

## Supplementary Materials

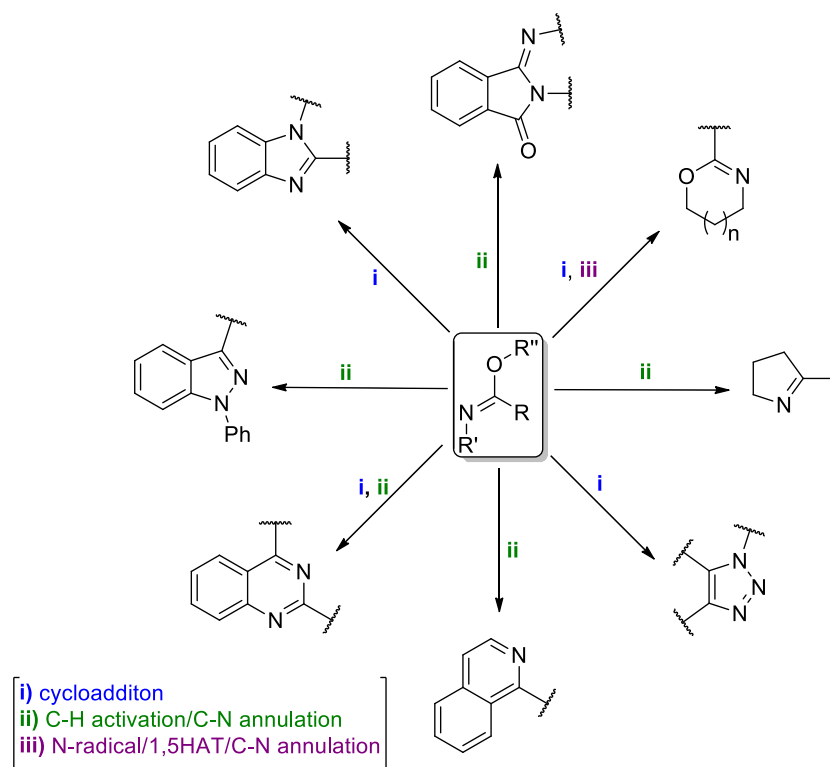
### Simple Synthetic Approach to *N*-(Pyridin-2-yl)imides from Nitrostyrenes and 2-Aminopyridines via the *N*-(Pyridin-2-yl)iminonitriles as Intermediates

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**Figure S1.** Synthetic approaches to N-heterocycles starting from imidates

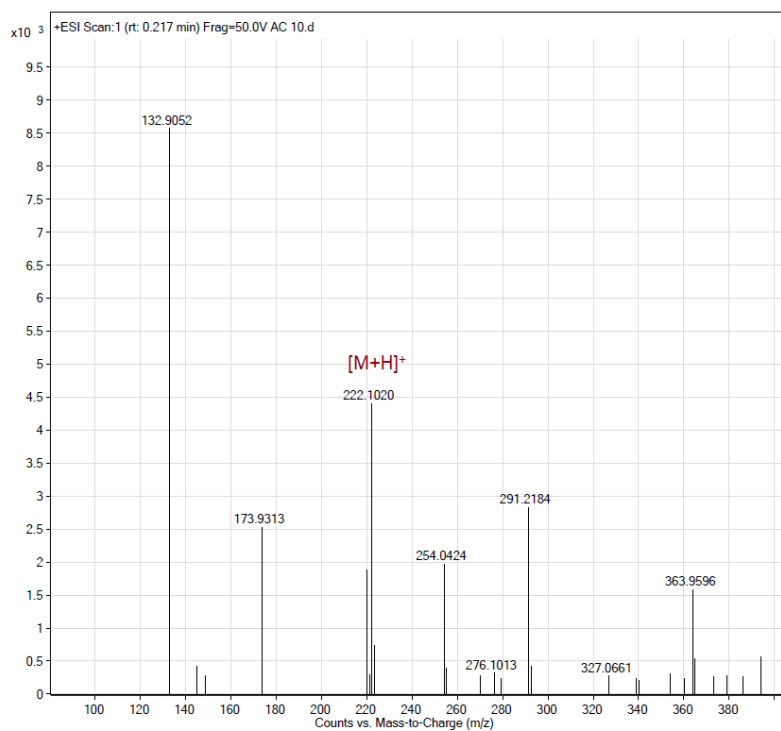
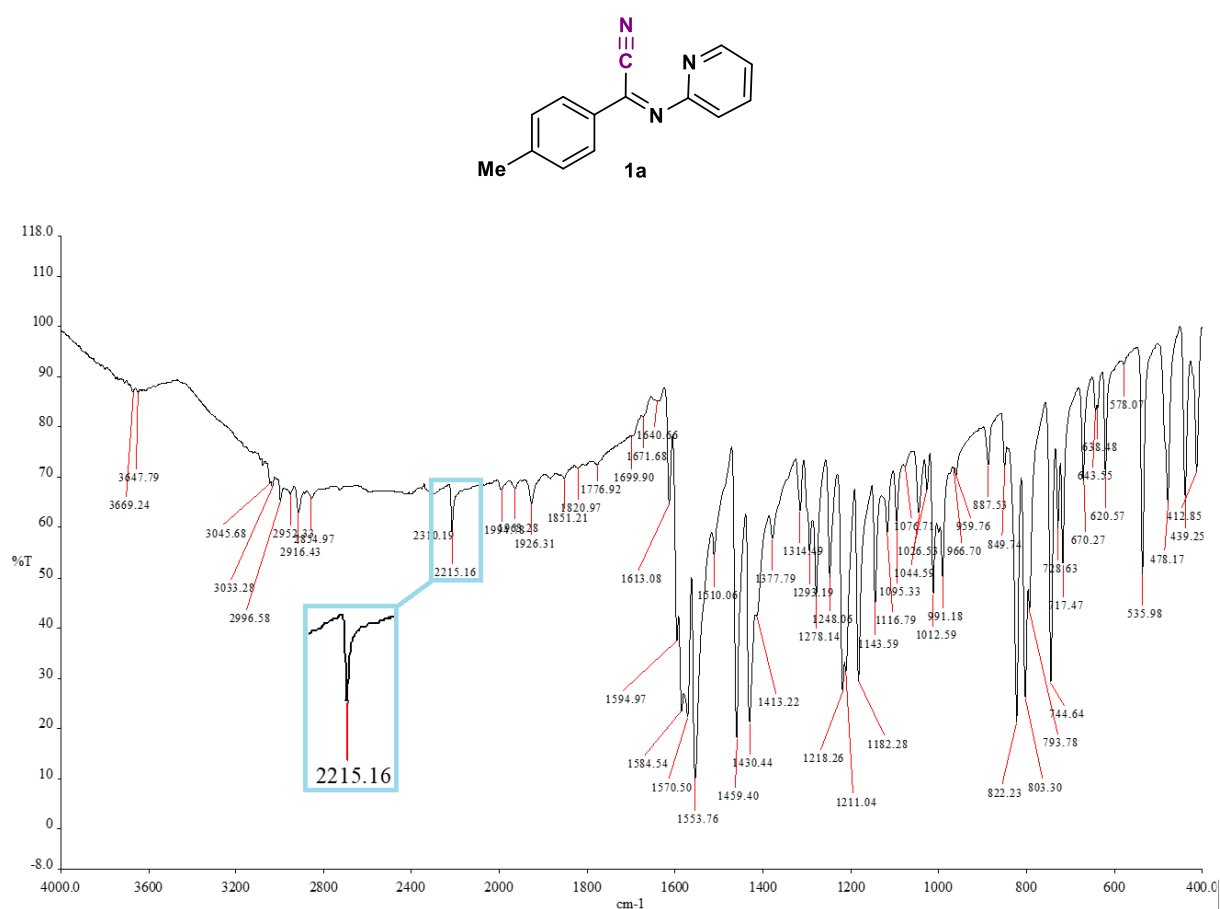
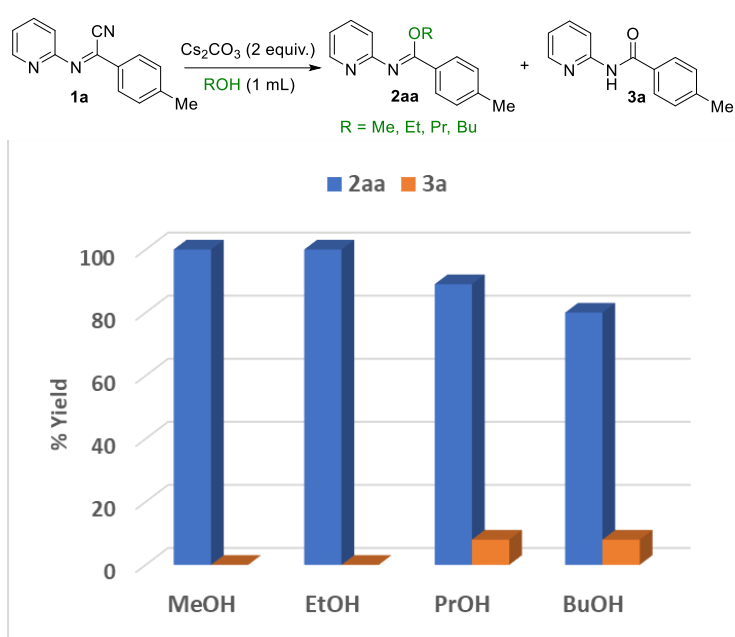
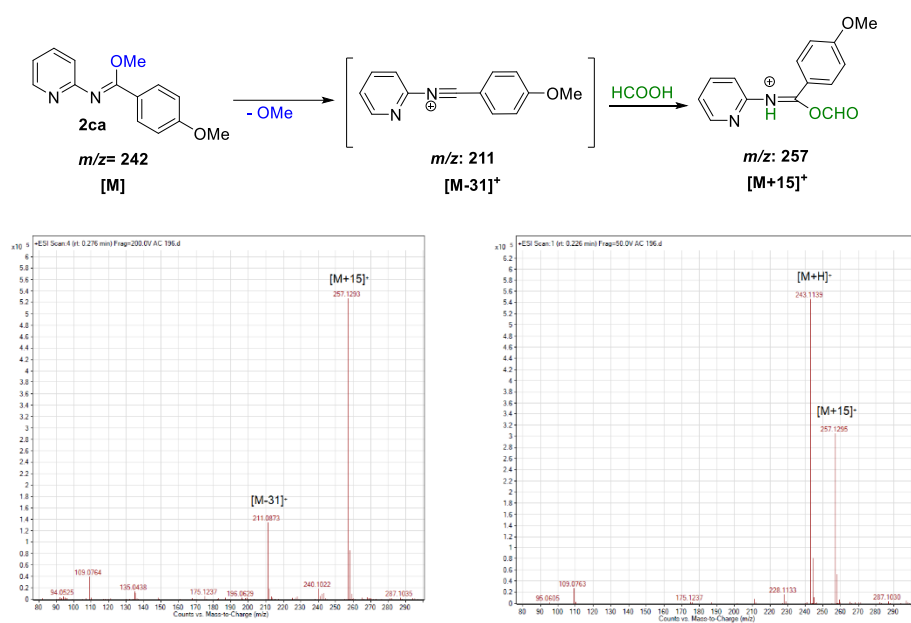


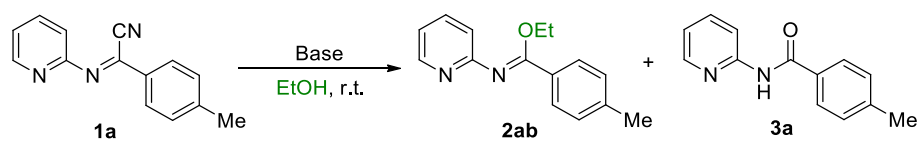
Figure S2. IR and HRMS spectra of the compound **1a**



**Figure S3.** Study of alcoholic solvent in the transformation of **1a** in the presence of  $\text{Cs}_2\text{CO}_3$ .

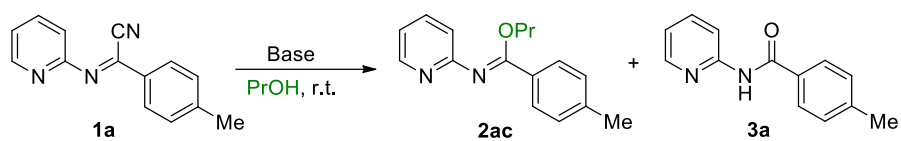


**Figure S4.** HRMS spectra of **2ca** at 50 V (left) and 200 V (right) and the corresponding observed fragments  $[M+H]^+$ ,  $[M-31]^+$  and  $[M+15]^+$

**Table S1.** Screening of base equivalents, with EtOH as solvent

Entry	Base	Base equiv.	Time (h)	Conversion (%) <sup>[b]</sup>	<b>2ab</b> (%) <sup>[b]</sup>	<b>3a</b> (%) <sup>[b]</sup>
1	Cs <sub>2</sub> CO <sub>3</sub>	2	4	100	100	0
2	DBU	2	24	100	100	0
3	Cs <sub>2</sub> CO <sub>3</sub>	1	24	100	91	9
4	DBU	1	24	100	84	16
5	Cs <sub>2</sub> CO <sub>3</sub>	0.5	24	100	92	8
6	DBU	0.5	48	100	73	7
7	Cs <sub>2</sub> CO <sub>3</sub>	0.2	48	95	77	6
8	DBU	0.2	48	96	75	5
9	-	-	24	17	17	0
10	-	-	48	28	28	0

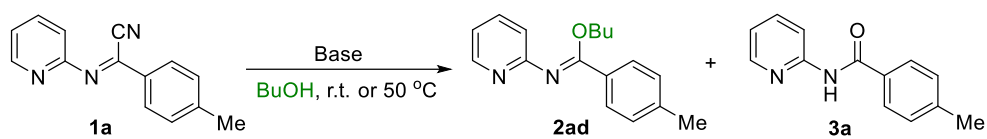
<sup>[a]</sup> Conditions: (Z)-4-methyl-N-(pyridin-2-yl)benzimidoyl cyanide **1a** (0,1 mmol), EtOH (1 ml). <sup>[b]</sup> Relative yields and conversion measured by <sup>1</sup>H NMR of the crude reaction mixture.

**Table S2.** Screening of base equivalents, with PrOH as solvent

Entry	Base	Base equiv.	Time (h)	Conversion (%) <sup>[b]</sup>	<b>2ac</b> (%) <sup>[b]</sup>	<b>3a</b> (%) <sup>[b]</sup>
1	Cs <sub>2</sub> CO <sub>3</sub>	2	24	100	89	6
2	DBU	2	24	100	80	15
3	Cs <sub>2</sub> CO <sub>3</sub>	1	24	100	84	11
4	DBU	1	24	100	79	16
5	Cs <sub>2</sub> CO <sub>3</sub>	0.5	24	100	73	22
6	DBU	0.5	24	100	71	24
7	-	-	24	14	14	0
8	-	-	48	27	27	0

<sup>[a]</sup> Conditions: (Z)-4-methyl-N-(pyridin-2-yl)benzimidoyl cyanide **1a** (0,1 mmol), PrOH (1 ml). <sup>[b]</sup>

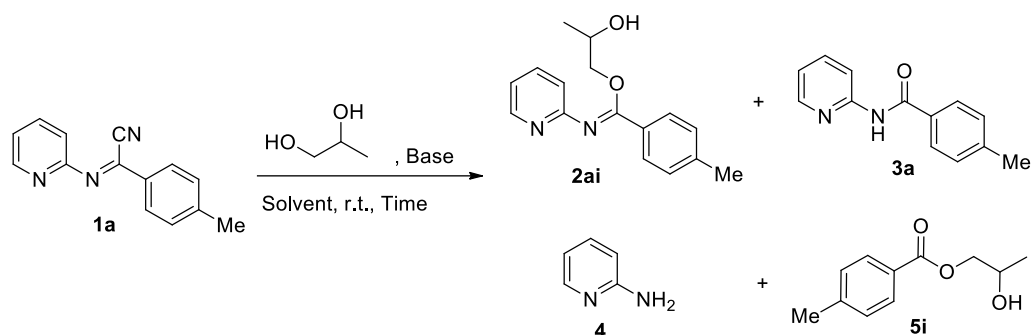
Relative yields and conversion measured by <sup>1</sup>H NMR of the crude reaction mixture, 2-aminopyridine and propyl 4-methylbenzoate of about 5% is observed in all reactions.

**Table S3.** Screening of base equivalents, with BuOH as solvent

Entry	Base	Base equiv.	Time (h)	Conversion (%) <sup>[c]</sup>	<b>2ad</b> (%) <sup>[c]</sup>	<b>3a</b> (%) <sup>[c]</sup>
1	CS <sub>2</sub> CO <sub>3</sub>	2	24	36	16	20
2	DBU	2	24	70	37	33
3	CS <sub>2</sub> CO <sub>3</sub>	1	24	50	15	15
4 <sup>[b]</sup>	CS <sub>2</sub> CO <sub>3</sub>	1	24	88	80	8
5	DBU	1	24	65	20	20
6	DBU	0.5	24	70	25	20
7 <sup>[b]</sup>	-	-	48	65	35	30

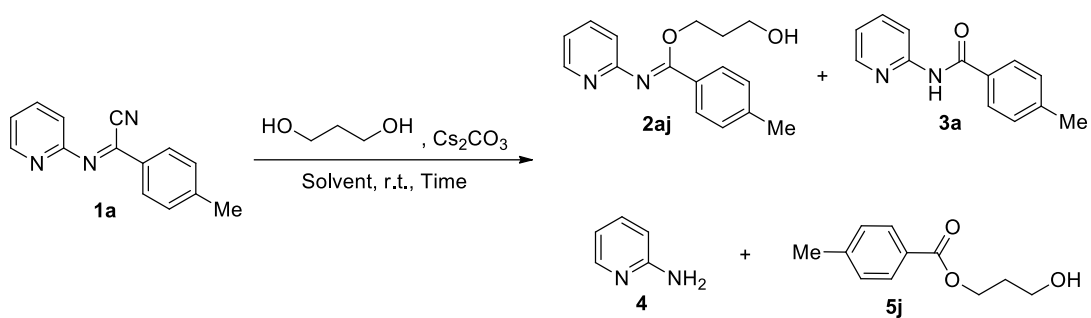
<sup>[a]</sup> Conditions: (Z)-4-methyl-N-(pyridin-2-yl)benzimidoyl cyanide **1a** (0,1 mmol), BuOH (1 ml). <sup>[b]</sup> The reaction was carried out at 50 °C. <sup>[c]</sup> Relative yields and conversion measured by <sup>1</sup>H NMR of the crude reaction mixture.



**Table S4.** Screening of reaction, in the presence of 1,2-propanediol

Entry	Base (equiv)	Solvent	Time (h)	Conversion (%) <sup>[b]</sup>	2ai (%) <sup>[b]</sup>	Byproducts (%) <sup>[b]</sup>
1	Cs <sub>2</sub> CO <sub>3</sub> (1)	DCE	24	90	20	3a (19), 4 (33), 5i (28)
2	Cs <sub>2</sub> CO <sub>3</sub> (2)	DCE	24	100	36	3a (17), 4 (24), 5i (23)
3	Cs <sub>2</sub> CO <sub>3</sub> (2)	Acetone	4	100	0	Unidentified products
4	-	DCE	24	0	0	0

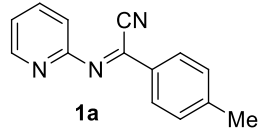
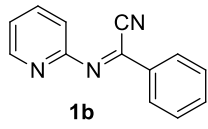
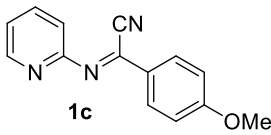
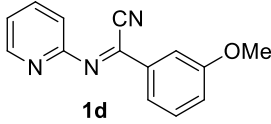
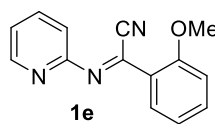
<sup>[a]</sup> Conditions: **1a** (0,1 mmol), 1,2-propanediol (0.2 ml), Solvent (0.8 mL). <sup>[b]</sup> Relative yields and conversion measured by <sup>1</sup>H NMR of the crude reaction mixture.

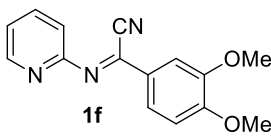
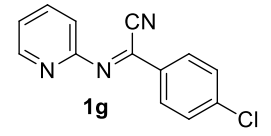
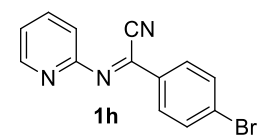
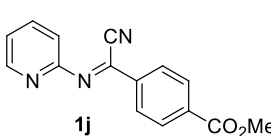
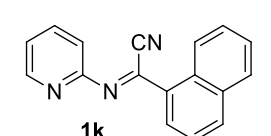
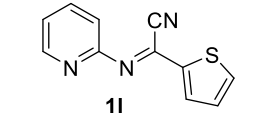
**Table S5.** Screening of reaction, in the presence of 1,3-propanediol

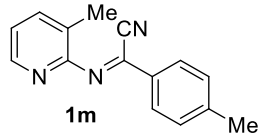
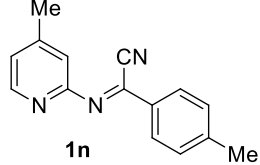
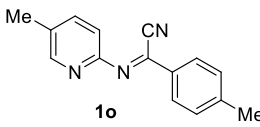
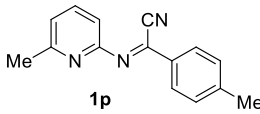
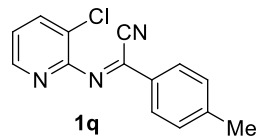
Entry	Solvent	$\text{Cs}_2\text{CO}_3$ equiv.	Time (h)	Conversion (%) <sup>[b]</sup>	<b>2aj</b> (%) <sup>[b]</sup>	Byproducts (%) <sup>[b]</sup>
1	DCE	1	48	53	36	<b>3a</b> (17)
2	DCE	2	48	69	42	<b>3a</b> (27)
3	Acetone	2	4	100	83	<b>3a</b> (17)
4	DMSO	2	4	100	72	<b>4</b> (12), <b>5j</b> (12)

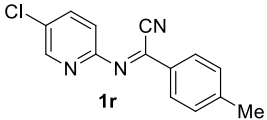
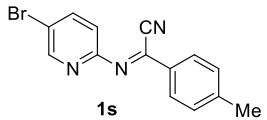
<sup>[a]</sup> Conditions: **1a** (0,1 mmol), 1,3-propanediol (0,2 ml), Solvent (0,8 ml). <sup>[b]</sup> Relative yields and conversion measured by  $^1\text{H}$  NMR of the crude reaction mixture.

**<sup>1</sup>H and <sup>13</sup>C{H} NMR data for  $\alpha$ -iminonitriles 1a-1h, 1j-1s**

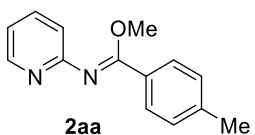
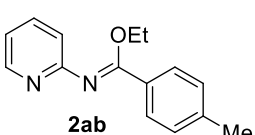
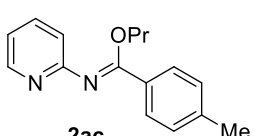
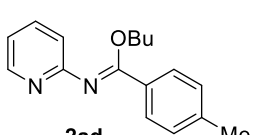
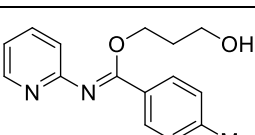
<p>(<i>Z</i>)-4-methyl-<i>N</i>-(pyridin-2-yl)benzimidoyl cyanide (<b>1a</b>):<sup>[S1]</sup> Yellow solid, 165 mg, yield 75%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 10/1); mp: (88–90 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) <math>\delta</math> 8.60 (dd, <math>J_1</math> = 5.0 Hz, <math>J_2</math> = 1.0 Hz, 1H), 8.12 (d, <math>J</math> = 8.0 Hz, 2H), 7.86 (td, <math>J_1</math> = 7.5 Hz, <math>J_2</math> = 2.0 Hz, 1H), 7.34 (d, <math>J</math> = 8.0 Hz, 2H), 7.32 – 7.22 (m, 2H), 2.46 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>): <math>\delta</math> 159.5, 149.0, 144.6, 141.3, 138.5, 131.2, 129.9, 128.9, 122.9, 118.3, 111.7, 21.9; HRMS (ESI) <math>m/z</math>: calcd for C<sub>14</sub>H<sub>12</sub>N<sub>3</sub> [M+H]<sup>+</sup> 222.1026, found: 222.1020.</p>	 <p style="text-align: center;"><b>1a</b></p>
<p>(<i>Z</i>)-<i>N</i>-(pyridin-2-yl)benzimidoyl cyanide (<b>1b</b>):<sup>[S1]</sup> Brown solid, 182 mg, yield 88%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 10/1); mp: (61–63 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) <math>\delta</math> 8.61 (d, <math>J</math> = 4.0 Hz, 1H), 8.23 (d, <math>J</math> = 8.0 Hz, 2H), 7.85 (t, <math>J</math> = 7.5 Hz, 1H), 7.62 (t, <math>J</math> = 7.5 Hz, 1H), 7.54 (t, <math>J</math> = 8.0 Hz, 2H), 7.30 – 7.26 (m, 2H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>): <math>\delta</math> 159.3, 149.0, 141.4, 138.5, 133.8, 133.5, 129.2, 128.9, 123.1, 118.5, 111.6; HRMS (ESI) <math>m/z</math>: calcd for C<sub>13</sub>H<sub>9</sub>N<sub>3</sub> [M+H]<sup>+</sup> 208.0869, found 208.0870.</p>	 <p style="text-align: center;"><b>1b</b></p>
<p>(<i>Z</i>)-4-methoxy-<i>N</i>-(pyridin-2-yl)benzimidoyl cyanide (<b>1c</b>):<sup>[S2]</sup> Yellow solid, 171 mg, yield 72%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 10/1); mp: (76–78 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) <math>\delta</math> 8.58 (d, <math>J</math> = 4.0 Hz, 1H), 8.18 (d, <math>J</math> = 8.5 Hz, 2H), 7.82 (t, <math>J</math> = 7.5 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.02 (d, <math>J</math> = 8.5 Hz, 2H), 3.91 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) <math>\delta</math> 164.1, 159.6, 148.9, 140.6, 138.5, 131.0, 126.7, 122.6, 118.2, 114.6, 111.7, 55.8; HRMS (ESI) <math>m/z</math>: calcd for C<sub>14</sub>H<sub>12</sub>N<sub>3</sub>O [M+H]<sup>+</sup> 238.0975; found 238.0979.</p>	 <p style="text-align: center;"><b>1c</b></p>
<p>(<i>Z</i>)-3-methoxy-<i>N</i>-(pyridin-2-yl)benzimidoyl cyanide (<b>1d</b>):<sup>[S1]</sup> Yellow oil, 178 mg, yield 75%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 10/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) <math>\delta</math> 8.59 (d, <math>J</math> = 4.0 Hz, 1H), 7.83 (dd, <math>J_1</math> = 8.0 Hz, <math>J_2</math> = 1.5 Hz, 1H), 7.79 (d, <math>J</math> = 8.0 Hz, 1H), 7.74 (s, 1H), 7.43 (t, <math>J</math> = 8.0 Hz, 1H), 7.30 – 7.26 (m, 2H), 7.14 (dd, <math>J_1</math> = 8.5 Hz, <math>J_2</math> = 2.5 Hz, 1H), 3.87 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>): <math>\delta</math> 160.2, 159.3, 149.0, 141.3, 138.5, 135.1, 130.2, 123.1, 122.2, 120.5, 118.3, 112.2, 111.6, 55.7; HRMS (ESI) <math>m/z</math>: calcd for C<sub>14</sub>H<sub>12</sub>N<sub>3</sub>O [M+H]<sup>+</sup> 238.0975; found 238.0979.</p>	 <p style="text-align: center;"><b>1d</b></p>
<p>(<i>Z</i>)-2-methoxy-<i>N</i>-(pyridin-2-yl)benzimidoyl cyanide (<b>1e</b>): Brown oil, 123 mg, yield 52%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 8/1 to 5/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) <math>\delta</math> 8.59 (d, <math>J</math> = 4.5 Hz, 1H), 7.91 (d, <math>J</math> = 8.0 Hz, 1H), 7.81 (t, <math>J</math> = 7.5 Hz, 1H), 7.54 (t, <math>J</math> = 8.0 Hz, 1H), 7.25 – 7.22 (m, 1H), 7.17 (d, <math>J</math> = 8.0 Hz, 1H), 7.07 (t, <math>J</math> = 7.5 Hz, 1H), 7.03 (d, <math>J</math> = 8.5 Hz, 1H), 3.97 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>): <math>\delta</math> 160.1, 159.1, 149.1, 140.4, 138.3, 134.4, 130.6, 123.6, 122.4, 121.2, 117.0, 112.2, 112.1, 56.0; HRMS (ESI) <math>m/z</math>: calcd for C<sub>14</sub>H<sub>12</sub>N<sub>3</sub>O [M+H]<sup>+</sup> 238.0975; found 238.0979.</p>	 <p style="text-align: center;"><b>1e</b></p>

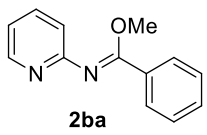
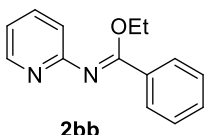
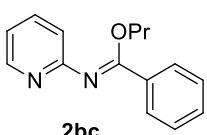
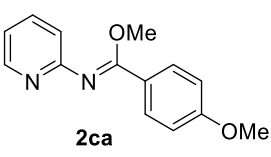
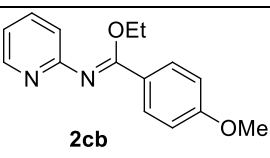
<p>(Z)-3,4-dimethoxy-N-(pyridin-2-yl)benzimidoyl cyanide (<b>1f</b>): Yellow solid, 203 mg, yield 76%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 7/1 to 5/1); mp: (88-90 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.59 (d, <i>J</i> = 4.5 Hz, 1H), 7.84 – 7.80 (m, 2H), 7.77 (s, 1H), 7.23 (d, <i>J</i> = 8.5 Hz, 2H), 6.98 (d, <i>J</i> = 8.5 Hz, 1H), 3.99 (s, 3H), 3.98 (s, 3H). <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 159.8, 154.0, 149.7, 149.1, 140.7, 138.4, 127.0, 124.7, 122.6, 117.9, 111.6, 110.7, 109.4, 56.4, 56.3; HRMS (ESI) <i>m/z</i>: calcd for C<sub>15</sub>H<sub>14</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 268.1081; found 268.1084.</p>	 <p style="text-align: center;"><b>1f</b></p>
<p>(Z)-4-chloro-N-(pyridin-2-yl)benzimidoyl cyanide (<b>1g</b>):<sup>[S2]</sup> Yellow solid, 222 mg, yield 92%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 10/1); mp: (120-121 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.61 (d, <i>J</i> = 5.0 Hz, 1H), 8.18 (d, <i>J</i> = 8.5 Hz, 2H), 7.87 (t, <i>J</i> = 7.5 Hz, 1H), 7.53 (d, <i>J</i> = 8.5 Hz, 2H), 7.33 – 7.28 (m, 2H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>): δ 158.8, 148.9, 140.1, 140.0, 138.7, 132.3, 130.1, 129.6, 123.4, 118.9, 111.5; HRMS (ESI) <i>m/z</i>: calcd for C<sub>13</sub>H<sub>9</sub>ClN<sub>3</sub> [M+H]<sup>+</sup> 242.048; found 242.0482.</p>	 <p style="text-align: center;"><b>1g</b></p>
<p>(Z)-4-bromo-N-(pyridin-2-yl)benzimidoyl cyanide (<b>1h</b>):<sup>[S2]</sup> Yellow solid, 172 mg, yield 60%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 10/1); mp: (110-111 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.61 (dd, <i>J</i><sub>1</sub> = 5.0 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 8.10 (d, <i>J</i> = 8.5 Hz, 2H), 7.86 (td, <i>J</i><sub>1</sub> = 7.5 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 7.69 (d, <i>J</i> = 8.5 Hz, 2H), 7.34 – 7.24 (m, 2H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 158.8, 149.0, 140.0, 138.5, 132.8, 132.5, 130.2, 128.7, 123.4, 119.0, 111.5; HRMS (ESI) <i>m/z</i>: calcd for C<sub>13</sub>H<sub>9</sub>BrN<sub>3</sub> [M+H]<sup>+</sup> 285.9974 and 287.9954; found 285.9975 and 287.9963.</p>	 <p style="text-align: center;"><b>1h</b></p>
<p>(Z)-methyl 4-(cyano(pyridin-2-ylimino)methyl)benzoate (<b>1j</b>): Brown oil, 228 mg, yield 86%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 10/1 to 7/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.62 (dd, <i>J</i><sub>1</sub> = 5.0 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 8.30 (d, <i>J</i> = 8.5 Hz, 2H), 8.19 (d, <i>J</i> = 8.5 Hz, 2H), 7.87 (td, <i>J</i><sub>1</sub> = 8.0 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 7.34 – 7.31 (m, 2H), 3.97 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 166.2, 158.7, 149.1, 140.0, 138.5, 137.4, 134.2, 130.2, 128.8, 123.7, 119.3, 111.6, 52.7; HRMS (ESI) <i>m/z</i>: calcd for C<sub>15</sub>H<sub>12</sub>N<sub>3</sub>O<sub>2</sub> [M+H]<sup>+</sup> 266.0924; found 266.0925.</p>	 <p style="text-align: center;"><b>1j</b></p>
<p>(Z)-N-(pyridin-2-yl)-1-naphthimidoyl cyanide (<b>1k</b>):<sup>[S3]</sup> Brown oil, 231 mg, yield 90%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 10/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 9.24 (d, <i>J</i> = 8.5 Hz, 1H), 8.66 (d, <i>J</i> = 4.0 Hz, 1H), 8.34 (d, <i>J</i> = 7.0 Hz, 1H), 8.08 (d, <i>J</i> = 8.0 Hz, 1H), 7.95 (d, <i>J</i> = 8.0 Hz, 1H), 7.88 (t, <i>J</i> = 7.5 Hz, 1H), 7.69 – 7.59 (m, 3H), 7.32 – 7.30 (m, 2H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 159.7, 149.1, 142.7, 138.5, 134.33, 134.25, 132.7, 130.5, 130.0, 129.1, 128.9, 127.1, 125.8, 124.9, 122.9, 117.9, 112.3; HRMS (ESI) <i>m/z</i>: calcd for C<sub>17</sub>H<sub>12</sub>N<sub>3</sub> [M+H]<sup>+</sup> 258.1026; found 258.1028.</p>	 <p style="text-align: center;"><b>1k</b></p>
<p>(E)-N-(pyridin-2-yl)thiophene-2-carbimidoyl cyanide (<b>1l</b>):<sup>[S1]</sup> Brown solid, 106 mg, yield 50%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 10/1); mp (56–58 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.59 (d, <i>J</i> = 4.0 Hz, 1H), 7.95 (d, <i>J</i> = 3.5 Hz, 1H), 7.83 (t, <i>J</i> = 7.0 Hz, 1H), 7.66</p>	 <p style="text-align: center;"><b>1l</b></p>

<p>(d, <math>J = 4.5</math> Hz, 1H), 7.31-7.26 (m, 2H), 7.21 (t, <math>J = 4.5</math> Hz, 1H); <math>^{13}\text{C}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 158.0, 148.6, 141.4, 138.7, 135.0, 134.5, 134.0, 128.7, 123.3, 119.7, 111.5; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{11}\text{H}_8\text{N}_3\text{S}</math> <math>[\text{M}+\text{H}]^+</math> 214.0433; found 214.0437.</p>	
<p>(<i>Z</i>)-4-methyl-<i>N</i>-(3-methylpyridin-2-yl)benzimidoyl cyanide (<b>1m</b>): Brown oil, 188 mg, 80%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 10/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.40 (d, <math>J = 3.5</math> Hz, 1H), 8.13 (d, <math>J = 8.2</math> Hz, 2H), 7.62 (d, <math>J = 7.5</math> Hz, 1H), 7.34 (d, <math>J = 8.2</math> Hz, 2H), 7.19 (dd, <math>J_1 = 7.5</math> Hz, <math>J_2 = 4.8</math> Hz, 1H), 2.46 (s, 3H), 2.36 (s, 3H); <math>^{13}\text{C}\{^1\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 157.8, 146.1, 144.3, 140.5, 139.2, 131.5, 129.9, 128.8, 128.0, 123.2, 112.0, 21.9, 17.4; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{15}\text{H}_{14}\text{N}_3</math> <math>[\text{M}+\text{H}]^+</math> 236.1182; found 236.1190.</p>	
<p>(<i>Z</i>)-4-methyl-<i>N</i>-(4-methylpyridin-2-yl)benzimidoyl cyanide (<b>1n</b>):<sup>[S3]</sup> Yellow oil, 153 mg, yield 65%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 10/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.43 (d, <math>J = 5.0</math> Hz, 1H), 8.09 (d, <math>J = 8.0</math> Hz, 2H), 7.32 (d, <math>J = 8.0</math> Hz, 2H), 7.07 (d, <math>J = 5.0</math> Hz, 1H), 7.05 (s, 1H), 2.44 (s, 3H), 2.41 (s, 3H); <math>^{13}\text{C}\{^1\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 159.5, 149.7, 148.5, 144.3, 140.96, 131.2, 129.7, 128.7, 123.8, 118.6, 111.6, 21.7, 21.0; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{15}\text{H}_{14}\text{N}_3</math> <math>[\text{M}+\text{H}]^+</math> 236.1182; found 236.1188.</p>	
<p>(<i>Z</i>)-4-methyl-<i>N</i>-(5-methylpyridin-2-yl)benzimidoyl cyanide (<b>1o</b>): Orange oil, 160 mg, yield 68%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 10/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.40 (d, <math>J = 0.7</math> Hz, 1H), 8.09 (d, <math>J = 8.0</math> Hz, 2H), 7.61 (dd, <math>J_1 = 8.0</math> Hz, <math>J_2 = 2.0</math> Hz, 1H), 7.31 (d, <math>J = 8.0</math> Hz, 2H), 7.17 (d, <math>J = 8.0</math> Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H); <math>^{13}\text{C}\{^1\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 157.0, 148.9, 144.1, 140.2, 138.7, 132.8, 131.3, 129.7, 128.6, 118.2, 111.9, 21.7, 18.2; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{15}\text{H}_{14}\text{N}_3</math> <math>[\text{M}+\text{H}]^+</math> 236.1182; found 236.1189.</p>	
<p>(<i>Z</i>)-4-methyl-<i>N</i>-(6-methylpyridin-2-yl)benzimidoyl cyanide (<b>1p</b>): Yellow oil, 185 mg, yield 79%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 10/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.10 (d, <math>J = 8.3</math> Hz, 2H), 7.71 (t, <math>J = 8.0</math> Hz, 1H), 7.33 (d, <math>J = 8.0</math> Hz, 2H), 7.12 (d, <math>J = 7.5</math> Hz, 1H), 7.03 (d, <math>J = 7.8</math> Hz, 1H), 2.62 (s, 3H), 2.45 (s, 3H); <math>^{13}\text{C}\{^1\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 158.9, 158.2, 144.3, 141.1, 138.5, 131.1, 129.7, 128.7, 122.2, 114.5, 111.4, 23.9, 21.7; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{15}\text{H}_{14}\text{N}_3</math> <math>[\text{M}+\text{H}]^+</math> 236.1182; found 236.1185.</p>	
<p>(<i>Z</i>)-<i>N</i>-(3-chloropyridin-2-yl)-4-methylbenzimidoyl cyanide (<b>1q</b>): Yellow oil, 210 mg, yield 82%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 10/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.47 (d, <math>J = 3.8</math> Hz, 1H), 8.15 (d, <math>J = 8.0</math> Hz, 2H), 7.84 (d, <math>J = 8.0</math> Hz, 1H), 7.36 (d, <math>J = 8.0</math> Hz, 2H), 7.23 (dd, <math>J_1 = 8.0</math> Hz, <math>J_2 = 5.0</math> Hz, 1H), 2.47 (s, 3H); <math>^{13}\text{C}\{^1\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 156.1, 146.7, 145.0, 142.4, 138.5, 130.9, 129.9, 129.1, 125.5, 123.5, 111.2, 21.8; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{14}\text{H}_{11}\text{ClN}_3</math> <math>[\text{M}+\text{H}]^+</math> 256.0636; found 256.0635.</p>	

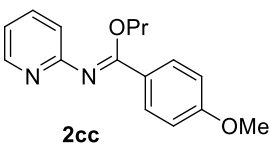
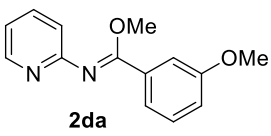
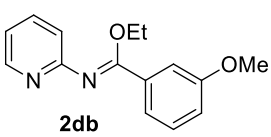
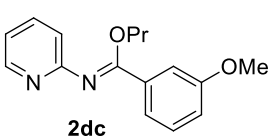
<p>(Z)-N-(5-chloropyridin-2-yl)-4-methylbenzimidoyl cyanide (<b>1r</b>): Orange oil, 166 mg, yield 65%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 10/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.51 (s, 1H), 8.07 (d, <i>J</i> = 8.0 Hz, 2H), 7.75 (dd, <i>J</i><sub>1</sub> = 8.5 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 7.31 (d, <i>J</i> = 8.0 Hz, 2H), 7.20 (d, <i>J</i> = 8.5 Hz, 1H), 2.43 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 157.3, 147.6, 144.7, 141.2, 137.9, 131.0, 130.8, 129.8, 128.8, 119.6, 111.5, 21.6; HRMS (ESI) <i>m/z</i>: calcd for C<sub>14</sub>H<sub>11</sub>ClN<sub>3</sub> [M+H]<sup>+</sup> 256.0636; found 256.0637.</p>	
<p>(Z)-N-(5-bromopyridin-2-yl)-4-methylbenzimidoyl cyanide (<b>1s</b>):<sup>[S3]</sup> Yellow oil, 210 mg, yield 70%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 10/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.63 (d, <i>J</i> = 2.1 Hz, 1H), 8.10 (d, <i>J</i> = 8.0 Hz, 2H), 7.93 (dd, <i>J</i><sub>1</sub> = 8.5 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 7.34 (d, <i>J</i> = 8.0 Hz, 2H), 7.16 (d, <i>J</i> = 8.5 Hz, 1H), 2.46 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 157.8, 149.9, 144.8, 141.3, 140.8, 131.0, 129.8, 128.9, 119.9, 119.3, 111.4, 21.8; HRMS (ESI) <i>m/z</i>: calcd for C<sub>14</sub>H<sub>11</sub>BrN<sub>3</sub> [M+H]<sup>+</sup> 300.0131 and 302.0110; found 300.0093 and 302.0117.</p>	

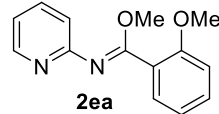
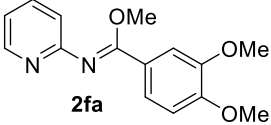
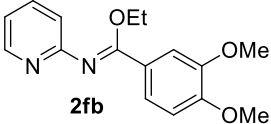
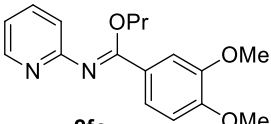
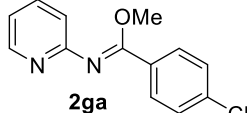
**<sup>1</sup>H and <sup>13</sup>C{H} NMR data for imidates 2aa-2ad, 2aj, 2ba-2hc, 2ja-2sa**

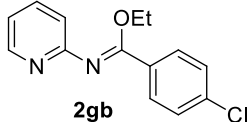
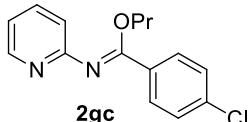
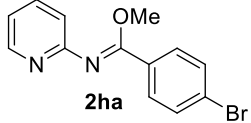
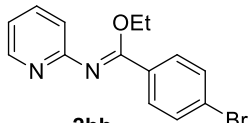
<p>(<i>Z</i>)-methyl 4-methyl-N-(pyridin-2-yl)benzimidate (<b>2aa</b>): Yellow oil, 37 mg, yield 82%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 7/1 to 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.33 (dd, <i>J</i><sub>1</sub> = 5.0 Hz, <i>J</i><sub>2</sub> = 1 Hz, 1H), 7.46 (td, <i>J</i><sub>1</sub> = 7.5 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 7.18 (d, <i>J</i> = 8.0 Hz, 2H), 7.01 (d, <i>J</i> = 8.0 Hz, 2H), 6.88 (ddd, <i>J</i><sub>1</sub> = 7.0, <i>J</i><sub>2</sub> = 5.0 Hz, <i>J</i><sub>3</sub> = 1.0 Hz, 1H), 6.55 (d, <i>J</i> = 8.0 Hz, 1H), 4.00 (s, 3H), 2.27 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 161.29, 161.25, 148.8, 140.6, 137.6, 129.1, 128.7, 128.2, 118.1, 116.3, 54.3, 21.4; HRMS (ESI) <i>m/z</i>: calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 227.1179; found 227.1203.</p>	 <p style="text-align: center;"><b>2aa</b></p>
<p>(<i>Z</i>)-ethyl 4-methyl-N-(pyridin-2-yl)benzimidate (<b>2ab</b>): Yellow oil, 35 mg, yield 74%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 7/1 to 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.33 (d, <i>J</i> = 5.0 Hz, 1H), 7.44 (td, <i>J</i><sub>1</sub> = 7.5 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 7.19 (d, <i>J</i> = 8.0 Hz, 2H), 7.01 (d, <i>J</i> = 8.0 Hz, 2H), 6.87 (dd, <i>J</i><sub>1</sub> = 7.0, <i>J</i><sub>2</sub> = 5.0 Hz, 1H), 6.54 (d, <i>J</i> = 8.0 Hz, 1H), 4.45 (q, <i>J</i> = 7.0 Hz, 2H), 2.27 (s, 3H), 1.43 (t, <i>J</i> = 7.0 Hz, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 161.5, 160.8, 148.8, 140.4, 137.5, 129.1, 128.7, 128.6, 118.0, 116.3, 62.8, 21.4, 14.3; HRMS (ESI) <i>m/z</i>: calcd for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 241.1335; found 241.1387.</p>	 <p style="text-align: center;"><b>2ab</b></p>
<p>(<i>Z</i>)-propyl 4-methyl-N-(pyridin-2-yl)benzimidate (<b>2ac</b>): Light yellow oil, 29 mg, yield 56%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 7/1 to 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.31 (dd, <i>J</i><sub>1</sub> = 5.0 Hz, <i>J</i><sub>2</sub> = 1.0 Hz, 1H), 7.43 (td, <i>J</i><sub>1</sub> = 7.5 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 7.18 (d, <i>J</i> = 8.0 Hz, 2H), 6.99 (d, <i>J</i> = 8.0 Hz, 2H), 6.85 (dd, <i>J</i><sub>1</sub> = 7.0, <i>J</i><sub>2</sub> = 5.0 Hz, 1H), 6.53 (d, <i>J</i> = 8.0 Hz, 1H), 4.33 (t, <i>J</i> = 6.5 Hz, 2H), 2.26 (s, 3H), 1.87 – 1.79 (m, 2H), 1.04 (t, <i>J</i> = 7.5 Hz, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 161.4, 161.0, 147.9, 140.7, 138.2, 129.1, 128.7, 128.4, 118.0, 116.6, 68.9, 22.0, 21.4, 10.7; HRMS (ESI) <i>m/z</i>: calcd for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 255.1492; found 255.1543.</p>	 <p style="text-align: center;"><b>2ac</b></p>
<p>(<i>Z</i>)-butyl 4-methyl-N-(pyridin-2-yl)benzimidate (<b>2ad</b>): Yellow oil, 41 mg, yield 77%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 7/1 to 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.32 (d, <i>J</i> = 5.0 Hz, 1H), 7.47 (td, <i>J</i><sub>1</sub> = 8.0 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 7.18 (d, <i>J</i> = 8.0 Hz, 2H), 7.01 (d, <i>J</i> = 8.0 Hz, 2H), 6.88 (dd, <i>J</i><sub>1</sub> = 7.0 Hz, <i>J</i><sub>2</sub> = 5.5 Hz, 1H), 6.55 (d, <i>J</i> = 8.0 Hz, 1H), 4.38 (t, <i>J</i> = 6.5 Hz, 2H), 2.27 (s, 3H), 1.83 – 1.76 (m, 2H), 1.51 (sextet, <i>J</i> = 7.5 Hz, 2H), 0.98 (t, <i>J</i> = 7.5 Hz, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 161.3, 161.1, 148.1, 140.6, 138.0, 129.1, 128.7, 128.4, 118.0, 116.5, 67.1, 30.7, 21.3, 19.4, 13.9; HRMS (ESI) <i>m/z</i>: calcd for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 269.1648; found 269.1655.</p>	 <p style="text-align: center;"><b>2ad</b></p>
<p>(<i>Z</i>)-3-hydroxypropyl 4-methyl-N-(pyridin-2-yl)benzimidate (<b>2aj</b>): Brown oil, 16 mg, yield 30%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 5/1 to 1/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.32 (d, <i>J</i> = 5.0 Hz, 1H), 7.48 (t, <i>J</i> = 8.0 Hz, 1H), 7.18 (d, <i>J</i> = 8.0 Hz, 2H), 7.02</p>	 <p style="text-align: center;"><b>2aj</b></p>

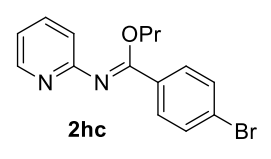
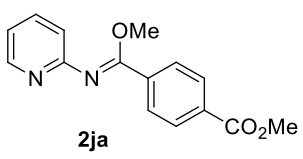
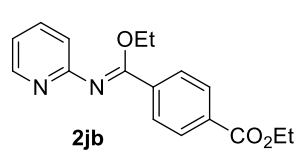
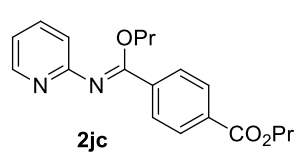
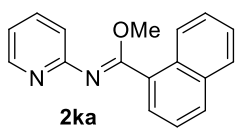
<p>(d, <math>J = 8.0</math> Hz, 2H), 6.90 (dd, <math>J_1 = 7.0</math> Hz, <math>J_2 = 5.5</math> Hz, 1H), 6.59 (d, <math>J = 8.0</math> Hz, 2H), 4.59 (t, <math>J = 6.0</math> Hz, 2H), 3.83 (t, <math>J = 6.0</math> Hz, 2H), 2.28 (s, 3H), 2.07 – 2.02 (m, 2H); <math>^{13}\text{C}\{\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 161.7, 160.9, 148.8, 140.8, 137.7, 129.1, 128.8, 128.2, 118.3, 116.4, 63.9, 59.3, 32.1, 21.4; MS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_2</math> <math>[\text{M}+\text{H}]^+</math> 271.14; found 271.19 (sensitive compound)</p>	
<p>(<i>Z</i>)-methyl <i>N</i>-pyridin-2-ylbenzimidate (<b>2ba</b>):<sup>[S4]</sup> Brown oil, 35 mg, yield 83%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 7/1 to 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.32 (dd, <math>J_1 = 5.0</math> Hz, <math>J_2 = 1.0</math> Hz, 1H), 7.46 (td, <math>J_1 = 8.0</math> Hz, <math>J_2 = 2.0</math> Hz, 1H), 7.32 – 7.28 (m, 3H), 7.23 – 7.18 (m, 2H), 6.88 (dd, <math>J_1 = 7.0</math> Hz, <math>J_2 = 5.0</math> Hz, 1H), 6.56 (d, <math>J = 8.0</math> Hz, 1H), 4.02 (s, 3H); <math>^{13}\text{C}\{\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 161.4, 161.0, 148.6, 137.8, 131.2, 130.3, 129.1, 128.0, 118.3, 116.4, 54.5; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}</math> <math>[\text{M}+\text{H}]^+</math> 213.1022; found 213.1026.</p>	 <p style="text-align: center;"><b>2ba</b></p>
<p>(<i>Z</i>)-ethyl <i>N</i>-pyridin-2-ylbenzimidate (<b>2bb</b>): Brown oil, 38 mg, yield 84%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 7/1 to 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.31 (dd, <math>J_1 = 5.0</math> Hz, <math>J_2 = 1.0</math> Hz, 1H), 7.43 (td, <math>J_1 = 8.0</math> Hz, <math>J_2 = 2.0</math> Hz, 1H), 7.31 – 7.27 (m, 3H), 7.20 (t, <math>J = 7.5</math> Hz, 2H), 6.85 (ddd, <math>J_1 = 7.0</math> Hz, <math>J_2 = 5.0</math> Hz, <math>J_3 = 1.0</math> Hz, 1H), 6.54 (d, <math>J = 8.0</math> Hz, 1H), 4.46 (q, <math>J = 7.0</math> Hz, 2H), 1.44 (t, <math>J = 7.0</math> Hz, 3H); <math>^{13}\text{C}\{\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 161.1, 161.0, 148.3, 137.8, 131.4, 130.2, 129.1, 128.0, 118.1, 116.5, 63.1, 14.2; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}</math> <math>[\text{M}+\text{H}]^+</math> 227.1179; found 227.1225.</p>	 <p style="text-align: center;"><b>2bb</b></p>
<p>(<i>Z</i>)-propyl <i>N</i>-pyridin-2-ylbenzimidate (<b>2bc</b>): Brown oil, 37 mg, yield 77%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 7/1 to 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.31 (dd, <math>J_1 = 5.0</math> Hz, <math>J_2 = 1.0</math> Hz, 1H), 7.44 (ddd, <math>J_1 = 8.0</math> Hz, <math>J_2 = 7.5</math> Hz, <math>J_3 = 2.0</math> Hz, 1H), 7.31 – 7.27 (m, 3H), 7.20 (t, <math>J = 8.0</math> Hz, 2H), 6.86 (ddd, <math>J_1 = 7.0</math> Hz, <math>J_2 = 5.0</math> Hz, <math>J_3 = 1.0</math> Hz, 1H), 6.55 (d, <math>J = 8.0</math> Hz, 1H), 4.36 (t, <math>J = 6.5</math> Hz, 2H), 1.89 – 1.81 (m, 2H), 1.05 (t, <math>J = 7.5</math> Hz, 3H); <math>^{13}\text{C}\{\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 161.2, 161.0, 148.7, 137.6, 131.6, 130.1, 129.1, 128.0, 118.1, 116.4, 68.7, 22.0, 10.7; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}</math> <math>[\text{M}+\text{H}]^+</math> 241.1335; found 241.1339.</p>	 <p style="text-align: center;"><b>2bc</b></p>
<p>(<i>Z</i>)-methyl 4-methoxy-<i>N</i>-(pyridin-2-yl)benzimidate (<b>2ca</b>): Yellow oil, 47 mg, yield 98%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.33 (dd, <math>J_1 = 5.0</math> Hz, <math>J_2 = 1.0</math> Hz, 1H), 7.47 (td, <math>J_1 = 8.0</math> Hz, <math>J_2 = 2.0</math> Hz, 1H), 7.24 (d, <math>J = 9.0</math> Hz, 2H), 6.88 (ddd, <math>J_1 = 7.0</math> Hz, <math>J_2 = 5.0</math> Hz, <math>J_3 = 1.0</math> Hz, 1H), 6.70 (d, <math>J = 9.0</math> Hz, 2H), 6.57 (d, <math>J = 8.0</math> Hz, 1H), 3.99 (s, 3H), 3.73 (s, 3H); <math>^{13}\text{C}\{\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 161.4, 161.0, 160.7, 148.8, 137.7, 130.9, 123.3, 118.0, 116.3, 113.3, 55.2, 54.3; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_2</math> <math>[\text{M}+\text{H}]^+</math> 243.1128; found 243.1136.</p>	 <p style="text-align: center;"><b>2ca</b></p>
<p>(<i>Z</i>)-ethyl 4-methoxy-<i>N</i>-(pyridin-2-yl)benzimidate (<b>2cb</b>): Brown oil, 49 mg, yield 96%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.33 (d, <math>J = 5.0</math></p>	 <p style="text-align: center;"><b>2cb</b></p>

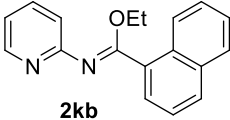
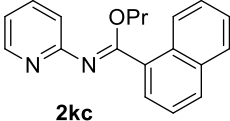
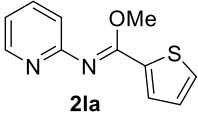
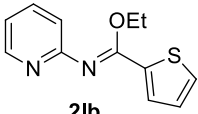


