Electronic Supplementary Information

Supramolecular gels based on boronate esters and imidazolyl donors

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Content :

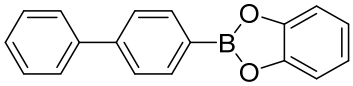
1. Experimental

1.1 General

All reactants and solvents were purchased from Sigma-Aldrich, Fisher Scientific, Acros, Fluorochem and Alfa Aesar, and were used without further purification. NMR spectra were recorded with a Bruker Avance DPX 400 spectrometer with the residual solvent as internal standard. ITC measurements were performed on a GE MicroCal VP-ITC system. Rheology data were measured on a Bohlin C-VOR shear rheometer. 4,4'-Diphenylacetylene-diboronic acid,[1] 4-phenylethynyl-benzene boronic acid,[2] 1,1'-(propane-2,2-diyl)bisimidazole,[3] bis(imidazole-1-yl)methane[4], 1,4-bis(imidazol-1-yl)butane[5], 1,4-bis(imidazol-1-yl)benzene[5], 2,6-naphthalenediboronic acid[6], 4-(benzo[*d*][1,3,2]dioxaborol-2-yl)benzonitrile,[7] 5,6-dichloro-2-phenylbenzo[*d*][1,3,2]dioxaborole,[8] and 2-phenylbenzo[*d*][1,3,2]dioxaborole[8] were synthetized according to literature procedures.

1.2 Synthesis and characterization

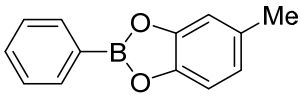
Synthesis of 2-([1,1'-biphenyl]-4-yl)benzo[*d*][1,3,2]dioxaborole



A mixture of catechol (110 mg, 1.0 mmol) and 4-biphenyl boronic acid (198 mg, 1.0 mmol) in toluene (50 mL) was heated under reflux using a Dean Stark apparatus for 4 h. After this time, the reaction was cooled to RT and the solvent was evaporated. The product was purified by recrystallization from toluene and collected by filtration (262 mg, 96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, J = 8.3 Hz, 2 H), 7.73 (d, J = 8.3 Hz, 2 H), 7.67 (d, J = 7.0 Hz, 2 H), 7.48 (t, J = 7.5 Hz, 2 H), 7.40 (t, J = 7.4 Hz, 1 H), 7.37 – 7.31 (m, 2 H), 7.18 – 7.11 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.56, 144.99, 140.63, 135.49, 128.88, 127.89, 127.26, 126.96, 122.80, 112.57 (B-C was not observed due to quadrupole broadening). ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.90. HRMS (APPI) calc'd for [M]+: 272.1012, found: 272.1003.

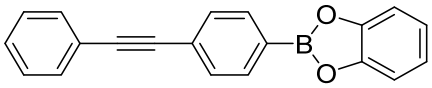
Synthesis of 5-methyl-2-phenylbenzo[*d*][1,3,2]dioxaborole



A mixture of 4-methylcatechol (124 mg, 1.0 mmol) and phenyl boronic acid (122 mg, 1.0 mmol) in toluene (50 mL) was heated under reflux using a Dean Stark apparatus for 4 h. After this time, the reaction was cooled to RT and the solvent was evaporated. The product was purified by recrystallization from toluene/pentane and collected by filtration (181 mg, 86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 6.7 Hz, 2 H), 7.62 – 7.53 (m, 1 H), 7.49 (t, J = 7.2 Hz, 2 H), 7.18 (d, J = 8.1 Hz, 1 H), 7.13 (s, 1 H), 6.92 (d, J = 9.0 Hz, 1 H), 2.42 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.54, 146.39, 134.93, 132.70, 132.26, 128.21, 123.09, 113.16, 111.82, 21.42 (B-C was not observed due to quadrupole broadening). ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.71. HRMS (APPI) calc'd for [M]+: 210.0854, found: 210.0844.

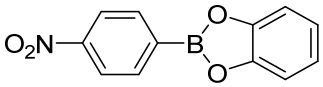
Synthesis of 2-(4-(phenylethynyl)phenyl)benzo[*d*][1,3,2]dioxaborole



A mixture of catechol (110 mg, 1.0 mmol) and 4-phenylethynyl-benzene boronic acid (222 mg, 1.0 mmol) in toluene (50 mL) was heated under reflux using a Dean Stark apparatus for 4 h. After this time, the reaction was cooled to RT and the solvent was evaporated. The product was purified by recrystallization from toluene and collected by filtration (272 mg, 92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 8.3 Hz, 2 H), 7.67 (d, J = 8.4 Hz, 2 H), 7.62 – 7.56 (m, 2 H), 7.42 – 7.37 (m, 3 H), 7.38 – 7.33 (m, 2 H), 7.20 – 7.13 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.47, 134.80, 131.72, 131.27, 128.58, 128.40, 127.24, 122.96, 122.89, 112.61, 91.66, 89.20 (B-C was not observed due to quadrupole broadening). ^{11}B NMR (128 MHz, $CDCl_3$): δ 32.71. HRMS (APPI) calc'd for [M]+: 296.1012, found: 296.1009.

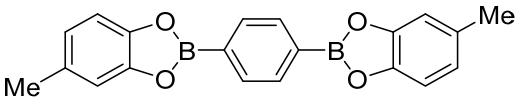
Synthesis of 2-(4-nitrophenyl)benzo[*d*][1,3,2]dioxaborole



A mixture of catechol (110 mg, 1.0 mmol) and 4-nitrophenyl boronic acid (167 mg, 1.0 mmol) in toluene (50 mL) was heated under reflux using a Dean Stark apparatus for 4 h. After this time, the reaction was cooled to RT and the solvent was evaporated. The product was purified by sublimation under vacuum (145 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, J = 8.7 Hz, 2 H), 8.29 (d, J = 8.7 Hz, 2 H), 7.43 – 7.35 (m, 2 H), 7.26 – 7.14 (m, 2 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.46, 148.24, 135.92, 123.36, 123.02, 112.88 (B-C was not observed due to quadrupole broadening). ^{11}B NMR (128 MHz, $CDCl_3$): δ 31.98. HRMS (APPI) calc'd for [M]+: 241.0549, found: 241.0553.

Synthesis of 1,4-bis(5-methylbenzo[*d*][1,3,2]dioxaborol-2-yl)benzene

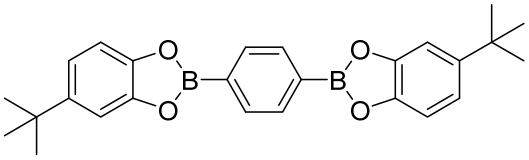


A mixture of 4-methylcatechol (74.5 mg, 0.6 mmol) and benzene-1,4-diboronic acid (49.7 mg, 0.3 mmol) in toluene (50 mL) was heated under reflux using a Dean Stark apparatus for 4 h. After this time, the reaction was cooled to RT and the solid was filtered off. The product was purified by recrystallization from toluene (83.1 mg, 81%).

The product displayed very low solubility at room temperature in standard NMR solvents. An indirect characterization of the N-methylimidazole (MIm) adduct was thus performed using a mixture of bis(dioxaborole) (3.0 mg, 8.8 μmol) and N-methylimidazole (1.4 μL, 17.5 μmol) in $CDCl_3$ (600 μL).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, J = 1.4 Hz, 2 H, MIm), 7.75 (s, 4 H), 7.17 (t, J = 1.5 Hz, 2 H, MIm), 6.86 (t, J = 1.6 Hz, 2 H, MIm), 6.86 – 6.78 (m, 4 H), 6.61 (d, J = 7.6 Hz, 2 H), 3.70 (s, 6 H, MIm), 2.30 (s, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.05, 148.83, 135.90 (MIm), 132.26, 129.79, 125.20 (MIm), 121.21 (MIm), 120.18, 111.74, 110.06, 77.48, 77.36, 77.16, 77.16, 76.84, 34.94 (MIm), 21.47 (B-C was not observed due to quadrupole broadening). HRMS (APPI) calc'd for [M]+: 342.12347, found: 342.12367.

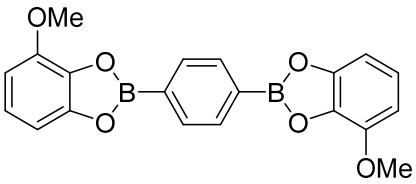
Synthesis of 1,4-bis(5-(tert-butyl)benzo[*d*][1,3,2]dioxaborol-2-yl)benzene



A mixture of 4-*tert*-butylcatechol (199 mg, 1.2 mmol) and benzene-1,4-diboronic acid (99.5 mg, 0.6 mmol) in toluene (50 mL) was heated under reflux using a Dean Stark apparatus for 4 h. After this time, the reaction was cooled to RT and the solvent was evaporated. The product was purified by recrystallization from a concentrated solution in toluene overnight at −20 °C (171 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 4 H), 7.32 (d, J = 1.9 Hz, 2 H), 7.16 (d, J = 8.3 Hz, 2 H), 7.10 (dd, J = 8.4, 2.0 Hz, 2 H), 1.29 (s, 18 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.50, 146.93, 146.30, 134.59, 119.80, 111.77, 110.14, 77.48, 77.36, 77.16, 76.84, 35.03, 31.90 (B-C was not observed due to quadrupole broadening). HRMS (APPI) calc'd for [M]+: 426.21737, found: 426.21766.

Synthesis of 1,4-bis(4-methoxybenzo[*d*][1,3,2]dioxaborol-2-yl)benzene

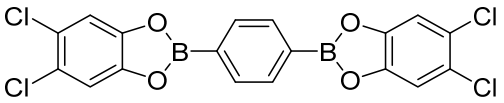


A mixture of 3-methoxycatechol (84.1 mg, 0.6 mmol) and benzene-1,4-diboronic acid (49.7 mg, 0.3 mmol) in toluene (50 mL) was heated under reflux using a Dean Stark apparatus for 4 h. After this time, the reaction was cooled to RT and the solid was filtered off. The product was purified by recrystallization from toluene (147 mg, 79%).

The product displayed very low solubility at room temperature in standard NMR solvents. An indirect characterization of the N-methylimidazole (MIm) adduct was thus performed using a mixture of bis(dioxaborole) (3.0 mg, 8.0 μmol) and N-methylimidazole (1.3 μL, 17.5 μmol) in $CDCl_3$ (600 μL).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (s, 2 H, MIm), 7.66 (s, 4 H), 7.14 (t, J = 1.5 Hz, 2 H, MIm), 6.80 (t, J = 1.6 Hz, 2 H, MIm), 6.67 (t, J = 8.0 Hz, 2 H), 6.59 (dd, J = 7.8, 1.2 Hz, 2 H), 6.45 (dd, J = 8.3, 1.2 Hz, 2 H), 3.89 (s, 6 H), 3.64 (s, 6 H, MIm). ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.96, 145.18, 139.73, 136.00 (MIm), 131.58, 125.15 (MIm), 121.06 (MIm), 118.93, 104.74, 104.48, 77.48, 77.36, 77.16, 76.84, 56.32, 34.85 (MIm) (B-C was not observed due to quadrupole broadening). HRMS (APPI) calc'd for [M+H]+: 375.12112, found: 375.12157.

Synthesis of 1,4-bis(5,6-dichlorobenzo[*d*][1,3,2]dioxaborol-2-yl)benzene

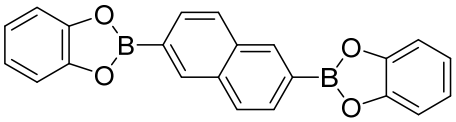


A mixture of 4,5-dichlorocatechol (107 mg, 0.6 mmol) and benzene-1,4-diboronic acid (49.7 mg, 0.3 mmol) in toluene:THF (4:1, 50 mL) was heated under reflux using a Dean Stark apparatus for 6 h. After this time, the reaction was cooled to RT and the product was filtered off. (203 mg, 90%).

The product displayed very low solubility at room temperature in standard NMR solvents. An indirect characterization of the N-methylimidazole (MIm) adduct was thus performed using a mixture of bis(dioxaborole) (3.0 mg, 6.6 μmol) and N-methylimidazole (1.1 μL, 13.2 μmol) in $C_2D_2Cl_4$ (600 μL).

^{1}H NMR (400 MHz, tetrachloroethane-d_2): δ 7.81 (s, 2 H, MIm), 7.48 (s, 4 H), 7.18 (s, 2 H, MIm), 6.95 (t, J = 1.6 Hz, 2 H, MIm), 6.84 (s, 4 H), 3.73 (s, 6 H, MIm). ^{13}C NMR (101 MHz, tetrachloroethane-d_2): δ 151.93, 135.29 (MIm), 130.87, 124.02 (MIm), 121.53 (MIm), 120.43, 110.63, 74.26, 74.05, 73.98, 73.78, 73.50, 35.06 (B-C was not observed due to quadrupole broadening). HRMS (APPI) calc'd for [M]+: 449.93628, found: 449.93639.

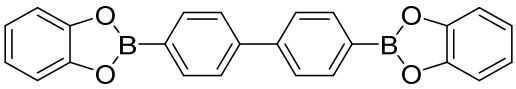
Synthesis of 2,6-bis(benzo[*d*][1,3,2]dioxaborol-2-yl)naphthalene



A mixture of catechol (66.6 mg, 0.6 mmol) and 2,6-naphthalenediboronic acid (64.7 mg, 0.3 mmol) in toluene (50 mL) was heated under reflux using a Dean Stark apparatus for 4 h. After this time, the reaction was cooled to RT and the solid was filtered off. The product was purified by recrystallization from toluene (99.4 mg, 91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 2 H), 8.23 – 8.13 (m, 2 H), 8.07 (d, J = 8.2 Hz, 2 H), 7.38 (dd, J = 5.9, 3.3 Hz, 4 H), 7.17 (dd, J = 5.9, 3.3 Hz, 4 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.73, 137.04, 134.95, 130.50, 128.72, 123.11, 112.83, 77.48, 77.36, 77.16, 76.84 (B-C was not observed due to quadrupole broadening). HRMS (APPI) calc'd for [M]+: 364.10782, found: 364.10812.

Synthesis of 4,4'-bis(benzo[*d*][1,3,2]dioxaborol-2-yl)-1,1'-biphenyl

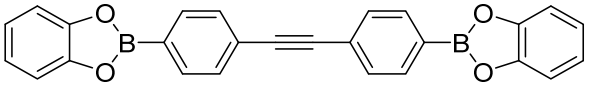


A mixture of catechol (66.1 mg, 0.6 mmol) and 4,4'-biphenyldiboronic acid (72.6 mg, 0.3 mmol) in toluene (50 mL) was heated under reflux using a Dean Stark apparatus for 4 h. After this time, the reaction was cooled to RT and the solid was filtered off. The product was purified by recrystallization from toluene (90.1 mg, 77%).

The product displayed very low solubility at room temperature in standard NMR solvents. An indirect characterization of the N-methylimidazole (MIm) adduct was thus performed using a mixture of bis(dioxaborole) (3.0 mg, 7.7 μmol) and N-methylimidazole (1.2 μL, 15.4 μmol) in $C_2D_2Cl_4$ (600 μL).

^{1}H NMR (400 MHz, tetrachloroethane- d_2): δ 7.92 (s, 2 H, MIm), 7.62 (d, J = 8.1 Hz, 4 H), 7.58 (d, J = 8.2 Hz, 4 H), 7.25 (t, J = 1.5 Hz, 2 H, MIm), 6.95 (t, J = 1.6 Hz, 2 H, MIm), 6.85 (dd, J = 5.6, 3.4 Hz, 4 H), 6.71 (dd, J = 5.6, 3.4 Hz, 4 H), 3.74 (s, 6 H, MIm). ^{13}C NMR (101 MHz, tetrachloroethane-d_2) δ 151.79, 140.36, 135.48 (MIm), 132.32, 126.10, 124.44 (MIm), 121.36 (MIm), 118.91, 109.84, 101.27, 74.07, 74.00, 73.80, 73.60, 73.53, 34.97 (MIm) (B-C was not observed due to quadrupole broadening). HRMS (APPI) calc'd for [M]+: 390.12347, found: 390.12377.

Synthesis of 1,2-bis(4-(benzo[*d*][1,3,2]dioxaborol-2-yl)phenyl)ethyne

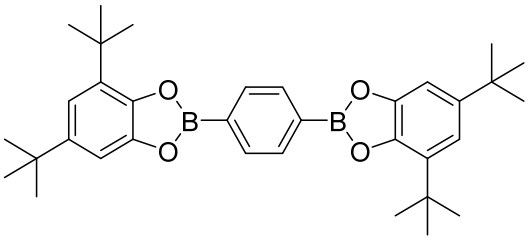


A mixture of catechol (66.1 mg, 0.6 mmol) and 4,4'-diphenylacetylene-diboronic acid (79.8 mg, 0.3 mmol) in toluene (50 mL) was heated under reflux using a Dean Stark apparatus for 4 h. After this time, the reaction was cooled to RT and the solid was filtered off. The product was purified by recrystallization from toluene (106 mg, 85%).

The product displayed very low solubility at room temperature in standard NMR solvents. An indirect characterization of the N-methylimidazole (MIm) adduct was thus performed using a mixture of bis(dioxaborole) (3.0 mg, 7.2 μmol) and N-methylimidazole (1.2 μL, 14.5 μmol) in $CDCl_3$ (600 μL).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 2 H, MIm), 7.58 (d, J = 8.2 Hz, 4 H), 7.47 (d, J = 8.0 Hz, 4 H), 7.16 (t, J = 1.5 Hz, 2 H, MIm), 6.88 (t, J = 1.7 Hz, 2 H, MIm), 6.87 – 6.80 (m, 4 H), 6.78 – 6.65 (m, 4 H), 3.70 (s, 6 H, MIm). ^{13}C NMR (101 MHz, $CDCl_3$): δ 151.80, 135.64 (MIm), 131.89, 130.91, 124.72 (MIm), 122.63, 121.48 (MIm), 119.38, 110.16, 89.89, 77.48, 77.36, 77.16, 76.84, 35.11 (MIm) (B-C was not observed due to quadrupole broadening). HRMS (APPI) calc'd for [M]+: 414.12347, found: 414.12405.

