Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Boronic, Diboronic and Boric Acid Esters of 1,8-Naphthalenediol – Synthesis, Structure and Formation of Boronium Salts

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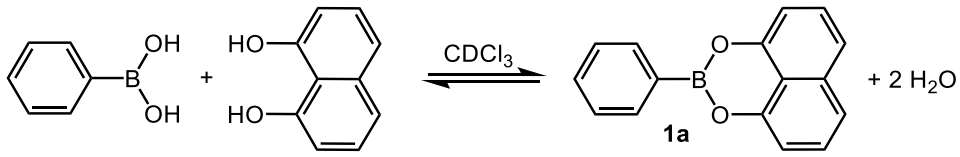
1. General Remarks

All air- and moisture-sensitive manipulations were carried out using standard vacuum line, Schlenk or cannula techniques or in a Vacuum Atmospheres OMNI inert atmosphere dry box containing an atmosphere of purified nitrogen. Toluene, hexanes and benzene were distilled under nitrogen from alkali metals and stored over 4 Å molecular sieves prior to use. All deuterated solvents were purchased from Cambridge Isotope Labs. C_6D_6 and $CDCl_3$ were dried and stored over 4 Å molecular sieves prior to use. All the non-sensitive reactions were carried out using the undried solvents. Catechol (Alfa Aesar), 2,2-bipyridine (Strem), 1,8-dihydroxynaphthalene (Accela), $PhB(OH)_2$ (Chem-Impex), 3,4,5-F_3-$C_6H_2B(OH)_2$ (Frontier Scientific), 2,4,6-F_3-$C_6H_2B(OH)_2$ (Combi-Blocks), 2,6-F_2-$C_6H_3B(OH)_2$ (Oakwood Chemicals), $C_6F_5B(OH)_2$ (BTC chemicals), $MesB(OH)_2$ (Matrix Scientifics) and 2,6-Cl_2-$C_6H_3B(OH)_2$ (Combi Blocks), B_2OH_4 (Boron Molecular), anhydrous 1,10-phenanthroline (Chem-Impex), $B(NMe_2)_3$ (Aldrich chemicals) , $B_2(NMe_3)_4$ (Oakwood Chemicals) 1 M BCl_3 in hexanes (Across Organics), $O=PEt_3$ (Across Organics), 2,6-$(MeO)_2$-$C_6H_3B(OH)_2$ (Alfa Aesar), n-Bu-$B(OH)_2$ (Oakwood Chemicals), $B(OMe)_3$ (Across Organics), $B(OH)_3$ (EMD chemicals), anhydrous pyridine (Chem-Impex), PhBPin (**1c**) (TCI) and 2 N HCl in ether (Across Organics) were purchased form commercial sources and used without further purification. 4-dimethylaminopyridine was purchased from Acros Organics and sublimed prior to use. The boronic catechol esters PhBCat (**1b**) [1], 3,4,5-F_3-C_6H_2BCat (**3b**) [2], 2,4,6-F_3-C_6H_2BCat (**4b**) [2], 2,6-F_2-C_6H_3BCat (5b) [2]. C_6F_5BCat (**2b**) [2], 2, 4, 6-Me_3-C_6H_2-BCat (**7b**) [3] and Ph-BDan [4] were prepared according to the literature. The ^{1}H-, ^{13}C-, ^{11}B- ^{19}F-NMR spectra were obtained from a JOEL ECS 400. All measurements, unless noted otherwise, were carried out at 298 K and NMR chemical shifts were given in ppm. The ^{11}B NMR spectra referenced to H_3BO_3 in D_2O (δ = 36 ppm), ^{19}F NMR spectrum was referenced to $C_6H_5CF_3$ in C_6D_6 (δ = 62.3 ppm), The ^{1}H-NMR spectra were referenced to the residual protonated solvent for ^{1}H and the ^{13}C NMR spectra were referenced to the deuterated solvent peaks. The following abbreviations were used to describe peak multiplicities in the reported NMR spectroscopic data: “s” for singlet, “d” for doublet, “t” for triplet, “q” for quartet, “sept” for septet, “m” for multiplet and “br” for broadened resonances. Elemental analyses were performed using a Perkin Elmer 2400 Series II CHNS/O Analyzer.

2. Experimental

2.1. Acid-ester equilibrium of phenyl boronic acid and 1,8-naphthalenediol



A standard NMR tube was charged with 1,8-naphthalenediol (3.3 mg, 0.02 mmol), phenyl boronic acid (2.5 mg, 0.02 mmol) and 0.5 mL of $CDCl_3$. After 10 minutes, the resulting solution was analyzed by ^{1}H-NMR (400 MHz, $CDCl_3$): 6.99 (d, $^3\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.41 (m, CH-phenyl, 4 H), 7.49 (t, $^3\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.58 (t, $^3\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-phenyl, 1 H), 8.13 (d, $^3\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H) ppm.

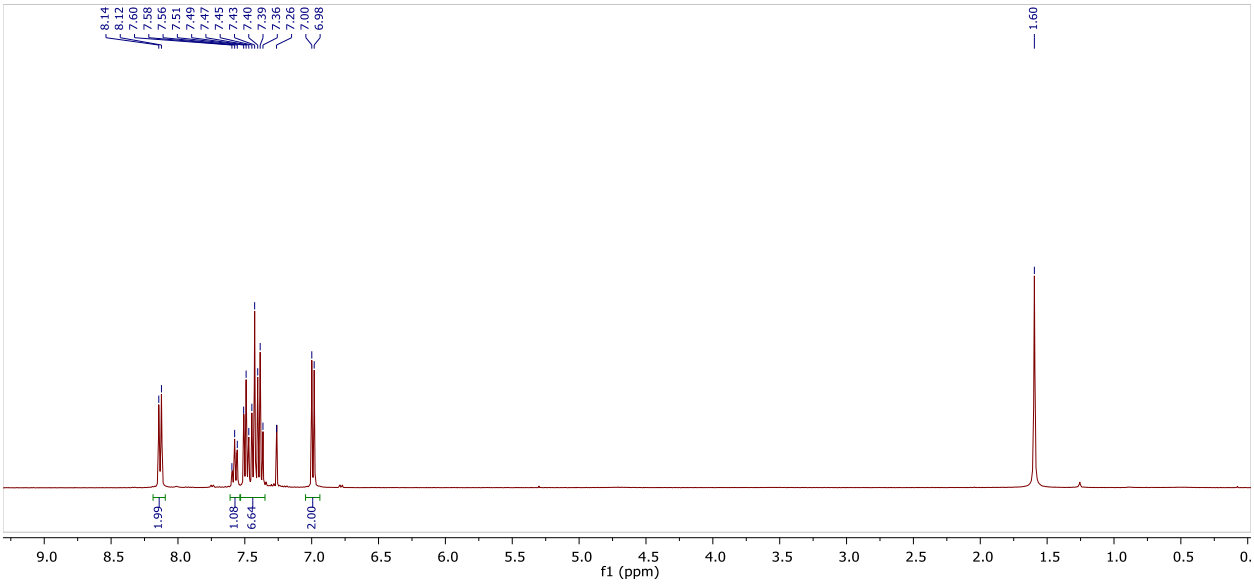
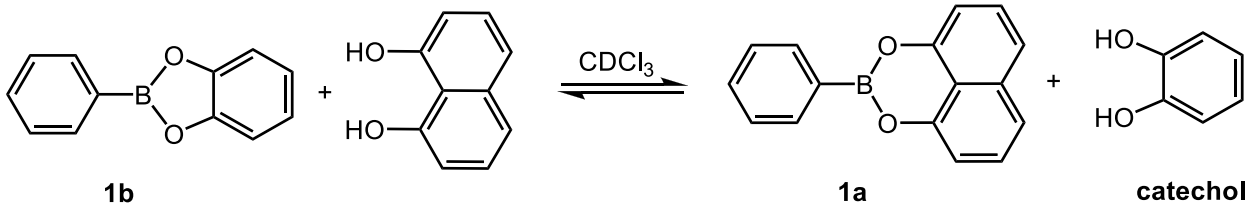


Figure S1. ^{1}H NMR spectrum of the reaction of phenyl boronic acid with 1,8-naphthalenediol (room temperature, $CDCl_3$).

2.2. Ligand exchange experiments

2.2.1 **1b** and 1,8-naphthalenediol

A standard NMR tube was charged with 1,8-naphthalenediol (6.5 mg, 0.04 mmol), **1b** (7.8 mg, 0.04 mmol) and 0.5 mL of $CDCl_3$. The progress of the reaction was monitored by ^{1}H-NMR spectroscopy. **Figure S2** shows the ^{1}H NMR spectrum of the reaction mixture after reaching equilibrium.



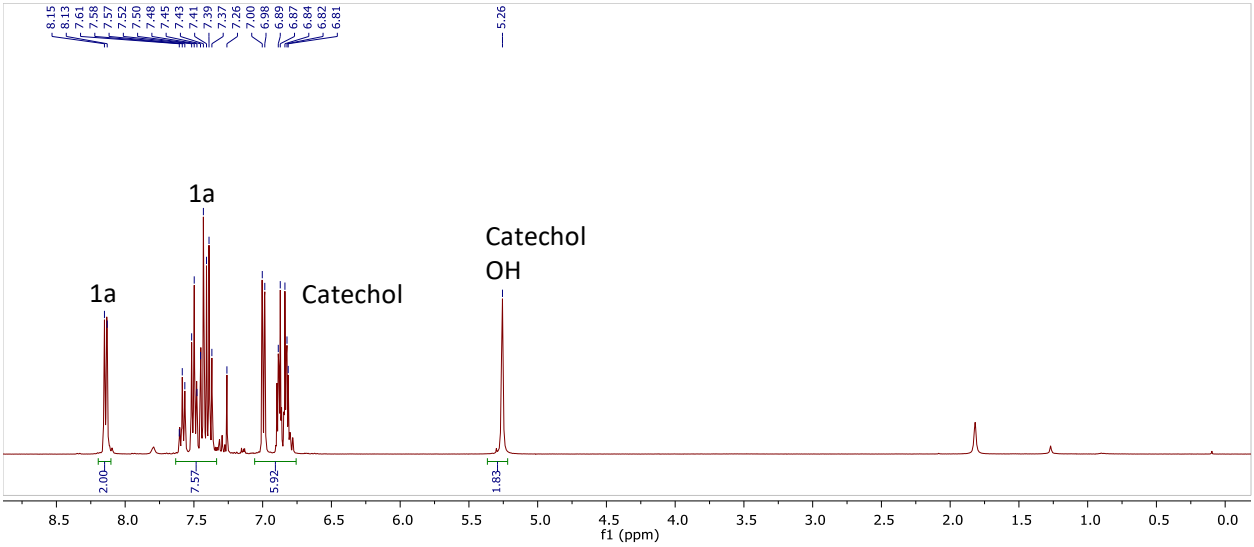
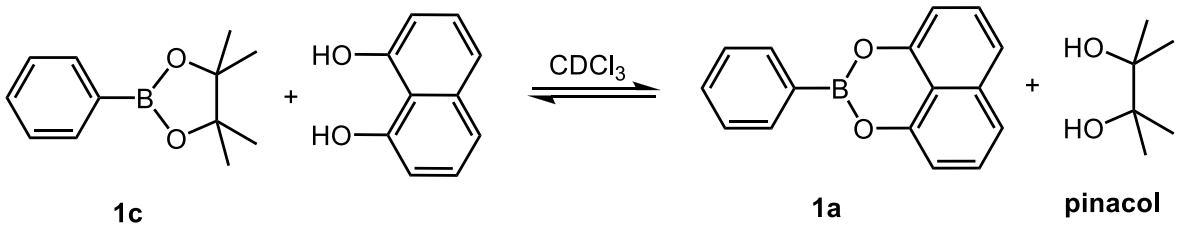


Figure S2. ^{1}H NMR spectrum of the reaction mixture of **1b** and 1,8-naphthalenediol after 1 hour at room temperature.

2.2.2 **1c** and 1,8-naphthalenediol

A standard NMR tube was charged with 1,8-naphthalenediol (6.5 mg, 0.04 mmol), **1c** (8.2 mg, 0.04 mmol) and 0.5 mL of $CDCl_3$. The progress of the reaction was monitored periodically by ^{1}H-NMR spectroscopy. **Figure S3** shows the ^{1}H NMR spectrum of the reaction mixture after reaching equilibrium.



1c **1a** **pinacol**

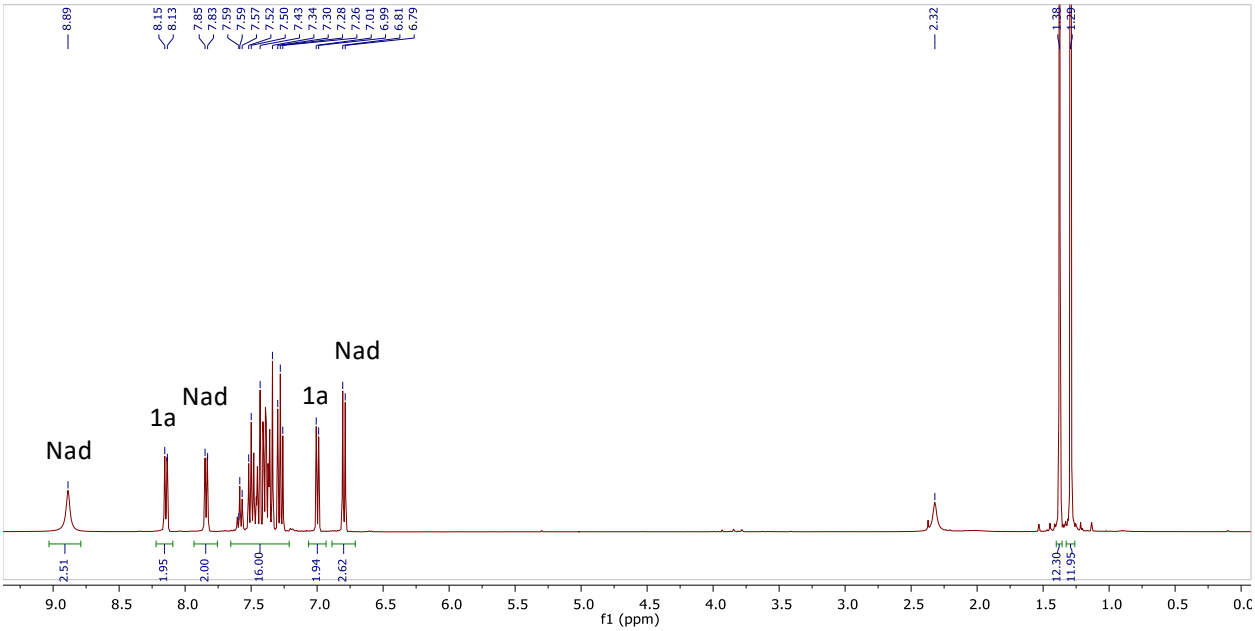
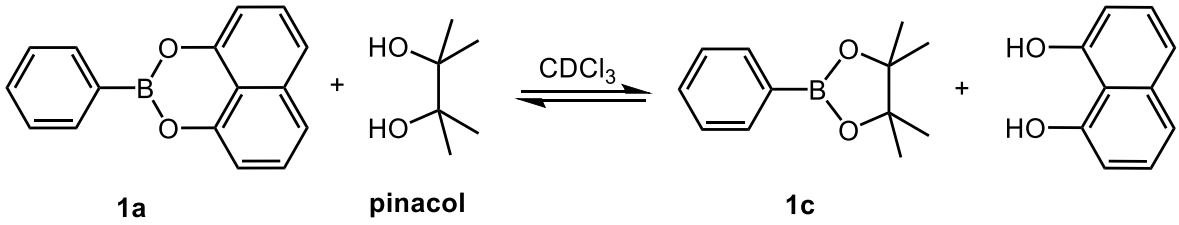


Figure S3. ^{1}H NMR spectrum of **1c** and 1,8-naphthalenediol after heating for 24 hours at 50 °C ($CDCl_3$).

2.2.3 **1a** and pinacol

A standard NMR tube was charged with pinacol (4.7 mg, 0.04 mmol), **1a** (9.8 mg, 0.04 mmol) and 0.5 mL of $CDCl_3$. The progress of the reaction was monitored periodically by ^{1}H-NMR spectroscopy. **Figure S4** shows the ^{1}H NMR spectrum of the reaction mixture after reaching equilibrium.



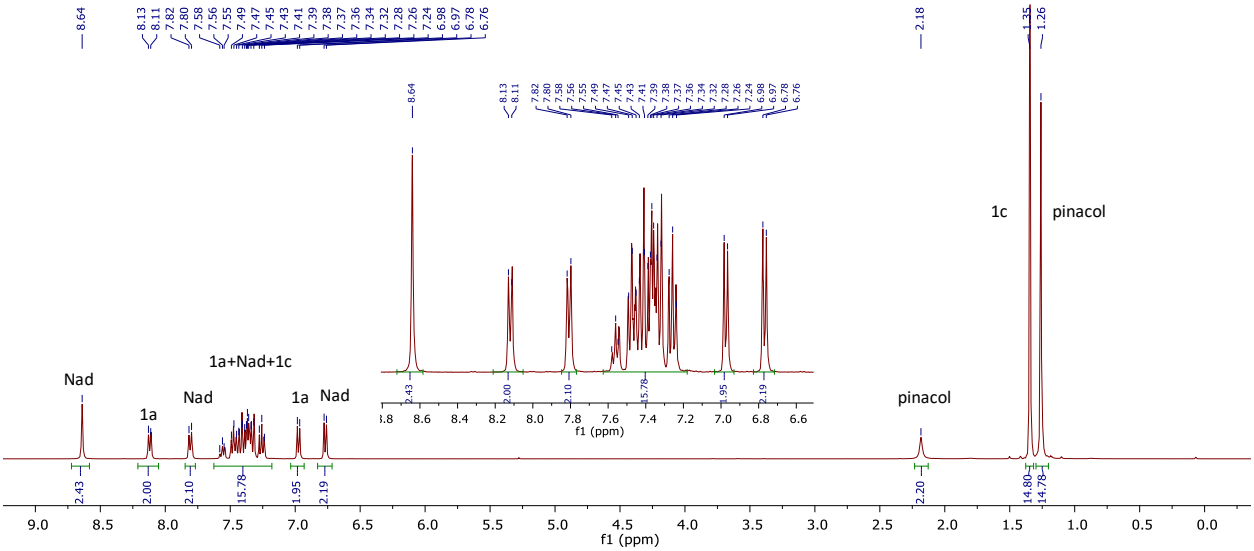
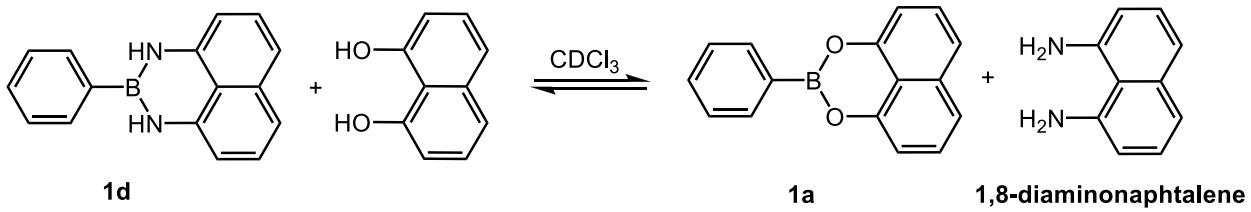


Figure S4. ^{1}H NMR spectrum of **1a** and pinacol after heating for 48 hours at 50 °C ($CDCl_3$).

2.2.4 **1d** and 1,8-naphthalenediol

A standard NMR tube was charged with 1,8-naphthalenediol (6.5 mg, 0.04 mmol), **1d** (9.8 mg, 0.04 mmol) and 0.5 mL of $CDCl_3$. The progress of the reaction was monitored periodically by ^{1}H-NMR spectroscopy. **Figure S4** shows the ^{1}H NMR spectrum of the reaction mixture after reaching equilibrium.



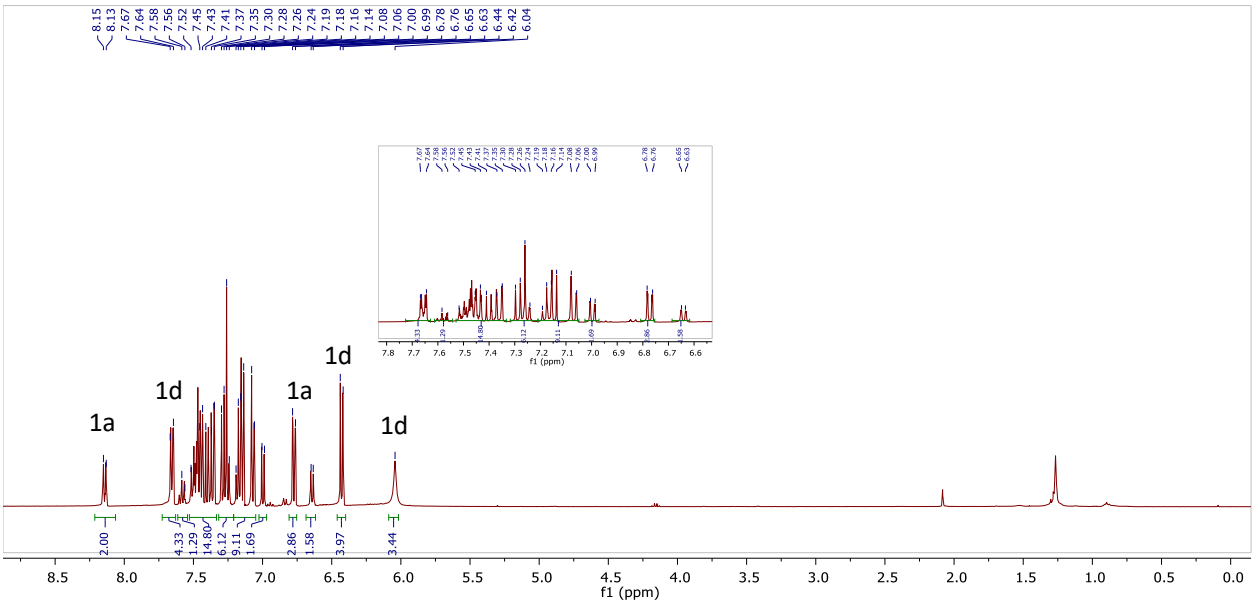
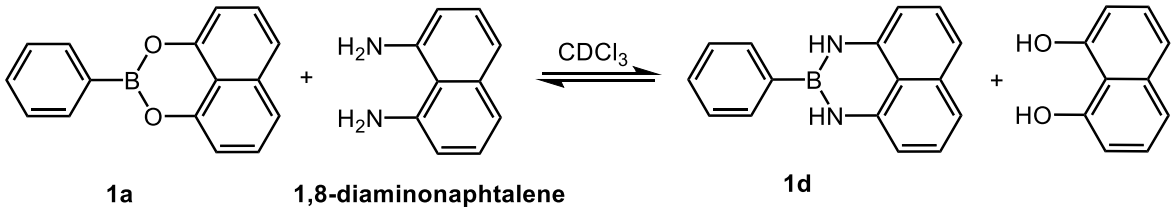


Figure S5. ^{1}H NMR spectrum of the reaction mixture of **1d** and 1,8-naphthalenediol after heating for 4 days at 50 °C ($CDCl_3$).

2.2.5 **1a** and 1,8-diaminonaphthalene

A standard NMR tube was charged with 1,8-diaminonaphthalene (6.4 mg, 0.04 mmol), **1d** (9.8 mg, 0.04 mmol) and 0.5 mL of $CDCl_3$. The progress of the reaction was monitored periodically by ^{1}H-NMR spectroscopy. **Figure S6** shows the ^{1}H NMR spectrum of the reaction mixture after reaching equilibrium.



1a **1,8-diaminonaphthalene** **1d**

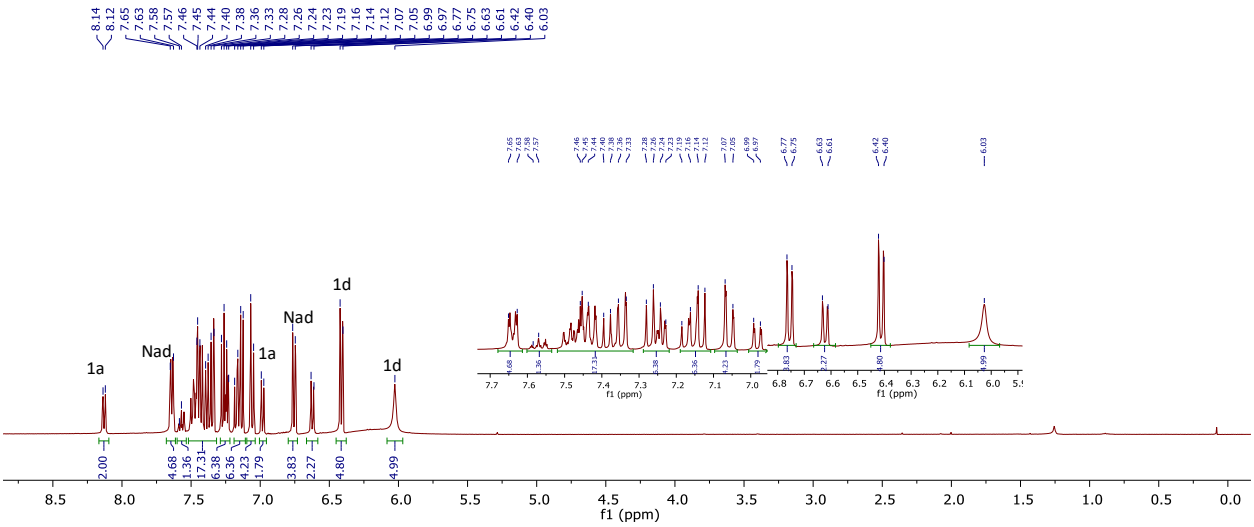
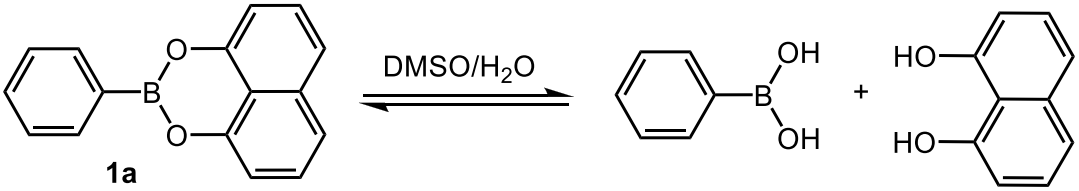


Figure S6. ^{1}H NMR spectrum of the reaction mixture of **1a** and 1,8-diaminonaphthalene after heating for 4 days at 50 °C ($CDCl_3$).

2.3 Hydrolytic stability of **1a-d**.

2.3.1 Hydrolysis of **1a**

A standard NMR tube was charged with **1a** (7.38 mg, 0.03 mmol) and 0.6 mL of a DMSO-D_6/water mixture (10 vol% H_2O). The progress of the hydrolysis was monitored periodically by ^1H NMR spectroscopy. The hydrolytic conversion was calculated from integrating distinguishable peaks of **1a** and 1,8-naphthalenediol.



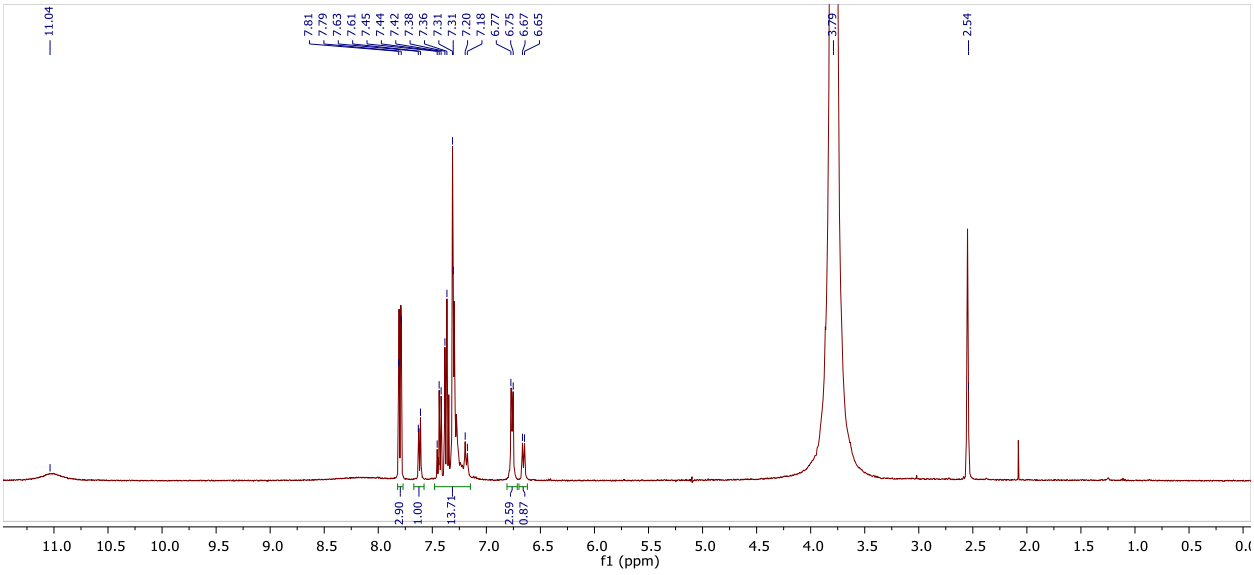


Figure S7. ^1H NMR spectrum of **1a** in 0.6 mL of DMSO-D_6/water mixture (10 vol% H_2O). after 2 weeks at room temperature.

2.3.2 Hydrolysis of **1b**

A standard NMR tube was charged with **1b** (5.88 mg, 0.03 mmol) and 0.6 mL of a DMSO-D_6/water mixture (10 vol% H_2O). The progress of the hydrolysis was monitored periodically by ^1H NMR spectroscopy. The hydrolytic conversion was calculated from integrating distinguishable peaks of **1b** and 1,8-naphthalenediol.

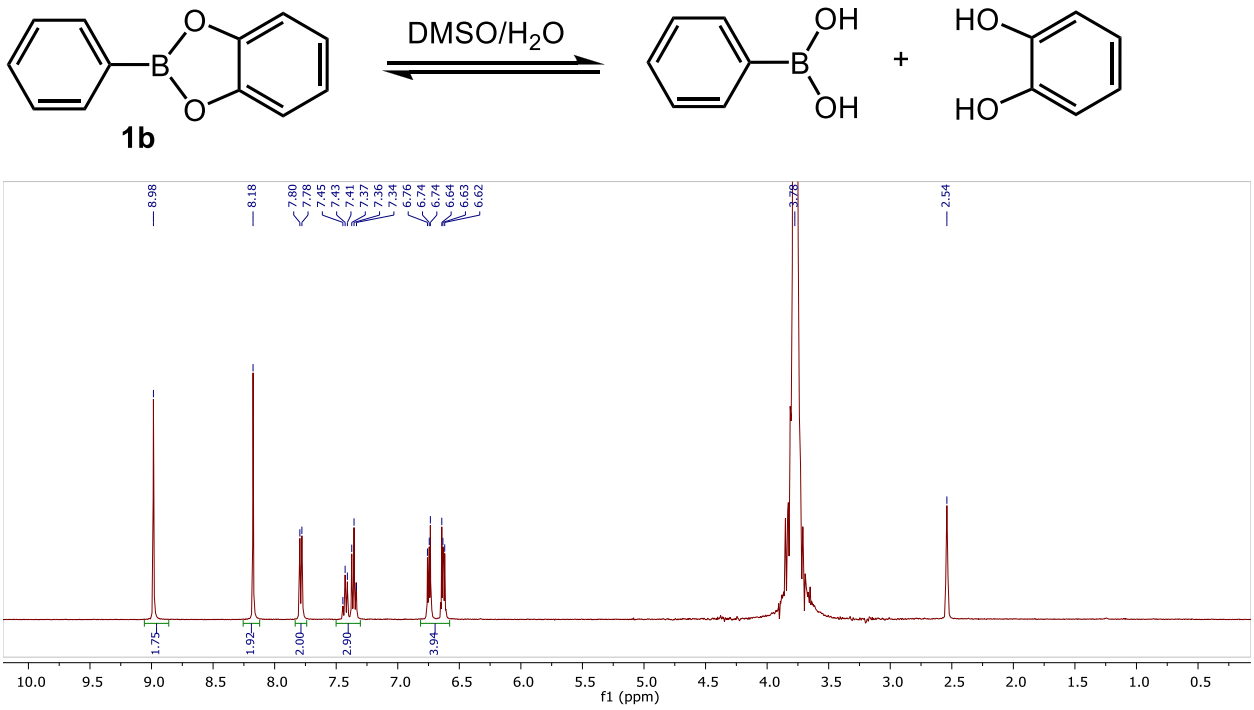
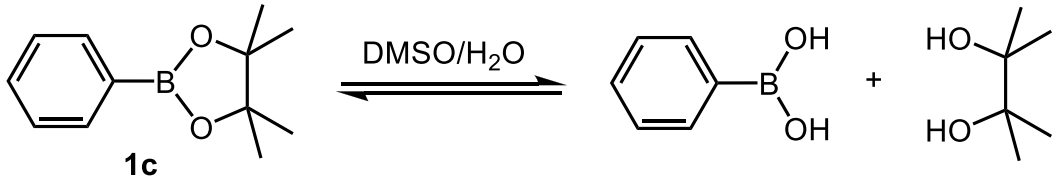


Figure S8. ^1H NMR spectrum of **1b** in DMSO-D_6/water mixture (10 vol% H_2O) after 30 min at room temperature.

2.3.3 Hydrolysis of **1c**

A standard NMR tube was charged with **1c** (6.12 mg, 0.03 mmol) and 0.6 mL of a DMSO-D_6/water mixture (10 vol% H_2O). The progress of the hydrolysis was monitored periodically by ^1H NMR spectroscopy. The hydrolytic conversion was calculated from integrating distinguishable peaks of **1c** and 1,8-naphthalenediol.



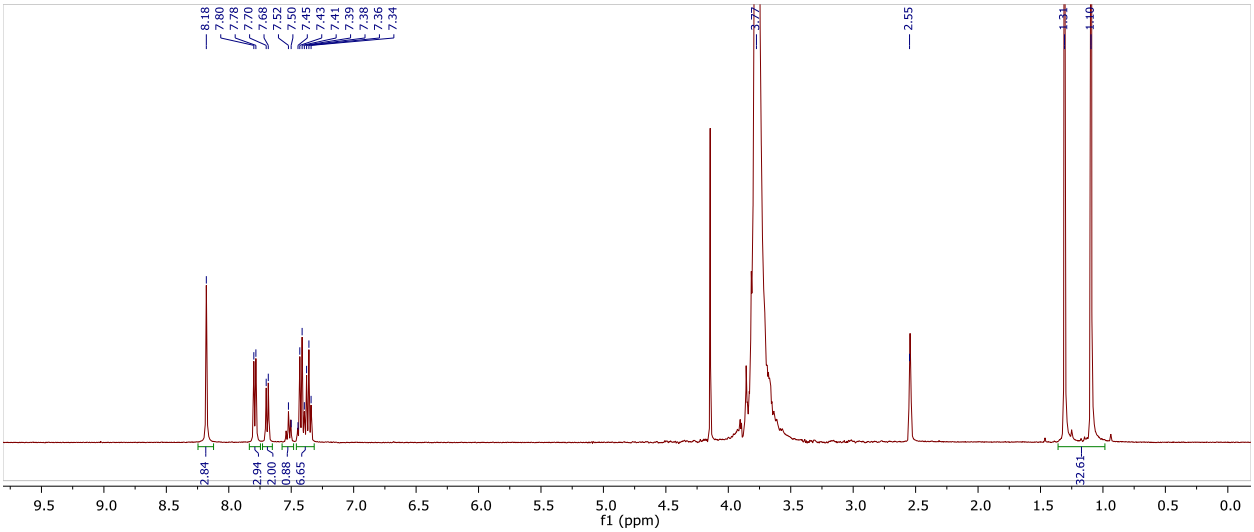
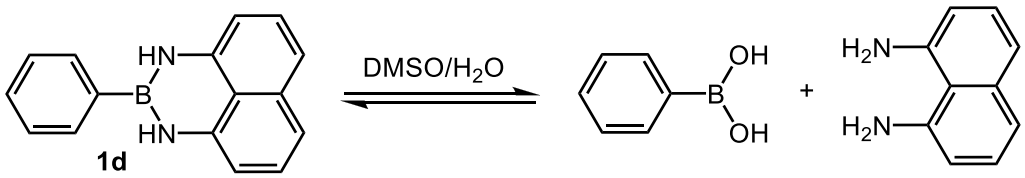


Figure S9. ^1H NMR spectrum of **1c** in DMSO/water mixture (10 vol% H_2O) after one week at room temperature.

2.3.4 Hydrolysis of **1d**

A standard NMR tube was charged with **1d** (7.32 mg, 0.03 mmol) and 0.6 mL of a DMSO-D_6/water mixture (10 vol% H_2O). The progress of the hydrolysis was monitored periodically by ^1H NMR spectroscopy. The hydrolytic conversion was calculated from integrating distinguishable peaks of **1d** and 1,8-naphthalenediol.



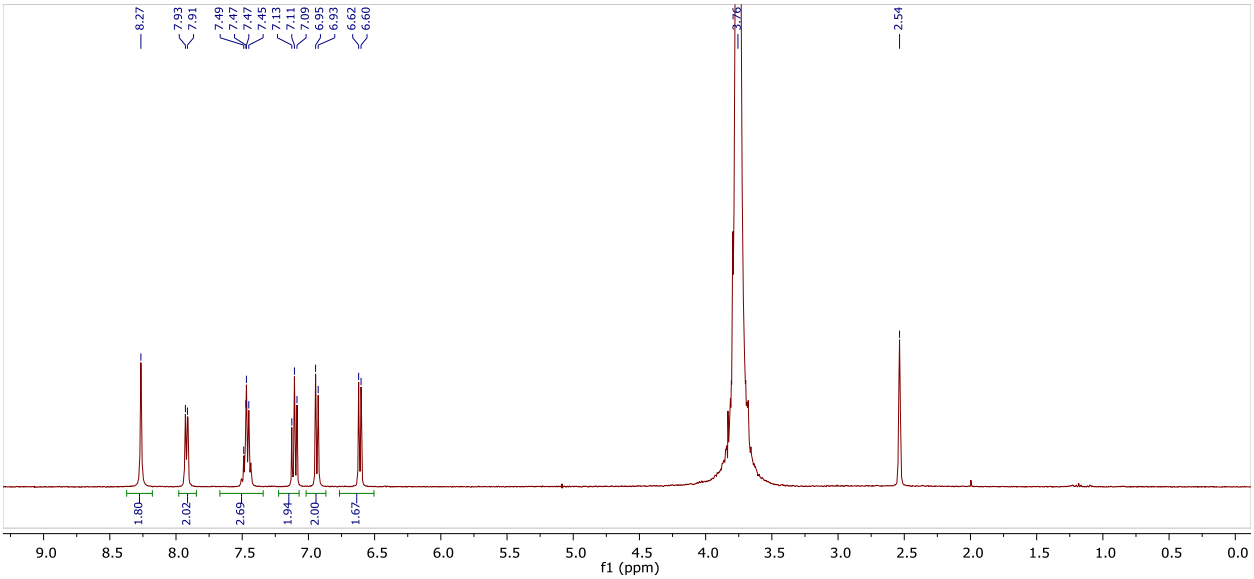


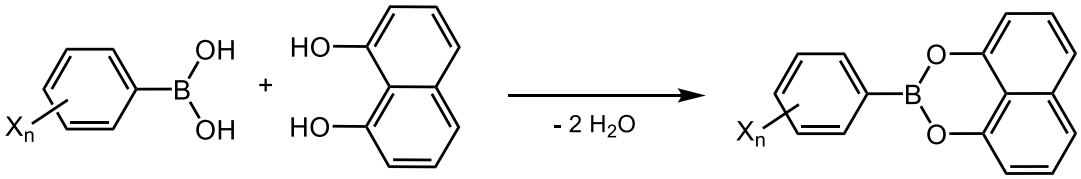
Figure S10. ^1H NMR spectrum of **1d** in DMSO/water mixture (10 vol% H_2O) after 12 days at room temperature.

