Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Highly luminescent antiaromatic diborinines with fused thiophene rings

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Experimental

Materials

All reactions were carried out under dry argon. For the reaction solvents, diethyl ether, THF, dichloromethane, and toluene were purchased from Kanto Chemical Co., Ltd. and were distilled from calcium hydride and stored over activated molecular sieves under argon until use. All other chemicals were purchased from FUJIFILM Wako Pure Chemical Industries, Ltd. and TCI Co., Ltd. Starting material triply(dimethoxy)borane and mesityl(dimethoxy)borane were prepared according to the literature procedure.[S1]

Analytical methods

NMR spectra were recorded on Varian System 500 and 400MR spectrometers. Abbreviations Th, Mes, and Tip used for the following NMR assignments stand for thiophene ring, mesityl, and tripyl groups, respectively. High-resolution mass spectra were obtained by the direct infusion method on a Thermo Fisher Scientific LTQ Orbitrap XL spectrometer at N-BARD, Hiroshima University. UV–vis absorption spectra were measured with a Shimadzu UV-3600 Plus spectrometer. Photoluminescence (PL) spectra were measured with a HORIBA FluoroMax-4 spectrophotometer. The absolute PL quantum yields were determined by using a HORIBA FluoroMax-4 spectrophotometer attached to an integrating sphere. CVs were measured with an AMETEK VersaSTAT 4 potentiostat/galvanostat in a solution of 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dichloromethane using a three-electrode system with a Pt plate counter electrode, a Pt wire working electrode, and an Ag/Ag^+ reference electrode.

Computational details

All the computational calculations were performed on the Gaussian 16 program. For the geometrical optimizations, vibrational frequency calculations, and TD-DFT calculations, the B3LYP/6-31G(d) level was used for $\mathbf{1}^{\mathbf{Br}}$ and $\mathbf{3}^{\mathbf{Br}}$, and the B3LYP-D3(BJ)/6-31G(d) level for other compounds. NICS

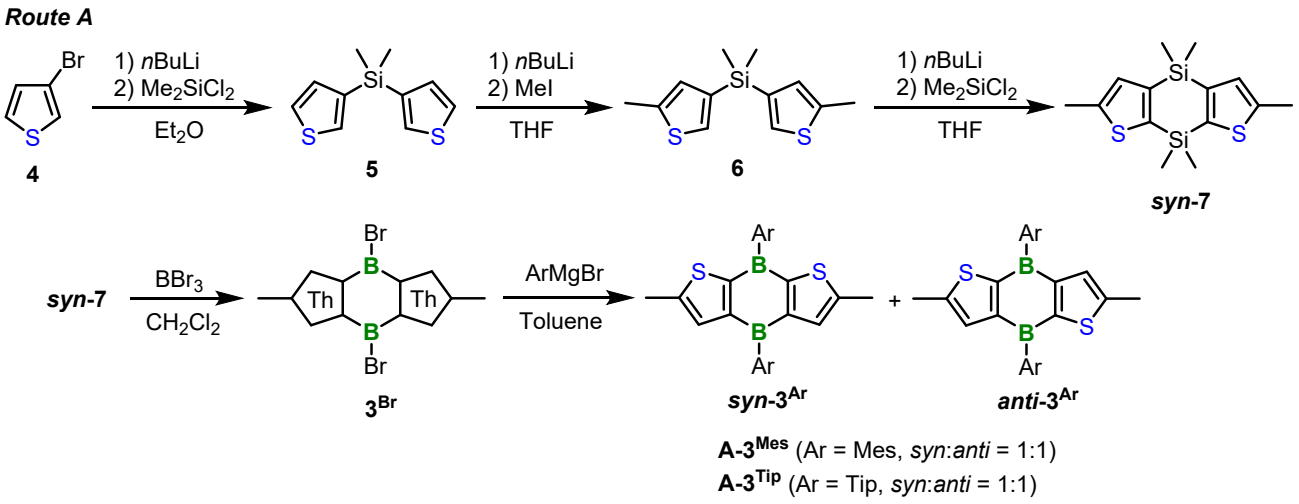
calculations were carried out at the B3LYP/6-31G(d,p) level toward the optimized geometries. Fluoride ion affinity (FIA) and global electrophilicity index (GEI) calculations were performed at M06-2X(D3zero)/def2-QZVPP//B3LYP-D3(BJ)/6-31G(d) level. FIA was value was calculated by using the experimental FIA value of Me_3Si^+ (952.5 kJ/mol) as a reference.

XRD measurements

Single crystal X-ray diffraction data was collected at 100 K on a Rigaku XtaLAB Synergy R,DW diffractometer at Natural Science Center for Basic Research and Development (N-BARD), Hiroshima University. The structure was solved by Intrinsic Phasing on the SHELXL 2018/2 program and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically, whereas hydrogen atoms were included but not refined (SHELXL 2018/3). Graphical crystal structures were generated using Mercury 4.3.1 (Cambridge Crystallographic Data Centre).

Titration experiments and ammonia vapor detection

Titration experiments with TBAF and DMAP were performed in 0.08 mM THF or toluene solutions for absorption and fluorescence measurements. In all the measurements, the samples were left for 1 minutes to equilibrate after each addition of the Lewis bases. The association constants were calculated by using HypSpec Graphs software.[S2] A filter paper was soaked in a dichloromethane solution of **A-3^{Mes}** or **B-3^{Tip}** at a concentration of 0.02 mM and dried under air for 1 hour. The test paper was held over a petri dish containing conc. ammonia water and the change in fluorescence was monitored.



Synthesis of ***5***

To a solution of 29.9 g (183 mmol) of **4** in 100 mL of diethyl ether was added dropwise 68.0 mL (184 mmol) of 2.70 M *n*-BuLi in hexane for 30 min at −80 °C, and the mixture was stirred for 1 h at the temperature. To this was slowly added 11.8 g (91.4mmol) of dimethyldichlorosilane at −80 °C, and the mixture was stirred at room temperature overnight. The resulting mixture was hydrolyzed with water, and extracted with hexane. The organic layer was washed with water then with brine. After drying over anhydrous magnesium sulfate, the solvent was evaporated. The residue was purified by silica gel chromatography with *n*-hexane as the eluent to afford compound **5** in 98% yield (20.1 g, 89.7 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.47 (dd, *J* = 2.6, 0.6 Hz, 2H, Th), 7.41 (dd, *J* = 4.8, 2.6 Hz, 2H, Th), 7.20 (dd, *J* = 4.8, 0.6 Hz, 2H, Th), 0.55 (s, 6H, $SiMe_2$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ = 138.8, 132.6, 131.6, 125.8, -1.1. EI-MS Calcd for $C_{10}H_{12}S_2Si$: M^+ : 224.01497, Found : 224.01505.

Synthesis of ***6***

To a solution of 8.00 g (35.7 mmol) of **5** in 80 mL of THF was added dropwise 28.0 mL (75.6 mmol) of 2.64 M *n*-BuLi in hexane for 15 min at 0 °C, and the mixture was stirred for 1 h at the temperature. To this was slowly added 5.60 mL (90.0 mmol) of iodomethane at −80 °C, and the mixture was stirred

at room temperature overnight. The resulting mixture was hydrolyzed with water, and extracted with hexane. The organic layer was washed with water then with brine. After drying over anhydrous magnesium sulfate, the solvent was evaporated. The residue was purified by silica gel chromatography with *n*-hexane as the eluent to afford compound **6** in 81% yield (7.31 g, 28.9 mmol) as a colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.20 (d, *J* = 1.3 Hz, 2H, Th), 6.81–6.80 (m, 2H, Th), 2.50 (d, *J* = 1.1 Hz, 6H, Th-Me), 0.47 (s, 6H, $SiMe_2$). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ = 140.2, 139.6, 130.8, 129.9, 14.7, -1.4. EI-MS Calcd for $C_{12}H_{16}S_2Si$: M^+ : 252.04627, Found : 252.04696.

*Synthesis of **syn-7***

To a solution of 3.94 g (15.6 mmol) of **6** in 35 mL of THF was added dropwise 12.0 mL (31.7 mmol) of 2.64 M *n*-BuLi in hexane for 15 min at 0 °C, and the mixture was stirred for 1 h at the temperature. To this was slowly added 2.00 mL (16.7 mmol) of dimethyldichlorosilane at −80 °C, and the mixture was stirred at room temperature overnight. The resulting mixture was hydrolyzed with water, and extracted with hexane. The organic layer was washed with water then with brine. After drying over anhydrous magnesium sulfate, the solvent was evaporated. The residue was purified by silica gel chromatography with *n*-hexane as the eluent to afford compound ***syn*-7** in 42% yield (2.03 g, 6.57 mmol) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 6.99 (d, *J* = 1.0 Hz, 2H, Th), 2.59 (d, *J* = 1.0 Hz, 6H, Th-Me), 0.48 (s, 6H, $SiMe_2$), 0.37 (s, 6H, $SiMe_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 148.4, 146.3, 143.2, 131.2, 14.7, 2.3, 0.3. FI-MS Calcd for $C_{14}H_{20}S_2Si_2$: M^+: 308.05449, Found: 308.05537. m.p. 147.7-149.0 °C.

*Synthesis of **A-3^{Mes}***

To a solution of ***syn*-7** (200 mg, 0.648 mmol) in 15 mL of toluene was slowly added 1.70 mL (1.70 mmol) of 1.0 mol/L BBr_3 in toluene for 5 min at 0 °C and stirred for overnight at 50 °C. All volatiles were removed in vacuum to give **3^{Br}** quantitively as a brown solid. The product was used in the next

step without further purification. NMR data of **3^{Br}**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.41–7.39 (m, 2H, Th), 2.56 (d, *J* = 0.7 Hz, 6H, Th-Me). ^{11}B NMR (160 MHz, $CDCl_3$) δ = 50.7.

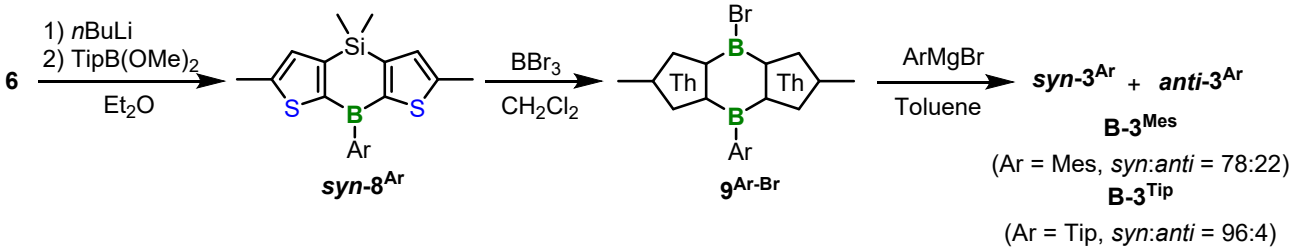
To a solution of **3^{Br}** synthesized above in 12 mL of toluene was slowly added dropwise 2.55 mL (2.55 mmol) of 1.0 M 2-mesitylmagnesium bromide in THF at −80 °C, then the mixture was stirred overnight at room temperature. The resulting mixture was hydrolyzed with saturated NH_4Cl aqueous solution, and the organic layer was washed twice with brine. After drying over anhydrous magnesium sulfate, the solvent was evaporated. The crude product was purified by silica gel chromatography using a mixed solvent (*n*-hexane : dichloromethane = 2 : 1) as the eluent to give 17.8 mg (39.4 μmol, 6% yield) of the title compound as an orangish powder as a ***syn*-3^{Mes}**: ***anti*-3^{Mes}** = 1:1 mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.90–6.86 (m, 12H, aromatic), 2.43–2.40 (m, 12H, Th-Me), 2.36 (s, 3H, *syn*-Mes), 2.35 (s, 6H, *anti*-Mes), 2.34 (s, 3H, *syn*-Mes), 2.24 (s, 6H, *syn*-Mes), 2.20 (s, 12H, *anti*-Mes), 2.15 (s, 6H, *syn*-Mes). ^{13}C NMR could not be recorded due to lack of sample. ^{11}B NMR (160 MHz, C_6D_6) δ = 56.7. m.p. 202.5-204.0 °C.

*Synthesis of **A-3^{Tip}***

A-3^{Tip} was prepared from **3^{Br}** synthesized from 1.62 mmol of ***syn*-7**, 7.00 mL (4.86 mmol) of 0.69 mol/L tripylmagnesium bromide in THF, and 10 mL of toluene as a yellowish powder as a ***syn*-3^{Tip}**: ***anti*-3^{Tip}** = 1:1 mixture (156 mg, 0.251 mmol, 16% yield in the two steps) in a manner similar to that of **A-3^{Mes}**. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.00 (s, 2H, *syn*-Tip), 6.99 (s, 4H, *anti*-Tip), 6.99 (s, 2H, *syn*-Tip), 6.91 (d, *J* = 0.9 Hz, 2H, *anti*-Th), 6.90 (d, *J* = 1.0 Hz, 2H, *syn*-Th), 3.00–2.88 (m, 4H, Tip), 2.75–2.53 (m, 8H, Tip), 2.43 (s, 12H, Th-Me), 1.34–1.29 (m, 24H, Tip), 1.20–1.15 (m, 24H, Tip), 1.14–1.10 (m, 24H, Tip). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 156.8 (*anti*, br, B−C), 156.0 (*syn*, br, B−C), 155.1 (*syn*, br, B−C), 154.4 (*anti*, br, B−C), 151.6 (*anti*), 151.2 (*syn*), 149.8 (*syn*), 149.5 (*anti*), 149.1 (*syn*), 148.5 (*syn*), 148.2 (*anti*), 148.0 (*syn*), 139.1 (*syn*, br, B−C), 138.1 (*anti*, br, B−C), 137.1 (*syn*, br, B−C), 136.0 (*syn*), 135.9 (*anti*), 119.87 (*syn*), 119.82 (*anti*), 119.78 (*syn*), 35.44 (*syn*), 35.40 (*anti*), 35.37 (*syn*), 34.24 (*syn*), 34.23 (*anti*), 34.21 (*syn*), 24.59 (*anti*), 24.47 (*syn*), 24.46 (*syn*), 24.33

(*anti*), 24.13 (*syn*), 24.12 (*anti*), 24.11 (*syn*), 15.37 (*anti*), 15.36 (*syn*). ^{11}B NMR (160 MHz, $CDCl_3$) δ = 55.5. m.p. 229.3-231.9 ℃.

Route B



Synthesis of ***syn-8^{Mes}***

***syn*-8^{Mes}** was prepared from 2.06 g (8.16 mmol) of **6** and 11.0 mL (17.5 mmol) of 1.59 mol/L *n*-butyllithium in *n*-hexane, 1.65 g (8.59 mmol) of mesityl(dimethoxy)borane, and 20 mL of THF as a white powder (1.69 g, 4.44 mmol, 54% yield) in a manner similar to that of ***syn*-7**. ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.18 (d, *J* = 0.9 Hz, 2H, Th), 6.86 (s, 2H, Mes), 2.57 (d, *J* = 0.9 Hz, 6H, Th-Me), 2.34 (s, 3H, Mes), 2.13 (s, 6H, Mes), 0.43 (s, 6H, $SiMe_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 154.6, 152.7, 150.9 (br, B−C), 140.5 (br, B−C), 138.2, 137.0, 132.8, 126.8, 22.7, 21.4, 15.4, -1.1. ^{11}B NMR (160 MHz, $CDCl_3$) δ = 51.7. EI-MS Calcd for $C_{21}H_{25}BS_2Si$: M^+ : 380.12642, Found : 380.12593. m.p. 171.8-172.3 ℃.

Synthesis of ***syn-8^{Tip}***

***syn*-8^{Tip}** was prepared from 1.30 g (5.15 mmol) of **6** and 3.90 mL (10.5 mmol) of 2.70 mol/L *n*-butyllithium in *n*-hexane, 1.95 g (7.06 mmol) of tripyl(dimethoxy)borane, and 10 mL of THF as a white powder (1.58 g, 3.63 mmol, 70% yield) in a manner similar to that above.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.16 (d, *J* = 0.9 Hz, 2H, Th), 6.98 (s, 2H, Tip), 2.99–2.88 (m, 1H, Tip), 2.57 (d, *J* = 0.8 Hz, 6H, Th-Me), 2.62–2.49 (m, 2H, Tip), 1.31 (d, *J* = 6.9 Hz, 6H, Tip), 1.11 (d, *J* = 6.7 Hz, 12H, Tip), 0.44 (s, 6H, $SiMe_2$). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 153.6, 152.6 (br, B−C), 152.2, 149.8, 148.3, 138.3 (br, B−C), 132.4, 119.8, 35.1, 34.2, 24.6, 24.1, 15.4, -0.9. ^{11}B NMR (160

MHz, $CDCl_3$) δ = 52.4. APCI-MS Calcd for $C_{27}H_{37}BS_2Si$: M^+: 464.21987, Found: 464.22076. m.p. 128.8-128.9 °C.

Synthesis of ***B-3^{Mes}***

9$^{Mes\text{-}Br}$ was prepared from 98.5 mg (0.259 mmol) of ***syn*-8^{Mes}** and 0.300 mL (0.300 mmol) of 1.0 mol/L BBr_3 in dichloromethane, and 7 mL of dichloromethane as a brown solid in a manner similar to that of **3^{Br}**. The product was used in the next step without further purification. NMR data of **9$^{Mes\text{-}Br}$**: ^{1}H NMR data of **9$^{Mes\text{-}Br}$** could not be obtained as the crude product contained many impurities. ^{11}B NMR (160 MHz, $CDCl_3$) δ = 53.2.

B-3^{Mes} was prepared from **9$^{Mes\text{-}Br}$** synthesized above, 0.200 mL (0.200 mmol) of 1.0 mol/L 2-mesitylmagnesium bromide in THF, and 7 mL of toluene as an orangish powder as a ***syn*-3^{Mes}**: ***anti*-3^{Mes}** = 78:22 (1:0.28) mixture (25.9 mg, 57.3 μmol, 22% yield in the two steps) in a manner similar to that of **A-3^{Mes}**. ^{1}H NMR (400 MHz, C_6D_6) δ = 6.98–6.95 (m, 2.6H, Th), 6.91 (br s, 2H, *syn*-Mes), 6.89 (br s, 1.1H, *anti*-Mes), 6.86 (br s, 2H, *syn*-Mes), 2.42 (s, 6H, *syn*-Mes), 2.36 (s, 3.4H, *anti*-Mes), 2.31 (s, 3H, *syn*-Mes), 2.28 (s, 6H, *syn*-Mes), 2.27 (s, 1.7H, *anti*-Mes), 2.23 (s, 3H, *syn*-Mes), 1.96 (d, *J* = 0.9 Hz, 7.7H, Th-Me). ^{13}C NMR could not be recorded due to lack of sample. ^{11}B NMR (160 MHz, CD_2Cl_2) δ = 55.5. APCI-MS Calcd for $C_{28}H_{30}B_2S_2$: M^+: 452.19794, Found: 452.19821. m.p. 202.5-205.0 °C.

Synthesis of ***B-3^{Tip}***

9$^{Tip\text{-}Br}$ was prepared from 465 mg (1.00 mmol) of ***syn*-8^{Tip}** and 1.00 mL (1.00 mmol) of 1.0 mol/L BBr_3 in dichloromethane, and 10 mL of dichloromethane as a brown solid in a manner similar to that of **3^{Br}**. The product was used in the next step without further purification. NMR data of **9$^{Tip\text{-}Br}$**: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.42 (d, *J* = 0.9, 2H, Th), 6.98 (s, 2H, Tip), 2.98–2.88 (m, 2H, Tip), 2.73–2.64 (m, 1H, Tip), 2.53 (d, *J* = 0.9 Hz, 6H, Th-Me), 1.31 (d, *J* = 6.9, 6H, Tip), 1.15 (d, *J* = 6.7 Hz, 12H, Tip). ^{11}B NMR (160 MHz, $CDCl_3$) δ = 52.5.

B-3^{Tip} was prepared from **9^{Tip-Br}** synthesized above, 2.10 mL (1.45 mmol) of 0.69 mol/L 2-tripylmagnesium bromide in THF, and 10 mL of toluene as a yellowish powder as a ***syn*-3^{Tip}**: ***anti*-3^{Tip}** = 96:4 mixture (173 mg, 0.279 mmol, 28% yield in the two steps) in a manner similar to that of **A-3^{Mes}**. NMR data of ***syn*-3^{Tip}**: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.00 (s, 2H, Tip), 6.99 (s, 2H, Tip), 6.90 (d, *J* = 1.0 Hz, 2H, Th), 3.00–2.88 (m, 2H, Tip), 2.76–2.66 (m, 2H, Tip), 2.61–2.52 (m, 2H, Tip), 2.43 (d, *J* = 0.8 Hz, 6H, Th-Me), 1.32 (d, *J* = 6.9 Hz, 12H, Tip), 1.31 (d, *J* = 6.9 Hz, 12H, Tip), 1.17 (d, *J* = 6.7 Hz, 12H, Tip), 1.12 (d, *J* = 6.7 Hz, 12H, Tip). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 156.0 (br, B−C), 155.1 (br, B−C), 151.2, 149.8, 149.1, 148.5, 148.0, 139.1 (br, B−C), 137.1 (br, B−C), 136.0, 119.9, 119.8, 35.4, 35.4, 34.24, 34.20, 24.47, 24.46, 24.14, 24.10, 15.4. ^{11}B NMR (160 MHz, $CDCl_3$) δ = 56.1. APCI-MS Calcd for $C_{40}H_{54}B_2S_2$: M^+: 620.38610, Found: 620.38715. m.p. 236.5-238.6 °C.

References

[S1] W.-M. Wan, F. Cheng and F. Jäkle, *Angew. Chem. Int. Ed.*, 2014, **53**, 8934.

[S2] P. Gans, A. Sabatini, A. Vacca, *Talanta* 1996, **43**, 1739.

Figures and Tables

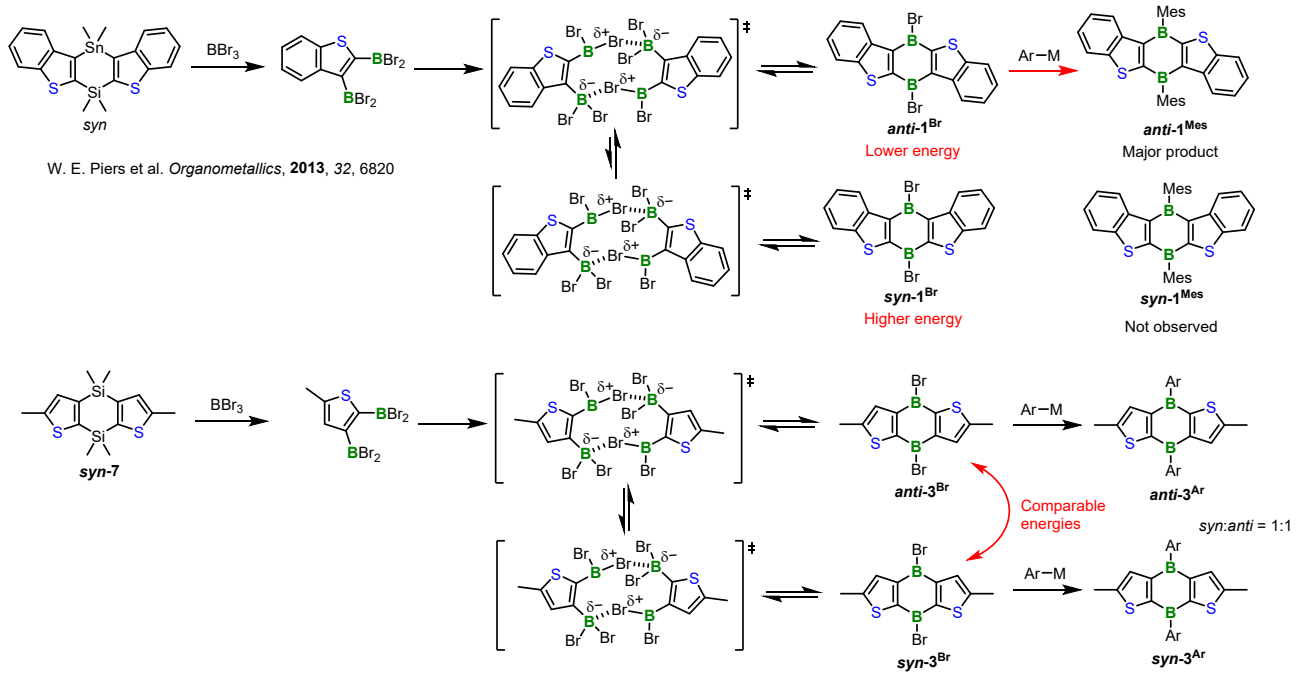


Figure S1 Plausible reaction mechanism for the formation of diborinines from *syn* precursors.

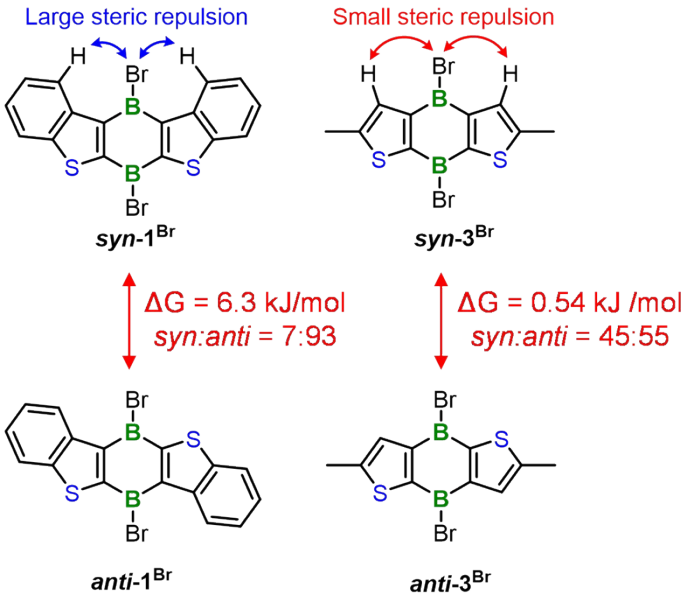


Figure S2 DFT-calculated Gibbs free energy differences at the B3LYP/6-31G(d) level at 298 K.