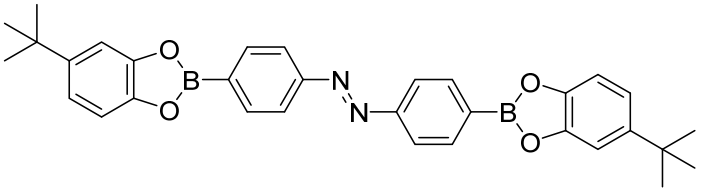
Synthesis of 1,4-bis(4,6-di-tert-butylbenzo[*d*][1,3,2]dioxaborol-2-yl)benzene



A mixture of 3,5-di-*tert*-butylcatechol (133 mg, 0.6 mmol) and benzene-1,4-diboronic acid (49.7 mg, 0.3 mmol) in toluene (50 mL) was heated under reflux using a Dean Stark apparatus for 4 h. After this time, the reaction was cooled to RT and the solvent was evaporated. The product was purified by recrystallization from toluene / pentane (126 mg, 78%).

^{1}H NMR (400 MHz, C_6D_6): δ 8.24 (s, 4 H), 7.26 (d, J = 1.9 Hz, 2 H), 7.23 (d, J = 1.9 Hz, 2 H), 1.57 (s, 18 H), 1.29 (s, 18 H). ^{13}C NMR (101 MHz, C_6D_6): δ 149.26, 146.28, 144.70, 135.29, 134.80, 128.30, 128.06, 127.82, 116.77, 108.47, 35.11, 34.73, 31.93, 30.09 (B-C was not observed due to quadrupole broadening). HRMS (APPI) calc'd for [M]+: 538.34257, found: 538.34323.

Synthesis of (E)-1,2-bis(4-(5-(tert-butyl)benzo[*d*][1,3,2]dioxaborol-2-yl)phenyl)diazene



A mixture of 4-*tert*-butylcatechol (99.7 mg, 0.6 mmol) and 4,4'-azobenzenediboronic acid[9] (81.0 mg, 0.3 mmol) in toluene / THF mixture (4:1, 50 mL) was heated under reflux using a Dean Stark apparatus for 4 h. After this time, the reaction was cooled to RT and the solvent was evaporated. The product was purified by recrystallization from toluene (130.4 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (d, J = 8.3 Hz, 4 H), 8.05 (d, J = 8.3 Hz, 4 H), 7.41 (d, J = 1.8 Hz, 2 H), 7.24 (s, 2 H), 7.18 (dd, J = 8.4, 1.9 Hz, 2 H), 1.37 (s, 18 H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 154.88, 148.36, 146.83, 146.16, 135.90, 122.64, 119.70, 111.63, 110.01, 77.33, 77.01, 76.70, 34.90, 31.75 (B-C was not observed due to quadrupole broadening). HRMS (APPI) calc'd for [M+H]+: 531.2628, found: 531.2622

1.3 Critical gel concentration determination

A 1.0 wt% sample of gel in the appropriate solvent was prepared in a glass vial with stoichiometric amounts of the bis(dioxaborole) (10 μmol) and the bis(imidazolyl) ligand (10 μmol). Gelation was induced by a heating-cooling cycle. After cooling down to room temperature, a vial-inversion test was used to confirm gelation (if the sample stands upside-down without any flow of matter). The sample was then diluted and the procedure repeated until the gelation was not strong enough for the sample to be self-supporting. The lowest concentration at which the gel could stand the vial-inversion was noted as the critical gel concentration.

1.4 Determination of $T_{sol\text{-}gel}$

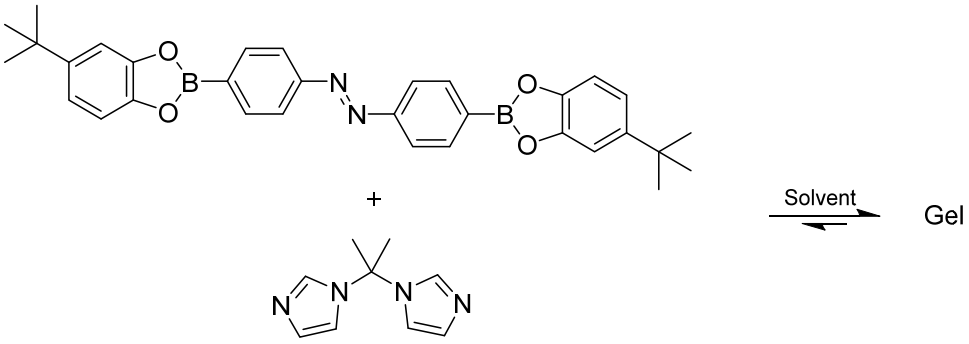
A 1.0 wt% sample of gel in the appropriate solvent was prepared in a glass vial with stoichiometric amounts of the bis(dioxaborole) (10 μmol) and the bis(imidazolyl) ligand (10 μmol). Gelation was induced by a heating-cooling cycle. The gels were then immersed in an oil bath warmed up at 30 °C for 5 min and then inversed. If the samples were still in the gel state, the oil bath temperature was increased by 5 °C and the procedure was repeated. The temperature at which a gel could no longer stand the vial-inversion test was noted as the $T_{sol\text{-}gel}$.

1.5 Preparation and testing of azobenzene-modified gels

To examine the behavior of the gel upon UV-irradiation, 0.05 and 0.1 wt% samples were prepared in 2.5 mL glass vials under inert and dry atmosphere by dissolving equimolar amount of boronate ester and bis-imidazolyl ligand in hot 1,2-dichlorobenzene (0.5 mL) and letting them cool down to afford gels. The vials were closed and sealed and placed upside-down under a standard lab UV-lab with irradiation at λ = 366 nm. After 5 min (0.05 wt% gel) or 15 min (0.1 wt% gel), the gel state broke down (they were not sticking anymore to the top of the vial). The same experiments were conducted in toluene instead of 1,2-dichlorobenzene as solvent, resulting in identical values.

The viscous solutions obtained after UV-irradiation were heated above $T_{sol\text{-}gel}$ (~100 °C) until clear and homogeneous solutions were obtained. Upon cooling, gels were reformed.

Table S1 Gelation properties of gel samples formed with azobenzene-modified diboronate ester and 1,1'-(propane-2,2-diyl)bisimidazole.



Solvent	$T_{sol\text{-}gel}$ @ 0.5 wt% [°C]	CGC [wt%]
Toluene	90	0.1
Chlorobenzene	85	0.1
1,2-Dichlorobenzene	90	0.05
1,2,4-Trichlorobenzene	90	0.05
Xylenes	95	0.1

1.6 Gel for TOC picture

1,1'-(Propane-2,2-diyl)bisimidazole (80 mmol, 14.0 mg) and 2-phenylbenzo[*d*][1,3,2]dioxaborole (80 mmol, 25 mg) were dissolved in hot 1,2-dichlorobenzene (30 mL, 39 mg). The mixture was poured in a flat-bottom recipient (10 x 4 x 1 cm) and allowed to cool to room temperature to afford a gel, which was cut into the desired shape.

2. Screening results

2.1 Gelation capability for various R, R' and R'' in toluene and 1,2-dichlorobenzene

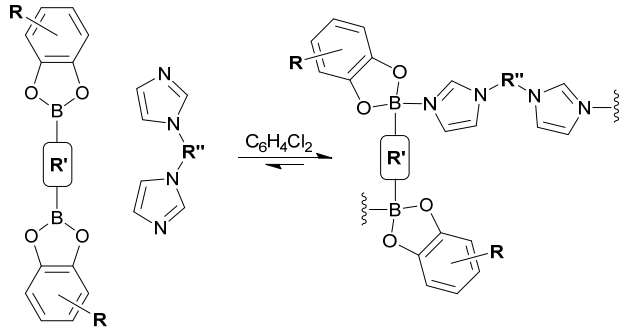


Table S2 Gelation capability for various **R**, **R'** and **R''** in toluene and 1,2-dichlorobenzene.

		Toluene				1,2-Dichlorobenzene			
		$T_{sol\text{-}gel}$ @ 1 wt% [°C]		CGC [wt%]		$T_{sol\text{-}gel}$ @ 1 wt% [°C]		CGC [wt%]	
R	**R'**	**R''** = CH_2	**R''** = CMe_2	**R''** = CH_2	**R''** = CMe_2	**R''** = CH_2	**R''** = CMe_2	**R''** = CH_2	**R''** = CMe_2
4-*t*Bu	*p*-C_6H_4	95[b]	60[b]	0.2[b]	1.0[b]	90[b]	50[b]	0.05[b]	1.0[b]
H	*p*-C_6H_4	bp[a]	105[a]	0.25[a]	0.05[a]	105[a]	105[a]	0.05[a]	0.02[a]
3,4-Cl	*p*-C_6H_4	ppt	ppt	ppt	ppt	ppt	55[b]	ppt	1.0[b]
H	4,4'-Biphenylene	80[b]	ppt	0.1[b]	ppt	65[b]	45[b]	0.05[b]	0.1[b]
3-OMe	*p*-C_6H_4	pg	80[a]	pg	0.05[a]	80[b]	100[a]	0.33[b]	0.04[a]
4-Me	*p*-C_6H_4	100[a]	105[b]	0.02[a]	0.05[b]	95[a]	90[a]	0.05[a]	0.02[a]
H	2,6-Naphthalene	40[b]	ppt	0.5[b]	ppt	pg	ppt	pg	ppt
H	4,4'-$C_6H_4CCC_6H_4$	ppt	ppt	ppt	ppt	45[b]	80[b]	1.0[b]	0.05[b]
3,5-*t*Bu	*p*-C_6H_4	ppt	liq	ppt	liq	ppt	liq	ppt	liq

bp = boiling point; ppt = precipitate was observed; pg = partial gel; liq = no gel formation. [a] transparent gel; [b] opaque gel.

2.2 Gelation capability in different solvents for R = 4-Me**, R'** = *p*-C_6H_4 **and R''** = CMe_2

Table S3 Gelation capability in various solvents for **R** = 4-Me**, R'** = *p*-C_6H_4 **and R''** = CMe_2

Solvent	$T_{sol\text{-}gel}$ @ 1 wt% [°C]	CGC [wt%]
1,2-Dichlorobenzene	90	0.02
Toluene	105	0.05
1,2,4-Trichlorobenzene	95	0.02
Benzene	80	0.1
Chloroform	50	0.1
Mesitylene	105	0.04
Xylenes	100	0.04
Chlorobenzene	90	0.02
Nitrobenzene	60	0.05
Dimethyl sulfoxide	-	-
Methanol	-	-
Dioxane	70	0.33
Tetrahydrofuran	50	0.5
Acetonitrile	65	0.25
Acetone	70	0.33
Ethyl Acetate	70	0.2

3. N-donor induced boronate ester condensation in THF-*d8*

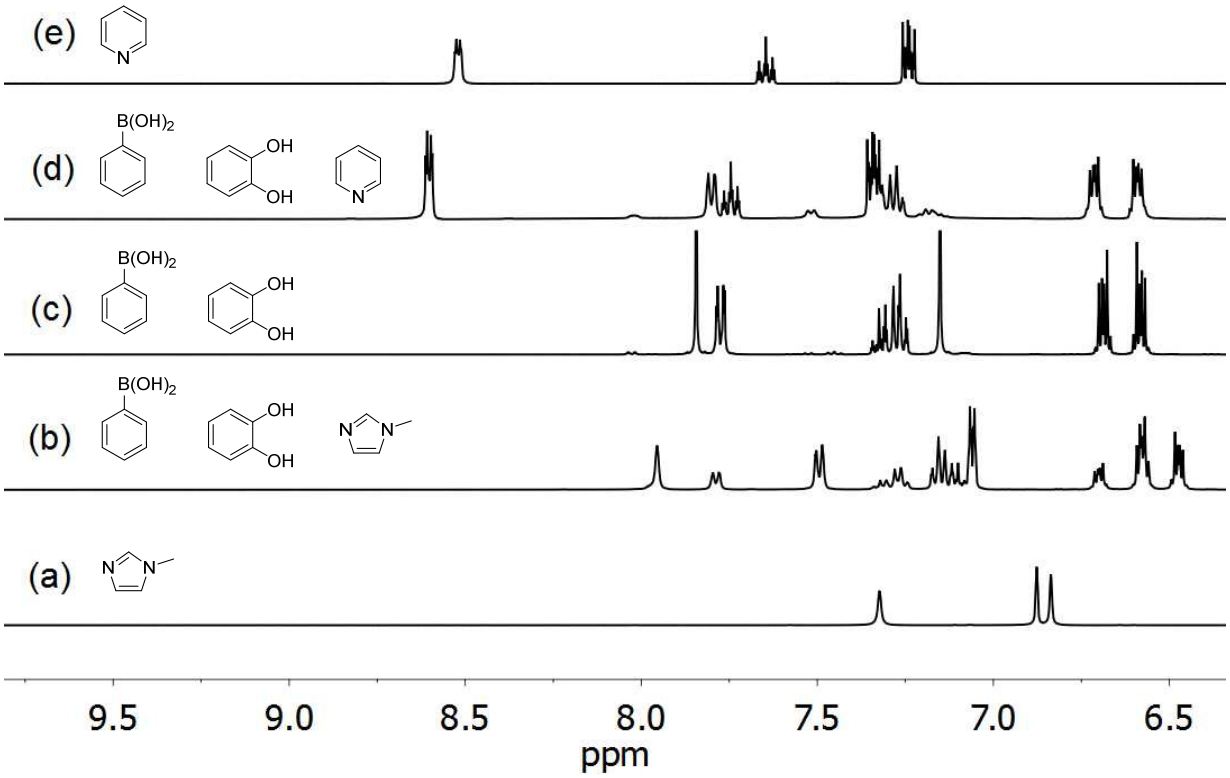


Fig. S1 Aromatic region of the ^{1}H-NMR spectra (THF-*d8*) of N-methylimidazole (a), an equimolar mixture of catechol, phenylboronic acid, and N-methylimidazole (b), an equimolar mixture of catechol and phenylboronic acid (c), an equimolar mixture of catechol, phenylboronic acid and pyridine (d), and pyridine (e). The spectra of the mixtures were recorded after an equilibration time of 4 h using a concentration of 200 mM for each compound.

4. Isothermal Titration Calorimetry

Freshly distilled solvent was used for the titrations. Injection of a solution of N-methylimidazole (20 mM) from the injector syringe to the measurement cell containing a solution of dioxaborole (0.5 mM) was done by 50 sequential additions of 2.5 µL separated by 240 seconds. The heat of injections, binding enthalpies and binding constants were obtained by data analysis with NITPIC (integration) and SEDPHAT (curve fitting).[10] For each sample, three independent measurements were performed from the same batch of ester. The results are presented with a stacking of the SVD-reconstructed thermogram (top) and the fitted integrated injection heats (bottom).

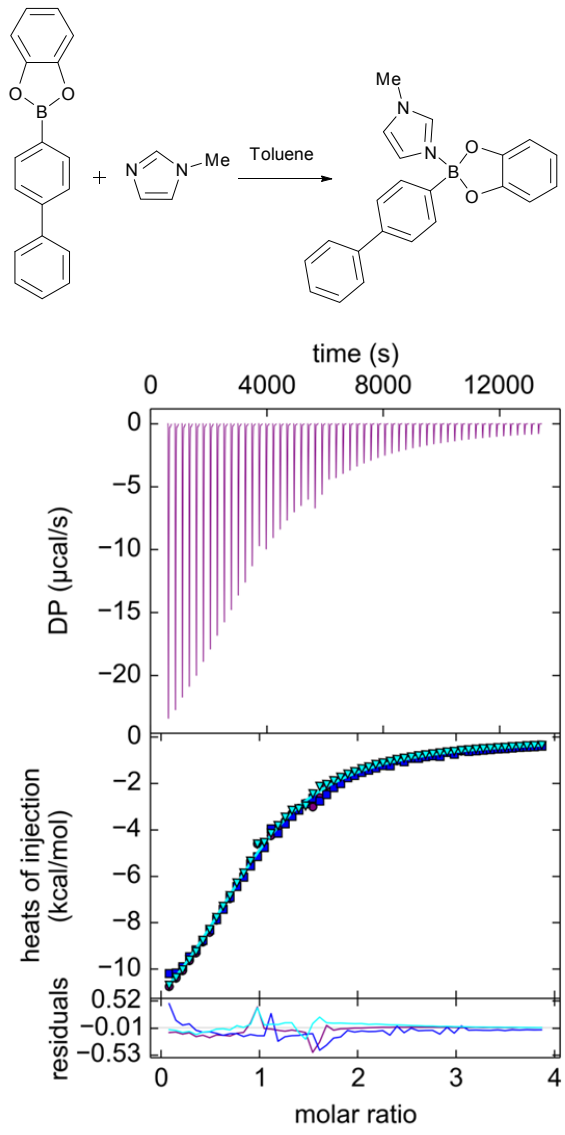


Fig. S2 ITC measurement of 2-([1,1'-biphenyl]-4-yl)benzo[*d*][1,3,2]dioxaborole with N-methylimidazole in toluene. K_a = 6.6(±0.4) x 10^3 M^{-1}

