Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

A New Synthesis of Symmetric Boraindacene (BODIPY) Dyes

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General Experimental Methods

All reactions were carried out under an atmosphere of dry nitrogen. Glassware was oven-dried prior to use. Unless otherwise indicated, common reagents or materials were obtained from commercial source and used without further purification. All the solvents were used after appropriate distillation or purification.

Flash column chromatography was performed using silica gel 60 (230-400 mesh). Analytical thin layer chromatography (TLC) was carried out on Merck silica gel plates with QF-254 indicator and visualized by UV. Fluorescence spectra were obtained on a Varian Cary Eclipse fluorescence spectrophotometer at room temperature. Absorbance spectra were obtained on a Varian 100 Bio UV-Vis spectrophotometer at room temperature.

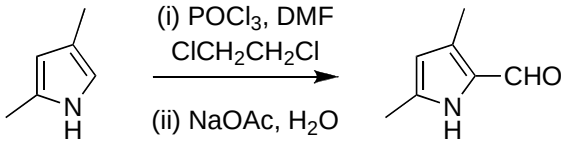
^{1}H and ^{13}C spectra were recorded on a Varian 300 (300 MHz ^{1}H; 75 MHz ^{13}C) or Varian 500 (500 MHz ^{1}H; 125 MHz ^{13}C) spectrometer at room temperature. Chemical shifts were reported in ppm relative to the residual $CDCl_3$ (δ 7.24 ppm ^{1}H; δ 77.0 ppm ^{13}C). ^{19}F NMR were acquired on a Varian 300 (300 MHz ^{1}H; 282 MHz ^{19}F) spectrometer. $CFCl_3$ was used as an external reference for the ^{19}F NMR spectra. H_3PO_4 was used as an external reference for the ^{31}P NMR spectra. Coupling constants (*J*) were reported in Hertz.

Photophysical Properties and Determination of Quantum Yields

Steady-state fluorescence spectroscopic studies were performed on a Cary Eclipse fluorometer. The slit width was 5 nm for both excitation and emission. The relative quantum yields of the samples were obtained by comparing the area under the corrected emission spectrum of the test sample with that of a standard. The quantum efficiencies of fluorescence were obtained from multiple measurements (N=3) with the following equation:

$$\Phi_x = \Phi_{st} (I_x/I_{st}) (A_{st}/A_x) (\eta_x^2/\eta_{st}^2)$$

Where Φ_{st} is the reported quantum yield of the standard, **I** is the area under the emission spectra, **A** is the absorbance at the excitation wavelength and η is the refractive index of the solvent used, measured on a pocket refractometer from ATAGO. **X** subscript denotes test sample, and **st** denotes standard.

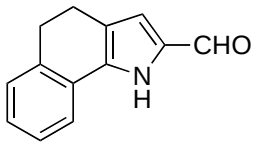


1a

Typical Procedure for the Synthesis of Pyrrole-2-carboxaldehyde[1]

$POCl_3$ (5.9 mL, 63.0 mmol) was added dropwise to DMF (4.9 mL, 63.0 mmol) at 0 ^oC. The mixture was warmed to room temperature and stirred for 15 min. The ice bath was replaced to cool the mixture back to 0 °C, then 30 mL of 1,2-dichloroethane was added to the mixture. A solution of 2,4-dimethyl pyrrole (5.0 g, 52.5 mmol) in 50 mL of 1,2-dichloroethane was added dropwise over 20 min at 0^oC. After the addition was complete, the reaction mixture was refluxed for 30 min and then cooled to room temperature. A solution of NaOAc (23.7 g, 289 mmol) in 100 mL of water was added. The reaction mixture was again refluxed for 30 min. The cooled mixture was washed with water (1 x 100 mL), saturated Na_2CO_3 solution (2 x 50 mL) and brine (1 x 50 mL). The organic layer was dried over Na_2SO_4 and the solvents were removed under reduced pressure. The residue was purified by flash chromatography (SiO_2, 20 % EtOAc/Hexanes) to afford the pure product as a light yellow solid (5.8 g, 89 %). ^1H NMR (300 MHz, $CDCl_3$) δ 9.96 (br, 1H), 9.44 (s, 1H), 5.84 (d, 1H, J = 2.6 Hz), 2.30 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.9, 138.4, 134.7, 128.7, 112.0, 13.2, 10.6.

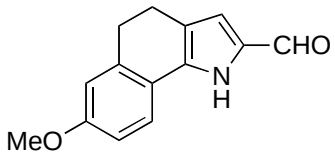
1b-**1h** were prepared using similar method as described for **1a**.



1b

4,5-Dihydro-1H-benzo[g]indole-2-carbaldehyde (1b)

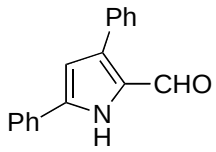
Yellow solid (910 mg, 85 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.74 (br, 1H), 9.48 (s, 1H), 7.71 (d, 1H, *J* = 7.4 Hz), 7.32-7.19 (m, 3H), 6.84 (d, 1H, *J* = 2.0 Hz), 2.96 (t, 2H, *J* = 7.5 Hz), 2.78 (t, 2H, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 137.2, 136.7, 132.5, 128.5, 128.0, 127.4, 127.0, 122.7, 121.7, 120.6, 29.6, 21.3. MS (ESI) m/z calcd for $(M+H)^+$ $C_{13}H_{12}NO$ 198.09; found 198.09.



1c

7-Methoxy-4,5-dihydro-1H-benzo[g]indole-2-carbaldehyde (1c)

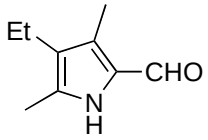
Light green solid (345 mg, 100 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.59 (br, 1H), 9.39 (s, 1H), 7.61 (d, 1H, *J* = 8.2 Hz), 6.82-6.78 (m, 3H), 3.81 (s, 3H), 2.91 (t, 2H, *J* = 7.5 Hz), 2.74 (t, 2H, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.8, 159.6, 139.3, 137.1, 132.0, 123.1, 121.4, 120.9, 120.5, 114.5, 112.0, 55.3, 30.0, 21.3. MS (ESI) m/z calcd for $(M+H)^+$ $C_{14}H_{14}NO_2$ 228.10; found 228.10.



1d

3,5-Diphenyl-1H-pyrrole-2-carbaldehyde (1d)

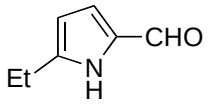
White solid (290 mg, 86 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.04 (br, 1H), 9.63 (s, 1H), 7.70-7.67 (m, 2H), 7.55-7.52 (m, 2H), 7.48-7.33 (m, 6H), 6.72 (d, 1H, *J* = 2.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 179.4, 139.1, 138.5, 133.5, 130.4, 129.2, 129.1, 129.0, 128.8, 128.7, 127.9, 125.3, 109.0. MS (ESI) m/z calcd for $(M+H)^+$ $C_{17}H_{14}NO$ 248.11; found 248.11.



1e

4-Ethyl-3,5-dimethyl-1H-pyrrole-2-carbaldehyde (1e)

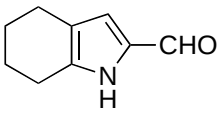
Brown solid (1.1 g, 85 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.08 (br, 1H), 9.42 (s, 1H), 2.36 (q, 2H, *J* = 7.5 Hz), 2.25 (s, 3H), 2.24 (s, 3H), 1.03 (t, 3H, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.5, 135.9, 132.2, 127.8, 124.8, 16.9, 15.0, 11.4, 8.7. MS (ESI) m/z calcd for $(M+H)^+$ $C_9H_{14}NO$ 152.11; found 152.10.



1f

5-Ethyl-1H-pyrrole-2-carbaldehyde (1f)

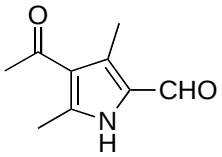
Red solid (1.0 g, 78 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.58 (br, 1H), 9.34 (s, 1H), 6.92-6.90 (m, 1H), 6.09-6.07 (m, 1H), 2.72 (q, 2H, *J* = 7.5 Hz), 1.26 (t, 3H, *J* =7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.2, 145.4, 131.8, 123.4, 108.8, 21.0, 13.1. MS (ESI) m/z calcd for $(M+H)^+$ $C_7H_{10}NO$ 124.08; found 124.07.



1g

4,5,6,7-Tetrahydro-1H-indole-2-carbaldehyde (1g)

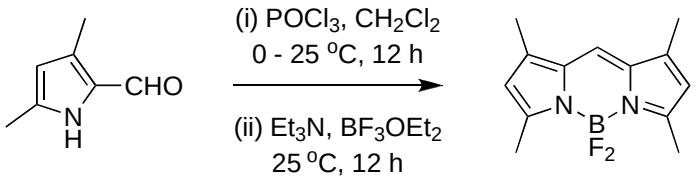
Yellow solid (960 mg, 78 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.21 (br, 1H), 9.29 (s, 1H), 6.69 (d, 1H, *J* = 2.4 Hz), 2.67 (t, 2H, *J* = 6.1 Hz), 2.51 (t, 2H, *J* = 6.0 Hz), 1.84-1.69 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 138.9, 131.2, 121.2, 121.1, 23.3, 23.0, 22.6 (2C: 22.61, 22.59). MS (ESI) m/z calcd for $(M+H)^+$ $C_9H_{12}NO$ 150.09; found 150.09.



1h

4-Acetyl-3,5-dimethyl-1H-pyrrole-2-carbaldehyde (1h)

Light yellow solid (481 mg, 40 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.20 (br, 1H), 9.62 (s, 1H), 2.58 (s, 3H), 2.56 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.9, 177.6, 143.1, 134.6, 128.2, 123.7, 31.3, 15.2, 11.4. MS (ESI) m/z calcd for $(M+H)^+$ $C_9H_{12}NO_2$ 166.09; found 166.09.

