Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Direct palladium-catalysed C–H arylation of BODIPY dyes at the 3- and 3,5-positions

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Contents

Experimental procedures and characterisation data

Chemicals where purchased from Acros Organics and Sigma Aldrich, and used as received. All reactions were carried out in flame dried glassware, but no special precautions were taken for the exclusion of moisture. Solvents were not dried prior to use, except *o*-xylene which was dried over molecular sieves. All reactions were carried out under a nitrogen atmosphere.

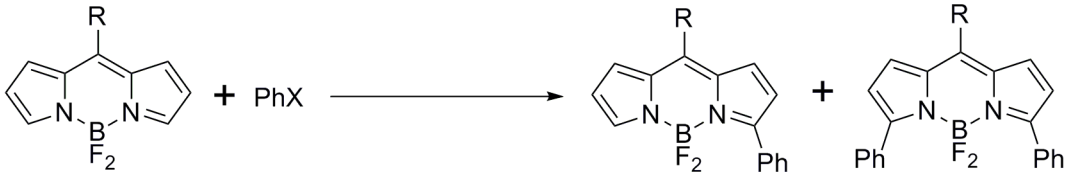
^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker Avance 300 instrument operating at a frequency of 300 MHz for ^{1}H and 75 MHz for ^{13}C. In the case of ambiguous assignments, spectra were run on a Bruker 400 or Bruker 600. ^{1}H NMR spectra in $CDCl_3$ were referenced to tetramethylsilane (0.00 ppm) as an internal standard. ^{13}C NMR spectra in $CDCl_3$ were referenced to the $CDCl_3$ (77.16 ppm) signal. Mass spectra were recorded on a Hewlett-Packard 5989A mass spectrometer (EI mode and CI mode). High-resolution mass data were obtained with a Kratos MS50TC instrument. Melting points were taken on a Reichert Thermovar and are uncorrected.

The electronic absorption spectra and absorbances were measured at 20 °C on a Perkin-Elmer Lambda 40 UV–vis spectrophotometer. Corrected steady-state excitation and emission spectra were recorded on a Spex Fluorolog instrument with temperature-controlled cell holder. Freshly prepared samples in 1 cm quartz cells were used to perform all UV–vis absorption and fluorescence measurements.

8-Arylated BODIPY dyes were prepared according to published literature procedures, through a water based dipyrromethane synthesis followed by oxidation and condensation.[1]

Optimisation of reaction protocol

Table S1 Optimisation of the reaction protocol for the direct C–H arylation of 8-(2,6-dichlorophenyl)-BODIPY



1 **2a** **3a**

Entry	Reaction condition[a,b]								Yield / %[c]		
	Catalyst	Ligand	Additive	Base	Solvent	PhX	Temp	Time	**1**	**2a**	**3a**
1	$Pd(OAc)_2$	PPh_3	/	K_2CO_3	toluene	PhBr-d5	110 °C	24 h	75	3	0
2	$Pd(OAc)_2$	PPh_3	/	K_2CO_3	toluene	PhBr-d5	110 °C	4 d	73	4	1
3	$Pd(OAc)_2$	PPh_3	PivOH	K_2CO_3	toluene	PhBr-d5	110 °C	24 h	59	15	3
4	$Pd(OAc)_2$	PPh_3	PivOH	K_2CO_3	toluene	PhBr-d5	110 °C	4 d	54	17	4
5	$Pd(OAc)_2$	$P(tBu)_3HBF_4$	PivOH	K_2CO_3	toluene	PhBr-d5	110 °C	24 h	94	0	0
6[d]	$Pd(OAc)_2$	PCy_3HBF_4	PivOH	K_2CO_3	toluene	PhBr-d5	110 °C	24 h	33	45	19
7	$Pd(OAc)_2$	DavePhos	PivOH	K_2CO_3	toluene	PhBr-d5	110 °C	24 h	68	0	0
8	$Pd_2(dba)_3$	PCy_3HBF_4	PivOH	K_2CO_3	toluene	PhBr-d5	110 °C	24 h	22	37	21
9	$Pd(TFA)_2$	PCy_3HBF_4	PivOH	K_2CO_3	toluene	PhBr-d5	110 °C	24 h	92	5	0
10	$Pd(OAc)_2$	PCy_3HBF_4	PivOH	Cs_2CO_3	toluene	PhBr-d5	110 °C	24 h	32	19	14
11	$Pd(OAc)_2$	PCy_3HBF_4	PivOH	Na_2CO_3	toluene	PhBr-d5	110 °C	24.5 h	92	5	1
12	$Pd(OAc)_2$	PCy_3HBF_4	PivOH	KOAc	toluene	PhBr-d5	110 °C	24 h	77	17	4

[1] V. Leen, M. Van der Auweraer, N. Boens and W. Dehaen, *Org. Lett.*, 2011, **13**, 1470.

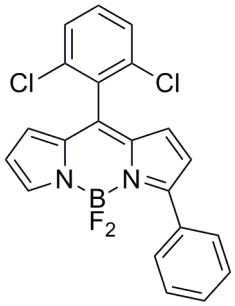
13	$Pd(OAc)_2$	PCy_3HBF_4	/	CsOPiv	toluene	PhBr-d5	110 °C	24 h	69	23	6
14	$Pd(OAc)_2$	PCy_3HBF_4	PivOH	K_2CO_3	*o*-xylene	PhBr-d5	110 °C	24 h	28	45	22
15	$Pd(OAc)_2$	PCy_3HBF_4	PivOH	K_2CO_3	*o*-xylene	PhBr-d5	144 °C	24 h	22	41	26
16	$Pd(OAc)_2$	PCy_3HBF_4	PivOH	K_2CO_3	1,4-dioxane	PhBr-d5	101 °C	24 h	56	30	9
17	$Pd(OAc)_2$	PCy_3HBF_4	PivOH	K_2CO_3	DMF	PhBr-d5	110 °C	3.5 h	20	0	0
18	$Pd(OAc)_2$	PCy_3HBF_4	PivOH	K_2CO_3	DMF	PhBr-d5	110 °C	24 h	0	0	0
19	$Pd(OAc)_2$	PCy_3HBF_4	PivOH	K_2CO_3	toluene	PhCl[e]	110 °C	4 d	94	2	0
20	$Pd(OAc)_2$	PCy_3HBF_4	PivOH	K_2CO_3	toluene	PhI[e]	110 °C	4 d	90	4	0

[a] Experimental condition: 5 mol% catalyst, 10 mol% ligand, 30 mol% additive, 3 eq base, 1.1 eq arylhalide, solvent (0.1 M solution). [b] R is 2,6-dichlorophenyl. [c] All yields were determined *via* NMR-spectroscopy using pentadeuterated phenylhalides to avoid overlapping peaks. [d] Highest yielding condition. [e] No deuterated phenylhalide was used.

General C–H arylation procedure

BODIPY **1** (one equivalent) was weighed together with K_2CO_3 (3 equivalents), $Pd(OAc)_2$ (5 mol%), PCy_3HBF_4 (10 mol%), pivalic acid (30 mol%, IUPAC name 2,2-dimethylpropanoic acid)) and, if a solid, the bromoarene (1.1 equivalents). This was placed in a Schlenk flask with a magnetic stirring bar and dissolved in toluene (or *o*-xylene) to form a 0.1 M solution. Next, the reaction vessel was thrice evacuated and backfilled with nitrogen. If the bromoarene (1.1 equivalents) was a liquid it was added next, using a syringe. This reaction mixture was heated to 110 °C for the indicated time. Upon completion, the reaction mixture was cooled to room temperature. Subsequently, the solution was poured in diethyl ether (100 ml), washed three times with water (100 ml), dried over $MgSO_4$, filtered, and evaporated to dryness. The crude product was purified chromatographically.

3-Phenyl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene 2a



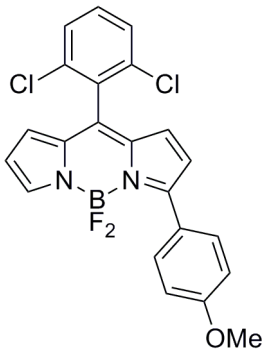
The compound was prepared following the general procedure using 0.4 mmol 8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene in *o*-xylene for 24 h. Bromobenzene was the bromoarene used. The crude product was purified *via* column chromatography (silica; petroleum ether/CH_2Cl_2; 2:1 v/v) providing the desired product **2a** in 44% (73 mg) and the diarylated product **3a** in 17% (34 mg) yield.

2a: Red crystals with a green lustre; Mp 278 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.06-7.95 (m, 2H), 7.85 (s, 1H), 7.56-7.39 (m, 6H), 6.75 (d, 1H, J = 3.96 Hz), 6.68 (d, 1H, J = 3.96 Hz), 6.62 (d, 1H, J = 3.00 Hz), 6.49 (s, 1H) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 161.8, 143.4, 135.6, 132.0, 131.8, 131.3, 131.1, 130.5, 129.8, 129.7, 129.6, 129.5, 128.5, 128.4, 128.1, 121.8, 118.6 ppm; MS (EI): 412; HRMS: Calculated for $C_{21}H_{13}BCl_2F_2N_2$: 412.05169, found 412.05171.

3a: Purple crystals with a copper lustre; Mp 140 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.96-7.86 (m, 4H), 7.54-7.37 (m, 9H), 6.66 (d, 2H, J = 4.14 Hz), 6.61 (d, 2H, J = 4.14 Hz) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 159.9, 135.8, 132.5, 132.2, 131.2, 129.9, 129.7, 129.7, 129.6,

129.2, 128.4, 128.3, 121.6 ppm; MS (EI): 488; HRMS: Calculated for $C_{27}H_{17}BCl_2F_2N_2$: 488.08299, found 488.08194.

3-*p*-Anisyl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene 2b

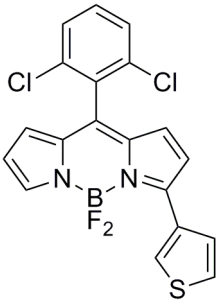


The compound was prepared following the general procedure using 0.4 mmol 8-(2,6-dichloropheny)l-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene in toluene for 43 h. 4-Bromoanisole was the bromoarene used. The crude product was purified *via* column chromatography (silica; petroleum ether/diethyl ether; 2:1 v/v) providing the desired product **2b** in 42% (74 mg) and the diarylated product **3b** in 10% (21 mg) yield.

2b: Dark red crystals with a copper lustre; Mp 70 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.04 (d, 2H, J = 8.85 Hz), 7.80 (s, 1H), 7.52-7.37 (m, 3H), 7.02 (d, 2H, J = 8.85 Hz), 6.76-6.69 (m, 2H), 6.56 (s, 1H), 6.46 (s, 1H), 3.89 (s, 3H) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 162.1, 161.8, 141.9, 137.5, 135.7, 132.0, 131.8, 131.7, 131.7, 131.4, 131.2, 128.3, 126.8, 124.2, 121.9, 118.0, 114.2, 55.5 ppm; MS (EI): 442; HRMS: Calculated for $C_{22}H_{15}BCl_2F_2N_2O$: 442.06226, found 442.06248.

3b: Purple crystals with a green lustre; Mp 63 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.93 (d, 4H, J = 8.85 Hz), 7.52-7.38 (m, 3H), 6.97 (d, 4H, J = 8.85 Hz), 6.60 (s, 4H), 3.86 (s, 6H) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 160.9, 159.1, 135.8, 132.2, 131.3, 131.3, 131.2, 130.9, 128.5, 128.2, 125.0, 120.9, 113.8, 55.3 ppm; MS (EI): 548; HRMS: Calculated for $C_{29}H_{21}BCl_2F_2N_2O_2$: 548.10412, found 548.10536.

3-Thien-3-yl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene 2d



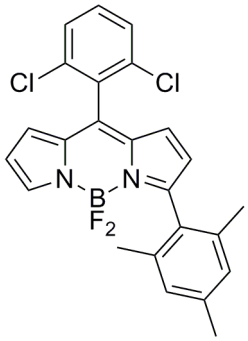
The compound was prepared following the general procedure using 0.1 mmol 8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene in toluene for 27 h. 3-Bromothiophene was the bromoarene used. The crude product was purified *via* column chromatography (silica; petroleum ether/CH_2Cl_2; 2:1 v/v) providing the desired product **2d** in 55% (23 mg) and the diarylated product **3d** in 10% (5 mg) yield.

2d: Dark purple crystals with a green lustre; Mp 214 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.44 (d, 1H, J = 1.53 Hz), 7.84 (s, 1H), 7.72 (d, 1H, J = 4.71 Hz), 7.53-7.35 (m, 4H), 6.80 (d, 1H, J = 4.32 Hz), 6.72 (d, 1H, J = 4.32 Hz), 6.58 (d, 1H, J = 3.39 Hz), 6.49 (s, 1H) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 155.7, 142.4, 137.2, 135.6, 133.6, 132.1, 131.9, 131.3, 131.2,

130.6, 130.5, 128.9, 128.4, 127.1, 125.9, 121.8, 118.3 ppm; MS (EI): 418; HRMS: Calculated for $C_{19}H_{11}BCl_2F_2N_2S$: 418.00811, found 418.00869.

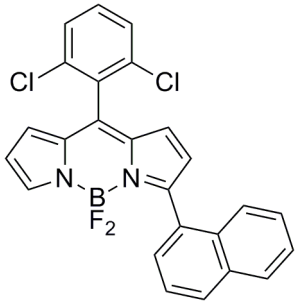
3d: Blue solid; Mp 205 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.37 (s, 2H), 7.69 (d, 2H, J = 4.71 Hz), 7.52-7.33 (m, 5H), 6.75 (d, 2H, J = 3.78 Hz), 6.59 (d, 2H, J = 3.78 Hz) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 153.2, 136.0, 135.9, 132.7, 131.1, 129.3, 129.2, 129.0, 129.0, 128.6, 128.3, 125.6, 121.1 ppm; MS (EI): 500; HRMS: Calculated for $C_{23}H_{13}BCl_2F_2N_2S_2$: 499.99583, found 499.99666.

3-Mesityl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene 2e



The compound was prepared following the general procedure using 0.1 mmol 8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene in toluene for 43 h. 2-Bromo-1,3,5-trimethylbenzene was the bromoarene used. The crude product was purified *via* column chromatography (silica; petroleum ether/CH_2Cl_2; 1:1 v/v) providing the desired product **2e** in 35% (16 mg) yield. Orange solid with a green lustre; Mp 152 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.72 (s, 1H), 7.55-7.39 (m, 3H), 6.96 (s, 2H), 6.79 (d, 1H, J = 4.14 Hz), 6.62 (d, 1H, J = 4.14 Hz), 6.44 (d, 1H, J = 3.75 Hz), 6.37 (d, 1H, J = 4.14 Hz), 2.34 (s, 3H), 2.17 (s, 6H) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 162.3, 143.6, 139.2, 139.1, 137.4, 135.7, 135.5, 131.8, 131.3, 131.1, 130.8, 129.1, 129.0, 128.4, 127.8, 121.7, 118.4, 21.4, 20.1 ppm; MS (EI): 454 (M), 434 (M-HF); HRMS: Calculated for $C_{24}H_{19}BCl_2F_2N_2$: 454.09864, found 454.09852.

