

Electronic Supplementary Information

## **Rhodium-catalysed direct formylmethylation using vinylene carbonate and sequential dehydrogenative esterification**

Moena Kato,<sup>a,b</sup> Koushik Ghosh,<sup>a,b</sup> Yuji Nishii,<sup>\*a</sup> and Masahiro Miura<sup>\*c</sup>

<sup>a</sup> Department of Applied Chemistry, Graduate School of Engineering,  
Osaka University, Suita, Osaka 565-0871, Japan.

<sup>b</sup> M.K. and K.G. contributed equally to this work.

<sup>c</sup> Innovative Catalysis Science Division, Institute for Open and Transdisciplinary  
Research Initiatives (ICS-OTRI), Osaka University, Suita, Osaka 565-0871, Japan.

y-nishii@chem.eng.osaka-u.ac.jp

miura@chem.eng.osaka-u.ac.jp

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## 1. General Information

All manipulations were performed under N<sub>2</sub> using standard Schlenk techniques unless otherwise noted. Toluene and 1,4-dioxane were dried and deoxygenated by a Glass Counter Solvent Dispensing System (Nikko Hansen & Co., Ltd.). DCE (1,2-dichloroethane) and DMSO (dimethylsulfoxide) were distilled from CaH<sub>2</sub> and stored with molecular sieves 4A. MeOH was purchased as dehydrated solvent and used as received. Silica gel column chromatography was performed using Wakosil<sup>®</sup> C-200 (64~210 μm). [Cp\*RhCl<sub>2</sub>]<sub>2</sub> and [Cp\*Rh(MeCN)<sub>3</sub>][SbF<sub>6</sub>]<sub>2</sub> were prepared according to the literature procedure.<sup>1</sup> Pyrazoles (**1a-1k**),<sup>2</sup> indolines (**4a-4j**, **6**),<sup>3</sup> and indoles (**8a-8h**)<sup>4</sup> were prepared according to the literature procedures. 2-Naphthylacetaldehyde (**10**) was prepared according to the literature procedure.<sup>5</sup> All other reagents were purchased from suppliers and used without further purification.

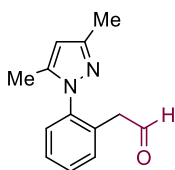
Nuclear magnetic resonance spectra were measured at 400 MHz (<sup>1</sup>H NMR), at 100 MHz (<sup>13</sup>C NMR), and at 376 MHz (<sup>19</sup>F NMR) in 5 mm NMR tubes. <sup>1</sup>H NMR chemical shifts were reported in ppm relative to the resonance of TMS (δ 0.00) or the residual solvent signals at δ 7.26 for CDCl<sub>3</sub>. <sup>13</sup>C NMR chemical shifts were reported in ppm relative to the residual solvent signals at δ 77.2 for CDCl<sub>3</sub>. Melting points were measured with Mettler Toledo MP90. High resolution mass spectra (HRMS) were recorded by APCI-TOF. Gas chromatography (GC) was conducted with Shimadzu GC-2010 plus equipped Dielectric-Barrier Discharge Ionization (BID) Detector and Shinwa Chemical Industries MICROPACKED-ST column (2.0 m × 1.0 mm I.D.). Preparative gel permeation chromatography (GPC) was conducted with two in-line YMC-GPC T2000 preparative columns (eluent: CHCl<sub>3</sub>).

## 2. Experimental Procedures and Identification Data

### 2-1. General Procedure for the Formylmethylation of **1** with **2** (Scheme 2)

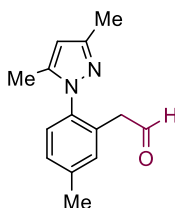
To an oven-dried 10 mL screw-top tube were added **1** (0.2 mmol), vinylene carbonate (**2**) (34.4 mg, 0.4 mmol), [Cp\*Rh(MeCN)<sub>3</sub>][SbF<sub>6</sub>]<sub>2</sub> (10.0 mg, 6.0 mol%), and DCE (1.0 mL). The tube was filled with N<sub>2</sub> and sealed with a Teflon cap. The mixture was heated at 130 °C with an oil bath for 16 h. After cooling to room temperature, volatiles were removed in vacuo. The residue was purified by silica gel column chromatography to give the corresponding product **3**.

#### 2-(2-(3,5-dimethyl-1*H*-pyrazol-1-yl)phenyl)acetaldehyde (**3a**)



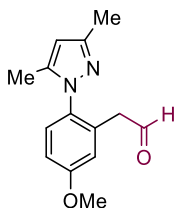
Isolated by silica gel column chromatography (eluent: chloroform/MeOH = 100/1), orange oil (35.1 mg, 82% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.58 (t, *J* = 1.5 Hz, 1H), 7.45-7.38 (m, 2H), 7.33 (dd, *J* = 2.1, 7.0 Hz, 1H), 7.28 (dd, *J* = 1.4, 7.6 Hz, 1H), 5.96 (s, 1H), 3.54 (d, *J* = 1.6 Hz, 2H), 2.26 (s, 3H), 2.10 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.7, 149.1, 140.6, 139.1, 131.6, 131.1, 129.2, 128.2, 128.0, 105.8, 46.3, 13.5, 11.4; HRMS *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>O 215.1179; Found 215.1177.

#### 2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-5-methylphenylacetaldehyde (**3b**)



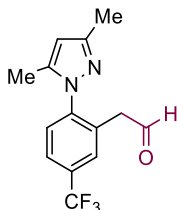
Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), orange oil (33.8 mg, 74% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.56 (t, *J* = 1.8 Hz, 1H), 7.20-7.15 (m, 2H), 7.12 (s, 1H), 5.95 (s, 1H), 3.48 (d, *J* = 1.8 Hz, 2H), 2.40 (s, 3H), 2.26 (s, 3H), 2.08 (d, *J* = 0.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 199.0, 149.0, 140.6, 139.2, 136.5, 132.2, 130.7, 128.8, 127.8, 105.6, 46.2, 21.2, 13.5, 11.4; HRMS *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O 229.1335; Found 229.1320.

2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-5-methoxyphenylacetaldehyde (**3c**)



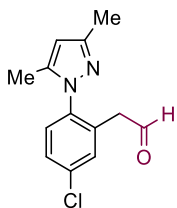
Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 1/1), yellow oil (23.6 mg, 48% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.56 (t, *J* = 1.8 Hz, 1H), 7.21 (d, *J* = 8.6 Hz, 1H), 6.91-6.88 (dd, *J* = 2.9, 8.6 Hz, 1H), 6.83 (d, *J* = 2.8 Hz, 1H), 5.94 (s, 1H), 3.84 (s, 3H), 3.46 (d, *J* = 1.8 Hz, 2H), 2.25 (s, 3H), 2.06 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.6, 159.8, 148.9, 140.8, 132.4, 132.0, 129.1, 116.6, 113.2, 105.5, 55.6, 46.4, 13.5, 11.4; HRMS *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> 245.1285; Found 245.1298.

2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-5-(trifluoromethyl)phenylacetaldehyde (**3d**)



Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 1/1), yellow oil (44.4 mg, 79% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.58 (t, *J* = 1.3 Hz, 1H), 7.68-7.66 (dd, *J* = 1.3, 8.2 Hz, 1H), 7.60 (d, *J* = 1.4 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 5.99 (s, 1H), 3.72 (s, 2H), 2.26 (s, 3H), 2.15 (d, *J* = 0.5 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 197.3, 149.9, 142.0, 140.7, 132.1, 130.0 (q, -CCF<sub>3</sub>, *J* = 32.9 Hz), 129.0 (q, -CCCF<sub>3</sub>, *J* = 3.5 Hz), 128.1, 125.2 (q, -CCCF<sub>3</sub>, *J* = 3.6 Hz), 123.6 (q, -CF<sub>3</sub>, *J* = 270.5 Hz), 106.6, 46.4, 13.5, 11.5; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.6; HRMS *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>13</sub>N<sub>2</sub>OF<sub>3</sub> 283.1052; Found 283.1043.

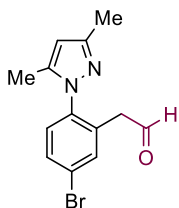
2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-5-chlorophenylacetaldehyde (**3e**)



Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), orange oil (32.8 mg, 66% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.55 (t, *J* = 1.5 Hz, 1H), 7.37 (dd, *J* = 2.4, 8.3 Hz, 1H), 7.33 (d, *J* = 2.2 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 5.96 (s, 1H), 3.55 (d, *J* = 1.4 Hz, 2H), 2.25 (s, 3H), 2.10 (d, *J* = 0.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 197.6, 149.5, 140.7, 137.6, 134.7, 133.0, 131.7, 129.0, 128.3,

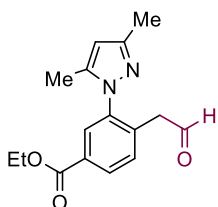
106.1, 46.1, 13.5, 11.4; HRMS  $m/z$ :  $[M+H]^+$  Calcd for  $C_{13}H_{13}N_2OCl$  249.0789; Found 249.0785.

2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-5-bromophenylacetaldehyde (**3f**)



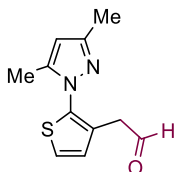
Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), yellow oil (22.5 mg, 38%, eluent);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  9.55 (t,  $J$  = 1.5 Hz, 1H), 7.53 (dd,  $J$  = 2.2, 8.3 Hz, 1H), 7.49 (d,  $J$  = 2.2 Hz, 1H), 7.14 (d,  $J$  = 8.3 Hz, 1H), 5.96 (s, 1H), 3.55 (d,  $J$  = 1.4 Hz, 2H), 2.25 (s, 3H), 2.10 (d,  $J$  = 0.5 Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  197.6, 149.6, 140.7, 138.1, 134.6, 133.3, 131.3, 129.2, 122.7, 106.2, 46.0, 13.5, 11.4; HRMS  $m/z$ :  $[M+H]^+$  Calcd for  $C_{13}H_{13}N_2OBr$  293.0284; Found 293.0269.

2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-4-ethoxycarbonylphenylacetaldehyde (**3g**)



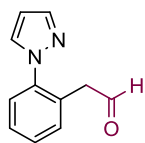
Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 2/1), orange oil (10.1 mg, 50% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  9.58 (t,  $J$  = 1.5 Hz, 1H), 8.10 (dd,  $J$  = 1.7, 8.0 Hz, 1H), 7.95 (d,  $J$  = 1.7 Hz, 1H), 7.41 (d,  $J$  = 8.0 Hz, 1H), 5.99 (s, 1H), 4.39 (q,  $J$  = 7.1 Hz, 2H), 3.66 (d,  $J$  = 1.4 Hz, 2H), 2.27 (s, 3H), 2.13 (s, 3H), 1.39 (t,  $J$  = 7.1 Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  197.6, 165.4, 149.6, 140.8, 139.2, 136.1, 131.8, 130.7, 130.0, 128.9, 106.2, 61.4, 46.4, 14.3, 13.5, 11.5; HRMS  $m/z$ :  $[M+H]^+$  Calcd for  $C_{16}H_{18}N_2O_3$  287.1390; Found 287.1401.

2-(3,5-Dimethyl-1*H*-pyrazol-1-yl)thiophene-3-ylacetaldehyde (**3h**)



Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 1/1), brown oil (29.1 mg, 66% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  9.64 (t,  $J$  = 1.8 Hz, 1H), 7.30 (d,  $J$  = 5.6 Hz, 1H), 6.93 (d,  $J$  = 5.6 Hz, 1H), 5.97 (s, 1H), 3.53 (d,  $J$  = 1.9 Hz, 2H), 2.26 (s, 3H), 2.16 (d,  $J$  = 0.6 Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  198.0, 150.3, 142.6, 137.4, 129.5, 127.4, 124.3, 106.5, 42.3, 13.6, 11.5; HRMS  $m/z$ :  $[M+H]^+$  Calcd for  $C_{11}H_{12}N_2OS$  221.0743; Found 221.0749.

2-(2-(1*H*-pyrazol-1-yl)phenyl)acetaldehyde (**3i**)

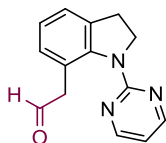


Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), yellow oil (18.7 mg, 50% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.66 (t, *J* = 1.6 Hz, 1H), 7.71 (d, *J* = 1.5 Hz, 1H), 7.64 (dd, *J* = 0.6, 2.4 Hz, 1H), 7.43-7.37 (m, 3H), 7.36-7.32 (m, 1H), 6.44 (t, *J* = 2.1 Hz, 1H), 3.74 (d, *J* = 1.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 198.8, 140.9, 140.1, 132.2, 130.4, 128.6, 128.6, 128.4, 125.7, 106.9, 46.8; HRMS *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O 187.0866; Found 187.0858.

### 2-3. General Procedure for the Formylmethylation of **4** with **2** (Scheme 3)

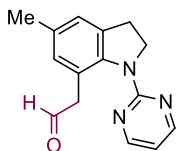
To an oven-dried 10 mL screw-top tube were added **4** (0.2 mmol), vinylene carbonate (**2**) (34.4 mg, 0.4 mmol),  $[\text{Cp}^*\text{Rh}(\text{MeCN})_3][\text{SbF}_6]_2$  (10.0 mg, 6.0 mol%), and DCE (1.0 mL). The tube was filled with  $\text{N}_2$  and sealed with a Teflon cap. The mixture was heated at 130 °C with an oil bath for 16 h. After cooling to room temperature, volatiles were removed in vacuo. The residue was purified by silica gel column chromatography to give the corresponding product **5**.

#### 2-(1-(Pyrimidin-2-yl)indolin-7-yl)acetaldehyde (**5a**)



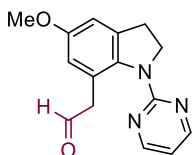
Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), brown solid (36.5 mg, 76% yield); m.p. 87.9-89.9 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.78 (t,  $J$  = 1.7 Hz, 1H), 8.32 (d,  $J$  = 4.8 Hz, 2H), 7.22 (dt,  $J$  = 1.2, 6.2 Hz, 1H), 7.13-1.07 (m, 2H), 6.69 (t,  $J$  = 4.8 Hz, 1H), 4.45 (t,  $J$  = 7.9 Hz, 2H), 3.44 (d,  $J$  = 1.7 Hz, 2H), 3.10 (t,  $J$  = 7.8 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.1, 160.5, 157.5, 143.2, 135.3, 130.1, 124.3, 123.8, 123.4, 112.6, 52.2, 48.0, 29.5; HRMS  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_3\text{O}$  240.1131; Found 240.1139.

#### 2-(5-Methyl-1-(pyrimidin-2-yl)indolin-7-yl)acetaldehyde (**5b**)



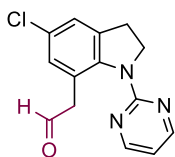
Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), yellow solid (38.8 mg, 77% yield); m.p. 119.0-121.0 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.78 (t,  $J$  = 1.7 Hz, 1H), 8.31 (d,  $J$  = 4.8 Hz, 2H), 7.04 (s, 1H), 6.92 (s, 1H), 6.67 (t,  $J$  = 4.8 Hz, 1H), 4.43 (t,  $J$  = 7.8 Hz, 2H), 3.42 (d,  $J$  = 1.7 Hz, 2H), 3.05 (t,  $J$  = 7.8 Hz, 2H), 2.35 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.2, 160.7, 157.5, 140.9, 135.4, 134.1, 130.5, 124.6, 123.1, 112.4, 52.2, 47.9, 29.5, 20.9; HRMS  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}$  254.1288; Found 254.1276.

#### 2-(5-Methoxy-1-(pyrimidin-2-yl)indolin-7-yl)acetaldehyde (**5c**)



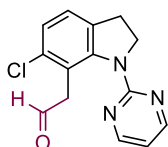
Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 2/1), white solid (12.9 mg, 24% yield); m.p. 85.5-87.5 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.79 (t, *J* = 1.7 Hz, 1H), 8.30 (d, *J* = 4.8 Hz, 2H), 6.81 (t, *J* = 1.3 Hz, 1H), 6.67 (d, *J* = 4.8 Hz, 1H), 6.65 (d, *J* = 1.8 Hz, 1H), 4.45 (t, *J* = 7.7 Hz, 2H), 3.82 (s, 3H), 3.44 (d, *J* = 1.7 Hz, 2H), 3.06 (t, *J* = 7.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.9, 160.8, 157.5, 157.0, 136.9, 136.8, 124.3, 114.6, 112.2, 110.1, 55.7, 52.3, 48.0, 30.0; HRMS *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub> 270.1237; Found 270.1225.

2-(5-Chloro-1-(pyrimidin-2-yl)indolin-7-yl)acetaldehyde (**5d**)



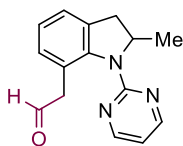
Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), yellow solid (32.3 mg, 59% yield); m.p. 154.4-156.4 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.76 (t, *J* = 1.5 Hz, 1H), 8.33 (d, *J* = 4.8 Hz, 2H), 7.19 (d, *J* = 1.8 Hz, 1H), 7.11 (d, *J* = 1.9 Hz, 1H), 6.72 (t, *J* = 4.8 Hz, 1H), 4.45 (t, *J* = 7.9 Hz, 2H), 3.42 (d, *J* = 1.4 Hz, 2H), 3.08 (t, *J* = 7.9 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.0, 160.4, 157.6, 142.1, 137.2, 129.8, 129.1, 124.6, 124.0, 112.9, 52.3, 47.7, 29.4; HRMS *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>12</sub>N<sub>3</sub>OCl 274.0742; Found 274.0739.

2-(6-Chloro-1-(pyrimidin-2-yl)indolin-7-yl)acetaldehyde (**5e**)



Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), brown solid (6.6 mg, 12% yield); m.p. 127.8-129.8 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.75 (t, *J* = 1.4 Hz, 1H), 8.33 (d, *J* = 4.8 Hz, 2H), 7.20-7.13 (m, 2H), 6.73 (t, *J* = 4.8 Hz, 1H), 4.49 (t, *J* = 7.8 Hz, 2H), 3.46 (d, *J* = 1.4 Hz, 2H), 3.08 (t, *J* = 8.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 200.8, 160.5, 157.6, 145.3, 134.3, 133.9, 124.9, 124.3, 122.5, 113.1, 52.8, 44.9, 29.3; HRMS *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>12</sub>N<sub>3</sub>OCl 274.0742; Found 274.0746.

2-(2-Methyl-1-(pyrimidin-2-yl)indolin-7-yl)acetaldehyde (**5f**)

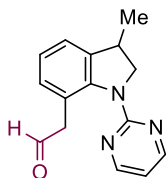


Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), orange oil (26.9 mg, 53% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.76 (dd, *J* = 0.8, 2.5 Hz, 1H), 8.32 (d, *J* = 4.8 Hz, 2H), 7.23-7.21 (m,



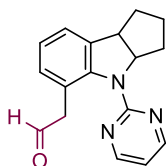
1H), 7.13-7.10 (m, 2H), 6.69 (t,  $J = 4.8$  Hz, 1H), 5.11-5.03 (m, 1H), 3.50-3.40 (m, 3H), 2.56 (d,  $J = 15.6$  Hz, 1H), 1.38 (d,  $J = 6.6$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.2, 160.1, 157.5, 141.7, 134.0, 131.5, 124.3, 124.3, 123.8, 112.7, 59.4, 48.1, 36.6, 21.1; HRMS  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}$  274.0742; Found 274.0739.

2-(3-Methyl-1-(pyrimidin-2-yl)indolin-7-yl)acetaldehyde (**5g**)



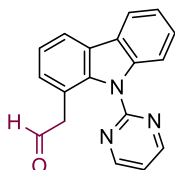
Isolated by silica gel column chromatography (eluent: chloroform/MeOH = 100/1), white solid (41.6 mg, 82% yield); m.p. 107.5-109.5 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.79 (t,  $J = 1.7$  Hz, 1H), 8.32 (d, 2H,  $J = 4.8$  Hz), 7.20-7.16 (m, 1H), 7.14-7.12 (m, 2H), 6.69 (t,  $J = 4.8$  Hz, 1H), 4.67 (dd,  $J = 8.2, 11.2$  Hz, 1H), 3.91 (dd,  $J = 7.5, 11.2$  Hz, 1H), 3.50-3.38 (m, 3H), 1.31 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.1, 160.7, 157.5, 143.0, 140.4, 130.2, 124.5, 123.4, 122.5, 112.6, 59.9, 47.9, 36.0, 18.6; HRMS  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}$  254.1288; Found 254.1296.

2-(4-(Pyrimidin-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indol-5-yl)acetaldehyde (**5h**)



Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), brown solid (47.8 mg, 86% yield); m.p. 83.4-85.4 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.77 (dd,  $J = 0.5, 2.7$  Hz, 1H), 8.33 (d,  $J = 4.8$  Hz, 2H), 7.17-7.10 (m, 3H), 6.71 (t,  $J = 4.8$  Hz, 1H), 5.05 (dd,  $J = 4.3, 8.2$  Hz, 1H), 3.94 (td,  $J = 2.4, 8.2$  Hz, 1H), 3.45 (dd,  $J = 2.7, 17.3$  Hz, 1H), 3.37 (d,  $J = 17.3$  Hz, 1H), 2.27-2.17 (m, 1H), 2.14-2.04 (m, 1H), 1.92-1.83 (m, 2H), 1.68-1.59 (m, 1H), 1.47-1.36 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.2, 160.5, 157.4, 142.7, 138.7, 131.5, 130.3, 124.4, 123.4, 122.6, 112.9, 68.7, 48.2, 45.3, 34.9, 33.6, 24.1; HRMS  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}$  280.1444; Found 280.1432.

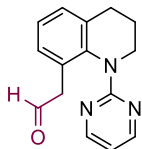
2-(9-(Pyrimidin-2-yl)-9*H*-carbazol-1-yl)acetaldehyde (**5i**)



Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 1/1), yellow oil (19.1 mg, 33% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.78 (t,  $J = 1.9$  Hz, 1H), 8.77 (d,  $J = 4.8$  Hz, 2H), 8.34 (d,  $J = 8.3$  Hz,

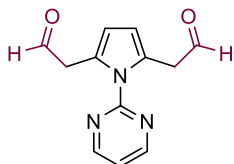
1H), 8.09-8.06 (m, 2H), 7.48-7.43 (m, 1H), 7.40 (d,  $J = 7.6$  Hz, 1H), 7.39-7.33 (m, 2H), 7.21 (t,  $J = 4.8$  Hz, 1H), 3.55 (d,  $J = 1.9$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.1, 158.6, 158.4, 140.9, 138.6, 131.5, 130.4, 127.5, 127.0, 125.5, 122.8, 122.6, 119.8, 119.5, 117.8, 113.6, 48.6; HRMS  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{18}\text{H}_{13}\text{N}_3\text{O}$  288.1131; Found 288.1137.

2-(1-(Pyrimidin-2-yl)-1,2,3,4-tetrahydroquinolin-8-yl)acetaldehyde (**5j**)



Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), brown oil (21.6 mg, 43% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) (broad peaks are observed due to the isomerism of piperidine moiety)  $\delta$  9.67 (t,  $J = 2.0$  Hz, 1H), 8.33 (d,  $J = 3.8$  Hz, 2H), 7.22-7.14 (m, 3H), 6.63 (t,  $J = 4.8$  Hz, 1H), 4.87 (br, 1H), 3.42 (d,  $J = 2.0$  Hz, 2H), 3.24 (br, 1H), 2.77 (br, 2H), 2.04 (br, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.5, 161.0, 158.1, 140.5, 134.6, 130.3, 128.3, 128.1, 125.7, 112.1, 46.6, 44.9, 26.5, 23.7; HRMS  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}$  274.0742; Found 274.0746.

2,2'-(1-(Pyrimidin-2-yl)-1H-pyrrole-2,5-diyl)diacetaldehyde (**7**)

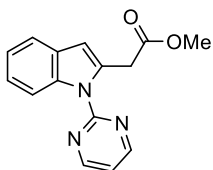


Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 1/1), brown oil (29.3 mg, 64% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.77 (t,  $J = 1.6$  Hz, 2H), 8.60 (d,  $J = 4.8$  Hz, 2H), 7.15 (t,  $J = 4.8$  Hz, 1H), 6.24 (s, 2H), 3.84 (d,  $J = 1.6$  Hz, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.1, 157.9, 127.1, 118.0, 113.5, 43.6, 29.7; HRMS  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{12}\text{H}_{11}\text{N}_3\text{O}_2$  230.0924; Found 230.0917.

#### 2-4. General Procedure for the Reaction of **8** with **2** (Scheme 4)

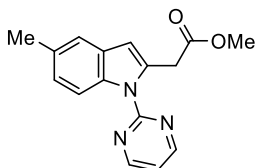
To an oven-dried 10 mL screw-top tube were added **8** (0.2 mmol), vinylene carbonate (**2**) (25.8 mg, 0.3 mmol), [Cp\*Rh(MeCN)<sub>3</sub>][SbF<sub>6</sub>]<sub>2</sub> (4.2 mg, 2.5 mol%), and MeOH (2.0 mL). The tube was filled with N<sub>2</sub> and sealed with a Teflon cap. The mixture was heated at 130 °C with an oil bath for 16 h. After cooling to room temperature, volatiles were removed in vacuo. The residue was purified by silica gel column chromatography and, if indicated, GPC to give the corresponding product **9**.

Methyl 2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate (**9a**)<sup>6</sup>



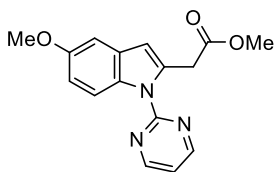
Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), white solid (42.2 mg, 79% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.69 (d, *J* = 4.8 Hz, 2H), 8.57 (dd, *J* = 0.8, 8.4 Hz, 1H), 7.56 (dd, *J* = 0.5, 7.7 Hz, 1H), 7.31-7.19 (m, 2H), 7.07 (t, *J* = 4.8 Hz, 1H), 6.59 (d, *J* = 0.6 Hz, 1H), 4.18 (s, 2H), 3.61 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 171.3, 158.2, 157.8, 136.9, 133.4, 129.1, 123.4, 122.2, 120.2, 116.6, 115.5, 109.8, 51.9, 37.1.

Methyl 2-(5-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate (**9b**)<sup>6</sup>



Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), white solid (54.5 mg, 97% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.66 (d, *J* = 4.8 Hz, 2H), 8.46 (d, *J* = 8.6 Hz, 1H), 7.34 (t, *J* = 0.8 Hz, 1H), 7.10 (dd, *J* = 1.4, 8.6 Hz, 1H), 7.03 (t, *J* = 4.8 Hz, 1H), 6.51 (d, *J* = 0.6 Hz, 1H), 4.16 (s, 2H), 3.61 (s, 3H), 2.44 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 171.4, 158.2, 157.7, 135.1, 133.4, 131.5, 129.3, 124.8, 120.0, 116.3, 115.3, 109.6, 51.9, 37.2, 21.3.

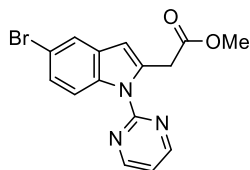
Methyl 2-(5-methoxy-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate (**9c**)<sup>6</sup>



Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), white solid (53.7 mg, 90% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.65 (d, *J* = 4.8 Hz, 2H), 8.51 (d, *J* = 9.1 Hz, 1H), 7.04-7.02 (m, 2H),

6.91 (dd,  $J = 2.6, 9.1$  Hz, 1H), 6.52 (d,  $J = 0.6$  Hz, 1H), 4.16 (s, 2H), 3.86 (s, 3H), 3.62 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.3, 158.1, 157.7, 155.5, 134.0, 131.7, 129.8, 116.6, 116.3, 112.4, 109.8, 102.5, 55.7, 51.9, 37.3.

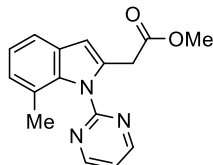
Methyl 2-(5-chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate (**9d**)<sup>6</sup>



Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 1/1), white solid (23.6 mg, 34% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.70 (d,  $J = 4.7$  Hz, 2H), 8.47 (d,  $J = 8.9$  Hz, 1H), 7.68 (d,  $J = 2.0$  Hz, 1H), 7.36 (dd,  $J = 2.1, 8.9$  Hz, 1H), 7.11 (t,  $J = 4.8$  Hz, 1H), 6.53 (d,  $J = 0.6$  Hz, 1H), 4.17 (s, 2H), 3.62 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.0, 157.9, 157.8, 135.5, 134.7, 130.8, 126.2, 122.7, 117.1, 116.9, 115.4, 109.0, 52.0, 37.0.

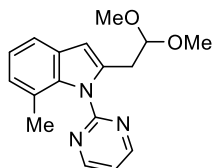
A mixture of **9e** and **9e'** (**9e/9e'** = 5/1) was obtained by silica gel column chromatography (eluent: hexane/EtOAc = 3/1) (45.3 mg, 80% yield). These two compounds were separated by GPC ( $\text{CHCl}_3$ ).

Methyl 2-(7-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate (**9e**)<sup>6</sup>



Brown oil (31.1 mg, 55% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.81 (d,  $J = 4.8$  Hz, 2H), 7.44 (d,  $J = 7.3$  Hz, 1H), 7.25 (t,  $J = 4.8$  Hz, 1H), 7.11 (t,  $J = 7.5$  Hz, 1H), 7.02 (d,  $J = 7.2$  Hz, 1H), 6.59 (s, 1H), 3.94 (s, 2H), 3.52 (s, 3H), 2.06 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 158.3, 136.5, 133.7, 129.5, 126.0, 125.6, 121.8, 118.6, 118.4, 107.3, 52.1, 34.4, 20.8 (1C overlapped).

2-(2,2-Dimethoxyethyl)-7-methyl-1-(pyrimidin-2-yl)-1H-indole (**9e'**)

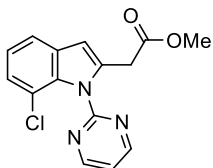


Colorless oil (8.4 mg, 14% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.87 (d,  $J = 4.8$  Hz, 2H), 7.44 (d,  $J = 7.7$  Hz, 1H), 7.33 (t,  $J = 4.8$  Hz, 1H), 7.07 (t,  $J = 7.4$  Hz, 1H), 6.95 (d,  $J = 7.2$  Hz, 1H), 6.56 (s, 1H), 4.63 (t,  $J = 5.6$  Hz, 1H), 3.26 (s, 6H), 3.07 (dd,  $J = 0.6, 9.3$  Hz, 2H), 1.95 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  158.8, 158.3, 136.7, 136.5, 129.6, 125.2, 121.8, 121.3, 119.1, 118.1, 105.1, 104.0, 53.5, 31.6, 20.1 (1C

overlapped); HRMS  $m/z$ :  $[M+H]^+$  Calcd for  $C_{17}H_{19}N_3O_2$  298.1550; Found 298.1545.

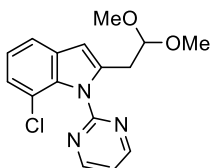
A mixture of **9f** and **9f'** (**9f/9f'** = 4/1) was obtained by silica gel column chromatography (eluent: hexane/EtOAc = 3/1) (47.0 mg, 77% yield). These two compounds were separated by GPC ( $CHCl_3$ ).

Methyl 2-(7-chloro-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)acetate (**9f**)



Brown oil (19.8 mg, 33% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.84 (d,  $J$  = 4.9 Hz, 2H), 7.51 (dd,  $J$  = 1.0, 7.8 Hz, 1H), 7.31 (t,  $J$  = 4.9 Hz, 1H), 7.21 (dd,  $J$  = 1.1, 7.7 Hz, 1H), 7.10 (t,  $J$  = 7.7 Hz, 1H), 6.62 (s, 1H), 3.90 (s, 2H), 3.54 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  170.0, 158.3, 157.4, 134.9, 133.6, 131.5, 124.6, 122.2, 119.3, 119.3, 117.9, 106.5, 52.2, 33.9; HRMS  $m/z$ :  $[M+H]^+$  Calcd for  $C_{15}H_{12}N_3O_2Cl$  302.0691; Found 302.0685.

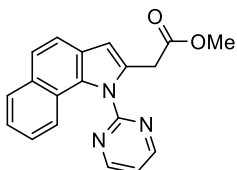
2-(2,2-Dimethoxyethyl)-7-chloro-1-(pyrimidin-2-yl)-1*H*-indole (**9f'**)



Brown oil (7.6 mg, 12% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.88 (d,  $J$  = 4.9 Hz, 2H), 7.49 (dd,  $J$  = 1.0, 7.7 Hz, 1H), 7.37 (t,  $J$  = 4.9 Hz, 1H), 7.14 (dd,  $J$  = 1.0, 7.7 Hz, 1H), 7.07 (t,  $J$  = 7.7 Hz, 1H), 6.58 (s, 1H), 4.66 (t,  $J$  = 5.6 Hz, 1H), 3.27 (s, 6H), 3.03 (d,  $J$  = 5.6 Hz, 2H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  158.4, 138.0, 133.6, 131.6, 123.7, 121.8, 119.7, 119.0, 117.3, 104.6, 103.5, 53.4, 31.3 (1C overlapped); HRMS  $m/z$ :  $[M+H]^+$  Calcd for  $C_{16}H_{16}N_3O_2Cl$  318.1004; Found 318.1009.