Table S1. Hydrolysis of the phenyl boronic acid esters **1a-c** and amino borate **1d**.

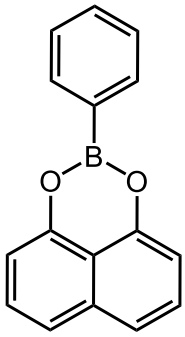
Time (days)	Conv. of **1b** [%]	Conv. of **1a** [%]	Conv. of **1c** [%]	Conv. of **1d** [%]
0.004	0	15.3	0.6	100
0.01	0	24.8	-	100
0.02	0	41.5	-	100
0.03	0	51.5	-	100
0.04	0	58.2	-	100
0.06	0	64.0	-	100
0.08	0	66.6	1.0	100
0.13	0	68.8	2.0	100
0.75	0	69.5	13.0	100
1	0	70.4	16.7	100
2	0	72.4	30.0	100
3	0	72.8	42.5	100
4	0	72.9	50.5	100
5	0	73.3	55.2	100
6	0	73.5	58.7	100
7	0	73.5	61.4	100
8	0	74.2	63.0	100
9	0	74.2	64.7	100
12	0	73.5	65.0	100

2.4 Synthetic procedures

2.4.1 Synthesis of **1a, 3a-5a** and **8a**



The aryl boronic acid esters **1a**, **3a-5a** and **8a** were synthesized in acetonitrile by mixing one equivalent of the aryl boronic acid with one equivalent of 1,8-naphthalenediol in a 20 mL scintillation vial with screw cap. The mixture was heated until all materials dissolved and subsequently cooled to room temperature. After the solutions were allowed to stand overnight (if not stated otherwise), crystalline precipitates formed, which were collected, washed once with cold acetonitrile and dried under vacuum to give the analytically pure products.



1a

1a. 1,8-naphthalenediol (85 mg, 0.7 mmol), phenyl boronic acid (112 mg, 0.7 mmol) and acetonitrile (5 mL). Colorless crystals. Yield 145 mg (84%). M.p. 152-153 °C. ^{1}H NMR [400 MHz, $CDCl_3$]: 6.99 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.41 (m, CH-phenyl, 4 H), 7.49 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.58 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-phenyl, 1 H), 8.13 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H) ppm. ^{13}C{H} NMR [100.4 MHz, $CDCl_3$]: 109.6 (CH-naphthyl), 117.8 (C-quart), 121.2 (CH-naphthyl), 128.0 (CH-phenyl), 128.1 (CH-naphthyl), 132.4 (CH-phenyl), 134.8 (C-quart), 135.3 (CH-naphthyl), 148.0 (C-quart) ppm. Note: The ipso carbon bound to boron could not be detected in the ^{13}C NMR. ^{11}B NMR [128.4 MHz, $CDCl_3$]: 28.0 ppm. Anal. Calc. for $C_{16}H_{11}BO_2$ (246.07): C, 78.10; H, 4.51; Found: C, 77.67; H, 4.17.

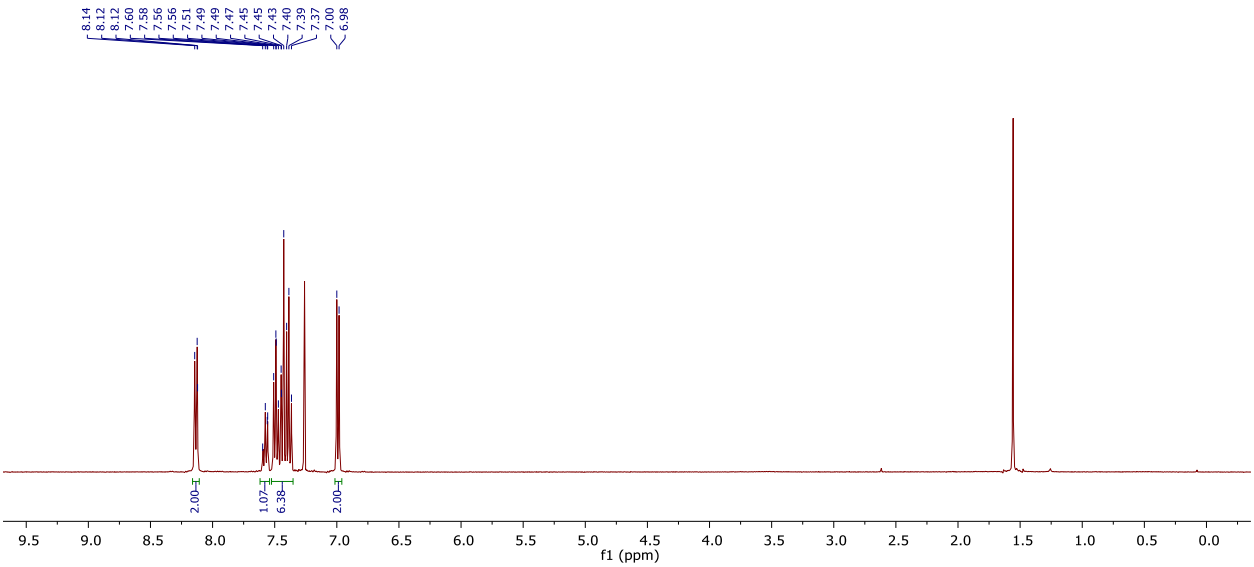


Figure S11. ^{1}H NMR spectrum of **1a** in $CDCl_3$ at room temperature.

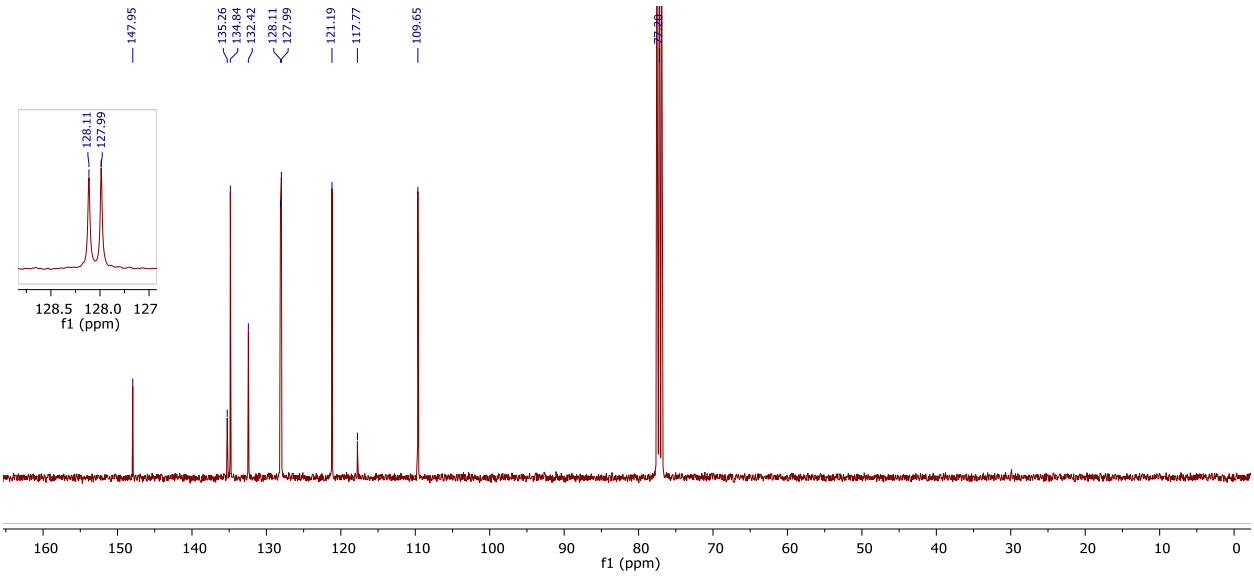


Figure S12. ^{13}C NMR spectrum of **1a** in $CDCl_3$ at room temperature.

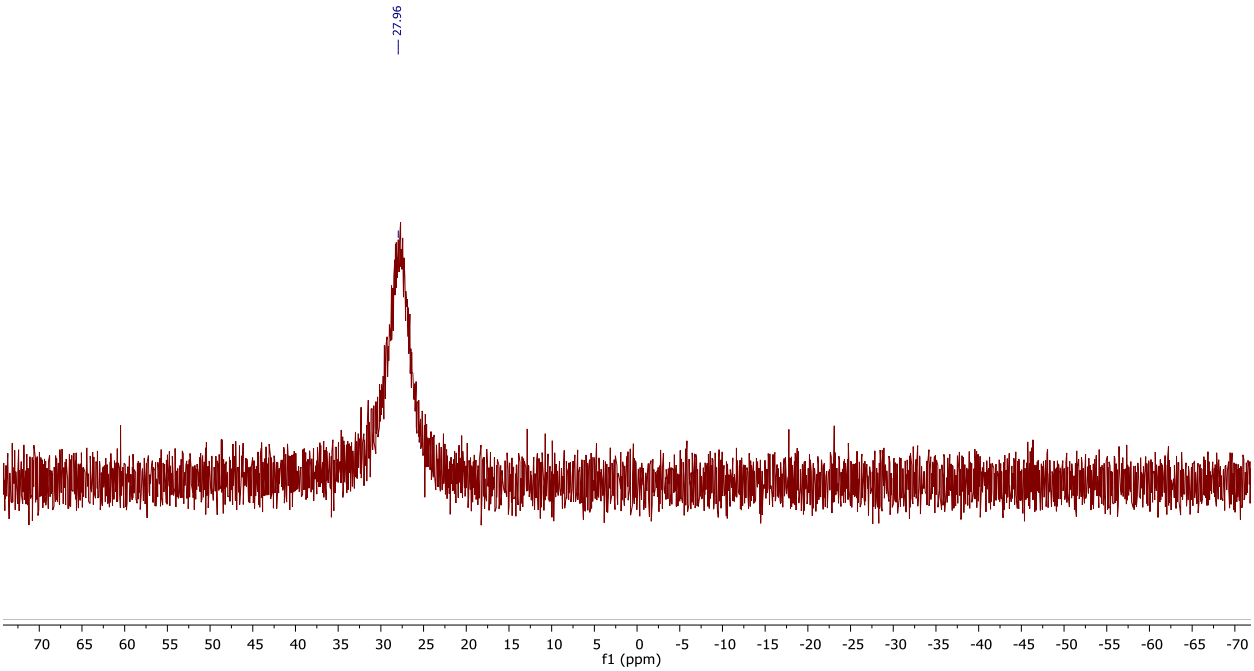
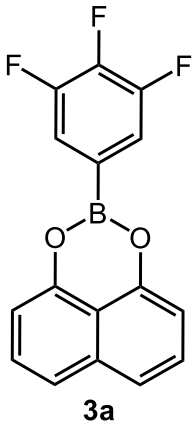


Figure S13. ^{11}B NMR spectrum of **1a** in $CDCl_3$ at room temperature.



3a

3a. 1,8-naphthalenediol (0.36 g, 2.05 mmol), 3,4,5-trifluorophenyl boronic acid (0.33 g, 2.05 mmol) and acetonitrile (12 mL). Colorless crystals. Yield 0.59 g (95%). M.p. 153-154 °C. ^{1}H NMR [400 MHz, $CDCl_3$]: 6.93 (d, $^{3}J_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.36 (t, $^{3}J_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.42 (d, $^{3}J_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.65 (d, $^{3}J_{H\text{-}H}$ = 8 Hz, CH-phenyl, 2 H) ppm. ^{13}C{H} NMR [100.4 MHz, $CDCl_3$]: 109.7 (CH-naphthyl), 117.4 (C-quart), 118.3 (dd, $^{2}J_{C\text{-}F}$ = 14 Hz, $^{3}J_{C\text{-}F}$ = 5 Hz, (CH-phenyl), 121.6, 127.9 (CH-naphthyl), 135.1 (C-quart.), 142.6 (dt, $^{1}J_{C\text{-}F}$ = 257 Hz, $^{2}J_{C\text{-}F}$ = 15.0 Hz, p-CF), 147.2, (C-quart), 151.1 (dd, $^{1}J_{C\text{-}F}$ = 251 Hz, $^{2}J_{C\text{-}F}$ = 12 Hz, m-CF) ppm. Note: The ipso carbon bound to boron could not be detected in the ^{13}C NMR. ^{11}B NMR [128.4 MHz, $CDCl_3$]: 27.0 ppm. ^{19}F NMR (376.3 MHz, $CDCl_3$): -134.3, -154.2 ppm. Anal. Calc. for $C_{16}H_8F_3BO_2$ (300.04): C, 64.05; H, 2.69; Found: C, 63.64; H, 2.29.

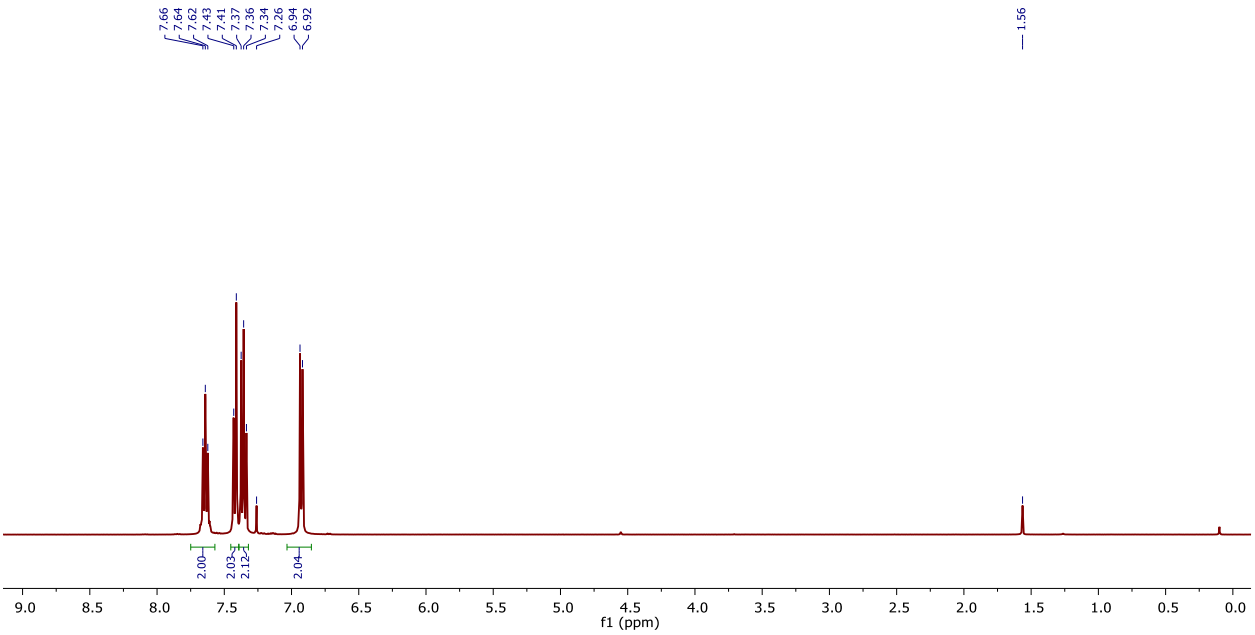


Figure S14. ^{1}H NMR spectrum of **3a** in $CDCl_3$ at room temperature.

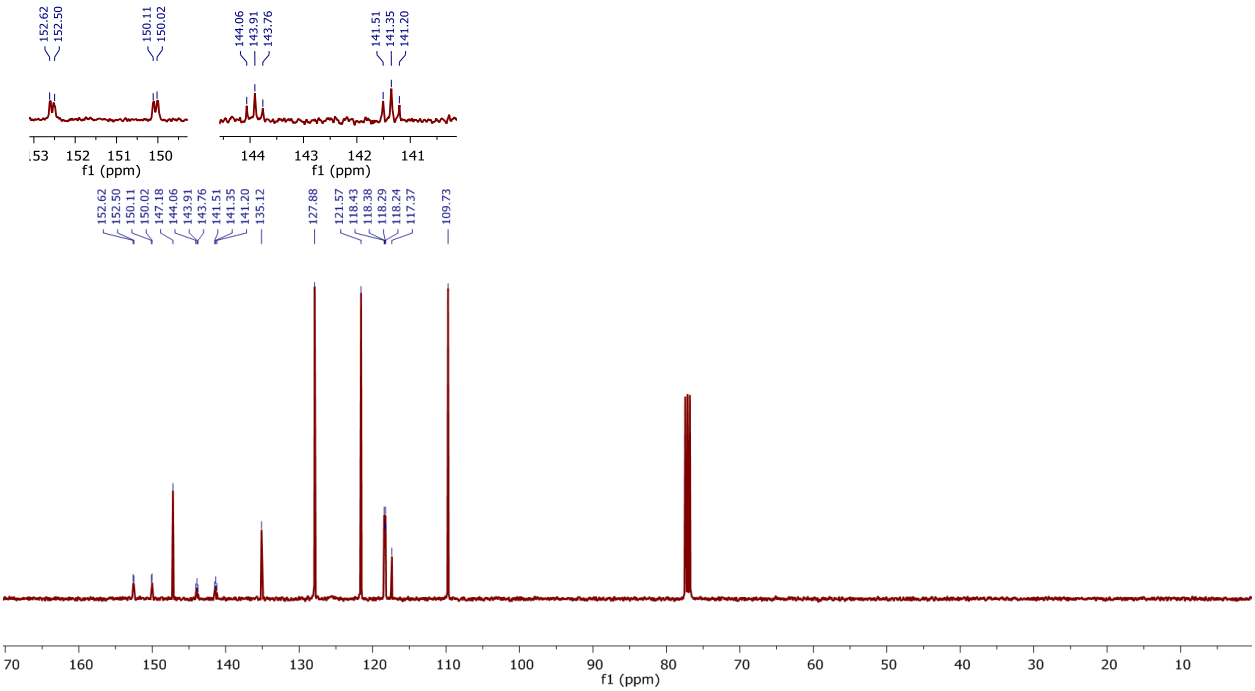


Figure S15. ^{13}C NMR spectrum of **3a** in $CDCl_3$ at room temperature.

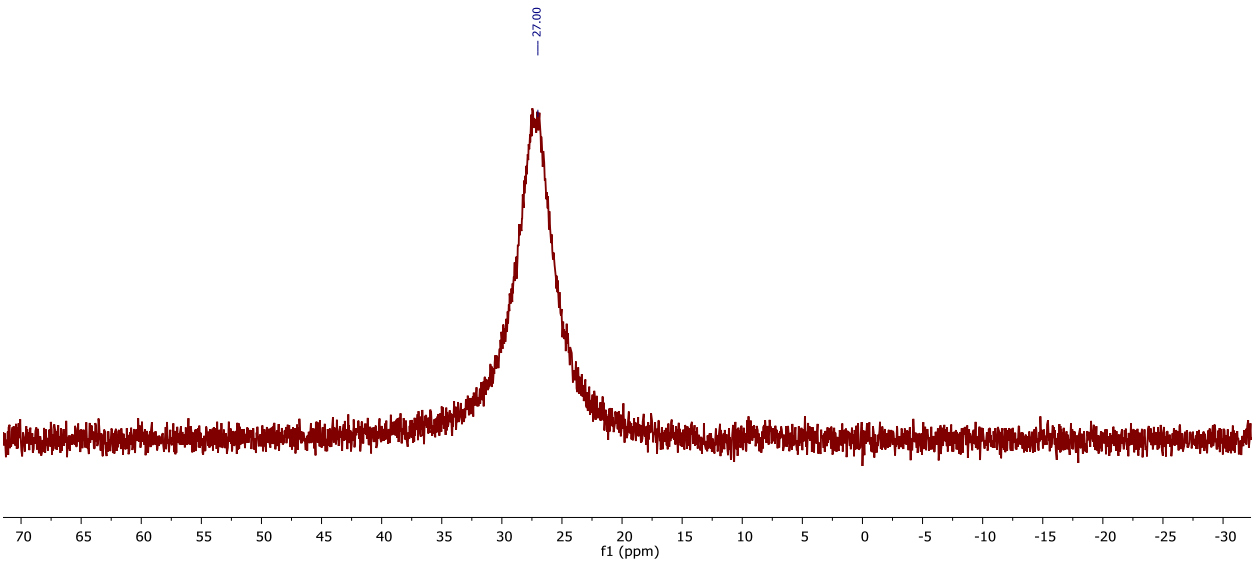


Figure S16. ^{11}B NMR spectrum of **3a** in $CDCl_3$ at room temperature.

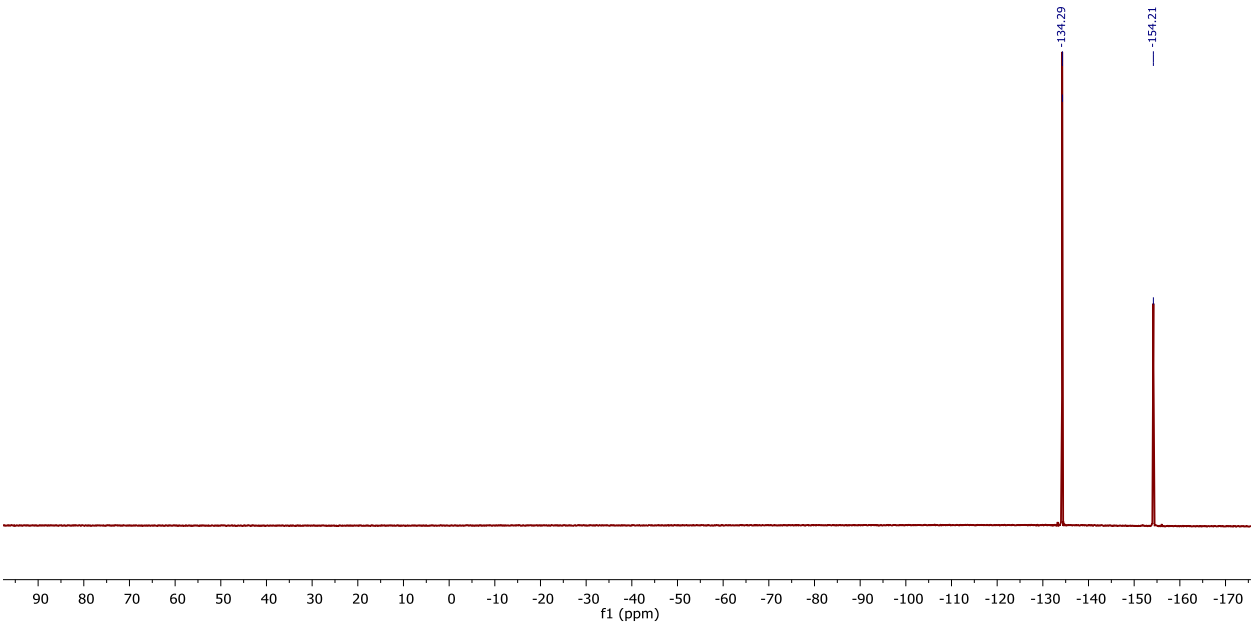
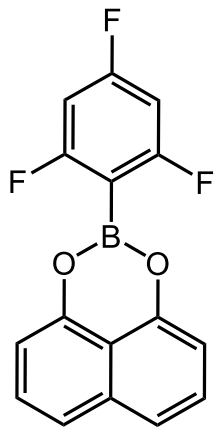


Figure S17. ^{19}F NMR spectrum of **3a** in $CDCl_3$ at room temperature.



4a

4a. 1,8-naphthalenediol (0.27 g, 1.7 mmol), 2,6-difluorophenyl boronic acid (0.3 g, 1.7 mmol) and acetonitrile (10 mL). Colorless crystals. Yield 0.47 g (92%). M.p. 140-141 °C. ^{1}H NMR [400 MHz, $CDCl_3$]: 6.70 (t, $^{3}\boldsymbol{J}_{H-H}$ = 8 Hz, CH-naphthyl, 2 H), 6.95 (d, $^{3}\boldsymbol{J}_{H-H}$ = 8 Hz, CH-naphthyl, 2 H), 7.37 (t, $^{3}\boldsymbol{J}_{H-H}$ = 8 Hz, CH-phenyl, 2 H), 7.45 (d, $^{3}\boldsymbol{J}_{H-H}$ = 8 Hz, CH-naphthyl, 2 H) ppm. ^{13}C{H} NMR [100.4 MHz, $CDCl_3$]: 100.7 (t, $^{2}\boldsymbol{J}_{C-F}$ = 26 Hz, CH-phenyl), 109.9 (CH-naphthyl), 117.08 (C-quart.), 121.6, 128.0 (CH-naphthyl), 135.1, 147.5 (C-quart.), 167.8 (dt, $^{1}J_{C-F}$ = 256 Hz, $^{2}J_{C-F}$ = 16.0 Hz, para-CF), 165.7 (dt, $^{1}J_{C-F}$ = 240 Hz, $^{2}J_{C-F}$ = 15 Hz, ortho-CF) ppm. Note: The ipso carbon bound to boron could not be detected in the ^{13}C NMR. ^{11}B NMR [128.4 MHz, $CDCl_3$]: 27.1 ppm. ^{19}F NMR [376.3 MHz, $CDCl_3$]: -96.8, -102.3 ppm. Anal. Calc. for $C_{16}H_8F_3BO_2$ (300.06): C, 64.05; H, 2.69; Found: C, 63.47; H, 2.52.

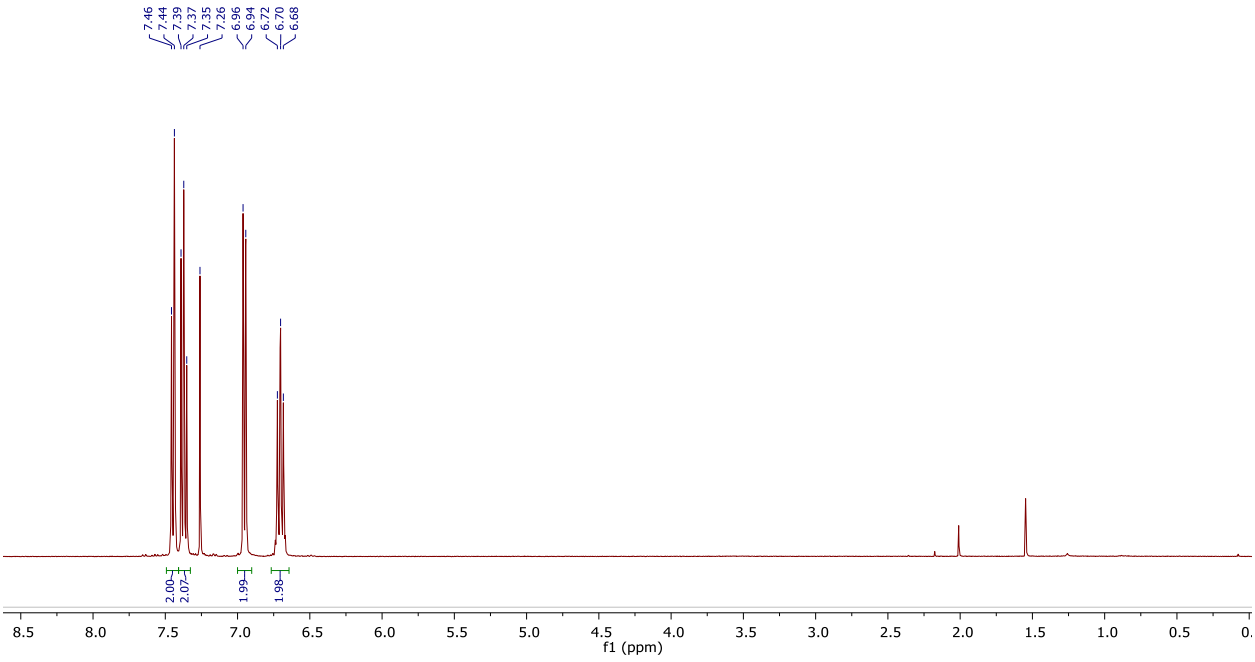


Figure S18. ^{1}H NMR spectrum of **4a** in $CDCl_3$ at room temperature.

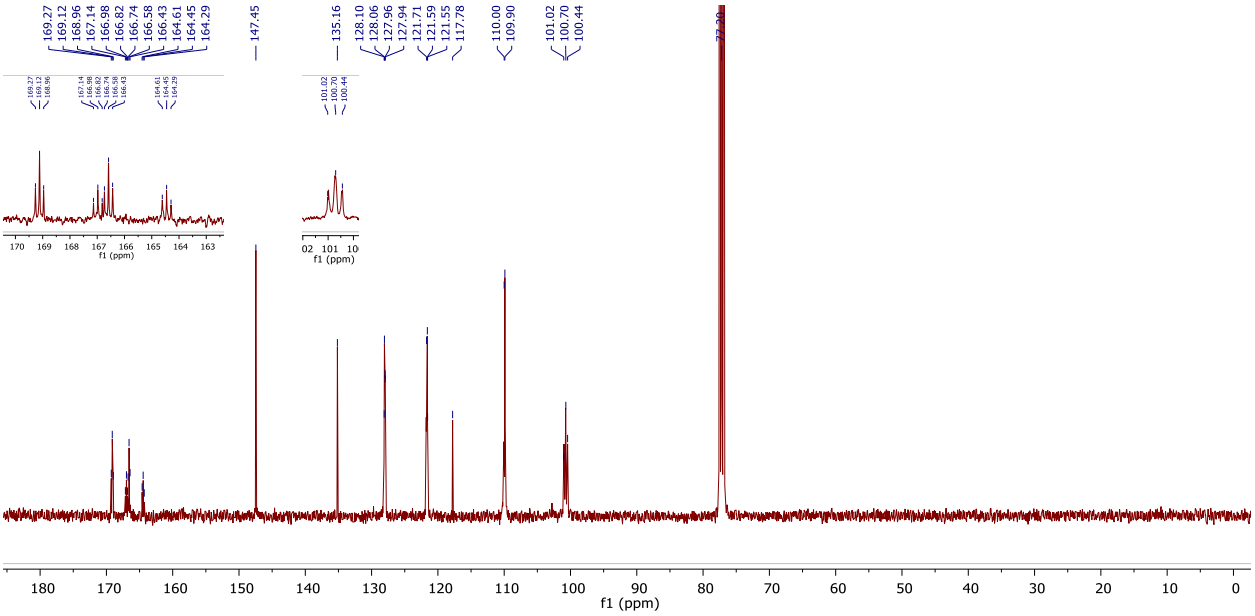


Figure S19. ^{13}C NMR spectrum of **4a** in $CDCl_3$ at room temperature.

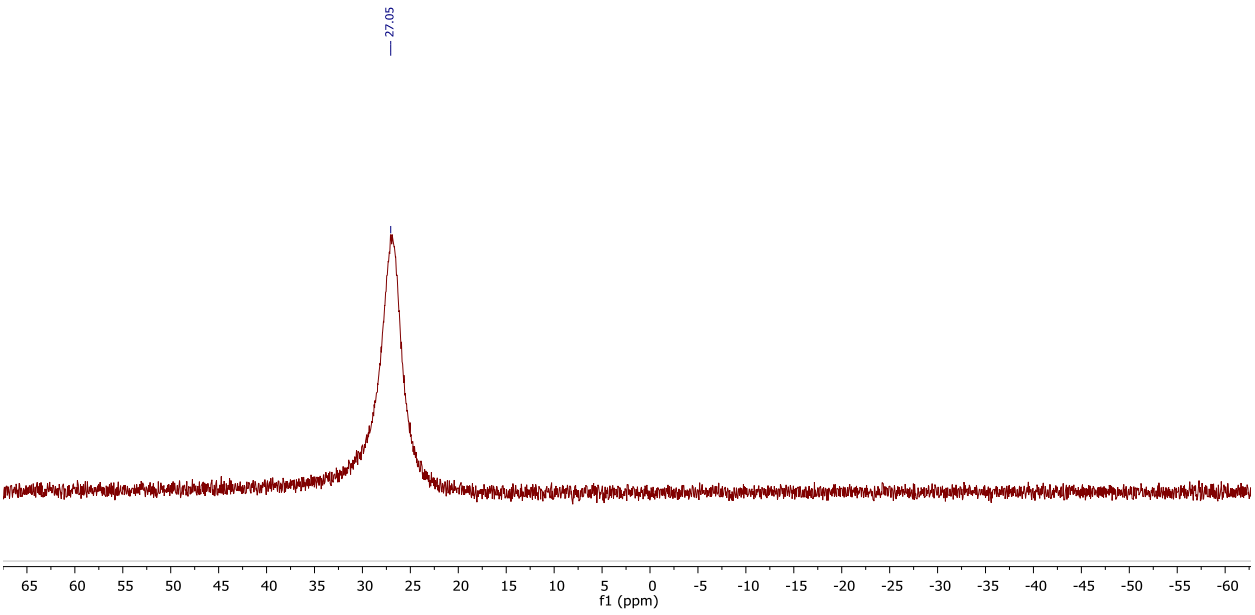


Figure S20. ^{11}B NMR spectrum of **4a** in $CDCl_3$ at room temperature.

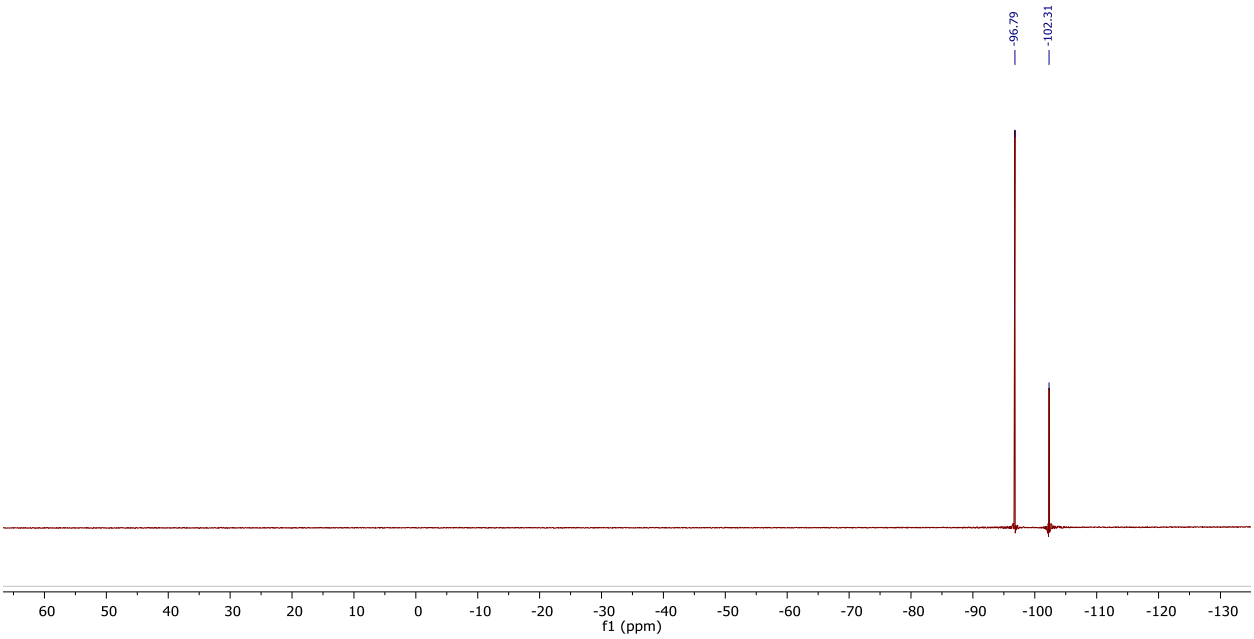
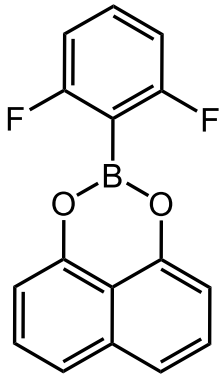


Figure S21. ^{19}F NMR spectrum of **4a** in $CDCl_3$ at room temperature.



5a

5a. 1,8-naphthalenediol (0.25 g, 1.5 mmol), 2,6-difluorophenyl boronic acid (0.24 g, 1.5 mmol), acetonitrile (10 mL). Colorless crystals. Yield 0.36 g (85%). M.p. 142-143 °C. ^{1}H NMR [400 MHz, $CDCl_3$]: 6.92-6.97 (m, 4H), 7.35-7.50 (m, 5 H) ppm. $^{13}C\{H\}$ NMR [100.4 MHz, $CDCl_3$]: 109.9 (d, $^{3}J_{C-F}$ = 11 Hz, CH), 111.6 (CH), 117.8 (C-quart.), 121.6, 128.0, 133.9 (CH), 135.2, 147.6 (C-quart.), 167.0 (dd, $^{1}J_{C-F}$ = 253 Hz, $^{2}J_{C-F}$ = 12.1 Hz ortho-CF) ppm. Note: The ipso carbon bound to boron could not be detected in the ^{13}C NMR. ^{11}B NMR [128.4 MHz, $CDCl_3$]. 27.0 ppm. ^{19}F NMR [376.3 MHz, $CDCl_3$]: -100.4 ppm. Anal. Calc. for $C_{16}H_9F_2BO_2$ (282.05): C, 68.13; H, 3.22; Found: C, 67.55; H, 3.05.

