Electronic Supplementary Material (ESI) for Dalton Transactions.

Contents

Analytical data

Compound 1

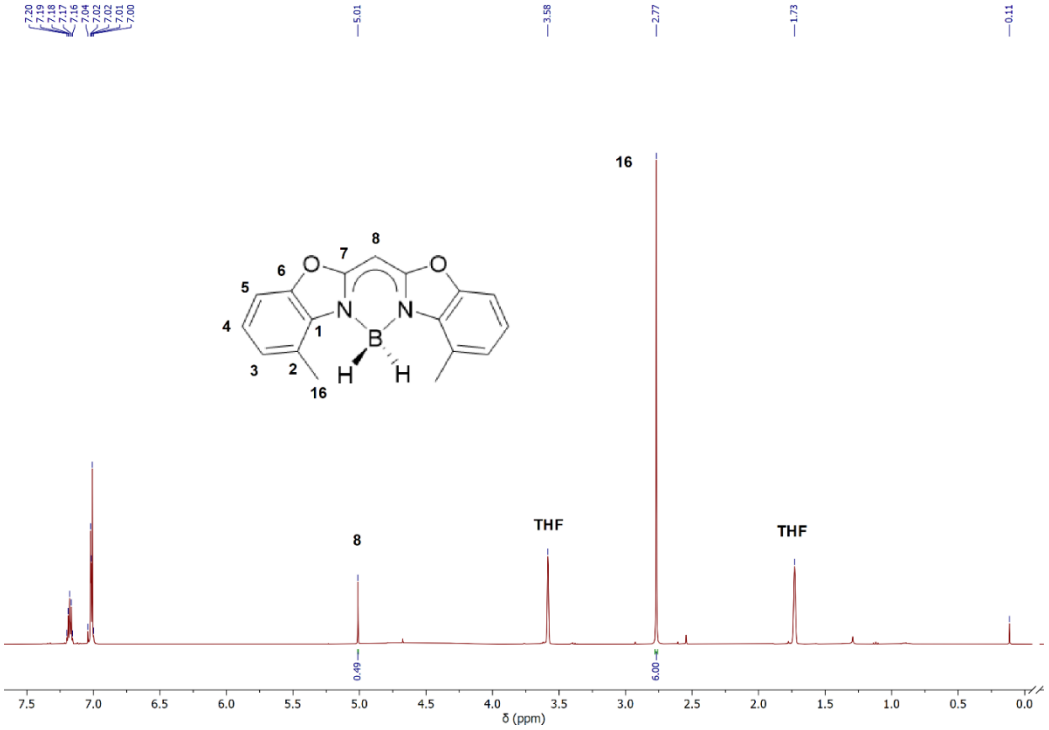
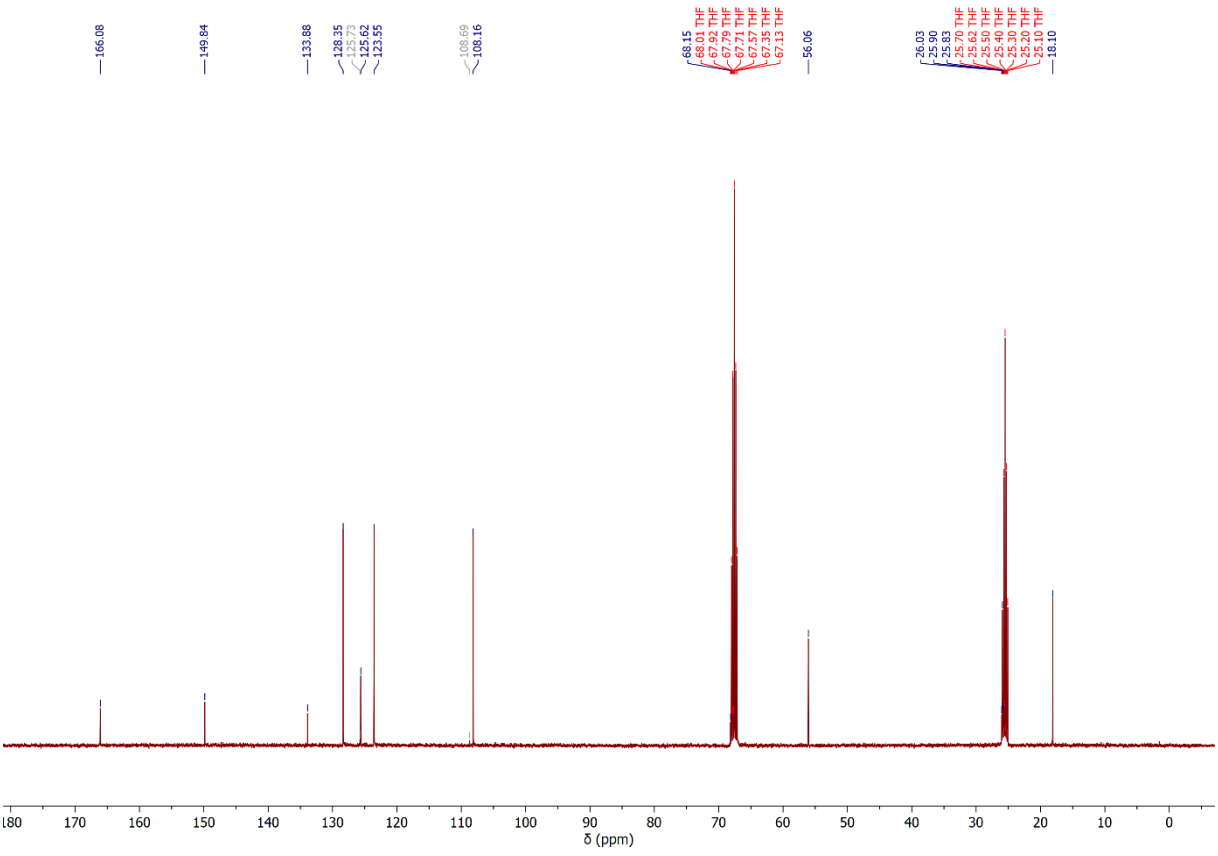


Figure S1: ^{1}H NMR spectrum of **1** in THF-d_8.

Figure S2: $^{13}C\{^{1}H\}$ NMR spectrum of **1** in THF-d_8.



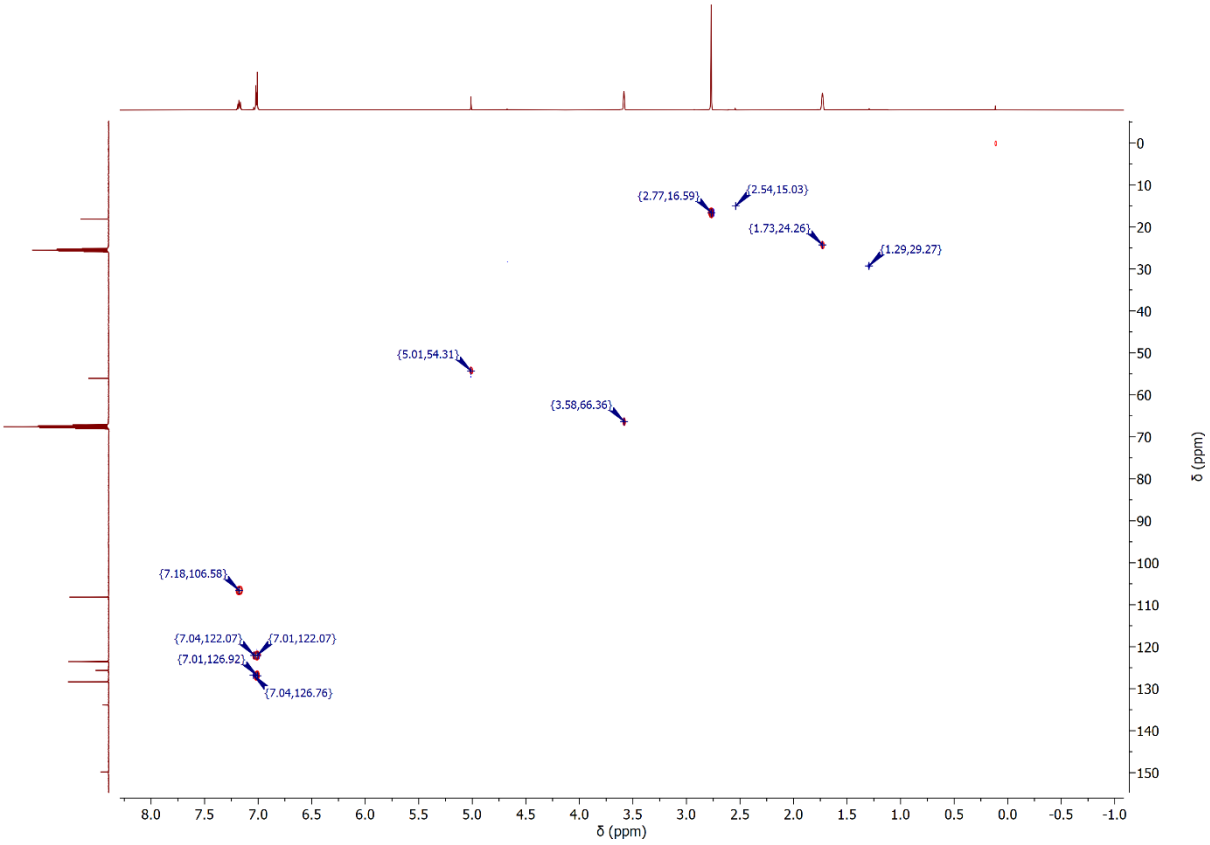


Figure S3: ^{1}H, ^{13}C HSQC NMR spectrum of **1** in THF-d_8.

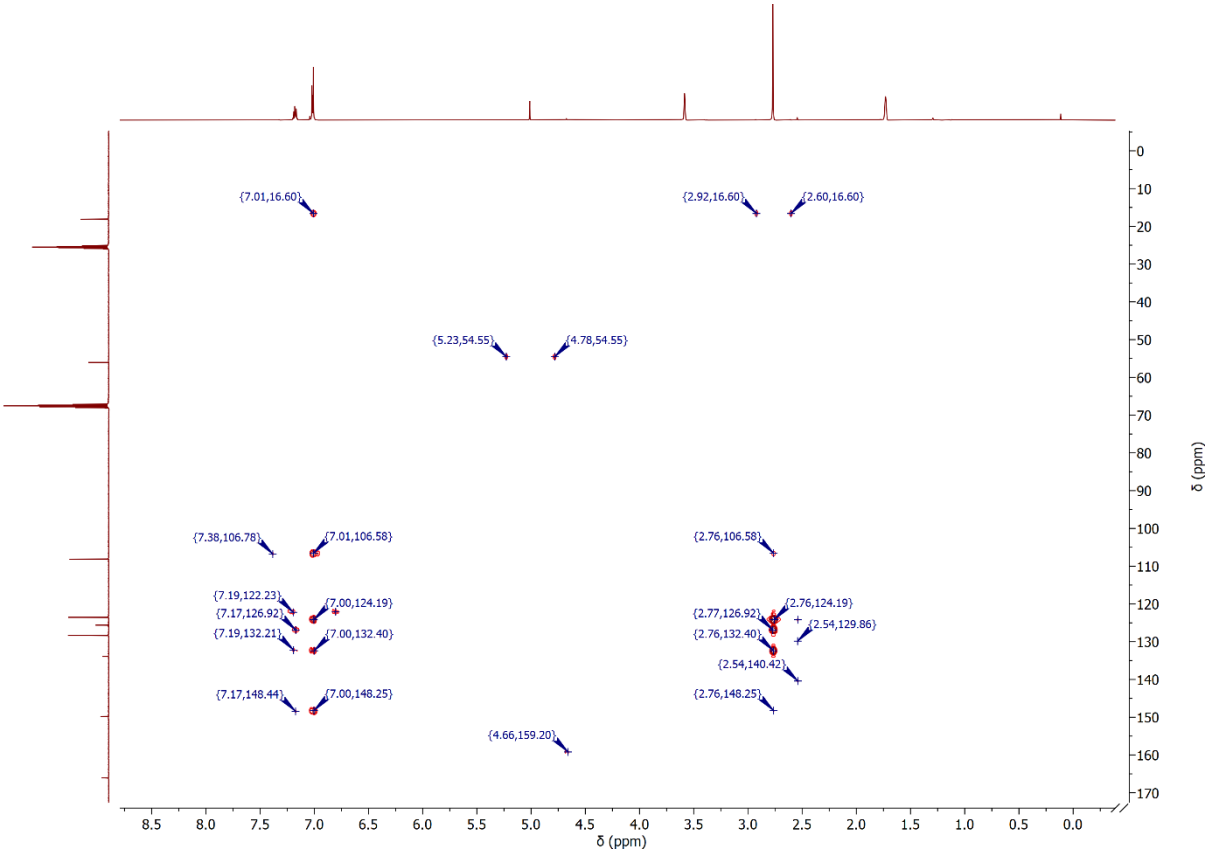


Figure S4: ^{1}H, ^{13}C HMBC NMR spectrum of **1** in THF-d_8.

