Synthesis of Boronocysteine

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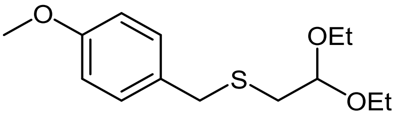
General Experimental Procedures

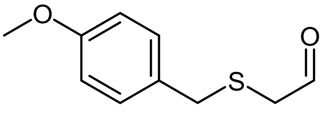
All solvents and chemicals were used as received. Column chromatography was carried out using either Merck Geduran Si 60 (40-63 µm) silica gel or a Biotage purification system using Biotage or Grace silica columns. Analytical thin layer chromatography was carried out using Merck TLC Silica Gel 60 F_{254} aluminium-backed plates. Components were visualised using combinations of ultra-violet lights, potassium permanganate or ninhydrin. Proton magnetic resonance spectra (^{1}H NMR) were recorded at 400, 500 or 600 MHz on a Bruker Avance spectrometer and are reported as follows: chemical shift δ in ppm (number of protons, multiplicity, coupling constant J in Hz, assignment). The solvent used was deuterated chloroform or deuterated methanol unless stated otherwise. Residual protic solvent was used as the internal reference, setting $CDCl_3$ to δ 7.26 and MeOD-d_4 to 3.31. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; m, mulitplet; br, broad or a combination of these. Carbon magnetic resonance spectra (^{13}C NMR) were recorded at 100, 125 or 150 MHz on a Bruker Avance spectrometer using deuterated chloroform or deuterated methanol and using the central reference of $CDCl_3$ to δ 77.0 or MeOD-d_4 to δ 49.15 as the internal standard. Mass Spectrometry data were collected on either TOF or magnetic sector analysers either at the Department of Chemistry, University College London or at the EPSRC UK National Mass Spectroscopy Facility at Swansea University. The ionization method is reported in the experimental data.

(2,2-Diethoxyethyl)(4-methoxybenzyl)sulfane (3b)[1,2]



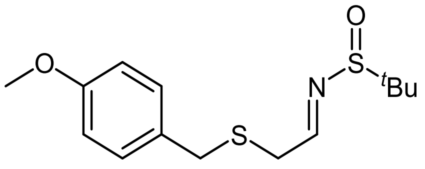
To a stirred solution of bromoacetaldehyde diethyl acetal (3.760 mL, 25 mmol) in EtOH (110 mL) and NaOH (1 M, 50 mL) at 0 °C was added *para*-methoxybenzyl mercaptan (3.831 mL, 27.5 mmol) dropwise and the reaction stirred for 2 days. A precipitate formed which was removed by filtration and the filtrate reduced *in vacuo*. The residue was dissolved in ether (25 mL) and washed with H_2O (25 mL) and then brine (20 mL). The organic layers were dried ($MgSO_4$) and reduced *in vacuo* to give **3b** as a light yellow oil (3.56 g, 13.2 mmol, 52%); **R$_f$** 0.28 (3:1 CH_2Cl_2:EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 (2H, d, *J* = 8.5, ArH), 6.83 (2H, d, *J* = 8.5, ArH), 4.54 (1H, t, J= 5.5, C**H**), 3.77 (3H, s, OCH_3), 3.74 (2H, s, ArC$\mathbf{H_2}$), 3.64 (2H, dq, J = 9.3, 7.1, 2 × OCH_2), 3.51 (2H, dq, J = 9.3, 7.1, 2 × OCH_2)2.57 (2H, d, J = 5.5, SC$\mathbf{H_2}$CH), 1.21 (6H, t, J = 7.1, 2 × CH_2C$\mathbf{H_3}$); **^{13}C NMR** δ (150 MHz, $CDCl_3$) δ 158.7, 130.5, 130.3, 114.0, 103.5, 62.3, 55.4, 36.2, 34.0, 15.5 ; **IR** υ_{max} 2973 (C-H), 1609 (Ar), 1509 (Ar), 1300 (C-O), 1244 (ArO-C).

2-((4-Methoxybenzyl)thio)acetaldehyde (4)[2]



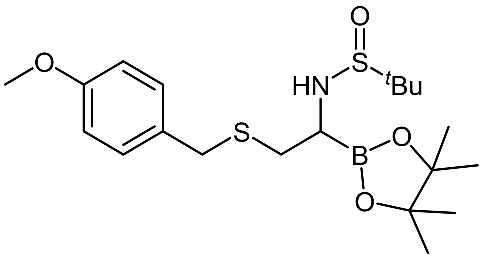
Dilute HCl (2 M, 15 mL) was added to **3b** (1.9336 g, 7.158 mmol) in acetone (15 mL) and the reaction stirred overnight. The solution was extracted (EtOAc, 2 × 10 mL) and the organic layer washed with H_2O (10 mL) and then brine (10 mL). The organic layer was dried ($MgSO_4$), filtered, and reduced *in vacuo* to give **20** as a colourless oil (1.39 g, 7.08 mmol, 99%). **R$_f$** 0.4 (9:1 petrol:EtOAc); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.40 (1H, t, *J* = 3.5, CHO), 7.21 (2H, d, *J* = 8.6, Ar**H**), 6.85 (2H, d, *J* = 8.6, Ar**H**), 3.79 (3H, s, OCH_3), 3.58 (2H, s, ArC$\mathbf{H_2}$), 3.07 (2H, d, *J* = 3.5, C$\mathbf{H_2}$CHO); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 194.1, 159.0, 130.5, 128.9, 114.2, 55.4, 40.3, 35.1; **IR** ν_{max} 3006 (C-H), 2834 (C(O)-H), 1714 (C=O), 1609, 1509, 1301, 1241, 1173, 1028.

(*E*)-*N*-(2-((4-methoxybenzyl)thio)ethylidene)-2-methylpropane-2-sulfinamide (5)



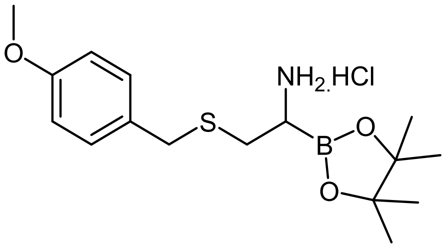
Copper(II) Sulfate (1.27 g, 7.94 mmol) and aldehyde **4** (779 mg, 3.97 mmol, 1.1 eq) were added to a solution of (±)-*tert*-butyl sulfonamide (438 mg, 3.61 mmol) in anhydrous CH_2Cl_2 (7.2 mL). The reaction was stirred at room temperature for 18 h, before filtering through Celite. The solvents were removed *in vacuo* and the residue obtained was purified by column chromatography to give **5** as an orange oil (865 mg, 2.89 mmol, 80%). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 7.98 (1H, t, *J* = 5.6, NCH), 7.23 (2H, d, *J* = 6.5, ArH), 6.85 (2H, d, *J* = 6.5, ArH), 3.79 (3H, s, OCH_3), 3.66 (2H, s, ArC**H$_2$**), 3.35 (1H, dd, *J* = 14.3, 6.0, 1 × SC**H$_2$**CH), 3.31 (1H, dd, *J* = 14.3, 5.3, 1 × SC**H$_2$**CH), 1.22 (9H, s, *t*Bu); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ 164.2, 158.9, 130.3, 129.2, 114.1, 57.0, 55.4, 35.02, 34.3, 22.5; **LRMS** (CI) 420 (100%), 300 (37%, $[M+H]^+$), 240 (30%), 195 (32%, $[M-SOtBu]^+$), 121 (88%, PMB^+); **HRMS** Found 300.10877, $C_{14}H_{22}NO_2S_2$ requires 300.10865; **IR** ν_{max} (film/cm^{-1}) 2958 (C-H), 1609 (C=C), 1510 (C=N), 1458 (C=C), 1083 (S=O).

N-(2-((4-Methoxybenzyl)thio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-2-methylpropane-2-sulfinamide (6)



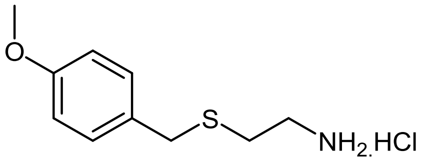
Using flame dried glassware under an argon atmosphere, CuCl (38.4 mg, 0.388 mmol), (±)-BINAP (111.1 mg, 0.1784 mmol) and B_2pin_2 (1.331 g, 5.242 mmol) were dissolved in anhydrous THF (4 mL). KOtBu (1 M in THF, 1.4 mL, 1.4 mmol) was added whilst stirring at room temperature. After 10 min, the reaction was cooled to −20 °C and aldehyde **5** (1.0338 g, 3.4522 mmol) was added followed by MeOH (300 μL, 7.41 mmol) and the reaction stirred overnight. The solvent was removed *in vacuo* and the resultant oil purified by flash column chromatography using EtOAc in CH_2Cl_2 (20 → 35%) to give **6** as an orange oil (878 mg, 2.06 mmol, 60%). **^{1}H NMR** ($CDCl_3$, 600 MHz) *δ* 7.24 (2H, d, *J* = 8.6, ArH), 6.82 (2H, d, *J* = 8.6, ArH), 3.78 (3H, s, OCH_3), 3.71 (1H, d, *J* = 5.6, NH), 3.69 (2H, s, ArC**H_2**S), 3.22-3.17 (1H, m, CHB), 2.77 (1H, dd, *J* = 13.4, 6.3, 1 × SC**H_2**CH), 2.72 (1H, dd, *J* = 13.4, 7.9, 1 × SC**H_2**CH), 1.25 (s, 6H, 2 × pinacol-CH_3), 1.23 (s, 9H, *t*Bu), 1.20 (s, 6H, 2 × pinacol-CH_3); **^{13}C NMR** ($CDCl_3$, 150 MHz) *δ* 158.7, 130.1, 130.0, 114.0, 84.3, 56.2, 55.3, 41.3 (br), 35.2, 34.6, 25.0, 24.9, 22.6; **LRMS** (CI) 428 (41%, $[M+H]^+$), 371 (18%, $[M-tBu]^+$), 322 (38%, $[M-SOtBu]^+$), 121 (100%, PMB^+); **HRMS** Found 428.2095, $C_{20}H_{34}BNO_4S_2$ requires 428.2095; **IR** ν_{max} (film/cm^{-1}) 2977 (C-H), 2930 (C-H), 1609 (C=C), 1511 (C=C), 1544(C=C), 1369 (B-O).

2-((4-Methoxybenzyl)thio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethanamine hydrochloride (7)



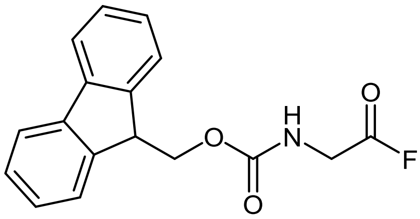
A solution of HCl in dioxane (4 M, 585 µL, 2.34 mmol) was added to **6** (99.7 mg, 0.233 mmol) dissolved in anhydrous MeOH (3 mL) to give a pale yellow solution. The reaction was stirred for 3 h. The solvent was removed *in vacuo* to give an orange residue (75.3 mg). The residue was washed with ether, sonicated, and centrifuged to give **7** as a light brown solid (68 mg, 0.190 mmol, 82%); mp 166-168 °C). **^{1}H NMR** (MeOD-*d*$_4$, 400 MHz) *δ* 7.29 (2H, d, *J* = 8.7, ArH), 6.89 (2H, d, *J* = 8.7, ArH) 3.80 (3H, s, OCH_3), 3.79 (2H, s, ArC**H_2**), 3.01 (1H, dd, *J* = 8.7, 4.7, CHB), 2.85 (1H, dd, *J* = 14.3,4.8, 1 × C**H_2**CH), 2.73 (1H, dd, *J* = 14.3, 8.8, 1 × C**H_2**CH), 1.33 (12H, s, 4 × CH_3); **^{13}C NMR** (MeOD-*d*$_4$, 100 MHz) *δ* 159.1, 129.9, 129.5, 113.7, 85.5, 74.4, 54.5, 35.1, 30.4, 23.8, 23.7; **LRMS** (CI) 323 (100%, $[M+H]^+$), 198 (18%, $[M-Bpin]^+$); **HRMS** Found 323.18359, $C_{16}H_{27}BNO_3S$ requires 323.1836; **IR** ν_{max} (solid/cm^{-1}) 2975 (C-H), 2958 (C-H), 2831 (C-H), 1607, 1583, 1411.