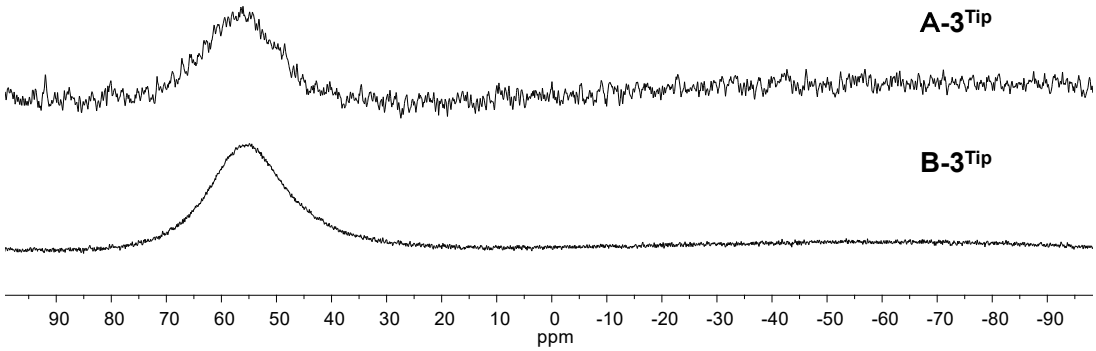


Figure S3 ^{11}B NMR spectra of **A-3^{Tip}** and **B-3^{Tip}** in $CDCl_3$ at room temperature.

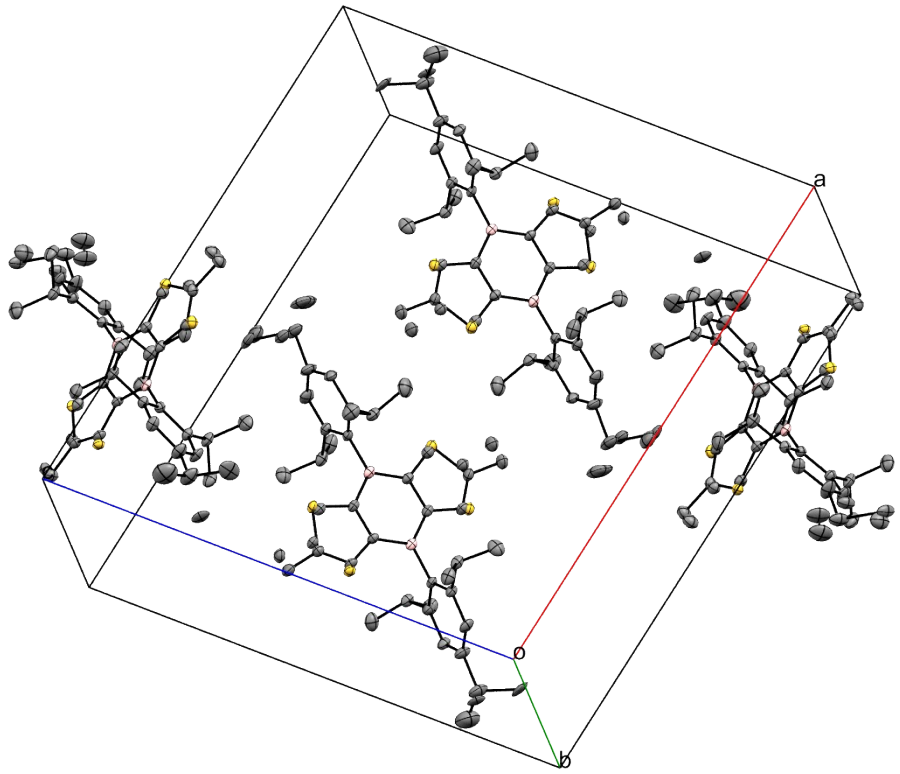


Figure S4 Crystal packing structure of ***syn*-3^{Tip}** obtained at 100 K. Thermal ellipsoids are at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table S1 Experimental and DFT-calculated bond lengths in diborinine rings of dithienodiborinines.

	***syn*-3^{Tip}**	***anti*-1^{Mes}**	**2^{Mes}**	***syn*-3^{Tip}**	***anti*-1^{Mes}**	**2^{Mes}**
	SC	SC	SC	DFT	DFT	DFT
B1-C1	1.551	1.552	1.551	1.543	1.552	1.548
C1-C2	1.398	1.388	1.463	1.395	1.387	1.462
C2-B2	1.552	1.556	1.552	1.558	1.554	1.548
B2-C3	1.554	1.552	1.551	1.558	1.552	1.548
C3-C4	1.393	1.388	1.463	1.395	1.387	1.462
C4-B1	1.551	1.556	1.552	1.543	1.554	1.548

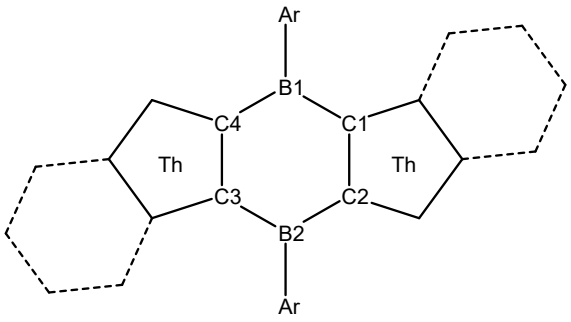


Table S2 TD-DFT results at the B3LYP-D3(BJ)/6-31G(d) level of theory.

Compound	Excited State	Composition	Contribution /%	Excitation energy /eV	Wavelength /nm	Oscillator strength
***syn*-3^{Mes}**	S0→S1	H→L	99	2.37	524	0.03
	S0→S3	H-2→L	99	2.59	479	0.02
	S0→S6	H-5→L	97	3.51	353	0.16
	S0→S7	H-6→L	96	3.58	346	0.03
		H→L+1	3			
	S0→S8	H-7→L	96	4.07	305	0.17
	S0→S13	H-4→L+2	17	5.13	242	0.13
		H-4→L+4	5			
		H-2→L+1	22			
		H-2→L+5	12			
		H-1→L+1	2			
		H-1→L+5	2			
		H→L+2	37			
	S0→S16	H-4→L+2	22	5.15	241	0.18
		H-4→L+4	8			
		H-2→L+5	18			
		H-1→L+5	3			
		H→L+2	46			
***anti*-3^{Mes}**	S0→S1	H→L	99	2.39	518	0
	S0→S2	H-1→L	99	2.51	495	0.01
	S0→S6	H-5→L	97	3.36	369	0.18
		H→L+1	3			
	S0→S8	H-7→L	95	4.04	307	0.22
		H→L+1	2			
	S0→S14	H-7→L	2	4.93	251	0.49
		H-5→L	3			
		H-2→L+1	5			
		H→L+1	86			

Table S3 Calculated NICS values at the B3LYP/6-31G(d,p) level based on the optimized structures.

Compound	NICS(1)		$NICS(1)_{zz}$		NICS(0)		$NICS(0)_{zz}$	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
***anti*-1^{Mes}**	8.0	−7.8	29.0	−16.3	13.4	−7.3	48.7	7.6
***syn*-3^{Mes}**	6.8	−7.5	25.0	−16.4	12.0	−7.1	43.7	7.5
***anti*-3^{Mes}**	6.8	−7.5	24.9	−16.4	12.0	−7.1	43.7	7.3
2^{Mes}	2.1	−7.3	9.9	−14.8	6.8	−7.1	26.9	9.0

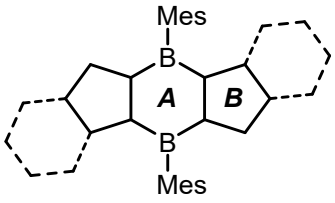


Table S4 Calculated FIA and GEI values based on the optimized structures.

Compound	FIA (kJ/mol)	GEI (eV)
Tris(pentafluorophenyl)borane	449.4	2.86
***syn*-3^{Mes}**	329.0	2.14
***syn*-3^{Mes}•F$^-$**	5.9	-
***anti*-3^{Mes}**	327.8	2.13
***anti*-3^{Mes}•F$^-$**	7.8	-
***anti*-1^{Mes}**	358.4	2.44
***anti*-1^{Mes}•F$^-$**	49.1	-
2^{Mes}	297.2	1.40
2^{Mes}•F$^-$	26.6	-
10	289.8	1.45

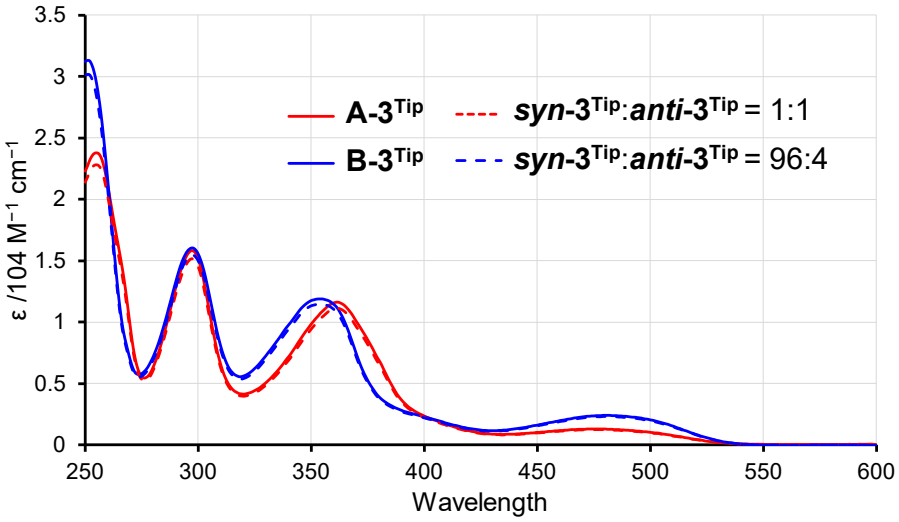


Figure S5 Comparison of synthesized absorption spectra from the estimated spectra of ***syn*-3^{Tip}** and ***anti*-3^{Tip}** with the experimental absorption spectra of **A-3^{Tip}** and **B-3^{Tip}**.

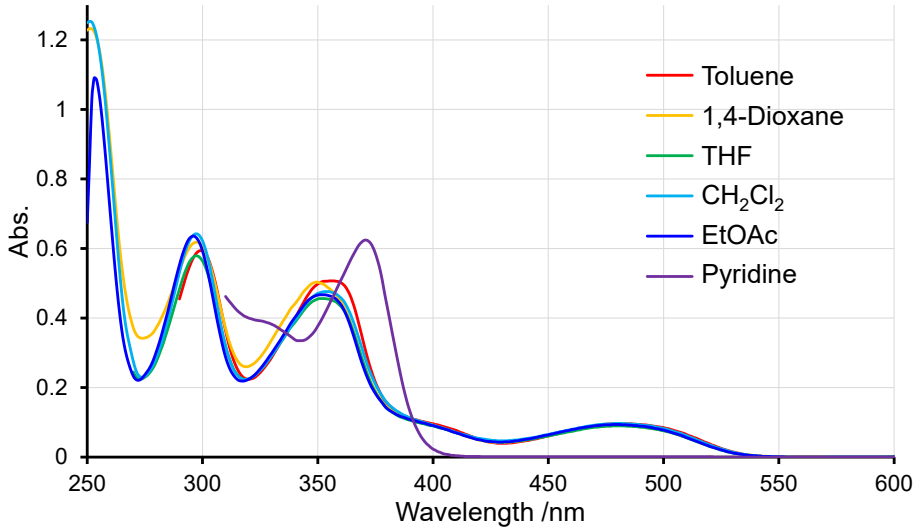


Figure S5 Absorption spectra of **B-3^{Tip}** in various solvents at the concentration of 0.04 mM.

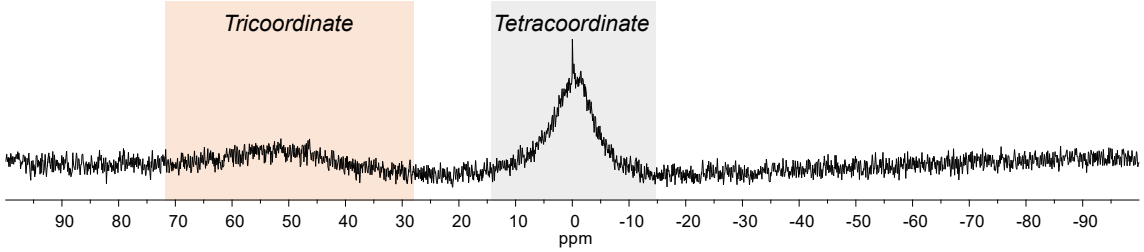


Figure S6 ^{11}B NMR spectrum of **B-3^{Tip}** in pyridine-d_5 at room temperature (160 MHz).

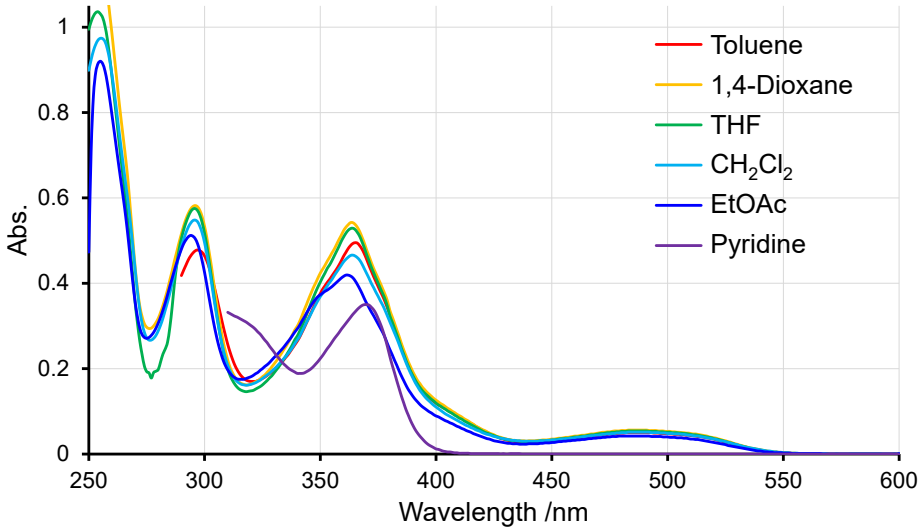


Figure S7 Absorption spectra of **A-3^{Mes}** in various solvents at the concentration of 0.04 mM.

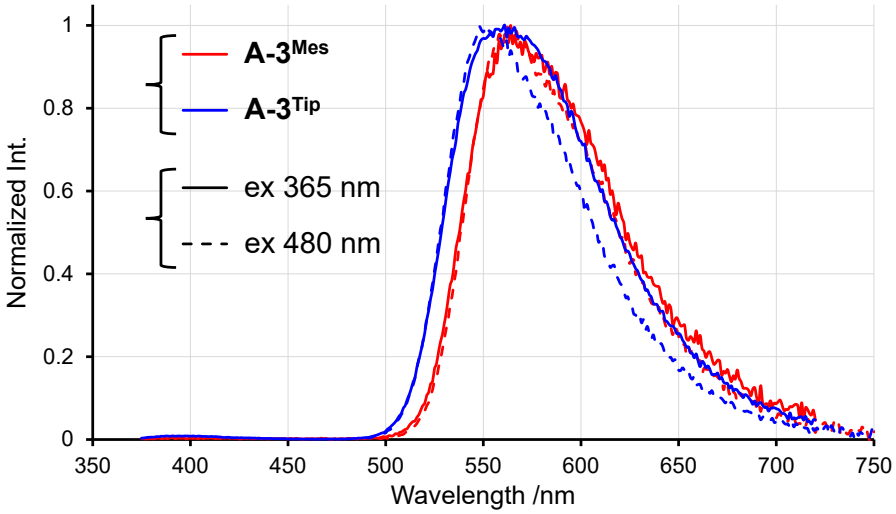


Figure S8 Excitation wavelength dependence of fluorescence spectra of **A-3^{Mes}** and **A-3^{Tip}** in dichloromethane.

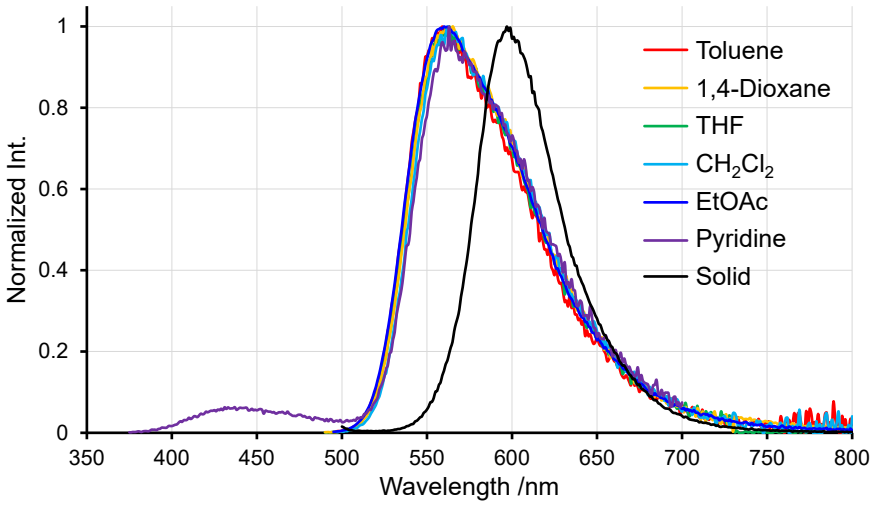


Figure S9 Fluorescence spectra of **A-3^{Mes}** in various solvents at the concentration of 0.04 mM.

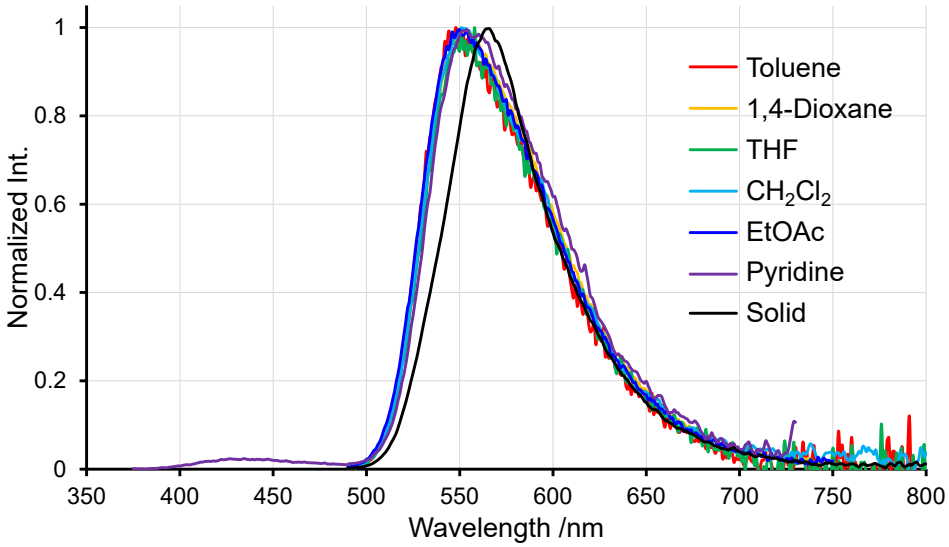


Figure S10 Fluorescence spectra of **B-3^{Tip}** in various solvents at the concentration of 0.04 mM.

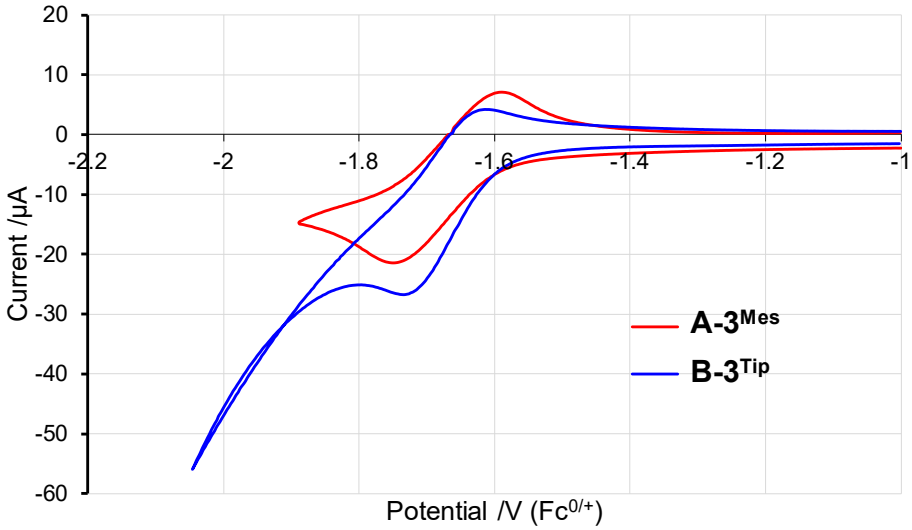


Figure S11 Cathodic voltammograms of **A-3^{Mes} and B-3^{Tip}** in dichloromethane with 0.1 M $TBAPF_6$ at the scan rate of 50 mV/s.

Table S5 Optical data of dithienodiborinines in various solvents.

	Solvent	λ_{Abs} [a] /nm	λ_{FL}^{480} [b] /nm	λ_{FL}^{365} [c] /nm	Φ_{FL}^{480} [d] /%	Φ_{FL}^{365} [e] /%	τ [f] /ns (%)
A-3^{Mes}	Toluene	297, 365, 486	560	564	72	50	69
	Dioxane	297, 364, 487	560	564	62	38	0.49 (18), 25 (82)
	THF	297, 364, 487	563	566	83	45	0.42 (29), 25 (71)
	CH_2Cl_2	297, 364, 487	564	564	71	45	77
	EtOAc	294, 362, 485	560	563	70	44	0.42 (41), 28 (59)
	Pyridine	305, 370	-	563	-	31	0.33 (92), 47 (8)
	Solid	-	597	593	20	20	23
A-3^{Tip}	Toluene	299, 363, 475	547	557	75	47	69
	Dioxane	297, 361, 473	551	565	70	46	0.42 (63), 56 (37)
	THF	297, 361, 475	555	565	67	40	39 (18), 81 (82)
	CH_2Cl_2	297, 361, 477	550	561	71	45	77
	EtOAc	295, 360, 473	550	560	65	44	0.4 (70), 76 (30)
	Pyridine	306, 371	-	557	0	31	0.18 (88), 59 (12)
	Solid	-	563	559	78	81	87
B-3^{Tip}	Toluene	299, 356, 482	548	550	82	82	67
	Dioxane	297, 350, 479	553	554	72	81	0.45 (46), 56 (54)
	THF	297, 352, 480	558	550	72	75	72
	CH_2Cl_2	297, 354, 480	553	553	81	81	74
	EtOAc	296, 352 ,479	550	552	61	76	0.30 (56), 76 (45)
	Pyridine	306, 371	-	553	-	42	0.70 (20), 3.6 (43), 82 (37)
	Solid	-	566	559	87	95	79

[a] Absorption maxima. [b] Fluorescence maxima when excited at 480 nm. [c] Fluorescence maxima when excited at 365 nm. [d] Absolute quantum yield when excited at 480 nm. [e] Absolute quantum yield when excited at 365 nm. [f] Emission lifetime and contribution.

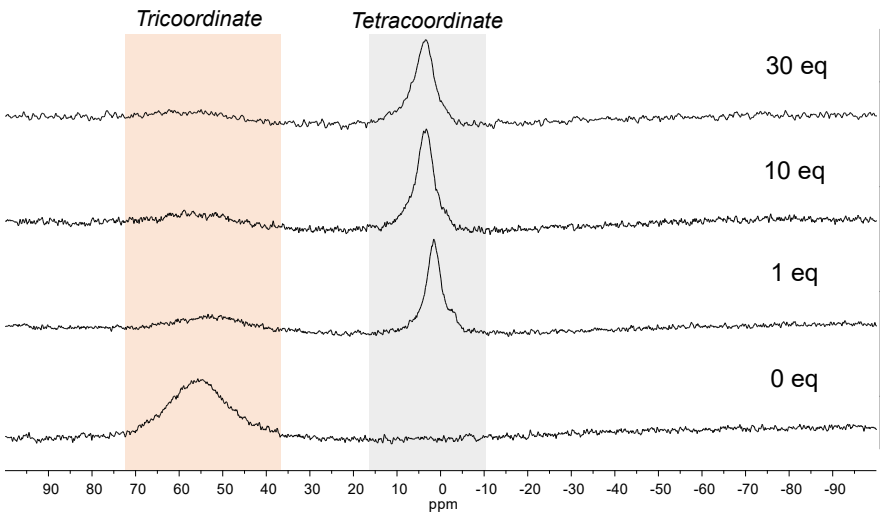


Figure S12. ^{11}B NMR spectra of **B-3^{Tip}** before and after the addition of TBAF in THF-d_8 at room temperature (160 MHz).