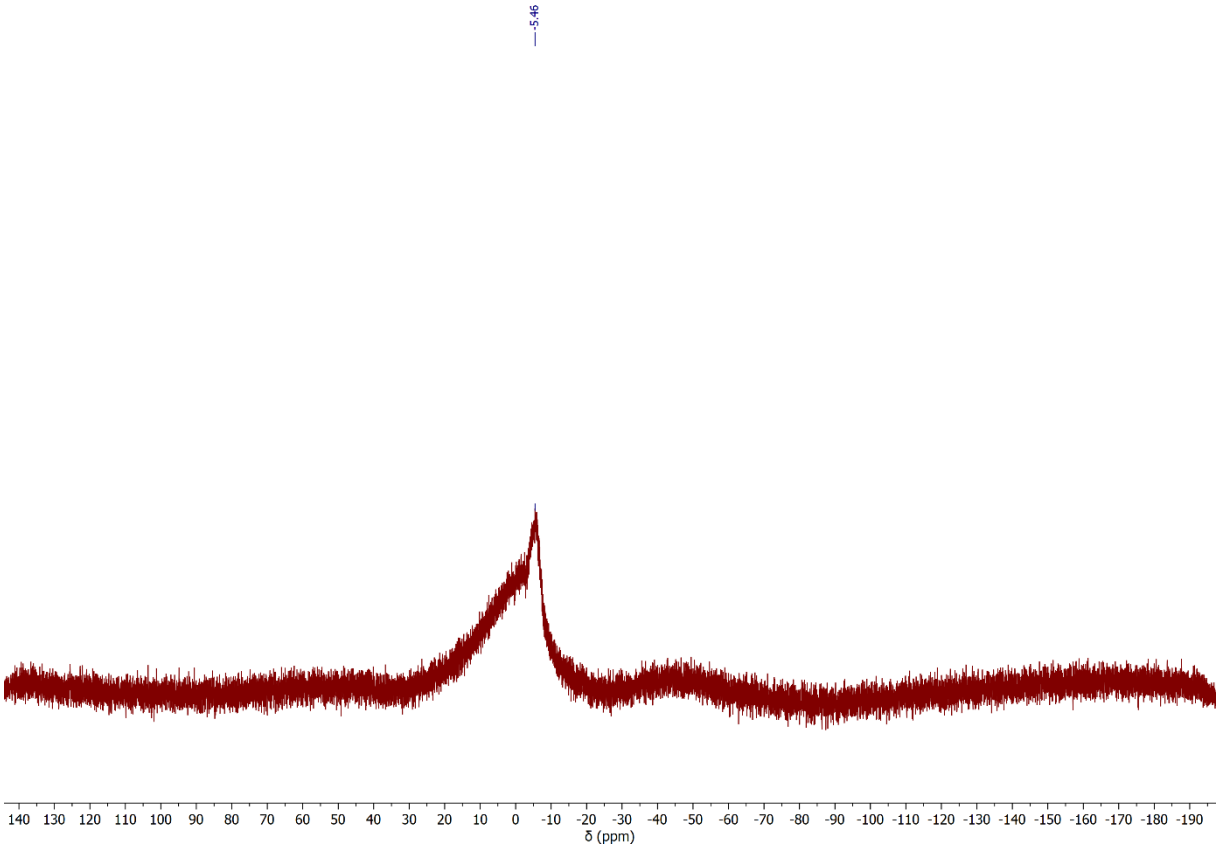


Figure S5: ^{11}B NMR spectrum of **1** in THF-d_8.

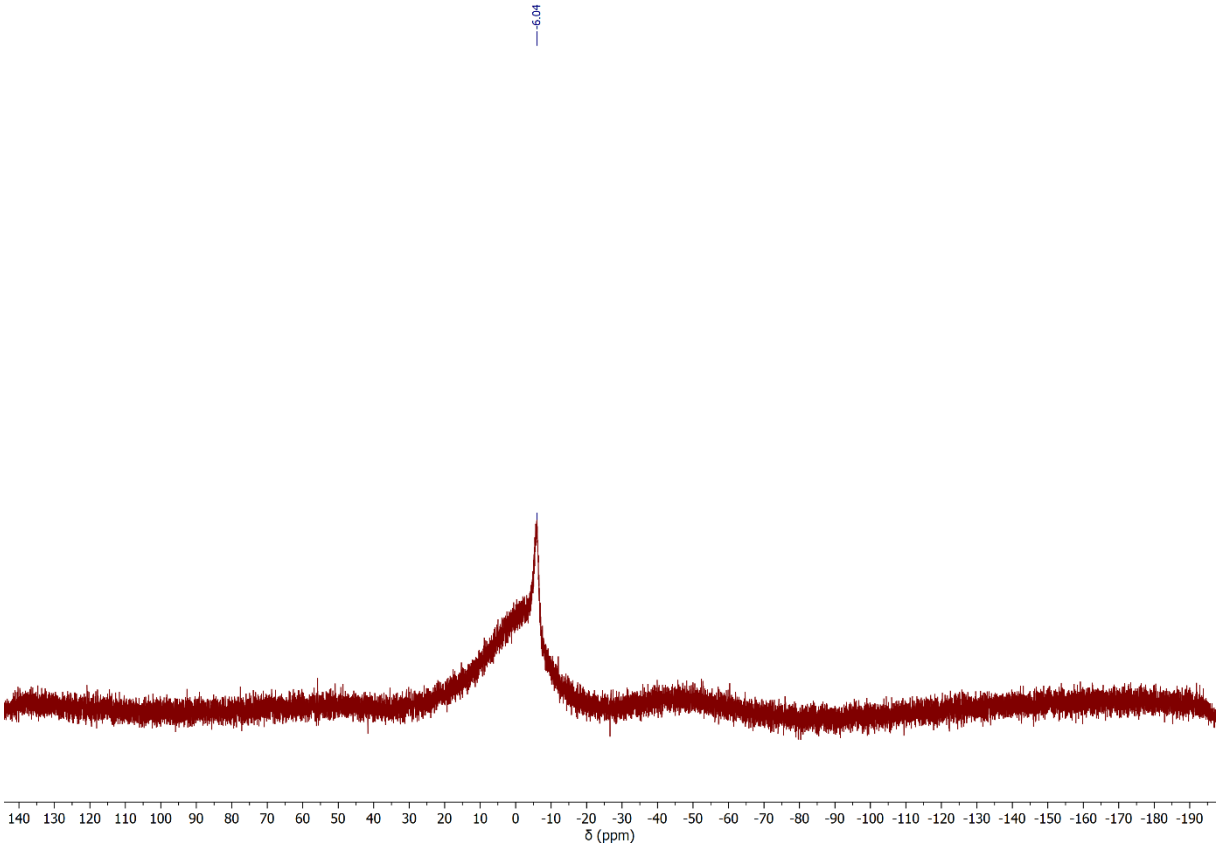


Figure S6*:* ^{11}B-H NMR spectrum of **1** in THF-d_8.

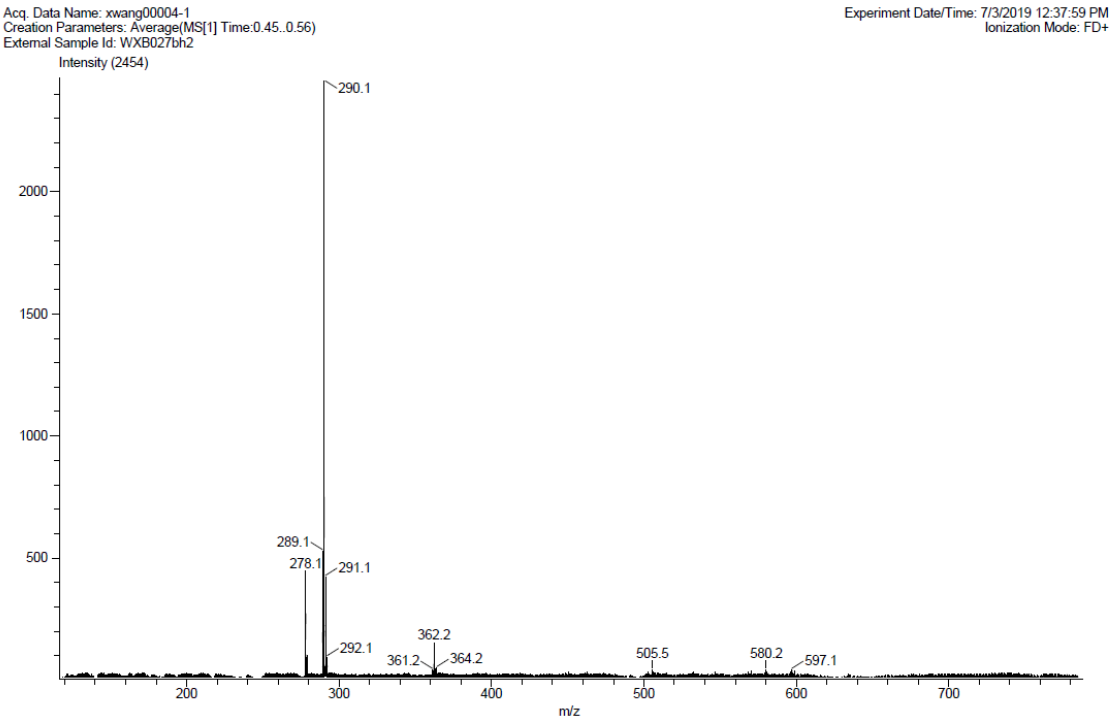


Figure S7: Mass spectrum (LIFDI[+], THF) of **1** (1 of 2).

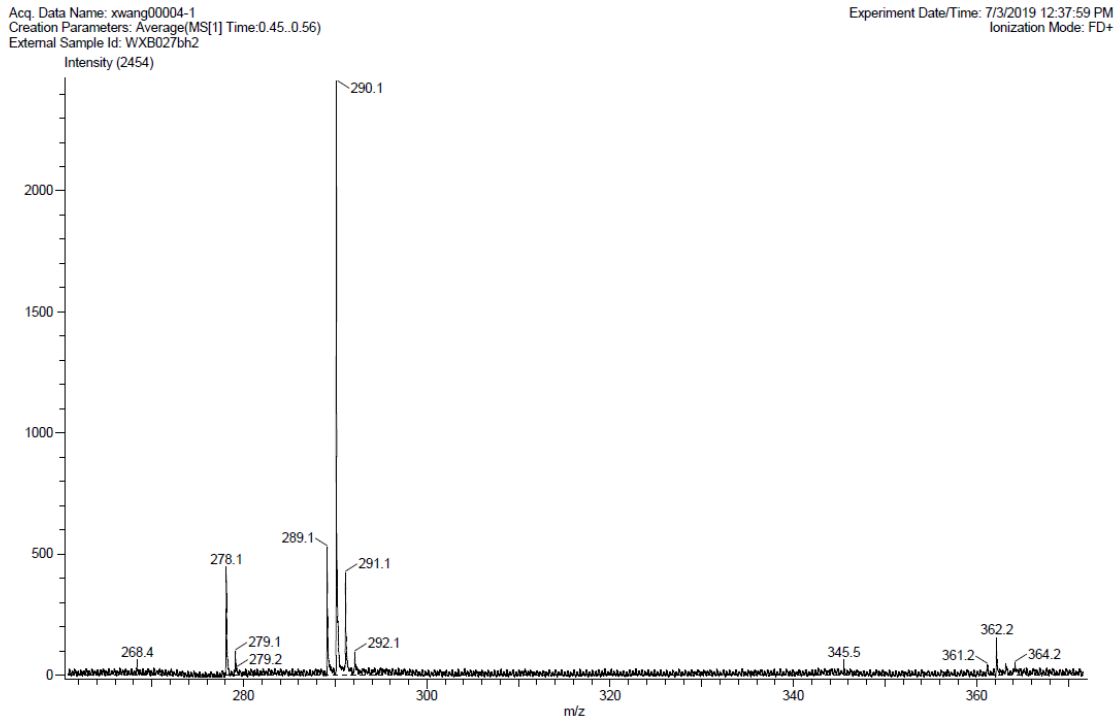


Figure S8: Mass spectrum (LIFDI[+], THF) of **1** (2 of 2).

Compound 2

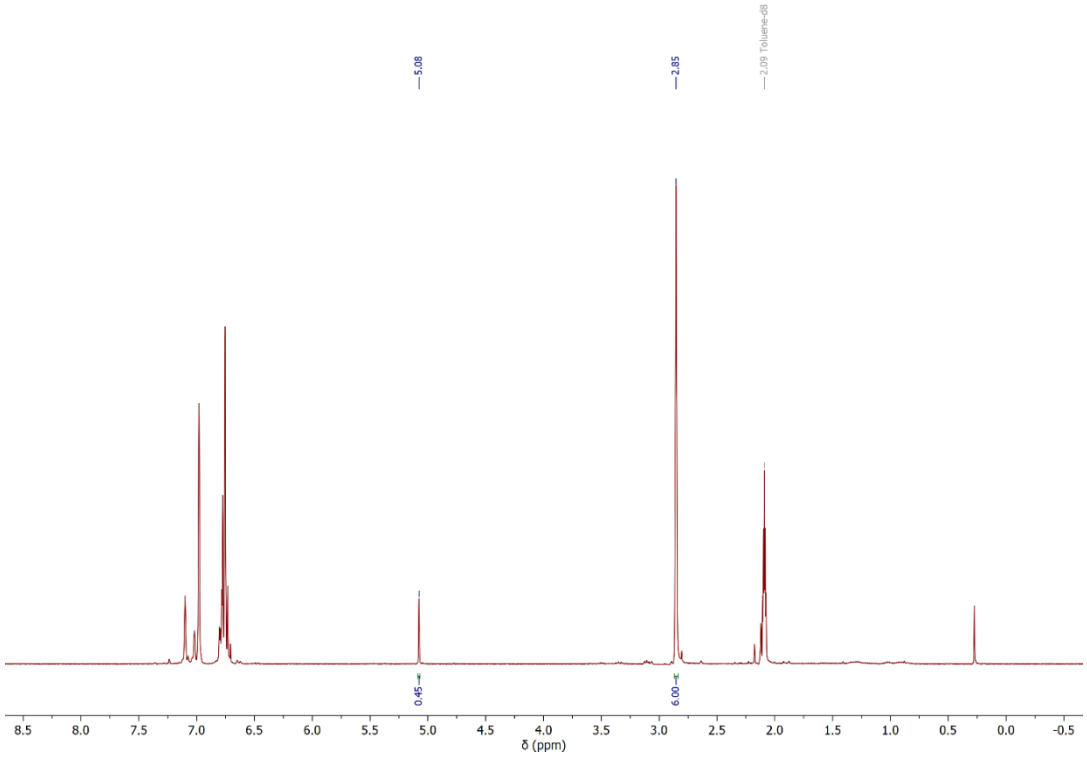


Figure S9: ^{1}H NMR spectrum of **2** in tol-d_8.

