Accessing Elaborated 2,1-Borazaronaphthalene Cores using Photoredox/Nickel Dual-Catalytic Functionalization

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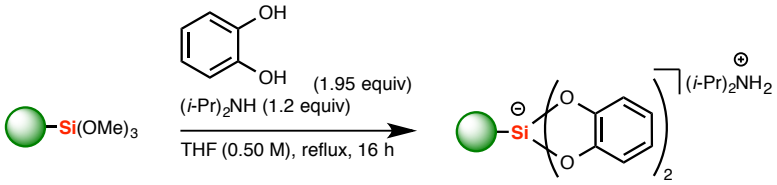
Supporting Information

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. NEt_3 and $(i\text{–}Pr)_2NH$ were distilled prior to use and stored over activated molecular sieves. Catechol (99%) was recrystallized from heptane. [$NiCl_2$(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. Photoredox reactions were irradiated with blue LED strips, and the temperature 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 (^1H, $^{13}C\{^1H\}$, ^{11}B, $^{19}F\{^1H\}$) were performed at 298 K. ^1H (500.4 MHz) and $^{13}C\{^1H\}$ (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 $^{19}F\{^1H\}$ 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 2,1-borazaronaphthalenes[2] were prepared according to literature procedures.

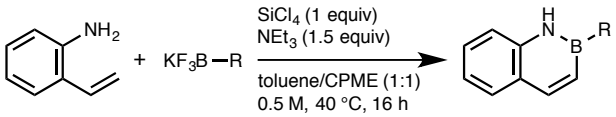
Procedure for synthesis of organobis(catecholato)silicates



Catechol (1.95 equiv) was introduced into a microwave vial with a stirring bar. The vial was sealed with a Teflon-coated septum cap, then purged with N_2 and evacuated four times. THF and $(i\text{–}Pr)_2NH$ (1.2 equiv) were introduced, and the resulting light pink solution was stirred at rt for 15 min before addition of organotrimethoxysilane derivative (1 equiv) (*Note: no base was added for the synthesis of alkylamine containing silane*). The reaction mixture was refluxed for 16 h. The vial was then cooled to rt, and the reaction mixture concentrated to a thick slurry before Et_2O (0.1 M) was introduced. The mixture was then sonicated 15 min to allow the corresponding product to precipitate as a white powder. The vial was finally unsealed, and the precipitate was collected by vacuum filtration. The filter cake was washed with Et_2O to afford silicate **11**. If required, the product was further purified by dissolving in CH_2Cl_2 followed by precipitation with pentane and vacuum filtration.

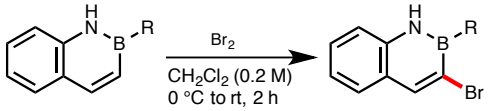
[1] (a) Jouffroy, M.; Primer, D. N.; Molander, G. A. *J. Am. Chem. Soc.* **2016**, 138, 475. (b) Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. *Org. Lett.*, DOI: 10.1021/acs.orglett.6b00024.
[2] Wisniewski, S. R.; Guenther, C. L.; Argintaru, O. A.; Molander, G. A. *J. Org. Chem.* **2014**, *79*, 365.

Procedure for synthesis of 2,1-borazaronaphthalenes



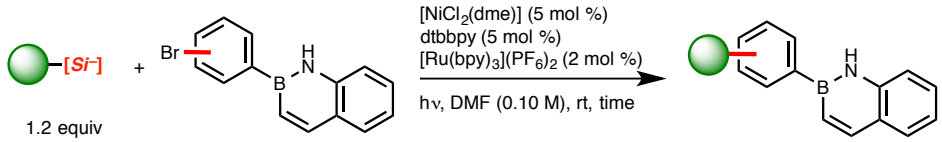
Aryltrifluoroborate (1.0 equiv) was introduced into a microwave vial with a stirring bar. The vial was sealed with a Teflon-coated septum cap, then purged with N_2 and evacuated four times. CPME/toluene mixture (0.5 M, 1:1, *v*/*v*) and 2-aminostyrene (1.2 equiv) were introduced *via* syringe, followed by NEt_3 (1.5 equiv) and $SiCl_4$ (1.0 equiv). The resulting suspension was heated to 40 °C under vigorous stirring for 16 h. The vial was finally cooled to rt, and the reaction mixture filtered through a plug of silica and flushed with hexanes/EtOAc mixture (20 times solvent volume, 4:1, *v*/*v*). Solvents were removed *in vacuo* to obtain product **10** in pure form. If required, the residue was further purified by column chromatography on silica gel, eluting with CH_2Cl_2 and hexanes.

Procedure for the bromation of 2,1-borazaronaphthalenes



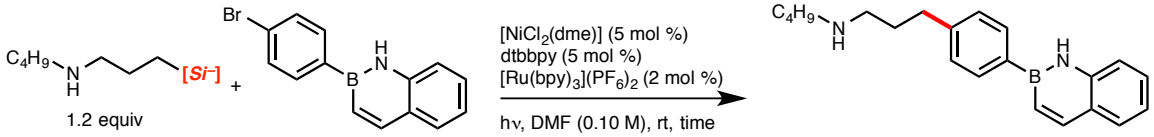
The 2,1-borazaronaphthalenes **10** (1.0 equiv) were introduced into a round-bottom flask equipped with a stirring bar. The flask was sealed with a rubber septum, then purged with inert gas and evacuated four times. CH_2Cl_2 (0.2 M) was introduced, and the flask was cooled to 0 °C before Br_2 (1.1 equiv) in CH_2Cl_2 (0.2 M) was added over 2 h. After addition, the reaction completion was monitored by HPLC. The crude reaction mixture condensed then purified by column chromatography on silica gel, eluting with CH_2Cl_2 and hexanes to afford product **1** in pure form.

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), and [$NiCl_2$(dme)] (5.5 mg, 0.025 mmol). The vial was capped and purged with nitrogen, then 1.5 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. 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, brominated azaborine **1** (0.5 mmol, 1.0 equiv) (liquid aryl bromides were added at the time of solvent addition), organosilicates (0.6 mmol, 1.2 equiv), and $[Ru(bpy)_3](PF_6)_2$ (8.6 mg, 0.01 mmol) were added in succession. The vial was then capped and purged four times. Under 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 (Figure S-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

12 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 (20 mL). The resulting suspension was extracted with EtOAc (3 × 10 mL), and the combined organic extracts were washed with a saturated solution of Na_2CO_3 (2 × 20 mL) then H_2O (20 mL), dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography on silica gel, eluting with EtOAc and hexanes, to obtain products in pure form. In the case of primary and secondary alkylamine-containing compounds, the residue was purified by column chromatography on silica gel, eluting with MeOH and CH_2Cl_2 containing NH_4OH (1 %, *v*/*v*).



Gram scale reaction: To a 100 mL round bottom flask equipped with a Teflon-coated magnetic stir bar was added [$NiCl_2$(dme)] (39 mg, 0.18 mmol) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (47 mg, 0.18 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, azaborine **1a** (1.000 g, 3.52 mmol), bis(catecholato)3-(butylammonio)propyl silicate **11d** (1.949 g, 4.23 mmol) and [$Ru(bpy)_3$](PF_6)$_2$ (61 mg, 0.07 mmol) were added in succession. The vial was then capped and purged four times. Under 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 (Figure S-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 (4 h), the crude reaction mixture was diluted with EtOAc (40 mL), filtered through approximately 6 cm x 4 cm cylindrical plug of Celite, washing with EtOAc (40 mL). The resulting solution was concentrated, retaken in EtOAc (50 mL), poured into a separatory funnel and washed with a saturated solution of Na_2CO_3 (2 × 40 mL) then H_2O (40 mL), dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography on silica gel, eluting with MeOH and CH_2Cl_2 containing NH_4OH (1%, *v*/*v*), to obtain azaborine **2m** in pure form (1070 mg, 96%).

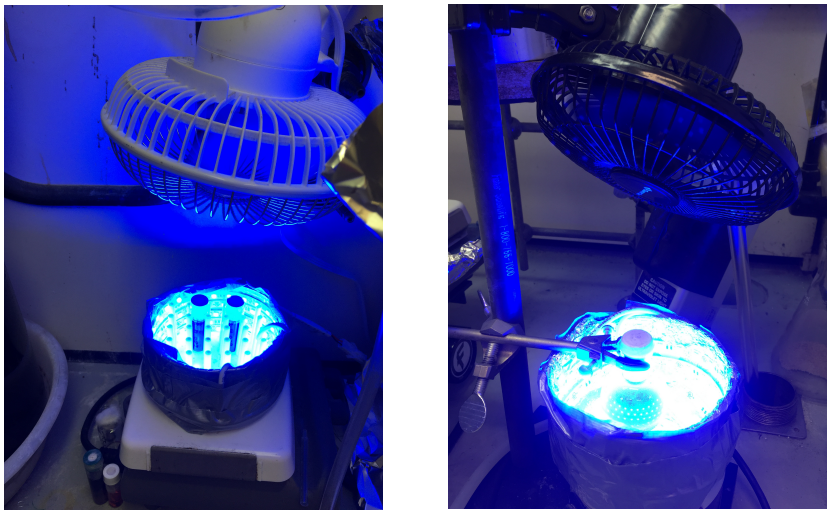
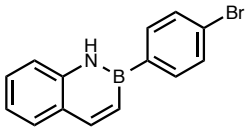
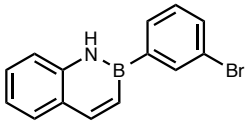


Figure S–1. 0.5 mmol (left) and gram (right) scale photoredox cross-coupling reaction set-up.

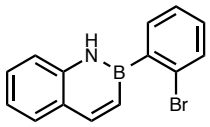
Compound Characterization Data



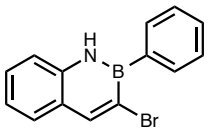
2-(4-Bromophenyl)-2,1-borazanaphthalene (1a): obtained as an off white powder (2.05 g, 72%, 10.00 mmol scale); mp = 158 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 10.5 (br s, 1 H), 8.15 (d, J = 12.0 Hz, 1 H), 8.02 (d, J = 8.2 Hz, 2 H), 7.72–7.64 (m, 4 H), 7.47 (ddd, J = 7.6, 7.5, 1.3 Hz, 1 H), 7.22 (dd, J = 11.6, 1.3 Hz, 1 H), 7.17 (ddd, J = 7.4, 7.5, 1.3 Hz, 1 H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 145.9, 141.2, 135.8, 131.2, 129.5, 128.8, 125.5, 123.9, 121.1, 119.1 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.0 ppm; IR: ν = 1612, 1576, 1557, 1490, 1434, 1390, 1345, 1280, 1206, 1134, 1077, 1067, 1007, 974, 808, 758 cm^{-1}; HRMS (ESI) m/z calc. for $C_{14}H_{11}BBrClN$ $[M + Cl]^-$ 317.9856, found 317.9857.



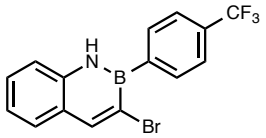
2-(3-Bromophenyl)-2,1-borazanaphthalene (1b): obtained as an off white powder (1.11 g, 56%, 7.00 mmol scale); mp = 75 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 9.93 (br s, 1 H), 8.21 (d, J = 10.7 Hz, 1 H), 8.17 (s, 1 H), 8.00 (d, J = 6.7 Hz, 1 H), 7.70 (d, J = 8.1 Hz, 1 H), 7.68 (d, J = 8.1 Hz, 1 H), 7.58 (d, J = 7.4 Hz, 1 H), 7.47 (ddd, J = 7.4, 7.4, 1.2 Hz, 1 H), 7.39 (t, J = 7.7 Hz, 1 H), 7.27 (dd, J = 7.4, 1.5 Hz, 1 H), 7.20 (ddd, J = 8.2, 6.7, 1.0 Hz, 1 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 145.8, 140.9, 135.4, 132.0, 131.9, 130.0, 129.1, 128.4, 125.7, 122.5, 121.0, 118.6 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 33.7 ppm; IR: ν = 1612, 1594, 1560, 1550, 1482, 1432, 1394, 1347, 1275, 1211, 1121, 1074, 987, 816, 786, 763 cm^{-1}; HRMS (ESI) m/z calc. for $C_{14}H_{10}BBrN$ $[M - H]^-$ 282.0090, found 282.0100.



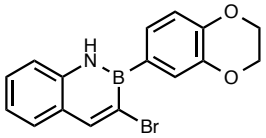
2-(2-Bromophenyl)-2,1-borazanaphthalene (1c): obtained as a viscous colorless oil (857 mg, 51%, 6.00 mmol scale); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.42 (br s, 1 H), 8.15 (d, J = 11.4 Hz, 1 H), 7.68 (d, J = 8.0 Hz, 1 H), 7.64–7.59 (m, 2 H), 7.46 (ddd, J = 7.5, 7.6, 1.3 Hz, 1 H), 7.37 (ddd, J = 7.5, 7.4, 1.0 Hz, 1 H), 7.33 (d, J = 8.1 Hz, 1 H), 7.27–7.20 (m, 2 H), 7.16 (dd, J = 11.7, 2.3 Hz, 1 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.3, 139.6, 135.7, 132.6, 130.3, 129.5, 128.5, 127.4, 126.9, 12.4, 121.5, 118.5 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.9 ppm; IR: ν = 1614, 1595, 1583, 1559, 1434, 1414, 1386, 1346, 1285, 1211, 1200, 1015, 978, 807, 748, 727 cm^{-1}; HRMS (ESI) m/z calc. for $C_{14}H_{12}BBrN$ $[M + H]^+$ 284.0246, found 284.0250.



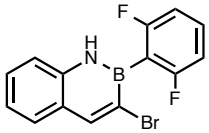
3-Bromo-2-phenyl-2,1-borazanaphthalene (1d): obtained as an off white powder (542 mg, 95%, 2.00 mmol scale) from 2-phenyl-2,1-borazanaphthalene;[2] mp = 81 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.46 (s, 1 H), 8.04 (br s, 1 H), 7.93–7.88 (m, 2 H), 7.62 (d, *J* = 7.8 Hz, 1 H), 7.50–7.46 (m, 4 H), 7.31 (d, *J* = 8.3 Hz, 1 H), 7.24 (t, *J* = 7.6 Hz, 1 H) ppm. Characterization data for this compound matched that reported in the literature.[3]



3-Bromo-2-(4-(trifluoromethyl)phenyl)-2,1-borazanaphthalene (1e): obtained as an off white powder (294 mg, 67%, 1.25 mmol scale) from **10a**; mp = 104 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 10.07 (br s, 1 H), 8.55 (s, 1 H), 8.07 (d, *J* = 7.9 Hz, 2 H), 7.77–7.67 (m, 4 H), 7.55–7.51 (m, 1 H), 7.28–7.24 (m, 1 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 147.0 139.9, 134.1, 130.1 (q, *J* = 31.7 Hz), 129.0, 128.6, 125.1, 124.6 (q, *J* = 270.9 Hz), 123.8 (q, *J* = 3.8 Hz), 122.0, 118.7 ppm; ^{19}F {^{1}H} NMR (acetone-d_6, 470.8 MHz): δ –63.1 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 33.4 ppm; IR: ν = 3321, 1554, 1328, 1225, 1166, 1156, 1130, 1118, 1104, 1070, 1007, 919, 847, 833, 761, 747, 719 cm^{-1}; HRMS (ESI) m/z calc. for $C_{15}H_9BBrF_3N$ $[M - H]^-$ 349.9964, found 349.9955.



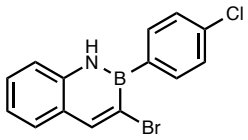
3-Bromo-2-(2,3-dihydro-1,4-benzodioxin-6-yl)-2,1-borazanaphthalene (1f): obtained as an off white powder (99 mg, 23%, 1.25 mmol scale) from **10b**; mp = 155 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 9.86 (br s, 1 H), 8.49 (s, 1 H), 7.72 (d, *J* = 7.8 Hz, 1 H), 7.62 (d, *J* = 8.4 Hz, 1 H), 7.50 (ddd, *J* = 8.2, 7.1, 1.3 Hz, 1 H), 7.24 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1 H), 7.09 (dd, *J* = 4.8, 3.8 Hz, 1 H), 6.90–6.83 (m, 2 H), 4.25 (s, 4 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 145.9, 145.8, 143.3, 139.7, 128.7, 128.5, 126.1, 124.9, 121.5, 120.7, 118.4, 117.7, 64.2, 64.1 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.5 ppm; IR: ν = 3324, 1556, 1458, 1441, 1422, 1286, 1249, 1211, 1200, 1081, 1039, 939, 922, 901, 881, 827, 771 cm^{-1}; HRMS (ESI) m/z calc. for $C_{17}H_{14}BBrNO_4$ $[M + HCOO]^-$ 386.0207, found 386.0199.



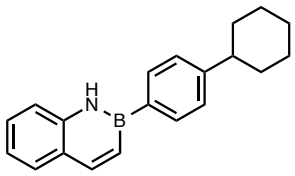
3-Bromo-2-(2,6-difluorophenyl)-2,1-borazanaphthalene (1g): obtained as an off white powder (241 mg, 60%, 1.25 mmol scale) from **10c**; mp = 173 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 10.37 (br s, 1 H), 8.59 (s, 1 H), 7.79 (d, *J* = 7.7 Hz, 1 H), 7.69 (d, *J* = 8.6 Hz, 1 H), 7.56 (ddd, *J* = 8.3, 7.3, 1.4 Hz, 1 H), 7.54–7.44 (m, 1 H), 7.31 (ddd, *J* = 8.1, 7.2, 1.0 Hz, 1 H), 7.08–7.00 (m, 2 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 164.5 (dd, *J* = 242.5,

[3] Molander, G. A.; Wisniewski, S. R. *J. Org. Chem.* **2014**, *79*, 6663.

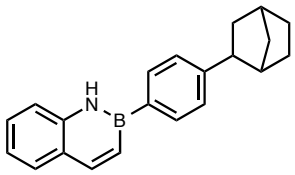
13.9 Hz), 146.1, 139.4, 131.7 (t, J = 10.0 Hz), 129.0, 128.7, 125.3, 122.2, 118.6, 110.7 (dd, J = 22.1, 5.9 Hz) ppm; ^{19}F NMR (acetone-d_6, 470.8 MHz): δ –102.9 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 33.1 ppm; IR: ν = 3339, 1616, 1596, 1557, 1450, 1427, 1345, 1221, 1210, 1156, 1018, 978, 910, 781, 764, 745 cm^{-1}; HRMS (CI) m/z calc. for $C_{14}H_9BBrF_2N$ $[M]^+$ 318.9979, found 318.9991.



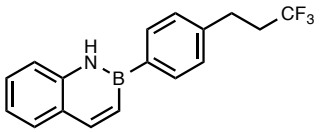
3-Bromo-2-(4-chlorophenyl)-2,1-borazanaphthalene (1h): obtained as an off white powder (310 mg, 78%, 1.25 mmol scale) from **10d**; mp = 77 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 9.88 (br s, 1 H), 8.48 (s, 1 H), 7.91 (d, J = 8.3 Hz, 2 H), 7.67–7.64 (m, 2 H), 7.49 (ddd, J = 8.3, 7.1, 1.3 Hz, 1 H), 7.44 (d, J = 8.3 Hz, 2 H), 7.22 (ddd, J = 8.1, 7.1, 1.3 Hz, 1 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 146.9, 140.0, 135.3, 134.8, 129.0, 128.5, 127.5, 125.0, 121.8, 118.6 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 33.6 ppm; IR: ν = 3369, 1614, 1589, 1554, 1421, 1388, 1340, 1227, 1201, 1087, 1006, 911, 845, 818, 756, 742 cm^{-1}; HRMS (ESI) m/z calc. for $C_{14}H_9BBrClN$ $[M - H]^-$ 315.9700, found 315.9690.



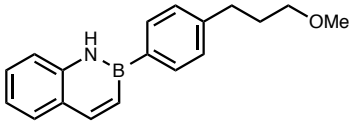
2-(4-Cyclohexylphenyl)-2,1-borazanaphthalene (2a): obtained as a white powder (139 mg, 97%); mp = 145°C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.12 (d, J = 10.5 Hz, 2 H), 7.87 (d, J = 8.4 Hz, 2 H), 7.66 (d, J = 8.4 Hz, 1 H), 7.44 (dd, J = 7.4, 7.4 Hz, 1 H), 7.37–7.32 (m, 3 H), 7.30–7.26 (m, 1 H), 7.19 (ddd, J = 7.6, 7.4, 1.1 Hz, 1 H), 2.62–2.53 (m, 1 H), 1.96–1.85 (m, 4 H), 1.78 (d, J = 6.0 Hz, 1 H), 1.52–1.37 (m, 4 H), 1.34–1.27 (m, 1 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 149.3, 145.1, 141.1, 133.2, 129.1, 128.1, 126.4, 125.6, 120.5, 118.5, 44.5, 34.2, 26.6, 25.9 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.6 ppm; IR: ν = 2920, 2849, 1612, 1596, 1564, 1439, 1404, 1388, 1347, 1284, 1218, 1174, 978, 808, 755, 737 cm^{-1}; HRMS (ESI) m/z calc. for $C_{20}H_{23}BN$ $[M + H]^+$ 288.1924, found 288.1924.



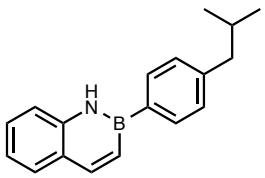
2-(4-(*exo*-Bicyclo[2.2.1]heptan-2-yl)phenyl)-2,1-borazanaphthalene (2b): obtained as a white powder (143 mg, 96%); mp = 159 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 9.67 (br s, 1 H), 8.15 (d, J = 12.5 Hz, 1 H), 7.96 (d, J = 7.2 Hz, 2 H), 7.69–7.63 (m, 2 H), 7.43 (dd, J = 7.2, 7.9 Hz, 1 H), 7.33–7.24 (m, 3 H), 7.16 (dd, J = 6.6, 7.2 Hz, 1 H), 2.82–2.76 (m, 1 H), 2.37–2.34 (m, 2 H), 1.82–1.75 (m, 1 H), 1.73–1.68 (m, 1 H), 1.64–1.54 (m, 3 H), 1.43–1.36 (m, 1 H), 1.31–1.28 (m, 1 H), 1.21–1.18 (m, 1 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 148.8, 145.1, 141.1, 133.1, 129.0, 128.1, 126.6, 125.6, 120.5, 118.4, 47.2, 42.9, 38.6, 36.6, 35.6, 30.2, 28.5 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.0 ppm; IR: ν = 2947, 2866, 1612, 1594, 1440, 1403, 1388, 1345, 1284, 1209, 1143, 978, 941, 806, 756, 697 cm^{-1}; HRMS (ESI) m/z calc. for $C_{21}H_{21}BN$ $[M - H]^-$ 298.1767, found 298.1763.



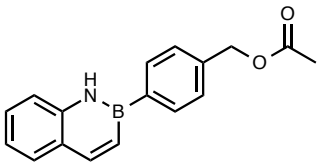
2-(4-(3,3,3-Trifluoropropyl)phenyl)-2,1-borazanaphthalene (2c): obtained as a white powder (138 mg, 92%) using silicate **11a**; mp = 151 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 9.73 (br s, 1 H), 8.17 (d, J = 11.3 Hz, 1 H), 8.00 (d, J = 7.7 Hz, 2 H), 7.70–7.63 (m, 2 H), 7.44 (dd, J = 7.5, 7.6 Hz, 1 H), 7.39 (d, J = 8.4 Hz, 2 H), 7.30–7.25 (m, 1 H), 7.17 (dd, J = 7.4, 7.4 Hz, 1 H), 2.95–2.89 (m, 2 H), 2.62–2.50 (m, 2 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.5, 140.5, 140.0, 133.1, 129.4, 128.3, 128.1, 126.7 (q, J = 276.3 Hz), 125.7, 121.0, 118.1, 35.5 (q, J = 28.7 Hz), 28.2 (q, J = 2.73 Hz) ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 33.9 ppm; ^{19}F {^{1}H} NMR (acetone-d_6, 470.8 MHz): –67.0 ppm; IR: ν = 1607, 1564, 1438, 1385, 1330, 1304, 1284, 1255, 1224, 1155, 1115, 1082, 975, 811, 760, 732 cm^{-1}; HRMS (ESI) m/z calc. for $C_{17}H_{16}BNF_3$ $[M + H]^+$ 302.1328, found 302.1334.



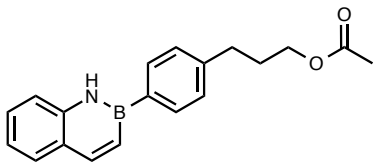
2-(4-(3-Methoxypropyl)phenyl)-2,1-borazanaphthalene (2d): obtained as an off white powder (133 mg, 96%); mp = 76 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 9.69 (br s, 1 H), 8.15 (d, J = 11.7 Hz, 1 H), 7.97 (d, J = 7.4 Hz, 2 H), 7.69–7.64 (m, 2 H), 7.44 (dd, J = 7.0, 7.0 Hz, 1 H), 7.30–7.28 (m, 3 H), 7.17 (dd, J = 7.6, 7.5 Hz, 1 H), 3.36 (t, J = 5.8 Hz, 2 H), 3.28 (s, 3 H), 2.70 (t, J = 7.2 Hz, 2 H), 1.87 (dt, J = 7.2, 5.8 Hz, 2 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 145.2, 143.6, 141.1, 133.2, 129.1, 128.2, 128.1, 125.6, 120.6, 118.5, 71.4, 57.5, 32.0, 31.2 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.3 ppm; IR: ν = 1605, 1595, 1562, 1437, 1389, 1346, 1282, 1208, 1193, 1118, 1067, 977, 952, 942, 813, 801 cm^{-1}; HRMS (ESI) m/z calc. for $C_{18}H_{20}BNO$ $[M]^+$ 277.1638, found 277.1632.



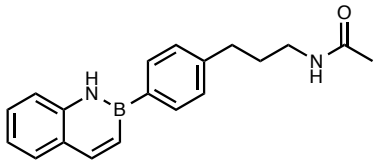
2-(4-Isobutylphenyl)-2,1-borazanaphthalene (2e): obtained as a white powder (122 mg, 94%); mp = 109 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 9.67 (br s, 1 H), 8.15 (d, J = 11.5 Hz, 1 H), 7.96 (d, J = 7.9 Hz, 2 H), 7.69–7.63 (m, 2 H), 7.44 (ddd, J = 7.4, 7.4, 1.0 Hz, 1 H), 7.29 (dd, J = 11.9, 1.0 Hz, 1 H), 7.25 (d, J = 8.2 Hz, 2 H), 7.17 (dd, J = 7.2, 7.3 Hz, 1 H), 2.52 (d, J = 7.0 Hz, 2 H), 1.91 (sept, J = 6.7 Hz, 1 H), 0.92 (d, J = 6.6 Hz, 6 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 145.2, 142.9, 141.1, 133.0, 129.1, 128.7, 128.2, 125.6, 120.6, 118.5, 45.1, 30.0, 21.8 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.2 ppm; IR: ν = 2952, 2865, 1612, 1596, 1566, 1460, 1440, 1402, 1384, 1346, 1284, 1200, 1118, 978, 813, 791 cm^{-1}; HRMS (ESI) m/z calc. for $C_{18}H_{21}BN$ $[M + H]^+$ 262.1767, found 262.1769.



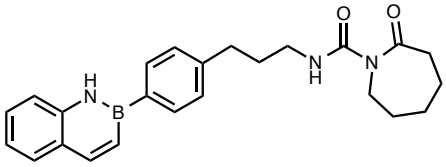
2-(4-(Acetoxymethyl)phenyl)-2,1-borazanaphthalene (2f): obtained as a white powder (104 mg, 75%) using silicate **11b**; mp = 95 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 9.79 (br s, 1 H), 8.18 (d, J = 11.6 Hz, 1 H), 8.05 (d, J = 8.0 Hz, 2 H), 7.70–7.64 (m, 2 H), 7.49–7.42 (m, 3 H), 7.29 (dd, J = 11.5, 2.1 Hz, 1 H), 7.18 (ddd, J = 7.9, 7.1, 1.1 Hz, 1 H), 5.15 (s, 2 H), 2.07 (s, 3 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 170.0, 145.4, 141.0, 137.7, 133.2, 129.1, 128.3, 127.5, 125.6, 120.8, 118.6, 65.5, 19.9 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.0 ppm; IR: ν = 1738, 1609, 1595, 1563, 1437, 1377, 1361, 1226, 1152, 1117, 1039, 1018, 988, 977, 939, 806 cm^{-1}; HRMS (ESI) m/z calc. for $C_{17}H_{16}BNNaO_2$ $[M + Na]^+$ 300.1172, found 300.1169.



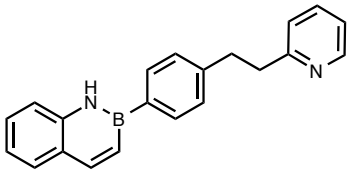
2-(4-(3-Acetoxypropyl)phenyl)-2,1-borazanaphthalene (2g): obtained as an off white powder (141 mg, 92%); mp = 71 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 9.70 (br s, 1 H), 8.15 (d, J = 8.6 Hz, 1 H), 7.98 (d, J = 7.8 Hz, 2 H), 7.69 (d, J = 8.1 Hz, 1 H), 7.66 (d, J = 8.1 Hz, 1 H), 7.45 (ddd, J = 8.1, 6.7, 1.3 Hz, 1 H), 7.31 (d, J = 7.8 Hz, 2 H), 7.28 (dd, J = 11.5, 1.8 Hz, 1 H), 7.17 (ddd, J = 8.0, 7.0, 1.3 Hz, 1 H), 4.07 (t, J = 6.6 Hz, 2 H), 2.74 (t, J = 7.7 Hz, 2 H), 2.00 (s, 3 H), 2.00–1.95 (m, 2 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 170.1, 145.2, 142.9, 141.0, 133.2, 129.1, 128.2, 128.0, 125.6, 120.6, 118.5, 63.2, 31.8, 30.1, 19.9 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.7 ppm; IR: ν = 3354, 1717, 1610, 1562, 1444, 1403, 1388, 136, 1344, 1253, 1191, 1154, 1033, 1002, 979, 815 cm^{-1}; HRMS (ESI) m/z calc. for $C_{19}H_{20}BNNaO_2$ $[M + Na]^+$ 328.1485, found 328.1481.



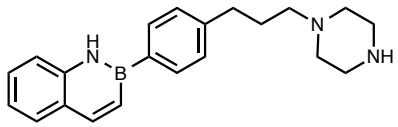
2-(4-(3-Acetamidopropyl)phenyl)-2,1-borazanaphthalene (2h): obtained as an off white powder (135 mg, 89%); mp = 157 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.17 (br s, 1 H), 8.13 (d, J = 11.3 Hz, 1 H), 7.86 (d, J = 7.8 Hz, 2 H), 7.68 (d, J = 8.3 Hz, 1 H), 7.45 (ddd, J = 7.9, 7.2, 1.4 Hz, 1 H), 7.35 (d, J = 8.5 Hz, 1 H), 7.30 (d, J = 7.5 Hz, 2 H), 7.27 (dd, J = 11.6, 2.1 Hz, 1 H), 7.20 (ddd, J = 7.9, 7.0, 0.9 Hz, 1 H), 5.49 (br s, 1 H), 3.33 (td, J = 6.8, 6.5 Hz, 2 H), 2.72 (t, J = 7.7 Hz, 2 H), 1.96 (s, 3 H), 1.90 (tt, J = 7.7, 6.8 Hz, 2 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 170.0, 145.4, 143.0, 140.1, 133.0, 132.9, 129.4, 128.3, 125.6, 120.9, 118.1, 39.3, 33.3, 31.0, 23.3 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.1 ppm; IR: ν = 1633, 1606, 1595, 1551, 1435, 1404, 1366, 1344, 1301, 1281, 1200, 1182, 810, 757, 745, 719 cm^{-1}; HRMS (ESI) m/z calc. for $C_{19}H_{22}BN_2O$ $[M + H]^+$ 305.1825, found 305.1816.



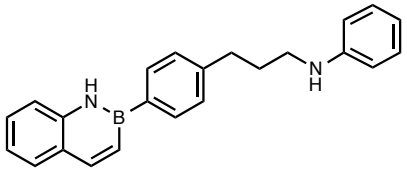
2-(4-(3-(2-Oxoazepane-1-carboxamido)propyl)phenyl)-2,1-borazanaphthalene (2i): obtained as an off white powder (192 mg, 96%); mp = 133 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 10.34 (br s, 1 H), 9.22 (br s, 1 H), 8.11 (d, J = 11.4 Hz, 1 H), 7.99 (d, J = 8.0 Hz, 2 H), 7.71 (d, J = 8.3 Hz, 1 H), 7.66 (d, J = 8.0 Hz, 1 H), 7.44 (t, J = 7.6 Hz, 1 H), 7.29 (d, J = 7.1 Hz, 2 H), 7.22 (d, J = 11.1 Hz, 1 H), 7.14 (t, J = 7.1 Hz, 1 H), 3.90 (d, J = 2.1 Hz, 2 H), 3.18–3.24 (m, 2 H), 2.71–2.68 (m, 2 H), 2.62 (t, J = 4.3 Hz, 2 H), 1.85–1.80 (m, 2 H), 1.68–1.62 (m, 4 H), 1.58–1.53 (m, 2 H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 179.4, 154.6, 145.5, 143.3, 141.4, 133.9, 129.4, 128.6, 128.3, 125.5, 120.9, 119.0, 43.2, 39.9, 39.3, 33.0, 30.9, 28.7, 28.3, 23.4 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 33.9 ppm; IR: ν = 3390, 3258, 1686, 1651, 1614, 1568, 1524, 1451, 1440, 1396, 1351, 1289, 1205, 1174, 1159, 814, 776, 748 cm^{-1}; HRMS (ESI) m/z calc. for $C_{24}H_{29}BN_3O_2$ $[M + H]^+$ 402.2344, found 402.2353.



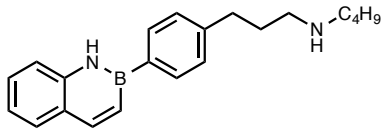
2-(4-(2-Pyridin-2-yl)ethyl)phenyl)-2,1-borazanaphthalene (2j): obtained as an off white powder (125 mg, 81%); mp = 117 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 9.73 (br s, 1 H), 8.52 (d, J = 4.9 Hz, 1 H), 8.16 (d, J = 11.2 Hz, 1 H), 7.95 (d, J = 7.3 Hz, 2 H), 7.69–7.60 (m, 3 H), 7.44 (ddd, J = 7.9, 7.4, 1.4 Hz, 1 H), 7.32–7.26 (m, 3 H), 7.21 (d, J = 8.0 Hz, 1 H) 7.19–7.12 (m, 2 H), 3.13–3.08 (m, 4 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 161.1, 149.1, 145.2, 143.3, 141.1, 136.0, 133.2, 129.1, 128.2, 128.1, 125.6, 122.7, 121.0, 120.6, 118.5, 39.6, 35.5 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 35.1 ppm; IR: ν = 3372, 1605, 1593, 1565, 1471, 1431, 1404, 1386, 1347, 1282, 1229, 1199, 1139, 977, 808, 756, 745 cm^{-1}; HRMS (ESI) m/z calc. for $C_{21}H_{20}BN_2$ $[M + H]^+$ 311.1720, found 311.1724.



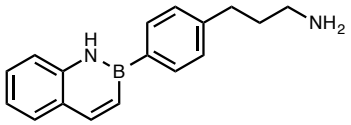
2-(4-(3-(Piperazin-1-yl)propyl)phenyl)-2,1-borazanaphthalene (2k): obtained as a colorless oil (78 mg, 47%) using silicate **11c**; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 8.16 (br s, 1 H), 8.13 (d, J = 11.5 Hz, 1 H), 7.66 (d, J = 7.7 Hz, 2 H), 7.66 (dd, J = 8.0, 1.1 Hz, 1 H), 7.44 (ddd, J = 8.3, 6.9, 1.2 Hz, 1 H), 7.35–7.30 (m, 3 H), 7.29 (d, J = 12 H, 1 H), 7.20 (t, J = 7.4 Hz, 1 H), 2.96–2.90 (m, 4 H), 2.71 (t, J = 7.7 Hz, 2 H), 2.51–2.37 (m, 6 H), 2.32–2.20 (br s, 1 H), 1.89 (tt, J = 8.5, 6.7 Hz, 2 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 145.3, 143.9, 140.2, 132.8, 129.4, 128.4, 128.3, 125.6, 120.9, 118.1, 58.6, 54.5, 46.0, 33.7, 28.2 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.2 ppm; IR: ν = 2939, 2806, 1612, 1595, 1563, 1437, 1345, 1283, 1233, 1217, 1199, 1188, 1142, 1116, 979, 801 cm^{-1}; HRMS (ESI) m/z calc. for $C_{21}H_{27}BN_3$ $[M + H]^+$ 332.2298, found 332.2307.



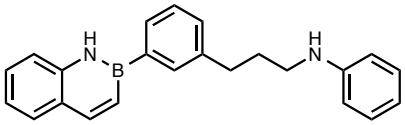
2-(4-(3-(Phenylamino)propyl)phenyl)-2,1-borazanaphthalene (2l): obtained as a white powder (154 mg, 91%); mp = 110 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 9.69 (br s, 1 H), 8.16 (d, J = 11.0 Hz, 1 H), 7.98 (d, J = 7.8 Hz, 2 H), 7.67 (t, J = 8.6 Hz, 2 H), 7.44 (ddd, J = 8.2, 7.2, 1.5 Hz, 1 H), 7.34–7.26 (m, 3 H), 7.17 (ddd, J = 8.0, 6.8, 1.2 Hz, 1 H), 7.10–7.05 (m, 2 H), 6.61 (dd, J = 8.2, 1.1 Hz, 2 H), 6.56 (t, J = 7.3 Hz, 1 H), 4.85 (br s, 1 H), 3.18–3.12 (m, 2 H), 2.78 (t, J = 7.7 Hz, 2 H), 2.00–1.94 (m, 2 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 149.1, 145.2, 143.6, 141.1, 133.2, 129.1, 128.8, 128.2, 128.1, 125.6, 120.6, 118.5, 115.9, 112.2, 42.8, 33.2, 30.9 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.4 ppm; IR: ν = 3350, 1596, 1561, 1503, 1480, 1438, 1405, 1311, 1282, 1236, 1183, 1163, 1148, 1118, 810, 757, 743 cm^{-1}; HRMS (ESI) m/z calc. for $C_{23}H_{24}BN_2$ $[M + H]^+$ 339.2033, found 339.2032.



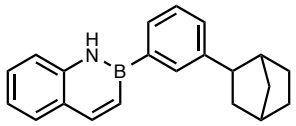
2-(4-(3-(Butylamino)propyl)phenyl)-2,1-borazanaphthalene (2m): obtained as a light brown powder (152 mg, 95%) using silicate **11d**; mp = 91 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.18–8.12 (m, 2 H), 7.88 (d, J = 7.8 Hz, 2 H), 7.67 (d, J = 7.8 Hz, 1 H), 7.46 (ddd, J = 8.6, 6.4, 1.4 Hz, 1 H), 7.36–7.27 (m, 4 H), 7.21 (ddd, J = 8.1, 7.5, 1.3 Hz, 1 H), 2.77–2.69 (m, 4 H), 2.64 (t, J = 7.2 Hz, 2 H), 2.19 (br s, 1 H), 1.90 (tt, J = 7.8, 7.2 Hz, 2 H), 1.51 (tt, J = 8.0, 7.2 Hz, 2 H), 1.40–1.33 (m, 2 H), 0.95 (t, J = 7.5 Hz, 3 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.3, 143.8, 140.2, 132.8, 129.4, 128.3, 128.2, 125.6, 120.9, 118.1, 49.7, 49.5, 33.7, 32.2, 31.5, 20.4, 13.9 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.6 ppm; IR: ν = 2988, 1608, 1597, 1563, 1437, 1405, 1345, 1282, 1234, 1211, 1183, 1103, 977, 881, 796, 758, 733 cm^{-1}; HRMS (ESI) m/z calc. for $C_{21}H_{28}BN_2$ $[M + H]^+$ 319.2346, found 319.2351.



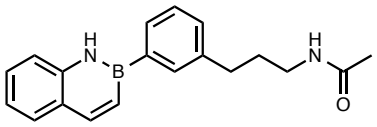
2-(4-(3-Aminopropyl)phenyl)-2,1-borazanaphthalene (2n): obtained as a white powder (89 mg, 68%); mp = 121 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 9.71 (br s, 1 H), 8.15 (d, J = 11.6 Hz, 1 H), 7.96 (d, J = 7.9 Hz, 2 H), 7.69–7.65 (m, 2 H), 7.43 (ddd, J = 8.5, 6.8, 1.4 Hz, 1 H), 7.31–7.26 (m, 3 H), 7.16 (ddd, J = 8.1, 6.8, 1.4 Hz, 1 H), 3.21 (t, J = 6.8 Hz, 2 H), 2.72 (t, J = 7.1 Hz, 2 H), 1.95–1.71 (m, 4 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 145.1, 144.1, 141.1, 133.1, 129.1, 128.2, 128.1, 125.6, 120.5, 118.5, 50.2, 33.4, 32.5 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.2 ppm; IR: ν = 2941, 1651, 1609, 1575, 1455, 1417, 1349, 1287, 1208, 1193, 978, 941, 893, 813, 790, 759 cm^{-1}; HRMS (ESI) m/z calc. for $C_{17}H_{20}BN_2$ $[M + H]^+$ 263.1720, found 263.1711.



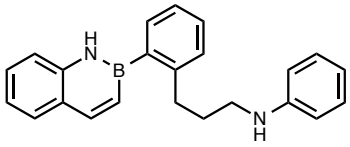
2-(3-(3-(Phenylamino)propyl)phenyl)-2,1-borazanaphthalene (3a): obtained as a white powder (153 mg, 90%); mp = 75 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.18 (d, *J* = 11.3 Hz, 1 H), 8.14 (br s, 1 H), 7.81 (dt, *J* = 7.2, 1.2 Hz, 1 H), 7.78 (s, 1 H), 7.70 (dd, *J* = 7.9, 1.3 Hz, 1 H), 7.51–7.44 (m, 2 H), 7.38–7.30 (m, 3 H), 7.27–7.20 (m, 3 H), 6.75 (tt, *J* = 7.2, 1.0 Hz, 1 H), 6.65 (dd, *J* = 8.4, 0.8 Hz, 2 H), 3.67 (s, 1 H), 3.24 (t, *J* = 7.1 Hz, 2 H), 2.87 (t, *J* = 7.6 Hz, 2 H), 2.06 (tt, *J* = 7.6, 7.1 Hz, 2 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 148.3, 145.5, 141.3, 140.1, 132.8, 130.4, 129.7, 129.4, 129.2, 128.3 [× 2], 125.7, 121.0, 118.2, 117.2, 112.7, 43.4, 33.5, 31.2 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.5 ppm; IR: ν = 3325, 1599, 1579, 1561, 1507, 135, 1389, 1346, 1334, 1283, 1262, 1245, 1210, 1184, 1153, 795, 762 cm^{-1}; HRMS (ESI) m/z calc. for $C_{23}H_{24}BN_2$ $[M + H]^+$ 339.2033, found 339.2036.



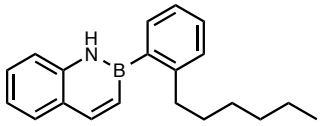
2-(3-(*exo*-Bicyclo[2.2.1]heptan-2-yl)phenyl)-2,1-borazanaphthalene (3b): obtained as a light brown powder (143 mg, 96%); mp = 115 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.13 (d, *J* = 11.7 Hz, 2 H), 7.75 (s, 1 H), 7.70 (d, *J* = 7.5 Hz, 1 H), 7.65 (d, *J* = 7.7 Hz, 1 H), 7.43 (ddd, *J* = 8.6, 7.2, 1.4 Hz, 1 H), 7.39 (t, *J* = 7.4 Hz, 1 H), 7.35–7.30 (m, 2 H), 7.27 (dd, *J* = 11.6, 2.2 Hz, 1 H), 7.18 (ddd, *J* = 7.9, 7.0, 1.1 Hz, 1 H), 2.84 (dd, *J* = 8.3, 5.8 Hz, 1 H), 2.45–2.43 (m, 1 H), 2.41–2.37 (m, 1 H), 1.86–1.80 (m, 1 H), 1.79–1.73 (m, 1 H), 1.67–1.55 (m, 3 H), 1.44–1.38 (m, 1 H), 1.34–1.28 (m, 1 H), 1.26–1.20 (m, 1 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 147.2, 145.4, 140.2, 131.8, 129.8, 129.5, 128.4, 128.3, 128.2, 125.8, 121.0, 118.3, 47.6, 43.1, 39.2, 36.9, 36.2, 30.7, 29.0 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.5 ppm; IR: ν = 2948, 2866, 1613, 1595, 1561, 1435, 1349, 1288, 1267, 1244, 1210, 1188, 1119, 818, 791, 756 cm^{-1}; HRMS (ESI) m/z calc. for $C_{21}H_{21}BN$ $[M - H]^-$ 298.1767, found 298.1756.



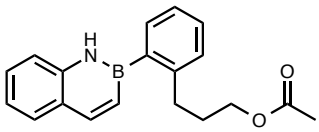
2-(3-(3-Acetamidopropyl)phenyl)-2,1-borazanaphthalene (3c): obtained as an off white powder (146 mg, 96%); mp = 78 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.49 (br s, 1 H), 8.11 (d, *J* = 11.4 Hz, 1 H), 7.76–7.71 (m, 2 H), 7.63 (d, *J* = 8.0 Hz, 1 H), 7.44–7.41 (m, 2 H), 7.37 (t, *J* = 7.5 Hz, 1 H), 7.26–7.21 (m, 2 H), 7.19–7.15 (m, 1 H), 5.65 (br s, 1 H), 3.30 (td, *J* = 6.6, 6.7 Hz, 2 H), 2.70 (t, *J* = 7.4 Hz, 2 H), 1.94 (s, 3 H), 1.87 (tt, *J* = 7.7, 7.1 Hz, 2 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 170.2, 145.4, 140.8, 140.4, 132.8, 130.6, 129.6, 129.3, 128.3, 128.2, 125.6, 120.9, 118.4, 39.3, 33.1, 31.0, 23.3 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.7 ppm; IR: ν = 3321, 1649, 1613, 1595, 1562, 1436, 1412, 1386, 1366, 1347, 1285, 1242, 1207, 1181, 810, 785, 759 cm^{-1}; HRMS (ESI) m/z calc. for $C_{19}H_{21}BN_2NaO$ $[M + Na]^+$ 327.1645, found 327.1635.