3-(1-Naphthyl)-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene 2f



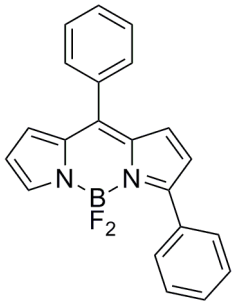
The compound was prepared following the general procedure using 0.4 mmol 8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene in *o*-xylene for 24 h. 1-Bromonaphthalene was the bromoarene used. The crude product was purified *via* column chromatography (silica; petroleum ether/CH_2Cl_2; 2:1 v/v) providing the diarylated product **3f** in 16% (37 mg) yield and impure **2f.** Analytically pure **2f** was obtained through HPLC purification (silica; toluene/CH_2Cl_2; 2:1 v/v), providing the desired product **2f** in 20% (37 mg) yield.

2f: Red crystals with a green lustre; Mp 282 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.03-7.95 (m, 2H), 7.94-7.84 (m, 2H), 7.77 (s, 1H), 7.62 (t, 1H, J = 7.73 Hz), 7.55-7.43 (m, 5H), 6.83 (d, 1H, J = 4.14 Hz), 6.65 (m, 2H), 6.46 (d, 1H, J = 3.03 Hz) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 160.1, 144.0, 139.3, 136.1, 135.6, 134.2, 133.6, 131.9, 131.8, 131.3, 130.3, 130.0,

129.8, 128.6, 128.4, 126.7, 126.2, 126.1, 125.0, 123.4, 118.8 ppm; MS (EI): 462; HRMS: Calculated for $C_{25}H_{15}BCl_2F_2N_2$: 462.06734, found 462.06839.

3f: Purple solid with a copper lustre; Mp: decomposition at 310 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.91-7.77 (m, 8H), 7.60-7.54 (m, 2H), 7.52-7.37 (m, 7H), 6.79 (d, 2H, J = 3.21 Hz), 6.59 (d, 2H, J = 3.39 Hz) ppm; ^{13}C-NMR: product is too insoluble to obtain a fully resolved spectrum; MS (EI): 588; HRMS: Calculated for $C_{35}H_{21}BCl_2F_2N_2$: 588.11429, found 588.11553.

3,8-Diphenyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene 2i

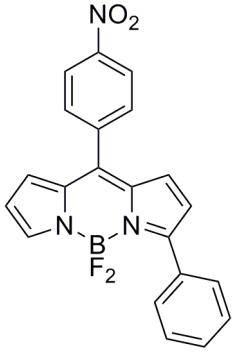


The compound was prepared following the general procedure using 0.2 mmol 8-phenyl-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene in *o*-xylene for 28 h. Bromobenzene was the bromoarene used. The crude product was purified *via* column chromatography (silica; petroleum ether/CH_2Cl_2; 2:1 v/v) providing the desired product **2i** in 31% (21 mg) and the diarylated product **3i** in 32% (27 mg) yield.

2i: Red solid with a green lustre; Mp 58 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.00-7.92 (m, 2H), 7.85 (s, 1H), 7.63-7.45 (m, 8H), 6.99 (d, 1H, J = 4.17 Hz), 6.86 (d, 1H, J = 3.60 Hz), 6.69 (d, 1H, J = 4.35 Hz), 6.52 (d, 1H, J = 2.46 Hz) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ 160.6, 145.8, 142.5, 137.3, 134.3, 132.9, 132.3, 130.7, 130.6, 130.1, 129.8, 129.6, 128.5, 128.5, 125.9, 121.1, 118.2 ppm; MS (EI): 344; HRMS: Calculated for $C_{21}H_{15}BF_2N_2$: 344.12964, found 344.13011.

3i: Dark purple solid; Mp 191 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.91-7.83 (m, 4H), 7.63-7.50 (m, 5H), 7.47-7.37 (m, 6H), 6.90 (d, 2H, J = 4.35 Hz), 6.63 (d, 2H, J = 4.17 Hz) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 159.0, 144.2, 136.5, 134.4, 132.7, 131.0, 130.7, 130.2, 129.6, 128.4, 128.3, 121.0 ppm (one carbon overlap); MS (EI): 420; HRMS: Calculated for $C_{27}H_{19}BF_2N_2$: 420.16094, found 420.16196.

3-Phenyl-8-(*p*-nitrophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene 2j

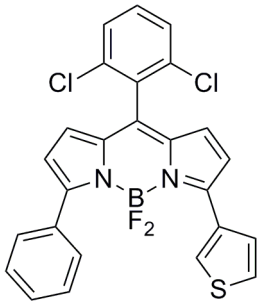


The compound was prepared following the general procedure using 0.2 mmol 8-(*p*-nitrophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene in *o*-xylene for 46 h. Bromobenzene was the bromoarene used. The crude product was purified *via* column chromatography (silica; petroleum ether/CH_2Cl_2; 1:1 v/v) providing the desired product **2j** in 28% (22 mg) and the diarylated product **3j** in 18% (17 mg) yield.

2j: Purple crystals with a green lustre; Mp 193 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.41 (d, 2H, J = 8.85 Hz), 8.00-7.93 (m, 2H), 7.89 (s, 1H), 7.77 (d, 2H, 8.67 Hz), 7.55-7.47 (m, 3H), 6.89 (d, 1H, J = 4.53 Hz), 6.79-6.70 (m, 2H), 6.55 (d, 1H, J = 3.21 Hz) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 149.1, 143.5, 140.4, 136.9, 133.7, 132.4, 131.8, 131.5, 130.6, 129.7, 129.6, 129.6, 129.2, 128.6, 123.8, 122.1, 118.9 ppm; MS (EI): 389; HRMS: Calculated for $C_{21}H_{14}BF_2N_3O_2$: 389.11471, found 389.11459.

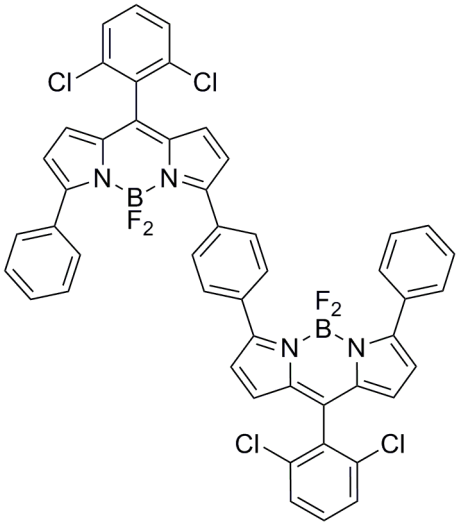
3j: Dark purple solid; Mp 99 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.42 (d, 2H, J = 8.67 Hz), 7.92-7.83 (m, 4H), 7.79 (d, 2H, J = 8.46 Hz), 7.49-7.39 (m, 6H), 6.79 (d, 2H, J = 4.14 Hz), 6.67 (d, 2H, J = 3.96 Hz) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 160.3, 140.8, 136.0, 132.3, 131.6, 130.4, 130.1, 129.7, 129.6, 129.6, 128.5, 123.7, 121.8 ppm; MS (EI): 465; HRMS: Calculated for $C_{27}H_{18}BF_2N_3O_2$: 465.14601, found 465.14769.

3-Phenyl-5-thien-3-yl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene 4



The compound was prepared following the general procedure using 0.2 mmol 3-phenyl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene **2a** in *o*-xylene for 48 h. 3-Bromothiophene was the bromoarene used. The crude product was purified *via* column chromatography (silica; petroleum ether/CH_2Cl_2; 3:1 v/v) providing the desired product in 62% (61 mg) yield. Dark purple solid; Mp 197 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.32 (s, 1H), 7.97 (d, 2H, J = 6.03 Hz), 7.65 (d, 1H, J = 4.71 Hz), 7.54-7.39 (m, 6H), 7.38-7.31 (m, 1H), 6.75 (d, 1H, J = 3.93 Hz), 6.68-6.58 (m, 3H) ppm; ^{13}C-NMR ($CDCl_3$, 75 MHz): δ 159.0, 154.0, 136.2, 135.9, 132.8, 132.4, 132.2, 131.1, 129.7, 129.7, 129.4, 129.0, 128.4, 128.3, 125.6, 121.4, 121.2 ppm; MS (EI): 494; HRMS: Calculated for $C_{25}H_{15}BCl_2F_2N_2S$: 494.03941, found 494.04022.

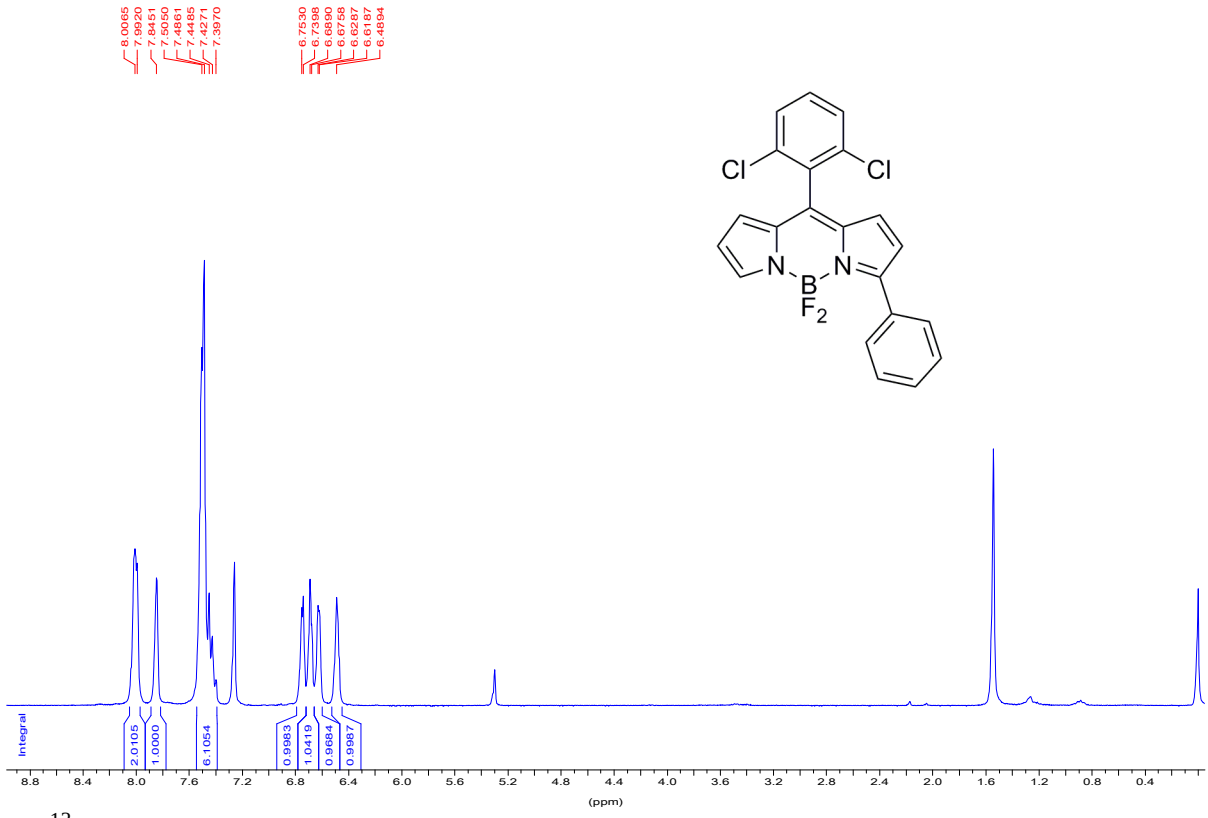
1,4-Di(3-phenyl-5-yl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene)benzene 5



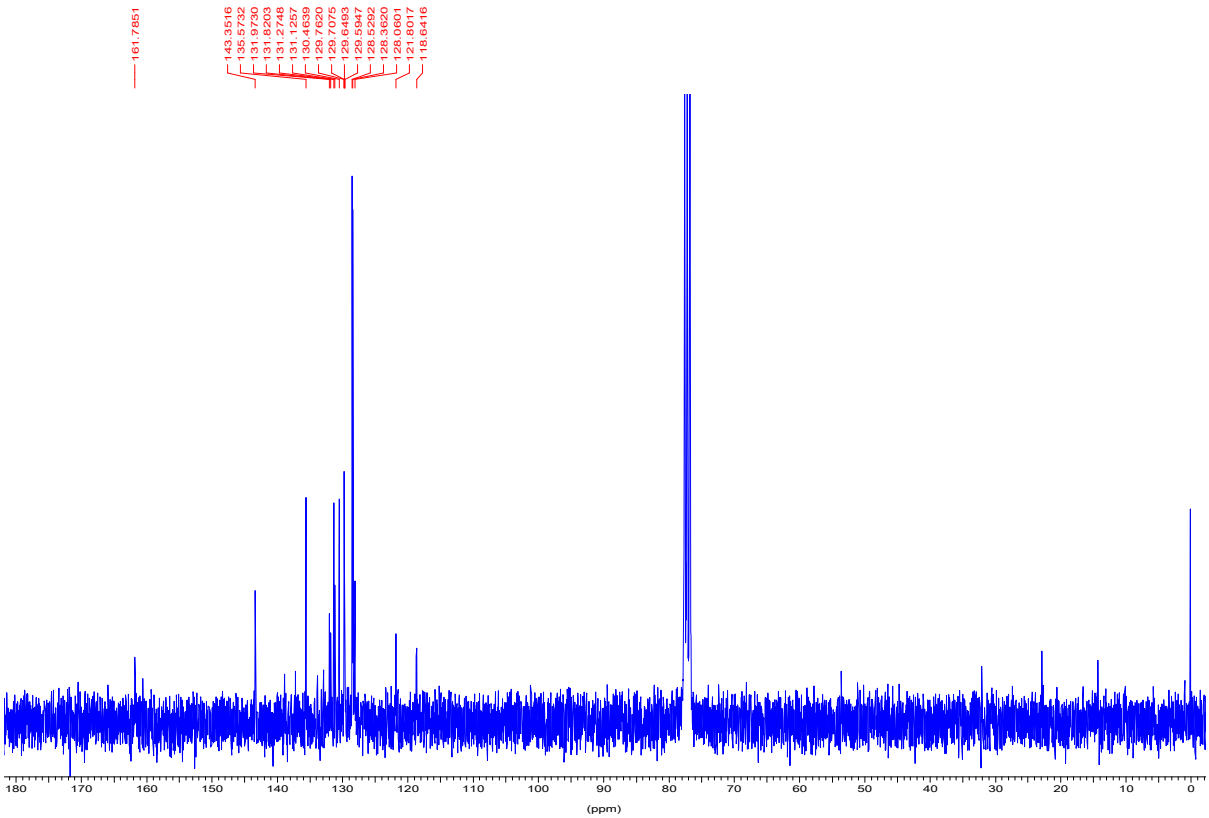
The compound was prepared following the general C–H arylation procedure using 0.36 mmol 3-phenyl-8-(2,6-dichlorophenyl)-4,4-difluoro-4-bora-3a,4a-diaza-*s*-indacene **2a** in toluene for 53 h. 1,4-Dibromobenzene (0.15 mmol, 0.42 equivalents) was used as bromoarene. The crude product was purified *via* column chromatography (silica; petroleum ether/ diethyl ether; 1:1 v/v) providing the desired product **5** in 23% (31 mg) yield. Dark crystals; Mp: decomposition at 290 °C; ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 8.02 (s, 4H), 7.93 (d, 4H, J = 5.85 Hz), 7.55-7.38 (m, 12 H), 6.71 (s, 2H), 6.67 (s, 4H), 6.63 (s, 2H) ppm; ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 160.2, 158.9, 137.1, 136.5, 136.3, 135.9, 133.4, 132.5, 132.1, 131.2, 129.9, 129.7, 129.2, 129.2, 128.4, 128.3, 121.9, 121.7 ppm (two carbons overlap); MS (ESI): 923 ($M^+ + Na^+$), 1823 ($M^+ + M^+ + Na^+$).