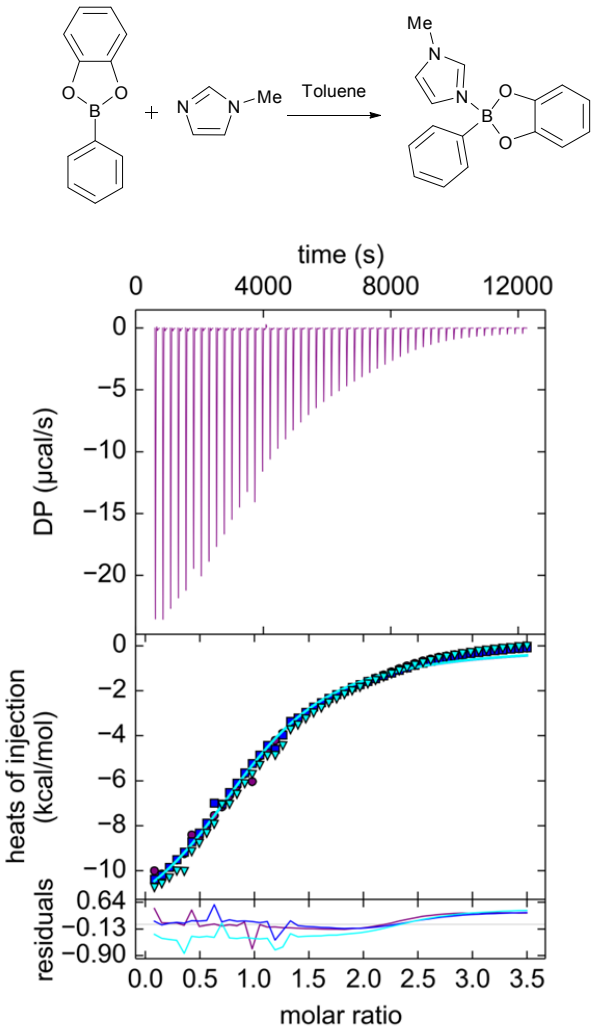


Fig. S3 ITC measurement of 2-phenylbenzo[*d*][1,3,2]dioxaborole with N-methylimidazole in toluene. K_a = 7.6(±0.3) x 10^3 M^{-1}

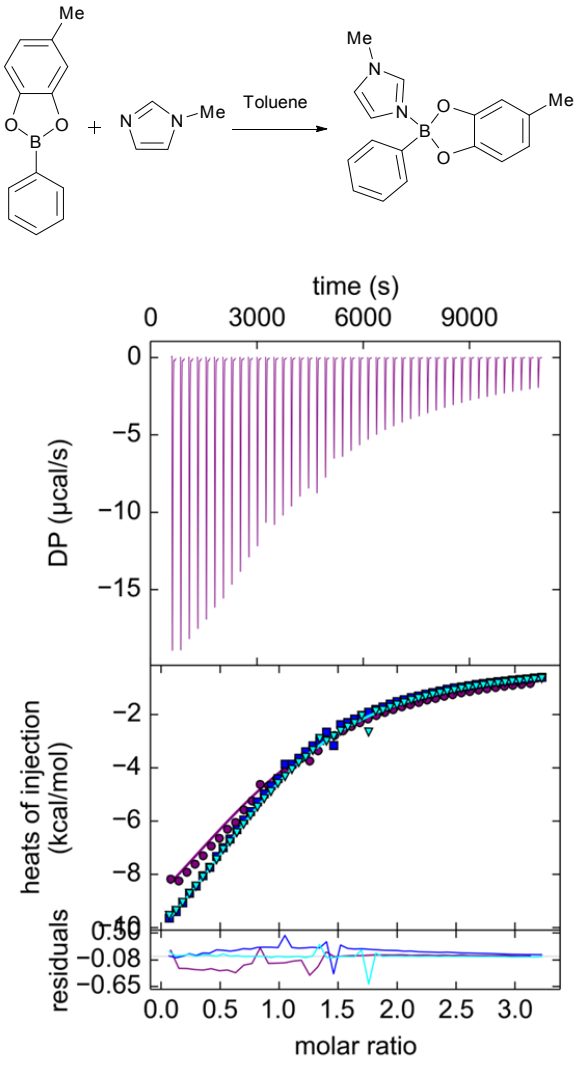


Fig. S4 ITC measurement of 5-methyl-2-phenylbenzo[*d*][1,3,2]dioxaborole with N-methylimidazole in toluene. K_a = 3.3(±0.3) x 10^3 M^{-1}

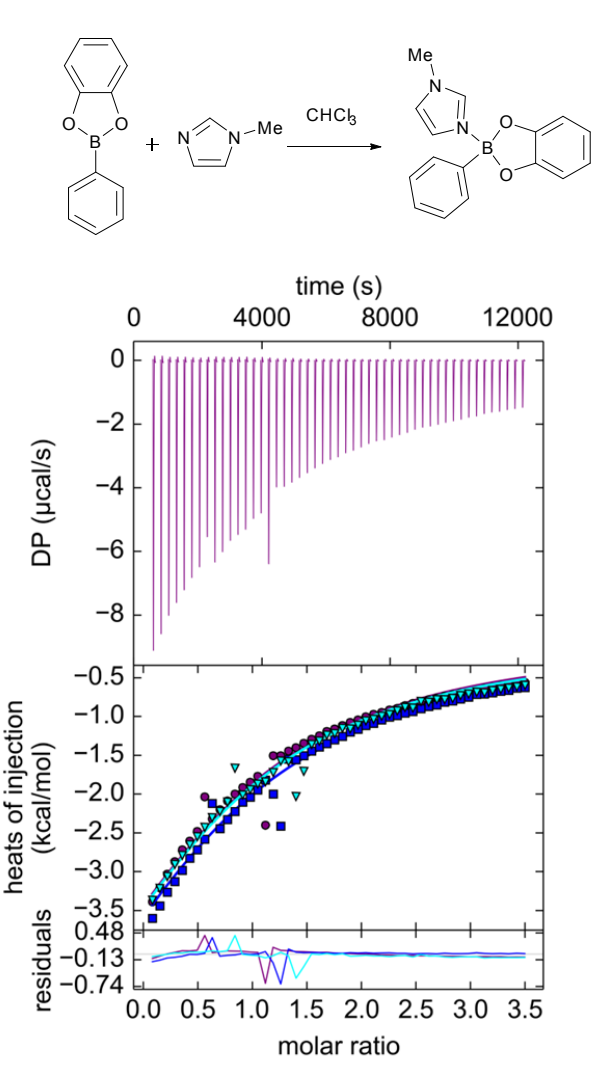


Fig. S5 ITC measurement of 2-phenylbenzo[*d*][1,3,2]dioxaborole with N-methylimidazole in toluene. K_a = 1.2(±0.3) x 10^3 M^{-1}

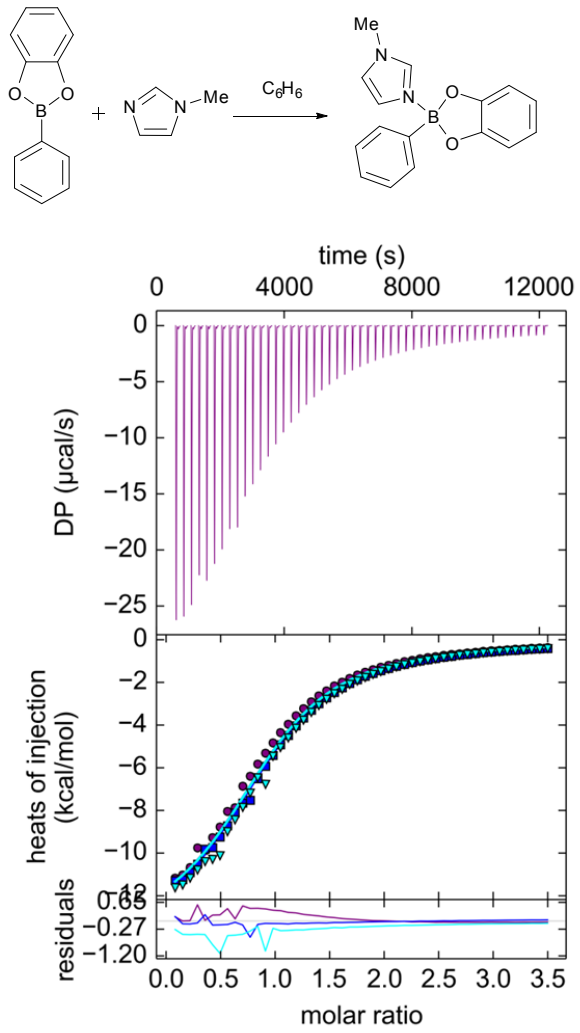


Fig. S6 ITC measurement of 2-phenylbenzo[*d*][1,3,2]dioxaborole with N-methylimidazole in toluene. K_a = 8.9(±0.6) x 10^3 M^{-1}

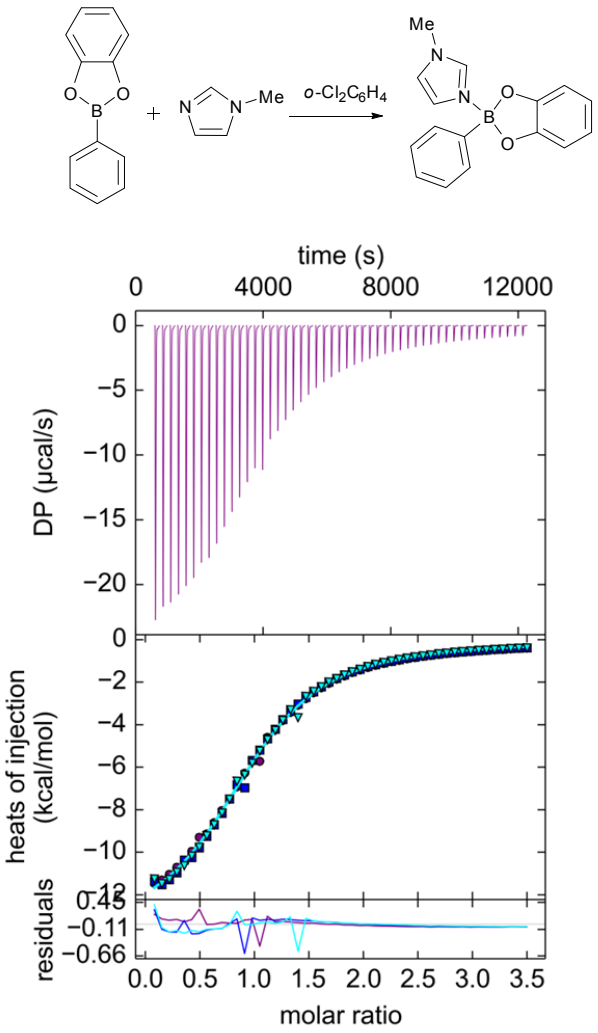


Fig. S7 ITC measurement of 2-phenylbenzo[*d*][1,3,2]dioxaborole with N-methylimidazole in toluene. K_a = 1.1(±0.1) x 10^4 M^{-1}

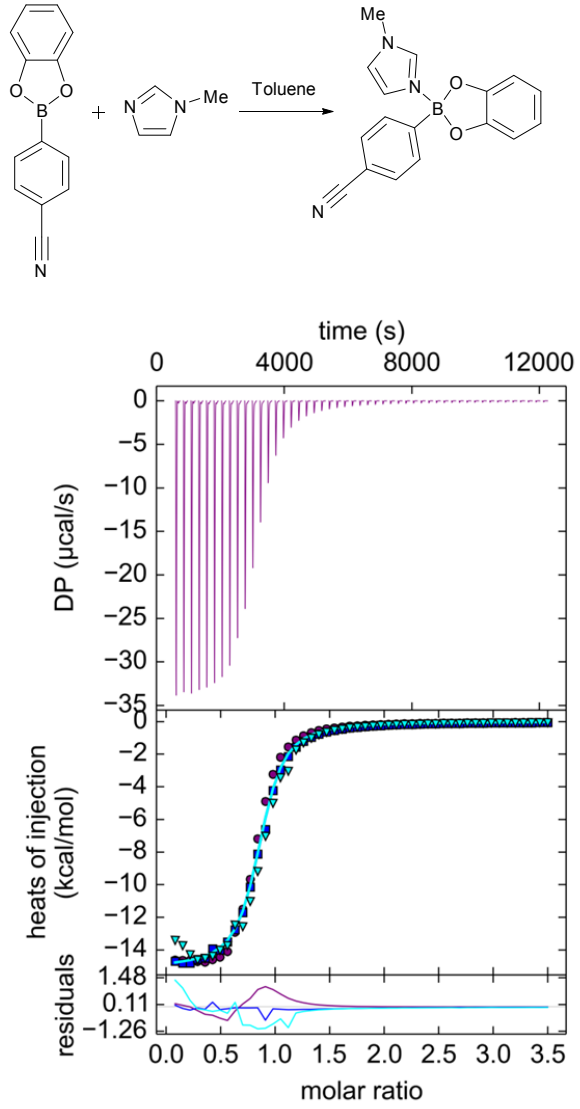


Fig. S8 ITC measurement of 4-(benzo[*d*][1,3,2]dioxaborol-2-yl)benzonitrile with N-methylimidazole in toluene. K_a = 1.2(±0.1) x 10^5 M^{-1}

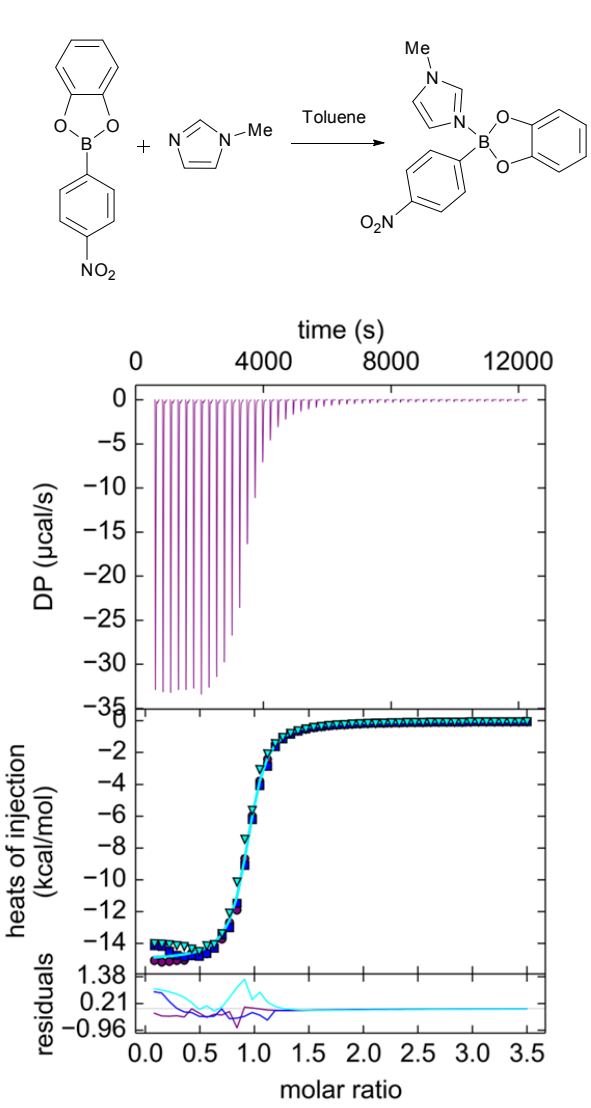


Fig. S9 ITC measurement of 2-(4-nitrophenyl)benzo[*d*][1,3,2]dioxaborole with N-methylimidazole in toluene. K_a = 2.1(±0.1) x 10^5 M^{-1}

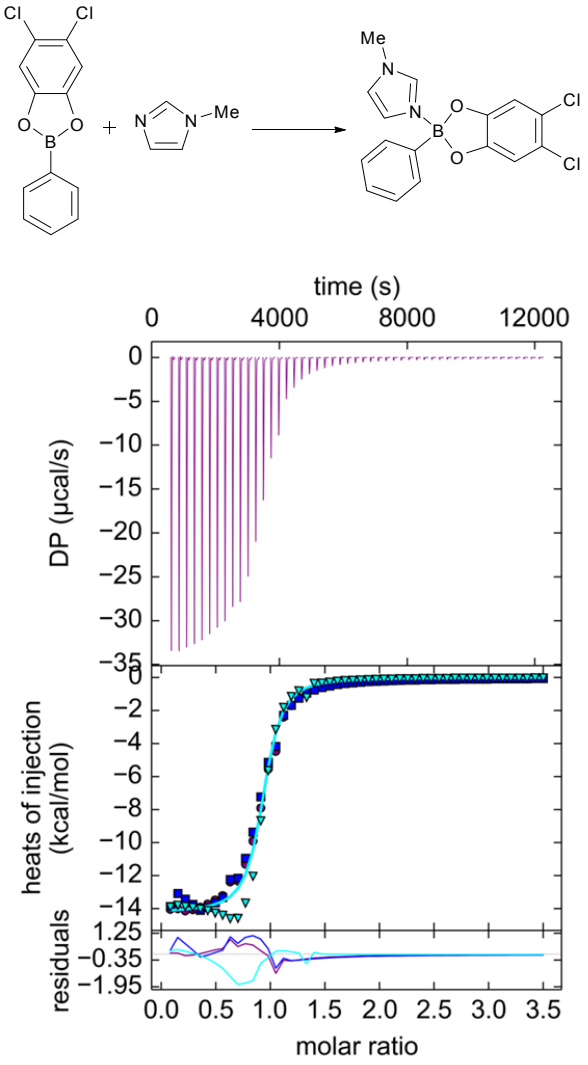
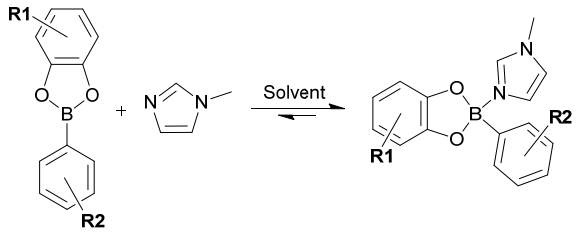


Fig. S10 ITC measurement of 5,6-dichloro-2-phenylbenzo[*d*][1,3,2]dioxaborole with N-methylimidazole in toluene. K_a = 1.8(±0.4) x 10^5 M^{-1}

Table S4 Association constants (K_a), binding enthalpies (ΔH), binding entropies (ΔS) and stoichiometry (n) of adducts between dioxaboroles and N-methylimidazole as determined by isothermal titration calorimetry (ITC). The values are averages of three independent measurements.



