

# Supporting Information

## Direct Access to Pyrrole Anhydrides via Oxidative Self-Coupling of Pyrrole Carboxaldehydes

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## 1. CRYSTAL STRUCTURE DATA OF 2n

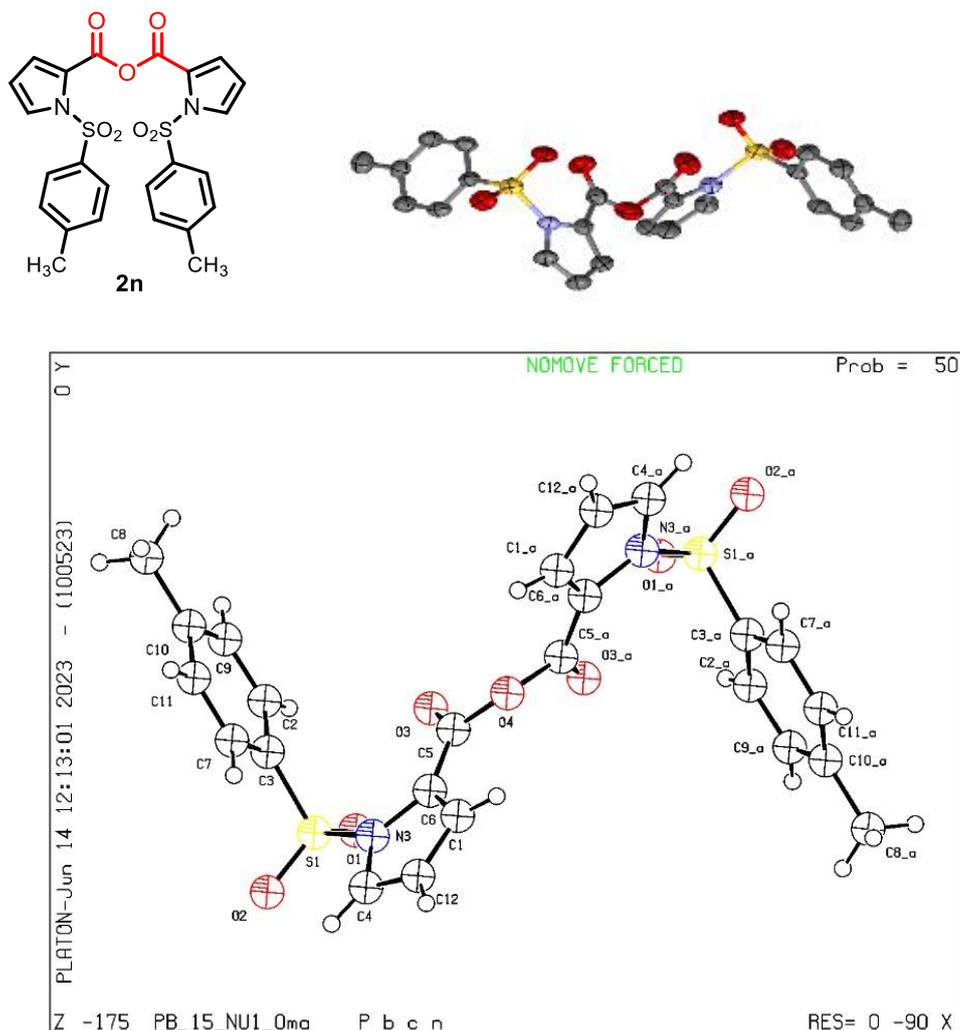


Figure 1. Crystal structure and ORTEP diagram of compound 2n

**Table 1 Crystal data and structure refinement for PB\_15\_NU1\_0ma.**

<b>Ccdc no.</b>	
<b>Empirical formula</b>	C <sub>24</sub> H <sub>20</sub> N <sub>2</sub> O <sub>7</sub> S <sub>2</sub>
<b>Formula weight</b>	512.54
<b>Temperature/K</b>	298
<b>Crystal system</b>	orthorhombic
<b>Space group</b>	Pbcn
<b>a/Å</b>	15.700(2)
<b>b/Å</b>	11.2137(13)
<b>c/Å</b>	13.4533(13)
<b>α/°</b>	90
<b>β/°</b>	90
<b>γ/°</b>	90
<b>Volume/Å<sup>3</sup></b>	2368.6(5)
<b>Z</b>	4
<b>ρ<sub>calc</sub>/cm<sup>3</sup></b>	1.437

$\mu/\text{mm}^{-1}$	0.273
<b>F(000)</b>	1064.0
<b>Crystal size/mm<sup>3</sup></b>	0.21 × 0.126 × 0.061
<b>Radiation</b>	MoK $\alpha$ ( $\lambda = 0.71073$ )
<b>2<math>\theta</math> range for data collection/<math>^\circ</math></b>	4.464 to 51.39
<b>Index ranges</b>	-19 ≤ h ≤ 19, -13 ≤ k ≤ 13, -16 ≤ l ≤ 16
<b>Reflections collected</b>	36961
<b>Independent reflections</b>	2258 [ $R_{\text{int}} = 0.1737$ , $R_{\text{sigma}} = 0.0580$ ]
<b>Data/restraints/parameters</b>	2258/0/162
<b>Goodness-of-fit on F<sup>2</sup></b>	1.029
<b>Final R indexes [<math>I \geq 2\sigma(I)</math>]</b>	$R_1 = 0.0418$ , $wR_2 = 0.0996$
<b>Final R indexes [all data]</b>	$R_1 = 0.0988$ , $wR_2 = 0.1246$
<b>Largest diff. peak/hole / e <math>\text{\AA}^{-3}</math></b>	0.20/-0.22

**Table 2 Fractional Atomic Coordinates ( $\times 10^4$ ) and Equivalent Isotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for PB\_15\_NU1\_0ma.  $U_{\text{eq}}$  is defined as 1/3 of the trace of the orthogonalised  $U_{\text{ij}}$  tensor.**

Atom	x	y	z	$U_{\text{eq}}$
<b>S1</b>	2889.5 (5)	6211.2 (6)	5347.6 (5)	56.8 (6)
<b>O1</b>	3369.1 (13)	7279.3 (16)	5428.9 (13)	68.1 (8)
<b>O4</b>	2400.4 (13)	6008.3 (19)	4474.2 (13)	74.1 (8)
<b>O3</b>	4120.6 (14)	6369 (2)	7199.6 (15)	80.9 (9)
<b>N1</b>	3572.3 (13)	5047.7 (19)	5374.1 (13)	52.7 (8)
<b>O2</b>	5000	4823 (3)	7500	87.0 (11)
<b>C13</b>	638.4 (19)	5455 (3)	8930 (2)	83.0 (11)
<b>C2</b>	1208.2 (17)	5638 (3)	8034.4 (19)	62.3 (10)
<b>C3</b>	1316.6 (18)	4748 (3)	7330 (2)	65.2 (10)
<b>C4</b>	1828.8 (17)	4923 (3)	6516 (2)	60.9 (9)
<b>C5</b>	2257.3 (16)	5994 (2)	6401.9 (18)	50.3 (9)
<b>C6</b>	4196.7 (16)	4741 (2)	6067.9 (19)	53.6 (8)
<b>C7</b>	4408.3 (18)	5446 (3)	6936 (2)	61.7 (9)
<b>C8</b>	2168.2 (18)	6881 (3)	7100 (2)	62.9 (9)
<b>C9</b>	1640.0 (19)	6699 (3)	7900 (2)	67.7 (10)
<b>C10</b>	4549.2 (19)	3693 (3)	5752 (2)	70.2 (10)
<b>C11</b>	4149 (2)	3346 (3)	4880 (2)	79.7 (11)
<b>C12</b>	3554 (2)	4161 (3)	4660 (2)	65.9 (10)

**Table 3 Anisotropic Displacement Parameters ( $\text{\AA}^2 \times 10^3$ ) for PB\_15\_NU1\_0ma. The Anisotropic displacement factor exponent takes the form: -  $2\pi^2[h^2a^2U_{11}+2hka*b*U_{12}+...]$ .**

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
<b>S1</b>	66.0 (8)	56.9 (7)	47.5 (7)	-0.5 (3)	-5.0 (3)	3.7 (4)
<b>O1</b>	84.6 (15)	54.5 (14)	65.2 (13)	2.6 (9)	2.9 (10)	-6.1 (11)
<b>O4</b>	82.8 (15)	91.6 (16)	47.8 (13)	-1.7 (10)	-18.2 (9)	8.9 (12)
<b>O3</b>	82.6 (16)	93.1 (17)	67.0 (14)	-	-	20.6 (14)
				25.7 (12)	18.2 (11)	

<b>N1</b>	57.6 (15)	55.0 (15)	45.6 (12)	-	-1.2 (10)	-0.2 (11)
				11.1 (11)		
<b>O2</b>	96 (2)	68 (2)	97 (2)	0	-48 (2)	0
<b>C13</b>	66 (2)	111 (3)	72 (2)	2.6 (19)	6.8 (16)	1 (2)
<b>C2</b>	50.1 (18)	80 (2)	56.5 (18)	0.4 (17)	-4.9 (14)	8.4 (16)
<b>C3</b>	66 (2)	59.3 (19)	70.4 (19)	4.6 (16)	-2.6 (16)	0.6 (16)
<b>C4</b>	72 (2)	52.0 (18)	58.9 (17)	-5.6 (14)	-6.8 (15)	8.2 (15)
<b>C5</b>	53.4 (17)	48.9 (17)	48.5 (16)	-1.9 (12)	-7.8 (12)	7.7 (13)
<b>C6</b>	47.9 (17)	57.0 (18)	56.0 (16)	-0.4 (14)	-3.1 (13)	-1.5 (14)
<b>C7</b>	55.9 (19)	71 (2)	58.7 (18)	4.6 (16)	-	-1.5 (17)
					10.8 (14)	
<b>C8</b>	71 (2)	56.4 (19)	61.5 (18)	-	1.6 (15)	-4.8 (15)
				11.6 (14)		
<b>C9</b>	69 (2)	72 (2)	62 (2)	-	0.0 (16)	3.0 (18)
				13.8 (16)		
<b>C10</b>	61.6 (19)	60 (2)	89 (2)	-3.0 (17)	-2.5 (18)	4.1 (16)
<b>C11</b>	80 (2)	63 (2)	97 (3)	-	11 (2)	-0.5 (19)
				26.5 (18)		
<b>C12</b>	70 (2)	71 (2)	56.8 (18)	-	2.8 (14)	-3.1 (18)
				19.8 (15)		

**Table 4 Bond Lengths for PB\_15\_NU1\_0ma.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
<b>S1</b>	<b>O1</b>	1.4190 (19)	<b>C2</b>	<b>C3</b>	1.387 (4)
<b>S1</b>	<b>O4</b>	1.4220 (19)	<b>C2</b>	<b>C9</b>	1.381 (4)
<b>S1</b>	<b>N1</b>	1.689 (2)	<b>C3</b>	<b>C4</b>	1.373 (4)
<b>S1</b>	<b>C5</b>	1.748 (3)	<b>C4</b>	<b>C5</b>	1.385 (4)
<b>O3</b>	<b>C7</b>	1.184 (3)	<b>C5</b>	<b>C8</b>	1.376 (3)
<b>N1</b>	<b>C6</b>	1.396 (3)	<b>C6</b>	<b>C7</b>	1.449 (4)
<b>N1</b>	<b>C12</b>	1.382 (3)	<b>C6</b>	<b>C10</b>	1.367 (4)
<b>O2</b>	<b>C7</b>	1.387 (3)	<b>C8</b>	<b>C9</b>	1.374 (4)
<b>O2</b>	<b>C7<sup>1</sup></b>	1.387 (3)	<b>C10</b>	<b>C11</b>	1.387 (4)
<b>C13</b>	<b>C2</b>	1.515 (4)	<b>C11</b>	<b>C12</b>	1.340 (4)

<sup>1</sup>1-X,+Y,3/2-Z

**Table 5 Bond Angles for PB\_15\_NU1\_0ma.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
<b>O1</b>	<b>S1</b>	<b>O4</b>	119.03 (12)	<b>C4</b>	<b>C5</b>	<b>S1</b>	119.1 (2)
<b>O1</b>	<b>S1</b>	<b>N1</b>	108.27 (11)	<b>C8</b>	<b>C5</b>	<b>S1</b>	120.7 (2)
<b>O1</b>	<b>S1</b>	<b>C5</b>	110.89 (12)	<b>C8</b>	<b>C5</b>	<b>C4</b>	120.1 (3)
<b>O4</b>	<b>S1</b>	<b>N1</b>	103.69 (11)	<b>N1</b>	<b>C6</b>	<b>C7</b>	124.5 (2)
<b>O4</b>	<b>S1</b>	<b>C5</b>	109.97 (13)	<b>C10</b>	<b>C6</b>	<b>N1</b>	106.7 (2)
<b>N1</b>	<b>S1</b>	<b>C5</b>	103.61 (11)	<b>C10</b>	<b>C6</b>	<b>C7</b>	128.8 (3)
<b>C6</b>	<b>N1</b>	<b>S1</b>	130.52 (17)	<b>O3</b>	<b>C7</b>	<b>O2</b>	122.1 (3)
<b>C12</b>	<b>N1</b>	<b>S1</b>	121.8 (2)	<b>O3</b>	<b>C7</b>	<b>C6</b>	129.1 (3)
<b>C12</b>	<b>N1</b>	<b>C6</b>	107.6 (2)	<b>O2</b>	<b>C7</b>	<b>C6</b>	108.7 (3)
<b>C7</b>	<b>O2</b>	<b>C7<sup>1</sup></b>	119.6 (3)	<b>C9</b>	<b>C8</b>	<b>C5</b>	119.3 (3)
<b>C3</b>	<b>C2</b>	<b>C13</b>	121.2 (3)	<b>C8</b>	<b>C9</b>	<b>C2</b>	121.8 (3)

<b>C9</b>	<b>C2</b>	<b>C13</b>	120.7 (3)	<b>C6</b>	<b>C10</b>	<b>C11</b>	108.7 (3)
<b>C9</b>	<b>C2</b>	<b>C3</b>	118.1 (3)	<b>C12</b>	<b>C11</b>	<b>C10</b>	108.1 (3)
<b>C4</b>	<b>C3</b>	<b>C2</b>	121.0 (3)	<b>C11</b>	<b>C12</b>	<b>N1</b>	108.8 (3)
<b>C3</b>	<b>C4</b>	<b>C5</b>	119.8 (3)				

<sup>1</sup>1-X,+Y,3/2-Z

**Table 6 Torsion Angles for PB\_15\_NU1\_0ma.**

<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>	<b>Angle/°</b>	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>	<b>Angle/°</b>
<b>S1</b>	<b>N1</b>	<b>C6</b>	<b>C7</b>	-2.7 (4)	<b>C2</b>	<b>C3</b>	<b>C4</b>	<b>C5</b>	1.2 (4)
<b>S1</b>	<b>N1</b>	<b>C6</b>	<b>C10</b>	178.0 (2)	<b>C3</b>	<b>C2</b>	<b>C9</b>	<b>C8</b>	-0.4 (4)
<b>S1</b>	<b>N1</b>	<b>C12</b>	<b>C11</b>	-178.5 (2)	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>S1</b>	-
									178.70 (19)
<b>S1</b>	<b>C5</b>	<b>C8</b>	<b>C9</b>	177.4 (2)	<b>C3</b>	<b>C4</b>	<b>C5</b>	<b>C8</b>	-0.2 (4)
<b>O1</b>	<b>S1</b>	<b>N1</b>	<b>C6</b>	54.4 (2)	<b>C4</b>	<b>C5</b>	<b>C8</b>	<b>C9</b>	-1.1 (4)
<b>O1</b>	<b>S1</b>	<b>N1</b>	<b>C12</b>	-128.9 (2)	<b>C5</b>	<b>S1</b>	<b>N1</b>	<b>C6</b>	-63.4 (2)
<b>O1</b>	<b>S1</b>	<b>C5</b>	<b>C4</b>	-	<b>C5</b>	<b>S1</b>	<b>N1</b>	<b>C12</b>	113.3 (2)
				171.66 (19)					
<b>O1</b>	<b>S1</b>	<b>C5</b>	<b>C8</b>	9.8 (3)	<b>C5</b>	<b>C8</b>	<b>C9</b>	<b>C2</b>	1.4 (4)
<b>O4</b>	<b>S1</b>	<b>N1</b>	<b>C6</b>	-178.3 (2)	<b>C6</b>	<b>N1</b>	<b>C12</b>	<b>C11</b>	-1.2 (3)
<b>O4</b>	<b>S1</b>	<b>N1</b>	<b>C12</b>	-1.5 (2)	<b>C6</b>	<b>C10</b>	<b>C11</b>	<b>C12</b>	-0.3 (4)
<b>O4</b>	<b>S1</b>	<b>C5</b>	<b>C4</b>	54.6 (2)	<b>C7<sup>1</sup></b>	<b>O2</b>	<b>C7</b>	<b>O3</b>	-34.0 (2)
<b>O4</b>	<b>S1</b>	<b>C5</b>	<b>C8</b>	-123.9 (2)	<b>C7<sup>1</sup></b>	<b>O2</b>	<b>C7</b>	<b>C6</b>	149.6 (2)
<b>N1</b>	<b>S1</b>	<b>C5</b>	<b>C4</b>	-55.7 (2)	<b>C7</b>	<b>C6</b>	<b>C10</b>	<b>C11</b>	-179.7 (3)
<b>N1</b>	<b>S1</b>	<b>C5</b>	<b>C8</b>	125.8 (2)	<b>C9</b>	<b>C2</b>	<b>C3</b>	<b>C4</b>	-0.9 (4)
<b>N1</b>	<b>C6</b>	<b>C7</b>	<b>O3</b>	-1.3 (5)	<b>C10</b>	<b>C6</b>	<b>C7</b>	<b>O3</b>	177.8 (3)
<b>N1</b>	<b>C6</b>	<b>C7</b>	<b>O2</b>	174.8 (2)	<b>C10</b>	<b>C6</b>	<b>C7</b>	<b>O2</b>	-6.0 (4)
<b>N1</b>	<b>C6</b>	<b>C10</b>	<b>C11</b>	-0.4 (3)	<b>C10</b>	<b>C11</b>	<b>C12</b>	<b>N1</b>	0.9 (4)
<b>C13</b>	<b>C2</b>	<b>C3</b>	<b>C4</b>	179.5 (2)	<b>C12</b>	<b>N1</b>	<b>C6</b>	<b>C7</b>	-179.7 (3)
<b>C13</b>	<b>C2</b>	<b>C9</b>	<b>C8</b>	179.2 (3)	<b>C12</b>	<b>N1</b>	<b>C6</b>	<b>C10</b>	1.0 (3)

<sup>1</sup>1-X,+Y,3/2-Z

**Table 7 Hydrogen Atom Coordinates ( $\text{\AA}\times 10^4$ ) and Isotropic Displacement Parameters ( $\text{\AA}^2\times 10^3$ ) for PB\_15\_NU1\_0ma.**

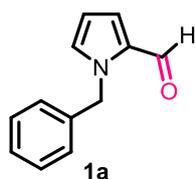
<b>Atom</b>	<b>x</b>	<b>y</b>	<b>z</b>	<b>U(eq)</b>
<b>H13A</b>	887.61	5835.02	9499.04	124
<b>H13B</b>	577.79	4616.42	9056.99	124
<b>H13C</b>	88.6	5795.8	8800.96	124
<b>H3</b>	1038.29	4022.14	7410.19	78
<b>H4</b>	1887.94	4323.72	6042.74	73
<b>H8</b>	2462.38	7595.74	7032.02	75
<b>H9</b>	1571.42	7306.17	8363.99	81
<b>H10</b>	4985.44	3281.18	6069.44	84
<b>H11</b>	4271.33	2665.45	4512.28	96
<b>H12</b>	3188.26	4135.11	4116.77	79

## 2. PROCEDURE FOR THE SAMPLE PREPARATION OF CRYSTAL (2n)

We opted for a solvent in which our compound (2n, 100 mg) readily dissolves, with popular choices being water, ethanol, or a solvent mixture. The compound (2n, 100 mg) was effectively dissolved in 2 mL of MeOH, ensuring thorough dissolution through a gradual addition process coupled with stirring. Controlled evaporation ensued, achieved by letting the solution stand at room temperature. Upon the formation of crystals, they were separated from the residual solution via filtration. A cleansing rinse with a cold solvent followed to eliminate impurities, and the crystals were subsequently dried completely. The Single Crystal X-ray diffraction (SC-XRD) was conducted using a Bruker D8 Venture instrument equipped with a photon counting detector, and APEX5 software was employed for chemical crystallography.

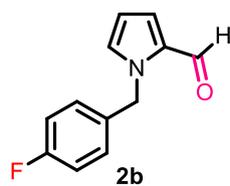
## 2. CHARACTERIZATION DATA OF SUBSTRATES

### *1-Benzyl-1H-Pyrrole-2-carbaldehyde (1a)*<sup>1</sup>



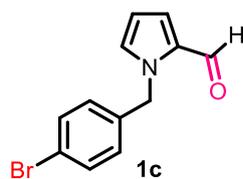
Brown oily liquid (185 mg, 99%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 9.56 (s, 1H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.26 (dd, *J* = 6.4, 4.1 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 2H), 6.97 (d, *J* = 3.3 Hz, 2H), 6.27 (t, *J* = 3.1 Hz, 1H), 5.56 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 179.6, 137.6, 131.5, 128.8, 127.8, 127.3, 124.9, 110.2, 52.0.

### *1-(4-Fluorobenzyl)-1H-Pyrrole-2-carbaldehyde (1b)*<sup>1</sup>



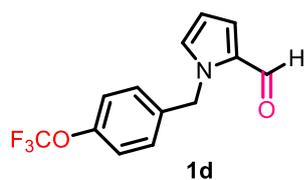
Yellow oily liquid (198 mg, 98%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 9.54 (s, 1H), 7.32 – 7.19 (m, 1H), 6.96 – 6.89 (m, 2H), 6.78 (d, *J* = 9.6 Hz, 1H), 6.31 – 6.27 (m, 1H), 5.54 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 179.6, 164.0, 162.1, 140.31 (d, <sup>3</sup>*J*<sub>C-F</sub> = 7.3 Hz), 131.55 (d, <sup>2</sup>*J*<sub>C-F</sub> = 5.2 Hz), 130.31 (d, <sup>3</sup>*J*<sub>C-F</sub> = 8.4 Hz), 125.1, 122.75 (d, <sup>4</sup>*J*<sub>C-F</sub> = 3.1 Hz), 114.69 (d, <sup>2</sup>*J*<sub>C-F</sub> = 21.2 Hz), 114.0 (d, <sup>2</sup>*J*<sub>C-F</sub> = 22.1 Hz), 110.4, 51.5.

### *1-(4-Bromobenzyl)-1H-Pyrrole-2-carbaldehyde (1c)*<sup>1</sup>



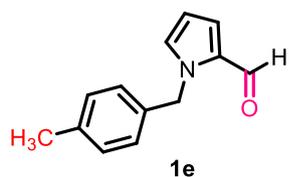
White solid (254 mg, 97%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 9.52 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 6.98 (dd, *J* = 18.3, 5.2 Hz, 4H), 6.27 (s, 1H), 5.49 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 179.6, 131.9, 131.46, 129.0, 125.1, 121.7, 110.4, 51.4.

**1-(4-Trifluoromethoxy)benzyl-1H-Pyrrole-2-carbaldehyde (1d)<sup>1</sup>**



Brown liquid (227 mg, 97%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 9.53 (s), 7.14 (q, *J* = 8.8 Hz), 7.02 – 6.92 (m), 6.31 – 6.24 (m), 5.54 (s). NMR (151 MHz,) δ 179.4, 148.5, 136.3, 131.3, 128.5, 125.0, 121.0, 110.3, 77.2, 77.0, 76.7, 51.1.

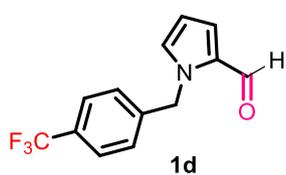
**1-(4-(Methyl)benzyl)-1H-Pyrrole-2-carbaldehyde (1e)<sup>1</sup>**



Brown solid (195 mg, 98%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 9.56 (s), 7.25 (s), 7.12 (d, *J* = 7.8 Hz), 7.07 (d, *J* = 7.4 Hz), 6.96 (d, *J* = 3.3 Hz), 6.26 (t, *J* = 2.8 Hz), 5.52 (s), 2.32 (s). NMR (151 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 179.61, 137.5, 134.6, 131.6, 131.4, 129.5, 127.5, 124.9, 110.1,

77.4, 77.2, 77.0, 51.8, 21.2.

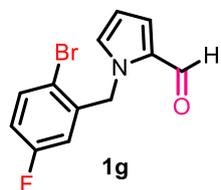
**1-(4-Trifluoromethyl)benzyl-1H-Pyrrole-2-carbaldehyde (1f)<sup>1</sup>**



Yellow oily liquid (248 mg, 98%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 9.54 (s, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.37 (s, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 3.6 Hz, 2H), 6.34 – 6.28 (m, 1H), 5.60 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 179.6, 138.7, 131.5,

130.5, 129.3, 125.2, 124.6 (d, 4*J*C–F = 3.3 Hz), 123.8 (d, 4*J*C–F = 3.4 Hz), 110.6, 51.5.

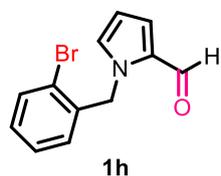
**1-(2-Bromo-5-fluorobenzyl)-1H-Pyrrole-2-carbaldehyde (1g)<sup>1</sup>**



White solid (198 mg, 95%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 7.49 (dd, *J* = 8.7, 5.2 Hz, 1H), 7.19 (dd, *J* = 4.1, 1.7 Hz, 1H), 7.05 – 6.98 (m, 1H), 6.84 (td, *J* = 8.3, 3.0 Hz, 1H), 6.30 (dd, *J* = 4.0, 2.6 Hz, 1H), 6.26 (dd, *J* = 9.3, 2.9 Hz, 1H), 5.57 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) NMR (151

MHz,) NMR (151 MHz, ) δ 163.0, 161.3, 155.4, 139.2, 133.6, 131.4, 121.3, 120.7, 115.8 (d, *J* = 30.8 Hz), 114.4 (d, 2*J*C–F = 24.6 Hz), 109.7, 52.1.

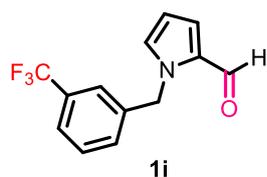
**1-(2-Bromobenzyl)-1H-Pyrrole-2-carbaldehyde (1h)<sup>1</sup>**



Brown solid (256 mg, 97%); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 9.56 (d, *J* = 15.0 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.05 – 7.02 (m, 1H), 6.92 (s, 1H), 6.60 (d, *J* = 7.7 Hz, 1H), 6.35 – 6.29 (m, 1H), 5.80 (s, 2H). <sup>13</sup>C NMR

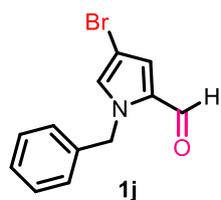
(126 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 179.6, 136.7, 132.5, 131.8, 127.5, 127.3, 127.1, 126.1, 126.1, 126.0, 126.0, 125.9, 125.4, 124.8, 123.3, 110.6, 77.3, 77.1, 76.8, 48.5.

### 1-(3-(Trifluoromethyl)benzyl)-1H-Pyrrole-2-carbaldehyde (1i)<sup>1</sup>



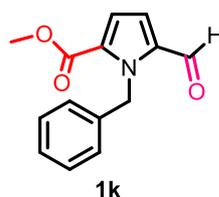
Yellow solid (248 mg, 98%); NMR (600 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 9.54 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.37 (s, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 3.9 Hz, 2H), 6.31 (s, 1H), 5.60 (s, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 179.6, 138.8, 131.5 (d, 3*J*C–F = 9.6 Hz), 130.5, 129.3, 125.2, 124.6 (d, 4*J*C–F = 3.7 Hz), 123.8 (d, 4*J*C–F = 3.6 Hz), 110.6, 51.5.

### 1-Benzyl-4-bromo-1H-Pyrrole-2-carbaldehyde (1j)<sup>1</sup>



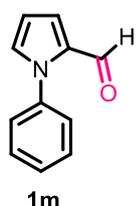
Pink solid (256 mg, 98%); NMR (600 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 9.49 (s, 1H), 7.34 – 7.31 (m), 7.30 – 7.28 (m), 7.16 (dd, *J* = 5.0, 3.3 Hz), 6.93 (d, *J* = 1.8 Hz), 6.93 – 6.91 (m), 5.51 (s). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 179.1, 136.6, 131.7, 130.5, 128.9, 128.2, 127.6, 125.4, 97.4, 52.3.

### Methyl-1-benzyl-5-formyl-1H-Pyrrole-2-carbaldehyde (1k)<sup>1</sup>



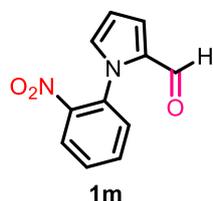
Orange oily liquid (238 mg, 98%); NMR (600 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 9.72 (s, 1H), 7.27 – 7.24 (m, 1H), 7.24 – 7.23 (m, 1H), 7.21 – 7.18 (m, 1H), 7.04 (d, *J* = 7.2 Hz, 2H), 7.01 (d, *J* = 4.3 Hz, 1H), 6.95 (d, *J* = 4.2 Hz, 1H), 6.11 (s, 2H), 3.82 (s, 3H). NMR (151 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 181.1, 161.1, 138.1, 135.3, 129.5, 128.5, 127.3, 126.5, 122.5, 117.6, 51.9, 49.3. HRMS (ESI) *m/z* calcd for C<sub>14</sub>H<sub>13</sub>NO<sub>3</sub>, [M+1]<sup>+</sup> 244.0974, found [M+H]<sup>+</sup> 244.0976.

### 1-(Phenyl-1H-Pyrrole-2-carbaldehyde (1l)<sup>2</sup>



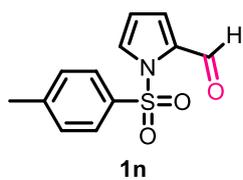
Brown liquid (162 mg, 95%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 9.56 (s), 7.48 – 7.44 (m), 7.44 – 7.40 (m), 7.36 – 7.33 (m), 7.16 (dd, *J* = 4.0, 1.7 Hz), 7.07 (t, *J* = 2.1 Hz), 6.40 (dd, *J* = 4.0, 2.6 Hz). NMR (151 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 179.18, 138.91, 132.72, 131.19, 129.25, 128.39, 126.22, 122.14, 111.01, 77.42, 77.21, 77.00.

### 1-(2-nitrophenyl)-1H-Pyrrole-2-carbaldehyde (1m)<sup>3</sup>



Yellow solid (213 mg, 99%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 9.48 (s, 1H), 8.11 (d, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 2.3 Hz, 1H), 7.00 (s, 1H), 6.51 – 6.44 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 178.8, 145.9, 133.7, 133.6, 132.7, 131.2, 129.8, 129.6, 125.3, 124.9, 111.7. HRMS (ESI) *m/z* calcd for C<sub>11</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>, [M+1]<sup>+</sup> 217.0613, found [M+H]<sup>+</sup> 217.0610.

