Boron calixphyrin complexes: exploring the coordination chemistry of a BODIPY/porphyrin hybrid

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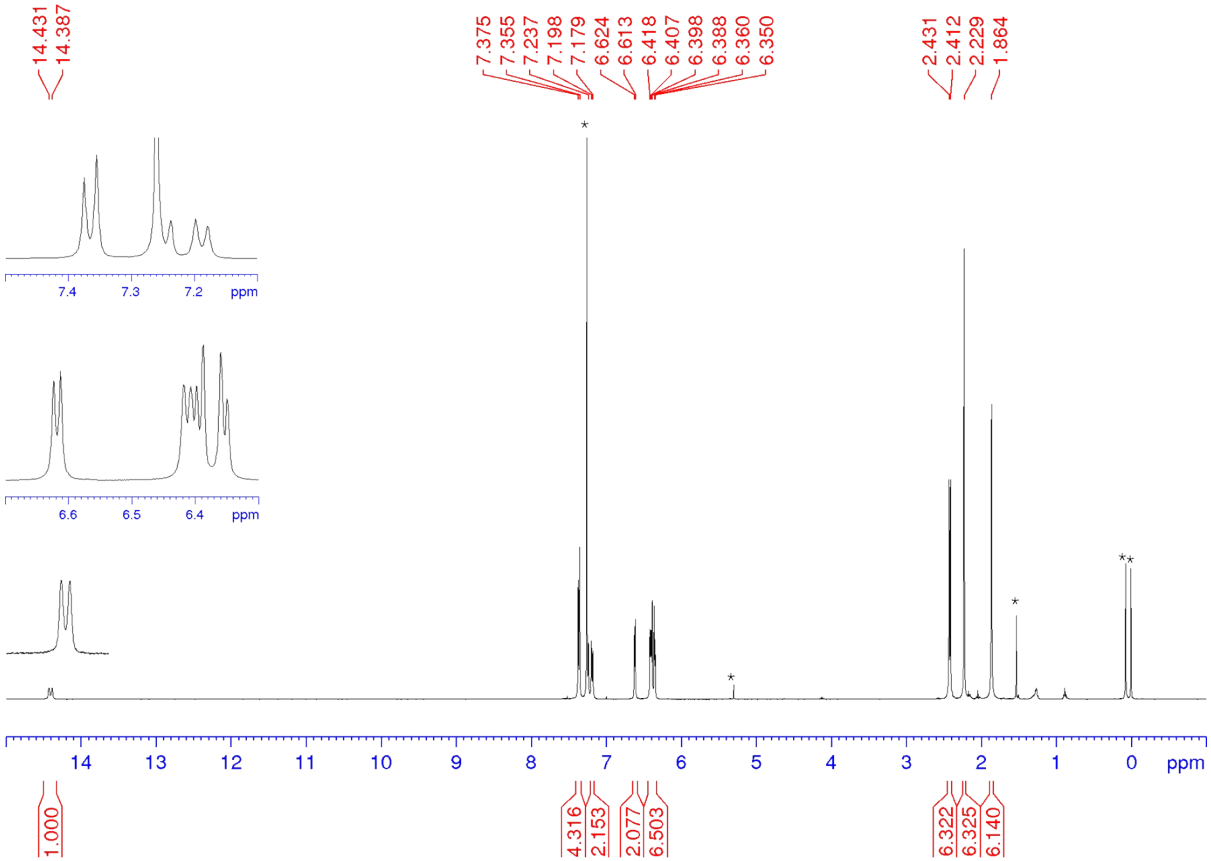


Figure S2: ^{13}C NMR spectrum of **2a** in $CDCl_3$ (100 MHz)

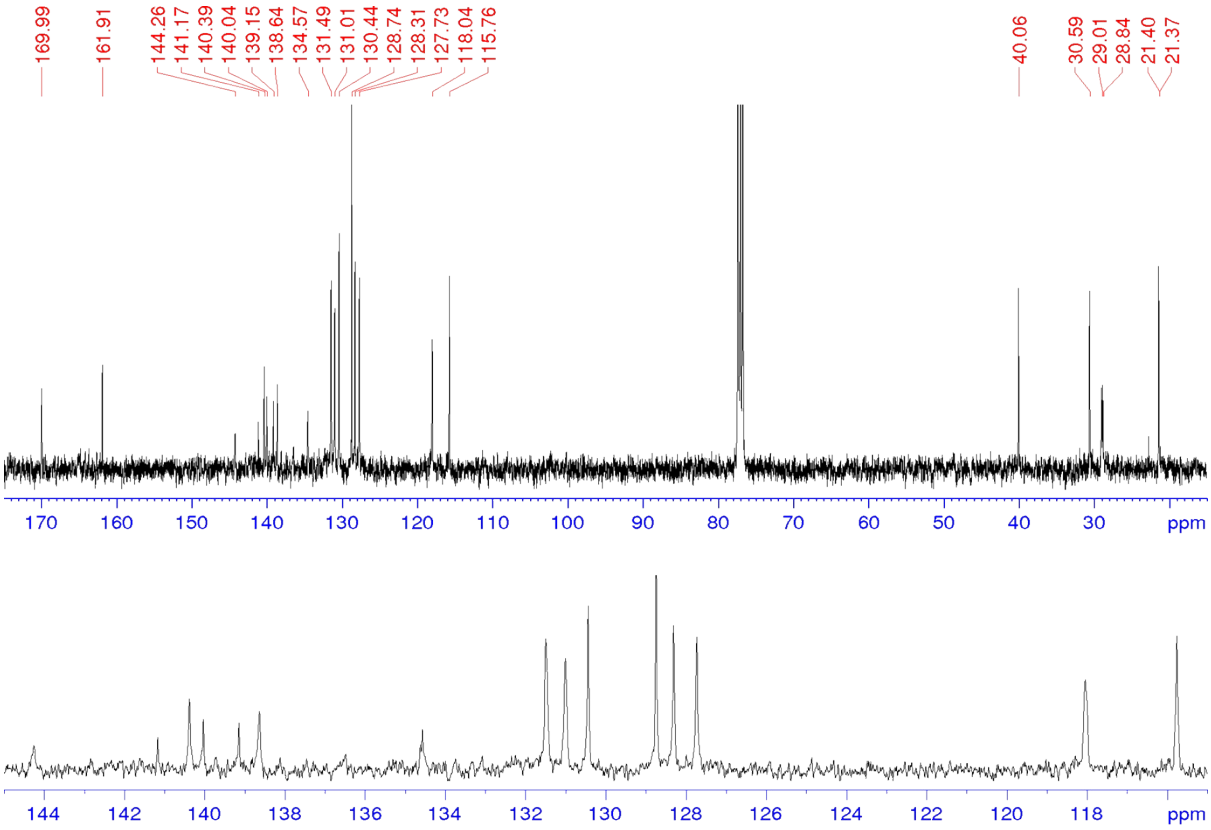


Figure S3: ^{11}B NMR spectrum of **2a** in $CDCl_3$ (128 MHz)

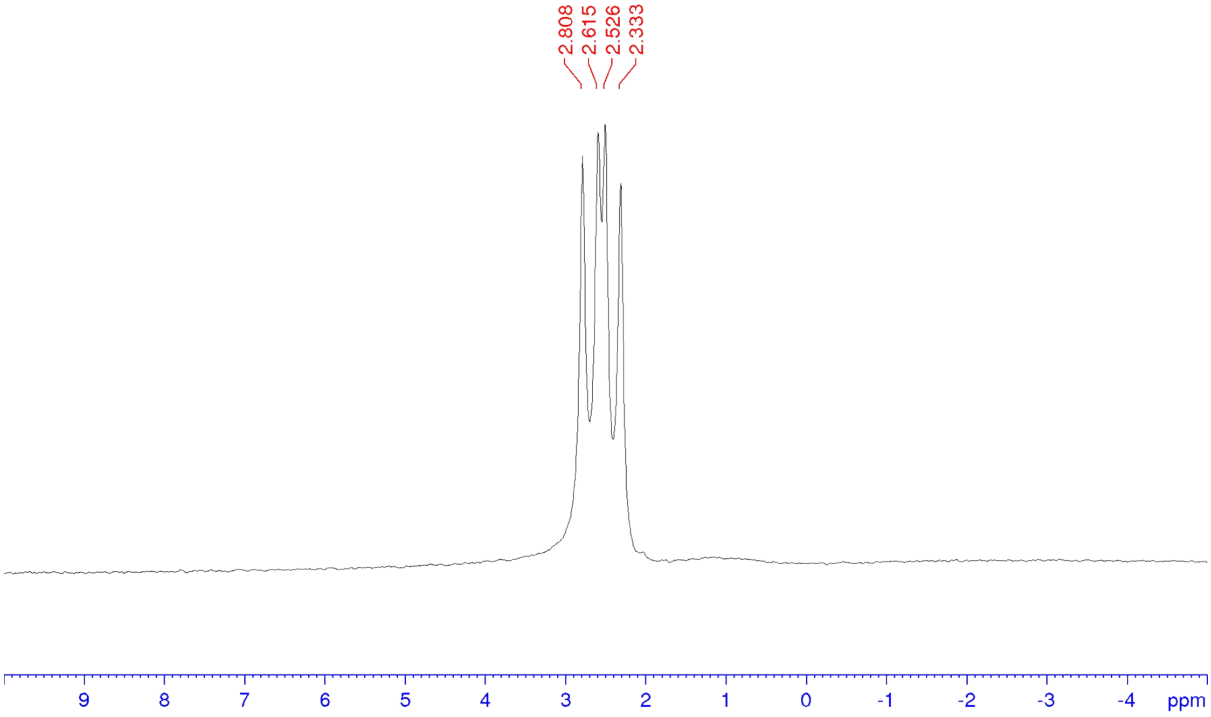


Figure S4: ^{19}F NMR spectrum of **2a** in $CDCl_3$ (376 MHz)

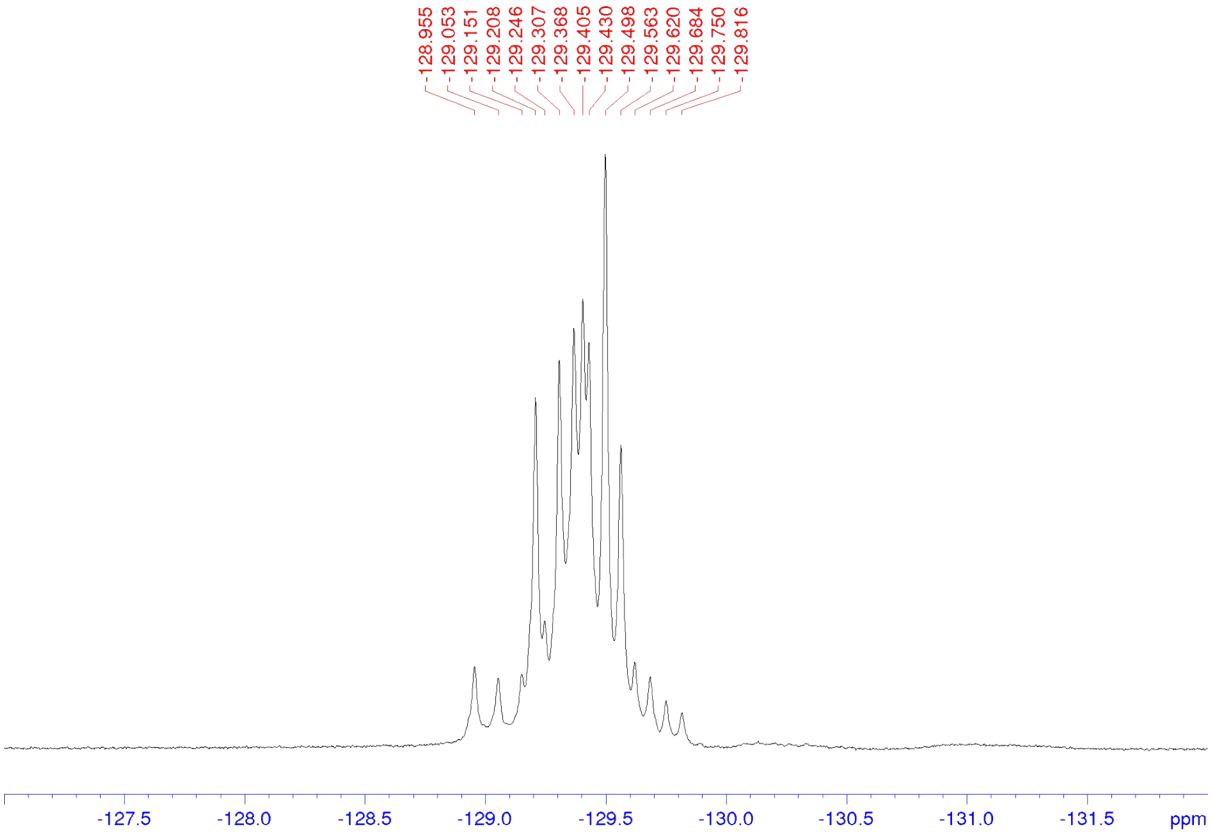


Figure S5: COSY NMR spectrum **2a** in $CDCl_3$

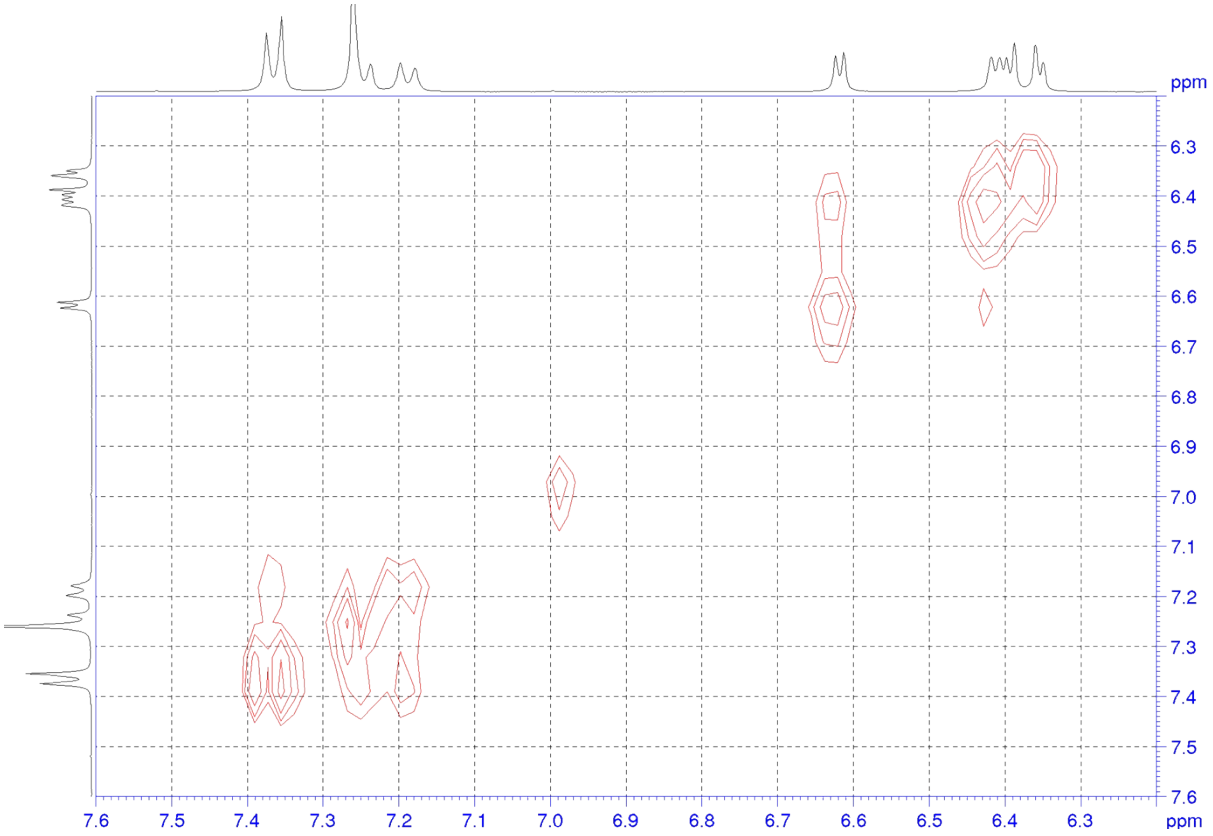


Figure S6: NOESY NMR spectrum of **2a** in $CDCl_3$

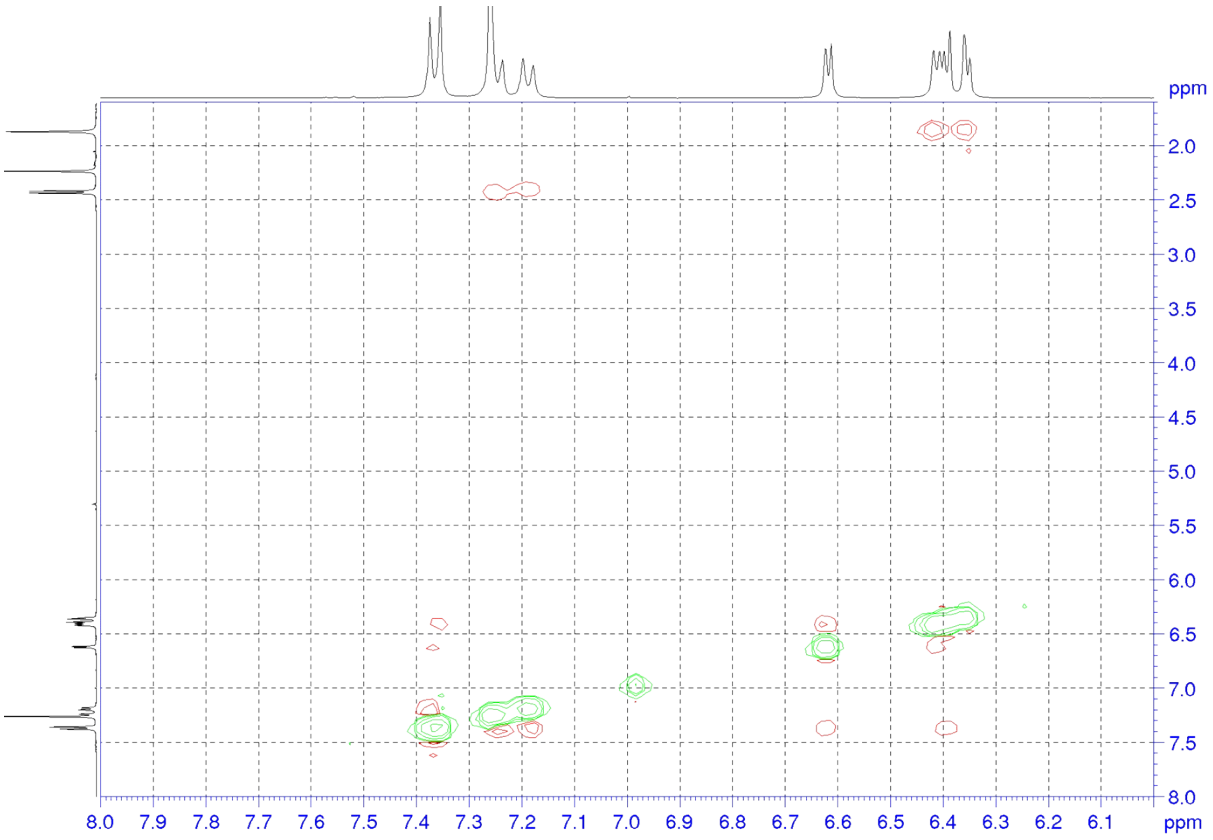


Figure S7: HSQC NMR spectrum of **2a** in $CDCl_3$

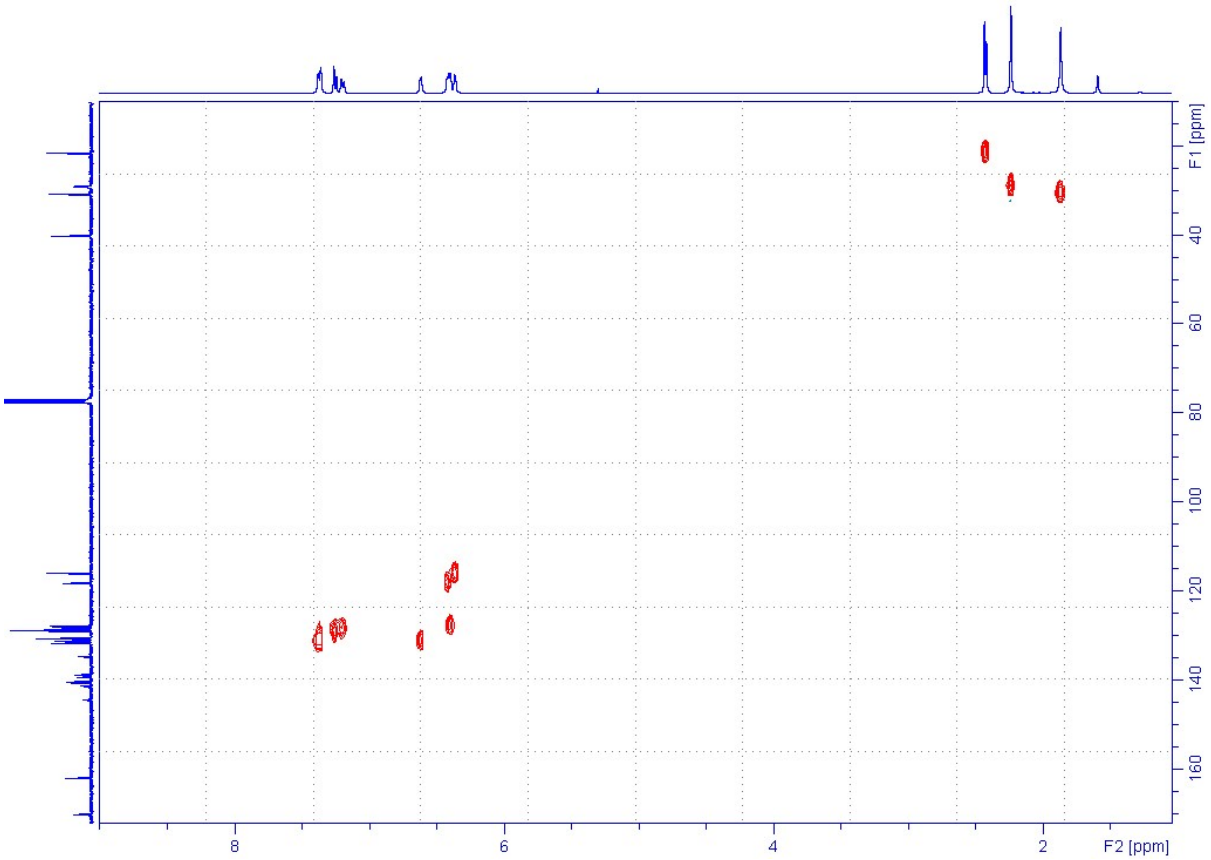


Figure S8: HMBC NMR spectrum of **2a** in $CDCl_3$

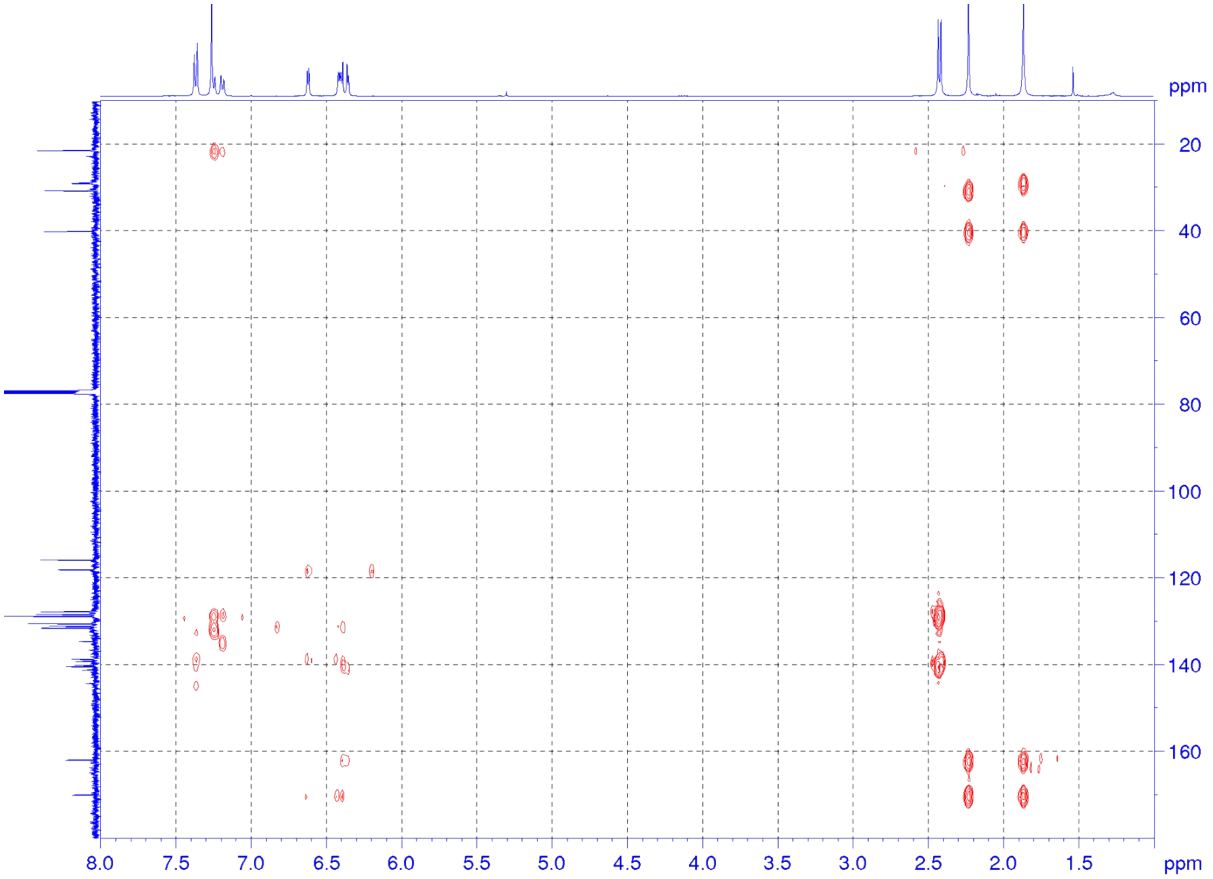


Figure S9: ^{1}H NMR spectrum of **2b** in $CDCl_3$ (400 MHz)