NMR-spectra of new compounds

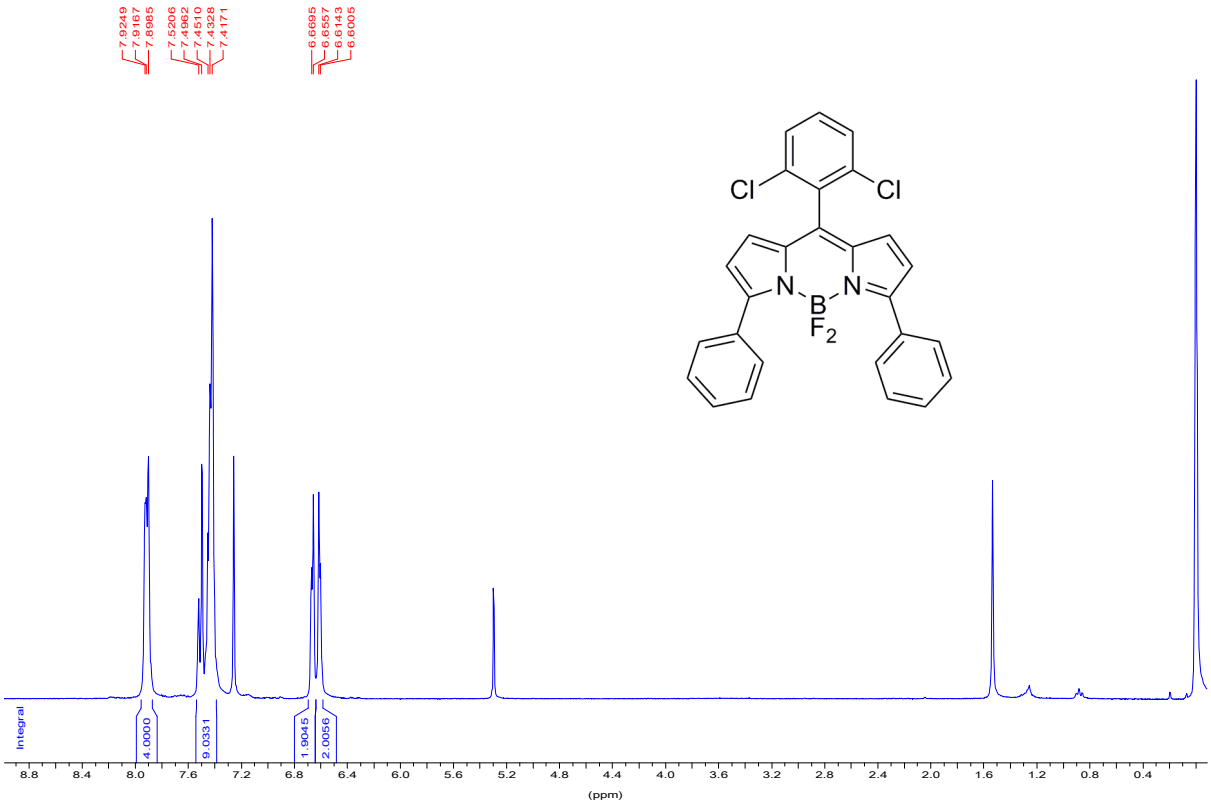
2a, ^{1}H, 300 MHz, $CDCl_3$



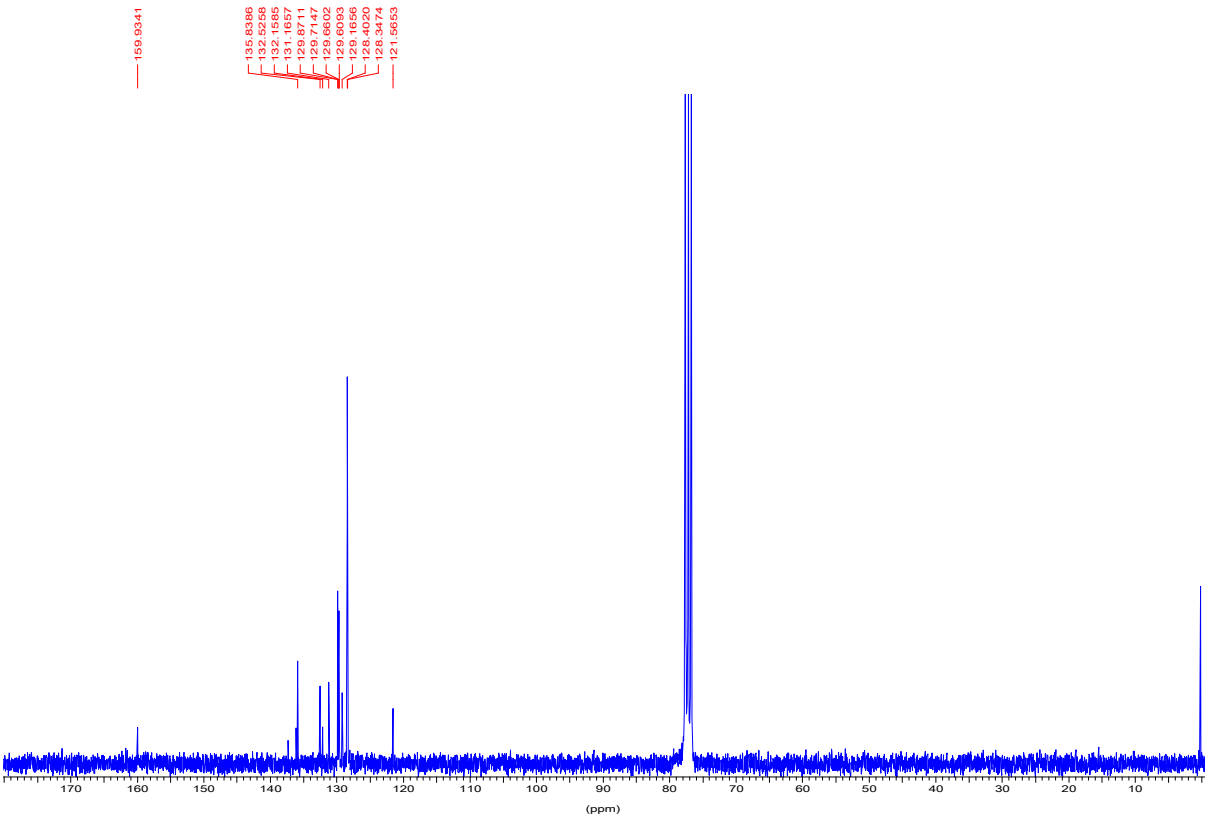
2a, ^{13}C, 75 MHz, $CDCl_3$



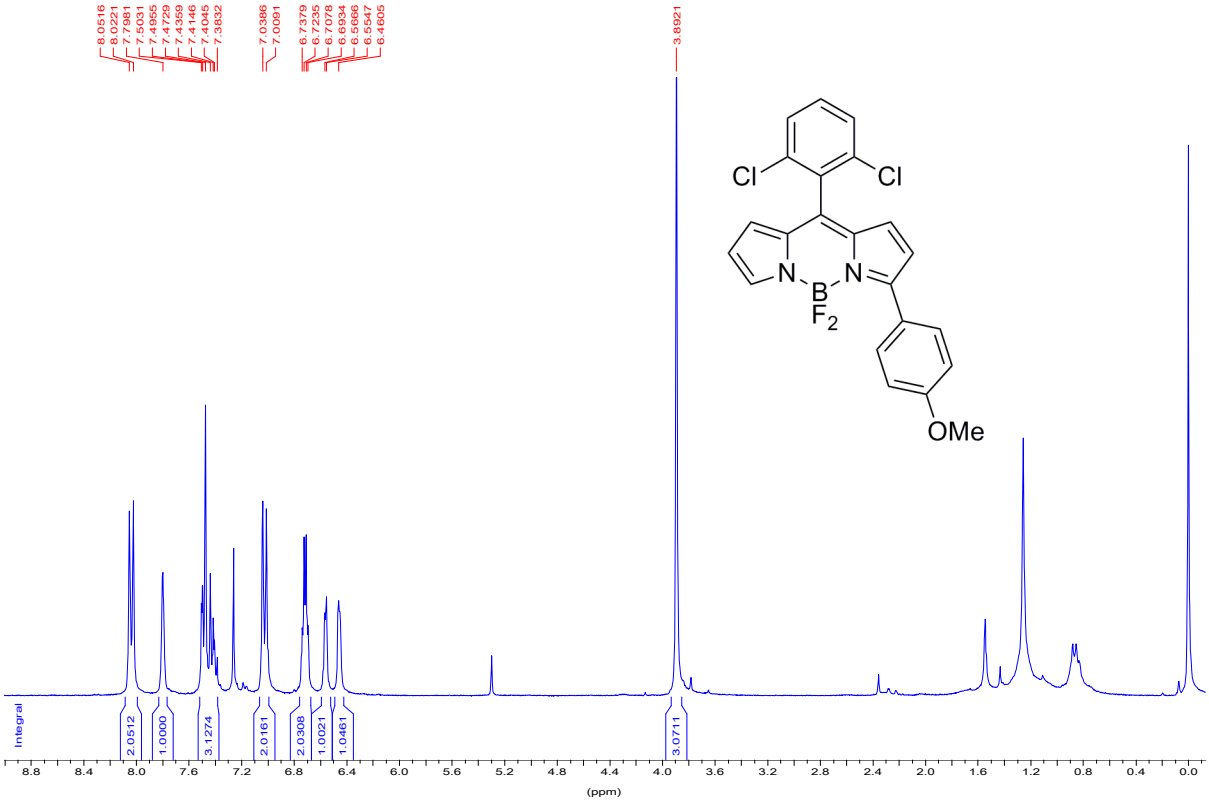
3a, ^{1}H, 300 MHz, $CDCl_3$



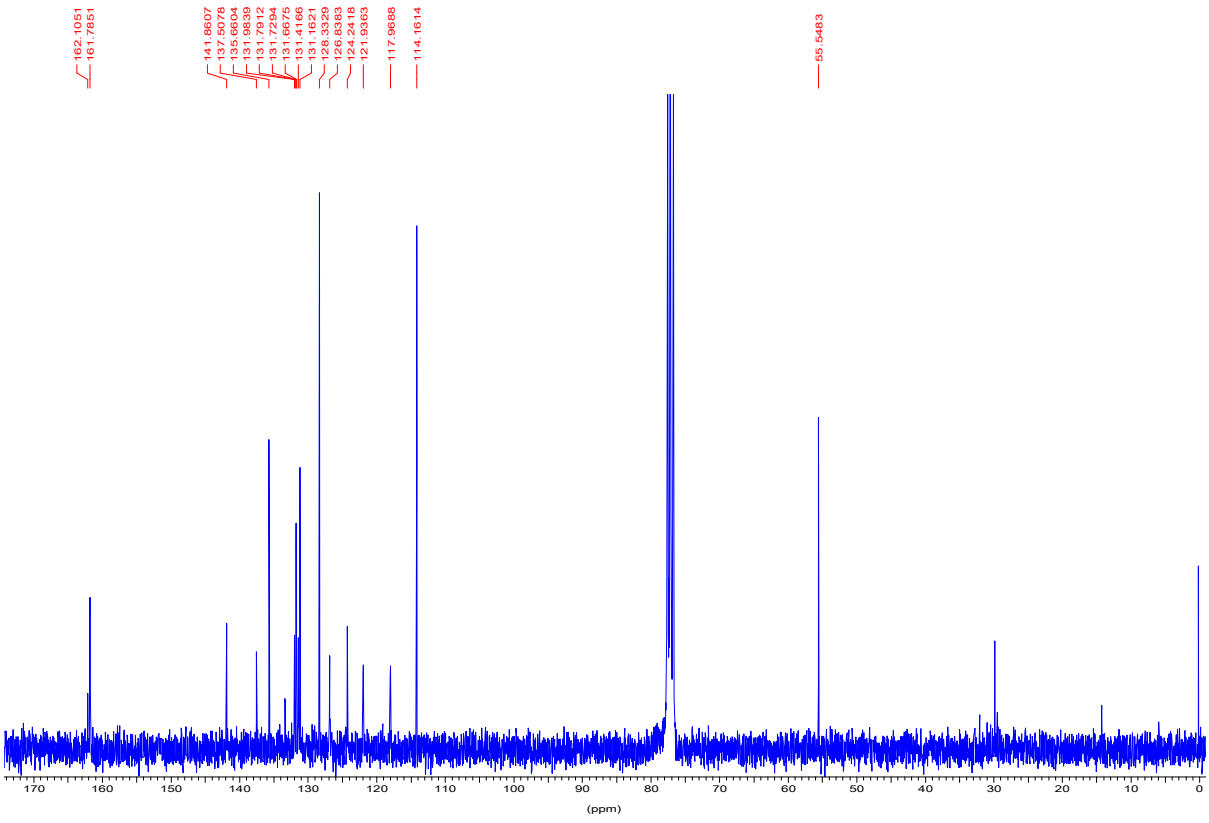
3a, ^{13}C, 75 MHz, $CDCl_3$



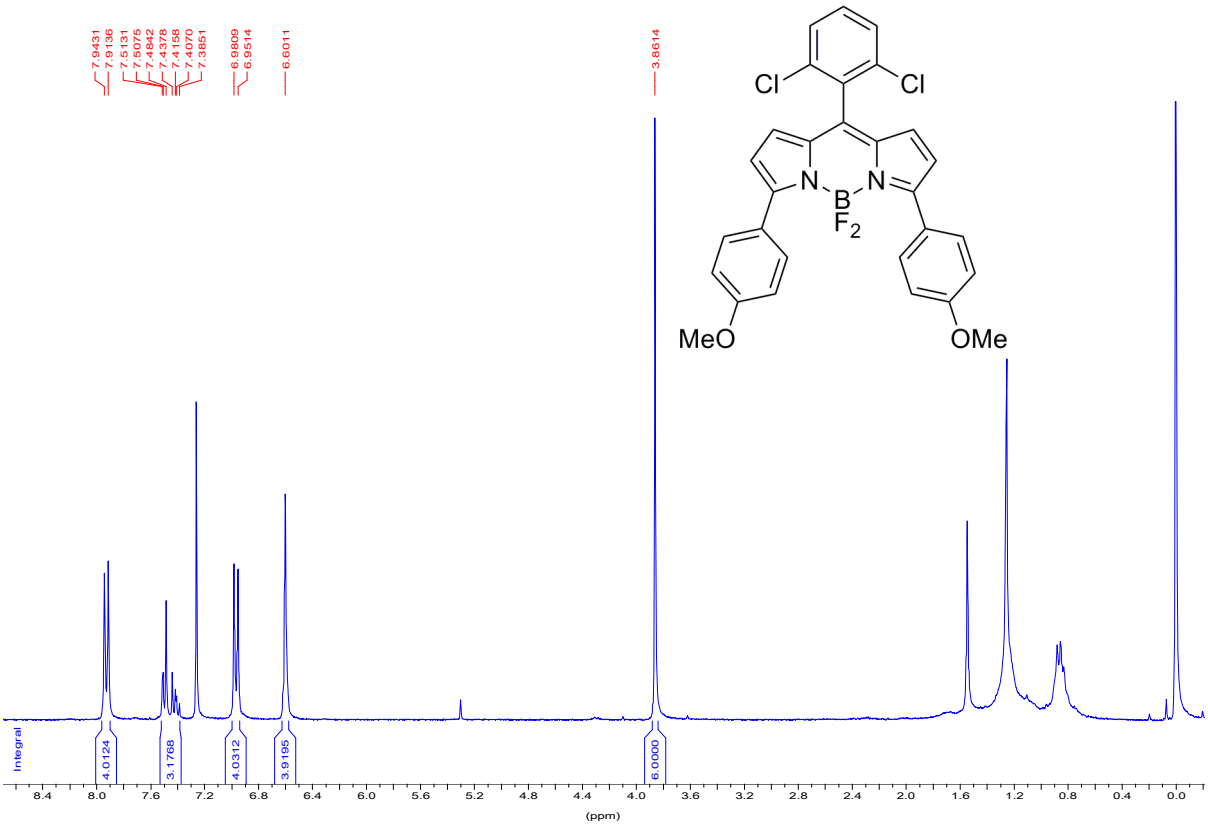
2b, ^{1}H, 300 MHz, $CDCl_3$



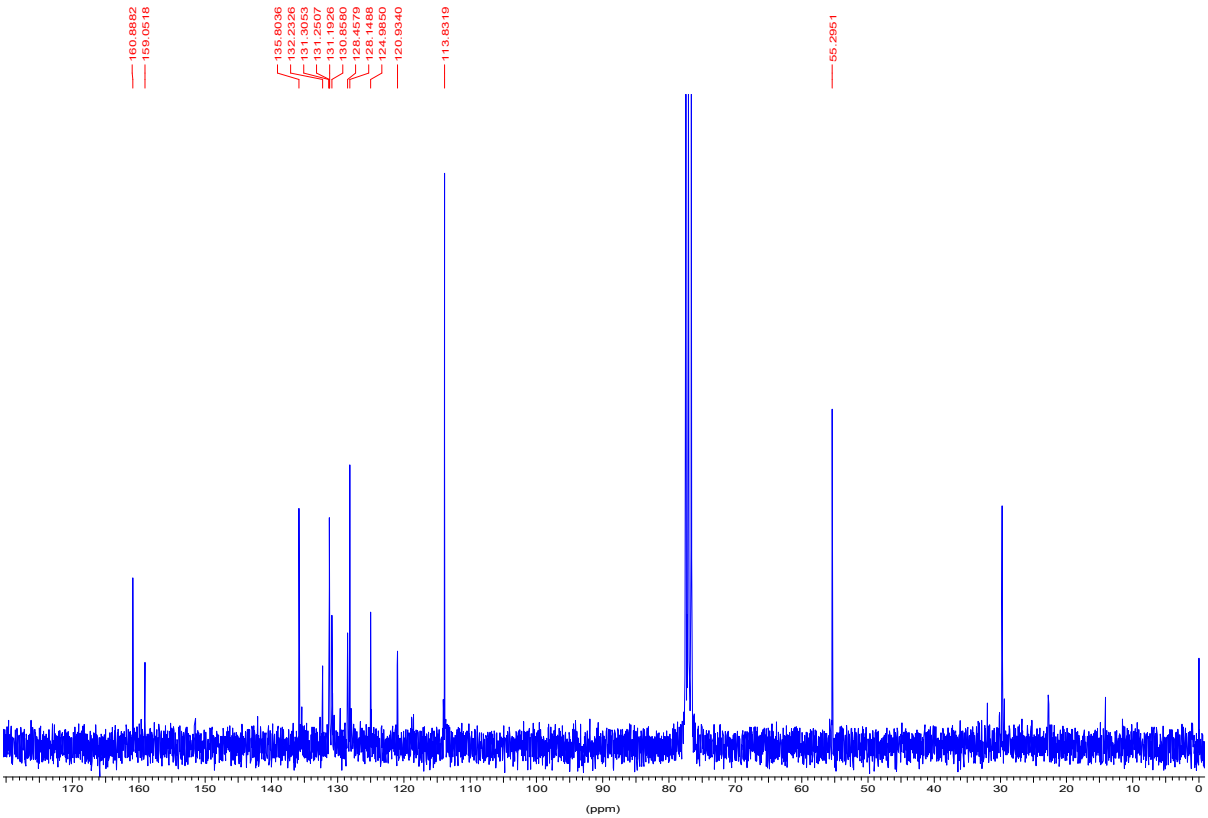
2b, ^{13}C, 75 MHz, $CDCl_3$



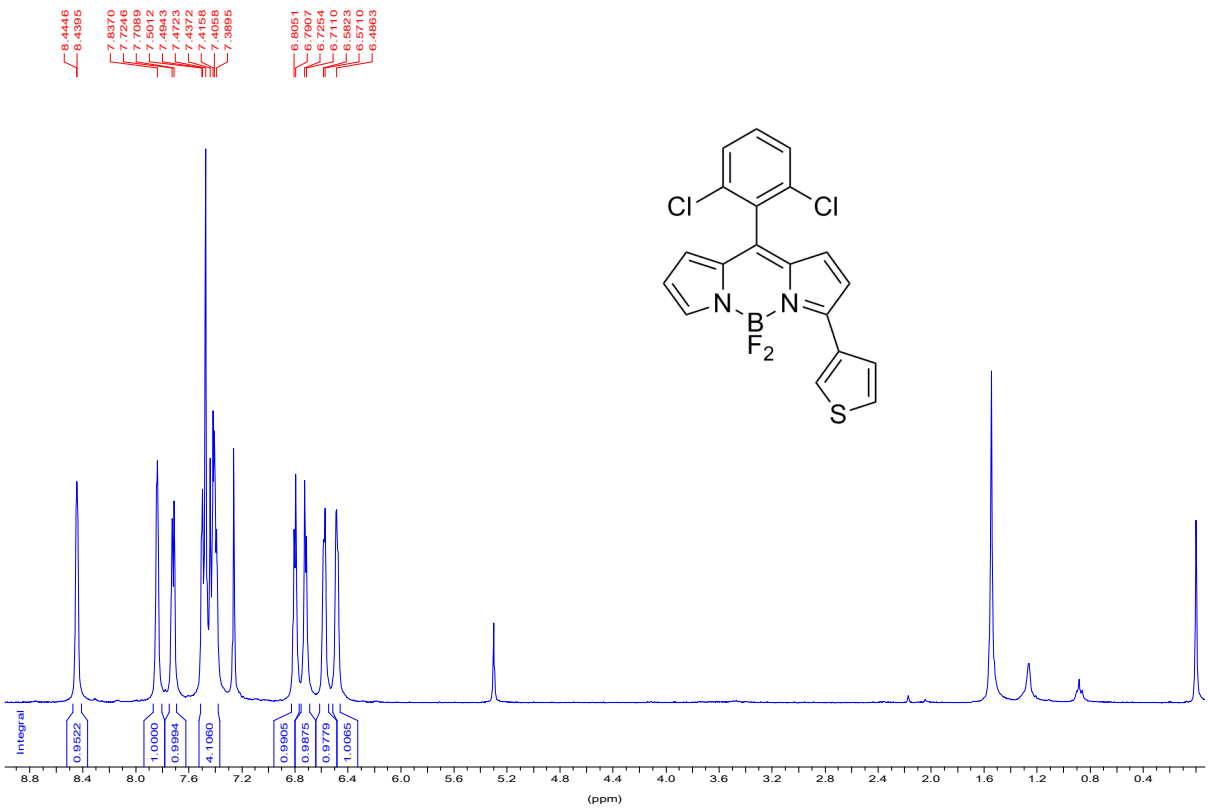
3b, ^{1}H, 300 MHz, $CDCl_3$