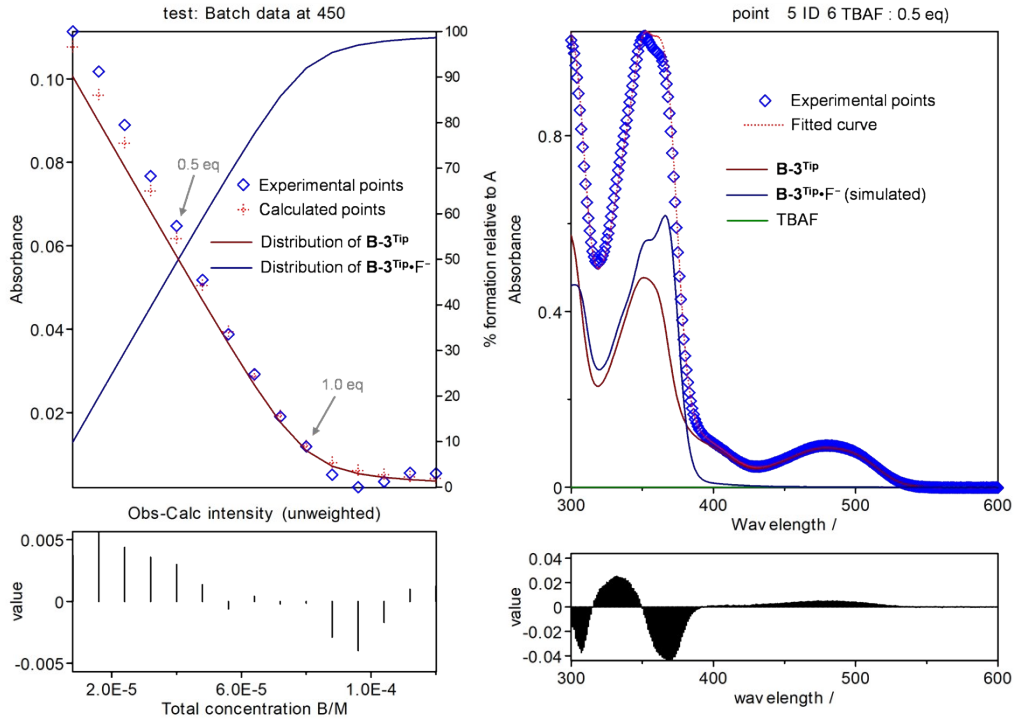


Figure S13 Images exported from HypSpec Graphs showing the fitting over the whole spectrum. The titration experiment of **B-3^{Tip}** with TBAF was performed in THF at the concentration of 0.08 mM at room temperature.

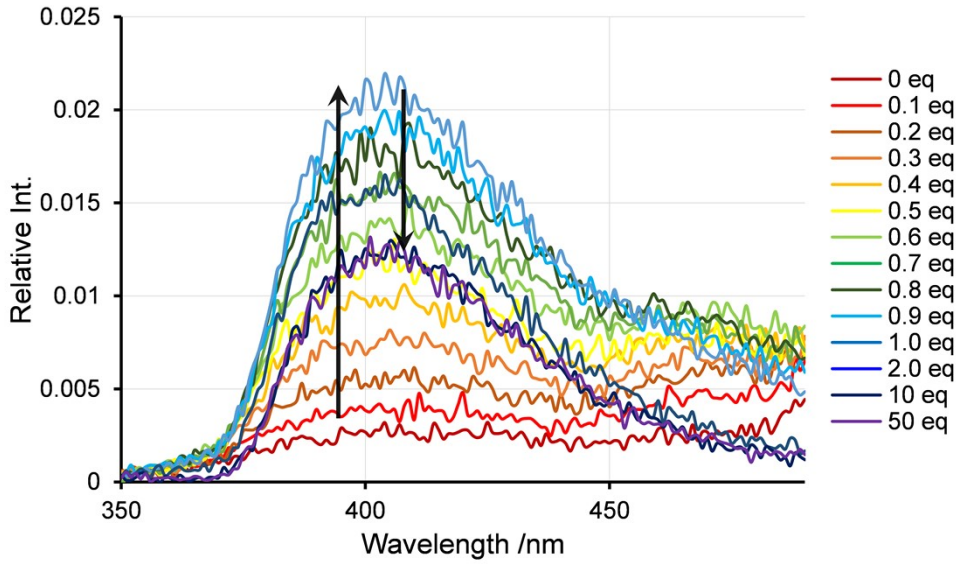


Figure S14 Fluorescence data excited at 320 nm for titrations of **B-3^{Tip}** with TBAF aliquots in THF at the concentration of 0.08 mM.

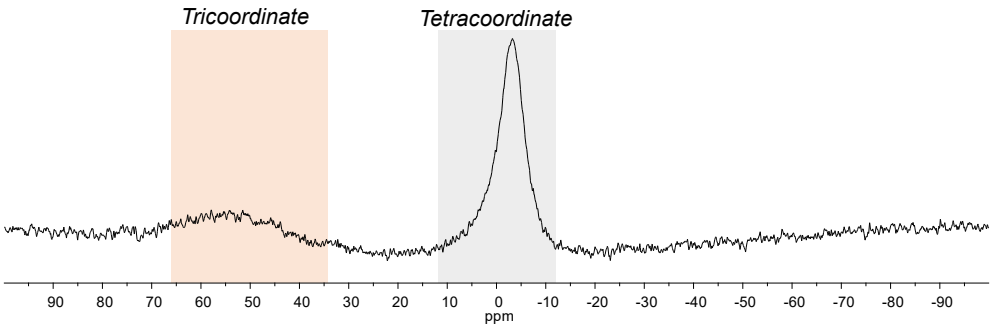


Figure S15 ^{11}B NMR spectrum of **B-3^{Tip}** in the presence of 140 equiv. of DMAP in $CDCl_3$ at room temperature (160 MHz).

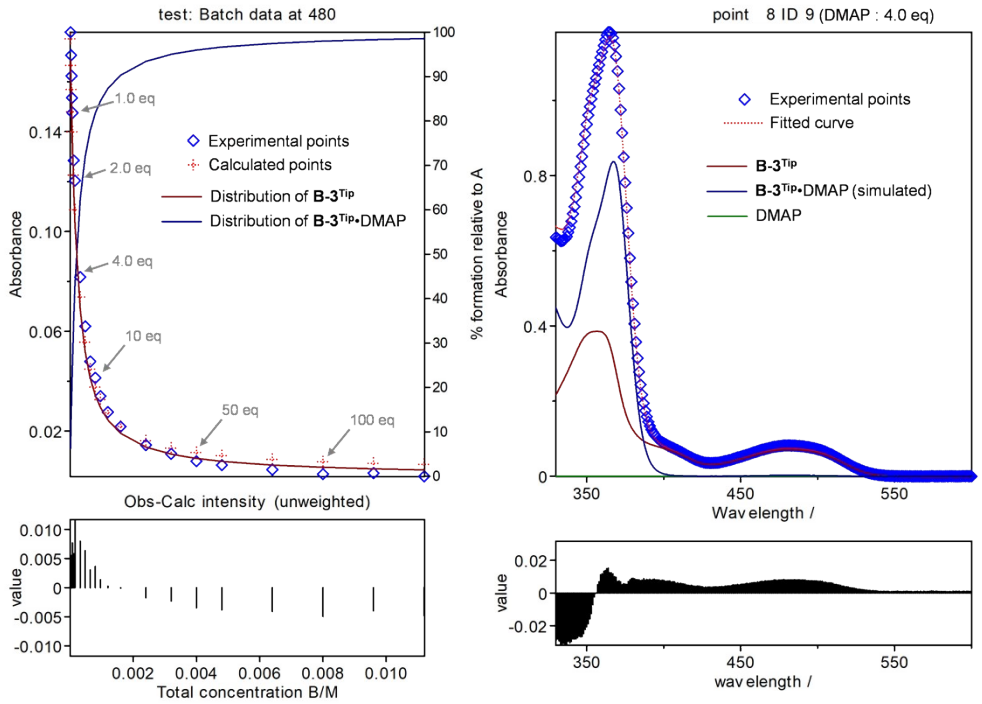


Figure S16 Images exported from HypSpec Graphs showing the fitting over the whole spectrum. The titration experiment of **B-3^{Tip}** with DMAP was performed in toluene at the concentration of 0.08 mM at room temperature.

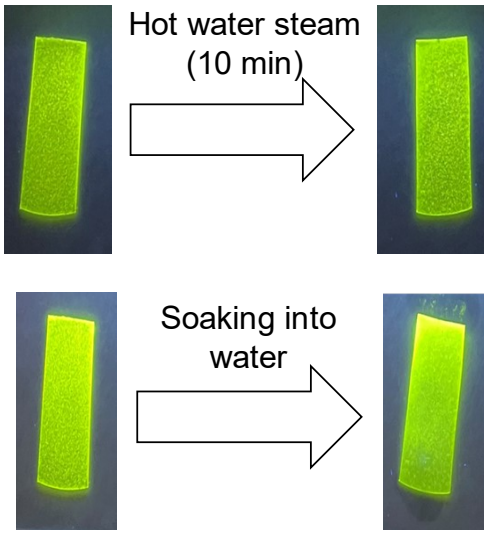


Figure S17 Response of filter paper strips containing **B-3^{Tip}** to water.

NMR spectra

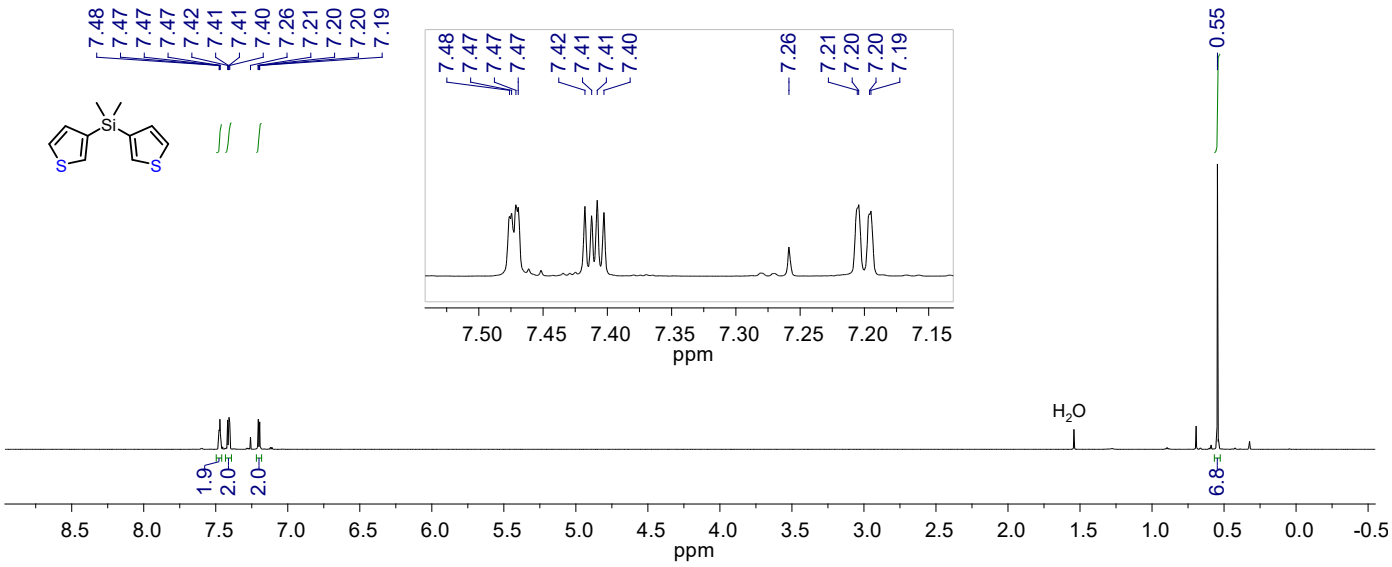


Figure S18 ^{1}H NMR spectrum of **5** in $CDCl_3$ at room temperature (500 MHz).

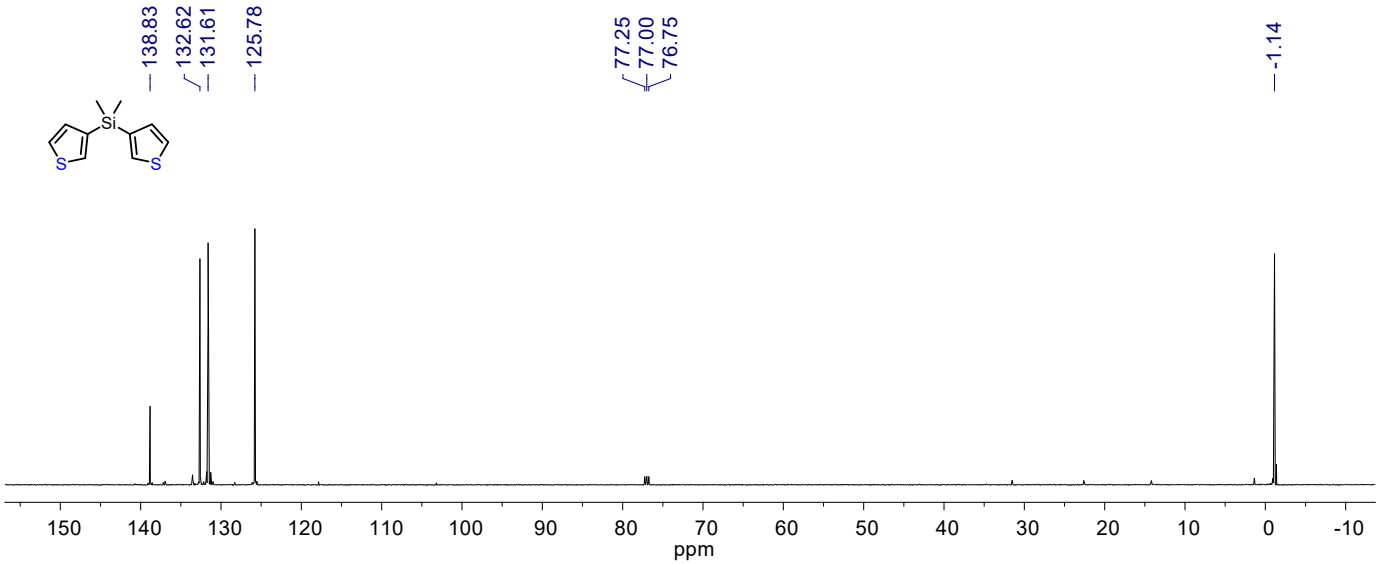


Figure S19 ^{13}C NMR spectrum of **5** in $CDCl_3$ at room temperature (126 MHz).

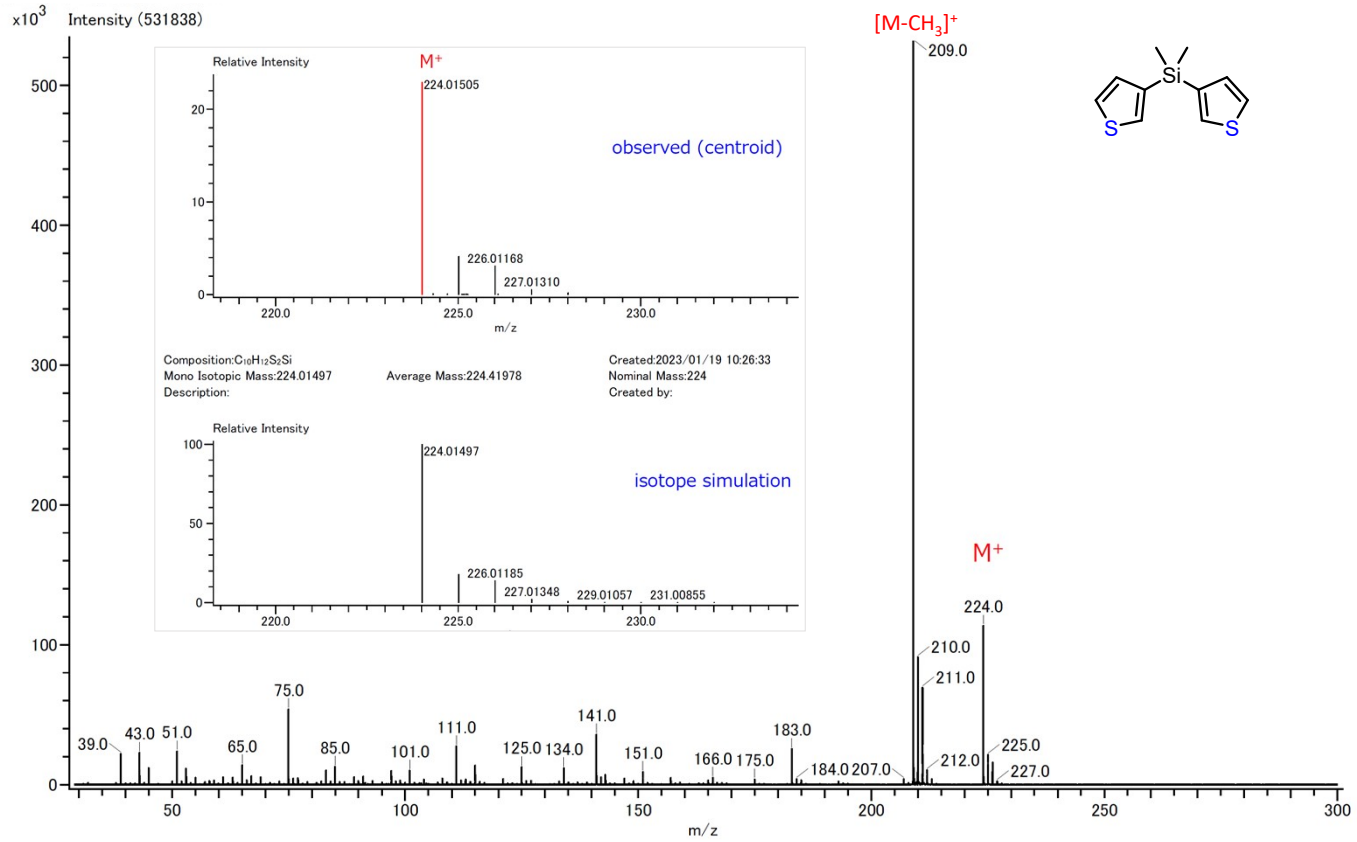


Figure S20 High resolution EI-mass spectrum of **5**.

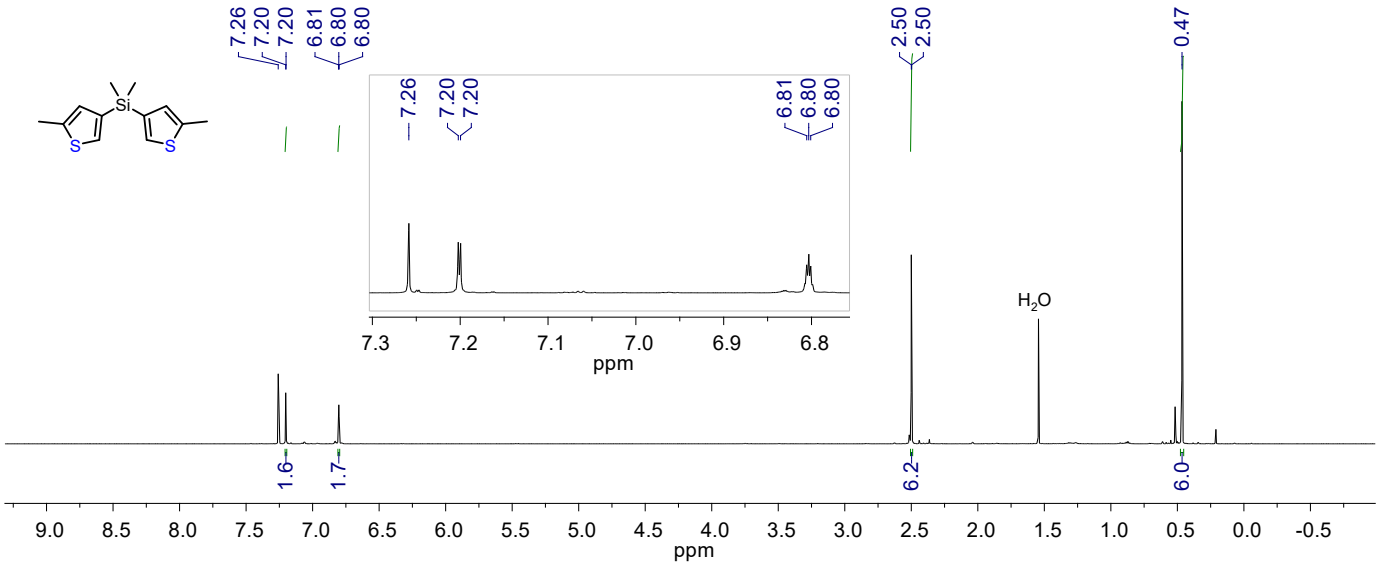


Figure S21 ^{1}H NMR spectrum of **6** in $CDCl_3$ at room temperature (500 MHz).

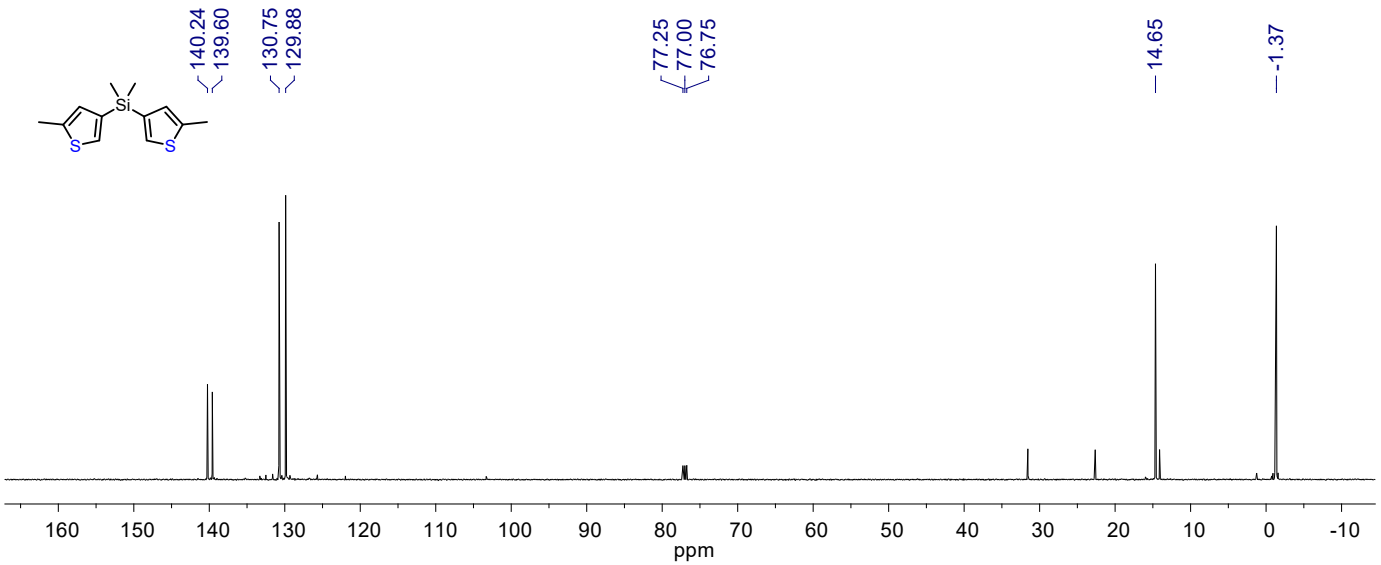


Figure S22 ^{13}C NMR spectrum of **6** in $CDCl_3$ at room temperature (126 MHz).

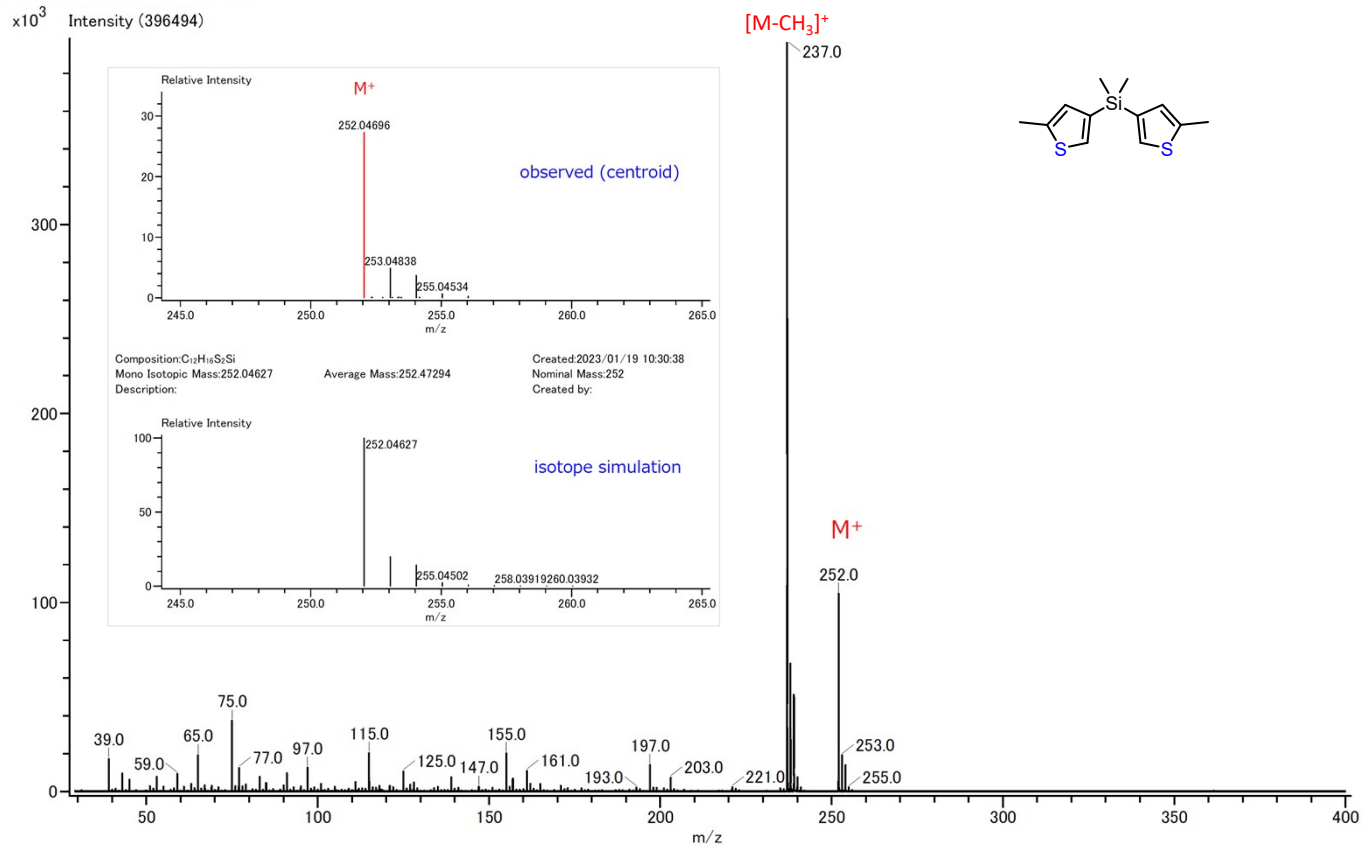


Figure S23 High resolution EI-mass spectrum of **6**.