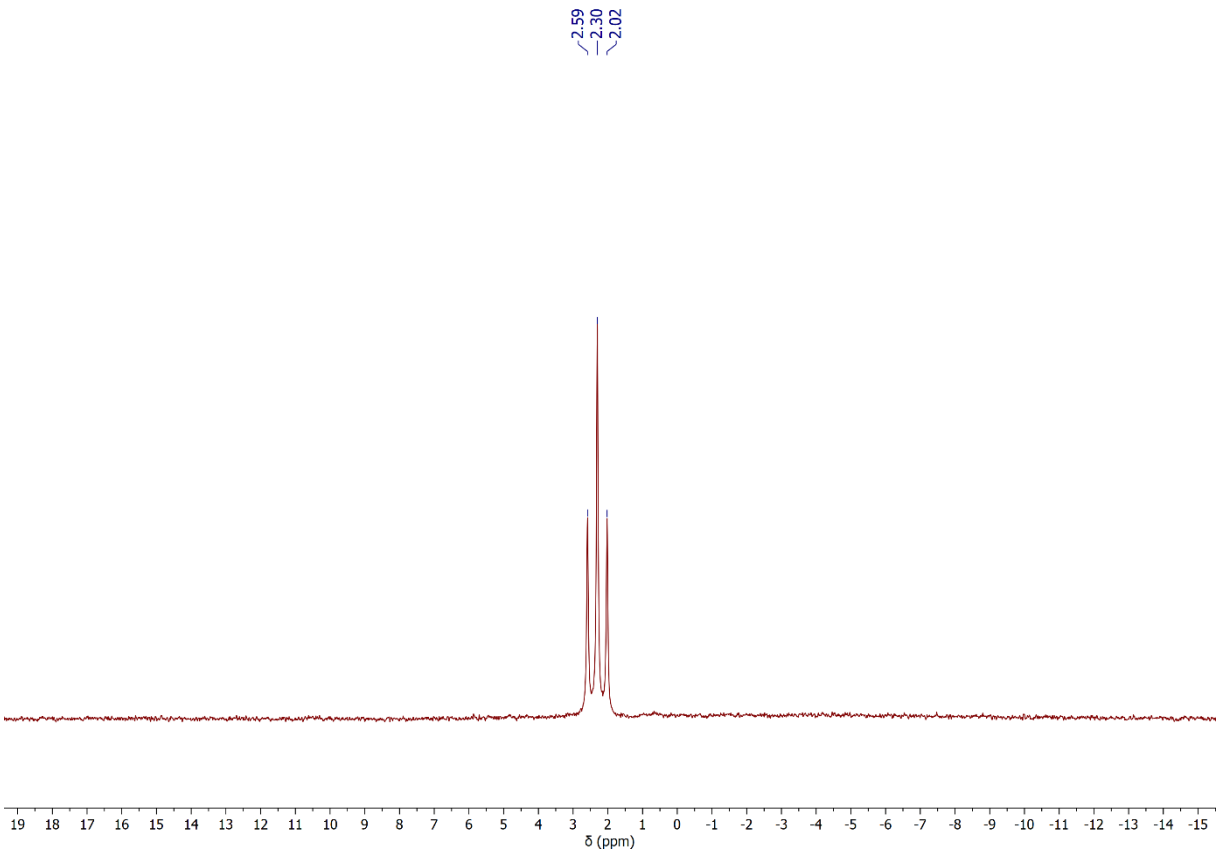


Figure S10: ^{11}B NMR spectrum of **2** in tol-d_8.

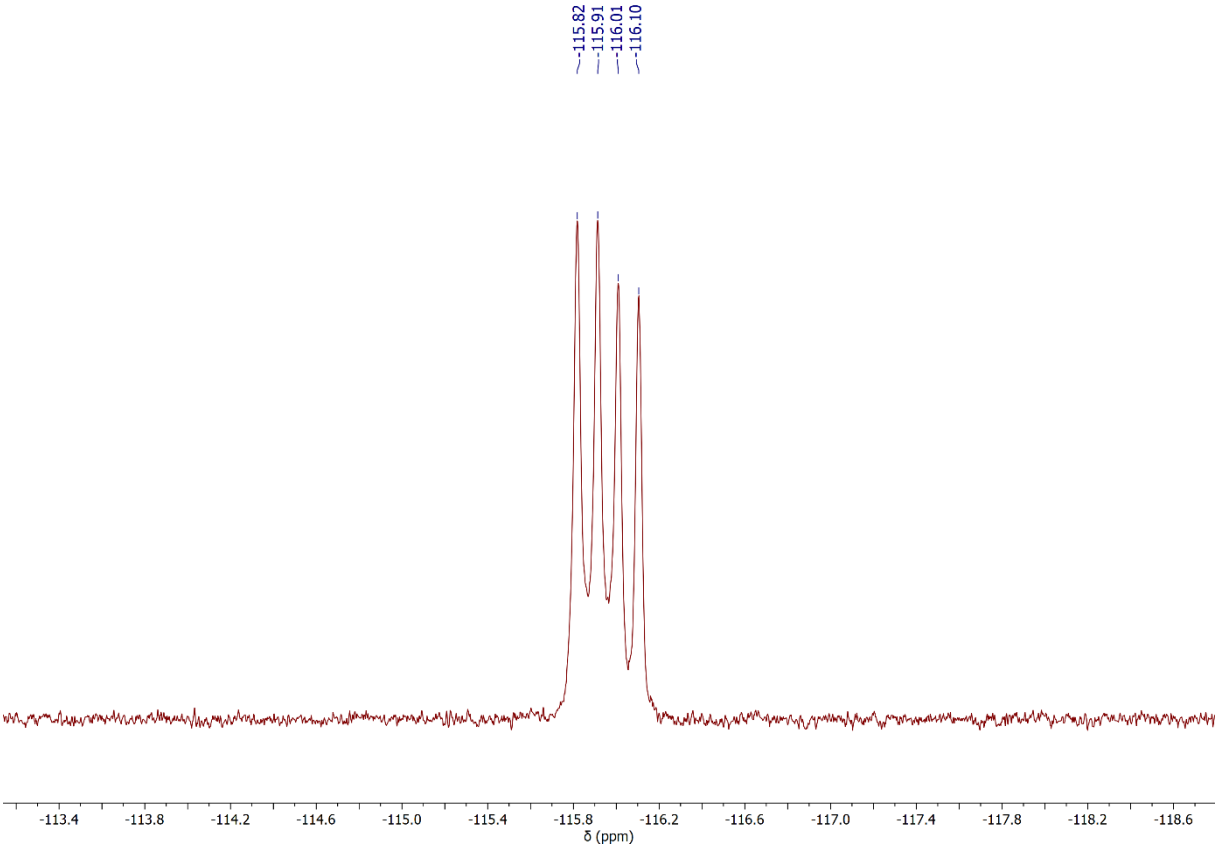


Figure S11: ^{19}F NMR spectrum of **2** in tol-d_8.

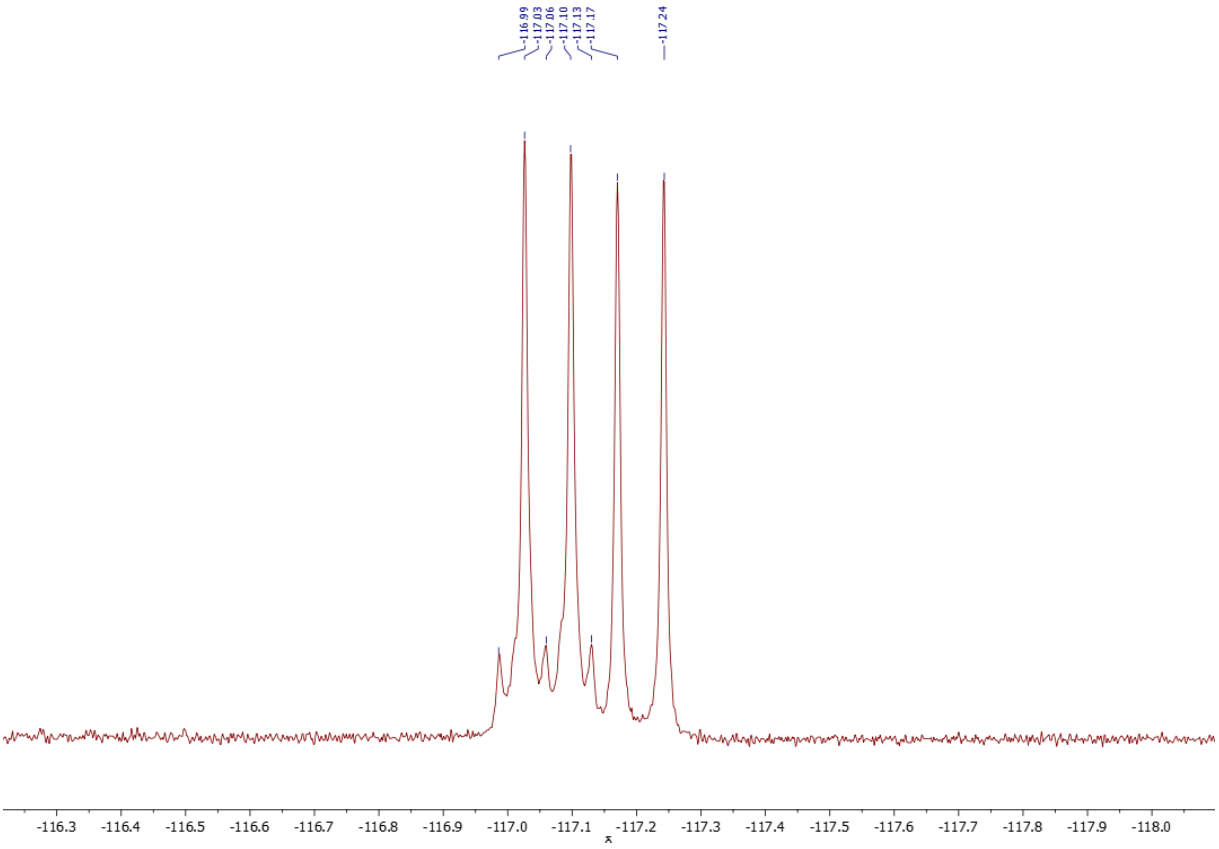


Figure S12: $^{19}F\{^{1}H\}$ NMR spectrum of **2** in THF-d_8.

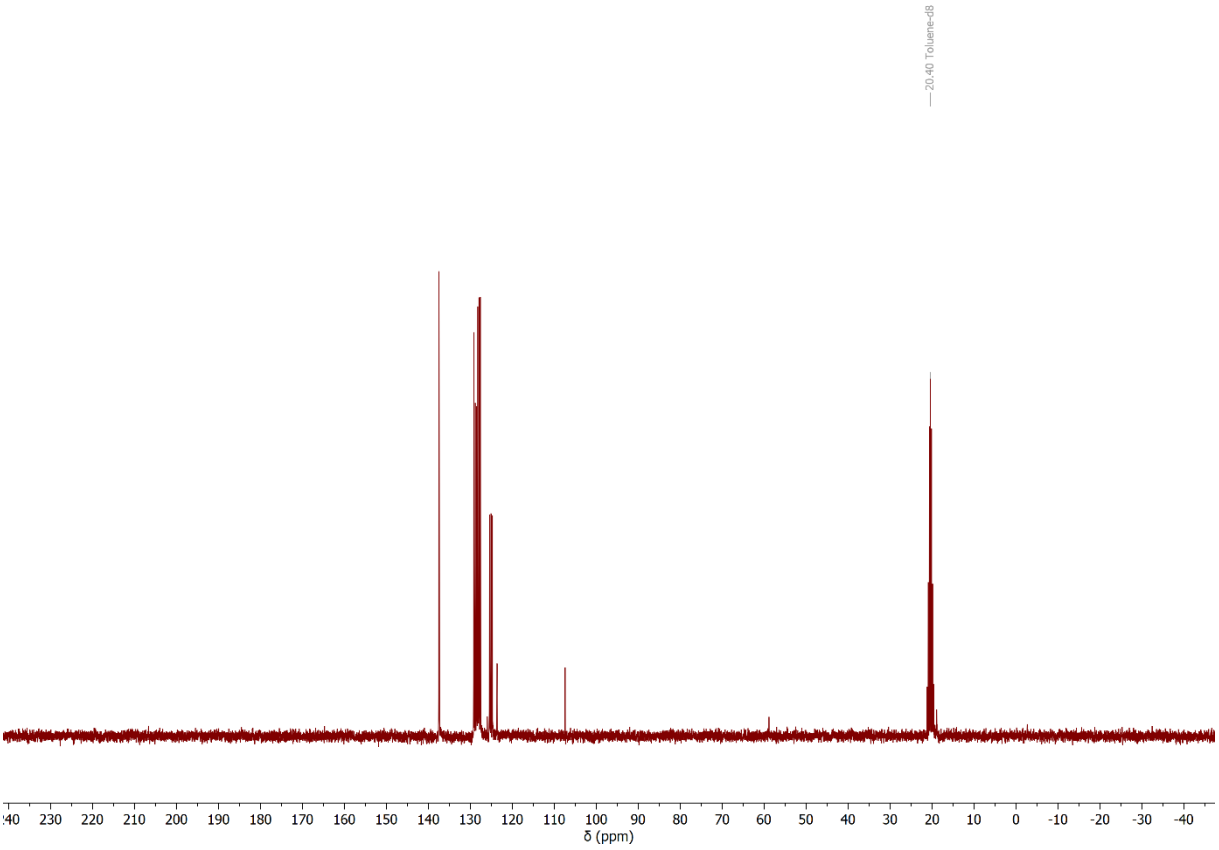


Figure S13: $^{13}C\{^{1}H\}$ NMR spectrum of **2** in tol-d_8.

