Electronic Supporting Information for:

Conjugated bis and poly(dioxaborole)s for optical sensing of Lewis bases based on main-chain perturbations

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Contents:

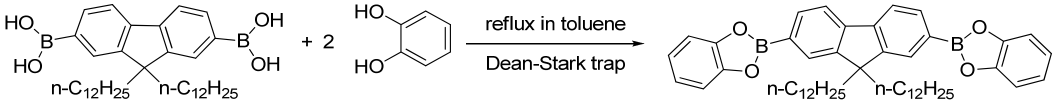
1. Materials

Sodium percarbonate, 9,9-didodecylfluorene-2,7-diboronic acid and 4-nitrocatechol were purchased from Sigma-Aldrich. Catechol, 2-hydroxy-4-methoxybenzaldehyde, tin and 2,5-dihydroxy-1,4-benzoquinone were purchased from Acros. Pinacol was purchased from Alfa Aesar. Acetic acid, ethyl ether, hydrochloric acid, sodium bicarbonate, sodium chloride, and magnisium sulfate, were purchased from Fisher Scientific. All chemicals were used without further purification. Toluene, tetrahydrofuran, dichloromethane and acetonitrile were obtained using purification systems from Innovative Technologies. 1,2,4,5-Tetrahydroxybenzene (THB),[1] 4-methoxycatechol[2] and polymer **3**[3] were obtained according to the literature procedure. Elemental analysis are notoriously poor for evaluating purity and exact mass of boronic acid containing compounds. Therefore, ^{1}H NMR analysis was used to assess purity of the boronate linked materials and spectra are included as evidence of purity.[4]

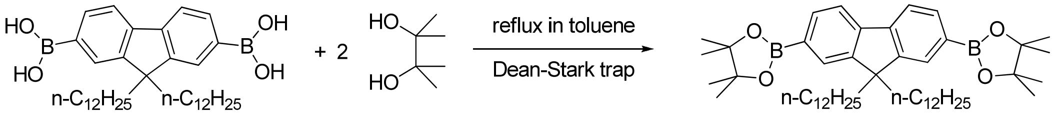
2. Instrumentation

FT-IR spectra were collected on a PerkinElmer Spectrum 100 FT-IR Spectrometer using a diamond/ZnSe crystal (~0.5 mg). The spectrometer scanned 4 times with a resolution of 4.00 cm^{-1} from 4000 cm^{-1} to 650 cm^{-1}. ^{1}H NMR and ^{13}C NMR spectra were collected on a Varian Mercury/VX 300 MHz Spectrometer. Mass spectra were obtained using a VG 70S Mass Spectrometer with the sample being introduced by direct exposure probe. UV-Vis absorbance data were recorded on a Beckman Coulter 640 DU Spectrophotometer.

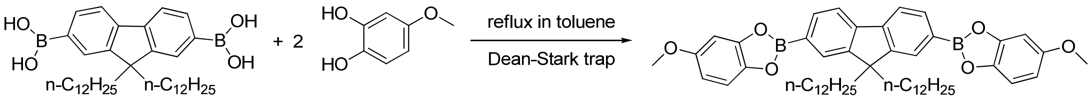
3. Synthesis and Characterization



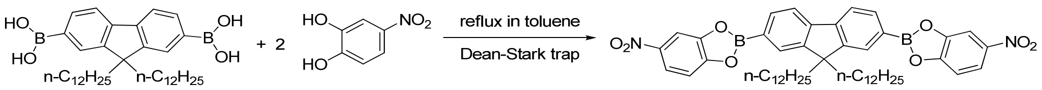
Synthesis of bis(dioxaborole) 1. Glassware was first dried in oven overnight. The starting materials were the mixture of 9,9-didodecylfluorene-2,7-diboronic acid (0.2960 g, 0.5013 mmol) and catechol (0.1238 g, 1.124 mmol). In a round-bottom flask with a Dean-Stark trap, starting materials as well as 50 mL of dry, degassed toluene were added. The solution was kept at reflux overnight under a nitrogen atmosphere. The resultant clear solution was cooled to room temperature. Then toluene was removed by rotary evaporation and the crude product was further purified by Kugelrohr distillation. The product was a white solid (0.3784 g, quantitative). Mp 48.6-51.5 °C. Solid IR: 2917, 2850, 1609, 1577, 1469, 1424, 1367, 1327, 1288, 1270, 1232, 1149, 1131, 1112, 1066, 1004, 911, 867, 827, 812, 738, 718, 695. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.09 (m, 4H), 7.90 (d, J = 6.6 Hz, 2H), 7.34 (m, 4H), 7.16 (m, 4H), 2.15-2.05 (m, 4H), 1.14-1.02 (br m, 36H), 0.83 (t, J = 6.9 Hz, 6H), 0.66-0.54 (br m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 151.3, 148.8, 144.9, 134.2, 129.5, 123.0, 120.5, 112.7, 55.6, 40.5, 32.1, 30.2, 29.8, 29.8, 29.5, 29.5, 24.0, 22.9, 14.3. MS calcd for $C_{49}H_{64}B_2O_4$: m/z = 738.5007; found: m/z = 738.5011 (E = 0.5 ppm).



Synthesis of bis(dioxaborole) 2. The starting materials, a mixture of 9,9-didodecylfluorene-2,7-diboronic acid (0.2949 g, 0.4994 mmol) and pinacol (0.1313 g, 1.111 mmol), along with 40 mL of dry, degassed toluene were placed in a round-bottom flask fitted with a Dean-Stark trap. The solution was kept at reflux overnight under a nitrogen atmosphere. The resultant clear solution was cooled to room temperature and the toluene was removed by rotary evaporation. The crude product was further purified using Kugelrohr distillation to remove unreacted starting catechol. The product was dried under vacuum to give a white solid (0.3769 g, quantitative). Mp 68.2-72.7 °C. Solid FT-IR: 2922, 2851, 1609, 1576, 1469, 1424, 1346, 1308, 1269, 1142, 1117, 1079, 1004, 964, 908, 855, 825, 760, 740, 722, 708, 697, 672. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.81-7.70 (m, 6H), 2.02-1.96 (m, 4H), 1.39 (s, 24H), 1.27-1.00 (br m, 36H), 0.86 (t, J = 6.9 Hz, 6H), 0.54 (br, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 150.7, 144.1, 133.9, 129.1, 119.6, 83.9, 55.4, 40.3, 32.1, 30.2, 29.8, 29.6, 29.5, 29.2, 23.9, 22.9, 14.3. MS calcd for $C_{49}H_{80}B_2O_4$: m/z = 754.6259; found: m/z = 754.6242 (E = 2.3 ppm).

