Electronic Supplementary Information (ESI)

Bis(pentafluorophenyl)-*o*-carborane and Its Arylthio Derivatives: Synthesis, Electrochemistry and Optical Properties

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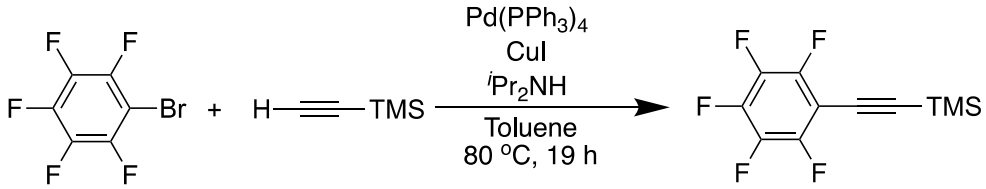
1. General considerations

Reagents and dehydrated solvents were obtained from commercial source and used without further purification. ^{1}H, ^{19}F and ^{11}B NMR spectra were recorded on JEOL JNM EX-270 (^{1}H: 270.05 MHz, ^{19}F: 254.05 MHz) spectrometer, JEOL ECP-300 (^{11}B: 96.00 MHz) and Bruker biospin AVANCE III HD500 (^{19}F: 470.59 MHz) spectrometer using $CDCl_3$ as a solvent. The chemical shifts for ^{1}H and ^{19}F NMR spectra are given in δ (ppm) relative to internal TMS, deuterated solvent, and monofluorobenzene respectively. The chemical shifts for ^{11}B NMR spectra are given in δ (ppm) relative to boron trifluoride diethyl etherate (0.0 ppm) as an external standard. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer. The cyclic voltammetry (CV) measurements were performed using BAS ALS Instruments model 600 A. All CV measurements were carried out in the three-electrode system equipped with glassy carbon (GC) disk working (φ = 3 mm), a Pt plate counter electrode (10 mm × 10 mm) and a saturated calomel electrode (SCE) as a reference electrode in DMF solution of 0.1 M Bu_4NClO_4 at scan rate of 10 mVs^{-1}. Spectroelectrochemistry measurements were carried out using SEC2000-UV/Vis spectrometer system (BAS). UV-vis absorption spectra were recorded with SHIMAZU UV-1800. In-solution photoluminescence (PL) spectra were obtained on a JASCO FP-6500 spectrophotomerter. The fluorescence quantum yield (Φ_F) of the compounds in a dilute solution (10^{-5} M) was determined on excitation at their λ_{max}^{abs} in comparison with the emission of quinine sulfate dihydrate/0.1 M sulfuric acid solution (Φ_F = 0.55) as a standard. Solid-state photoluminescence spectra were recorded on a Shimadzu RF-6000 spectrometer equipped with an integrating sphere. The single crystal X-ray analysis was carried out on a Rigaku RAXIS RAPID-F Imaging Plate diffractometer (Mo-K α radiation, λ = 0.71075 Å). An empirical absorption correction was carried out by the ABSCOR method.[1] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. Molecular orbital DFT calculations were performed at the B3LYP/6-31G(d) level by using the GAUSSIAN16 suite of programs.

2. Synthesis

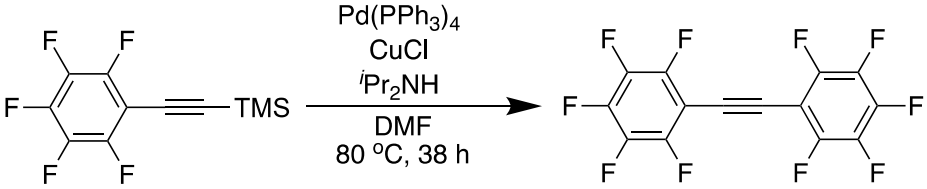
Synthesis of trimethyl((pentafluorophenyl)ethynyl)silane



Trimethyl((pentafluorophenyl)ethynyl)silane was prepared according to the reported procedure.[2] Under argon atmosphere, to a stirred solution of tetrakis(triphenylphosphine)palladium(0) (2.61 g, 2.25 mmol), CuI (428 mg, 2.25 mmol) in toluene (120 mL) was added bromopentafluorobenzene (11.1 g, 45 mmol), diisopropylamine (18 mL), trimethylsilylacetylene (6.93 mL, 49.5 mmol). The solution was reacted at 80 °C for 19 h. After cooling to room temperature, solvent was evaporated under reduced pressure. The residue was dissolved in EtOAc, then washed with saturated NH_4Cl aq. and brine. The organic layer was dried over anhydrous $MgSO_4$. After filtration and removal of the solvent, the residue was purified by silica gel column chromatography (hexane) to give trimethyl((pentafluorophenyl)ethynyl)silane as an yellow oil in 96% yield (11.4 g, 43.1 mmol).

Trimethyl((pentafluorophenyl)ethynyl)silane: yellow oil. ^{1}H NMR (270 MHz, $CDCl_3$): δ (ppm) 0.28 (s, 9H, TMS). ^{19}F NMR (254 MHz, $CDCl_3$): δ (ppm) −161.9 (m, 2F), −152.4 (t, J = 20.3 Hz, 1F), −135.8 (m, 2F).

*Sythesis of 1,2-Bis(perfluorophenyl)ethyne (**1**)*

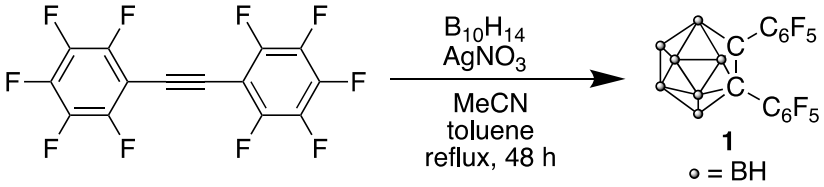


Perfluorotolane was prepared according to the reported procedure.[2] Under argon atmosphere, to a stirred solution of tetrakis(triphenylphosphine)palladium(0) (2.26 g, 1.96 mmol), CuCl (4.53 g, 45.7 mmol) in DMF (100 mL) was added trimethyl((pentafluorophenyl)ethynyl)silane (12.0 g, 45.3 mmol), pentafluoroiodobenzene (9.24 g, 31.4 mmol) diisopropylamine (7.55 mL). The solution was stirred at 80 °C for 38 h. After cooling to room temperature, solvent was evaporated under reduced pressure. The residue was dissolved in AcOEt, then washed with saturated NH_4Cl aq. and brine. The organic layer was dried over anhydrous $MgSO_4$. After filtration and removal of the solvent, the residue was purified by silica gel column chromatography

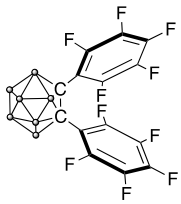
(hexane). The material was further purified by the recrystallization from hexane to give perfluorotolane as a white solid in 61% yield (6.83 g, 19.1 mmol).

Perfluorotolane: white solid. ^{19}F NMR (254 MHz, $CDCl_3$): δ (ppm) −160.65 (m, 4F, Ar), −149.37 (t, *J* = 20.3 Hz, 2F, Ar), −134.33 (m, 4F, Ar).

*1,2-Bis(pentafluorophenyl)-1,2-closo-$C_2B_{10}H_{10}$ (**1**)*

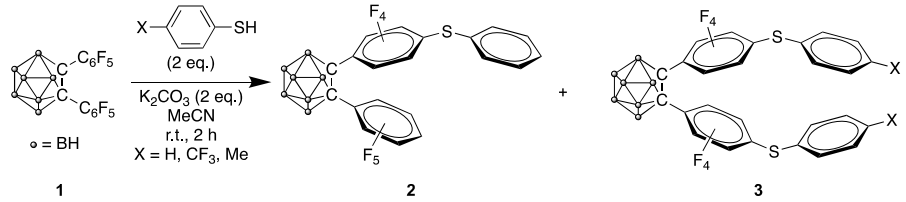


1 was prepared under similar conditions to the previous reports.[3,4] Under argon atmosphere, decaborane (388 mg, 3.12 mmol), **1** (998 mg, 2.79 mmol), silver nitrate (23.8 mg, 0.14 mmol) were dissolved in MeCN (0.5 mL) and toluene (27 mL) mixture The solution was refluxed for 48 h. After cooling to room temperature, the mixture was passed through celite, then. solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (hexane) to give **2** as a white solid in 26% yield (351 mg, 0.738 mmol).



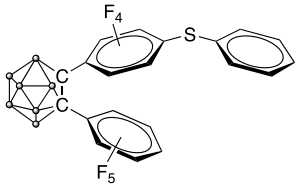
1: white solid. ^{1}H NMR (270.05 MHz, $CDCl_3$): δ (ppm) 3.7-1.5 (br, 10H, B-H). ^{19}F NMR (254.05 MHz, $CDCl_3$): δ (ppm) −129.4 (br, 4F), −145.2 (m, 2F), −158.0 (m, 4F). ^{11}B NMR (96.00 MHz, $CDCl_3$): δ (ppm) −0.12 (2B), −1.57 (2B), −8.13 (4B), −9.61 (2B). HRMS (APCI) calcd. for $C_{14}H_{10}B_{10}F_{10}$ $[M]^+$:478.1572, found 478.1562.

General procedure for arylthiolation



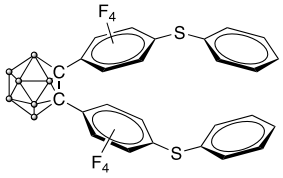
Under argon atmosphere, to a stirred solution of **2** (50 mg, 0.105 mmol) in MeCN (9 mL) was added 2 eq. of thiol (0.210 mmol) and 2 eq. of K_2CO_3 (29 mg, 0.210 mmol). The solution was stirred at room temperature for 2 h. After the reaction, chloroform was added to the reaction mixture and then filtrated. The filtrate was evaporated under reduced pressure. The residue was purified by silica gel column chromatography using hexane as an eluent.

1-(2,3,5,6-Tetrafluoro-4-(phenylthio)phenyl)-2-(2,3,4,5,6-pentafluorophenyl)-1,2-*closo*-$C_2B_{10}H_{10}$ (2a)



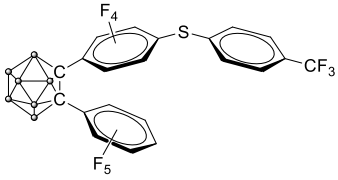
2a: 29 mg, 49% yield, white solid. ^{1}H NMR (270 MHz, $CDCl_3$): δ (ppm) 7.41 (m, 2H, Ar), 7.34 (m, 3H, Ar), 3.7-1.5 (br, 10H, B-H). ^{19}F NMR (254 MHz, $CDCl_3$): δ (ppm) −158.2 (m, 2F), −145.5 (m, 1F), −130.9 (m, 2F), −130.3 (s, 2F), −129.2 (s, 2F). ^{11}B NMR (96.0 MHz, $CDCl_3$): δ (ppm) −0.321, −1.79, −8.25, −9.59. HRMS (FAB) calcd. for $C_{20}H_{15}B_{10}F_9S$ $[M]^+$: 568.1681, found 568.1699.