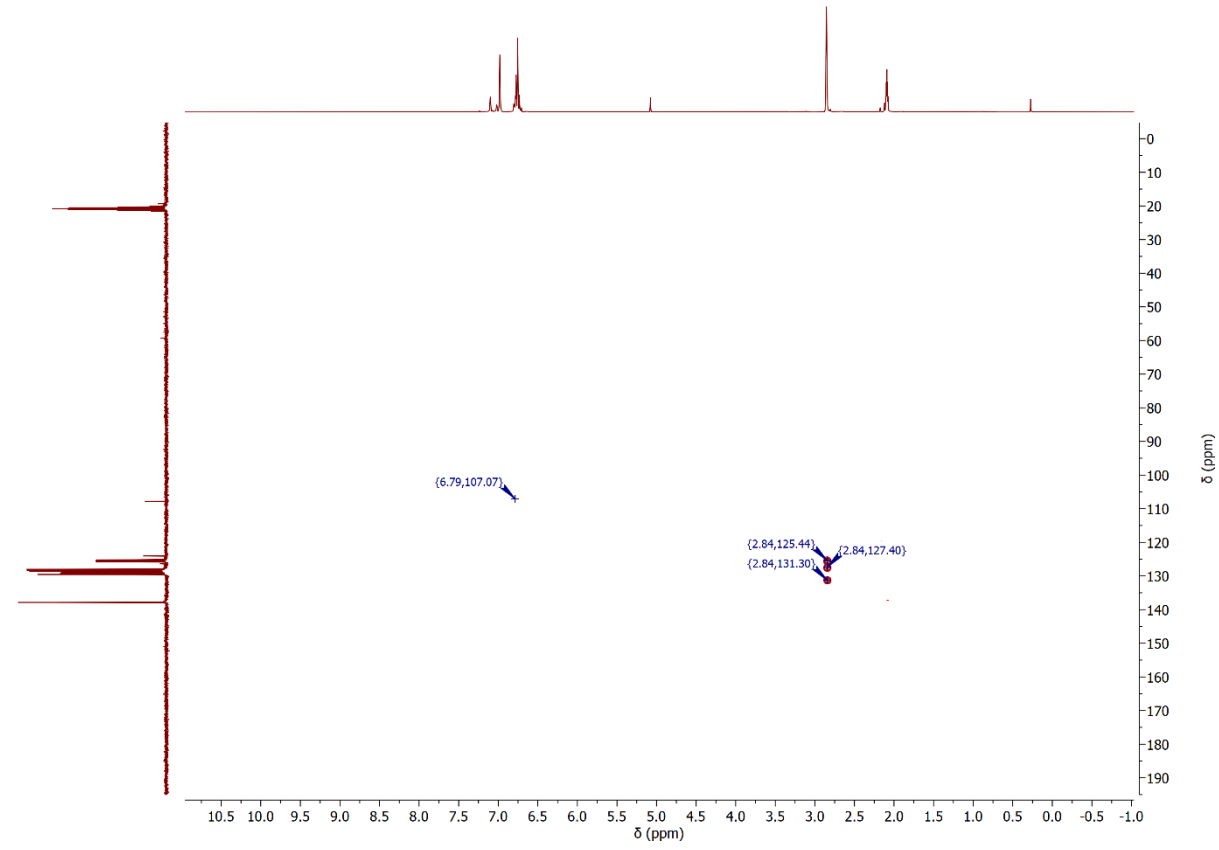


Figure S14: ^{1}H, ^{13}C HMBC NMR spectrum of **2** in tol-d_8.

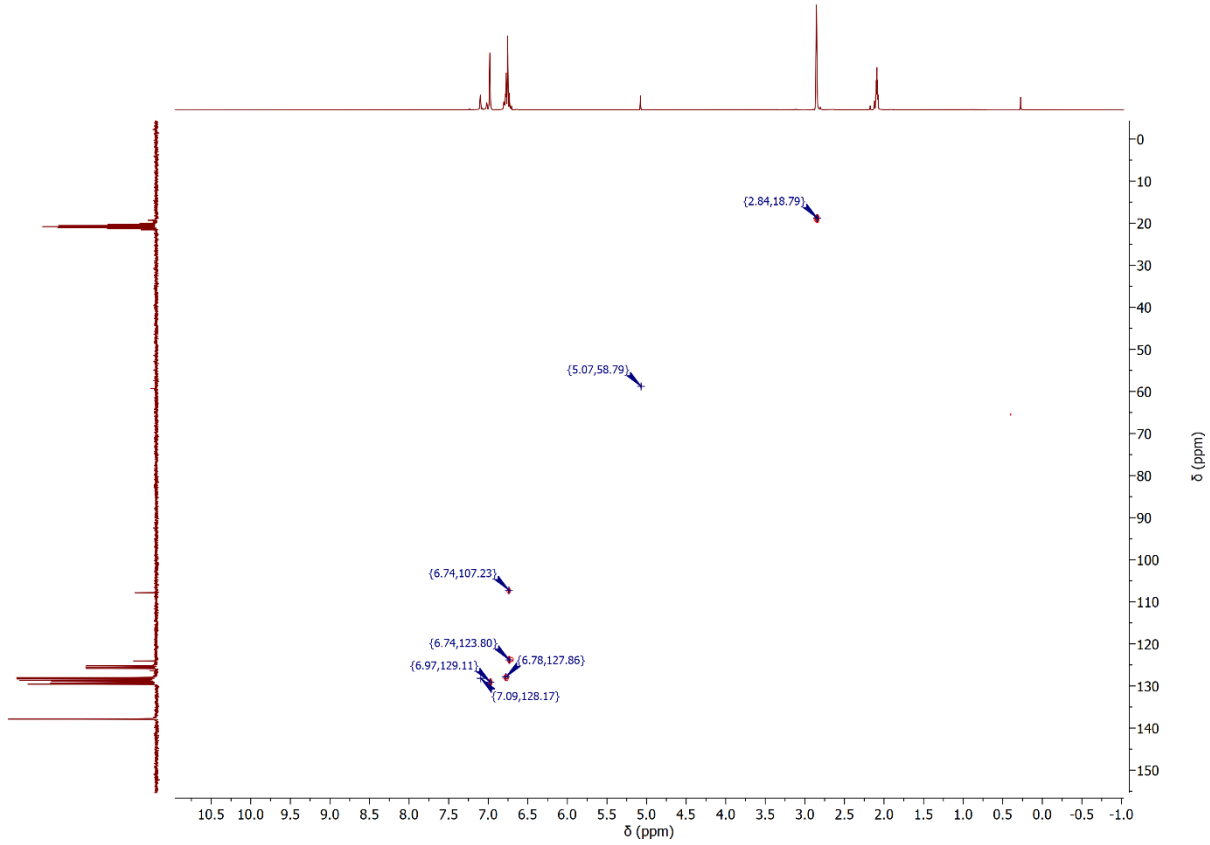


Figure S15: ^{1}H, ^{13}C HSQC NMR spectrum of **2** in tol-d_8.

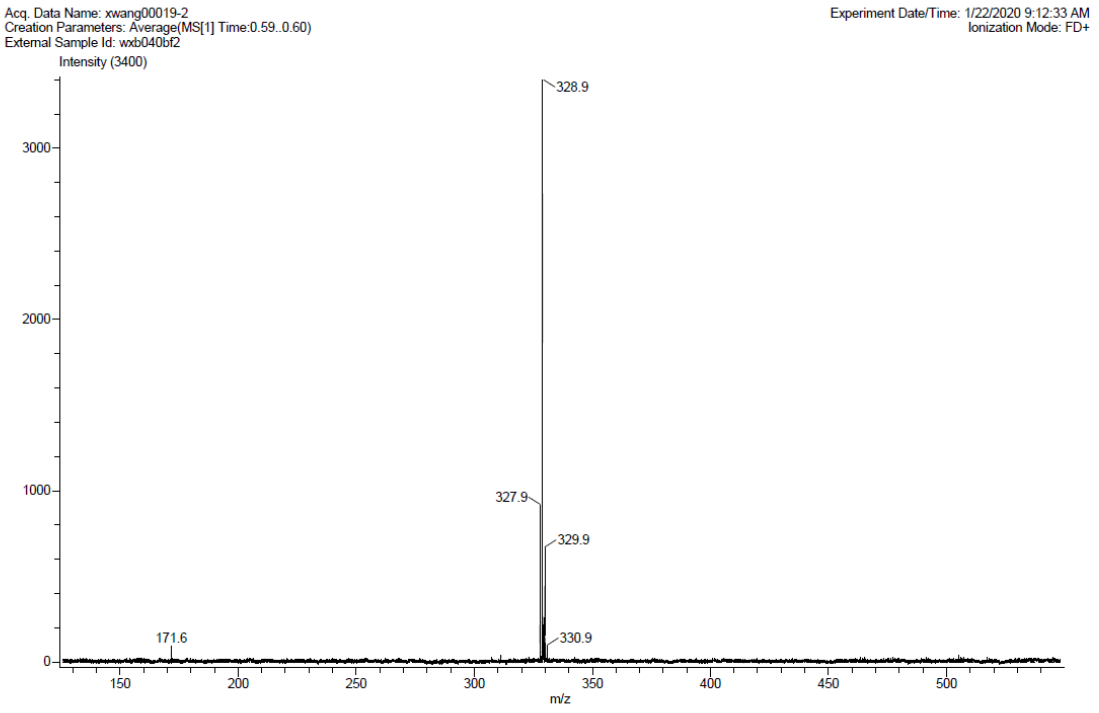


Figure S16: Mass spectrum (LIFDI[+], toluene) of **2**.

Compound 3

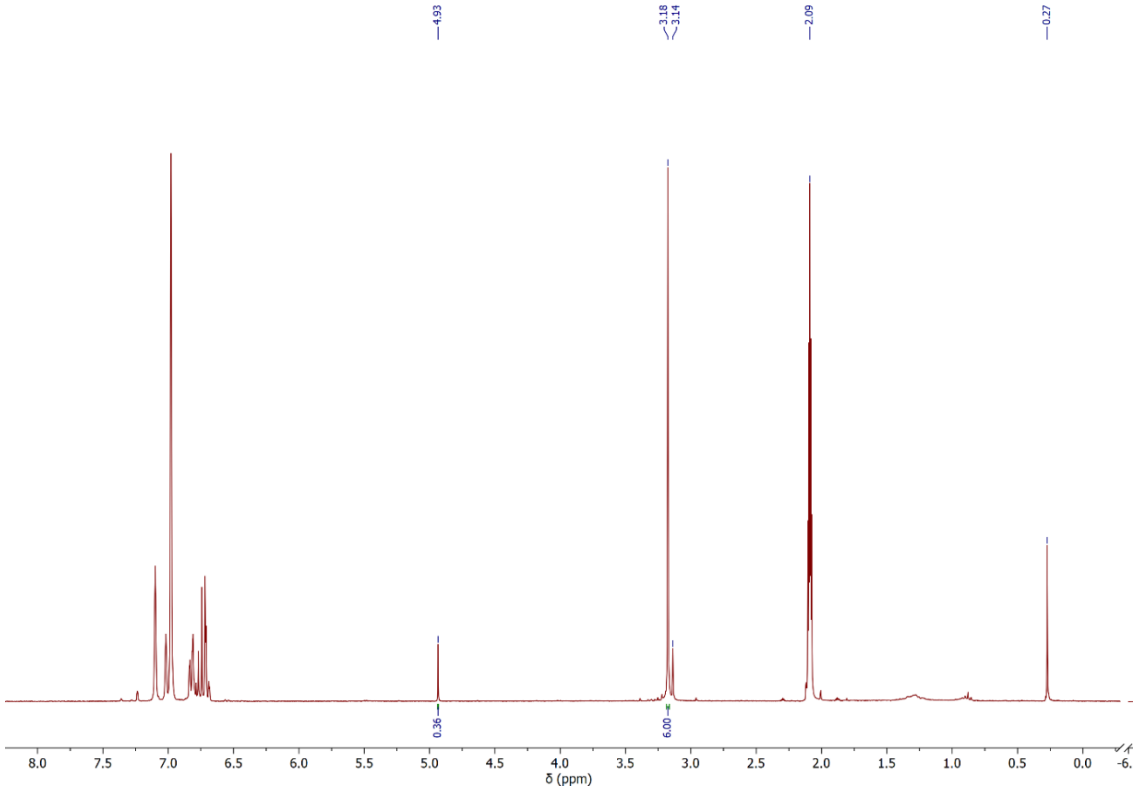


Figure S17: ^{1}H NMR spectrum of **3** in tol-d_8.