Entry	**R1**	**R2**	Solvent	K_a [M^{-1}]	ΔH [kcal mol^{-1}]	ΔS [cal mol^{-1} K^{-1}]	n
1	H	H	Chloroform	1.2(±0.3) x 10^3	−13.6(±0.4)	−31.3(±1.2)	0.89
2	H	H	Benzene	8.9(±0.6) x 10^3	−15.0(±0.3)	−32.4(±0.9)	0.91
3	H	H	*o*-Dichlorobenzene	1.1(±0.1) x 10^4	−14.0(±0.2)	−28.3(±0.7)	0.99
4	H	H	Toluene	7.6(±0.3) x 10^3	−13.4(±0.3)	−27.1(±0.8)	1.03
5	4-Me	H	Toluene	3.3(±0.3) x 10^3	−14.2(±0.7)	−31.4(±0.6)	0.94
6	4-Ph	H	Toluene	6.6(±0.4) x 10^3	−14.5(±0.4)	−31.2(±1.4)	0.92
7	H	4-CN	Toluene	1.2(±0.1) x 10^5	−15.1(±0.3)	−27.5(±1.0)	0.88
8	H	4-NO_2	Toluene	2.1(±0.1) x 10^5	−15.0(±0.4)	−26.1(±1.4)	0.93
9	3,4-Cl	H	Toluene	1.8(±0.4) x 10^5	−4.0(±0.1)	−23.4(±0.7)	0.92

5. Variable Temperature NMR

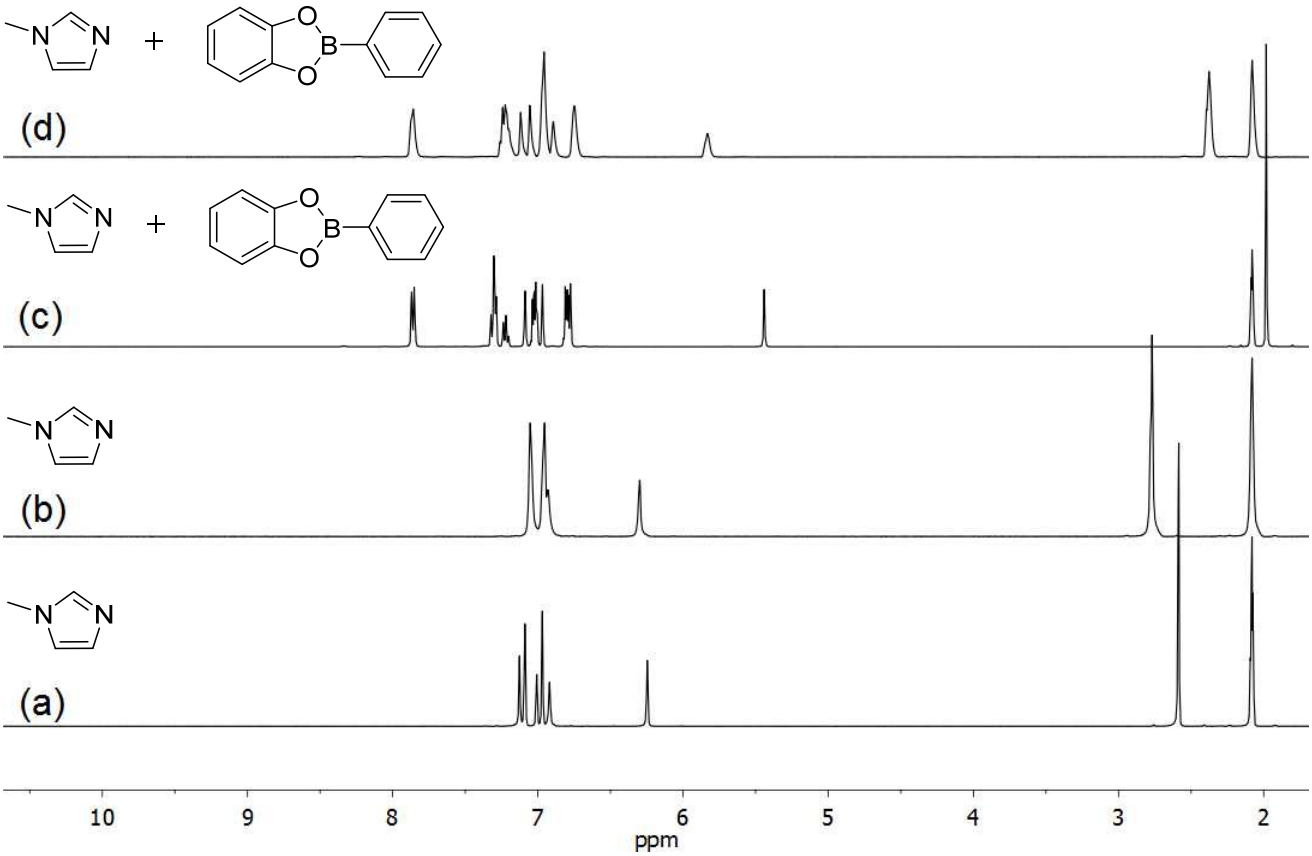


Fig. S11 [1]H-NMR spectra of N-methylimidazole in toluene-*d8* at 25 °C (a) and 100 °C (b), and of an equimolar mixture of N-methylimidazole and 2-phenylbenzo[*d*][1,3,2]dioxaborole in toluene at 25 °C (c) and 100 °C (d).

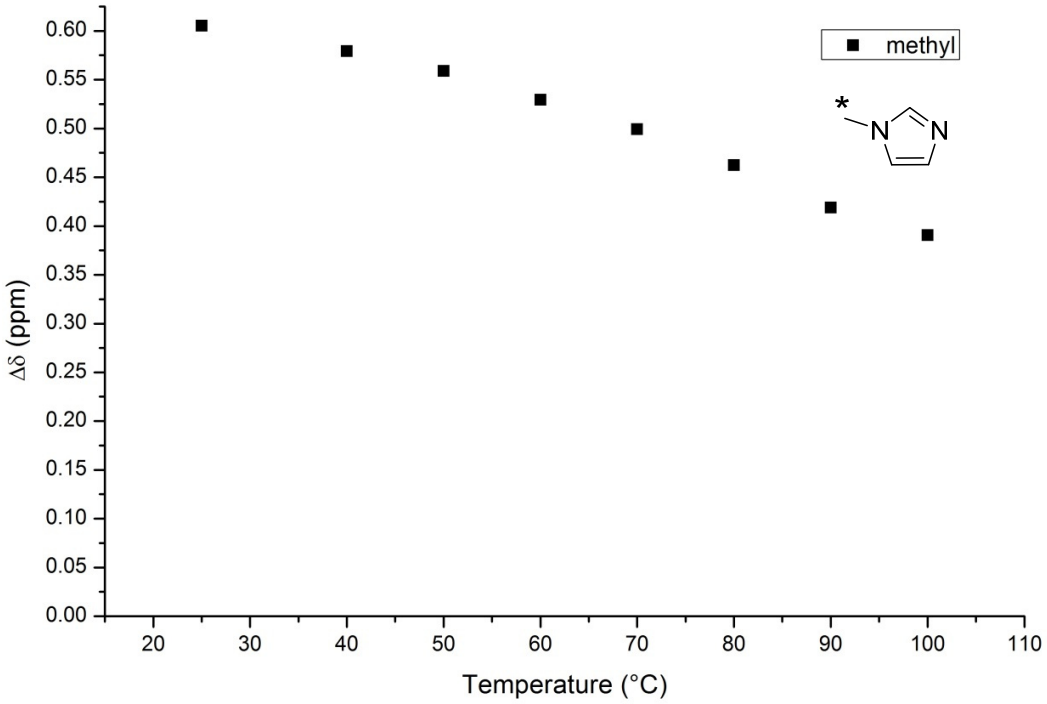


Fig. S12 Difference of the chemical shifts of the signal of the NCH_3 group for toluene-*d8* solutions containing N-methylimidazole (20 mM) or a mixture of N-methylimidazole and 2-phenylbenzo[*d*][1,3,2]dioxaborole (20 mM each) as a function of temperature.

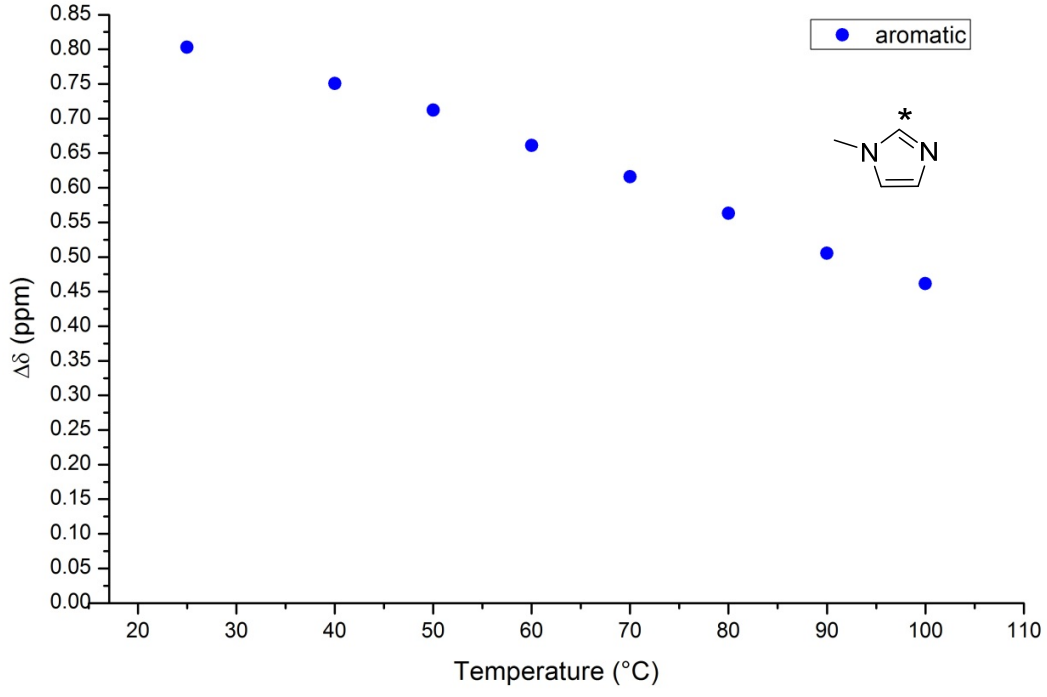


Fig. S13 Difference of the chemical shifts of the signal of the NCHN proton for toluene-*d8* solutions containing N-methylimidazole (20 mM) or a mixture of N-methylimidazole and 2-phenylbenzo[*d*][1,3,2]dioxaborole (20 mM each) as a function of temperature.

6. Scanning electron microscopy

The selected gels were wiped on an aluminum stub and freeze-dried for 4 days. A 7 nm layer of osmium was then coated onto the samples to improve the contrast of the measurement and the stability of the samples. Observations were done with a Zeiss NVision 40 scanning electron microscope with 2.0 kV operating voltage. In all cases, we observed fibrous structures with various degree of crystallinity.

7. Rheology

Rheology samples were prepared from the appropriate selected gels. Discs of 1.0 cm diameter and 3.3 mm height were prepared by pouring a hot liquid solution of the gel into a Teflon cast with the appropriate dimensions. The normal gap of the rheometer was fixed to 3.0 mm. The oscillation frequency sweep was performed at 25 °C from 0.1 Hz to 10 Hz with a strain of 2.56 %. Three measurements were performed for each gel and the average values were used in the present paper.

8. B-N bond length vs. THC

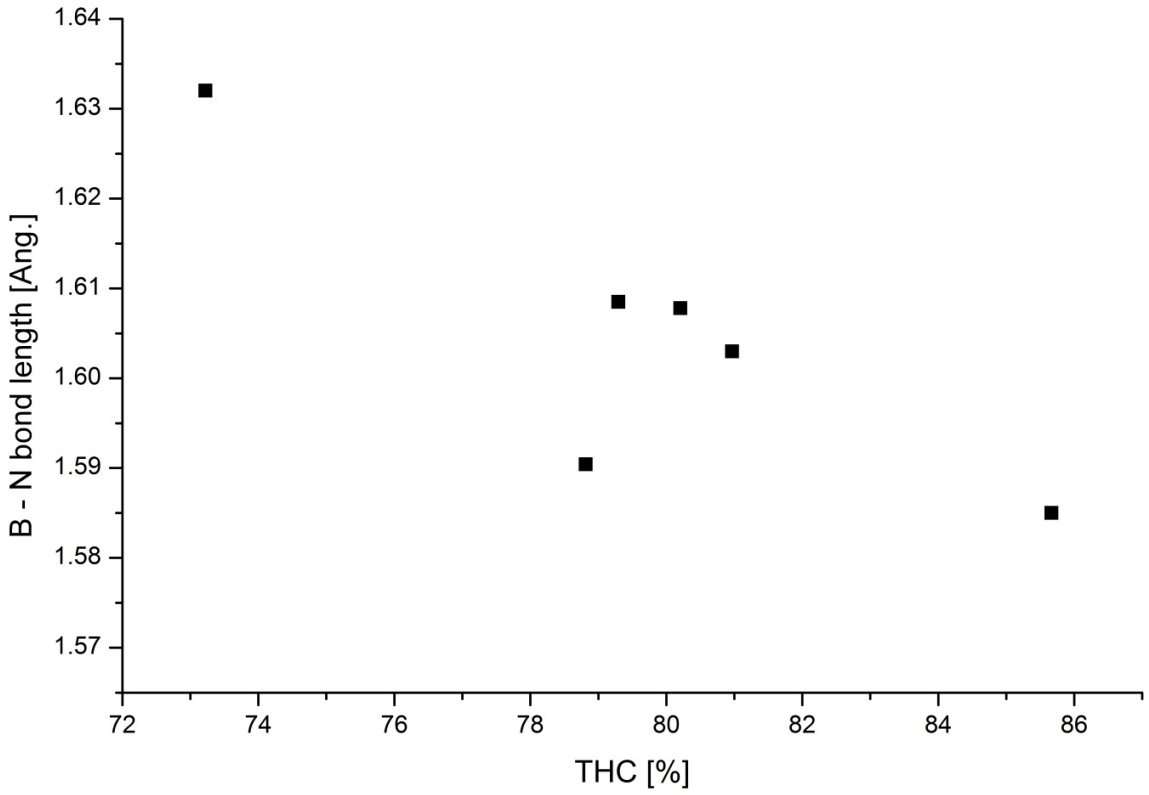


Fig. S14 B – N bond length as a function of tetrahedral character. Both values were determined from refined crystal data.

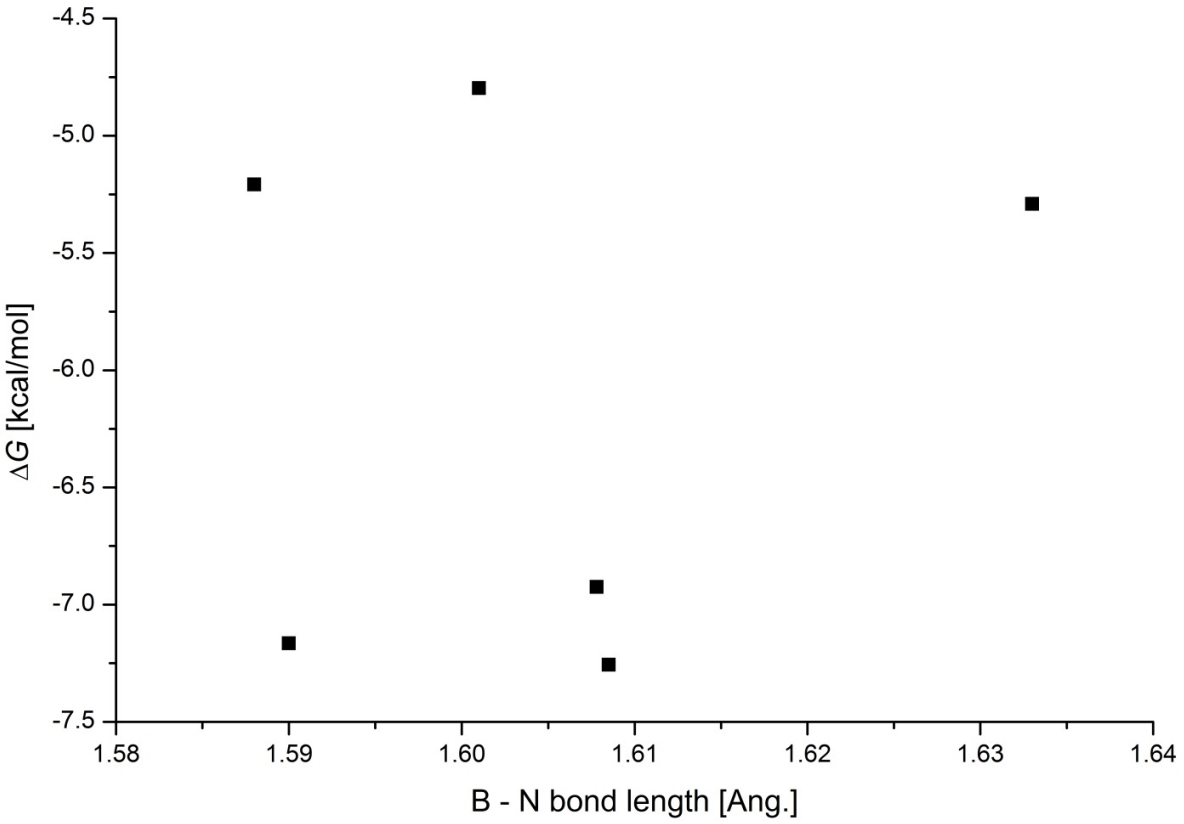


Fig. S15 Gibbs free energy of binding (determined from ITC measurements) as a function of B – N bond length (determined from refined crystal data).

