C(sp^3)-C(sp^2) Cross-Coupling of Alkylsilicates with Borylated Aryl Bromides – An Iterative Platform to Alkylated Aryl- and Heteroaryl Boronates

Brandon A. Vara,[‡] Matthieu Jouffroy,[‡] and Gary A. Molander*

Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania, 231 South 34th Street, Philadelphia, Pennsylvania 19104-6323, United States

*To whom correspondence should be addressed. E-mail: gmolandr@sas.upenn.edu

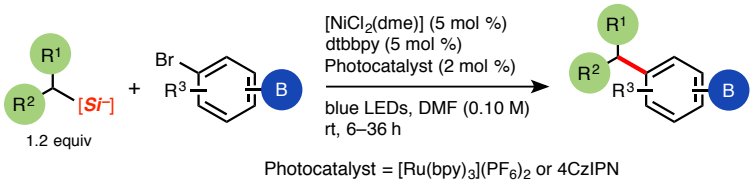
Supporting Information

General considerations

All reactions were carried out under an inert atmosphere of nitrogen or argon in oven-dried glassware, unless otherwise noted. Conventional solvents (THF, Et_2O, CH_2Cl_2, toluene, CPME) were dried using a J. C. Meyer solvent system. DMF (99.9%, extra dry) was used as received. [$NiCl_2$(dme)] was purchased from commercial sources, and all other reagents were purchased commercially and used as received, unless otherwise noted. Column chromatography was performed by Combiflash$^{(R)}$ using RediSep Rf Gold Normal-Phase Silica$^{(R)}$ columns or RediSep Rf Alumina Neutral$^{(R)}$. Photoredox reactions were irradiated with blue LED strips, and the temperature (~ 30 °C) was controlled using an external fan. Melting points (°C) are uncorrected. Mass spectra (ESI- or CI-TOF) were recorded using CH_2Cl_2, MeCN or MeOH as the solvent. NMR Spectra (^{1}H, ^{13}C {^{1}H}, ^{11}B, ^{19}F {^{1}H}) were performed at 298 K. ^{1}H (500.4 MHz) and ^{13}C {^{1}H} (125.8 MHz) NMR chemical shifts are reported relative to internal TMS (δ = 0.00 ppm) or to residual protiated solvent. ^{11}B (128.4 MHz) and ^{19}F {^{1}H} NMR (470.8 MHz) chemical shifts were referenced to external BF_3•Et_2O (0.0 ppm) and $CFCl_3$ (0.0 ppm), respectively. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad), coupling constant *J* (Hz) and integration. Ammonium organobis(catecholato)silicates [1] and 4CzIPN [2] photocatalyst were prepared according to literature procedures.

[1] (a) Jouffroy, M.; Primer, D. N.; Molander, G. A. *J. Am. Chem. Soc.* **2016**, *138*, 475. (b) Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. *Org. Lett.* **2016**, *18*, 764. (c) Jouffroy, M.; Kelly, C. B.; Molander, G. A. *Org. Lett.* **2016**, *18*, 876. (d) Jouffroy, M.; Davies, G. H. M.; Molander, G. A. *Org. Lett.* **2016**, *18*, 1606.
[2] Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. *Nature* **2012**, *492*, 234.

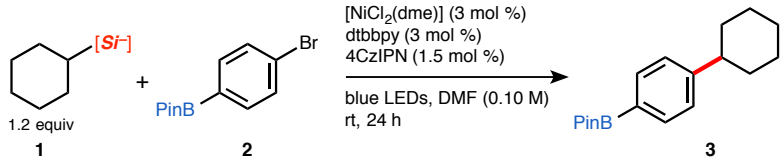
General procedure for photoredox cross-coupling reactions



0.5 mmol scale reaction: To an 8 mL clear glass vial equipped with a Teflon-coated magnetic stir bar was added 4,4'-di-*tert*-butyl-2,2'-bipyridine (6.7 mg, 0.025 mmol, 0.05 equiv), and [$NiCl_2$(dme)] (5.5 mg, 0.025 mmol, 0.05 equiv). The vial was capped and purged with nitrogen, then 1 mL of THF was introduced. The resulting suspension was heated briefly with a heat gun until the nickel complex and ligand were fully solubilized, yielding a pale green solution.[3] The solution was cooled in an ice bath, resulting in the immediate precipitation of an evergreen solid. Solvents were then evaporated in vacuo to give a fine coating of the ligated nickel complex. Once dry, borylated aryl bromide (0.5 mmol, 1.0 equiv), ammonium organobis(catecholato)silicate (0.6 mmol, 1.2 equiv), and photocatalyst ([$Ru(bpy)_3$]$(PF_6)_2$ *or* 4CzIPN) (0.01 mmol, 0.02 equiv) were added in succession. The vial was then capped and purged three times. Under an inert atmosphere, DMF (5 mL) was introduced. The vial containing all the reagents was further sealed with Parafilm and stirred approximately 4 cm away from the LED strips (see Figure SI-1). A fan was blown across the reaction setup to suppress the heat generated by the latter (the reaction temperatures were estimated to be ~30 °C). After several hours (2-36 h), an aliquot was taken and analyzed by HPLC to monitor reaction completion. The crude reaction mixture was poured into a separatory funnel and diluted with H_2O (10 mL) before addition of a saturated solution of Na_2CO_3 (10 mL). The resulting suspension was extracted with Et_2O (3 × 15 mL), and the

[3] We subsequently showed it was not essential to precomplex the [$NiCl_2$(dtbbpy)] active catalyst species and adding [$NiCl_2$(dme)] and dtbbpy separately to the reaction mixture before the reaction was suitable to obtaining identically high yield. It should be noted, this experiment was performed on only one substrate combination and may not be a general solution to all the reactions examined in this work. We find pre-complexation to be more reliable.

combined organic extracts were washed with a saturated solution of Na_2CO_3 (2 × 20 mL) then brine (20 mL), dried ($MgSO_4$), and concentrated. When needed, the residue was purified by column chromatography on silica gel or alumina, eluting with hexanes or CH_2Cl_2 and EtOAc, to obtain products in pure form.



Gram scale reaction: To a 100 mL round bottom flask equipped with a Teflon-coated magnetic stir bar was added [$NiCl_2$(dme)] (23 mg, 0.10 mmol) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (29 mg, 0.10 mmol). The flask was capped and purged with nitrogen, then 3.0 mL of THF was introduced. The resulting suspension was heated briefly with a heat gun until the nickel and ligand were fully solubilized, yielding a pale green solution. The solution was cooled in an ice bath, resulting in the immediate precipitation of an evergreen solid. Solvents were then evaporated in vacuo to give a fine coating of the ligated nickel complex. Once dry, 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane **2** (1.00 g, 3.53 mmol), diisopropylammonium bis(catecholato)cyclohexylsilicate **1** (1.82 g, 4.24 mmol) and 4CzIPN (42 mg, 0.05 mmol) were added in succession. The vial was then capped and purged four times. Under an inert atmosphere, DMF (35 mL) was introduced. The vial containing all the reagents was further sealed with Parafilm and stirred in the presence of coiled blue LEDs (see Figure SI-1). A fan was blown across the reaction setup to suppress the heat generated by the LEDs, stabilizing at 30 °C after 1 h. Reaction completion was monitored by sampling the reaction mixture and analyzing by HPLC. After completion (24 h), the crude reaction mixture was poured into a separatory funnel and diluted with H_2O (30 mL) before addition of a saturated solution of Na_2CO_3 (30 mL). The resulting suspension was extracted with Et_2O (3 × 30 mL), and the combined organic extracts were washed with a saturated solution of Na_2CO_3

(2 × 40 mL) then brine (20 mL), dried ($MgSO_4$), and concentrated. The residue was purified by filtration through approximately 6 cm x 4 cm cylindrical plug of silica (SiO_2; CH_2Cl_2/hexanes, 50:50, *v/v*), to obtain **3** in pure form (974 mg, 96%).

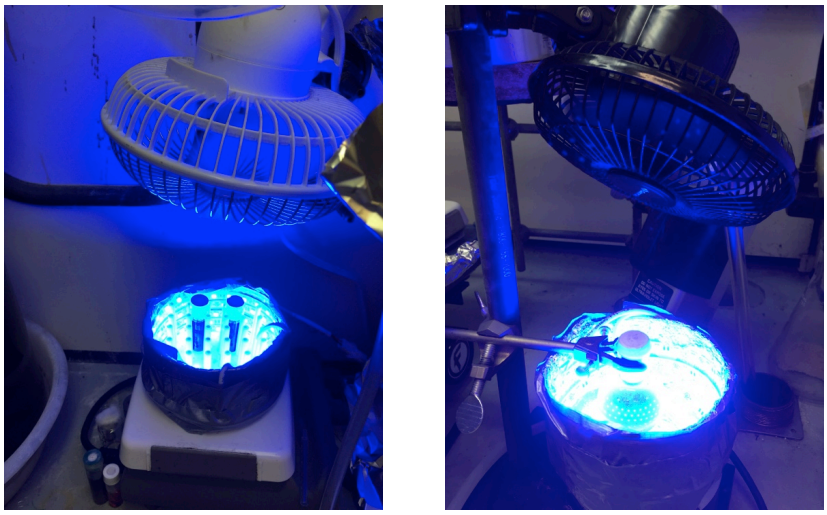
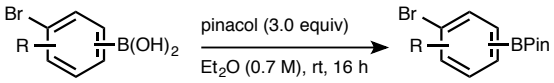
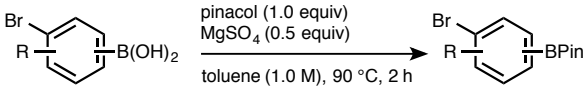


Figure SI–1. 0.5 mmol (left) and gram (right) scale photoredox cross-coupling reaction set-up.

General procedure for the preparation of pinacol boronate esters

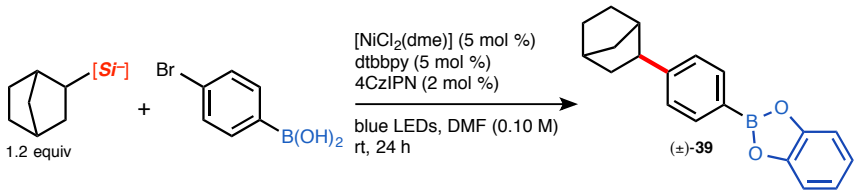


Method A: A round bottom flask was charged with a Teflon-coated magnetic stir bar, the corresponding bromo arylboronic acid (1 equiv), pinacol (3 equiv), and anhyd Et_2O (0.7 M). The reaction was capped and allowed to stir overnight at rt. Following complete consumption of the boronic acid starting material as determined by HPLC analysis, the reaction was diluted with Et_2O and transferred to a separatory funnel. The organics were washed with H_2O (× 3), dried ($MgSO_4$), filtered, and concentrated. When needed, the resulting pinacol boronate was purified by column chromatography on silica gel, eluting with hexanes or CH_2Cl_2 and EtOAc, to obtain products in pure form.



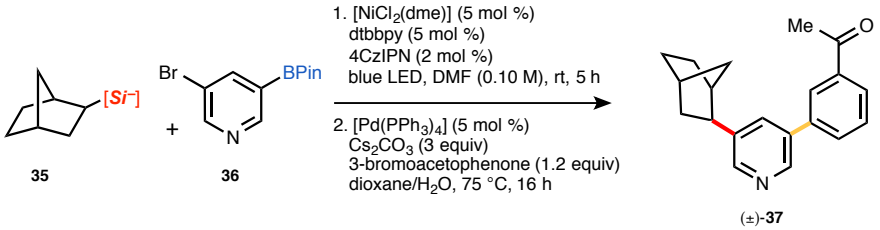
Method B: A round bottom flask was charged with a Teflon-coated magnetic stir bar, the corresponding bromo arylboronic acid (1 equiv) and pinacol (1 equiv). The flask was then capped and purged three times. Under inert atmosphere, toluene (1.0 M) was introduced, and the resulting mixture was stirred and heated to 90 °C. After several hours (1-4 h), an aliquot was taken and analyzed by HPLC to monitor reaction completion. Following complete consumption of the boronic acid starting material, the reaction was cooled to rt, then $MgSO_4$ (0.5 equiv) was added, and the reaction was stirred for another 15 min, before being filered and concentrated. When needed, the residue was purified by column chromatography on silica gel, eluting with hexanes or CH_2Cl_2 and EtOAc, to obtain products in pure form.

Procedure for the synthesis of 39



2-(4-(Bicyclo[2.2.1]heptan-2-yl)phenyl)benzo[*d*][1,3,2]dioxaborole (39): The reaction was carried out following the general cross-coupling procedure (0.5 mmol scale), using the 4CzIPN (**4**) photocatalyst, and 4-bromophenylboronic acid in place of 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2**). The reaction was analyzed by HPLC to monitor consumption of the aryl bromide. After 14 h, the crude reaction mixture was poured into a separatory funnel and diluted with H_2O (10 mL). The resulting suspension was extracted with Et_2O (3 × 15 mL), and the combined organic extracts were washed again with H_2O (2 × 10 mL), then brine (20 mL), dried ($MgSO_4$) and concentrated to yield a light yellow solid (quantitative conversion). The crude residue contained **39** with residual catechol, and traces of an unknown aryl-containing compound (~ 15%). This material was carried forward without further purification. ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.03 (d, J = 8.0 Hz, 2 H), 7.36 (d, J = 8.0 Hz, 2 H), 7.34–7.32 (m, 2 H), 7.15–7.13 (m, 2 H), 2.83 (m, 1H), 2.46 (br s, 1 H), 2.41 (br s, 1 H), 1.86–1.82 (m, 1 H), 1.74–1.58 (m, 4 H), 1.41 (t, J = 10.0 Hz, 1 H) 1.35–1.24 (m, 2 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 148.5, 135.0, 127.0, 122.6, 121.1, 112.4, 47.6, 42.7, 39.0, 36.8, 36.1, 30.5, 28.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 32.2 ppm. The extent to which this compound was prone to decomposition precluded acquisition of the remaining analytical data.

Procedure for iterative cross-coupling

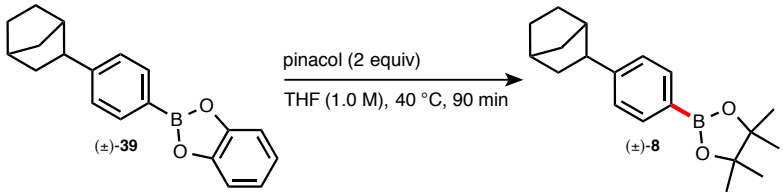


35 36 (±)-37

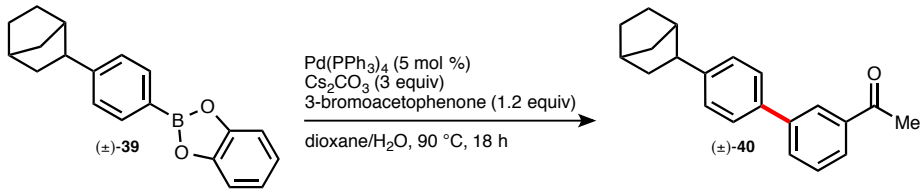
1-(3-(5-(Bicyclo[2.2.1]heptan-2-yl)pyridin-3-yl)phenyl)ethan-1-one (37): 3-Bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**36**) (141 mg, 0.5 mmol) and diisopropylammonium bis(catecholato)*exo*-2-bicyclo[2.2.1]heptylsilicate (**35**) (264 mg, 0.6 mmol) were reacted together following the general procedure for photoredox cross-coupling reactions (see above). After a standard work up procedure, an 8 mL vial was charged with the crude reaction mixture and a Teflon-coated magnetic stir bar. $[Pd(PPh_3)_4]$ (28 mg, 0.025 mmol), 3-bromoacetophenone (119 mg, 0.60 mmol), and Cs_2CO_3 (488 mg, 1.50 mmol) were added, and the vial was capped and evacuated/purged 3 times with argon. Dioxane/H_2O (5 mL, 4:1, *v/v*) was introduced and the vial was purged with argon. The vial containing all the reagents was sealed with parafilm and stirred at 75 °C and monitored by TLC. After 18 h, the reaction was cooled, diluted with H_2O (5 mL) and the aqueous layer was extracted with Et_2O (3 × 10 mL). The organics were combined, dried ($MgSO_4$), filtered, and concentrated to a brown residue. The crude residue was purified by flash column chromatography (SiO_2; hexanes/EtOAc, 95:5 to 70:30, *v/v*) affording the title compound (**37**) as a light yellow oil (104 mg, 72% over 2 steps). ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.65 (s, 1 H), 8.51 (s, 1 H), 8.15 (s, 1 H), 7.97 (d, J = 8.0 Hz, 1 H), 7.76 (d, J = 8.0 Hz, 1 H), 7.71 (s, 1 H), 7.58 (t, J = 8.0 Hz, 1 H), 2.83 (dd, J = 8.5, 6.0 Hz, 1 H), 2.66 (s, 3 H), 2.43 (br m, 2 H), 1.88–1.84 (m, 1 H), 1.72–1.58 (m, 3 H), 1.54 (d, J = 10.0 Hz, 1 H), 1.44–1.40 (m, 1 H), 1.25–1.22 (m, 2 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 197.8, 148.3, 145.2, 142.7, 138.8, 137.8, 135.3, 133.1, 131.8, 129.3, 127.9, 126.9, 45.0, 42.8, 38.9, 36.9, 36.2, 30.5, 28.7, 26.7 ppm; IR: ν = 2952,

2870, 1686, 1583, 1429, 1407, 1357, 1298, 1251, 1025, 958, 890, 801, 720 cm^{-1}; HRMS (ESI) m/z calc. for $C_{20}H_{22}NO$ [M+H] 292.1701, found 292.1706.

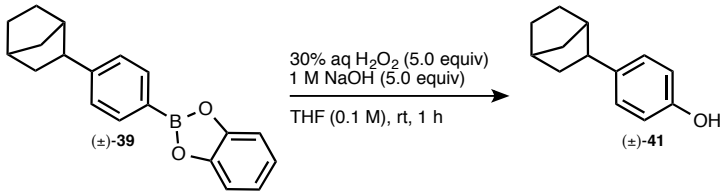
Procedure for further transformation of 39



2-(4-(Bicyclo[2.2.1]heptan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8): An 8 mL clear glass vial was charged with a Teflon-coated magnetic stir bar, crude catecholborane **39** (0.32 mmol), pinacol (37 mg, 0.64 mmol), and anhydrous THF (320 μL, 1.0 M) under air. The reaction mixture was stirred and gently heated to 40 °C and quickly darkened. The reaction was monitored by HPLC, and after 90 min, the mixture was concentrated then redissolved in EtOAc (15 mL). The organics were washed with saturated aq Na_2CO_3 (2 x 5 mL) and H_2O (2 x 10 mL), dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography (SiO_2; hexanes/EtOAc, 100:0 to 90:10, *v/v*) affording the title compound (**8**) as a white solid (66 mg, 70%).

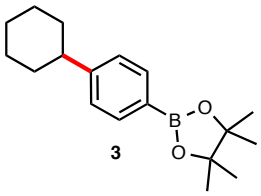


1-(4'-(Bicyclo[2.2.1]heptan-2-yl)-[1,1'-biphenyl]-3-yl)ethan-1-one (40): An 8 mL clear glass vial was charged with crude catecholborane **39** (147 mg, 0.25 mmol) and a Teflon-coated magnetic stir bar. [$Pd(PPh_3)_4$] (28 mg, 0.025 mmol), 3-bromoacetophenone (60 mg, 0.30 mmol), and Cs_2CO_3 (244 mg, 0.75 mmol) were added, and the vial was capped and evacuated/purged 3 times with argon. Dioxane/H_2O (2.5 mL, 4:1, *v/v*) was introduced, and the vial was purged with argon. The vial containing all the reagents was sealed with parafilm and stirred at 90 °C and monitored by TLC. After 18 h, the reaction was cooled, diluted with H_2O (3 mL) and the aqueous layer was extracted with Et_2O (3 × 10 mL). The organics were combined, dried ($MgSO_4$), filtered, and concentrated to a brown residue. The crude residue was purified by flash chromatography (SiO_2; hexanes/EtOAc, 100:0 to 80:20, *v/v*) affording the title compound (**40**) as a colorless oil (52 mg, 72% over 2 steps). ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.18 (t, *J* = 1.5 Hz, 1 H), 7.90 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.78 (dd, *J* = 8.0, 1.5 Hz, 1 H), 7.56–7.51 (m, 3 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 2.80 (dd, *J* = 8.5, 5.5 Hz, 1 H), 2.66 (s, 3 H), 2.42–2.40 (m, 2 H), 1.82–1.80 (m, 1 H), 1.74–1.71 (m, 1 H), 1.65–1.57 (m, 3 H), 1.41–1.31 (m, 2 H), 1.23 (d, *J* = 10.0 Hz, 1 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 198.1, 147.4, 141.6, 137.6, 137.2, 131.5, 128.9, 129.6, 126.9, 126.8, 126.7, 47.0, 43.0, 39.1, 36.8, 36.1, 30.6, 28.9, 26.7 ppm; IR: ν = 2949, 2868, 1684, 1599, 1582, 1477, 1454, 1434, 1402, 1355, 1297, 1234, 957, 828, 792, 764, 693 cm^{-1}; HRMS (CI) m/z calc. for $C_{21}H_{22}O$ [M+] 290.1671, found 290.1669.



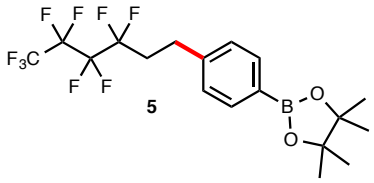
4-(Bicyclo[2.2.1]heptan-2-yl)phenol (41): A 25 mL flask was charged with a Teflon-coated magnetic stir bar, crude catecholborane **39** (0.5 mmol), THF (5 mL, 0.1 M), 30% aq H_2O_2 (290 μL, 2.5 mmol), and 1 M NaOH (2.5 mL, 2.5 mmol) under air. The reaction mixture immediately darkened upon the addition of base and was stirred vigorously for 1 h. The reaction was diluted with H_2O (2 mL) and quenched with 1 M HCl (3 mL). The aqueous layer was extracted three times with CH_2Cl_2, and the organics were combined, dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography (SiO_2; hexanes/EtOAc, 100:0 to 90:10, *v/v*) affording the title compound (**41**) as a white solid (78 mg, 80%); mp = 105-106 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.09 (d, *J* = 8.5 Hz, 2 H), 6.75 (d, *J* = 8.5 Hz, 2 H), 4.71 (s, 1 H), 2.68 (dd, *J* = 9.0, 5.5 Hz, 1 H), 2.34–2.31 (m, 2 H), 1.77–1.70 (m, 1 H), 1.64–1.50 (m, 4 H), 1.36–1.32 (1 H), 1.28–1.24 (m, 1 H), 1.18–1.15 (m, 1 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 153.1, 140.0, 128.1, 114.9, 46.5, 43.2, 39.2, 36.8, 35.9, 30.5, 28.9 ppm; IR: ν = 3231, 3023, 2950, 2868, 1611, 1598, 1511, 1450, 1369, 1296, 1240, 1178, 1101, 909, 837, 816, 762 cm^{-1}; HRMS (CI) m/z calc. for $C_{13}H_{16}O$ [M+] 188.1201, found 188.1196.

Compound Characterization Data



3

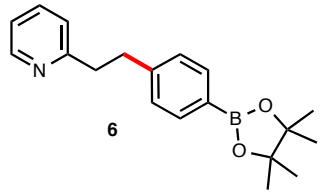
2-(4-Cyclohexylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3): obtained as a crystalline solid (139 mg, 97%) by purification over a short plug of silica (hexanes/EtOAc, 95:5, *v/v*); mp = 93–95 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.77 (d, *J* = 7.5 Hz, 2 H), 7.25 (d, *J* = 7.5 Hz, 2 H), 2.58–2.49 (m, 1 H), 1.93–1.83 (m, 4 H), 1.80–1.74 (m, 1 H), 1.51–1.39 (m, 4 H), 1.36 (s, 12 H), 1.32–1.21 (m, 1 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 151.3, 134.8, 126.2, 83.5, 44.8, 34.2, 26.8, 26.1, 24.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.5 ppm; IR: ν = 2978, 2922, 2851, 1611, 1399, 1359, 1321, 1299, 1270, 1214, 1165, 1142, 1089, 1019, 963, 860 cm^{-1}; HRMS (CI) m/z calc. for $C_{18}H_{27}BO_2$ $[M]^+$ 286.2104, found 286.2111.



5

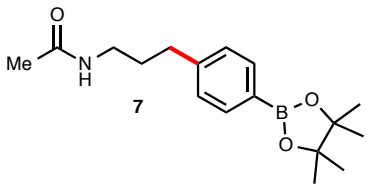
4,4,5,5-Tetramethyl-2-(4-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)phenyl)-1,3,2-dioxaborolane (5): obtained as colorless oil (128 mg, 57%) by purification over silica (hexanes/EtOAc, 90:10 to 60:40, *v/v*); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.79 (d, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 7.5 Hz, 2 H), 2.93 (dd, *J* = 11.5, 8.0 Hz, 2 H), 2.38 (m, 2 H), 1.35 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 142.4, 135.3, 127.7, 83.8, 32.2 (t, $^{2}J_{CF}$ = 22 Hz), 26.6, 24.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.7 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): –81.1, –114.8, –124.4, –126.0 ppm; IR: ν = 2954, 1400, 1359, 1320, 1272, 1217, 1165, 1144,

1132, 1089, 1048, 1022, 1008, 963, 881, 860, 840, 826 cm^{-1}; HRMS (CI) m/z calc. for $C_{18}H_{20}BF_9O_2$ [M+] 451.1491, found 451.1501.



6

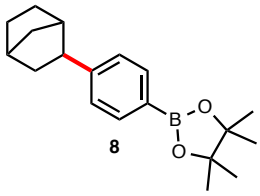
2-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenethyl)pyridine (6): obtained as a light yellow oil (125 mg, 81%) by purification over silica (hexanes/EtOAc, 90:10 to 60:40, *v/v*); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.55 (d, *J* = 4.9 Hz, 1 H), 7.72 (d, *J* = 7.5 Hz, 2 H), 7.54 (td, *J* = 7.8, 1.6 Hz, 1 H), 7.20 (d, *J* = 7.5 Hz, 2 H), 7.10 (dd, *J* = 7.8, 4.9 Hz, 1 H), 7.05 (d, *J* = 7.9 Hz, 1 H), 3.12–3.02 (m, 4 H), 1.33 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 161.0, 149.2, 133.8, 136.2, 134.8, 127.9, 122.9, 121.0, 83.6, 39.9, 36.1, 24.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.4 ppm; IR: ν = 1611, 1595, 1514, 1471, 1437, 1397, 1357, 1321, 1262, 1213, 1168, 1140, 1087, 857, 821, 768 cm^{-1}; HRMS (ESI) m/z calc. for $C_{19}H_{25}BNO_2$ $[M + H]^+$ 310.1978, found 310.1970.



7

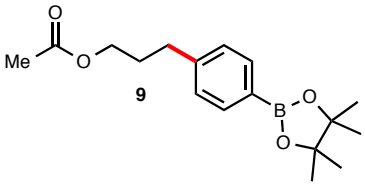
***N*-(3-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)acetamide (7)**: obtained as a light yellow oil (115 mg, 76%) by purification over silica (hexanes/EtOAc, 90:10 to 60:40, *v/v*); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.71 (d, *J* = 7.5 Hz, 2 H), 7.17 (d, *J* = 7.5 Hz, 2 H), 5.71 (br s, 1 H), 3.25 (dd, *J* = 13.0, 7.0 Hz, 2 H), 2.64 (t, *J* = 7.0 Hz, 2 H), 1.93 (s, 3 H), 1.81 (tt, *J* = 7.0, 7.0 Hz, 2 H), 1.32 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 171.0, 144.8, 134.9, 127.7, 83.6, 39.2, 33.4, 30.9, 24.7, 23.1 ppm; ^{11}B NMR ($CDCl_3$,

128.4 MHz): δ 30.4 ppm; IR: ν = 1650, 1412, 1555, 1519, 1438, 1398, 1358, 1319, 1272, 1166, 1143, 1108, 1089, 1021, 962, 859, 824 cm^{-1}; HRMS (ESI) m/z calc. for $C_{17}H_{27}BNO_3$ [M+H] 304.2084, found 304.2083.



8

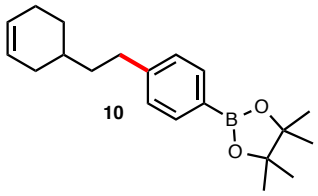
2-(4-(Bicyclo[2.2.1]heptan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (8): obtained as colorless crystals (133 mg, 90%) by purification over silica (hexanes/EtOAc, 90:10 to 60:40, *v/v*); mp = 93–95 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.73 (d, *J* = 8.0 Hz, 2 H), 7.23 (d, *J* = 8.0 Hz, 2 H), 2.76 (dd, *J* = 8.5, 5.5 Hz, 1 H), 2.38–2.36 (m, 2 H), 1.80–1.75 (ddd, *J* = 12.0, 9.0, 2.0 Hz, 1 H), 1.70–1.66 (m, 1 H), 1.64–1.52 (m, 3 H), 1.34 (s, 12 H), 1.29–1.27 (m, 2 H), 1.20–1.18 (m, 1 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 151.0, 134.8, 126.5, 83.6, 47.5, 42.8, 39.0, 36.8, 36.1, 30.6, 28.9, 24.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.5 ppm; IR: ν = 2948, 2870, 1610, 1399, 1390, 1359, 1320, 1272, 1144, 1090, 1018, 861 cm^{-1}; HRMS (ESI) m/z calc. for $C_{19}H_{27}BO_2$ [M+] 298.2104, found 298.2115.



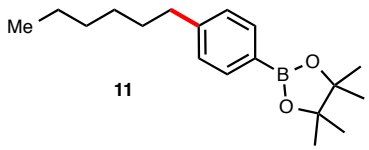
9

3-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl acetate (9): obtained as a light yellow oil (127 mg, 84%) by purification over silica (hexanes/EtOAc, 90:10 to 60:40, *v/v*); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.74 (d, *J* = 7.5 Hz, 2 H), 7.20 (d, *J* = 7.5 Hz, 2 H), 4.07 (t, *J* = 6.5 Hz, 2 H), 2.70 (t, *J* = 7.0 Hz, 2 H), 2.04 (s, 3 H), 1.98–1.94 (m, 2 H), 1.34 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 170.9, 144.5, 135.0, 127.7, 83.6, 63.4,

32.3, 30.0, 24.8, 20.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.4 ppm; IR: ν = 2978, 1738, 1611, 1398, 1390, 1358, 1320, 1270, 1235, 1166, 1143, 1108, 1089, 1038, 1024, 962, 859 cm^{-1}; HRMS (ESI) m/z calc. for $C_{17}H_{25}BO_4$ [M+] 327.1744, found 327.1751.

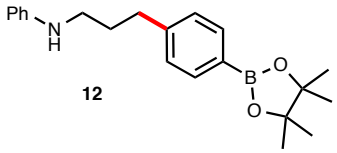


2-(4-(2-(Cyclohex-3-en-1-yl)ethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10): obtained as a colorless oil (120 mg, 77%) by purification over silica (hexanes/EtOAc, 90:10 to 60:40, *v/v*); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.75 (d, *J* = 7.5 Hz, 2 H), 7.22 (d, *J* = 7.5 Hz, 2 H), 5.67 (br s, 2 H), 2.68 (t, *J* = 7.5 Hz, 2 H), 2.15 (d, *J* = 17.0 Hz, 1 H), 2.05 (m, 2 H), 1.81–1.78 (m, 1 H), 1.74–1.69 (m, 1 H), 1.64–1.59 (m, 3 H), 1.35 (s, 12 H), 1.30–1.28 (m, 1 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.4, 134.9, 127.8, 127.0, 126.4, 83.6, 38.3, 33.5, 33.0, 31.8, 28.8, 25.1, 24.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.8 ppm; IR: ν = 2978, 2915, 2855, 1611, 1518, 1436, 1398, 1389, 1357, 1319, 1271, 1214, 1143, 1089, 1022, 963, 860 cm^{-1}; HRMS (ESI) m/z calc. for $C_{20}H_{29}BO_2$ [M+] 312.2261, found 312.2267.



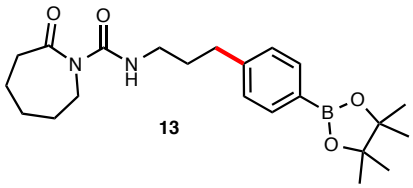
2-(4-Hexylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11): obtained as a colorless oil (141 mg, 98%) by purification over a short plug of silica (hexanes/EtOAc, 95:5, *v/v*); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.76 (d, *J* = 7.4 Hz, 2 H), 7.22 (d, *J* = 7.4 Hz, 2 H), 2.64 (t, *J* = 8.0 Hz, 2 H), 1.68–1.60 (m, 2 H), 1.42–1.28 (m, 18 H), 0.93–0.88 (m, 3 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.3, 134.7, 127.8, 83.5, 36.1, 31.7, 31.2, 28.9, 24.7, 22.5, 14.0 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.8 ppm; IR: ν = 2977, 2957, 2927, 2857, 1611,

1466, 1398, 1357, 1318, 1271, 1214, 1143, 1110, 1088, 1021, 962, 859 cm^{-1}; HRMS (CI) m/z calc. for $C_{18}H_{30}BO_2$ $[M + H]^+$ 289.2339, found 289.2339.



12

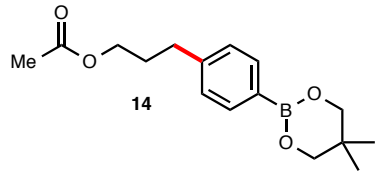
***N*-(3-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)aniline (12):** obtained as an off white solid (159 mg, 86%) by purification over a short plug of silica (hexanes/CH_2Cl_2, 50:50, *v/v*); mp = 105–106 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.74 (d, *J* = 7.7 Hz, 2 H), 7.20 (d, *J* = 7.7 Hz, 2 H), 7.17–7.13 (m, 2 H), 6.67 (t, *J* = 7.6 Hz, 1 H), 6.56 (d, *J* = 7.9 Hz, 2 H), 3.60 (br s , 1 H), 3.11 (t, *J* = 7.2 Hz, 2 H), 2.72 (t, *J* = 7.2 Hz, 2 H), 1.92 (tt, *J* = 7.2, 7.2 Hz, 2 H), 1.33 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 148.3, 145.0, 134.9, 129.2, 127.8, 117.2, 112.7, 83.6, 43.3, 33.5, 30.9, 24.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.5 ppm; IR: ν = 3368, 1604, 1512, 1473, 1395, 1355, 1315, 1271, 1258, 1178, 1139, 1087, 1024, 856, 824, 755 cm^{-1}; HRMS (ESI) m/z calc. for $C_{21}H_{28}BNO_2Na$ $[M + Na]^+$ 360.2111, found 360.2108



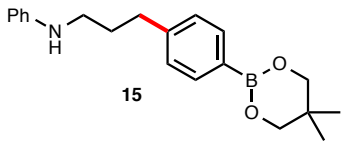
13

***N*-[(3-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)-2-aza-1-oxopentyl]caprolactam (13):** obtained as a colorless oil (164 mg, 82%) by purification over silica (hexanes/EtOAc, 100:0 to 20:80, *v/v*); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 9.31 (br s, 1 H), 7.73 (d, *J* = 7.6 Hz, 2 H), 7.20 (d, *J* = 7.6 Hz, 2 H), 4.00–3.96 (m, 2 H), 3.33–3.27 (m, 2 H), 2.72–2.66 (m, 4 H), 1.93–1.85 (m, 2 H), 1.80–1.66 (m, 6 H), 1.33 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 179.3, 154.8, 144.8, 134.9, 127.8, 83.5, 43.7, 40.0, 39.7, 33.4,

30.8, 29.0, 28.3, 24.8, 23.4 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.8 ppm; IR: ν = 1695, 1654, 1611, 1530, 1487, 1437, 1397, 1358, 1333, 1319, 1270, 1243, 1213, 1164, 1143, 1088, 967 cm^{-1}; HRMS (ESI) m/z calc. for $C_{22}H_{34}BN_2O_4$ $[M + H]^+$ 401.2612, found 401.2617.

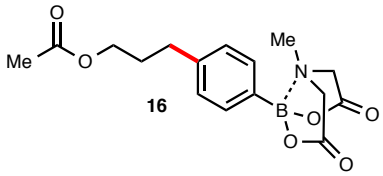


3-(4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)propyl Acetate (14): obtained as a white solid (114 mg, 79%) by purification over a short plug of silica (hexanes/EtOAc, 95:5, *v/v*); mp = 38–40 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.72 (d, *J* = 7.4 Hz, 2 H), 7.18 (d, *J* = 7.4 Hz, 2 H), 4.08 (t, *J* = 6.7 Hz, 2 H), 3.75 (s, 4 H), 2.69 (t, *J* = 7.6 Hz, 2 H), 2.04 (s, 3 H), 1.98–1.93 (m, 2 H), 1.01 (s, 6 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 171.0, 143.8, 134.0, 127.6, 72.2, 63.8, 32.3, 31.8, 30.0, 21.8, 20.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 26.7 ppm; IR: ν = 2959, 1737, 1611, 1477, 1420, 1377, 1367, 1343, 1314, 1306, 1241, 1183, 1131, 1037, 1021, 840, 812 cm^{-1}; HRMS (ESI) m/z calc. for $C_{16}H_{24}BO_4$ $[M + H]^+$ 291.1768, found 291.1766.

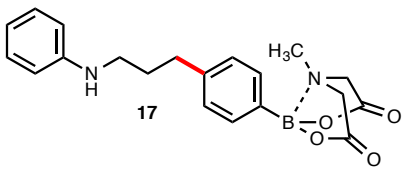


***N*-(3-(4-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)propyl)aniline (15):** obtained as a white solid (129 mg, 80%) by purification over a short plug of silica (hexanes/EtOAc, 90:10, *v/v*); mp = 107–109 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.73 (d, *J* = 7.5 Hz, 2 H), 7.18 (d, *J* = 7.5 Hz, 2 H), 7.14 (t, *J* = 7.8 Hz, 2 H), 6.67 (t, *J* = 7.8 Hz, 1 H), 6.55 (d, *J* = 7.8 Hz, 2 H), 3.74 (s, 4 H), 3.58 (br s, 1 H), 3.11 (t, *J* = 6.6 Hz, 2 H), 2.72 (t, *J* = 7.6 Hz, 2 H), 1.96–1.88 (m, 2 H), 1.00 (s, 6 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 148.3, 144.3, 134.0,

129.2, 127.7, 117.1, 112.7, 72.3, 43.4, 33.5, 31.9, 30.9, 21.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 26.4 ppm; IR: ν = 1601, 1506, 1477, 1422, 1378, 1342, 1302, 1273, 1250, 1177, 1127, 815, 746, 706 cm^{-1}; HRMS (ESI) m/z calc. for $C_{20}H_{27}BNO_2$ $[M + H]^+$ 324.2135, found 324.2127.

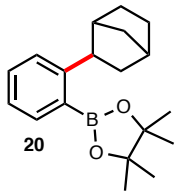


3-(4-(6-Methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)phenyl)propyl Acetate (16): obtained as colorless crystals. Crystallized from MeCN in Et_2O (88 mg, 53%). Bmida **16** decomposed on silica gel using EtOAc/hexanes as the eluent, but other eluents were not examined further after this initial failed attempt. **16** was prone to crystallization and thus this method of purification seemed ideal; mp = 164–165 °C; ^{1}H NMR (d_6-DMSO, 500.4 MHz): δ 7.36 (d, *J* = 8.0 Hz, 2 H), 7.20 (d, *J* = 8.0 Hz, 2 H), 4.32 (d, *J* = 17.0 Hz, 2 H), 4.09 (d, *J* = 17.0 Hz, 2 H), 3.99 (t, *J* = 6.5 Hz, 2 H), 2.64 (t, *J* = 7.5 Hz, 2 H), 2.50 (s, 3 H), 2.00 (s, 3 H), 1.88 (dt, *J* = 7.5, 6.5 Hz, 2 H) ppm; ^{13}C {^{1}H} NMR (d_6-DMSO, 125.8 MHz): δ 170.4, 169.3, 141.8, 132.5, 127.7, 63.2, 63.7, 47.5, 31.3, 29.6, 20.7 ppm; ^{11}B NMR (d_6-DMSO, 128.4 MHz): δ 11.8 ppm; IR: ν = 3007, 2990, 1759, 1738, 1611, 1454, 1404, 1389, 1366, 1336, 1288, 1229, 1202, 1190, 1034, 989, 889, 863 cm^{-1}; HRMS (ESI) m/z calc. for $C_{16}H_{20}BNNaO_6$ [M+Na] 356.1281, found 356.1285.



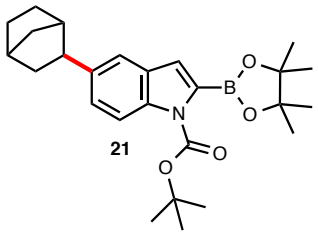
6-Methyl-2-(4-(3-(phenylamino)propyl)phenyl)-1,3,6,2-dioxazaborocane-4,8-dione (17): obtained as a light tan oil (130 mg, 71%) by purification over silica (MeCN/EtOAc, 15:85,

v/v); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.38 (d, *J* = 8.0 Hz, 2 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 7.13 (t, *J* = 7.5 Hz, 2 H), 6.66 (t, *J* = 7.5 Hz, 1 H), 6.55 (d, *J* = 7.5 Hz, 2 H), 4.14 (d, *J* = 17.0 Hz, 2 H), 3.75 (d, *J* = 17.0 Hz, 2 H), 3.09 (t, *J* = 7.0 Hz, 2 H), 2.68 (t, *J* = 7.0 Hz, 2 H), 2.41 (s, 3 H), 1.90 (tt, *J* = 7.0, 7.0 Hz, 2 H), 1.27 (m, 1 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 168.9, 148.3, 143.3, 132.4, 129.2, 128.3, 117.1, 112.7, 61.7, 47.7, 43.3, 33.2, 30.8, 29.6 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 11.1 ppm; IR: ν = 1760, 1602, 1506, 1334, 1289, 1254, 1229, 1202, 1188, 1036, 1024, 989, 907, 888, 863, 826 cm^{-1}; HRMS (ESI) m/z calc. for $C_{20}H_{24}BN_2O_4$ [M+H] 367.1829, found 367.1826.



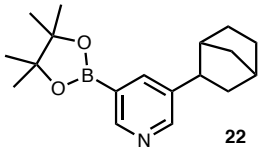
20

2-(2-(Bicyclo[2.2.1]heptan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (20): obtained as colorless crystals (140 mg, 94%) by purification over SiO_2 (hexanes/EtOAc, 100:0 to 20:80, *v/v*); mp = 58–59 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.78 (d, *J* = 8.5 Hz, 1 H), 7.41–7.29 (m, 2 H), 7.17 (t, *J* = 6.0 Hz, 1 H), 3.48 (t, *J* = 6.0 Hz, 1 H), 2.37 (m, 1 H), 2.28 (m, 1 H), 1.77-1.74 (m, 2 H), 1.59–1.52 (m, 4 H), 1.38 (s, 12 H), 1.16 (d, *J* = 6.0 Hz, 1 H), 0.90 (m, 1 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 153.3, 136.0, 130.5, 124.7, 124.5, 83.3, 45.5, 44.4, 38.3, 37.0, 35.9, 30.4, 29.1, 24.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.1 ppm; IR: ν = 2952, 2925, 2869, 1456, 1443, 1379, 1371, 1344, 1309, 1273, 1256, 1145, 1108, 1068, 1054, 862 cm^{-1}; HRMS (ESI) m/z calc. for $C_{19}H_{27}BO_2$ [M+] 298.2104, found 298.2104.



21

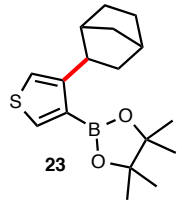
***tert*-Butyl 5-(Bicyclo[2.2.1]heptan-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-1-carboxylate (21)**: obtained as a colorless oil (120 mg, 55%) by purification over SiO_2 (hexanes/EtOAc, 100:0 to 20:80, *v/v*); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.83 (d, *J* = 9.0 Hz, 1 H), 7.36 (s, 1 H), 7.15 (dd, *J* = 9.0, 1.5 Hz, 1 H), 6.80 (s, 1 H), 2.84–2.81 (m, 1 H), 2.40 (m, 1 H), 2.37 (m, 1 H), 1.83–1.78 (m, 1 H), 1.73–1.71 (m, 2 H), 1.68 (s, 9 H), 1.63-1.57 (m, 3 H), 1.40 (s, 12 H), 1.30–1.28 (m, 1 H), 1.23–1.19 (m, 1 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 151.1, 141.7, 134.8, 131.2, 124.5, 118.5, 115.9, 114.5, 84.0, 83.8, 47.1, 43.2, 39.4, 36.8, 36.0, 30.6, 28.9, 28.2, 24.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.1 ppm; IR: ν = 2951, 1721, 1439, 1369, 1349, 1319, 1271, 1238, 1216, 1164, 1133, 1060, 966, 909, 851, 835 cm^{-1}; HRMS (ESI) m/z calc. for $C_{26}H_{37}BNO_4$ [M+H] 438.2816, found 438.2810.



22

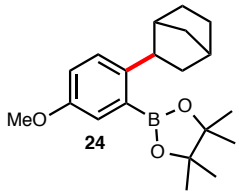
3-(Bicyclo[2.2.1]heptan-2-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (22): The crude reaction mixture was diluted with Et_2O (15 mL), washed with H_2O (5 x 5 mL), brine (10 mL), and the combined organic layers were dried ($MgSO_4$), filtered, and concentrated to a light brown oil which was >95% pure by ^{1}H NMR (contains residual DMF and trace dtbbpy ligand). This material was used without further purification: (148 mg, 99% (crude)); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.72 (d, *J* = 1.5 Hz, 1 H), 8.52 (d, *J* = 2.0 Hz, 1 H), 7.87 (s, 1 H), 2.73 (m, 1 H), 2.36 (m, 2 H), 1.79–1.75 (m, 1 H), 1.61–1.50 (m, 4 H), 1.34 (s, 12 H), 1.22–1.20 (m, 3 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 152.4, 151.1, 141.5,

140.5, 84.0, 44.9, 42.7, 38.5, 36.8, 36.0, 30.4, 28.7, 24.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.7 ppm. The extent to which this compound was prone to decomposition precluded acquisition of the remaining analytical data.



23

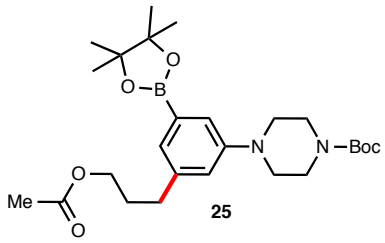
2-(4-(Bicyclo[2.2.1]heptan-2-yl)thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (23): obtained as colorless crystals (147 mg, 98%) by purification over SiO_2 (hexanes/EtOAc, 100:0 to 20:80, *v/v*); mp = 70–71 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.87 (d, *J* = 2.5 Hz, 1 H), 6.87 (d, *J* = 2.5 Hz, 1 H), 3.24 (dd, *J* = 8.0, 6.0 Hz, 1 H), 2.32 (m, 1 H), 2.22 (m, 1 H), 1.72–1.34 (m, 6 H), 1.33 (s, 12 H), 1.30–1.29 (m, 1 H), 1.09 (d, *J* = 9.5 Hz, 1 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 153.3, 137.7, 118.3, 83.2, 44.2, 42.6, 37.9, 36.9, 35.4, 29.8, 29.0, 24.9, 24.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 28.6 ppm; IR: ν = 2948, 1517, 1444, 1372, 1340, 1307, 1287, 1260, 1209, 1164, 1140, 1111, 1027, 962, 863, 853, 805 cm^{-1}; HRMS (CI) m/z calc. for $C_{17}H_{25}BO_2S$ [M+] 304.1668, found 304.1678.



24

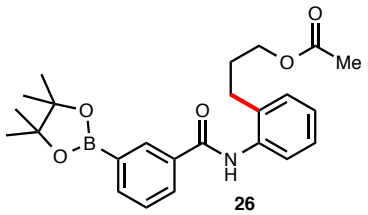
2-(2-(Bicyclo[2.2.1]heptan-2-yl)-5-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (24): obtained as colorless crystals (156 mg, 95%) by purification over SiO_2 (hexanes/EtOAc, 100:0 to 20:80, *v/v*); mp = 62–63 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.31 (d, *J* = 2.5 Hz, 1 H), 7.20 (d, *J* = 8.5 Hz, 1 H), 6.90 (dd, *J* = 8.5, 2.5 Hz, 1 H), 3.80 (s, 3 H),

3.38 (dd, J = 14.5, 4.0 Hz, 1 H), 2.33 (m, 1 H), 2.19 (m, 1 H), 1.71–1.67 (m, 2 H), 1.59–1.45 (m, 4 H), 1.36 (s, 12 H), 1.32–1.26 (m, 1 H), 1.10 (d, J = 10.0 Hz, 1 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 156.5, 145.6, 125.9, 120.7, 116.1, 83.4, 55.3, 44.8, 44.6, 38.4, 37.0, 35.8, 30.3, 29.1, 24.9, 24.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.9 ppm; IR: ν = 2950, 2869, 1572, 1492, 1466, 1444, 1413, 1390, 1371, 1335, 1308, 1274, 1256, 1236, 1220, 1145, 1059 cm^{-1}; HRMS (ESI) m/z calc. for $C_{20}H_{29}BO_3$ [M+] 328.2210, found 328.2220.