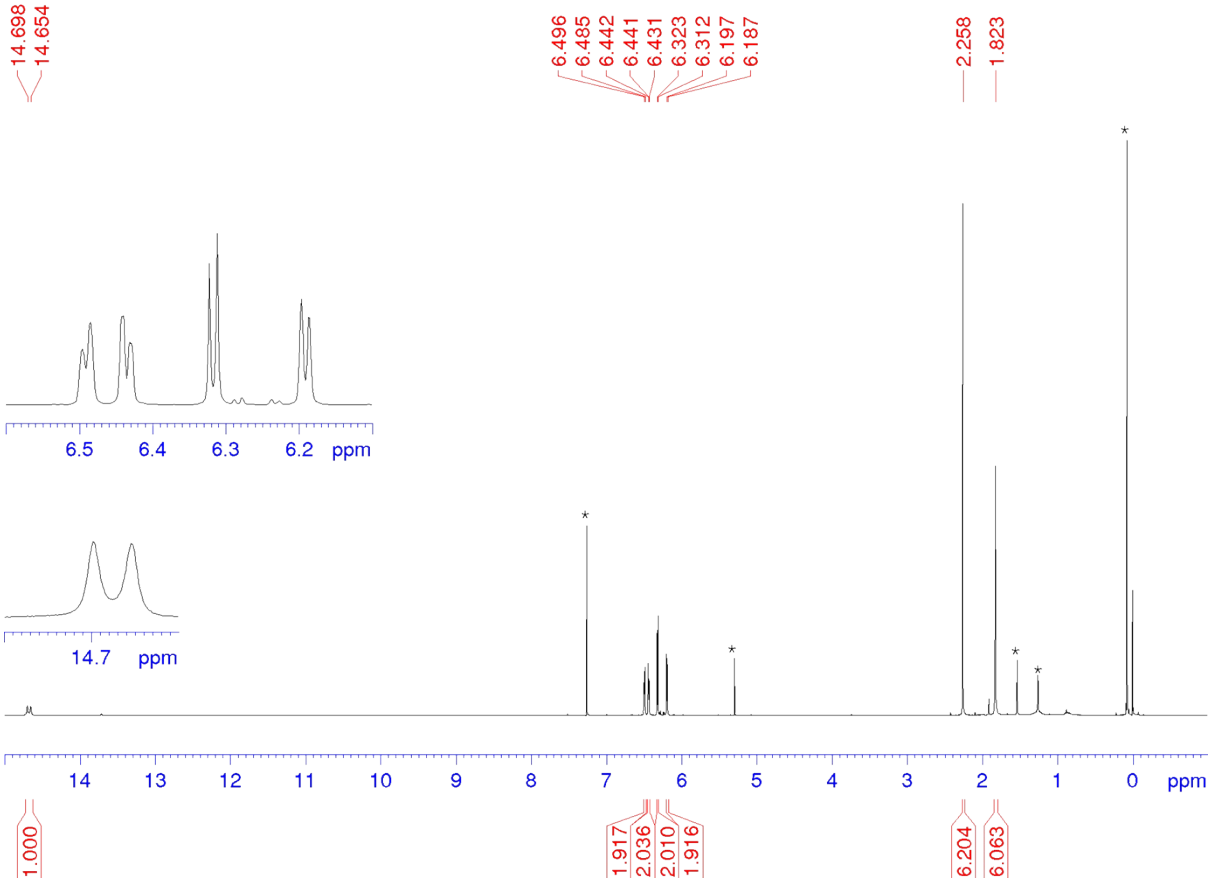


Figure S10: ^{11}B NMR spectrum of **2b** in $CDCl_3$ (128 MHz)

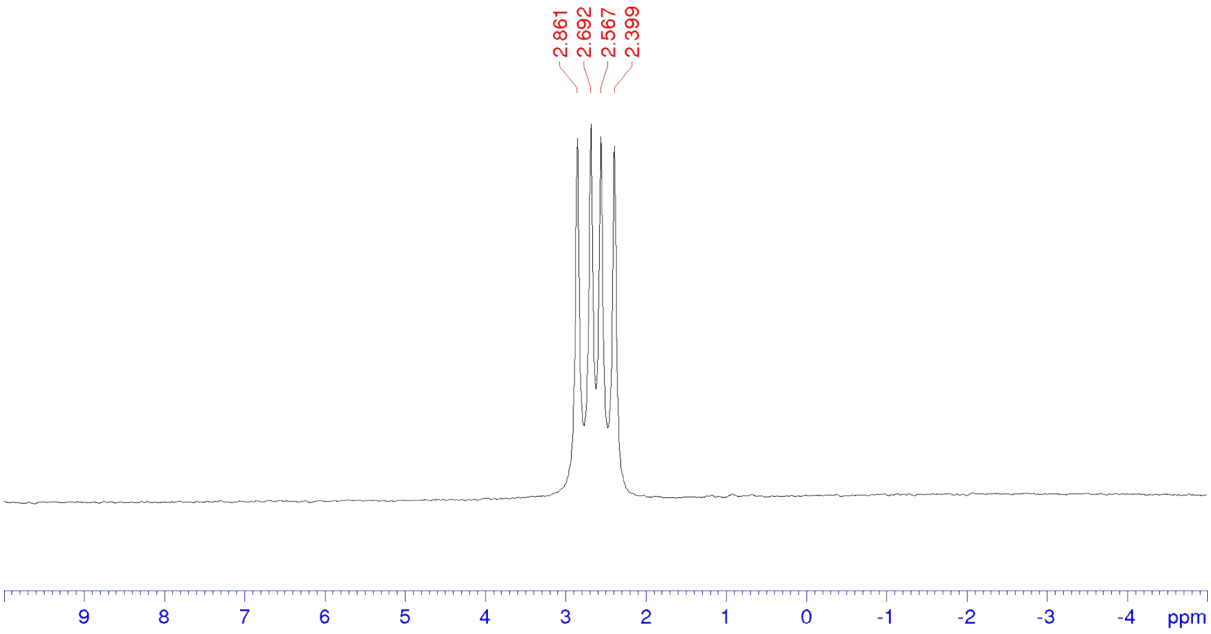


Figure S11: ^{19}F NMR spectrum of **2b** in $CDCl_3$ (376 MHz)

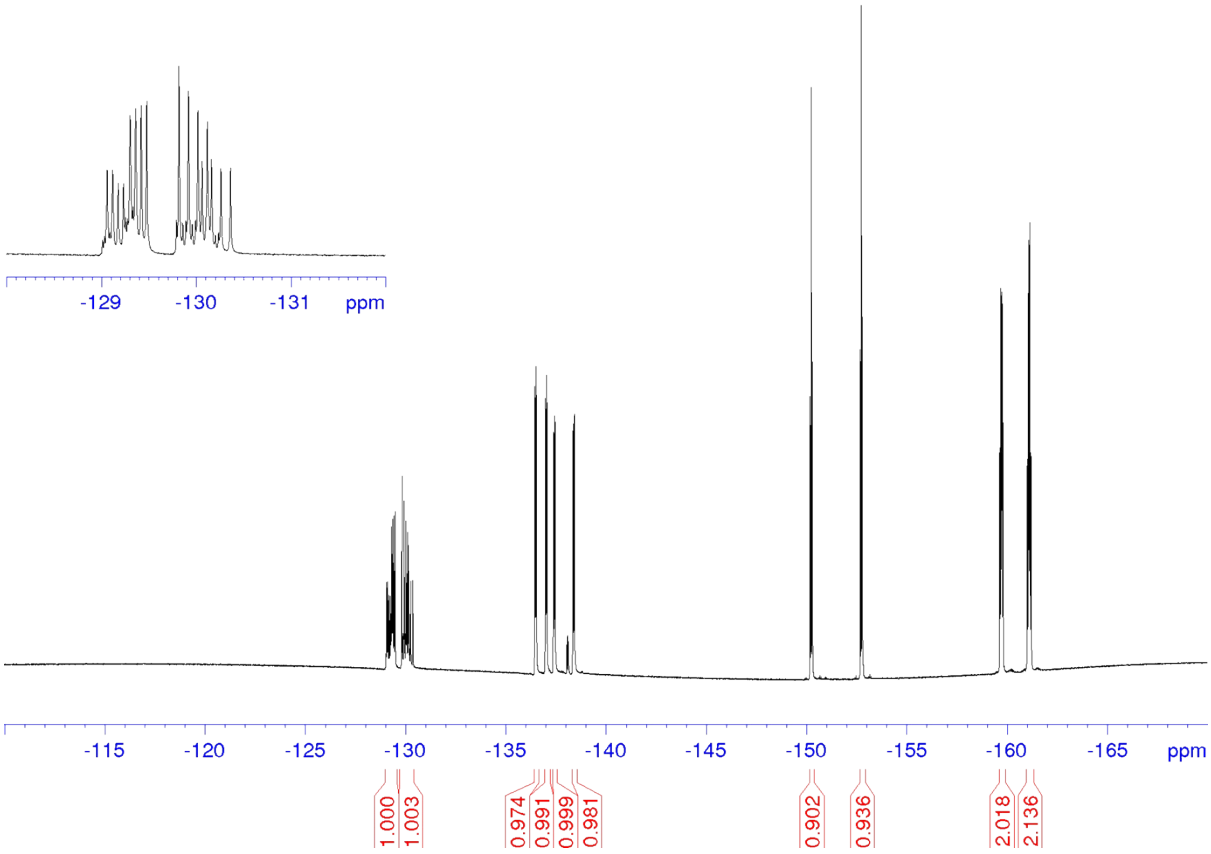


Figure S12: ^{1}H NMR spectrum of **2c** in $CDCl_3$ (400 MHz)

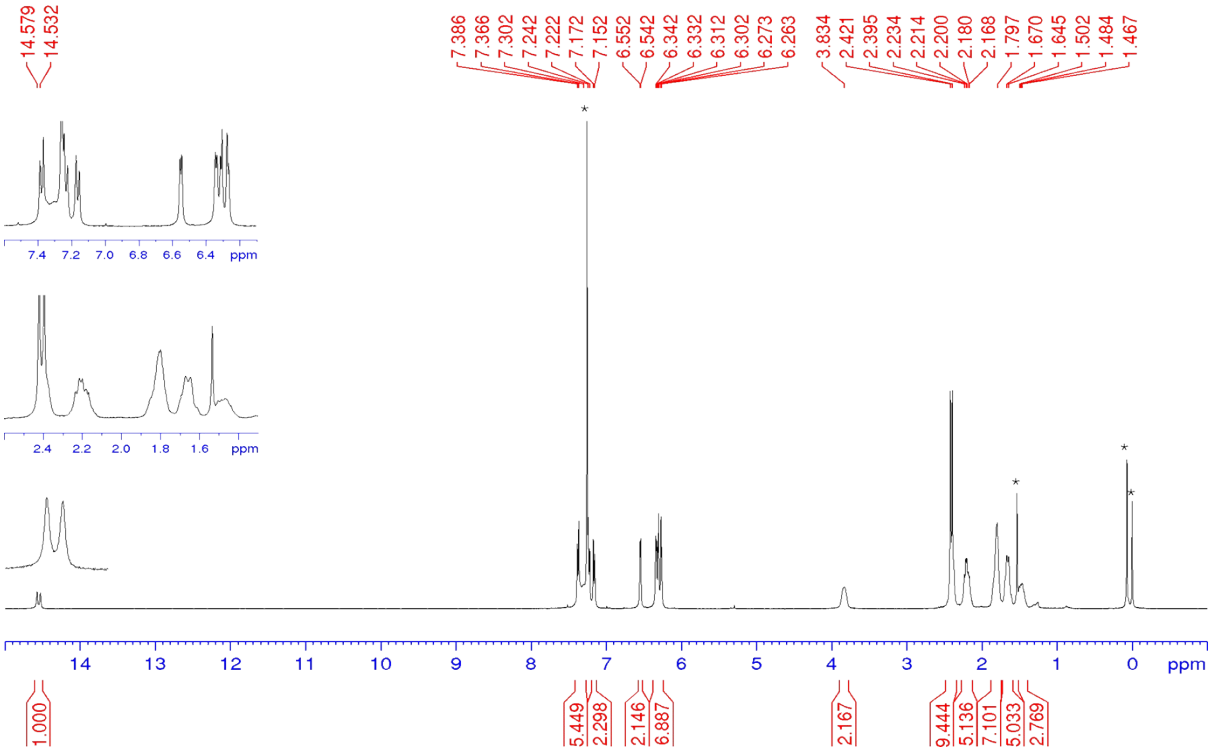


Figure S13: ^{13}C NMR spectrum of **2c** in $CDCl_3$ (100 MHz)

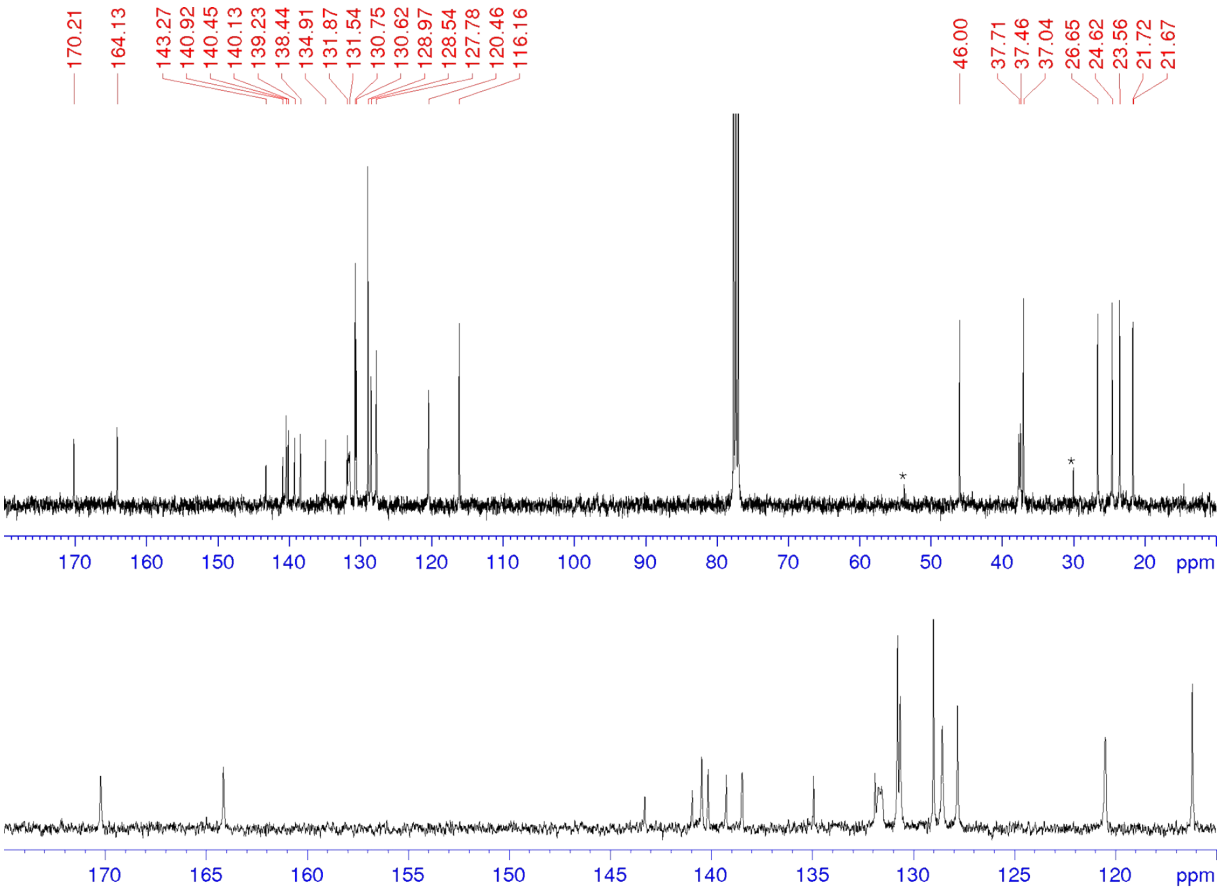


Figure S14: ^{11}B NMR spectrum of **2c** in $CDCl_3$ (128 MHz)

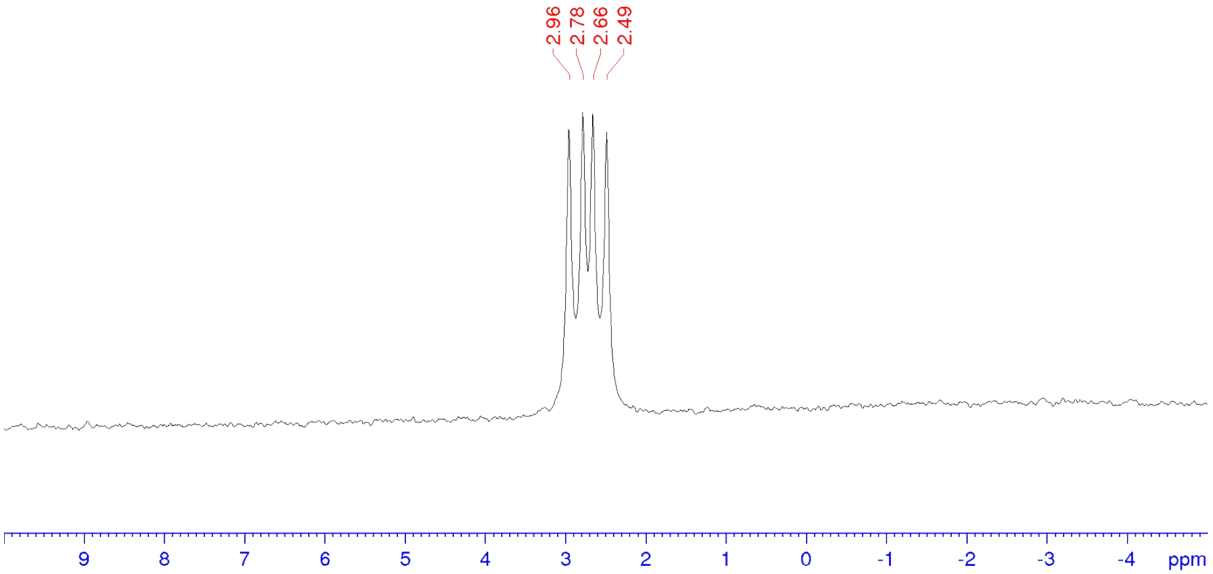


Figure S15: ^{19}F NMR spectrum of **2c** in $CDCl_3$ (376 MHz)