**1-(Phenylsulfonyl)-1H-Pyrrole-2-carbaldehyde (1n)<sup>4</sup>**



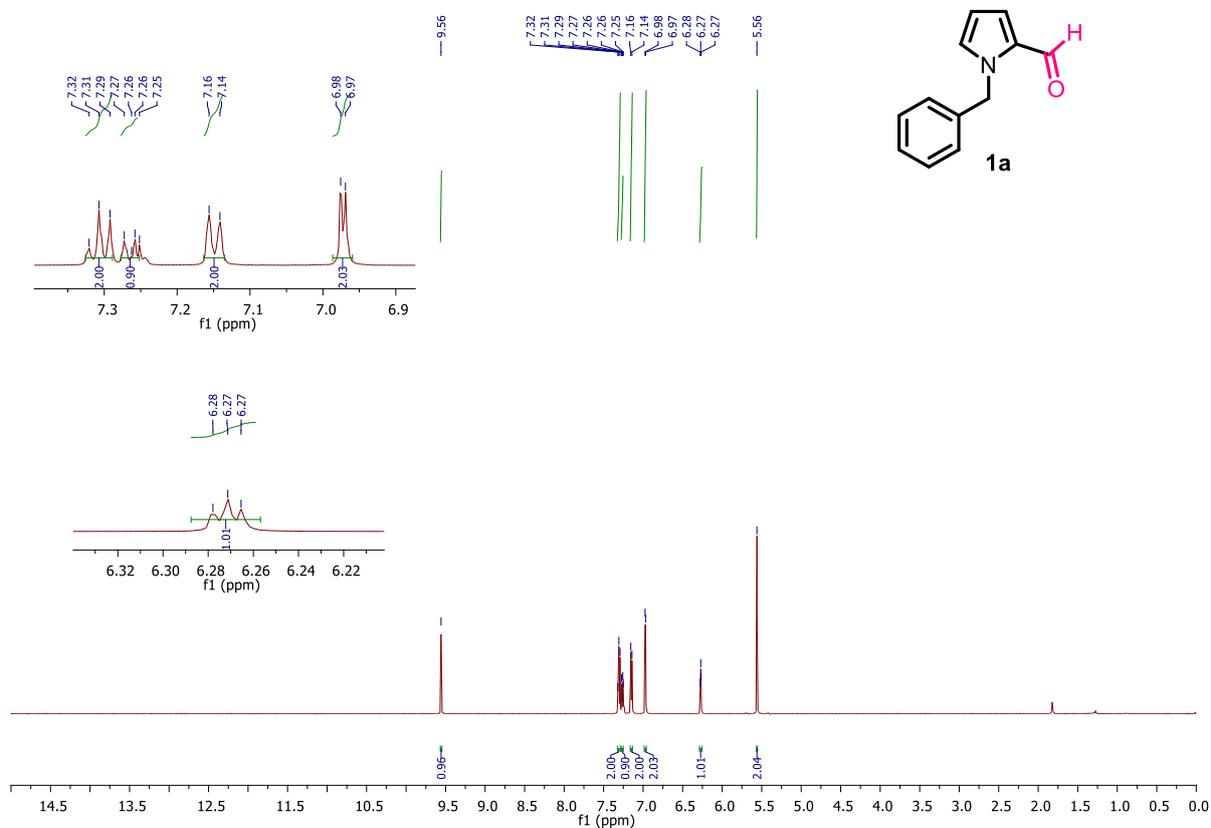
white solid (223 mg, 95%); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 9.96 (s, 1H), 7.79 (d, *J* = 7.8 Hz, 2H), 7.61 (s, 1H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.15 (s, 1H), 6.39 (s, 1H), 2.41 (s, 4H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>-d<sub>6</sub>) δ 179.0, 146.0, 135.2, 133.5, 130.2, 129.5, 127.5, 124.5, 112.4, 21.7.

### 3. REFERENCES

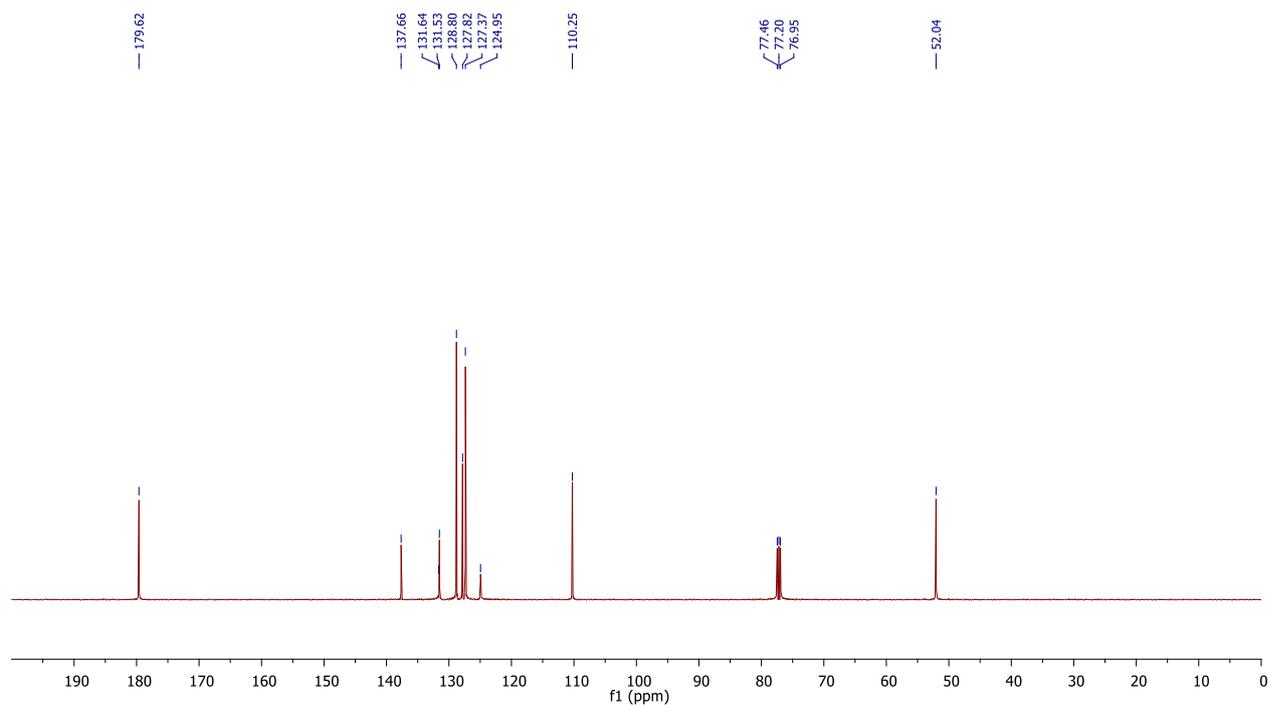
1. Z. Li, M. Luo, B. Cai, M. Huang, J. Jiang, L. Wang, L. Wu, *Eur. J. Med. Chem.*, 2018, **157**, 665-682.
2. L. Liua, F. Wua, Y. Liua, J. Xiea, B. Daia, Z. Zhou, *J. Chem. Res.*, 2014, **38**, 180-182.
3. J. Ni, Y. Jiang, Z. Qi, R. Yan, *Chem. Asian J.*, 2019, **14**, 2898–2902.
4. K. Wang and Z. Liu, *Synth. Commun.*, 2010, **40**, 144-150.

## 4. $^1\text{H}$ and $^{13}\text{C}$ Spectra

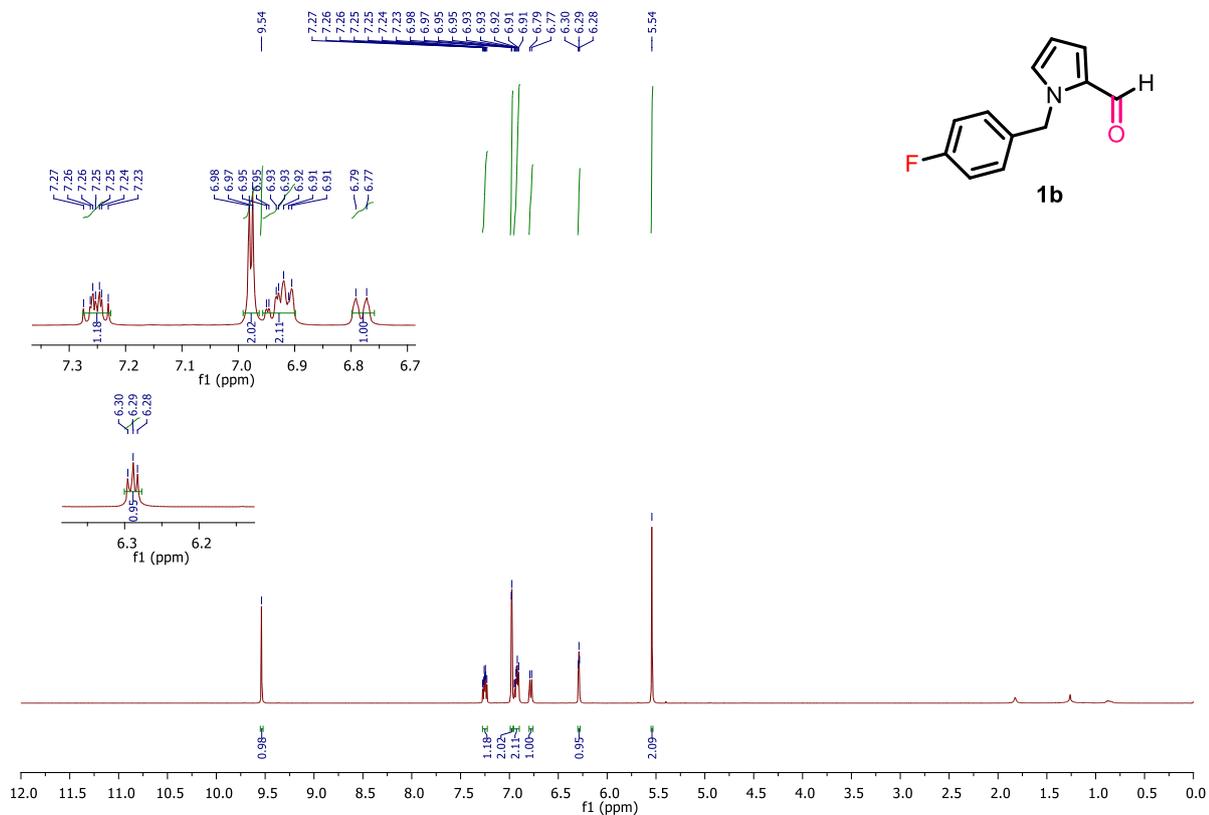
### 1a $^1\text{H}$ NMR ( $\text{CDCl}_3$ )



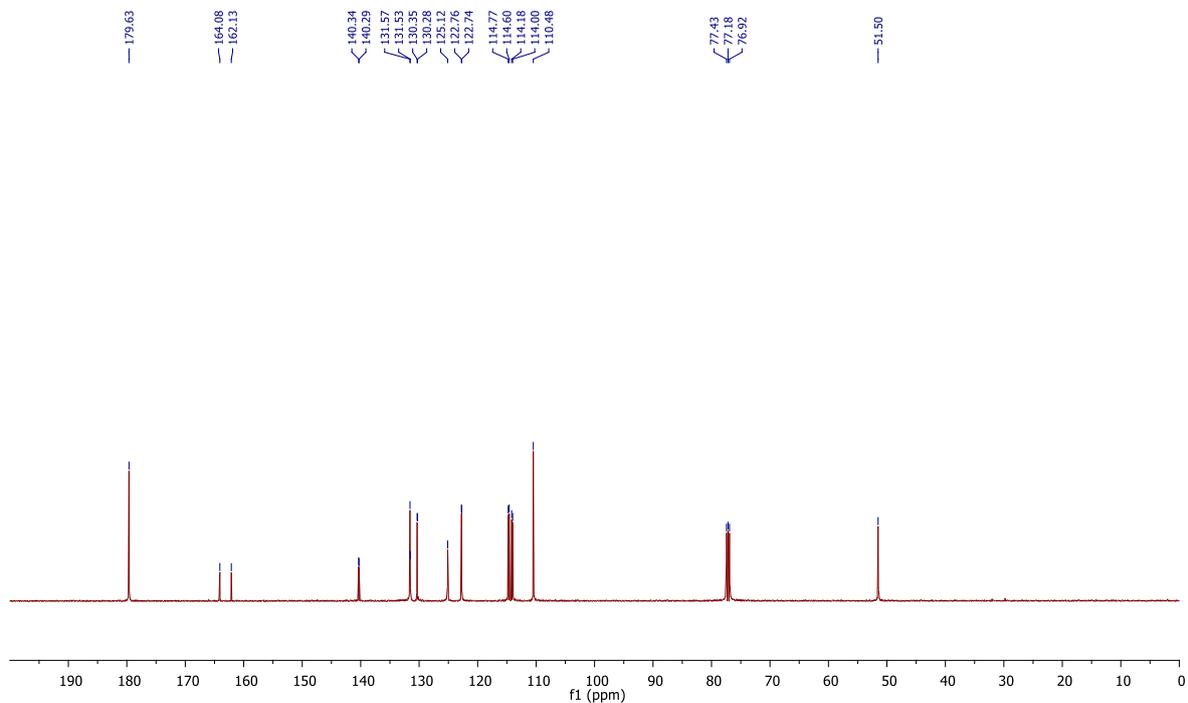
### $^{13}\text{C}\{^1\text{H}\}$ NMR ( $\text{CDCl}_3$ )



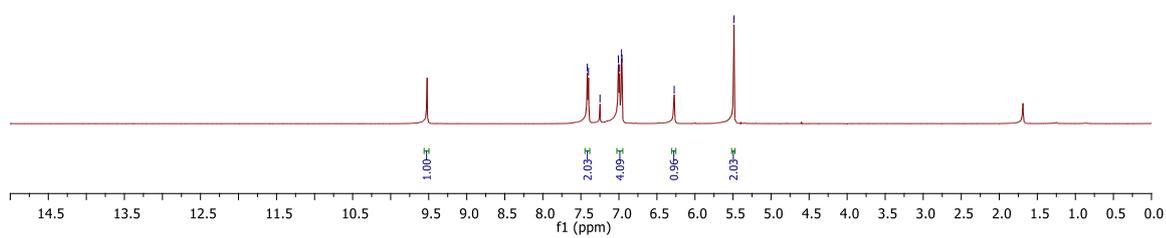
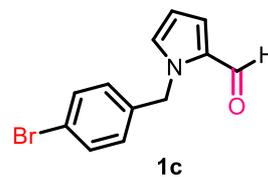
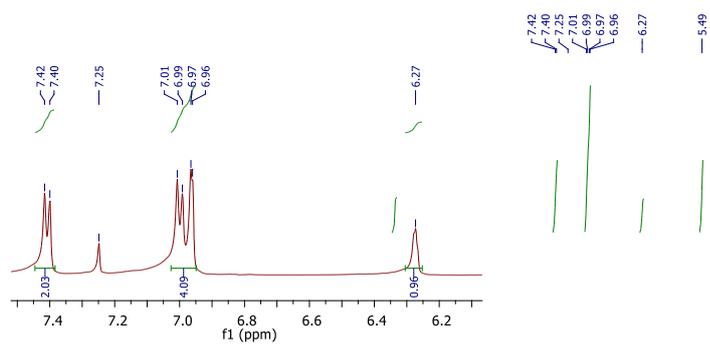
# 1b <sup>1</sup>H NMR (CDCl<sub>3</sub>)



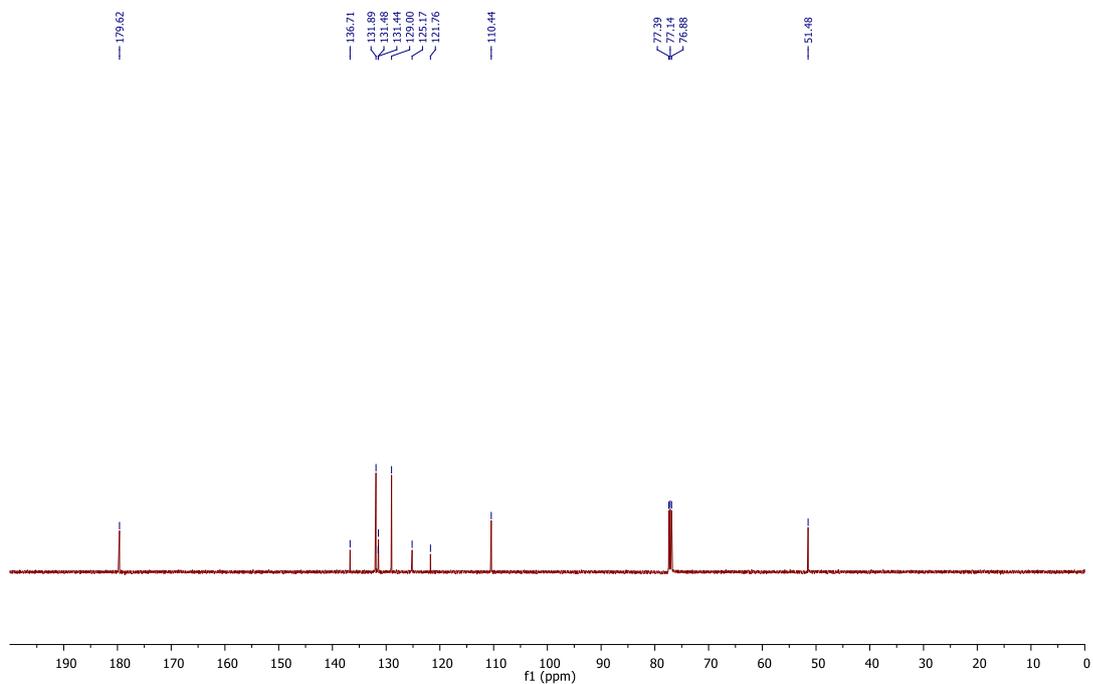
# <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



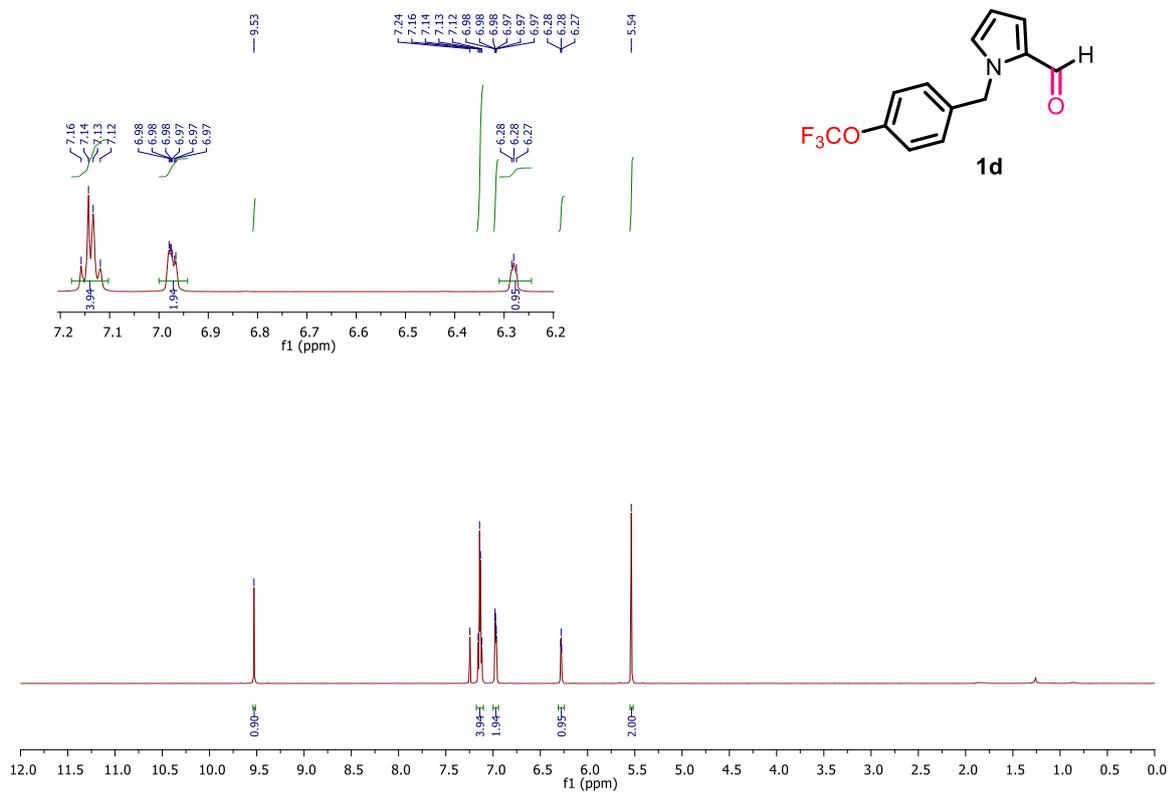
### 1c <sup>1</sup>H NMR (CDCl<sub>3</sub>)



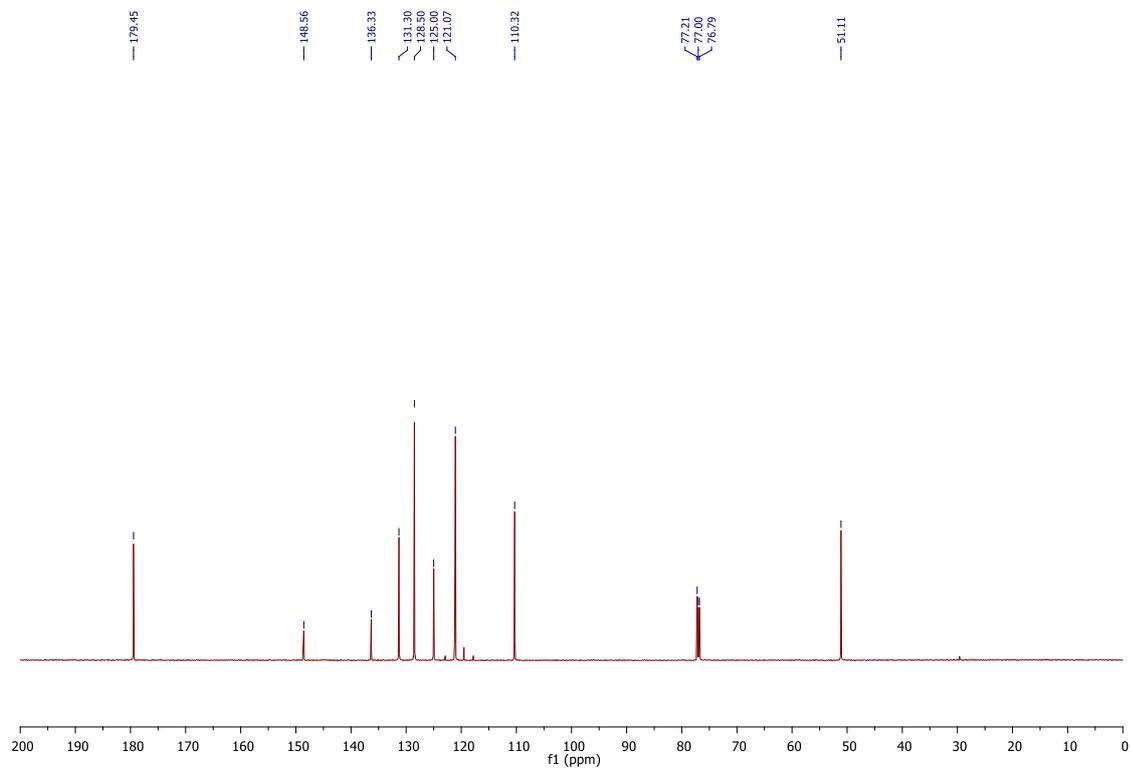
### <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



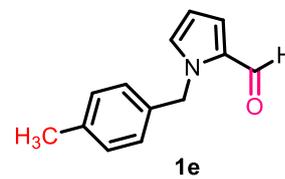
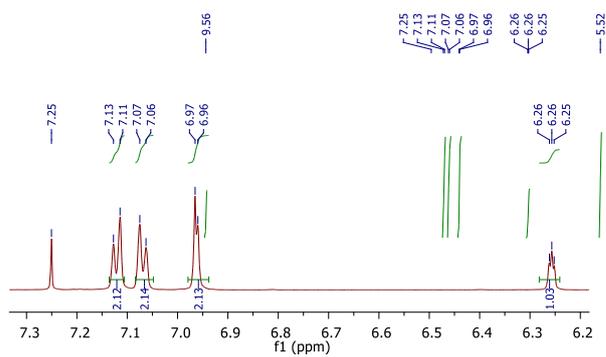
# 1d <sup>1</sup>H NMR (CDCl<sub>3</sub>)



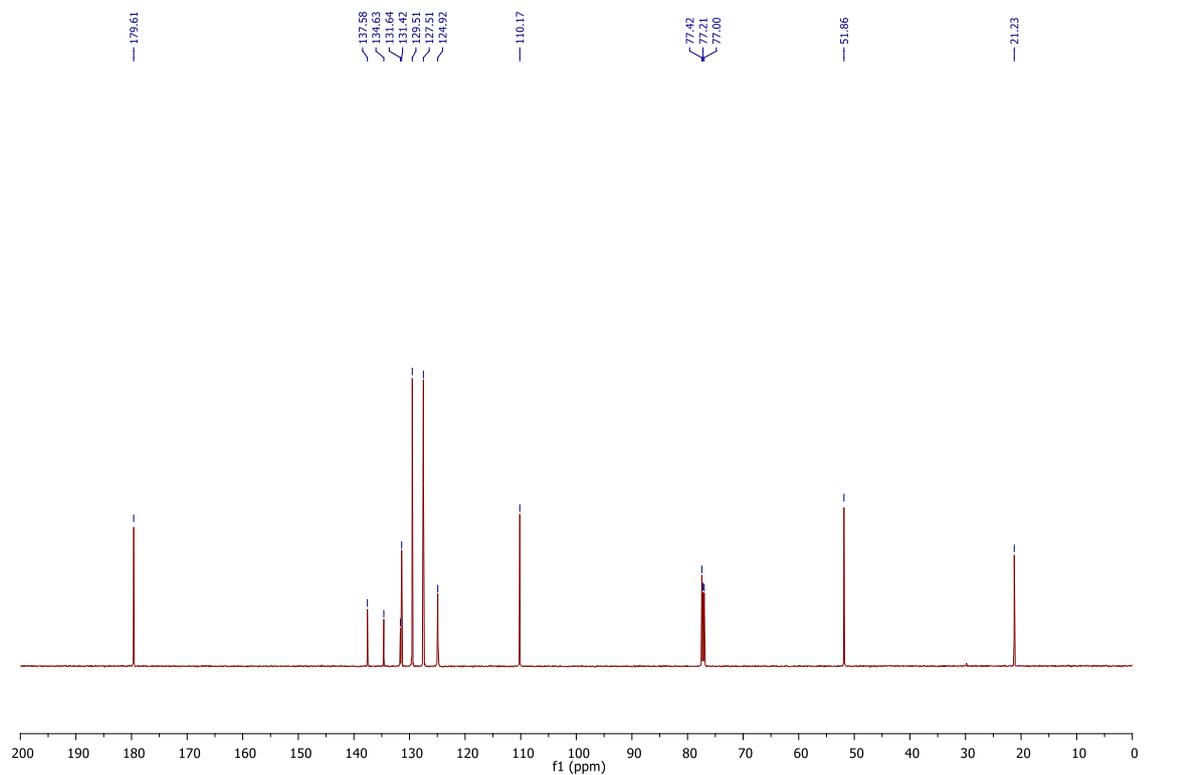
# <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



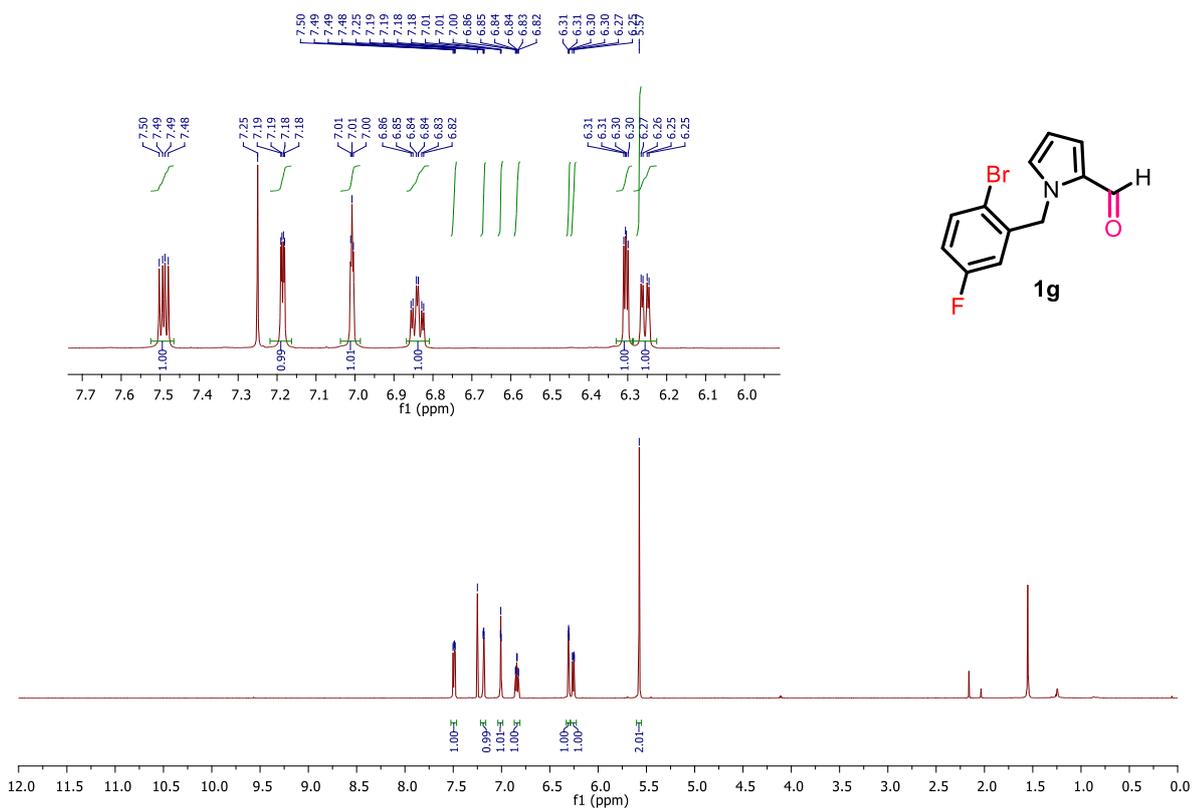
# 1e <sup>1</sup>H NMR (CDCl<sub>3</sub>)



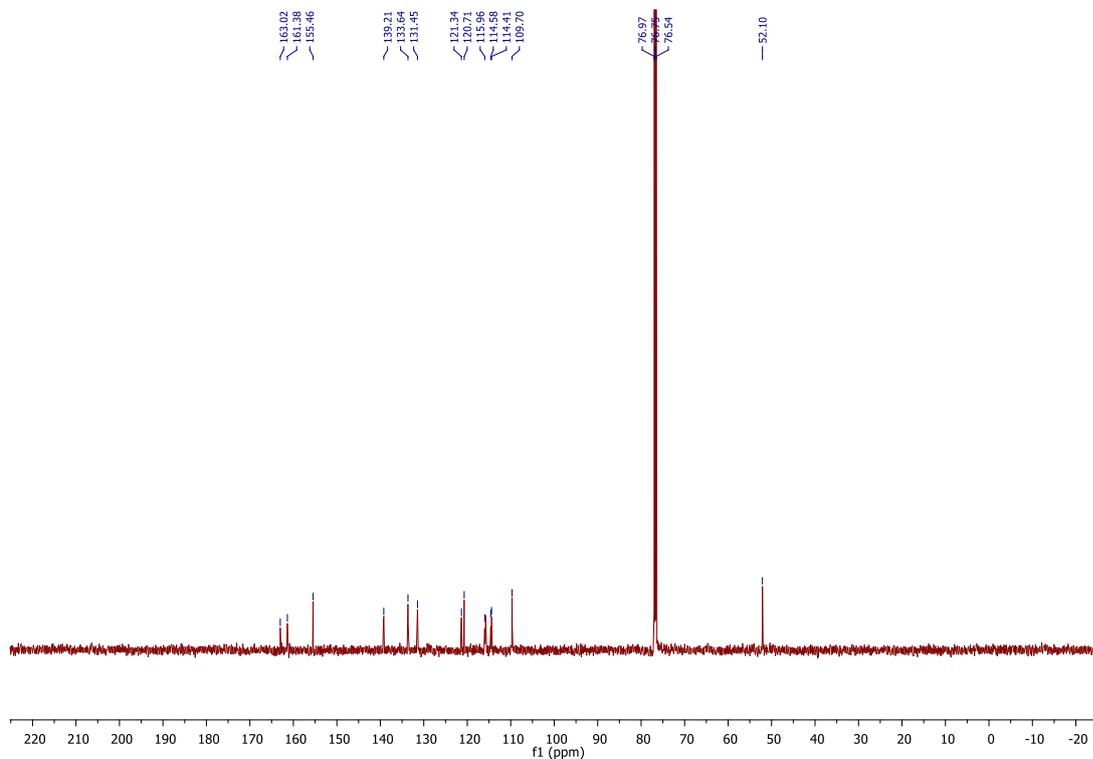
# <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



