Supporting Information to

Synthesis and Ligand-Based Reduction Chemistry of Boron Difluoride Complexes with Redox-Active Formazanate Ligands

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Contents

Experimental Section

General Considerations.

All manipulations were carried out under nitrogen atmosphere using standard glovebox, Schlenk, and vacuum-line techniques. Toluene and hexane (Aldrich, anhydrous, 99.8%) were passed over columns of Al_2O_3 (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). THF (Aldrich, anhydrous, 99.8%) was dried by percolation over columns of Al_2O_3 (Fluka). All solvents were degassed prior to use and stored under nitrogen. C_6D_6 (Aldrich) and d_8-toluene (Aldrich) was vacuum transferred from Na/K alloy and stored under nitrogen. The compounds $(PhNNC(p\text{-tolyl})NNPh)_2Zn$ (**1a**) and $[MesN_2]^+[BF_4]^-$ were synthesized according to published procedures.[1] NMR spectra were recorded on a Varian Gemini 400 spectrometer. The ^1H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported in ppm relative to TMS (0 ppm); *J* is reported in Hz. Elemental analyses were performed at the Microanalytical Department of the University of Groningen or Kolbe Microanalytical Laboratory (Mülheim an der Ruhr, Germany). UV-Vis spectra were recorded in THF solution (~ 10^{-5} M) using a Perkin Elmer Lambda 900 in a quartz cell that was sealed under N_2 atmosphere. EPR spectra were recorded on a Bruker EMXplus spectrometer at 20 K in THF. All electrochemical measurements were performed under an inert N_2 atmosphere in a glove box using an Autolab PGSTAT 100 computer-controlled potentiostat. Cyclic voltammetry (CV) was performed using a three-electrode configuration comprising of a Pt wire counter electrode, a Ag wire pseudoreference electrode and a Pt disk working electrode (CHI102, CH Instruments, diameter = 2 mm). The Pt working electrode was polished before experiment using alumina slurry (0.05 µm), rinsed with distilled water and subjected to brief ultrasonication to remove any adhered alumina microparticles. The electrodes were then dried in an oven at 75 °C overnight to remove any residual traces of water. The CV data was calibrated by adding ferrocene in THF solution at the end of experiments. In all cases, there is no indication that addition of ferrocene influences the electrochemical behaviour of products. All electrochemical measurements were performed at ambient temperatures under an inert N_2 atmosphere in THF containing 0.1 M $[nBu_4N][PF_6]$ as the supporting electrolyte. Data were recorded with Autolab NOVA software (v.1.8).

$PhNHNC(C_6F_5)H$

This compound was prepared using a modified literature procedure. [2]

2,3,4,5,6-pentafluorobenzaldehyde (1.96 g, 10 mmol) and phenylhydrazine (1.08 g, 10 mmol) were stirred at room temperature in ethanol (30 mL) for 3 hours. After the reaction 60 mL water was added to the reaction mixture, and stirred for 1 hour. The light yellow solid that precipitated was collected and washed with water and hexane. After drying under reduced pressure overnight 2.8 g light yellow solid of $PhNHNC(C_6F_5)H$ (0.96 mmol, 96%) was obtained. ^1H NMR (C_6D_6): δ 7.18 (t, 2H, *J*= 8 Hz, Ph *m*-H), 7.04 (d, 2H, *J*= 8 Hz, Ph *o*-H), 6.84 (t, 1H, *J*= 8 Hz, Ph *p*-H), 6.75 (s, 1H, NH), 6.62 (s, 1H, NHNC*H*). ^{13}C NMR (C_6D_6): δ 144.8 (dm, *J*= 252 Hz, C_6F_5), 144.3 (Ph *i*-C), 140.3 (dtt, *J*= 252, 14, 5 Hz, C_6F_5 *p*-F), 138.2 (dm, *J*= 245 Hz, C_6F_5), 130.0 (Ph *m*-C), 123.6 (q, *J*= 3 Hz, NHN*C*), 121.9 (Ph *p*-C), 113.6(Ph *o*-C), 111.5 (td, *J*= 12, 4 Hz, C_6F_5 *i*-C). ^{19}F NMR (C_6D_6): δ -144.1 (dd, 2F, *J*= 22, 8 Hz, C_6F_5 *m*-F), -157.0 (t, 1F, *J*= 21 Hz, C_6F_5 *p*-F), -163.6 (td, 2F, *J*= 21, 8 Hz, , C_6F_5 *o*-F) ppm. Anal. calcd for $C_{13}H7N_2F_5$: C, 54.56; H, 2.47; N, 9.79. Found: C, 54.59; H, 2.44; N, 9.75.

PhNNC(C_6F_5)NNHMes

A flask was charged with PhNHNC(C_6F_5)H (1.72 g, 6 mmol), sodium hydroxide (2.00 g, 50 mmol), water (100 mL) and acetone (160 mL) and the mixture cooled to 0 °C. At this temperature, $[MesN_2]^+[BF_4]^-$ (1.40 g, 6 mmol) was added slowly with stirring. The reaction mixture was slowly warmed up to RT and stirred for an additional 30 mins. Acetic acid was added to the reaction mixture until pH = 7. The reaction mixture was stirred for another 2 hours. The crude organic product was extracted into CH_2Cl_2 and the solution was concentrated. The product was purified by recrystallization from CH_2Cl_2/MeOH at -30 °C for 2 days to give 1.2 g of PhNNC(C_6F_5)NNHMes (2.7 mmol, 45%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 12.21 (s, 1H, NH), 7.41- 7.35 (m, 4H, Ph *o*-H, Ph *m*-H), 7.31 (t, 1H, *J*= 6.6, Ph *p*-H), 6.95 (s, 2H, Mes *m*-H), 2.41 (s, 6H, Mes *o*-CH_3), 2.31 (s, 3H, Mes *p*-CH_3). ^{19}F NMR (376.4 MHz, C_6D_6, 25 °C) δ -139.3 (dd, 2F, *J*= 23.3, 7.5, C_6F_5 *m*-F), -154.5 (t, 1F, *J*= 20.9, C_6F_5 *p*-F), -162.9 (td, 2F, *J*= 23.0, 5.6, C_6F_5 *o*-F).^{13}C NMR (400 MHz, $CDCl_3$, 25 °C) δ 145.5 (dm, *J*= 251.8, C_6F_5), 145.2 (Ph *i*-C), 144.8 (Mes *i*-C), 141.4 (dm, *J*= 259.0, C_6F_5), 140.0 (Mes *p*-C), 137.8 (dm, *J*= 249.6, C_6F_5), 135.8 (NN*C*NN), 132.8 (Mes *o*-C), 130.8 (Ph *m*-C), 129.7 (Mes *m*-C), 125.3 (Ph *p*-C), 116.7(Ph *o*-C), 111.5-111.1 (m, C_6F_5), 21.4 (Mes *p*-CH_3), 20.6 (Mes *o*-CH_3). Anal. calcd for $C_{19}H_{11}N_4F_5$: C, 61.11; H, 3.96; N, 12.96. Found: C, 61.23; H, 3.98; N, 12.80.

(PhNHNC(C_6F_5)NNMes)$_2$Zn (1b)

A schlenk flask was charged with PhNNC(C_6F_5)NNHMes (258.7 mg, 0.60 mmol), 1.2M solution of Me_2Zn in toluene (0.25 mL, 0.60 mmol) and toluene 10 mL. The reaction mixture was stirred at RT overnight after which all volatiles were removed under vacuo. The crude product was dissolved in 10 mL of hexane and all volatiles was removed under vacuo again. After drying under vacuo, 210.5 mg deep orange solid of (PhNHNC(C_6F_5)NNMes)$_2$Zn (0.55 mmol, 76%) could be obtained. The isolated product is about 95 % pure with some unidentified impurity and free ligand present. Because of good solubility in all the common organic solvents, **1b** is very hard to purify further and was used as such in subsequent reactions. ^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ 7.75 (d, 2H, *J* = 7.9, Ph *o*-H), 7.21 (t, 2H, *J* = 7.9, Ph *m*-H), 6.92 (t, 1H, *J* = 7.6, Ph *p*-H), 6.33 (s, 2H, Mes *m*-H), 1.95 (s, 3H, Mes *p*-CH_3), 1.82 (bs, 6H, Mes *o*-CH_3). ^{19}F NMR (376.4 MHz, C_6D_6, 25 °C) δ -143.67 (dd, 2F, *J* = 24.7, 7.9, C_6F_5 *m*-F), -156.4 (t, 1F, *J* = 21.5, C6F$_5$ *p*-F), -163.0 (td, 2F, *J* = 21.7, 8.1, C_6F_5 *o*-F). ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C) δ 151.8 (Ph *i*-C), 148.0 (Mes *i*-C), 148.1-147.7 (m, C_6F_5), 145.7-145.3 (m, C_6F_5), 143.0-142.4 (m, C_6F_5), 140.4-139.9 (m, C_6F_5), 139.9-139.3 (m, C_6F_5), 137.4 (Mes *p*-C), 133.7 (NN*C*NN), 130.4 (Ph *o*-C), 130.1 (bs, Mes *o*-C), 129.3 (Mes *m*-C), ~128.5 (overlapped, Ph *p*-C), 120.9 (Ph *o*-C), 115.8 (td, J = 17.3, 4.0, C_6F_5 *i*-C), 21.1 (Mes *p*-CH_3), 18.5 (bs, Mes *o*-CH_3). The NMR spectra are shown below. (Figure S4)

