15) |
| C(6)-B(1) | 1.6058(15) |
| C(6)-H(6A) | 1.0000 |
| C(7)-C(8) | 1.5305(15) |
| C(7)-C(12) | 1.5345(15) |

| | |
|---|---|
| C(7)-H(7A) | 1.0000 |
| C(8)-C(9) | 1.5262(16) |
| C(8)-H(8A) | 0.9900 |
| C(8)-H(8B) | 0.9900 |
| C(9)-C(10) | 1.5233(17) |
| C(9)-H(9A) | 0.9900 |
| C(9)-H(9B) | 0.9900 |
| C(10)-C(11) | 1.5202(17) |
| C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 |
| C(11)-C(12) | 1.5292(16) |
| C(11)-H(11A) | 0.9900 |
| C(11)-H(11B) | 0.9900 |
| C(12)-H(12A) | 0.9900 |
| C(12)-H(12B) | 0.9900 |
| C(13)-H(13A) | 0.9500 |
| N(1S)-C(1S) | 1.137(2) |
| C(1S)-C(2S) | 1.450(2) |
| C(2S)-H(2S1) | 0.9800 |
| C(2S)-H(2S2) | 0.9800 |
| C(2S)-H(2S3) | 0.9800 |

| | |
|---|---|
| C(2)-O(1)-B(1) | 113.51(9) |
| C(4)-O(3)-B(1) | 112.54(9) |
| N(2)-O(5)-H(5O) | 101.5(11) |
| C(1)-N(1)-C(5) | 112.84(9) |
| C(1)-N(1)-C(3) | 111.77(9) |
| C(5)-N(1)-C(3) | 110.06(9) |
| C(1)-N(1)-B(1) | 103.81(8) |
| C(5)-N(1)-B(1) | 116.66(8) |
| C(3)-N(1)-B(1) | 101.05(8) |
| C(13)-N(2)-O(5) | 112.03(9) |
| N(1)-C(1)-C(2) | 104.80(9) |
| N(1)-C(1)-H(1A) | 110.8 |
| C(2)-C(1)-H(1A) | 110.8 |
| N(1)-C(1)-H(1B) | 110.8 |

| | |
|---|---|
| C(2)-C(1)-H(1B) | 110.8 |
| H(1A)-C(1)-H(1B) | 108.9 |
| O(2)-C(2)-O(1) | 124.29(11) |
| O(2)-C(2)-C(1) | 124.65(11) |
| O(1)-C(2)-C(1) | 111.04(9) |
| N(1)-C(3)-C(4) | 106.19(9) |
| 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) | 108.7 |
| O(4)-C(4)-O(3) | 124.09(12) |
| O(4)-C(4)-C(3) | 125.03(11) |
| O(3)-C(4)-C(3) | 110.87(9) |
| 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 |
| C(13)-C(6)-C(7) | 112.17(9) |
| C(13)-C(6)-B(1) | 108.99(9) |
| C(7)-C(6)-B(1) | 112.07(8) |
| C(13)-C(6)-H(6A) | 107.8 |
| C(7)-C(6)-H(6A) | 107.8 |
| B(1)-C(6)-H(6A) | 107.8 |
| C(8)-C(7)-C(12) | 110.45(9) |
| C(8)-C(7)-C(6) | 110.70(9) |
| C(12)-C(7)-C(6) | 114.36(9) |
| C(8)-C(7)-H(7A) | 107.0 |
| C(12)-C(7)-H(7A) | 107.0 |
| C(6)-C(7)-H(7A) | 107.0 |
| C(9)-C(8)-C(7) | 112.00(9) |
| C(9)-C(8)-H(8A) | 109.2 |
| C(7)-C(8)-H(8A) | 109.2 |
| C(9)-C(8)-H(8B) | 109.2 |

| | |
|---|---|
| C(7)-C(8)-H(8B) | 109.2 |
| H(8A)-C(8)-H(8B) | 107.9 |
| C(10)-C(9)-C(8) | 110.54(10) |
| C(10)-C(9)-H(9A) | 109.5 |
| C(8)-C(9)-H(9A) | 109.5 |
| C(10)-C(9)-H(9B) | 109.5 |
| C(8)-C(9)-H(9B) | 109.5 |
| H(9A)-C(9)-H(9B) | 108.1 |
| C(11)-C(10)-C(9) | 111.01(10) |
| C(11)-C(10)-H(10A) | 109.4 |
| C(9)-C(10)-H(10A) | 109.4 |
| C(11)-C(10)-H(10B) | 109.4 |
| C(9)-C(10)-H(10B) | 109.4 |
| H(10A)-C(10)-H(10B) | 108.0 |
| C(10)-C(11)-C(12) | 111.30(10) |
| C(10)-C(11)-H(11A) | 109.4 |
| C(12)-C(11)-H(11A) | 109.4 |
| C(10)-C(11)-H(11B) | 109.4 |
| C(12)-C(11)-H(11B) | 109.4 |
| H(11A)-C(11)-H(11B) | 108.0 |
| C(11)-C(12)-C(7) | 111.56(9) |
| C(11)-C(12)-H(12A) | 109.3 |
| C(7)-C(12)-H(12A) | 109.3 |
| C(11)-C(12)-H(12B) | 109.3 |
| C(7)-C(12)-H(12B) | 109.3 |
| H(12A)-C(12)-H(12B) | 108.0 |
| N(2)-C(13)-C(6) | 121.29(10) |
| N(2)-C(13)-H(13A) | 119.4 |
| C(6)-C(13)-H(13A) | 119.4 |
| O(3)-B(1)-O(1) | 110.98(9) |
| O(3)-B(1)-C(6) | 114.01(9) |
| O(1)-B(1)-C(6) | 113.04(9) |
| O(3)-B(1)-N(1) | 102.25(8) |
| O(1)-B(1)-N(1) | 98.61(8) |
| C(6)-B(1)-N(1) | 116.52(9) |
| N(1S)-C(1S)-C(2S) | 179.58(18) |