A mixture of **9g** and **9g'** (**9g/9g'** = 5/3) was obtained by silica gel column chromatography (eluent: hexane/EtOAc = 2/1) (41.9 mg, 65% yield). These two compounds were separated by GPC ( $CHCl_3$ ).

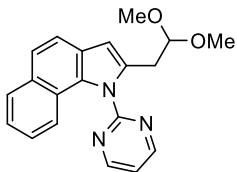
Methyl 2-(1-(pyrimidin-2-yl)-1*H*-benzo[*g*]indol-2-yl)acetate (**9g**)



Brown oil (22.8 mg, 36% yield);  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.90 (d,  $J$  = 4.9 Hz, 2H), 7.89 (d,  $J$  = 8.1 Hz, 1H), 7.67 (d,  $J$  = 8.5 Hz, 1H), 7.61 (d,  $J$  = 8.5 Hz, 1H), 7.38 (t,  $J$  = 4.8 Hz, 1H), 7.36-7.32 (m, 1H), 7.22-7.18 (m, 1H), 7.06 (d,  $J$  = 8.6 Hz, 1H), 6.72 (s, 1H), 3.98 (s, 2H), 3.53 (s, 3H);  $^{13}C$  NMR (100 MHz,

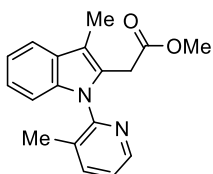
CDCl<sub>3</sub>)  $\delta$  170.5, 159.4, 159.1, 133.0, 131.9, 131.3, 129.2, 126.3, 124.7, 123.6, 123.3, 122.3, 121.8, 120.2, 119.6, 107.9, 52.1, 34.3; HRMS  $m/z$ : [M+H]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub> 318.1237; Found 318.1245.

2-(2,2-Dimethoxyethyl)-1-(pyrimidin-2-yl)-1*H*-benzo[*g*]indole (**9g'**)



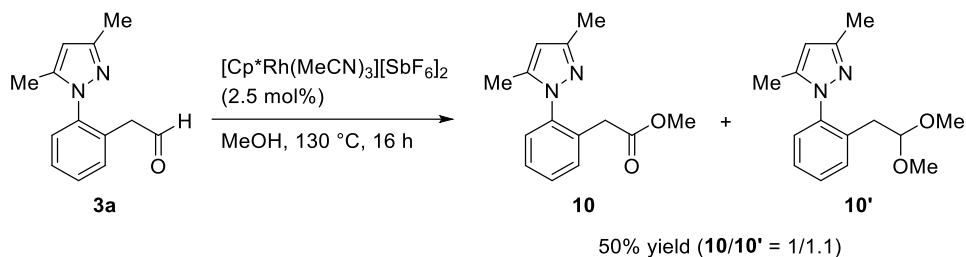
Brown oil (12.9 mg, 20% yield); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.96 (d,  $J$  = 4.8 Hz, 2H), 7.88 (d,  $J$  = 8.0 Hz, 1H), 7.68 (d,  $J$  = 8.5 Hz, 1H), 7.58 (d,  $J$  = 8.5 Hz, 1H), 7.45 (t,  $J$  = 4.9 Hz, 1H), 7.32-7.28 (m, 1H), 7.18-7.14 (m, 1H), 6.82 (d,  $J$  = 7.9 Hz, 1H), 6.70 (s, 1H), 4.65 (t,  $J$  = 5.6 Hz, 1H), 3.27 (s, 6H), 3.12 (dd,  $J$  = 0.6, 5.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.8, 159.2, 135.9, 131.6, 131.1, 129.2, 126.2, 124.7, 123.3, 122.8, 122.1, 121.0, 120.2, 120.0, 105.9, 104.2, 53.6, 31.6; HRMS  $m/z$ : [M+H]<sup>+</sup> Calcd for C<sub>20</sub>H<sub>19</sub>N<sub>3</sub>O<sub>2</sub> 334.1550; Found 334.1538.

Methyl 2-(3-methyl-1-(3-methylpyridin-2-yl)-1*H*-indol-2-yl)acetate (**9h**)



Isolated by silica gel column chromatography (eluent: hexane/EtOAc = 3/1), white solid (52.2 mg, 89% yield); m.p. 92.7-94.7 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.45 (dd,  $J$  = 1.4, 4.8 Hz, 1H), 7.73 (dd,  $J$  = 1.1, 7.6 Hz, 1H), 7.60-7.58 (m, 1H), 7.30 (dd,  $J$  = 4.8, 7.6 Hz, 1H), 7.14-7.12 (m, 2H), 6.82-6.80 (m, 1H), 3.87 (d,  $J$  = 16.5 Hz, 1H), 3.74 (d,  $J$  = 16.5 Hz, 1H), 3.49 (s, 3H), 2.35 (s, 3H), 2.11 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.4, 150.1, 147.3, 140.0, 136.3, 132.1, 128.7, 128.7, 123.4, 122.2, 119.8, 118.9, 111.4, 110.0, 51.9, 30.9, 17.5, 8.8; HRMS  $m/z$ : [M+H]<sup>+</sup> Calcd for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> 295.1441; Found 295.1456.

## 2-5. Control Experiment: Oxidative Esterification (Scheme 5)



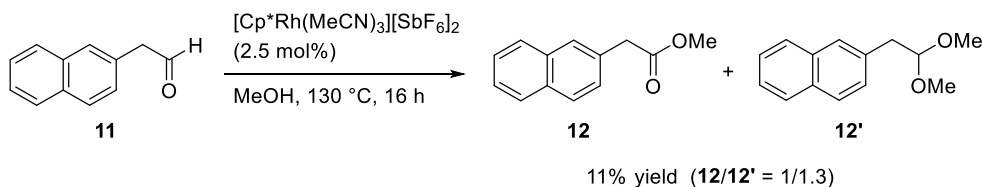
To an oven-dried 10 mL screw-top tube were added **3a** (32.1 mg, 0.15 mmol),  $[\text{Cp}^*\text{Rh}(\text{MeCN})_3][\text{SbF}_6]_2$  (3.1 mg, 2.5 mol%), and MeOH (1.5 mL). The tube was filled with  $\text{N}_2$  and sealed with a Teflon cap. The mixture was heated at 130 °C with an oil bath for 16 h. After cooling to room temperature, volatiles were removed in vacuo. A mixture of **10** and **10'** (**10/10'** = 1/1.1) was obtained by silica gel column chromatography (eluent: hexane/EtOAc = 3/1) (19.0 mg, 50% yield). These two compounds were separated by GPC ( $\text{CHCl}_3$ ).

### Methyl 2-(2-(3,5-dimethyl-1H-pyrazol-1-yl)phenyl)acetate (**10**)

Colorless oil (6.0 mg, 15% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.39 (m, 2H), 7.38-7.34 (m, 1H), 7.23 (d,  $J = 7.2$  Hz, 1H), 5.95 (s, 1H), 3.58 (s, 3H), 3.53 (s, 2H), 2.27 (s, 3H), 2.09 (d,  $J = 0.5$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.4, 148.9, 140.8, 138.8, 132.8, 131.4, 129.0, 127.9, 127.9, 105.3, 51.9, 36.7, 13.9, 11.3; HRMS  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_2$  245.1285; Found 245.1268.

### 1-(2-(2,2-dimethoxyethyl)phenyl)-3,5-dimethyl-1H-pyrazole (**10'**)

Colorless oil (6.4 mg, 17% yield);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 (dd,  $J = 1.4$  Hz, 1H), 7.37 (td,  $J = 1.5, 7.5$  Hz, 1H), 7.31 (td,  $J = 1.7, 7.5$  Hz, 1H), 7.20 (dd,  $J = 1.3, 7.7$  Hz, 1H), 5.97 (s, 1H), 4.30 (t,  $J = 5.6$  Hz, 1H), 3.23 (s, 6H), 2.69 (d,  $J = 5.6$  Hz, 2H), 2.28 (s, 3H), 2.08 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.5, 140.5, 138.8, 135.5, 131.7, 128.9, 127.9, 127.1, 105.2, 105.0, 53.9, 35.1, 13.5, 11.4; HRMS  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{15}\text{H}_{20}\text{N}_2\text{O}_2$  261.1598; Found 261.1613.

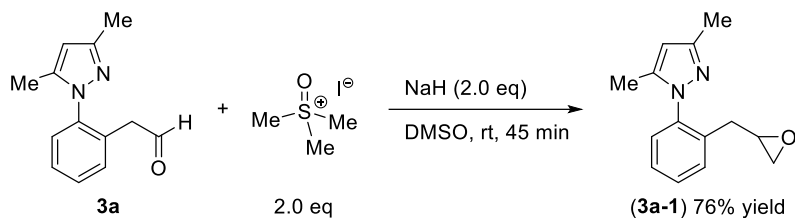


To an oven-dried 10 mL screw-top tube were added **11** (25.5 mg, 0.15 mmol),  $[\text{Cp}^*\text{Rh}(\text{MeCN})_3][\text{SbF}_6]_2$

(3.1 mg, 2.5 mol%), and MeOH (1.5 mL). The tube was filled with N<sub>2</sub> and sealed with a Teflon cap. The mixture was heated at 130 °C with an oil bath for 16 h. After cooling to room temperature, volatiles were removed in vacuo. A mixture of **12** and **12'** (**12/12'** = 1/1.3) was obtained by silica gel column chromatography (eluent: hexane/EtOAc = 3/1) (3.5 mg, 11% yield). These two compounds were reported in the literatures.<sup>7</sup>



## 2-6. Epoxidation of **3a** (Scheme 7)

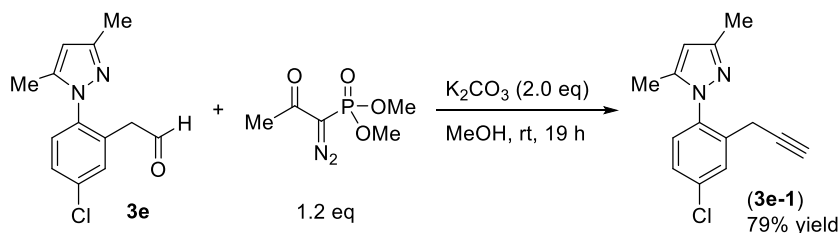


To a two-neck round-bottom flask were added NaH (24.0 mg, 0.6 mmol) and DMSO (1.0 mL). After stirring at room temperature for 15 min, trimethylsulfoxonium iodide (132.0 mg, 0.6 mmol) was added in portionwise. After stirring at this temperature for additional 30 min, a DMSO (1.0 mL) solution of **3a** (64.3 mg, 0.3 mmol) was added via syringe. The mixture was stirred for another 45 min and poured into ice-water. The suspension was extracted with Et<sub>2</sub>O three times, and the combined organic layers was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The crude material was purified by GPC (EtOAc) to give **3a-1** as brown oil (34.8 mg, 76% yield).

### 3,5-Dimethyl-1-(2-(oxiran-2-ylmethyl)phenyl)-1H-pyrazole (**3a-1**)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46 (dd, *J* = 1.5, 7.6 Hz, 1H), 7.41 (td, *J* = 1.4, 7.5 Hz, 1H), 7.34 (td, *J* = 1.7, 7.5 Hz, 1H), 7.23 (dd, *J* = 1.3, 7.7 Hz, 1H), 5.97 (s, 1H), 3.03-2.98 (m, 1H), 2.72-2.67 (m, 2H), 2.58 (dd, *J* = 5.7, 14.6 Hz, 1H), 2.36 (dd, *J* = 2.6, 4.9 Hz, 1H), 2.28 (s, 3H), 2.07 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 148.7, 140.4, 138.7, 135.7, 130.7, 129.2, 128.2, 127.5, 105.3, 51.7, 47.2, 34.3, 13.6, 11.4; HRMS *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O 229.1335; Found 229.1319.

## 2-7. Alkynylation **3e** with an Ohira-Bestmann Reagent (Scheme 7)

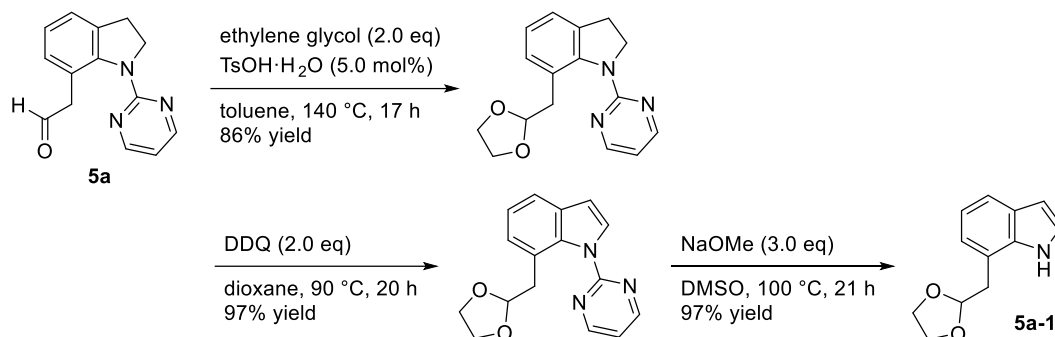


To a two-neck round-bottom flask were added **3e** (42.2 mg, 0.17 mmol), K<sub>2</sub>CO<sub>3</sub> (46.9 mg, 0.34 mmol), and MeOH (2.0 mL). Dimethyl-1-diazo-2-oxopropylphosphonate (30 μL, 0.20 mmol) was added via the syringe, and the solution was stirred at room temperature for 19 h. The resulting mixture was diluted with Et<sub>2</sub>O and washed with water. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica gel chromatography (eluent: hexane/EtOAc = 3/1) to give **3e-1** in as brown solid (32.7 mg, 79% yield).

### 1-(4-Chloro-2-(prop-2-yn-1-yl)phenyl)-3,5-dimethyl-1*H*-pyrazole (**3e-1**)

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 (d,  $J = 2.2$  Hz, 1H), 7.17 (dd,  $J = 8.4, 2.3$  Hz, 1H), 7.11 (d,  $J = 8.4$  Hz, 1H), 5.90 (s, 1H), 5.60 (t,  $J = 6.8$  Hz, 1H), 5.07 (d,  $J = 6.8$  Hz, 2H), 2.21 (s, 3H), 1.99 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.3, 140.1, 134.1, 133.9, 133.1, 128.5, 126.4, 126.3, 104.6, 87.5, 78.3, 28.7, 12.6, 10.3; HRMS  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_2\text{Cl}$  245.0840; Found 245.0829.

### 2-8. Oxidation and Directing Group Removal of **5a** (Scheme 7)



To a round-bottom flask equipped with a reflux condenser were added **5a** (50.6 mg, 0.21 mmol), ethylene glycol (20  $\mu\text{L}$ , 0.42 mmol), toluene (10 mL), *p*-toluenesulfonic acid monohydrate (2.4 mg, 5.0 mol%). The mixture was refluxed (oil bath temp.  $130\text{ }^\circ\text{C}$ ) for 17 h. After cooling to room temperature, volatiles were removed in vacuo. The crude material was purified by silica gel column chromatography (eluent: hexanes/EtOAc = 1/1) to give the corresponding acetal as orange solid (51.3 mg, 86% yield).

### 7-((1,3-Dioxolan-2-yl)methyl)-1-(pyrimidin-2-yl)indoline

m.p.  $112.2\text{--}114.2\text{ }^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.42 (d,  $J = 4.8$  Hz, 2H), 7.27 (d,  $J = 7.2$  Hz, 1H), 7.15 (dd,  $J = 0.9, 7.3$  Hz, 1H), 7.05 (t,  $J = 7.5$  Hz, 1H), 6.69 (t,  $J = 4.8$  Hz, 1H), 5.12 (t,  $J = 5.0$  Hz, 1H), 4.43 (t,  $J = 7.7$  Hz, 2H), 3.95-3.89 (m, 2H), 3.85-3.79 (m, 2H), 3.07-3.02 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.2, 157.7, 142.9, 135.0, 129.2, 126.9, 124.4, 123.0, 112.4, 104.0, 64.8, 53.2, 38.8, 29.9; HRMS  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{16}\text{H}_{17}\text{N}_3\text{O}_2$  284.1394; Found 284.1394.

In a round-bottom flask, the obtained acetal (43.7 mg, 0.15 mmol) was dissolved in 1,4-dioxane (3.0 mL). To this solution was added 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (68.1 mg, 0.30 mmol) portionwise, and mixture was heated at  $90\text{ }^\circ\text{C}$  with an oil bath for 18 h. Solvent was removed in vacuo and the residue was purified by silica gel column chromatography (eluent: hexane/EtOAc = 1/1) to give the corresponding indole as white solid (40.9 mg, 97% yield).

7-((1,3-Dioxolan-2-yl)methyl)-1-(pyrimidin-2-yl)-1*H*-indole

m.p. 114.1-116.1 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.76 (d, *J* = 4.8 Hz, 2H), 7.84 (d, *J* = 3.6 Hz, 1H), 7.54 (dd, *J* = 1.3, 7.6 Hz, 1H), 7.26 (d, *J* = 7.1 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 4.9 Hz, 1H), 6.70 (d, *J* = 3.6 Hz, 1H), 4.99 (t, *J* = 4.7 Hz, 1H), 3.73-3.70 (m, 2H), 3.68-3.65 (m, 2H), 3.41 (d, *J* = 4.7 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.3, 134.2, 132.4, 130.0, 127.4, 122.8, 122.3, 120.0, 117.3, 106.9, 104.5, 64.7, 39.9 (1C overlapped); HRMS *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub> 282.1237; Found 282.1241.

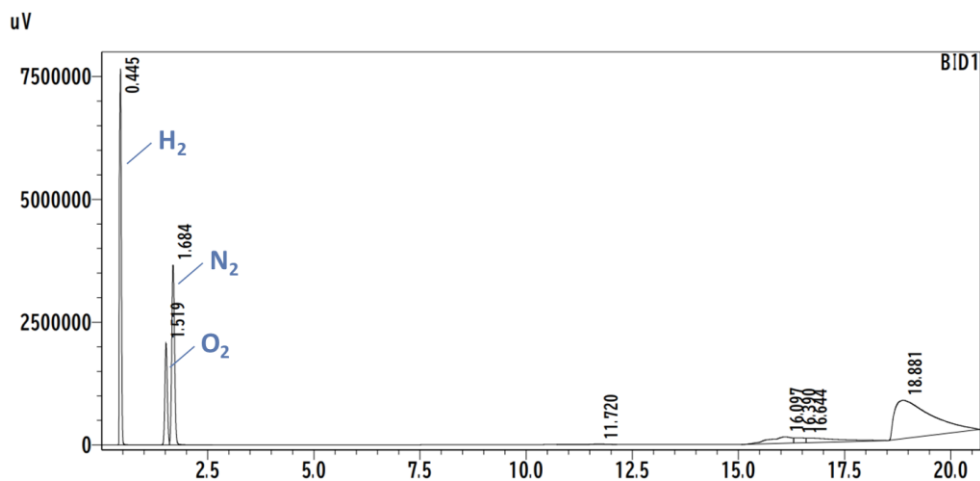
To a two-neck round-bottom flask were added NaOMe (4.9 mg, 0.09 mmol), DMSO (3.0 mL), and the obtained indole (9.6 mg, 0.03 mmol). The solution was heated at 100 °C with an oil bath for 21 h. The resulting mixture was poured into water, and extracted with EtOAc three times. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated in vacuo, and purified by silica gel chromatography (eluent: hexane/EtOAc = 3/1) to give **5a-1** as brown oil (5.9 mg, 97% yield).

7-((1,3-Dioxolan-2-yl)methyl)-1*H*-indole (**5a-1**)

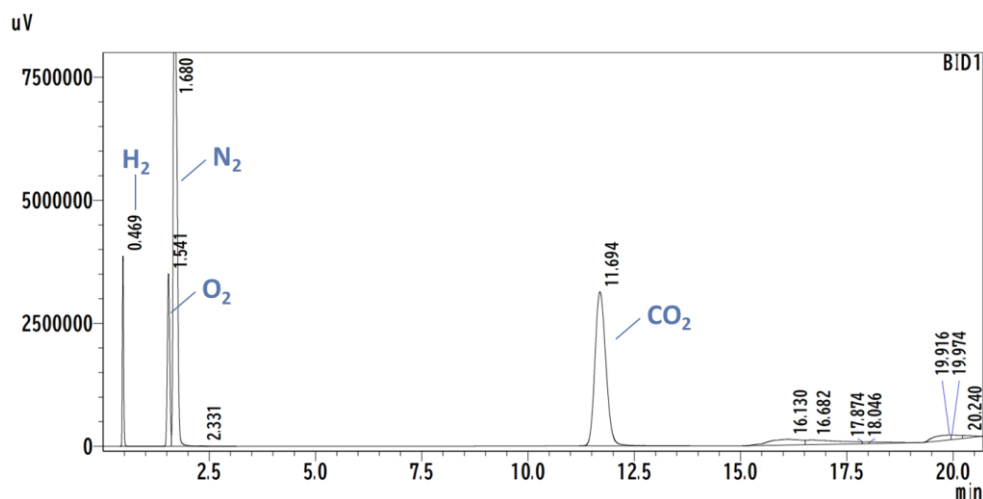
<sup>1</sup>H NMR (400 Hz, CDCl<sub>3</sub>) δ 9.18 (br, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 2.8 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 6.0 Hz, 1H), 6.55 (dd, *J* = 2.1, 1.6 Hz, 1H), 5.12 (t, *J* = 4.2 Hz, 1H), 4.02-3.96 (m, 2H), 3.93-3.87 (m, 2H), 3.26 (d, *J* = 4.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 135.9, 128.1, 124.3, 123.9, 119.7, 119.7, 118.9, 105.0, 102.6, 65.1, 38.2; HRMS *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>13</sub>NO<sub>2</sub> 204.1019; Found 204.1013.

### 3. Detection of H<sub>2</sub> and CO<sub>2</sub>

To an oven-dried 10 mL screw-top tube were added **8a** (0.2 mmol), **2** (0.3 mmol), [Cp\*Rh(MeCN)<sub>3</sub>][SbF<sub>6</sub>]<sub>2</sub> (6.0 mmol), and MeOH (2.0 mL). The tube was filled with N<sub>2</sub> and sealed with a Teflon cap. The mixture was heated at 130 °C with an oil bath for 15 h. After cooling to room temperature, the gas component in the tube was sampled with a gas tight syringe and analyzed by GC.



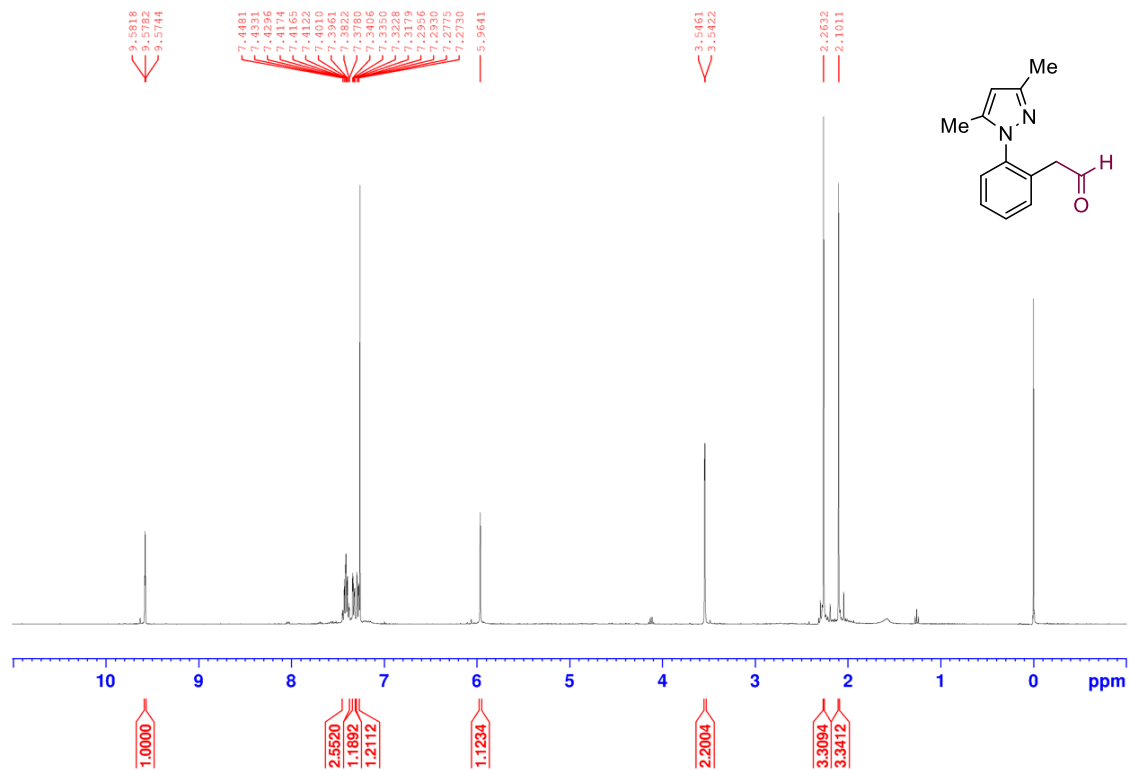
**Figure S1.** GC chart for an authentic H<sub>2</sub> sample filled in a vial with several drops of MeOH.



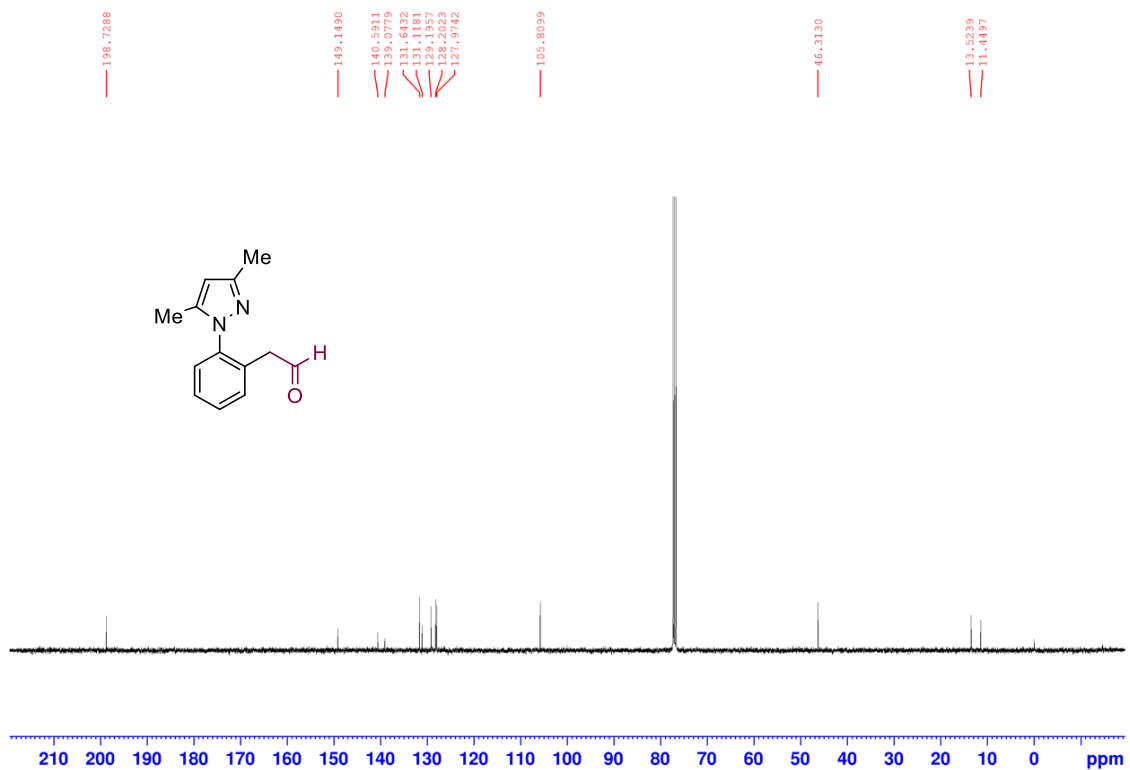
**Figure S2.** GC chart for the gas component in the reaction tube.

## 4. Copy of NMR Spectra

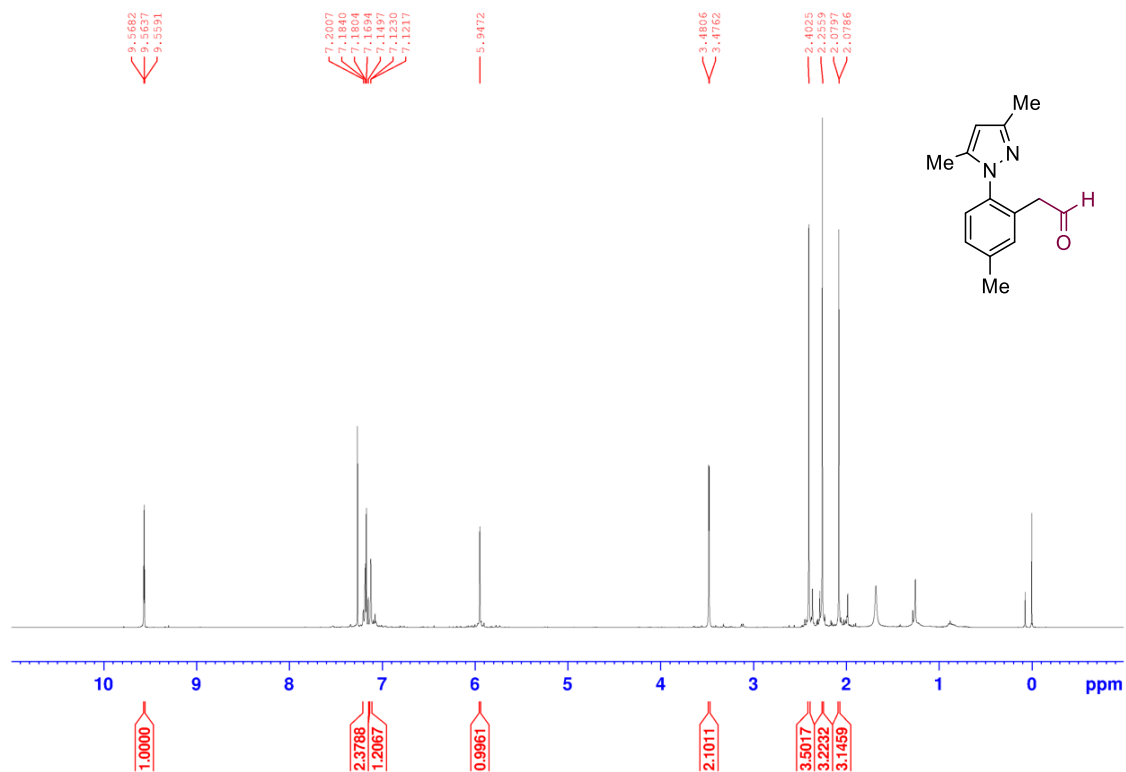
$^1\text{H}$  NMR of **3a** (400 MHz,  $\text{CDCl}_3$ )



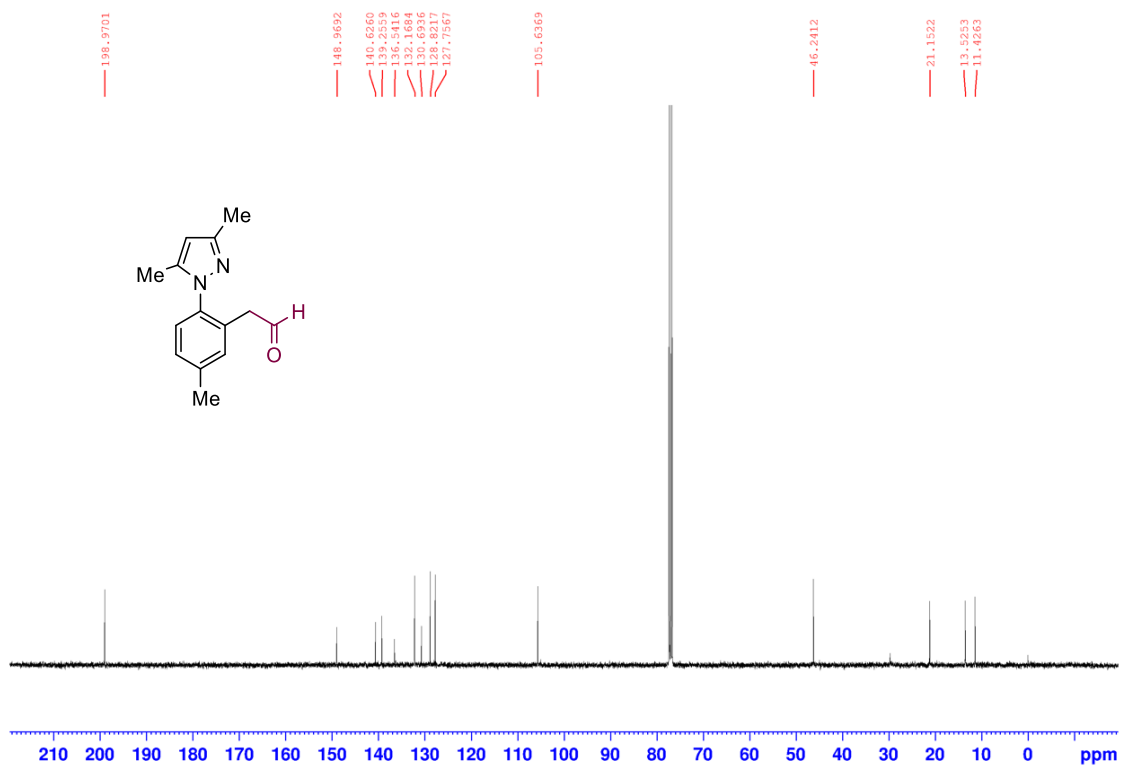
$^{13}\text{C}$  NMR of **3a** (100 MHz,  $\text{CDCl}_3$ )