(PhNNC(*p*-tol)NNPh)BF$_2$ (2a)

A schlenk flask was charged with **1a** (610 mg, 0.83 mmol), $BF_3 \cdot Et_2O$ (0.4 mL, 3.24 mmol) and 10 mL of toluene. The reaction mixture was stirred at 70°C overnight after which the color had changed from blue to purple and all volatiles were removed under reduced pressure. To the residue was added 10 mL of toluene and $BF_3 \cdot Et_2O$ (0.4 mL, 3.24 mmol), and the mixture was stirred at 70 °C overnight, upon which the color had changed to red. The volatiles were removed in vacuo and the residue was taken up into hexane and recrystallized by slowly cooling the clear red solution to -30 °C to afford 517 mg of (PhNNC(*p*-tol)NNPh)BF$_2$ (1.43 mmol, 86%) as red crystalline material. ^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ 8.06 (d, 2H, *J* = 8.2, p-tolyl CH), 7.91 (d, 4H, *J* = 8.4, Ph *o*-H), 7.09 (d, 2H, *J* = 8.2, p-tolyl CH), 7.01 (t, 4H, *J* = 7.1, Ph *m*-H), 6.95 (t, 2H, *J* = 7.2, Ph *p*-H), 2.13 (s, 3H, p-tolyl CH_3). ^{19}F NMR (376.4 MHz, C_6D_6, 25 °C) δ -144.4 (q, 2F, *J* = 28.8, BF_2). ^{11}B NMR (128.3 MHz, C_6D_6, 25 °C) δ -0.06 (t, 1B, *J* = 28.7, BF_2). ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C) δ 150.3 (Ph *i*-C), 144.8 (N*C*N), 139.8 (*p*-tolyl *i*-C), 131.8 (*p*-tolyl *C*Me), 130.1 (Ph *m*-CH), 130.0 (*p*-tolyl CH), 129.6 (Ph *p*-CH), 126.4 (*p*-tolyl CH), 124.2 (Ph *o*-CH), 21.6 (*p*-tolyl CH_3). Anal. Calcd for $C_{20}H_{17}BF_2N_4$: C, 66.32; H, 4.73; N, 15.47. Found: C, 66.39; H, 4.75; N, 15.30. The NMR spectra are shown below. (Figure S5)

[(PhNNC(*p*-tol)NNPh)BF$_2$][Cp$_2$Co](THF) (3a)

A mixture of solid (PhNNC(*p*-tol)NNPh)BF_2 (24.9 mg, 0.069 mmol) and Cp_2Co (14.9 mg, 0.079 mmol) was prepared. After addition of 2 mL THF, the color of the reaction mixture changed to green. Slow diffusion of hexane (4 mL) into the THF solution precipitated 42 mg of [(PhNNC(*p*-tol)NNPh)BF_2][Cp_2Co](THF) as green crystalline material (0.067 mmol, 98%). Anal. Calcd for $C_{34}H_{35}BCoF_2N_4O$: C, 65.50; H, 5.66; N, 8.99. Found: C, 65.47; H, 5.71; N, 8.99.

(PhNNC(C$_6$F$_5$)NN(BF$_3$)Mes)$_2$Zn (4b)

A mixture of **1b** (100.0 mg, 0.108 mmol), $BF_3{\cdot}Et_2O$ (0.04 mL, 0.32 mmol) and 10 mL of toluene was prepared. The reaction mixture was stirred at 70°C for 2 hours after which the color had changed to orange. Slow diffusion of 5 mL of hexane into the toluene solution at -30 °C for 4 days resulted in precipitation of 98 mg orange crystals of **4b** (0.092 mmol, 85%). ^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ 7.76 (d, 2H, *J* = 8.1, Ph *o*-H), 7.01 (t, 2H, *J* = 7.7, Ph *m*-H), 6.89 (t, 1H, *J* = 7.4, Ph *p*-H), 6.35 (s, 1H, Mes *m*-H), 6.14 (s, 1H, Mes *m*-H), 2.48 (s, 3H, Mes *o*-CH_3), 2.29 (s, 3H, Mes *o*-CH_3), 1.79 (s, 3H, Mes *p*-CH_3), ^{11}B NMR (128.3 MHz, C_6D_6, 25 °C) δ 0.78 (s, 1B, BF_3). ^{19}F NMR (376.4 MHz, C_6D_6, 25 °C) δ -130.3 (d, 1F, *J* = 23.9, C_6F_5 *m*-F), -136.7 (d, 1F, *J* = 23.9, C_6F_5 *m*-F), -148.4 (s, 3F, BF_3), -152.7 (t, 1F, *J* = 21.8, C_6F_5 *p*-F), -161.6 (td, 1F, *J* = 22.6, 7.3, C_6F_5 *o*-F), -163.0 (td, 1F, *J* = 22.7, 7.7, C_6F_5 *o*-F). ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C) δ 148.6 (Ph *i*-C), 144.7 (dm, $^{1}J_{CF}$ ~ 253, C_6F_5 *o*-C), 142.1 (dm, $^{1}J_{CF}$ ~ 260, C_6F_5 *p*-C) 139.2 (Mes *i*-C), 137.2 (dm, $^{1}J_{CF}$ ~ 252, C_6F_5 *m*-C), 136.3 (Mes *o*-C), 136.0 (Mes *o*-C), 134.5 (Ph *p*-C), 132.4 (Mes *p*-C), 130.5 (NN*C*NN), 129.7 (Ph *m*-C), 129.1 (Mes *m*-C), ~128.5 (overlapped, Mes *m*-C), 122.4 (Ph *o*-C), 108.9 (td, *J* = 19.4, 4.0, C_6F_5 *i*-C), 19.9 (Mes *p*-CH_3), 17.9 (Mes *o*-CH_3). Anal. Calcd for $C_{44}H_{32}B_2F_{16}N_8Zn$: C, 49.68; H, 3.03; N, 10.53. Found: C, 50.18; H, 3.15; N, 10.18. The NMR spectra are shown below. (Figure S6)

(PhNNC(C$_6$F$_5$)NNMes)BF$_2$ (2b)

A solution of (PhNNC(C_6F_5)NN(BF_3)Mes)$_2$Zn (**4b**) (103.1 mg, 0.097 mmol) in toluene (10 mL) was stirred at 130°C for 12 hours after which all volatiles were removed under vacuo. The crude product was dissolved in hexane and separated from solid by filtration. The product was further purified by silica column chromatography with CH_2Cl_2/hexane (1:10)(r = 0.2). The fractions were collected and removing solvent *in vacuo* afforded the product as red solid (51 mg, 0.104 mmol, 54%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.85-7.78 (m, 2H, Ph *o*-H), 7.52-7.43 (m, 3H, Ph *m*-H and *p*-H), 6.90 (s, 2H, Mes *m*-H), 2.27 (s, 3H, Mes *p*-CH_3), 2.05 (s, 6H, Mes *o*-CH_3). ^{11}B NMR (128.3 MHz, $CDCl_3$, 25 °C) δ -1.34 (t, 1B, *J* = 23.8, BF_2). ^{19}F NMR (376.4 MHz, $CDCl_3$, 25 °C) δ -140.9 - -141.1 (m, 2F, C_6F_5 *m*-F), -151.8 (tt, 1F, *J* = 21.0, 2.2, C_6F_5 *p*-F), -153.2 (q, 2F, *J* = 23.7, BF_2), -161.2 - -161.4 (m, 2F, C_6F_5 *o*-F). ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 147.2-146.7 (m, C_6F_5), 144.7-144.2 (m, C_6F_5), 143.8-143.2 (m, C_6F_5), 142.8 (Ph, *i*-C), 141.1-140.7 (m, C_6F_5), 140.7-140.4 (m, C_6F_5), 139.7 (NN*C*NN), 139.3 (Mes *i*-C). 139.5-139.1 (m,

C_6F_5), 137.1-136.6 (m, C_6F_5), 134.4 (Mes o-C), 130.7 (Ph *p*-C), 129.6 (Mes *m*-C and Ph *m*-C), 123.9 (Ph *o*-C), 109.8 (td, J = 15.6, 4.1, C_6F_5 *i*-C), 21.3 (Mes *p*-CH_3), 17.8 (Mes *o*-CH_3). Anal. Calcd for $C_{19}H_{10}BF_7N_4$: C, 55.03; H, 3.36; N, 11.67. Found: C, 55.20; H, 3.53; N, 11.26. The NMR spectra are shown below. (Figure S7)

X-ray crystallography

Suitable crystals of **2a**, **3a**, and **4b** were mounted on a cryo-loop in a drybox and transferred, using inert-atmosphere handling techniques, into the cold nitrogen stream of a Bruker D8 Venture diffractometer. The final unit cell was obtained from the xyz centroids of 9981 (**2a**), 9687 (**3a**) and 9950 (**4b**) reflections after integration. Intensity data were corrected for Lorentz and polarisation effects, scale variation, for decay and absorption: a multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS)*.[5] The structures were solved by direct methods using the program *SHELXS*.[6] The hydrogen atoms were generated by geometrical considerations and constrained to idealised geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Structure refinement was performed with the program package *SHELXL.*[6] Crystal data and details on data collection and refinement are presented in Table S1.