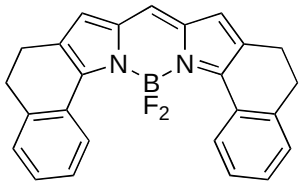


1a **2a**

Typical Procedure for the Synthesis of Symmetric BODIPYs

3,5-Dimethyl-1H-pyrrole-2-carbaldehyde **1a** (246 mg, 2 mmol) was dissolved in 10 mL CH_2Cl_2 and $POCl_3$ (0.22 mL, 2.4 mmol) was added dropwise over 1 min at 0 ^oC. The solution was warmed to room temperature slowly and stirred for 12 h. The mixture was cooled to 0 ^oC and Et_3N (1.4 mL, 10 mmol) was added dropwise over 5 min. After stirring for 15 min, BF_3OEt_2 (2.0 mL, 16 mmol) was added dropwise to the solution over 5 min. The reaction mixture was warmed to room temperature and stirred for 12 h. The mixture was passed through a short pad of silica gel eluting with CH_2Cl_2 to remove the polar impurities. The solvents were removed under reduced pressure. The residue was dissolved in CH_2Cl_2 and water was added, and the mixture was stirred at room temperature overnight. (to decompose excess BF_3OEt_2 and other impurities). The organic layer was washed with water, brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (5 % EtOAc/hexanes) to give the pure product **2a** (229 mg, 92 %) as a red solid. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.01 (s, 1H), 6.02 (s, 2H), 2.51 (s, 6H), 2.22 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.7, 141.2, 133.4, 120.0, 119.0, 14.6, 11.2; ^{19}F NMR ($CDCl_3$, 282 MHz) δ 30.68 (q, J = 33.5 Hz). HRMS (ESI) m/z calcd for $(M+H)^+$ $C_{13}H_{16}BF_2N_2$ 249.1375; found 249.1373.

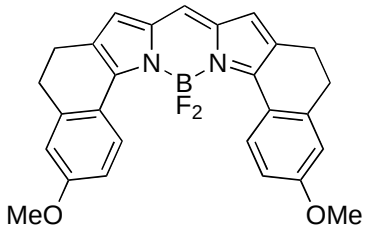
2b-**2h** were prepared using similar methods as described for **2a**.



2b

BODIPY 2b

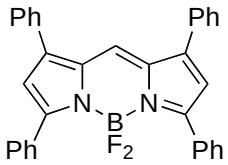
Green solid (360 mg, 91 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73 (d, 2H, *J* = 8.0 Hz), 7.45-7.39 (m, 2H), 7.33-7.23 (m, 4H), 6.98 (s, 1H), 6.76 (s, 2H), 2.90 (t, 4H, *J* = 7.0 Hz), 2.72 (t, 4H, *J* = 7.0 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 140.5, 136.3, 133.1, 129.7, 128.3, 128.2, 128.1, 127.5, 124.8, 124.1, 30.5, 22.3; ^{19}F NMR ($CDCl_3$, 282 MHz) δ 39.67 (q, *J* = 33.6 Hz). MS (MALDI) m/z calcd for M^+ $C_{25}H_{19}BF_2N_2$ 396.16; found 395.88.



2c

BODIPY 2c

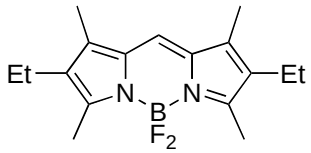
Blue solid (194 mg, 85 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (d, 2H, *J* = 9.0 Hz), 6.95 (dd, 2H, *J* = 9.0, 2.8 Hz), 6.86 (s, 1H), 6.78 (d, 2H, *J* = 2.8 Hz), 6.69 (s, 2H), 3.85 (s, 6H), 2.87 (t, 4H, *J* = 6.9 Hz), 2.70 (t, 4H, *J* = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6, 151.9, 142.8, 135.9, 131.9, 129.9 (t, *J* = 11.1 Hz), 124.2, 122.2, 121.4, 114.3, 112.4, 55.3, 30.8, 22.3; ^{19}F NMR ($CDCl_3$, 282 MHz) δ 39.15 (q, *J* = 33.6 Hz). MS (MALDI) m/z calcd for M^+ $C_{27}H_{23}BF_2N_2O_2$ 456.18; found 455.88.



2d

BODIPY 2d

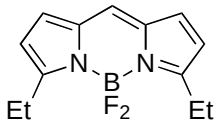
Green solid (52 mg, 21 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98-7.95 (m, 4H), 7.54-7.42 (m, 17H), 6.73 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8, 145.7, 134.4, 133.3, 132.3, 129.7, 129.4 (t, *J* = 3.5 Hz), 129.1, 128.7 (2C), 128.2, 127.7, 119.0; ^{19}F NMR ($CDCl_3$, 282 MHz) δ 45.58 (q, *J* = 33.5 Hz). MS (MALDI) m/z calcd for M^+ $C_{33}H_{23}BF_2N_2$ 496.19; found 495.93.



2e

BODIPY 2e

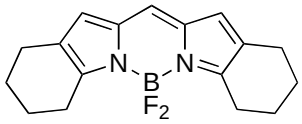
Organge solid (227 mg, 75 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (s, 1H), 2.47 (s, 6H), 2.36 (q, 4H, *J* = 7.5 Hz), 2.14 (s, 6H), 1.04 (t, 6H, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 136.6, 132.4, 131.6, 118.5, 17.3, 14.6, 12.5, 9.4; ^{19}F NMR ($CDCl_3$, 282 MHz) δ 30.93 (q, *J* = 33.6 Hz). MS (MALDI) m/z calcd for M^+ $C_{17}H_{23}BF_2N_2$ 304.19; found 303.96.



2f

BODIPY 2f

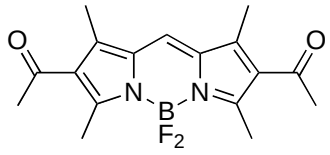
Orange solid (70 mg, 28 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (s, 1H), 6.94 (d, 2H, *J* = 4.2 Hz), 6.32 (d, 2H, *J* = 4.2 Hz), 3.02 (q, 4H, *J* = 7.5 Hz), 1.31 (t, 6H, *J* = 7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 134.4, 130.1, 127.1, 117.4, 22.0, 12.6; ^{19}F NMR ($CDCl_3$, 282 MHz) δ 31.94 (q, *J* = 33.4 Hz). MS (MALDI) m/z calcd for M^+ $C_{13}H_{15}BF_2N_2$ 248.13; found 247.85.



2g

BODIPY 2g

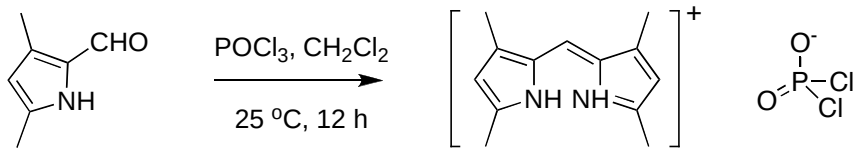
Red solid (65 mg, 22 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.89 (s, 1H), 6.59 (s, 2H), 3.01 (t, 4H, *J* = 6.2 Hz), 2.52 (t, 4H, *J* = 6.2 Hz), 1.86-1.78 (m, 4H), 1.76-1.68 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0, 134.0, 129.3, 125.9, 125.3, 24.7, 23.1, 22.8, 22.3; ^{19}F NMR ($CDCl_3$, 282 MHz) δ 27.29 (q, *J* = 33.5 Hz). MS (MALDI) m/z calcd for M^+ $C_{17}H_{19}BF_2N_2$ 300.16; found 299.91.



2h

BODIPY 2h

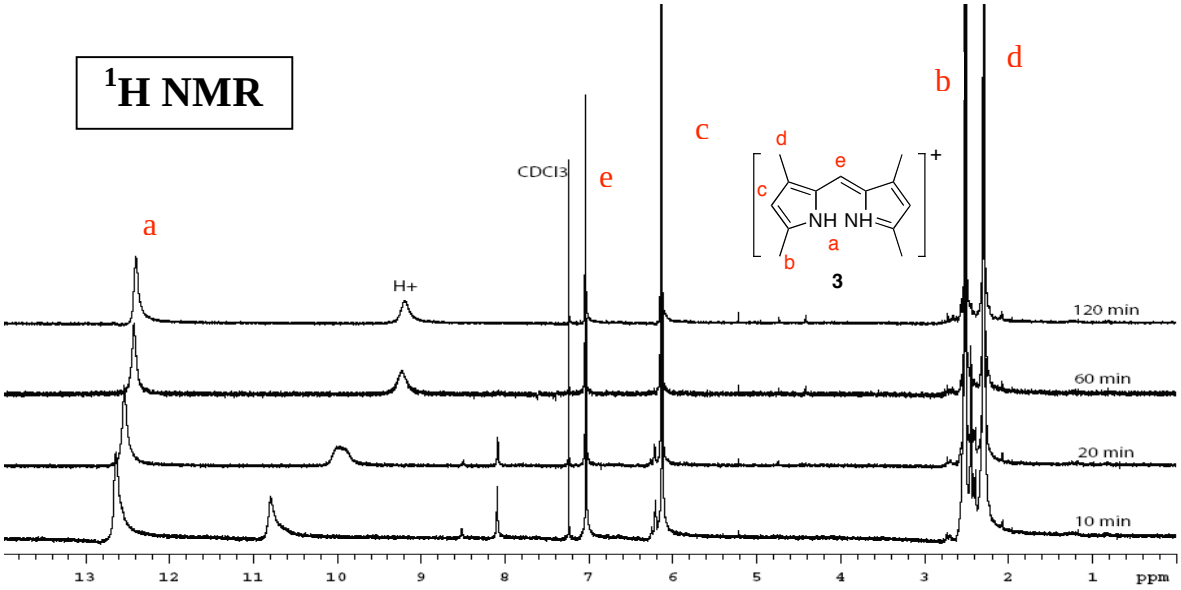
Messy reaction, obtained complex mixtures.