| | |
|---|---|
| C(1S)-C(2S)-H(2S1) | 109.5 |
| C(1S)-C(2S)-H(2S2) | 109.5 |
| H(2S1)-C(2S)-H(2S2) | 109.5 |
| C(1S)-C(2S)-H(2S3) | 109.5 |
| H(2S1)-C(2S)-H(2S3) | 109.5 |
| H(2S2)-C(2S)-H(2S3) | 109.5 |

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for d1574. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| O(1) | 25(1) | 21(1) | 21(1) | -3(1) | 5(1) | 0(1) |
| O(2) | 41(1) | 22(1) | 41(1) | -3(1) | 18(1) | 6(1) |
| O(3) | 26(1) | 24(1) | 21(1) | 4(1) | 3(1) | 4(1) |
| O(4) | 53(1) | 28(1) | 28(1) | 10(1) | 4(1) | 7(1) |
| O(5) | 43(1) | 23(1) | 39(1) | -3(1) | -17(1) | 12(1) |
| N(1) | 24(1) | 18(1) | 24(1) | 0(1) | 4(1) | 0(1) |
| N(2) | 29(1) | 21(1) | 26(1) | 1(1) | -3(1) | 6(1) |
| C(1) | 22(1) | 23(1) | 34(1) | 1(1) | 7(1) | 3(1) |
| C(2) | 30(1) | 21(1) | 25(1) | 3(1) | 10(1) | 2(1) |
| C(3) | 35(1) | 19(1) | 27(1) | 3(1) | 10(1) | -2(1) |
| C(4) | 38(1) | 19(1) | 19(1) | -1(1) | 6(1) | 2(1) |
| C(5) | 30(1) | 25(1) | 28(1) | -4(1) | 1(1) | -5(1) |
| C(6) | 22(1) | 18(1) | 18(1) | -1(1) | 1(1) | 0(1) |
| C(7) | 21(1) | 22(1) | 18(1) | 0(1) | 2(1) | 0(1) |
| C(8) | 25(1) | 31(1) | 19(1) | -1(1) | 3(1) | -3(1) |
| C(9) | 26(1) | 36(1) | 26(1) | 0(1) | 6(1) | -4(1) |
| C(10) | 24(1) | 28(1) | 36(1) | 1(1) | 2(1) | -5(1) |
| C(11) | 27(1) | 35(1) | 28(1) | -7(1) | -2(1) | -5(1) |
| C(12) | 24(1) | 32(1) | 22(1) | -6(1) | 1(1) | -2(1) |
| C(13) | 25(1) | 21(1) | 20(1) | 1(1) | 2(1) | -1(1) |
| B(1) | 20(1) | 18(1) | 20(1) | -1(1) | 1(1) | 1(1) |
| N(1S) | 50(1) | 40(1) | 74(1) | 5(1) | 18(1) | 3(1) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(1S) | 30(1) | 27(1) | 65(1) | 3(1) | 5(1) | 0(1) |
| C(2S) | 51(1) | 70(1) | 61(1) | -2(1) | 9(1) | -12(1) |