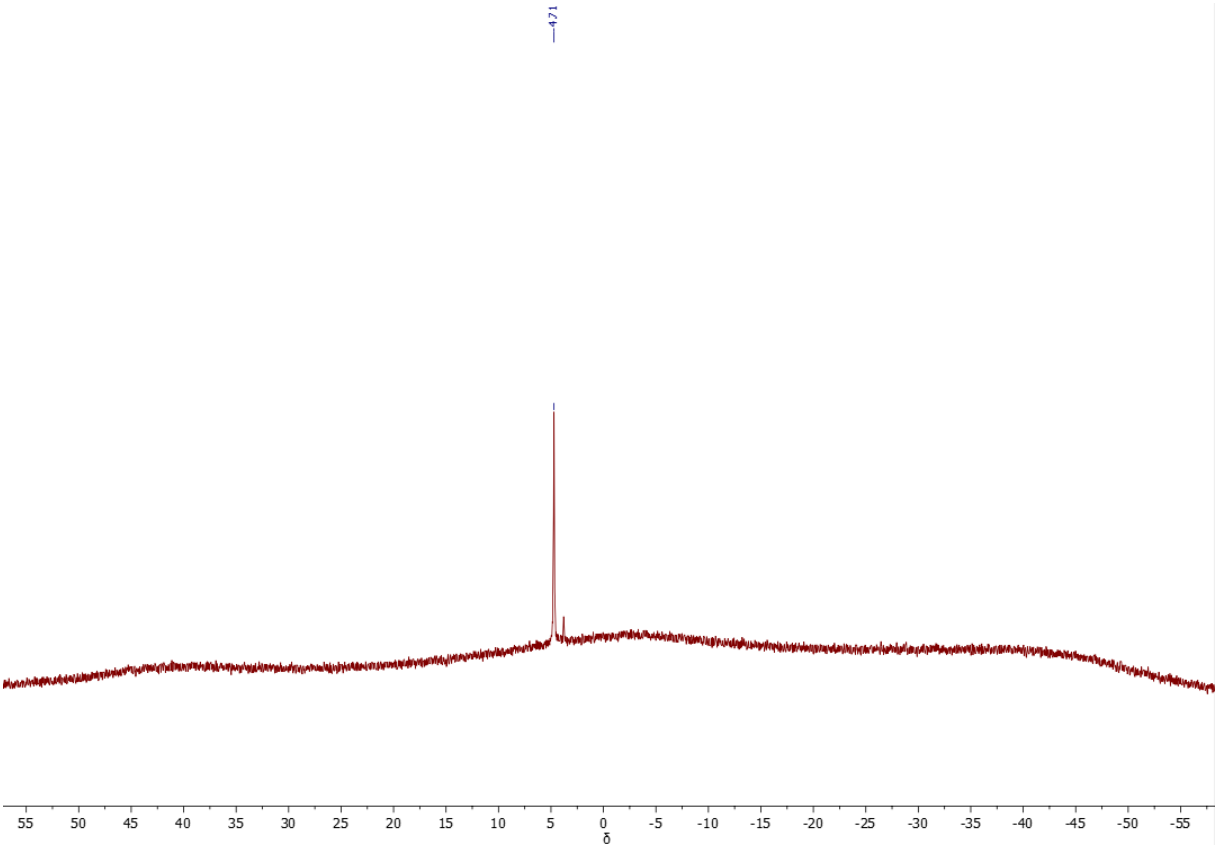


Figure S18: ^{11}B NMR spectrum of **3** in tol-d_8.

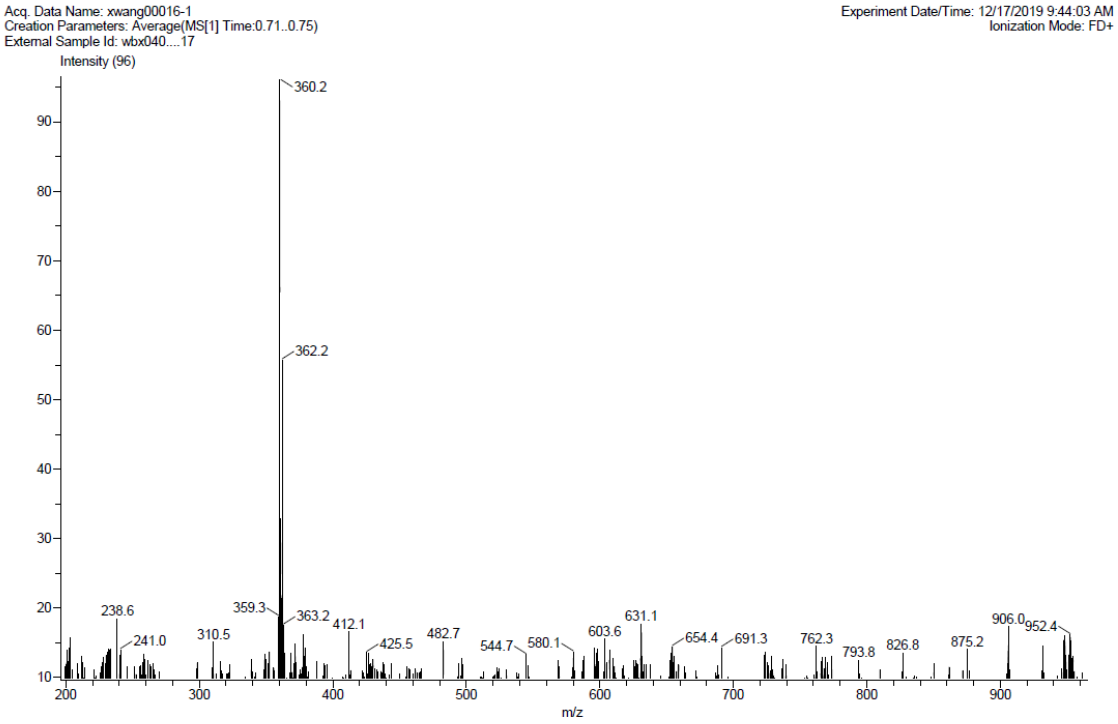


Figure S19: Mass spectrum (LIFDI[+], toluene) of **3** (1 of 2).

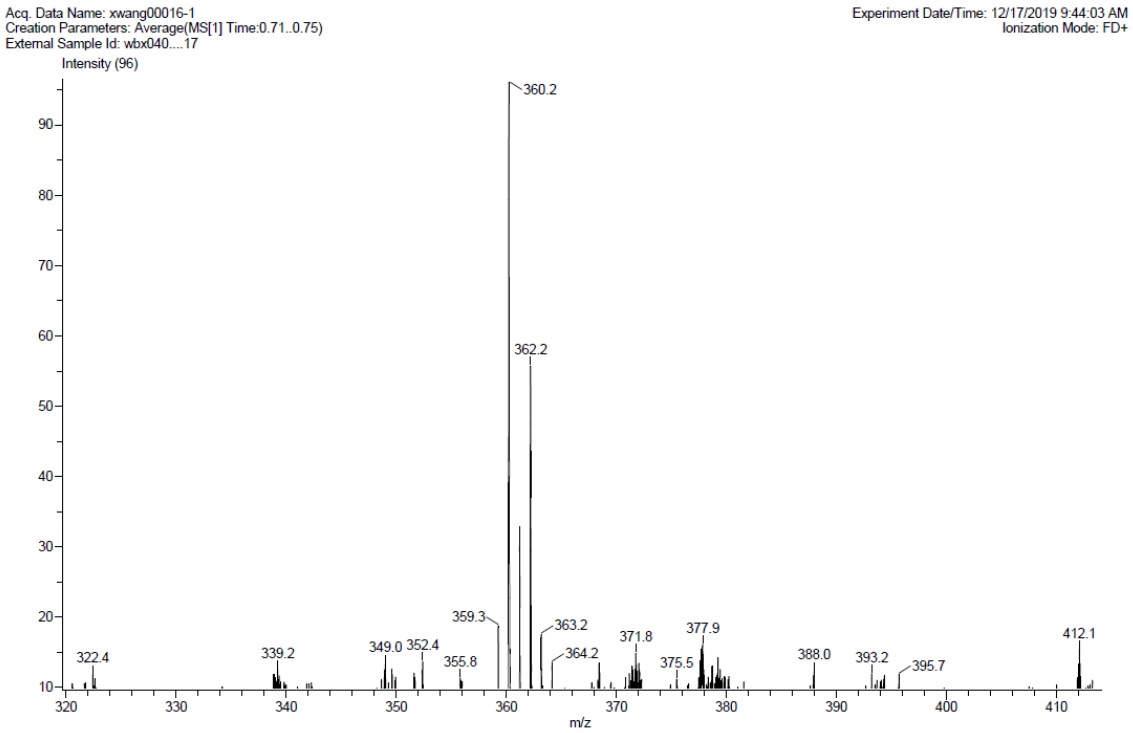


Figure S20*:* Mass spectrum (LIFDI[+], toluene) of **3** (2 of 2).

Compound 4

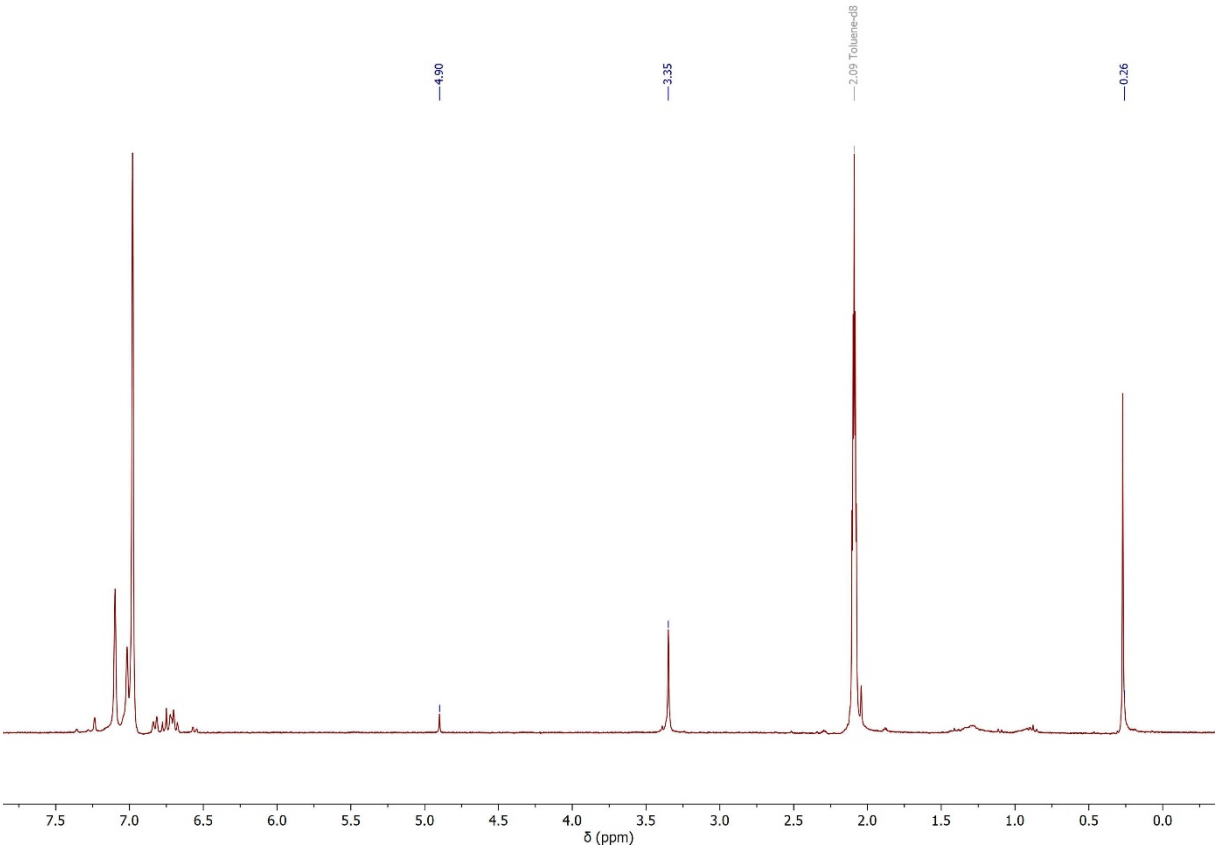


Figure S21: ^{1}H NMR spectrum of **4** in tol-d_8.