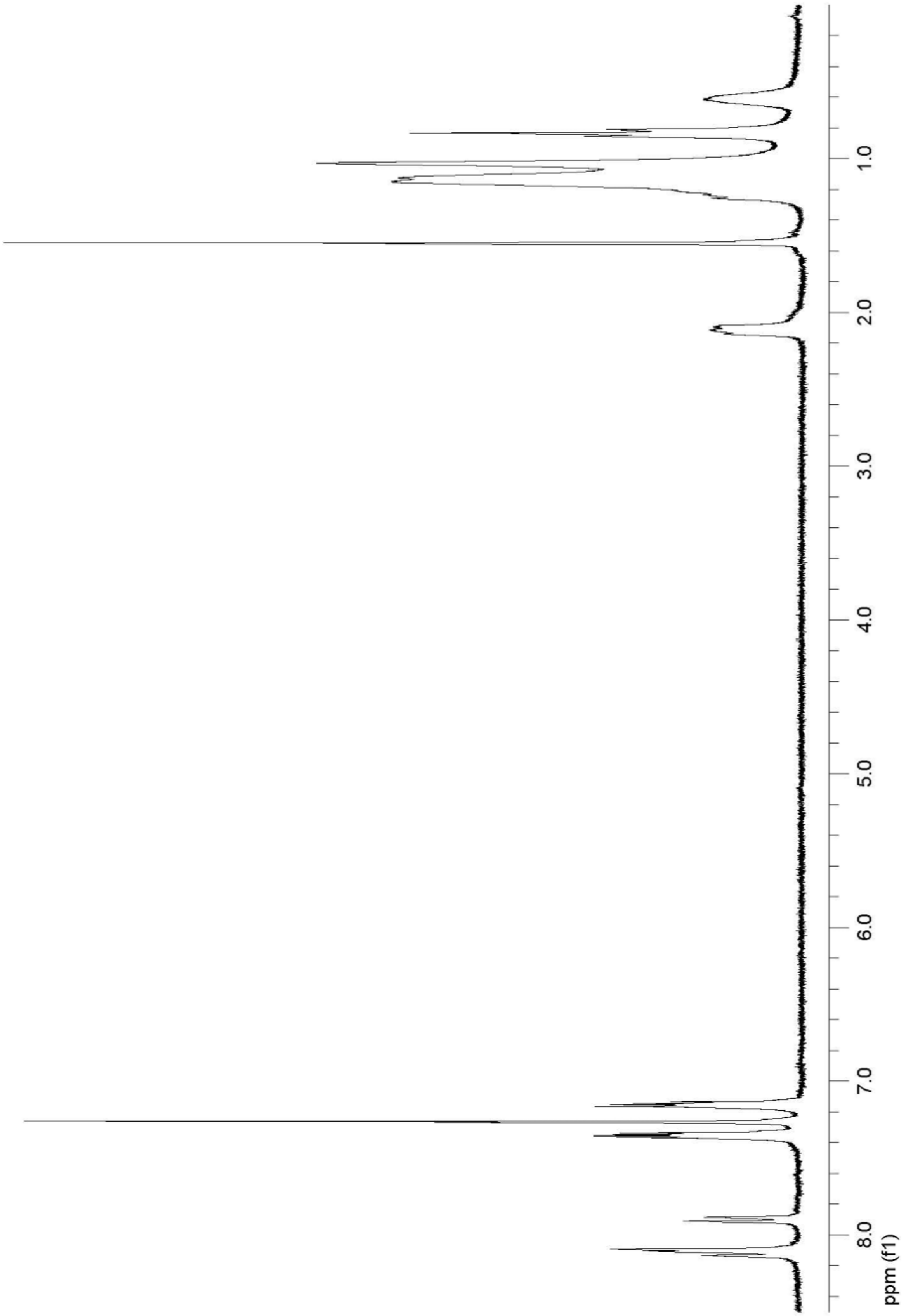


Synthesis of bis(dioxaborole) 4. 4-Methoxycatechol was used as described above. The starting materials, a mixture of 9,9-didodecylfluorene-2,7-diboronic acid (0.2948 g, 0.4992 mmol) and 4-methoxycatechol (0.1551 g, 1.107 mmol), along with 40 mL of dry, degassed toluene were placed in a round-bottom flask fitted with a Dean-Stark trap. The solution was kept at reflux overnight under a nitrogen atmosphere. The resultant clear solution was cooled to room temperature and the toluene was removed by rotary evaporation. The crude product was further purified by Kugelrohr distillation to remove unreacted starting catechol. The product was a yellow solid (0.4153 g, quantitative). Solid IR: 2923, 2852, 1609, 1577, 1490, 1422, 1353, 1335, 1319, 1269, 1253, 1230, 1191, 1157, 1133, 1086, 1064, 1027, 938, 824, 791, 741, 693. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11-8.06 (m, 4H), 7.89 (d, J = 7.5 Hz, 2H), 7.20 (d, J = 8.7 Hz, 2H), 6.96 (d, J = 2.4 Hz, 2H), 6.68 (dd, J = 8.4, 2.7 Hz, 2H), 3.84 (s, 6H), 2.12-2.07 (m, 4H), 1.25-1.02 (br m, 36H), 0.83 (t, J = 6.9 Hz, 6H), 0.70-0.50 (br m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 156.2, 151.3, 149.4, 144.8, 142.9, 134.1, 129.4, 120.5, 112.2, 107.9, 99.9, 56.3, 55.5, 40.5, 32.1, 30.2, 29.8, 29.8, 29.5, 29.5, 24.0, 22.9, 14.3. MS calcd for $C_{51}H_{68}B_2O_6$: m/z = 798.5218; found: m/z = 798.5248 (E = 3.8 ppm)