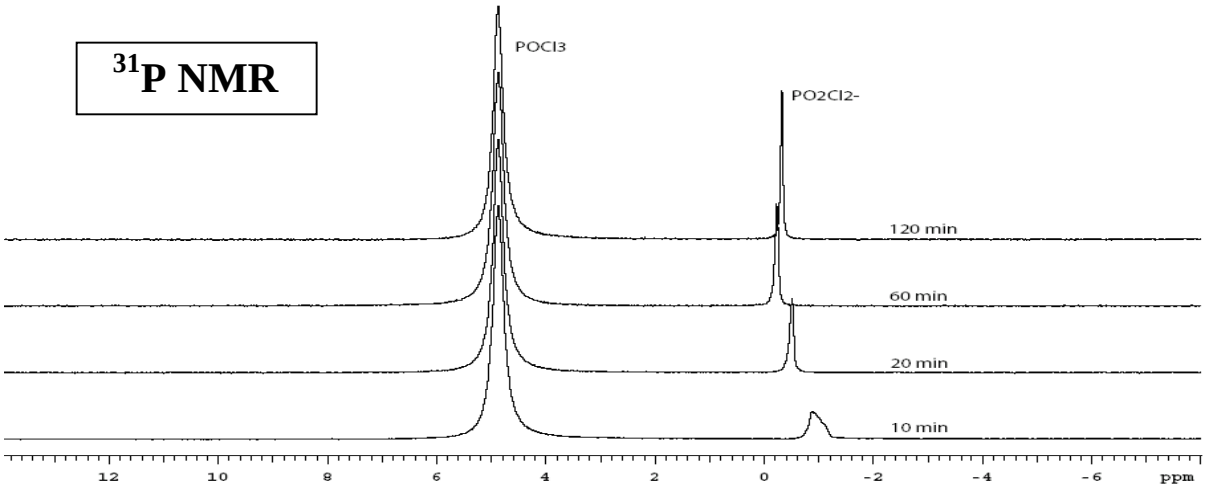


1a **3**

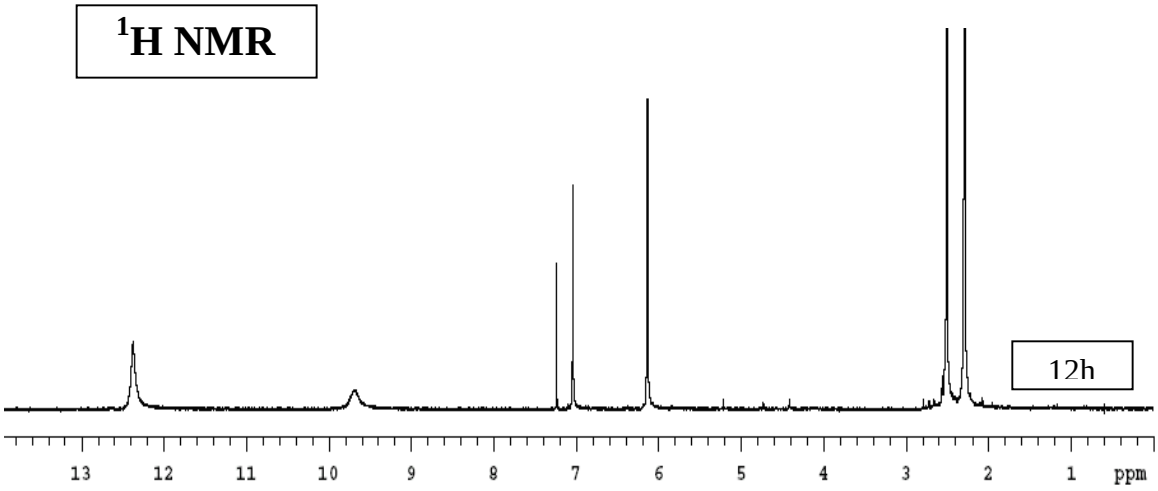
NMR and MS Study of the Self-condensation Reaction:

Compound **1a** (25 mg, 0.2 mmol) was dissolved in 1 mL of $CDCl_3$ and then $POCl_3$ (50 μL) was added. The reaction was monitored by ^{1}H, ^{13}C and ^{31}P over 10 min intervals at room temperature.