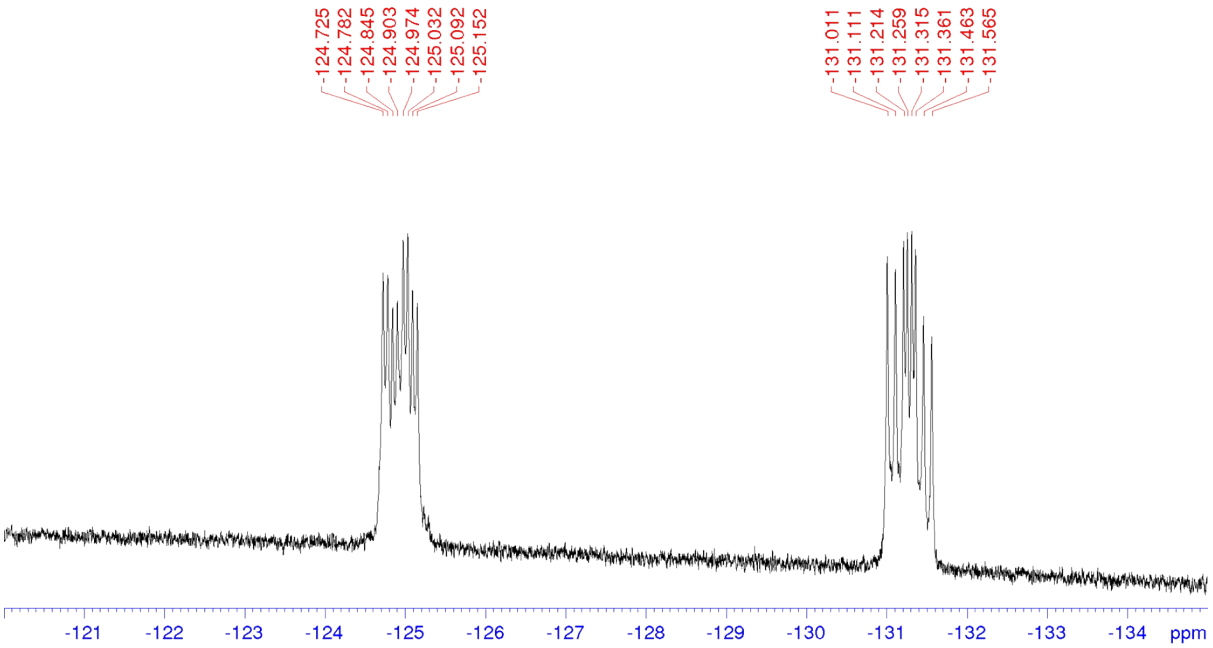


Figure S16: COSY NMR spectrum of **2c** in $CDCl_3$

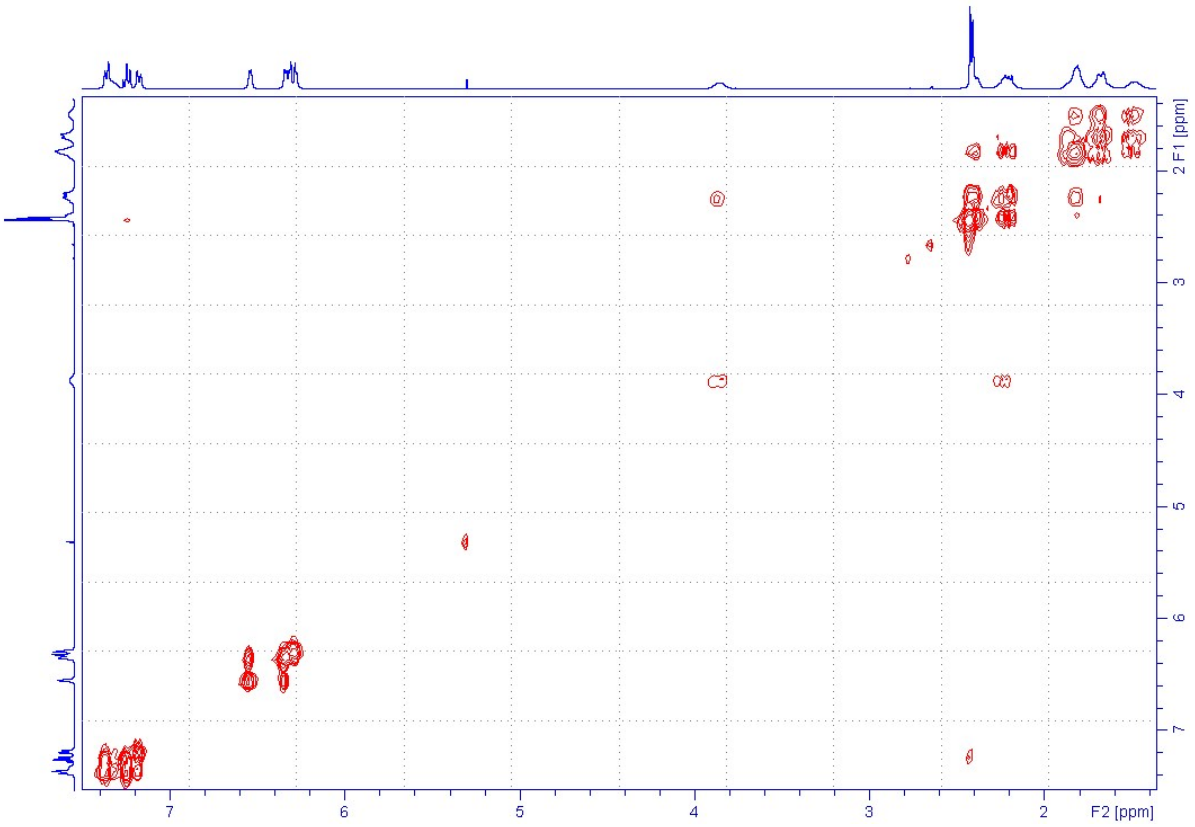


Figure S17: NOESY NMR spectrum of **2c** in $CDCl_3$

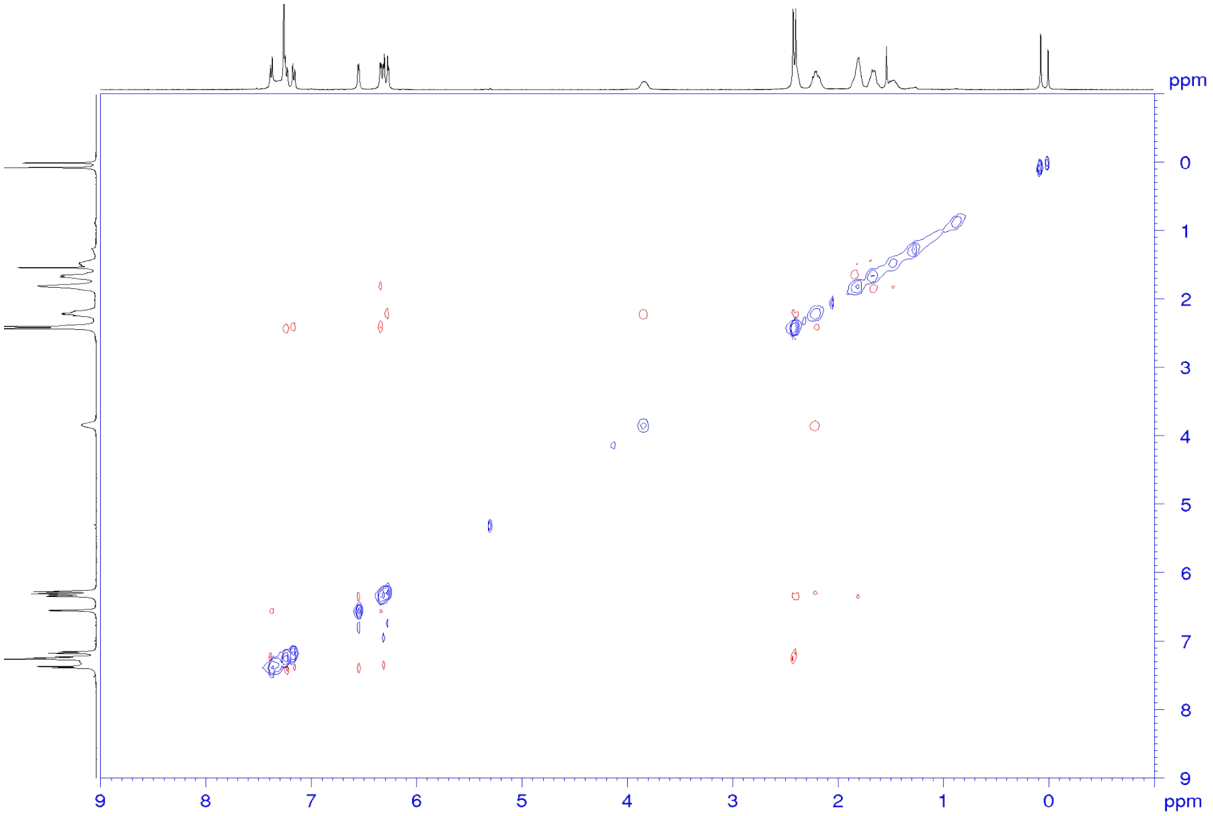


Figure S18: HSQC NMR spectrum of **2c** in $CDCl_3$

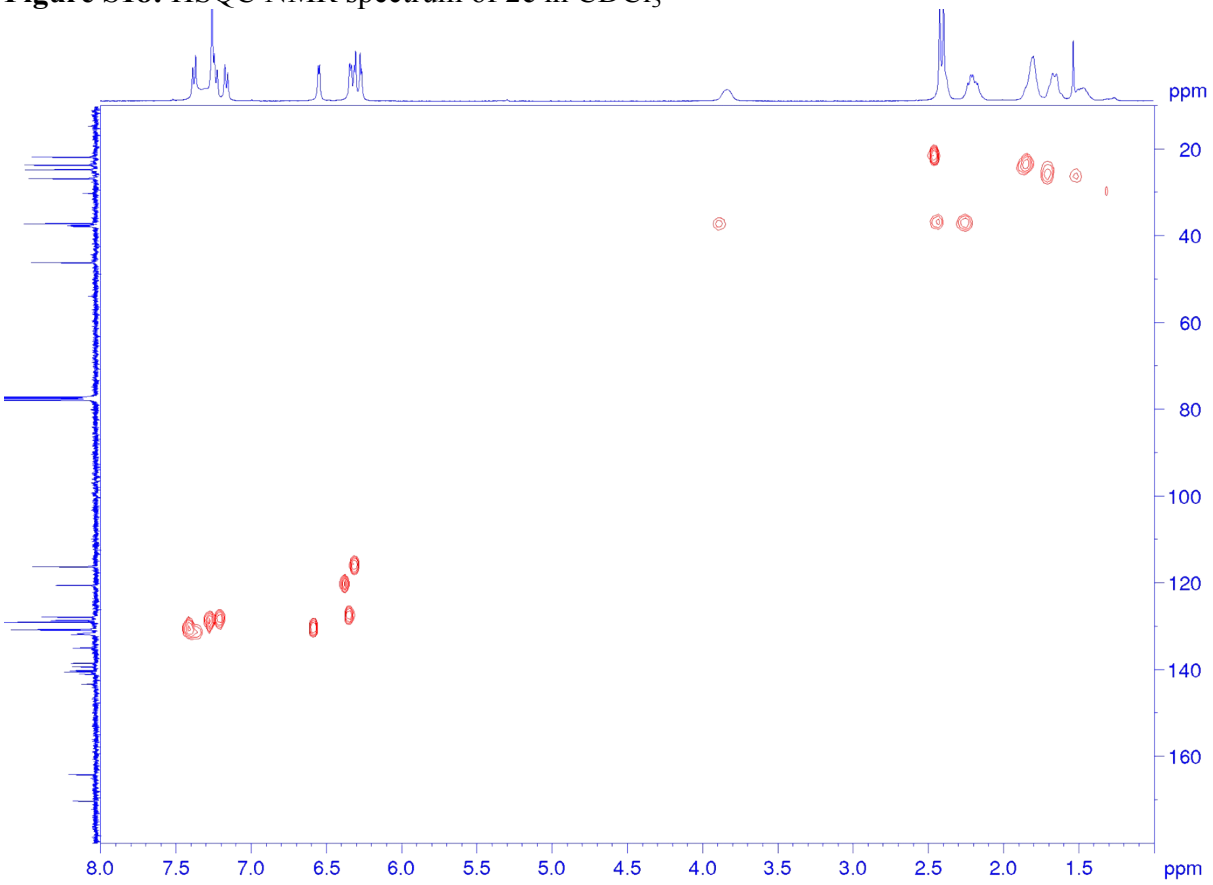


Figure S19: HMBC NMR spectrum of **2c** in $CDCl_3$

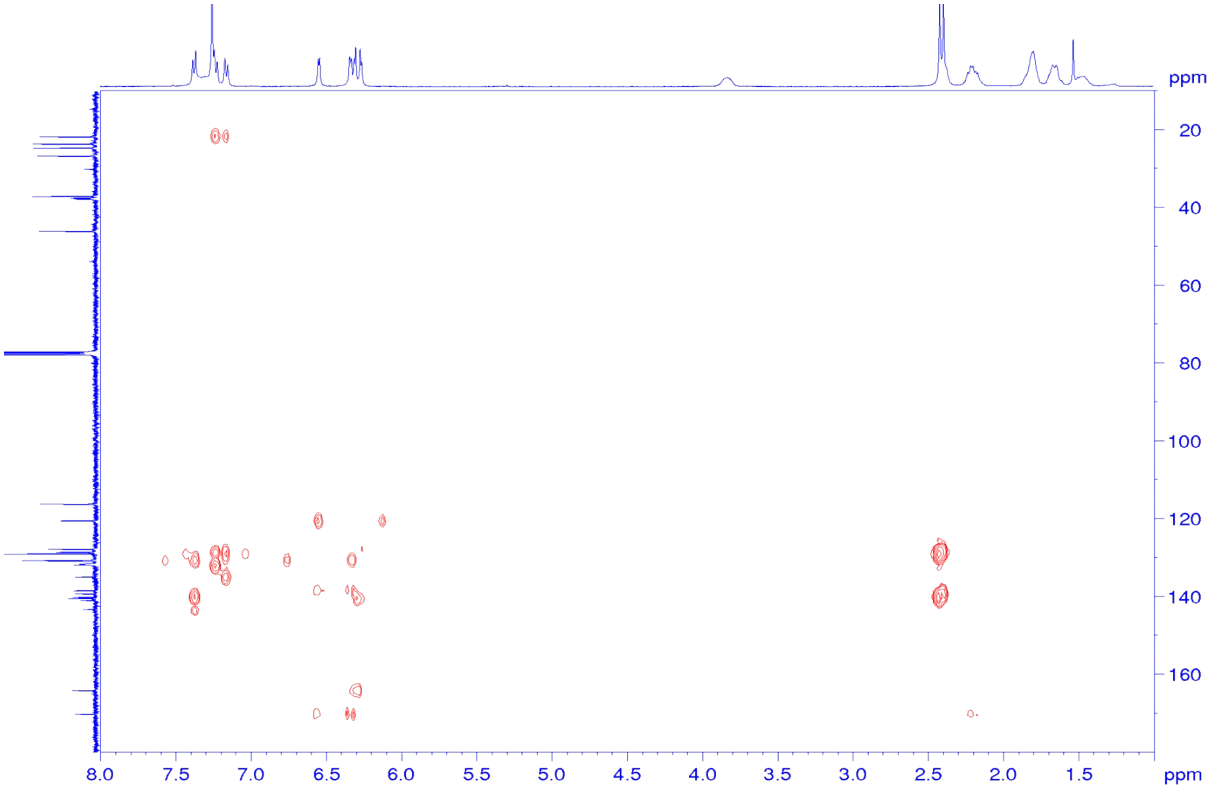


Figure S20: ^{1}H NMR spectrum of **2d** in $CDCl_3$ (400 MHz)

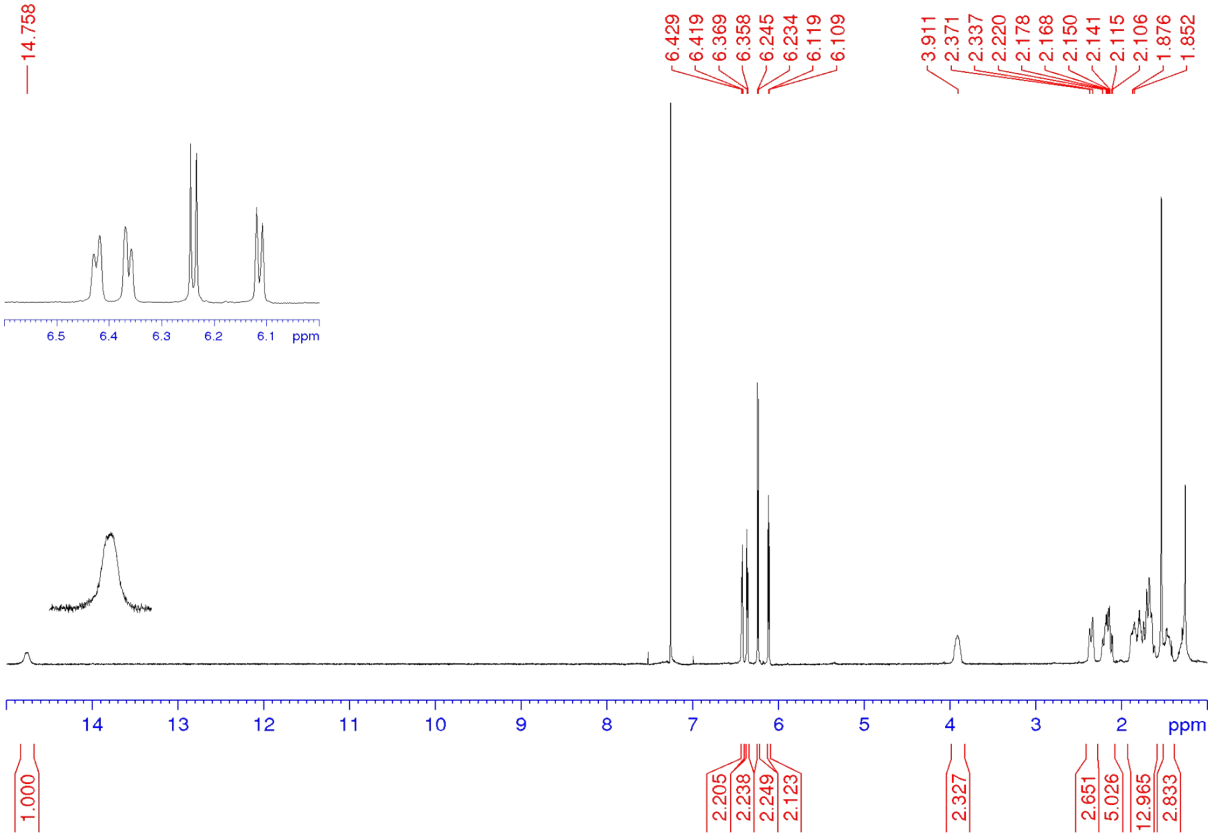


Figure S21: ^{11}B NMR spectrum of **2d** in $CDCl_3$ (128 MHz)

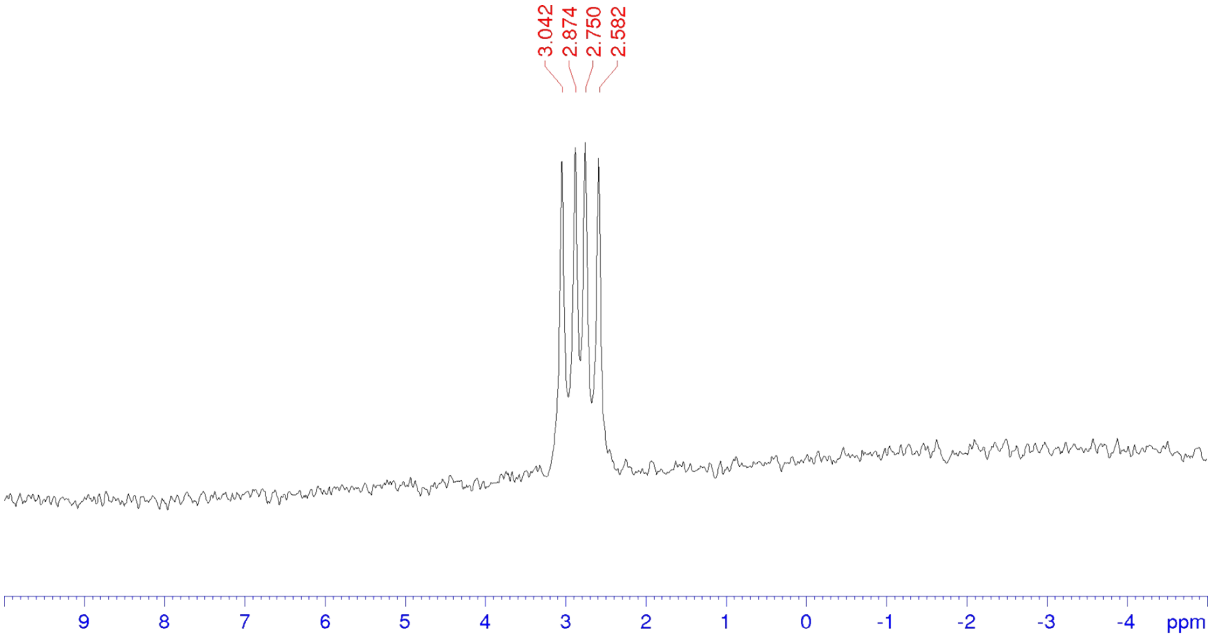


Figure S22: ^{19}F NMR spectrum of **2d** in $CDCl_3$ (376 MHz)

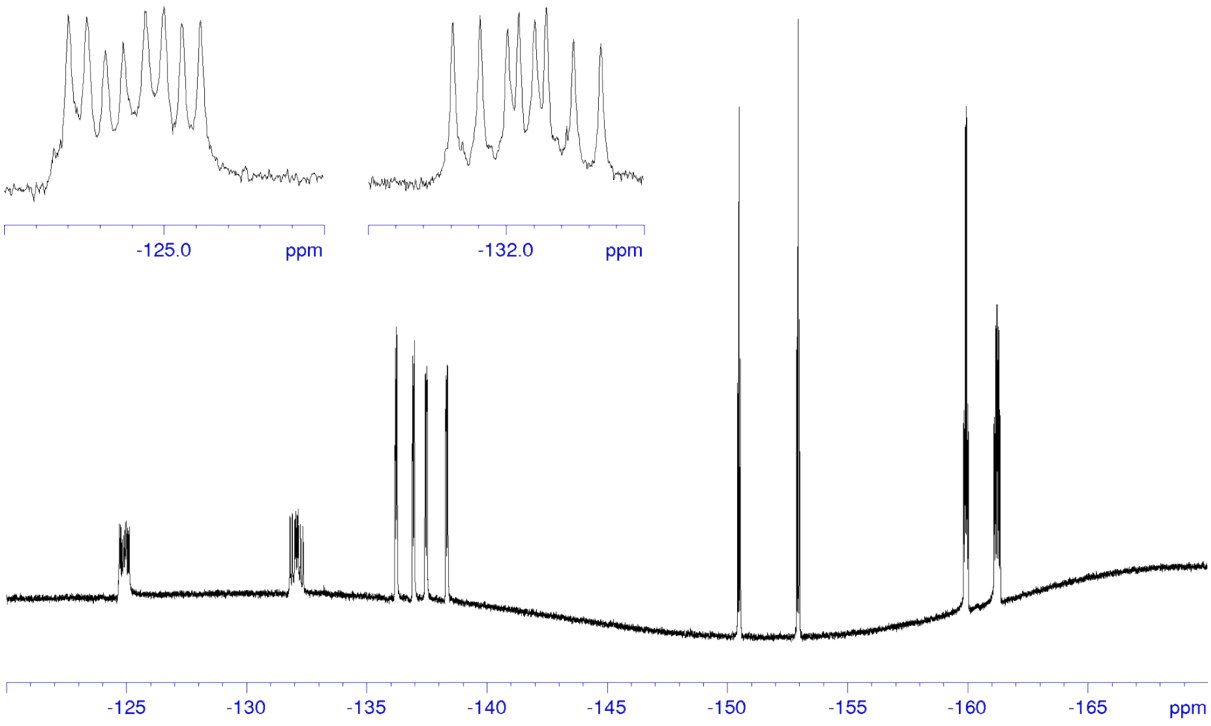


Figure S23: ^{1}H NMR spectrum of **3a** in $CDCl_3$ (400 MHz)

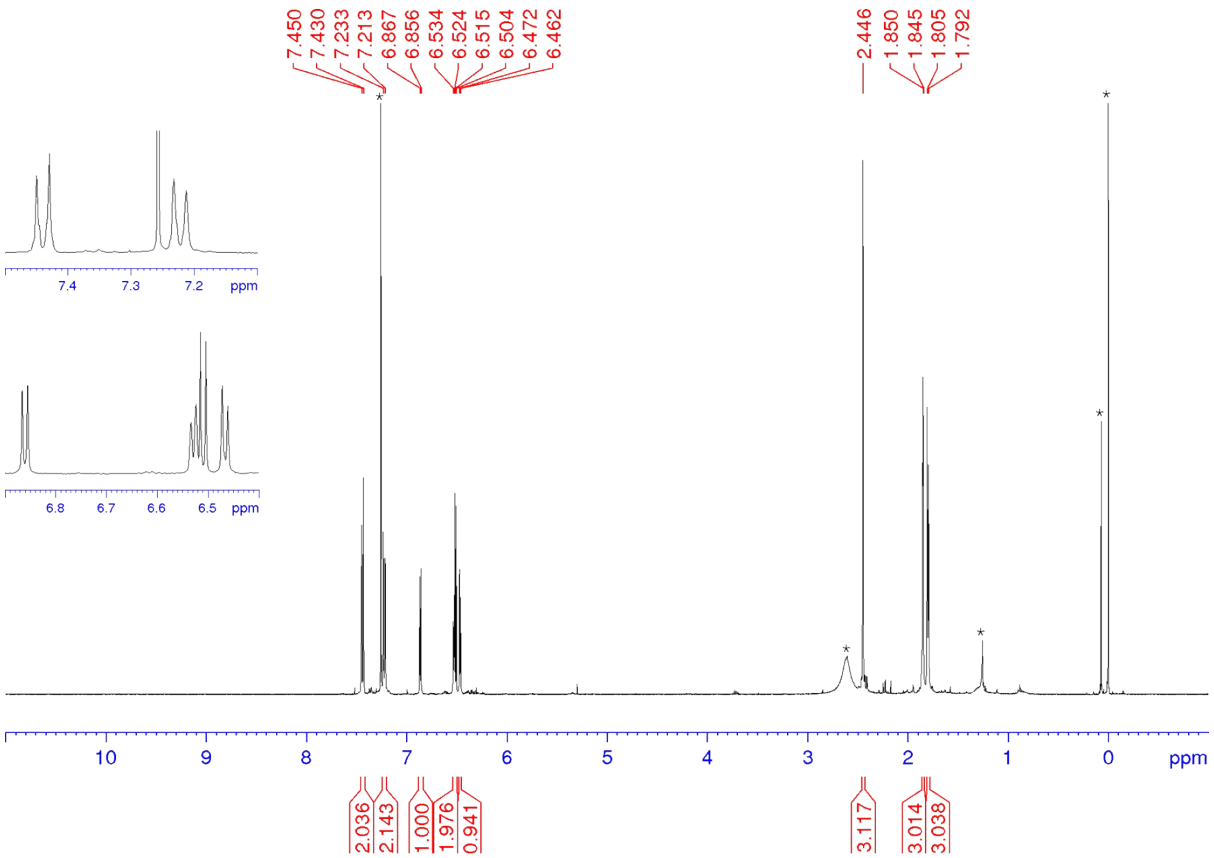


Figure S24: ^{11}B NMR spectrum of **3a** in $CDCl_3$ (128 MHz)