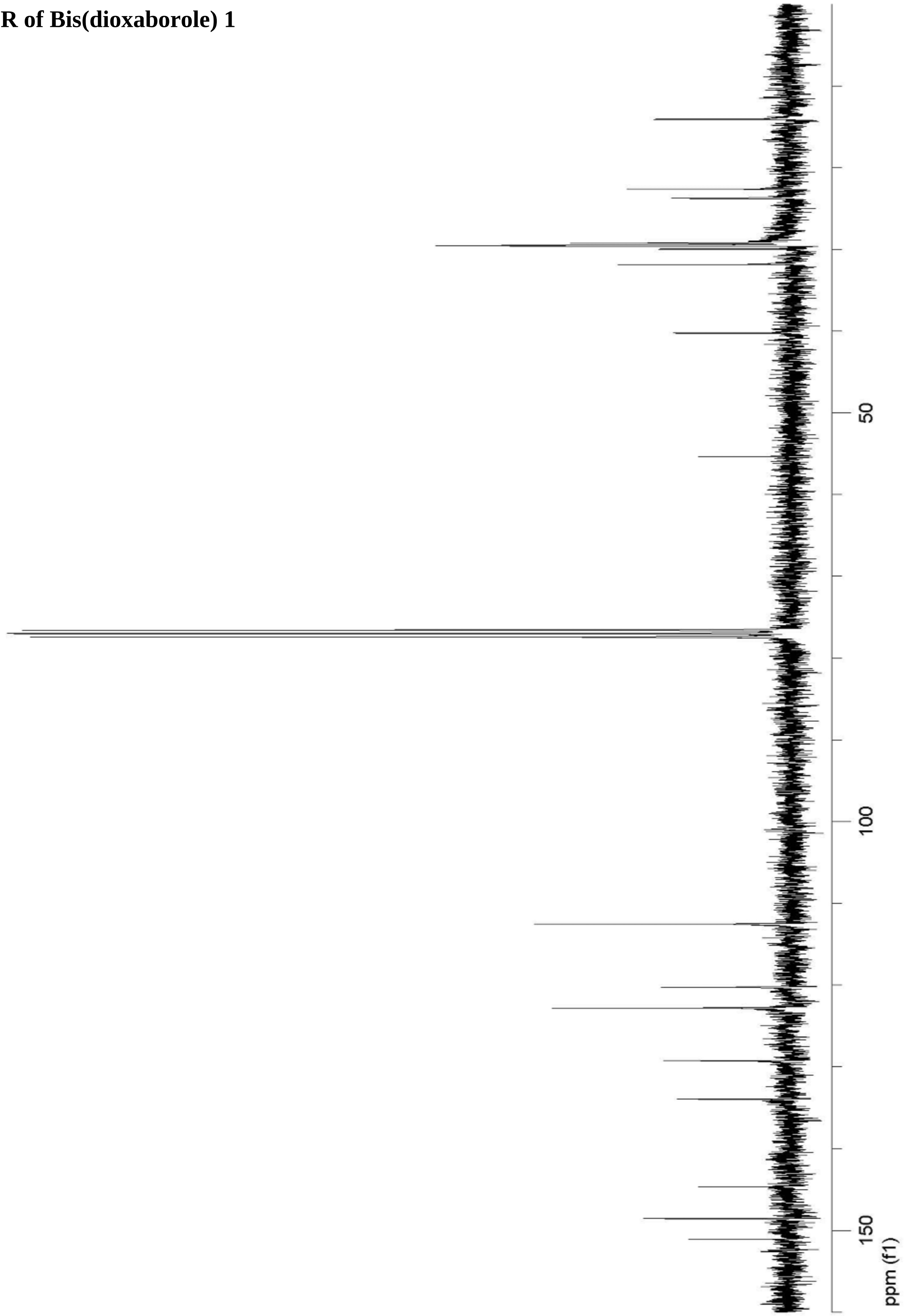


Synthesis of bis(dioxaborole) 5. The starting materials, a mixture of 9,9-didodecylfluorene-2,7-diboronic acid (0.2959 g, 0.5011 mmol) and 4-nitrocatechol (0.1680 g, 1.083 mmol), along with 40 mL of dry, degassed toluene were placed in a round-bottom flask fitted with a Dean-Stark trap. The solution was kept at reflux overnight under a nitrogen atmosphere. The resultant clear solution was cooled to room temperature and the toluene was removed by rotary evaporation. The crude product was further purified by Kugelrohr distillation to remove unreacted starting catechol. The product was a yellow solid (0.4152 g, yield 93.69%). Mp 107.5-115.0 °C. Solid IR: 2922, 2852, 1609, 1576, 1524, 1470, 1422, 1378, 1330, 1256, 1231, 1131, 1117, 1066, 1053, 1004, 934, 876, 818, 747, 730, 686. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.24-8.11 (m, 8H), 7.95 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H), 2.16-2.10 (m, 4H), 1.25-1.03 (br m, 36H), 0.83 (t, J = 6.9 Hz, 6H), 0.66-0.54 (br m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$, δ): 153.9, 151.6, 148.8, 145.4, 144.0, 134.6, 129.8, 120.9, 120.3, 112.3, 109.0, 55.7, 40.4, 32.1, 30.1, 29.8, 30.0, 29.7, 29.5, 29.4, 24.0, 22.9, 14.3. MS calcd for $C_{49}H_{62}B_2N_2O_8$: m/z = 828.4708; found: m/z = 828.4676)E = 3.9 ppm).