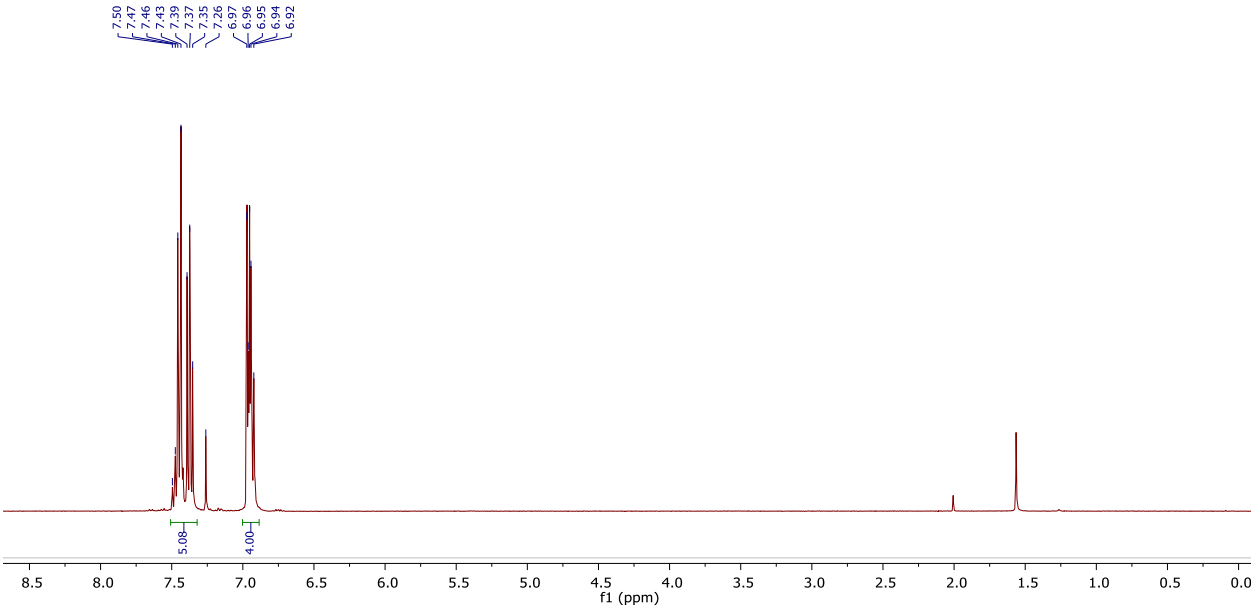


Figure S22. ^{1}H NMR spectrum of **5a** in $CDCl_3$ at room temperature.

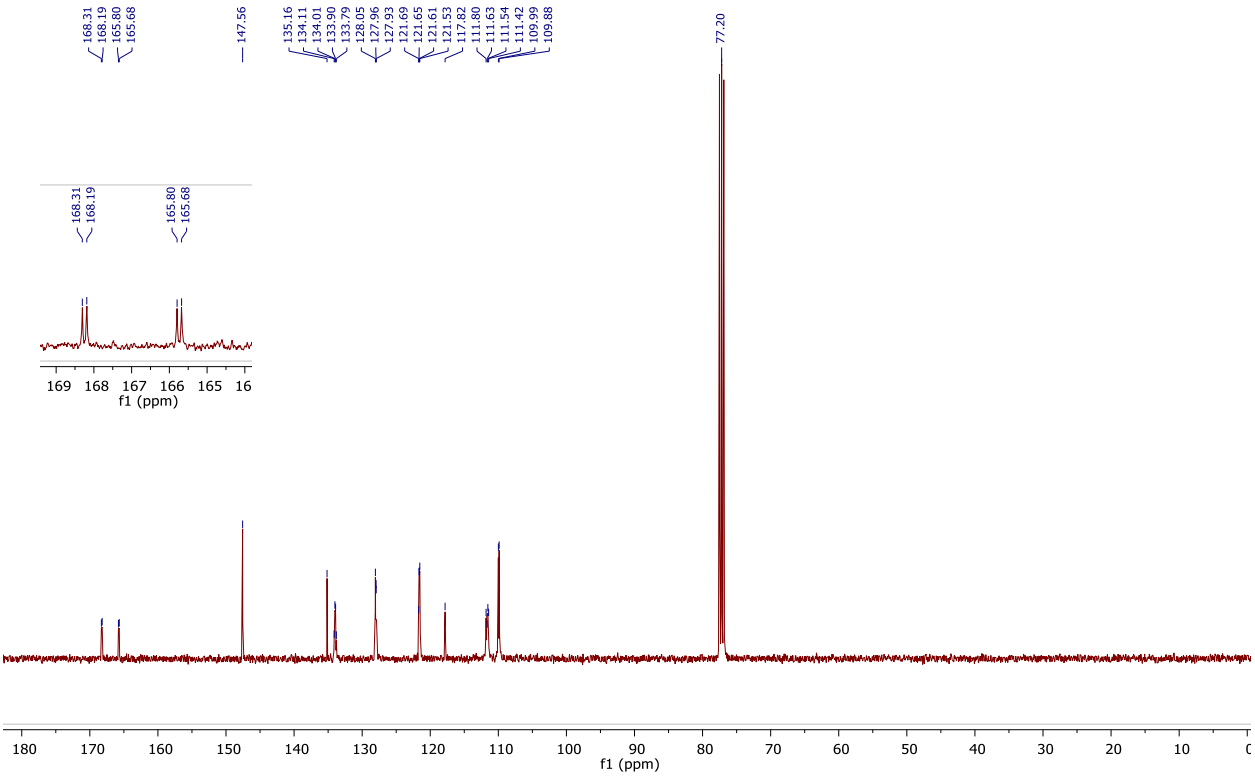


Figure S23. ^{13}C NMR spectrum of **5a** in $CDCl_3$ at room temperature.

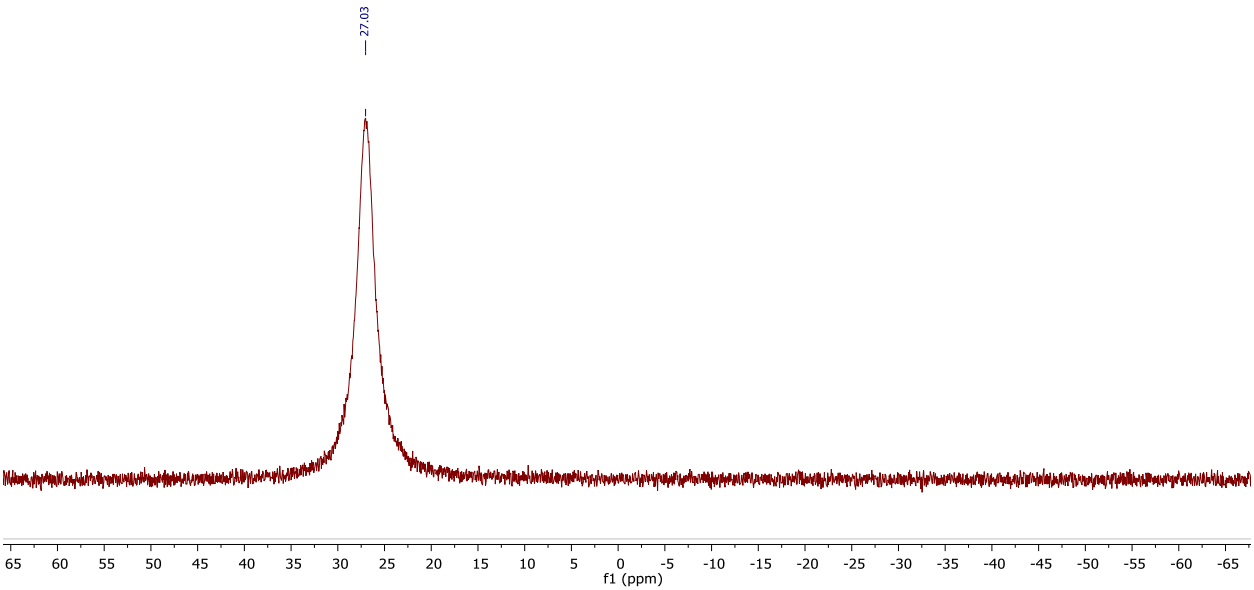


Figure S24. ^{11}B NMR spectrum of **5a** in $CDCl_3$ at room temperature.

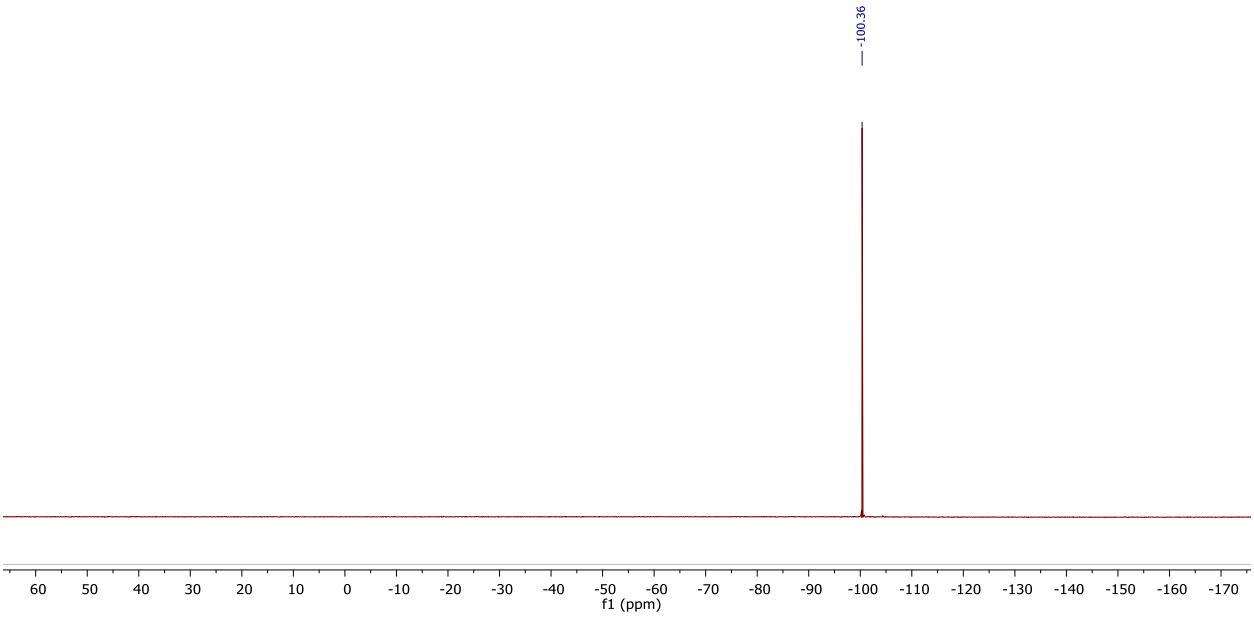
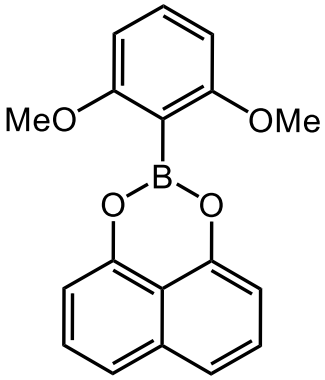


Figure S25. ^{19}F NMR spectrum of **5a** in $CDCl_3$ at room temperature.



8a

8a. 1,8-naphthalenediol (0.14 g, 0.76 mmol), phenyl boronic acid (0.12 g, 0.76 mmol), acetonitrile (10 mL). Stored for 2 days in a fridge. Colorless crystals. Yield 0.23 g (75 %). M.p. 202-203°C. ^{1}H NMR [400 MHz, $CDCl_3$]: 3.80 (s, CH_3, 6 H), 6.57 (d, $^{3}J_{H\text{-}H}$ = 12 Hz, CH-naphthyl, 2 H), 6.94 (d, $^{3}J_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.32-7.44 (m, CH-naphthyl, CH-phenyl, 5 H) ppm; ^{13}C{H} NMR [100.4 MHz, $CDCl_3$]: 55.9 (OCH_3), 103.7 (CH-phenyl), 109.7 (CH-naphthyl), 117.9 (C-quart), 121.1, 127.9 (CH-naphthyl), 132.1 (CH-phenyl), 135.2, 148.3, 163.4 (C-quart) ppm. Note: The ipso carbon bound to boron could not be detected in the ^{13}C NMR. ^{11}B NMR [128.4 MHz, $CDCl_3$]: 28.3 ppm. Anal. Calc. for $C_{16}H_{11}BO_2$ (306.12): C, 70.62; H, 4.94; Found: C, 70.43; H, 4.78.

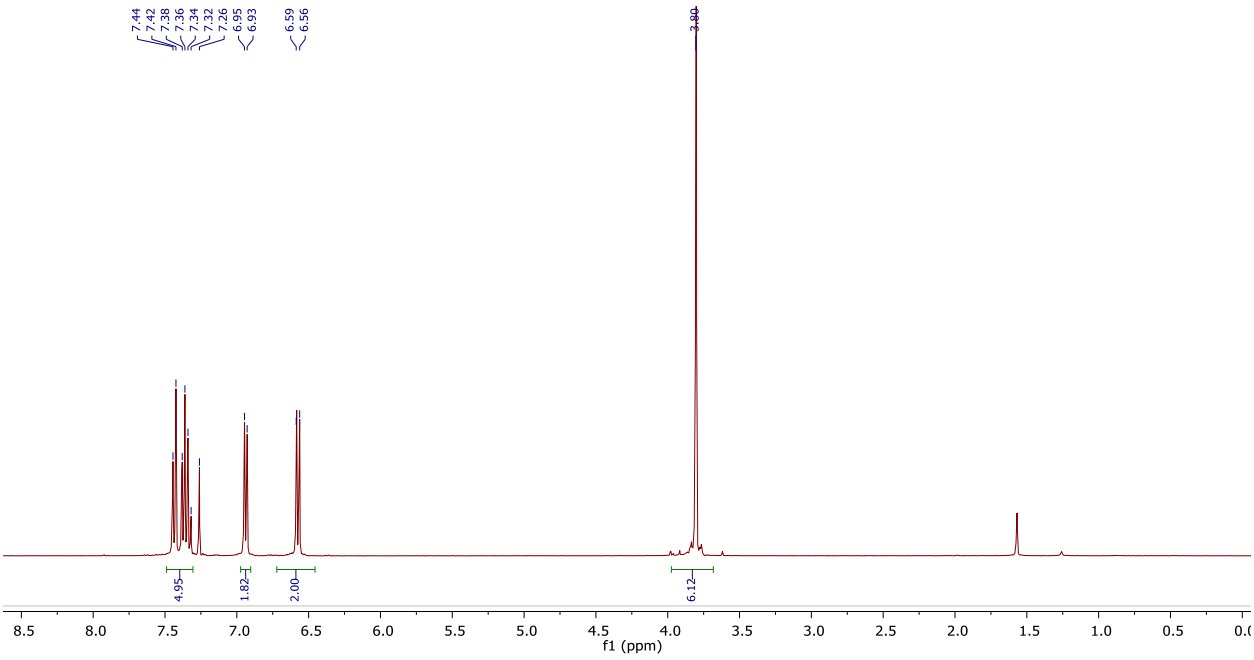


Figure S26. ^{1}H NMR spectrum of **8a** in $CDCl_3$ at room temperature.

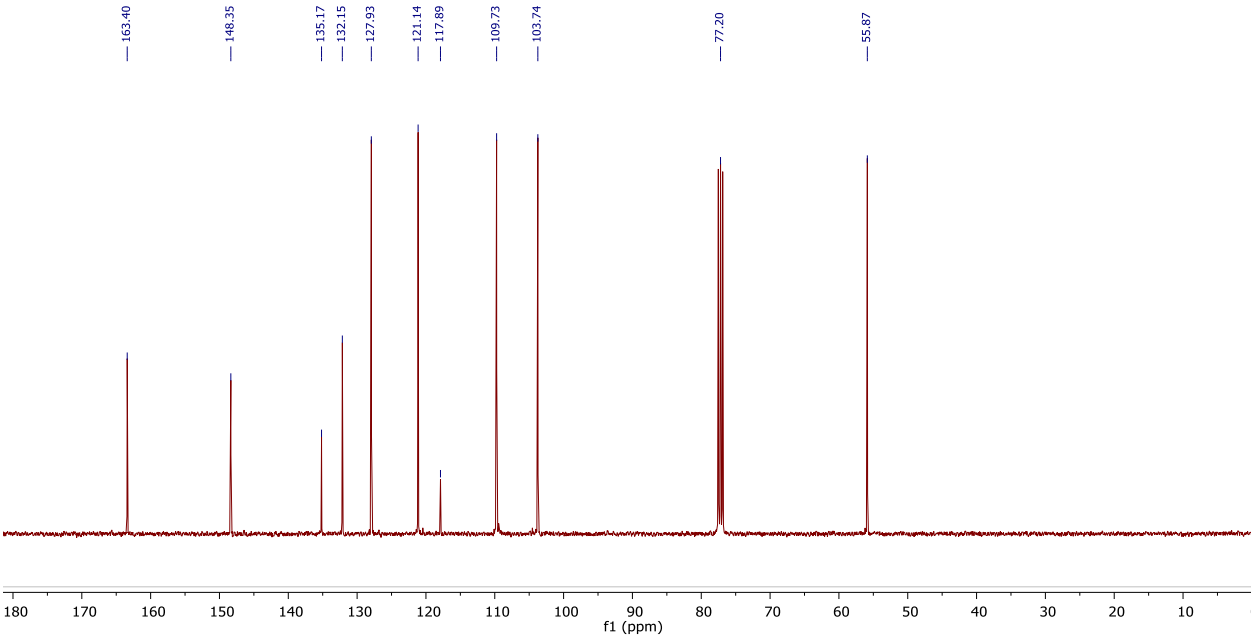


Figure S27. ^{13}C NMR spectrum of **8a** in $CDCl_3$ at room temperature.

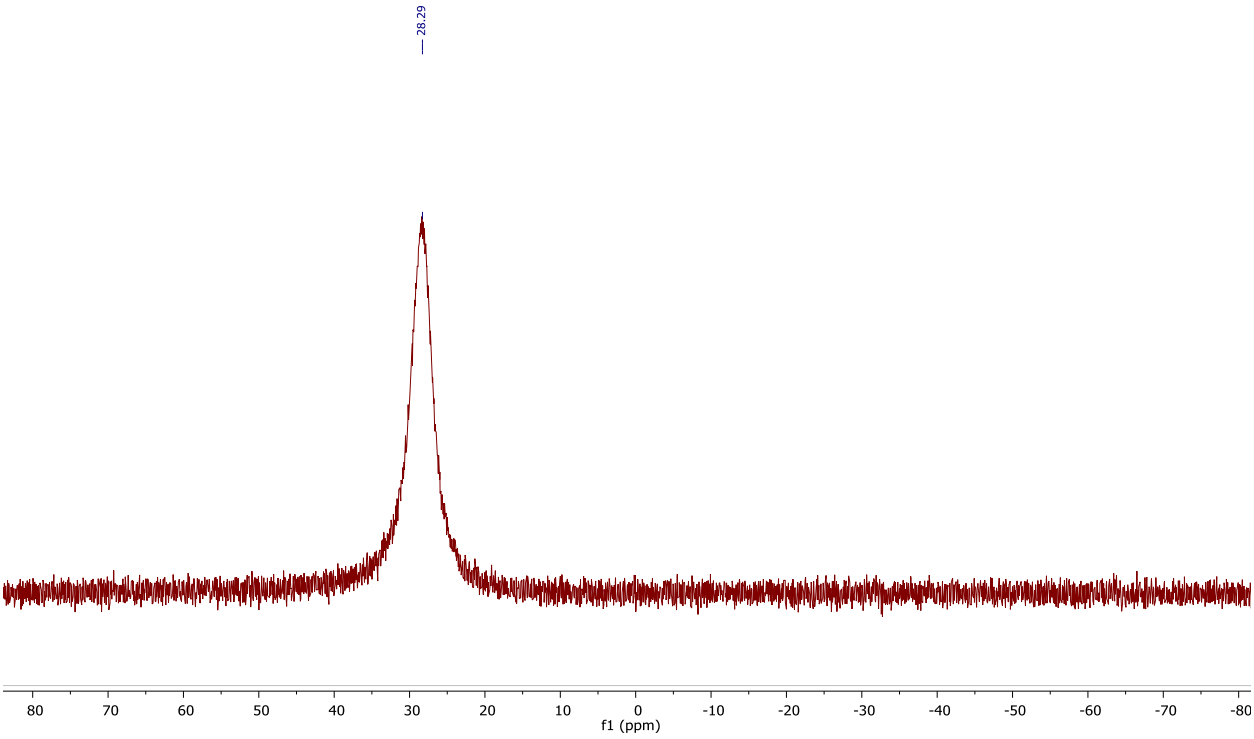
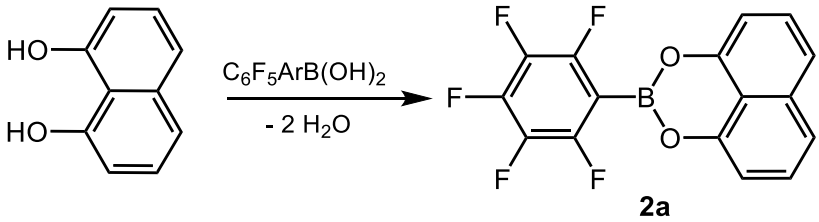


Figure S28. ^{11}B NMR spectrum of **8a** in $CDCl_3$ at room temperature.

2.4.2 Synthesis of **2a**



2a

1,8-naphthalenediol (0.26 g, 1.6 mmol), $C_6F_5B(OH)_2$ (0.35 g, 1.6 mmol) and 15 mL of dry DCM were added to a 60 mL Schlenk flask with a magnetic stir bar under nitrogen. After stirring the mixture for about 20 hours at room temperature, all volatiles were removed under vacuum and the solid residue was recrystallized from acetonitrile to give **2a** as colorless crystals. Yield 0.34 g (60%). M.p. 167-168 °C. ^{1}H NMR [400 MHz, $CDCl_3$]: 6.97 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.39 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.47 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H) ppm. ^{13}C{H} NMR [100.4 MHz, $CDCl_3$]: 110.2 (CH-naphthyl), 117.6 (C-quart.), 122.0, 128.0 (CH-naphthyl), 135.2 (C-quart.), 137.6 (d, $^{1}J_{C\text{-}F}$ = 253 Hz, C-F), 143.6 (d, $^{1}J_{C\text{-}F}$ = 258 Hz, C-F), 147.0 (C-quart.), 149.9 (d, $^{1}J_{C\text{-}F}$ = 252 Hz, C-F) ppm. Note: The ipso carbon bound to boron could not be detected in the ^{13}C NMR. ^{11}B NMR [128.4 MHz, $CDCl_3$]: 27.9 ppm. ^{19}F NMR [376 MHz, $CDCl_3$]: -129.3, -148.1, -161.2 ppm. Anal. Calc. for $C_{16}H_6BF_5O_2$ (336.02): C, 57.19; H, 1.8. Found: C, 56.92; H, 1.26.

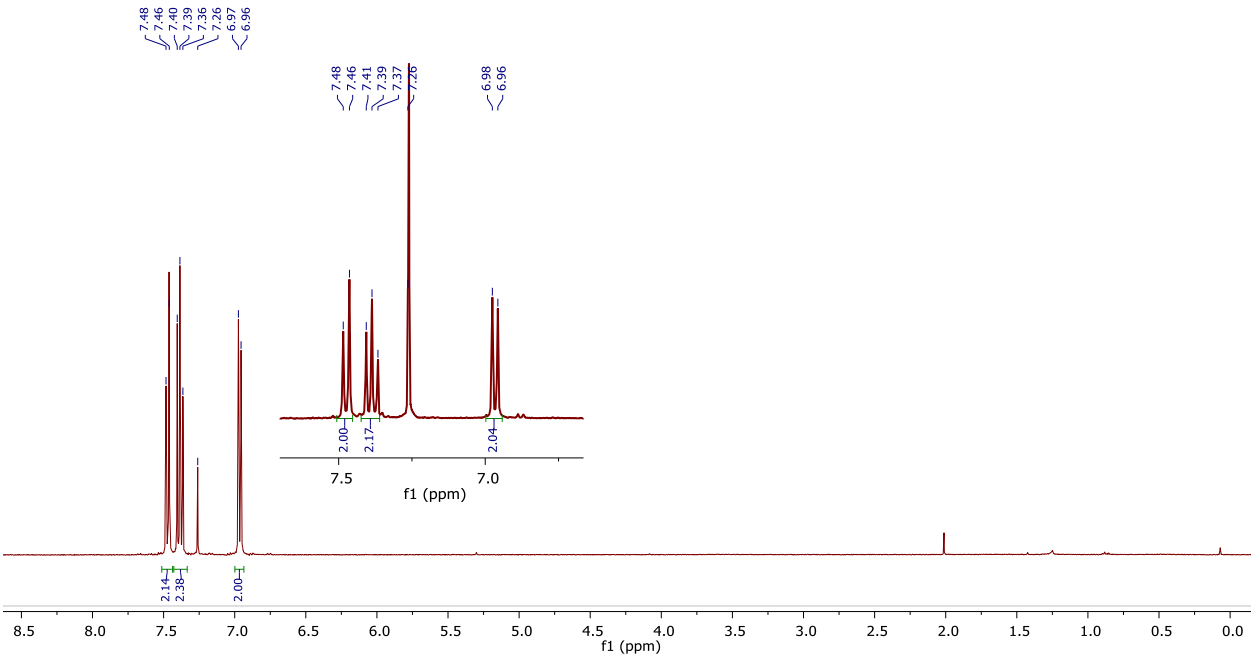


Figure S29. ^{1}H NMR spectrum of **2a** in $CDCl_3$ at room temperature.

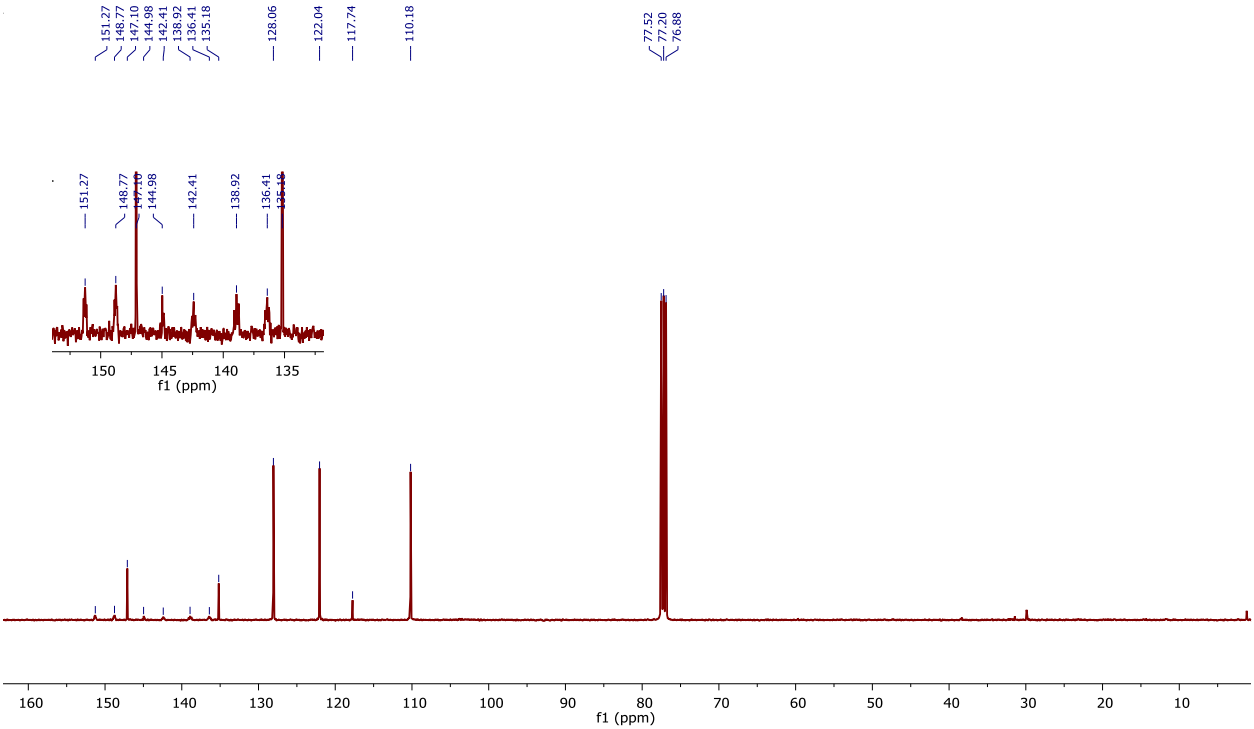


Figure S30. ^{13}C NMR spectrum of **2a** in $CDCl_3$ at room temperature.

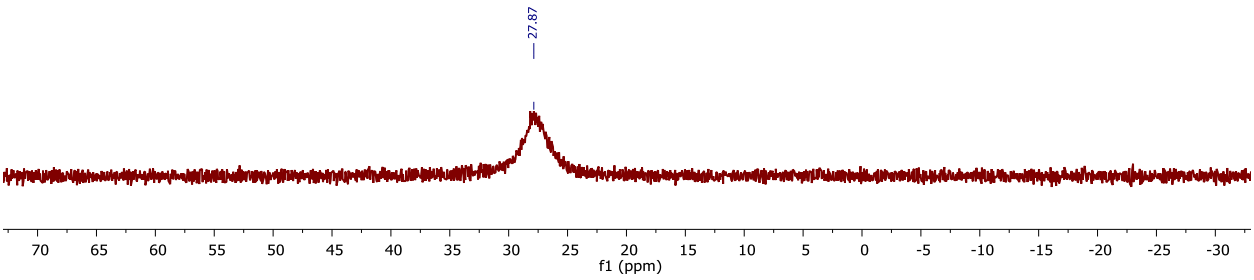


Figure S31. ^{11}B NMR spectrum of **2a** in $CDCl_3$ at room temperature.

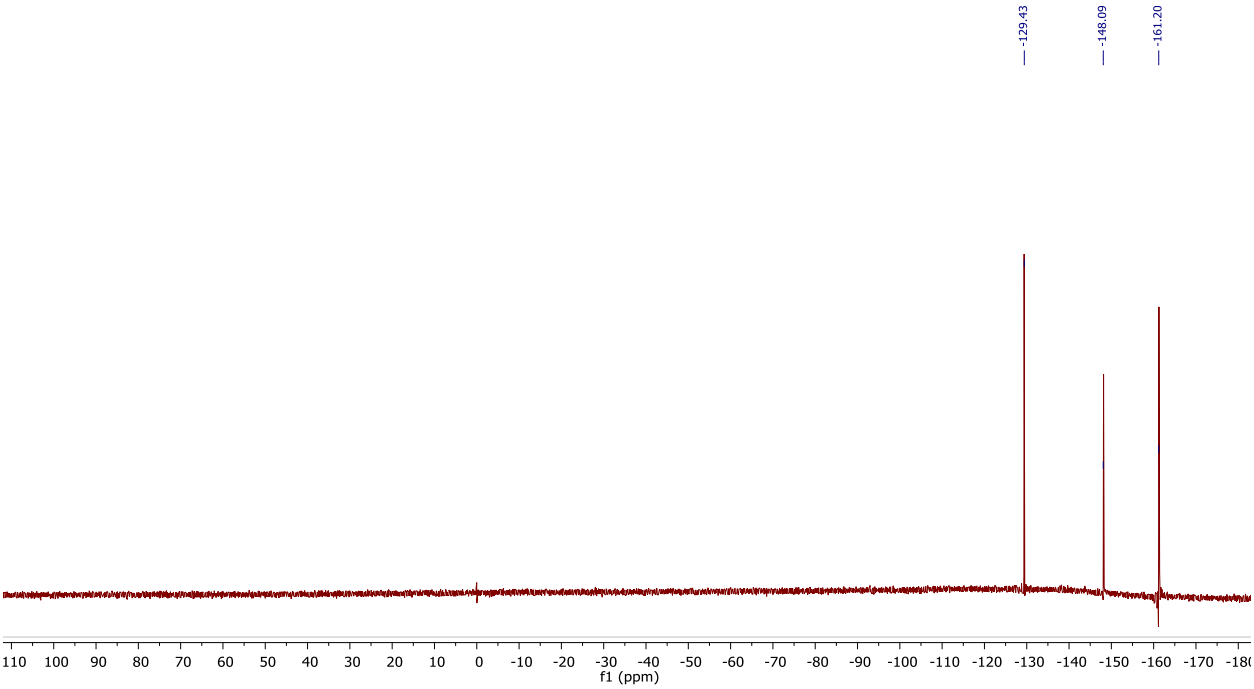
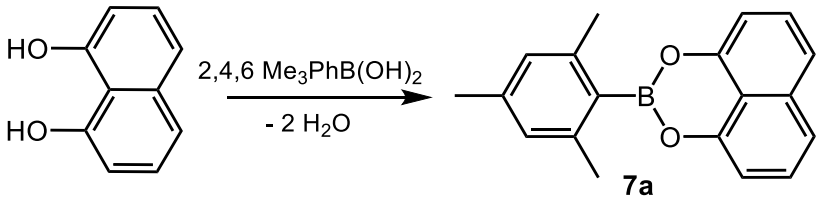


Figure S32. ^{19}F NMR spectrum of **2a** in $CDCl_3$ at room temperature.

2.4.3 Synthesis of **7a**



1,8-naphthalenediol (0.24 g, 1.5 mmol), 2,4,6-trimethylphenyl boronic acid (0.246 g, 1.5 mmol) and 15 mL of toluene were added to a 20 mL scintillation vial with magnetic stir bar. After stirring the mixture for one day at room temperature, all volatiles were removed under vacuum and the residue was recrystallized from acetonitrile to give 0.26 g (63%) of **7a** as a colorless crystalline solid. M.p. 98-100 °C. ^{1}H NMR [400 MHz, $CDCl_3$]: 2.31 (s, para-CH_3, 3 H), 2.49 (s, ortho-CH_3, 6 H), 6.89 (s, CH-phenyl, 2 H), 6.92 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.37 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.45 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H) ppm; ^{13}C{H} NMR [100.4 MHz, $CDCl_3$]: 21.5 (p-CH_3), 22.6 (m-CH_3), 109.6 (CH-naphthyl), 117.7 (C-quart.), 121.3 (CH-naphthyl), 127.9, 128.0 (CH-phenyl), 135.2, 139.9, 142.0, 147.9 (C-quart.) ppm. Note: The ipso carbon bound to boron could not be detected in the ^{13}C NMR. ^{11}B NMR [128.4 MHz, $CDCl_3$]: 29.9 ppm. Anal. Calc. for $C_{19}H_{17}BO_2$ (288.15): C, 79.20; H, 5.95. Found: C, 78.74; H, 5.87.

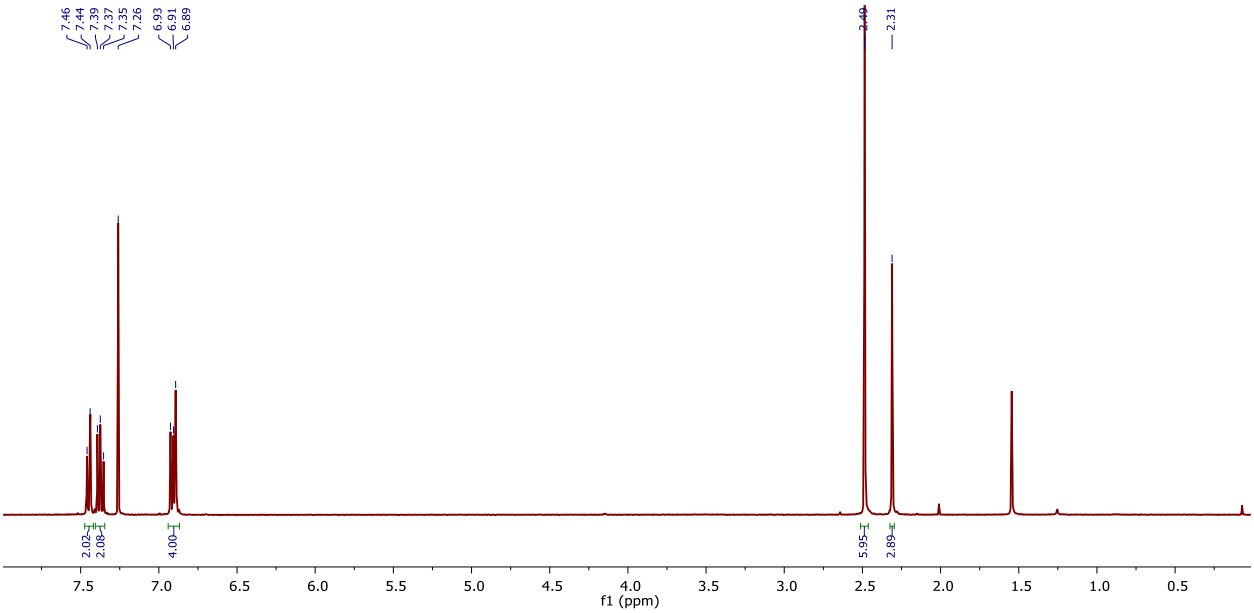


Figure S33. ^{1}H NMR spectrum of **7a** in $CDCl_3$ at room temperature.

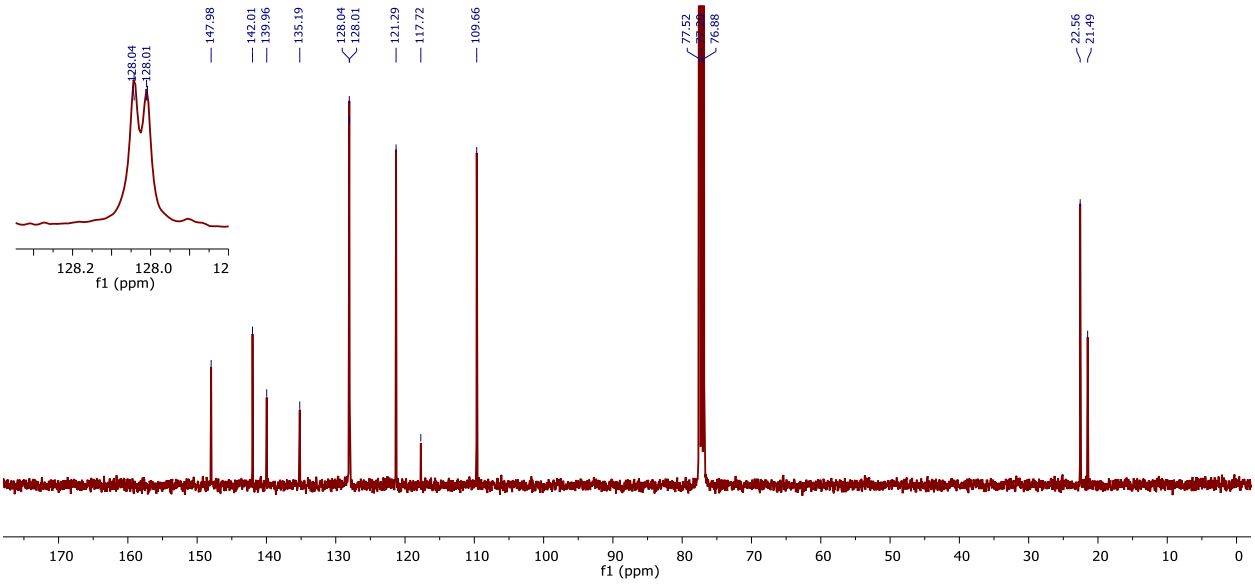


Figure S34. ^{13}C NMR spectrum of **7a** in $CDCl_3$ at room temperature.