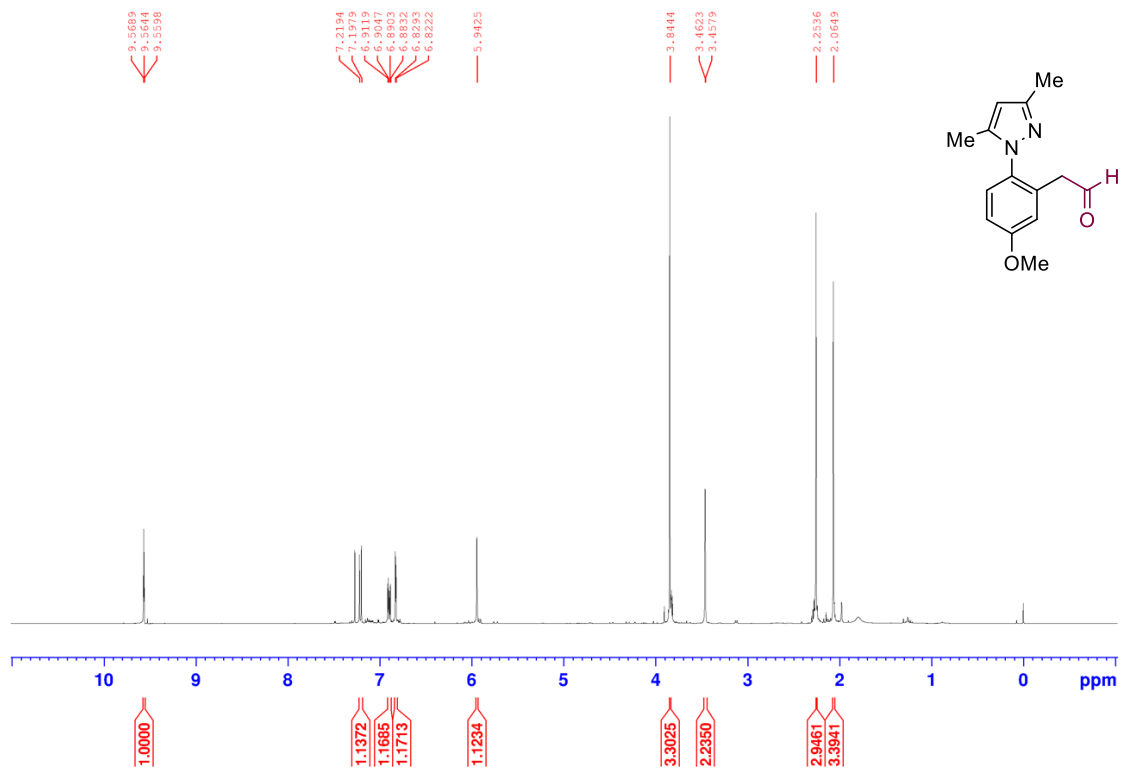
<sup>1</sup>H NMR of **3b** (400 MHz, CDCl<sub>3</sub>)



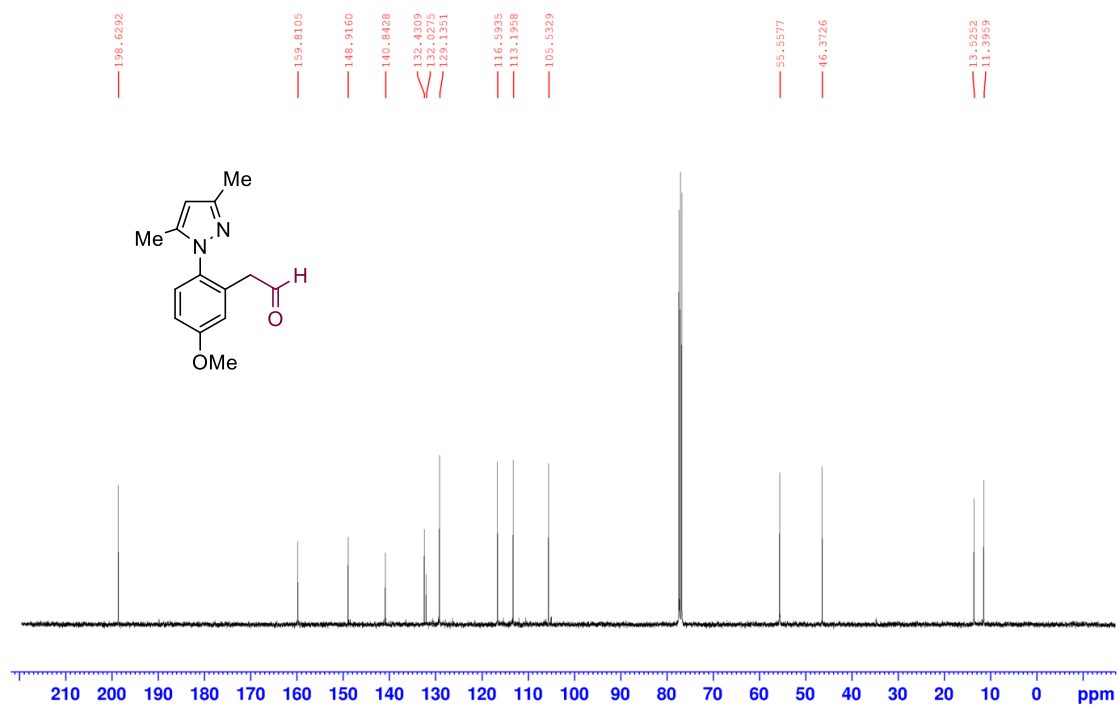
<sup>13</sup>C NMR of **3b** (100 MHz, CDCl<sub>3</sub>)



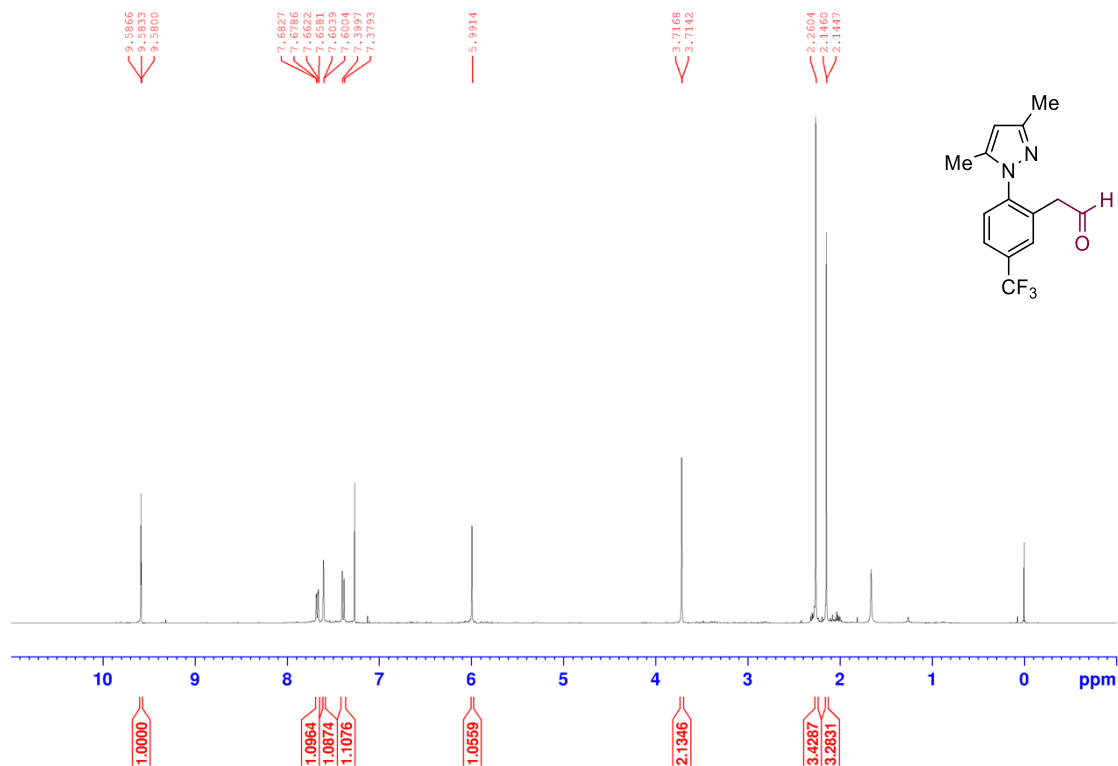
<sup>1</sup>H NMR of **3c** (400 MHz, CDCl<sub>3</sub>)



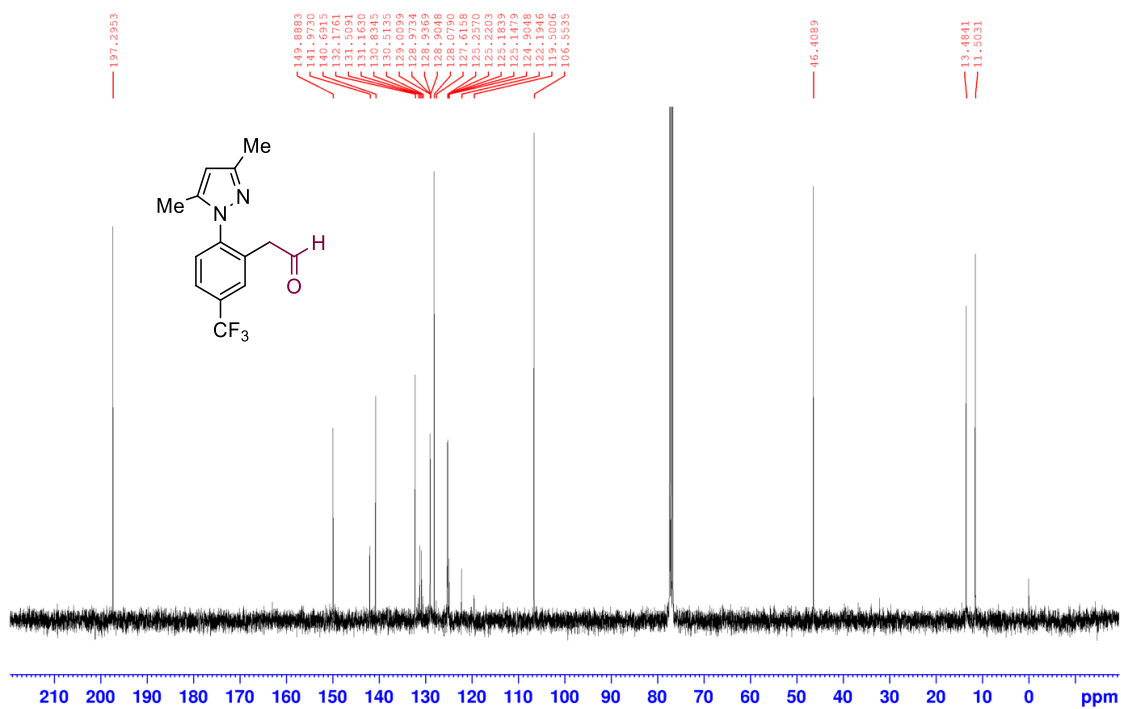
<sup>13</sup>C NMR of **3c** (100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **3d** (400 MHz, CDCl<sub>3</sub>)

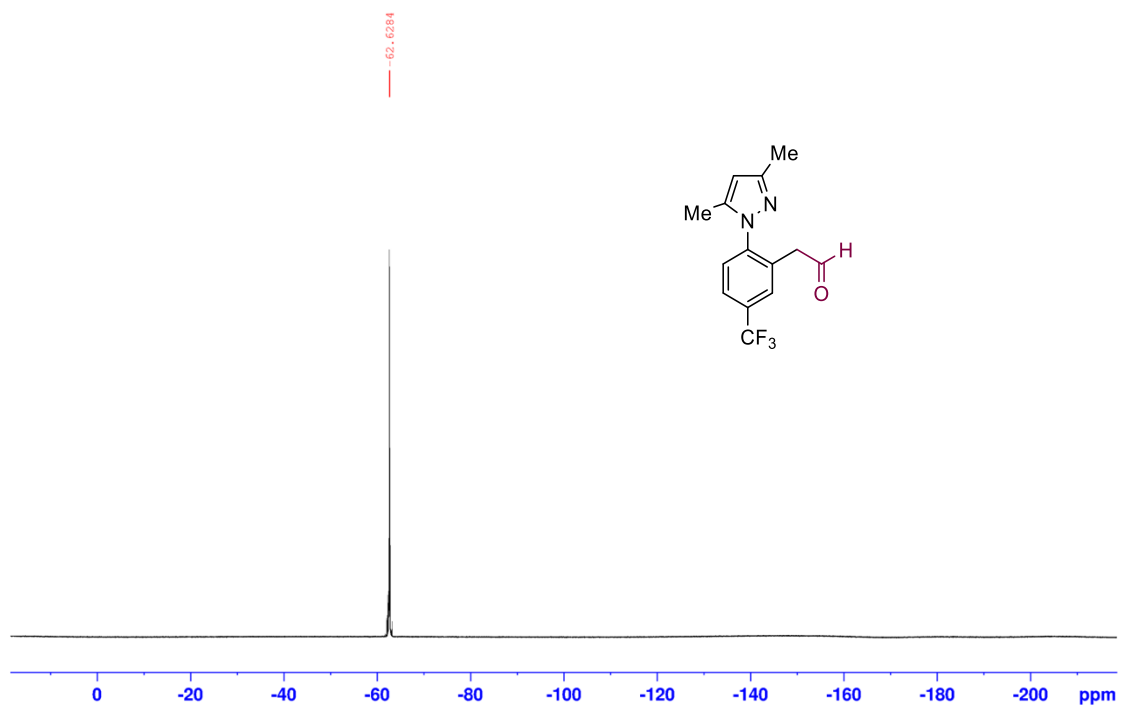


<sup>13</sup>C NMR of **3d** (100 MHz, CDCl<sub>3</sub>)

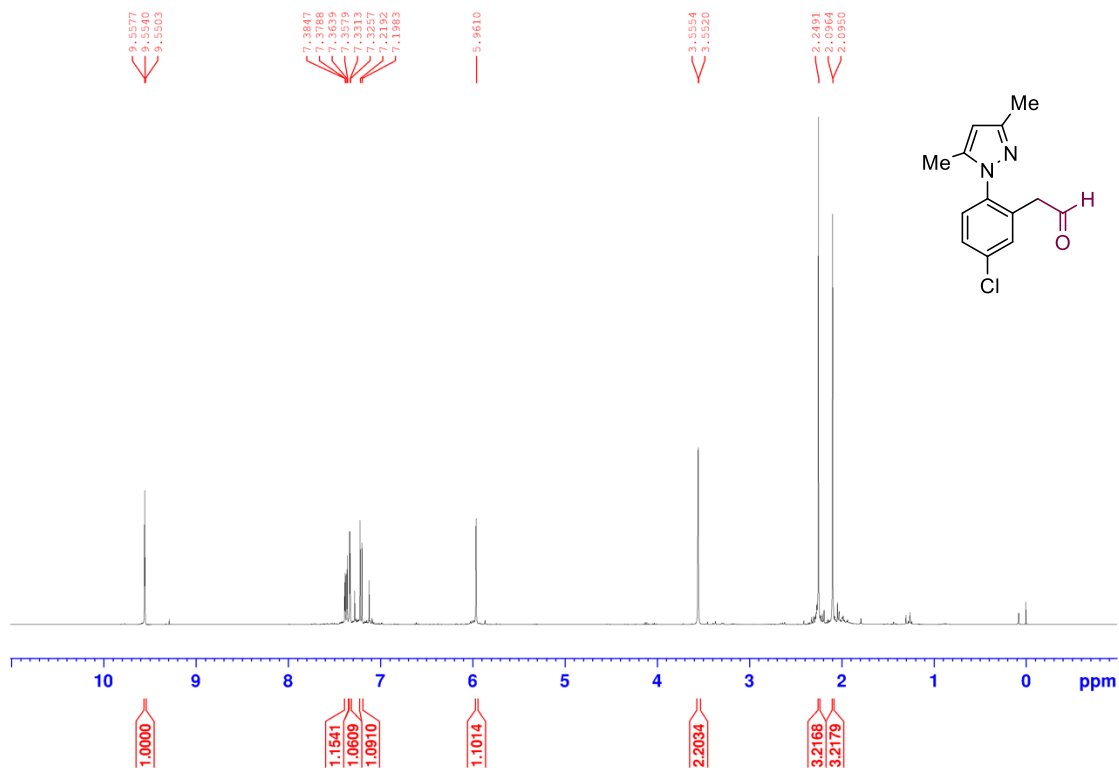




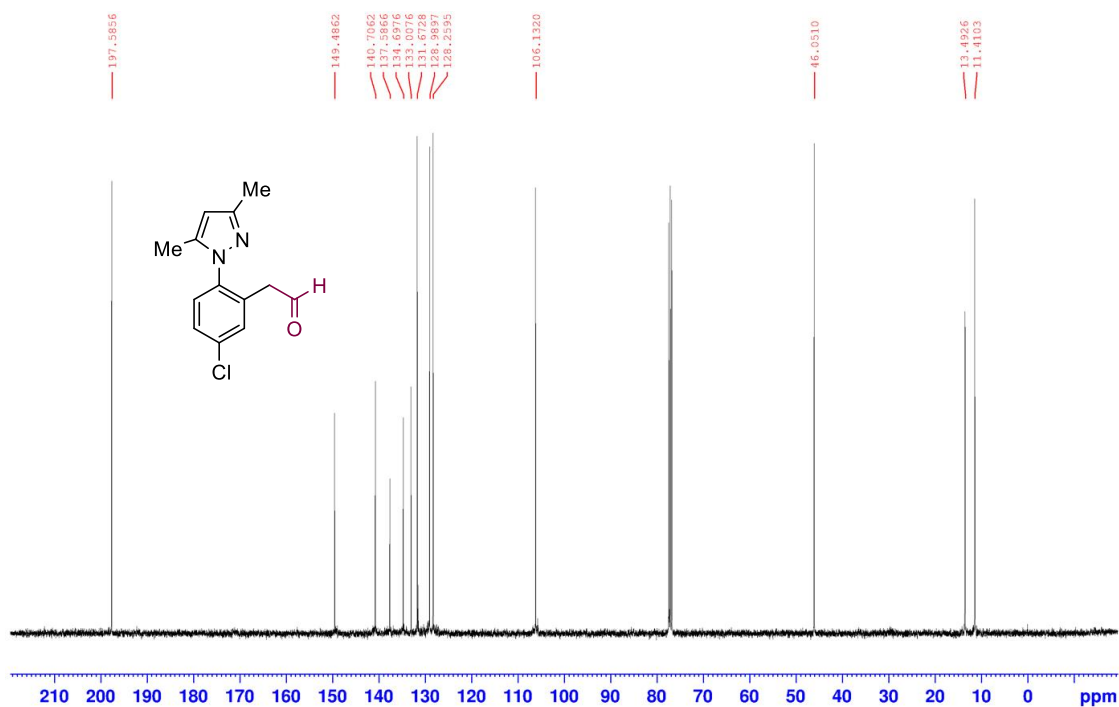
$^{19}\text{F}$  NMR of **3d** (376 MHz,  $\text{CDCl}_3$ )



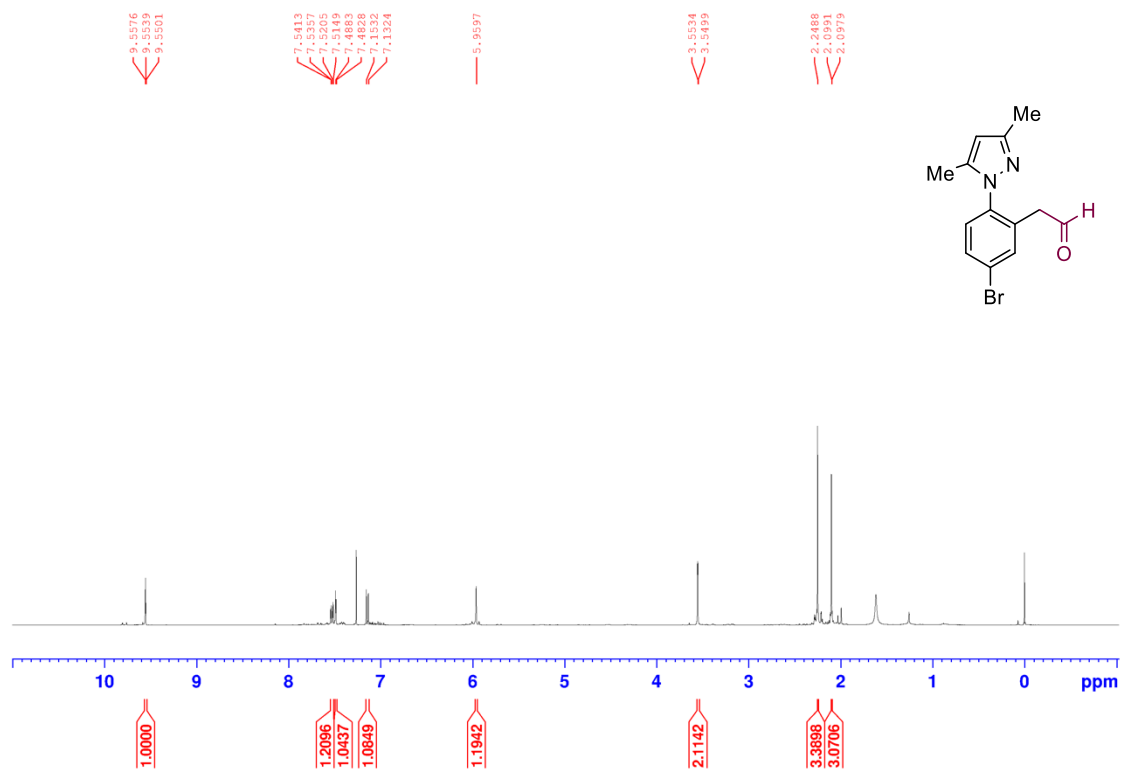
<sup>1</sup>H NMR of **3e** (400 MHz, CDCl<sub>3</sub>)



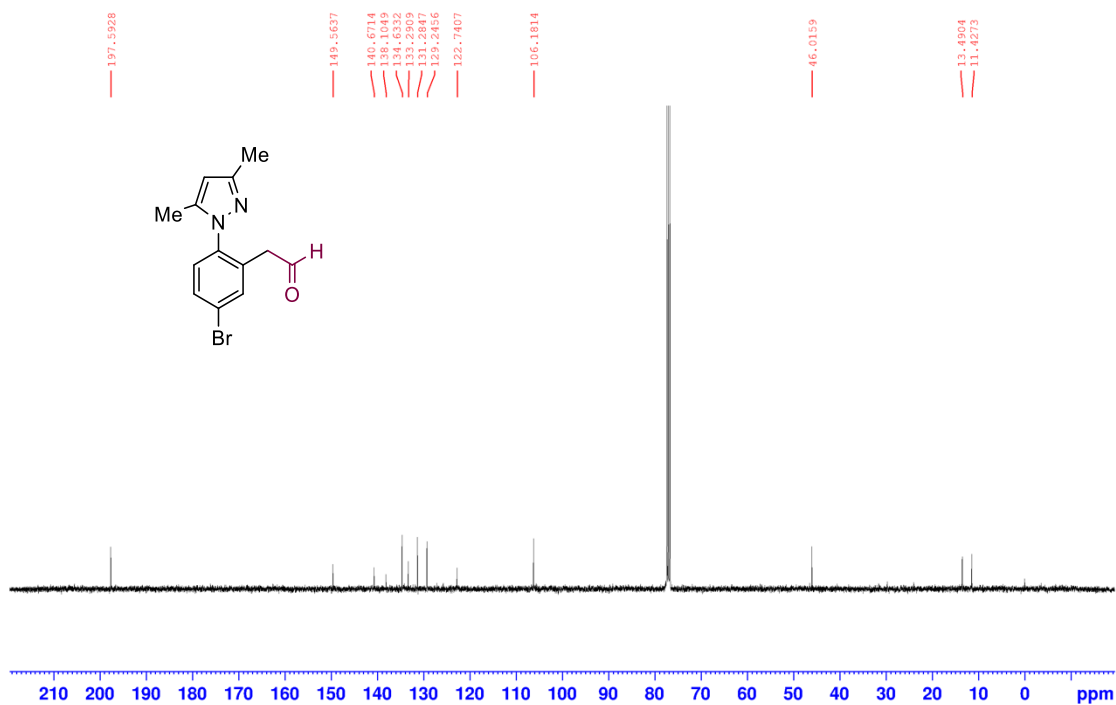
<sup>13</sup>C NMR of **3e** (100 MHz, CDCl<sub>3</sub>)



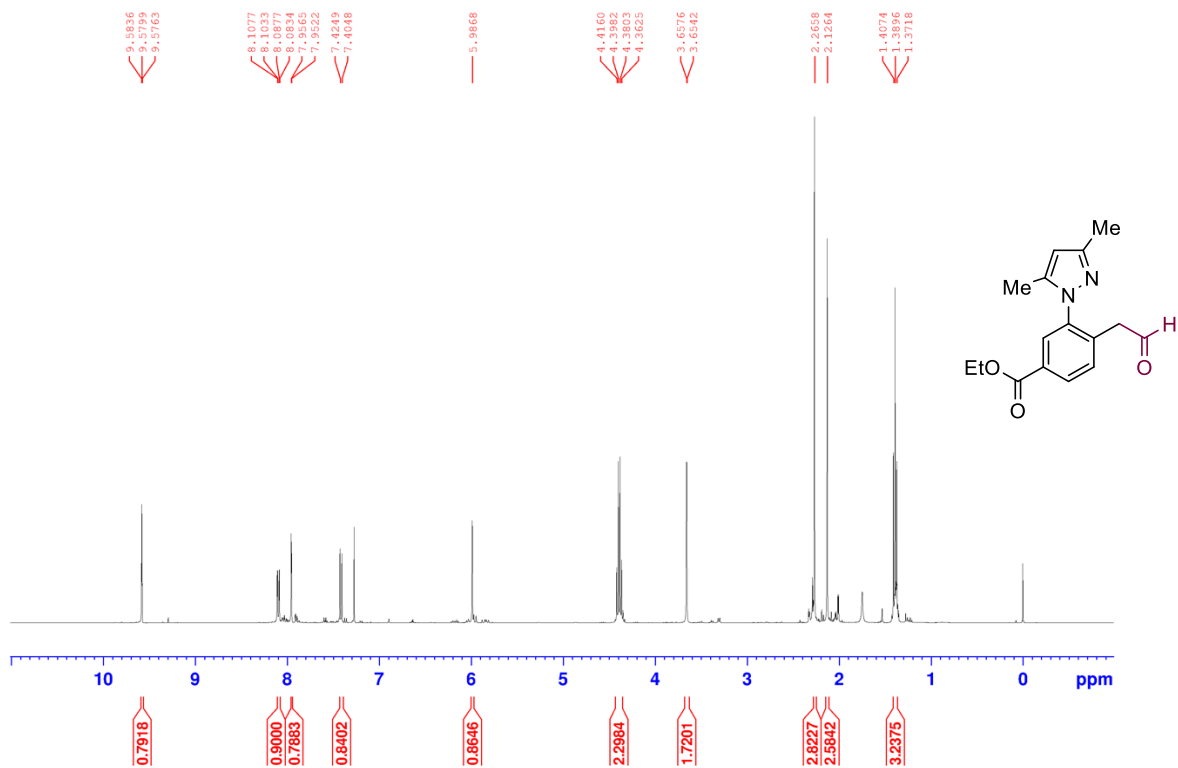
<sup>1</sup>H NMR of **3f** (400 MHz, CDCl<sub>3</sub>)



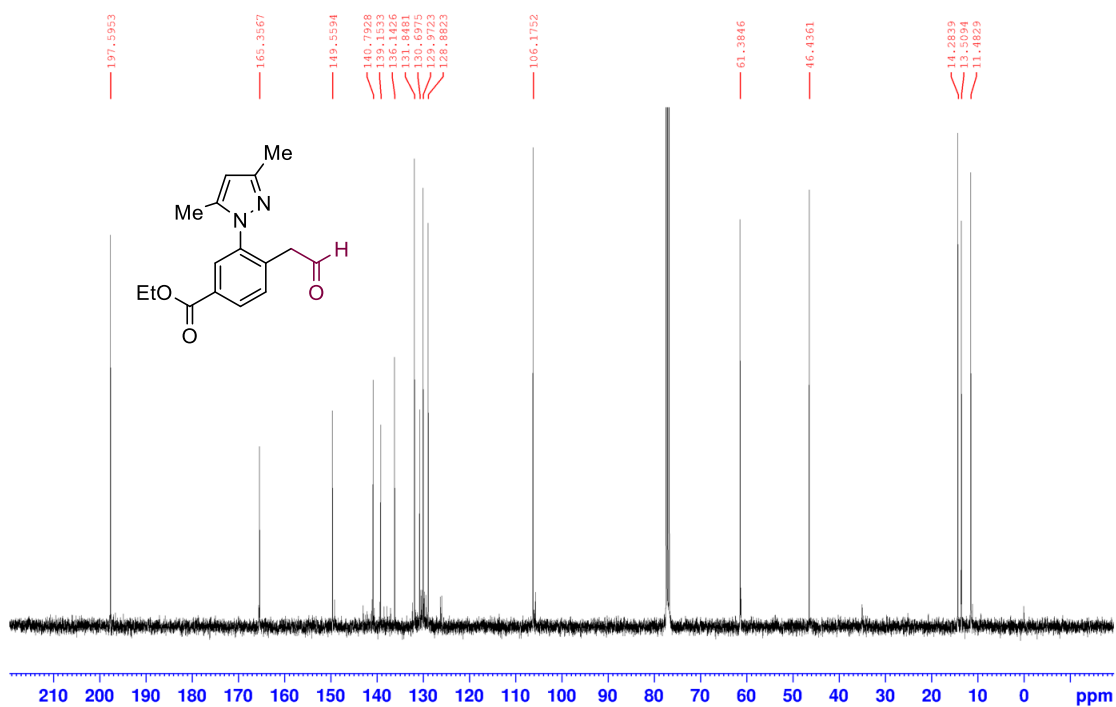
<sup>13</sup>C NMR of **3f** (100 MHz, CDCl<sub>3</sub>)



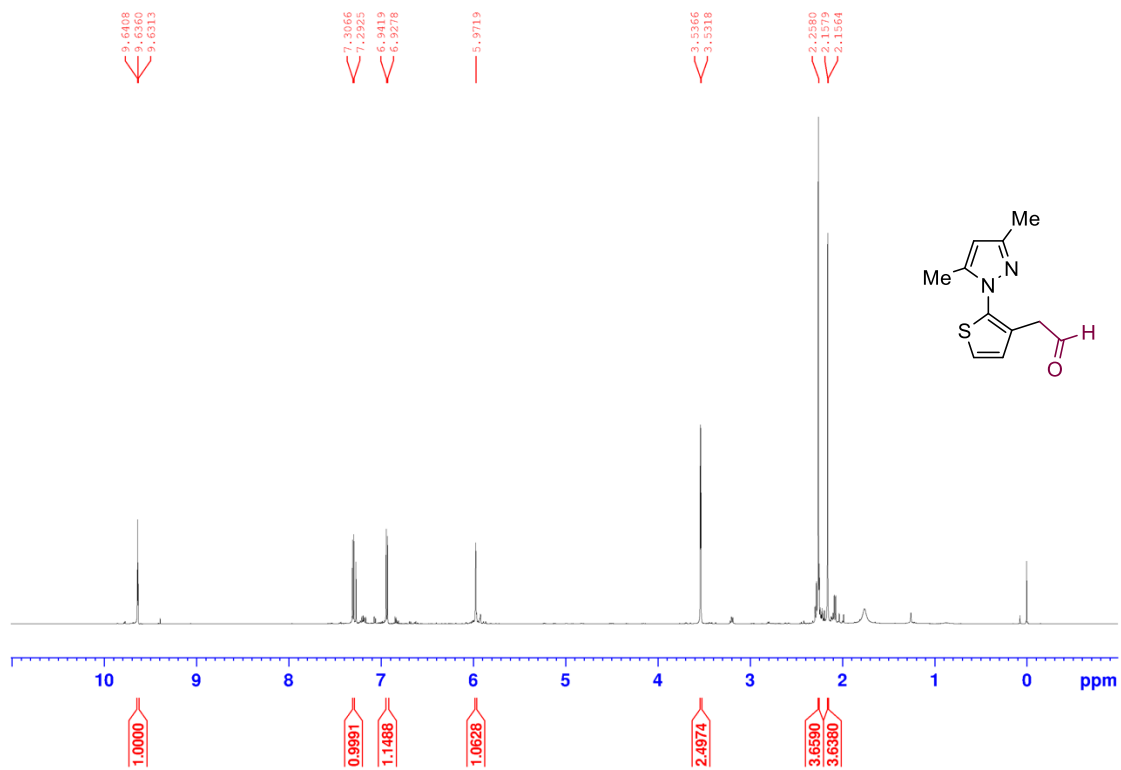
<sup>1</sup>H NMR of **3g** (400 MHz, CDCl<sub>3</sub>)