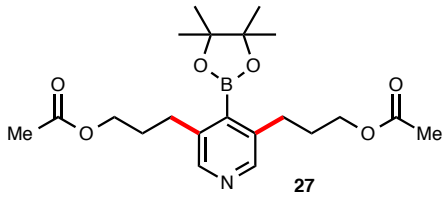
25

***tert*-Butyl 4-(3-(3-Acetoxypropyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)piperazine-1-carboxylate (25)**: obtained as a colorless oil (200 mg, 82%) by purification over SiO_2 (hexanes/EtOAc, 100:0 to 20:80, *v/v*); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.19 (d, J = 2.0 Hz, 1 H), 7.16 (s, 1 H), 6.84 (s, 1 H), 4.05 (t, J = 7.0 Hz, 2 H), 3.56–3.54 (m, 4 H), 3.12 (m, 4 H), 2.63 (t, J = 8.0 Hz, 2 H), 2.02 (s, 3 H), 1.92 (dt, J = 8.0, 7.0 Hz, 2 H), 1.46 (s, 9 H), 1.31 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 171.0, 154.6, 150.9, 141.5, 126.8, 120.5, 119.9, 83.6, 79.7, 63.9, 49.5, 43.6 (br s), 32.3, 30.2, 28.3, 24.7, 20.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.2 ppm; IR: ν = 2995, 2992, 17.38, 1693, 1461, 1425, 1379, 1366, 1317, 1296, 1238, 1166, 1144, 1123, 1039, 998, 968, 910, 853 cm^{-1}; HRMS (ESI) m/z calc. for $C_{26}H_{42}BN_2O_6$ [M+H] 489.3136, found 489.3136.



26

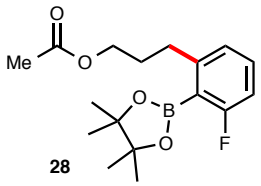
3-(2-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzamido)phenyl)propyl Acetate (26): obtained as a colorless oil (113 mg, 54%) by purification over SiO_2 (hexanes/EtOAc, 100:0 to 20:80, *v/v*); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.27 (s, 1 H), 8.01 (d, *J* = 8.0 Hz, 1 H), 7.97 (d, *J* = 7.0 Hz, 1 H), 7.93 (s, 1 H), 7.68 (d, *J* = 7.5 Hz, 1 H), 7.48 (t, *J* = 7.5 Hz, 1 H), 7.24-7.22 (m, 2 H), 7.19-7.15 (m, 1 H), 4.07 (t, *J* = 6.0 Hz, 2 H), 2.71 (t, *J* = 7.5 Hz, 2 H), 1.94 (dt, *J* = 7.5, 6.0 Hz, 2 H), 1.89 (s, 3 H), 1.35 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 170.9, 166.1, 138.1, 135.2, 134.2, 134.1, 132.6, 130.4, 129.5, 128.2, 127.0, 126.1, 125.2, 84.1, 63.5, 28.8, 27.7, 24.8, 20.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 29.9 ppm; IR: ν = 2995, 2993, 2885, 1737, 1676, 1600, 1535, 1500, 1484, 1441, 1418, 1388, 1359, 1317, 1235, 1166, 1143, 1034, 1001, 965, 861 cm^{-1}; HRMS (ESI) m/z calc. for $C_{24}H_{30}BNNaO_5$ [M+Na] 446.2115, found 446.2115.



27

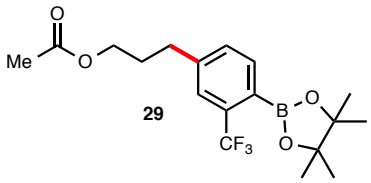
(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine-3,5-diyl)bis(propane-3,1-diyl) Diacetate (27): obtained as a light yellow oil (93 mg, 46%) by purification over SiO_2 (hexanes/EtOAc, 100:0 to 20:80, *v/v*); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.21 (s, 2 H), 4.04 (t, *J* = 6.5 Hz, 4 H), 2.67 (dd, *J* = 10.0, 6.0 Hz, 4 H), 1.99 (s, 6 H), 1.89–1.86 (m, 4 H), 1.35 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 170.8, 147.2, 139.7, 84.4, 63.7, 31.1, 30.0, 24.8, 20.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.0 ppm; IR: ν = 2979, 1736, 1468,

1415, 1366, 1341, 1320, 1264, 1233, 1168, 1141, 1087, 1039, 962, 907, 855 cm^{-1}; HRMS (ESI) m/z calc. for $C_{21}H_{33}BNO_6$ [M+H] 406.2401, found 406.2406.



28

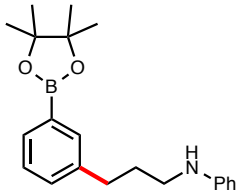
3-(3-Fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl Acetate (28): obtained as a colorless oil (131 mg, 82%) by purification over SiO_2 (hexanes/EtOAc, 100:0 to 20:80, *v/v*); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.26 (dd, *J* = 8.0, 6.0 Hz, 1 H), 6.93 (d, *J* = 7.5 Hz, 1 H), 6.84 (t, *J* = 7.5 Hz, 1 H), 4.09 (t, *J* = 6.5 Hz, 2 H), 2.80 (m, 2 H), 2.05 (s, 3 H), 1.92 (m, 2 H), 1.38 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 171.1, 166.6 (d, $^2J_{CF}$ = 250 Hz), 148.5 (d, $^3J_{CF}$ = 7.5 Hz), 131.5 (d, $^3J_{CF}$ = 9.4 Hz), 124.6 (d, $^2J_{CF}$ = 25.0 Hz), 112.5 (d, $^2J_{CF}$ = 24.3 Hz), 84.0, 64.0, 32.5, 31.3, 24.8, 20.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 28.6 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): –103.7 ppm; IR: ν = 2979, 1738, 1612, 1567, 1452, 1372, 1340, 1317, 1230, 1166, 1142, 1102, 1084, 1037, 963, 856, 829 cm^{-1}; HRMS (ESI) m/z calc. for $C_{17}H_{24}BFNaO_4$ [M+Na] 345.1649, found 345.1661.



29

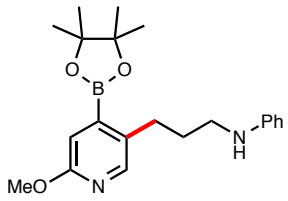
3-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trifluoromethyl)phenyl)propyl Acetate (29): obtained as a colorless oil (120 mg, 66%) by purification over SiO_2 (hexanes/EtOAc, 100:0 to 20:80, *v/v*); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.90 (br s, 1 H), 7.80 (br s, 1 H), 7.51 (s, 1 H), 4.09 (t, *J* = 6.0 Hz, 2 H), 2.77–2.74 (m, 2 H), 2.05 (s, 3 H), 2.00-1.97 (m, 2 H), 1.35 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 171.0, 141.4, 138.0,

130.2 (q, $^{2}J_{CF}$ = 33 Hz), 129.1 (q, $^{3}J_{CF}$ = 3.6 Hz), 127.6 (q, $^{3}J_{CF}$ = 3.6 Hz), 124.3 (q, $^{1}J_{CF}$ = 270 Hz), 84.3, 63.7, 32.0, 30.1, 24.8, 20.9 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.1 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): –62.5 ppm; IR: ν = 1741, 1472, 1412, 1390, 1368, 1329, 1298, 1269, 1235, 1202, 1163, 1143, 1121, 1041, 966, 901, 871 cm^{-1}; HRMS (CI) m/z calc. for $C_{18}H_{25}BF_3O_4$ [M+H] 373.1798, found 373.1808.



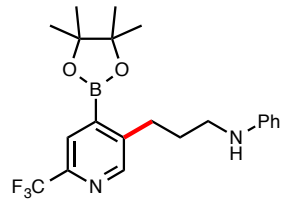
30

***N*-(3-(3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)aniline (30):** obtained as a white solid (165 mg, 98%) by purification over a short plug of silica (hexanes/EtOAc, 90:10, *v/v*); mp = 103–105 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.67–7.63 (m, 2 H), 7.31–7.27 (m, 2 H), 7.15 (t, *J* = 7.9 Hz, 2 H), 6.67 (t, *J* = 7.9 Hz, 1 H), 6.57 (d, *J* = 7.9 Hz, 2 H), 3.60 (br s, 1 H), 3.13 (t, *J* = 6.9 Hz, 2 H), 2.76–2.70 (m, 2 H), 1.97–1.91 (m, 2 H), 1.34 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 148.3, 140.9, 134.6, 132.4, 131.4, 129.2, 127.8, 117.1, 112.7, 83.7, 43.5, 33.3, 31.1, 24.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 31.3 ppm; IR: ν = 1602, 1512, 1479, 1423, 1390, 1380, 1359, 1319, 1270, 1260, 1202, 1142, 1100, 1085, 962, 849 cm^{-1}; HRMS (ESI) m/z calc. for $C_{21}H_{29}BNO_2$ $[M + H]^+$ 338.2291, found 338.2306.



31

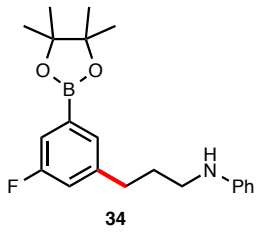
***N*-(3-(6-Methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-yl)propyl)aniline (31)**: obtained as an off white solid (159 mg, 86%) by purification over neutral alumina (CH_2Cl_2/EtOAc, 100:0 to 90:10, *v/v*); mp = 100–102 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.99 (s, 1 H), 7.16 (t, *J* = 7.9 Hz, 2 H), 7.12 (s, 1 H), 6.68 (t, *J* = 7.9 Hz, 1 H), 6.60 (d, *J* = 8.0 Hz, 2 H), 3.90 (s, 3 H), 3.75 (br s, 1 H), 3.15 (t, *J* = 6.6 Hz, 2 H), 2.85–2.80 (m, 2 H), 1.89–1.82 (m, 2 H), 1.35 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 182.4, 148.5, 146.6, 134.5, 129.1, 117.1, 116.9, 112.3, 84.2, 53.2, 43.5, 32.7, 29.5, 24.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 29.5 ppm; IR: ν = 1602, 1513, 1476, 1436, 1377, 1336, 1263, 1203, 1170, 1142, 1113, 1071, 1035, 890, 852, 755 751 cm^{-1}; HRMS (ESI) m/z calc. for $C_{21}H_{30}BN_2O_3$ $[M + H]^+$ 369.2344, found 369.2355.



33

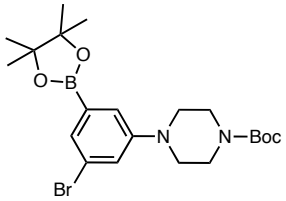
***N*-(3-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trifluoromethyl)pyridin-2-yl)propyl)aniline (33)**: obtained as a light yellow oil (154 mg, 76%) by purification over a short plug of neutral alumina (CH_2Cl_2/EtOAc, 90:10, *v/v*); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.57 (s, 1 H), 7.99 (s, 1 H), 7.17 (t, *J* = 8.0 Hz, 2 H), 6.70 (t, *J* = 7.9 Hz, 1 H), 6.60 (d, *J* = 8.0 Hz, 2 H), 3.77 (br s, 1 H), 3.20 (t, *J* = 6.8 Hz, 2 H), 3.06–3.02 (m, 2 H), 1.94–1.88 (m, 2 H), 1.38 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 150.5, 148.2, 146.4, 129.2, 126.1, 117.2, 112.6, 85.8, 43.4, 32.4, 30.4, 24.8 ppm; ^{19}F NMR ($CDCl_3$, 470.8 MHz): δ –67.6 ppm;

^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.3 ppm; IR: ν = 1602, 1507, 1432, 1373, 1320, 1286, 1270, 1177, 1166, 1135, 1100, 1074, 963, 915, 885 cm^{-1}; HRMS (ESI) m/z calc. for $C_{21}H_{27}BF_3N_2O_2$ $[M + H]^+$ 407.2118, found 407.2107.



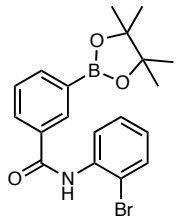
34

***N*-(3-(3-Fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)aniline (34)**: obtained as an off white solid (170 mg, 96%) by purification over a short plug of neutral alumina eluted with CH_2Cl_2; mp = 105–108 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.42 (s, 1 H), 7.32 (dd, *J* = 9.1, 2.8 Hz, 1 H), 7.16 (t, *J* = 7.9 Hz, 2 H), 7.00–6.95 (m, 1 H), 6.68 (t, *J* = 7.9 Hz, 1 H), 6.57 (d, *J* = 8.0 Hz, 2 H), 3.60 (br s, 1 H), 3.14 (t, *J* = 6.6 Hz, 2 H), 2.73 (t, *J* = 6.6 Hz, 2 H), 1.98–1.90 (m, 2 H), 1.34 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 162.6 (d, *J* = 242 Hz), 148.2, 143.6 (d, *J* = 7 Hz), 130.2, 129.2, 118.5 (d, *J* = 20 Hz), 118.0 (d, *J* = 21 Hz), 117.2, 112.7, 84.0, 43.3, 33.0, 30.9, 24.8 ppm; ^{19}F NMR ($CDCl_3$, 470.8 MHz): δ –114.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.3 ppm; IR: ν = 1602, 1587, 1512, 1480, 1425, 1364, 1326, 1303, 1261, 1237, 1141, 1104, 965, 934, 848, 751 cm^{-1}; HRMS (ESI) m/z calc. for $C_{21}H_{28}BFNO_2$ $[M + H]^+$ 356.2197, found 356.2198.

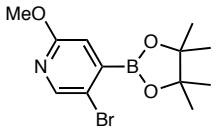


***tert*-Butyl 4-(3-Bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)piperazine-1-carboxylate (S1)**: Method A. Obtained as a tan solid (1.16 g, 96%, 2.6 mmol scale); mp =

105–106 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.41 (s, 1 H), 7.25 (d, *J* = 2.0 Hz, 1 H), 7.10 (d, *J* = 2.0 Hz, 1 H), 3.54 (br t, *J* = 5.0 Hz, 4 H), 3.14 (m, 4 H), 1.47 (s, 9 H), 1.32 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 154.6, 151.9, 128.7, 123.1, 121.8, 121.0, 118.4, 84.0, 79.9, 49.0, 28.4, 24.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.4 ppm; IR: ν = 1692, 1420, 1380, 1363, 1319, 1286, 1264, 1278, 1231, 1165, 1143, 1125, 986, 968, 951, 908, 861 cm^{-1}; HRMS (ESI) m/z calc. for $C_{21}H_{32}BBrN_2NaO_4$ [M+Na] 489.1536, found 489.1546.

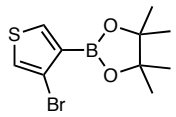


***N*-(2-Bromophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (S2)**: Method A. Obtained as a tan solid (1.06 g, 85%, 3.1 mmol scale); mp = 76–77 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.49 (dd, *J* = 8.0, 1.5 Hz, 1 H), 8.44 (s, 1 H), 8.36 (s, 1 H), 8.04–8.00 (m, 2 H), 7.57 (dd, *J* = 8.0, 1.0 Hz, 1 H), 7.52 (t, *J* = 8.0 Hz, 1 H), 7.36 (t, *J* = 7.5 Hz, 1 H), 7.01 (dd, *J* = 7.5, 1.5 Hz, 1 H), 1.36 (s, 12 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 165.4, 138.3, 135.8, 133.9, 133.0, 135.2, 129.9, 128.4, 128.3, 125.3, 122.1, 113.9, 84.1, 24.8 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 30.2 ppm; IR: ν = 2996, 1682, 1588, 1519, 1435, 1417, 1389, 1380, 1387, 1317, 1299, 1273, 1242, 1142, 909, 859, 751 cm^{-1}; HRMS (ESI) m/z calc. for $C_{19}H_{21}BBrNNaO_3$ [M+Na] 424.0696, found 424.0698.

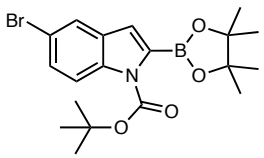


5-Bromo-2-methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (S3): Method A. Obtained as a white solid (777 mg, 82%, 3.0 mmol scale); mp = 53–54 °C; ^{1}H

NMR ($CDCl_3$, 500.4 MHz): δ 8.19 (s, 1 H), 6.93 (s, 1 H), 3.86 (s, 3 H), 1.34 (s, 12 H) ppm; ^{13}C {^1H} NMR ($CDCl_3$, 125.8 MHz): δ 162.5, 148.0, 117.8, 115.8, 84.8, 53.6, 24.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 28.3 ppm; IR: ν = 3015, 2998, 2992, 1527, 1439, 1402, 1375, 1321, 1300, 1273, 1259, 1208, 1166, 1140, 1110, 1015, 962, 892 cm^{-1}; HRMS (ESI) m/z calc. for $C_{12}H_{18}BBrNO_3$ [M+H] 314.0563, found 314.0561.



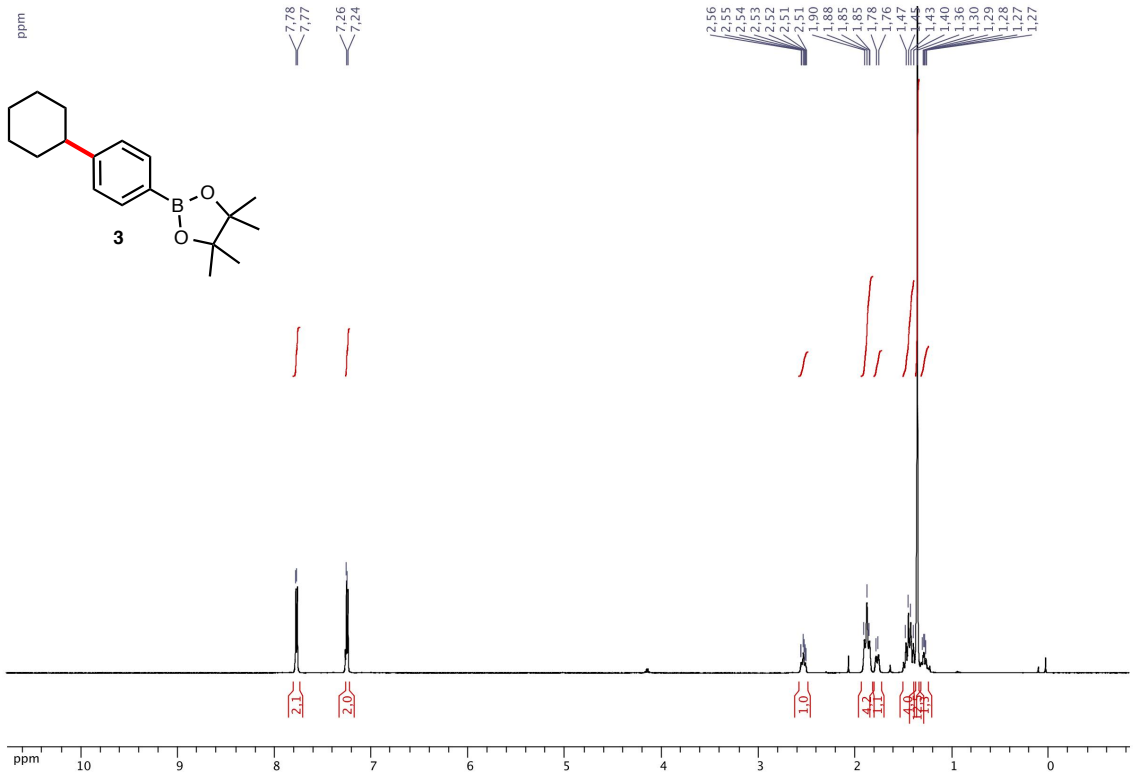
2-(4-Bromothiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (S4): Method A. Obtained as a white solid (685 mg, 99%, 2.4 mmol scale); mp = 81–82 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 7.82 (d, *J* = 3.0 Hz, 1 H), 7.25 (d, *J* = 3.0 Hz, 1 H), 1.34 (s, 12 H) ppm; ^{13}C {^1H} NMR ($CDCl_3$, 125.8 MHz): δ 137.7, 123.8, 115.1, 83.8, 24.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 28.5 ppm; IR: ν = 3008, 2998, 2992, 1493, 1410, 1372, 1353, 1316, 1282, 1264, 1212, 1139, 1108, 968, 938, 850, 821 cm^{-1}; HRMS (CI) m/z calc. for $C_{10}H_{14}BBrO_2S$ [M+] 287.9991, found 287.9992.



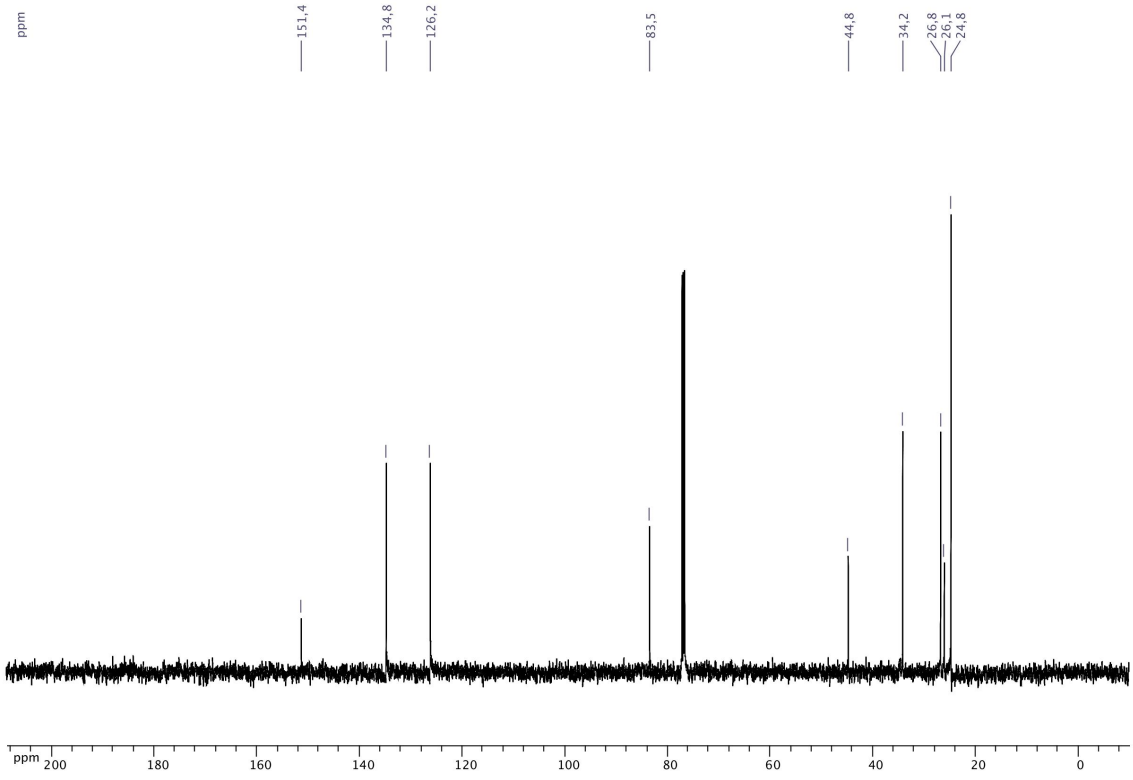
***tert*-Butyl 5-Bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-1-carboxylate (S5)**: Method A. Obtained as a tan solid (590 mg, 93%, 1.5 mmol scale); mp = 63–65 °C; ^1H NMR ($CDCl_3$, 500.4 MHz): δ 7.80 (d, *J* = 8.5 Hz, 1 H), 7.65 (d, *J* = 1.5 Hz, 1 H), 7.35 (dd, *J* = 8.5, 1.5 Hz, 1 H), 6.77 (s, 1 H), 1.68 (s, 9 H), 1.39 (s, 12 H) ppm; ^{13}C {^1H} NMR ($CDCl_3$, 125.8 MHz): δ 150.7, 135.2, 132.9, 129.2, 123.5, 116.3, 115.7, 114.7, 84.7, 84.3, 28.1, 24.7 ppm; ^{11}B NMR ($CDCl_3$, 128.4 MHz): δ 28.8 ppm; IR: ν = 2996, 2993, 1721,

1557, 1431, 1364, 1350, 1329, 1316, 1287, 1229, 1195, 1161, 1138, 1061, 1051, 964 cm^{-1}; HRMS (CI) m/z calc. for $C_{19}H_{25}BBrNO_4$ [M+] 421.1060, found 421.1049.

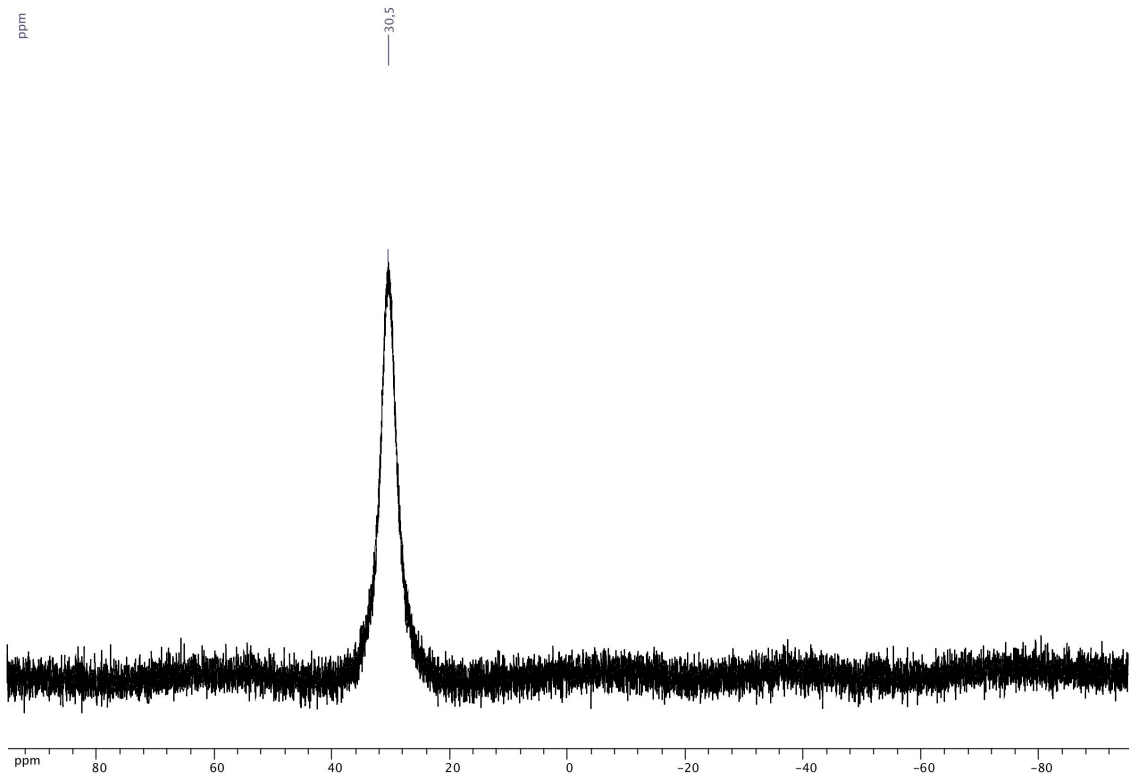
Spectral data



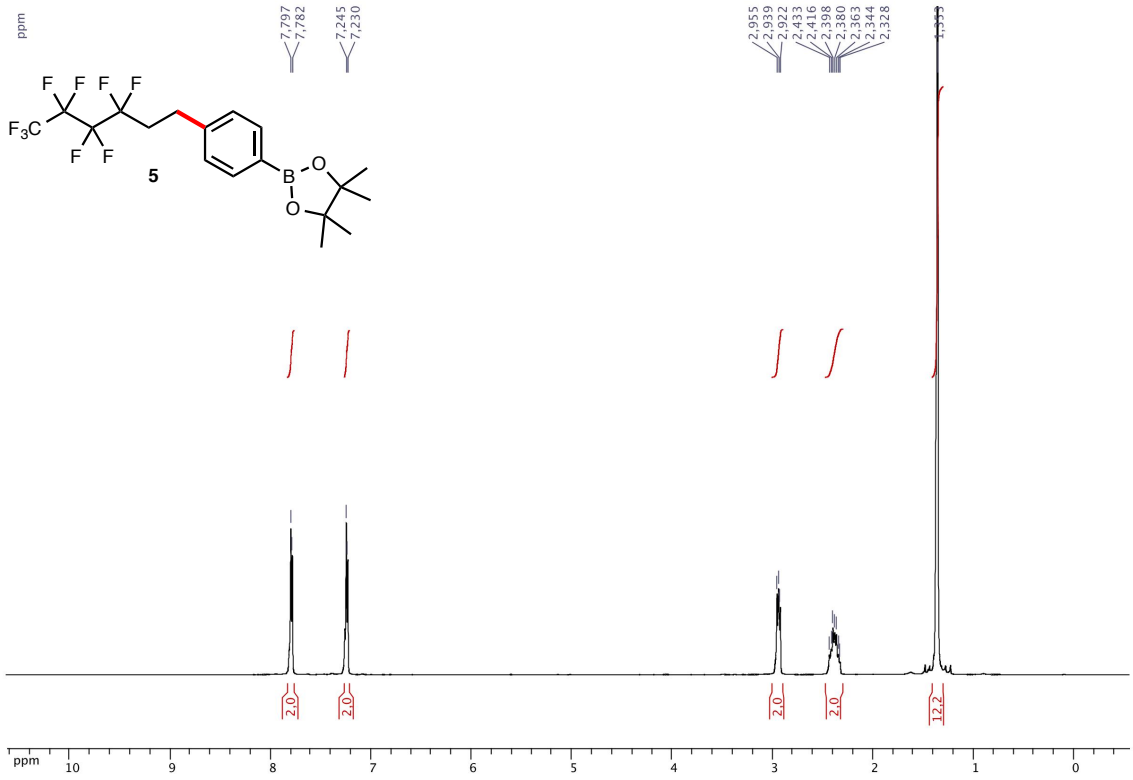
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(4-cyclohexylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**)



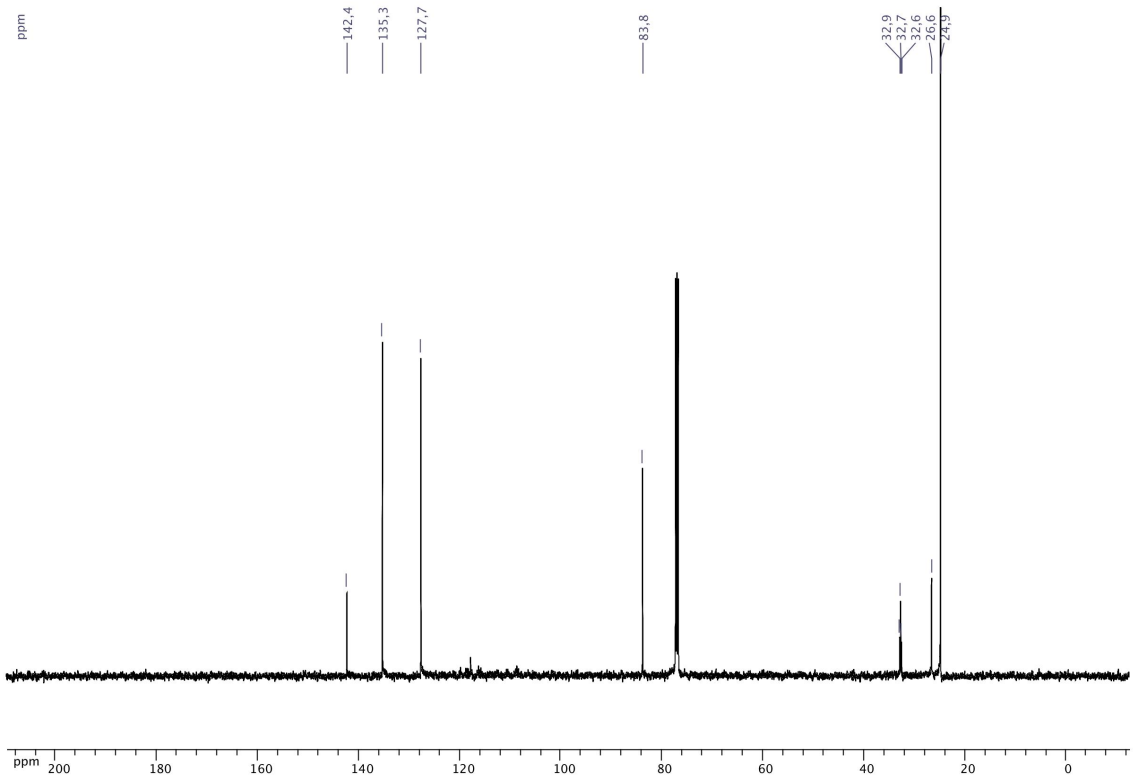
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(4-cyclohexylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**)



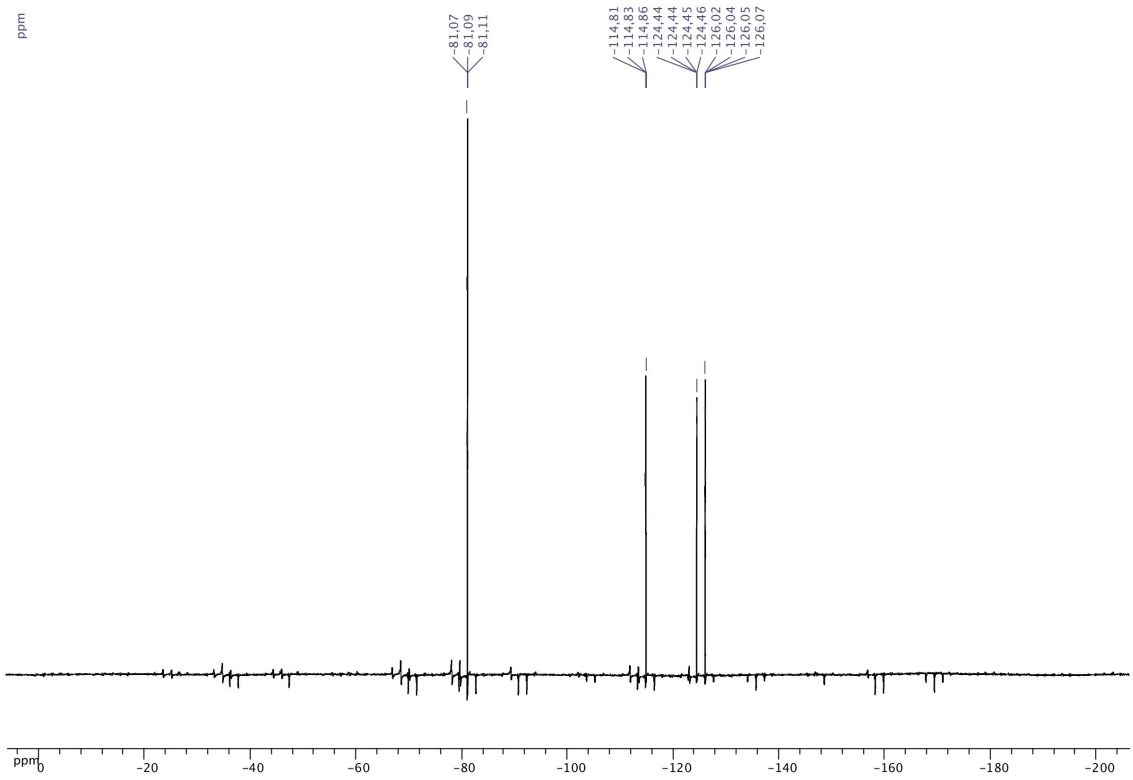
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 2-(4-cyclohexylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**)



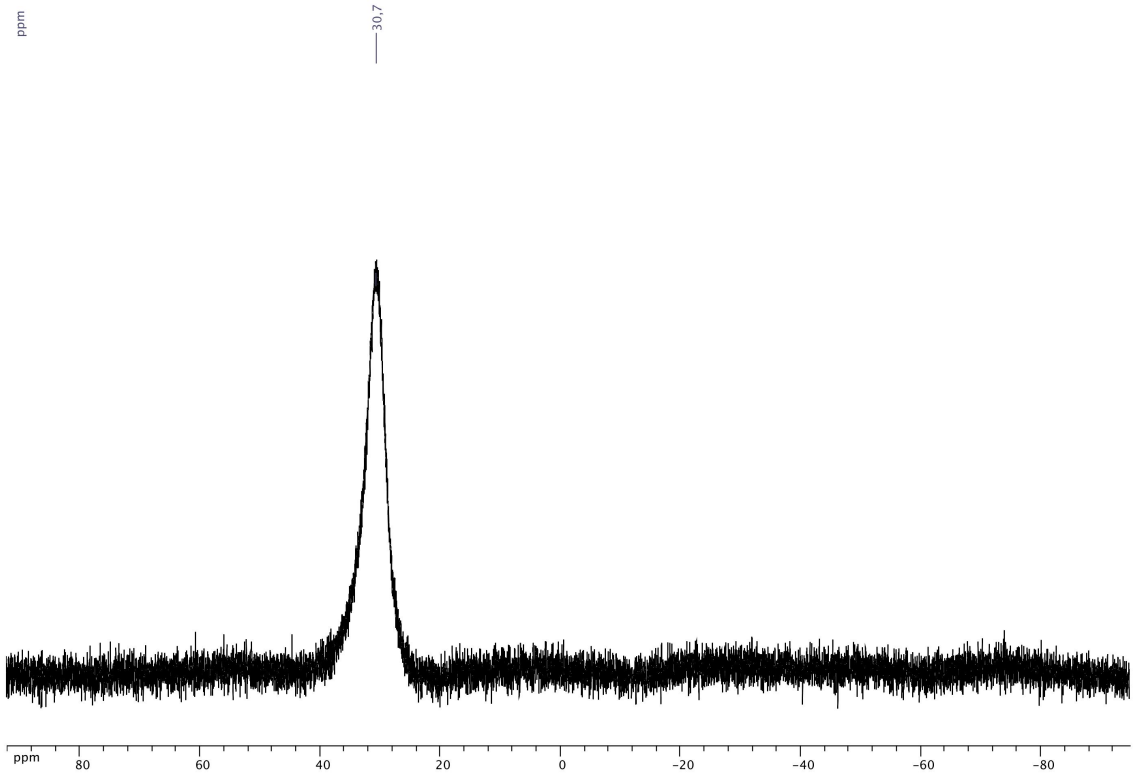
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 4,4,5,5-tetramethyl-2-(4-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)phenyl)-1,3,2-dioxaborolane (**5**)



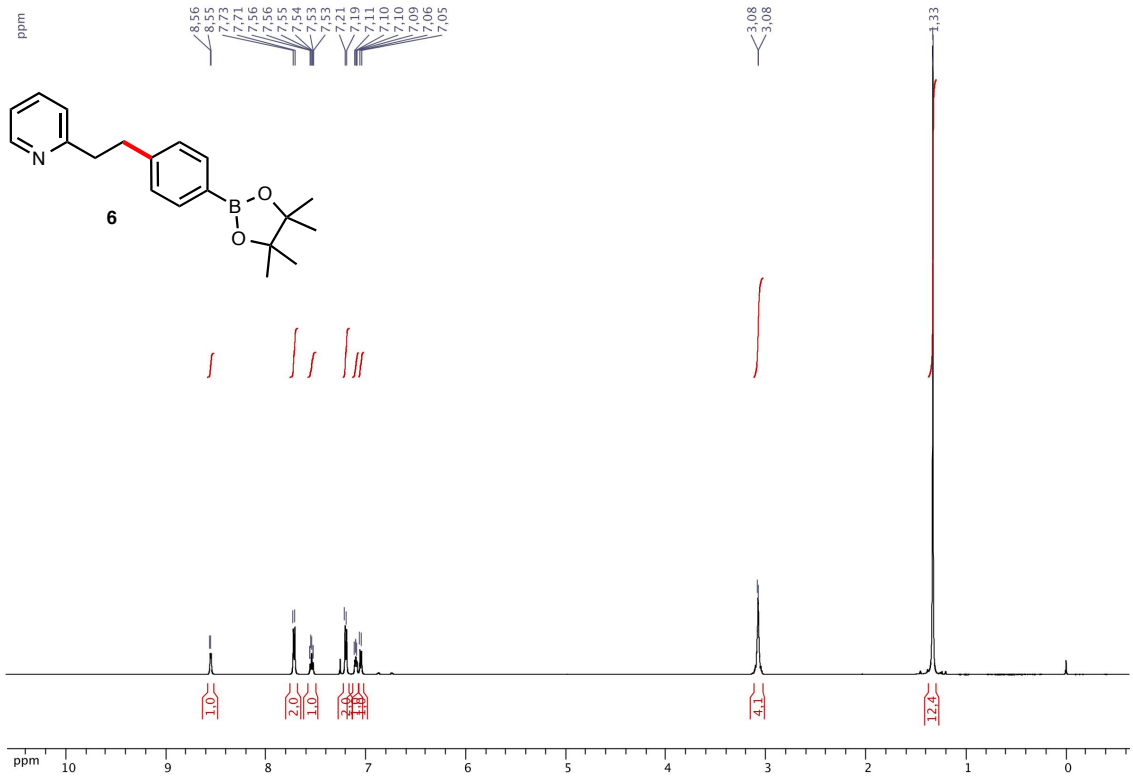
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 4,4,5,5-tetramethyl-2-(4-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)phenyl)-1,3,2-dioxaborolane (**5**)



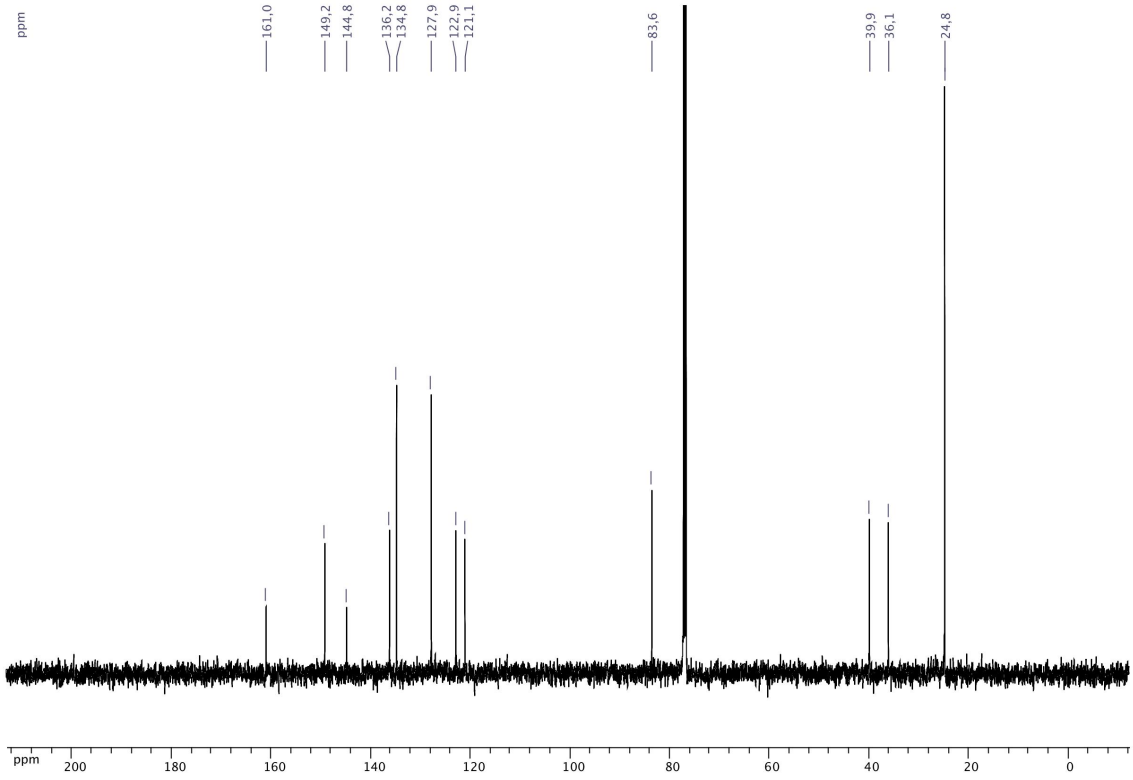
^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz) of 4,4,5,5-tetramethyl-2-(4-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)phenyl)-1,3,2-dioxaborolane (**5**)



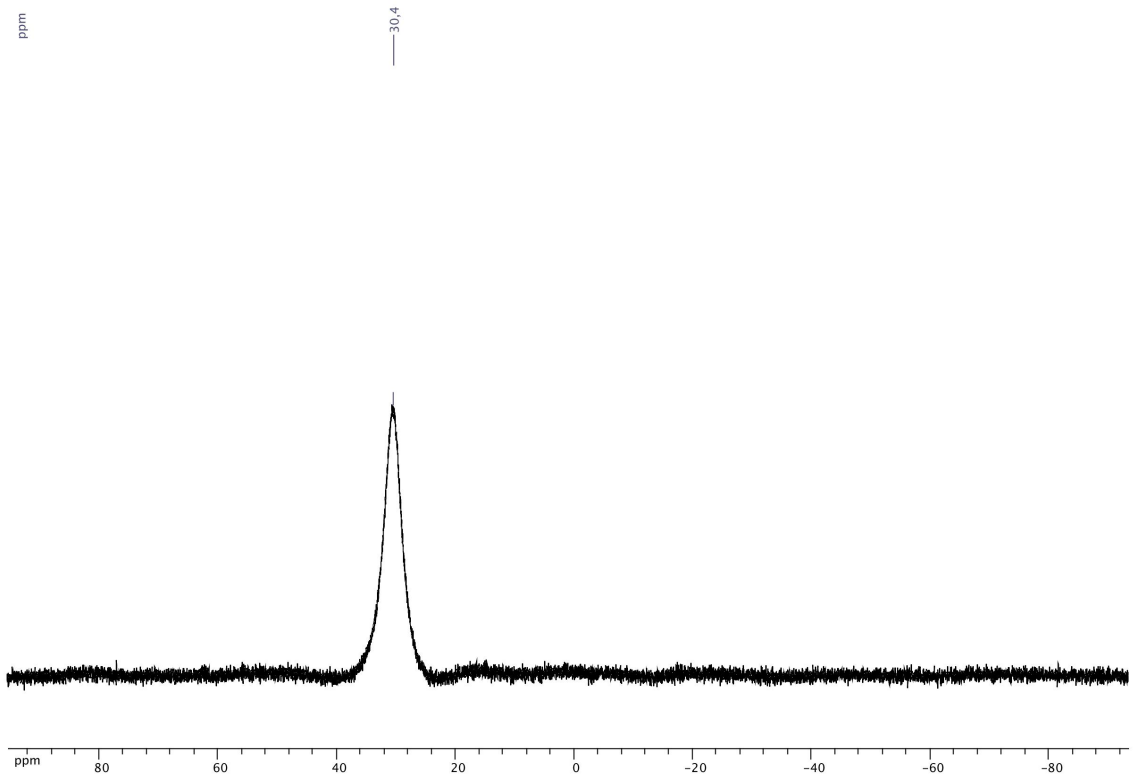
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 4,4,5,5-tetramethyl-2-(4-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)phenyl)-1,3,2-dioxaborolane (**5**)