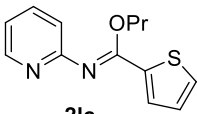
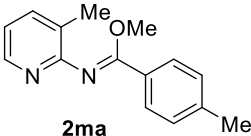
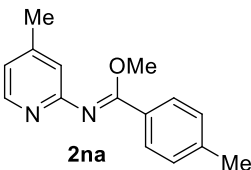
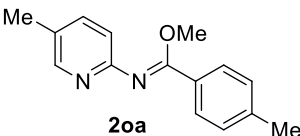
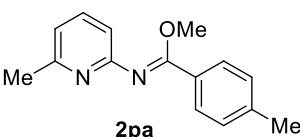
<p>Hz, 1H), 7.46 (t, <math>J = 8.0</math> Hz, 1H), 7.26 (d, <math>J = 9.0</math> Hz, 2H), 6.87 (dd, <math>J_1 = 7.0</math> Hz, <math>J_2 = 5.0</math> Hz, 1H), 6.70 (d, <math>J = 9</math> Hz, 2H), 6.55 (d, <math>J = 8.0</math> Hz, 1H), 4.43 (q, <math>J = 7.0</math> Hz, 2H), 3.74 (s, 3H), 1.43 (t, <math>J = 7.0</math> Hz, 3H); <math>^{13}\text{C}\{\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 161.5, 160.9, 160.3, 148.7, 137.6, 131.0, 123.6, 117.9, 116.3, 113.3, 62.8, 55.2, 14.3; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_2</math> <math>[\text{M}+\text{H}]^+</math> 257.1285; found 257.1290.</p>	
<p>(<i>Z</i>)-propyl 4-methoxy-<i>N</i>-(pyridin-2-yl)benzimidate (<b>2cc</b>): Yellow oil, 49 mg, yield 91%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 7/1 to 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.32 (d, <math>J = 5.0</math> Hz, 1H), 7.46 (td, <math>J_1 = 8.0</math> Hz, <math>J_2 = 2.0</math> Hz, 1H), 7.25 (d, <math>J = 9.0</math> Hz, 2H), 6.86 (dd, <math>J_1 = 7.0</math> Hz, <math>J_2 = 5.0</math> Hz, 1H), 6.70 (d, <math>J = 9.0</math> Hz, 2H), 6.56 (d, <math>J = 8.0</math> Hz, 1H), 4.33 (t, <math>J = 6.5</math> Hz, 2H), 3.73 (s, 3H), 1.87 – 1.80 (m, 2H), 1.05 (t, <math>J = 7.5</math> Hz, 3H); <math>^{13}\text{C}\{\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 161.5, 161.0, 160.4, 148.7, 137.7, 131.0, 123.6, 117.9, 116.3, 113.3, 68.6, 55.2, 22.0, 10.7; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_2</math> <math>[\text{M}+\text{H}]^+</math> 271.1441; found 271.1448.</p>	 <p style="text-align: center;"><b>2cc</b></p>
<p>(<i>Z</i>)-methyl 3-methoxy-<i>N</i>-(pyridin-2-yl)benzimidate (<b>2da</b>): Yellow oil, 43 mg, yield 89%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 7/1 to 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.33 (dd, <math>J_1 = 5.0</math> Hz, <math>J_2 = 1.0</math> Hz, 1H), 7.46 (td, <math>J_1 = 7.5</math> Hz, <math>J_2 = 1.5</math> Hz, 1H), 7.11 (t, <math>J = 8.0</math> Hz, 1H), 6.90 – 6.86 (m, 2H), 6.85 – 6.81 (m, 2H), 6.56 (d, <math>J = 8.0</math> Hz, 1H), 4.01 (s, 3H), 3.60 (s, 3H); <math>^{13}\text{C}\{\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 161.1, 161.0, 159.0, 148.7, 137.7, 132.3, 129.1, 121.5, 118.2, 116.9, 116.3, 113.9, 55.1, 54.4; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_2</math> <math>[\text{M}+\text{H}]^+</math> 243.1128; found 243.1168.</p>	 <p style="text-align: center;"><b>2da</b></p>
<p>(<i>Z</i>)-ethyl 3-methyl-<i>N</i>-(pyridin-2-yl)benzimidate (<b>2db</b>): Brown oil, 46 mg, yield 91%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.32 (dd, <math>J = 5.0</math> Hz, 1.0 Hz, 1H), 7.45 (td, <math>J_1 = 7.5</math> Hz, <math>J_2 = 1.5</math> Hz, 1H), 7.11 (t, <math>J = 8.0</math> Hz, 1H), 6.90 – 6.82 (m, 4H), 6.55 (d, <math>J = 8.0</math> Hz, 1H), 4.45 (q, <math>J = 7.0</math> Hz, 2H), 3.60 (s, 3H), 1.43 (t, <math>J = 7.0</math> Hz, 3H); <math>^{13}\text{C}\{\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 161.2, 160.7, 159.0, 148.5, 137.8, 132.6, 129.1, 121.5, 118.1, 116.7, 116.4, 114.0, 63.1, 55.1, 14.2; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{15}\text{H}_{17}\text{N}_2\text{O}_2</math> <math>[\text{M}+\text{H}]^+</math> 257.1285; found 257.1336.</p>	 <p style="text-align: center;"><b>2db</b></p>
<p>(<i>Z</i>)-propyl 3-methoxy-<i>N</i>-(pyridin-2-yl)benzimidate (<b>2dc</b>): Yellow oil, 46 mg, yield 86%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 7/1 to 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.33 (dd, <math>J = 5.0</math> Hz, 1.0 Hz, 1H), 7.47 (t, <math>J = 7.5</math> Hz, 1H), 7.13 (t, <math>J = 8.0</math> Hz, 1H), 6.91 – 6.82 (m, 4H), 6.56 (d, <math>J = 8.0</math> Hz, 1H), 4.36 (t, <math>J = 6.5</math> Hz, 2H), 3.61 (s, 3H), 1.89 – 1.82 (m, 2H), 1.06 (t, <math>J = 7.5</math> Hz, 3H); <math>^{13}\text{C}\{\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 161.2, 160.8, 158.9, 148.6, 137.7, 132.7, 129.1, 121.5, 118.1, 116.6, 116.4, 114.0, 68.8, 55.1, 22.0, 10.7; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{16}\text{H}_{19}\text{N}_2\text{O}_2</math> <math>[\text{M}+\text{H}]^+</math> 271.1441; found 271.1443.</p>	 <p style="text-align: center;"><b>2dc</b></p>

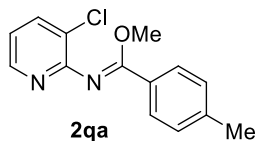
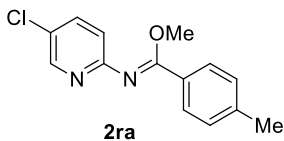
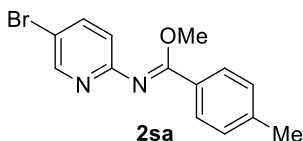
<p>(<i>Z</i>)-methyl 2-methoxy-<i>N</i>-(pyridin-2-yl)benzimidate (<b>2ea</b>): Brown oil, 39 mg, yield 82%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 7/1 to 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.23 (dd, <i>J</i><sub>1</sub> = 5.0 Hz, <i>J</i><sub>2</sub> = 1.0 Hz, 1H), 7.38 (td, <i>J</i><sub>1</sub> = 8.0 Hz, <i>J</i><sub>2</sub> = 1.5 Hz, 1H), 7.29 – 7.23 (m, 2H), 6.86 (t, <i>J</i> = 7.5 Hz, 1H), 6.79 (dd, <i>J</i><sub>1</sub> = 7.0 Hz, <i>J</i><sub>2</sub> = 5.5 Hz, 1H), 6.71 (d, <i>J</i> = 8.5 Hz, 1H), 6.57 (d, <i>J</i> = 8.0 Hz, 1H), 4.03 (s, 3H), 3.54 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 161.5, 160.9, 155.9, 148.2, 136.9, 131.1, 130.0, 121.7, 120.3, 118.2, 116.1, 110.8, 55.2, 54.4; HRMS (ESI) <i>m/z</i>: calcd for C<sub>14</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup> 243.1128; found 243.1133.</p>	 <p style="text-align: center;"><b>2ea</b></p>
<p>(<i>Z</i>)-methyl 3,4-dimethoxy-<i>N</i>-(pyridin-2-yl)benzimidate (<b>2fa</b>): Yellow oil, 53 mg, yield 98%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.34 (dd, <i>J</i><sub>1</sub> = 5.0 Hz, <i>J</i><sub>2</sub> = 1.0 Hz, 1H), 7.47 (td, <i>J</i><sub>1</sub> = 8.0 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 6.96 (dd, <i>J</i><sub>1</sub> = 8.0 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 6.88 (ddd, <i>J</i><sub>1</sub> = 7.0 Hz, <i>J</i><sub>2</sub> = 5.0 Hz, <i>J</i><sub>3</sub> = 1.0 Hz, 1H), 6.76 (d, <i>J</i> = 2.0 Hz, 1H), 6.69 (d, <i>J</i> = 8.5 Hz, 1H), 6.57 (d, <i>J</i> = 8.0 Hz, 1H), 3.99 (s, 3H), 3.81 (s, 3H), 3.58 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 161.6, 160.5, 150.6, 148.8, 148.0, 137.7, 123.3, 122.7, 118.0, 116.3, 112.2, 110.2, 55.8, 55.6, 54.3; HRMS (ESI) <i>m/z</i>: calcd for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 273.1234; found 273.1282.</p>	 <p style="text-align: center;"><b>2fa</b></p>
<p>(<i>Z</i>)-ethyl 3,4-dimethoxy-<i>N</i>-(pyridin-2-yl)benzimidate (<b>2fb</b>): Brown oil, 56 mg, yield 98%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.33 (dd, <i>J</i><sub>1</sub> = 5.0, <i>J</i><sub>2</sub> = 1.0 Hz, 1H), 7.45 (td, <i>J</i><sub>1</sub> = 8.0 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 6.99 (dd, <i>J</i><sub>1</sub> = 8.0 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 6.86 (ddd, <i>J</i><sub>1</sub> = 7.5 Hz, <i>J</i><sub>2</sub> = 5.0 Hz, <i>J</i><sub>3</sub> = 1.0 Hz, 1H), 6.73 (d, <i>J</i> = 2.0 Hz, 1H), 6.69 (d, <i>J</i> = 8.5 Hz, 1H), 6.55 (d, <i>J</i> = 8.0 Hz, 1H), 4.43 (q, <i>J</i> = 7.0 Hz, 2H), 3.80 (s, 3H), 3.56 (s, 3H), 1.43 (t, <i>J</i> = 7.0 Hz, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 161.8, 160.1, 150.5, 148.8, 148.0, 137.7, 123.6, 122.7, 117.9, 116.3, 112.3, 110.2, 62.8, 55.8, 55.5, 14.3; HRMS (ESI) <i>m/z</i>: calcd for C<sub>16</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 287.1390; found 287.1434.</p>	 <p style="text-align: center;"><b>2fb</b></p>
<p>(<i>Z</i>)-propyl 3,4-dimethoxy-<i>N</i>-(pyridin-2-yl)benzimidate (<b>2fc</b>): Brown oil, 54 mg, yield 90%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 7/1 to 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.33 (ddd, <i>J</i><sub>1</sub> = 5.0 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, <i>J</i><sub>3</sub> = 1.0 Hz, 1H), 7.45 (ddd, <i>J</i><sub>1</sub> = 8.0 Hz, <i>J</i><sub>2</sub> = 7.5 Hz, <i>J</i><sub>3</sub> = 2.0 Hz, 1H), 7.00 (dd, <i>J</i><sub>1</sub> = 8.5 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 6.86 (ddd, <i>J</i><sub>1</sub> = 7.5 Hz, <i>J</i><sub>2</sub> = 5.0, <i>J</i><sub>3</sub> = 1.0 Hz, 1H), 6.73 (d, <i>J</i> = 2.0 Hz, 1H), 6.70 (d, <i>J</i> = 8.5 Hz, 1H), 6.55 (d, <i>J</i> = 8.0 Hz, 1H), 4.32 (t, <i>J</i> = 6.5 Hz, 2H), 3.80 (s, 3H), 3.56 (s, 3H), 1.88 – 1.80 (m, 2H), 1.04 (t, <i>J</i> = 7.5 Hz, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 161.8, 160.2, 150.5, 148.7, 147.9, 137.7, 123.7, 122.7, 117.9, 116.3, 112.3, 110.2, 68.6, 55.8, 55.5, 22.0, 10.7; HRMS (ESI) <i>m/z</i>: calcd for C<sub>17</sub>H<sub>21</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 301.1547; found 301.1440.</p>	 <p style="text-align: center;"><b>2fc</b></p>
<p>(<i>Z</i>)-methyl 4-chloro-<i>N</i>-(pyridin-2-yl)benzimidate (<b>2ga</b>):<sup>[S5]</sup> Brown oil, 48 mg, yield 98%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.31 (dd, <i>J</i><sub>1</sub> = 5.0</p>	 <p style="text-align: center;"><b>2ga</b></p>

<p>Hz, <math>J_2 = 1.0</math> Hz, 1H), 7.48 (td, <math>J_1 = 7.5</math> Hz, <math>J_2 = 2.0</math> Hz, 1H), 7.23 (d, <math>J = 8.5</math> Hz, 2H), 7.18 (d, <math>J = 8.5</math> Hz, 2H), 6.90 (dd, <math>J_1 = 7.0</math> Hz, <math>J_2 = 5.5</math> Hz, 1H), 6.58 (d, <math>J = 8.0</math> Hz, 1H), 4.00 (s, 3H); <math>^{13}\text{C}\{^1\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 160.8, 160.1, 148.9, 137.8, 136.4, 130.5, 129.6, 128.3, 118.4, 116.2, 54.5; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{13}\text{H}_{12}\text{ClN}_2\text{O}</math> <math>[\text{M}+\text{H}]^+</math> 247.0633 and 249.0603; found 247.0682 and 249.0635.</p>	
<p>(<i>Z</i>)-ethyl 4-chloro-<i>N</i>-(pyridin-2-yl)benzimidate (<b>2gb</b>): White oil, 48 mg, yield 92%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 7/1 to 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.31 (dd, <math>J_1 = 5.0</math> Hz, <math>J_2 = 1.0</math> Hz, 1H), 7.48 (td, <math>J_1 = 7.5</math> Hz, <math>J_2 = 2.0</math> Hz, 1H), 7.24 (d, <math>J = 8.5</math> Hz, 2H), 7.18 (d, <math>J = 8.5</math> Hz, 2H), 6.89 (ddd, <math>J_1 = 7.0</math> Hz, <math>J_2 = 5.0</math> Hz, <math>J_3 = 1.0</math> Hz, 1H), 6.57 (d, <math>J = 8.0</math> Hz, 1H), 4.45 (q, <math>J = 7.0</math> Hz, 2H), 1.43 (t, <math>J = 7.0</math> Hz, 3H); <math>^{13}\text{C}\{^1\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 160.9, 159.6, 148.9, 137.7, 136.3, 130.5, 129.9, 128.3, 118.3, 116.2, 63.1, 14.2; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{14}\text{H}_{14}\text{ClN}_2\text{O}</math> <math>[\text{M}+\text{H}]^+</math> 261.0790 and 263.0760; found 261.0843 and 263.0819.</p>	 <p style="text-align: center;"><b>2gb</b></p>
<p>(<i>Z</i>)-propyl 4-chloro-<i>N</i>-(pyridin-2-yl)benzimidate (<b>2gc</b>): Brown oil, 43 mg, yield 78%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 7/1 to 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.32 (d, <math>J = 5.0</math> Hz, 1H), 7.53 (td, <math>J_1 = 8.0</math> Hz, <math>J_2 = 2.0</math> Hz, 1H), 7.25 (d, <math>J = 8.5</math> Hz, 2H), 7.20 (d, <math>J = 8.5</math> Hz, 2H), 6.93 (dd, <math>J_1 = 7.0</math> Hz, <math>J_2 = 5.0</math> Hz, 1H), 6.60 (d, <math>J = 8.0</math> Hz, 1H), 4.36 (t, <math>J = 6.5</math> Hz, 2H), 1.89 – 1.81 (m, 2H), 1.06 (t, <math>J = 7.5</math> Hz, 3H); <math>^{13}\text{C}\{^1\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 160.6, 160.1, 148.3, 138.2, 136.5, 130.5, 129.8, 128.4, 118.4, 116.5, 69.1, 22.0, 10.7; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{15}\text{H}_{16}\text{ClN}_2\text{O}</math> <math>[\text{M}+\text{H}]^+</math> 275.0946; found 275.0952.</p>	 <p style="text-align: center;"><b>2gc</b></p>
<p>(<i>Z</i>)-methyl 4-bromo-<i>N</i>-(pyridin-2-yl)benzimidate (<b>2ha</b>): Yellow oil, 54 mg, yield 93%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 7/1 to 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.31 (dd, <math>J_1 = 5.0</math> Hz, <math>J_2 = 1.0</math> Hz, 1H), 7.51 (td, <math>J_1 = 8.0</math> Hz, <math>J_2 = 2.0</math> Hz, 1H), 7.35 (d, <math>J = 8.5</math> Hz, 2H), 7.16 (d, <math>J = 8.5</math> Hz, 2H), 6.92 (ddd, <math>J_1 = 7.0</math> Hz, <math>J_2 = 5.0</math> Hz, <math>J_3 = 1.0</math> Hz, 1H), 6.59 (d, <math>J = 8.0</math> Hz, 1H), 4.00 (s, 3H); <math>^{13}\text{C}\{^1\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 161.23, 159.82, 147.17, 139.17, 131.47, 130.71, 129.68, 125.32, 118.56, 116.87, 55.00; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{13}\text{H}_{12}\text{BrN}_2\text{O}</math> <math>[\text{M}+\text{H}]^+</math> 291.0128 and 293.0107; found 291.0186 and 293.0164.</p>	 <p style="text-align: center;"><b>2ha</b></p>
<p>(<i>Z</i>)-ethyl 4-bromo-<i>N</i>-(pyridin-2-yl)benzimidate (<b>2hb</b>): Brown oil, 58 mg, yield 96%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.30 (dd, <math>J_1 = 5.0</math> Hz, <math>J_2 = 1.0</math> Hz, 1H), 7.49 (ddd, <math>J_1 = 8.0</math> Hz, <math>J_2 = 7.5</math> Hz, <math>J_3 = 2.0</math> Hz, 1H), 7.34 (d, <math>J = 8.5</math> Hz, 2H), 7.17 (d, <math>J = 8.5</math> Hz, 2H), 6.89 (ddd, <math>J_1 = 7.0</math> Hz, <math>J_2 = 5.0</math> Hz, <math>J_3 = 1.0</math> Hz, 1H), 6.57 (d, <math>J = 8.0</math> Hz, 1H), 4.44 (q, <math>J = 7.0</math> Hz, 2H), 1.43 (t, <math>J = 7.0</math> Hz, 3H); <math>^{13}\text{C}\{^1\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 160.7, 159.9, 148.6, 137.9, 131.3, 130.7, 130.3, 124.8, 118.3, 116.3, 63.2, 14.2; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{14}\text{H}_{14}\text{BrN}_2\text{O}</math> <math>[\text{M}+\text{H}]^+</math> 305.0284 and 307.0264; found 305.0347 and 307.0328.</p>	 <p style="text-align: center;"><b>2hb</b></p>

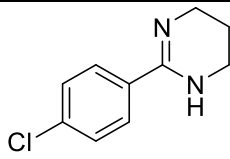
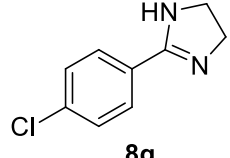
<p>(<i>Z</i>)-propyl 4-bromo-<i>N</i>-(pyridin-2-yl)benzimidate (<b>2hc</b>): Brown oil, 58 mg, yield 91%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 7/1 to 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.30 (dd, <i>J</i><sub>1</sub> = 5.0 Hz, <i>J</i><sub>2</sub> = 1.0 Hz, 1H), 7.49 (td, <i>J</i><sub>1</sub> = 8.0 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 7.34 (d, <i>J</i> = 8.5 Hz, 2H), 7.17 (d, <i>J</i> = 8.5 Hz, 2H), 6.89 (dd, <i>J</i><sub>1</sub> = 7.0 Hz, <i>J</i><sub>2</sub> = 5.0 Hz, 1H), 6.58 (d, <i>J</i> = 8.0 Hz, 1H), 4.34 (t, <i>J</i> = 6.5 Hz, 2H), 1.87 – 1.79 (m, 2H), 1.04 (t, <i>J</i> = 7.5 Hz, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 160.7, 160.0, 148.6, 137.9, 131.3, 130.7, 130.4, 124.8, 118.3, 116.3, 69.0, 22.0, 10.7; HRMS (ESI) <i>m/z</i>: calcd for C<sub>15</sub>H<sub>16</sub>BrN<sub>2</sub>O [M+H]<sup>+</sup> 319.0441 and 321.0420; found 319.0470 and 321.0488.</p>	 <p style="text-align: center;"><b>2hc</b></p>
<p>(<i>Z</i>)-methyl 4-(methoxy(pyridin-2-ylimino)methyl)benzoate (<b>2ja</b>): Yellow oil, 44 mg, yield 82%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 8/1 to 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.28 (d, <i>J</i> = 5.0 Hz, 1H), 7.86 (d, <i>J</i> = 8.0 Hz, 2H), 7.46 (t, <i>J</i> = 7.5 Hz, 1H), 7.34 (d, <i>J</i> = 8.0 Hz, 2H), 6.88 (t, <i>J</i> = 5.0 Hz, 1H), 6.57 (d, <i>J</i> = 8.0 Hz, 1H), 4.02 (s, 3H), 3.85 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 166.2, 160.52, 160.49, 148.7, 137.8, 135.4, 131.4, 129.2, 129.0, 118.6, 116.3, 54.6, 52.3; HRMS (ESI) <i>m/z</i>: calcd for C<sub>15</sub>H<sub>15</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 271.1077; found 271.1079.</p>	 <p style="text-align: center;"><b>2ja</b></p>
<p>(<i>Z</i>)-ethyl 4-(ethoxy(pyridin-2-ylimino)methyl)benzoate (<b>2jb</b>): Yellow oil, 51 mg, yield 86%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 7/1 to 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.29 (d, <i>J</i> = 5.0 Hz, 1H), 7.88 (d, <i>J</i> = 8.0 Hz, 2H), 7.47 (td, <i>J</i><sub>1</sub> = 7.5 Hz, <i>J</i><sub>2</sub> = 1.0 Hz, 1H), 7.36 (d, <i>J</i> = 8.0 Hz, 2H), 6.89 (dd, <i>J</i><sub>1</sub> = 7.0 Hz, <i>J</i><sub>2</sub> = 5.0 Hz, 1H), 6.57 (d, <i>J</i> = 8.0 Hz, 1H), 4.48 (q, <i>J</i> = 7.0 Hz, 2H), 4.33 (q, <i>J</i> = 7.0 Hz, 2H), 1.45 (t, <i>J</i> = 7.0 Hz, 3H), 1.35 (t, <i>J</i> = 7.0 Hz, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 165.8, 160.6, 160.2, 148.6, 137.9, 135.6, 131.7, 129.2, 129.0, 118.4, 116.4, 63.3, 61.2, 14.24, 14.21; HRMS (ESI) <i>m/z</i>: calcd for C<sub>17</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 299.1390; found 299.1392.</p>	 <p style="text-align: center;"><b>2jb</b></p>
<p>(<i>Z</i>)-propyl 4-(propoxy(pyridin-2-ylimino)methyl)benzoate (<b>2jc</b>): Brown oil, 63 mg, yield 96%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.28 (dd, <i>J</i><sub>1</sub> = 5.0 Hz, <i>J</i><sub>2</sub> = 1.0 Hz, 1H), 7.88 (d, <i>J</i> = 8.0 Hz, 2H), 7.46 (td, <i>J</i><sub>1</sub> = 7.5 Hz, <i>J</i><sub>2</sub> = 1.0 Hz, 1H), 7.35 (d, <i>J</i> = 8.0 Hz, 2H), 6.88 (dd, <i>J</i><sub>1</sub> = 7.0 Hz, <i>J</i><sub>2</sub> = 5.0 Hz, 1H), 6.57 (d, <i>J</i> = 8.0 Hz, 1H), 4.36 (t, <i>J</i> = 6.5 Hz, 2H), 4.22 (t, <i>J</i> = 6.5 Hz, 2H), 1.88 – 1.80 (m, 2H), 1.77 – 1.69 (m, 2H), 1.04 (t, <i>J</i> = 7.5 Hz, 3H), 0.97 (t, <i>J</i> = 7.5 Hz, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 165.8, 160.7, 160.3, 148.7, 137.8, 135.7, 131.7, 129.1, 129.0, 118.4, 116.3, 69.0, 66.8, 22.00, 21.97, 10.7, 10.5; HRMS (ESI) <i>m/z</i>: calcd for C<sub>19</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup> 327.1703; found 327.1704.</p>	 <p style="text-align: center;"><b>2jc</b></p>
<p>(<i>Z</i>)-methyl <i>N</i>-pyridin-2-yl-1-naphthimide (<b>2ka</b>): Brown oil, 50 mg, yield 96%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.21 (d, <i>J</i> = 4.0 Hz, 1H), 7.94 (d, <i>J</i> = 8.5 Hz, 1H), 7.76 (dd, <i>J</i><sub>1</sub> = 8.0 Hz, <i>J</i><sub>2</sub> = 5.0 Hz, 2H), 7.51 (t, <i>J</i> = 7.5 Hz, 1H), 7.45 (t, <i>J</i> = 7.5 Hz, 1H), 7.37 (d, <i>J</i> = 7.0 Hz, 1H), 7.29 (t, <i>J</i> = 7.5 Hz,</p>	 <p style="text-align: center;"><b>2ka</b></p>

<p>1H), 7.22 – 7.18 (m, 1H), 6.70 (t, <math>J = 6.0</math> Hz, 1H), 6.42 (d, <math>J = 8.0</math> Hz, 1H), 4.17 (s, 3H); <math>^{13}\text{C}\{\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 163.5, 160.4, 148.3, 137.3, 133.1, 130.4, 130.2, 129.8, 128.2, 127.1, 126.8, 126.2, 125.4, 124.6, 118.4, 116.0, 54.5; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{17}\text{H}_{15}\text{N}_2\text{O}</math> <math>[\text{M}+\text{H}]^+</math> 263.1179; found 263.1186.</p>	
<p>(<i>Z</i>)-ethyl <i>N</i>-pyridin-2-yl-1-naphthimide (<b>2kb</b>): Brown oil, 52 mg, yield 95%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.20 (d shown as s, 1H), 7.98 (d, <math>J = 8.5</math> Hz, 1H), 7.76 (t, <math>J = 8.0</math> Hz, 2H), 7.51 (t, <math>J = 7.5</math> Hz, 1H), 7.45 (t, <math>J = 7.5</math> Hz, 1H), 7.38 (d, <math>J = 7.0</math> Hz, 1H), 7.29 (t, <math>J = 7.5</math> Hz, 1H), 7.18 (d, <math>J = 6.5</math> Hz, 1H), 6.69 (d shown as s, 1H), 6.41 (d, <math>J = 6.5</math> Hz, 1H), 4.66 (d, <math>J = 6.5</math> Hz, 2H), 1.50 (t, <math>J = 7.0</math> Hz, 3H); <math>^{13}\text{C}\{\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 162.9, 160.6, 148.3, 137.3, 133.2, 130.6, 130.2, 129.7, 128.2, 127.1, 126.8, 126.1, 125.3, 124.7, 118.3, 116.0, 63.2, 14.3; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}</math> <math>[\text{M}+\text{H}]^+</math> 277.1335; found 277.1342.</p>	 <p style="text-align: center;"><b>2kb</b></p>
<p>(<i>Z</i>)-propyl <i>N</i>-pyridin-2-yl-1-naphthimide (<b>2kc</b>): Brown oil, 51 mg, yield 89%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 7/1 to 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.20 (dd, <math>J_1 = 5.0</math> Hz, <math>J_2 = 1.0</math> Hz, 1H), 7.98 (d, <math>J = 8.5</math> Hz, 1H), 7.76 (t, <math>J = 8.0</math> Hz, 2H), 7.51 (t, <math>J = 7.5</math> Hz, 1H), 7.45 (t, <math>J = 7.5</math> Hz, 1H), 7.38 (dd, <math>J_1 = 7.0</math>, <math>J_2 = 1.0</math> Hz, 1H), 7.29 (dd, <math>J_1 = 8.0</math> Hz, <math>J_2 = 7.5</math> Hz, 1H), 7.19 (td, <math>J_1 = 8.0</math> Hz, <math>J_2 = 2.0</math> Hz, 1H), 6.69 (ddd, <math>J_1 = 7.0</math> Hz, <math>J_2 = 5.0</math> Hz, <math>J_3 = 1.0</math> Hz, 1H), 6.41 (d, <math>J = 8.0</math> Hz, 1H), 4.55 (t, <math>J = 6.5</math> Hz, 2H), 1.93 – 1.85 (m, 2H), 1.07 (t, <math>J = 7.5</math> Hz, 3H); <math>^{13}\text{C}\{\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 163.2, 160.6, 148.3, 137.2, 133.2, 130.7, 130.3, 129.7, 128.2, 127.1, 126.7, 126.1, 125.4, 124.7, 118.2, 116.0, 69.0, 22.0, 10.7; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}</math> <math>[\text{M}+\text{H}]^+</math> 291.1492; found 291.1502.</p>	 <p style="text-align: center;"><b>2kc</b></p>
<p>(<i>Z</i>)-methyl <i>N</i>-pyridin-2-ylthiophene-2-carbimide (<b>2la</b>): Brown oil, 37 mg, yield 85%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 7/1 to 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.42 (dd, <math>J_1 = 5.0</math> Hz, <math>J_2 = 1.5</math> Hz, 1H), 7.63 (td, <math>J_1 = 7.5</math> Hz, <math>J_2 = 2.0</math> Hz, 1H), 7.32 (d, <math>J = 5.0</math> Hz, 1H), 7.03 (dd, <math>J_1 = 7.5</math> Hz, <math>J_2 = 5.0</math> Hz, 1H), 6.86 – 6.83 (m, 1H), 6.82 – 6.79 (m, 2H), 3.99 (s, 3H); <math>^{13}\text{C}\{\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 160.8, 154.2, 149.1, 138.2, 131.7, 131.6, 129.8, 126.9, 118.9, 116.1, 54.3; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{11}\text{H}_{11}\text{N}_2\text{OS}</math> <math>[\text{M}+\text{H}]^+</math> 219.0587; found 219.0592.</p>	 <p style="text-align: center;"><b>2la</b></p>
<p>(<i>Z</i>)-ethyl <i>N</i>-pyridin-2-ylthiophene-2-carbimide (<b>2lb</b>): Brown oil, 44 mg, yield 95%; Purified by flash column chromatography (<math>\text{SiO}_2</math>, elution system Hexane/EtOAc 2/1); <math>^1\text{H}</math> NMR (500 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 8.41 (ddd, <math>J_1 = 5.0</math> Hz, <math>J_2 = 1.5</math> Hz, <math>J_3 = 1.0</math> Hz, 1H), 7.61 (ddd, <math>J_1 = 8.0</math> Hz, <math>J_2 = 7.5</math> Hz, <math>J_3 = 2.0</math> Hz, 1H), 7.30 (dd, <math>J_1 = 5.0</math> Hz, <math>J_2 = 1.0</math> Hz, 1H), 7.00 (ddd, <math>J_1 = 7.5</math> Hz, <math>J_2 = 5.0</math> Hz, <math>J_3 = 1.0</math> Hz, 1H), 6.84 – 6.81 (m, 2H), 6.79 – 6.77 (m, 1H), 4.43 (q, <math>J = 7.0</math> Hz, 2H), 1.43 (t, <math>J = 7.0</math> Hz, 3H); <math>^{13}\text{C}\{\text{H}\}</math> NMR (125 MHz, <math>\text{CDCl}_3</math>) <math>\delta</math> 160.9, 153.7, 149.1, 138.1, 132.0, 131.6, 129.7, 126.9, 118.7, 116.0, 62.8, 14.2; HRMS (ESI) <math>m/z</math>: calcd for <math>\text{C}_{12}\text{H}_{13}\text{N}_2\text{OS}</math> <math>[\text{M}+\text{H}]^+</math> 233.0743; found 233.0753.</p>	 <p style="text-align: center;"><b>2lb</b></p>

<p>(<i>Z</i>)-propyl <i>N</i>-pyridin-2-ylthiophene-2-carbimide (<b>2lc</b>): Brown oil, 48 mg, yield 98%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.41 (dd, <i>J</i><sub>1</sub> = 5.0 Hz, <i>J</i><sub>2</sub> = 1.0 Hz, 1H), 7.61 (td, <i>J</i><sub>1</sub> = 7.5 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 7.30 (dd, <i>J</i><sub>1</sub> = 5.0, <i>J</i><sub>2</sub> = 1.0 Hz, 1H), 7.01 (dd, <i>J</i><sub>1</sub> = 7.0 Hz, <i>J</i><sub>2</sub> = 5.5 Hz, 1H), 6.85 – 6.82 (m, 1H), 6.81 – 6.77 (m, 2H), 4.33 (t, <i>J</i> = 6.5 Hz, 2H), 1.88 – 1.80 (m, 2H), 1.06 (t, <i>J</i> = 7.5 Hz, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 160.9, 153.8, 149.1, 138.1, 132.1, 131.5, 129.7, 126.9, 118.7, 116.1, 68.6, 22.0, 10.7; HRMS (ESI) <i>m/z</i>: calcd for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>OS [M+H]<sup>+</sup> 247.0900; found 247.0688.</p>	 <p style="text-align: center;"><b>2lc</b></p>
<p>(<i>Z</i>)-methyl 4-methyl-<i>N</i>-(3-methylpyridin-2-yl)benzimidate (<b>2ma</b>): Brown oil, 16 mg, yield 33%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 8/1 to 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.14 (d, <i>J</i> = 5.0 Hz, 1H), 7.36 (d, <i>J</i> = 7.5 Hz, 1H), 7.18 (d, <i>J</i> = 8.0 Hz, 2H), 6.99 (d, <i>J</i> = 8.0 Hz, 2H), 6.83 (dd, <i>J</i><sub>1</sub> = 7.5 Hz, <i>J</i><sub>2</sub> = 5.0 Hz, 1H), 4.02 (s, 3H), 2.26 (s, 3H), 2.02 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 159.9, 159.8, 146.1, 140.6, 138.4, 128.8, 128.7, 128.5, 123.7, 118.4, 54.2, 21.4, 17.6; HRMS (ESI) <i>m/z</i>: calcd for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 241.1335; found 241.1338.</p>	 <p style="text-align: center;"><b>2ma</b></p>
<p>(<i>Z</i>)-methyl 4-methyl-<i>N</i>-(4-methylpyridin-2-yl)benzimidate (<b>2na</b>): Brown oil, 47 mg, yield 98%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.15 (d, <i>J</i> = 5.0 Hz, 1H), 7.19 (d, <i>J</i> = 8.0 Hz, 2H), 6.99 (d, <i>J</i> = 8.0 Hz, 2H), 6.69 (dd, <i>J</i><sub>1</sub> = 5.0 Hz, <i>J</i><sub>2</sub> = 0.5 Hz, 1H), 6.41 (s, 1H), 3.96 (s, 3H), 2.25 (s, 3H), 2.17 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 161.2, 160.8, 148.8, 148.3, 140.5, 129.1, 128.6, 128.3, 119.4, 116.6, 54.2, 21.3, 20.9; HRMS (ESI) <i>m/z</i>: calcd for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 241.1335; found 241.1339.</p>	 <p style="text-align: center;"><b>2na</b></p>
<p>(<i>Z</i>)-methyl 4-methyl-<i>N</i>-(5-methylpyridin-2-yl)benzimidate (<b>2oa</b>): Brown oil, 44 mg, yield 92%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.14 (s, 1H), 7.25 (dd, <i>J</i><sub>1</sub> = 8.0 Hz, <i>J</i><sub>2</sub> = 2.0 Hz, 1H), 7.17 (d, <i>J</i> = 8.0 Hz, 2H), 6.99 (d, <i>J</i> = 8.0 Hz, 2H), 6.44 (d, <i>J</i> = 8.0 Hz, 1H), 3.97 (s, 3H), 2.25 (s, 3H), 2.20 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 161.3, 158.9, 148.5, 140.4, 138.5, 129.1, 128.7, 128.4, 127.2, 115.7, 54.2, 21.3, 17.7; HRMS (ESI) <i>m/z</i>: calcd for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 241.1335; found 241.1339.</p>	 <p style="text-align: center;"><b>2oa</b></p>
<p>(<i>Z</i>)-methyl 4-methyl-<i>N</i>-(6-methylpyridin-2-yl)benzimidate (<b>2pa</b>): Yellow oil, 34 mg, yield 71%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 7/1 to 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.32 (t, <i>J</i> = 7.5 Hz, 1H), 7.19 (d, <i>J</i> = 8.0 Hz, 2H), 7.01 (d, <i>J</i> = 8.0 Hz, 2H), 6.75 (d, <i>J</i> = 7.5 Hz, 1H), 6.26 (d, <i>J</i> = 8.0 Hz, 1H), 4.00 (s, 3H), 2.49 (s, 3H), 2.27 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 161.3, 160.6, 157.5, 140.6, 138.1, 129.1, 128.7, 128.2, 117.4, 113.0, 54.4, 24.3, 21.4; HRMS (ESI) <i>m/z</i>: calcd for C<sub>15</sub>H<sub>17</sub>N<sub>2</sub>O [M+H]<sup>+</sup> 241.1335; found 241.1339.</p>	 <p style="text-align: center;"><b>2pa</b></p>

<p>(<i>Z</i>)-methyl <i>N</i>-(3-chloropyridin-2-yl)-4-methylbenzimidate (<b>2qa</b>): Light yellow oil, 23 mg, yield 44%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 8/1 to 1/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.20 (d, <i>J</i> = 5.0 Hz, 1H), 7.57 (d, <i>J</i> = 8.0 Hz, 1H), 7.23 (d, <i>J</i> = 8.0 Hz, 2H), 7.02 (d, <i>J</i> = 8.0 Hz, 2H), 6.86 (dd, <i>J</i><sub>1</sub> = 8.0 Hz, <i>J</i><sub>2</sub> = 5.0 Hz, 1H), 4.05 (s, 3H), 2.28 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 162.1, 158.0, 146.7, 140.9, 137.9, 128.8, 128.7, 128.5, 122.5, 119.0, 54.7, 21.4; HRMS (ESI) <i>m/z</i>: calcd for C<sub>14</sub>H<sub>14</sub>ClN<sub>2</sub>O [M+H]<sup>+</sup> 261.0789; found 261.0787.</p>	 <p style="text-align: center;"><b>2qa</b></p>
<p>(<i>Z</i>)-methyl <i>N</i>-(5-chloropyridin-2-yl)-4-methylbenzimidate (<b>2ra</b>): Brown oil, 46 mg, yield 89%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 7/1 to 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.27 (s, 1H), 7.41 (dd, <i>J</i><sub>1</sub> = 8.5 Hz, <i>J</i><sub>2</sub> = 1.5 Hz, 1H), 7.16 (d, <i>J</i> = 8.0 Hz, 2H), 7.02 (d, <i>J</i> = 8.0 Hz, 2H), 6.50 (d, <i>J</i> = 8.5 Hz, 1H), 3.98 (s, 3H), 2.27 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 162.0, 159.7, 147.2, 140.1, 137.5, 129.0, 128.9, 127.9, 125.7, 117.2, 54.5, 21.4; HRMS (ESI) <i>m/z</i>: calcd for C<sub>14</sub>H<sub>14</sub>ClN<sub>2</sub>O [M+H]<sup>+</sup> 261.0789; found 261.0792.</p>	 <p style="text-align: center;"><b>2ra</b></p>
<p>(<i>Z</i>)-methyl <i>N</i>-(5-bromopyridin-2-yl)-4-methylbenzimidate (<b>2sa</b>): Brown oil, 60 mg, yield 98%; Purified by flash column chromatography (SiO<sub>2</sub>, elution system Hexane/EtOAc 2/1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.36 (s, 1H), 7.53 (dd, <i>J</i><sub>1</sub> = 8.5 Hz, <i>J</i><sub>2</sub> = 2.5 Hz, 1H), 7.17 (d, <i>J</i> = 7.5 Hz, 2H), 7.03 (d, <i>J</i> = 7.5 Hz, 2H), 6.45 (dd, <i>J</i><sub>1</sub> = 8.5, <i>J</i><sub>2</sub> = 1.0 Hz, 1H), 3.98 (s, 3H), 2.28 (s, 3H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 161.9, 160.1, 149.6, 140.9, 140.1, 129.1, 128.9, 127.9, 117.8, 113.8, 54.5, 21.4; HRMS (ESI) <i>m/z</i>: calcd for C<sub>14</sub>H<sub>14</sub>BrN<sub>2</sub>O [M+H]<sup>+</sup> 305.0284 and 307.0264; found 305.0438 and 307.0445.</p>	 <p style="text-align: center;"><b>2sa</b></p>

**<sup>1</sup>H and <sup>13</sup>C{H} NMR data for *N,N*-heterocycles 7g, 8g**

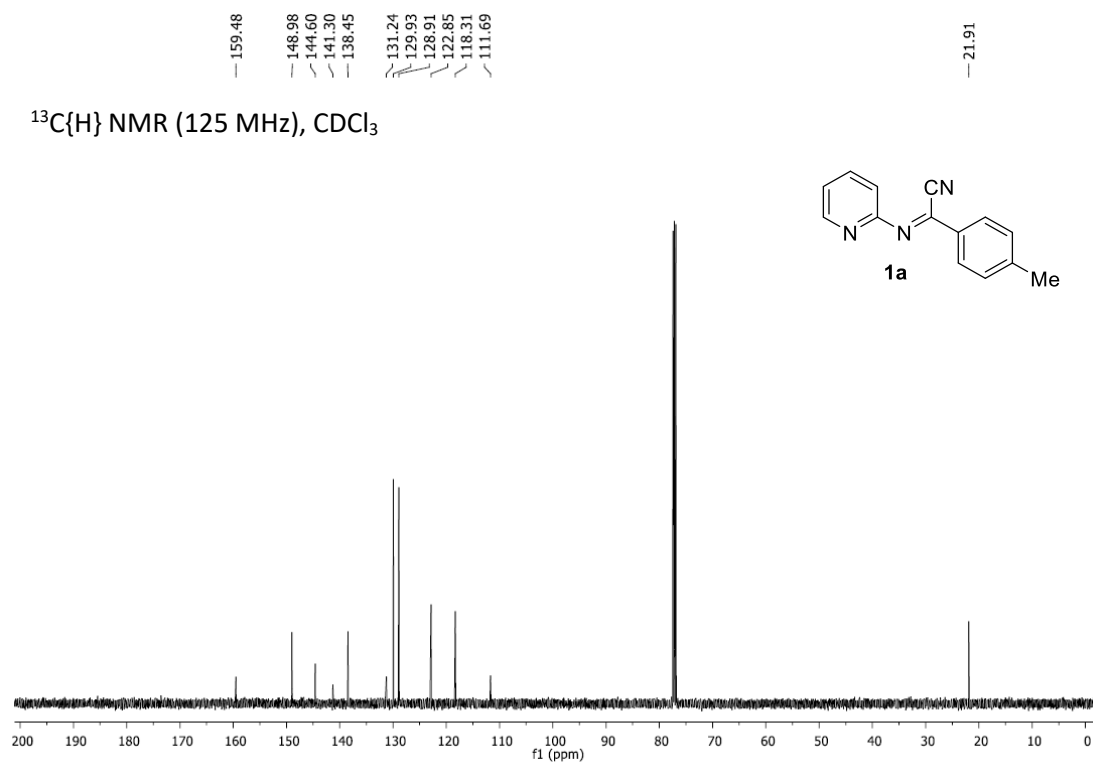
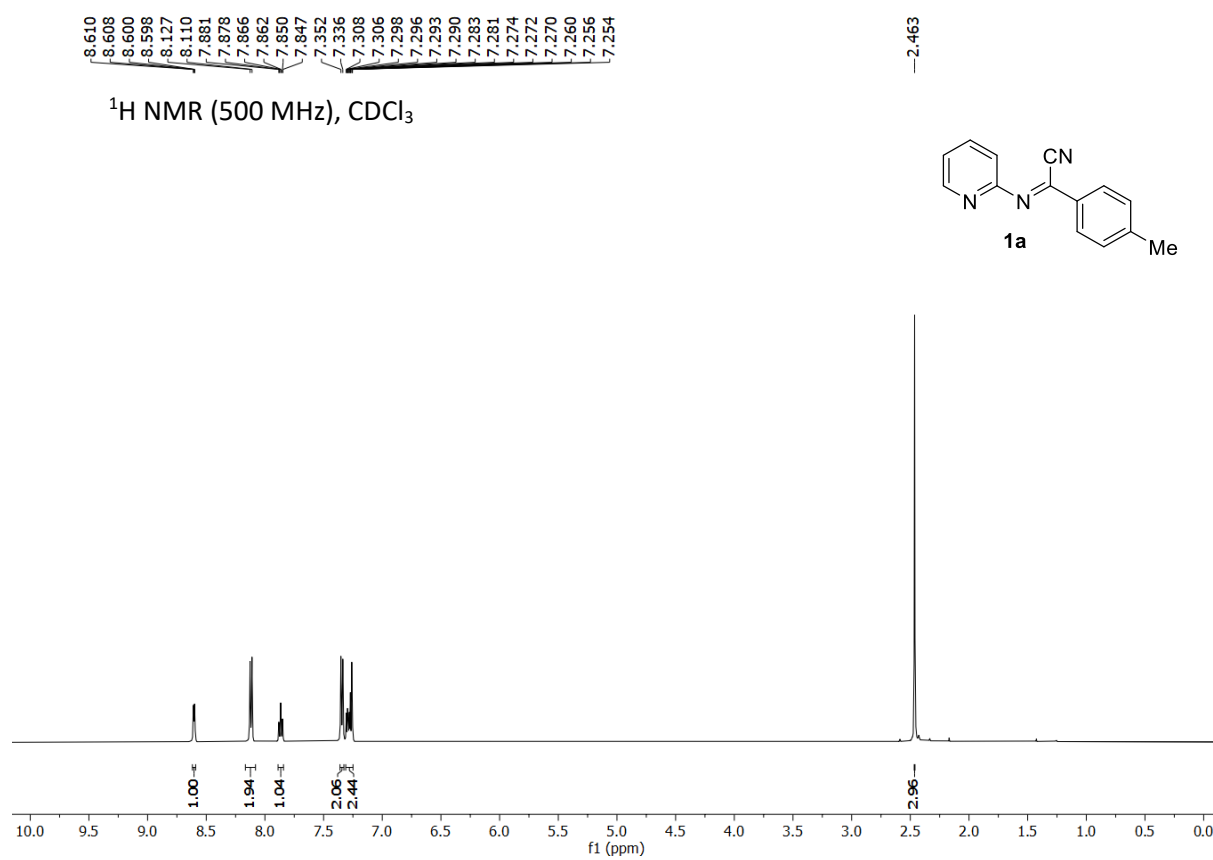
<p>2-(4-chlorophenyl)-1,4,5,6-tetrahydropyrimidine (<b>7g</b>):<sup>[S6]</sup> White solid, 13 mg, yield 35%; mp (144-145 °C); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.61 (d, <i>J</i> = 8.5 Hz, 2H), 7.31 (d, <i>J</i> = 8.5 Hz, 2H), 5.05 (brs, 1H), 3.46 (t, <i>J</i> = 5.5 Hz 4H), 1.86 (quin, <i>J</i> = 5.5 Hz, 2H); <sup>13</sup>C{H} NMR (125 MHz, CDCl<sub>3</sub>) δ 155.0, 136.6, 133.8, 128.7, 128.0, 41.7, 20.2.</p>	 <p style="text-align: center;"><b>7g</b></p>
<p>2-(4-chlorophenyl)-4,5-dihydro-1H-imidazole (<b>8g</b>):<sup>[S7]</sup> White solid, 20 mg, yield 55%; mp (186-187 °C); <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>OD) δ 7.76 (d, <i>J</i> = 8.5 Hz, 2H), 7.45 (d, <i>J</i> = 8.5 Hz, 2H), 3.76 (s, 4H); <sup>13</sup>C{H} NMR (125 MHz, CD<sub>3</sub>OD): δ 172.1, 144.4, 138.8, 138.3, 137.7, 59.1.</p>	 <p style="text-align: center;"><b>8g</b></p>

The spectroscopic data are in agreement with the literature reported data in ref [S6 and S7]

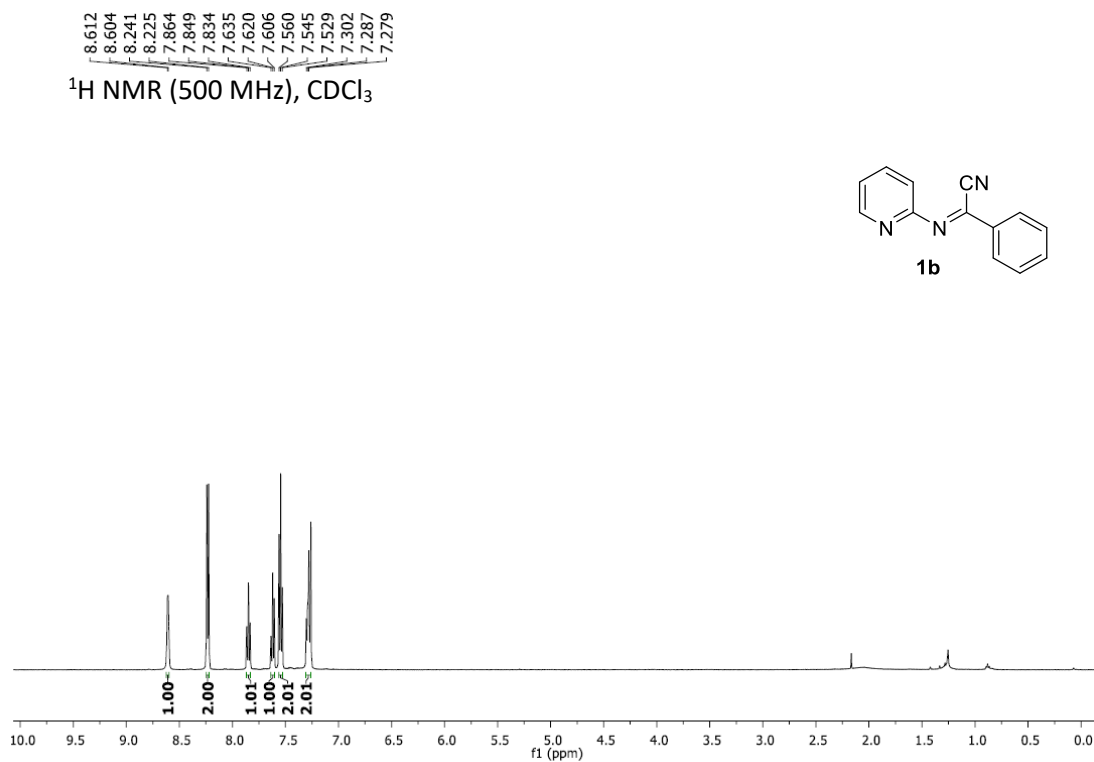


## References

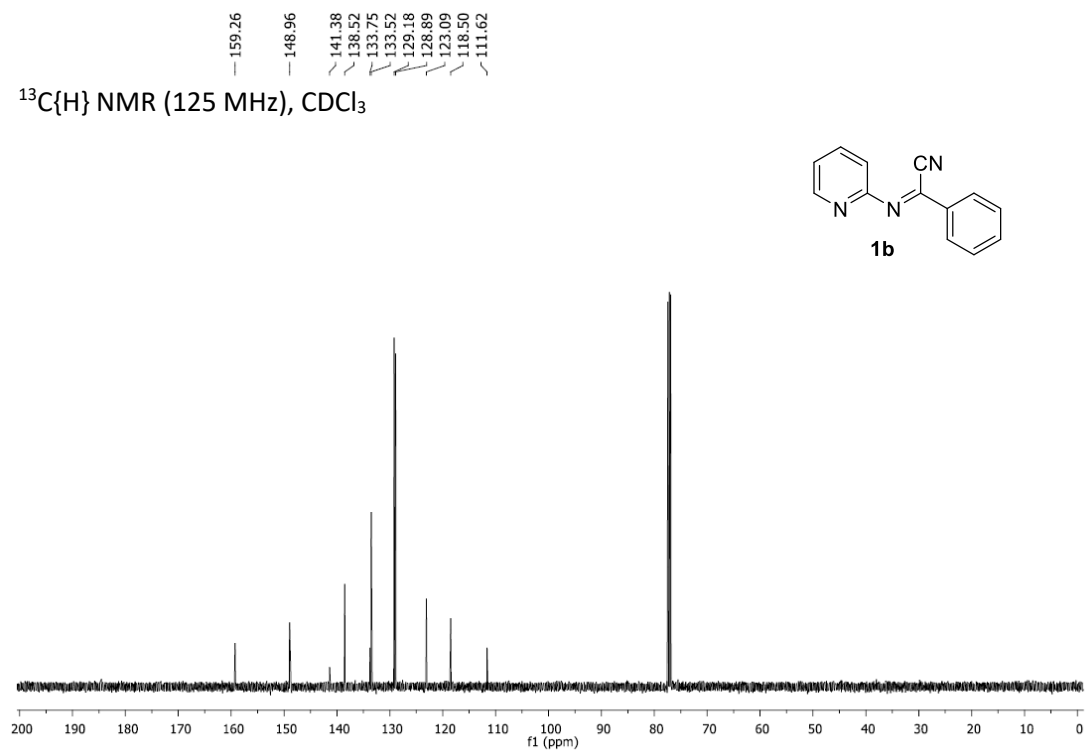
- S1. Wang, R.; Wang, S.; Li, D.; Ye, F.; Leng, Y.; Wu, Y.; Chang, J.; Wu, Y. Radical Ring Opening Reaction of Pyridine Fused Heterocycles with IBA-N<sub>3</sub> Catalyzed by Tetra-n-Butylammonium Iodide. *Tetrahedron* **2019**, 75, 2298–2305. <https://doi.org/10.1016/j.tet.2019.02.061>
- S2. Chen, Z.; Liang, P.; Zheng, J.; Zhou, Z.; Wen, X.; Liu, T.; Ye, M. Cyanide-Free Ce(III)-Catalyzed Highly Efficient Synthesis of  $\alpha$ -Iminonitriles from 2-Aminopyridines and Nitroalkenes via Intermolecular Dehydration Reaction. *ACS Omega* **2018**, 3, 12520–12529. <https://doi.org/10.1021/acsomega.8b02214>
- S3. Kalbandhe, A.H.; Kavale, A.C.; Karade, N.N. Ring-Opening Reaction of Imidazo[1,2-a]Pyridines Using (Diacetoxyiodo)Benzene and NaN<sub>3</sub>: The Synthesis of  $\alpha$ -Iminonitriles. *Eur. J. Org. Chem.* **2017**, 2017, 1318–1322. <https://doi.org/10.1002/ejoc.201601480>
- S4. Birch, D.J.; Guildford, A.J.; Tometzki, M.A.; Turner, R.W. Reaction of 3-Nitroso-2-Phenylimidazo[1,2-a]Pyridine with Triethyl Phosphite. A Revised Structure for the Product. *J. Org. Chem.* **1982**, 47, 3547–3548. <https://doi.org/10.1021/jo00139a034>
- S5. Wang, G.; Wei, C.; Hong, X.; Fu, Z.; Huang, W. Sodium Pyruvate as a Peroxide Scavenger in Aerobic Oxidation under Carbene Catalysis. *Green Chem.* **2020**, 22, 6819–6826. <https://doi.org/10.1039/d0gc02555k>
- S6. Nenajdenko G.V.; Muzalevskiy M.V.; Shastin A.V.; Balenkova S.E.; Kondrashov E.V.; Ushakov I.A.; Rulev A.Y. Fragmentation of Trifluoromethylated Alkenes and Acetylenes by N,N-Binucleophiles. Synthesis of Imidazolines or Imidazolidines (Oxazolidines) Controlled by Substituent. *J. Org. Chem.* **2010**, 5679–5688 <https://doi.org/10.1021/jo101107t>
- S7. Hegedus A.; Vigh I.; Hell Z. Zeolite-catalyzed simple synthesis of different heterocyclic rings part 2, *Heteroat. Chem.* **2004**, 15, 428 <https://doi.org/10.1002/hc.20036>