2-((4-Methoxybenzyl)thio)ethanamine hydrochloride (8)



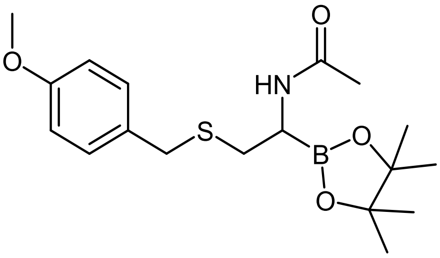
Following procedure for **7**, leaving the reaction mixture overnight gave **8**. mp 136.9-138.3 °C; **^{1}H NMR** (600 MHz, MeOD) δ 7.27 (2H, d, *J* = 8.7, ArH), 6.87 (2H, d, *J* = 8.7, ArH), 3.77 (3H, s, OCH_3), 3.74 (2H, s, ArC**H**$_2$), 3.01 (2H, t, *J* = 6.9, CH_2N), 2.68 (2H, t, *J* = 6.9, SC**H**$_2$$CH_2$); **^{13}C NMR** (150 MHz, MeOD) δ 160.5, 131.2, 131.0, 115.1, 55.7, 39.7, 35.9, 29.1; **LRMS** (CI) m/z 198 ($M+H^+$), 121 (PMB^+). Data in accordance with the literature.[3]

(9H-Fluoren-9-yl)methyl (2-fluoro-2-oxoethyl)carbamate (FMoc-Gly-F)[4]



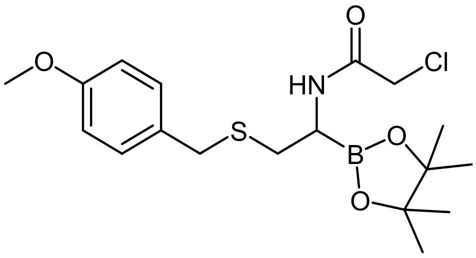
Using flame dried glassware and under an argon atmosphere, to a solution of Fmoc-Gly-OH (2.973 g, 10.0 mmol) in anhydrous CH_2Cl_2 (50 mL) and anhydrous THF (15 mL) was added pyridine (810 µL, 10 mmol) followed by the dropwise addition of cyanuric fluoride (1.72 mL, 20 mmol). The reaction was stirred overnight. The precipitate and yellow solution were washed with ice water (2 × 50 mL) and then brine (50 mL). The organic layer was reduced *in vacuo*. Addition of CH_2Cl_2 and hexane precipitated **FMoc-Gly-F** as a yellow solid (2.5903 g, 8.654 mmol, 87%); **R**$_f$ 0.26 (1:9 MeOH:$CHCl_3$); mp 127.5-128.4 °C (lit. 134-135 °C[14]); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77 (2H, d, *J* = 7.6, ArH), 7.59 (2H, d, *J* = 7.4, ArH), 7.41 (2H, td, *J* = 7.4, 1.4, ArH), 7.32 (2H, td, *J* = 7.5, 1.0, ArH), 5.24 (1H, br s, NH), 4.47 (2H, d, *J* = 6.9, FmocC**H**$_2$), 4.24 (1H, t, *J* = 6.9, FmocC**H**CH_2), 4.18 (2H, m, NHC**H**$_2$); **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.7 (d, $J_{C\text{-}F}$ = 363 Hz), 156.1, 143.6, 141.4, 127.9, 127.2, 125.0, 120.1, 67.6, 47.1, 41.2 (d, $J_{C\text{-}F}$ = 87 Hz); **IR** υ_{max} 3333 (N-H), 3212, 2970 (C-H), 1865, 1840 (C=O), 1678 (C=O), 1534, 1262, 734 (C-F).

N-(2-((4-Methoxybenzyl)thio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)acetamide (9a)



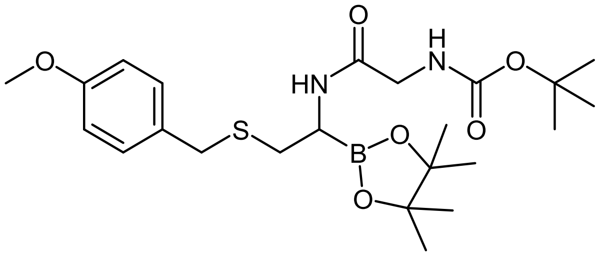
Acetyl chloride (65 µL, 0.42 mmol) was added to a solution of **7** (30 mg, 84 µmol) in acetonitrile (1 mL) followed by pyridine (40 µL, 0.50 mmol). The reaction was stirred for 18 h. Solvent was removed *in vacuo* and EtOAc (3 mL) added. The reaction mixture was filtered and the filtrate washed with H_2O (3 mL), phosphoric acid (1% in H_2O, 3 mL), potassium carbonate (2% in H_2O, 3 mL) and then brine (3 mL). All aqueous layers were back extracted with EtOAc. Removal of solvent *in vacuo* gave an orange oil which was purified by column chromatography (20% EtOAc in CH_2Cl_2) to give **9a** as an orange oil (6.7 mg, 22%). **^{1}H NMR** ($CDCl_3$, 600 MHz) 7.21 (2H, d, *J* = 8.6, ArH), 7.00 (1H, br s, NH), 6.83 (2H, d, *J* = 8.6, ArH), 3.78 (3H, s, OCH_3), 3.66 (1H, d, *J* = 13.6, 1 × ArC**H**$_2$), 3.63 (1H, d, *J* = 13.6, 1 × ArC**H**$_2$), 2.81 (1H, dd, *J* =14.3, 2.8, 1 × C**H**$_2$CH), 2.65 (1H, br d, *J* = 12.2, C**H**B), 2.45 (1H, dd, *J* = 14.3, 12.8, 1 × C**H**$_2$CH), 2.05 (3H, s, C(O)C**H**$_3$), 1.16 (6H, s, 2 × pinacol-CH_3), 1.15 (6H, s, 2 × pinacol-CH_3); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ 176.0, 158.8, 130.7, 130.1, 114.1, 80.4, 55.4, 44.4, 35.2, 34.2, 25.3, 24.9, 18.1; **LRMS** (CI) 366 (40%, $[M+H]^+$), 266 (51%), 243 (33%), 212 (57%, $[M-SPMB]^+$), 121 (100%, PMB^+); **HRMS** Found 366.19151, $C_{18}H_{28}BNO_4S$ requires 366.19103; **IR** ν_{max} (film/cm^{-1}) 3260 (N-H), 2960(C-H), 2924 (C-H), 2853 (C-H), 1609 (C=O), 1511.

2-Chloro-*N*-(2-((4-methoxybenzyl)thio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)acetamide (9b)



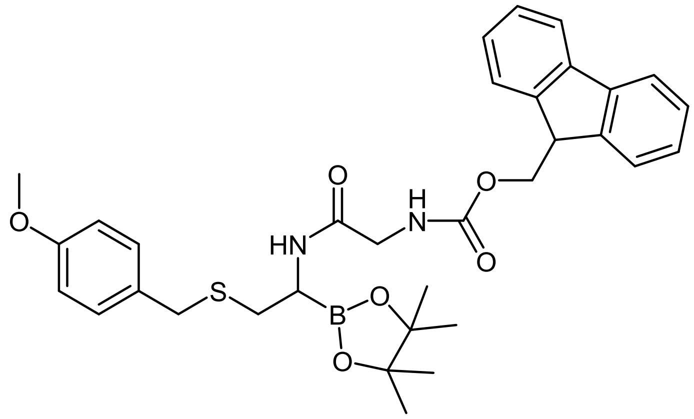
Using flame dried glassware and under an argon atmosphere, a solution of **7** (82.3 mg, 0.193 mmol) in anhydrous CH_2Cl_2 (1 mL) was cooled to 0 °C. Chloroacetyl chloride (17 µL, 0.231 mmol) was added followed by the dropwise addition of NMM (30 µL, 0.270 mmol). The solution was allowed to warm to room temperature and stirred for 90 min. The reaction was cooled to 0 °C and HCl (0.2 M, 7 mL) added. The reaction mixture was diluted with EtOAc and the organic layer was separated, dried ($MgSO_4$), filtered and concentrated *in vacuo* to give a brown oil. On addition of Et_2O a brown solid formed which was filtered. The filtrate was concentrated *in vacuo* to give **9b** as a brown oil (65.4 mg, 85%). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 7.66 (1H, br s, NH), 7.21 (2H, d, J = 8.7, ArH), 6.83 (2H, d, J = 8.7, ArH), 4.15 (2H, s, CH_2Cl), 3.78 (3H, s, OCH_3), 3.67 (2H, s, $ArCH_2$), 2.97 (1H, br d, J = 11.1, CHB), 2.76 (1H, dd, J = 14.0, 3.0, 1 × C**H**$_2$CHB), 2.52 (1H, dd, J = 14.0, 11.6, 1 × C**H**$_2$CHB), 1.21 (6H, s, 2 × pinacol-CH_3), 1.19 (6H, s, 2 × pincaol-CH_3); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ 171.1, 158.8, 130.1 (2C), 114.1, 82.5, 55.4, 41.6 (br), 41.3, 35.4, 33.0, 24.9, 24.63; **LRMS** (CI) 402 (41%, $[M+H]^+$, Cl^{37}), 404 (100%, $[M+H]^+$, Cl^{35}); **HRMS** Found 399.1552, $C_{18}H_{28}BClNO_4S$ requires 399.1551; **IR** ν_{max} (film/cm^{-1}) 2923 (C-H), 1733 (C=O), 1661, 1593, 1494, 1434.

***tert*-Butyl (2-((2-((4-methoxybenzyl)thio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)amino)-2-oxoethyl)carbamate (10a)**



