

## Supporting Information

# Redox-Neutral Dehydrogenative Cross-Coupling of Alcohols and Amines Enabled by Nickel Catalysis

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### Table of Contents

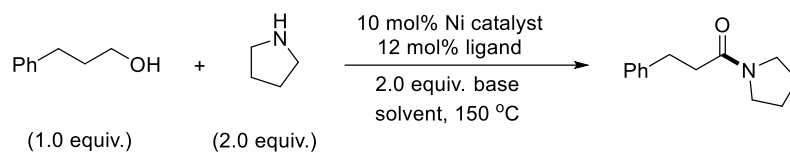
1. General Considerations	S2
2. Supplementary Table	S3
3. General procedure for the preparation of allylic alcohols	S4
4. General procedures for the redox-neutral nickel-catalyzed dehydrogenative cross-coupling reactions	S4
5. Characterization data for the products	S4
6. Mechanism Studies	S16
7. Supplementary References	S16
8. <sup>1</sup> H NMR, <sup>13</sup> C NMR, and <sup>19</sup> F NMR spectra	S17

## 1. General Considerations

Unless noted otherwise, all solvents were dried by filtration through a Pure-Solv MD-5 Solvent Purification System (Innovative Technology). Toluene was carefully freeze-pump-thawed and dried by 4A molecular sieves (activated at 350 °C for 8h). Reaction temperatures were reported as the temperatures of the bath surrounding the flasks or cylindrical pressure vessel. Sensitive reagents and solvents were transferred under nitrogen into a nitrogen-filled glovebox with standard techniques. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (silica gel 60, F254, Leyan chemical). Cylindrical pressure vessel (26 x 109 mm (15 mL) with PTFE lined cap attached) were purchased from Synthware. Nuclear magnetic resonance spectra (<sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR) were recorded with a Bruker Model DMX 500 (500 MHz, <sup>1</sup>H at 500 MHz, <sup>13</sup>C at 126 MHz). Chemical shifts were reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ=0.00ppm) and were referenced to residual solvent (CDCl<sub>3</sub>, δ=7.26 ppm (<sup>1</sup>H) and 77.00 ppm (<sup>13</sup>C)). All the <sup>19</sup>F chemical shifts were not referenced. Coupling constants were reported in Hertz (Hz). Data for <sup>1</sup>H NMR spectra were reported as follows: chemical shift (ppm, referenced to protium, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). All other materials were obtained from Rhawn Corporation, Aladdin Bio-Chem Technology or Energy chemical and were used as received.

## 2. Supplementary Table

### Optimization of Reaction Conditions<sup>[a]</sup>



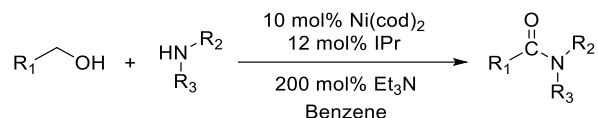
Entry	Catalyst	Ligand	Base	Solvent	Yield <sup>b</sup>
1	Ni(cod) <sub>2</sub>	IPr	Et <sub>3</sub> N	benzene	88%
2	Ni(OTf) <sub>2</sub>	IPr	Et <sub>3</sub> N	benzene	11%
3	Ni(PPh <sub>3</sub> ) <sub>4</sub>	IPr	Et <sub>3</sub> N	benzene	7%
4	Ni(cod) <sub>2</sub>	IMes	Et <sub>3</sub> N	benzene	19%
5	Ni(cod) <sub>2</sub>	Triphos	Et <sub>3</sub> N	benzene	trace
6	Ni(cod) <sub>2</sub>	PCy <sub>3</sub>	Et <sub>3</sub> N	benzene	trace
7	Ni(cod) <sub>2</sub>	dppp	Et <sub>3</sub> N	benzene	trace
8	Ni(cod) <sub>2</sub>	Sphos	Et <sub>3</sub> N	benzene	trace
9	Ni(cod) <sub>2</sub>	IPr	DIPEA	benzene	64%
10	Ni(cod) <sub>2</sub>	IPr	TMP	benzene	61%
11	Ni(cod) <sub>2</sub>	IPr	Na <sub>2</sub> CO <sub>3</sub>	benzene	64%
12	Ni(cod) <sub>2</sub>	IPr	K <sub>2</sub> HPO <sub>4</sub>	benzene	62%
13	Ni(cod) <sub>2</sub>	IPr	K <sub>3</sub> PO <sub>4</sub>	benzene	48%
14	Ni(cod) <sub>2</sub>	IPr	DABCO	benzene	65%
15	Ni(cod) <sub>2</sub>	IPr	Et <sub>3</sub> N	toluene	29%
16	Ni(cod) <sub>2</sub>	IPr	Et <sub>3</sub> N	cyclopentyl methyl ether	48%
17	Ni(cod) <sub>2</sub>	IPr	Et <sub>3</sub> N	Xylene	34%
18	Ni(cod) <sub>2</sub>	IPr	Et <sub>3</sub> N	THF	17%
19	Ni(cod) <sub>2</sub>	IPr	Et <sub>3</sub> N	TBME	39%
20	Ni(cod) <sub>2</sub>	IPr	Et <sub>3</sub> N	1,4-dioxane	trace

[a] Reaction condition: alcohol (0.3 mmol, 1.0 equiv.), amine (0.6 mmol, 2.0 equiv.), base (2.0 equiv.), solvent (2 mL), 150 °C under N<sub>2</sub> for 20 h. [b] Yield was detected by NMR.

### 3. General procedure for the Preparation of allylic alcohols

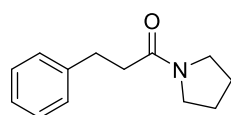
Allylic alcohols **1b–1z**, **1a'–1c'** were prepared according to previous literature procedures <sup>[1]</sup>.

### 4. General procedures for the redox-neutral nickel-catalyzed dehydrogenative cross-coupling reactions

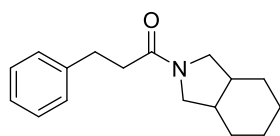


A flame-dried 15 mL cylindrical pressure vessel was charged with alcohol (0.3 mmol, 1.0 equiv.) and amine (0.6 mmol, 2.0 equiv.). The cylindrical pressure vessel was directly transferred into a nitrogen-filled glovebox without caps. Then, Ni(cod)<sub>2</sub> (8.3 mg, 0.03 mmol, 10 mol%), IPr (14.0 mg, 0.036 mmol, 12 mol%), Et<sub>3</sub>N (60.7 mg, 0.6 mmol, 2.0 equiv.) and 2.0 mL dry benzene were added. Then the cylindrical pressure vessel was tightly sealed, transferred out of the glovebox and stirred at 130 °C or 150 °C with corresponding reaction time. After the completion of reaction, the solvent was removed in vacuo and the residue was purified by flash column chromatography on silica gel to give the desired amide products.

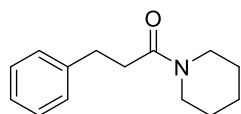
### 5. Characterization data for the products



**3a** (CAS: 151647-54-0). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.31–7.17 (m, 5H), 3.46 (t, *J* = 6.8 Hz, 2H), 3.28 (t, *J* = 6.7 Hz, 2H), 3.03–2.94 (m, 2H), 2.61–2.51 (m, 2H), 1.92–1.77 (m, 4H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.8, 141.6, 128.5, 128.4, 126.1, 46.6, 45.7, 36.8, 31.2, 26.1, 24.4.

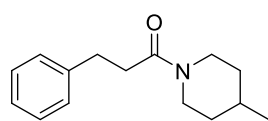


**3b** (CAS: 1789209-15-9). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.32–7.27 (m, 2H), 7.23–7.17 (m, 3H), 3.56 (t, *J* = 5.5 Hz, 2H), 3.33 (t, *J* = 5.5 Hz, 2H), 2.97 (t, *J* = 8.1 Hz, 2H), 2.62 (t, *J* = 8.0 Hz, 2H), 1.63–1.57 (m, 2H), 1.54–1.48 (m, 2H), 1.40–1.32 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 171.5, 141.5, 128.5, 128.5, 126.1, 50.6, 49.6, 37.6, 36.6, 35.9, 31.4, 25.7, 22.7, 22.7.

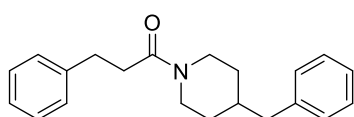


**3c** (CAS: 21924-11-8). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.42–7.34 (m, 3H), 7.31–7.26 (m, 3H), 7.24–7.17 (m, 3H), 3.27 (t, *J* = 7.7 Hz, 2H), 3.05 (t, *J* = 7.7 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.2, 141.3, 128.3, 128.3, 125.9, 46.4, 42.5, 35.0, 31.5,

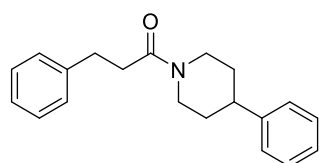
26.2, 25.4, 24.4.



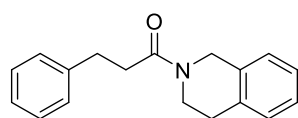
**3d** (CAS: 349643-98-7).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33–7.28 (m, 2H), 7.28–7.18 (m, 3H), 4.64–4.59 (m, 1H), 3.80–3.74 (m, 1H), 3.00–2.95 (m, 2H), 2.93–2.89 (m, 1H), 2.66–2.62 (m, 2H), 2.58–2.52 (m, 1H), 1.69–1.55 (m, 3H), 1.12–1.03 (m, 1H), 1.01–0.95 (m, 1H), 0.94 (d,  $J = 6.4$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.4, 141.5, 128.5, 128.5, 126.1, 45.9, 42.1, 35.2, 34.5, 33.8, 31.7, 31.1, 21.7.



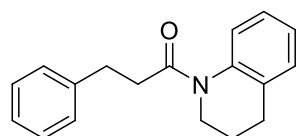
**3e** (CAS: 349419-32-5).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34–7.05 (m, 10H), 4.64–4.60 (m, 1H), 3.77–3.72 (m, 1H), 2.96 (t,  $J = 7.4$  Hz, 2H), 2.87–2.81 (m, 1H), 2.63–2.43 (m, 5H), 1.73–1.64 (m, 2H), 1.61–1.57 (m, 1H), 1.16–1.07 (m, 1H), 1.01–0.92 (m, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 141.5, 140.0, 129.1, 128.5, 128.3, 126.1, 126.1, 45.9, 43.0, 42.1, 38.2, 35.2, 32.4, 31.8, 31.7.



**3f** (CAS: 2183648-12-4).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36–7.32 (m, 4H), 7.30–7.22 (m, 4H), 7.22–7.16 (m, 2H), 4.87–4.83 (m, 1H), 3.97–3.92 (m, 1H), 3.16–2.96 (m, 3H), 2.81–2.59 (m, 4H), 1.96–1.81 (m, 2H), 1.66–1.58 (m, 1H), 1.51–1.42 (m, 1H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.6, 145.2, 141.4, 128.6, 128.5, 128.5, 126.8, 126.5, 126.2, 46.3, 42.8, 42.6, 35.2, 33.8, 32.9, 31.7.

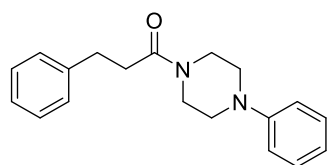


**3g** (CAS: 349431-73-8).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ) (amide rotamers 1.3:1)  $\delta$  7.35–7.06 (m, 9H), 4.78 (s, 1.12H), 4.57 (s, 0.87H), 3.87 (t,  $J = 6.0$  Hz, 0.88H), 3.63 (t,  $J = 5.9$  Hz, 1.12H), 3.08–3.02 (m, 2H), 2.89–2.83 (m, 2H), 2.79–2.71 (m, 2H).  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ , 60 °C)  $\delta$  7.28–7.24 (m, 4H), 7.20–7.15 (m, 5H), 4.62 (s, 2H), 3.75–3.67 (brs, 2H), 2.89 (t,  $J = 7.7$  Hz, 2H), 2.80 (brs, 2H), 2.72 (t,  $J = 7.7$  Hz, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ ) (mixture of rotamers, all peaks listed)  $\delta$  171.2, 171.1, 141.4, 141.4, 135.1, 134.1, 133.6, 132.6, 129.0, 128.6, 128.5, 128.5, 128.5, 128.3, 126.9, 126.7, 126.6, 126.6, 126.3, 126.2, 126.2, 126.1, 47.3, 44.3, 43.2, 39.7, 35.83, 35.6, 31.5, 31.4, 29.5, 28.6.

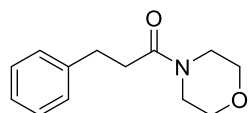


**3h** (CAS: 349644-04-8).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53–6.87 (m, 9H), 3.79 (t,  $J = 6.6$  Hz, 2H), 3.04 (t,  $J = 7.7$  Hz, 2H), 2.88–2.85 (m, 2H), 2.62 (t,  $J = 7.1$  Hz, 2H), 1.91–1.85 (m, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  172.0,

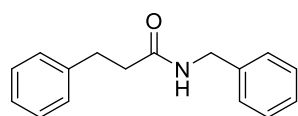
141.1, 139.1, 128.5, 128.5, 128.4, 126.1, 126.1, 125.3, 124.7, 42.9, 36.2, 32.1, 26.7, 24.1.



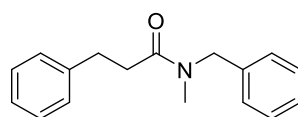
**3i** (CAS: 303066-54-8).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36–7.20 (m, 7H), 7.02–6.82 (m, 3H), 3.81 (t,  $J = 5.3$  Hz, 2H), 3.56 (t,  $J = 5.3$  Hz, 2H), 3.20–3.11 (m, 2H), 3.11–2.98 (m, 4H), 2.78–2.62 (m, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.7, 151.0, 141.2, 129.3, 128.6, 128.5, 126.3, 120.6, 116.7, 49.6, 49.4, 45.5, 41.6, 35.1, 31.6.



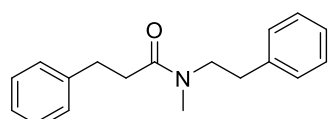
**3j** (CAS: 17077-46-2).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31–7.27 (m, 2H), 7.25–7.15 (m, 3H), 3.64–3.61 (m, 4H), 3.54–3.48 (m, 2H), 3.39–3.32 (m, 2H), 3.02–2.94 (m, 2H), 2.63–2.60 (m, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.9, 141.1, 128.6, 128.5, 126.3, 66.9, 66.5, 46.0, 42.0, 34.8, 31.5.



**3k** (CAS: 10264-10-5).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35–7.26 (m, 5H), 7.26–7.19 (m, 3H), 7.19–7.13 (m, 2H), 5.71 (s, 1H), 4.42 (d,  $J = 5.7$  Hz, 2H), 3.02 (t,  $J = 7.6$  Hz, 2H), 2.54 (t,  $J = 7.6$  Hz, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  171.9, 140.8, 138.2, 128.7, 128.6, 128.4, 127.8, 127.5, 126.3, 43.6, 38.5, 31.7.

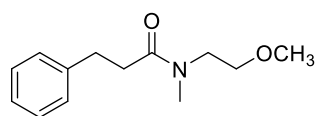


**3l** (CAS: 61751-42-6).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ) (amide rotamers 1.4:1)  $\delta$  7.38–7.19 (m, 9H), 7.18–7.06 (m, 1H), 4.63 (s, 1.15H), 4.49 (s, 0.84H), 3.10–3.01 (m, 2H), 2.98 (s, 1.15H), 2.88 (s, 1.81H), 2.73–2.69 (m, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ ) (mixture of rotamers, all peaks listed)  $\delta$  172.6, 172.3, 141.4, 141.3, 137.4, 136.6, 128.9, 128.6, 128.5, 128.5, 128.1, 127.6, 127.3, 126.3, 126.2, 126.1, 53.3, 50.9, 35.4, 35.0, 34.8, 34.0, 31.6, 31.4.



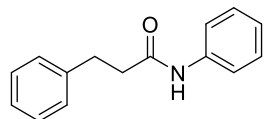
**3m** (CAS: 152328-83-1).  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ , 60 °C)  $\delta$  7.32–7.10 (m, 10H), 3.50 (t,  $J = 7.4$  Hz, 2H), 2.91–2.81 (m, 4H), 2.80–2.74 (m, 2H), 2.70 (t,  $J = 7.6$  Hz, 1H), 2.57 (t,  $J = 7.7$  Hz, 1H), 2.37 (t,  $J = 7.8$  Hz, 1H).

$^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ ) (mixture of rotamers, all peaks listed)  $\delta$  172.1, 171.9, 141.5, 139.2, 138.2, 128.9, 128.8, 128.5, 128.5, 128.4, 126.8, 126.3, 126.1, 126.0, 51.5, 50.1, 36.1, 35.5, 34.8, 34.7, 33.8, 33.6, 31.4, 31.3.

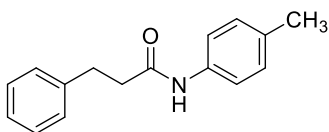


**3n**: Yellow oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ ) (amide rotamers 1.6:1)  $\delta$  7.33–7.20 (m, 5H), 3.59–3.53 (m, 2H), 3.44 (s, 2H), 3.36 (s, 1.81H), 3.33 (s, 1.12H), 3.05–2.94 (m, 5H), 2.71–2.62 (m, 2H).  $^1\text{H NMR}$  (500 MHz,  $\text{DMSO}-d_6$ , 60 °C)  $\delta$  7.28–7.20 (m, 4H), 7.20–7.15 (m, 1H), 3.46–3.40 (m, 4H), 3.17 (s, 3H), 3.17 (s, 3H),

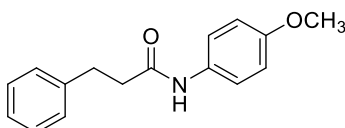
2.96 (s, 2H), 2.83 (t,  $J = 7.7$  Hz, 3H), 2.64-2.58 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ ) (mixture of rotamers, all peaks listed)  $\delta$  172.6, 172.3, 141.7, 141.5, 128.5, 128.4, 126.1, 126.0, 71.1, 70.2, 59.1, 58.8, 49.6, 47.8, 36.9, 35.5, 34.9, 34.0, 31.5, 31.3. HRMS (ESI): Calculated for  $\text{C}_{13}\text{H}_{19}\text{NO}_2$   $[\text{M}+\text{Na}]^+$ : 244.1318, found: 244.1308.



**3o** (CAS: 3271-81-6).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (d,  $J = 8.0$  Hz, 2H), 7.32-7.28 (m, 4H), 7.26-7.19 (m, 3H), 7.09 (t,  $J = 7.4$  Hz, 1H), 7.00 (s, 1H), 3.06 (t,  $J = 7.6$  Hz, 2H), 2.66 (t,  $J = 7.6$  Hz, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.3, 140.6, 137.7, 129.0, 128.7, 128.4, 126.4, 124.3, 119.9, 39.6, 31.6.

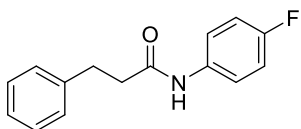


**3p** (CAS: 71231-25-9).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (t,  $J = 7.3$  Hz, 4H), 7.24-7.20 (m, 3H), 7.09 (d,  $J = 8.2$  Hz, 2H), 7.02 (s, 1H), 3.04 (t,  $J = 7.6$  Hz, 2H), 2.64 (t,  $J = 7.6$  Hz, 2H), 2.30 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.3, 140.7, 135.2, 134.0, 129.5, 128.7, 128.4, 126.4, 120.1, 39.5, 31.6, 20.9.



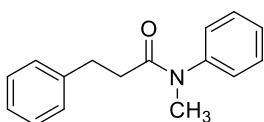
**3q** (CAS: 97754-31-9).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35-7.27 (m, 4H), 7.25-7.19 (m, 3H), 7.01 (s, 1H), 6.85-6.79 (m, 2H), 3.77 (s, 3H), 3.04 (t,  $J = 7.6$  Hz, 2H), 2.63 (t,  $J = 7.7$  Hz, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )

$\delta$  170.3, 156.4, 140.8, 128.6, 128.4, 126.4, 122.0, 114.1, 55.5, 39.3, 31.7.



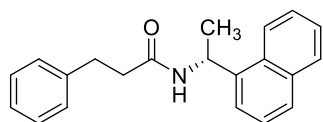
**3r** (CAS: 5298-86-2).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-737 (m, 2H), 7.33-7.28 (m, 3H), 7.27-7.23 (m, 3H), 7.00-6.97 (m, 2H), 3.06 (t,  $J = 7.6$  Hz, 2H), 2.66 (t,  $J = 7.6$  Hz, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.5, 159.4 (d,  $J =$

243.2 Hz), 140.6, 133.7, 128.7, 128.4, 126.5, 121.9 (d,  $J = 8.1$  Hz), 115.6 (d,  $J = 22.3$  Hz), 39.3, 31.6.  $^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )  $\delta$  -118.0.

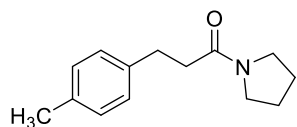


**3s** (CAS: 18859-20-6).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.41-7.33 (m, 2H), 7.30 (t,  $J = 7.5$  Hz, 1H), 7.22 (t,  $J = 7.4$  Hz, 2H), 7.16 (t,  $J = 7.4$  Hz, 1H), 7.06 (d,  $J = 7.5$  Hz, 2H), 7.02 (d,  $J = 7.6$  Hz, 2H), 3.25 (s, 3H), 2.91 (t,  $J = 7.9$  Hz, 2H), 2.37 (t,

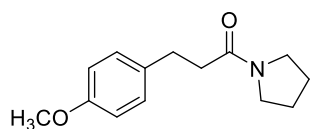
$J = 7.9$  Hz, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  172.2, 144.0, 141.3, 129.8, 128.4, 128.4, 127.8, 127.3, 126.0, 37.4, 36.0, 31.8.



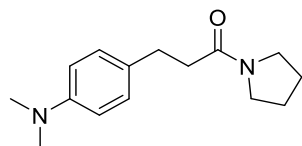
**3t:** White solid. Melting point: 166–167 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.11–8.06 (m, 1H), 7.92–7.86 (m, 1H), 7.84–7.79 (m, 1H), 7.58–7.50 (m, 2H), 7.46–7.38 (m, 2H), 7.28–7.23 (m, 2H), 7.23–7.12 (m, 3H), 5.98–5.88 (m, 1H), 5.60 (d, *J* = 8.3 Hz, 1H), 3.07–2.91 (m, 2H), 2.48 (t, *J* = 7.5 Hz, 2H), 1.61 (d, *J* = 6.7 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.9, 140.8, 138.2, 133.9, 131.1, 128.8, 128.5, 128.5, 128.4, 128.4, 126.6, 126.2, 125.9, 125.2, 123.5, 122.5, 44.6, 38.5, 31.7, 20.6. HRMS (ESI): Calculated for C<sub>21</sub>H<sub>21</sub>NO [M+H]<sup>+</sup>: 304.1703, found: 304.1696.



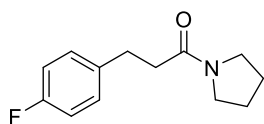
**4a** (CAS: 932163-41-2). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.15–7.09 (m, 4H), 3.48 (t, *J* = 6.8 Hz, 2H), 3.31 (t, *J* = 6.7 Hz, 2H), 2.99–2.92 (m, 2H), 2.59–2.52 (m, 2H), 2.33 (s, 3H), 1.94–1.87 (m, 2H), 1.85–1.80 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.9, 138.5, 135.5, 129.1, 128.3, 46.6, 45.6, 37.0, 30.8, 26.1, 24.4, 21.0.



**4b** (CAS: 56004-07-0). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.14 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.3 Hz, 2H), 3.78 (s, 3H), 3.46 (t, *J* = 6.8 Hz, 2H), 3.29 (t, *J* = 6.7 Hz, 2H), 2.99–2.85 (m, 2H), 2.59–2.47 (m, 2H), 1.91–1.78 (m, 4H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.9, 133.6, 129.4, 113.8, 55.3, 46.6, 45.6, 37.0, 30.3, 26.1, 24.4.

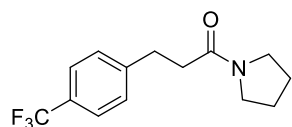


**4c** (CAS: 1379169-29-5). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.10 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 3.46 (t, *J* = 6.8 Hz, 2H), 3.30 (t, *J* = 6.7 Hz, 2H), 2.91 (s, 6H), 2.91–2.87 (m, 2H), 2.55–2.48 (m, 2H), 1.89–1.85 (m, 2H), 1.84–1.79 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 171.2, 129.7, 129.1, 113.1, 46.6, 45.6, 40.9, 37.3, 30.3, 26.1, 24.4.

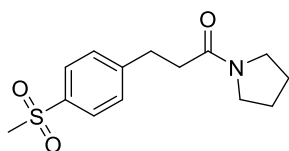


**4d** (CAS: 1090435-97-4). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.21–7.15 (m, 2H), 6.98–6.92 (m, 2H), 3.45 (t, *J* = 6.8 Hz, 2H), 3.29 (t, *J* = 6.7 Hz, 2H), 2.95 (t, *J* = 7.8 Hz, 2H), 2.53 (t, *J* = 7.7 Hz, 2H), 1.92–1.86 (m, 2H), 1.84–1.77 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.5, 161.4 (d, *J* = 243.6 Hz), 137.2 (d, *J* = 3.0 Hz), 129.9 (d, *J* = 7.5 Hz), 115.2 (d, *J* = 21.1 Hz), 46.6, 45.6, 36.7, 30.3, 26.1, 24.4. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -117.4.

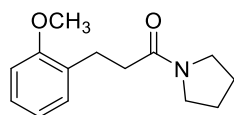




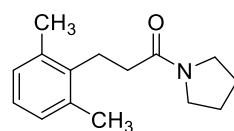
**4e** (CAS: 2322107-62-8). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.53 (d, *J* = 7.9 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 3.47 (t, *J* = 6.8 Hz, 2H), 3.32 (t, *J* = 6.7 Hz, 2H), 3.05 (t, *J* = 7.7 Hz, 2H), 2.58 (t, *J* = 7.7 Hz, 2H), 1.94–1.88 (m, 2H), 1.86–1.79 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.0, 145.7, 128.8, 128.4 (q, *J* = 32.7 Hz), 125.2 (q, *J* = 3.7 Hz), 124.2 (q, *J* = 274.5 Hz), 46.4, 45.6, 36.0, 30.7, 26.0, 24.3. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -62.4.



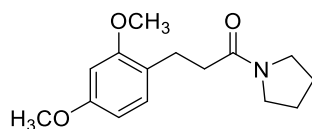
**4f** (CAS: 2326249-72-1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.85 (d, *J* = 7.9 Hz, 2H), 7.44 (d, *J* = 7.9 Hz, 2H), 3.46 (t, *J* = 6.8 Hz, 2H), 3.33 (t, *J* = 6.7 Hz, 2H), 3.09 (t, *J* = 7.5 Hz, 2H), 3.04 (s, 3H), 2.60 (t, *J* = 7.5 Hz, 2H), 1.96–1.89 (m, *J* = 6.7 Hz, 2H), 1.87–1.80 (m, *J* = 6.7 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 169.8, 148.3, 138.3, 129.5, 127.6, 46.6, 45.8, 44.6, 35.8, 30.8, 26.1, 24.4.