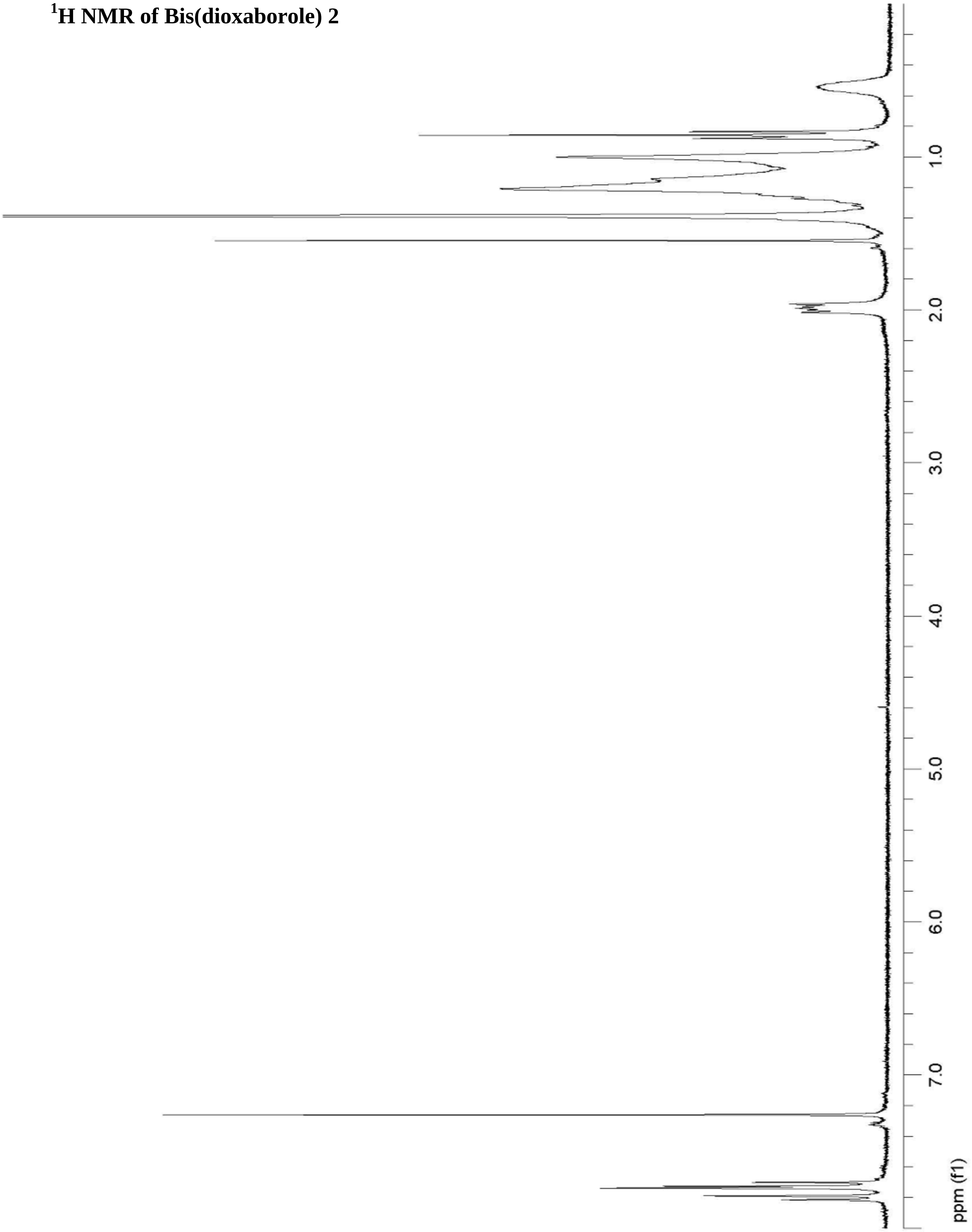
^{1}H NMR of Bis(dioxaborole) 1



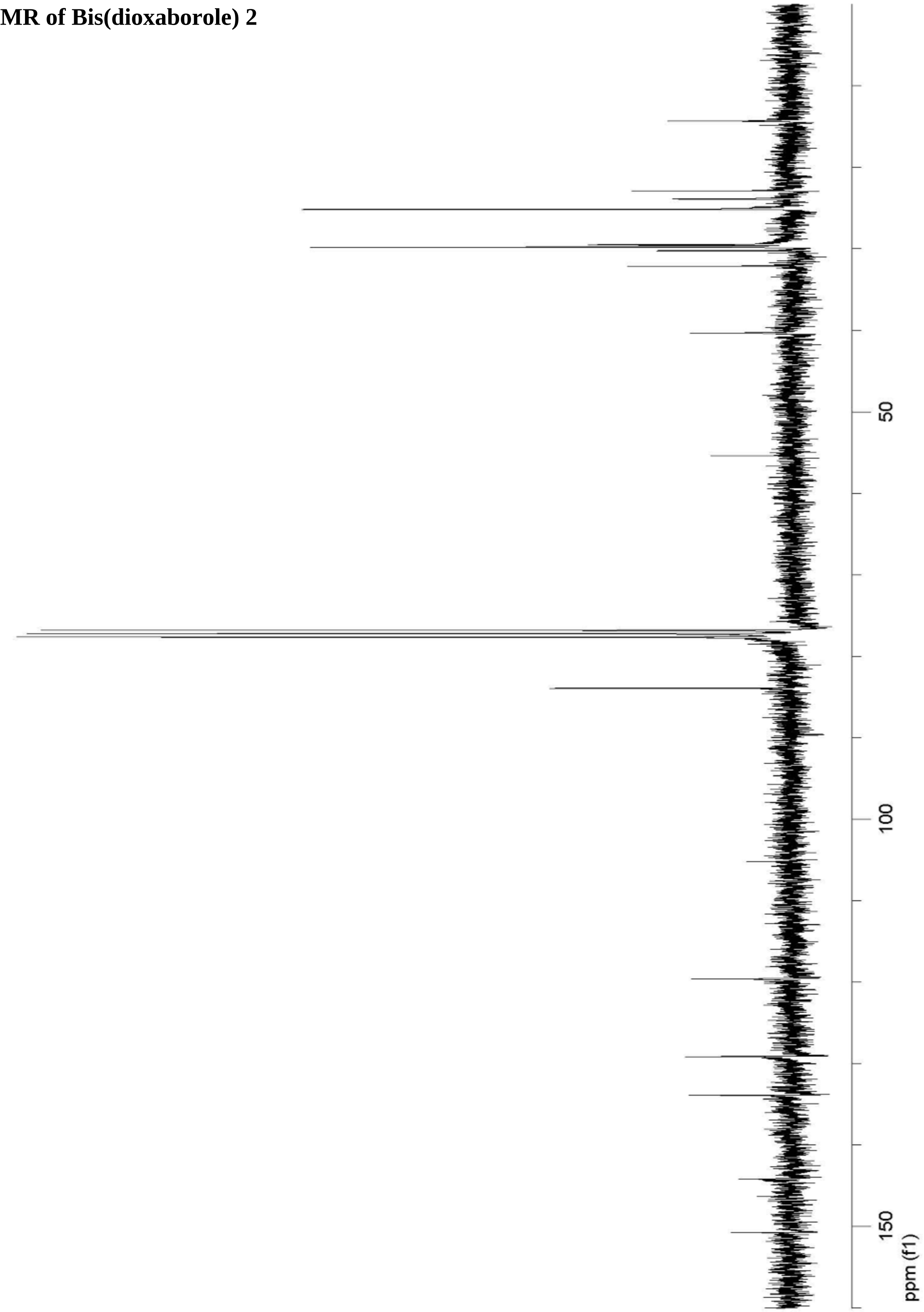
^{13}C NMR of Bis(dioxaborole) 1



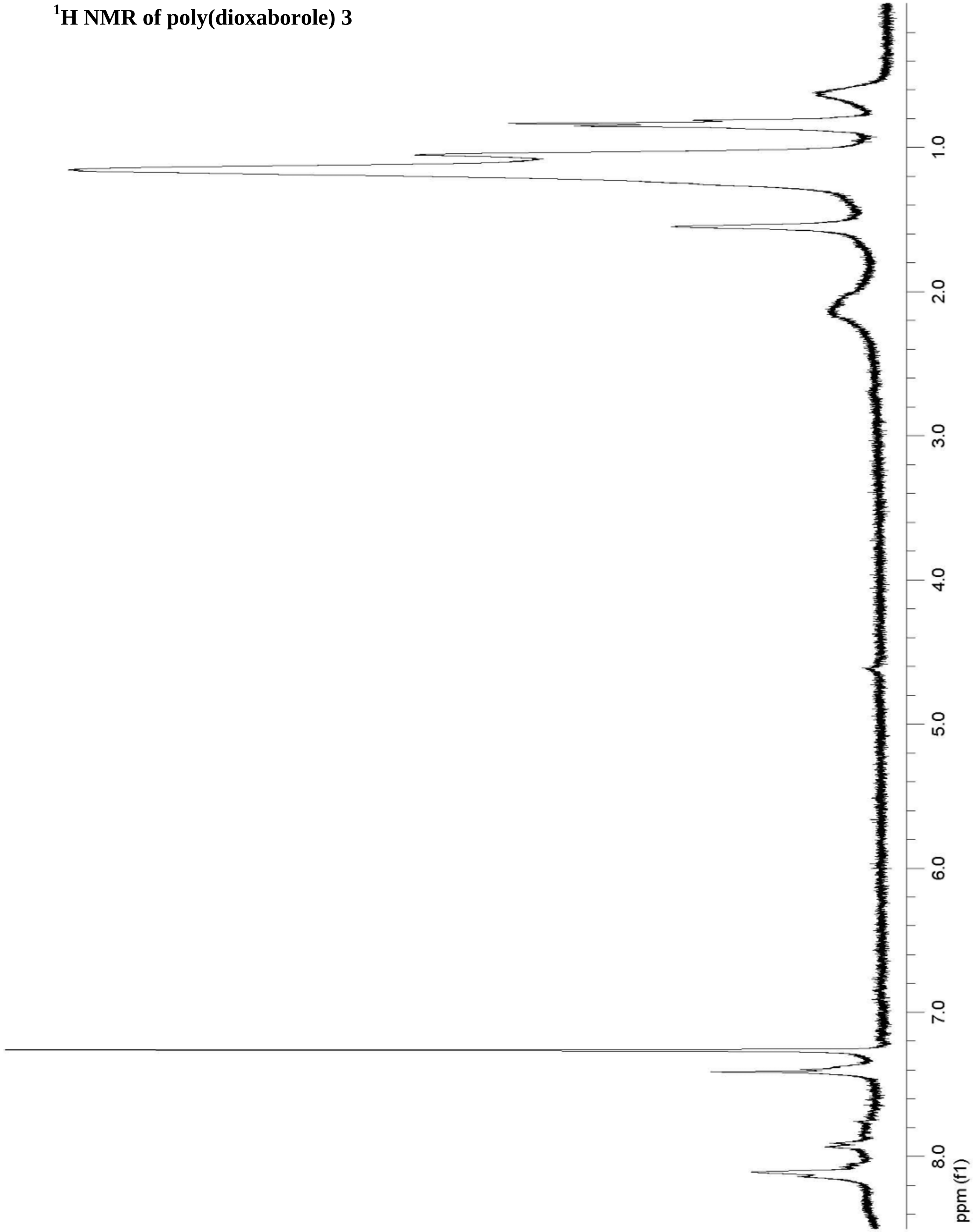
^{1}H NMR of Bis(dioxaborole) 2



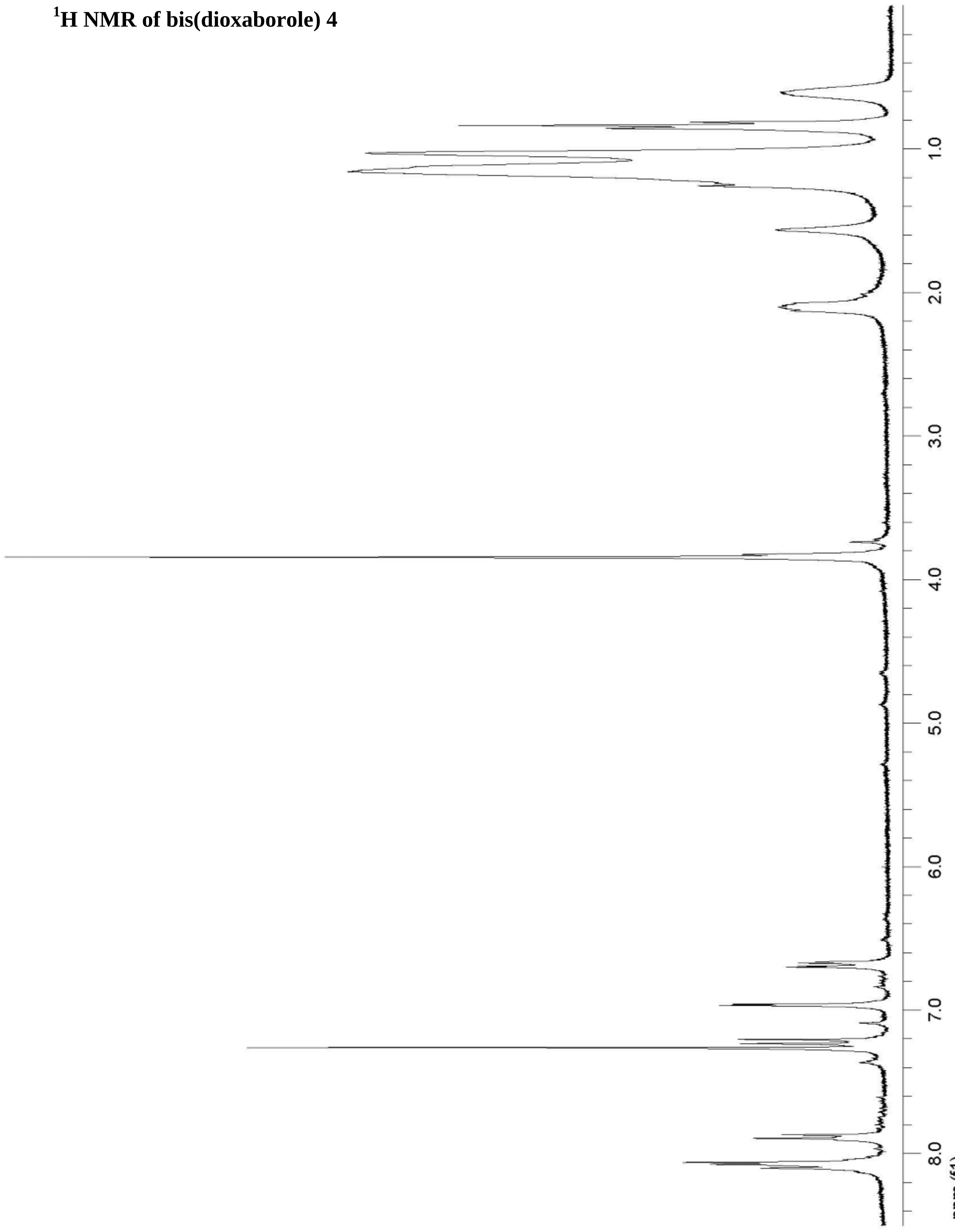
^{13}C NMR of Bis(dioxaborole) 2



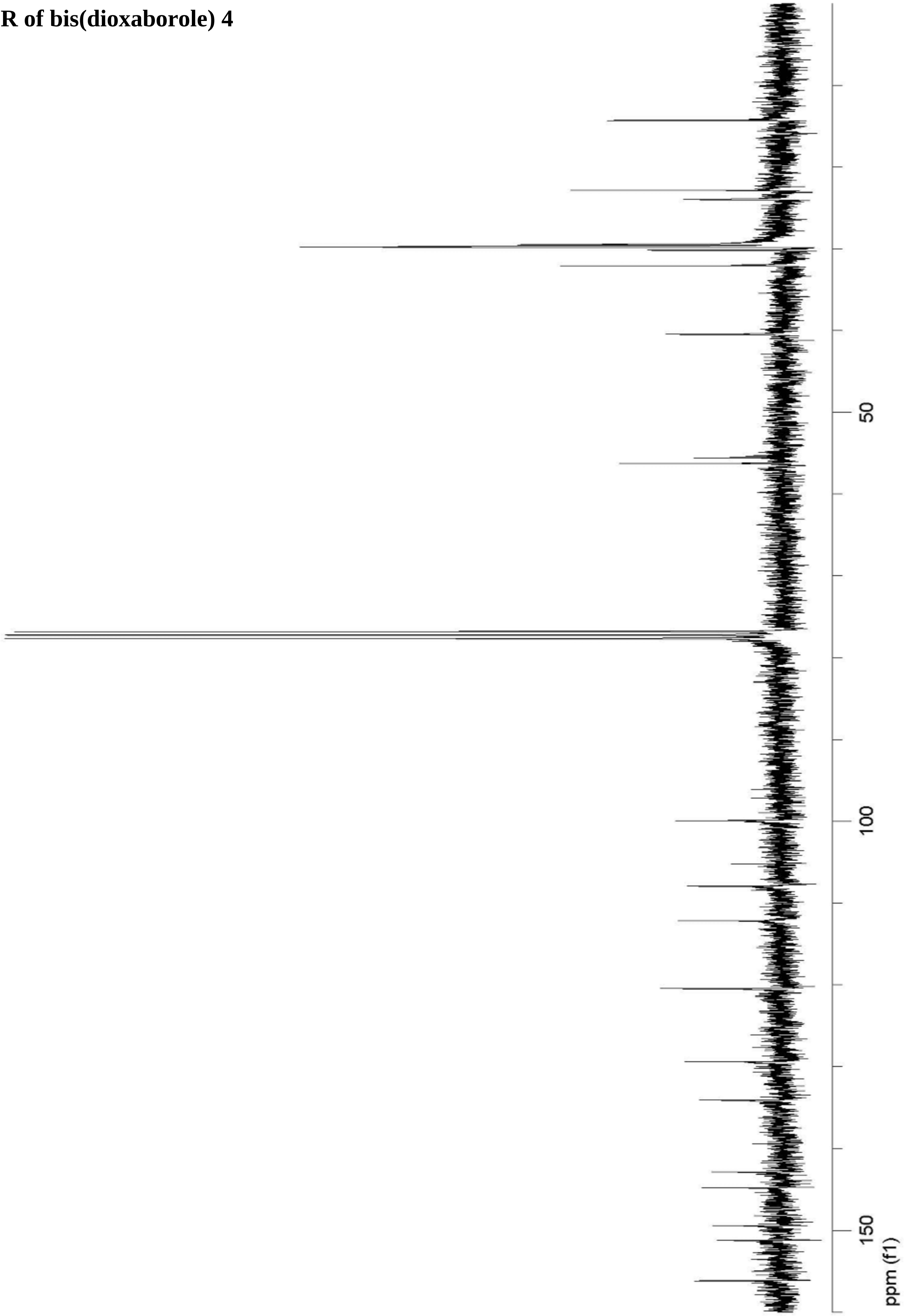
^{1}H NMR of poly(dioxaborole) 3



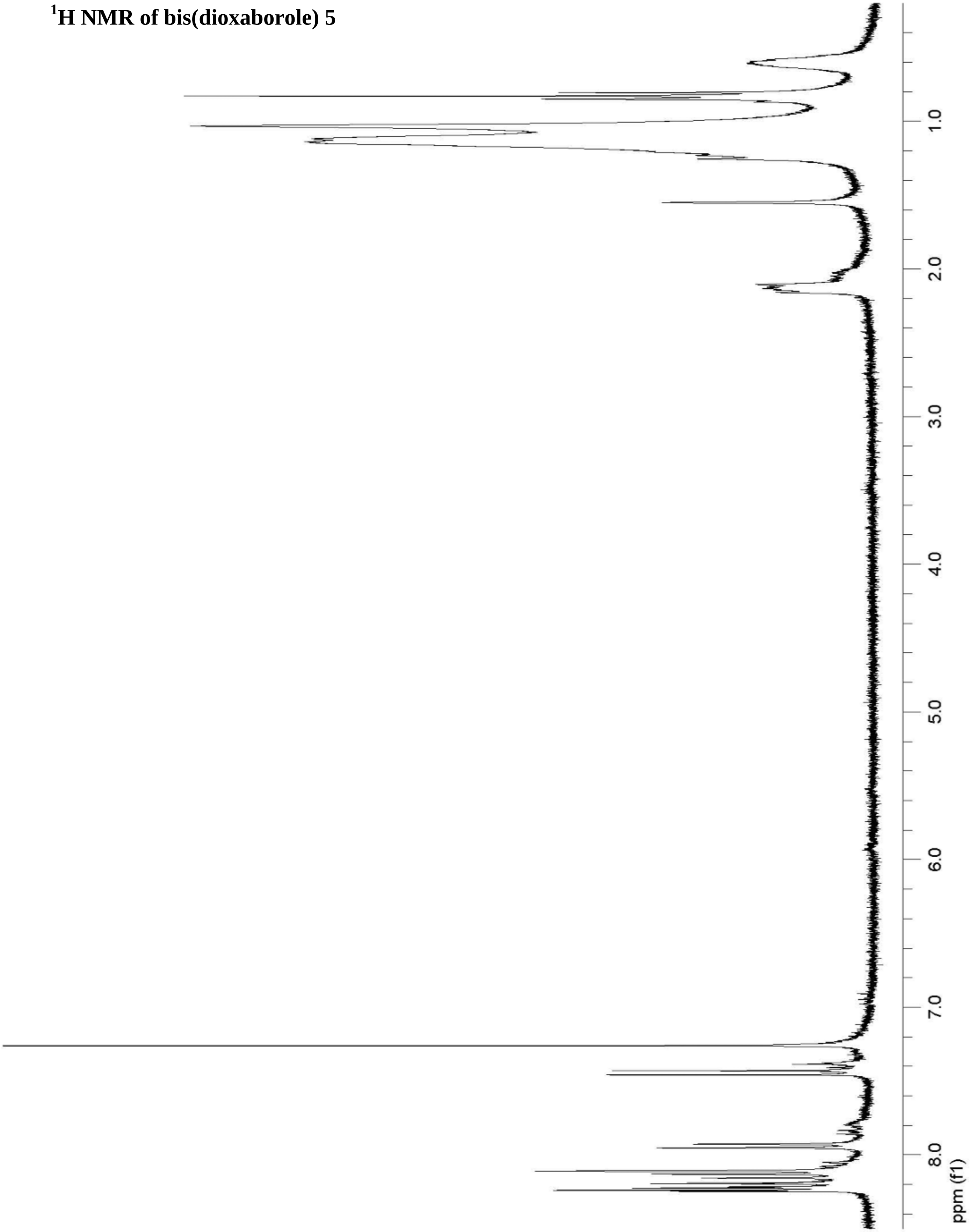
^{1}H NMR of bis(dioxaborole) 4



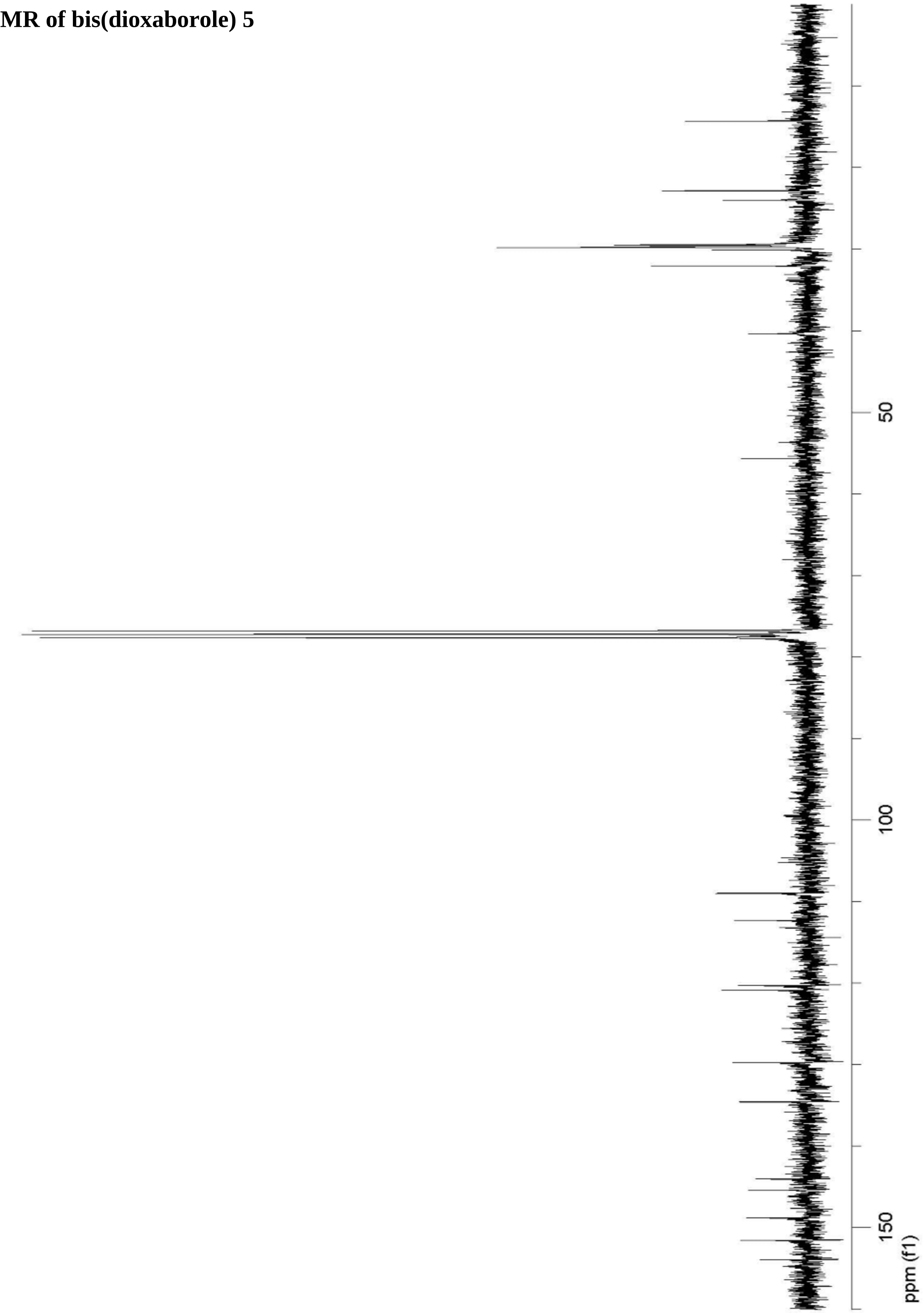
^{13}C NMR of bis(dioxaborole) 4



^{1}H NMR of bis(dioxaborole) 5



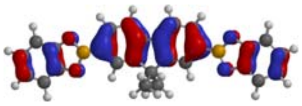