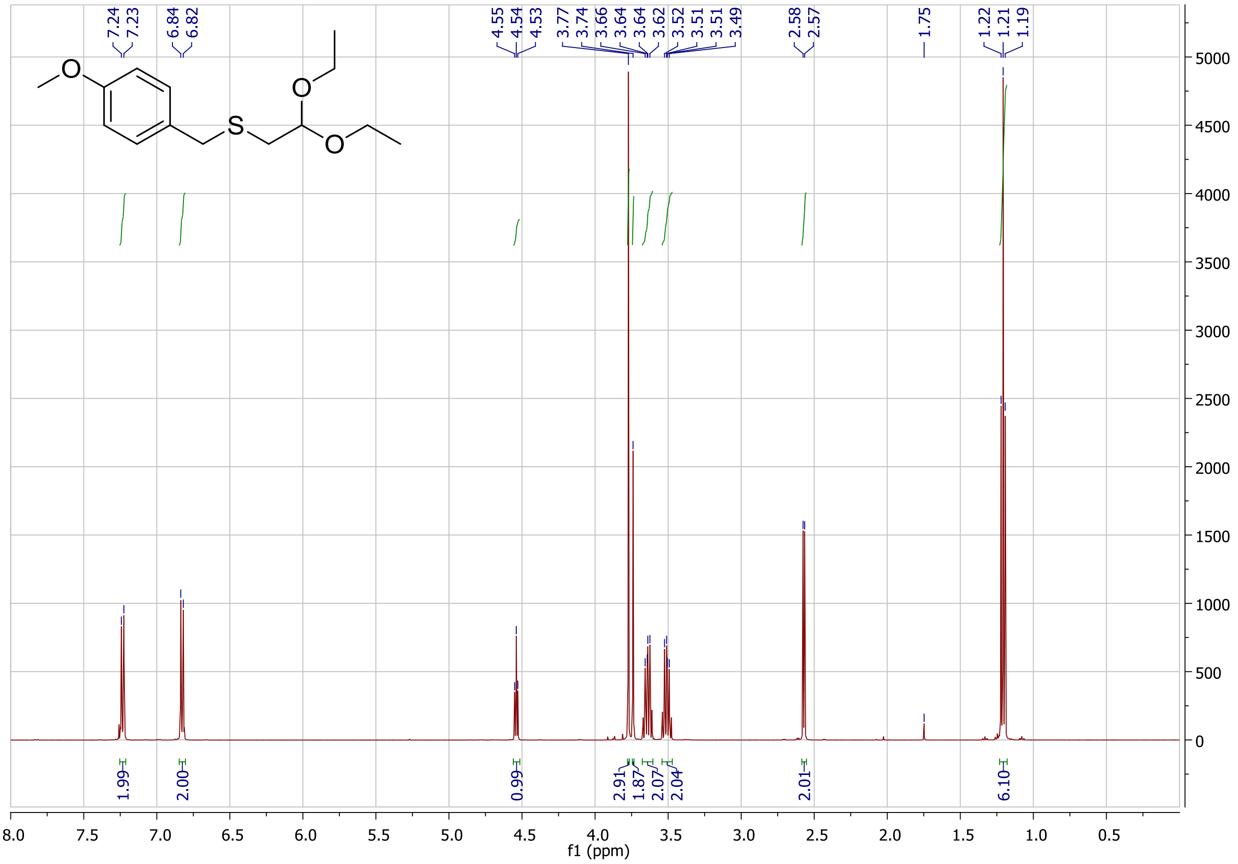
Using flame dried glassware under an argon atmosphere, Boc-Gly-OH (87.5 mg, 0.50 mmol) was dissolved in anhydrous CH_2Cl_2 (1.5 mL) and cooled to −20 °C. NMM (66 µL, 0.60 mmol) was added followed by IBCF (58 µL, 0.45 mmol) and the reaction stirred for 5 h at −20 °C. HCl salt **23** (23.4 mg, 65.1 µmol) was added followed by NMM (7 µL, 65 µmol) and the reaction allowed to warm to rt and stirred for 18 h. The reaction mixture was concentrated *in vacuo* and the resultant oil purified by column chromatography (2% MeOH in EtOAc) using deactivated silica (35% H_2O w/w) to give **36** as a pale yellow oil (27.9 mg, 89%). **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 7.51 (1H, br s, CHN**H**), 7.21 (2H, d, J = 8.7, ArH), 6.82 (2H, d, J = 8.7, ArH), 5.29 (1H, br s, CH_2N**H**), 3.93 (2H, d, J = 5.7, NHC**H$_2$**), 3.78 (3H, s, OCH_3), 3.65 (2H, s, $ArCH_2$), 2.81 (1H, br d, J = 11.5, CHB), 2.75 (1H, dd, J = 14.1, 3.2, 1 × SC**H**$_2$CH), 2.46 (1H, dd, J = 14.1, 11.5, 1 × SC**H$_2$**CH), 1.44 (9H, s, Bu), 1.18 (6H, s, 2 × pinacol-CH_3), 1.16 (6H, s, 2 × pinacol-CH_3); **^{13}C NMR** ($CDCl_3$, 150 MHz) δ 174.9, 158.7, 130.3, 130.1, 114.1, 81.6, 55.4, 54.0, 41.4, 35.2, 33.6, 29.8, 28.4, 25.0, 24.9, 14.3; **LRMS** (CI) 481 (100%, $[M+H]^+$); **HRMS** Found 480.2575, $C_{23}H_{37}BN_2O_6S$ requires 480.2574; **IR** (film/cm^{-1}) 2970 (C-H), 2926 (C-H), 1697 (br, C=O), 1609 (C=O), 1511, 1456.

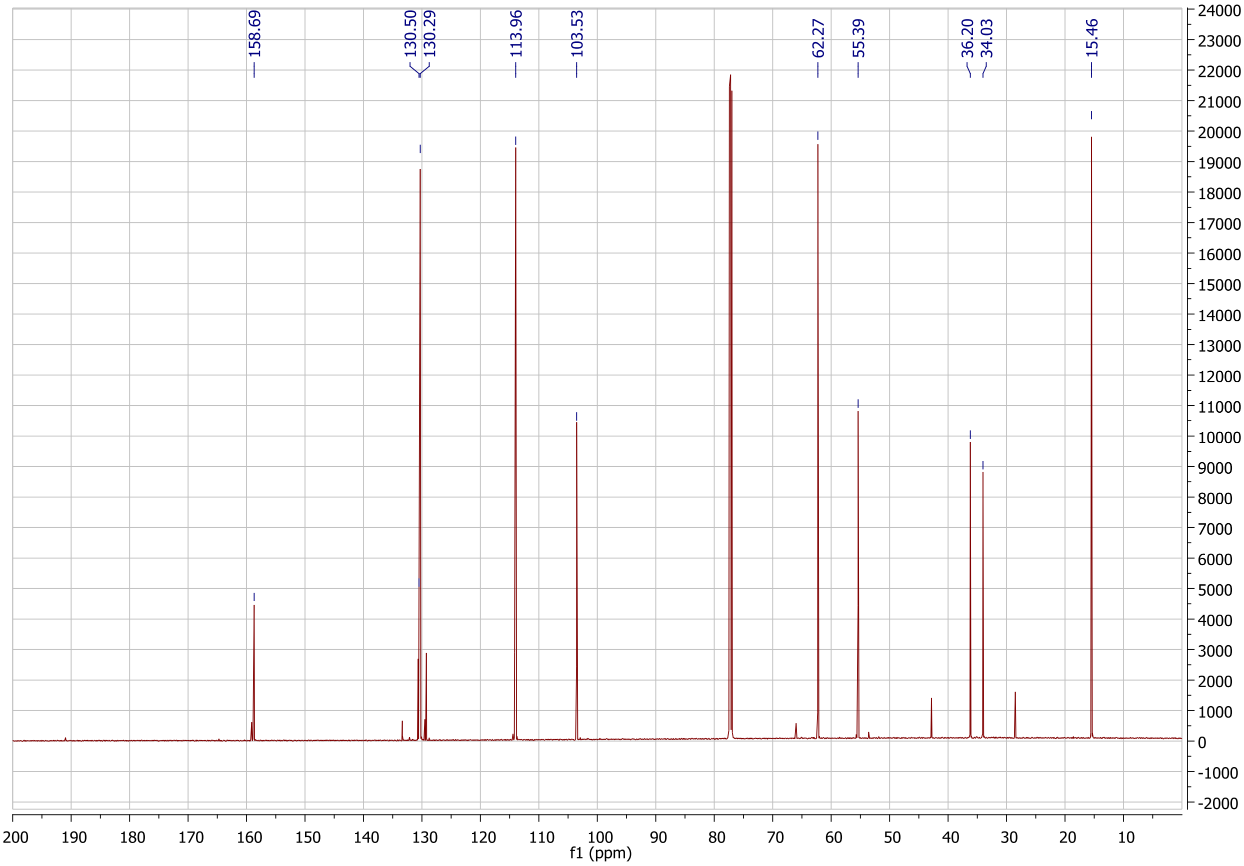
(9*H*-Fluoren-9-yl)methyl(2-((2-((4-methoxybenzyl)thio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)amino)-2-oxoethyl)carbamate (10b)



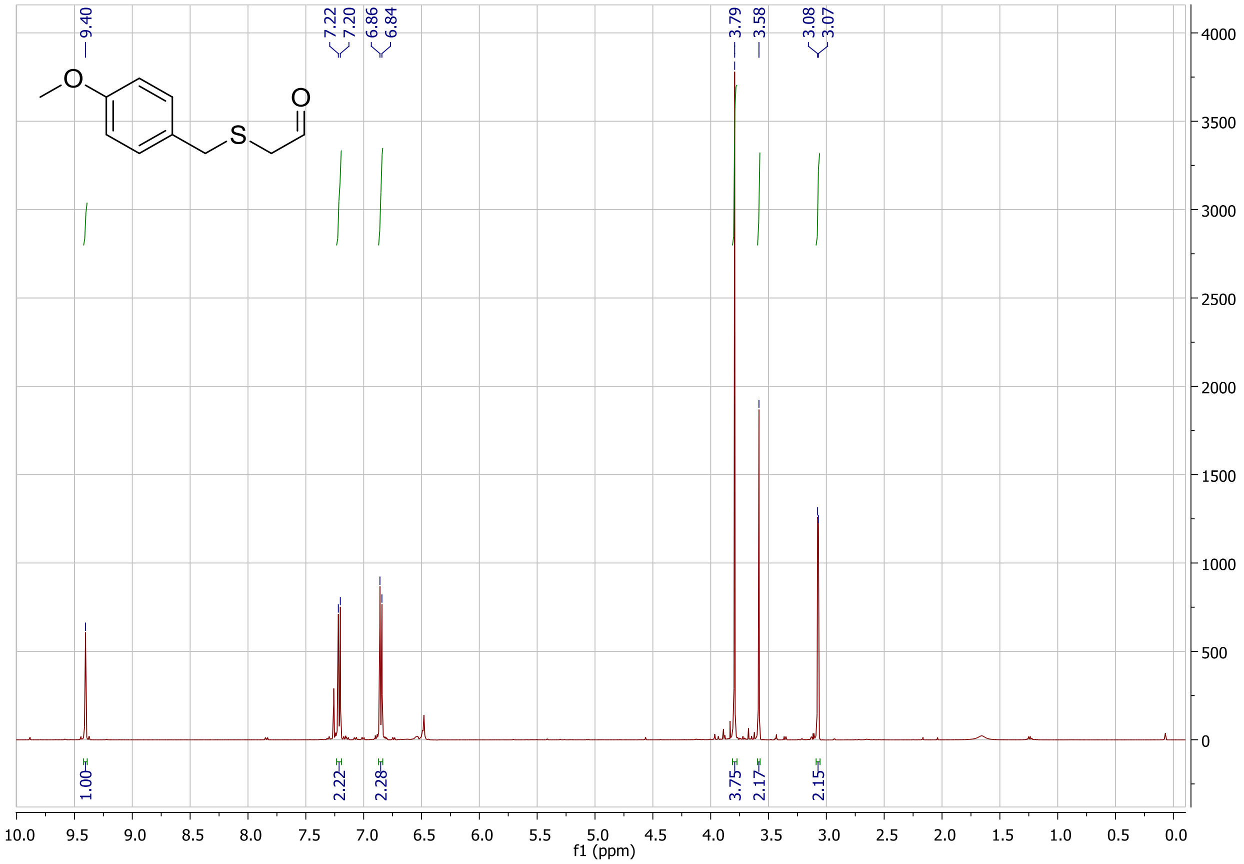
Using flame dried glassware and under an argon atmosphere FMoc-Gly-F (15.9 mg, 53.0 μmol) was added to a solution of HCl salt **7** (15.9 mg, 44.2 μmol) in anhydrous CH_2Cl_2 (1.5 mL) followed by DIPEA (15 μL, 88 μmol). The reaction was stirred for 18 h. The solution was washed with HCl (2 M, 2 × 3 mL), H_2O (2 × 3 mL), sodium bicarbonate (2 × 3 mL) and H_2O (2 × 3 mL). All aqueous layers were back extracted with CH_2Cl_2. The combined organic layers were dried ($MgSO_4$), filtered and concentrated *in vacuo* to give an orange residue which was purified by column chromatography (1% MeOH in $CHCl_3$) using deactivated silica (35% H_2O w/w) to give **39** as an orange gum (16.0 mg, 60%). **^{1}H NMR** ($CDCl_3$, 600 MHz) *δ* 7.77 (2H, d, *J* = 7.6, FmocH), 7.58 (2H, d, *J* = 7.4, FmocH), 7.40 (2H, t, *J* = 7.6, FmocH), 7.31 (2H, t, *J* = 7.4, FmocH), 7.18 (2H, d, *J* = 8.6, ArH), 7.03 (1H, br s, CHN**H**), 6.79 (2H, d, *J* = 8.6, ArH), 5.33 (1H, br s, CH_2N**H**), 4.46 (2H, d, *J* = 6.7, FmocCH_2), 4.22 (1H, d, *J* = 6.7, FmocCH_2C**H**), 3.98 (1H, dd, *J* = 17.3, 5.8, 1 × C**H**$_2$NH), 3.92 (1H, dd, *J* = 17.3, 5.7, 1 × C**H**$_2$NH), 3.74 (3H, s, OCH_3), 3.63 (2H, s, ArC**H₂**S), 2.89 (1H, br d, *J* = 10.0, CHB), 2.80 (1H, dd, *J* = 13.7, 3.4, 1 × C**H**$_2$CHB), 2.50 (1H, dd, *J* = 13.7, 11.6, 1 × C**H**$_2$CHB), 1.20 (6H, s, 2 × pinacol-CH_3), 1.19 (6H, s, 2 × pinacol-CH_3); **^{13}C NMR** ($CDCl_3$, 150 MHz) *δ* 173.0, 158.7, 156.5, 143.7, 141.4, 130.4, 130.1, 127.9, 127.3, 125.1, 120.2, 114.1, 82.2, 67.4, 55.4, 47.2, 42.3, 41.0 (br), 35.5, 33.7, 25.1, 24.9; **LRMS** (CI) 603 (3%, $[M+H]^+$), 503 (3%), 381 (9%), 325 (8%), 281 (7%), 207 (7%), 179 (100%, $[Fmoc-CO_2]^+$), 147 (8%), 121 (36%, PMB^+), 103 (17%); **HRMS** Found 603.27061, $C_{33}H_{39}BN_2O_6S$ requires 603.27001; **IR** ν_{max} (film/cm^{-1}) 3300 (N-H), 2970 (C-H), 2928 (C-H), 1711 (C=O), 1680 (C=O), 1610, 1536, 1511, 1462, 1450.