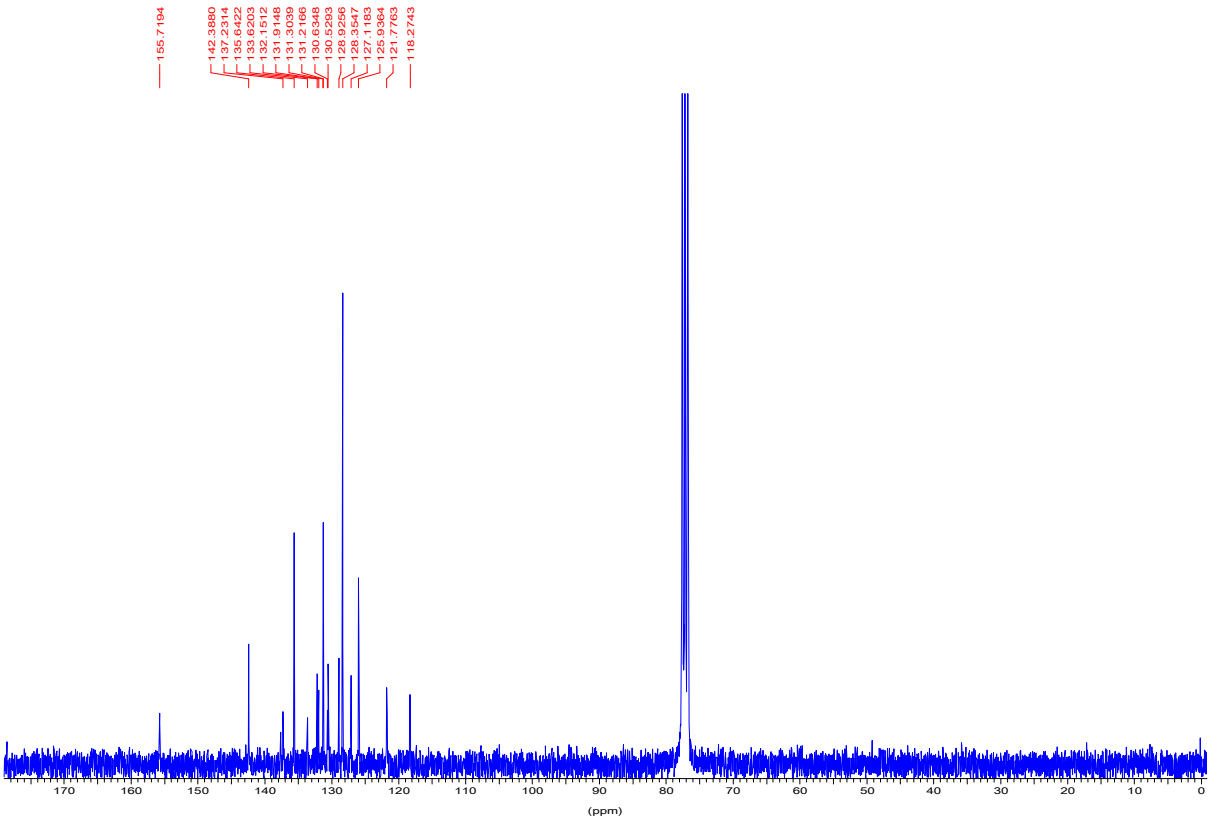
3b, ^{13}C, 75 MHz, $CDCl_3$



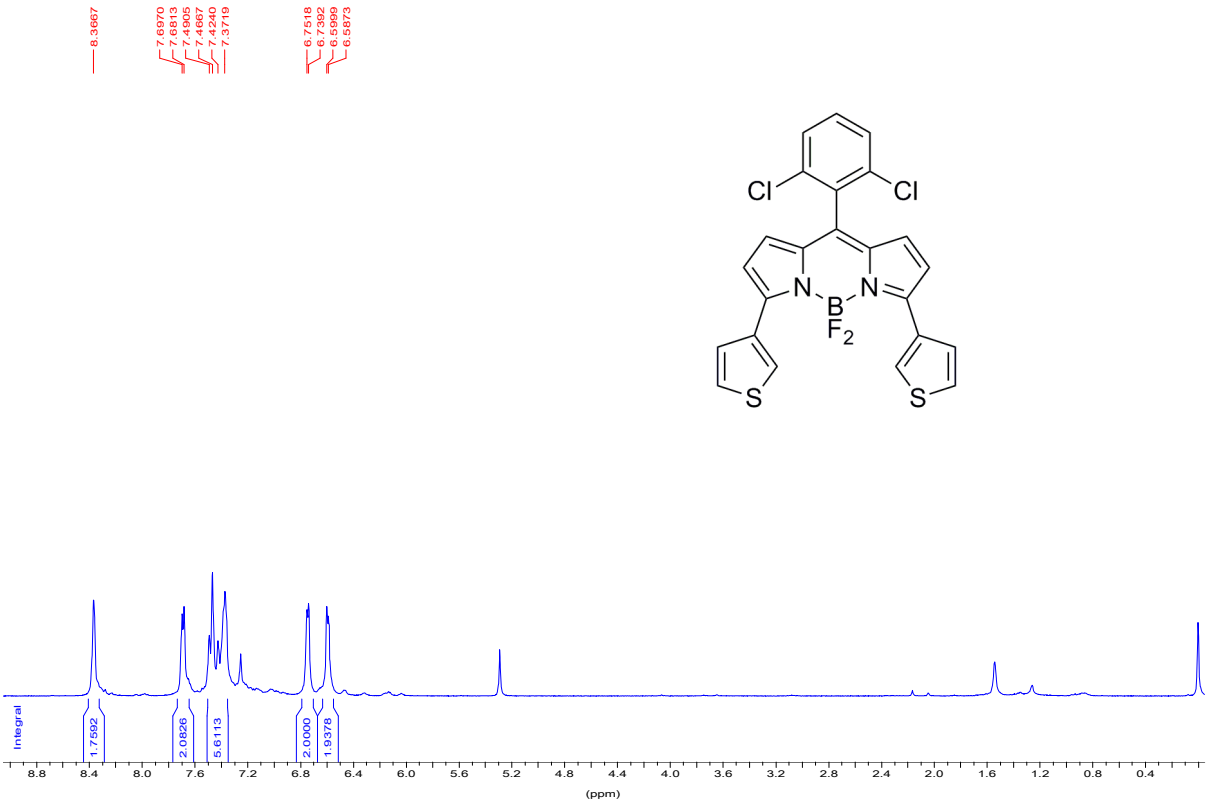
2d, ^{1}H, 300 MHz, $CDCl_3$



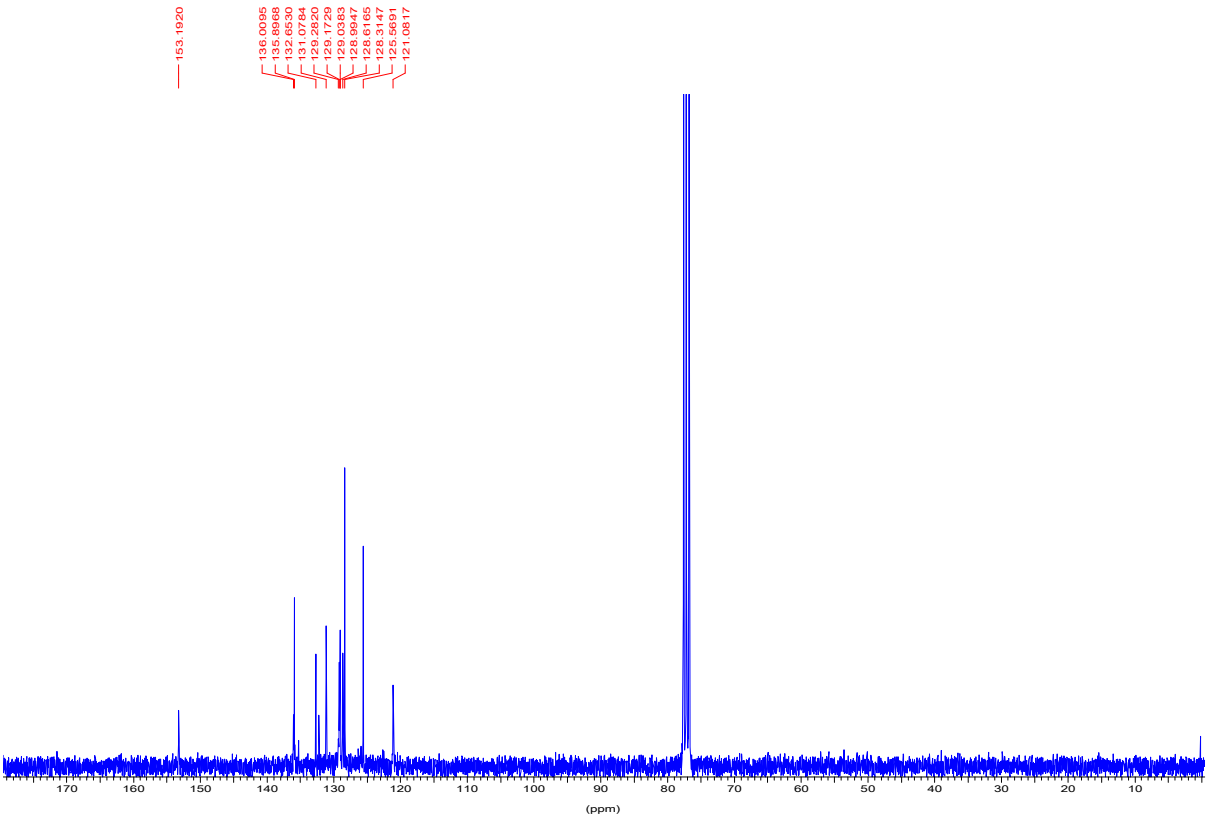
2d, ^{13}C, 75 MHz, $CDCl_3$



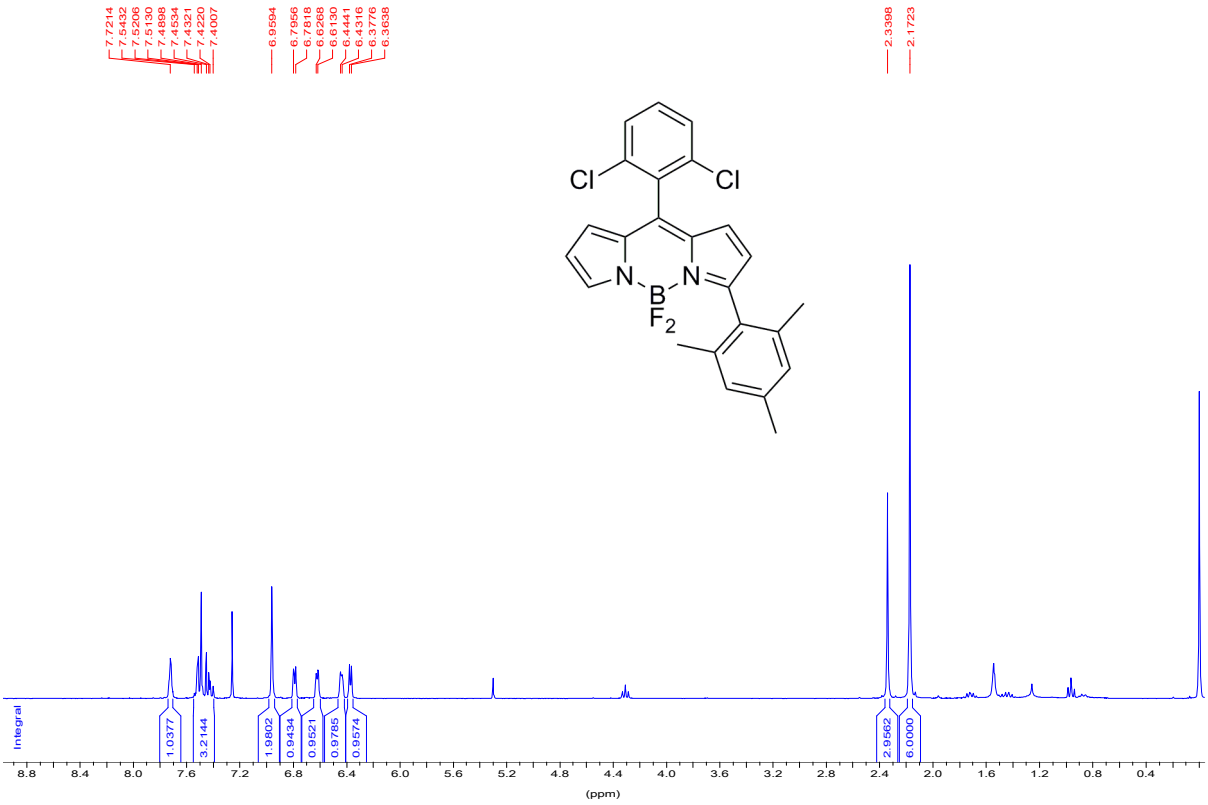
3d, ^{1}H, 300 MHz, $CDCl_3$



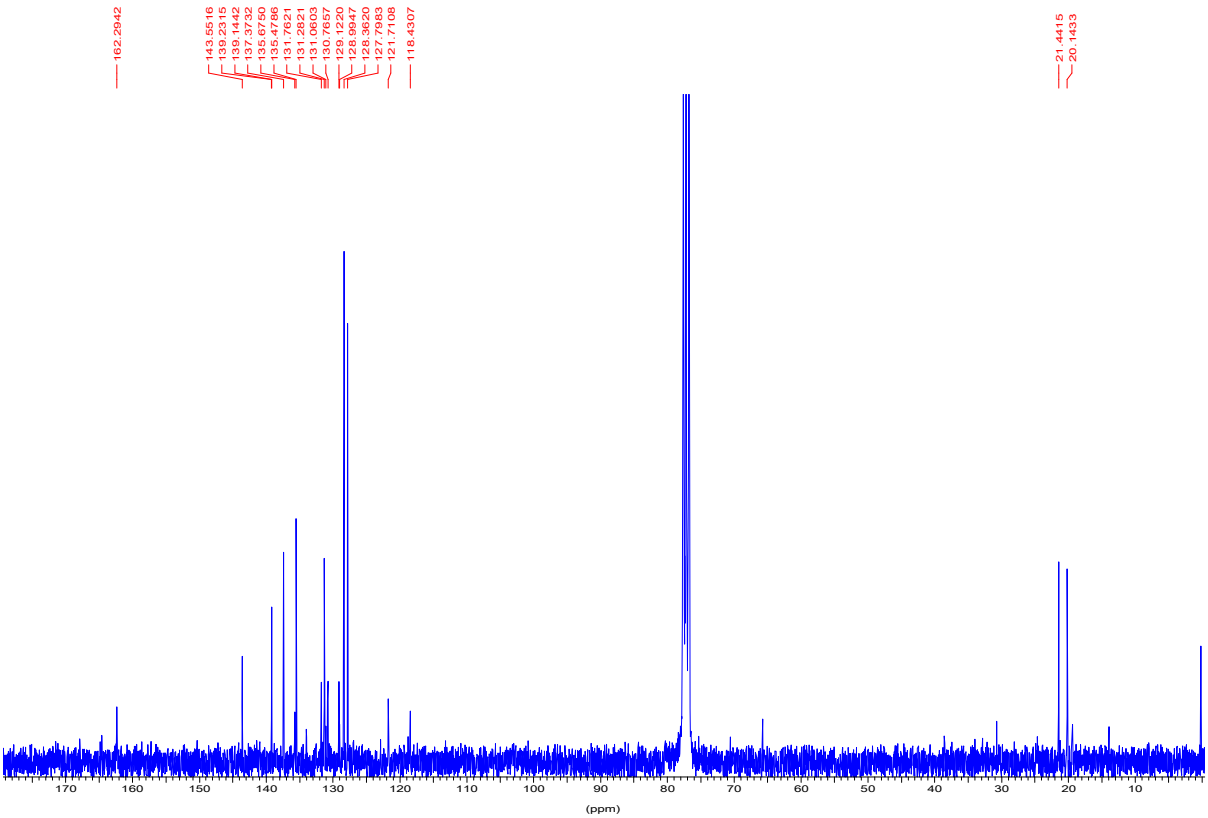
3d, ^{13}C, 75 MHz, $CDCl_3$



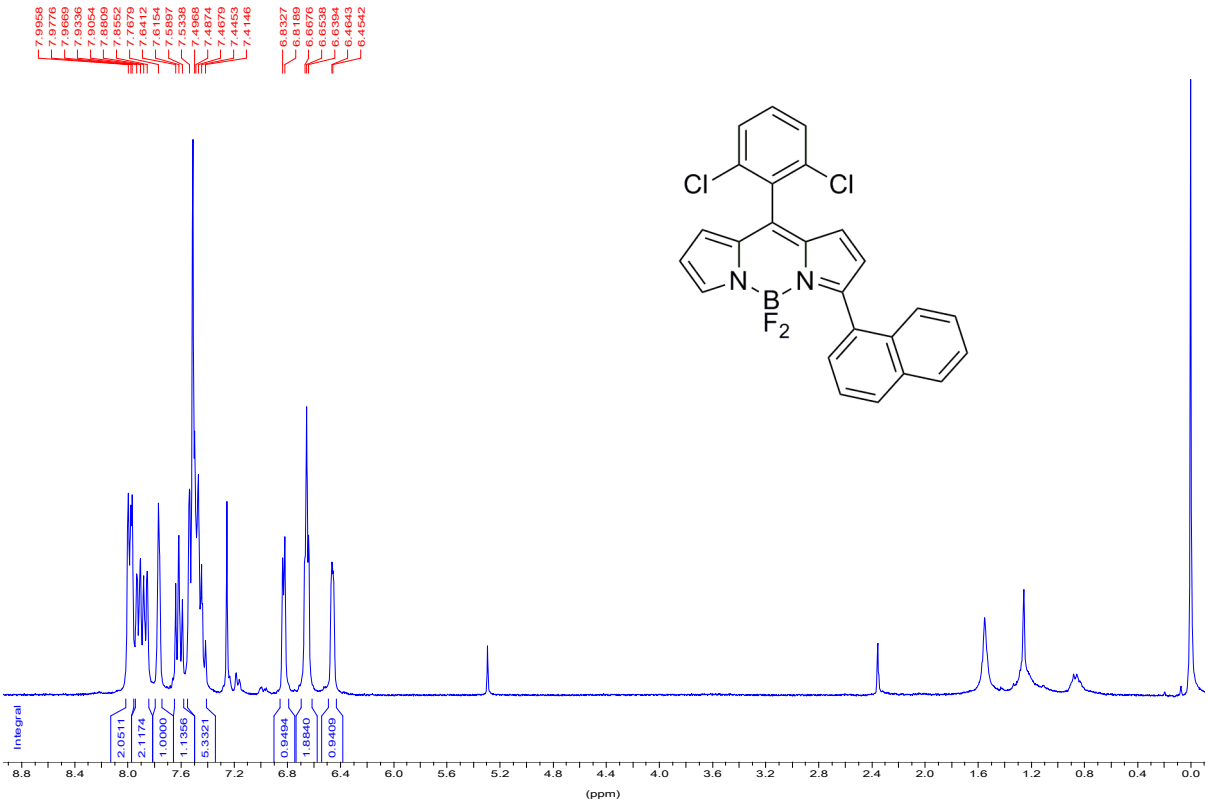
2e, ^{1}H, 300 MHz, $CDCl_3$



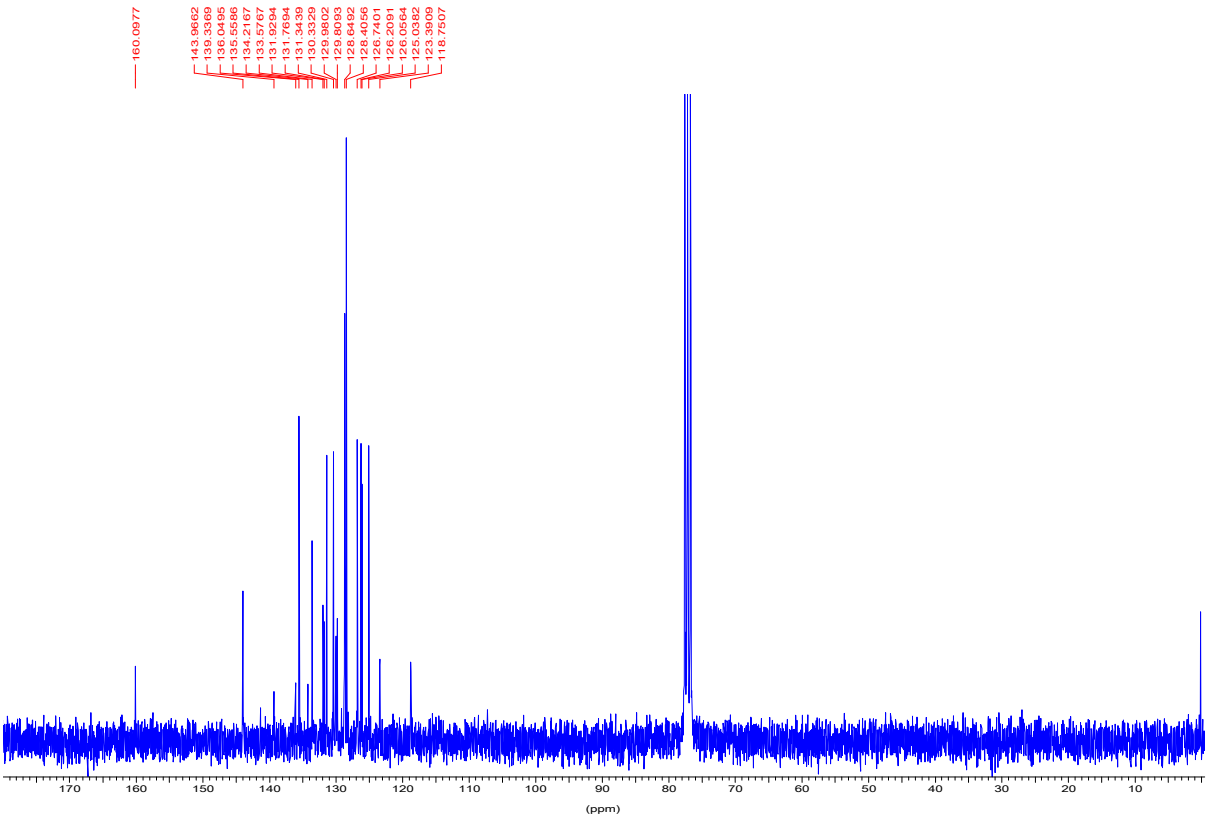
2e, ^{13}C, 75 MHz, $CDCl_3$



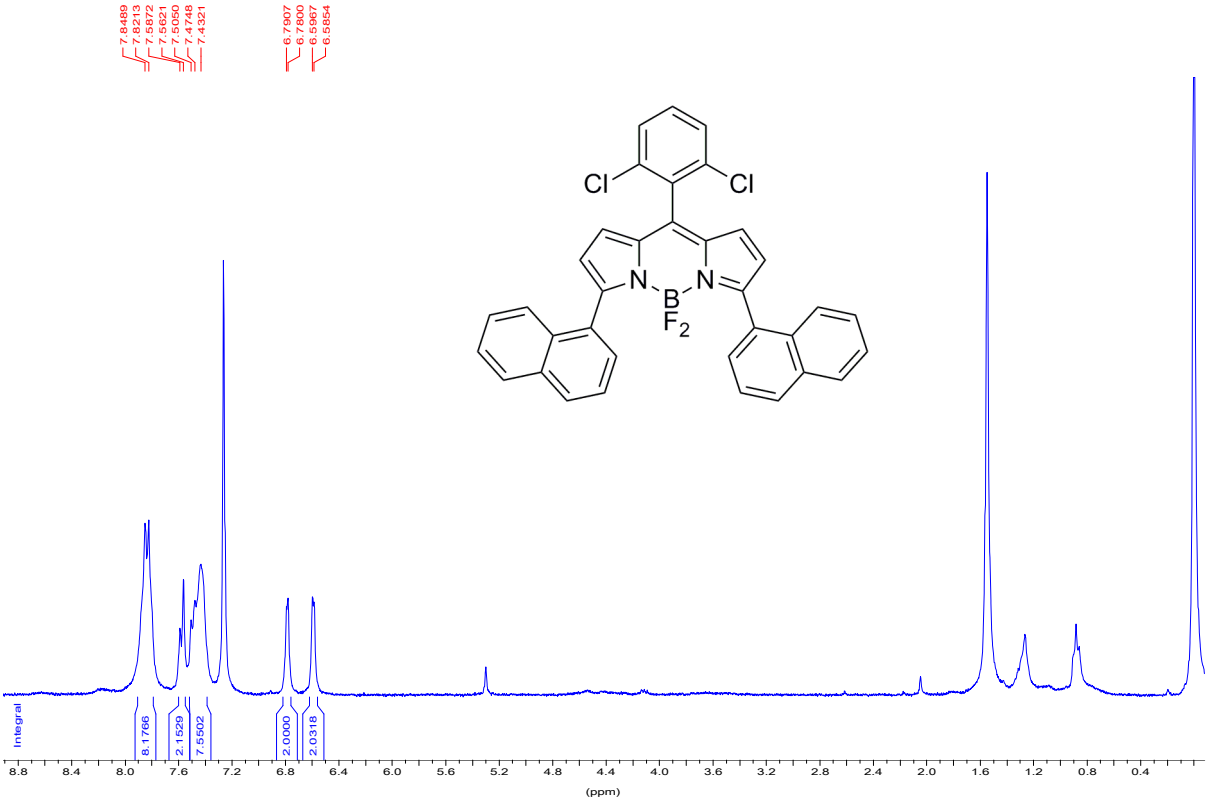