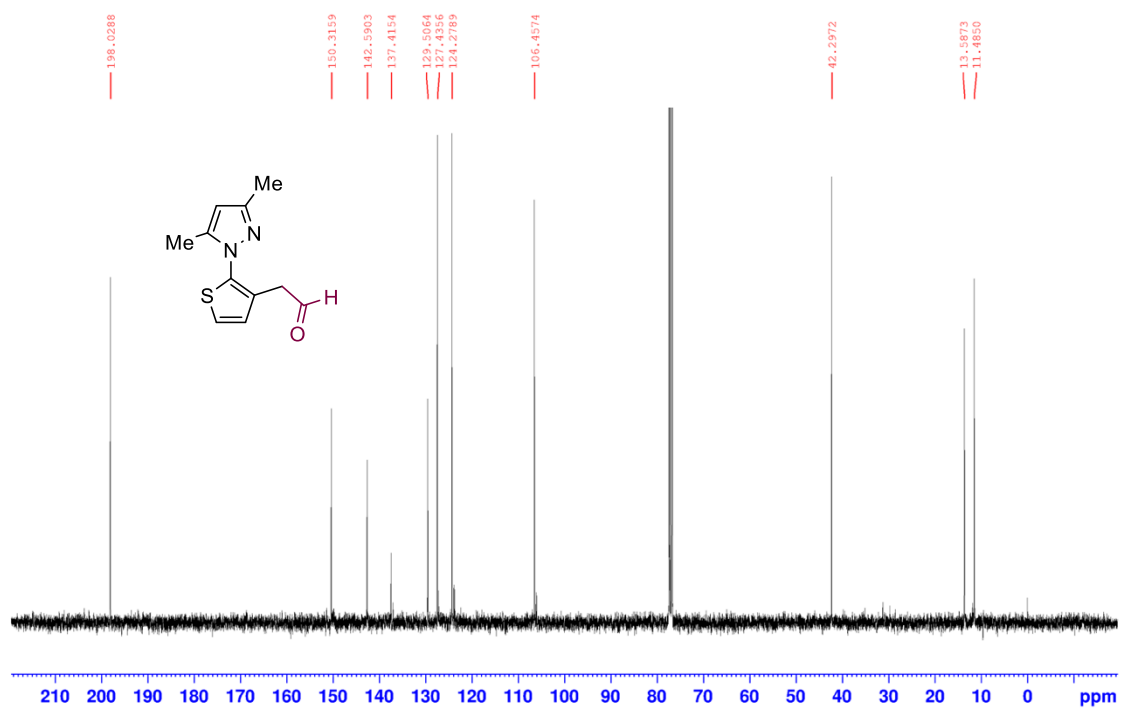
<sup>13</sup>C NMR of **3g** (100 MHz, CDCl<sub>3</sub>)



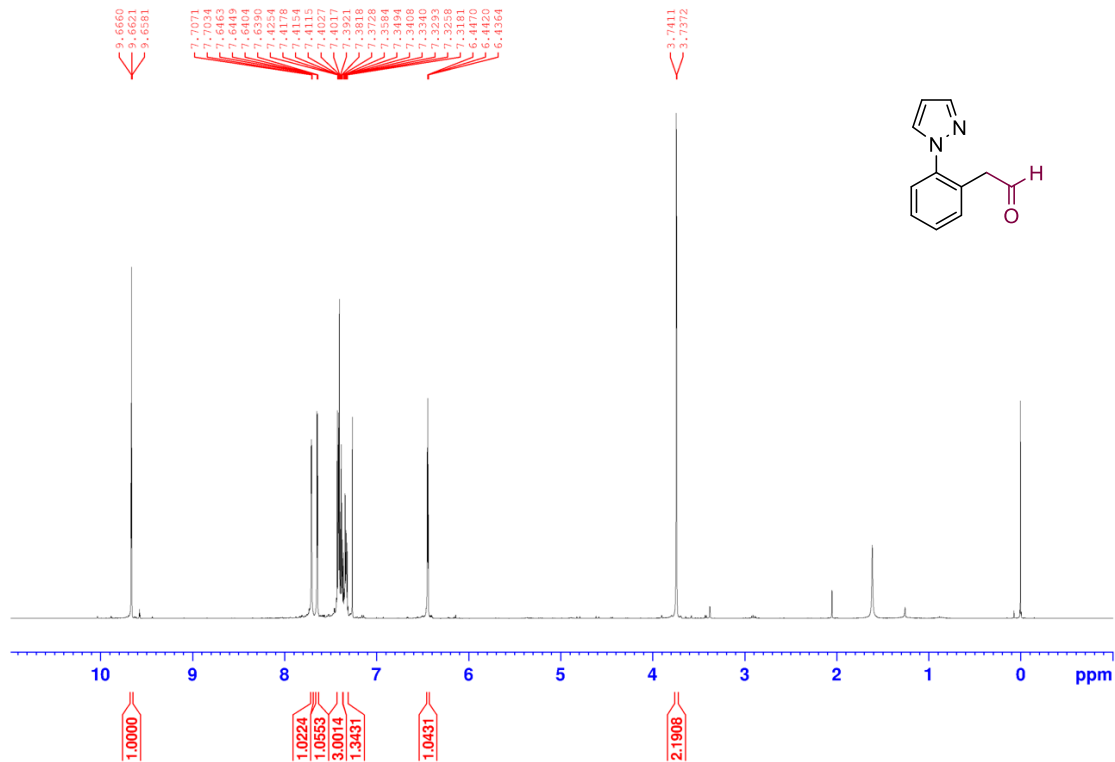
<sup>1</sup>H NMR of **3h** (400 MHz, CDCl<sub>3</sub>)



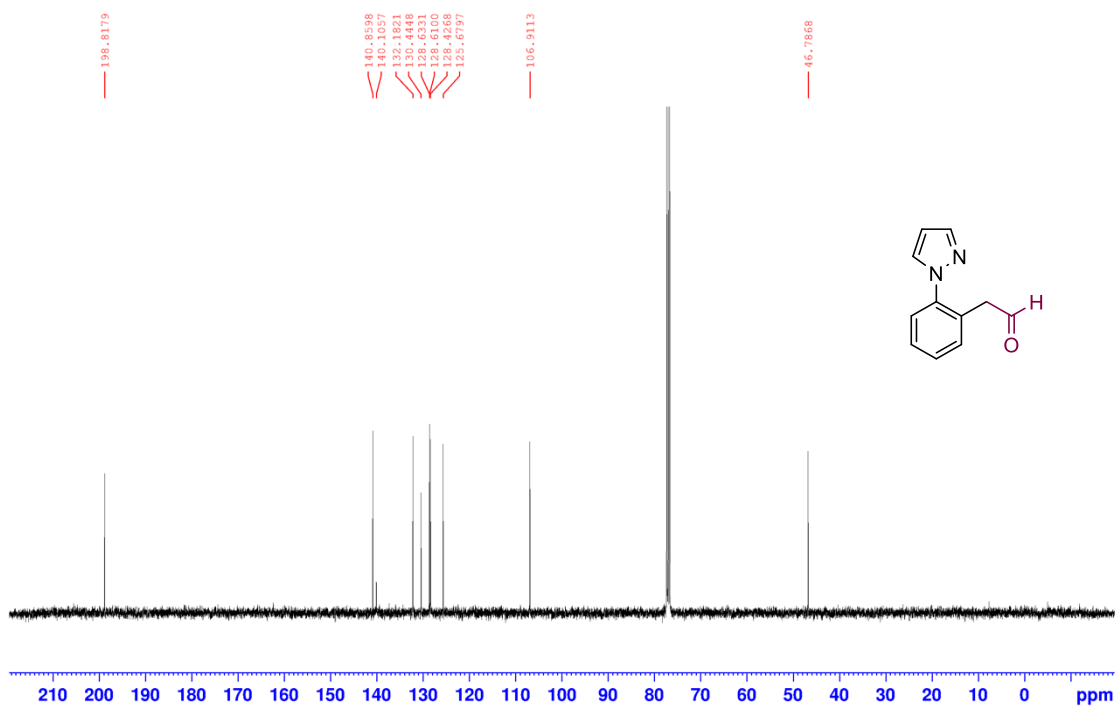
<sup>13</sup>C NMR of **3h** (100 MHz, CDCl<sub>3</sub>)



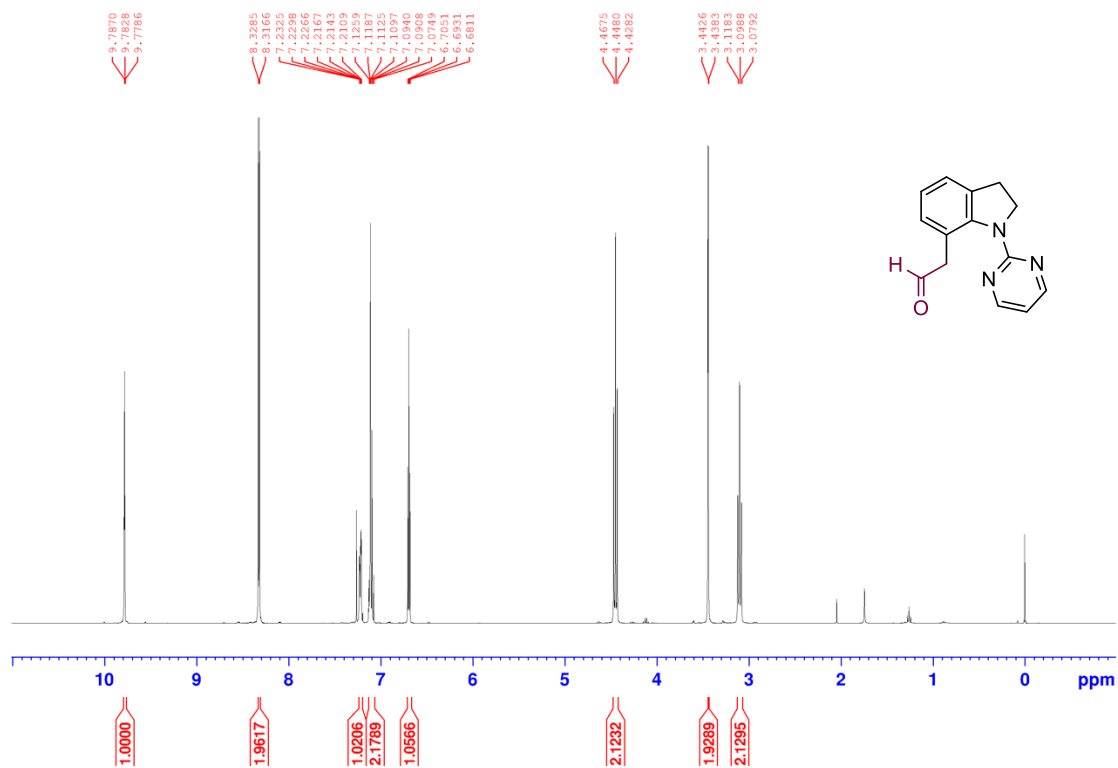
<sup>1</sup>H NMR of **3i** (400 MHz, CDCl<sub>3</sub>)



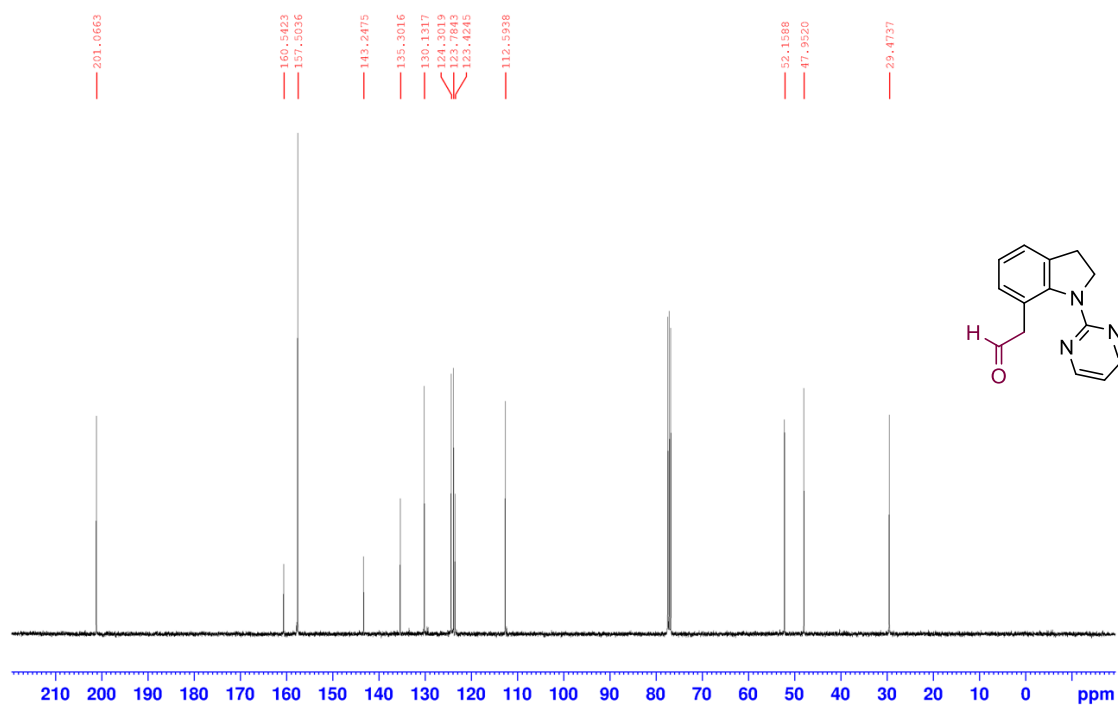
<sup>13</sup>C NMR of **3i** (100 MHz, CDCl<sub>3</sub>)



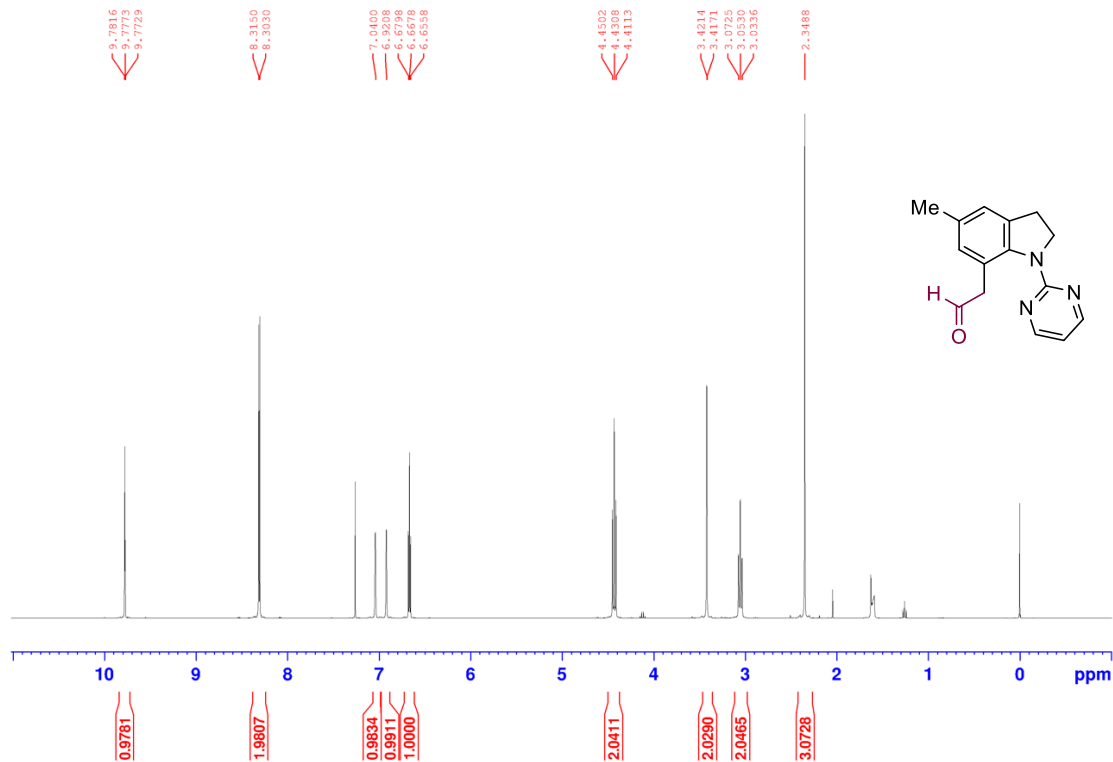
<sup>1</sup>H NMR of **5a** (400 MHz, CDCl<sub>3</sub>)



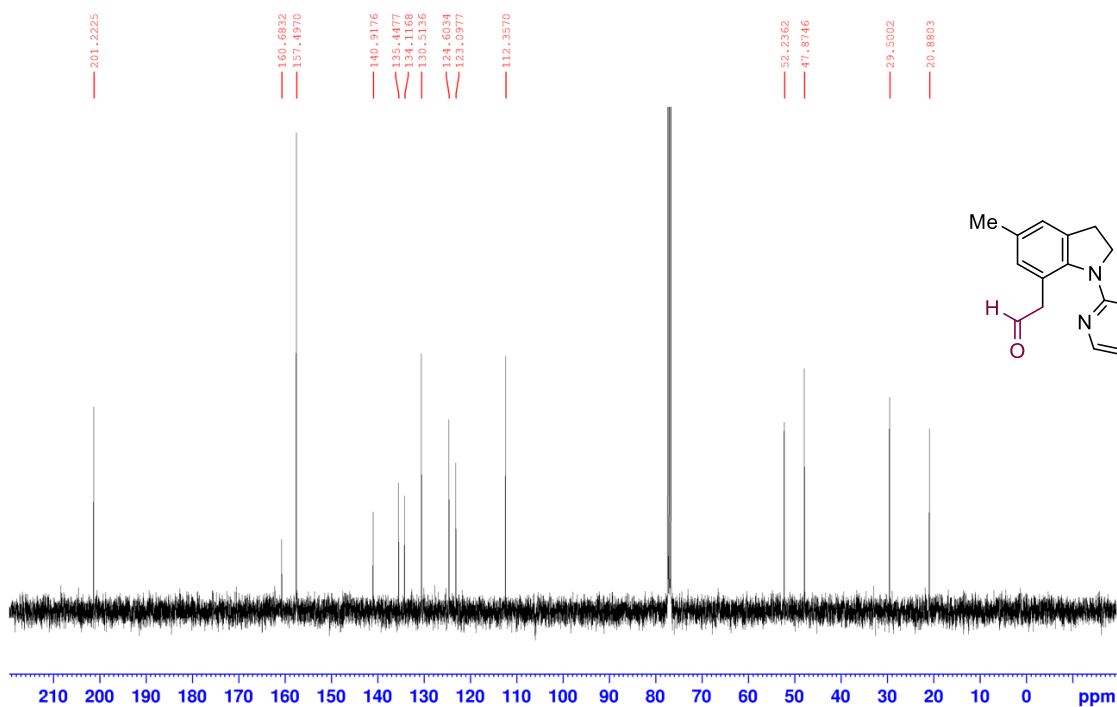
<sup>13</sup>C NMR of **5a** (100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **5b** (400 MHz, CDCl<sub>3</sub>)

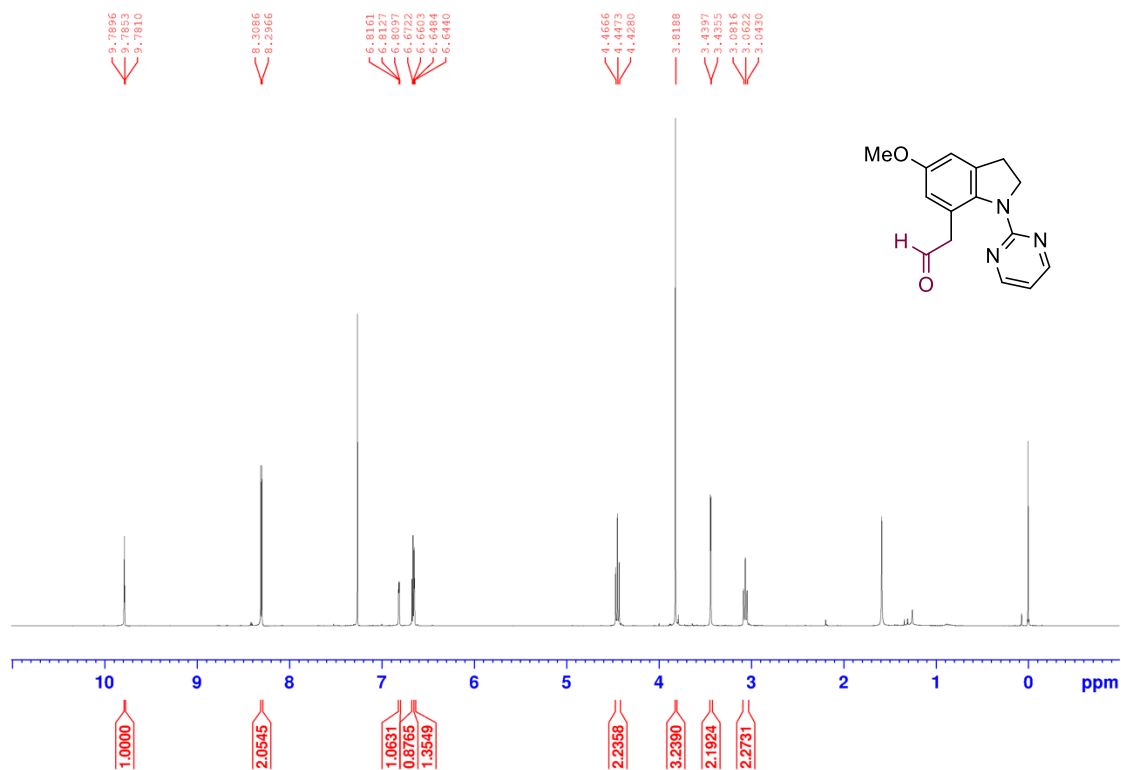


<sup>13</sup>C NMR of **5b** (100 MHz, CDCl<sub>3</sub>)

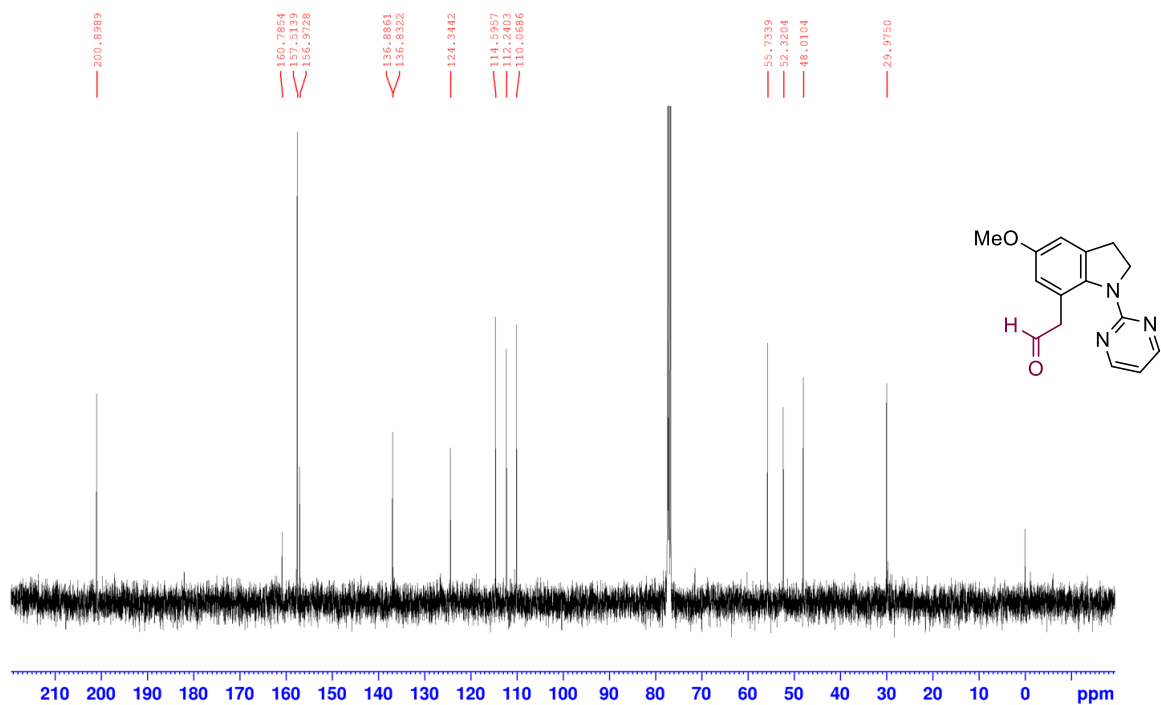




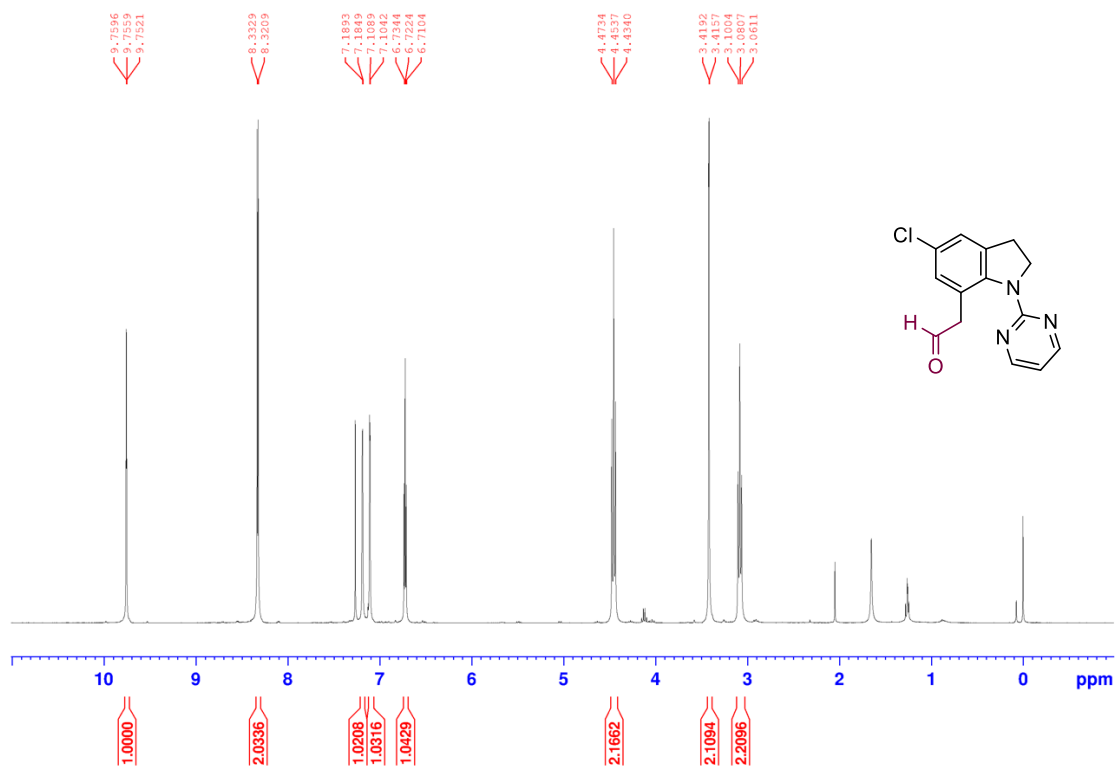
<sup>1</sup>H NMR of **5c** (400 MHz, CDCl<sub>3</sub>)



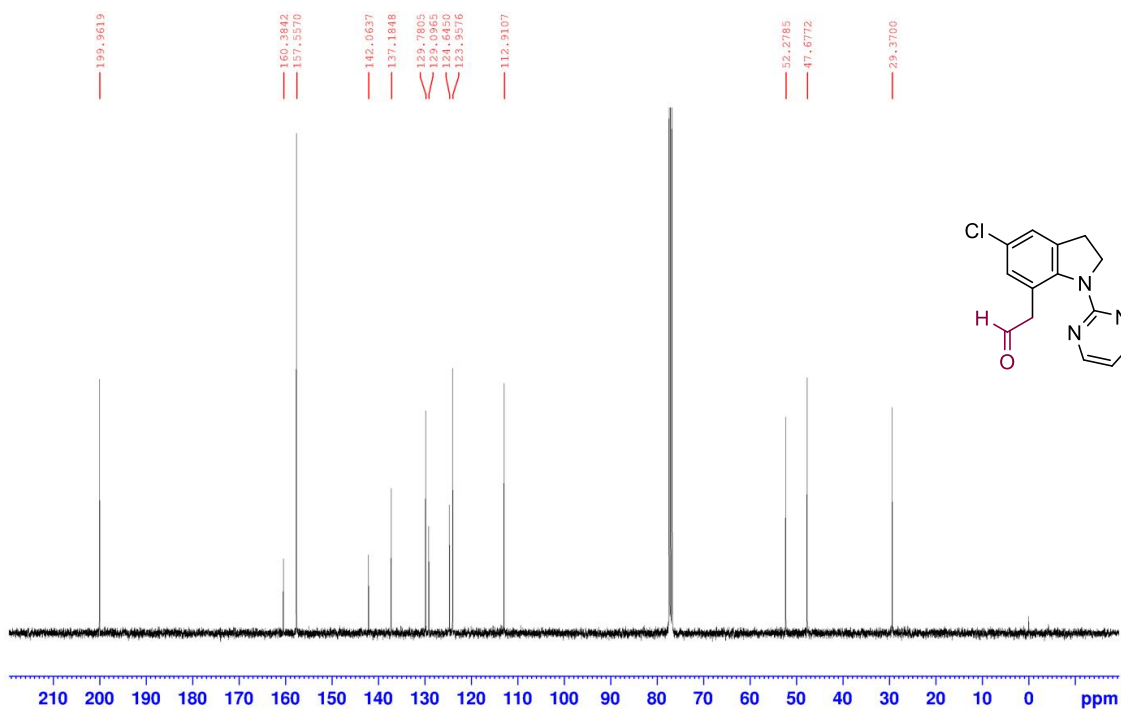
<sup>13</sup>C NMR of **5c** (100 MHz, CDCl<sub>3</sub>)



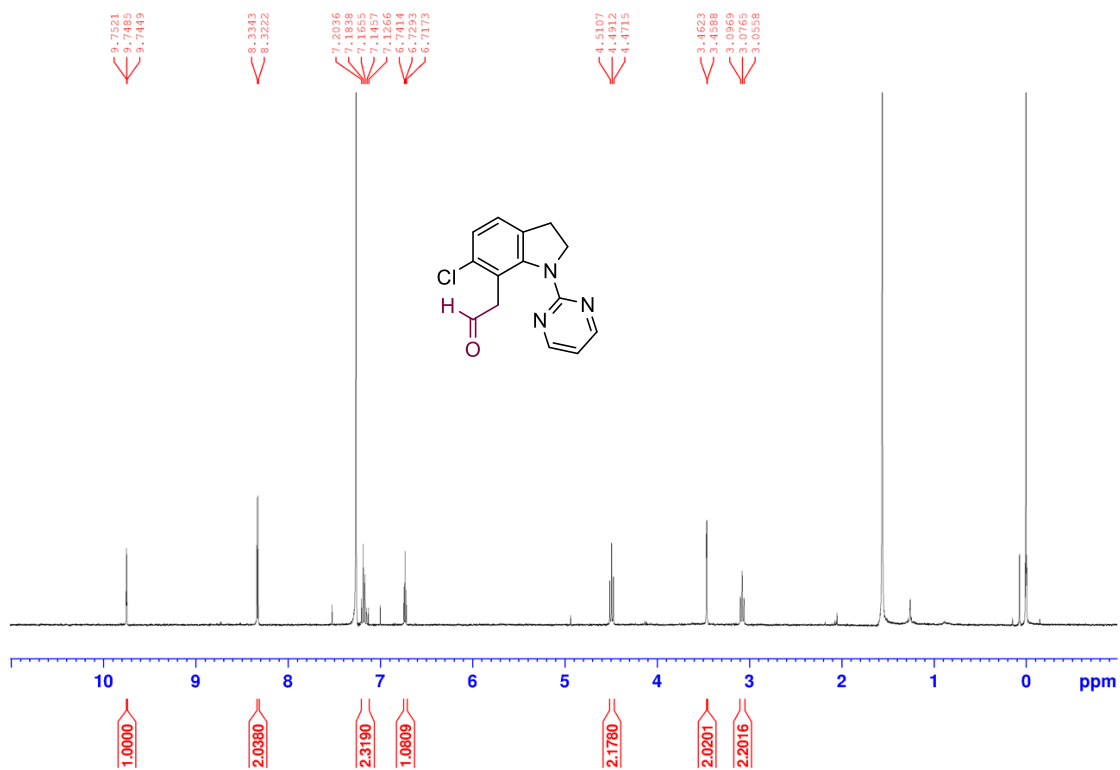
<sup>1</sup>H NMR of **5d** (400 MHz, CDCl<sub>3</sub>)