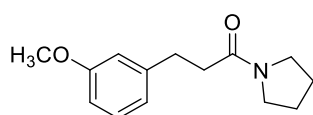
**4g** (CAS: 1458527-03-1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.21–7.16 (m, 2H), 6.91–6.81 (m, 2H), 3.82 (s, 3H), 3.46 (t, *J* = 6.8 Hz, 2H), 3.32 (t, *J* = 6.7 Hz, 2H), 3.01–2.91 (m, 2H), 2.59–2.46 (m, 2H), 1.91–1.86 (m, 2H), 1.85–1.79 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 171.4, 157.5, 130.2, 129.8, 127.4, 120.5, 110.2, 55.2, 46.5, 45.6, 35.1, 26.3, 26.1, 24.4.



**4h**: Yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.04–6.97 (m, 3H), 3.49 (t, *J* = 6.8 Hz, 2H), 3.29 (t, *J* = 6.7 Hz, 2H), 3.04–2.98 (m, 2H), 2.43–2.38 (m, 2H), 2.34 (s, 6H), 1.94–1.82 (m, 4H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.8, 138.0, 136.1, 128.1, 125.8, 46.4, 45.6, 33.7, 26.0, 24.8, 24.3, 19.7. HRMS (ESI): Calculated for C<sub>15</sub>H<sub>21</sub>NO [M+H]<sup>+</sup>: 232.1706, found: 232.1696.

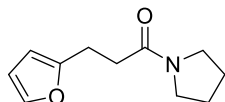


**4i**: Yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.08 (d, *J* = 8.2 Hz, 1H), 6.44 (d, *J* = 2.3 Hz, 1H), 6.41 (dd, *J* = 8.3, 2.4 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 3H), 3.46 (t, *J* = 6.8 Hz, 2H), 3.32 (t, *J* = 6.7 Hz, 2H), 2.95–2.84 (m, 2H), 2.55–2.45 (m, 2H), 1.91–1.84 (m, 4H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 171.5, 159.4, 158.4, 130.4, 122.2, 103.8, 98.5, 55.4, 55.2, 46.5, 45.6, 35.4, 26.1, 25.7, 24.4. HRMS (ESI): Calculated for C<sub>15</sub>H<sub>21</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 264.1600, found: 264.1594.

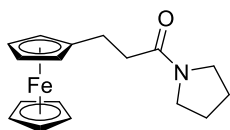


**4j** (CAS: 131656-86-5). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.21 (t, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.79 (s, 1H), 6.75 (dd, *J* = 8.2, 2.6 Hz, 1H),

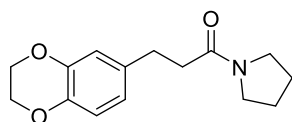
3.80 (s, 3H), 3.47 (t,  $J = 6.8$  Hz, 2H), 3.31 (t,  $J = 6.7$  Hz, 2H), 2.97 (t,  $J = 8.0$  Hz, 2H), 2.57 (t,  $J = 7.9$  Hz, 2H), 1.93-1.80 (m, 4H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.7, 159.6, 143.1, 129.3, 120.7, 114.1, 111.3, 55.1, 46.5, 45.6, 36.6, 31.2, 26.0, 24.3.



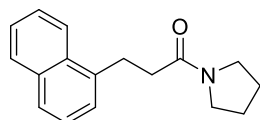
**4k** (CAS: 154011-61-7).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.32 – 7.28 (m, 1H), 6.29-6.27(m, 1H), 6.05-6.01 (m, 1H), 3.47 (t,  $J = 6.9$  Hz, 2H), 3.36 (t,  $J = 6.8$  Hz, 2H), 3.00(t,  $J = 7.7$  Hz, 2H), 2.60(t,  $J = 7.7$  Hz, 2H), 1.96-1.90 (m, 2H), 1.87-1.81(m, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.2, 155.1, 141.90, 110.2, 105.2, 46.5, 45.7, 33.2, 26.1, 24.4, 23.5.



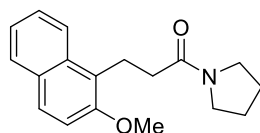
**4l**: Yellow solid. Melting point: 78–79 °C.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  4.09 (s, 5H), 4.07 (s, 2H), 4.03 (s, 2H), 3.44 (t,  $J = 6.8$  Hz, 2H), 3.29 (t,  $J = 6.7$  Hz, 2H), 2.68 (t,  $J = 7.9$  Hz, 2H), 2.43 (t,  $J = 7.8$  Hz, 2H), 1.91-1.84 (m, 2H), 1.83-1.79 (m, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.9, 88.0, 68.4, 68.0, 67.2, 46.5, 45.5, 36.5, 26.0, 25.0, 24.3. HRMS (ESI): Calculated for  $\text{C}_{17}\text{H}_{21}\text{FeNO}$   $[\text{M}+\text{Na}]^+$ : 334.0872, found: 334.0865.



**4m** (CAS: 1088196-64-8).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  6.76 (d,  $J = 8.2$  Hz, 1H), 6.71 (s, 1H), 6.68 (d,  $J = 8.2$  Hz, 1H), 4.22 (s, 4H), 3.45 (t,  $J = 6.9$  Hz, 2H), 3.30 (t,  $J = 6.7$  Hz, 2H), 2.86 (t,  $J = 8.0$  Hz, 2H), 2.50 (t,  $J = 8.0$  Hz, 2H), 1.91-1.80(m, 4H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.8, 143.3, 141.8, 134.8, 121.3, 117.1, 117.0, 64.4, 64.3, 46.6, 45.7, 36.9, 30.4, 26.1, 24.4.

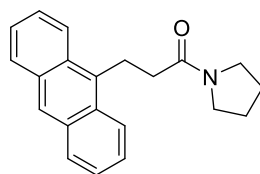


**4n** (CAS: 2363125-90-8).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.07 (d,  $J = 8.4$  Hz, 1H), 7.85 (d,  $J = 8.1$  Hz, 1H), 7.79 – 7.67 (m, 1H), 7.52-7.45 (m, 2H), 7.40-7.36(m, 2H), 3.46 (t,  $J = 7.6$  Hz, 4H), 3.26 – 3.04 (m, 2H), 2.68 (t,  $J = 8.1$  Hz, 2H), 1.80-1.75 (m, 4H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.9, 137.7, 131.7, 128.8, 126.9, 126.2, 126.0, 125.7, 125.6, 123.7, 46.5, 45.7, 36.0, 28.3, 26.0, 24.4.



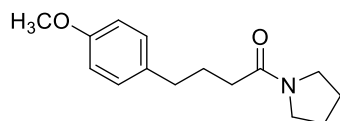
**4o**: Colorless oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (d,  $J = 8.6$  Hz, 1H), 7.80 (d,  $J = 8.2$  Hz, 1H), 7.76 (d,  $J = 8.9$  Hz, 1H), 7.50 (t,  $J = 7.7$  Hz, 1H), 7.35 (t,  $J = 7.5$  Hz, 1H), 7.30 – 7.27 (m, 1H), 3.97 (s, 3H), 3.50-3.44 (m, 4H), 3.25 (t,  $J = 6.4$  Hz, 2H), 2.57 (t,  $J = 8.2$  Hz, 2H), 1.86 – 1.77 (m, 4H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  171.4, 154.3, 132.7, 129.1, 128.4, 127.8, 126.4, 123.2, 123.0, 122.6, 113.1, 56.4, 46.4, 45.6, 34.8, 26.0, 24.3, 20.6. HRMS (ESI):

Calculated for  $C_{18}H_{21}NO_2$   $[M+Na]^+$ : 306.1474, found: 306.1465.



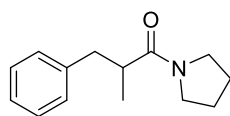
**4p**: Colorless oil.  $^1H$ NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.36 (s, 1H), 8.31 (d,  $J = 8.8$  Hz, 2H), 8.01 (d,  $J = 8.3$  Hz, 2H), 7.55-7.50 (m, 2H), 7.50 – 7.43 (m, 2H), 4.07 – 3.97 (m, 2H), 3.47 (t,  $J = 6.6$  Hz, 2H), 3.02 (t,  $J = 6.4$  Hz, 2H), 2.76 – 2.69 (m,

2H), 1.77 – 1.68 (m, 4H).  $^{13}C$ NMR (126 MHz,  $CDCl_3$ )  $\delta$  170.9, 133.7, 131.6, 129.6, 129.2, 126.1, 125.8, 125.0, 124.2, 46.4, 45.8, 35.79, 25.9, 24.3, 23.2. HRMS (ESI): Calculated for  $C_{21}H_{21}NO$   $[M+H]^+$ : 304.1705, found: 304.1696.



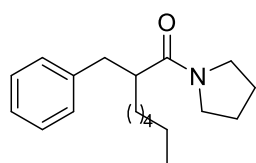
**4q** (CAS: 2340760-34-9).  $^1H$ NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.12 (d,  $J = 8.6$  Hz, 2H), 6.84 (d,  $J = 8.6$  Hz, 2H), 3.80 (s, 3H), 3.47 (t,  $J = 6.9$  Hz, 2H), 3.34 (t,  $J = 6.8$  Hz, 2H), 2.64 (t,  $J = 7.5$  Hz, 2H), 2.26 (t,  $J = 7.5$  Hz, 2H),

2.01-1.90 (m, 4H), 1.88-1.81 (m, 2H).  $^{13}C$ NMR (126 MHz,  $CDCl_3$ )  $\delta$  171.4, 157.8, 133.9, 129.4, 113.7, 55.3, 46.5, 45.6, 34.4, 33.9, 26.5, 26.1, 24.4.



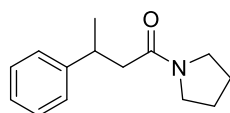
**4r** (CAS: 200283-03-0).  $^1H$ NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.23 (t,  $J = 7.5$  Hz, 2H), 7.24 – 7.19 (m, 3H), 3.44 – 3.32 (m, 2H), 3.28-3.23(m, 1H), 2.98-2.89 (m, 2H), 2.78-2.73 (m, 1H), 2.62 (dd,  $J = 13.1, 6.4$  Hz, 1H), 1.80-1.61 (m, 4H), 1.14 (d,  $J = 6.7$  Hz,

3H).  $^{13}C$ NMR (126 MHz,  $CDCl_3$ )  $\delta$  174.2, 140.1, 128.9, 128.1, 126.0, 46.2, 45.5, 40.5, 40.4, 25.8, 24.1, 17.3.



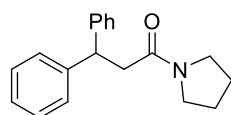
**4s**: Colorless oil.  $^1H$ NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.26 – 7.20 (m, 2H), 7.20 – 7.09 (m, 3H), 3.41 – 3.34 (m, 2H), 3.22 – 3.18 (m, 1H), 2.97 – 2.87 (m, 1H), 2.77 – 2.64 (m, 3H), 1.81 – 1.42 (m, 6H), 1.28-1.23 (m, 8H), 0.87 (t,  $J = 6.7$  Hz, 3H).

$^{13}C$ NMR (126 MHz,  $CDCl_3$ ) 140.3, 128.9, 128.2, 126.1, 46.8, 46.3, 45.4, 39.7, 33.0, 31.8, 29.4, 27.7, 25.9, 24.2, 22.6, 14.1. HRMS (ESI): Calculated for  $C_{25}H_{39}NO$   $[M+Na]^+$ : 392.2927, found: 392.2924.

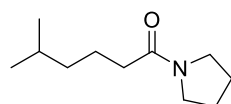


**4t** (CAS: 243466-37-7).  $^1H$ NMR (500 MHz,  $CDCl_3$ )  $\delta$  7.31 – 7.24 (m, 4H), 7.21-7.17 (m, 1H), 3.47 – 3.37 (m, 3H), 3.35 – 3.29 (m, 1H), 3.14-3.09 (m, 1H), 2.57 – 2.45 (m, 2H), 1.88 – 1.73 (m, 4H), 1.34 (d,  $J = 7.0$  Hz, 3H).  $^{13}C$ NMR (126 MHz,  $CDCl_3$ )

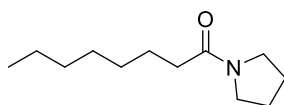
$\delta$  170.3, 146.6, 128.4, 126.9, 126.2, 46.7, 45.6, 43.6, 36.4, 26.0, 24.4, 21.4.



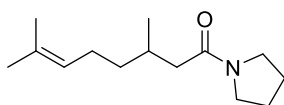
**4u** (CAS: 348607-78-3).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29-7.22 (m, 8H), 7.19-7.14 (m, 2H), 4.71 (t,  $J = 7.5$  Hz, 1H), 3.37 (t,  $J = 6.6$  Hz, 2H), 3.19 (t,  $J = 6.5$  Hz, 2H), 2.98 (d,  $J = 7.5$  Hz, 2H), 1.79-1.71 (m, 4H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  169.7, 144.3, 128.4, 127.9, 126.3, 47.0, 46.6, 45.6, 41.0, 26.0, 24.3.



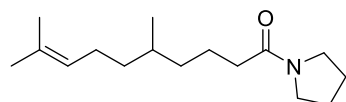
**4v** (CAS: 2134594-44-6).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.46 (t,  $J = 6.9$  Hz, 2H), 3.41 (t,  $J = 6.8$  Hz, 2H), 2.24 (t,  $J = 7.7$  Hz, 2H), 1.98-1.91 (m, 2H), 1.89-1.81 (m, 2H), 1.69-1.63 (m, 2H), 1.59-1.53 (m, 1H), 1.25-1.18 (m, 2H), 0.89 (d,  $J = 6.6$  Hz, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  171.9, 46.6, 45.6, 38.8, 35.1, 27.9, 26.1, 24.4, 22.8, 22.6.



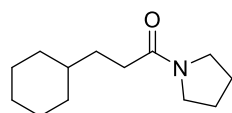
**4w** (CAS: 20299-80-3).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.46 (t,  $J = 6.9$  Hz, 2H), 3.41 (t,  $J = 6.8$  Hz, 2H), 2.25 (t,  $J = 7.7$  Hz, 2H), 1.97-1.92 (m, 2H), 1.87-1.81 (m, 2H), 1.68-1.61 (m, 2H), 1.33-1.27 (m, 8H), 0.88 (t,  $J = 6.6$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  171.9, 46.6, 45.6, 34.9, 31.7, 29.5, 29.1, 26.2, 25.0, 24.4, 22.63, 14.1.



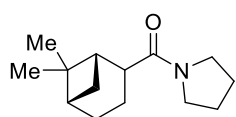
**4x** (CAS: 80016-69-9).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.09 (t,  $J = 7.3$  Hz, 1H), 3.45 (t,  $J = 6.9$  Hz, 2H), 3.40 (t,  $J = 6.8$  Hz, 2H), 2.29-2.22 (m, 1H), 2.09-1.91 (m, 6H), 1.87-1.80 (m, 2H), 1.66 (s, 3H), 1.58 (s, 3H), 1.41-1.35 (m, 1H), 1.26-1.15 (m, 1H), 0.94 (d,  $J = 6.0$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  2171.2, 131.2, 124.5, 46.7, 45.5, 42.1, 37.1, 29.8, 26.1, 25.6, 25.5, 24.4, 19.8, 17.6.



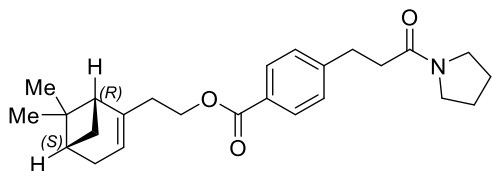
**4y**: Yellow oil.  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.08 (t,  $J = 7.2$  Hz, 1H), 3.45 (t,  $J = 6.9$  Hz, 2H), 3.40 (t,  $J = 6.8$  Hz, 2H), 2.27-2.20 (m, 2H), 1.98-1.89 (m, 4H), 1.86-1.82 (m, 2H), 1.66 (s, 3H), 1.59 (s, 3H), 1.47-1.28 (m, 4H), 1.28-1.21 (m, 1H), 1.19-1.09 (m, 2H), 0.87 (d,  $J = 6.6$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  171.7, 130.9, 124.7, 46.5, 45.6, 36.9, 36.7, 35.1, 32.2, 26.0, 25.6, 25.4, 24.3, 22.4, 19.4, 17.5. HRMS (ESI): Calculated for  $\text{C}_{16}\text{H}_{29}\text{NO}$   $[\text{M}+\text{H}]^+$ : 252.2330, found: 252.2322.



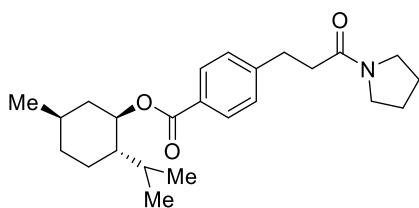
**4z** (CAS: 72299-21-9).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.45-3.37 (m, 4H), 2.24 (t,  $J = 8.0$ , 2H), 1.94-1.80 (m, 4H), 1.77-1.57 (m, 5H), 1.58-1.46 (m, 2H), 1.30-1.06 (m, 4H), 0.93-0.84 (m, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  172.2, 46.6, 45.6, 37.5, 33.2, 32.3, 28.9, 26.6, 26.3, 26.1, 25.9, 24.4.



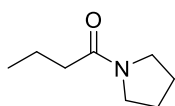
**4a'**: Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.75 – 3.16 (m, 4H), 2.97 (t, J = 8.7 Hz, 1H), 2.36 – 2.20 (m, 1H), 2.15-2.09 (m, 1H), 2.07 – 1.62 (m, 9H), 1.58-1.51 (m, 1H), 1.22 (s, 3H), 0.88 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 174.6, 46.0, 45.8, 43.8, 40.1, 39.7, 39.3, 26.6, 26.2, 24.2, 24.1, 23.8, 20.1, 16.4. HRMS (ESI): Calculated for C<sub>14</sub>H<sub>23</sub>NO [M+Na]<sup>+</sup>: 244.1680, found: 244.1672.



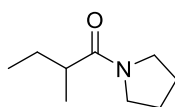
**4b'**: Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.95 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 5.37 (s, 1H), 4.35-4.29 (m, 2H), 3.47 (t, J = 6.8 Hz, 2H), 3.31 (t, J = 6.7 Hz, 2H), 3.05 (t, J = 7.8 Hz, 2H), 2.59 (t, J = 7.8 Hz, 2H), 2.44-2.36 (m, 3H), 2.29-2.19 (m, 2H), 2.15-2.09 (m, 2H), 1.93-1.80 (m, 4H), 1.28 (s, 3H), 1.18 (d, J = 8.6 Hz, 1H), 0.85 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.2, 166.5, 147.0, 144.3, 129.8, 128.5, 128.4, 118.9, 63.2, 46.6, 45.8, 45.7, 40.7, 38.0, 36.2, 36.1, 31.7, 31.4, 31.1, 26.3, 26.1, 24.4, 21.2. HRMS (ESI): Calculated for C<sub>25</sub>H<sub>33</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 396.2537, found: 396.2533.



**4c'**: Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.98 (d, J = 7.8 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 4.96-4.90 (m, 1H), 3.48 (t, J = 6.9 Hz, 2H), 3.33 (t, J = 6.7 Hz, 2H), 3.06 (t, J = 7.8 Hz, 2H), 2.59 (t, J = 7.8 Hz, 2H), 2.14-2.10 (m, 1H), 2.00-1.95 (m, 1H), 1.92-1.89 (m, 2H), 1.86-1.81 (m, 2H), 1.77 – 1.72 (m, 2H), 1.60-1.53 (m, 2H), 1.21 – 1.04 (m, 3H), 0.94 (d, J = 7.3 Hz, 3H), 0.93 (d, J = 7.3 Hz, 3H), 0.80 (d, J = 6.9 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.2, 166.1, 146.9, 129.8, 128.8, 128.5, 74.7, 47.3, 46.6, 45.7, 41.0, 36.2, 34.4, 31.5, 31.1, 26.5, 26.1, 24.4, 23.7, 22.1, 20.8, 16.6. HRMS (ESI): Calculated for C<sub>24</sub>H<sub>35</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 386.2699, found: 386.2690.

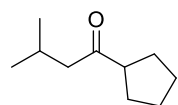


**6a** (CAS: 33527-93-4). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.47 (t, J = 6.9 Hz, 2H), 3.42 (t, J = 6.8 Hz, 2H), 2.25 (t, J = 7.6 Hz, 2H), 1.98–1.92 (m, 2H), 1.89–1.82 (m, 2H), 1.68 (h, J = 7.4 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 171.9, 46.7, 45.6, 36.8, 26.1, 24.4, 18.4, 14.0.

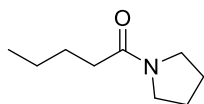


**6b** (CAS: 349422-58-8). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 3.51-3.43 (m, 4H), 2.49-2.41 (m, 1H), 1.98-1.92 (m, 2H), 1.89 – 1.82 (m, 2H), 1.74-1.66 (m, 1H), 1.46 – 1.37 (m, 1H), 1.11 (d, J = 6.8 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR δ 175.3, 46.5, 45.7, 39.6, 27.0,

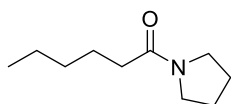
26.2, 24.3, 16.9, 12.1.



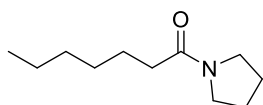
**6c** (CAS: 60026-17-7).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.47 (t,  $J = 6.9$  Hz, 2H), 3.42 (t,  $J = 6.8$  Hz, 2H), 2.22–2.14 (m, 3H), 1.98–1.91 (m, 2H), 1.89–1.82 (m, 2H), 0.97 (d,  $J = 6.2$  Hz, 6H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  171.3, 46.8, 45.5, 43.7, 26.1, 25.5, 24.4, 22.7.



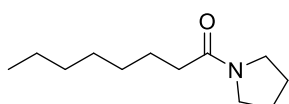
**6d** (CAS: 4419-57-2).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.46 (t,  $J = 6.9$  Hz, 2H), 3.42 (t,  $J = 6.8$  Hz, 2H), 2.29–2.23 (m, 2H), 1.98–1.92 (m, 2H), 1.88–1.81 (m, 2H), 1.66–1.60 (m, 2H), 1.41–1.33 (m, 2H), 0.93 (t,  $J = 7.3$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  172.0, 46.6, 45.6, 34.6, 27.1, 26.1, 24.4, 22.6, 13.9.



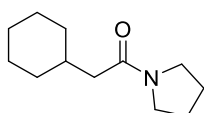
**6e** (CAS: 3389-56-8).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.46 (t,  $J = 6.9$  Hz, 2H), 3.41 (t,  $J = 6.8$  Hz, 2H), 2.30–2.21 (m, 2H), 1.97–1.92 (m, 2H), 1.88–1.82 (m, 2H), 1.69–1.62 (m, 2H), 1.37–1.30 (m, 4H), 0.90 (t,  $J = 6.9$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  171.9, 46.6, 45.6, 34.8, 31.7, 26.1, 24.6, 24.4, 22.5, 14.0.



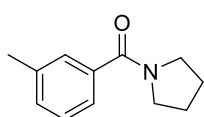
**6f** (CAS: 70974-42-4).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.44 (t,  $J = 6.9$  Hz, 2H), 3.40 (t,  $J = 6.8$  Hz, 2H), 2.26–2.21 (m, 2H), 1.96–1.90 (m, 2H), 1.86–1.80 (m, 2H), 1.65–1.59 (m, 2H), 1.35–1.26 (m, 6H), 0.86 (t,  $J = 6.7$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  171.9, 46.6, 45.6, 34.8, 31.6, 29.2, 26.1, 24.9, 24.4, 22.5, 14.0.



**6g** (CAS: 20299-80-3).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.46 (t,  $J = 7.0$  Hz, 2H), 3.41 (t,  $J = 6.8$  Hz, 2H), 2.25 (t,  $J = 7.7$  Hz, 2H), 1.98–1.91 (m, 2H), 1.89–1.81 (m, 2H), 1.68–1.61 (m, 2H), 1.34–1.25 (m, 8H), 0.88 (t,  $J = 6.7$  Hz, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  172.0, 46.6, 45.6, 34.9, 31.7, 29.5, 29.1, 26.1, 25.0, 24.4, 22.6, 14.1.

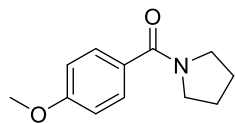


**6h** (CAS: 72299-06-0).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  3.46 (t,  $J = 6.9$  Hz, 2H), 3.42 (t,  $J = 6.7$  Hz, 2H), 2.14 (d,  $J = 6.8$  Hz, 2H), 1.97–1.90 (m, 2H), 1.87–1.81 (m, 3H), 1.78–1.73 (m, 2H), 1.70–1.61 (m, 3H), 1.31–1.26 (m, 2H), 1.17–1.08 (m, 1H), 0.98–0.90 (m, 2H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  171.4, 46.9, 45.6, 42.5, 34.9, 33.4, 26.3, 26.2, 26.1, 24.4.



**6i** (CAS: 164918-75-6).  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36–7.20 (m, 4H), 3.65 (t,  $J = 7.0$  Hz, 2H), 3.42 (t,  $J = 6.7$  Hz, 2H), 2.38 (s, 3H), 1.99–1.93 (m, 2H), 1.90–1.84 (m,

2H).  $^{13}\text{C}$ NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  170.0, 138.1, 137.2, 130.5, 128.1, 127.7, 124.0, 49.6, 46.1, 26.4, 24.5, 21.4.



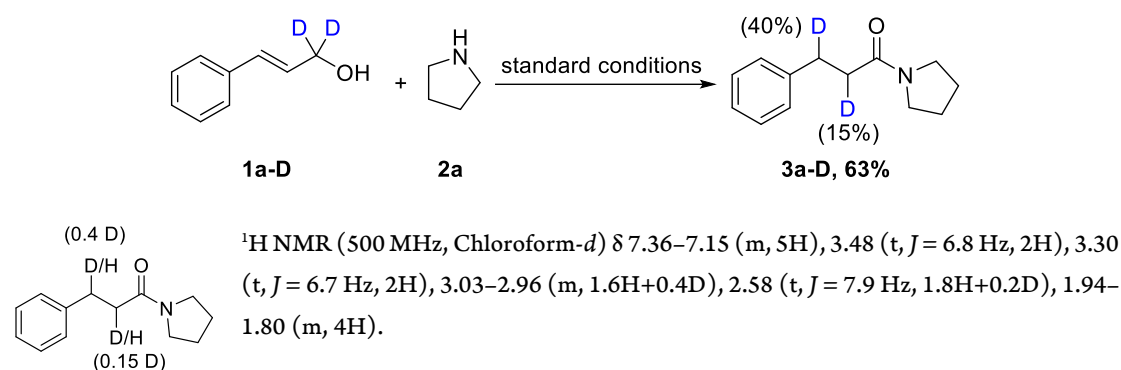
6j (CAS: 69838-98-8).  $^1\text{H}$ NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56–7.49 (m, 2H), 6.94–6.88

(m, 2H), 3.84 (s, 3H), 3.64 (t,  $J = 7.0$  Hz, 2H), 3.49 (t,  $J = 6.6$  Hz, 2H), 1.98–1.92

(m, 2H), 1.91–1.86 (m, 2H).  $^{13}\text{C}$ NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  169.5, 160.8, 129.4,

129.2, 113.4, 55.3, 49.8, 46.4, 26.5, 24.5.