1,2-Bis(2,3,5,6-tetrafluoro-4-(phenylthio)phenyl)-1,2-*closo*-$C_2B_{10}H_{10}$ (3a)



3a: 34 mg, 49% yield, yellow solid. ^{1}H NMR (270 MHz, $CDCl_3$): δ (ppm) 7.34 (m, 10H, Ar), 3.7-1.5 (br, 10H, B-H). ^{19}F NMR (254 MHz, $CDCl_3$): δ (ppm) −131.2 (m, 4F, Ar), −130.2 (s, 4F, Ar). ^{11}B NMR (96.0 MHz, $CDCl_3$): δ (ppm) −0.52, −1.81, −8.18, −9.59. HRMS (FAB) calcd. for $C_{26}H_{20}B_{10}F_8S_2$ $[M]^+$:658.1809, found 658.1812.

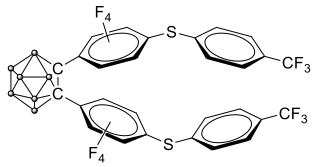
1-(2,3,5,6-Tetrafluoro-4-((4-trifluoromethyl)phenylthio)phenyl)-2-(2,3,4,5,6-pentafluorophenyl)-1,2-*closo*-$C_2B_{10}H_{10}$ (2b)



(**2b**): 11 mg, 14% yield, white solid. ^{1}H NMR (270 MHz, $CDCl_3$): δ (ppm) 7.58 (m, 2H, Ar), 7.44 (m, 2H, Ar), 3.8-1.5 (br, 10H, B-H). ^{19}F NMR (254 MHz, $CDCl_3$): δ (ppm) −158.1 (m, 2F, Ar), −145.3 (m, 1F, Ar), −129.8 (m, 2F, Ar), −129.4 (s, 2F, Ar), −129.2 (s, 2F, Ar), −62.78 (s, 3F, CF_3).

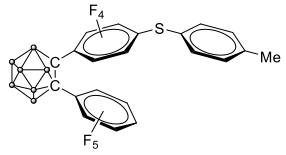
^{11}B NMR (96.0 MHz, $CDCl_3$): δ (ppm) −0.285, −1.67, −8.16, −9.59. HRMS (FAB) calcd. for $C_{21}H_{14}B_{10}F_{12}S_1$ $[M]^+$:636.1555, found 636.1557.

1,2-Bis(2,3,5,6-tetrafluoro-4-((4-trifluoromethyl)phenylthio)phenyl)-1,2-*closo*-$C_2B_{10}H_{10}$ (3b)



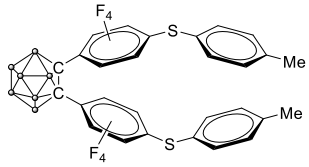
(**3b**): 39 mg, 47% yield, white solid. ^{1}H NMR (270 MHz, $CDCl_3$): δ (ppm) 7.54 (m, 4H, Ar), 7.35 (m, 4H, Ar). ^{19}F NMR (254 MHz, $CDCl_3$): δ (ppm) −130.0 (m, 4F, Ar), −129.1 (s, 4F, Ar), −62.8 (s, 6F, CF_3). ^{11}B NMR (96.0 MHz, $CDCl_3$): δ (ppm) −0.124, −1.39, −8.21, −9.51. HRMS (APCI) calcd. for $C_{28}H_{18}B_{10}F_{14}S_2$ $[M]^+$:794.1575, found 794.1568.

1-(2,3,5,6-Tetrafluoro-4-((4-methyl)phenylthio)phenyl)-2-(2,3,4,5,6-pentafluorophenyl)-1,2-*closo*-$C_2B_{10}H_{10}$ (2c)



2c: 12 mg, 20% yield. white solid. ^{1}H NMR (270 MHz, $CDCl_3$): δ (ppm) 7.36 (m, 2H, Ar), 7.12 (m, 2H, Ar), 2.35 (s, 3H, Me). ^{19}F NMR (254 MHz, $CDCl_3$): δ (ppm) −158.3 (m, 2F), −145.7 (m, 1F), −131.5 (m, 2F), −130.6 (s, 2F), −129.3 (s, 2F). ^{11}B NMR (96.0 MHz, $CDCl_3$): δ (ppm) −0.268, −1.82, −8.24, −9.66. HRMS (FAB) calcd. for $C_{21}H_{17}B_{10}F_9S_1$ $[M]^+$:582.1838, found 582.1829.

1,2-Bis(2,3,5,6-tetrafluoro-4-((4-methyl)phenylthio)phenyl)-1,2-*closo*-$C_2B_{10}H_{10}$ (3c)



3c: 56 mg, 78% yield, yellow solid. ^{1}H NMR (270 MHz, $CDCl_3$): δ (ppm) 7.29 (m, 4H), 7.29 (m, 4H), 2.33 (s, 6H, Me). ^{19}F NMR (254 MHz, $CDCl_3$): δ (ppm) −131.7 (m, 4F), −130.5 (s, 4F). ^{11}B NMR (96.0 MHz, $CDCl_3$): δ (ppm) −0.468, −1.84, −8.27, −9.74. HRMS (FAB) calcd. for $C_{28}H_{24}B_{10}F_8S_2$ $[M]^+$:686.2122, found 686.2098.

3. CV of hexafluorobenzene

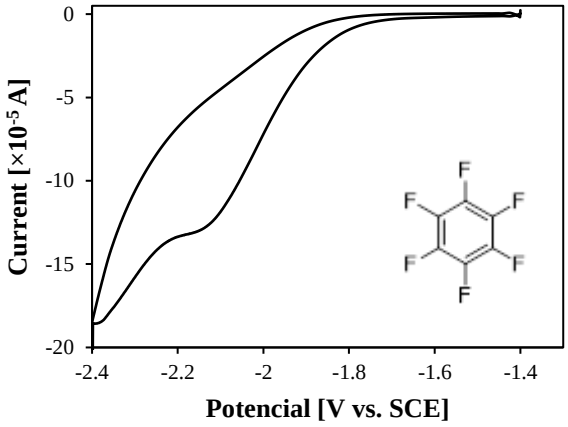


Fig. S1 CV of hexafluorobenzene (10 mM) in 0.1 M Bu_4NClO_4/DMF using a GC working electrode at a scan rate of 100 mV/s.

4. Electrochemical stability of 1

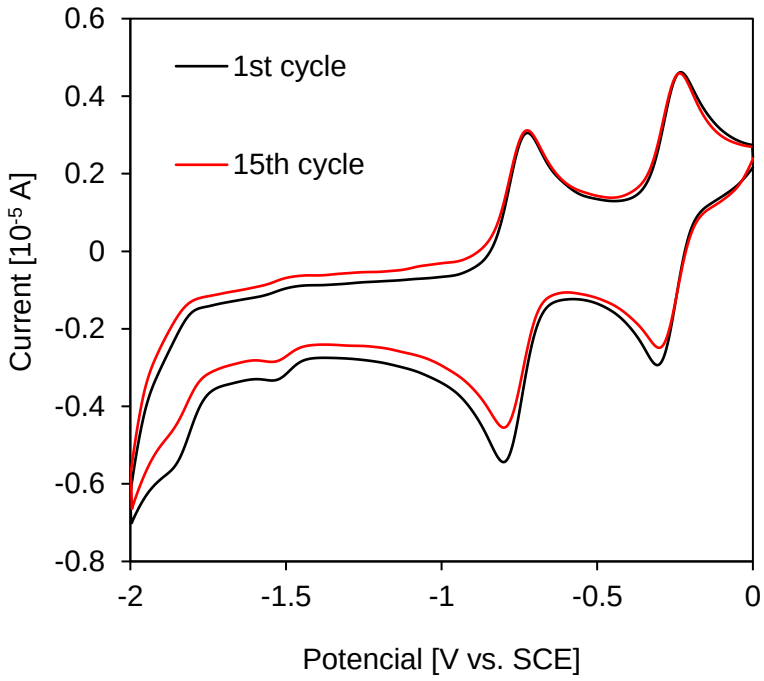


Fig. S2 CV of **1** (1 mM) in 0.1 M Bu_4NClO_4/DMF using a GC working electrode at a scan rate of 10 mV/sec.

5. CVs of 1, 2a, 3a-c

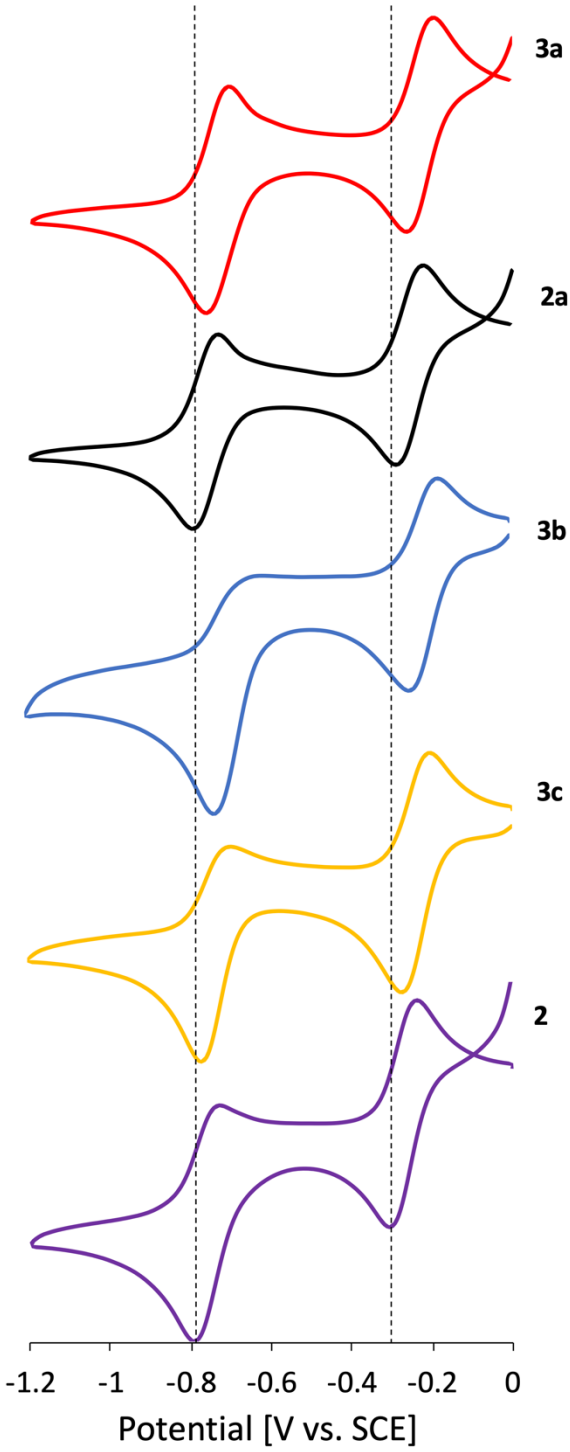


Fig. S3 CVs of **1, 2a, 3a-c** (1 mM) in 0.1 M Bu_4NClO_4/DMF using a GC working electrode at a scan rate of 10 mV/sec.