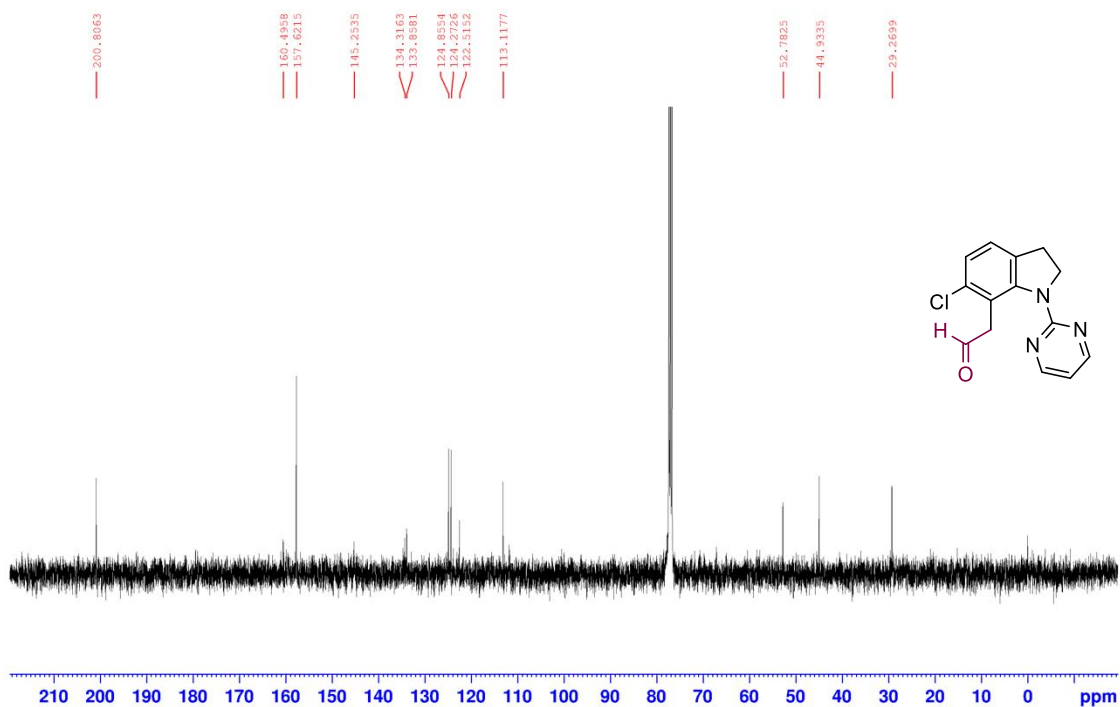
<sup>13</sup>C NMR of **5d** (100 MHz, CDCl<sub>3</sub>)



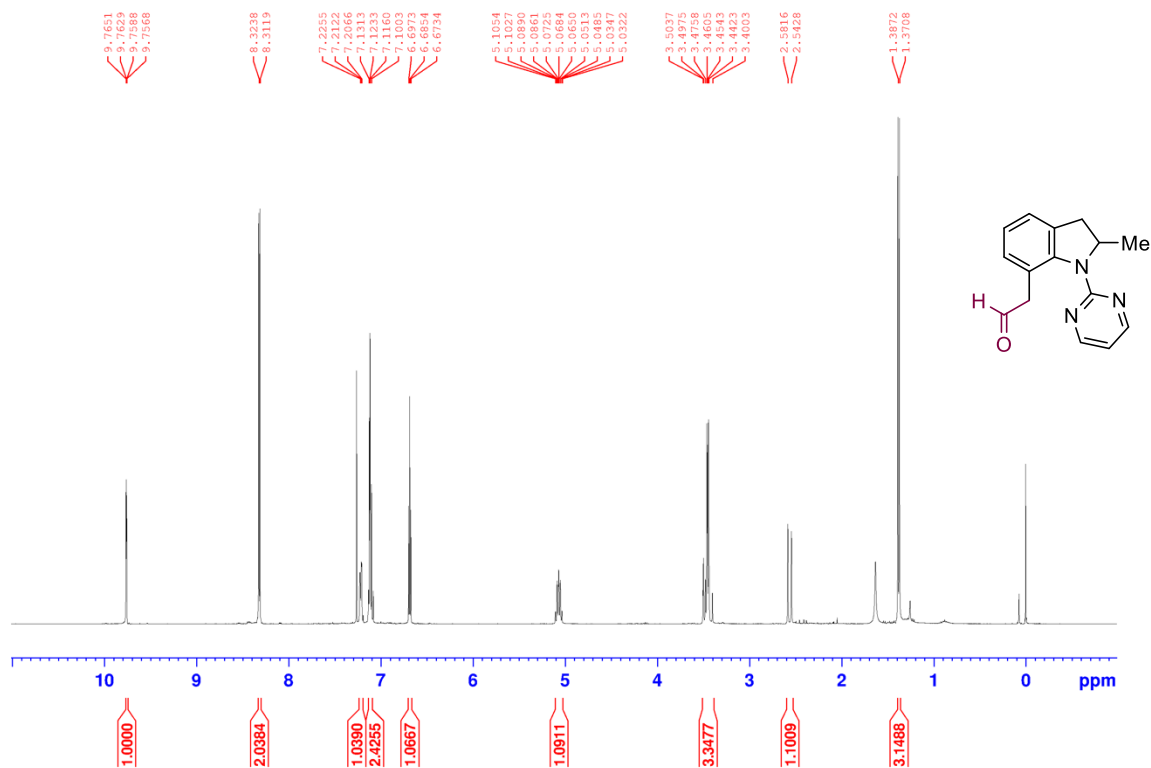
<sup>1</sup>H NMR of **5e** (400 MHz, CDCl<sub>3</sub>)



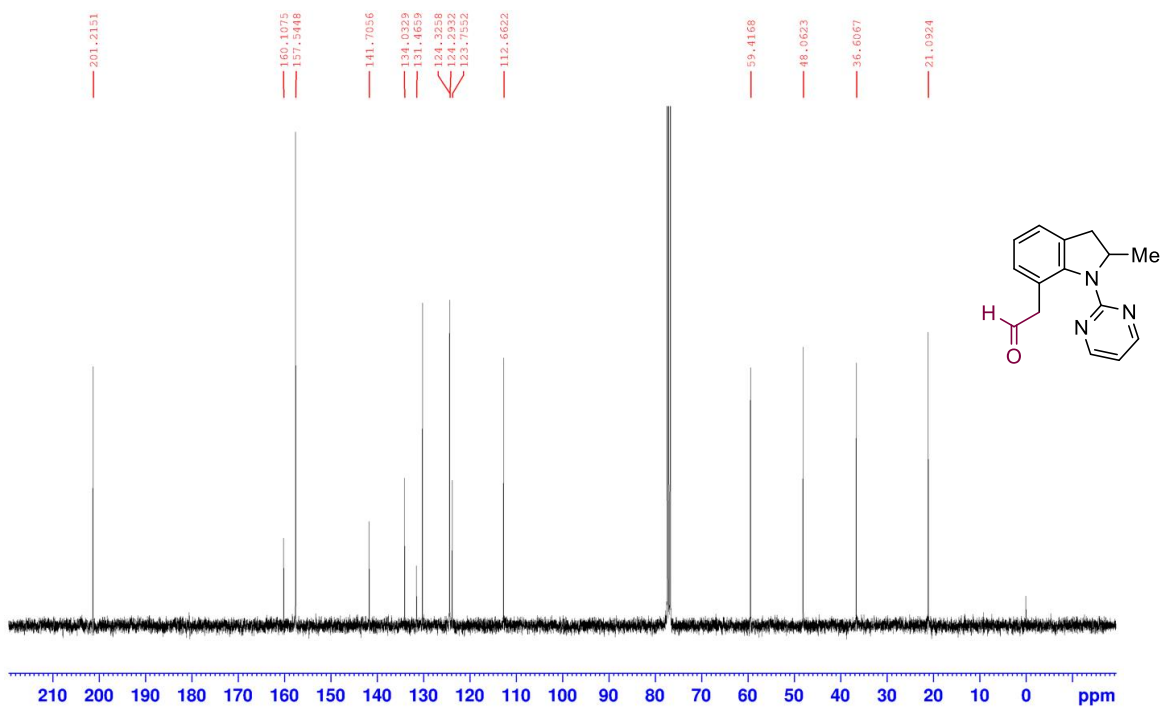
<sup>13</sup>C NMR of **5e** (100 MHz, CDCl<sub>3</sub>)



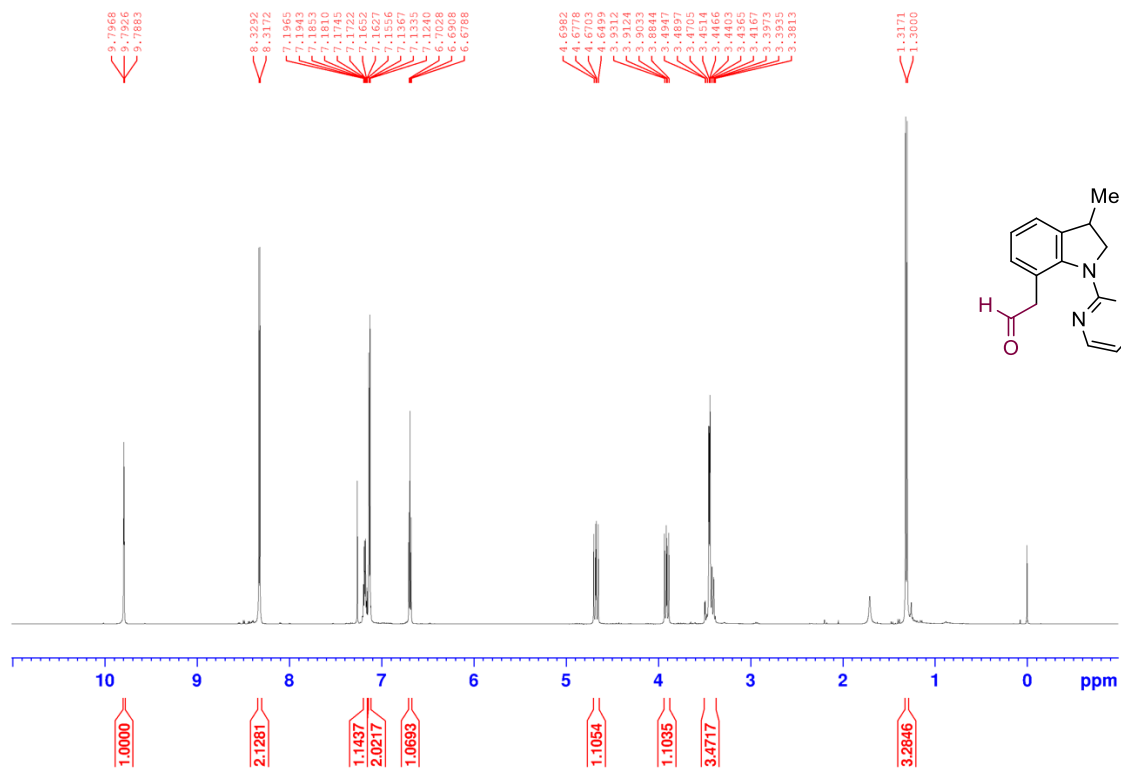
<sup>1</sup>H NMR of **5f** (400 MHz, CDCl<sub>3</sub>)



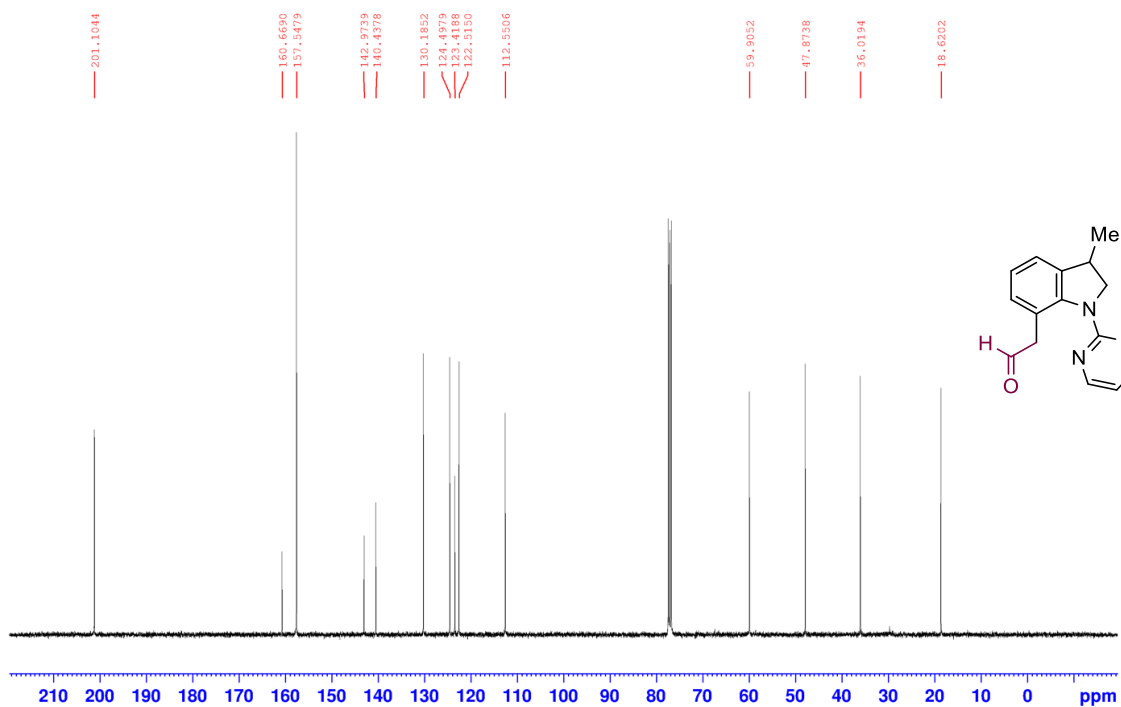
<sup>13</sup>C NMR of **5f** (100 MHz, CDCl<sub>3</sub>)



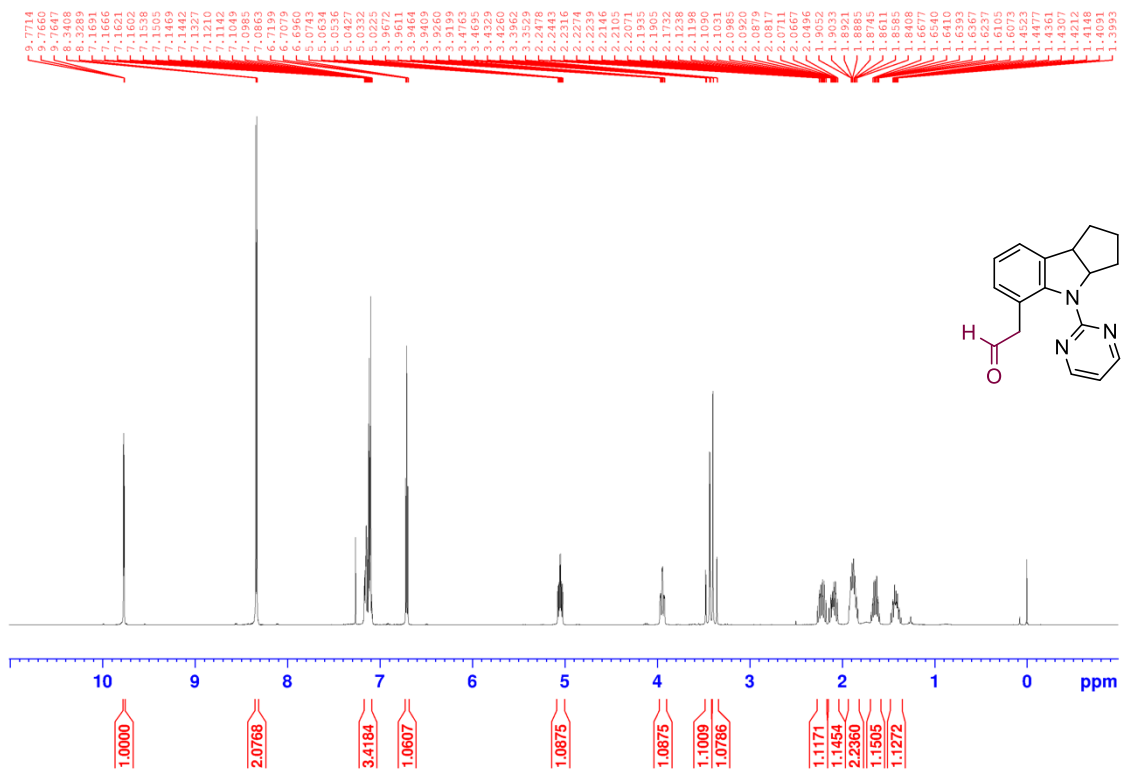
<sup>1</sup>H NMR of **5g** (400 MHz, CDCl<sub>3</sub>)



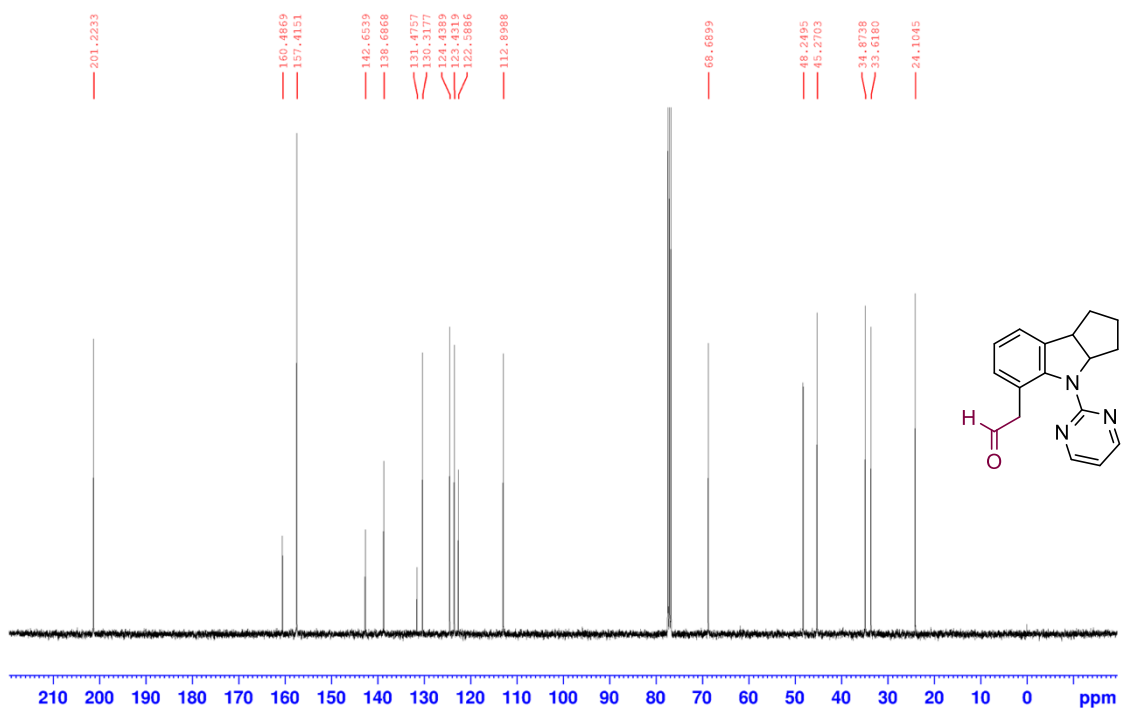
<sup>13</sup>C NMR of **5g** (100 MHz, CDCl<sub>3</sub>)



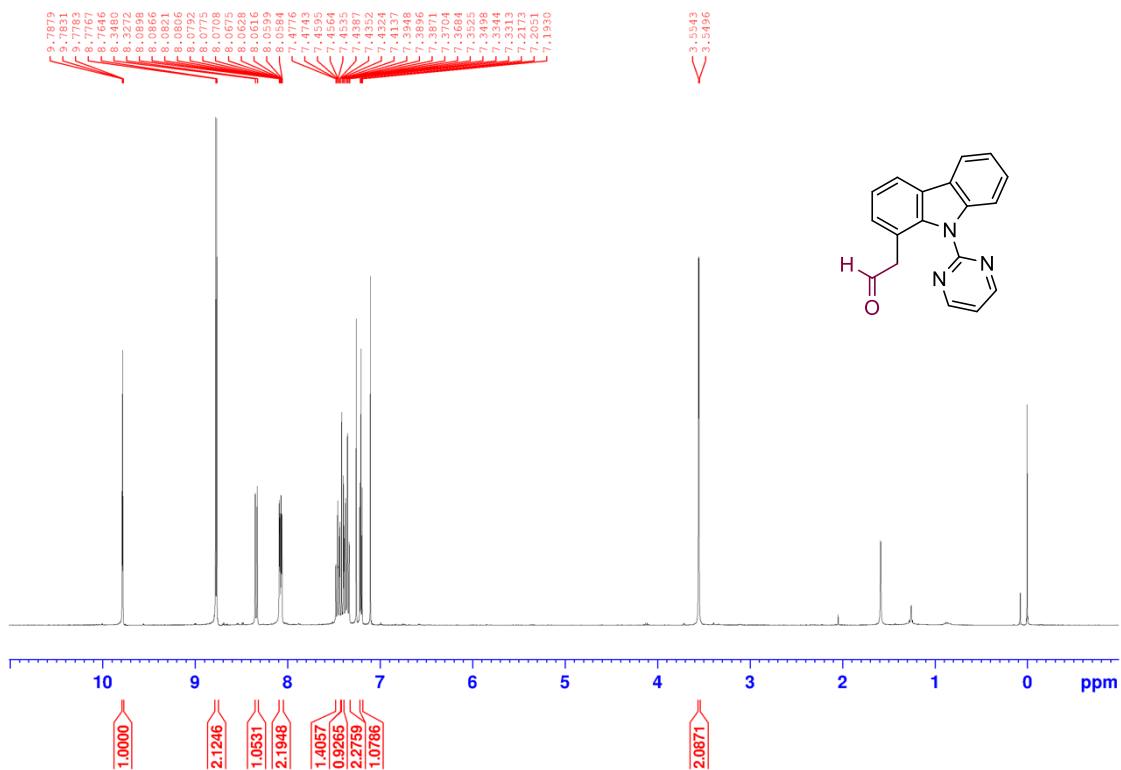
<sup>1</sup>H NMR of **5h** (400 MHz, CDCl<sub>3</sub>)



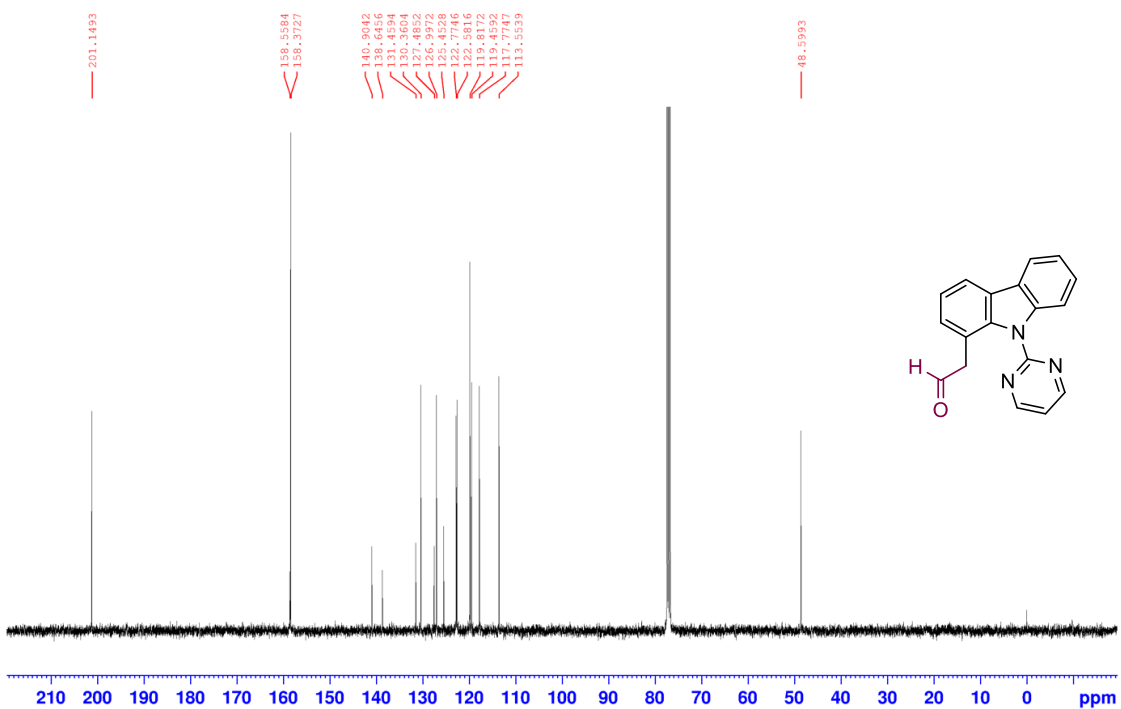
<sup>13</sup>C NMR of **5h** (100 MHz, CDCl<sub>3</sub>)



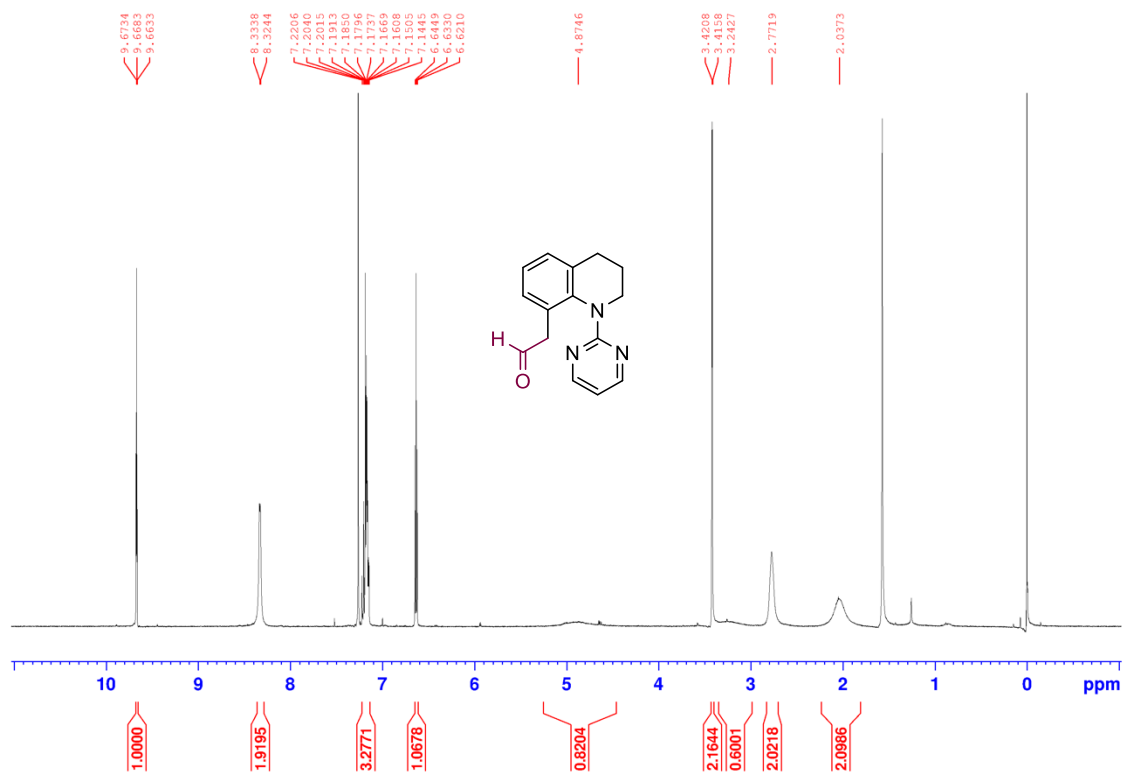
<sup>1</sup>H NMR of **5i** (400 MHz, CDCl<sub>3</sub>)



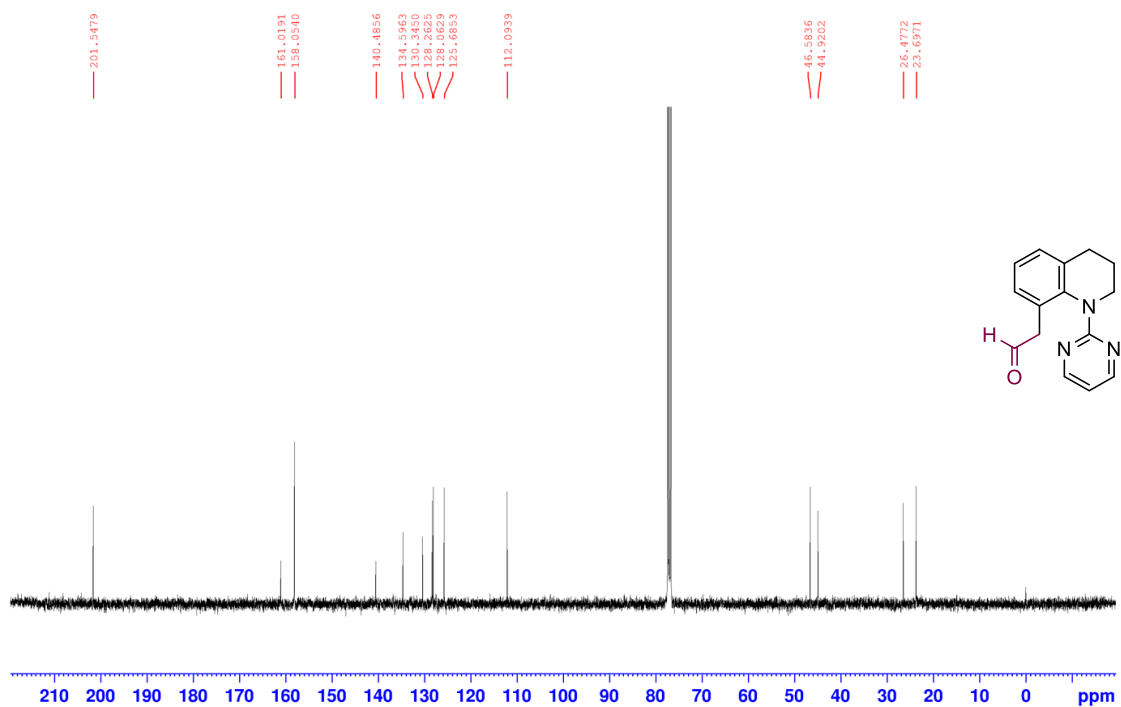
<sup>13</sup>C NMR of **5i** (100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **5j** (400 MHz, CDCl<sub>3</sub>)

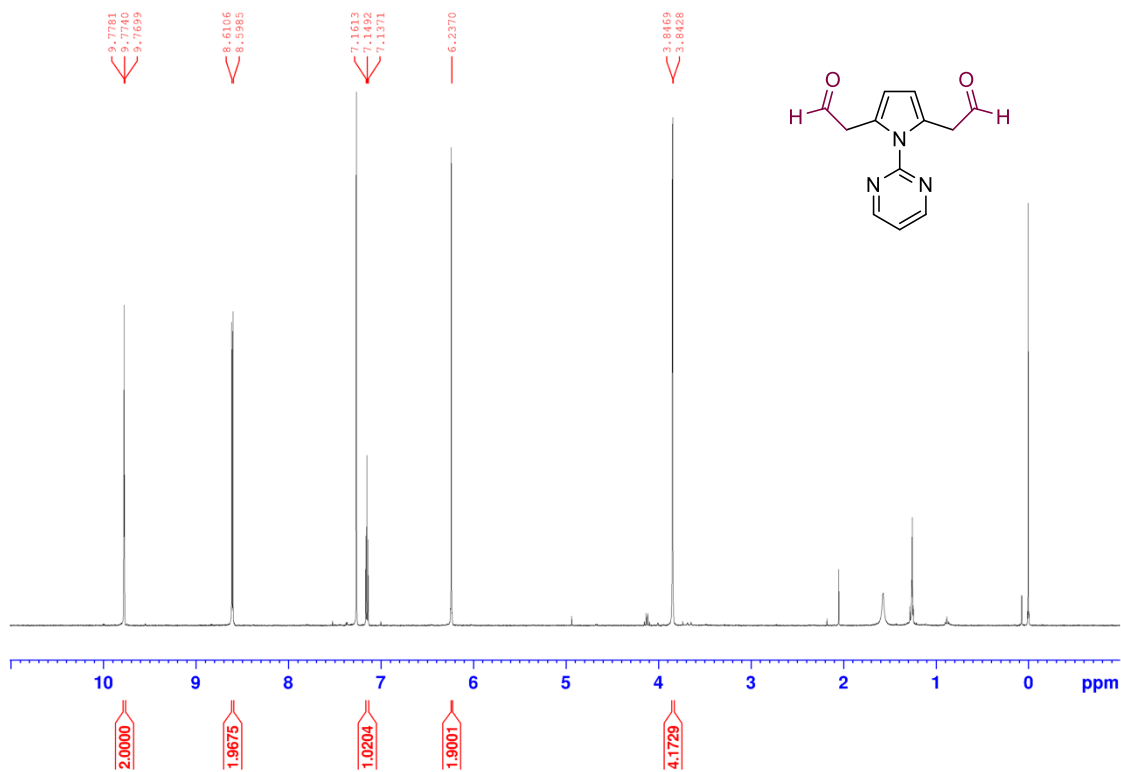


<sup>13</sup>C NMR of **5j** (100 MHz, CDCl<sub>3</sub>)