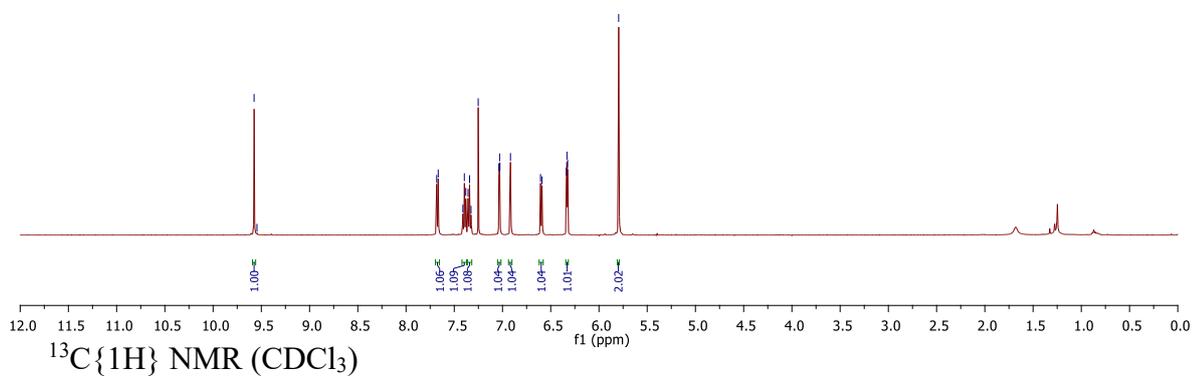
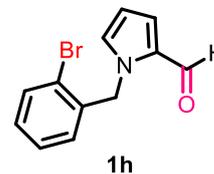
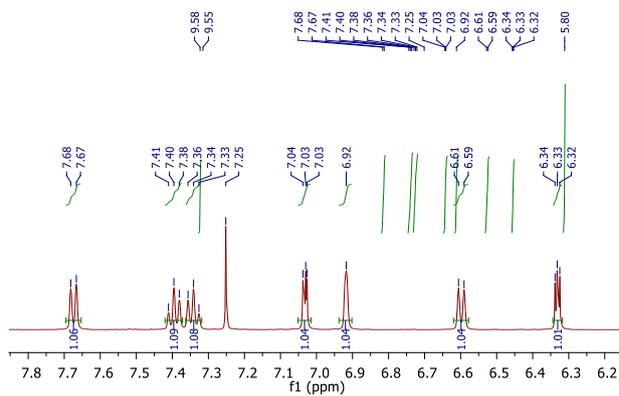
# 1g <sup>1</sup>H NMR (CDCl<sub>3</sub>)



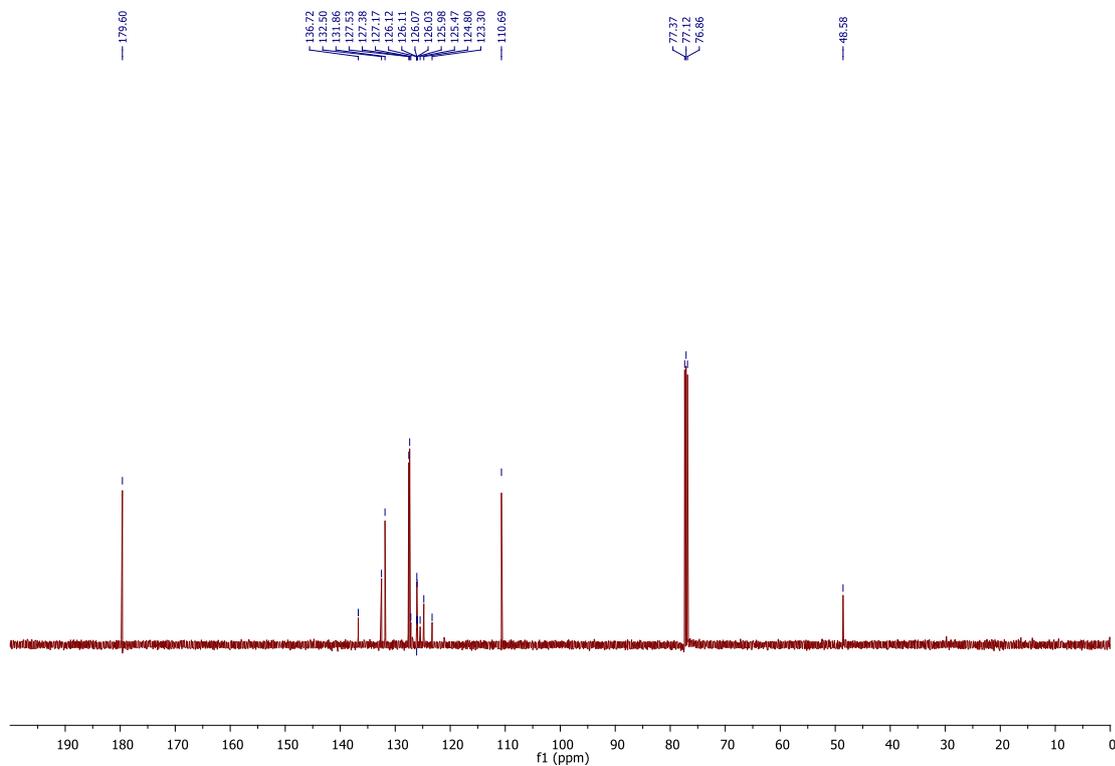
# <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



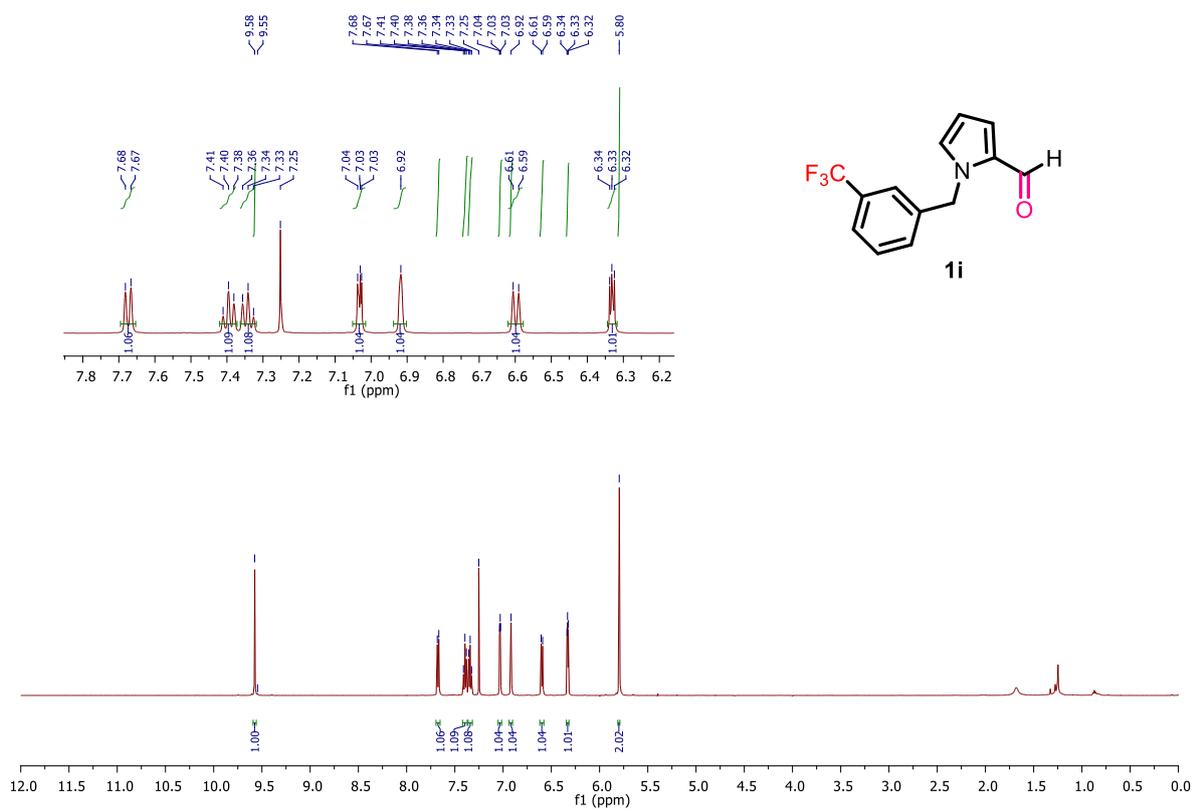
# 1h <sup>1</sup>H NMR (CDCl<sub>3</sub>)



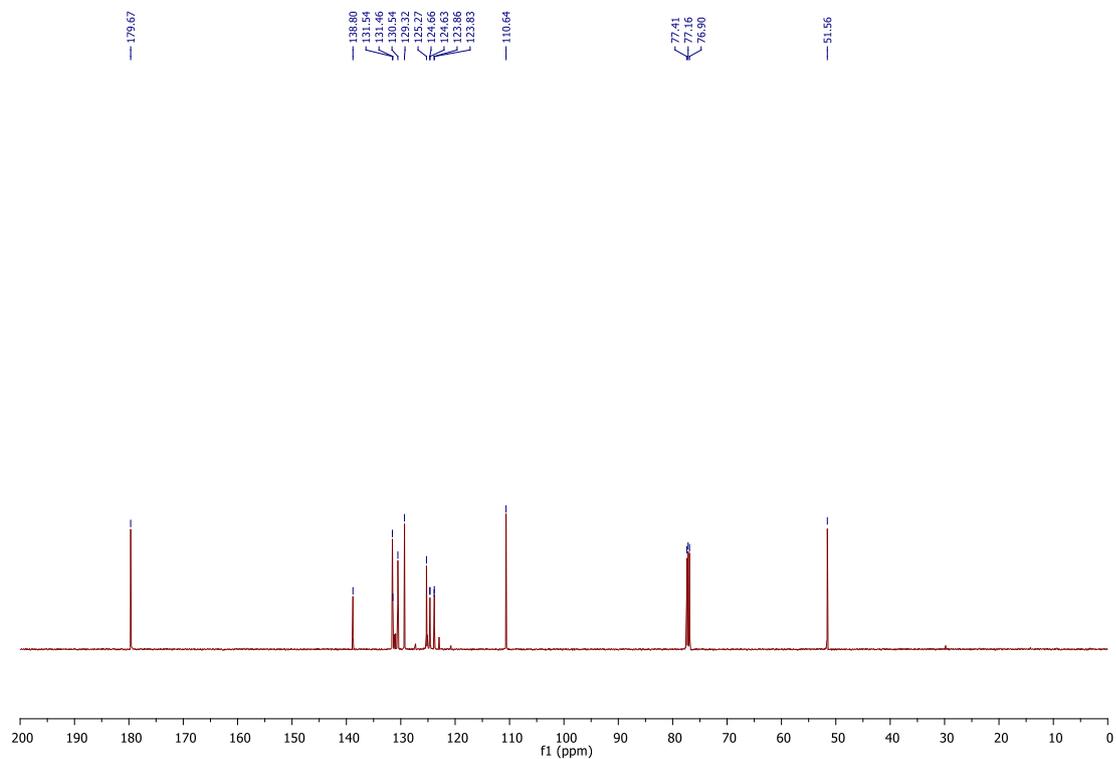
# <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



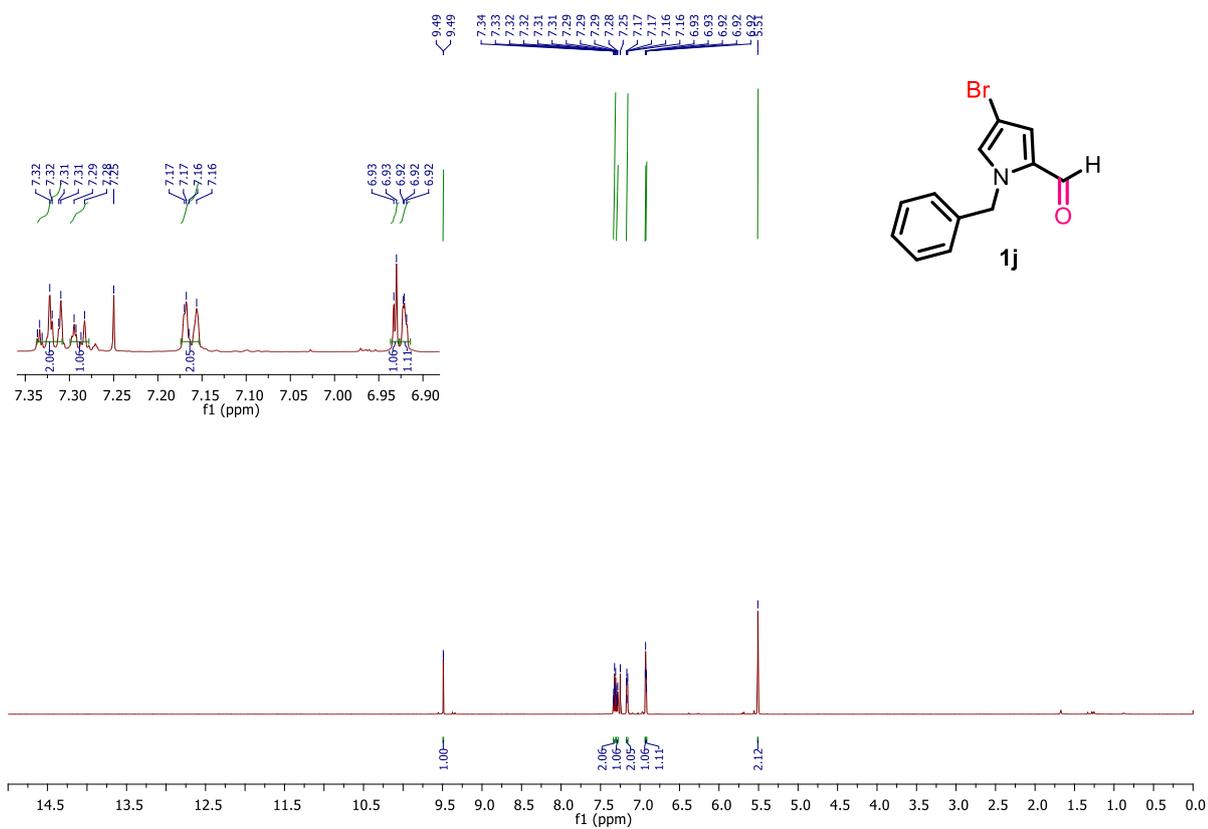
# 1i <sup>1</sup>H NMR (CDCl<sub>3</sub>)



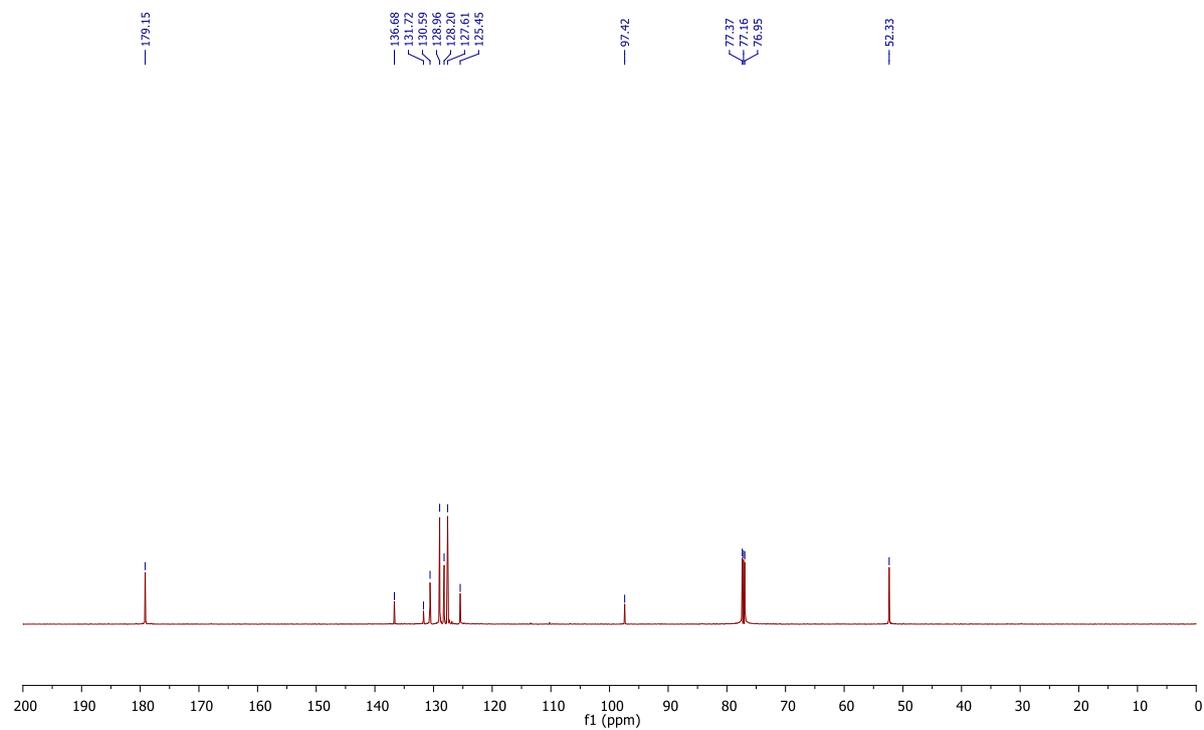
# <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



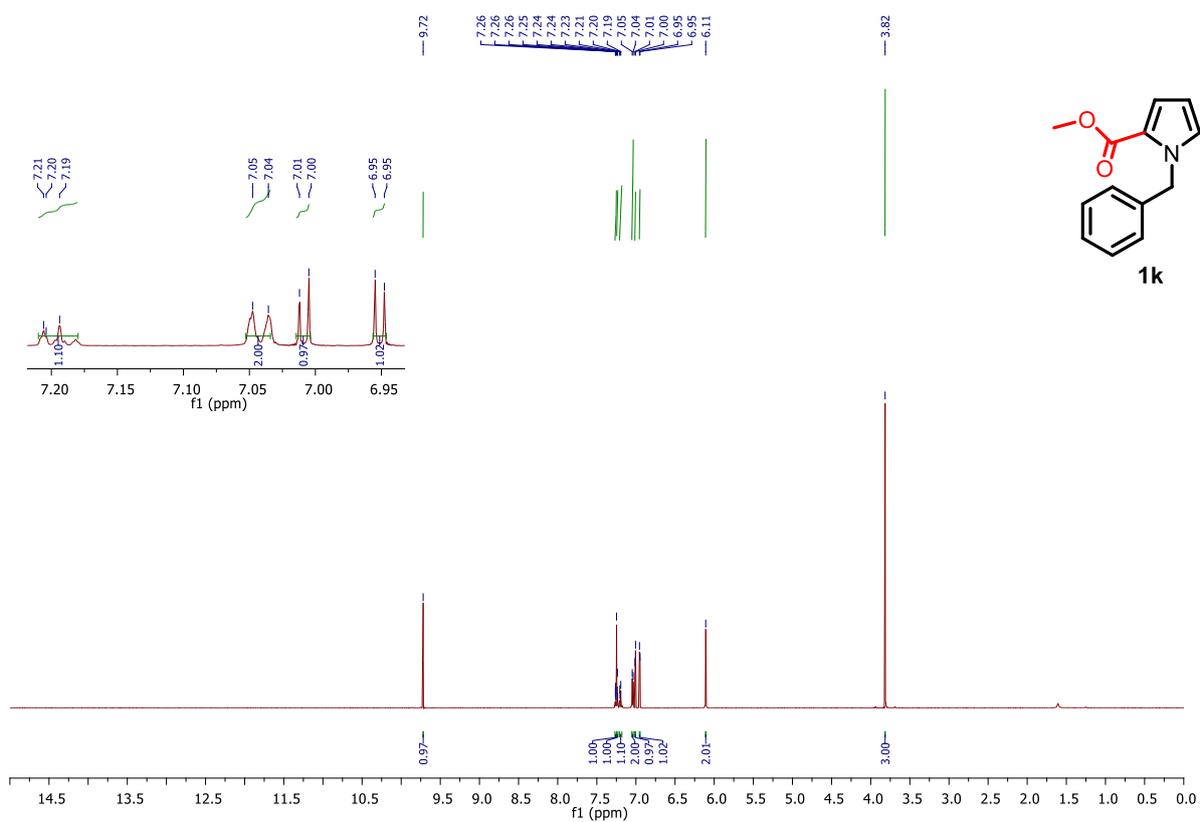
# 1j <sup>1</sup>H NMR (CDCl<sub>3</sub>)



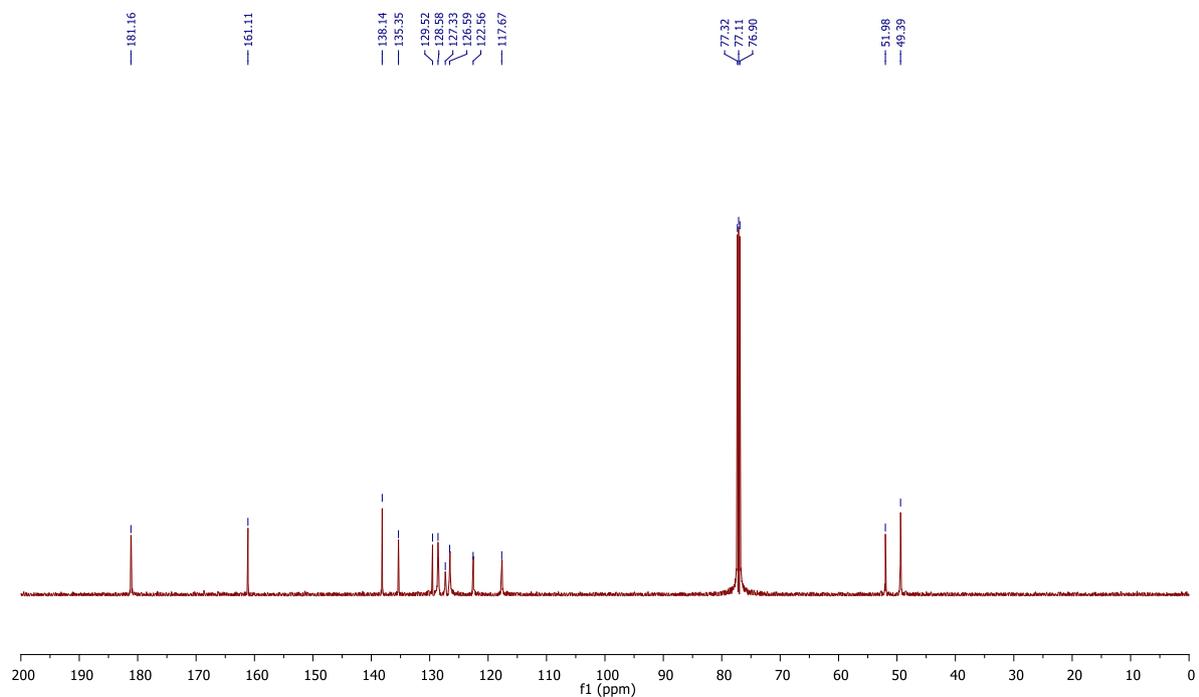
# <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



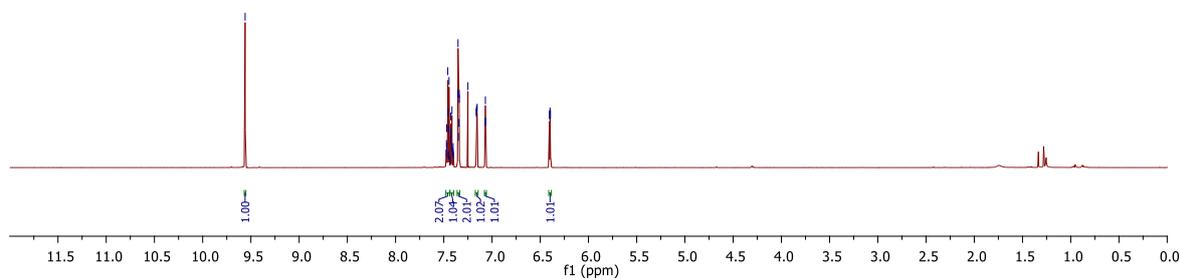
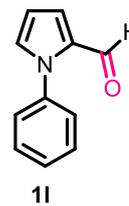
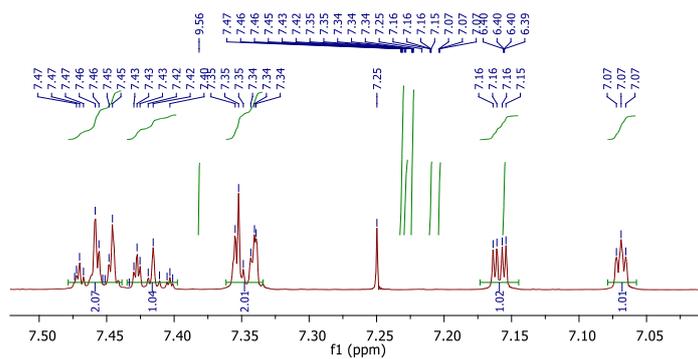
# 1k <sup>1</sup>H NMR (CDCl<sub>3</sub>)



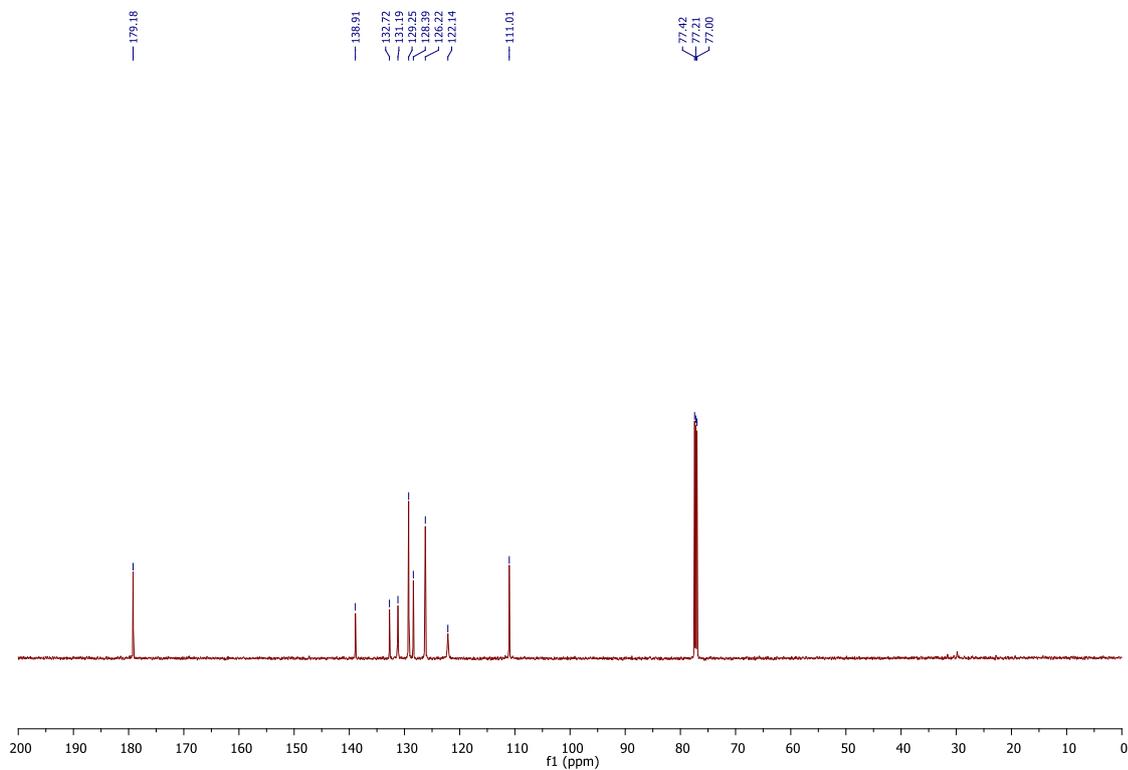
# <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



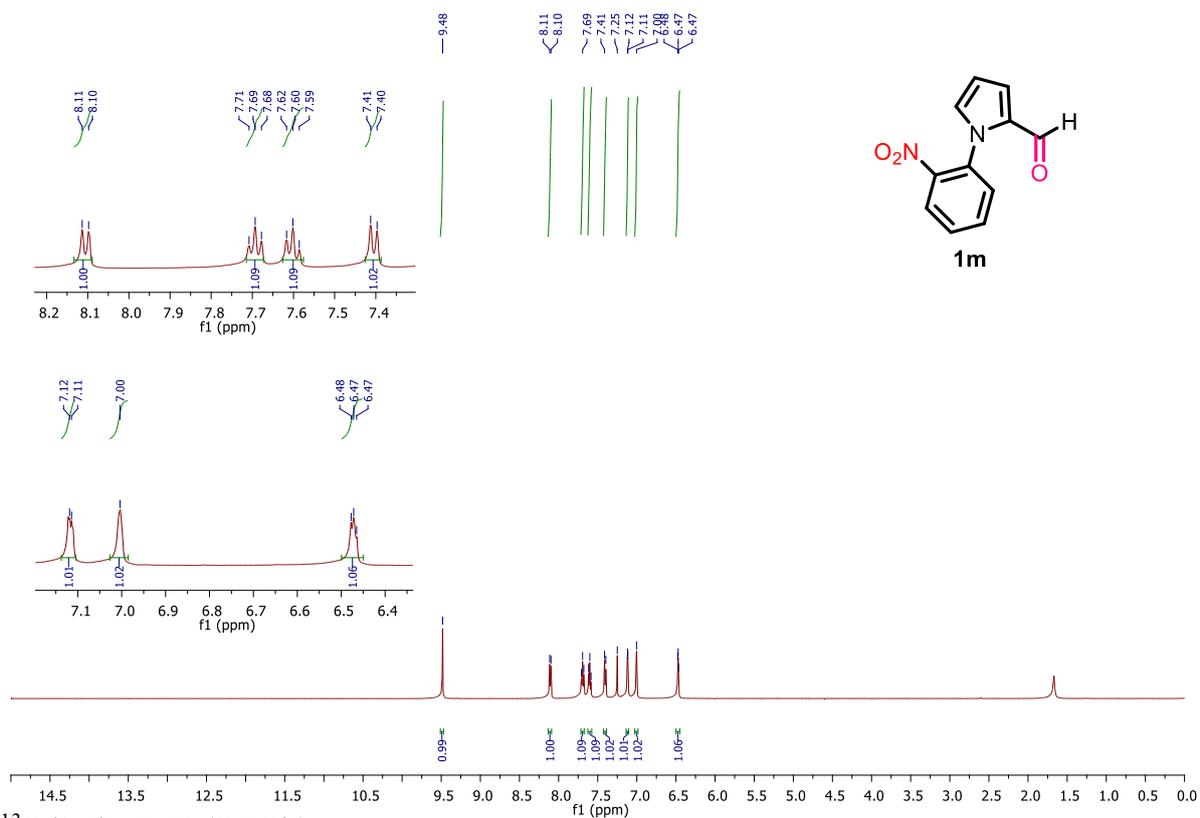
# 11 <sup>1</sup>H NMR (CDCl<sub>3</sub>)