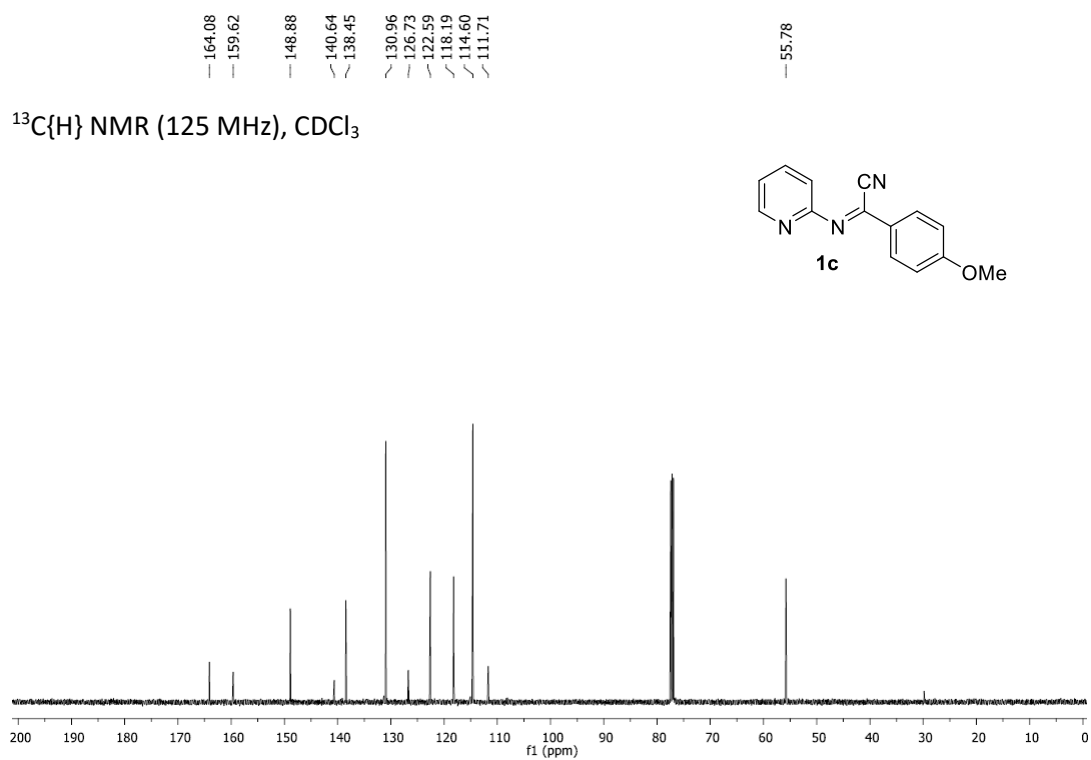
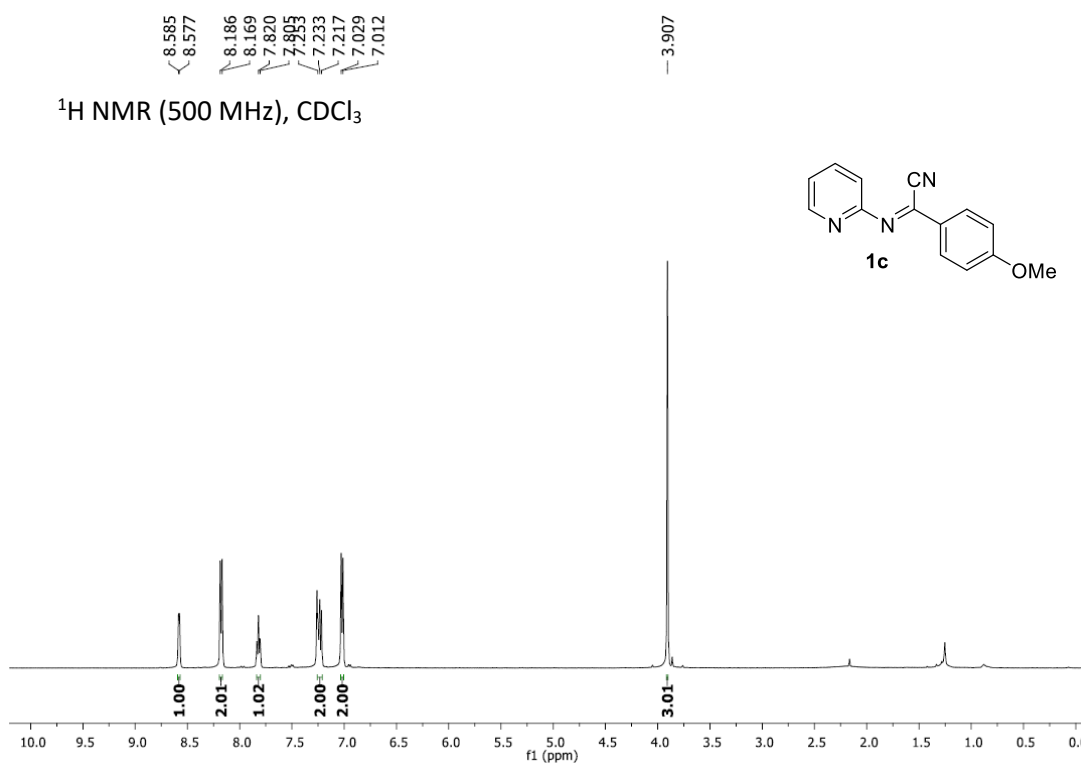
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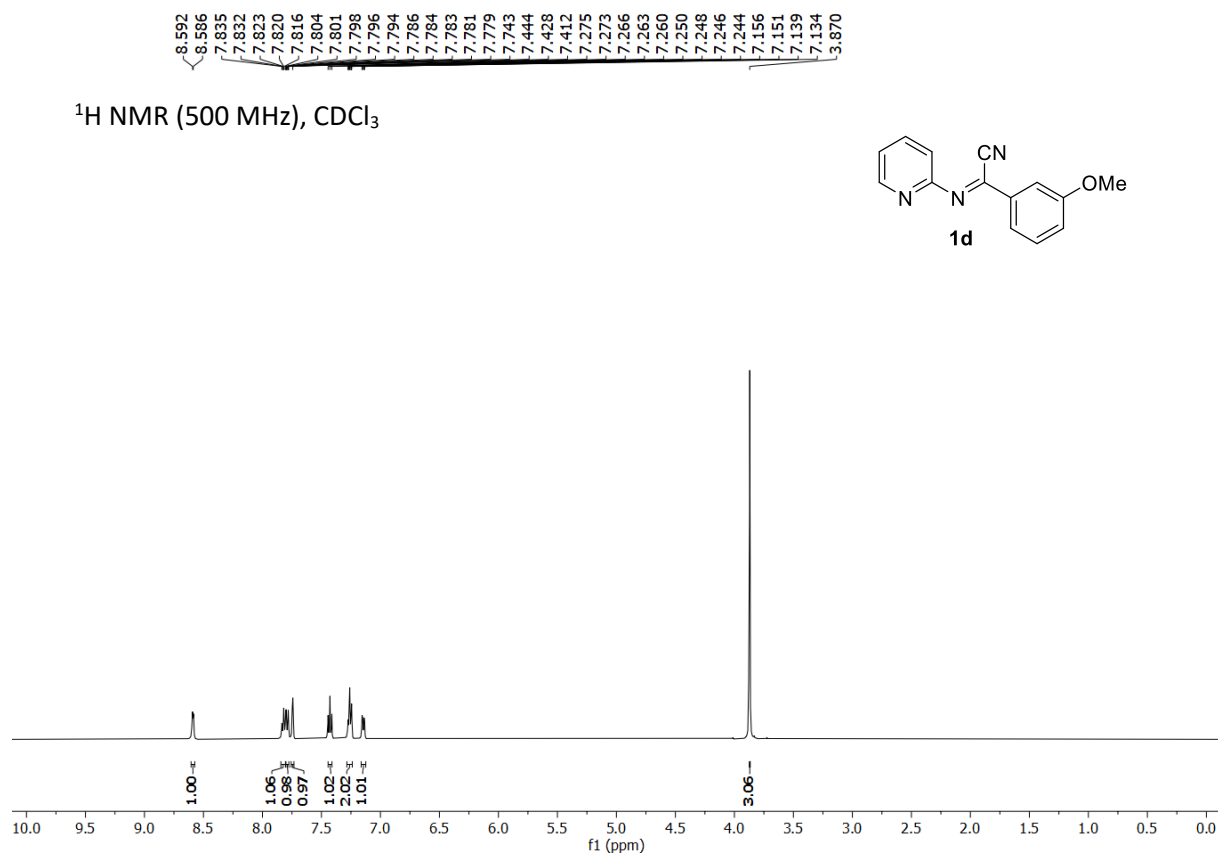
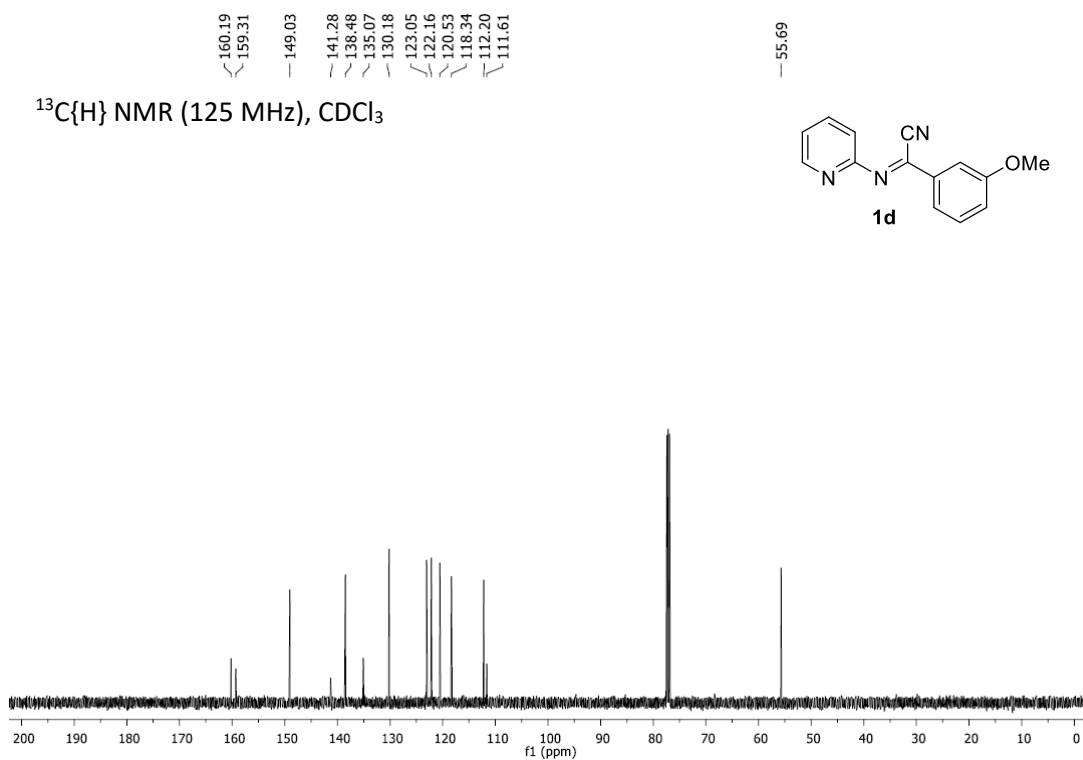
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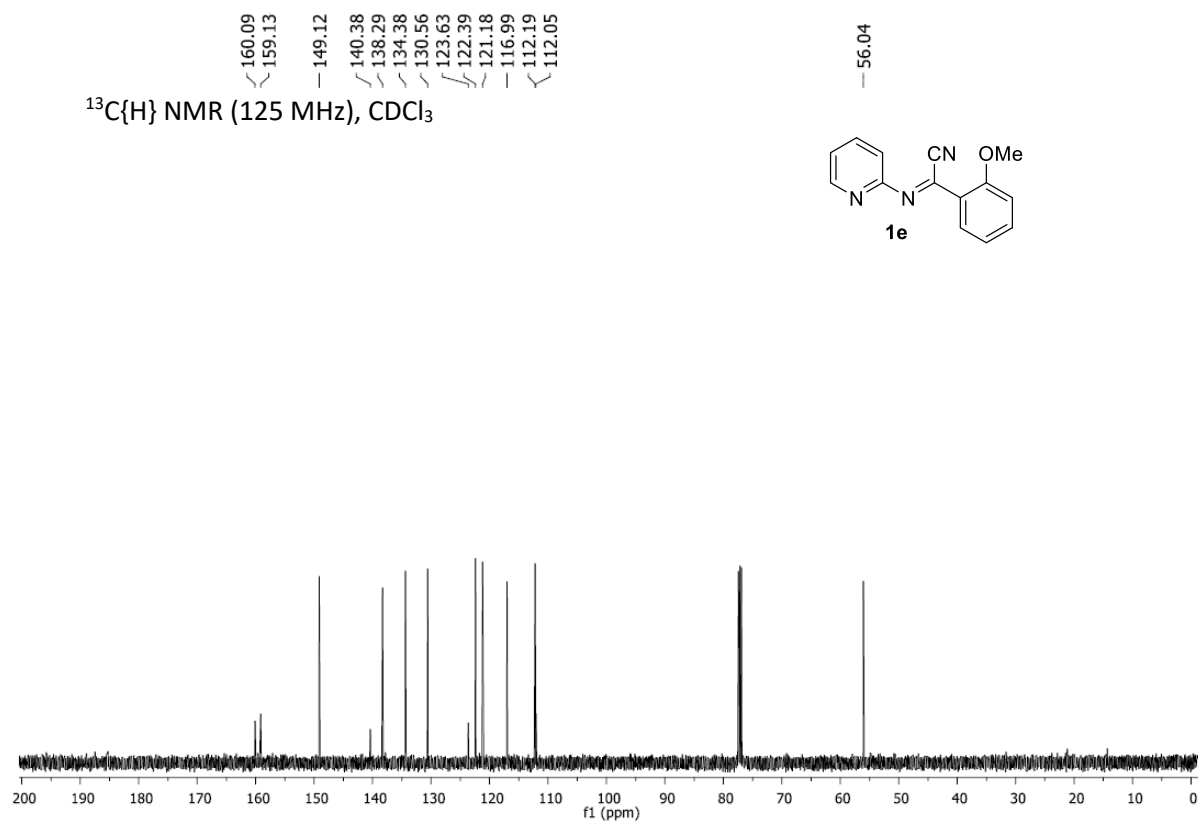
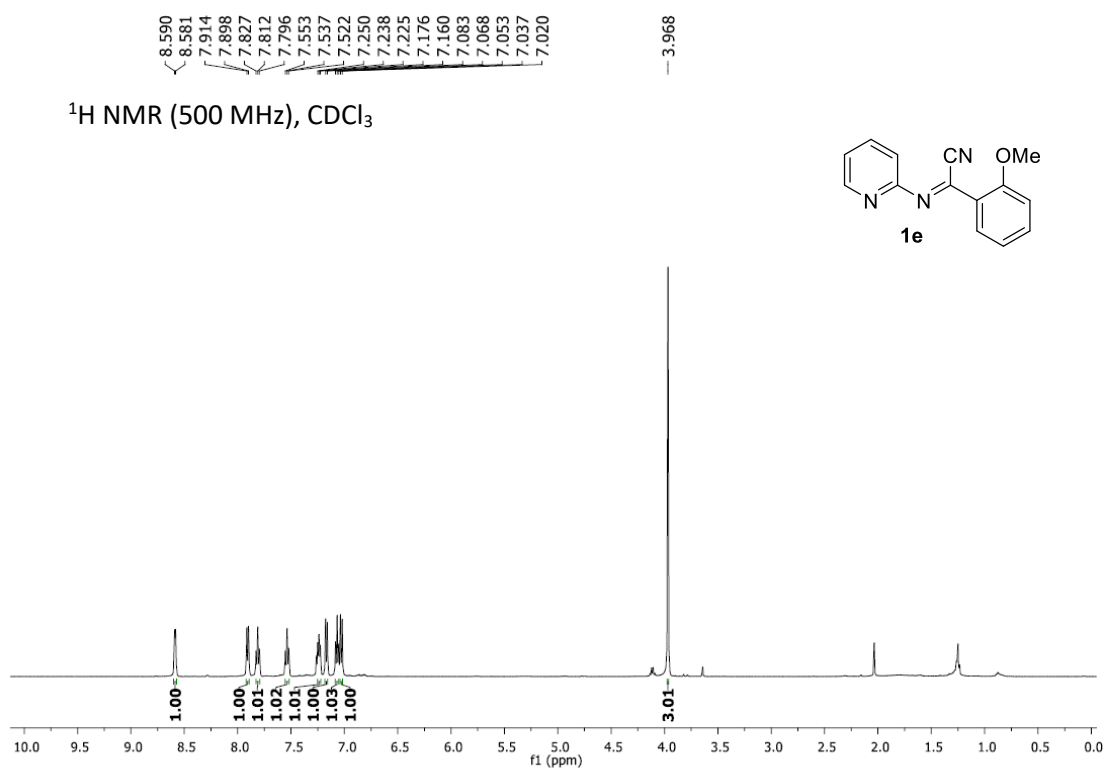


<sup>13</sup>C{H} NMR (125 MHz), CDCl<sub>3</sub>

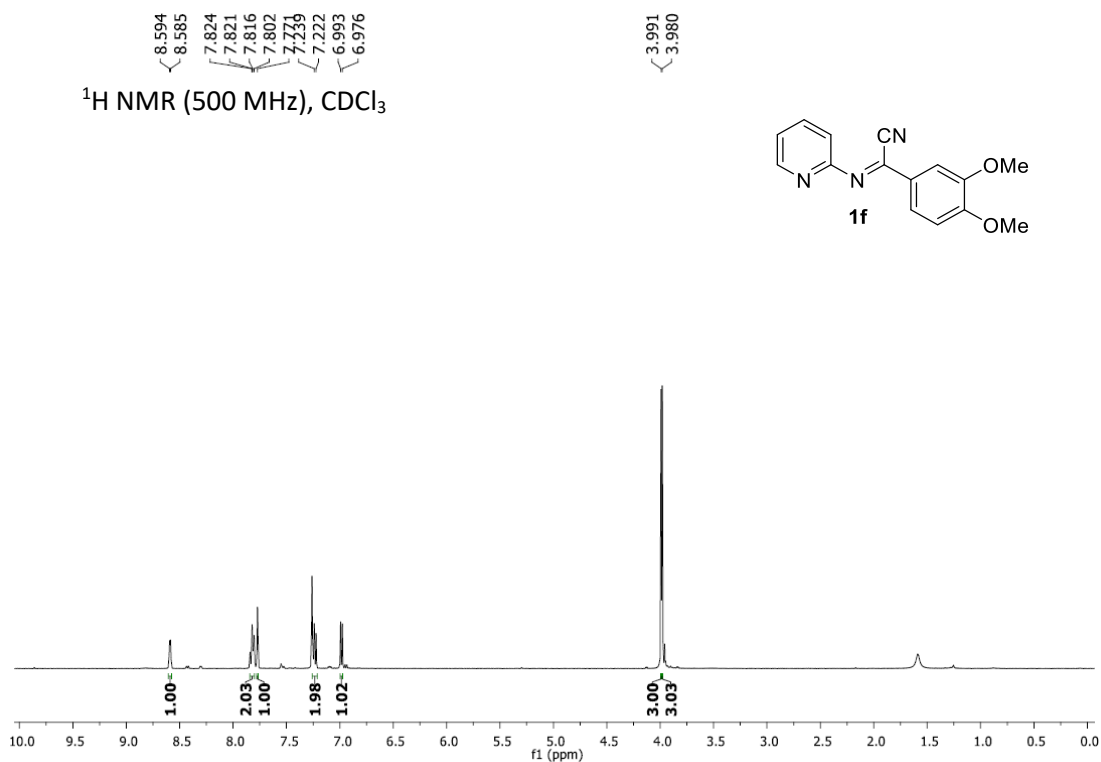




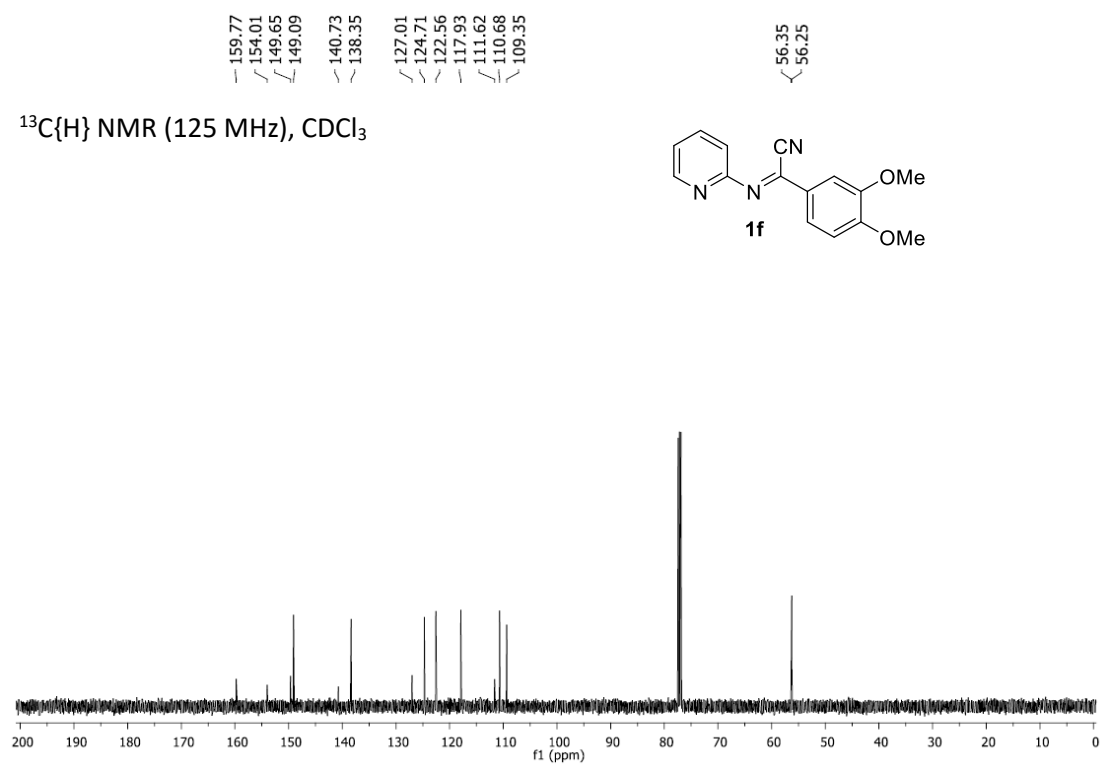
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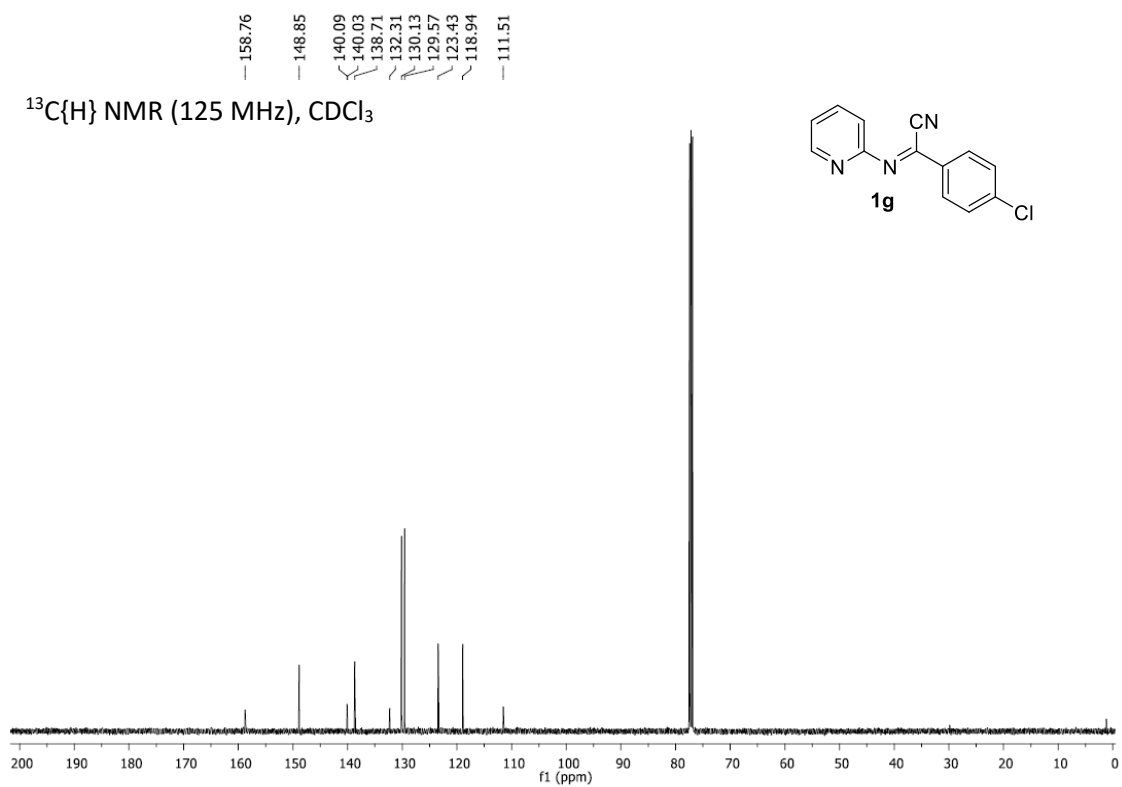
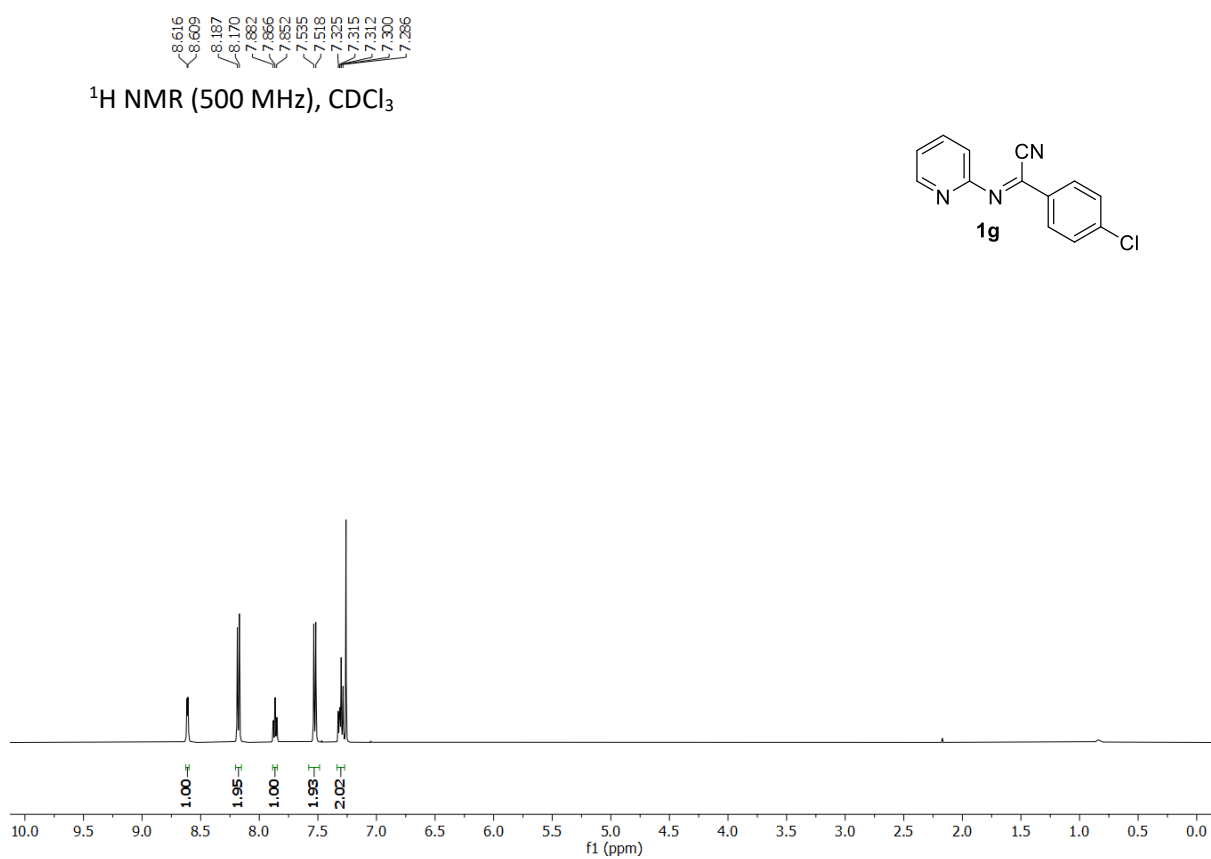


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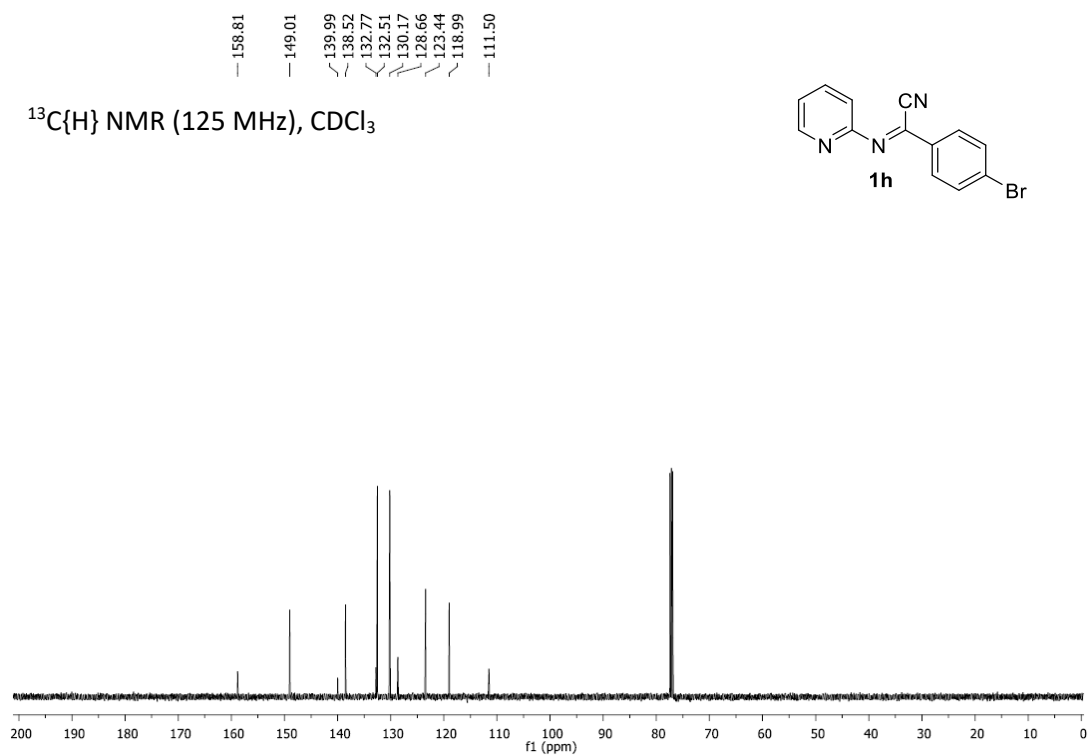
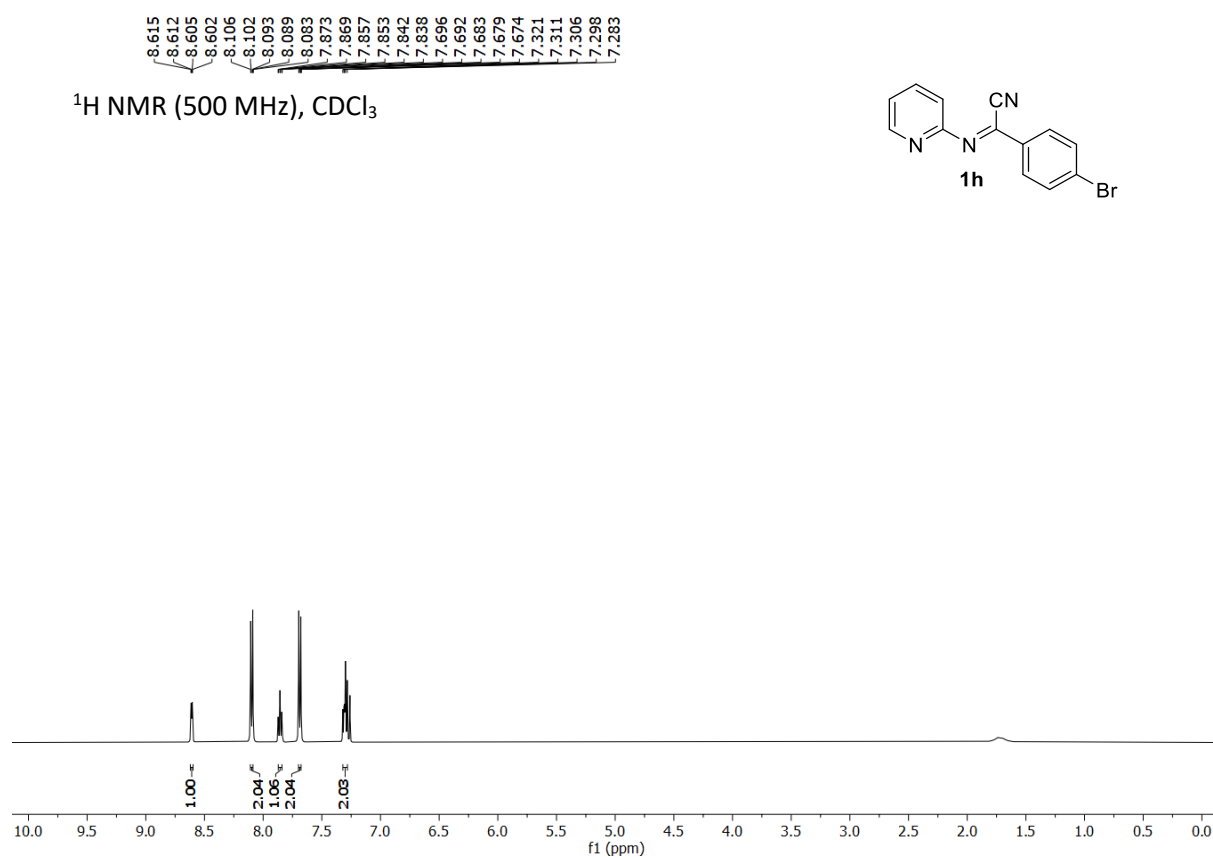


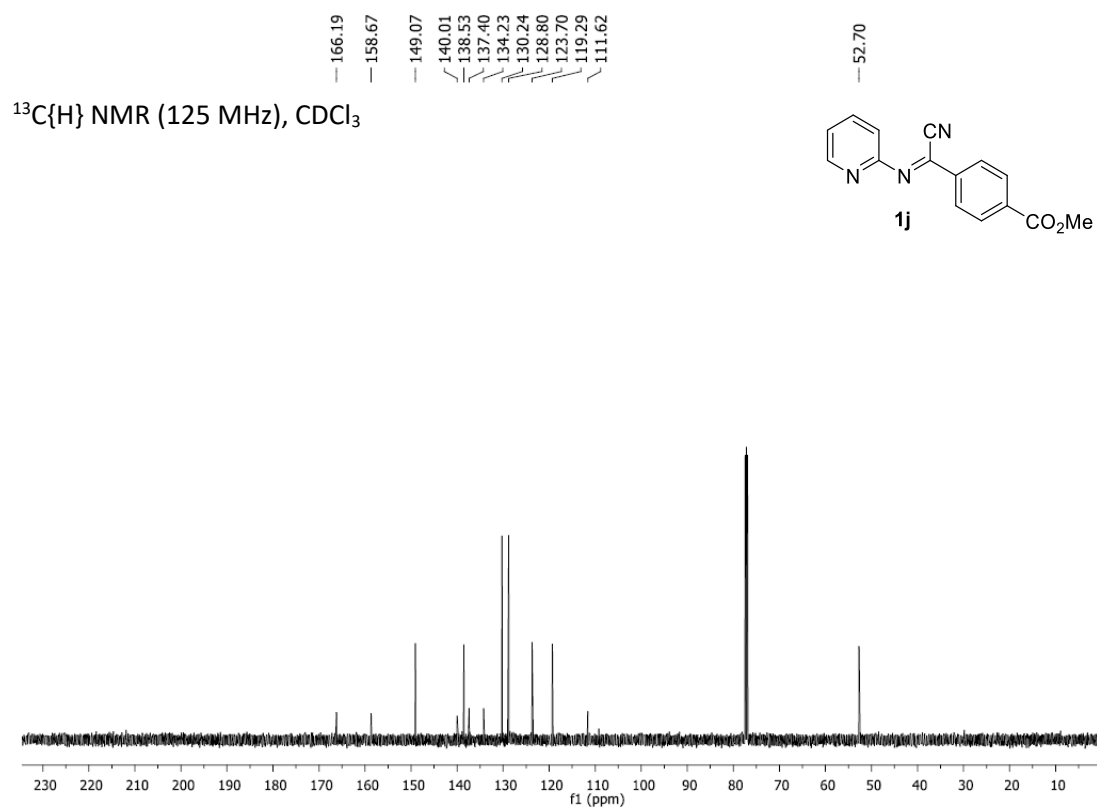
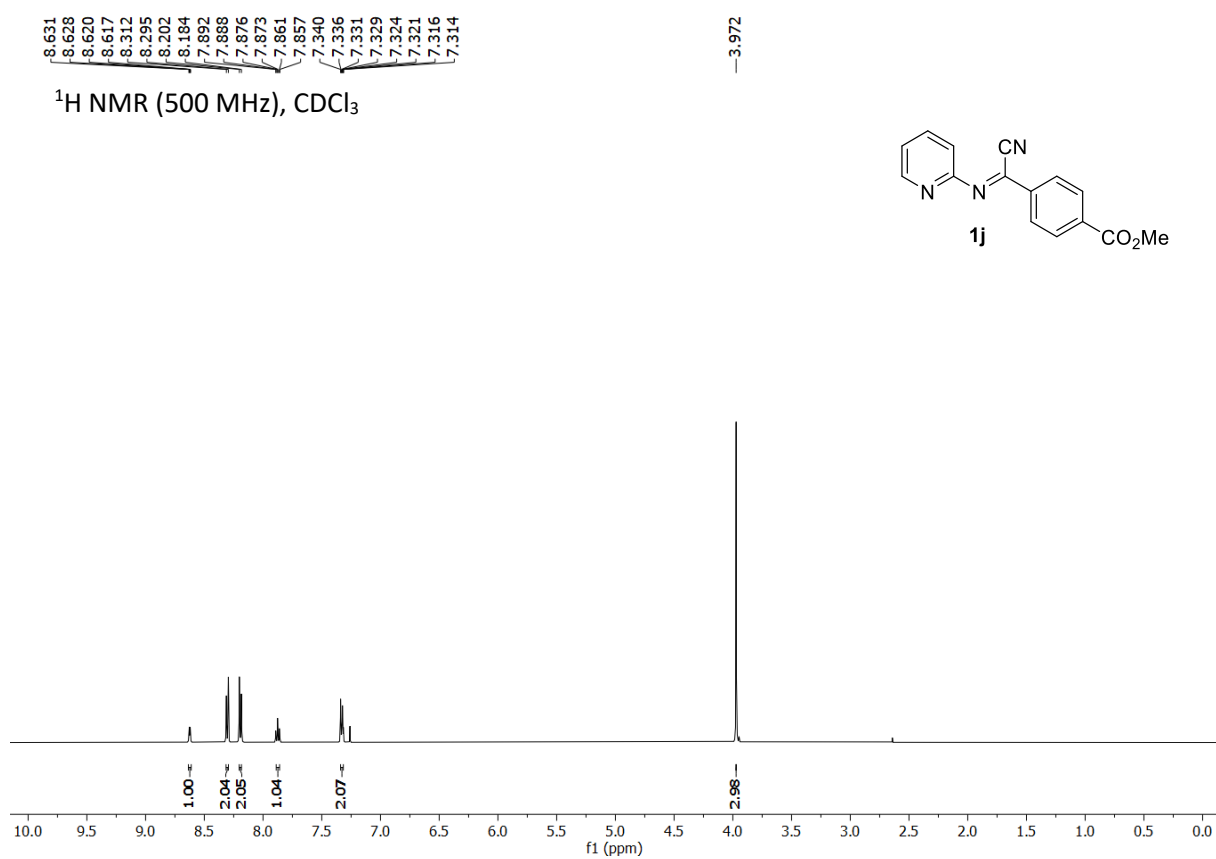
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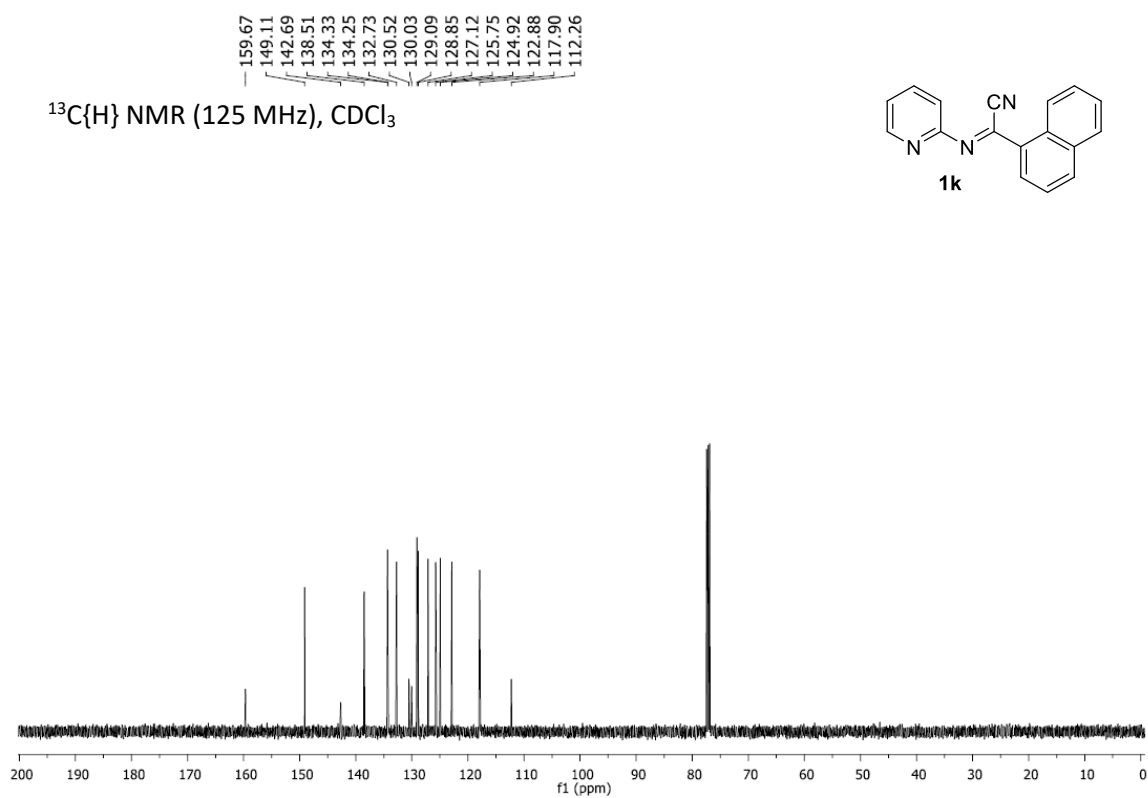
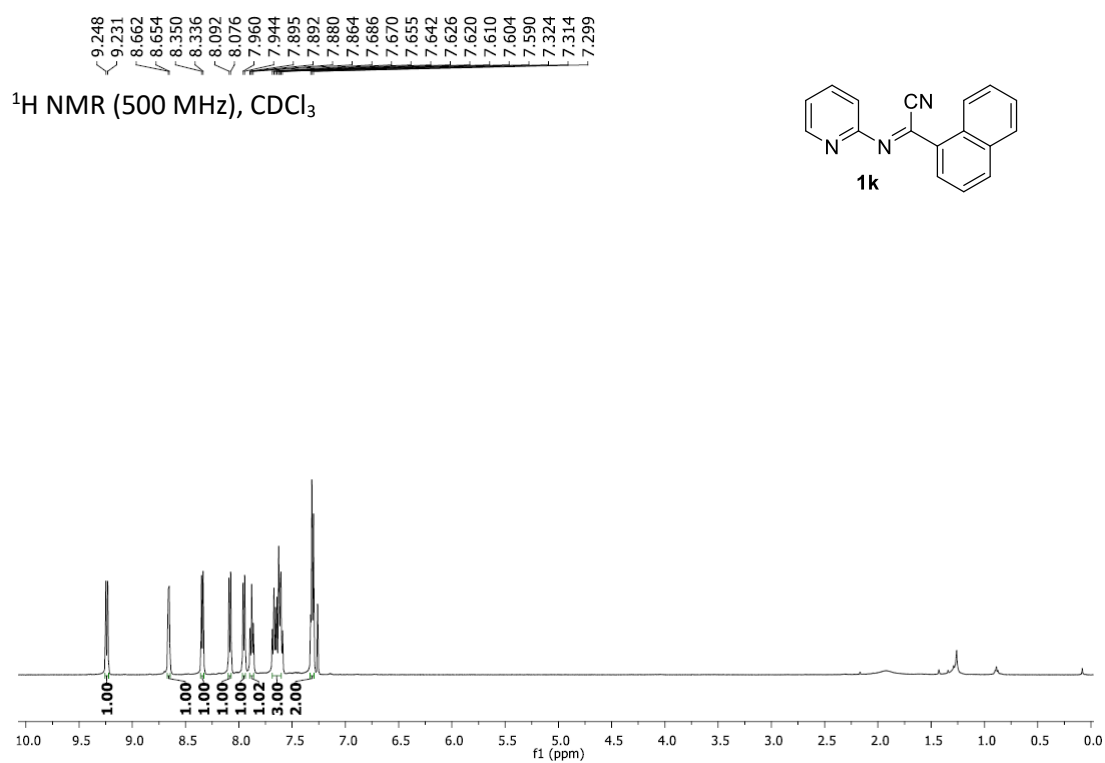




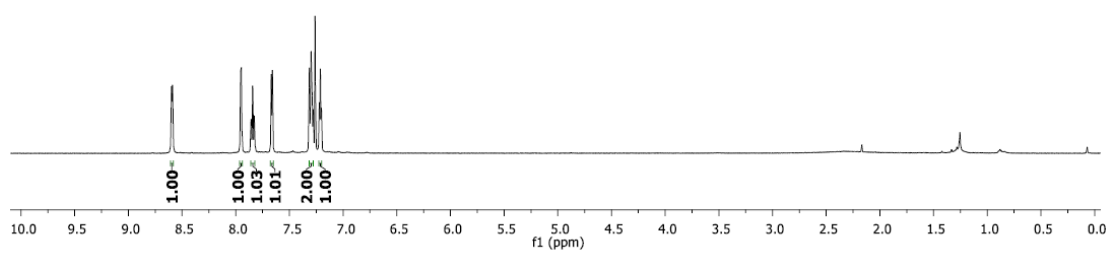
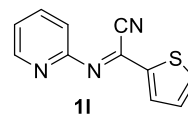




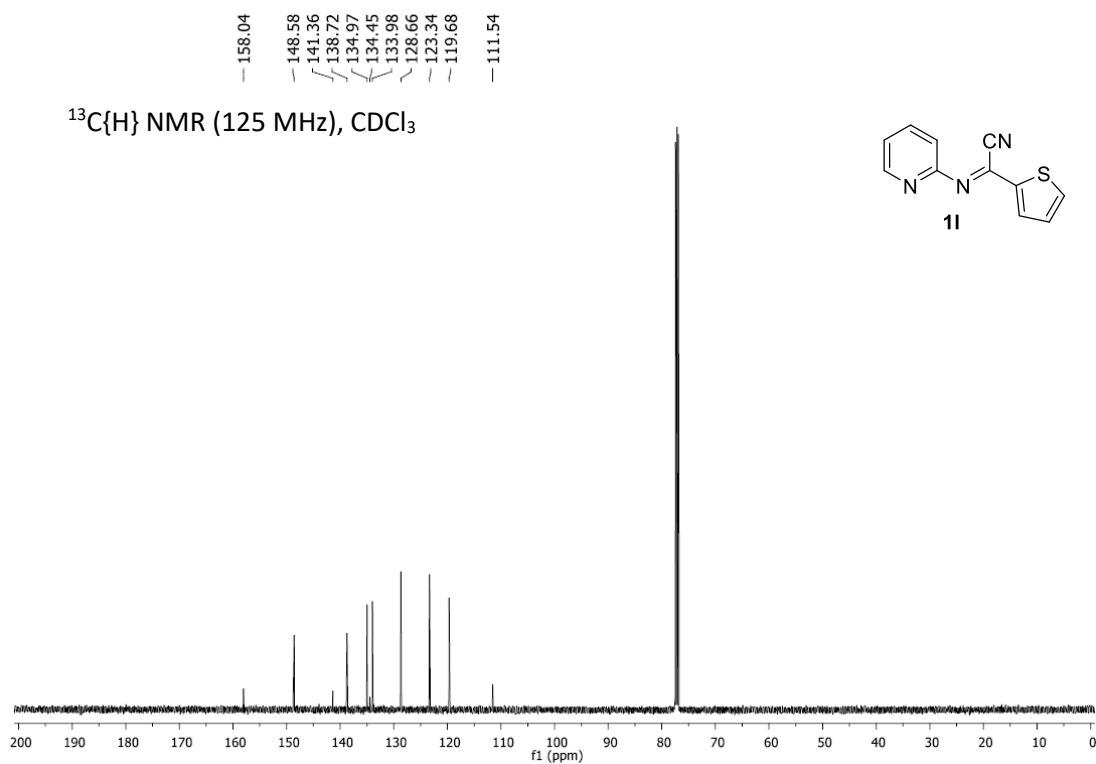
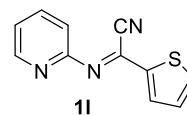


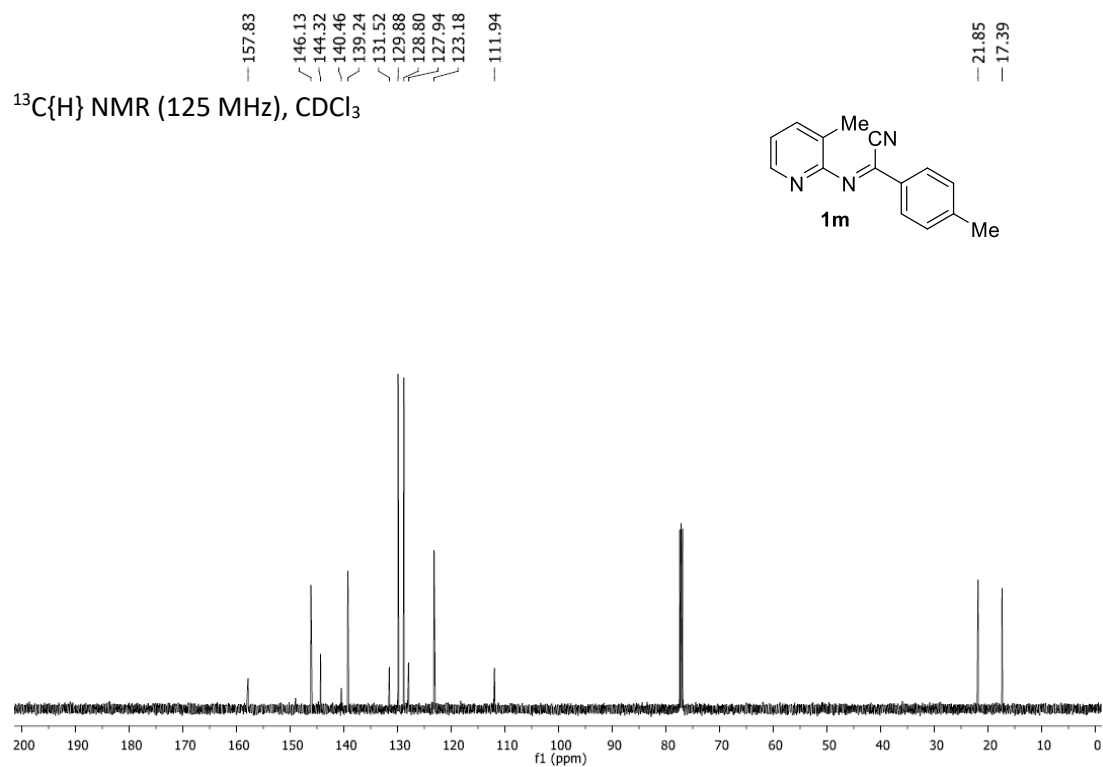
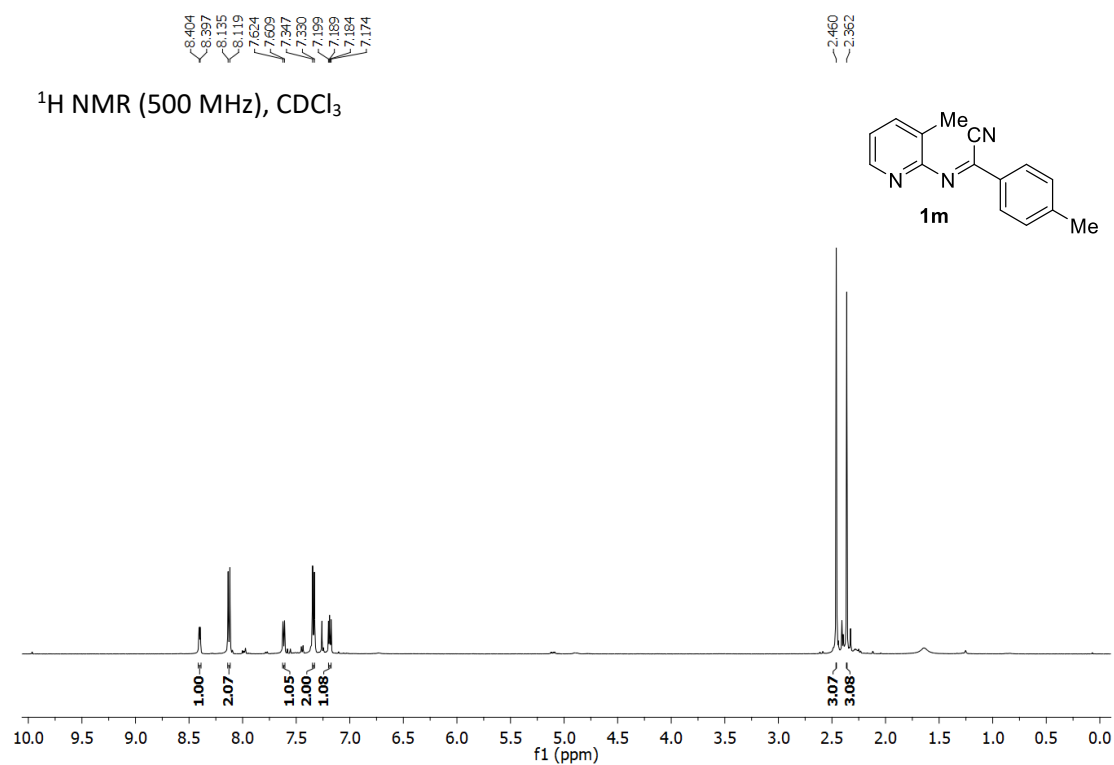