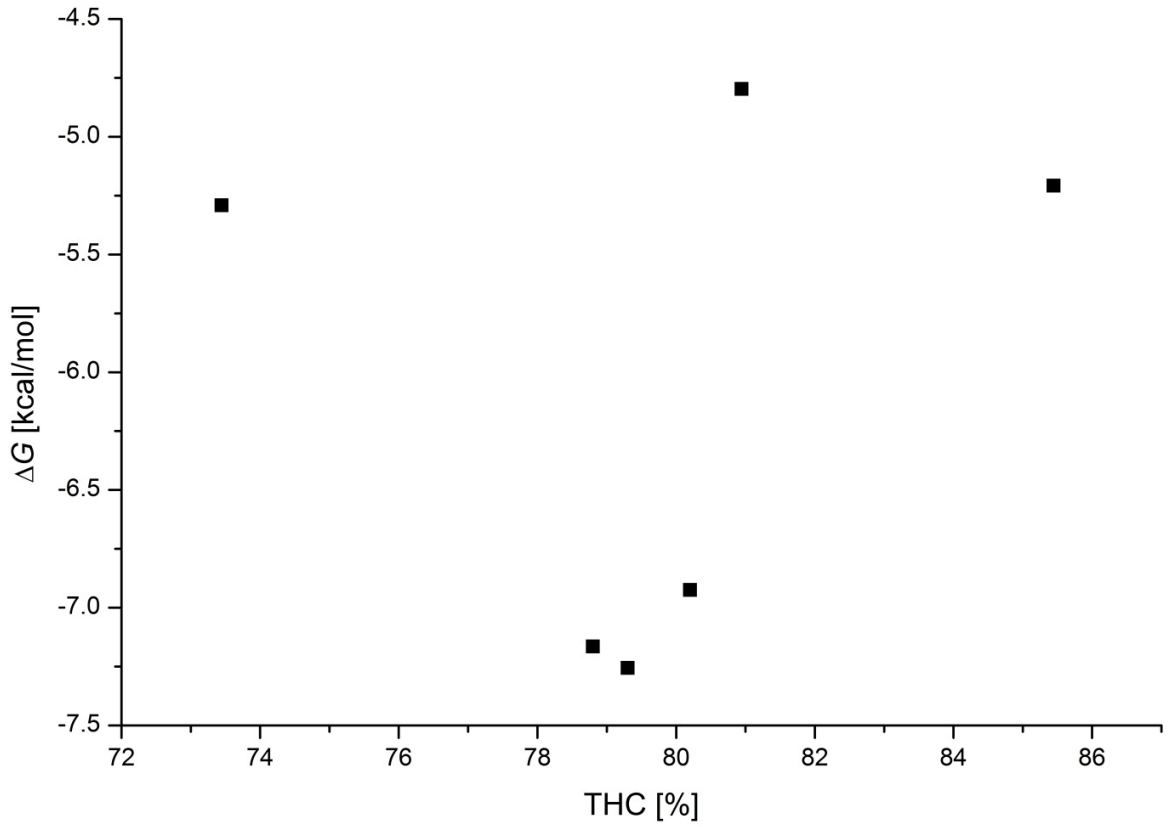


Fig. S16 Gibbs free energy of binding (determined from ITC measurements) as a function of tetrahedral character (determined from refined crystal data).

9. NMR spectra

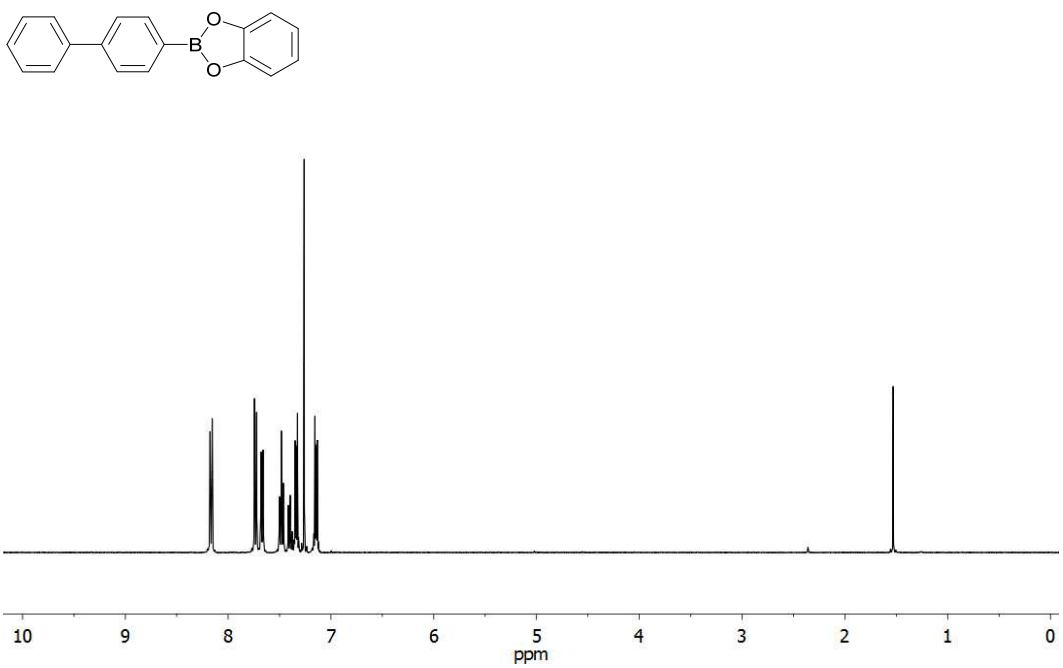


Fig. S17 ^{1}H NMR spectra of 2-([1,1'-biphenyl]-4-yl)benzo[*d*][1,3,2]dioxaborole in $CDCl_3$

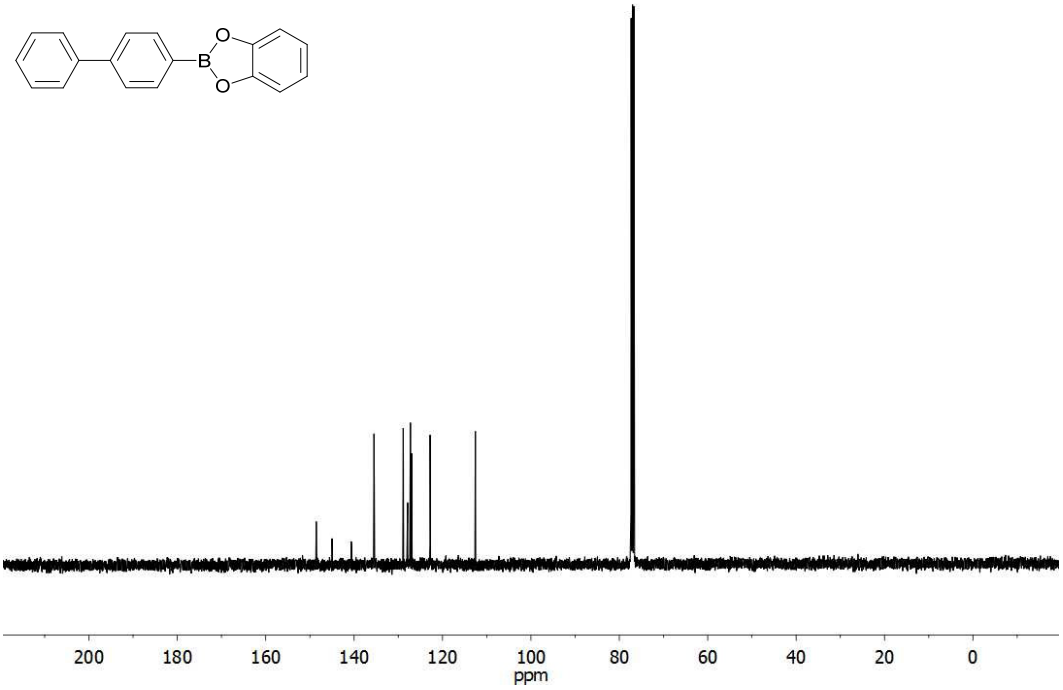


Fig. S18 ^{13}C NMR spectra of 2-([1,1'-biphenyl]-4-yl)benzo[*d*][1,3,2]dioxaborole in $CDCl_3$

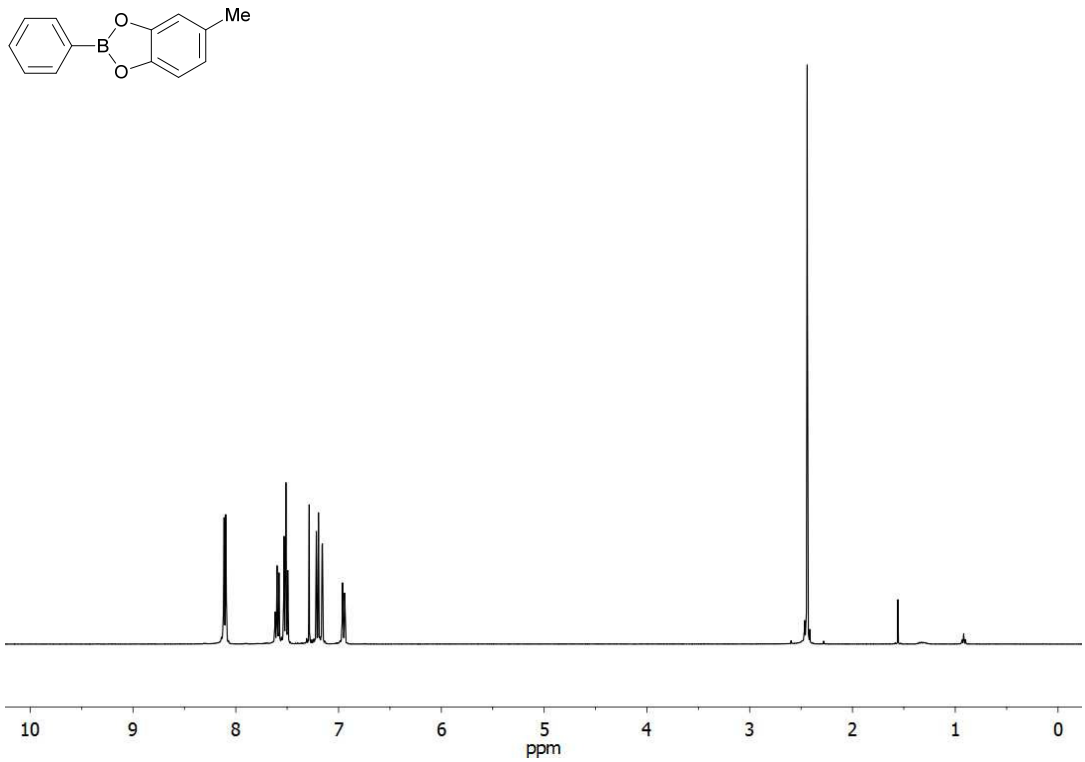


Fig. S19 ^{1}H NMR spectra of 5-methyl-2-phenylbenzo[*d*][1,3,2]dioxaborole in $CDCl_3$

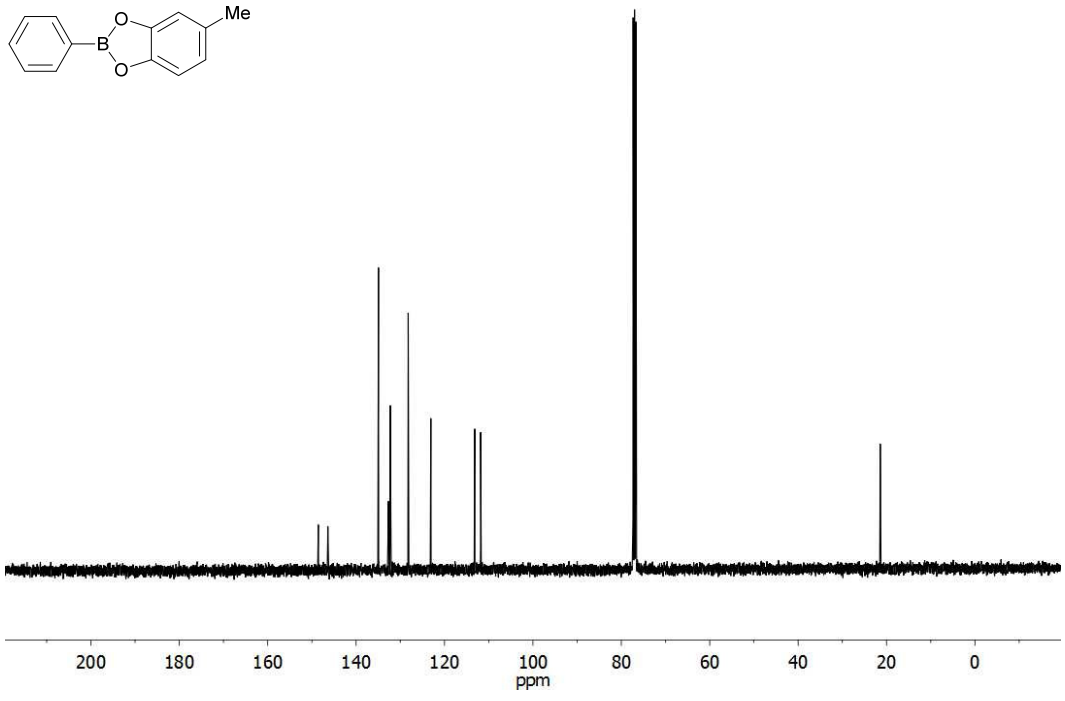


Fig. S20 ^{13}C NMR spectra of 5-methyl-2-phenylbenzo[*d*][1,3,2]dioxaborole in $CDCl_3$

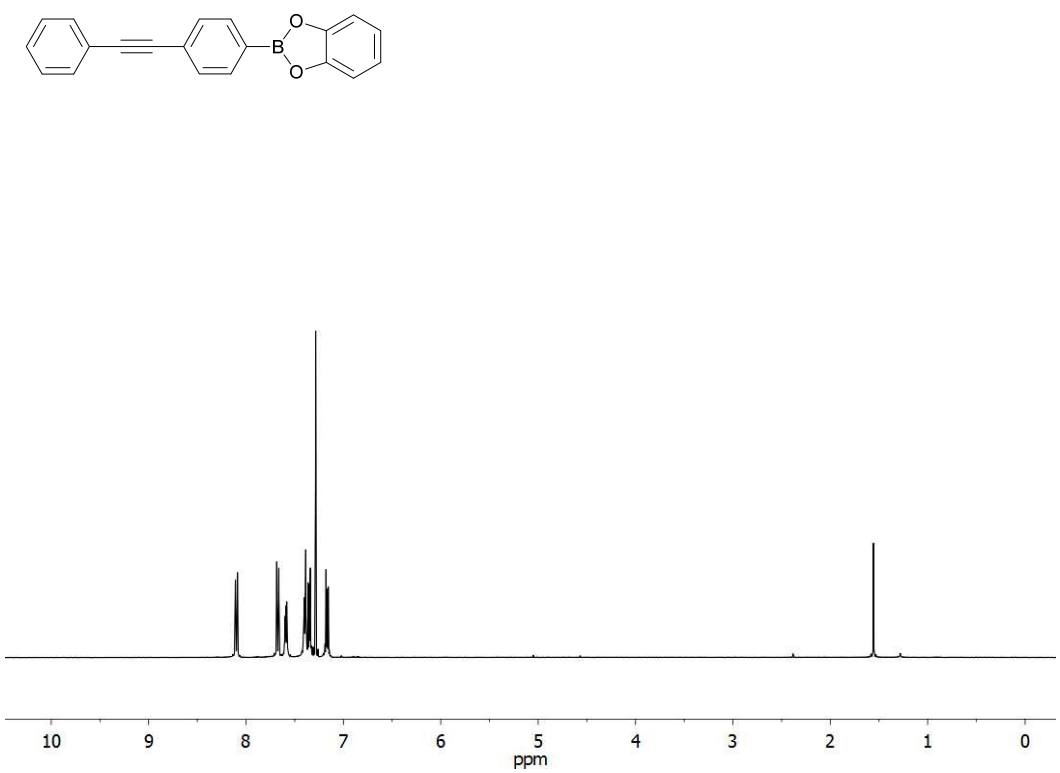


Fig. S21 ^{1}H NMR spectra of 1,2-bis(4-(benzo[*d*][1,3,2]dioxaborol-2-yl)phenyl)ethyne in $CDCl_3$

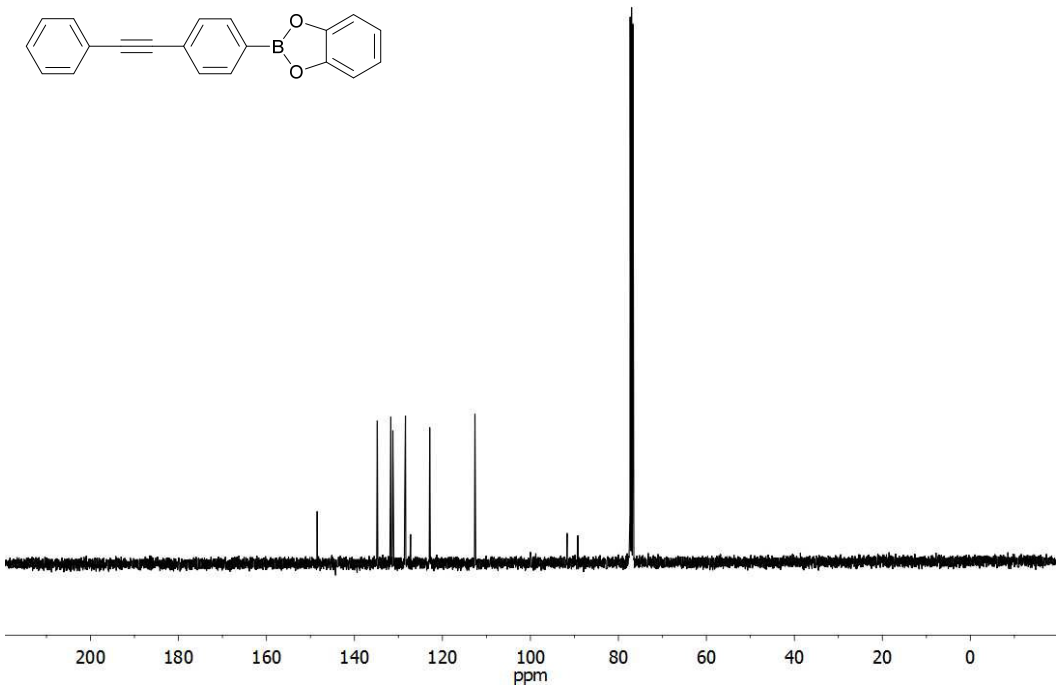
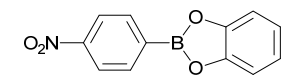