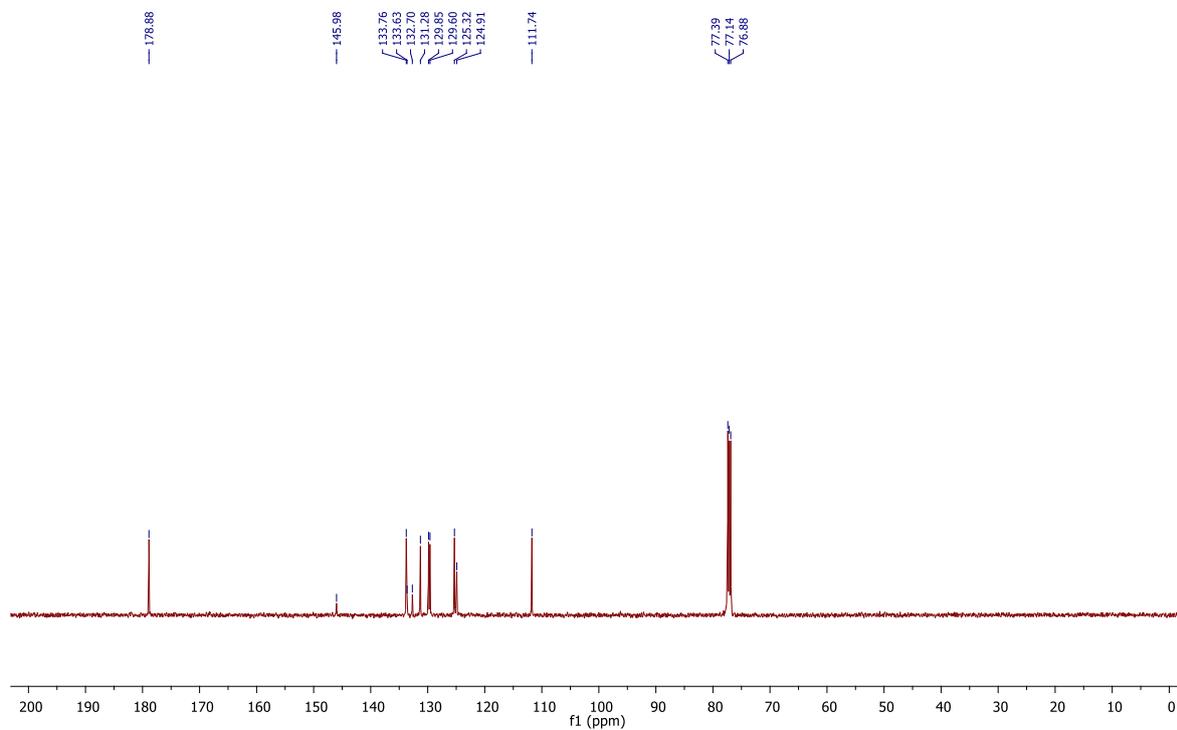
# 13C{1H} NMR (CDCl<sub>3</sub>)



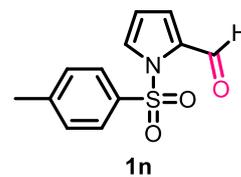
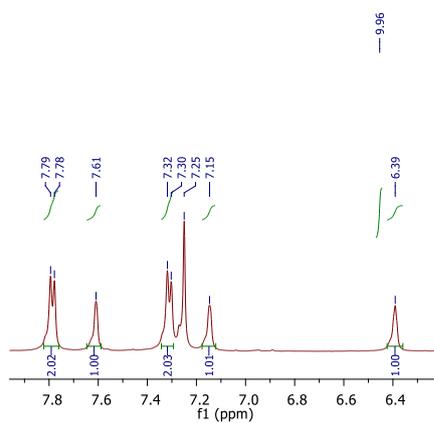
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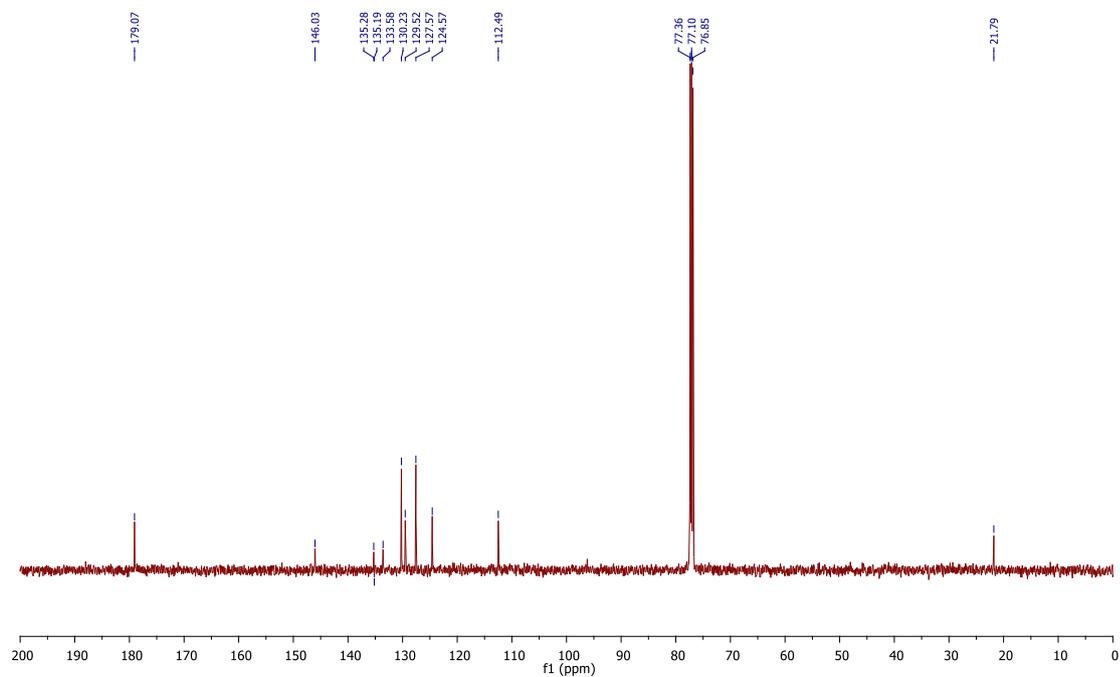
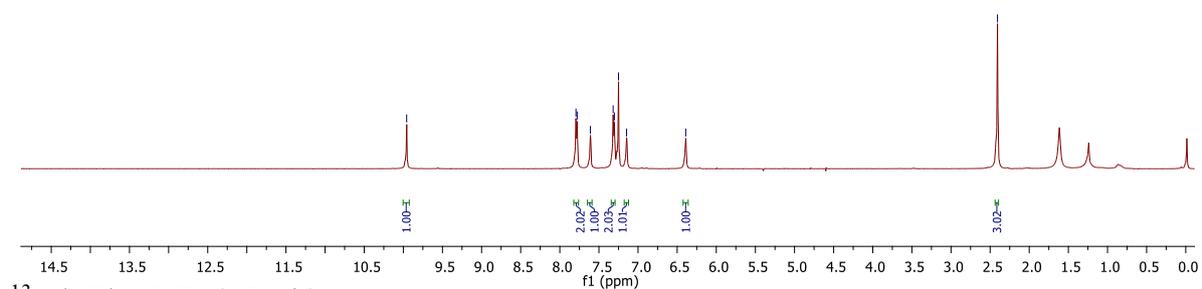
# <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



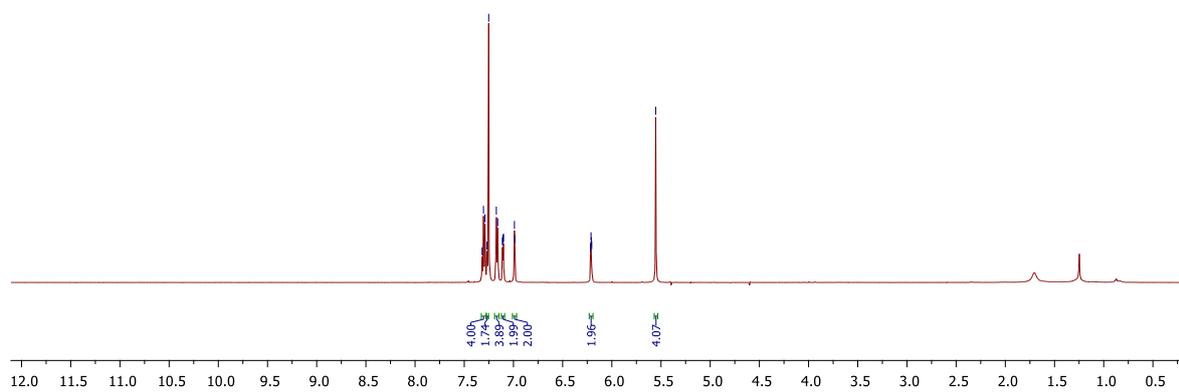
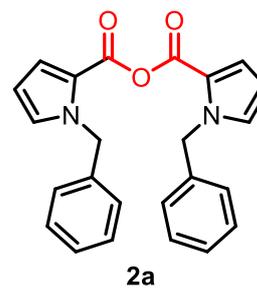
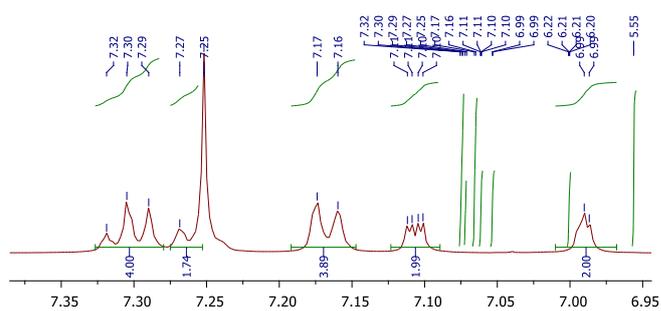
# 1n <sup>1</sup>H NMR (CDCl<sub>3</sub>)



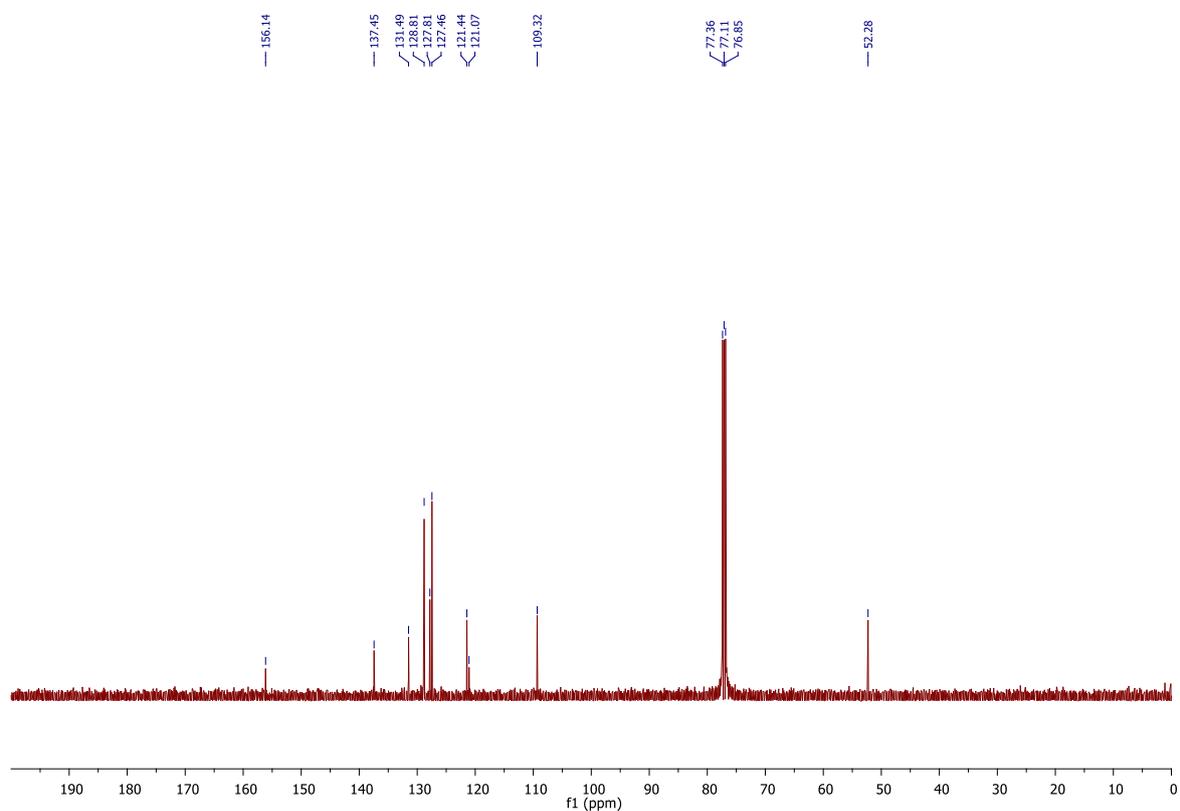
# <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



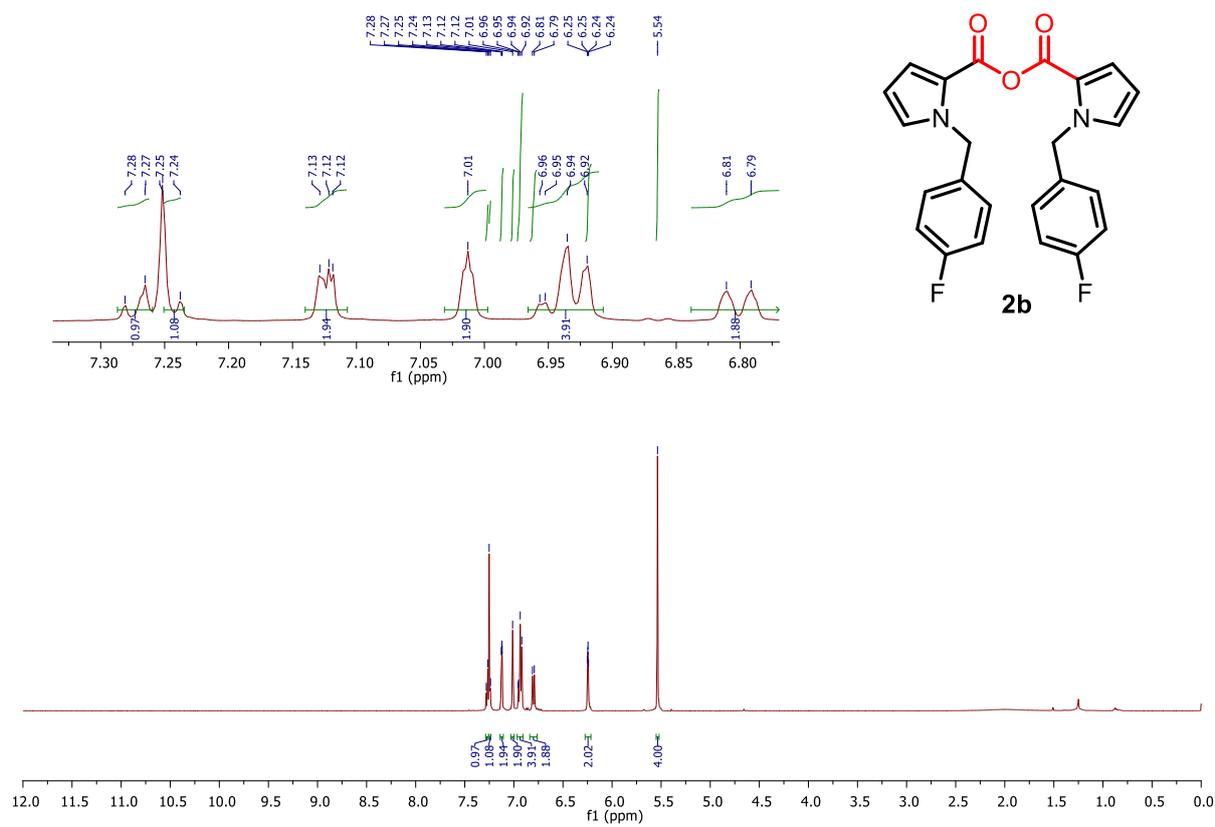
## 2a <sup>1</sup>H NMR (CDCl<sub>3</sub>)



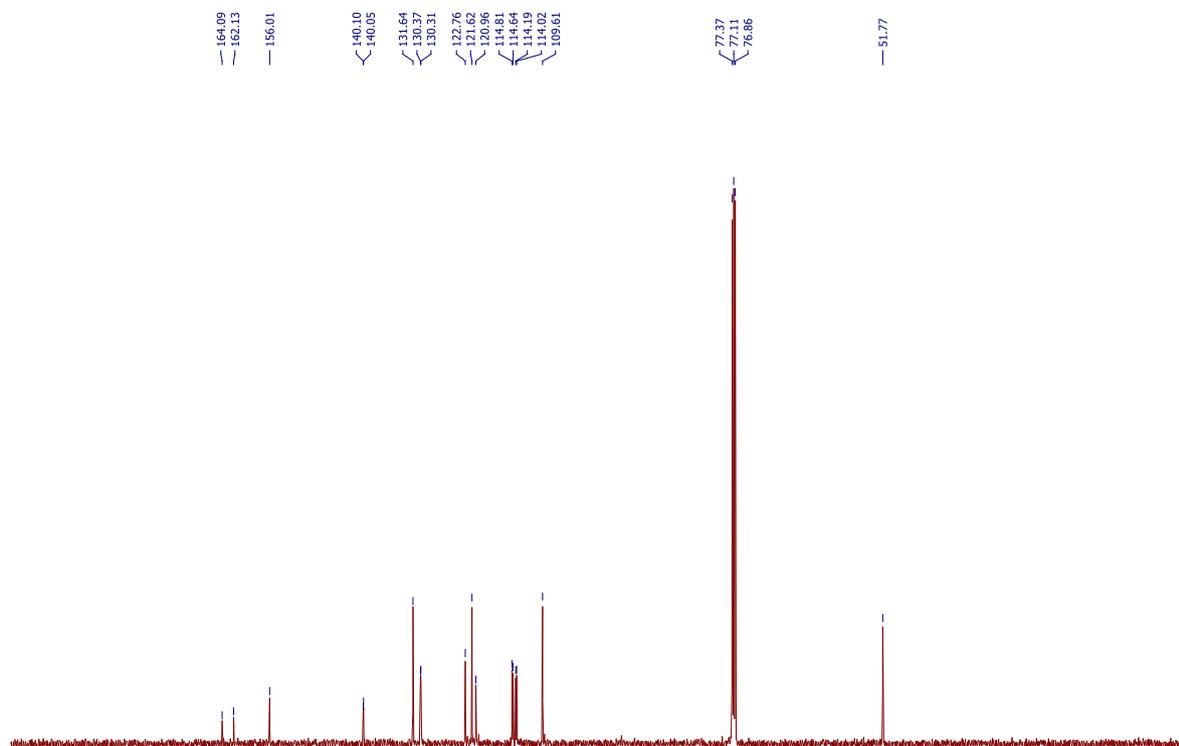
## <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



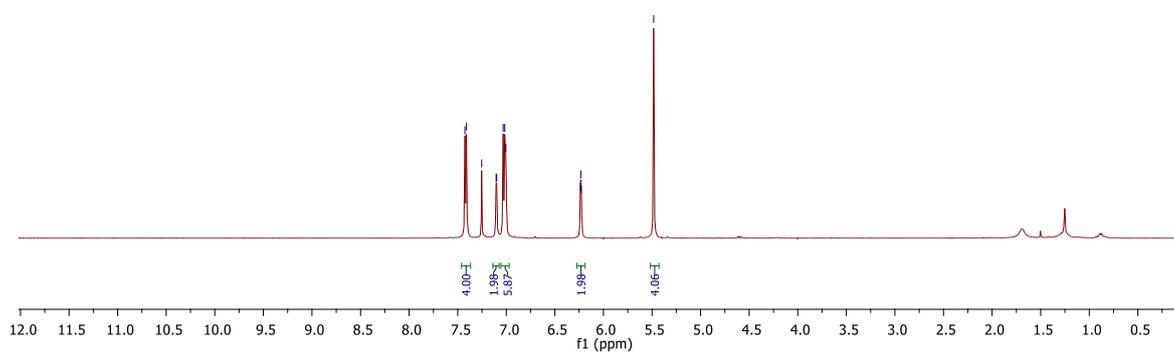
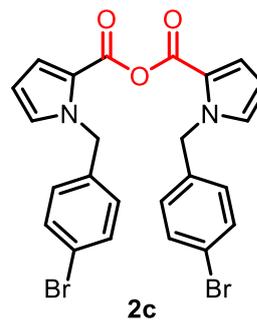
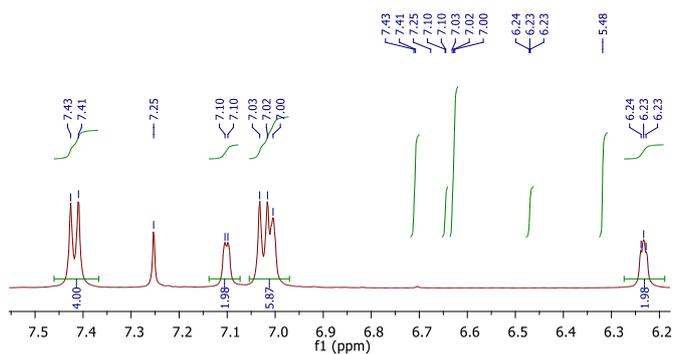
## 2b <sup>1</sup>H NMR (CDCl<sub>3</sub>)



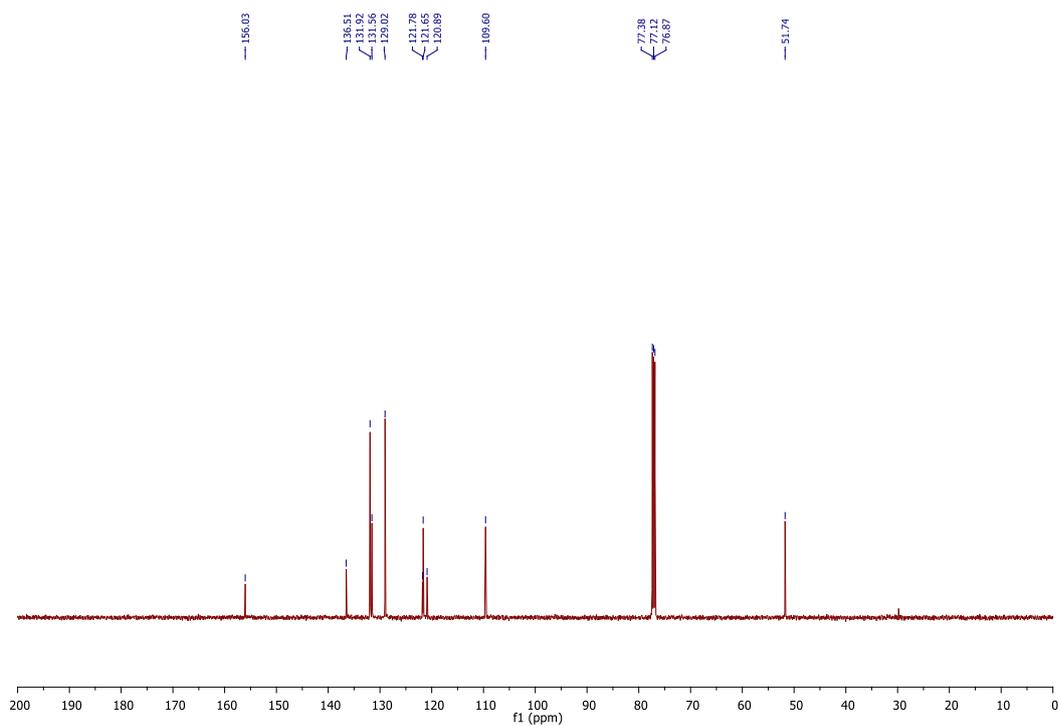
## <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



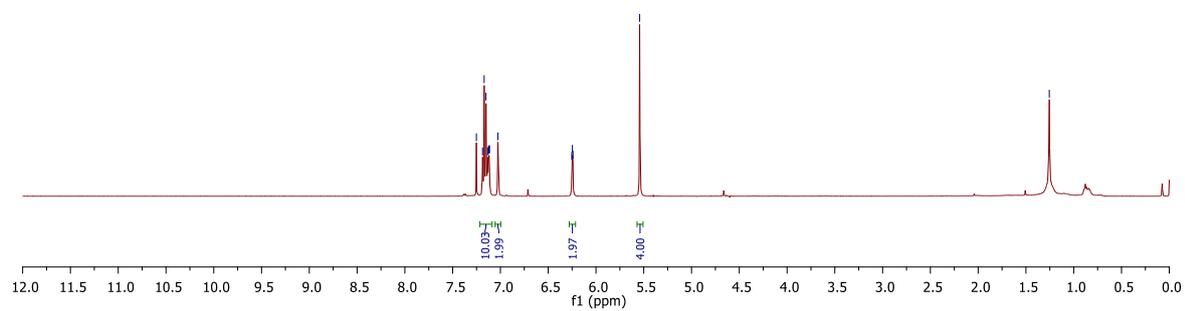
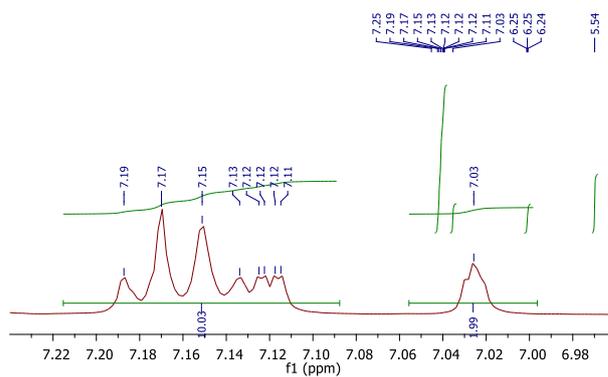
### 2c <sup>1</sup>H NMR (CDCl<sub>3</sub>)



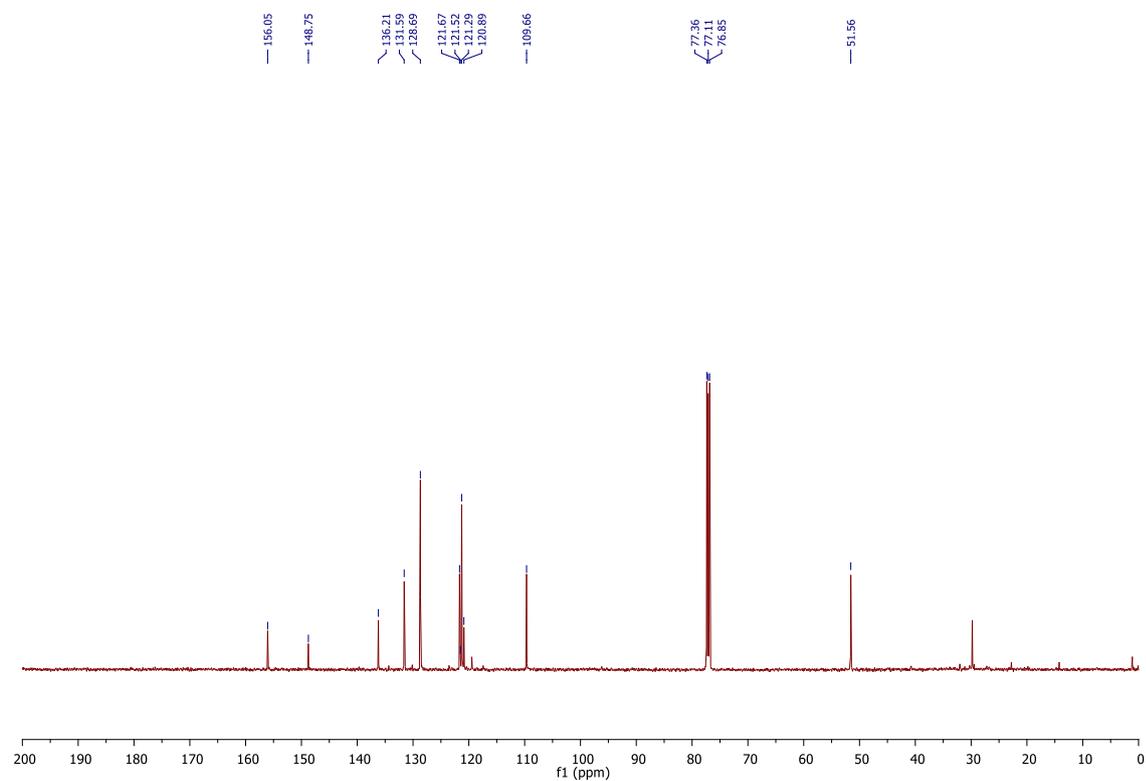
### <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



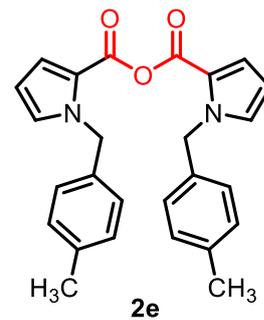
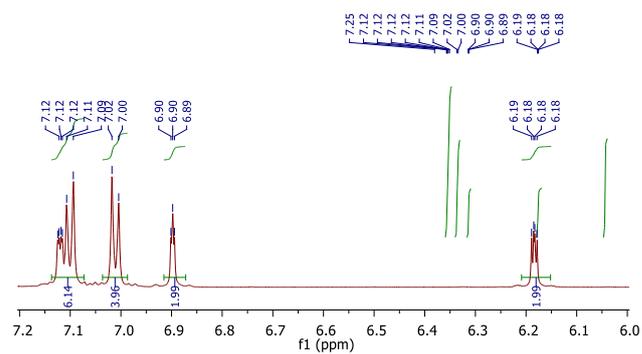
## 2d <sup>1</sup>H NMR (CDCl<sub>3</sub>)



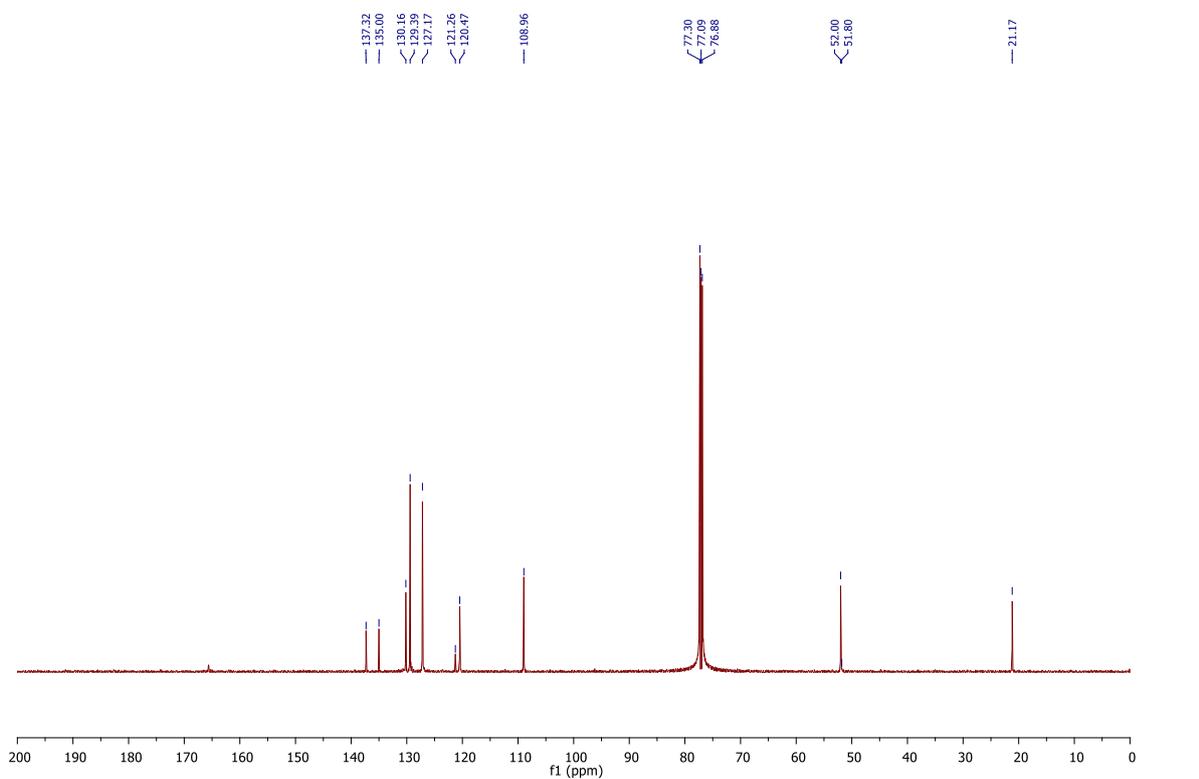
## <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