6. UV-absorption and fluorescent spectra of 2a, 3a-c

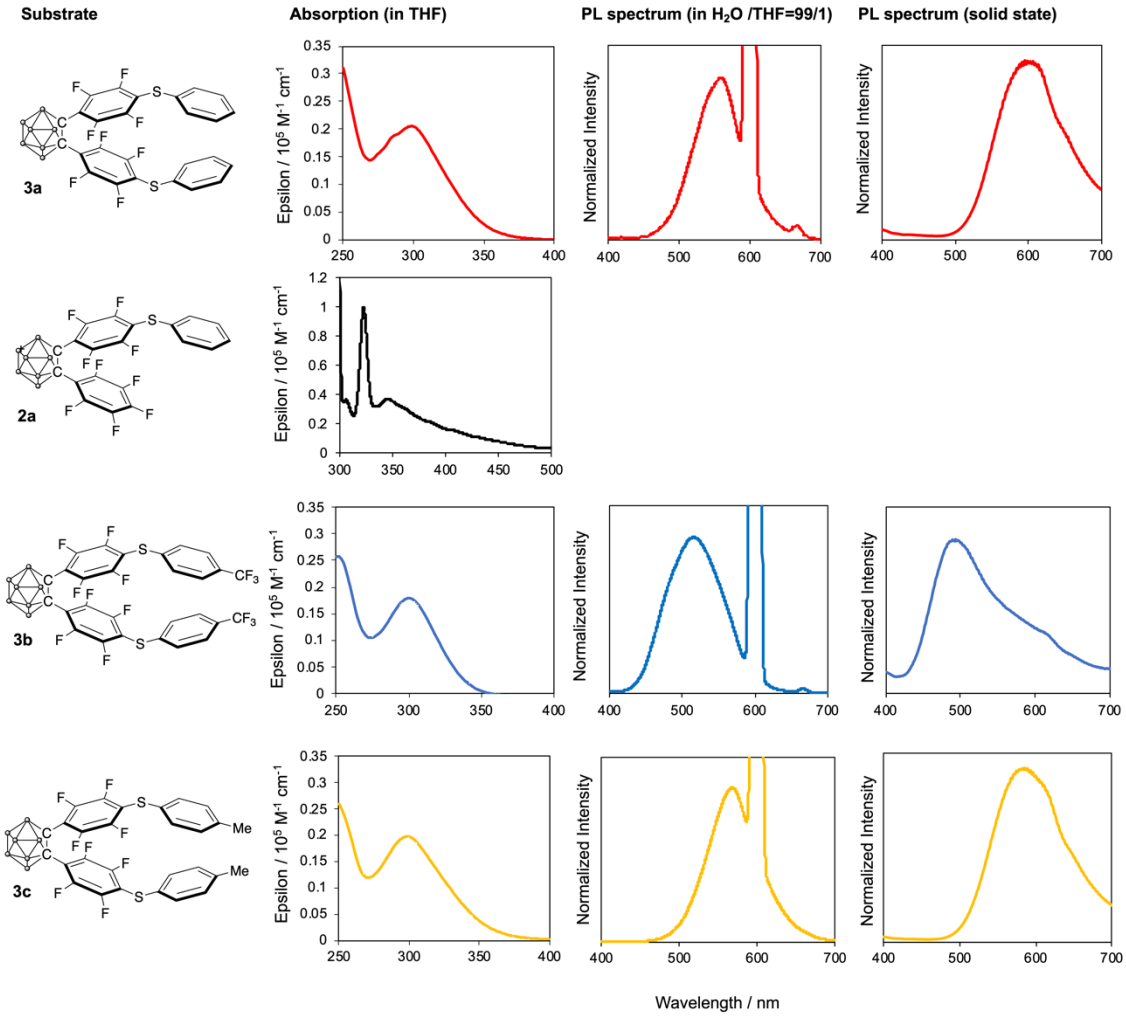


Fig. S4 UV-absorption and fluorescent spectra of **2a, 3a-c**. Absorption spectra were recorded with 1.0×10^{-5} M solution in THF. Fluorescent spectra were recorded both in H_2O/THF = 99/1 (v/v) (1.0×10^{-5} M) excited at 300 nm, or in solid state excited at the absorption peak in THF solution.

7. Single crystal X-ray diffraction analysis of 1

*Note: For the refinement of **3a**, unreasonably diffraction peaks, which presumably derived from crack of a single crystal or on-surface contaminates, were omitted.*

Table S1. Crystallographic data of **1** and **3a**.

Crystal data	**1**	**3a**
CCDC	2010815	2010816
Empirical Formula	C14H10B10F10	C26H20B10F8S2
Formula Weight	476.3	656.6
Crystal Dimension, mm^{-3}	0.30, 0.30, 0.30	0.15, 0.10, 0.10
Crystal System	triclinic	orthorhombic
Space Group	P-1	$Pna2_1$
a, Å	9.7685(13)	28.3905(12)
b, Å	10.2940(14)	7.0545(4)
c, Å	11.1361(15)	28.8336(15)
α, deg	116.860(3)	90
β, deg	94.106(4)	90
γ, deg	90.486(4)	90
Volume, Å	995.4(2)	5774.8(5)
D_{calcd}, g cm^{-3}	1.589	1.511
Z	2	8
F(000)	468	2640
Data Collection	Data Collection	Data Collection
Temperature, deg	23	-180
2θmax, deg	55.02	55.22
Tmin/Tmax	0.7298 / 1.0000	0.4179 / 1.0000
Refinement	Refinement	Refinement
No. of Observed Data	2055	10537
No. of Parameters	347	829
R1[a], wR2[b]	0.0612, 0.2085	0.1171, 0.3603
Goodness of Fit Indictor	1.092	1.459

[a] $R1 = \sum ||Fo| - |Fc|| / \sum |Fo|$ [b] $wR2 = [\sum w ((Fo^2 - Fc^2)^2 / \sum w (Fo^2)^2]^{1/2}$ $w = [\sigma^2(Fo^2)]^{-1}$

8. DFT calculation

Table S2. Cartesian coordinates of the optimized structure for **1**.

	X	Y	Z
B	0.8850321	4.2912163	-0.011622
B	1.4633461	2.8562242	0.8693371
B	0.018153	3.7138653	1.4401591
B	1.4412451	2.8558322	-0.9072821
B	-0.8849381	4.2912243	0.010904
B	0.017271	1.9418921	1.3936371
B	-0.018064	3.7137533	-1.4408221
B	-1.4411611	2.8559322	0.9066771
B	-0.017198	1.9417932	-1.3941581
B	-1.4632651	2.8561552	-0.8699411
C	-0.9416511	1.5088421	0.011541
C	0.9417211	1.5088281	-0.01202
H	-2.4589902	2.7198622	-1.4952611
H	-2.4209022	2.7176722	1.5567881
H	-1.5342901	5.2849874	0.018791
H	-0.031642	4.2795793	-2.4837202
H	1.5343921	5.2849734	-0.019581
H	2.4209742	2.7174452	-1.5573941
H	2.4590732	2.7200282	1.4946601
H	0.031736	4.2797913	2.4830032
H	0.030673	1.2453691	2.3286162
H	-0.030614	1.2453051	-2.3291452
C	-1.7106041	0.212497	0.017705
C	-2.1703862	-0.408014	-1.1666521
C	-2.1171102	-0.432898	1.2080481
C	-2.8959782	-1.5977261	-1.1708391
C	-2.8418582	-1.6231021	1.2196431
C	-3.2299832	-2.2191112	0.026128
C	1.7106441	0.212457	-0.017879
C	2.1166952	-0.433589	-1.2080201
C	2.1708432	-0.407446	1.1666441
C	2.8413462	-1.6238581	-1.2192461
C	2.8963542	-1.5972031	1.1712001
C	3.2298582	-2.2192612	-0.025558
F	-3.9272123	-3.3550093	0.029882
F	-3.1813822	-2.1832942	2.3862122
F	-1.8561141	0.078301	2.4169562
F	-3.2880983	-2.1332392	-2.3324052
F	-1.9629322	0.128683	-2.3747372
F	1.9638902	0.129911	2.3745202
F	3.2888812	-2.1321162	2.3329042
F	3.9270063	-3.3552103	-0.028956
F	3.1804092	-2.1846922	-2.3856422
F	1.8553461	0.077005	-2.4171082

Table S3. Cartesian coordinates of the optimized structure for **1**$^{\bullet-}$.

	X	Y	Z
B	0.876649	4.155059	-0.000134
B	1.503239	2.75353	0.901051
B	-0.000003	3.508007	1.431795
B	1.503303	2.753633	-0.90135
B	-0.876672	4.155091	-0.00012
B	-0.000118	1.687318	1.215848
B	-0.000045	3.507911	-1.432006
B	-1.503377	2.753746	0.901188
B	0.000003	1.687235	-1.215935
B	-1.503311	2.753523	-0.901211
C	-1.218267	1.418652	0.000102
C	1.218151	1.41861	-0.000174
H	-2.468438	2.745361	-1.59616
H	-2.468521	2.745633	1.596108
H	-1.490623	5.178752	-0.000186
H	-0.000162	4.067048	-2.485576
H	1.490636	5.178698	-0.000137
H	2.468447	2.745436	-1.596271
H	2.468365	2.745375	1.596003
H	0.000132	4.067216	2.485326
H	0.00006	0.967557	2.151006
H	-0.000211	0.967409	-2.151044
C	-2.082125	0.226216	0.000121
C	-2.546688	-0.390954	-1.18601
C	-2.546604	-0.391045	1.186252
C	-3.343826	-1.531402	-1.194601
C	-3.343743	-1.531491	1.194822
C	-3.745862	-2.117391	0.000102
C	2.081997	0.226159	-0.000122
C	2.546445	-0.391192	-1.186222
C	2.546734	-0.390828	1.186037
C	3.343643	-1.531596	-1.194732
C	3.343942	-1.531228	1.194688
C	3.745883	-2.117348	0.000019
F	-4.513483	-3.224642	0.000086
F	-3.74401	-2.067924	2.365534
F	-2.249496	0.119547	2.39452
F	-3.744162	-2.067757	-2.365326
F	-2.249658	0.119742	-2.394255
F	2.24995	0.120094	2.394245
F	3.744475	-2.06738	2.365438
F	4.513608	-3.224527	0.000094
F	3.74389	-2.068104	-2.365417
F	2.249317	0.119314	-2.39452

Table S4. Cartesian coordinates of the optimized structure for $\mathbf{1}^{2-}$.