Fig. S22 ^{13}C NMR spectra of 1,2-bis(4-(benzo[*d*][1,3,2]dioxaborol-2-yl)phenyl)ethyne in $CDCl_3$



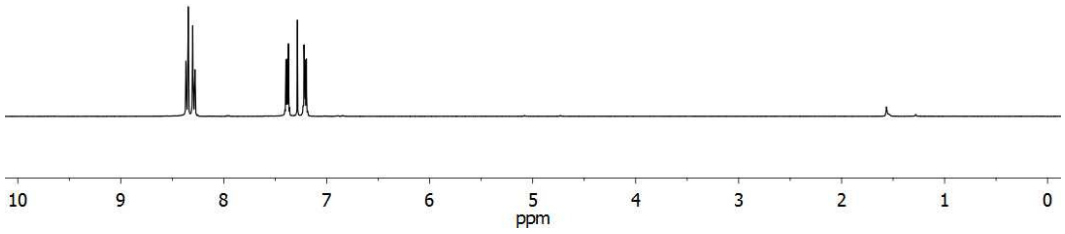


Fig. S23 ^{1}H NMR spectra of 2-(4-nitrophenyl)benzo[*d*][1,3,2]dioxaborole in $CDCl_3$

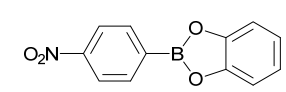


Fig. S24 ^{13}C NMR spectra of 2-(4-nitrophenyl)benzo[*d*][1,3,2]dioxaborole in $CDCl_3$

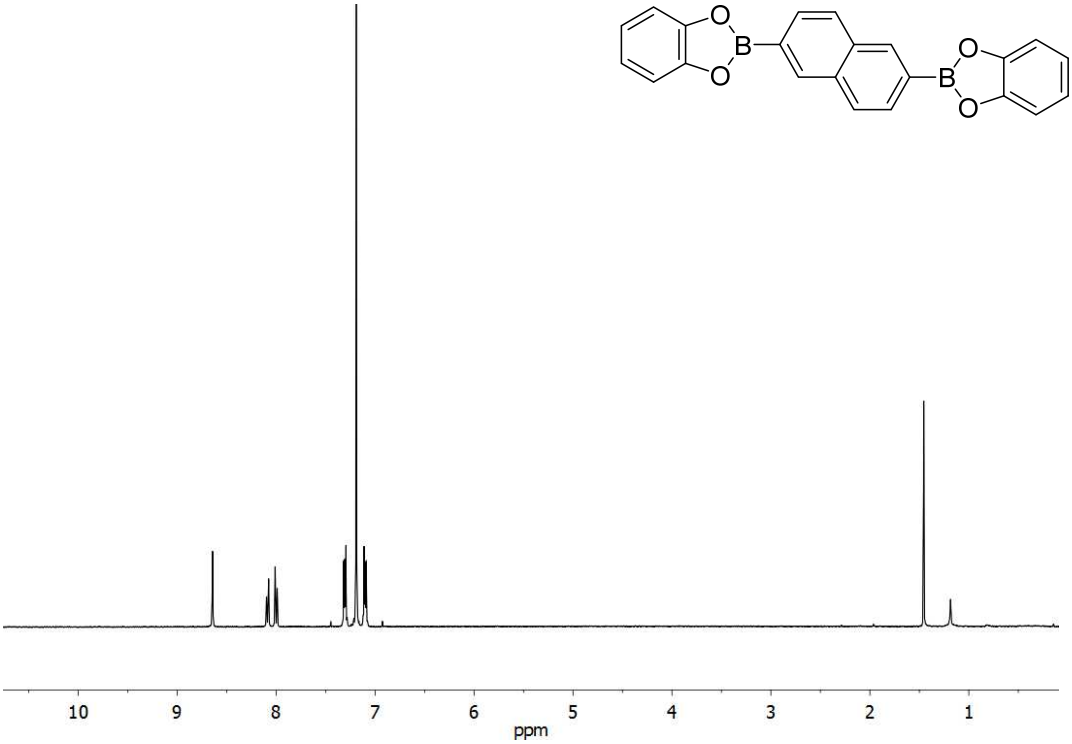


Fig. S25 ^{1}H NMR spectra of 2,6-bis(benzo[*d*][1,3,2]dioxaborol-2-yl)naphthalene in $CDCl_3$

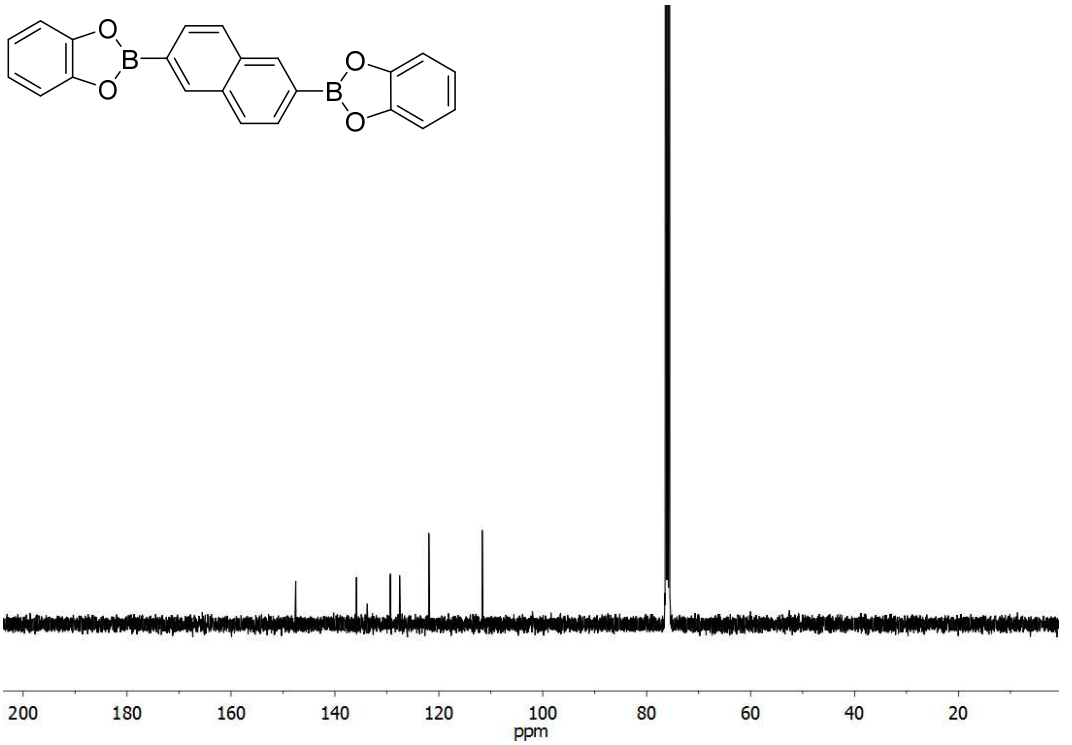


Fig. S26 ^{13}C NMR spectra of 2,6-bis(benzo[*d*][1,3,2]dioxaborol-2-yl)naphthalene in $CDCl_3$

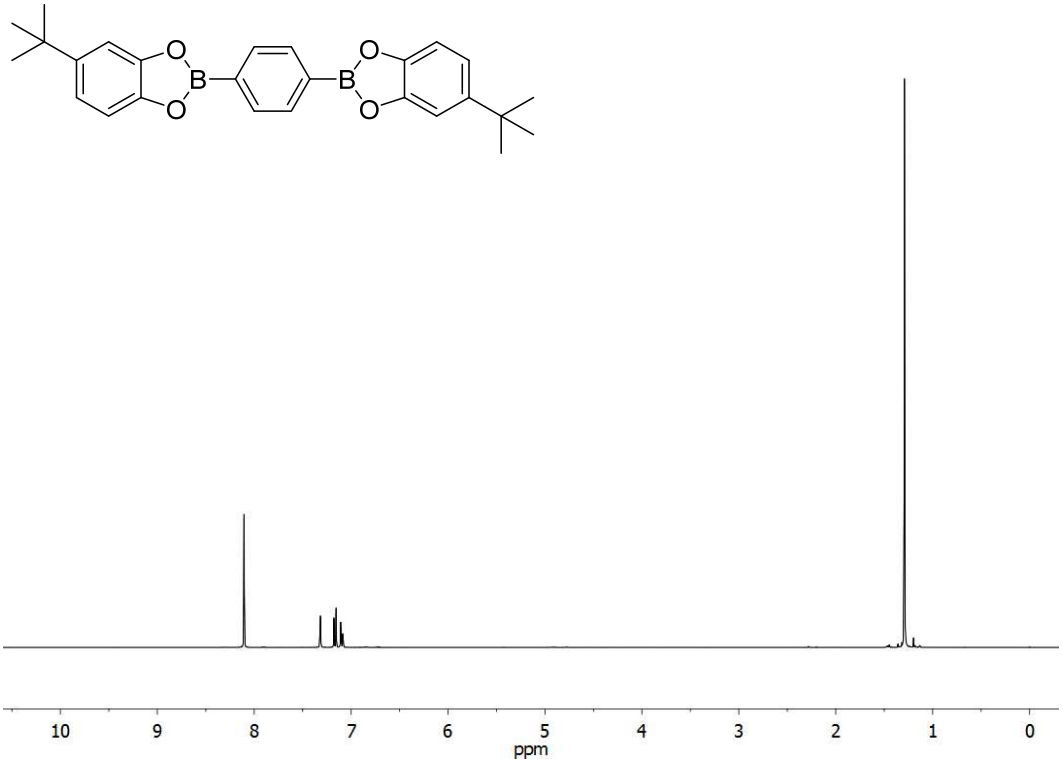


Fig. S27 ^{1}H NMR spectra of 1,4-bis(5-(tert-butyl)benzo[*d*][1,3,2]dioxaborol-2-yl)benzene in $CDCl_3$

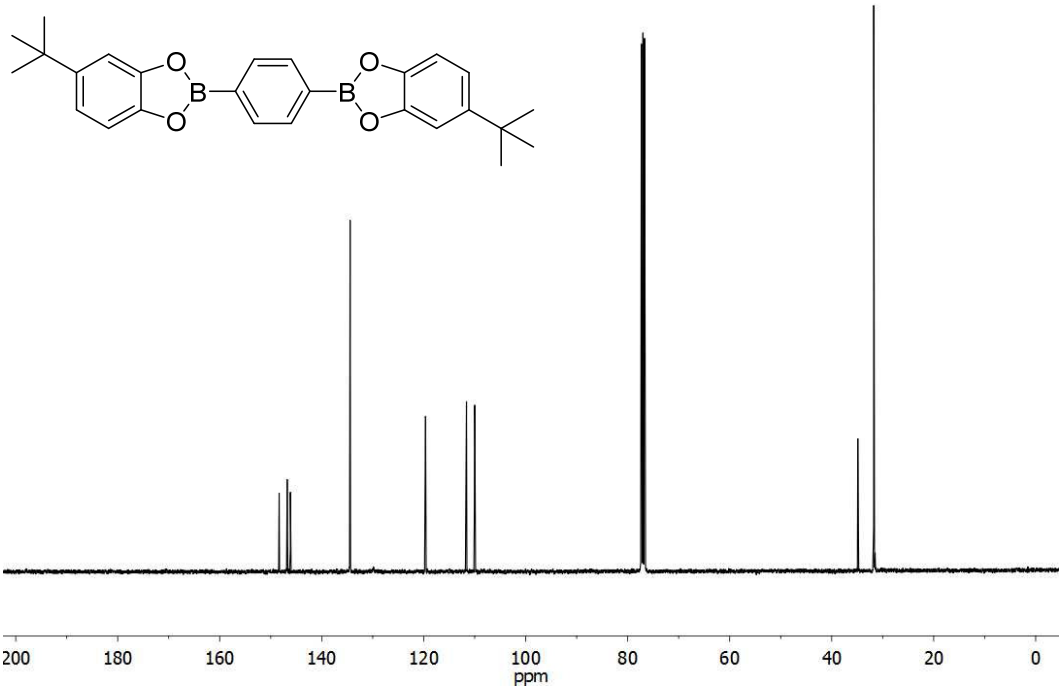


Fig. S28 ^{13}C NMR spectra of 1,4-bis(5-(tert-butyl)benzo[*d*][1,3,2]dioxaborol-2-yl)benzene in $CDCl_3$

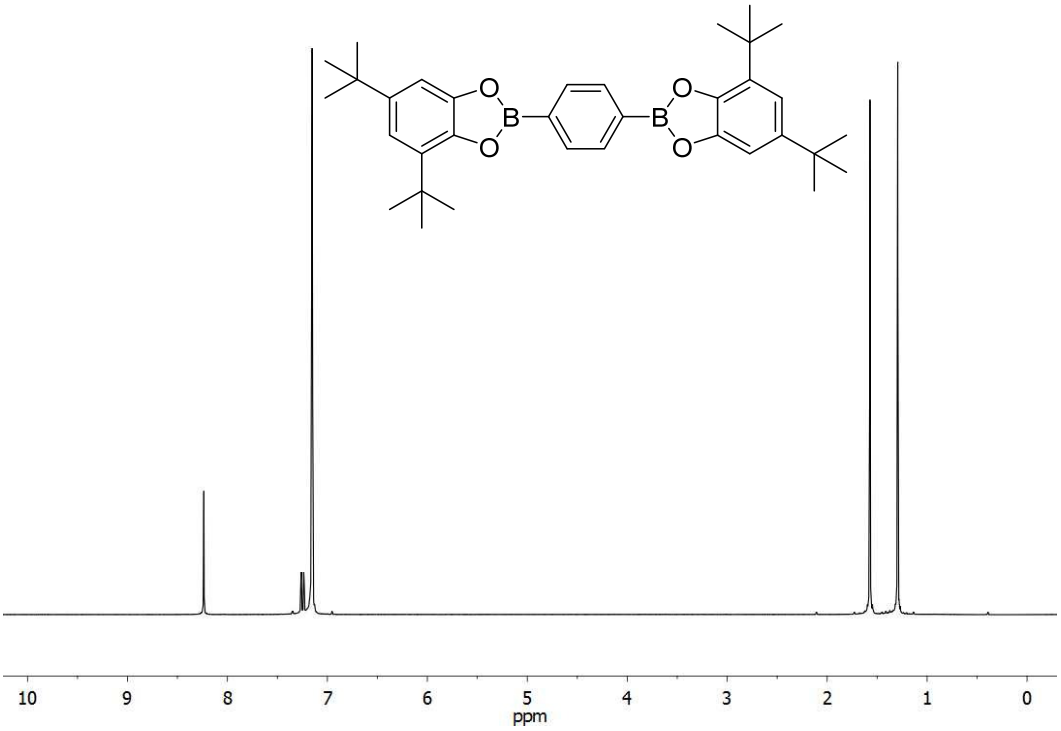


Fig. S29 ^{1}H NMR spectra of 1,4-bis(4,6-di-tert-butylbenzo[*d*][1,3,2]dioxaborol-2-yl)benzene in C_6D_6

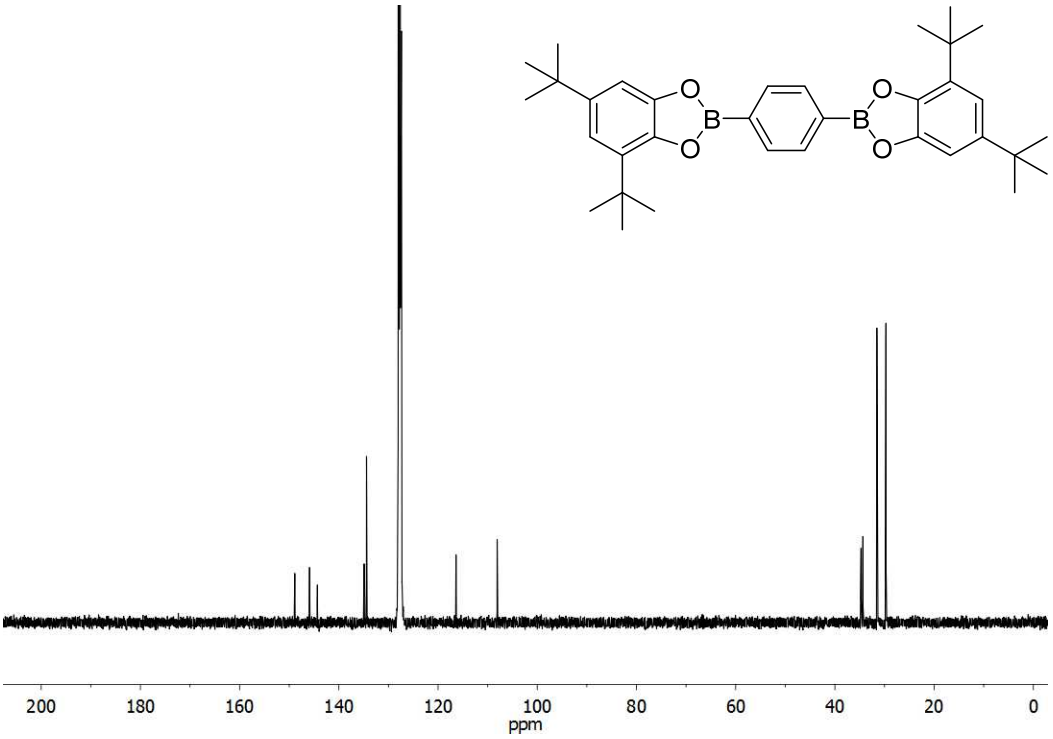


Fig. S30 ^{13}C NMR spectra of 1,4-bis(4,6-di-tert-butylbenzo[*d*][1,3,2]dioxaborol-2-yl)benzene in C_6D_6