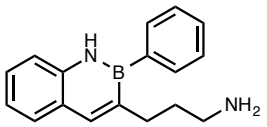
2-(2-(3-(Phenylamino)propyl)phenyl)-2,1-borazanaphthalene (4a): obtained as a light yellow oil (158 mg, 93%); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.08 (d, *J* = 11.7 Hz, 1 H), 7.92 (br s, 1 H), 7.66 (d, *J* = 8.3 Hz, 1 H), 7.48–7.44 (m, 1 H), 7.40 (ddd, *J* = 8.2, 7.1, 1.5 Hz, 1 H), 7.37–7.32 (m, 1 H), 7.28–7.23 (m, 2 H), 7.19 (ddd, *J* = 7.9, 7.0, 1.1 Hz, 1 H), 7.15 (d, *J* = 8.3 Hz, 1 H), 7.09–7.02 (m, 3 H), 6.64 (tt, *J* = 7.3, 1.1 Hz, 1 H), 6.38 (dd, *J* = 8.6, 1.1 Hz, 2 H), 3.37 (br s, 1 H), 3.03 (t, *J* = 6.8 Hz, 2 H), 2.90 (t, *J* = 7.6 Hz, 2 H), 1.85 (tt, *J* = 7.6, 6.8 Hz, 2 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 148.2, 144.9, 140.0, 133.0 ,129.4, 129.1, 128.7, 128.6, 128.4 [× 2], 125.5, 125.3, 121.2, 118.3, 117.2, 112.7, 43.4, 33.6, 31.9 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 36.1 ppm; IR: ν =3331, 1614, 1597, 1559, 1504, 1430, 1345, 1320, 1280, 1262, 1235, 1203, 1179, 978, 907, 811, 746 cm^{-1}; HRMS (ESI) m/z calc. for $C_{23}H_{24}BN_2$ $[M + H]^+$ 339.2033, found 339.2034.



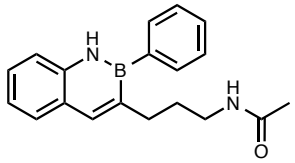
2-(2-Hexylphenyl)-2,1-borazanaphthalene (4b): obtained as a colorless oil (140 mg, 97%); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.09 (d, *J* = 11.4 Hz, 1 H), 7.93 (br s, 1 H), 7.67 (d, *J* = 8.3 Hz, 1 H), 7.47 (dd, *J* = 7.3, 1.3 Hz, 1 H), 7.43 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1 H), 7.33 (ddd, *J* = 7.6, 7.4, 1.3 Hz, 1 H), 7.29–7.16 (m, 4 H), 7.07 (dd, *J* = 11.4, 2.1 Hz, 1 H), 2.77 (t, *J* = 8.3 Hz, 2 H), 1.60–1.51 (m, 2 H), 1.31–1.17 (m, 6 H), 0.8 (t, *J* = 6.8 Hz, 3 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 146.3, 144.7, 140.1, 133.0, 129.5, 128.7, 128.5, 128.3, 125.4, 125.3, 121.1, 118.2, 36.2, 32.7, 31.7, 29.3, 22.6, 14.1 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 36.3 ppm; IR: ν = 2952, 2924, 2854, 1614, 1596, 1559, 1430, 1383, 1345, 1278, 1232, 1213, 1203, 1114, 978, 809 cm^{-1}; HRMS (ESI) m/z calc. for $C_{20}H_{23}BN$ $[M - H]^-$ 288.1924, found 288.1942.



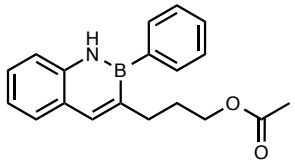
2-(2-(3-Acetoxypropyl)phenyl)-2,1-borazanaphthalene (4c): obtained as a colorless oil (142 mg, 93%); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.10 (d, *J* = 11.2 Hz, 1 H), 7.80 (br s, 1 H), 7.68 (d, *J* = 8.0 Hz, 1 H), 7.50–7.41 (m, 2 H), 7.37–7.30 (m, 2 H), 7.28–7.24 (m, 2 H), 7.22 (ddd, *J* = 8.0, 7.0, 1.2 Hz, 1 H), 7.06 (dd, *J* = 11.6, 1.8 Hz, 1 H), 3.99 (t, *J* = 6.6 Hz, 2 H), 2.87 (t, *J* = 7.8 Hz, 2 H), 1.91–1.85 (m, 2 H), 1.84 (s, 3 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 171.1, 144.8, 144.4, 140.2, 133.0, 129.4, 128.6, 128.5, 128.4, 125.6, 125.3, 121.2, 118.3, 63.8, 32.3, 31.2, 20.7 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 36.1 ppm; IR: ν = 1723, 1614, 1596, 1560, 1432, 1286, 1365, 1347, 1236, 1031, 979, 908, 812, 753, 729, 662 cm^{-1}; HRMS (ESI) m/z calc. for $C_{19}H_{21}BNO_2$ $[M + H]^+$ 306.1665, found 306.1666.



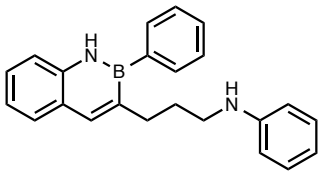
3-(3-Aminopropyl)-2-phenyl-2,1-borazanaphthalene (5a): obtained as a brown oil (124 mg, 95%); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.95 (br s, 1 H), 7.86 (s, 1 H), 7.70–7.65 (m, 2 H), 7.63 (dd, *J* = 7.8, 0.9 Hz, 1 H), 7.48–7.37 (m, 4 H), 7.27 (d, *J* = 7.4 Hz, 1 H), 7.20 (t, *J* = 7.5 Hz, 1 H), 2.78 (t, *J* = 7.6 Hz, 2 H), 2.68 (t, *J* = 7.6 Hz, 2 H), 1.72 (br s, 2 H), 1.66 (tt, *J* = 7.6 Hz, 2 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 141.9, 139.0, 132.3, 128.7, 128.4, 127.9, 127.4, 125.3, 121.1, 117.6, 41.8, 34.9, 32.4 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 36.1 ppm; IR: ν = 2926, 2854, 1661, 1614, 1597, 1567, 1453, 1427, 1372, 1347, 1285, 1240, 1208, 945, 909, 751 cm^{-1}; HRMS (ESI) m/z calc. for $C_{17}H_{20}BN_2$ $[M + H]^+$ 263.1720, found 263.1724.



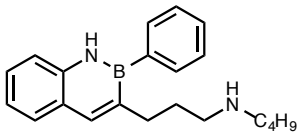
3-(3-Acetamidopropyl)-2-phenyl-2,1-borazanaphthalene (5b): obtained as an off white solid (146 mg, 96%); mp = 92 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.99 (br s, 1 H), 7.83 (s, 1 H), 7.65 (dd, *J* = 7.6, 1.4 Hz, 2 H), 7.60 (d, *J* = 7.7 Hz, 1 H), 7.46–7.40 (m, 3 H), 7.37 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1 H), 7.26 (d, *J* = 7.8 Hz, 1 H), 7.17 (ddd, *J* = 7.9, 7.3, 1.1 Hz, 1 H), 5.26 (br s, 1 H), 3.13 (td, *J* = 6.4, 6.3 Hz, 2 H), 2.73 (t, *J* = 7.6 Hz, 2 H), 1.80 (s, 3 H), 1.63 (tt, *J* = 7.4, 7.2 Hz, 2 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 169.9, 142.5, 139.1, 132.3, 128.8, 128.4, 128.0, 127.6, 125.3, 121.1, 117.7, 39.0, 32.1, 31.1, 23.2 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 35.8 ppm; IR: ν = 3281, 1650, 1614, 1597, 1565, 1453, 1429, 1365, 1347, 1286, 1239, 1208, 948, 752, 731, 701 cm^{-1}; HRMS (ESI) m/z calc. for $C_{19}H_{22}BN_2O$ $[M + H]^+$ 305.1825, found 305.1830.



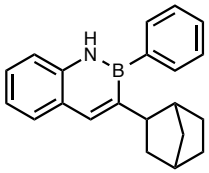
3-(3-Acetoxypropyl)-2-phenyl-2,1-borazanaphthalene (5c): obtained as a thick white wax (139 mg, 91%); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.93 (br s, 1 H), 7.85 (s, 1 H), 7.67 (dd, *J* = 7.8, 1.6 Hz, 2 H), 7.62 (d, *J* = 7.7 Hz, 1 H), 7.46–7.41 (m, 3 H), 7.39 (ddd, *J* = 8.2, 7.2, 1.4 Hz, 1 H), 7.26 (d, *J* = 8.2 Hz, 1 H), 7.19 (ddd, *J* = 7.8, 7.1, 1.0 Hz, 1 H), 4.02 (t, *J* = 6.6 Hz, 2 H), 2.80 (t, *J* = 7.9 Hz, 2 H), 1.98 (s, 3 H), 1.81 (tt, *J* = 7.8, 6.4 Hz, 2 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 171.1, 142.3, 139.1, 132.3, 128.8, 128.4, 128.0, 127.6, 125.3, 121.2, 117.7, 64.1, 31.4, 29.9, 20.9 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 36.2 ppm; IR: ν = 1721, 1614, 1597, 1567, 1452, 1427, 1385, 1364, 1347, 1238, 1035, 999, 946, 918, 854, 751 cm^{-1}; HRMS (ESI) m/z calc. for $C_{19}H_{20}BNNaO_2$ $[M + Na]^+$ 328.1485, found 328.1496.



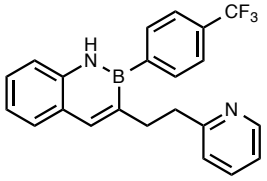
3-(3-(Phenylamino)propyl)-2-phenyl-2,1-borazanaphthalene (5d): obtained as a brown oil (147 mg, 87%); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.00 (br s, 1 H), 7.96 (s, 1 H), 7.79–7.75 (m, 2 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.58–7.54 (m, 3 H), 7.48 (t, *J* = 7.4 Hz, 1 H), 7.33–7.21 (m, 4 H), 6.78 (t, *J* = 7.2 Hz, 1 H), 6.59 (d, *J* = 8.1 Hz, 2 H), 3.51 (br s, 1 H), 3.15 (t, *J* = 7.0 Hz, 2 H), 2.94 (t, *J* = 7.5 Hz, 2 H), 1.87 (tt, *J* = 7.5, 7.0 Hz, 2 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 148.4, 142.3, 139.2, 132.4, 129.2, 128.9, 128.6, 128.1, 127.6, 125.4, 121.3, 117.8, 117.0, 112.7, 43.5, 32.7, 31.0 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 35.9 ppm; IR: ν =1613, 1600, 1565, 1504, 1473, 1451, 1423, 1345, 1320, 1282, 1255, 1240 ,1206, 1179, 944, 765 cm^{-1}; HRMS (ESI) m/z calc. for $C_{23}H_{24}BN_2$ $[M + H]^+$ 339.2031, found 339.2033.



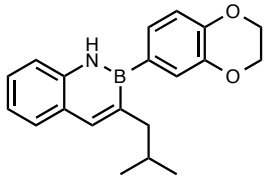
3-(3-(Butylamino)propyl)-2-phenyl-2,1-borazanaphthalene (5e): obtained as a light brown powder (141 mg, 89%); ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.98 (br s, 1 H), 7.88 (s, 1 H), 7.70 (dd, *J* = 7.8, 1.5 Hz, 2 H), 7.65 (d, *J* = 8.2 Hz, 1 H), 7.49–7.43 (m, 3 H), 7.40 (ddd, 8.1, 7.4, 1.7 Hz, 1 H), 7.27 (d, *J* = 8.3 Hz, 1 H), 7.21 (ddd, *J* = 7.8, 7.2, 1.0 Hz, 1 H), 2.79 (t, *J* = 8.1 Hz, 2 H), 2.62 (t, *J* = 7.3 Hz, 2 H), 2.54 (t, *J* = 7.5 Hz, 2 H), 1.98 (br s, 1 H), 1.73 (tt, *J* = 7.5, 7.3 Hz, 2 H), 1.48–1.40 (m, 2 H), 1.37–1.27 (m, 2 H), 0.92 (t, *J* = 7.5 Hz, 3 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 142.0, 139.1, 132.3, 128.7, 128.4, 127.9, 127.4, 125.4, 121.1, 117.6, 49.6, 49.4, 32.8, 32.0, 31.3, 20.4, 14.0 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 35.0 ppm; IR: ν = 2954, 2927, 2857, 1615, 1597, 1567, 1454, 1423, 1346, 1283, 1240, 1207, 954, 943, 910, 764 cm^{-1}; HRMS (ESI) m/z calc. for $C_{21}H_{28}BN_2$ $[M + H]^+$ 319.2346, found 319.2333.



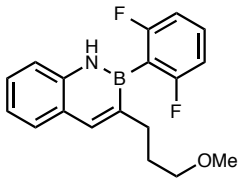
3-(*exo*-Bicyclo[2.2.1]heptan-2-yl)-2-phenyl-2,1-borazanaphthalene (5f): obtained as an off white solid (144 mg, 96%); mp = 62 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 7.84 (br s, 1 H), 7.81 (s, 1 H), 7.68–7.61 (m, 3 H), 7.46–7.38 (m, 3 H), 7.34 (ddd, *J* = 8.2, 6.9, 1.5 Hz, 1 H), 7.22–7.19 (m, 1 H), 7.17 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1 H), 2.98 (dd, *J* = 8.9, 6.0 Hz, 1 H), 2.35–2.33 (m, 1 H), 2.32–2.30 (m, 1 H), 1.66–1.44 (m, 5 H), 1.30–1.23 (m, 1 H), 1.21–1.11 (m, 2 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 138.6, 137.4, 132.4, 1291, 128.1, 127.8, 127.2, 125.4, 121.1, 117.5, 44.9, 42.4, 38.7, 37.2, 35.5, 30.2, 29.0 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 36.6 ppm; IR: ν = 2946, 2866, 1612, 1597, 1563, 1453, 1419, 1345, 1307, 1235, 1206, 940, 909, 763, 747, 700 cm^{-1}; HRMS (ESI) m/z calc. for $C_{21}H_{23}BN$ $[M + H]^+$ 300.1924, found 300.1928.



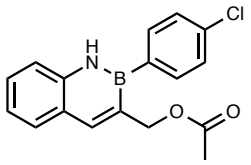
3-(2-Pyridin-2-yl)ethyl)-2-(4-trifluoromethylphenyl)-2,1-borazanaphthalene (6): obtained as a white solid (145 mg, 77%); mp = 100 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 9.71 (br s, 1 H), 8.44 (d, J = 4.2 Hz, 1 H), 8.01–7.87 (m, 3 H), 7.71 (d, J = 8.6 Hz, 2 H), 7.67 (d, J = 7.7 Hz, 1 H), 7.61 (d, J = 7.8 Hz, 1 H), 7.57 (ddd, J = 7.8, 7.7, 1.8 Hz, 1 H), 7.40 (ddd, J = 7.9, 7.5, 1.7 Hz, 1 H), 7.18 (t, J = 7.9 Hz, 1 H), 7.09–7.00 (m, 2 H), 3.13 (d, J = 8.6 Hz, 2 H), 2.93 (dd, J = 9.6, 7.3 Hz, 2 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 161.5, 149.0, 142.5, 139.8, 135.9, 133.2, 129.4 (q, J = 32.4 Hz), 128.7, 127.6, 125.5, 124.7 (q, J = 271.8 Hz), 124.0 (q, J = 4.0 Hz), 122.5, 121.1, 120.9, 118.2, 39.5, 34.9 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 35.2 ppm; ^{19}F {^{1}H} NMR (acetone-d_6, 470.8 MHz): –62.9 ppm; IR: ν = 1595, 1571, 1459, 1438, 1322, 1293, 1150, 1112, 1104, 1063, 1019, 969, 953, 835, 763, 749 cm^{-1}; HRMS (ESI) m/z calc. for $C_{22}H_{19}BF_3N_2$ $[M + H]^+$ 379.1593, found 379.1599.



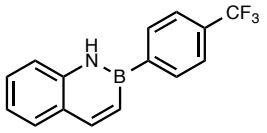
3-(Isobutyl)-2-(2,3-dihydro-1,4-benzodioxin-6-yl)-2,1-borazanaphthalene (7): obtained as a white solid (78 mg, 94%), starting from **1f** (69 mg, 0.26 mmol); mp = 78 °C; ^{1}H NMR ($CDCl_3$, 500.4 MHz): δ 8.09 (br s, 1 H), 7.77 (s, 1 H), 7.60 (d, J = 7.5 Hz, 1 H), 7.33 (ddd, J = 8.2, 7.0, 1.1 Hz, 1 H), 7.20 (d, J = 8.3 Hz, 1 H), 7.15 (t, J = 7.2 Hz, 1 H), 8.97 (dd, J = 5.8, 3.2 Hz, 1 H), 6.92–6.86 (m, 2 H), 4.26–4.17 (m, 4 H), 2.52 (d, J = 7.2 Hz, 2 H), 1.67 (tsept, 6.6, 7.2 Hz, 1 H), 0.79 (d, J = 6.6 Hz, 6 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 145.3, 143.1, 142.3, 138.8, 128.7, 127.1, 125.8, 125.4, 121.3, 121.0, 117.6, 117.5, 64.3, 64.2, 45.1, 29.2, 22.6 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 36.5 ppm; IR: ν = 2946, 1614, 1597, 1565, 1454, 1437, 1422, 1377, 1280, 1252, 1217, 1200, 1093, 1082, 930, 895, 843 cm^{-1}; HRMS (ESI) m/z calc. for $C_{20}H_{23}BNO_2$ $[M + H]^+$ 320.1822, found 320.1836.



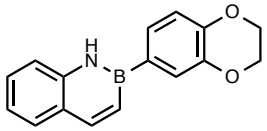
3-(3-Methoxypropyl)-2-(2,6-difluorophenyl)-2,1-borazanaphthalene (8): obtained as a white solid from (150 mg, 96%); mp = 73 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 9.91 (br s, 1 H), 7.96 (s, 1 H), 7.71 (d, J = 9.1 Hz, 1 H), 7.61 (d, J = 8.0 Hz, 1 H), 7.47–7.40 (m, 2 H), 7.22 (ddd, J = 8.1, 7.0, 1.1 Hz, 1 H), 7.03–6.95 (m, 2 H), 3.25 (t, J = 6.7 Hz, 2 H), 3.15 (s, 3 H), 2.63 (t, J = 8.2 Hz, 2 H), 1.69 (tt, J = 8.3, 6.7 Hz, 2 H) ppm; ^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz): δ 164.4 (dd, J = 238.9, 16.7 Hz), 141.7, 139.4, 131.0 (t, J = 10.1 Hz), 128.7, 127.5, 125.6, 121.3, 118.1, 110.7 (dd, J = 21.8, 5.7 Hz), 71.8, 57.3, 31.4, 30.6 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 33.6 ppm; ^{19}F {^{1}H} NMR (acetone-d_6, 470.8 MHz): –103.2 ppm; IR: ν = 3274, 1617, 1573, 1462, 1444, 1227, 1213, 1110, 1101, 1060, 976, 966, 943, 852, 777, 760 cm^{-1}; HRMS (ESI) m/z calc. for $C_{18}H_{19}BF_2NO$ $[M + H]^+$ 314.1528, found 314.1536.



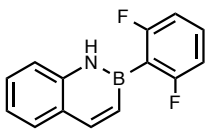
3-(Acetoxymethyl)-2-(4-chlorophenyl)-2,1-borazanaphthalene (9): obtained as a white solid (94 mg, 60%); mp = 122 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 9.73 (br s, 1 H), 8.13 (s, 1 H), 7.76–7.71 (m, 3 H), 7.65 (d, J = 8.7 Hz, 1 H), 7.50–7.42 (m, 3 H), 7.22 (ddd, J = 8.2, 6.7, 1.1 Hz, 1 H), 5.19 (s, 2 H), 2.03 (s, 3 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 169.9, 142.9, 140.5, 134.6, 134.2, 129.2, 128.6, 127.7, 124.6, 121.2, 118.3, 66.2, 20.0 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.9 ppm; IR: ν = 3324, 1720, 1616, 1587, 1575, 1454, 1431, 1367, 1340, 1246, 1210, 1100, 1088, 1034, 1013, 961, 792 cm^{-1}; HRMS (ESI) m/z calc. for $C_{17}H_{15}BClNNaO_2$ $[M + Na]^+$ 334.0782, found 334.0796.



2-(4-(Trifluoromethyl)phenyl)-2,1-borazanaphthalene (10a): obtained as an off white powder (0.42 g, 27%, 5.00 mmol scale); mp = 154 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 10.67 (br s, 1 H), 8.28 (d, J = 6.6 Hz, 2 H), 8.22 (d, J = 12.1 Hz, 1 H), 7.82 (d, J = 7.7 Hz, 2 H), 7.75 (t, J = 8.8 Hz, 2 H), 7.51 (ddd, J = 8.7, 7.3, 1.7 Hz, 1 H), 7.28 (dd, J = 11.9, 1.5 Hz, 1 H), 7.22 (ddd, J = 7.8, 7.4, 1.5 Hz, 1 H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 146.2, 141.1, 134.4, 130.0 (q, J = 31.1 Hz), 129.5, 128.9, 125.7, 124.9 (q, J = 273.3 Hz), 124.8 (q, J = 5.3 Hz), 121.4, 119.2 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 33.8 ppm; ^{19}F {^{1}H} NMR (DMSO-d_6, 470.8 MHz): –61.2 ppm; IR: ν = 1614, 1560 ,1434, 1326, 1205, 1168, 1159, 1117, 1104, 1069, 1015, 989, 978, 838, 811, 761 cm^{-1}; HRMS (ESI) m/z calc. for $C_{15}H_{10}BF_3N$ $[M - H]^+$ 272.0858, found 272.0853.

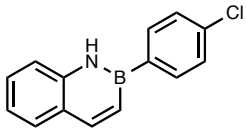


2-(2,3-Dihydro-1,4-benzodioxin-6-yl)-2,1-borazanaphthalene (10b): obtained as an off white powder (1.73 g, 84%, 7.80 mmol scale) from **10b**; mp = 89 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 10.23 (br s, 1 H), 8.07 (d, J = 10.6 Hz, 1 H), 7.68 (d, J = 8.7 Hz, 1 H), 7.64 (d, J = 7.8 Hz, 1 H), 7.62–7.59 (m, 1 H), 7.54 (dd, J = 8.1, 1.4 Hz, 1 H), 7.42 (ddd, J = 8.4, 6.9, 1.4 Hz, 1 H), 7.17 (dd, J = 11.2, 1.6 Hz, 1 H), 7.13 (ddd, J = 8.4, 7.2, 1.0 Hz, 1 H), 6.93 (d, J = 7.9 Hz, 1 H), 4.28 (s, 4 H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 145.4, 145.3, 143.7, 141.7, 129.3, 128.6, 127.2, 125.3, 122.2, 120.8, 118.9, 117.2, 64.7, 64.4 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 33.8 ppm; IR: ν = 3341, 1613, 1605, 1596, 1564, 1510, 1455, 1438, 1303, 1284, 1250, 1216, 1127, 1068, 1047, 898, 803 cm^{-1}; HRMS (CI) m/z calc. for $C_{16}H_{14}BNO_2$ $[M]^+$ 263.1118, found 263.1132.

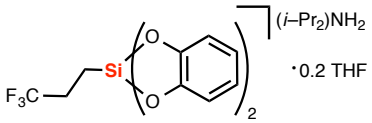


2-(2,6-Difluorophenyl)-2,1-borazanaphthalene (10c): obtained as an off white powder (0.67 g, 56%, 5.00 mmol scale); mp = 54 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 10.69 (br s,

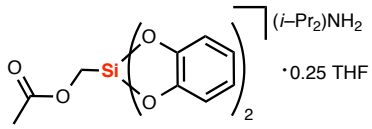
1 H), 8.20 (d, J = 10.9 Hz, 1 H), 7.76 (d, J = 7.3 Hz, 1 H), 7.68 (d, J = 8.5 Hz, 1 H), 7.55–7.48 (m, 2 H), 7.24 (t, J = 7.6 Hz, 1 H), 7.12 (t, J = 7.3 Hz, 2 H), 7.02 (d, J = 11.5 Hz, 1 H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 165.0 (dd, J = 240.1, 16.1 Hz), 145.5, 140.7, 132.5 (t, J = 12.0 Hz), 129.5, 128.9, 125.4, 121.6, 119.2, 111.5 (dd, J = 22.1, 5.9 Hz) ppm; ^{19}F NMR (DMSO-d_6, 470.8 MHz): δ –102.7 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 32.3 ppm; IR: ν = 1615, 1558, 1463, 1452, 1429, 1385, 1345, 1276, 1247, 1217, 1202, 990, 973, 943, 810, 779 cm^{-1}; HRMS (CI) m/z calc. for $C_{14}H_{10}BF_2N$ $[M]^+$ 241.0874, found 241.0871.



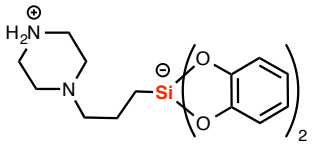
2-(4-Chlorophenyl)-2,1-borazanaphthalene (10d): obtained as an off white powder (0.40 g, 83%, 2.00 mmol scale); mp = 140 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 10.50 (br s, 1 H), 8.17 (d, J = 11.5 Hz, 1 H), 8.10 (d, J = 8.1 Hz, 2 H), 7.73 (d, J = 8.3 Hz, 1 H), 7.70 (d, J = 7.7 Hz, 1 H), 7.53 (d, J = 8.3 Hz, 2 H), 7.48 (ddd, J = 8.5, 7.2, 1.5 Hz, 1 H), 7.24 (dd, J = 11.6, 1.8 Hz, 1 H), 7.19 (ddd, J = 8.1, 6.6, 1.1 Hz, 1 H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 145.8, 141.2, 135.6, 135.0, 129.4, 128.8, 128.3, 125.5, 121.1, 119.0 ppm; ^{11}B NMR (acetone, 128.4 MHz): δ 34.1 ppm; IR: ν = 1611, 1582, 1556, 1494, 1434, 1392, 1345, 1280, 1223, 1205, 1117, 1089, 1010, 975, 822, 808 cm^{-1}; HRMS (ESI) m/z calc. for $C_{14}H_{11}BCl_2N$ $[M + Cl]^-$ 274.0362, found 274.0363.



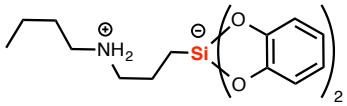
Diisopropylammonium bis(catecholato)3,3,3-trifluoropropylsilicate (11a): obtained as a white powder (6.31 g, 92%, 15.00 mmol scale), crystallized with 0.2 equiv THF, mp 237 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 8.02 (br s, 2 H), 6.59–6.55 (m, 4 H), 6.49–6.45 (m, 4 H), 3.34 (sept, J = 6.9 Hz, 2 H), 2.04–1.96 (m, 2 H), 1.19 (d, J = 6.9 Hz, 12 H), 0.68–0.62 (m, 2 H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 150.6, 128.8 (q, J = 277.9 Hz), 117.9, 110.2, 46.8, 28.9 (q, J = 28.9 Hz), 19.2, 9.54 ppm; ^{19}F {^{1}H} NMR ($CDCl_3$, 470.8 MHz): –67.3 ppm; IR: ν = 2987, 1707, 1599, 1484, 1392, 1349, 1321, 1297, 1238, 1167, 1149, 1098, 1014, 938, 891, 811 cm^{-1}; HRMS (ESI) m/z calc. for $C_{15}H_{12}F_3O_4Si$ $[M - i\text{-}Pr_2NH_2]^-$ 341.0457, found 341.0462.



Diisopropylammonium bis(catecholato)acetoxymethylsilicate (11b): obtained as a white powder (1.71 g, 76%, 5.15 mmol scale), mp 127 °C; ^{1}H NMR (acetone-d_6, 500.4 MHz): δ 7.43 (br s, 2 H), 6.69–6.63 (m, 4 H), 6.54–6.50 (m, 4 H), 3.82 (sept, J = 6.7 Hz, 2 H), 3.80 (s, 2 H), 1.74 (s, 3 H), 1.43 (d, J = 6.7 Hz, 12 H) ppm; ^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz): δ 170.5, 150.0, 118.0, 110.3, 56.2, 48.3, 19.9, 18.6 ppm; IR: ν = 1725, 1483, 1393, 1365, 1347, 1294, 1235, 1148, 1098, 1038, 1014, 887, 814, 771, 738, 707 cm^{-1}; HRMS (ESI) m/z calc. for $C_{15}H_{13}O_6Si$ $[M - i\text{-}Pr_2NH_2]^-$ 317.0481, found 317.0482.

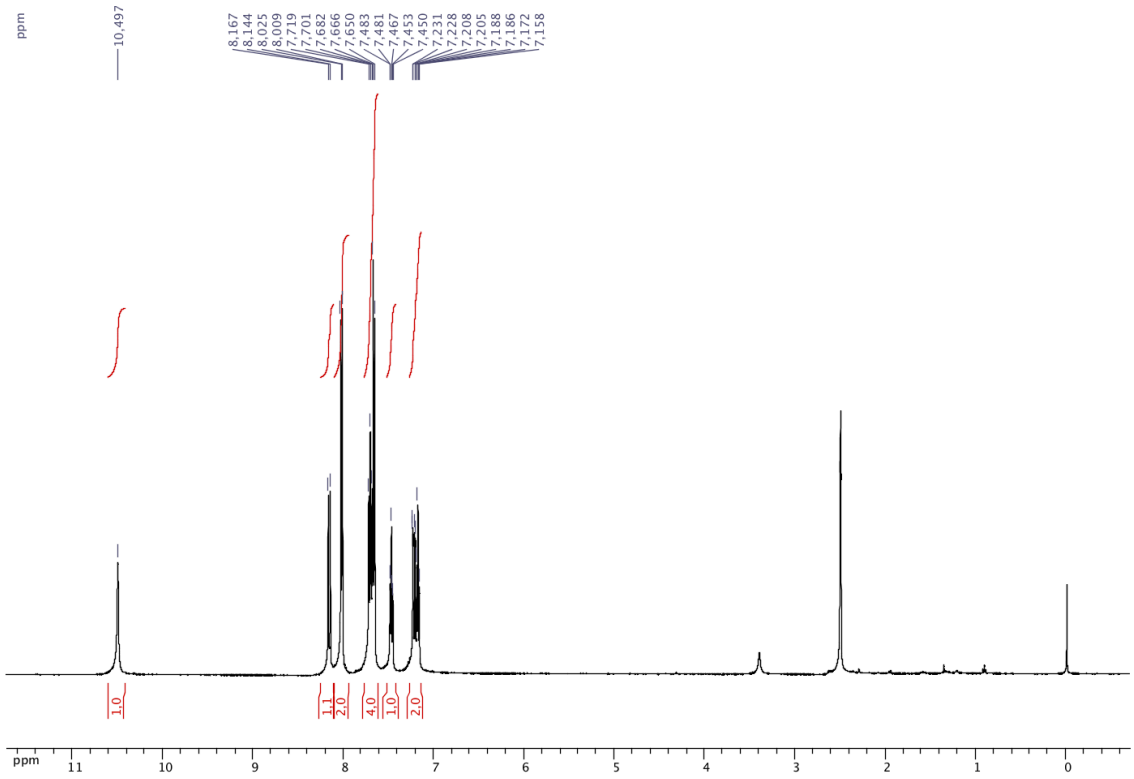


Bis(catecholato)3-(piperazin-1-ium-1-yl)propyl silicate (11c): obtained as a white powder (909 mg, 71%, 3.44 mmol scale), mp >260 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 8.16 (br s, 2 H), 6.53–6.50 (m, 4 H), 6.46–6.41 (m, 4 H), 2.98–2.96 (m, 4 H), 2.43–2.42 (m, 4 H), 2.20 (t, J = 7.0 Hz, 2 H), 1.36 (tt, J = 7.7, 7.7 Hz, 2 H), 0.47 (t, J = 7.0 Hz, 2 H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 150.9, 117.5, 109.9, 61.1, 49.9, 43.4, 21.4, 15.7 ppm; IR: ν = 2812, 1488, 1457, 1352, 1243, 1223, 1198, 1174, 1104, 1015, 889, 828, 769, 738, 724, 716 cm^{-1}; HRMS (ESI) m/z calc. for $C_{19}H_{24}N_2O_4Si$ $[M]^+$ 372.1505, found 372.1506.

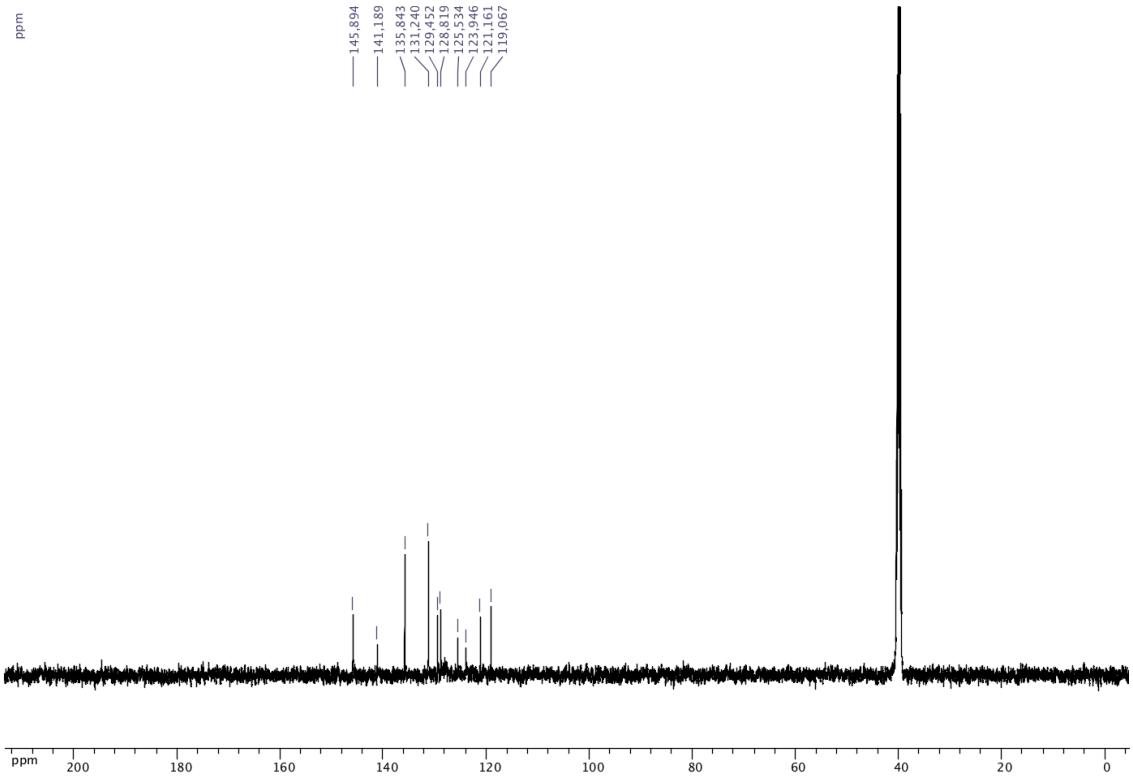


Bis(catecholato)3-(butylammonio)propyl silicate (11d): obtained as a white powder (6.86 g, 90%, 21.25 mmol scale), mp 225 °C; ^{1}H NMR (DMSO-d_6, 500.4 MHz): δ 8.00 (br s, 2 H), 6.57–6.51 (m, 4 H), 6.48–6.42 (m, 4 H), 2.76–2.68 (m, 4 H), 1.58–1.49 (m, 2 H), 1.48–1.40 (m, 2 H), 1.25 (tt, J = 7.0, 7.0 Hz, 2 H), 0.84 (t, J = 7.4 Hz, 3 H), 0.52 (t, J = 8.0 Hz, 2 H) ppm; ^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz): δ 150.7, 117.7, 110.1, 50.3, 46.9, 27.8, 21.9, 19.6, 15.3, 13.8 ppm; IR: ν = 3031, 1485, 1460, 1435, 1352, 1257, 1236, 1222, 1194, 1102, 1015, 888, 830, 753, 730, 697, 656 cm^{-1}; HRMS (ESI) m/z calc. for $C_{19}H_{24}NO_4Si$ $[M - H]^-$ 358.1475, found 358.1479.

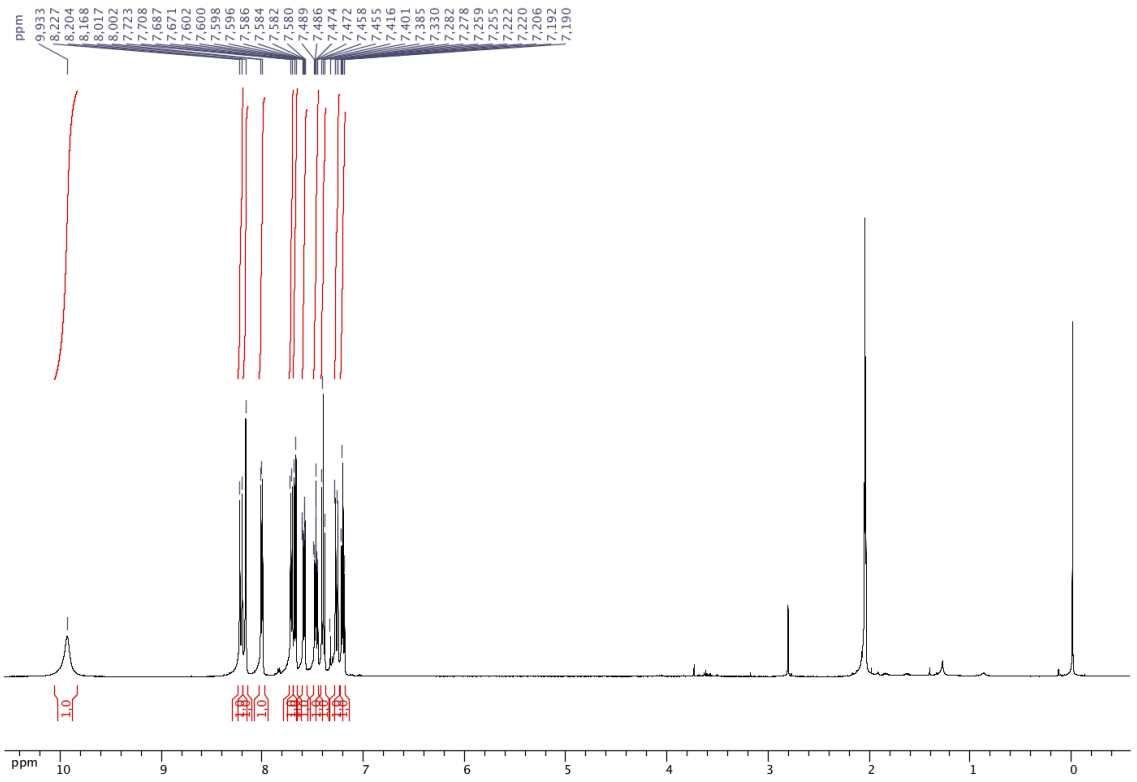
Spectral data



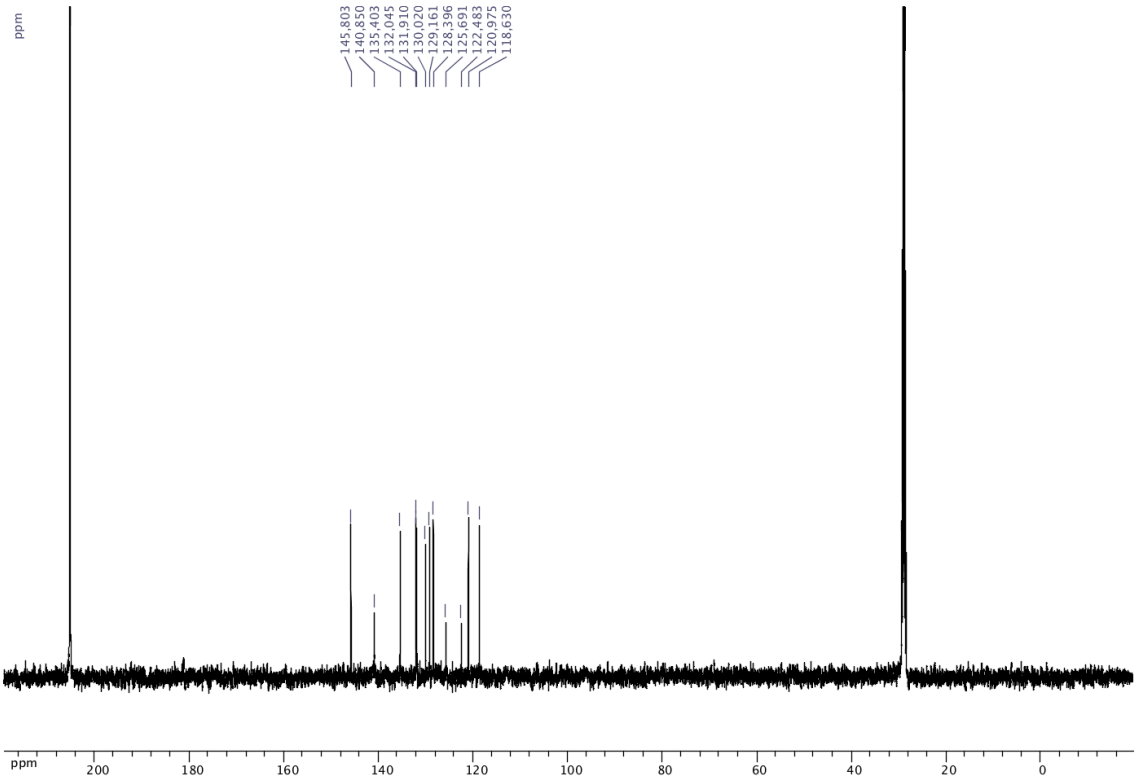
^{1}H NMR (DMSO-d_6, 500.4 MHz) of 2-(4-bromophenyl)-2,1-borazanaphthalene (**1a**)



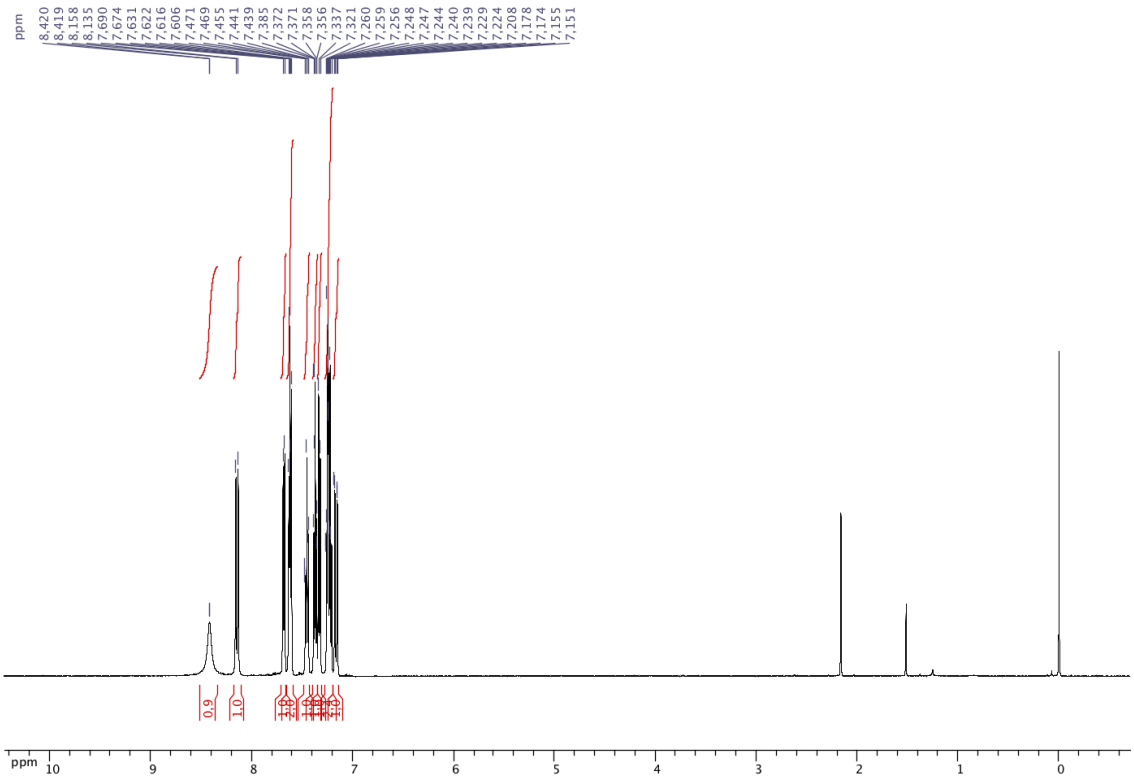
^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz) of 2-(4-bromophenyl)-2,1-borazanaphthalene (**1a**)



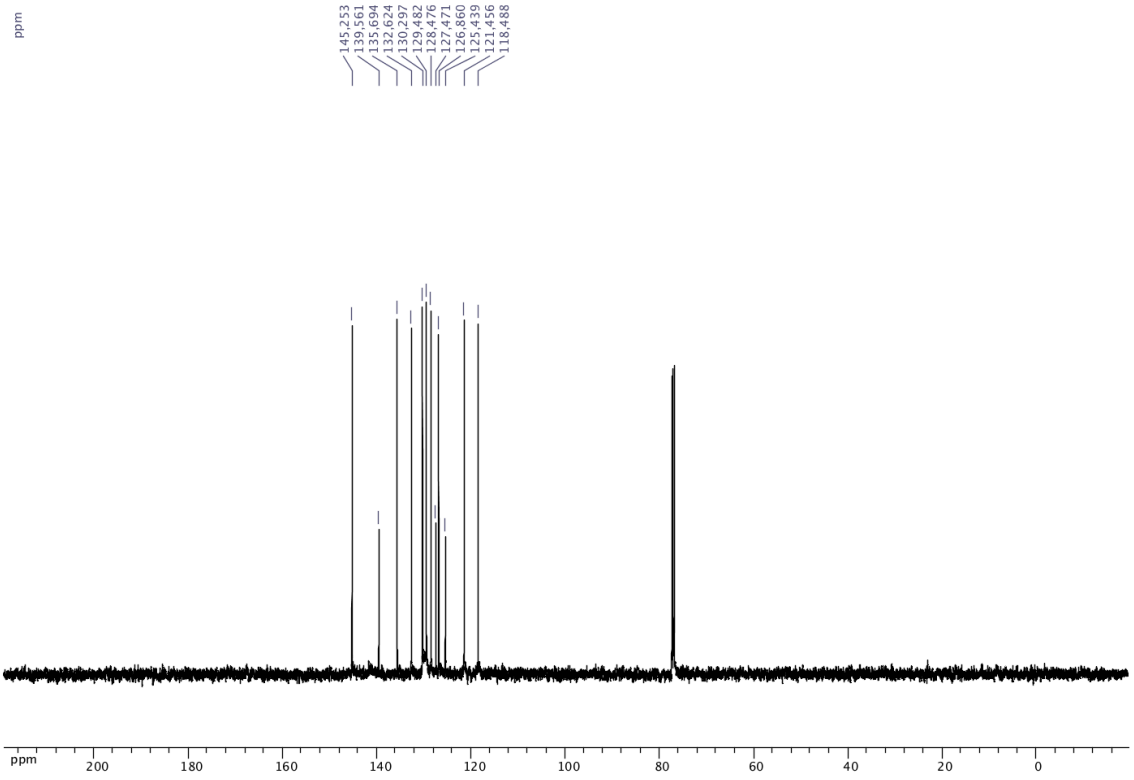
^{1}H NMR (acetone-d_6, 500.4 MHz) of 2-(3-bromophenyl)-2,1-borazanaphthalene (**1b**)