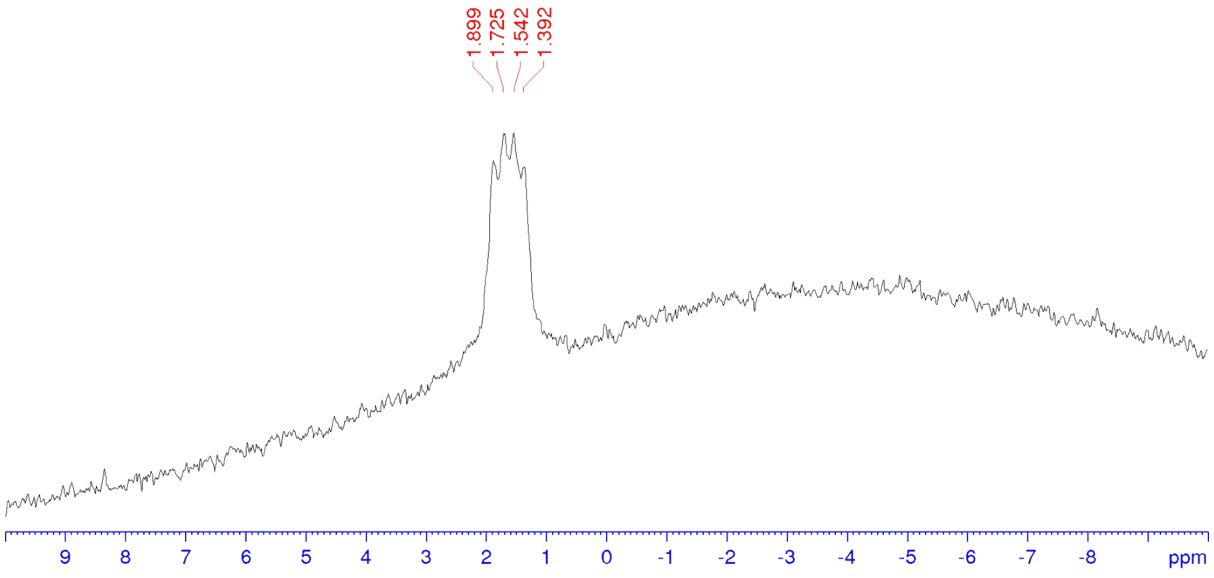


Figure S25: ^{19}F NMR spectrum of **3a** in $CDCl_3$ (376 MHz)

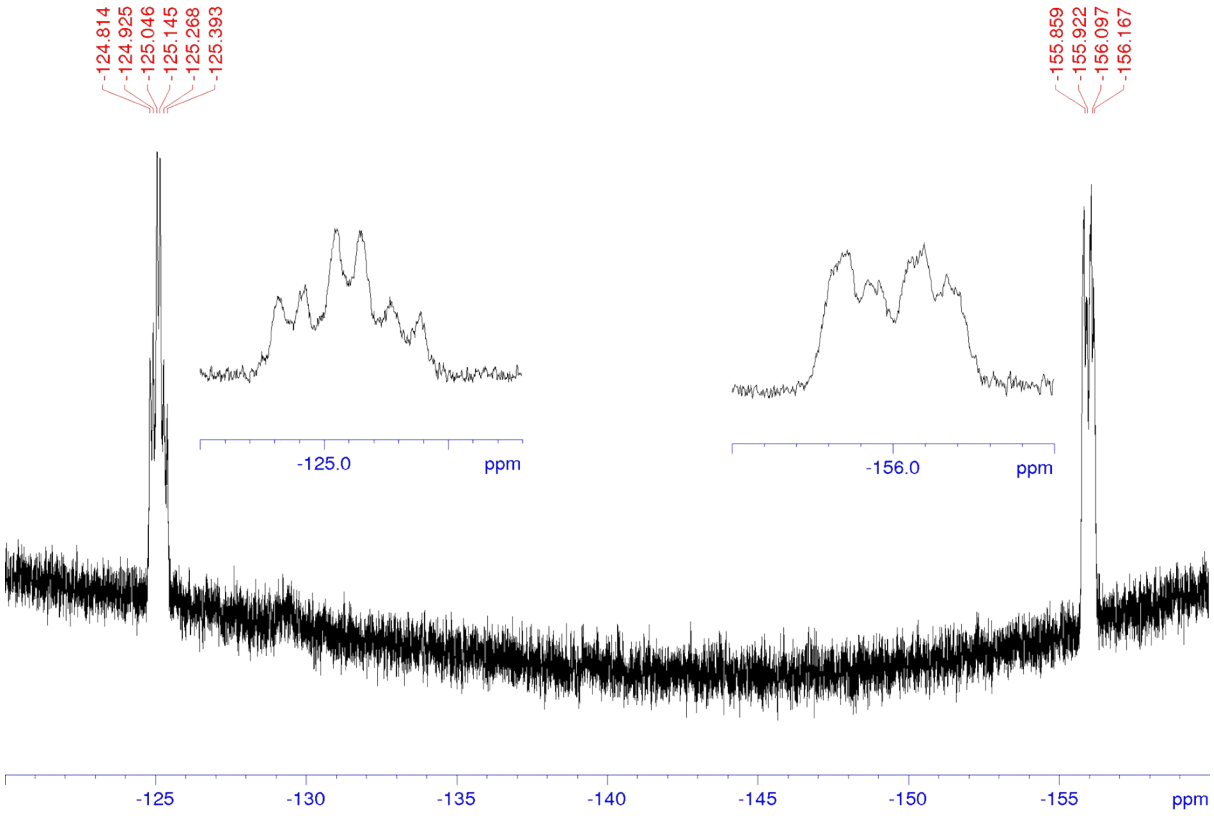


Figure S26: ^{1}H NMR spectrum of **4a** in $CDCl_3$ (400 MHz)

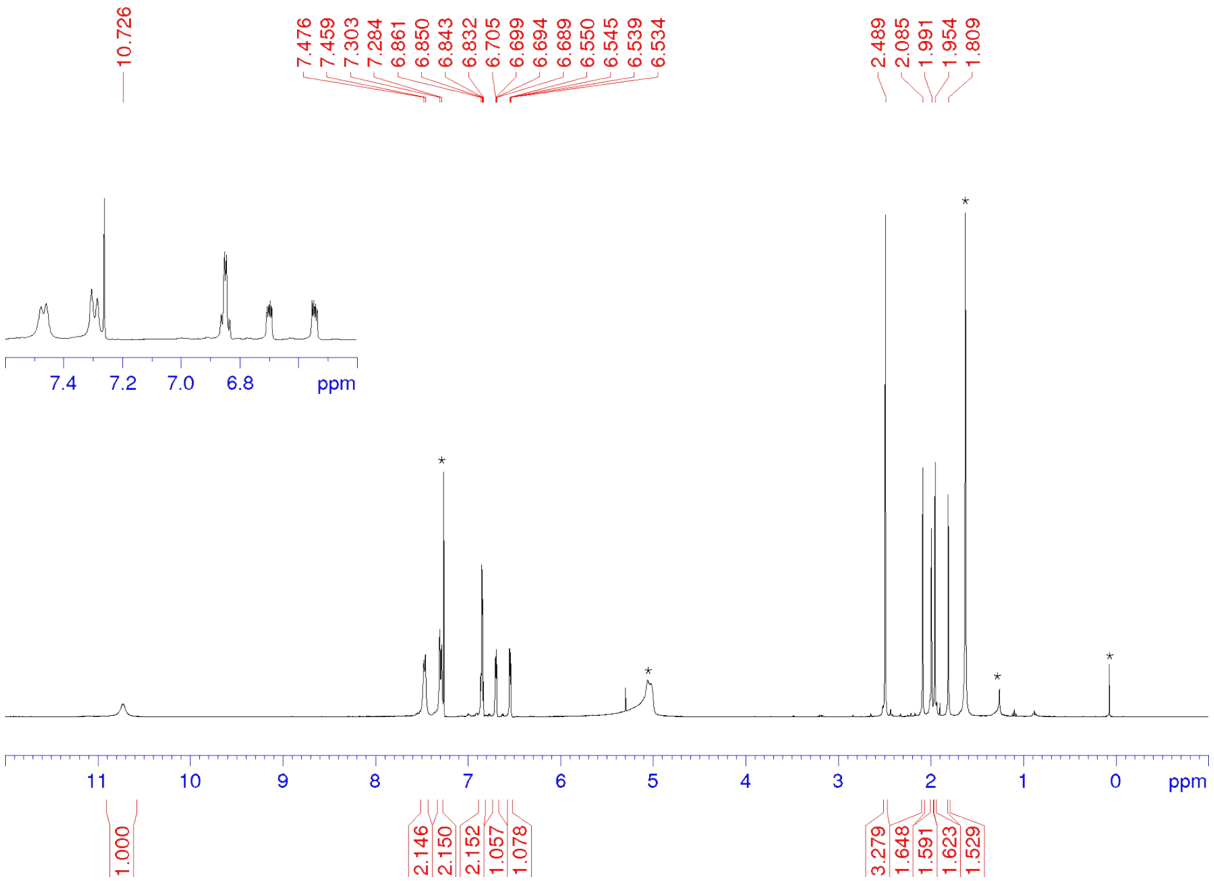


Figure S27: ^{11}B NMR spectrum of **4a** in $CDCl_3$ (128 MHz)

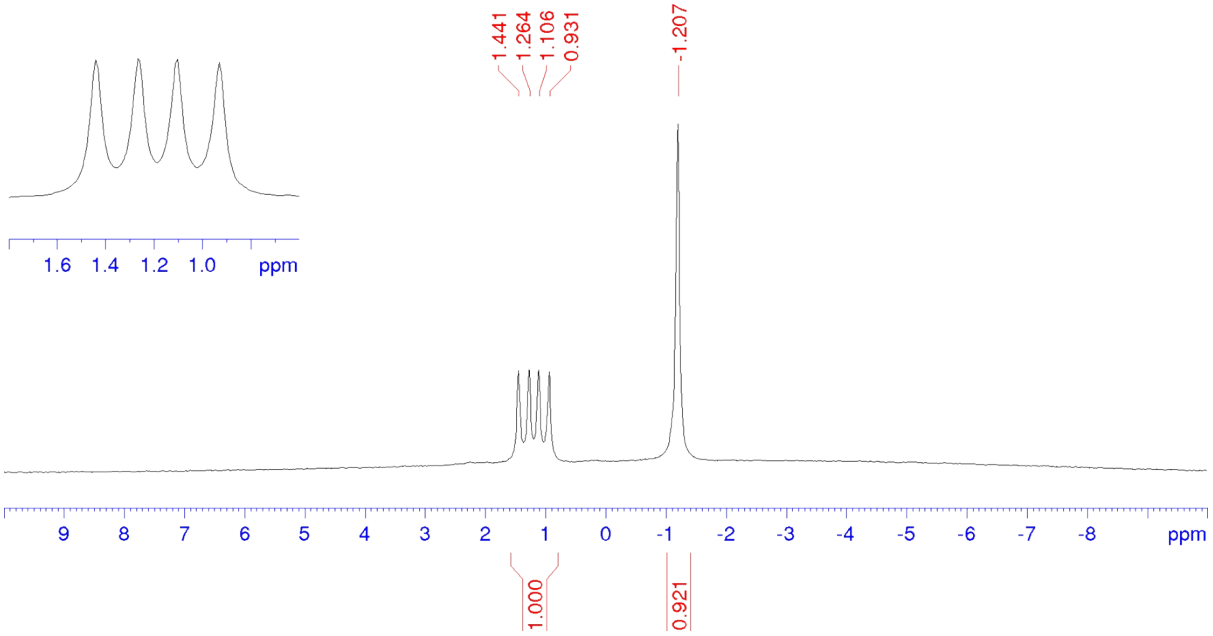


Figure S28: ^{19}F NMR spectrum of **4a** in $CDCl_3$ (376 MHz)

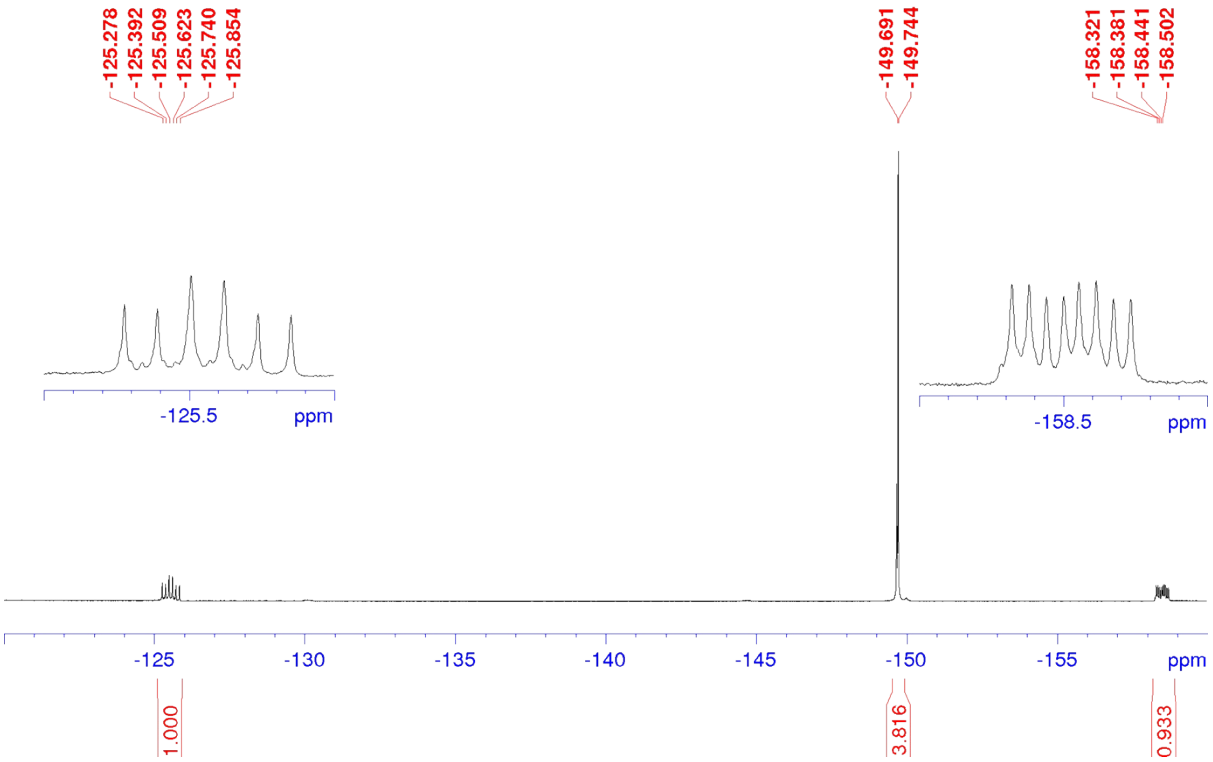


Figure S29: ^{1}H NMR spectrum of **5a** in $CDCl_3$ (400 MHz)

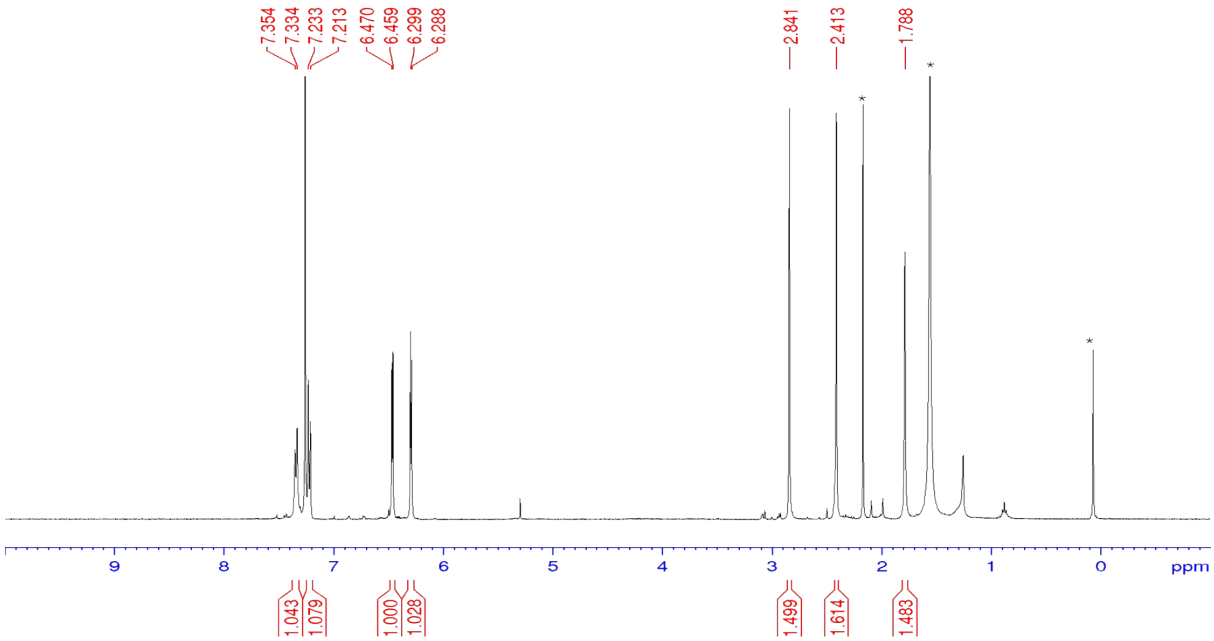


Figure S30: ^{11}B NMR spectrum of **5a** in $CDCl_3$ (128 MHz)

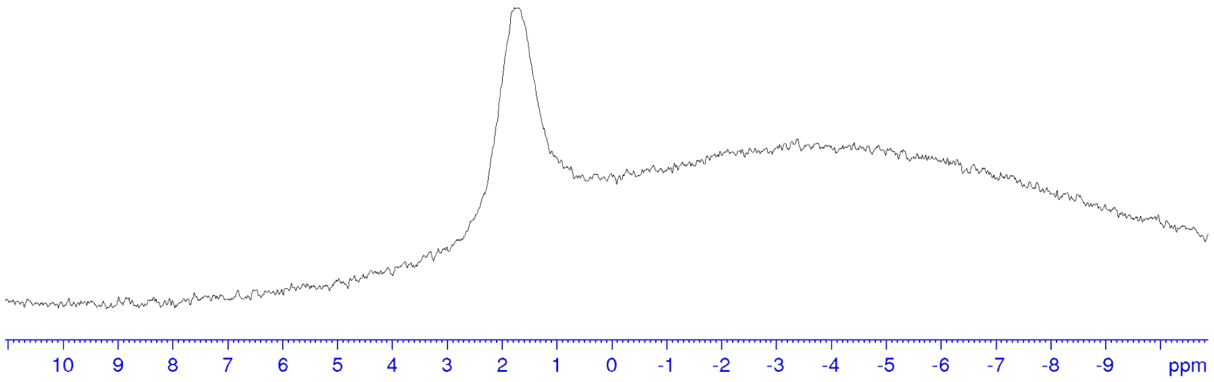


Figure S31: ^{19}F NMR spectrum of **5a** in $CDCl_3$ (376 MHz)

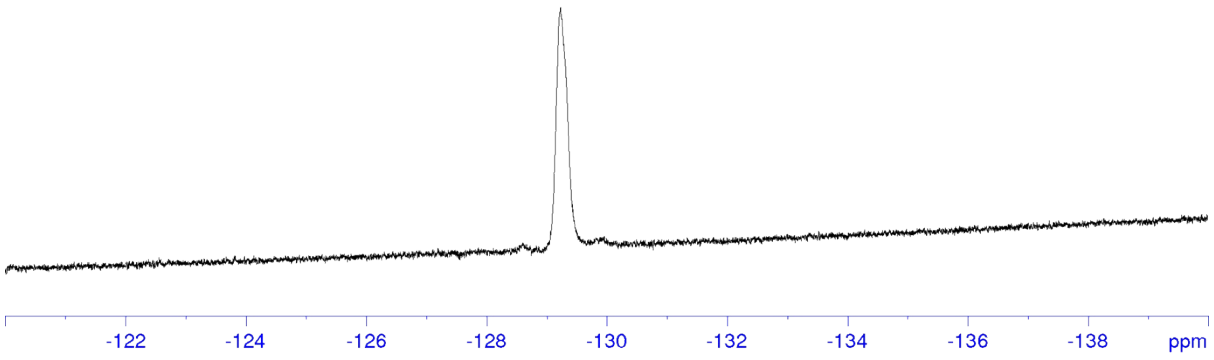


Figure S32: ^{1}H NMR spectrum of **6a** in $CDCl_3$ (400 MHz)

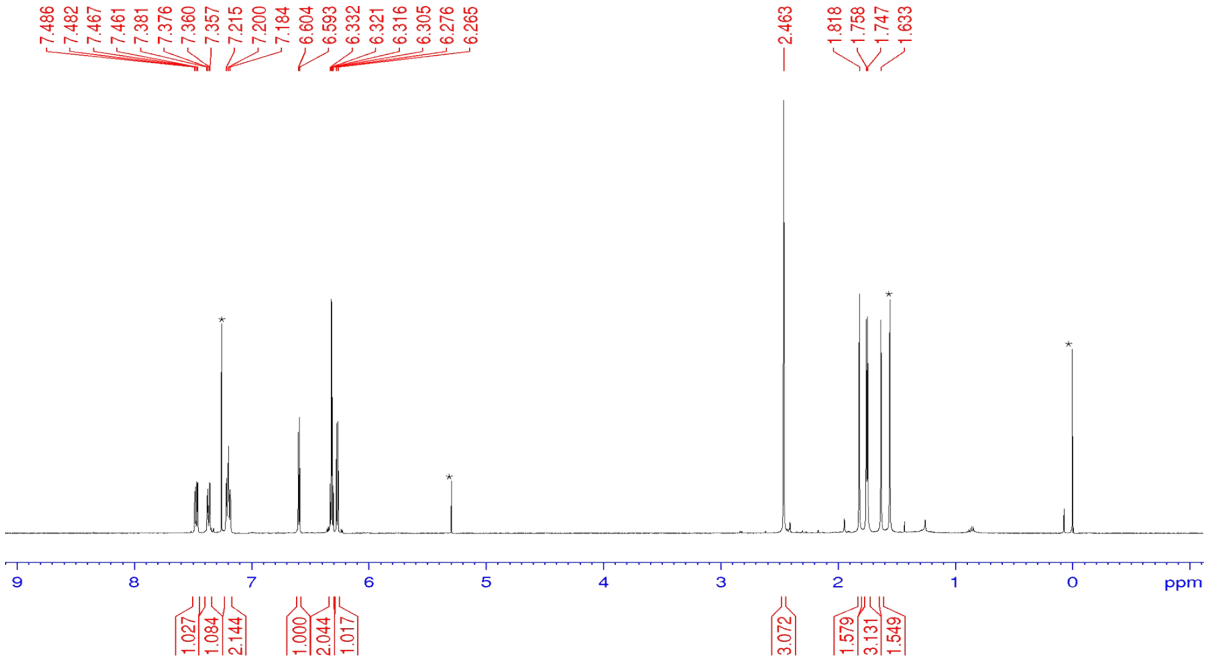


Figure S33: ^{11}B NMR spectrum of **6a** in $CDCl_3$ (128 MHz)

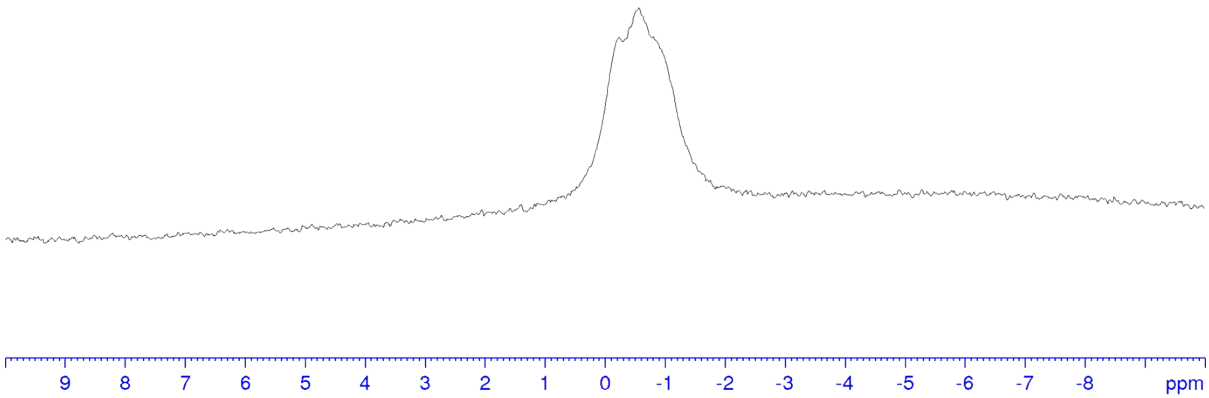


Figure S34: ^{19}F NMR spectrum of **6a** in $CDCl_3$ (376 MHz)