For compound **3a**, refinement was frustrated by disorder problems. From the solution it was clear that the THF solvate molecule was partly occupied (81%) and disordered: the electron density of the atoms appeared to be spread out. The THF C atom that showed the most unrealistic displacement parameters was described by two site occupancy factors with separately refined displacement parameters. The s.o.f. of the major/minor fractions refined to 0.52/0.29, respectively. The remaining atoms of the THF solvate molecule also showed large displacement parameters, but attempts to model this with a two-site occupancy model did not lead to significant improvements. In addition, one of the cyclopentadienyl rings of the Cp_2Co^+ fragment suffered from rotational disorder. A two-site occupancy model was applied: both s.o.f. for the major fraction refined to 0.54.

For compound **4b**, refinement was frustrated by disorder problems. The two independent molecules in the asymmetric unit both showed a different kind of disorder. For one of them, it was clear from the solution that a phenyl ring was disordered over two positions. A difference Fourier synthesis allowed the location of the minor orientation, and a two-site occupancy model was applied. The s.o.f. of both refined to a value of 0.50. One of the BF_3 units in this molecule showed large displacement parameters, but this could not be satisfactorily modelled by a disorder model. The second independent molecule also showed unrealistic displacement parameters for a BF_3 fragment: for two of the F atoms in this group, a two-site occupancy model was applied, the major fraction of which refined to a s.o.f. of 0.61.

Table S1. Crystallographic data for **2a**, **3a** and **4b**

	2a	**3a**	**4b**
chem formula	$C_{20}H_{17}BF_2N_4$	$C_{33.25}H_{33}BCoF_2N_4O$	$C_{44}H_{32}B_2F_{16}N_8Zn$
M_r	362.19	612.88	1063.76
cryst syst	monoclinic	monoclinic	monoclinic
color, habit	red, needle	green, platelet	orange, platelet
size (mm)	0.34 x 0.24 x 0.05	0.30 x 0.18 x 0.06	0.20 x 0.16 x 0.03
space group	*P21/c*	*P21/n*	*P21/c*
a (Å)	10.4160(6)	12.2031(7)	28.1225(14)
b (Å)	18.8213(11)	17.4363(9)	20.6482(10)
c (Å)	9.2633(5)	14.4788(7)	15.3728(7)
α (°)			
β (°)	101.539(2)	97.446(2)	93.868(2)
γ (°)			
V ($Å^3$)	1779.30(17)	3054.8(3)	8906.3(7)
Z	4	4	8
ρ_{calc}, $g.cm^{-3}$	1.352	1.333	1.587
μ(Mo K_α), mm^{-1}	0.096	0.607	0.663
F(000)	752	1276	4288
temp (K)	100(2)	200(2)	100(2)
θ range (°)	5.80–55.82	5.675-53.32	5.878-52.737
data collected (h,k,l)	-13:13, -24:24, -11:12	-15:15, -22:22, -18:17	-36:36, -26:26, -20:19
min, max transm	0.9680, 0.9952	0.8389, 0.9645	0.6950, 0.7456
rflns collected	49978	105601	285779
indpndt reflns	4282	6775	20514
observed reflns $F_o \geq 2.0\, \sigma (F_o)$	3564	5657	15776
R(F) (%)	3.74	4.37	5.26
wR(F^2) (%)	8.92	12.67	11.07
GooF	1.037	1.070	1.083
weighting a,b	0.0416, 0.7967	0.0770, 1.6064	0.0422, 16.6302
params refined	245	455	1353
min, max resid dens	-0.219, 0.379	-0.512, 0.960	-0.914, 2.757

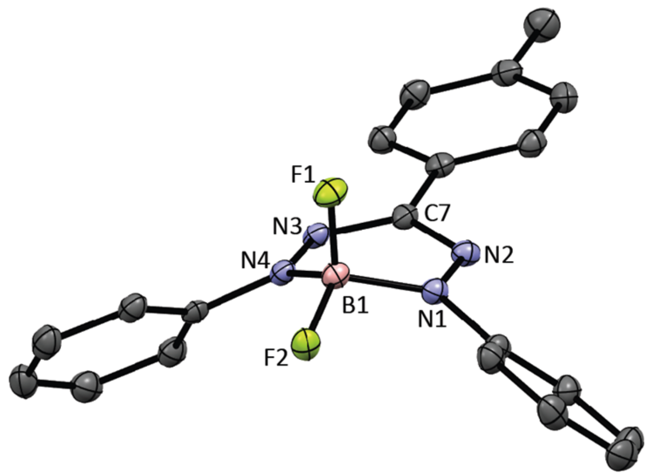
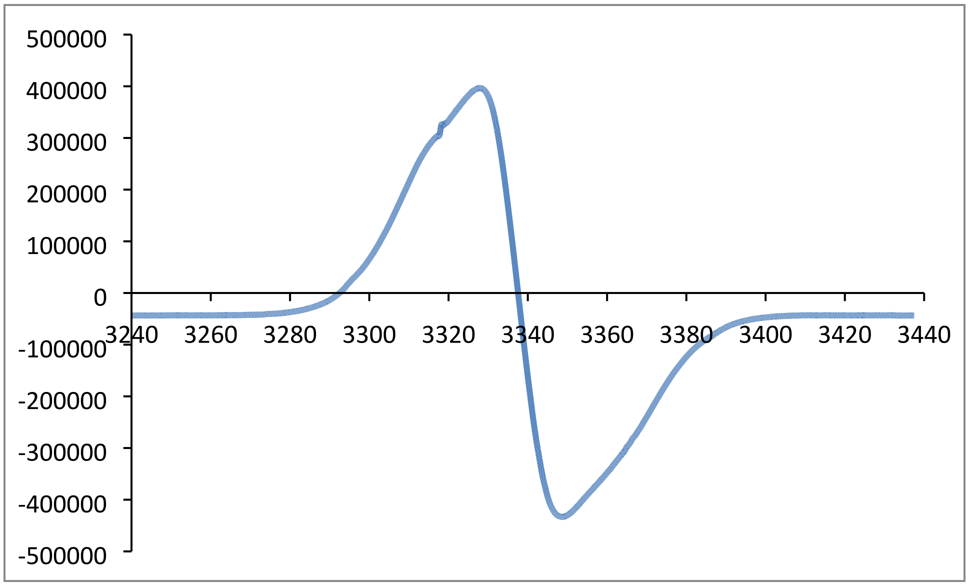


***Figure S1*.** Molecular structure of **2a** showing 50% probability ellipsoid. The hydrogen atoms are omitted for clarity

EPR spectrum of 3a

Figure S2. EPR of **3a** (frozen THF solution at 20K)



UV-VIS data

Figure S2a. UV-Vis of **2a**, **2b** and **3a** in THF.