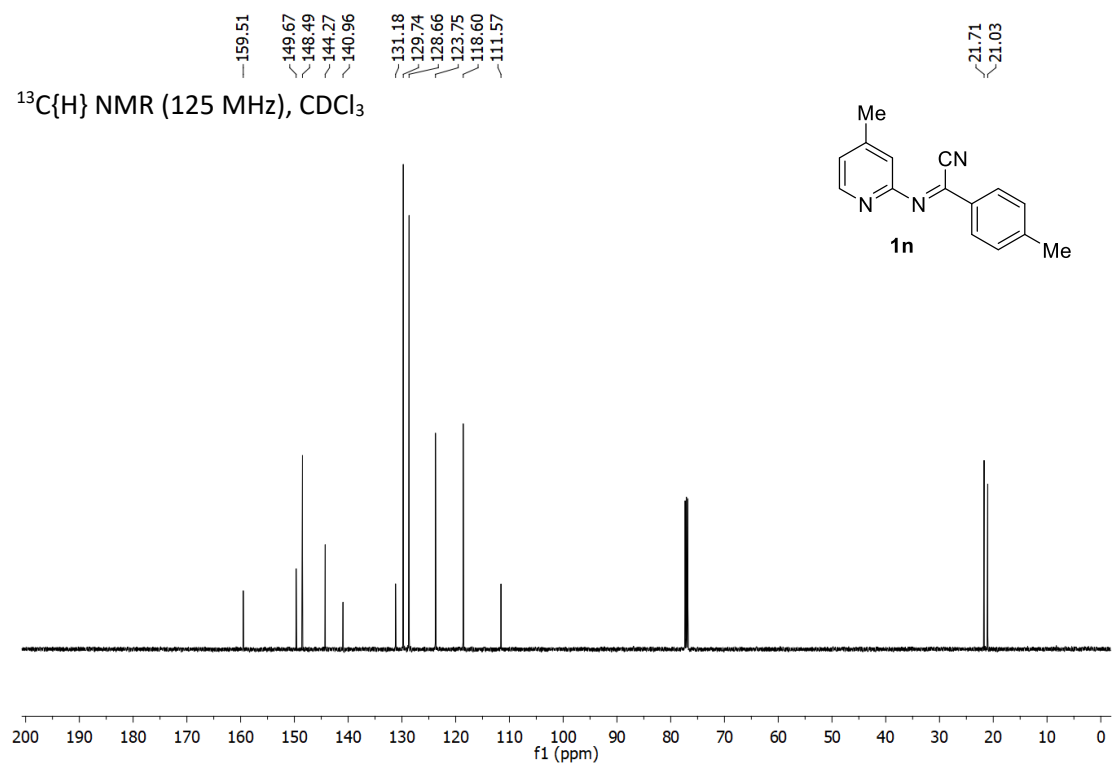
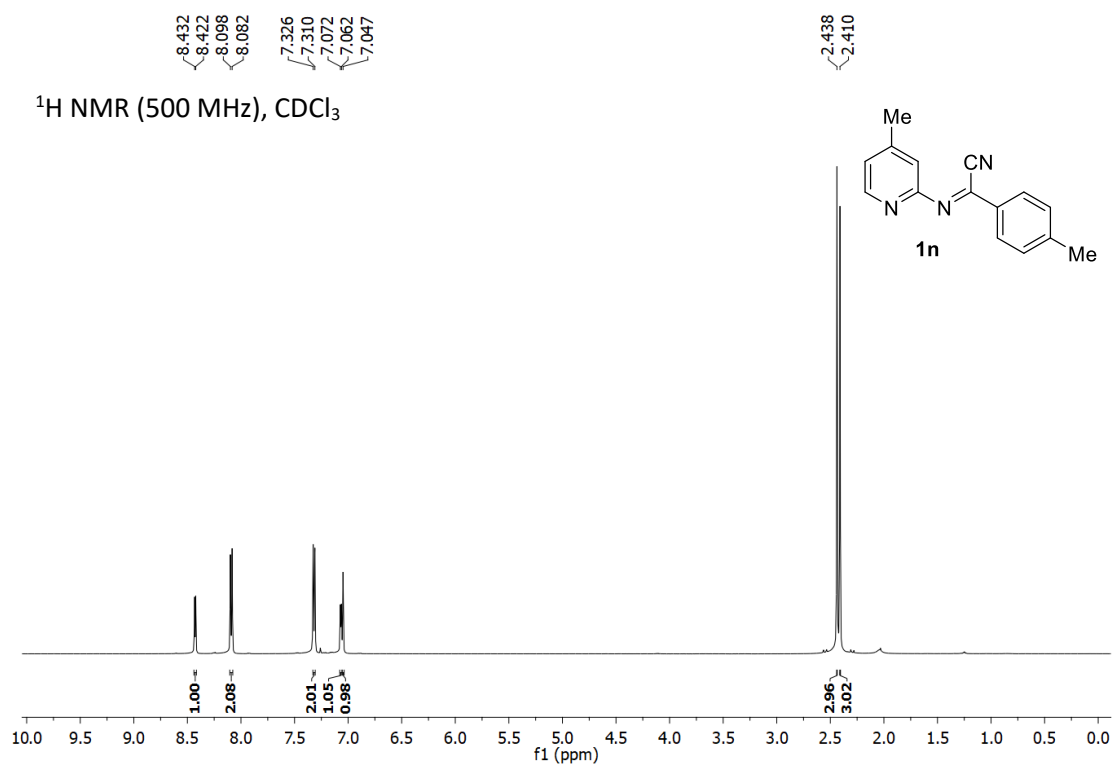
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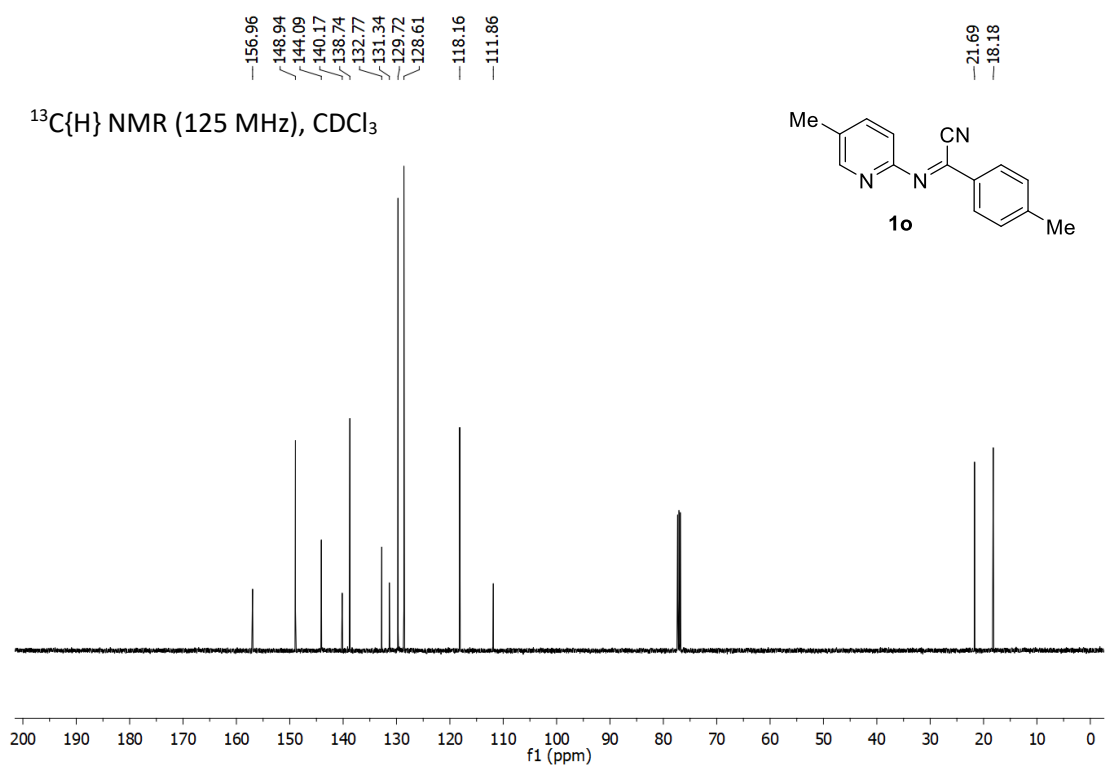
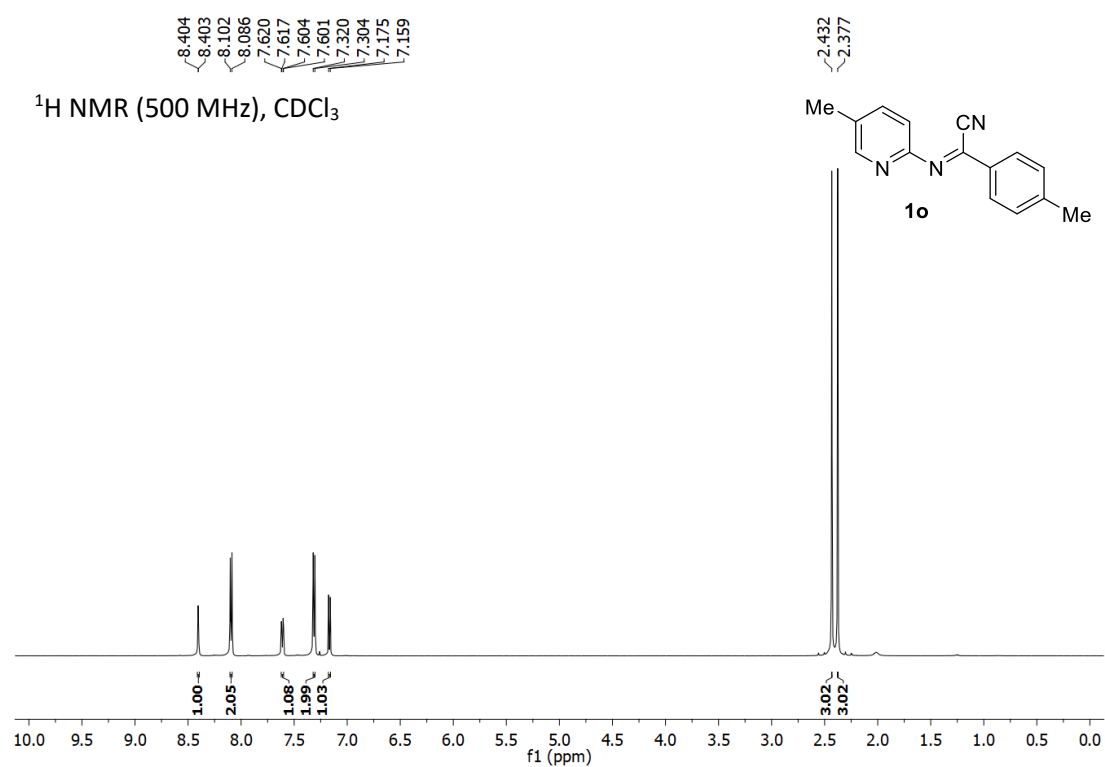


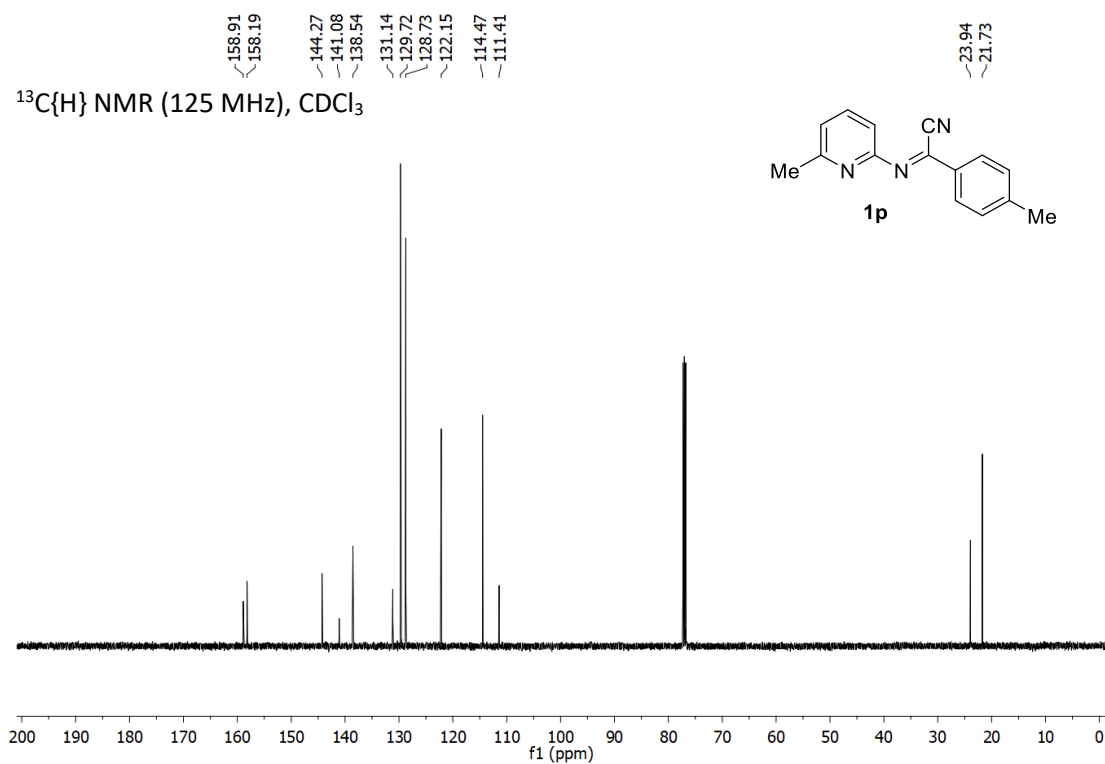
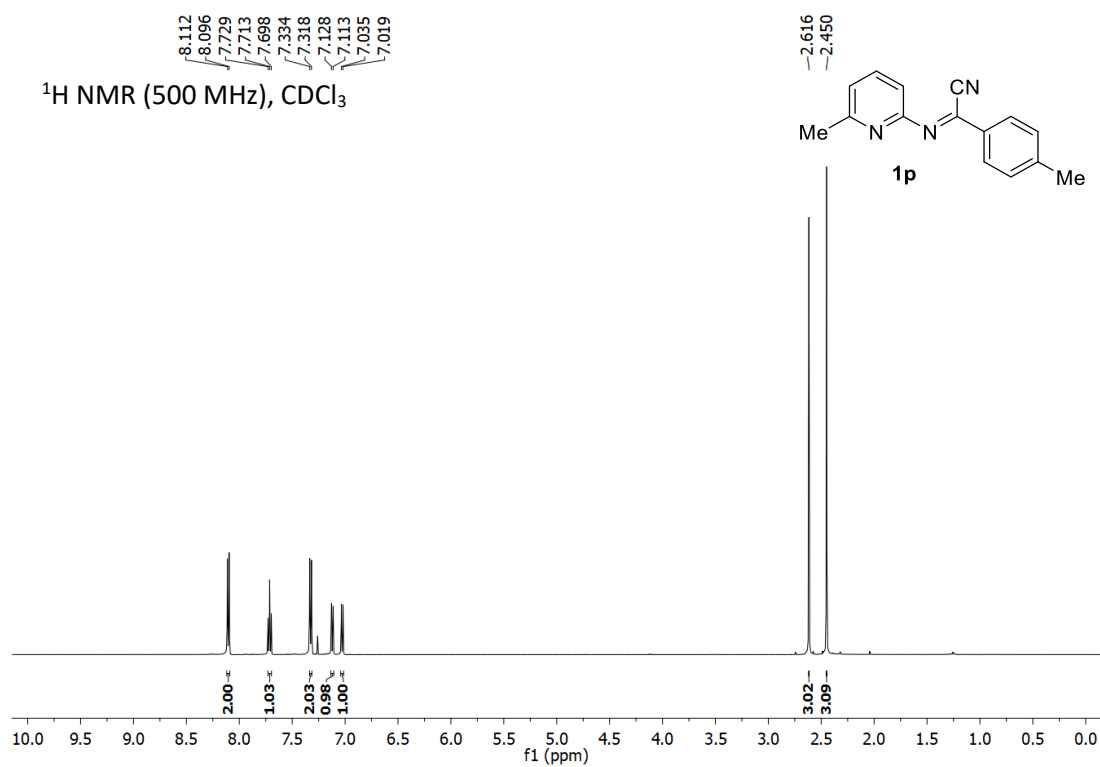
<sup>13</sup>C{H} NMR (125 MHz), CDCl<sub>3</sub>



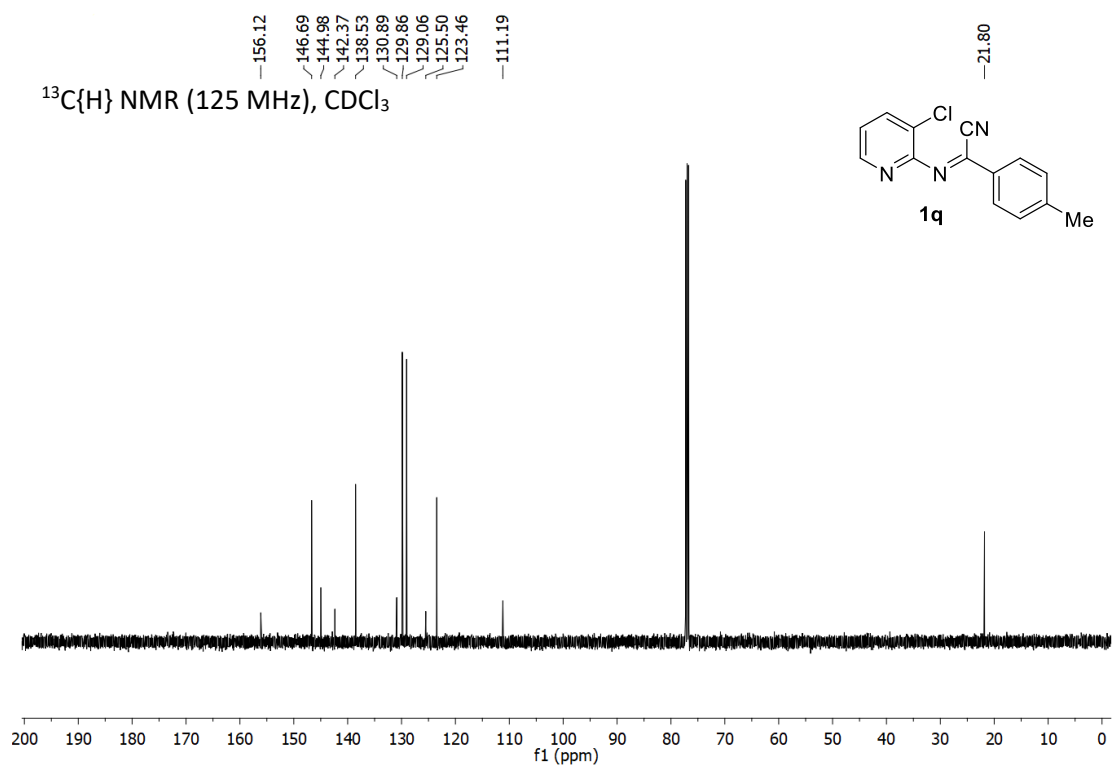
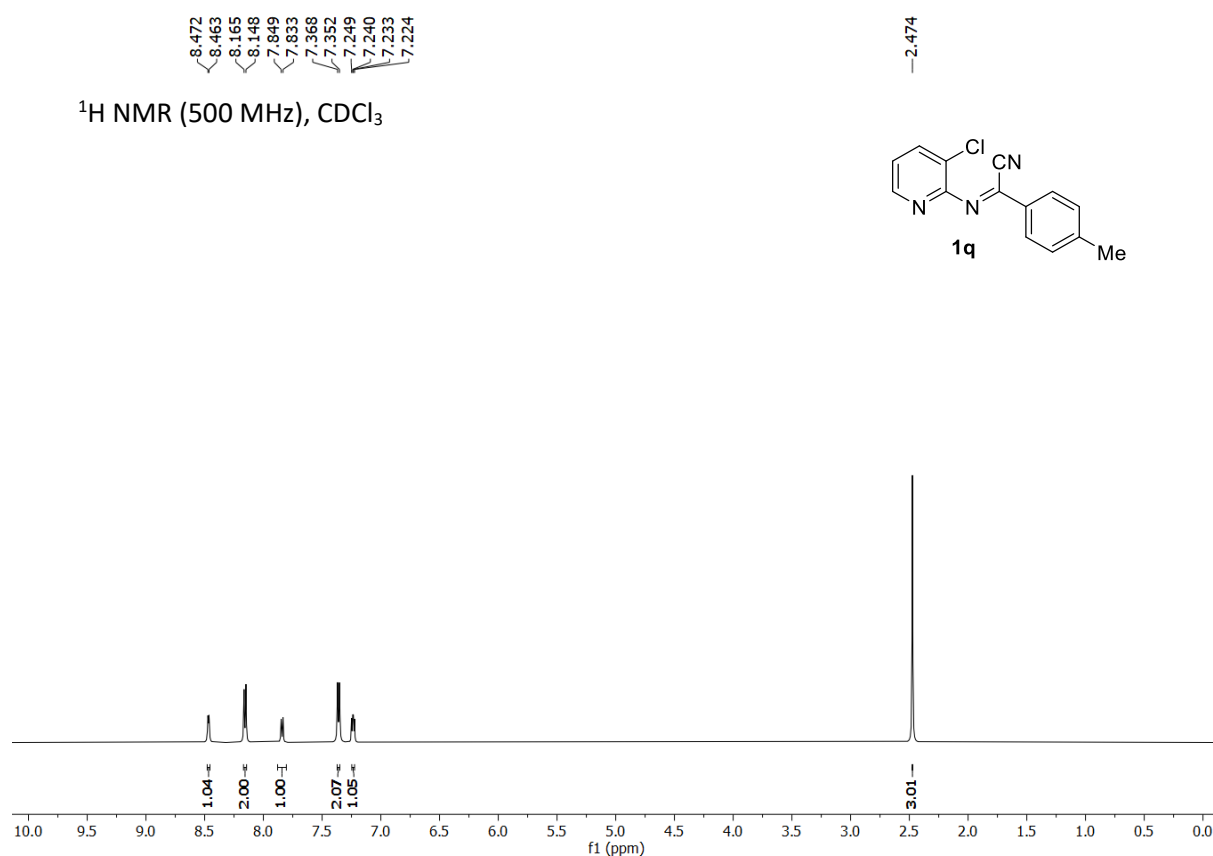


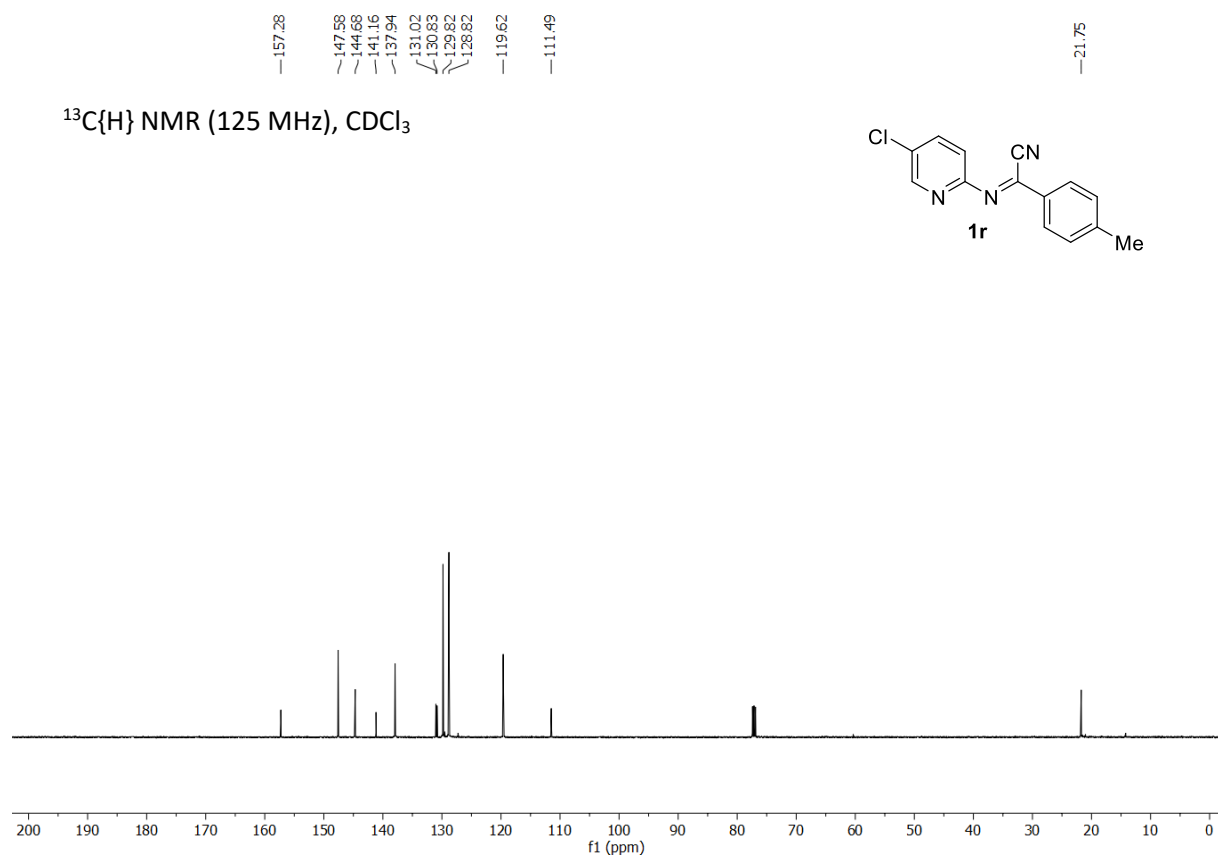
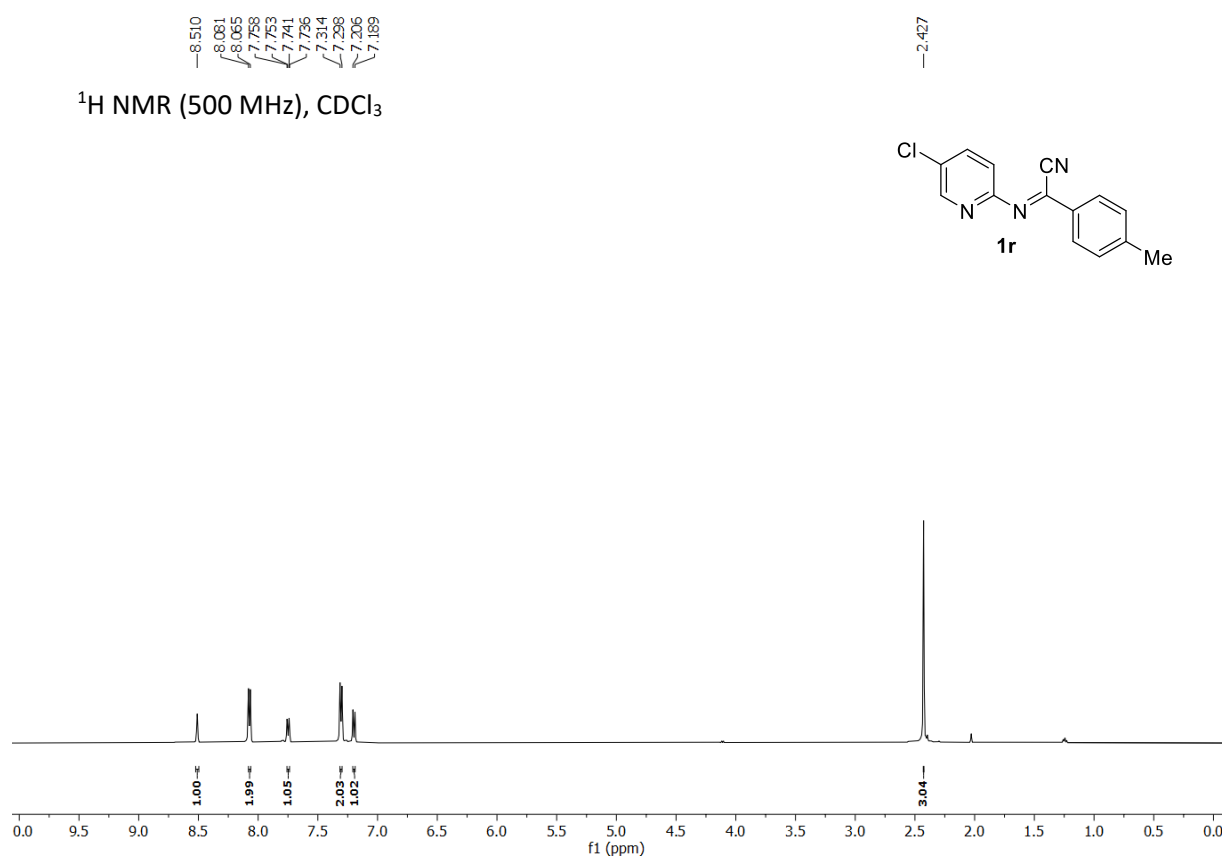




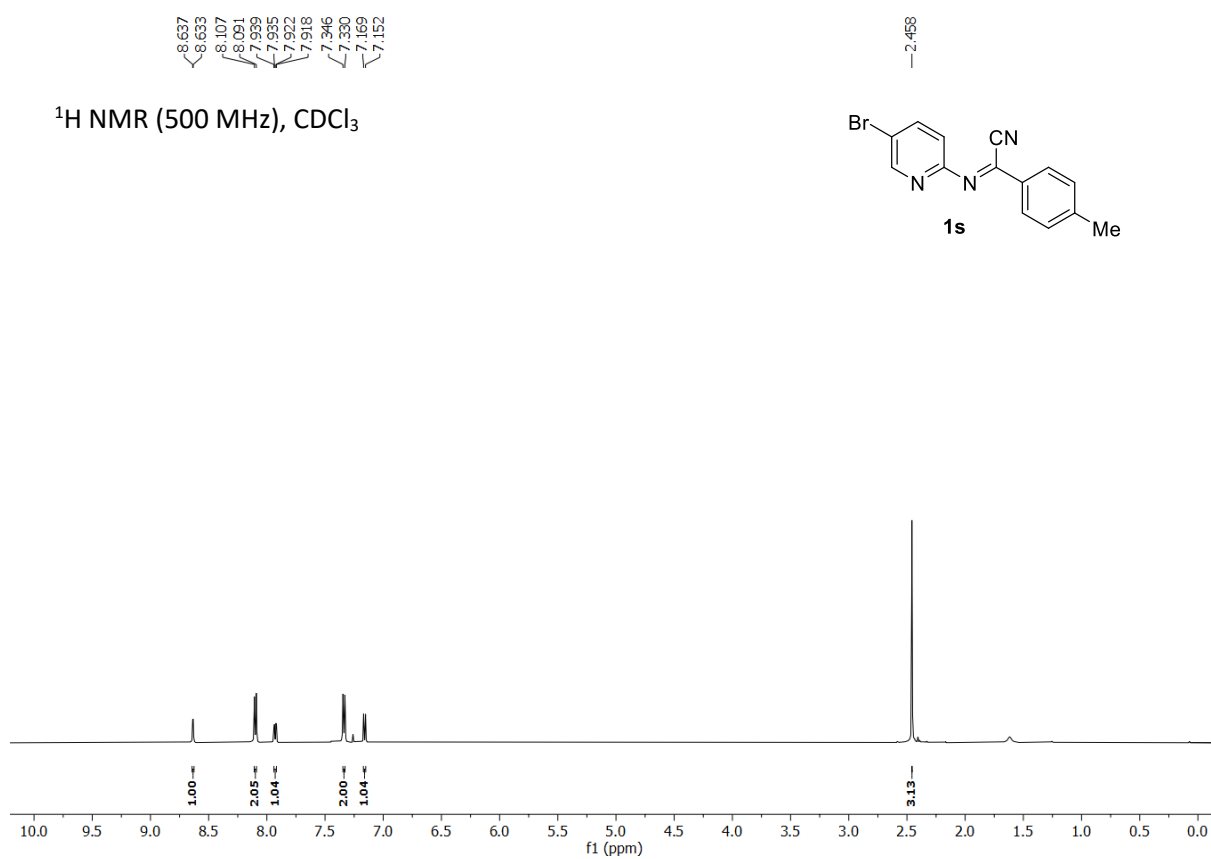




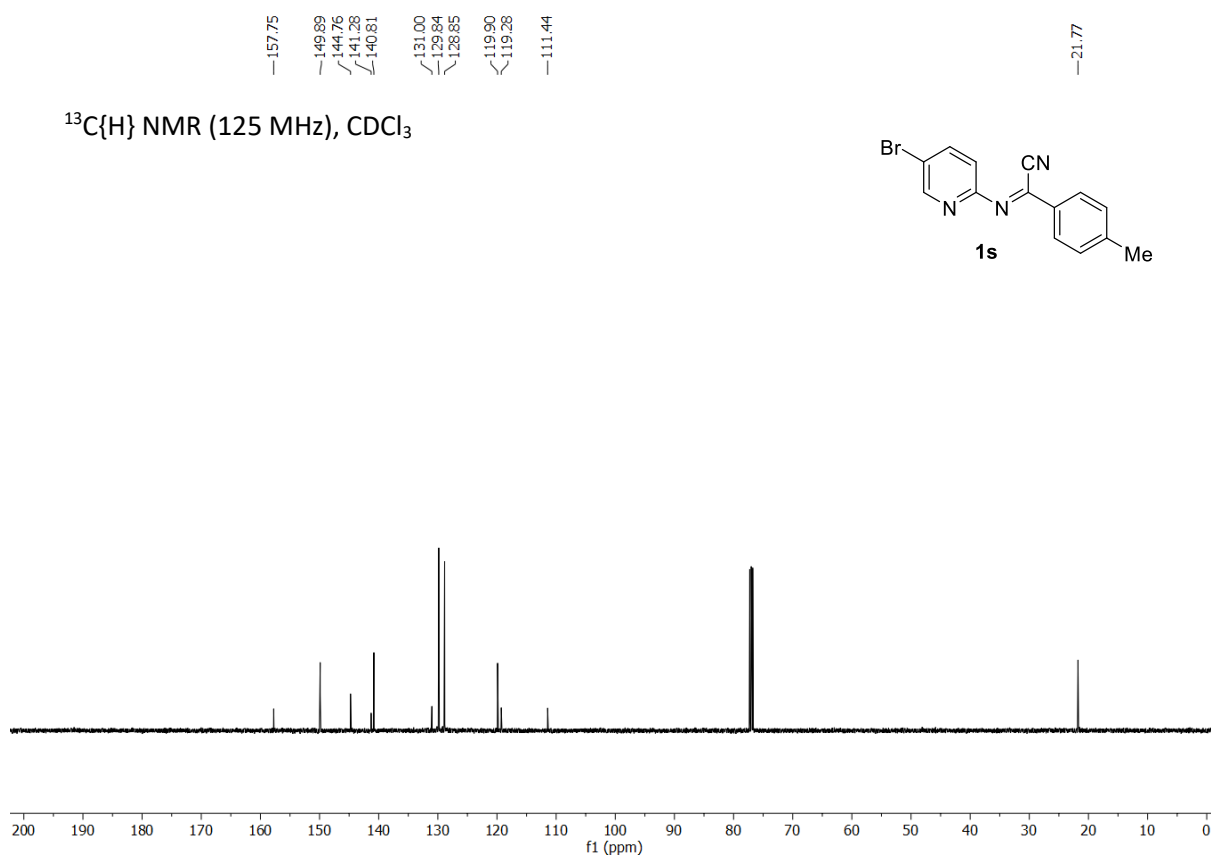


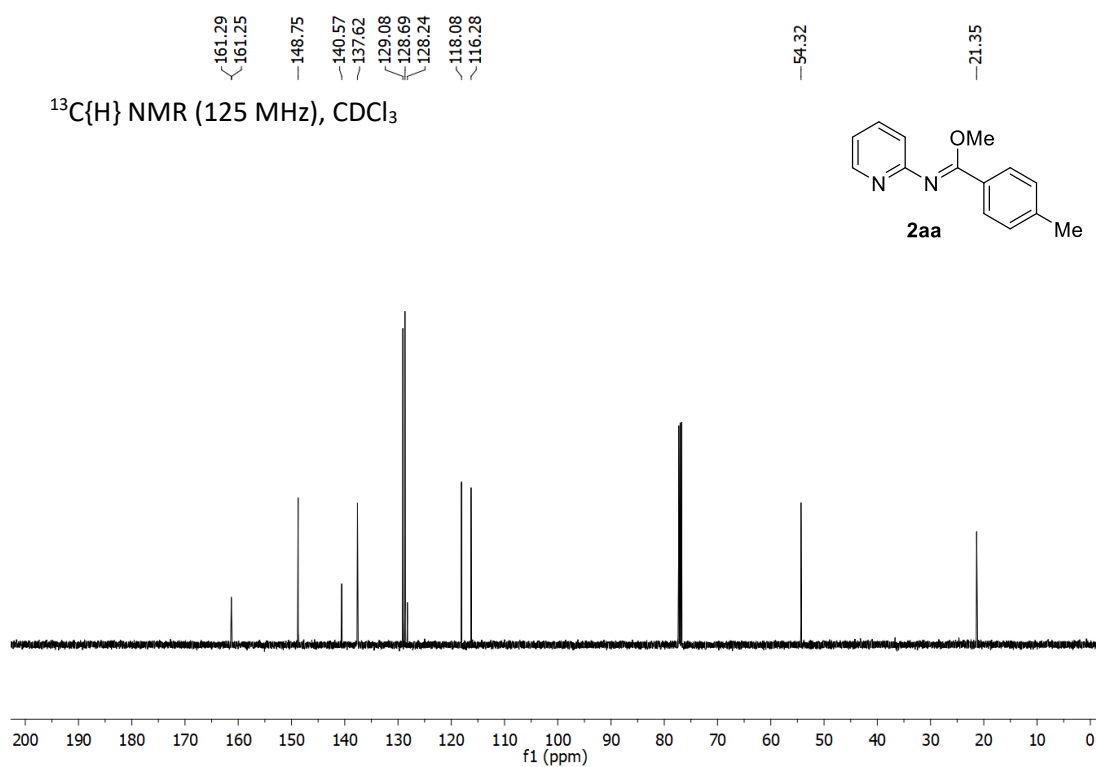
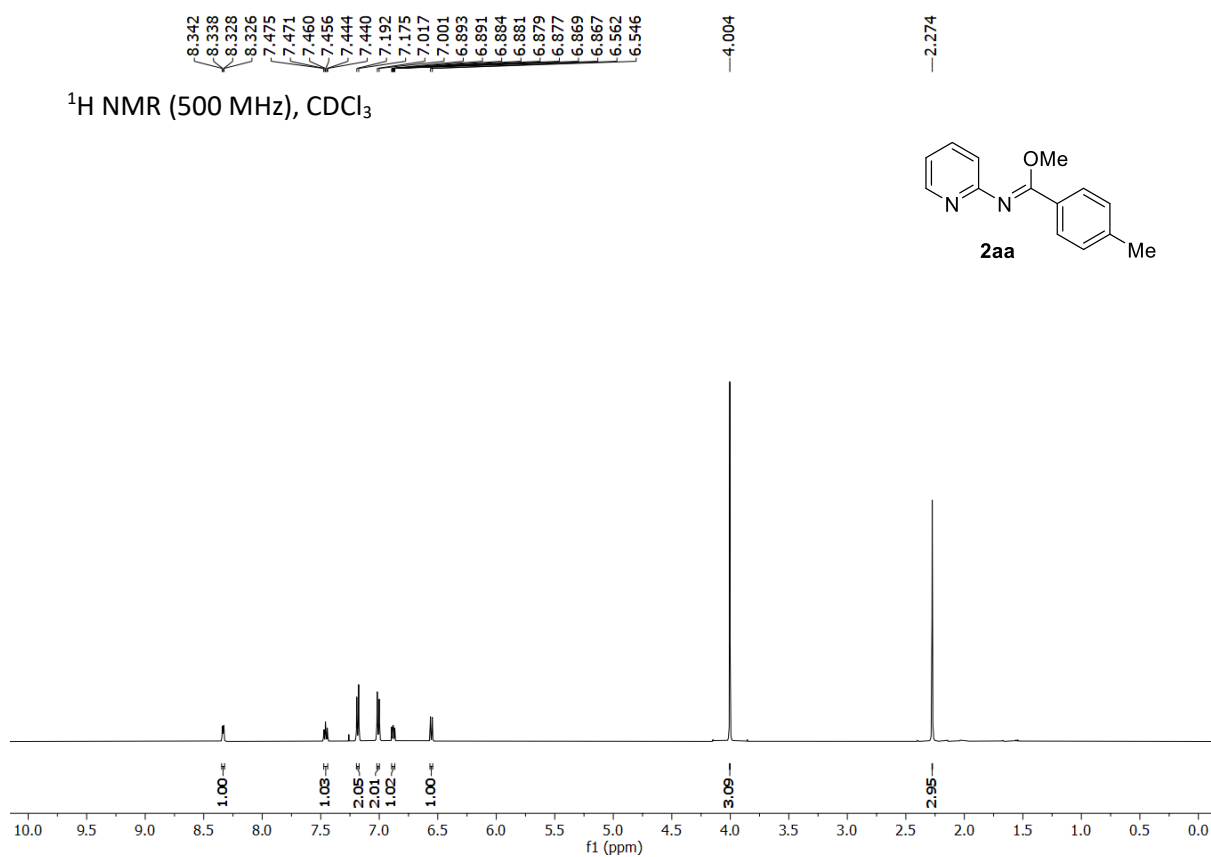


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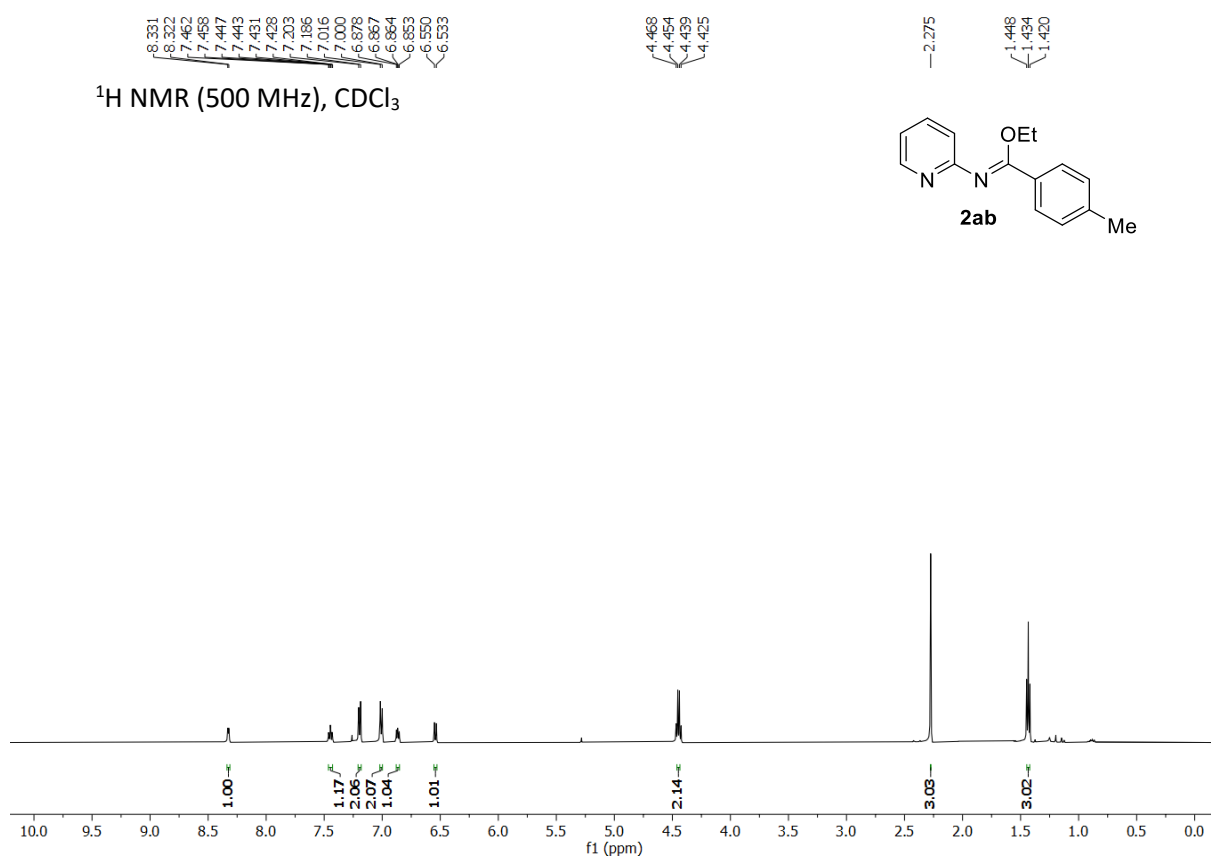
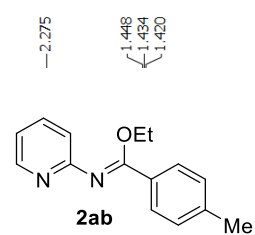


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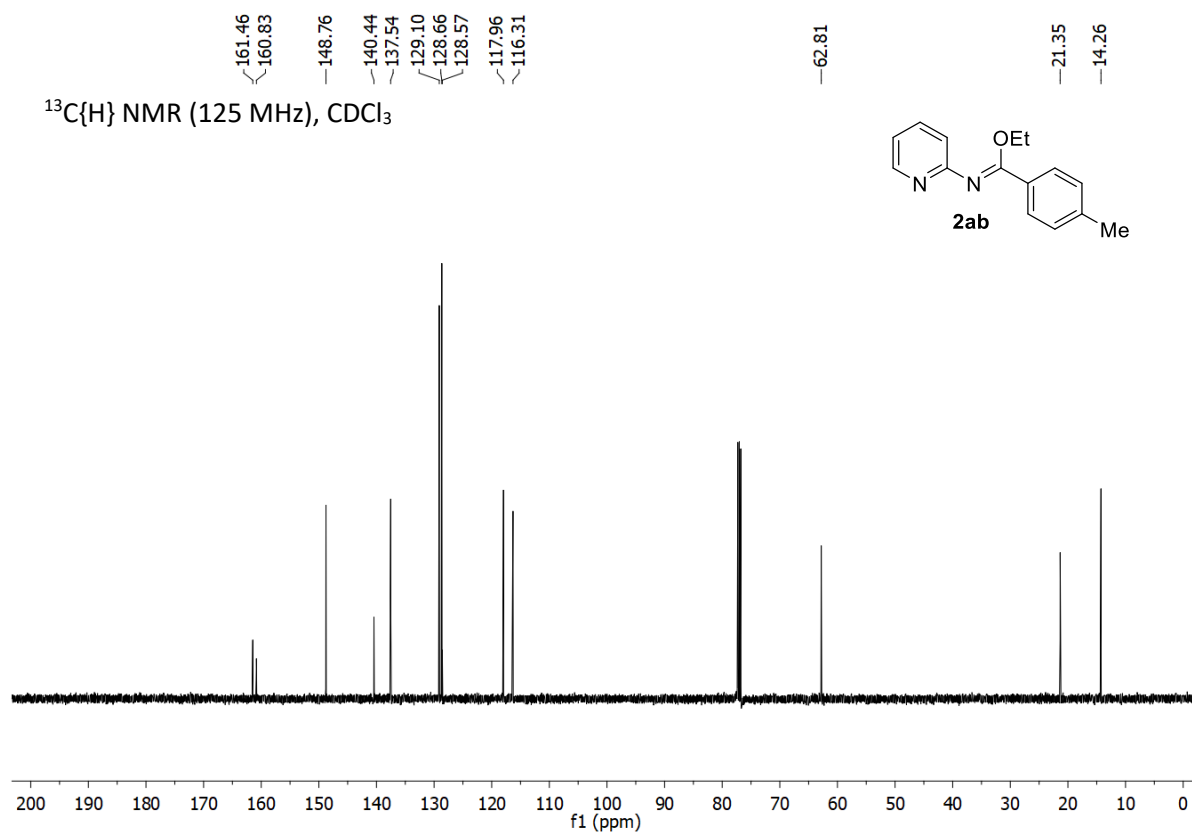
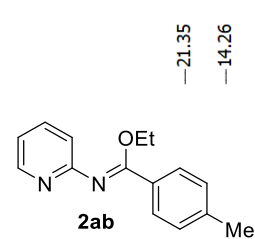


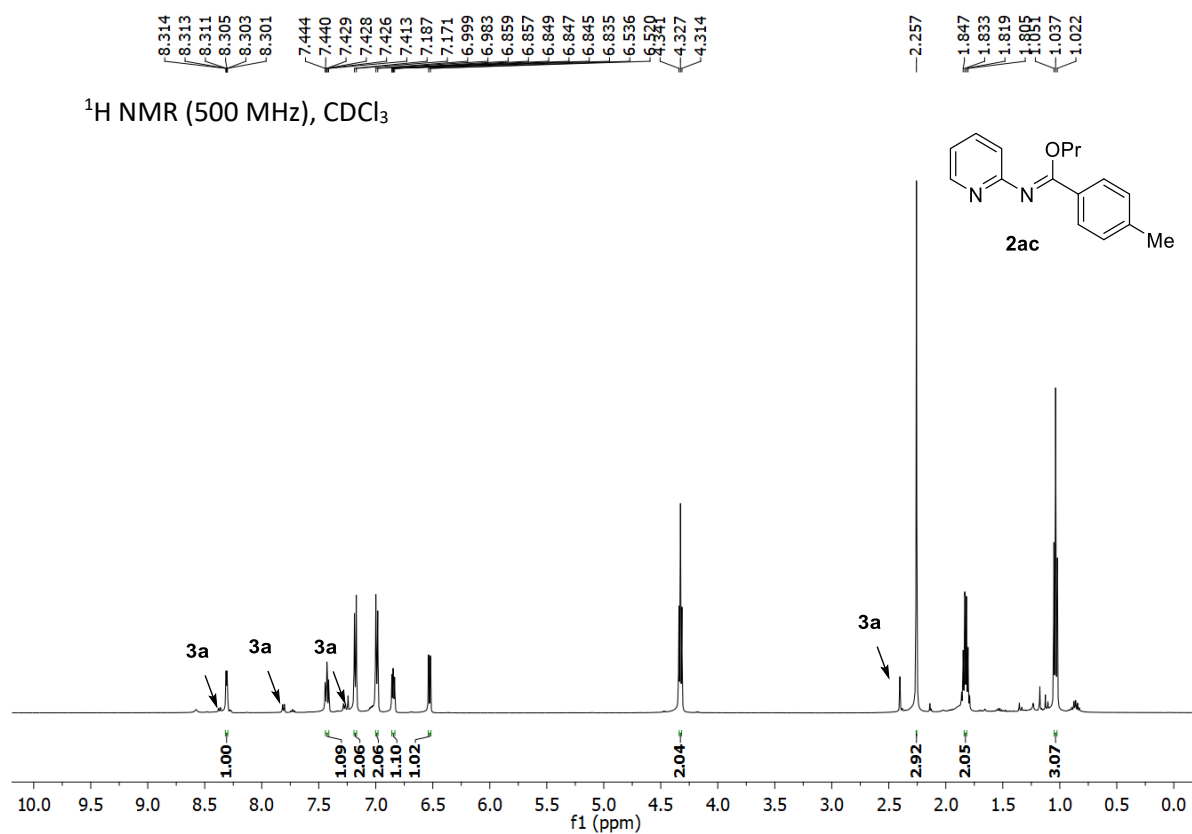
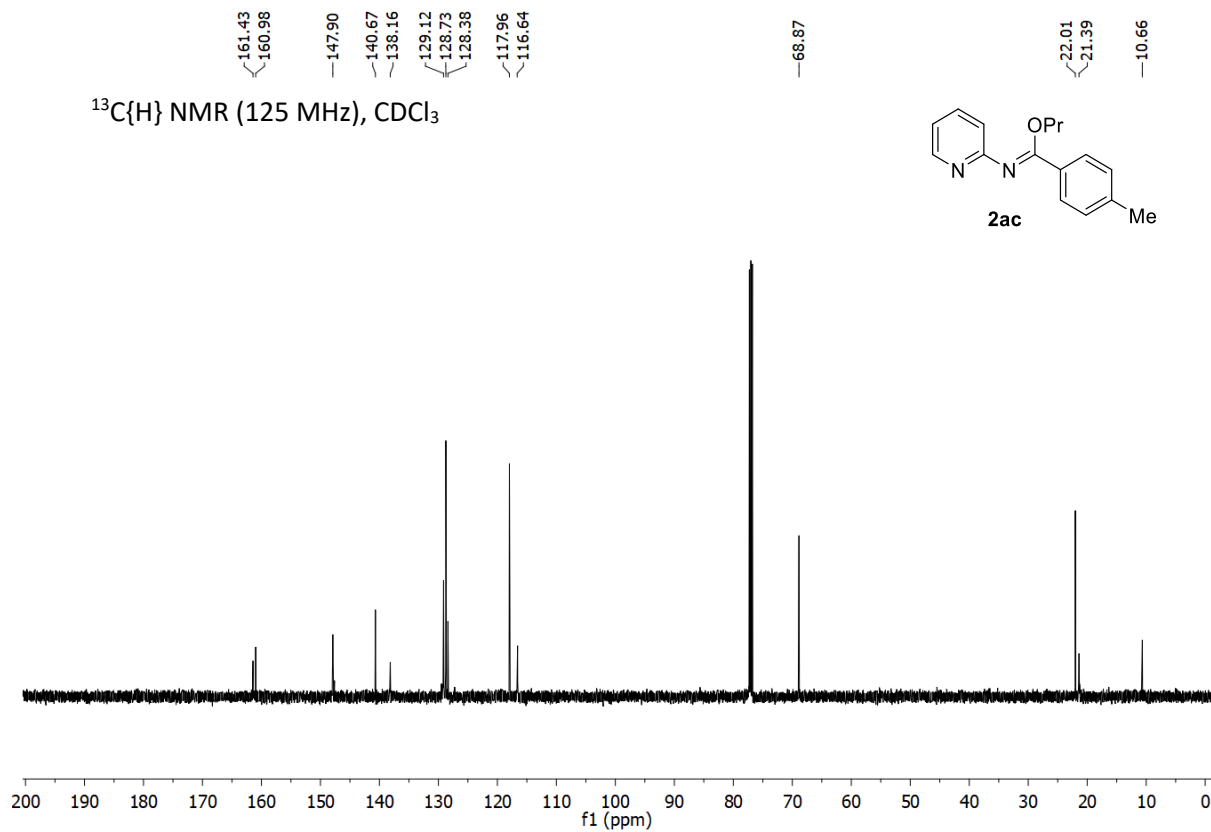
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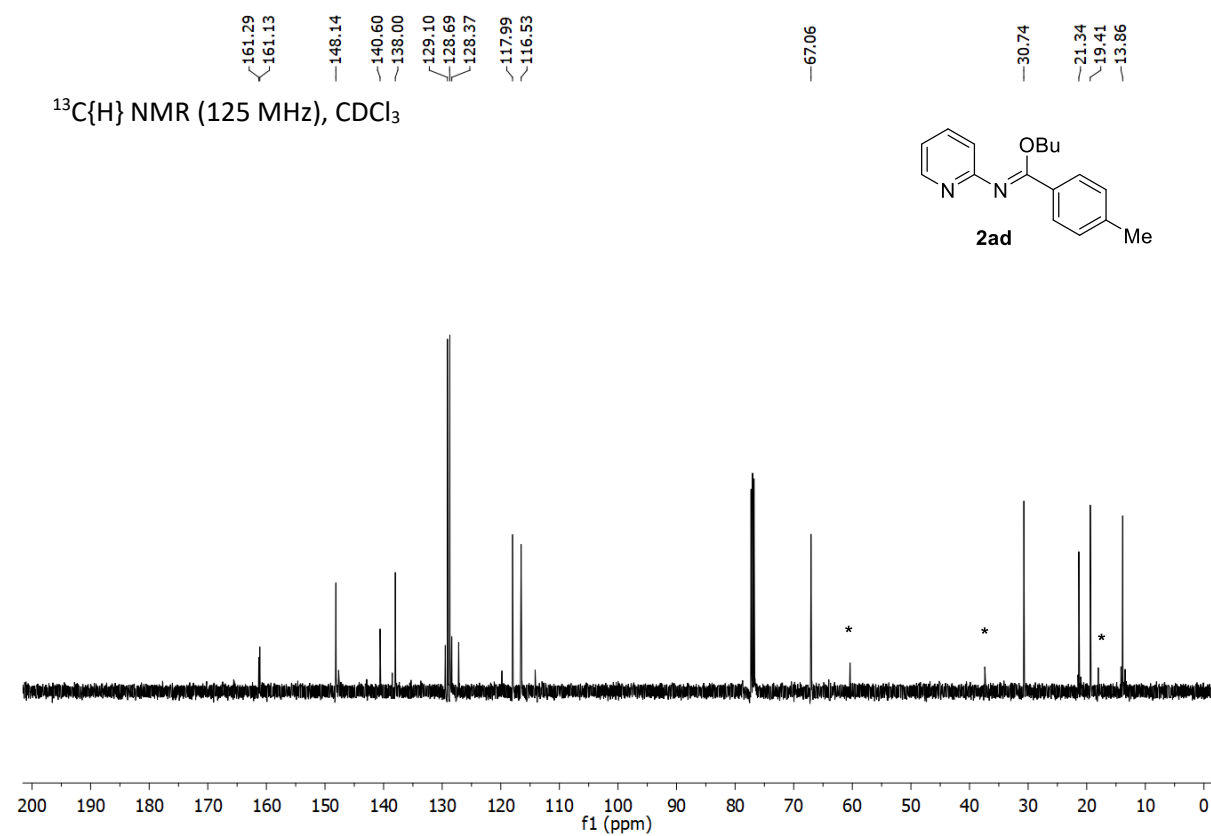
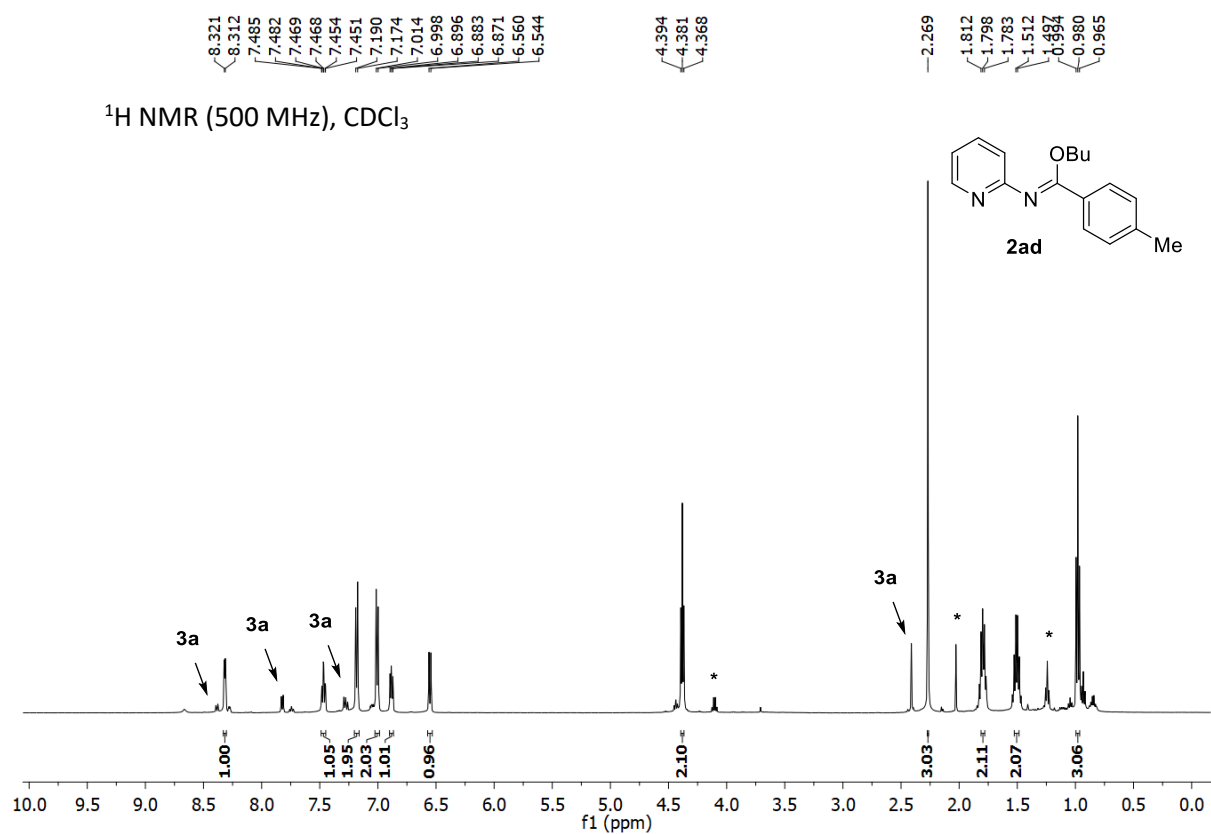
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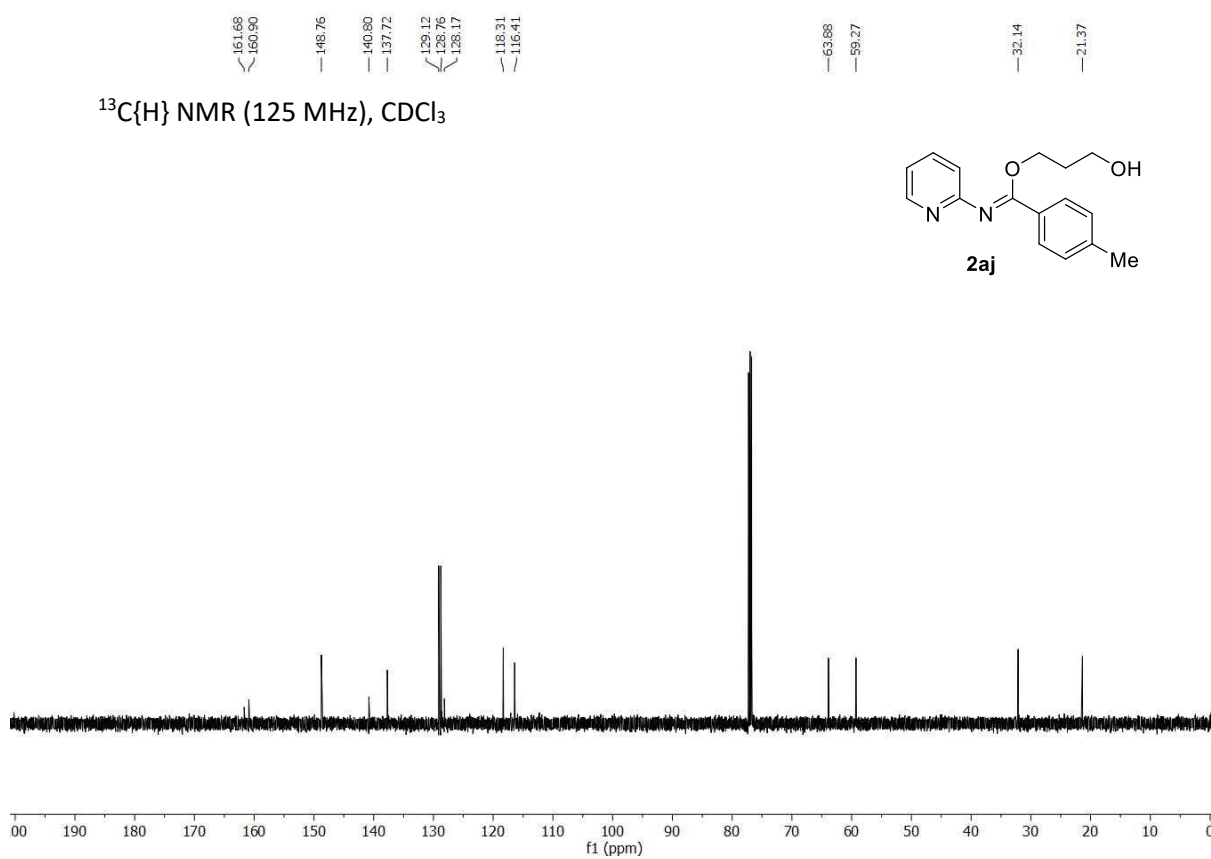
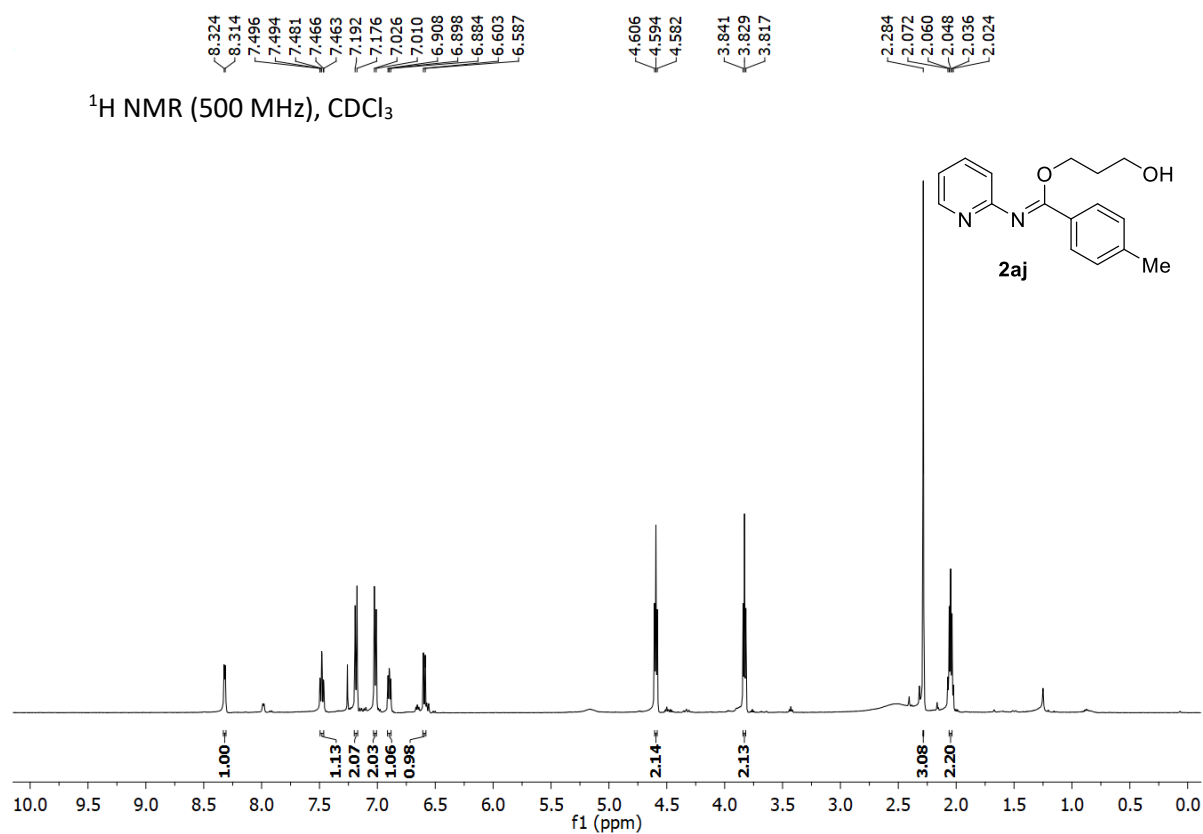
<sup>13</sup>C{H} NMR (125 MHz), CDCl<sub>3</sub>