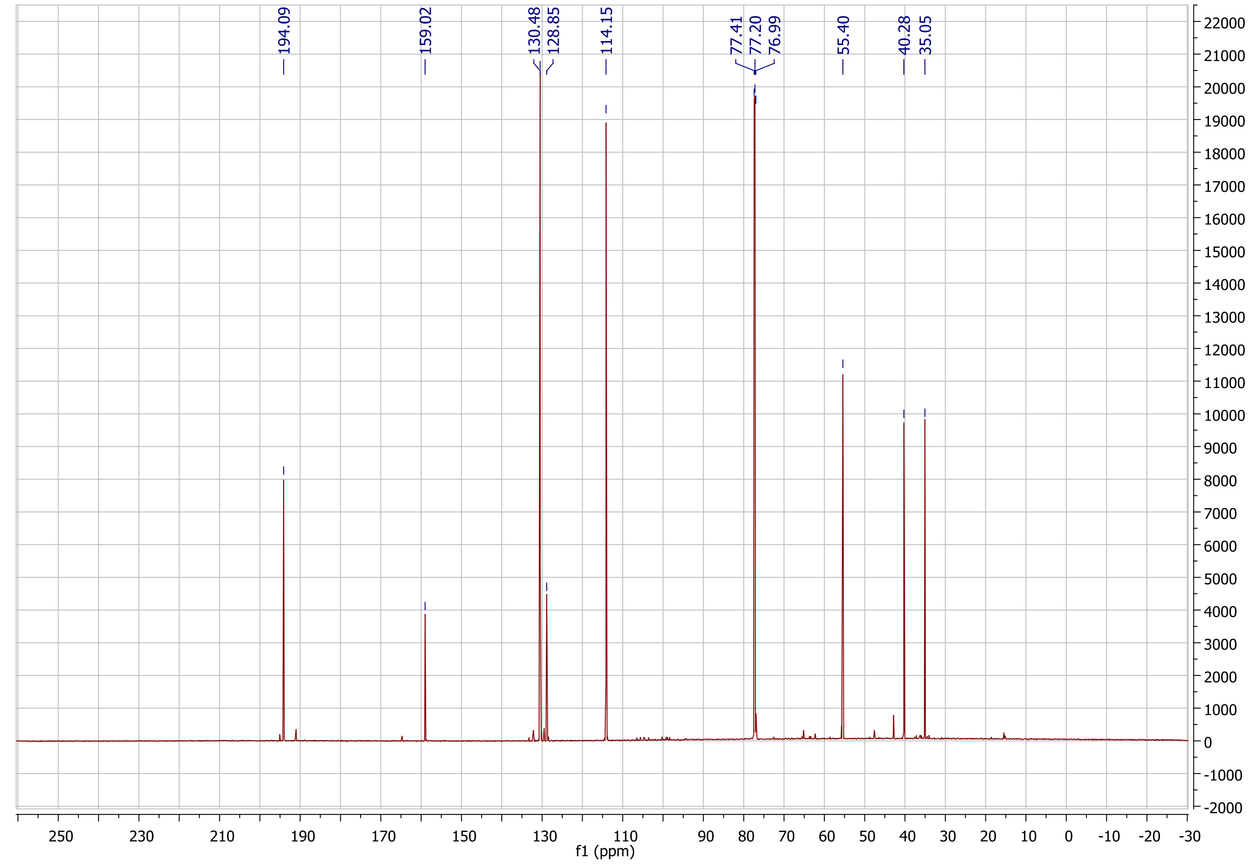
(2,2-Diethoxyethyl)(4-methoxybenzyl)sulfane (3b)



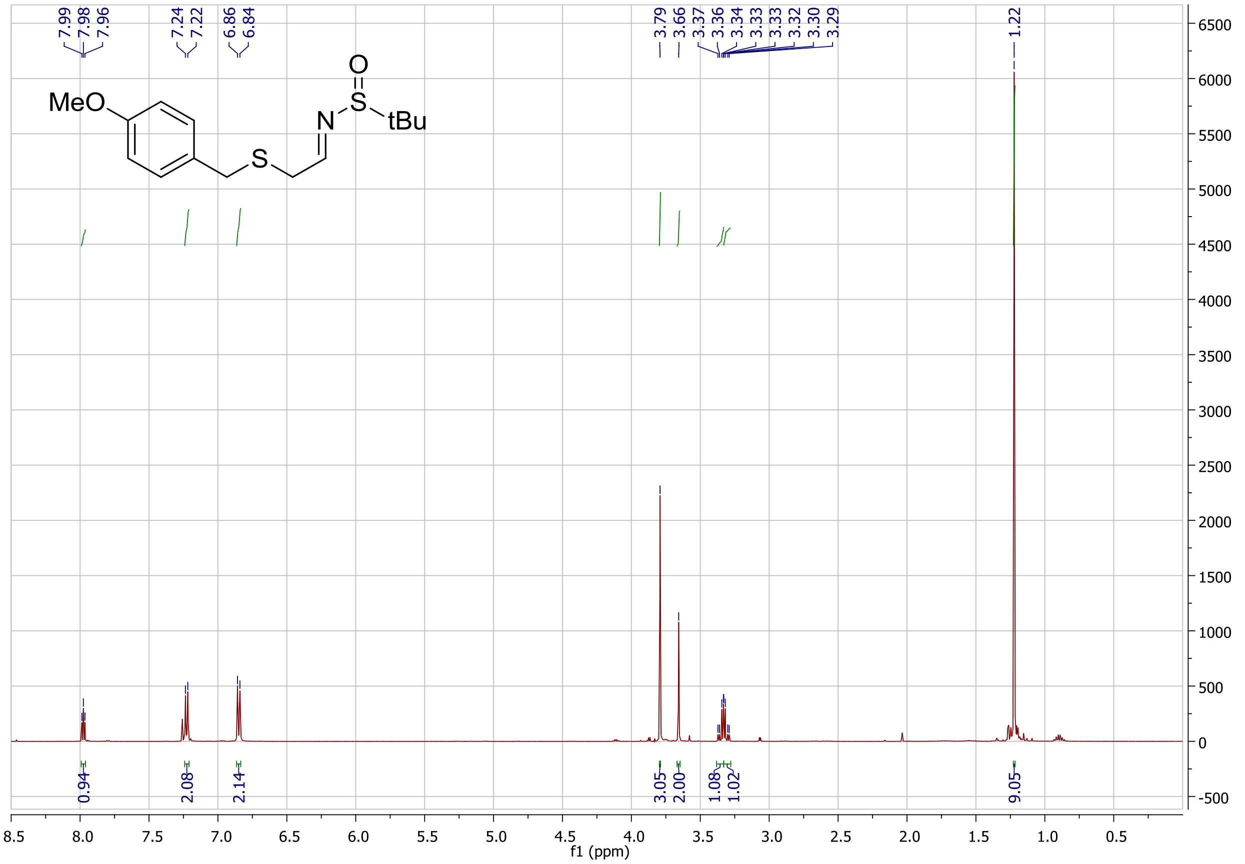


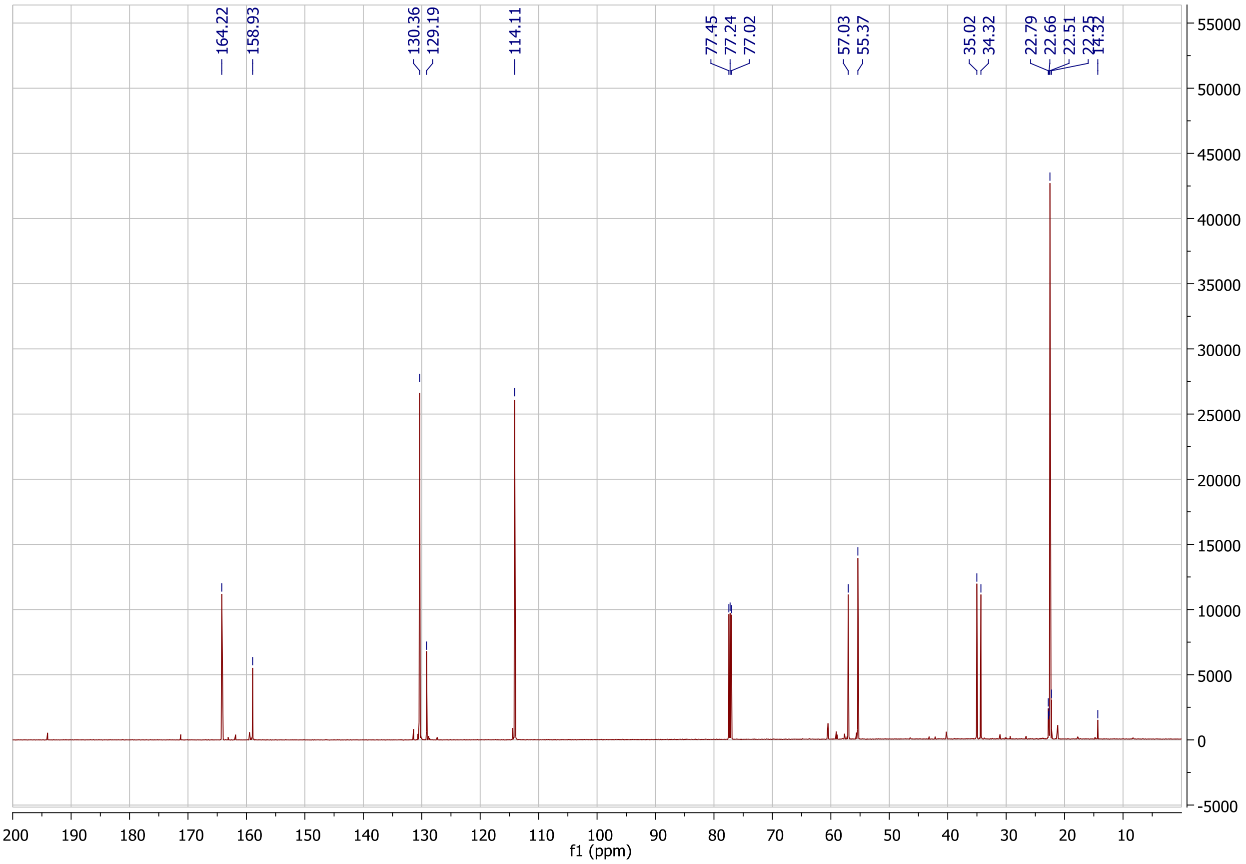
2-((4-methoxybenzyl)thio)acetaldehyde (4)