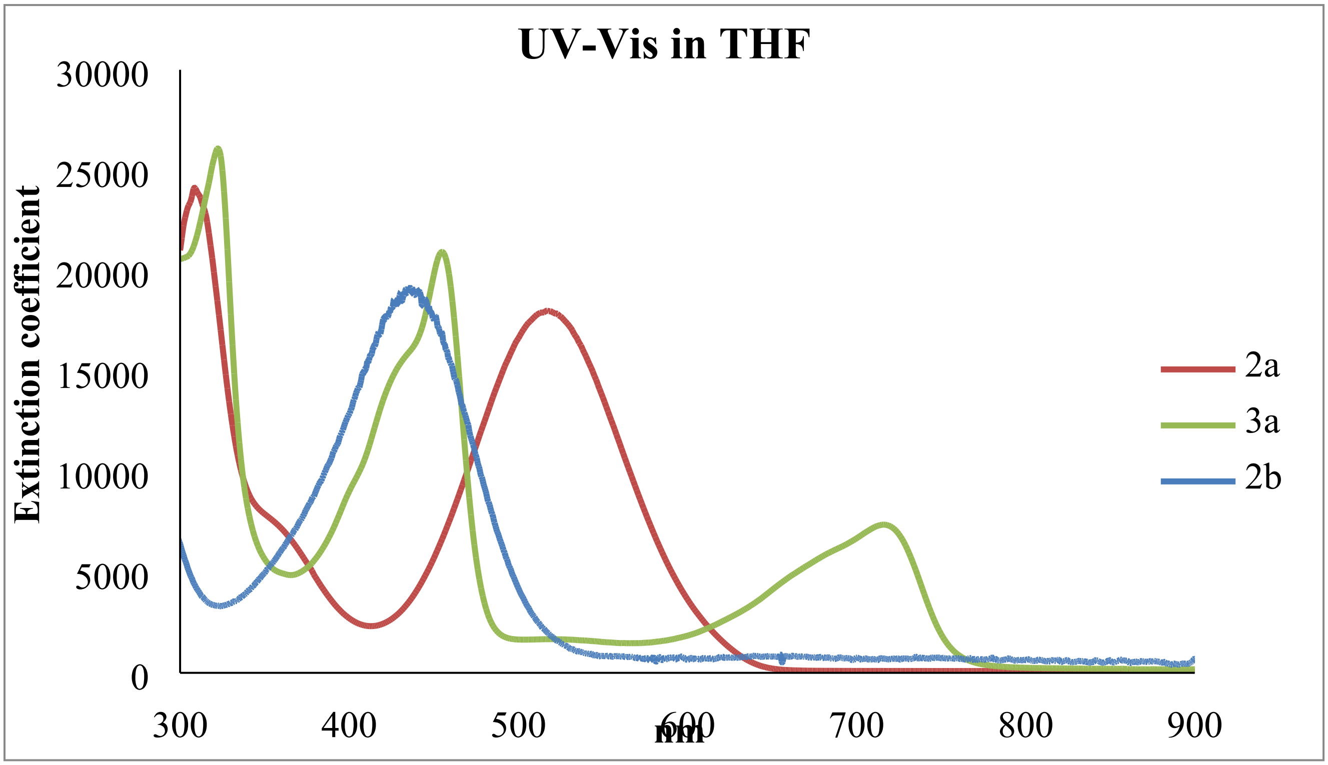
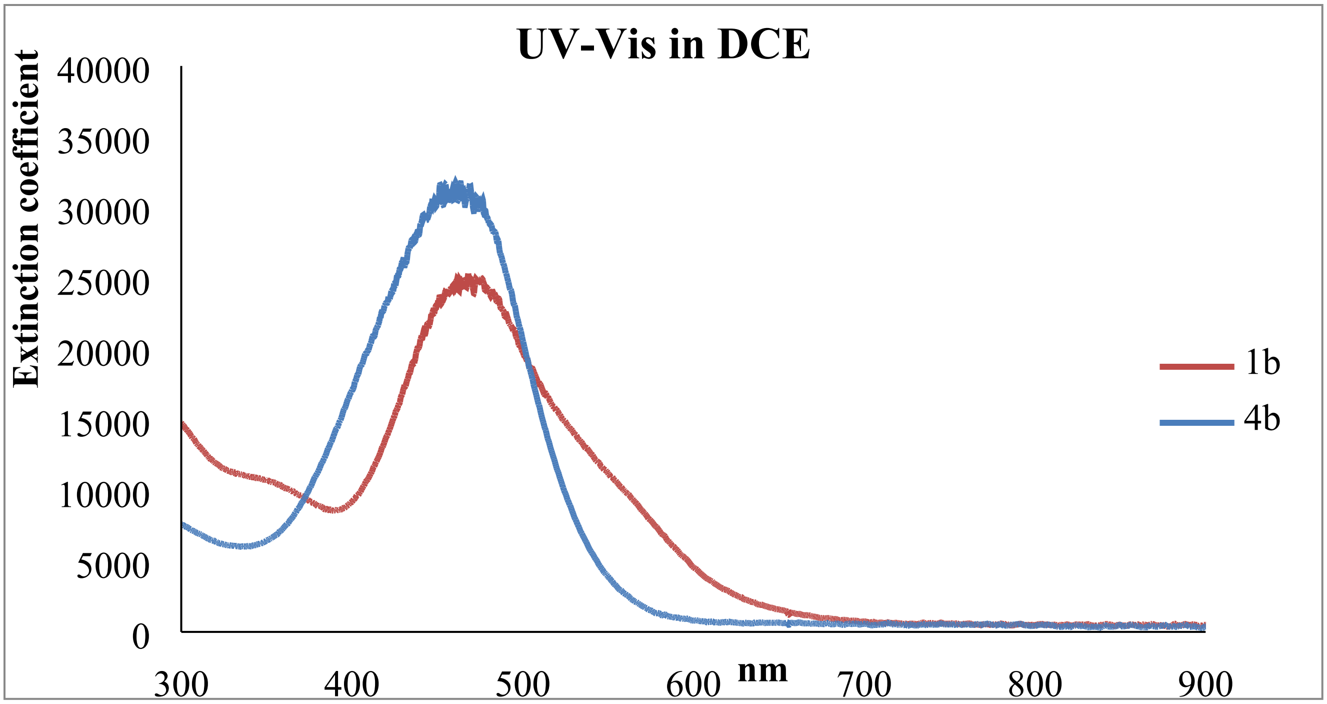


Figure S2b. UV-Vis of **1b** and **4b** in 1,2-dichloroethane.



NMR spectra for compounds 1b, 2a, 4b and 2b.