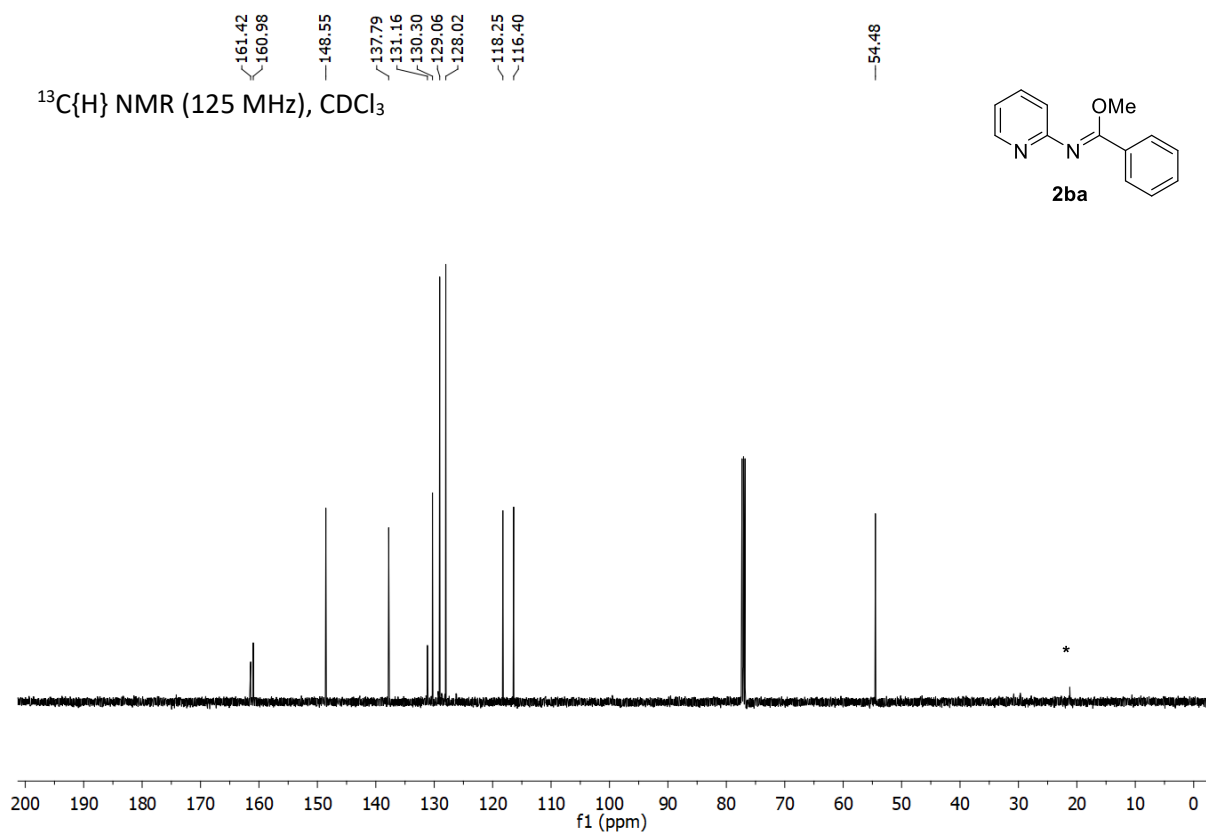
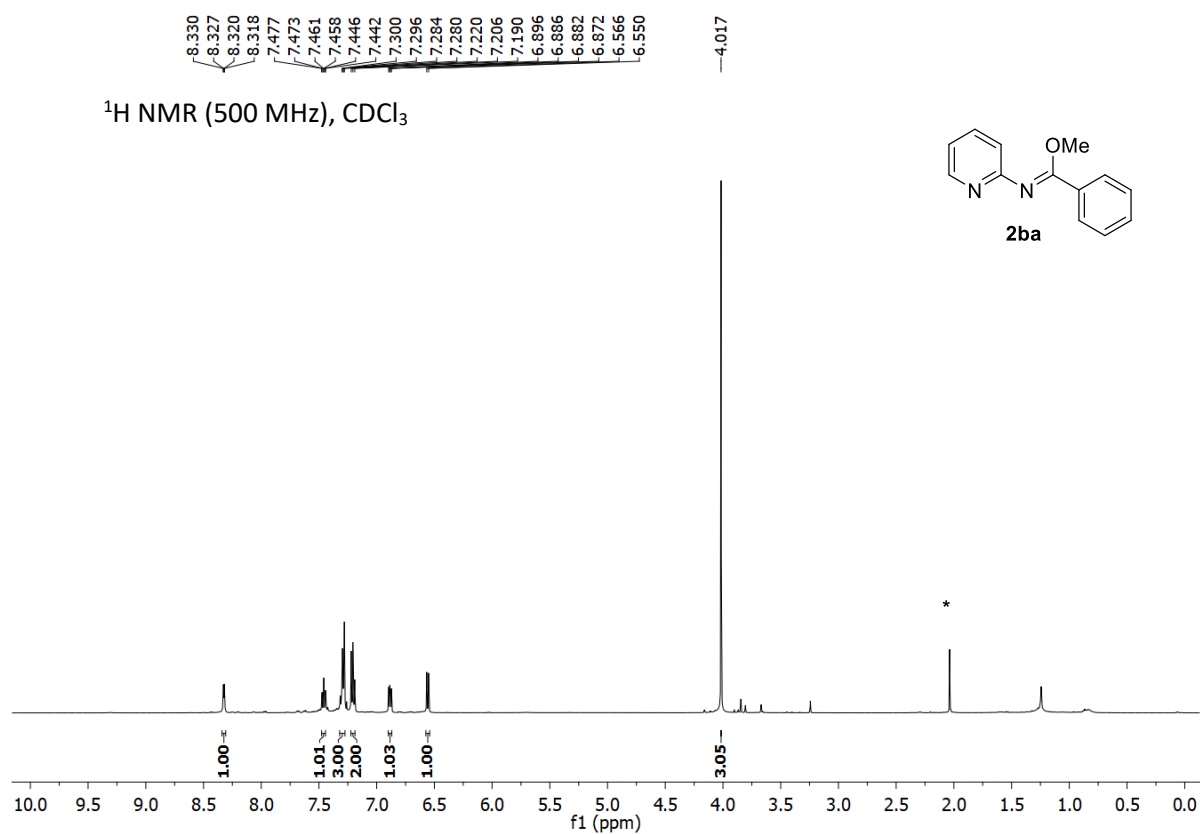
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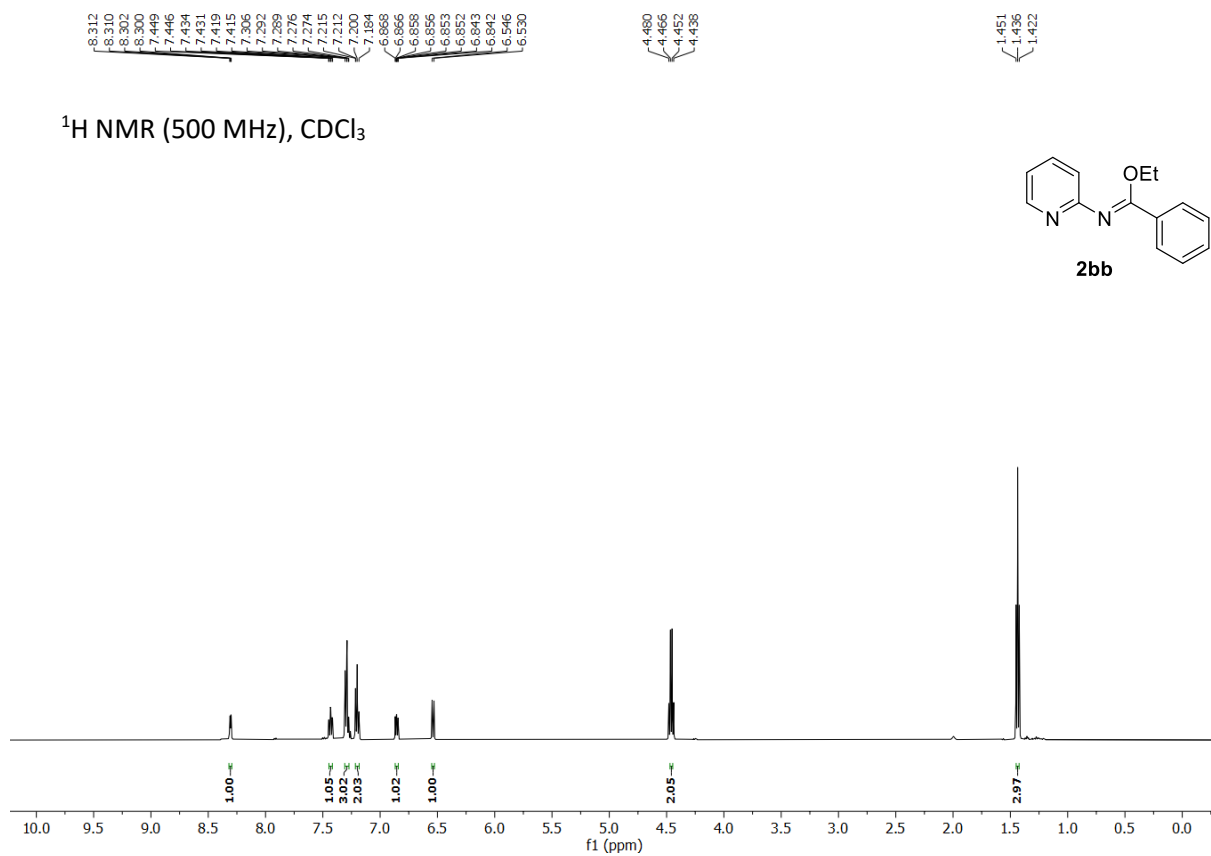
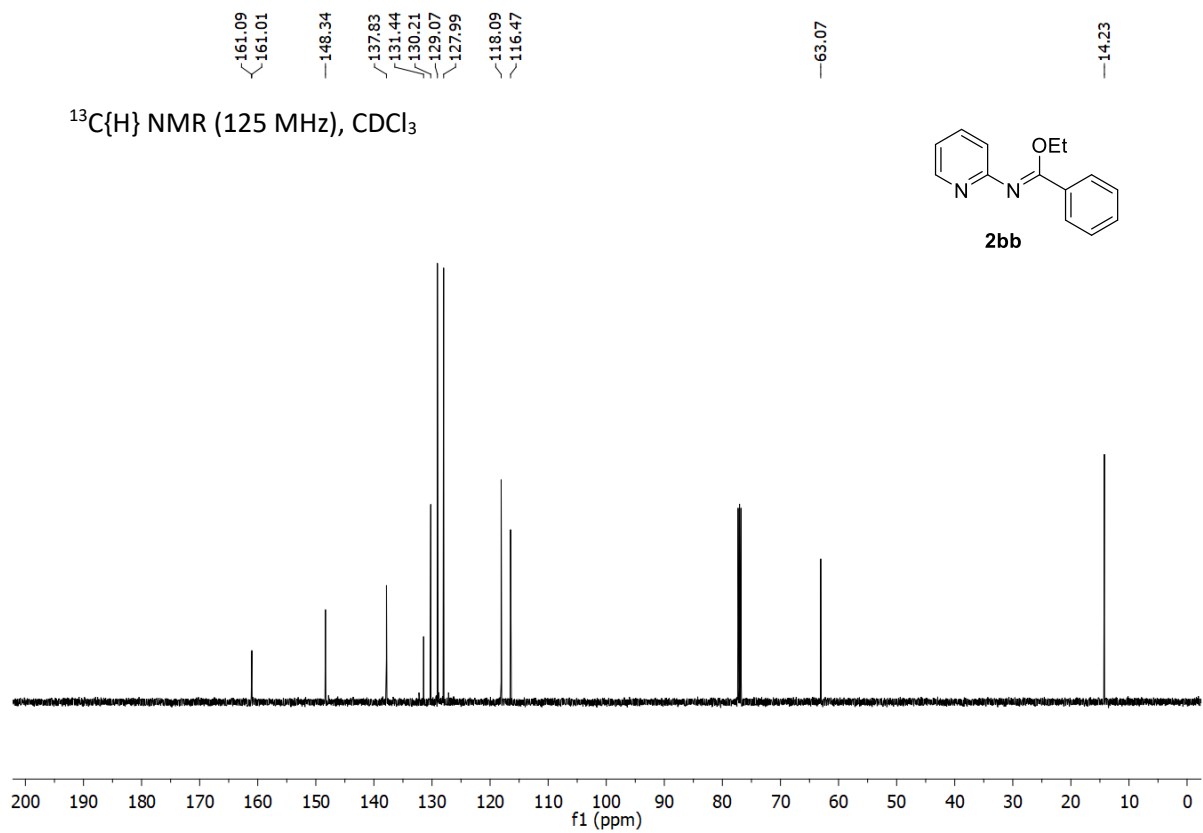
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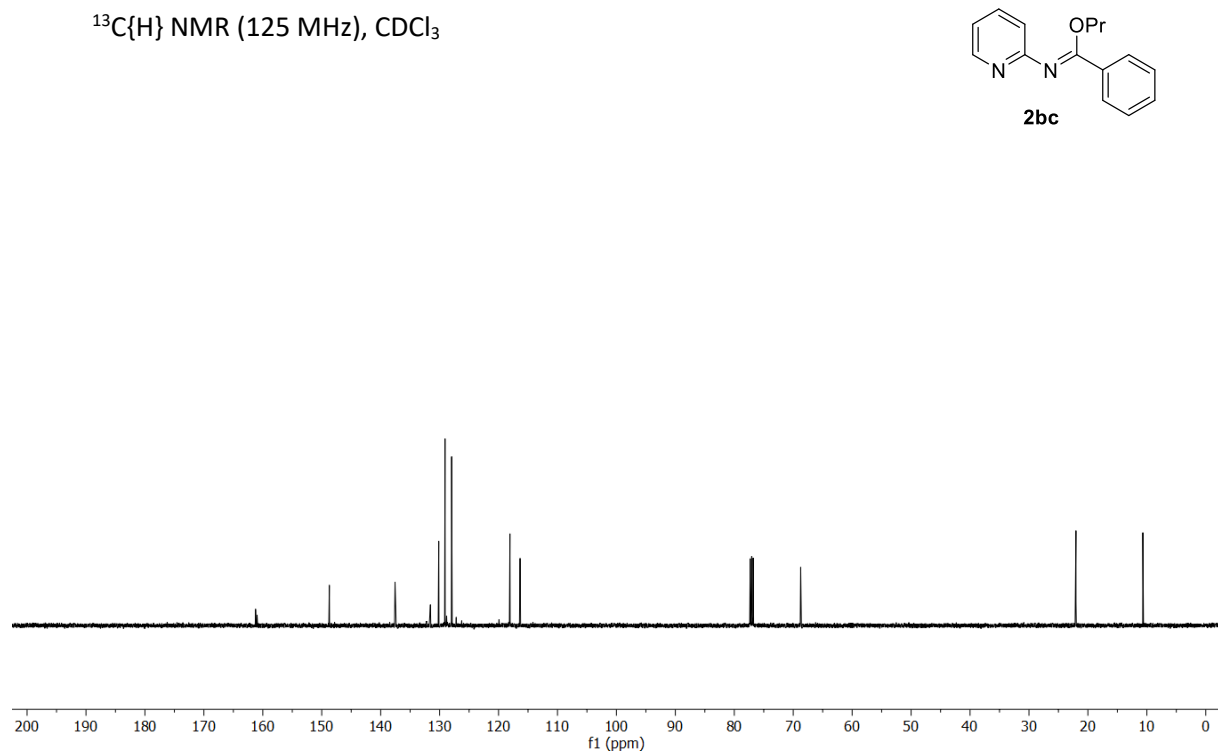
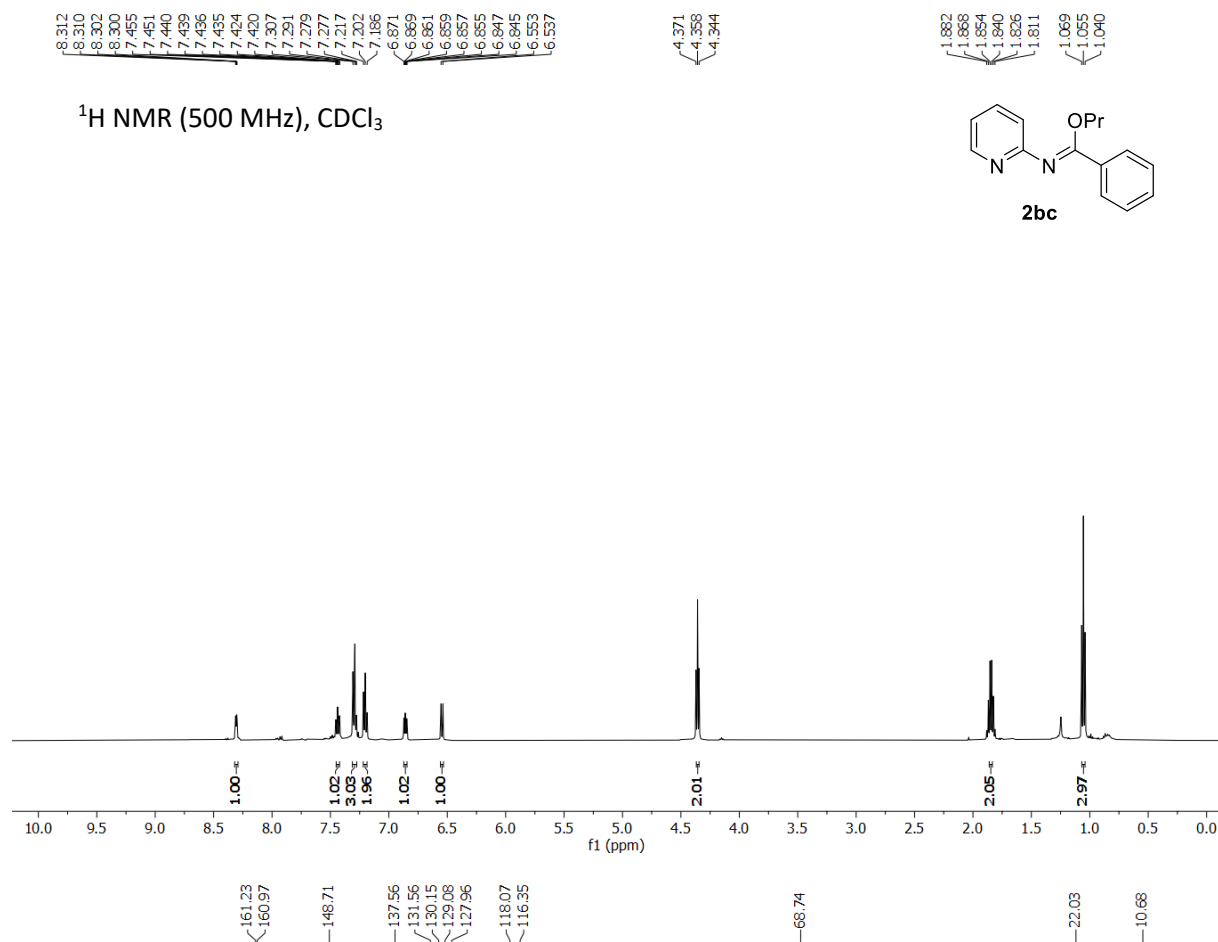


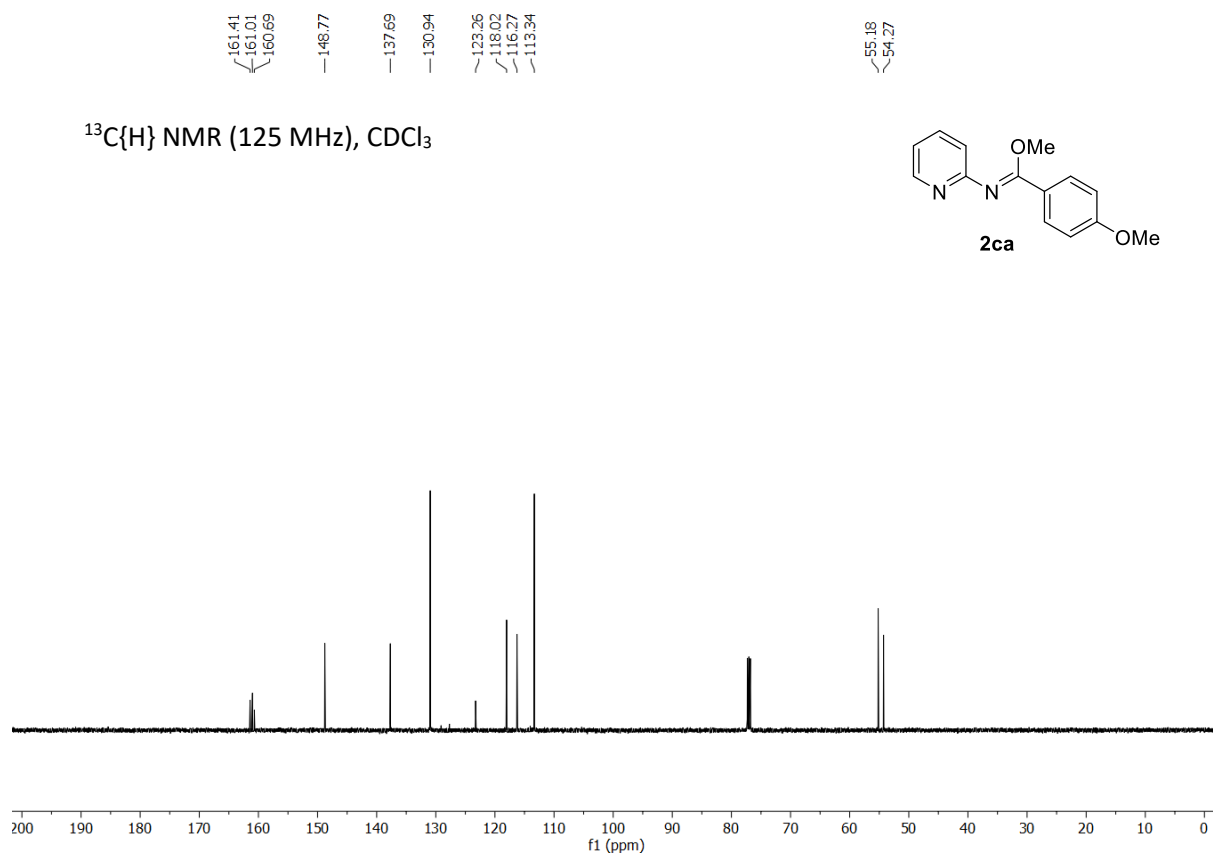
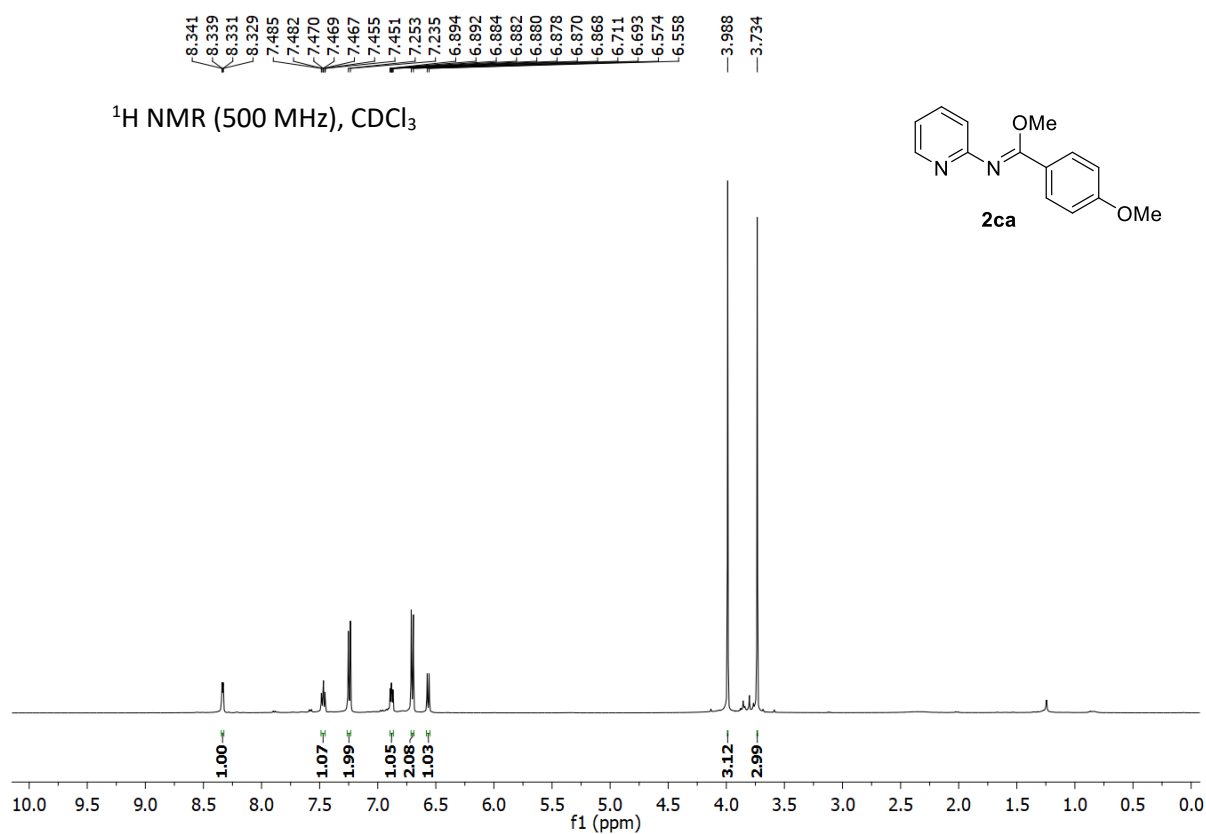


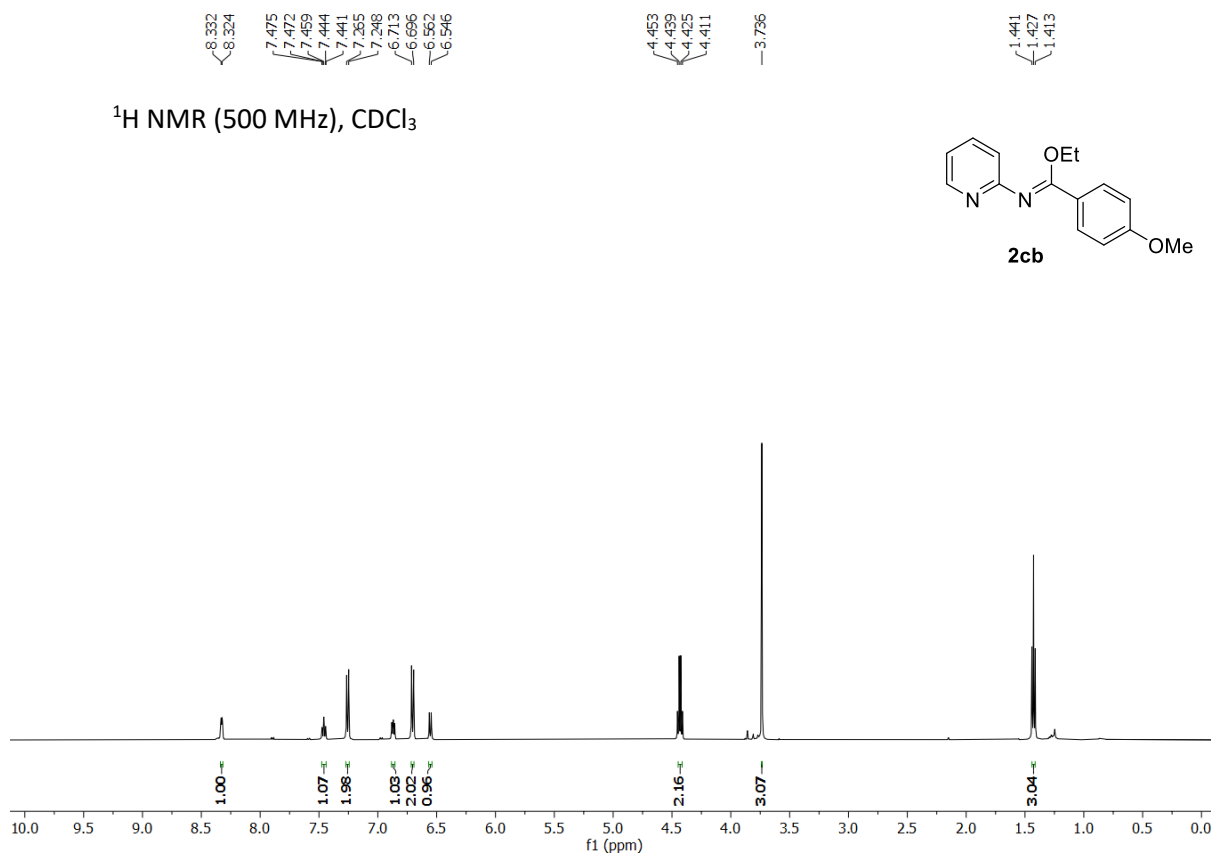
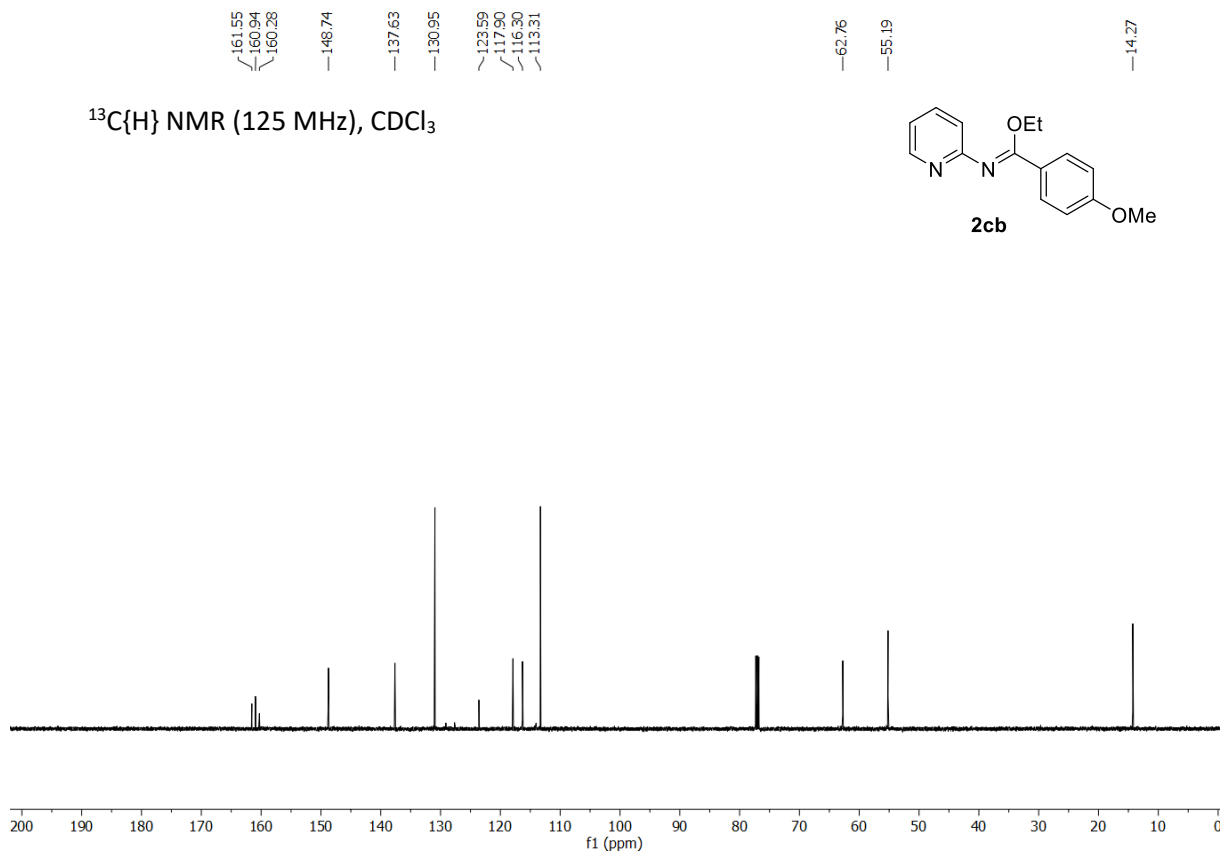


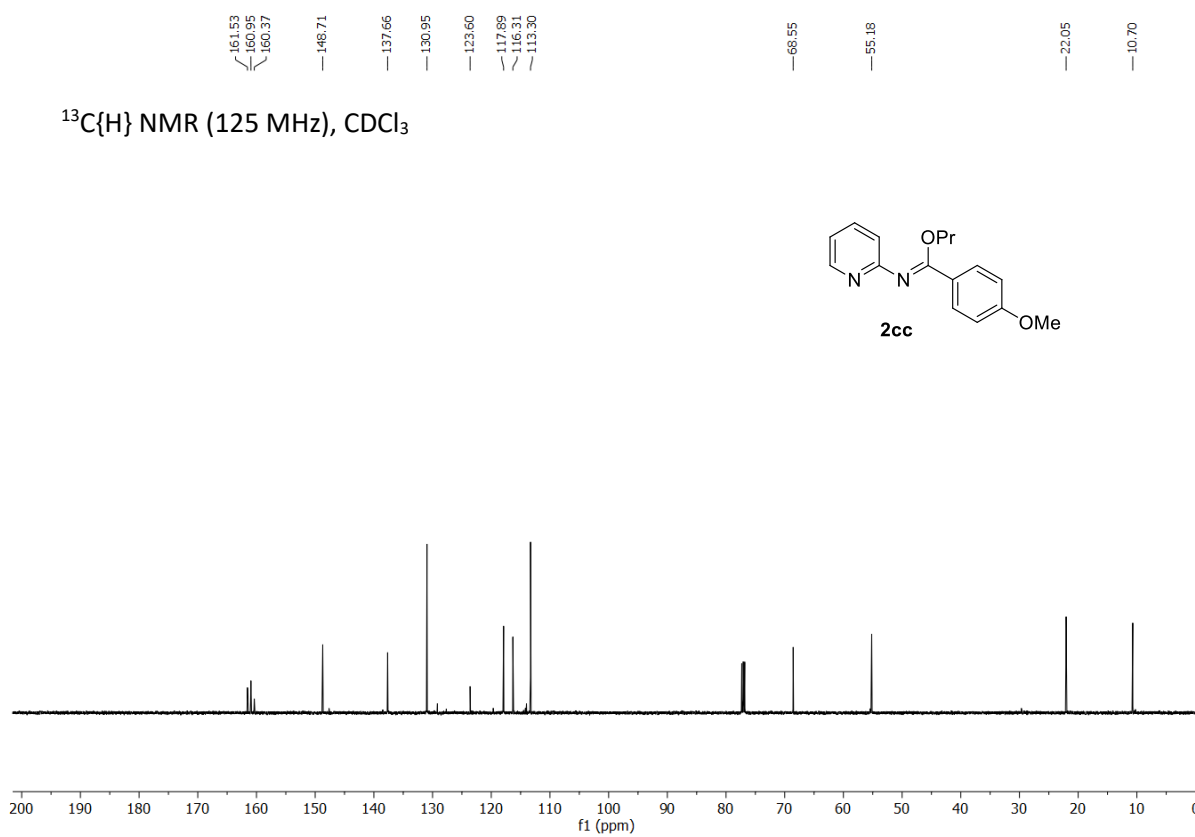
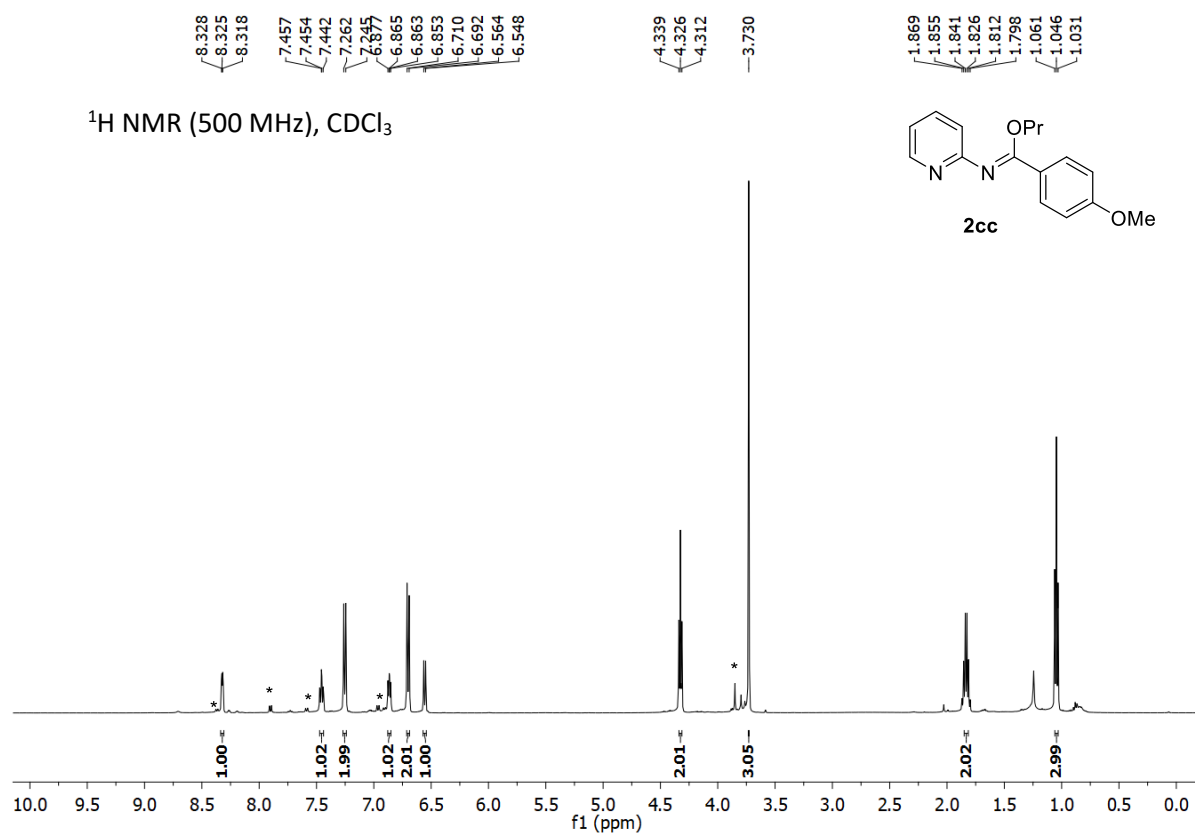
\*acetone

<sup>1</sup>H NMR (500 MHz), CDCl<sub>3</sub><sup>13</sup>C{H} NMR (125 MHz), CDCl<sub>3</sub>

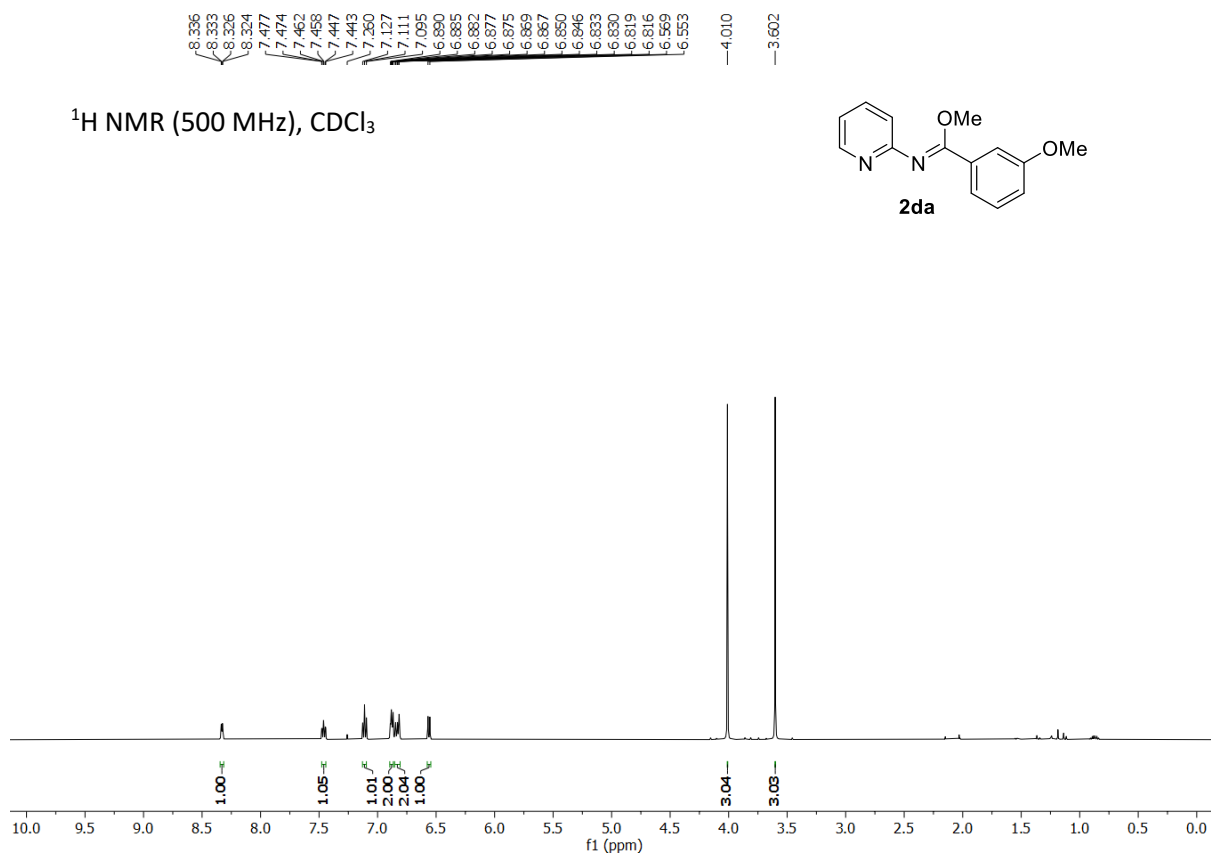
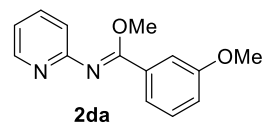
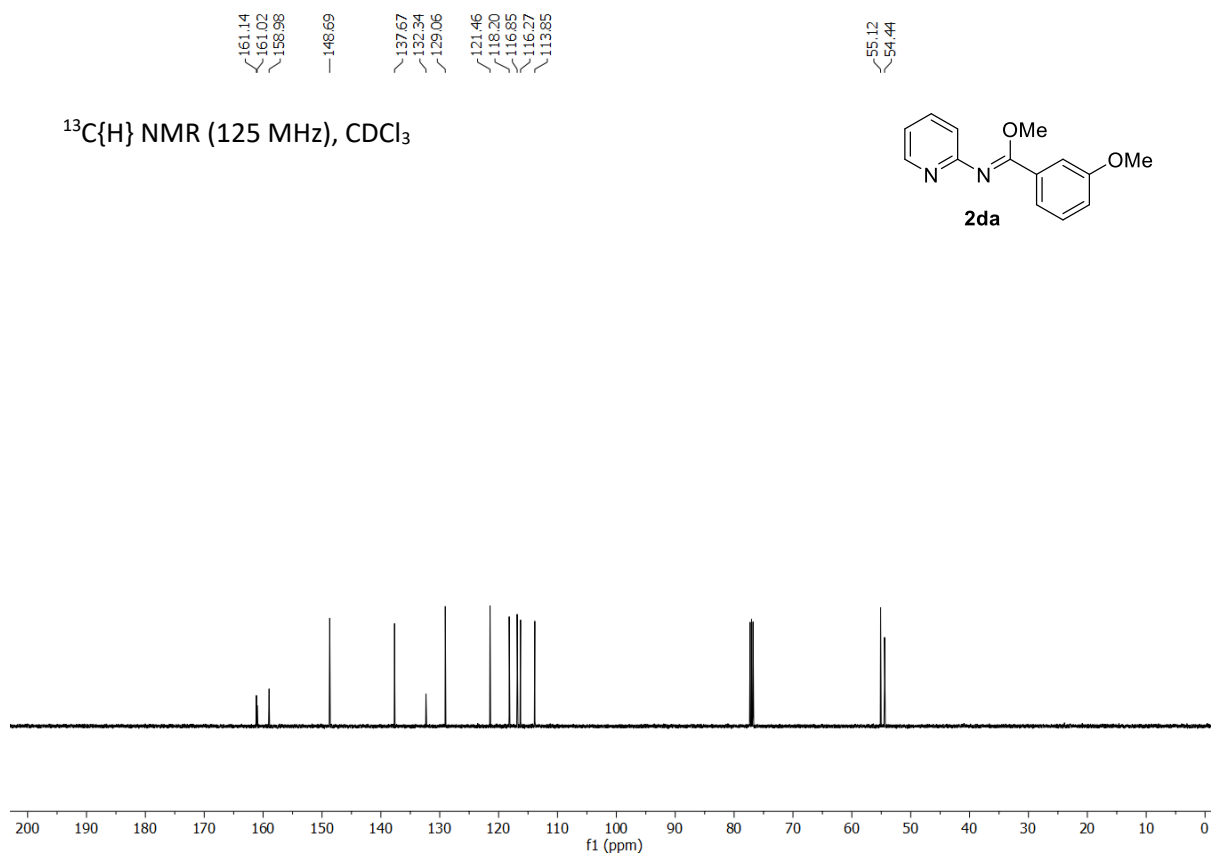
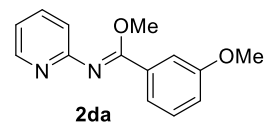


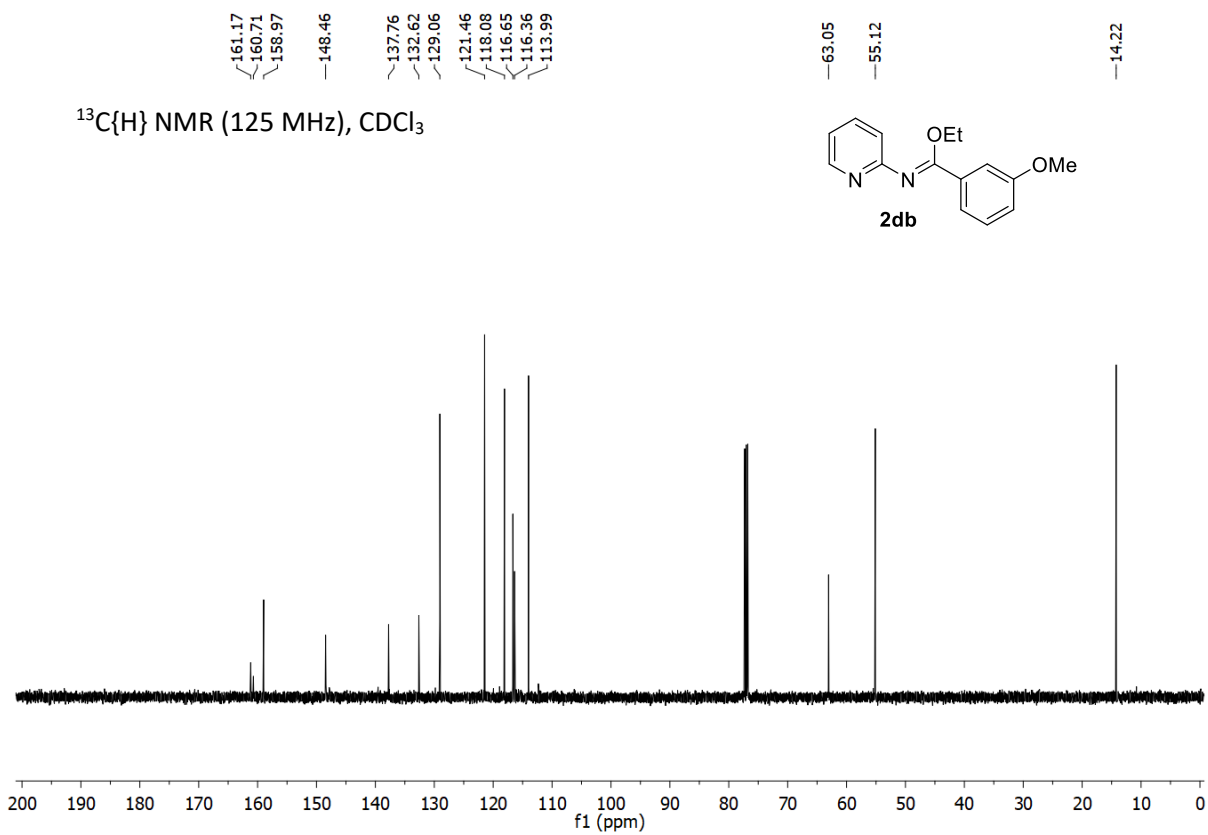
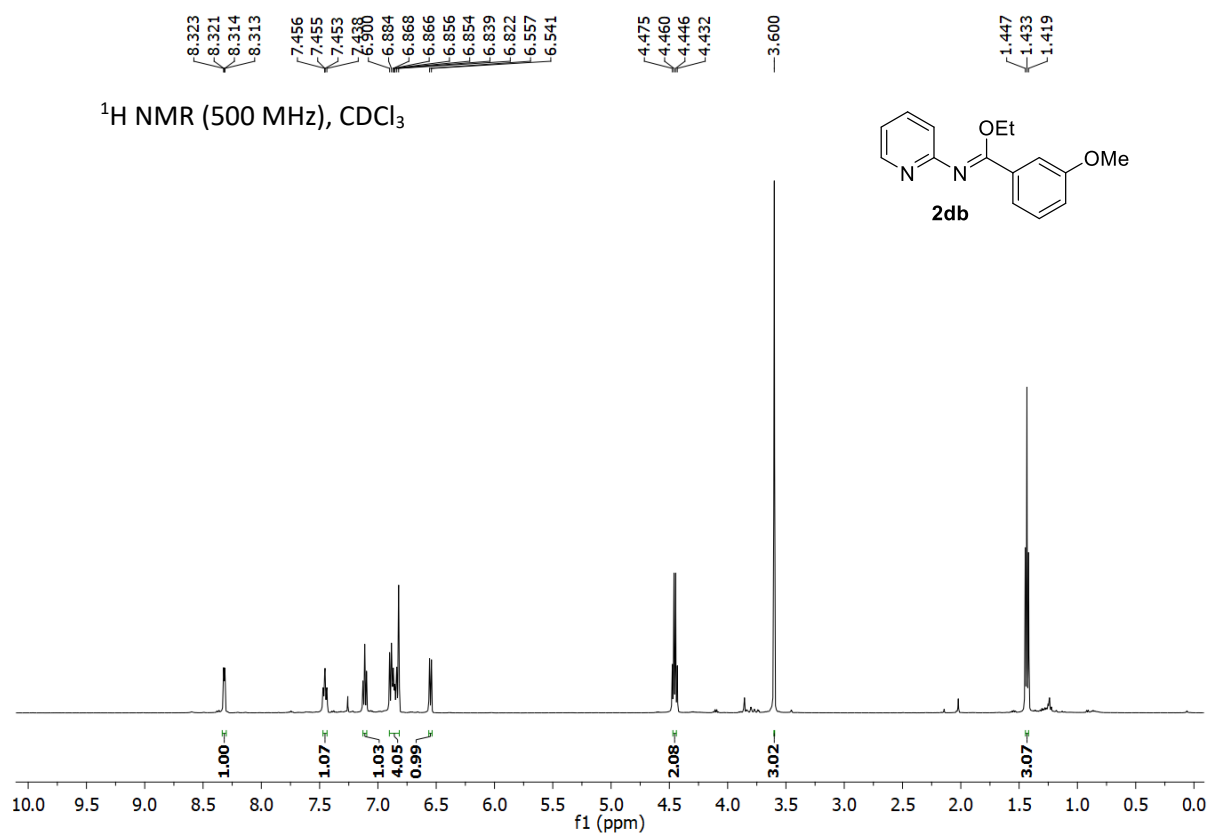