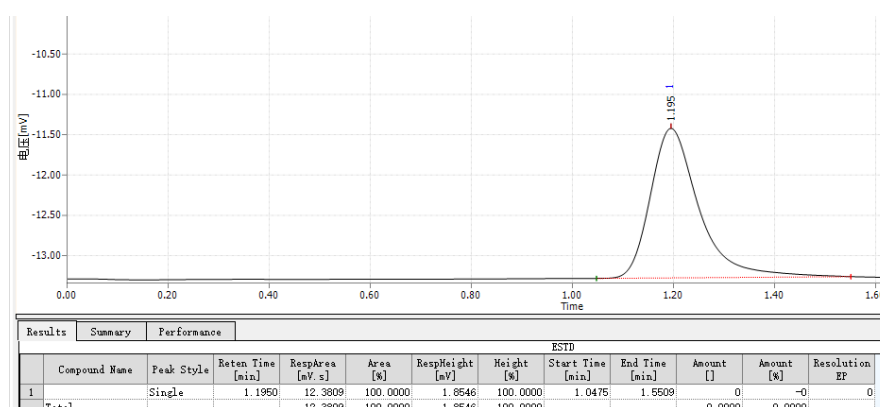
## 6. Mechanism studies



In order to determine the source and transfer route of hydrogen during the reaction, an isotopic labeling experiment was carried out. When the deuterated cinnamyl alcohol **1a-D** was reacted with pyrrolidine **2a** under standard reaction conditions, the deuteration was found in the corresponding product **3a-D**, and the deuterated amide was obtained with an isolated yield of 63%. The  $^1\text{H NMR}$  analysis of **3a-D** indicated that deuterium hydrogen was inserted at C1 and C2 respectively. These studies showed that the hydrogen atoms on methylene of allylic alcohol participate in the reduction of unsaturated double bond.

In addition, hydrogen gas signal was detected by gas chromatography after the end of the reaction (Figure S1), suggesting a dehydrogenative process involved in this cross-coupling of alcohols and amines.

Figure S1. Monitoring of hydrogen gas signal.

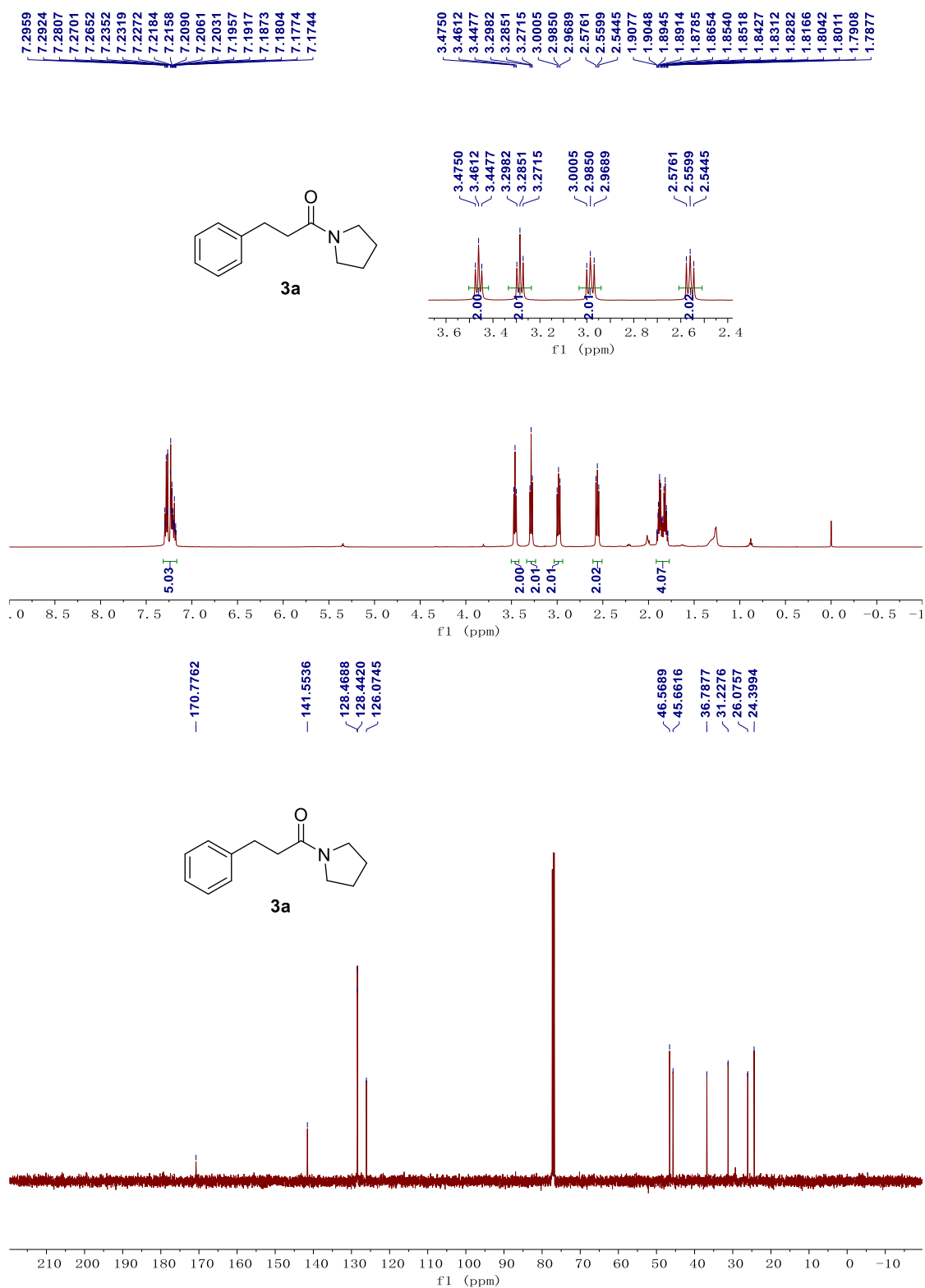


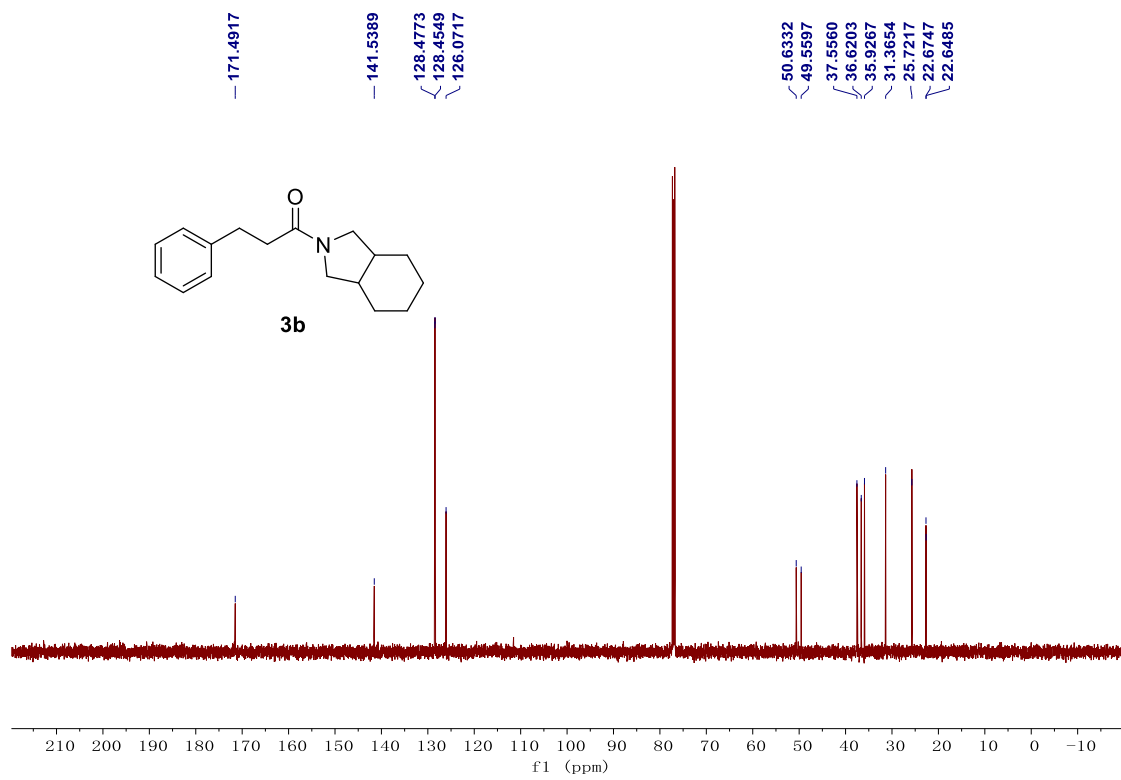
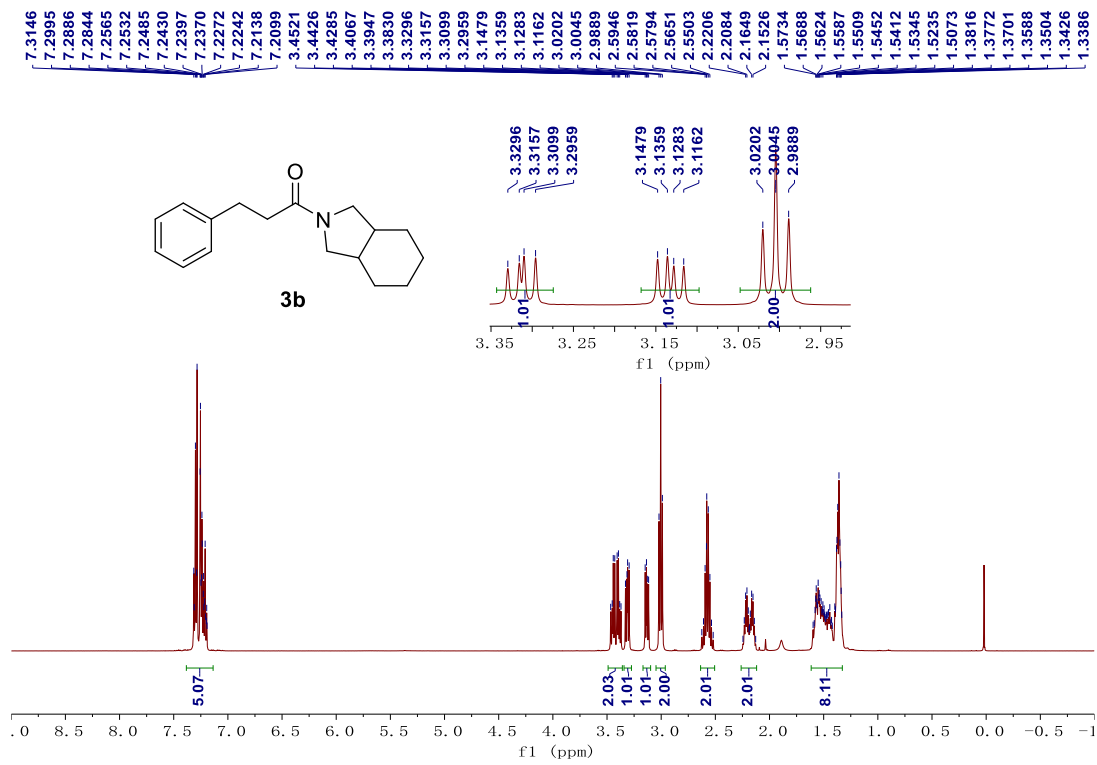
## 7. Supplementary References

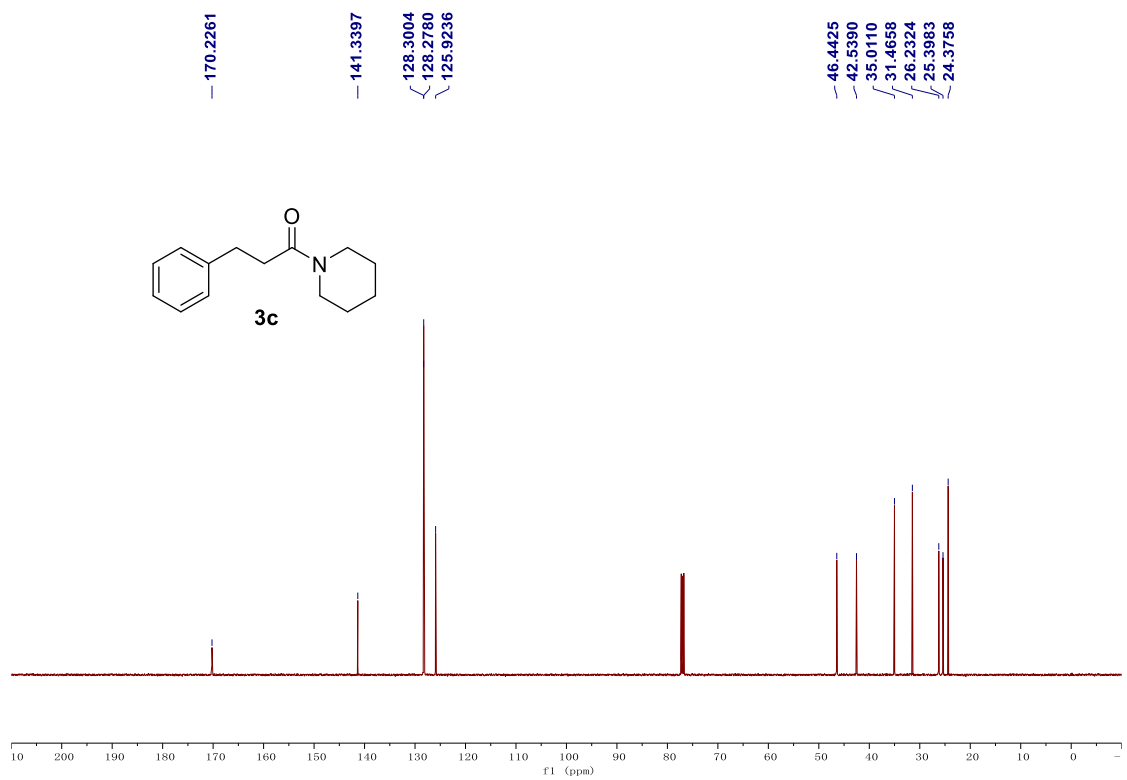
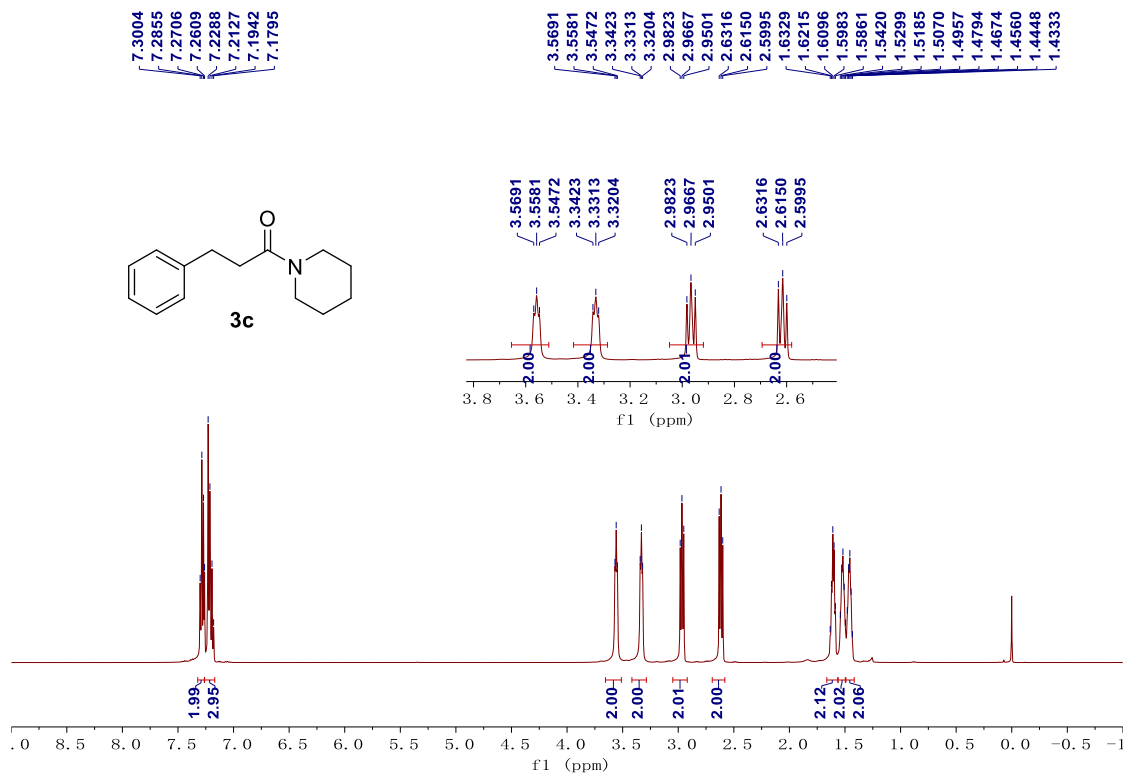
- [1] (a) Wang, Y.; Shao, Z.; Zhang, K.; Liu, Q. Manganese-Catalyzed Dual-Deoxygenative Coupling of Primary Alcohols with 2-Arylethanol. *Angew. Chem. Int. Ed.* **2018**, *57*, 15143-15147. (b) Peng, X.; Xu, J.; Li, T.; Chi, Y. R.; Jin, Z. Chemo-selective cross reaction of two enals via carbene-catalyzed dual activation. *Chem. Sci.* **2020**, *11*, 12533-12539. (c) Wang, X.; Liu, F.; Yan, Z.; Qiang, Q.; Huang, W.; Rong, Z.-Q. Redox-Neutral Nickel-Catalyzed Cross-Coupling Reactions of (Homo)allylic Alcohols and Aryltriflates. *ACS Catal.* **2021**, *11*, 7319-7326.



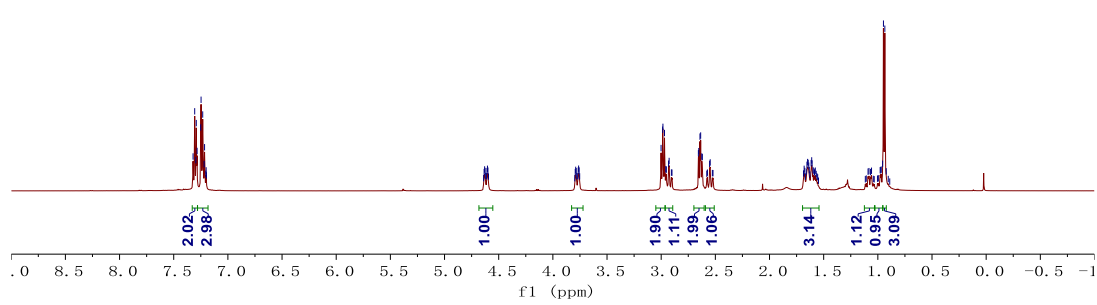
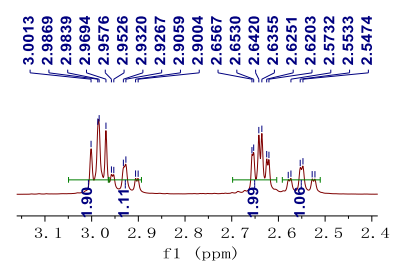
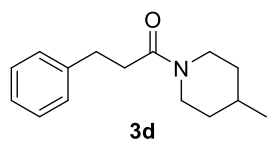
## 8. <sup>1</sup>H NMR, <sup>13</sup>C NMR, and <sup>19</sup>F NMR spectra



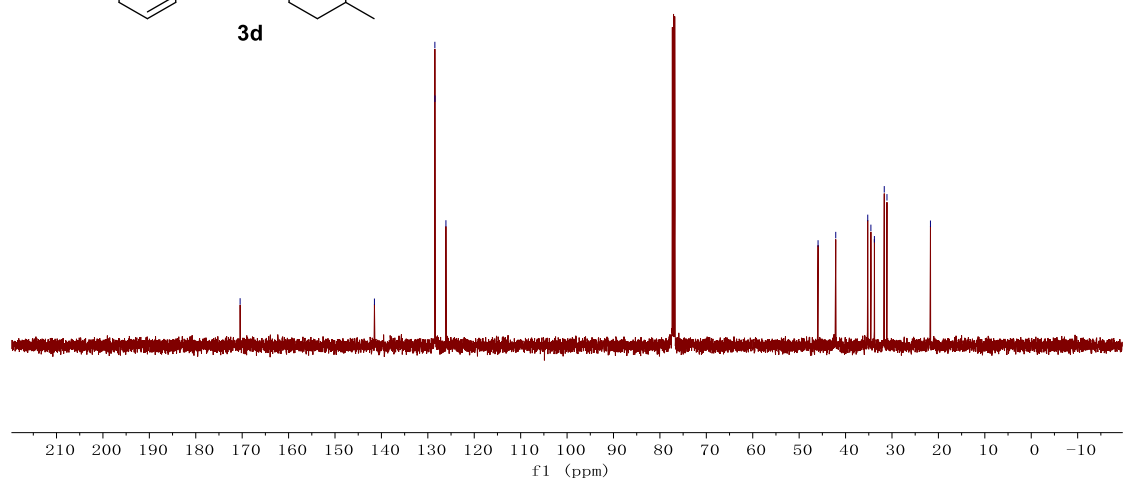
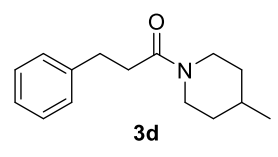




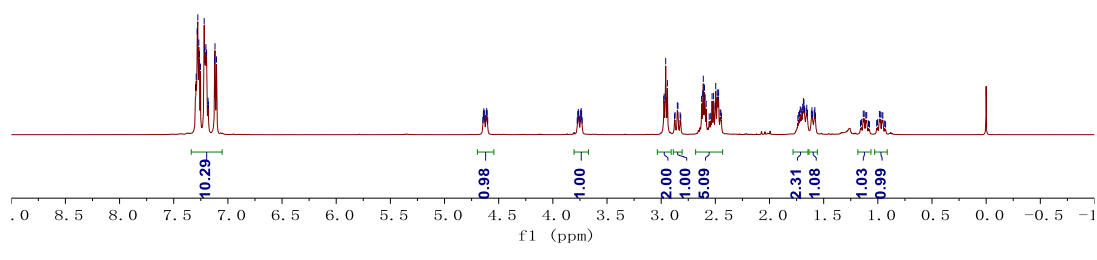
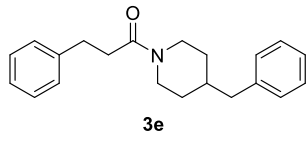
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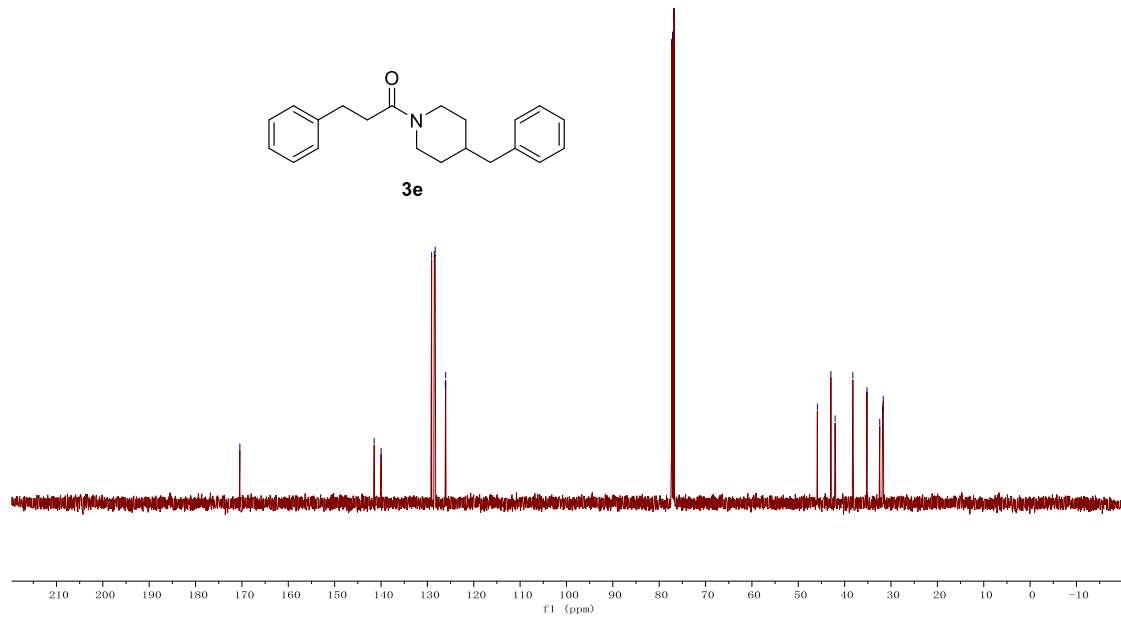
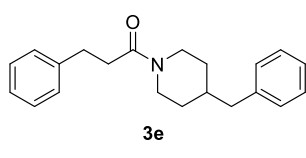
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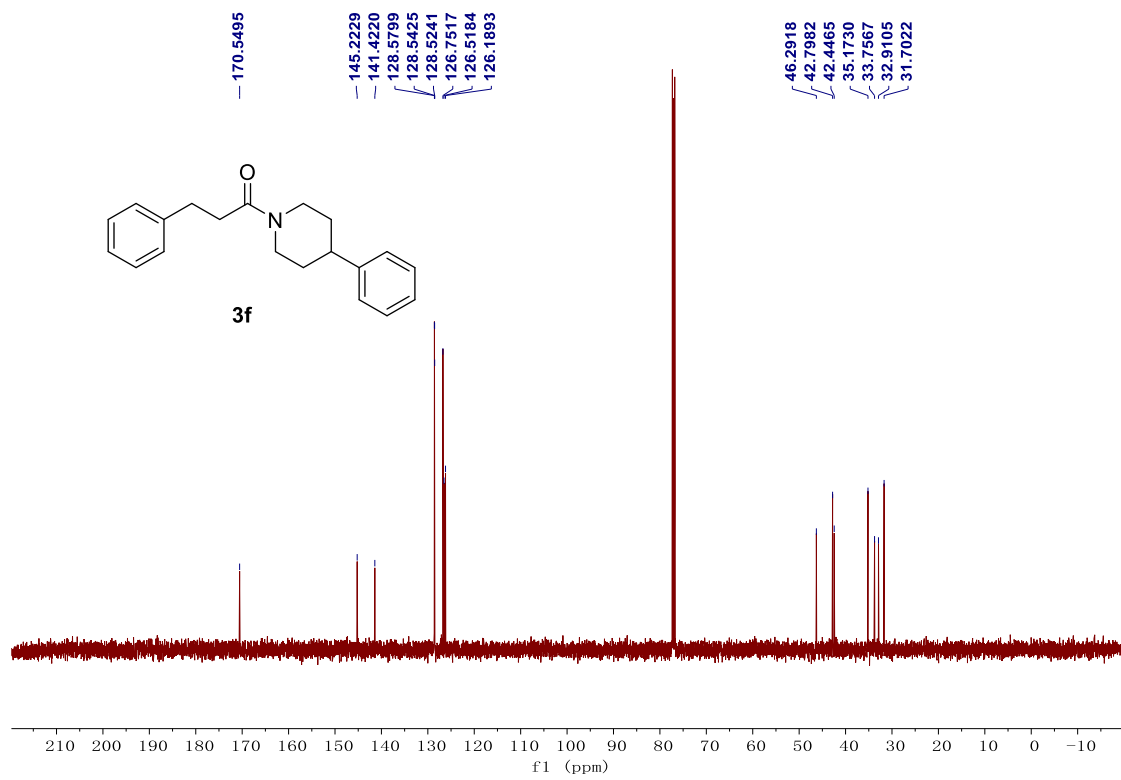
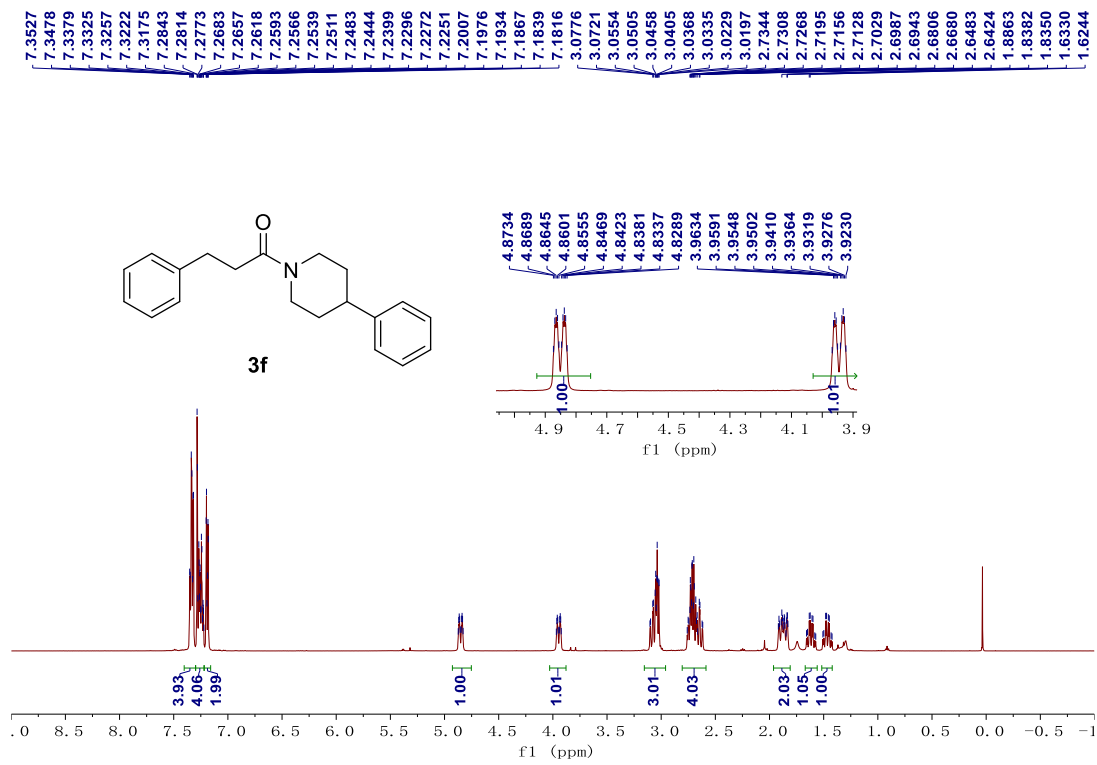