	X	Y	Z
B	0.8815344	4.0959742	0.0002805
B	1.5291774	2.7282437	0.8933032
B	-0.0006072	3.412945	1.436607
B	1.5302348	2.7285888	-0.8923359
B	-0.8815322	4.095975	-0.0004297
B	-0.0005006	1.5798962	1.148079
B	0.0006087	3.4128871	-1.4367287
B	-1.5302341	2.7286257	0.8922412
B	0.0004999	1.5798496	-1.1481268
B	-1.5291763	2.7282095	-0.8933979
C	-1.2655033	1.3637144	-0.0001005
C	1.2655025	1.3637133	0.0000604
H	-2.5168687	2.7671229	-1.5671854
H	-2.5186482	2.7679301	1.56497
H	-1.4592494	5.1495861	-0.0007299
H	0.0007557	3.9763938	-2.4974149
H	1.4592523	5.1495848	0.0005382
H	2.518649	2.7678661	-1.5650659
H	2.5168702	2.767182	1.5670891
H	-0.0007541	3.9764942	2.4972706
H	-0.0005172	0.8534499	2.087979
H	0.0005159	0.8533649	-2.0879982
C	-2.1739521	0.2298444	-0.0002658
C	-2.6743308	-0.383809	-1.1843698
C	-2.6749149	-0.3832453	1.1838629
C	-3.5115384	-1.4921715	-1.1912194
C	-3.5121349	-1.4915856	1.1908414
C	-3.9426511	-2.068272	-0.000161
C	2.1739503	0.2298429	0.0002651
C	2.6748596	-0.383324	-1.183846
C	2.6743832	-0.3837323	1.1843868
C	3.5120789	-1.4916649	-1.1907906
C	3.5115936	-1.4920927	1.1912704
C	3.9426515	-2.0682717	0.00023
F	-4.7290262	-3.1811863	-0.0000835
F	-3.9372305	-2.0187934	2.3705472
F	-2.364248	0.1168454	2.4012694
F	-3.9359697	-2.0200061	-2.3708854
F	-2.3629145	0.1154383	-2.4019198
F	2.363036	0.1156041	2.4019177
F	3.9360829	-2.0198471	2.3709514
F	4.7290283	-3.1811847	0.0001895
F	3.9371185	-2.0189514	-2.3704814
F	2.364124	0.1166785	-2.4012713

Table S5. Cartesian coordinates of the optimized structure for **2a**.

	X	Y	Z
B	2.0804831	4.3734389	0.5613432
B	1.2090431	3.6026586	1.9099402
B	0.3011665	4.4964076	0.6739662
B	2.5374913	2.7395399	1.1044451
B	1.0974506	4.2265631	-0.9028007
B	-0.3079482	2.9303136	1.2386399
B	2.4550404	3.0971733	-0.6321968
B	-0.4056724	3.3618954	-0.4945369
B	1.7728723	1.5788542	-0.0229902
B	0.9226703	2.4983491	-1.2999377
C	0.0488863	1.8002208	-0.0318707
C	1.1008683	1.9585757	1.5328551
H	0.8032462	1.9879177	-2.3612139
H	-1.4808509	3.4730857	-0.9764712
H	1.0993763	5.0383006	-1.769319
H	3.4409972	3.0830888	-1.2924946
H	2.8030997	5.2925613	0.7683641
H	3.513584	2.3919759	1.677236
H	1.2305371	3.8759136	3.061613
H	-0.2721784	5.4954982	0.9593151
H	-1.2603881	2.7751252	1.8935774
H	2.2181387	0.5186163	-0.2157235
C	-0.8490124	0.6092563	-0.2306243
C	-0.4384046	-0.5609223	-0.9057754
C	-2.2073919	0.5974861	0.1606769
C	-1.2738456	-1.6603595	-1.0865878
C	-3.0414878	-0.4989241	-0.0343453
C	-2.5968559	-1.6788184	-0.6383234
C	1.0534825	0.8947593	2.599035
C	1.9447317	-0.2022354	2.6264969
C	0.1761822	0.9596815	3.7057573
C	1.9122862	-1.1850097	3.614018
C	0.131937	-0.0154755	4.7002699
C	0.9961224	-1.1022	4.6550231
F	-4.3201904	-0.3822646	0.3546154
F	-2.7943057	1.6769508	0.6982797
F	-0.7669244	-2.7284692	-1.7243549
F	0.7876738	-0.6774091	-1.4355422
F	-0.6563635	1.9904542	3.8916961
F	-0.7346086	0.1056617	5.7131284
F	2.7799781	-2.2029676	3.568686
F	2.9113085	-0.3537442	1.7139151
S	-3.6293796	-3.0927818	-0.9566369
C	-4.4218776	-3.367971	0.6390102
C	-5.8159312	-3.2859594	0.7257647
C	-3.665564	-3.7560943	1.7528177
C	-6.4526617	-3.5877498	1.932886
H	-6.3947474	-2.9768183	-0.1394529
C	-4.3076942	-4.0352241	2.9608211
H	-2.5859528	-3.8475025	1.6723052
C	-5.7011176	-3.95499	3.0518159
H	-7.5354296	-3.5230162	1.999021
H	-3.7199999	-4.3305423	3.8261222
H	-6.198233	-4.1814273	3.9911852
F	0.9607596	-2.0380182	5.6049114

Table S6. Cartesian coordinates of the optimized structure for **3a**.

	X	Y	Z
B	-1.2946321	4.5176253	1.3067141
B	-2.3453532	4.8925013	-0.084519
B	-1.4549821	6.1980945	0.7267761
B	-1.2996821	3.4578613	-0.120347
B	0.136479	5.5572784	1.2300491
B	-1.5167551	6.1508334	-1.0414321
B	0.240727	3.8689793	0.659682
B	0.001809	6.5983105	-0.204727
B	0.129898	3.8931703	-1.1067521
B	1.0470471	5.1633974	-0.251465
C	0.03866	5.5716254	-1.5525281
C	-1.4679941	4.4663183	-1.4718841
H	2.2124792	5.2315234	-0.451452
H	0.422209	7.6924966	-0.36241
H	0.707861	5.9475734	2.1951382
H	0.8804351	3.0287862	1.2015011
H	-1.7693401	4.1405923	2.3278402
H	-1.7329841	2.3620562	-0.221073
H	-3.5247143	4.8225333	-0.169128
H	-2.0395571	7.0457375	1.3171281
H	-2.0949231	6.9065645	-1.7153331
H	0.639595	3.1283532	-1.8244331
C	0.56701	6.0366734	-2.8843812
C	1.4944211	5.3057484	-3.6571813
C	0.233433	7.2964855	-3.4335552
C	1.9651071	5.7496374	-4.8902824
C	0.7236551	7.7447206	-4.6562643
C	1.5824751	6.9734015	-5.4448474
C	-2.1213422	3.9825983	-2.7401992
C	-1.8444741	2.7125272	-3.2973942
C	-3.1146322	4.7052603	-3.4347882
C	-2.4489922	2.2466322	-4.4608853
C	-3.7003663	4.2436353	-4.6108073
C	-3.3754642	3.0091622	-5.1782334
F	0.36282	8.9735287	-5.0563494
F	-0.54129	8.1695026	-2.7742662
F	2.8259212	4.9559414	-5.5511424
F	1.9954431	4.1336713	-3.2411162
F	-3.5700683	5.8866824	-2.9935602
F	-4.6164563	5.0308424	-5.2013454
F	-2.1310812	1.0098901	-4.8727054
F	-1.0131671	1.8470981	-2.6998822
S	2.2754402	7.4986895	-6.9959775
S	-4.2115433	2.4618912	-6.6491265
C	0.8522041	8.1811116	-7.8639966
C	0.9259821	9.4957447	-8.3370226
C	-0.267394	7.3895865	-8.1508706
C	-0.125155	10.0178877	-9.0962626
H	1.7914651	10.1082707	-8.1019336
C	-1.3236071	7.9262355	-8.8890126
H	-0.310571	6.3616735	-7.8016566
C	-1.2526331	9.2389867	-9.3667087
H	-0.066032	11.0394488	-9.4621747
H	-2.1962862	7.3142585	-9.1015847
H	-2.0731122	9.6509617	-9.9478687
C	-2.8760492	1.7625261	-7.6350786
C	-2.9961312	0.441797	-8.0808286
C	-1.7855471	2.5458592	-8.0344916
C	-2.0203601	-0.094639	-8.9258726
H	-3.8377913	-0.164278	-7.7586296
C	-0.8027911	1.9951491	-8.8587036
H	-1.7078831	3.5782703	-7.7049896
C	-0.9205061	0.676227	-9.3094236
H	-2.1152772	-1.1209301	-9.2703936
H	0.048277	2.6008272	-9.1588827
H	-0.157769	0.253211	-9.9574537

Table S7. Cartesian coordinates of the optimized structure for **3b**.

	X	Y	Z
B	0.8881025	3.7469864	-0.8951062
B	1.4252521	2.8051502	0.5127255
B	2.0983893	4.4218922	0.2352302
B	-0.2953657	2.8316277	0.0739305
B	0.7999612	5.451838	-0.4284951
B	1.6230919	3.949265	1.8759697
B	-0.6926726	4.4684326	-0.4850329
B	1.2787384	5.5973353	1.282439
B	-1.0855309	3.992521	1.1766751
B	-0.4389228	5.6268903	0.8328865
C	0.1105398	4.7521784	2.1790329
C	0.2123544	2.9550687	1.6894315
H	-1.1336771	6.5571794	1.0572455
H	1.8055489	6.5022534	1.8357989
H	1.0077502	6.3449766	-1.1826809
H	-1.5638236	4.6385367	-1.2726926
H	1.1665968	3.3853793	-1.9911668
H	-0.8927466	1.8494634	-0.2106119
H	2.0560324	1.8049435	0.5318089
H	3.2469201	4.554826	-0.0320579
H	2.3576704	3.7409267	2.7570928
H	-2.1611772	3.8277206	1.5958643
C	-0.2763714	5.1820574	3.5729367
C	-1.5883612	5.5938558	3.8962327
C	0.6532453	5.34995	4.6230736
C	-1.9376284	6.0936173	5.1498343
C	0.2988711	5.8535554	5.871609
C	-1.0071467	6.2402319	6.1797049
C	-0.02866	1.8408348	2.6782751
C	-1.3040517	1.2911297	2.9360725
C	1.0304529	1.1596963	3.3182844
C	-1.4980539	0.1927575	3.7691399
C	0.8290724	0.06258	4.154456
C	-0.4407595	-0.4576723	4.4088422
F	1.273787	5.996246	6.7833249
F	1.9572966	5.0839863	4.4620959
F	-3.2162457	6.454124	5.3379368
F	-2.5826128	5.5592902	2.9990841
F	2.31057	1.5092909	3.1346117
F	1.9139607	-0.5025614	4.7055431
F	-2.7529838	-0.259975	3.9179671
F	-2.4102974	1.7640761	2.3446341
S	-1.4595952	7.0265956	7.7174521
S	-0.6441535	-1.9552121	5.3599208
C	-1.073821	5.7490629	8.9326067
C	0.0501363	5.8886052	9.7520692
C	-1.9565366	4.6761741	9.1225842
C	0.3037333	4.9474545	10.7533336
H	0.7289952	6.7219922	9.6036915
C	-1.7013861	3.7355386	10.1174779
H	-2.8447103	4.5864177	8.5045839
C	-0.5684979	3.8718399	10.9304132
H	1.1781749	5.05267	11.3863783
H	-2.3904491	2.9104038	10.2701825
C	-1.6996126	-1.4094138	6.718644
C	-3.0475621	-1.7793755	6.741397
C	-1.1425839	-0.7072419	7.7971342
C	-3.846427	-1.4349531	7.8349423
H	-3.473823	-2.3257197	5.9064285
C	-1.9397512	-0.360126	8.885165
H	-0.0885141	-0.4470303	7.7907048
C	-3.2928687	-0.723096	8.9007496
H	-4.8933818	-1.7179745	7.8510845
H	-1.505383	0.1750873	9.7241797
C	-0.3151592	2.8336574	11.9929565
C	-4.1315542	-0.3265802	10.0883646
F	-0.1492289	1.5937168	11.4460092
F	0.7922164	3.0897504	12.7236719
F	-1.3537647	2.7301933	12.8578925
F	-5.4087683	-0.7578754	9.9965495
F	-3.6255534	-0.8092595	11.2495685
F	-4.1824193	1.0305617	10.2293381

Table S8. Cartesian coordinates of the optimized structure for **3c**.