$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 

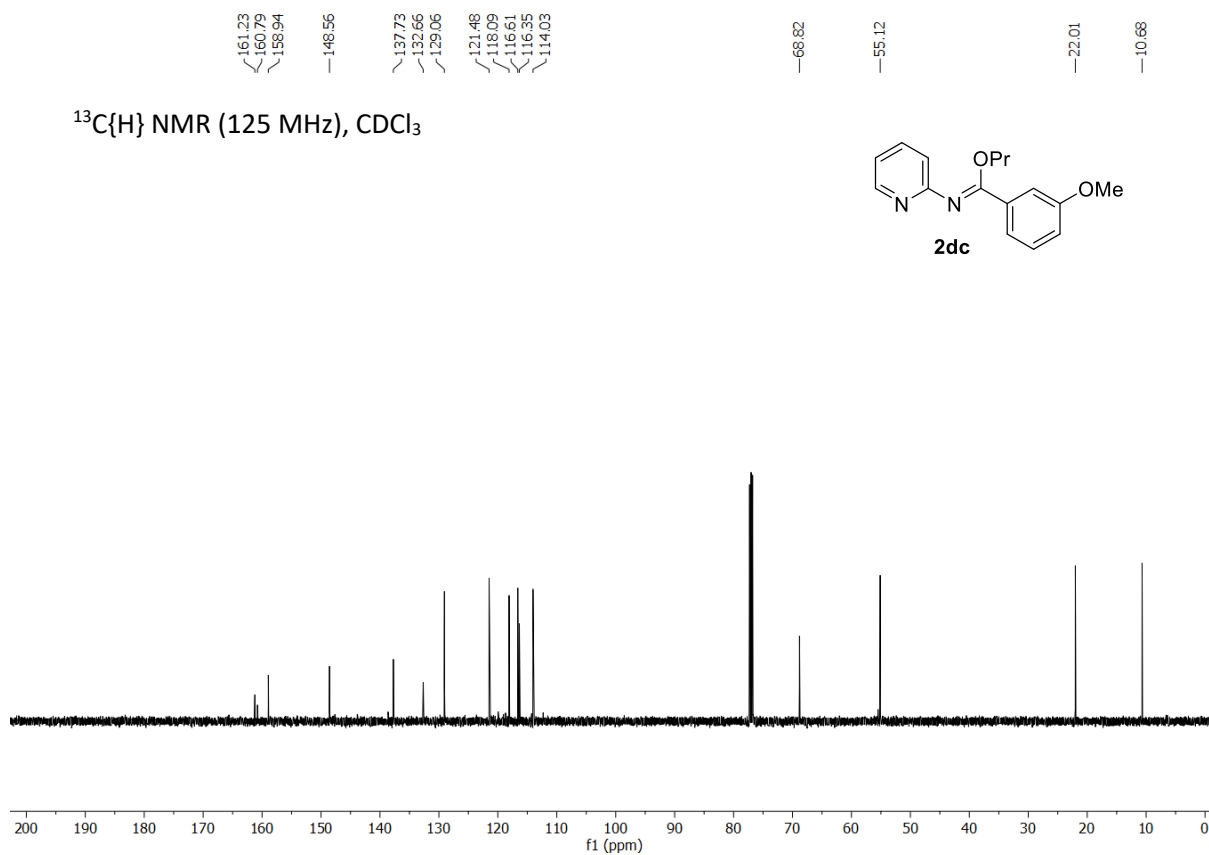
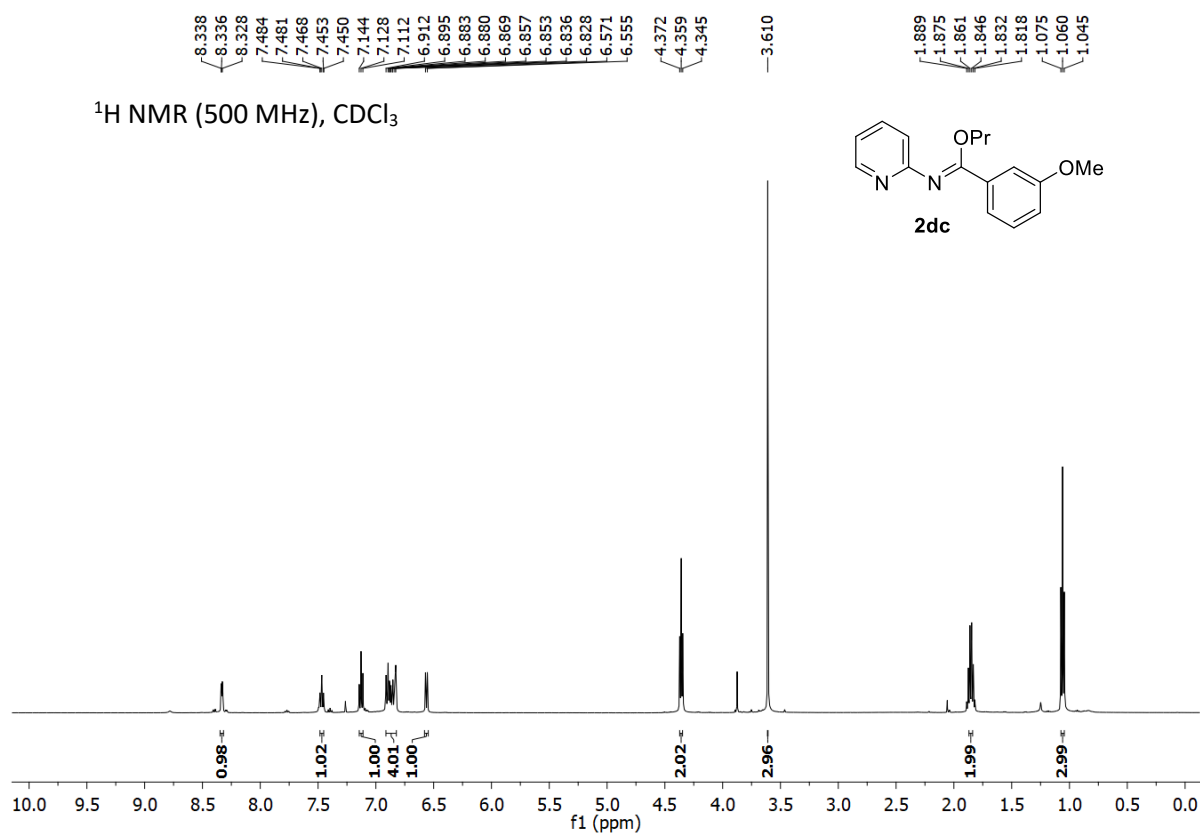


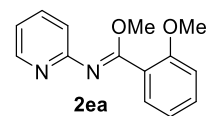
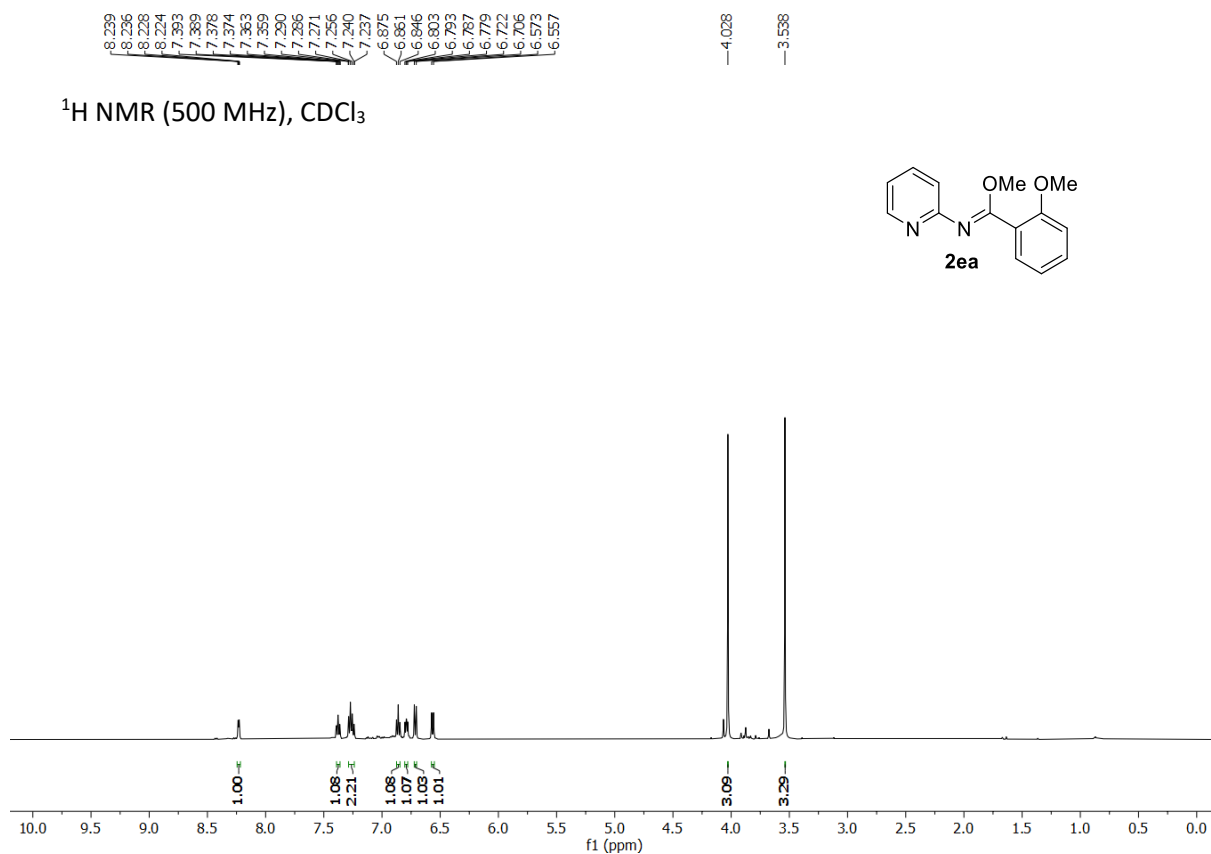
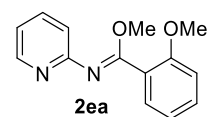
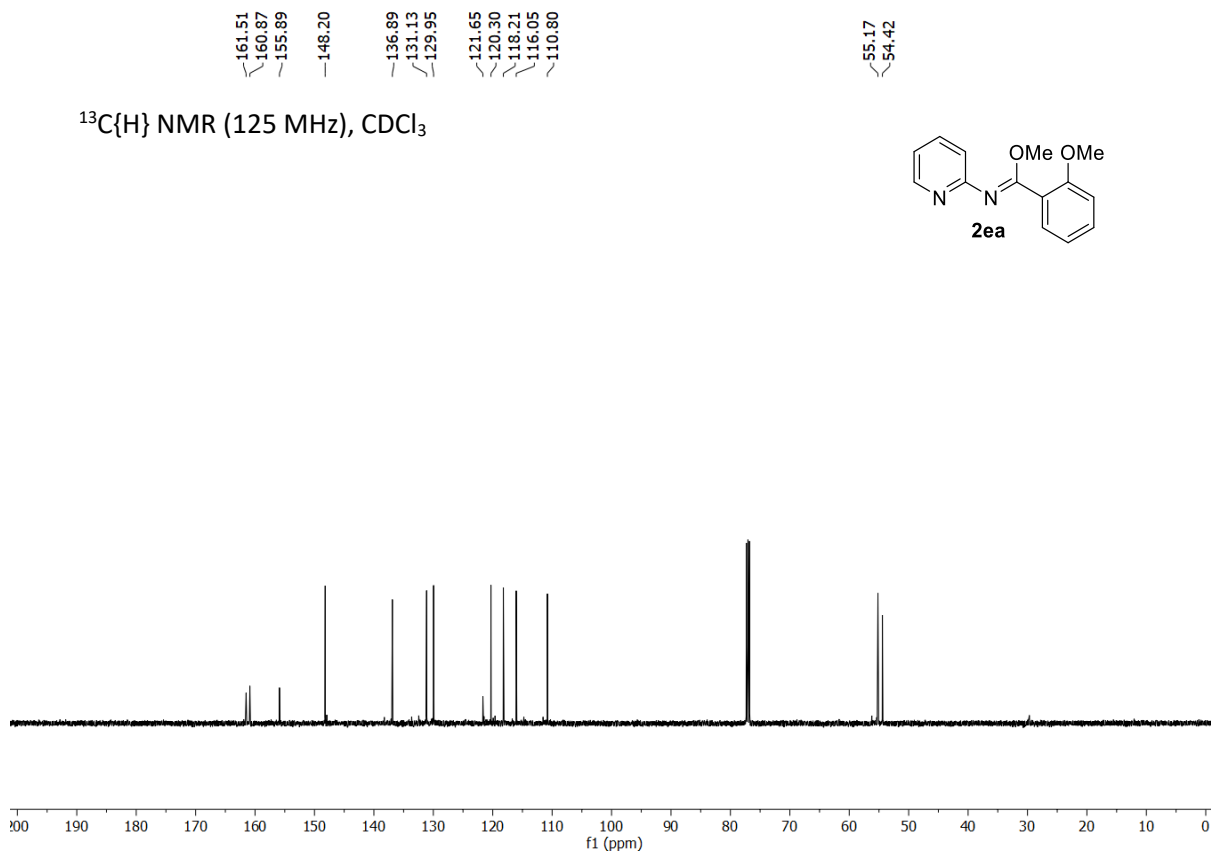
\*corresponding amide

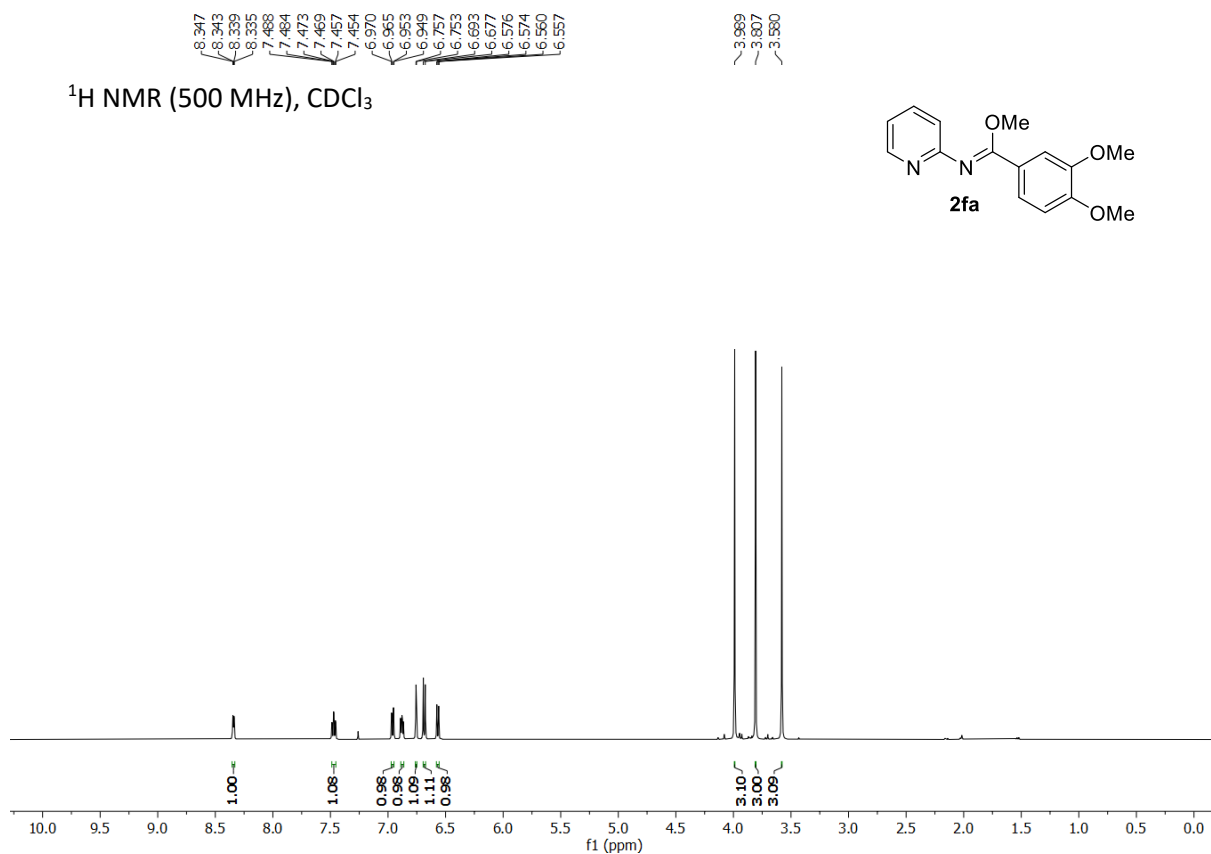
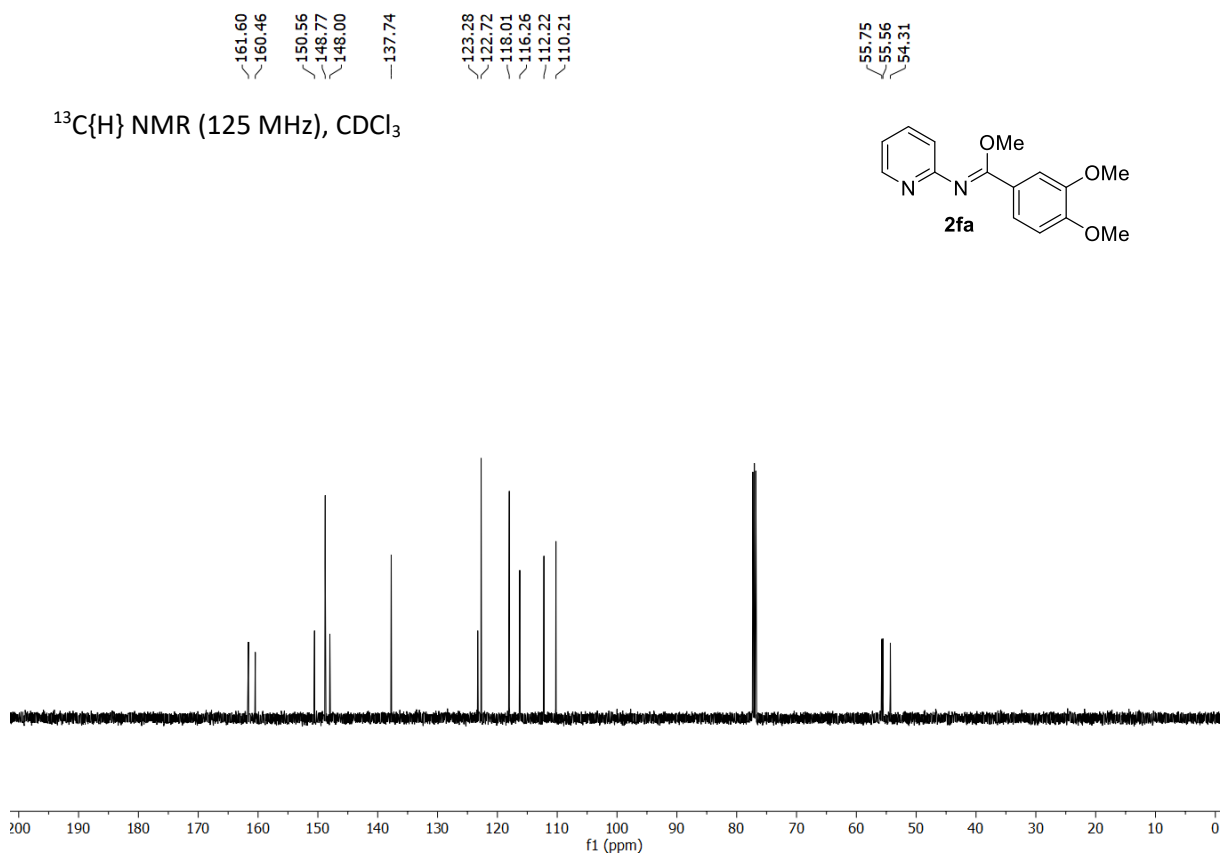
$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 

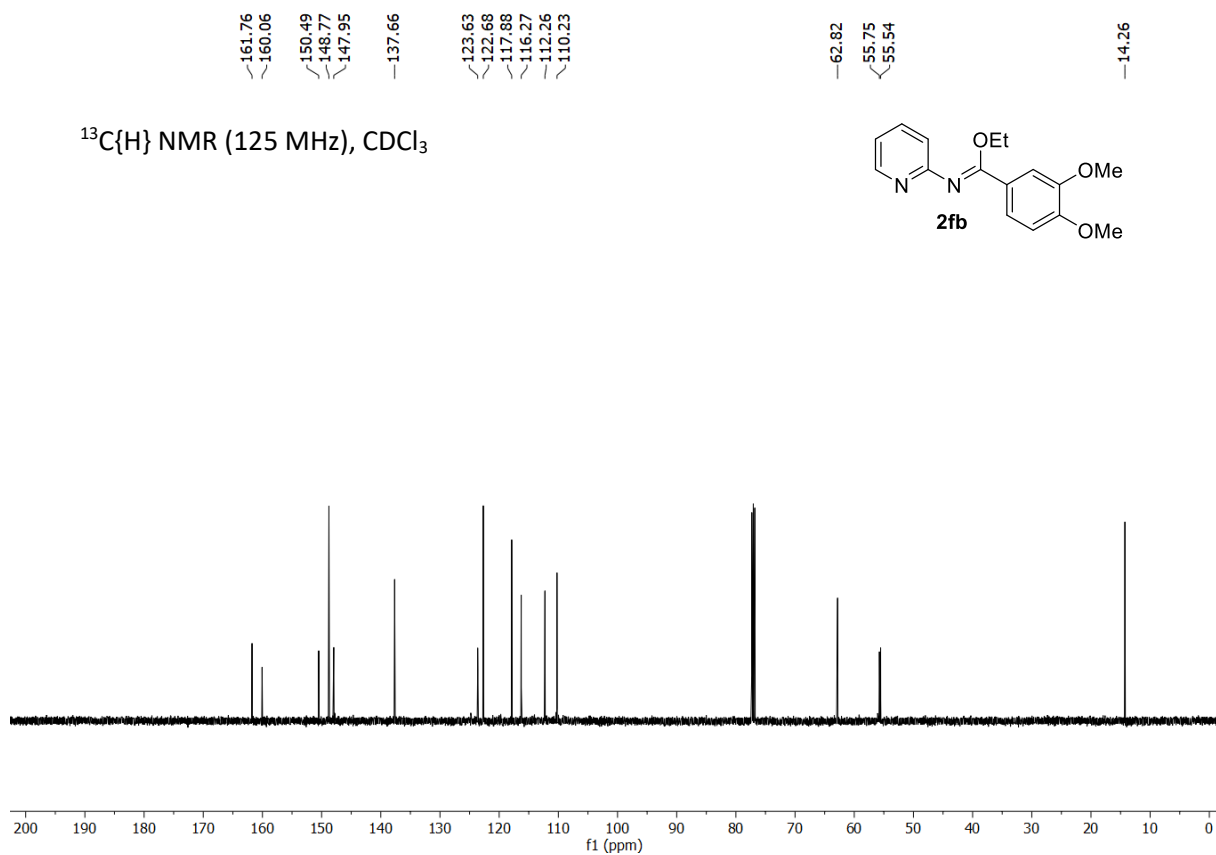
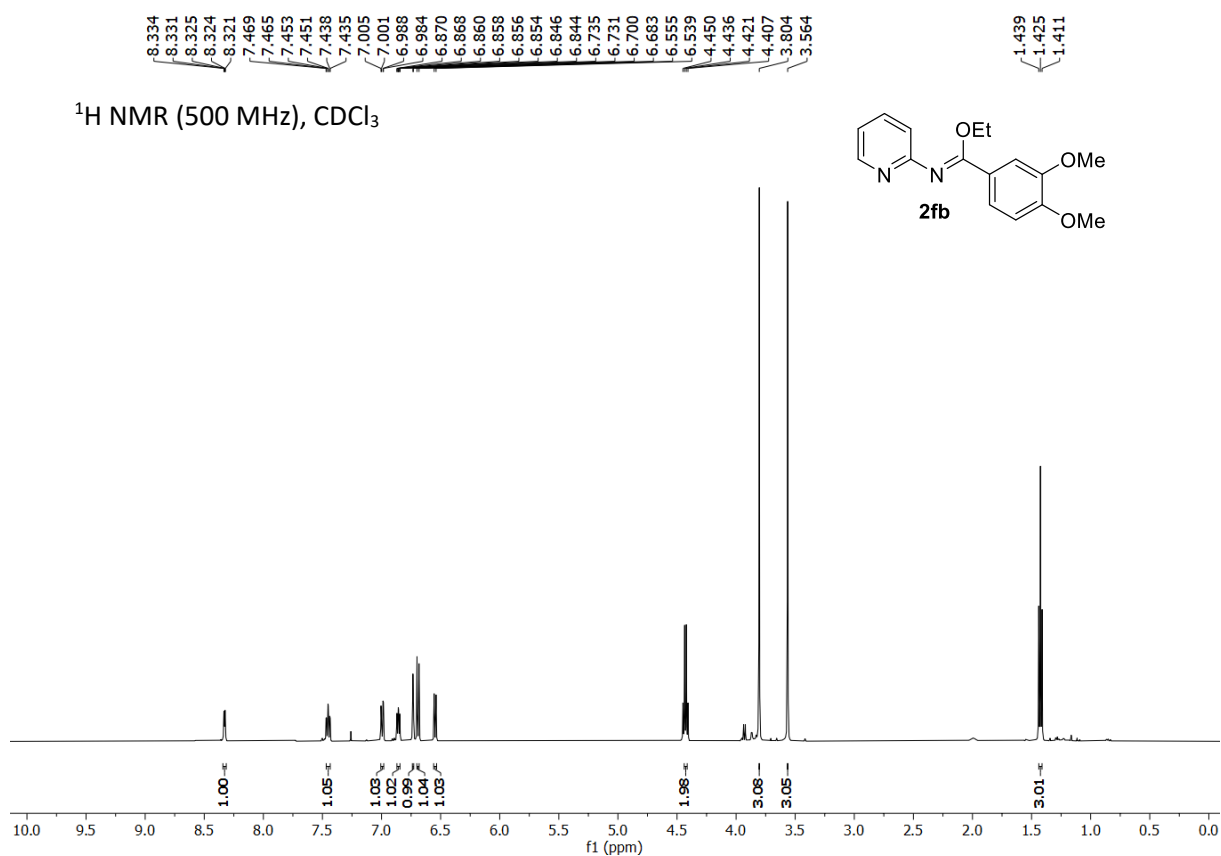


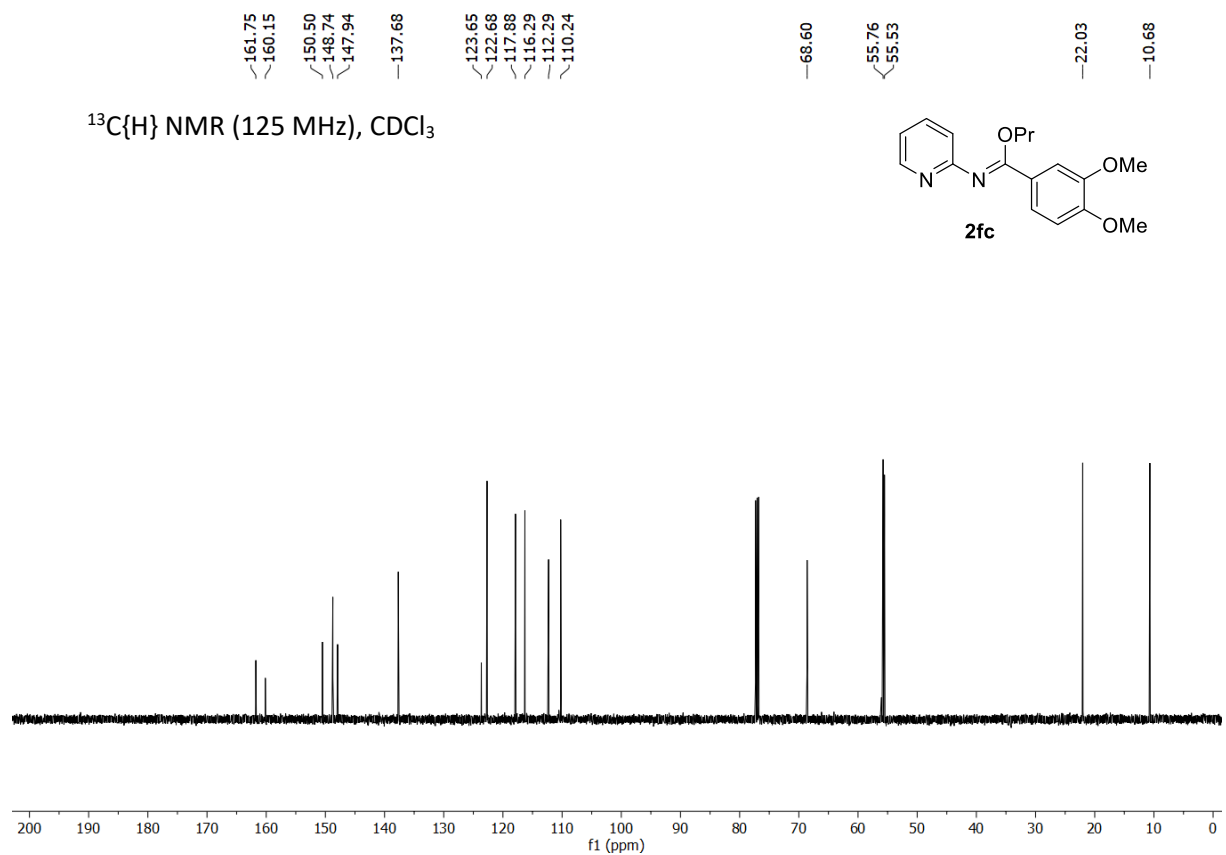
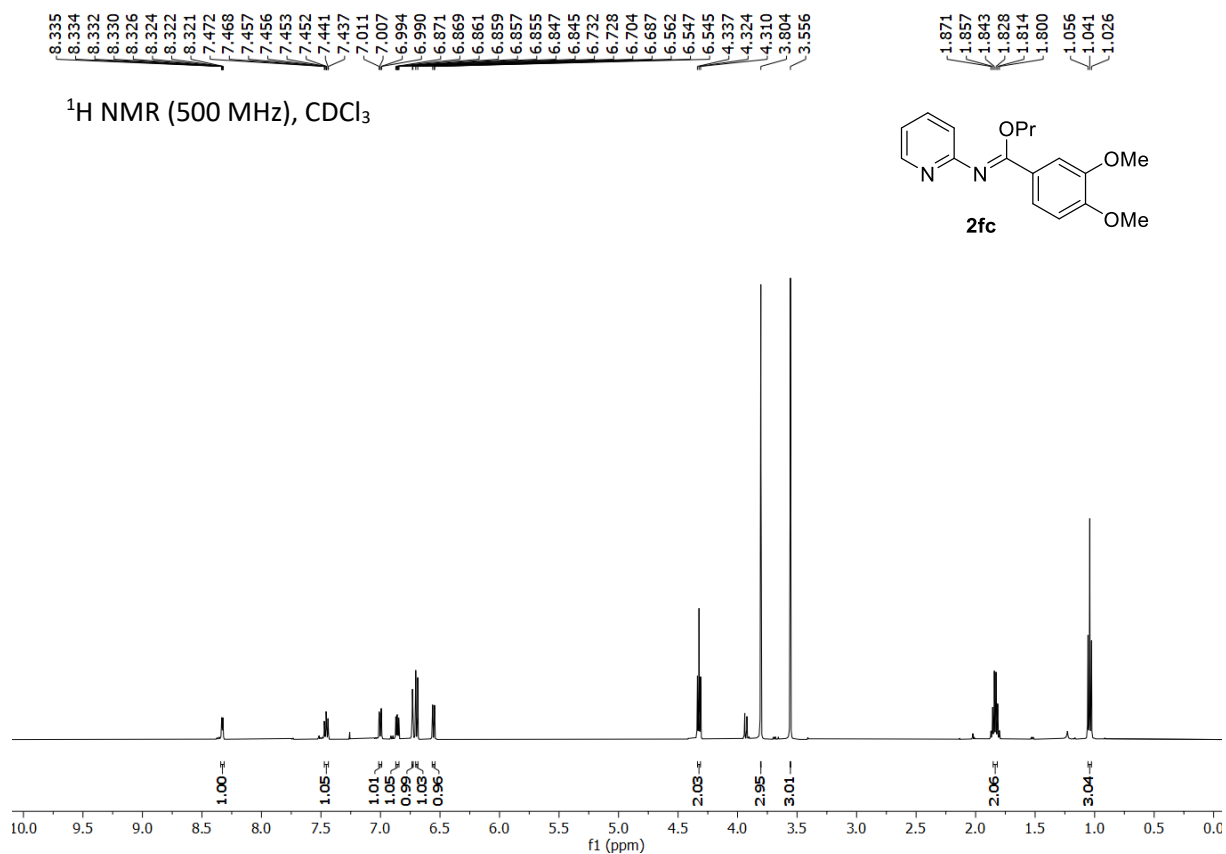


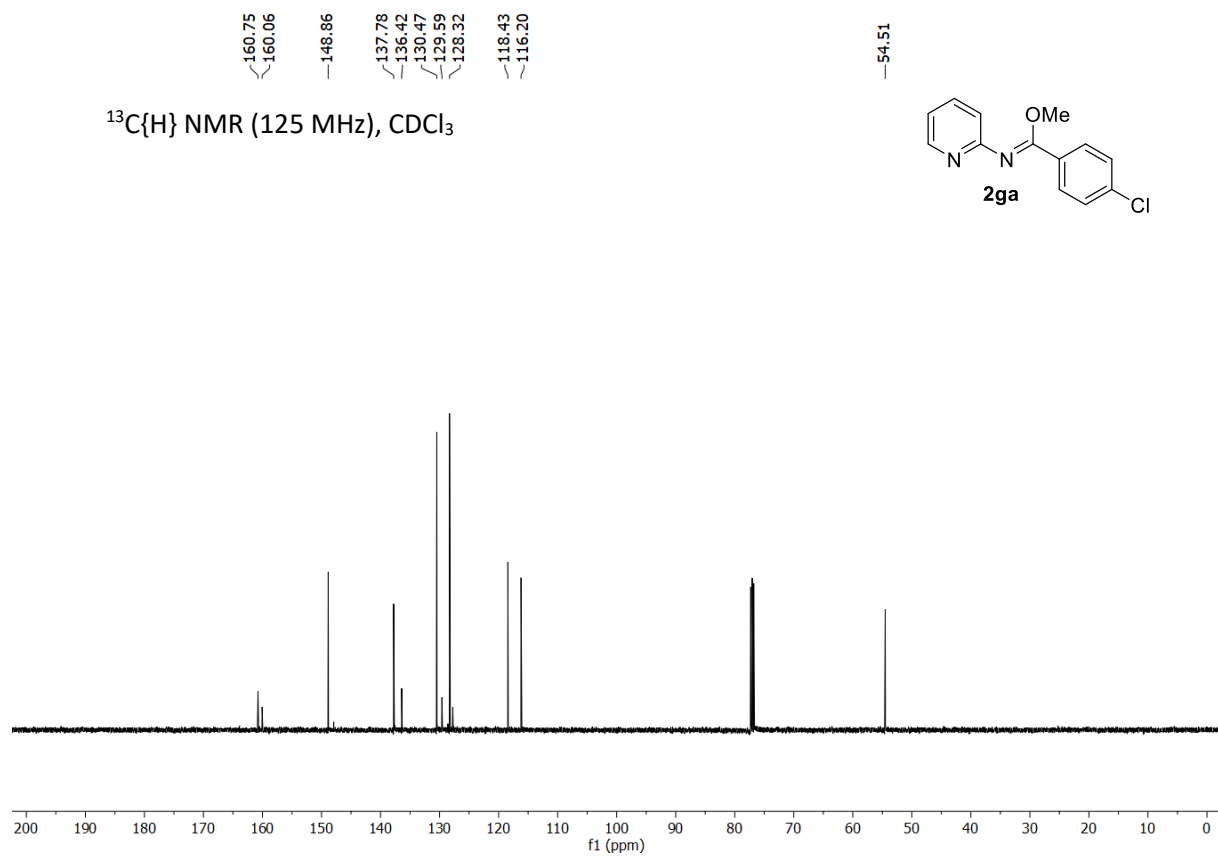
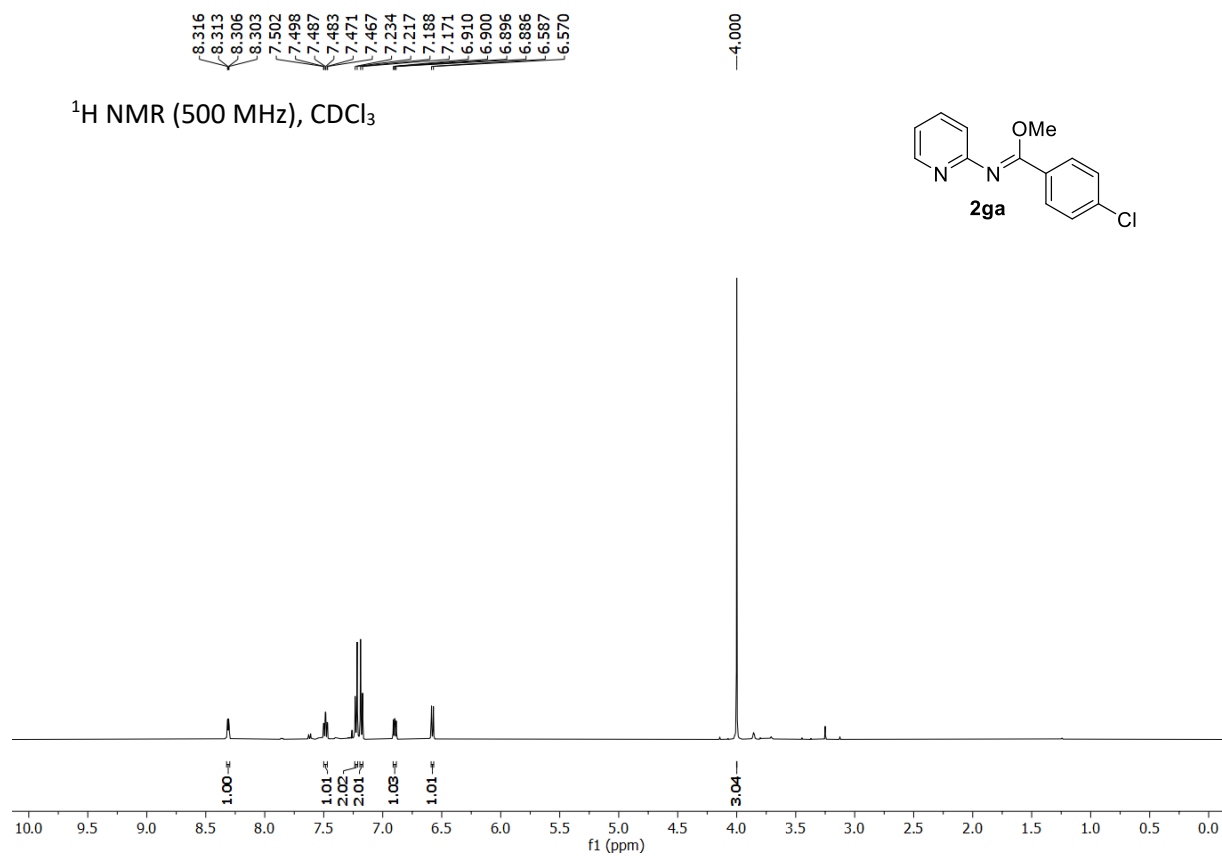


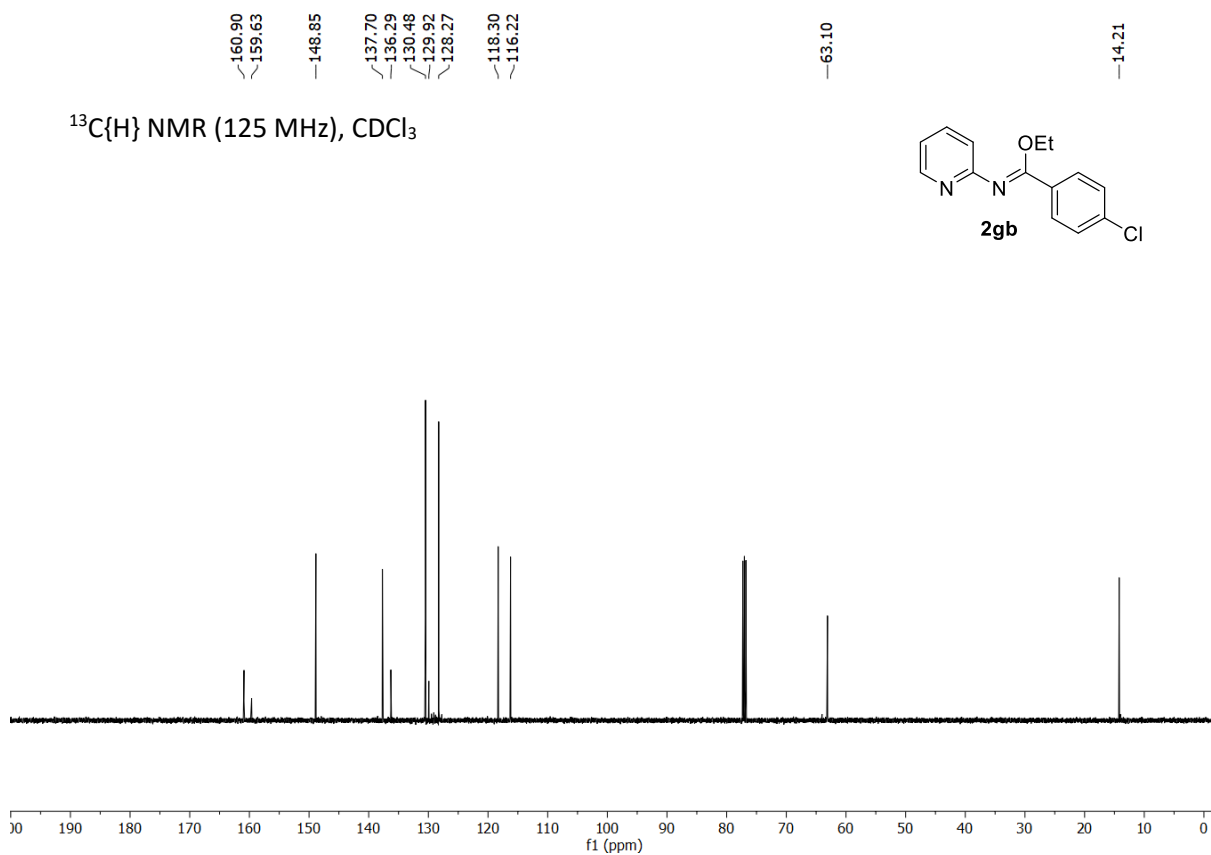
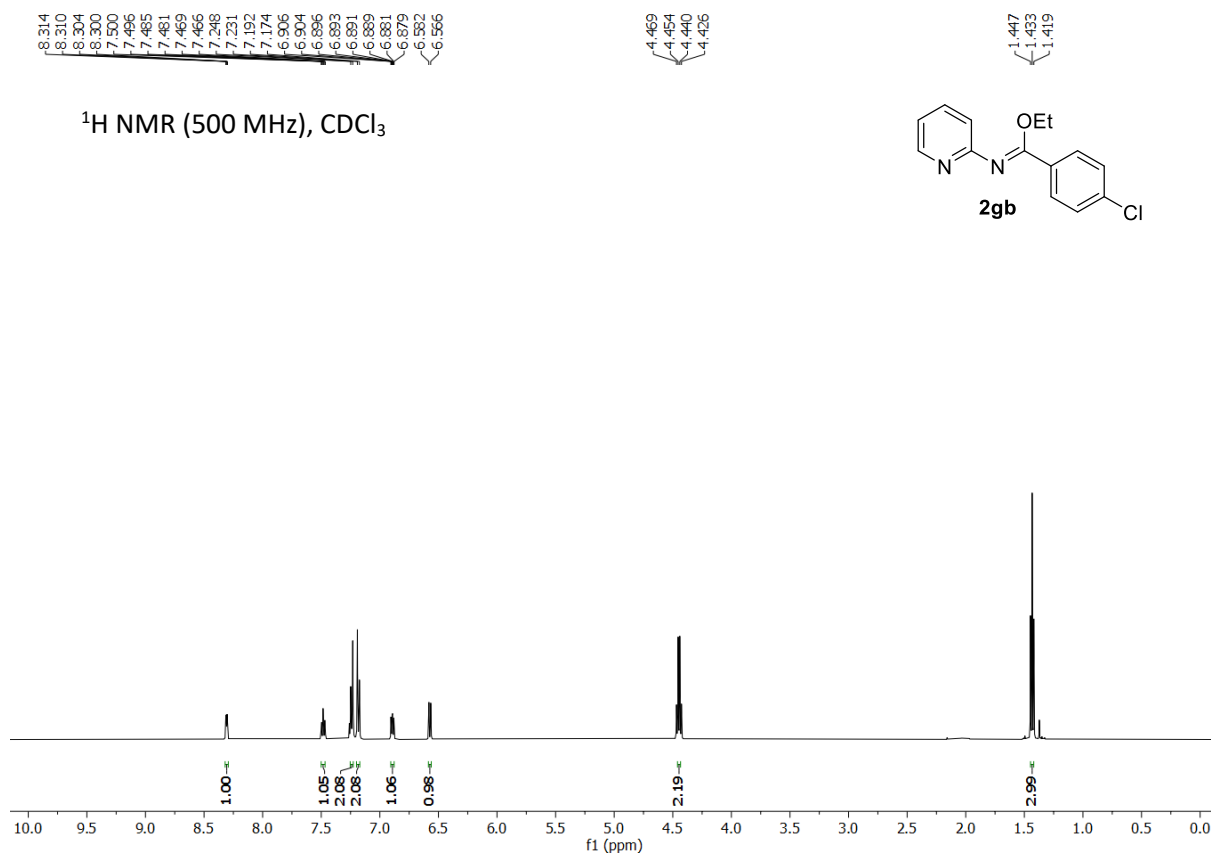
$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 

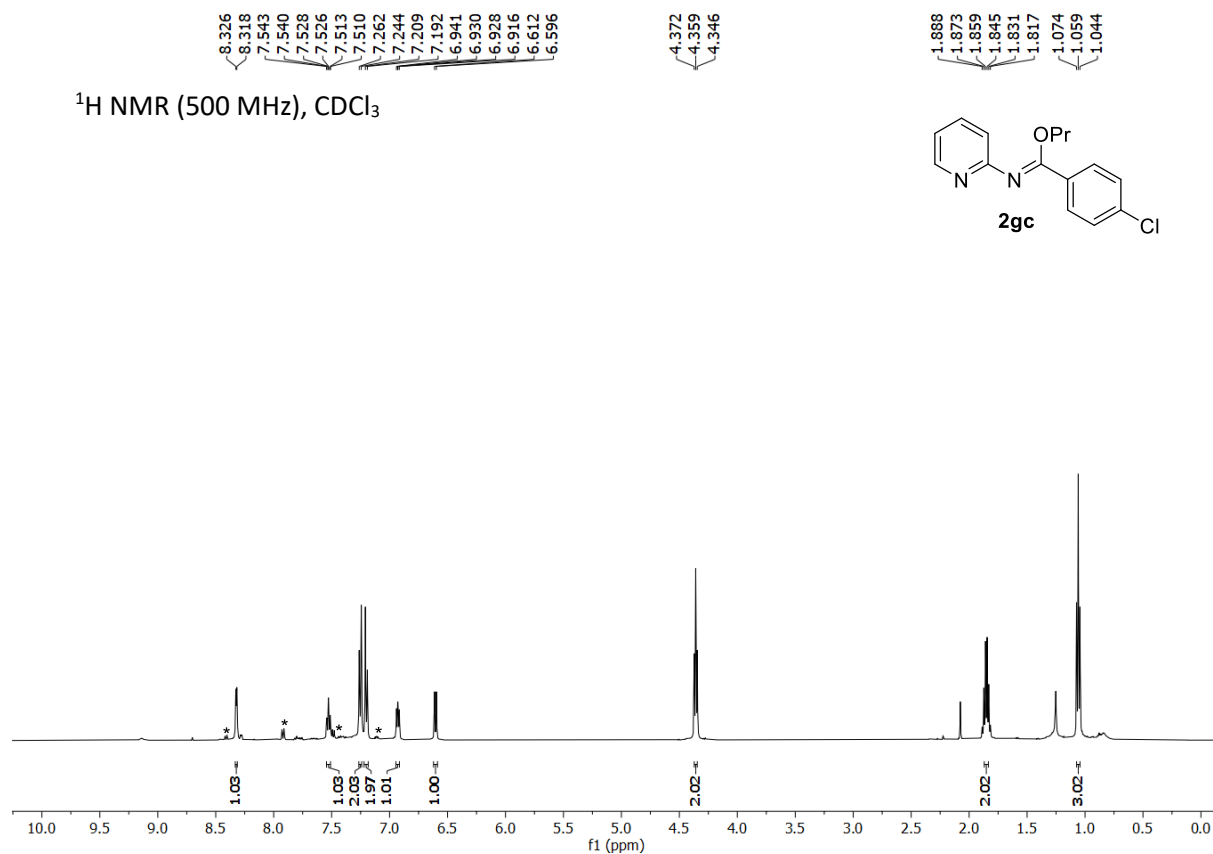
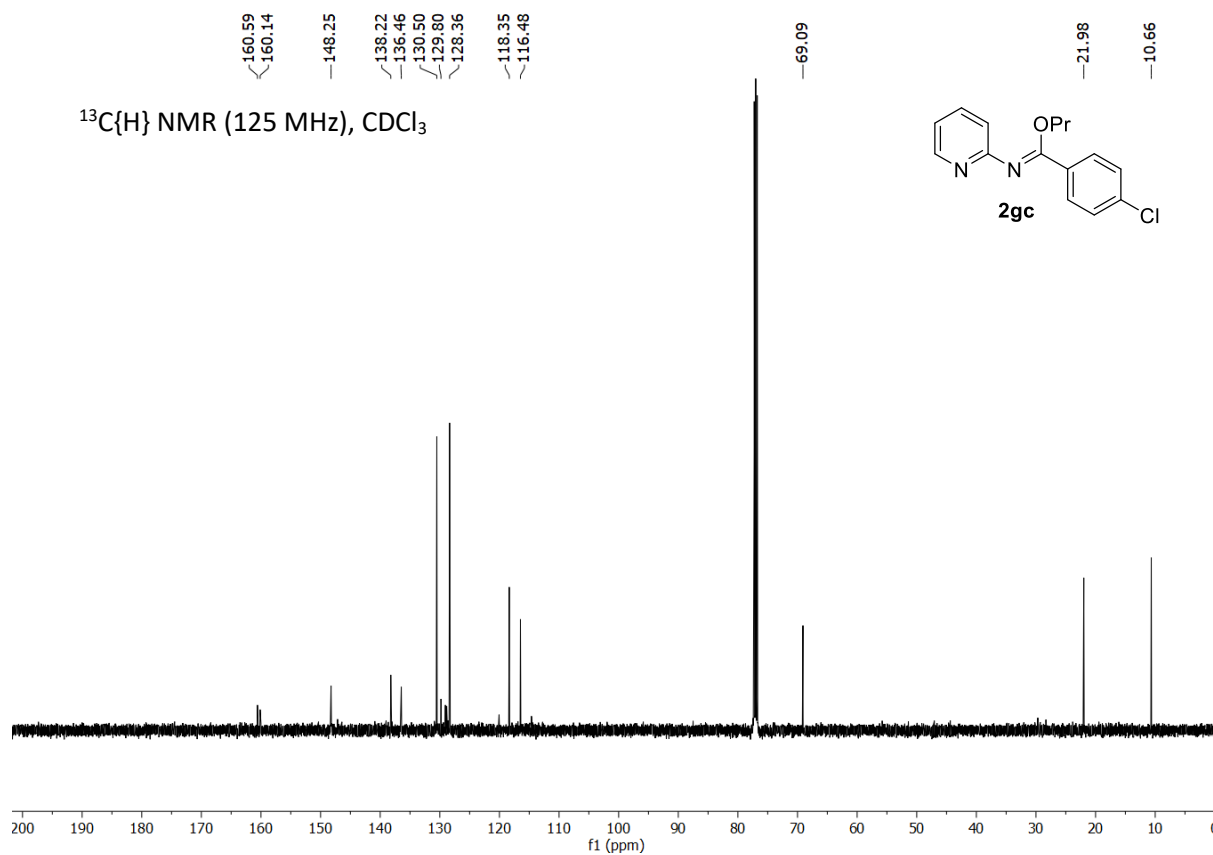
$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 





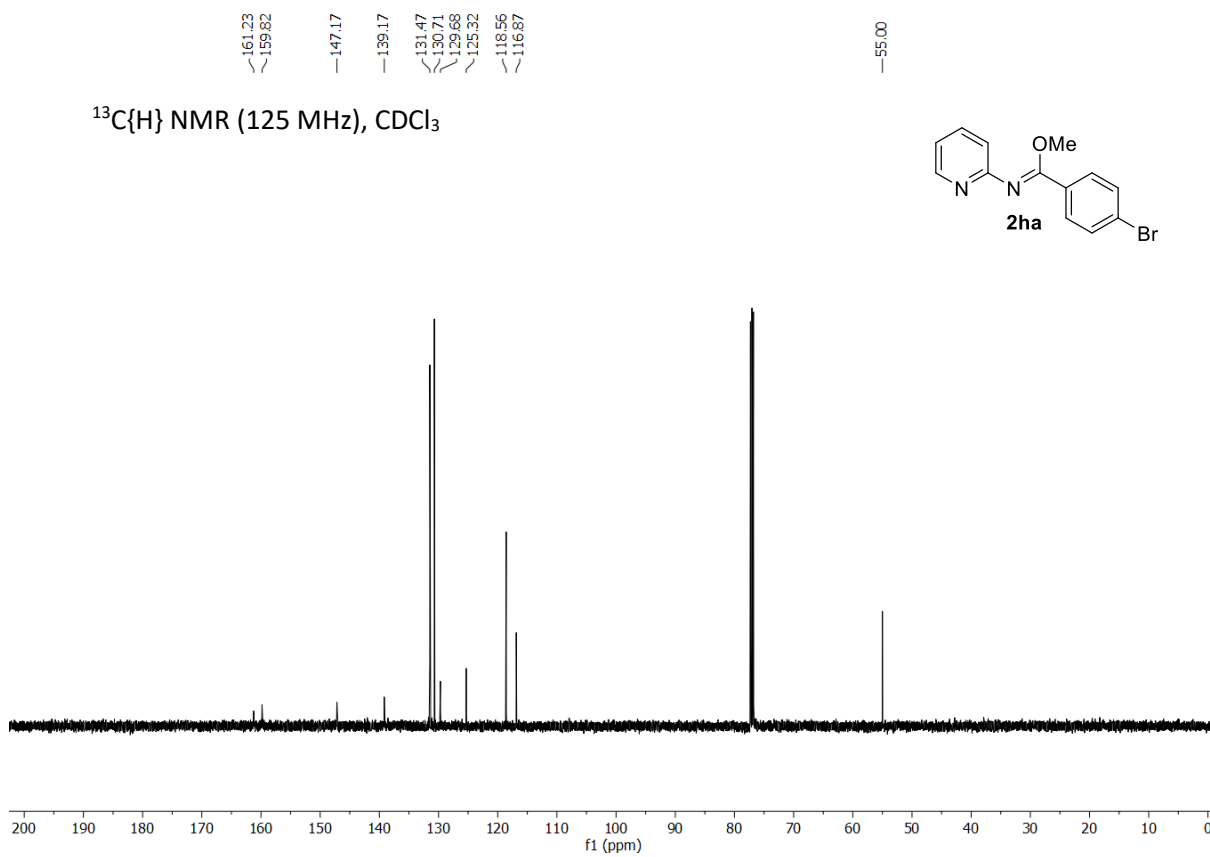
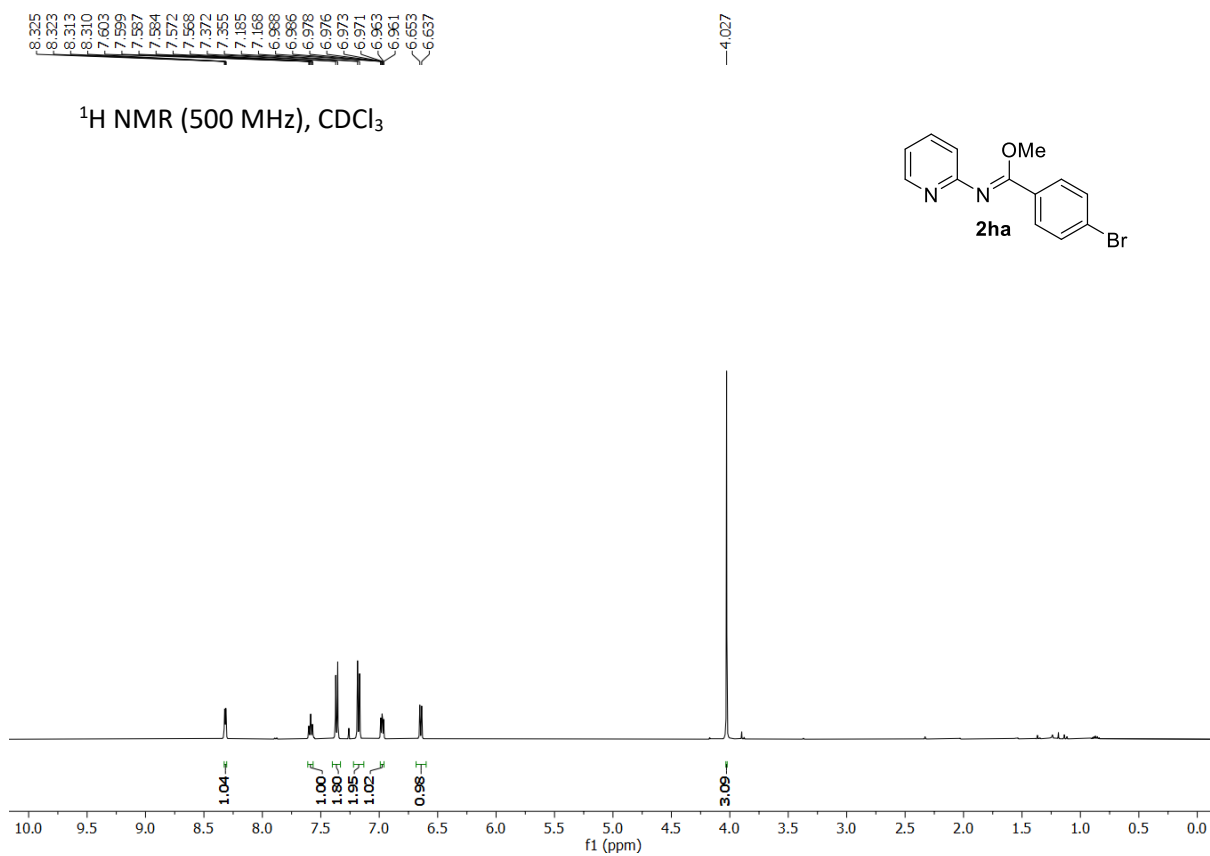