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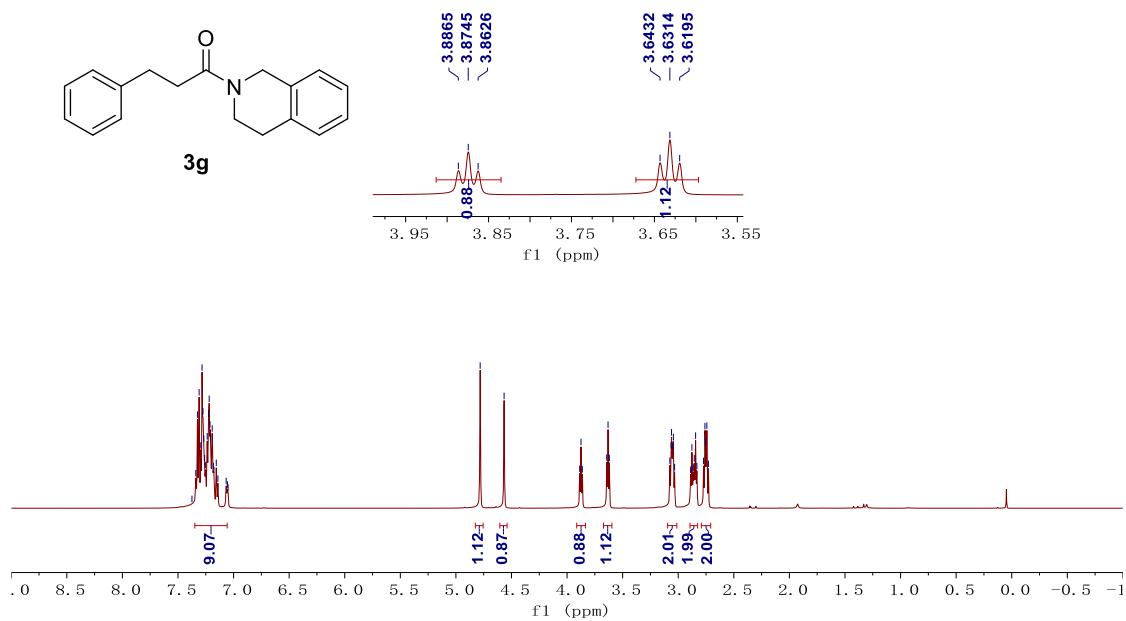
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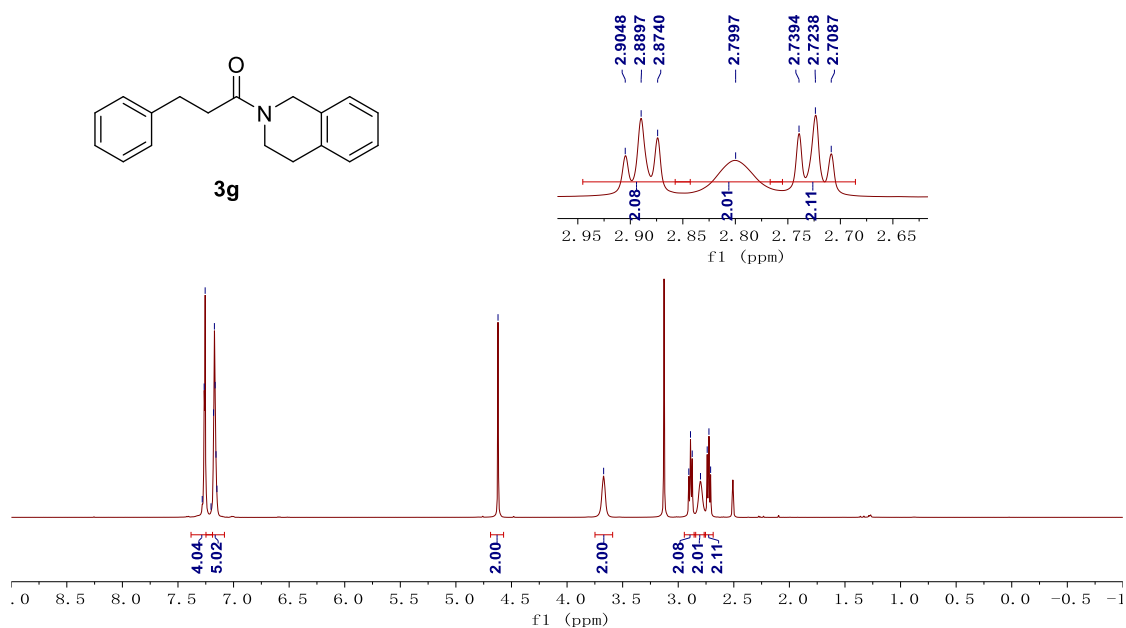
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) (amide rotamers 1.3:1)

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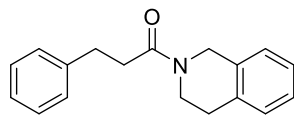
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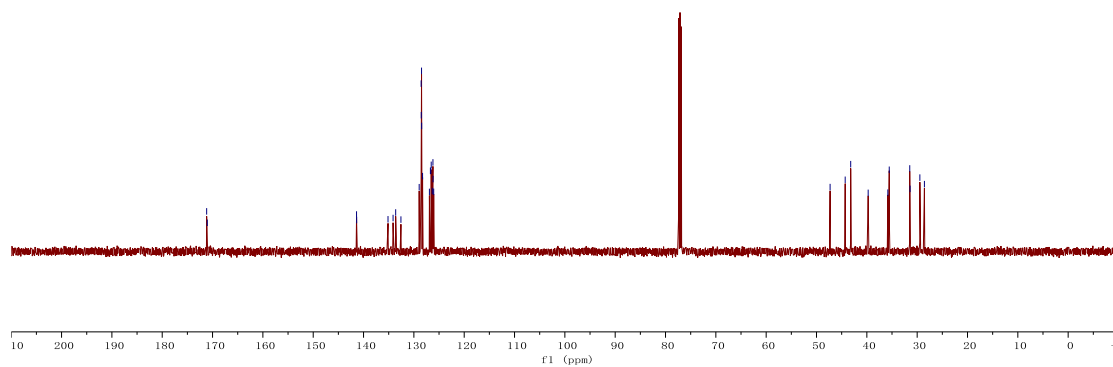


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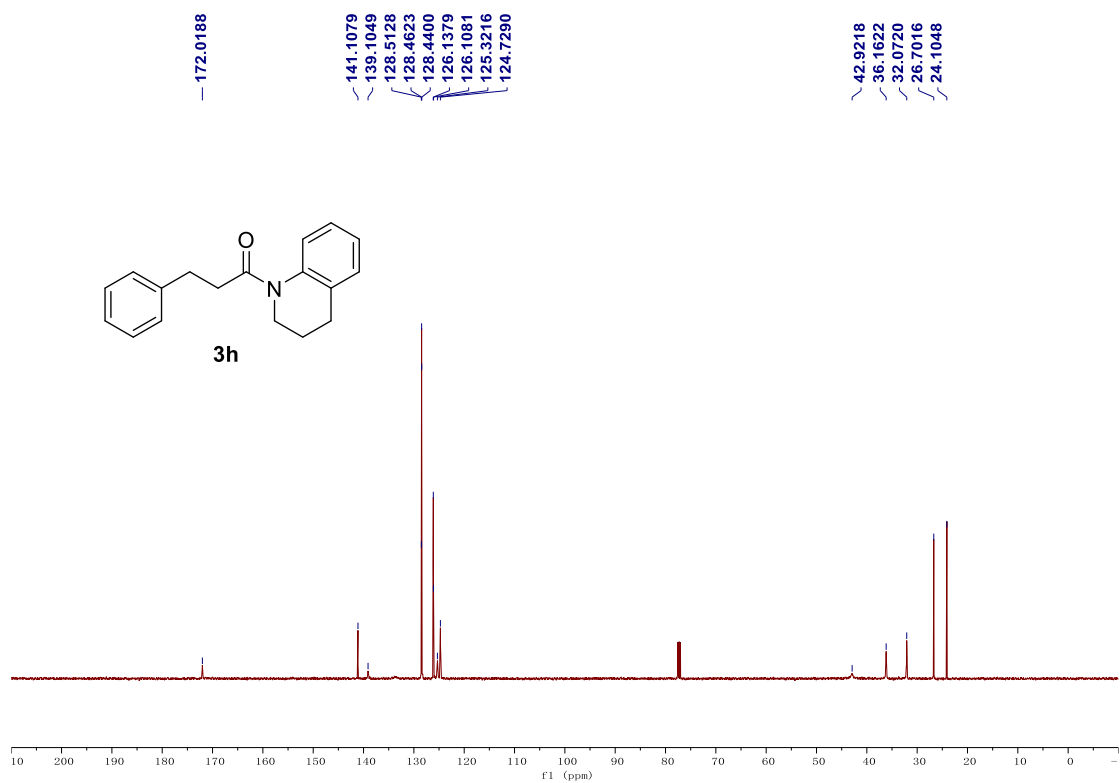
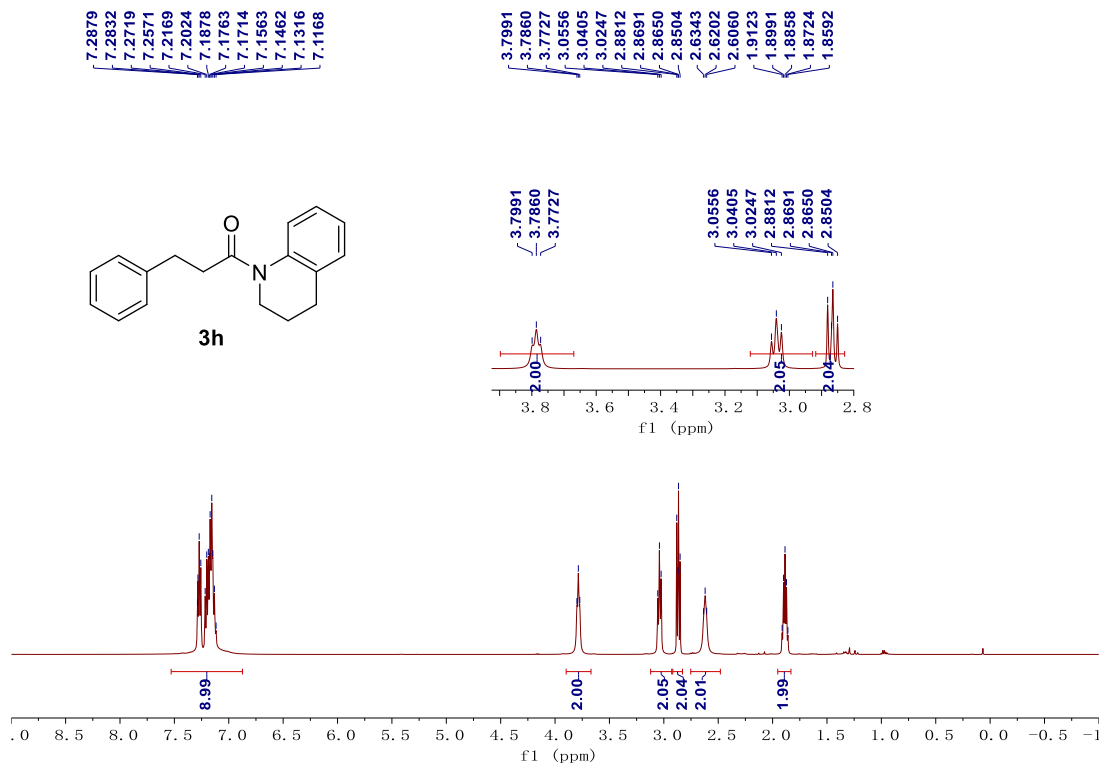
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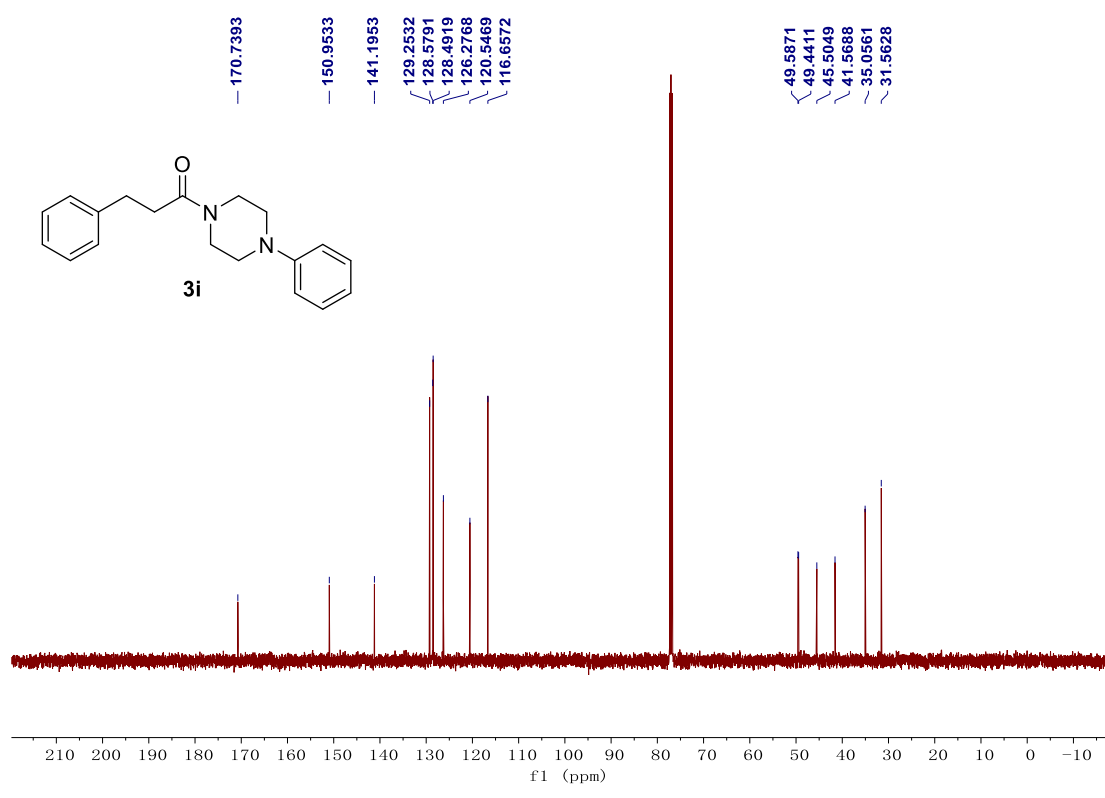
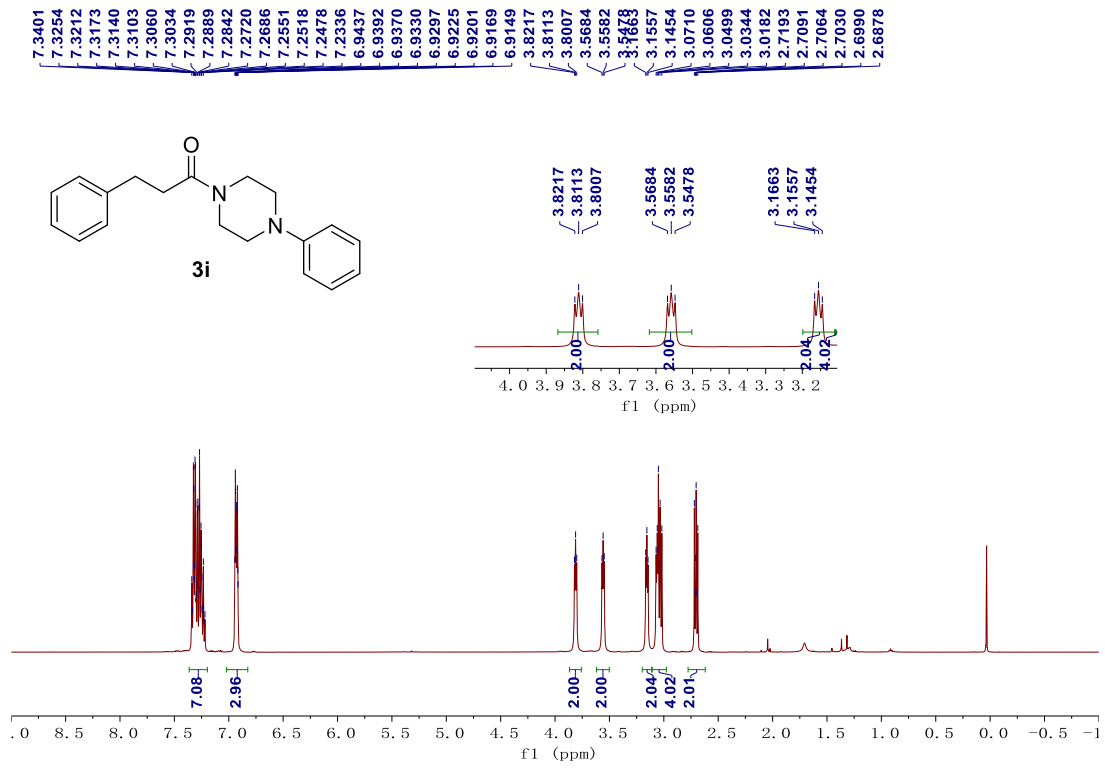


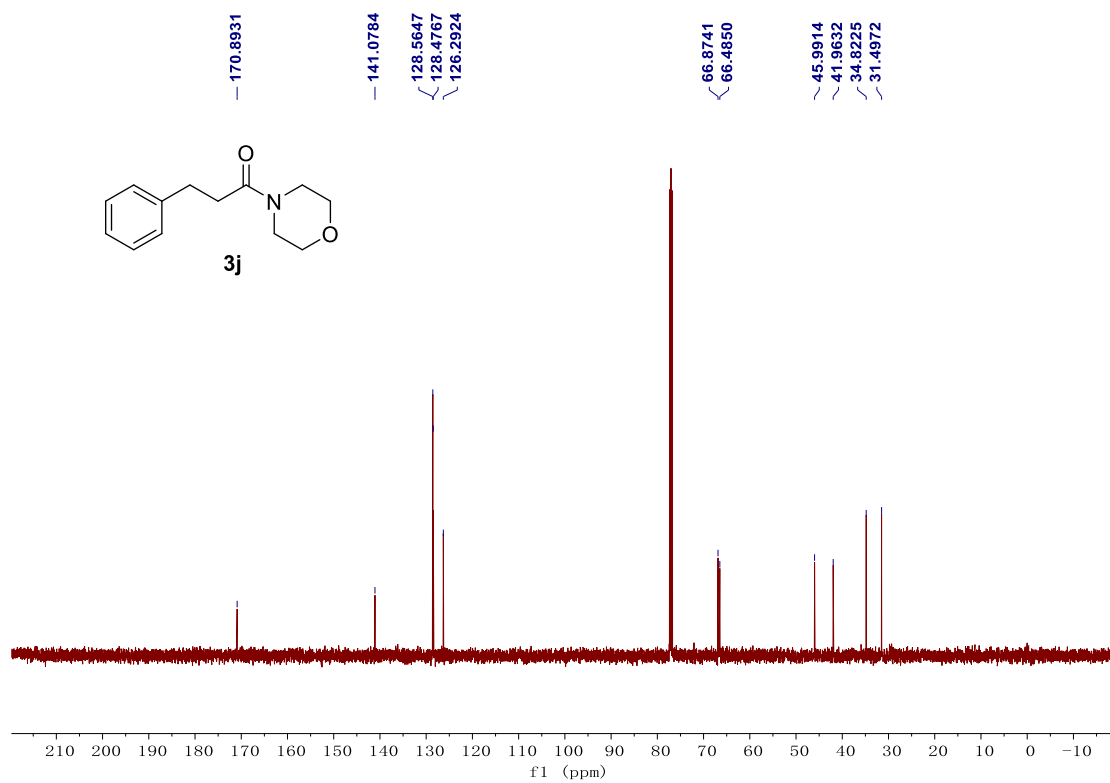
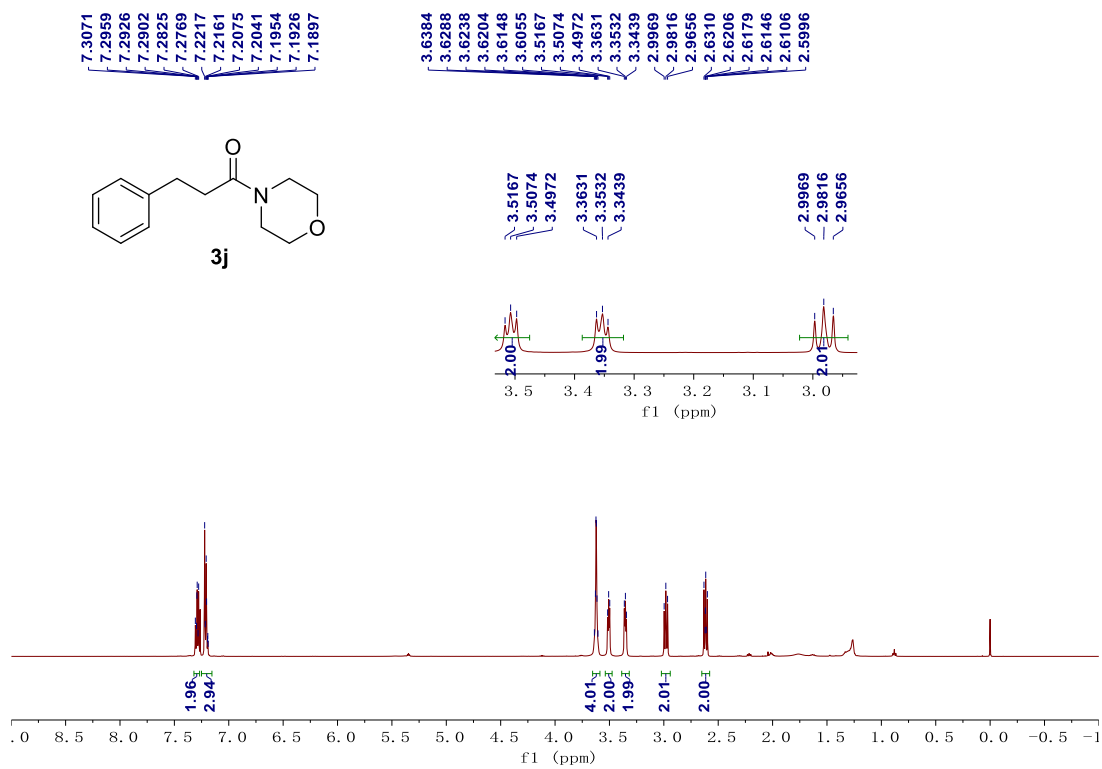
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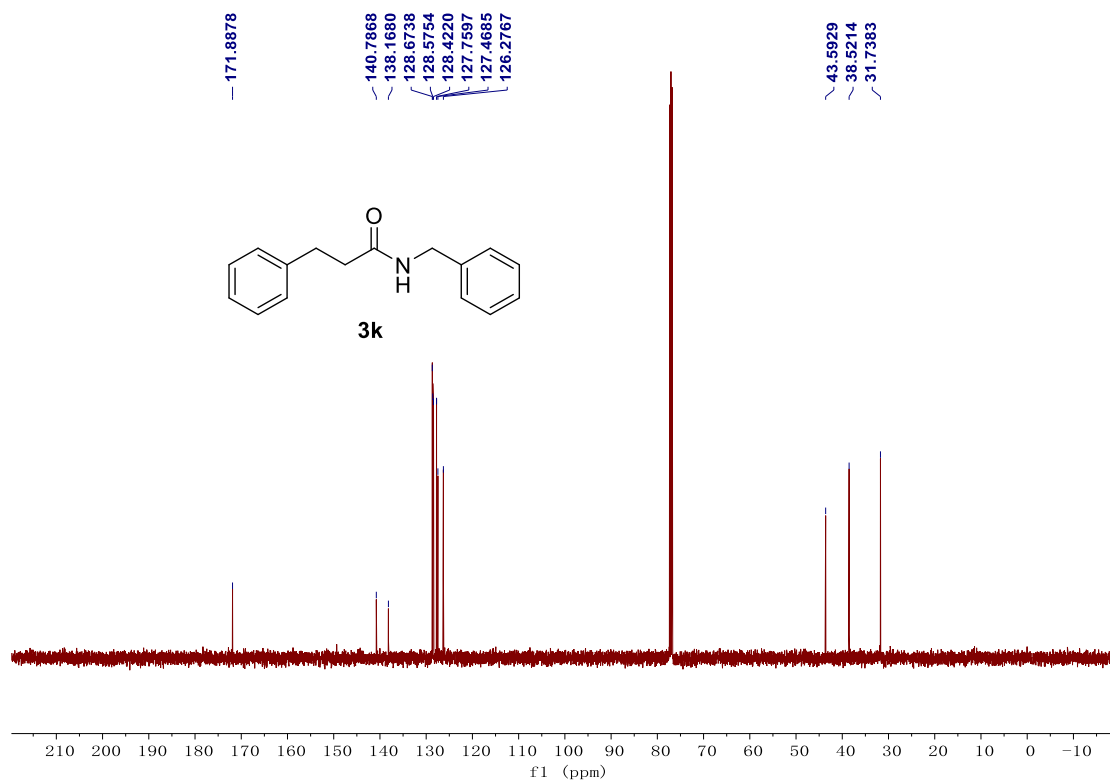
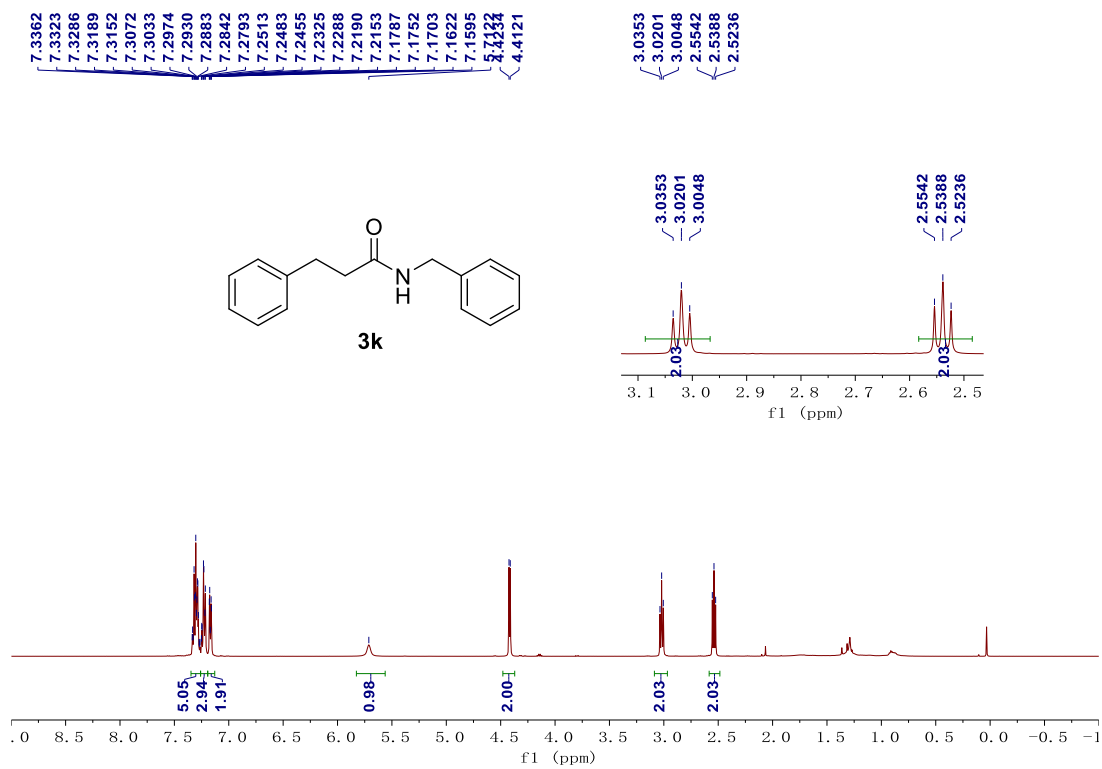