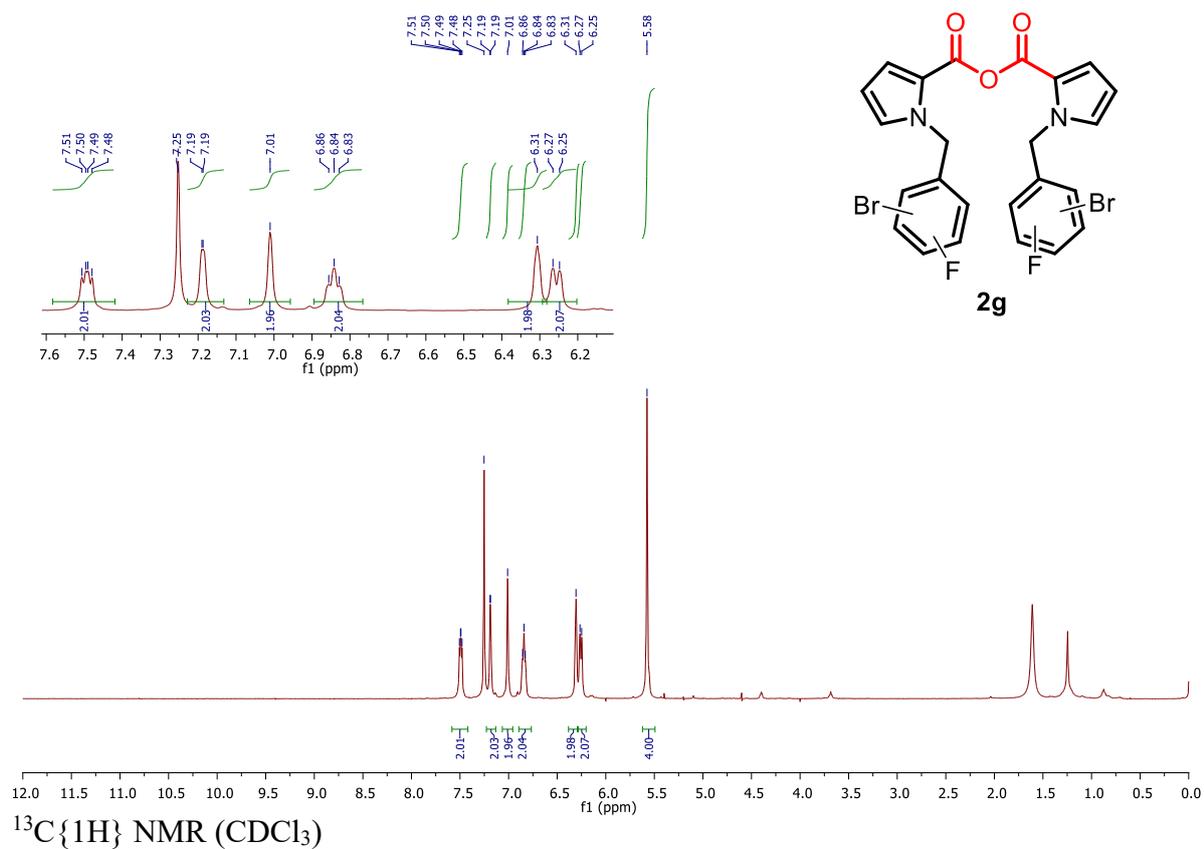
**2e**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )



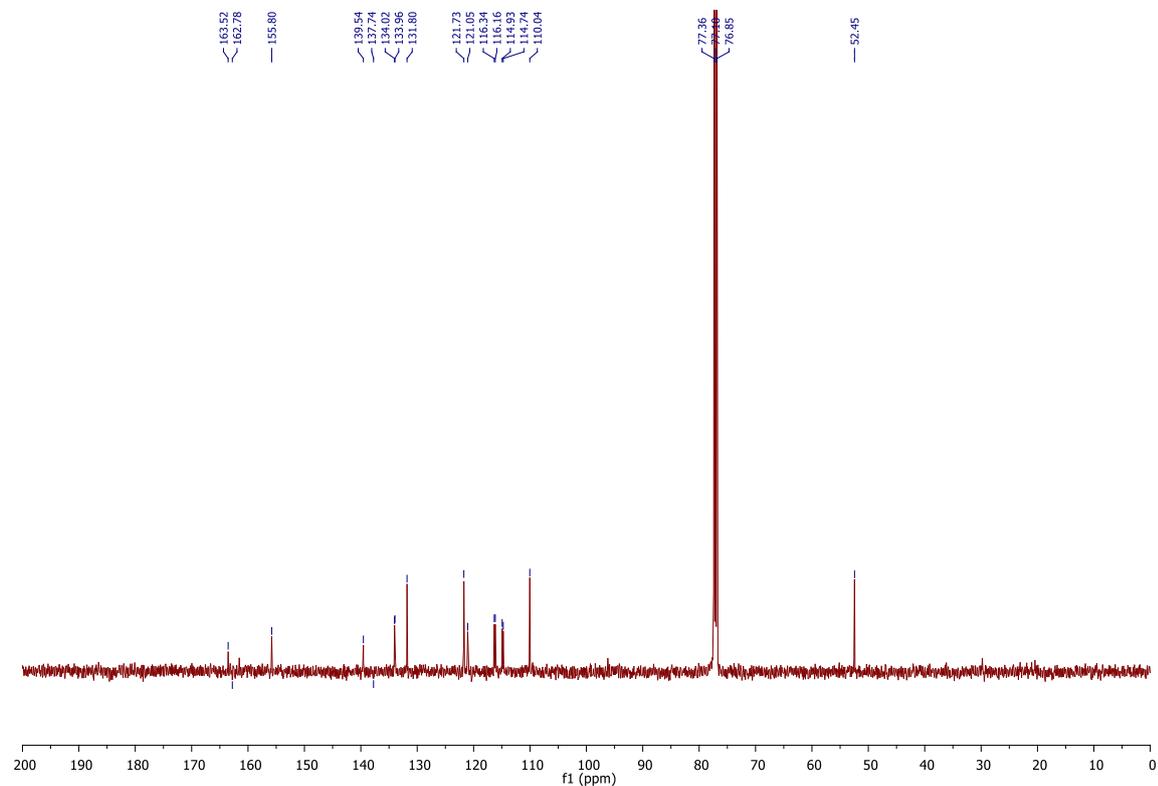
$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )



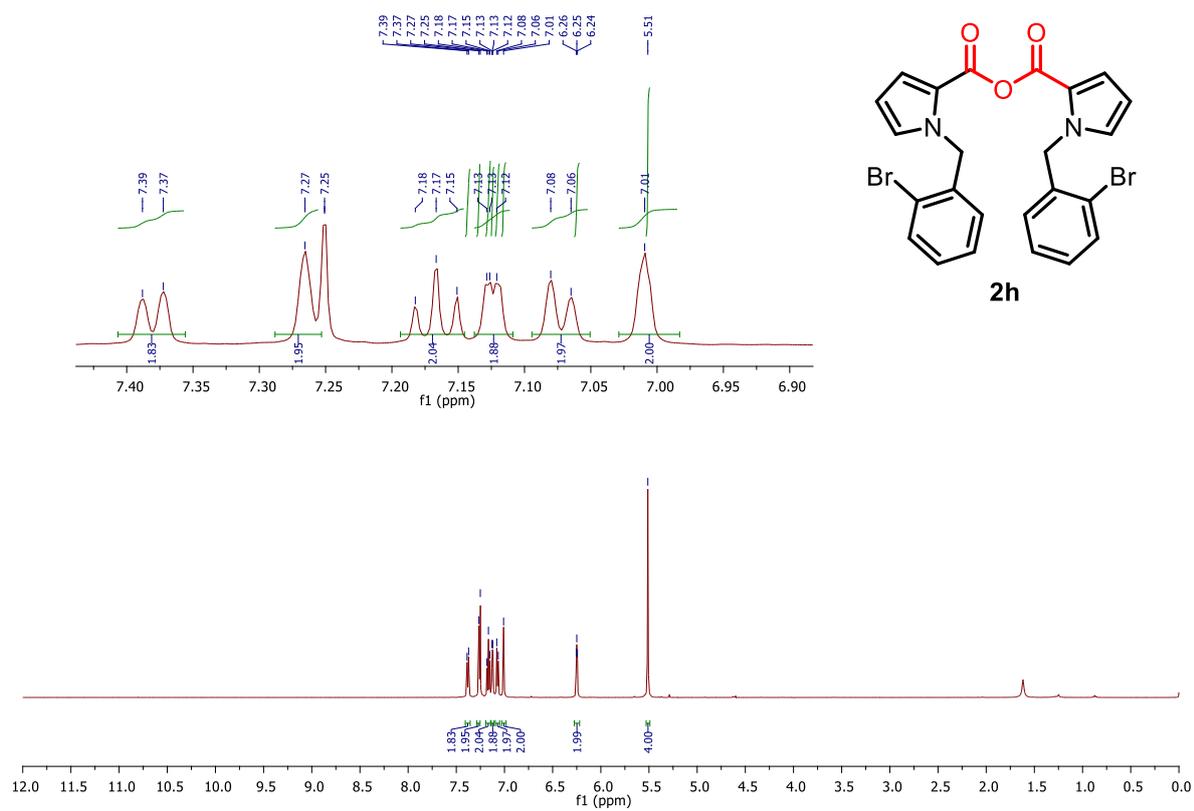
### 2g <sup>1</sup>H NMR (CDCl<sub>3</sub>)



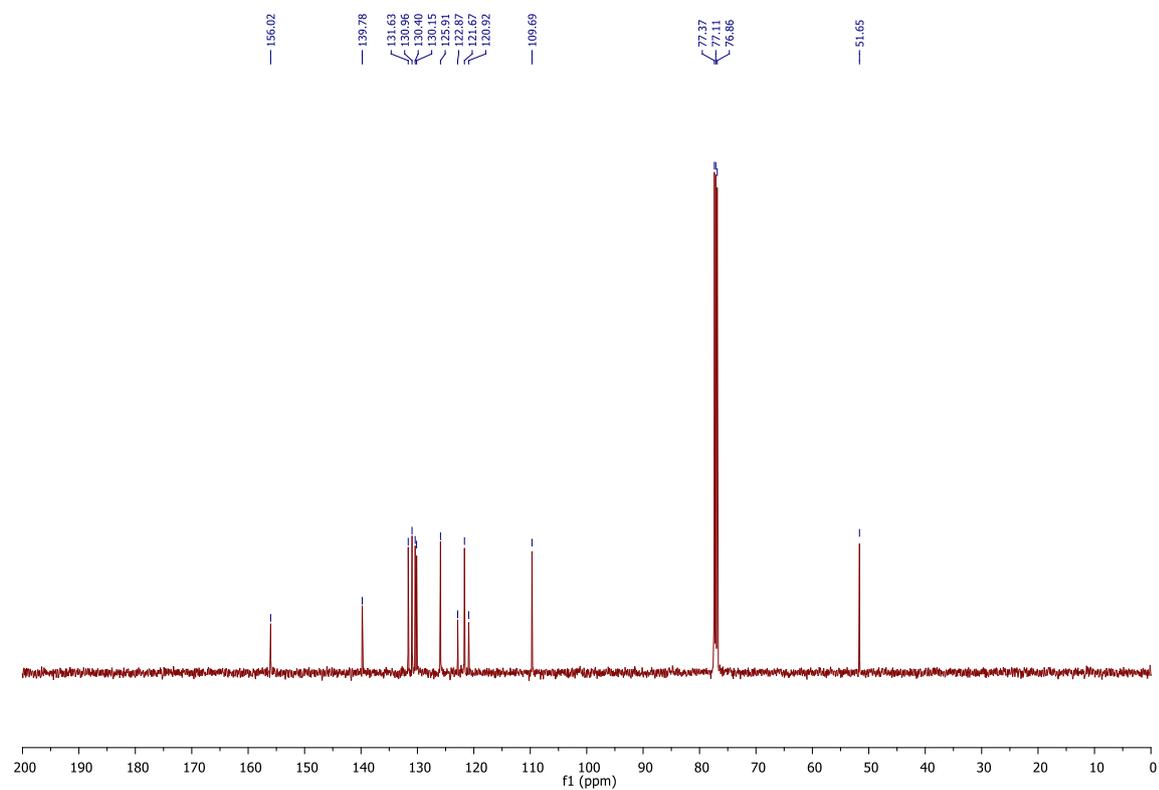
### <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



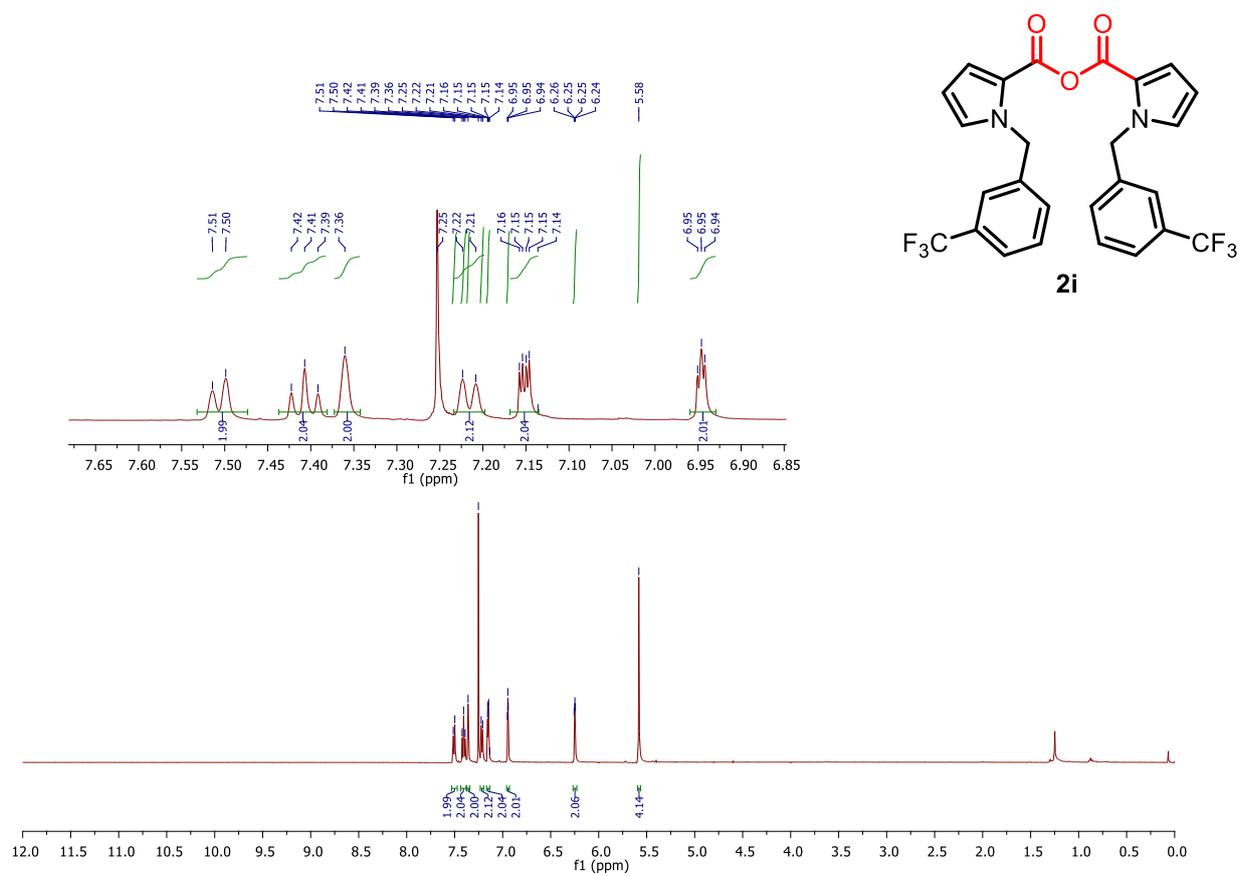
## 2h <sup>1</sup>H NMR (CDCl<sub>3</sub>)



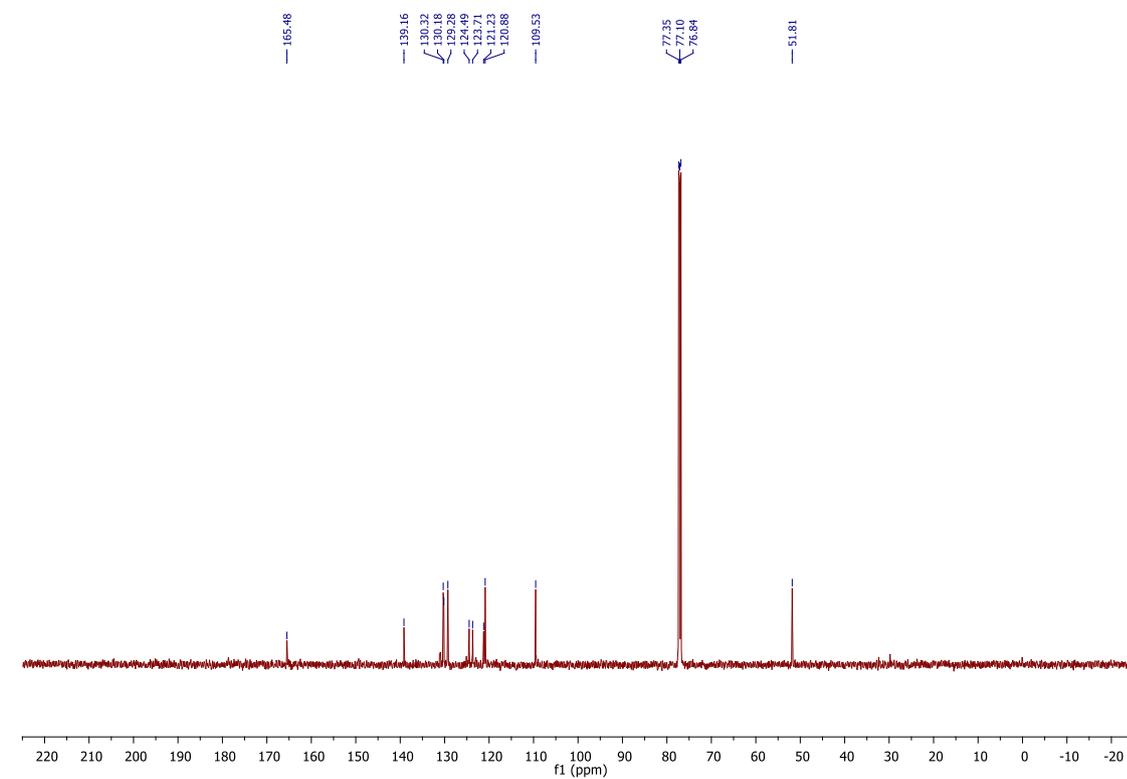
## <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



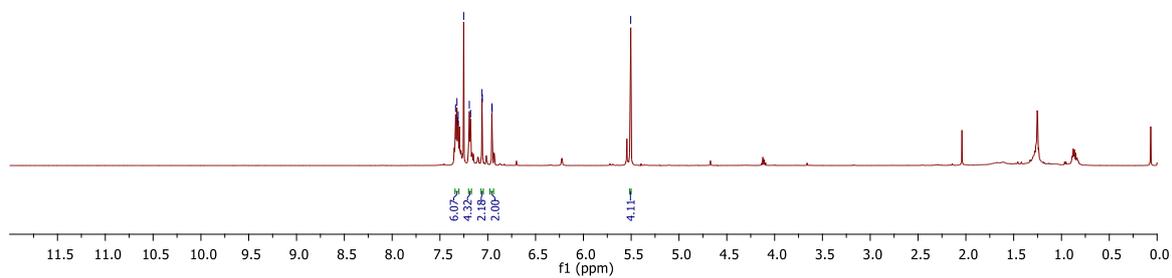
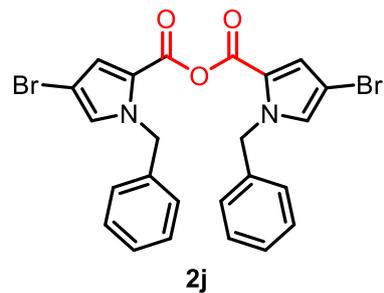
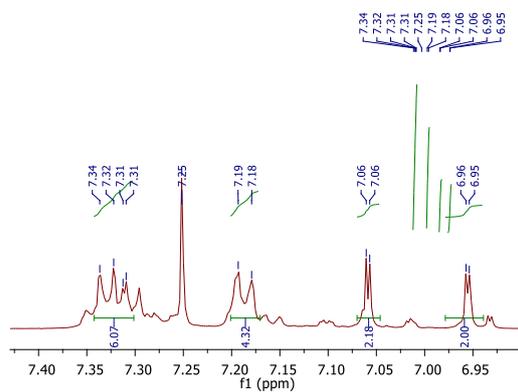
**2i** <sup>1</sup>H NMR (CDCl<sub>3</sub>)



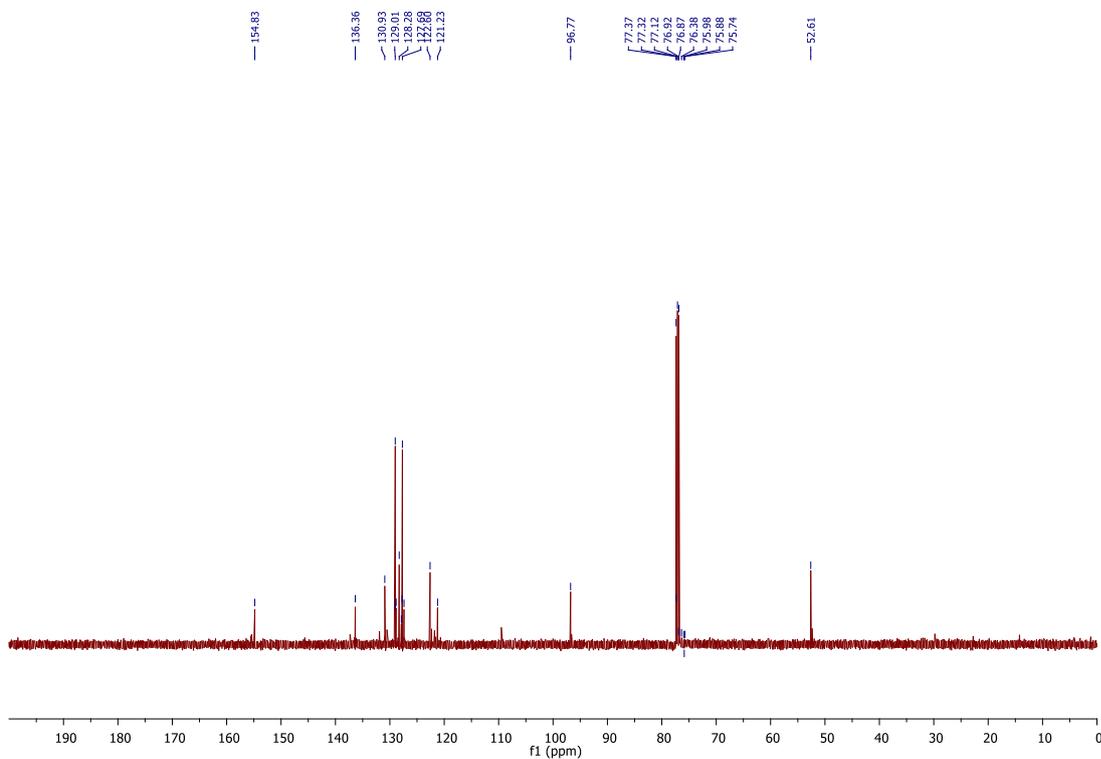
**2i** <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



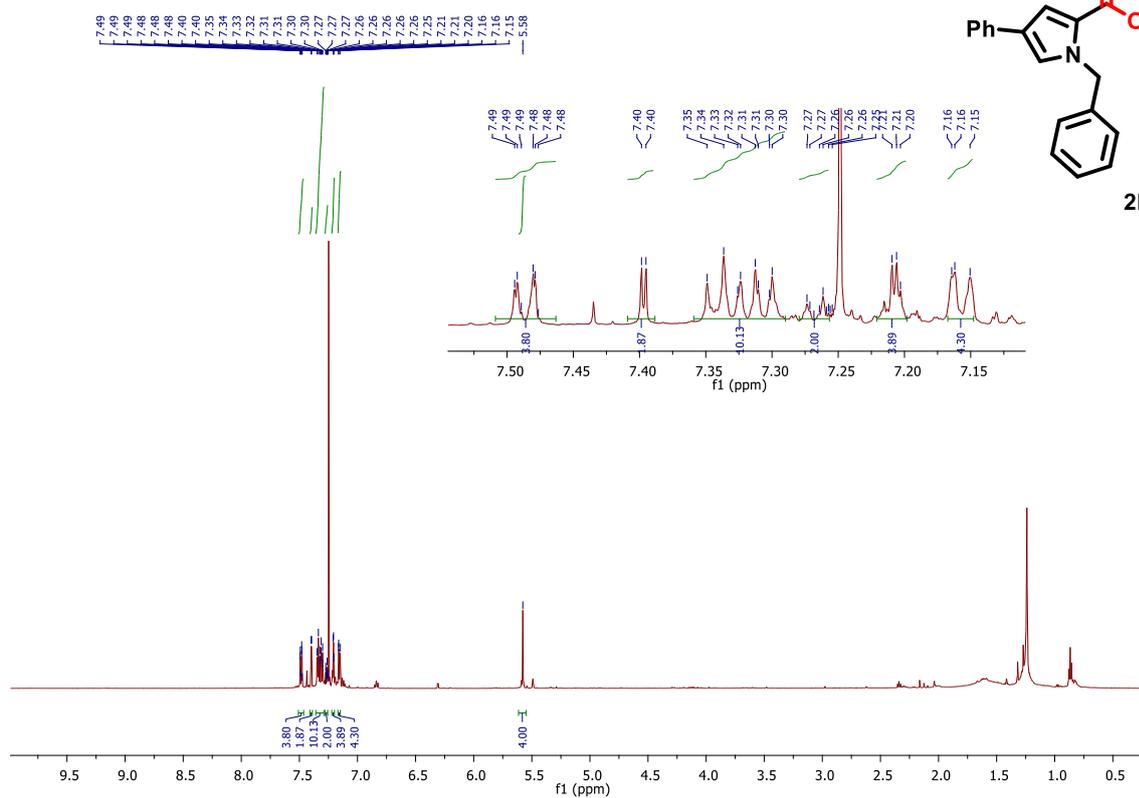
**2j**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )



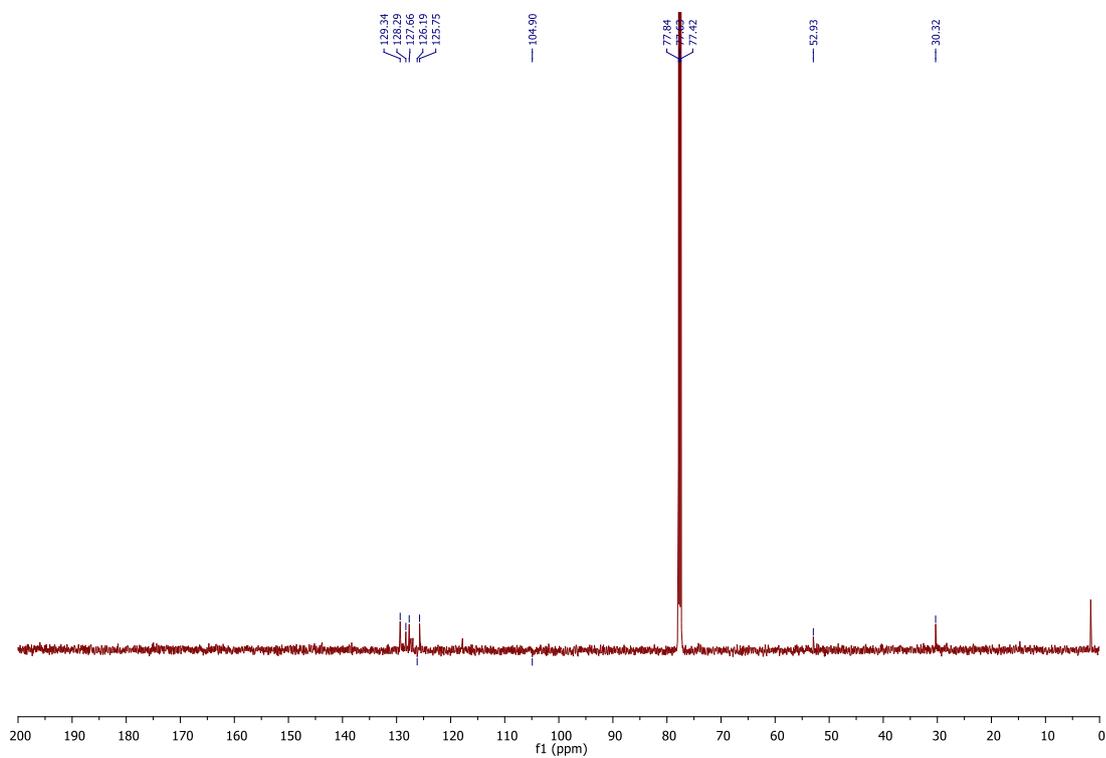
$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )



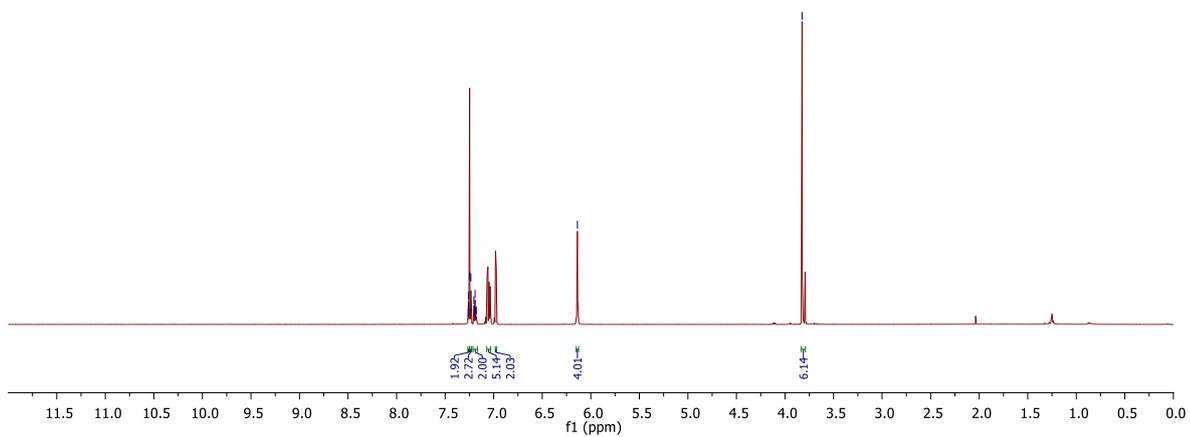
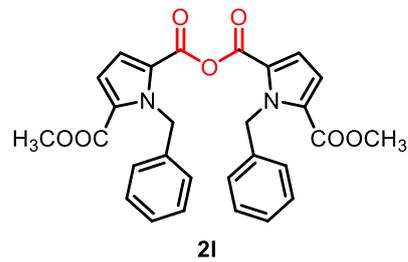
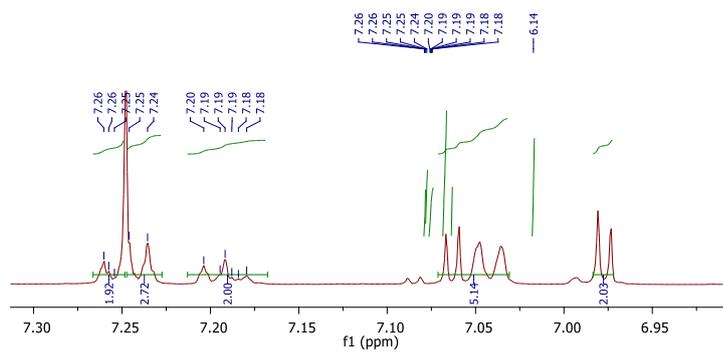
### 2k <sup>1</sup>H NMR (CDCl<sub>3</sub>)