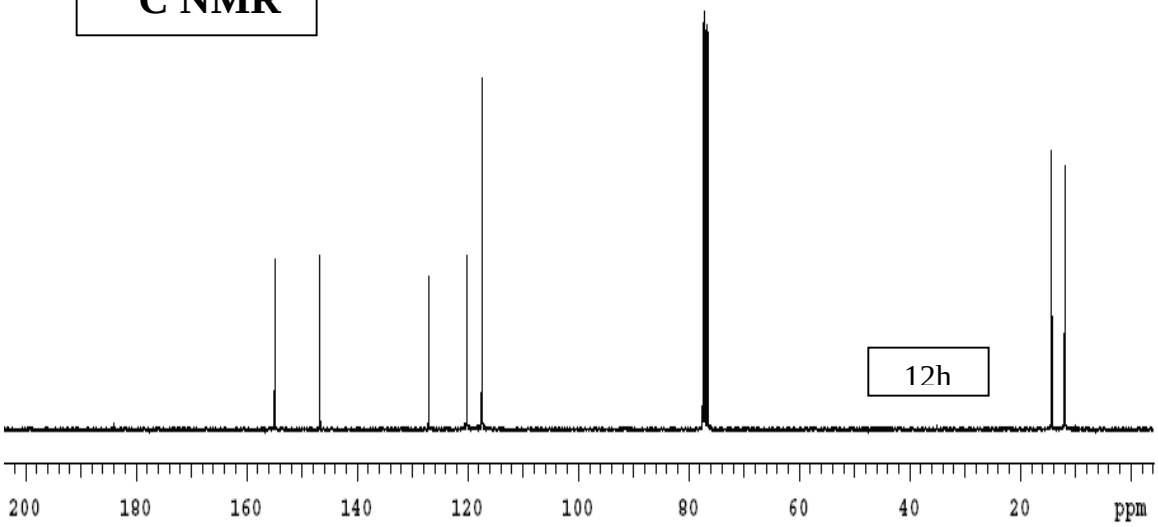


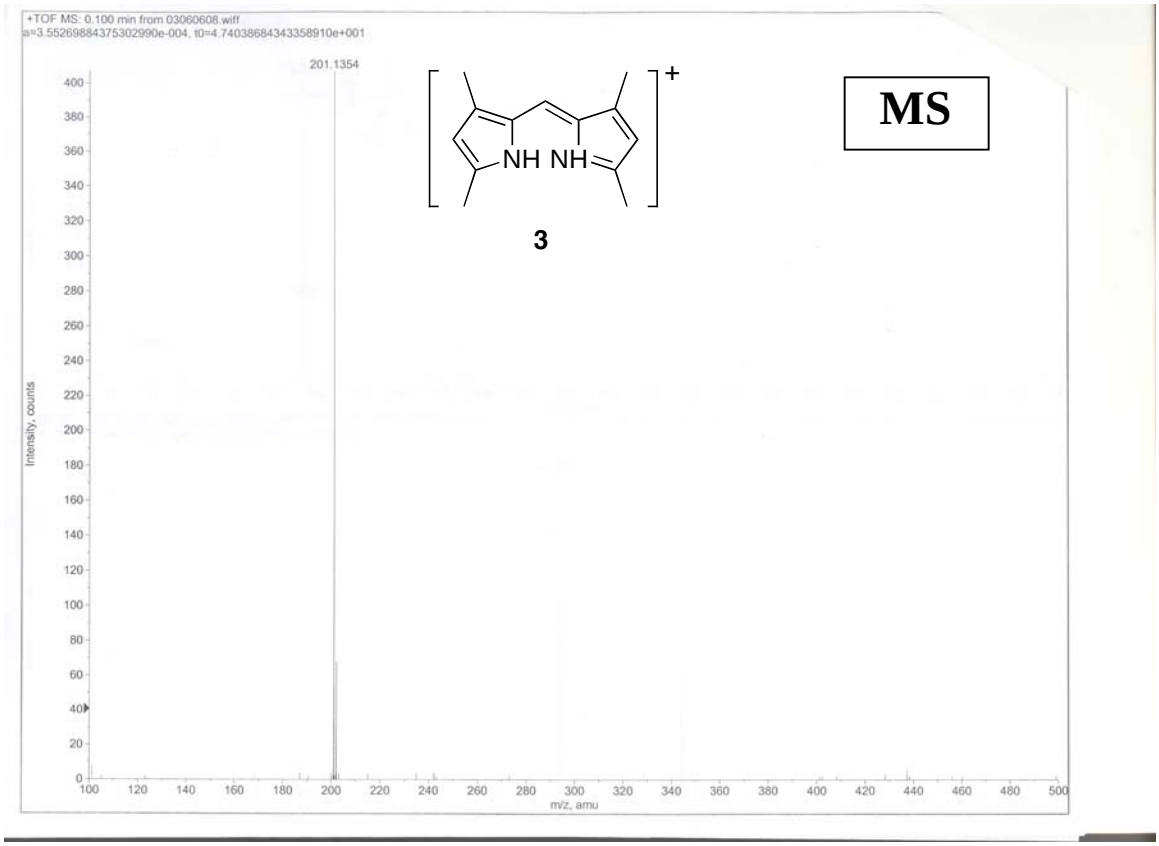


^{1}H NMR



^{13}C NMR

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m/z, amu
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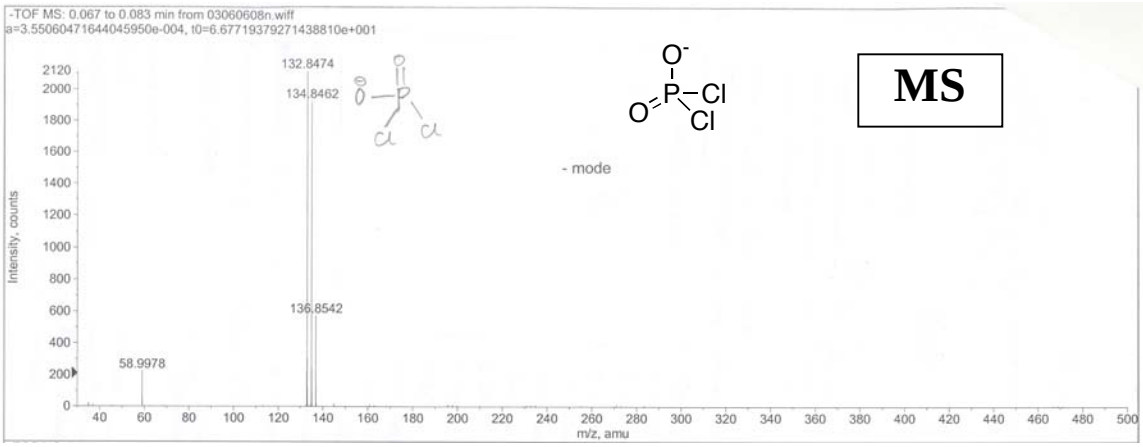
+
3
MS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132.8474
134.8462
136.8542
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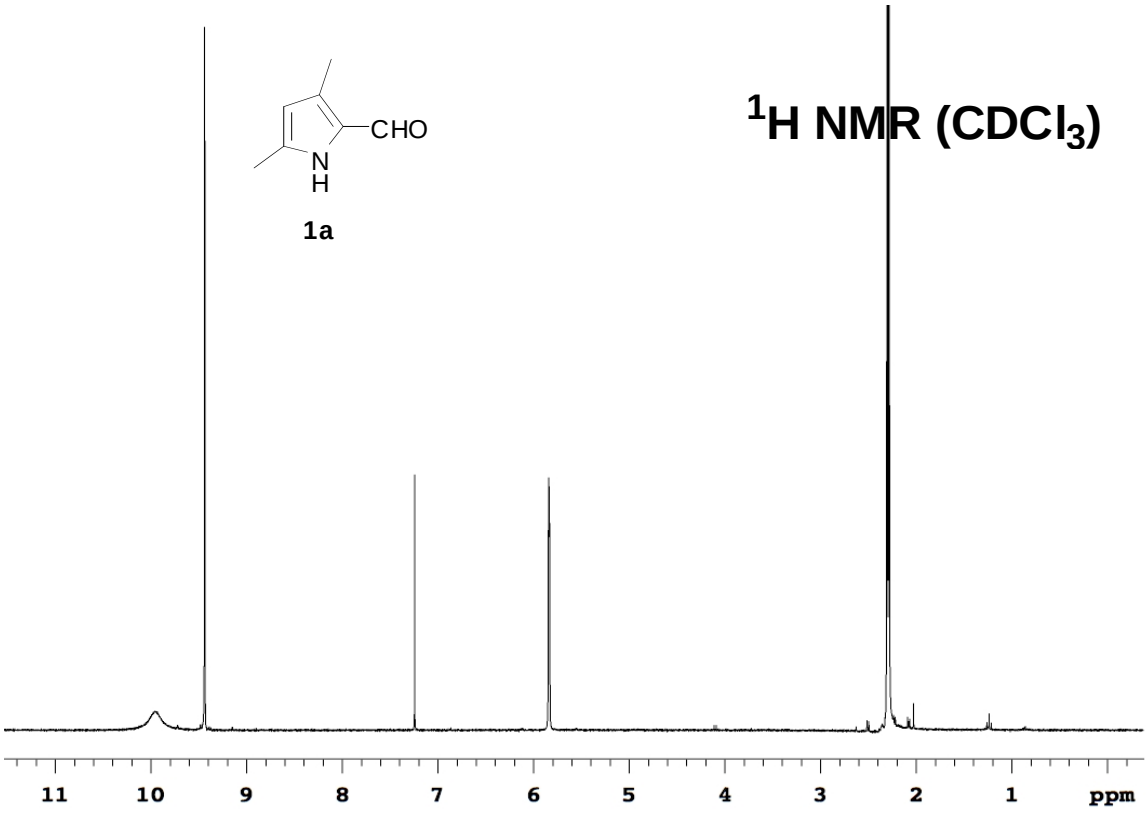
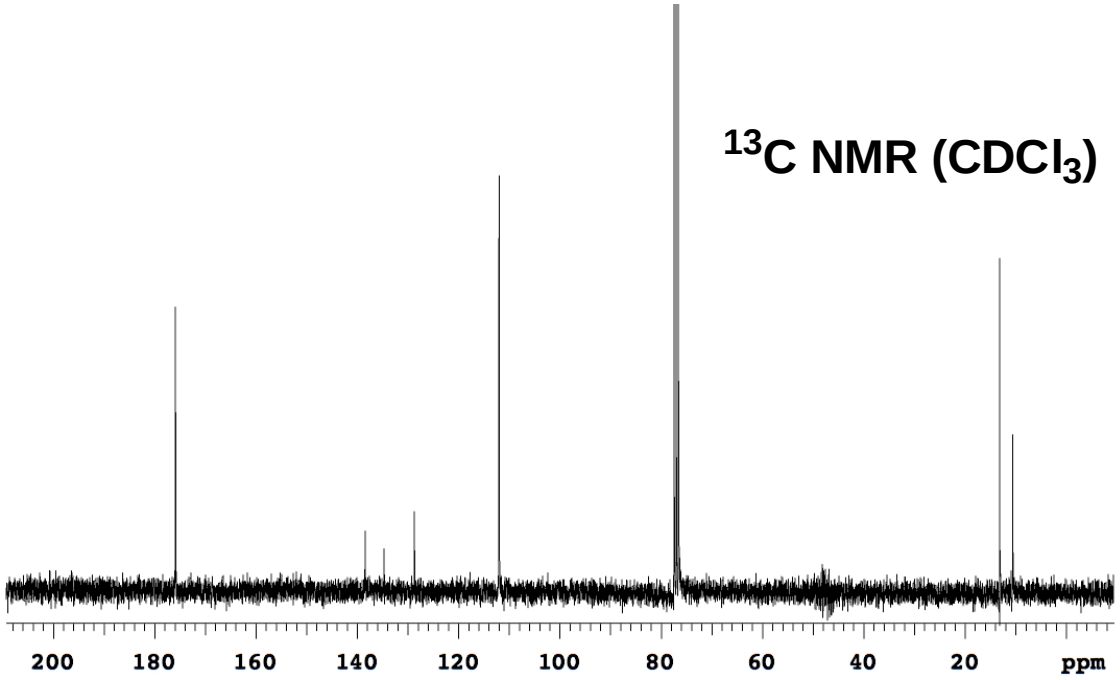
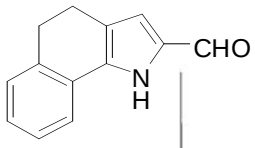
- mode
Intensity, counts
m/z, amu
MS

References:

1. R. Silverstein, E. Ryskiewicz and C. Willard, *Org. Synth.*, 1963, **4**, 831-833.

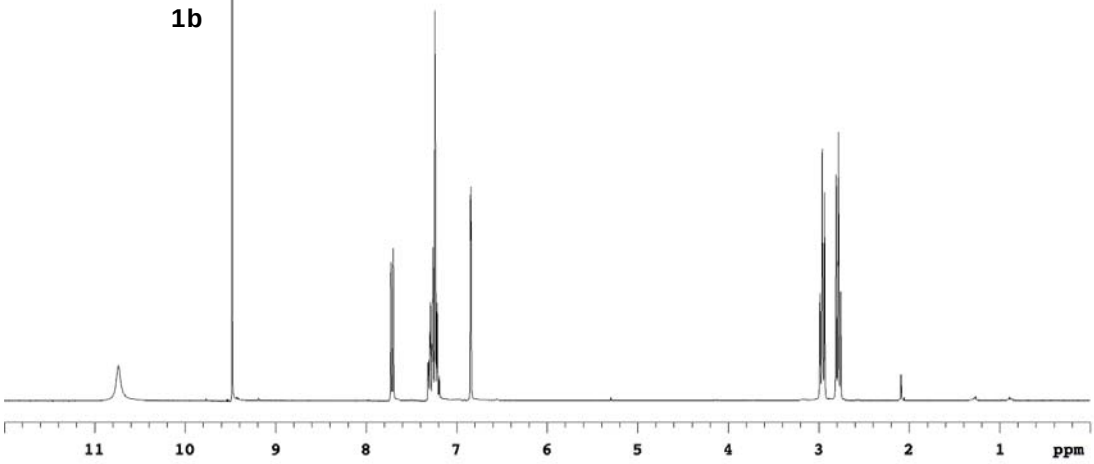

CHO
N
H
1a
^{1}H NMR (CDCl$_3$)
11
10
9
8
7
6
5
4
3
2
1
ppm


^{13}C NMR (CDCl$_3$)
200
180
160
140
120
100
80
60
40
20
ppm



1b

^{1}H NMR ($CDCl_3$)



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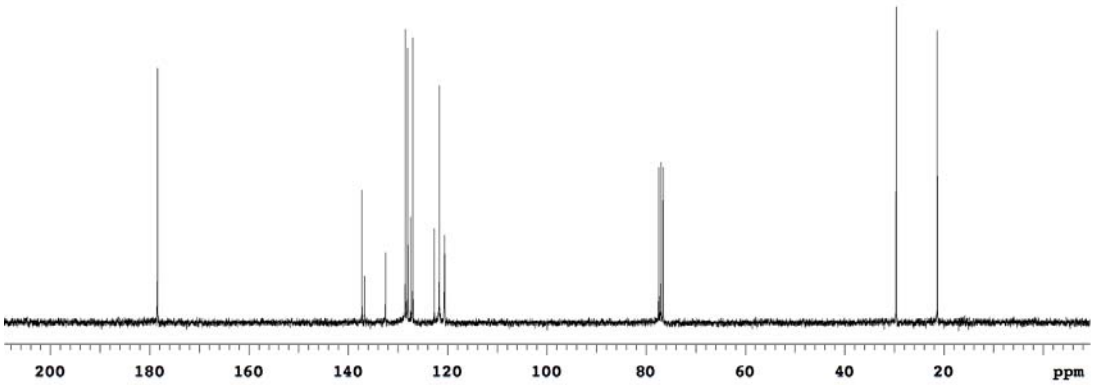
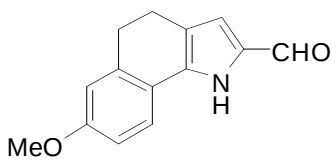
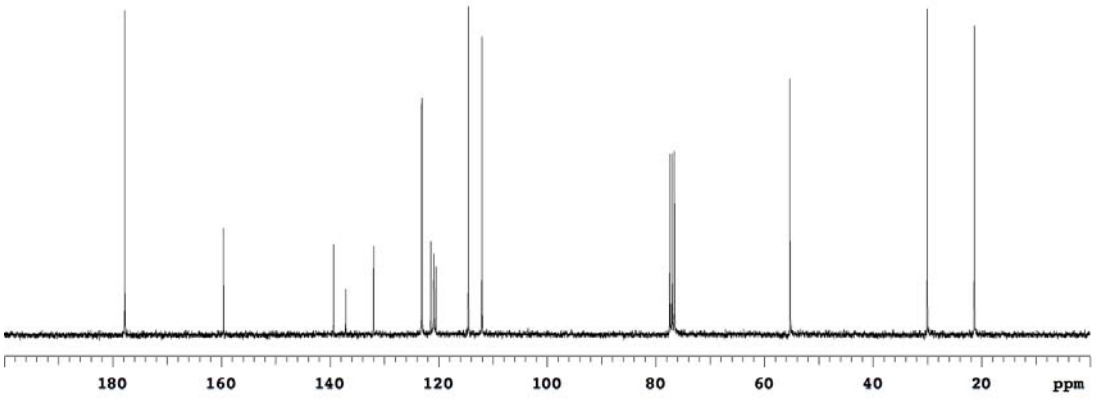