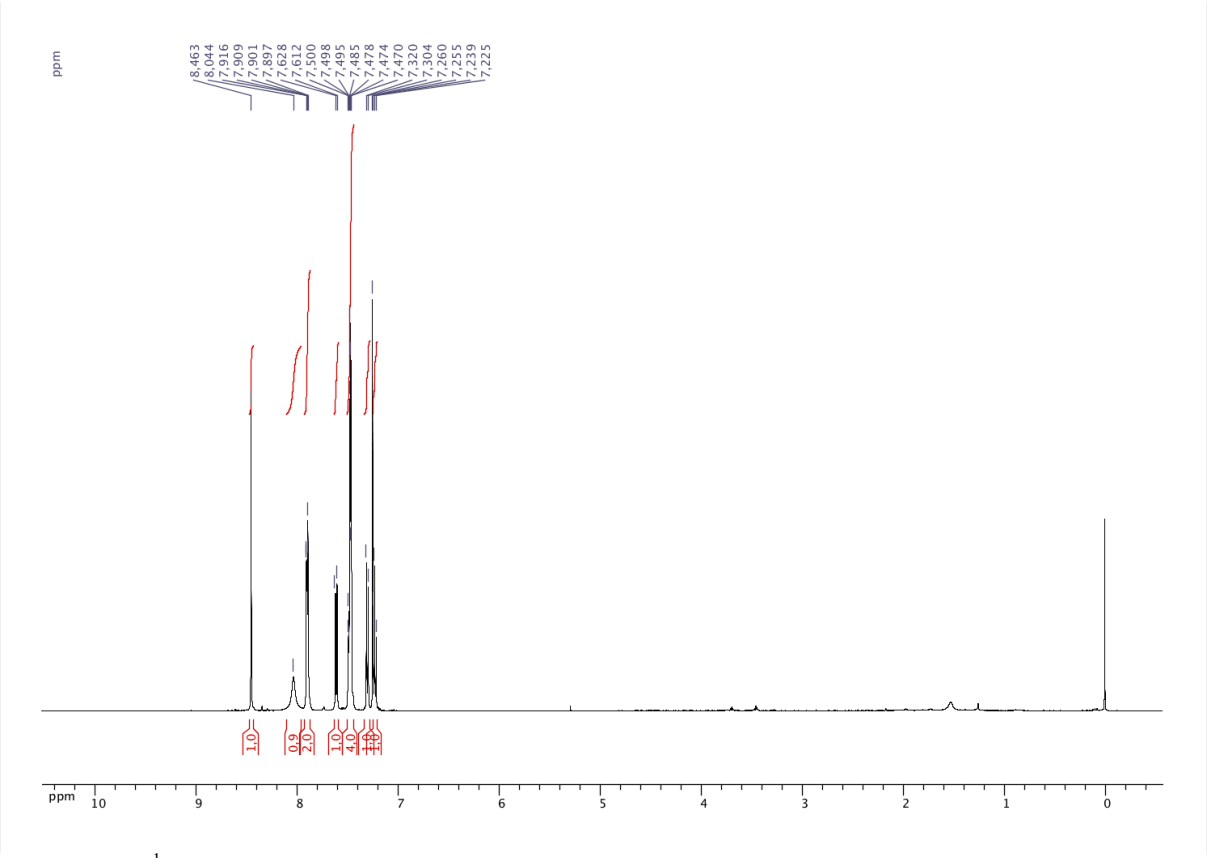
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of 2-(3-bromophenyl)-2,1-borazanaphthalene (**1b**)



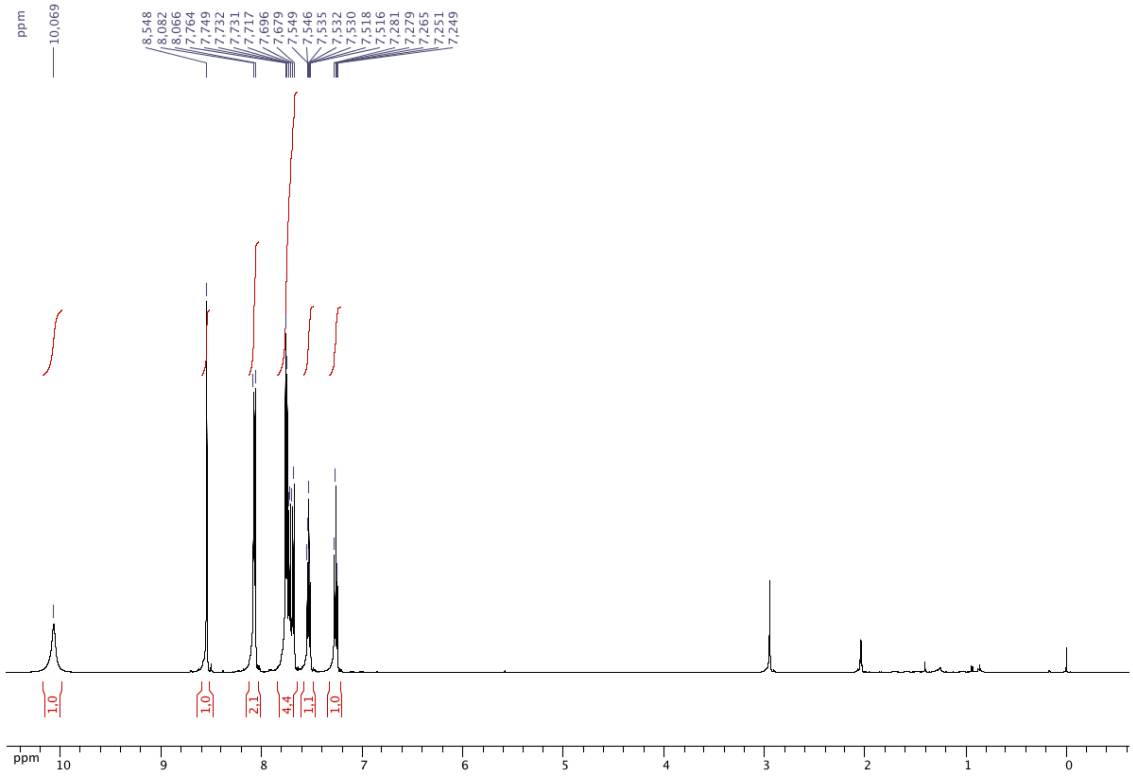
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(2-bromophenyl)-2,1-borazanaphthalene (**1c**)



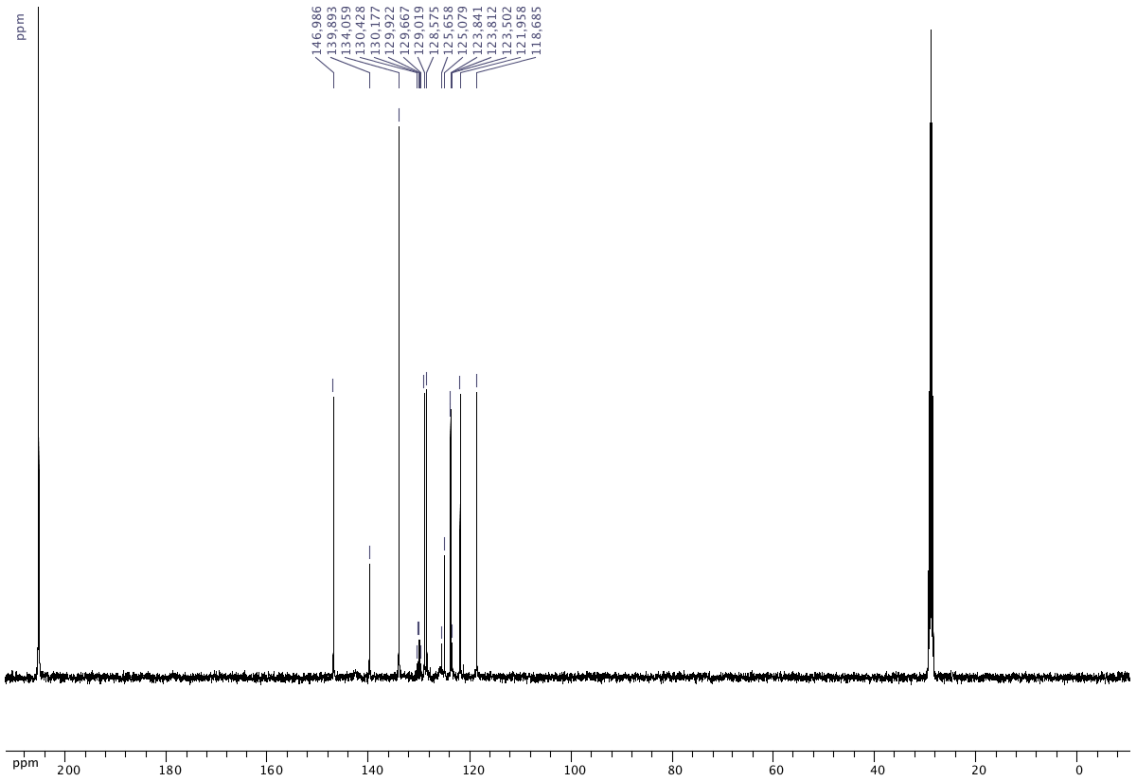
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(2-bromophenyl)-2,1-borazanaphthalene (**1c**)



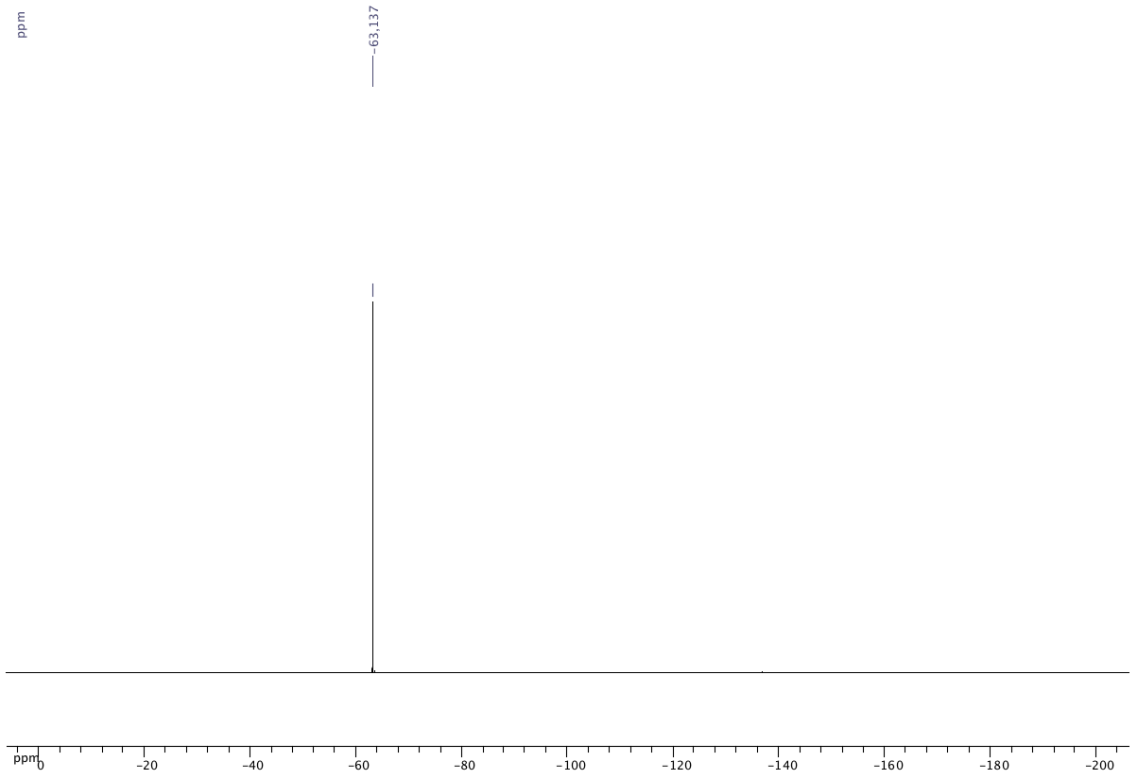
^{1}H NMR (acetone-d_6, 500.4 MHz) of 3-bromo-2-phenyl-2,1-borazanaphthalene (**1d**)



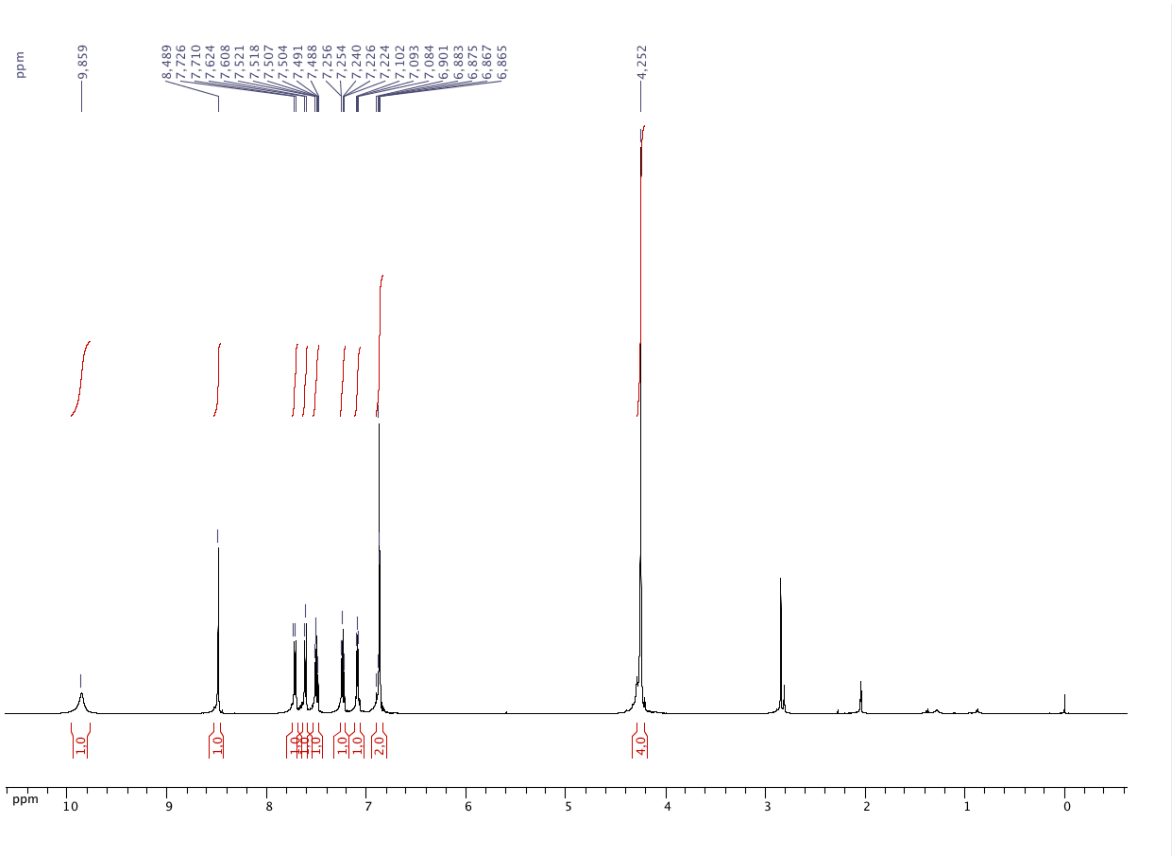
^{1}H NMR (acetone-d_6, 500.4 MHz) of 3-bromo-2-(4-(trifluoromethyl)phenyl)-2,1-borazanaphthalene (**1e**)



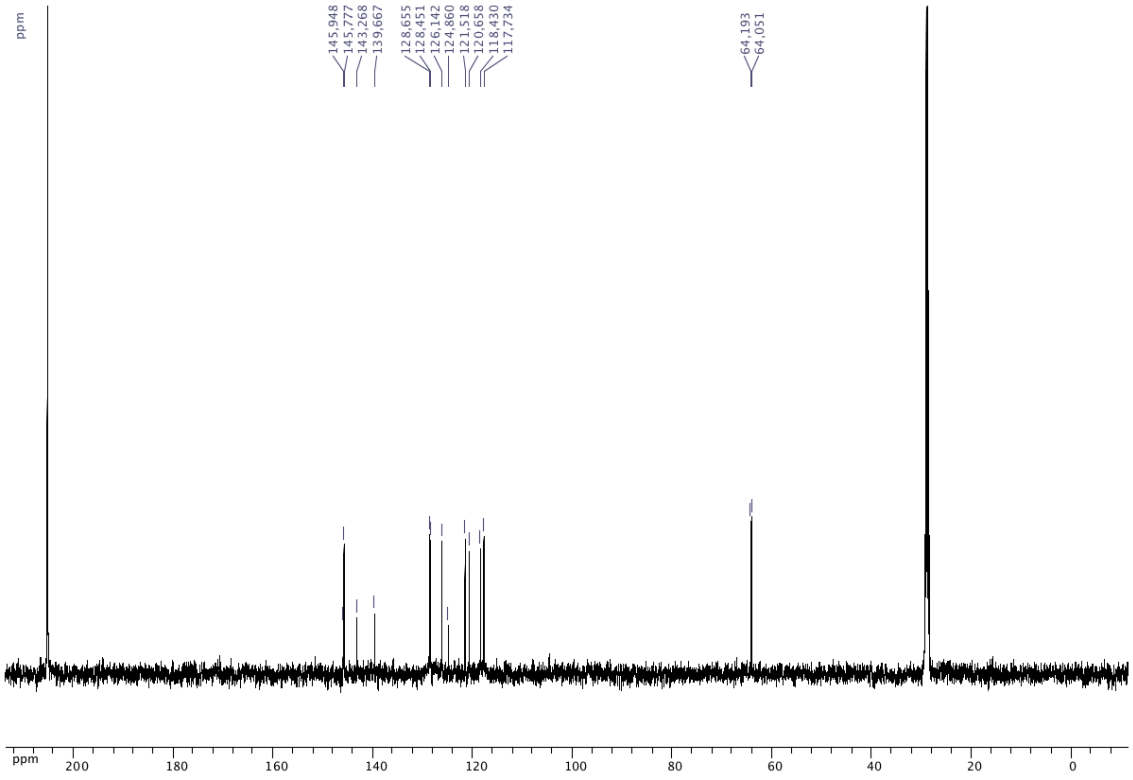
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of 3-bromo-2-(4-(trifluoromethyl)phenyl)-2,1-borazanaphthalene (**1e**)



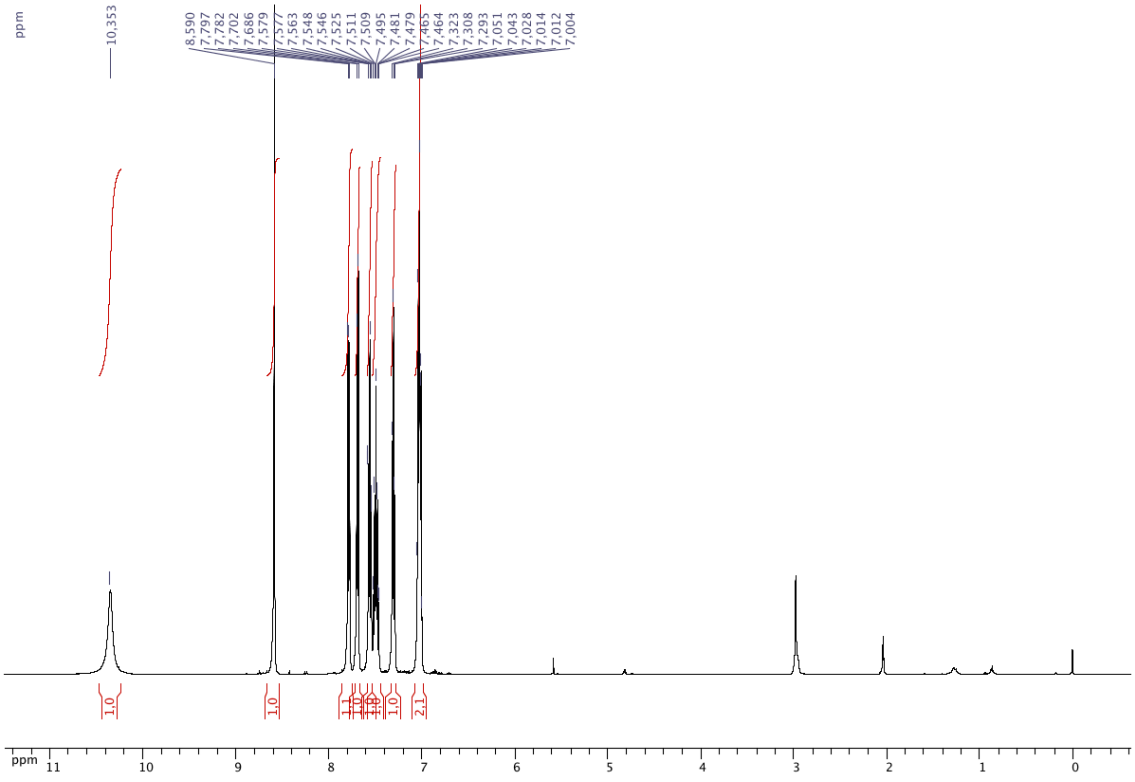
^{19}F {^{1}H} NMR (acetone-d_6, 470.8 MHz) of 3-bromo-2-(4-(trifluoromethyl)phenyl)-2,1-borazanaphthalene (**1e**)



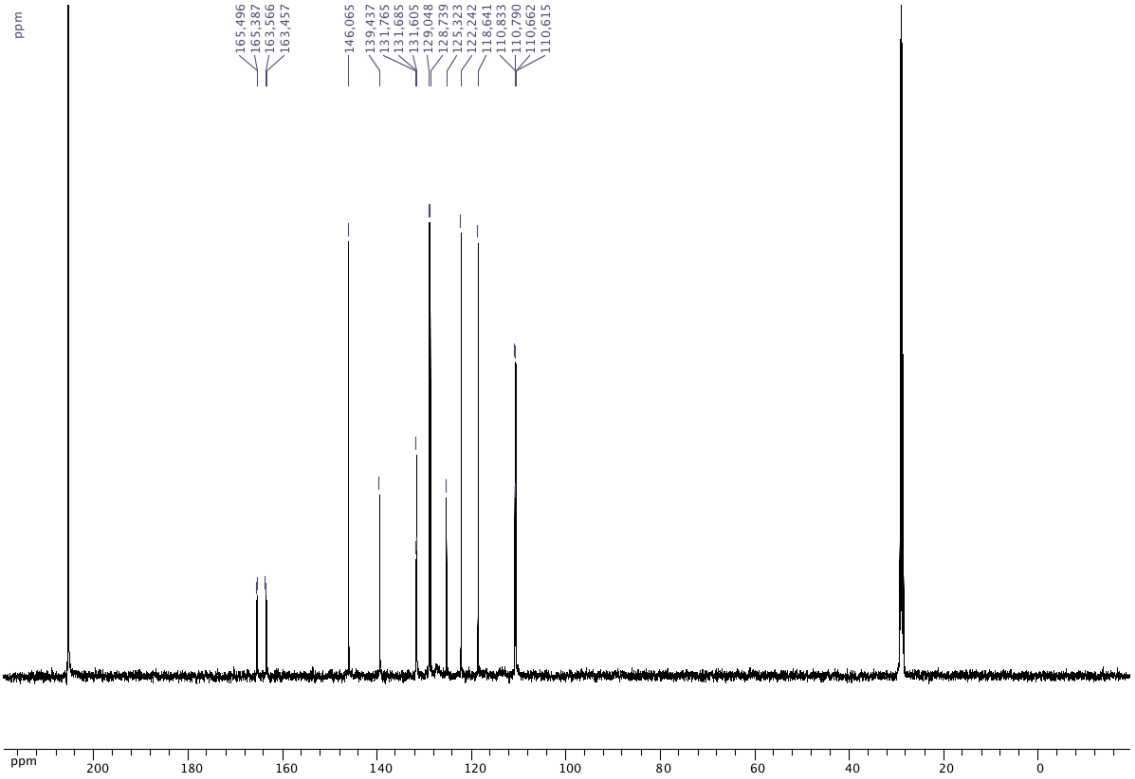
^{1}H NMR (acetone-d_6, 500.4 MHz) of 3-bromo-2-(2,3-dihydro-1,4-benzodioxin-6-yl)-2,1-borazanaphthalene (**1f**)



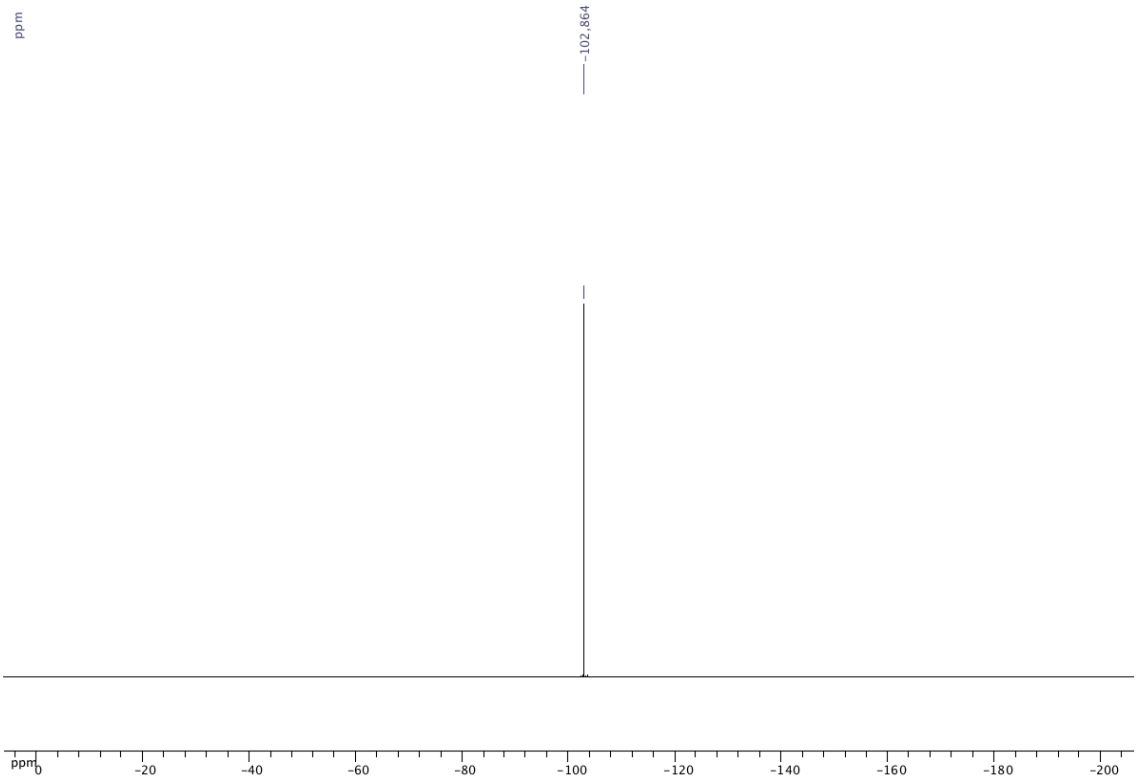
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of 3-bromo-2-(2,3-dihydro-1,4-benzodioxin-6-yl)-2,1-borazanaphthalene (**1f**)



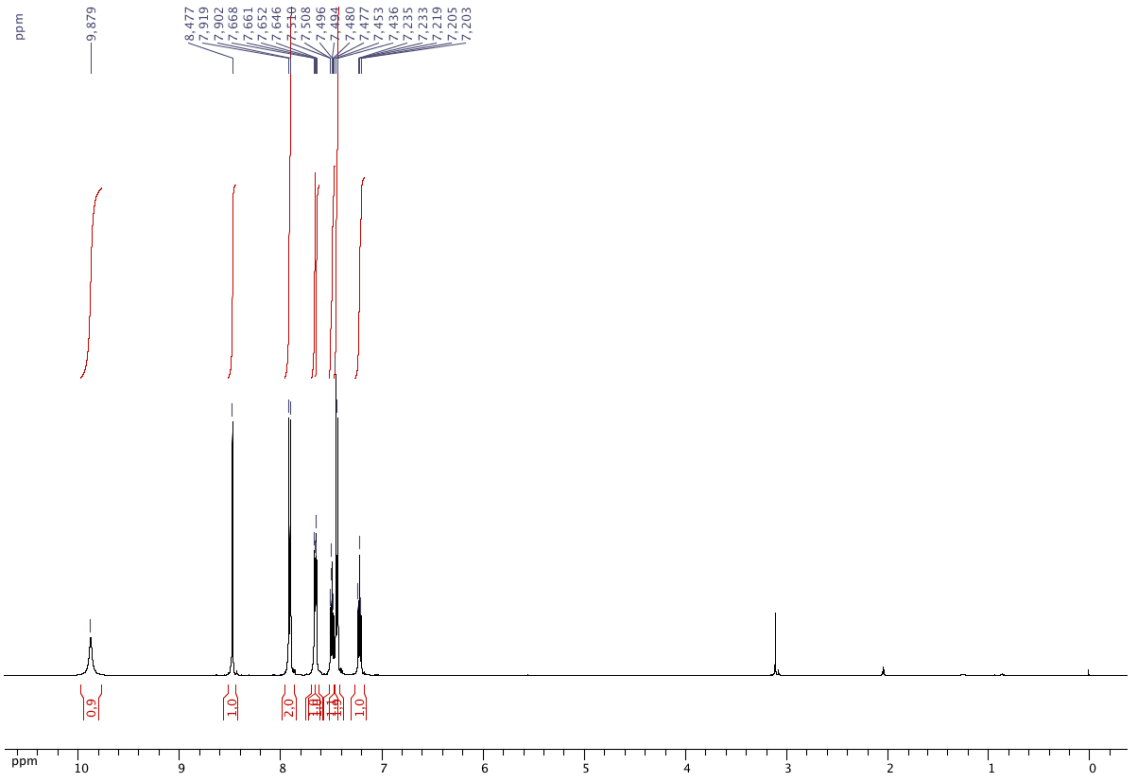
^{1}H NMR (acetone-d_6, 500.4 MHz) of 3-bromo-2-(2,6-difluorophenyl)-2,1-borazanaphthalene (**1g**)



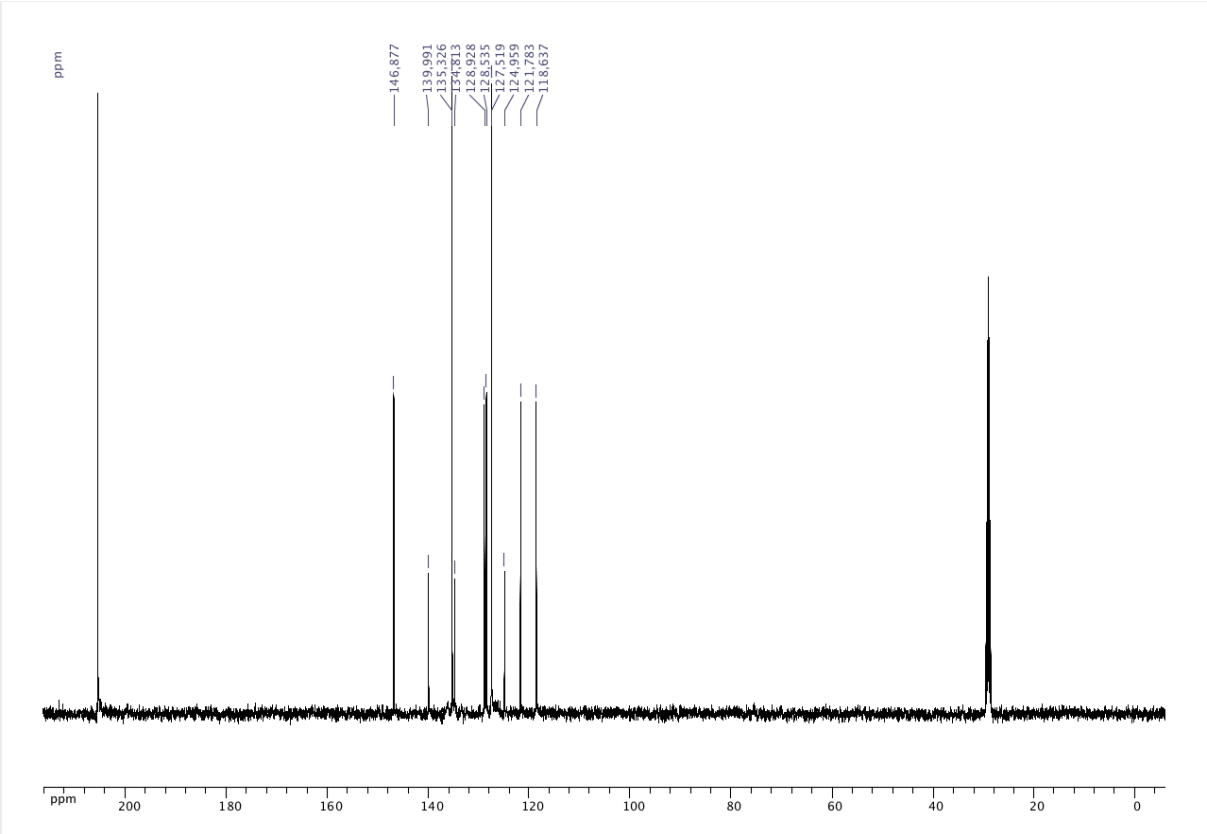
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of 3-bromo-2-(2,6-difluorophenyl)-2,1-borazanaphthalene (**1g**)



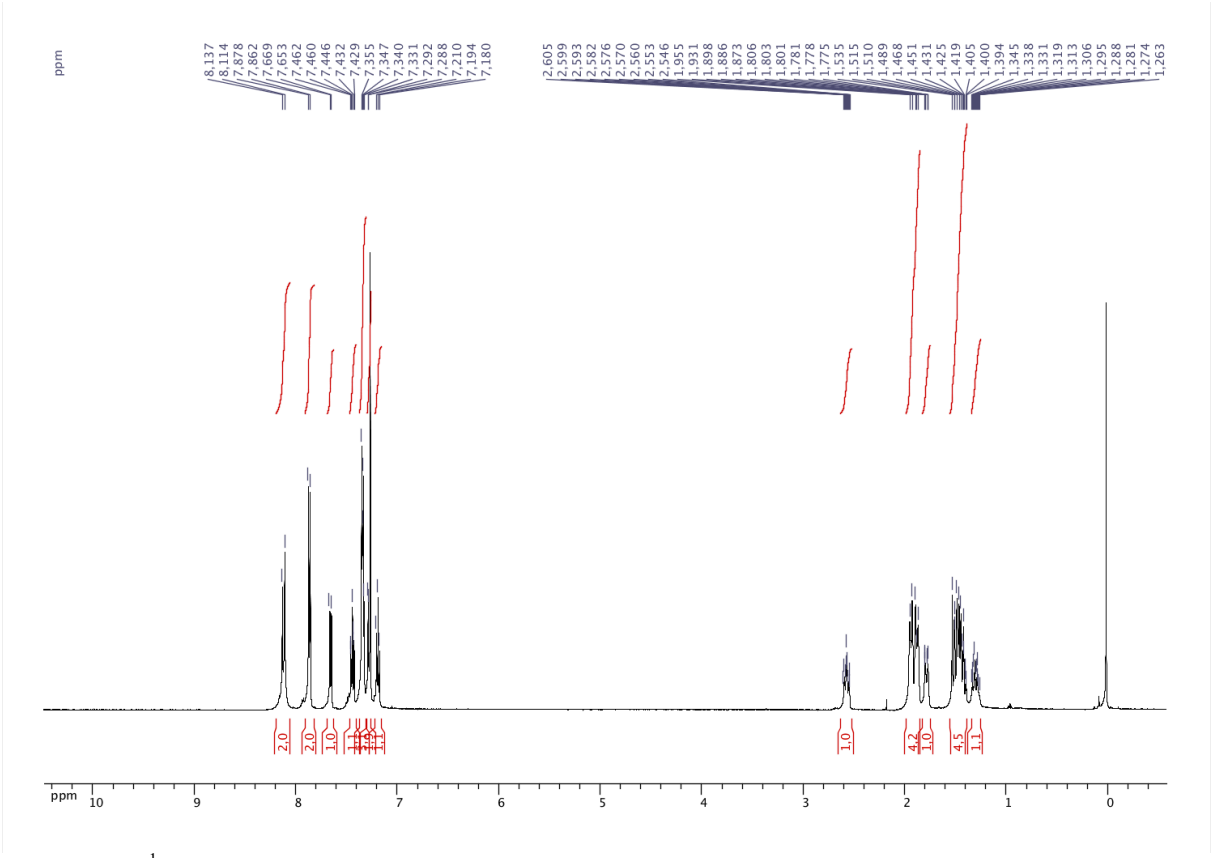
^{19}F $\{^{1}H\}$ NMR (acetone-d_6, 470.8 MHz) of 3-bromo-2-(2,6-difluorophenyl)-2,1-borazanaphthalene (**1g**)



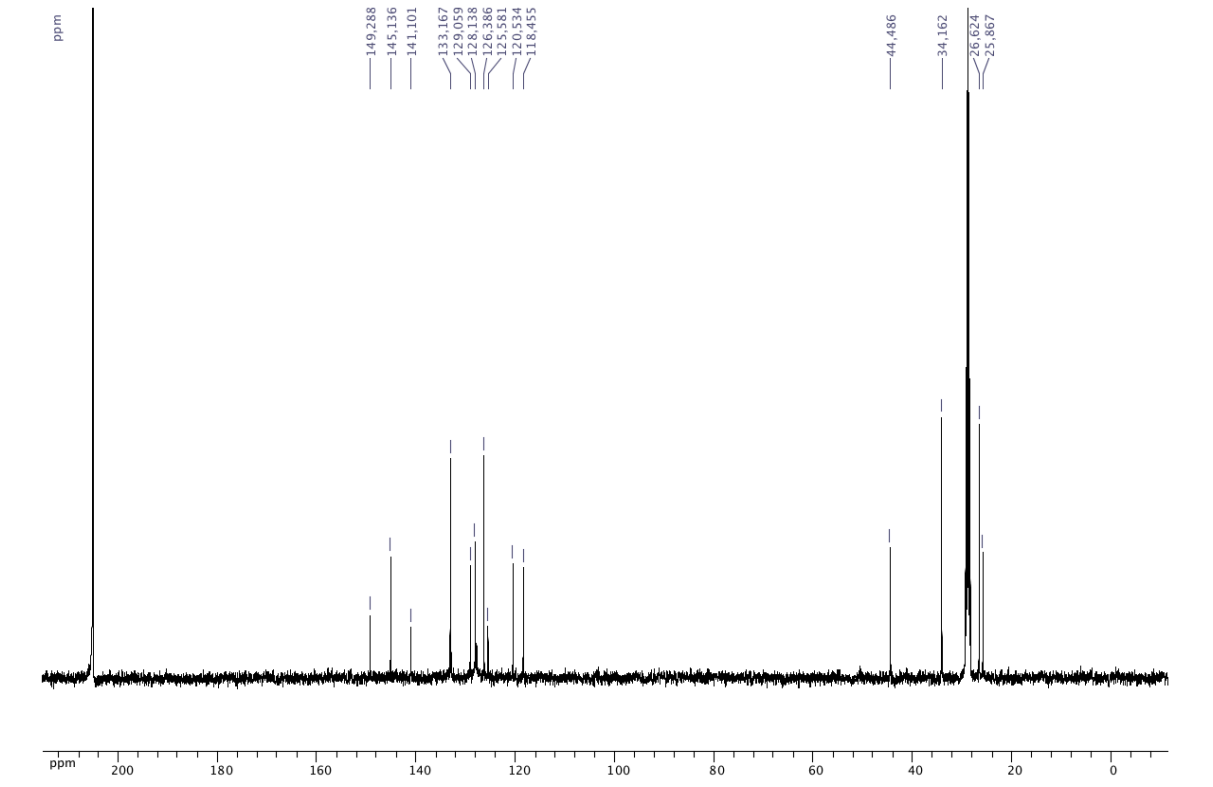
^{1}H NMR (acetone-d_6, 500.4 MHz) of 3-bromo-2-(4-chlorophenyl)-2,1-borazanaphthalene (**1h**)



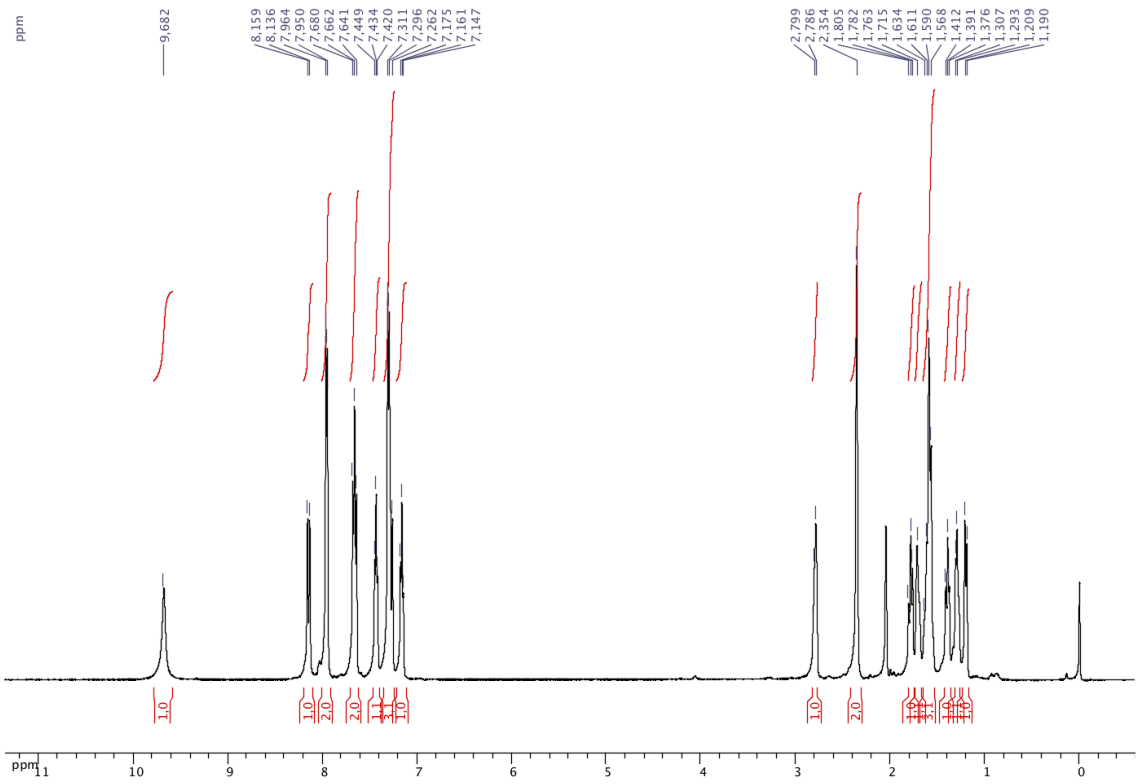
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of 3-bromo-2-(4-chlorophenyl)-2,1-borazanaphthalene (**1h**)



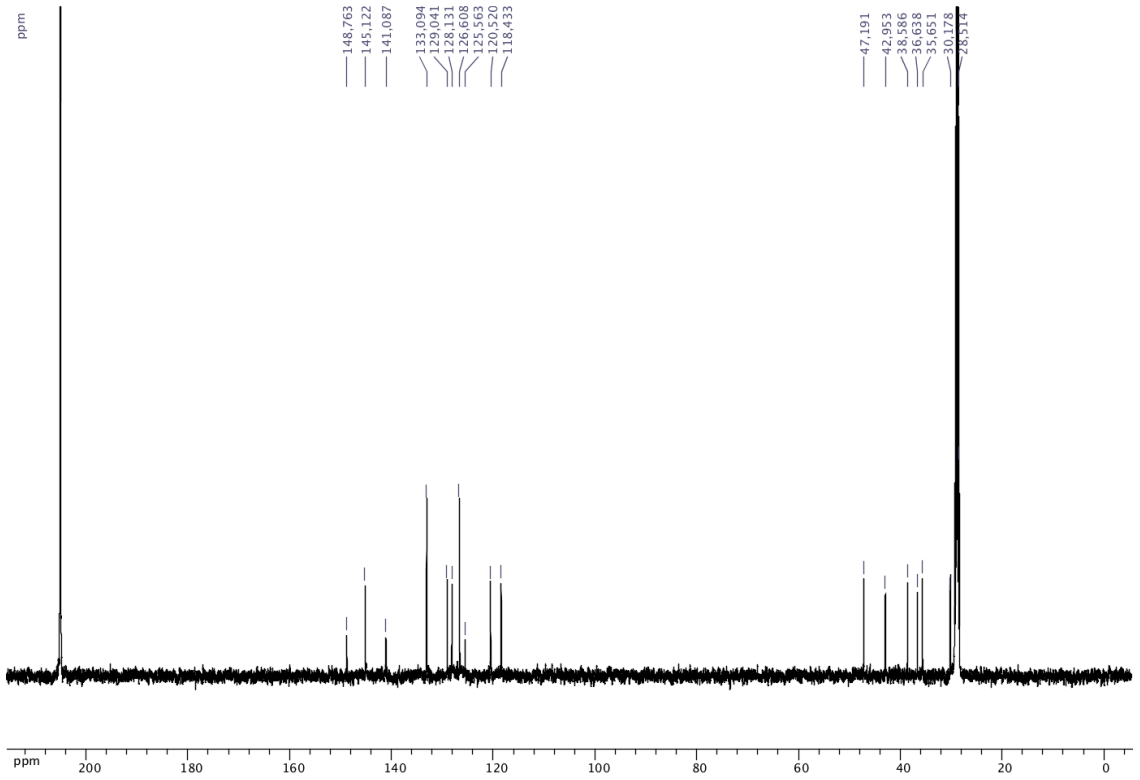
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(4-cyclohexylphenyl)-2,1-borazanaphthalene (**2a**)