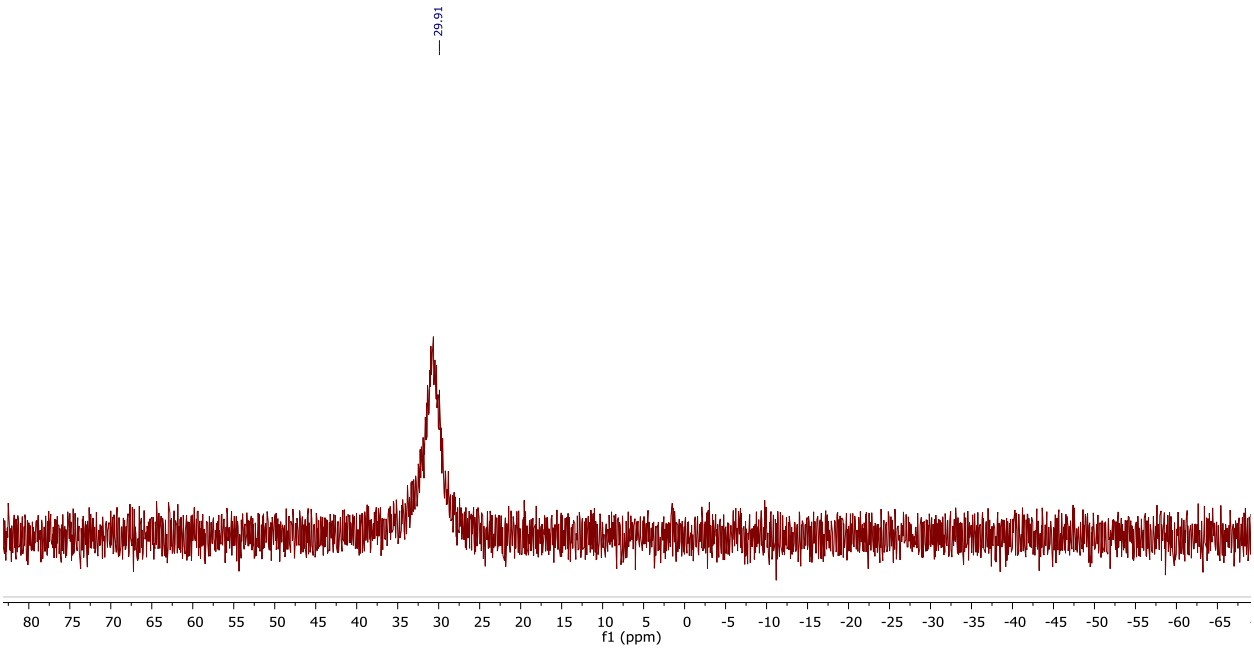
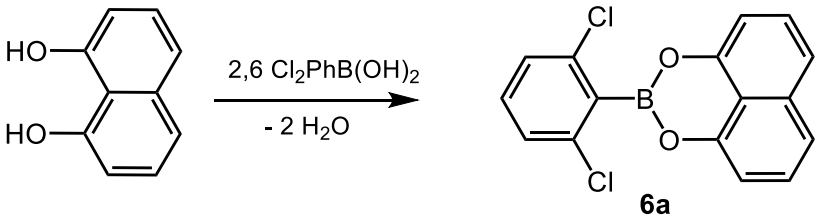


Figure S35. ^{11}B NMR spectrum of **7a** in $CDCl_3$ at room temperature.

2.4.4 Synthesis of **6a**



6a

1,8-naphthalenediol (0.29 g, 1.5 mmol), 2,6-dichlorophenyl boronic acid (0.242 g, 1.5 mmol), Na_2SO_4 (2 g) and 15 mL of $CHCl_3$ were added to a 100 mL round bottom flask equipped with a magnetic stir bar. The mixture was stirred for ca. 20 hours at room temperature and filtered to separate Na_2SO_4. Then all volatiles were evaporated under vacuum (rotavap) and the solid residue was extracted with circa 100 mL of hexanes. After removal of hexanes under vacuum (rotavap) the raw product was distilled under vacuum using a Kugelrohrofen (180°C, 10^{-1} mbar) to give **6a** as a colorless crystalline solid. Yield 0.4 g (84%). M.p. 158-159 °C. ^1H NMR [400 MHz, $CDCl_3$]: 6.96 (d, $^3\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.32 (s, CH-naphthyl, 3 H), 7.39 (t, $^3\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl), 2 H), 7.48

(d, $^{3}J_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H) ppm. $^{13}C\{H\}$ NMR [100.4 MHz, $CDCl_3$] 110.0 (CH-naphthyl), 117.8 (C-quart), 121.8, 127.2 (CH-naphthyl), 128.0 (m-CH-phenyl), 131.8 (p-CH-phenyl), 135.2, 137.9, 147.7 (C-quart.) ppm. Note: The ipso carbon bound to boron could not be detected in the ^{13}C NMR. ^{11}B NMR [128.4 MHz, $CDCl_3$]: 27.6 ppm. Anal. Calc. for $C_{16}H_9BCl_2O_2$ (314.96): C, 61.02; H, 2.88. Found: C, 60.76; H, 2.61.

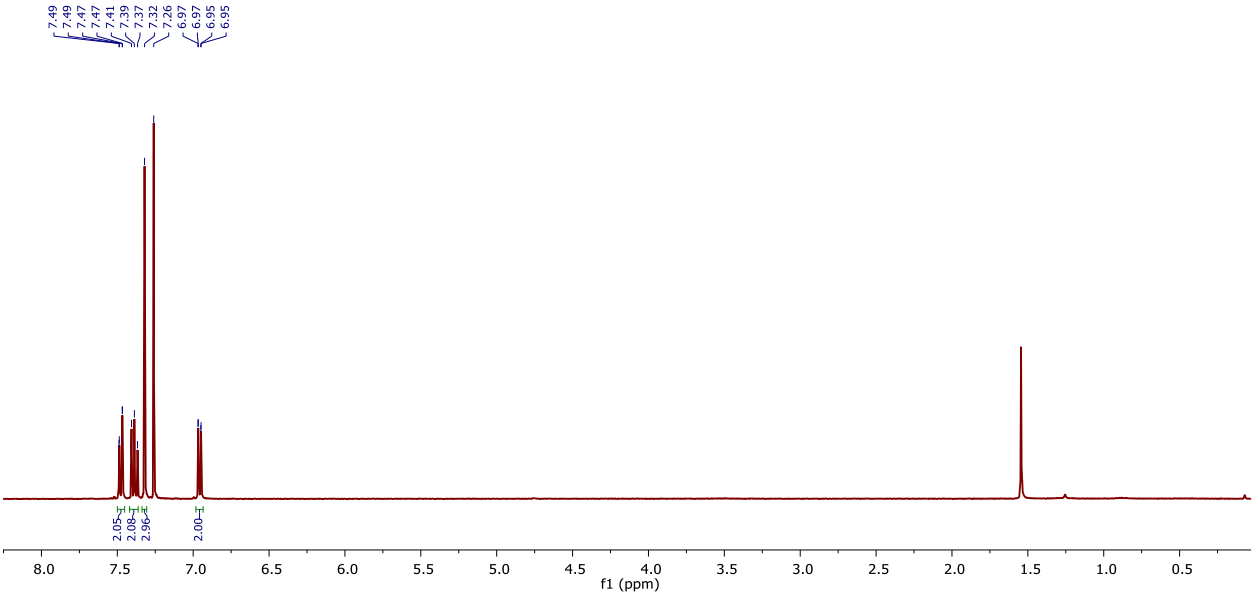


Figure S36. ^{1}H NMR spectrum of **6a** in $CDCl_3$ at room temperature.

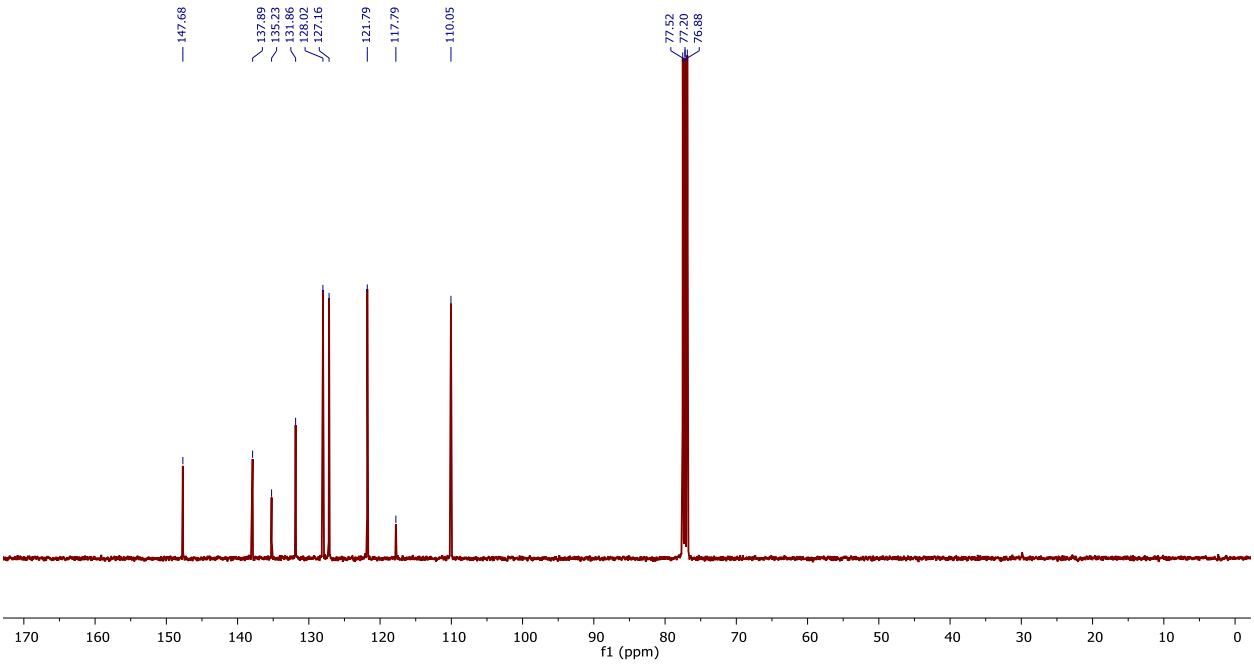


Figure S37. ^{13}C NMR spectrum of **6a** in $CDCl_3$ at room temperature.

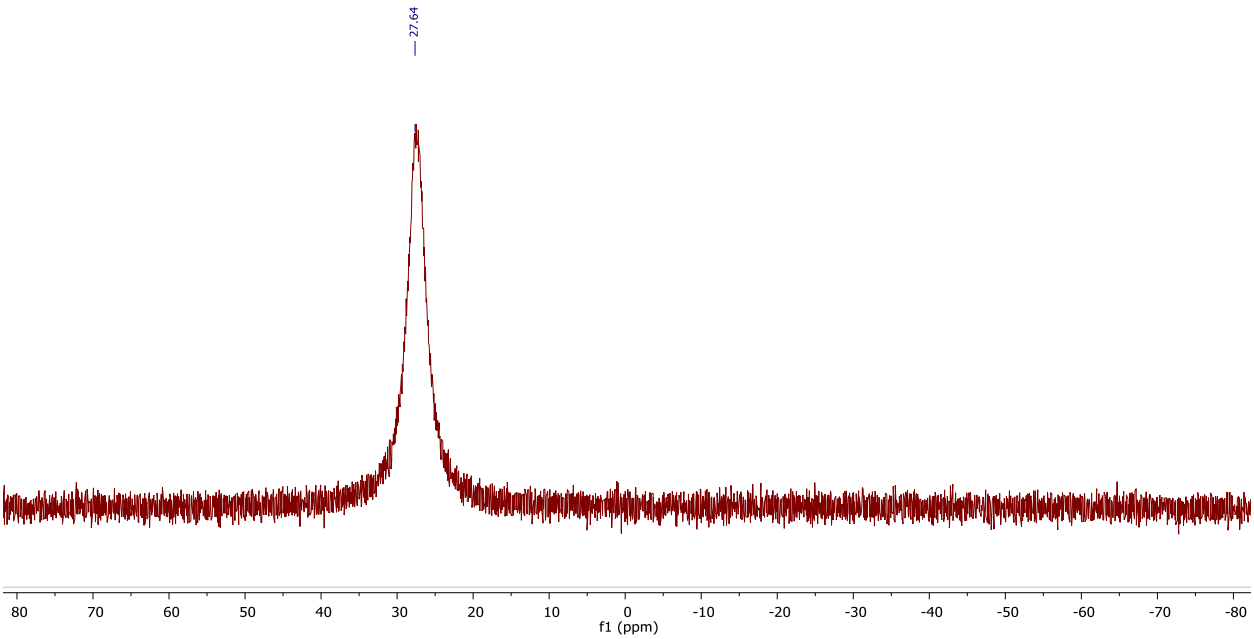
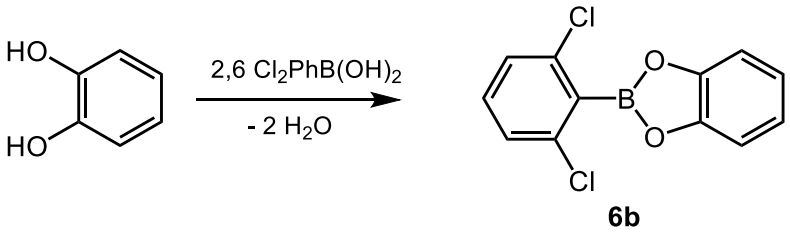


Figure S38. ^{11}B NMR spectrum of **6a** in $CDCl_3$ at room temperature.

2.4.5 Synthesis of **6b**



6b

Catechol (0.12 g, 1.05 mmol), 2,6-dichlorophenyl boronic acid (0.2 g, 1.05 mmol) and acetonitrile (10 mL) were added to a 20 mL scintillation vial. The mixture was heated overnight at 80°C. After cooling to room temperature, all the volatiles were removed under vacuum. The residue was sublimed under vacuum using a Kugelrohrofen (180°C, 10^{-1} mbar) to give **6b** as a colorless crystalline solid. Yield 0.15 g (65%). M.p: 85-86°C. ^{1}H NMR [400 MHz, C_6D_6]: 6.45 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-phenyl, 1 H), 6.78 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8.0 Hz, CH-catechol, 4 H), 7.09 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 4 Hz, CH-phenyl, 2 H) ppm. $^{13}C\{H\}$ NMR [100.4 MHz, C_6D_6]: 113.0, 123.2, 126.9, 132.2 (CH), 139.0, 148.3 (C-quart) ppm. Note: The ipso carbon bound to boron could not be detected in the ^{13}C NMR. ^{11}B NMR (128.4 MHz,

C_6D_6): 30.7 ppm. Anal. Calc. for $C_{12}H_7BCl_2O_2$ (264.9): C, 54.41; H, 2.66; Found: C, 53.49, H, 2.52.

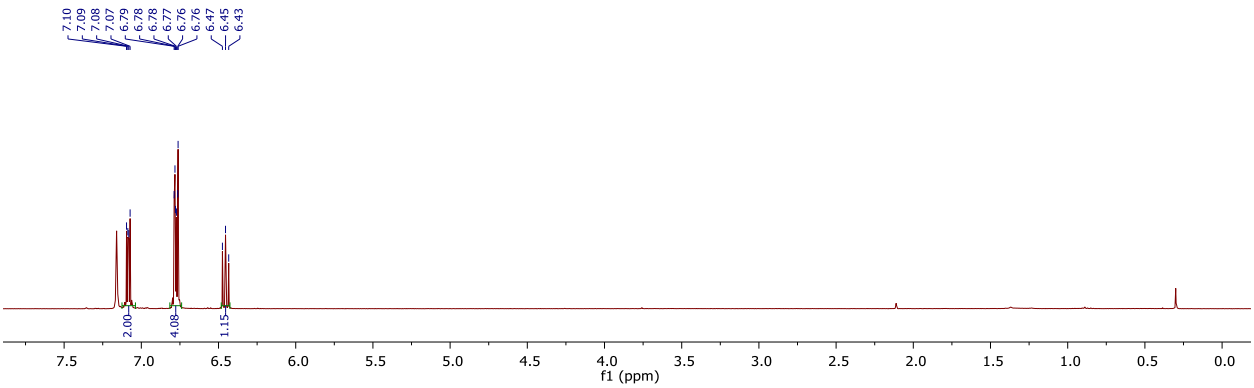


Figure S39. ^{1}H NMR spectrum of **6b** in $CDCl_3$ at room temperature.

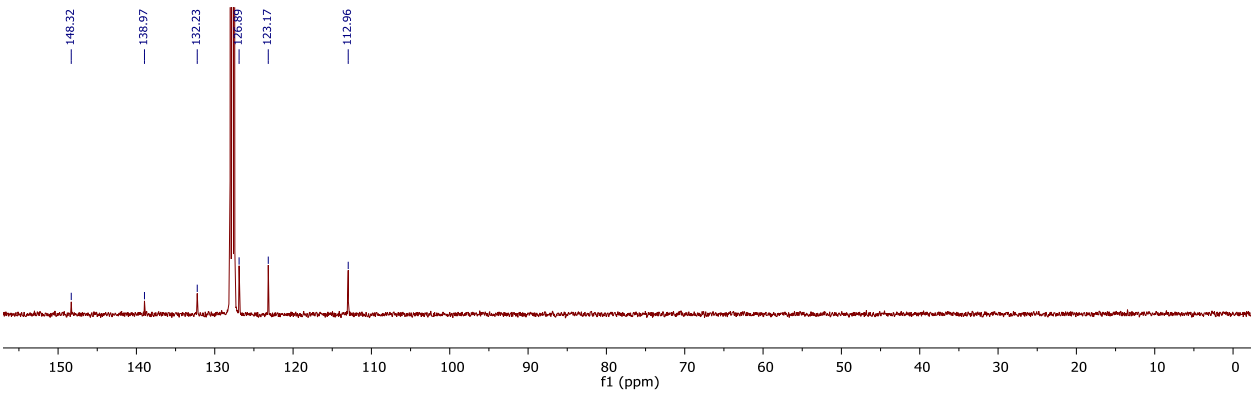


Figure S40. ^{13}C NMR spectrum of **6b** in $CDCl_3$ at room temperature.

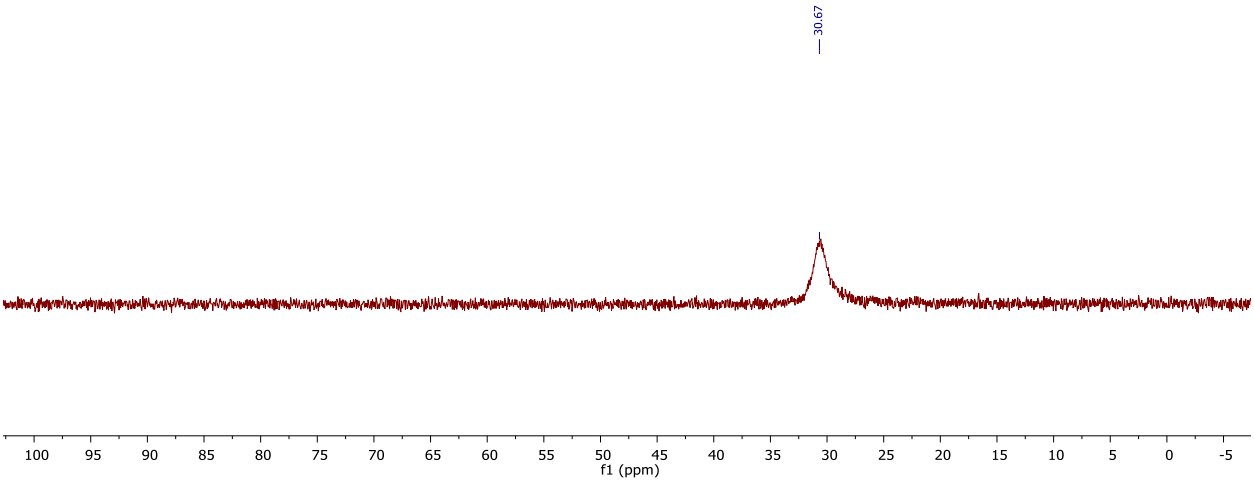
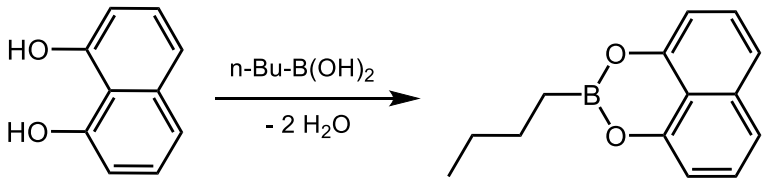


Figure S41. ^{11}B NMR spectrum of **6b** in $CDCl_3$ at room temperature.

2.4.6 Synthesis of **9a**



9a

1,8-naphthalenediol (0.16 g, 0.1 mmol), n-butyl-boronic acid (0.1 g, 0.1 mmol) and acetonitrile (10 mL) were added to a 20 mL scintillation vial with screw cap. After heating the reaction mixture at 80°C overnight, all volatiles were removed under vacuum. The residue was distilled under vacuum using a Kugelrohrofen (130°C, 10^{-1} mbar) to give 210 mg (93 %) of **9a** as colorless oil. ^{1}H NMR [400 MHz, $CDCl_3$]: 0.96 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8.0 Hz, CH_3, 3 H), 1.10 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, BCH_2, 2 H), 1.42 (m, CH_2, 2 H),1.58 (m, CH_2, 2 H), 6.84 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.35 (m, CH-naphthyl, 4 H). ^{13}C{H} NMR [100.4 MHz, $CDCl_3$] 14.1 (CH_3), 14.9, 25.5, 25.7 (CH_2), 109.3 (CH-naphthyl), 117.6 (C-quart), 121.0, 127.9 (CH-naphthyl), 135.8, 147.9 (C-quart) ppm. ^{11}B NMR [128.4 MHz, $CDCl_3$]: 31.9 ppm. Anal. Calc. for $C_{16}H_{11}BO_2$ (MW. 226.08) C, 74.38; H, 6.69; Found: C, 74.52; H, 7.11.

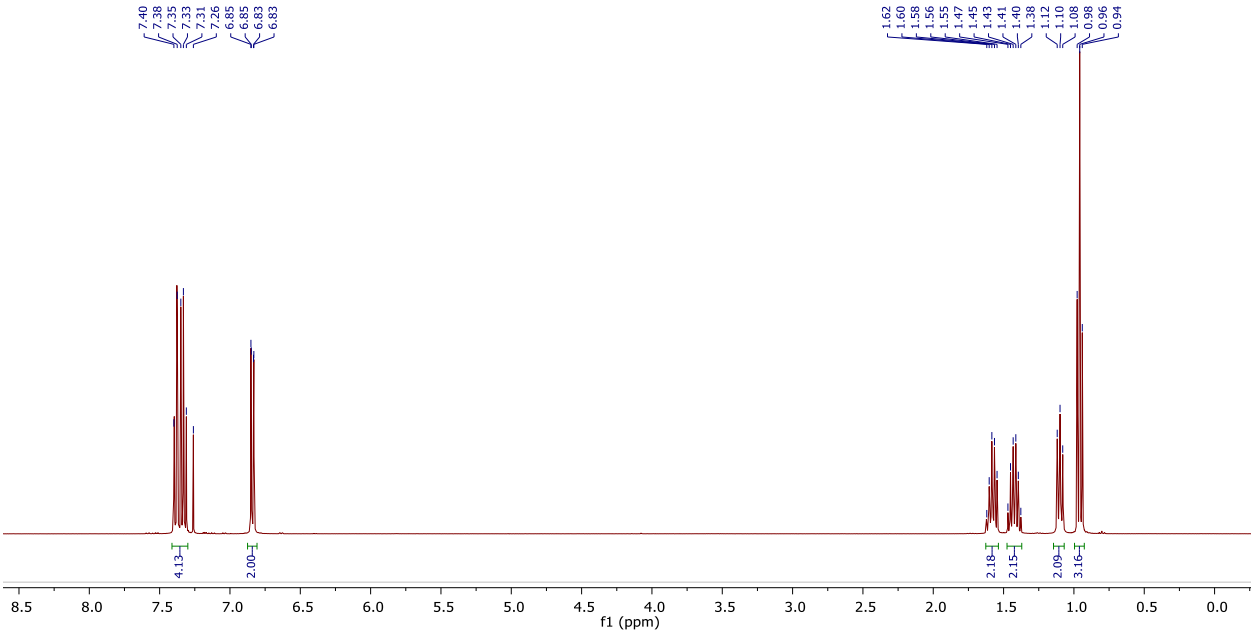


Figure S42. ^{1}H NMR spectrum of **9a** in $CDCl_3$ at room temperature.

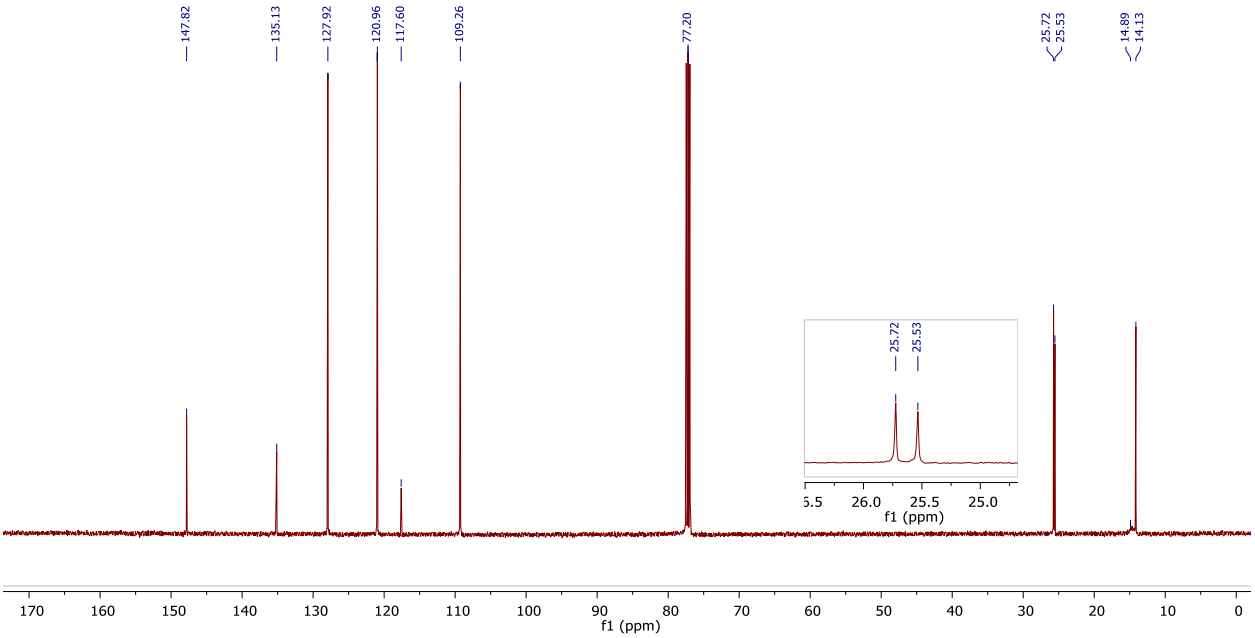


Figure S43. ^{13}C NMR spectrum of **9a** in $CDCl_3$ at room temperature.

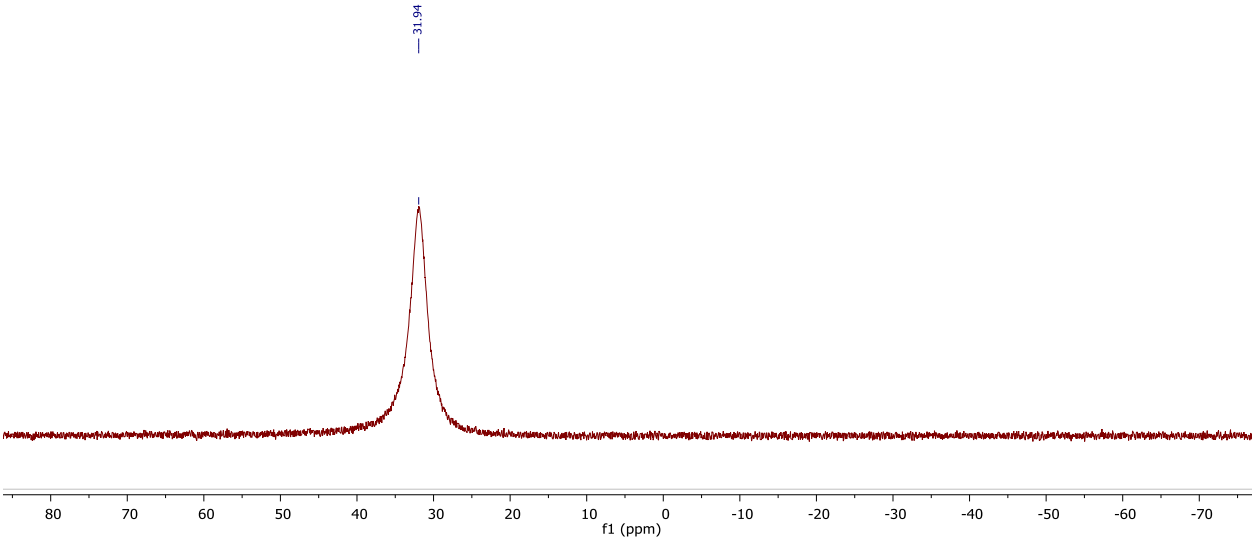
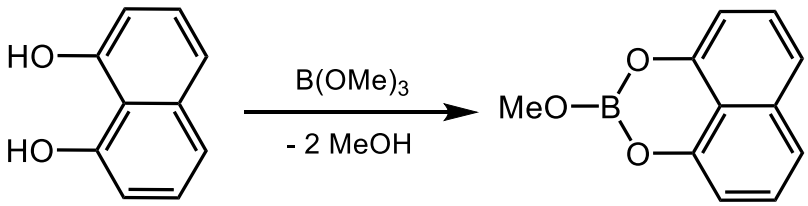


Figure S44. ^{11}B NMR spectrum of **9a** in $CDCl_3$ at room temperature.

2.4.7 Synthesis of **10a**



10a

1,8-naphthalenediol (1 g, 6.2 mmol) was added portion-wise to a stirred solution of $B(OMe)_3$ (1.9 g, 18.6 mmol) in anhydrous CH_2Cl_2 (10 mL). After stirring the reaction mixture overnight at room temperature, all volatiles were removed under vacuum. The residue was distilled under vacuum using a Kugelrohrofen (140°C, 10^{-2} mbar) to give **10a** as a colorless crystalline solid. Yield 1.22 g (98%). ^{1}H NMR [400 MHz, $CDCl_3$]: 3.86 (s, CH_3, 3 H), 6.88 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.34 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.40 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H) ppm. ^{13}C{H} NMR [100.4 MHz, $CDCl_3$] 52.1 (OCH_3), 109.6 (CH-naphthyl), 116.3 (C-quart), 121.0, 127.9 (CH-naphthyl), 135.3, 148.9 (C-quart) ppm. ^{11}B NMR [128.4 MHz, $CDCl_3$]: 17.8 ppm. Anal. Calc. for $C_{11}H_9BO_3$ (200.0): C, 66.06; H, 4.54; Found: 65.50; H, 4.25.

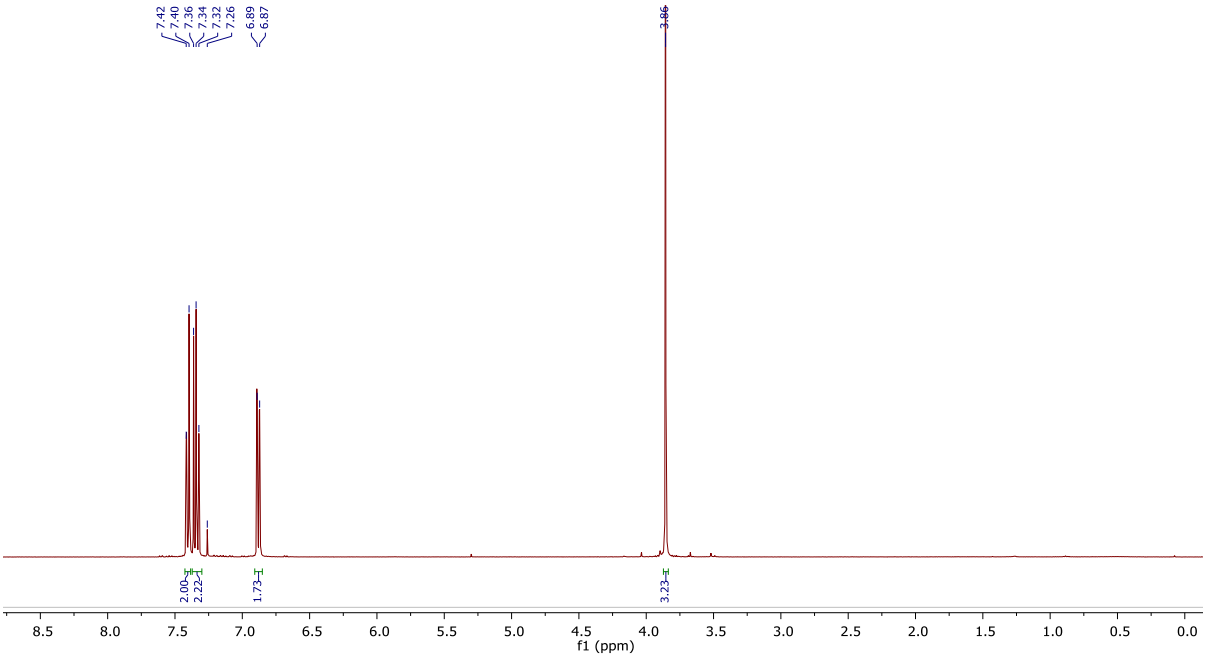


Figure S45. ^{1}H NMR spectrum of **10a** in $CDCl_3$ at room temperature.

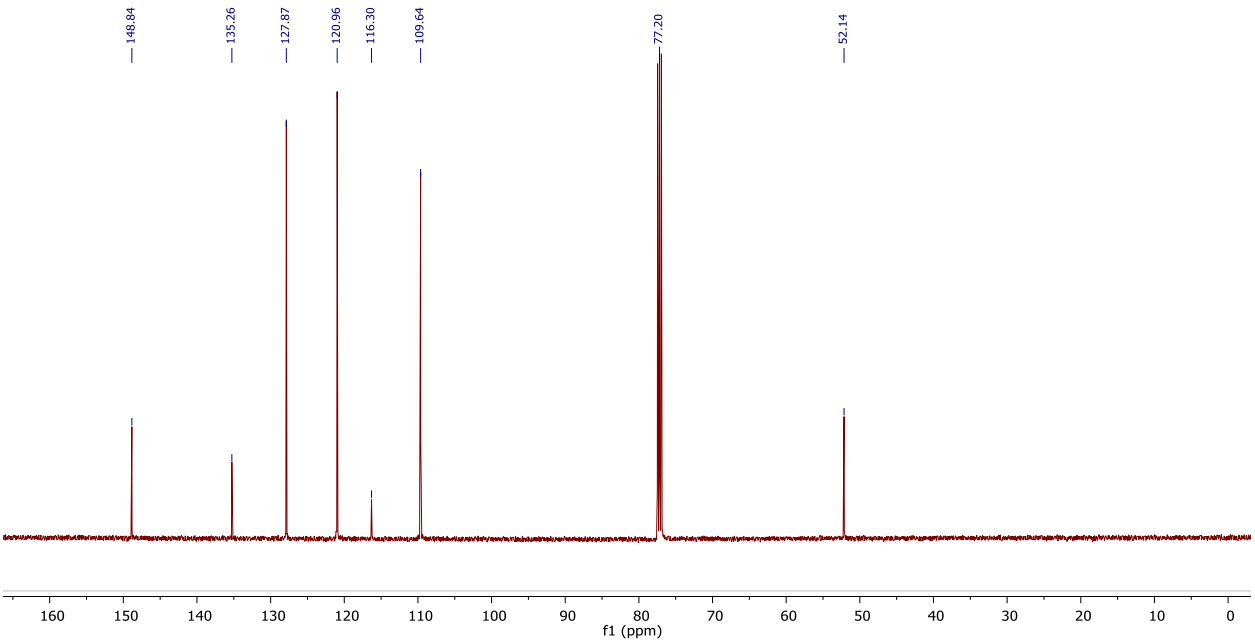


Figure S46. ^{13}C NMR spectrum of **10a** in $CDCl_3$ at room temperature.

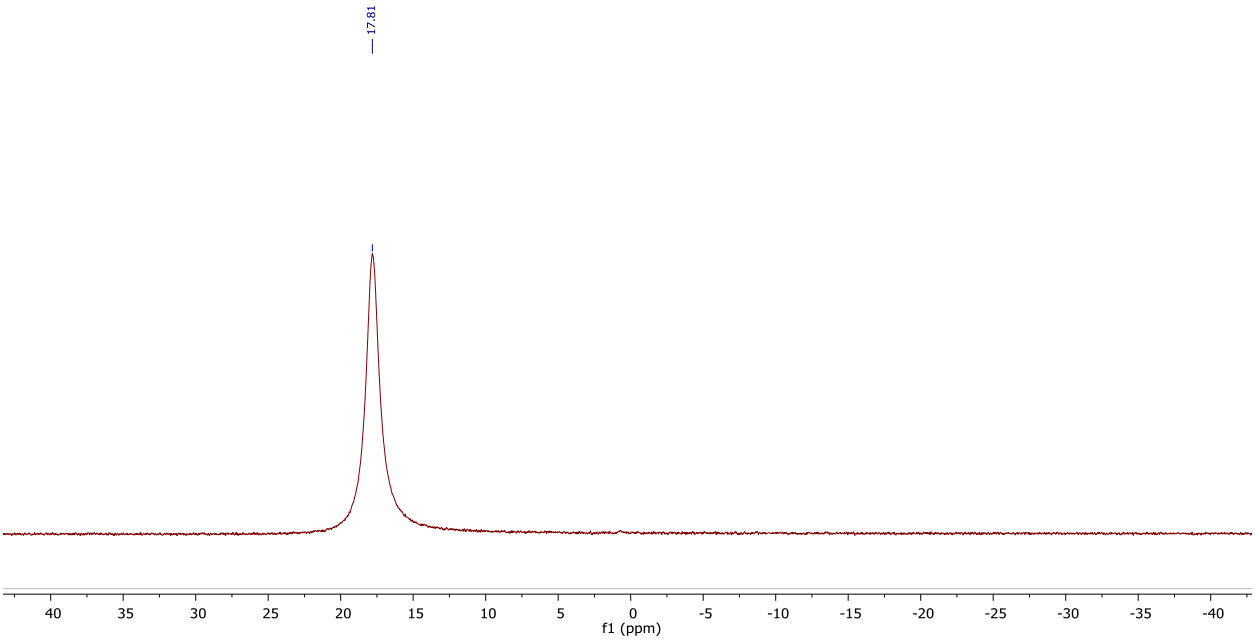
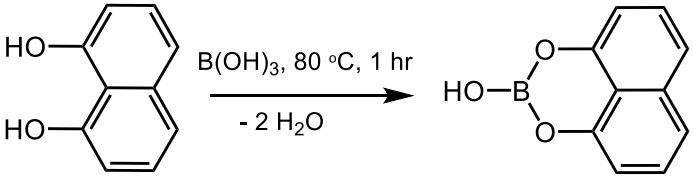


Figure S47. ^{11}B NMR spectrum of **10a** in $CDCl_3$ at room temperature.