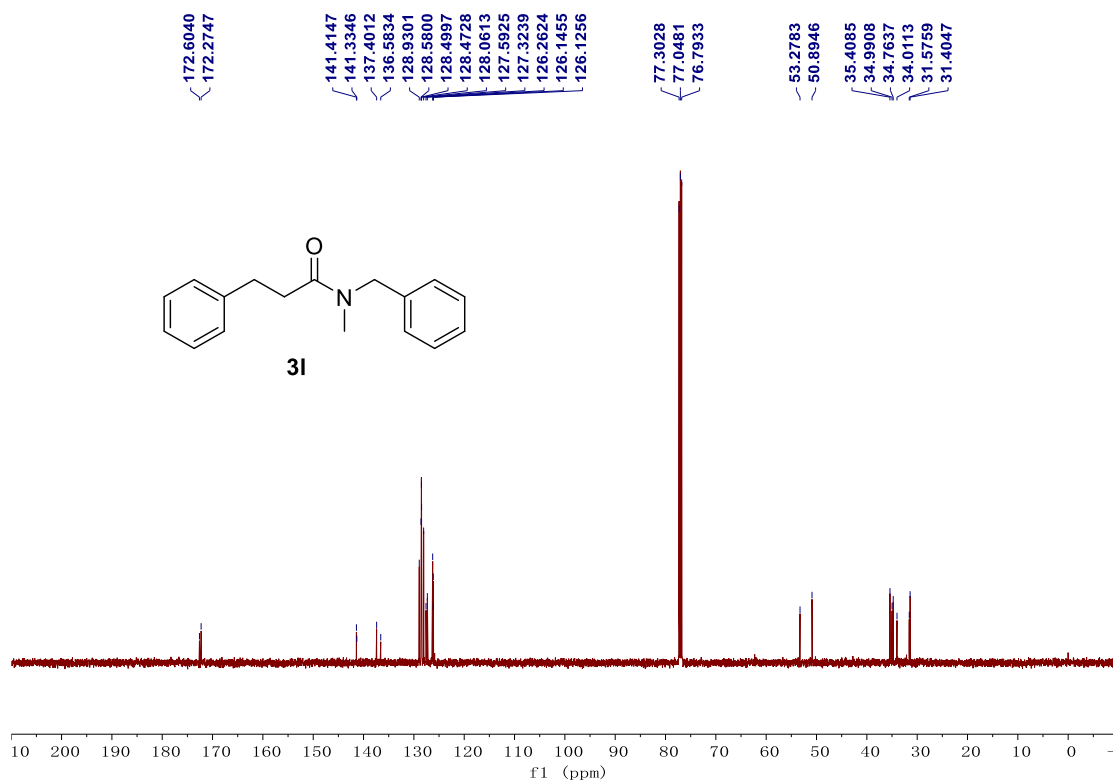
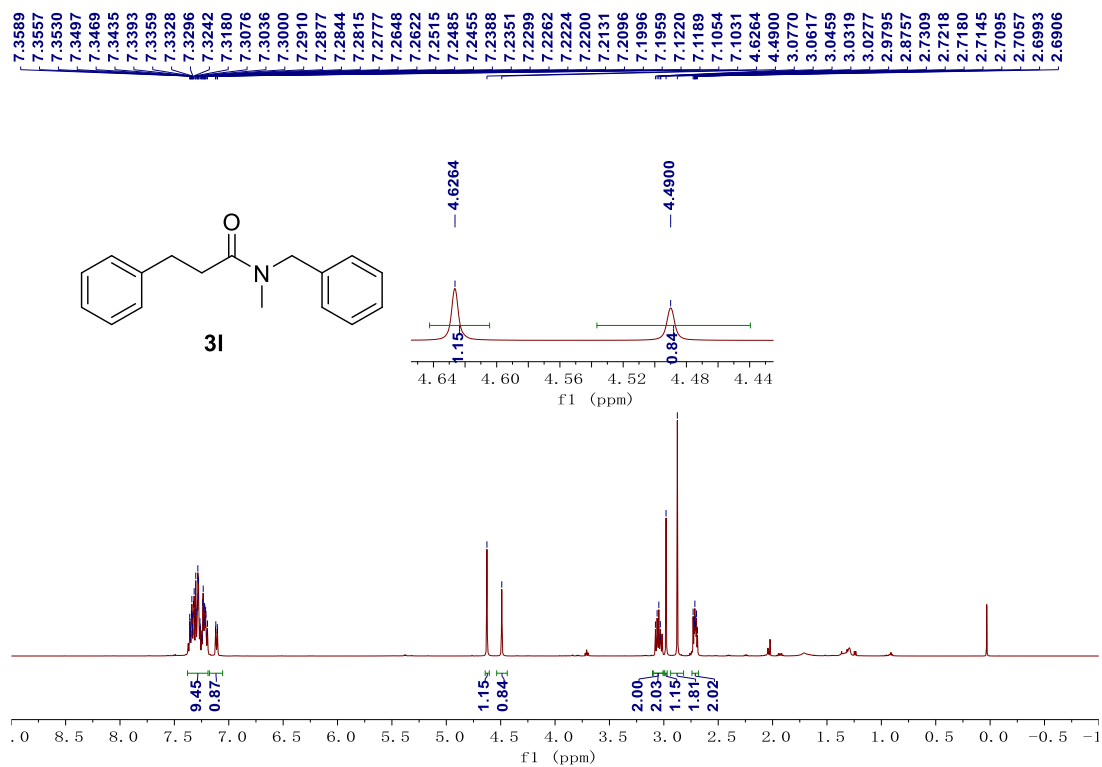




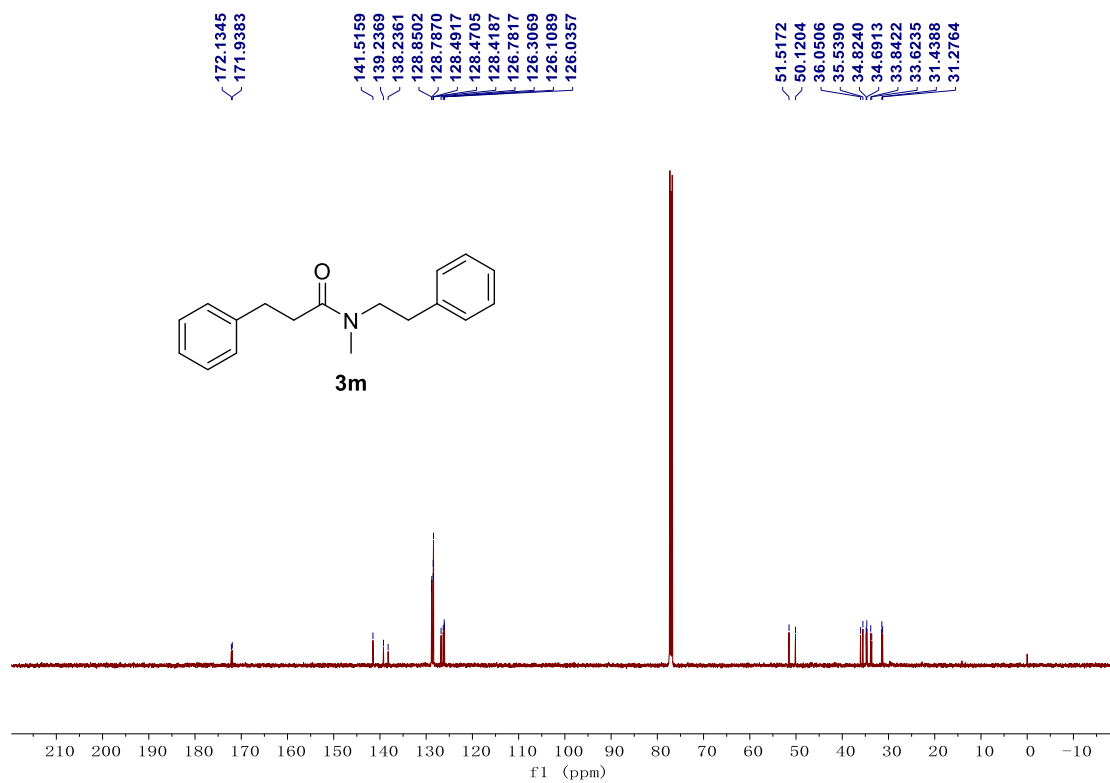
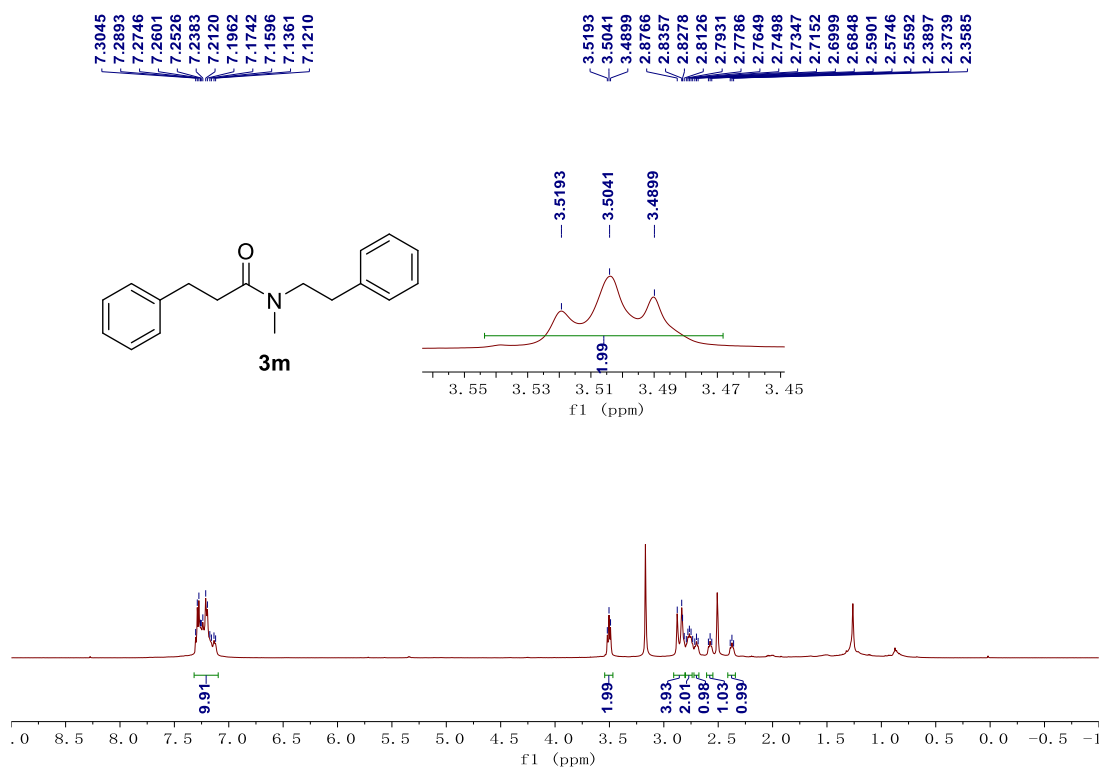




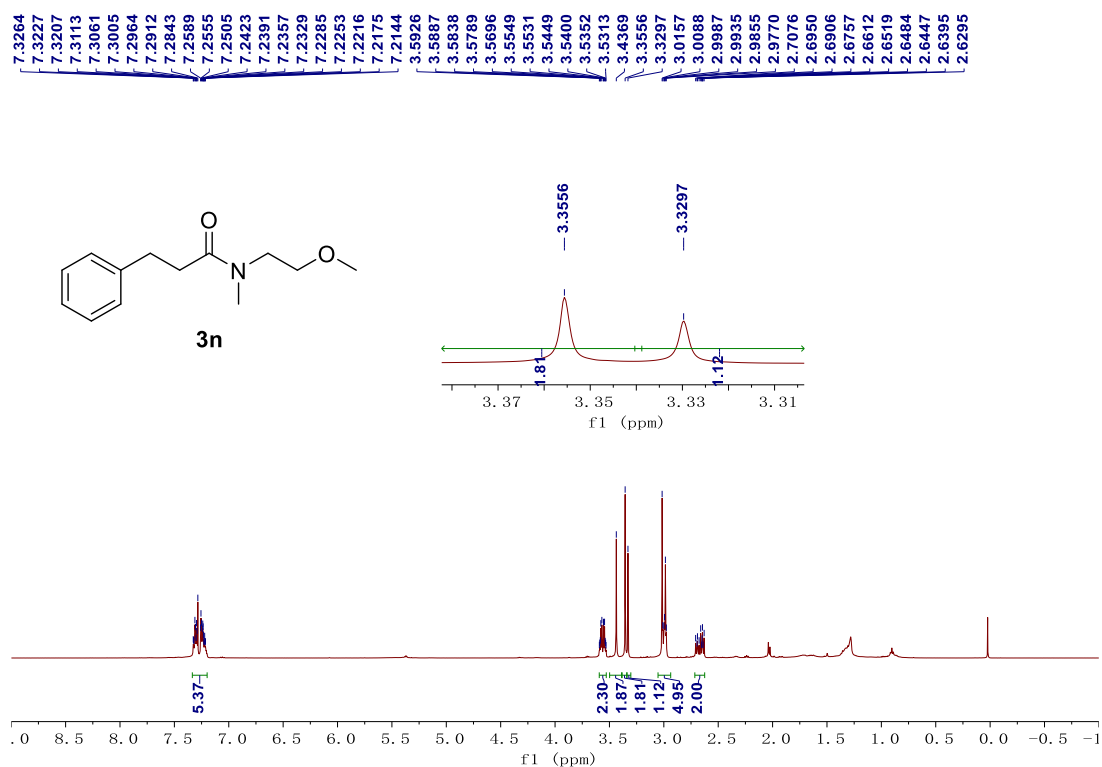
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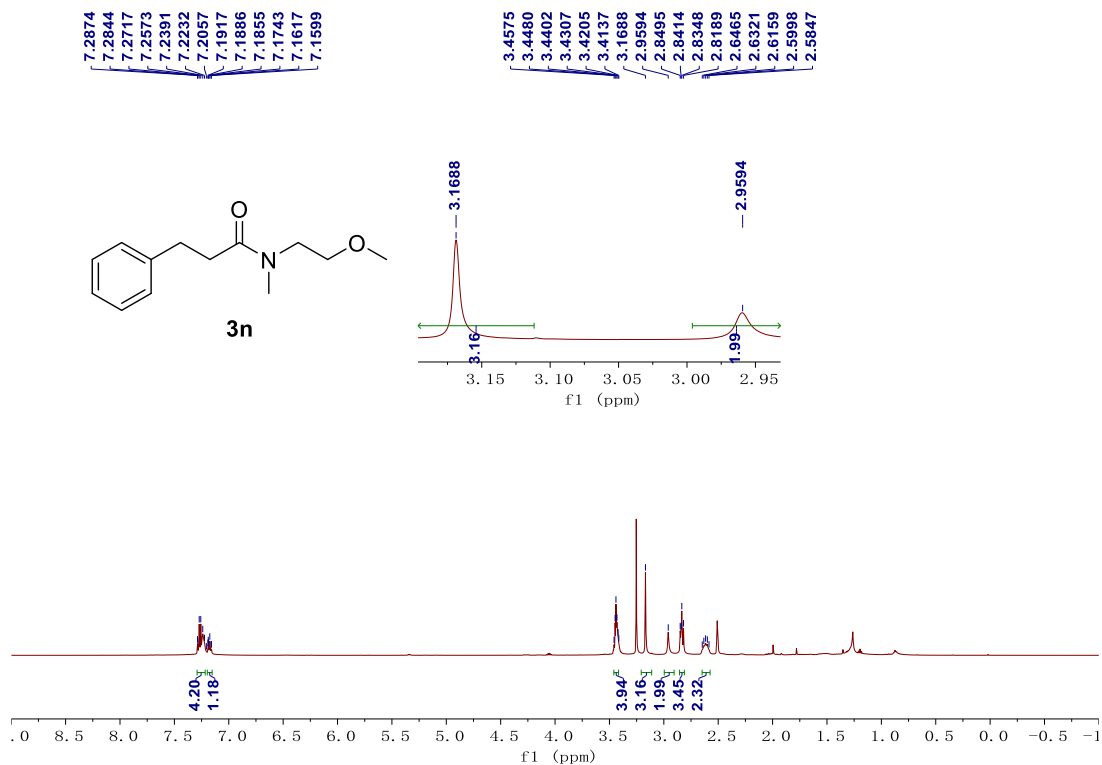
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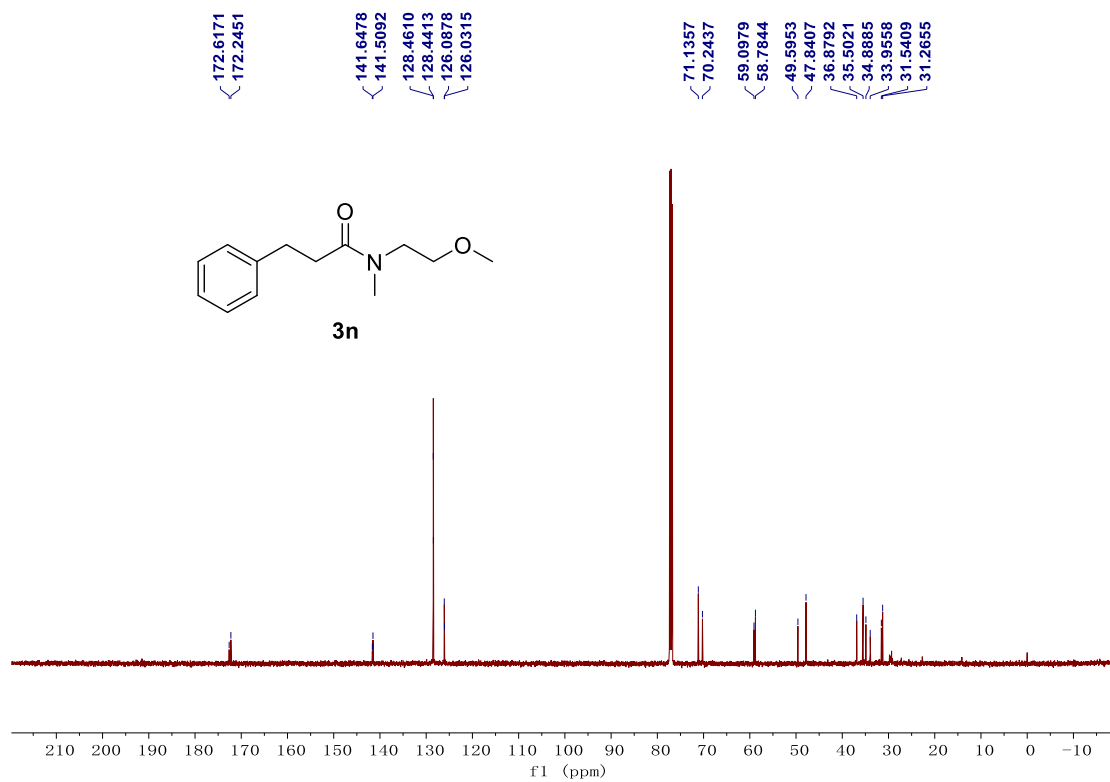


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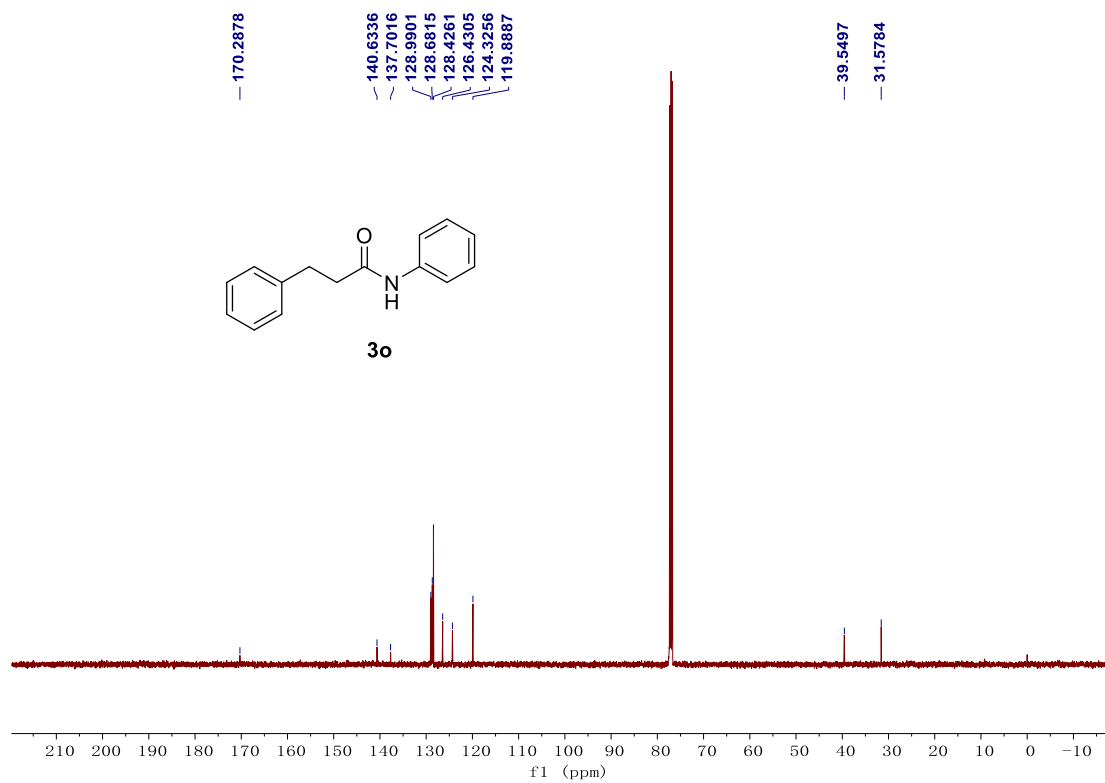
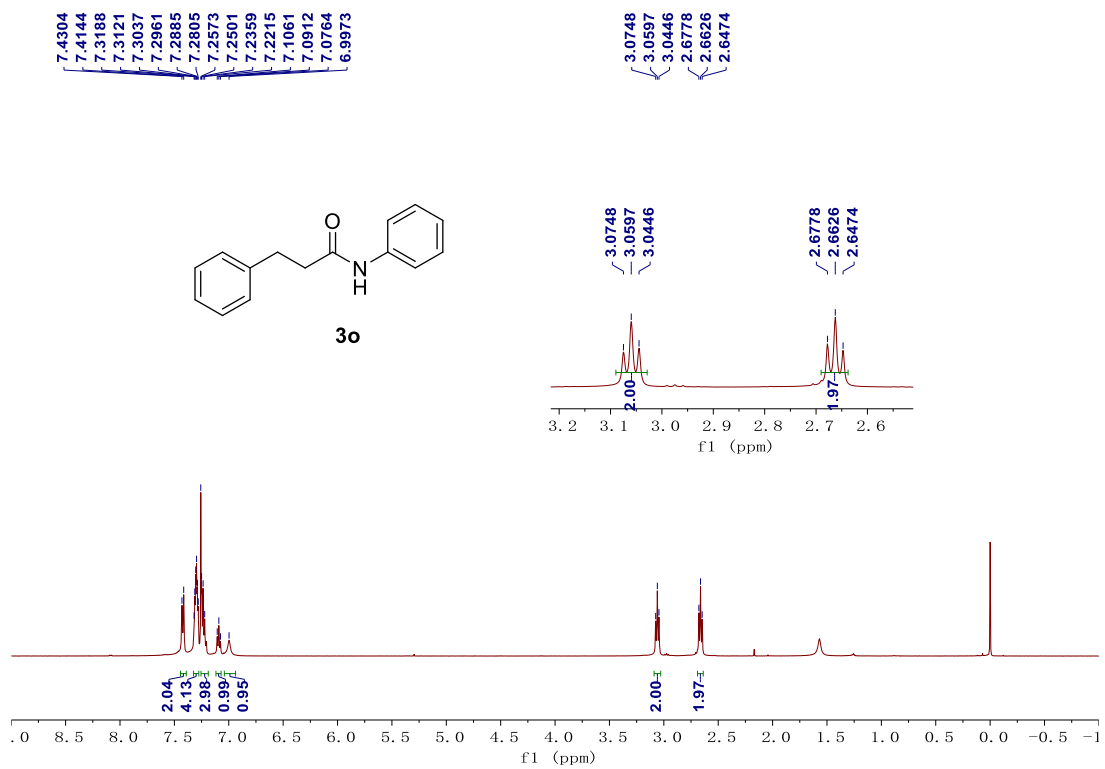