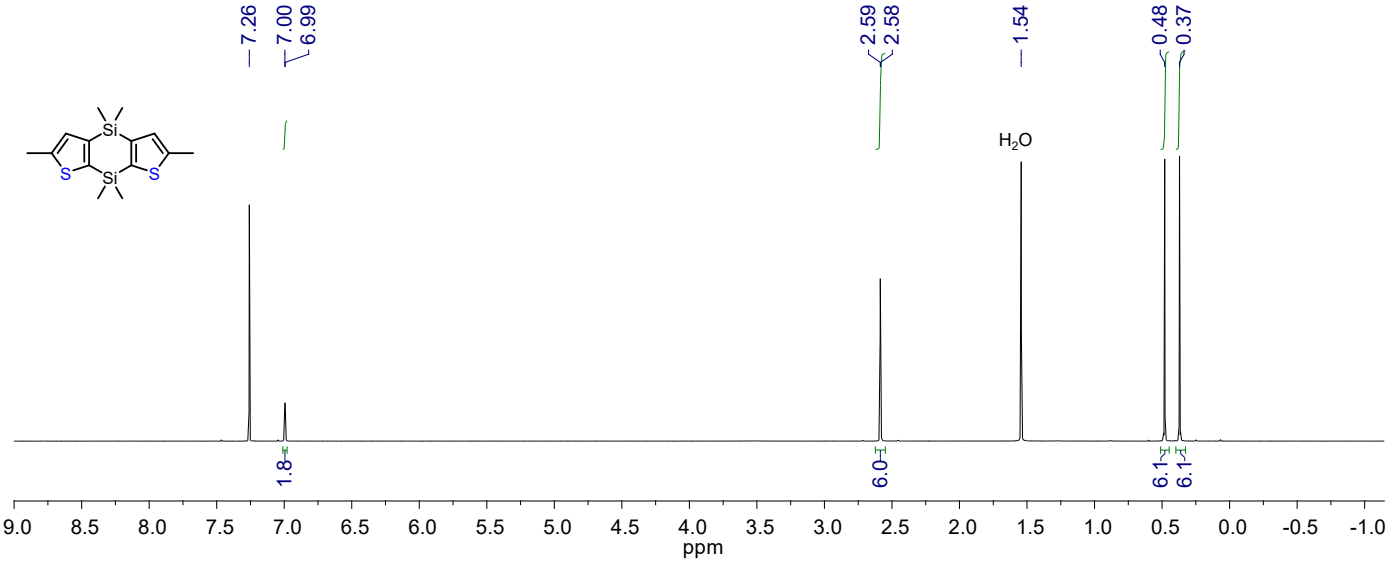


Figure S24 ^{1}H NMR spectrum of ***syn*-7** in $CDCl_3$ at room temperature (500 MHz).

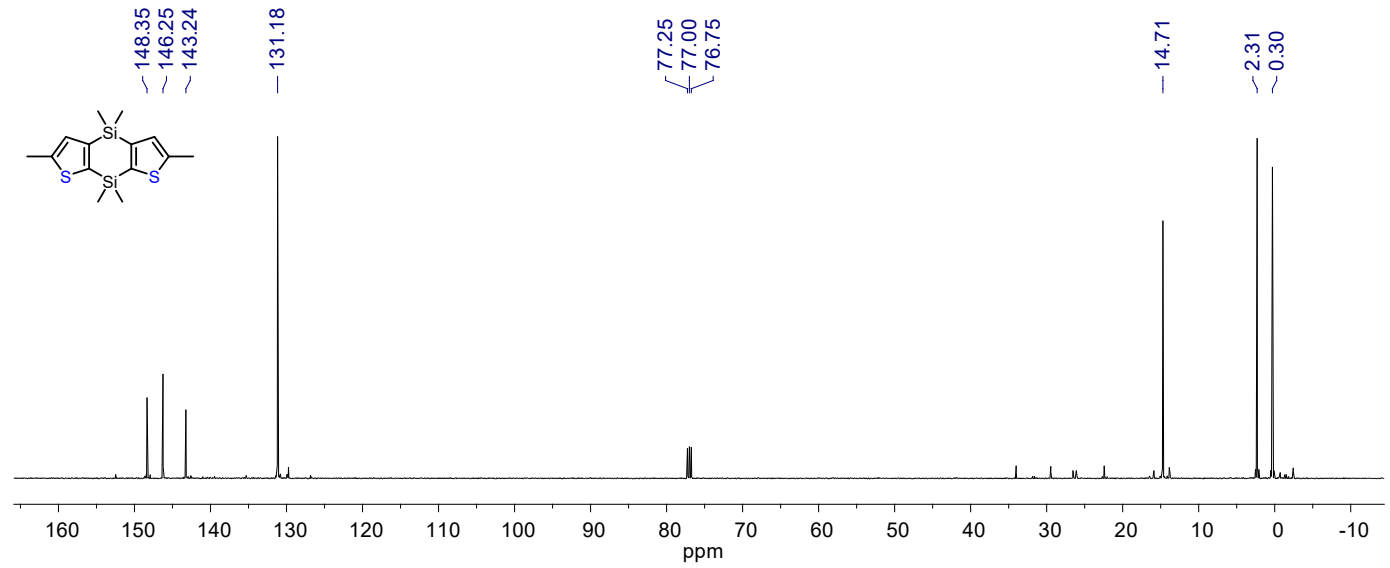


Figure S25 ^{13}C NMR spectrum of ***syn*-7** in $CDCl_3$ at room temperature (126 MHz).

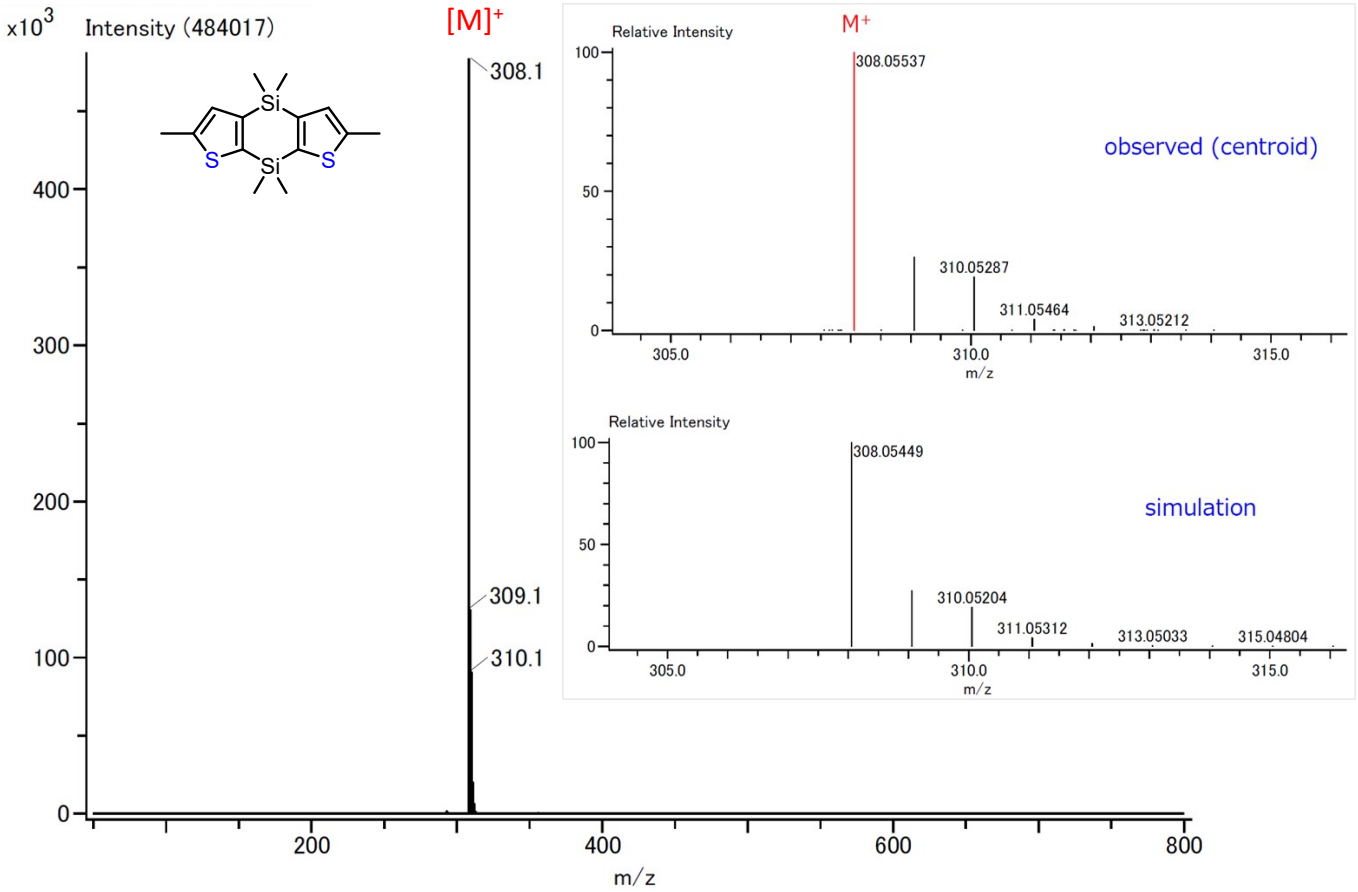


Figure S26 High resolution FI-mass spectrum of ***syn*-7**.

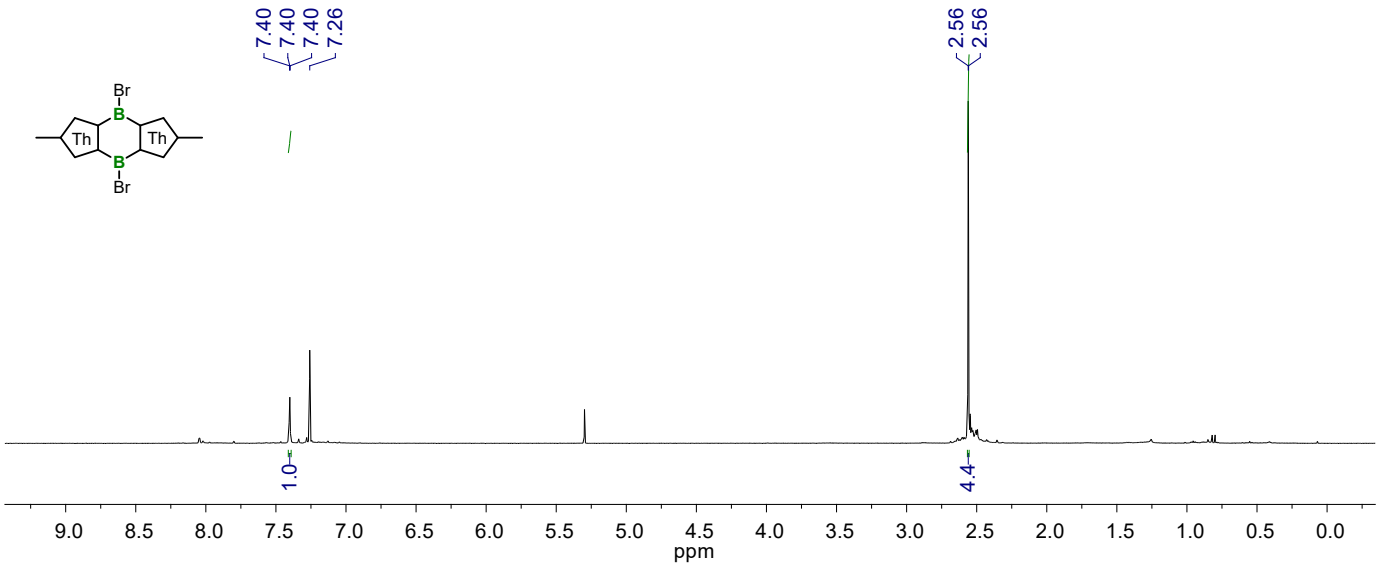


Figure S27 ^{1}H NMR spectrum of $\mathbf{3^{Br}}$ in $CDCl_3$ at room temperature (500 MHz).

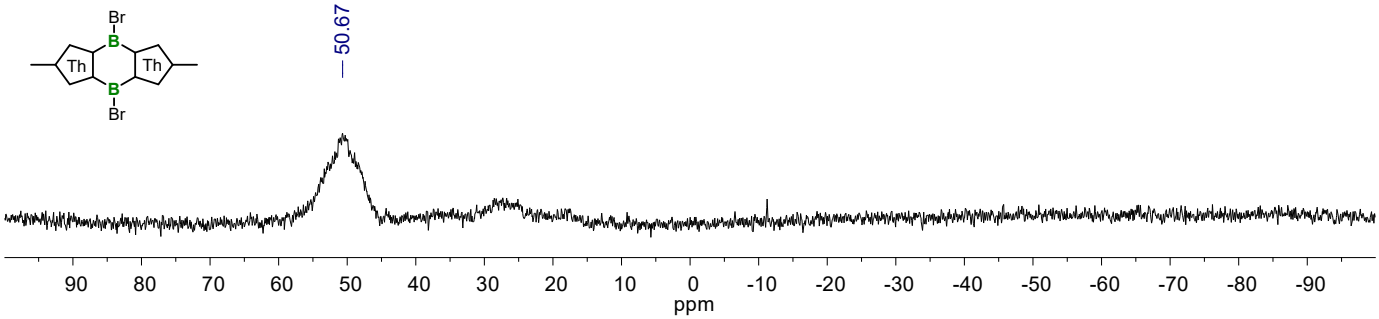


Figure S28 ^{11}B NMR spectrum of **3^{Br}** in $CDCl_3$ at room temperature (160 MHz).

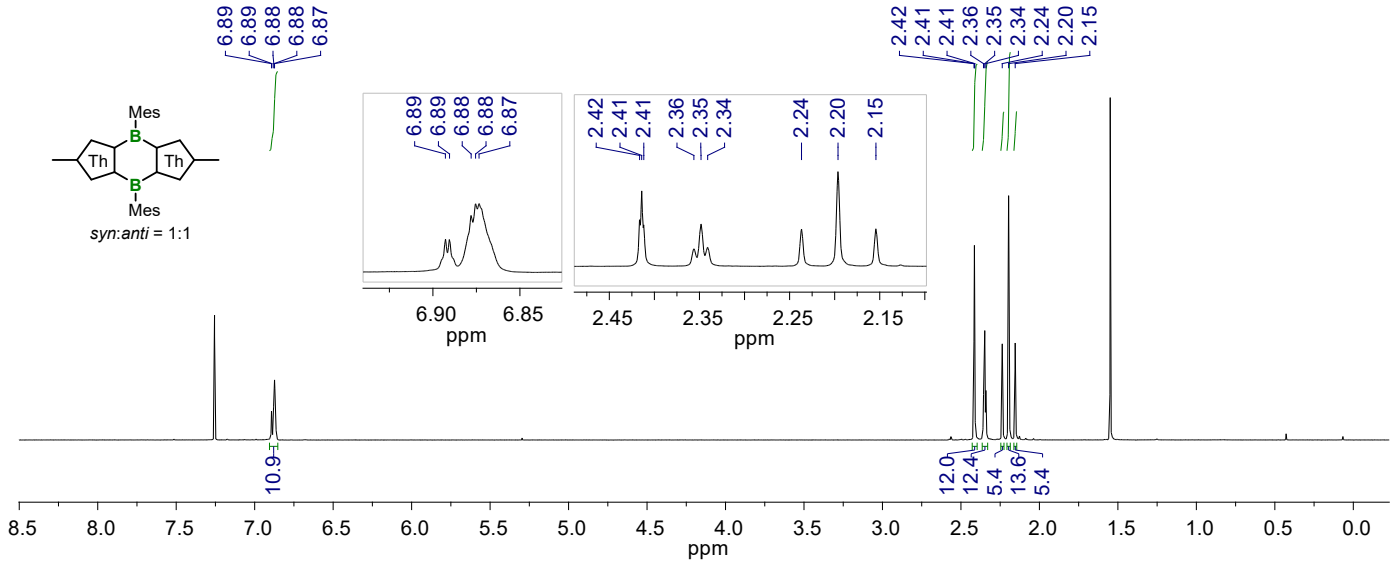


Figure S29 ^{1}H NMR spectrum of **A-3^{Mes}** in $CDCl_3$ at room temperature (400 MHz).

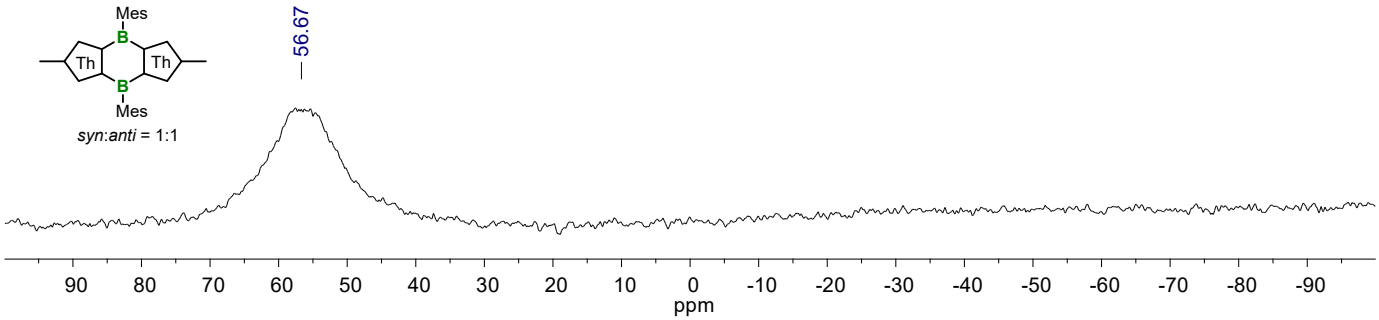


Figure S30 ^{11}B NMR spectrum of **A-3^{Mes}** in C_6D_6 at room temperature (160 MHz).

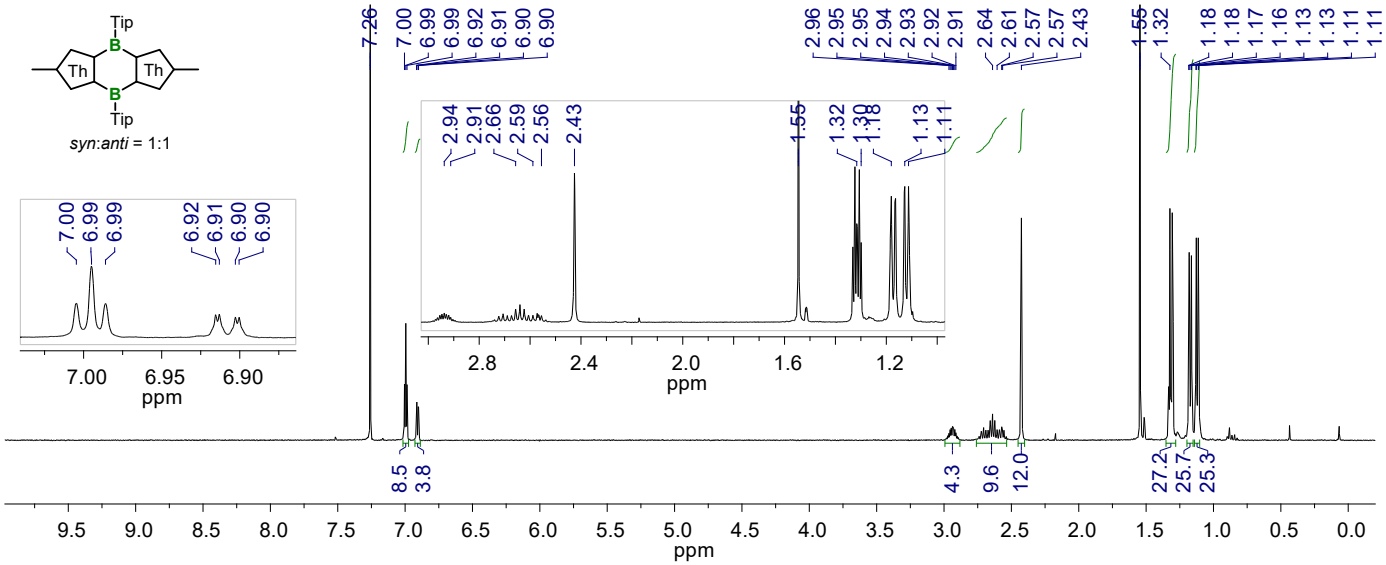


Figure S31 ^{1}H NMR spectrum of **A-3^{Tip}** in $CDCl_3$ at room temperature (400 MHz).

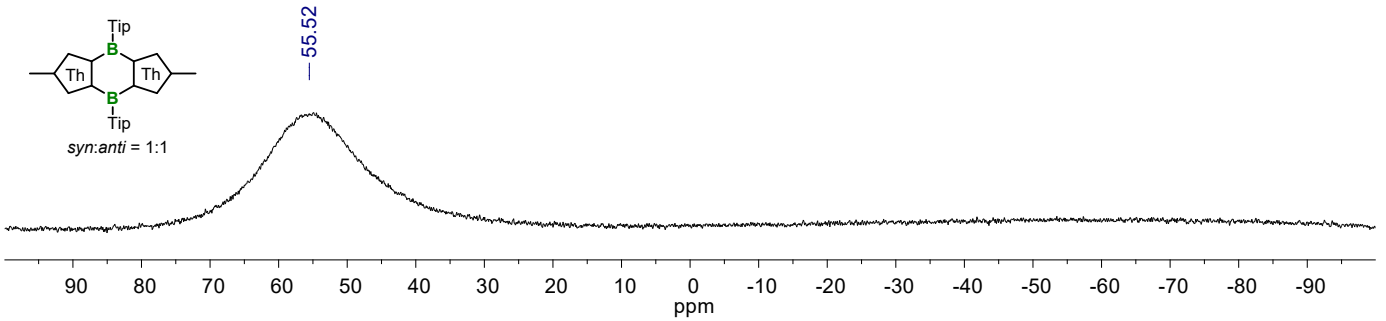


Figure S32 ^{11}B NMR spectrum of **A-3^{Tip}** in $CDCl_3$ at room temperature (160 MHz).

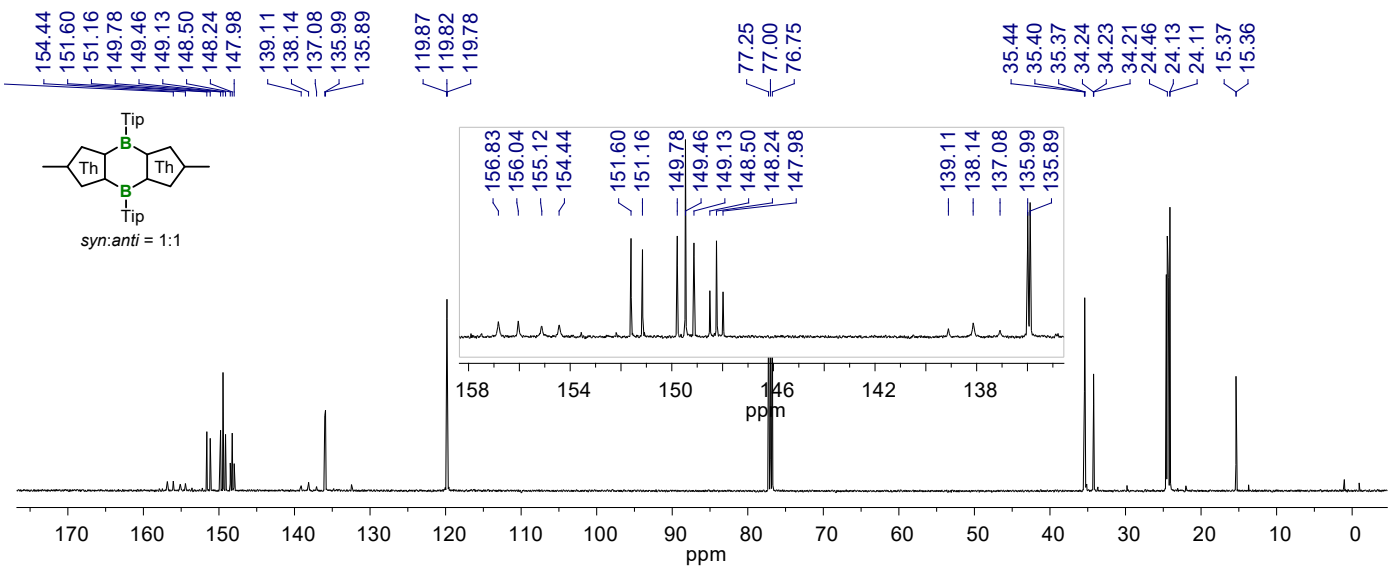


Figure S33 ^{13}C NMR spectrum of **A-3^{Tip}** in $CDCl_3$ at room temperature (126 MHz).