2.4.8 Synthesis of **11a**



11a

Powdered boric acid (0.73, 1.25 mmol) and 1,8-naphthalenediol (0.2 g, 1.25 mmol) were dissolved in acetonitrile (10 mL) in a 20 mL scintillation vial. The solution was gently heated until all the starting material dissolved and then heated 80°C for one hour. After cooling to room temperature, all volatiles were removed under vacuum. After the residue was extracted twice with toluene, the solvent of the combine extracts was removed under vacuum to give **11a** as a colorless solid. Yield 0.21 g (93%). ^{1}H NMR [400 MHz, CD_3CN]: 6.42 (br, OH, 1 H), 6.85 (d, $^{3}J_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.38 (t, $^{3}J_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.44 (d, $^{3}J_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H) ppm. ^{13}C{H} NMR [125 MHz, CD_3CN]: 110.4 (CH), 117.4 (C-quart), 121.7, 129.2 (CH), 136.5, 150.4 (C-quart) ppm. ^{11}B NMR (128.4 MHz, CD_3CN): 18.0 ppm. ^{11}B NMR (128.4 MHz, $CDCl_3$): 18.4 ppm Anal. Calc. for $C_{12}H_9BO_3$ (185.97): C, 64.58, H, 3.79 Found: C, 64.90; H, 4.00.

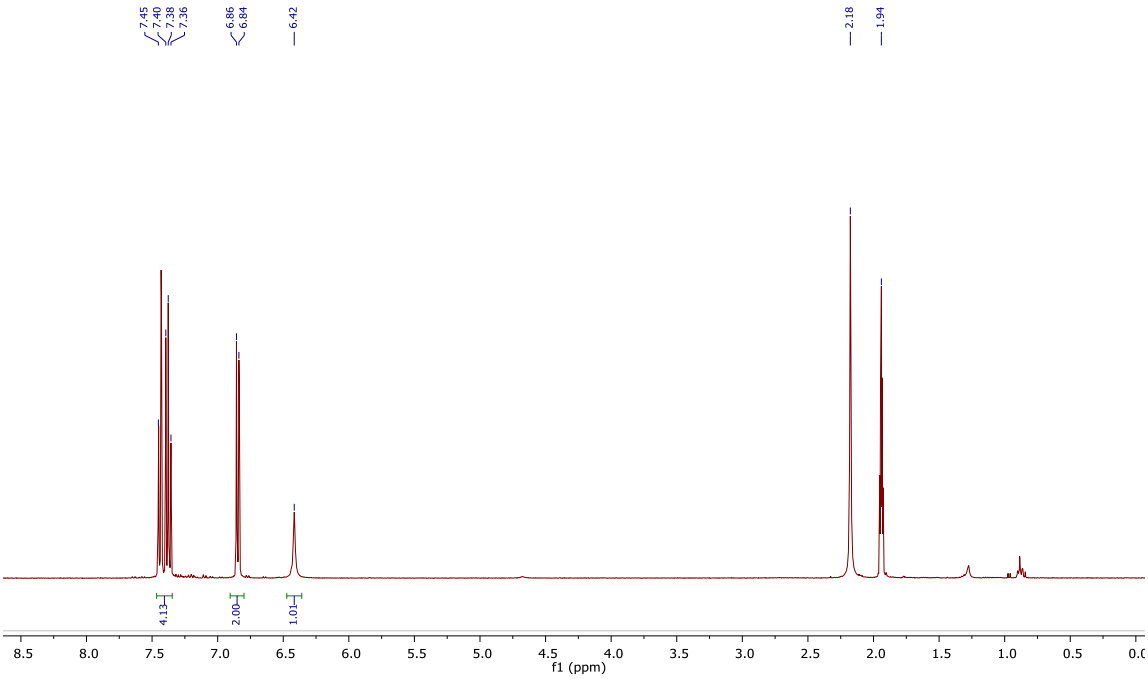


Figure S48. ^{1}H NMR spectrum of **11a** in $CDCl_3$ at room temperature.

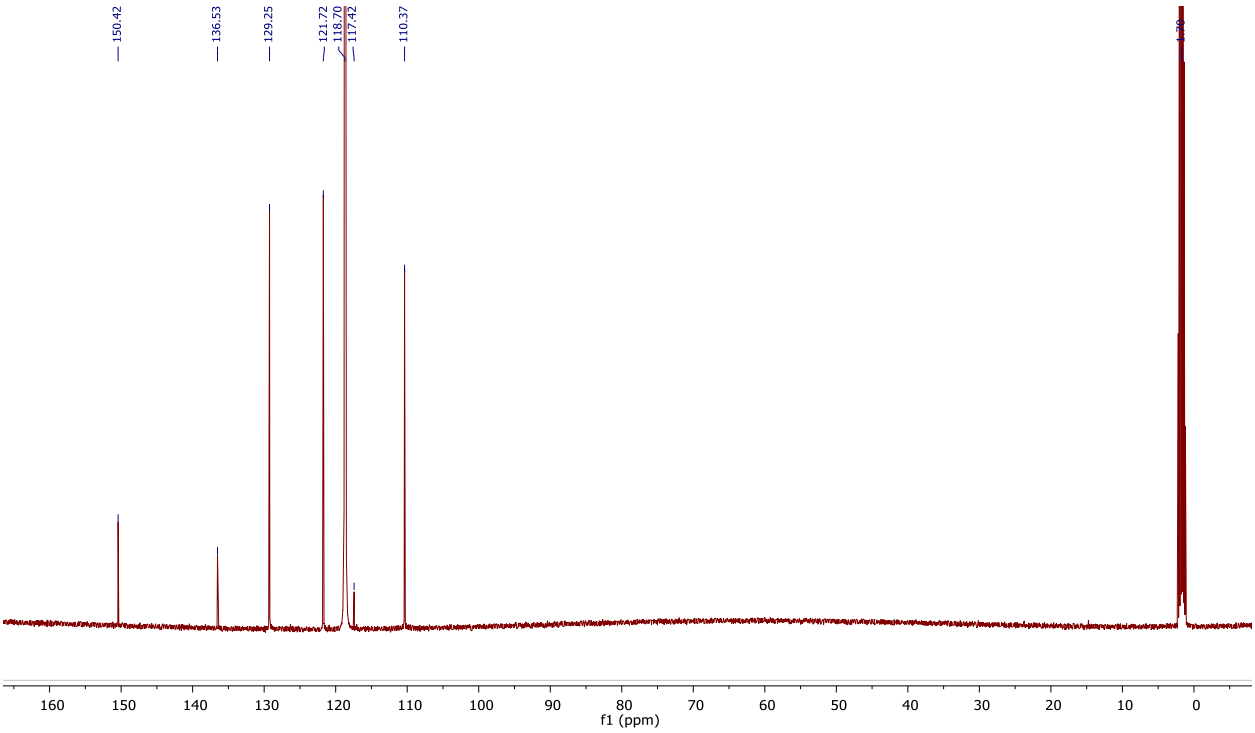


Figure S49. ^{13}C NMR spectrum of **11a** in $CDCl_3$ at room temperature.

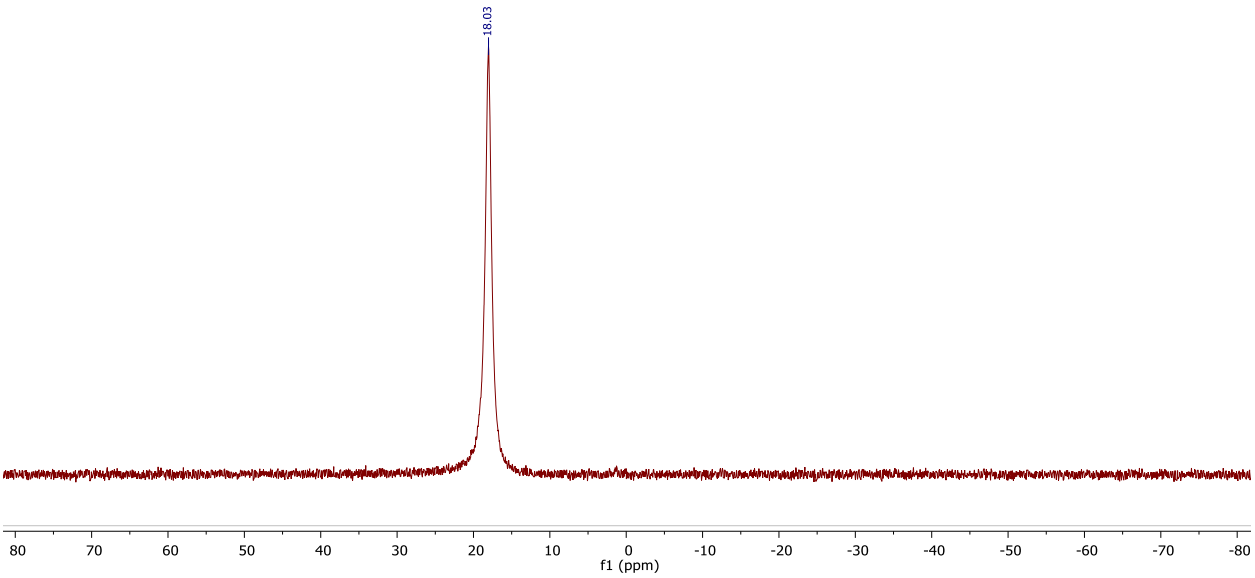
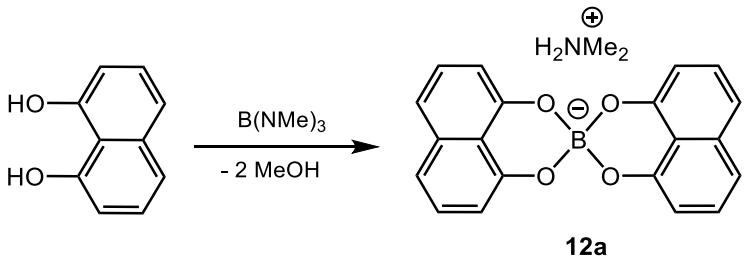


Figure S50. ^{11}B NMR spectrum of **11a** in $CDCl_3$ at room temperature.

2.4.9 Synthesis of **12a**



1,8-naphthalenediol (134 mg, 0.84 mmol) was added to a solution of $B(NMe_2)_3$ (60 mg, 0.42 mmol) in THF (5 mL) and resulting suspension was stirred for an hour. The precipitate was filtered, washed with THF and dried under vacuum to give **12a** as a white powder. Yield 0.15 g (96 %). ^{1}H NMR [400 MHz, DMSO-D_6]: 2.57 (s, CH_3, 6 H), 6.41 (d, $^{3}J_{H-H}$ = 4 Hz, CH-naphthyl, 4 H), 7.10 (d, $^{3}J_{H-H}$ = 8 Hz, CH-naphthyl, 4 H), 7.21 (t, $^{3}J_{H-H}$ = 8 Hz, CH-naphthyl, 4 H), 8.16 (br, NH, 2 H); ^{13}C{H} NMR [100.4 MHz, DMSO-D_6]: 34.5 (CH_3), 106.7, 115.4 (CH), 116.5 (C-quart), 127.4 (CH), 135.5, 154.9 (C-quart) ppm. ^{11}B NMR [128.4 MHz, DMSO-D_6]: 0.5 ppm. Anal. Calc. for $C_{22}H_{20}BNO_4$ (373.15): C, 70.80; H, 5.40; N, 3.75 Found: C, 69.87; H, 5.10; N, 3.84.

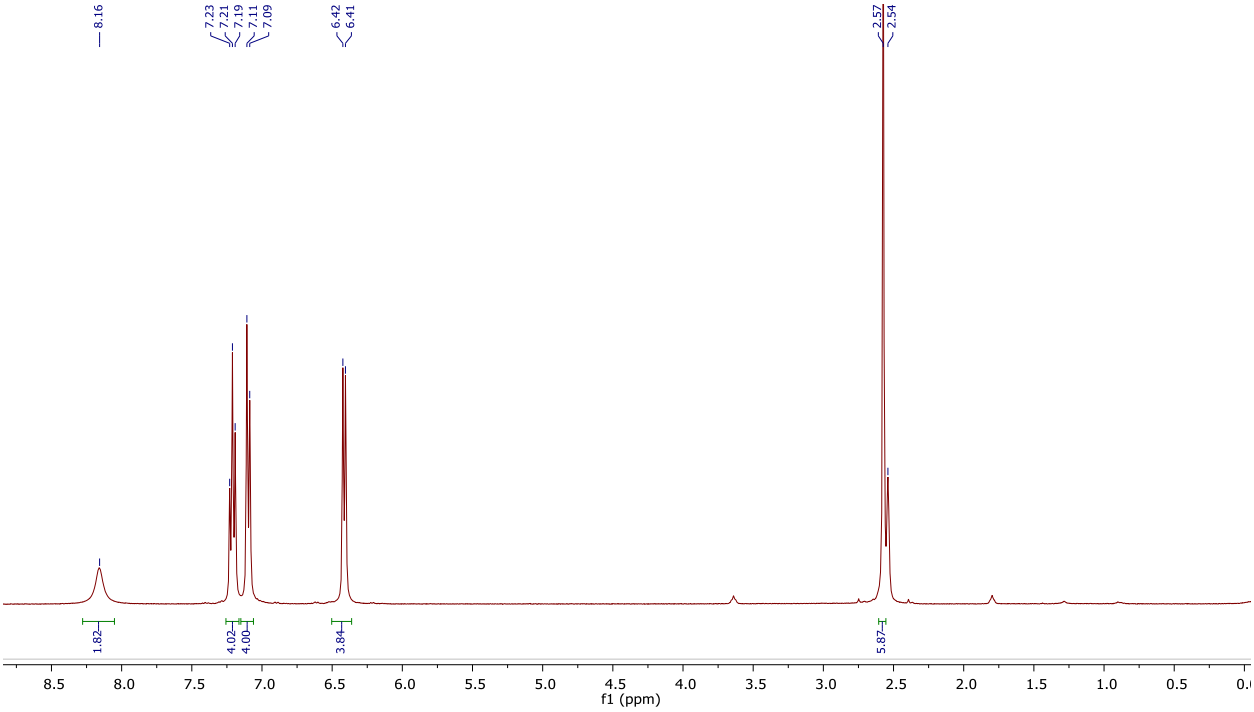


Figure S51. ^{1}H NMR spectrum of **12a** in $CDCl_3$ at room temperature.

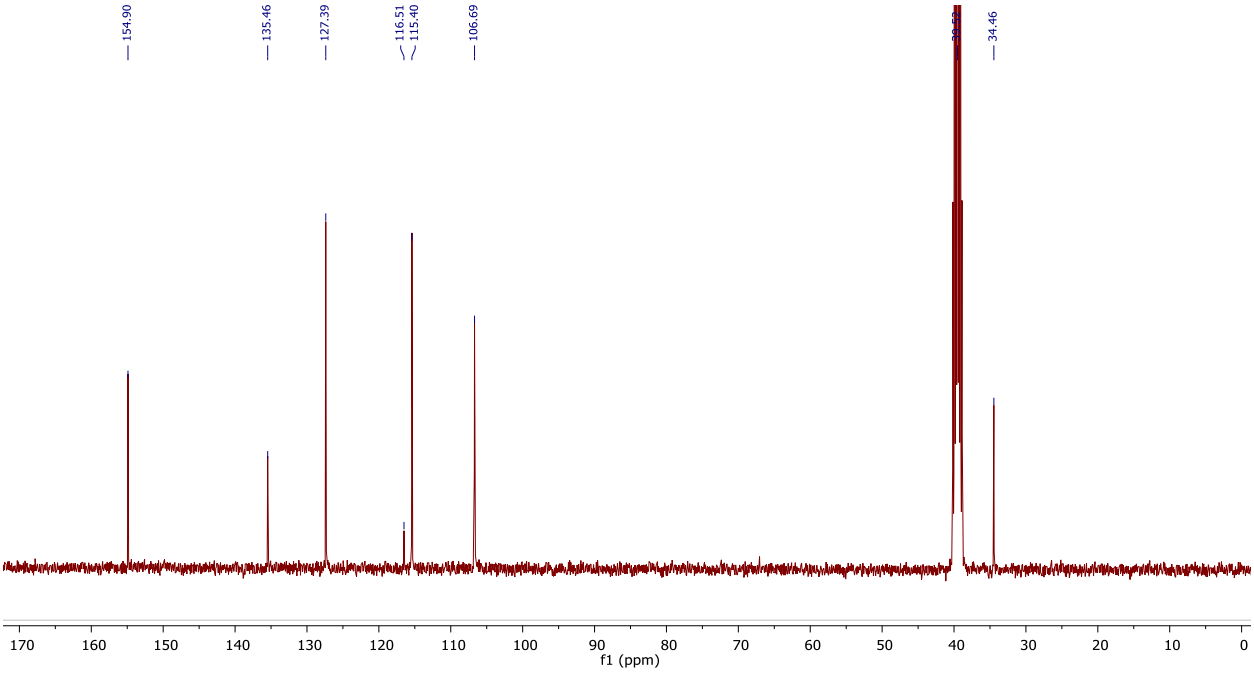


Figure S52. ^{13}C NMR spectrum of **12a** in $CDCl_3$ at room temperature.

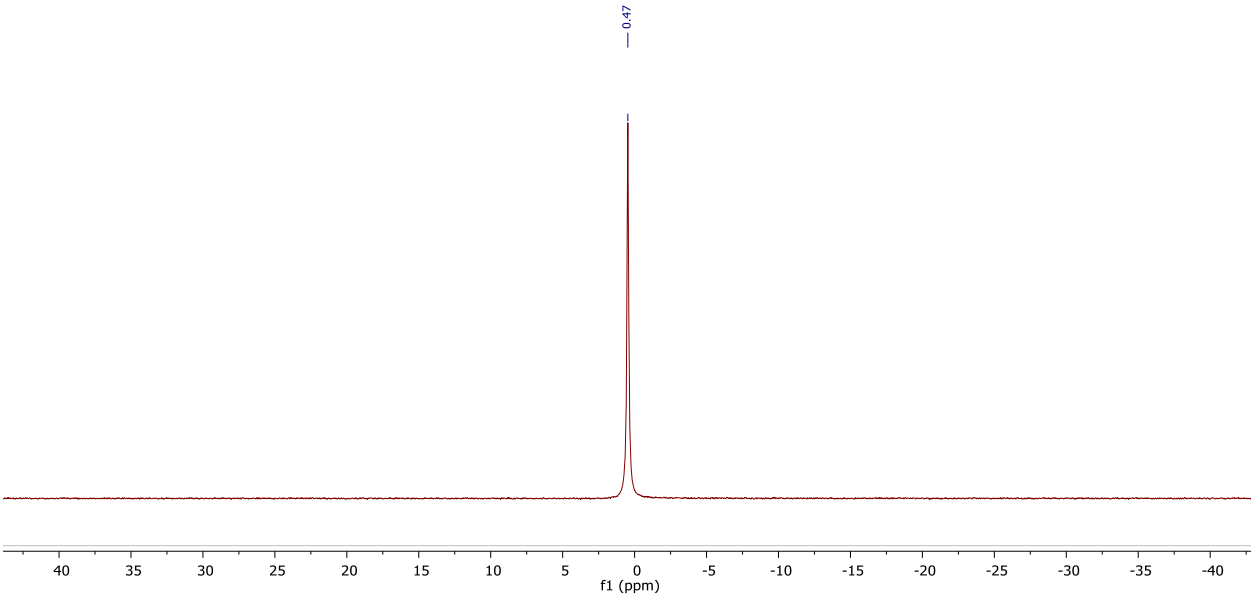


Figure S53. ^{11}B NMR spectrum of **12a** in $CDCl_3$ at room temperature.

2.4.10 Synthesis of **13a**

13a

1,8-naphthalenediol (0.7 g, 4.4 mmol) was added portion-wise to a 1 M hexanes solution of BCl_3 (13.2 ml, 13.2 mmol) in CH_2Cl_2 (10 mL) at -78°C. After the reaction mixture was allowed to warm to room temperature, all volatiles were quickly removed under vacuum to give **13a** as colorless solid, slightly contaminated with CH_2Cl_2. Yield 0.85 g (95%). ^{1}H NMR [400 MHz, $CDCl_3$]: 6.94 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.37 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8.0 Hz, CH-naphthyl, 2 H), 7.47 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H) ppm. ^{13}C{H} NMR [125 MHz, $CDCl_3$]: 110.4 (CH), 117.1 (C-quart), 122.2, 128.2 (CH), 135.5, 148.1 (C-quart) ppm. ^{11}B NMR [128.4 MHz, $CDCl_3$]: 24.8 ppm. Attempts to obtain accurate microanalysis have failed due to the extreme water sensitivity of this molecule.

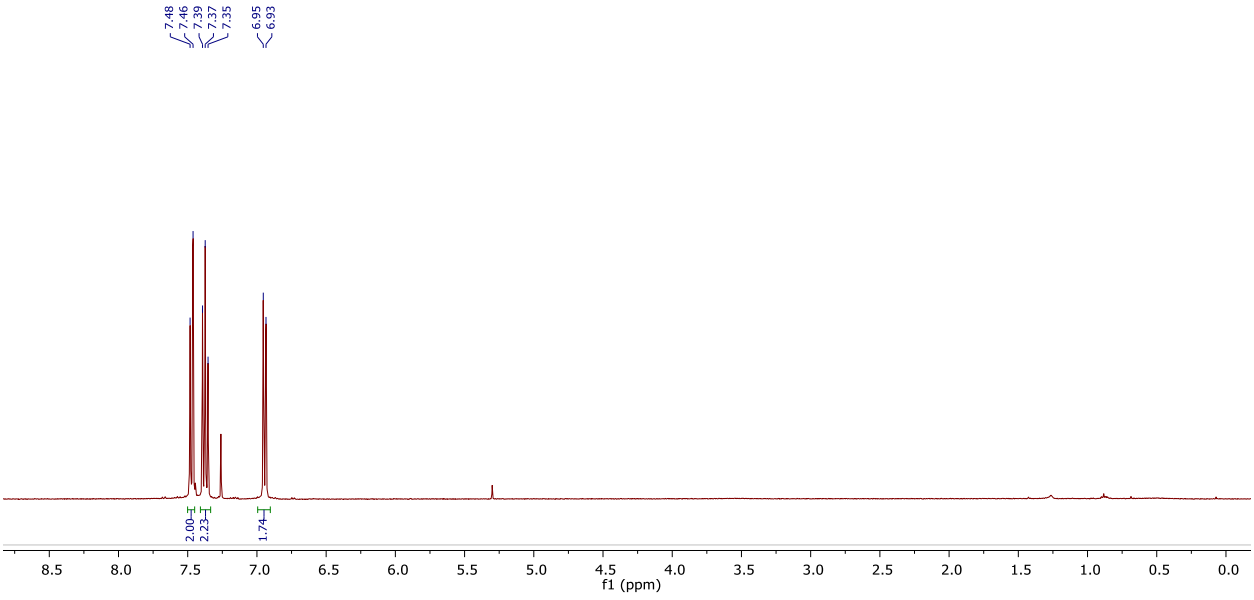


Figure S54. ^{1}H NMR spectrum of **13a** in $CDCl_3$ at room temperature.

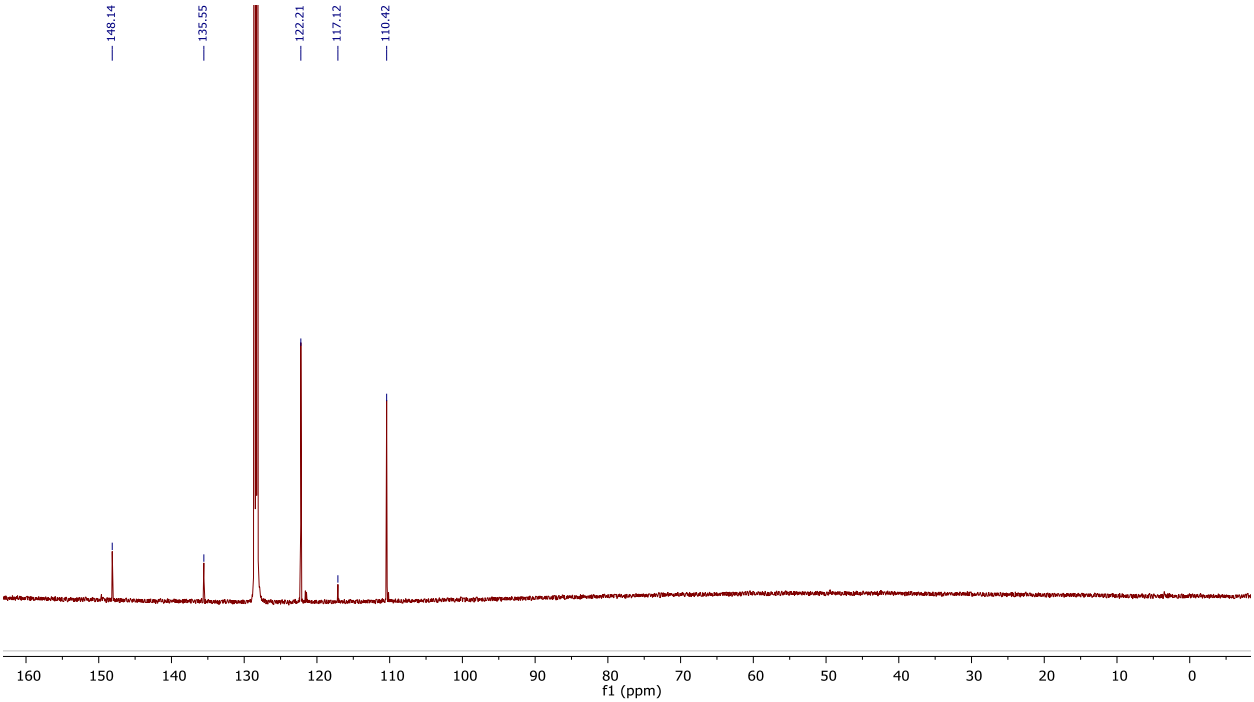


Figure S55. ^{13}C NMR spectrum of **13a** in $CDCl_3$ at room temperature.

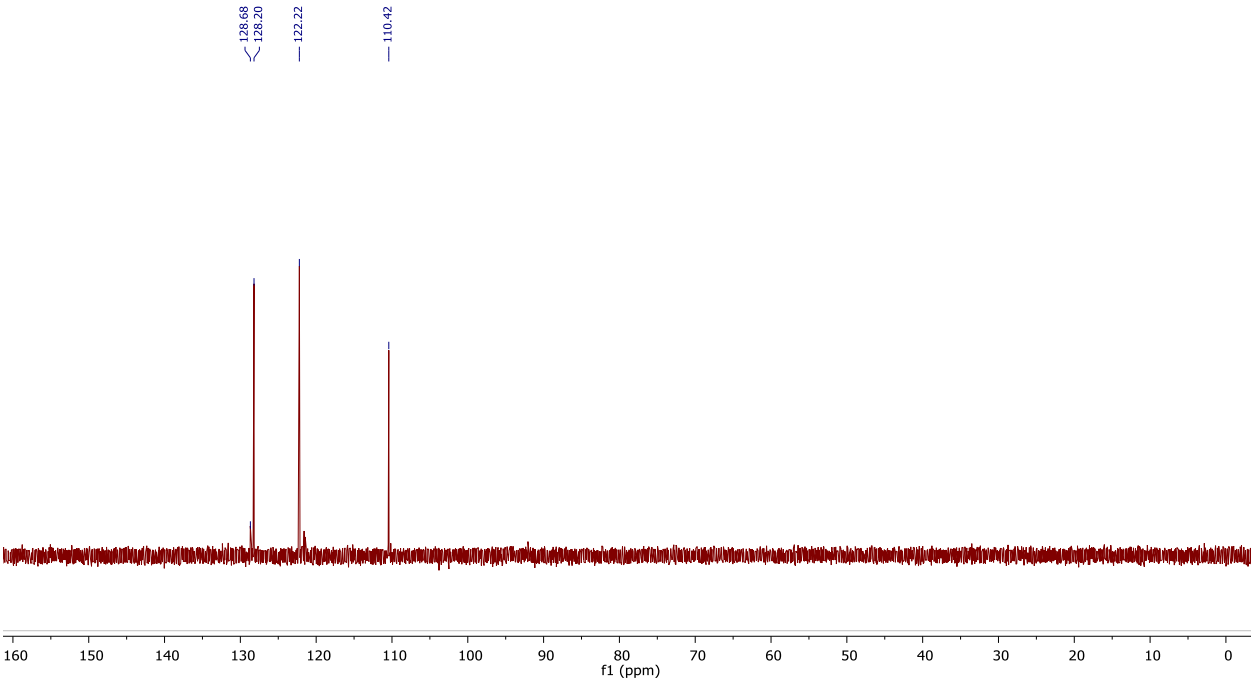


Figure S56. ^{13}C DEPT NMR spectrum of **13a** in $CDCl_3$ at room temperature.

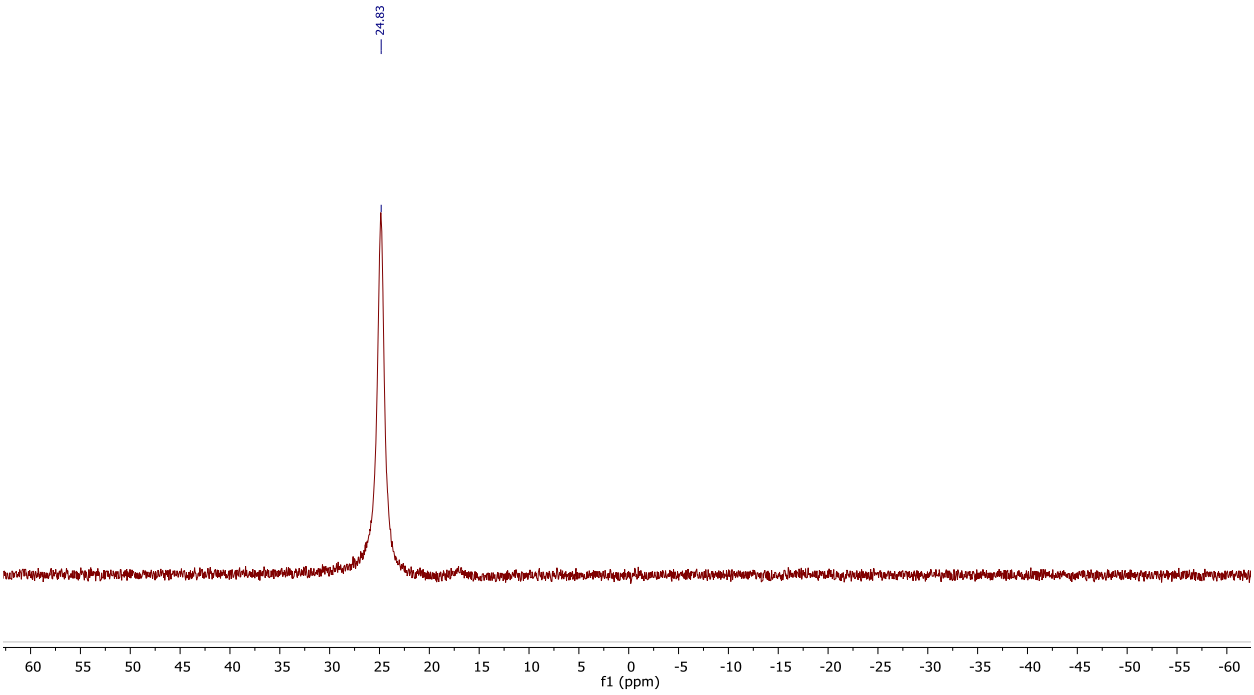
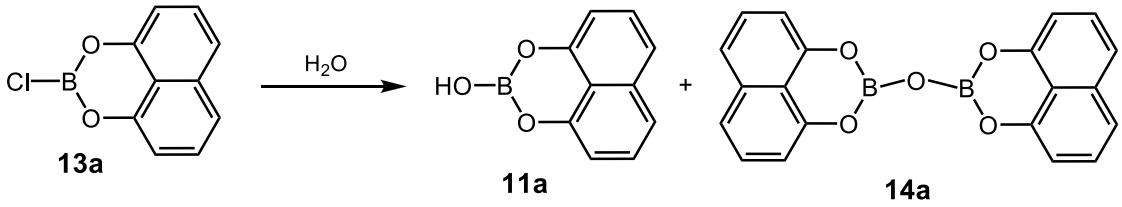


Figure S57. ^{11}B NMR spectrum of **13a** in $CDCl_3$ at room temperature.

2.4.11 Hydrolysis of **13a** in $CDCl_3$



In the Glove box, a standard NMR tube was charged with ca. 20 mg of **13a** and dry $CDCl_3$ (0.5 mL), removed from the glove box and stored on the bench. After ca. 10 days, a crystalline precipitate formed. Analysis of the isolated crystals by multi-nuclear NMR spectroscopy revealed the formation of **11a** and **14a** (see also Figures **S56** and **S57**). Single crystals of **14a** suitable for X-ray analysis were grown from benzene. The NMR spectroscopic data of **14a** are shown in Figures **S58-S61**. ^{1}H NMR [400 MHz, C_6D_6]: 6.74 (d, $^3J_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.01 (t, $^3J_{H\text{-}H}$ = 8.0 Hz, CH-naphthyl, 2 H), 7.15 (d, $^3J_{H\text{-}}$

$_H$ = 8 Hz, CH-naphthyl, 2 H) ppm. $^{13}C\{H\}$ NMR [100.4 MHz, C_6D_6]: 110.0 (CH), 116.8 (C-quart), 121.2, 127.9 (CH), 135.5, 149.1 (C-quart) ppm. ^{11}B NMR [128.4 MHz, C_6D_6]: 16.9 ppm.

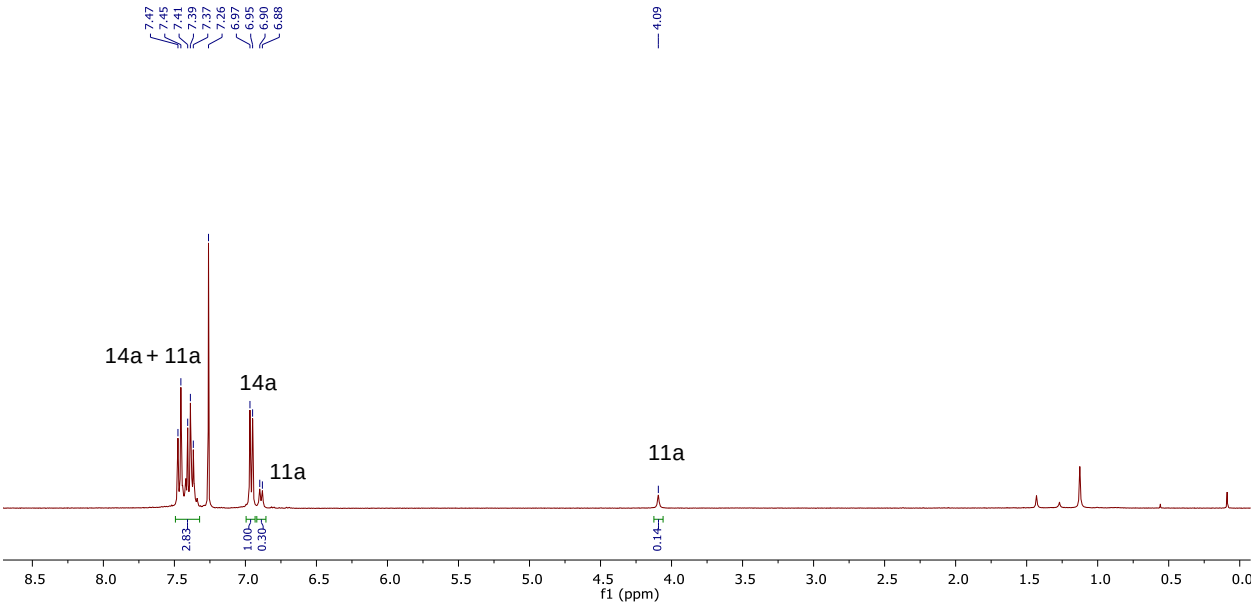


Figure S58. ^{11}H NMR spectrum of the mixture of **11a**/**14a** in $CDCl_3$ at room temperature.

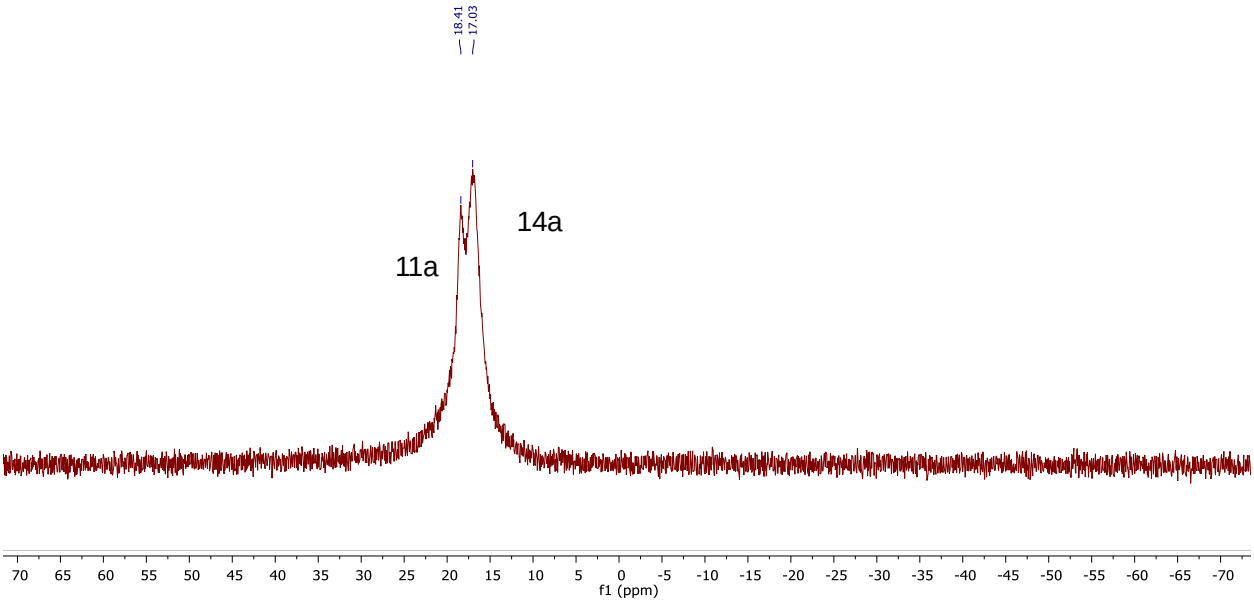


Figure S59. ^{11}B NMR spectrum of the mixture of **11a**/**14a** in $CDCl_3$ at room temperature.