2f, ^{1}H, 300 MHz, $CDCl_3$



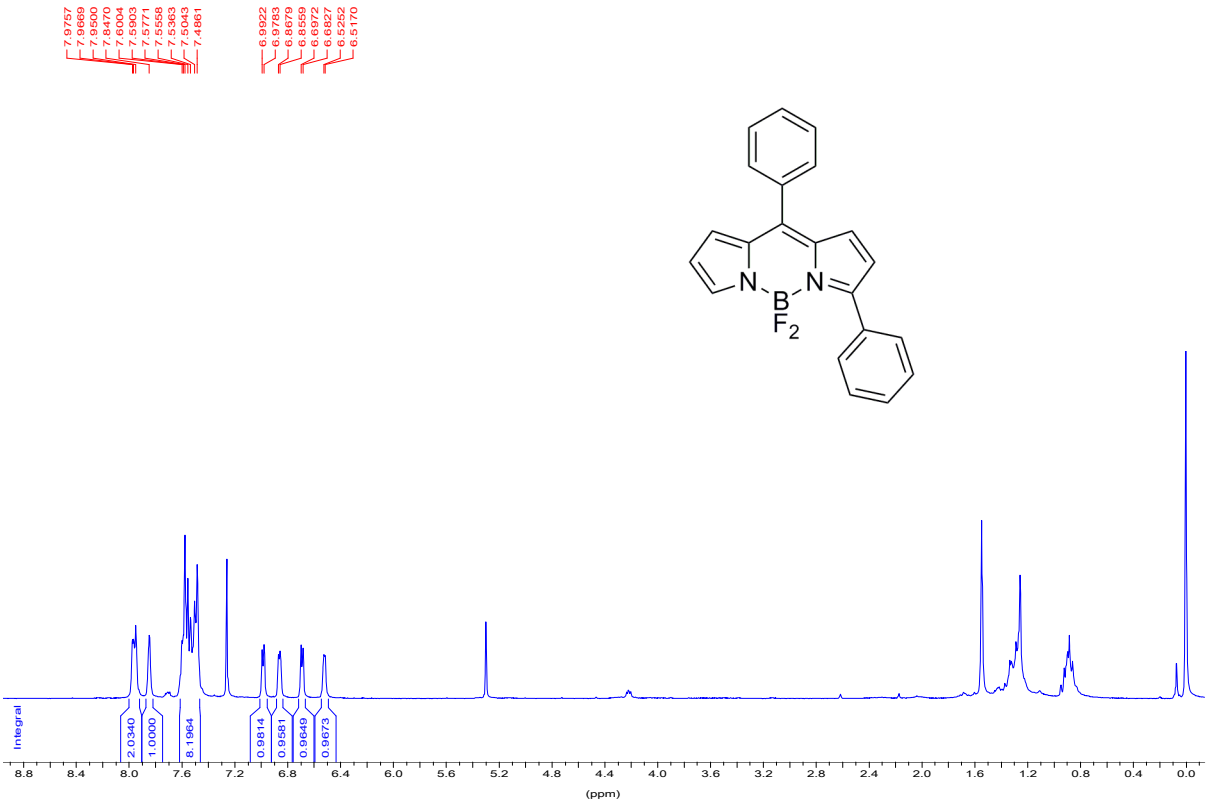
2f, ^{13}C, 75 MHz, $CDCl_3$



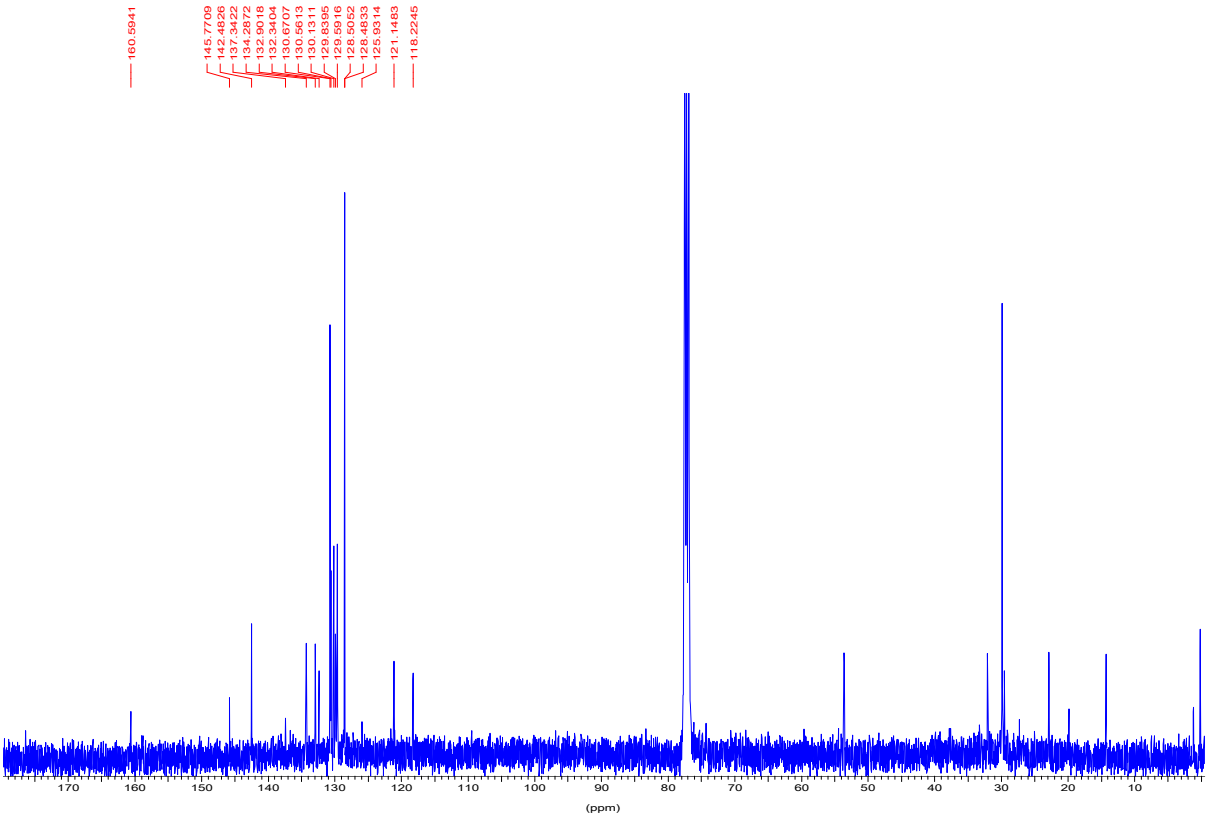
3f, ^{1}H, 300 MHz, $CDCl_3$



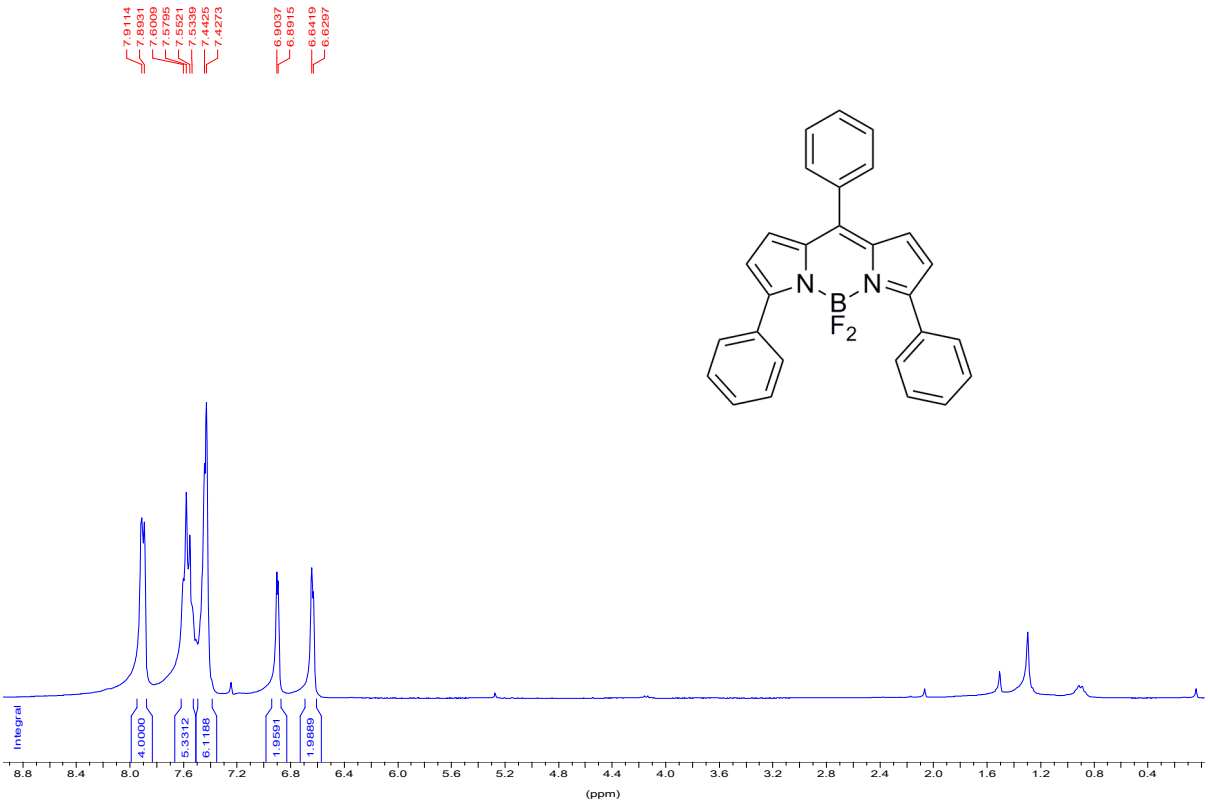
2i, ^{1}H, 300 MHz, $CDCl_3$



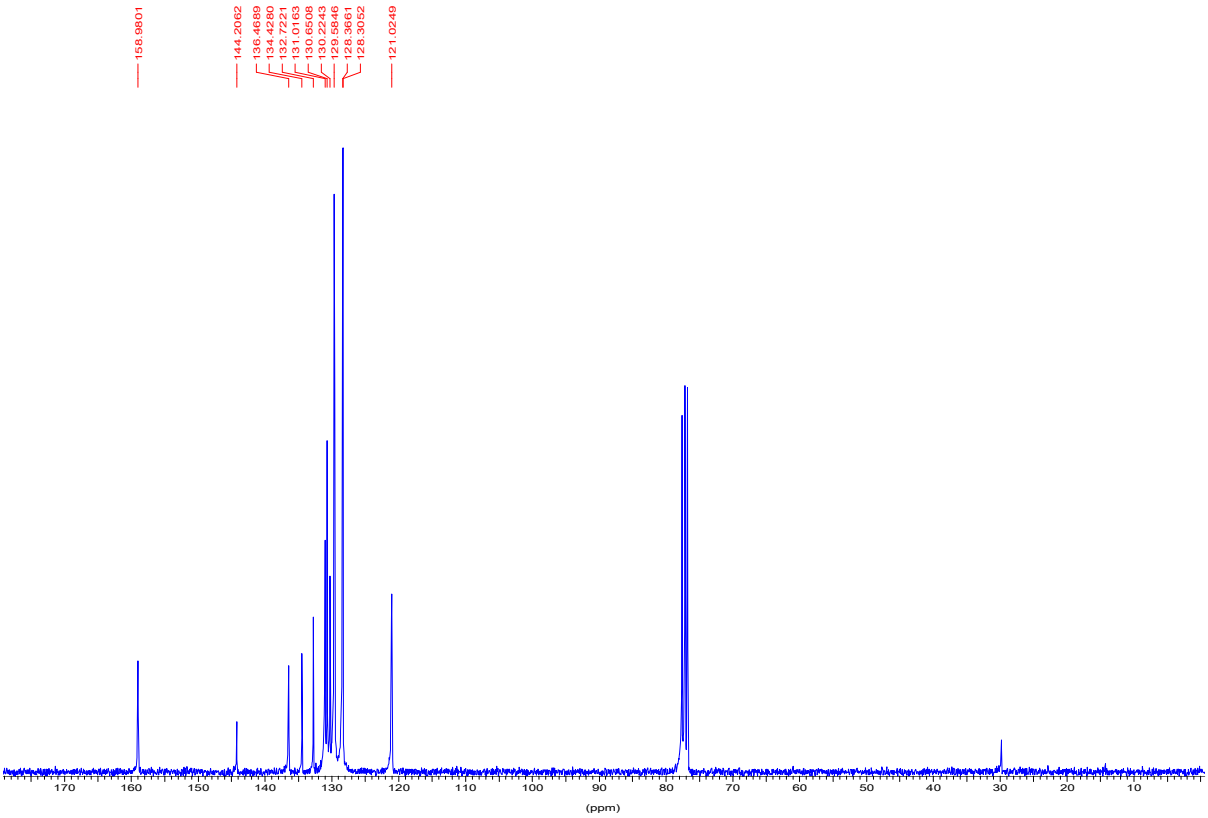
2i, ^{13}C, 100 MHz, $CDCl_3$



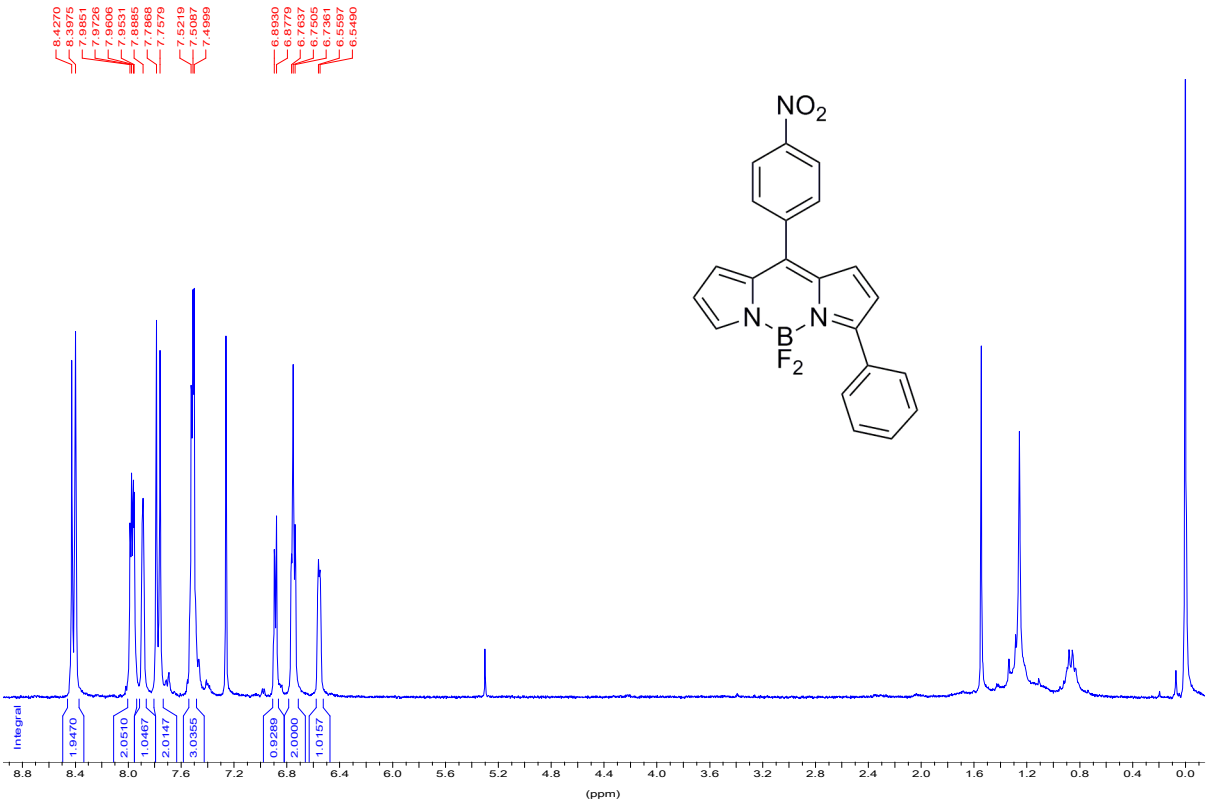
3i, ^{1}H, 300 MHz, $CDCl_3$



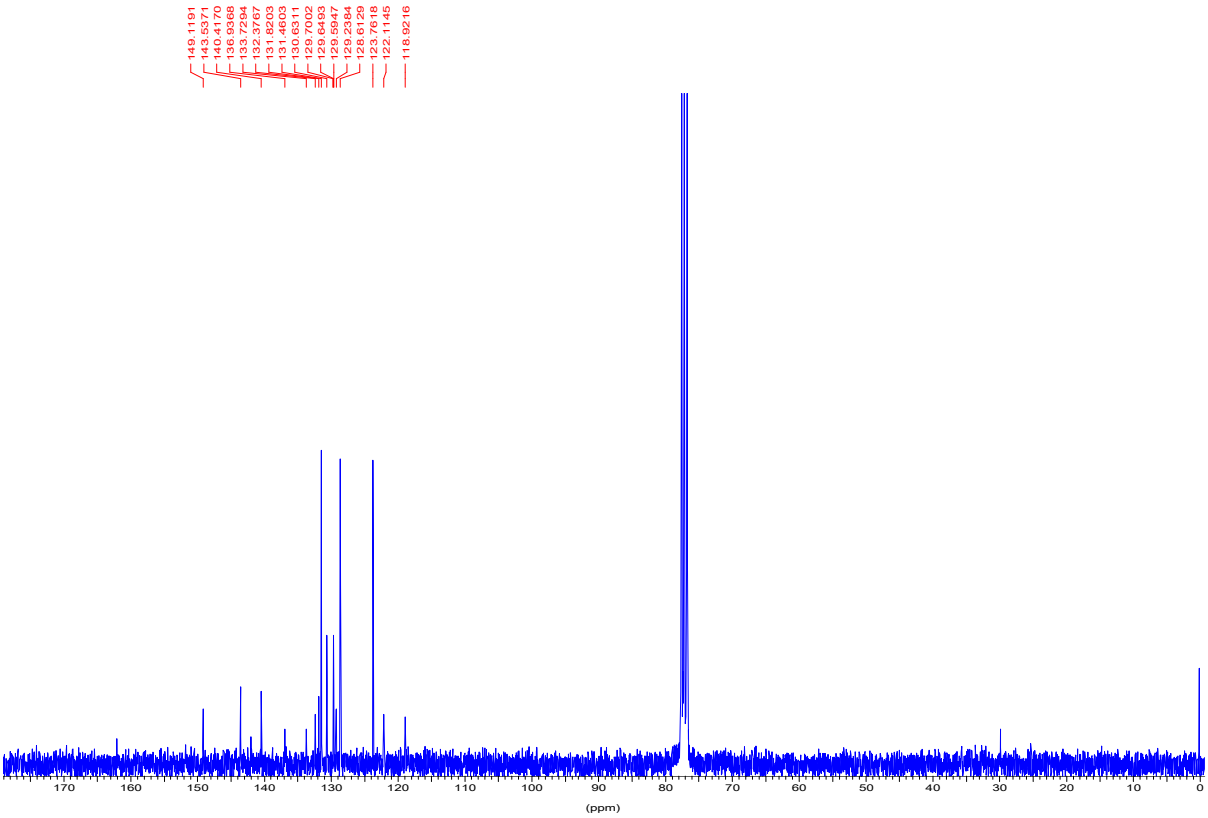
3i, ^{13}C, 75 MHz, $CDCl_3$



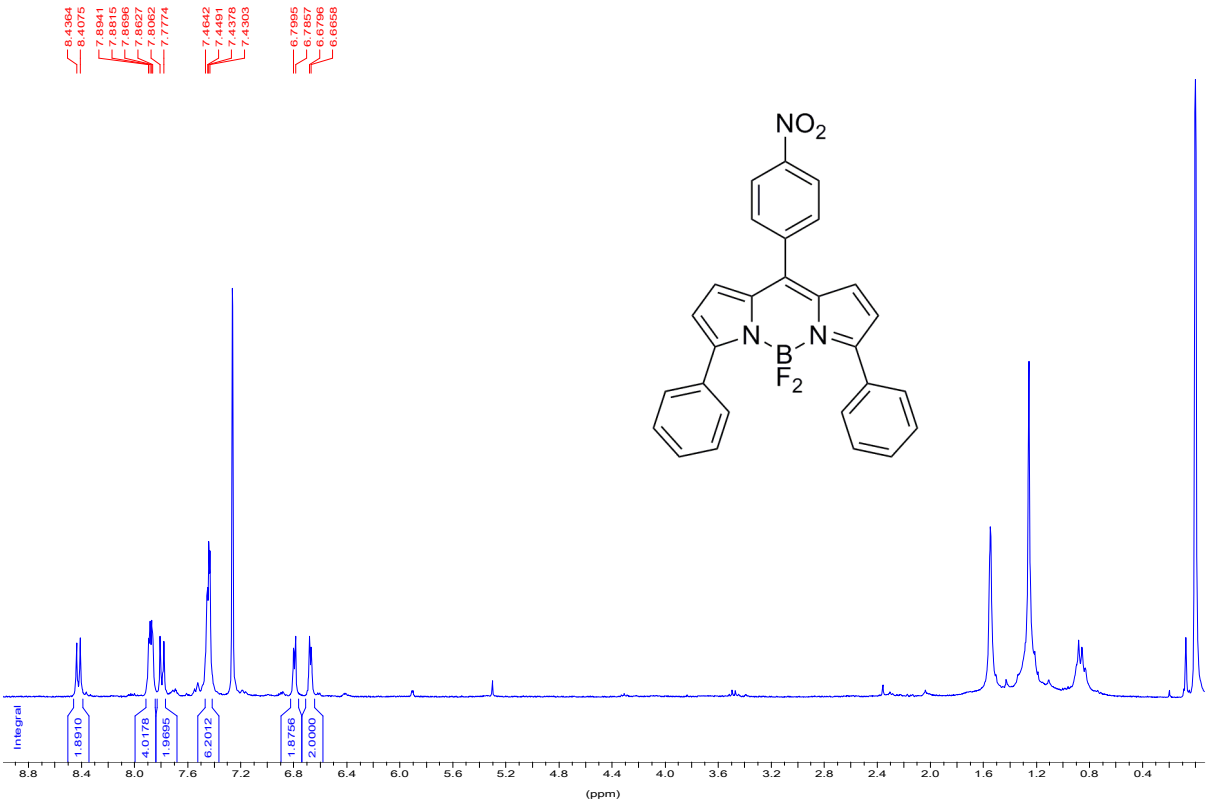