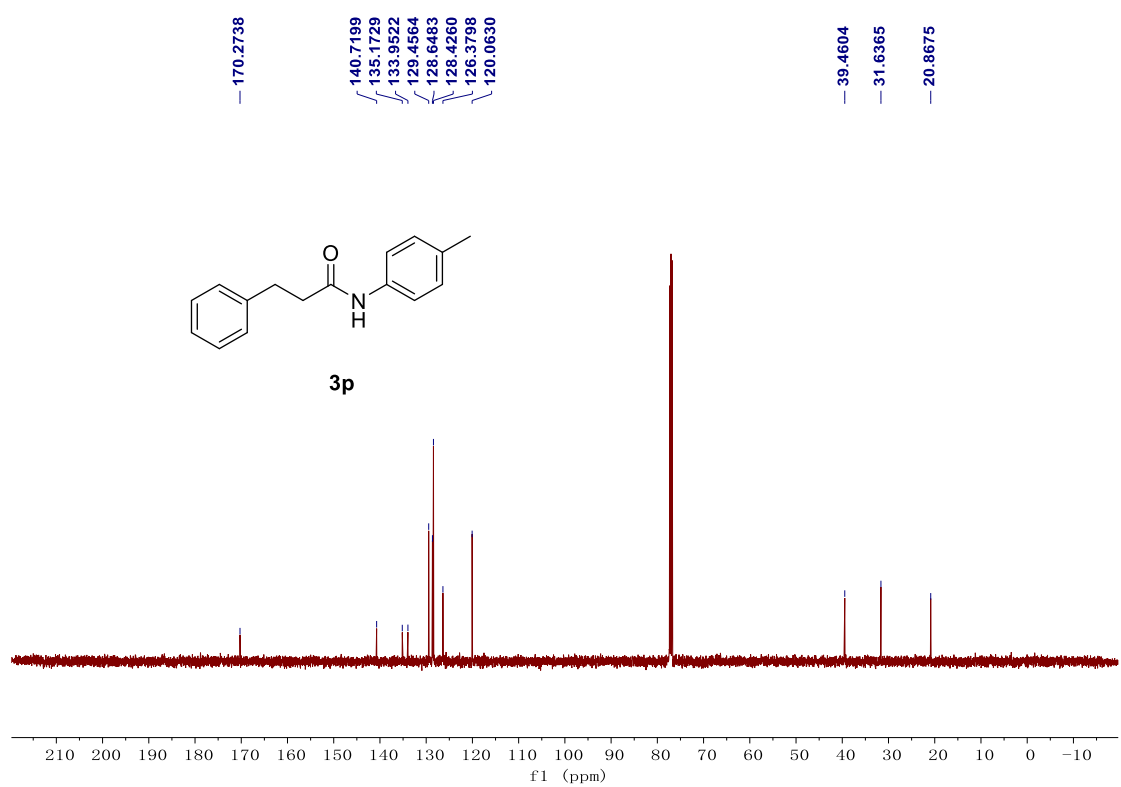
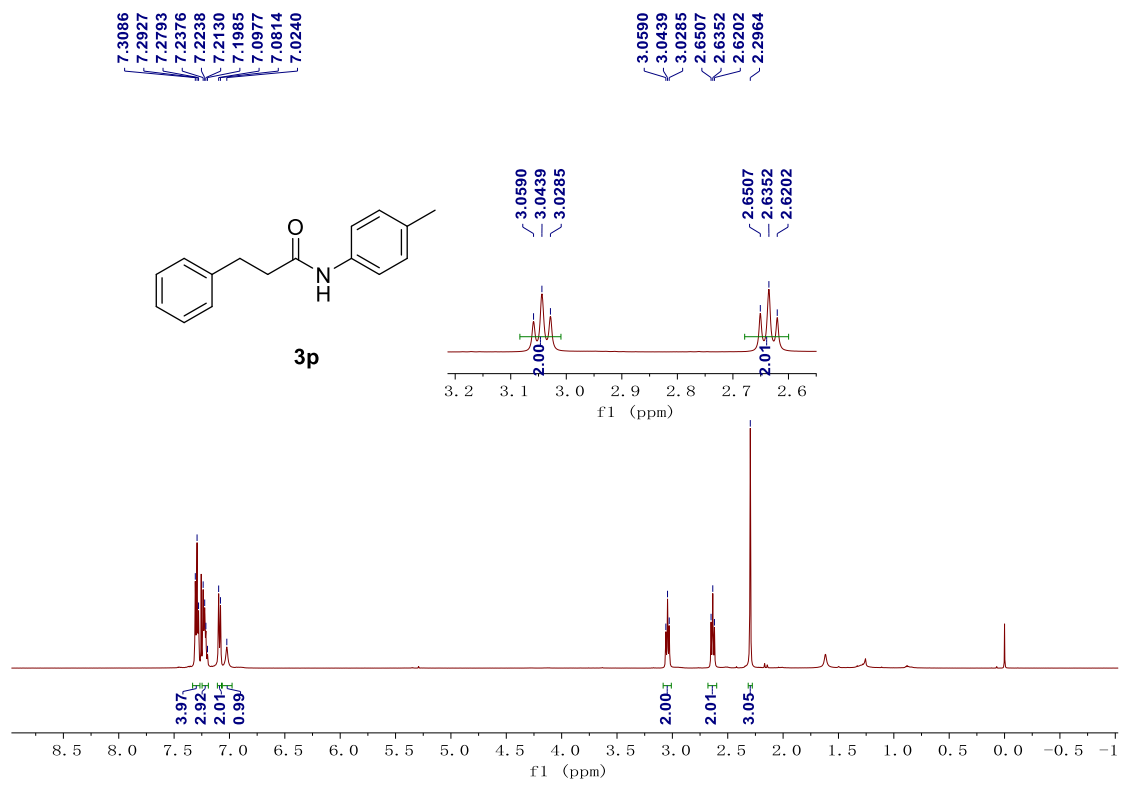
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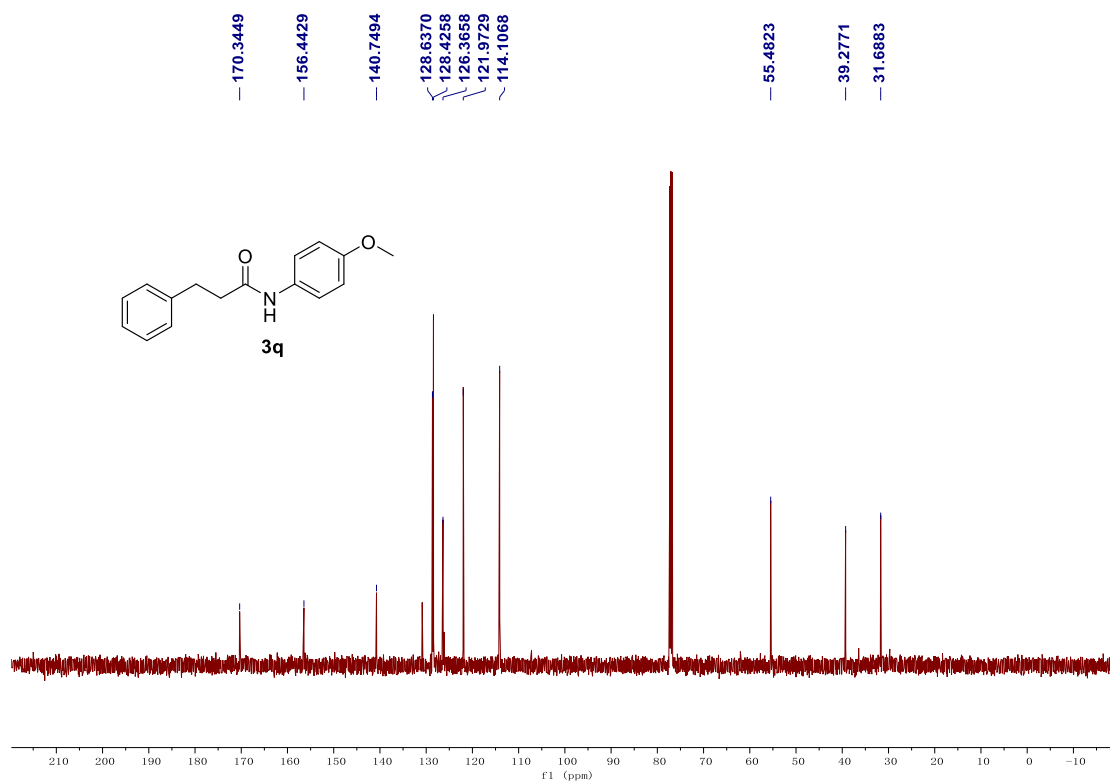
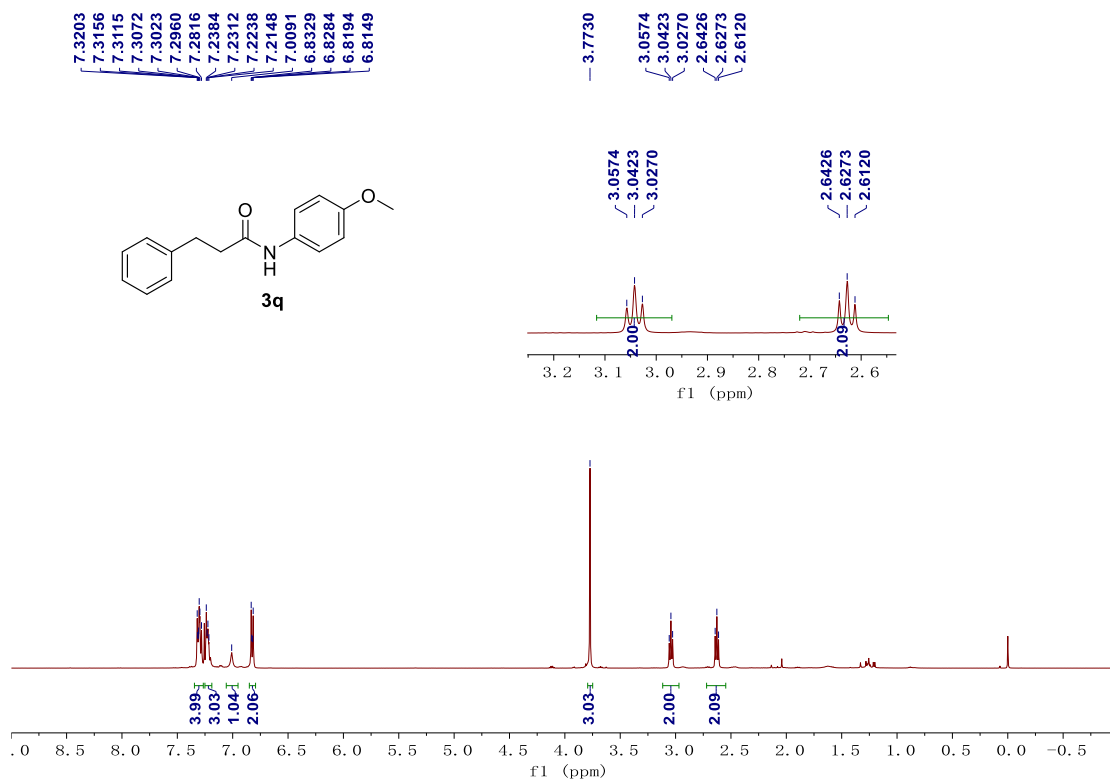


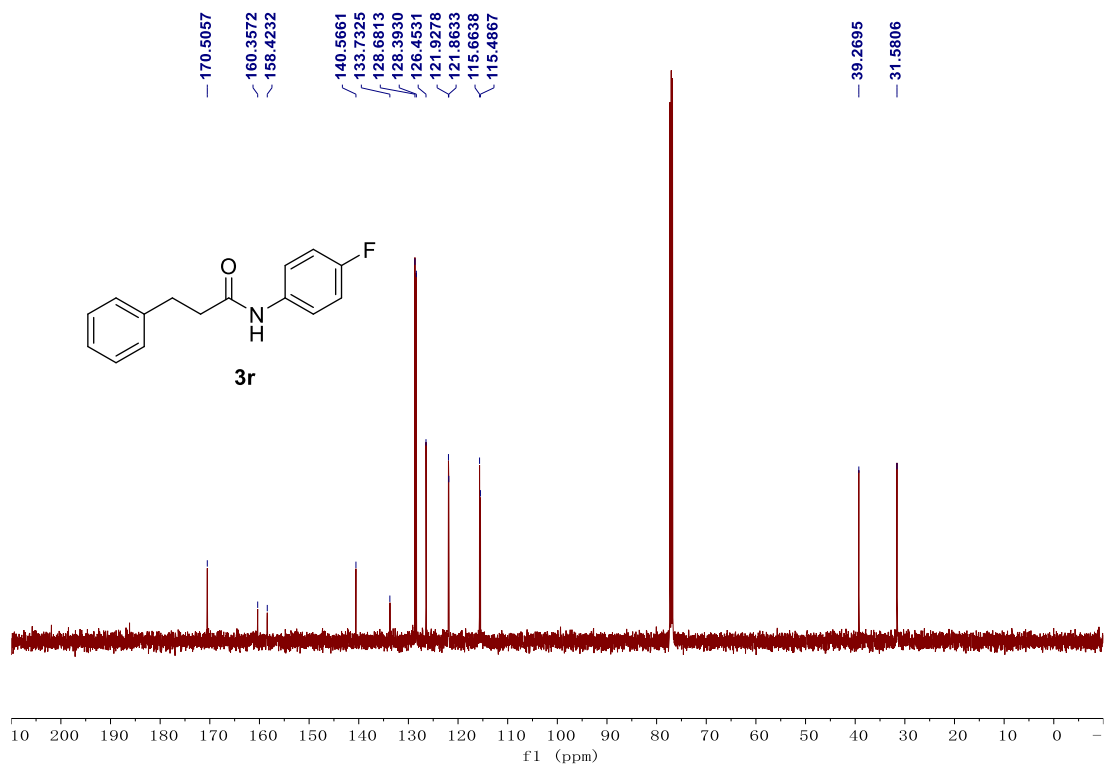
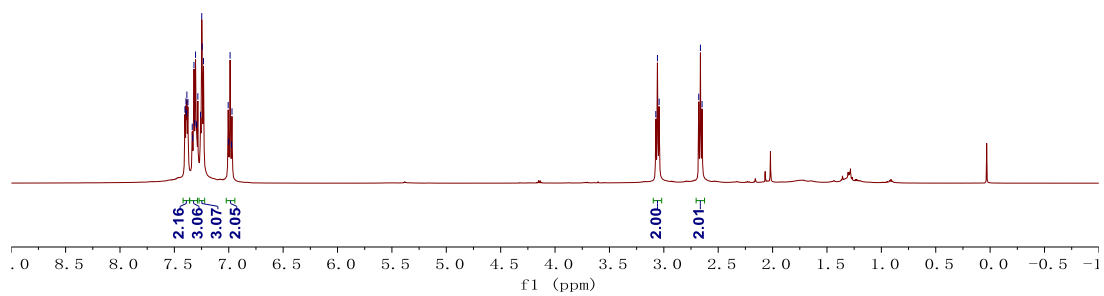
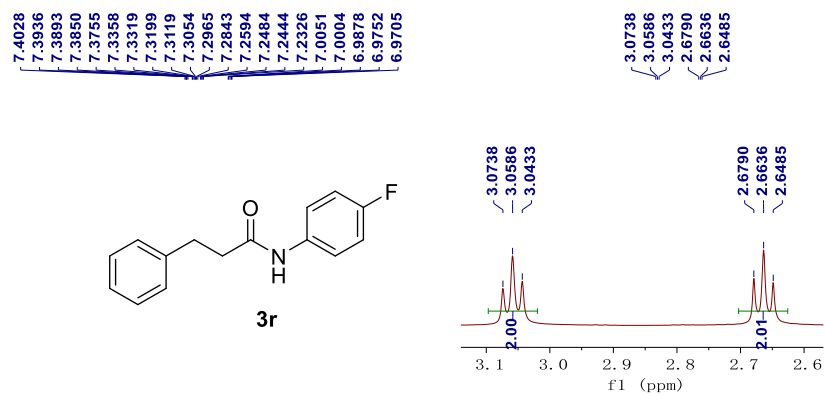


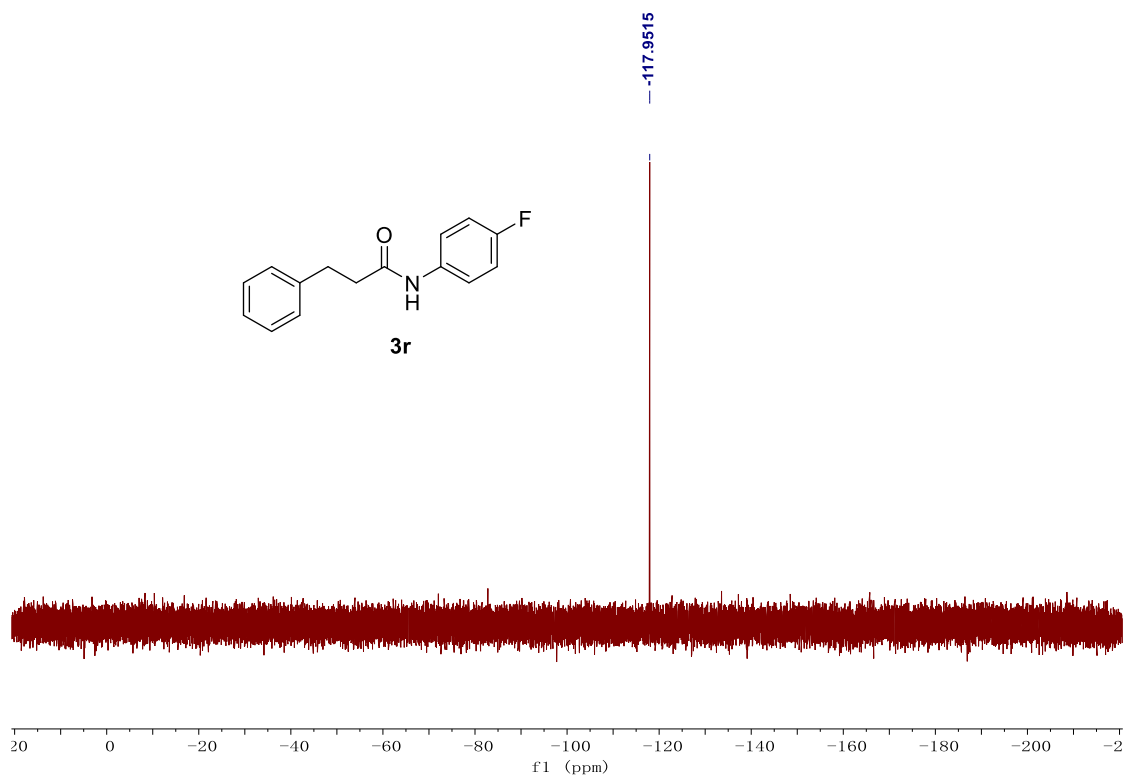


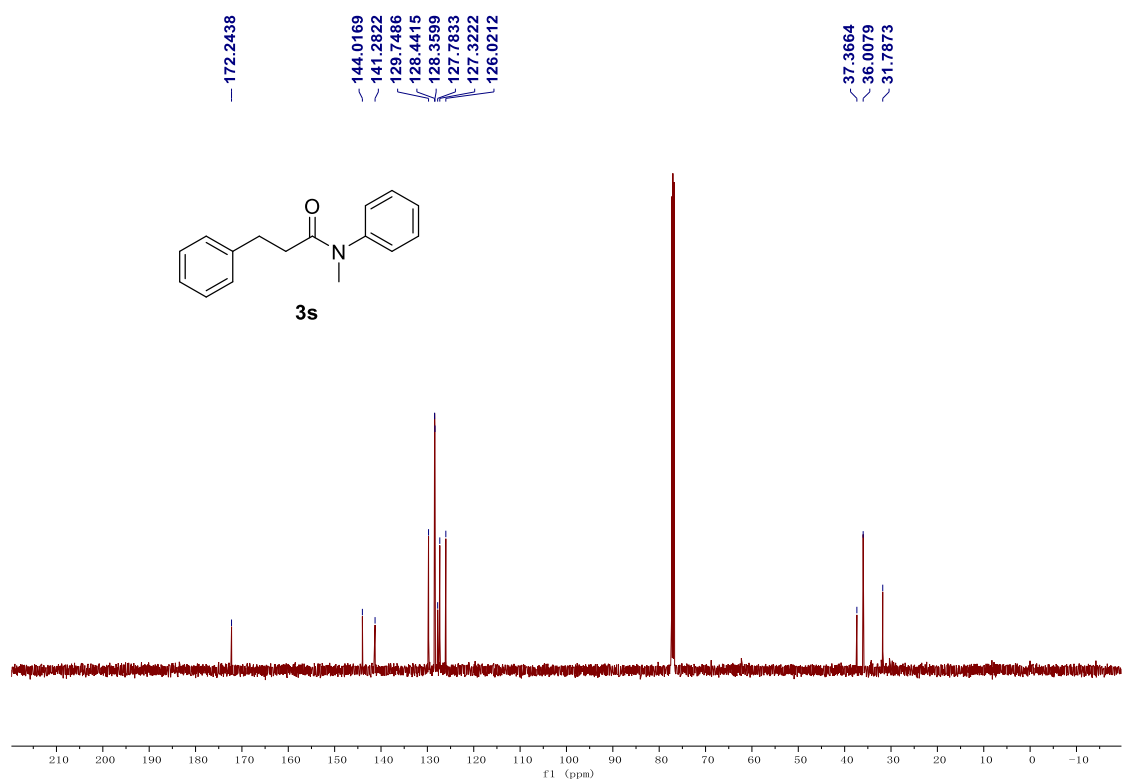
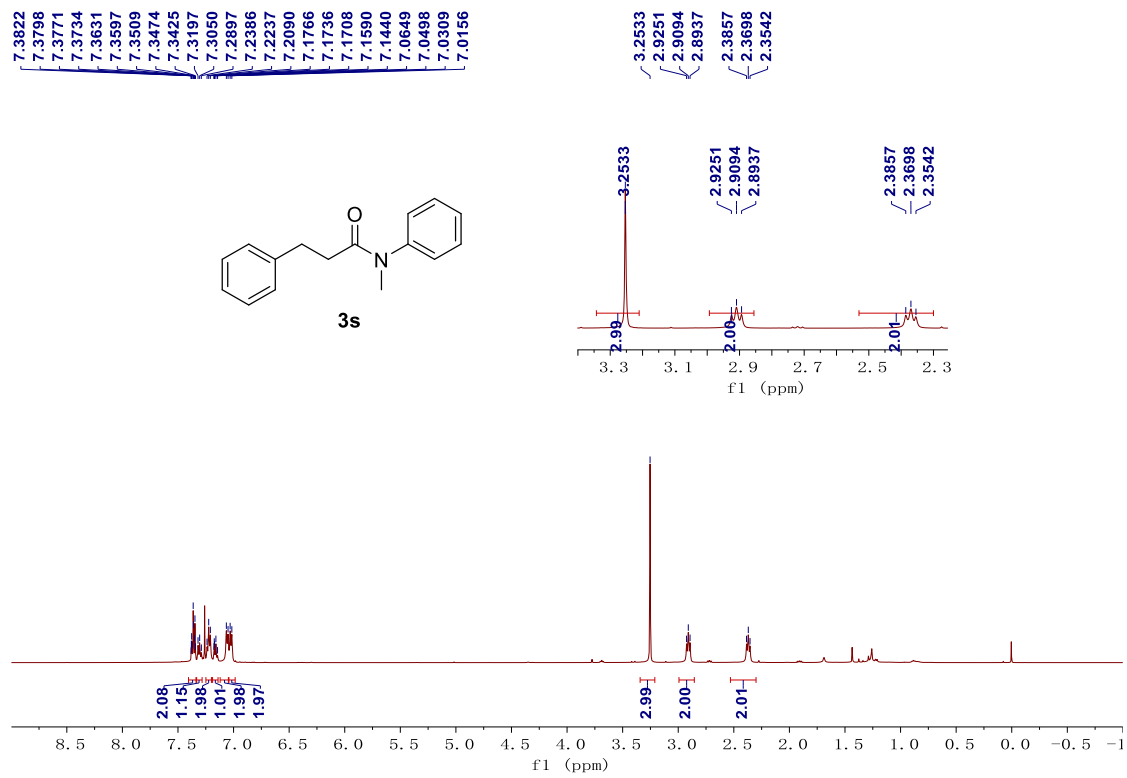


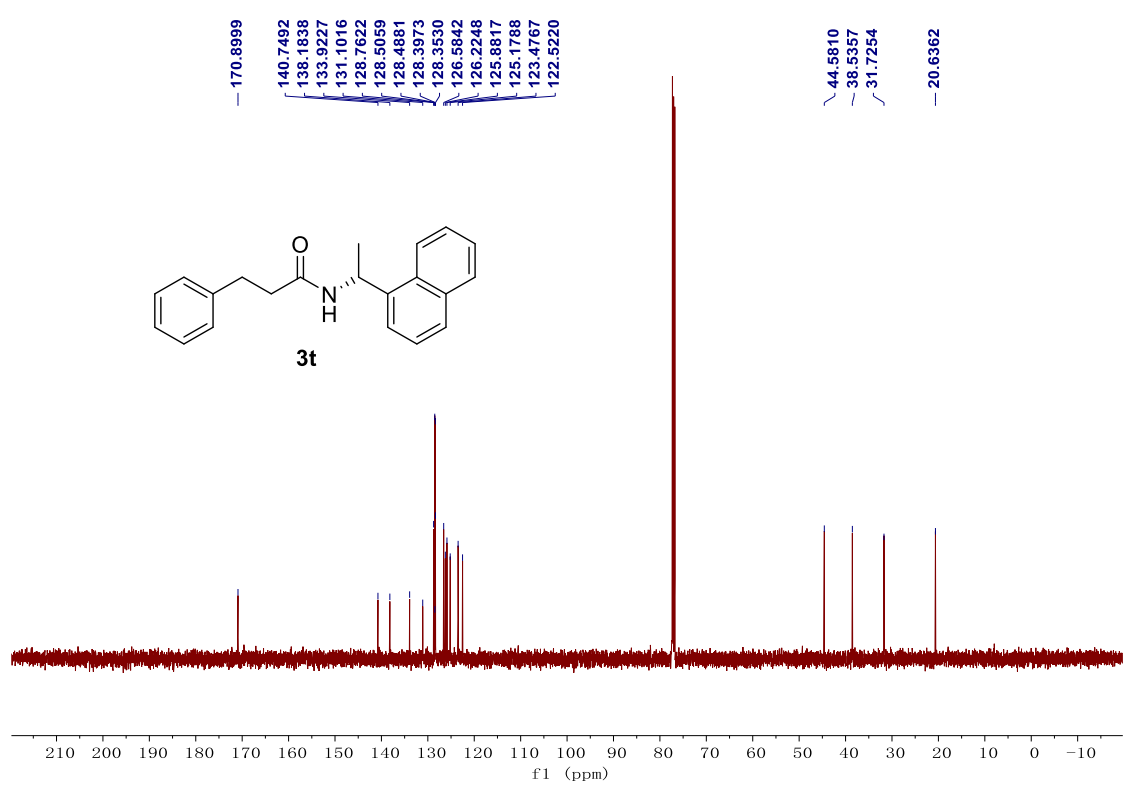
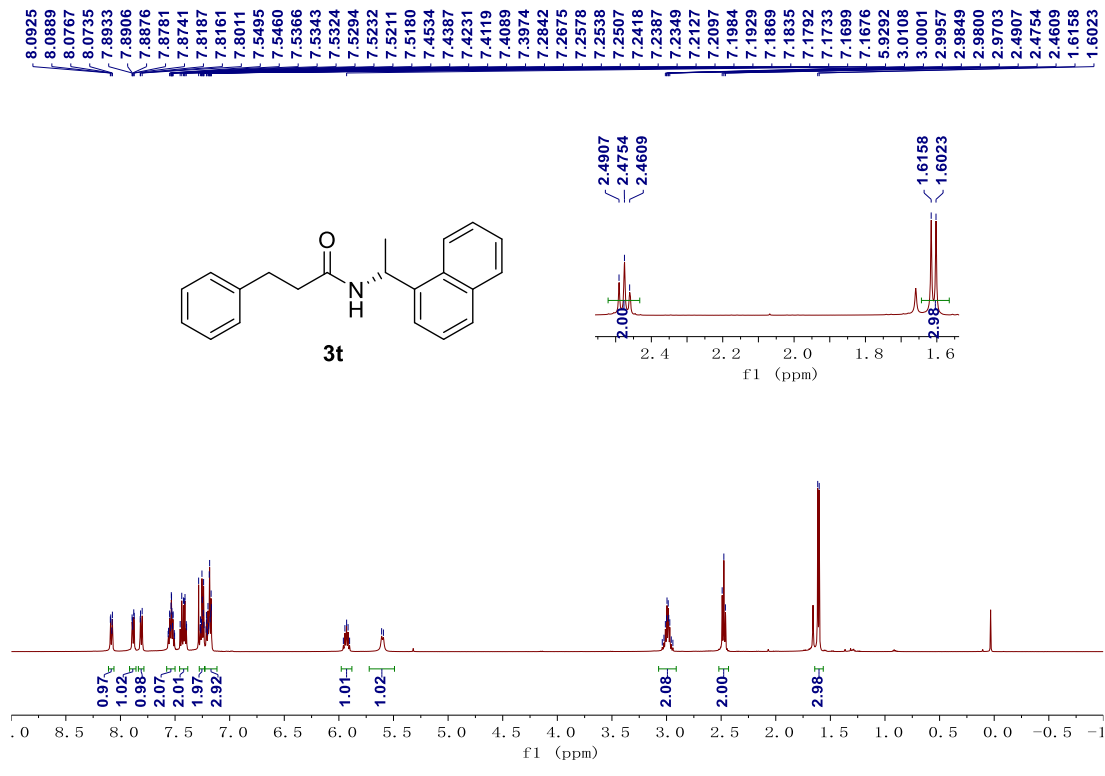