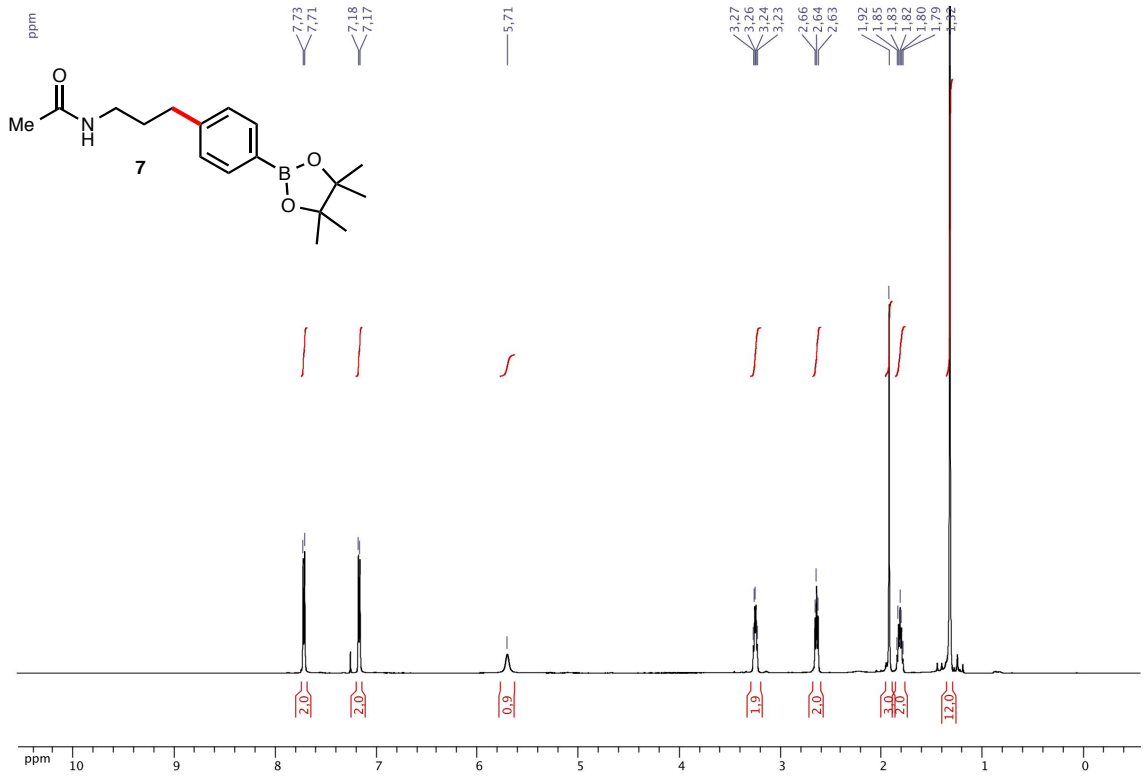
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenethyl)pyridine (**6**)



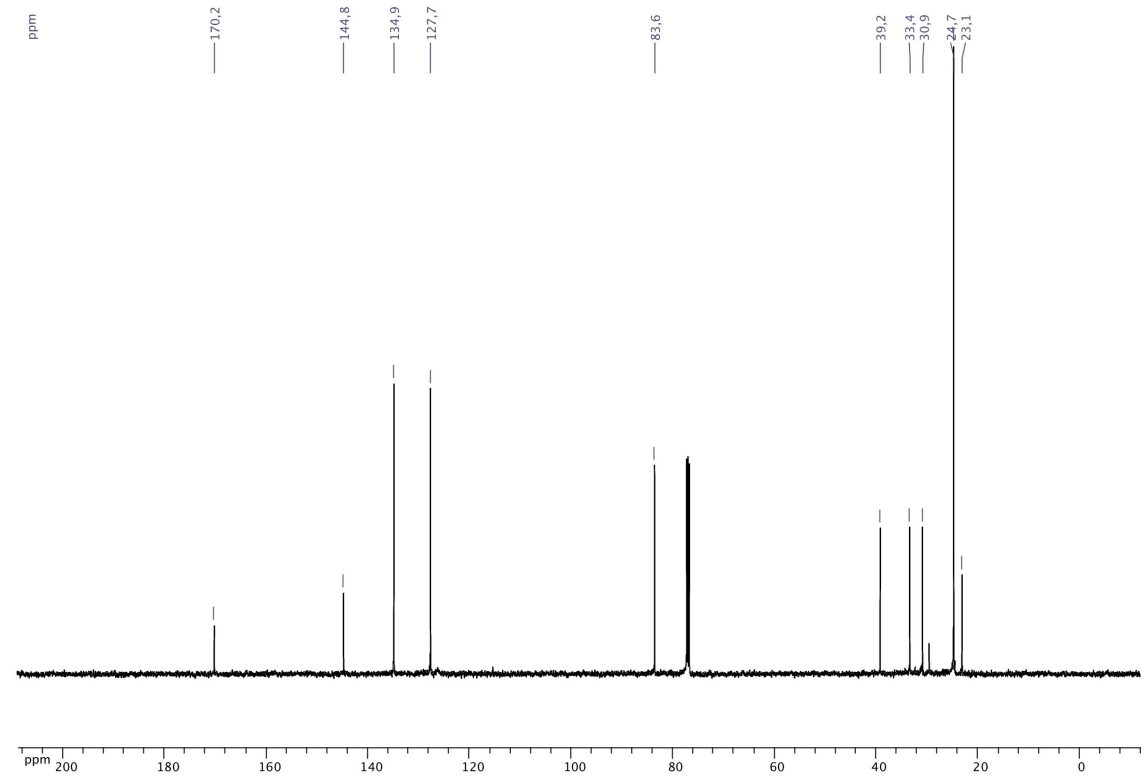
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenethyl)pyridine (**6**)



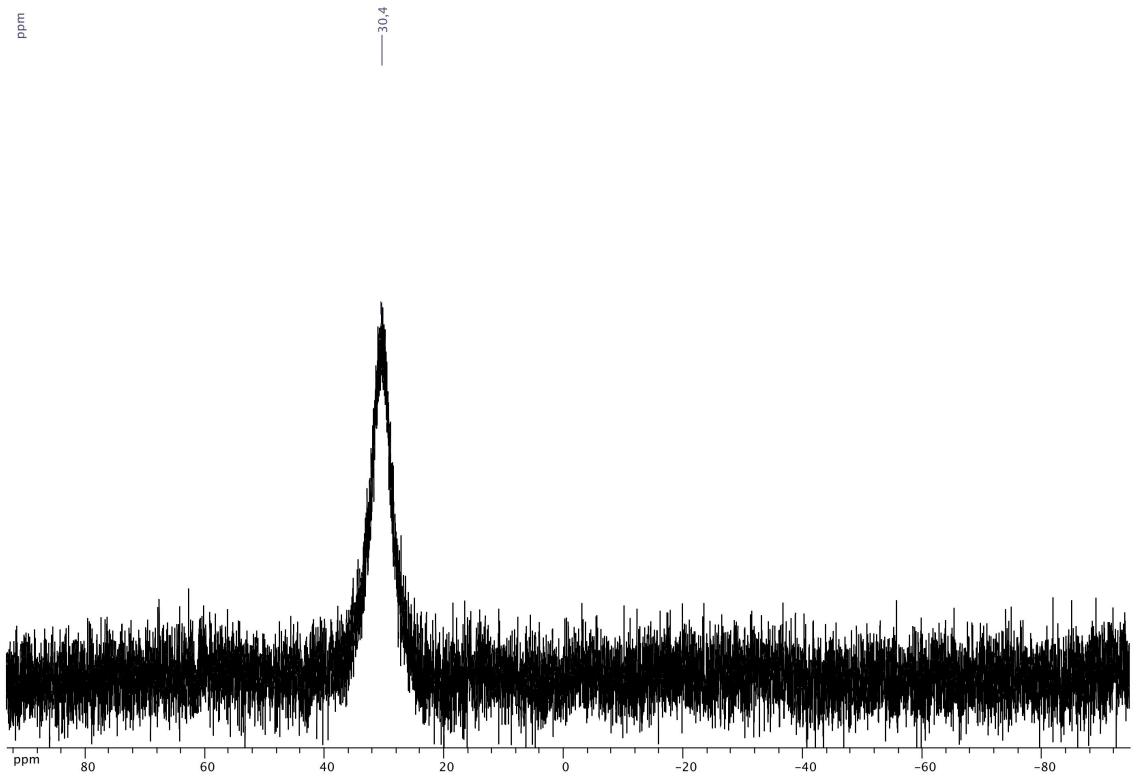
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 2-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenethyl)pyridine (**6**)



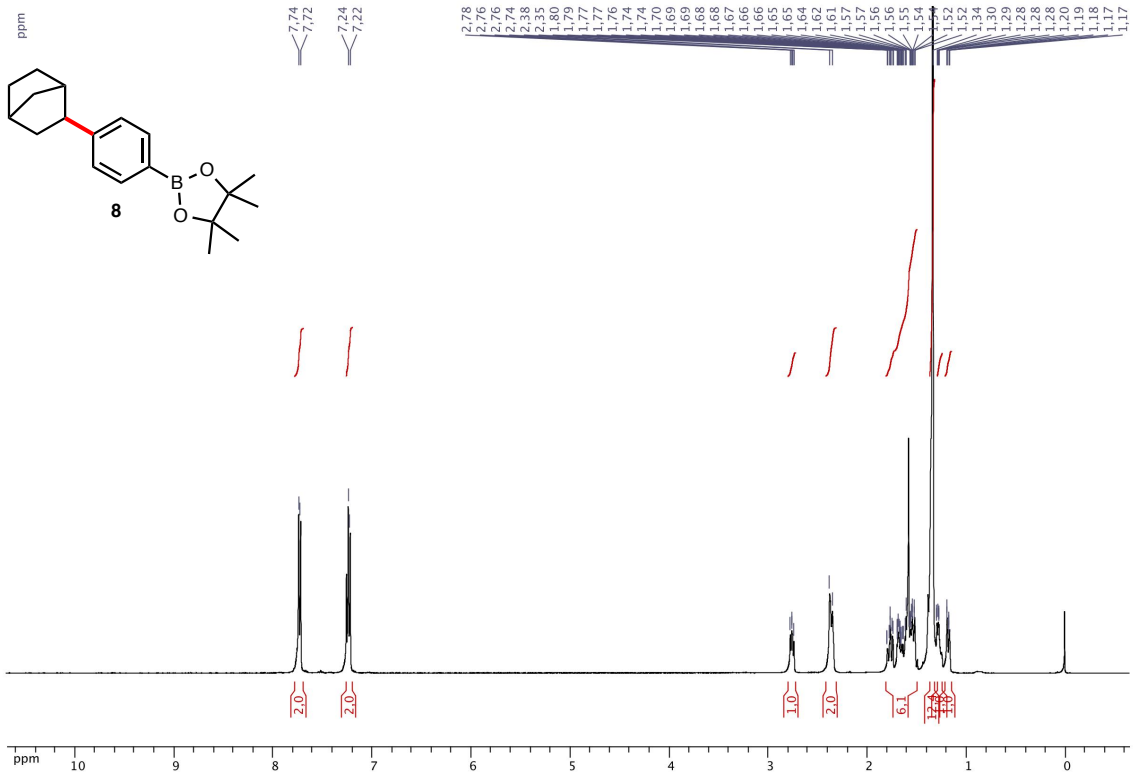
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *N*-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)acetamide (**7**)



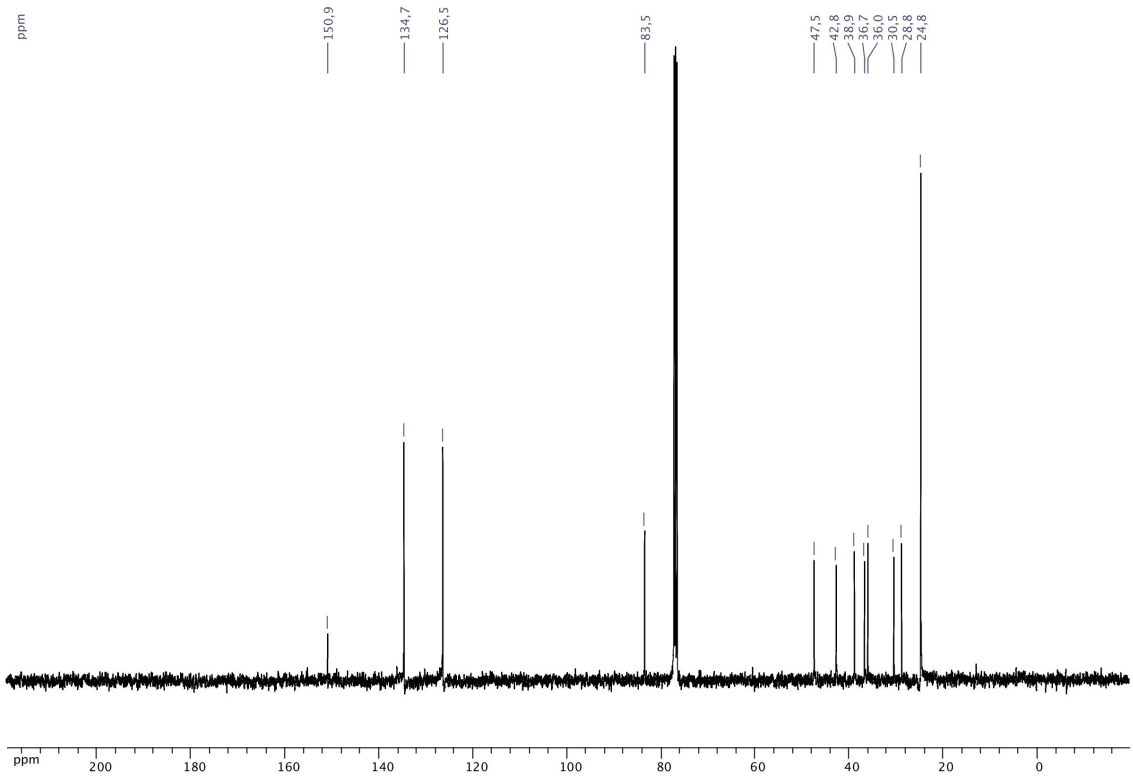
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *N*-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)acetamide (**7**)



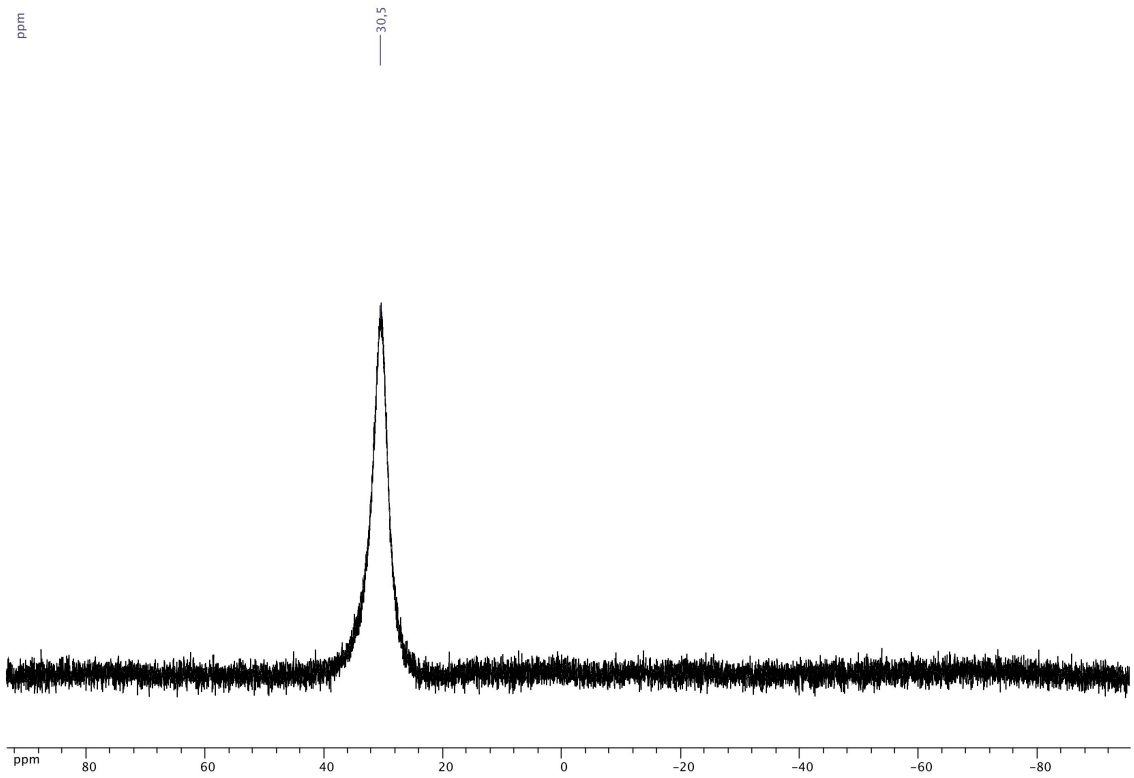
^{11}B NMR ($CDCl_3$, 128.4 MHz) of *N*-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)acetamide (**7**)



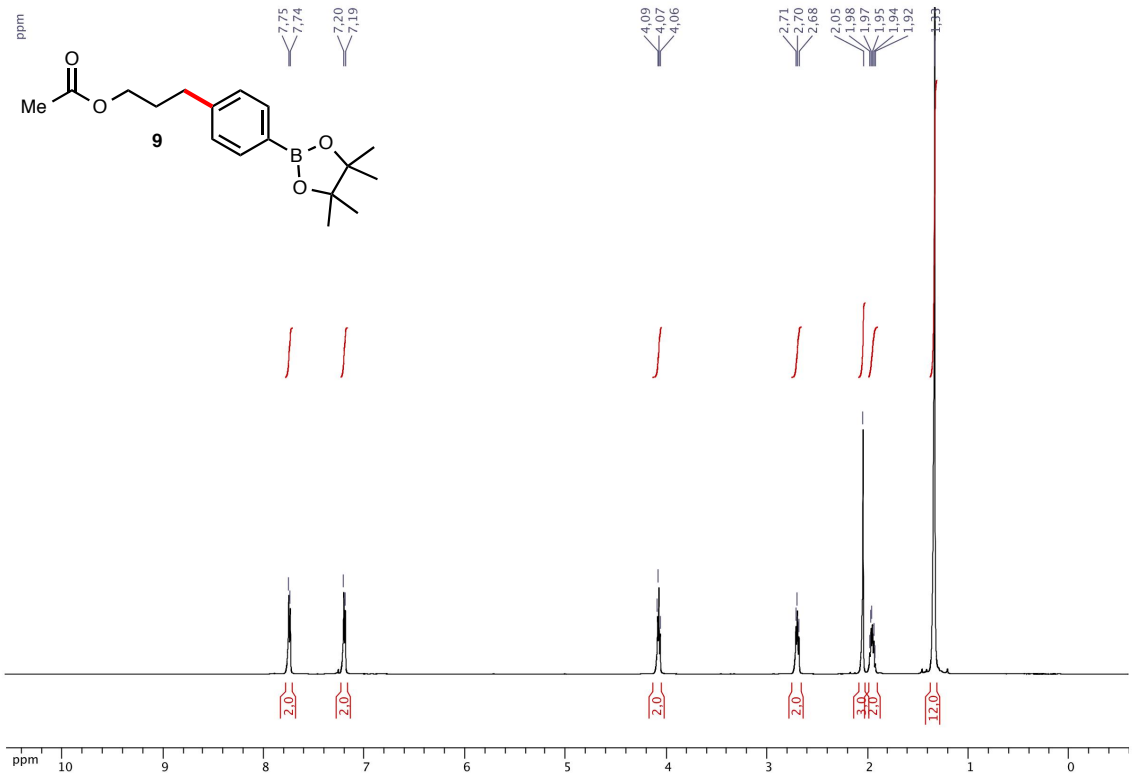
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(4-(bicyclo[2.2.1]heptan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8**)



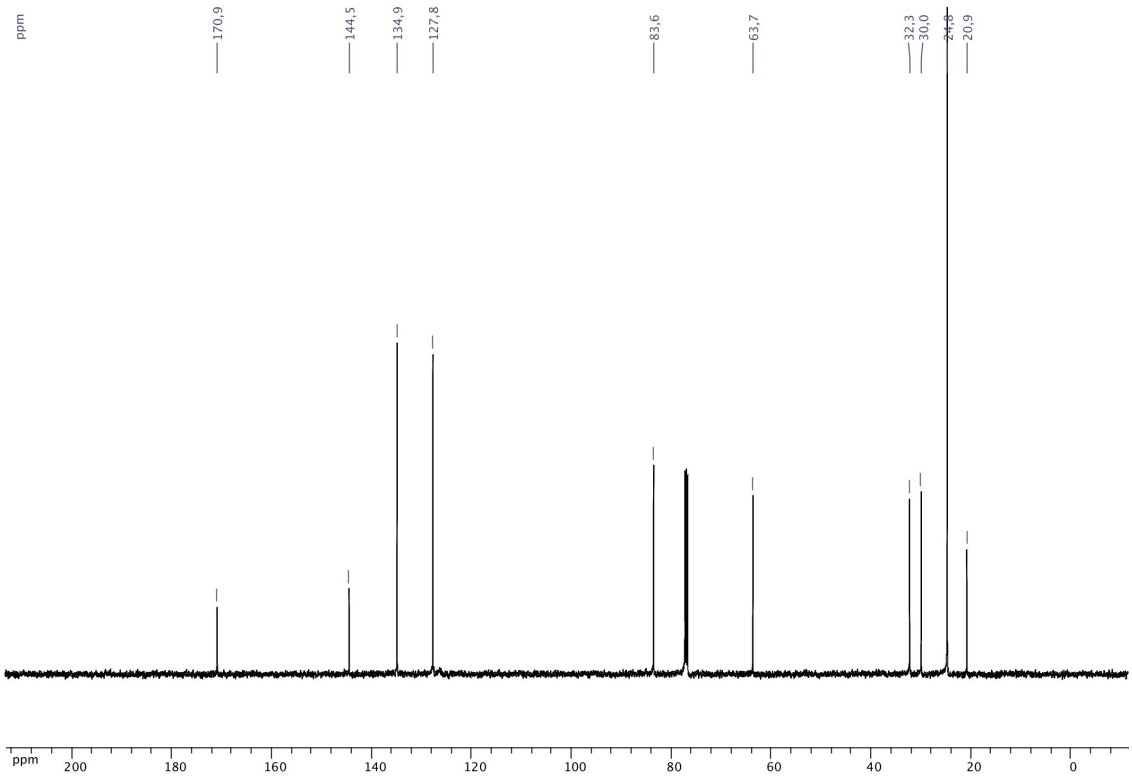
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(4-(bicyclo[2.2.1]heptan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8**)



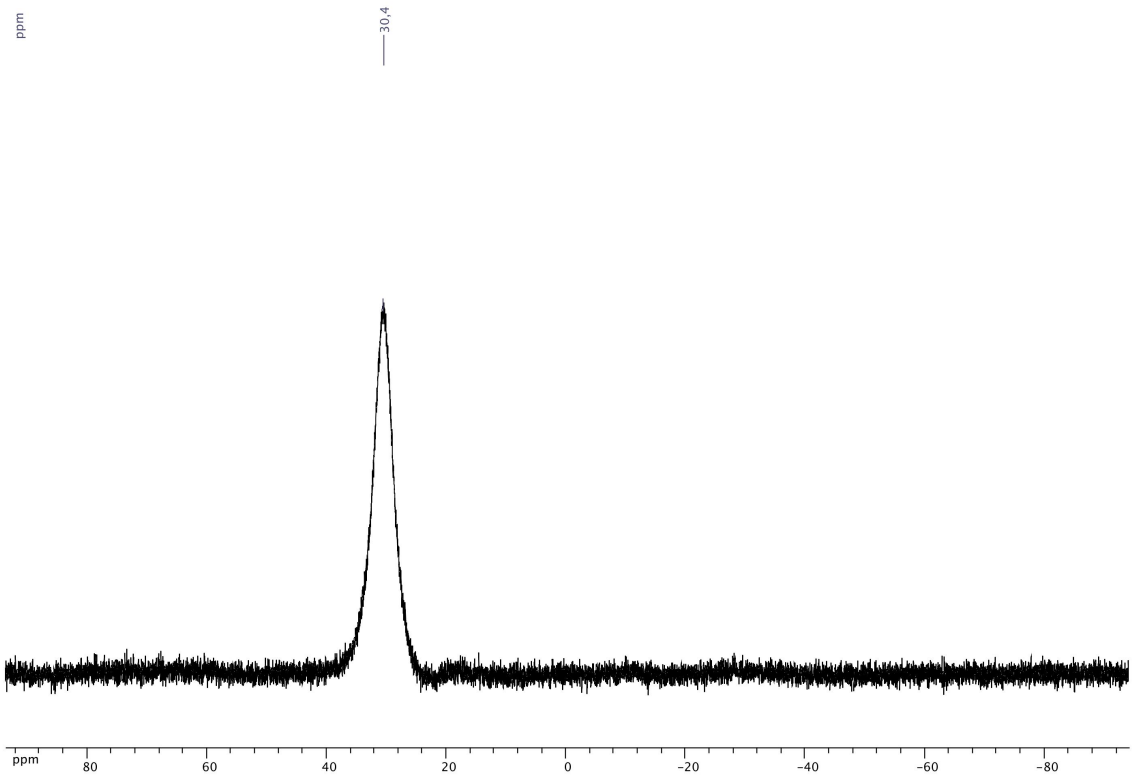
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 2-(4-(bicyclo[2.2.1]heptan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**8**)



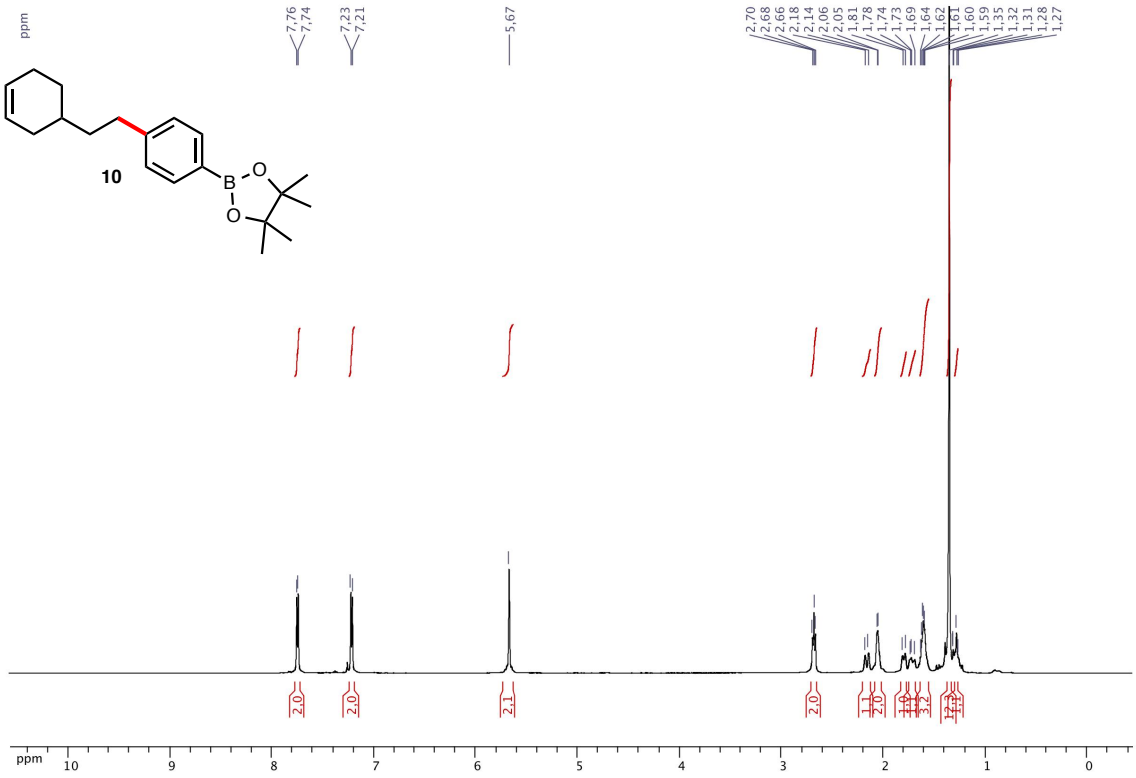
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl acetate (**9**)



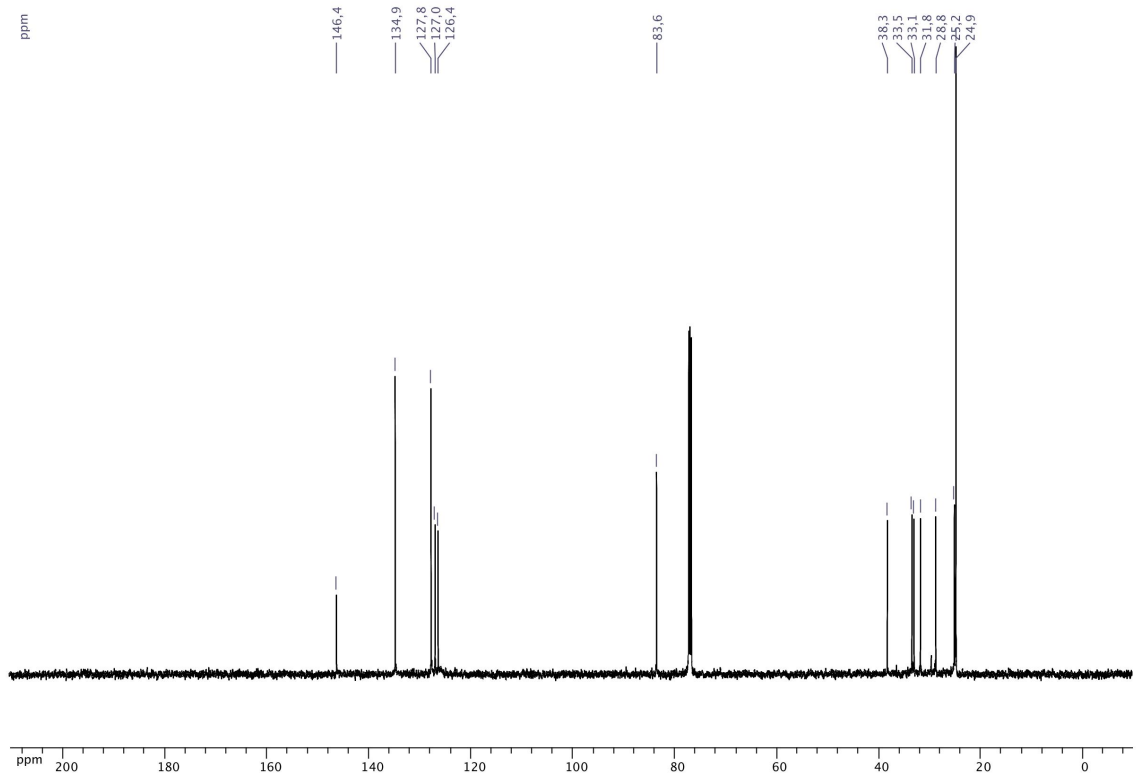
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl acetate (**9**)



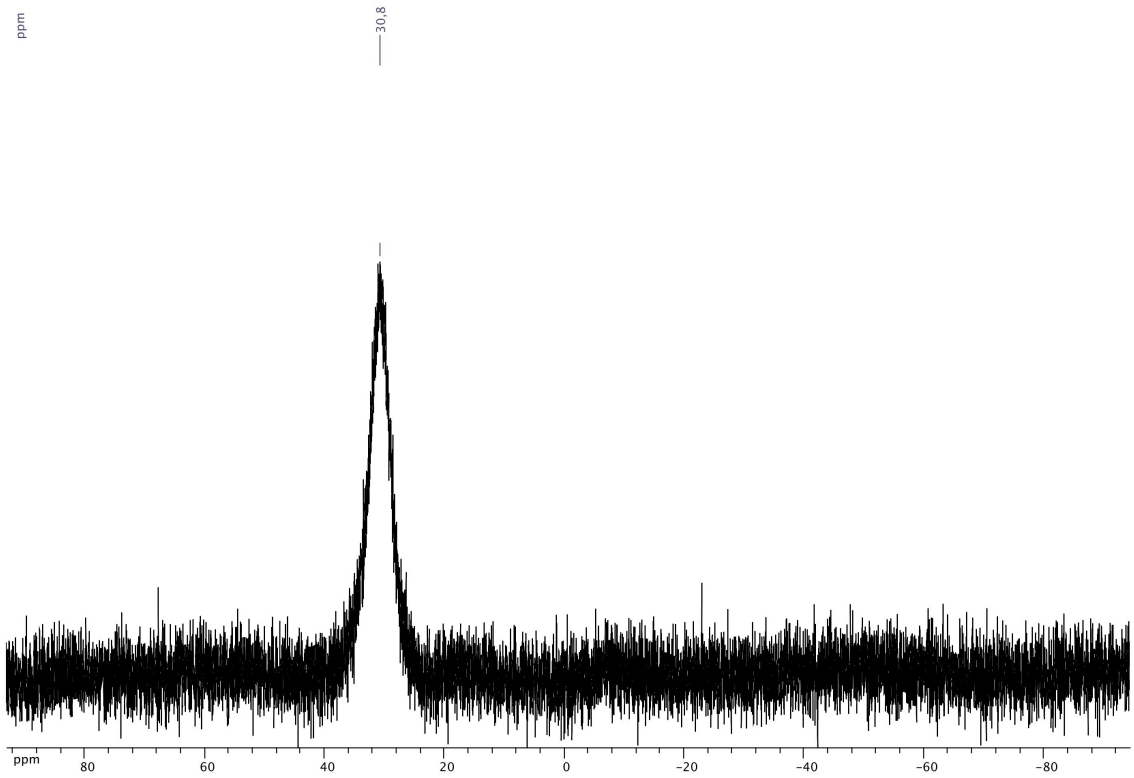
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl acetate (**9**)



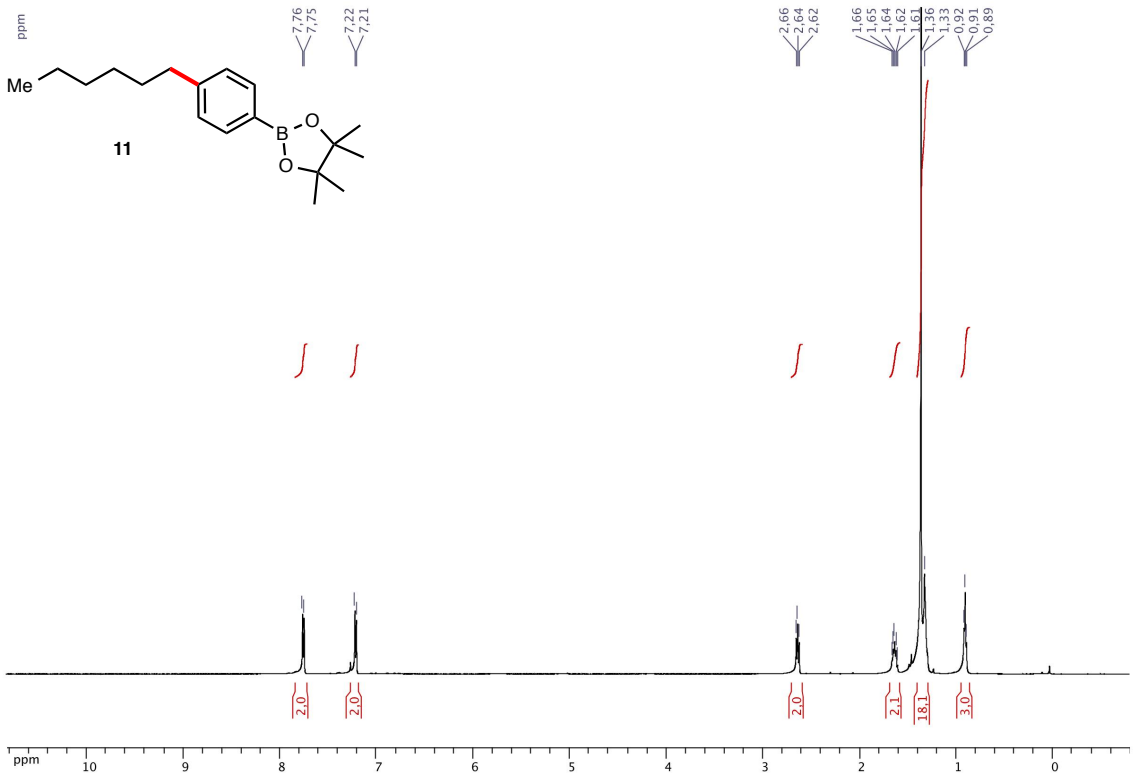
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(4-(2-(Cyclohex-3-en-1-yl)ethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10**)



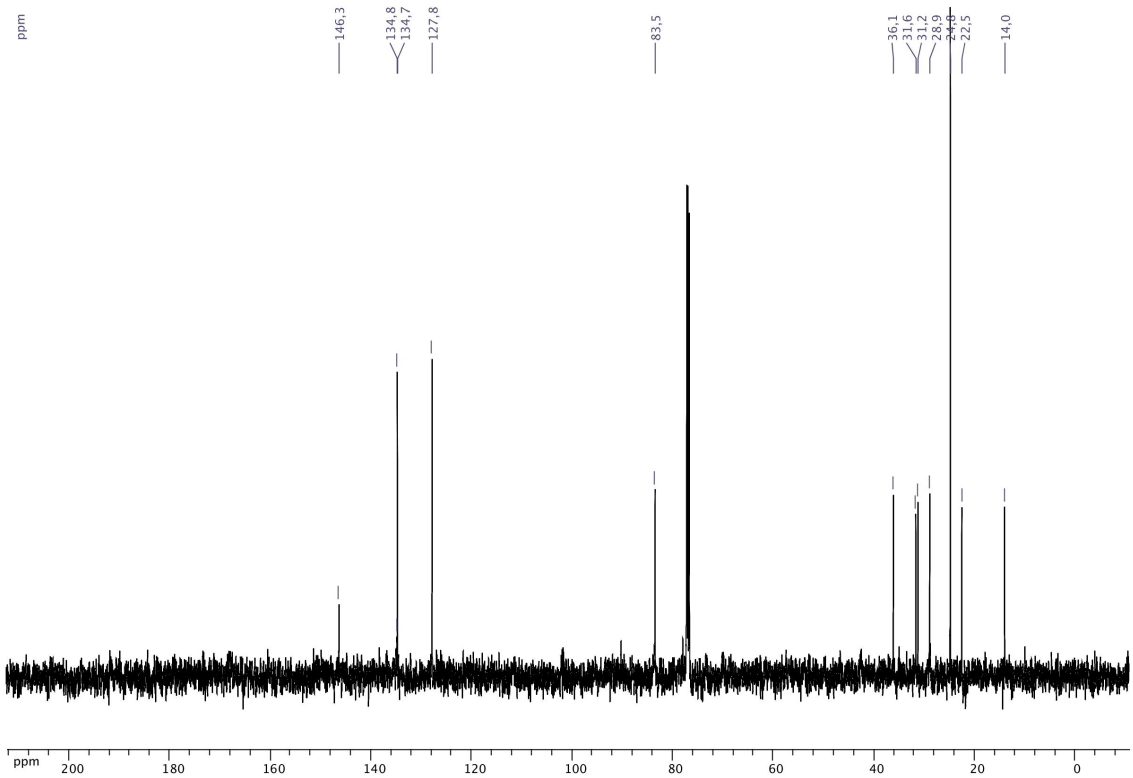
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(4-(2-(cyclohex-3-en-1-yl)ethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10**)



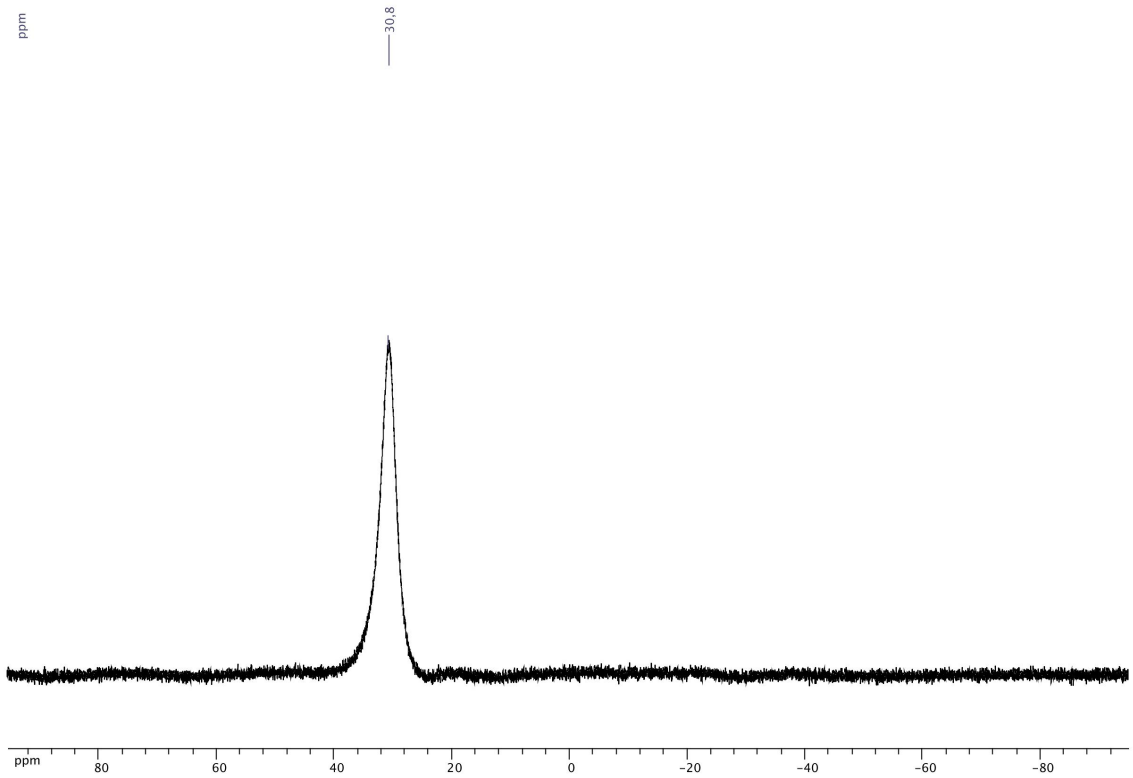
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 2-(4-(2-(Cyclohex-3-en-1-yl)ethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**10**)



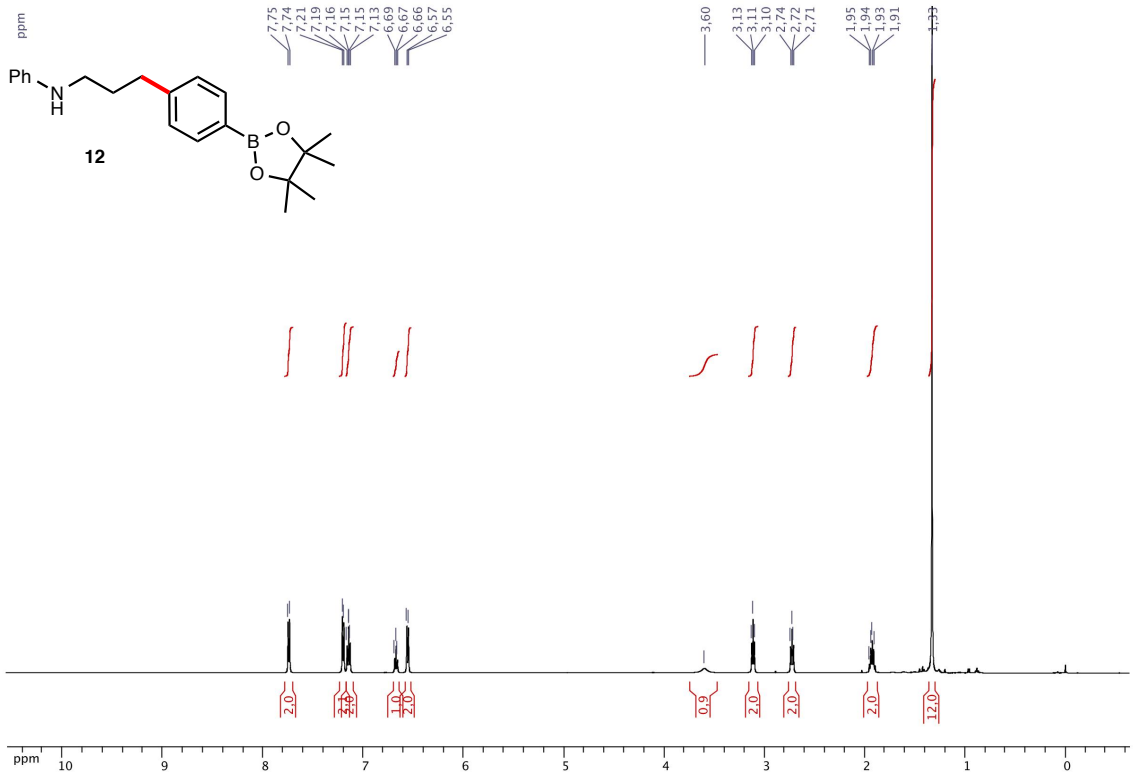
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(4-hexylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11**)



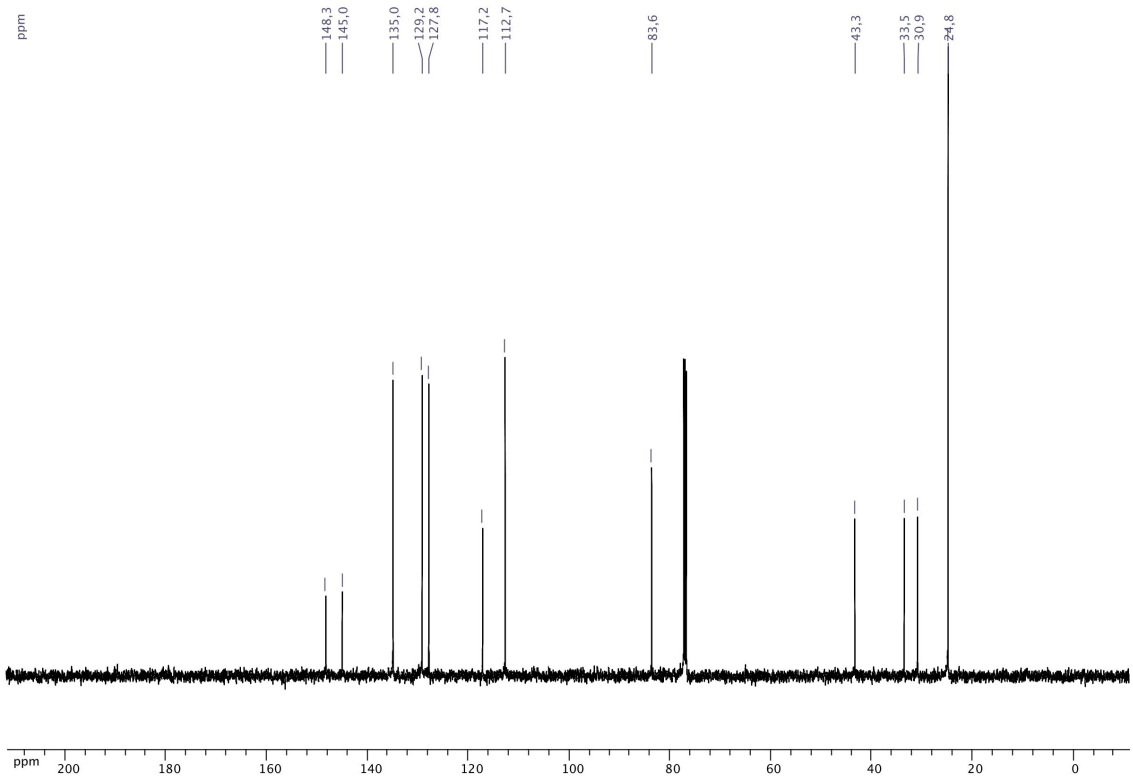
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(4-hexylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11**)



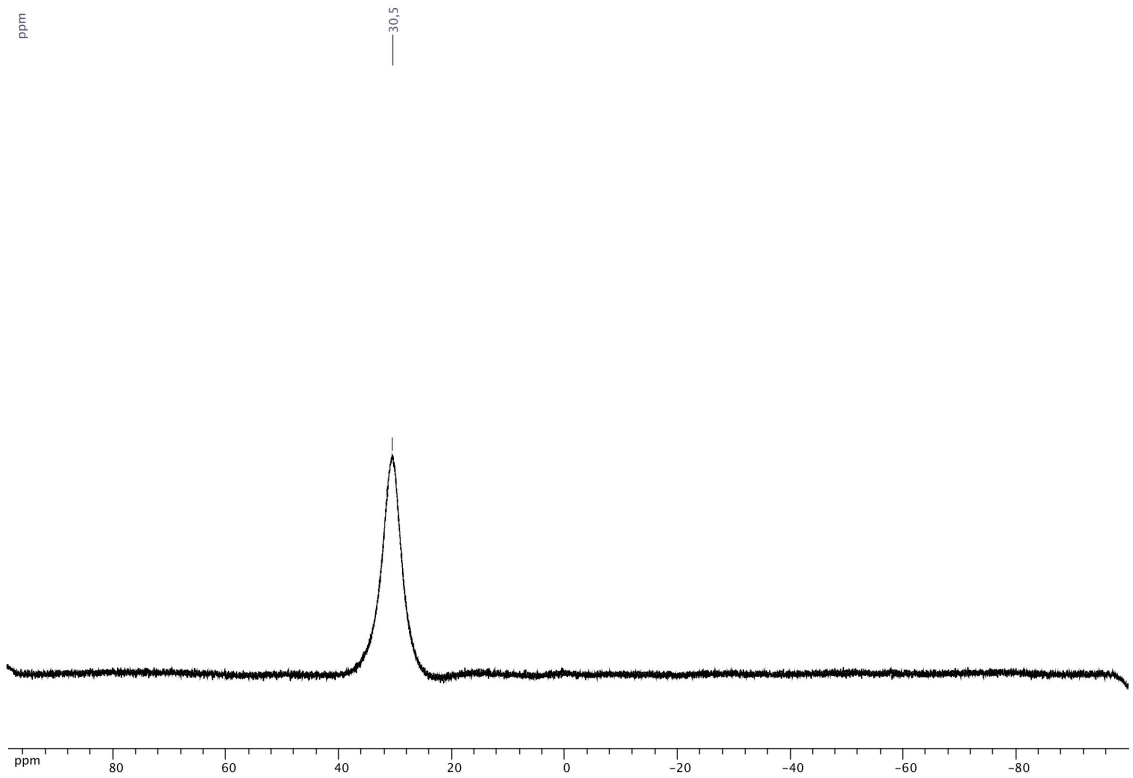
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 2-(4-hexylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**11**)