2j, ^{1}H, 300 MHz, $CDCl_3$



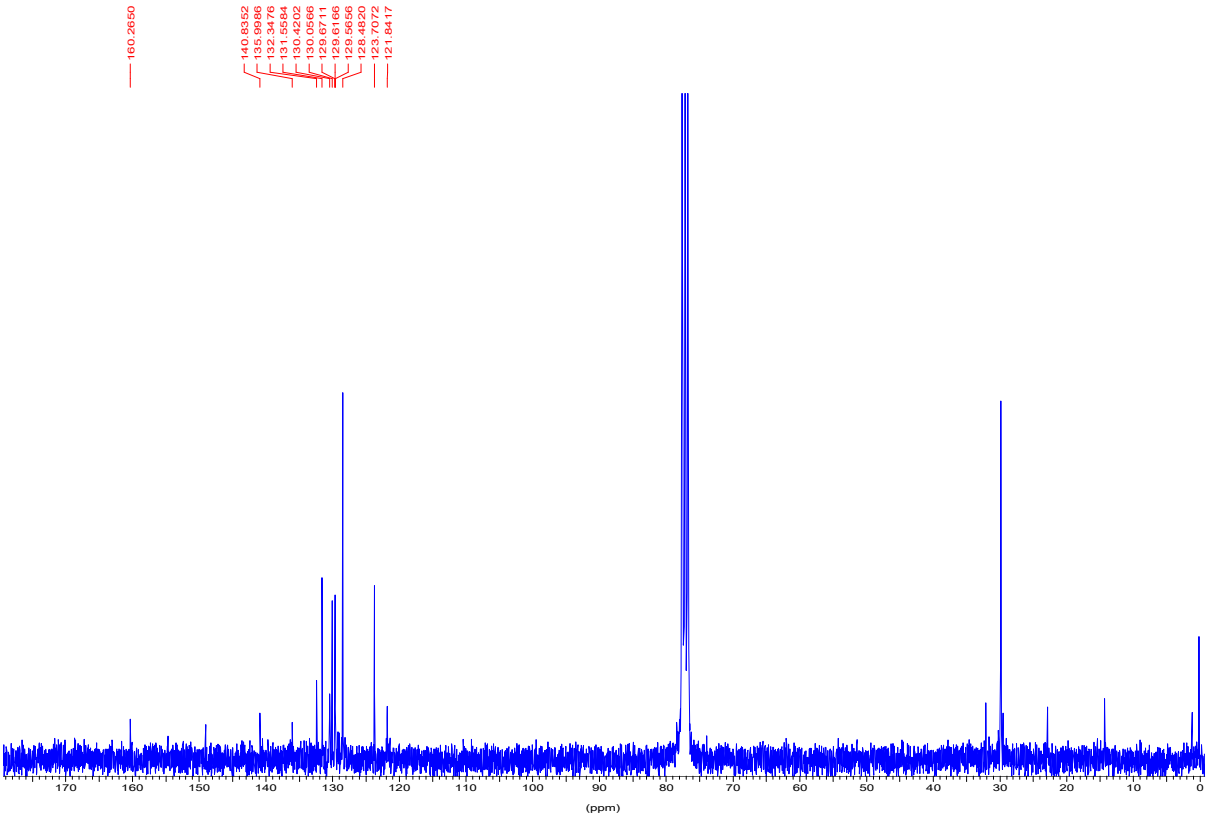
2j, ^{13}C, 75 MHz, $CDCl_3$



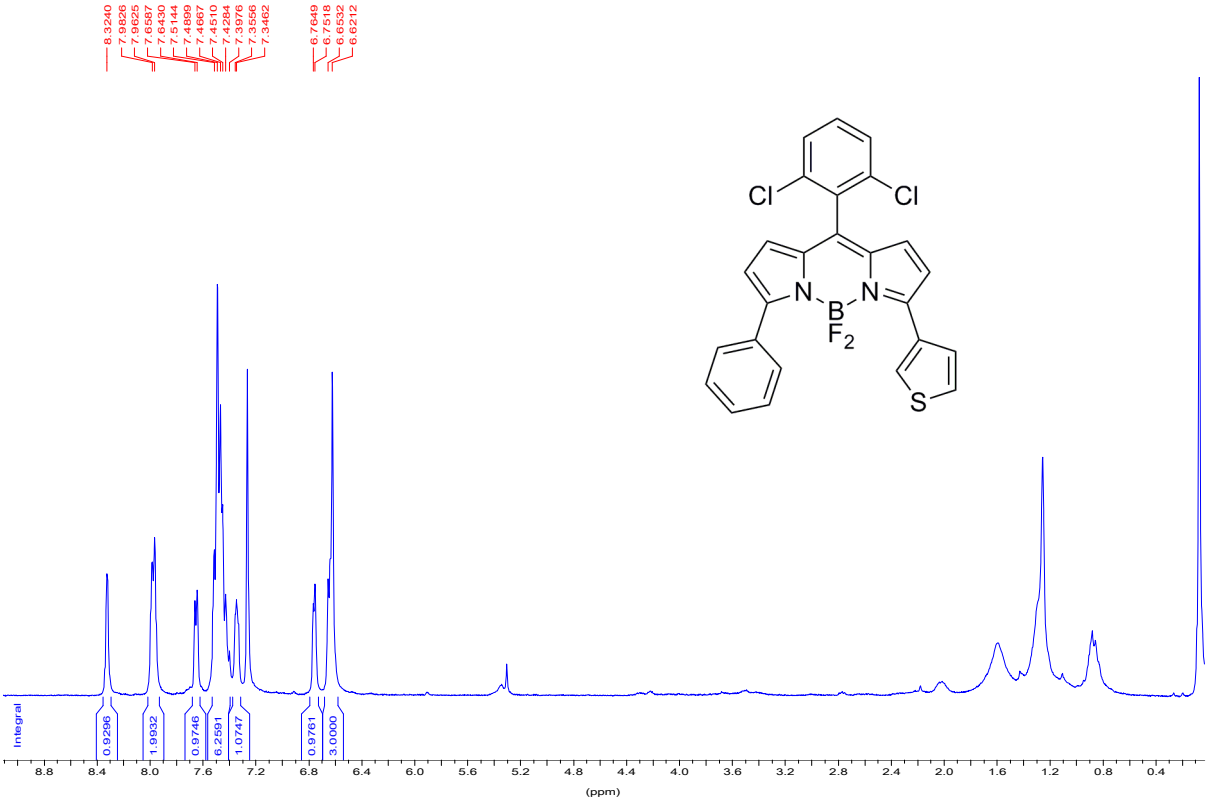
3j, ^{1}H, 300 MHz, $CDCl_3$



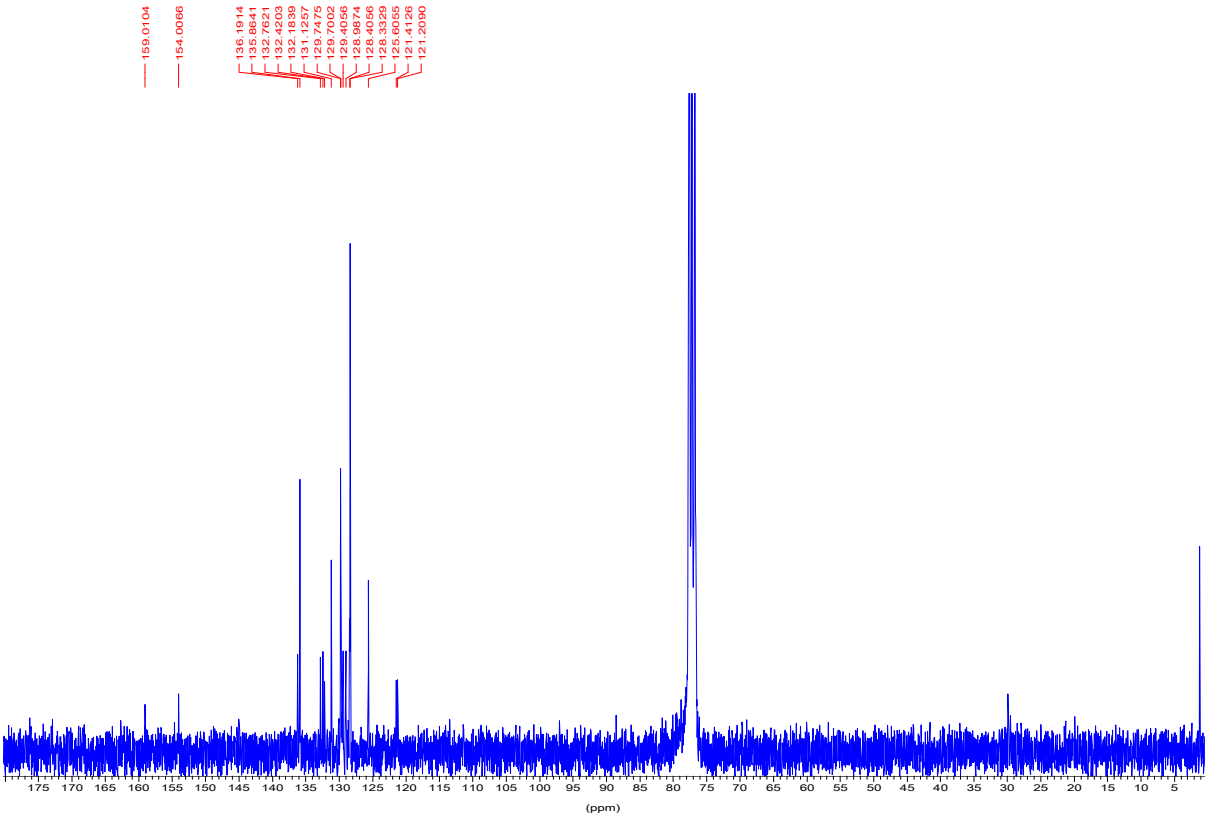
3j, ^{13}C, 75 MHz, $CDCl_3$



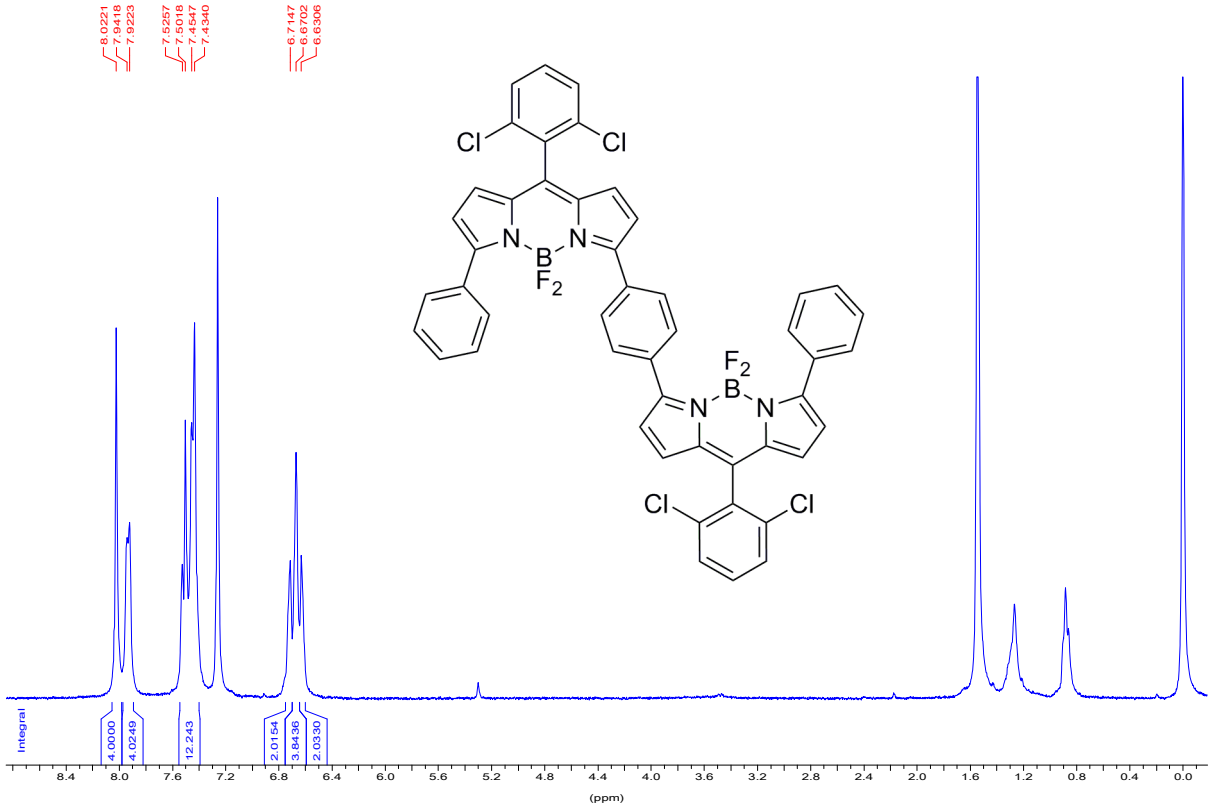
4, ^{1}H, 300 MHz, $CDCl_3$



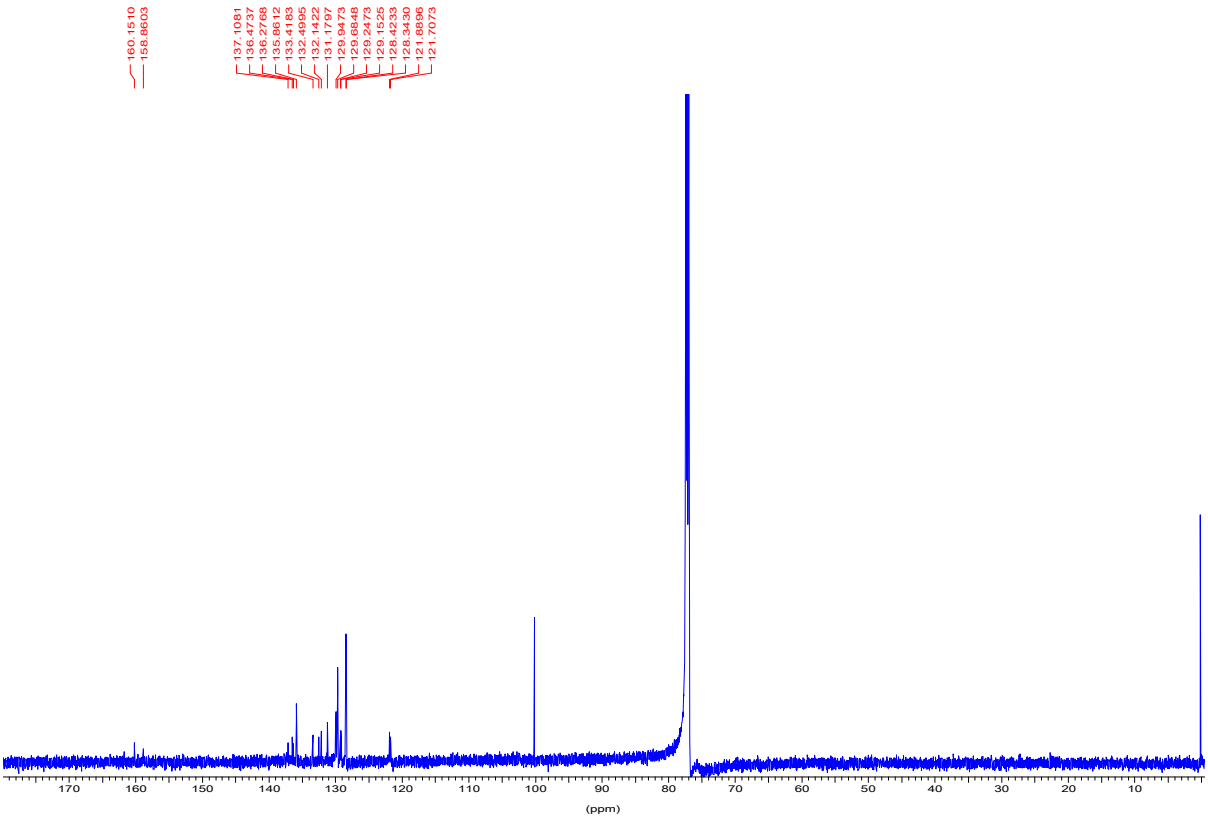
4, ^{13}C, 75 MHz, $CDCl_3$



5, ^{1}H, 300 MHz, $CDCl_3$



5, ^{13}C, 150 MHz, $CDCl_3$



Spectroscopic data

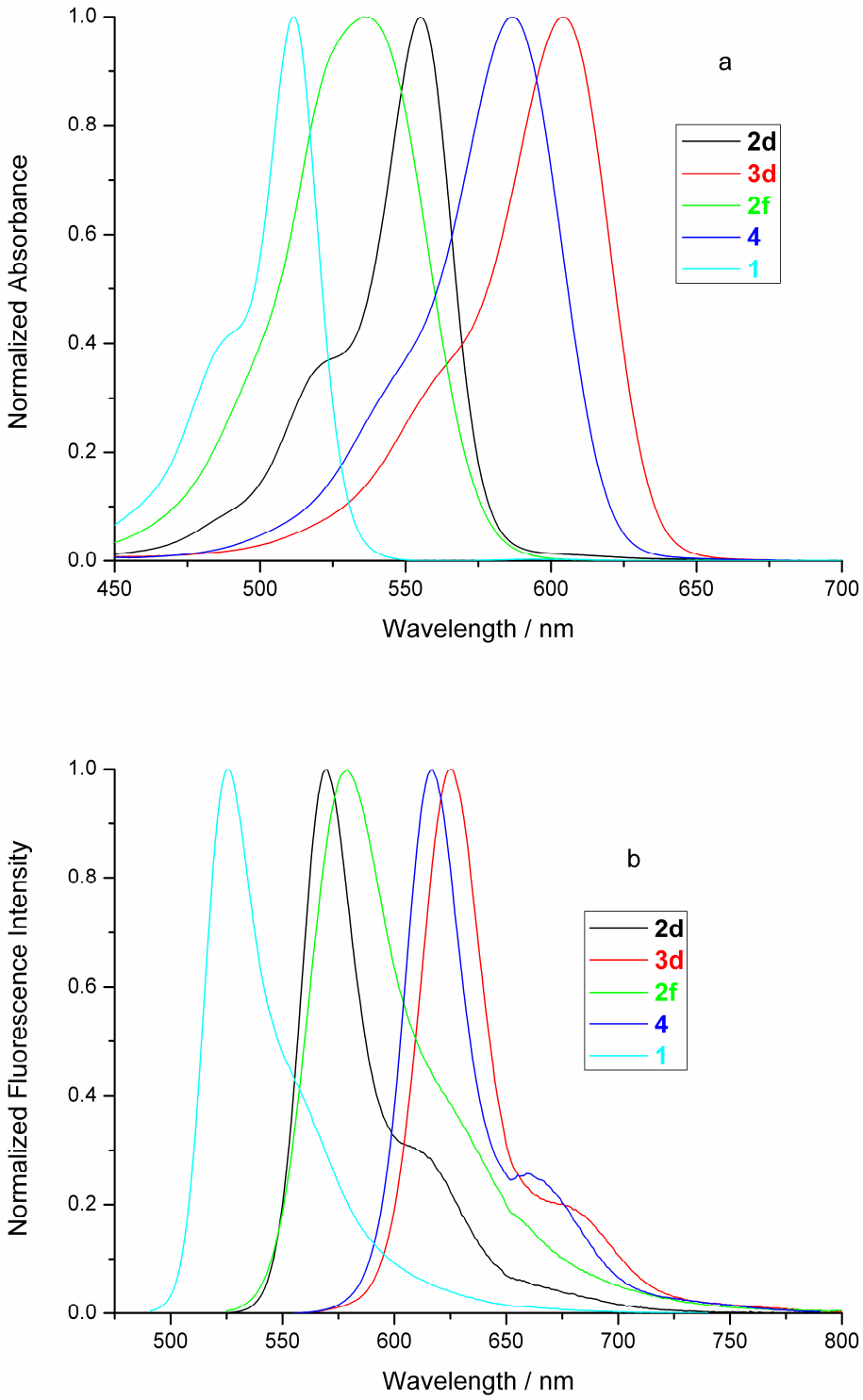