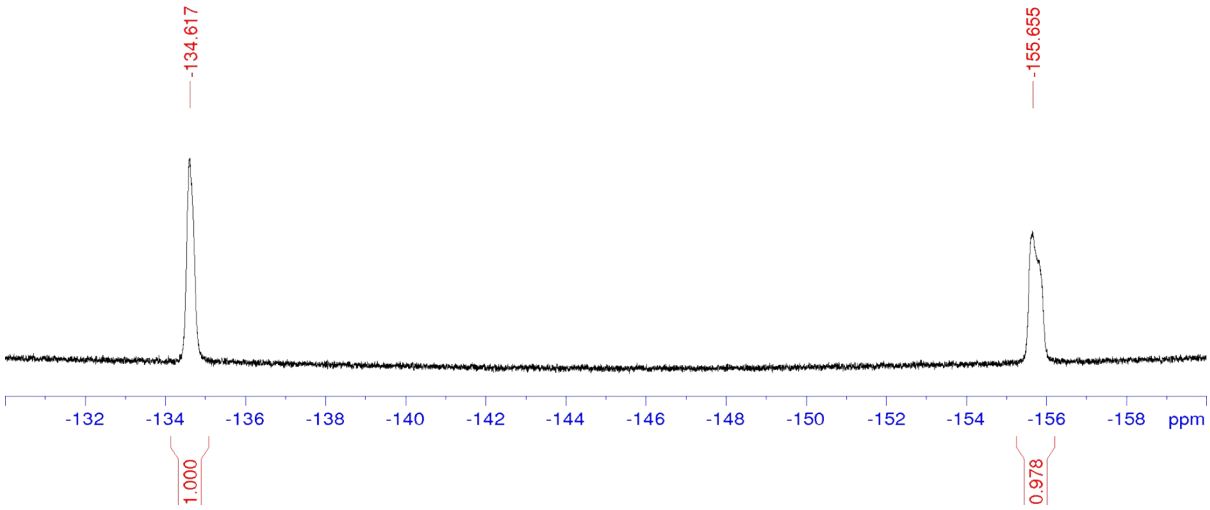


Figure S35: ^{1}H NMR spectrum of **6b** in $CDCl_3$ (400 MHz)

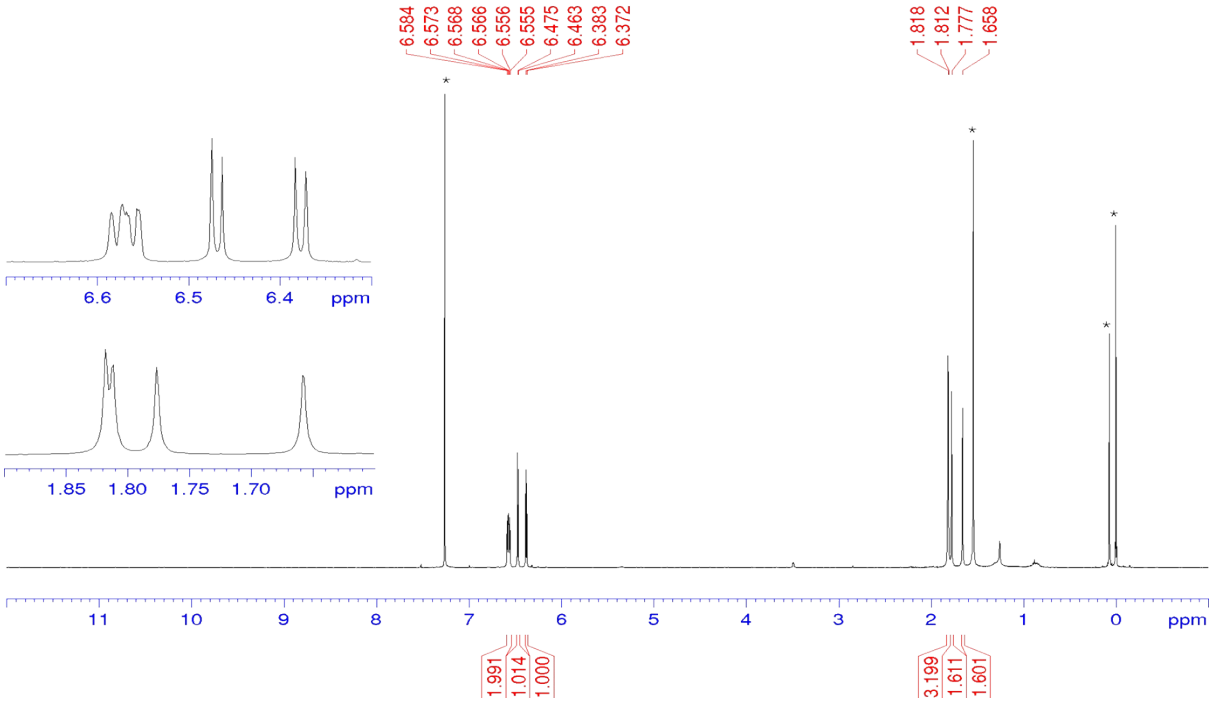


Figure S36: ^{11}B NMR spectrum of **6b** in $CDCl_3$ (128 MHz)

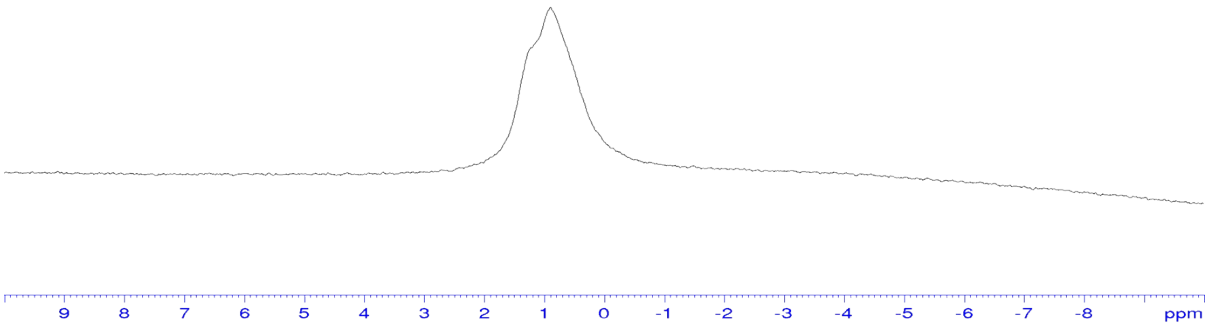


Figure S37: ^{19}F NMR spectrum of **6b** in $CDCl_3$ (376 MHz)

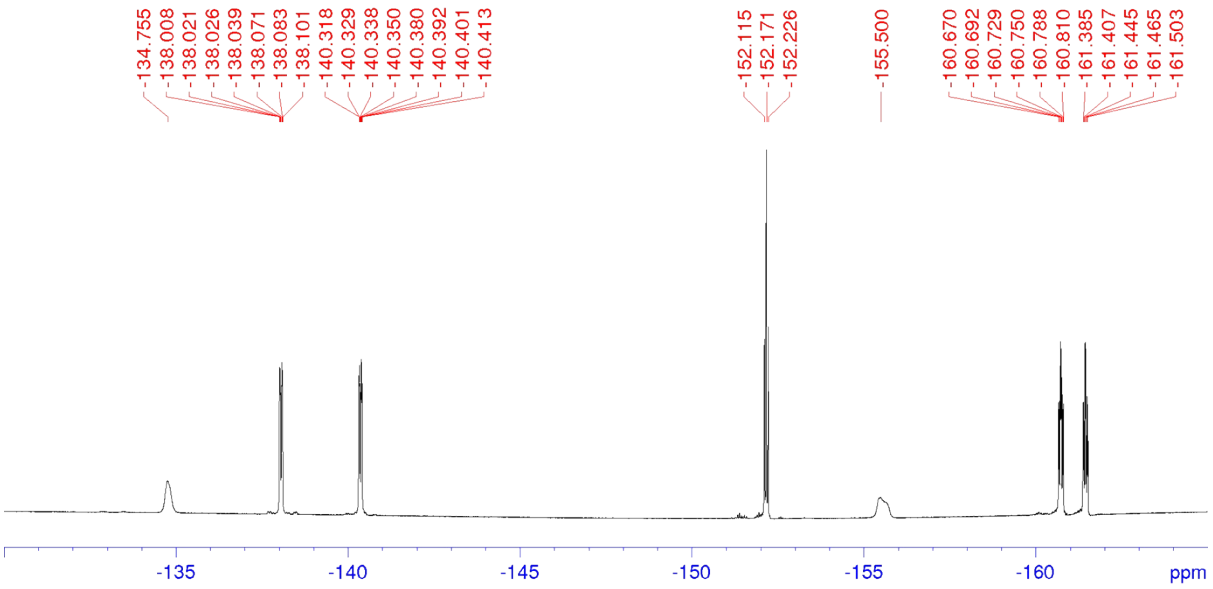


Figure S38: ^{1}H NMR spectrum of **6c** in $CDCl_3$ (400 MHz)

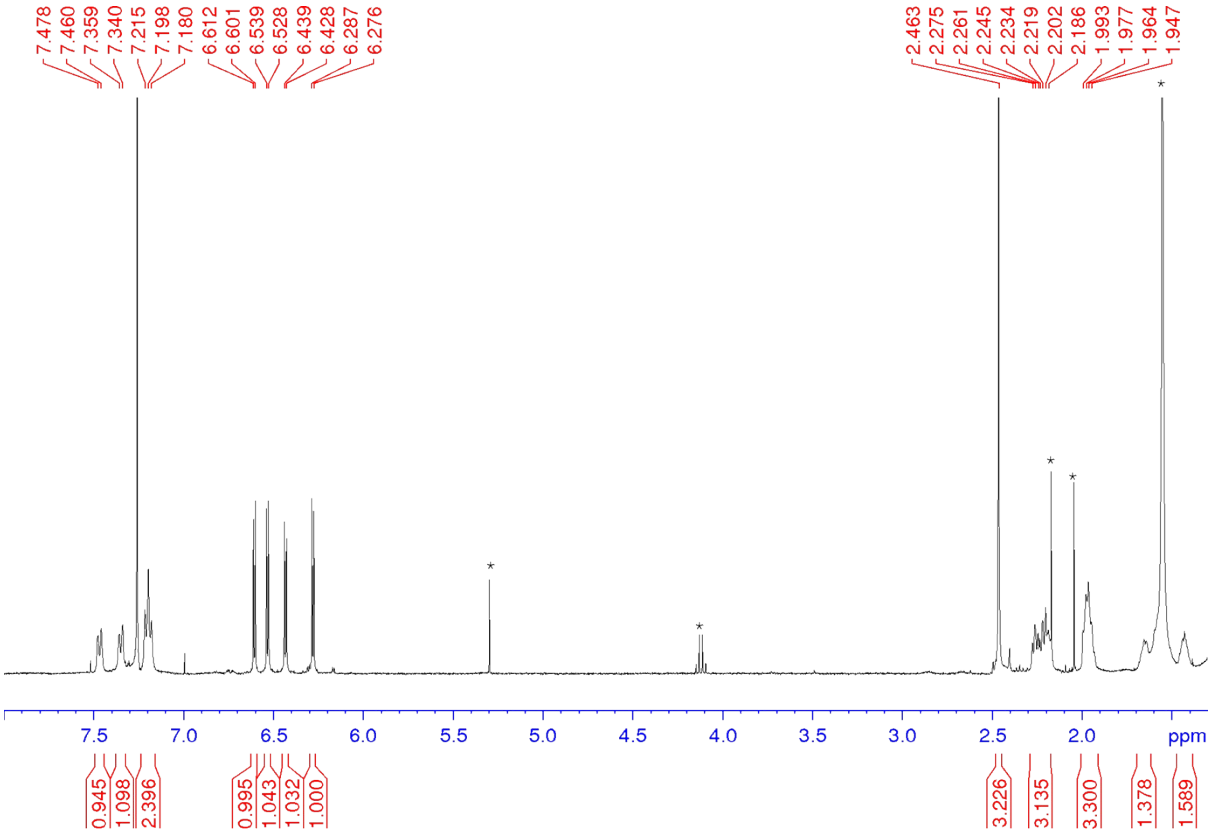


Figure S39: ^{11}B NMR spectrum of **6c** in $CDCl_3$ (128 MHz)

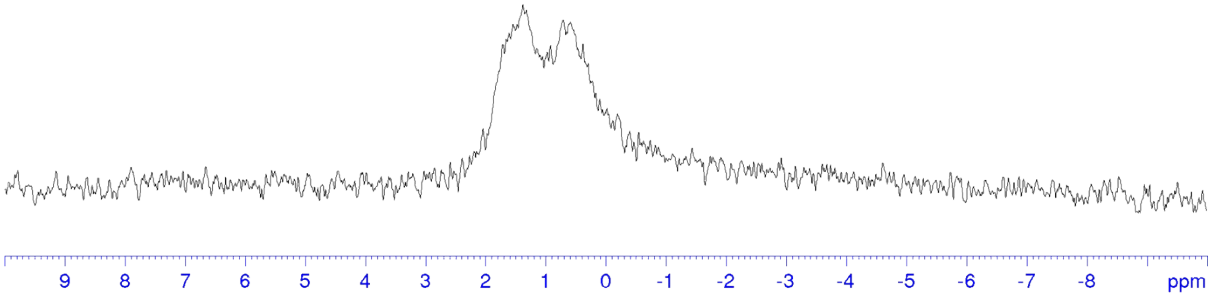


Figure S40: ^{19}F NMR spectrum of **6c** in $CDCl_3$ (376 MHz)

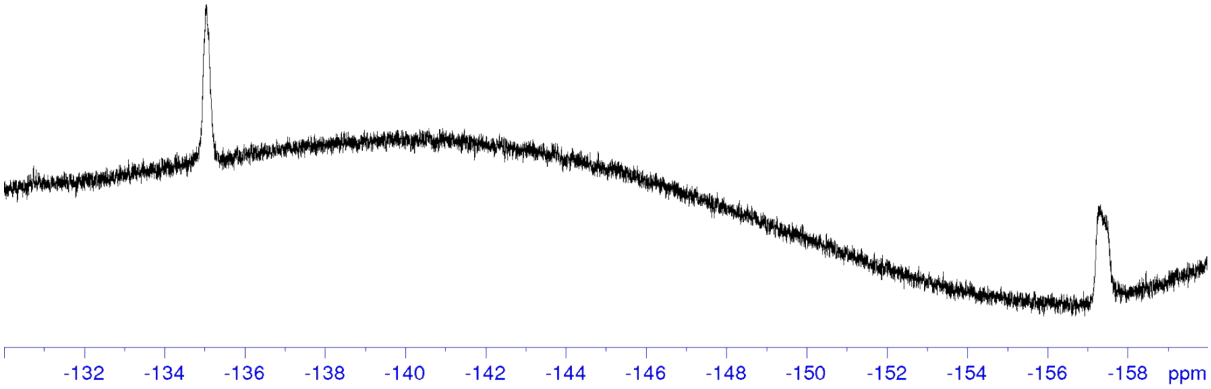


Figure S41: ^{1}H NMR spectrum of **6d** in $CDCl_3$ (400 MHz)

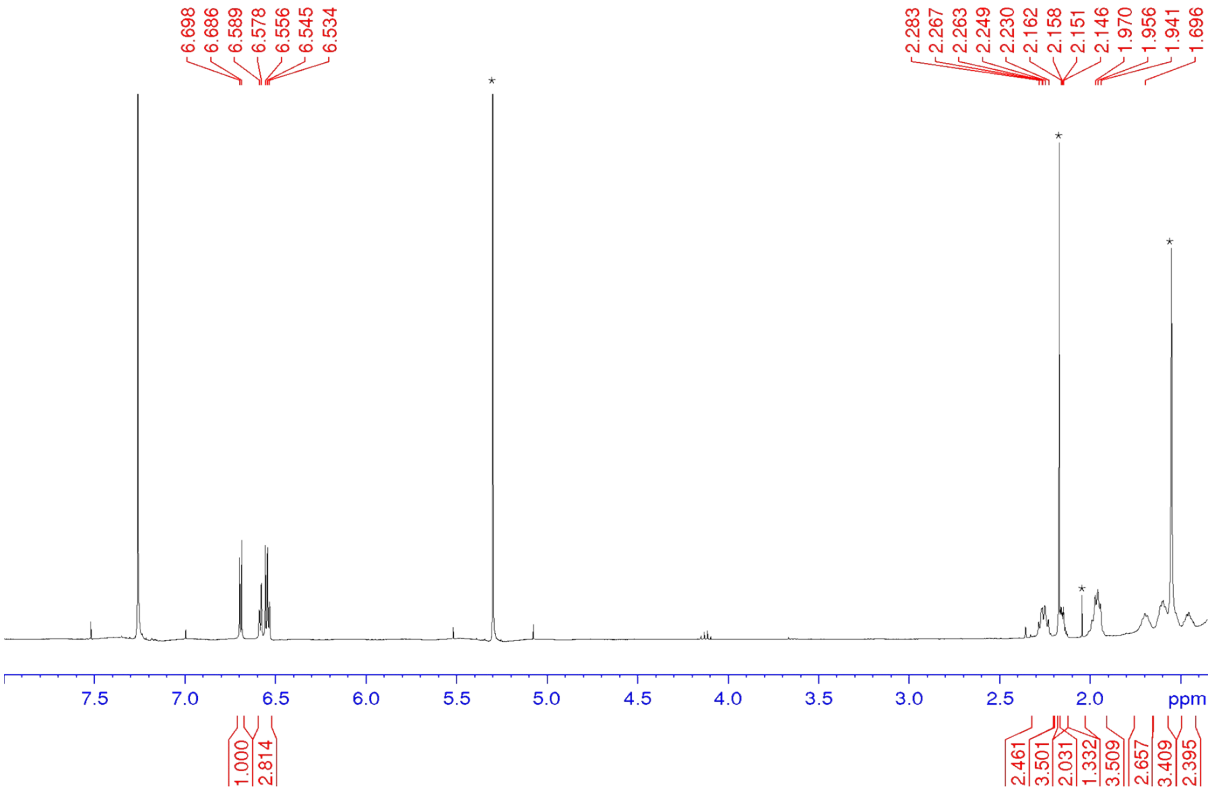


Figure S42: ^{11}B NMR spectrum of **6d** in $CDCl_3$ (128 MHz)

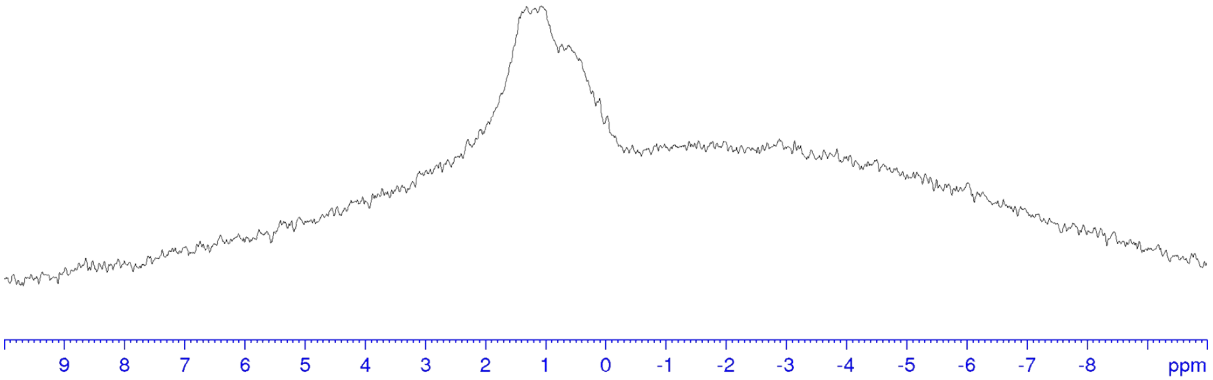


Figure S43: ^{19}F NMR spectrum of **6d** in $CDCl_3$ (376 MHz)