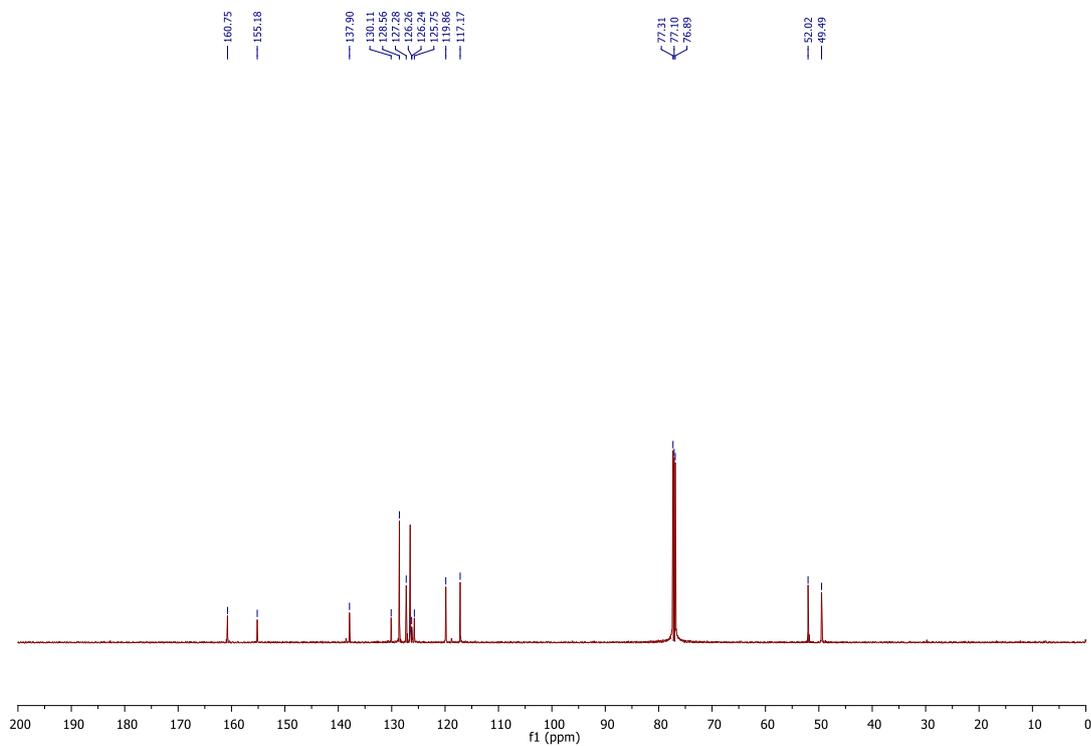
### <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



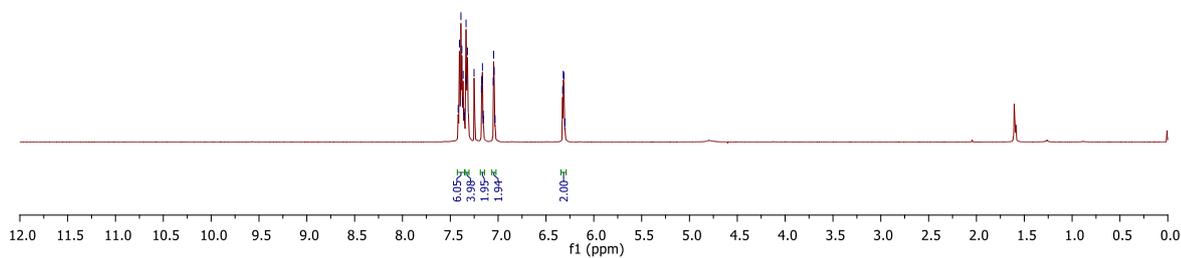
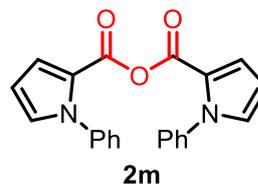
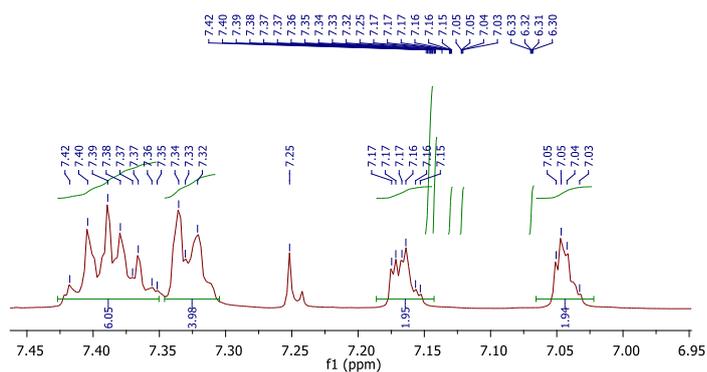
21 <sup>1</sup>H NMR (CDCl<sub>3</sub>)



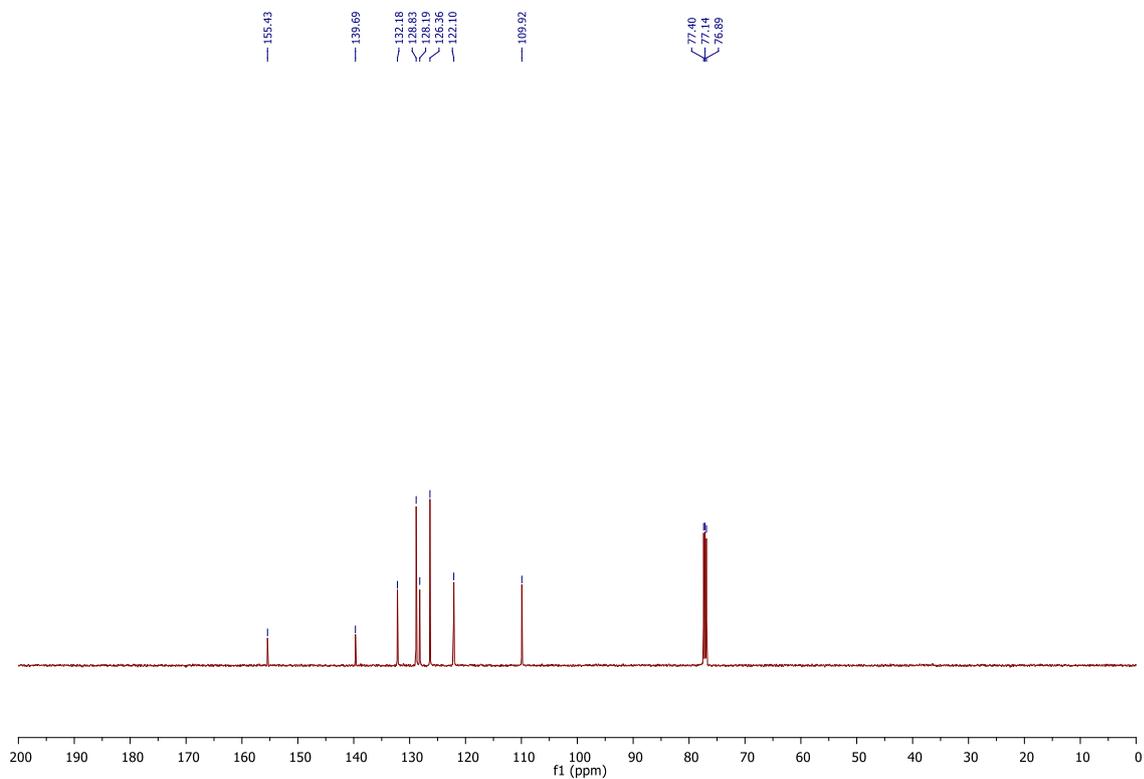
<sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



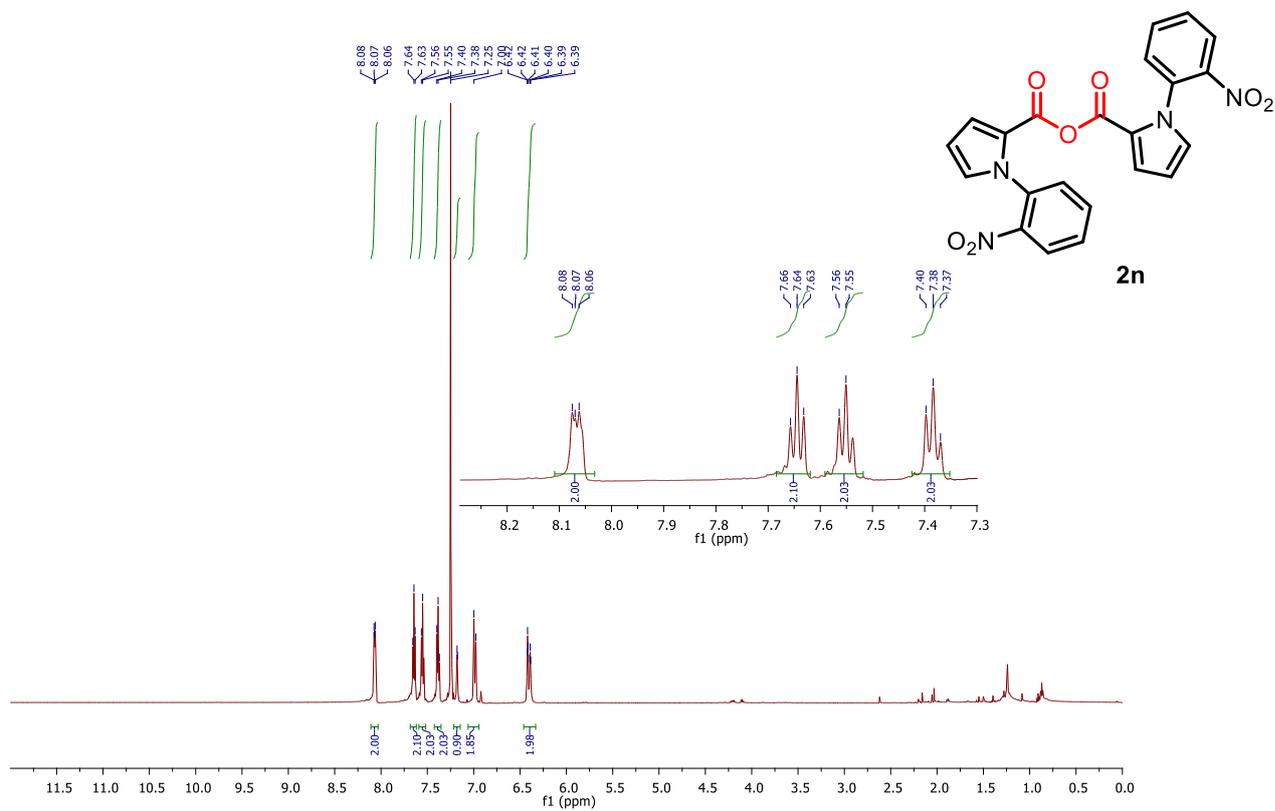
## 2m <sup>1</sup>H NMR (CDCl<sub>3</sub>)



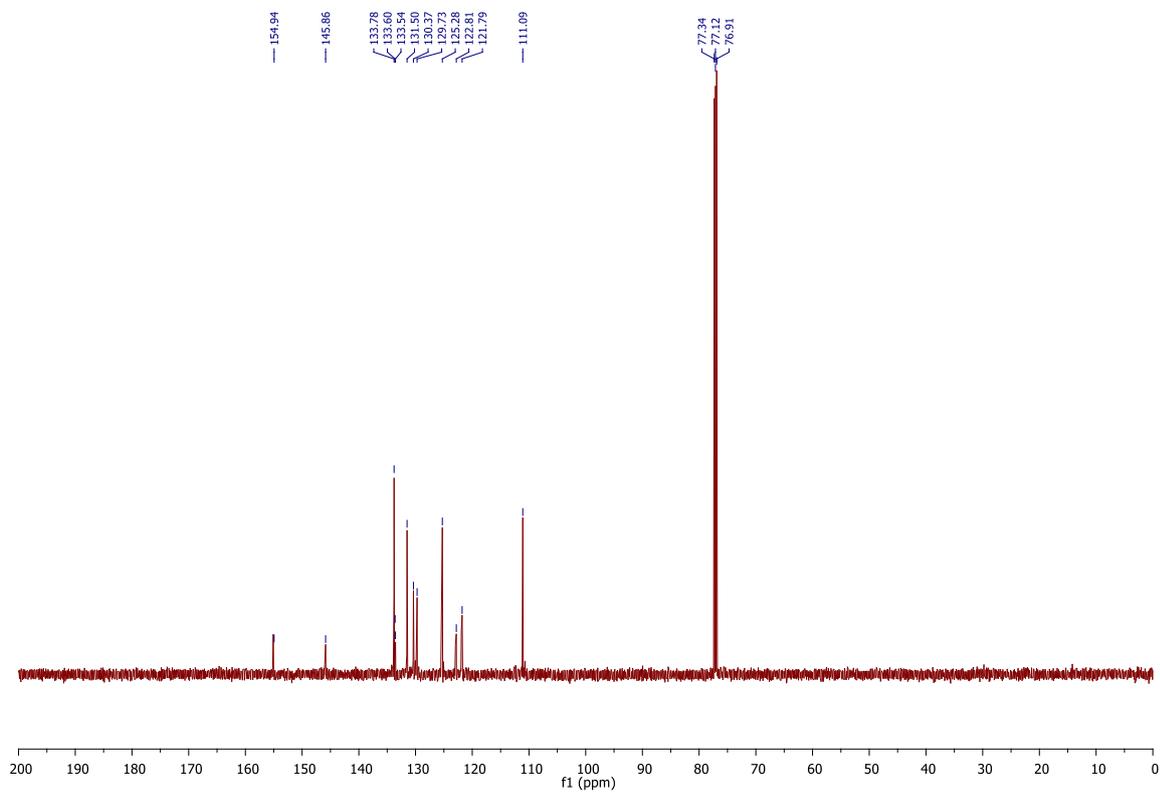
## <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



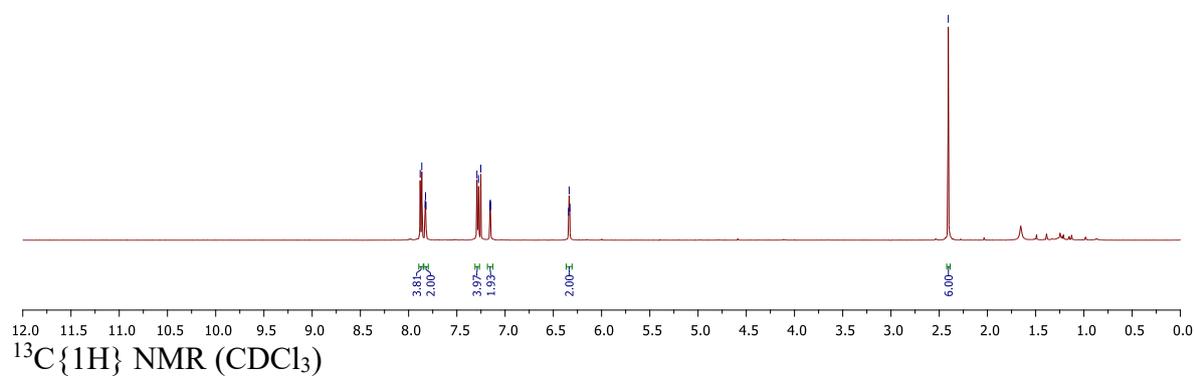
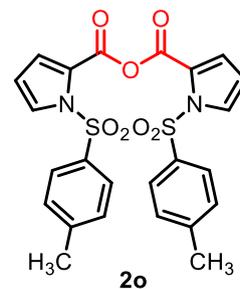
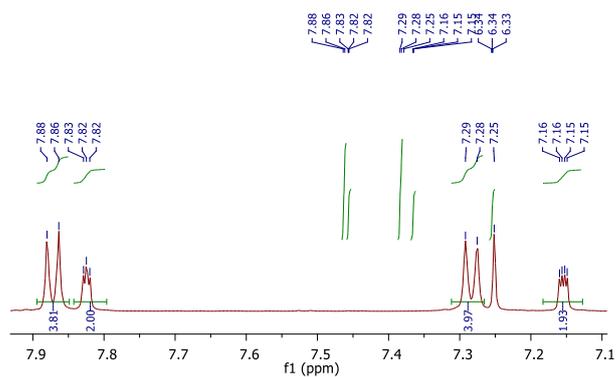
**2n**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )



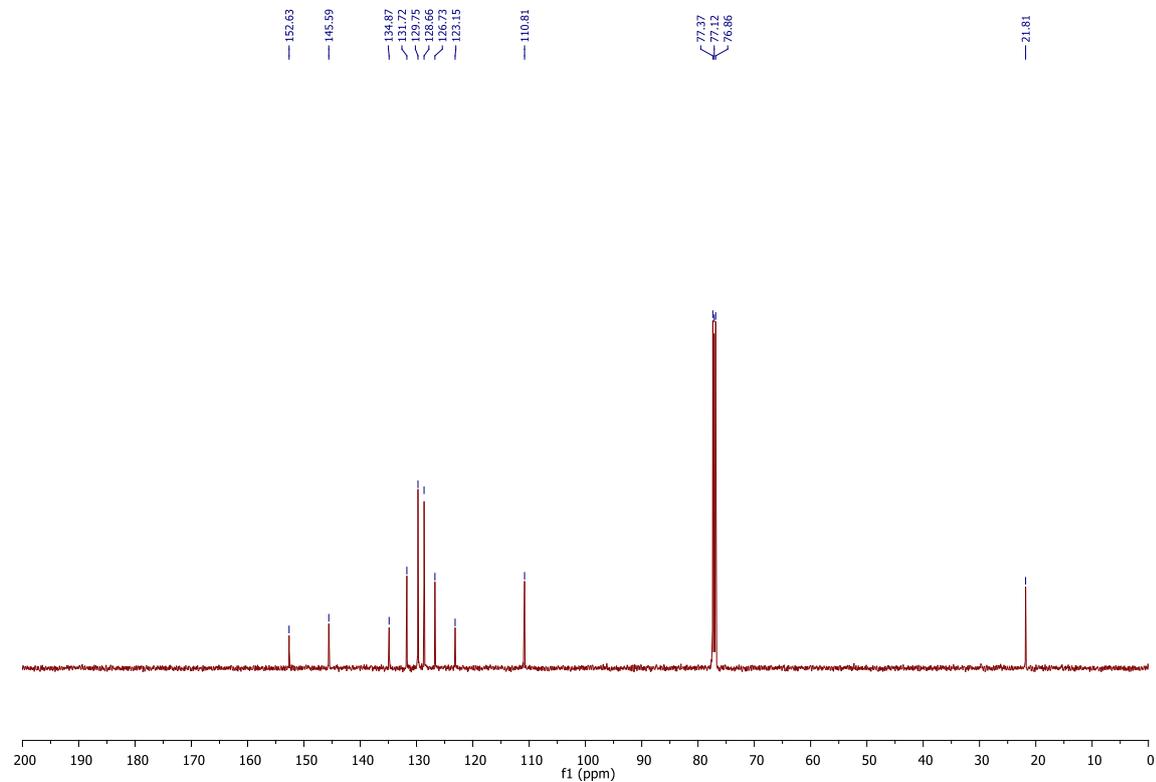
$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )



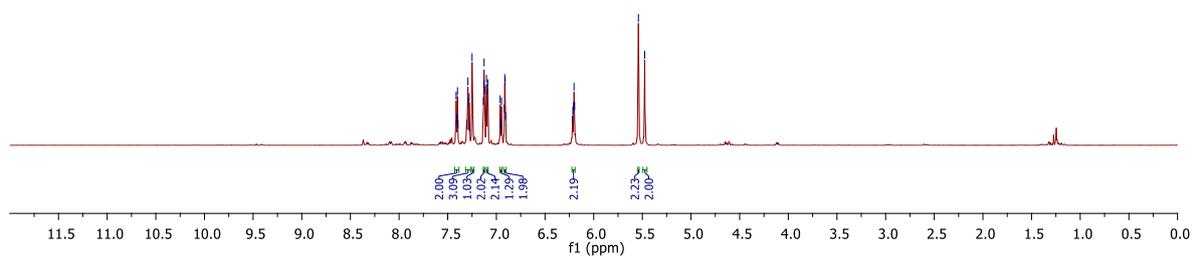
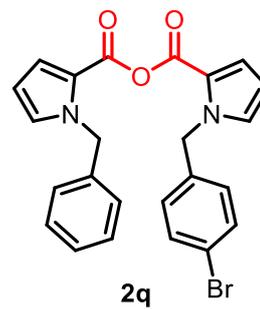
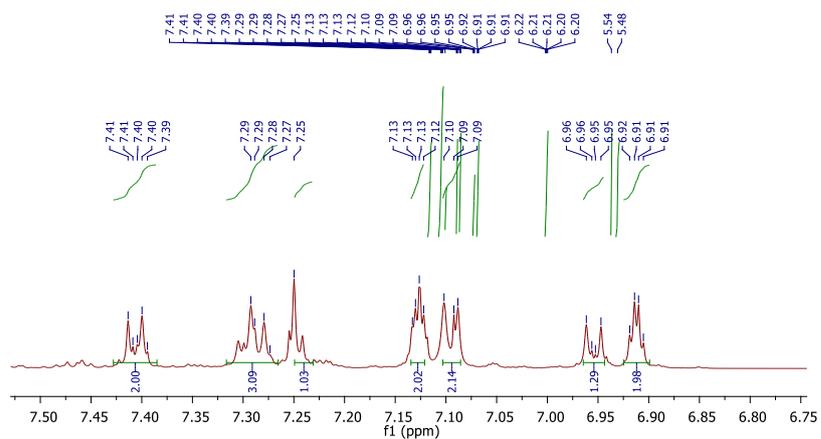
**2o**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )



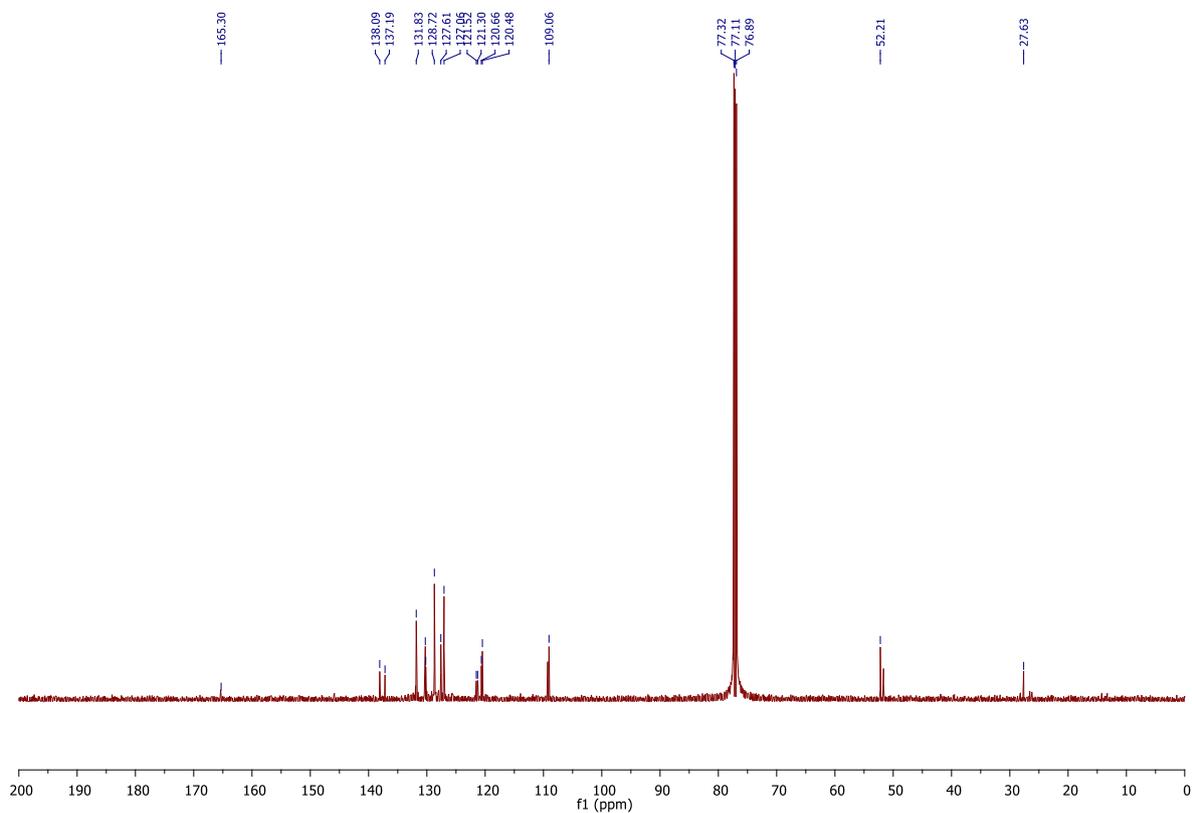
$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )



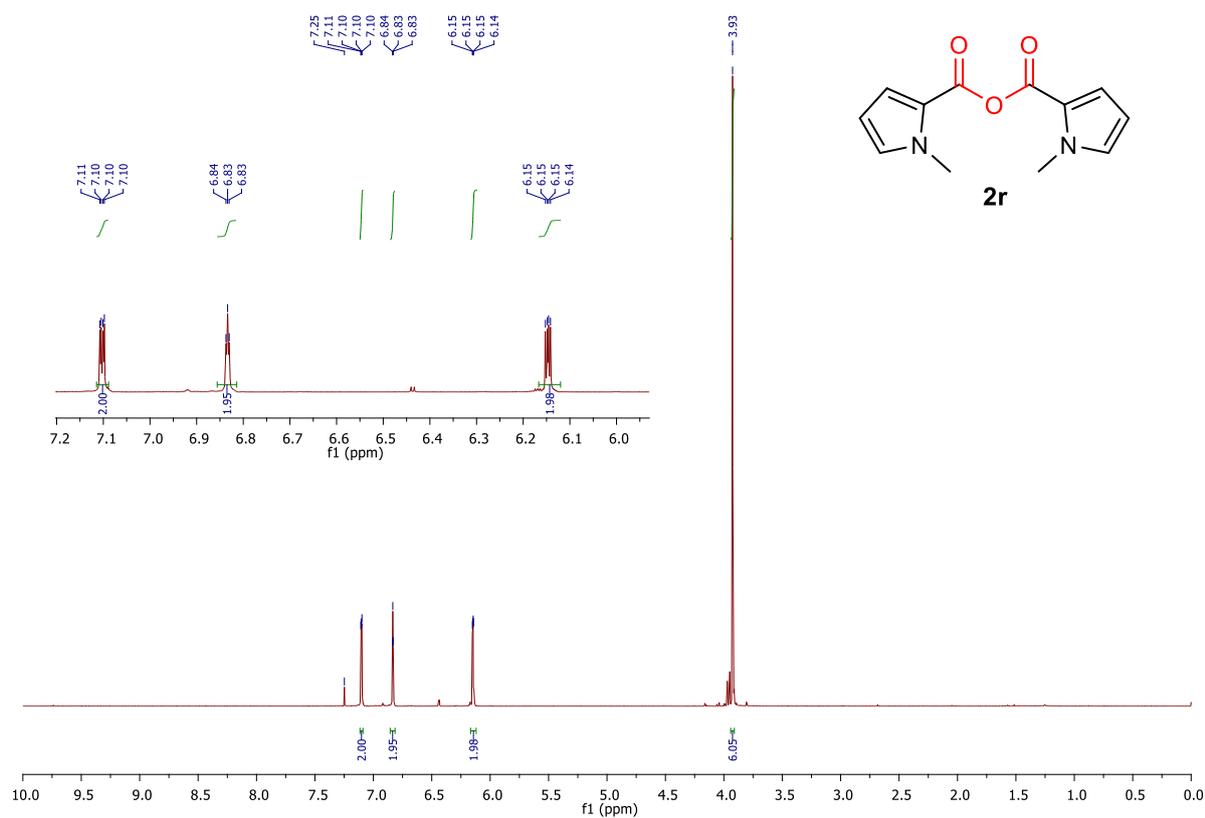
## 2q <sup>1</sup>H NMR (CDCl<sub>3</sub>)



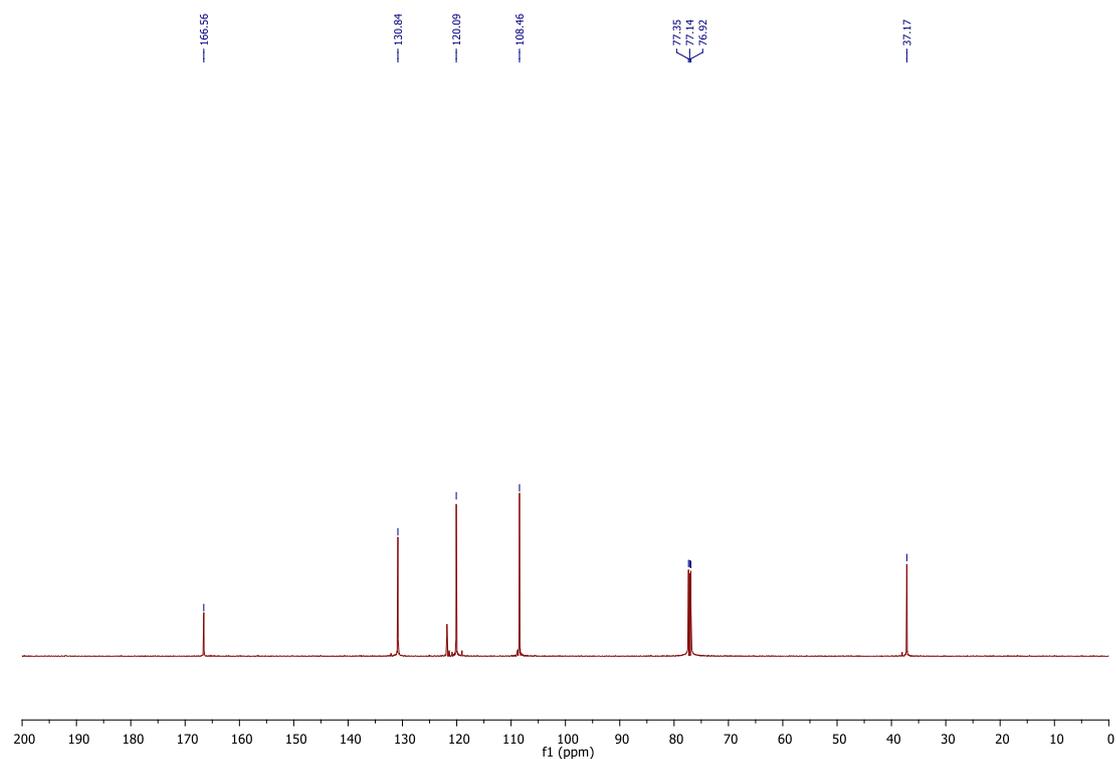
## <sup>13</sup>C {<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