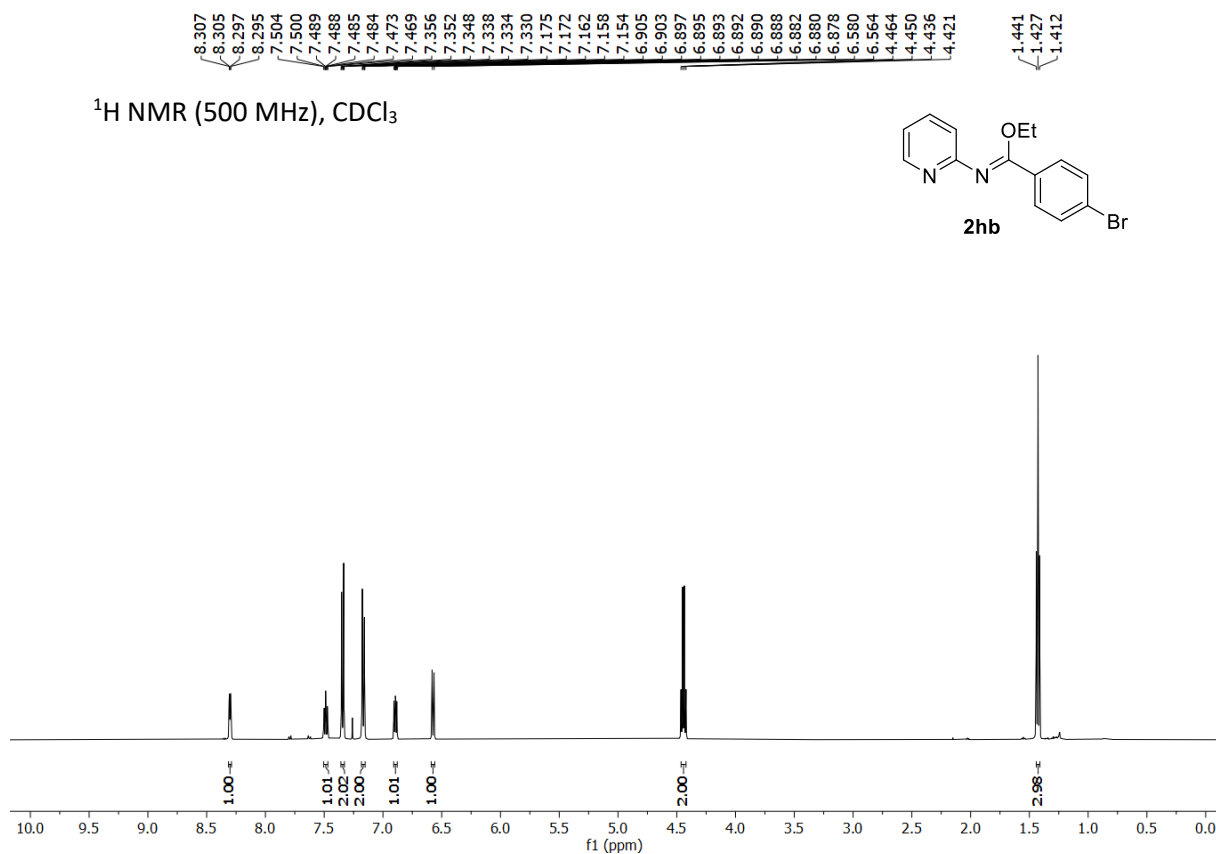
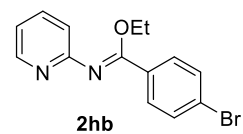
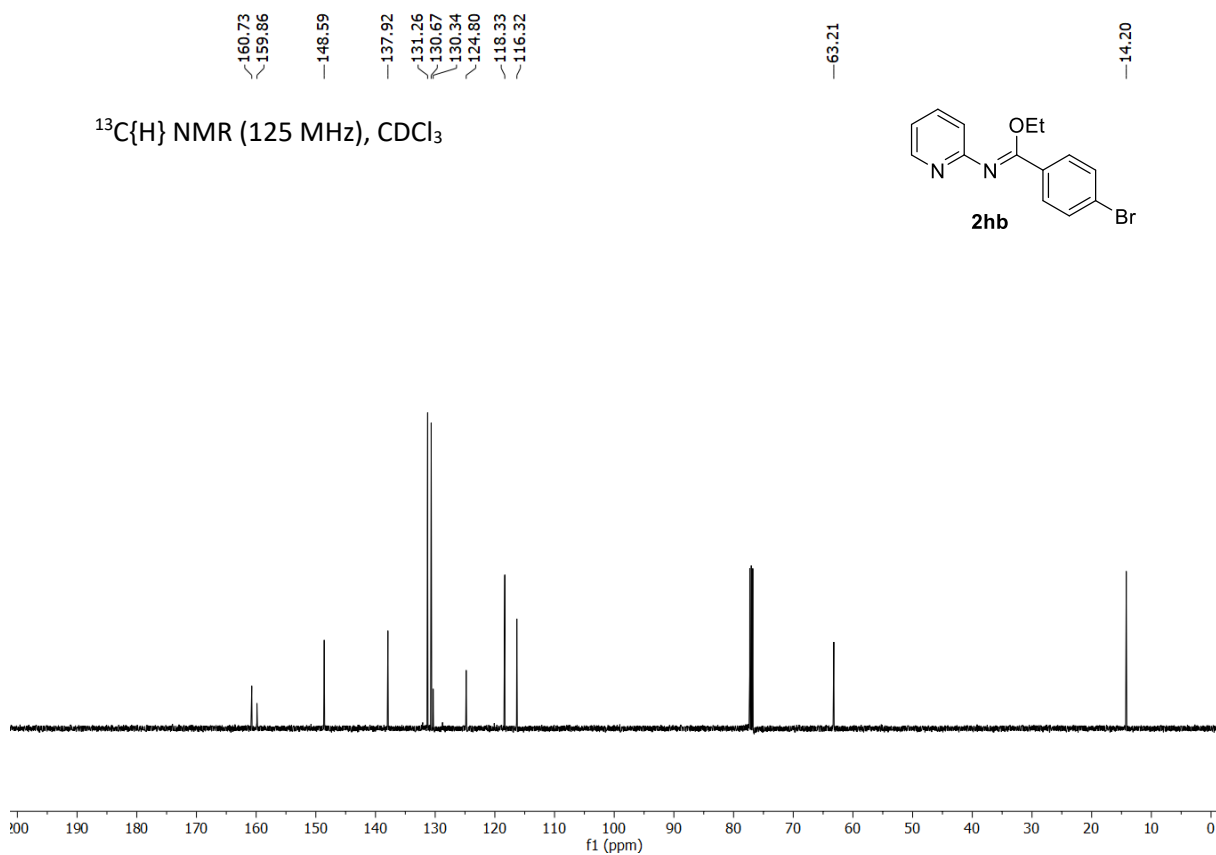
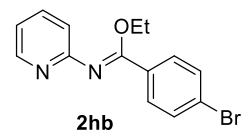


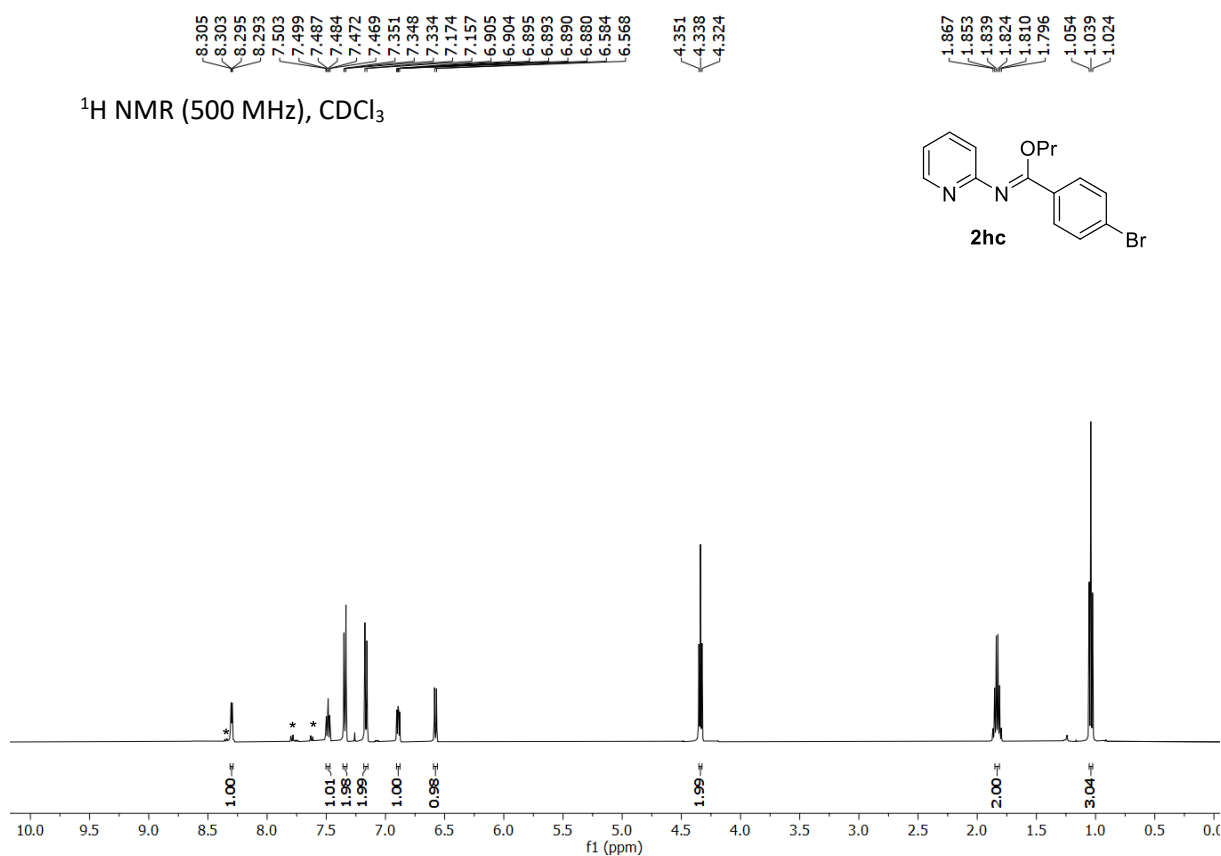
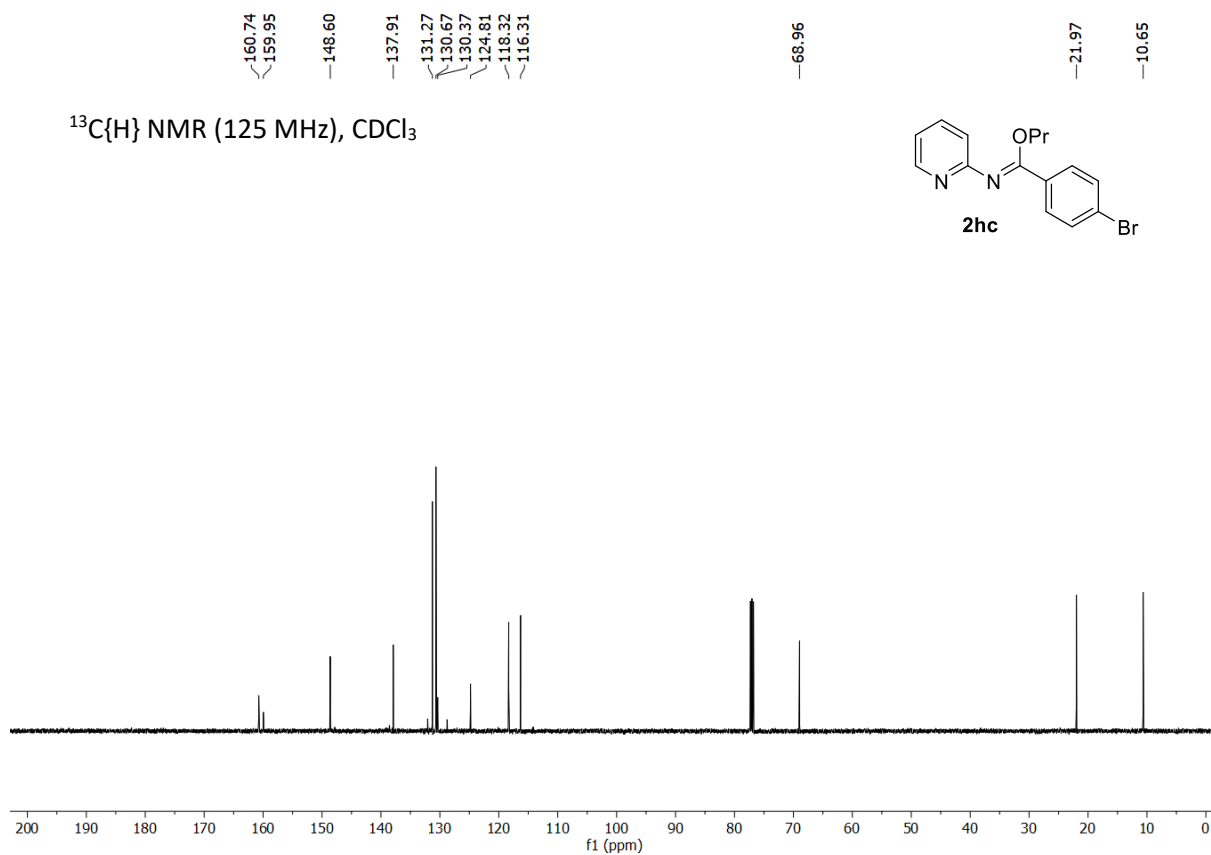
$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 

\*corresponding amide

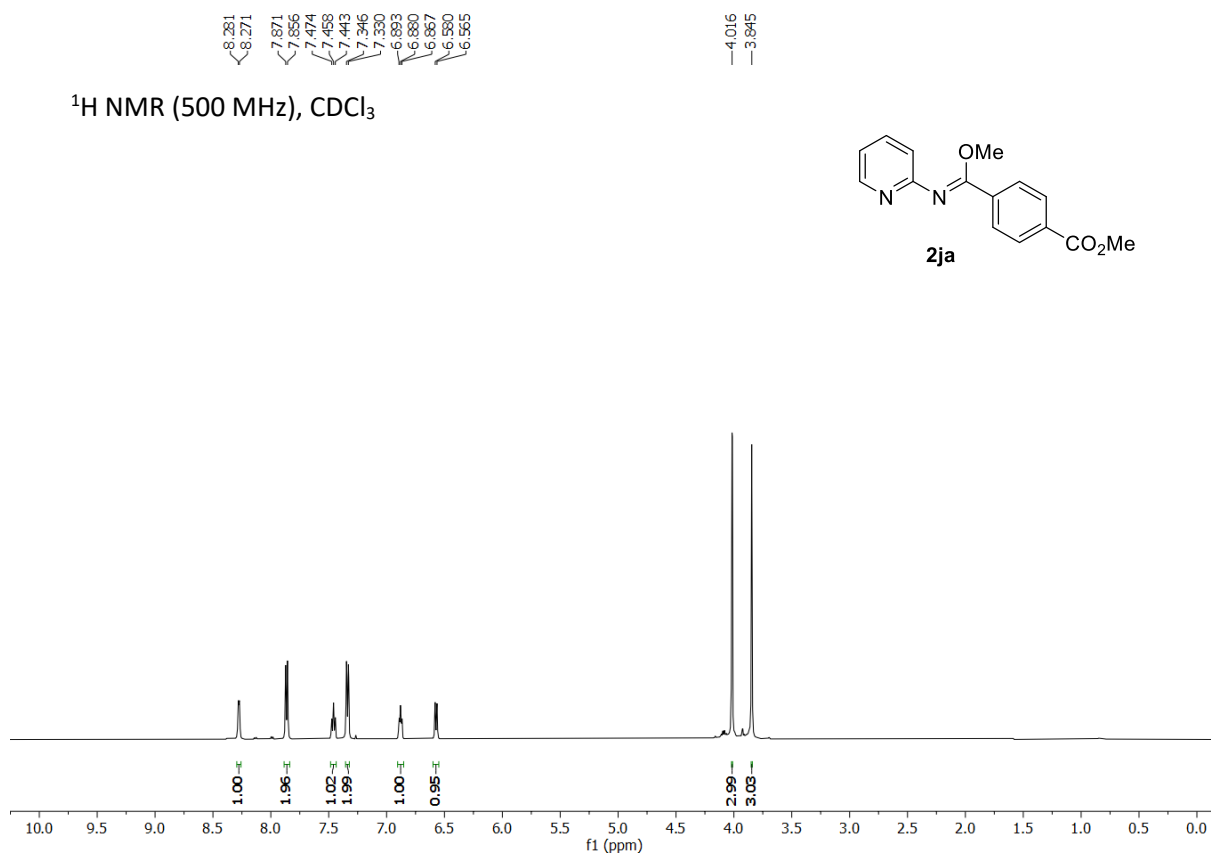
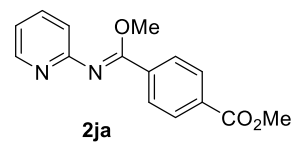
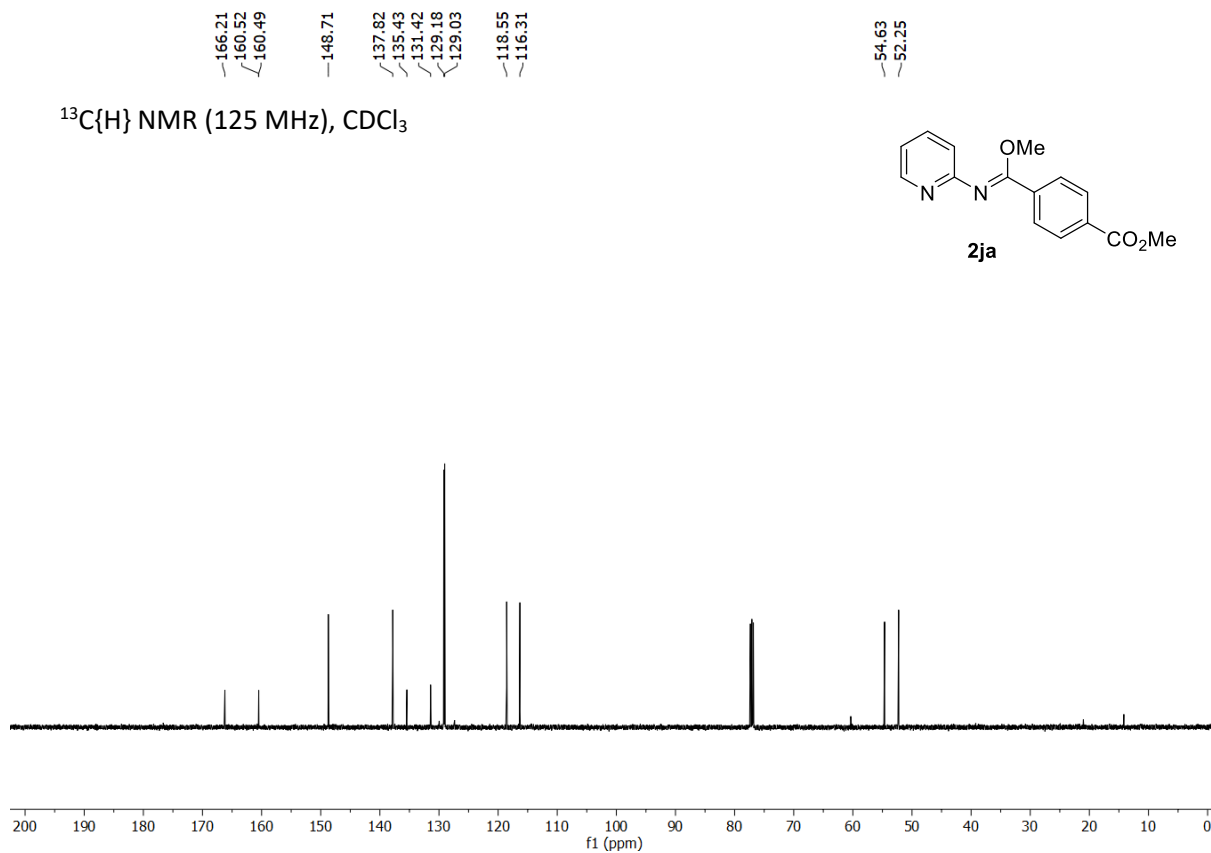
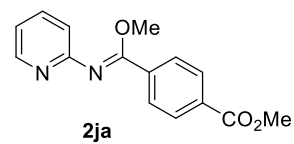


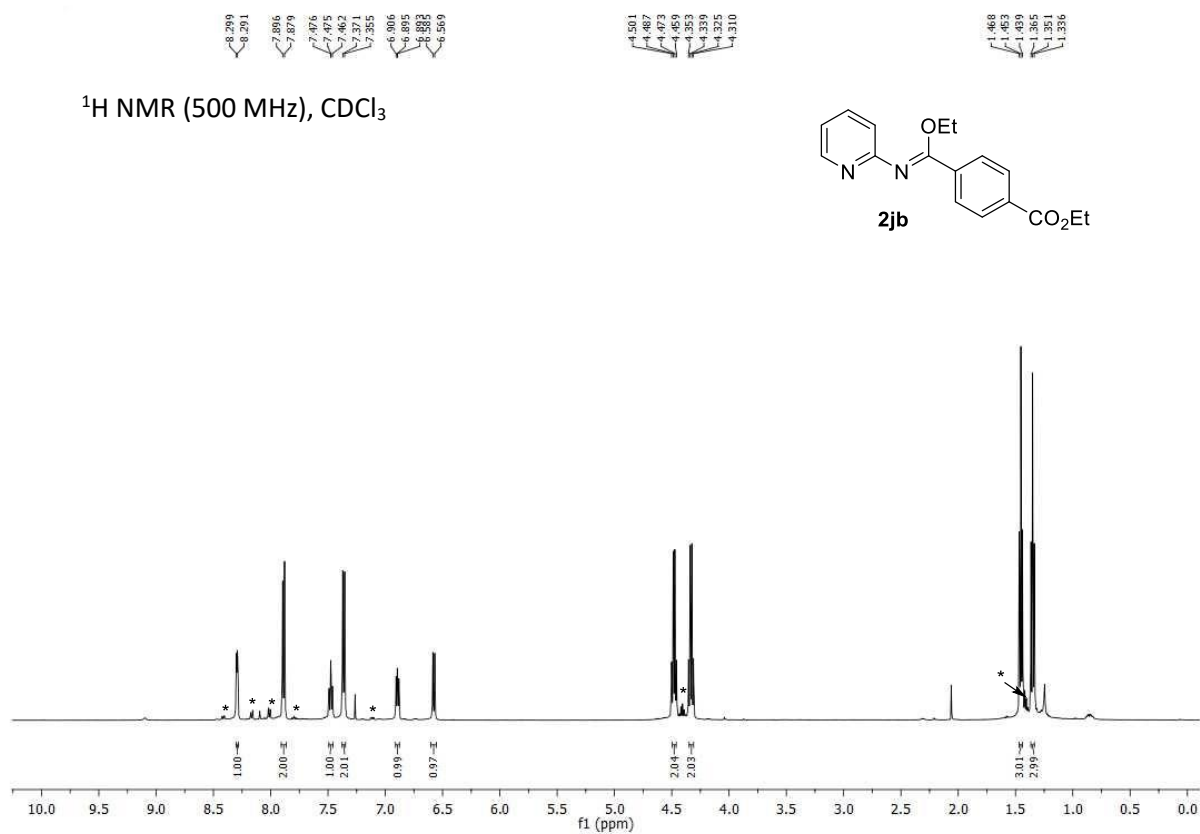
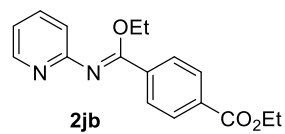
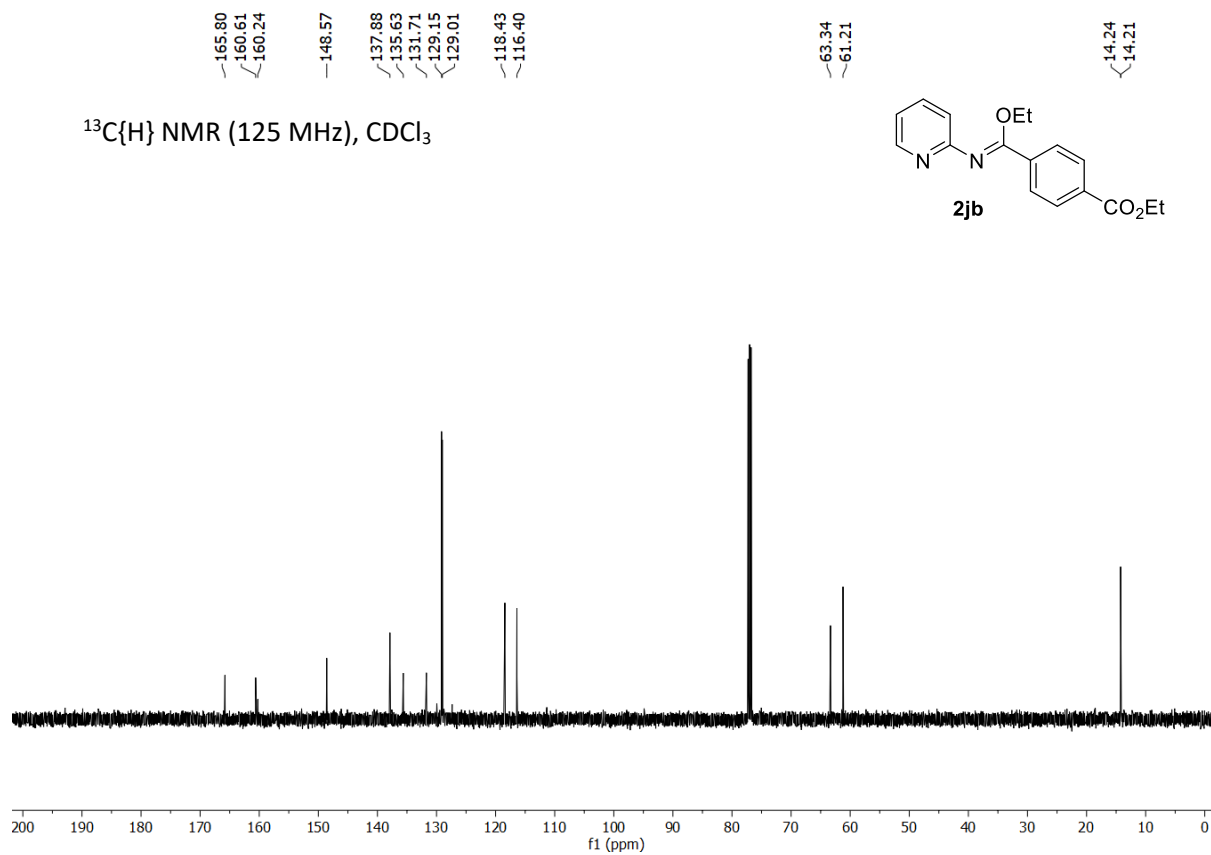
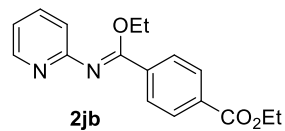


$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 

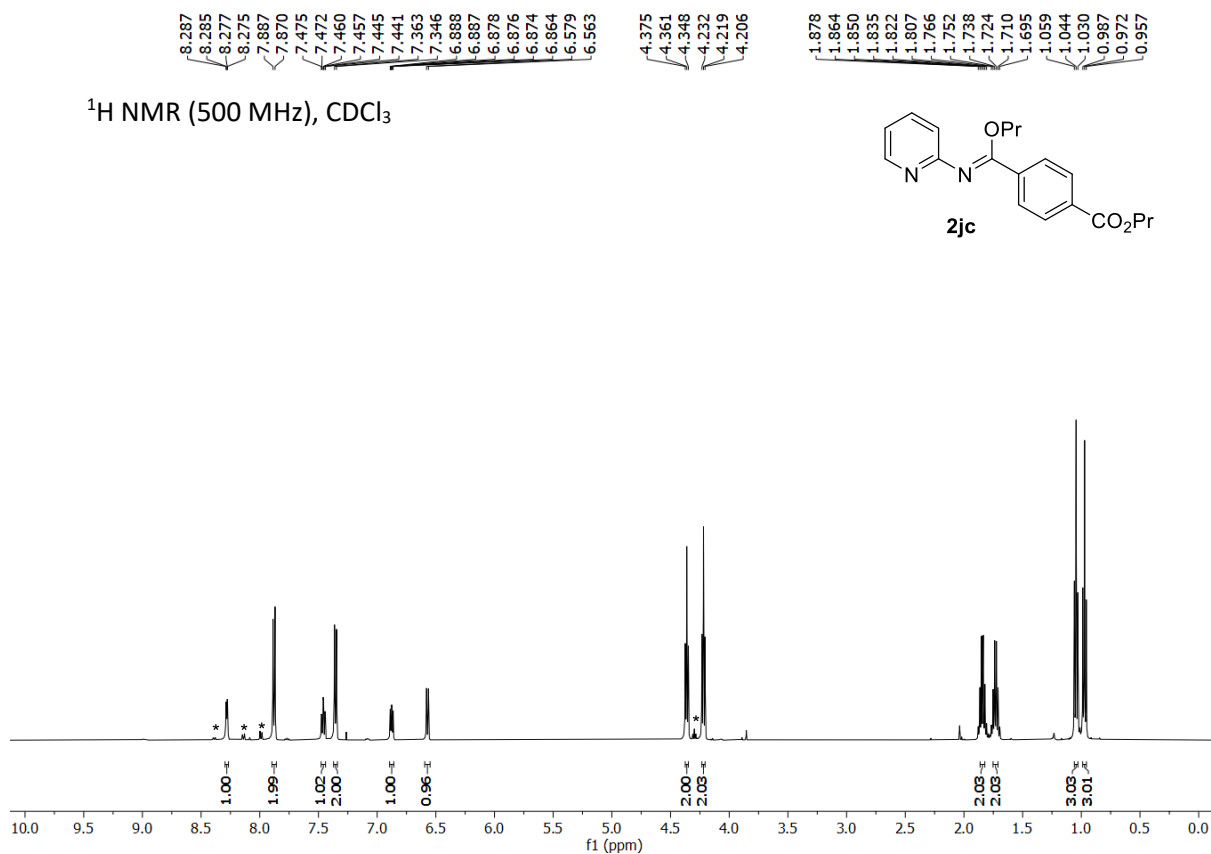
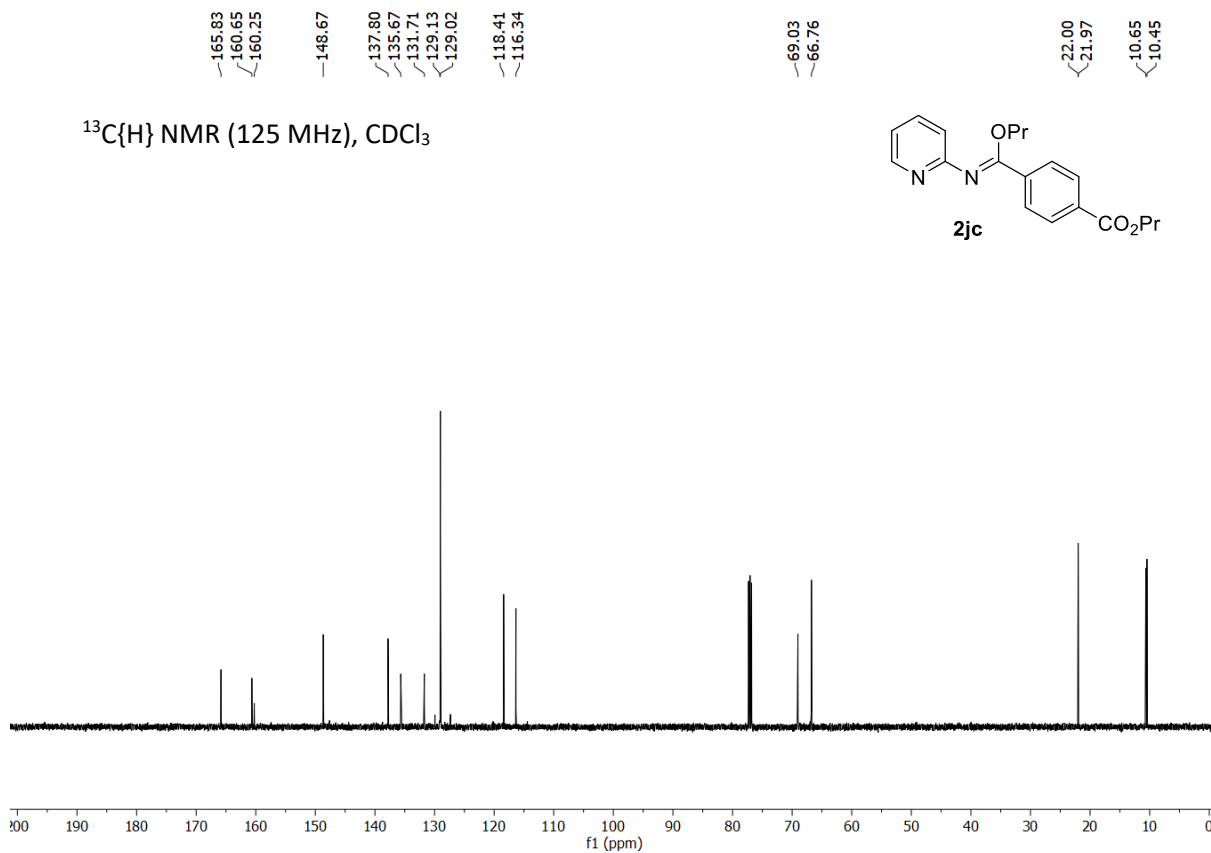
$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 

\*corresponding amide

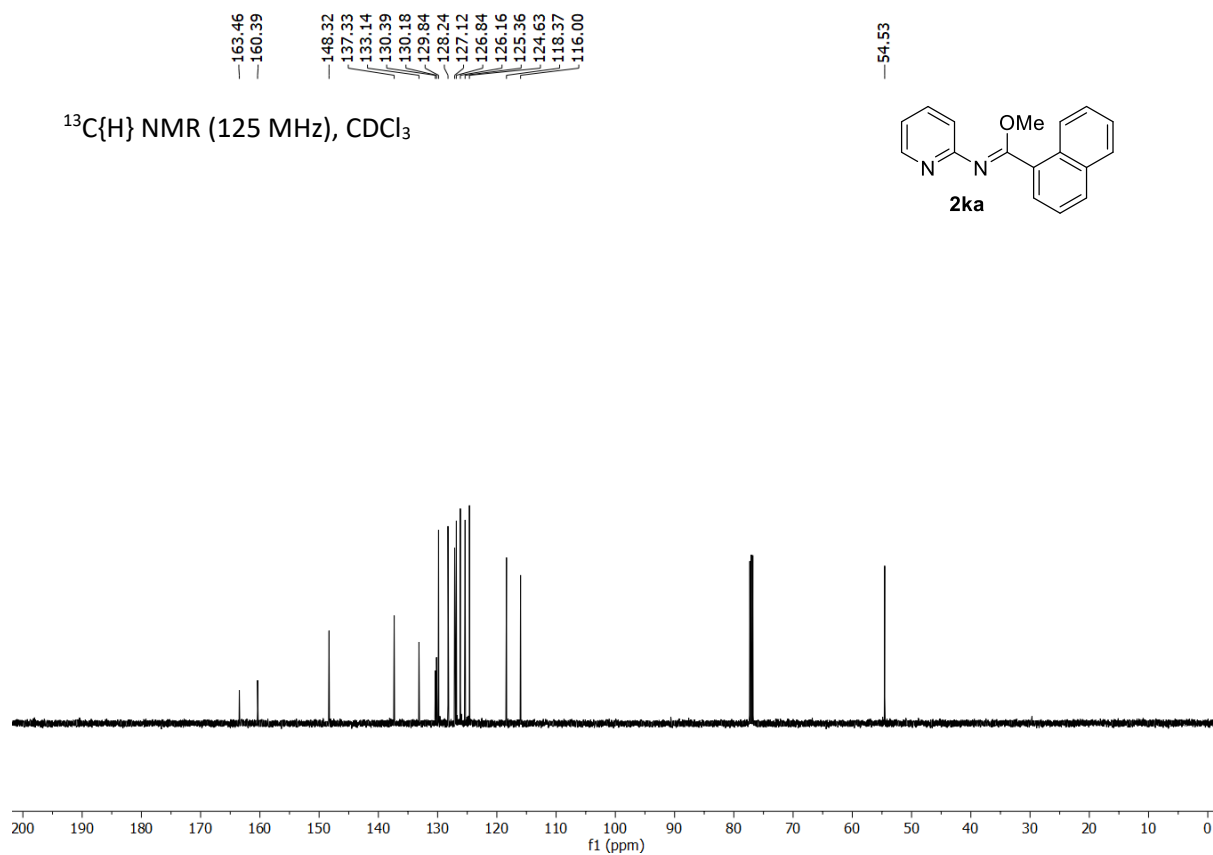
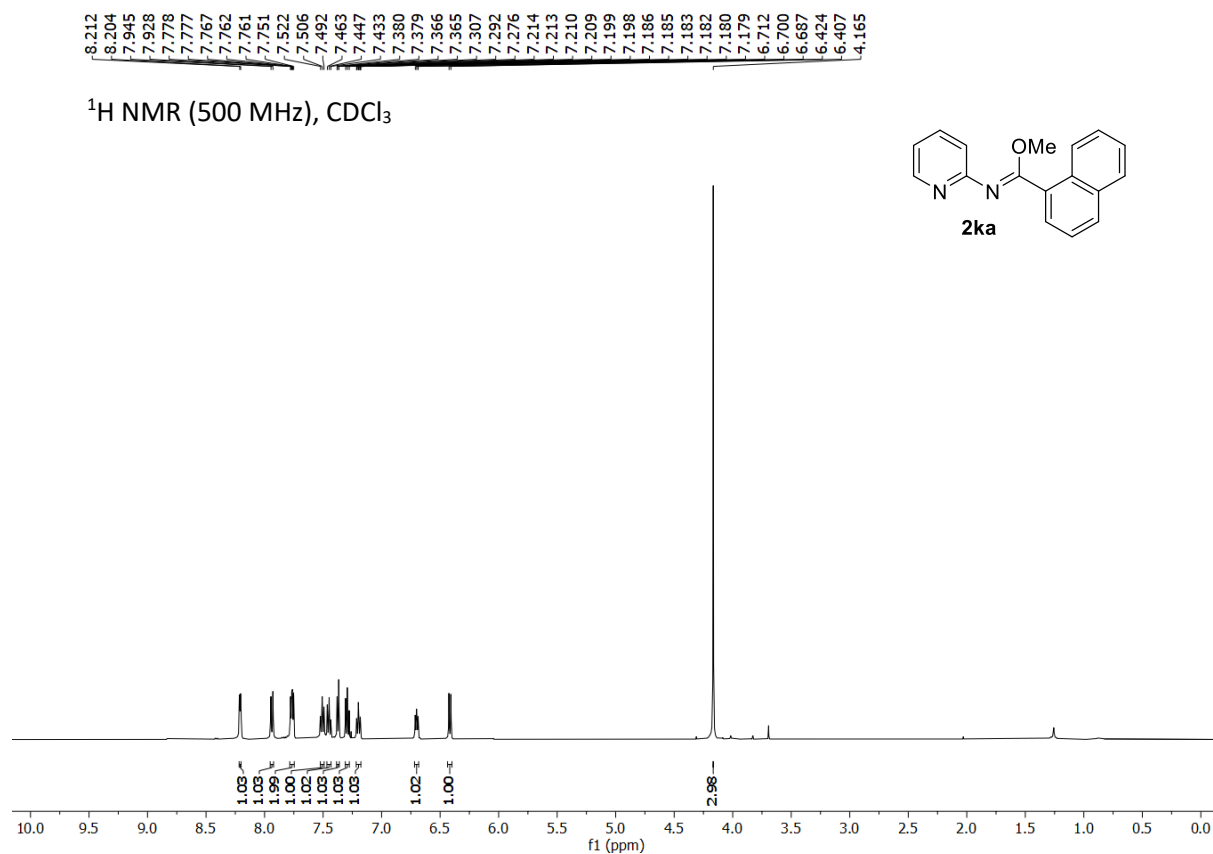
$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 

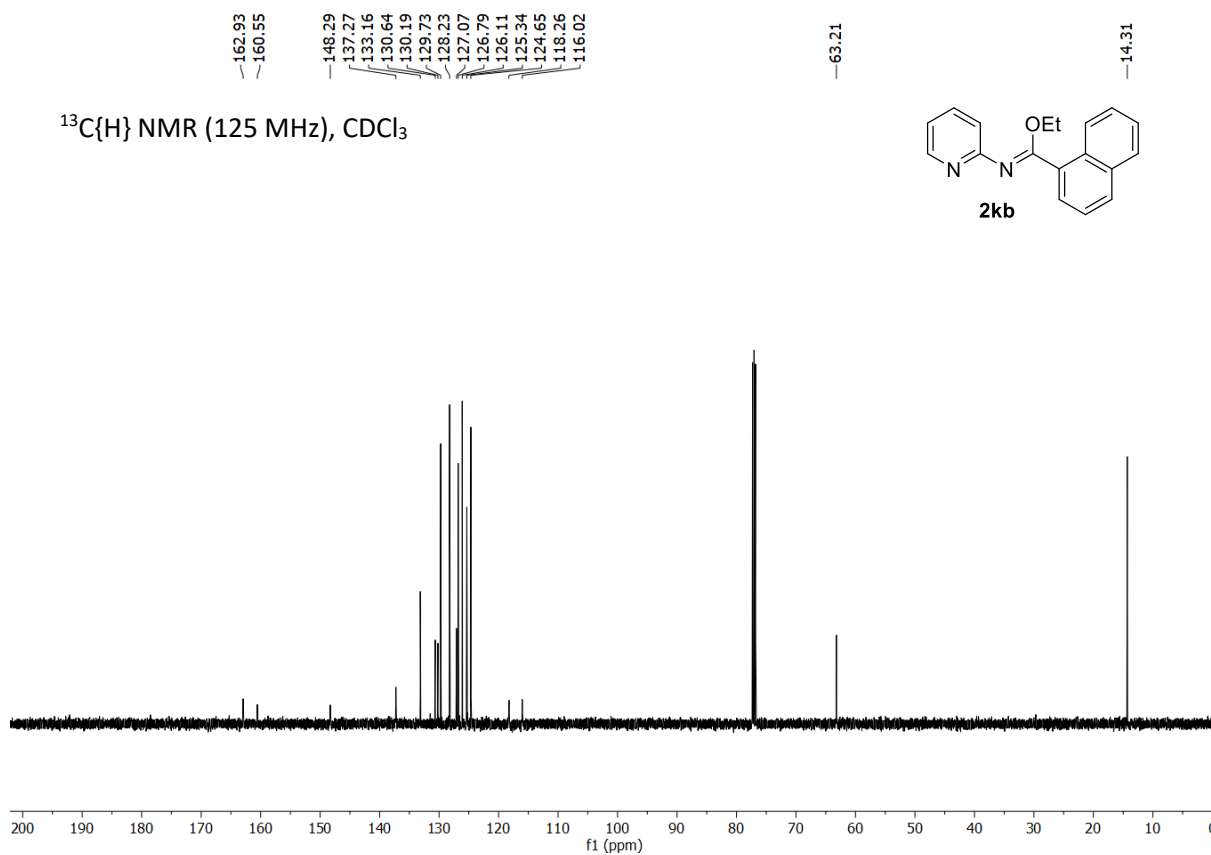
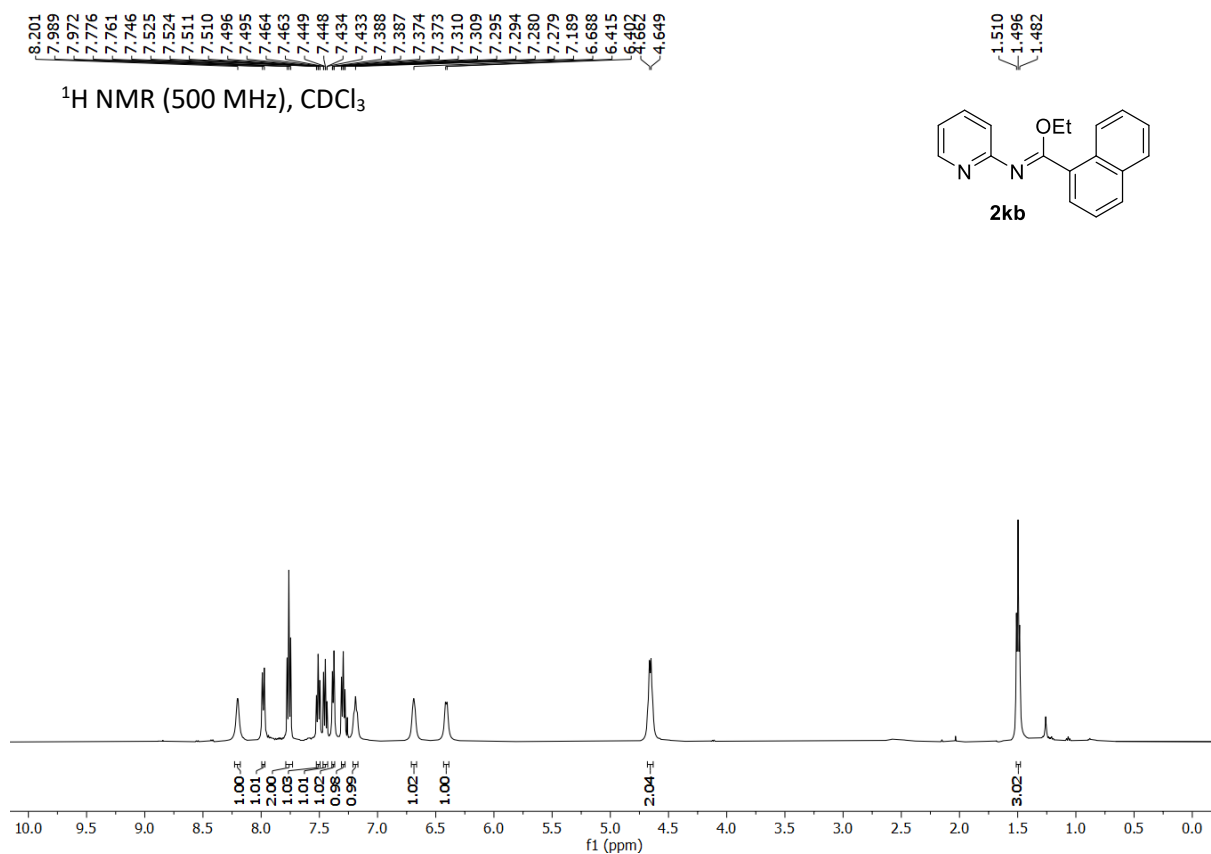
$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 

\*corresponding amide

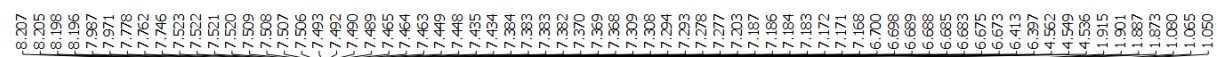
$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 

\*corresponding amide

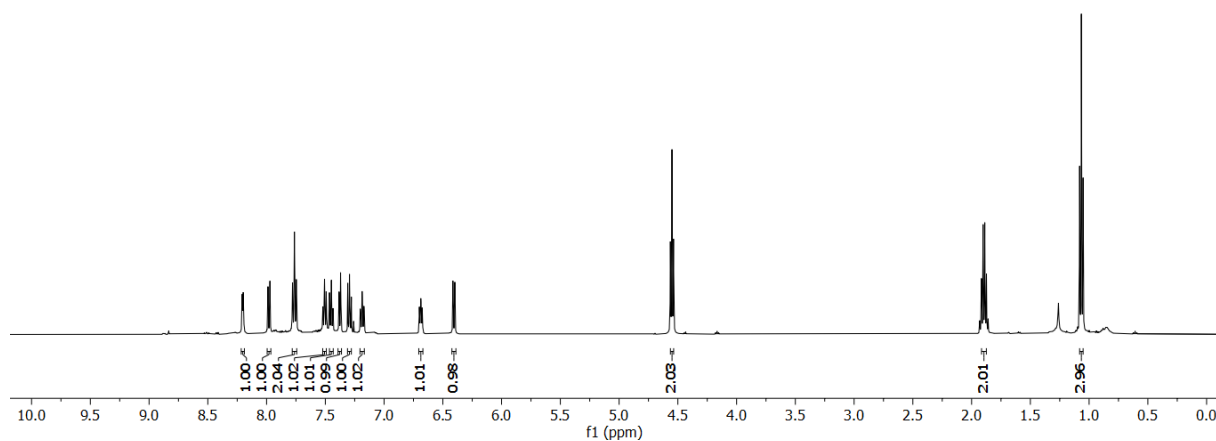
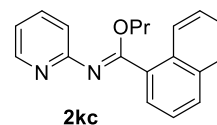




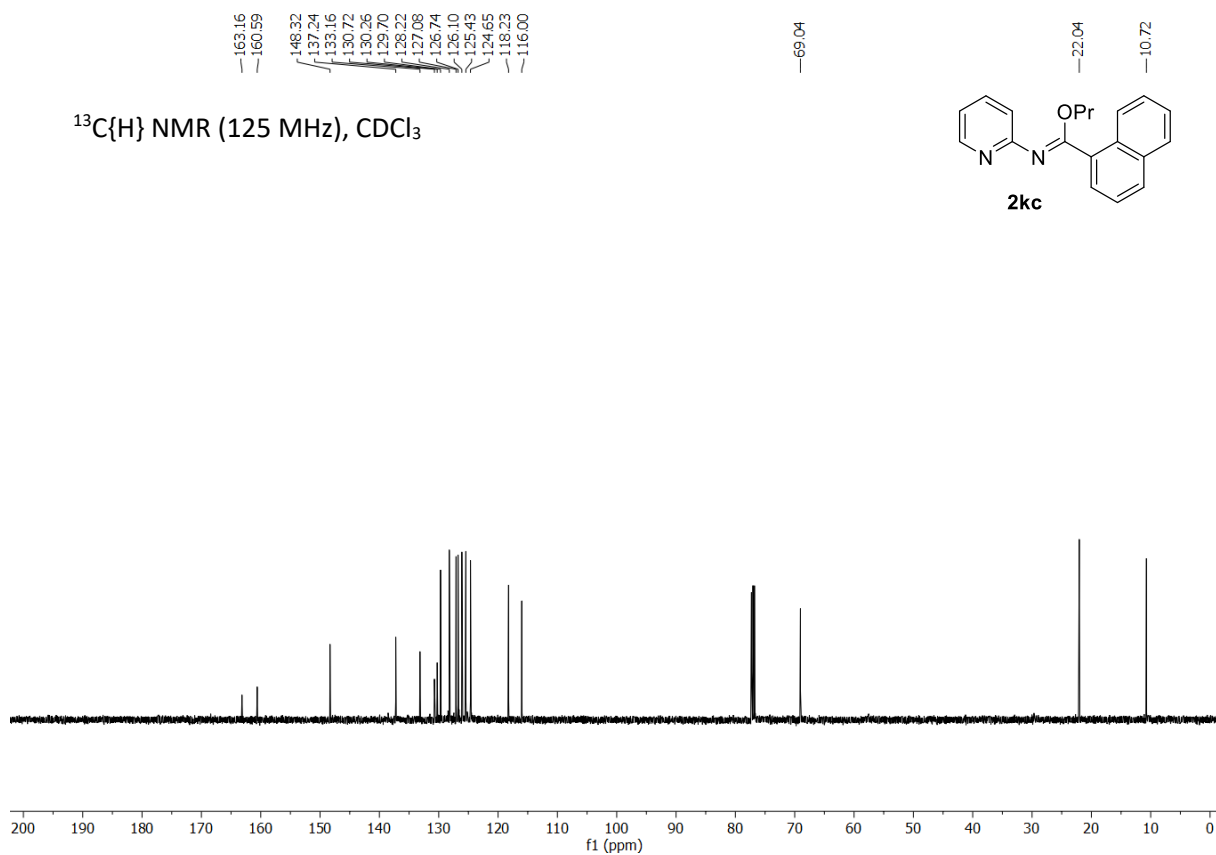
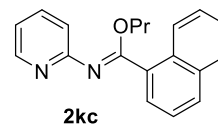


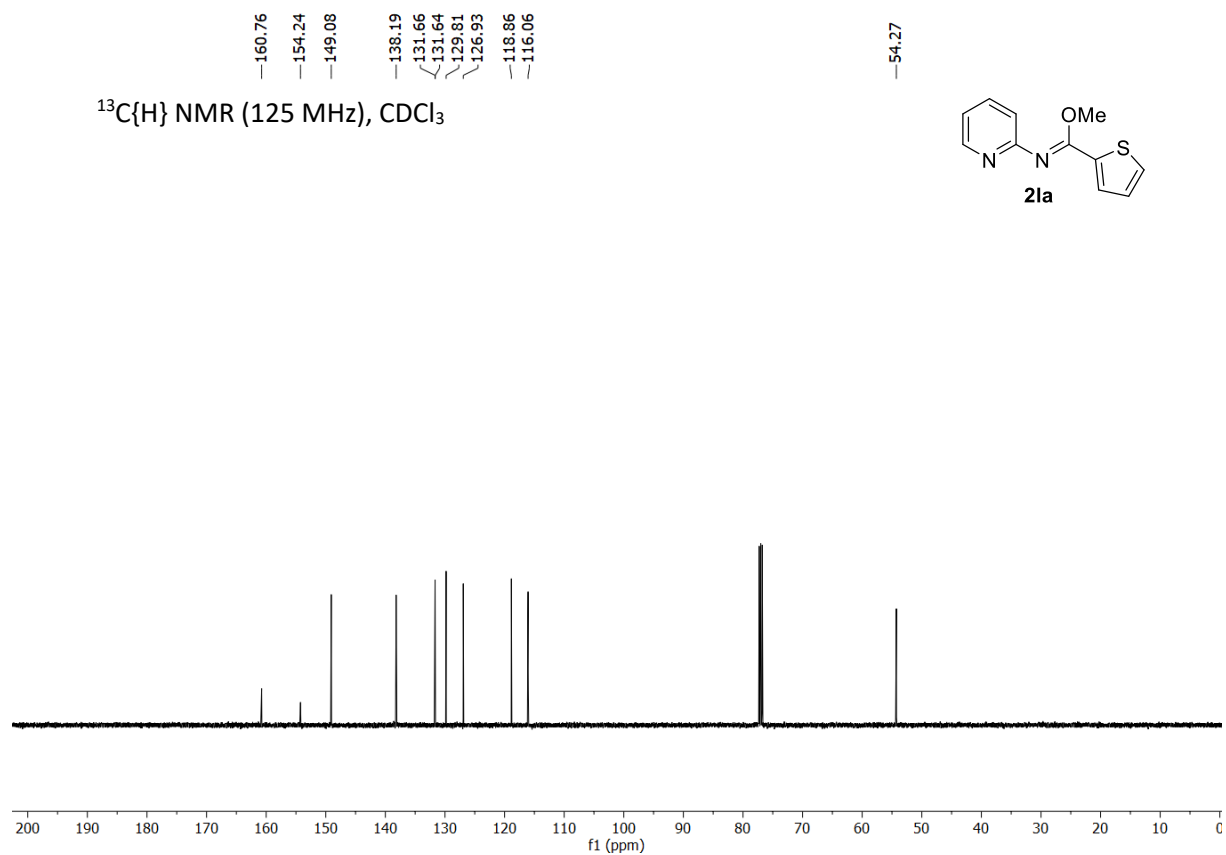
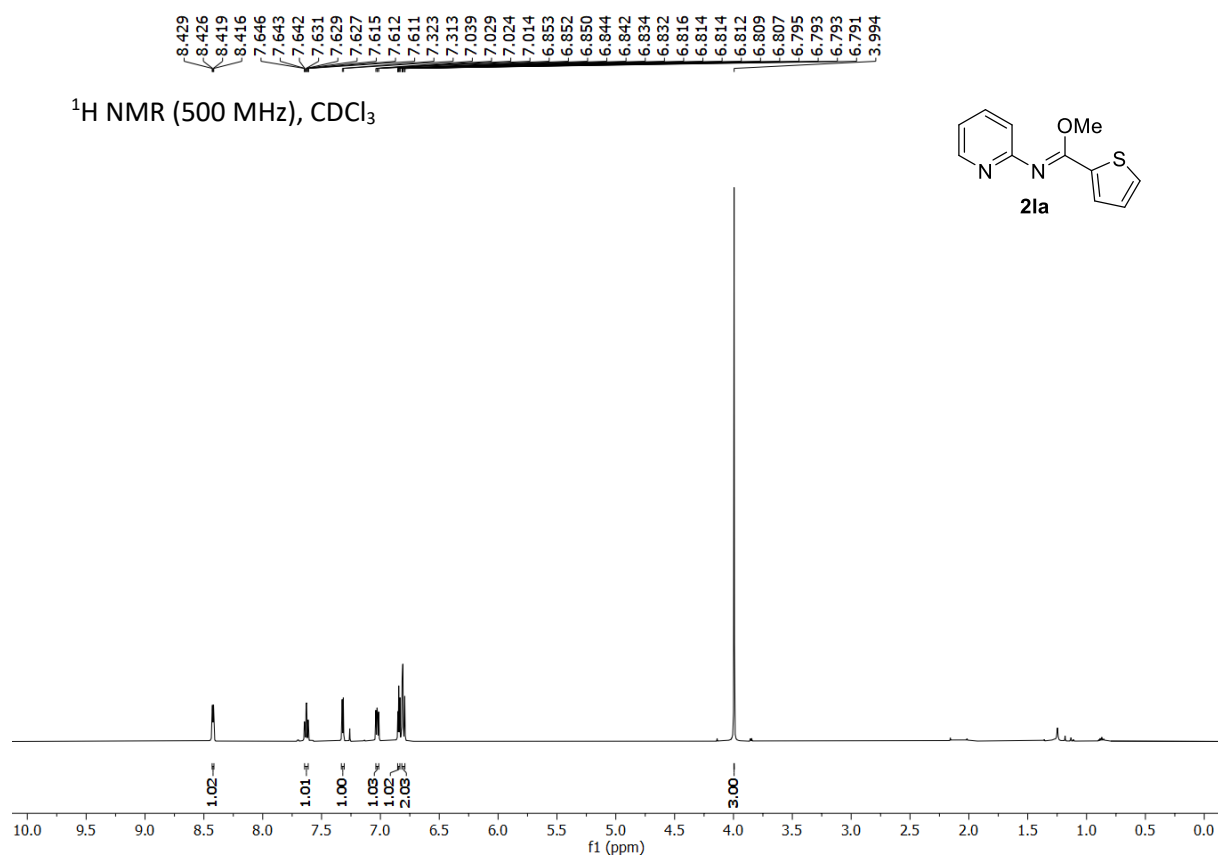