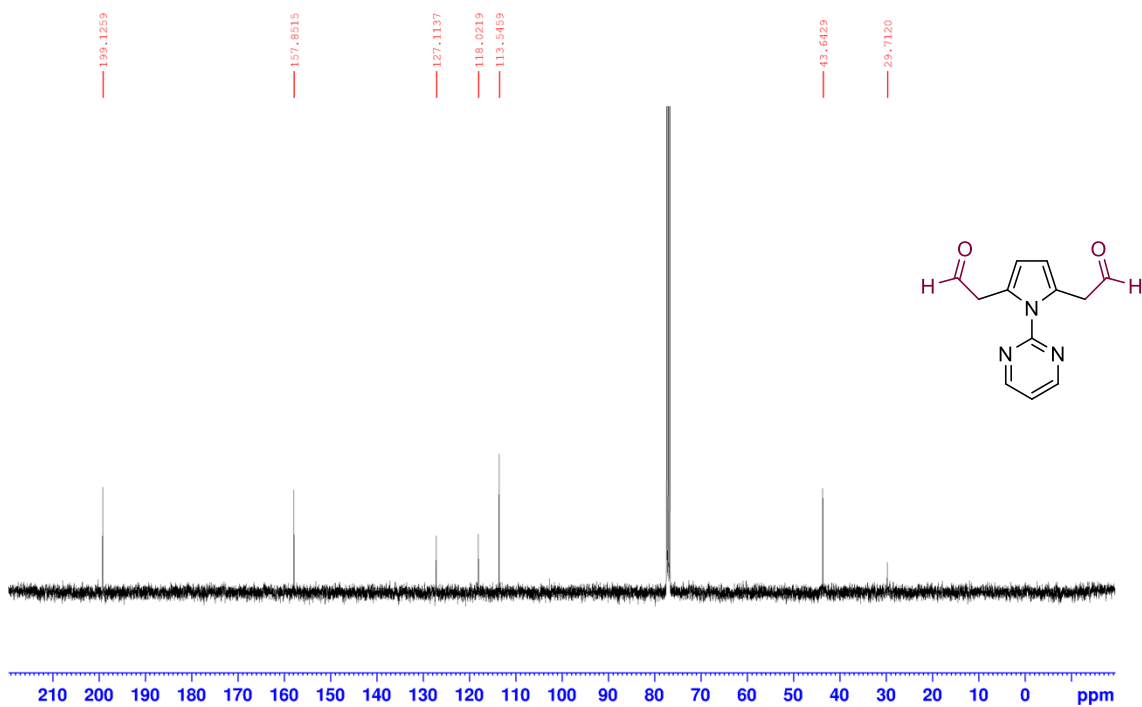




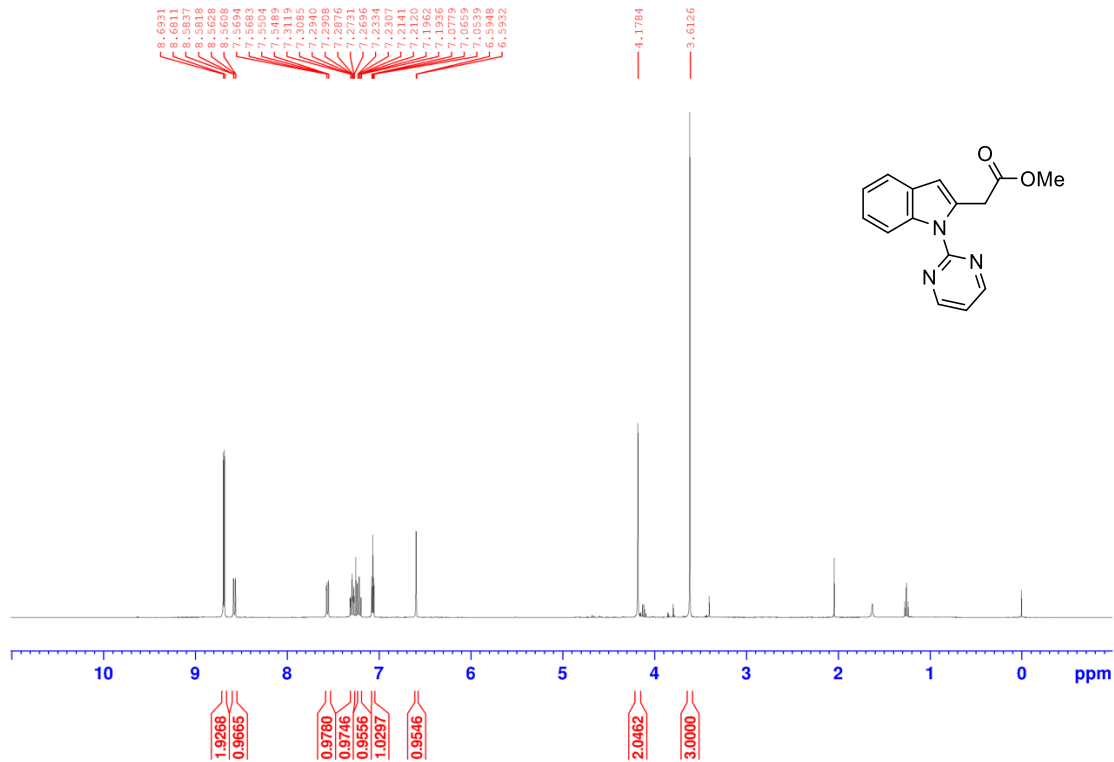
<sup>1</sup>H NMR of 7 (400 MHz, CDCl<sub>3</sub>)



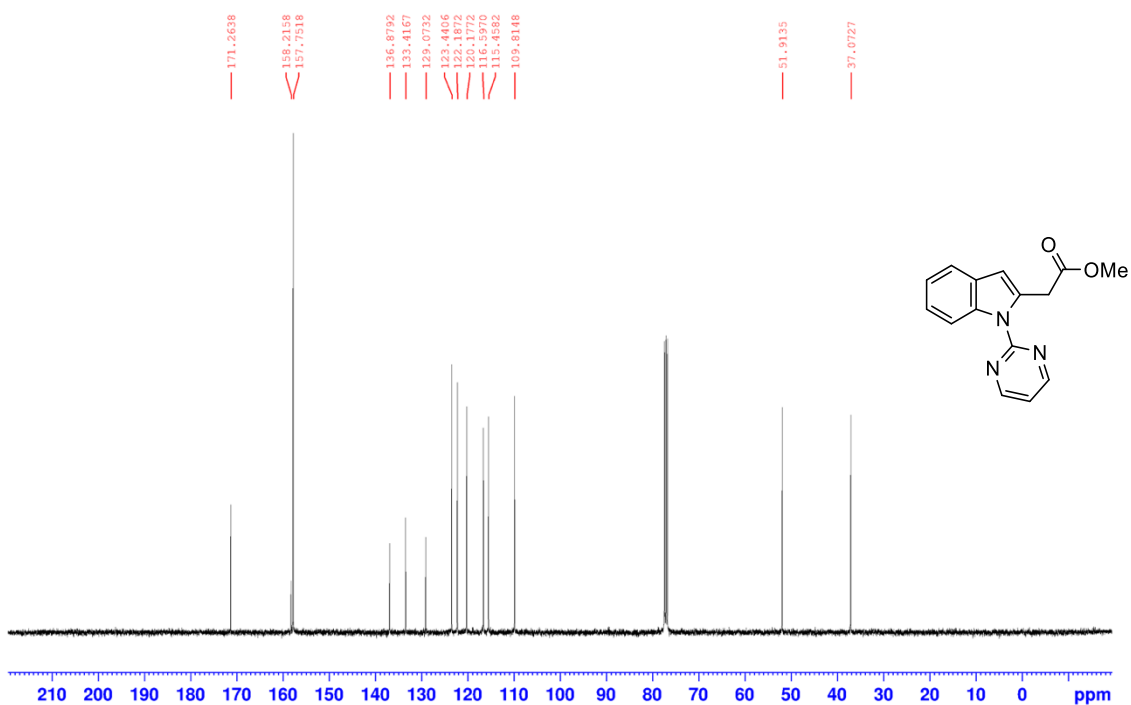
<sup>13</sup>C NMR of 7 (100 MHz, CDCl<sub>3</sub>)



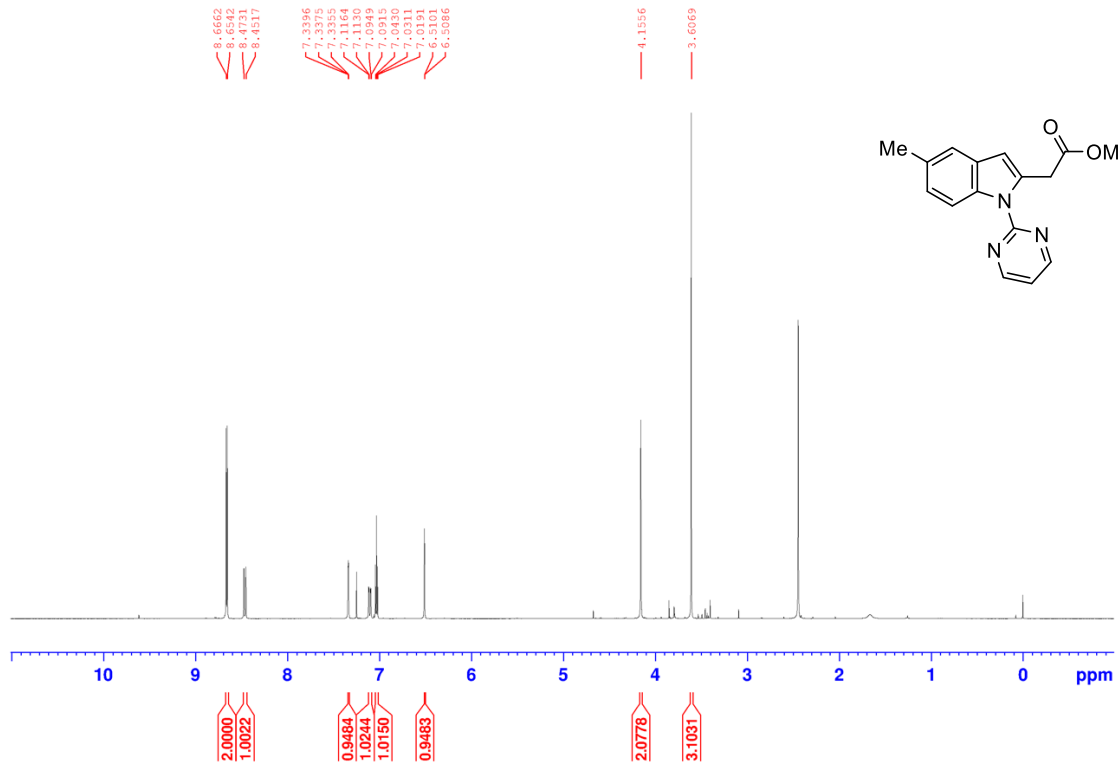
<sup>1</sup>H NMR of **9a** (400 MHz, CDCl<sub>3</sub>)



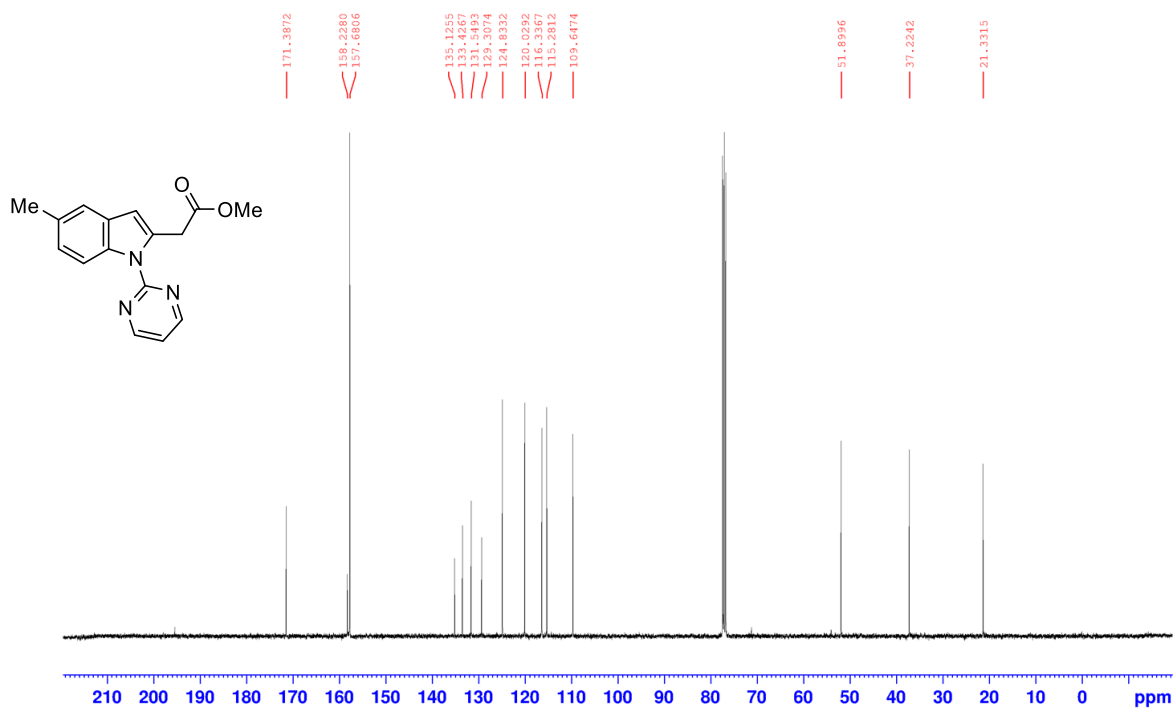
<sup>13</sup>C NMR of **9a** (100 MHz, CDCl<sub>3</sub>)



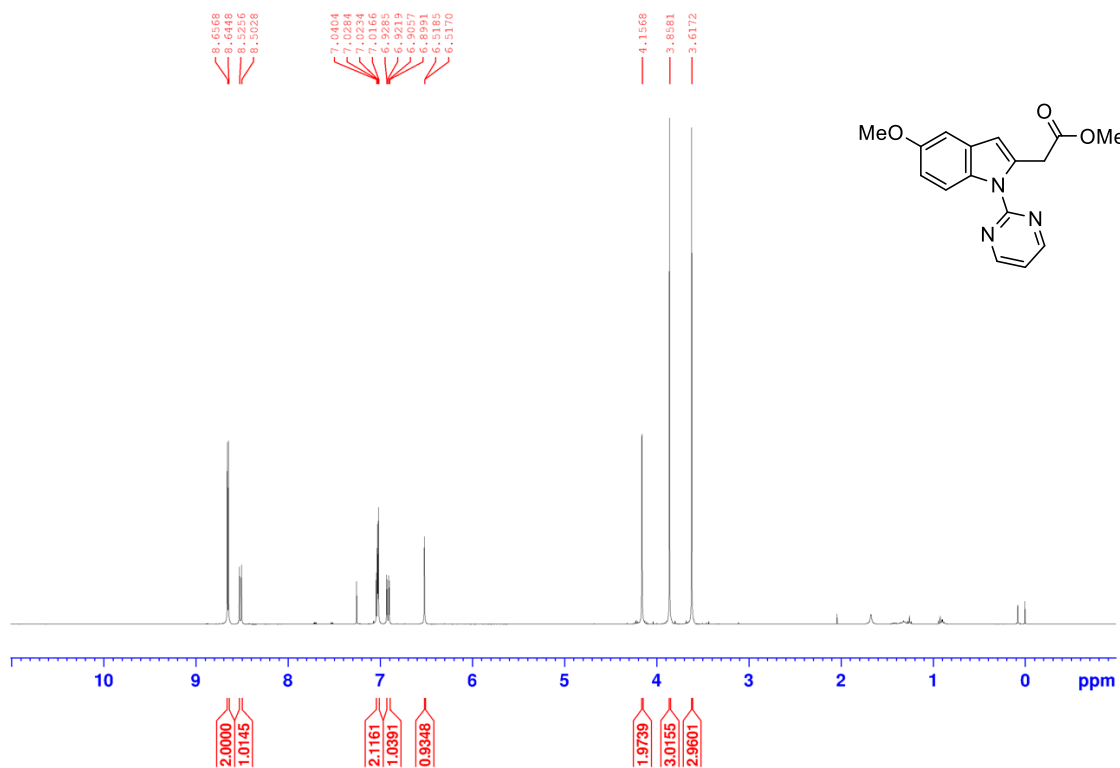
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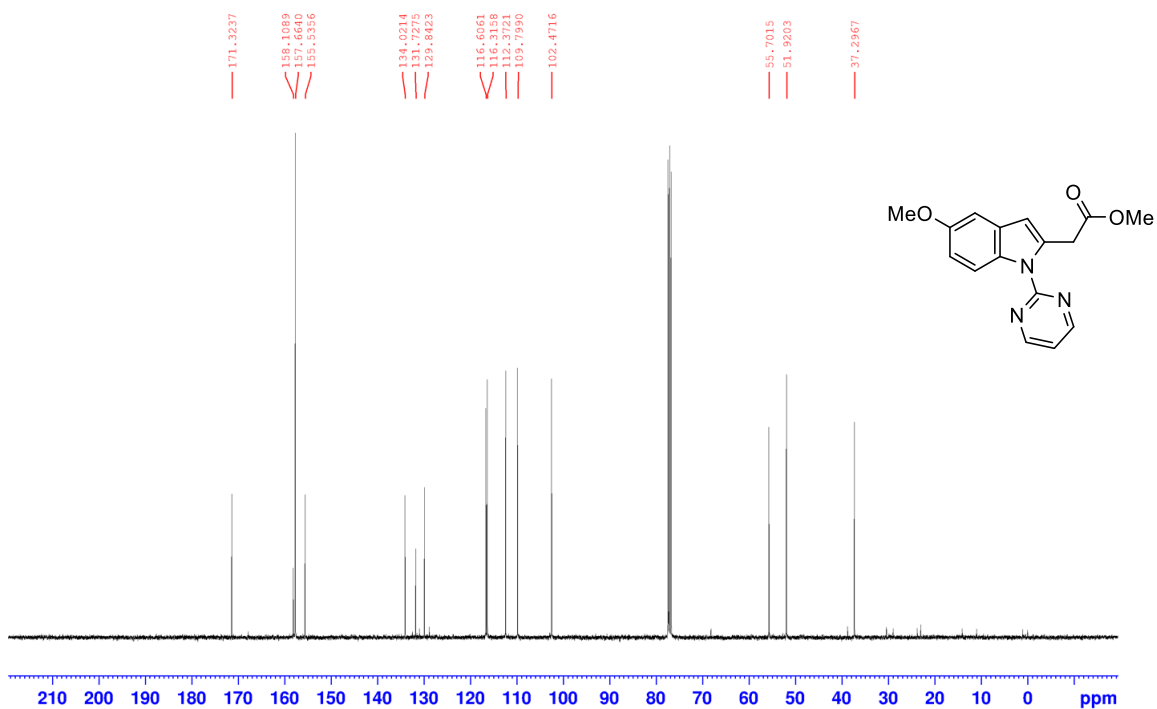
<sup>13</sup>C NMR of **9b** (100 MHz, CDCl<sub>3</sub>)



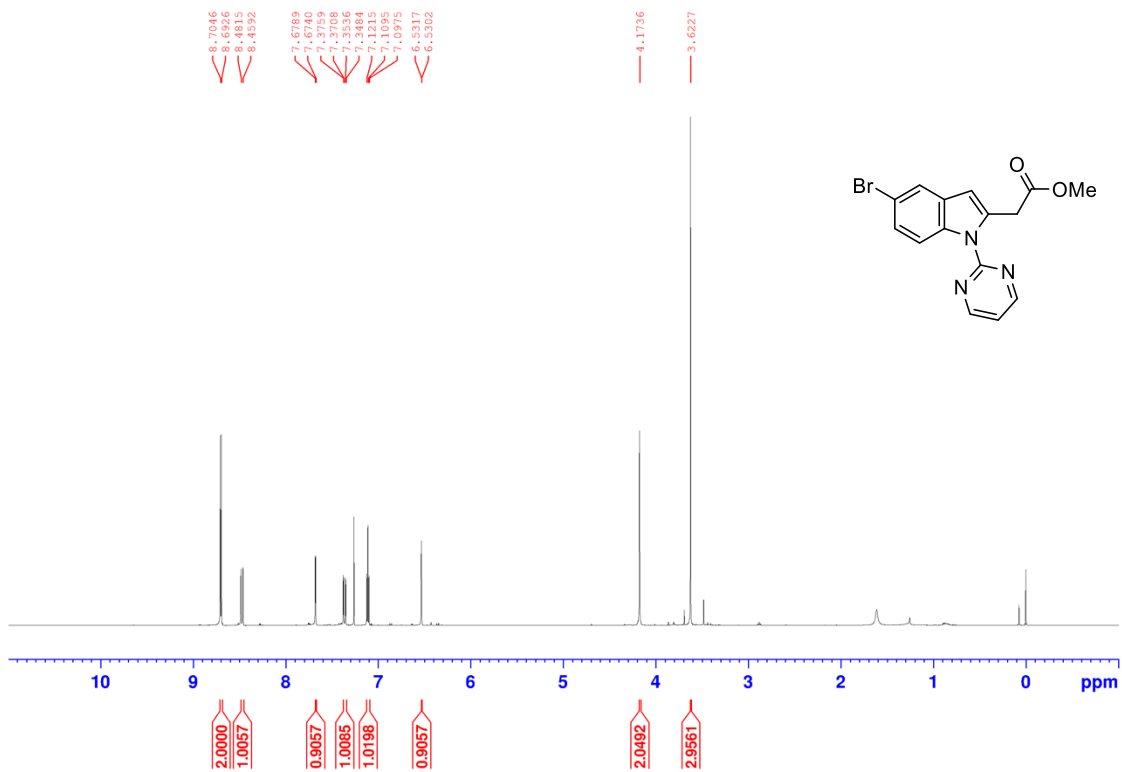
<sup>1</sup>H NMR of **9c** (400 MHz, CDCl<sub>3</sub>)



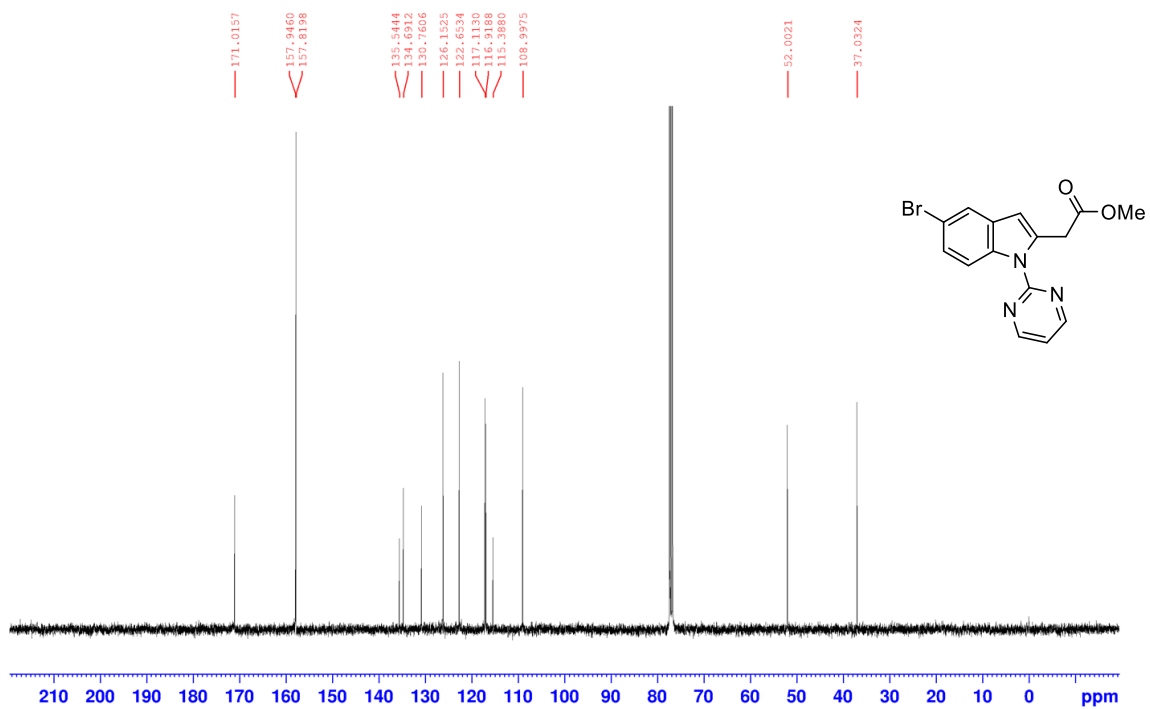
<sup>13</sup>C NMR of **9c** (100 MHz, CDCl<sub>3</sub>)



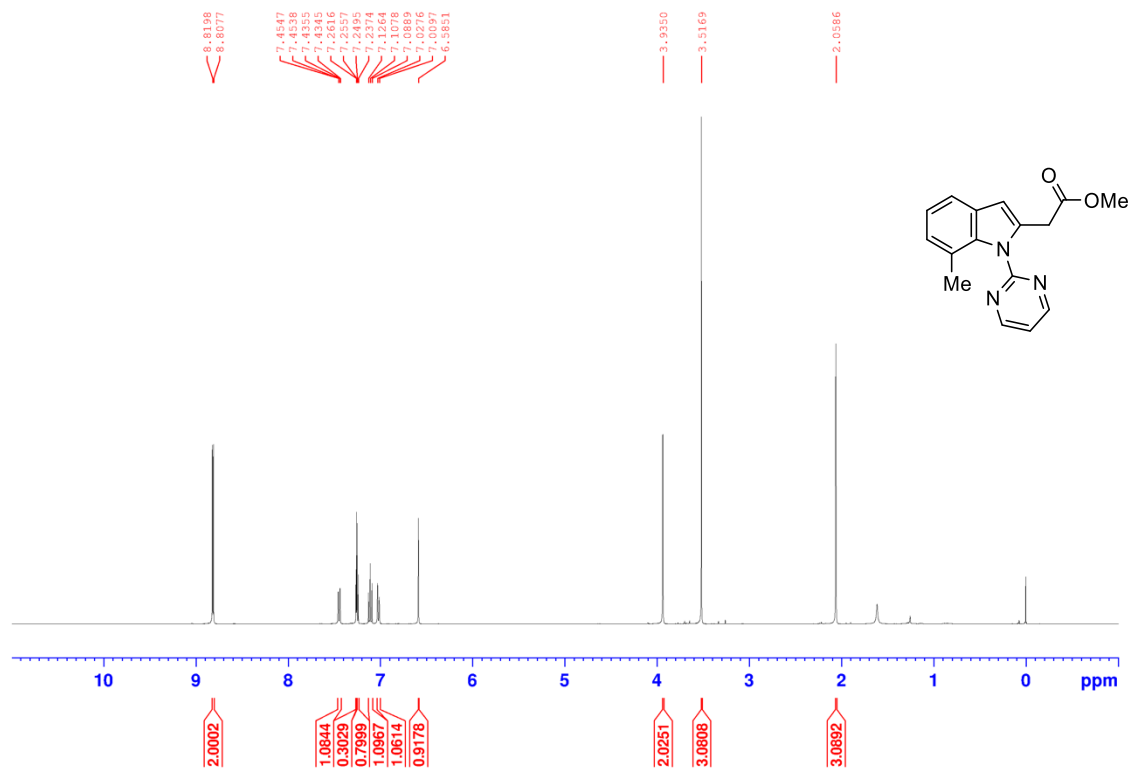
<sup>1</sup>H NMR of **9d** (400 MHz, CDCl<sub>3</sub>)



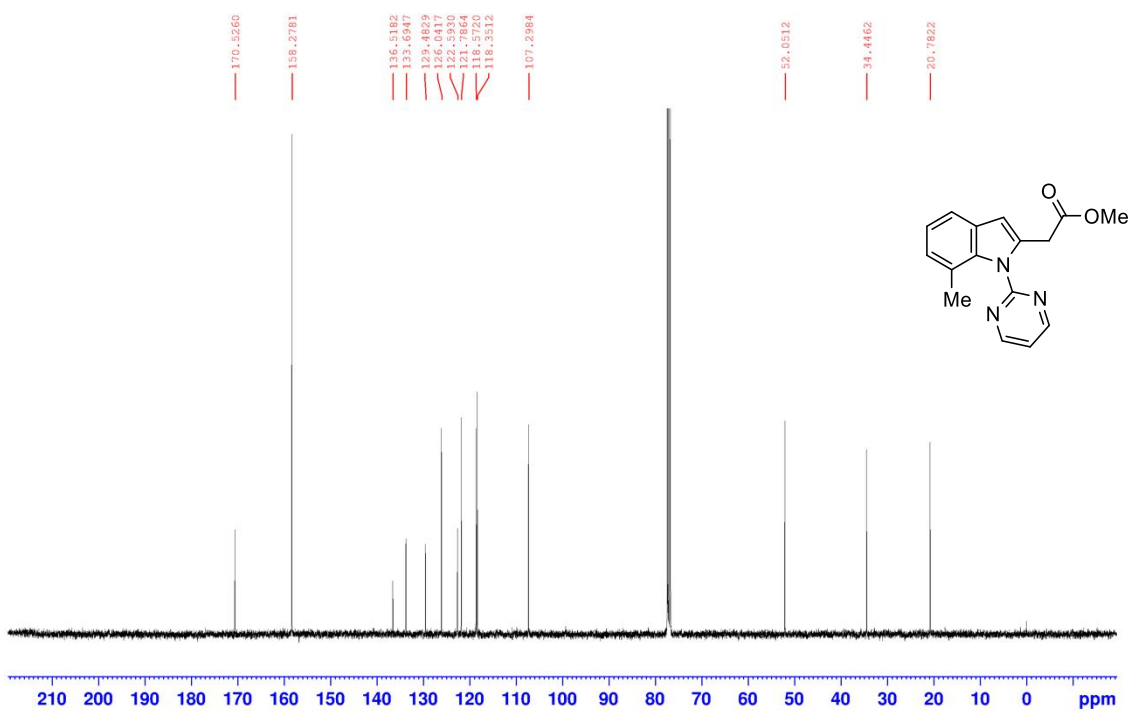
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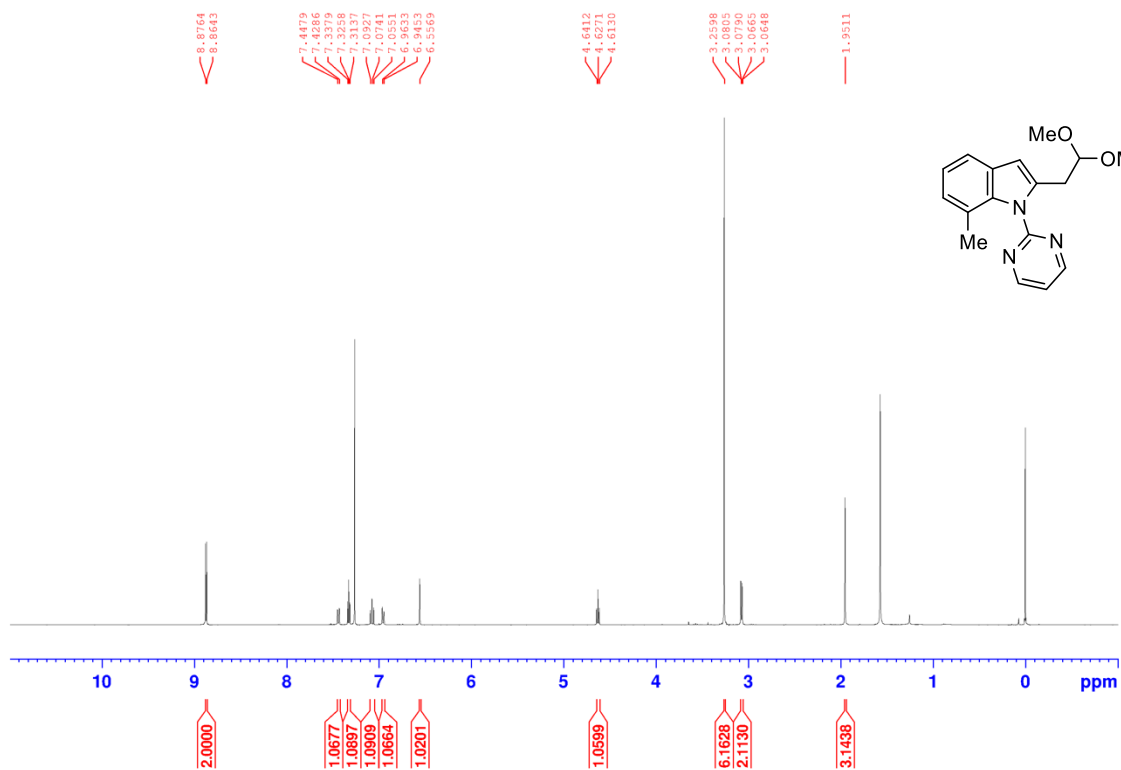
<sup>1</sup>H NMR of **9e** (400 MHz, CDCl<sub>3</sub>)