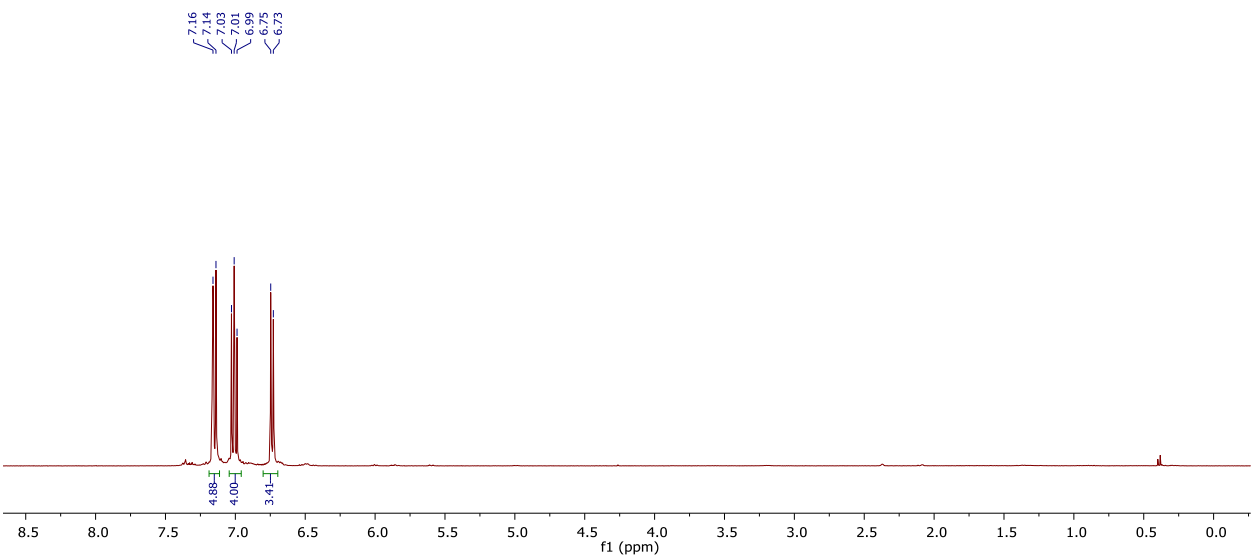


Figure S60. ^{11}H NMR spectrum of the mixture of **14a** in C_6D_6 at room temperature.

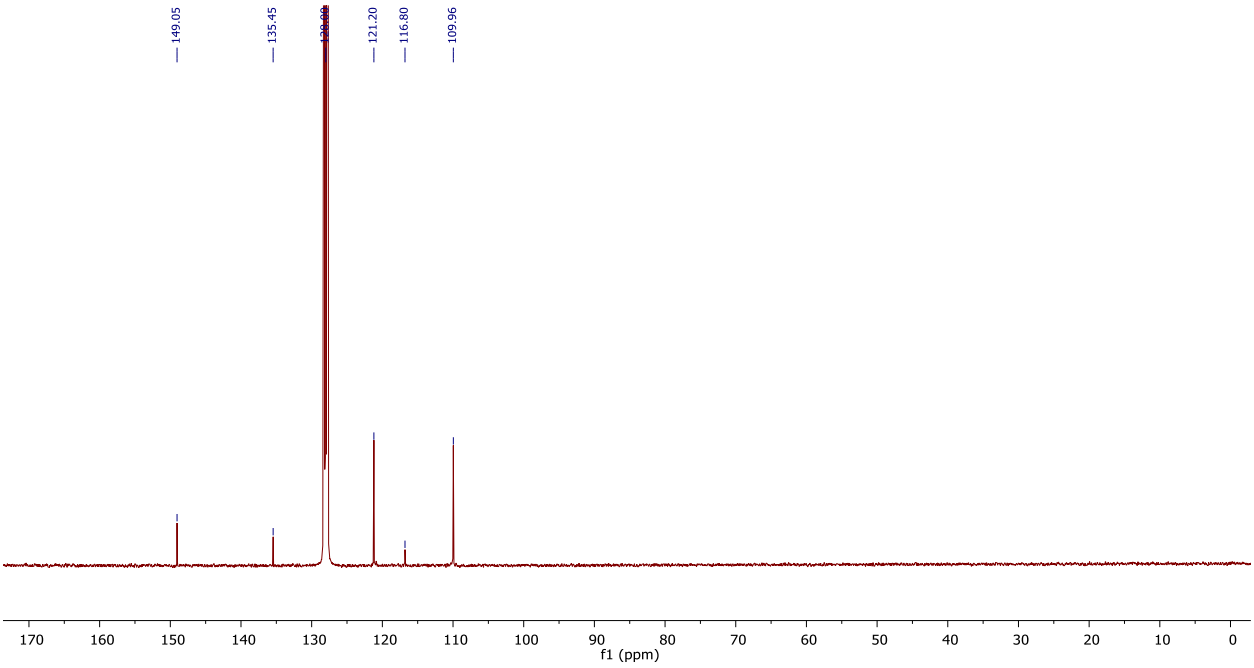


Figure S61. ^{13}C NMR spectrum of the mixture of **14a** in C_6D_6 at room temperature.

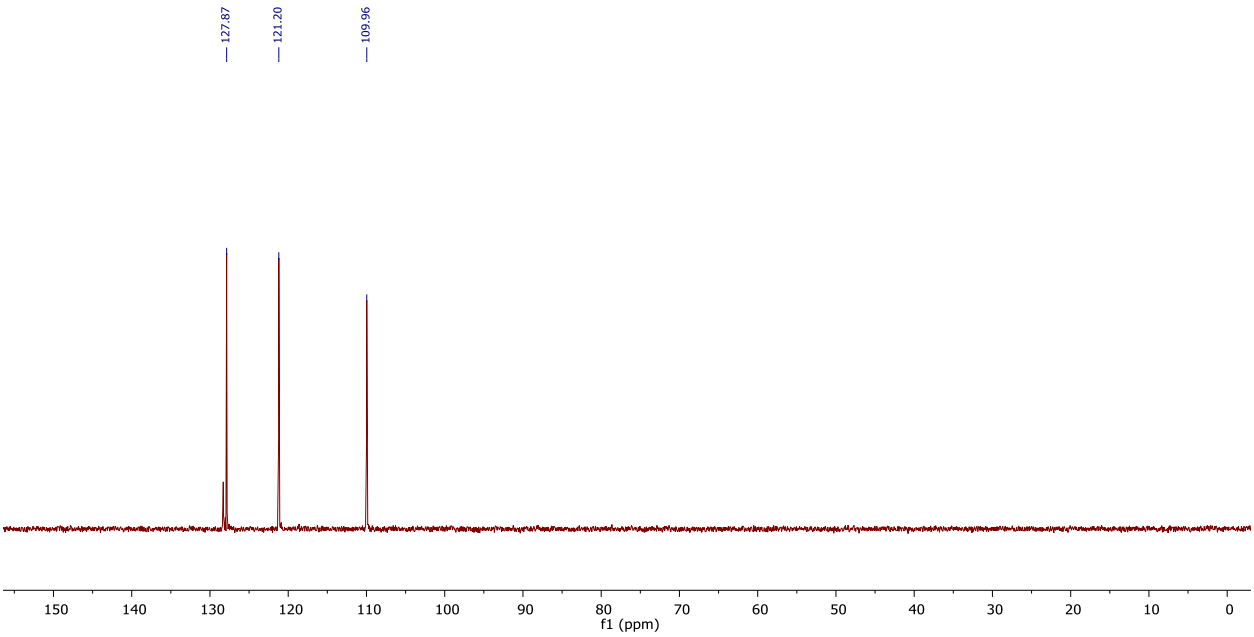


Figure S62. ^{13}C DEPT NMR spectrum of the mixture of **14a** in C_6D_6 at room temperature.

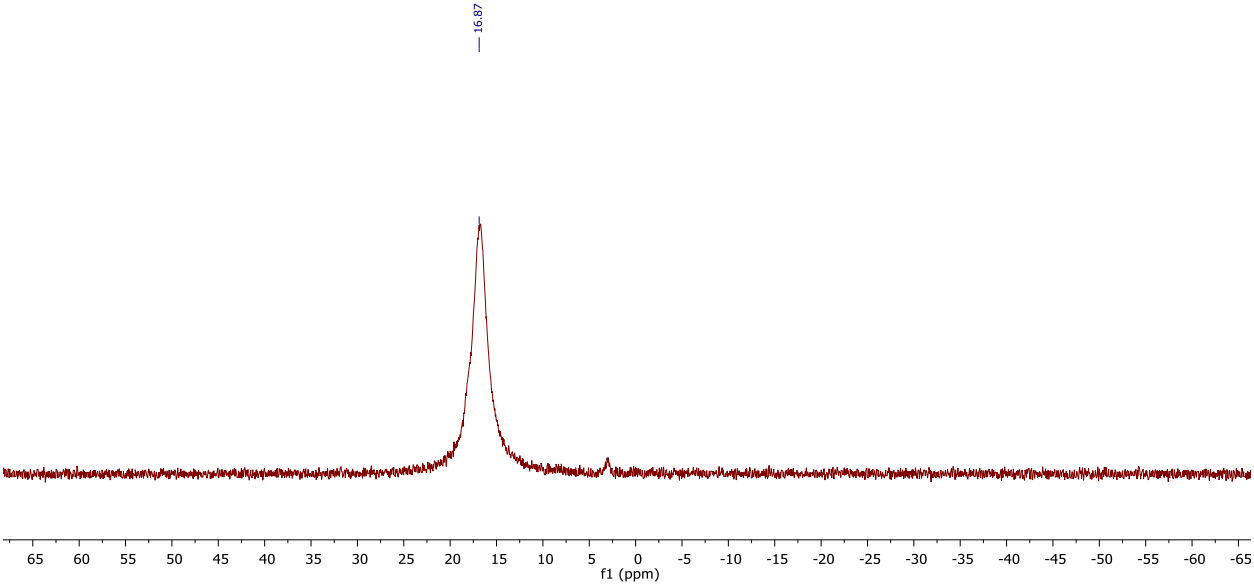
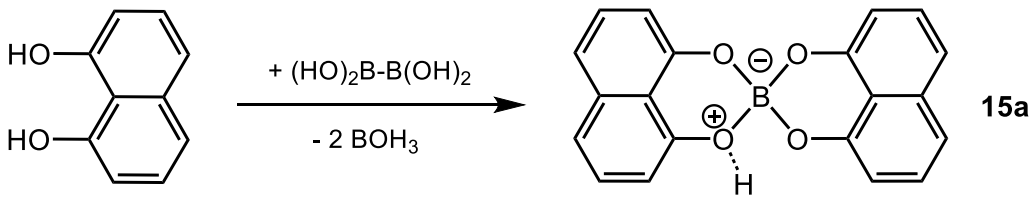


Figure S63. ^{11}B NMR spectrum of the mixture of **14a** in C_6D_6 at room temperature.

2.4.12 Attempted synthesis of diboronic acid ester **16a**



A standard NMR tube was charged with 1,8-naphthalenediol (51 mg, 0.32 mmol), $(HO)_2B$-$B(OH)_2$ (14 mg, 0.16 mmol) and 0.6 mL of DMSO-D_6. The reaction mixture was heated at 80°C for 1 hour and subsequently analyzed by NMR spectroscopy. ^{1}H NMR [400 MHz, DMSO-D_6]: 6.42 (d, $^3J_{H-H}$ = 8 Hz, CH-naphthyl, 4 H), 6.09 (d, $^3J_{H-H}$ = 8 Hz, CH-naphthyl, 4 H), 7.20 (t, $^3J_{H-H}$ = 8 Hz, CH-naphthyl, 4 H) ppm. ^{13}C{H} NMR [100.4 MHz, DMSO-D_6] 106.9, 115.6 (CH-naphthyl), 116.7 (C-quart), 127.6 (CH-naphthyl), 135.6, 155.1 (C-quart) ppm. ^{11}B NMR [128.4 MHz, DMSO-D_6]: 0.46 (**15a**), 18.9 (boric acid) ppm.

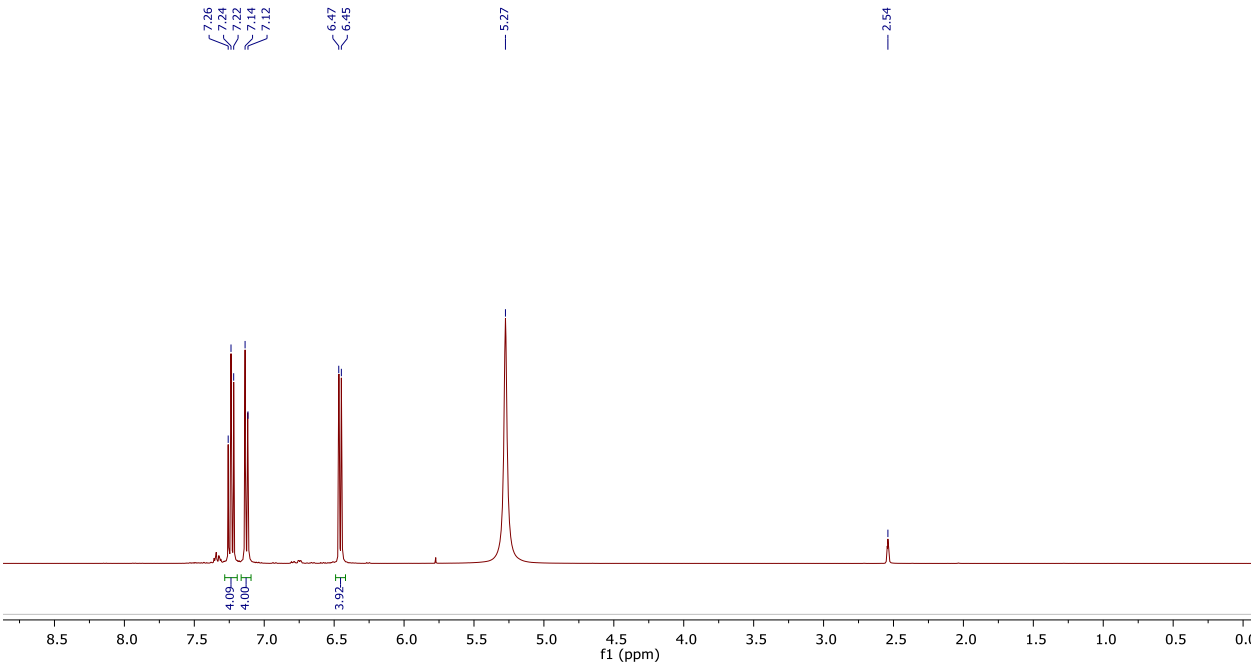


Figure S64. ^{1}H NMR spectrum of **15a i**n $CDCl_3$ at room temperature.

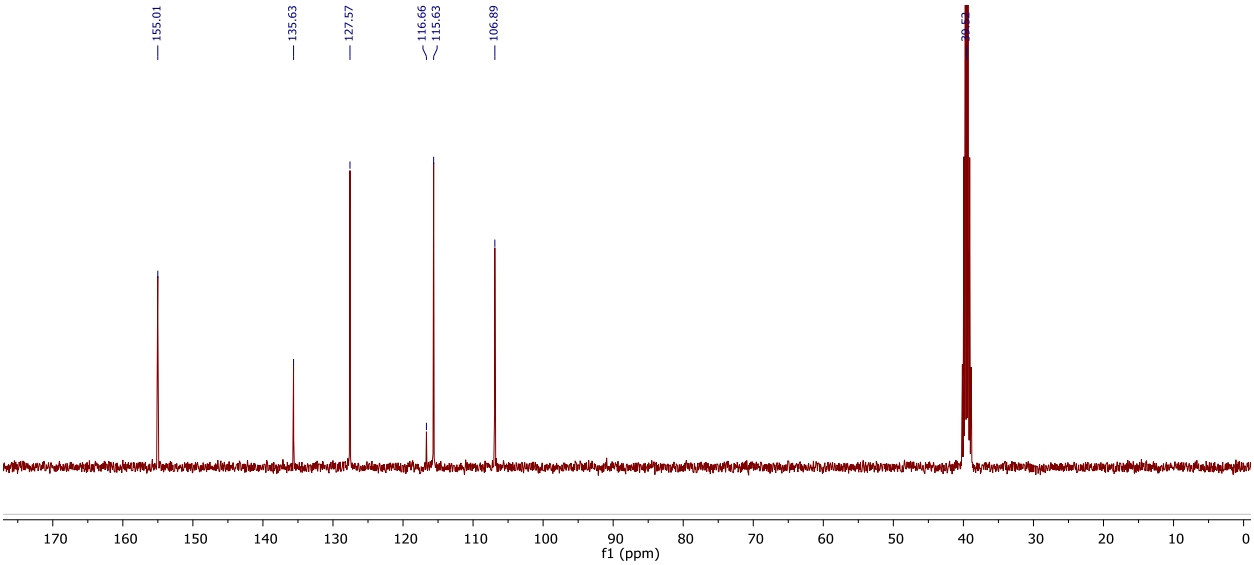


Figure S65. ^{13}C NMR spectrum of **15a** in $CDCl_3$ at room temperature.

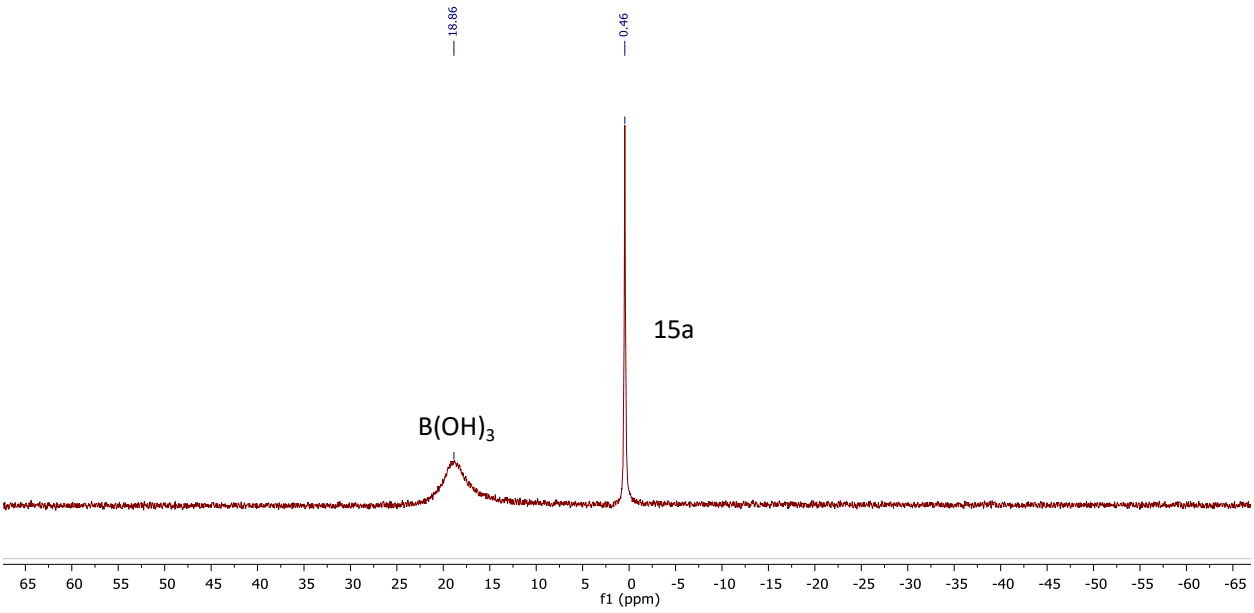
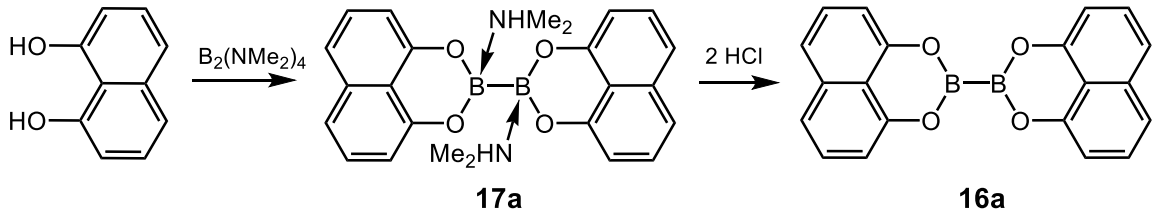


Figure S66. ^{11}B NMR spectrum of **15a** in $CDCl_3$ at room temperature.

2.4.13 Synthesis of **16a**



In the glove box, a 30 mL Schlenk flask was charged with a magnetic stir bar, 1,8-naphthalenediol (0.1 g, 0.62 mmol) and diethyl ether (7 mL). In addition, a 20 mL scintillation vial was charged with $B_2(NMe_2)_4$ (0.063 g, 0.31 mmol) and diethyl ether (3 mL). Upon adding $B_2(NMe_2)_4$ solution to 1,8-naphthalenediol, a precipitate formed, which was identified by NMR spectroscopy as **17a**: ^{1}H NMR [400 MHz, C_6D_6]: 1.8 (s, 12 H), 2.8 (br, NH, 2 H) 6.99 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naptyl, 4 H), 7.31-7.39 (m,CH-naptyl, 8 H), ppm. ^{13}C{H} NMR [125 MHz, C_6D_6]: 36.3 (CH_3, N-Me), 108.3 (CH-naphthyl), 115.9 (C-quart), 117.5 (CH-naphthyl), 127.8 (CH-naphthyl), 136.6 (C-quart), 153.0 (C-quart) ppm. ^{11}B NMR [128.4 MHz, C_6D_6]: 4.4 ppm. After stirring the ethereal suspension of **17a** for one hour, an ether solution of HCl (2 N, 0.7 mL, 1.4 mmol) was added at 0 °C. The reaction mixture was stirred for another hour at room temperature and 5 mL of deionized water were added. The obtained precipitate was immediately filtered over a frit, washed with acetone to remove all water and dried under vacuum to give **16a** as a colorless solid (Note! **16a** contains ca. 5-10% diethyl ether. Attempts to remove residual diethyl ether under dynamic vacuum (50°C, 10^{-2} mbar, 24 hours) failed. Yield 71 mg (70%). ^{1}H NMR [400 MHz, DMSO-D_6]: 6.79 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 4 H), 7.31-7.38 (m, CH-naphthyl, 8 H) ppm. ^{13}C{H} NMR [100.4 MHz, DMSO-D_6]: 108.1 (CH-naphthyl), 117.6 (C-quart), 118.4 (CH-naphthyl), 127.8 (CH-naphthyl), 134.9 (C-quart), 159.6 (C-quart) ppm. ^{11}B NMR [128.4 MHz, DMSO-D_6]: 4.8 ppm. Anal. Calc. for $C_{20}H_{12}B_2O_4$ (337.93): C, 71.09; H, 3.58; Found: C, 70.50; H, 3.45.

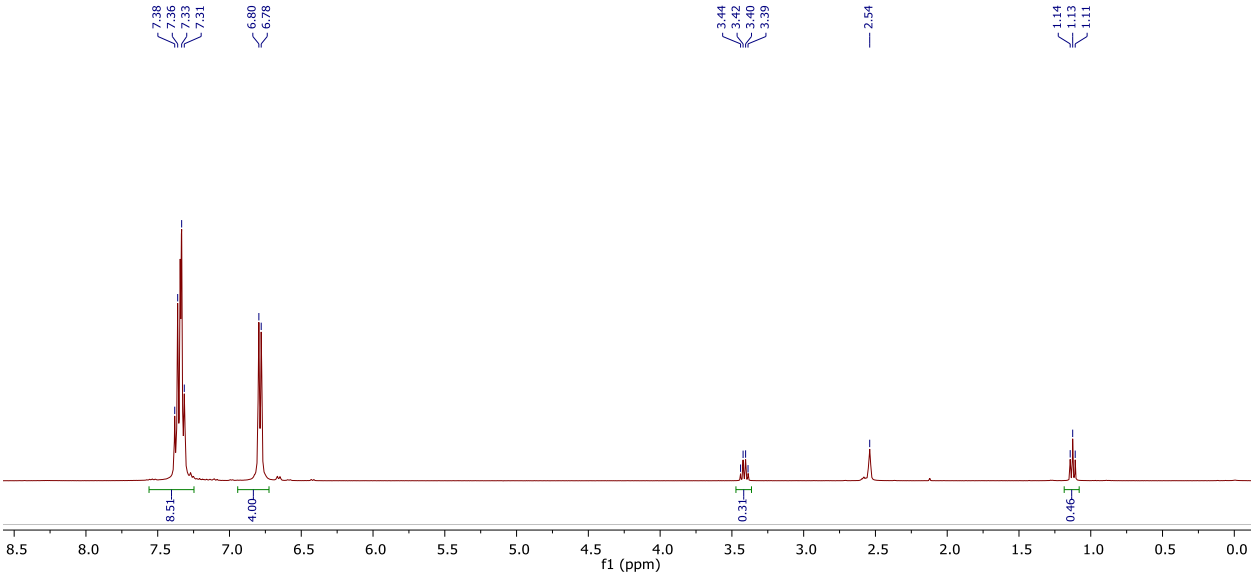


Figure S67. ^{1}H NMR spectrum of **16a i**n $CDCl_3$ at room temperature.

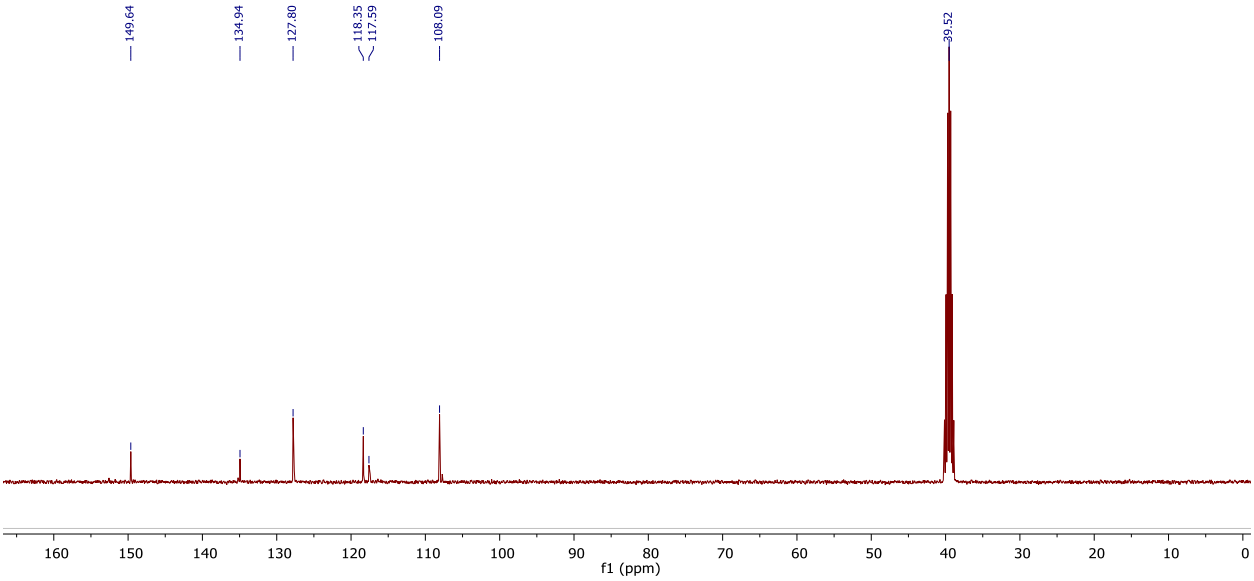


Figure S68. ^{13}C NMR spectrum of **16a** in $CDCl_3$ at room temperature.

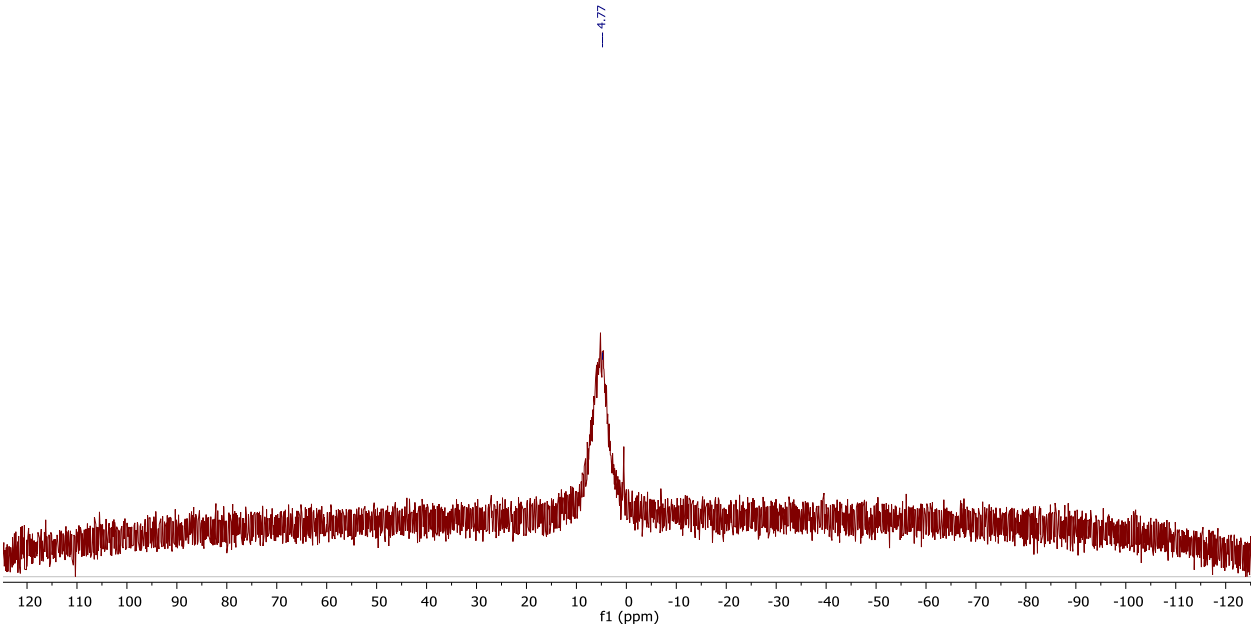


Figure S69. ^{11}B NMR spectrum of **16a** in $CDCl_3$ at room temperature.

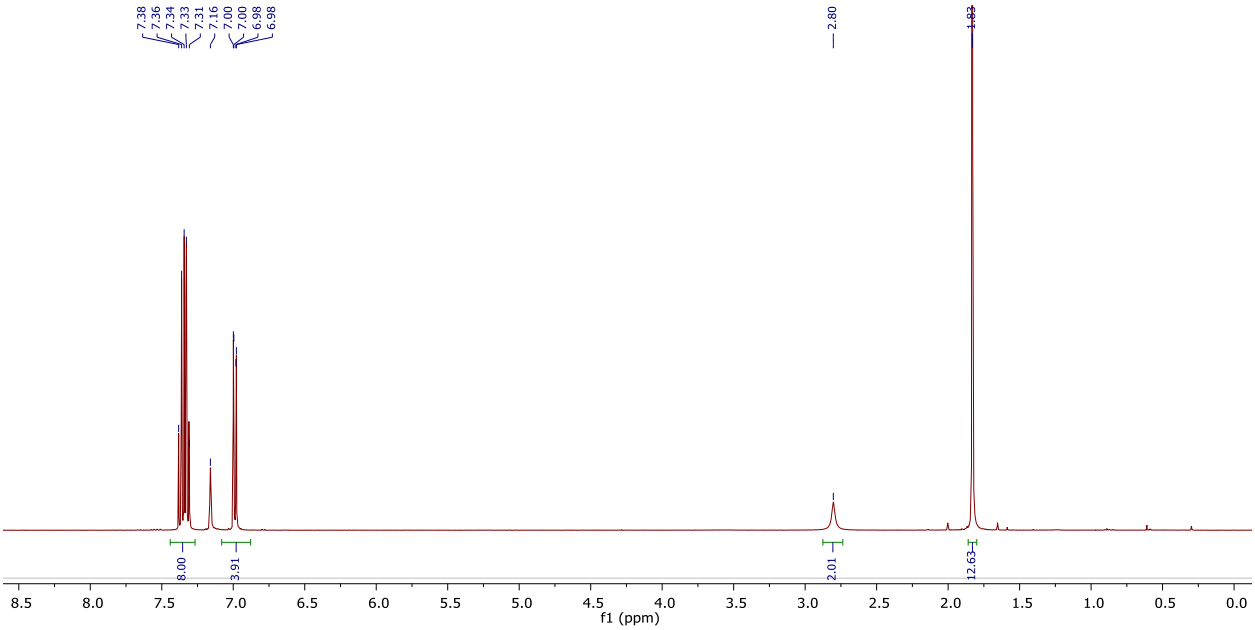


Figure S70. ^{1}H NMR spectrum of **17a i**n $CDCl_3$ at room temperature.

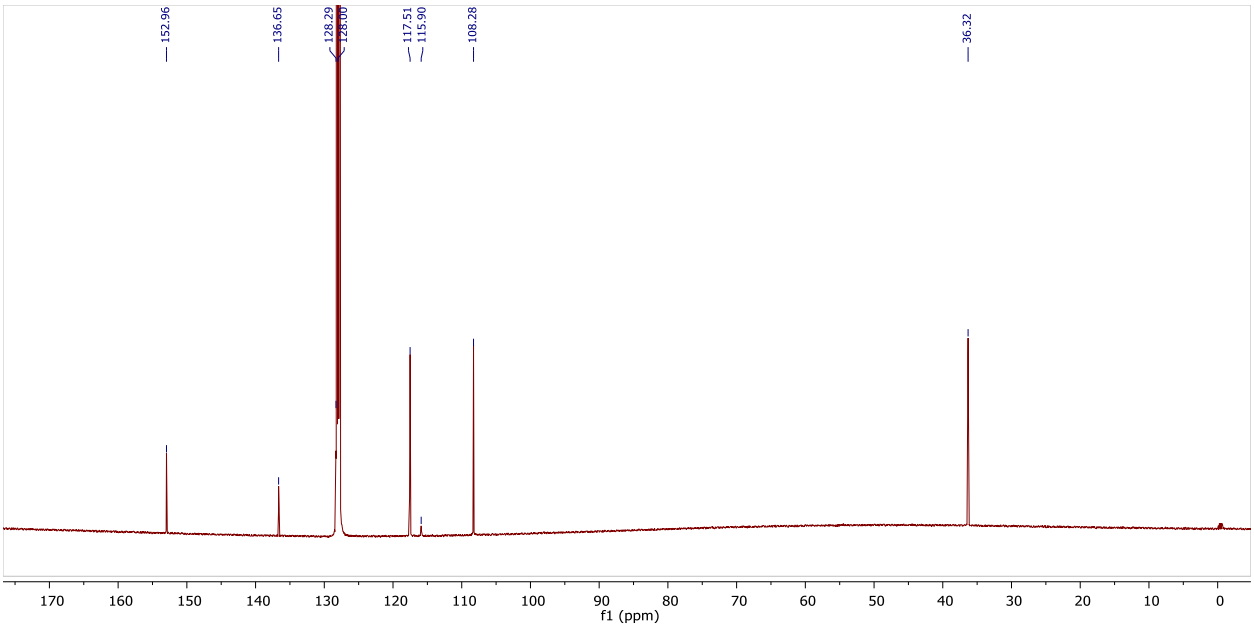


Figure S71. ^{13}C NMR spectrum of **17a** in $CDCl_3$ at room temperature.

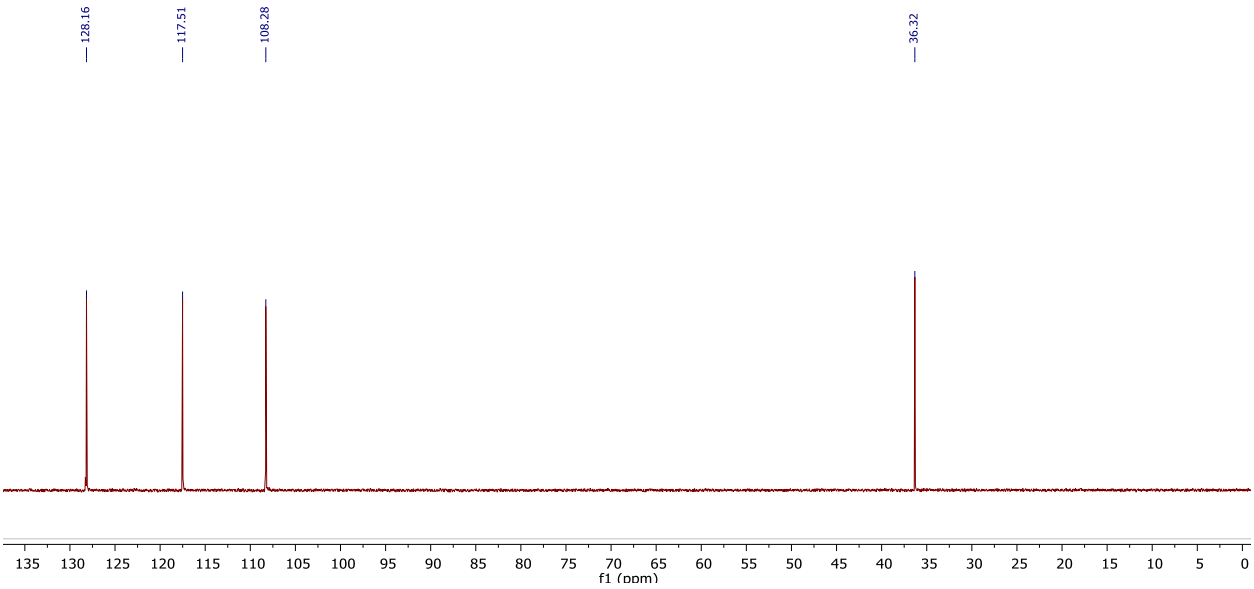


Figure S72. ^{13}C DEPT NMR spectrum of **17a** in $CDCl_3$ at room temperature.