Table 5. Hydrogen coordinates ( x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for d1574.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H(5O) | 4700(20) | 10729(14) | 114(15) | 63(5) |
| H(1A) | 4129 | 9193 | 3589 | 31 |
| H(1B) | 4504 | 9634 | 2507 | 31 |
| H(3A) | 5486 | 7339 | 3909 | 32 |
| H(3B) | 5601 | 8263 | 4660 | 32 |
| H(5A) | 4544 | 7696 | 2175 | 42 |
| H(5B) | 6131 | 7511 | 2095 | 42 |
| H(5C) | 5359 | 8417 | 1526 | 42 |
| H(6A) | 7787 | 8840 | 1693 | 23 |
| H(7A) | 9980 | 9019 | 2677 | 24 |
| H(8A) | 9797 | 9304 | 855 | 30 |
| H(8B) | 9531 | 10414 | 1031 | 30 |
| H(9A) | 12056 | 9434 | 1763 | 35 |
| H(9B) | 11848 | 10201 | 826 | 35 |
| H(10A) | 12952 | 10909 | 2423 | 36 |
| H(10B) | 11514 | 11423 | 2023 | 36 |
| H(11A) | 11684 | 11131 | 3846 | 36 |
| H(11B) | 11957 | 10022 | 3669 | 36 |
| H(12A) | 9416 | 10996 | 2968 | 32 |
| H(12B) | 9643 | 10216 | 3890 | 32 |
| H(13A) | 7285 | 10831 | 1990 | 26 |
| H(2S1) | 1933 | 8210 | 5507 | 91 |
| H(2S2) | 2004 | 7072 | 5472 | 91 |
| H(2S3) | 599 | 7609 | 5035 | 91 |

Table 6. Torsion angles [°] for d1574.

| | |
|---|---|
| C(5)-N(1)-C(1)-C(2) | -151.17(9) |
| C(3)-N(1)-C(1)-C(2) | 84.15(11) |
| B(1)-N(1)-C(1)-C(2) | -23.95(11) |
| B(1)-O(1)-C(2)-O(2) | -169.17(11) |
| B(1)-O(1)-C(2)-C(1) | 9.21(12) |
| N(1)-C(1)-C(2)-O(2) | -170.63(11) |
| N(1)-C(1)-C(2)-O(1) | 11.01(12) |
| C(1)-N(1)-C(3)-C(4) | -133.31(9) |
| C(5)-N(1)-C(3)-C(4) | 100.47(10) |
| B(1)-N(1)-C(3)-C(4) | -23.44(10) |
| B(1)-O(3)-C(4)-O(4) | -174.13(11) |
| B(1)-O(3)-C(4)-C(3) | 4.77(12) |
| N(1)-C(3)-C(4)-O(4) | -167.33(11) |
| N(1)-C(3)-C(4)-O(3) | 13.78(12) |
| C(13)-C(6)-C(7)-C(8) | -60.62(12) |
| B(1)-C(6)-C(7)-C(8) | 176.40(9) |
| C(13)-C(6)-C(7)-C(12) | 64.90(12) |
| B(1)-C(6)-C(7)-C(12) | -58.07(12) |
| C(12)-C(7)-C(8)-C(9) | 54.88(13) |
| C(6)-C(7)-C(8)-C(9) | -177.42(9) |
| C(7)-C(8)-C(9)-C(10) | -56.35(13) |
| C(8)-C(9)-C(10)-C(11) | 56.67(13) |
| C(9)-C(10)-C(11)-C(12) | -56.52(14) |
| C(10)-C(11)-C(12)-C(7) | 55.39(14) |
| C(8)-C(7)-C(12)-C(11) | -54.05(13) |
| C(6)-C(7)-C(12)-C(11) | -179.71(9) |
| O(5)-N(2)-C(13)-C(6) | 174.46(9) |
| C(7)-C(6)-C(13)-N(2) | 134.05(11) |
| B(1)-C(6)-C(13)-N(2) | -101.25(12) |
| C(4)-O(3)-B(1)-O(1) | 85.06(11) |
| C(4)-O(3)-B(1)-C(6) | -145.91(9) |
| C(4)-O(3)-B(1)-N(1) | -19.26(11) |

| | |
|---|---|
| C(2)-O(1)-B(1)-O(3) | -129.63(9) |
| C(2)-O(1)-B(1)-C(6) | 100.83(10) |
| C(2)-O(1)-B(1)-N(1) | -22.89(10) |
| C(13)-C(6)-B(1)-O(3) | -171.77(9) |
| C(7)-C(6)-B(1)-O(3) | -47.01(12) |
| C(13)-C(6)-B(1)-O(1) | -43.79(12) |
| C(7)-C(6)-B(1)-O(1) | 80.97(11) |
| C(13)-C(6)-B(1)-N(1) | 69.42(11) |
| C(7)-C(6)-B(1)-N(1) | -165.82(9) |
| C(1)-N(1)-B(1)-O(3) | 141.56(8) |
| C(5)-N(1)-B(1)-O(3) | -93.64(10) |
| C(3)-N(1)-B(1)-O(3) | 25.64(10) |
| C(1)-N(1)-B(1)-O(1) | 27.76(10) |
| C(5)-N(1)-B(1)-O(1) | 152.57(9) |
| C(3)-N(1)-B(1)-O(1) | -88.16(9) |
| C(1)-N(1)-B(1)-C(6) | -93.43(10) |
| C(5)-N(1)-B(1)-C(6) | 31.37(13) |
| C(3)-N(1)-B(1)-C(6) | 150.64(9) |

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for d1574 [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(5)-H(5O)...N(2)#1 | 0.96(2) | 1.87(2) | 2.7790(13) | 156.7(17) |

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+2,-z