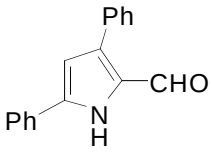


1c

^{1}H NMR ($CDCl_3$)

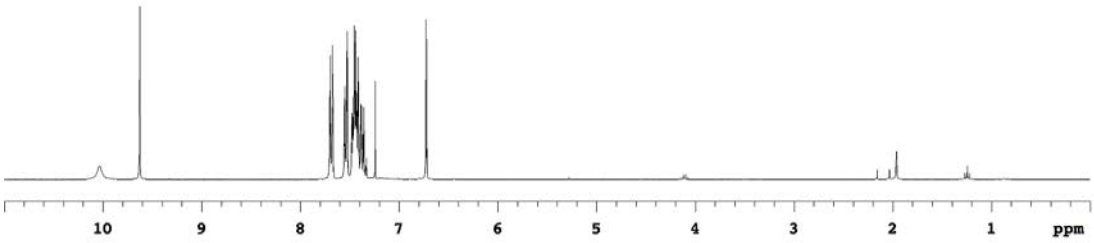
^{13}C NMR ($CDCl_3$)





1d

^{1}H NMR ($CDCl_3$)



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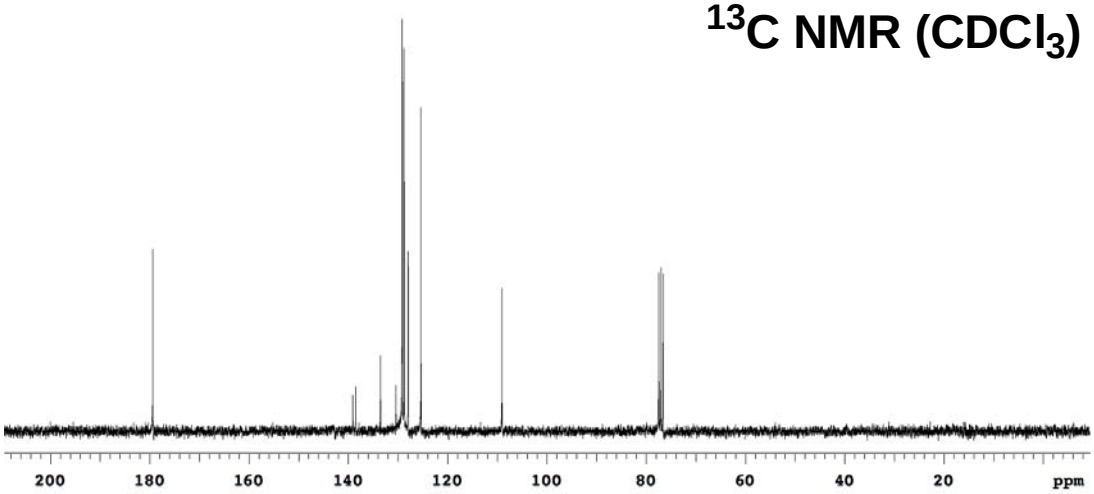
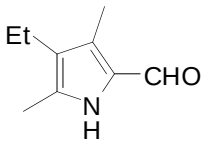
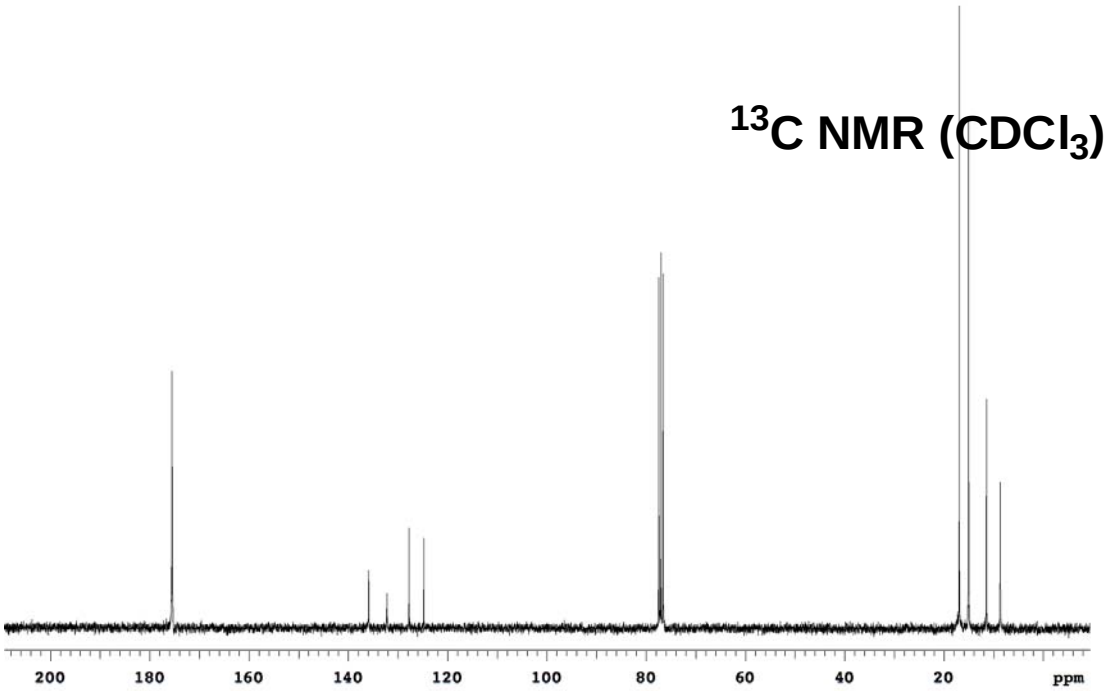


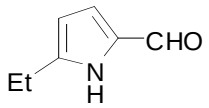


1e

^{1}H NMR ($CDCl_3$)

^{13}C NMR ($CDCl_3$)

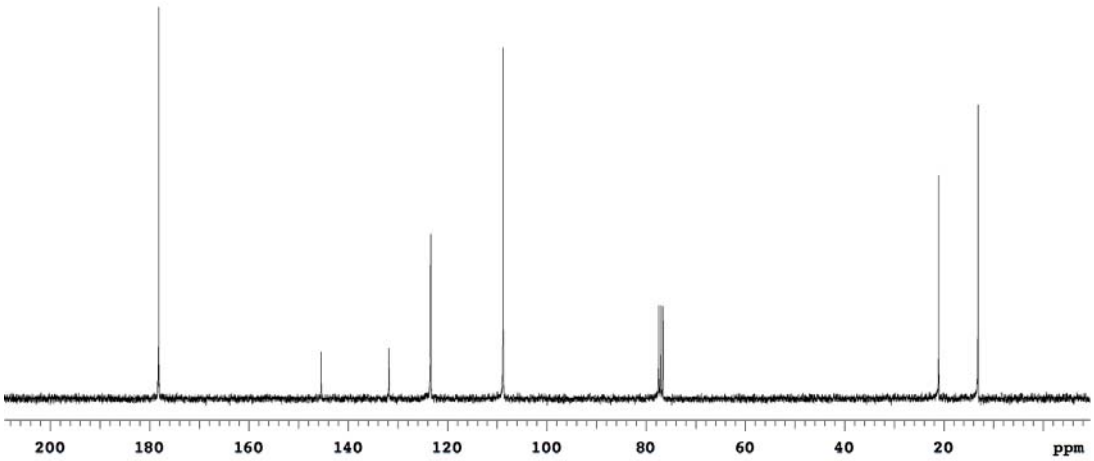


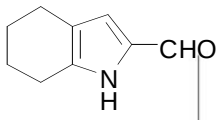


1f

^{1}H NMR ($CDCl_3$)

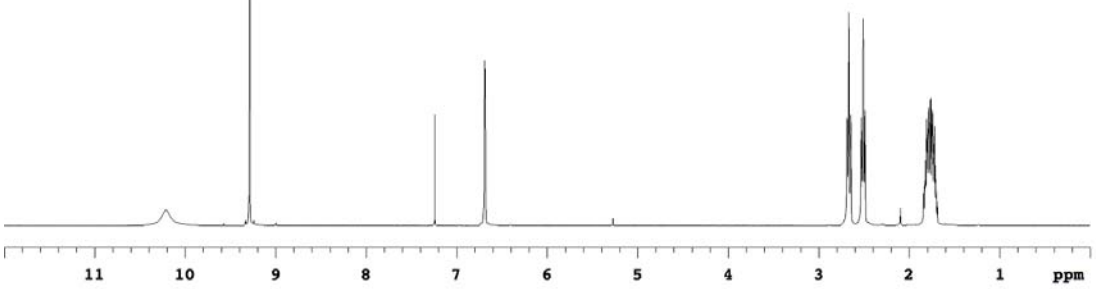
^{13}C NMR ($CDCl_3$)





1g

^{1}H NMR ($CDCl_3$)



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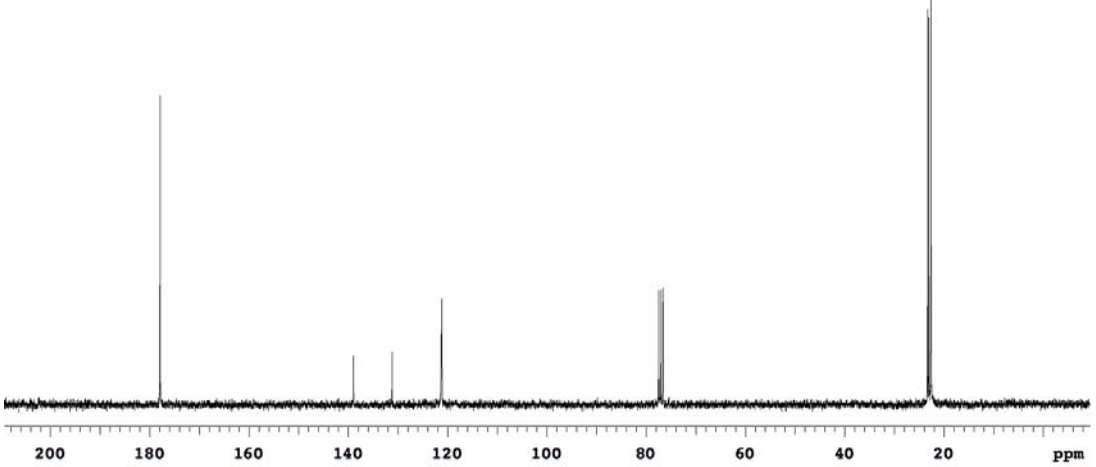
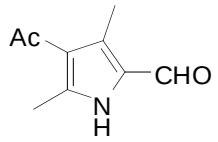
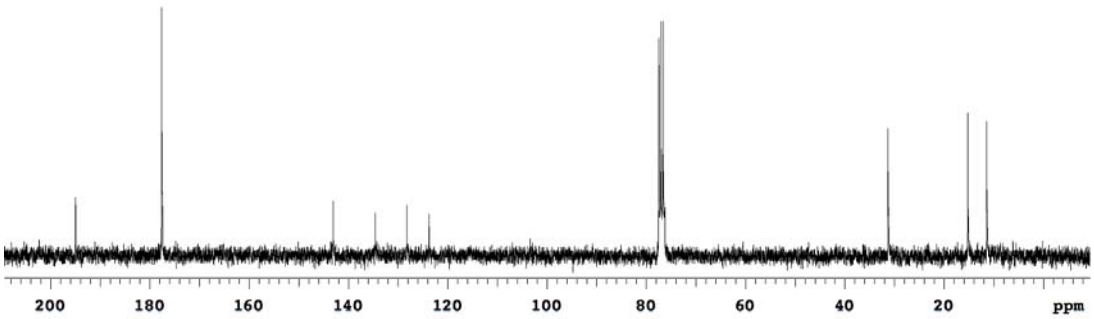