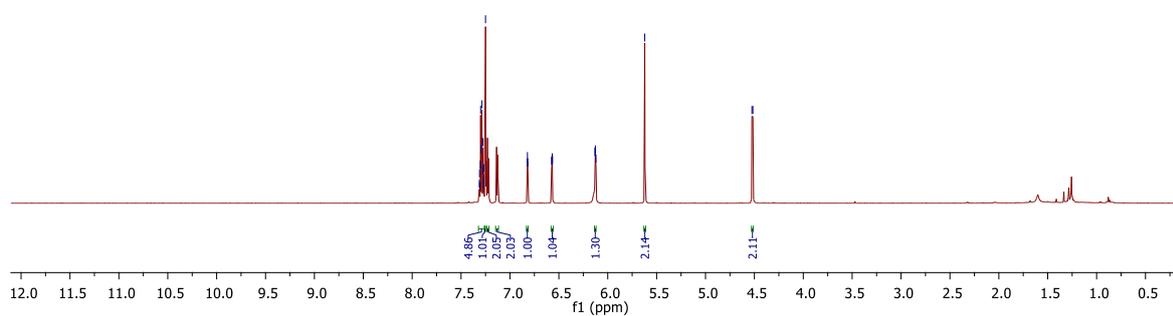
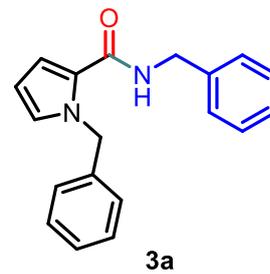
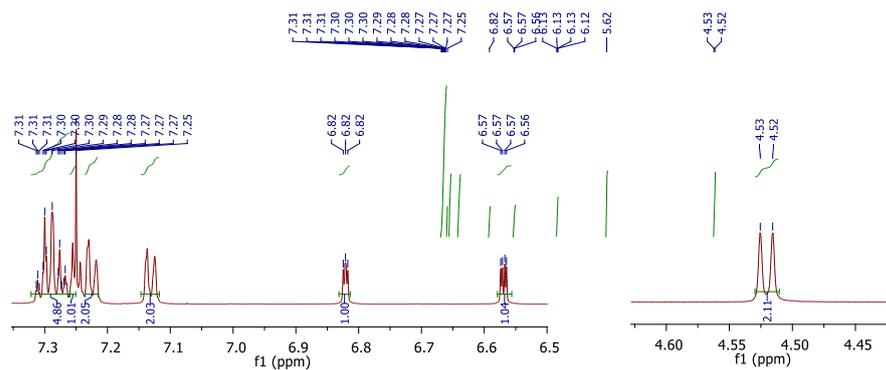
**2r**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )



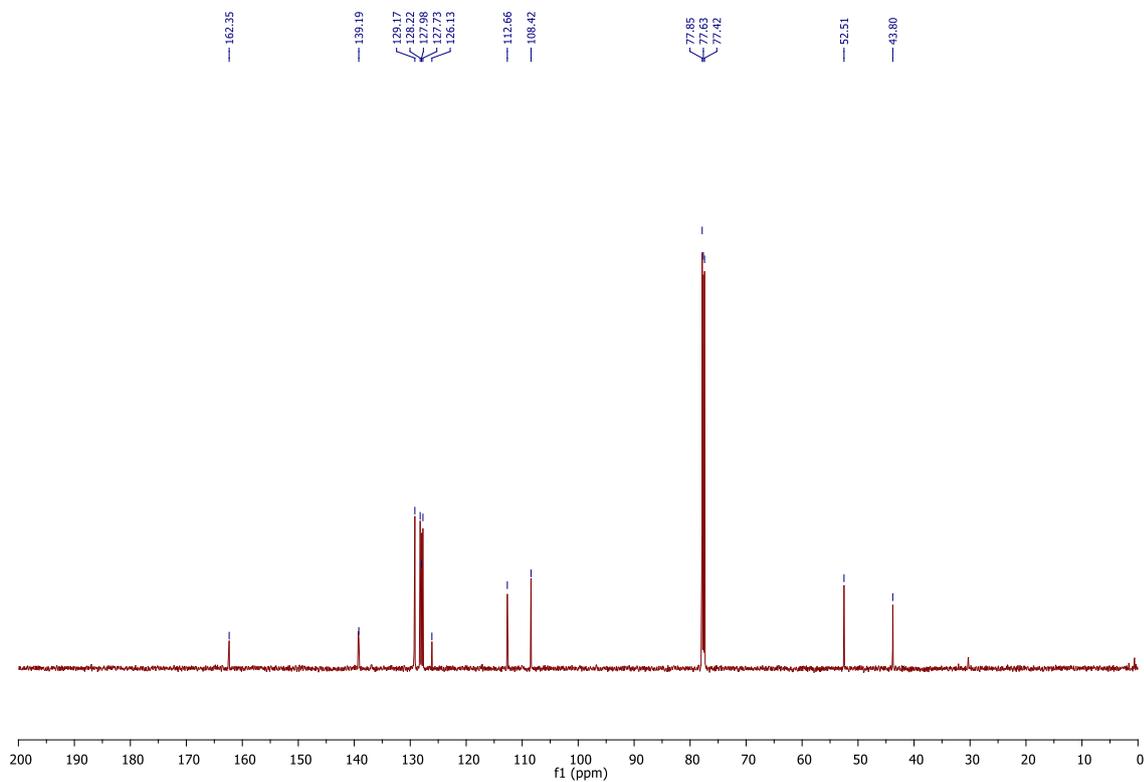
$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )



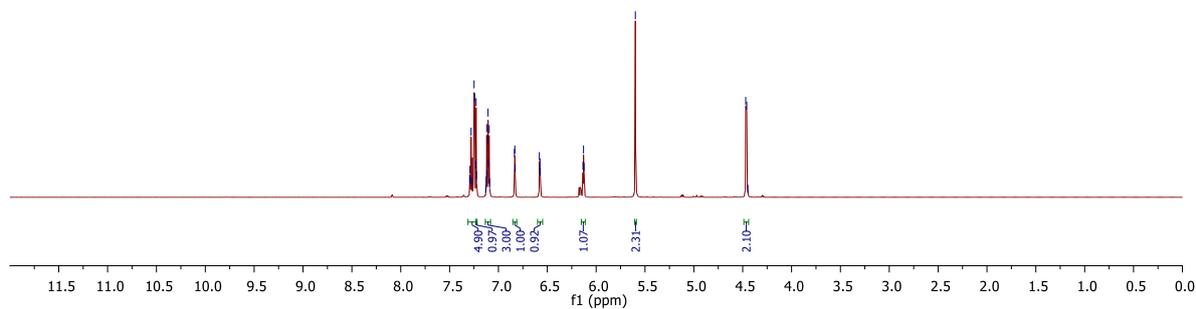
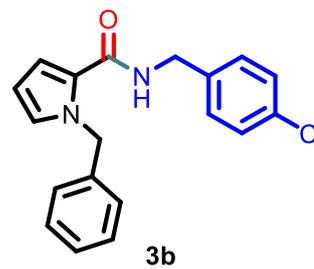
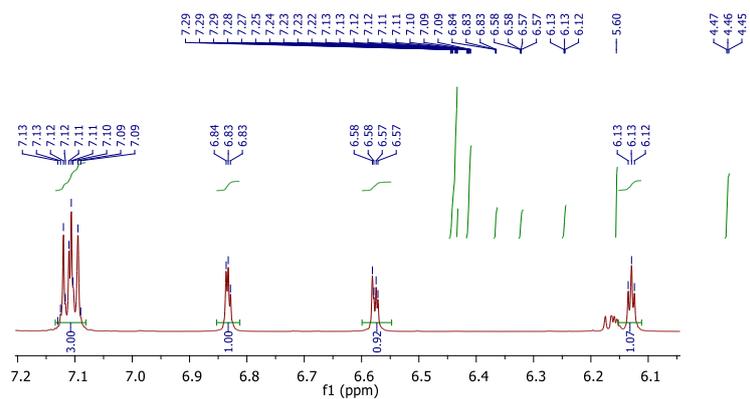
**3a**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )



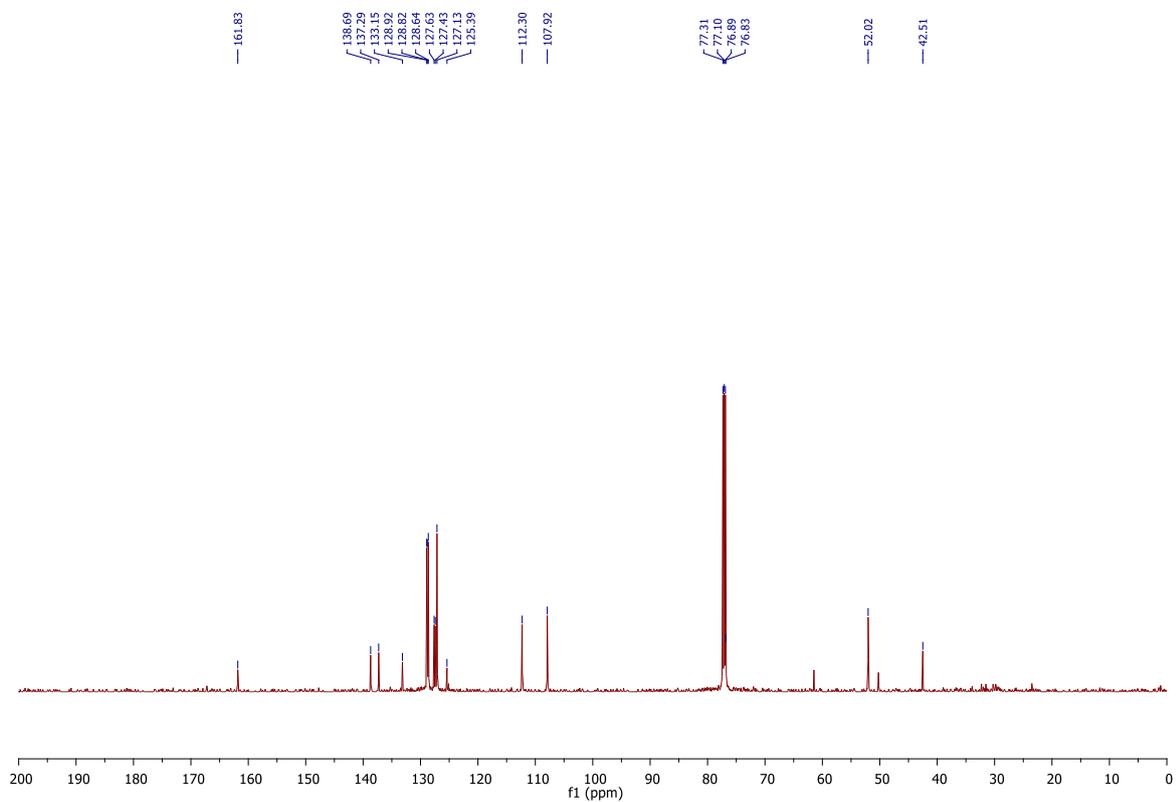
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )



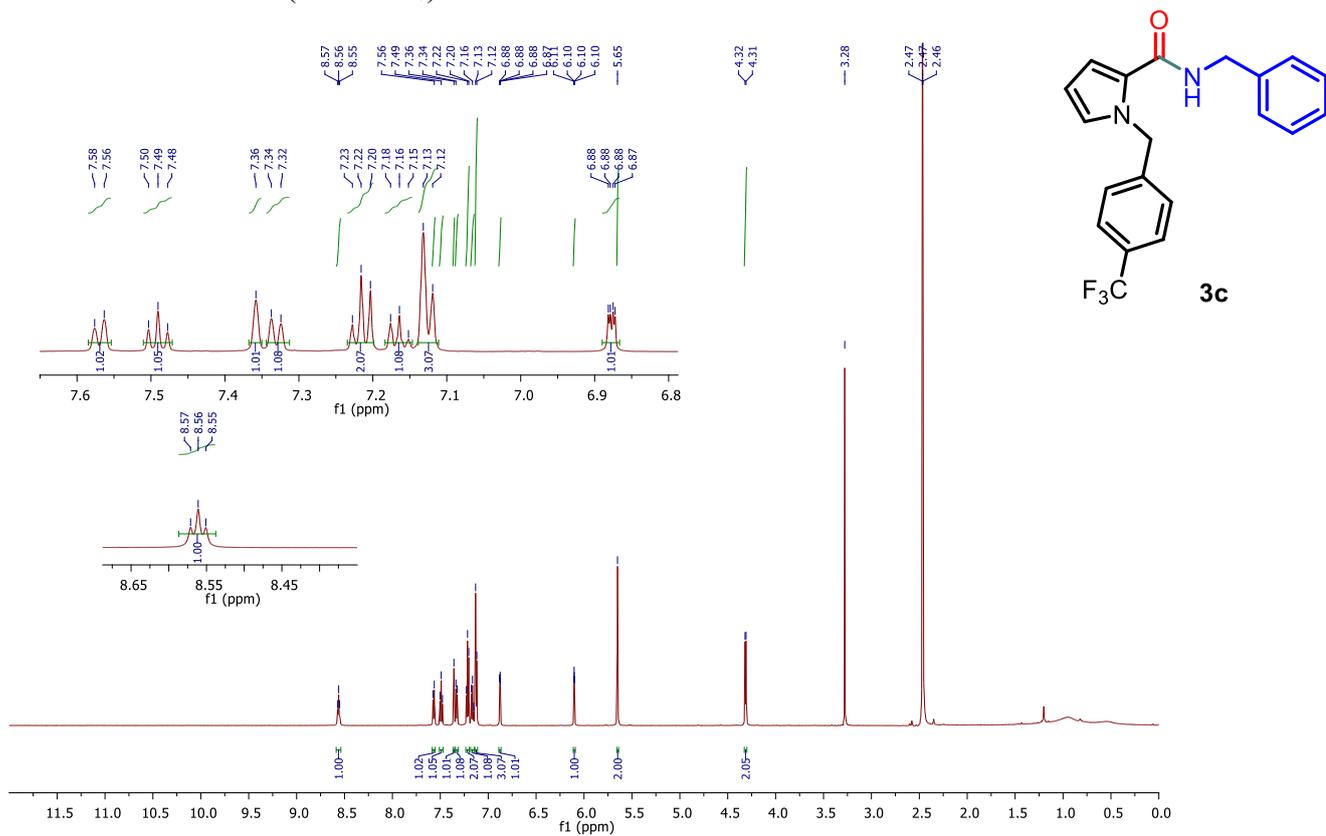
### 3b <sup>1</sup>H NMR (CDCl<sub>3</sub>)



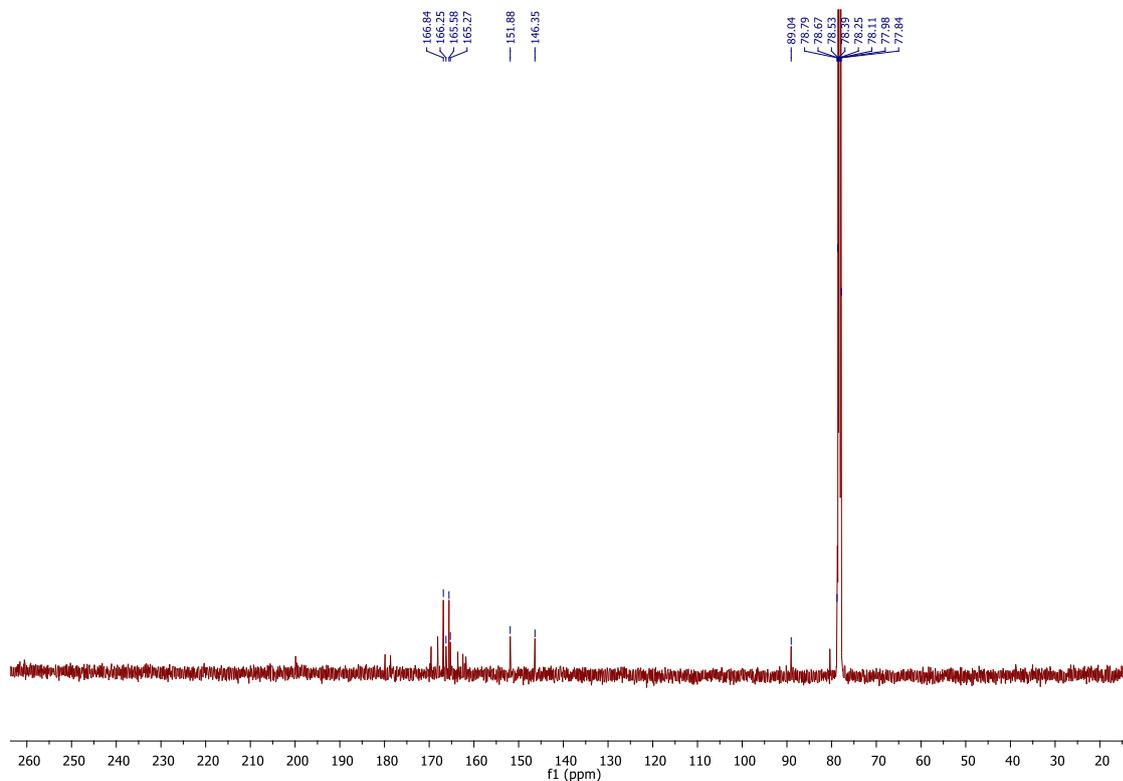
### <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



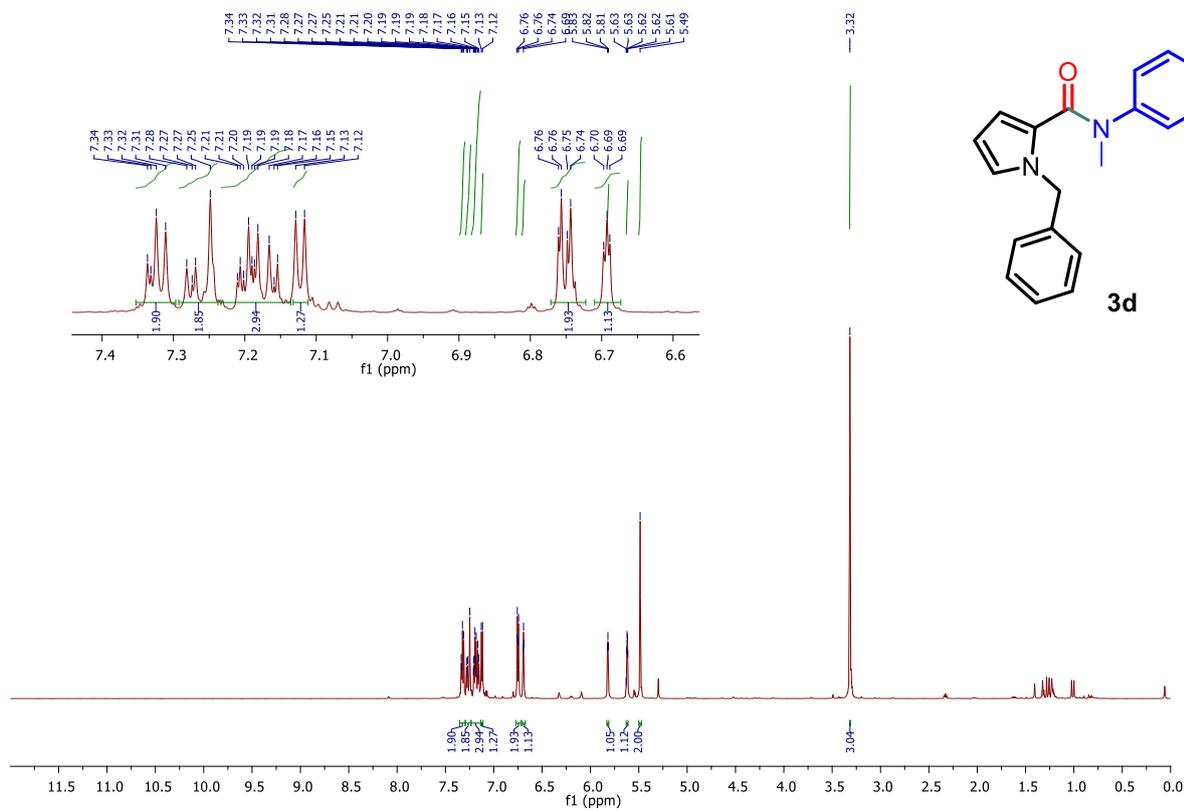
### 3c <sup>1</sup>H NMR (DMSO-d<sub>6</sub>)



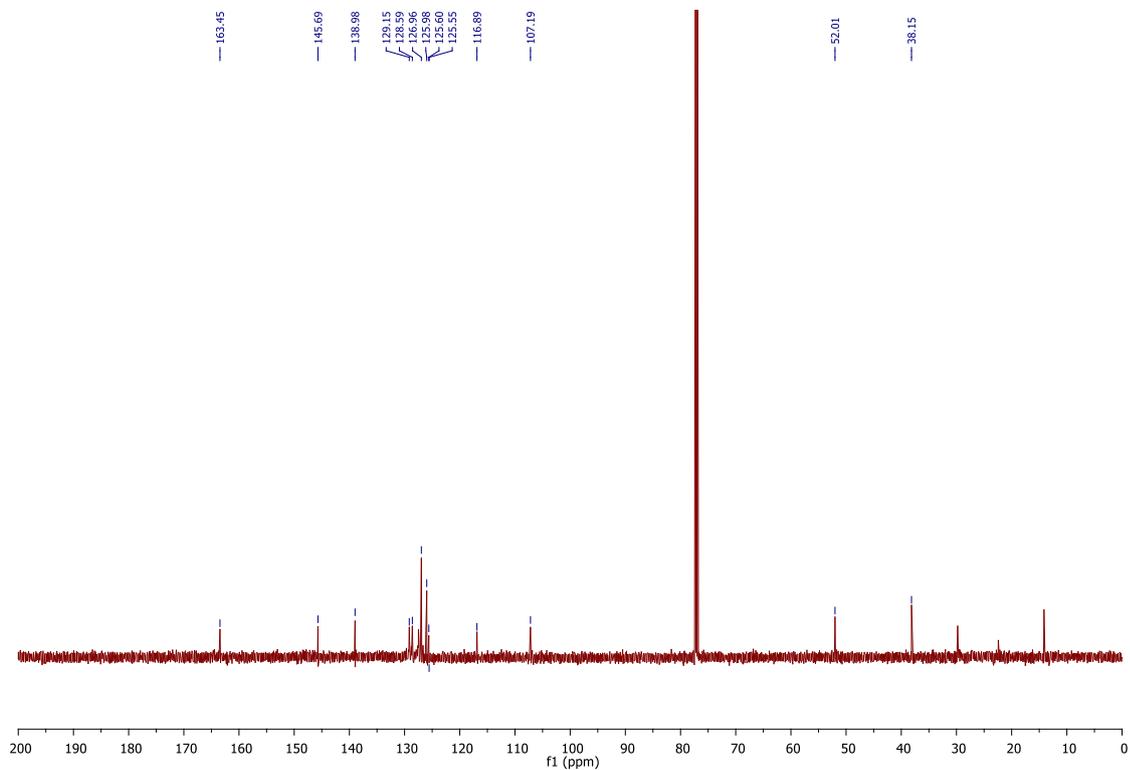
### <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-d<sub>6</sub>)



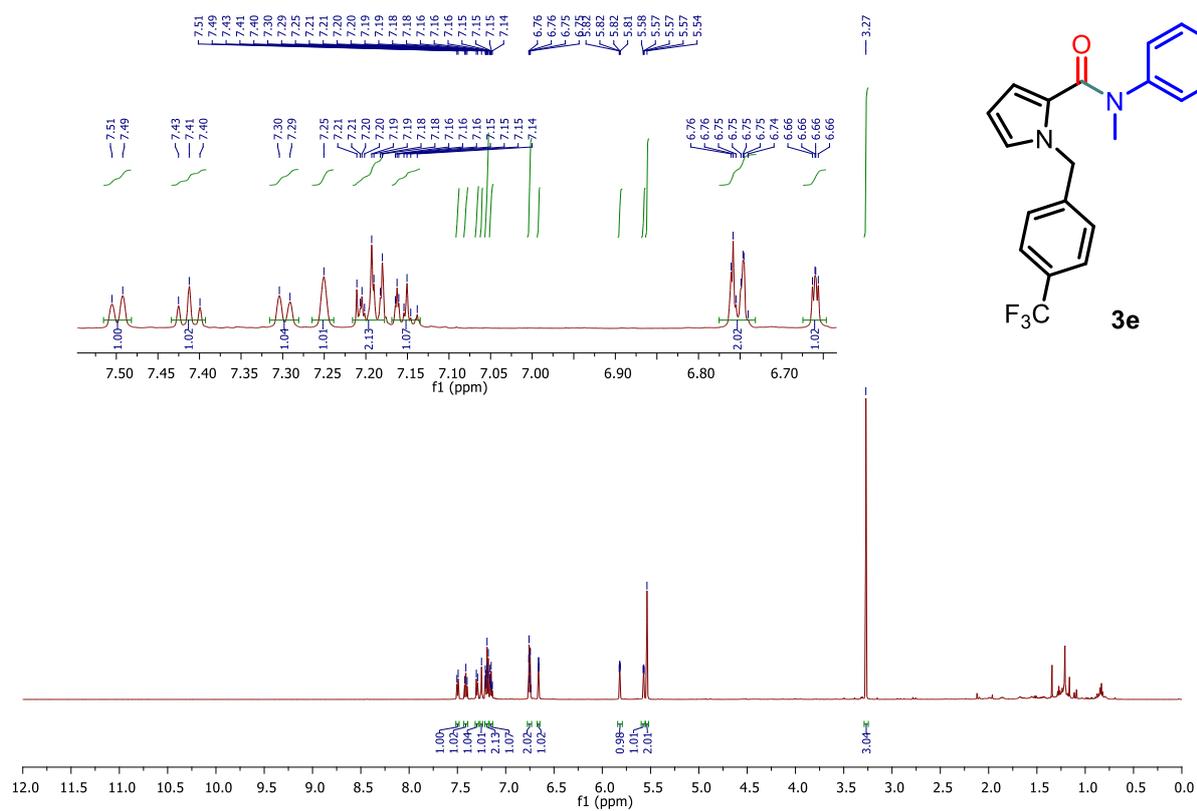
### 3d <sup>1</sup>H NMR (CDCl<sub>3</sub>)



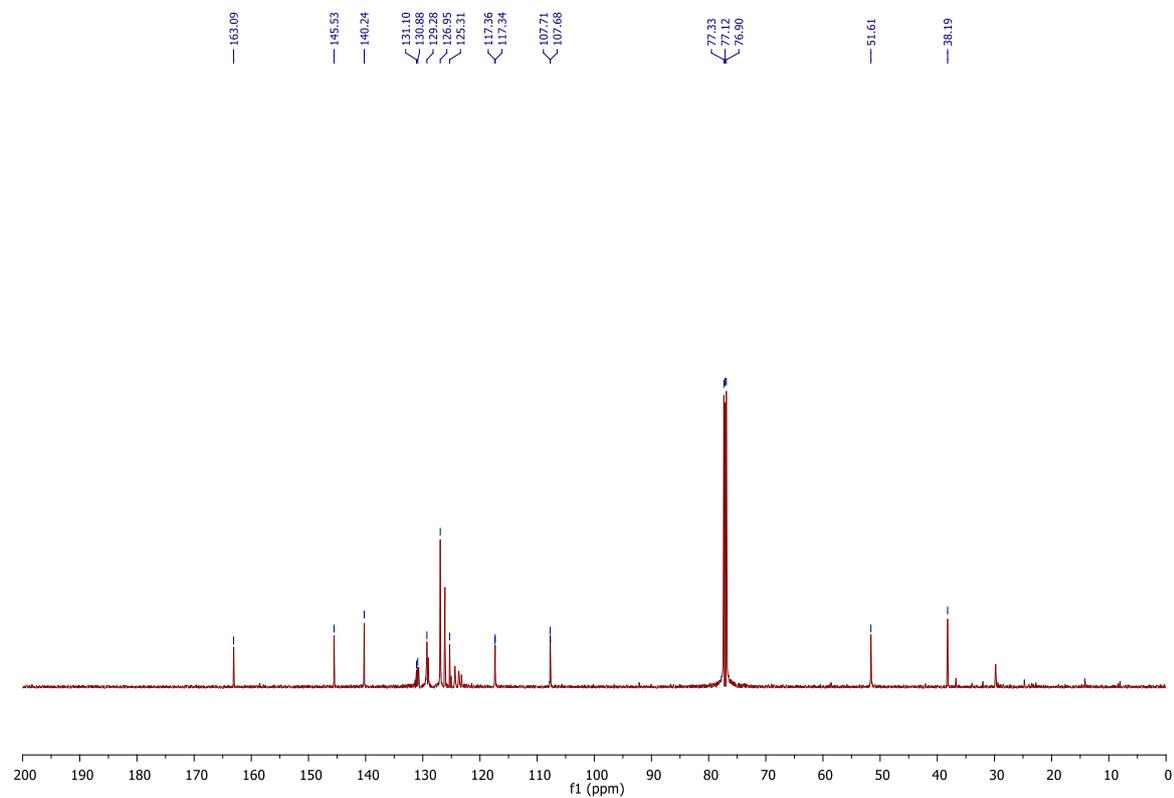
### <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



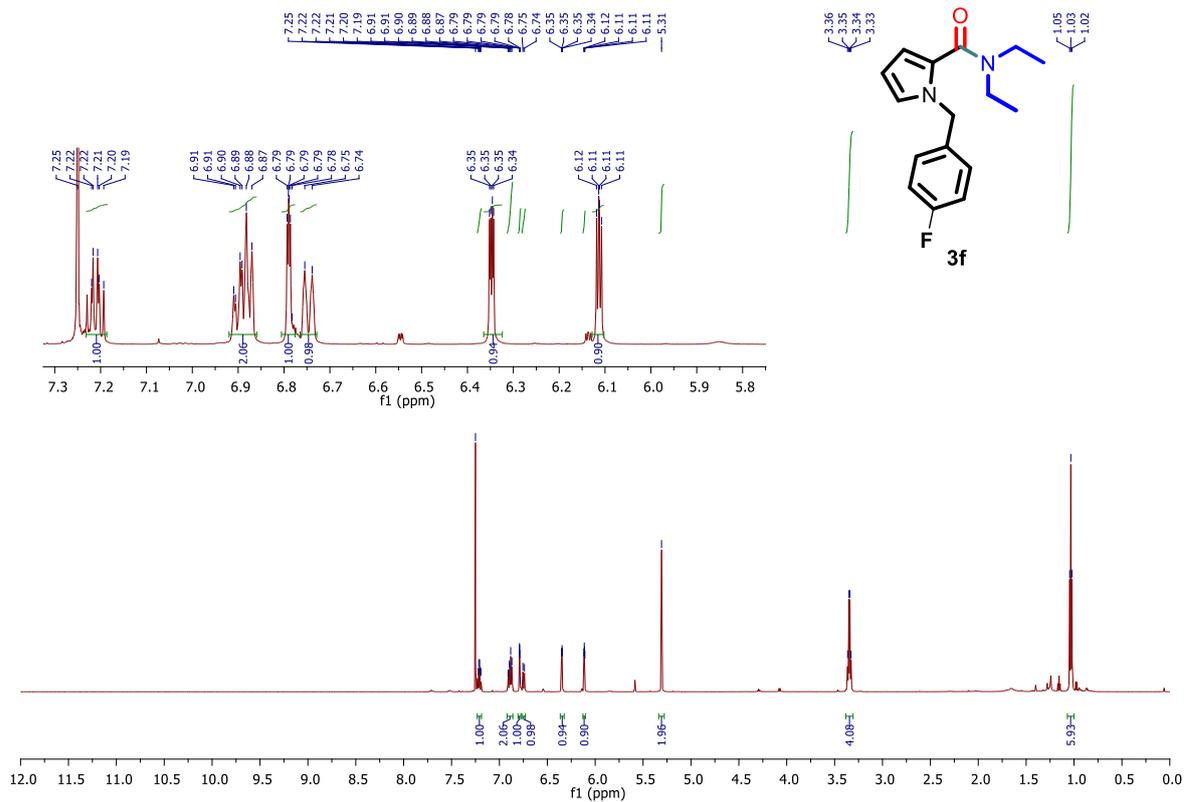
**3e**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )