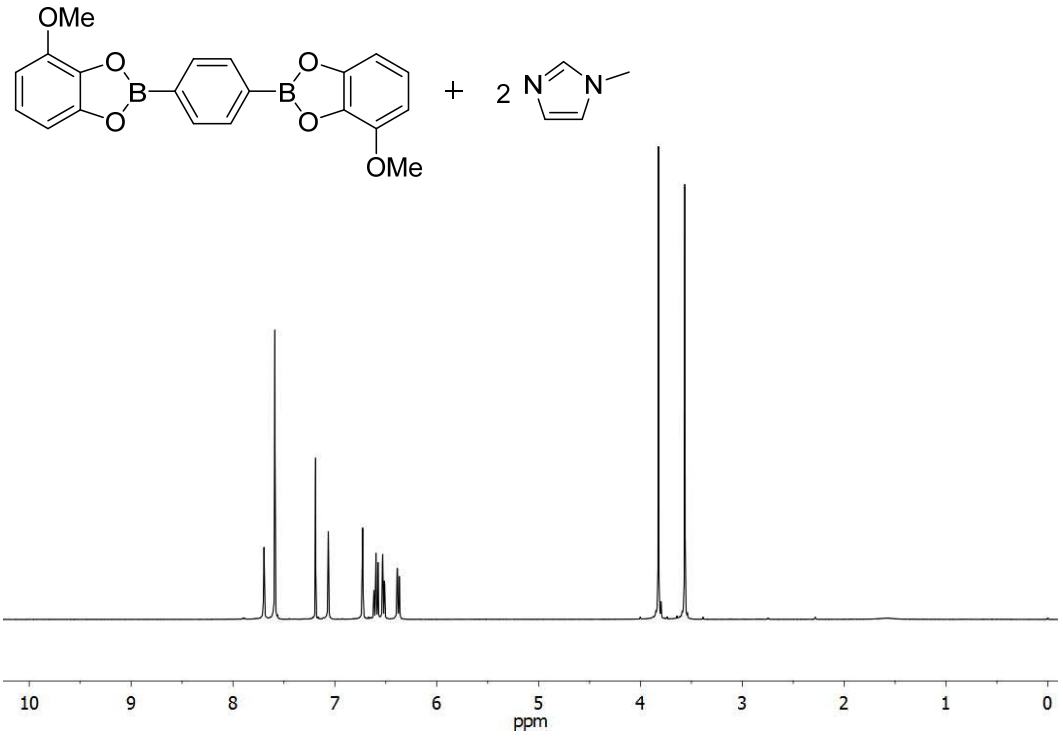


Fig. S31 ^{1}H NMR spectra of N-methylimidazole - 1,4-bis(4-methoxybenzo[*d*][1,3,2]dioxaborol-2-yl)benzene adduct in $CDCl_3$

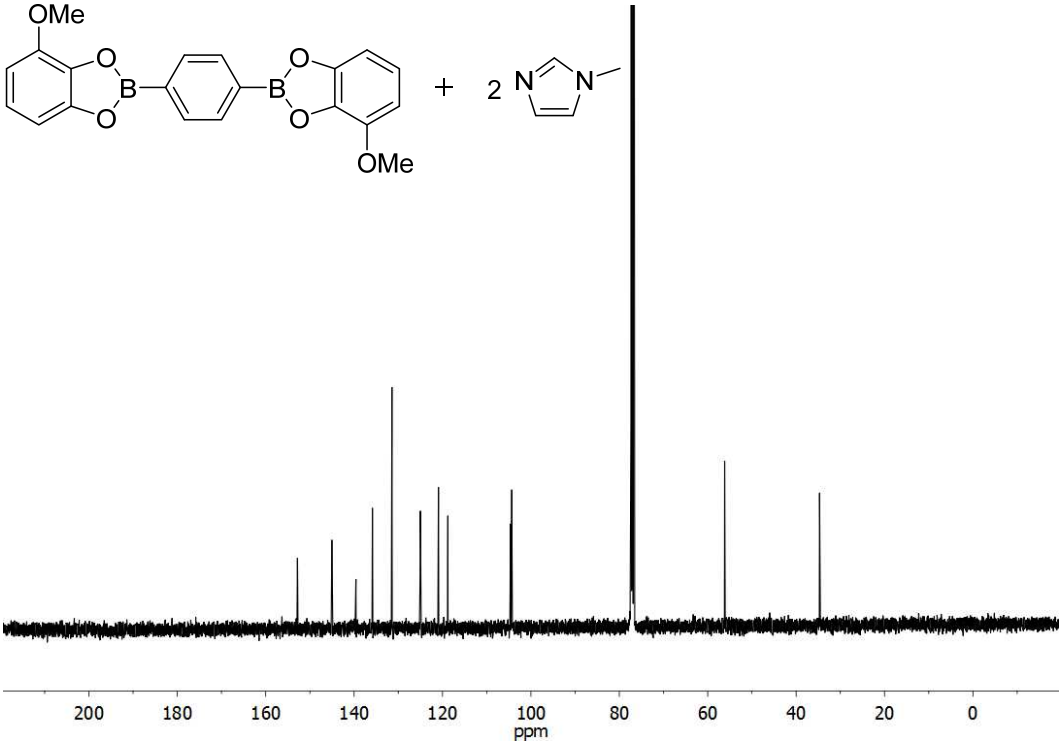


Fig. S32 ^{13}C NMR spectra of N-methylimidazole - 1,4-bis(4-methoxybenzo[*d*][1,3,2]dioxaborol-2-yl)benzene adduct in $CDCl_3$

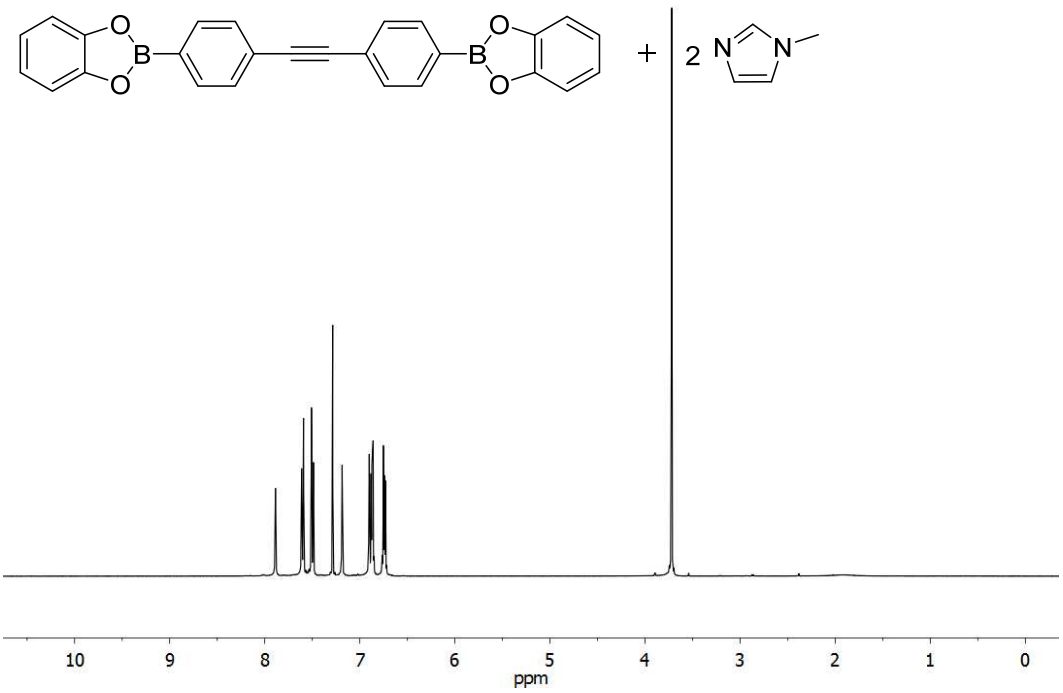


Fig. S33 ^{1}H NMR spectra of N-methylimidazole - 1,2-bis(4-(benzo[*d*][1,3,2]dioxaborol-2-yl)phenyl)ethyne adduct in $CDCl_3$

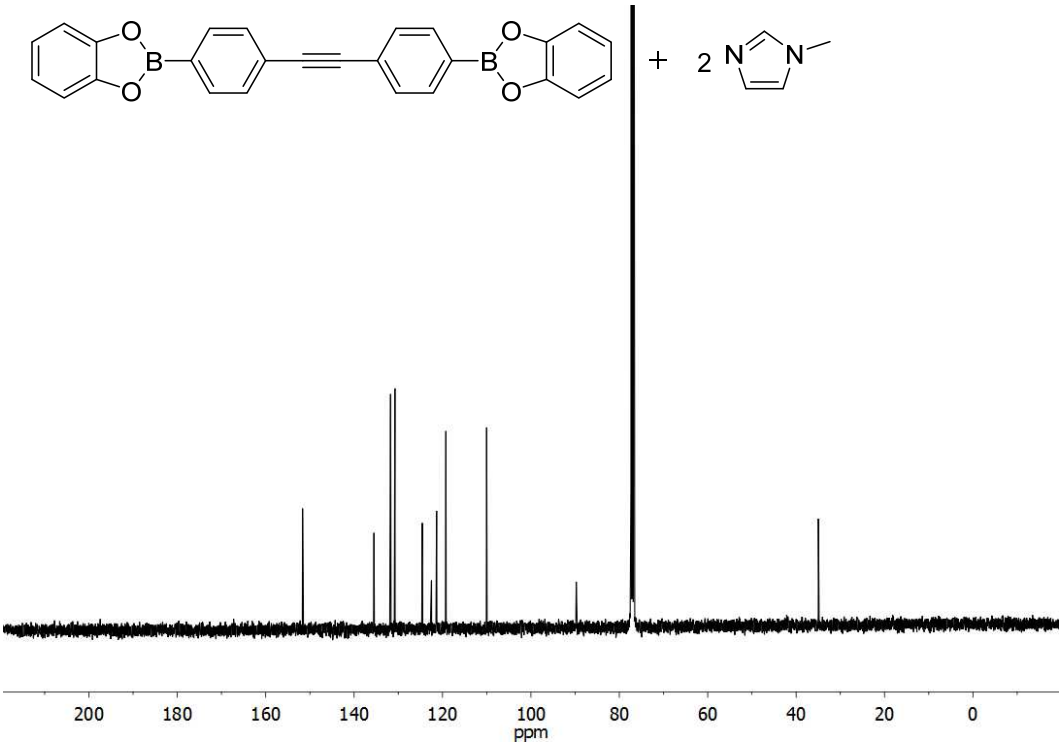


Fig. S34 ^{13}C NMR spectra of N-methylimidazole - 1,2-bis(4-(benzo[*d*][1,3,2]dioxaborol-2-yl)phenyl)ethyne adduct in $CDCl_3$

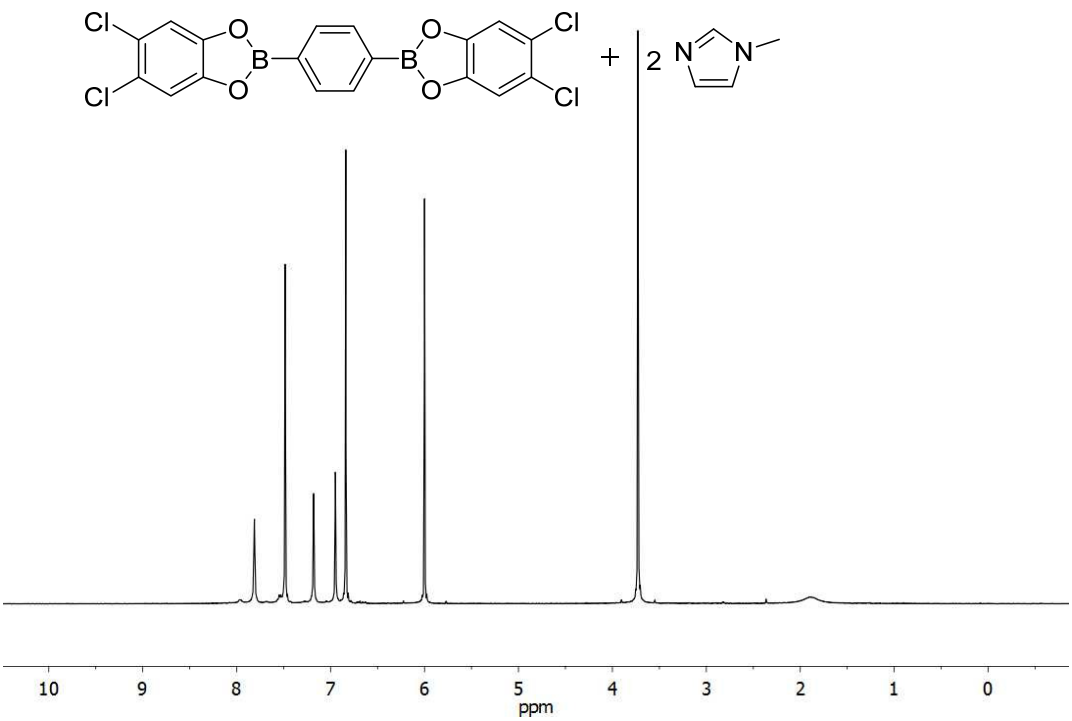


Fig. S35 ^{1}H NMR spectra of N-methylimidazole - 1,4-bis(5,6-dichlorobenzo[*d*][1,3,2]dioxaborol-2-yl)benzene adduct in TCE-d_2

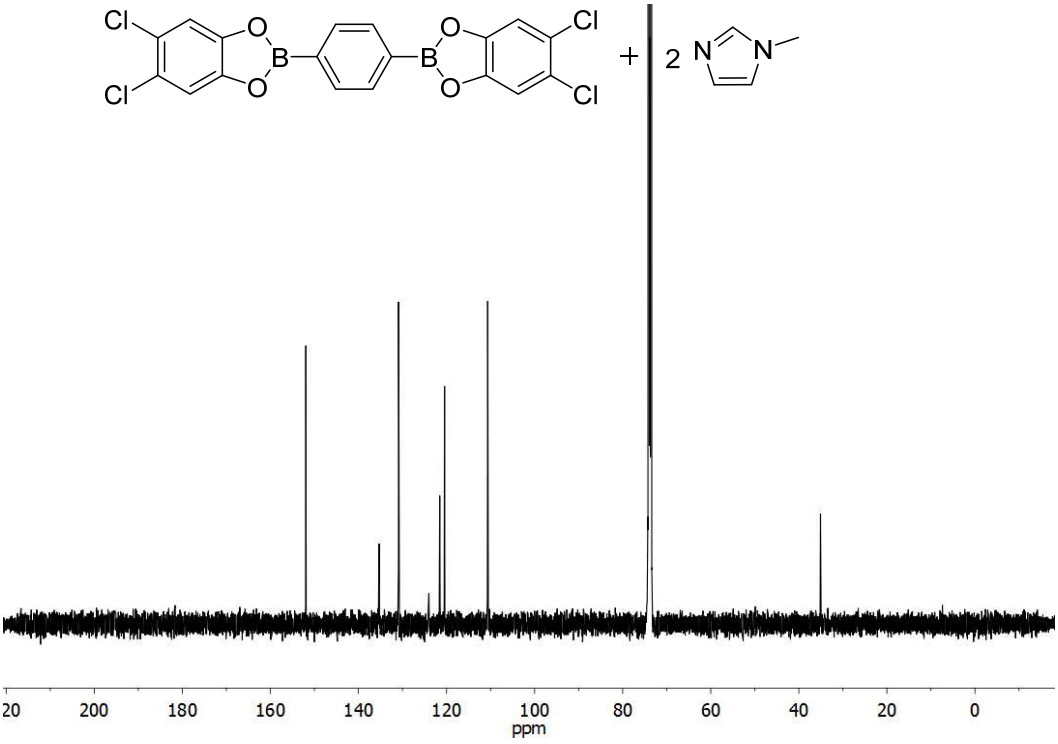


Fig. S36 ^{13}C NMR spectra of N-methylimidazole - 1,4-bis(5,6-dichlorobenzo[*d*][1,3,2]dioxaborol-2-yl)benzene adduct in TCE-d_2