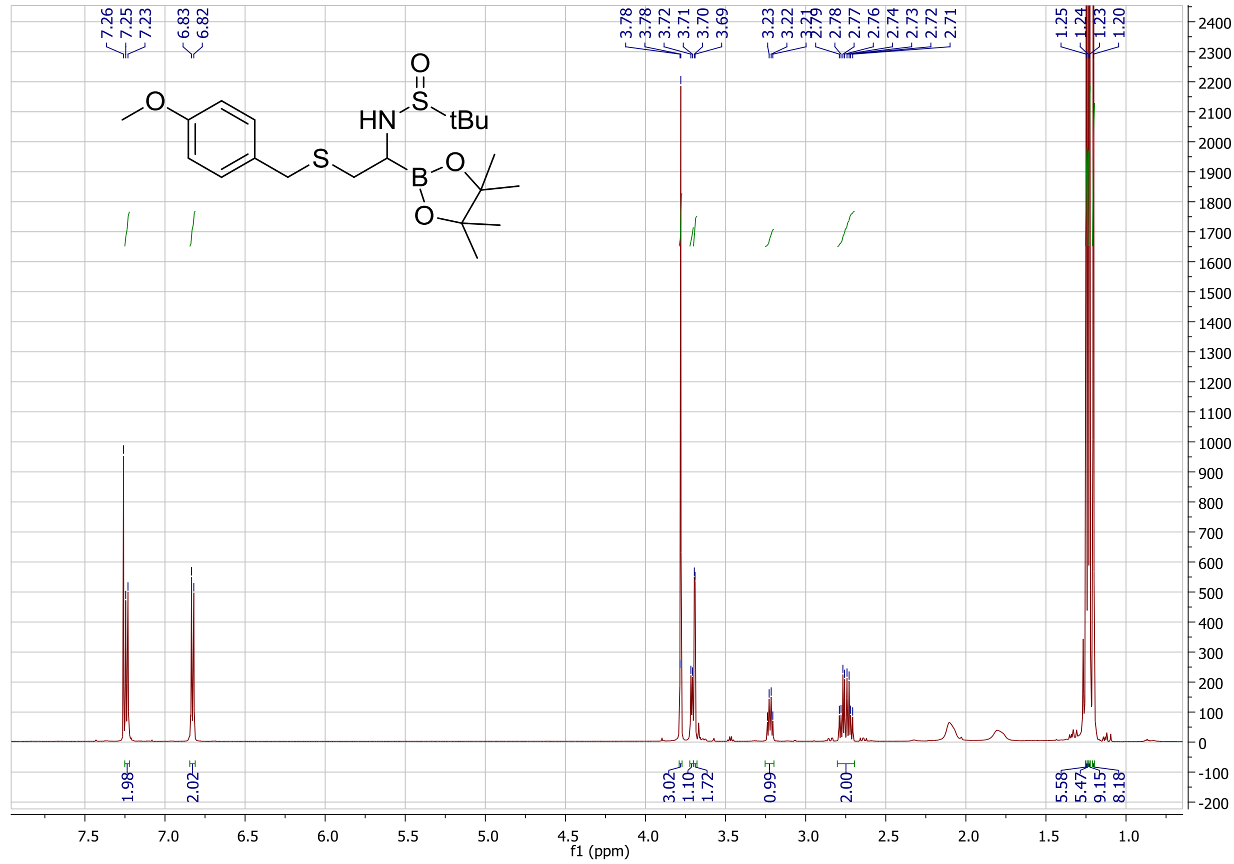


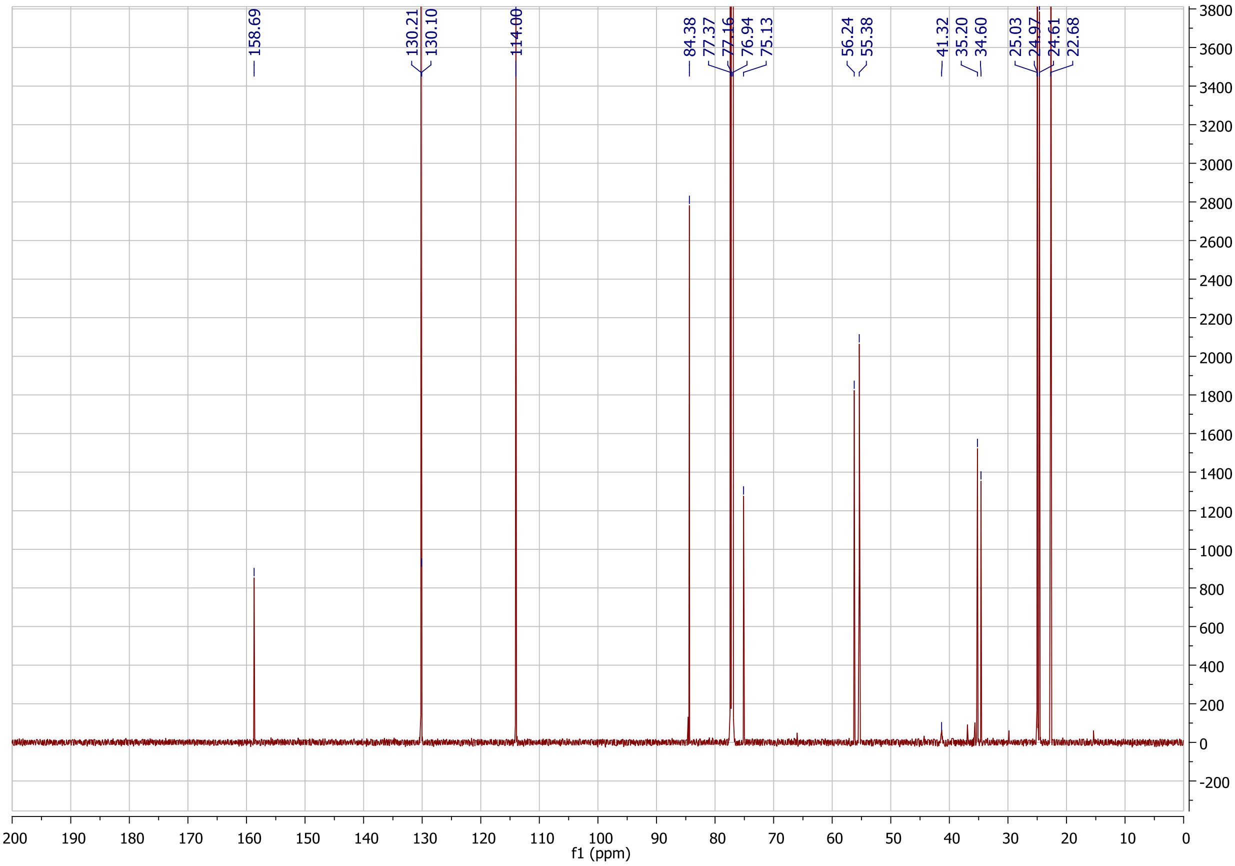
(*E*)-*N*-(2-((4-Methoxybenzyl)thio)ethylidene)-2-methylpropane-2-sulfinamide (5)