Figure S4. (a) ^{1}H-NMR of **1b** in C_6D_6

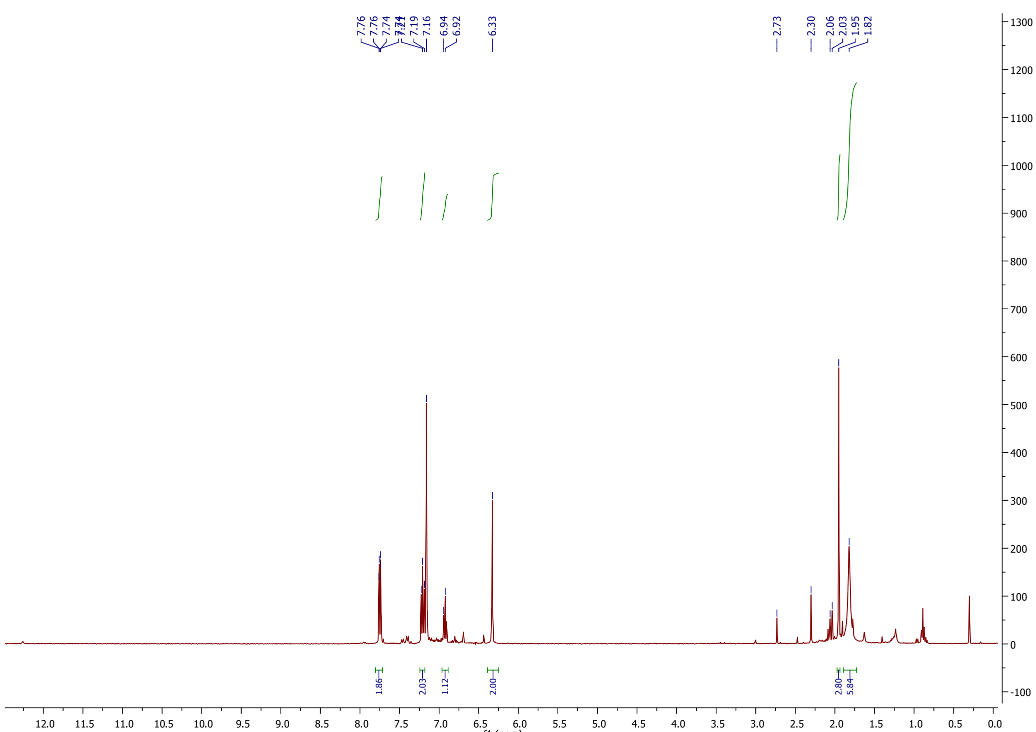


Figure S4.(b) ^{19}F-NMR of **1b** in C_6D_6

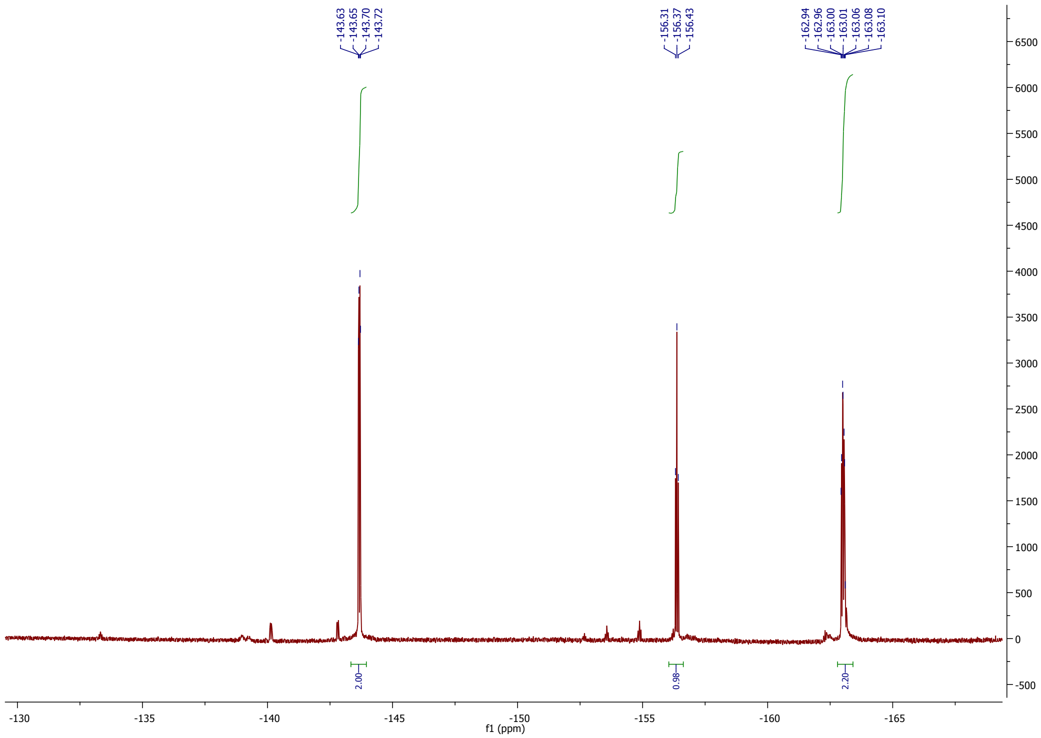


Figure S5. (a) ^{1}H-NMR of **2a** in C_6D_6

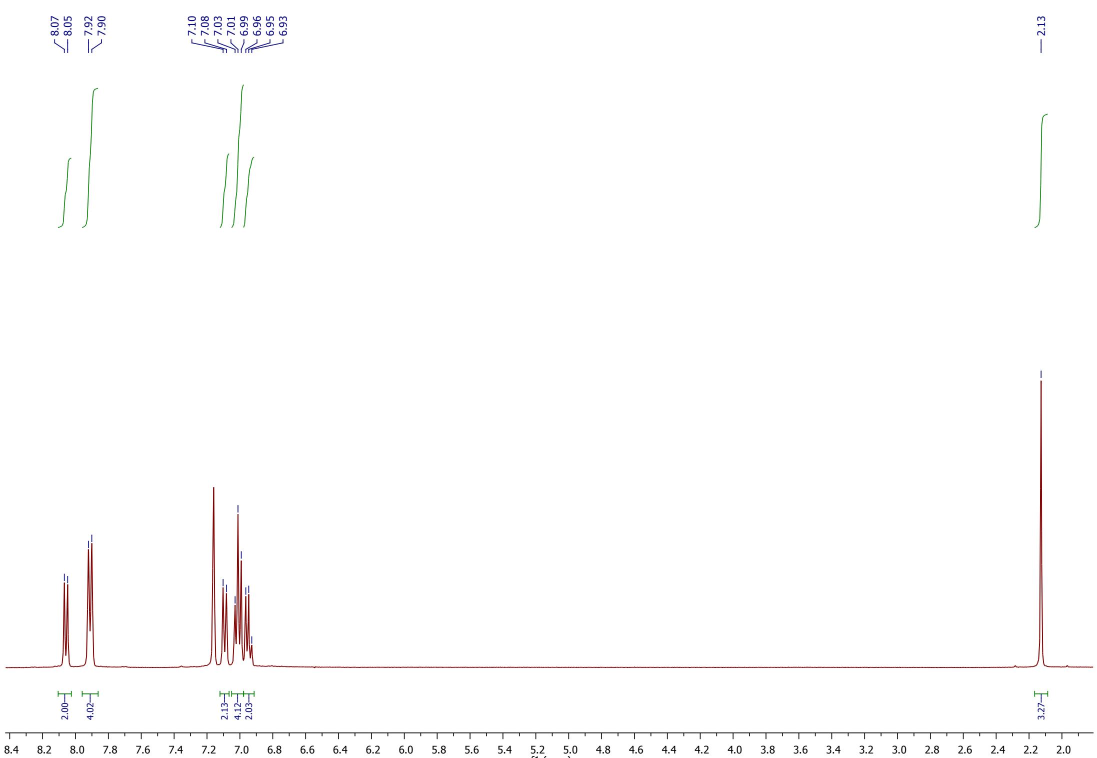


Figure S5. (b) ^{19}F-NMR of **2a** in C_6D_6