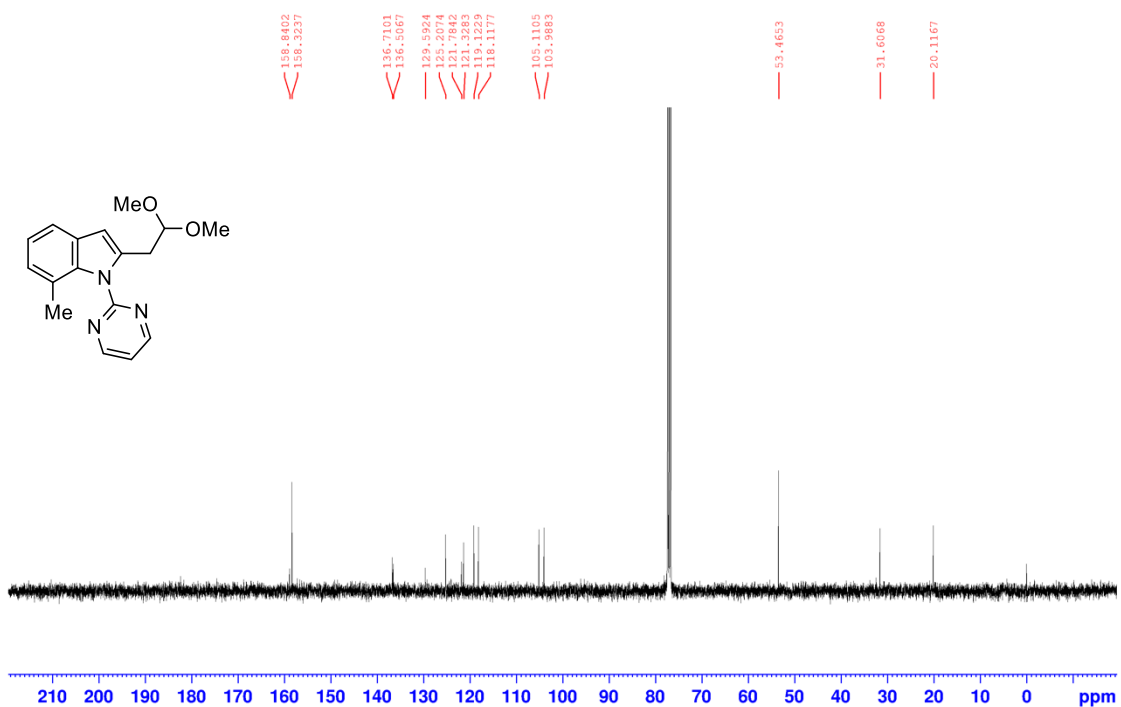
<sup>13</sup>C NMR of **9e** (100 MHz, CDCl<sub>3</sub>)



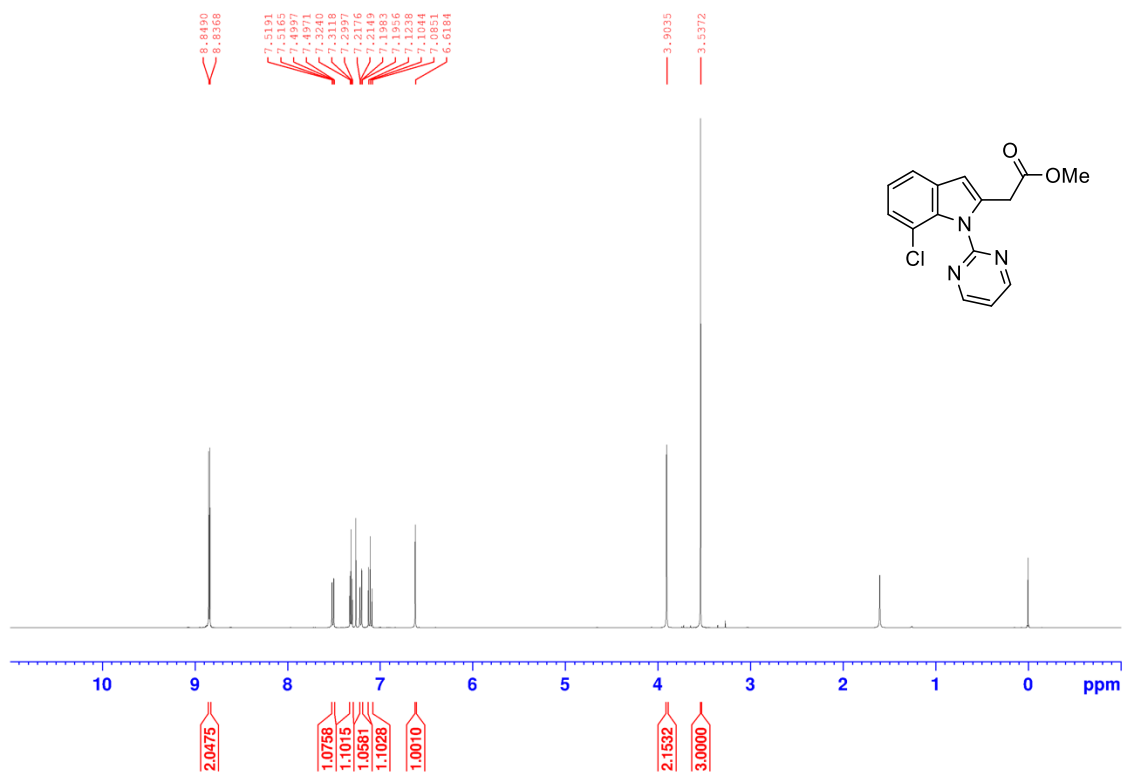
<sup>1</sup>H NMR of **9e'** (400 MHz, CDCl<sub>3</sub>)



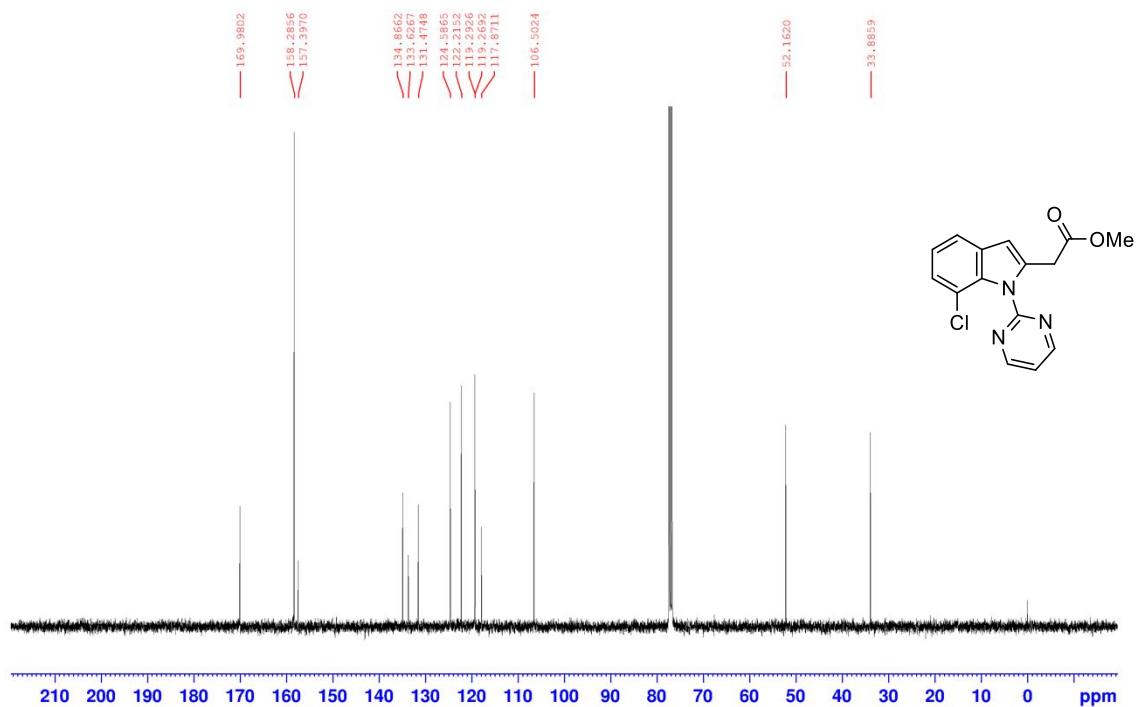
<sup>13</sup>C NMR of **9e'** (100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **9f** (400 MHz, CDCl<sub>3</sub>)

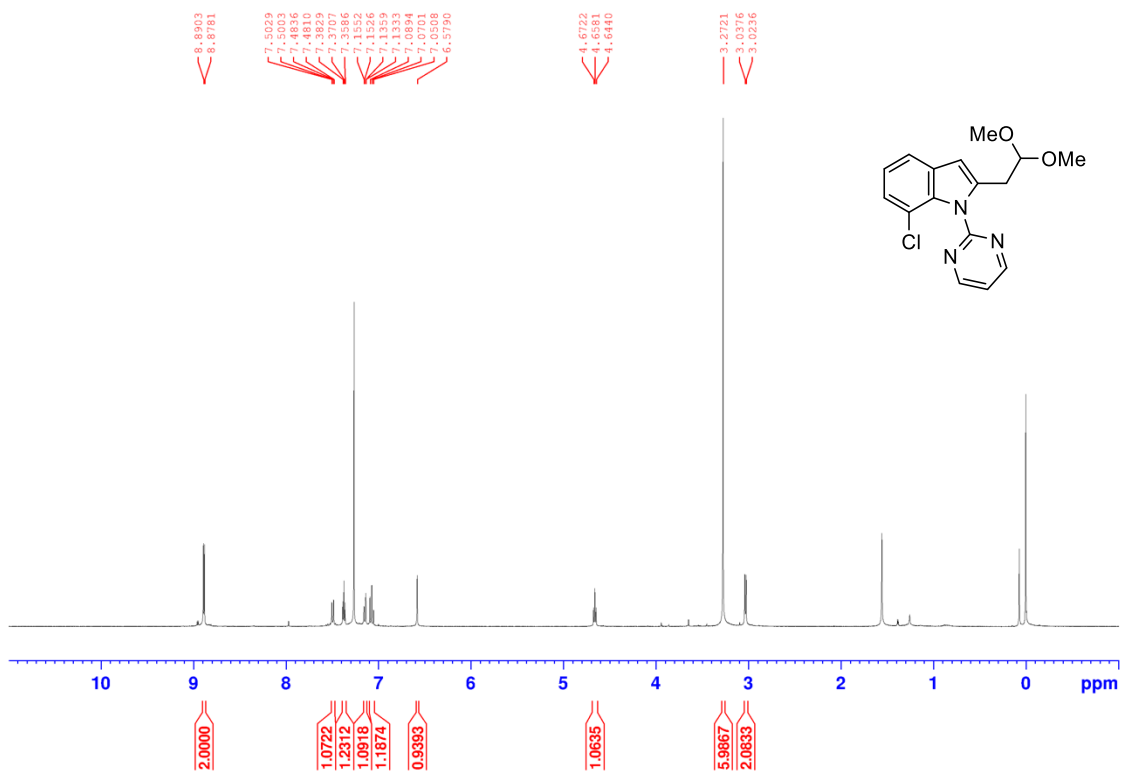


<sup>13</sup>C NMR of **9f** (100 MHz, CDCl<sub>3</sub>)

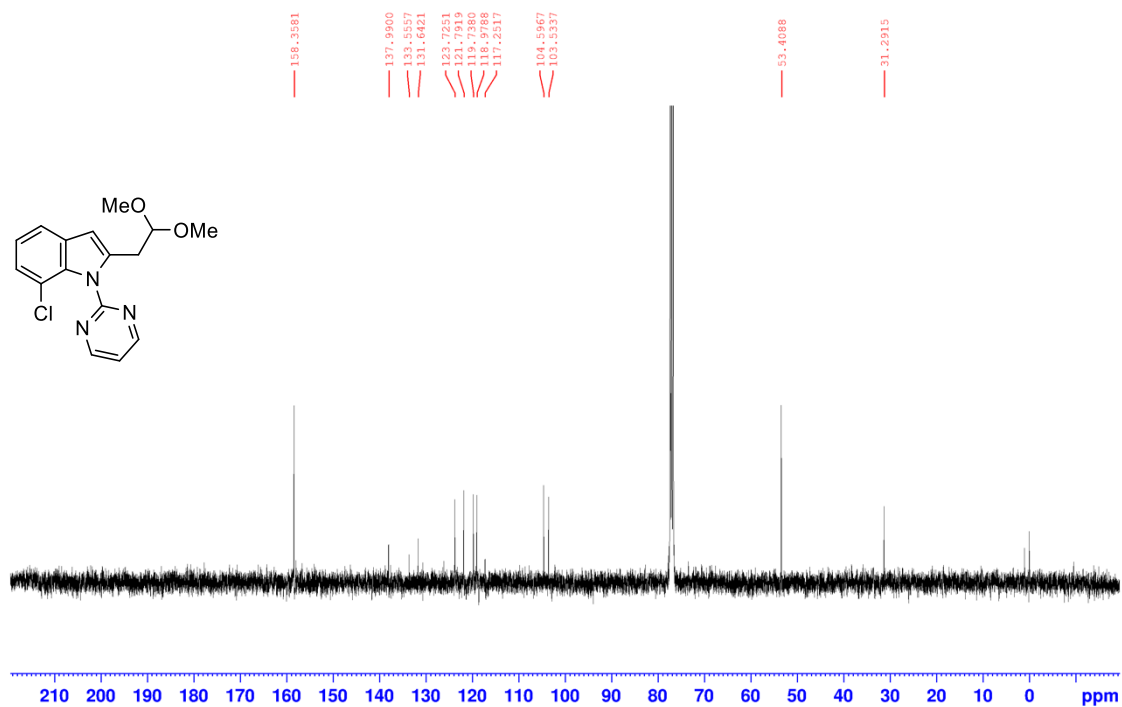




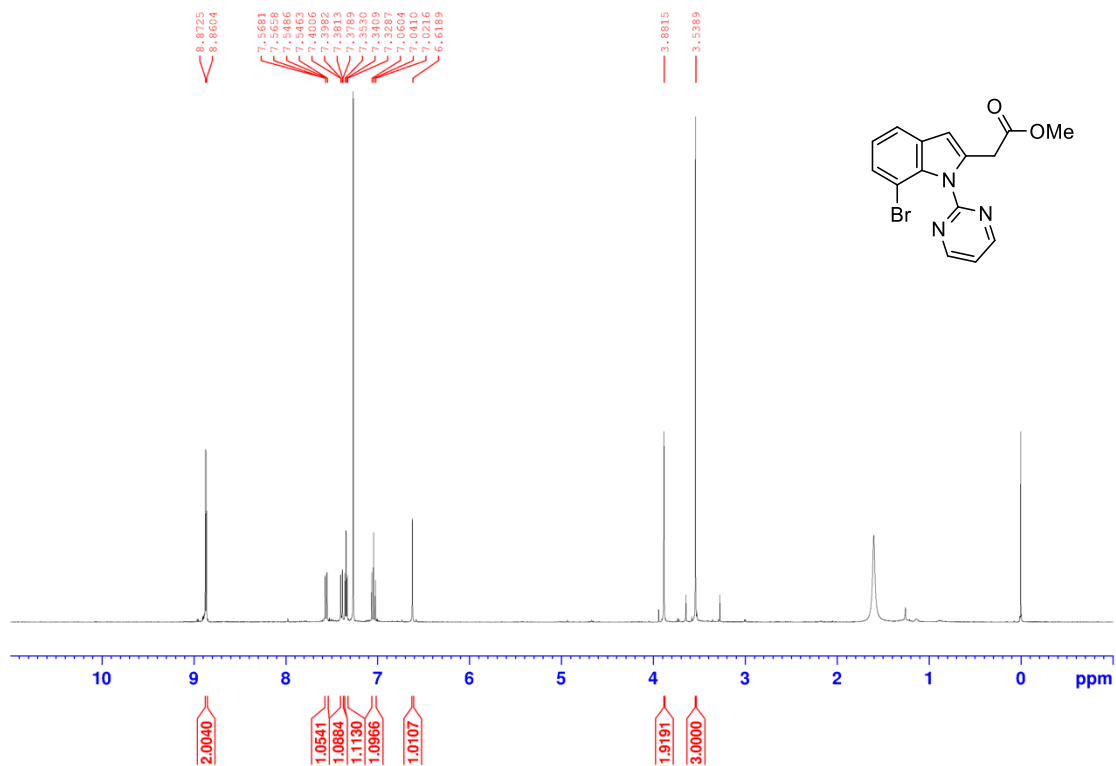
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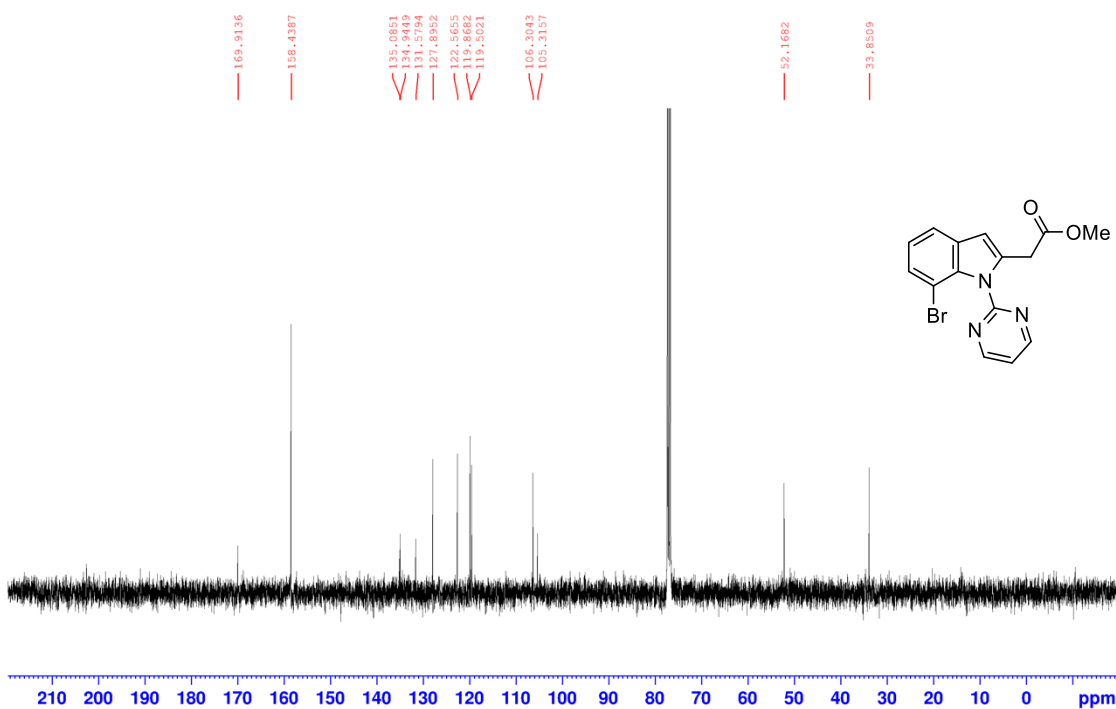
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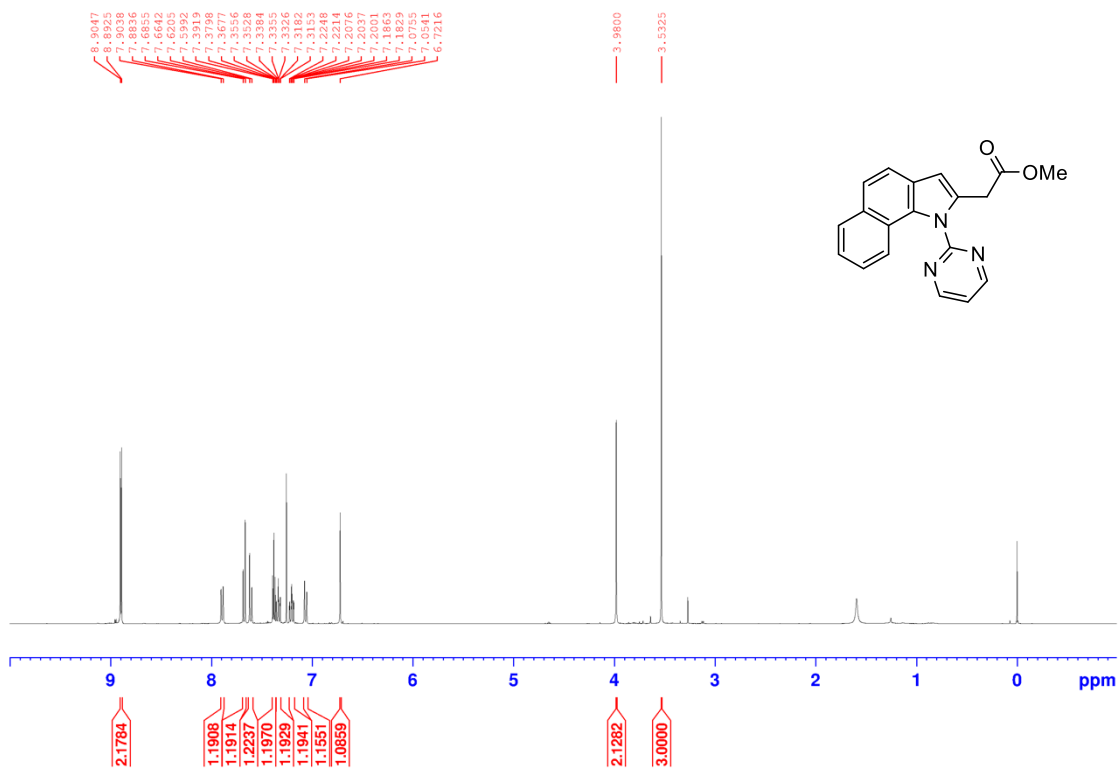
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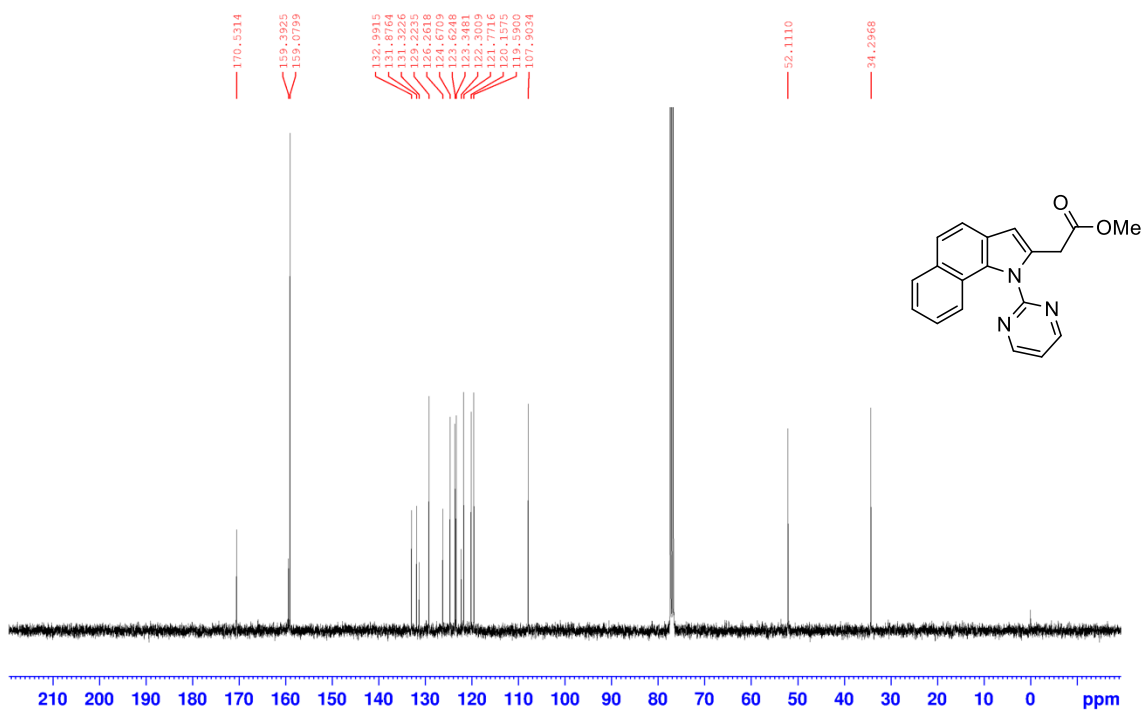
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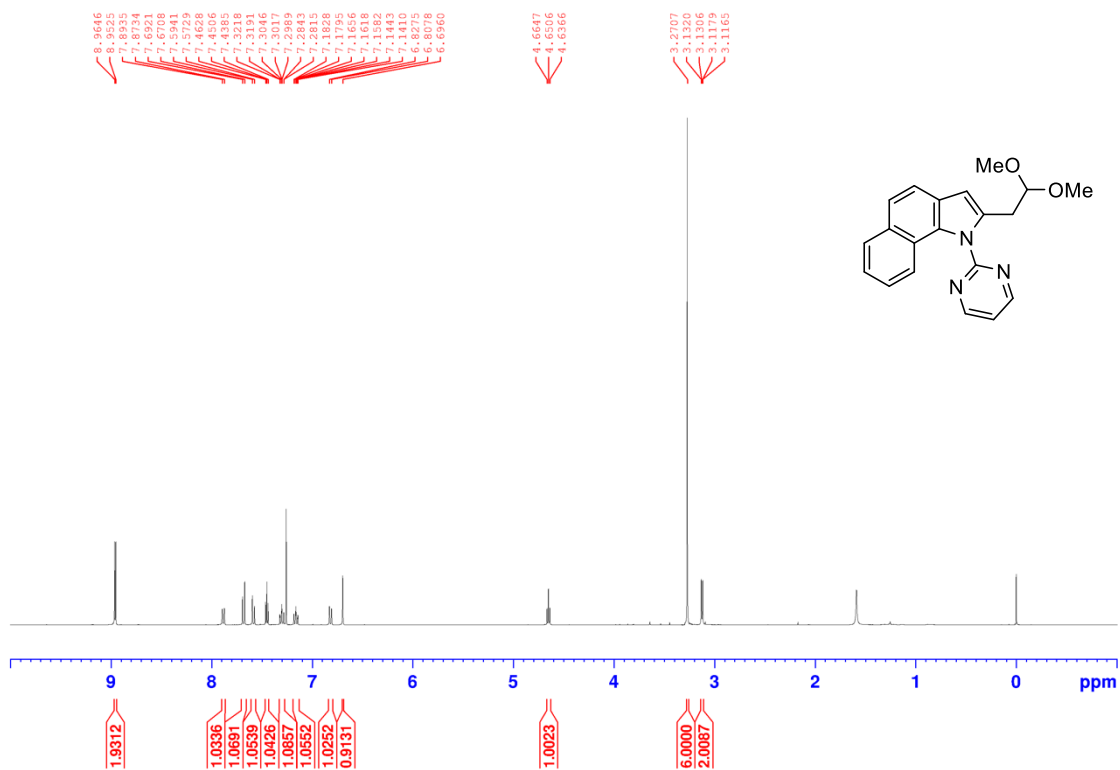
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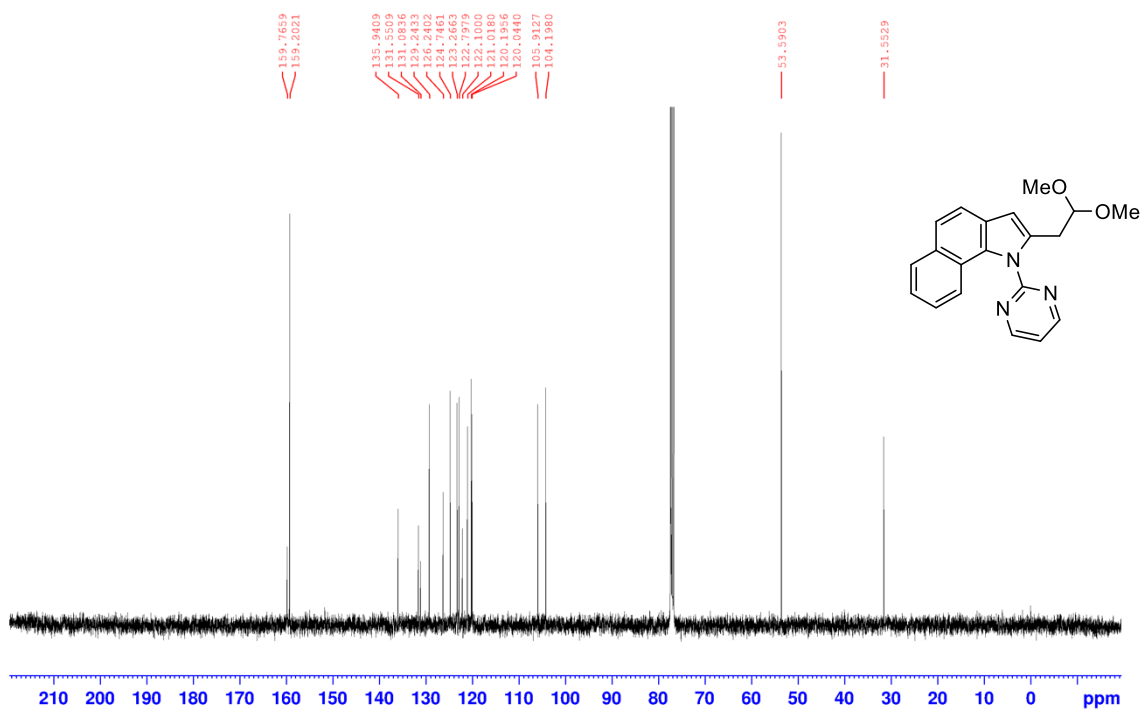
<sup>13</sup>C NMR of **9g'** (100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **9g'** (400 MHz, CDCl<sub>3</sub>)

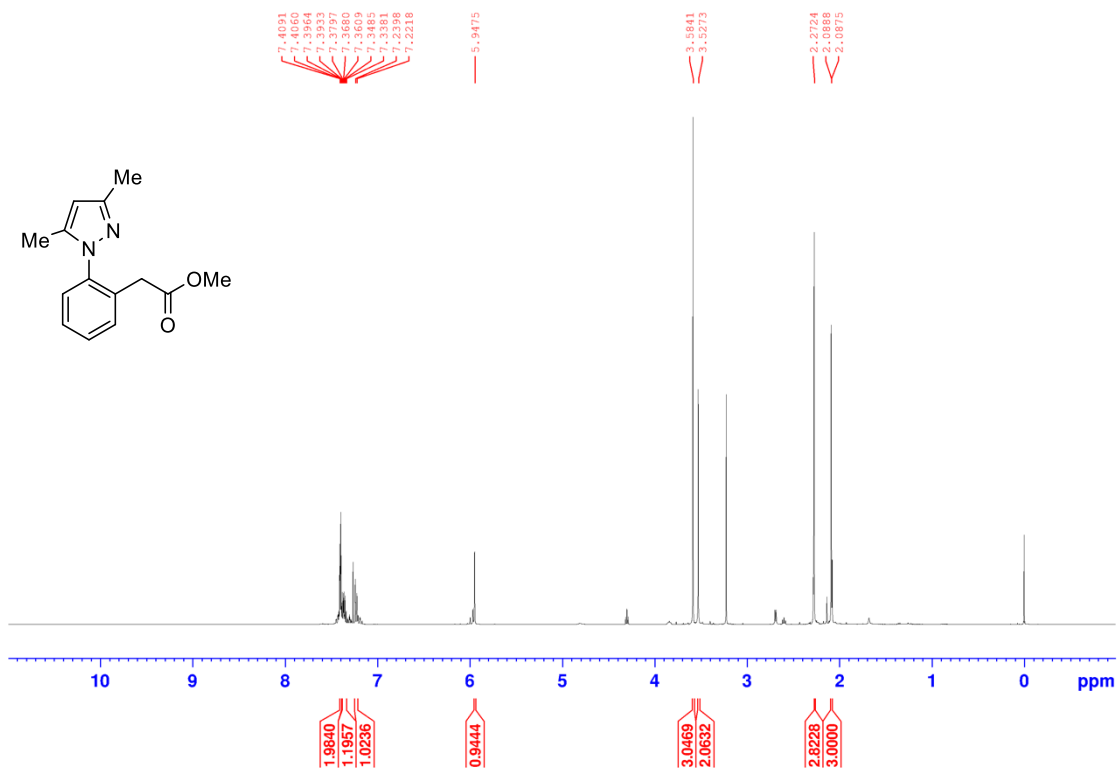


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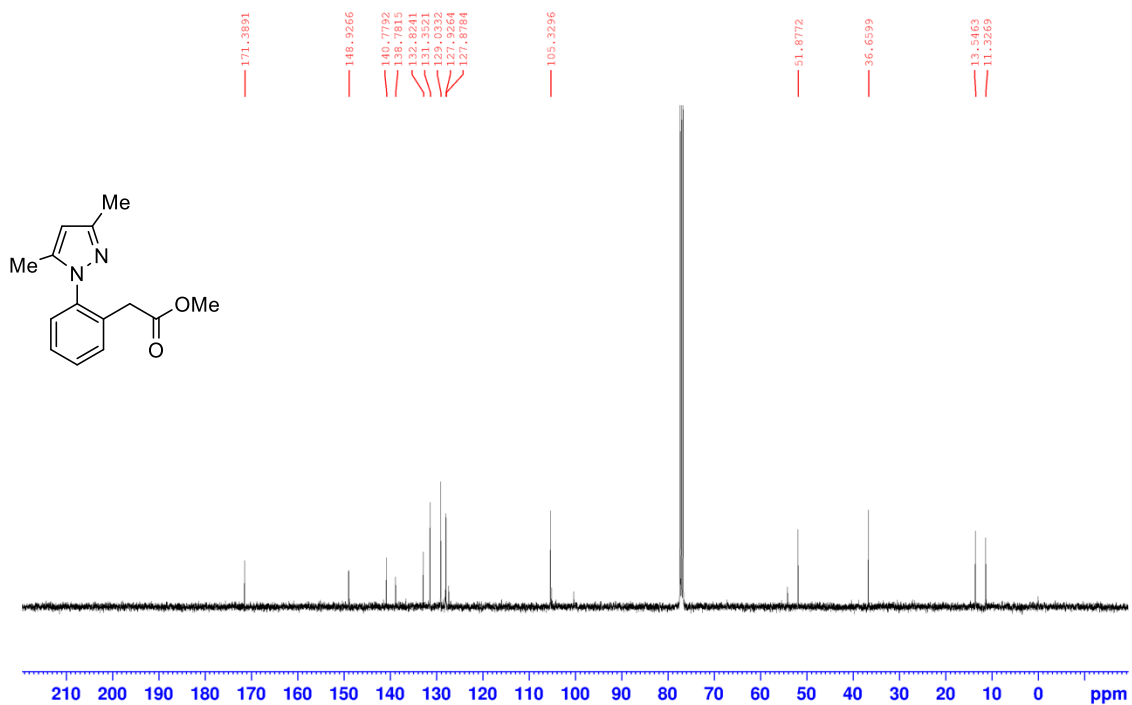