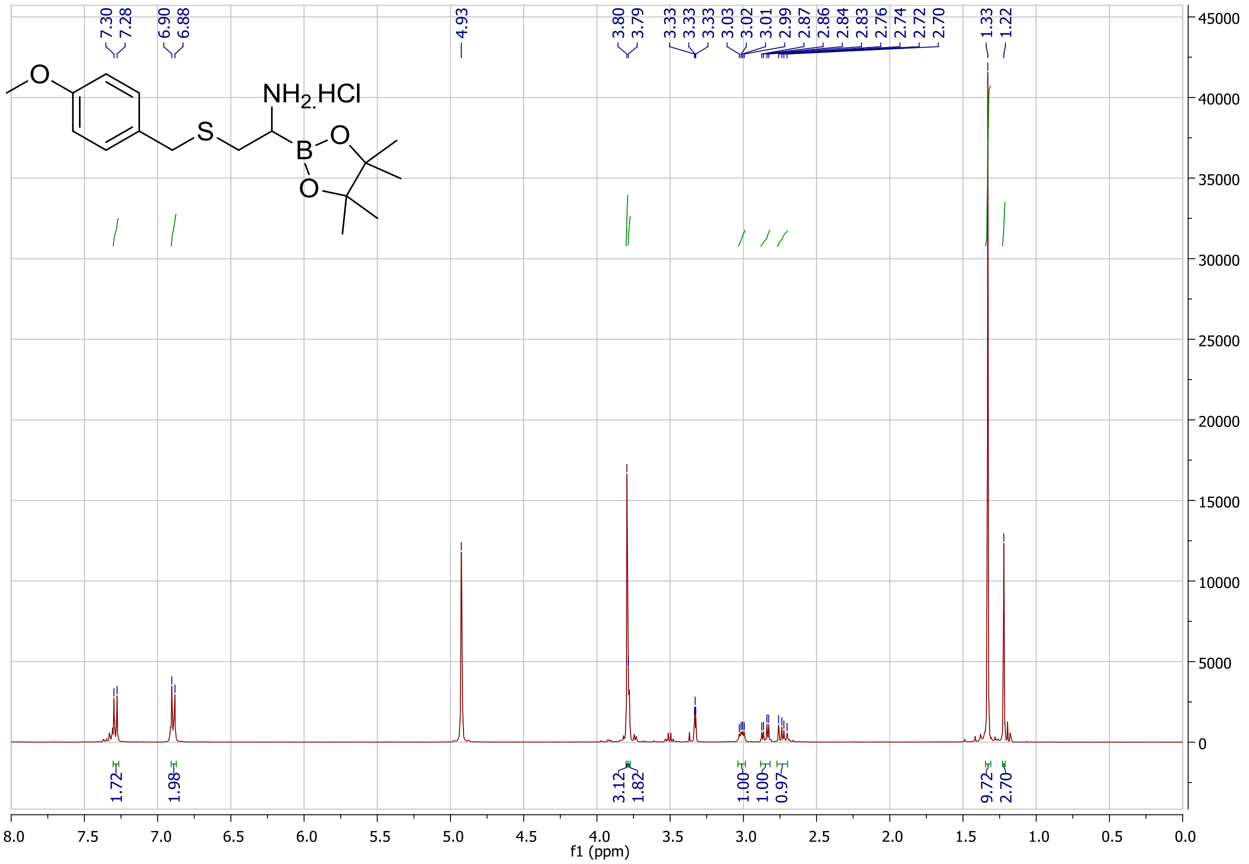


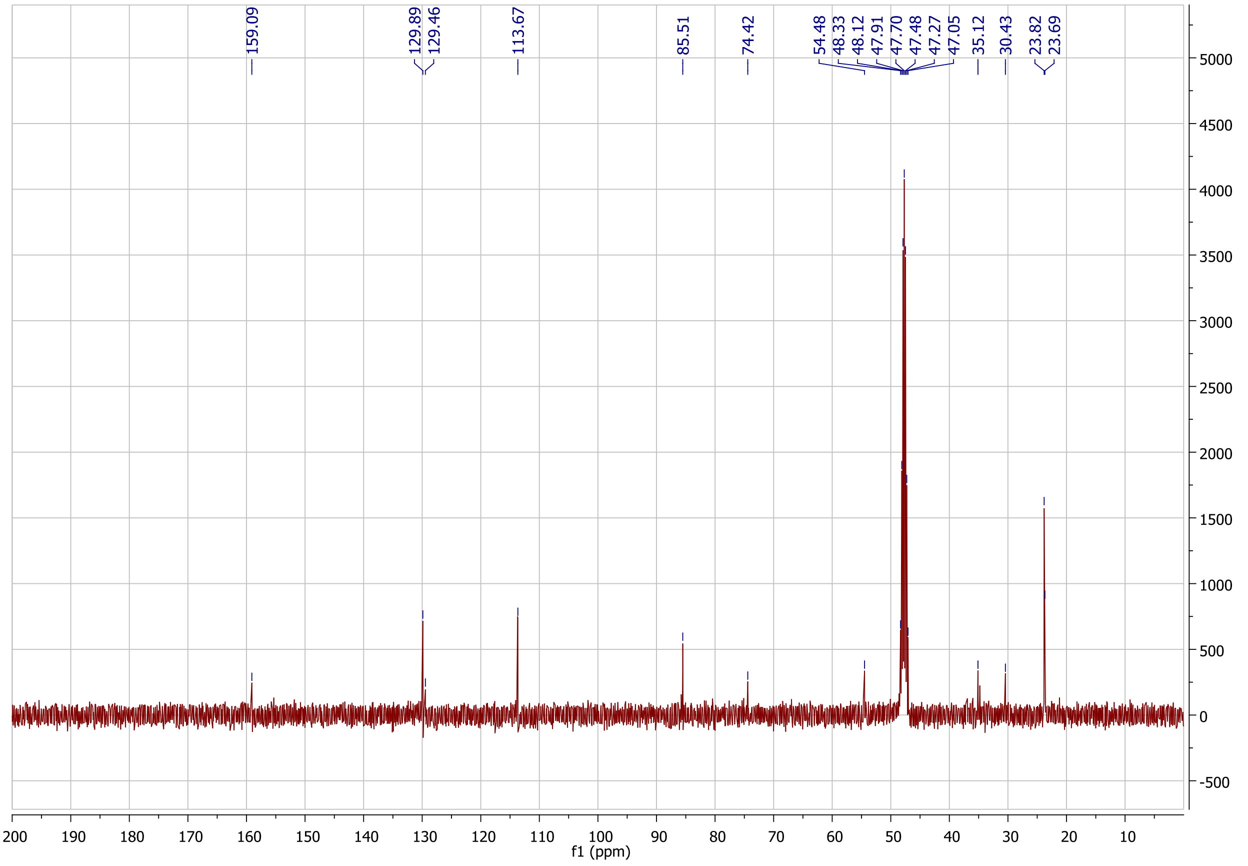
N-(2-((4-Methoxybenzyl)thio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)-2-methylpropane-2-sulfinamide (6)



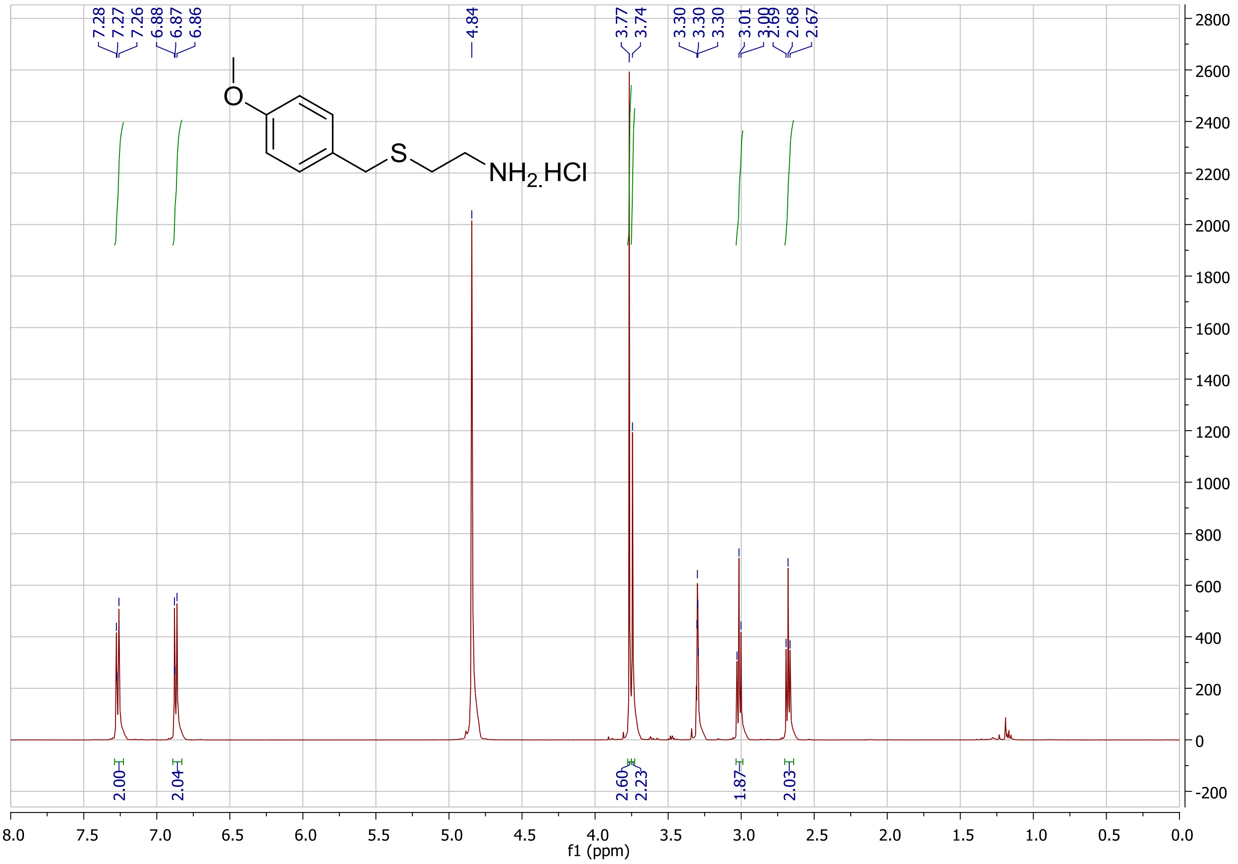


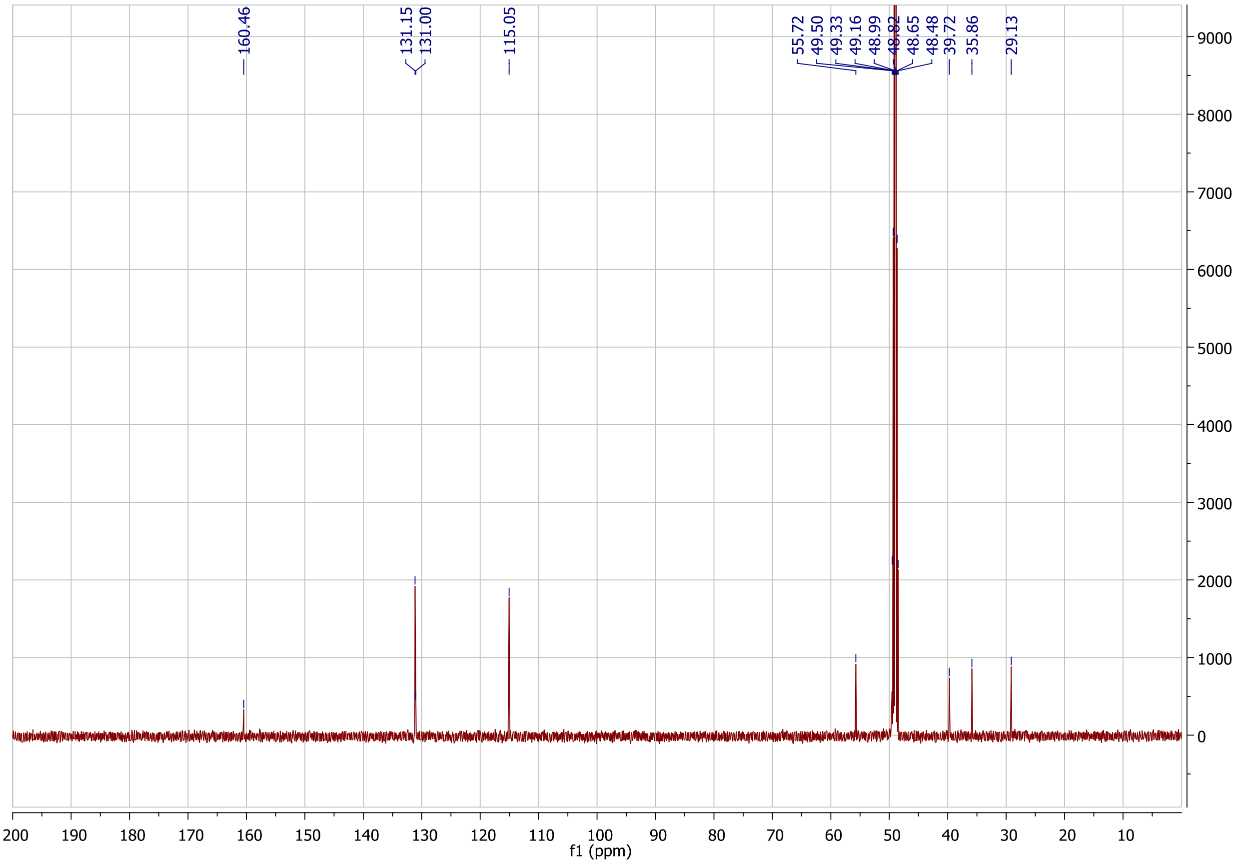
2-((4-Methoxybenzyl)thio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethanamine hydrochloride (7)