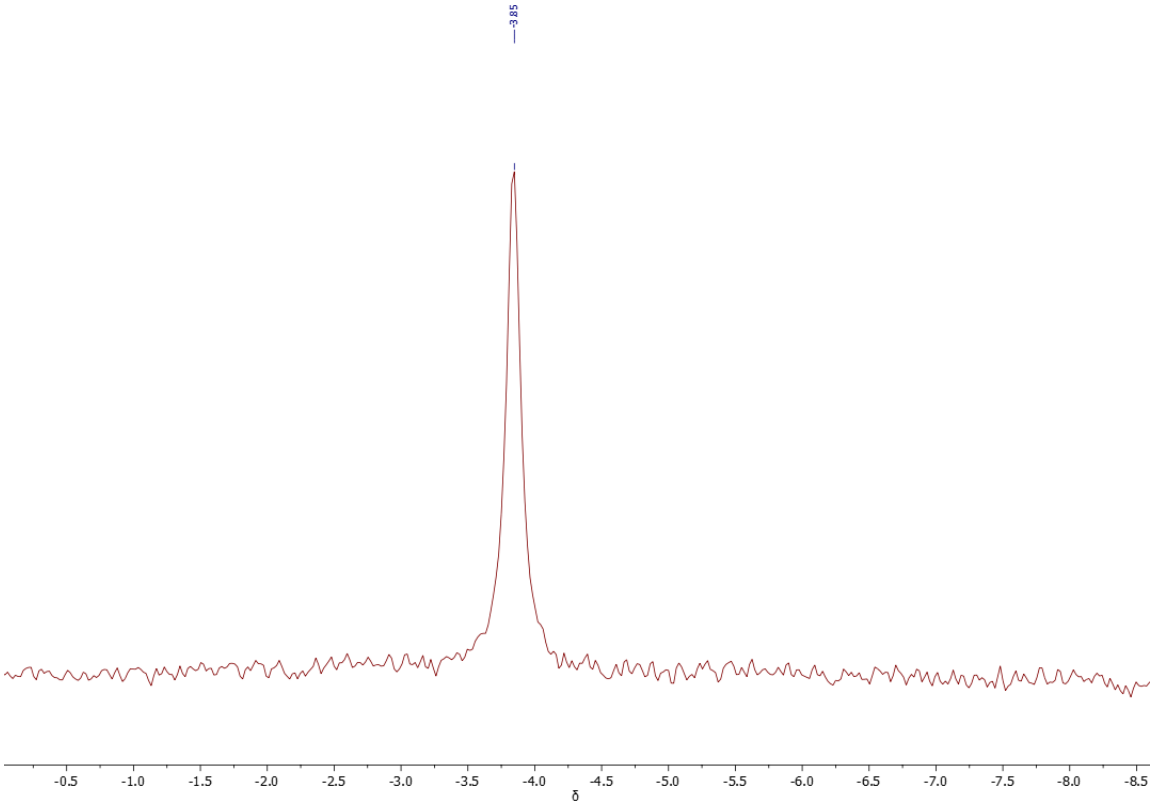


Figure S22: ^{11}B NMR spectrum of **4** in THF-d_8.

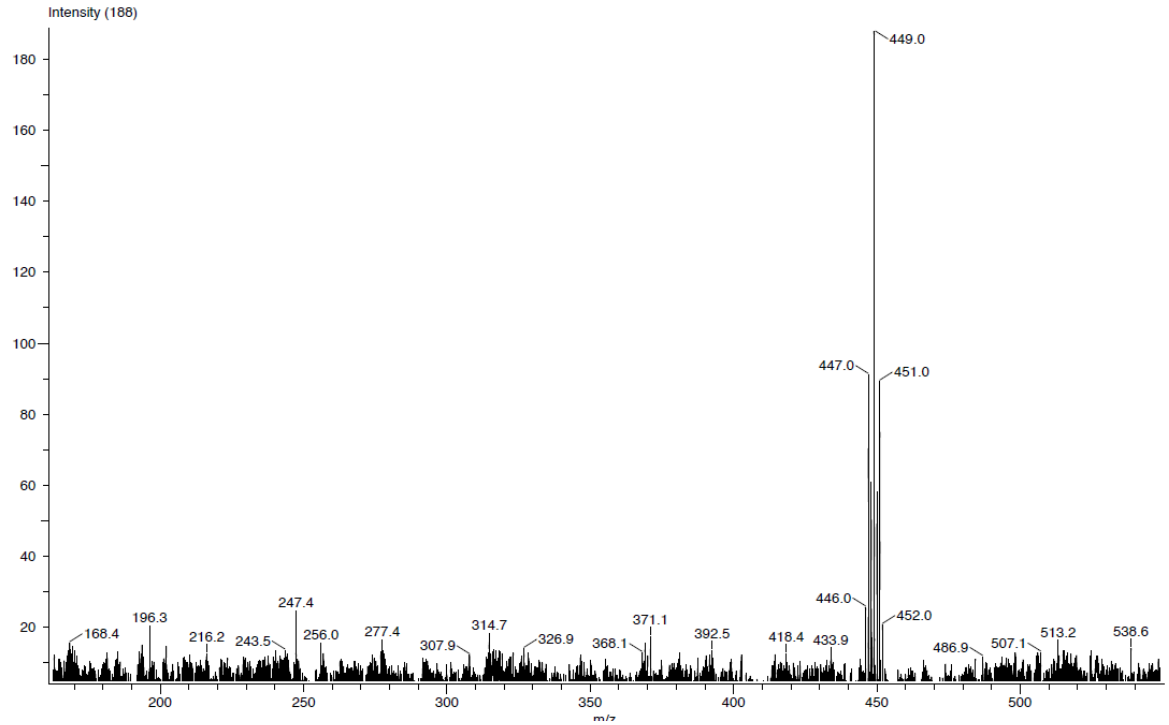


Figure S23: Mass spectrum (LIFDI[+], toluene) of **4**.

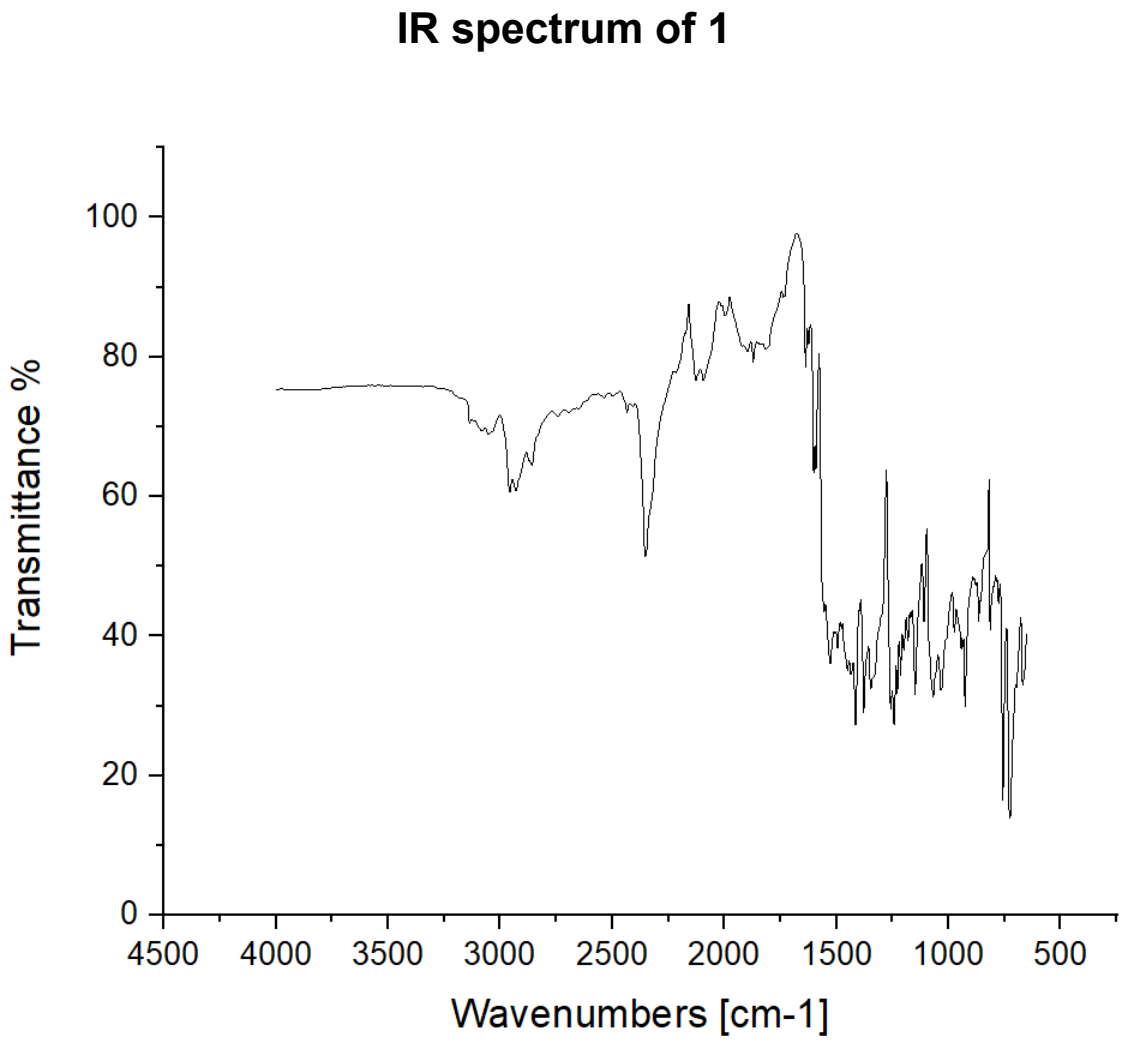


Figure S24: ATR−IR spectra (solid, 650–4000 cm^{-1}) of compound **1**.

Crstallographic data

General Data Acquisition and Processing

The diffraction data were collected using Incoatec Mo Microsource radiation and a Bruker APEX II detector. The data were integrated with SAINT.[1] A multi-scan absorption correction was applied using SADABS[2] and TWINABS[3](**4**). The structures were solved by SHELXT[4] and refined on F^2 using SHELXL[5] in the graphical user interface ShelXle.[6] All hydrogen atoms were placed according to geometrical criteria and refined with a riding model except those mentioned below. An overview of the crystallographic data for **1**, **2**, **3**, **4** can be found in **Table S1** while individual bond lengths and angles are listed in **Table S2-S5**, respectively.

Table S1: Crystal data and structure refinement for compound **1**, **2**, **3**, **4** at 100(2)K.

Compound	**1**	**2**	**3**	**4**
CCDC	2333148	2333149	2333150	2333151
Empirical Formula	$C_{17}H_{15}BN_2O_2$	$C_{17}H_{13}BF_2N_2O_2$	$C_{17}H_{13}BCl_2N_2O_2$	$C_{17}H_{13}BBr_2N_2O_2$
Formula weight	290.12	326.10	359.00	447.92
***T* [K]**	100(2)	100(2)	100(2)	100(2)
***λ* [Å]**	0.71073	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic
Space group	*P*nma	*P*nma	$P2_1/m$	$P2_1$
***a* [Å]**	15.336(3)	15.378(3)	7.935(2)	6.877(2)
***b* [Å]**	6.707(2)	6.800(2)	6.703(2)	14.447(3)
***c* [Å]**	13.506(2)	13.574(3)	14.407(3)	7.970(2)
***β* [°]**	-	-	94.76(2)	93.81(2)
***V* [Å^3]**	1389.2(5)	1419.4(6)	763.6(3)	790.1(3)
Z	4	4	2	2
***μ* [mm^{-1}]**	0.091	0.118	0.437	5.142
***F*(000)**	608	672	368	440
Crystal size [mm]	0.708x0.254x0.163	0.412x0.094x0.046	0.243x0.155x0.1	0.279x0.263x0.127
***Θ* max [°]**	2.009 to 27.126	2.001 to 27.114	2.576 to 27.144	2.561 to 29.749
Reflections collected	38676	34861	17901	21013
Independent reflections	1678	1707	1843	4055
R_{int}	0.0238	0.0332	0.0266	0.0590
Data/restraints/parameters	1678/0/139	1707/0/144	1843/0/145	4055/1/226
GooF	1.046	1.060	1.032	1.057

***R*1 [*I* >2*σ*(*I*)]**	0.0348	0.0336	0.0262	0.0354
***wR*2 [all data]**	0.0992	0.0944	0.0716	0.0686
Extinction coefficient	-	-	0.015(2)	
ρ_{max}/ρ_{min} [e A^{-3}]	0.317/-0.232	0.367/-0.285	0.368/-0.243	0.827/-0.748
Shape and color	yellow needle	yellow needle	colorless needle	colorless plate

[a]$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$

Crystal structure of 1

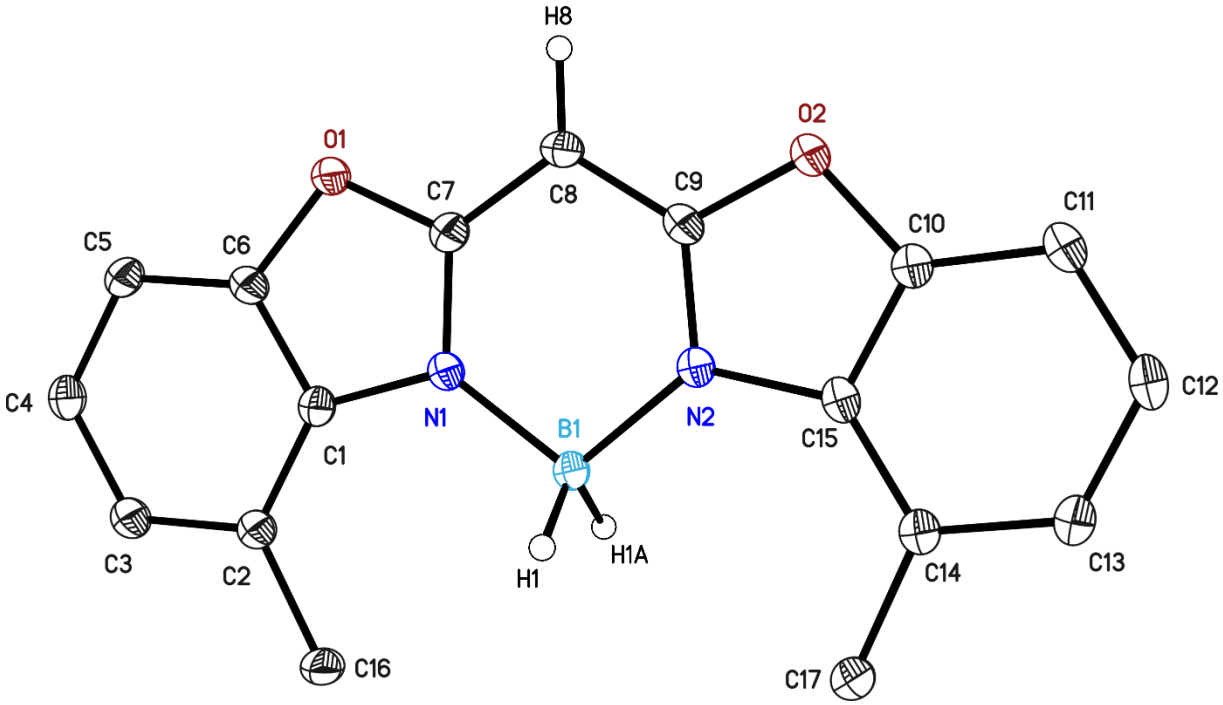


Figure S25: Molecular structure of compound **1**. Anisotropic displacement parameters are depicted at the 50% probability level. All hydrogen atoms are omitted for clarity except for the bridging (methylene) and boron dihydride. The hydrogens attached to boron were refined freely.