	X	Y	Z
B	0.460757	4.8788714	-0.053824
B	-0.306744	3.6843633	-1.1328071
B	0.077802	3.2406402	0.543642
B	-0.8582701	5.3727224	-1.1393611
B	-0.19851	4.6738213	1.5761611
B	-1.4832101	2.7706922	-0.148132
B	-0.8238941	5.9773004	0.528903
B	-1.3842291	3.3489062	1.5440411
B	-2.3571892	5.4204924	-0.16014
B	-1.9445391	5.0342694	1.5336471
C	-2.6499252	3.8565233	0.541017
C	-1.9524551	4.0817723	-1.1894311
H	-2.6347742	5.4822004	2.3855772
H	-1.6661541	2.5921282	2.4082382
H	0.429806	4.8845803	2.5616242
H	-0.654368	7.1323965	0.7430811
H	1.5708351	5.2450854	-0.26347
H	-0.8018881	6.0548444	-2.1040781
H	0.137257	3.1547932	-2.0947122
H	0.8988341	2.4143032	0.7714831
H	-1.8021391	1.6797051	-0.408776
H	-3.2561052	6.1074444	-0.442819
C	-4.0584483	3.3592552	0.7297321
C	-5.1883664	4.2040943	0.7668611
C	-4.3562793	1.9974041	0.9670391
C	-6.4848585	3.7230463	0.9289081
C	-5.6521474	1.5248221	1.1498961
C	-6.7678405	2.3660762	1.1037951
C	-2.8186102	3.8229533	-2.3934772
C	-3.5071263	4.8569843	-3.0690302
C	-2.9580112	2.5557052	-2.9988452
C	-4.3056713	4.6327503	-4.1862513
C	-3.7748033	2.3335422	-4.1042983
C	-4.4956143	3.3567512	-4.7251183
F	-5.8039404	0.215668	1.4027241
F	-3.3897402	1.0758971	1.0871421
F	-7.4876666	4.6190703	0.9196881
F	-5.0799794	5.5365474	0.66112
F	-2.2944032	1.4800051	-2.5506702
F	-3.8523183	1.0778531	-4.5793723
F	-4.8808173	5.7003374	-4.7609423
F	-3.3855282	6.1407074	-2.7015022
S	-8.4476646	1.8374251	1.3549851
S	-5.4774954	3.0007222	-6.1651355
C	-8.5586436	0.350853	0.346402
C	-8.9141377	-0.8562261	0.9536331
C	-8.3924806	0.405536	-1.0439281
C	-9.0962887	-2.0004001	0.17187
H	-9.0370926	-0.9062911	2.0316401
C	-8.5541916	-0.7481071	-1.8086201
H	-8.1410836	1.3469101	-1.5250101
C	-8.9108287	-1.9711811	-1.2161101
H	-9.3740497	-2.9336682	0.656399
H	-8.4138356	-0.695163	-2.8863762
C	-6.9837595	3.9403303	-5.8690584
C	-7.3795075	4.9003064	-6.8037985
C	-7.8109116	3.6557043	-4.7742163
C	-8.5938246	5.5724894	-6.6383095
H	-6.7388295	5.1308594	-7.6500245
C	-9.0075706	4.3500843	-4.6088183
H	-7.5206316	2.8924782	-4.0572393
C	-9.4225607	5.3188594	-5.5381674
H	-8.8910056	6.3169385	-7.3733965
H	-9.6370907	4.1267603	-3.7497883
C	-9.0742286	-3.2156202	-2.0571291
H	-9.7022817	-3.0249562	-2.9354722
H	-8.1034506	-3.5731293	-2.4246752
H	-9.5319107	-4.0286883	-1.4846501
C	-10.720692	6.0666804	-5.3424744
H	-11.554451	5.3782474	-5.1592174
H	-10.661492	6.7405695	-4.4779633
H	-10.970039	6.6723685	-6.2194975

Table S9. Cartesian coordinates of the optimized structure for diphenyl-*o*-carborane.

	X	Y	Z
B	3.50874	0.887985	-0.038834
B	2.071697	1.404458	-0.951838
B	2.943476	-0.062806	-1.44228
B	2.070187	1.479474	0.821276
B	3.508745	-0.887964	0.038856
B	1.176895	-0.060301	-1.409333
B	2.943471	0.062825	1.442296
B	2.070199	-1.479458	-0.821266
B	1.176882	0.060309	1.409333
B	2.071697	-1.404443	0.951852
C	0.721881	-0.880572	0.040302
C	0.721875	0.880574	-0.040285
H	1.918017	-2.378492	1.608494
H	1.92279	-2.507578	-1.390591
H	4.502559	-1.538053	0.065609
H	3.516323	0.111109	2.481654
H	4.502547	1.538084	-0.065576
H	1.922757	2.507584	1.390614
H	1.917995	2.378507	-1.608474
H	3.51633	-0.111096	-2.481638
H	0.453156	-0.110748	-2.337952
H	0.453169	0.110748	2.337974
C	-0.588351	-1.628361	0.057157
C	-1.283611	-1.853254	1.255844
C	-1.109281	-2.171143	-1.128988
C	-2.473136	-2.583458	1.264706
H	-0.895918	-1.467792	2.191048
C	-2.29727	-2.902992	-1.118586
H	-0.581764	-2.034202	-2.065992
C	-2.987733	-3.108683	0.077851
H	-2.993249	-2.743613	2.205367
H	-2.678615	-3.315169	-2.049014
H	-3.912935	-3.678815	0.086217
C	-0.58836	1.628357	-0.057161
C	-1.109347	2.171064	1.128994
C	-1.283569	1.853317	-1.255865
C	-2.29734	2.902907	1.118582
H	-0.581869	2.034071	2.066012
C	-2.473098	2.583514	-1.264736
H	-0.895832	1.467916	-2.191076
C	-2.987752	3.108665	-0.077872
H	-2.678728	3.315026	2.049019
H	-2.99317	2.743723	-2.205411
H	-3.912957	3.67879	-0.086245

9. NMR Charts

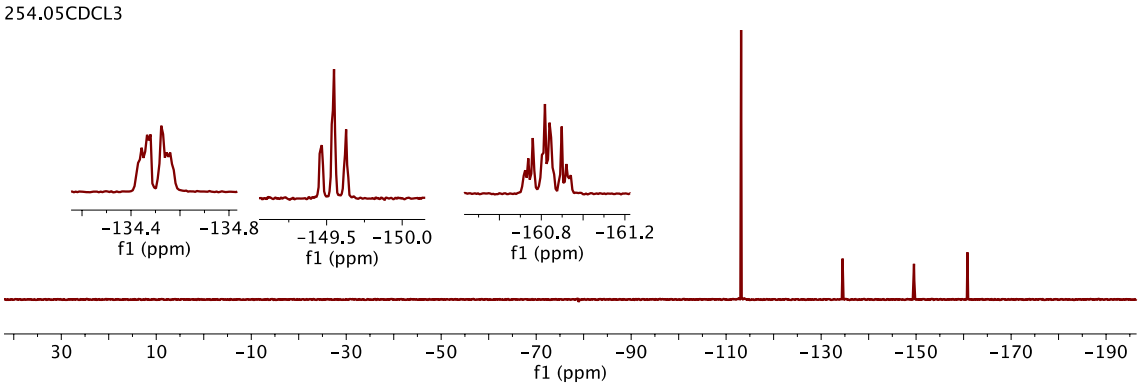


Fig. S5 ^{19}F NMR spectrum (254.05 MHz, $CDCl_3$, 25 °C) of perfluorotolane.

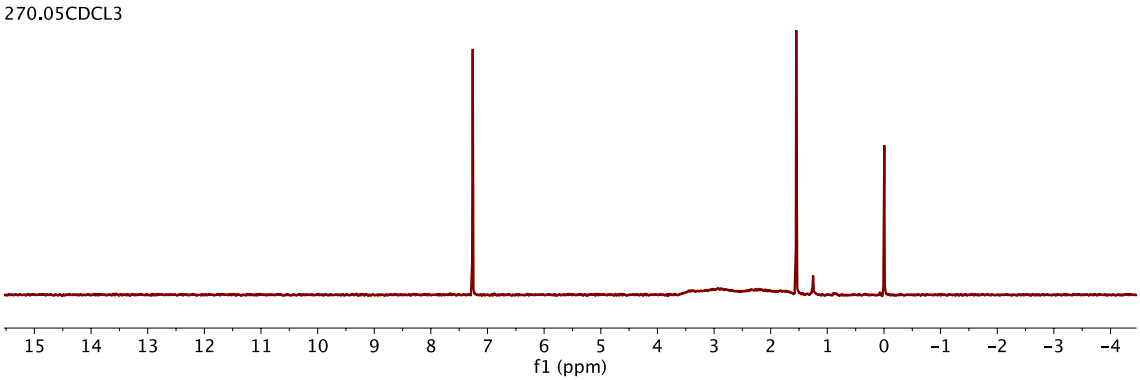


Fig. S6 ^{1}H NMR spectrum (270.05 MHz, $CDCl_3$, 25 °C) of **1**.