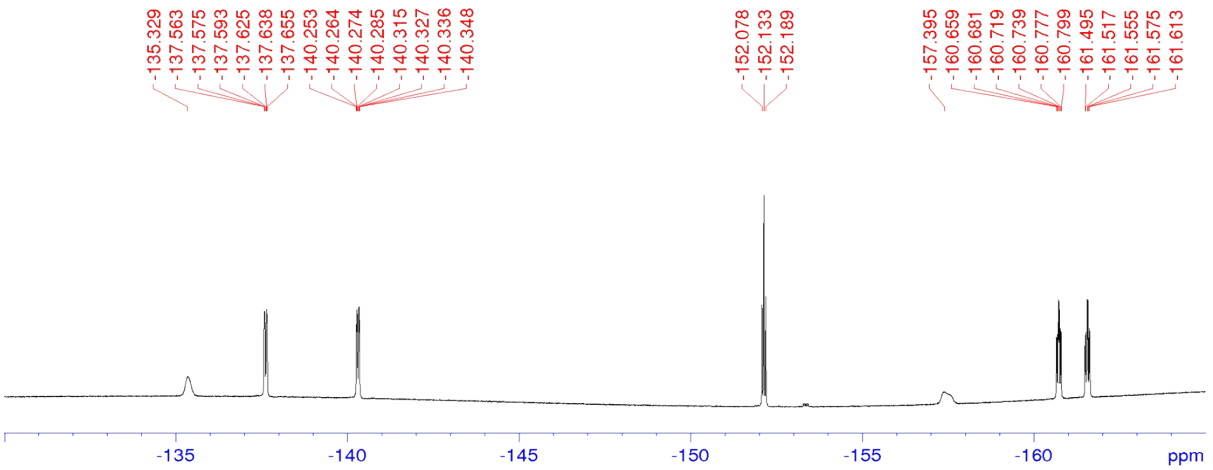


Figure S44: UV-vis absorbance spectrum of **2a** in CH_2Cl_2

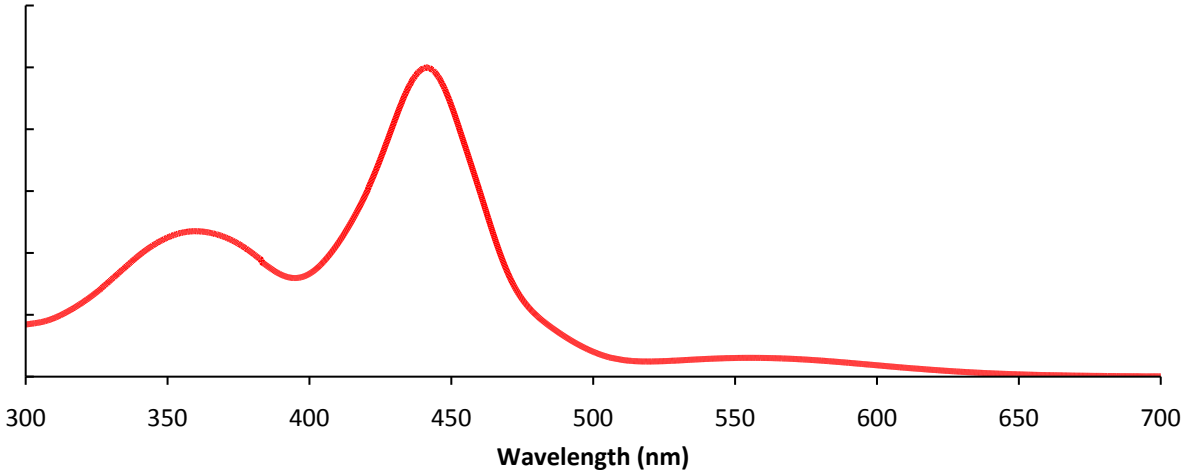


Figure S45: UV-vis absorbance spectrum of **2b** in CH_2Cl_2

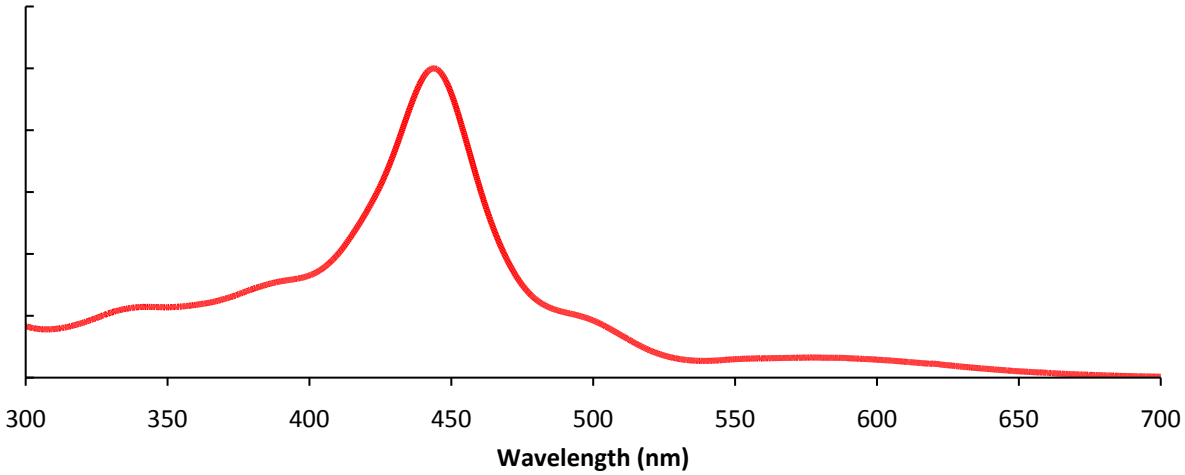


Figure S46: UV-vis absorbance spectrum of **2c** in CH_2Cl_2

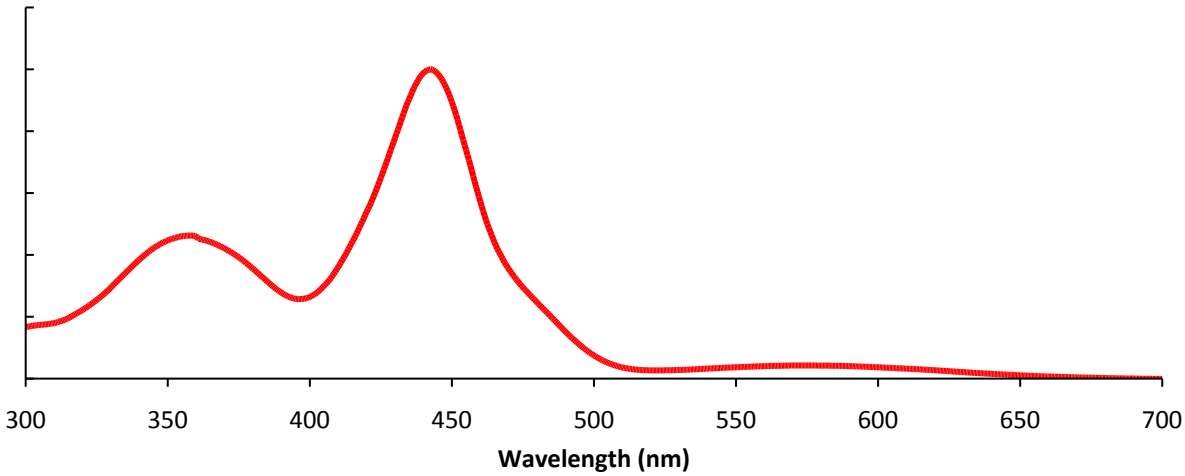


Figure S47: UV-vis absorbance spectrum of **2d** in CH_2Cl_2

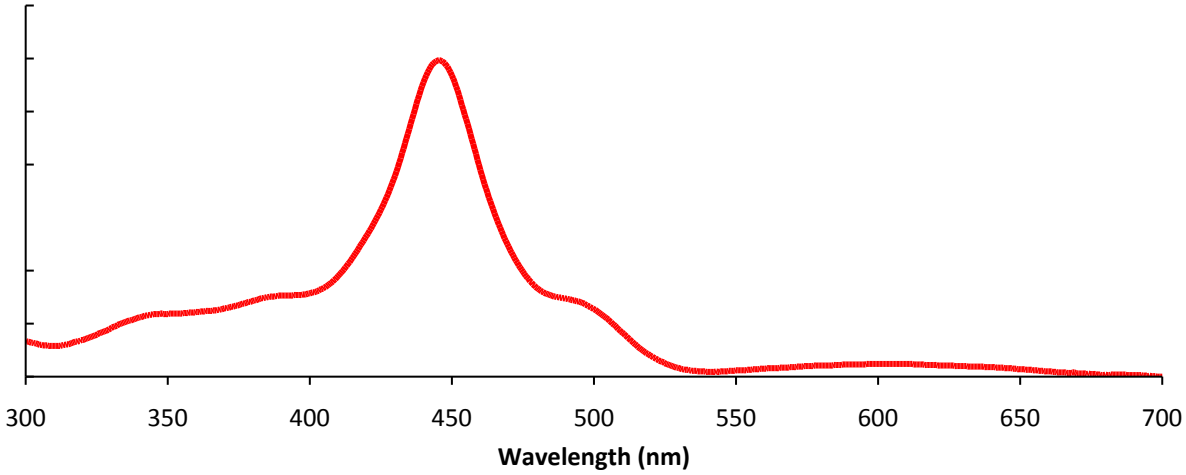


Figure S48: UV-vis absorbance spectrum of **3a** in CH_2Cl_2

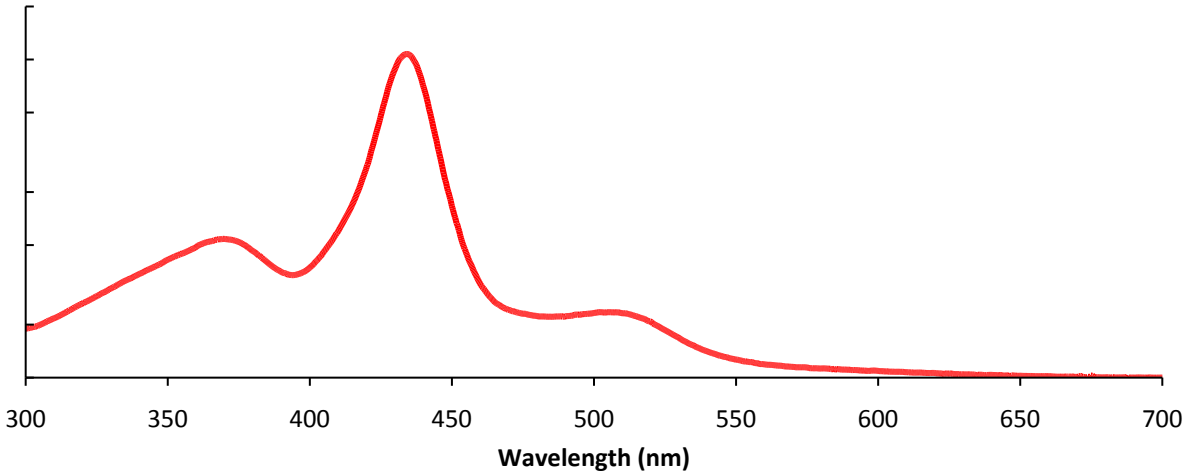


Figure S49: UV-vis absorbance spectrum of **4a** in CH_2Cl_2

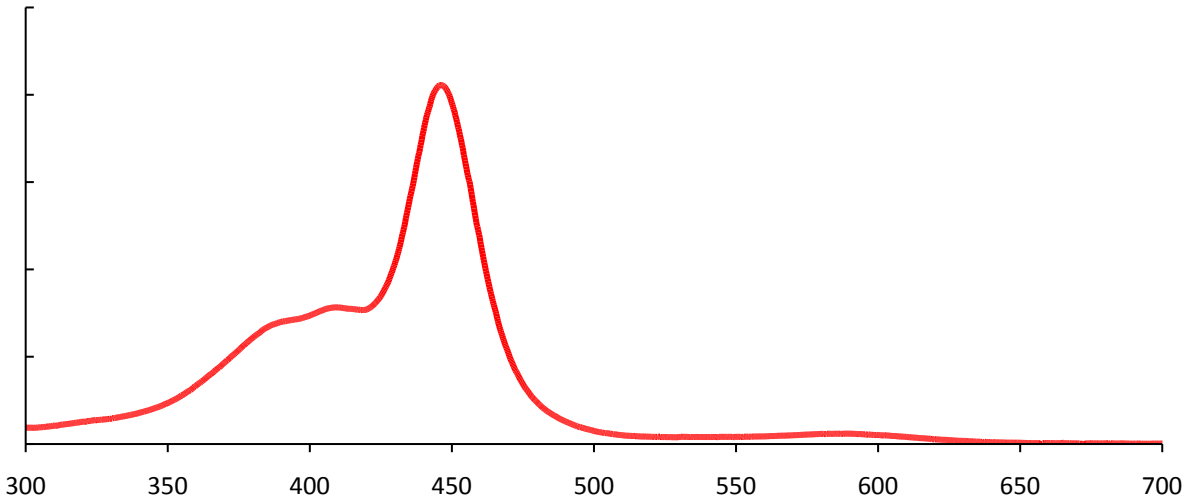


Figure S50: UV-vis absorbance spectrum of **5a** in CH_2Cl_2

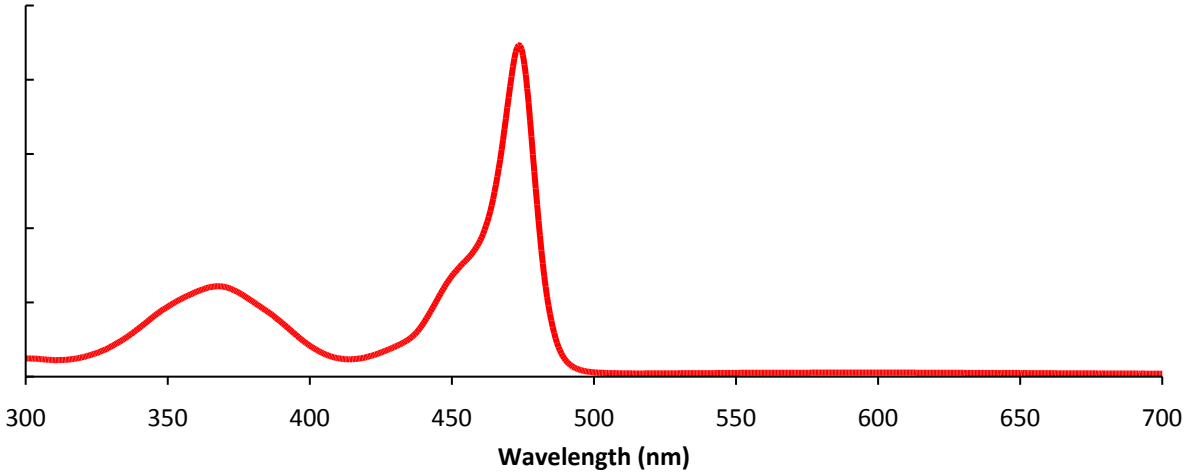


Figure S51: UV-vis absorbance spectrum of **6a** in CH_2Cl_2

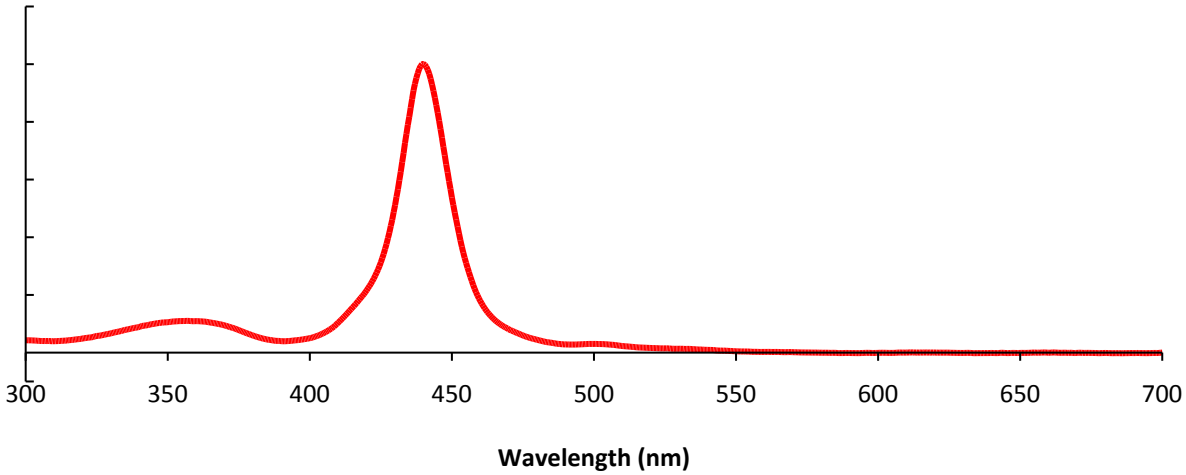


Figure S52: UV-vis absorbance spectrum of **6b** in CH_2Cl_2

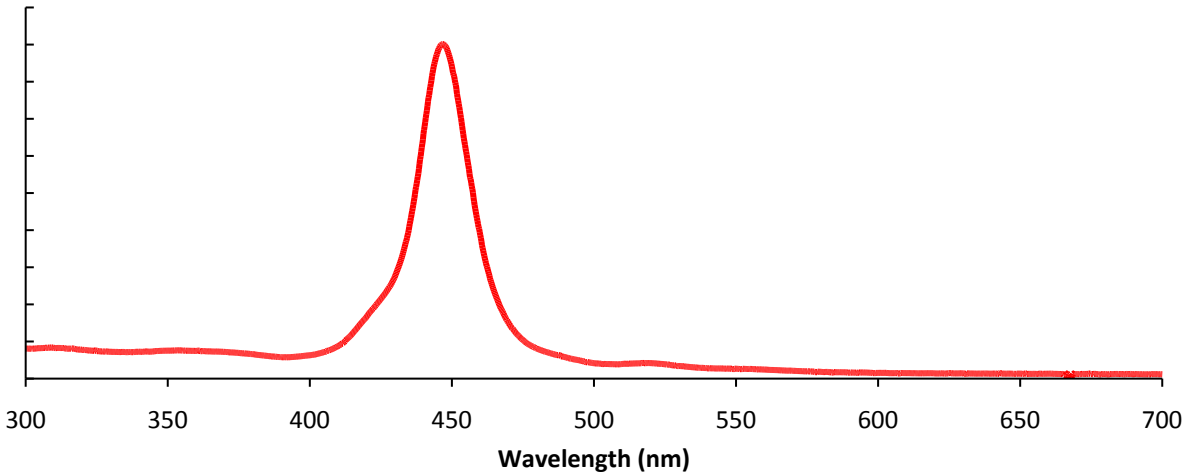


Figure S53: UV-vis absorbance spectrum of **6c** in CH_2Cl_2

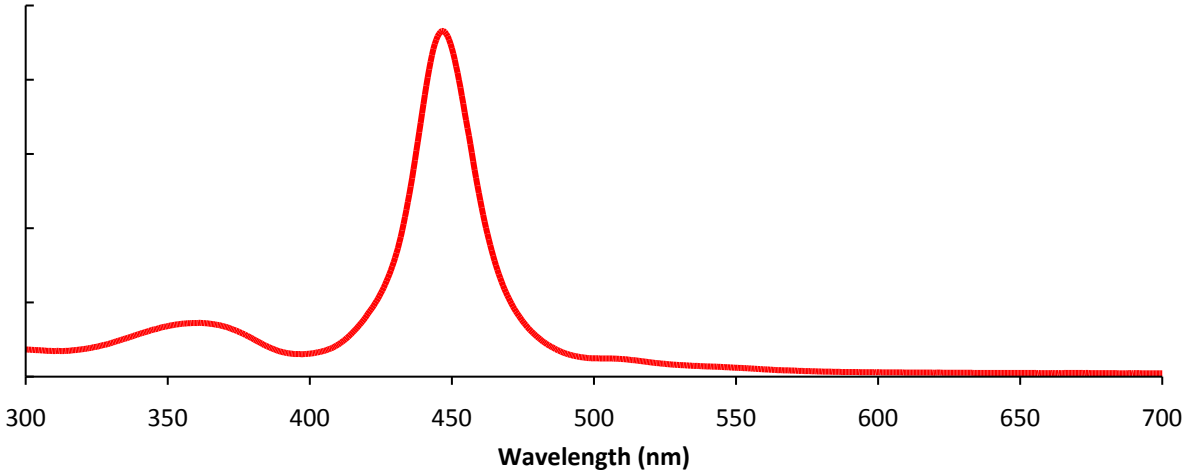


Figure S54: UV-vis absorbance spectrum of **6d** in CH_2Cl_2

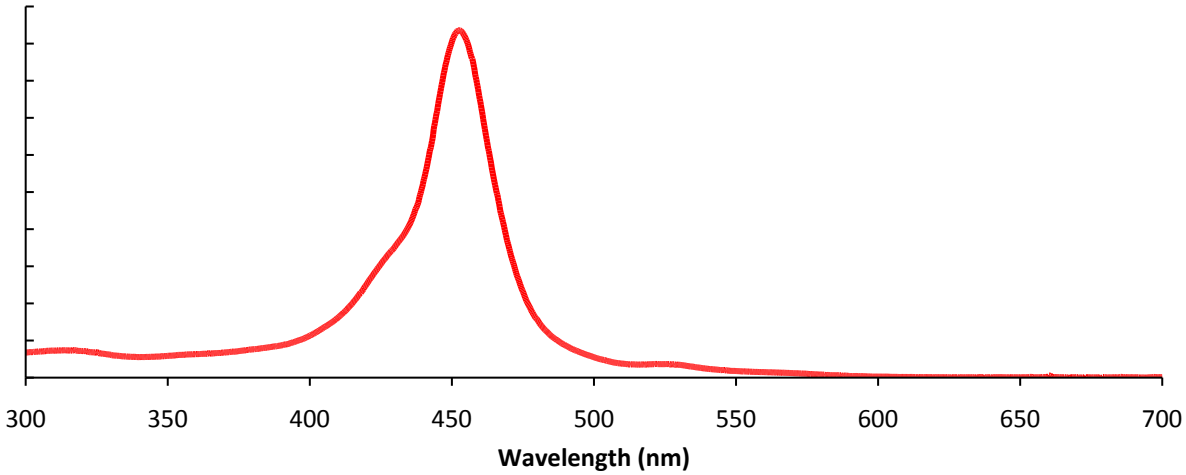
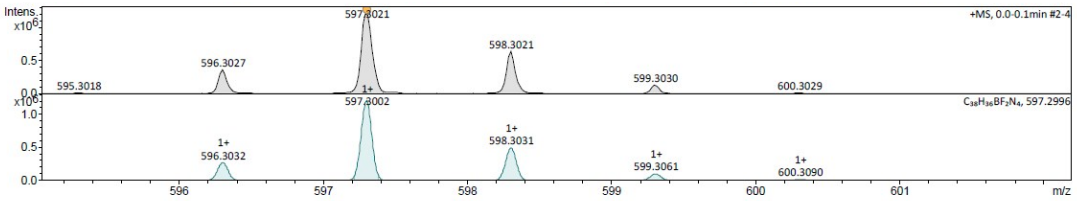
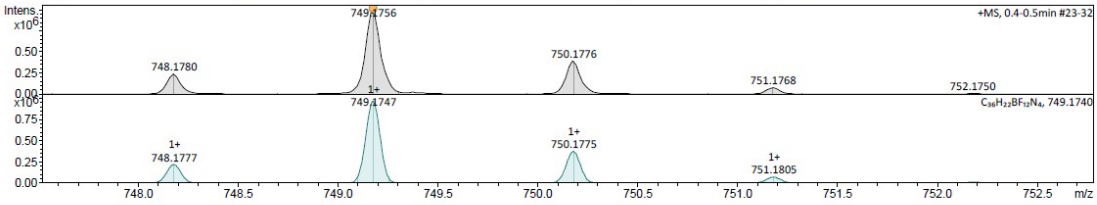


Figure S55: HRMS of BF_2[H(DMPTCx)] (**2a**)



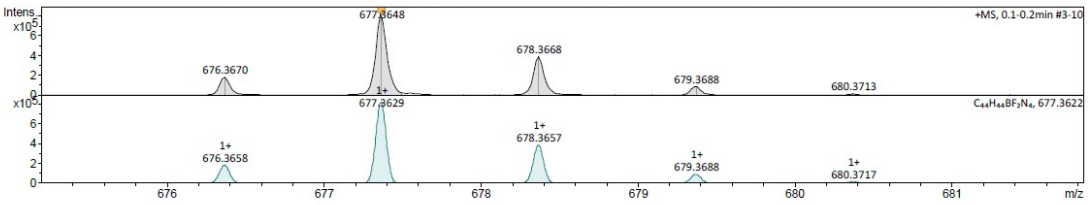
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
597.3021	1	C38H36BF2N4	597.3002	-3.2	64.5	1	100.00	22.5	even	ok
	1	C38H36BF2N4	597.3002	-3.2	64.5	1	100.00	22.5	even	ok

Figure S56: HRMS of BF_2[H(DMPFPCx)] (**2b**)



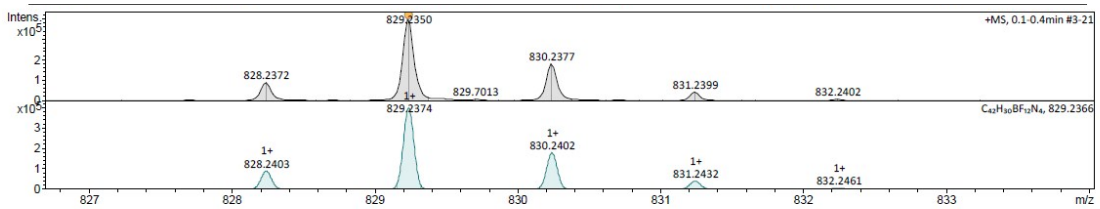
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
749.1756	1	C36H22BF12N4	749.1747	1.3	14.4	1	100.00	22.5	even	ok
	1	C36H22BF12N4	749.1747	1.3	14.4	1	100.00	22.5	even	ok
	1	C36H22BF12N4	749.1747	1.3	14.4	1	100.00	22.5	even	ok
	1	C36H25BF12NNaO	749.1736	2.7	17.7	1	100.00	19.0	odd	ok

Figure S57: HRMS of BF_2[H(CHPTCx)] (**2c**)



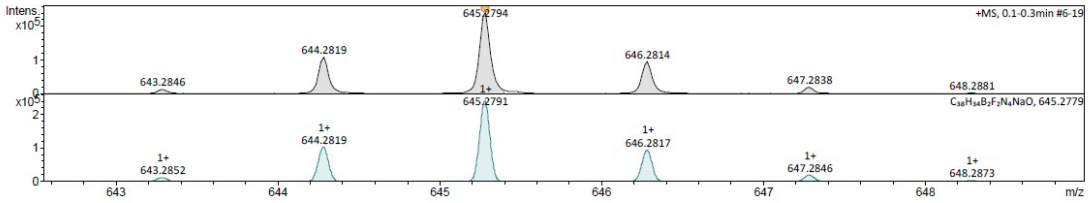
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
677.3648	1	C44H44BF2N4	677.3629	2.8	3.7	1	100.00	24.5	even	ok
	1	C44H44BF2N4	677.3629	2.8	3.7	1	100.00	24.5	even	ok
	1	C44H47BF2NNaO	677.3618	-4.3	7.0	1	100.00	21.0	odd	ok

Figure S58: HRMS of BF_2[H(CHPFPCx)] (**2d**)