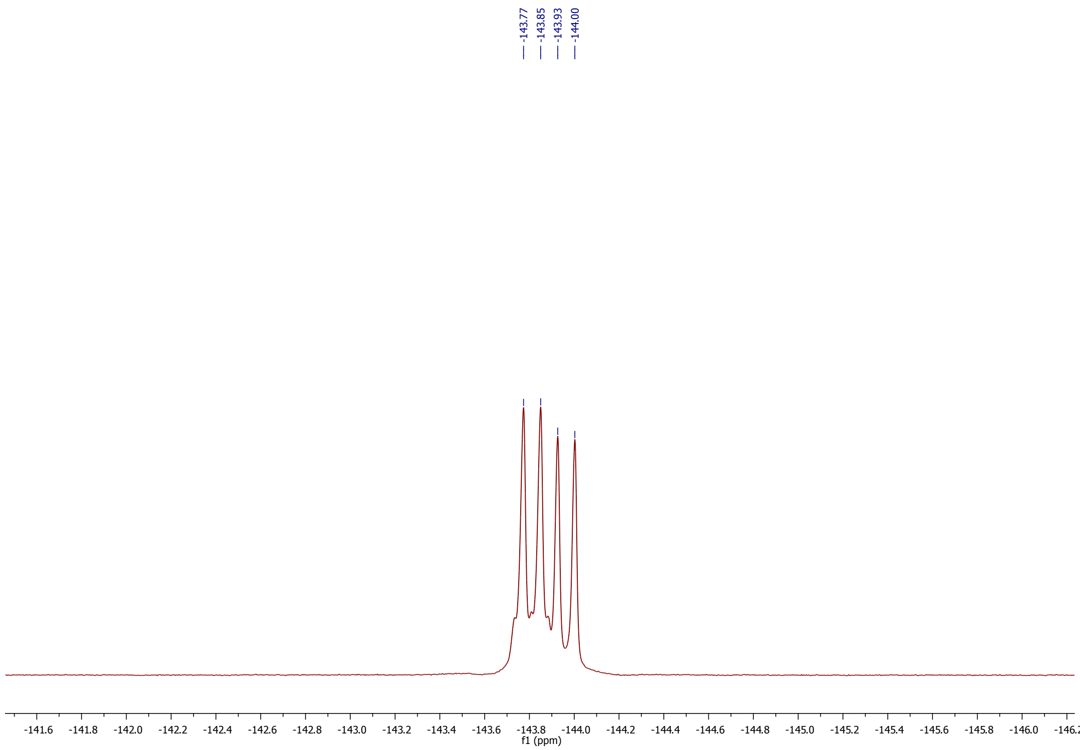


Figure S5. (c) ^{11}B-NMR of **2a** in C_6D_6

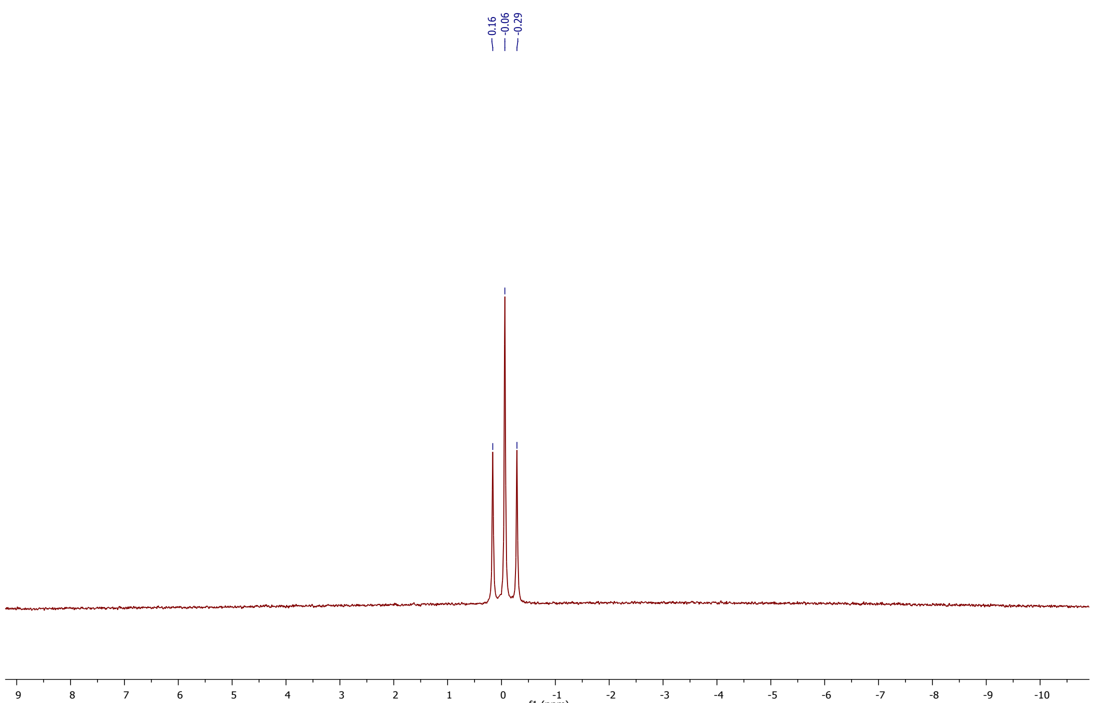


Figure S5. (d) ^{13}C-NMR of **2a** in C_6D_6

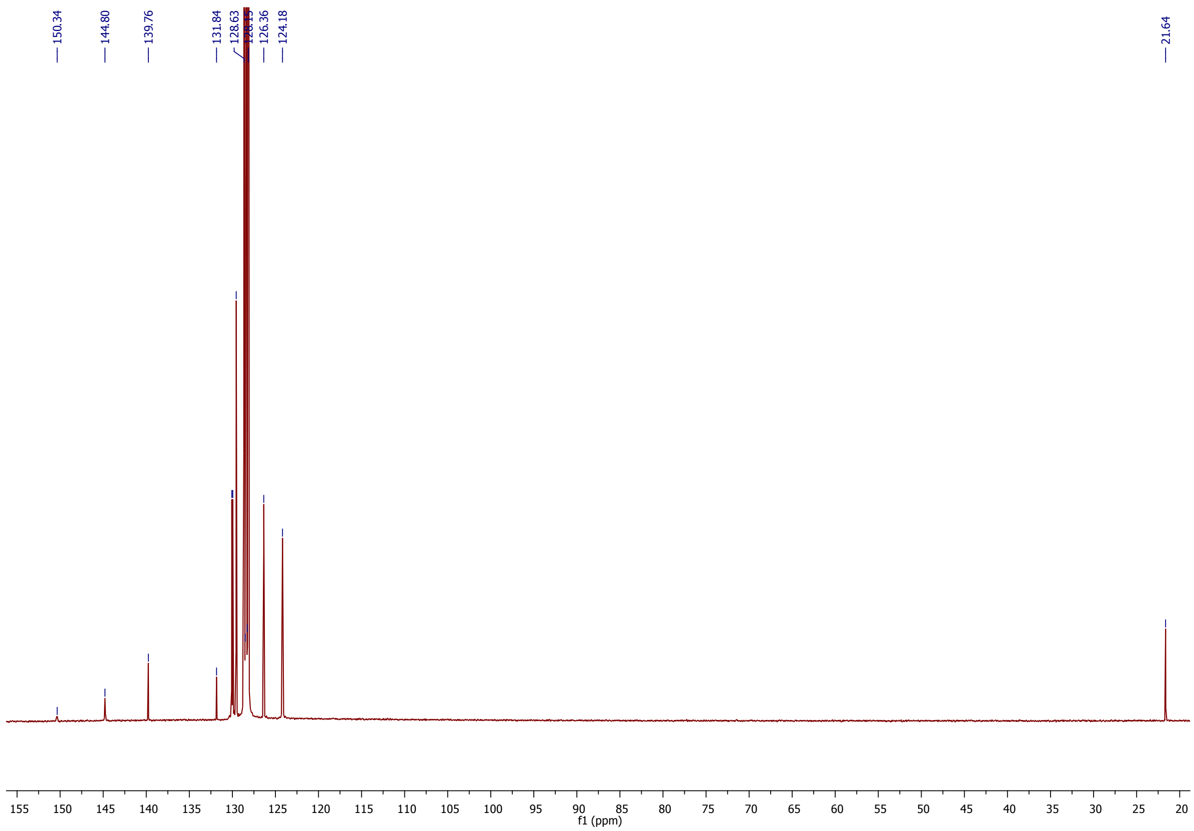


Figure S6. (a) ^{1}H-NMR of **4b** in C_6D_6