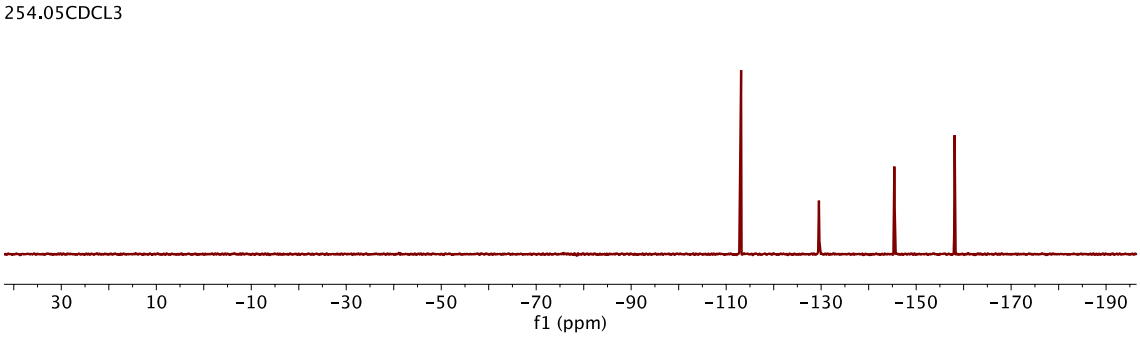


Fig. S7 ^{19}F NMR spectrum (254.05 MHz, $CDCl_3$, 25 °C) of **1**.

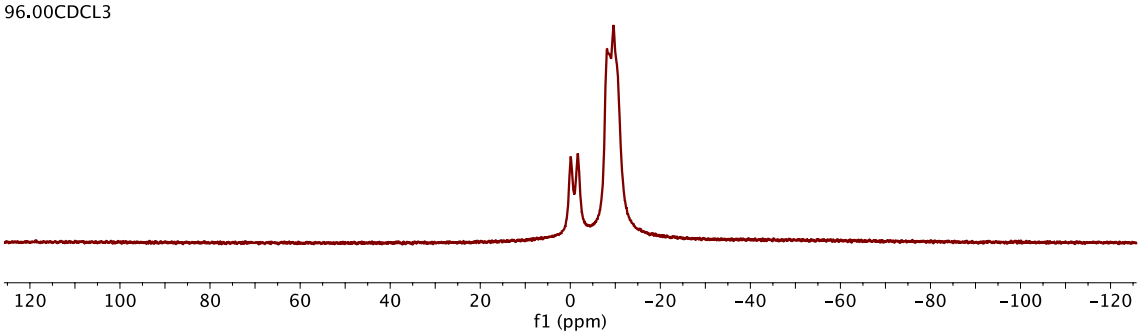


Fig. S8 ^{11}B NMR spectrum (96.00 MHz, $CDCl_3$, 25 °C) of **1**.

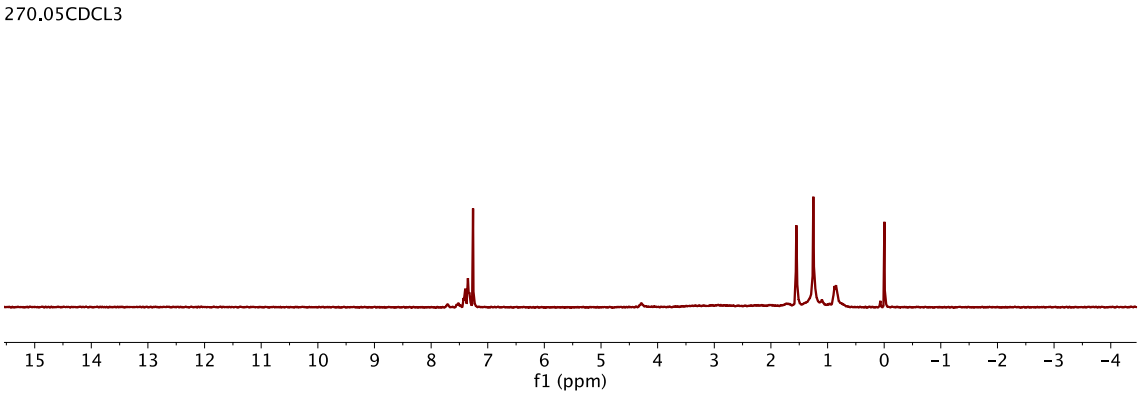


Fig. S9 ^{1}H NMR spectrum (270.05 MHz, $CDCl_3$, 25 °C) of **2a**.

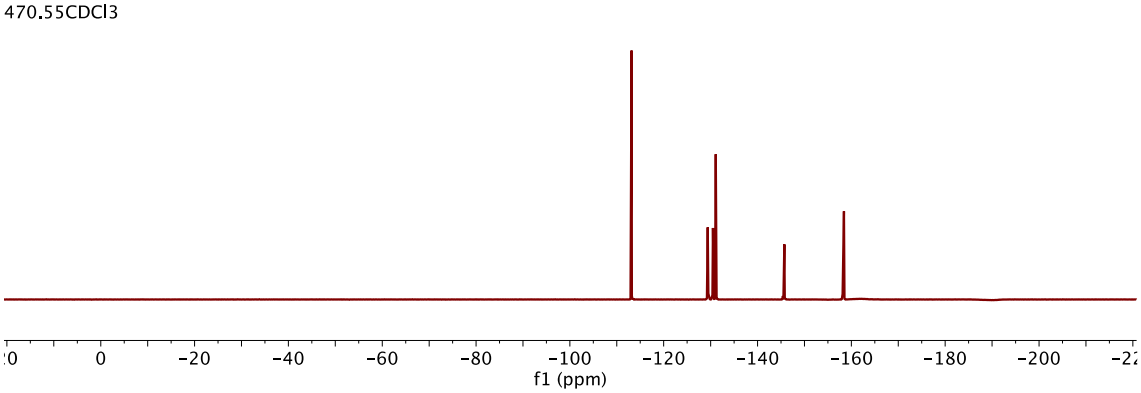


Fig. S10 ^{19}F NMR spectrum (470.55 MHz, $CDCl_3$, 25 °C) of **2a**.

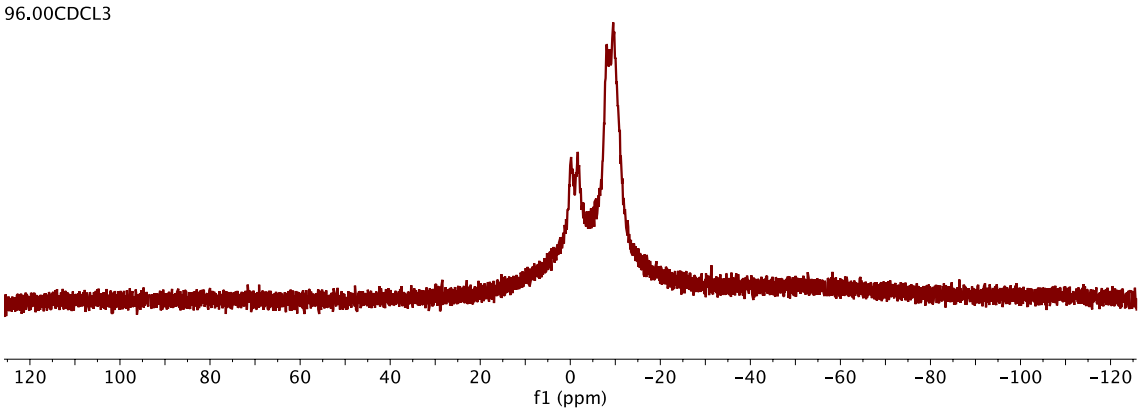


Fig. S11 ^{11}B NMR spectrum (96.00 MHz, $CDCl_3$, 25 °C) of **2a**.

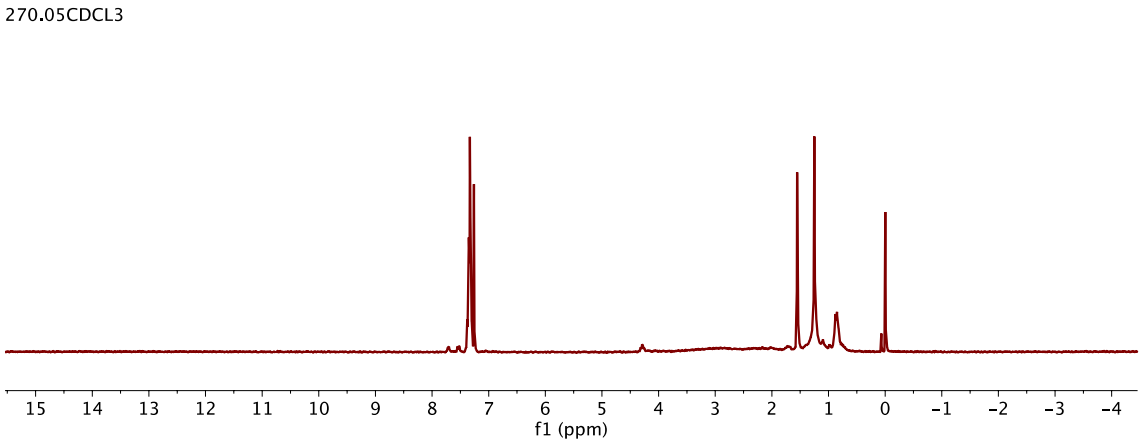


Fig. S12 ^{1}H NMR spectrum (270.05 MHz, $CDCl_3$, 25 °C) of **3a**.

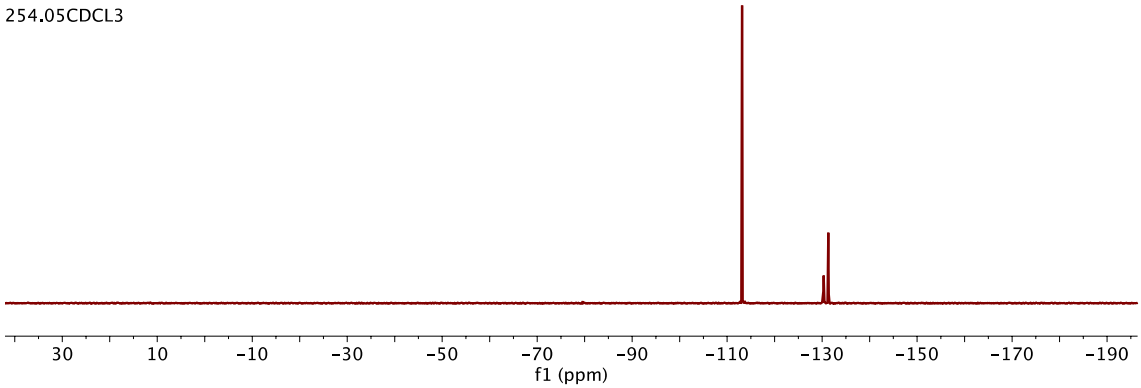


Fig. S13 ^{19}F NMR spectrum (254.05 MHz, $CDCl_3$, 25 °C) of **3a**.