Table S2: Bond lengths [Å] and angles [°] for **1**.

O(1)-C(7)	1.3548(16)	C(8)-C(9)	1.3901(19)
O(1)-C(6)	1.3887(15)	C(10)-C(11)	1.3788(18)
O(2)-C(9)	1.3609(16)	C(10)-C(15)	1.3905(18)
O(2)-C(10)	1.3892(16)	C(11)-C(12)	1.399(2)
N(1)-C(7)	1.3373(17)	C(12)-C(13)	1.3977(19)
N(1)-C(1)	1.4069(16)	C(13)-C(14)	1.4008(18)
N(1)-B(1)	1.5770(18)	C(14)-C(15)	1.3985(19)
N(2)-C(9)	1.3381(17)	C(14)-C(17)	1.5055(19)
N(2)-C(15)	1.4062(16)	B(1)-H(1)	1.118(13)
N(2)-B(1)	1.5824(18)		
C(1)-C(6)	1.3912(18)	C(7)-O(1)-C(6)	105.63(10)
C(1)-C(2)	1.4014(18)	C(9)-O(2)-C(10)	105.50(10)
C(2)-C(3)	1.3992(18)	C(7)-N(1)-C(1)	106.69(11)
C(2)-C(16)	1.5066(18)	C(7)-N(1)-B(1)	124.33(11)
C(3)-C(4)	1.3986(19)	C(1)-N(1)-B(1)	128.98(11)
C(4)-C(5)	1.3921(19)	C(9)-N(2)-C(15)	106.80(11)
C(5)-C(6)	1.3788(18)	C(9)-N(2)-B(1)	124.00(11)
C(7)-C(8)	1.3883(18)	C(15)-N(2)-B(1)	129.20(10)

C(6)-C(1)-C(2)	120.53(12)	O(2)-C(9)-C(8)	121.54(12)
C(6)-C(1)-N(1)	106.46(11)	C(11)-C(10)-O(2)	126.08(12)
C(2)-C(1)-N(1)	133.01(12)	C(11)-C(10)-C(15)	125.01(13)
C(3)-C(2)-C(1)	115.21(12)	O(2)-C(10)-C(15)	108.91(11)
C(3)-C(2)-C(16)	120.61(12)	C(10)-C(11)-C(12)	114.93(13)
C(1)-C(2)-C(16)	124.18(13)	C(13)-C(12)-C(11)	121.10(13)
C(4)-C(3)-C(2)	123.29(13)	C(12)-C(13)-C(14)	123.24(13)
C(5)-C(4)-C(3)	121.10(13)	C(15)-C(14)-C(13)	115.44(12)
C(6)-C(5)-C(4)	115.34(12)	C(15)-C(14)-C(17)	124.35(12)
C(5)-C(6)-O(1)	126.68(12)	C(13)-C(14)-C(17)	120.21(13)
C(5)-C(6)-C(1)	124.53(12)	C(10)-C(15)-C(14)	120.29(12)
O(1)-C(6)-C(1)	108.79(11)	C(10)-C(15)-N(2)	106.53(11)
N(1)-C(7)-O(1)	112.43(11)	C(14)-C(15)-N(2)	133.18(12)
N(1)-C(7)-C(8)	126.09(12)	H(1)-B(1)-N(1)	110.5(6)
O(1)-C(7)-C(8)	121.48(12)	H(1)-B(1)-N(2)	109.9(6)
C(7)-C(8)-C(9)	114.69(12)	N(1)-B(1)-N(2)	104.71(10)
N(2)-C(9)-O(2)	112.27(12)	H(1)-B(1)-H(1)#1	111.3(12)
N(2)-C(9)-C(8)	126.19(12)		

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z

Crystal structure of 2

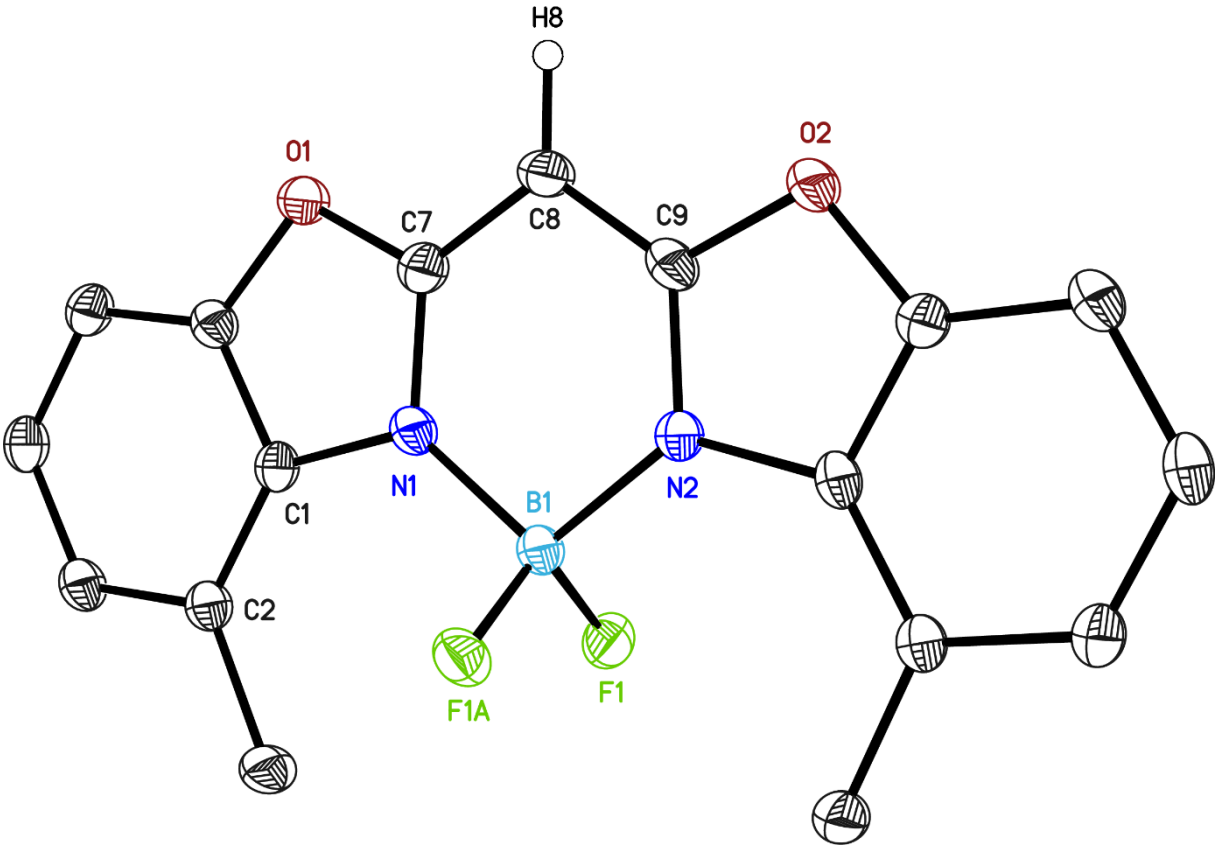


Figure S26: Molecular structure of compound **2**. Anisotropic displacement parameters are depicted at the 50% probability level. All hydrogen atoms are omitted for clarity except for the bridging (methylene).

Table S3: Bond lengths [Å] and angles [°] for **2**.

F(1)-B(1)	1.3853(13)	C(4)-C(5)	1.388(3)
B(1)-N(1)	1.558(2)	C(5)-C(6)	1.378(2)
B(1)-N(2)	1.569(2)	C(7)-C(8)	1.388(2)
O(1)-C(7)	1.349(2)	C(9)-C(8)	1.384(3)
O(1)-C(6)	1.391(2)	C(10)-C(11)	1.378(2)
N(1)-C(7)	1.341(2)	C(10)-C(15)	1.387(2)
N(1)-C(1)	1.417(2)	C(11)-C(12)	1.398(3)
C(1)-C(6)	1.390(2)	C(12)-C(13)	1.394(3)
C(1)-C(2)	1.402(2)	C(13)-C(14)	1.402(2)
N(2)-C(9)	1.346(2)	C(14)-C(15)	1.399(2)
N(2)-C(15)	1.418(2)	C(14)-C(17)	1.501(2)
O(2)-C(9)	1.356(2)		
O(2)-C(10)	1.393(2)	F(1)#1-B(1)-F(1)	110.15(14)
C(2)-C(3)	1.398(2)	F(1)-B(1)-N(1)	109.86(10)
C(2)-C(16)	1.504(2)	F(1)-B(1)-N(2)	110.44(10)
C(3)-C(4)	1.398(3)	N(1)-B(1)-N(2)	106.01(13)

C(7)-O(1)-C(6)	105.86(13)	N(1)-C(7)-O(1)	112.50(15)
C(7)-N(1)-C(1)	106.53(14)	N(1)-C(7)-C(8)	125.71(16)
C(7)-N(1)-B(1)	123.99(14)	O(1)-C(7)-C(8)	121.79(16)
C(1)-N(1)-B(1)	129.49(14)	N(2)-C(9)-O(2)	112.18(15)
C(6)-C(1)-C(2)	120.44(16)	N(2)-C(9)-C(8)	126.15(16)
C(6)-C(1)-N(1)	106.17(15)	O(2)-C(9)-C(8)	121.66(16)
C(2)-C(1)-N(1)	133.39(16)	C(9)-C(8)-C(7)	114.95(16)
C(9)-N(2)-C(15)	106.41(14)	C(11)-C(10)-C(15)	125.38(17)
C(9)-N(2)-B(1)	123.19(14)	C(11)-C(10)-O(2)	125.79(16)
C(15)-N(2)-B(1)	130.40(14)	C(15)-C(10)-O(2)	108.83(15)
C(9)-O(2)-C(10)	105.94(13)	C(10)-C(11)-C(12)	114.63(16)
C(3)-C(2)-C(1)	114.94(16)	C(13)-C(12)-C(11)	121.17(16)
C(3)-C(2)-C(16)	120.59(16)	C(12)-C(13)-C(14)	123.44(17)
C(1)-C(2)-C(16)	124.47(16)	C(15)-C(14)-C(13)	115.17(16)
C(4)-C(3)-C(2)	123.51(17)	C(15)-C(14)-C(17)	124.30(15)
C(5)-C(4)-C(3)	121.20(17)	C(13)-C(14)-C(17)	120.52(16)
C(6)-C(5)-C(4)	115.07(16)	C(10)-C(15)-C(14)	120.21(16)
C(5)-C(6)-C(1)	124.83(17)	C(10)-C(15)-N(2)	106.65(15)
C(5)-C(6)-O(1)	126.23(16)	C(14)-C(15)-N(2)	133.14(15)
C(1)-C(6)-O(1)	108.94(15)		