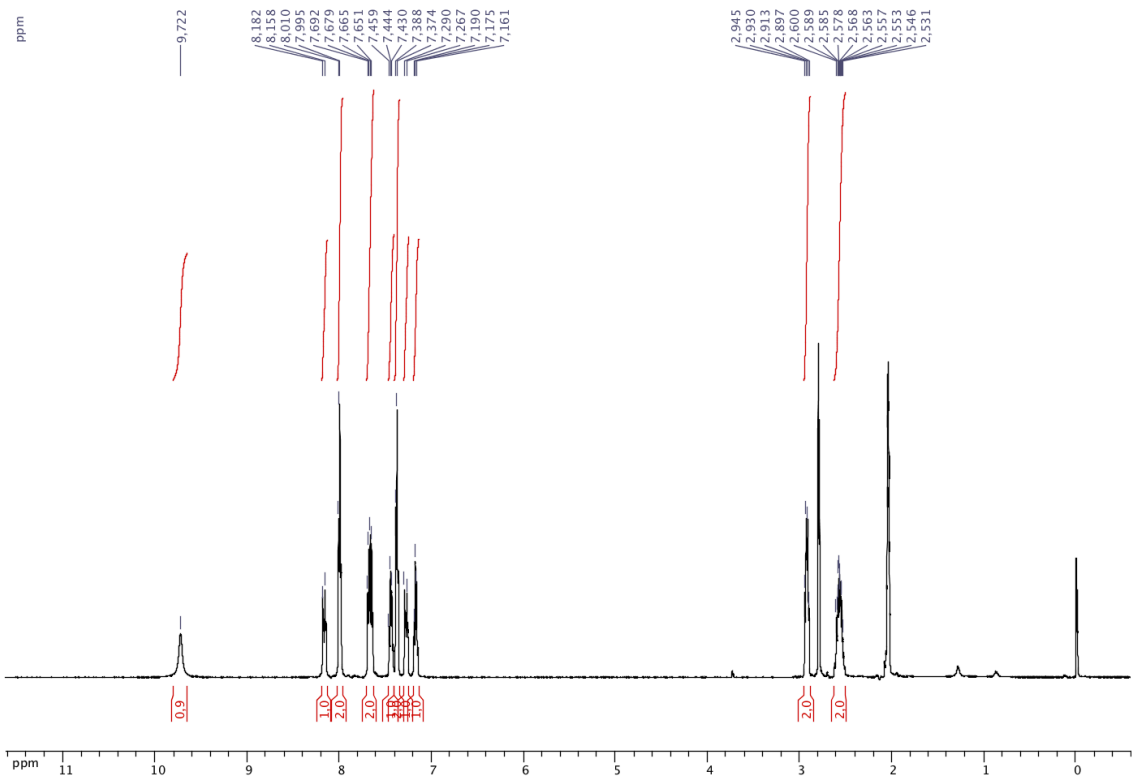
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(4-cyclohexylphenyl)-2,1-borazanaphthalene (**2a**)



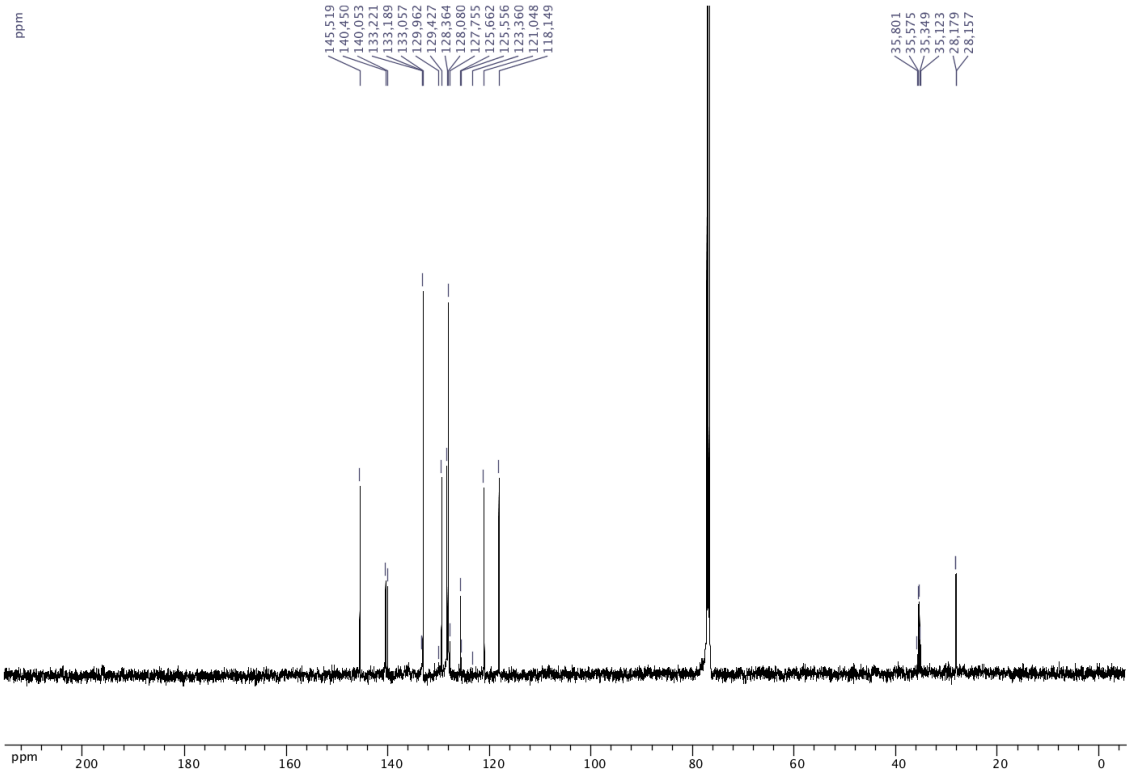
^{1}H NMR (acetone-d_6, 500.4 MHz) of 2-(4-(*exo*-bicyclo[2.2.1]heptan-2-yl)phenyl)-2,1-borazanaphthalene (**2b**)



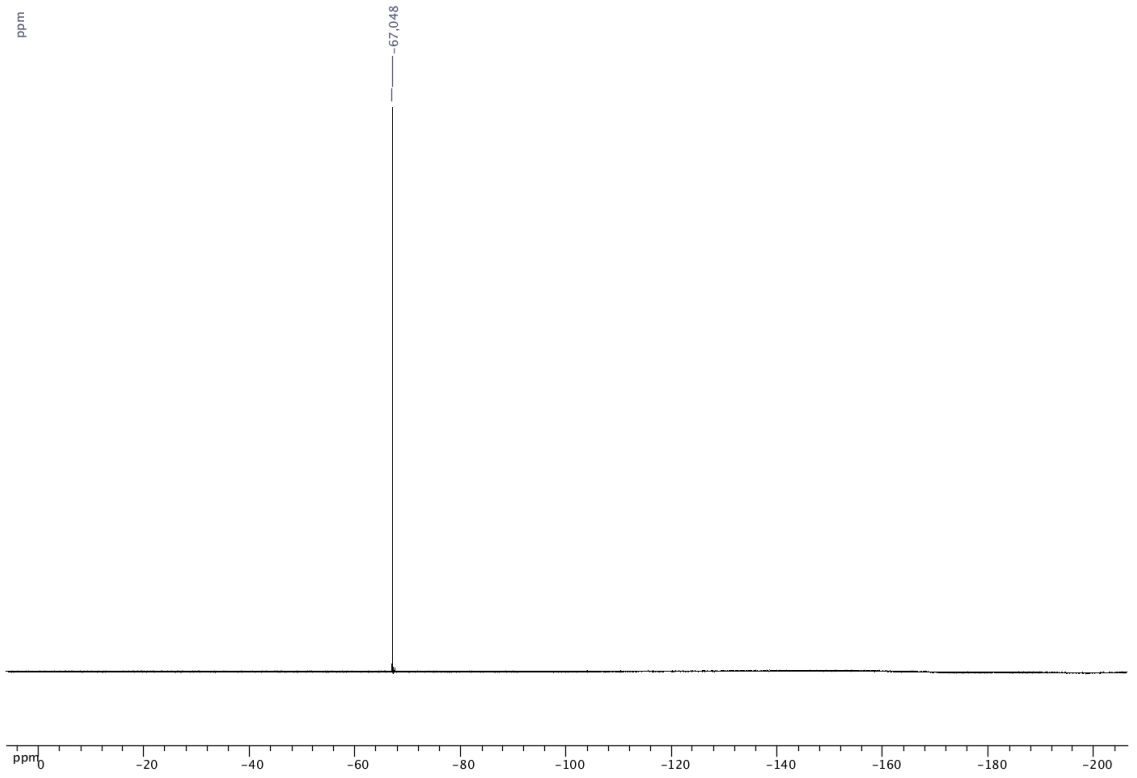
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of 2-(4-(*exo*-bicyclo[2.2.1]heptan-2-yl)phenyl)-2,1-borazanaphthalene (**2b**)



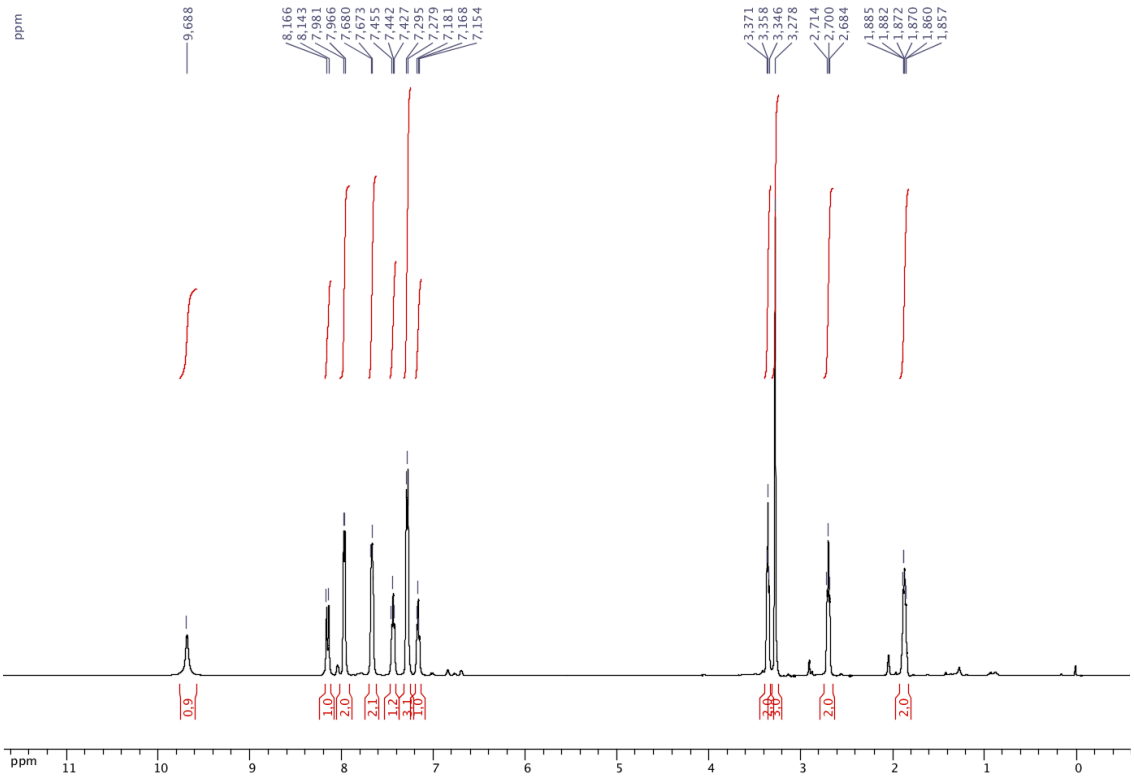
^{1}H NMR (acetone-d_6, 500.4 MHz) of 2-(4-(3,3,3-trifluoropropyl)phenyl)-2,1-borazanaphthalene (**2c**)



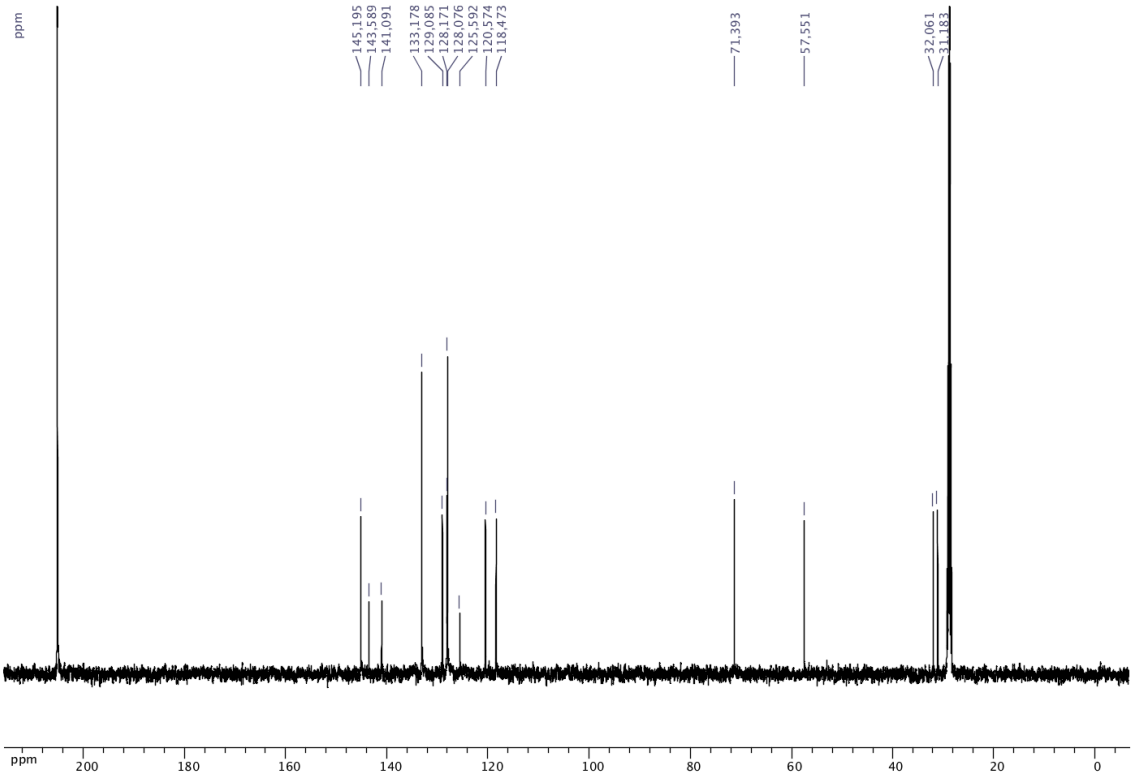
^{13}C {^{1}H} ($CDCl_3$, 125.8 MHz) of 2-(4-(3,3,3-trifluoropropyl)phenyl)-2,1-borazanaphthalene (**2c**)



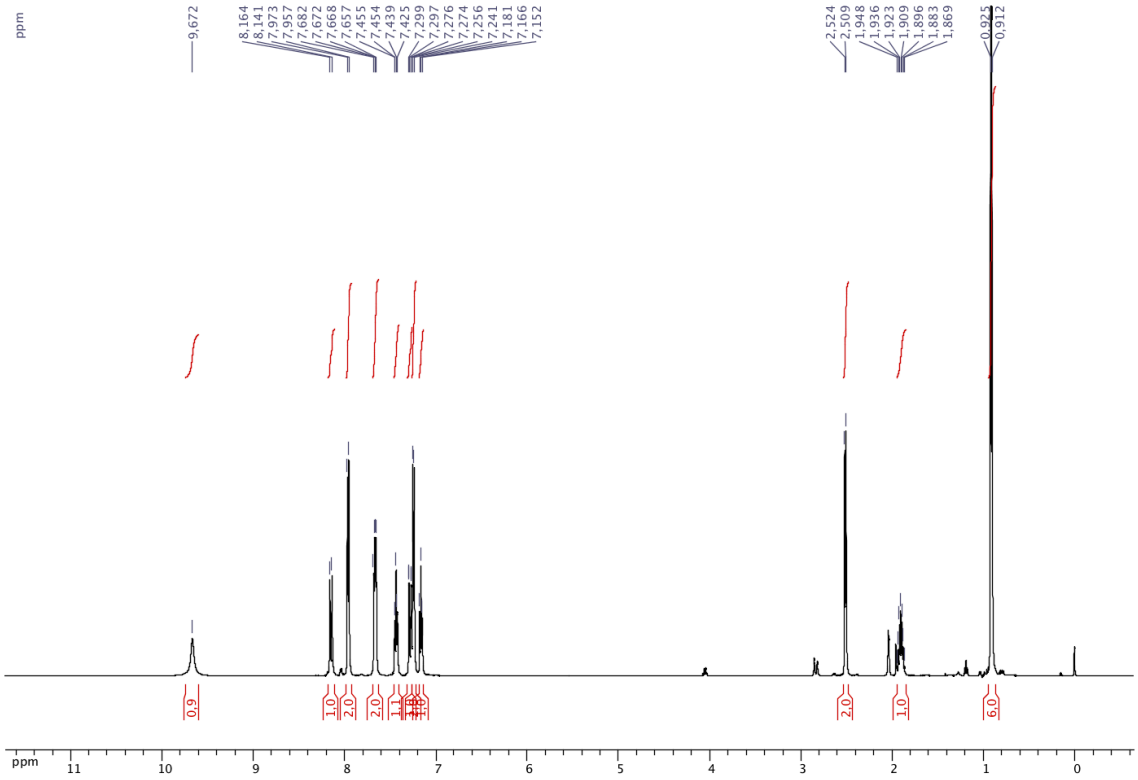
^{19}F {^{1}H} NMR (acetone-d_6, 470.8 MHz) of 2-(4-(3,3,3-trifluoropropyl)phenyl)-2,1-borazanaphthalene (**2c**)



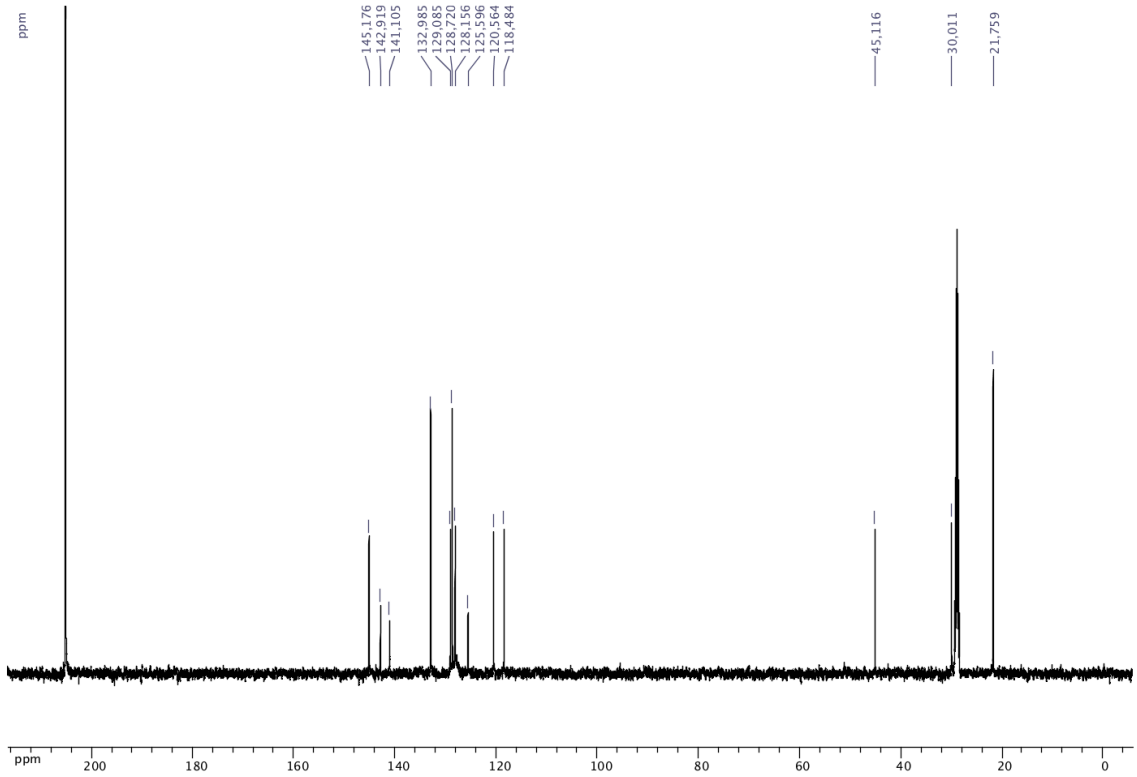
^{1}H NMR (acetone-d_6, 500.4 MHz) of 2-(4-(3-methoxypropyl)phenyl)-2,1-borazanaphthalene (**2d**)



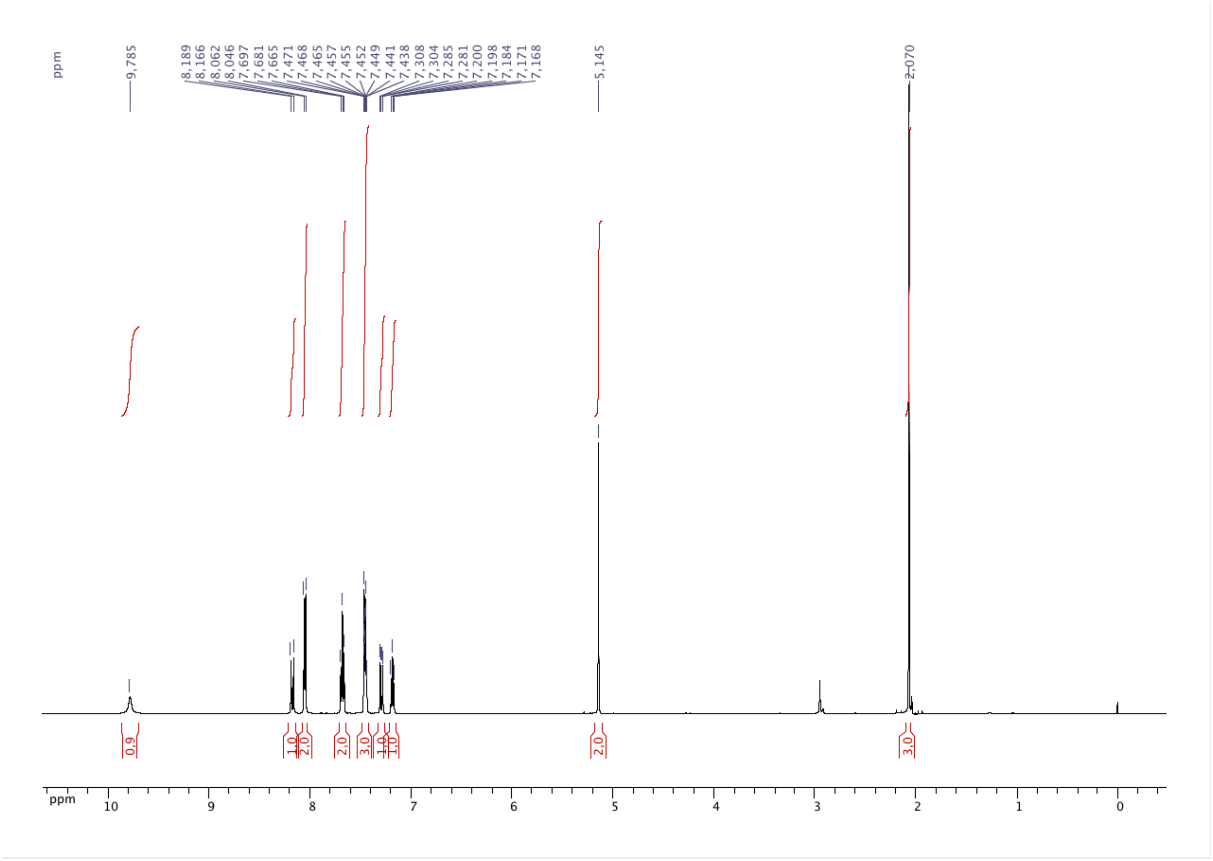
^{13}C {^{1}H} (acetone-d_6, 125.8 MHz) of 2-(4-(3-methoxypropyl)phenyl)-2,1-borazanaphthalene (**2d**)



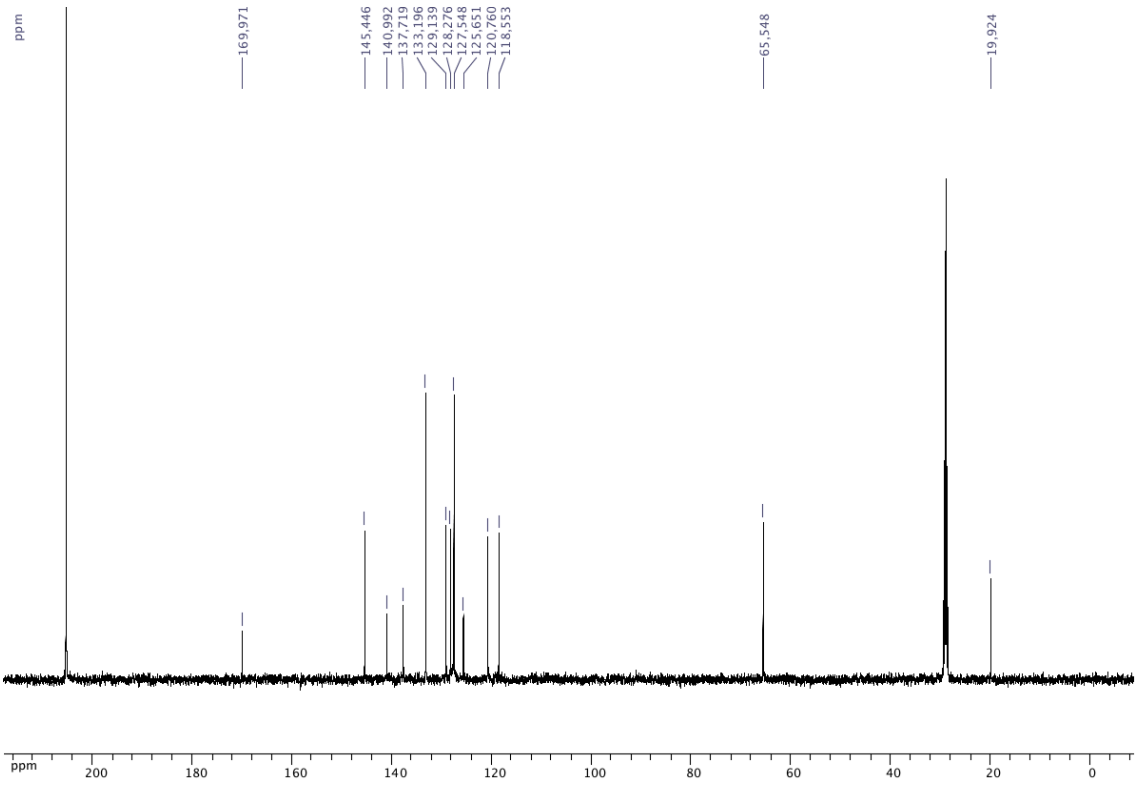
^{1}H NMR (acetone-d_6, 500.4 MHz) of 2-(4-isobutylphenyl)-2,1-borazanaphthalene (**2e**)



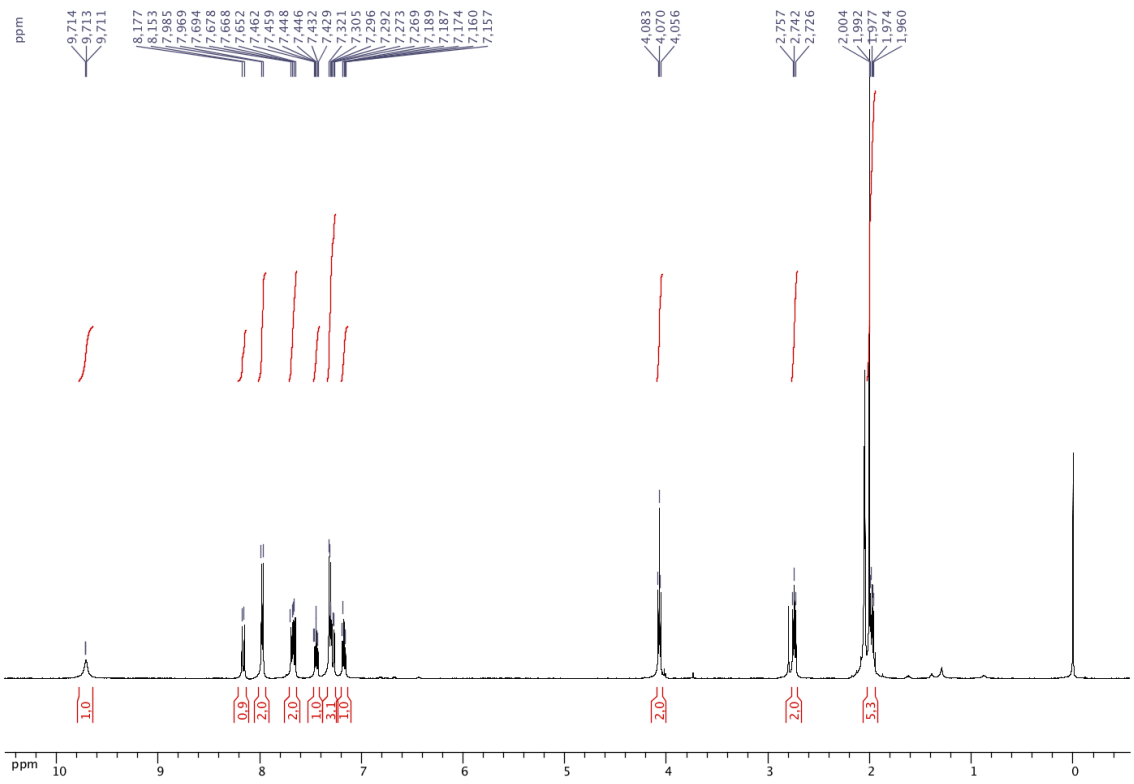
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of 2-(4-isobutylphenyl)-2,1-borazanaphthalene (**2e**)



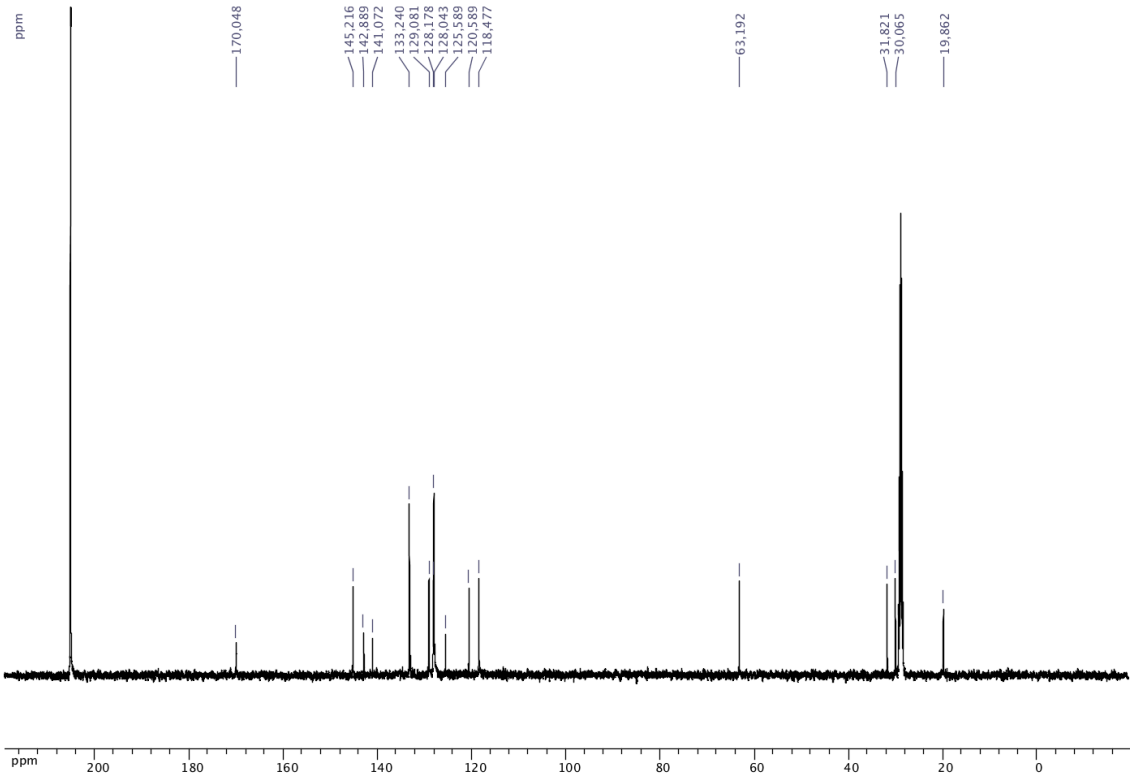
^{1}H NMR (acetone-d_6, 500.4 MHz) of 2-(4-(acetoxymethyl)phenyl)-2,1-borazanaphthalene (**2f**)



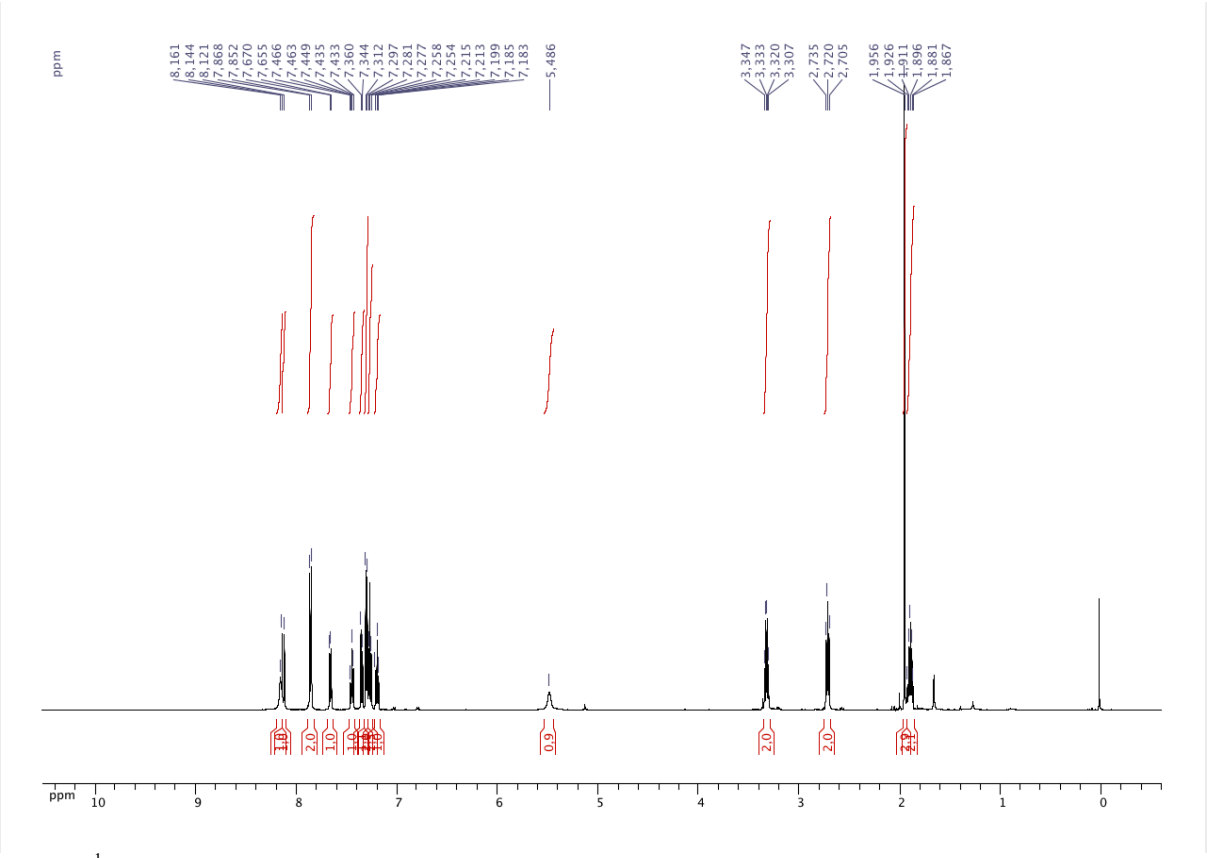
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of 2-(4-(acetoxymethyl)phenyl)-2,1-borazanaphthalene (**2f**)



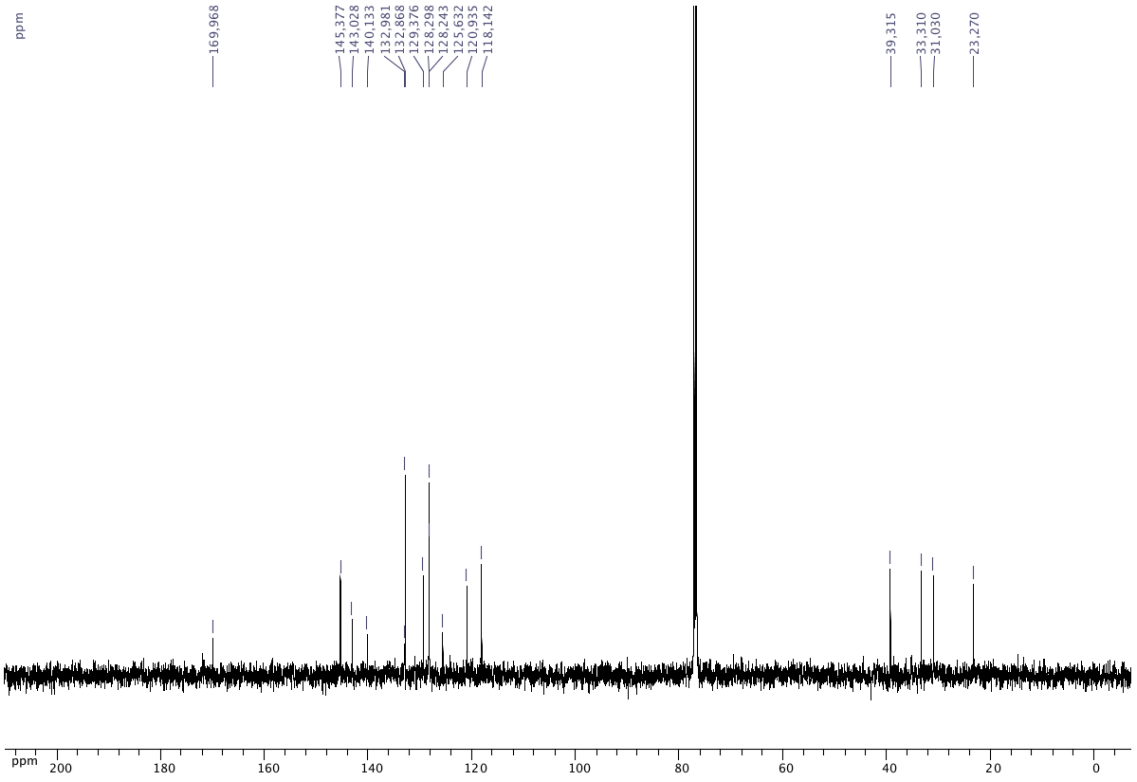
^{1}H NMR (acetone-d_6, 500.4 MHz) of 2-(4-(3-acetoxypropyl)phenyl)-2,1-borazanaphthalene (**2g**)



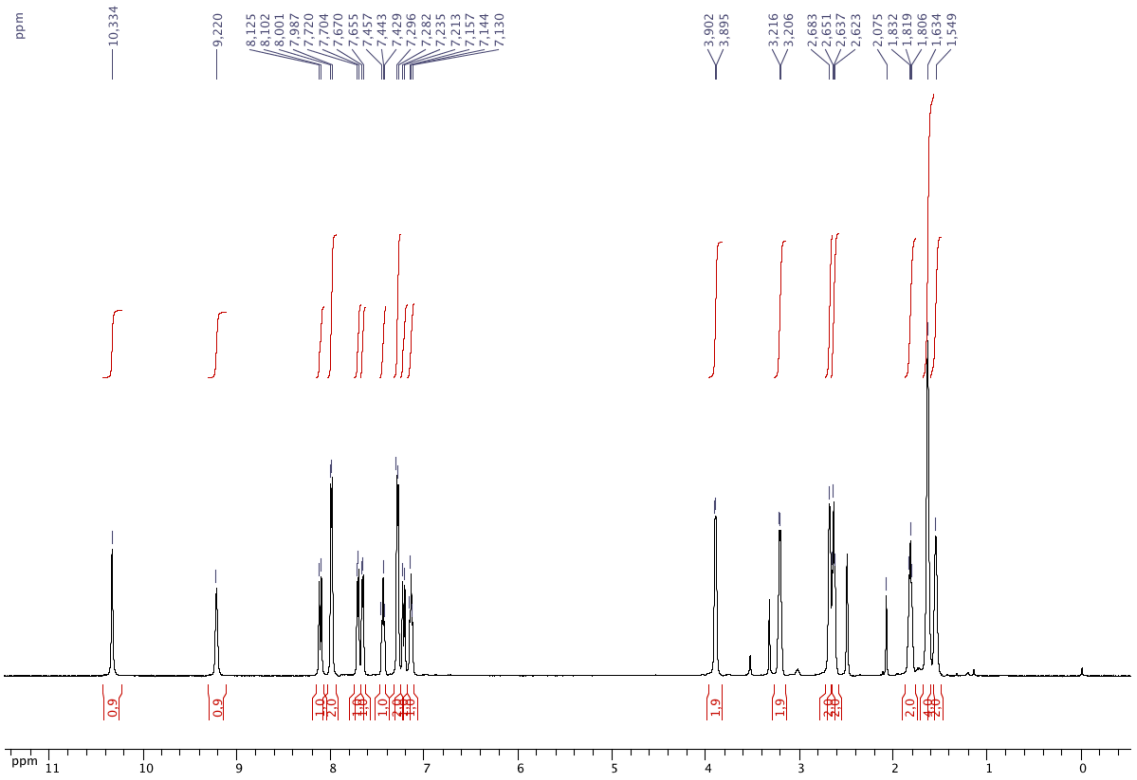
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of 2-(4-(3-acetoxypropyl)phenyl)-2,1-borazanaphthalene (**2g**)



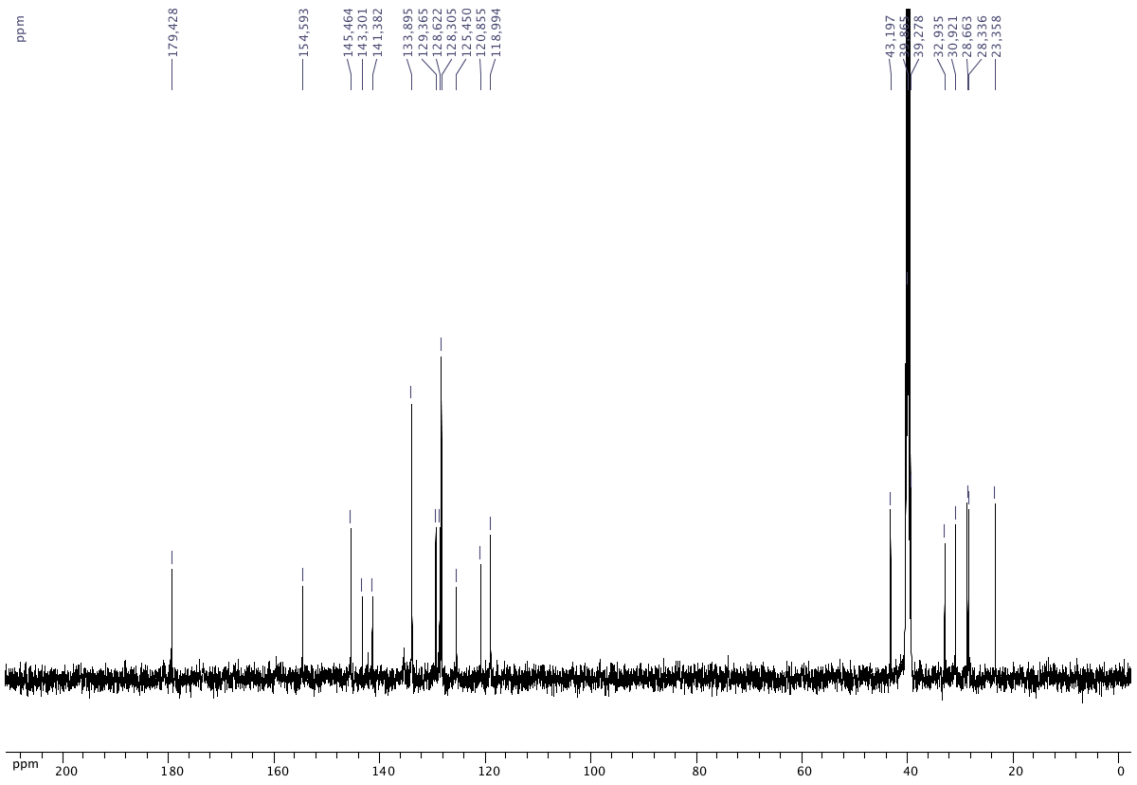
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(4-(3-acetamidopropyl)phenyl)-2,1-borazanaphthalene (**2h**)



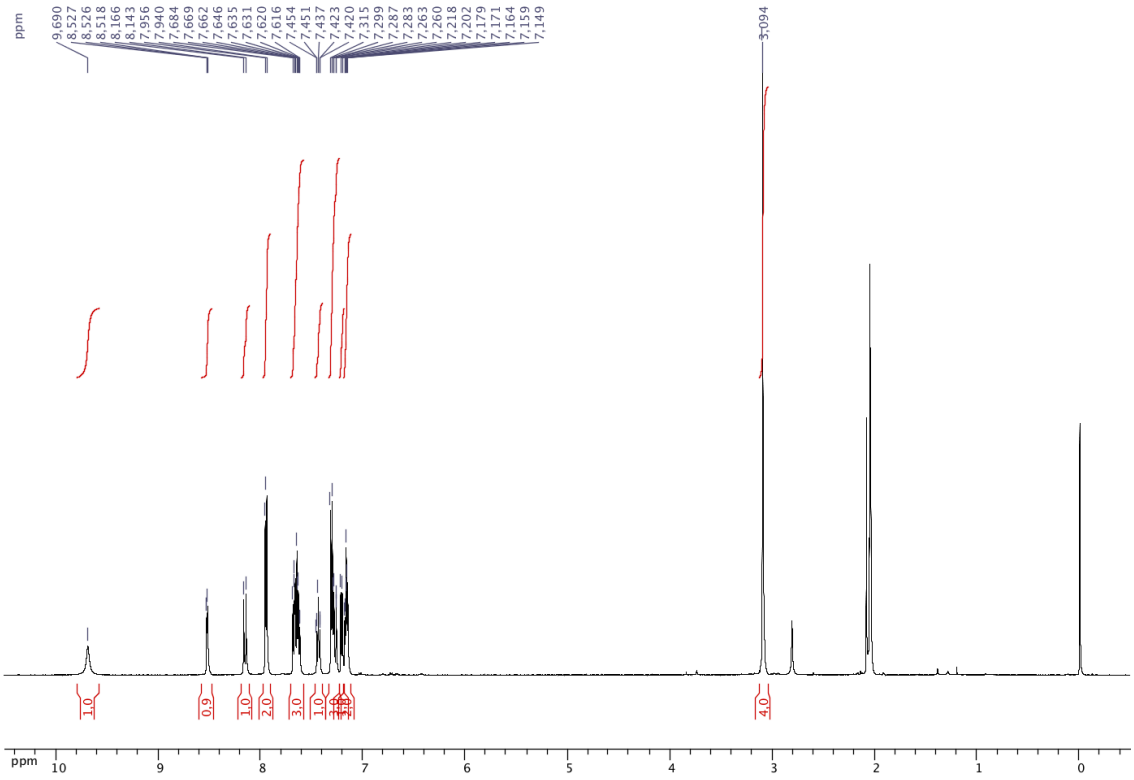
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(4-(3-acetamidopropyl)phenyl)-2,1-borazanaphthalene (**2h**)