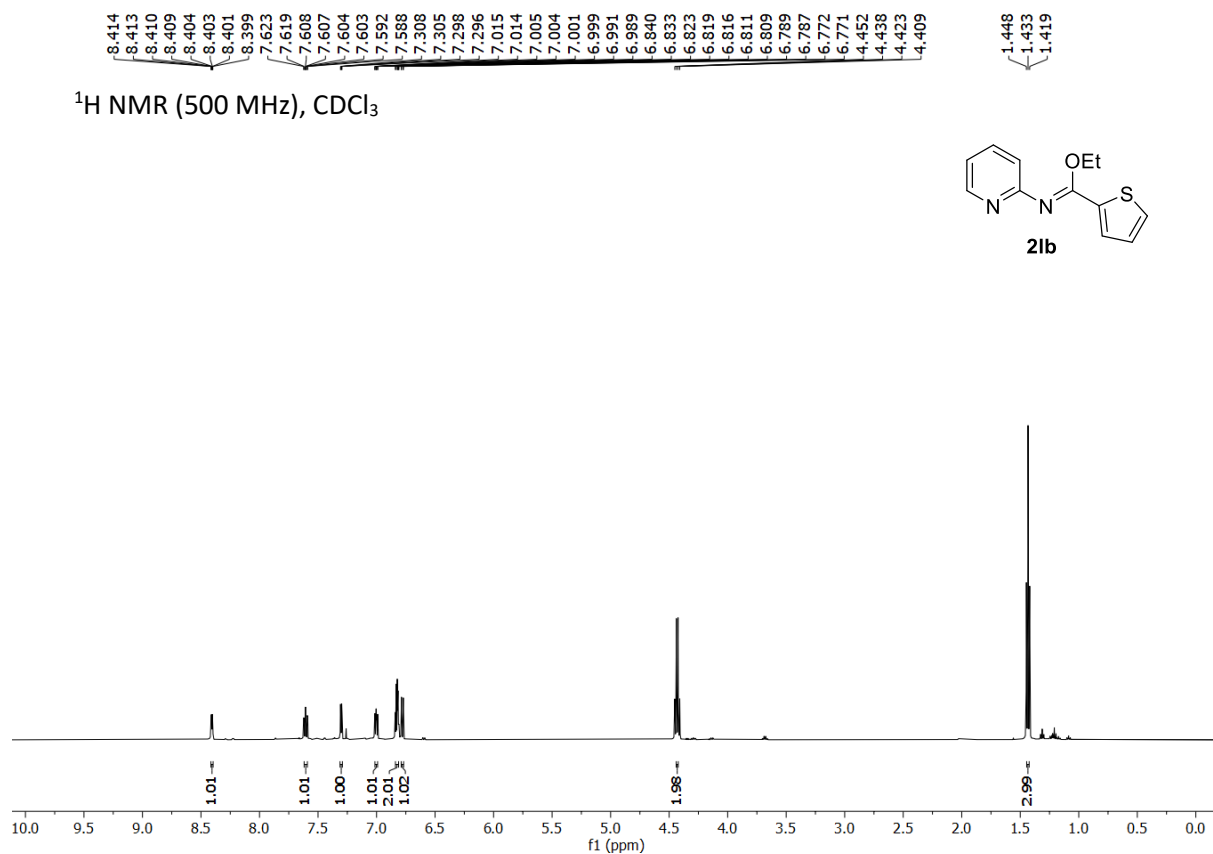
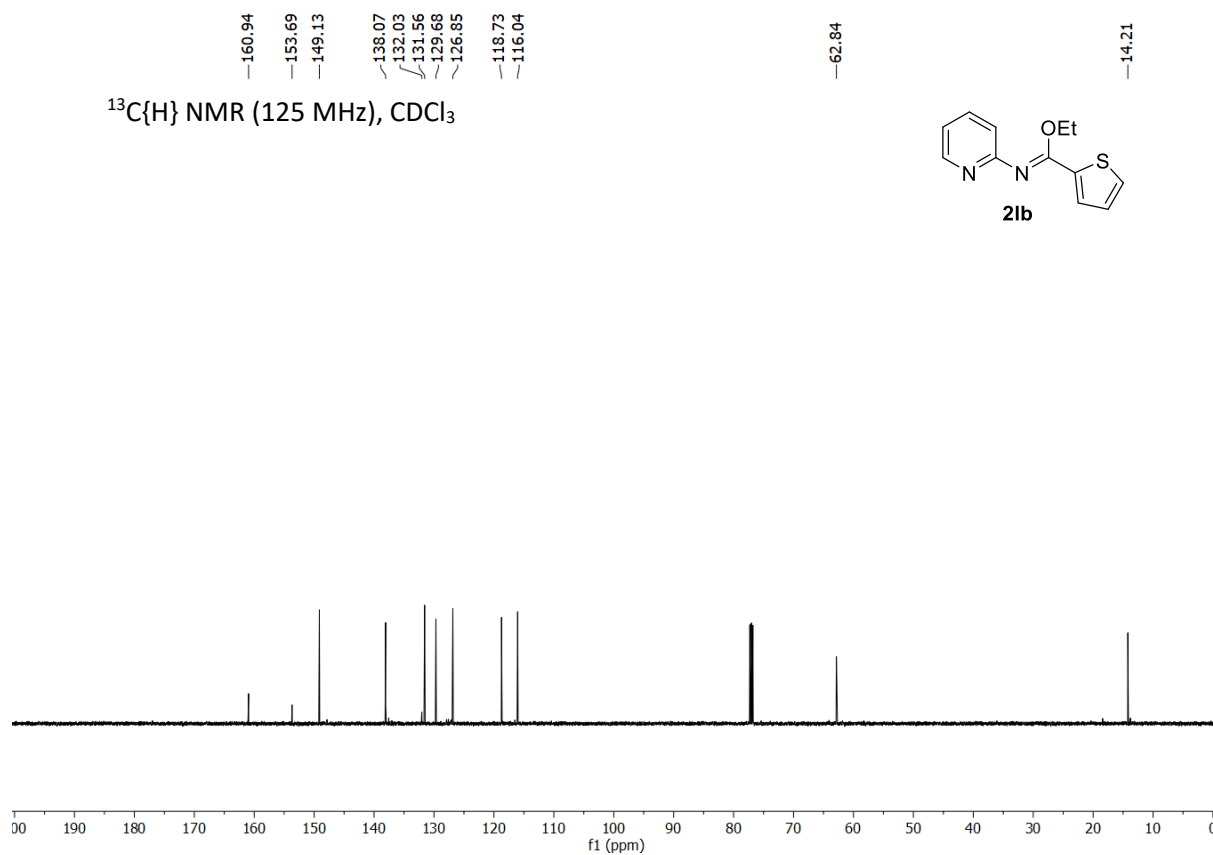
$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$

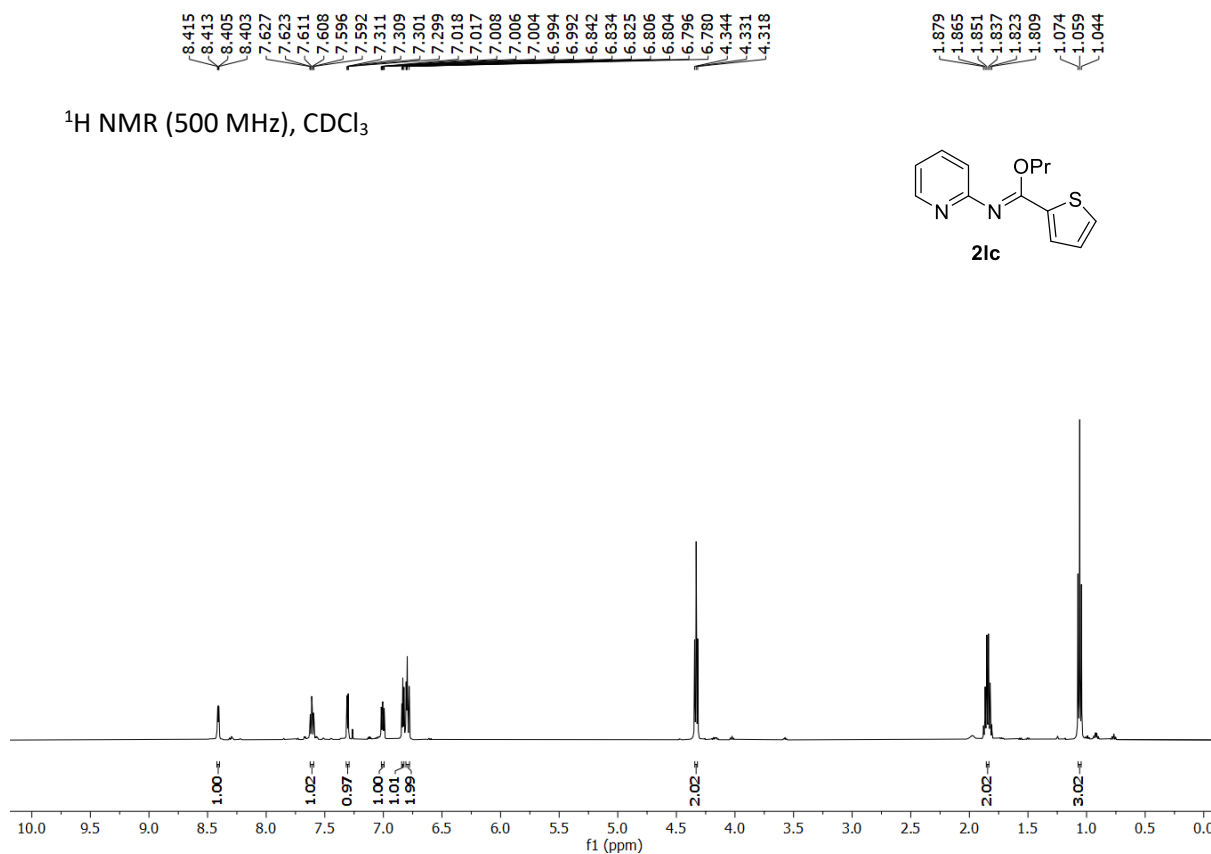
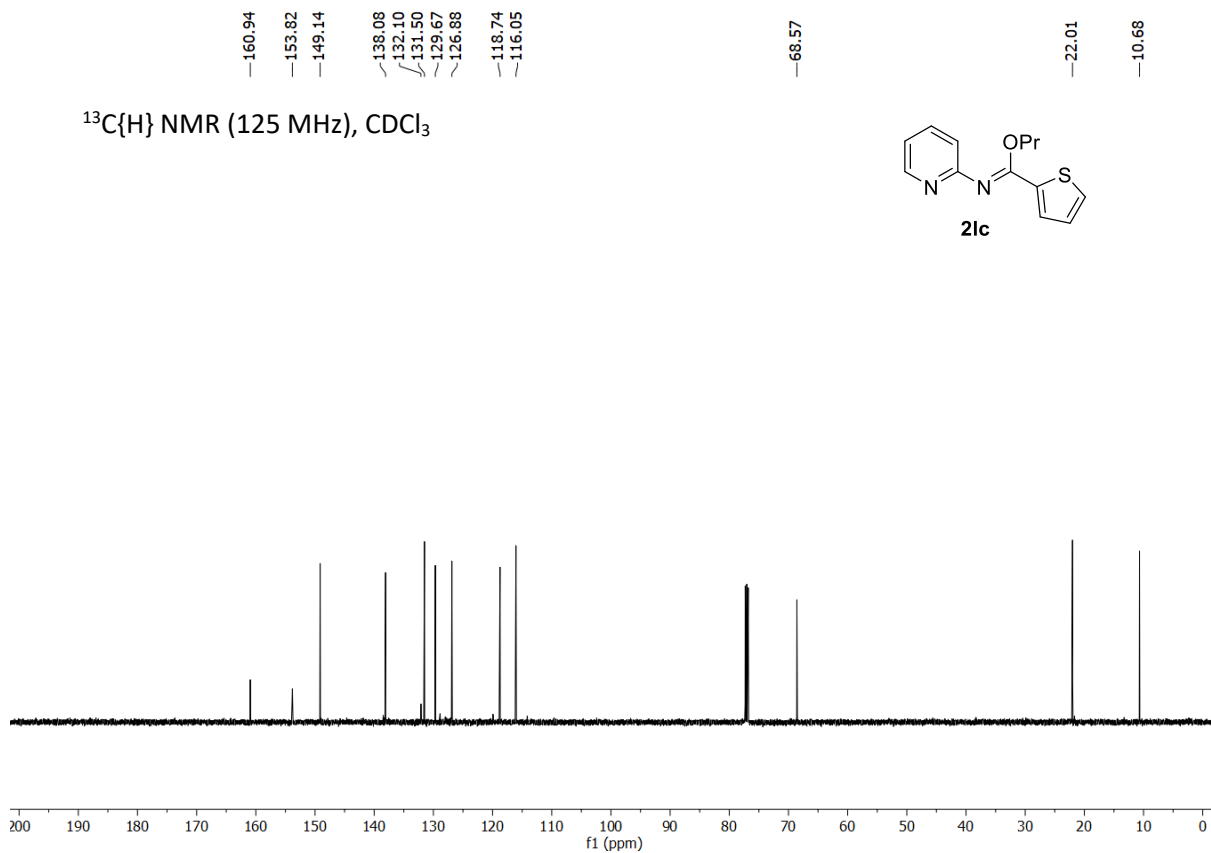


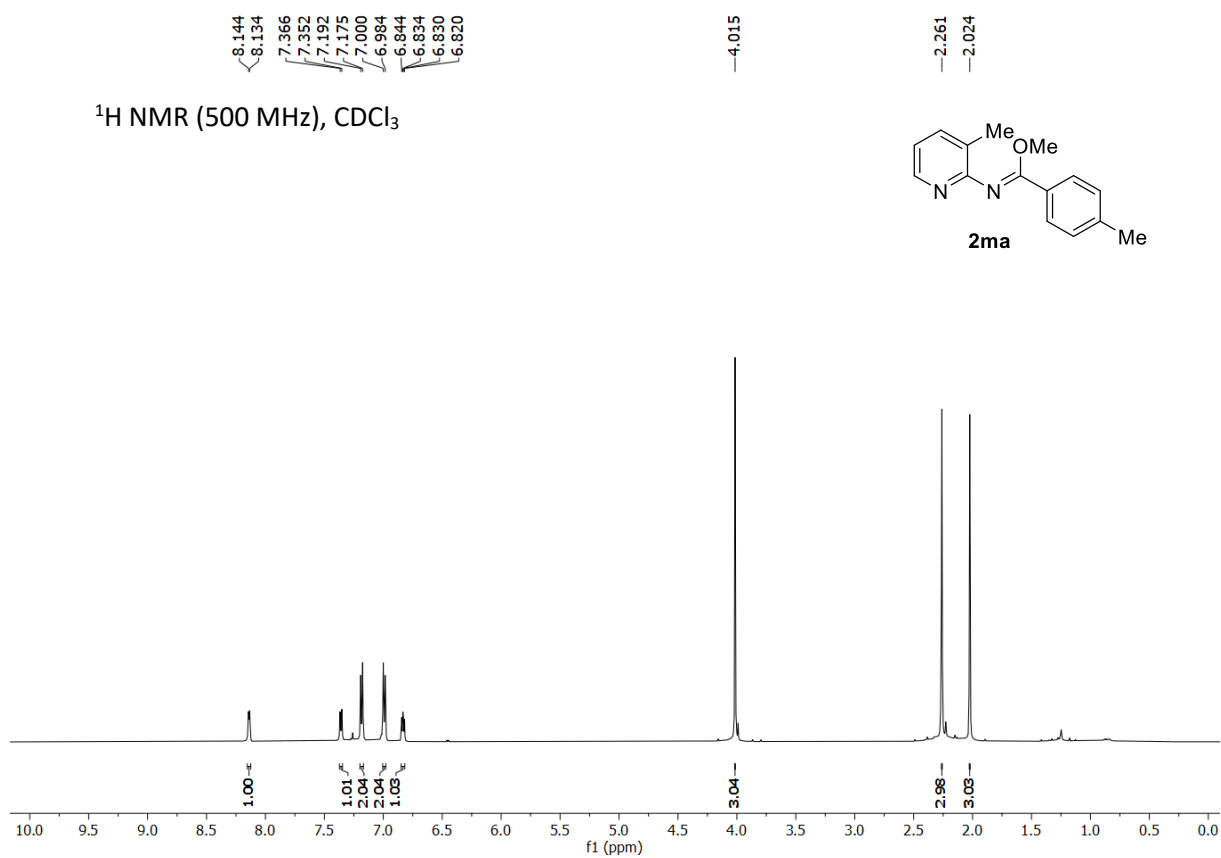
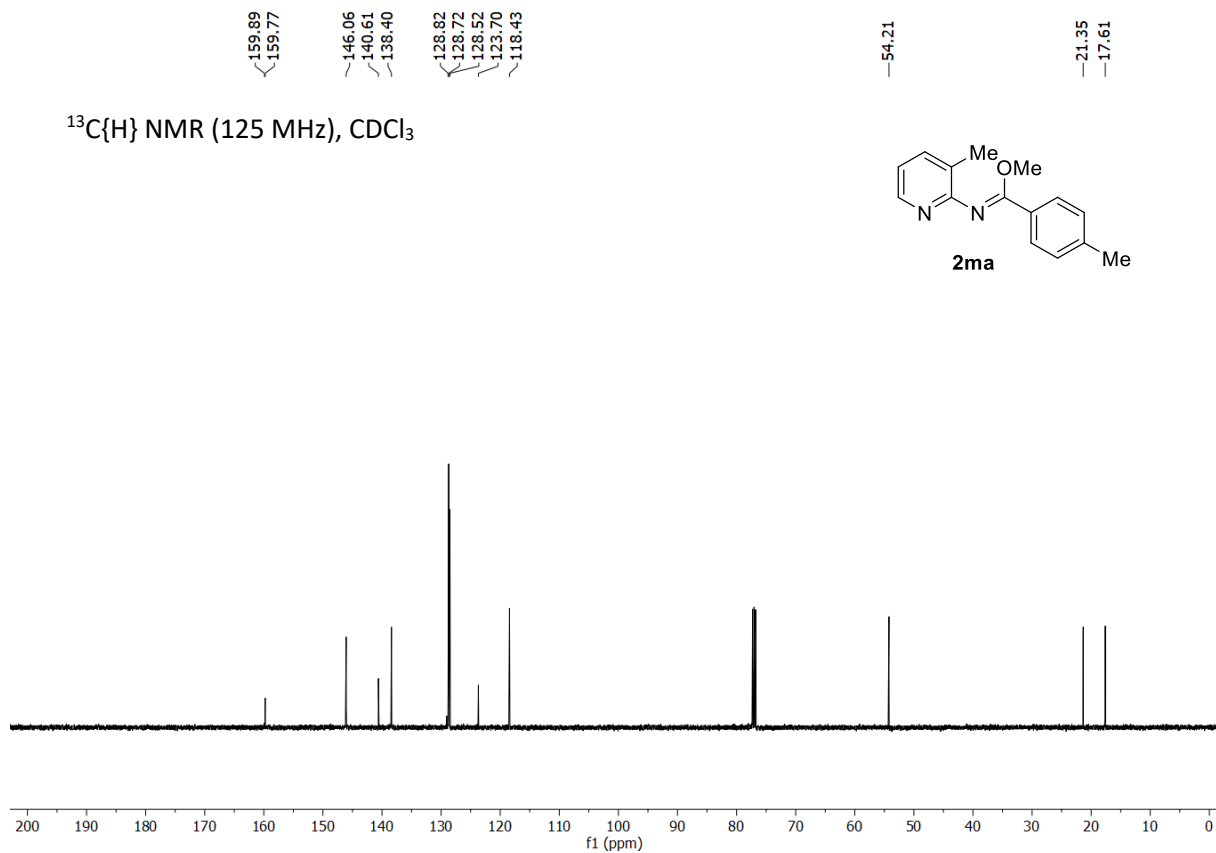
$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$

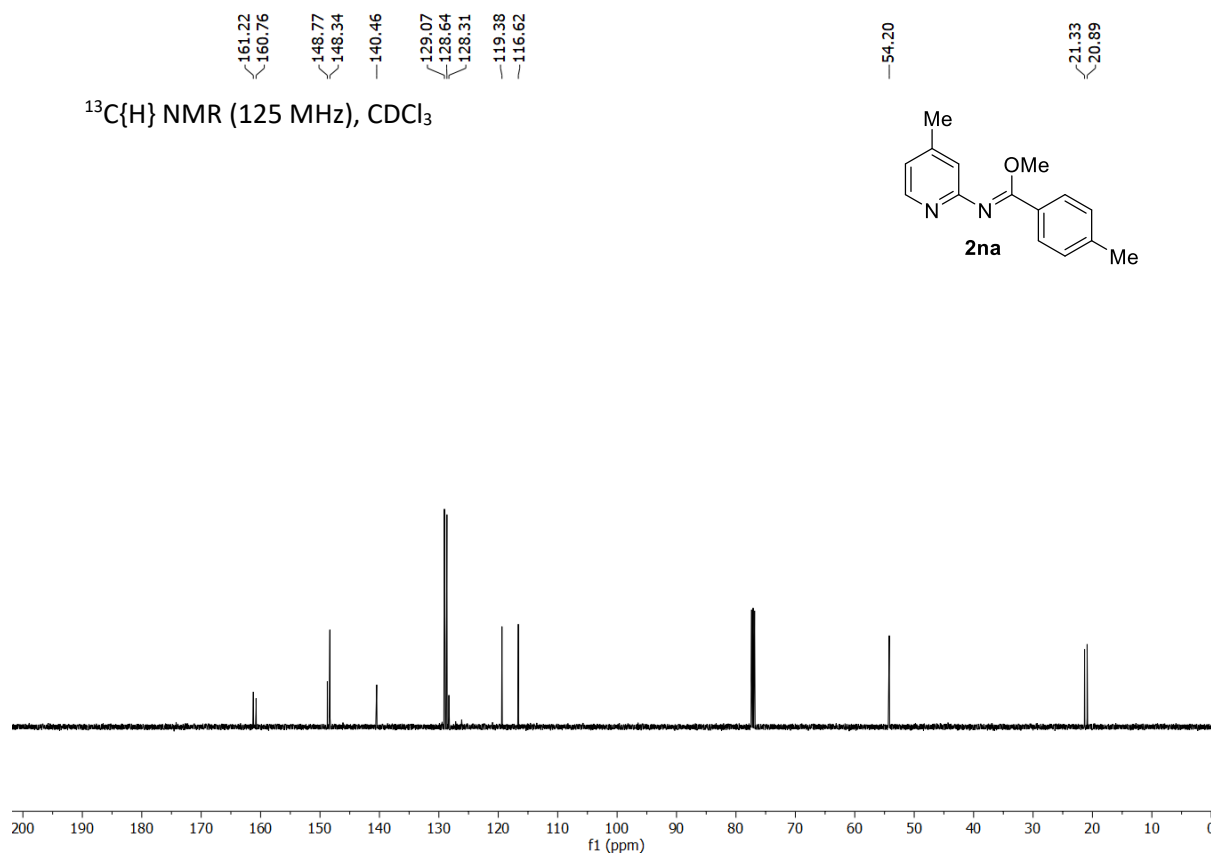
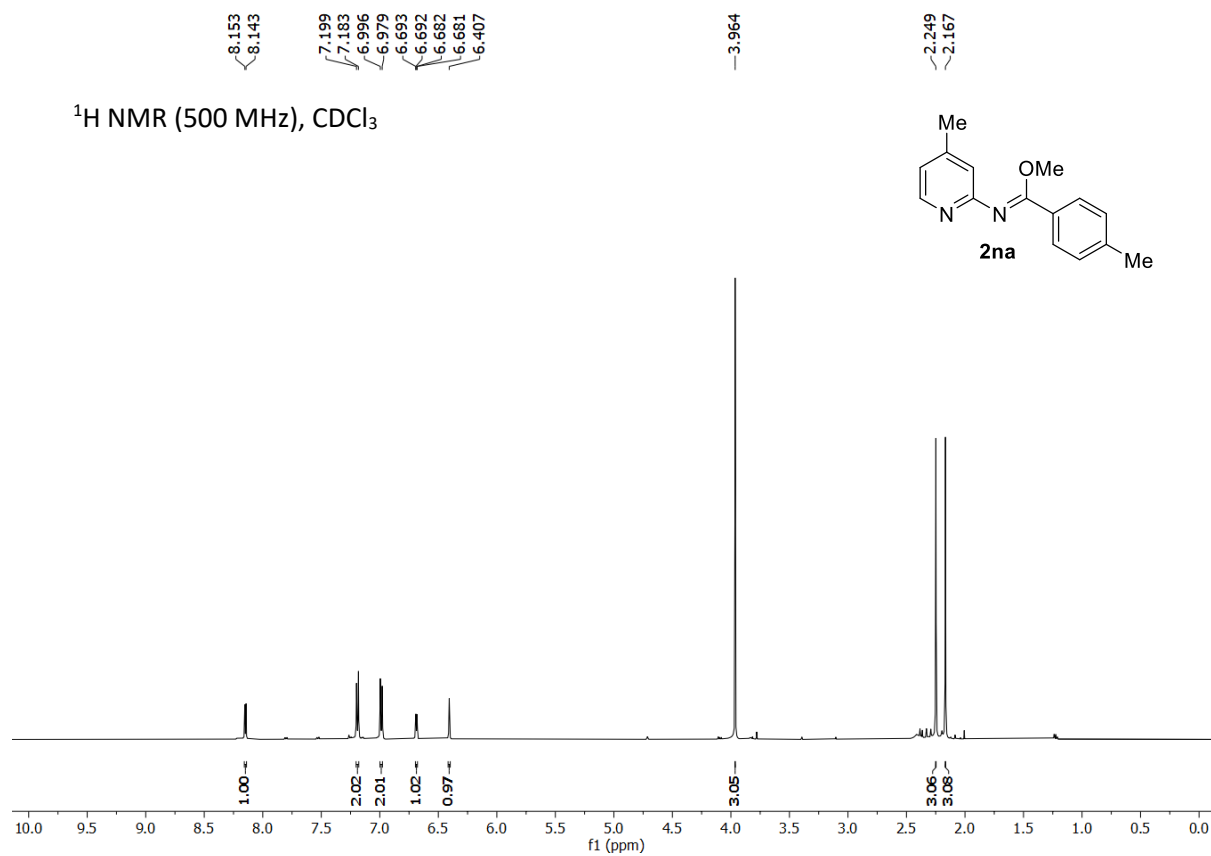


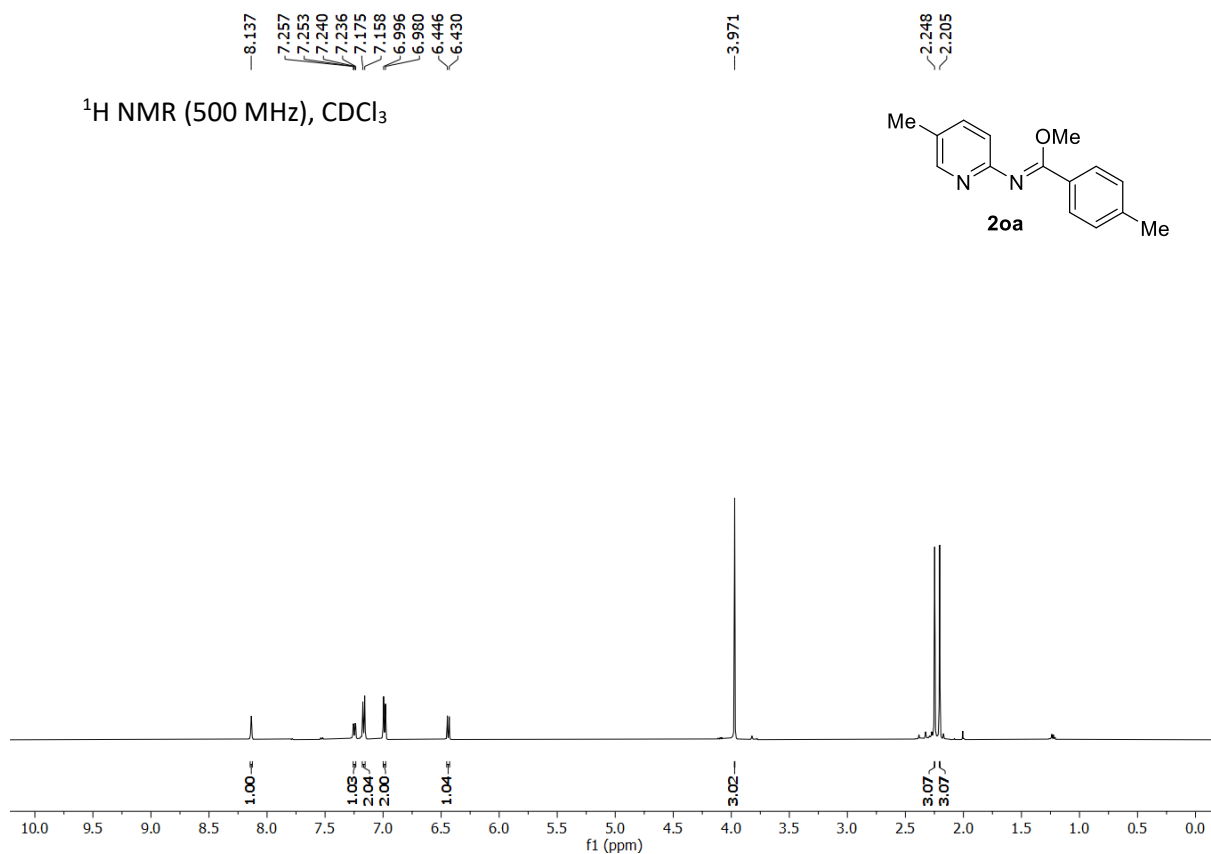
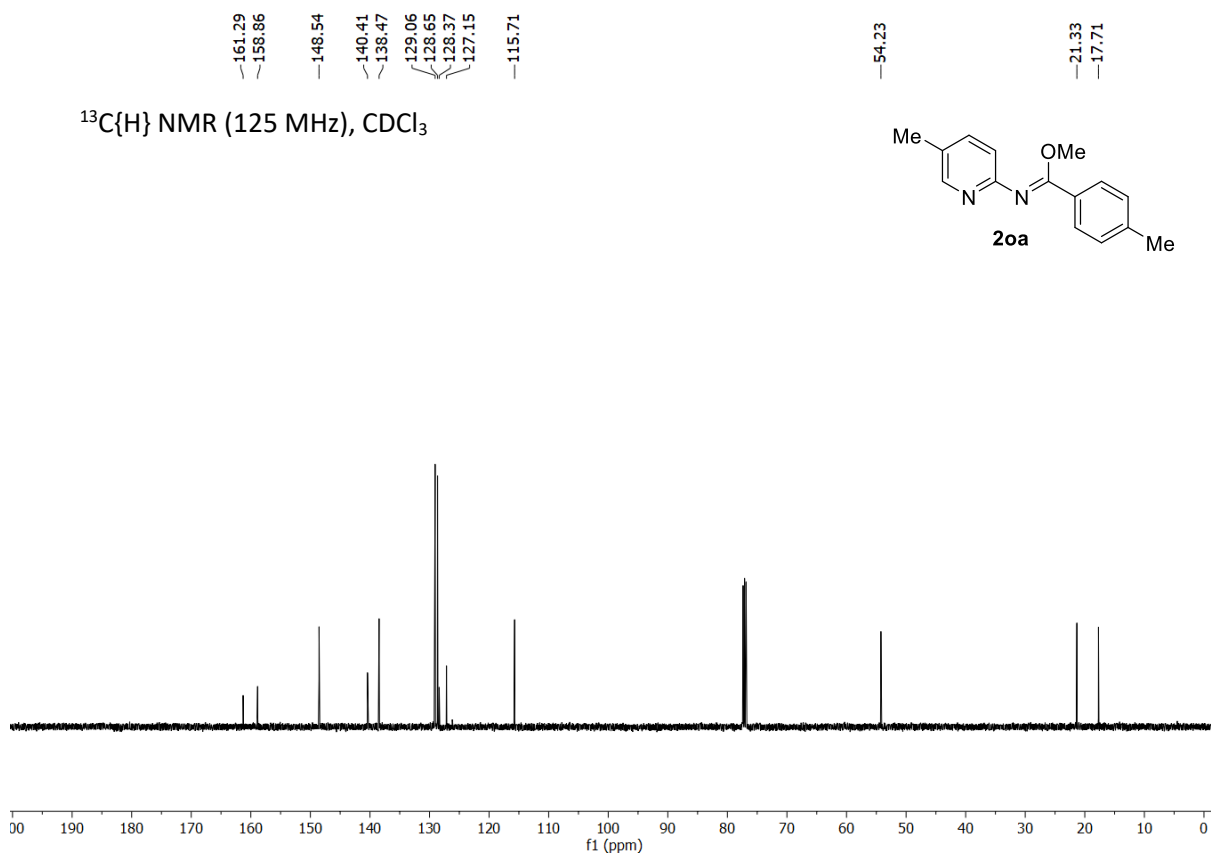


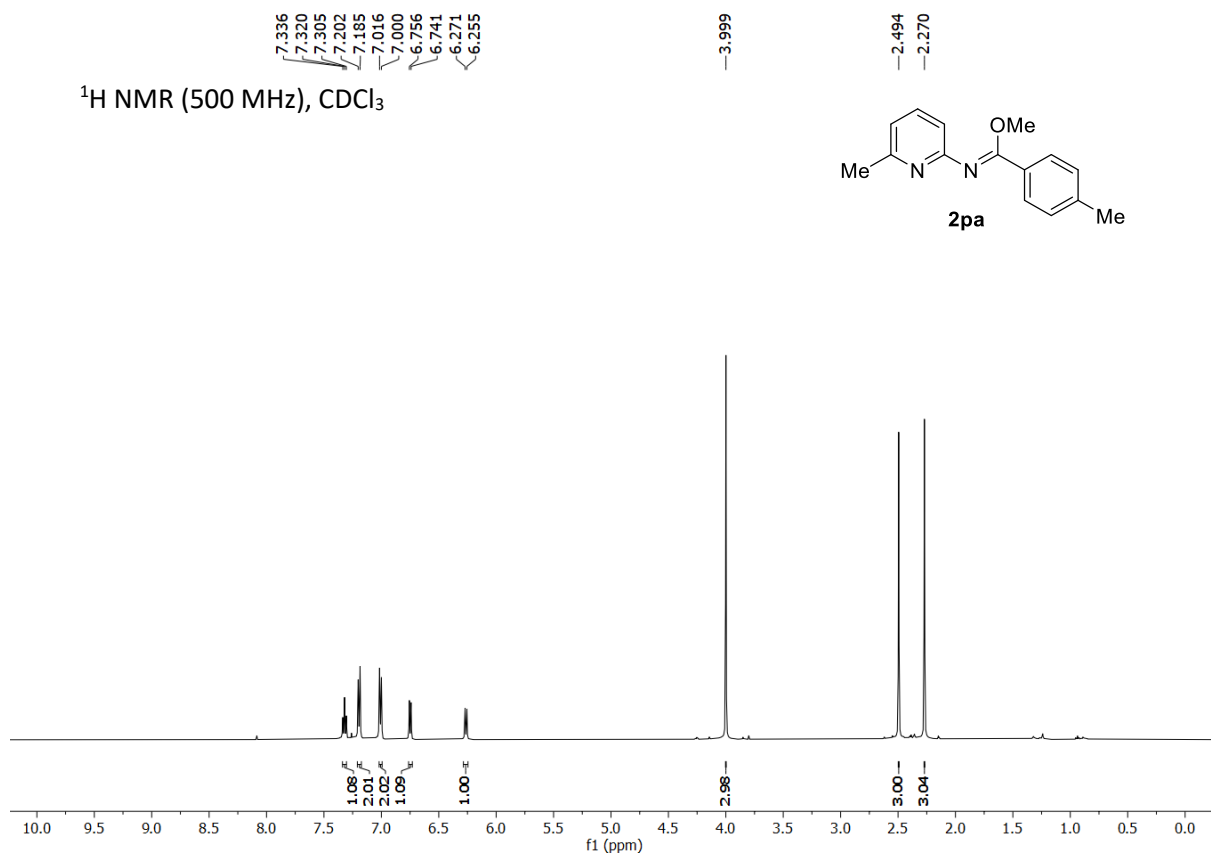
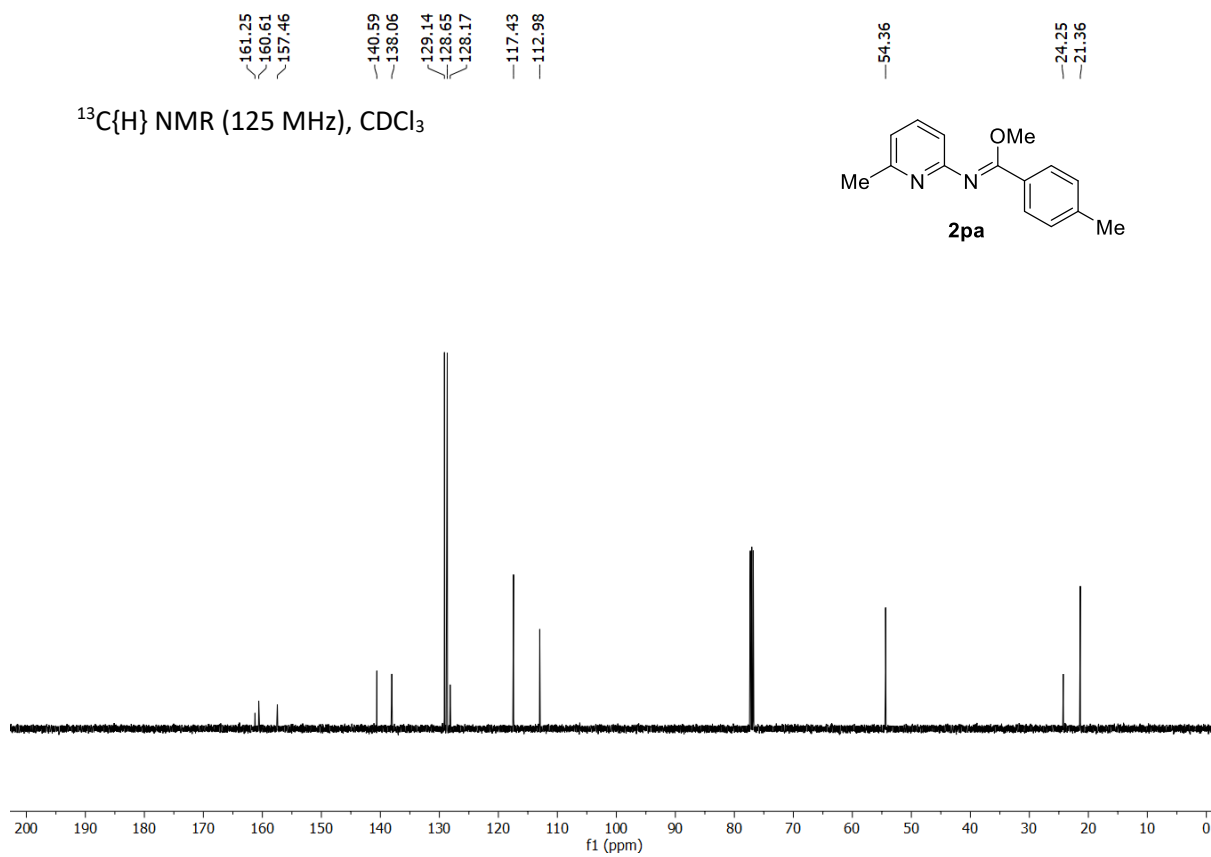
$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 

$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 

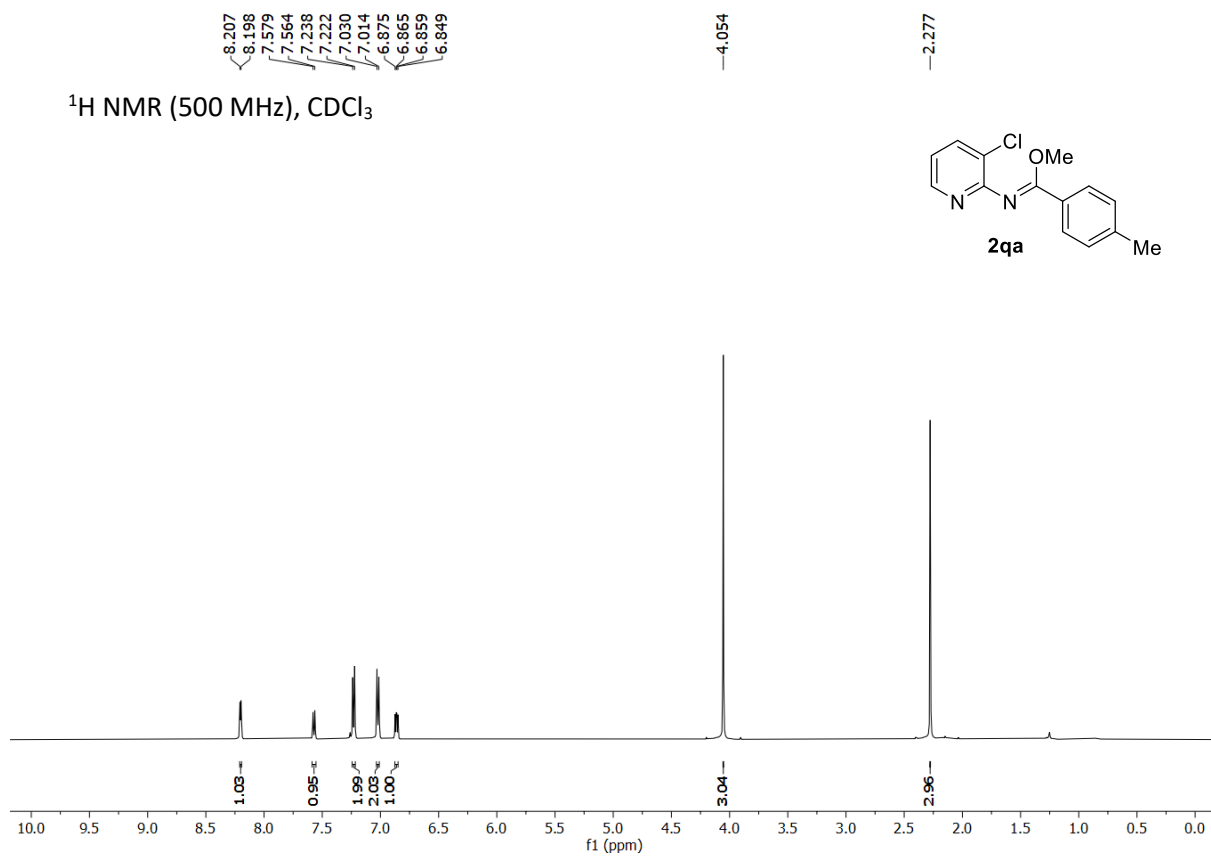
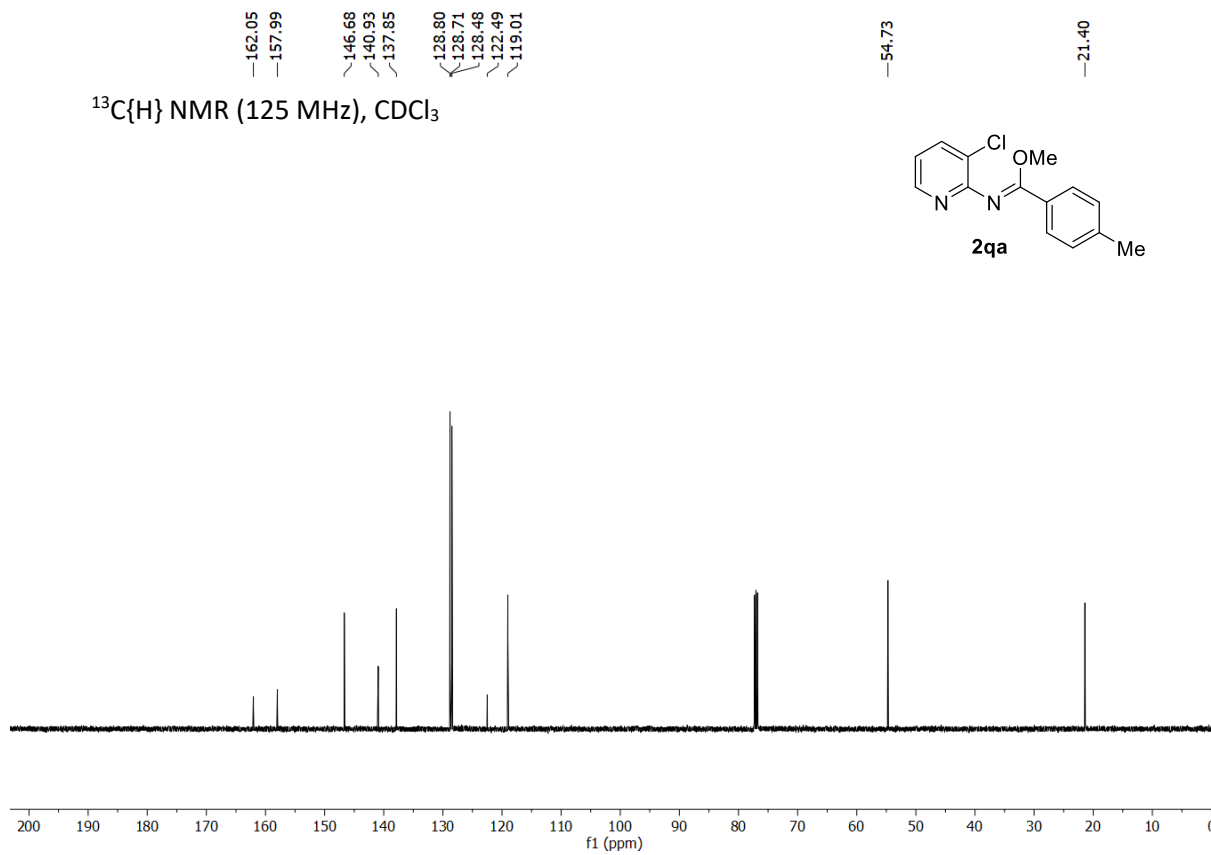
$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 

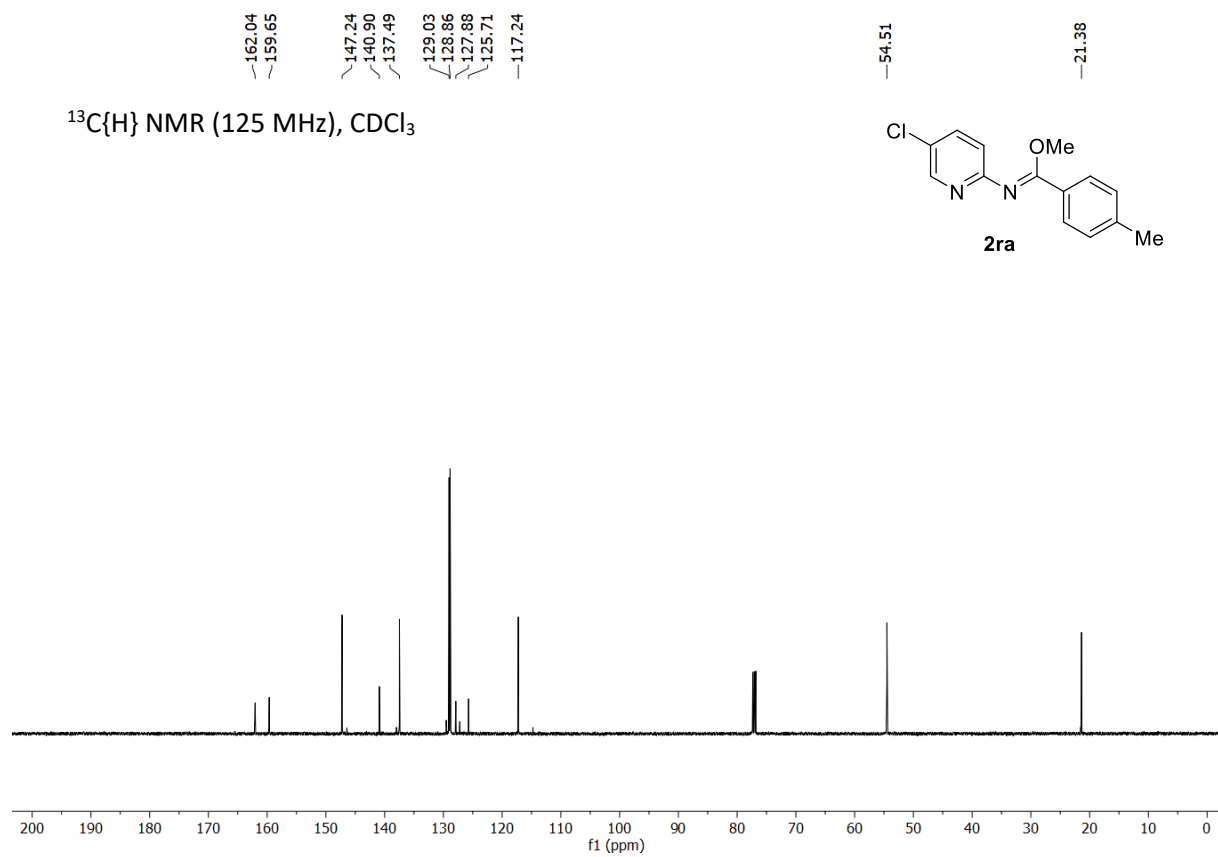
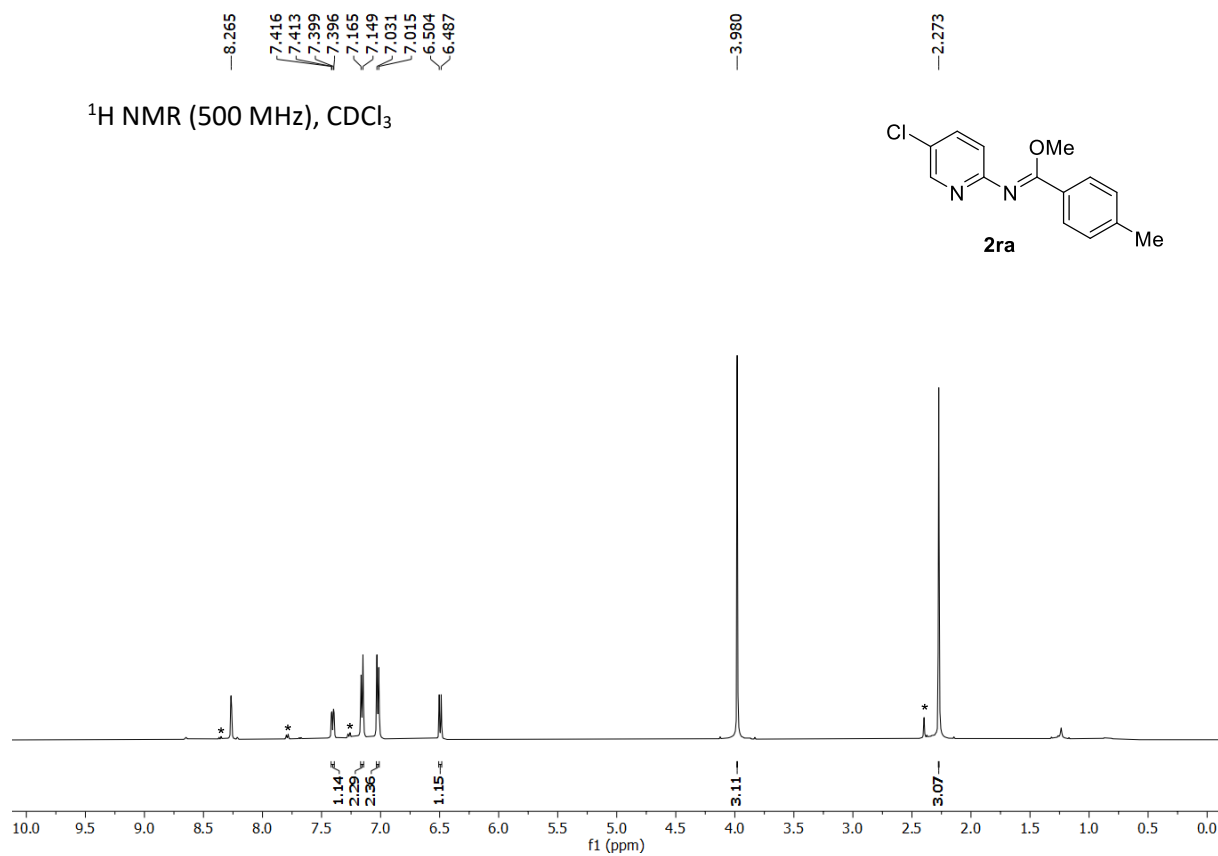


$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 

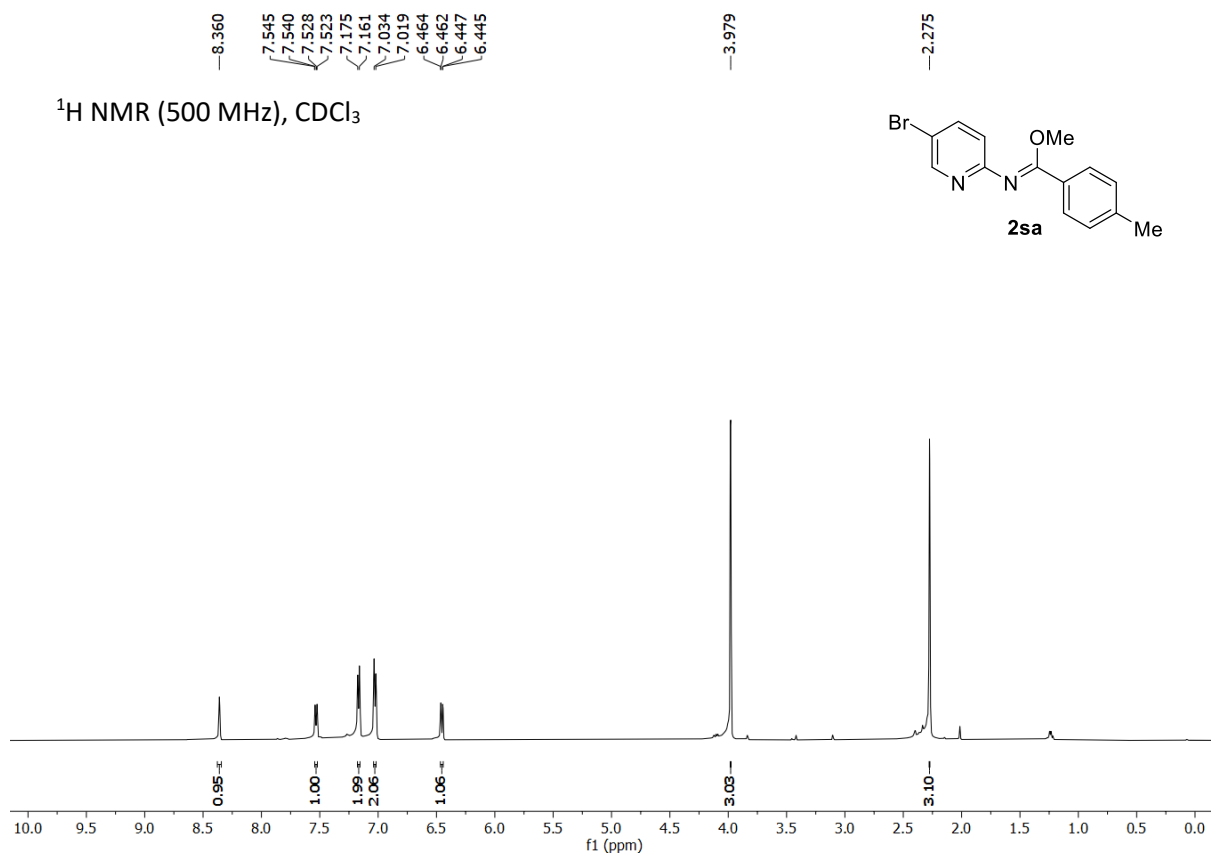
$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 



$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 



\*corresponding amide

$^1\text{H}$  NMR (500 MHz),  $\text{CDCl}_3$  $^{13}\text{C}\{\text{H}\}$  NMR (125 MHz),  $\text{CDCl}_3$ 