Figure S1 (a) Normalized, visible absorption spectra of a selection of *meso*-(2,6-dichlorophenyl) substituted BODIPY dyes (**1**, **2d**, **2f**, **3d**, **4**) in THF. (b) Corresponding normalized fluorescence emission spectra. Note that merging figures (a) and (b) produces the 'congested' Figure 1.

Table S2 Spectroscopic and fluorescence quantum yield data of bis-BODIPY **5** as a function of solvent. The solvents are listed from top to bottom according to increasing refractive index *n*.

Product	Solvent	λ_{abs}(max) [a] / nm	λ_{em}(max) [b] / nm	$\Delta\bar{\nu}$ [c] / cm^{-1}	Φ [d]
	MeOH	621	707	1959	[e]
	MeCN	612	707	2196	[e]
5	Ethyl acetate	625	708	1876	0.58 ± 0.01
	THF	636	717	1776	0.524 ± 0.003
	Toluene	638	718	1746	0.634 ± 0.004

[a] Absorption maximum.
[b] Fluorescence emission maximum.
[c] Stokes shift (=$1/\lambda_{abs}$(max) – $1/\lambda_{em}$(max)).
[d] Fluorescence quantum yield ± one standard uncertainty. Φ determined vs. cresyl violet in methanol (Φ_r = 0.55) as reference.
[e] Not possible to obtain reliable Φ values due to very limited solubility in the solvents indicated.