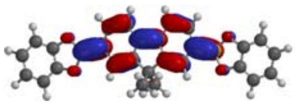
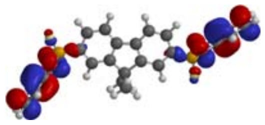
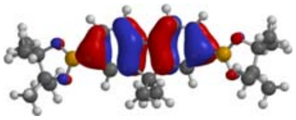
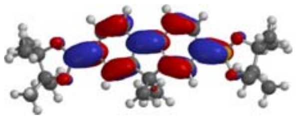
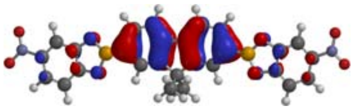
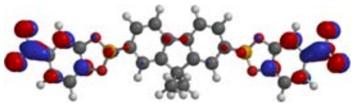
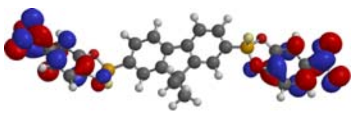
^{13}C NMR of bis(dioxaborole) 5



4. Computational Studies

Computational studies were performed using Spartan 08. The geometries were first optimized using semi-empirical AM1 calculations. The molecular orbitals and band gap energies were calculated using DFT B3LYP with a 6-31G* basis set. No distance, angle or dihedral constraints were applied though molecular symmetry was employed wherever possible to simplify the calculations. The band gaps were calculated as the difference in energies between HOMO-1 and LUMO-1.

Table 1 Computed orbitals and energies for model compounds

Compound	HOMO	LUMO	E_{cal} (eV)	E_{exp} (eV)
1	 -5.79 eV	 -1.64 eV	4.15	3.75
1-F[a]	 0.14 eV	 4.55 eV	4.41	3.99
2	 -5.63 eV	 -1.16 eV	4.47	3.91
4	 -6.36 eV	 -2.48 eV	3.88	3.69
4-F[a]	 -0.71 eV	 2.92 eV	3.63	3.08

[a] The depicted HOMO is a combination of degenerate orbitals HOMO and HOMO(-1).