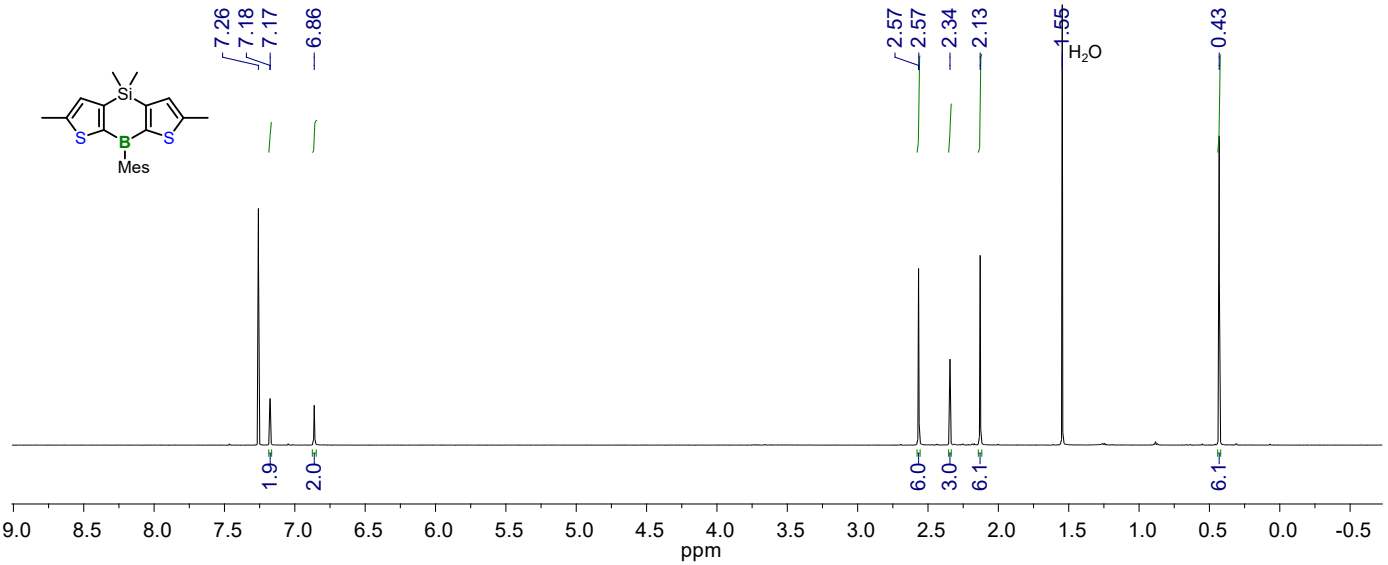


Figure S34 ^{1}H NMR spectrum of ***syn*-8^{Mes}** in $CDCl_3$ at room temperature (500 MHz).

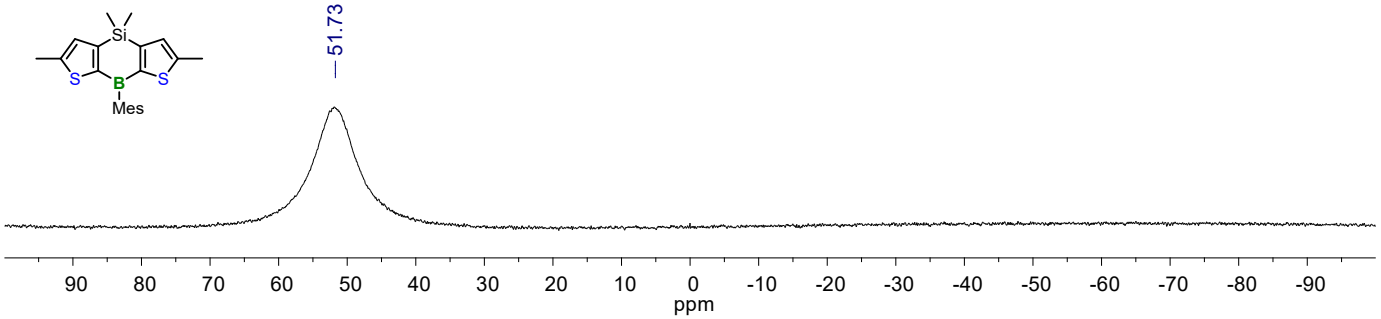


Figure S35 ^{11}B NMR spectrum of ***syn*-8^{Mes}** in $CDCl_3$ at room temperature (160 MHz).

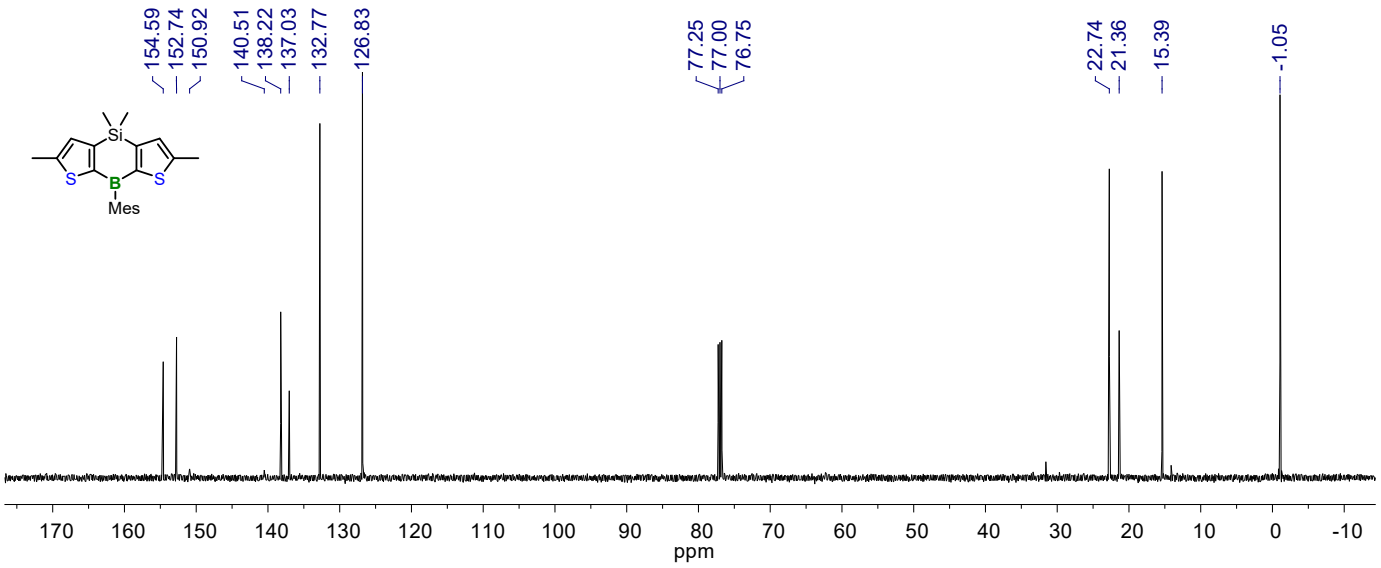


Figure S36 ^{13}C NMR spectrum of ***syn*-8^{Mes}** in $CDCl_3$ at room temperature (126 MHz).

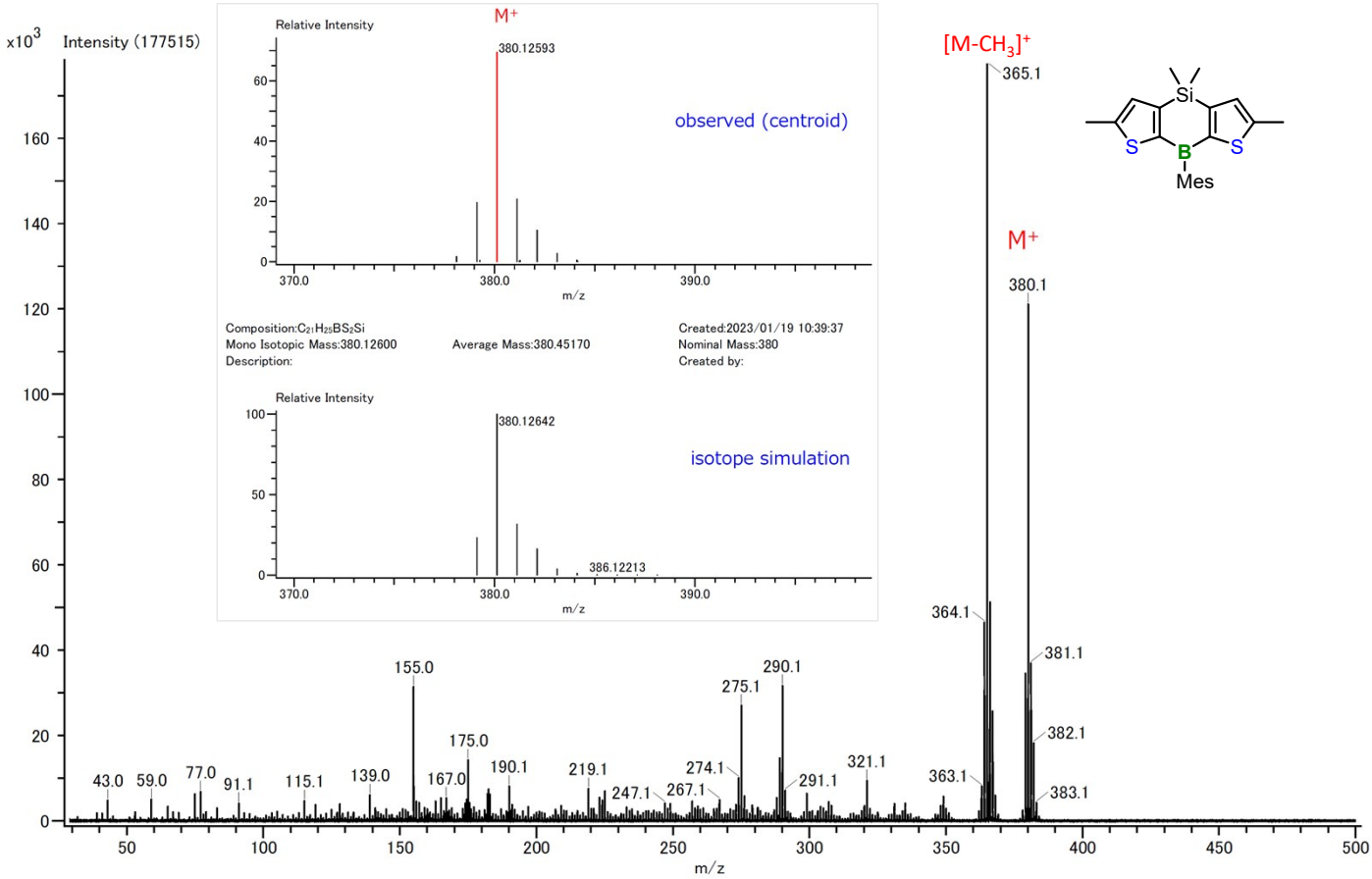


Figure S37 High resolution APCI-mass spectrum of ***syn*-8^{Mes}**.

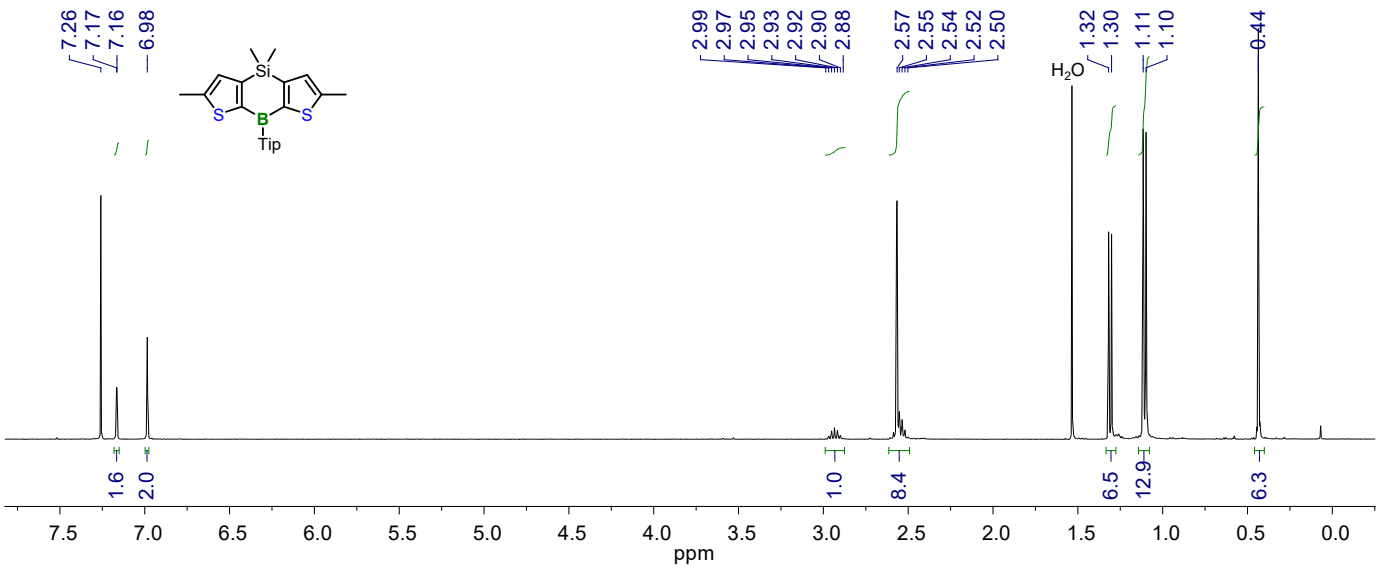


Figure S38 ^{1}H NMR spectrum of ***syn*-8^{Tip}** in $CDCl_3$ at room temperature (400 MHz).

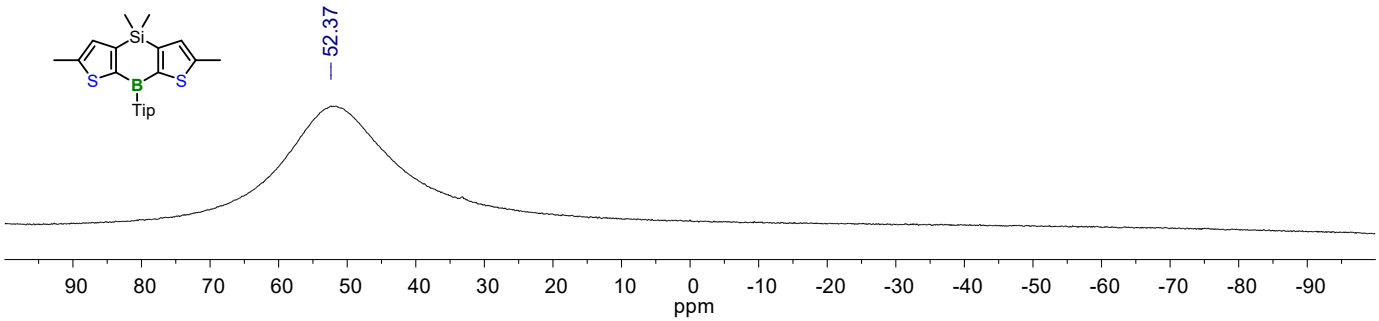


Figure S39 ^{11}B NMR spectrum of ***syn*-8^{Tip}** in $CDCl_3$ at room temperature (160 MHz).

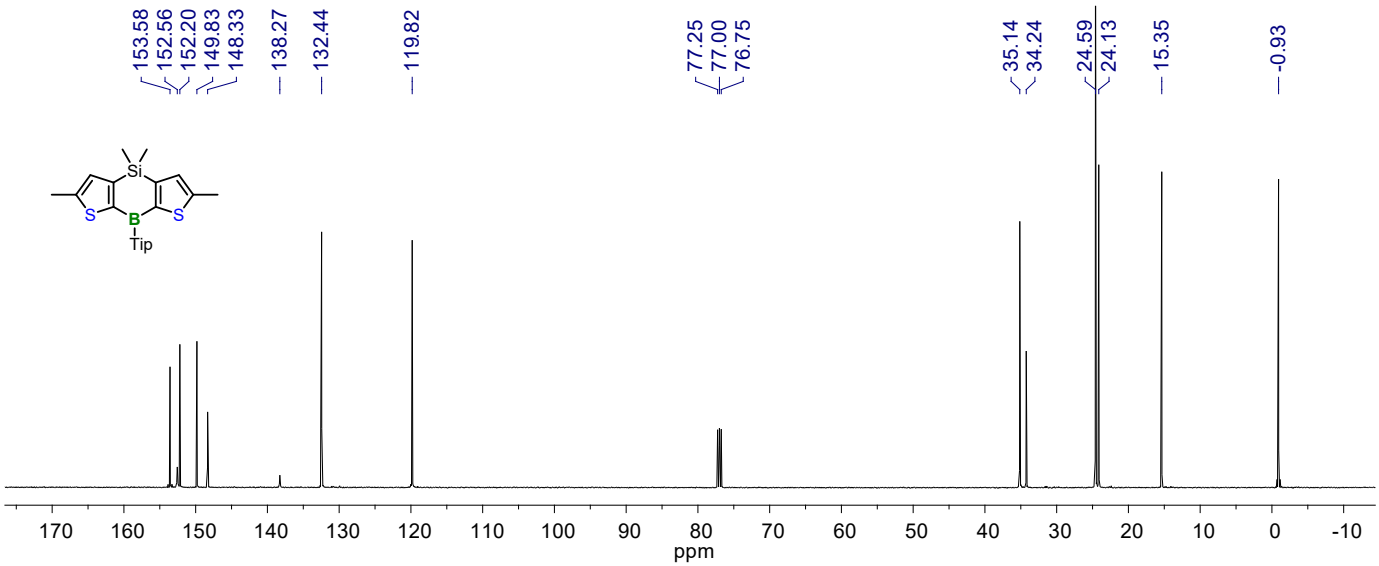


Figure S40 ^{13}C NMR spectrum of ***syn*-8^{Tip}** in $CDCl_3$ at room temperature (126 MHz).

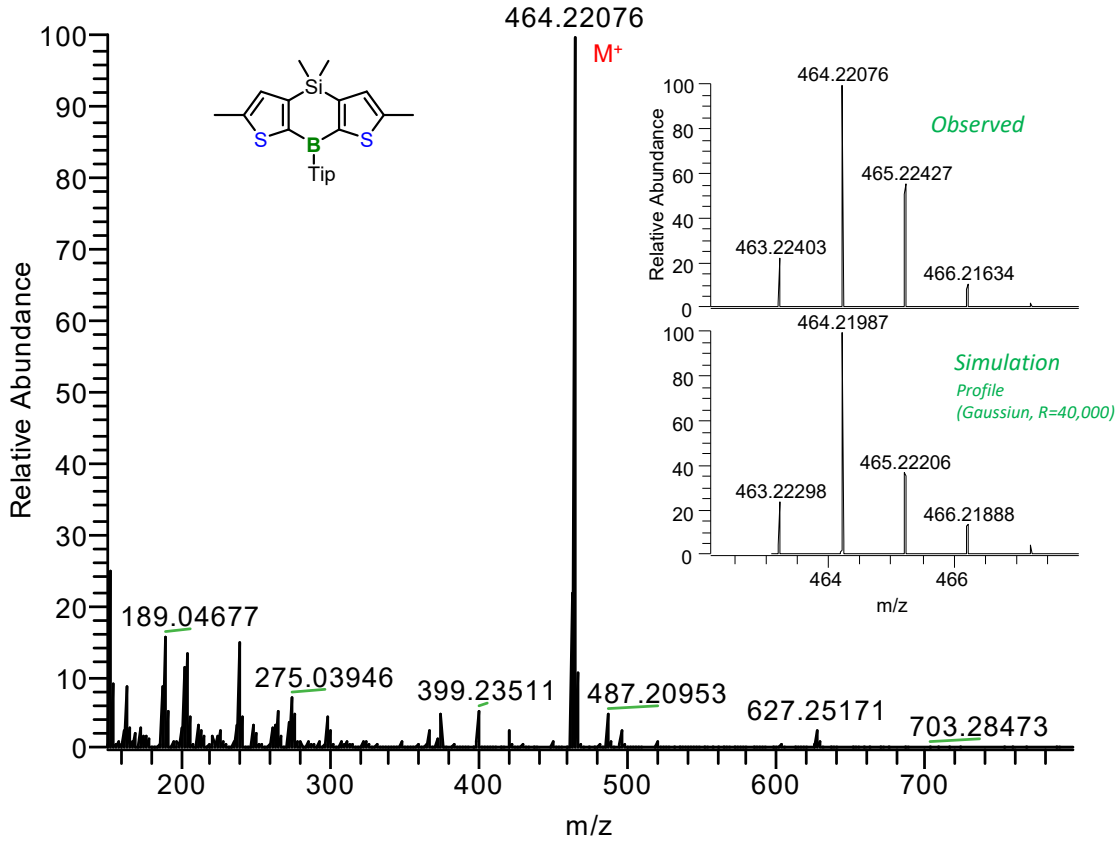


Figure S41 High resolution APCI-mass spectrum of ***syn*-8^{Tip}**.

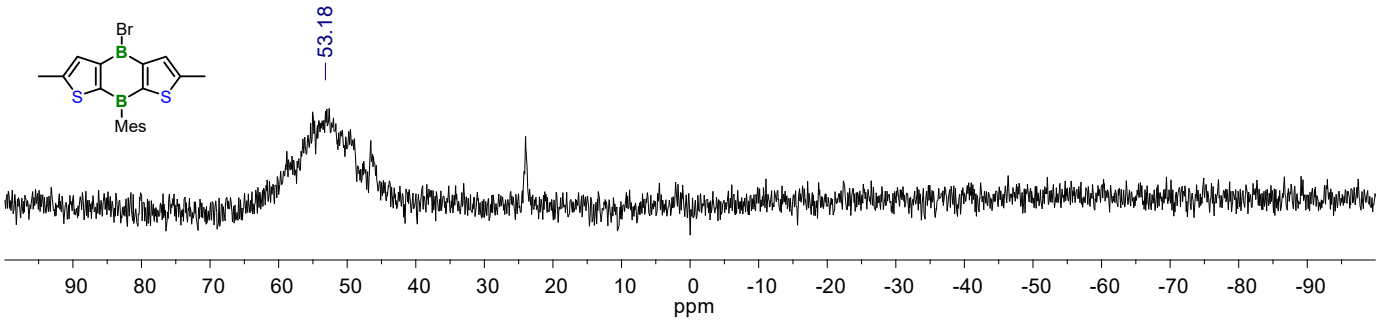


Figure S42 ^{11}B NMR spectrum of **9^{Mes-Br}** in $CDCl_3$ at room temperature (160 MHz).

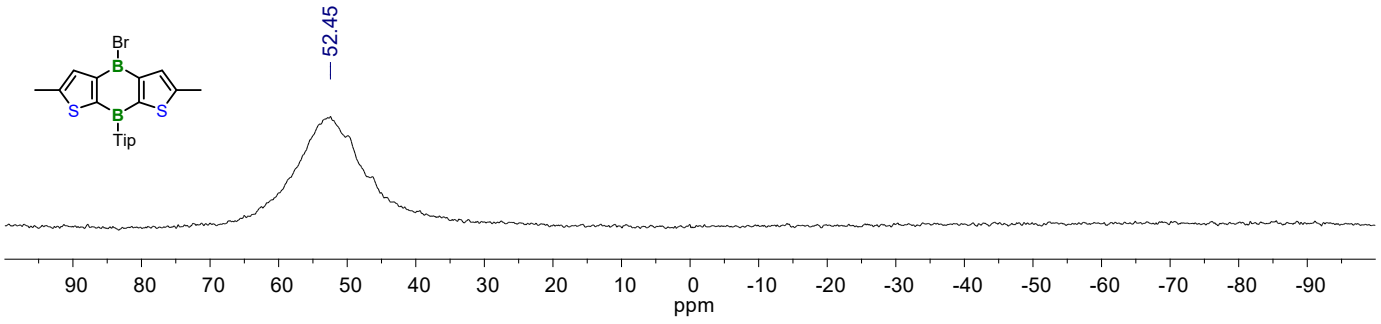


Figure S43 ^{11}B NMR spectrum of **9^{Tip-Br}** in $CDCl_3$ at room temperature (160 MHz).