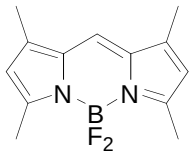


1h

^{1}H NMR ($CDCl_3$)

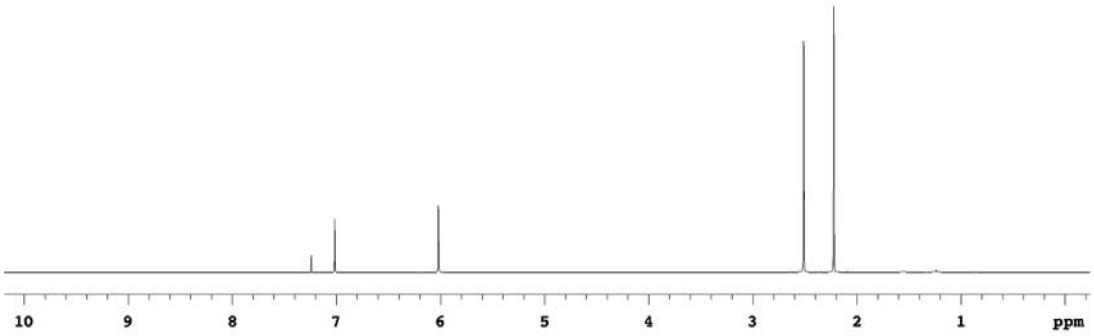
^{13}C NMR ($CDCl_3$)





2a

^{1}H NMR ($CDCl_3$)



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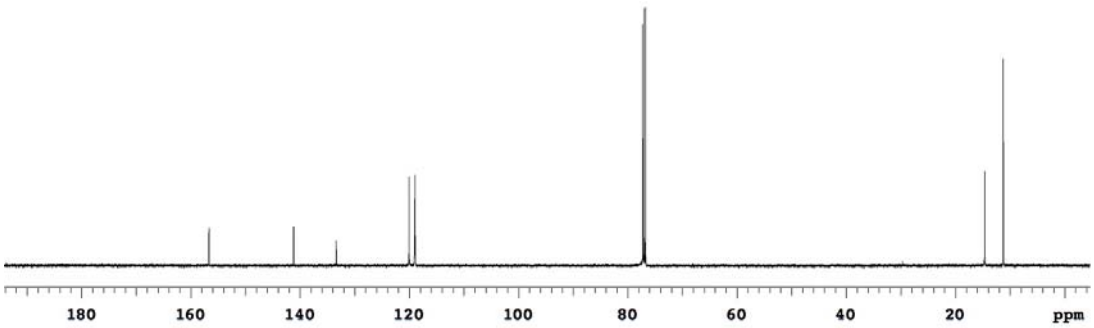
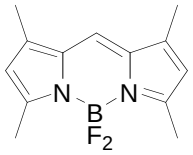
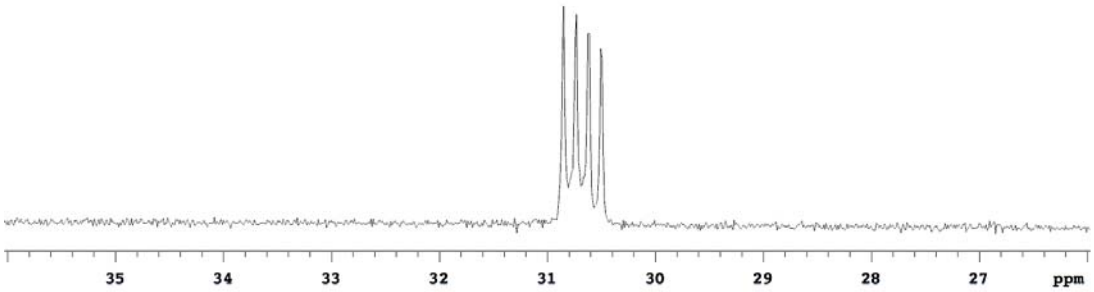
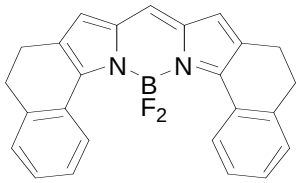




2a

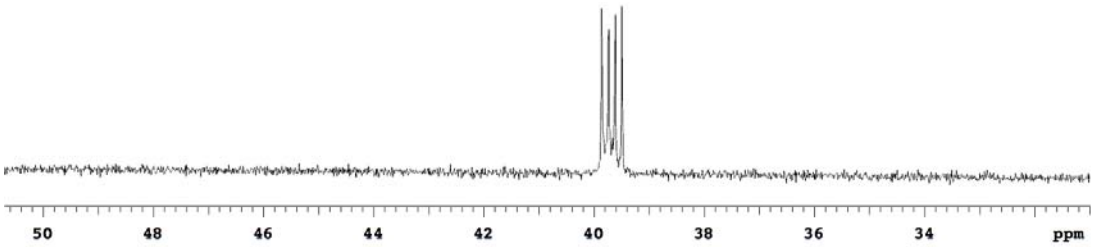
^{19}F NMR ($CDCl_3$)

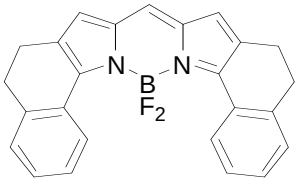




2b

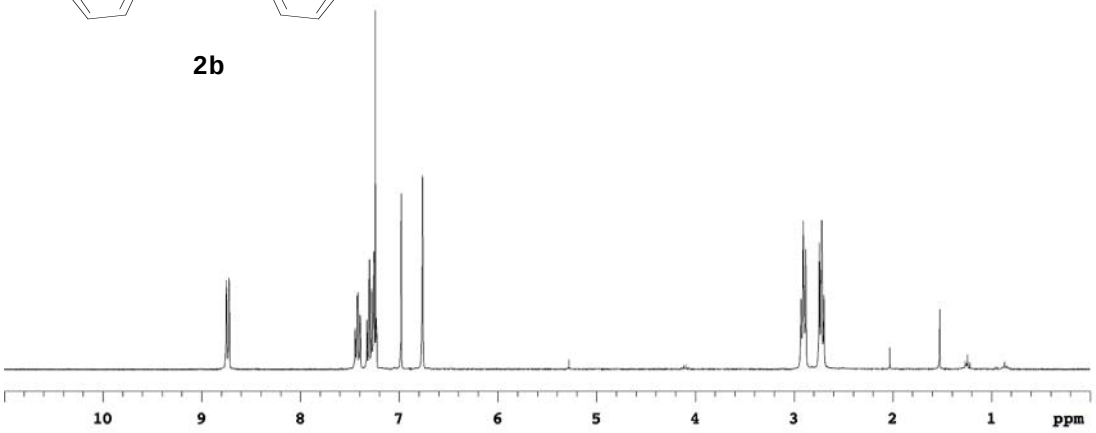
^{19}F NMR ($CDCl_3$)





2b

^{1}H NMR ($CDCl_3$)



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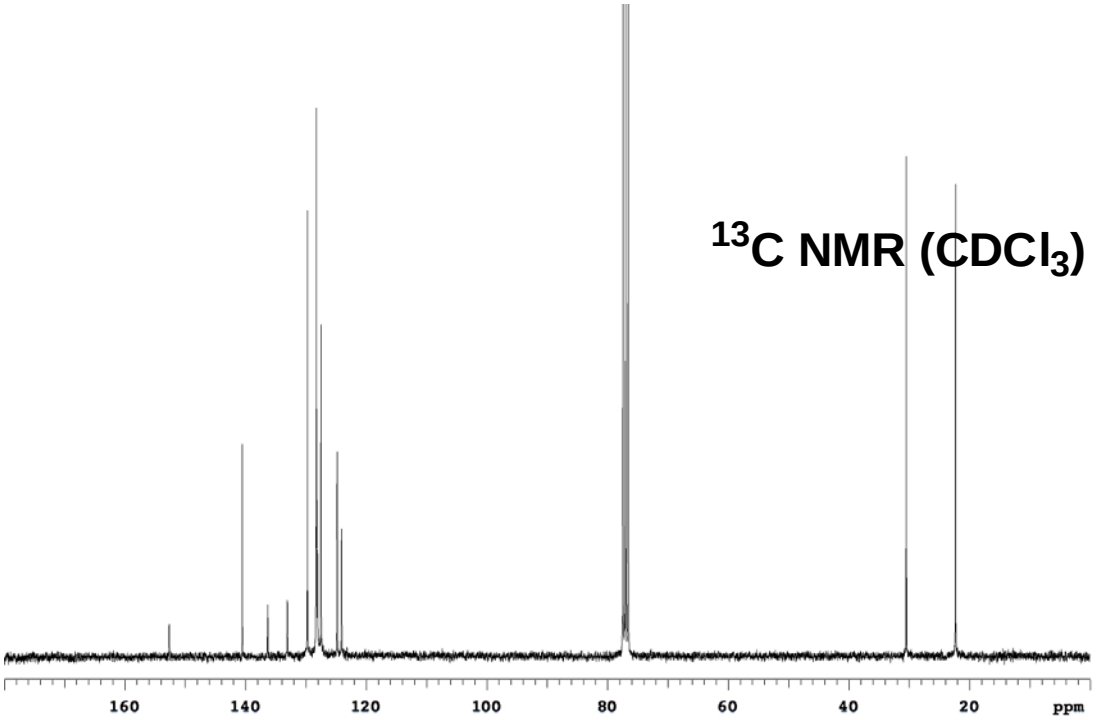
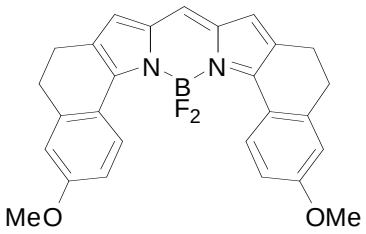
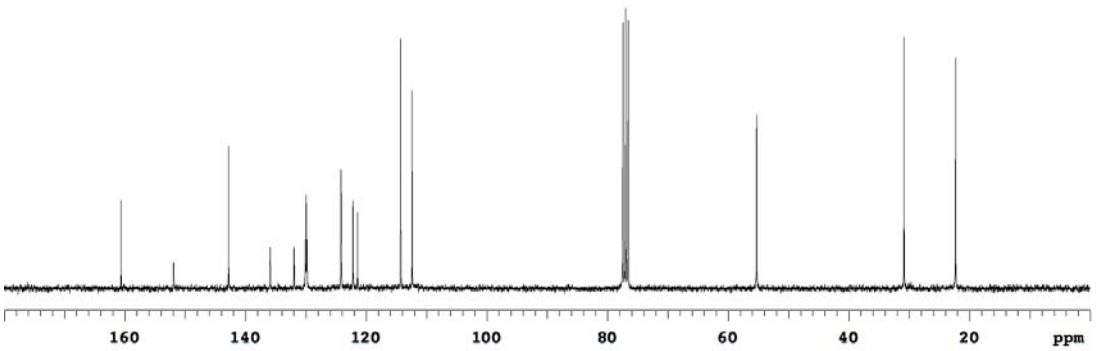