5. Absorption Measurements

Dichloromethane was used as a solvent and stock solutions were made in volumetric flasks. The solution of bis(dioxaborole) (1.0 x 10^{-5} M, 2 mL in a quartz cuvette) was titrated with the incremental amounts (3-5 μL) of a TBAF solution using a micro-syringe and absorbance data were recorded after each addition.

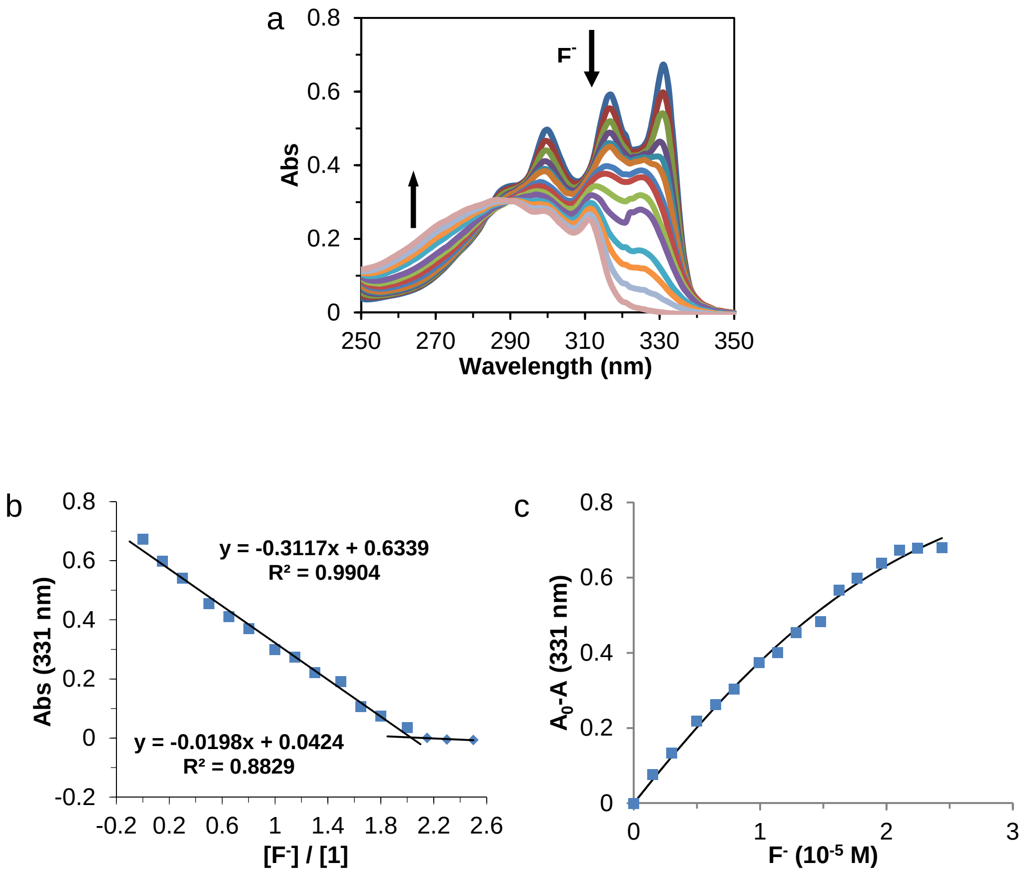


Fig. S1 (a) Absorption titration, (b) mole ratio plot, and (c) binding isotherm of bis(dioxaborole) **1** (1.0 x 10^{-5} M) upon fluoride addition in CH_2Cl_2.

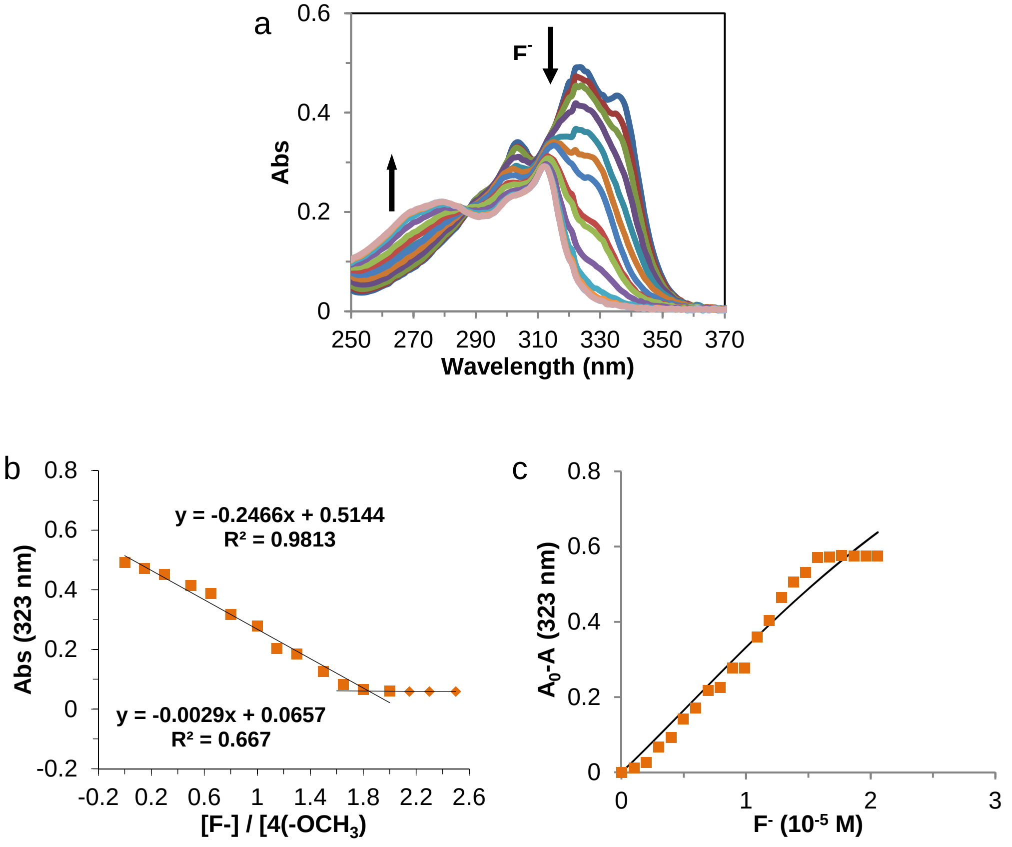


Fig. S2 (a) Absorption titration, (b) mole ratio plot, and (c) binding isotherm of bis(dioxaborole) **4**(-OCH$_3$) (1.0 x 10^{-5} M) upon fluoride addition in CH$_2$Cl$_2$.