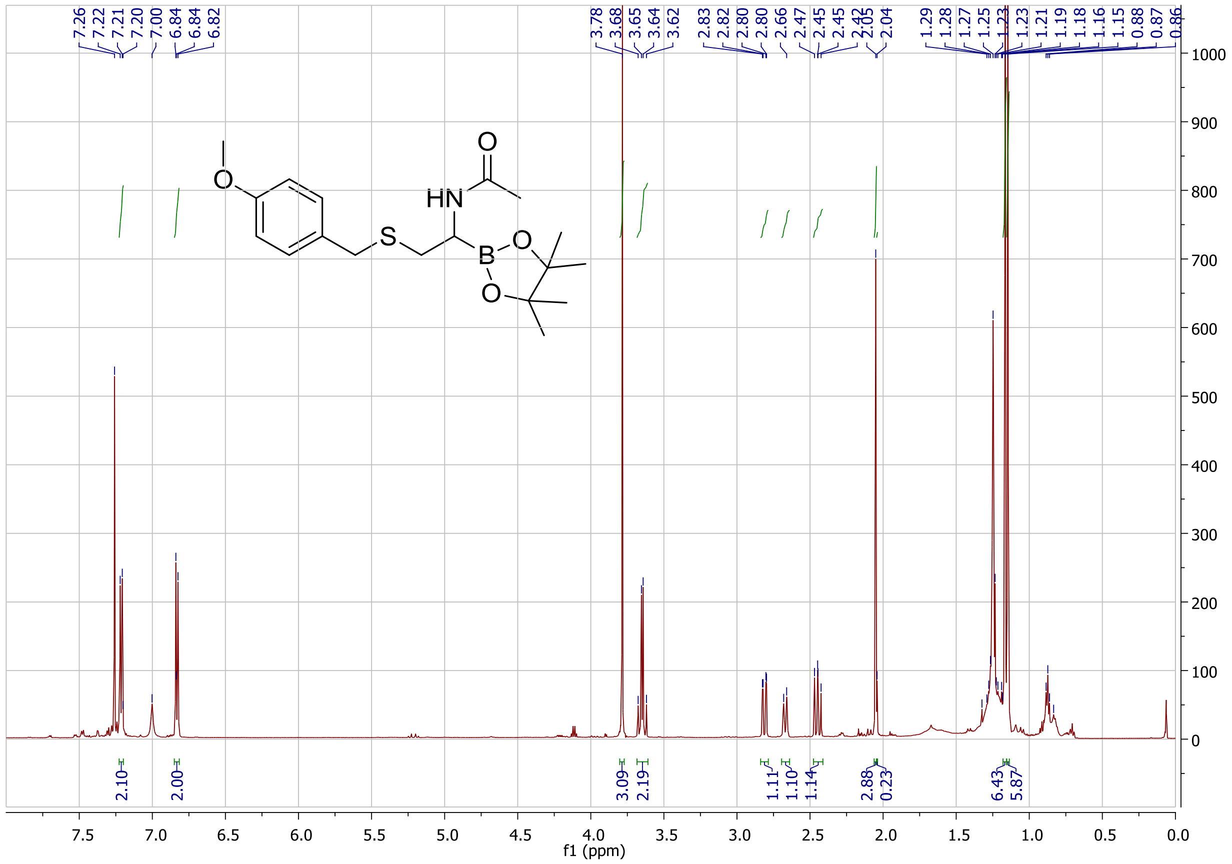


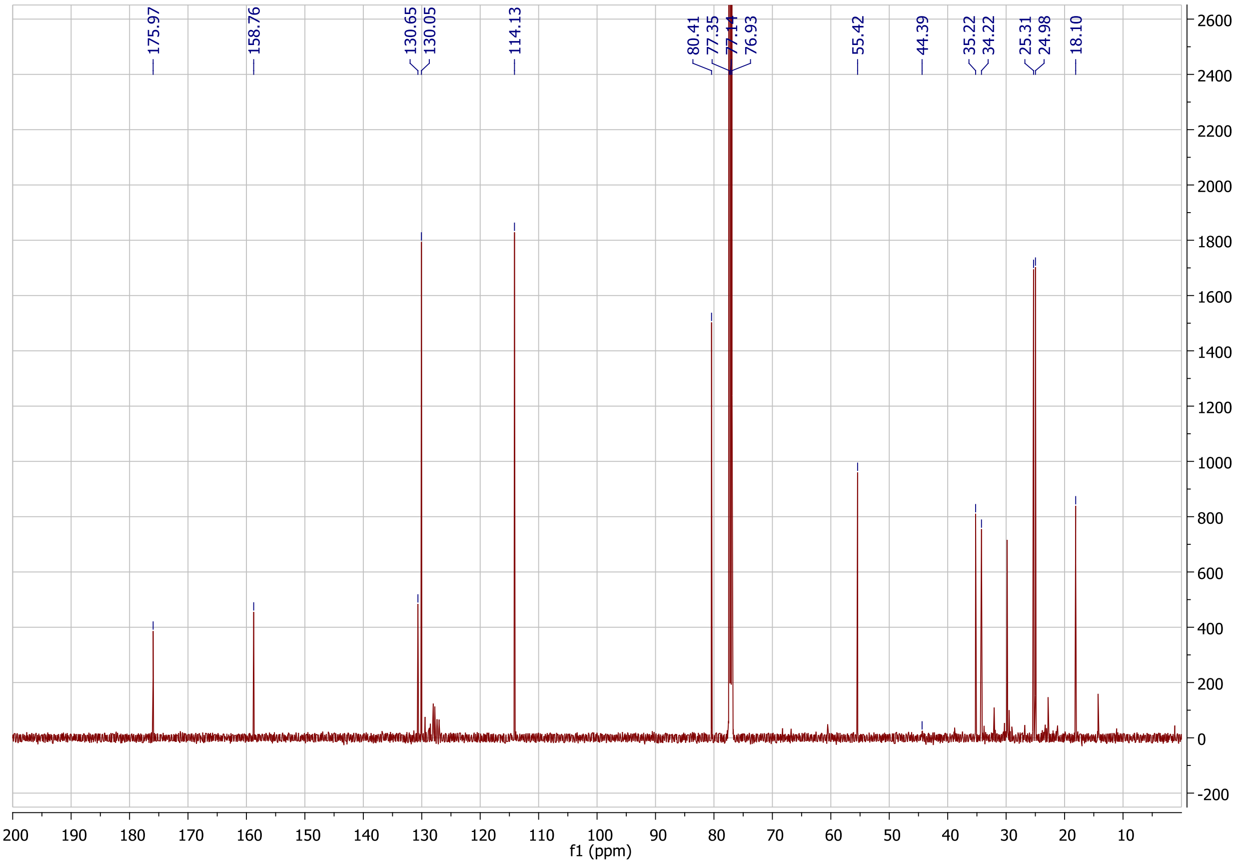
2-((4-Methoxybenzyl)thio)ethanamine hydrochloride (8)



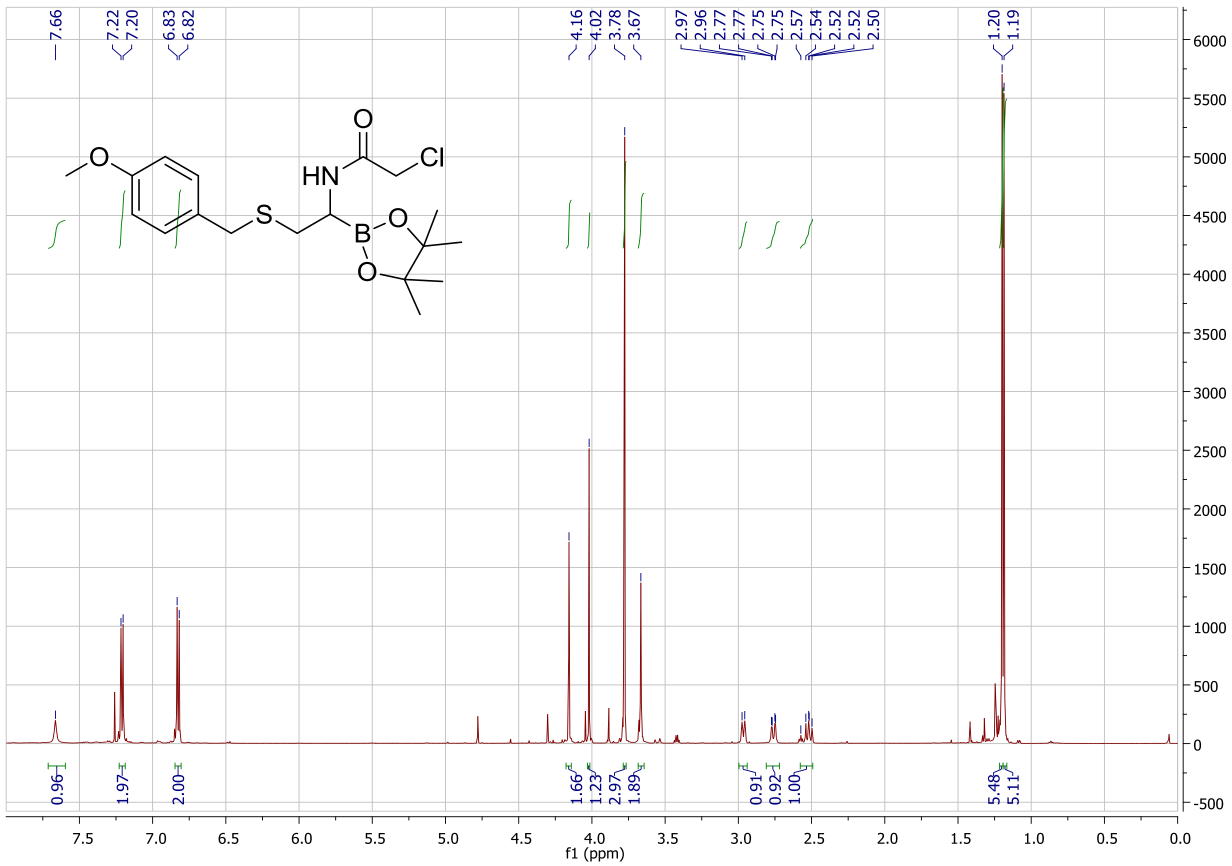


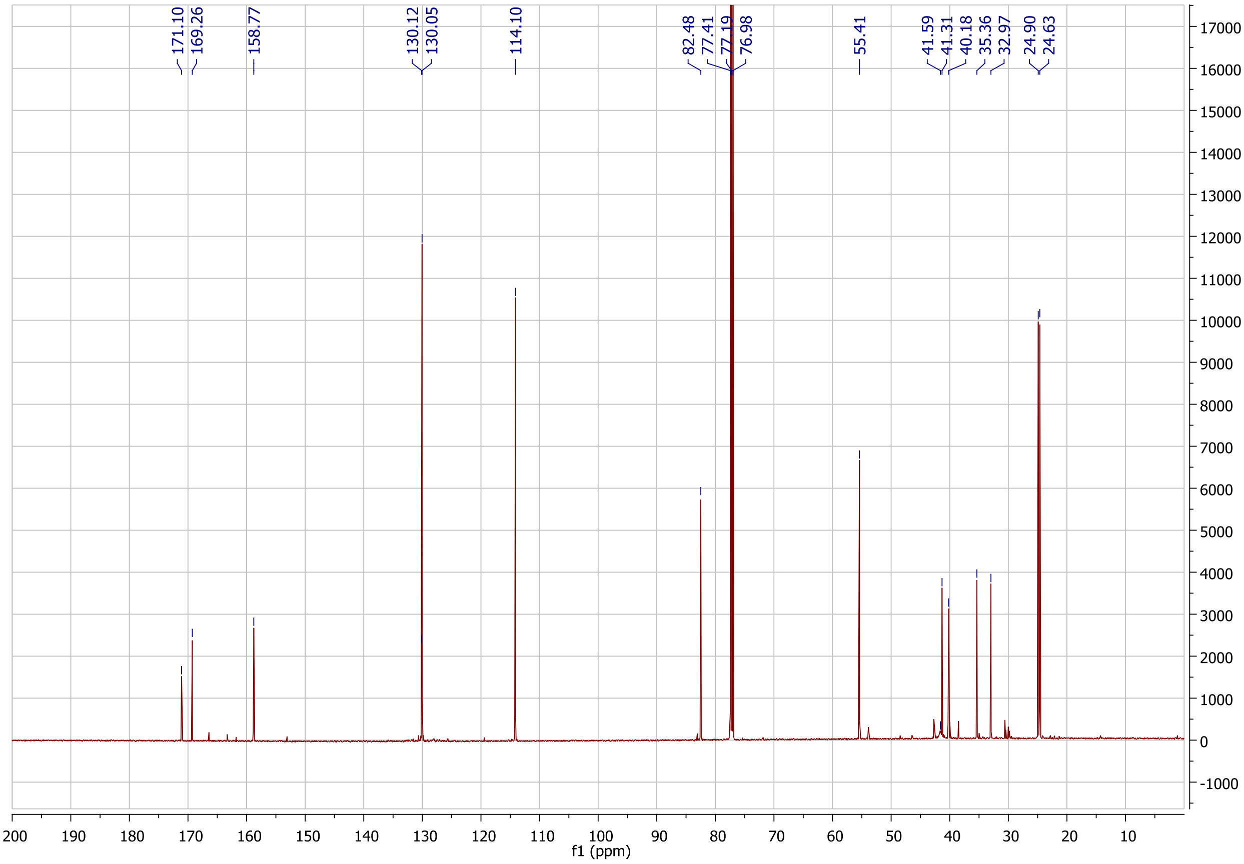
N-(2-((4-Methoxybenzyl)thio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)acetamide (9a)