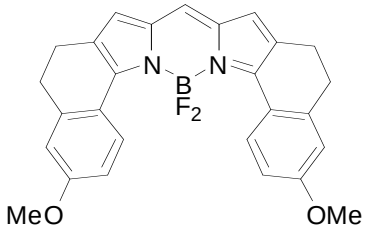


2c

^{1}H NMR ($CDCl_3$)

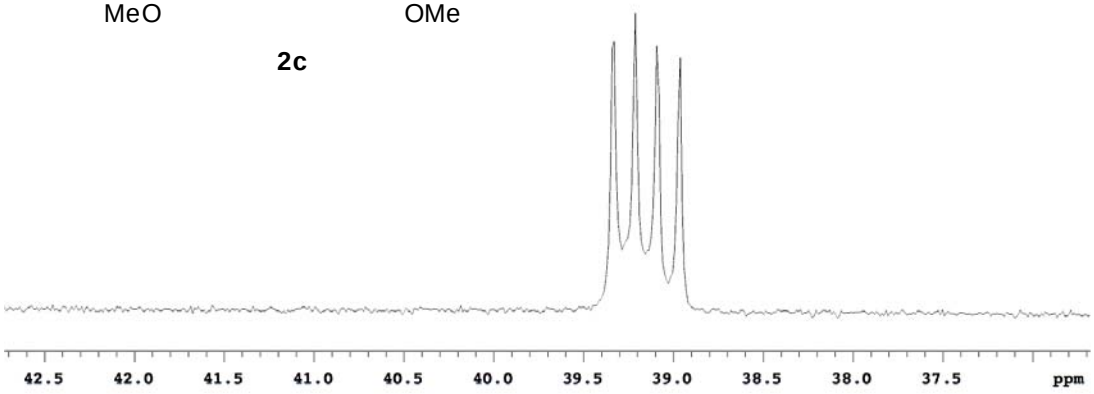
^{13}C NMR ($CDCl_3$)

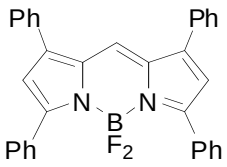




2c

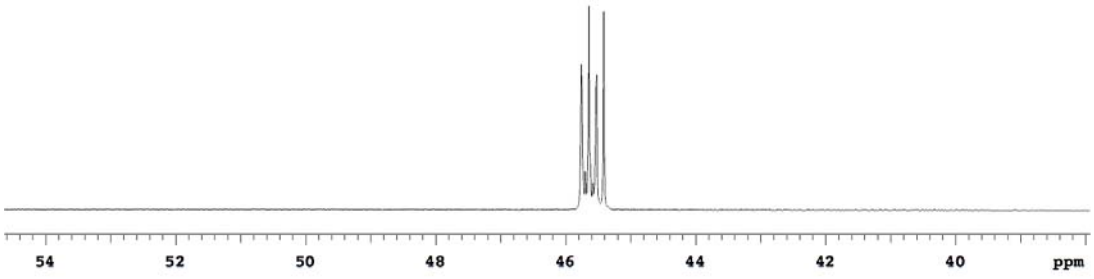
^{19}F NMR ($CDCl_3$)

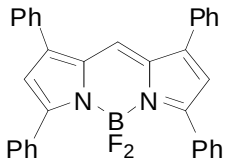




2d

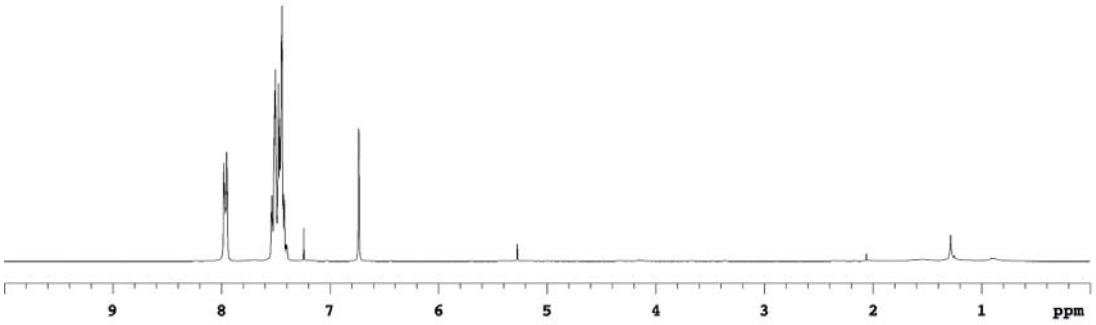
^{19}F NMR ($CDCl_3$)





2d

^{1}H NMR ($CDCl_3$)



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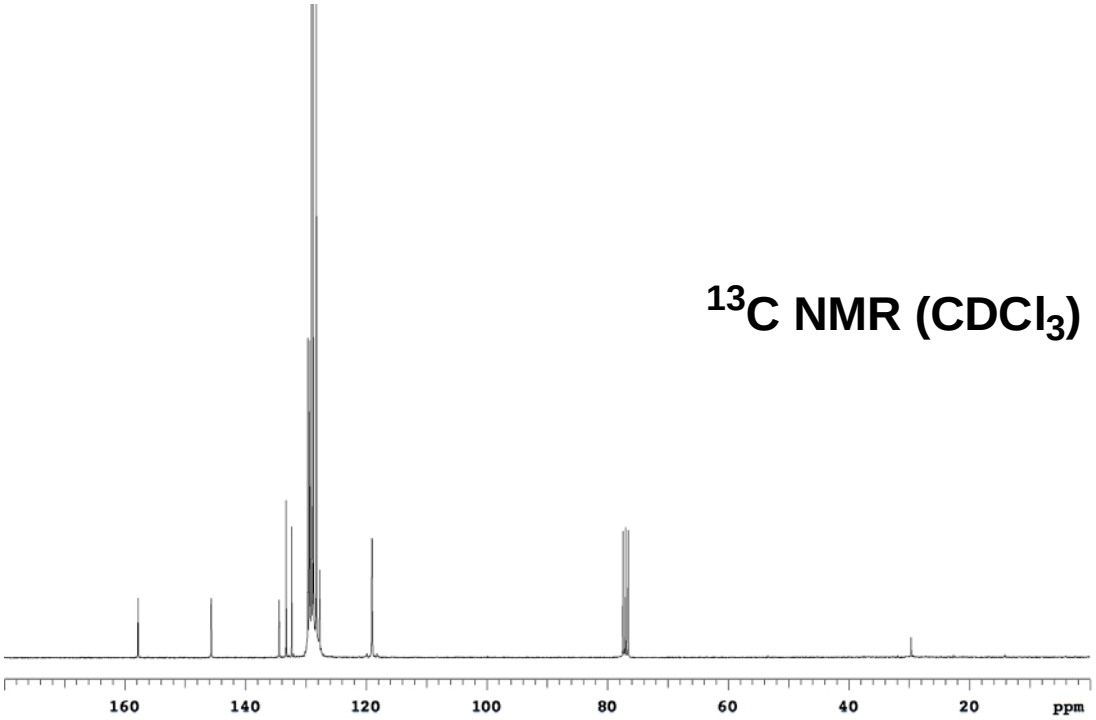
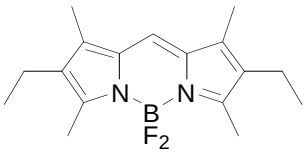
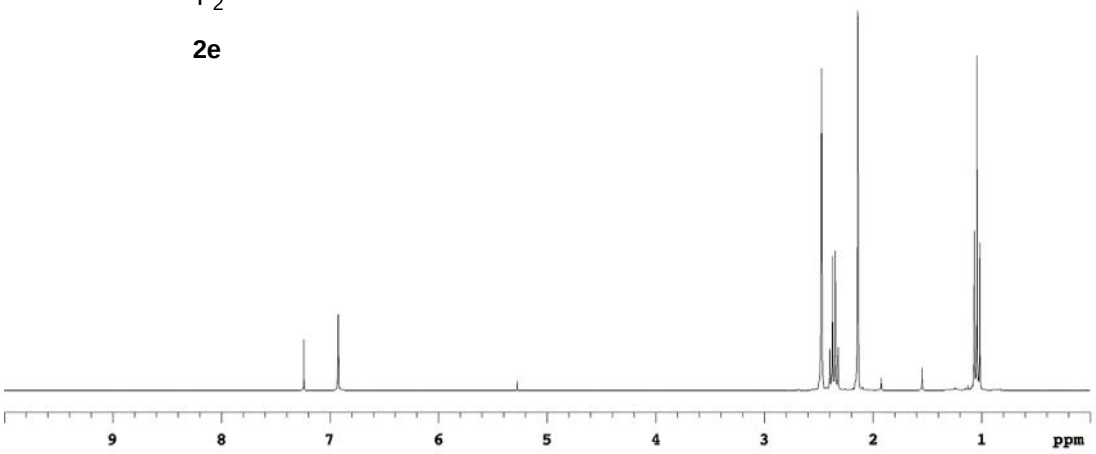