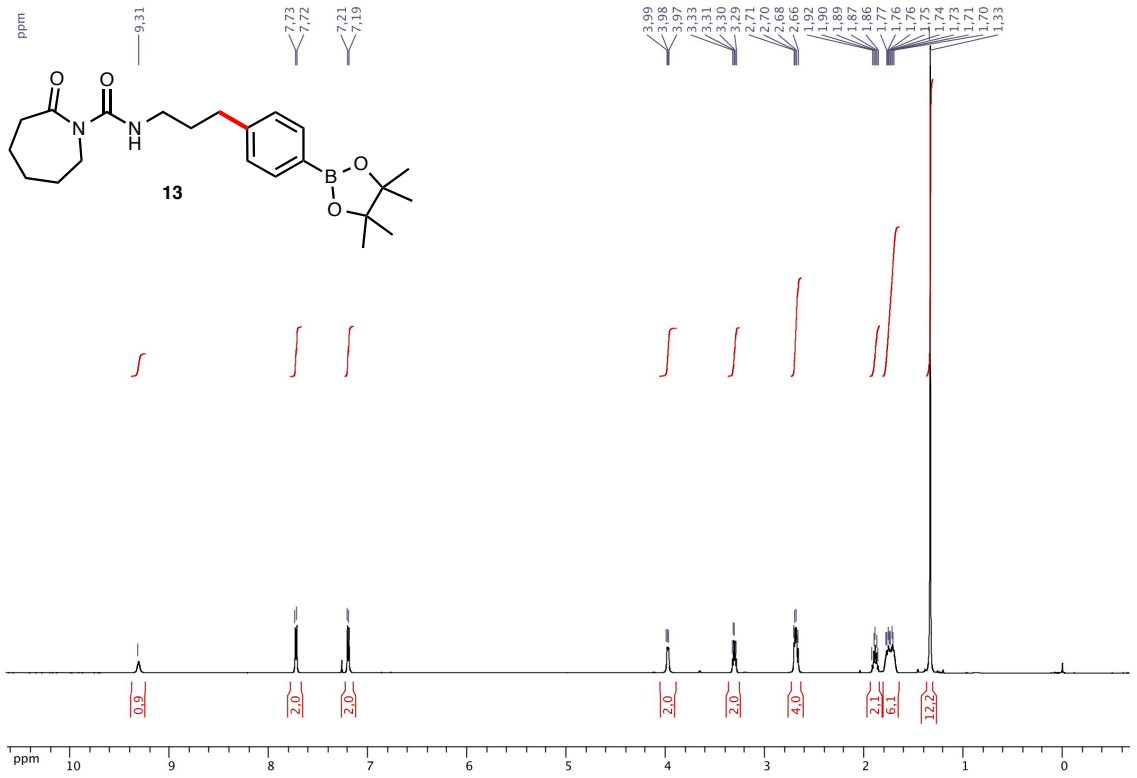
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *N*-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)aniline (**12**)



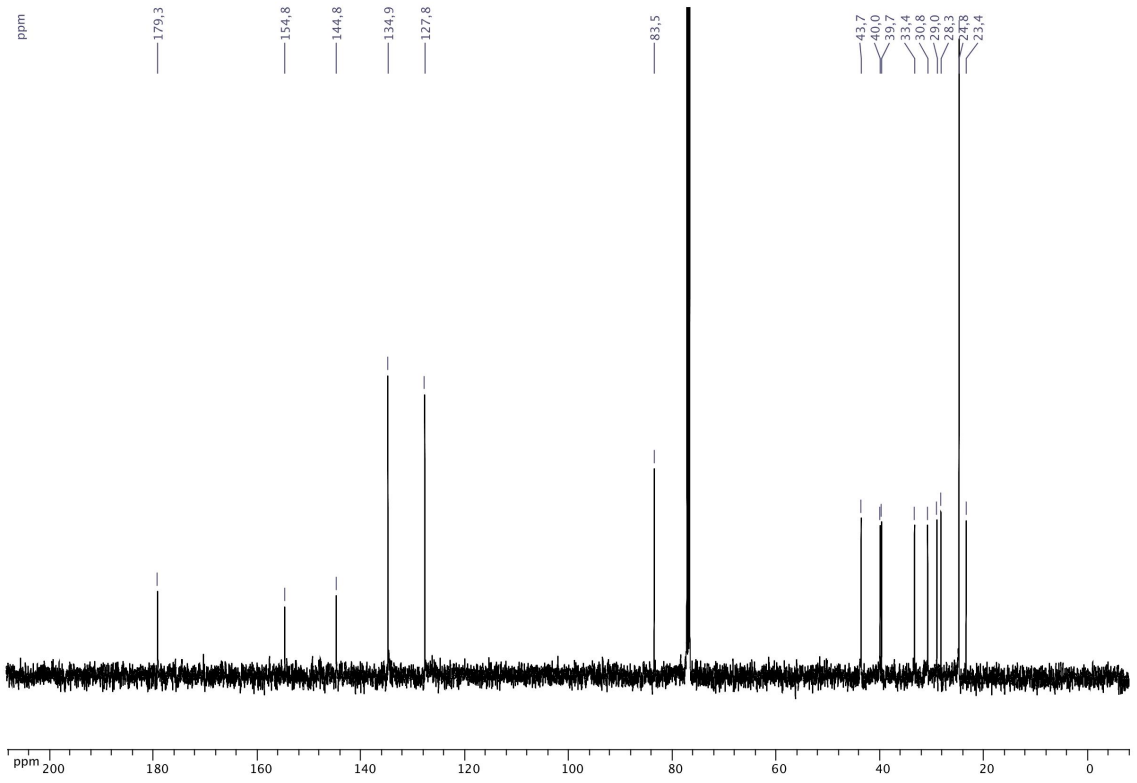
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *N*-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)aniline (**12**)



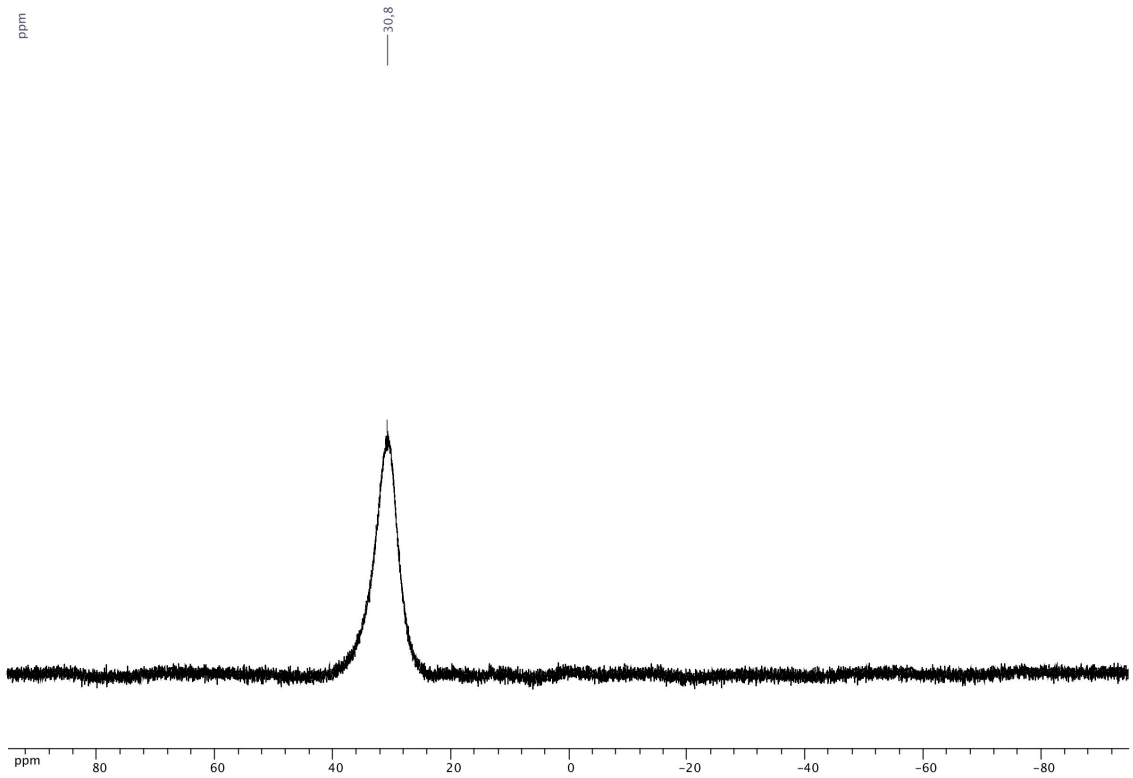
^{11}B NMR ($CDCl_3$, 128.4 MHz) of *N*-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)aniline (**12**)



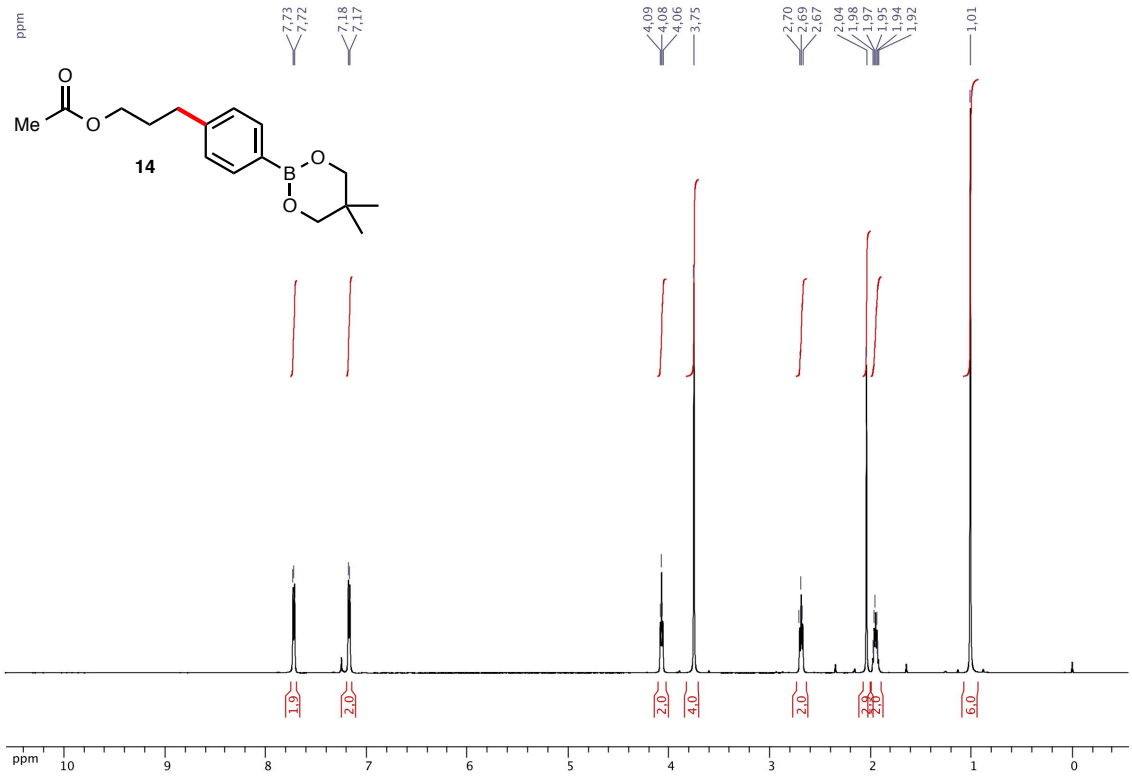
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *N*-[(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)-2-aza-1-oxopentyl]caprolactam (**13**)



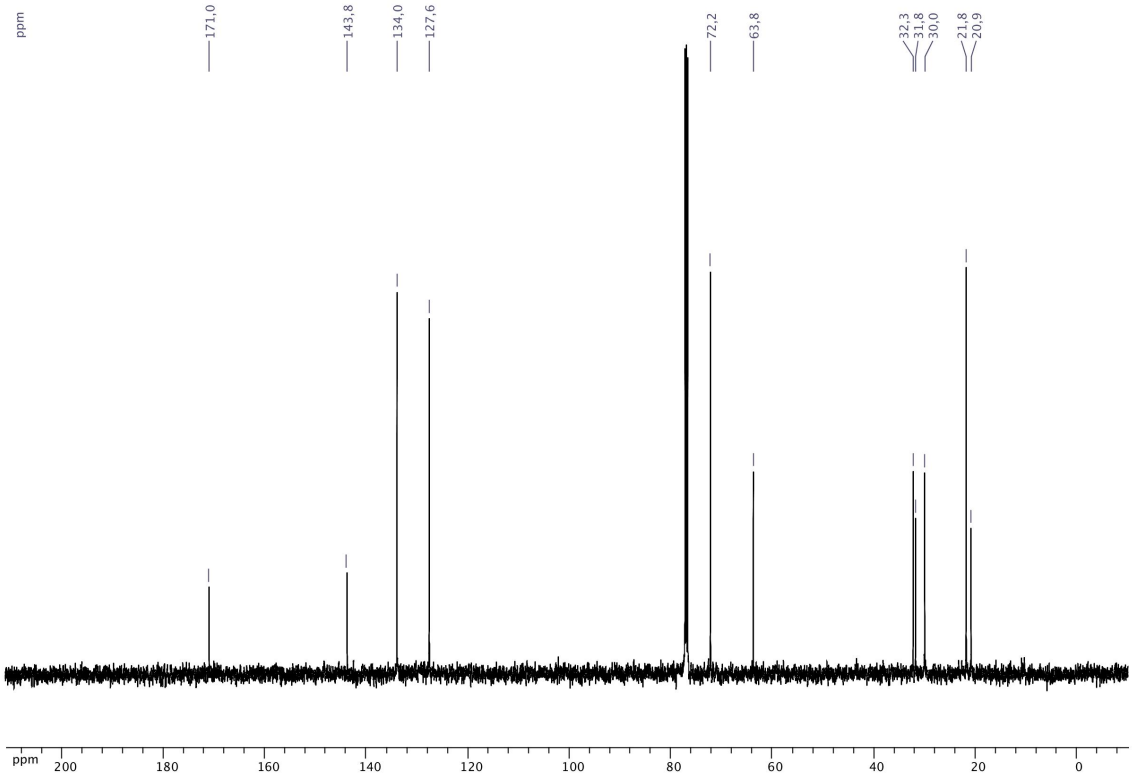
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *N*-[(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)-2-aza-1-oxopentyl]caprolactam (**13**)



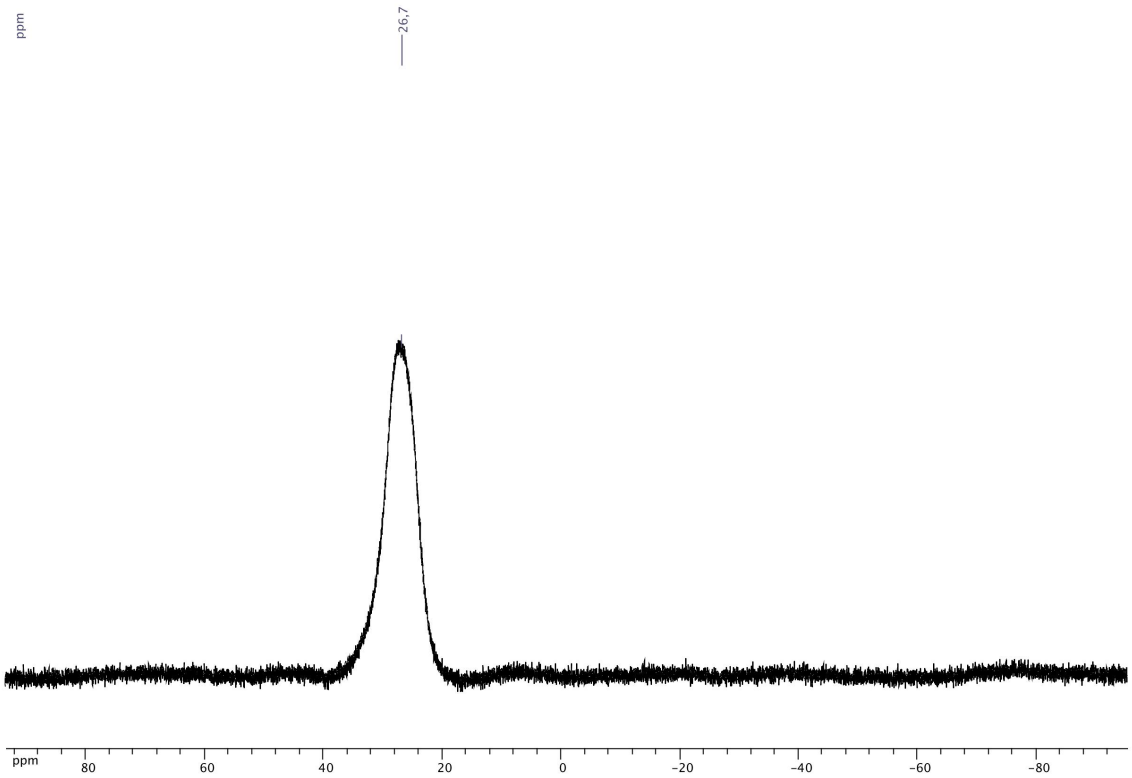
^{11}B NMR ($CDCl_3$, 128.4 MHz) of *N*-[(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)-2-aza-1-oxopentyl]caprolactam (**13**)



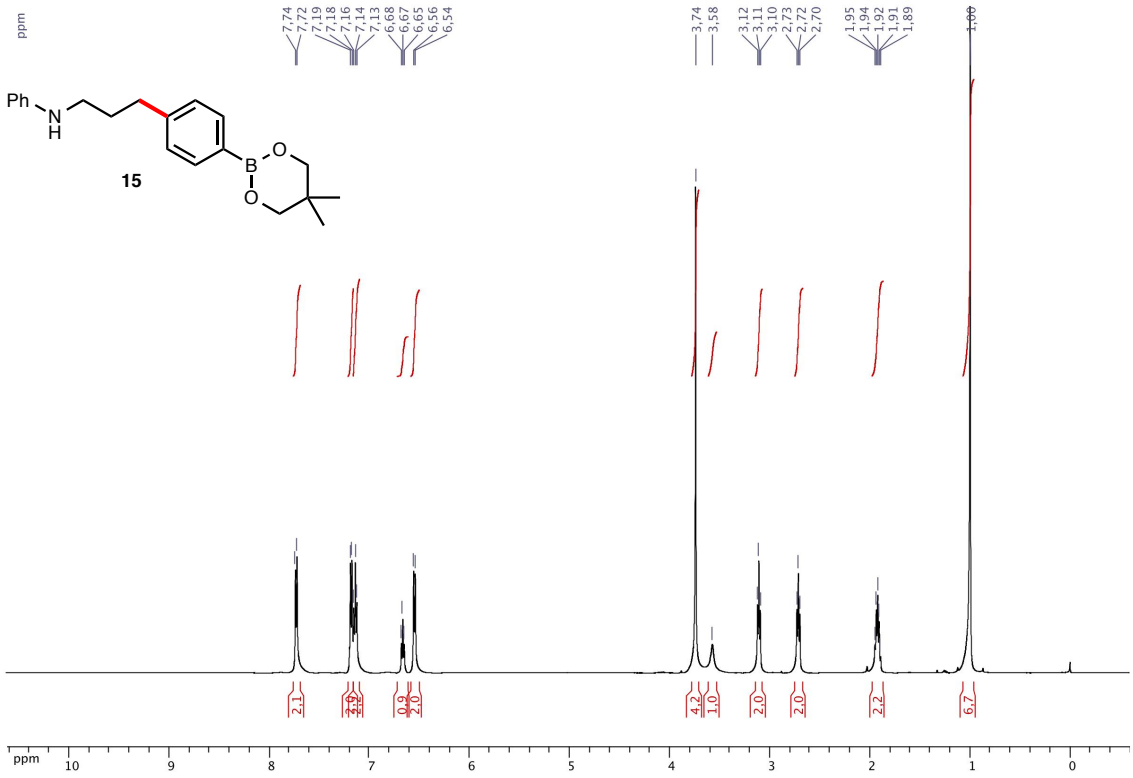
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 3-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)propyl acetate (**14**)



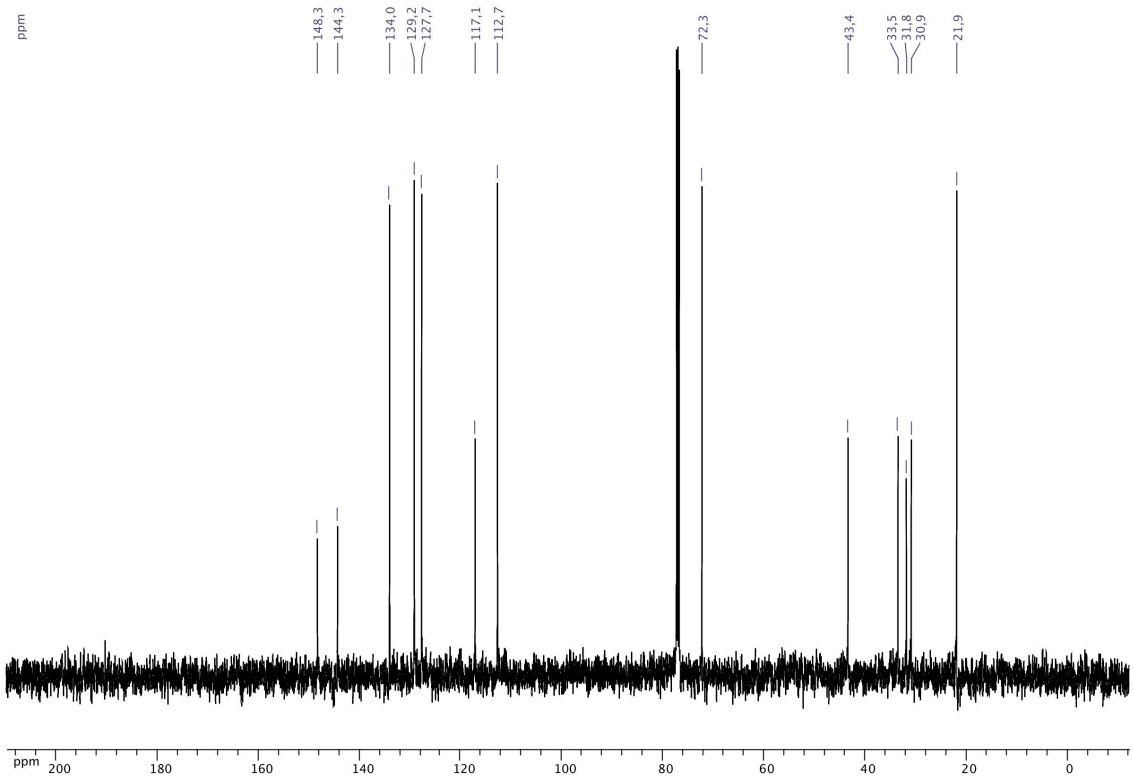
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 3-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)propyl acetate (**14**)



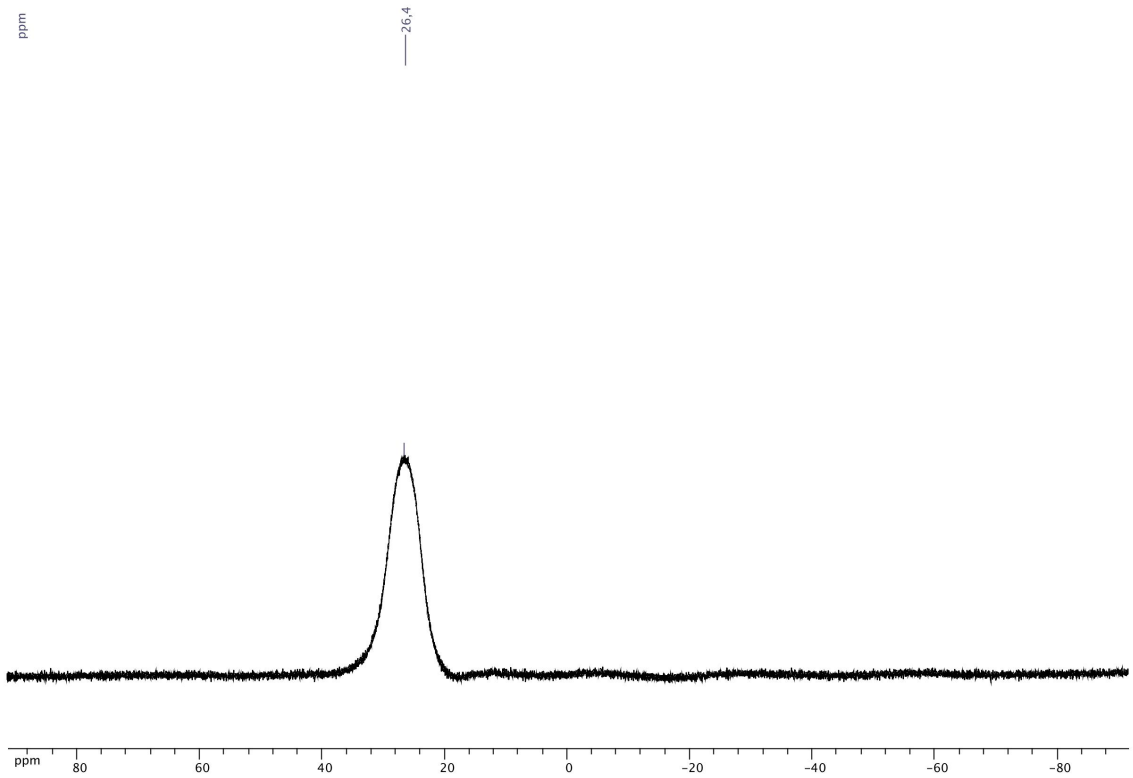
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 3-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)propyl acetate (**14**)



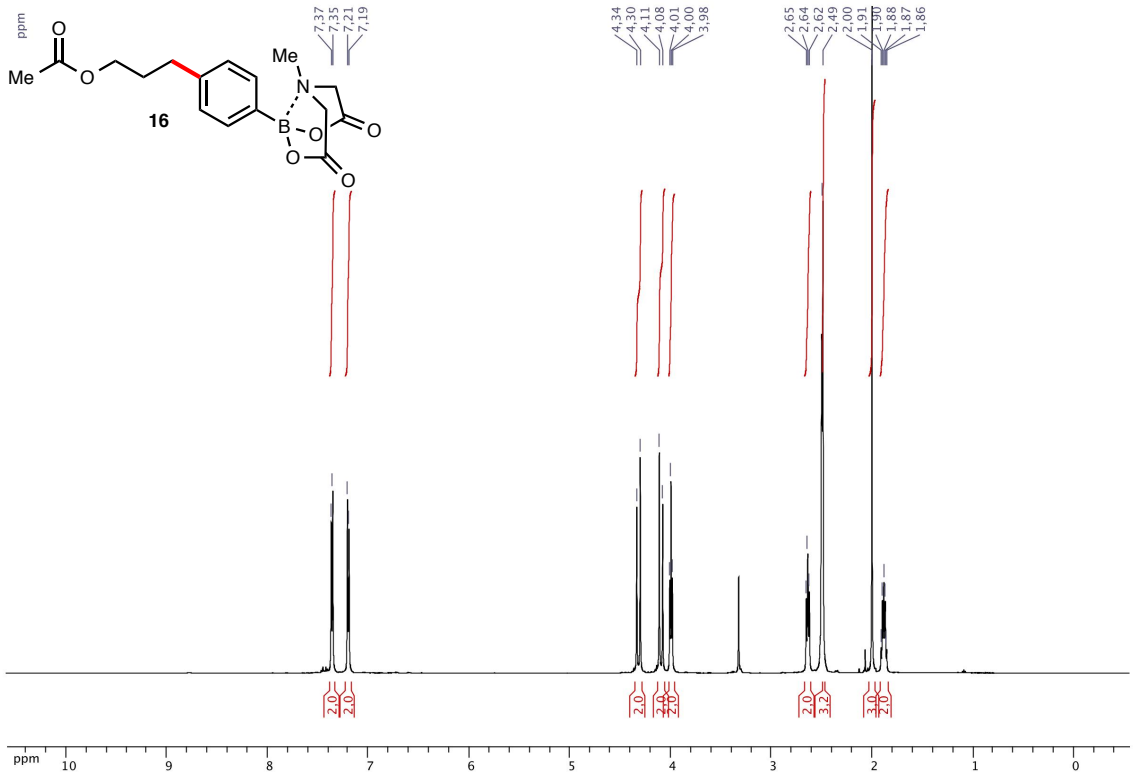
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *N*-(3-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)propyl)aniline (**15**)



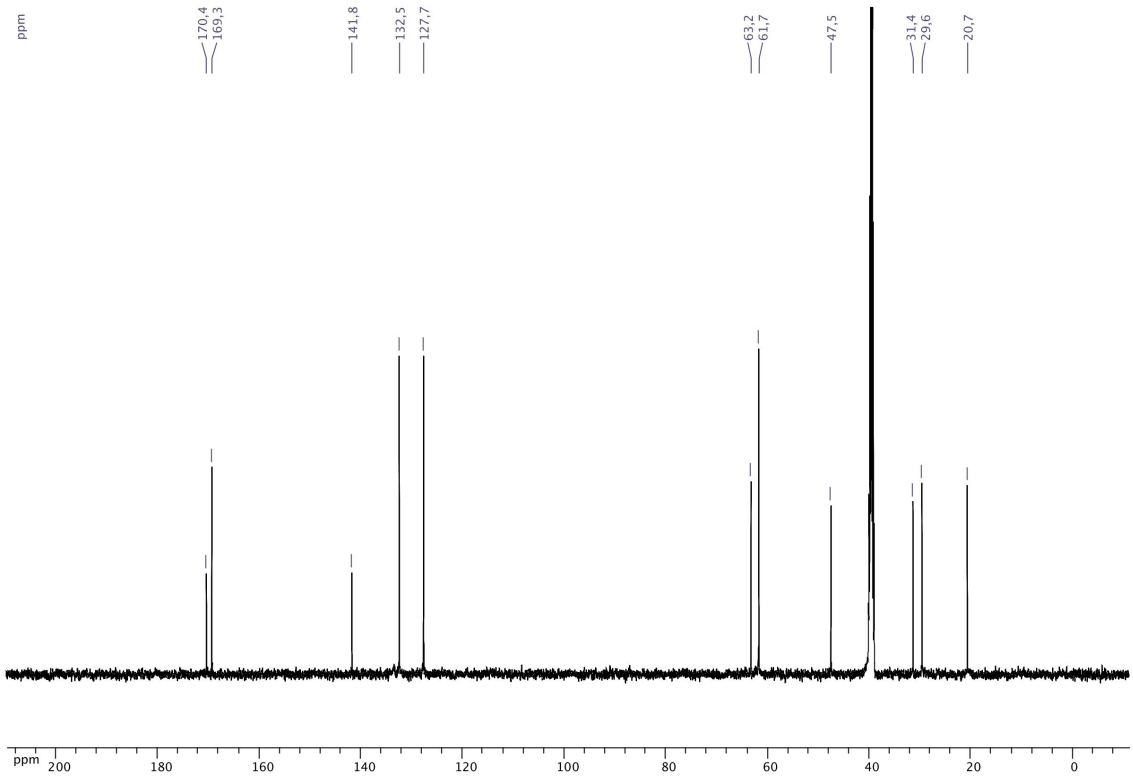
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *N*-(3-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)propyl)aniline (**15**)



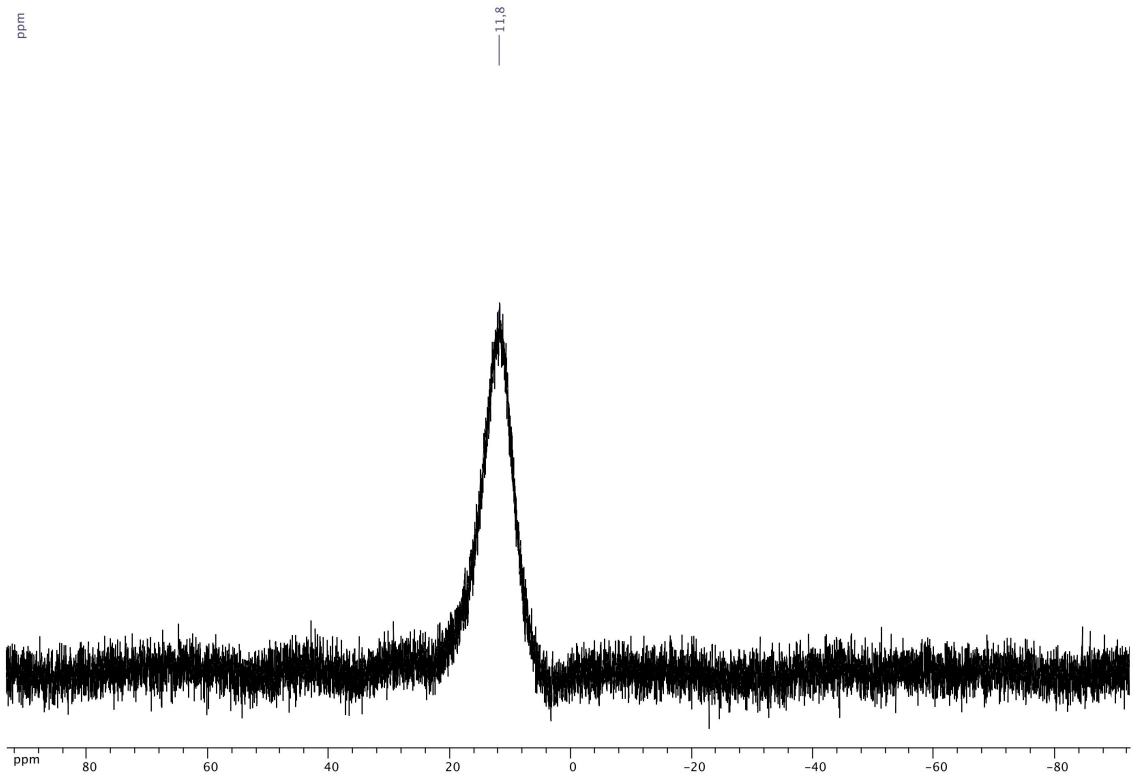
^{11}B NMR ($CDCl_3$, 128.4 MHz) of *N*-(3-(4-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)propyl)aniline (**15**)



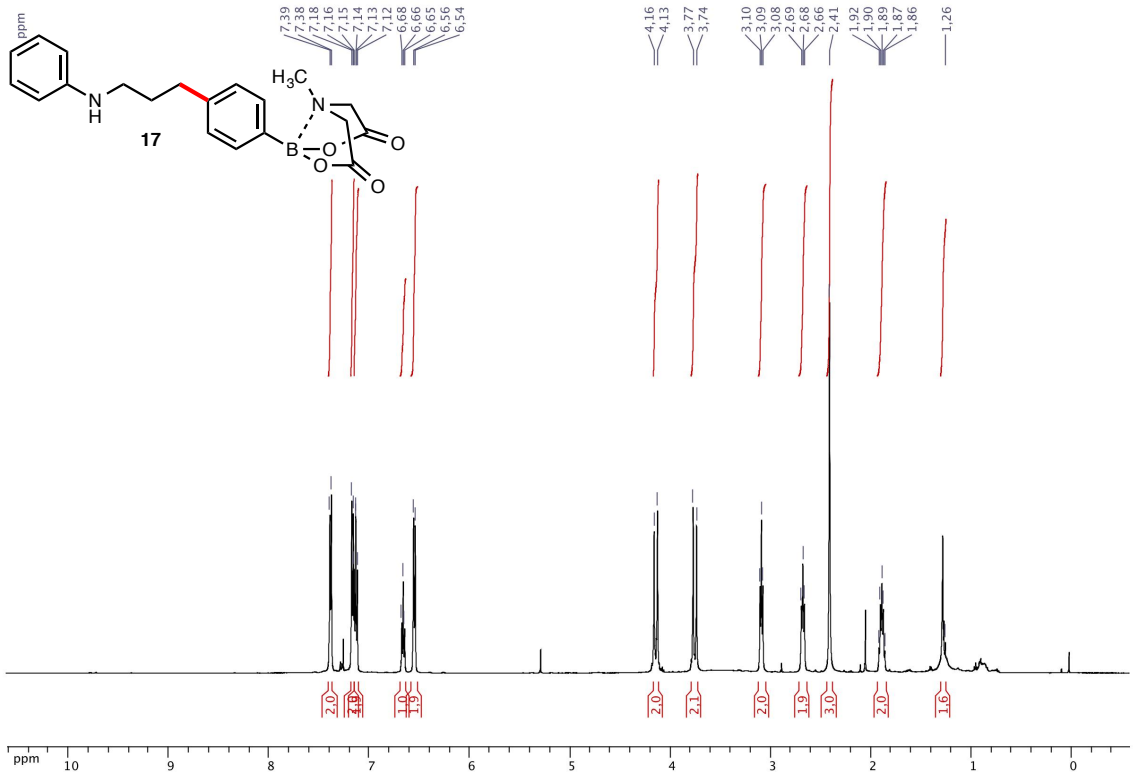
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 3-(4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)phenyl)propyl acetate (**16**)



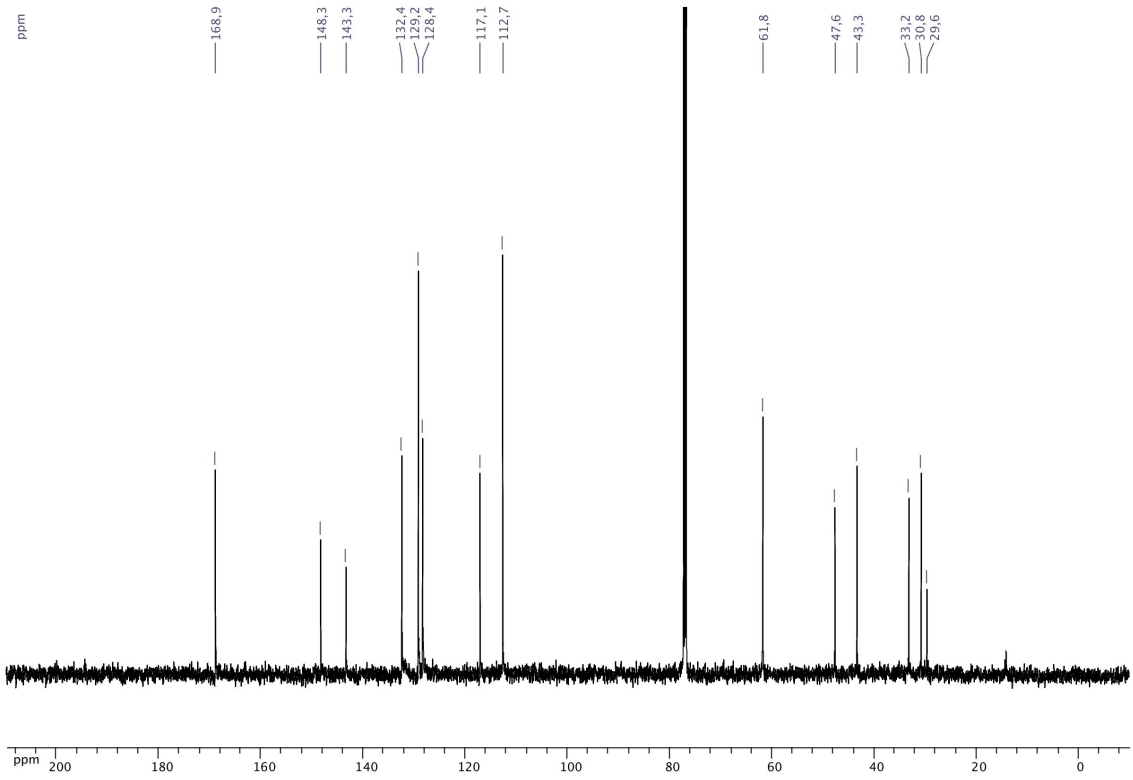
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 3-(4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)phenyl)propyl acetate (**16**)



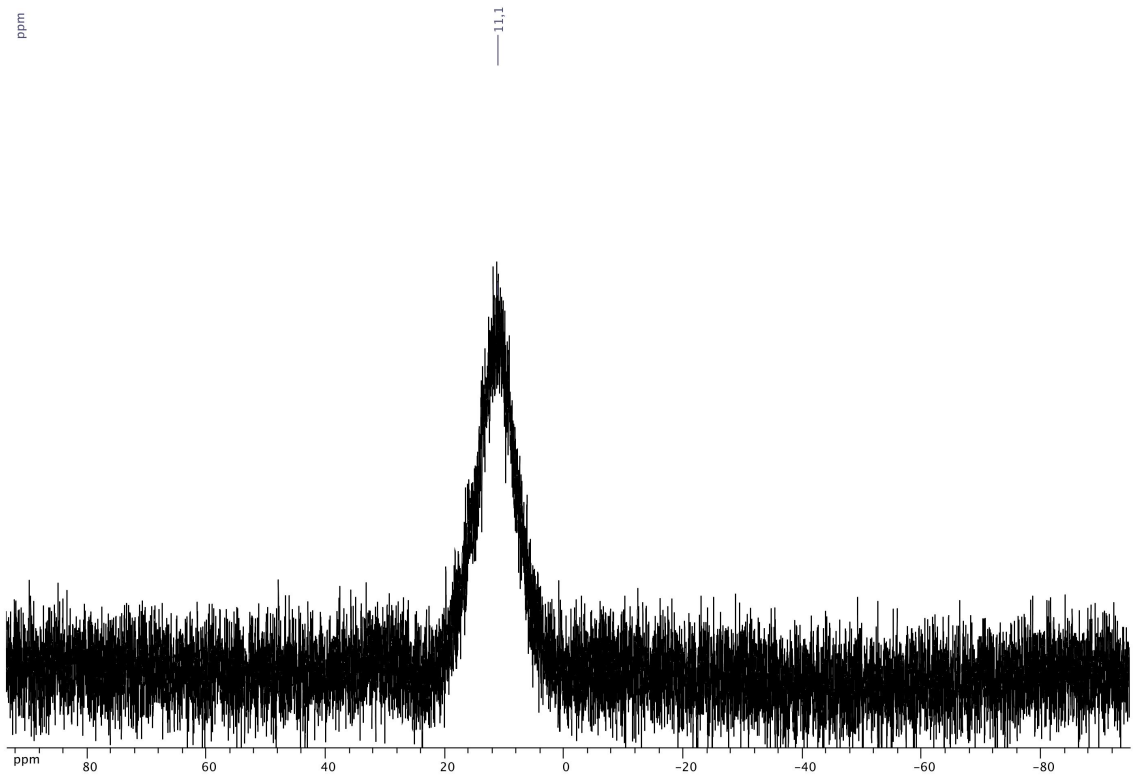
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 3-(4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)phenyl)propyl acetate (**16**)



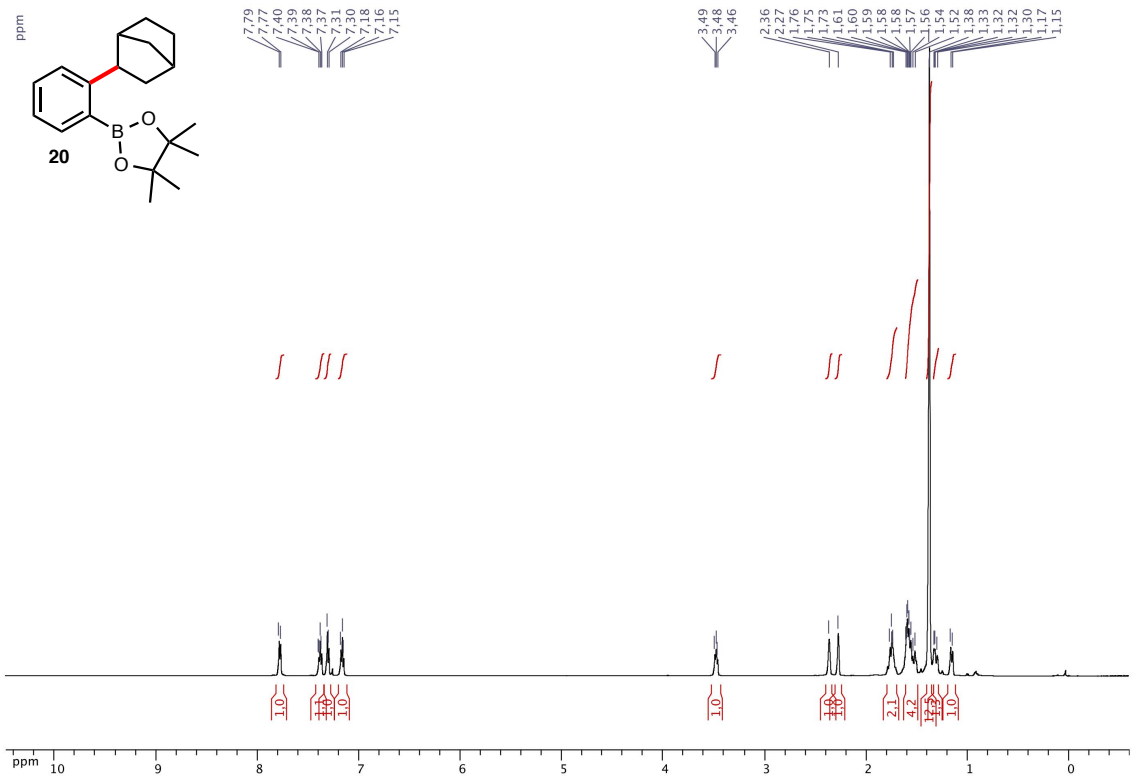
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 6-methyl-2-(4-(3-(phenylamino)propyl)phenyl)-1,3,6,2-dioxazaborocane-4,8-dione (**17**)



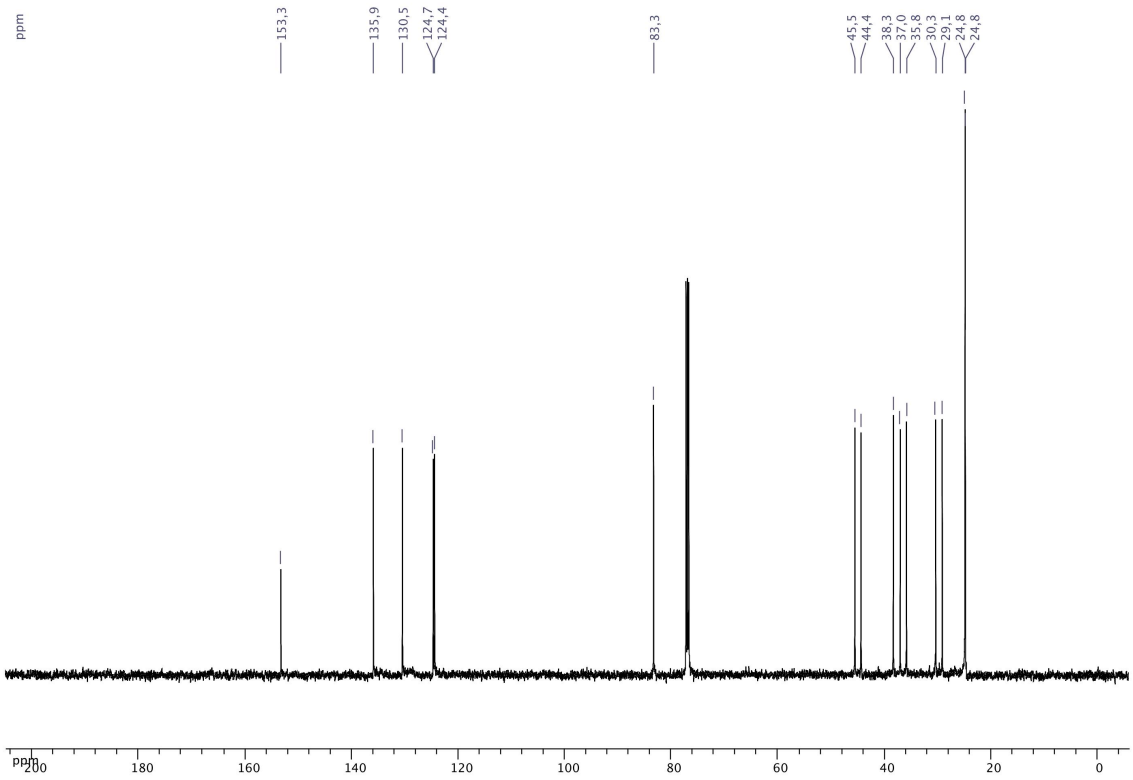
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 6-methyl-2-(4-(3-(phenylamino)propyl)phenyl)-1,3,6,2-dioxazaborocane-4,8-dione (**17**)