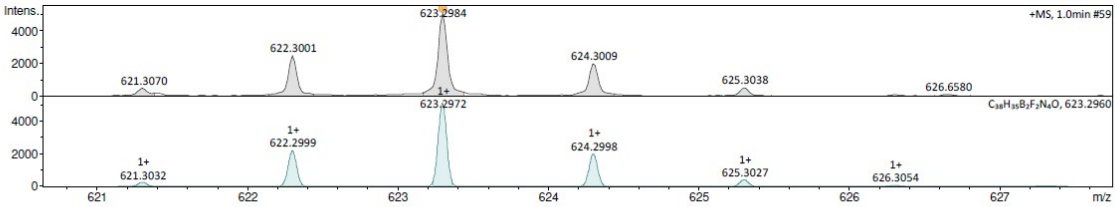
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
829.2350	1	C42H30BF12N4	829.2374	2.9	3.7	1	100.00	24.5	even	ok
	1	C42H30BF12N4	829.2374	2.9	3.7	1	100.00	24.5	even	ok
	1	C42H30BF12N4	829.2374	2.9	3.7	1	100.00	24.5	even	ok
	1	C42H33BF12NNaO	829.2363	1.6	7.7	1	100.00	21.0	odd	ok

Figure S59: HRMS of B_2OF_2(DMPTCx) (**5a**)



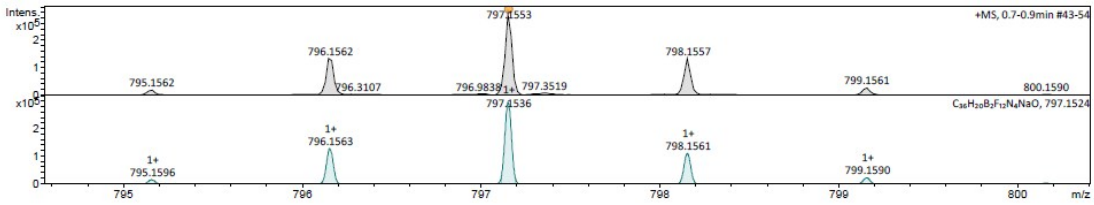
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
645.2794	1	C38H31B2F2N7	645.2802	-0.6	9.1	1	84.84	27.0	odd	ok
	2	C37H35B2F2N3O4	645.2789	-2.7	9.2	2	100.00	22.0	odd	ok
	1	C38H31B2F2N7	645.2802	-0.6	9.1	1	84.84	27.0	odd	ok
	2	C37H35B2F2N3O4	645.2789	-2.7	9.2	2	100.00	22.0	odd	ok
	1	C38H34B2F2N4NaO	645.2792	-2.3	8.6	1	100.00	23.5	even	ok

Figure S60: HRMS of B_2OF_2(DMPTCx) (**6a**)



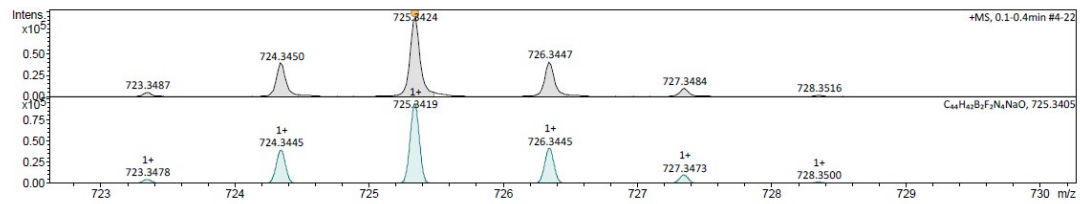
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
623.2984	1	C38H35B2F2N4O	623.2972	-3.9	31.0	1	100.00	23.5	even	ok
	1	C38H35B2F2N4O	623.2972	-3.9	31.0	1	100.00	23.5	even	ok

Figure S61: HRMS of B_2OF_2(DMPFPCx) (**6b**)



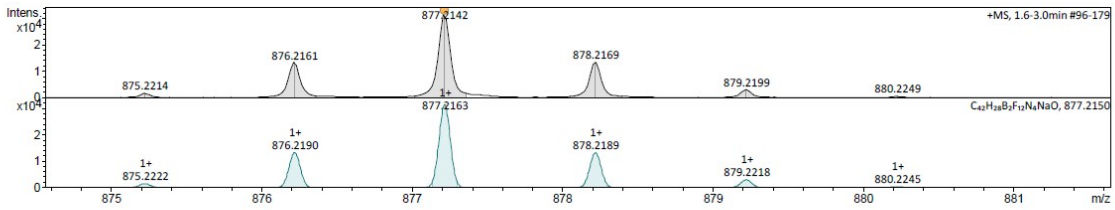
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
797.1553	1	C36H17B2F12N7	797.1546	-2.3	30.5	1	100.00	27.0	odd	ok
	1	C36H17B2F12N7	797.1546	-2.3	30.5	1	100.00	27.0	odd	ok
	1	C36H20B2F12N4NaO	797.1536	-3.7	33.4	1	100.00	23.5	even	ok

Figure S62: HRMS of B_2OF_2(CHPTCx) (**6c**)



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
725.3424	1	C44H39B2F2N7	725.3430	-1.2	6.0	1	100.00	29.0	odd	ok
	1	C44H39B2F2N7	725.3430	-1.2	6.0	1	100.00	29.0	odd	ok
	1	C44H39B2F2N7	725.3430	-1.2	6.0	1	100.00	29.0	odd	ok
	1	C44H42B2F2N4NaO	725.3419	-2.7	3.1	1	100.00	25.5	even	ok

Figure S63: HRMS of B_2OF_2(CHPFPCx) (**6d**)



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
877.2142	1	C42H25B2F12N7	877.2174	2.1	3.6	1	100.00	29.0	odd	ok
	1	C42H25B2F12N7	877.2174	2.1	3.6	1	100.00	29.0	odd	ok
	1	C42H28B2F12N4NaO	877.2163	0.9	1.7	1	100.00	25.5	even	ok

Table S1: Details of collected X-ray data for compounds **2a** and **4a**.

	2a	4a
Empirical formula	C38 H35 B F2 N4	C39.50 H37.50 B2 Cl4.50 F6 N4
Formula weight	596.51	863.38
Temperature	99(2) K	99(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	Pccn
Unit cell dimensions	a = 11.9721(11) Å α = 90° b = 14.8594(13) Å β = 90° c = 17.2769(17) Å γ = 90°	a = 21.5460(9) Å α = 90° b = 31.9600(12) Å β = 90° c = 11.6400(4) Å γ = 90°
Volume	3073.5(5) $Å^3$	8015.4(5) $Å^3$
Z, Calculated density	4, 1.289 Mg/m^3	8, 1.431 Mg/m^3
Absorption coefficient	0.084 mm^{-1}	0.392 mm^{-1}
F(000)	1256	3544
Crystal size	0.320 x 0.100 x 0.100 mm	0.44 x 0.05 x 0.04 mm
Theta range for data collection	1.808 to 27.959°	1.274 to 27.950°
Limiting indices	-15<=h<=15, -19<=k<=19, -21<=l<=22	-28<=h<=28, -42<=k<=42, -15<=l<=15
Reflections collected / unique	36247 / 7300 [R(int) = 0.1107]	109808 / 9554 [R(int) = 0.1654]
Completeness to theta max	99.6%	100.0%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	7300 / 0 / 426	9554 / 53 / 544
Goodness-of-fit on F2	1.004	0.999
Final R indices [I>2σ(I)]	R1 = 0.0628, wR2 = 0.1280	R1 = 0.0697, wR2 = 0.1569
R indices (all data)	R1 = 0.1619, wR2 = 0.1582	R1 = 0.1827, wR2 = 0.2183
Absolute structure parameter	0.9(7)	n/a
Extinction coefficient	0.021(2)	n/a
Largest diff. peak and hole	0.236 and -0.210 e $Å^{-3}$	1.005 and -0.952
CCDC number	1587635	1587636

Table S2: Details of collected X-ray data for compounds **5a** and **6b**.

	5a	6b
Empirical formula	C38 H34 B2 F2 N4 O	C36 H20 B2 F12 N4 O
Formula weight	622.31	774.18
Temperature	99(2) K	99(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Triclinic
Space group	$Cmc2_1$	P-1
Unit cell dimensions	a = 23.237(2) Å α = 90° b = 10.5234(10) Å β = 90° c = 12.0981(12) Å γ = 90°	a = 16.1693(10) Å α = 83.225(4)° b = 17.8717(11) Å β = 79.773(4)° c = 18.1564(11) Å γ = 67.472(4)°
Volume	2958.4(5) $Å^3$	4762.1(5) $Å^3$
Z, Calculated density	4, 1.397 Mg/m^3	6, 1.620 Mg/m^3
Absorption coefficient	0.093 mm^{-1}	0.147 mm^{-1}
F(000)	1304	2340
Crystal size	0.38 x 0.22 x 0.05 mm	0.20 x 0.12 x 0.10 mm
Theta range for data collection	2.124 to 27.734°	1.141 to 27.928°
Limiting indices	-30<=h<=30, -13<=k<=11, -13<=l<=15	-21<=h<=21, -23<=k<=23, -23<=l<=23
Reflections collected / unique	9674 / 3154 [R(int) = 0.0821]	151819 / 22188 [R(int) = 0.1883]
Completeness to theta max	99.9%	99.3%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3154 / 1 / 223	22188 / 0 / 1475
Goodness-of-fit on F2	0.984	0.943
Final R indices [I>2σ(I)]	R1 = 0.0579, wR2 = 0.1212	R1 = 0.0767, wR2 = 0.1676
R indices (all data)	R1 = 0.1062, wR2 = 0.1395	R1 = 0.3002, wR2 = 0.2546
Absolute structure parameter	n/a	n/a
Extinction coefficient	n/a	0.0022(2)
Largest diff. peak and hole	0.303 and -0.254e $Å^{-3}$	0.530 and -0.329
CCDC number	1587634	1587637

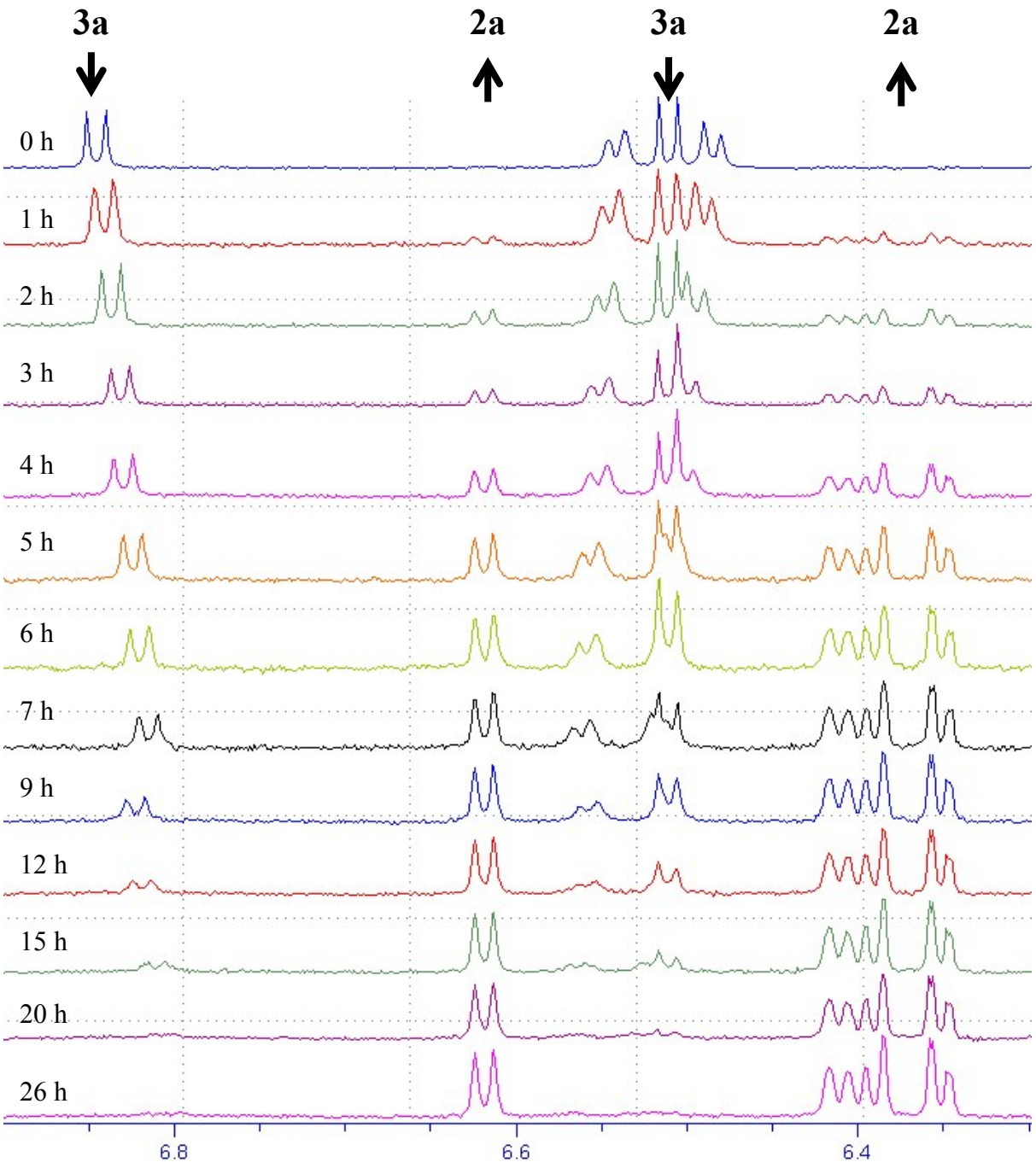


Figure S64: Conversion of **3a** into **2a** as observed via ^{1}H NMR spectroscopy (40°C).

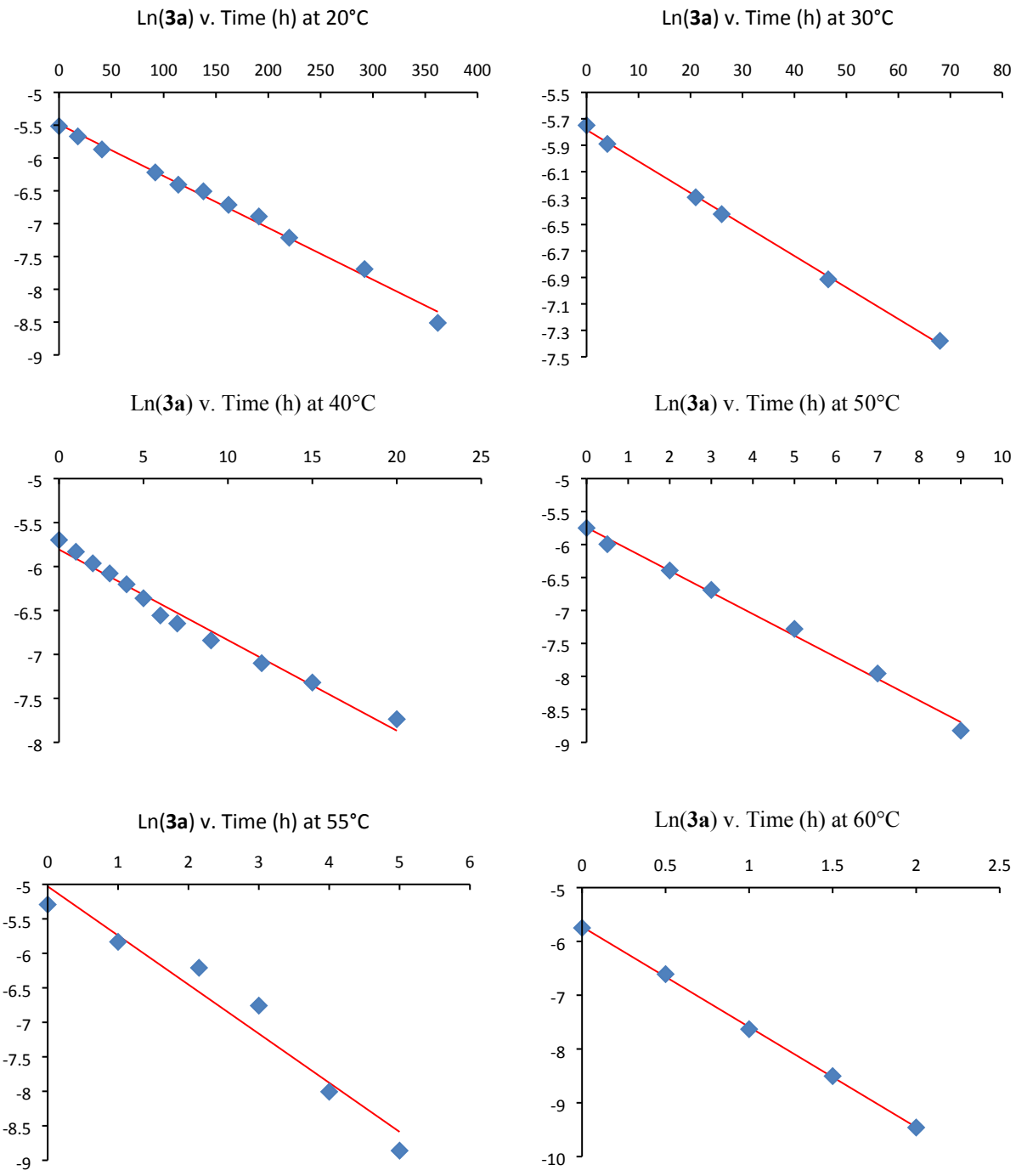


Figure S65: Plots of ln(**3a**) versus time (hours) for conversion of **3a** into **2a** at 20°C, 30°C, 40°C, 50°C, 55°C and 60°C.

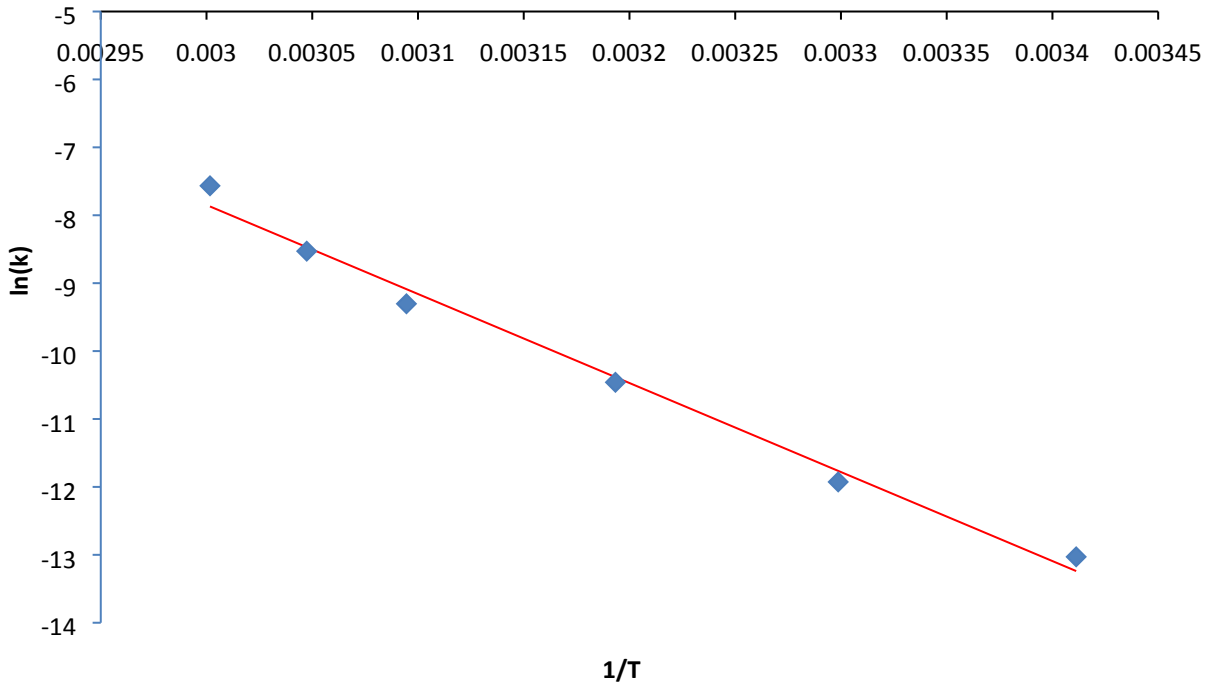


Figure S66: Arrhenius plot of the isomerism of **3a** into **2a**.

DFT Optimised Cartesian Coordinates for TS Calculations

3a

C	-2.54734600	-1.45918600	0.10887900
C	-3.13579800	-0.20622700	-0.01350900
C	-4.47520800	-0.09468200	-0.64729500
C	-5.52319100	-0.97532000	-0.32685900
H	-5.35823800	-1.74347600	0.42095700
C	-6.77319700	-0.84792600	-0.92853000
H	-7.57125900	-1.53129700	-0.64889800
C	-7.02413700	0.15267100	-1.87590800
C	-8.36838000	0.26722800	-2.55317000
H	-9.16270300	-0.17518300	-1.94507900
H	-8.36905900	-0.25269600	-3.51955700
H	-8.63102800	1.31144000	-2.74890200
C	-5.98178500	1.03740100	-2.18810800
H	-6.15104900	1.82663900	-2.91653400
C	-4.73597800	0.92658000	-1.57976200
H	-3.94329600	1.62242700	-1.83398000
C	-2.60895500	1.03071800	0.51137600
C	-3.40531200	1.97163300	1.18516800
H	-4.47152700	1.87917300	1.33387500
C	-2.56181600	2.95678700	1.70488500
H	-2.85073900	3.80914600	2.30302900
C	-1.26861800	2.63397100	1.29310600
C	-0.02169900	3.47693100	1.45155300
C	-0.09229300	4.68513400	0.46672800
H	-0.14508200	4.32564200	-0.56200800
H	0.78986700	5.32407700	0.57655700
H	-0.98418300	5.28130200	0.67998500
C	0.05755800	4.01164200	2.90378500
H	-0.82700100	4.61079800	3.13393000
H	0.93311700	4.65324200	3.03703700
H	0.11350600	3.19172600	3.62464500
C	1.23414600	2.69377000	1.14705200
C	2.56246700	3.11325500	1.36739800
H	2.86993000	4.00909700	1.88650700
C	3.38100200	2.15968200	0.79371600
H	4.46004400	2.12763300	0.81715300
C	2.55162400	1.12261900	0.27771600
C	3.09216700	-0.12491100	-0.12176300
C	4.46855900	-0.05524100	-0.69044600
C	4.72427600	0.79117600	-1.78318800
H	3.90898000	1.36952500	-2.20513200
C	5.99935600	0.87487800	-2.33452400
H	6.16840000	1.52555500	-3.18854800
C	7.06881500	0.13933200	-1.80531000
C	8.44514800	0.21928700	-2.41925100
H	8.54843400	-0.49445500	-3.24609500
H	9.22451000	-0.01429800	-1.68836100
H	8.64522200	1.21526800	-2.82527200
C	6.81652600	-0.68473200	-0.70006200
H	7.63374000	-1.24621900	-0.25470800
C	5.53972500	-0.78924600	-0.15395300
H	5.37358500	-1.41852300	0.71415100
C	2.53660900	-1.41005400	0.05041400
C	3.09301900	-2.65937400	-0.33688700
H	3.99195000	-2.78154800	-0.92084800

C	2.28250900	-3.67000000	0.16419000
H	2.42733000	-4.73365300	0.05182800
C	1.21408100	-3.05235100	0.84471800
C	-0.01277400	-3.64196800	1.51579600
C	-0.02683400	-3.25339600	3.01619800
H	0.88161600	-3.60542700	3.51620500
H	-0.89253300	-3.71140200	3.50435500
H	-0.10793900	-2.17218800	3.13706000
C	-0.00437400	-5.17358100	1.38422500
H	0.04001700	-5.49271500	0.33923200
H	-0.91272400	-5.59049000	1.82745900
H	0.85445700	-5.60226600	1.90986800
C	-1.21364200	-3.01984800	0.80588700
C	-2.11150000	-3.66213100	-0.12733700
H	-2.10911400	-4.70258400	-0.42191600
C	-2.95791700	-2.67839200	-0.56048000
H	-3.74948700	-2.76688200	-1.29038600
B	-0.08237000	1.17200800	-0.37342200
N	-1.45952600	-1.72923900	0.94068800
N	-1.28074300	1.46170900	0.58609400
N	1.21615400	1.49858500	0.50825900
N	1.39308300	-1.71596100	0.78087100
H	0.61336100	-1.08579300	0.96955600
F	-0.03379100	-0.11520300	-0.84823800
F	-0.10099000	2.08586400	-1.42844400