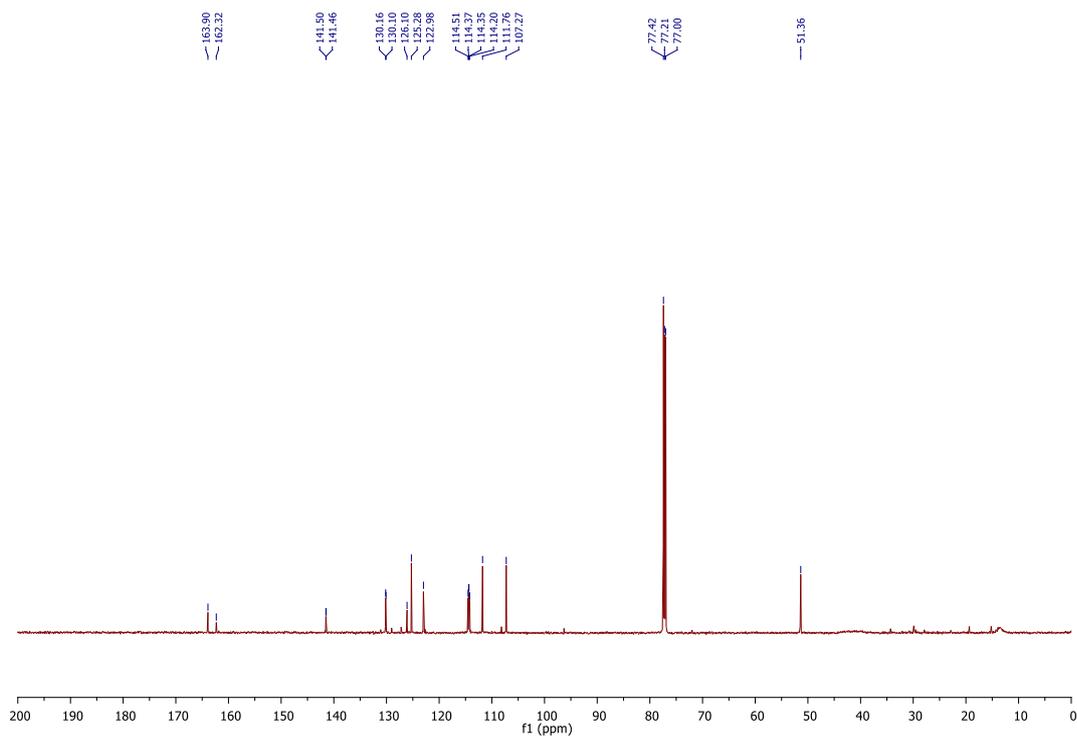
$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )



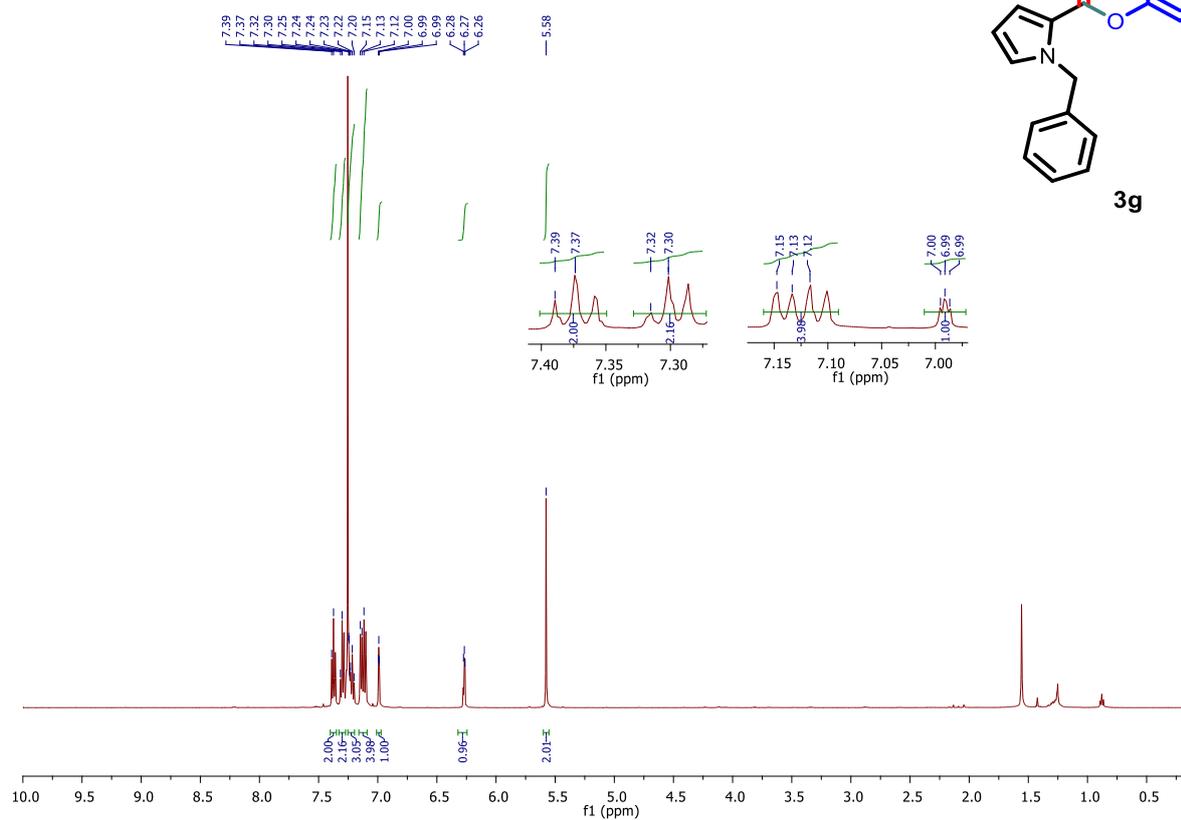
### 3f <sup>1</sup>H NMR (CDCl<sub>3</sub>)



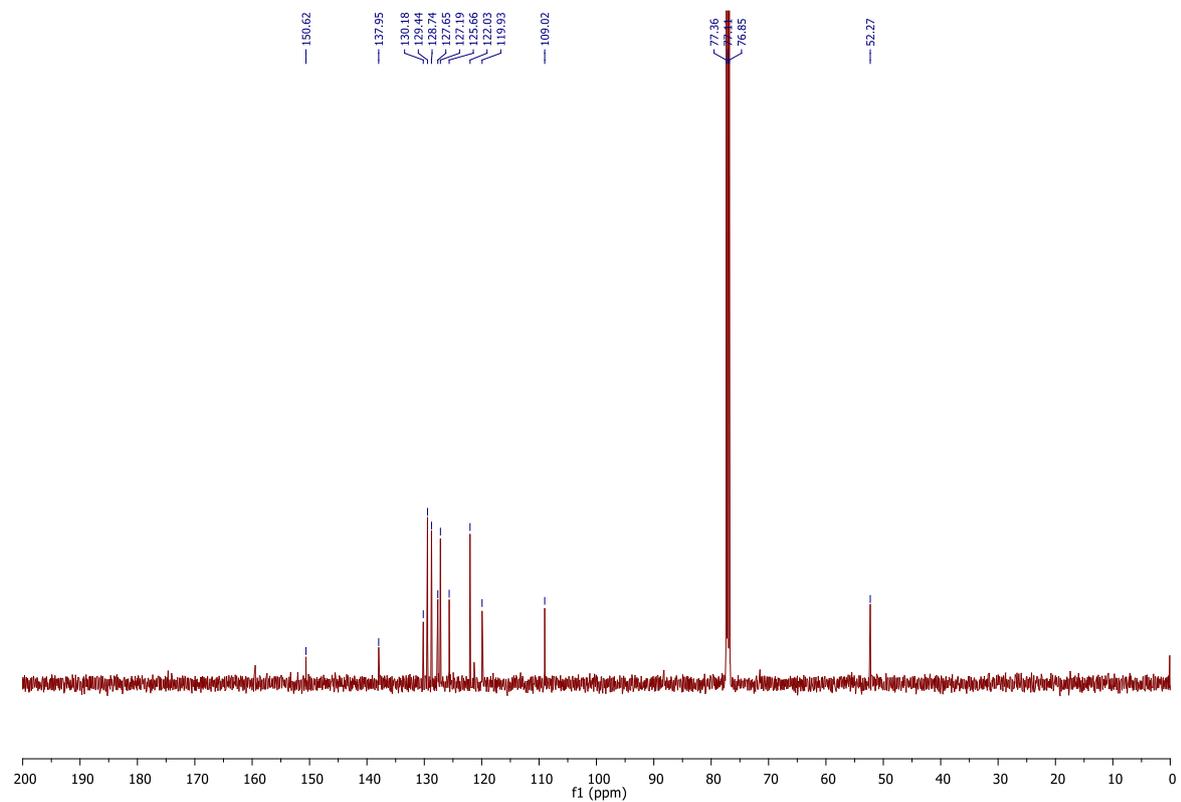
### <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



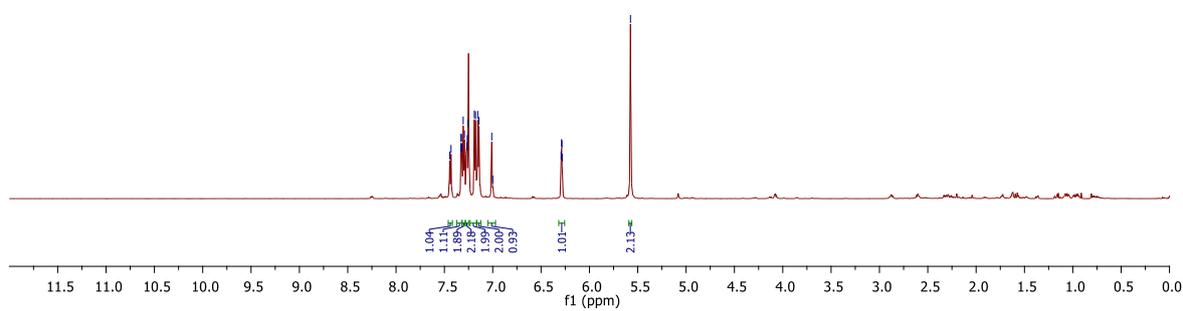
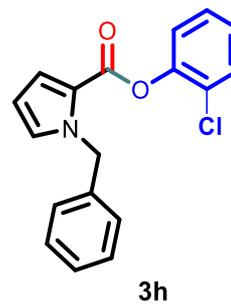
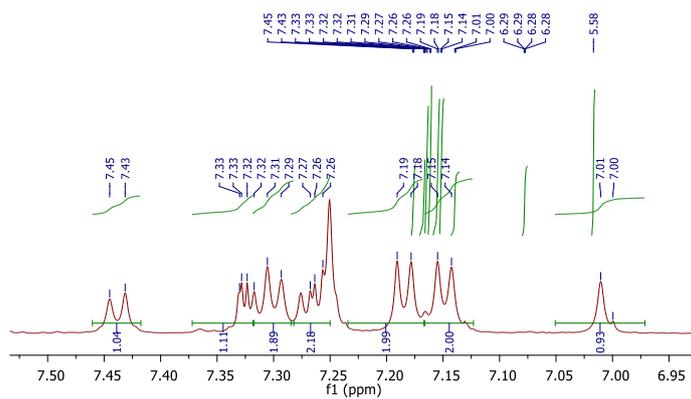
### 3g <sup>1</sup>H NMR (CDCl<sub>3</sub>)



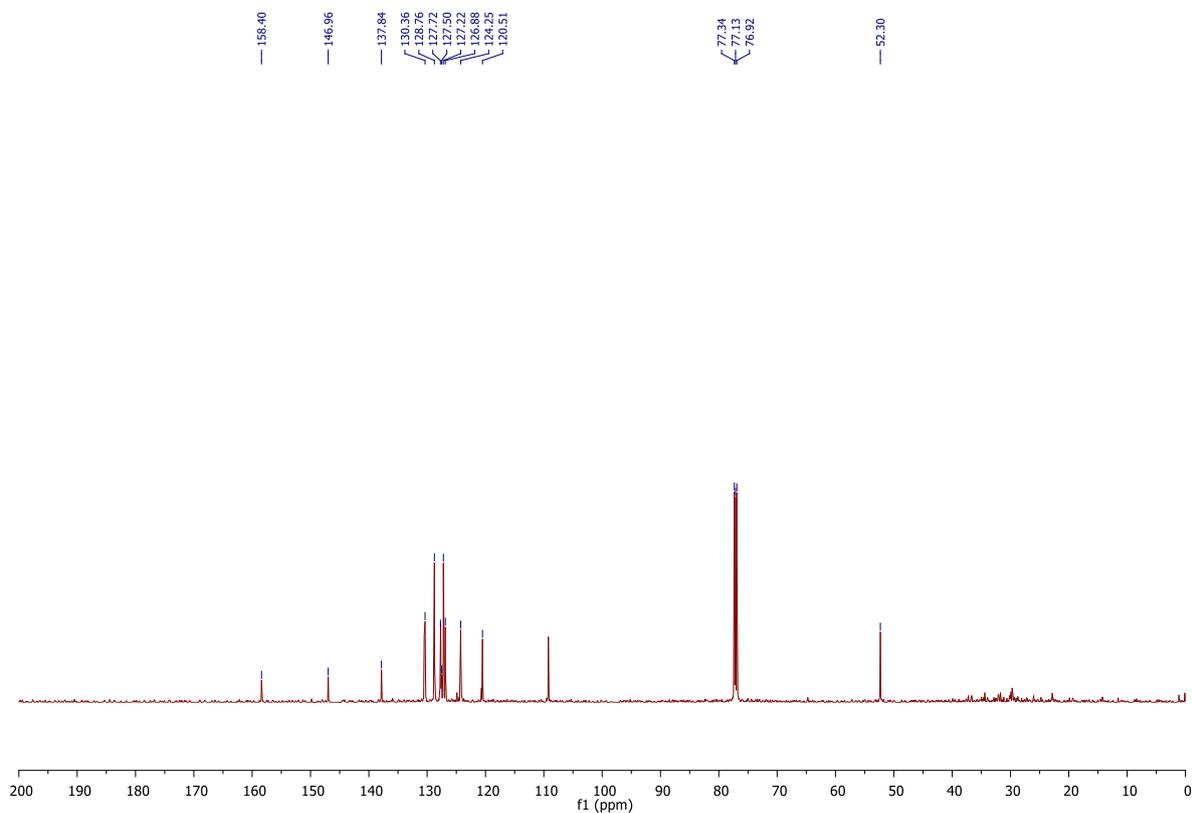
### <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



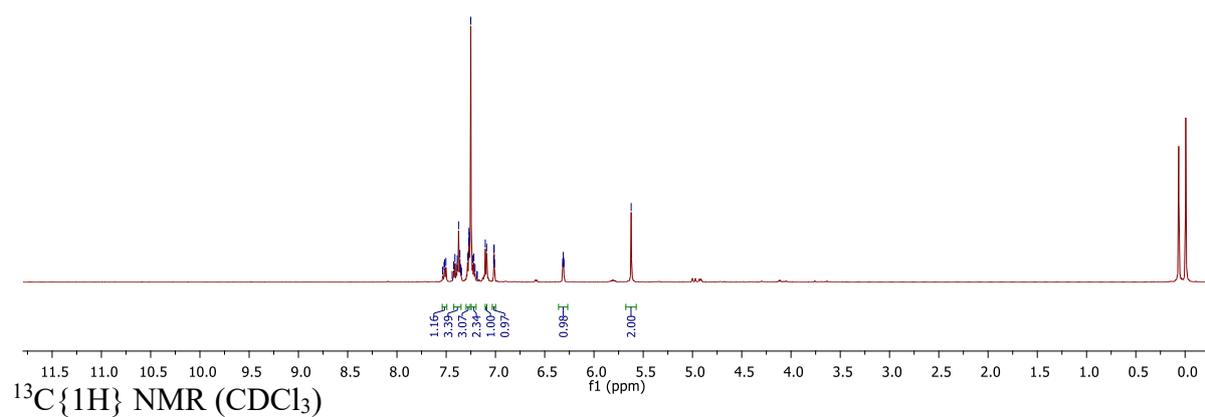
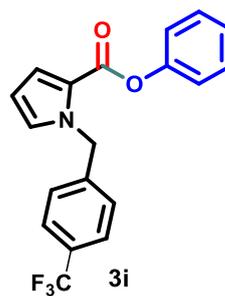
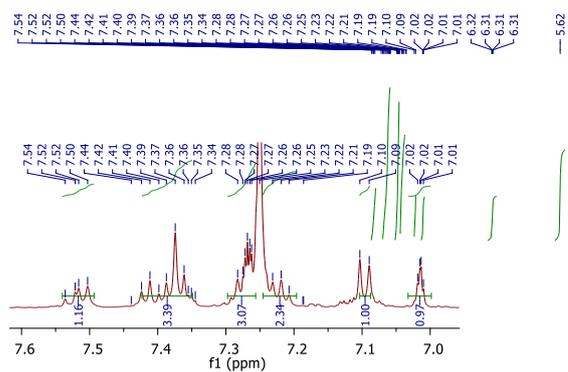
### 3h <sup>1</sup>H NMR (CDCl<sub>3</sub>)



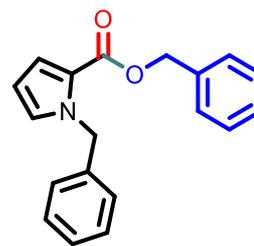
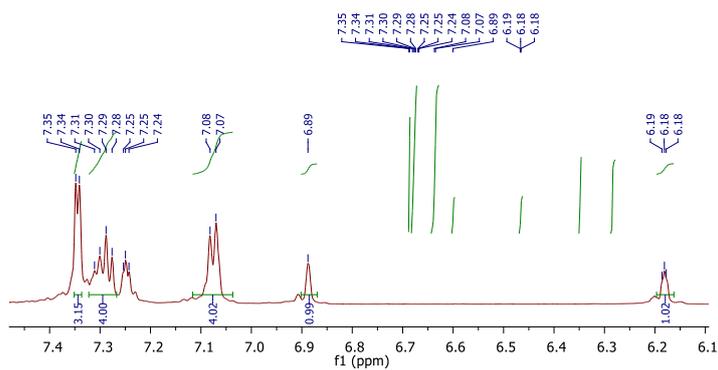
### <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>)



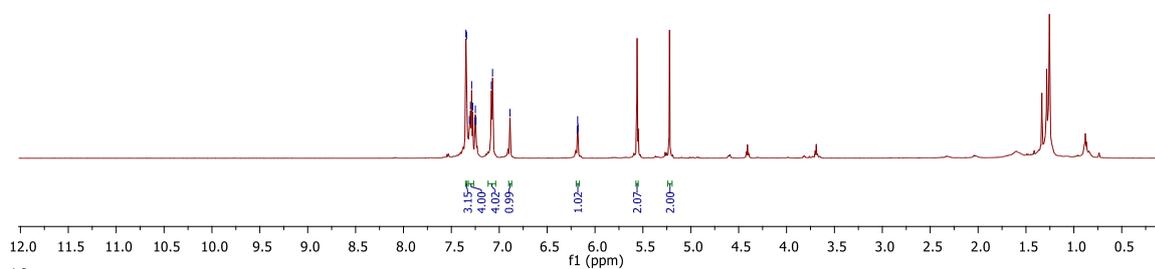
### 3i <sup>1</sup>H NMR (CDCl<sub>3</sub>)



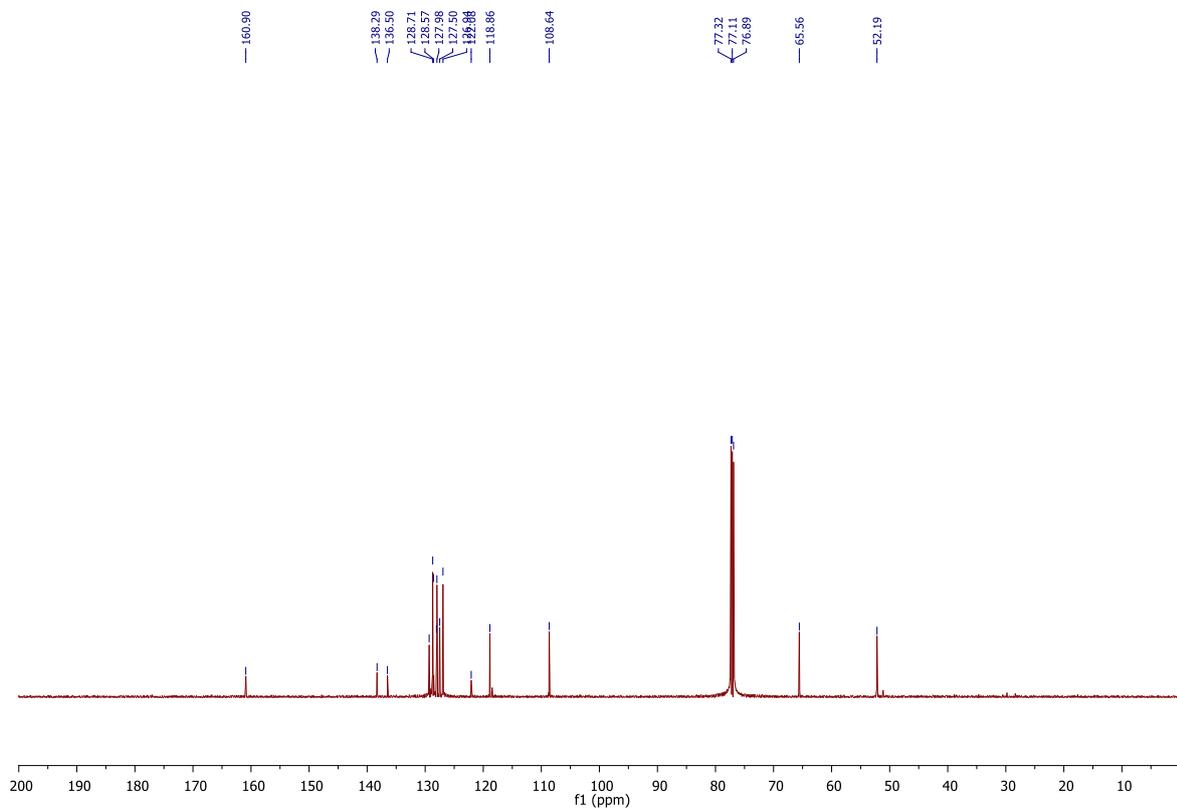
**3j**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )



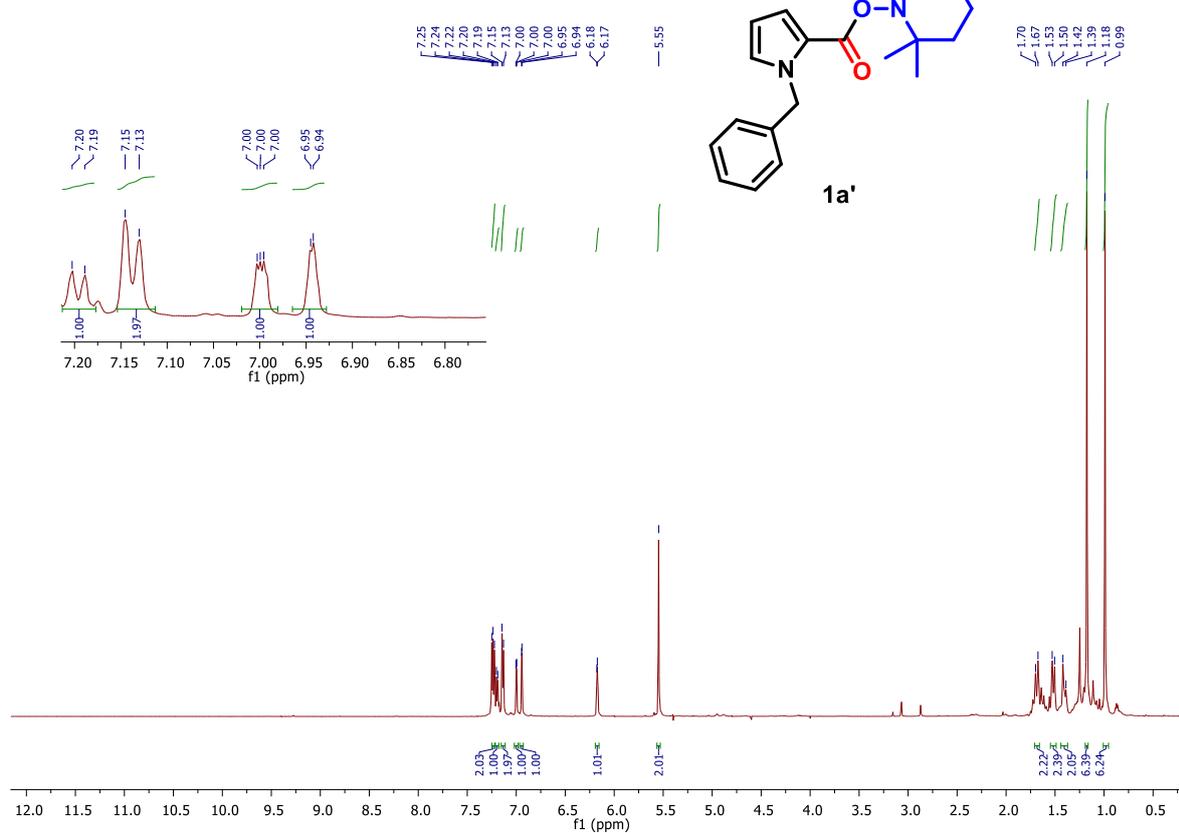
**3j**



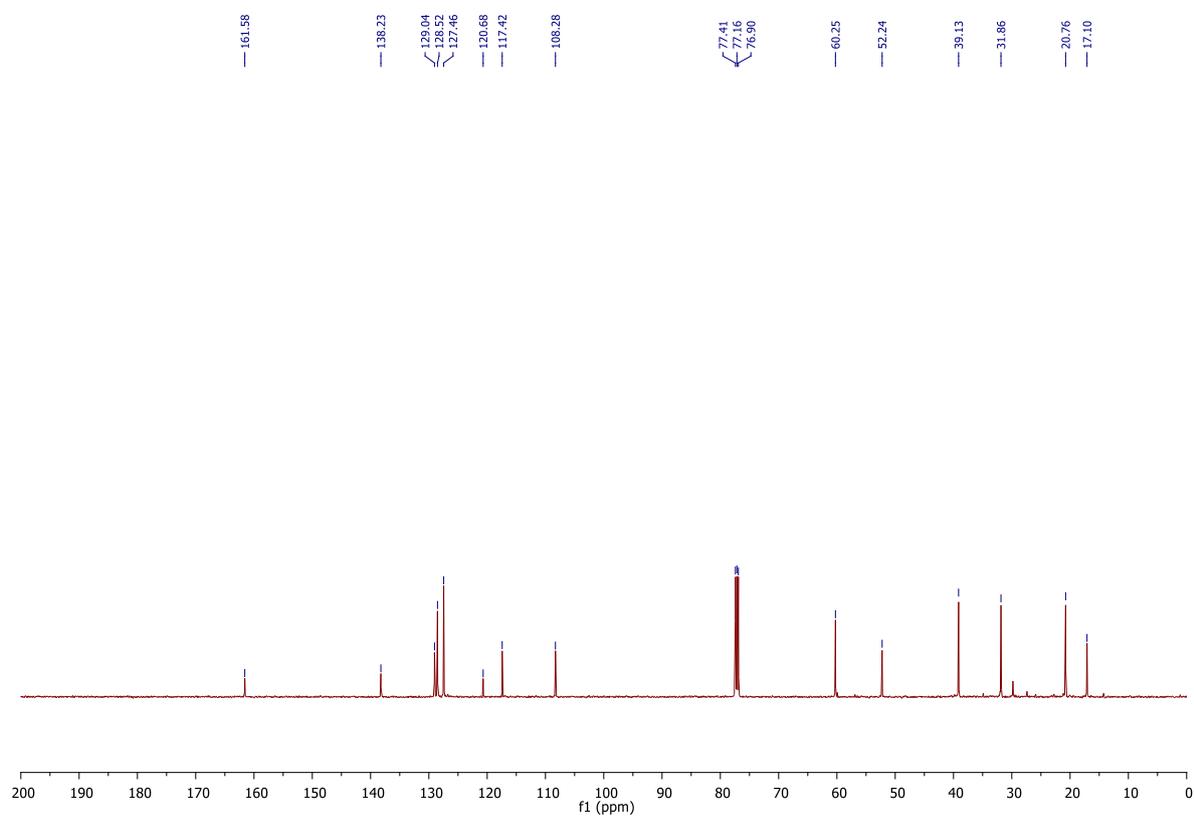
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )



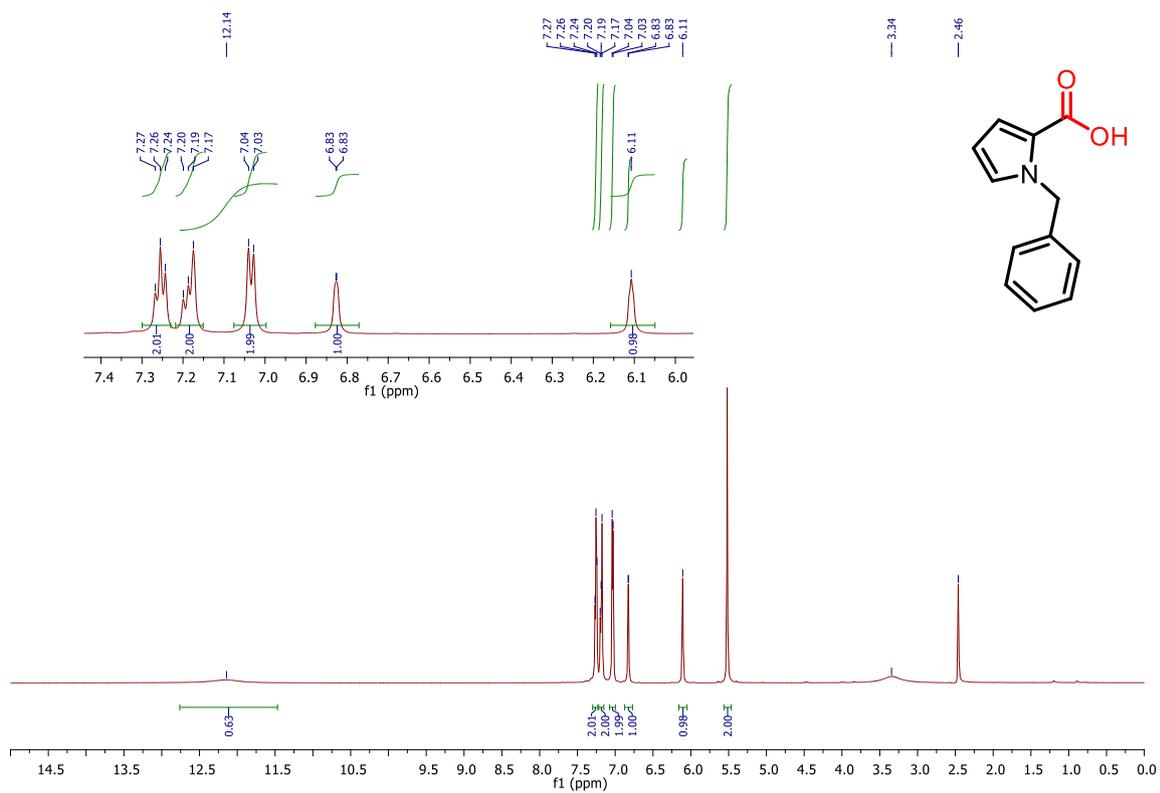
**1a'**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )



**1a'**  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ )



# $^1\text{H}$ NMR (DMSO- $d_6$ )



# $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- $d_6$ )