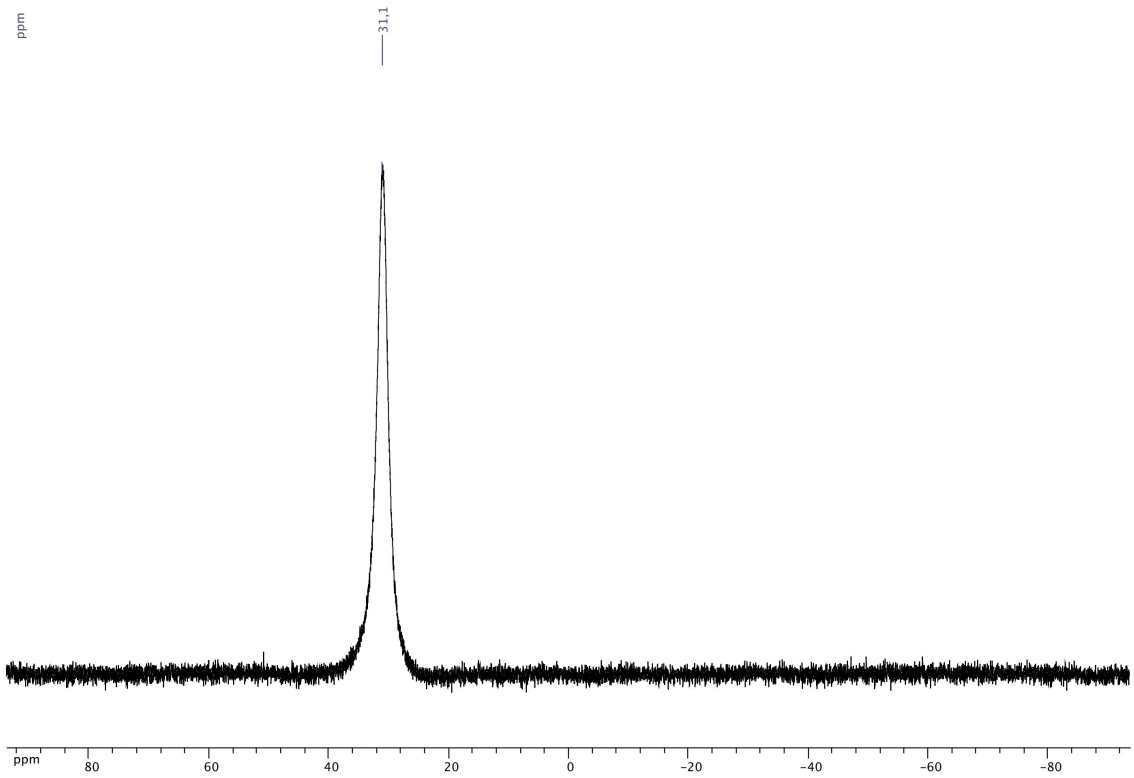
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 6-methyl-2-(4-(3-(phenylamino)propyl)phenyl)-1,3,6,2-dioxazaborocane-4,8-dione (**17**)



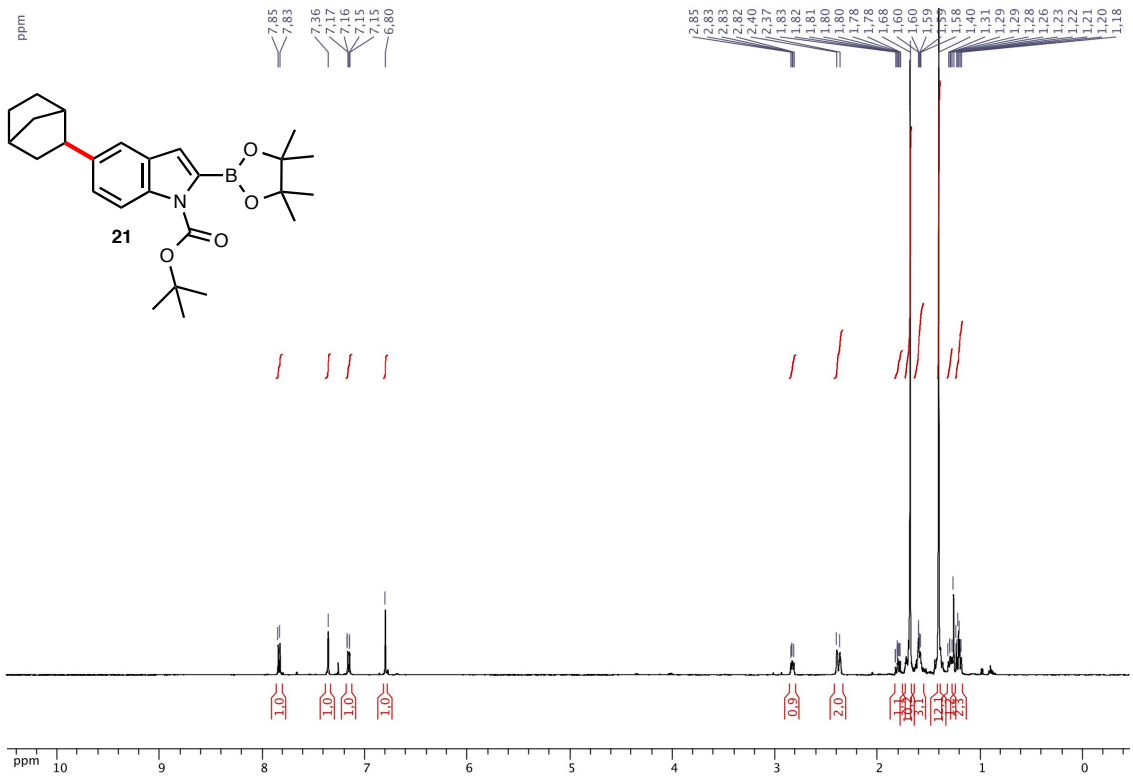
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(2-(bicyclo[2.2.1]heptan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**20**)



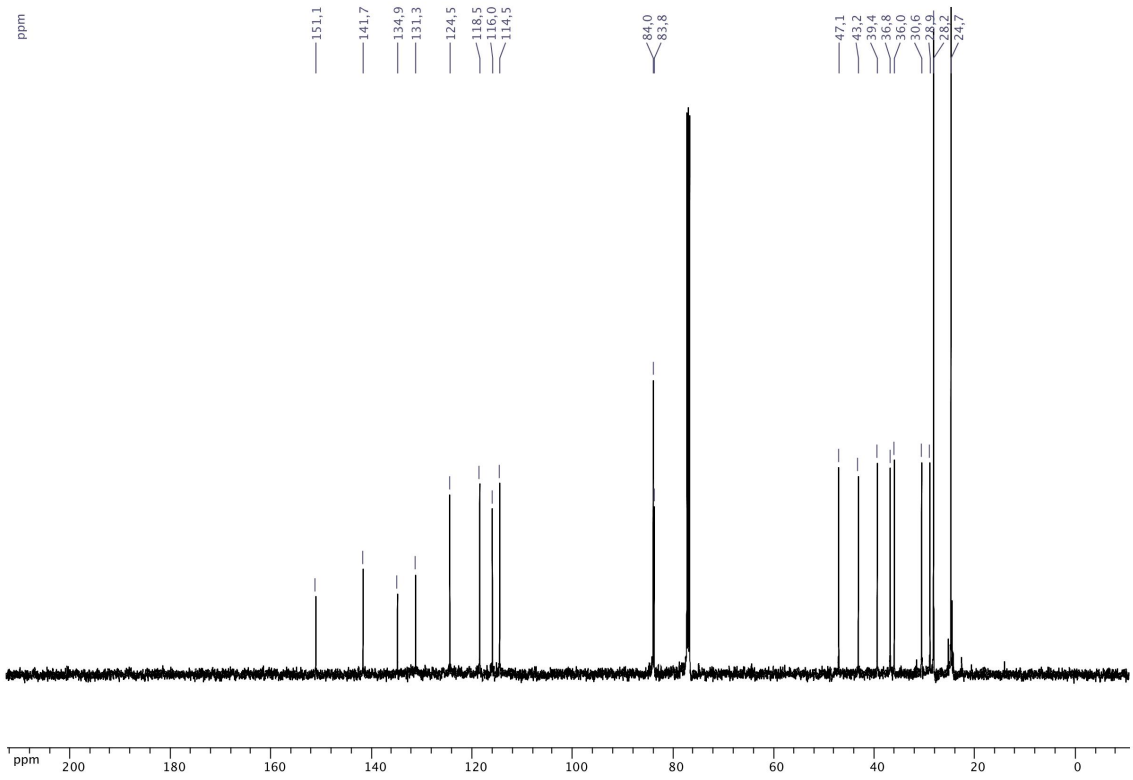
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(2-(bicyclo[2.2.1]heptan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**20**)



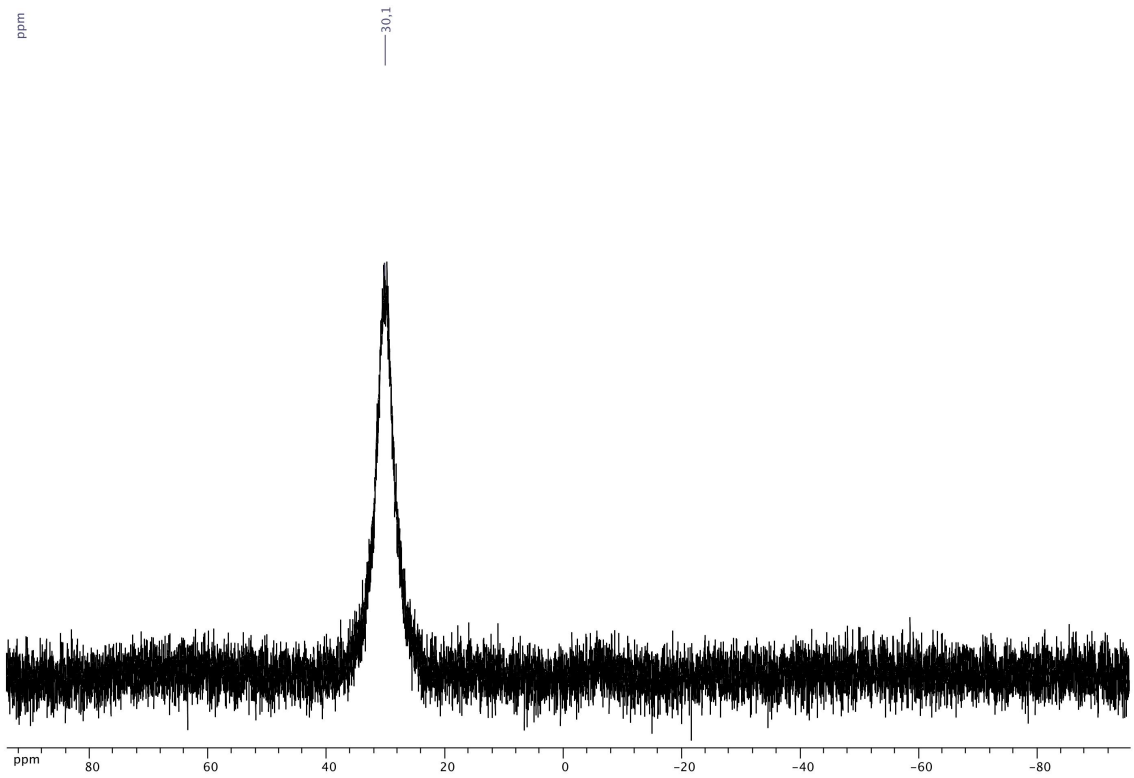
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 2-(2-(bicyclo[2.2.1]heptan-2-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**20**)



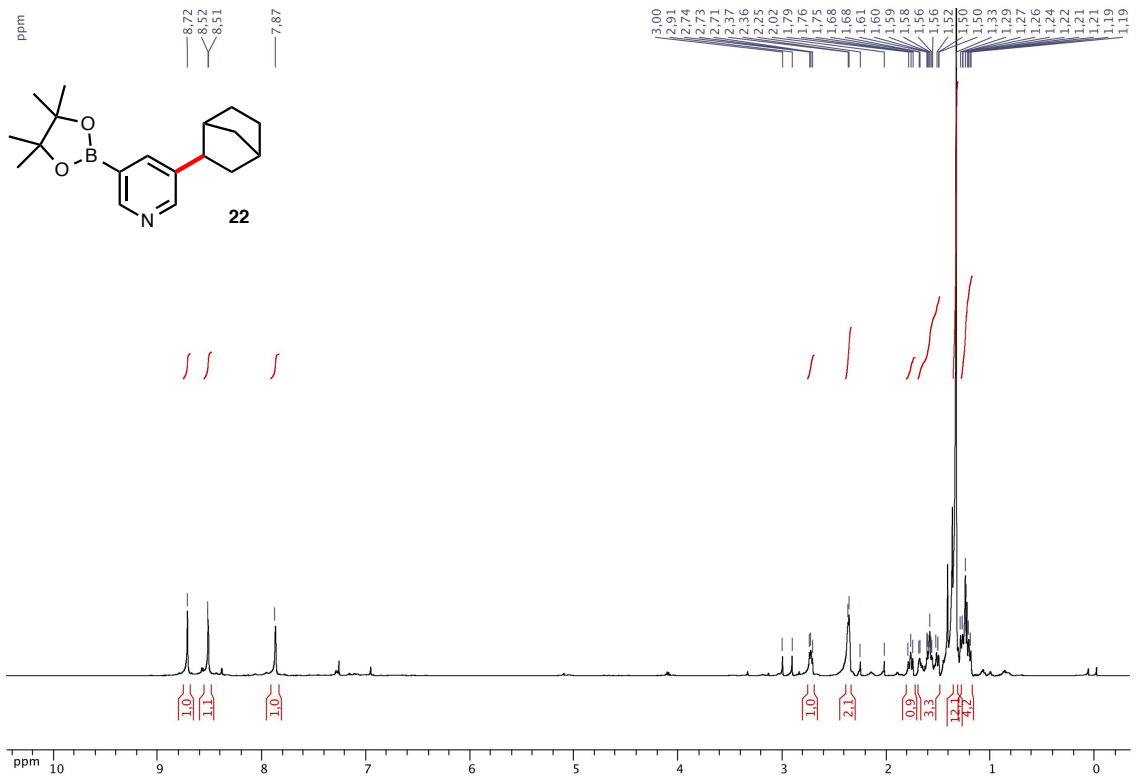
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *tert*-butyl 5-(bicyclo[2.2.1]heptan-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-1-carboxylate (**21**)



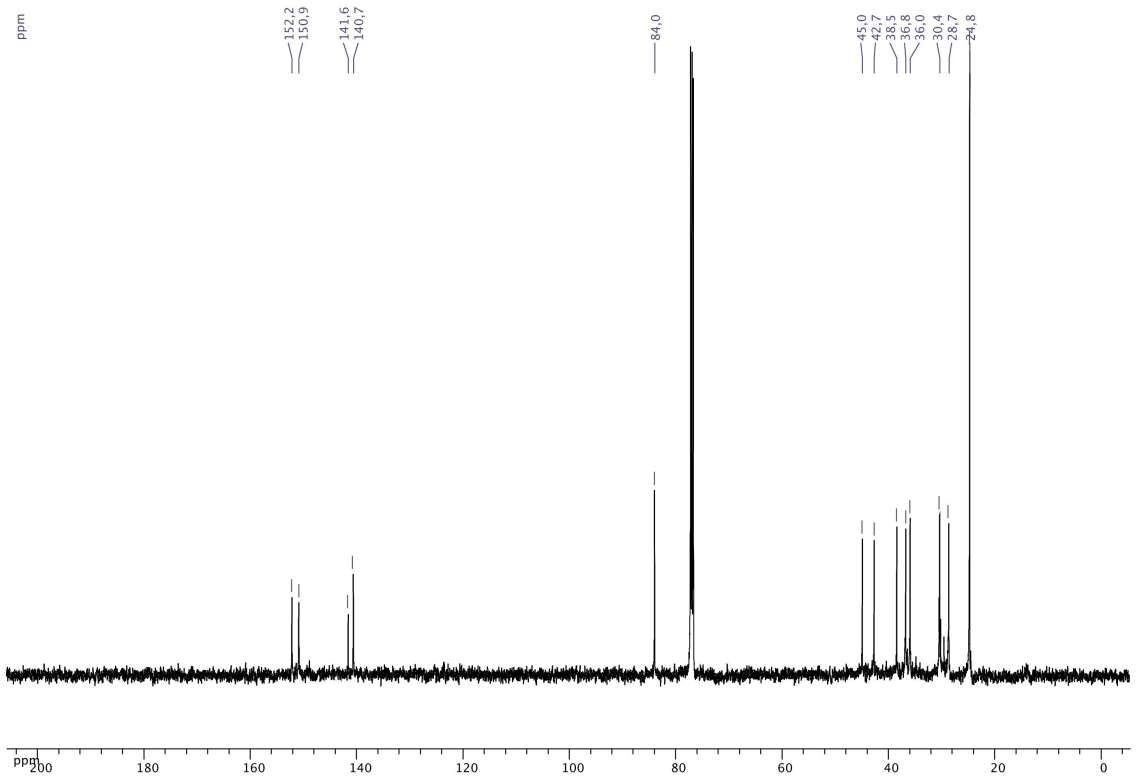
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *tert*-butyl 5-(bicyclo[2.2.1]heptan-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-1-carboxylate (**21**)



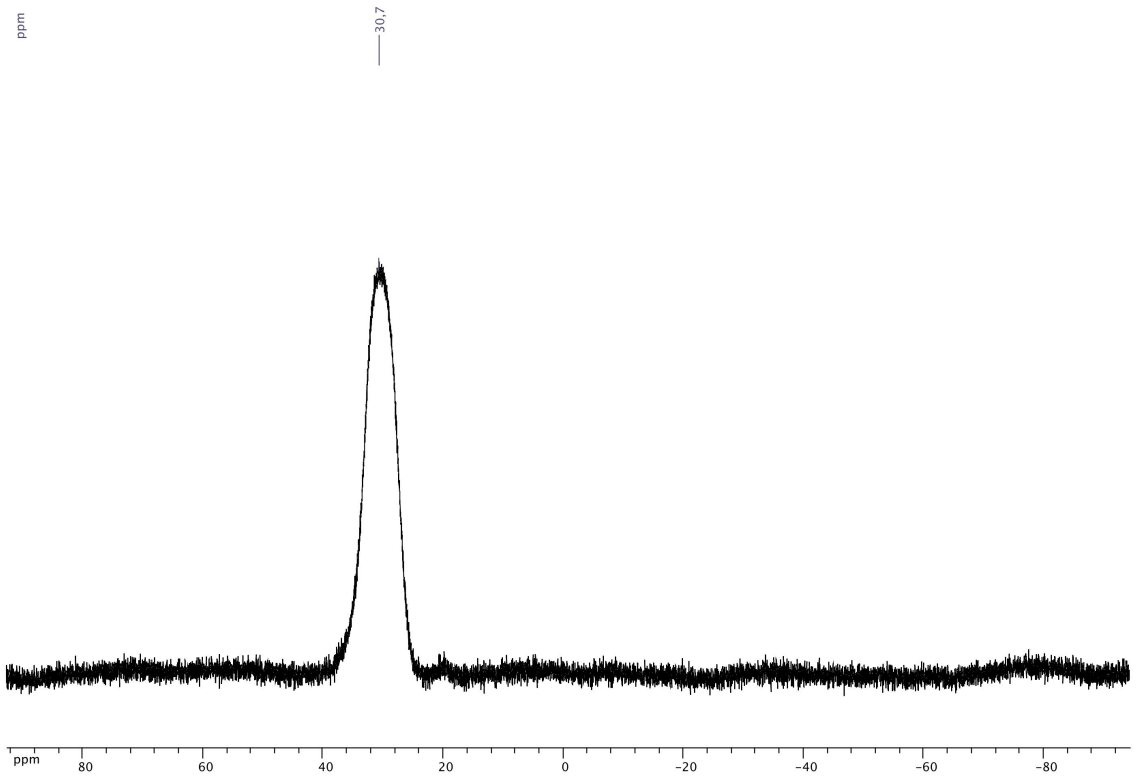
^{11}B NMR ($CDCl_3$, 128.4 MHz) of *tert*-butyl 5-(bicyclo[2.2.1]heptan-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-1-carboxylate (**21**)



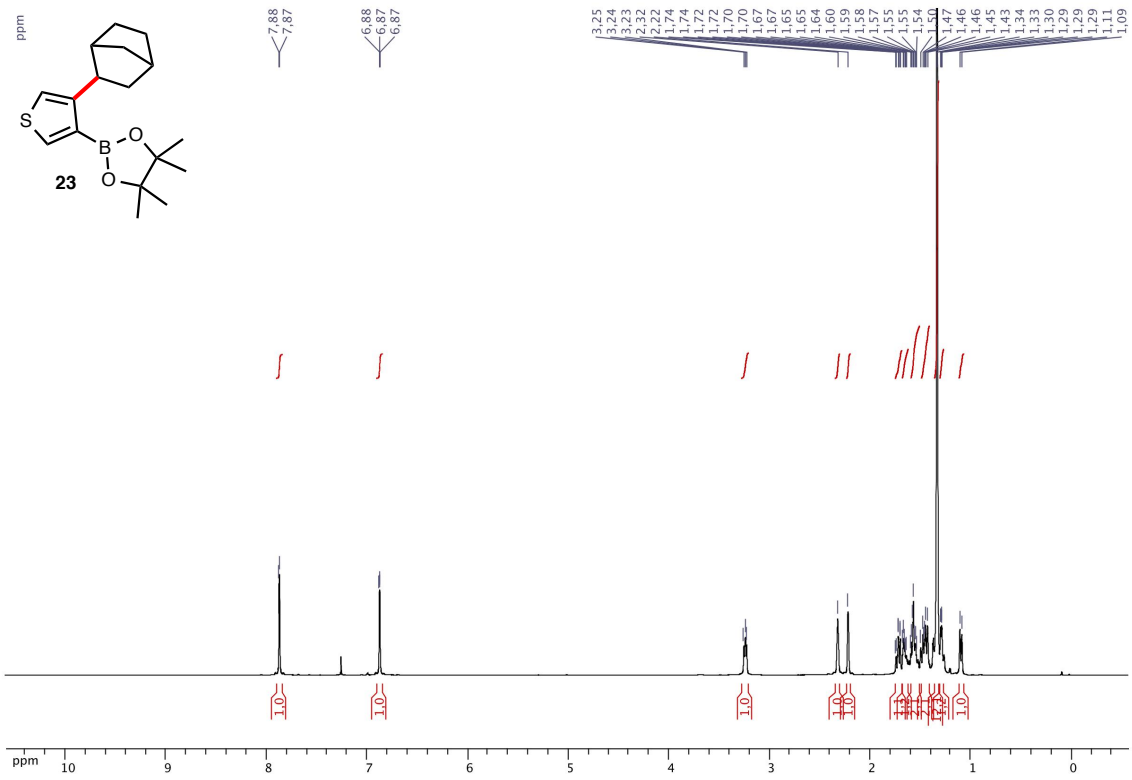
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 3-(bicyclo[2.2.1]heptan-2-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**22**)



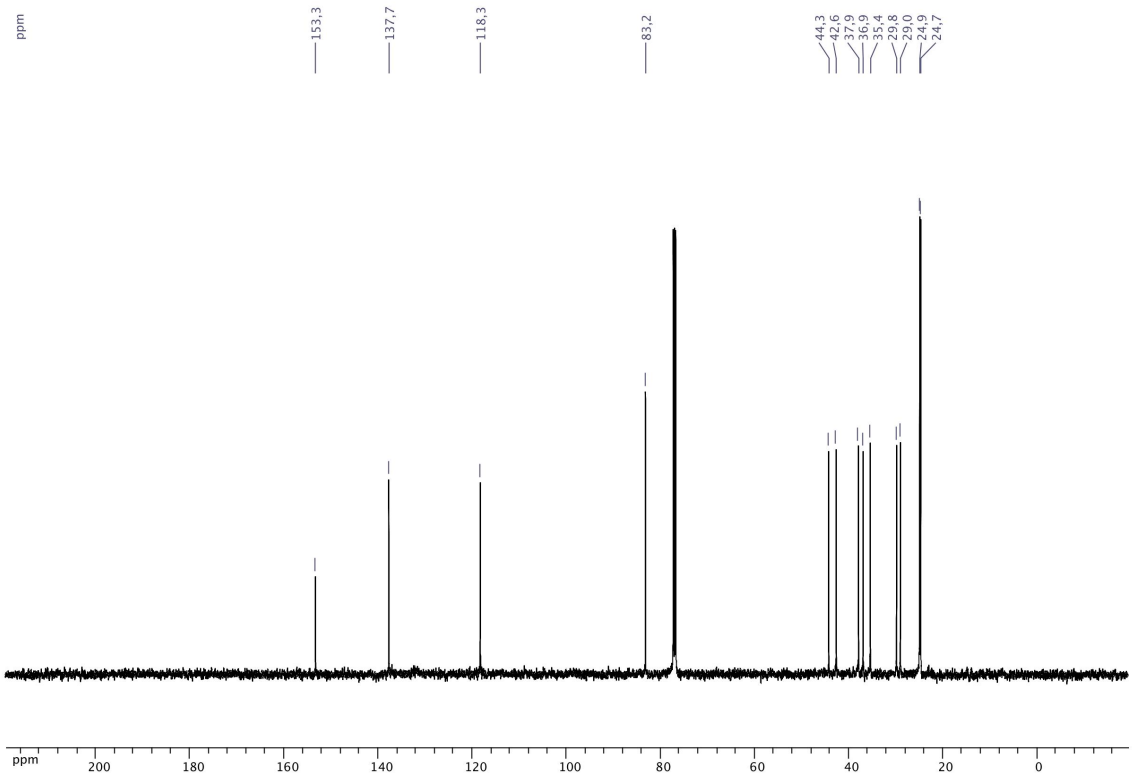
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 3-(bicyclo[2.2.1]heptan-2-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**22**)



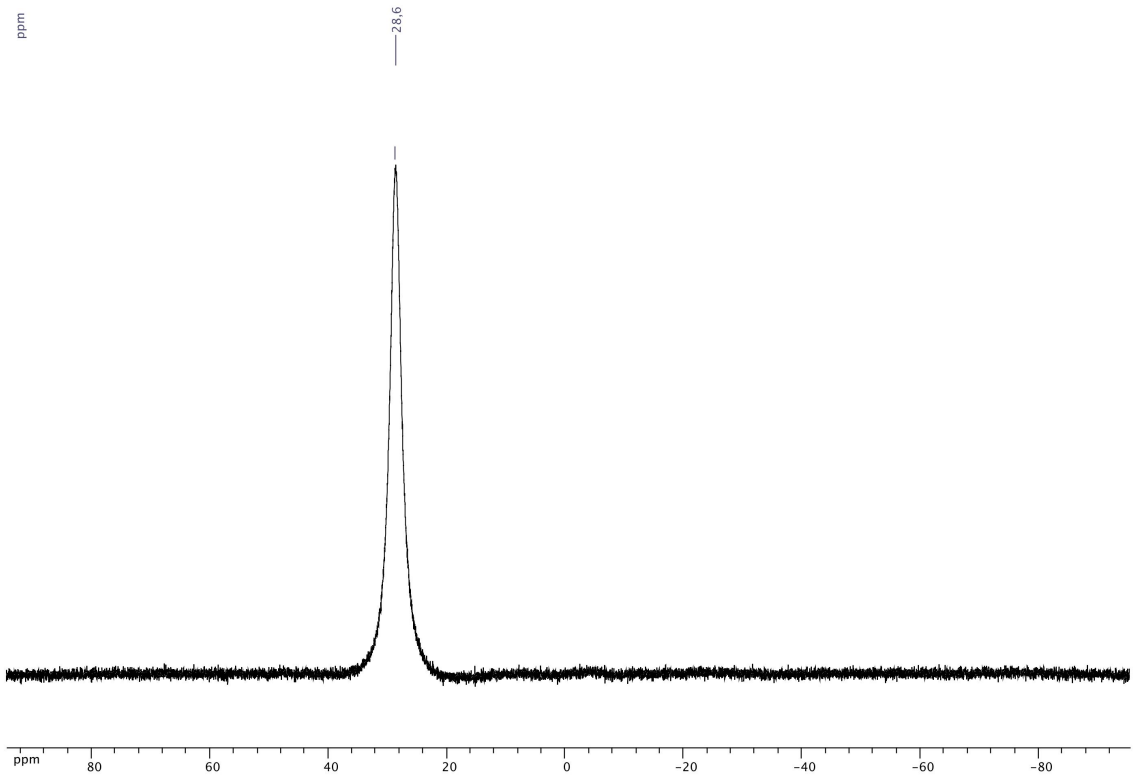
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 3-(bicyclo[2.2.1]heptan-2-yl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**22**)



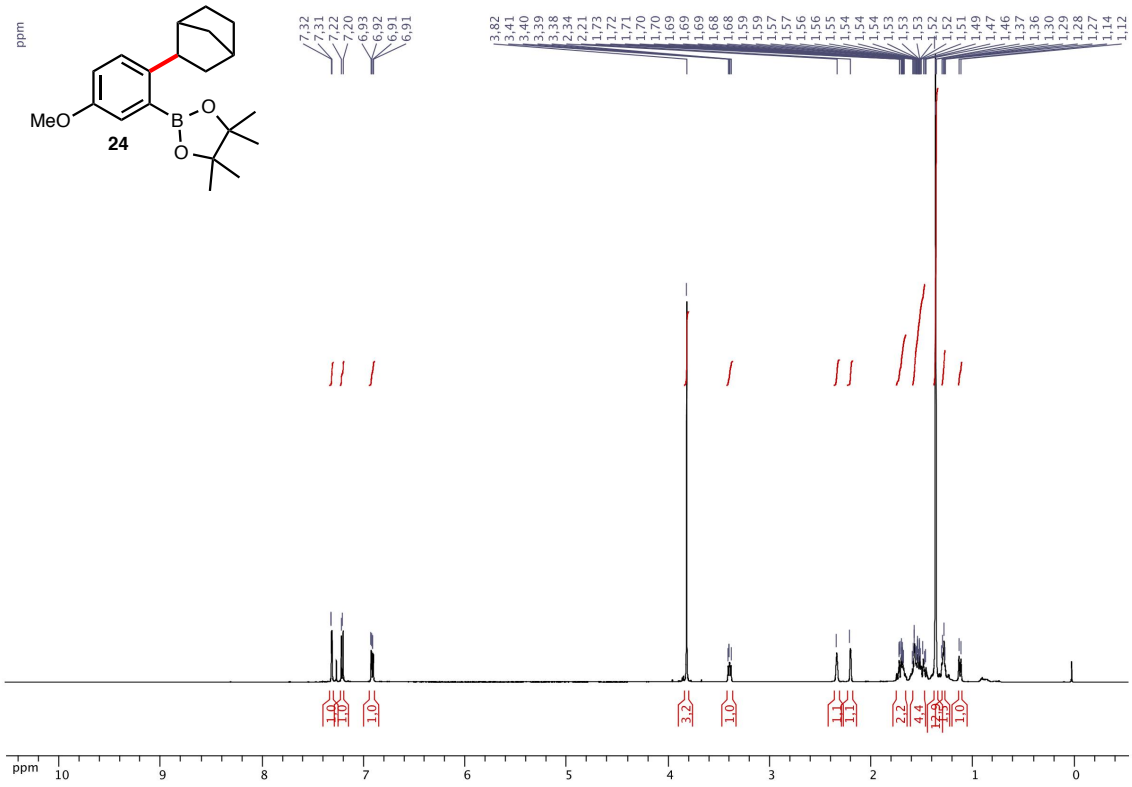
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(4-(bicyclo[2.2.1]heptan-2-yl)thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**23**)



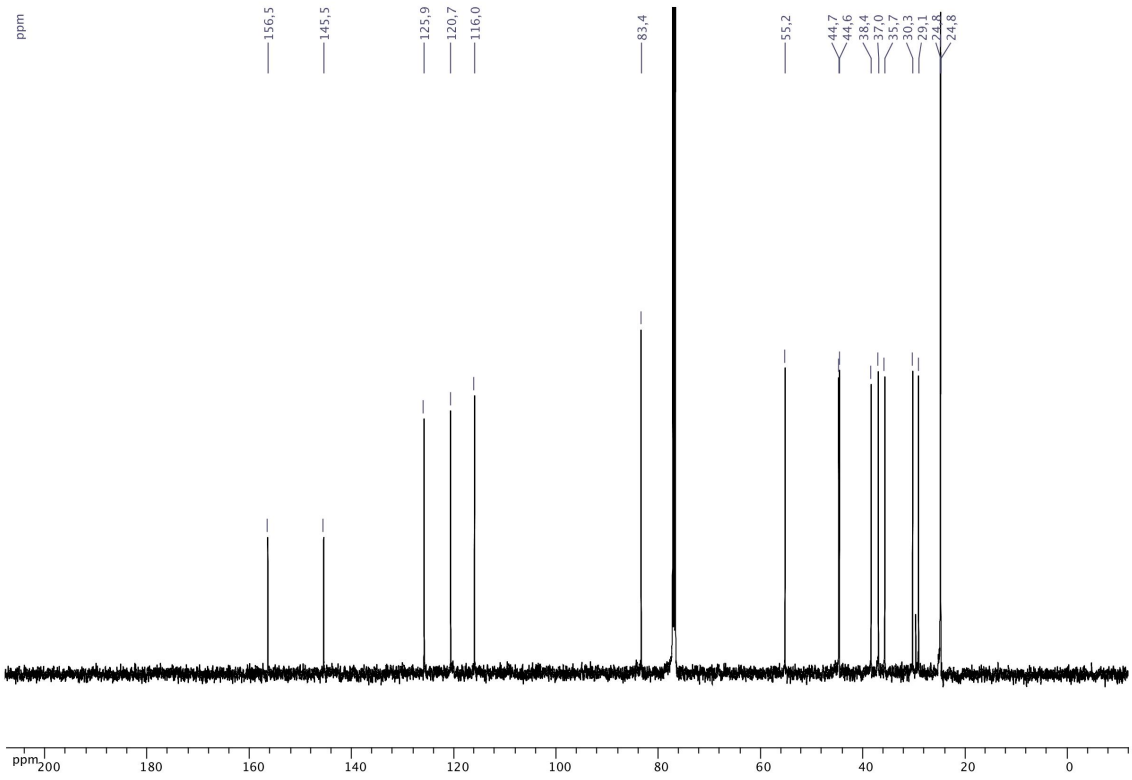
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(4-(bicyclo[2.2.1]heptan-2-yl)thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**23**)



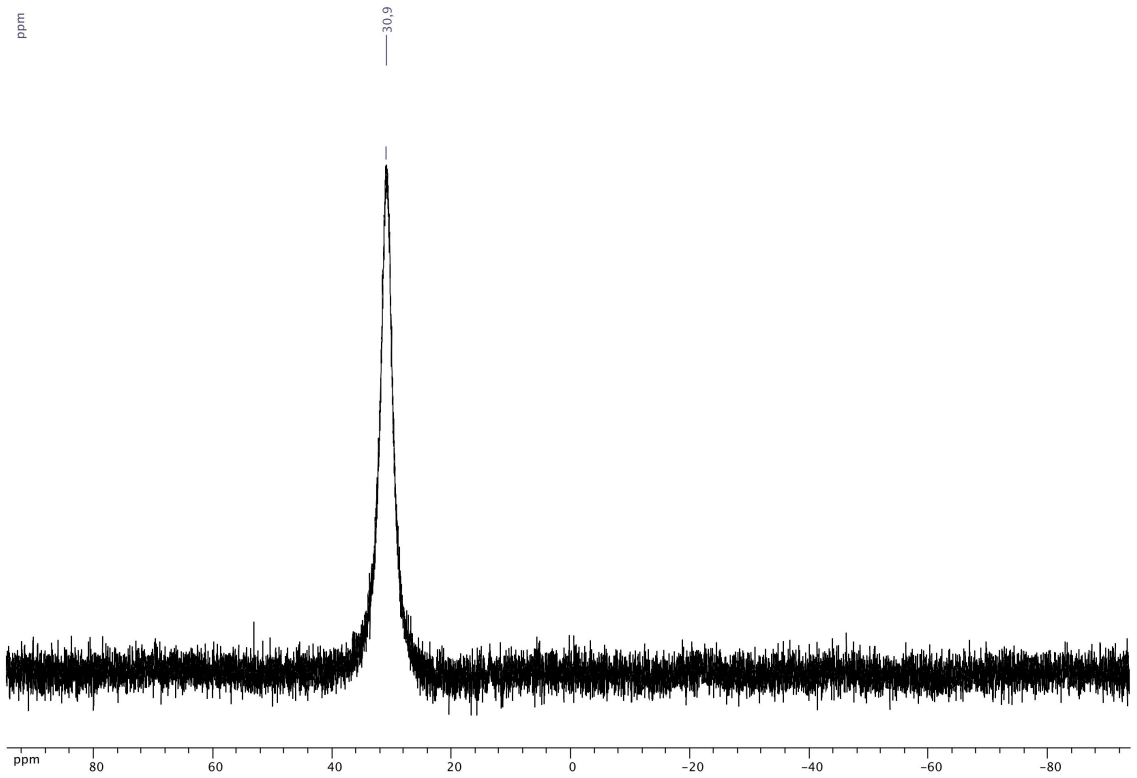
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 2-(4-(bicyclo[2.2.1]heptan-2-yl)thiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**23**)



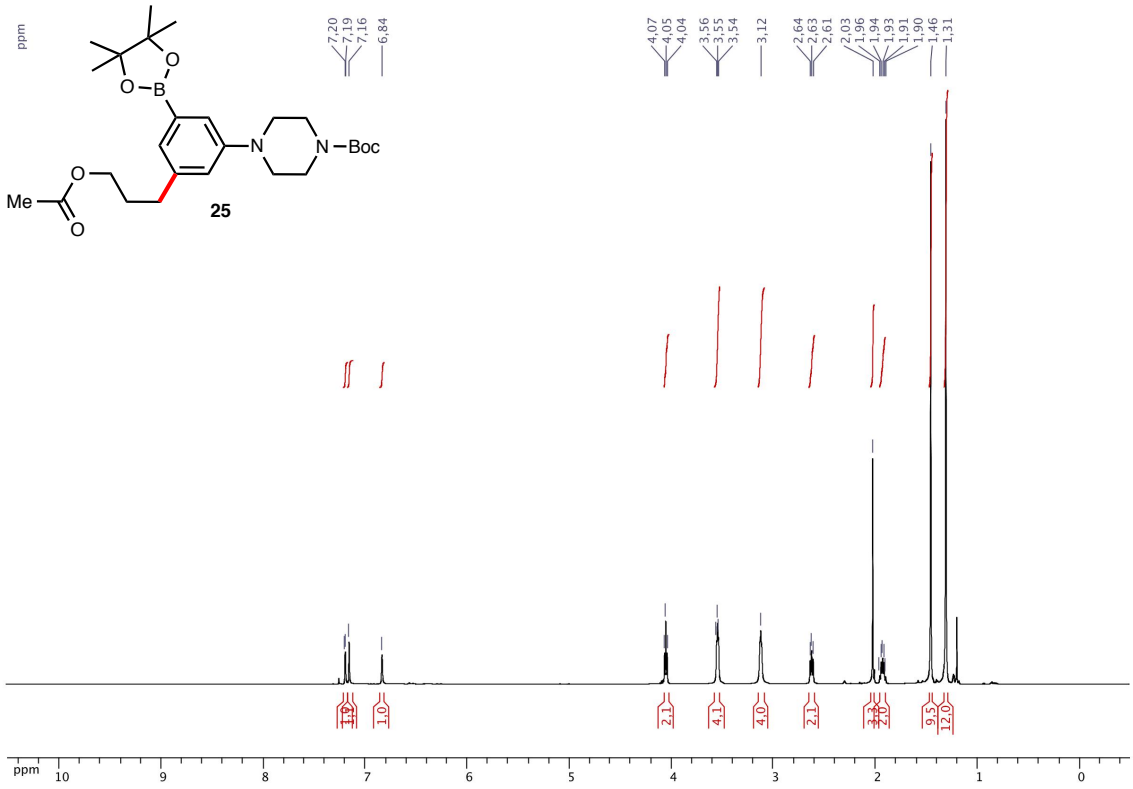
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(2-(bicyclo[2.2.1]heptan-2-yl)-5-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**24**)



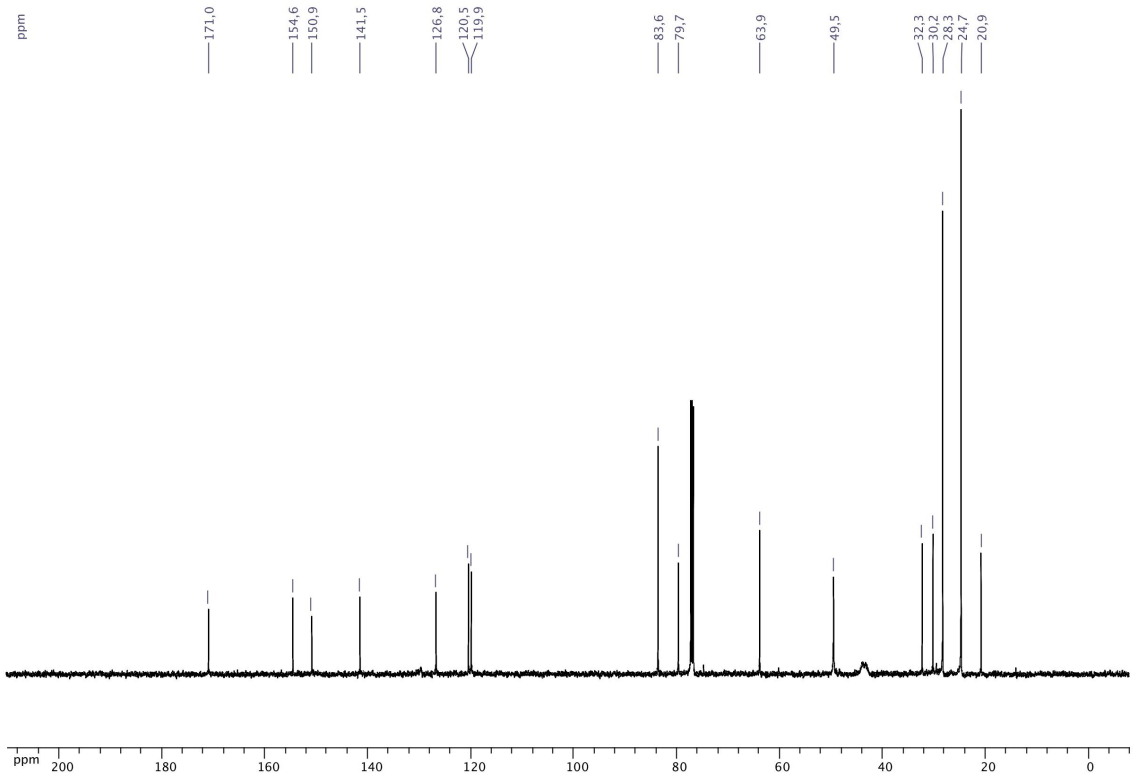
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(2-(bicyclo[2.2.1]heptan-2-yl)-5-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**24**)



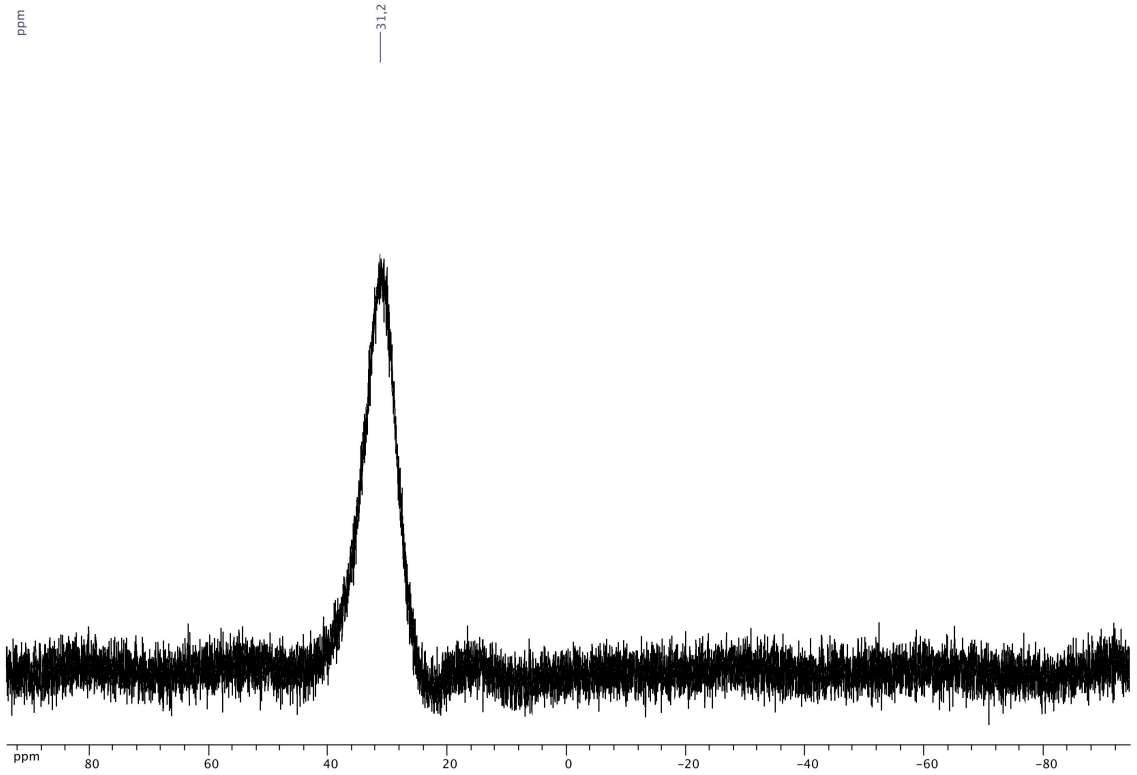
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 2-(2-(bicyclo[2.2.1]heptan-2-yl)-5-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**24**)



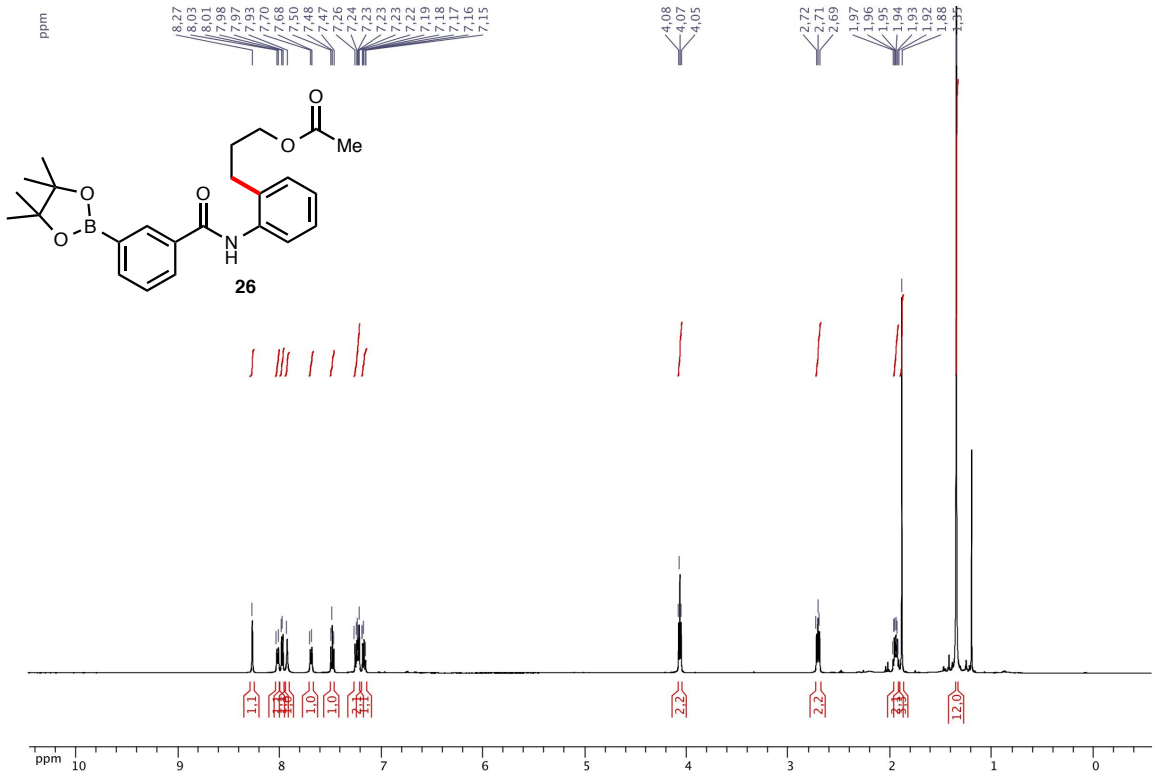
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *tert*-butyl 4-(3-(3-acetoxypropyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)piperazine-1-carboxylate (**25**)