2e

^{1}H NMR ($CDCl_3$)



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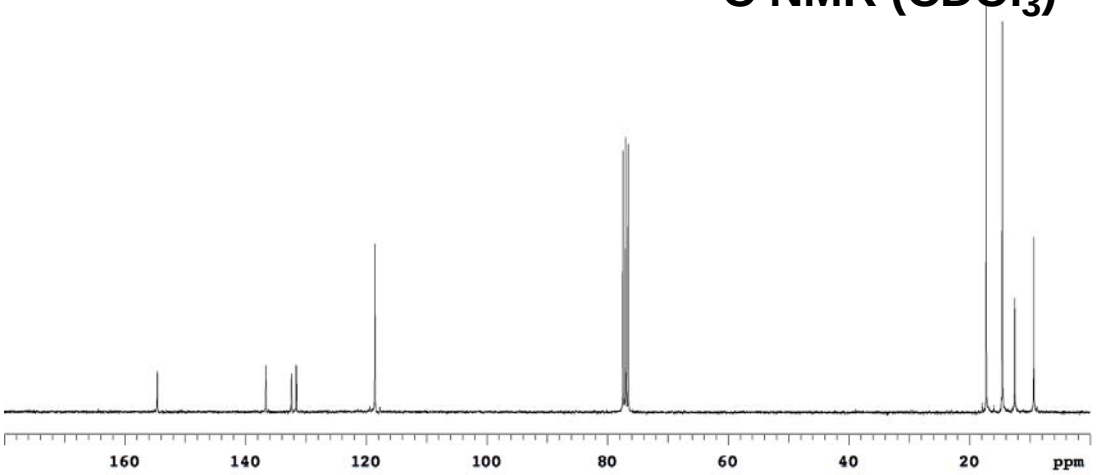
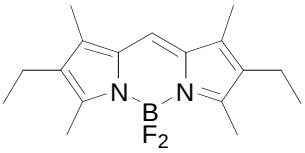
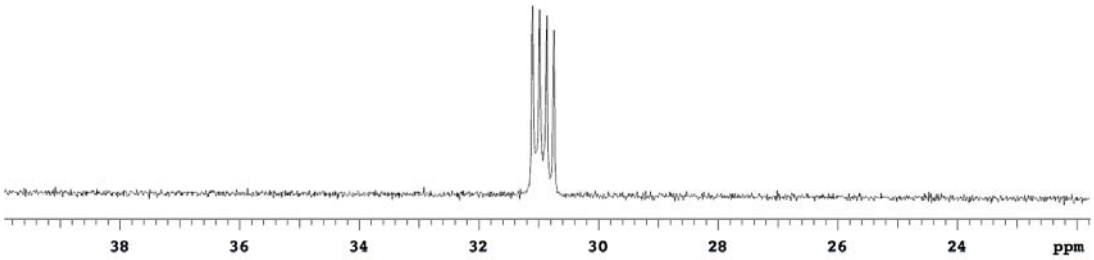
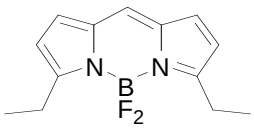




2e

^{19}F NMR ($CDCl_3$)





2f

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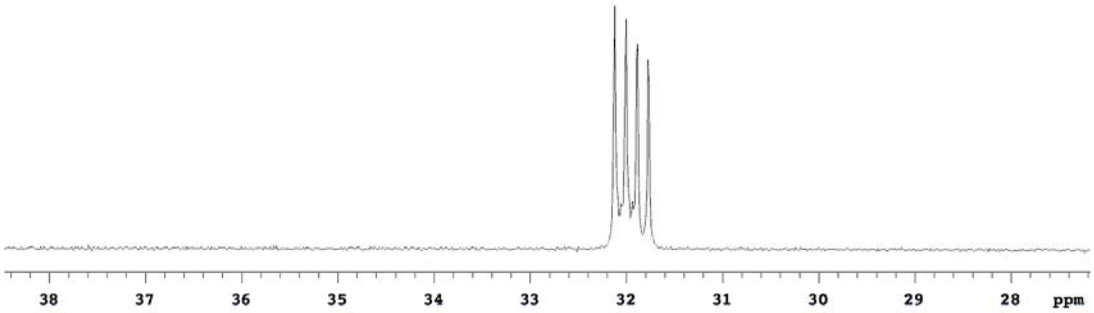
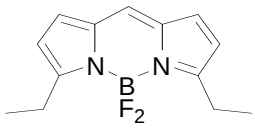
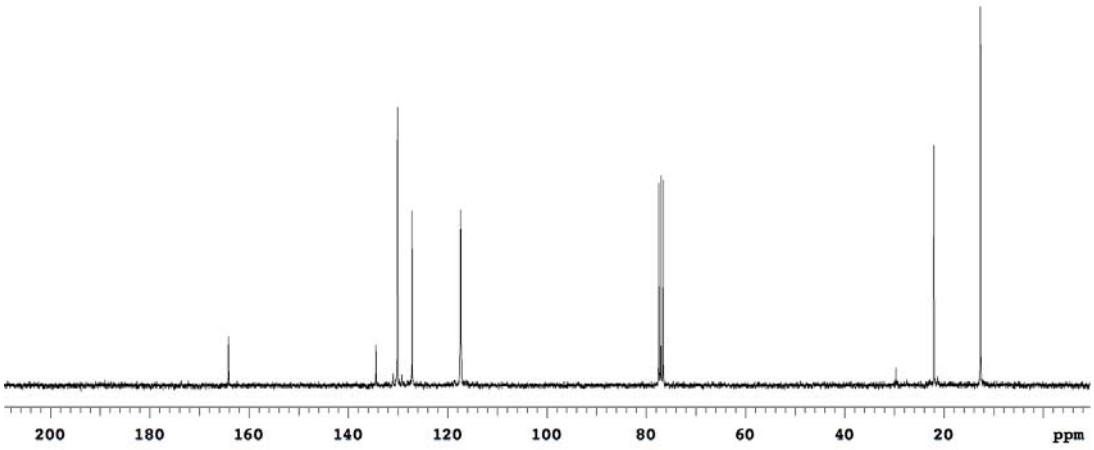


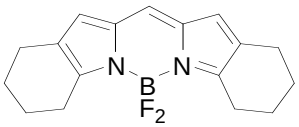


2f

^{1}H NMR ($CDCl_3$)

^{13}C NMR ($CDCl_3$)





2g

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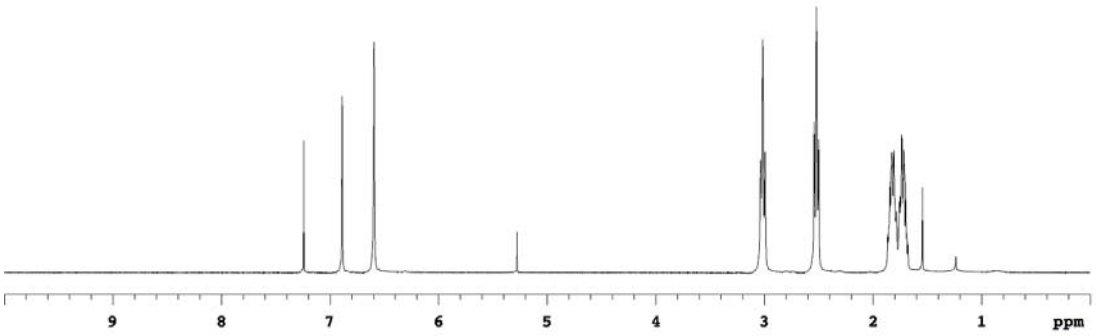

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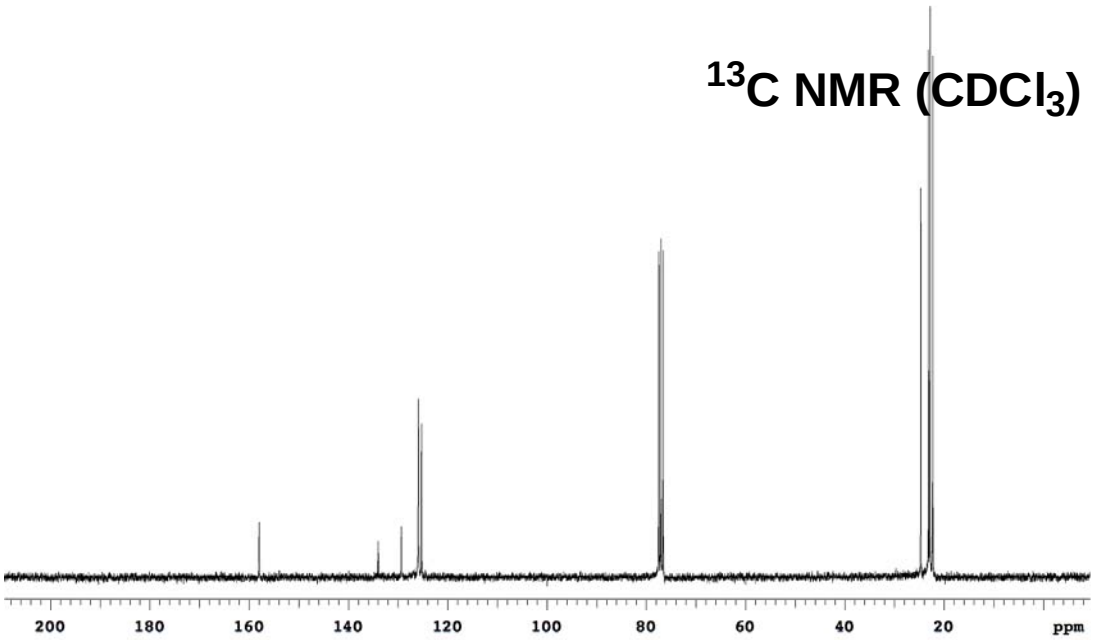

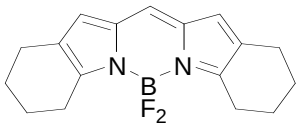

2g

^{19}F NMR ($CDCl_3$)