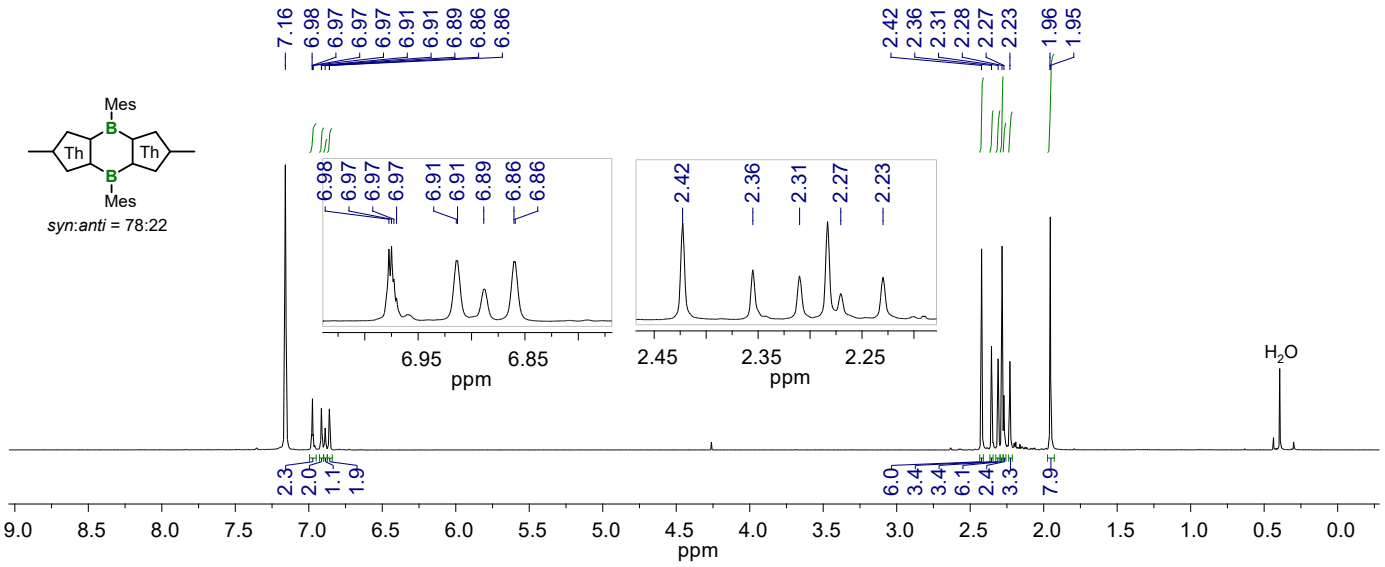


Figure S44 ^{1}H NMR spectrum of **B-3^{Mes}** in $CDCl_3$ at room temperature (400 MHz).

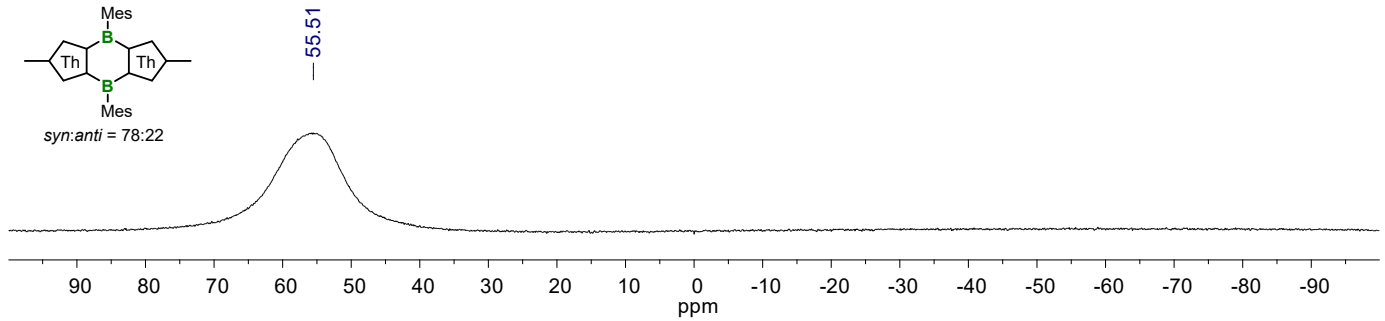


Figure S45 ^{11}B NMR spectrum of **B-3^{Mes}** in $CDCl_3$ at room temperature (160 MHz).

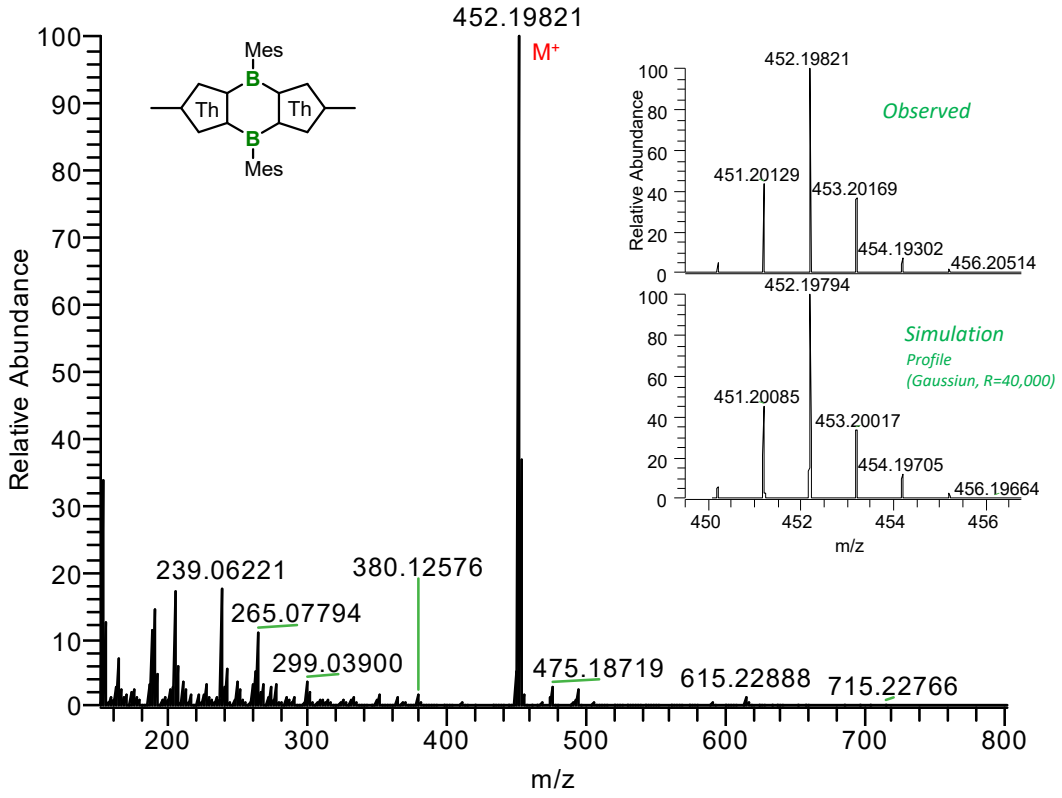


Figure S46 High resolution APCI-mass spectrum of **B-3^{Mes}**.

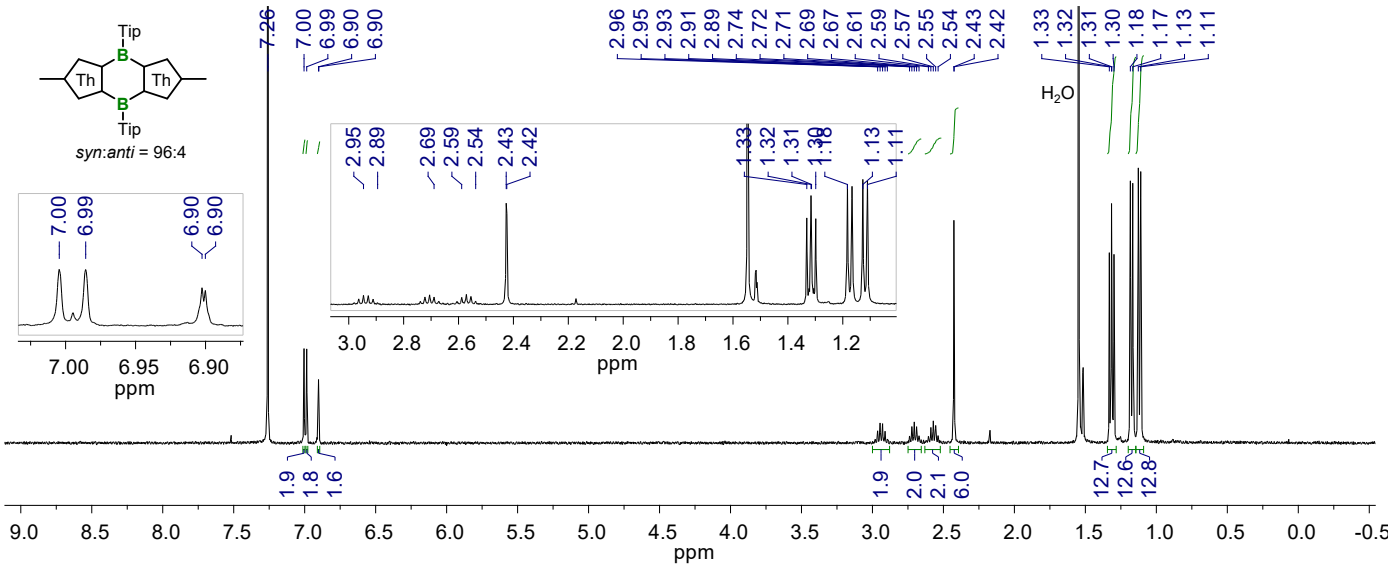


Figure S47 ^{1}H NMR spectrum of **B-3^{Tip}** in $CDCl_3$ at room temperature (400 MHz).

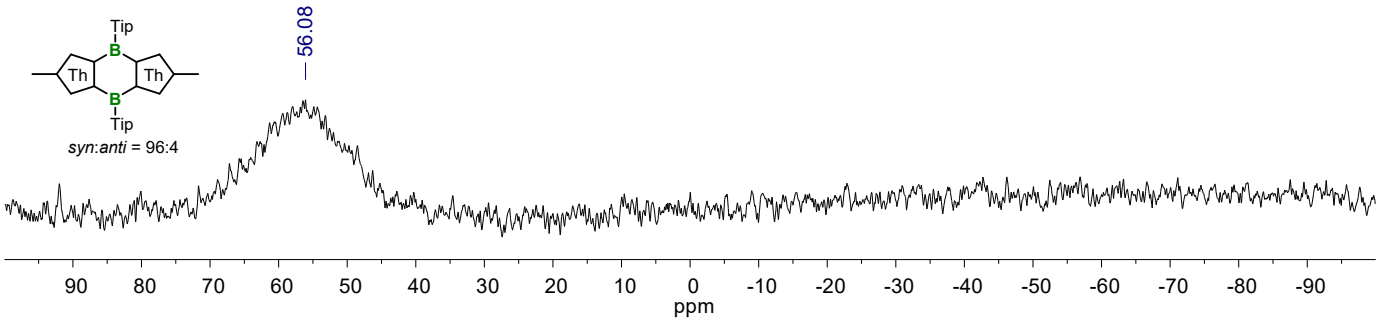


Figure S48 ^{11}B NMR spectrum of **B-3^{Tip}** in $CDCl_3$ at room temperature (160 MHz).

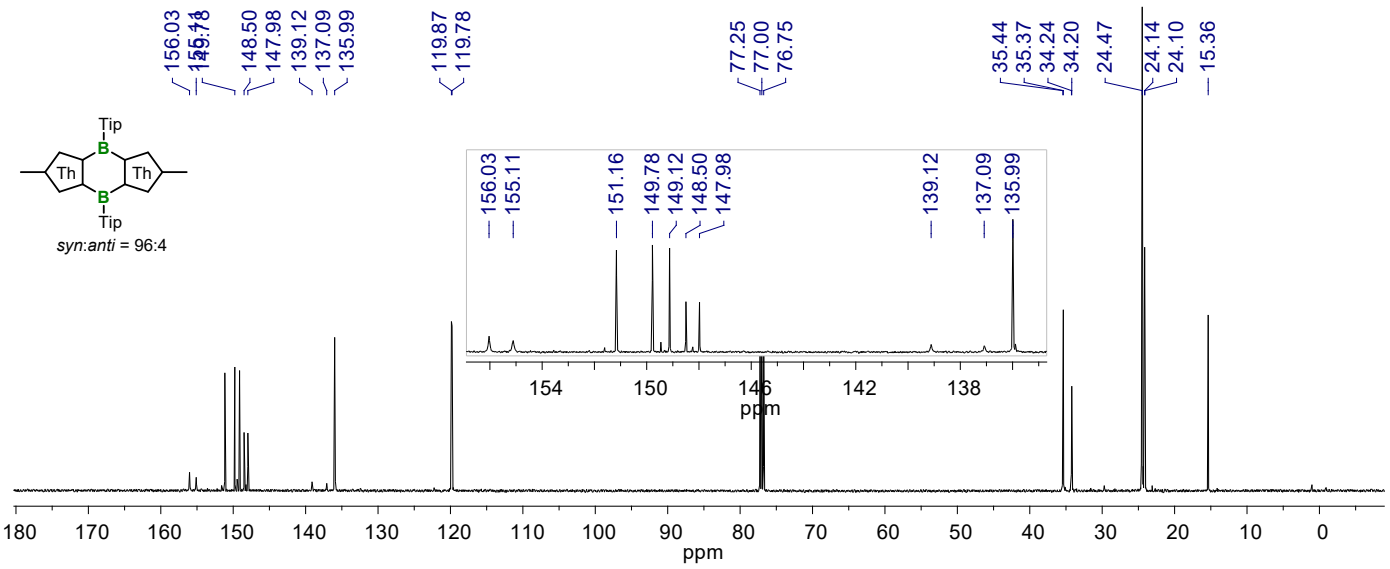


Figure S49 ^{13}C NMR spectrum of **B-3^{Tip}** in $CDCl_3$ at room temperature (126 MHz).

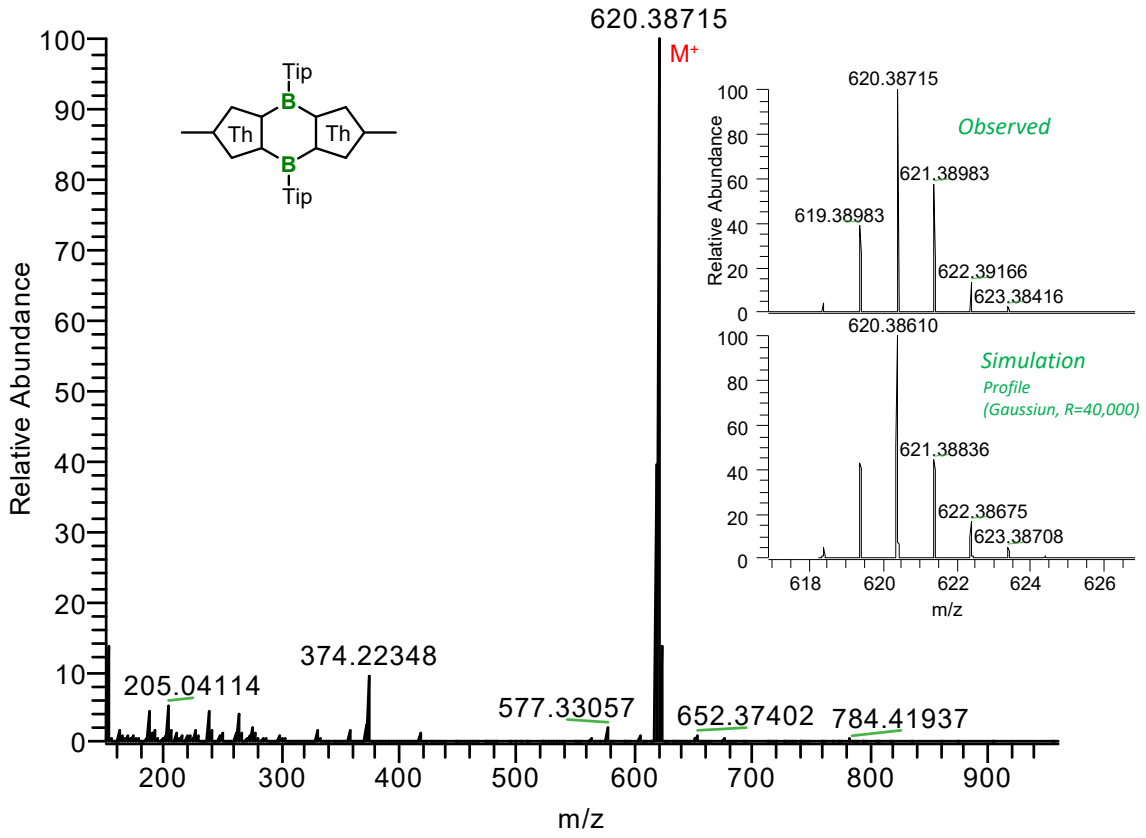


Figure S50 High resolution APCI-mass spectrum of **B-3^{Tip}**.

Cartesian coordinates for optimized structures

Table S6 Optimized cartesian coordinates of ***syn*-3^{Br}**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.342437	0.781242	-0.000314
2	6	0	-1.308288	-0.616025	-0.000186
3	6	0	1.308292	-0.616016	-0.000197
4	6	0	1.342433	0.781250	-0.000327
5	16	0	2.917994	-1.269153	-0.000045
6	6	0	3.644000	0.315523	-0.000058
7	6	0	2.672523	1.290201	-0.000236
8	16	0	-2.917986	-1.269171	0.000003
9	6	0	-3.644002	0.315501	-0.000022
10	6	0	-2.672531	1.290185	-0.000201
11	5	0	0.000004	-1.418157	-0.000288
12	5	0	-0.000005	1.550160	-0.000509
13	6	0	5.132872	0.495352	0.000130
14	1	0	5.597485	0.042163	0.884100
15	1	0	5.597835	0.041236	-0.883175
16	1	0	5.378354	1.561548	-0.000375
17	6	0	-5.132874	0.495321	0.000112
18	1	0	-5.597736	0.041687	-0.883498
19	1	0	-5.597584	0.041644	0.883777
20	1	0	-5.378363	1.561515	0.000158
21	35	0	-0.000011	3.480951	-0.000545
22	35	0	0.000011	-3.344409	0.000274
23	1	0	2.903488	2.350788	-0.000303
24	1	0	-2.903502	2.350770	-0.000258

Table S7 Optimized cartesian coordinates of ***anti*-3^{Br}**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.404982	0.454546	-0.000296
2	6	0	1.203123	-0.928592	-0.000066
3	16	0	3.103448	0.825329	0.000180
4	6	0	3.549422	-0.858368	0.000155
5	6	0	2.426641	-1.655473	0.000101
6	5	0	0.251473	1.462658	-0.000801
7	5	0	-0.251473	-1.462658	-0.000123
8	6	0	-1.404982	-0.454546	-0.000286
9	6	0	-1.203122	0.928592	-0.000508
10	16	0	-3.103447	-0.825329	-0.000478
11	6	0	-2.426641	1.655473	-0.000324
12	6	0	-3.549422	0.858368	-0.000125
13	6	0	4.985888	-1.289377	0.000348
14	1	0	5.521215	-0.920840	-0.882938
15	1	0	5.520706	-0.921664	0.884289
16	1	0	5.046380	-2.381766	-0.000139

17	6	0	-4.985888	1.289377	0.000143
18	1	0	-5.521080	0.921385	-0.883454
19	1	0	-5.520841	0.921119	0.883774
20	1	0	-5.046379	2.381766	0.000315
21	35	0	-0.595116	-3.360455	-0.000419
22	35	0	0.595116	3.360454	0.000231
23	1	0	-2.474982	2.739846	-0.000318
24	1	0	2.474983	-2.739846	0.000169

Table S8 Optimized cartesian coordinates of ***syn*-1^{Br}**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	2.881979	1.771554	-0.024454
2	6	0	1.312631	1.015550	0.008531
3	6	0	1.363637	-0.374828	-0.030978
4	6	0	2.734602	-0.852937	-0.109545
5	6	0	3.673289	0.218553	-0.116255
6	5	0	0.000031	-1.131174	0.053840
7	6	0	-3.673324	0.218393	-0.116222
8	6	0	-2.734599	-0.853067	-0.109549
9	6	0	-1.363644	-0.374911	-0.030964
10	6	0	-1.312700	1.015475	0.008554
11	16	0	-2.882076	1.771421	-0.024392
12	35	0	0.000168	-3.046095	0.358751
13	5	0	-0.000055	1.808059	0.053898
14	6	0	-3.249114	-2.166649	-0.201819
15	6	0	-5.055616	0.008454	-0.196321
16	35	0	-0.000107	3.727655	0.125756
17	6	0	5.055586	0.008647	-0.196357
18	6	0	5.520523	-1.294960	-0.278914
19	6	0	4.616335	-2.374310	-0.284073
20	6	0	3.249139	-2.166511	-0.201762
21	6	0	-4.616306	-2.374481	-0.284129
22	6	0	-5.520523	-1.295160	-0.278921
23	1	0	-2.572924	-3.010589	-0.205536
24	1	0	-5.743946	0.848496	-0.197433
25	1	0	5.743894	0.848707	-0.197500
26	1	0	6.588454	-1.483589	-0.343510
27	1	0	4.997010	-3.389372	-0.354759
28	1	0	2.572956	-3.010465	-0.205435
29	1	0	-4.996955	-3.389551	-0.354854
30	1	0	-6.588450	-1.483814	-0.343516

Table S9 Optimized cartesian coordinates of ***anti*-1^{Br}**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	16	0	2.084474	-2.429796	0.000032
2	6	0	0.936860	-1.116311	-0.000001
3	6	0	1.549026	0.133881	-0.000026
4	6	0	2.995677	0.034078	-0.000017

5	6	0	3.433657	-1.318939	0.000014
6	5	0	0.595991	1.347632	-0.000058
7	6	0	-5.729986	0.644693	0.000027
8	6	0	-5.322511	-0.703454	0.000043
9	6	0	-4.790408	1.665551	0.000001
10	6	0	-3.979810	-1.046439	0.000033
11	35	0	1.206860	3.179669	0.000027
12	5	0	-0.595991	-1.347632	0.000002
13	35	0	-1.206860	-3.179669	-0.000019
14	6	0	4.790408	-1.665551	0.000028
15	6	0	5.729986	-0.644693	0.000010
16	6	0	5.322511	0.703454	-0.000021
17	6	0	3.979810	1.046439	-0.000035
18	16	0	-2.084474	2.429796	-0.000041
19	6	0	-0.936860	1.116311	-0.000034
20	6	0	-1.549026	-0.133881	-0.000007
21	6	0	-2.995677	-0.034077	0.000007
22	6	0	-3.433657	1.318939	-0.000009
23	1	0	-6.788723	0.888216	0.000035
24	1	0	-6.073823	-1.488148	0.000063
25	1	0	-5.097568	2.707223	-0.000012
26	1	0	-3.679621	-2.086695	0.000046
27	1	0	5.097568	-2.707223	0.000052
28	1	0	6.788723	-0.888216	0.000020
29	1	0	6.073823	1.488148	-0.000035
30	1	0	3.679621	2.086695	-0.000059

Table S10 Optimized cartesian coordinates of ***syn*-3^{Mes}**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.764483	-1.326586	-0.061543
2	6	0	-0.629788	-1.288833	-0.059493
3	6	0	-0.630154	1.288802	0.058984
4	6	0	0.764107	1.327021	0.060938
5	16	0	-1.291277	2.896569	0.150045
6	6	0	0.290540	3.627242	0.191310
7	6	0	1.267993	2.658177	0.139140
8	16	0	-1.290394	-2.896741	-0.151759
9	6	0	0.291671	-3.626841	-0.193869
10	6	0	1.268823	-2.657518	-0.140834
11	5	0	-1.475393	-0.000156	0.000055
12	5	0	1.578590	0.000301	0.000304
13	6	0	-3.040032	-0.000120	0.000509
14	6	0	-3.753355	0.097537	-1.210892
15	6	0	-5.149938	0.091516	-1.194631
16	6	0	-5.866836	-0.005407	0.001009
17	6	0	-5.149130	-0.105246	1.195945
18	6	0	-3.752557	-0.103237	1.211941
19	6	0	3.143932	0.000587	0.000849
20	6	0	3.859285	0.324524	-1.170418
21	6	0	5.256171	0.311631	-1.157292
22	6	0	5.974649	-0.004627	-0.001187
23	6	0	5.256641	-0.323512	1.154513
24	6	0	3.859771	-0.328469	1.170418
25	1	0	2.327825	2.894151	0.157878
26	1	0	2.328731	-2.893133	-0.159942

27	1	0	-5.691288	0.162564	-2.136269
28	1	0	-5.689852	-0.187499	2.137039
29	1	0	5.796706	0.551524	-2.071204
30	1	0	5.797692	-0.574422	2.065183
31	6	0	3.115568	-0.668988	2.442583
32	1	0	2.459450	0.154129	2.753616
33	1	0	2.476100	-1.549983	2.309878
34	1	0	3.805600	-0.874297	3.266927
35	6	0	7.483776	0.023506	0.006475
36	1	0	7.862282	1.017259	0.281223
37	1	0	7.893789	-0.690192	0.729031
38	1	0	7.893757	-0.217907	-0.979989
39	6	0	3.114458	0.659340	-2.443758
40	1	0	2.455968	-0.163739	-2.749812
41	1	0	2.477312	1.542613	-2.314953
42	1	0	3.804081	0.858826	-3.269878
43	6	0	-3.003404	0.199007	-2.519874
44	1	0	-2.354260	1.083341	-2.539335
45	1	0	-2.357311	-0.673935	-2.677425
46	1	0	-3.688642	0.266746	-3.370484
47	6	0	-7.375975	0.024254	0.004071
48	1	0	-7.753547	1.052001	0.090270
49	1	0	-7.786470	-0.395438	-0.920511
50	1	0	-7.785733	-0.543294	0.846393
51	6	0	-3.001767	-0.211266	2.519912
52	1	0	-2.354670	-1.097156	2.536183
53	1	0	-2.353507	0.659695	2.679550
54	1	0	-3.686466	-0.279858	3.370887
55	6	0	0.468407	5.112397	0.275145
56	1	0	0.016566	5.625222	-0.582359
57	1	0	0.010974	5.526306	1.181705
58	1	0	1.534393	5.358111	0.292304
59	6	0	0.470020	-5.111852	-0.279179
60	1	0	0.018509	-5.625650	0.577916
61	1	0	0.012531	-5.525022	-1.186044
62	1	0	1.536084	-5.357183	-0.296793