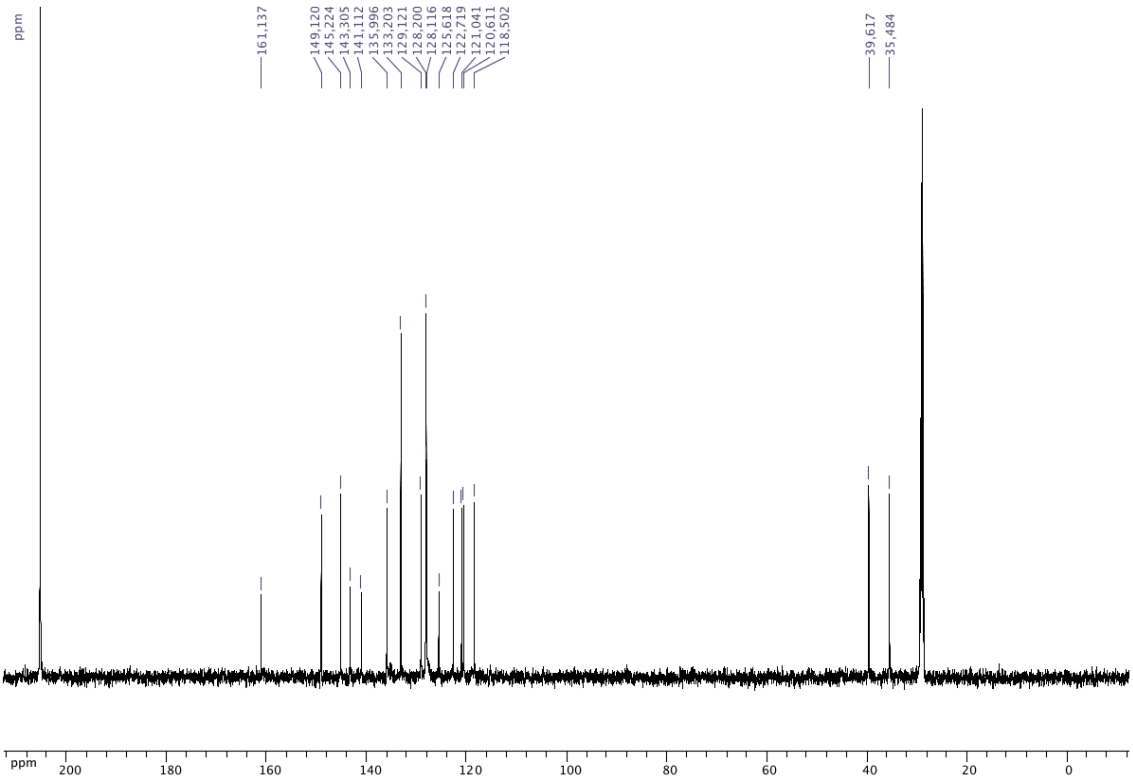
^{1}H NMR (DMSO-d_6, 500.4 MHz) 2-(4-(3-(2-oxoazepane-1-carboxamido)propyl)phenyl)-2,1-borazanaphthalene (**2i**)



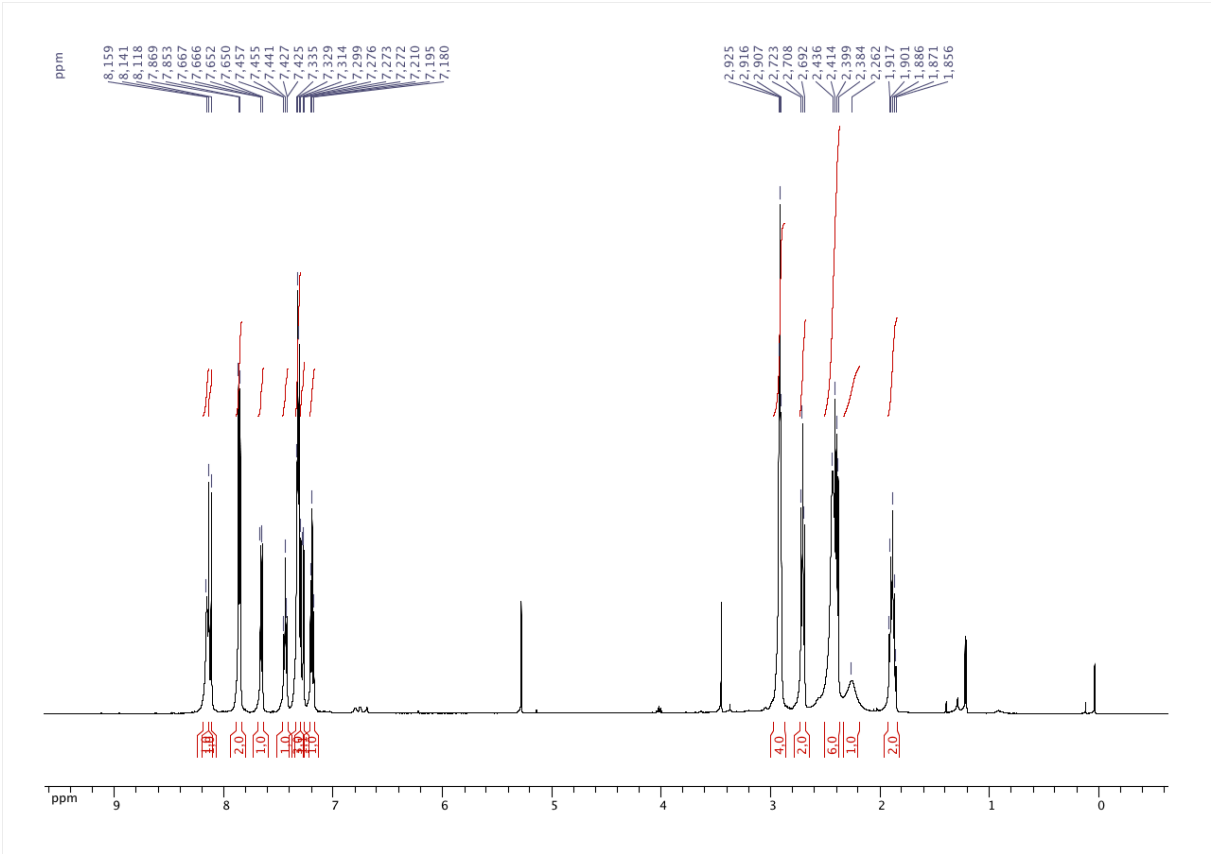
^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz) 2-(4-(3-(2-oxoazepane-1-carboxamido)propyl)phenyl)-2,1-borazanaphthalene (**2i**)



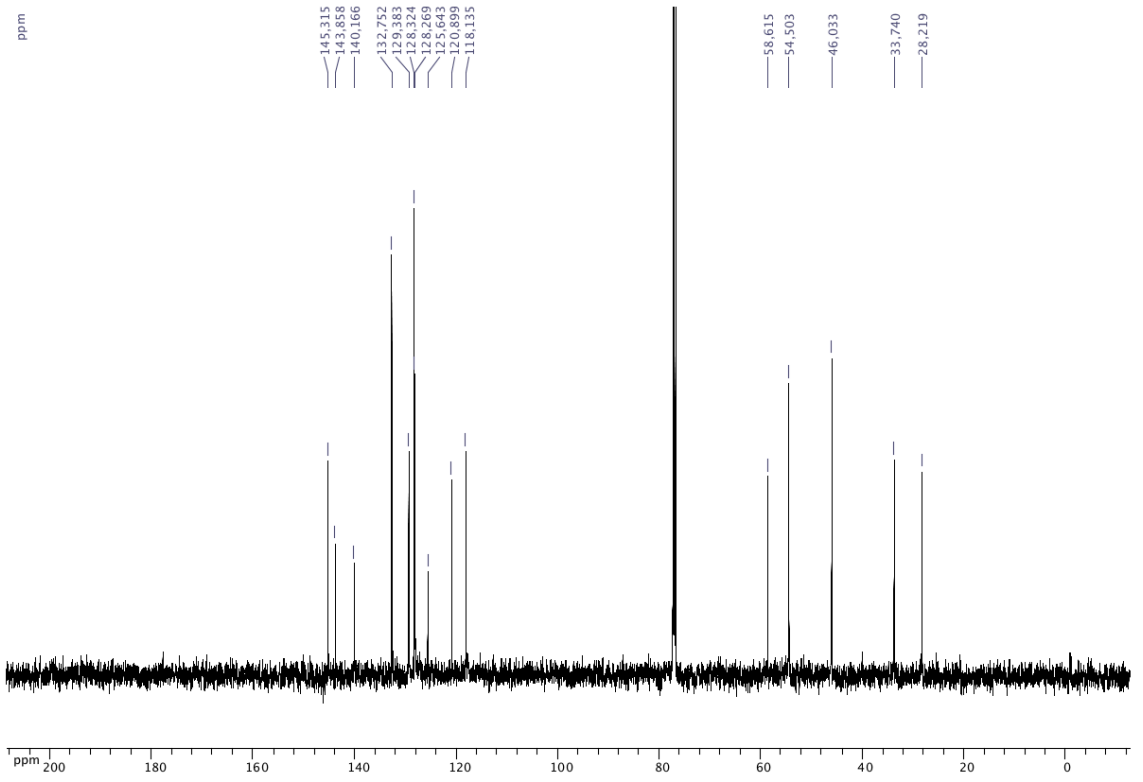
^{1}H NMR (acetone-d_6, 500.4 MHz) of 2-(4-(2-pyridin-2-yl)ethyl)phenyl)-2,1-borazanaphthalene (**2j**)



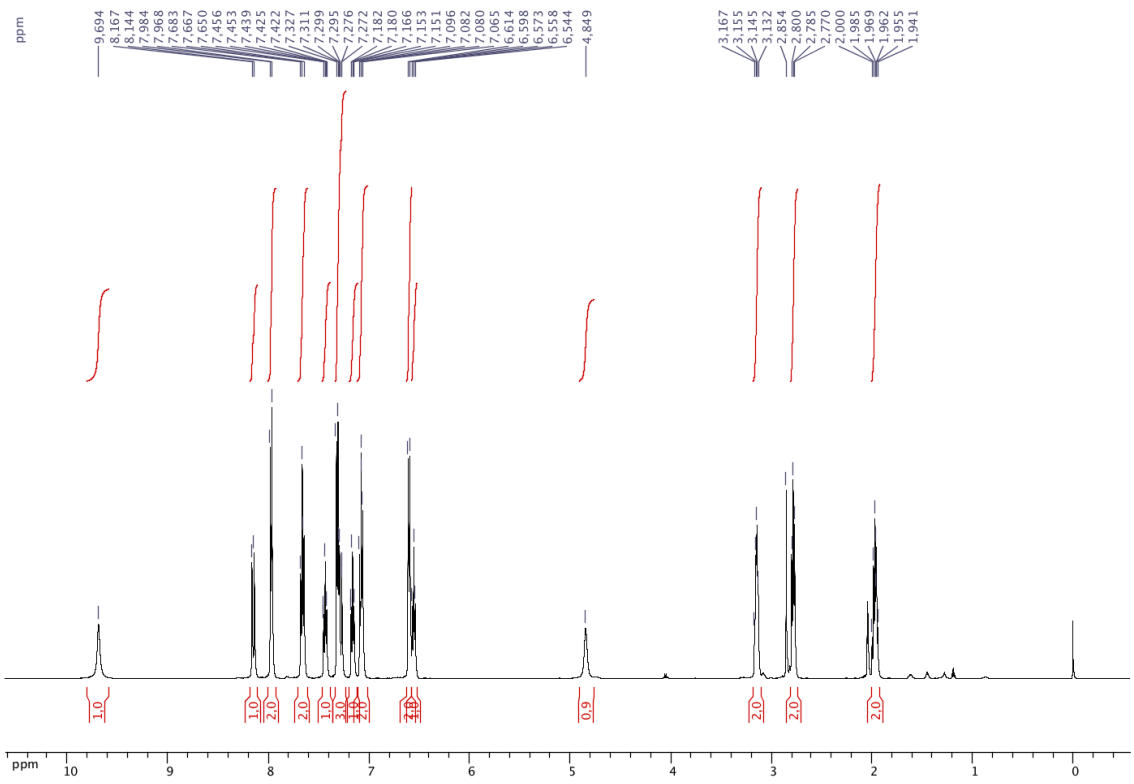
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of 2-(4-(2-pyridin-2-yl)ethyl)phenyl)-2,1-borazanaphthalene (**2j**)



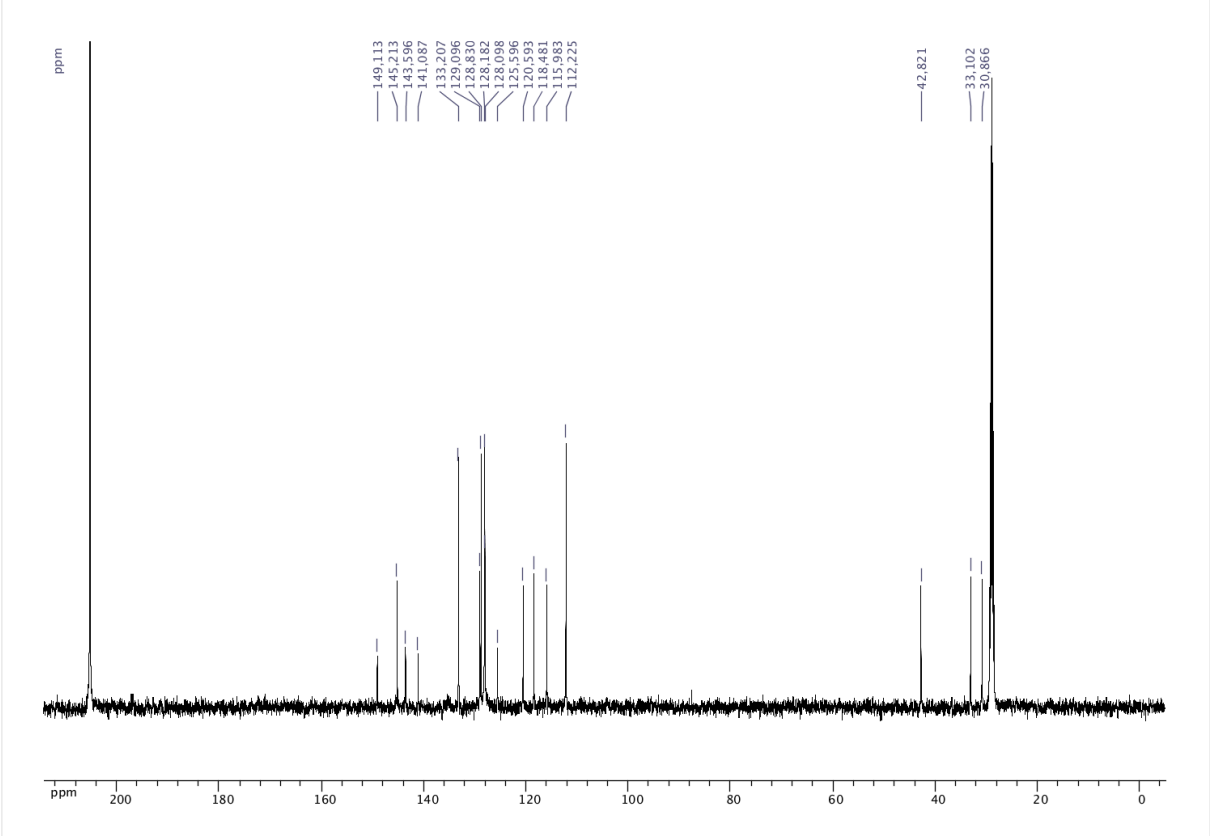
^{1}H NMR (acetone-d_6, 500.4 MHz) of 2-(4-(3-(piperazin-1-yl)propyl)phenyl)-2,1-borazanaphthalene (**2k**)



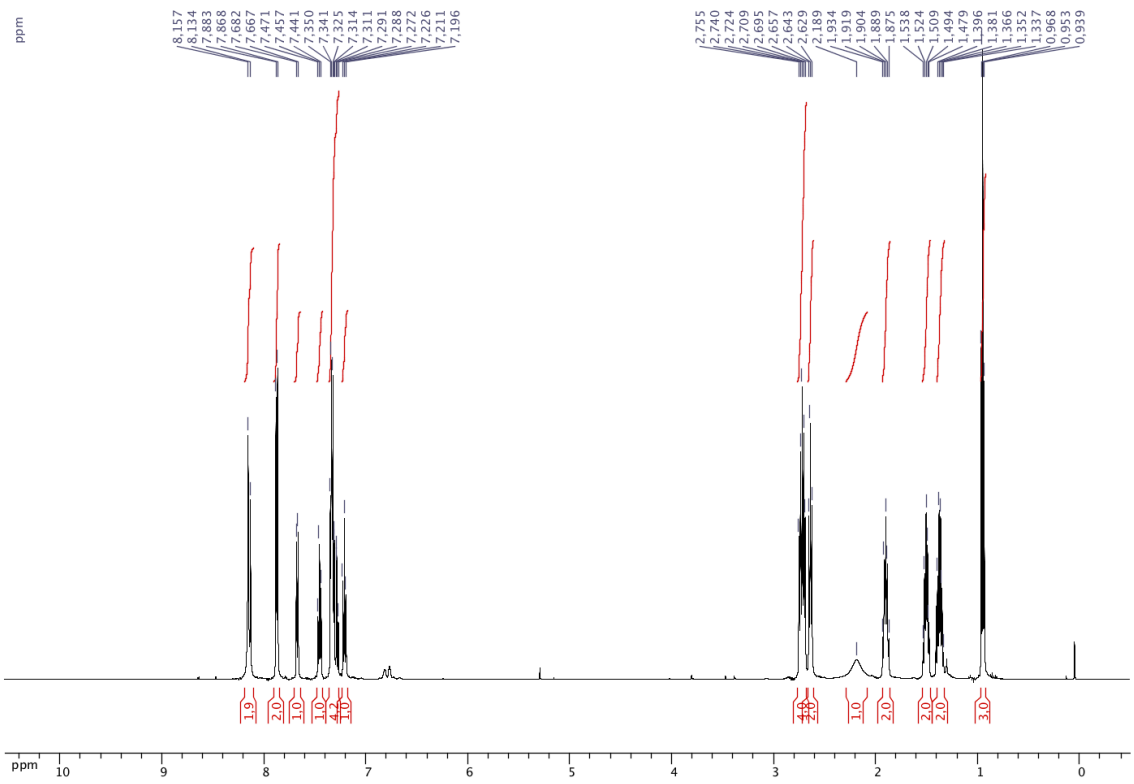
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of 2-(4-(3-(piperazin-1-yl)propyl)phenyl)-2,1-borazanaphthalene (**2k**)



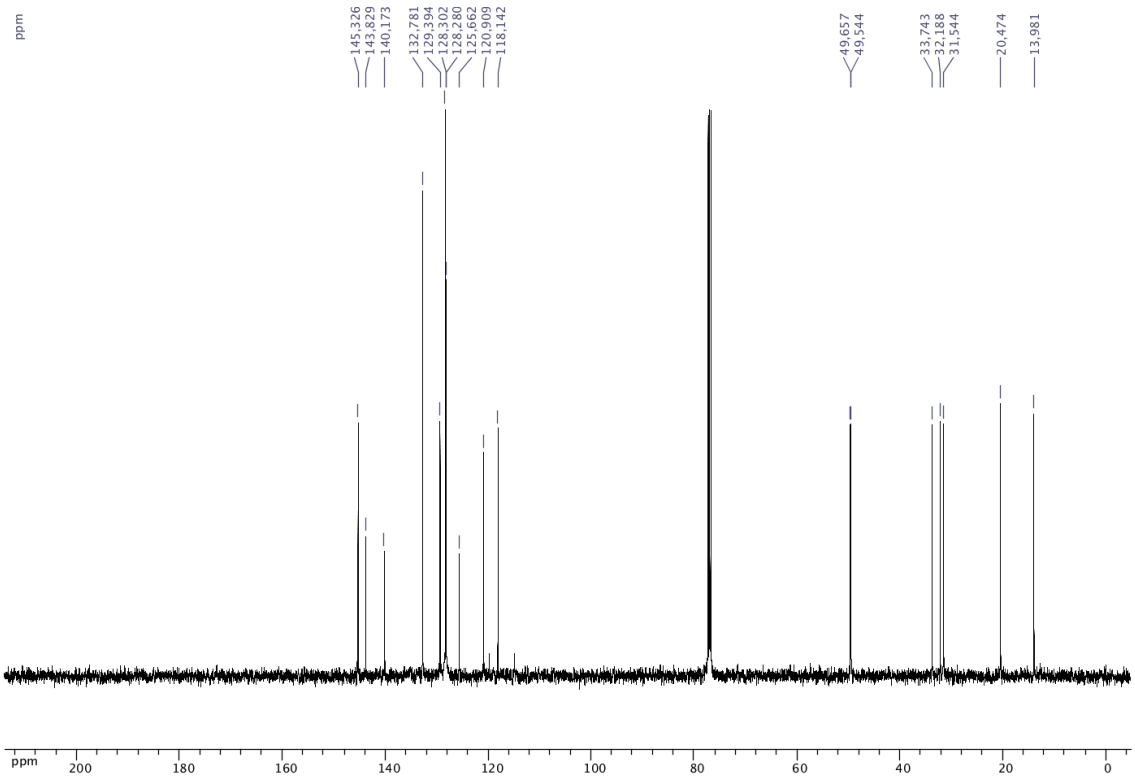
^{1}H NMR (acetone-d_6, 500.4 MHz) of 2-(4-(3-(phenylamino)propyl)phenyl)-2,1-borazanaphthalene (**2l**)



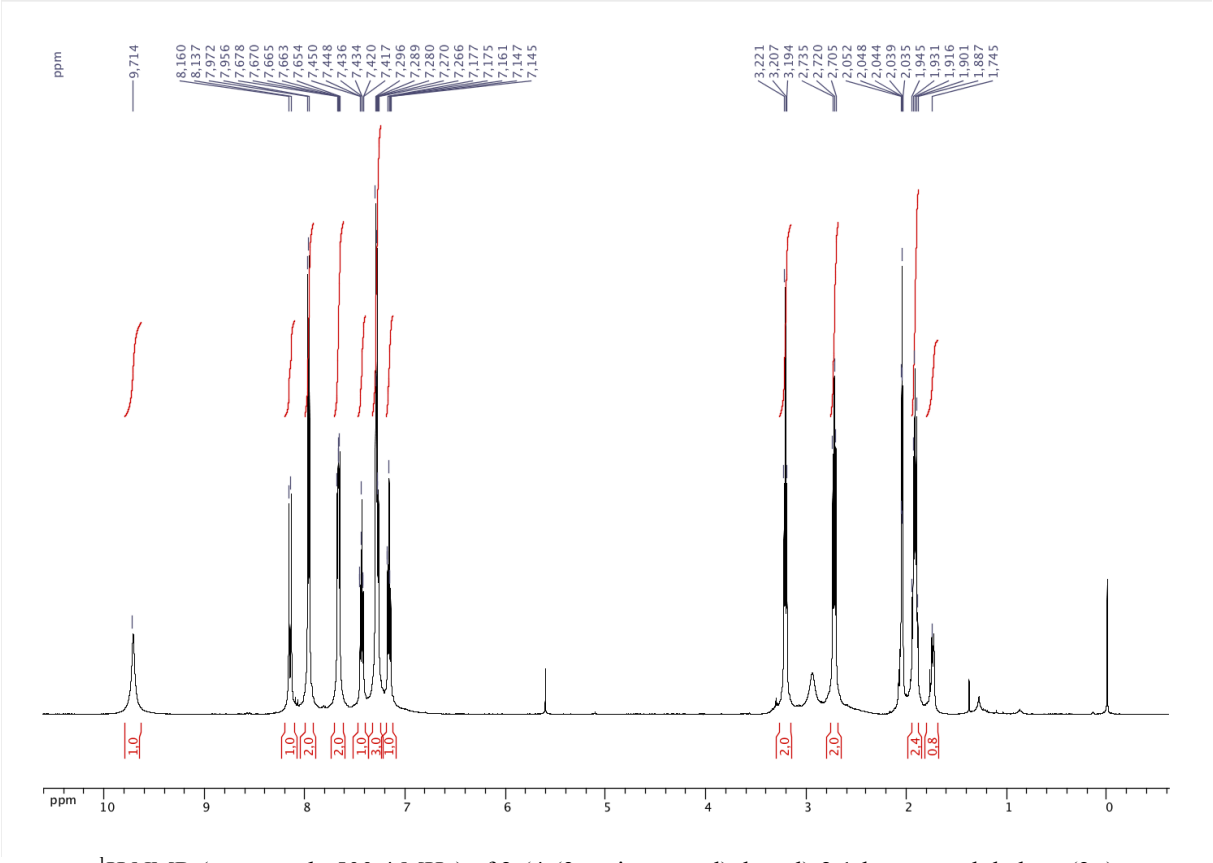
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of 2-(4-(3-(phenylamino)propyl)phenyl)-2,1-borazanaphthalene (**2l**)



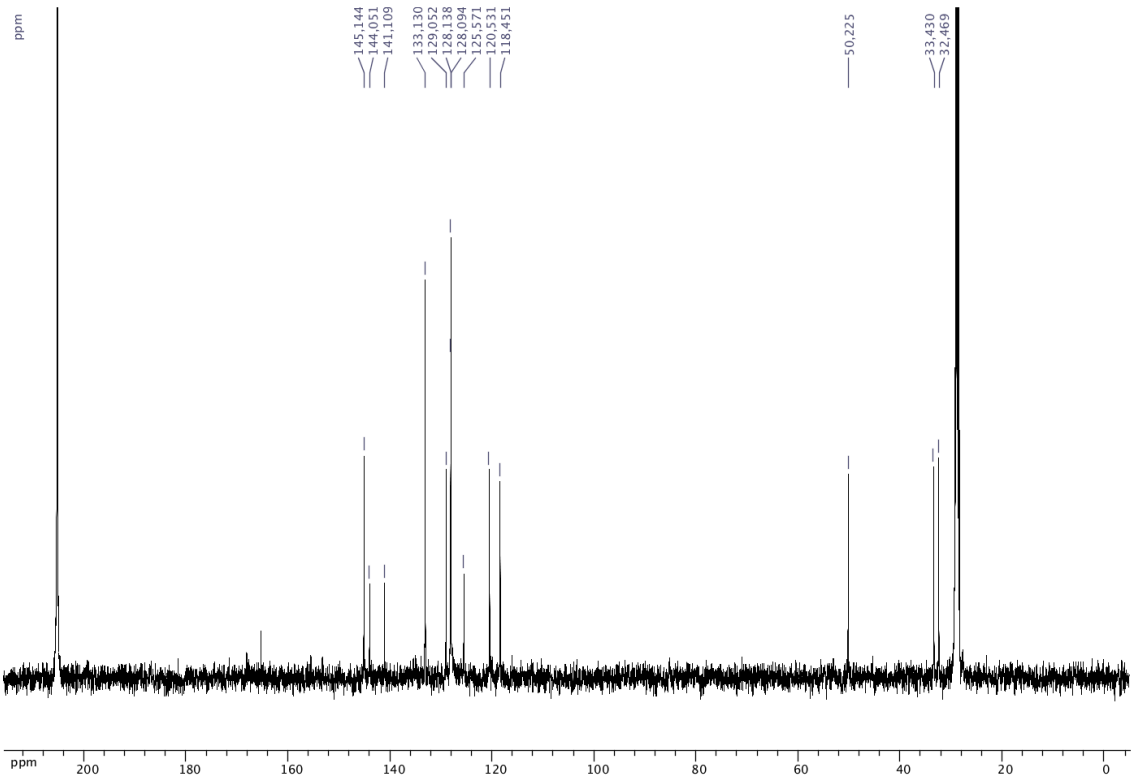
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(4-(3-(butylamino)propyl)phenyl)-2,1-borazanaphthalene (**2m**)



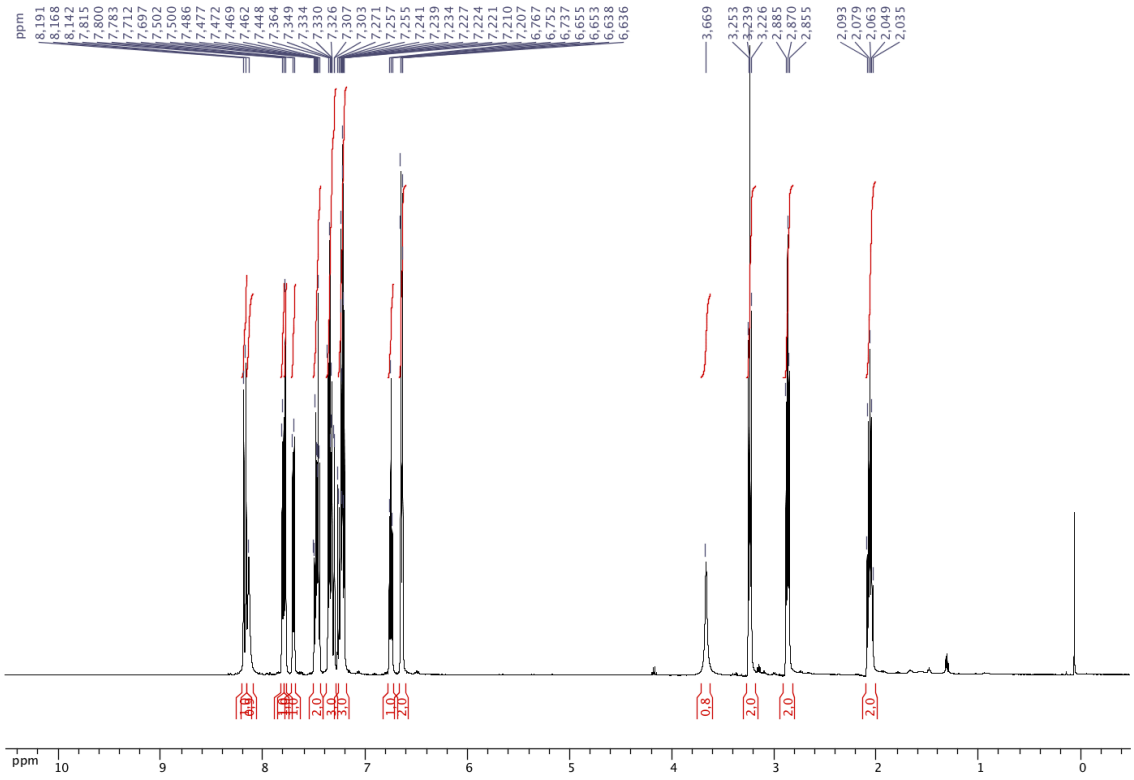
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(4-(3-(butylamino)propyl)phenyl)-2,1-borazanaphthalene (**2m**)



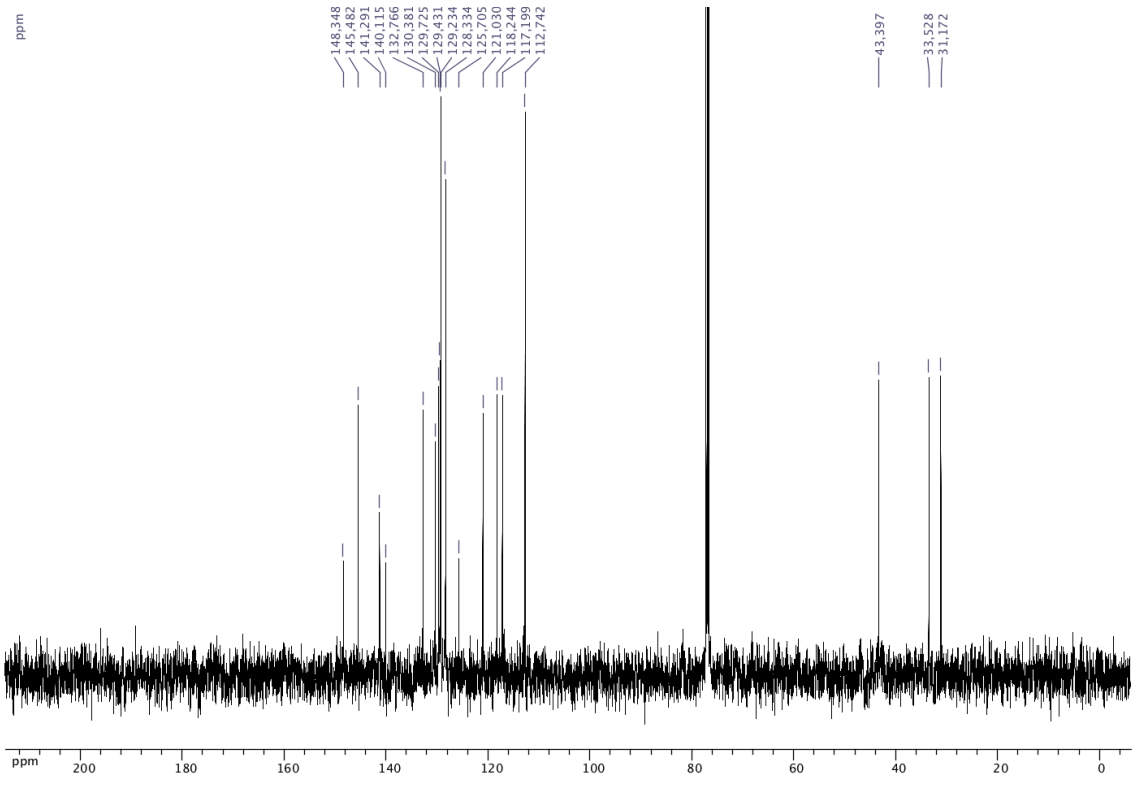
^{1}H NMR (acetone-d_6, 500.4 MHz) of 2-(4-(3-aminopropyl)phenyl)-2,1-borazanaphthalene (**2n**)



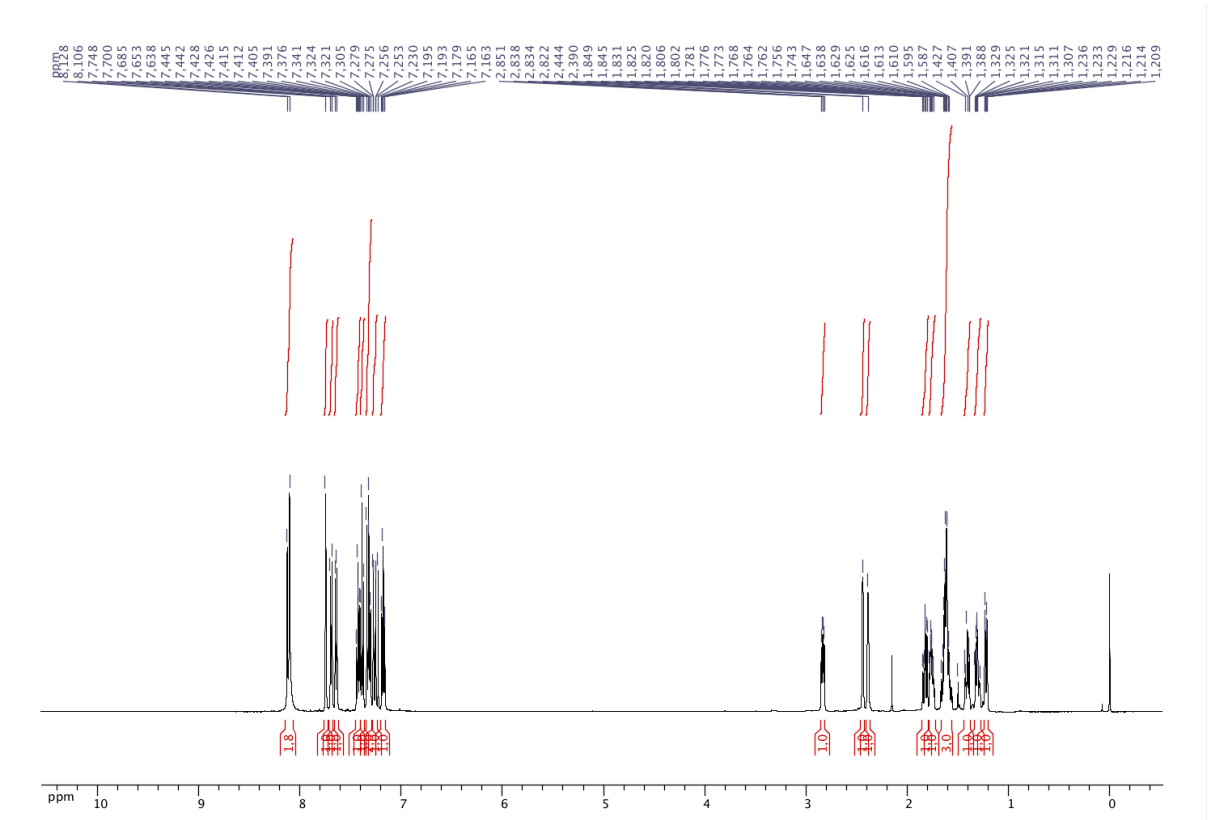
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of 2-(4-(3-aminopropyl)phenyl)-2,1-borazanaphthalene (**2n**)



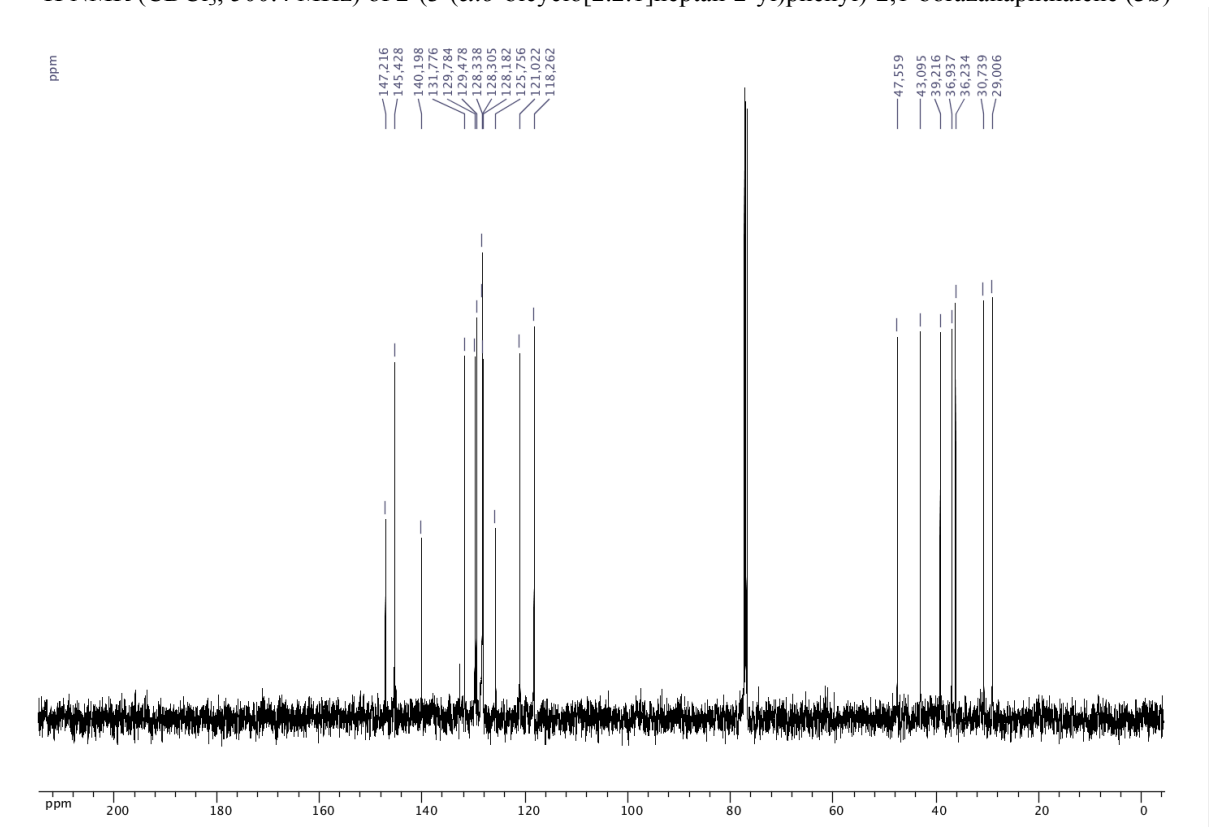
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(3-(3-(phenylamino)propyl)phenyl)-2,1-borazanaphthalene (**3a**)



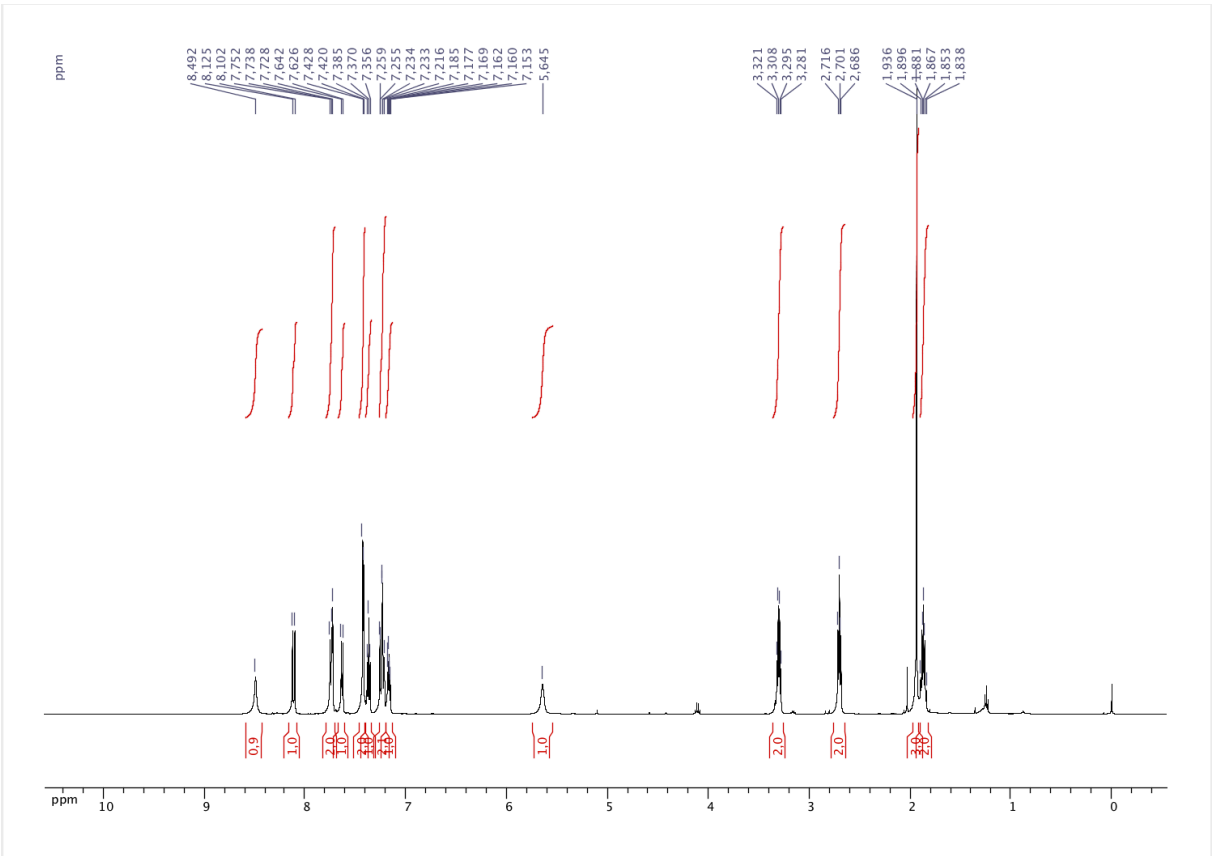
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(3-(3-(phenylamino)propyl)phenyl)-2,1-borazanaphthalene (**3a**)



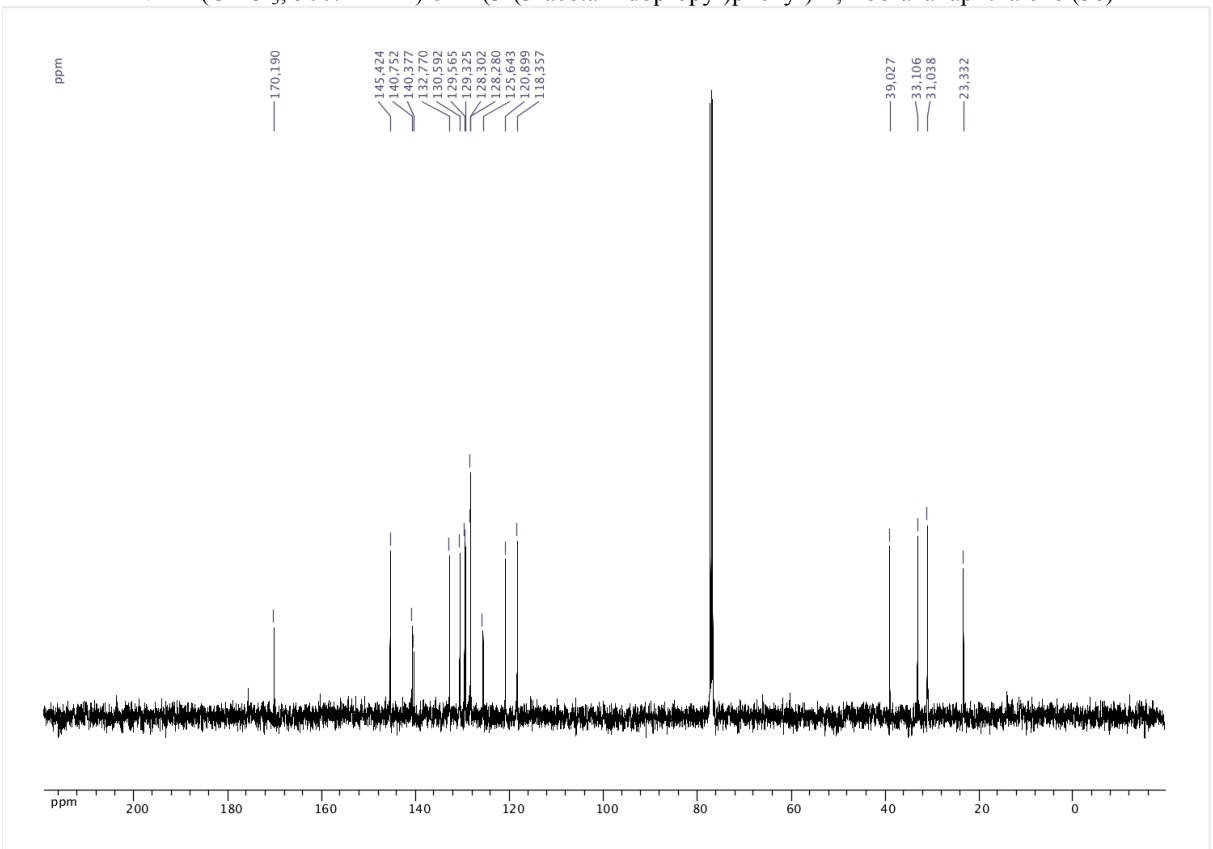
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(3-(*exo*-bicyclo[2.2.1]heptan-2-yl)phenyl)-2,1-borazanaphthalene (**3b**)