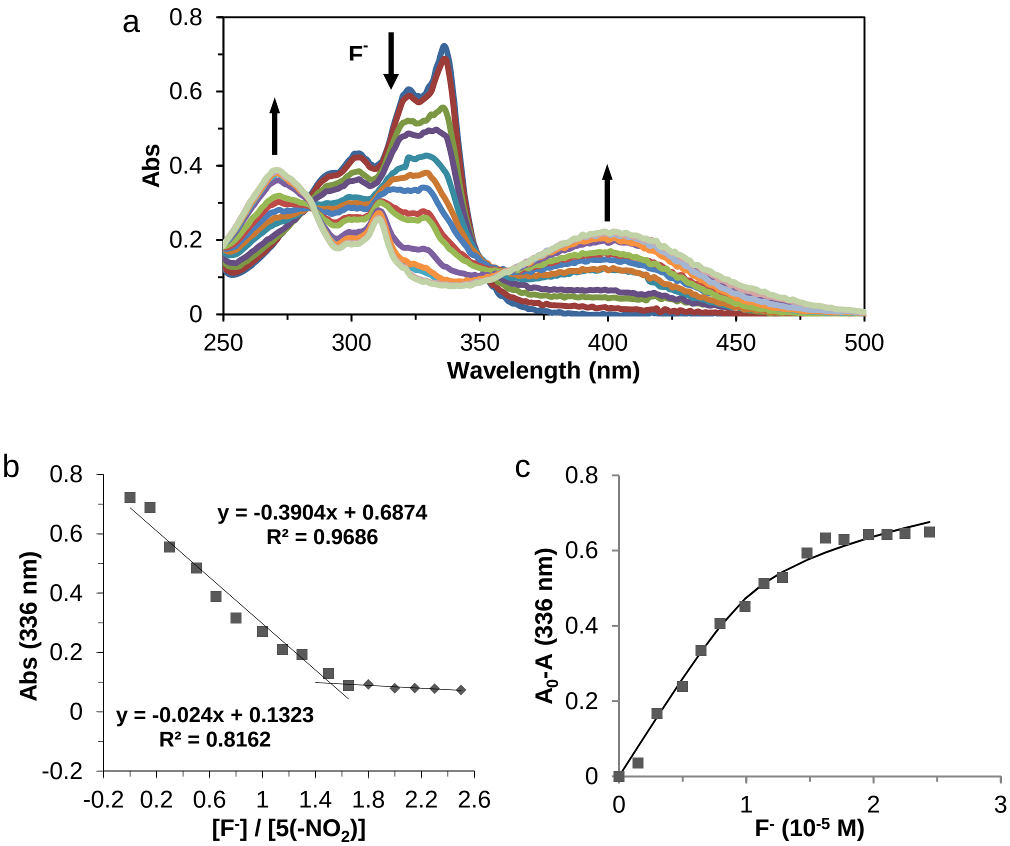


Fig. S3 (a) Absorption titration, (b) mole ratio plot, and (c) binding isotherm of bis(dioxaborole) **5**(-NO$_2$) (1.0 x 10^{-5} M) upon fluoride addition in CH$_2$Cl$_2$.

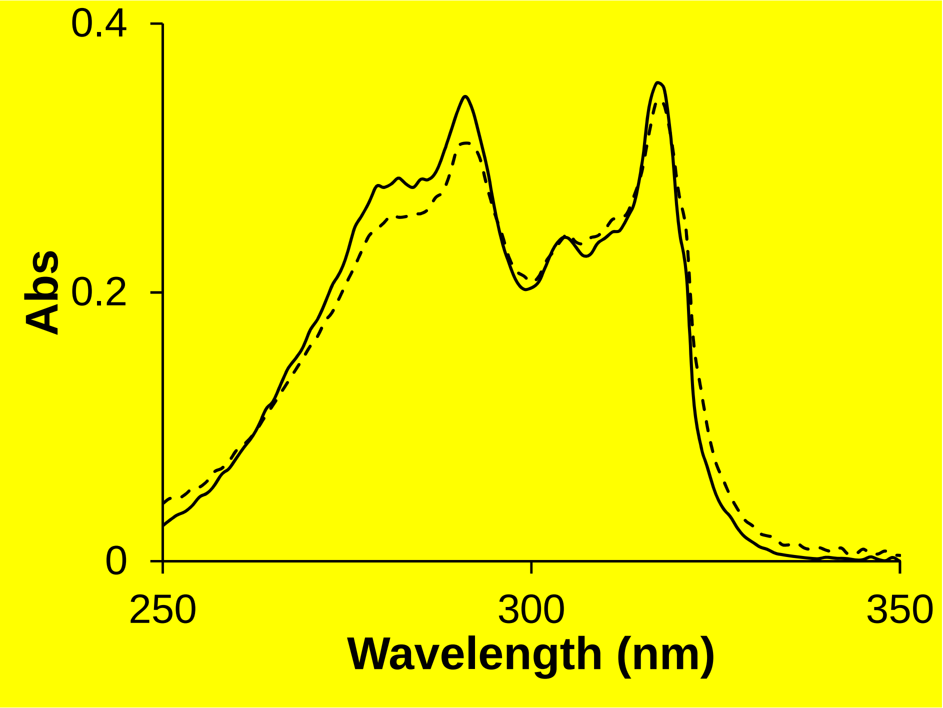


Fig. S4 Absorption spectra of **2** (1 x 10^{-5} M) in the absence (—) and presence (- - -) of fluoride.

Table 2 Binding affinity of bis(dioxaborole)s toward fluoride in CH_2Cl_2

Compound	Dynamic range[a] (10^{-6} M)	Slope[b]	Ratio[c]	K_1 (M^{-1})	K_2 (M^{-1})
1	0.15 -2.10	0.312	2.02	3.53×10^5	3.43×10^4
4	0.15-1.96	0.252	1.84	8.07×10^4	8.07×10^4
5	0.15-1.59	0.405	1.52	4.14×10^6	8.45×10^4

a Dynamic range of the concentration of fluoride was determined from the linear regression part of calibration curve (Fig. 4 inserts); b Slope of linear regression part; c Mole ratio of fluoride to bis(dioxaborole).

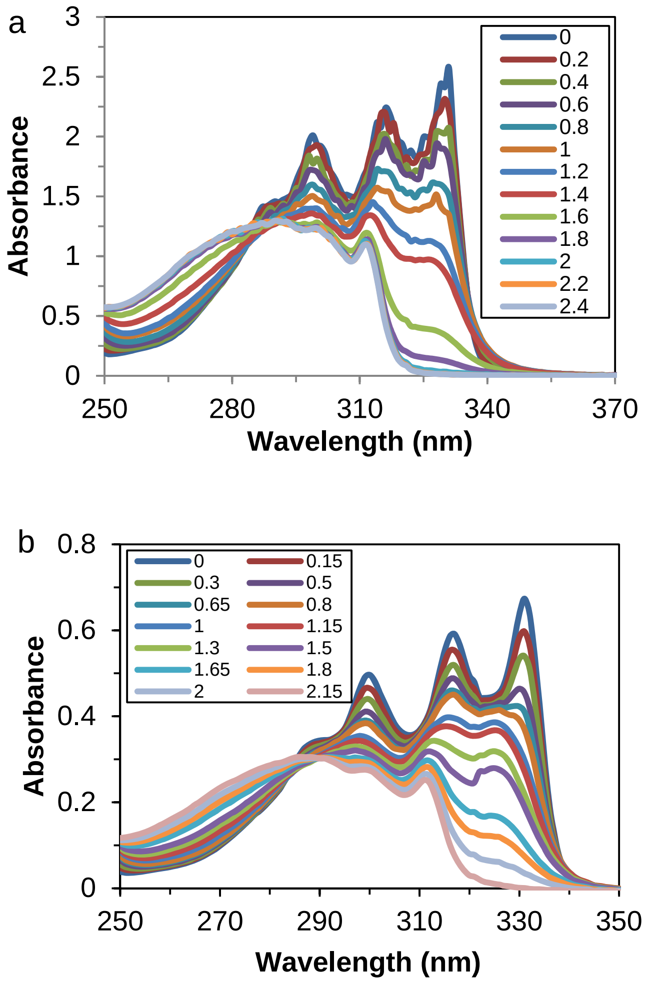


Fig. S5 (a) Absorption spectra of 5.0 x 10^{-5} M bis(dioxaborole) **1** in THF with increasing amounts of fluoride (added as TBAF). (b) Absorption spectra of 5.0 x 10^{-5} M bis(dioxaborole) **1** in $CH_2Cl_2$with increasing amounts of fluoride (added as TBAF). Legends in each plot indicates the ratio of TBAF to bis(dioxaborole) **1**.

6. References

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