Table S11 Optimized cartesian coordinates of ***syn*-3^{Mes}•F^{-}**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.741360	1.341143	-0.304890
2	6	0	0.617142	1.330505	-0.604974
3	6	0	0.598786	-1.272993	-0.763637
4	6	0	-0.760998	-1.300813	-0.474358
5	16	0	1.205923	-2.896396	-0.942591
6	6	0	-0.367255	-3.622537	-0.630454
7	6	0	-1.288948	-2.641648	-0.403895
8	16	0	1.243586	2.956352	-0.595589
9	6	0	-0.319530	3.660473	-0.196865
10	6	0	-1.251623	2.670760	-0.074870
11	5	0	-1.517842	0.015348	-0.231386
12	6	0	2.918292	-0.010207	-0.094789
13	6	0	4.211013	0.133301	-0.661038
14	6	0	5.355579	0.088078	0.148413
15	6	0	5.287690	-0.092992	1.527305
16	6	0	4.019713	-0.218235	2.092092

17	6	0	2.857795	-0.180435	1.314184
18	6	0	-3.058343	0.003916	0.121385
19	6	0	-4.029383	0.269705	-0.864368
20	6	0	-5.387871	0.257292	-0.534033
21	6	0	-5.820597	-0.013253	0.766694
22	6	0	-4.853014	-0.268309	1.741940
23	6	0	-3.488659	-0.265924	1.436199
24	1	0	-2.333025	-2.854969	-0.186016
25	1	0	-2.290414	2.869247	0.179197
26	1	0	6.333295	0.203079	-0.320173
27	1	0	3.928265	-0.346254	3.170956
28	1	0	-6.125440	0.464833	-1.308927
29	1	0	-5.168064	-0.472400	2.764980
30	6	0	-2.465022	-0.542056	2.514453
31	1	0	-1.863337	-1.425483	2.270411
32	1	0	-1.760645	0.292854	2.614630
33	1	0	-2.940189	-0.706555	3.488122
34	6	0	-7.292737	-0.057115	1.102569
35	1	0	-7.709281	-1.066064	0.971591
36	1	0	-7.475168	0.233330	2.143784
37	1	0	-7.870959	0.615630	0.458489
38	6	0	-3.589954	0.570001	-2.279495
39	1	0	-2.960061	1.466869	-2.314293
40	1	0	-2.983998	-0.248846	-2.686443
41	1	0	-4.447761	0.724383	-2.943812
42	6	0	4.452062	0.351767	-2.144237
43	1	0	4.081637	-0.482863	-2.744320
44	1	0	3.934498	1.240285	-2.514713
45	1	0	5.526450	0.470162	-2.334328
46	6	0	6.535945	-0.172683	2.373617
47	1	0	6.850279	-1.213137	2.542159
48	1	0	7.376653	0.344350	1.895836
49	1	0	6.381421	0.277877	3.361885
50	6	0	1.540513	-0.323044	2.045409
51	1	0	0.850663	0.487915	1.795042
52	1	0	1.029669	-1.254610	1.781034
53	1	0	1.698788	-0.318263	3.130423
54	6	0	-0.565234	-5.107539	-0.634325
55	1	0	-0.325013	-5.556047	-1.608045
56	1	0	0.060841	-5.611958	0.114300
57	1	0	-1.611166	-5.343516	-0.407883
58	6	0	-0.498339	5.138067	-0.025649
59	1	0	0.132961	5.542583	0.777254
60	1	0	-0.250882	5.694980	-0.939730
61	1	0	-1.541493	5.359157	0.227074
62	9	0	1.830185	0.113856	-2.399985
63	5	0	1.540577	0.040267	-0.993018

Table S12 Optimized cartesian coordinates of ***syn*-3^{Mes}•2F$^-$**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.697354	1.326866	0.273226
2	6	0	0.524275	1.288841	-0.360134
3	6	0	0.595371	-1.300561	-0.227107
4	6	0	-0.625570	-1.343025	0.406878
5	16	0	1.214716	-2.947086	-0.483935

6	6	0	-0.194479	-3.673808	0.265020
7	6	0	-1.053586	-2.690050	0.677694
8	16	0	1.064988	2.935499	-0.758042
9	6	0	-0.375777	3.655398	-0.063039
10	6	0	-1.189790	2.670262	0.428630
11	6	0	2.953907	0.042283	-0.287794
12	6	0	4.077587	-0.071323	-1.145991
13	6	0	5.385833	-0.030291	-0.637542
14	6	0	5.649724	0.115259	0.721359
15	6	0	4.551485	0.223421	1.574884
16	6	0	3.235434	0.188494	1.100789
17	6	0	-3.015379	-0.044001	0.352633
18	6	0	-3.322821	-0.229988	-1.025909
19	6	0	-4.646245	-0.244442	-1.481177
20	6	0	-5.729538	-0.079845	-0.617208
21	6	0	-5.441270	0.116350	0.730801
22	6	0	-4.124694	0.139249	1.218748
23	1	0	-2.000086	-2.917415	1.167861
24	1	0	-2.147802	2.893205	0.898152
25	1	0	6.224084	-0.117907	-1.331908
26	1	0	4.720773	0.339008	2.647110
27	1	0	-4.833933	-0.385507	-2.547406
28	1	0	-6.266373	0.262515	1.431426
29	6	0	-3.972819	0.382545	2.711067
30	1	0	-3.481737	-0.455842	3.210827
31	1	0	-3.344516	1.252582	2.917684
32	1	0	-4.960255	0.541670	3.169110
33	6	0	-7.153110	-0.132804	-1.120737
34	1	0	-7.501215	-1.164993	-1.284565
35	1	0	-7.846261	0.329405	-0.405853
36	1	0	-7.264594	0.391576	-2.079791
37	6	0	-2.236320	-0.420872	-2.061055
38	1	0	-1.455187	0.338876	-1.979875
39	1	0	-1.722399	-1.377657	-1.928555
40	1	0	-2.659861	-0.389176	-3.074325
41	6	0	3.954331	-0.246096	-2.650067
42	1	0	3.375170	-1.136690	-2.906324
43	1	0	3.428325	0.591562	-3.113963
44	1	0	4.953760	-0.332309	-3.101140
45	6	0	7.063611	0.125605	1.254190
46	1	0	7.341383	-0.833362	1.719062
47	1	0	7.789288	0.316928	0.453159
48	1	0	7.203715	0.898844	2.022331
49	6	0	2.130849	0.318754	2.124837
50	1	0	1.553674	1.236239	1.978558
51	1	0	1.401710	-0.491275	2.043662
52	1	0	2.546362	0.323096	3.141841
53	6	0	-0.355003	-5.157536	0.400972
54	1	0	-0.351223	-5.676227	-0.570425
55	1	0	0.442042	-5.618155	1.005526
56	1	0	-1.311081	-5.383849	0.890294
57	6	0	-0.608886	5.135652	-0.055863
58	1	0	0.169647	5.686232	0.495192
59	1	0	-0.639885	5.566205	-1.069000
60	1	0	-1.570632	5.357153	0.424434
61	9	0	1.356583	-0.075372	-2.269302
62	5	0	1.385745	-0.009529	-0.816451
63	9	0	-1.390485	0.055700	2.315037
64	5	0	-1.434075	-0.004134	0.854108

Table S13 Optimized cartesian coordinates of ***anti*-3^{Mes}**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.702976	-1.279666	-0.000656
2	6	0	0.690734	-1.338828	0.002800
3	16	0	-1.385224	-2.882492	0.012759
4	6	0	0.185602	-3.634647	0.017726
5	6	0	1.177243	-2.677520	0.010754
6	5	0	-1.526608	0.021638	-0.002736
7	6	0	-3.091714	0.033094	-0.007498
8	6	0	-3.805947	0.183985	1.198085
9	6	0	-5.202461	0.202870	1.179463
10	6	0	-5.919567	0.077029	-0.013480
11	6	0	-5.201324	-0.063743	-1.203936
12	6	0	-3.804727	-0.091019	-1.216645
13	1	0	2.233772	-2.928261	0.011475
14	1	0	-5.743628	0.319193	2.116783
15	1	0	-5.741647	-0.152481	-2.144720
16	6	0	-3.056131	0.317295	2.504461
17	1	0	-2.438885	-0.568704	2.700891
18	1	0	-2.377663	1.179506	2.489550
19	1	0	-3.740399	0.441838	3.349475
20	6	0	-7.428979	0.067537	-0.012960
21	1	0	-7.820334	-0.951898	0.104482
22	1	0	-7.832962	0.666358	0.810345
23	1	0	-7.832310	0.463332	-0.951150
24	6	0	-3.055235	-0.240768	-2.521606
25	1	0	-2.347839	0.584717	-2.672809
26	1	0	-2.469962	-1.168314	-2.540864
27	1	0	-3.738223	-0.257340	-3.376620
28	5	0	1.526610	-0.021607	-0.002803
29	6	0	0.702974	1.279701	-0.000060
30	6	0	3.091716	-0.033071	-0.007547
31	6	0	-0.690739	1.338862	0.003436
32	16	0	1.385218	2.882524	0.013750
33	6	0	3.805896	-0.184981	1.197947
34	6	0	3.804781	0.092011	-1.216561
35	6	0	-1.177248	2.677552	0.011660
36	6	0	-0.185609	3.634679	0.018830
37	6	0	5.202411	-0.203843	1.179364
38	6	0	3.056022	-0.319929	2.504123
39	6	0	5.201373	0.064672	-1.203821
40	6	0	3.055372	0.243306	-2.521396
41	1	0	-2.233775	2.928299	0.012525
42	6	0	5.919564	-0.077059	-0.013448
43	1	0	5.743550	-0.320897	2.116608
44	1	0	2.435227	0.563815	2.699457
45	1	0	2.380938	-1.184811	2.489733
46	1	0	3.740401	-0.441042	3.349545
47	1	0	5.741743	0.154132	-2.144511
48	1	0	2.345059	-0.579807	-2.671757
49	1	0	2.473349	1.172892	-2.541193
50	1	0	3.738148	0.256875	-3.376637
51	6	0	7.428979	-0.067584	-0.012885
52	1	0	7.820343	0.951877	0.104305
53	1	0	7.832931	-0.666216	0.810568
54	1	0	7.832332	-0.463605	-0.950974
55	6	0	0.344594	-5.124296	0.029012

56	1	0	-0.115547	-5.575441	0.916210
57	1	0	-0.116716	-5.588977	-0.850552
58	1	0	1.407277	-5.384319	0.030277
59	6	0	-0.344609	5.124325	0.030344
60	1	0	0.116365	5.575441	0.917119
61	1	0	0.115861	5.589049	-0.849642
62	1	0	-1.407294	5.384332	0.032612

Table S14 Optimized cartesian coordinates of ***anti*-3^{Mes}•F^{-}**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.652911	-1.269874	-0.382096
2	6	0	0.698808	-1.320434	-0.694130
3	16	0	-1.309980	-2.897013	-0.125334
4	6	0	0.242882	-3.624722	-0.442695
5	6	0	1.184173	-2.662433	-0.720791
6	5	0	-1.470613	0.011702	-0.243768
7	6	0	-3.006213	-0.012227	0.120330
8	6	0	-3.424070	0.112042	1.460260
9	6	0	-4.786638	0.106216	1.772865
10	6	0	-5.762446	-0.022571	0.781144
11	6	0	-5.341474	-0.140156	-0.546020
12	6	0	-3.985219	-0.138969	-0.884599
13	1	0	2.221590	-2.911463	-0.930104
14	1	0	-5.093782	0.205162	2.813662
15	1	0	-6.086573	-0.233998	-1.335587
16	6	0	-2.388587	0.250488	2.552958
17	1	0	-1.729313	-0.625634	2.582727
18	1	0	-1.742612	1.118974	2.377478
19	1	0	-2.854737	0.360684	3.538536
20	6	0	-7.230078	-0.062755	1.136505
21	1	0	-7.574213	-1.090236	1.321799
22	1	0	-7.438627	0.515196	2.044384
23	1	0	-7.849583	0.343170	0.328256
24	6	0	-3.555468	-0.268115	-2.328018
25	1	0	-2.932002	0.581817	-2.631359
26	1	0	-2.947088	-1.168336	-2.476218
27	1	0	-4.417672	-0.320429	-3.002380
28	6	0	0.640236	1.322204	-0.744768
29	6	0	2.955802	0.019279	-0.113043
30	6	0	-0.717981	1.337452	-0.444214
31	16	0	1.238482	2.953087	-0.877750
32	6	0	2.894556	0.167484	1.298336
33	6	0	4.245206	-0.174110	-0.673075
34	6	0	-1.250265	2.672741	-0.323204
35	6	0	-0.333891	3.663804	-0.525959
36	6	0	4.052662	0.144735	2.083090
37	6	0	1.579691	0.347567	2.025947
38	6	0	5.386094	-0.189722	0.142648
39	6	0	4.485447	-0.382541	-2.158110
40	1	0	-2.292708	2.874345	-0.087289
41	6	0	5.317890	-0.024731	1.523795
42	1	0	3.959914	0.258729	3.163477
43	1	0	1.122569	1.317284	1.803138
44	1	0	0.849922	-0.412168	1.733418
45	1	0	1.727407	0.283813	3.110709

46	1	0	6.360916	-0.339856	-0.322328
47	1	0	3.915872	-1.229074	-2.550472
48	1	0	4.172709	0.483776	-2.745987
49	1	0	5.552010	-0.564766	-2.342298
50	6	0	6.563401	-0.009296	2.377732
51	1	0	6.927687	1.013823	2.551795
52	1	0	6.380888	-0.454813	3.363502
53	1	0	7.380913	-0.565318	1.903267
54	6	0	0.442439	-5.109345	-0.389329
55	1	0	0.194145	-5.522515	0.597222
56	1	0	-0.180196	-5.635275	-1.125328
57	1	0	1.489415	-5.351306	-0.600972
58	6	0	-0.536668	5.147368	-0.478853
59	1	0	0.094525	5.629124	0.280395
60	1	0	-0.306738	5.628764	-1.439311
61	1	0	-1.581253	5.372133	-0.235371
62	9	0	1.884974	0.013505	-2.430356
63	5	0	1.580922	0.016976	-1.021522

Table S15 Optimized cartesian coordinates of ***anti*-3^{Mes}•2F^{-}**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.542766	1.308393	-0.353451
2	6	0	0.676742	1.322026	0.284724
3	16	0	-1.063431	2.968550	-0.718825
4	6	0	0.380675	3.659875	-0.001325
5	6	0	1.183074	2.656252	0.471566
6	6	0	-2.981707	0.070319	-0.321773
7	6	0	-4.097914	-0.090103	-1.183230
8	6	0	-5.409711	-0.081626	-0.682750
9	6	0	-5.685650	0.079225	0.672416
10	6	0	-4.595147	0.223071	1.530576
11	6	0	-3.275733	0.220942	1.063665
12	1	0	2.141526	2.858811	0.949189
13	1	0	-6.240971	-0.208952	-1.379595
14	1	0	-4.773455	0.337448	2.601505
15	6	0	-3.959870	-0.289291	-2.683221
16	1	0	-3.469689	0.562410	-3.160663
17	1	0	-3.338274	-1.155941	-2.922111
18	1	0	-4.952074	-0.429351	-3.136938
19	6	0	-7.104690	0.118982	1.189707
20	1	0	-7.456031	1.147578	1.368110
21	1	0	-7.802393	-0.338575	0.476228
22	1	0	-7.204065	-0.416708	2.143767
23	6	0	-2.180651	0.382694	2.094038
24	1	0	-1.414251	-0.390901	2.002577
25	1	0	-1.648828	1.330257	1.967206
26	1	0	-2.599485	0.350070	3.109260
27	6	0	0.542750	-1.308373	0.353202
28	6	0	2.981670	-0.070278	0.321857
29	6	0	-0.676785	-1.322005	-0.284923
30	16	0	1.063446	-2.968533	0.718528
31	6	0	3.275869	-0.220854	-1.063561
32	6	0	4.097779	0.090031	1.183459
33	6	0	-1.183082	-2.656233	-0.471809
34	6	0	-0.380648	-3.659862	0.001019

35	6	0	4.595341	-0.222946	-1.530299
36	6	0	2.180955	-0.382721	-2.094087
37	6	0	5.409640	0.081552	0.683149
38	6	0	3.959542	0.289084	2.683450
39	1	0	-2.141551	-2.858811	-0.949392
40	6	0	5.685742	-0.079182	-0.671994
41	1	0	4.773787	-0.337228	-2.601216
42	1	0	1.649615	-1.330624	-1.967654
43	1	0	1.414157	0.390450	-2.002438
44	1	0	2.599878	-0.349551	-3.109249
45	1	0	6.240813	0.208756	1.380120
46	1	0	3.338287	1.155995	2.922316
47	1	0	3.468879	-0.562443	3.160689
48	1	0	4.951719	0.428680	3.137370
49	6	0	7.104842	-0.118940	-1.189120
50	1	0	7.456261	-1.147543	-1.367332
51	1	0	7.204284	0.416614	-2.143248
52	1	0	7.802445	0.338760	-0.475636
53	6	0	0.628372	5.137180	0.038922
54	1	0	0.668186	5.589164	-0.964546
55	1	0	-0.147182	5.683557	0.598367
56	1	0	1.590062	5.338819	0.527995
57	6	0	-0.628286	-5.137172	-0.039359
58	1	0	0.147228	-5.683453	-0.598955
59	1	0	-0.667964	-5.589273	0.964062
60	1	0	-1.590022	-5.338800	-0.528345
61	9	0	1.371860	0.001346	2.296507
62	5	0	1.407846	-0.024190	0.838469
63	9	0	-1.372177	-0.001320	-2.296631
64	5	0	-1.407926	0.024198	-0.838602

Table S16 Optimized cartesian coordinates of ***anti*-1$^{\mathbf{Mes}}$**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.712363	-0.768727	1.215910
2	6	0	3.017172	-0.617117	0.000025
3	6	0	3.712330	-0.769137	-1.215831
4	6	0	5.076414	-1.068395	-1.199673
5	6	0	5.776389	-1.225374	0.000090
6	6	0	5.076447	-1.068002	1.199815
7	6	0	-0.951125	-1.193930	0.000130
8	6	0	0.422417	-1.386270	0.000099
9	6	0	-0.422412	1.386292	-0.000116
10	6	0	0.951131	1.193952	-0.000136
11	5	0	1.493687	-0.260095	-0.000007
12	5	0	-1.493682	0.260116	0.000006
13	6	0	-5.076239	1.069220	1.199663
14	6	0	-5.776391	1.225363	-0.000104
15	6	0	-5.076625	1.067160	-1.199825
16	6	0	-3.712545	0.767868	-1.215911
17	6	0	-3.017169	0.617133	-0.000023
18	6	0	-3.712147	0.769997	1.215829
19	6	0	-1.680773	-2.441929	0.000298
20	6	0	-0.812535	-3.570145	0.000348
21	16	0	0.867066	-3.077517	0.000243
22	6	0	1.680777	2.441951	-0.000269

23	6	0	0.812540	3.570167	-0.000377
24	16	0	-0.867062	3.077538	-0.000336
25	6	0	3.073184	2.669419	-0.000294
26	6	0	3.555246	3.968624	-0.000417
27	6	0	2.677131	5.069888	-0.000526
28	6	0	1.302064	4.881019	-0.000509
29	6	0	-3.073180	-2.669397	0.000411
30	6	0	-3.555242	-3.968603	0.000543
31	6	0	-2.677126	-5.069866	0.000574
32	6	0	-1.302059	-4.880998	0.000480
33	1	0	3.754810	1.827084	-0.000215
34	1	0	4.627471	4.142009	-0.000430
35	1	0	3.079822	6.078686	-0.000622
36	1	0	0.622700	5.727996	-0.000598
37	1	0	-3.754806	-1.827063	0.000405
38	1	0	-4.627466	-4.141988	0.000631
39	1	0	-3.079817	-6.078665	0.000682
40	1	0	-0.622697	-5.727975	0.000511
41	1	0	-5.606260	1.176912	-2.144315
42	1	0	-5.605590	1.180559	2.144126
43	1	0	5.605957	-1.178380	2.144301
44	1	0	5.605894	-1.179084	-2.144141
45	6	0	2.980270	-0.581725	-2.524846
46	1	0	3.642224	-0.737868	-3.382078
47	1	0	2.141198	-1.282834	-2.616666
48	1	0	2.563227	0.430734	-2.603157
49	6	0	2.980390	-0.580689	2.524885
50	1	0	3.642150	-0.737447	3.382157
51	1	0	2.564279	0.432153	2.603188
52	1	0	2.140674	-1.281031	2.616650
53	6	0	7.243132	-1.581205	0.000111
54	1	0	7.387471	-2.669857	-0.000539
55	1	0	7.750938	-1.186319	-0.886232
56	1	0	7.750647	-1.187389	0.887090
57	6	0	-2.980765	0.578886	-2.524854
58	1	0	-3.642533	0.735491	-3.382146
59	1	0	-2.140756	1.278820	-2.617041
60	1	0	-2.565089	-0.434176	-2.602676
61	6	0	-2.979927	0.583388	2.524873
62	1	0	-2.563268	-0.429170	2.603945
63	1	0	-2.140571	1.284244	2.615981
64	1	0	-3.641672	0.740480	3.382096
65	6	0	-7.243132	1.581199	-0.000174
66	1	0	-7.387467	2.669851	-0.001415
67	1	0	-7.751006	1.185818	-0.886256
68	1	0	-7.750583	1.187882	0.887065

Table S17 Optimized cartesian coordinates of ***anti*-1$^{\mathbf{Mes}}$•F$^-$**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.107740	-1.078757	-0.584070
2	6	0	-2.883916	-0.648688	-0.010291
3	6	0	-2.844322	-0.550116	1.405611
4	6	0	-3.966536	-0.846004	2.185275
5	6	0	-5.172146	-1.252325	1.615125
6	6	0	-5.216293	-1.361569	0.227982

7	6	0	0.964343	-1.166396	-0.387809
8	6	0	-0.376352	-1.391253	-0.665748
9	6	0	0.384029	1.389438	-0.309197
10	6	0	-0.951708	1.189500	-0.572783
11	5	0	1.441274	0.283783	-0.196942
12	6	0	5.180418	1.253072	-0.584334
13	6	0	5.619244	1.331877	0.740171
14	6	0	4.698226	1.068011	1.757482
15	6	0	3.370286	0.738648	1.472370
16	6	0	2.935760	0.663174	0.134580
17	6	0	3.858057	0.926225	-0.896587
18	6	0	1.738235	-2.400012	-0.308442
19	6	0	0.939897	-3.552323	-0.537362
20	16	0	-0.733122	-3.098005	-0.828951
21	6	0	-1.692297	2.427598	-0.573556
22	6	0	-0.884133	3.567866	-0.302602
23	16	0	0.785913	3.112877	-0.047044
24	6	0	-3.072254	2.615274	-0.787658
25	6	0	-3.612364	3.892177	-0.741802
26	6	0	-2.795161	5.008242	-0.479890
27	6	0	-1.431124	4.855295	-0.257854
28	6	0	3.108374	-2.591298	-0.047959
29	6	0	3.641542	-3.875825	-0.020885
30	6	0	2.831850	-4.999638	-0.249709
31	6	0	1.473038	-4.842498	-0.509244
32	1	0	-3.697567	1.748980	-0.973839
33	1	0	-4.677692	4.034655	-0.905295
34	1	0	-3.235222	6.002412	-0.446740
35	1	0	-0.802654	5.717697	-0.051485
36	1	0	3.745745	-1.732891	0.130044
37	1	0	4.701786	-4.009921	0.180641
38	1	0	3.265211	-5.996654	-0.224422
39	1	0	0.837895	-5.706534	-0.686968
40	1	0	5.022127	1.117528	2.796436
41	1	0	5.884578	1.448668	-1.392251
42	1	0	-6.143792	-1.683383	-0.245762
43	1	0	-3.894505	-0.754906	3.269195
44	6	0	-1.594175	-0.115997	2.140391
45	1	0	-1.702628	-0.284923	3.218072
46	1	0	-0.711491	-0.661799	1.796668
47	1	0	-1.383652	0.947789	1.986198
48	6	0	-4.309625	-1.262645	-2.078040
49	1	0	-5.317057	-1.650911	-2.273080
50	1	0	-4.185115	-0.325967	-2.627554
51	1	0	-3.582136	-1.957987	-2.504438
52	6	0	-6.368992	-1.592023	2.471155
53	1	0	-6.280214	-2.592915	2.917547
54	1	0	-6.486217	-0.882851	3.300113
55	1	0	-7.294920	-1.579383	1.884570
56	6	0	2.396862	0.434885	2.587539
57	1	0	2.859698	0.561737	3.572322
58	1	0	1.518928	1.089638	2.534386
59	1	0	2.027459	-0.595778	2.515047
60	6	0	3.408157	0.827314	-2.335545
61	1	0	3.060104	-0.186902	-2.568174
62	1	0	2.566136	1.501911	-2.531614
63	1	0	4.217893	1.077950	-3.029591
64	6	0	7.042416	1.720445	1.063826
65	1	0	7.151041	2.809686	1.163054
66	1	0	7.373848	1.275751	2.009222
67	1	0	7.734576	1.397780	0.277506