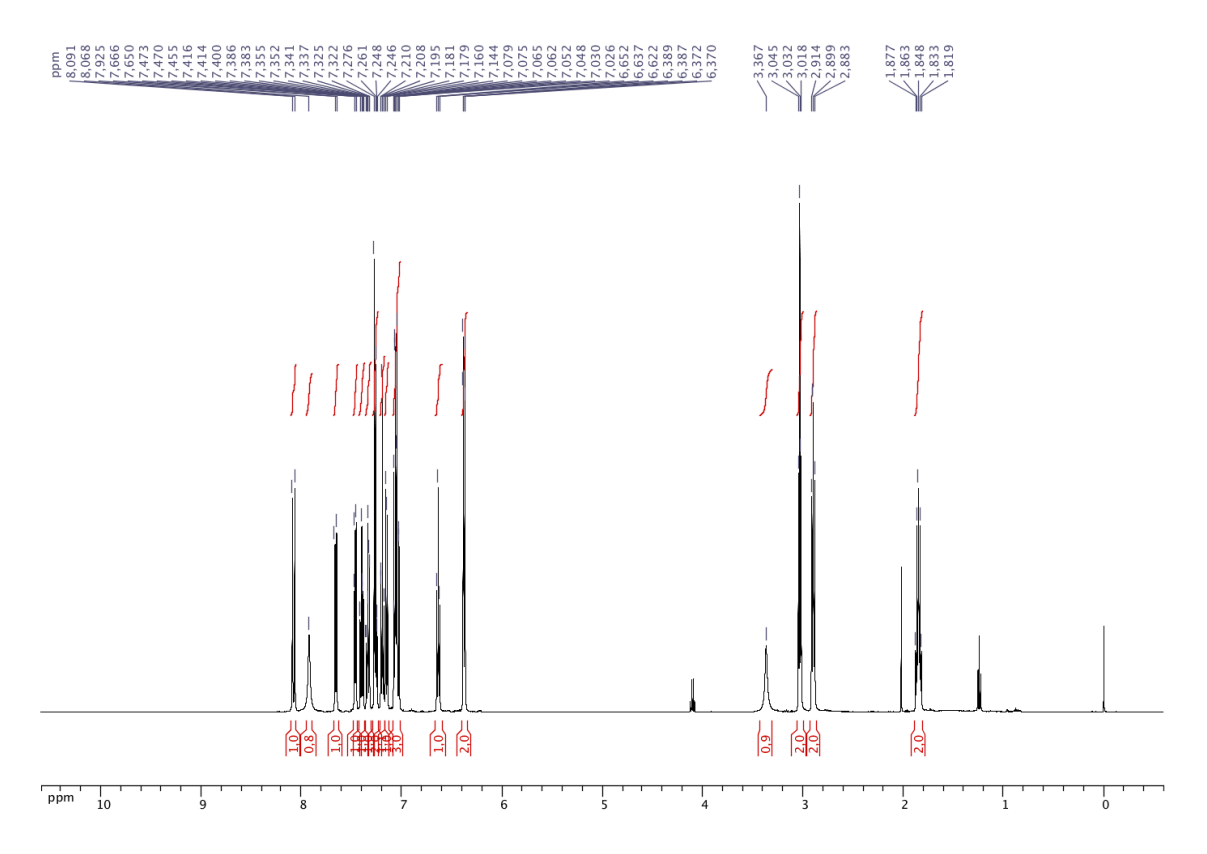
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(3-(*exo*-bicyclo[2.2.1]heptan-2-yl)phenyl)-2,1-borazanaphthalene (**3b**)



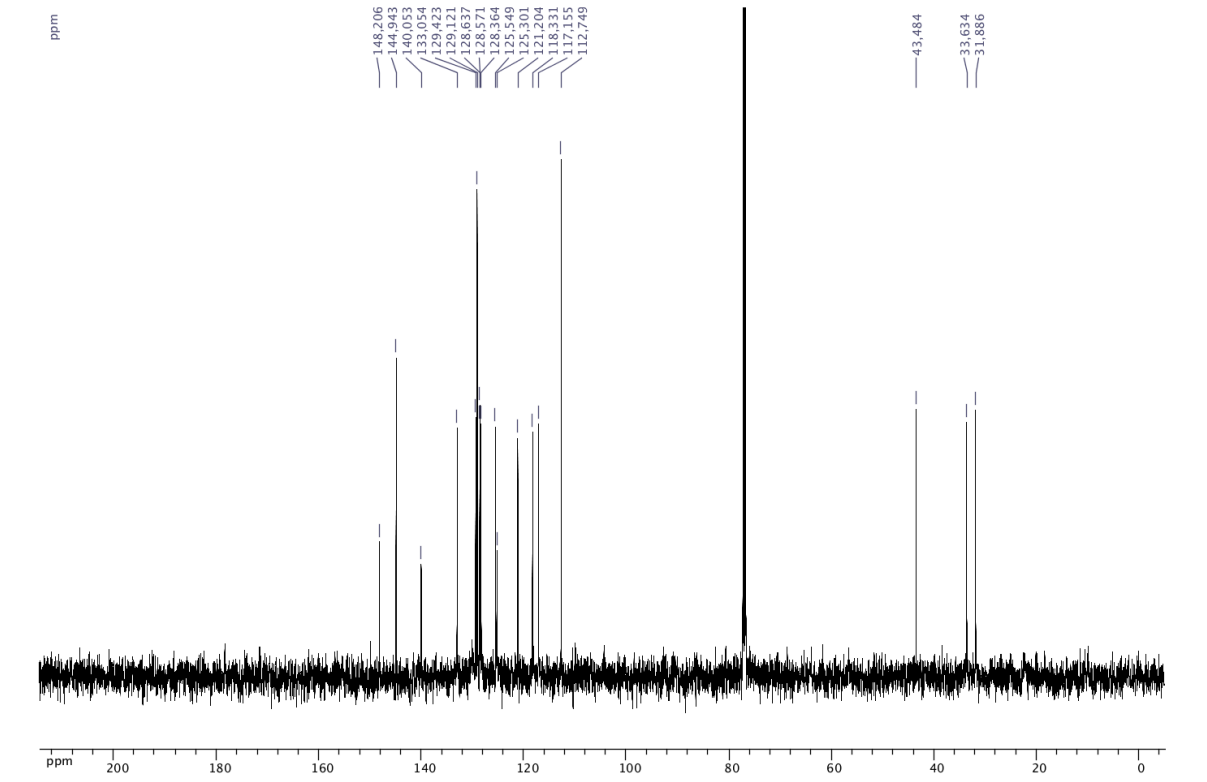
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(3-(3-acetamidopropyl)phenyl)-2,1-borazanaphthalene (**3c**)



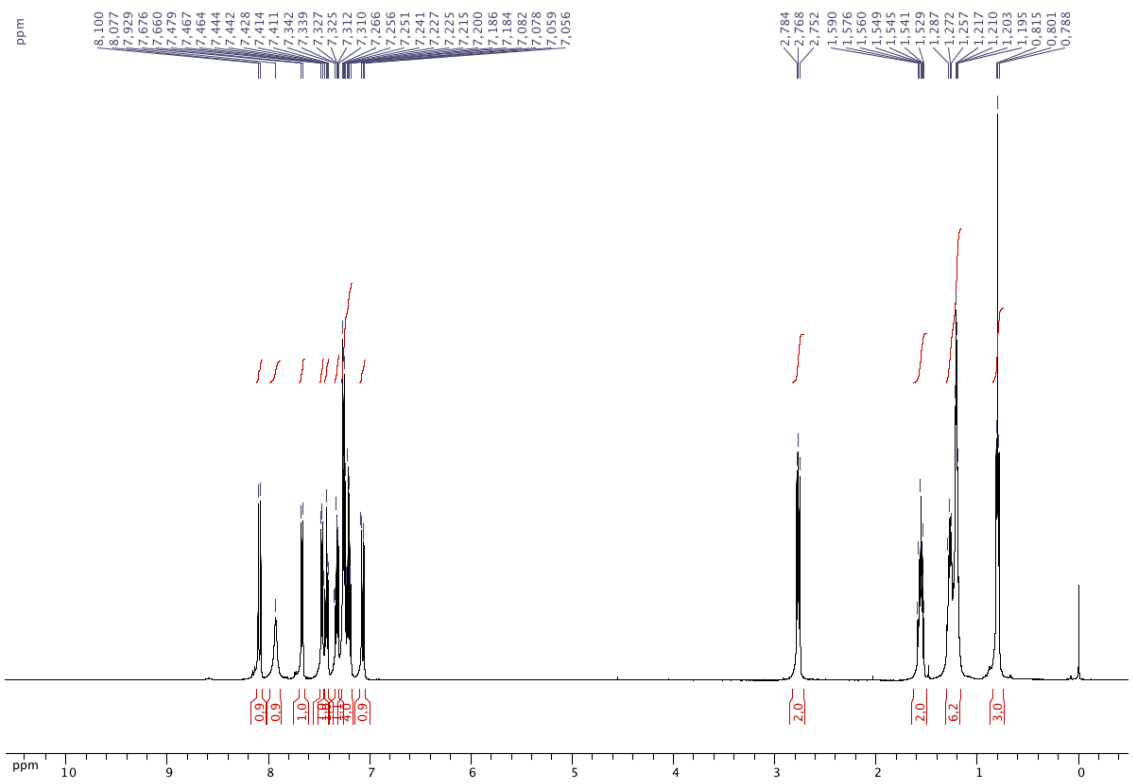
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(3-(3-acetamidopropyl)phenyl)-2,1-borazanaphthalene (**3c**)



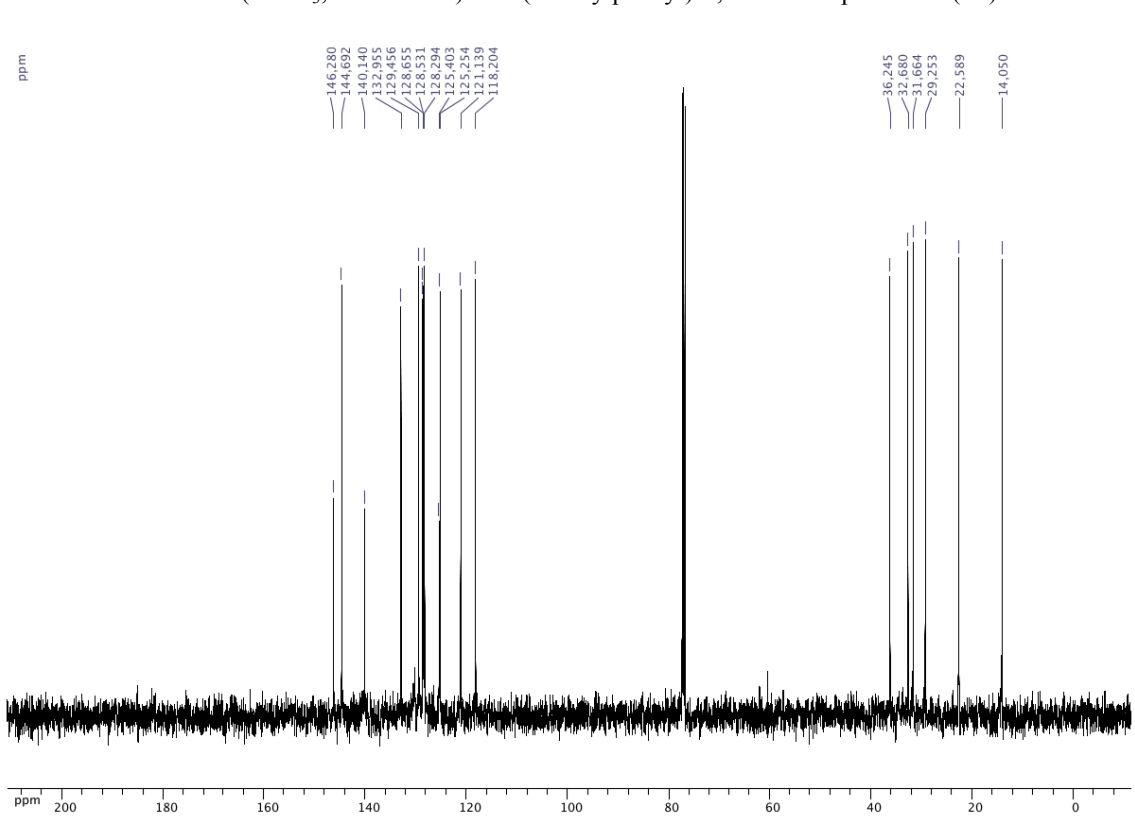
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(2-(3-(phenylamino)propyl)phenyl)-2,1-borazanaphthalene (**4a**)



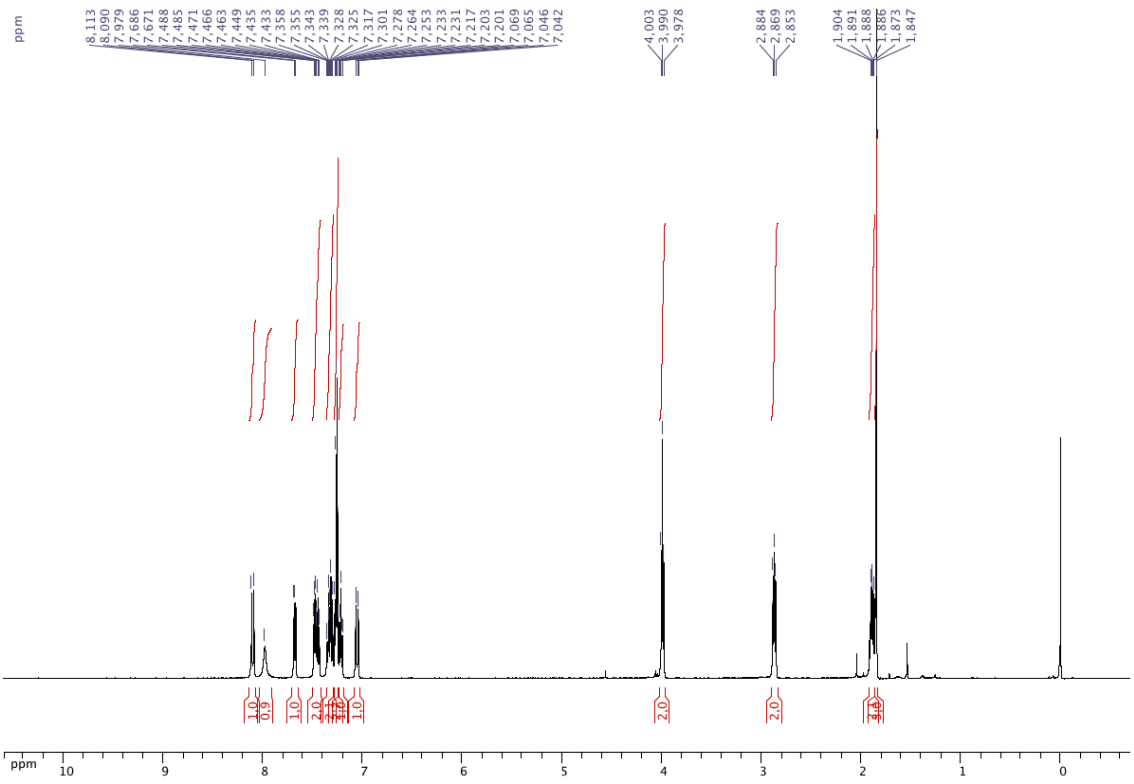
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(2-(3-(phenylamino)propyl)phenyl)-2,1-borazanaphthalene (**4a**)



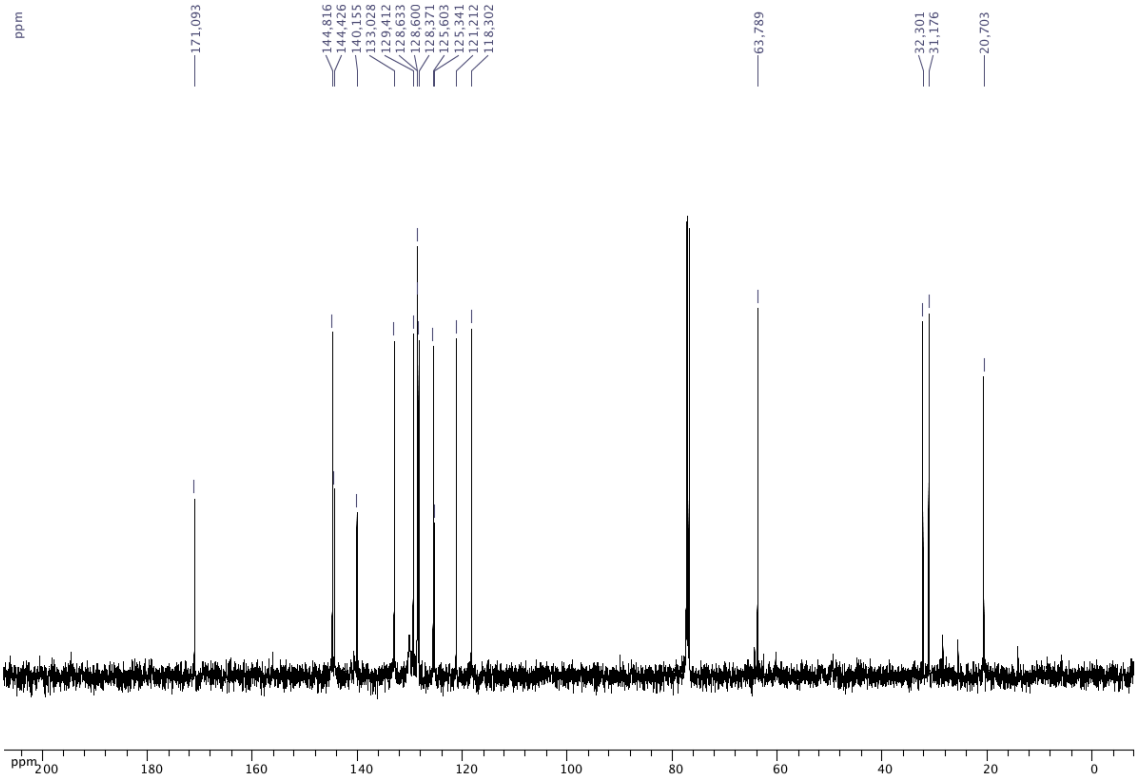
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(2-hexylphenyl)-2,1-borazanaphthalene (**4b**)



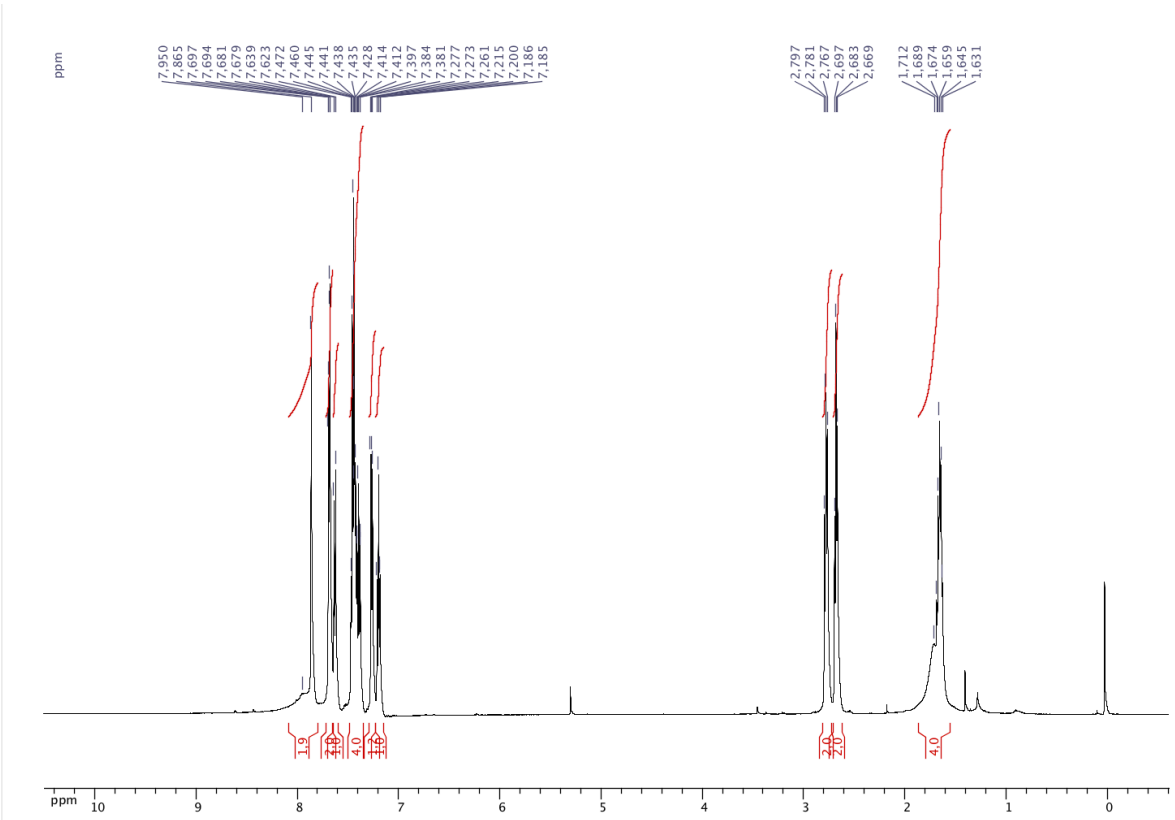
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(2-hexylphenyl)-2,1-borazanaphthalene (**4b**)



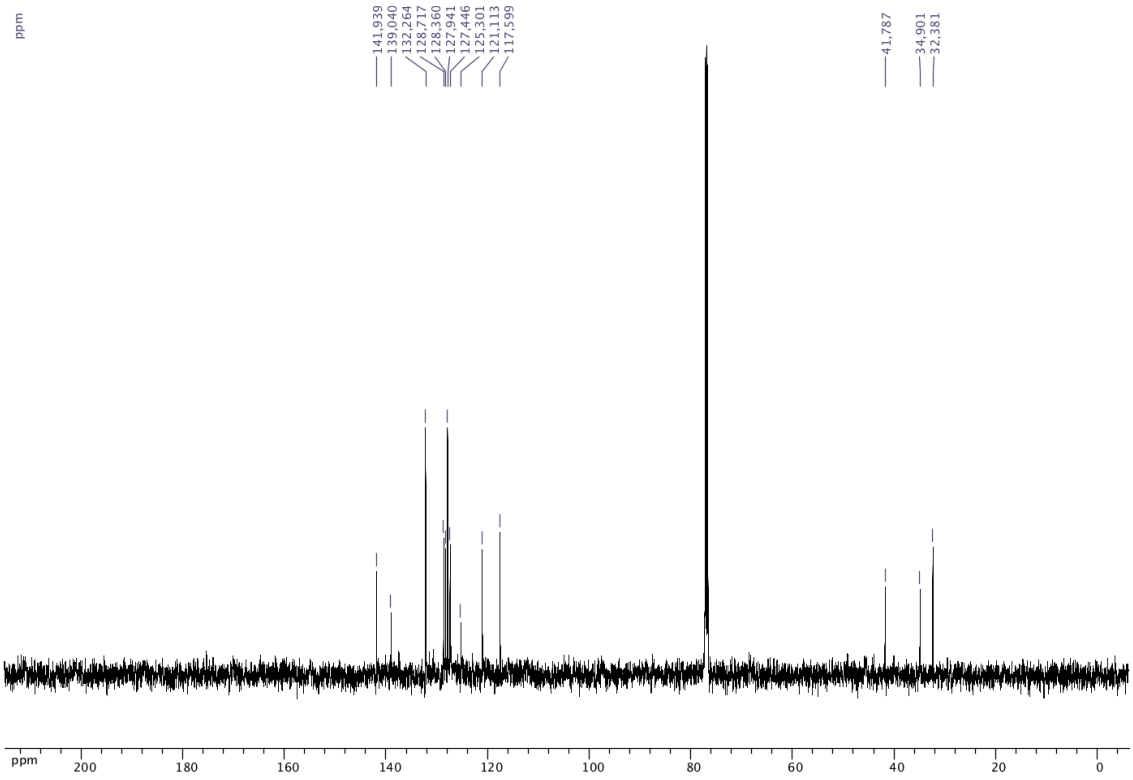
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 2-(2-(3-acetoxypropyl)phenyl)-2,1-borazanaphthalene (**4c**)



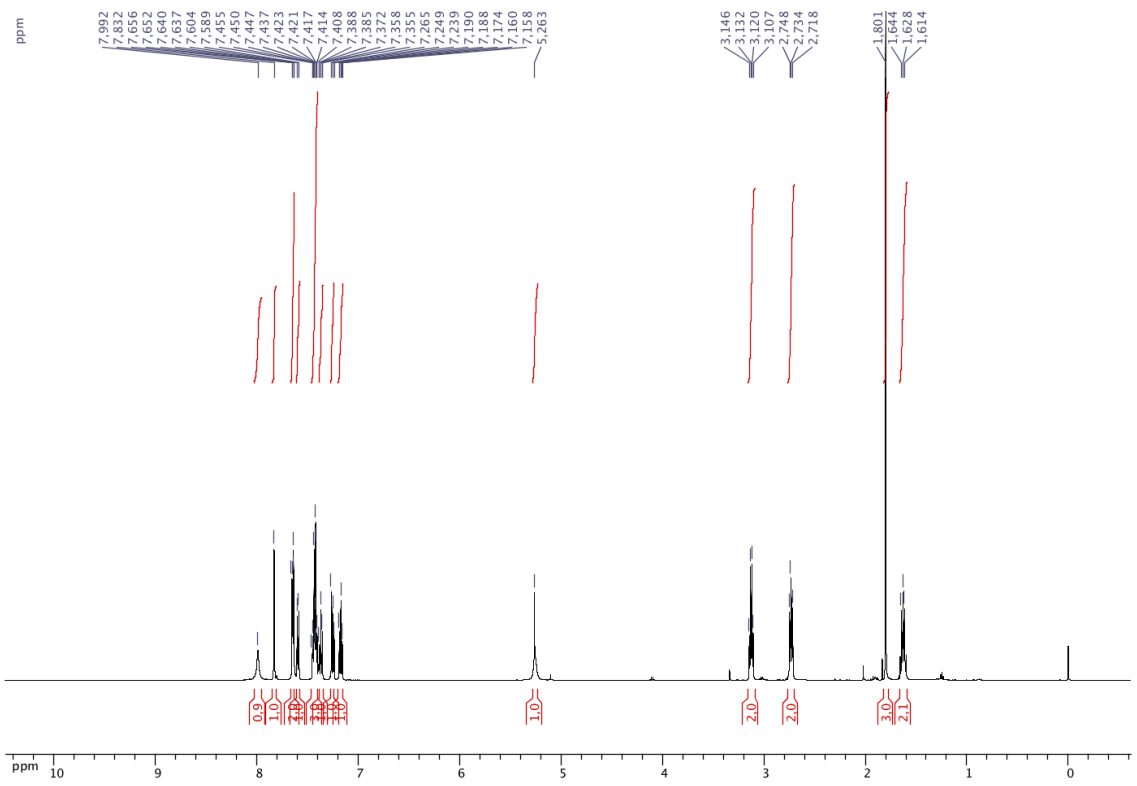
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 2-(2-(3-acetoxypropyl)phenyl)-2,1-borazanaphthalene (**4c**)



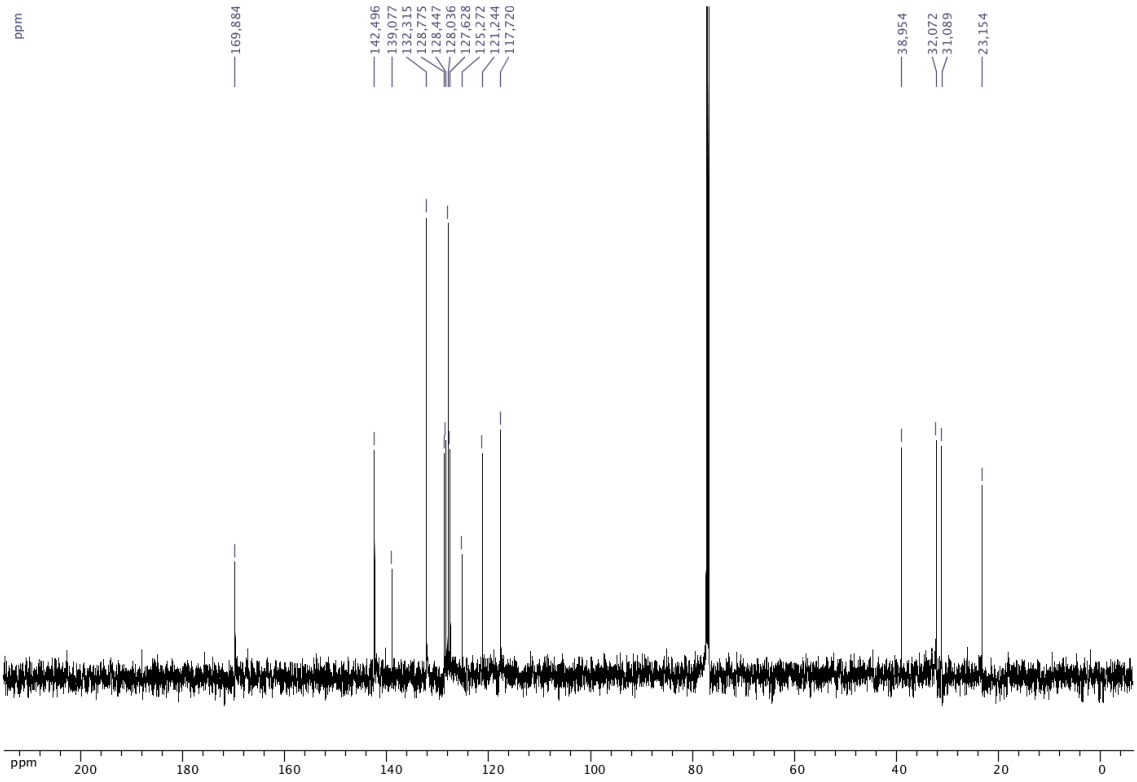
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 3-(3-aminopropyl)-2-phenyl-2,1-borazanaphthalene (**5a**)



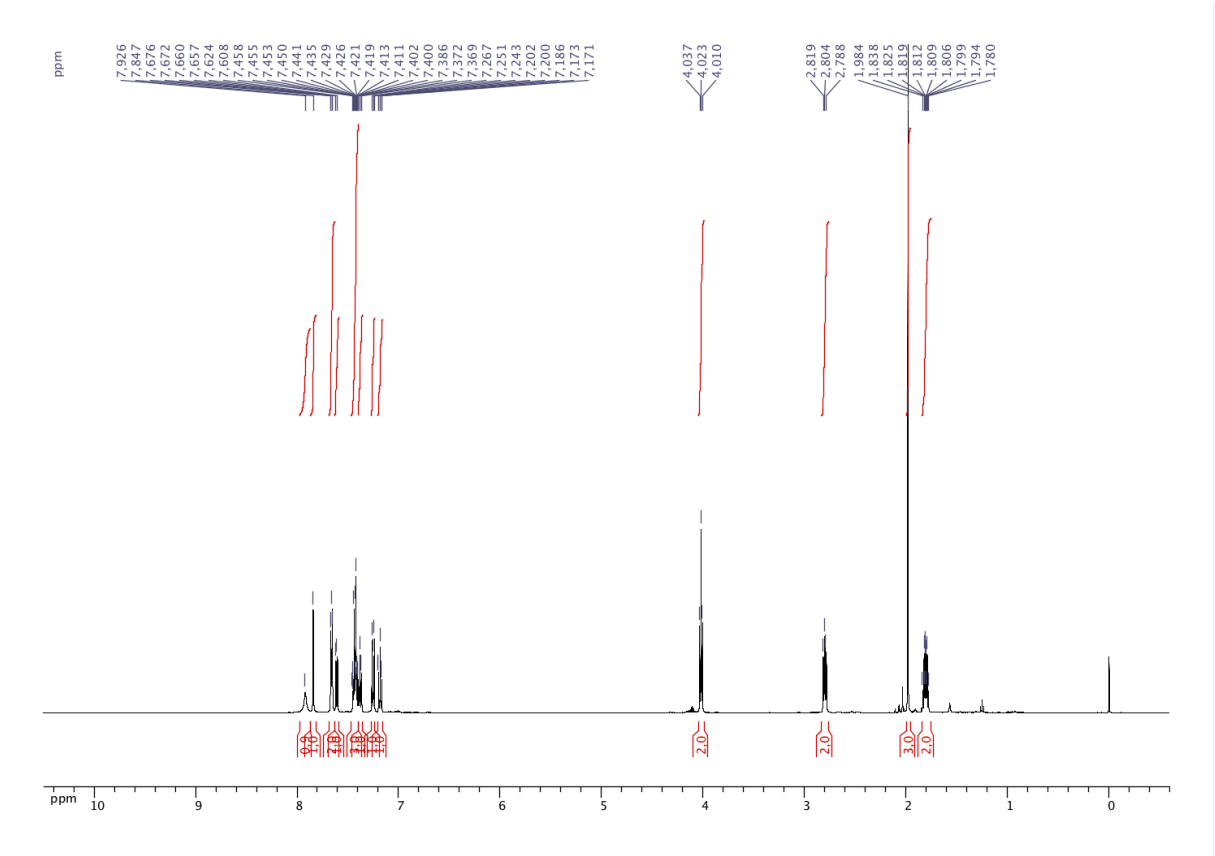
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 3-(3-aminopropyl)-2-phenyl-2,1-borazanaphthalene (**5a**)



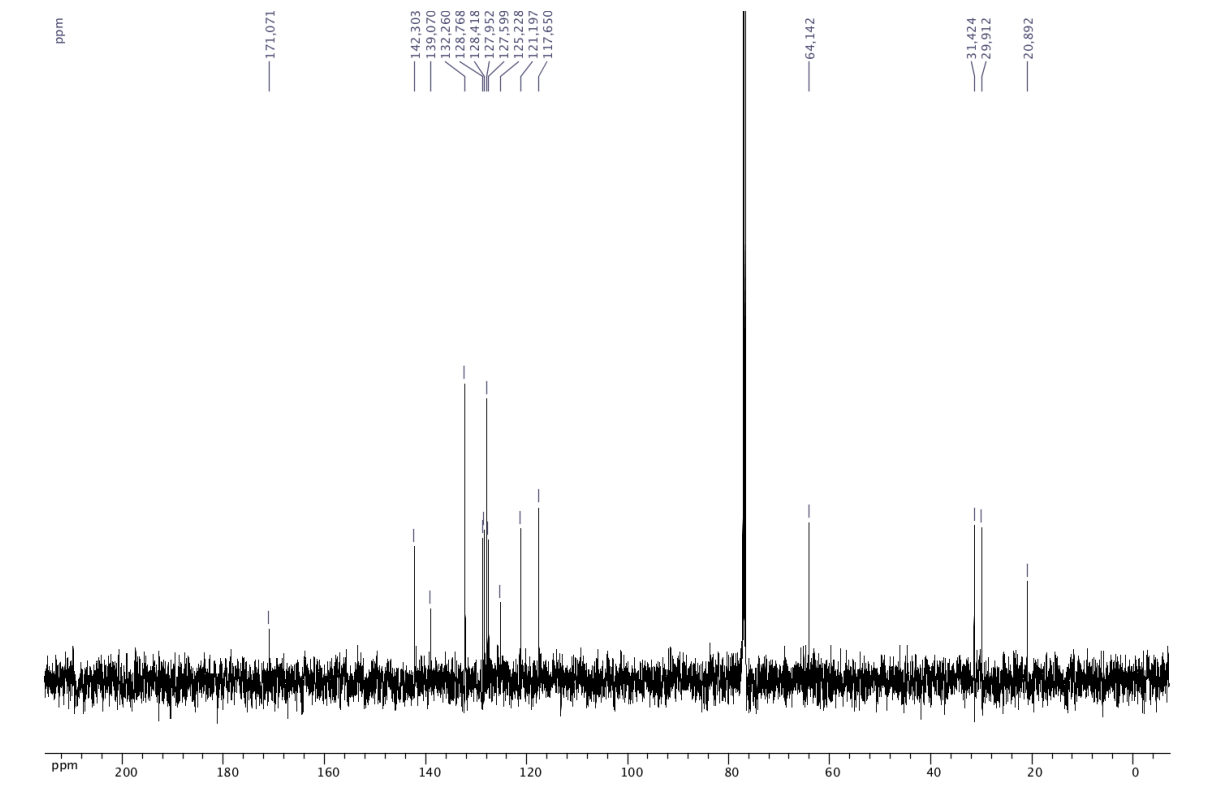
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 3-(3-acetamidopropyl)-2-phenyl-2,1-borazanaphthalene (**5b**)



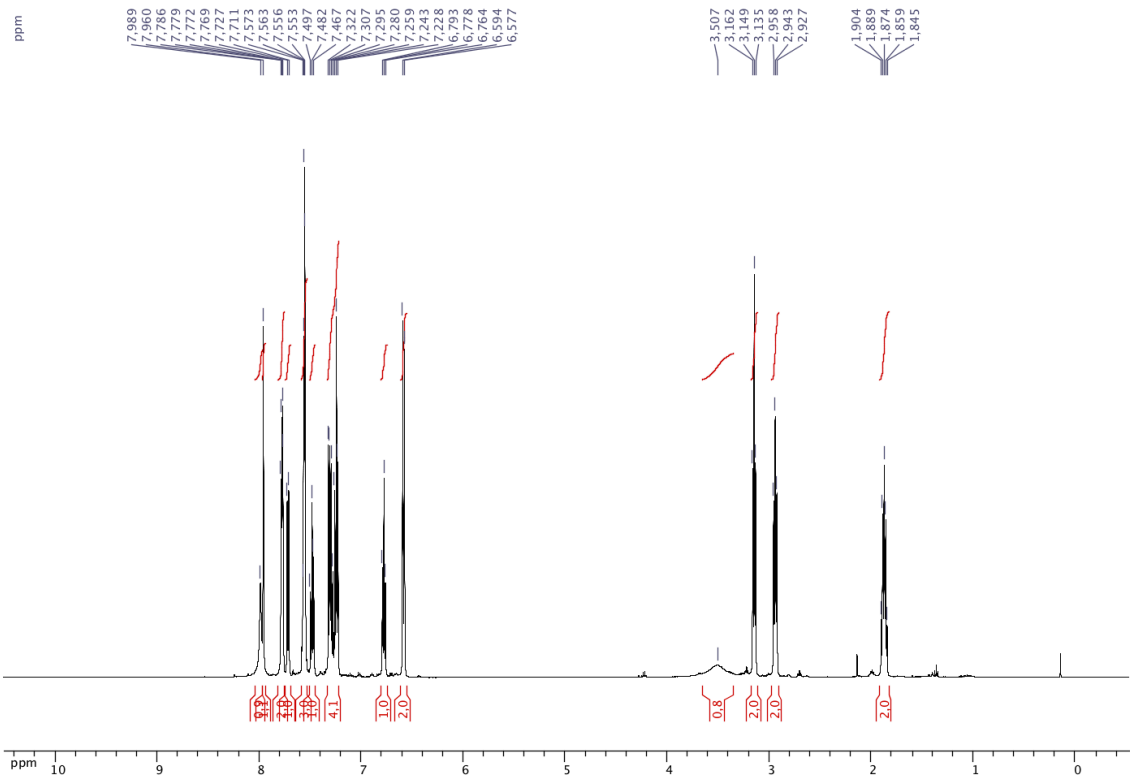
^{13}C {^{1}H} ($CDCl_3$, 125.8 MHz) of 3-(3-acetamidopropyl)-2-phenyl-2,1-borazanaphthalene (**5b**)



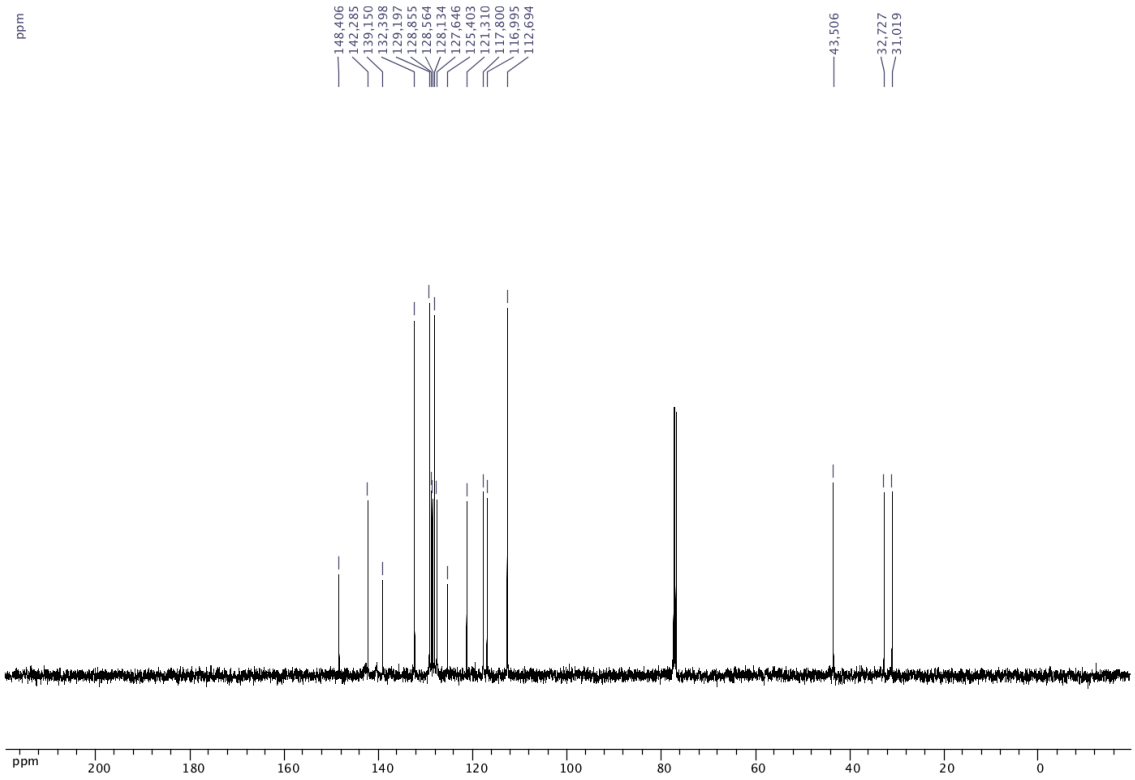
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 3-(3-acetoxypropyl)-2-phenyl-2,1-borazanaphthalene (**5c**)



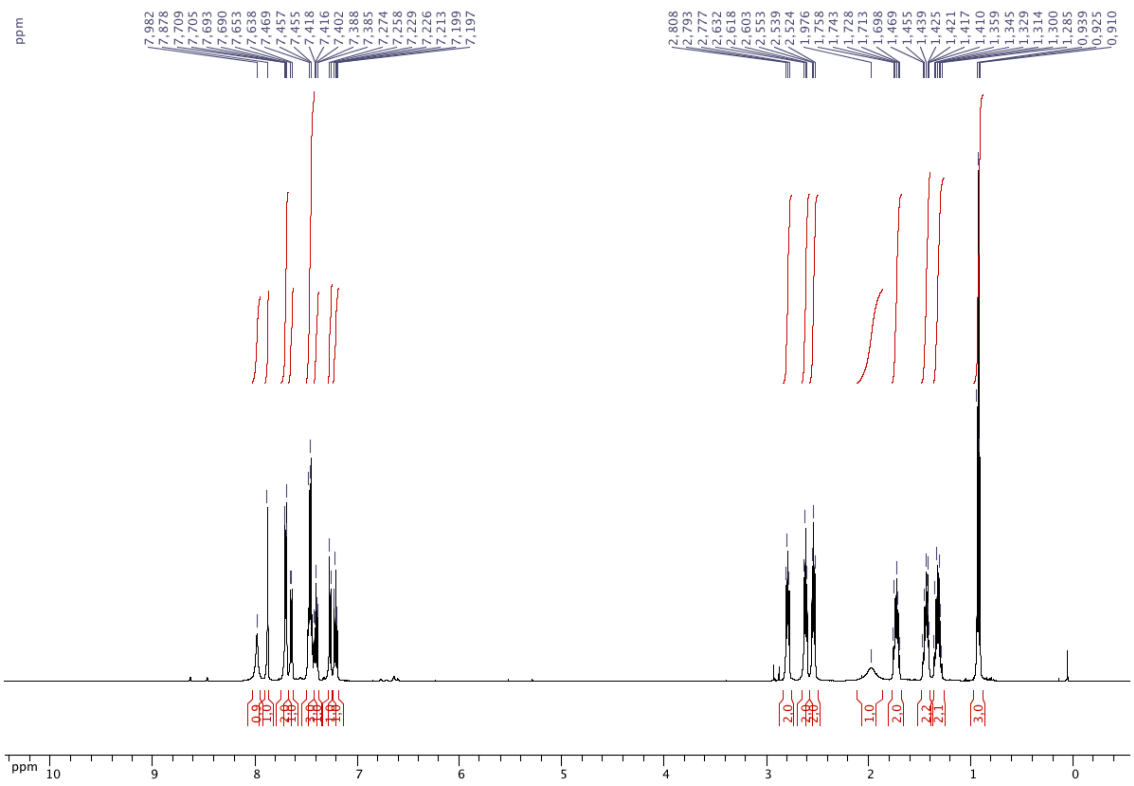
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 3-(3-acetoxypropyl)-2-phenyl-2,1-borazanaphthalene (**5c**)



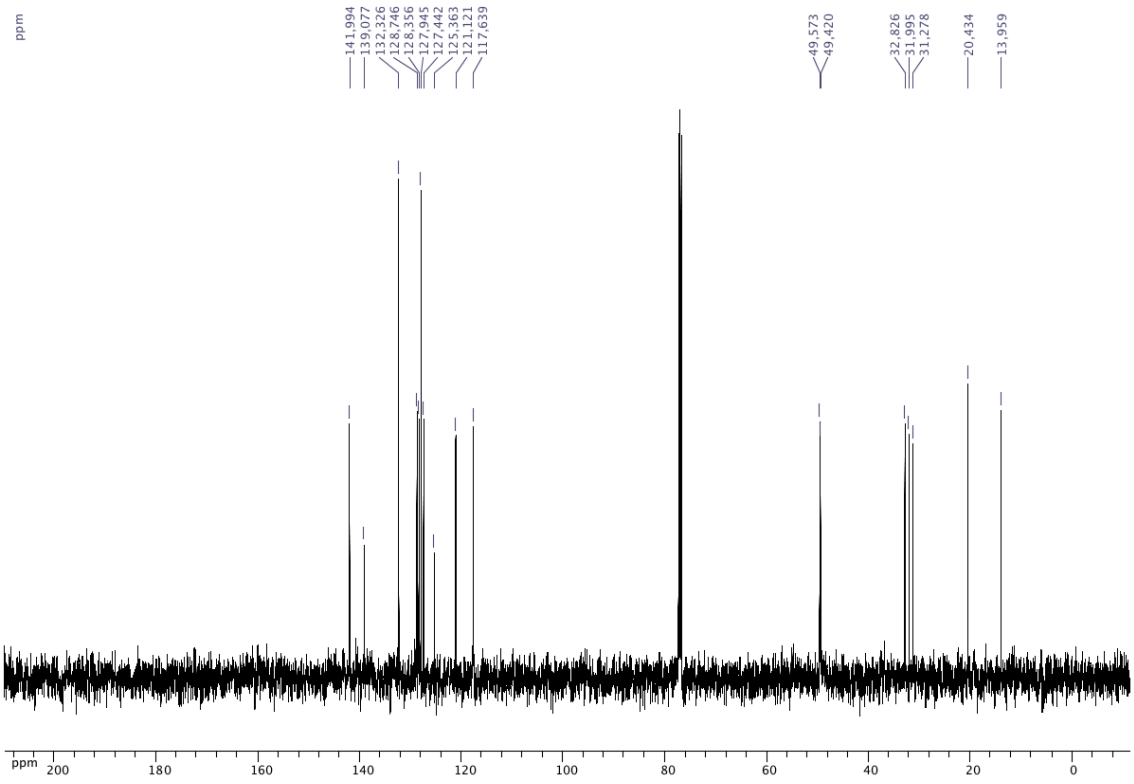
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 3-(3-(phenylamino)propyl)-2-phenyl-2,1-borazanaphthalene (**5d**)