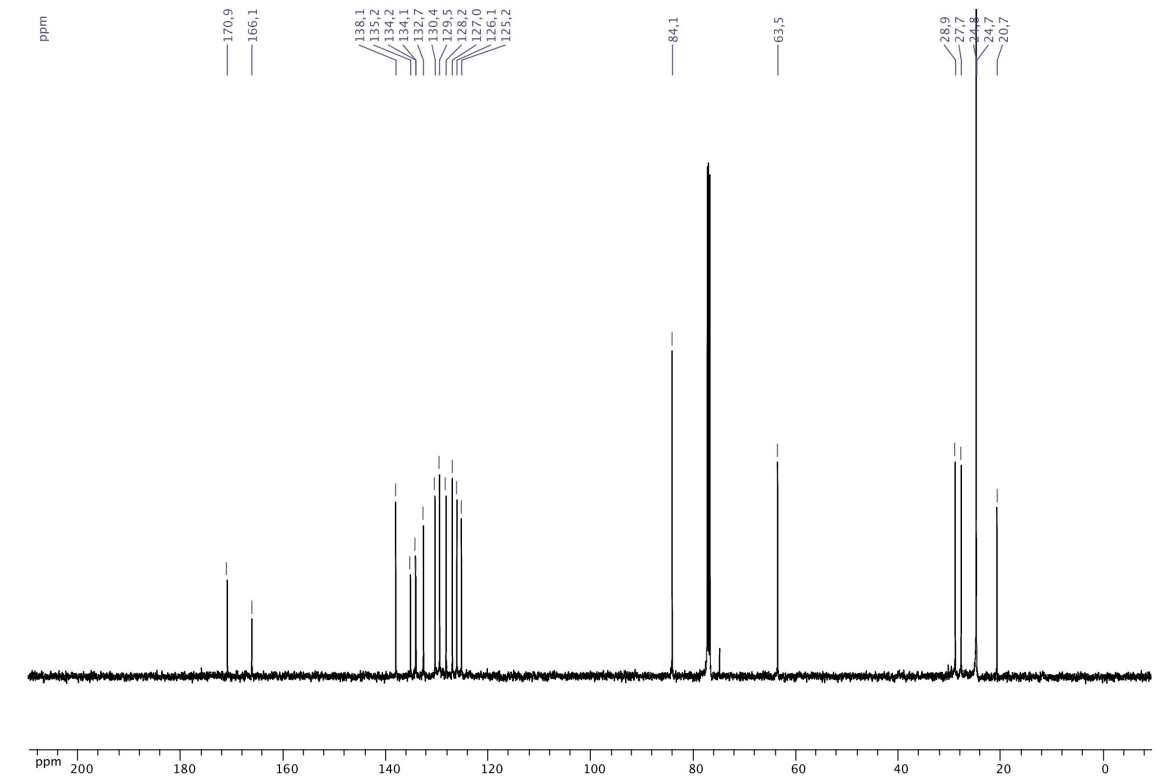
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *tert*-butyl 4-(3-(3-acetoxypropyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)piperazine-1-carboxylate (**25**)



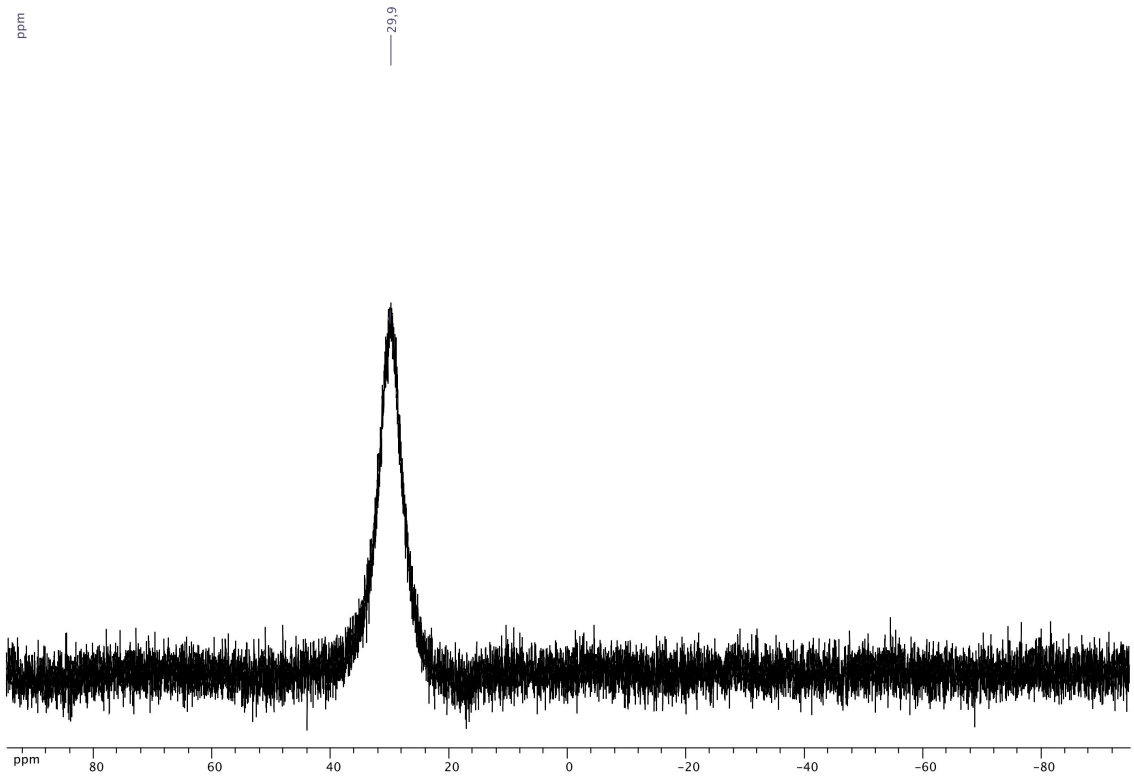
^{11}B NMR ($CDCl_3$, 128.4 MHz) of *tert*-butyl 4-(3-(3-acetoxypropyl)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)piperazine-1-carboxylate (**25**)



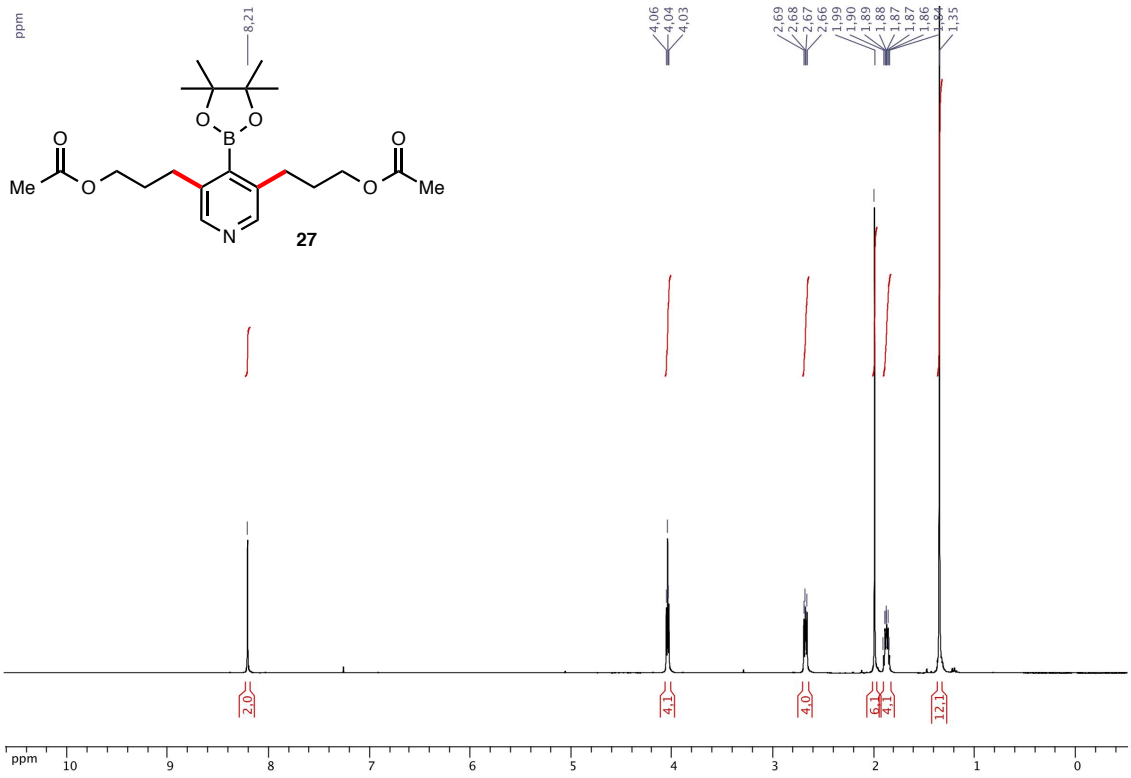
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 3-(2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamido)phenyl)propyl acetate (**26**)



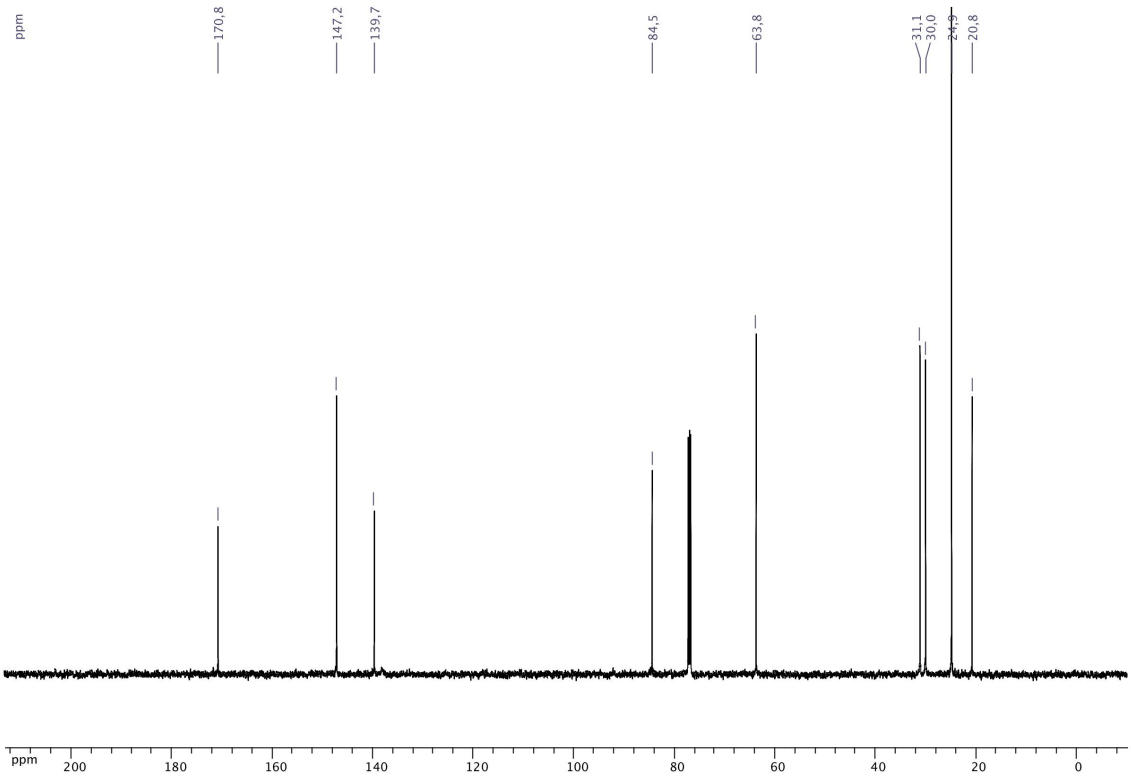
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 3-(2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamido)phenyl)propyl acetate (**26**)



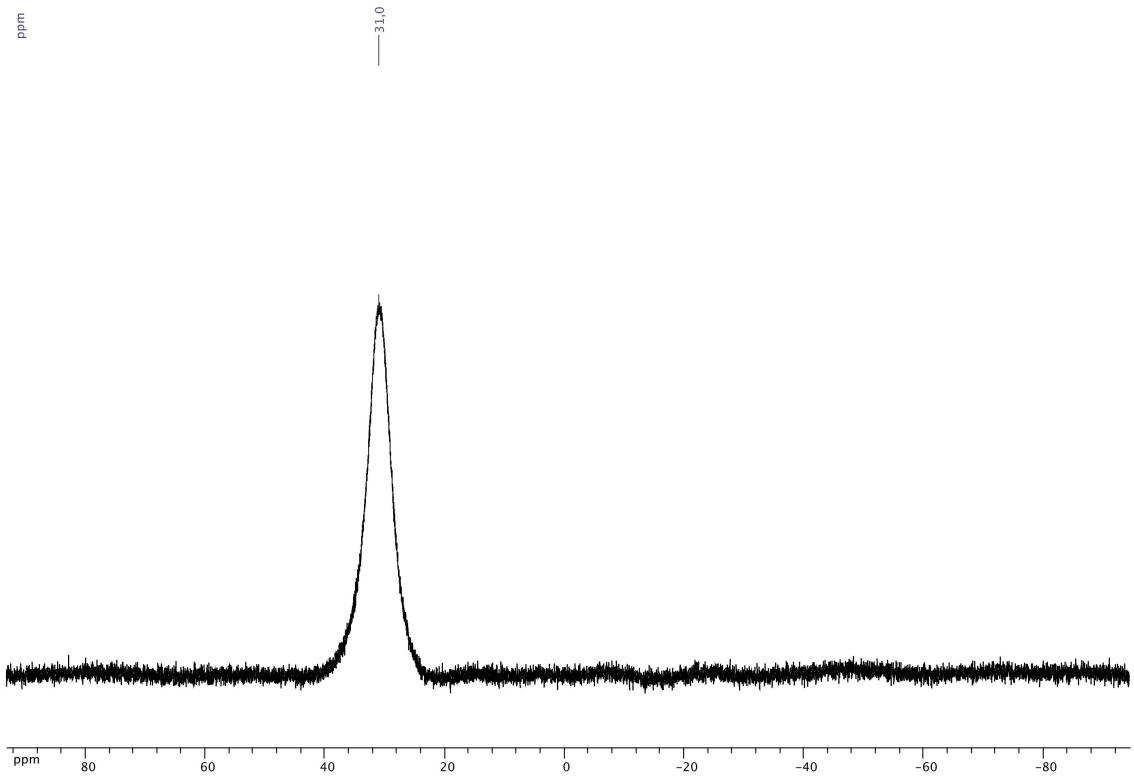
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 3-(2-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamido)phenyl)propyl acetate (**26**)



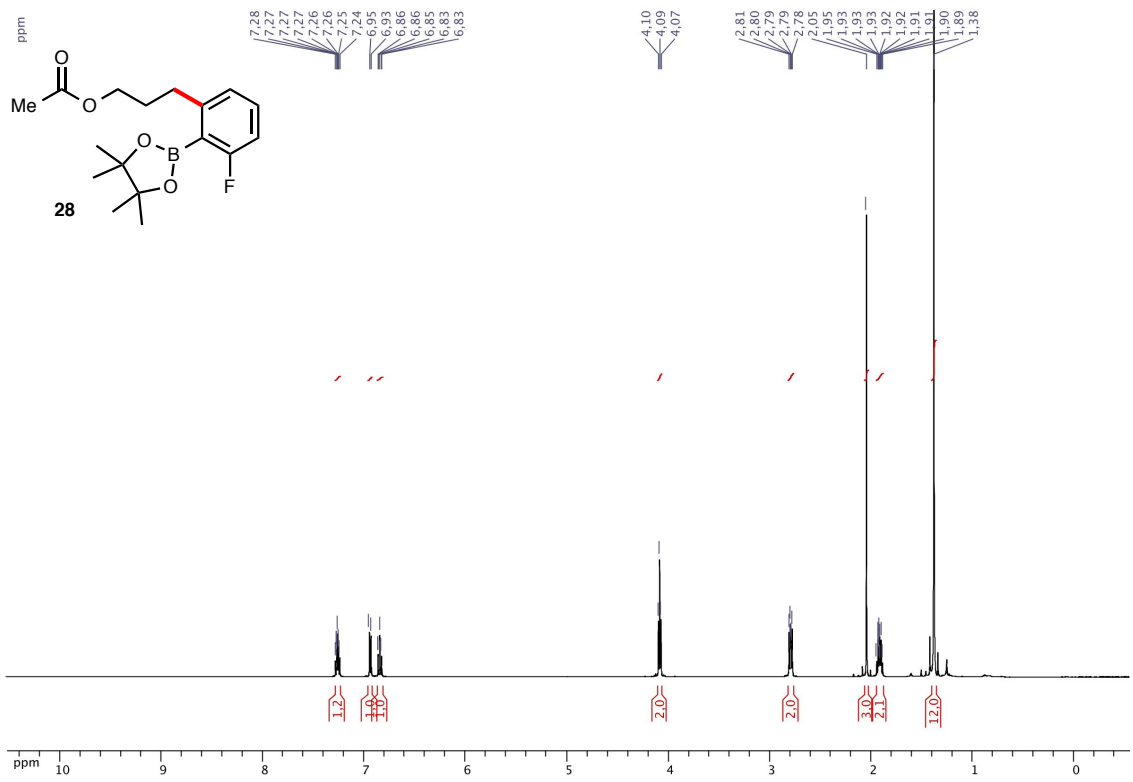
^{1}H NMR ($CDCl_3$, 500.4 MHz) of (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine-3,5-diyl)bis(propane-3,1-diyl) diacetate (**27**)



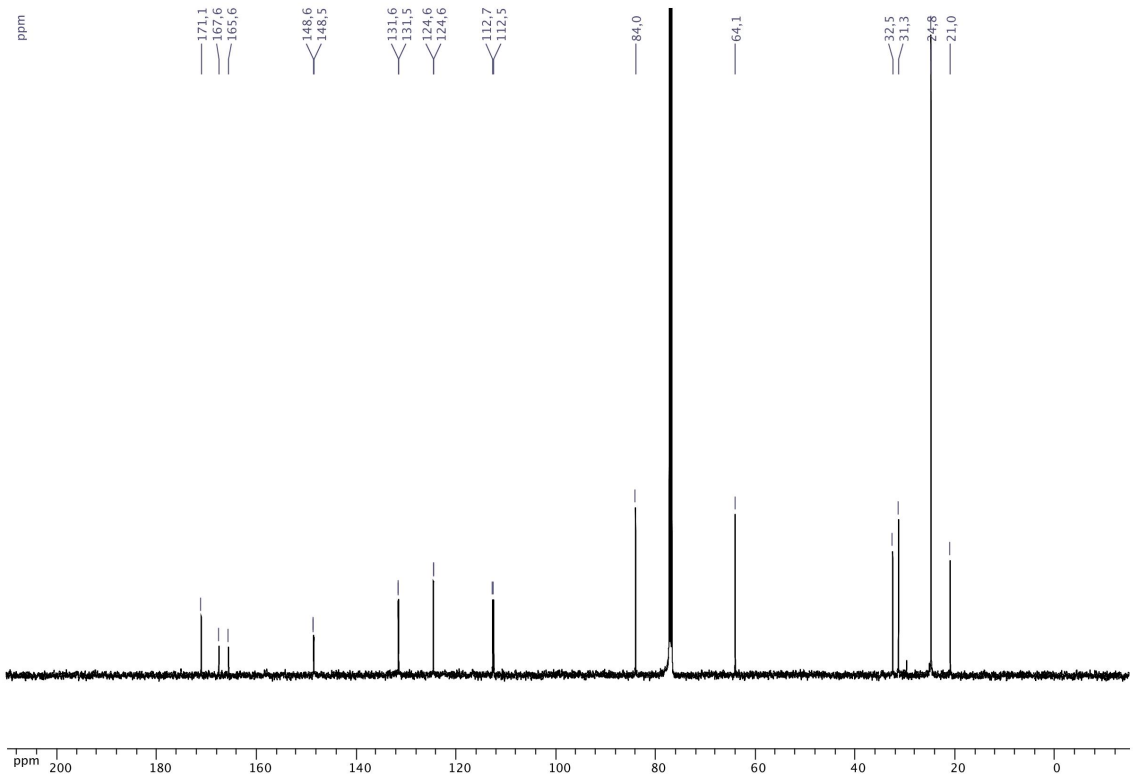
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine-3,5-diyl)bis(propane-3,1-diyl) diacetate (**27**)



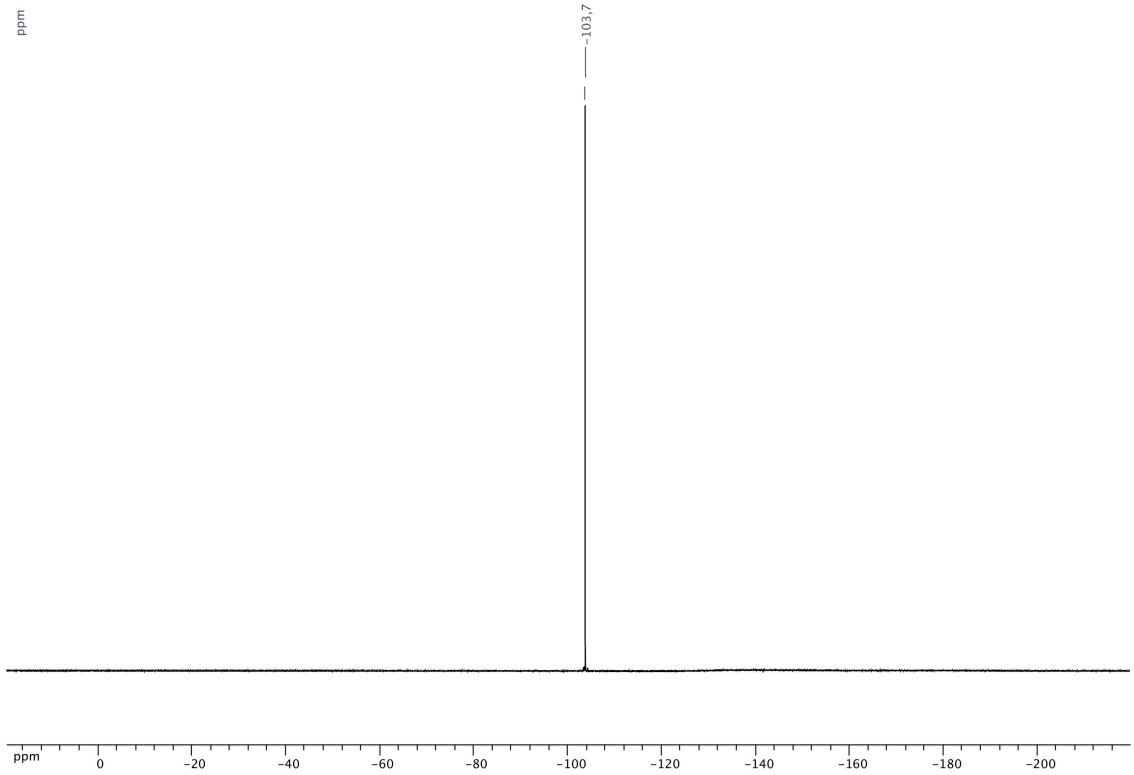
^{11}B NMR ($CDCl_3$, 128.4 MHz) of (4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine-3,5-diyl)bis(propane-3,1-diyl) diacetate (**27**)



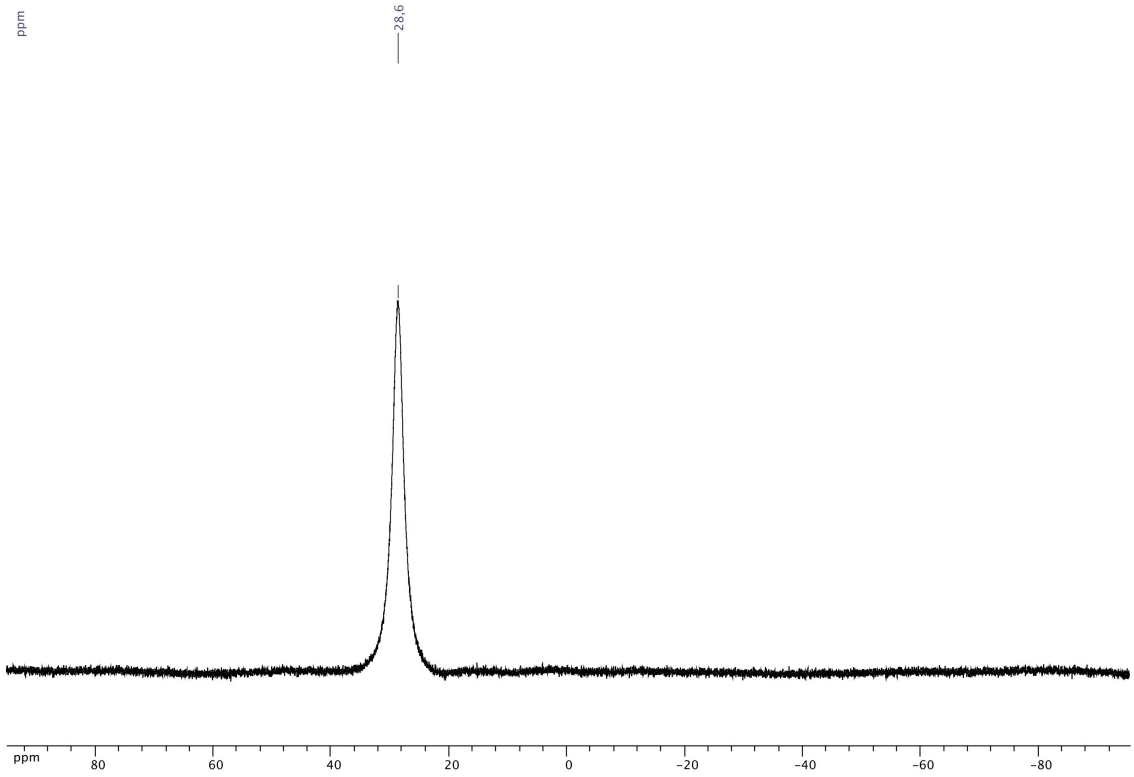
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 3-(3-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl acetate (**28**)



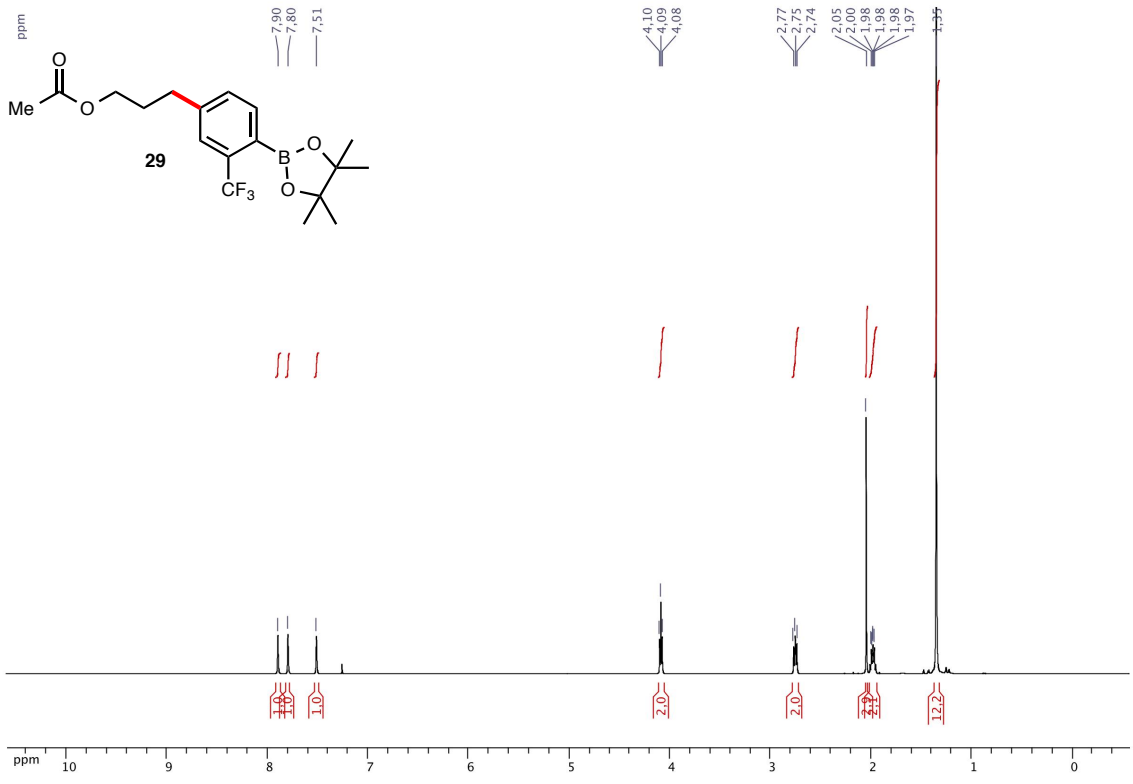
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 3-(3-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl acetate (**28**)



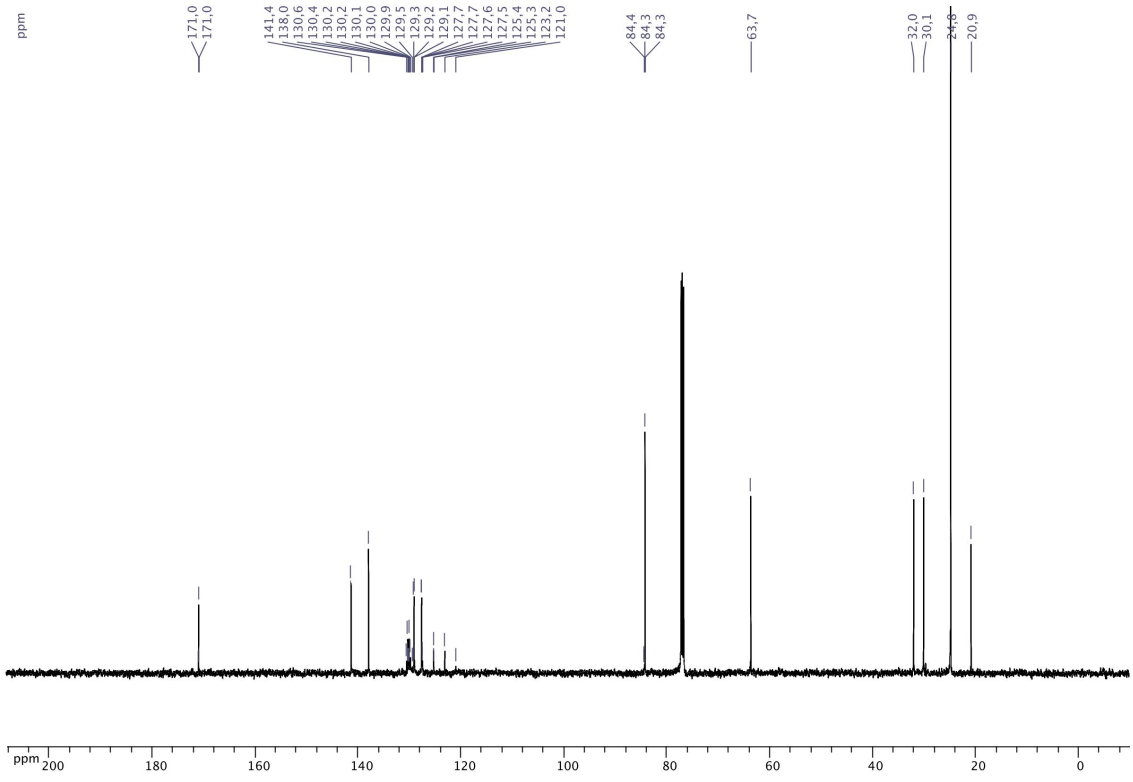
^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz) of 3-(3-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl acetate (**28**)



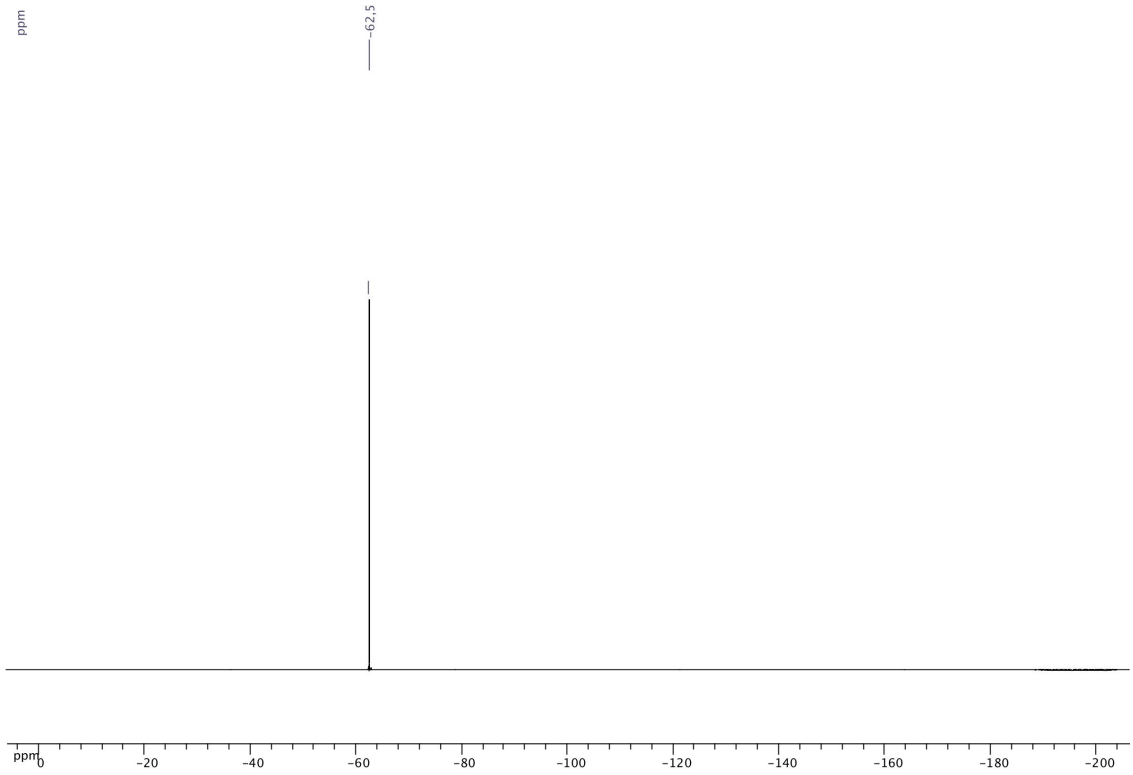
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 3-(3-fluoro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl acetate (**28**)



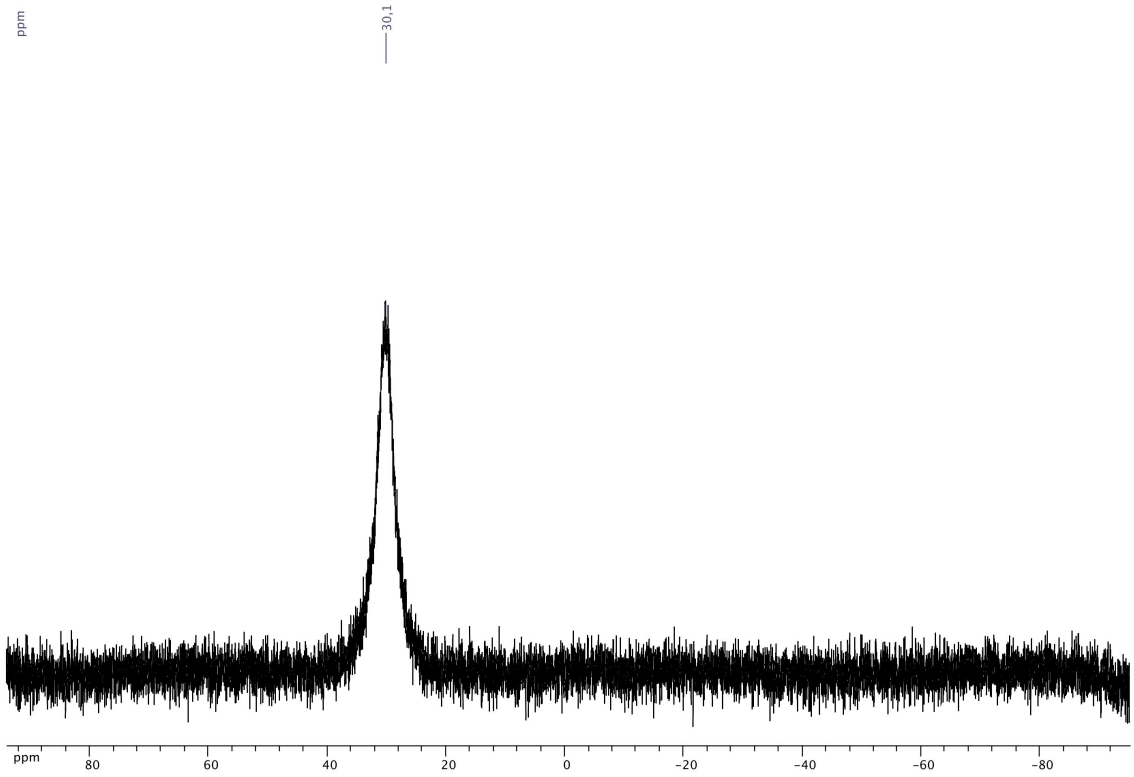
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trifluoromethyl)phenyl)propyl acetate (**29**)



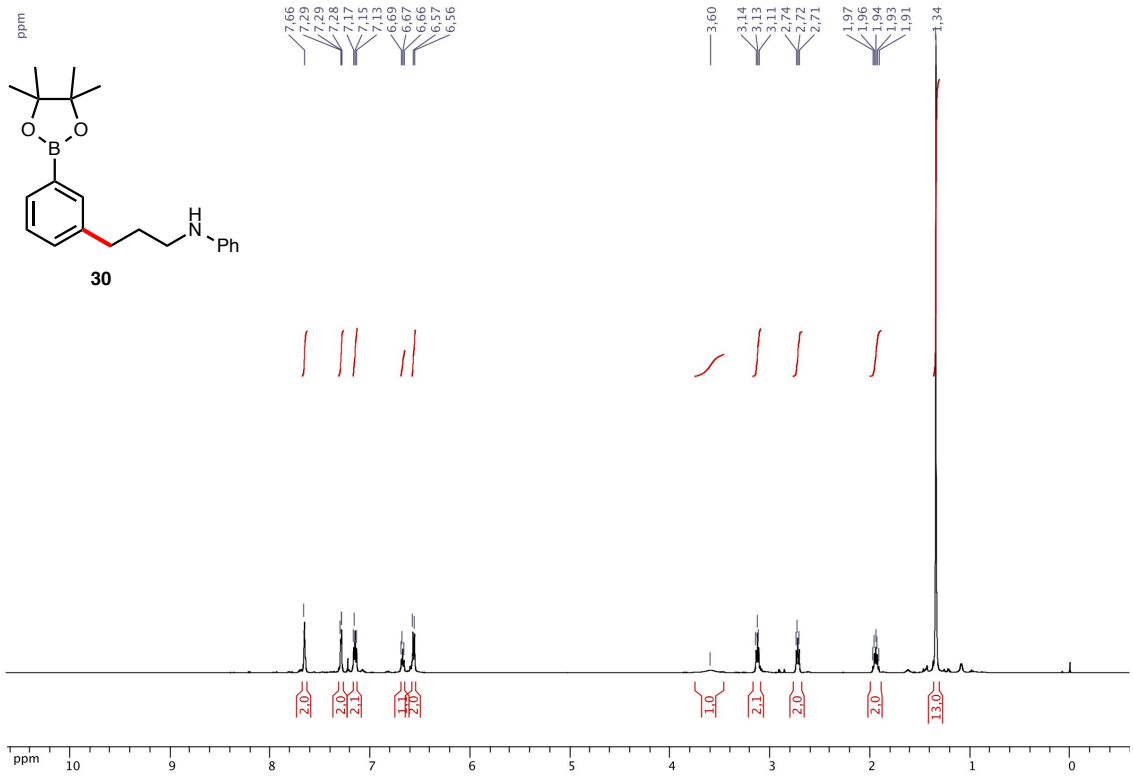
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trifluoromethyl)phenyl)propyl acetate (**29**)



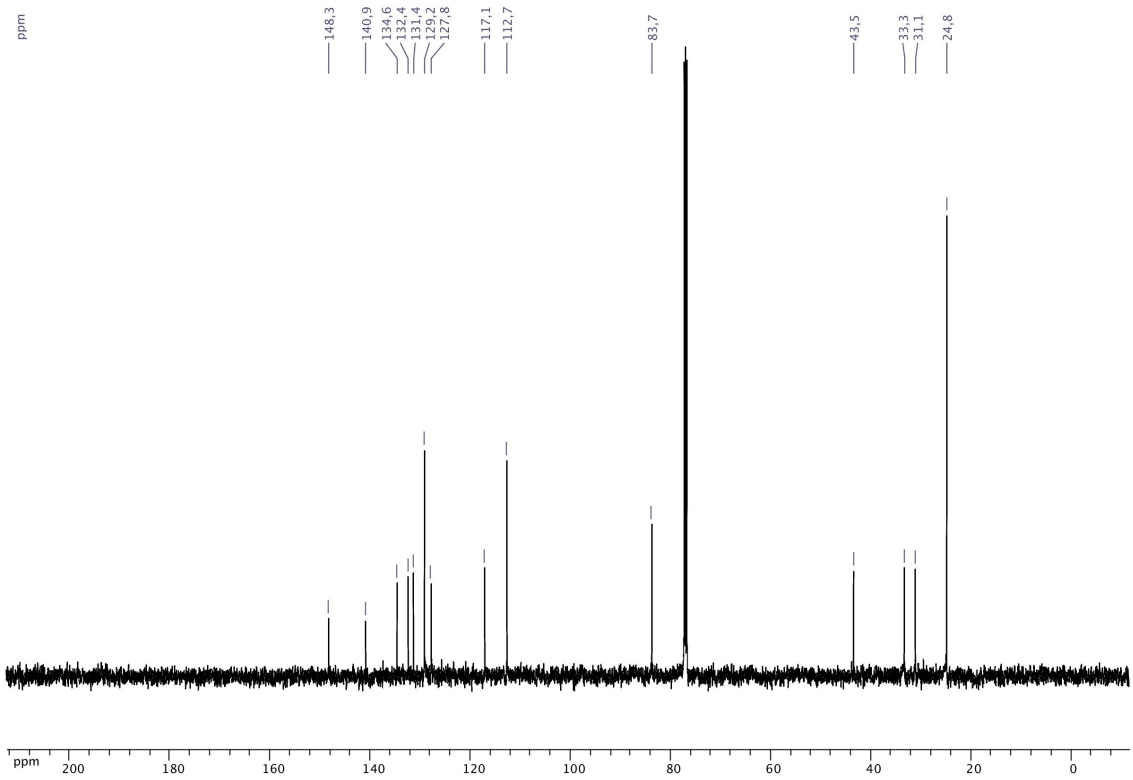
^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz) of 3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trifluoromethyl)phenyl)propyl acetate (**29**)



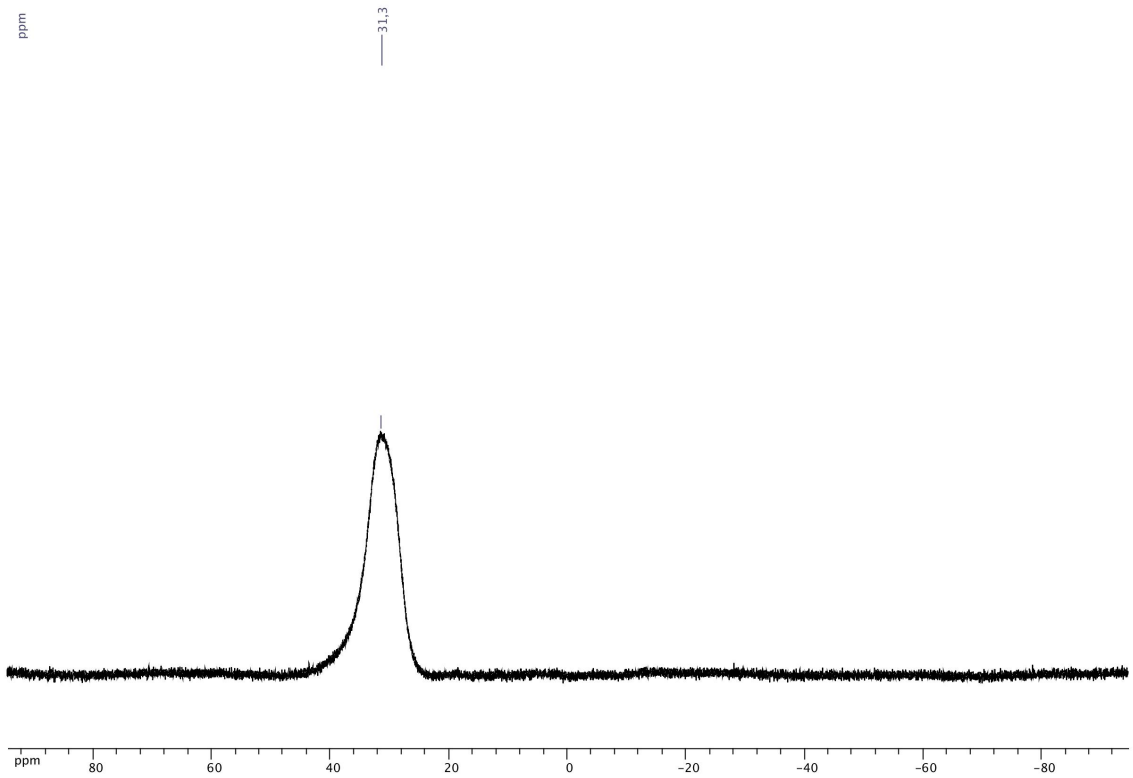
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trifluoromethyl)phenyl)propyl acetate (**29**)



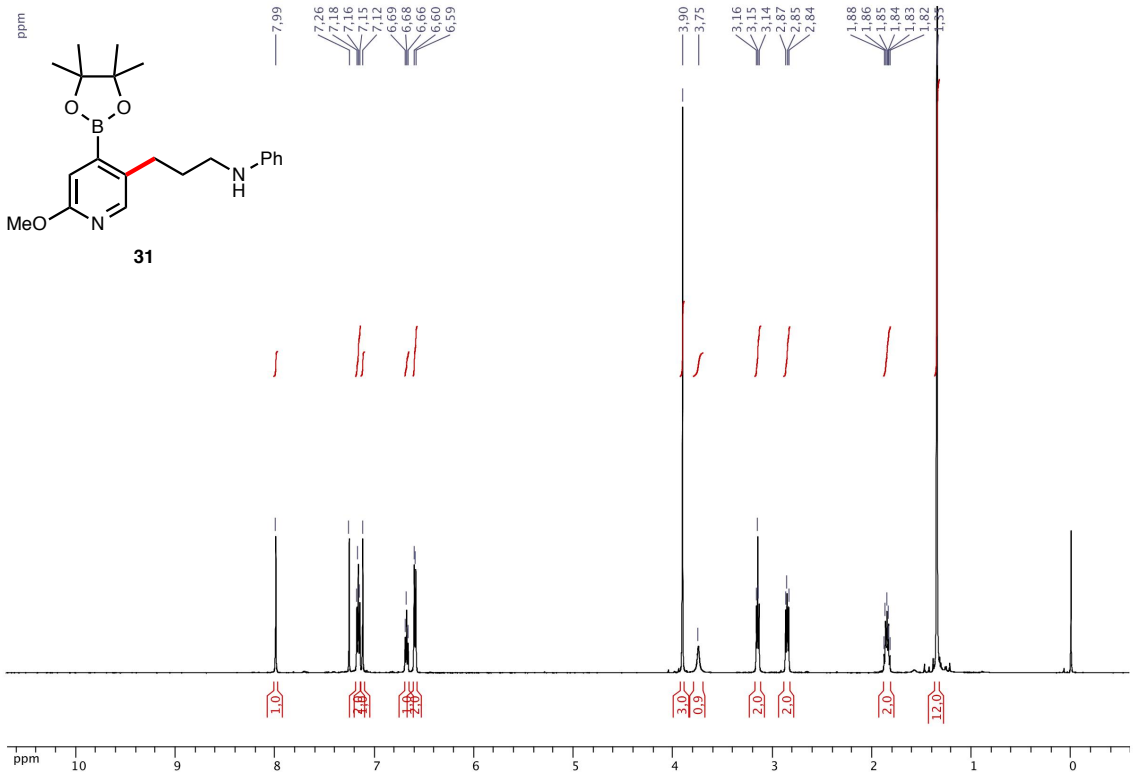
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *N*-(3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)aniline (**30**)