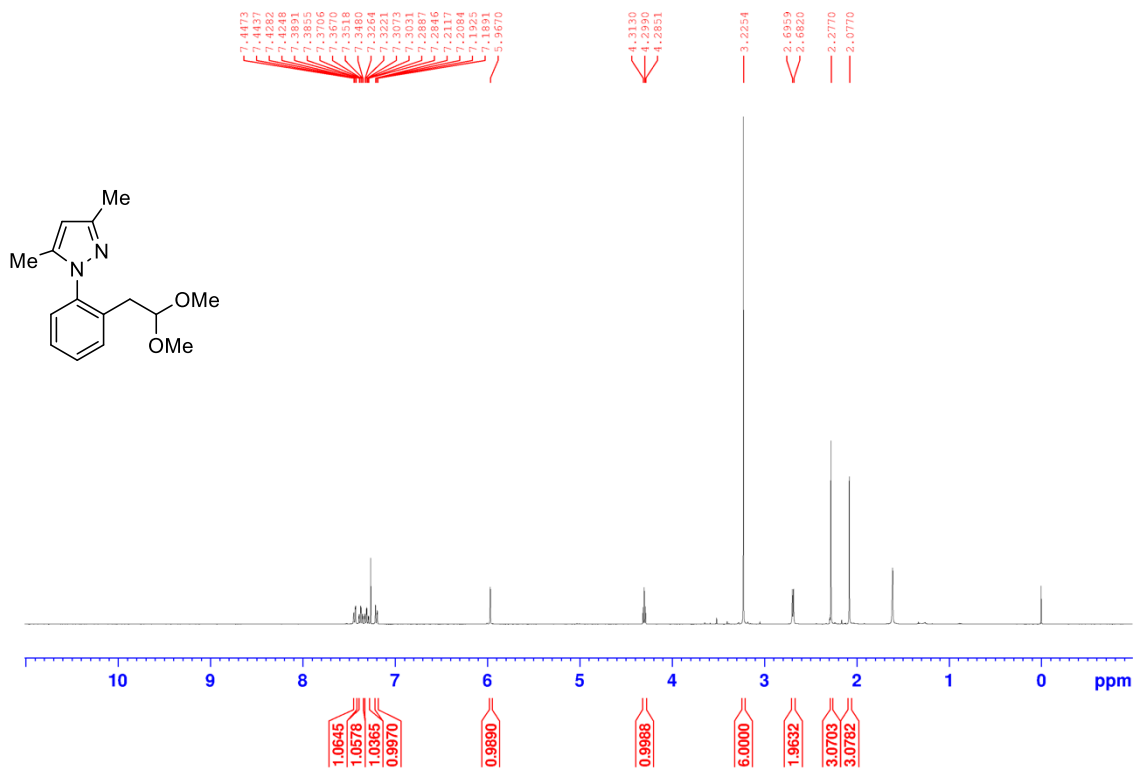
<sup>1</sup>H NMR of **10** (400 MHz, CDCl<sub>3</sub>)



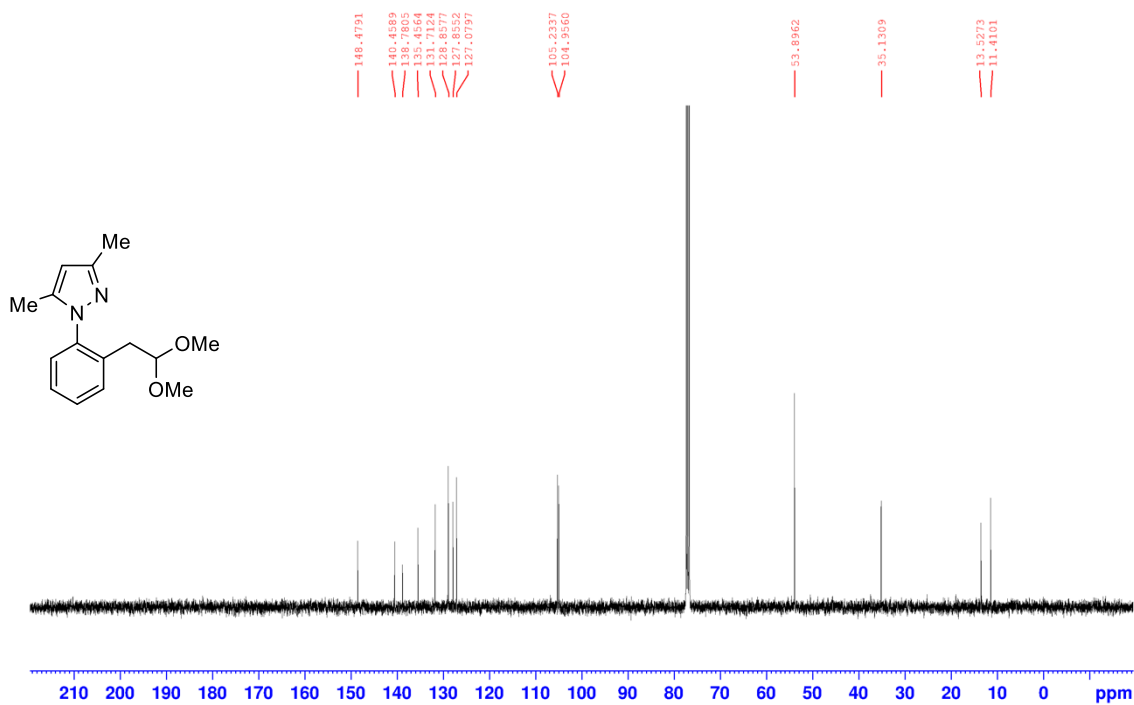
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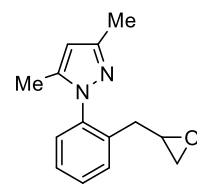
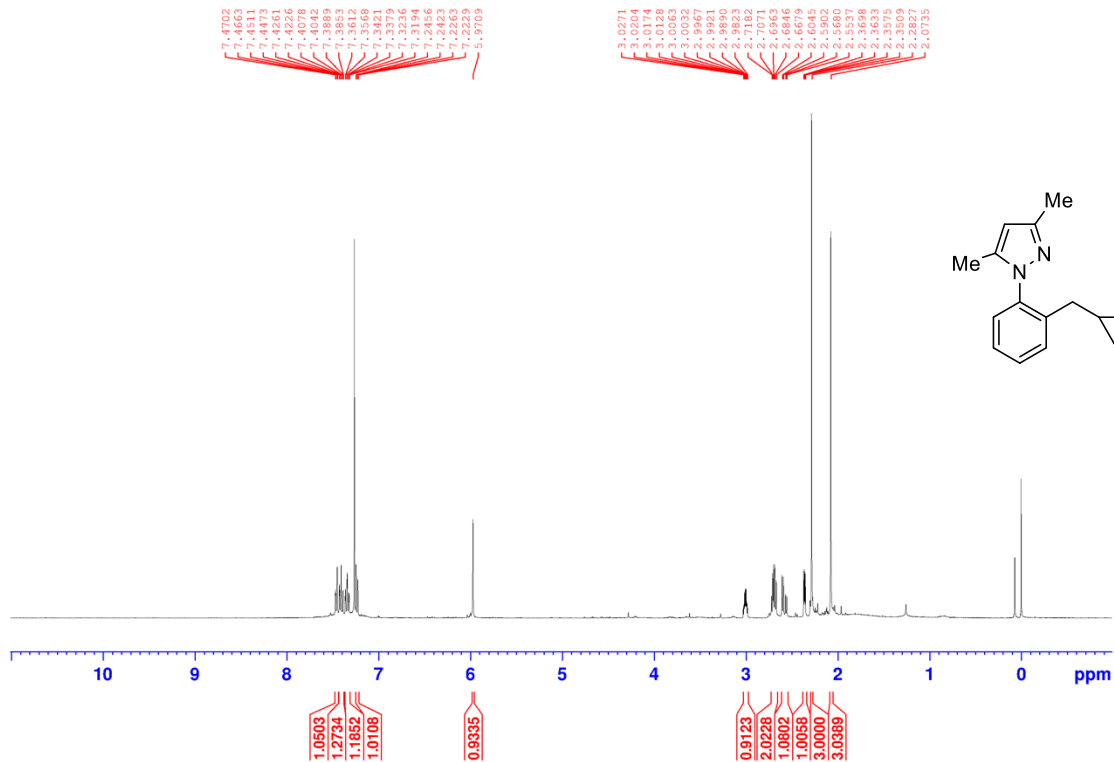
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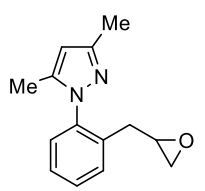
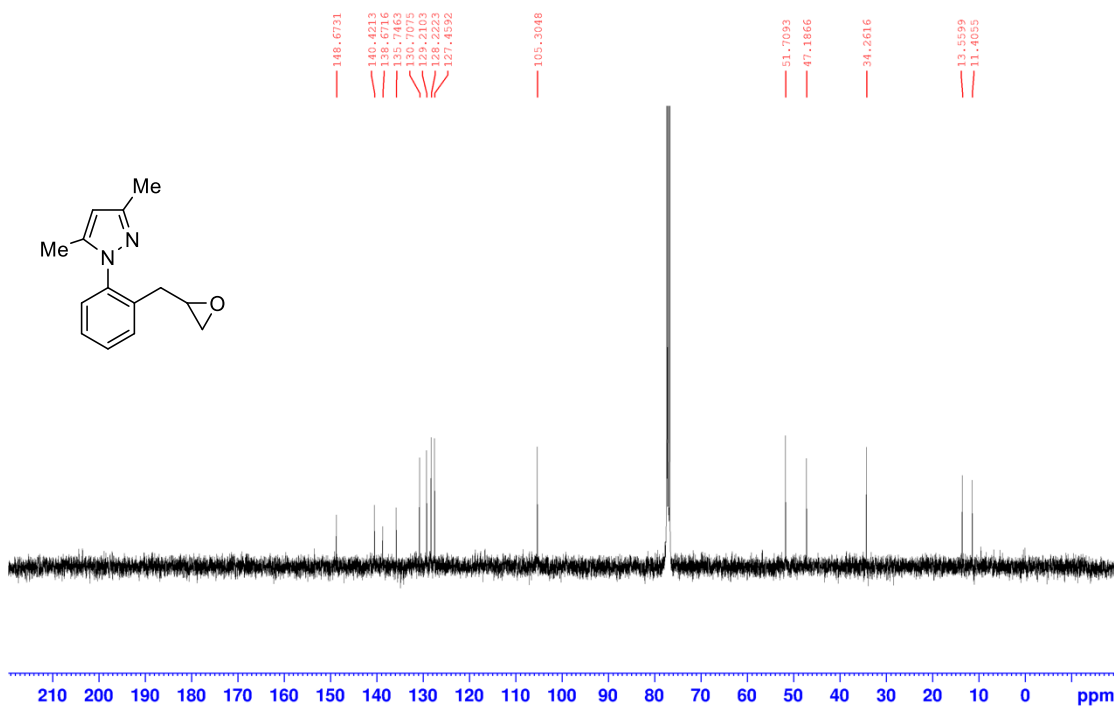
<sup>13</sup>C NMR of **10'** (100 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **3a-1** (400 MHz, CDCl<sub>3</sub>)

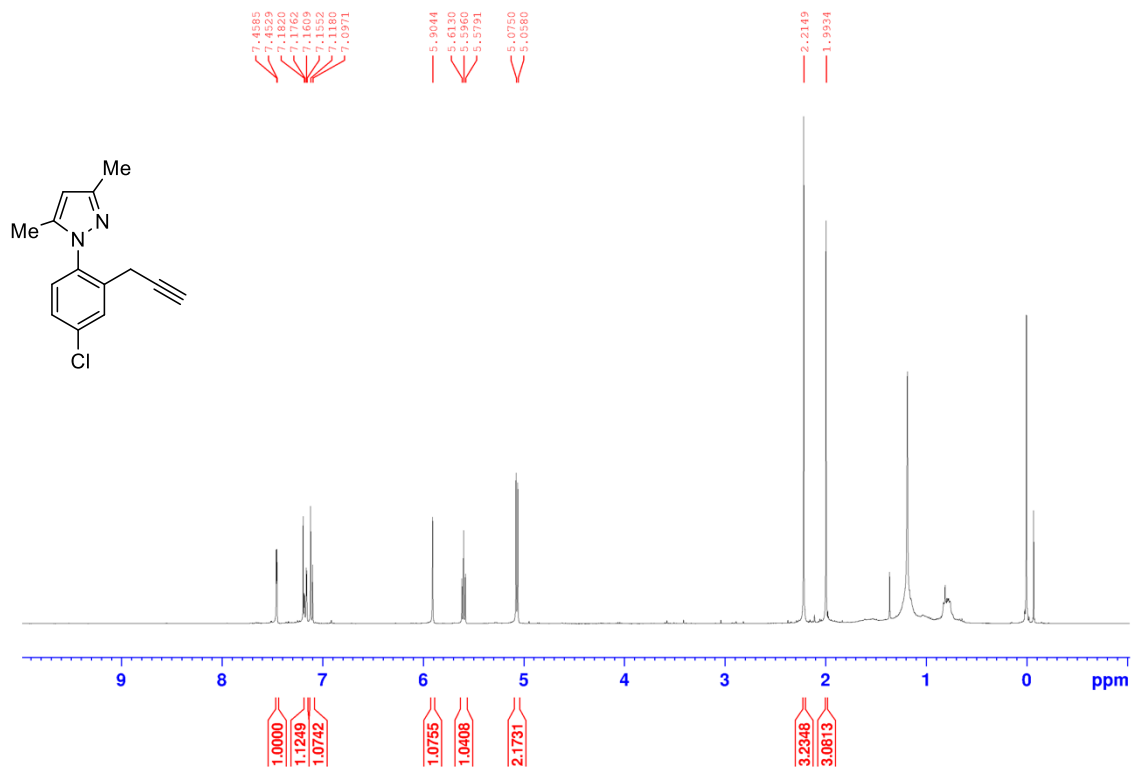


<sup>13</sup>C NMR of **3a-1** (100 MHz, CDCl<sub>3</sub>)

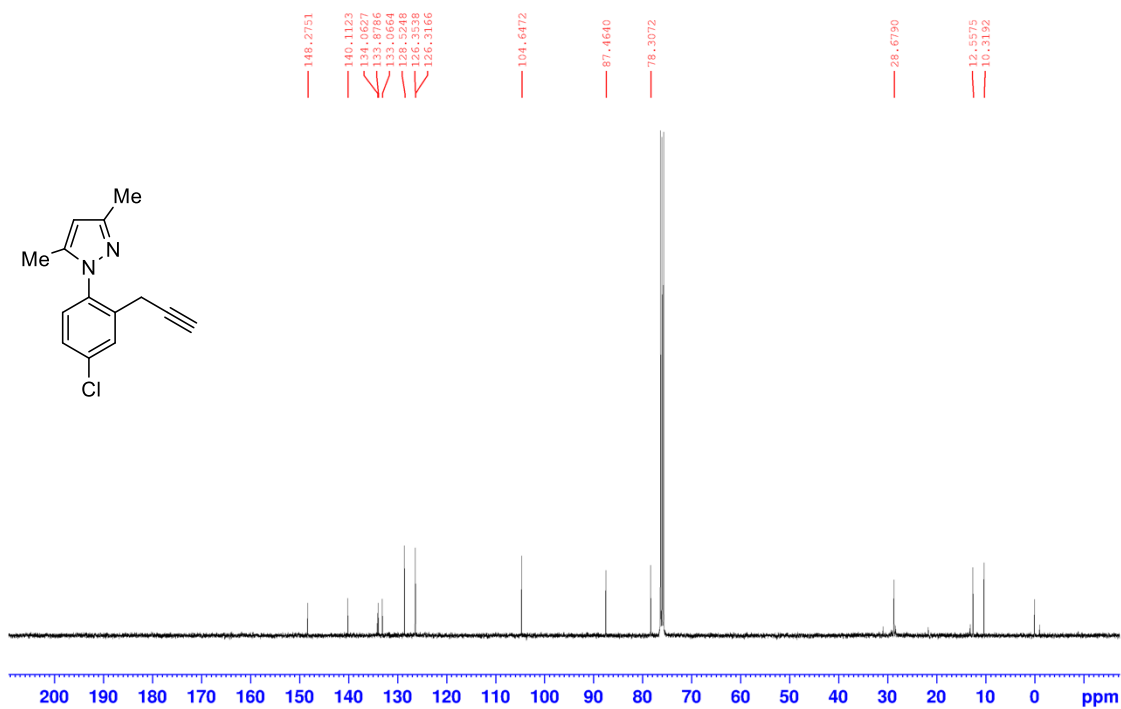




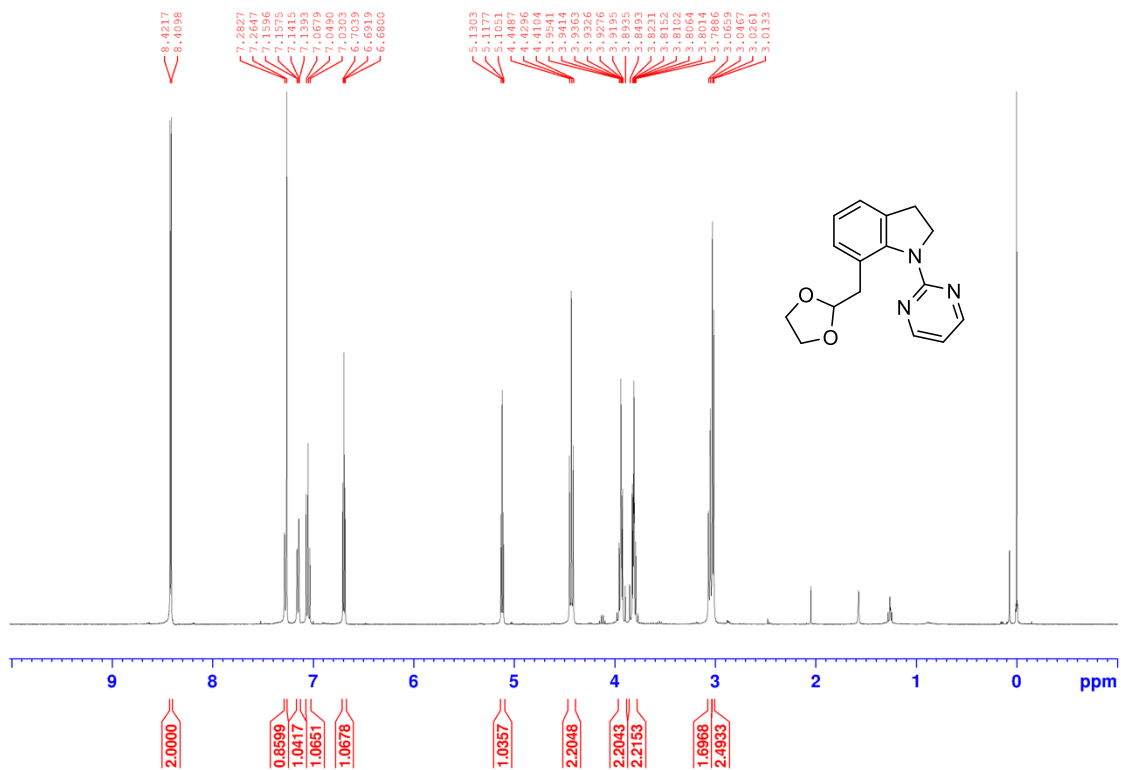
<sup>1</sup>H NMR of **5e-1** (400 MHz, CDCl<sub>3</sub>)



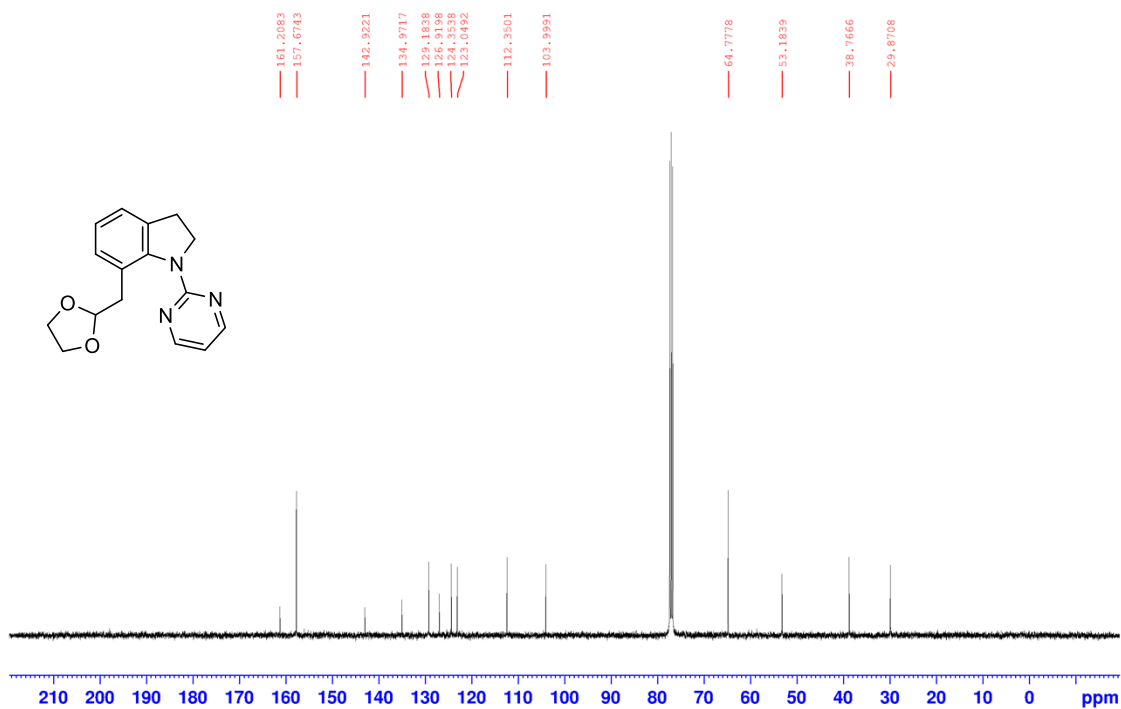
<sup>13</sup>C NMR of **5e-1** (100 MHz, CDCl<sub>3</sub>)



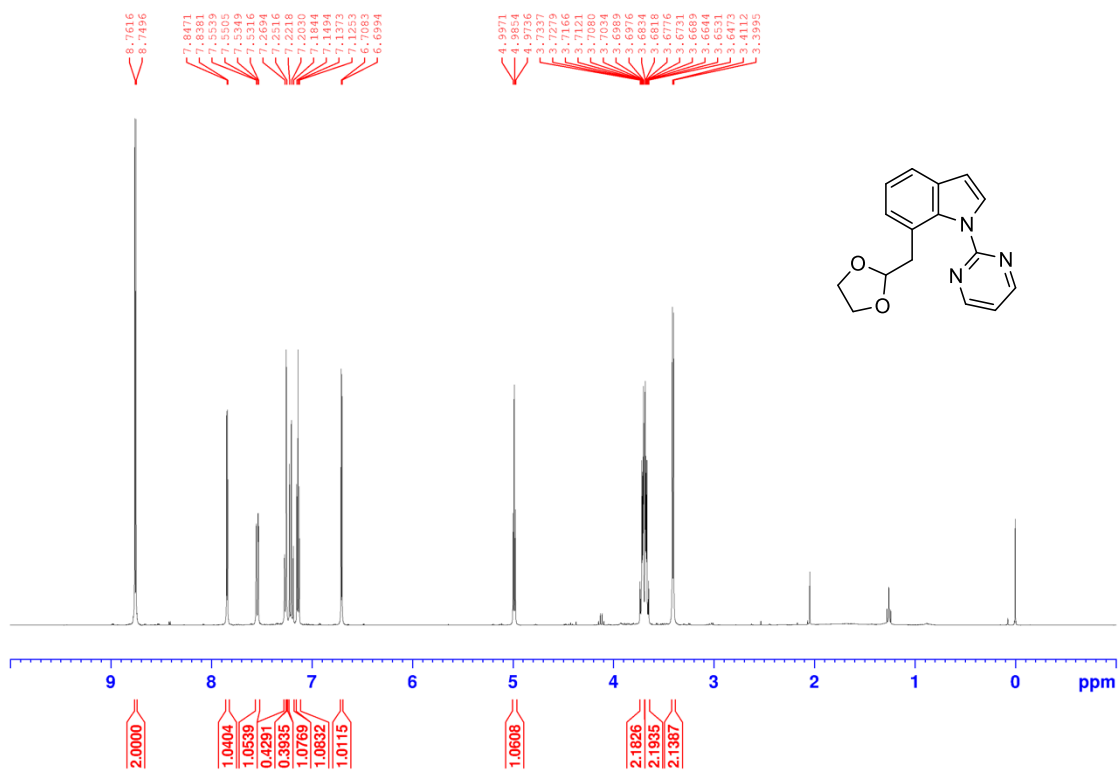
<sup>1</sup>H NMR of **5a-acetal** (400 MHz, CDCl<sub>3</sub>)



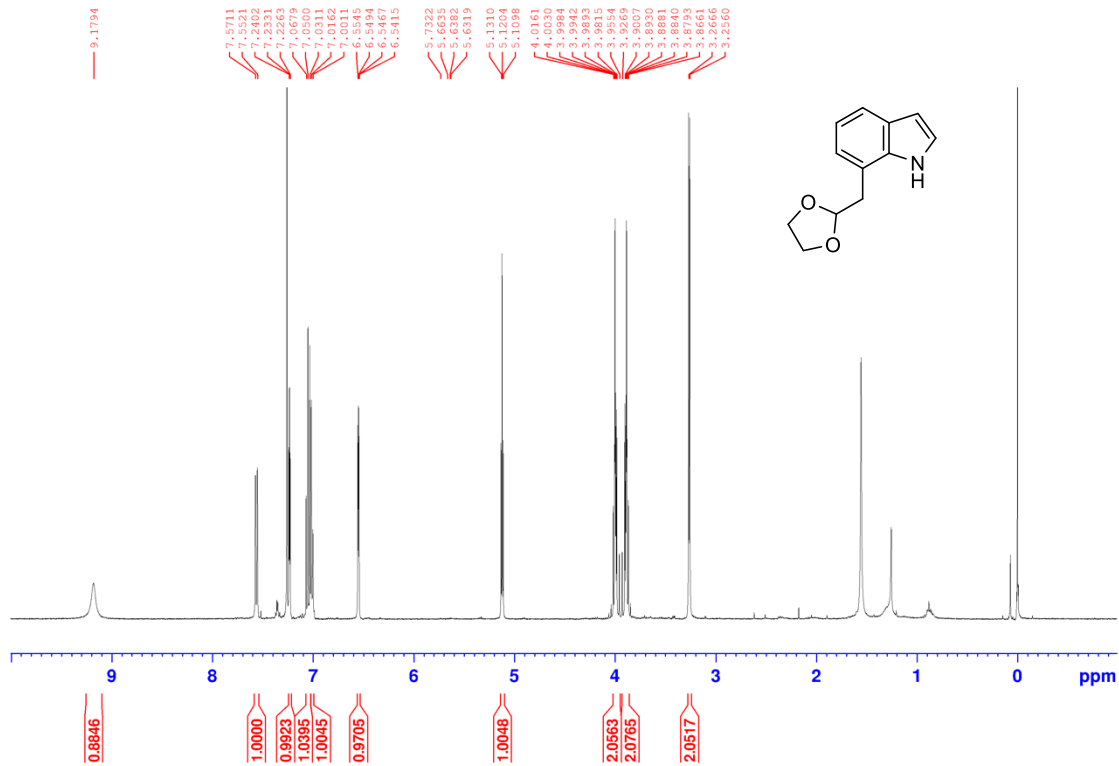
<sup>13</sup>C NMR of **5a-acetal** (100 MHz, CDCl<sub>3</sub>)



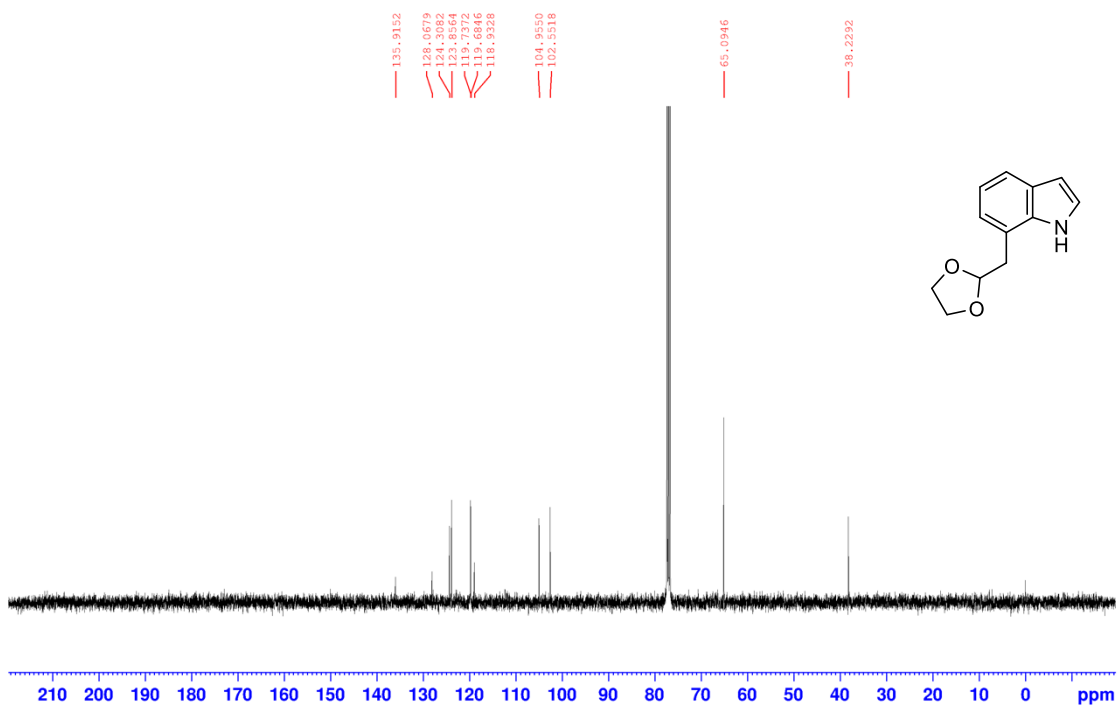
<sup>1</sup>H NMR of **5a-indole** (400 MHz, CDCl<sub>3</sub>)



<sup>1</sup>H NMR of **5a-1** (400 MHz, CDCl<sub>3</sub>)



<sup>13</sup>C NMR of **5a-1** (100 MHz, CDCl<sub>3</sub>)



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