3ai

C	-2.60857100	-1.38567500	0.28278000
C	-3.12027900	-0.11558500	0.01629300
C	-4.36019600	-0.06240400	-0.81392100
C	-5.48092300	-0.83848600	-0.47547600
H	-5.44141200	-1.45976300	0.41315600
C	-6.63683800	-0.80623400	-1.25350100
H	-7.49292100	-1.40973800	-0.96188700
C	-6.71563500	-0.00855100	-2.40130900
C	-7.97580900	0.04450900	-3.23137900
H	-8.57835900	-0.85931500	-3.10302800
H	-7.74890500	0.15328500	-4.29654500
H	-8.60323400	0.89848300	-2.94618800
C	-5.59419800	0.76124900	-2.74315100
H	-5.62328700	1.37930700	-3.63739600
C	-4.44303100	0.74560800	-1.96170900
H	-3.58646000	1.34689100	-2.24775100
C	-2.60969200	1.18092800	0.41877900
C	-3.39956300	2.34454900	0.50170300
H	-4.46389500	2.37854200	0.32441100
C	-2.58104300	3.41599700	0.87065200
H	-2.88660600	4.44079600	1.02252000
C	-1.28654200	2.90828700	0.99349800
C	-0.01799000	3.63108000	1.41260300
C	-0.06095700	5.10000000	0.94414600
H	-0.11776500	5.16903500	-0.14539400
H	0.82698600	5.64136300	1.28233400
H	-0.93089200	5.60872600	1.36673500
C	0.07529400	.59222700	2.97276800
H	-0.80180100	4.08182700	3.40584300
H	0.97523100	4.11235200	3.31660600
H	0.10783300	2.55913000	3.32559400
C	1.22718400	2.94918600	0.87847000

C	2.51872600	3.48817700	0.67672300
H	2.80867300	4.51922900	0.81385600
C	3.32950600	2.44107500	0.27908700
H	4.38595400	2.48798600	0.06335200
C	2.54710600	1.24643900	0.25323400
C	3.07623400	-0.04063600	-0.06039600
C	4.34998300	-0.03157000	-0.83605100
C	4.47420400	0.72071000	-2.01744700
H	3.62541300	1.29697000	-2.36985700
C	5.66045900	0.71280100	-2.74494700
H	5.72653400	1.29219300	-3.66223900
C	6.76972000	-0.03080900	-2.31802100
C	8.04666100	-0.05223500	-3.12216500
H	8.01964300	-0.84373000	-3.88152900
H	8.91691200	-0.24104000	-2.48710300
H	8.20573400	0.89439900	-3.64677900
C	6.64755000	-0.77269700	-1.13537500
H	7.49727800	-1.34593500	-0.77375800
C	5.45837000	-0.78437900	-0.41132100
H	5.38836000	-1.35945900	0.50611100
C	2.57998600	-1.33683200	0.23368000
C	2.84836400	-2.53997600	-0.48422800
H	3.55610400	-2.63051800	-1.29405000
C	1.98899300	-3.52281100	-0.01642700
H	1.91066500	-4.53725600	-0.37697600
C	1.19924800	-2.94723400	1.00894800
C	-0.02202400	-3.49012200	1.74647700
C	-0.03270100	-3.01755300	3.21756300
H	0.88839800	-3.31664000	3.72911200
H	-0.87986000	-3.47521800	3.73672500
H	-0.15806700	-1.93633100	3.28268100
C	-0.02269100	-5.02814200	1.69934000
H	-0.00262200	-5.41055200	0.67534800
H	-0.92566700	-5.41342700	2.18104500
H	0.84661200	-5.43080400	2.22872100
C	-1.23564000	-2.90509500	1.00144700
C	-1.99844600	-3.53474800	-0.06461600
H	-1.88624300	-4.54278300	-0.44108400
C	-2.88408700	-2.58857100	-0.49607400
H	-3.59362200	-2.67565000	-1.30632700
B	-0.02440700	0.73064000	0.79000400
N	-1.61323700	-1.66254800	1.21217200
N	-1.29874400	1.56920900	0.73715500
N	1.24420200	1.62910800	0.62493100
N	1.61324100	-1.67695000	1.16871600
H	1.12271100	-1.00314500	1.75977100
F	0.12538700	0.22607300	2.12737400
F	0.00261200	-0.19151800	-0.23080800

TS

C	2.79985400	-1.29147700	-0.21439600
C	3.31177300	-0.04191100	0.12609500
C	4.61326100	0.01481400	0.84755400
C	5.74925400	-0.62741600	0.32861200
H	5.67544800	-1.14847100	-0.62036400
C	6.96463200	-0.58654500	1.00800000
H	7.83086600	-1.08499500	0.57996600
C	7.09128400	0.08688700	2.22975100
C	8.41702000	0.15148800	2.94907900

H	8.28128100	0.24897800	4.03013800
H	9.00605000	1.01541800	2.61608800
H	9.01924100	-0.74238200	2.76104000
C	5.95431700	0.72015100	2.74969500
H	6.02019700	1.23795100	3.70335100
C	4.73883400	0.69384200	2.07070900
H	3.86950000	1.18371900	2.49702200
C	2.67931300	1.20966000	-0.16811600
C	3.28061500	2.47737300	-0.09419700
H	4.29474900	2.66478100	0.22396900
C	2.35459000	3.41950500	-0.53816700
H	2.51094100	.48472800	-0.60450400
C	1.18166300	2.73852800	-0.88731400
C	-0.07153000	3.36767000	-1.49572100
C	-0.05532700	4.88997900	-1.23995500
H	-0.06365000	5.12199200	-0.17126600
H	-0.92862900	5.35686000	-1.70143000
H	0.82722600	5.35119700	-1.68960100
C	-0.04351700	3.14036300	-3.04102200
H	0.86215700	3.58303900	-3.46784300
H	-0.91449700	3.61698600	-3.50259200
H	-0.06152100	2.07674300	-3.27771200
C	-1.36992300	2.77256200	-0.96276400
C	-2.63336400	3.44329600	-0.76590500
H	-2.84615900	4.49057100	-0.92639300
C	-3.51043200	2.48294700	-0.33583500
H	-4.56068000	2.60947300	-0.11671400
C	-2.78493100	1.23086000	-0.28830700
C	-3.32724300	-0.01123700	0.07672800
C	-4.61744600	-0.02846300	0.81529400
C	-4.84728600	0.82666900	1.90785000
H	-4.05982000	1.50207600	2.22419200
C	-6.05637000	0.79503500	2.59698500
H	-6.20403200	1.45959100	3.44457800
C	-7.08225600	-0.08395600	2.22425900
C	-8.38210800	-0.13154900	2.99005600
H	-9.20843300	-0.46503300	2.35550800
H	-8.64219700	0.84895700	3.40008800
H	-8.31722600	-0.82965300	3.83397800
C	-6.85228200	-0.93748900	1.13651200
H	-7.63461100	-1.62312700	0.82087500
C	-5.64120300	-0.92101700	0.45092700
H	-5.48644800	-1.58760800	-0.39102200
C	-2.73256400	-1.29995100	-0.14098600
C	-2.80421500	-2.44184800	0.68300200
H	-3.44898000	-2.54607100	1.54305300
C	-1.83724600	-3.35133900	0.24079700
H	-1.61017500	-4.30915000	0.68440000
C	-1.19050100	-2.78606400	-0.87019700
C	0.03875000	-3.27628700	-1.63935600
C	-0.00805100	-2.85805300	-3.12953600
H	-0.93327100	-3.21240500	-3.59640500
H	0.83599600	-3.31166100	-3.65784700
H	0.06847600	-1.77973800	-3.25319300
C	0.06031600	-4.81921800	-1.58720600
H	0.09640300	-5.19941000	-0.56348300
H	0.93466200	-5.20369600	-2.12007000
H	-0.83664500	-5.22130800	-2.06625200
C	1.31512300	-2.71117400	-0.97432200
C	2.30831700	-3.48490500	-0.25973600

H	2.31134300	-4.55699100	-0.12461300
C	3.23990500	-2.59755900	0.21208300
H	4.11025700	-2.81415600	0.81426100
B	0.34619800	0.30347400	-0.80384300
N	1.63533300	-1.42088000	-0.95800000
N	1.37823200	1.39617900	-0.66607400
N	-1.46504000	1.48509400	-0.69479400
N	-1.79214900	-1.59229400	-1.10980800
H	-1.44871200	-0.91429500	-1.77646200
F	-0.04126200	0.06998400	-2.11518800
F	-0.05661400	-0.28576200	0.34291200

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C	-2.90514300	-1.25049300	0.01965700
C	-3.51508800	-0.00313200	-0.22845500
C	-4.86377900	0.03702600	-0.84608300
C	-5.93810700	-0.67027000	-0.28106700
H	-5.78162600	-1.23822700	0.63024400
C	-7.20174200	-0.62687600	-0.86378900
H	-8.01929700	-1.17419400	-0.40153100
C	-7.43947200	0.11125900	-2.03120300
C	-8.81758100	0.17466800	-2.64363600
H	-9.41301900	0.97751700	-2.19127800
H	-9.36644600	-0.75961200	-2.49272400
H	-8.76938300	0.37147300	-3.71835500
C	-6.36312600	0.80670400	-2.59722100
H	-6.51483600	1.37463500	-3.51144100
C	-5.09815200	0.77901200	-2.01518300
H	-4.27555200	1.31145600	-2.48126000
C	-2.87404600	1.20625400	0.10545600
C	-3.33793100	2.54187500	0.01969400
H	-4.30734400	2.84904400	-0.34311500
C	-2.32929400	3.35127600	0.50889600
H	-2.36289500	4.42593100	0.58785600
C	-1.24216900	2.52634900	0.91459000
C	0.03439100	3.04898800	1.62199000
C	-0.00265000	4.59596500	1.59385900
H	-0.03983800	4.99401800	0.57592100
H	0.89527200	4.98651200	2.07839600
H	-0.86627700	4.97599100	2.14576500
C	-0.00893500	2.63169500	3.12046500
H	-0.94626800	2.96705300	3.57758200
H	0.82165000	3.11125800	3.64797700
H	0.07942700	1.55595200	3.23294000
C	1.37264100	2.59040900	1.00407000
C	2.32454700	3.43182900	0.28673000
H	2.22482500	4.48516300	0.06493300
C	3.37866700	2.62714500	-0.04575400
H	4.27547700	2.91032400	-0.57734000
C	3.02810700	1.29510900	0.41583700
C	3.62462300	0.08388900	0.07533000
C	4.89778000	0.07885800	-0.70267300
C	5.01134500	0.71247600	-1.94927300
H	4.14336100	1.20487100	-2.37484400
C	6.21321500	0.68832100	-2.65500800
H	6.27044700	1.17715300	-3.62452500
C	7.34313100	0.03756400	-2.14458900
C	8.65368400	0.04399700	-2.89462100
H	8.49843100	0.15890900	-3.97140700

H	9.21481100	-0.88093100	-2.72962100
H	9.29341900	0.87344200	-2.56763200
C	7.22307200	-0.60661300	-0.90593000
H	8.08147200	-1.12762400	-0.48877300
C	6.02259200	-0.59529500	-0.20009500
H	5.95178000	-1.10512300	0.75569500
C	3.03121900	-1.21169200	0.29428900
C	3.25258600	-2.38932700	-0.44470900
H	4.05997800	-2.54705600	-1.14386000
C	2.20081000	-3.27055000	-0.16245300
H	2.06784000	-4.25523000	-0.58386600
C	1.34517000	-2.64398800	0.75700300
C	0.03203100	-3.18384100	1.34813300
C	-0.02137800	-2.95989300	2.88694300
H	0.85178700	-3.42968400	3.35037300
H	-0.92131000	-3.43162500	3.29458400
H	-0.03844400	-1.90620000	3.15023500
C	0.03945000	-4.71919600	1.13918100
H	0.00728900	-4.99574900	0.08238900
H	-0.81708200	-5.17744400	1.63990000
H	0.94797600	-5.14028200	1.57509800
C	-1.26579800	-2.62701700	0.69820200
C	-2.31912300	-3.41847500	0.16364400
H	-2.32748300	-4.49493700	0.09994800
C	-3.32893000	-2.57132200	-0.26418500
H	-4.26119700	-2.84874600	-0.73288200
B	-0.75160300	-0.06177000	0.74954300
N	-1.64799200	-1.32426800	0.60821500
N	-1.59716700	1.23407300	0.66941200
N	1.81999400	1.35941800	1.10974300
N	1.90414400	-1.43795800	1.05664700
H	1.45606500	-0.67030200	1.55225600
F	-0.19253000	-0.13836200	2.03729500
F	0.12057900	-0.07873200	-0.32082000

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C	2.80364300	-1.18772500	-0.10481600
C	3.35592900	0.06080000	0.23344400
C	4.56787900	0.09686700	1.09153900
C	5.74411200	-0.54649600	0.67422300
H	5.76061200	-1.05358000	-0.28516700
C	6.88768300	-0.52092100	1.46895800
H	7.78920600	-1.01762300	1.11959800
C	6.89659400	0.13148700	2.70869100
C	8.14519600	0.17718900	3.55589900
H	8.78105200	-0.69501400	3.37893800
H	7.90438600	0.21243700	4.62243200
H	8.74368500	1.06810500	3.32819800
C	5.71505600	0.75661300	3.12904000
H	5.68731700	1.25212100	4.09616800
C	4.57013100	0.74658900	2.33613600
H	3.66067600	1.21788100	2.69409100
C	2.72856200	1.25007000	-0.16048800
C	2.99762600	2.57938400	0.23730400
H	3.82043700	2.89705600	0.85947900
C	1.99258800	3.36107500	-0.29224600
H	1.87563700	4.42329800	-0.15391300
C	1.12436100	2.52678700	-1.04898200
C	-0.12969000	3.05563600	1.75845700

C	-0.10083300	4.60393400	-1.72615100
H	-0.16818500	5.00329500	-0.71084500
H	-0.94714600	4.99541100	-2.29497600
H	0.81227500	4.98231300	-2.19329200
C	-0.18255200	2.65903900	-3.26074200
H	0.72614900	2.99701800	-3.77027200
H	-1.03995500	3.15392400	-3.72737300
H	-0.28576600	1.58833400	-3.39623900
C	-1.39905700	2.57094700	-1.03976000
C	-2.55555100	3.38655800	-0.70104500
H	-2.68099600	4.44445100	-0.88339000
C	-3.45890500	2.54629400	-0.11034100
H	-4.44836900	2.79168900	0.24844100
C	-2.84501700	1.23473900	-0.10414500
C	-3.40056800	0.02424200	0.30113600
C	-4.70974000	0.02099300	1.00698200
C	-4.91307900	0.81760400	2.14551000
H	-4.09480200	1.42489000	2.51822700
C	-6.14010900	0.82109300	2.80529900
H	-6.26791400	1.44162000	3.68881500
C	-7.20943200	0.03733900	2.35411700
C	-8.52926000	0.02111200	3.08718500
H	-8.56598000	-0.79646400	3.81815500
H	-9.36781700	-0.12290800	2.39913400
H	-8.69507200	0.95368700	3.63430100
C	-7.00715700	-0.75198000	1.21375200
H	-7.82455700	-1.35914500	0.83251100
C	-5.78073900	-0.76855100	0.55489600
H	-5.65229200	-1.37906400	-0.33290500
C	-2.77813100	-1.24706800	0.06347600
C	-3.12254200	-2.52979200	0.52758900
H	-3.95699600	-2.76042700	1.17252300
C	-2.17653400	-3.43154700	0.02358300
H	-2.15792300	-4.49674800	0.19531400
C	-1.25581200	-2.70270900	-0.74712600
C	-0.02130800	-3.20111200	-1.50275800
C	-0.13522700	-2.94912800	-3.03116600
H	-0.99503700	-3.50448200	-3.41796600
H	0.76501700	-3.32058800	-3.53143500
H	-0.25897300	-1.90123400	-3.27973800
C	0.04051500	-4.73979300	-1.33980200
H	0.05766600	-5.05309100	-0.29391300
H	0.92845800	-5.13768000	-1.83748300
H	-0.83883800	-5.18750600	-1.80877900
C	1.24595900	-2.59113900	-0.87390900
C	2.12462600	-3.32101100	-0.03442900
H	2.03243300	-4.36586700	0.21263800
C	3.09329200	-2.45581700	0.43959500
H	3.88995400	-2.67332700	1.13523200
B	1.38369100	-0.05278000	-1.86171200
N	1.67343100	-1.29274200	-0.92150600
N	1.58534400	1.24539500	-0.97448900
N	-1.57606900	1.31634500	-0.68262900
N	-1.64118300	-1.40214000	-0.70747900
H	-1.16960800	-0.59111300	-1.11361700
F	2.32761400	-0.03518700	-2.87273600
F	0.10317500	-0.12985700	-2.38765900

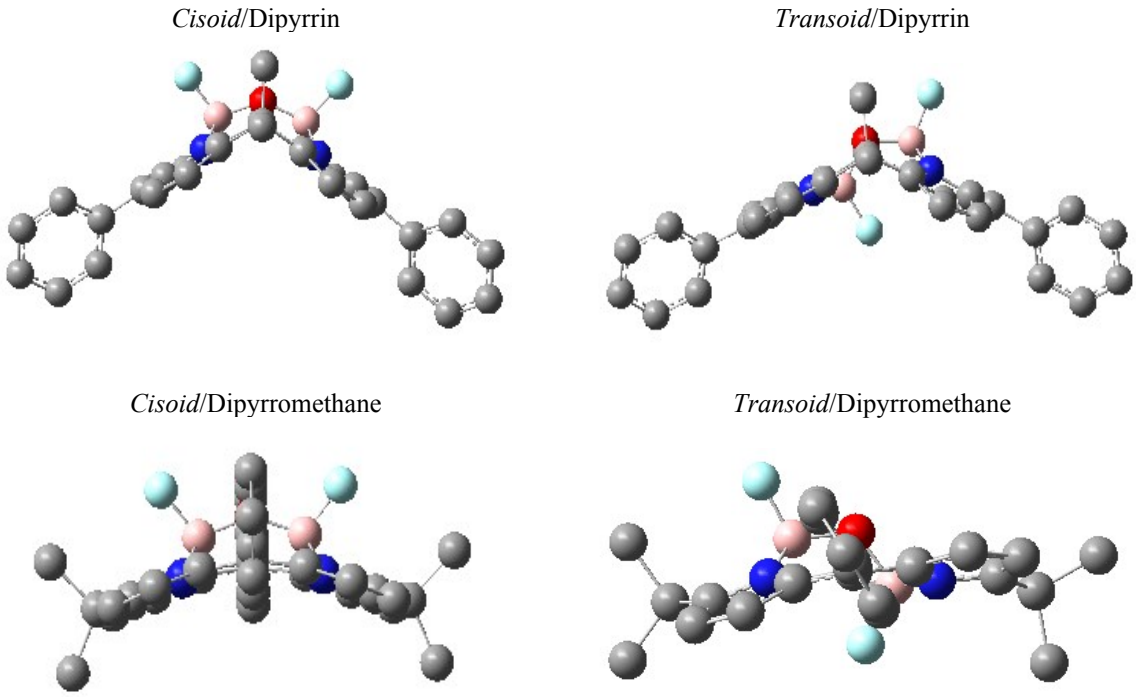

Figure S67: DFT optimised structures of B_2OF_2(DMPCx).

Table S3: Relative Energies of the Optimised Structures of B_2OF_2 (Calix).

Ligand	Isomer	Bonding Site	Relative Energy (kcal mol^{-1})
DMPCx	*Cisoid*	Dipyrrin	0.00
DMPCx	*Transoid*	Dipyrrin	3.72
DMPCx	*Transoid*	Dipyrromethane	11.12
DMPCx	*Cisoid*	Dipyrromethane	21.88
DMPFPCx	*Cisoid*	Dipyrrin	0.00
DMPFPCx	*Transoid*	Dipyrrin	3.83
DMPFPCx	*Transoid*	Dipyrromethane	9.91
DMPFPCx	*Cisoid*	Dipyrromethane	19.87
CHPCx	*Cisoid*	Dipyrrin	0.00
CHPCx	*Transoid*	Dipyrrin	4.05
CHPCx	*Transoid*	Dipyrromethane	14.84
CHPCx	*Cisoid*	Dipyrromethane	27.57

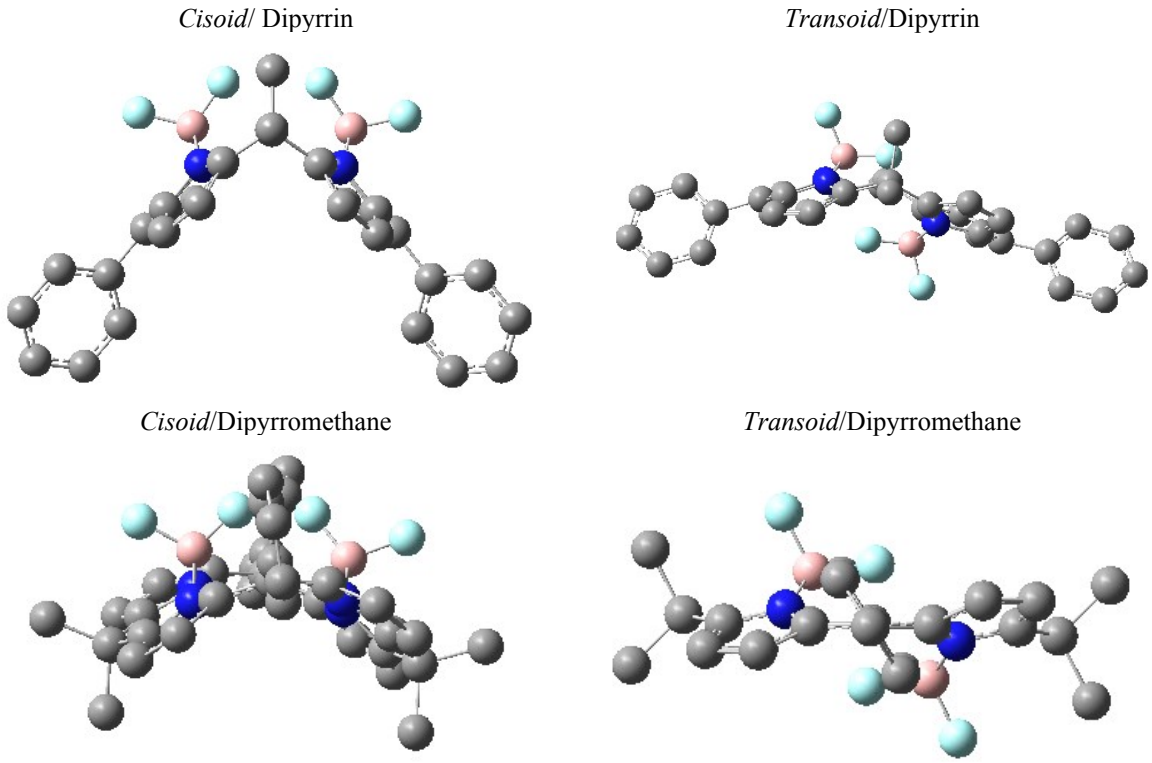

Figure S68: DFT optimised structures of $(BF_2)_2$(DMPCx).

Table S4: Relative Energies of the Isomers of $(BF_2)_2$(Calix).

Ligand	Isomer	Bonding Site	Relative Energy (kcal mol^{-1})
DMPCx	*Transoid*	Dipyrromethane	0.00
DMPCx	*Transoid*	Dipyrrin	7.73
DMPCx	*Cisoid*	Dipyrrin	11.91
DMPCx	*Cisoid*	Dipyrromethane	56.22
DMPFPCx	*Transoid*	Dipyrromethane	0.00
DMPFPCx	*Transoid*	Dipyrrin	7.65
DMPFPCx	*Cisoid*	Dipyrrin	12.41
DMPFPCx	*Cisoid*	Dipyrromethane	54.09
CHPCx	*Transoid*	Dipyrromethane	0.00
CHPCx	*Cisoid*	Dipyrrin	4.74
CHPCx	*Transoid*	Dipyrrin	5.57
CHPCx	*Cisoid*	Dipyrromethane	55.52