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z

Crystal structure of 3

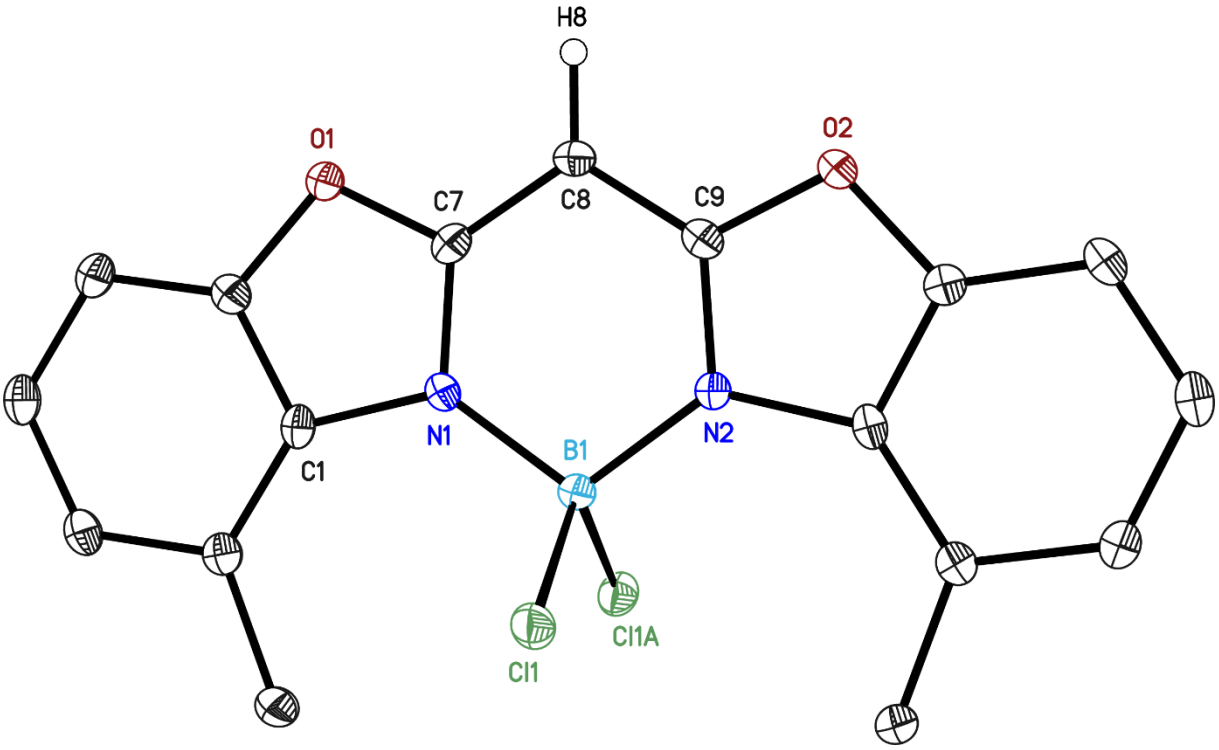


Figure S27: Molecular structure of complex **3**. Anisotropic displacement parameters are depicted at the 50% probability level. All hydrogen atoms are omitted for clarity except for the bridging (methylene).

Table S4: Bond lengths [Å] and angles [°] for **3**.

C(1)-C(6)	1.390(2)	C(11)-C(12)	1.389(2)
C(1)-C(2)	1.405(2)	C(12)-C(13)	1.390(2)
C(1)-N(1)	1.430(2)	C(13)-C(14)	1.404(2)
C(2)-C(3)	1.409(2)	C(14)-C(15)	1.402(2)
C(2)-C(17)	1.503(2)	C(14)-C(16)	1.504(2)
C(3)-C(4)	1.392(3)	C(15)-N(2)	1.429(2)
C(4)-C(5)	1.390(2)	B(1)-N(1)	1.542(2)
C(5)-C(6)	1.372(2)	B(1)-N(2)	1.542(2)
C(6)-O(1)	1.384(2)	B(1)-Cl(1)	1.8692(11)
C(7)-O(1)	1.345(2)		
C(7)-N(1)	1.349(2)	C(6)-C(1)-C(2)	119.55(15)
C(7)-C(8)	1.377(2)	C(6)-C(1)-N(1)	105.21(14)
C(8)-C(9)	1.382(2)	C(2)-C(1)-N(1)	135.24(15)
C(9)-O(2)	1.342(2)	C(1)-C(2)-C(3)	114.87(15)
C(9)-N(2)	1.349(2)	C(1)-C(2)-C(17)	126.93(15)
C(10)-C(11)	1.378(2)	C(3)-C(2)-C(17)	118.20(15)
C(10)-O(2)	1.385(2)	C(4)-C(3)-C(2)	123.84(16)
C(10)-C(15)	1.396(2)	C(5)-C(4)-C(3)	120.84(16)

C(6)-C(5)-C(4)	115.02(16)	C(15)-C(14)-C(16)	127.36(15)
C(5)-C(6)-O(1)	124.24(15)	C(13)-C(14)-C(16)	117.81(15)
C(5)-C(6)-C(1)	125.88(16)	C(10)-C(15)-C(14)	119.62(15)
O(1)-C(6)-C(1)	109.88(14)	C(10)-C(15)-N(2)	105.39(14)
O(1)-C(7)-N(1)	112.25(14)	C(14)-C(15)-N(2)	134.99(15)
O(1)-C(7)-C(8)	121.08(15)	N(1)-B(1)-N(2)	108.37(13)
N(1)-C(7)-C(8)	126.67(15)	N(1)-B(1)-Cl(1)	109.37(7)
C(7)-C(8)-C(9)	114.77(15)	N(2)-B(1)-Cl(1)	109.10(7)
O(2)-C(9)-N(2)	112.44(14)	Cl(1)#1-B(1)-Cl(1)	111.48(9)
O(2)-C(9)-C(8)	121.46(15)	C(7)-N(1)-C(1)	106.61(13)
N(2)-C(9)-C(8)	126.10(15)	C(7)-N(1)-B(1)	121.83(13)
C(11)-C(10)-O(2)	124.81(15)	C(1)-N(1)-B(1)	131.56(14)
C(11)-C(10)-C(15)	125.75(16)	C(9)-N(2)-C(15)	106.45(13)
O(2)-C(10)-C(15)	109.43(14)	C(9)-N(2)-B(1)	122.27(13)
C(10)-C(11)-C(12)	114.57(16)	C(15)-N(2)-B(1)	131.29(13)
C(11)-C(12)-C(13)	121.20(16)	C(7)-O(1)-C(6)	106.05(13)
C(12)-C(13)-C(14)	124.04(16)	C(9)-O(2)-C(10)	106.29(13)
C(15)-C(14)-C(13)	114.83(15)		

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z

Crystal structure of 4

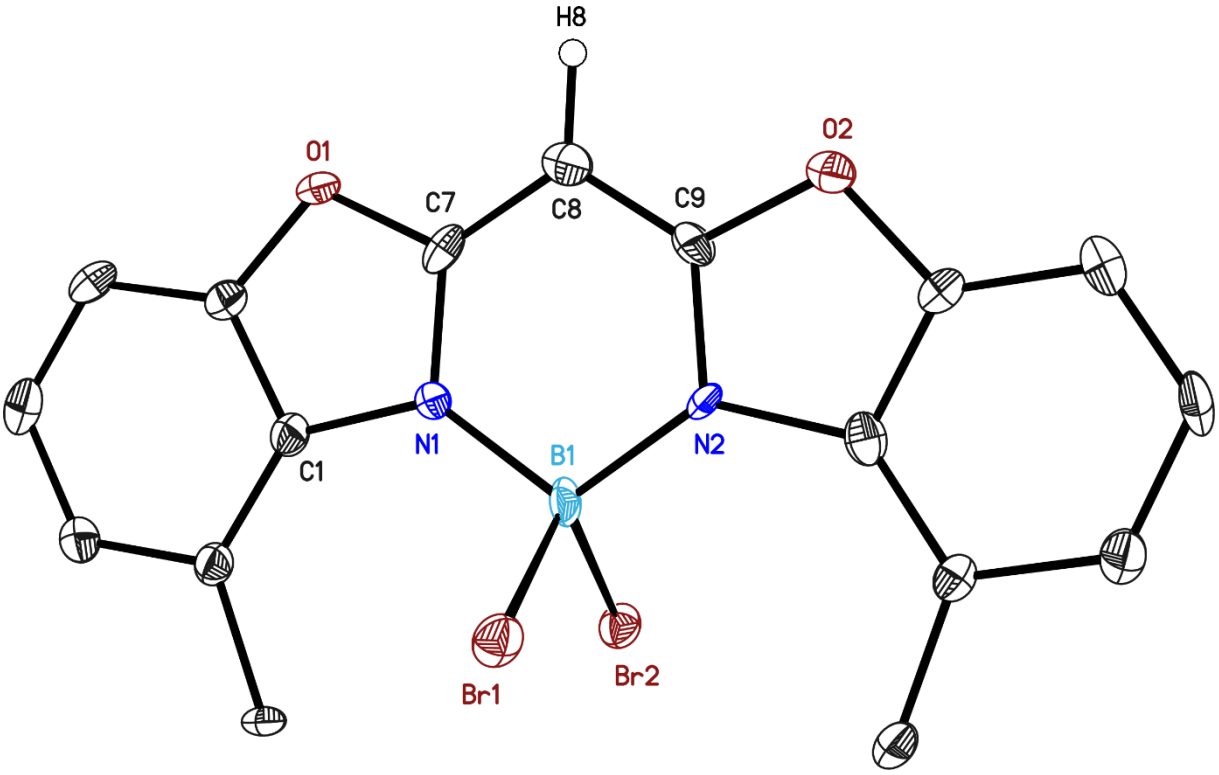


Figure S28: Molecular structure of complex **4**. Anisotropic displacement parameters are depicted at the 50% probability level. All hydrogen atoms are omitted for clarity except for the bridging (methylene). The data were collected on a non-merohedrally twinned crystal with the twin law 1 0 0 0 -1 0 -0.154 0 -1. Additional inversion twinning was taken into account. The fractional contribution refined to nearly identical values: 0.255(17), 0.252(10) and 0.253(17).

Table S5: Bond lengths [Å] and angles [°] for **4**.

Br(1)-B(1)	2.046(7)	B(1)-N(2)	1.538(8)
C(1)-C(2)	1.406(8)	N(2)-C(9)	1.363(8)
C(1)-C(6)	1.410(8)	N(2)-C(15)	1.447(8)
C(1)-C(16)	1.510(8)	C(12)-C(13)	1.397(9)
O(1)-C(7)	1.348(7)	C(5)-C(4)	1.382(9)
O(1)-C(5)	1.362(8)	C(5)-C(6)	1.393(8)
Br(2)-B(1)	2.028(6)	C(14)-C(15)	1.391(9)
C(2)-C(3)	1.384(8)	C(14)-C(13)	1.404(8)
O(2)-C(9)	1.348(7)	C(14)-C(17)	1.507(8)
O(2)-C(10)	1.394(8)	C(4)-C(3)	1.381(9)
C(11)-C(10)	1.357(9)	C(15)-C(10)	1.404(9)
C(11)-C(12)	1.372(9)	C(8)-C(9)	1.362(9)
N(1)-C(7)	1.356(8)	C(8)-C(7)	1.365(9)
N(1)-C(6)	1.431(8)		
N(1)-B(1)	1.537(9)	C(2)-C(1)-C(6)	114.5(6)

C(2)-C(1)-C(16)	117.5(5)	C(15)-C(14)-C(13)	114.8(6)
C(6)-C(1)-C(16)	128.0(5)	C(15)-C(14)-C(17)	127.4(6)
C(7)-O(1)-C(5)	107.7(5)	C(13)-C(14)-C(17)	117.7(6)
C(3)-C(2)-C(1)	124.3(6)	C(3)-C(4)-C(5)	115.2(6)
C(9)-O(2)-C(10)	106.5(5)	C(4)-C(3)-C(2)	121.1(7)
C(10)-C(11)-C(12)	115.3(6)	C(14)-C(15)-C(10)	119.6(6)
C(7)-N(1)-C(6)	106.8(5)	C(14)-C(15)-N(2)	135.9(6)
C(7)-N(1)-B(1)	121.0(5)	C(10)-C(15)-N(2)	104.5(5)
C(6)-N(1)-B(1)	132.2(5)	C(9)-C(8)-C(7)	115.5(5)
N(1)-B(1)-N(2)	109.5(4)	O(1)-C(7)-N(1)	110.8(5)
N(1)-B(1)-Br(2)	109.0(4)	O(1)-C(7)-C(8)	122.6(5)
N(2)-B(1)-Br(2)	109.2(4)	N(1)-C(7)-C(8)	126.6(6)
N(1)-B(1)-Br(1)	108.9(4)	C(5)-C(6)-C(1)	119.8(6)
N(2)-B(1)-Br(1)	108.4(4)	C(5)-C(6)-N(1)	105.1(5)
Br(2)-B(1)-Br(1)	111.8(3)	C(1)-C(6)-N(1)	135.0(5)
C(9)-N(2)-C(15)	107.0(5)	C(11)-C(10)-O(2)	124.4(6)
C(9)-N(2)-B(1)	120.9(5)	C(11)-C(10)-C(15)	125.5(6)
C(15)-N(2)-B(1)	132.1(5)	O(2)-C(10)-C(15)	110.1(6)
C(11)-C(12)-C(13)	121.2(7)	O(2)-C(9)-C(8)	121.6(5)
O(1)-C(5)-C(4)	125.3(6)	O(2)-C(9)-N(2)	111.9(6)
O(1)-C(5)-C(6)	109.6(6)	C(8)-C(9)-N(2)	126.4(6)
C(4)-C(5)-C(6)	125.1(6)	C(12)-C(13)-C(14)	123.5(6)

References

1 Bruker AXS Inc., *SAINT v8.40B*, Madison (WI), USA, 2019.

2 L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3–10.

3 M. Sevvana, M. Ruf, I. Usón, G. M. Sheldrick and R. Herbst-Irmer, *Acta Crystallogra. D*, 2019, **75**, 1040–1050.

4 G. M. Sheldrick, *Acta Crystallogra. A*, 2015, **71**, 3–8.

5 G. M. Sheldrick, *Acta Crystallogra. C*, 2015, **71**, 3–8.

6 C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogra.*, 2011, **44**, 1281–1284.