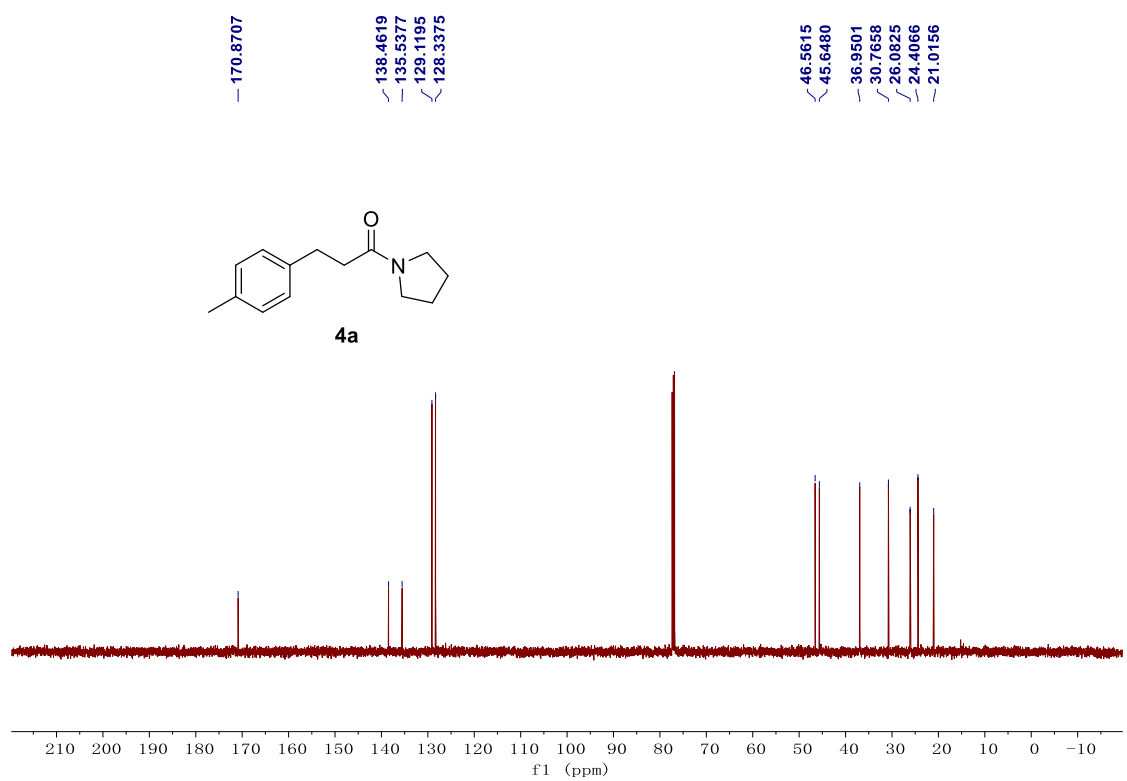
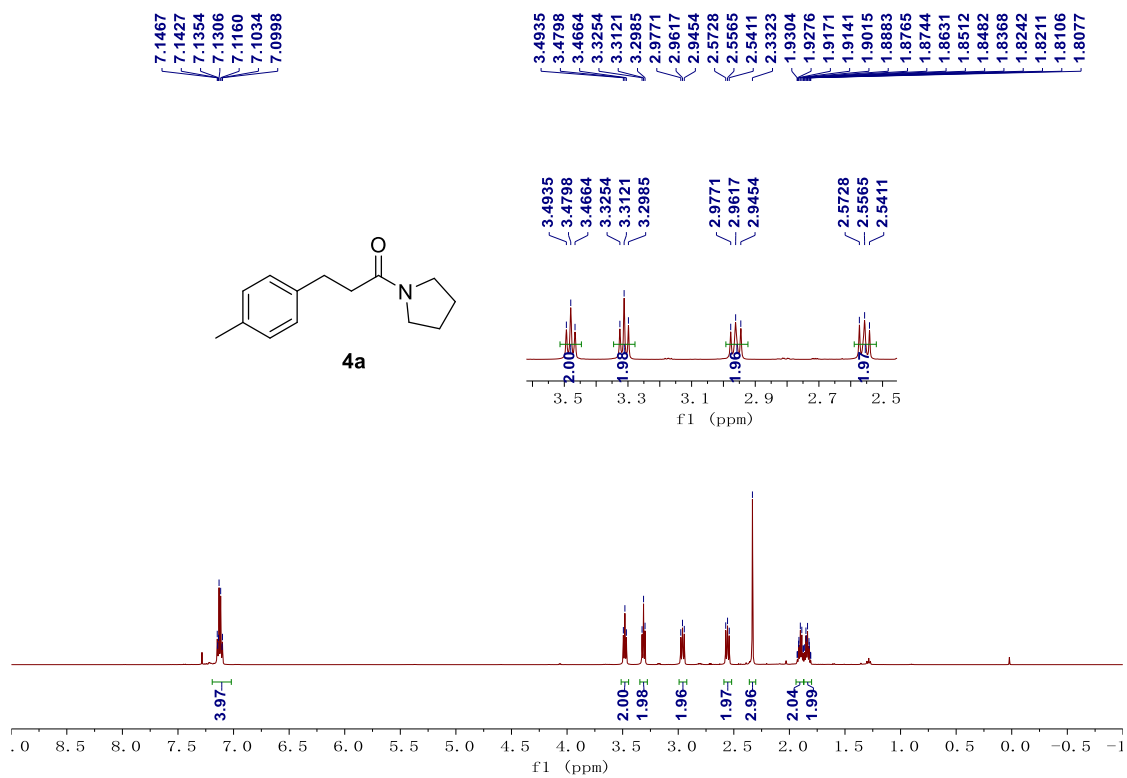




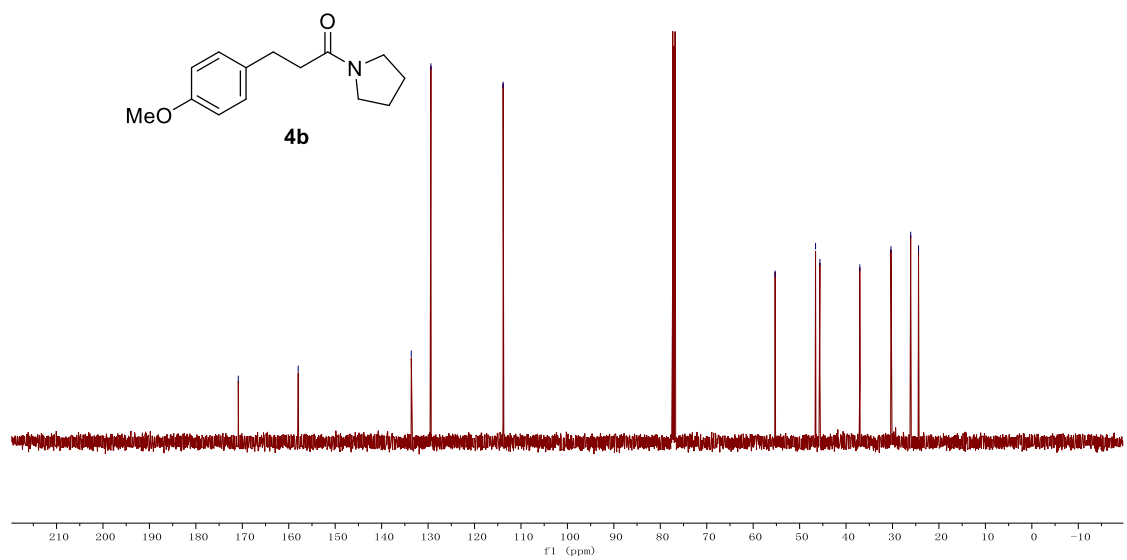
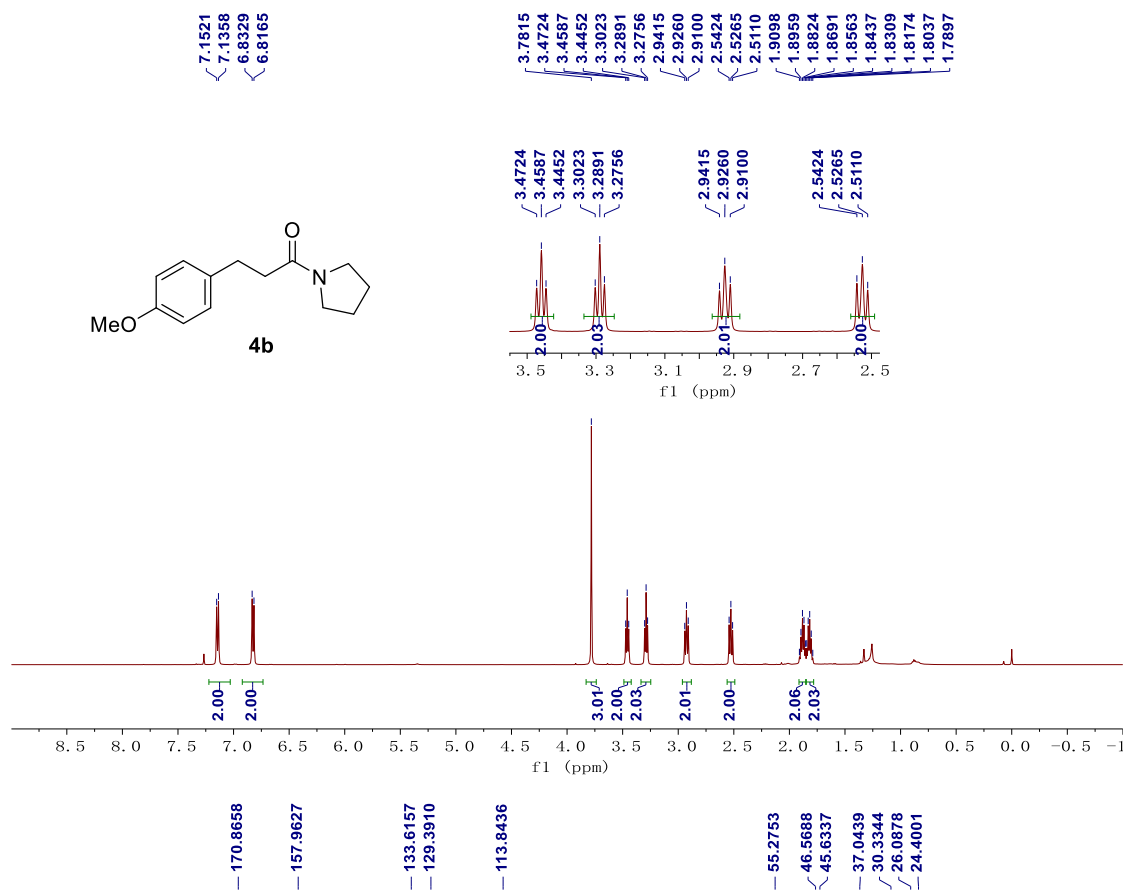


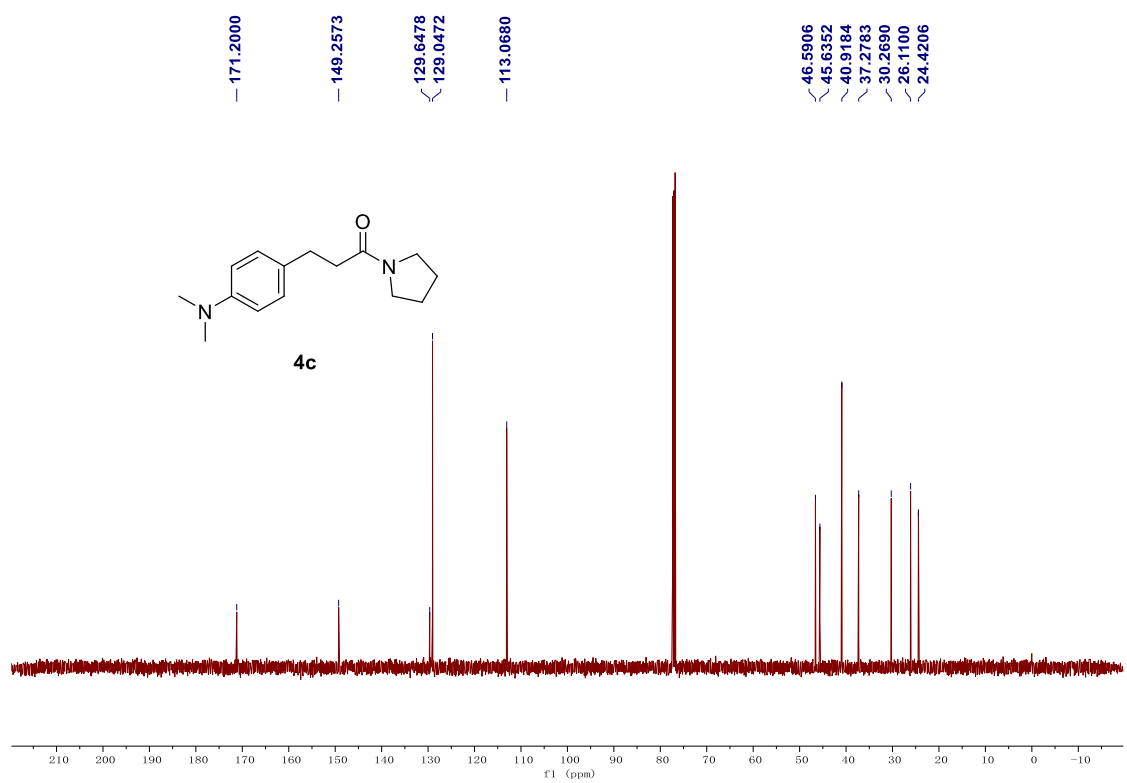
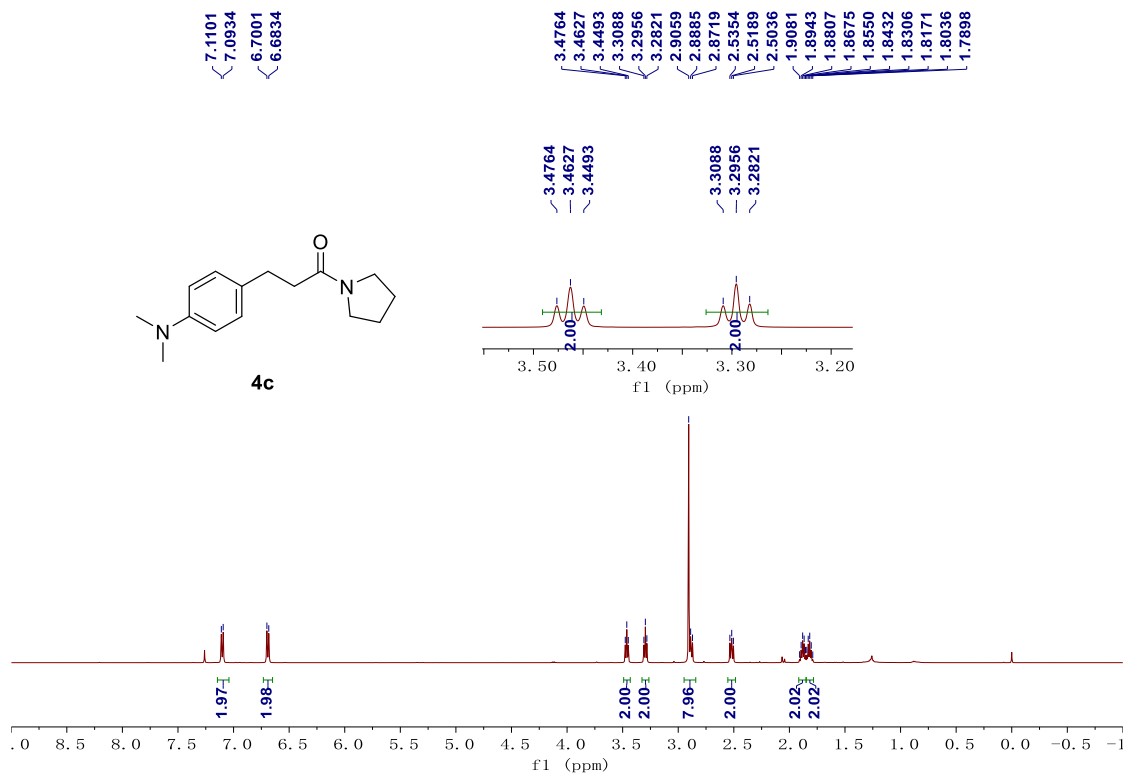






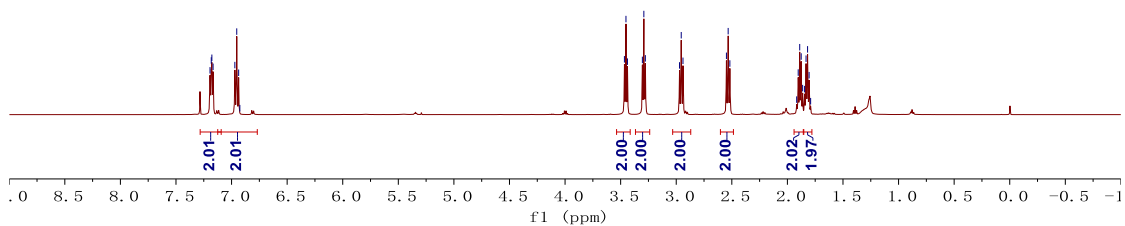
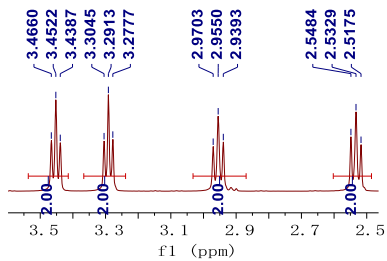
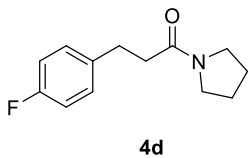






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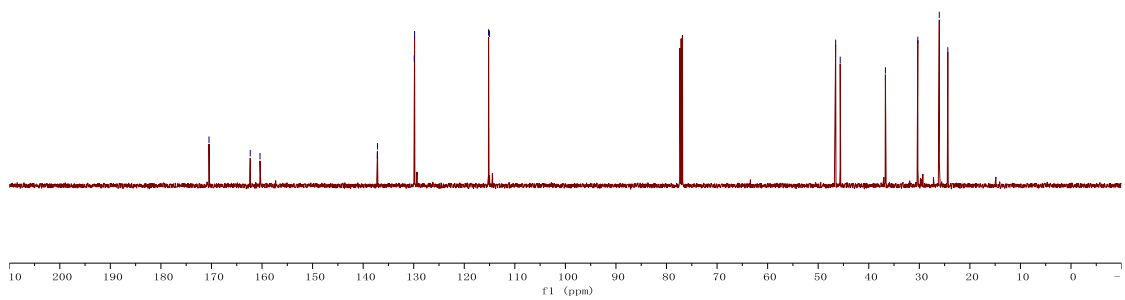
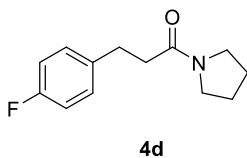