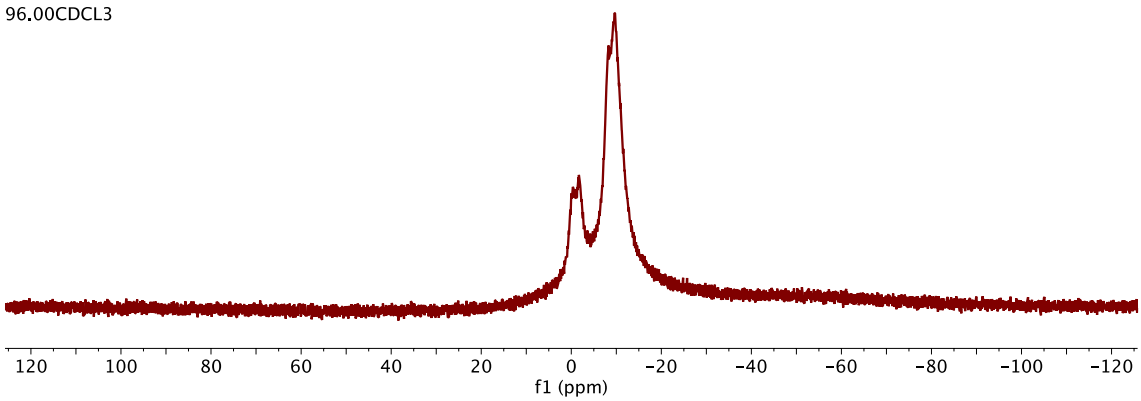


Fig. S14 ^{11}B NMR spectrum (96.00 MHz, $CDCl_3$, 25 °C) of **3a**.

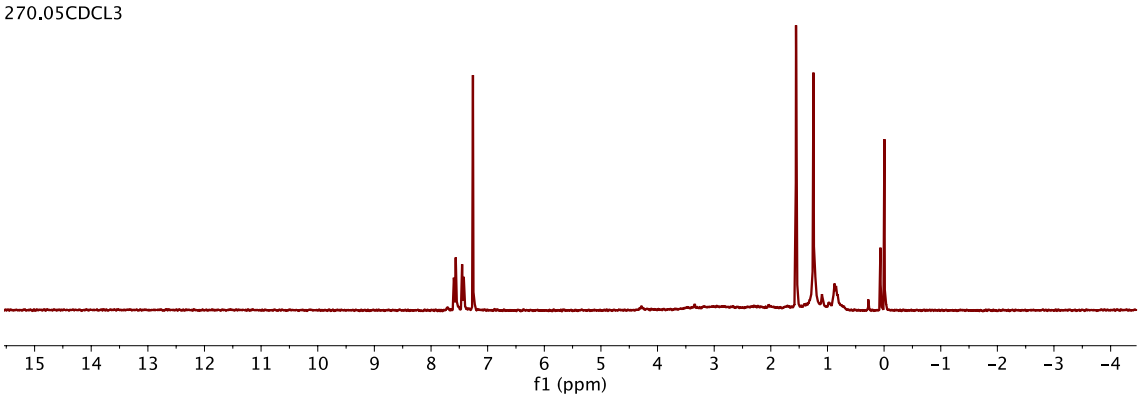


Fig. S15 ^{1}H NMR spectrum (270.05 MHz, $CDCl_3$, 25 °C) of **2b**.

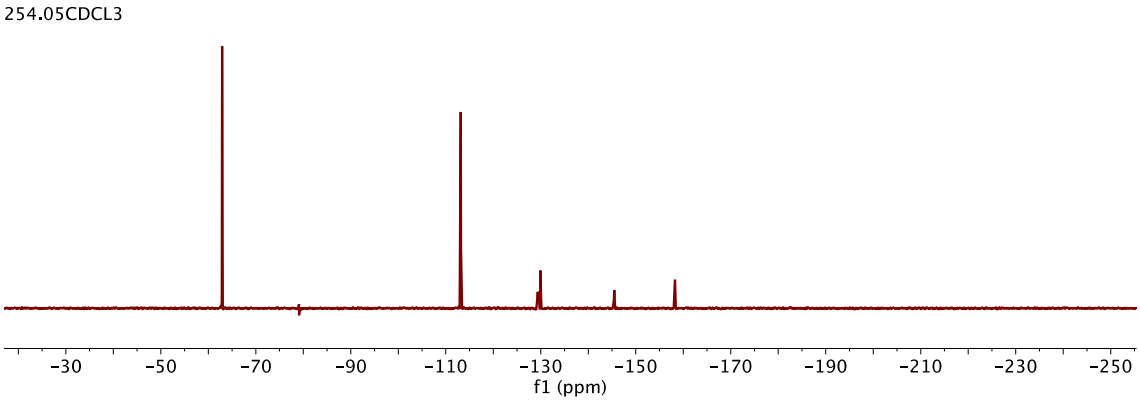


Fig. S16 ^{19}F NMR spectrum (254.05 MHz, $CDCl_3$, 25 °C) of **2b**.

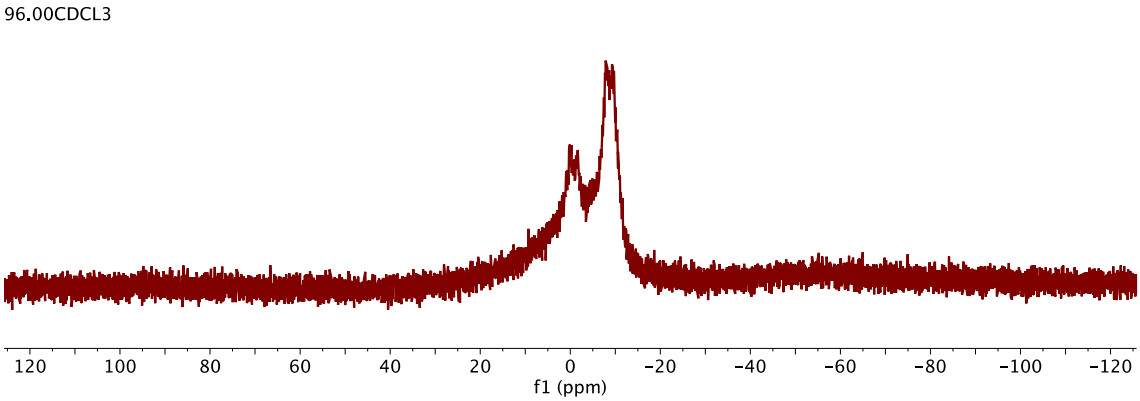


Fig. S17 ^{11}B NMR spectrum (96.00 MHz, $CDCl_3$, 25 °C) of **2b**.

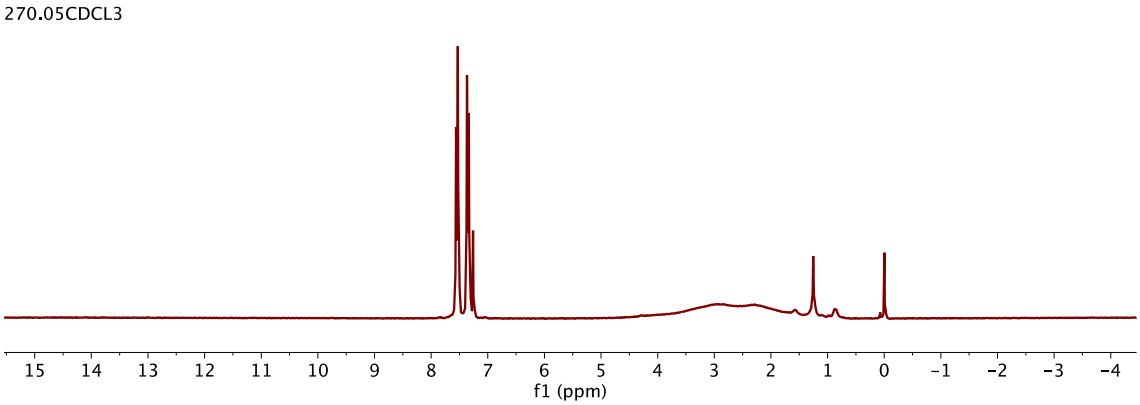


Fig. S18 ^{1}H NMR spectrum (270.05 MHz, $CDCl_3$, 25 °C) of **3b**.

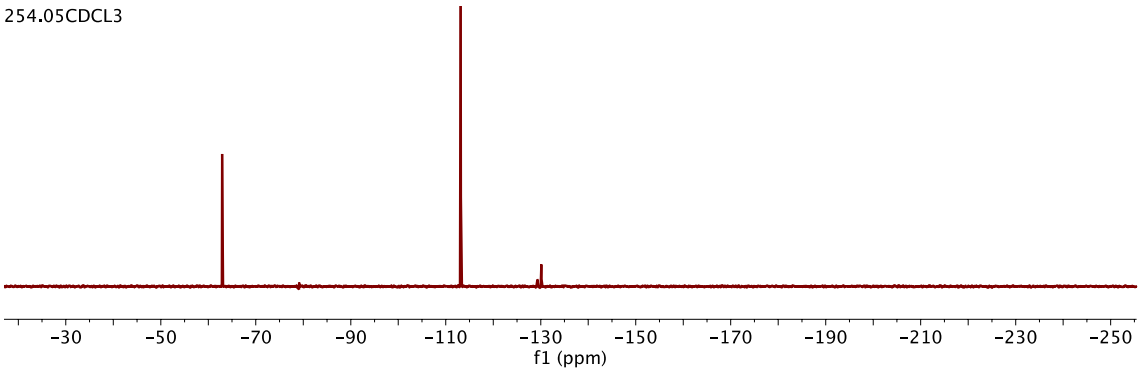


Fig. S19 ^{19}F NMR spectrum (254.05 MHz, $CDCl_3$, 25 °C) of **3b**.

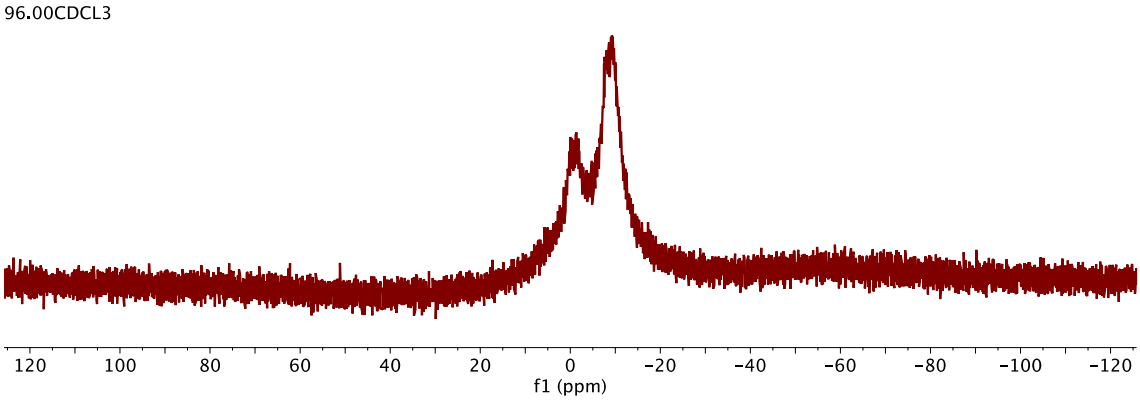


Fig. S20 ^{11}B NMR spectrum (96.00 MHz, $CDCl_3$, 25 °C) of **3b**.