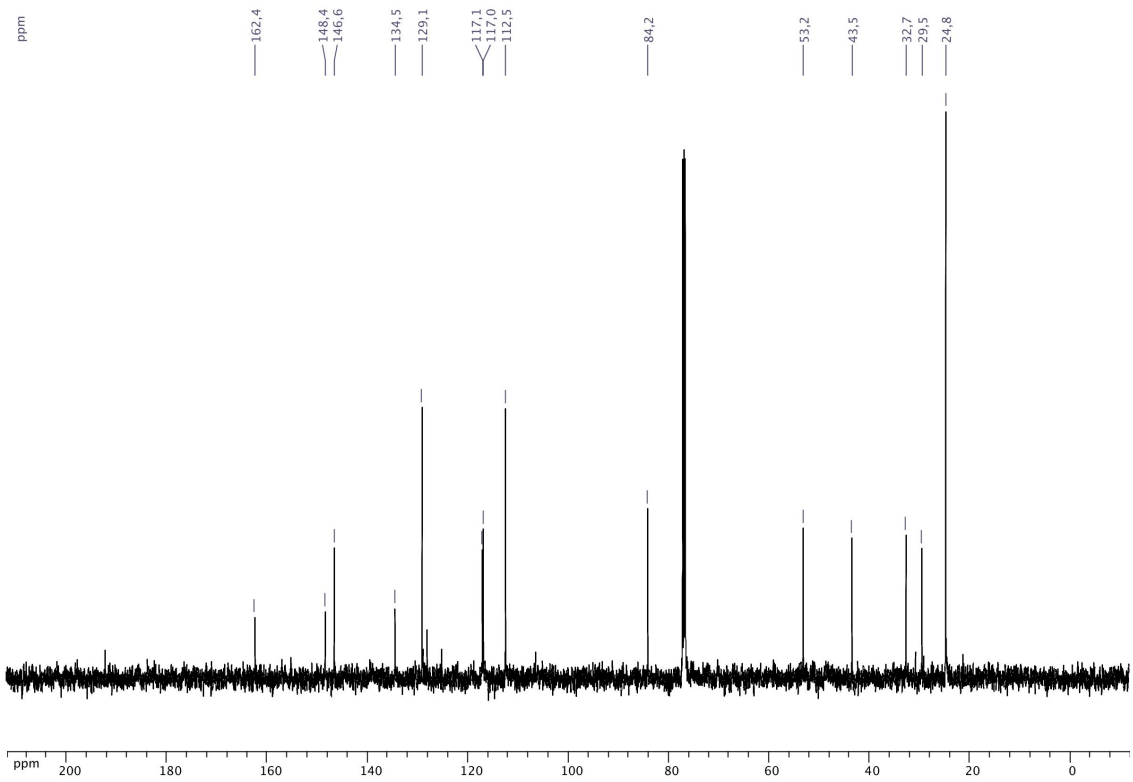
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *N*-(3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)aniline (**30**)



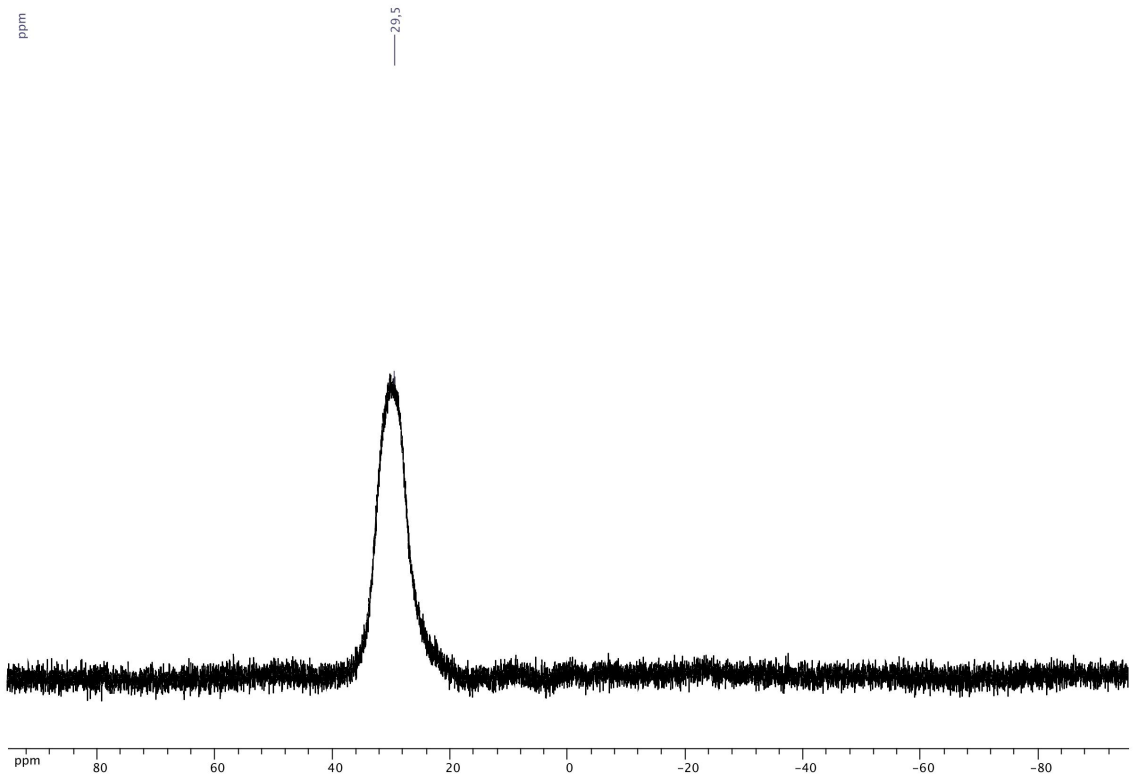
^{11}B NMR ($CDCl_3$, 128.4 MHz) of *N*-(3-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)aniline (**30**)



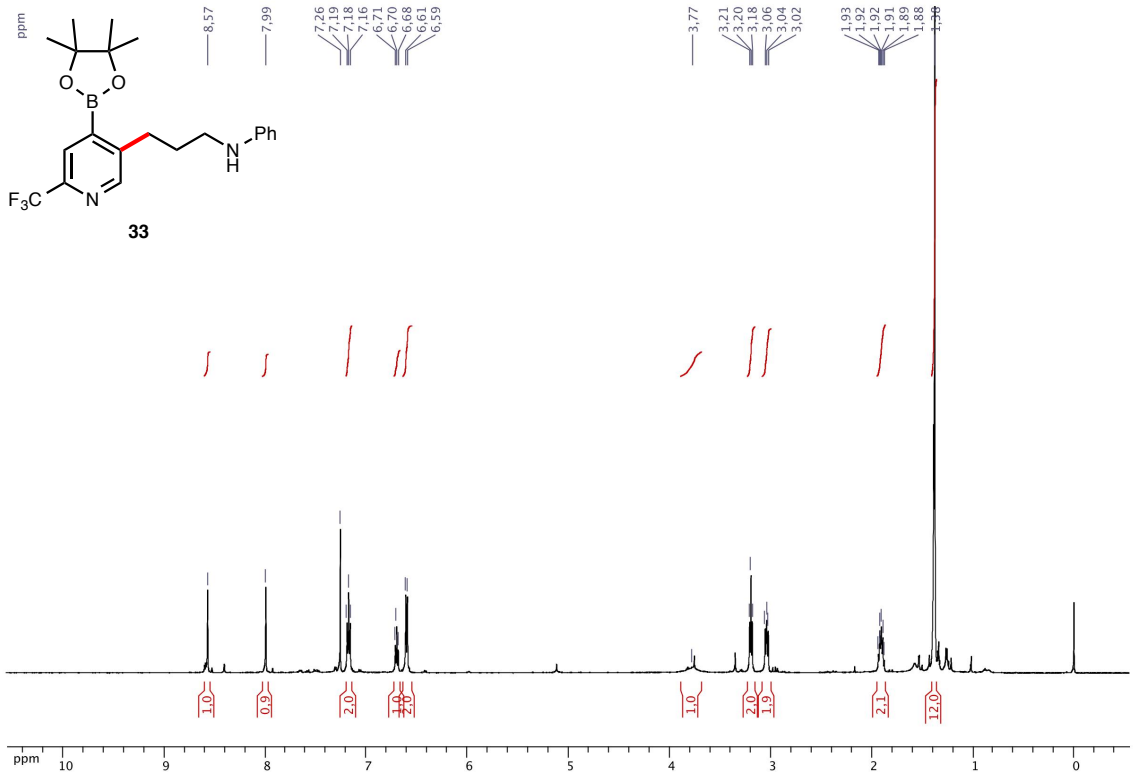
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *N*-(3-(6-methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-yl)propyl)aniline (**31**)



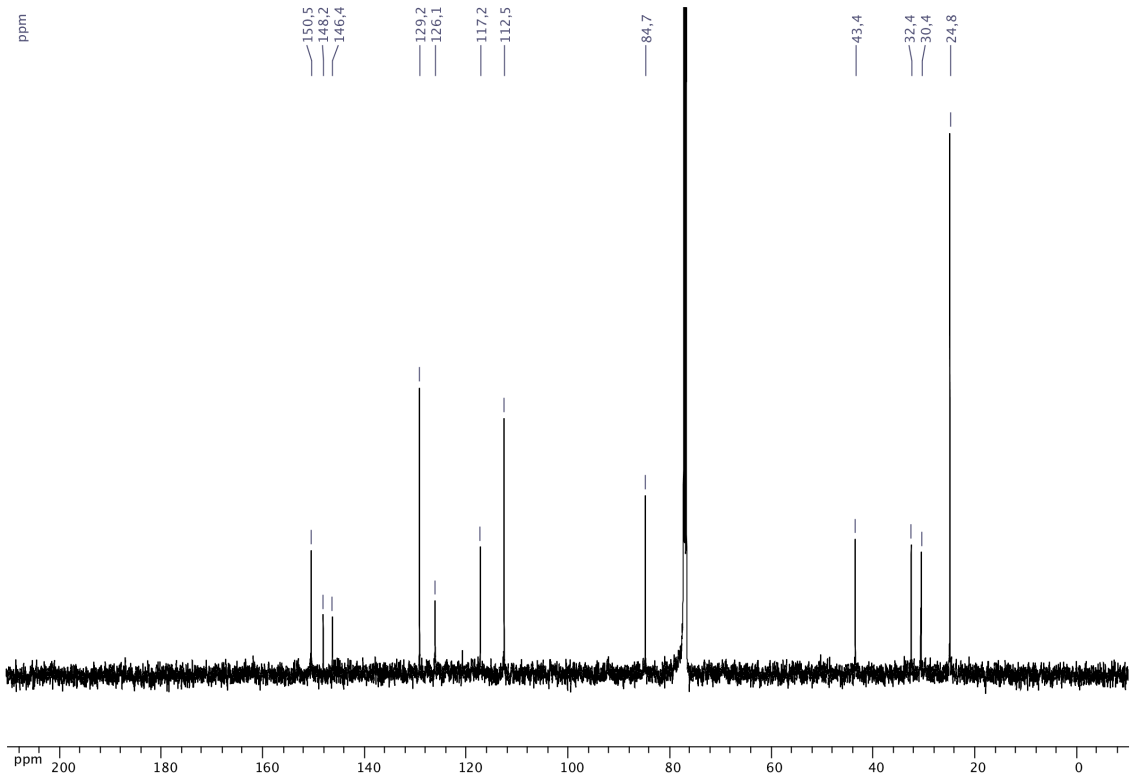
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *N*-(3-(6-methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-yl)propyl)aniline (**31**)



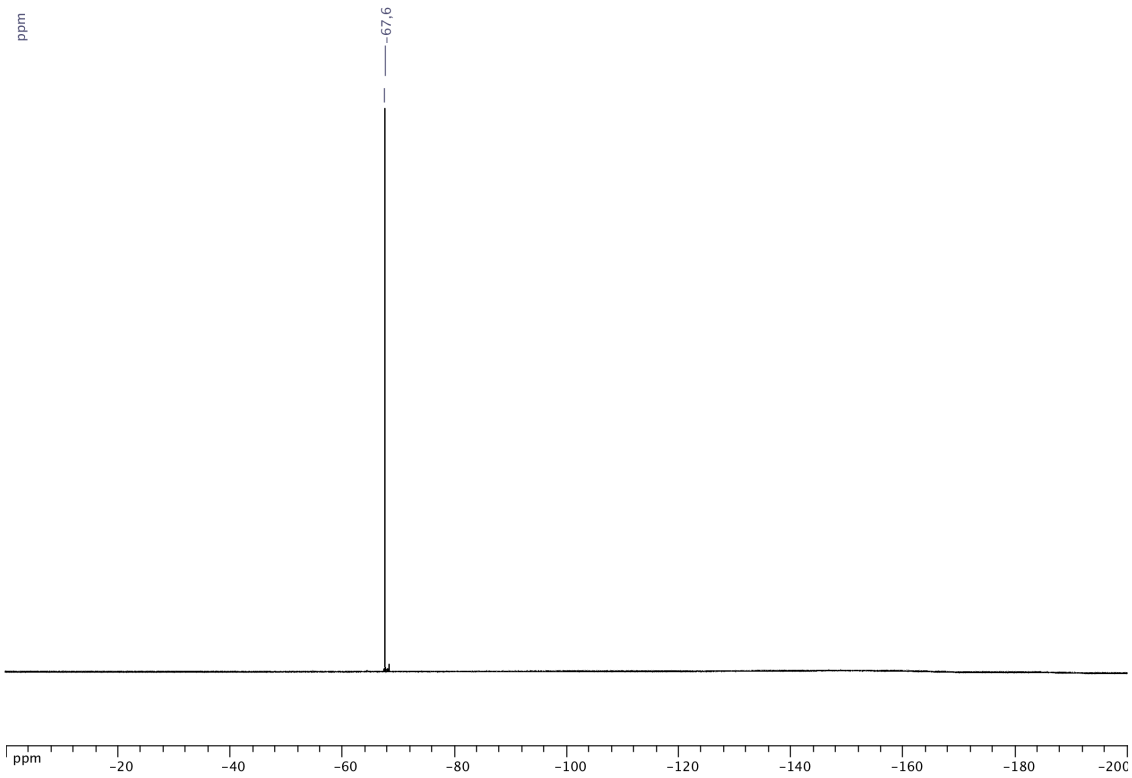
^{11}B NMR ($CDCl_3$, 128.4 MHz) of *N*-(3-(6-methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-yl)propyl)aniline (**31**)



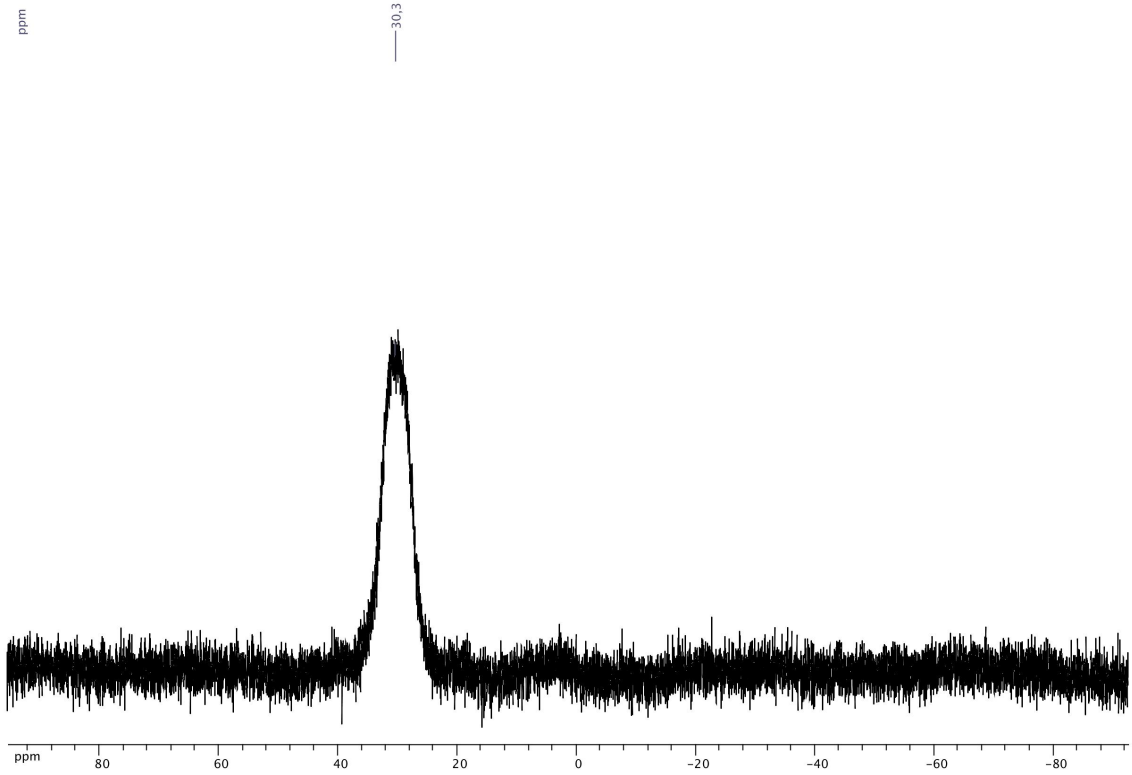
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *N*-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trifluoromethyl)pyridin-2-yl)propyl)aniline (**33**)



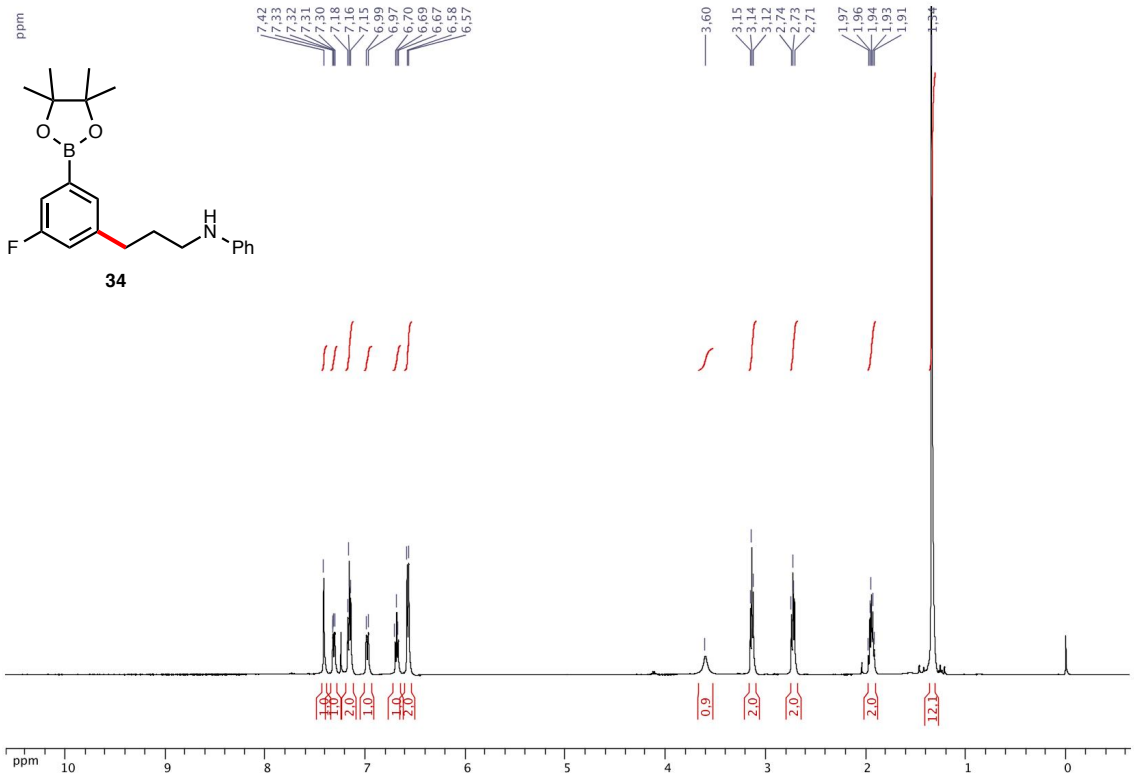
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *N*-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trifluoromethyl)pyridin-2-yl)propyl)aniline (**33**)



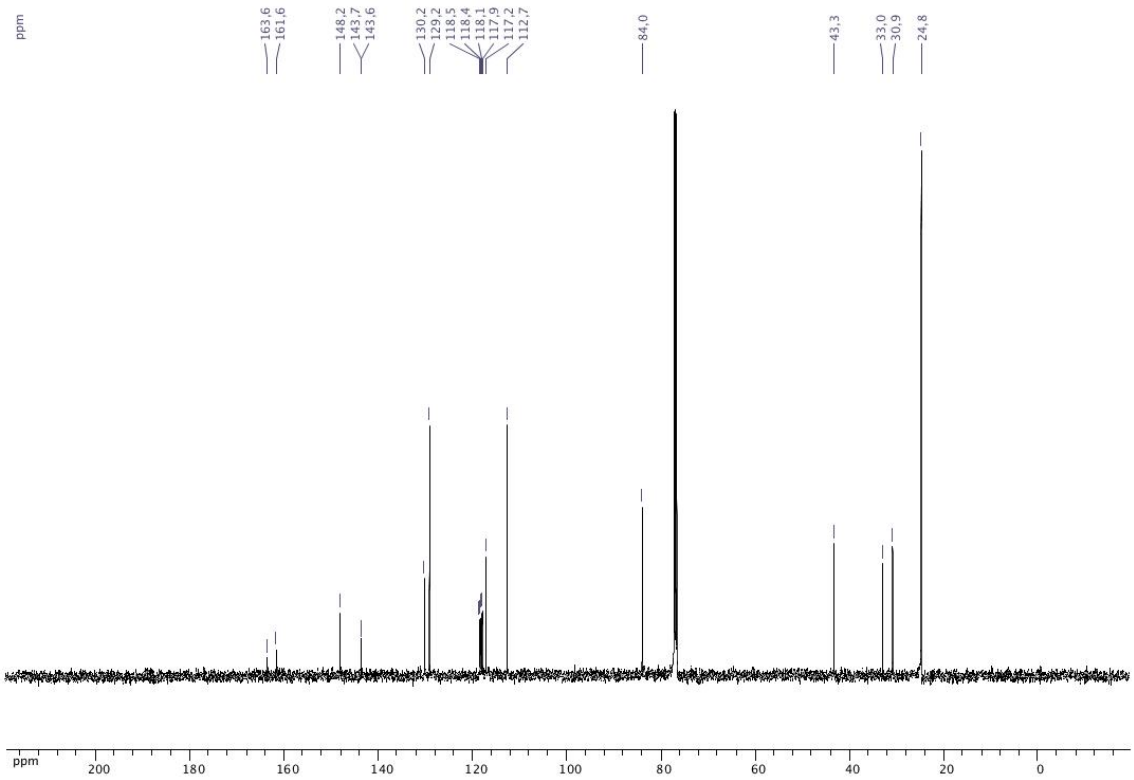
^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz) of *N*-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trifluoromethyl)pyridin-2-yl)propyl)aniline (**33**)



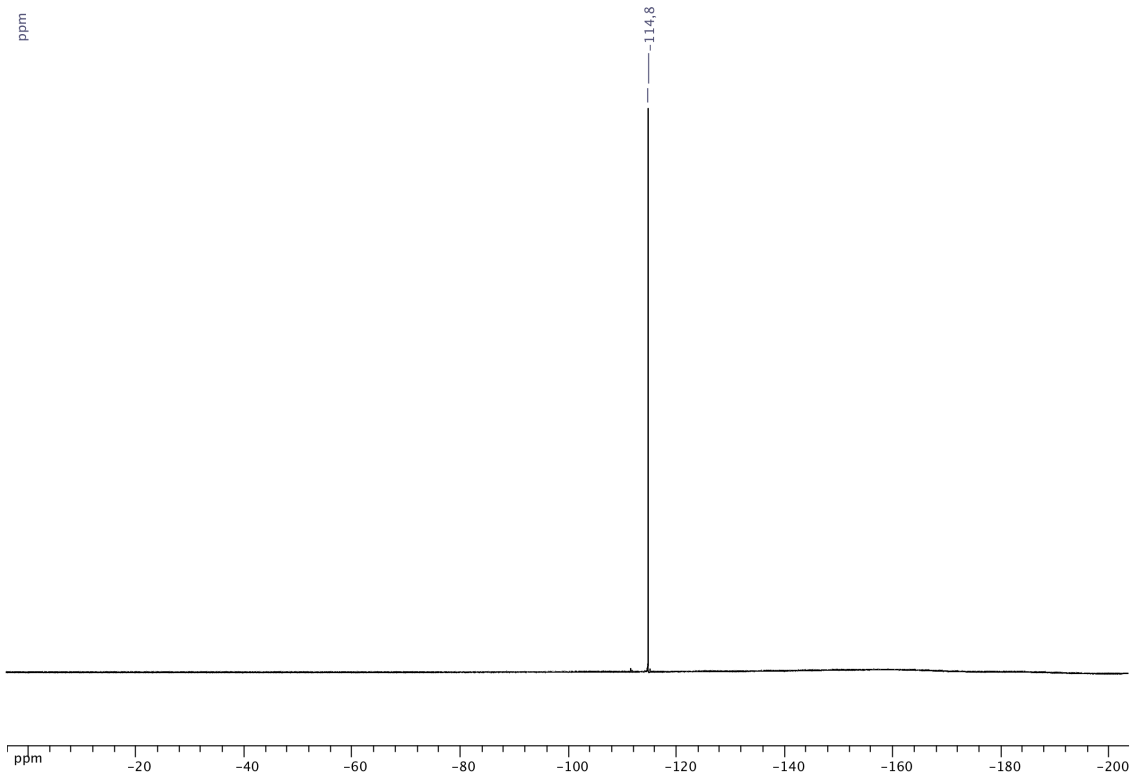
^{11}B NMR ($CDCl_3$, 128.4 MHz) of *N*-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(trifluoromethyl)pyridin-2-yl)propyl)aniline (**33**)



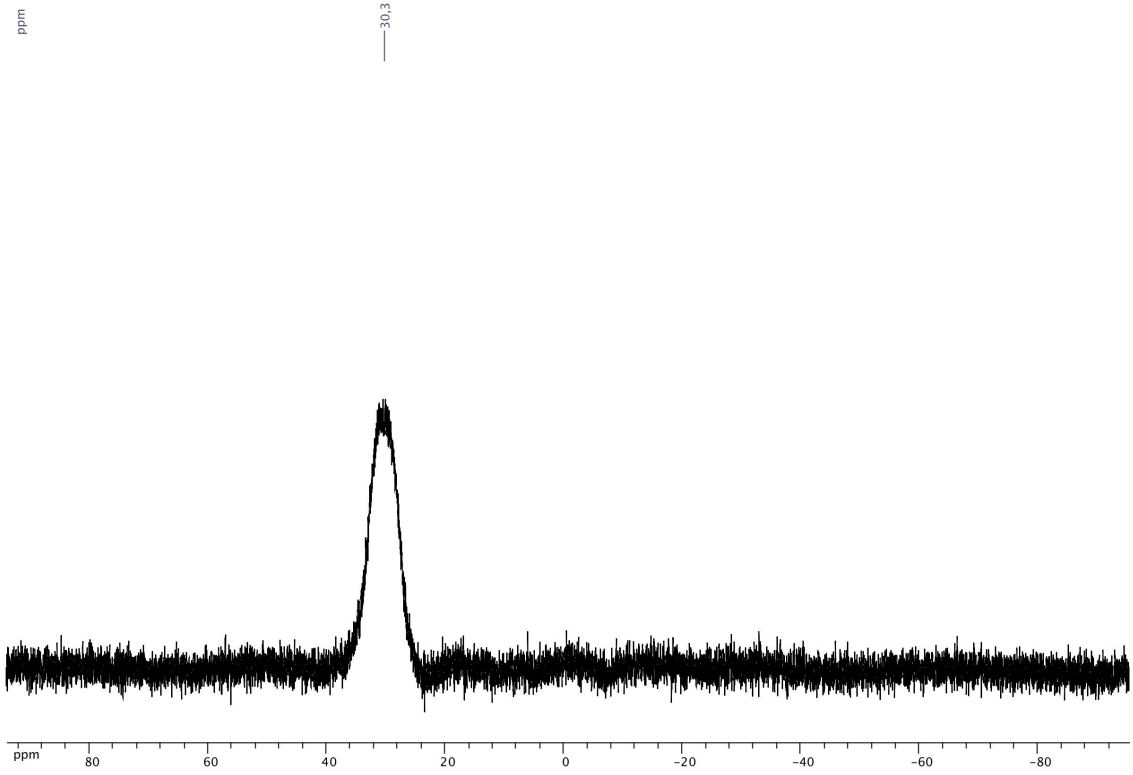
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *N*-(3-(3-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)aniline (**34**)



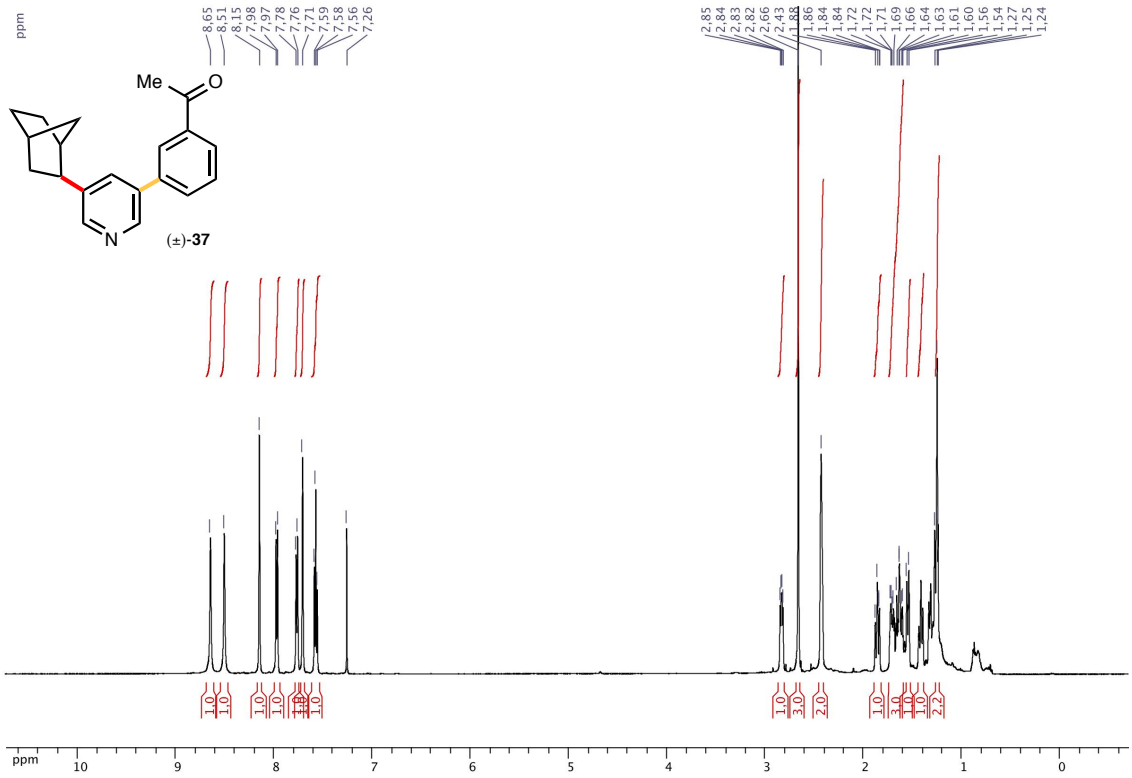
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *N*-(3-(3-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)aniline (**34**)



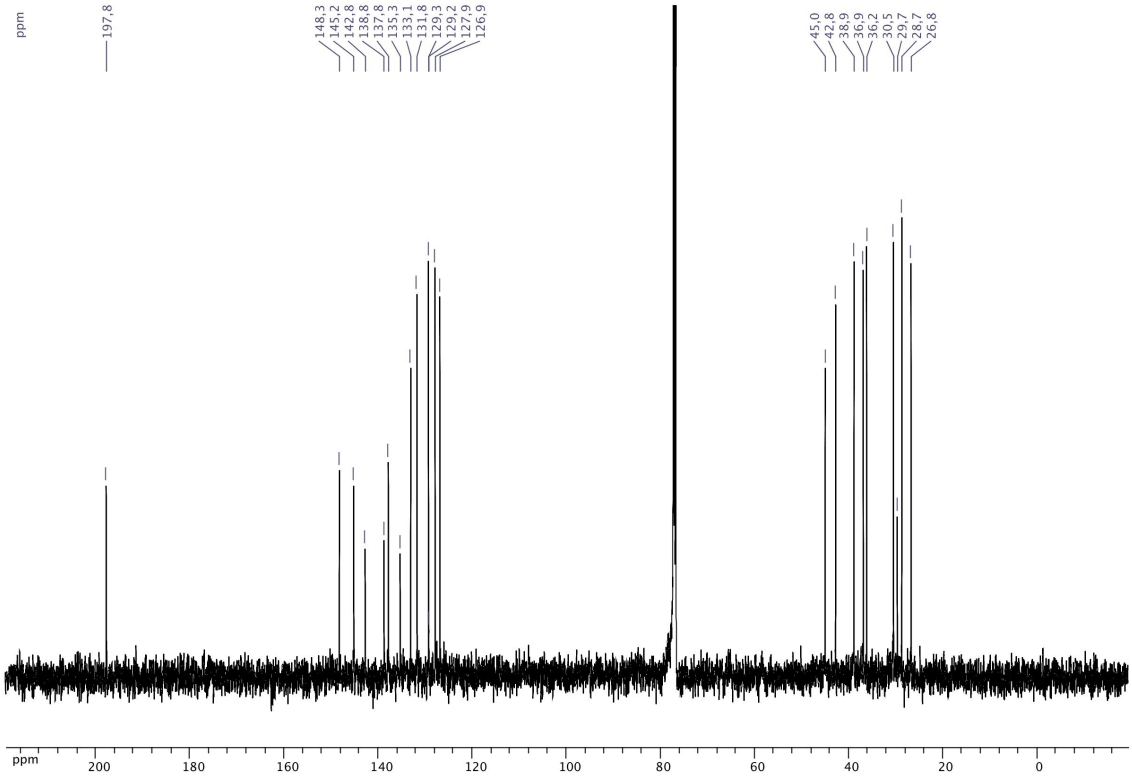
^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz) of *N*-(3-(3-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)aniline (**34**)



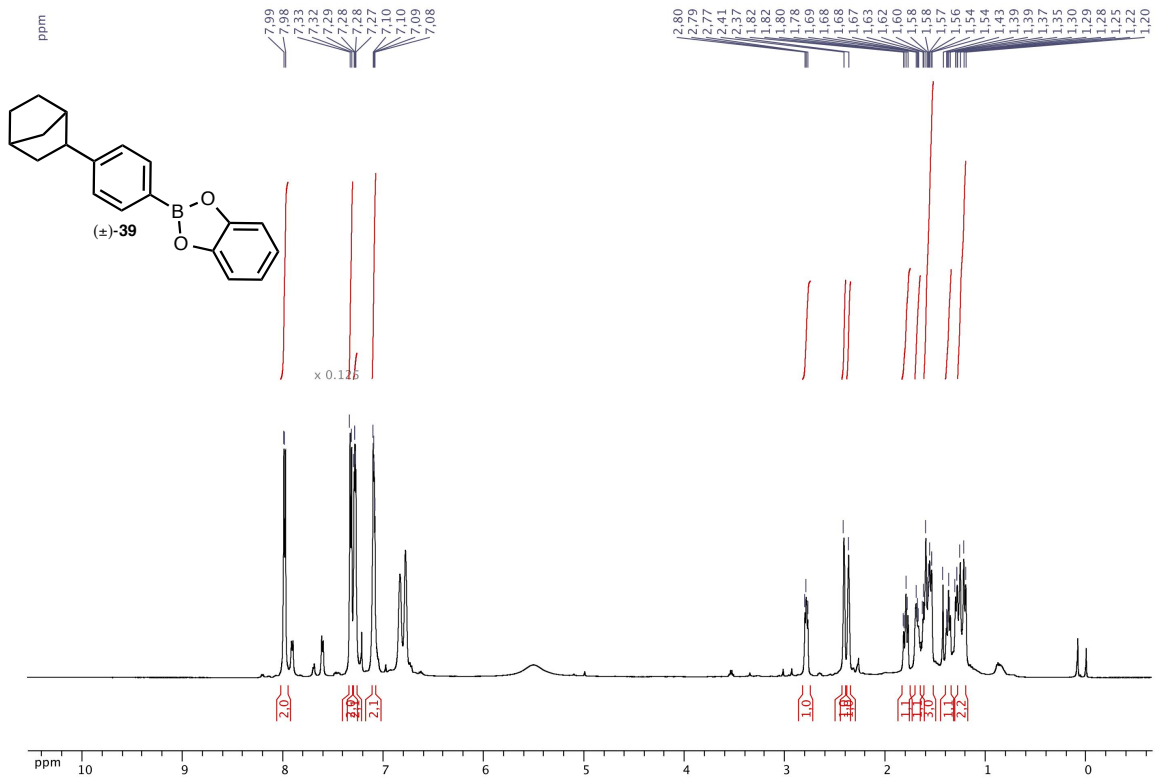
^{11}B NMR ($CDCl_3$, 128.4 MHz) of *N*-(3-(3-fluoro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl)aniline (**34**)



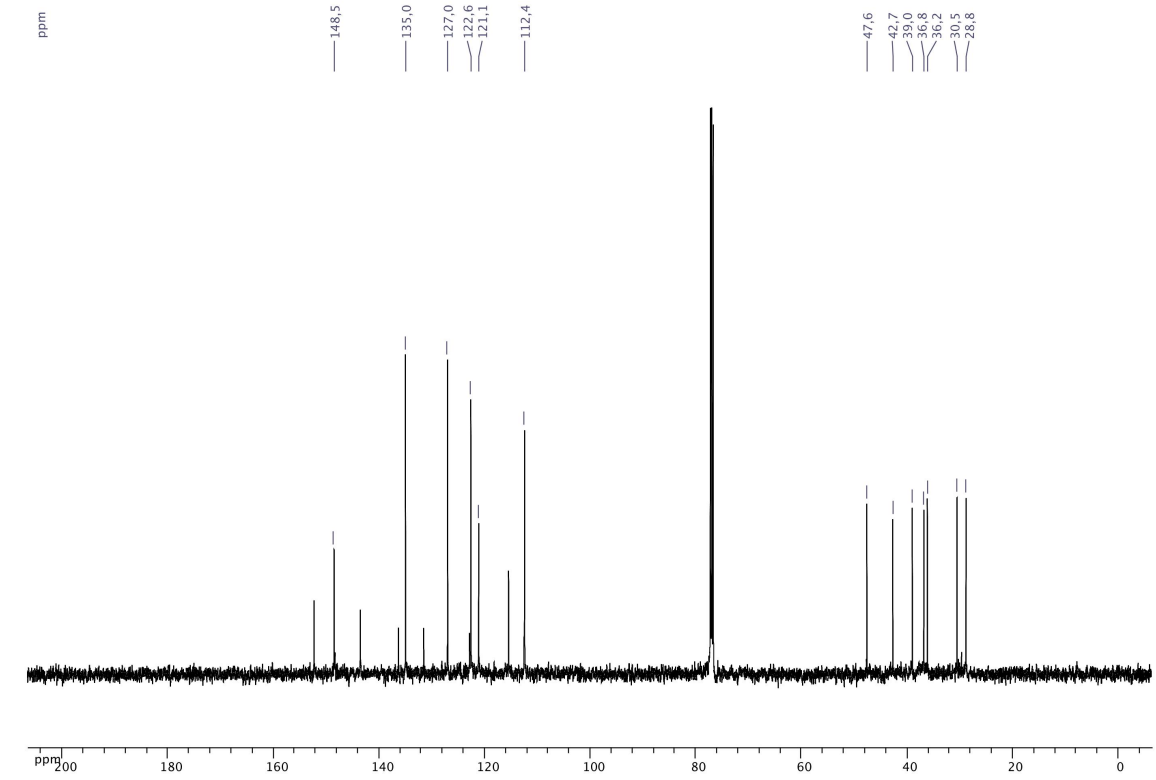
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 1-(3-(5-(bicyclo[2.2.1]heptan-2-yl)pyridin-3-yl)phenyl)ethan-1-one (**37**)



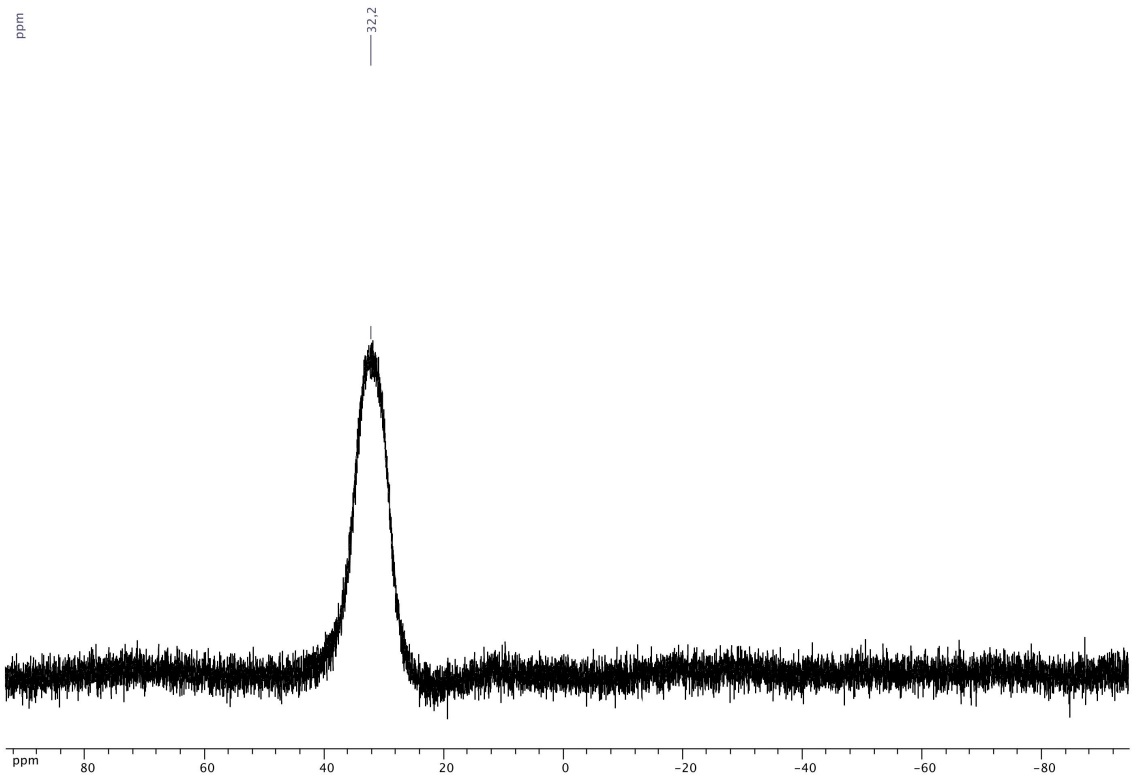
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 1-(3-(5-(bicyclo[2.2.1]heptan-2-yl)pyridin-3-yl)phenyl)ethan-1-one (**37**)



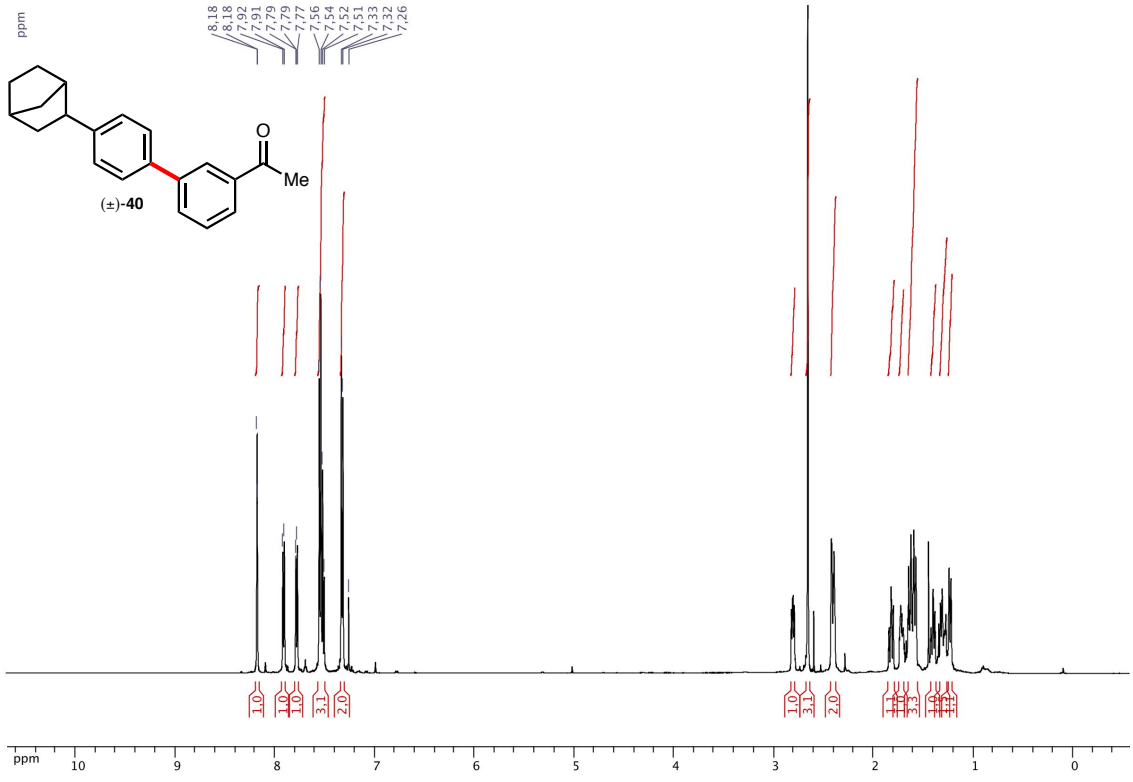
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(4-(bicyclo[2.2.1]heptan-2-yl)phenyl)benzo[*d*][1,3,2]dioxaborole (**39**)



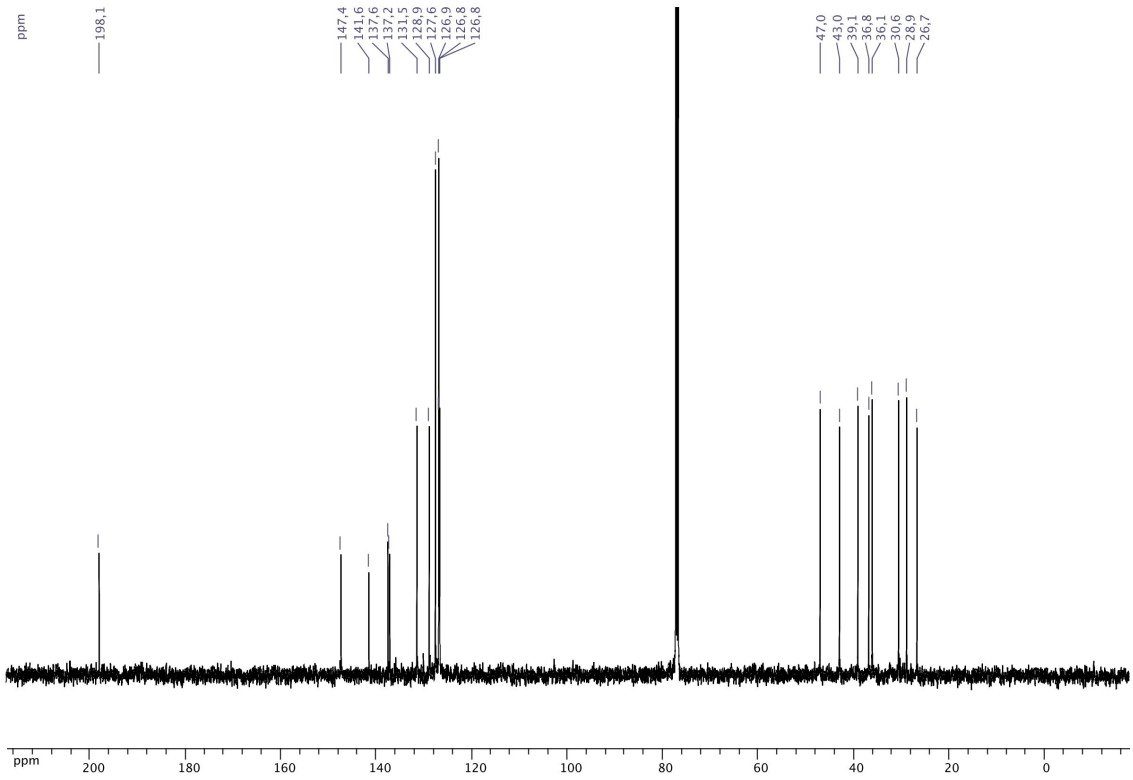
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(4-(bicyclo[2.2.1]heptan-2-yl)phenyl)benzo[*d*][1,3,2]dioxaborole (**39**)