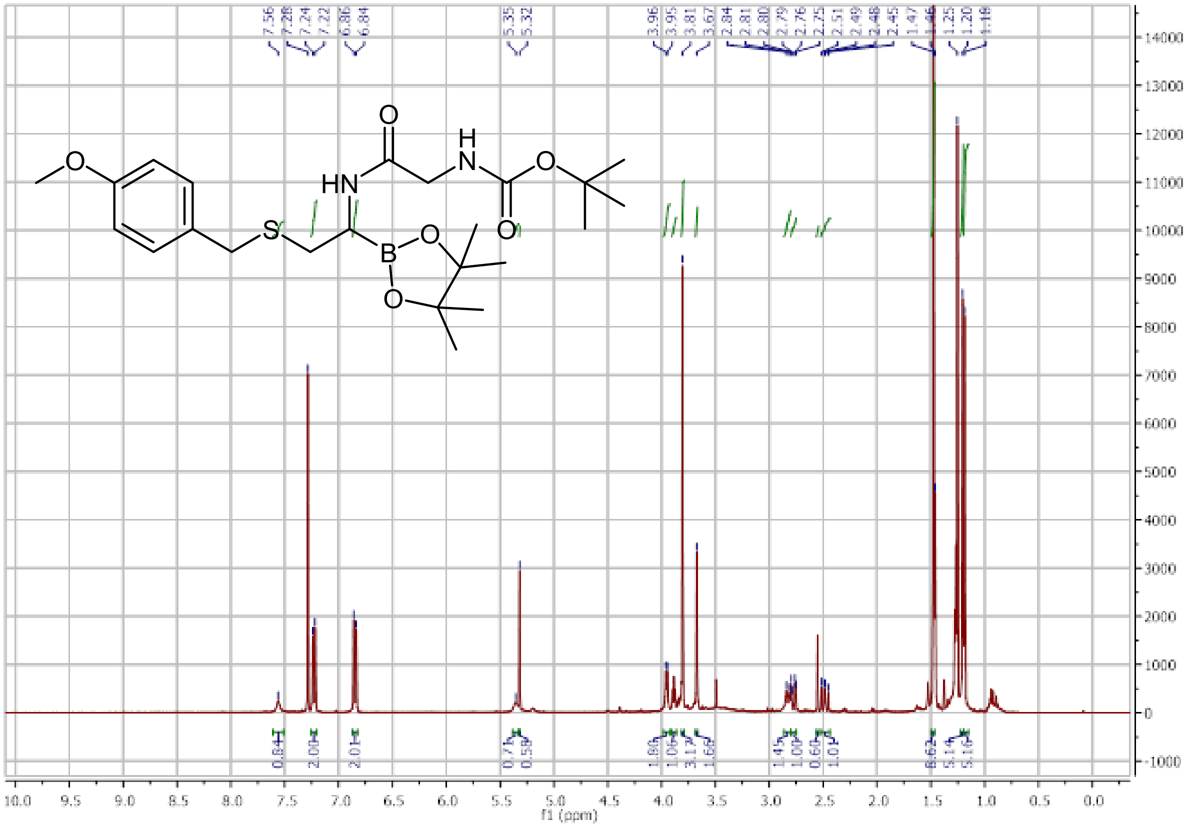


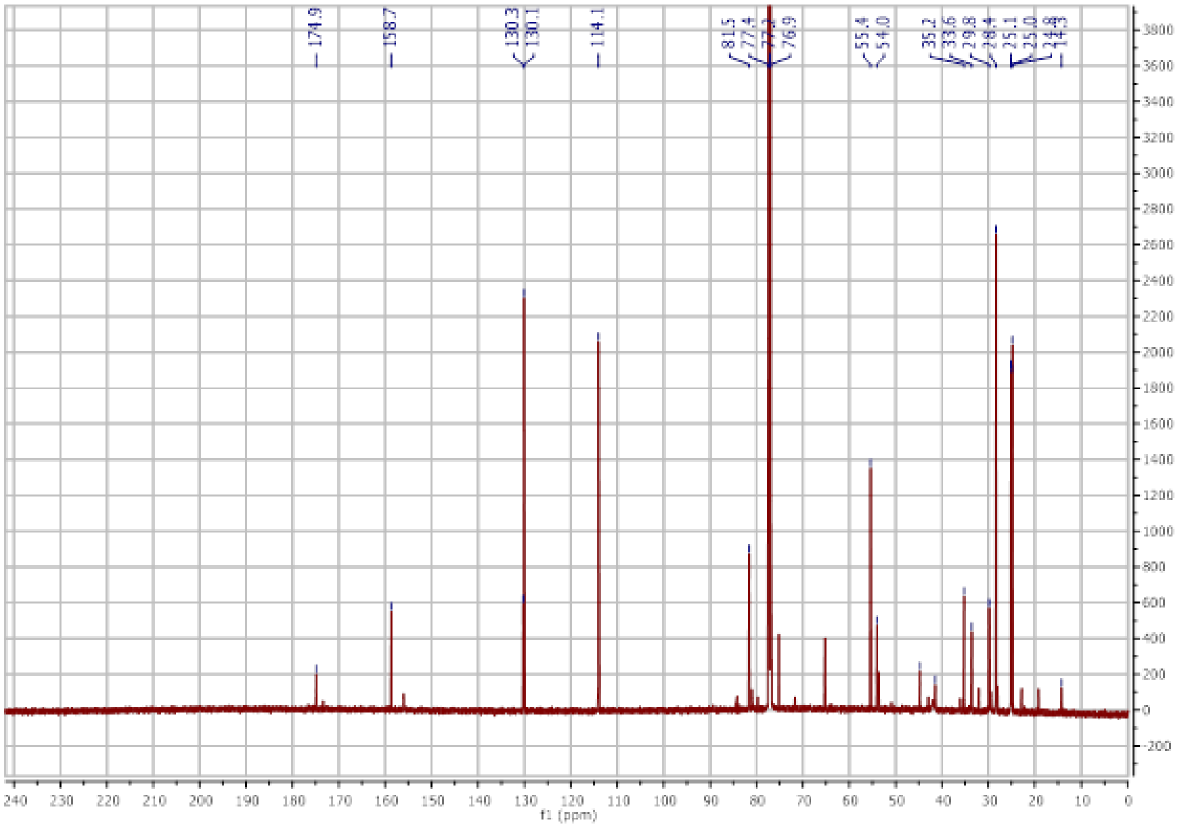
2-Chloro-*N*-(2-((4-methoxybenzyl)thio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)acetamide (9b)



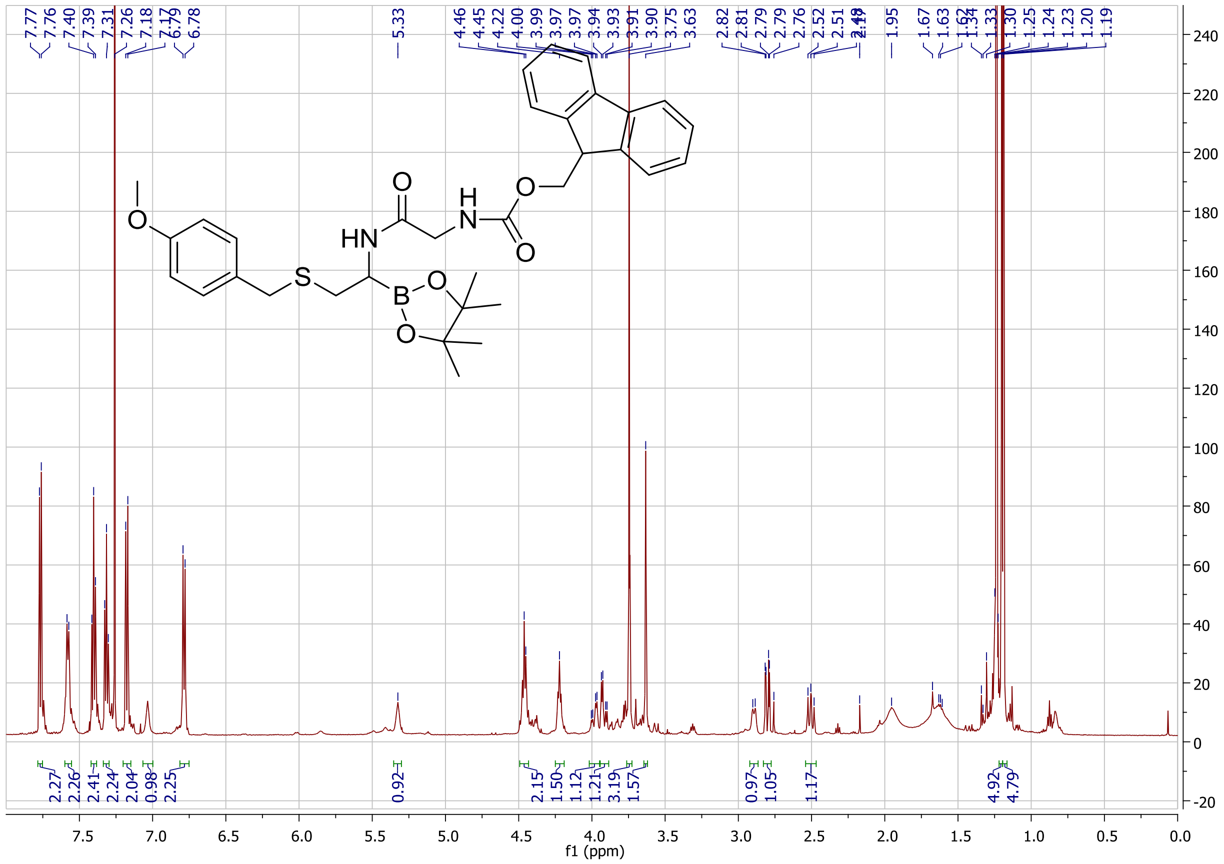


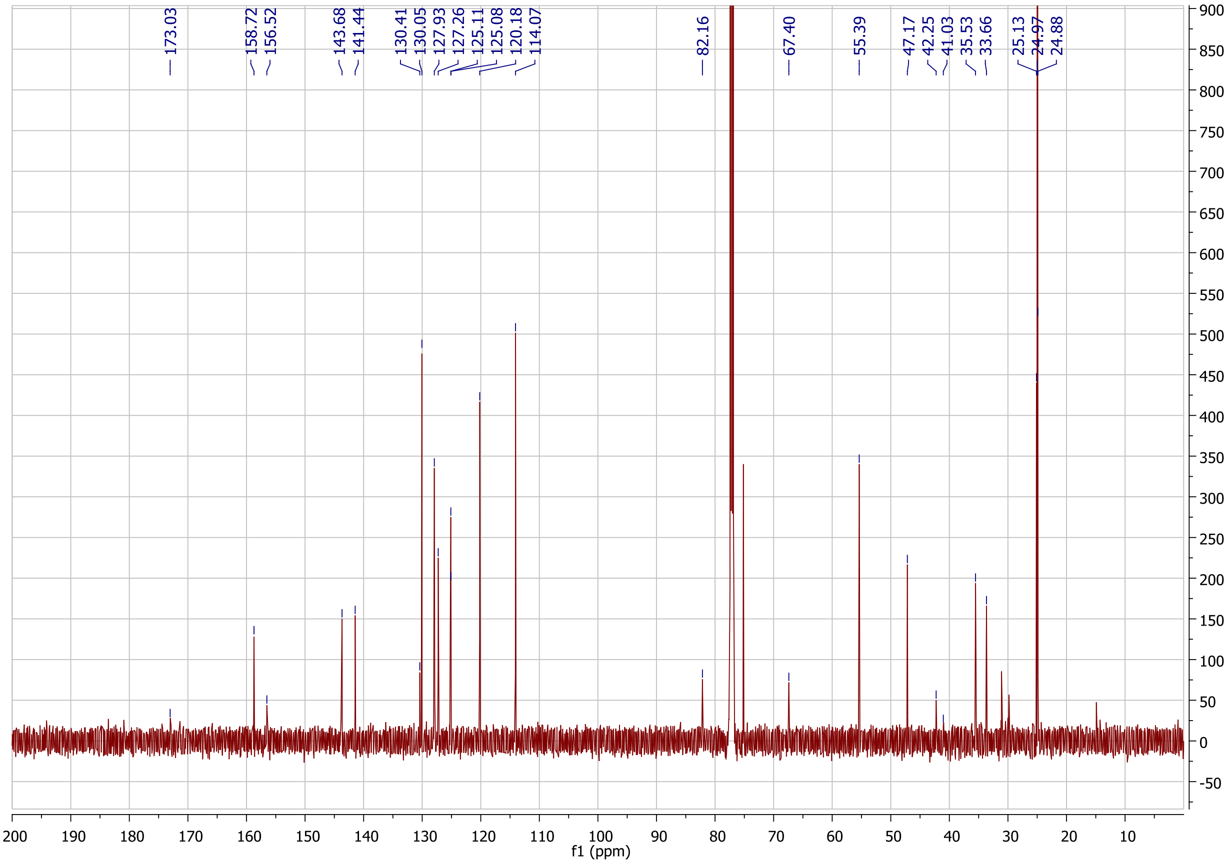
***tert*-Butyl (2-((2-((4-methoxybenzyl)thio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)amino)-2-oxoethyl)carbamate (10a)**





(9*H*-Fluoren-9-yl)methyl(2-((2-((4-methoxybenzyl)thio)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)amino)-2-oxoethyl)carbamate (10b)





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