68	5	0	-1.556326	-0.285576	-0.912732
69	9	0	-1.856793	-0.294166	-2.320708

Table S18 Optimized cartesian coordinates of ***anti*-1^{Mes}•2F^{-}**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.009691	-0.942430	1.080277
2	6	0	2.930340	-0.594767	0.227280
3	6	0	3.193155	-0.632753	-1.170232
4	6	0	4.458476	-0.974085	-1.660678
5	6	0	5.520428	-1.290428	-0.813732
6	6	0	5.268464	-1.273976	0.555416
7	6	0	-0.885077	-1.220009	-0.180741
8	6	0	0.349027	-1.354043	0.394924
9	6	0	-0.349033	1.354029	-0.394925
10	6	0	0.885069	1.219999	0.180741
11	6	0	-4.458456	0.974149	1.660710
12	6	0	-5.520416	1.290479	0.813769
13	6	0	-5.268473	1.273978	-0.555381
14	6	0	-4.009710	0.942403	-1.080250
15	6	0	-2.930349	0.594765	-0.227258
16	6	0	-3.193145	0.632791	1.170258
17	6	0	-1.600216	-2.477977	-0.265644
18	6	0	-0.874238	-3.582828	0.268727
19	16	0	0.687286	-3.053045	0.858366
20	6	0	1.600216	2.477963	0.265623
21	6	0	0.874244	3.582811	-0.268763
22	16	0	-0.687282	3.053029	-0.858398
23	6	0	2.887096	2.724034	0.781863
24	6	0	3.417067	4.010269	0.770297
25	6	0	2.681157	5.087144	0.244998
26	6	0	1.405924	4.875266	-0.277117
27	6	0	-2.887095	-2.724048	-0.781884
28	6	0	-3.417059	-4.010285	-0.770334
29	6	0	-2.681142	-5.087165	-0.245053
30	6	0	-1.405910	-4.875287	0.277063
31	1	0	3.460425	1.891549	1.176382
32	1	0	4.414817	4.185393	1.170397
33	1	0	3.107456	6.089611	0.242611
34	1	0	0.832256	5.704283	-0.687838
35	1	0	-3.460431	-1.891559	-1.176386
36	1	0	-4.414810	-4.185409	-1.170434
37	1	0	-3.107435	-6.089634	-0.242681
38	1	0	-0.832236	-5.704306	0.687770
39	1	0	-6.074141	1.534909	-1.244211
40	1	0	-4.615841	0.994148	2.740391
41	1	0	6.074125	-1.534925	1.244247
42	1	0	4.615872	-0.994056	-2.740358
43	6	0	2.125522	-0.305286	-2.191265
44	1	0	2.466491	-0.571927	-3.200469
45	1	0	1.185708	-0.824718	-1.990952
46	1	0	1.879179	0.761036	-2.183830
47	6	0	3.883359	-0.991470	2.593422
48	1	0	4.828557	-1.334839	3.037410
49	1	0	3.631333	-0.014394	3.013283
50	1	0	3.082631	-1.664418	2.909995

51	6	0	6.890629	-1.617561	-1.359545
52	1	0	6.828169	-2.225717	-2.271921
53	1	0	7.460805	-0.712612	-1.621035
54	1	0	7.489477	-2.174123	-0.627293
55	6	0	-3.883406	0.991373	-2.593400
56	1	0	-4.828627	1.334675	-3.037390
57	1	0	-3.082714	1.664341	-2.910021
58	1	0	-3.631340	0.014287	-3.013214
59	6	0	-2.125501	0.305337	2.191283
60	1	0	-1.879117	-0.760975	2.183823
61	1	0	-1.185705	0.824805	1.990978
62	1	0	-2.466476	0.571944	3.200494
63	6	0	-6.890606	1.617641	1.359592
64	1	0	-6.828114	2.225590	2.272102
65	1	0	-7.489365	2.174430	0.627438
66	1	0	-7.460894	0.712697	1.620855
67	5	0	1.422349	-0.195729	0.778996
68	9	0	1.440939	-0.064204	2.227989
69	9	0	-1.440965	0.064206	-2.227983
70	5	0	-1.422364	0.195720	-0.778983

Table S19 Optimized cartesian coordinates of **2^{Mes}**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.730843	1.320035	0.000001
2	6	0	0.730620	1.320276	-0.000016
3	6	0	1.264478	2.596660	-0.000019
4	5	0	-1.538675	-0.000161	-0.000034
5	6	0	-3.109090	-0.000328	-0.000015
6	6	0	-3.823467	-0.003261	-1.213059
7	6	0	-5.220736	-0.008908	-1.198991
8	6	0	-5.939522	-0.008715	0.000006
9	6	0	-5.220720	-0.009472	1.198983
10	6	0	-3.823443	-0.003842	1.213033
11	1	0	-5.761600	-0.014889	-2.143776
12	1	0	-5.761570	-0.015887	2.143772
13	6	0	-3.070448	-0.005622	-2.524393
14	1	0	-2.418951	0.873455	-2.610906
15	1	0	-2.419191	-0.885123	-2.608498
16	1	0	-3.751738	-0.006657	-3.380913
17	6	0	-7.448767	0.018674	0.000003
18	1	0	-7.829234	1.048988	-0.000807
19	1	0	-7.858171	-0.478203	-0.886031
20	1	0	-7.858140	-0.476830	0.886813
21	6	0	-3.070408	-0.006708	2.524359
22	1	0	-2.418600	-0.885859	2.607808
23	1	0	-2.419464	0.872718	2.611518
24	1	0	-3.751691	-0.008781	3.380883
25	5	0	1.538673	0.000168	-0.000014
26	6	0	0.730842	-1.320027	0.000007
27	6	0	3.109088	0.000332	0.000021
28	6	0	-0.730621	-1.320271	-0.000030
29	6	0	3.823480	0.003498	-1.213015
30	6	0	3.823424	0.003606	1.213078
31	6	0	-1.264476	-2.596657	-0.000065
32	6	0	5.220748	0.009129	-1.198928

33	6	0	3.070475	0.006044	-2.524357
34	6	0	5.220702	0.009236	1.199047
35	6	0	3.070372	0.006283	2.524394
36	6	0	5.939519	0.008703	0.000079
37	1	0	5.761624	0.015285	-2.143705
38	1	0	2.419331	-0.873264	-2.611200
39	1	0	2.418868	0.885313	-2.608146
40	1	0	3.751775	0.007651	-3.380868
41	1	0	5.761540	0.015473	2.143844
42	1	0	2.418822	0.885602	2.608105
43	1	0	2.419166	-0.872975	2.611269
44	1	0	3.751642	0.007901	3.380929
45	6	0	7.448764	-0.018694	0.000087
46	1	0	7.829225	-1.049010	-0.001004
47	1	0	7.858182	0.478424	-0.885806
48	1	0	7.858129	0.476564	0.887037
49	16	0	0.000584	-3.799722	-0.000037
50	16	0	-0.000577	3.799729	0.000003
51	6	0	1.265139	-2.596199	0.000011
52	6	0	-1.265136	2.596209	0.000018
53	6	0	2.692721	-3.067258	0.000037
54	1	0	3.232378	-2.698099	-0.877013
55	1	0	3.232326	-2.698155	0.877144
56	1	0	2.747274	-4.160040	0.000006
57	6	0	-2.691784	-3.068538	-0.000068
58	1	0	-3.231608	-2.700350	0.877279
59	1	0	-3.231938	-2.699343	-0.876776
60	1	0	-2.745661	-4.161346	-0.000667
61	6	0	-2.692716	3.067275	-0.000045
62	1	0	-3.232057	2.698904	-0.877632
63	1	0	-3.232640	2.697391	0.876524
64	1	0	-2.747263	4.160057	0.000849
65	6	0	2.691790	3.068531	-0.000026
66	1	0	3.231803	2.699764	0.876955
67	1	0	3.231749	2.699905	-0.877101
68	1	0	2.745675	4.161339	0.000057

Table S20 Optimized cartesian coordinates of $\mathbf{2}^{\mathbf{Mes}}\bullet F^-$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.731692	-1.339896	-0.712646
2	6	0	0.692897	-1.325571	-0.394919
3	6	0	1.244535	-2.599235	-0.286381
4	6	0	-2.970912	0.003923	0.029275
5	6	0	-2.816645	0.002975	1.442908
6	6	0	-3.921432	0.003523	2.299468
7	6	0	-5.229913	0.002947	1.816061
8	6	0	-5.394704	0.007473	0.434547
9	6	0	-4.306591	0.007015	-0.453750
10	1	0	-3.753203	0.005531	3.376916
11	1	0	-6.405120	0.012171	0.024772
12	6	0	-1.449489	0.004836	2.091256
13	1	0	-0.863629	-0.869115	1.791657
14	1	0	-0.867661	0.883108	1.796353
15	1	0	-1.536870	0.001616	3.184350
16	6	0	-6.413493	-0.024011	2.753645

17	1	0	-6.568560	-1.021742	3.189410
18	1	0	-6.281168	0.671189	3.592718
19	1	0	-7.338944	0.250635	2.234039
20	6	0	-4.657971	0.012916	-1.931281
21	1	0	-4.246356	0.884352	-2.445621
22	1	0	-4.250158	-0.857033	-2.451128
23	1	0	-5.748498	0.015714	-2.055986
24	5	0	1.462342	-0.000853	-0.213190
25	6	0	0.696357	1.326203	-0.392288
26	6	0	3.001807	-0.002770	0.140587
27	6	0	-0.728171	1.344993	-0.709806
28	6	0	3.428854	-0.007720	1.482063
29	6	0	3.973564	-0.005249	-0.877917
30	6	0	-1.208712	2.619492	-0.838640
31	6	0	4.793710	-0.013811	1.784116
32	6	0	2.398155	-0.011645	2.587495
33	6	0	5.332700	-0.011348	-0.551656
34	6	0	3.530118	-0.006723	-2.322830
35	6	0	5.763811	-0.012143	0.777921
36	1	0	5.107912	-0.021272	2.827408
37	1	0	1.743336	0.865776	2.519675
38	1	0	1.741872	-0.887401	2.512851
39	1	0	2.866502	-0.015804	3.577913
40	1	0	6.072350	-0.016835	-1.351763
41	1	0	2.909066	-0.883810	-2.543268
42	1	0	2.909667	0.870446	-2.544599
43	1	0	4.384483	-0.007491	-3.008712
44	6	0	7.235224	0.017329	1.117467
45	1	0	7.610658	1.046833	1.204152
46	1	0	7.435790	-0.480100	2.073408
47	1	0	7.834408	-0.479984	0.345992
48	16	0	0.054554	3.822669	-0.574914
49	16	0	0.044677	-3.819931	-0.584103
50	6	0	1.251274	2.598145	-0.280523
51	6	0	-1.215471	-2.612821	-0.844928
52	6	0	2.652663	3.042744	0.043382
53	1	0	2.984005	2.665108	1.016133
54	1	0	3.376093	2.676624	-0.692685
55	1	0	2.718614	4.135913	0.065250
56	6	0	-2.585661	3.084103	-1.213070
57	1	0	-2.742057	3.028396	-2.298344
58	1	0	-3.334606	2.443656	-0.740865
59	1	0	-2.769467	4.118583	-0.898943
60	6	0	-2.593211	-3.073052	-1.221710
61	1	0	-3.340565	-2.426905	-0.754915
62	1	0	-2.746013	-3.022112	-2.307768
63	1	0	-2.782752	-4.105153	-0.903085
64	6	0	2.644636	-3.048494	0.036670
65	1	0	3.369440	-2.682101	-0.697877
66	1	0	2.976726	-2.674954	1.010736
67	1	0	2.707673	-4.141887	0.055128
68	9	0	-2.041779	0.005930	-2.348044
69	5	0	-1.638761	0.004072	-0.957556

Table S21 Optimized cartesian coordinates of $\mathbf{2}^{\mathbf{Mes}}\bullet 2F^{-}$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-0.636664	-1.343809	-0.364006
2	6	0	0.629606	-1.349673	0.358176
3	6	0	1.078130	-2.619228	0.626536
4	6	0	-2.976072	0.006547	-0.215111
5	6	0	-3.172748	0.003590	1.197091
6	6	0	-4.455540	0.002977	1.753853
7	6	0	-5.608044	0.004245	0.965862
8	6	0	-5.430561	0.009971	-0.413547
9	6	0	-4.155588	0.010501	-1.006147
10	1	0	-4.555680	0.002541	2.840796
11	1	0	-6.310890	0.014624	-1.059482
12	6	0	-2.006841	0.003400	2.159784
13	1	0	-1.359494	-0.864939	2.012649
14	1	0	-1.361440	0.873660	2.015547
15	1	0	-2.362520	0.001171	3.198734
16	6	0	-6.985250	-0.015342	1.586594
17	1	0	-7.207785	-0.976520	2.074960
18	1	0	-7.098774	0.760602	2.357081
19	1	0	-7.762924	0.152318	0.830633
20	6	0	-4.133946	0.017578	-2.525038
21	1	0	-3.599070	0.883697	-2.920208
22	1	0	-3.618134	-0.856913	-2.927790
23	1	0	-5.162364	0.029741	-2.914434
24	6	0	0.636722	1.343953	0.363625
25	6	0	2.976145	-0.006560	0.215160
26	6	0	-0.629599	1.349738	-0.358481
27	6	0	4.155504	-0.010500	1.006435
28	6	0	3.173099	-0.003723	-1.197006
29	6	0	-1.078242	2.619238	-0.626845
30	6	0	5.430605	-0.010094	0.414105
31	6	0	4.133499	-0.017393	2.525333
32	6	0	4.456002	-0.003239	-1.753492
33	6	0	2.007378	-0.003514	-2.159921
34	6	0	5.608354	-0.004514	-0.965268
35	1	0	6.310790	-0.014724	1.060234
36	1	0	3.617415	0.857052	2.927836
37	1	0	3.598641	-0.883544	2.920465
38	1	0	5.161823	-0.029351	2.914982
39	1	0	4.556378	-0.002891	-2.840415
40	1	0	1.361933	-0.873761	-2.015789
41	1	0	1.360029	0.864844	-2.012893
42	1	0	2.363253	-0.001297	-3.198803
43	6	0	6.985673	0.014899	-1.585751
44	1	0	7.208227	0.975883	-2.074486
45	1	0	7.763212	-0.152390	-0.829571
46	1	0	7.099399	-0.761368	-2.355886
47	16	0	0.011756	3.850292	0.008759
48	16	0	-0.011986	-3.850185	-0.009078
49	6	0	1.093276	2.609056	0.638701
50	6	0	-1.093319	-2.608851	-0.639124
51	6	0	2.310930	3.024550	1.415252
52	1	0	2.206113	2.769656	2.478577
53	1	0	3.200728	2.501825	1.048679
54	1	0	2.494420	4.104469	1.342638
55	6	0	-2.292996	3.047497	-1.400585
56	1	0	-2.174053	2.842196	-2.473536
57	1	0	-3.176370	2.494341	-1.065629
58	1	0	-2.496518	4.119974	-1.283195
59	6	0	-2.311141	-3.024063	-1.415590
60	1	0	-3.201534	-2.503942	-1.046667

61	1	0	-2.207672	-2.765667	-2.478165
62	1	0	-2.492708	-4.104502	-1.346078
63	6	0	2.292725	-3.047709	1.400378
64	1	0	3.175688	-2.492935	1.067091
65	1	0	2.172870	-2.844752	2.473699
66	1	0	2.497522	-4.119730	1.280989
67	9	0	-1.493345	0.009032	-2.296955
68	5	0	-1.430545	0.006074	-0.837782
69	9	0	1.492984	-0.008893	2.296728
70	5	0	1.430511	-0.005976	0.837529

Table S22 Optimized cartesian coordinates of **4^{Mes}**.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.351723	-0.702712	-1.052475
2	6	0	0.037083	-0.699381	-1.048456
3	5	0	0.892499	0.003901	0.005920
4	6	0	0.034717	0.705768	1.059325
5	6	0	-1.354097	0.706712	1.061784
6	6	0	-1.907562	-1.430316	-2.143680
7	6	0	-0.944891	-1.972288	-2.957567
8	16	0	0.653575	-1.606291	-2.409543
9	16	0	0.648123	1.613889	2.420991
10	6	0	-0.951583	1.977187	2.967184
11	6	0	-1.912414	1.433457	2.152298
12	6	0	2.458113	0.005085	0.006540
13	6	0	3.171886	-1.004013	0.683354
14	6	0	4.568523	-0.987440	0.678385
15	6	0	5.285426	0.010088	0.012110
16	6	0	4.567664	1.008098	-0.652237
17	6	0	3.170886	1.018185	-0.665055
18	1	0	-2.972502	-1.546878	-2.317783
19	1	0	-1.097534	-2.566531	-3.849017
20	1	0	-1.106232	2.571285	3.858385
21	1	0	-2.977747	1.548197	2.325203
22	1	0	5.109999	-1.769702	1.207262
23	1	0	5.108417	1.797370	-1.171314
24	6	0	-2.159496	0.001221	0.004267
25	1	0	-2.832244	0.725731	-0.479461
26	1	0	-2.831224	-0.724646	0.487386
27	6	0	2.423340	-2.095428	1.414491
28	1	0	1.775481	-2.659620	0.731902
29	1	0	3.109920	-2.804019	1.888027
30	1	0	1.776450	-1.679433	2.197085
31	6	0	2.421451	2.112205	-1.391380
32	1	0	1.774171	1.698546	-2.174896
33	1	0	1.773867	2.673944	-0.706517
34	1	0	3.107460	2.822519	-1.863156
35	6	0	6.794638	-0.005593	-0.011884
36	1	0	7.204815	-0.456520	0.898091
37	1	0	7.173150	-0.588519	-0.862305
38	1	0	7.203988	1.006026	-0.104270

Table S23 Optimized cartesian coordinates of $\mathbf{4}^{\mathbf{Mes}}\bullet F^-$.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.447231	-0.637753	-1.063399
2	6	0	-0.096225	-0.774177	-0.842115
3	6	0	-0.274294	0.829587	1.140309
4	6	0	-1.624339	0.956011	0.906687
5	6	0	-1.950260	-1.464008	-2.124644
6	6	0	-0.981820	-2.229280	-2.712248
7	16	0	0.564002	-1.945304	-1.963332
8	16	0	0.156039	1.728645	2.579384
9	6	0	-1.480058	2.263429	2.840064
10	6	0	-2.309010	1.769681	1.871613
11	6	0	1.799811	-0.934730	1.108141
12	6	0	1.250417	-1.988384	1.889059
13	6	0	2.066990	-2.833185	2.648227
14	6	0	3.453032	-2.687845	2.676794
15	6	0	3.999958	-1.654393	1.921319
16	6	0	3.210345	-0.788950	1.149372
17	1	0	-2.995265	-1.483512	-2.426624
18	1	0	-1.090976	-2.934826	-3.526276
19	1	0	-1.737576	2.895991	3.680246
20	1	0	-3.378130	1.968469	1.838995
21	1	0	1.603694	-3.626740	3.235430
22	1	0	5.080852	-1.510285	1.930460
23	6	0	-0.239851	-2.250013	1.945933
24	1	0	-0.789770	-1.371090	2.295781
25	1	0	-0.644284	-2.490432	0.957839
26	1	0	-0.457993	-3.086465	2.621179
27	6	0	4.325117	-3.628947	3.473615
28	1	0	3.851346	-3.911929	4.422115
29	1	0	4.527671	-4.562142	2.927511
30	1	0	5.295646	-3.174150	3.705546
31	6	0	3.958309	0.290405	0.386604
32	1	0	3.794431	0.214650	-0.691080
33	1	0	3.626401	1.292491	0.669002
34	1	0	5.035236	0.209532	0.583968
35	9	0	1.583870	1.026442	-0.503052
36	5	0	0.817277	0.046453	0.223848
37	6	0	-2.326627	0.278044	-0.245653
38	1	0	-2.772729	1.042675	-0.904317
39	1	0	-3.186099	-0.295258	0.140887

Table S24 Optimized cartesian coordinates of tris(pentafluorophenyl)borane.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	0.000026	0.000024	-0.000306
2	6	0	1.521533	0.354049	-0.000124
3	6	0	2.467392	-0.412147	-0.696200
4	6	0	2.031788	1.459085	0.696152
5	6	0	3.822595	-0.107602	-0.715050
6	6	0	3.382198	1.784135	0.715388
7	6	0	4.281471	0.996261	0.000290

8	6	0	-0.454012	-1.494681	-0.000270
9	6	0	-1.590190	-1.930762	-0.696811
10	6	0	0.247603	-2.489070	0.696246
11	6	0	-2.004165	-3.256628	-0.715672
12	6	0	-0.146242	-3.821057	0.715502
13	6	0	-1.277993	-4.205916	0.000084
14	6	0	-1.067409	1.140596	-0.000173
15	6	0	-2.280040	1.029496	0.695155
16	6	0	-0.876387	2.343312	-0.695342
17	6	0	-3.236727	2.036487	0.714484
18	6	0	-1.817709	3.364693	-0.714116
19	6	0	-3.003575	3.209718	0.000366
20	9	0	-3.913188	4.181923	0.000727
21	9	0	-4.371190	1.891972	1.405897
22	9	0	-2.551827	-0.074788	1.409009
23	9	0	1.211481	2.245882	1.410965
24	9	0	3.824442	2.838302	1.407561
25	9	0	5.578212	1.297971	0.000531
26	9	0	4.685023	-0.858085	-1.407109
27	9	0	2.078817	-1.480114	-1.411300
28	9	0	1.338930	-2.172058	1.411378
29	9	0	0.545212	-4.731125	1.408043
30	9	0	-1.665208	-5.479741	0.000343
31	9	0	-3.085096	-3.628220	-1.408105
32	9	0	-2.320518	-1.060292	-1.412209
33	9	0	0.243297	2.541433	-1.409443
34	9	0	-1.598455	4.487284	-1.405242

Table S25 Optimized cartesian coordinates of tris(pentafluorophenyl)borane •F^-.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.188061	1.000285	1.563497
2	6	0	2.331666	1.499851	2.539814
3	6	0	4.541533	1.255713	1.789190
4	6	0	2.765506	2.225589	3.648804
5	6	0	5.020948	1.972921	2.880888
6	6	0	4.121738	2.467454	3.819081
7	6	0	1.140957	0.346149	-0.113766
8	6	0	0.165848	-0.638515	0.012100
9	6	0	0.669743	1.578398	-0.569311
10	6	0	-1.175827	-0.441969	-0.313395
11	6	0	-0.658647	1.821573	-0.904519
12	6	0	-1.591193	0.797888	-0.779416
13	6	0	3.183845	-1.411228	0.292860
14	6	0	3.212716	-2.168170	-0.879421
15	6	0	3.550391	-2.105188	1.441858
16	6	0	3.599702	-3.503837	-0.927337
17	6	0	3.947255	-3.442065	1.442426
18	6	0	3.975859	-4.146666	0.246765
19	5	0	2.752157	0.178746	0.200467
20	9	0	0.995933	1.293073	2.472829
21	9	0	5.474196	0.767763	0.946148
22	9	0	2.817152	-1.624531	-2.048467
23	9	0	3.529716	-1.509440	2.656812
24	9	0	1.507645	2.630099	-0.671451
25	9	0	0.470852	-1.870678	0.481436

26	9	0	3.461058	0.750757	-0.887128
27	9	0	6.341322	2.187002	3.048238
28	9	0	1.885860	2.692330	4.557437
29	9	0	4.300575	-4.058374	2.588087
30	9	0	3.606408	-4.185885	-2.090078
31	9	0	-2.073544	-1.438594	-0.179119
32	9	0	-1.056786	3.034231	-1.338314
33	9	0	4.562234	3.165974	4.882483
34	9	0	-2.881711	1.009409	-1.099741
35	9	0	4.356177	-5.438037	0.224276

Table S26 Optimized cartesian coordinates of Me_3SiF.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	1.768259	0.077450	0.042705
2	6	0	-0.106130	0.105685	-0.006114
3	1	0	-0.524817	-0.401062	0.872100
4	1	0	-0.489870	1.132143	-0.012777
5	1	0	-0.489958	-0.402134	-0.898149
6	6	0	2.419674	-1.680342	-0.006438
7	1	0	2.069246	-2.211170	-0.898819
8	1	0	3.515348	-1.700006	-0.012605
9	1	0	2.081048	-2.244308	0.871412
10	6	0	2.419689	0.998420	1.540731
11	1	0	3.515358	1.013960	1.554453
12	1	0	2.068920	2.036537	1.554819
13	1	0	2.081426	0.519618	2.467922
14	9	0	2.311767	0.846262	-1.288444

Table S27 Optimized cartesian coordinates of Me_3Si^+.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	0.371308	0.483907	0.061909
2	6	0	-0.529691	2.089268	0.033729
3	1	0	0.139316	2.952276	0.087469
4	1	0	-1.135719	2.160993	-0.881160
5	1	0	-1.240565	2.133148	0.871669
6	6	0	2.209045	0.461662	0.171251
7	1	0	2.535375	0.990749	1.078430
8	1	0	2.621494	-0.550783	0.180497
9	1	0	2.639772	1.017176	-0.674517
10	6	0	-0.564949	-1.099267	-0.019437
11	1	0	-0.231276	-1.685782	-0.887799
12	1	0	-0.338443	-1.712380	0.864997
13	1	0	-1.646156	-0.950360	-0.083145