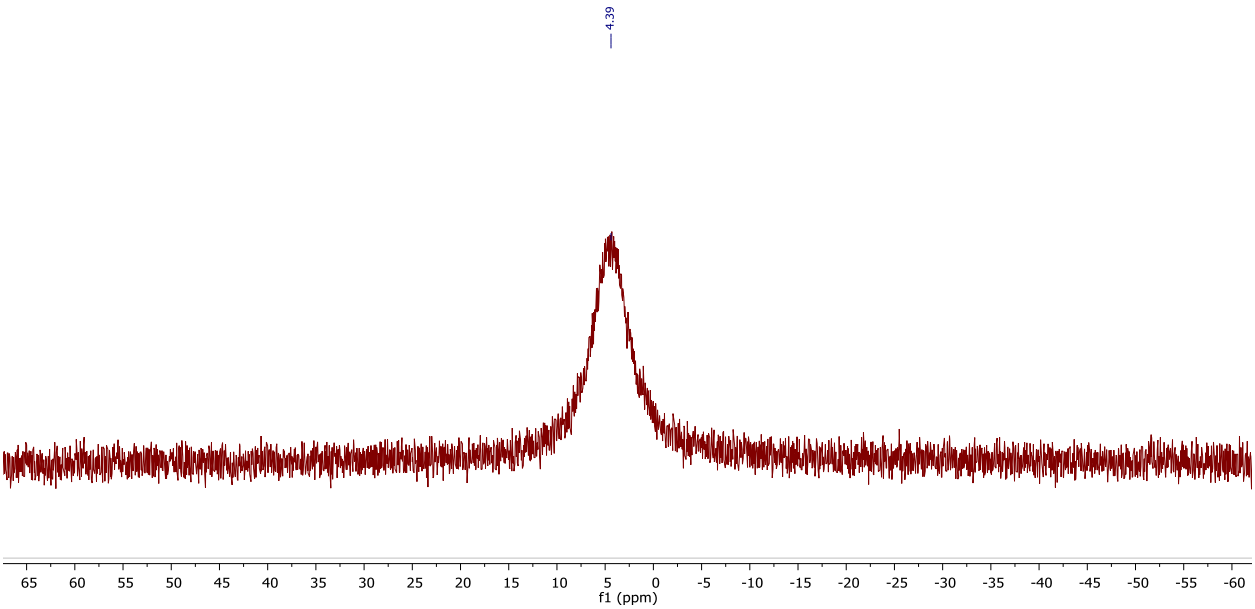
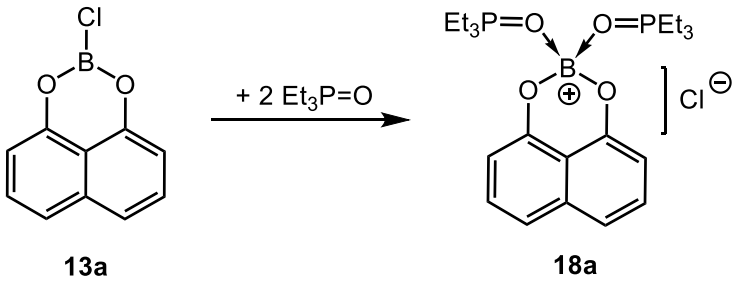


Figure S73. ^{11}B NMR spectrum of **17a** in $CDCl_3$ at room temperature.

2.4.13 Synthesis of **18a**



In the glove box, **13a** (102 mg, 0.5 mmol), $O=PEt_3$ (134 mg, 1 mmol) and anhydrous benzene (10 mL) were added to a 30 mL Schlenk flask under nitrogen. After stirring the mixture for one hour, crystalline precipitate was washed two times with benzene and dried under vacuum to give **18a** as a colorless solid. Yield 0.2 g (85 %) ^1H NMR [400 MHz, CD_2Cl_2]: 6.66 (d, $^3\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.26-7.32 (m, CH-naphthyl, 4 H), 2.24 (m, CH_2, 12 H), 1.17 (m, CH_3, 18 H) ppm. $^{13}C\{H\}$ NMR [125 MHz, CD_2Cl_2]: 5.5 (CH_3), 17.7 (d, $^1\boldsymbol{J}_{P\text{-}C}$ = 204 Hz, P-$\underline{C}H_2$), 108.6 (CH-naphthyl), 115.7 (CH-phenyl), 119.0 (CH-naphthyl), 128.2 (CH-phenyl), 136.1, 151.1 (C-quart) ppm. ^{11}B NMR [128.4 MHz, CD_2Cl_2]: 0.1 ppm.

^{31}P NMR [161.9 MHz, CD_2Cl_2]: 84.0 ppm. Attempts to obtain accurate microanalysis have failed due to the extreme water sensitivity of this compound.

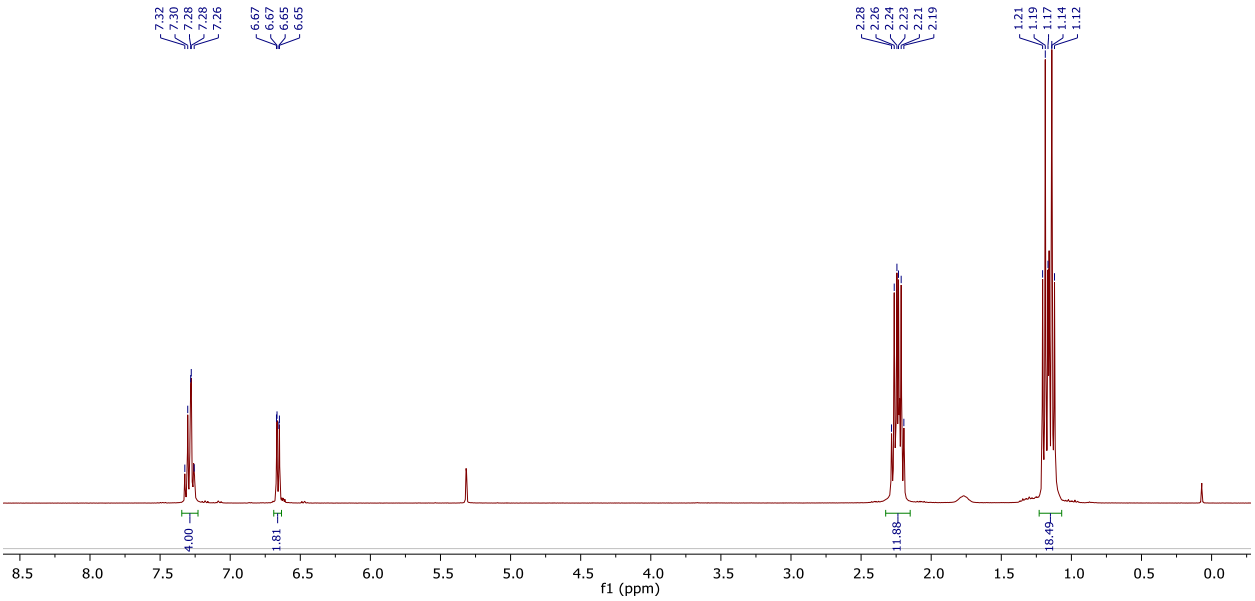


Figure S74. ^{1}H NMR spectrum of **18a i**n $CDCl_3$ at room temperature.

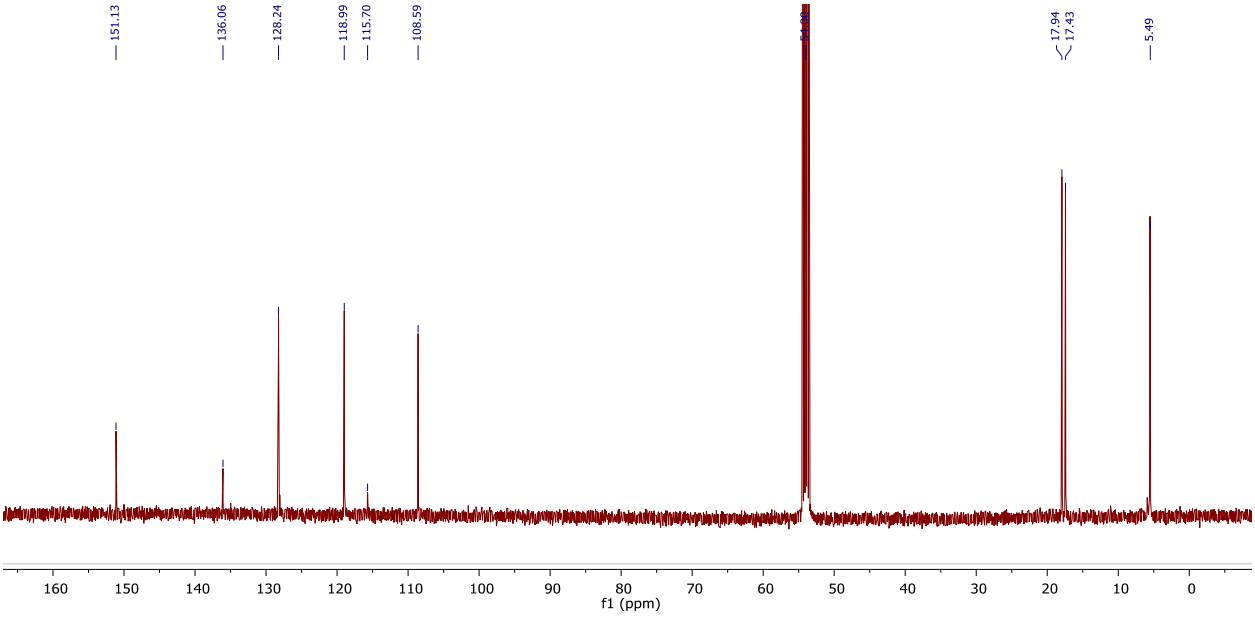


Figure S75. ^{13}C NMR spectrum of **18a** in $CDCl_3$ at room temperature.

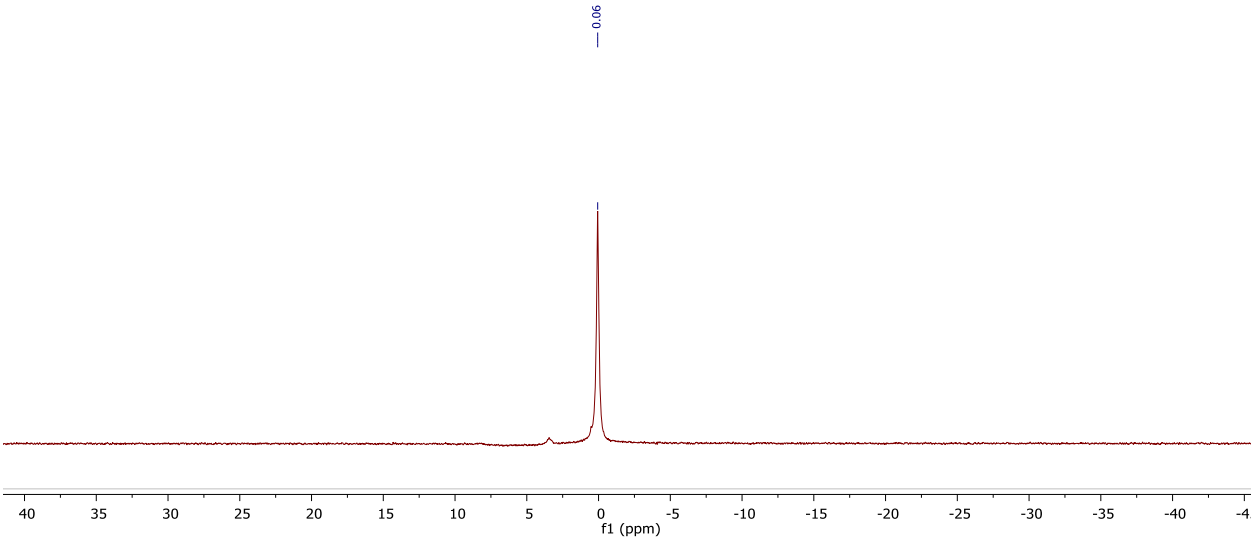


Figure S76. ^{11}B NMR spectrum of **18a** in $CDCl_3$ at room temperature.

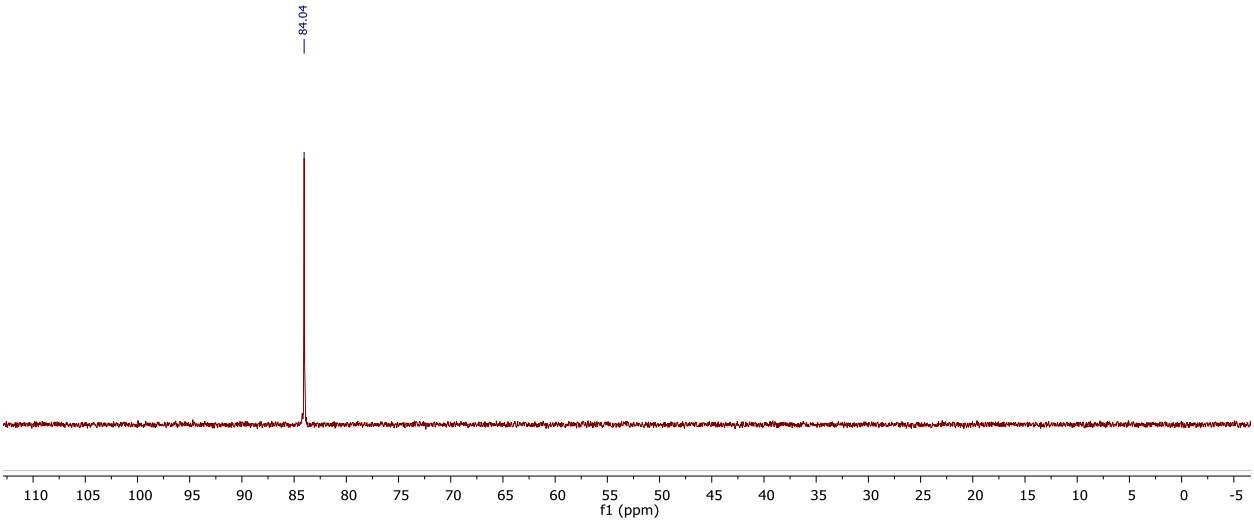
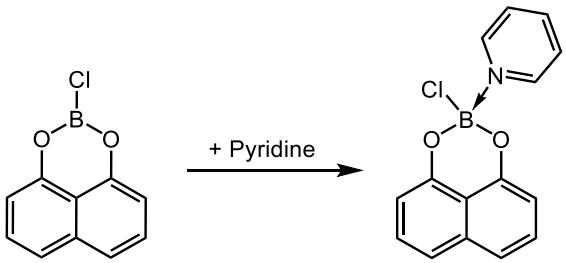


Figure S77. ^{31}P NMR spectrum of **17a** in $CDCl_3$ at room temperature.

2.4.14 Synthesis of **19a**



13a **19a**

In the glove box, **13a** (51 mg, 0.25 mmol), pyridine (19.8 mg, 0.25 mol) and dry CH_2Cl_2 (5 mL) were added to a 30 mL Schlenk flask. After the mixture was stirred for one hour, all volatiles were removed under vacuum. The solid residue was washed once with benzene and dried under vacuum to give **19a** as a colorless solid. Yield 50 mg (70%). ^{1}H NMR [400 MHz, C_6D_6]: 6.15 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-py, 4 H), 6.47 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-py, 1 H), 7.11 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$, CH-naphthyl, 2 H), 7.27-7.34 (m, CH-naphthyl, 4 H), 8.62 (d, $^{3}J_{H\text{-}H}$ = 4 Hz, CH-py, 2 H) ppm. ^{13}C{H} NMR [100.4 MHz, C_6D_6] 109.2 (CH-py), 117.1 (C-quart), 119.3, 125.0, 127.9 (CH-naphthyl) 136.2 (C-quart), 142.7, 143.2 (CH-py), 151.3 (C-quart) ppm. ^{11}B NMR [128.4 MHz, C_6D_6]: 5.2 ppm. Attempts to obtain accurate microanalysis have failed due to the extreme water sensitivity of this compound.

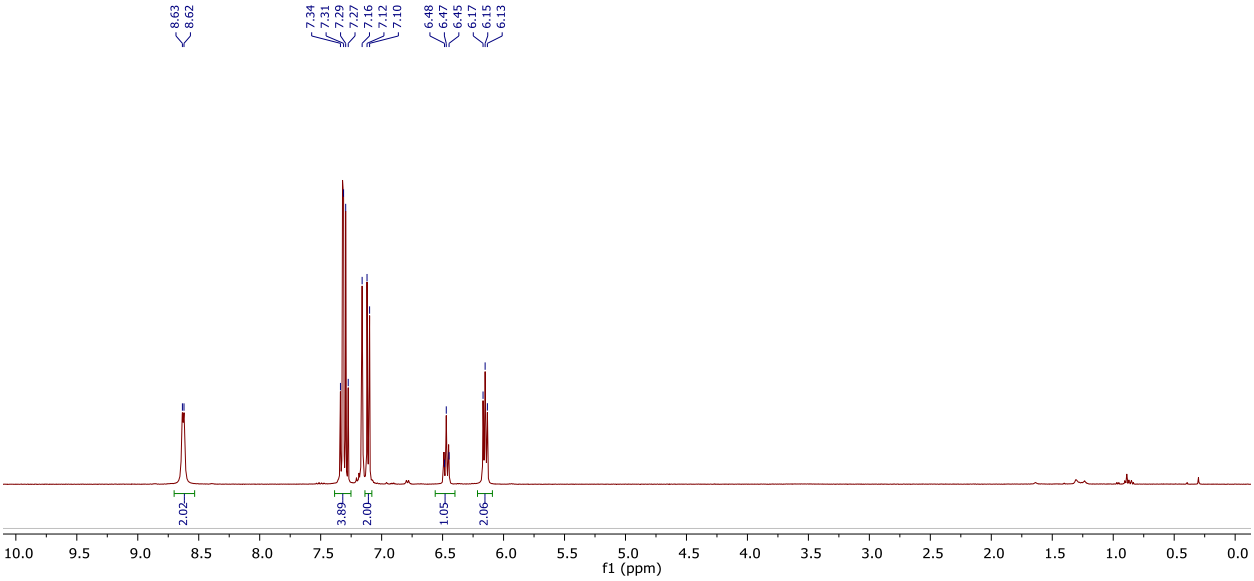


Figure S78. ^{1}H NMR spectrum of **19a i**n $CDCl_3$ at room temperature.

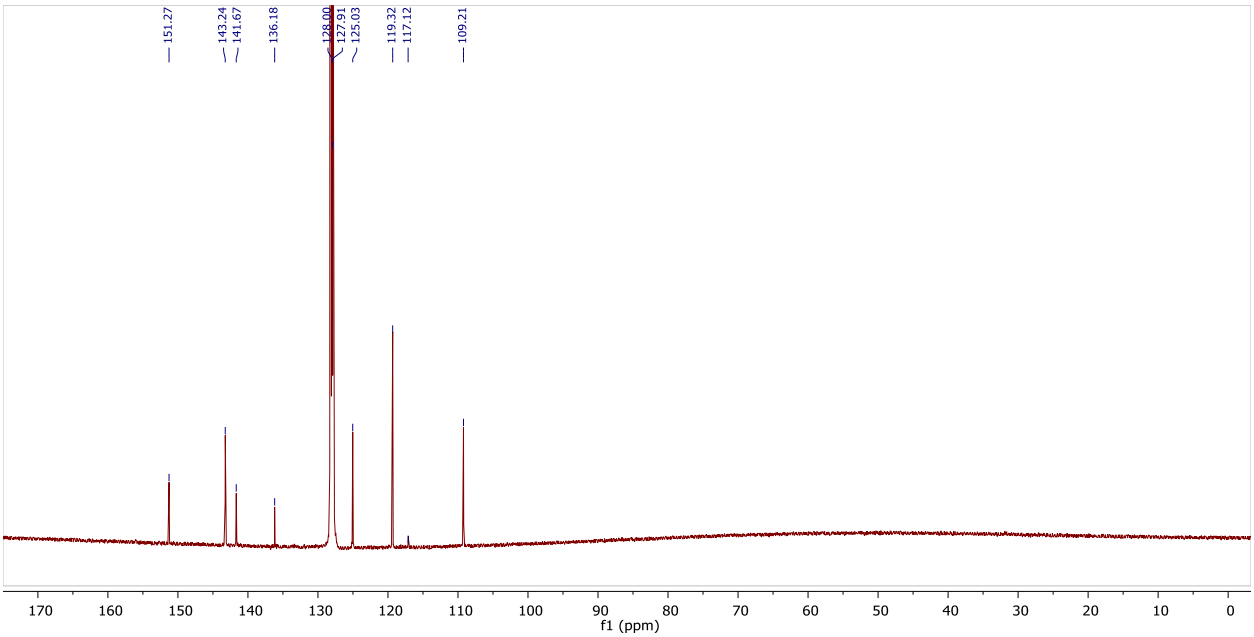


Figure S79. ^{13}C NMR spectrum of **19a** in $CDCl_3$ at room temperature.

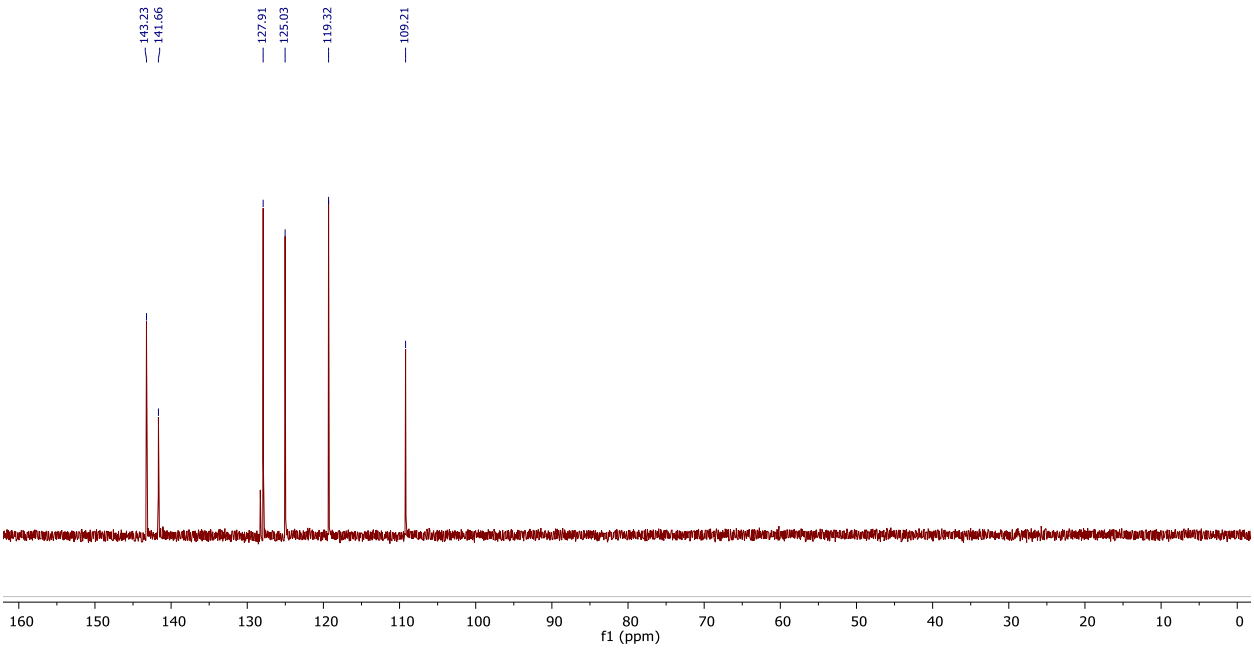


Figure S80. ^{13}C DEPT NMR spectrum of **19a** in $CDCl_3$ at room temperature.

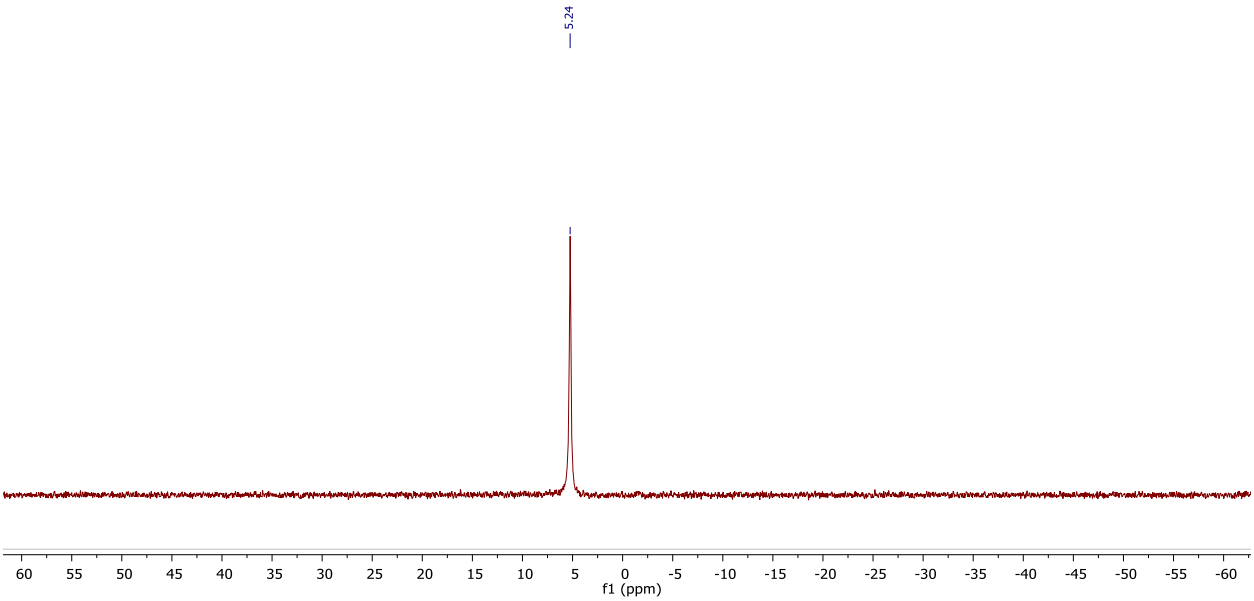
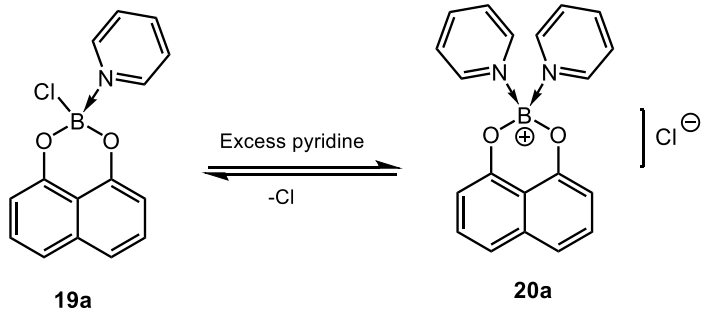


Figure S81. ^{11}B NMR spectrum of **19a** in $CDCl_3$ at room temperature.

2.4.15 Reaction of **19** with pyridine - attempted synthesis of **20a**



19a **20a**

In the glove box, a J-Young NMR tube was charged with **19a** (6 mg, 0.02 mmol), one equivalent of anhydrous pyridine (1.5 mg, 0.02 mmol) and $CDCl_3$ (0.5 mL) and a ^1H NMR spectrum of the resulting solution was taken. Then another equivalent of anhydrous pyridine (1.5 mg, 0.02 mmol) was added and again a ^1H NMR spectrum of the solution was taken.

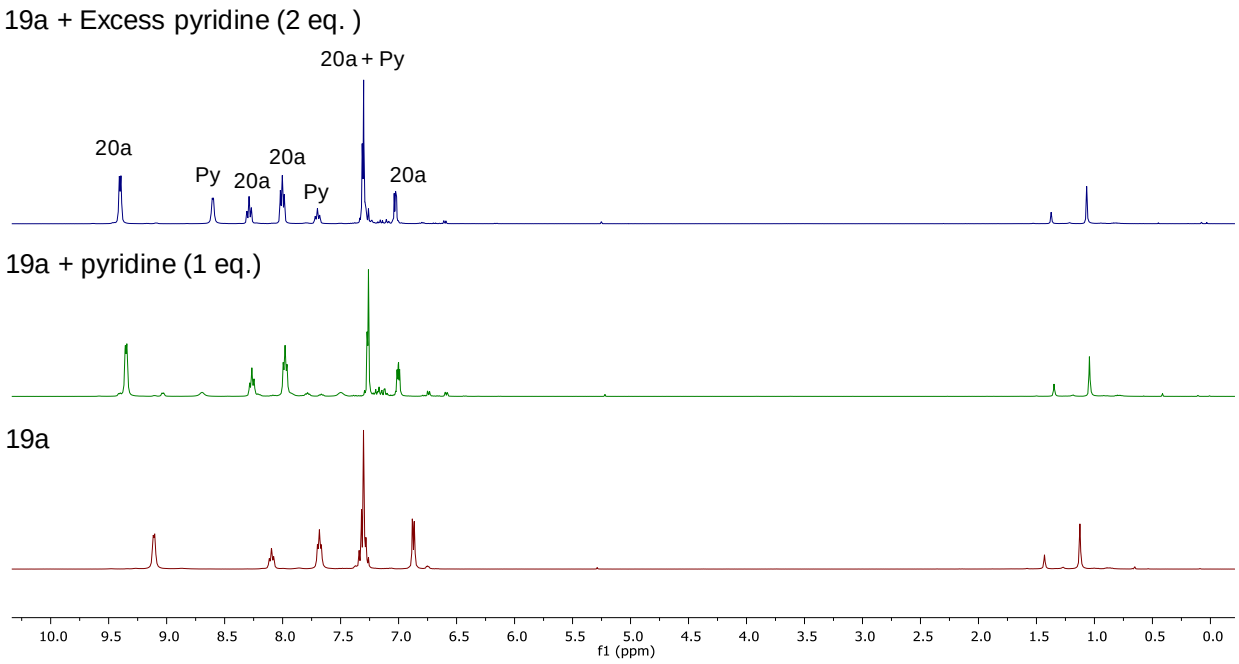
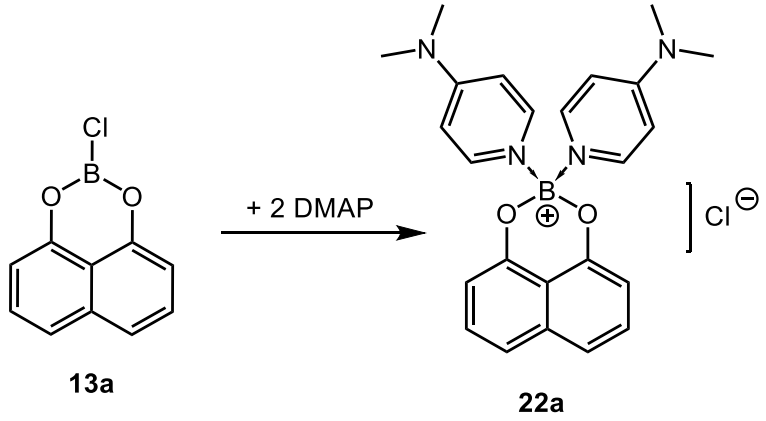


Figure S82. ^{1}H NMR stack plot of **19a** with excess pyridine in $CDCl_3$ at room temperature.

2.4.16 Synthesis of **22a**



13a **22a**

In the glove box, **13a** (0.51 mg, 0.25 mmol), DMAP (60 mg, 0.5mmol) and dry CH_2Cl_2 (5 mL) were added to a 30 mL Schlenk flask. The mixture was stirred one hour, and all volatiles were removed under vacuum. The resulting precipitate was washed once with benzene and dried under vacuum to give **22a** as a white solid. Yield 95 mg (85 %). ^{1}H

NMR [400 MHz, $CDCl_3$]: 3.10 (s, CH_3, 12 H), 6.75 (d, $^3\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-DMAP, 4 H), 6.84 (d, $^3\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.22-7.27 (m, CH-naphthyl, 4 H), 8.18 (d, $^3\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-DMAP, 4 H) ppm. $^{13}C\{H\}$ NMR [100.4 MHz, $CDCl_3$]: 40.2 (CH_3), 107.8 (CH-DMAP), 109.3 (CH-naphthyl), 116.1 (CH-naphthyl), 119.2 (C-quart), 127.7 (CH-naphthyl), 135.3 (C-quart), 141.5 (CH-DMAP), 149.6, 156.7 (C-quart) ppm. ^{11}B NMR [128.4 MHz, $CDCl_3$]: 1.1 ppm. Attempts to obtain accurate microanalysis have failed due to the extreme water sensitivity of this compound.

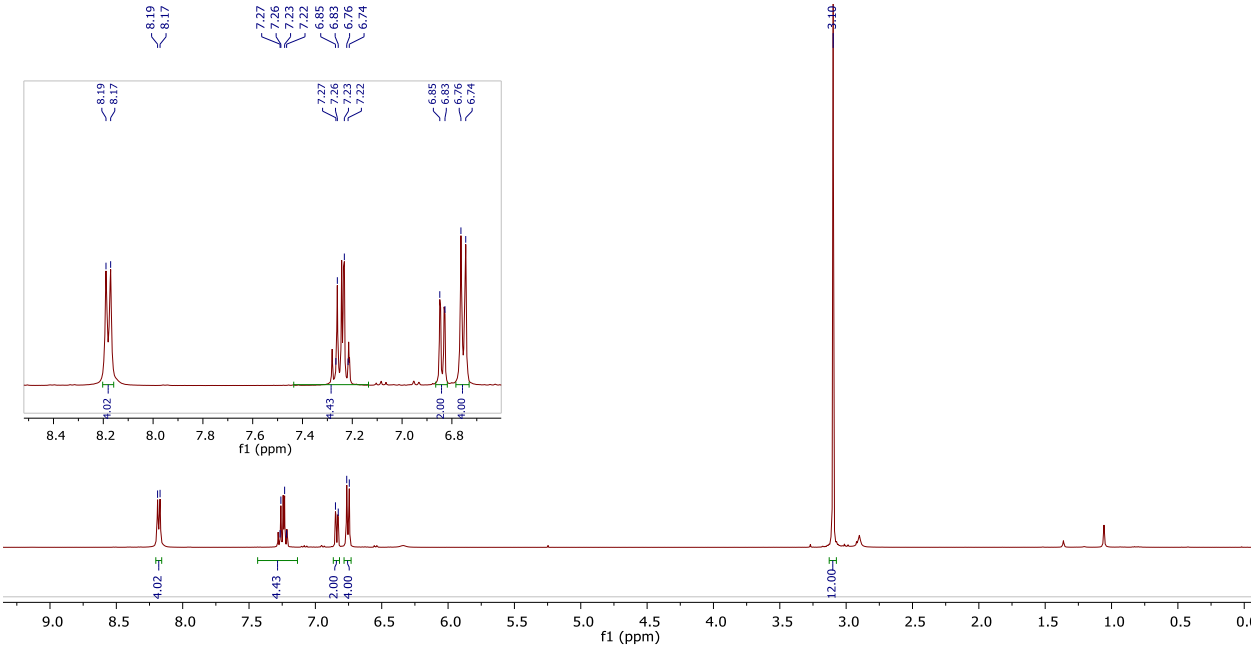


Figure S83. ^1H NMR spectrum of **22a i**n $CDCl_3$ at room temperature.

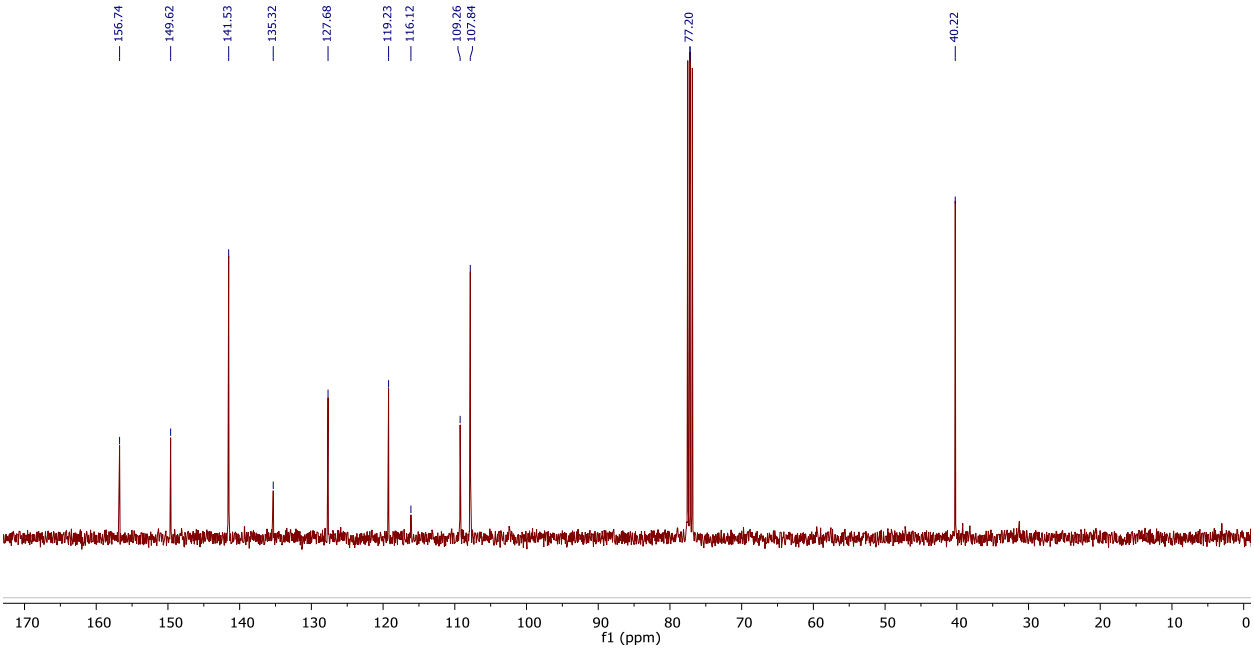


Figure S84. ^{13}C NMR spectrum of **22a** in $CDCl_3$ at room temperature.