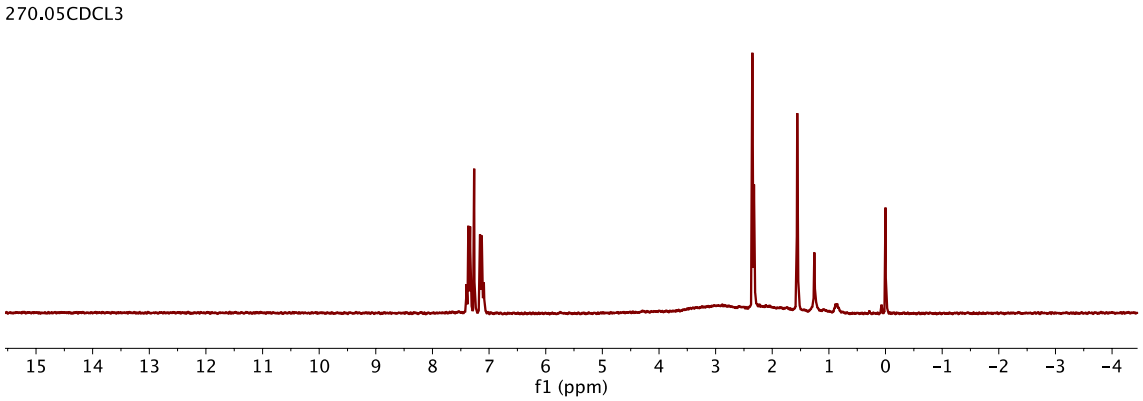


Fig. S21 ^{1}H NMR spectrum (270.05 MHz, $CDCl_3$, 25 °C) of **2c**.

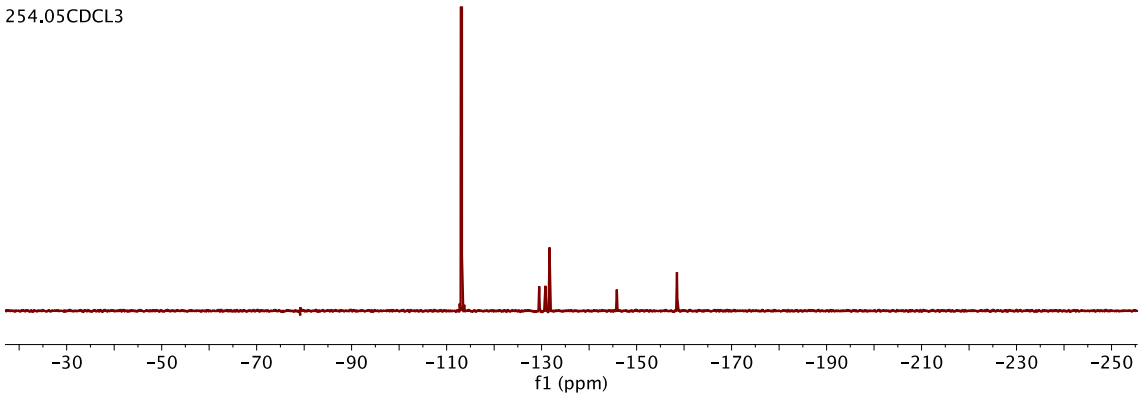


Fig. S22 ^{19}F NMR spectrum (254.05 MHz, $CDCl_3$, 25 °C) of **2c**.

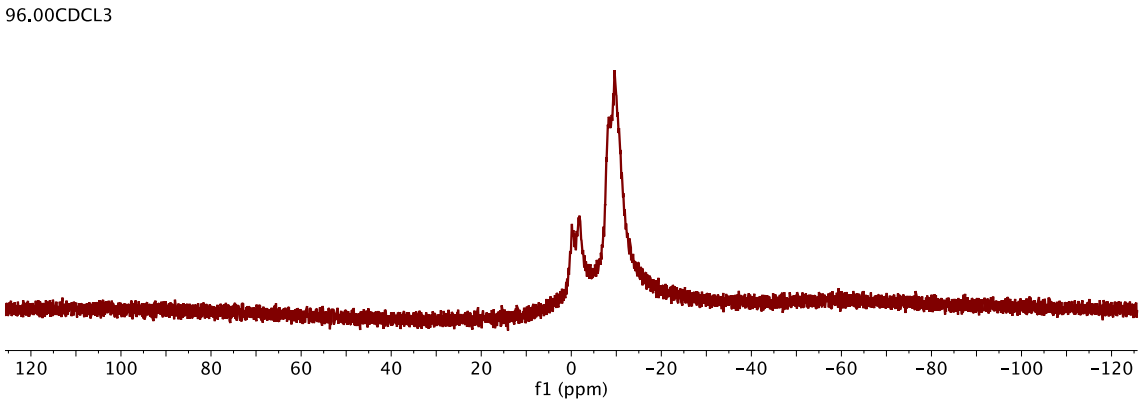


Fig. S23 ^{11}B NMR spectrum (96.00 MHz, $CDCl_3$, 25 °C) of **2c**.

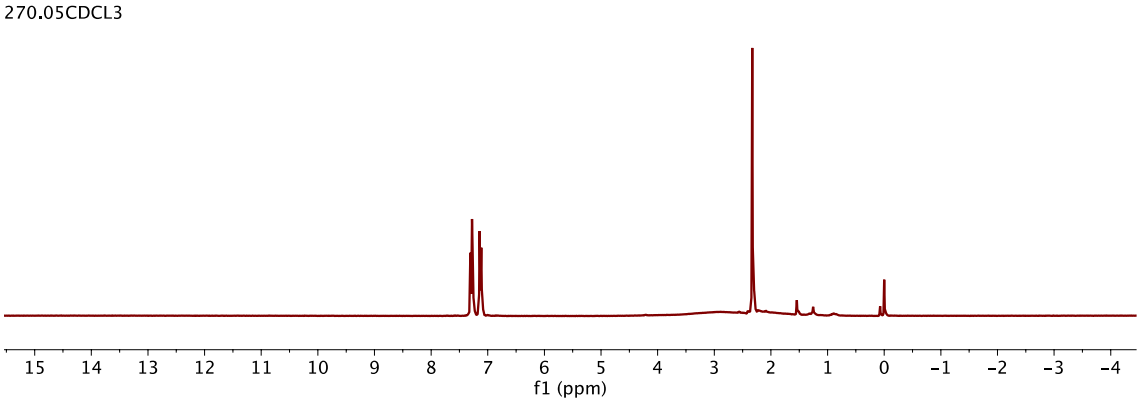


Fig. S24 ^{1}H NMR spectrum (270.05 MHz, $CDCl_3$, 25 °C) of **3c**.

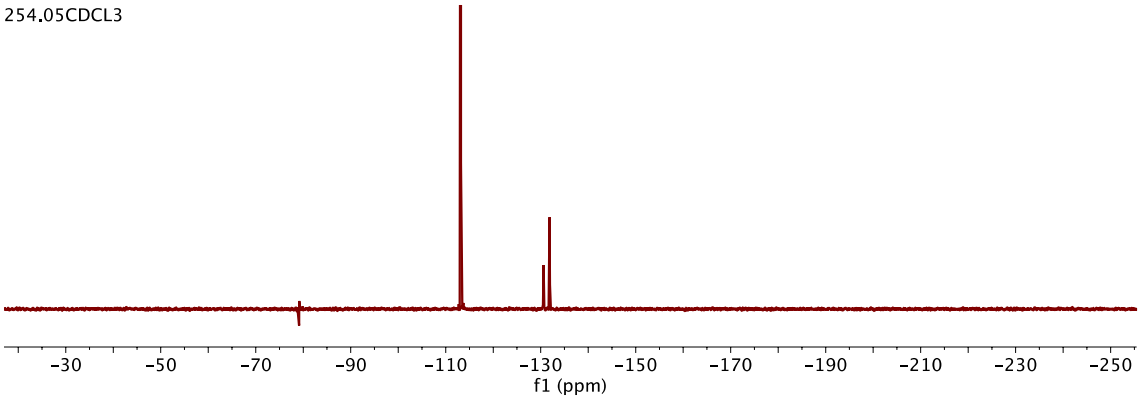


Fig. S25 ^{19}F NMR spectrum (254.05 MHz, $CDCl_3$, 25 °C) of **3c**.

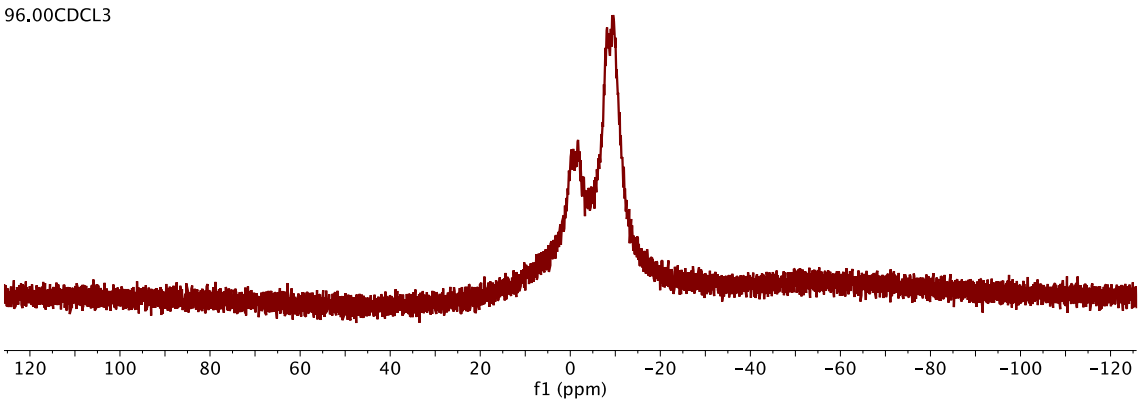


Fig. S26 ^{11}B NMR spectrum (96.00 MHz, $CDCl_3$, 25 °C) of **3c**.

10. Supporting References

(1) T. Higashi, ABSCOR. Program for Absorption Correction.; Rigaku Corporation: Japan, 1995.

(2) D. Matsuo, X. Yang, X. A Harada, K. Morimoto, T. Kato, M. Yahiro, C. Adachi, A. Orita, J. Otera, *Chem. Lett*., 2010, **39**, 1300-1302.

(3) M. E. El-Zaria, K. Keskar, A. R. Genady, J. A. Ioppolo, J. McNulty, J. F. Valliant, *Angew. Chem. Int. Ed.*, 2014, **126**, 5256-5260.

(4) H. Naito, Y. Morisaki, Y. Chujo, *Angew. Chem. Int. Ed.*, 2015, **54**, 5084-5087.