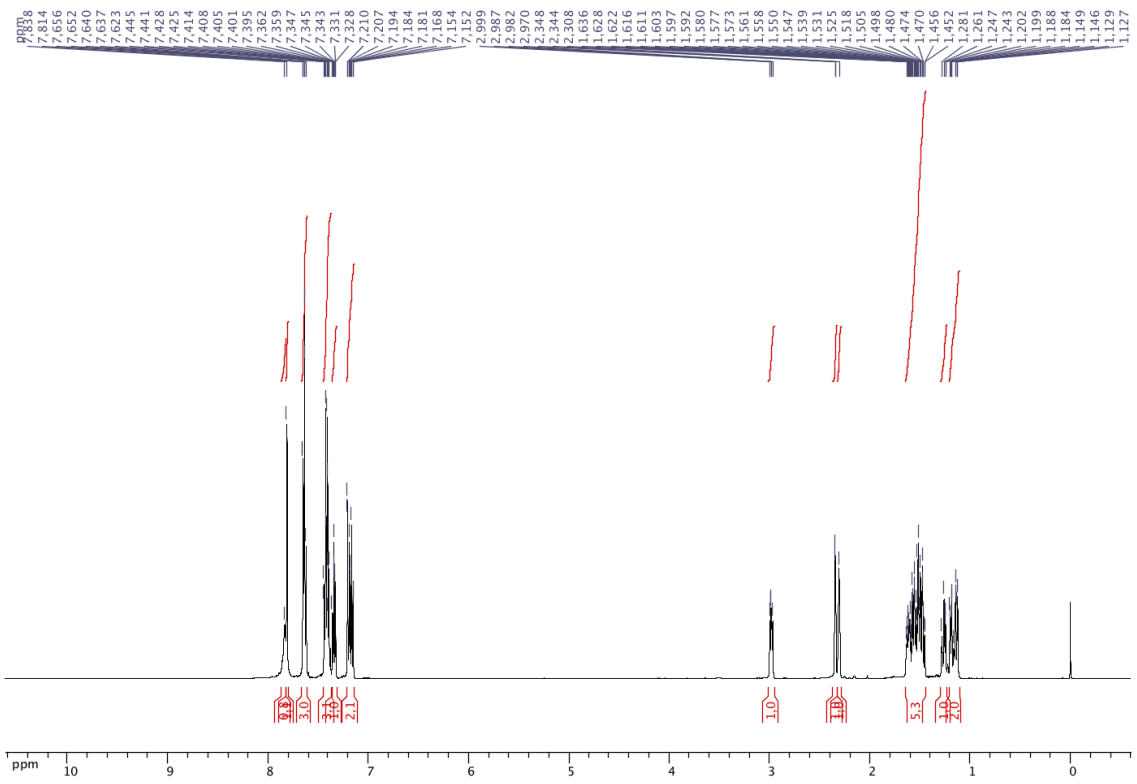
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 3-(3-(phenylamino)propyl)-2-phenyl-2,1-borazanaphthalene (**5d**)



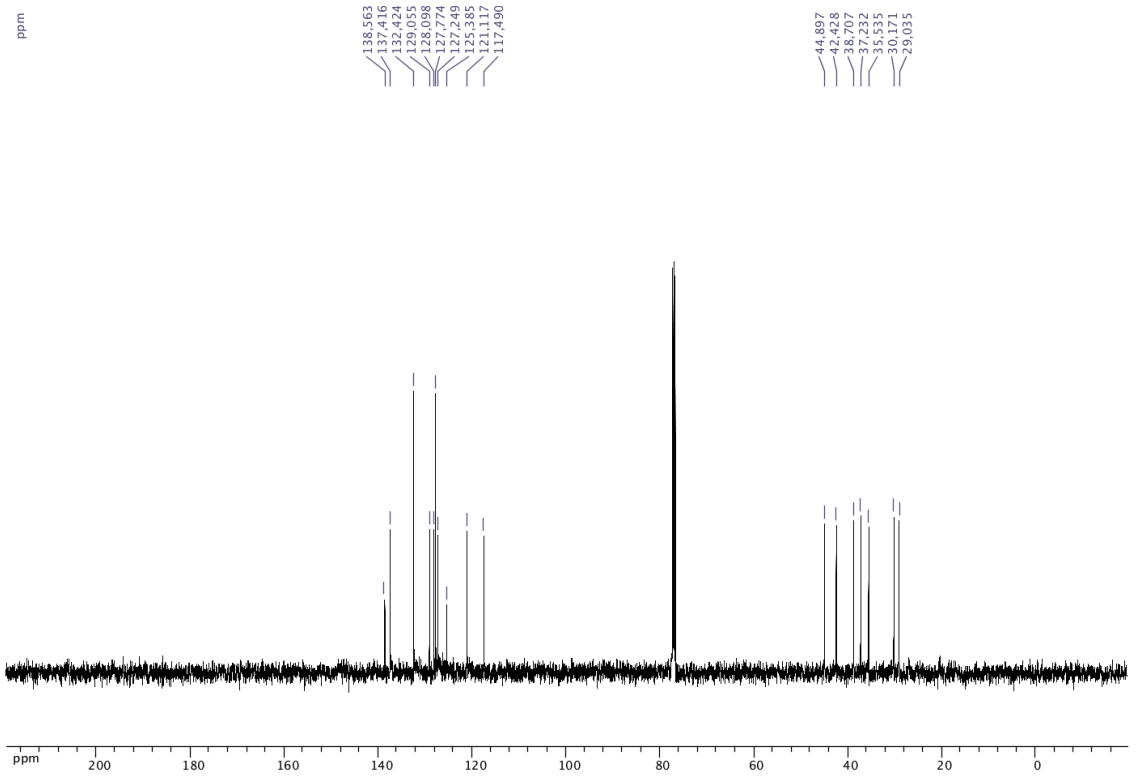
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 3-(3-(butylamino)propyl)-2-phenyl-2,1-borazanaphthalene (**5e**)



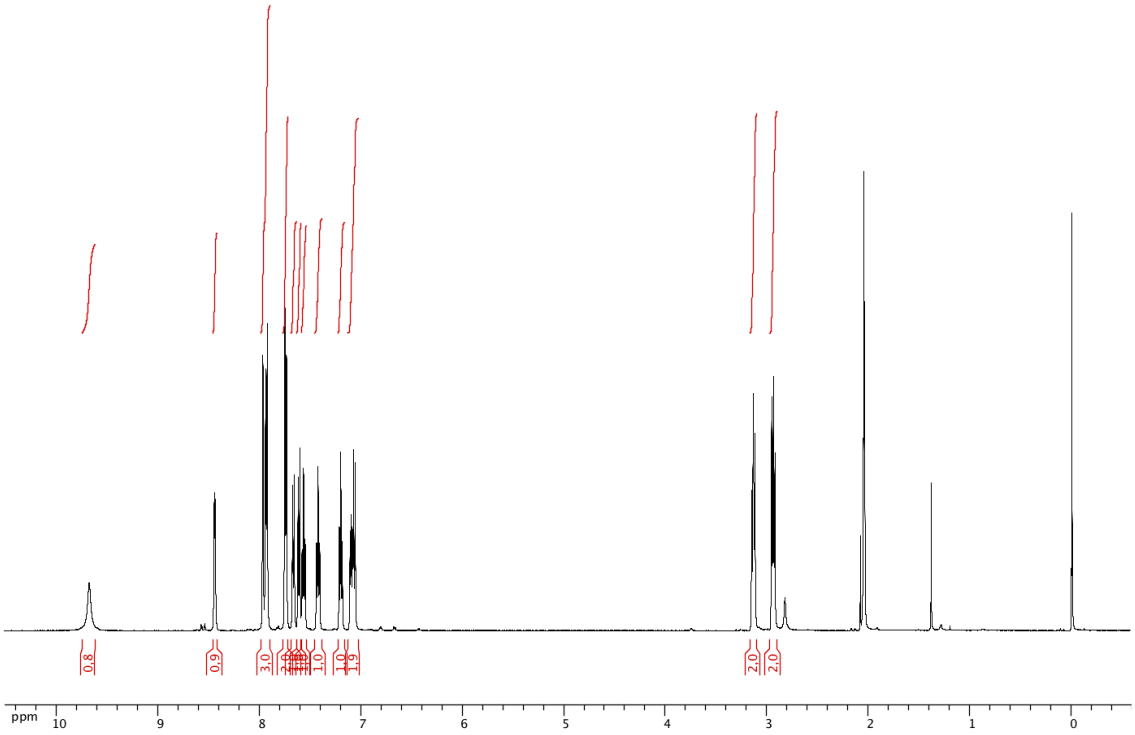
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 3-(3-(butylamino)propyl)-2-phenyl-2,1-borazanaphthalene (**5e**)



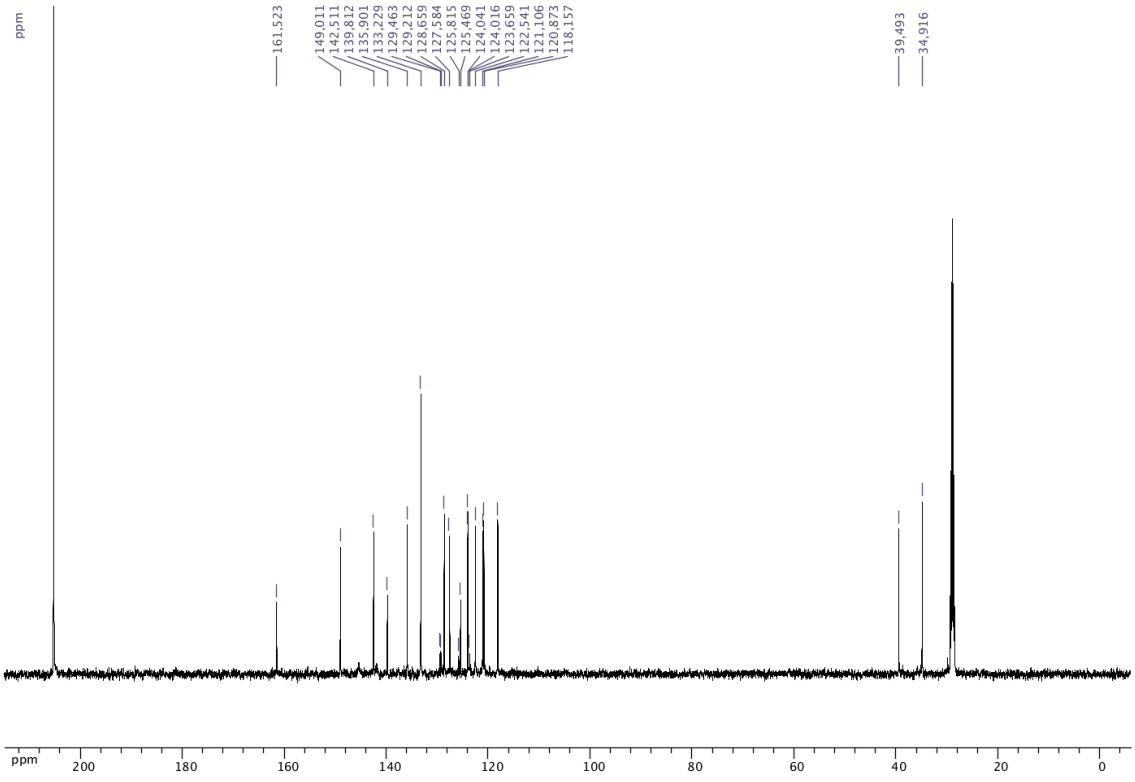
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 3-(*exo*-bicyclo[2.2.1]heptan-2-yl)-2-phenyl-2,1-borazanaphthalene (**5f**)



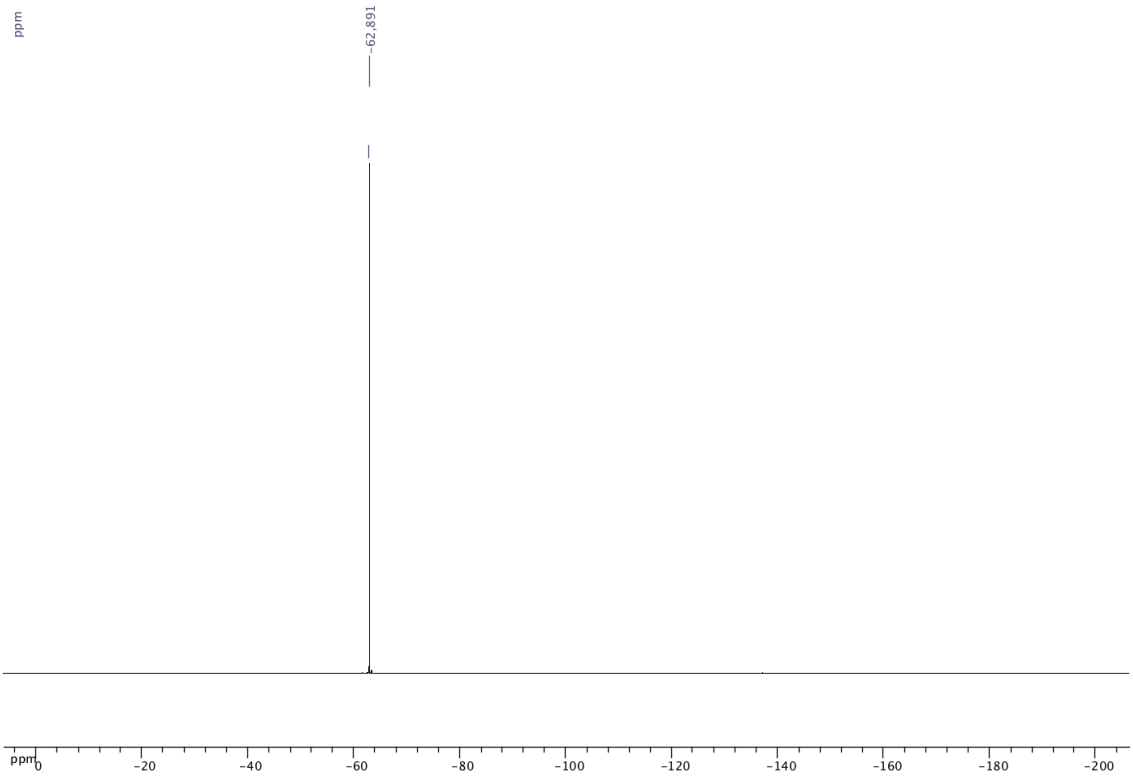
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 3-(*exo*-bicyclo[2.2.1]heptan-2-yl)-2-phenyl-2,1-borazanaphthalene (**5f**)



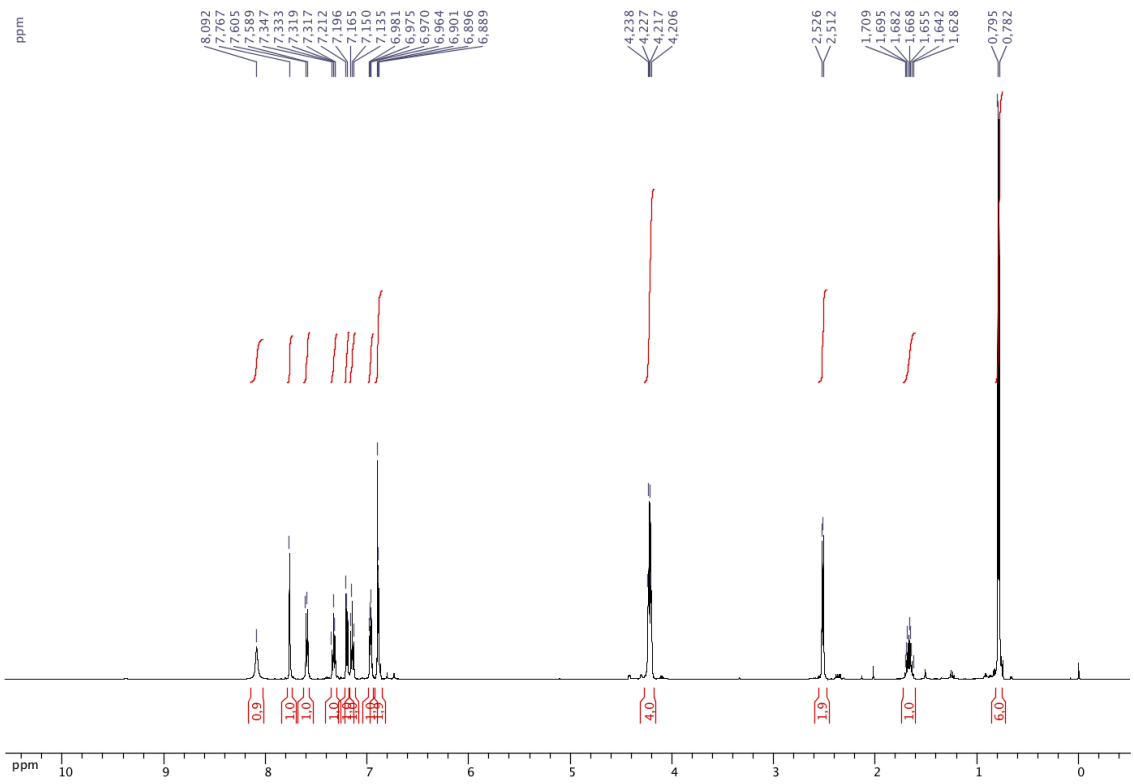
^{1}H NMR (acetone-d_6, 500.4 MHz) of 3-(2-pyridin-2-yl)ethyl)-2-(4-trifluoromethylphenyl)-2,1-borazanaphthalene (**6**)



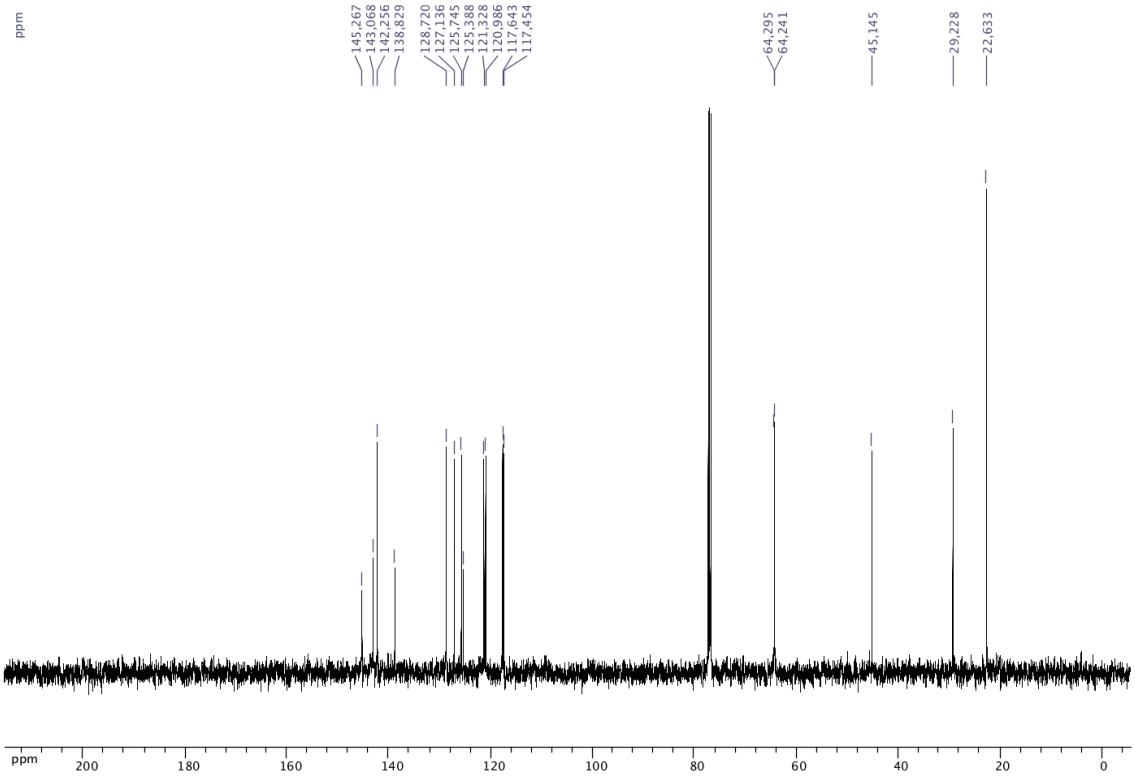
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of 3-(2-pyridin-2-yl)ethyl)-2-(4-trifluoromethylphenyl)-2,1-borazanaphthalene (**6**)



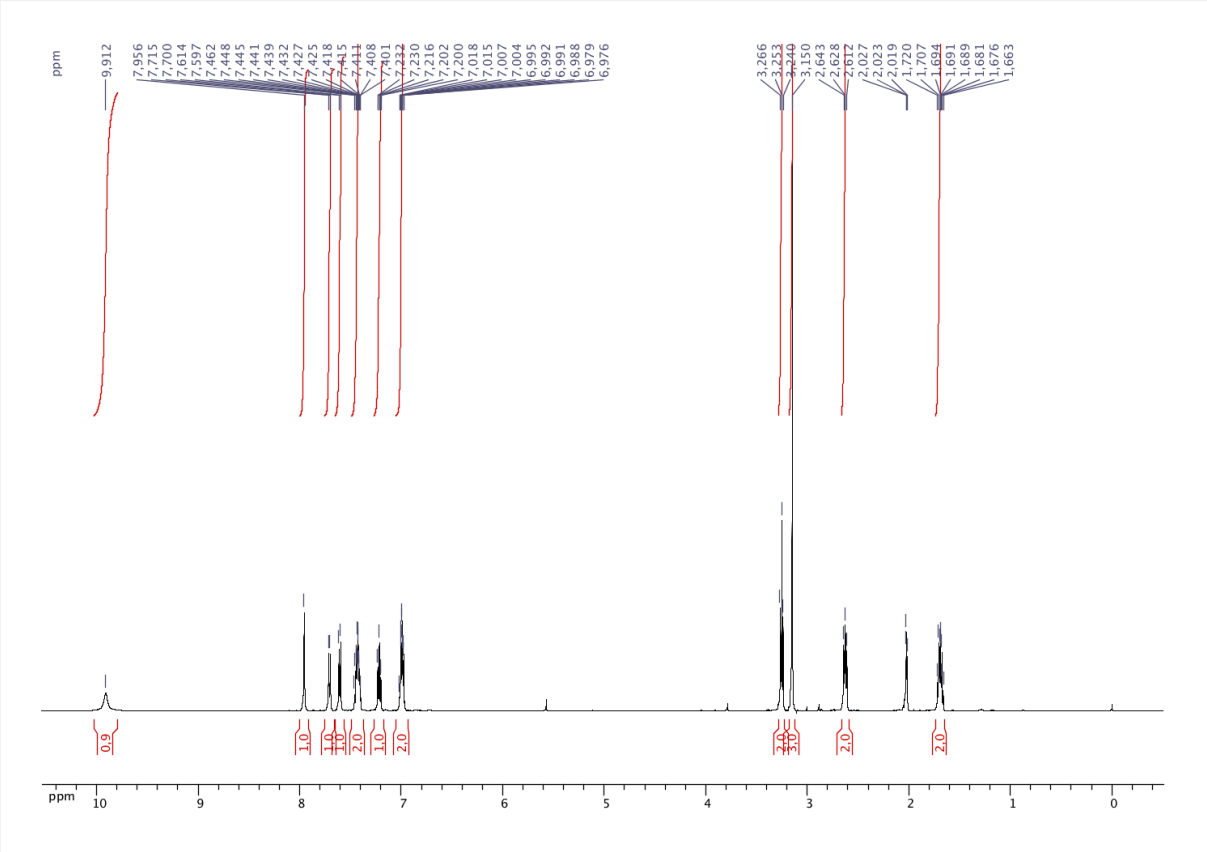
^{19}F {^{1}H} NMR (acetone-d_6, 470.8 MHz) of 3-(2-pyridin-2-yl)ethyl)-2-(4-trifluoromethylphenyl)-2,1-borazanaphthalene (**6**)



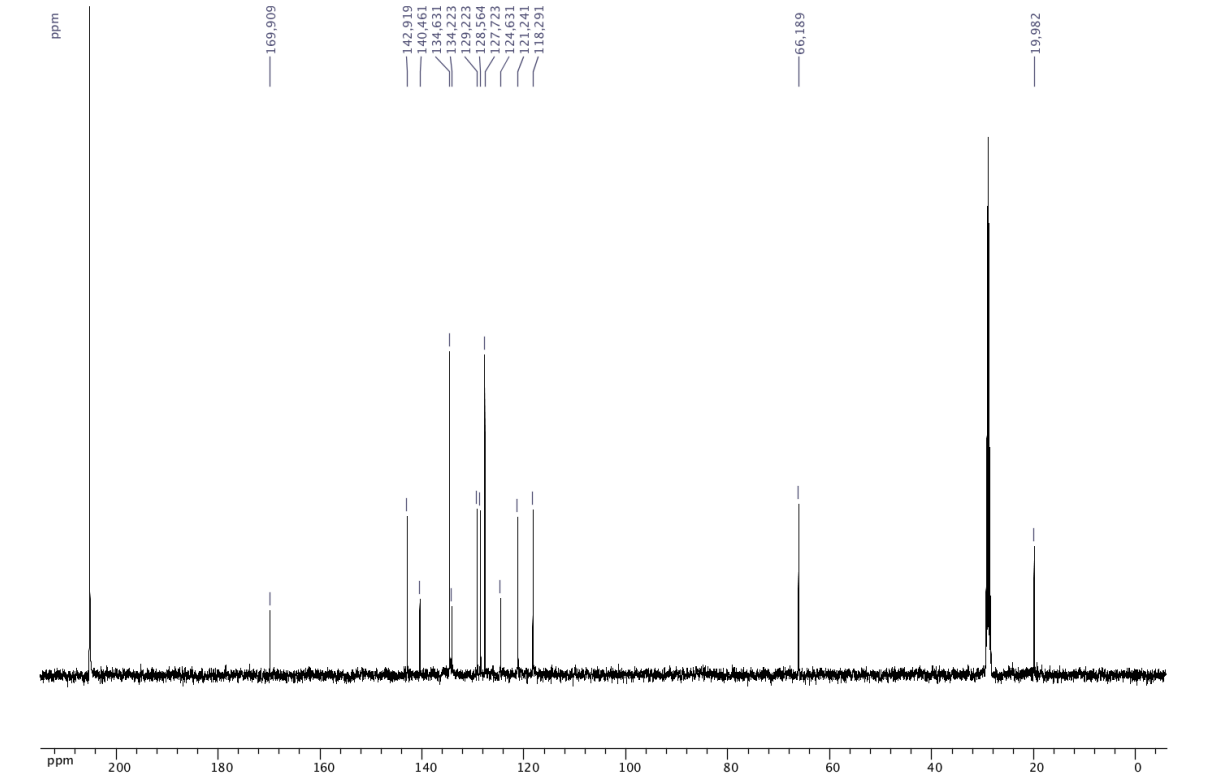
^{1}H NMR ($CDCl_3$, 500.4 MHz) of 3-(isobutyl)-2-(2,3-dihydro-1,4-benzodioxin-6-yl)-2,1-borazanaphthalene (**7**)



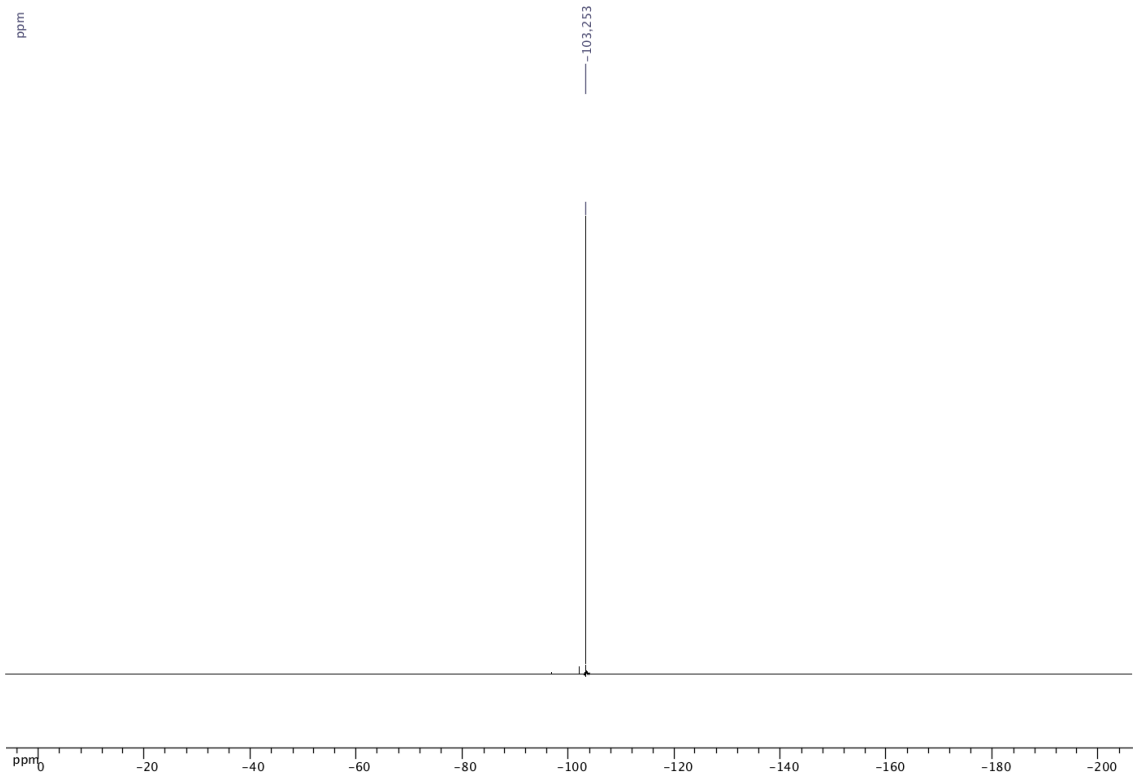
^{13}C {^{1}H} NMR ($CDCl_3$, 125.8 MHz) of 3-(isobutyl)-2-(2,3-dihydro-1,4-benzodioxin-6-yl)-2,1-borazanaphthalene (**7**)



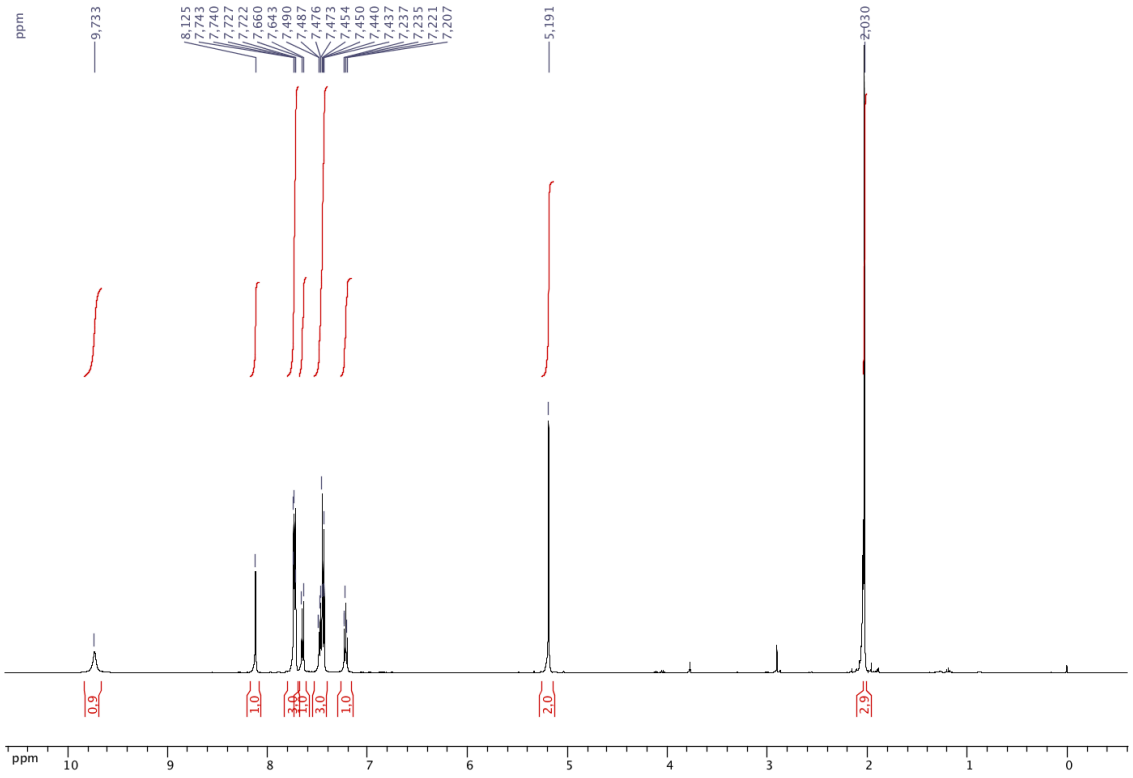
^{1}H NMR (acetone-d_6, 500.4 MHz) of 3-(3-methoxypropyl)-2-(2,6-difluorophenyl)-2,1-borazanaphthalene (**8**)



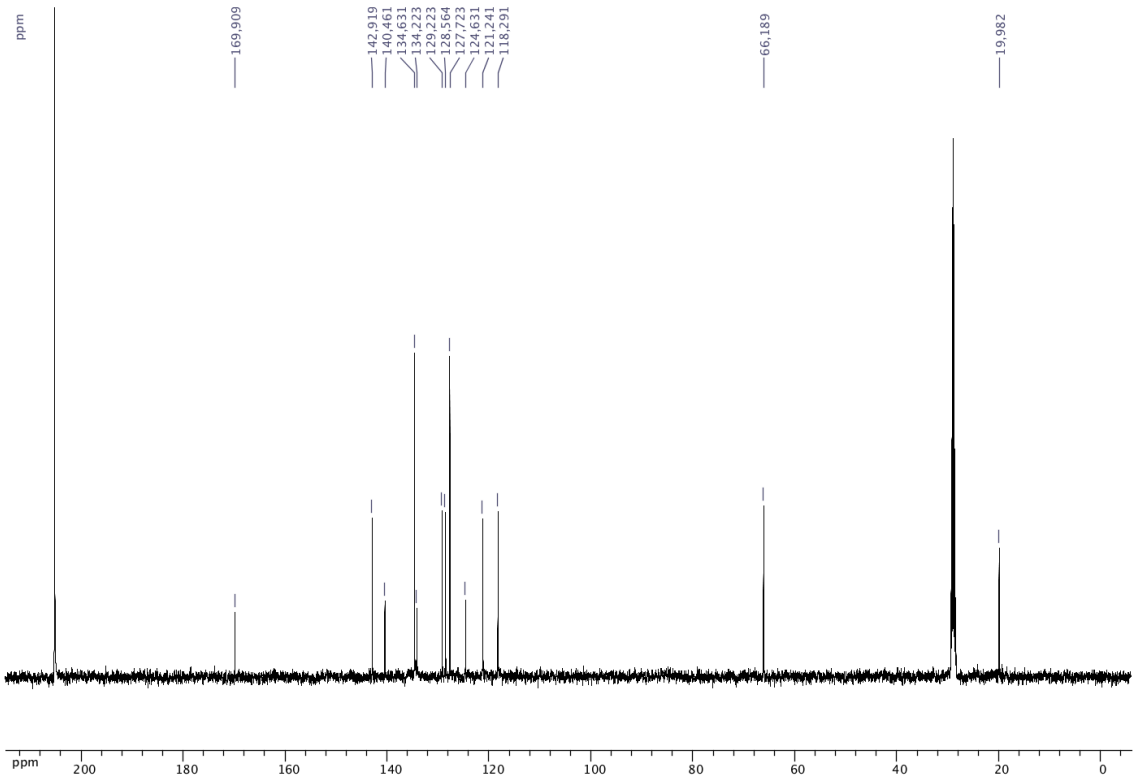
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of 3-(3-methoxypropyl)-2-(2,6-difluorophenyl)-2,1-borazanaphthalene (**8**)



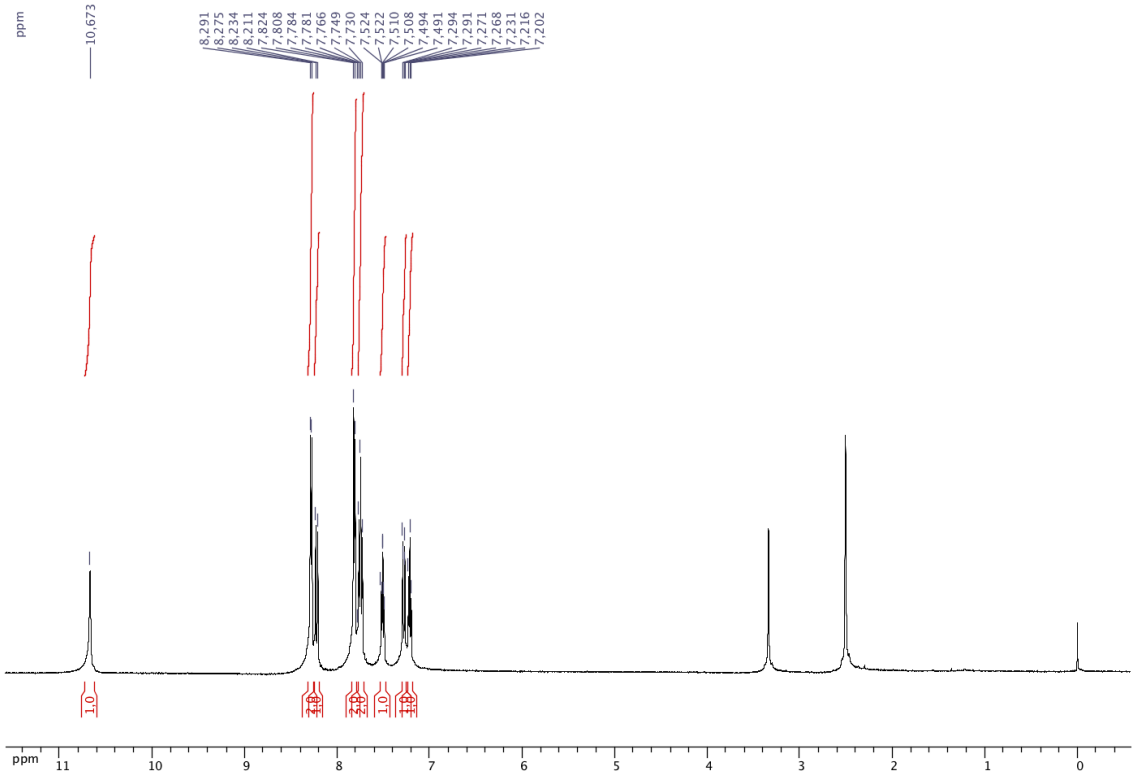
^{19}F {^{1}H} NMR (acetone-d_6, 470.8 MHz) of 3-(3-methoxypropyl)-2-(2,6-difluorophenyl)-2,1-borazanaphthalene (**8**)



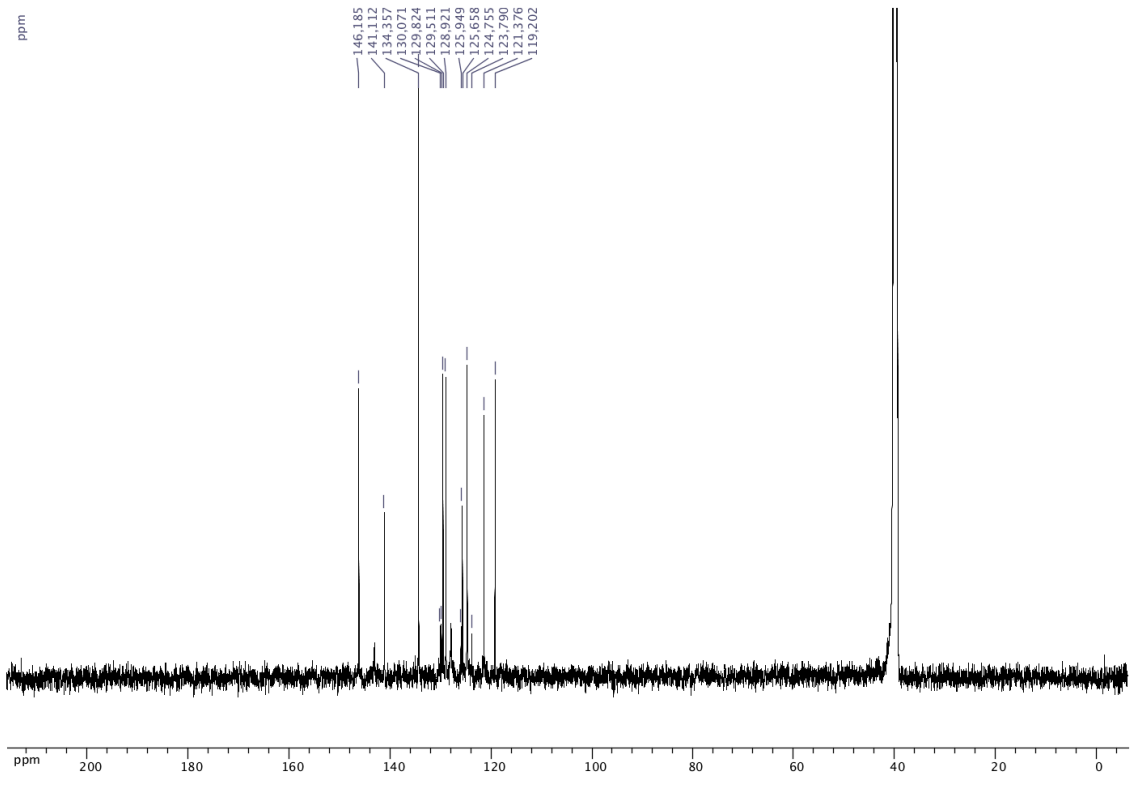
^{1}H NMR (acetone-d_6, 500.4 MHz) of 3-(acetoxymethyl)-2-(4-chlorophenyl)-2,1-borazanaphthalene (**9**)



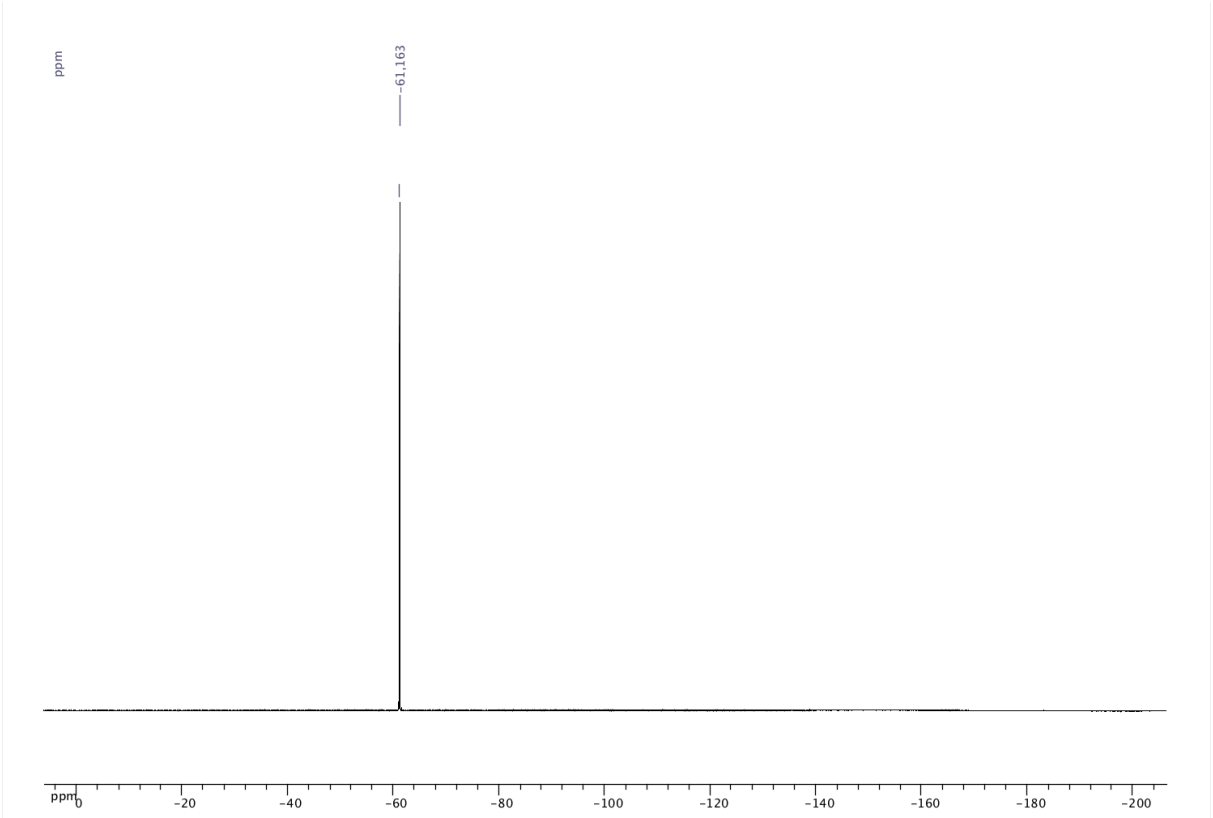
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of 3-(acetoxymethyl)-2-(4-chlorophenyl)-2,1-borazanaphthalene (**9**)



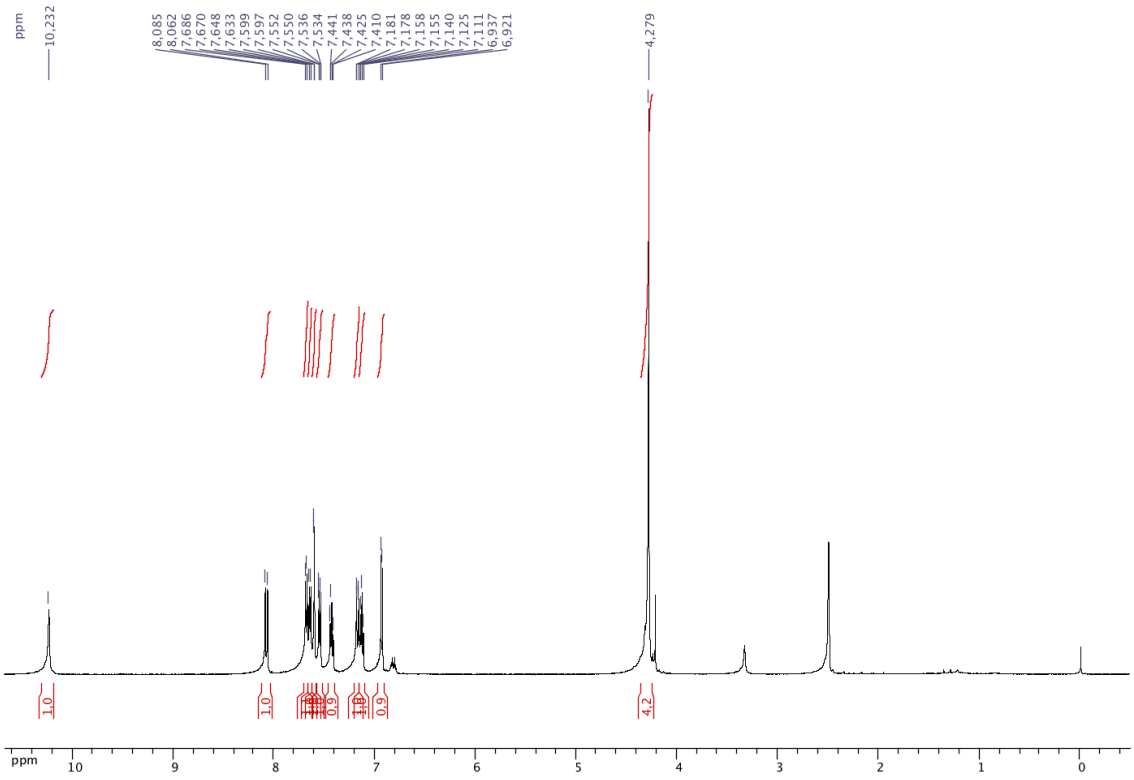
^{1}H NMR (DMSO-d_6, 500.4 MHz) of 2-(4-(trifluoromethyl)phenyl)-2,1-borazanaphthalene (**10a**)