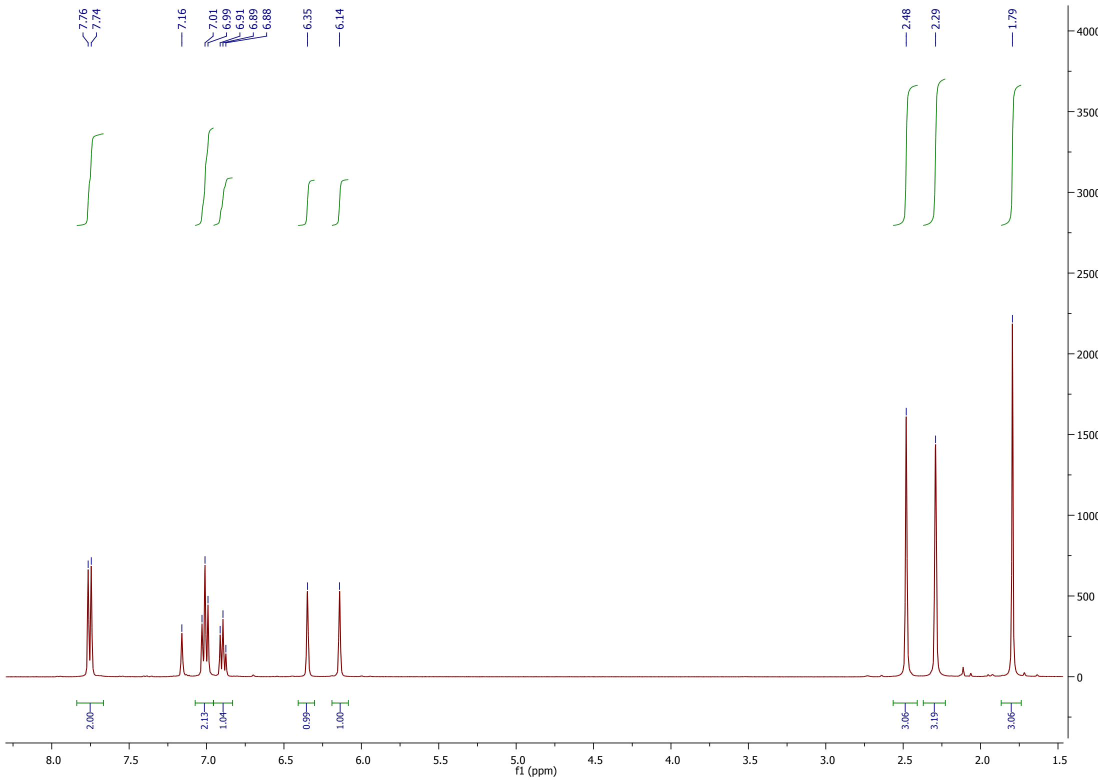


Figure S6. (b) ^{19}F-NMR of **4b** in C_6D_6

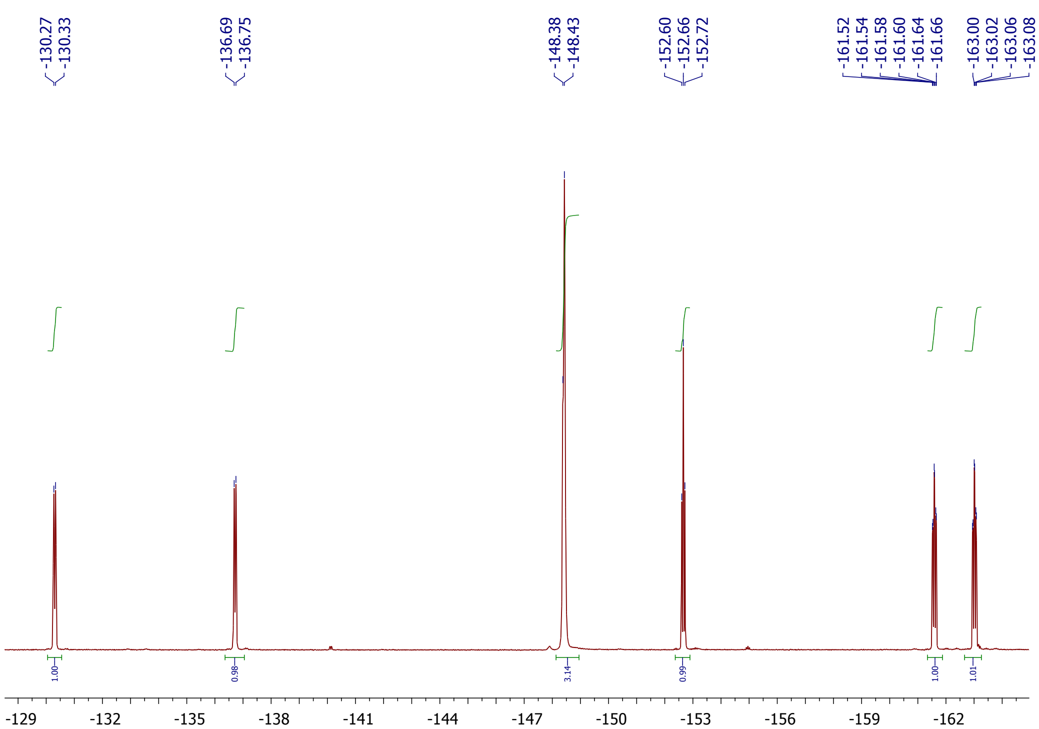


Figure S6. (c) ^{11}B-NMR of **4b** in C_6D_6

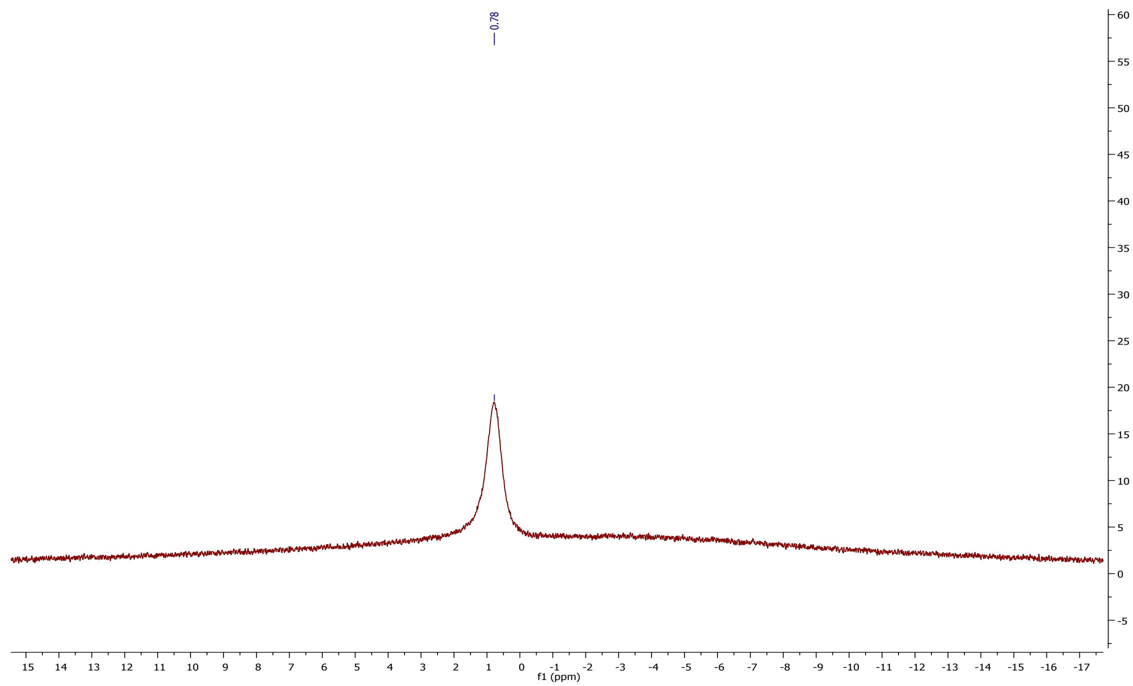


Figure S6. (d) ^{13}C-NMR of **4b** in C_6D_6 (inset highlighting resonances due to C_6F_5 group)