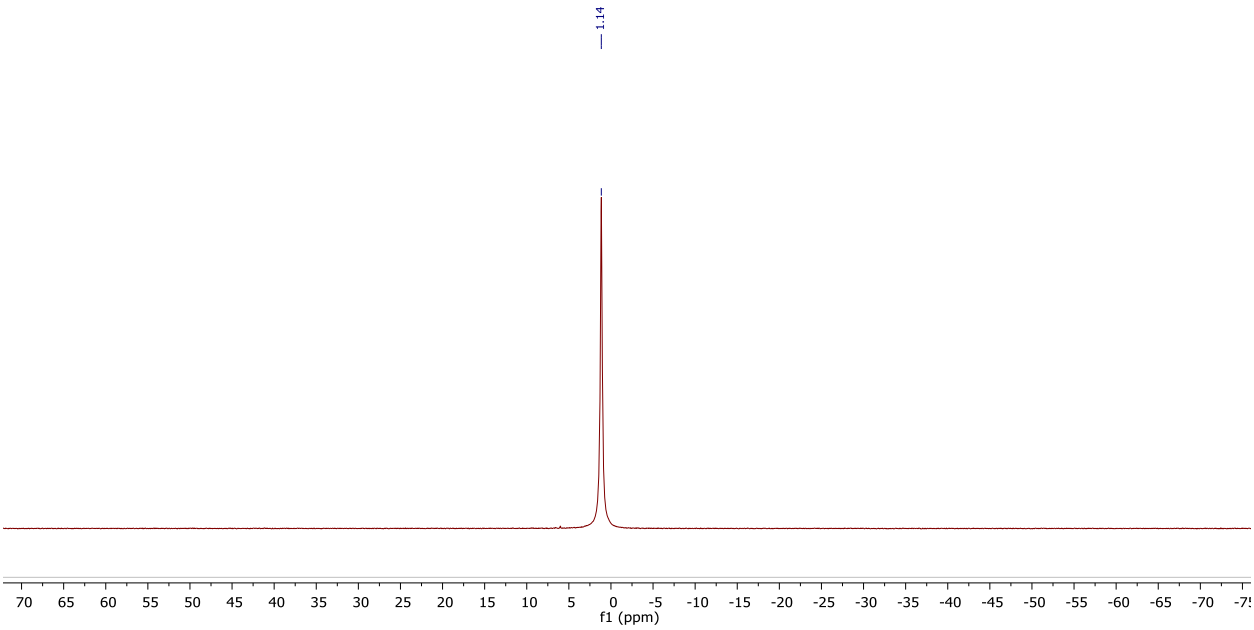
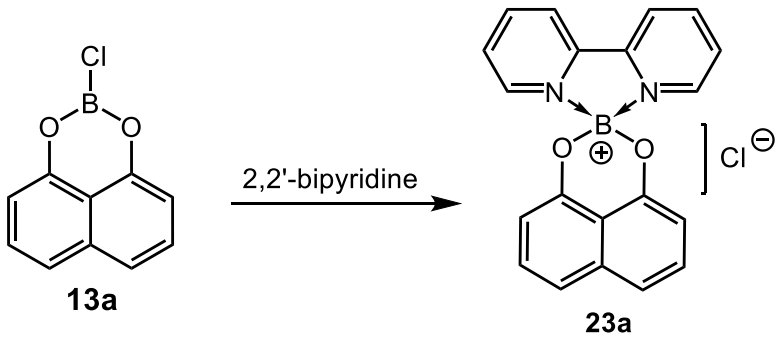


Figure S85. ^{11}B NMR spectrum of **22a** in $CDCl_3$ at room temperature.

2.4.18 Synthesis of **23a**



13a **23a**

In a glove box, **13a** (86 mg, 0.42 mmol) was dissolved in toluene (10 mL) in a 30 mL Schlenk flask. Separately, anhydrous 2,2-bipyridine (62 mg, 0.4 mmol) was dissolved in toluene (5 mL) in a shell vial. The resulting solution was slowly transferred to the solution of **13a**, upon which an orange colored solid precipitated immediately. The orange suspension was stirred overnight, and the precipitate washed twice with toluene and dried under vacuum to give **23a**·½toluene as an orange solid. Note! Attempts to fully remove toluene by heating the solid under dynamic vacuum for one day failed as partial degradation of **23a** occurred. Yield 140 mg (86 % toluene included). ^{1}H NMR [400 MHz, $CDCl_3$]: 6.80 (d, $^{3}J_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.40 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8.0 Hz, CH-naphthyl, 2 H), 7.48 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8.0 Hz, CH-naphthyl, 2 H), 8.01 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-bipy, 2 H), 8.53 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-bipy, 2 H), 8.79 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-bipy, 2 H), 10.57 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-bipy, 2 H) ppm. ^{13}C{H} NMR [100.4 MHz, $CDCl_3$]: 110.1 (CH), 114.6 (C-quart), 120.5, 127.4, 128.2 (CH), 129.3 (C-quart), 135.5, 142.2 (CH), 145.2, 148.2 (C-quart), 148.3 (CH) ppm. ^{11}B NMR [128.4 MHz, $CDCl_3$]: 5.9 ppm. Attempts to obtain accurate microanalysis have failed due to the extreme water sensitivity of this compound.

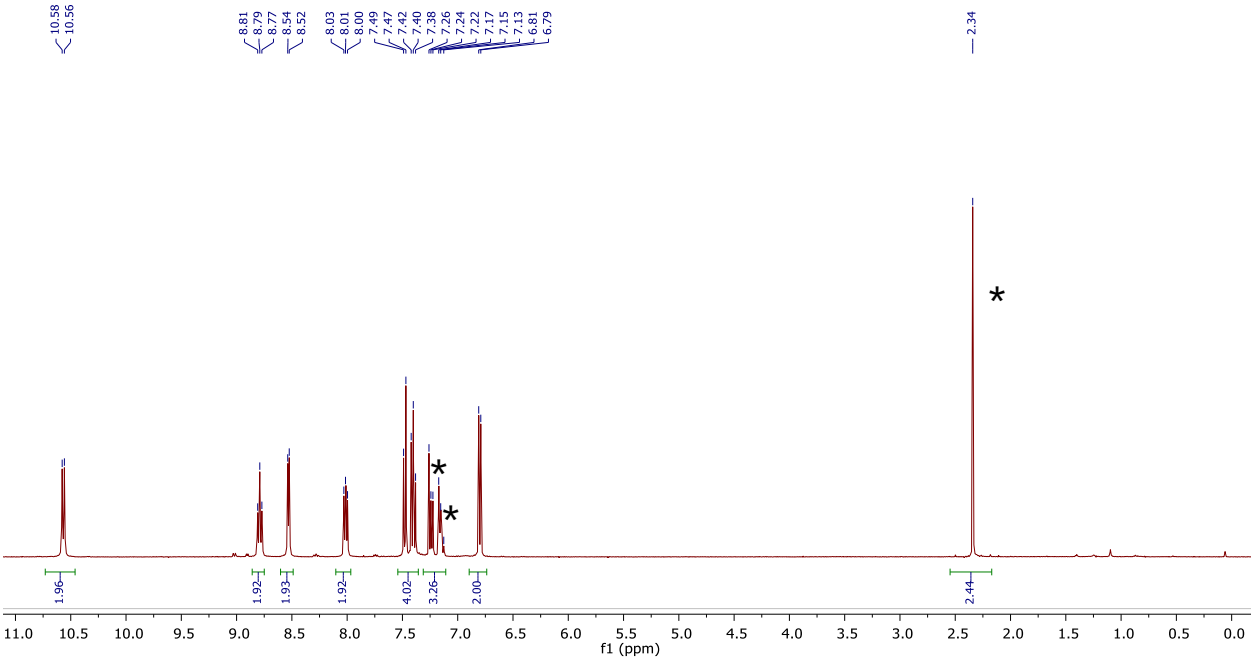


Figure S86. ^{1}H NMR spectrum of **23a i**n $CDCl_3$ at room temperature (toluene signals labelled with asterisks).

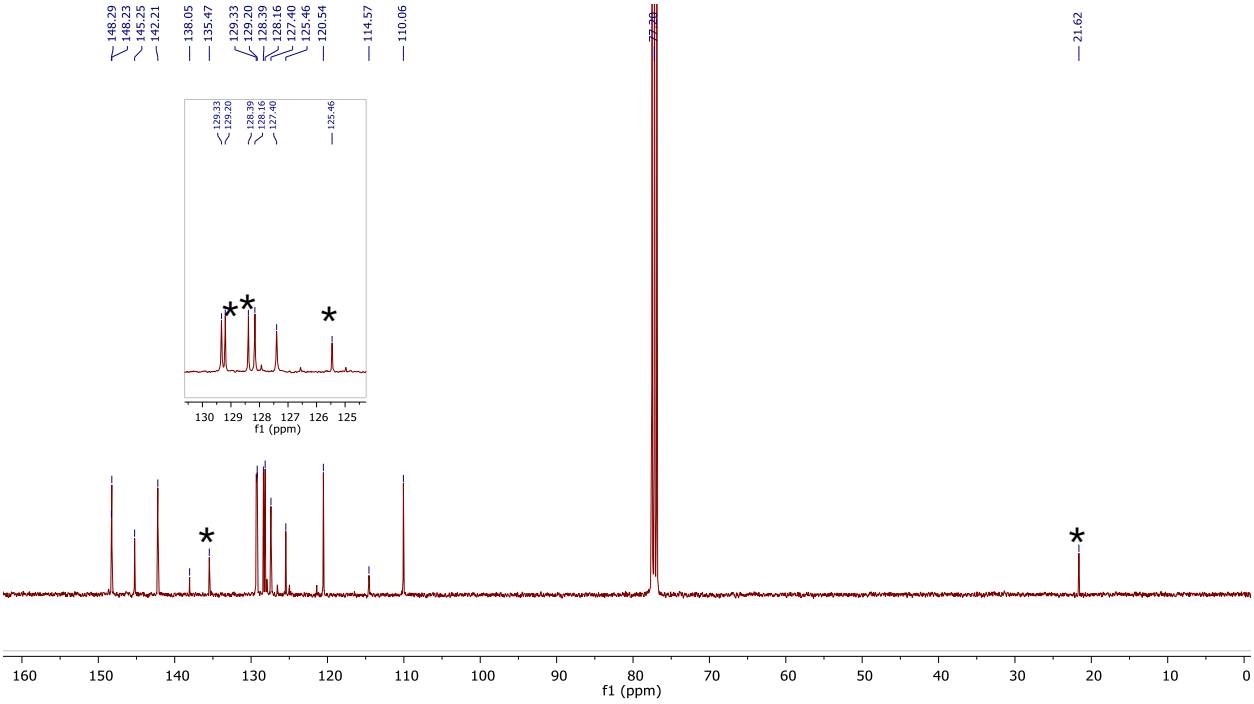


Figure S87. ^{13}C NMR spectrum of **23a** in $CDCl_3$ at room temperature (toluene signals labelled with asterisks).

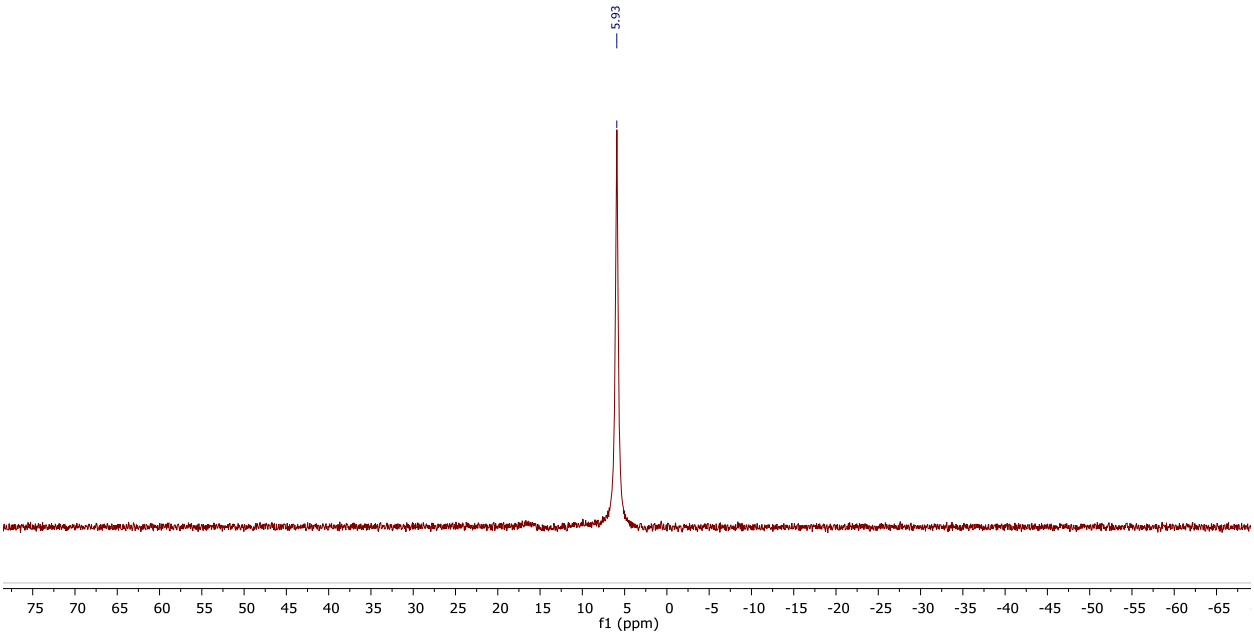
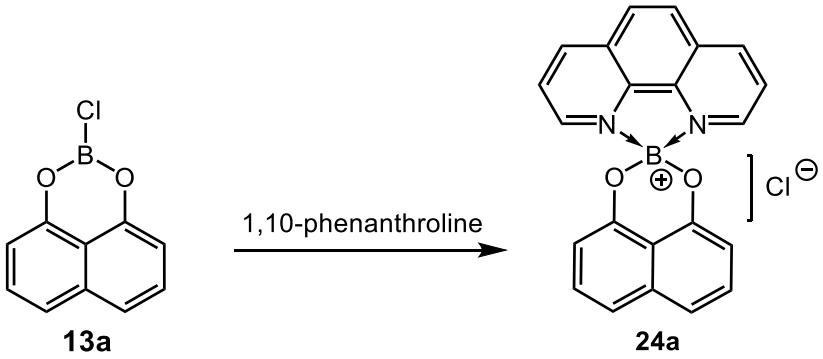


Figure S88. ^{11}B NMR spectrum of **23a** in $CDCl_3$ at room temperature.

2.4.17 Synthesis of **24a**



In a glove box, **13a** (53 mg, 0.26 mmol) was dissolved in toluene (5 mL) in 30 mL Schlenk flask. Separately, anhydrous 1,10-phenanthrolene (43 mg, 0.24 mmol) was dissolved in dry toluene (5 mL) in a shell vial. The resulting solution was slowly transferred to the solution of **13a**, upon which an orange colored solid precipitated immediately. The orange suspension was stirred overnight, and the precipitate washed twice with toluene and dried under vacuum to give **24a**·0.4toluene as an orange solid. Note! Attempts to fully remove

toluene by heating the solid under dynamic vacuum for one day failed as partial of degradation of **24a** occurred. Yield 91 mg (90 % toluene included). ^{1}H NMR [400 MHz, $CDCl_3$]: 6.94 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.37 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 7.44 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-naphthyl, 2 H), 8.05 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-phen, 2 H), 8.11 (s, CH-phen, 2 H), 8.74 (t, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-phen, 2 H), 9.64 (d, $^{3}\boldsymbol{J}_{H\text{-}H}$ = 8 Hz, CH-phen, 2 H) ppm. ^{13}C{H} NMR [100.4 MHz, $CDCl_3$]: 110.0 (CH), 116.5 (C-quart.), 121.4, 125.3, 127.6, 127.9 (CH), 129.8, 135.3, 138.3 (C-quart.), 140.9, 148.7 (CH) ppm. ^{11}B NMR [128.4 MHz, $CDCl_3$]: 16.7 ppm. Attempts to obtain accurate microanalysis have failed due to the extreme water sensitivity of this compound.

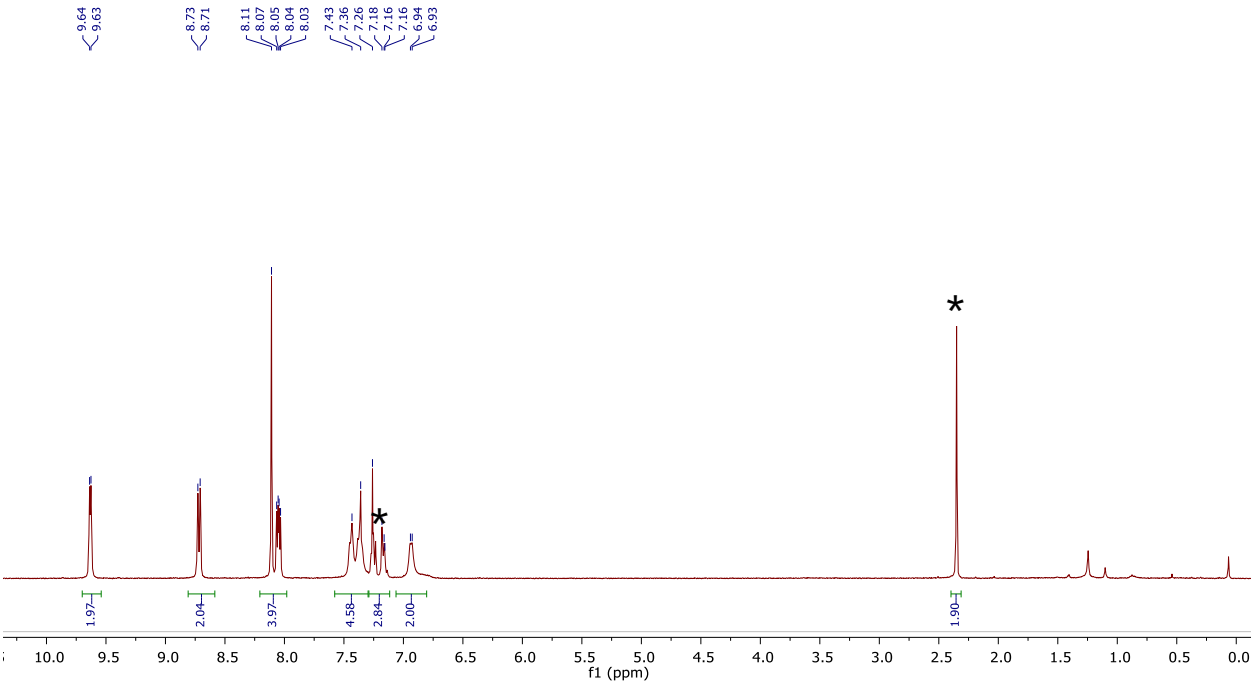


Figure S89. ^{1}H NMR spectrum of **24a i**n $CDCl_3$ at room temperature (toluene signals labelled with asterisks).

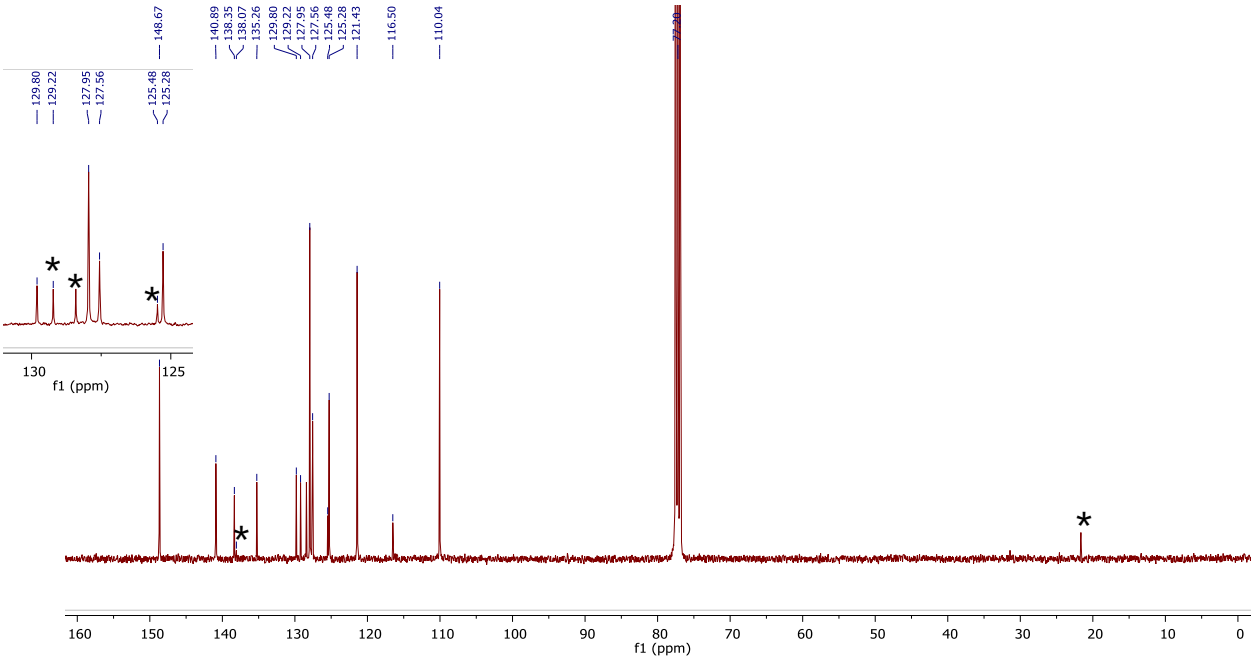


Figure S90. ^{13}C NMR spectrum of **24a** in $CDCl_3$ at room temperature (toluene signals labelled with asterisks).

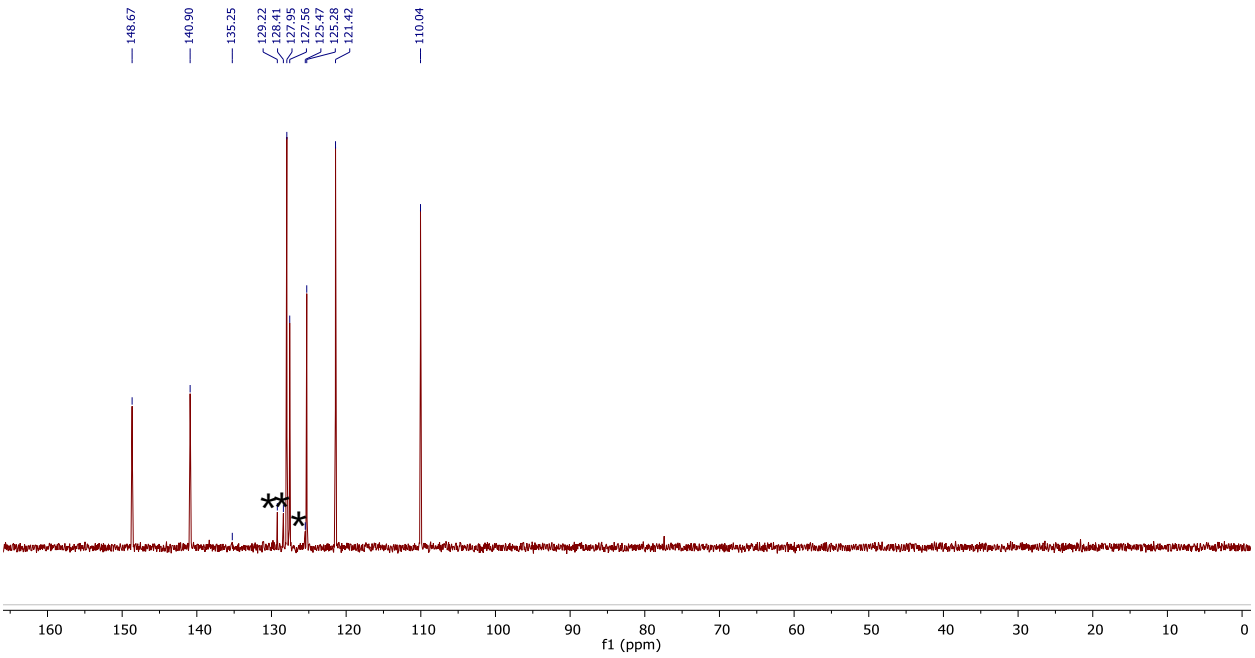


Figure S91. ^{13}C DEPT NMR spectrum of **24a** in $CDCl_3$ at room temperature (toluene signals labelled with asterisks).

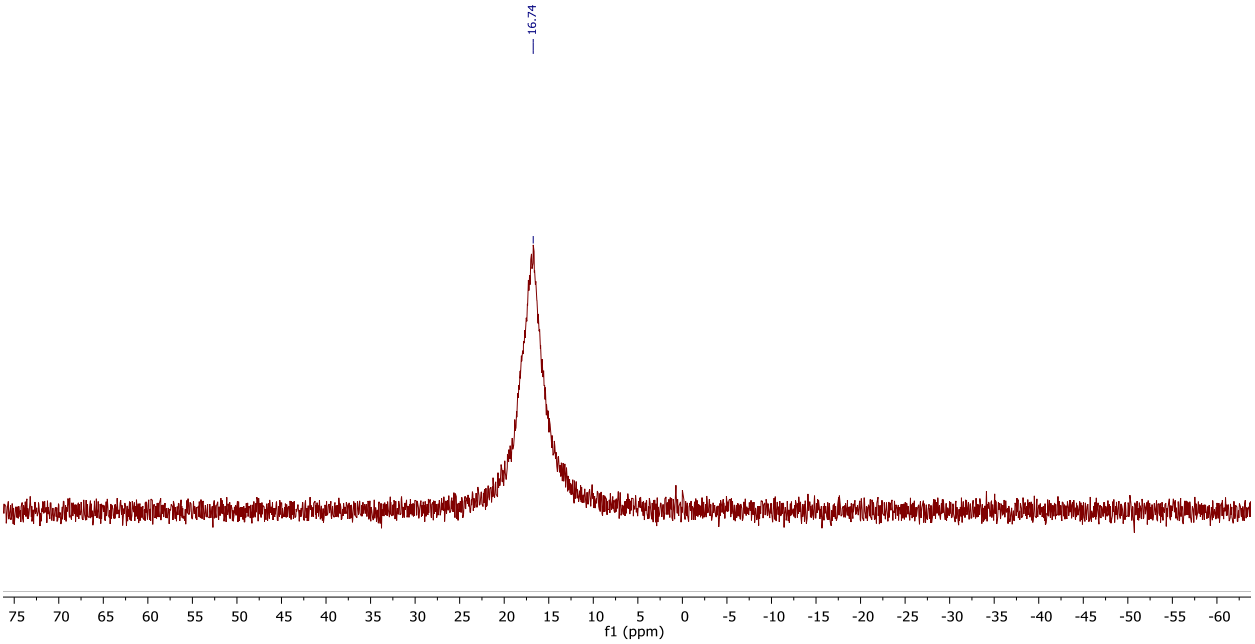


Figure S92. ^{11}B NMR spectrum of **24a** in $CDCl_3$ at room temperature.

2.5 Estimation of the Lewis acid strength of **1a-7a** and **1b-7b** via the Gutmann-Beckett method

All samples for ^{31}P NMR chemical shift measurements with different Lewis acids to $O{=}PEt_3$ ratios were prepared in the Glove box using dry C_6D_6. To a solution of ca. ≈ 3 mg of $OPEt_3$ in 0.5 mL of C_6D_6, variable amounts of Lewis acids were added and ^{31}P NMR spectra were taken. For all the measured Lewis acids (LAs), the equilibrium between LA←$O{=}PEt_3$ complex and free LA and $O{=}PEt_3$ is fast within the NMR time scale. Consequently, the observed signal is a weighted average of the LA←$O{=}PEt_3$ complex and free acid and $O{=}PEt_3$. To determine accurate ^{31}P NMR chemical shifts for these LA←$O{=}PEt_3$ complexes, additional equivalents of Lewis acid were added until the ^{31}P NMR chemical shift did not change significantly.

Table S2. ^{31}P NMR chemical shift measured for different Lewis acids to $O{=}PEt_3$ ratios in C_6D_6 [$\delta_{O=PEt3}$ = 46.2 ppm].

Lewis Acid: $OPEt_3$	(1:1) δ_{31P}	(2:1) δ_{31P}	(3:1) δ_{31P}	(4:1) δ_{31P}	(5:1) δ_{31P}
C_6H_5-BNad (**1a**)	58.9	65.3	66.8	67.3	**67.9**[a]
C_6F_5-BNad (**2a**)	75.5	77.5	**77.5**	-	-
3,4,5-F_3-C_6H_2-BNad (**3a**)	64.5	73.4	73.7	**73.8**	-
2,4,6-F_3-C_6H_2-BNad (**4a**)	69.3	74.6	74.2	**74.3**	-
2,6-F_2-C_6H_3-BNad (**5a**)	67.1	73.7	73.5	**73.6**	-
2,6-Cl_2-C_6H_3-BNad (**6a**)	55.8	59.1	62.2	64.4	**65.2**[a]
2,4,6-Me_3-C_6H_2-BNad (**7a**)	46.2	**46.3**	-	-	-

Values marked in red were used for the calculation of the acceptor number (AN); a …..

Table S3. ^{31}P NMR chemical shift measured for different Lewis acids to $O{=}PEt_3$ ratios in C_6D_6 [$\delta_{O=PEt3}$ = 46.2 ppm].

Lewis Acid: $OPEt_3$	(1:1) δ_{31P}	(2:1) δ_{31P}	(3:1) δ_{31P}	(4:1) δ_{31P}	(5:1) δ_{31P}	(6:1) δ_{31P}	(7:1) δ_{31P}	(8:1) δ_{31P}	(9:1) δ_{31P}
C_6H_5-BCat (**1b**)	56.9	62.3	66.7	68.9	-	-	69.1	**69.2**	-
C_6F_5-BCat (**2b**)	68.1	76.4	-	**76.6**	-	-	-	-	-
3,4,5-F_3-C_6H_2-BCat (**3b**)	71.1	74.7	-	74.9	**74.9**	-	-	-	-
2,4,6-F_3-C_6H_2-BCat (**4b**)	69.9	-	74.1	-	**74.1**	-	-	-	-
2,6-F_2-C_6H_3-BCat (**5b**)	65.9	-	73.7	73.7	-	73.8	-	**73.9**	-
2,6-Cl_2-C_6H_3-BCat (**6b**)	55.4	61.9	-	67.1	68.1	68.9	-	69.8	**70.2**
2,4,6-Me_3-C_6H_2-BCat (**7b**)	46.2	-	**46.5**	-	-	-	-	-	-

Values marked in red were used for the calculation of the acceptor number (AN).

3. X-ray crystallography

CCDC1962509 (**1a**), CCDC1962510 (**2a**), CCDC1962511 (**3a**), CCDC1962512 (**4a**), CCDC1962513 (**5a**), CCDC1962514 (**8a**), CCDC1962515 (**10a**), CCDC1962516 (**14a**), CCDC1965596 (**16a**), CCDC1962517 (**17a**), CCDC1962518 (**18a**), and CCDC1962519 (**23a**) contain the supplementary crystallographic data for this paper.

These data can be obtained from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

3.1 General Data Collection

Data for complexes **3a** and **8a** were collected on a Bruker PLATFORM three circle diffractometer equipped with an APEX II CCD detector and operated at 1500 W (50kV, 30 mA) to generate (graphite monochromated) Mo Kα radiation (λ = 0.71073 Å). For structures **2a**, **4a**, **5a**, **10a**, **14a**, **16a**, **17a**, **18a,** and **23a** data were collected on collected on a Rigaku XtaLAB Synergy-*i* Kappa diffractometer equipped with a PhotonJet-*i* X-ray source operated at 50 W (50kV, 1 mA) to generate Cu Kα radiation (λ = 1.54178 Å) and a HyPix-6000HE HPC detector. In all cases, crystals were transferred from the mother liquor and placed on a glass slide in polyisobutylene. A Zeiss Stemi 305 microscope was used to identify a suitable specimen for X-ray diffraction from a representative sample of the material. The crystal and a small amount of the oil were collected on either a MiTiGen cryoloop or a Hampton nylon loop and transferred to the instrument where it was placed under a cold nitrogen stream (Oxford) maintained at 100K throughout the duration of the experiment. The samples were optically centered with the aid of a video camera to insure that no translations were observed as the crystal was rotated through all positions.

A unit cell collection was then carried out. After it was determined that the unit cell was not present in the CCDC database a sphere of data was collected. For **3a**, and **8a,** omega

scans were carried out with a 10 sec/frame exposure time and a rotation of 0.50° per frame. For structures **2a**, **4a**, **5a**, **10a**, **14a**, **16a**, **17a**, **18a,** and **23a** a data collection strategy was calculated by *CrysAlis*^{Pro} [5] using omega, phi, and kappa scans. After data collection, the crystal was measured for size, morphology, and color. These values are reported in Tables **S4-S6**.

3.2 Refinement Details

After data collection, the unit cell was re-determined using a subset of the full data collection. Intensity data for **3a** and **8a** were corrected for Lorentz, polarization, and background effects using the Bruker program APEX 3. A semi-empirical correction for adsorption was applied using the program *SADABS* [6]. Intensity data for **2a**, **4a**, **5a**, **10a**, **14a**, **16a**, **17a**, **18a,** and **23a** were corrected for Lorentz, polarization, and background effects using the *CrysAlis*^{Pro} [5]. A numerical absorption correction was applied based on a Gaussian integration over a multifaceted crystal and followed by a semi-empirical correction for adsorption applied using the program *SCALE3 ABSPACK* [7]. The *SHELXL-2014* [8], series of programs was used for the solution and refinement of the crystal structures.

For **1a**, hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands. Inconsistent reflections -7 3 4 and -7 3 6 were omitted during the final refinements.

For **2a**, hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands. Inconsistent reflection 4 0 0 was omitted during the final refinements.

For **3a**, hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands. Inconsistent reflections 1 3 4, -4 2 4, and -6 0 4 were omitted during the final refinements.

For structures **4a**, **5a**, **8a**, and **14a** hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands.

For **10a**, hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands. The Z' value for the structure is 3.

For **16a**, every atom position was disordered over two sites. The site occupancies were 0.92 and 0.08 for **PART 1** and **PART 2**, respectively. To help maintain reasonable ADP values for the minor component, RIGU and SIMU restraints were applied. Inconsistent reflections 1 0 8 and 3 3 8 were omitted during the final refinements. Hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands.

For **17a**, once the atom positions of the main molecule and an interstitial acetonitrile molecule were determined, it was suspected that a highly disordered acetonitrile molecule existed about an inversion center on a three-fold axis. This disordered electron density was treated as diffuse scattering using the SQUEEZE [9] routine within PLATON [10], which resulted in a total of three void spaces each containing electron count of 24. Based on the electron density of acetonitrile, this is approximately one molecule of acetonitrile per void space. However, due to the lack of any other empirical evidence, this information was not added to the CIF. Hydrogen atoms bound to carbon atoms were geometrically constrained using the appropriate AFIX commands.

For **18a**, the ethyl groups bound to P2 (C17 < C22) were positionally disordered over two sites (A and B). The sites occupancies for the A and B sites were 0.93 and 0.07, respectively. To help maintain reasonable ADP values and atom positions for the minor components, SIMU, DELU, DFIX and EADP restraints and constraints were applied where needed. Hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands.

For **23a**, the interstitial benzene ring (C47 < C52) was disordered and was modeled as split sites A and B. To help maintain reasonable ADP values and C-C bond lengths,

SIMU, RIGU, and AFIX 66 restraints and constraints were applied. There was also a 1,8-naphthalenediol complexed to a B-OH group disordered about an inversion center, resulting in the SOF values of the atoms being set to 0.5. Hydrogen atoms bound to carbon atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands, while the hydrogen atom bound to oxygen (O5) was restrained with a DFIX command. The Z' value for the structure was 2.

Table S4. Crystallographic data for compounds **1a-4a**.

	1a	**2a**	**3a**	**4a**
Formula	$C_{16}H_{11}BO_2$	$C_{16}H_6BF_5O_2$	$C_{16}H_8BF_3O_2$	$C_{16}H_8BF_3O_2$
Molecular weight	246.06	336.02	300.03	300.03
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	13.8170(2)	9.30604(7)	9.000(2)	14.68950(10)
b (Å)	4.72630(10)	9.01092(6)	9.222(2)	4.72070(10)
c (Å)	18.1904(3)	15.64505(12)	15.177(3)	18.1961(2)
β (°)	102.366(2)	103.8492(7)	102.643(3)	102.4210(10)
Volume ($Å^3$)	1160.33(4)	1273.792(16)	1229.1(5)	1232.27(3)
Z	4	4	4	4
ρ_{calcd} (g cm^{-3})	1.409	1.752	1.621	1.617
Temperature (K)	100	100	100	100
μ (mm^{-1})	0.722	1.439	0.135	1.164
Reflections collected	19552	23436	7797	32221
Unique reflections	2402	2676	2270	2579
(R_{int})	(0.0352)	(0.0366)	(0.0464)	(0.0426)
R_1 [$I>2\sigma(I)$]	0.0394	0.0329	0.0419	0.0348
wR_2 (all data)	0.1135	0.0955	0.1066	0.1033
Goodness-of-fit on F^2	1.098	1.055	1.052	1.067

Table S5. Crystallographic data for compounds **5a**, **8a**, **10a** and **14a**.

	5a	**8a**	**10a**	**14a**
Formula	$C_{16}H_9BF_2O_2$	$C_{18}H_{15}BO_4$	$C_{11}H_9BO_3$	$C_{20}H_{12}B_2O_5$
Molecular weight	282.04	306.11	199.99	353.92
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	8.57980(10)	7.7613(5)	22.9961(2)	7.4723(2)
b (Å)	11.10590(10)	23.5453(15)	8.76840(10)	8.48060(10)
c (Å)	12.94850(10)	8.1854(5)	14.2648(2)	13.3696(3)
β (°)	99.9770(10)	98.4110(10)	102.7300(10)	82.555(2)
Volume ($Å^3$)	1215.16(2)	1479.73(16)	2805.64(6)	776.61(3)
Z	4	4	12	2
ρ_{calcd} (g cm^{-3})	1.542	1.374	1.420	1.513
Temperature (K)	100	100	100	100
μ (mm^{-1})	1.017	0.095	0.833	0.878
Reflections collected	14851	18004	36569	21542
Unique reflections	2543	3537	5830	3205
(R_{int})	(0.0224)	(0.0198)	(0.0404)	(0.0312)
R_1 [$I>2\sigma(I)$]	0.0311	0.0352	0.0343	0.0333
wR_2 (all data)	0.0853	0.0962	0.0940	0.0950
Goodness-of-fit on F^2	1.060	1.054	1.059	1.090

Table S6. Crystallographic data for compounds **16a**, **17a**, **18a** and **23a**.

	16a	**17a**	**18a**	**23a**
Formula	$C_{20}H_{12}B_2O_4$	$C_{76}H_{84}B_6N_8O_{12}$	$C_{22}H_{36}BClO_4P_2$	$C_{114}H_{88}B_5C_{l4}N_8O_{11}$
Molecular weight	337.92	1366.37	472.71	1941.77
Space group	$P2_1/c$	$R\bar{3}$	$P2_1/c$	$P\bar{1}$
a (Å)	12.3335(2)	16.70350(10)	11.88720(10)	12.7300(2)
b (Å)	5.12500(10)	16.70350(10)	19.09820(10)	13.2386(2)
c (Å)	12.2086(3)	23.0950(2)	11.32260(10)	15.2532(2)
β (°)	100.641(2)	90	102.3290(10)	74.9410(10)
Volume (Å^3)	758.43(3)	5580.38(8)	2511.22(3)	2470.56(6)
Z	2	3	4	1
ρ_{calcd} (g cm^{-3})	1.448	1.220	1.250	1.305
Temperature (K)	100	100	100	100
μ (mm^{-1})	0.819	0.654	2.749	1.627
Reflections collected	10355	15221	47551	64243
Unique reflections	1559	2608	5232	10099
(R_{int})	(0.0290)	(0.0241)	(0.0518)	(0.0410)
R_1 [$I>2\sigma(I)$]	0.0394	0.0384	0.0373	0.0396
wR_2 (all data)	0.0981	0.1051	0.0985	0.1097
Goodness-of-fit on F^2	1.177	1.045	1.039	1.045

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