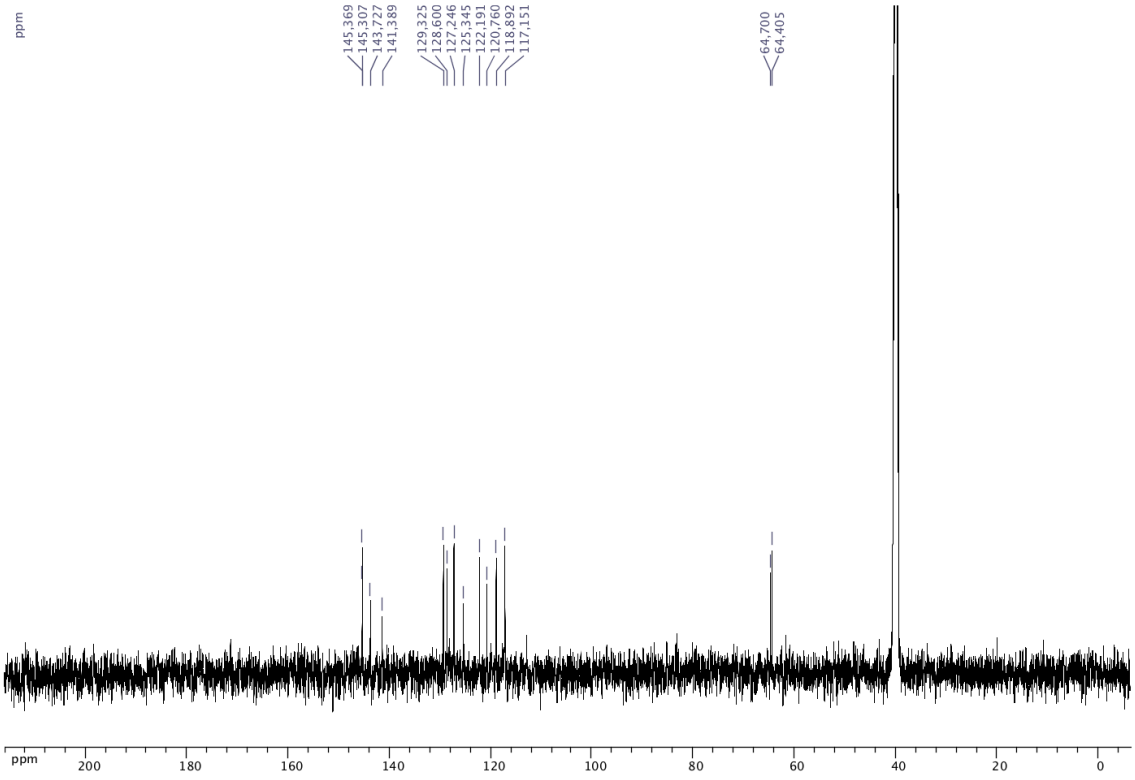
^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz) of 2-(4-(trifluoromethyl)phenyl)-2,1-borazanaphthalene (**10a**)



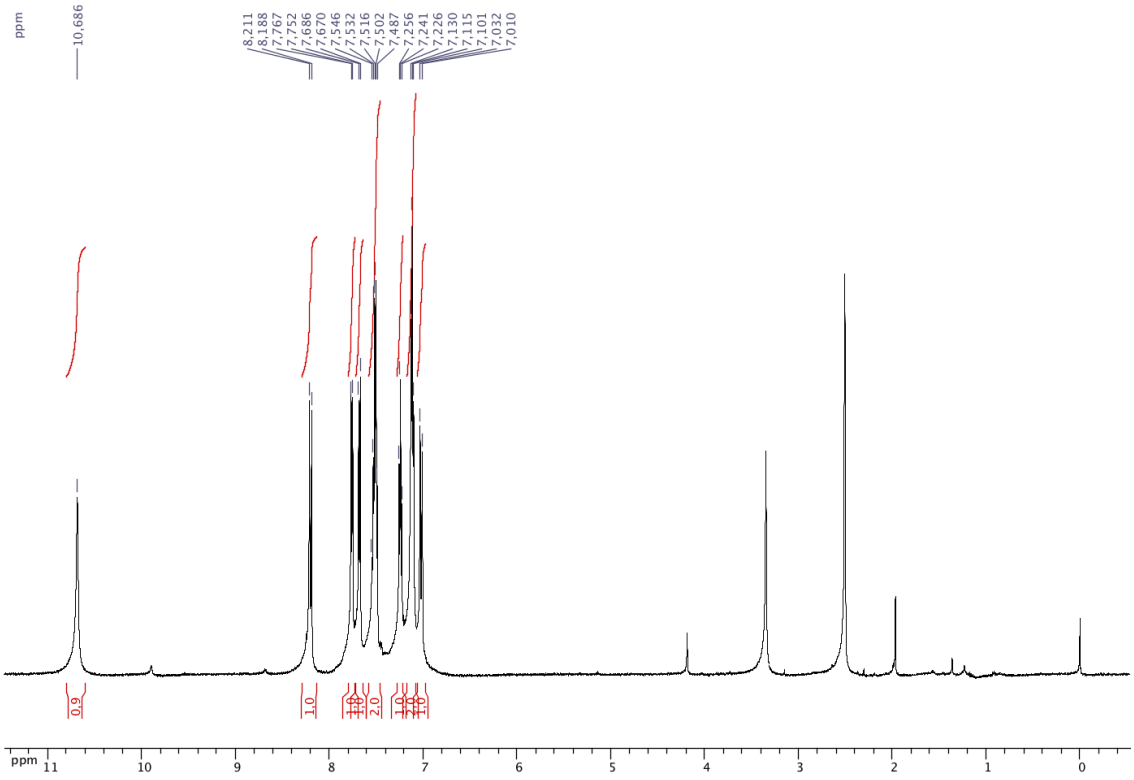
^{19}F {^{1}H} NMR (DMSO-d_6, 470.8 MHz) of of 2-(4-(trifluoromethyl)phenyl)-2,1-borazanaphthalene (**10a**)



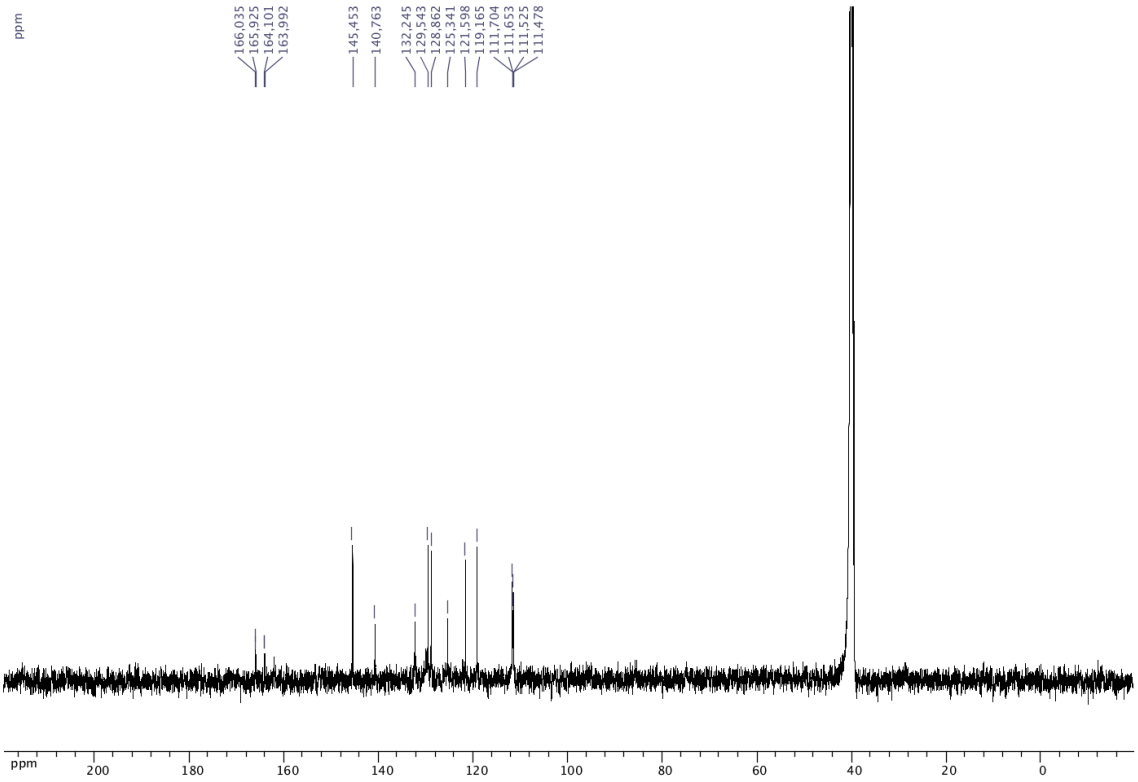
^{1}H NMR (DMSO-d_6, 500.4 MHz) of 2-(2,3-dihydro-1,4-benzodioxin-6-yl)-2,1-borazanaphthalene (**10b**)



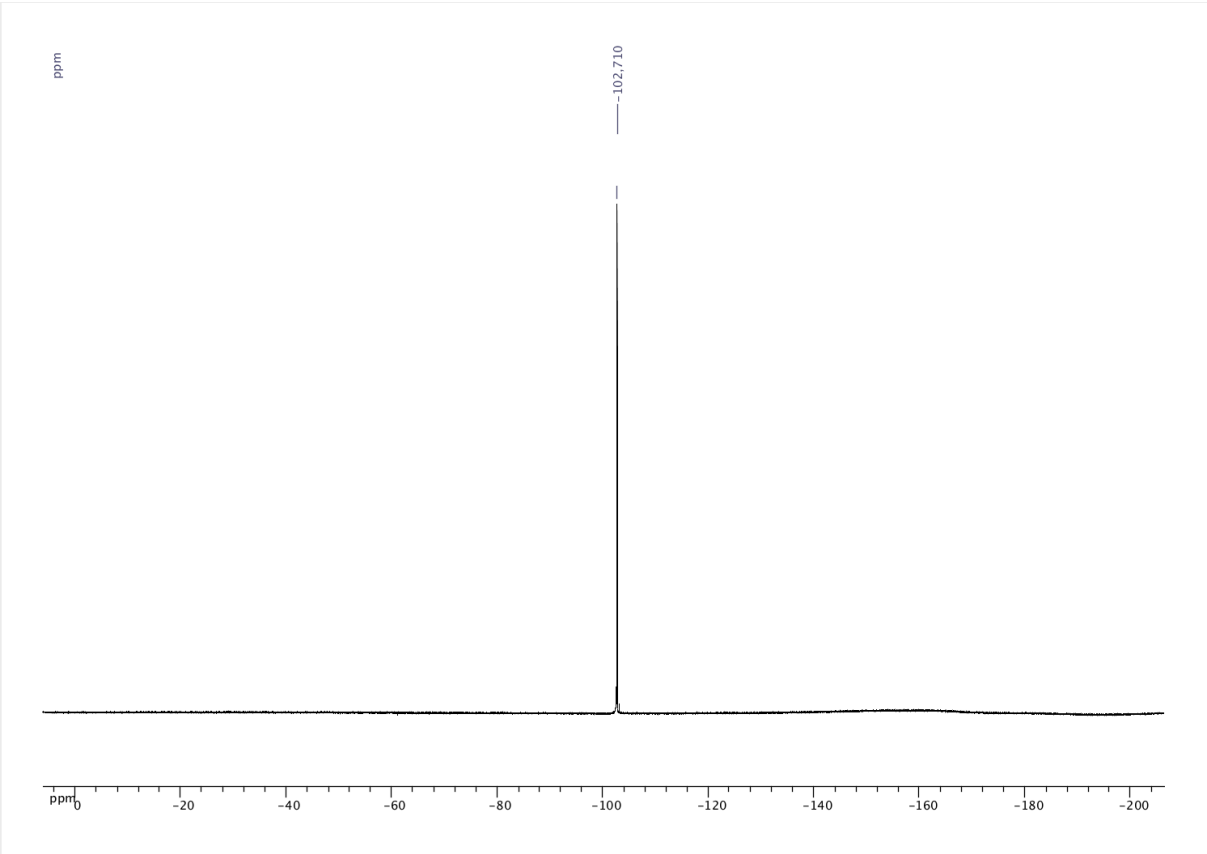
^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz) of 2-(2,3-dihydro-1,4-benzodioxin-6-yl)-2,1-borazanaphthalene (**10b**)



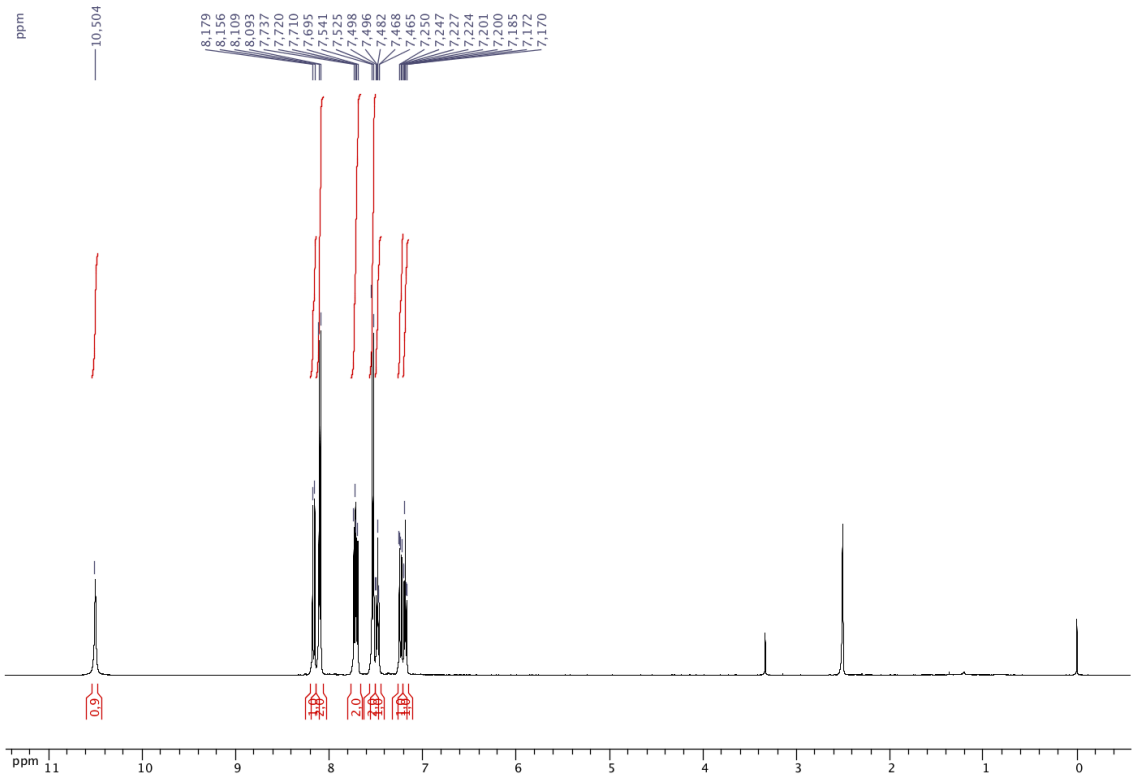
^{1}H NMR (DMSO-d_6, 500.4 MHz) of 2-(2,6-difluorophenyl)-2,1-borazanaphthalene (**10c**)



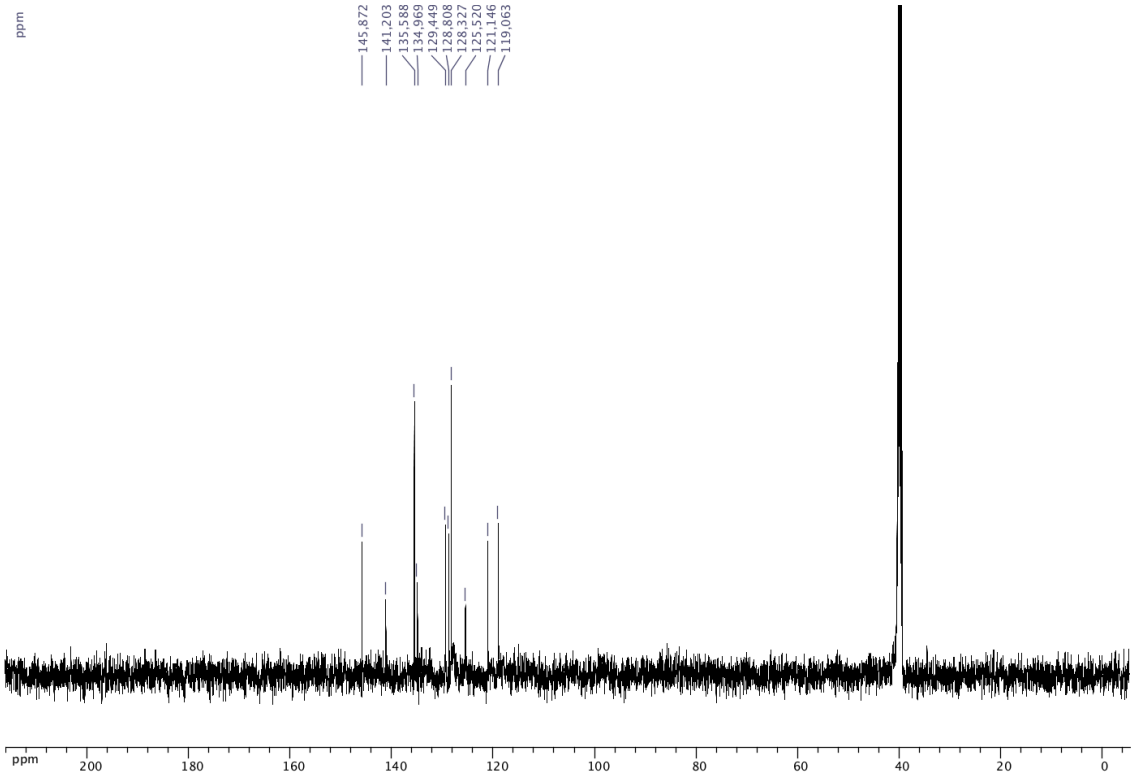
^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz) of 2-(2,6-difluorophenyl)-2,1-borazanaphthalene (**10c**)



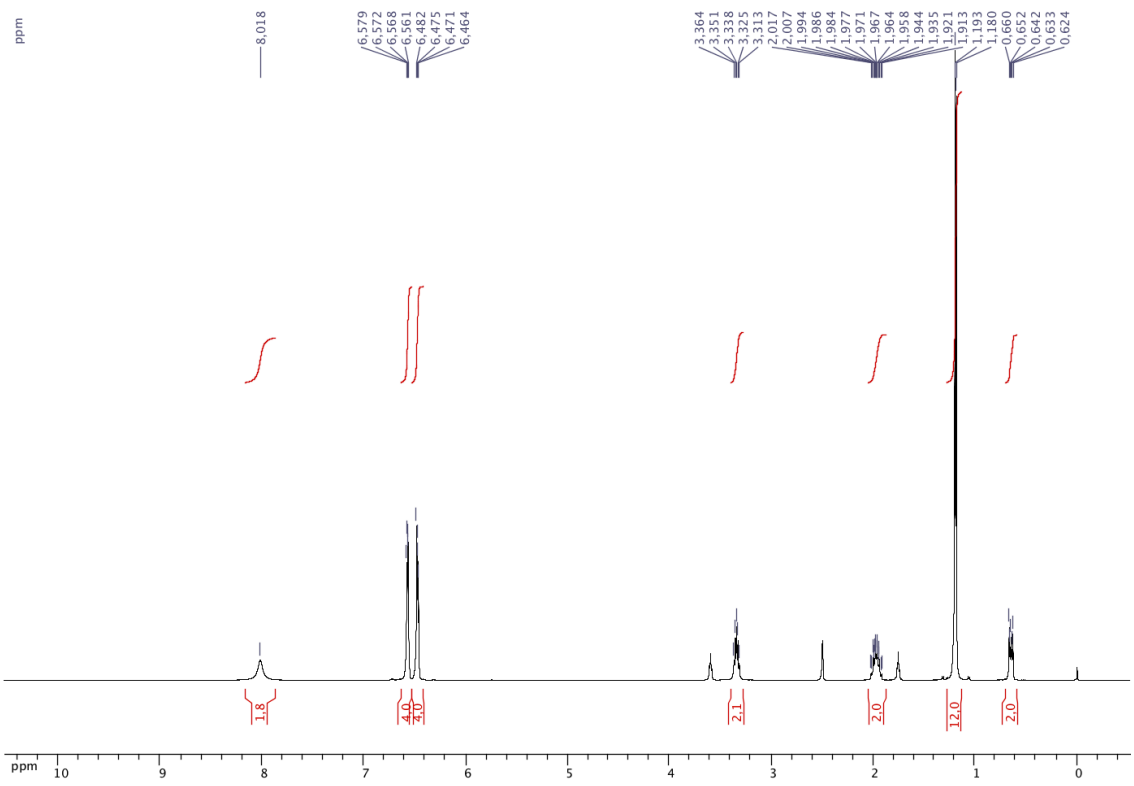
^{19}F $\{^{1}H\}$ NMR (DMSO-d_6, 470.8 MHz) of 2-(2,6-difluorophenyl)-2,1-borazanaphthalene (**10c**)



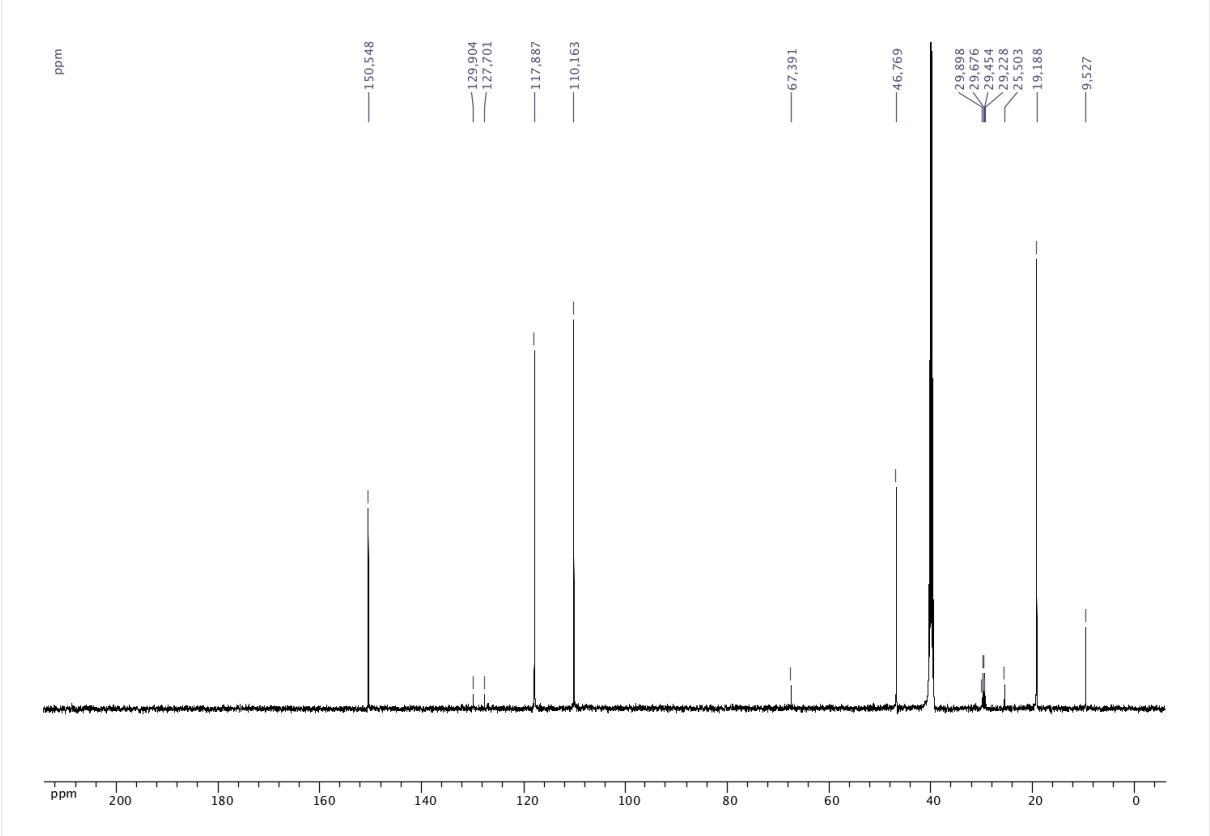
^{1}H NMR (DMSO-d_6, 500.4 MHz) of 2-(4-chlorophenyl)-2,1-borazanaphthalene (**10d**)



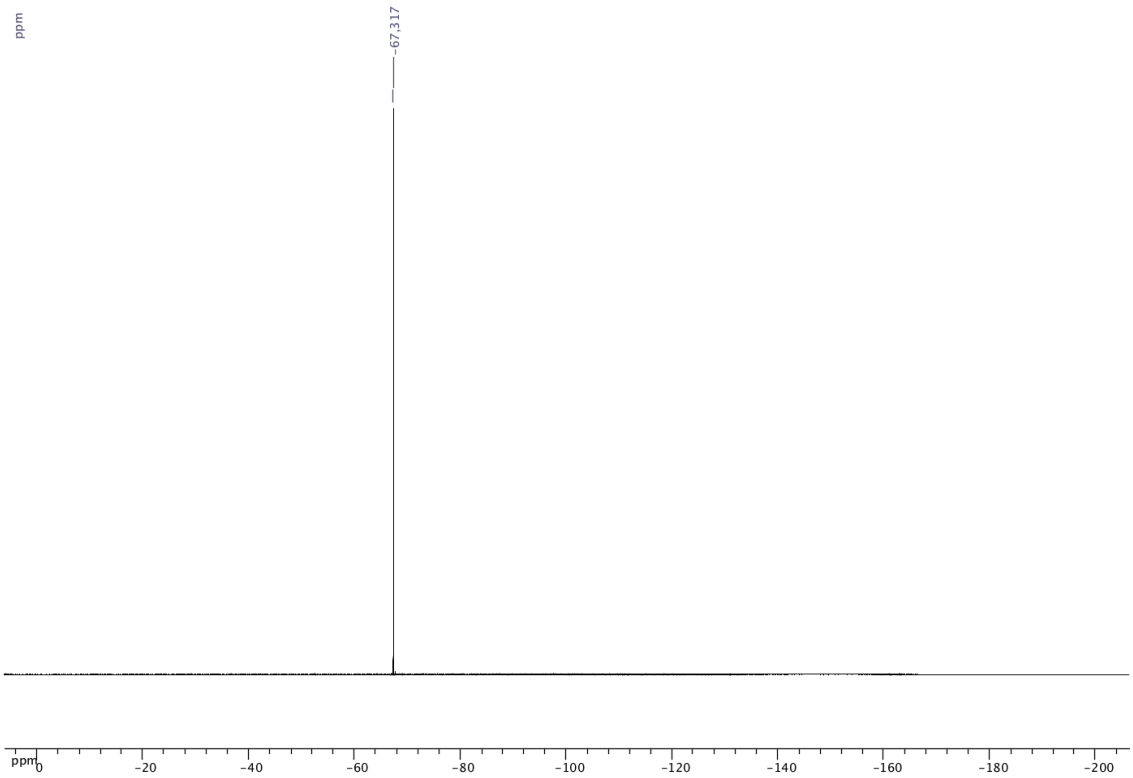
^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz) of 2-(4-chlorophenyl)-2,1-borazanaphthalene (**10d**)



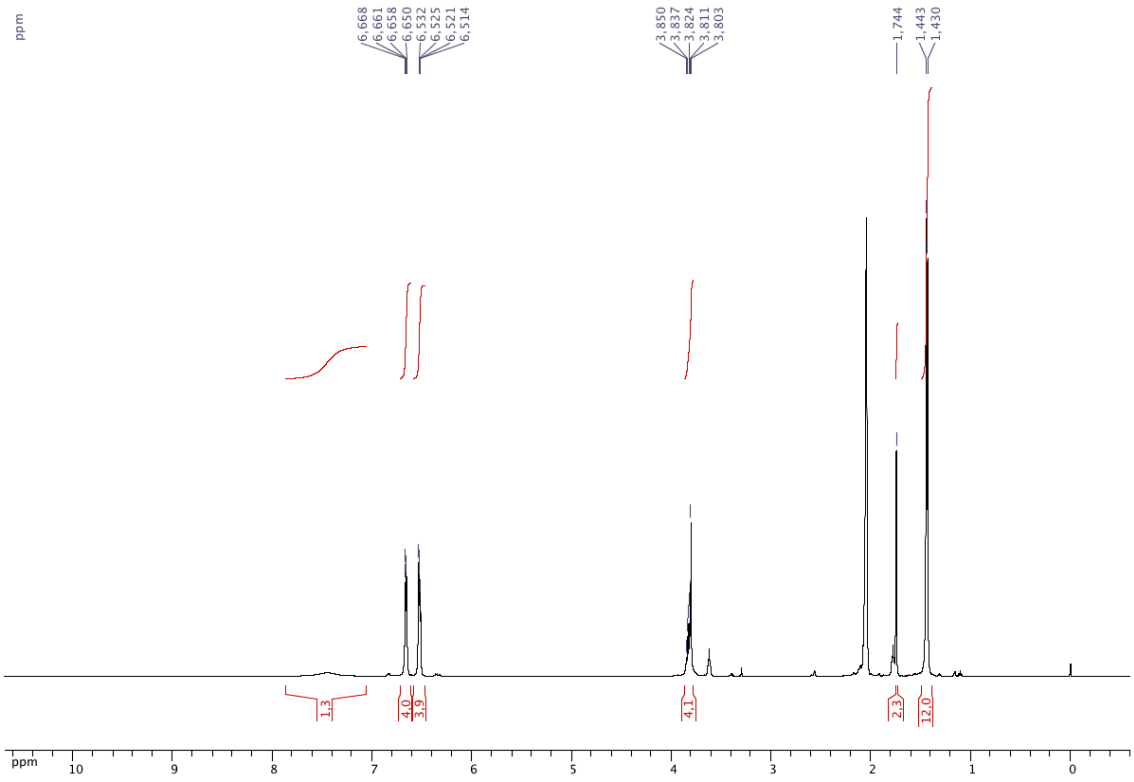
^{1}H NMR (DMSO-d_6, 500.4 MHz) of diisopropylammonium 3,3,3-trifluoropropylbis(catecholato)silicate (**11a**)



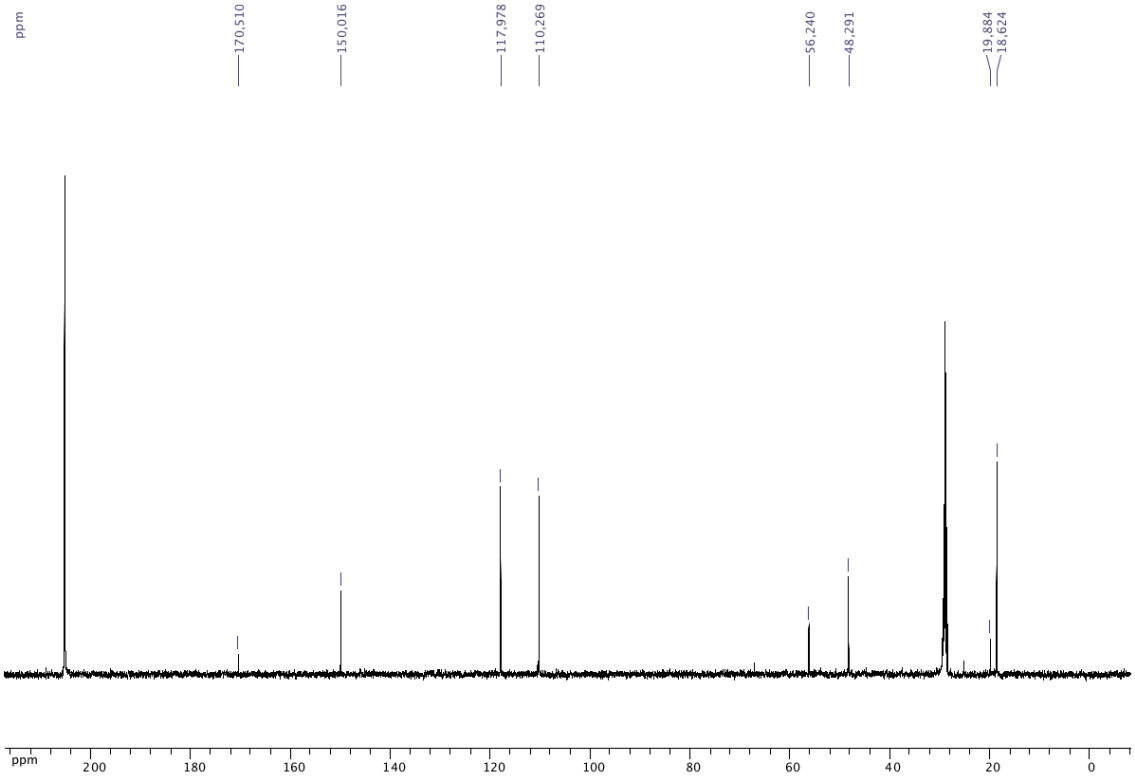
^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz) of diisopropylammonium 3,3,3-trifluoropropylbis(catecholato)silicate (**11a**)



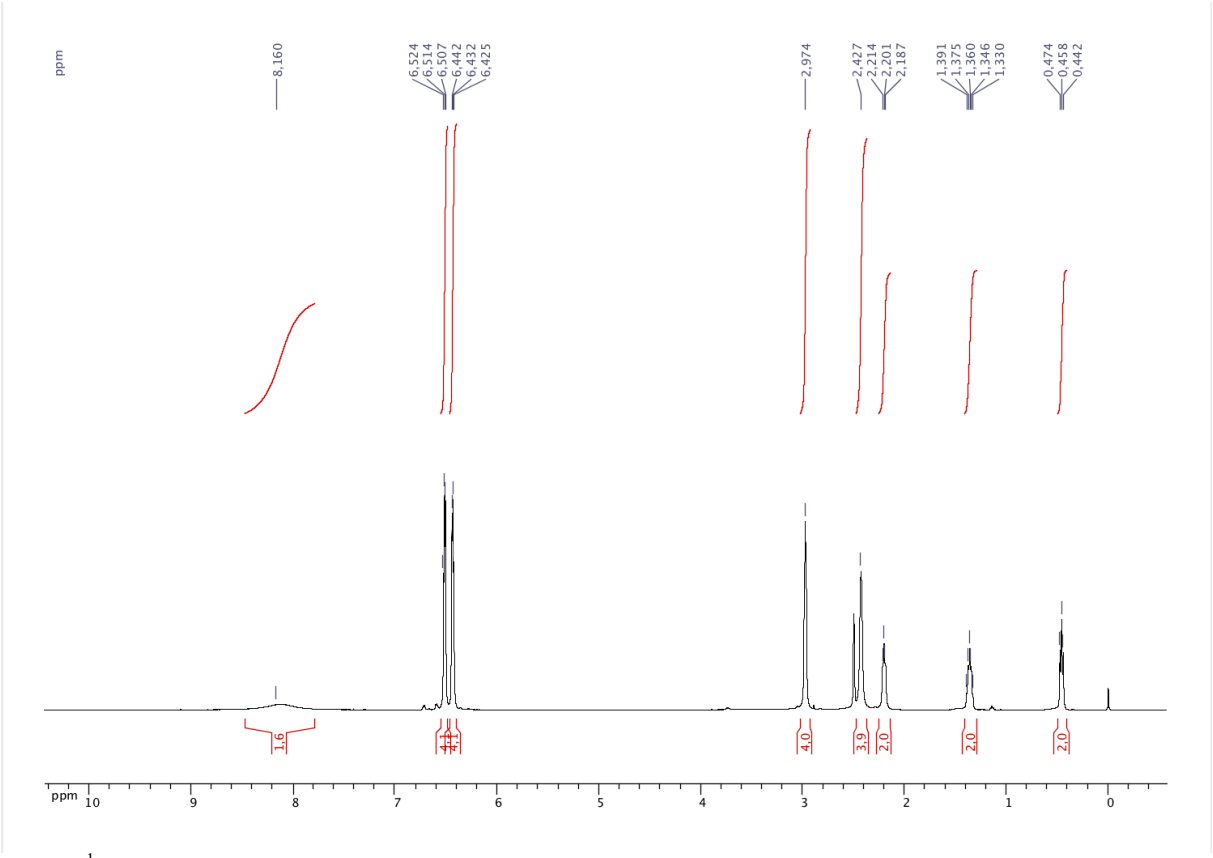
^{19}F {^{1}H} NMR (DMSO-d_6, 470.8 MHz) of diisopropylammonium 3,3,3-trifluoropropylbis(catecholato)silicate (**11a**)



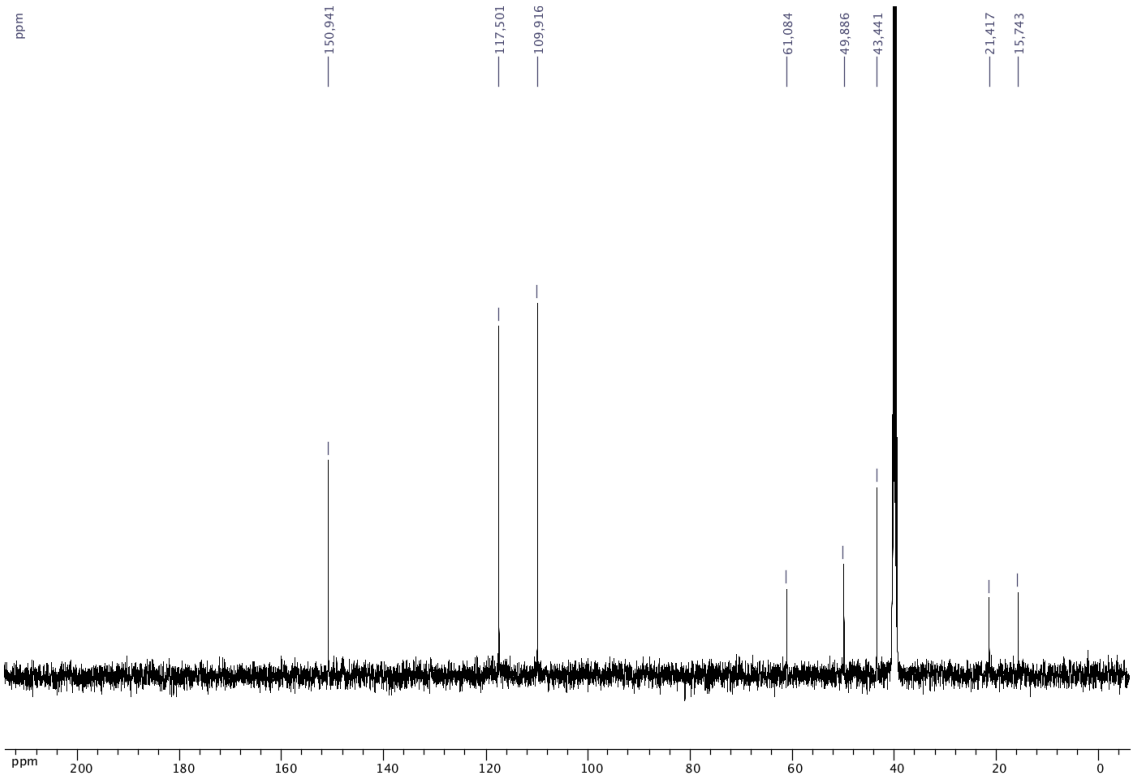
^{1}H NMR (acetone-d_6, 500.4 MHz) of diisopropylammonium acetoxymethylbis(catecholato)silicate (**11b**)



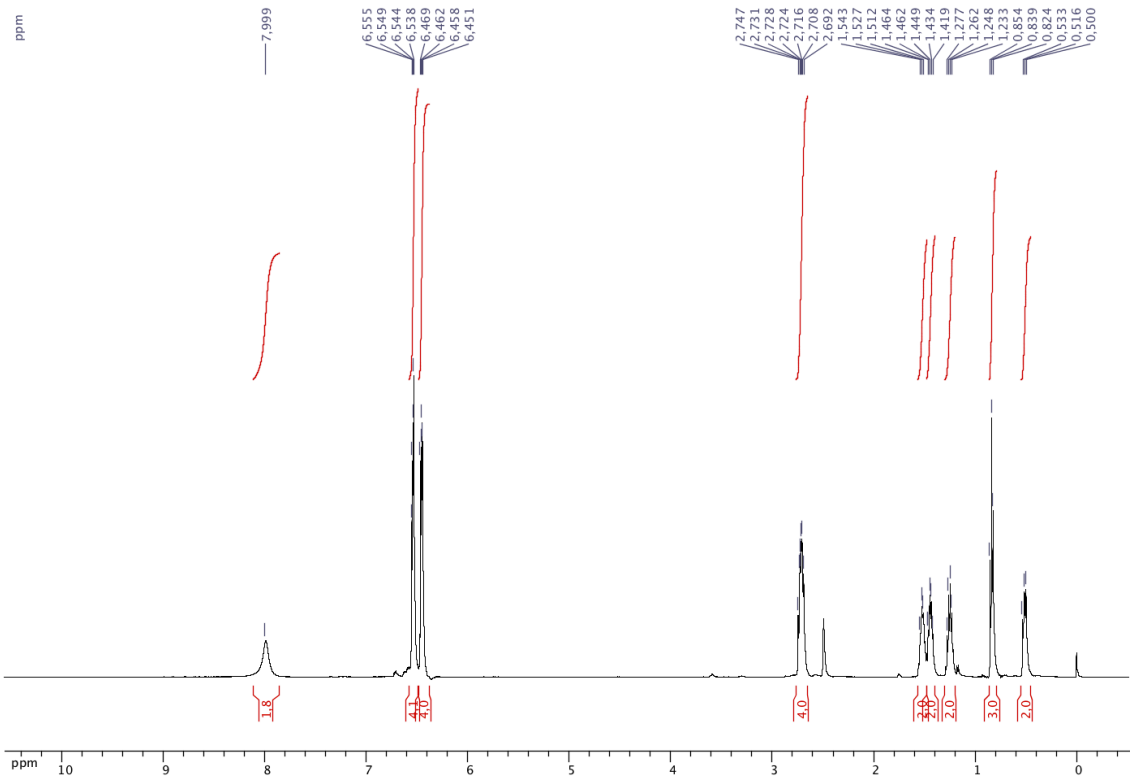
^{13}C {^{1}H} NMR (acetone-d_6, 125.8 MHz) of diisopropylammonium acetoxymethylbis(catecholato)silicate (**11b**)



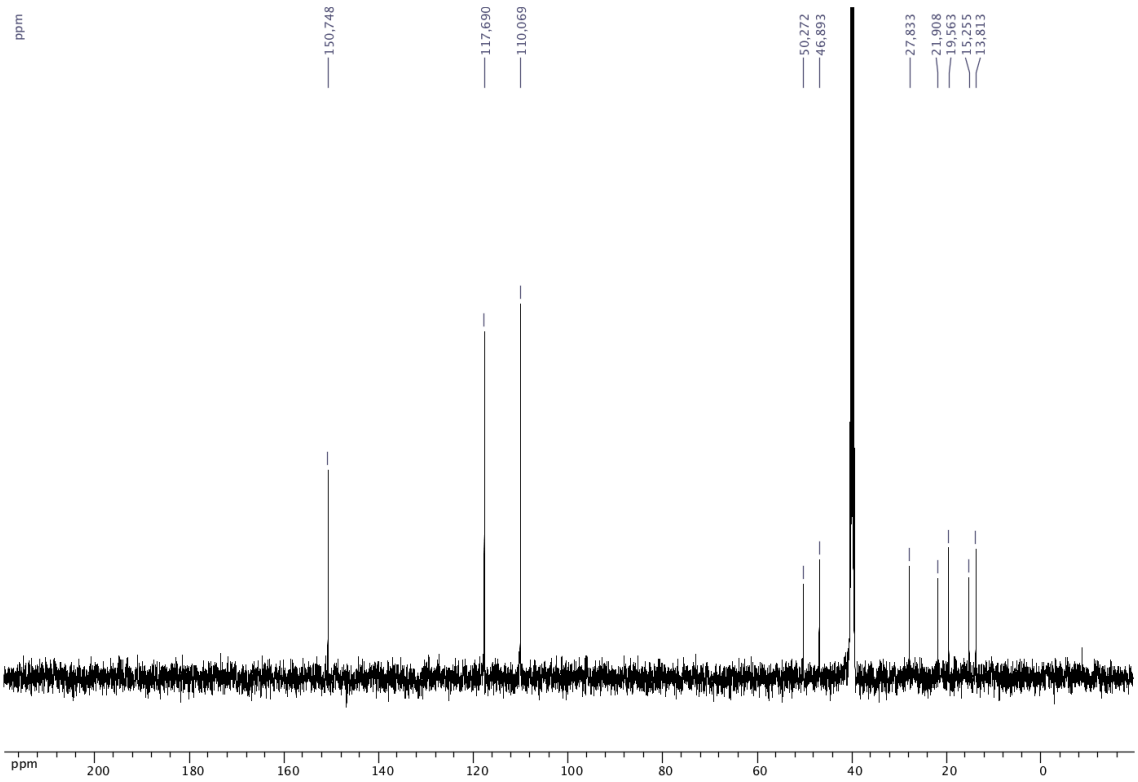
^{1}H NMR (DMSO-d_6, 500.4 MHz) of 3-(piperazin-1-ium-1-yl)propylbis(catecholato)silicate (**11c**)



^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz) of 3-(piperazin-1-ium-1-yl)propylbis(catecholato)silicate (**11c**)



^{1}H NMR (DMSO-d_6, 500.4 MHz) of 3-(butylammonio)propylbis(catecholato)silicate (**11d**)



^{13}C {^{1}H} NMR (DMSO-d_6, 125.8 MHz) of 3-(butylammonio)propylbis(catecholato)silicate (**11d**)