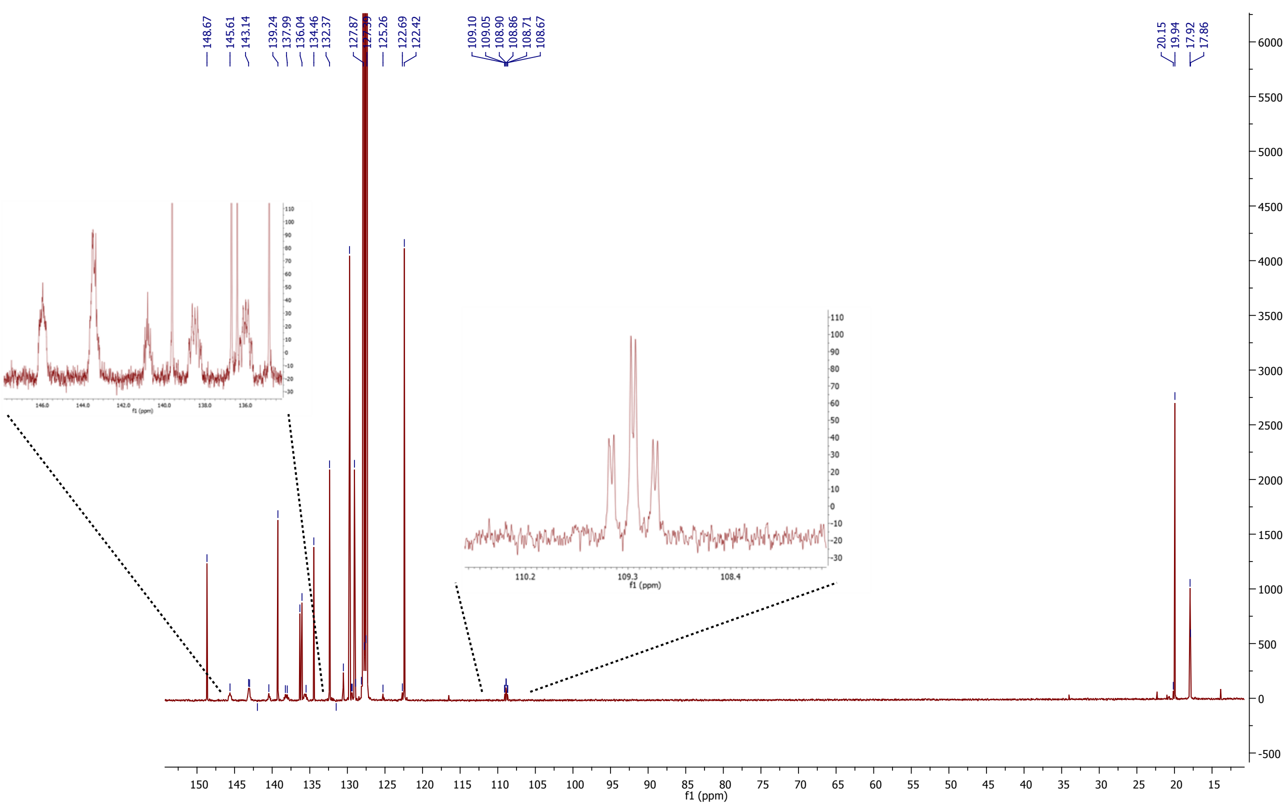


Figure S7. (a) ^{1}H-NMR of **2b** in $CDCl_3$

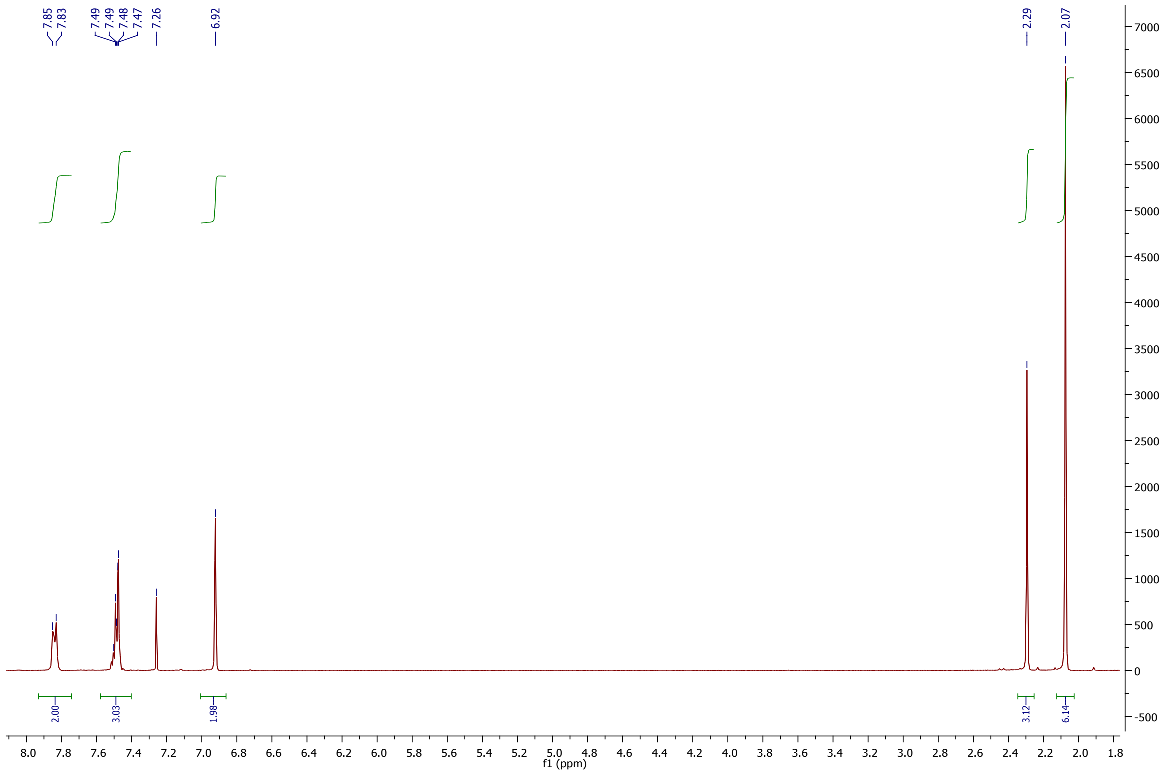


Figure S7. (b) ^{19}F-NMR of **2b** in $CDCl_3$

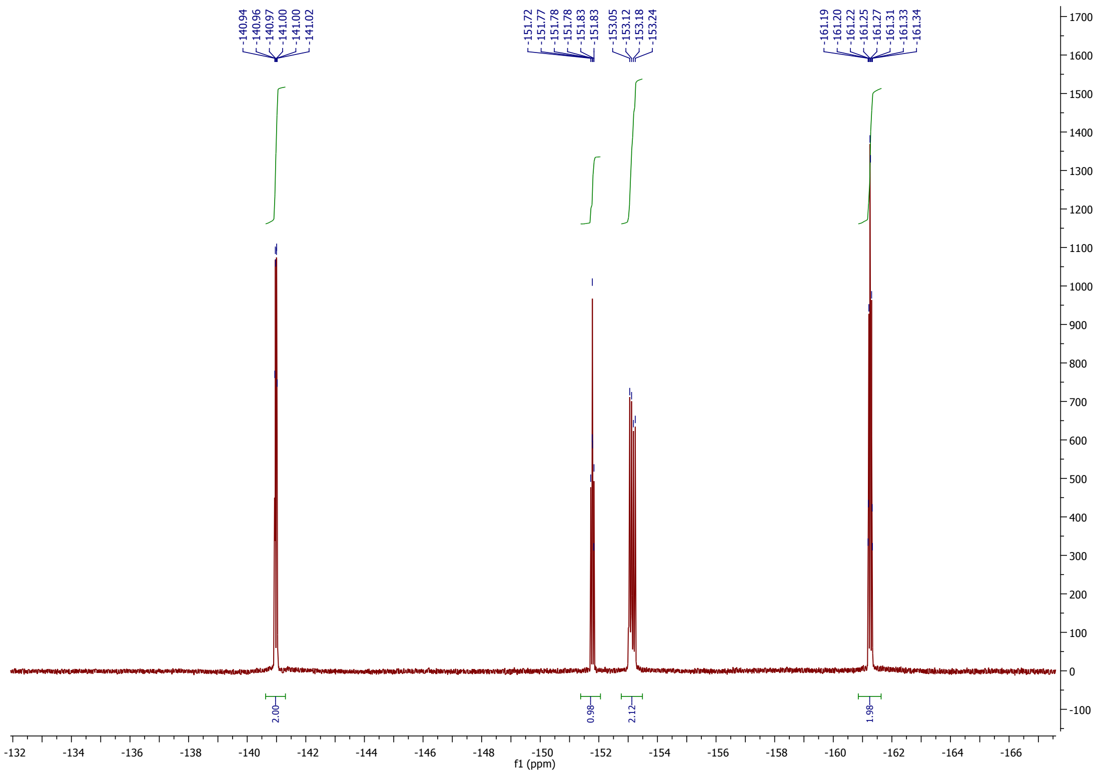


Figure S7. (c) ^{11}B-NMR of **2b** in $CDCl_3$

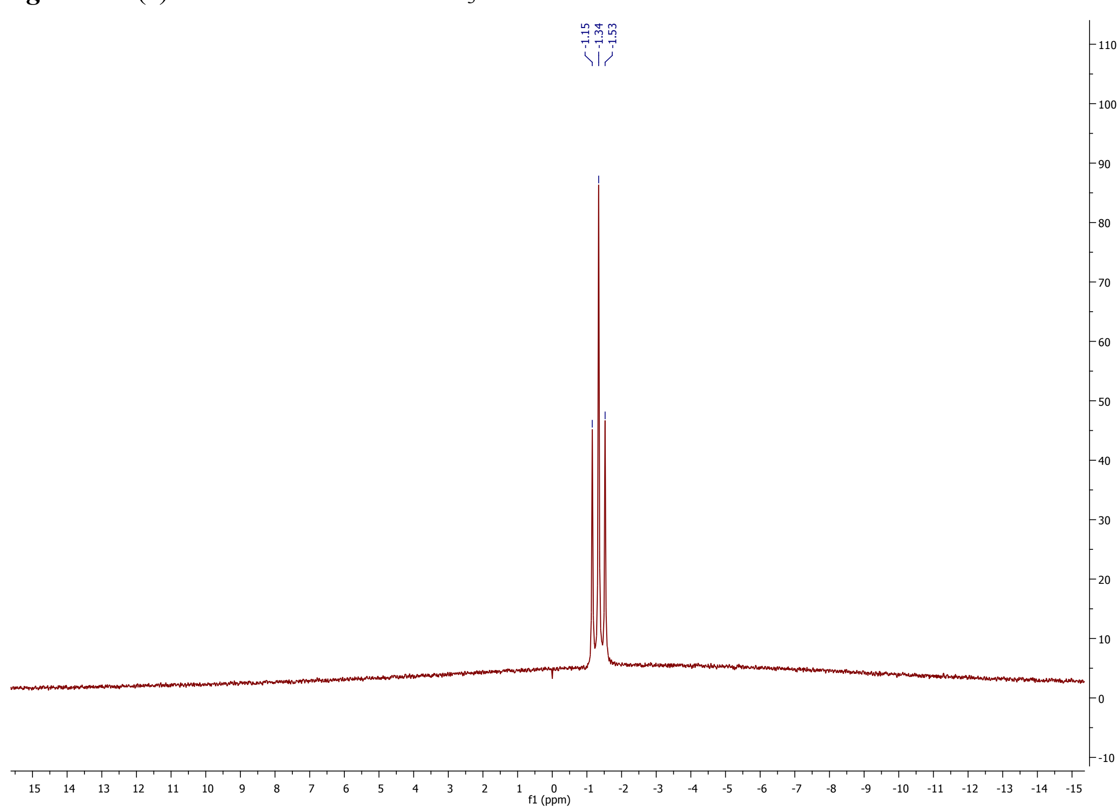
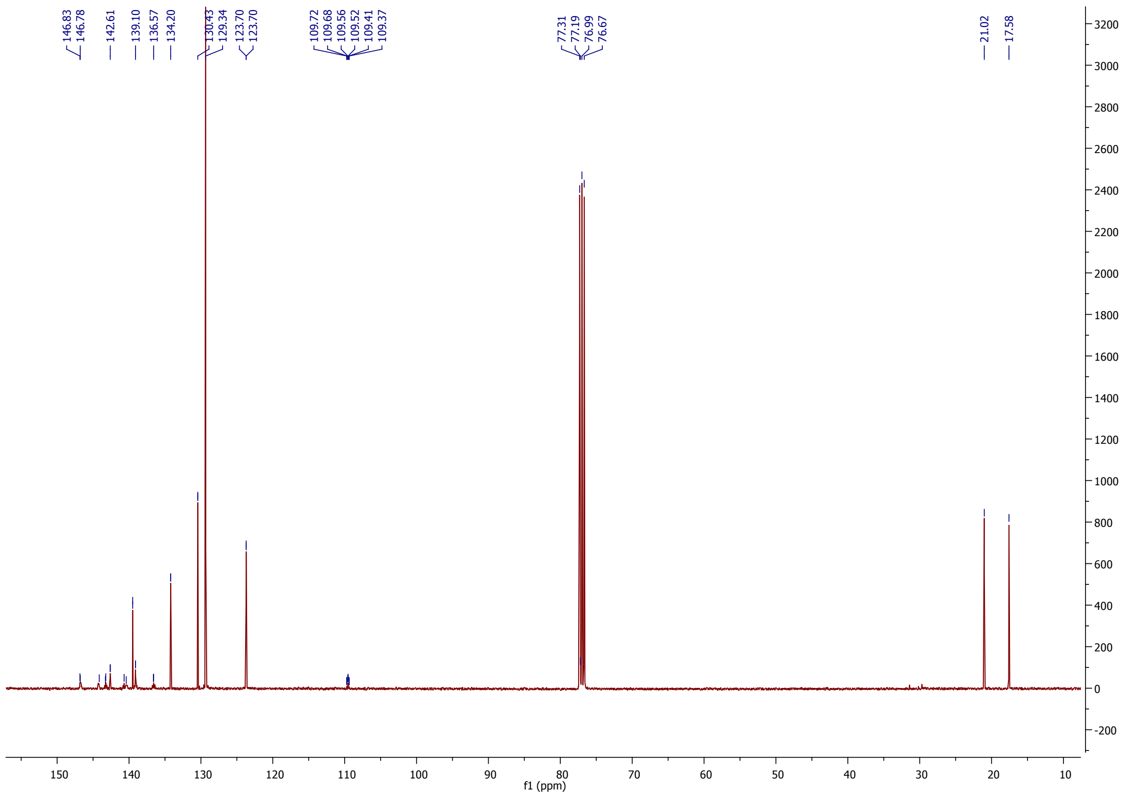


Figure S7. (d) ^{13}C-NMR of **2b** in $CDCl_3$



References

1. (a) M. P. Doyle, W. J. Bryker, *J. Org. Chem.* **1979**, *44*, 1572. (b) M.-C. Chang, T. Dann, D. P. Day, M. Lutz, G. G. Wildgoose, and E. Otten, *Angew. Chem. Int. Ed.*, **2014**, *53*, 4118.

2. N. I. Petrenko and T. N. Gerasimova, *J. Fluorine Chem.* **1990**, *19*, 359.