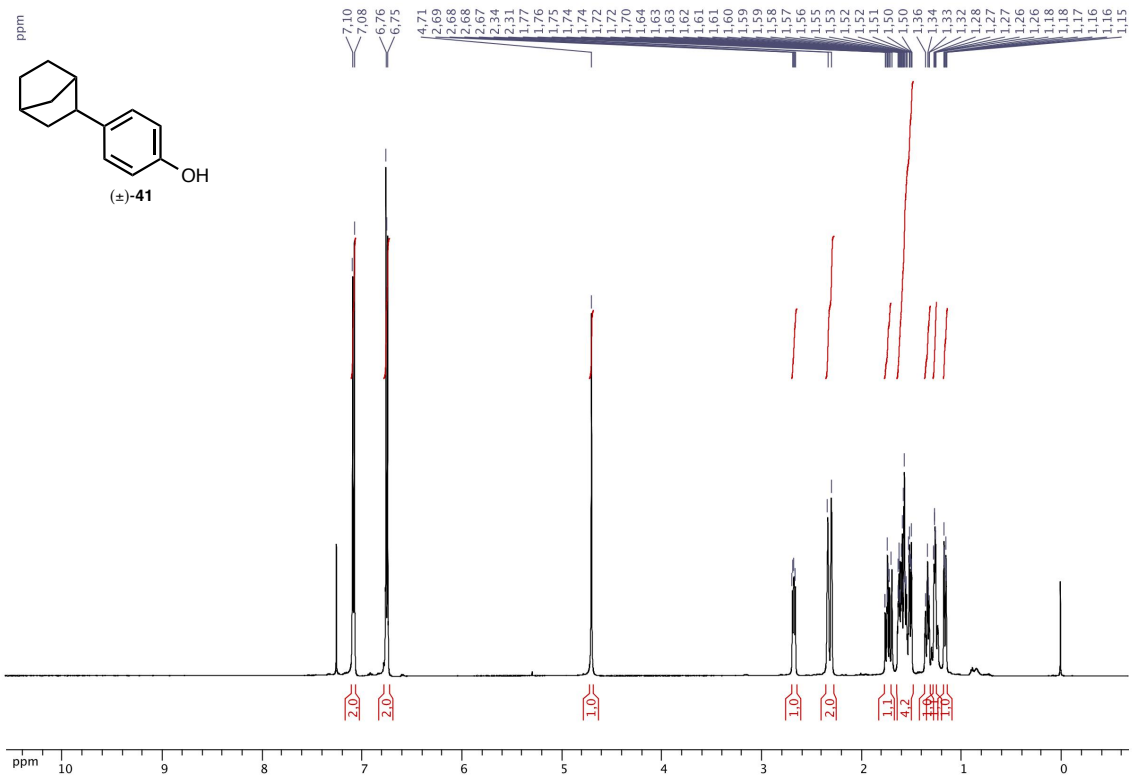
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 2-(4-(bicyclo[2.2.1]heptan-2-yl)phenyl)benzo[*d*][1,3,2]dioxaborole (**39**)



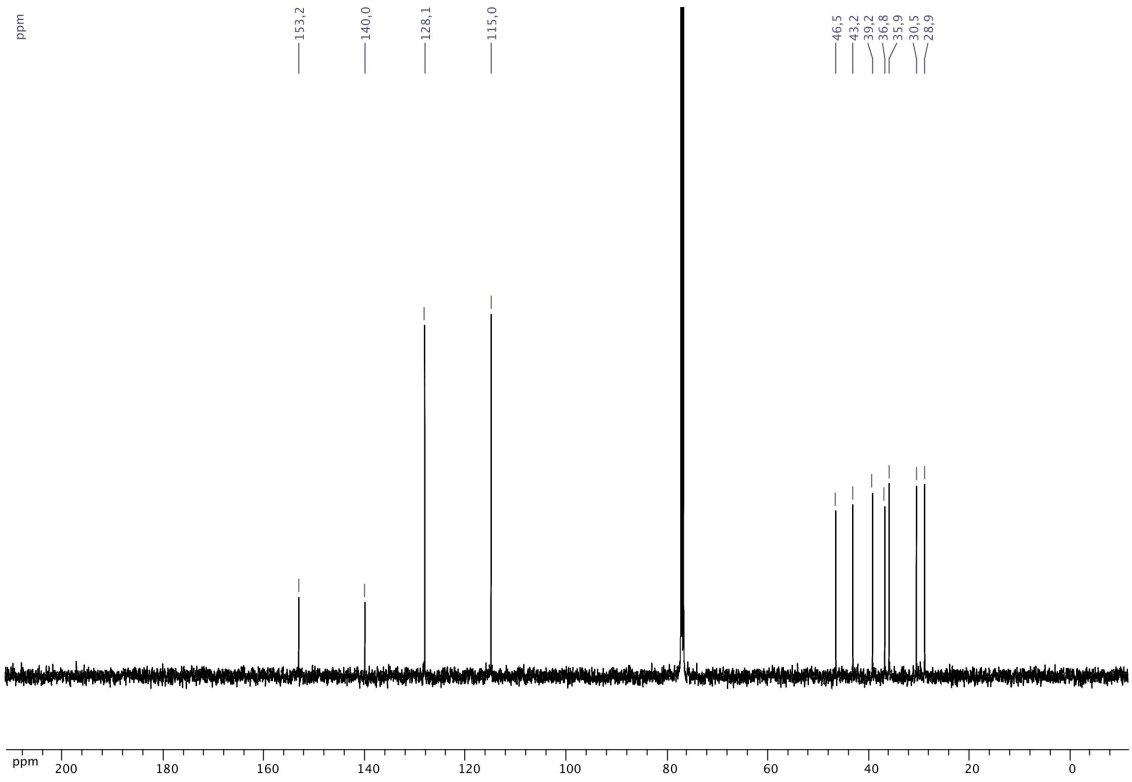
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 1-(4'-(bicyclo[2.2.1]heptan-2-yl)-[1,1'-biphenyl]-3-yl)ethan-1-one (**40**)



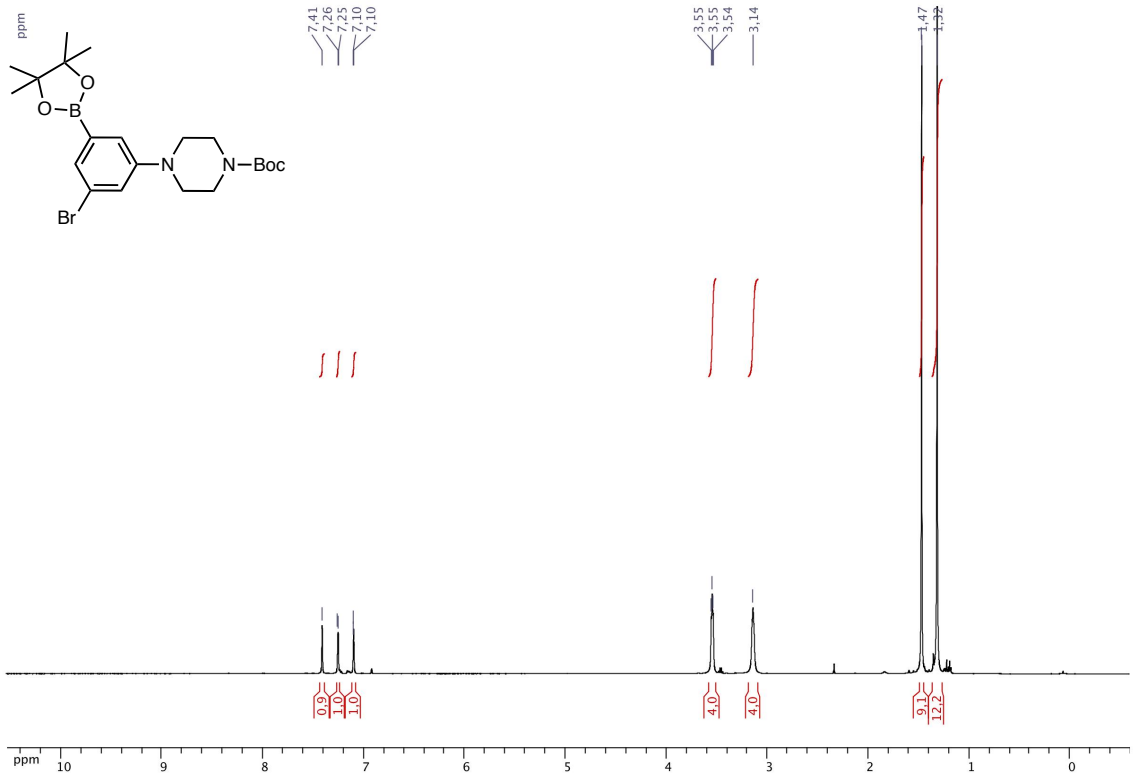
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 1-(4'-(bicyclo[2.2.1]heptan-2-yl)-[1,1'-biphenyl]-3-yl)ethan-1-one (**40**)



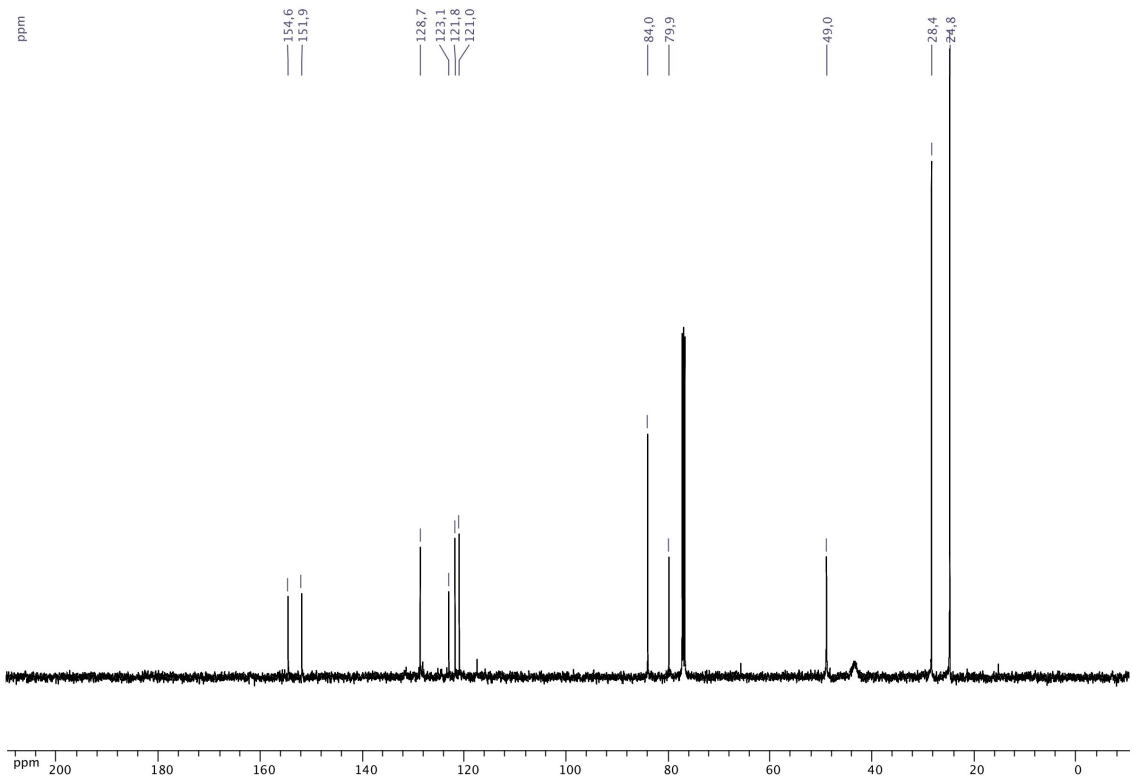
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 4-(bicyclo[2.2.1]heptan-2-yl)phenol (**41**)



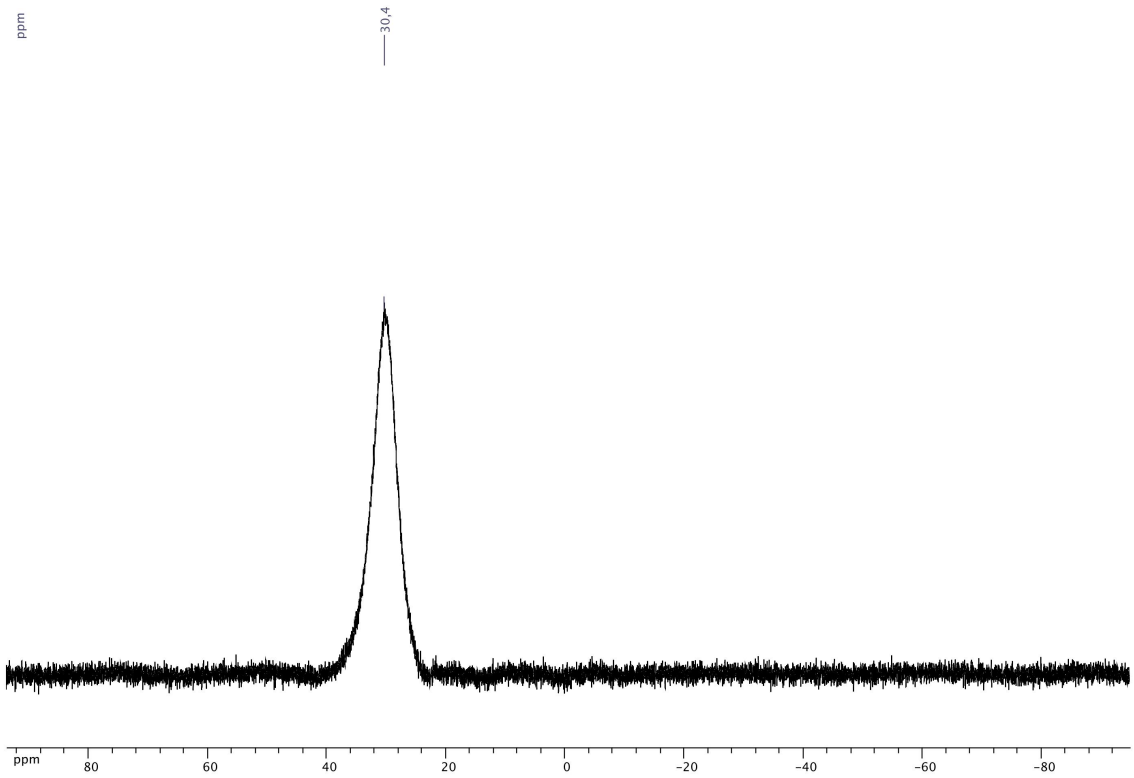
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 4-(bicyclo[2.2.1]heptan-2-yl)phenol (**41**)



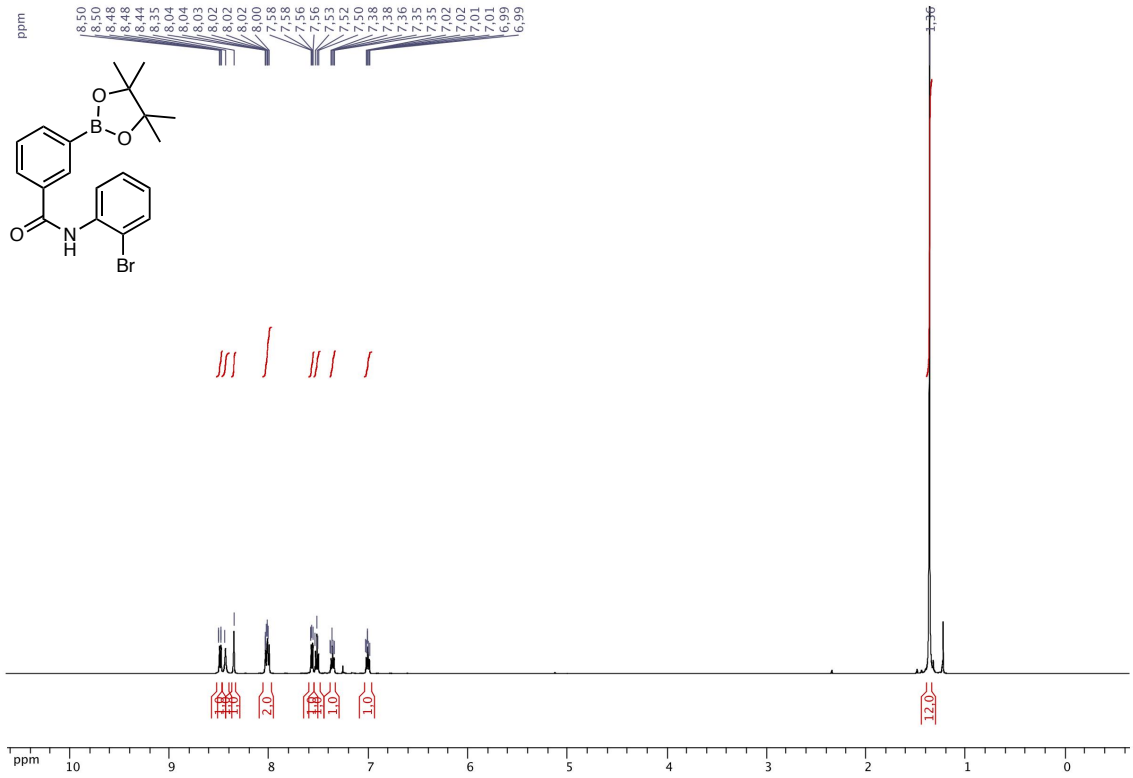
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *tert*-butyl 4-(3-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)piperazine-1-carboxylate (**S1**)



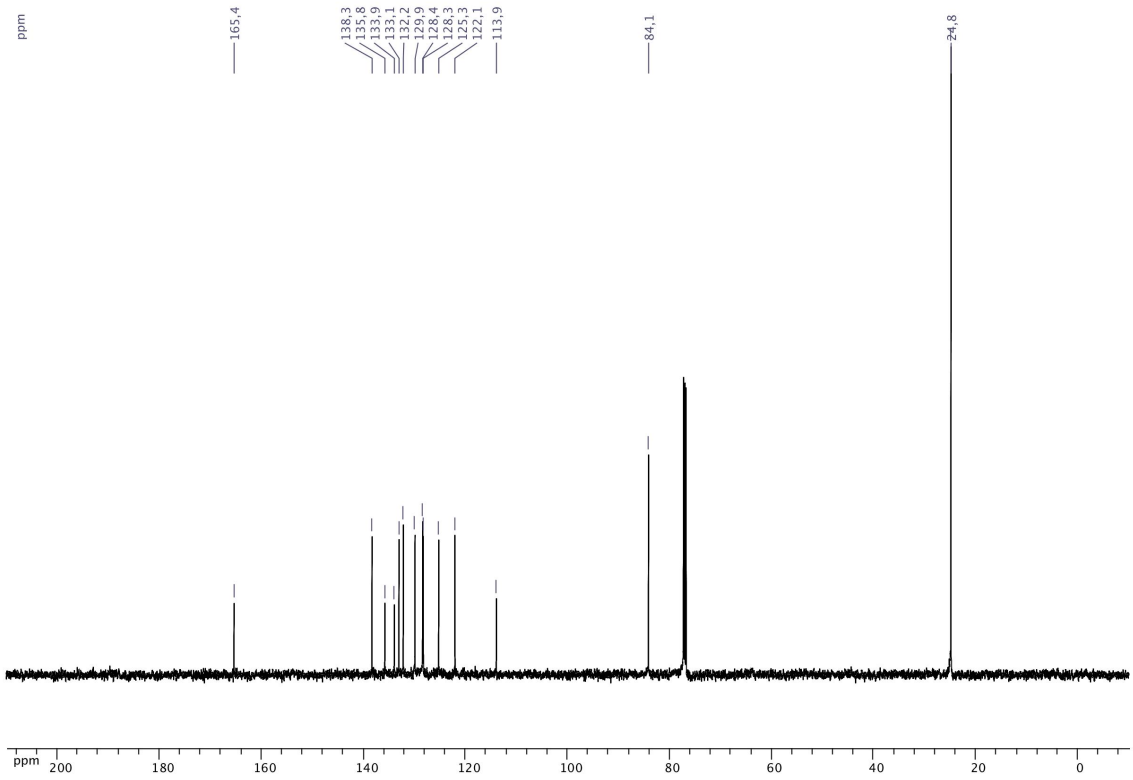
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *tert*-butyl 4-(3-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)piperazine-1-carboxylate (**S1**)



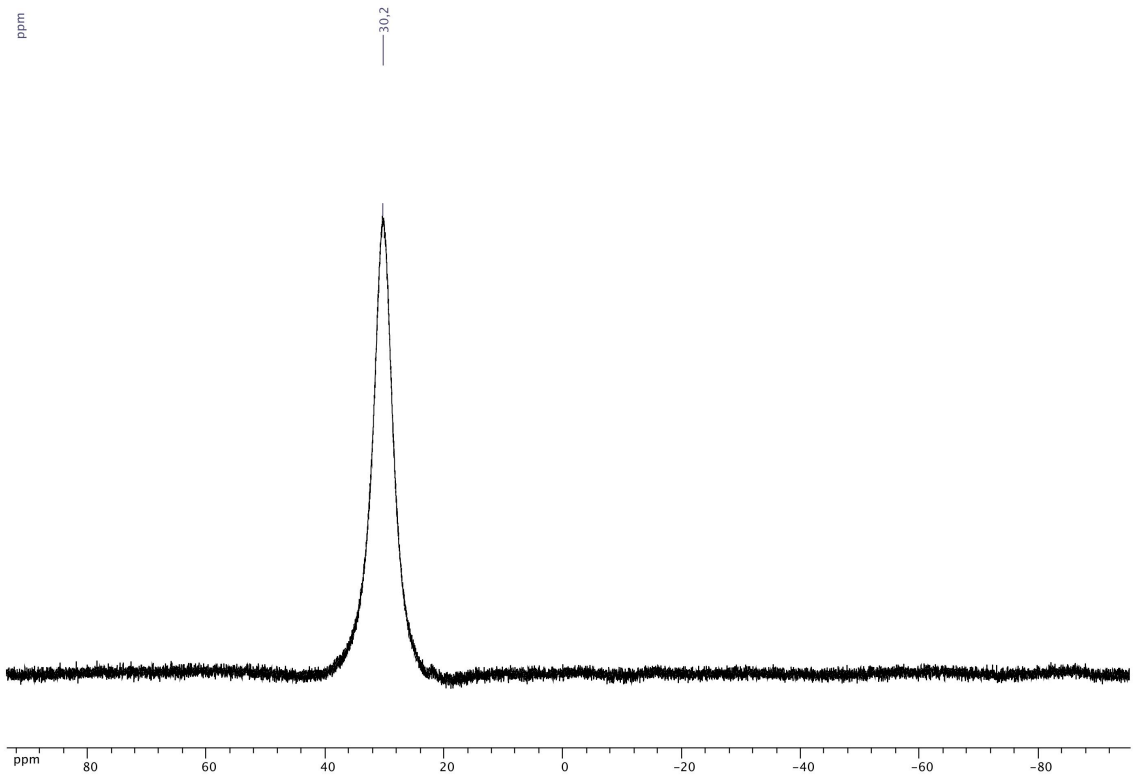
^{11}B NMR ($CDCl_3$, 128.4 MHz) of *tert*-butyl 4-(3-bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)piperazine-1-carboxylate (**S1**)



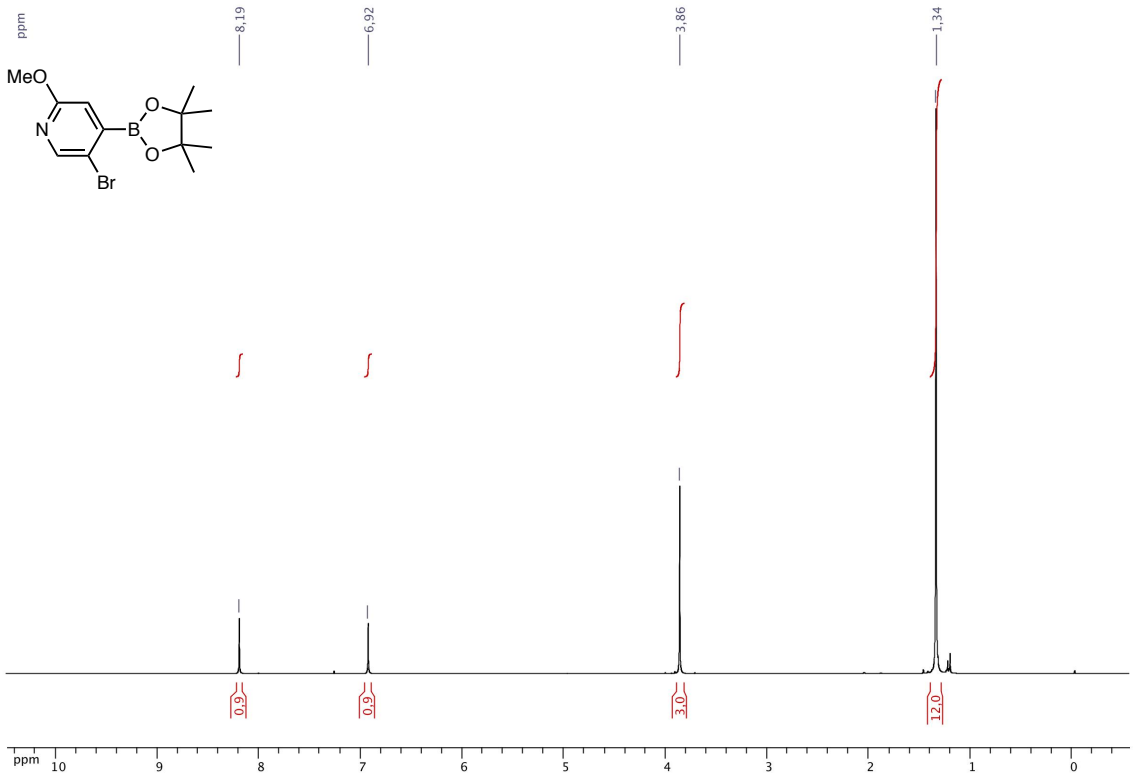
^{1}H NMR ($CDCl_3$, 500.4 MHz) of *N*-(2-bromophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**S2**)



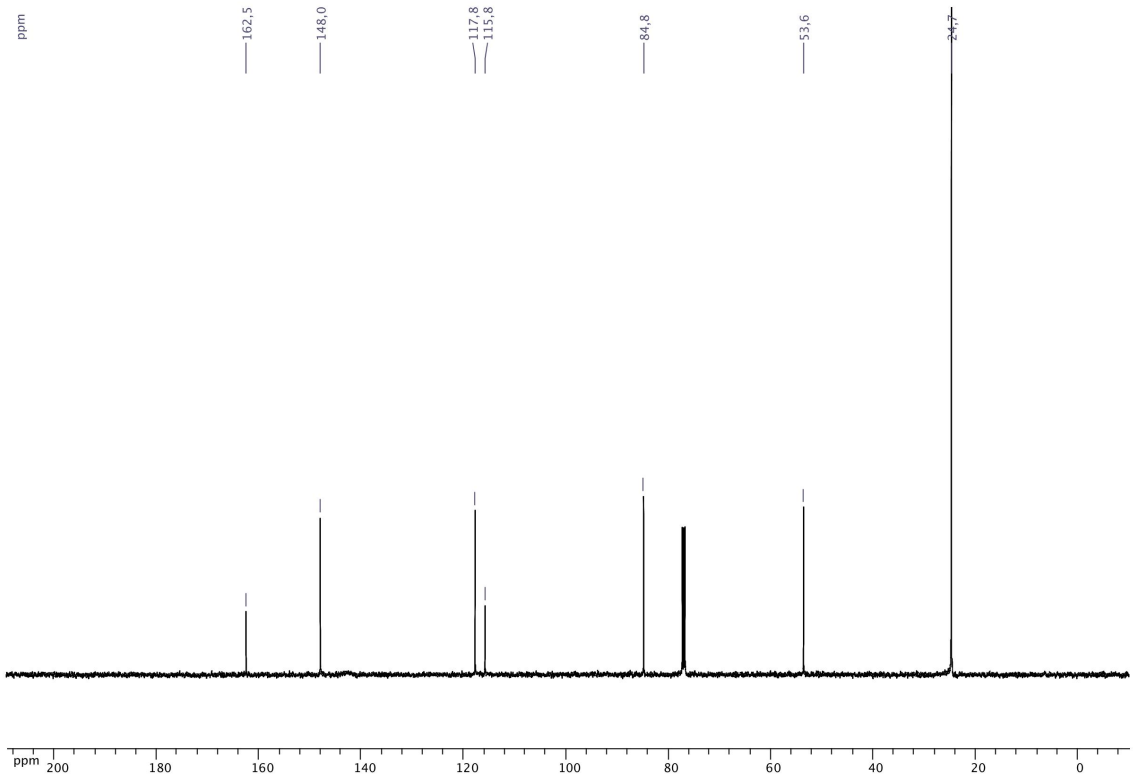
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *N*-(2-bromophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**S2**)



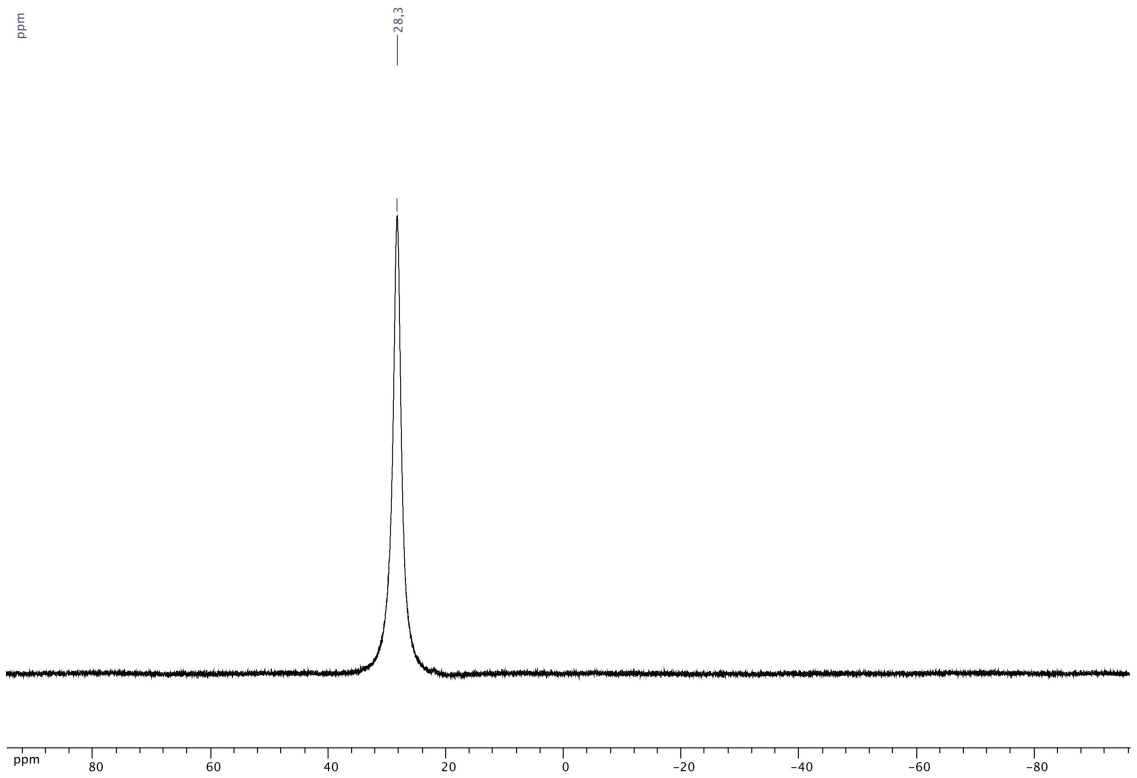
^{11}B NMR ($CDCl_3$, 128.4 MHz) of *N*-(2-bromophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**S2**)



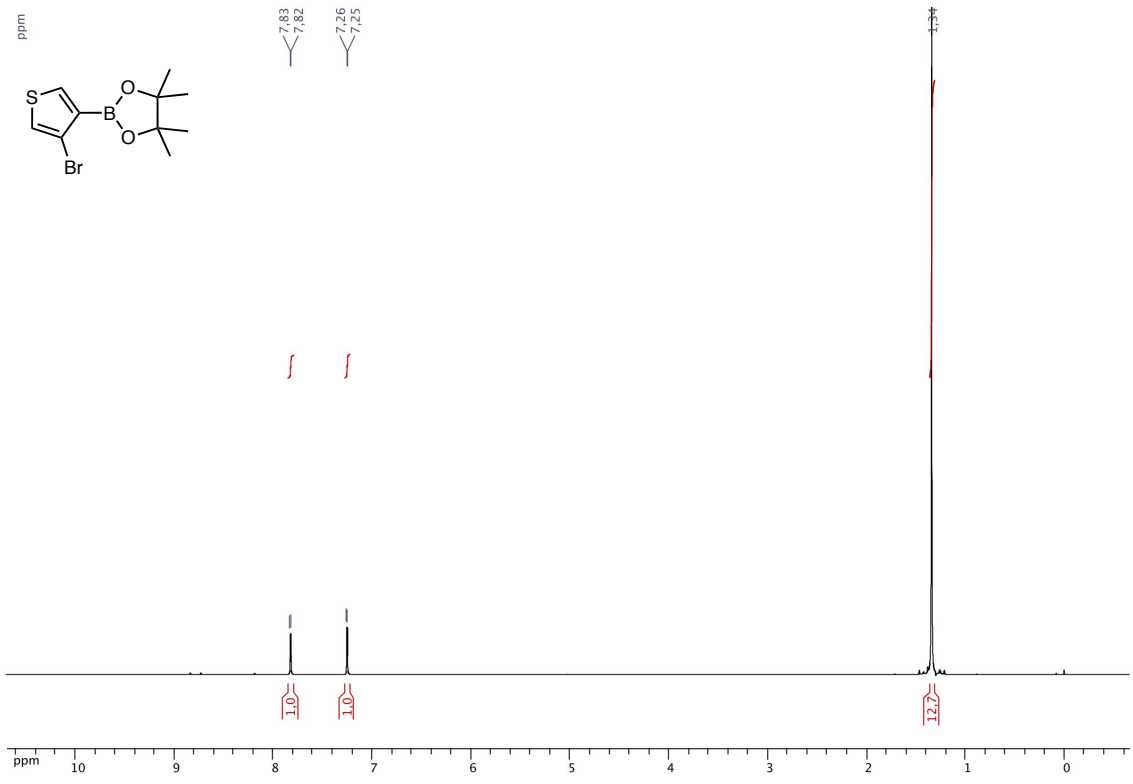
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 5-bromo-2-methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**S3**)



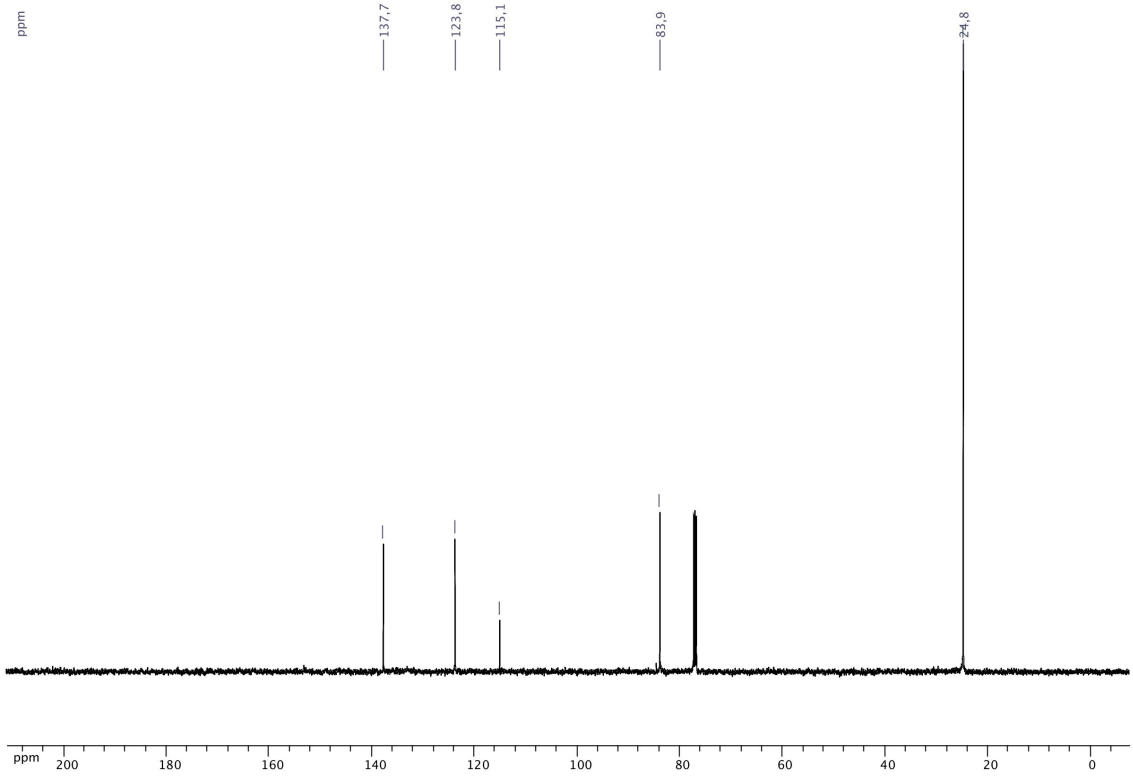
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 5-bromo-2-methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**S3**)



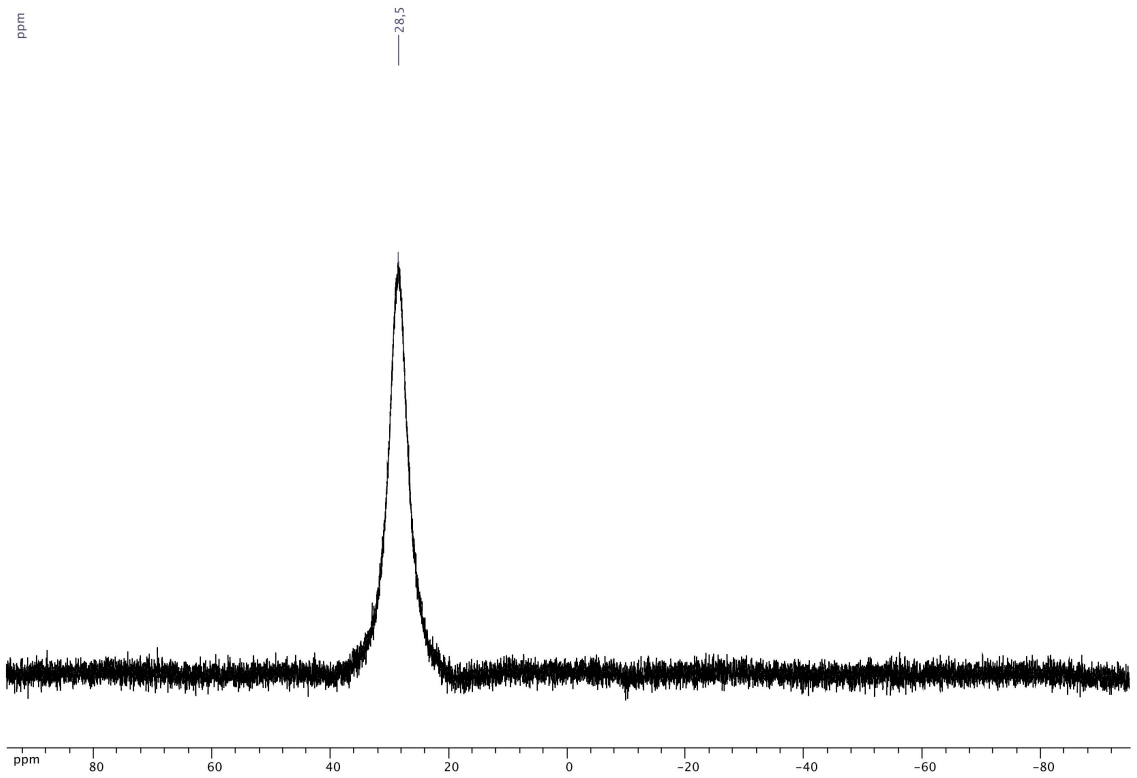
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 5-bromo-2-methoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**S3**)



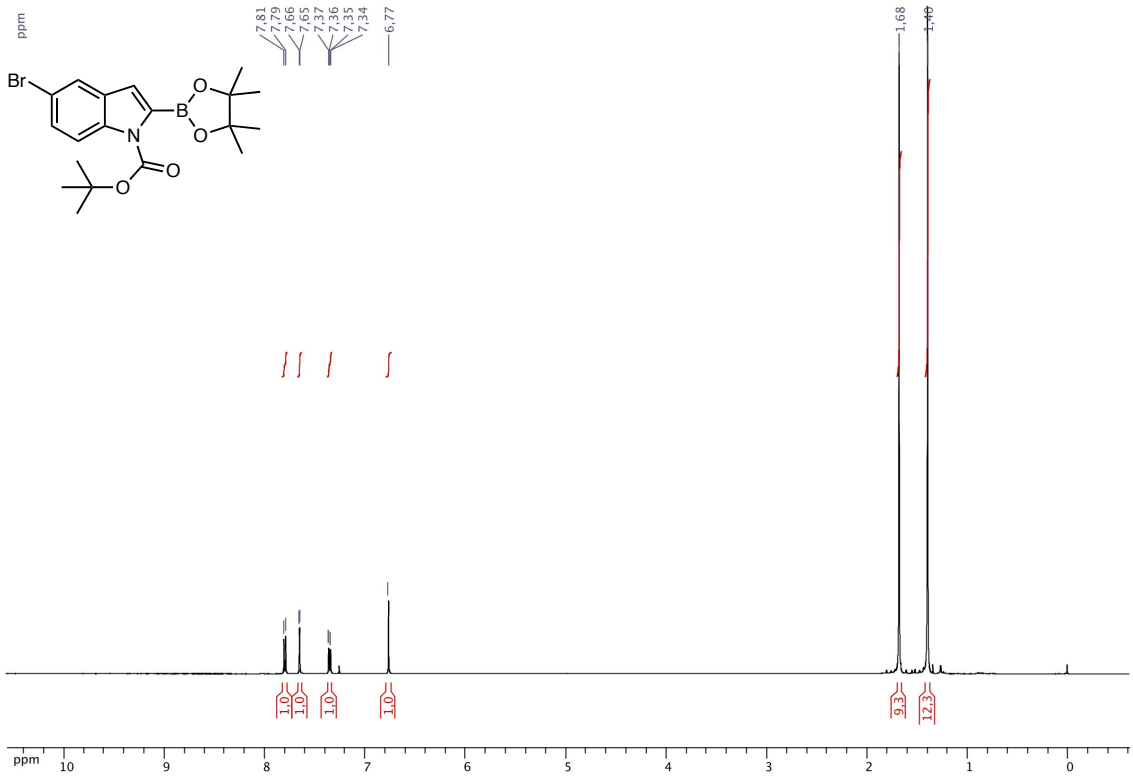
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(4-bromothiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**S4**)



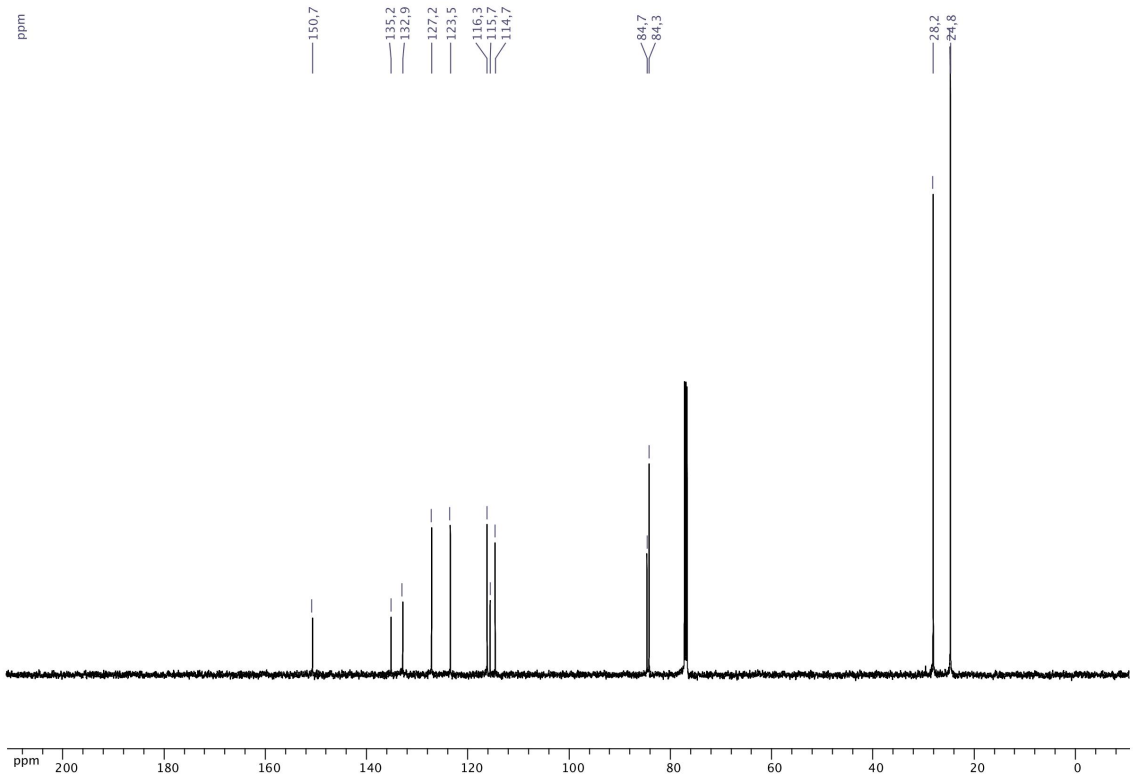
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(4-bromothiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**S4**)



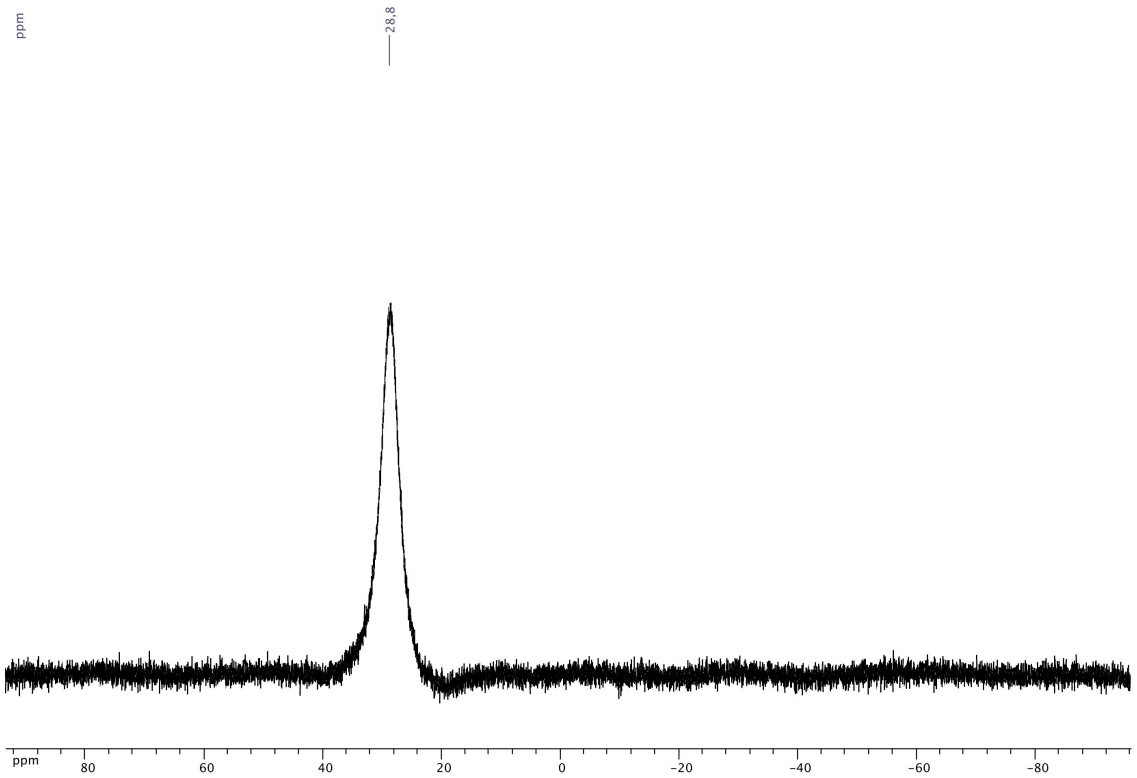
^{11}B NMR ($CDCl_3$, 128.4 MHz) of 2-(4-bromothiophen-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**S4**)



^{1}H NMR ($CDCl_3$, 500.4 MHz) of *tert*-butyl 5-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-1-carboxylate (**S5**)



^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of *tert*-butyl 5-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-1-carboxylate (**S5**)



^{11}B NMR ($CDCl_3$, 128.4 MHz) of *tert*-butyl 5-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole-1-carboxylate (**S5**)