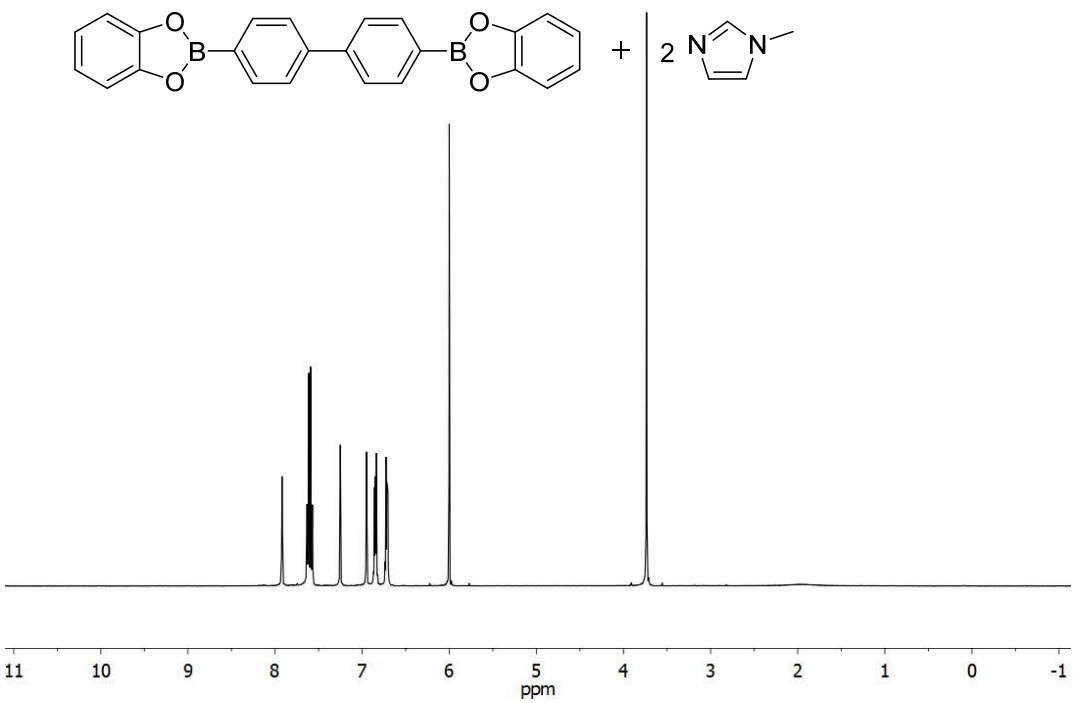


Fig. S37 ^{1}H NMR spectra of N-methylimidazole - 4,4'-bis(benzo[*d*][1,3,2]dioxaborol-2-yl)-1,1'-biphenyl adduct in TCE-d_2

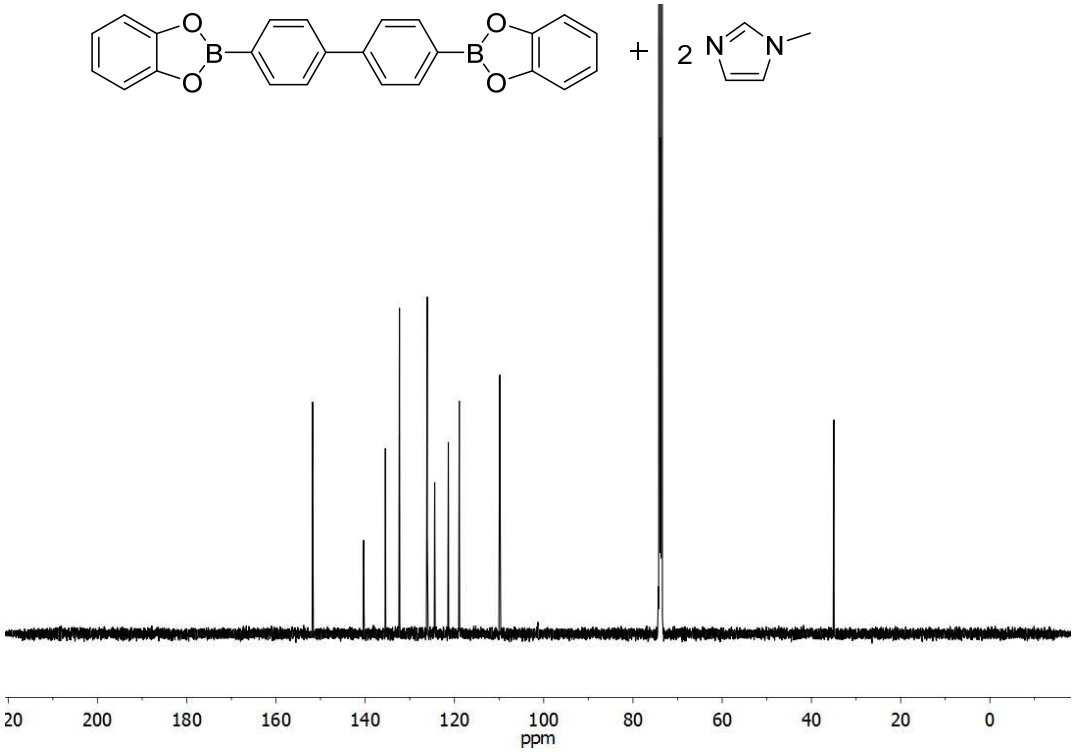


Fig. S38 ^{13}C NMR spectra of N-methylimidazole - 4,4'-bis(benzo[*d*][1,3,2]dioxaborol-2-yl)-1,1'-biphenyl adduct in TCE-d_2

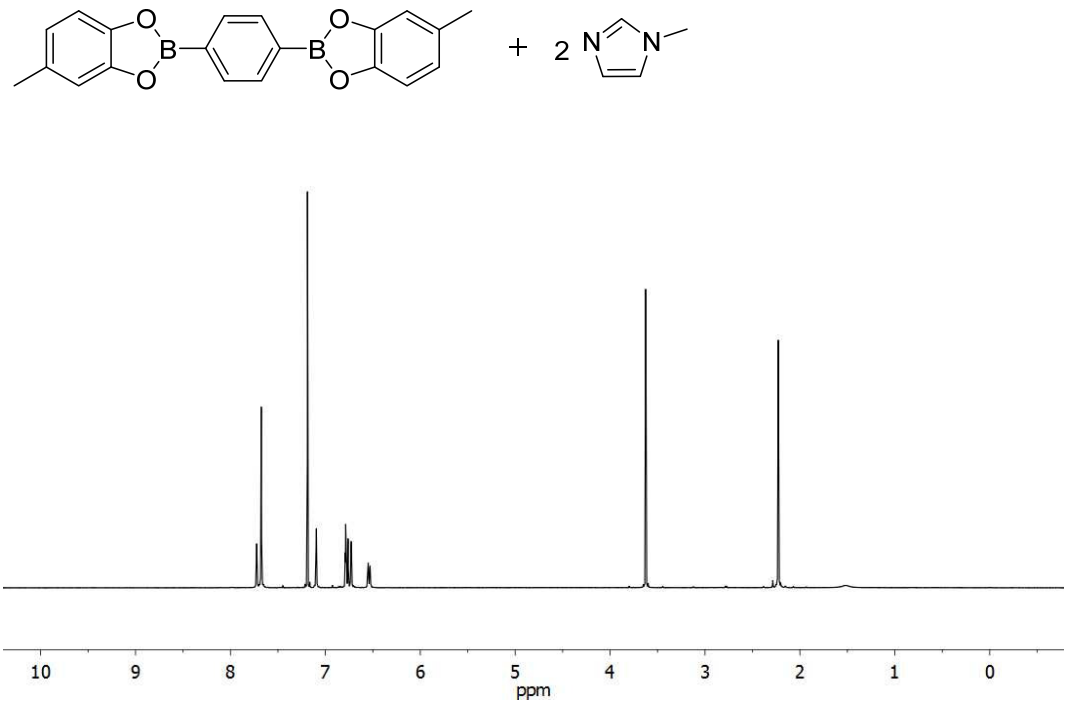


Fig. S39 ^{1}H NMR spectra of N-methylimidazole - 1,4-bis(5-methylbenzo[*d*][1,3,2]dioxaborol-2-yl)benzene adduct in $CDCl_3$

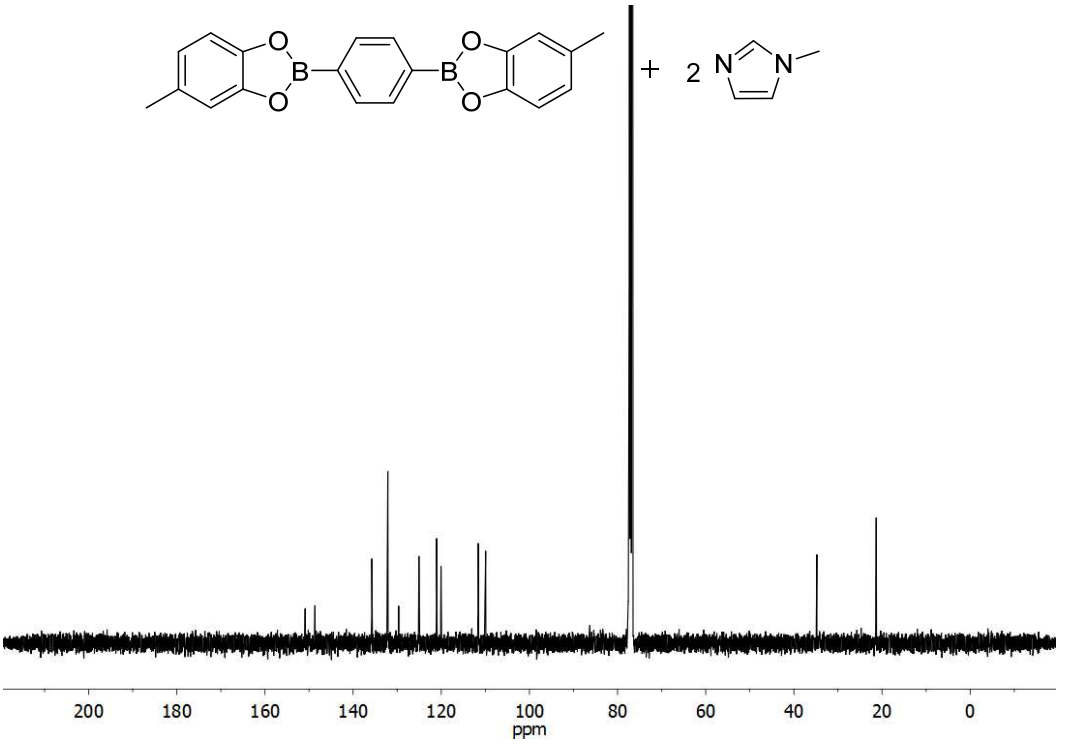


Fig. S40 ^{13}C NMR spectra of N-methylimidazole - 1,4-bis(5-methylbenzo[*d*][1,3,2]dioxaborol-2-yl)benzene adduct in $CDCl_3$

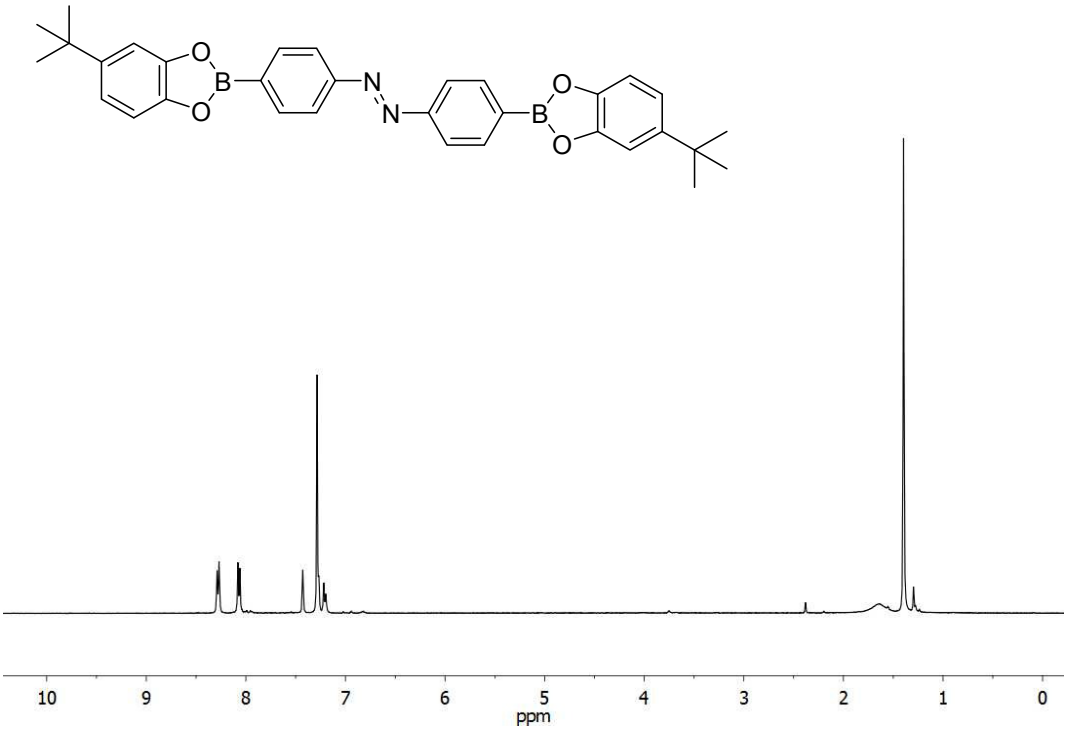


Fig. 41 ^{1}H NMR spectra of (E)-1,2-bis(4-(5-(tert-butyl)benzo[*d*][1,3,2]dioxaborol-2-yl)phenyl)diazene in $CDCl_3$

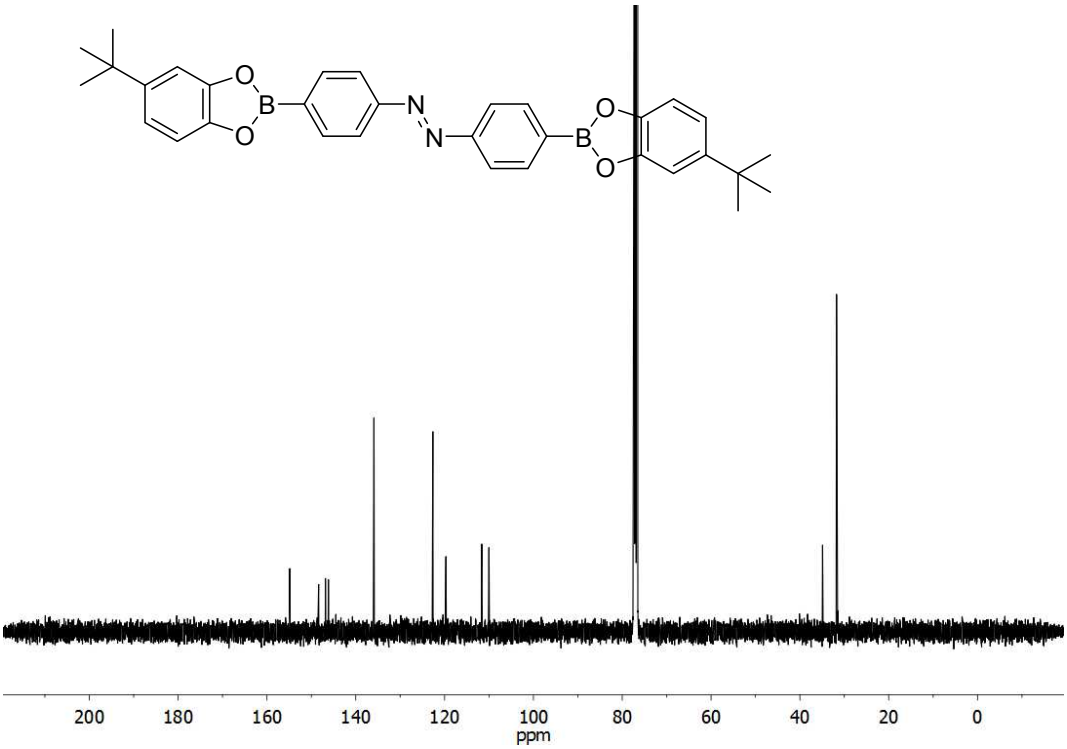
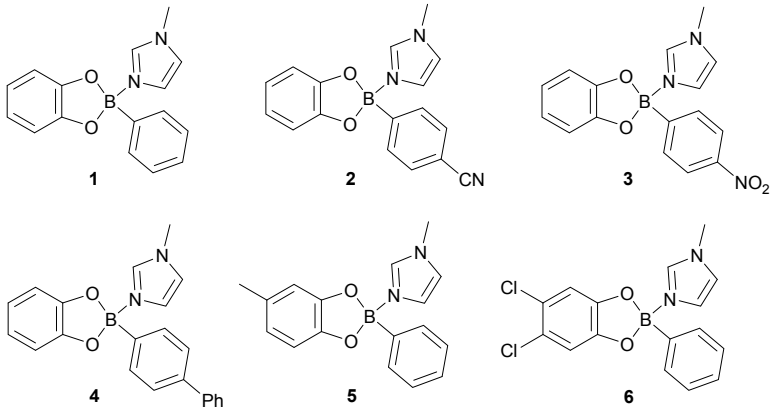


Fig. 42 ^{13}C NMR spectra of (E)-1,2-bis(4-(5-(tert-butyl)benzo[*d*][1,3,2]dioxaborol-2-yl)phenyl)diazene in $CDCl_3$

10. X-ray crystallography

Single crystals were obtained by following procedure: A stoichiometric mixture of the boronate ester (30 µmol) and N-methylimidazole (30 µmol) were dissolved in toluene. Slow diffusion of pentane or resting in the fridge at 4 °C afforded single crystal suited for X-ray crystallography.

For the discussion below, the following numbering scheme is used:



The diffraction data of all crystal structures (except compound **6**) were measured at low temperature [100(2) K] using Mo K_α radiation on a Bruker APEX II CCD diffractometer equipped with a kappa geometry goniometer. The datasets were reduced by EvalCCD[11] and then corrected for absorption.[12] The data collection of compound **6** was measured at room temperature, using Cu K_α radiation on an Agilent Technologies SuperNova dual system in combination with an Atlas CCD detector. The data reduction was carried out by Crysalis PRO.[13] The solutions and refinements were performed by SHELX.[14] The crystal structures were refined using full-matrix least-squares based on F^2 with all non hydrogen atoms anisotropically defined. Hydrogen atoms were placed in calculated positions by means of the "riding" model. Pseudo merohedral twinning was found for compound **2** and treated by the TWINROTMAT algorithm of PLATON,[15] obtaining one BASF value: 0.320(8).

Crystallographic data have been deposited with the CCDC numbers 1423210 (**1**), 1423213 (**2**), 1423209 (**3**), 1423208 (**4**), 1423205 (**5**) and 1423199 (**6**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, U.K. (fax, (internat.) +44-1223-336033; E-mail, deposit@ccdc.cam.ac.uk).

11. References

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