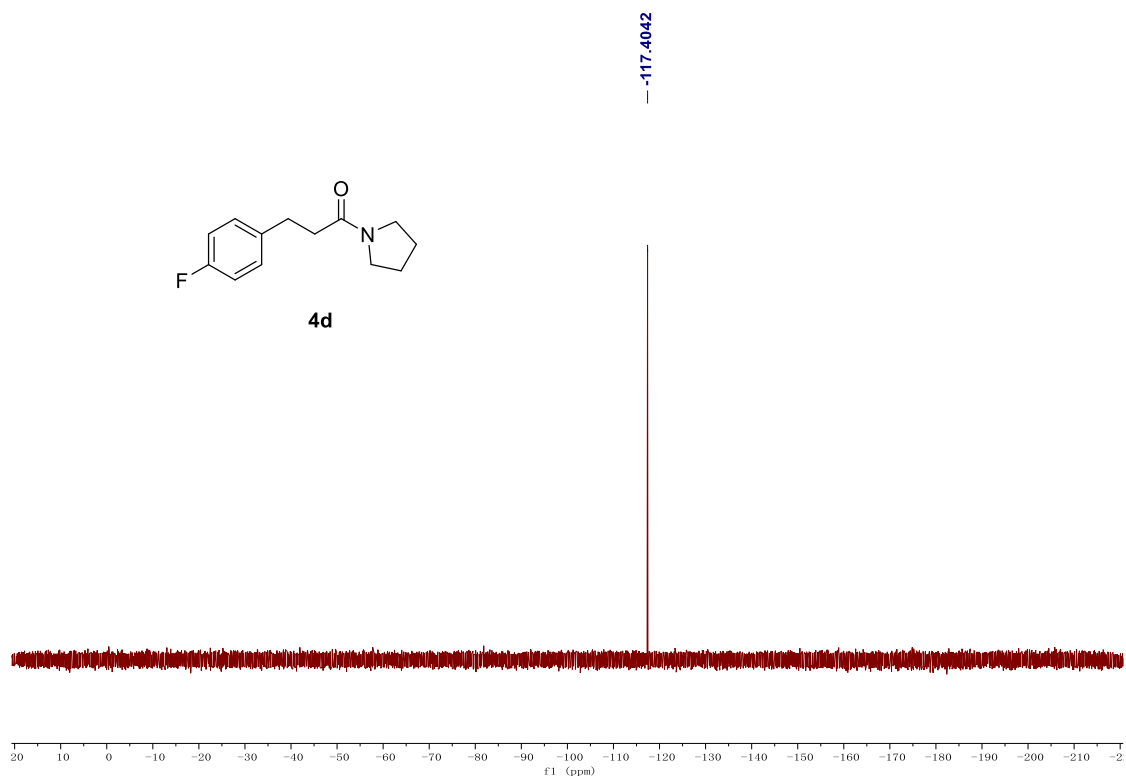
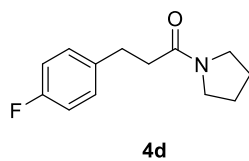
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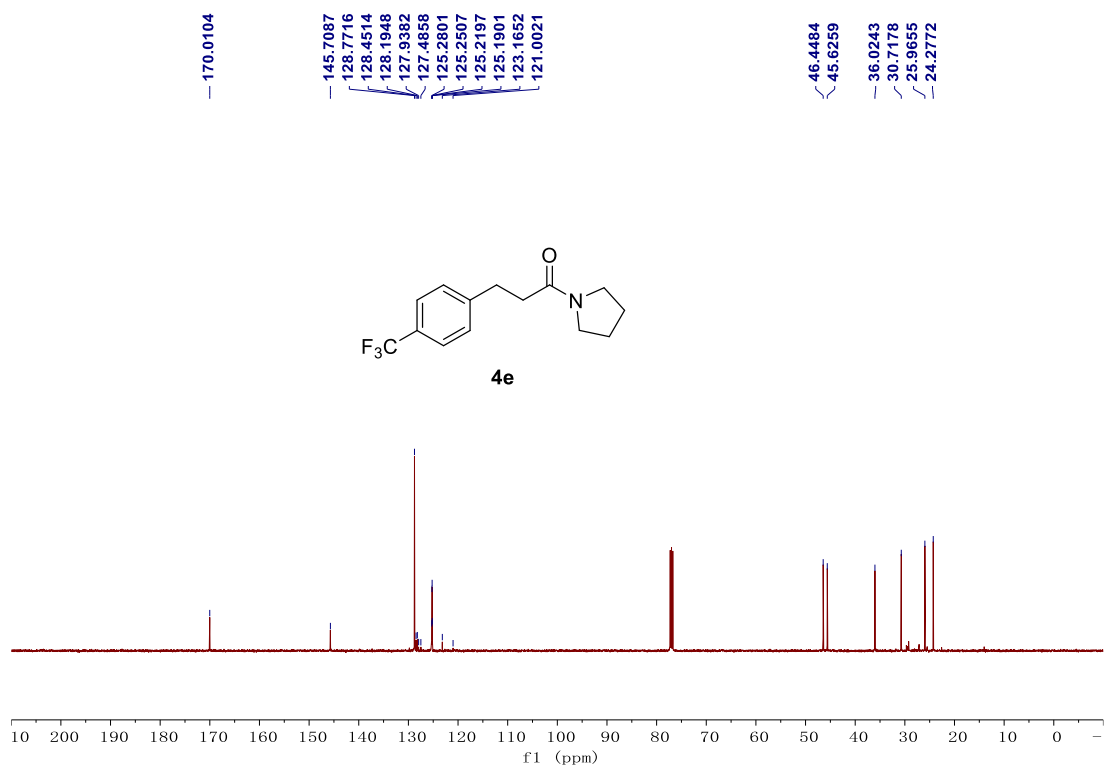
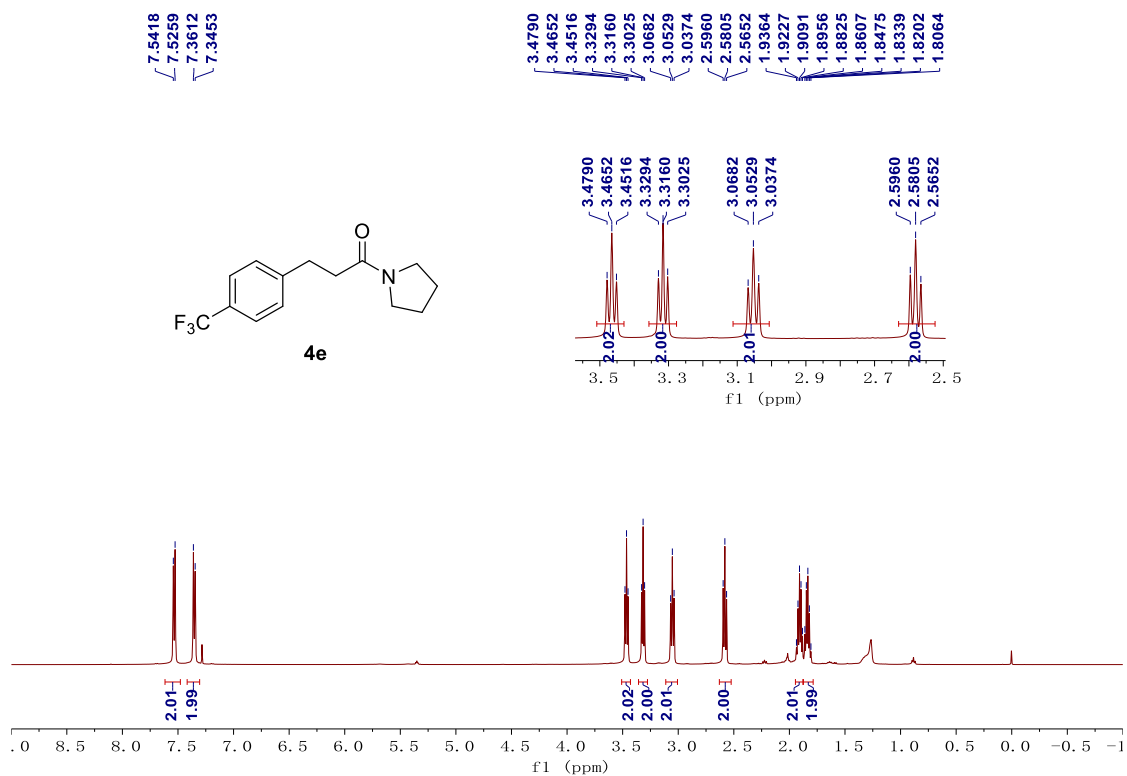
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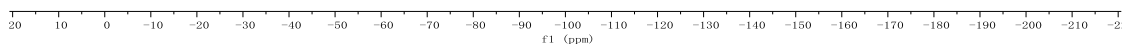
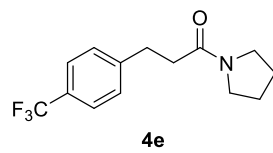
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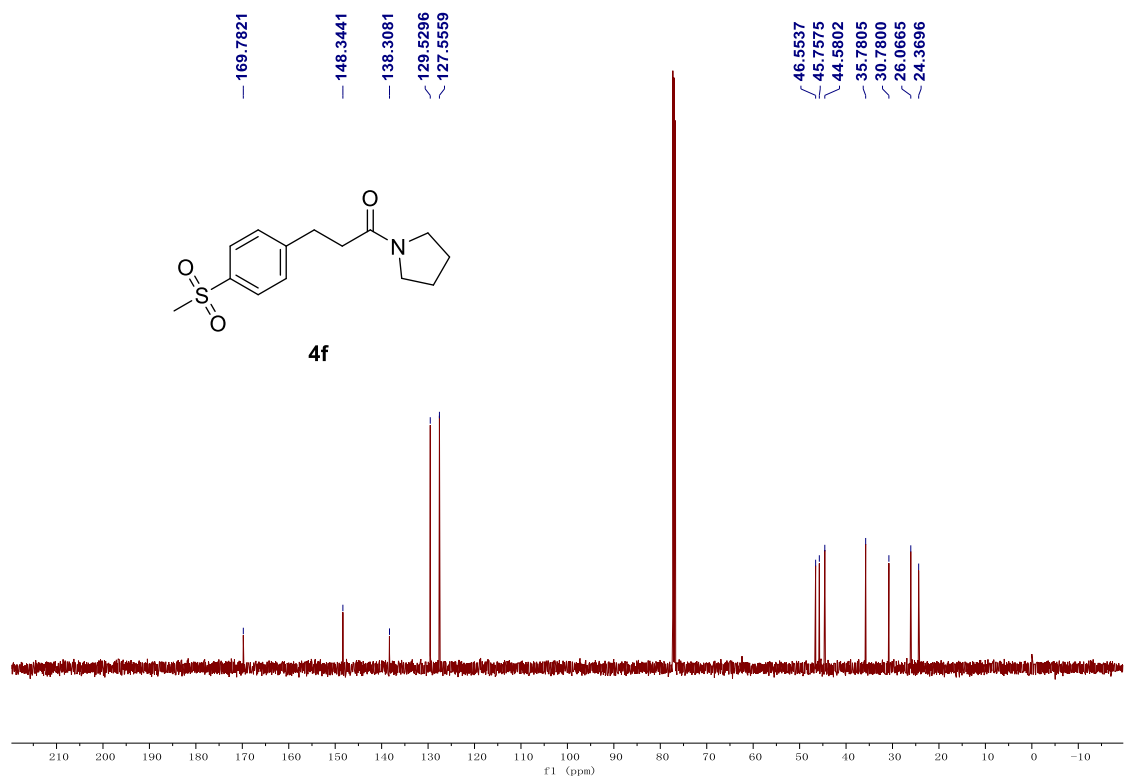
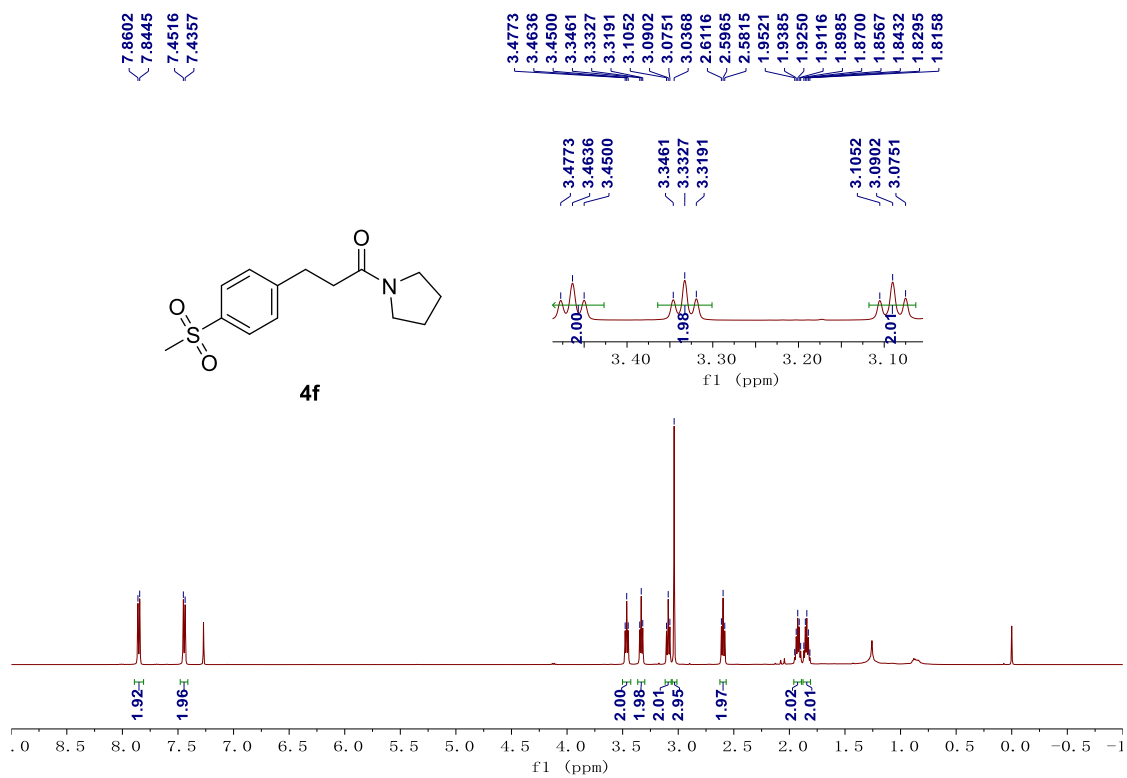


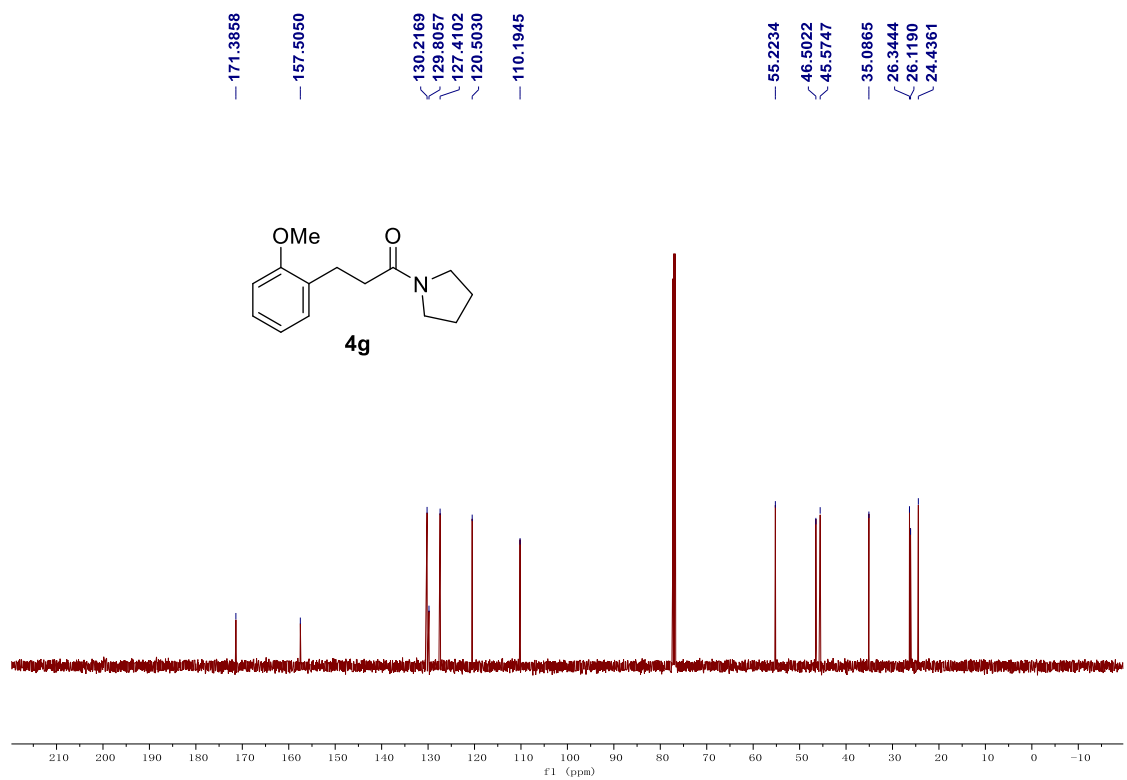
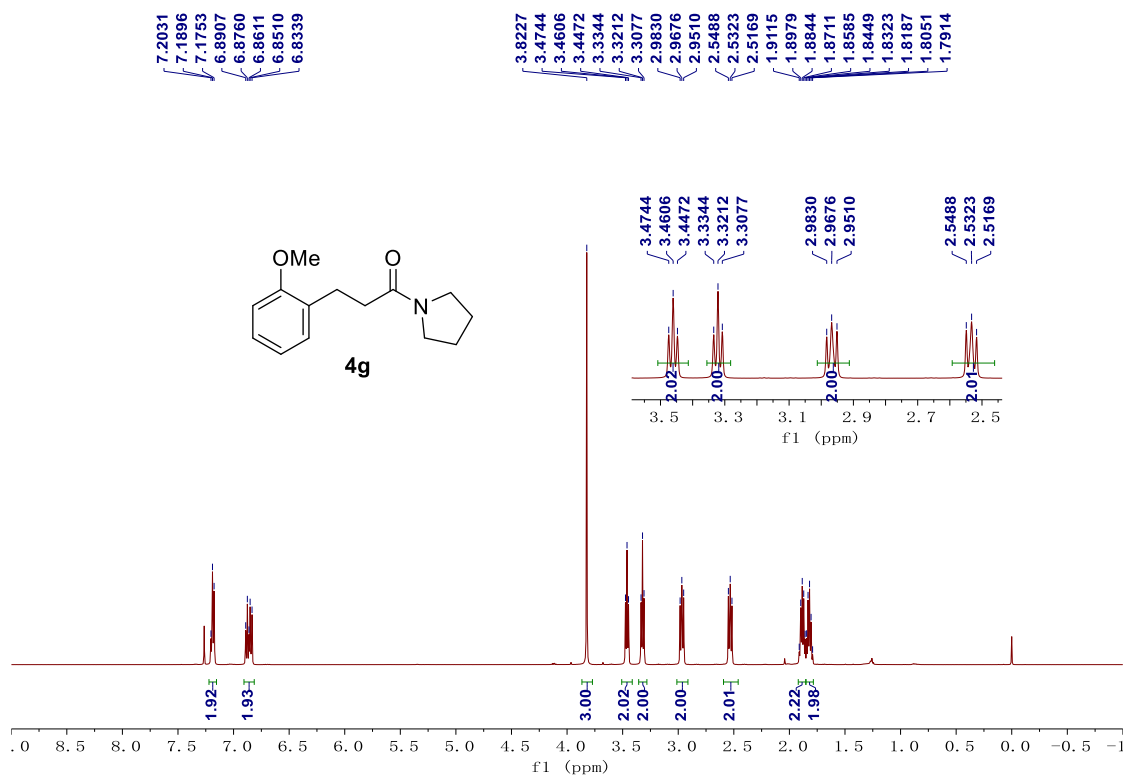




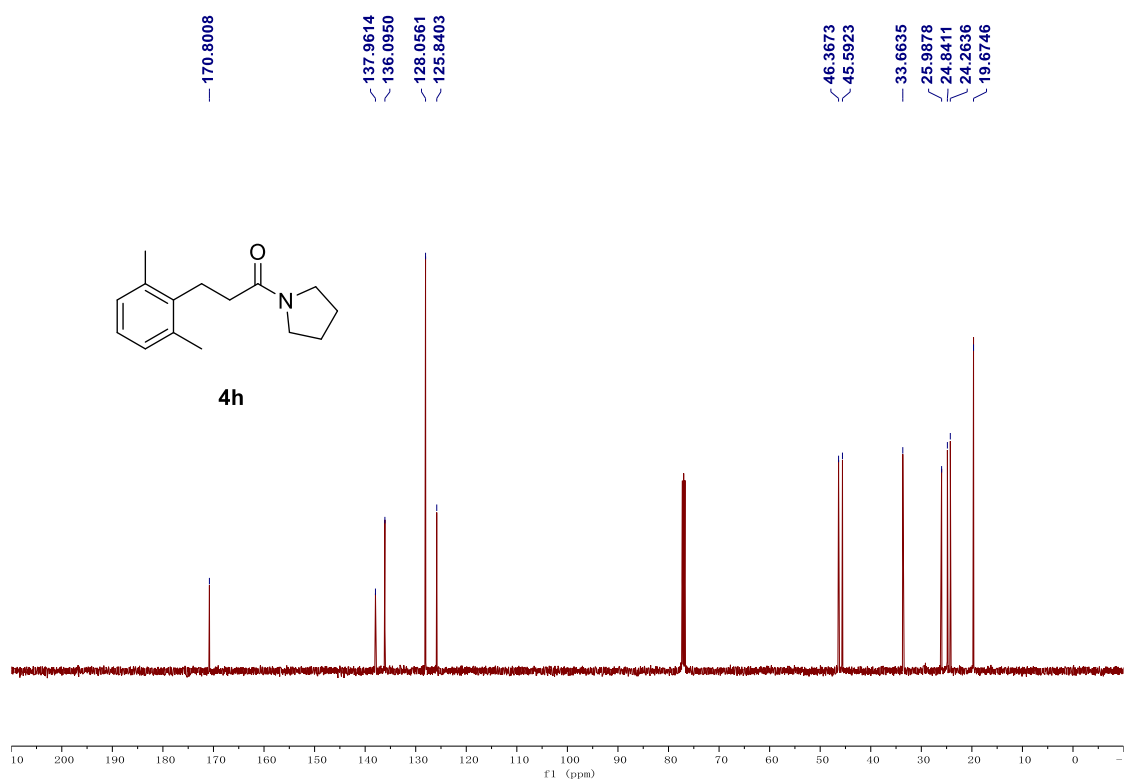
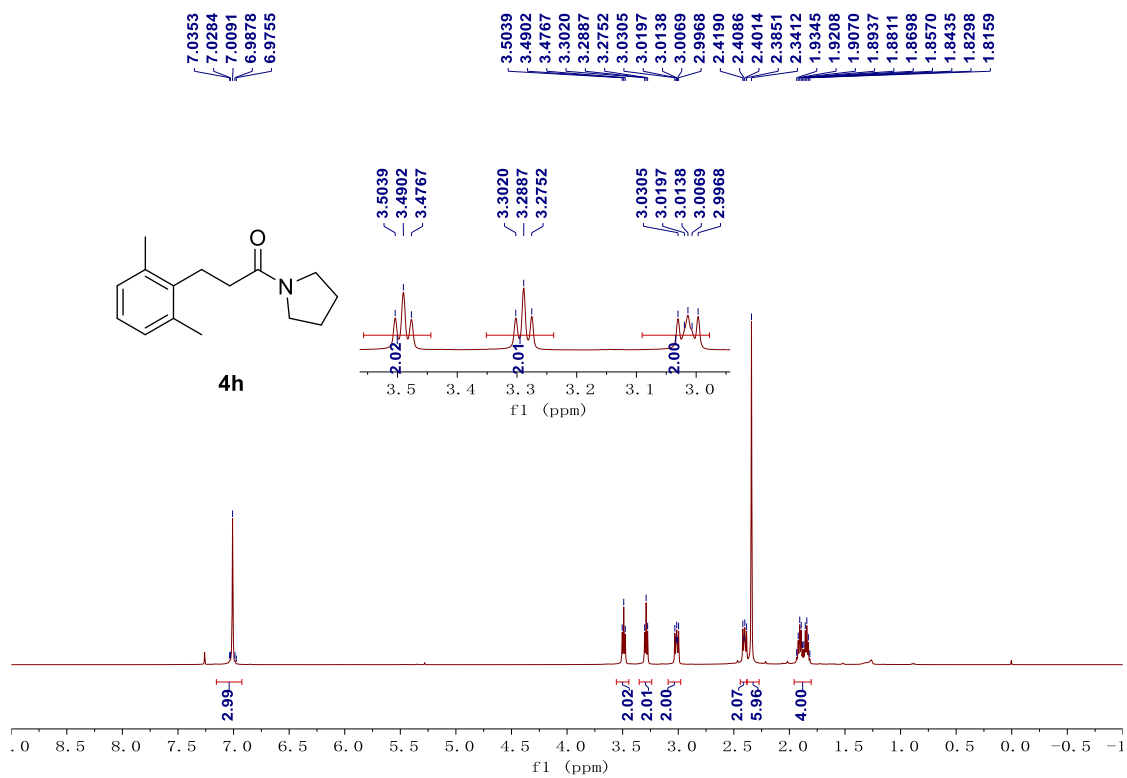
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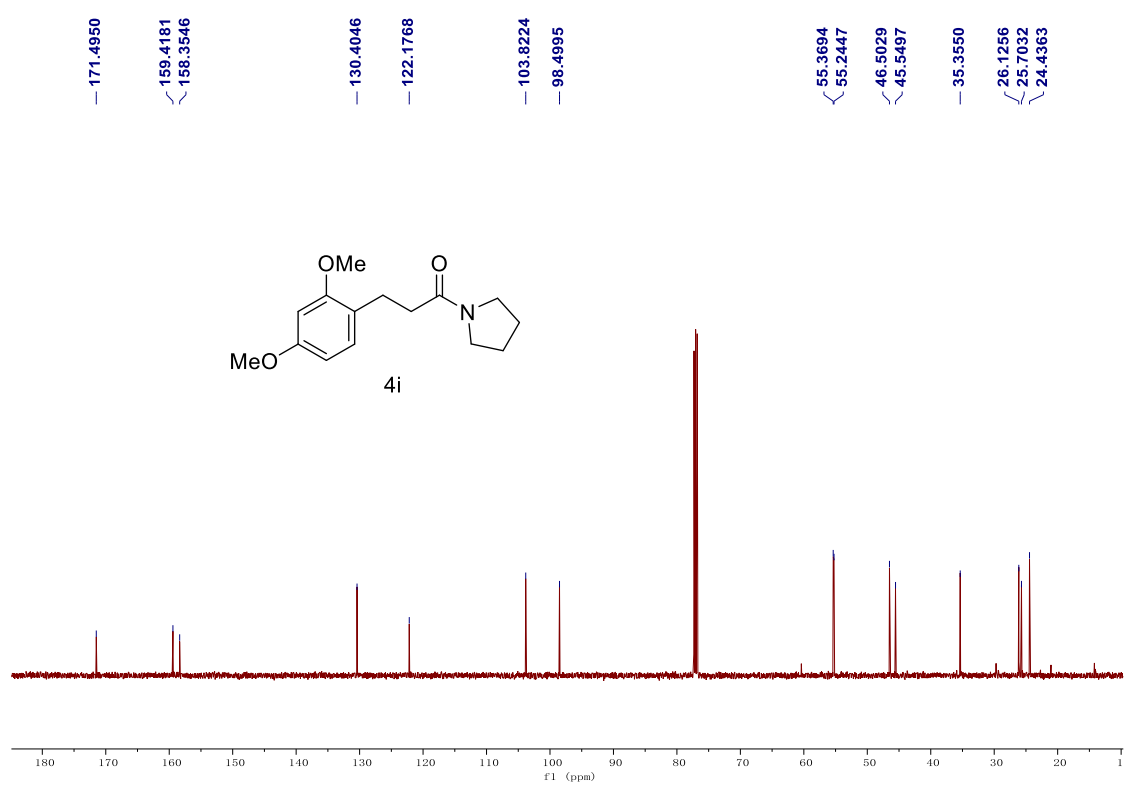
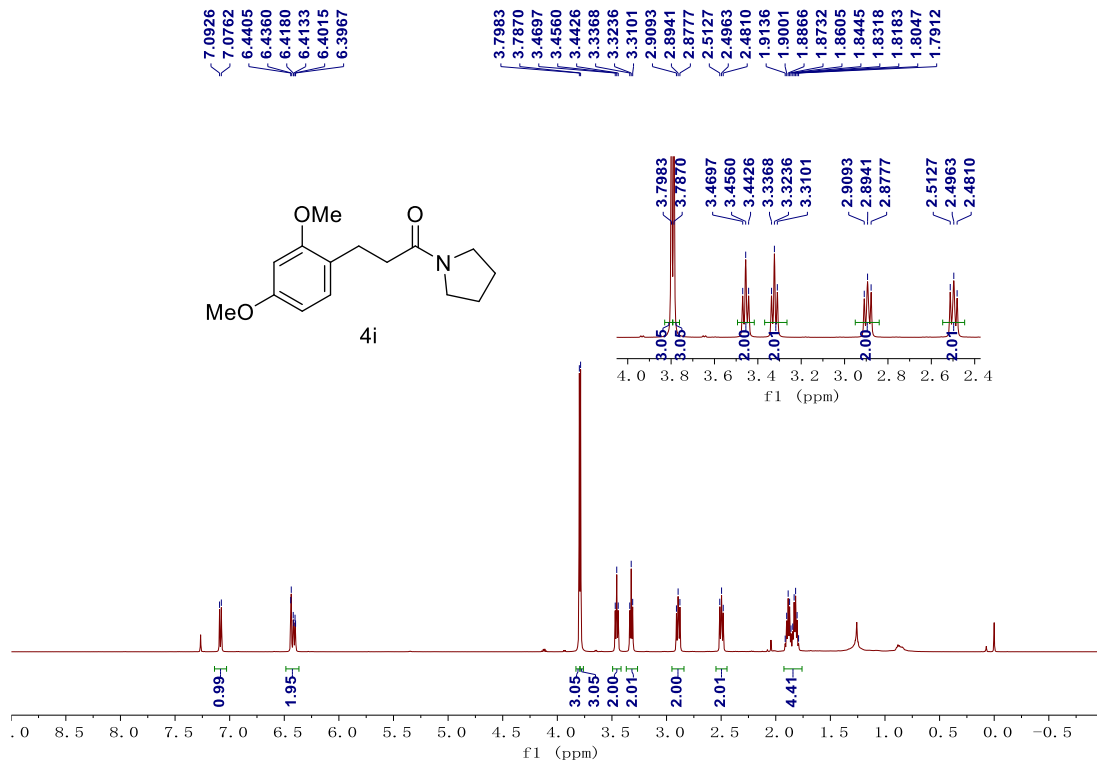


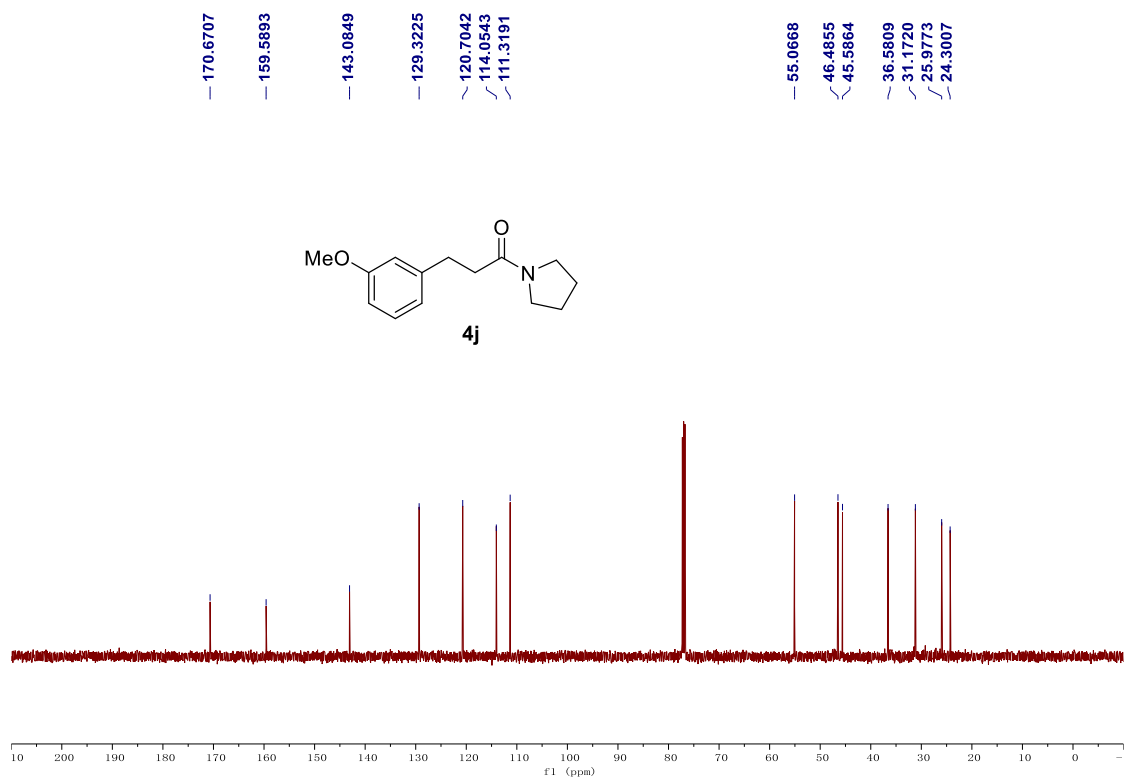
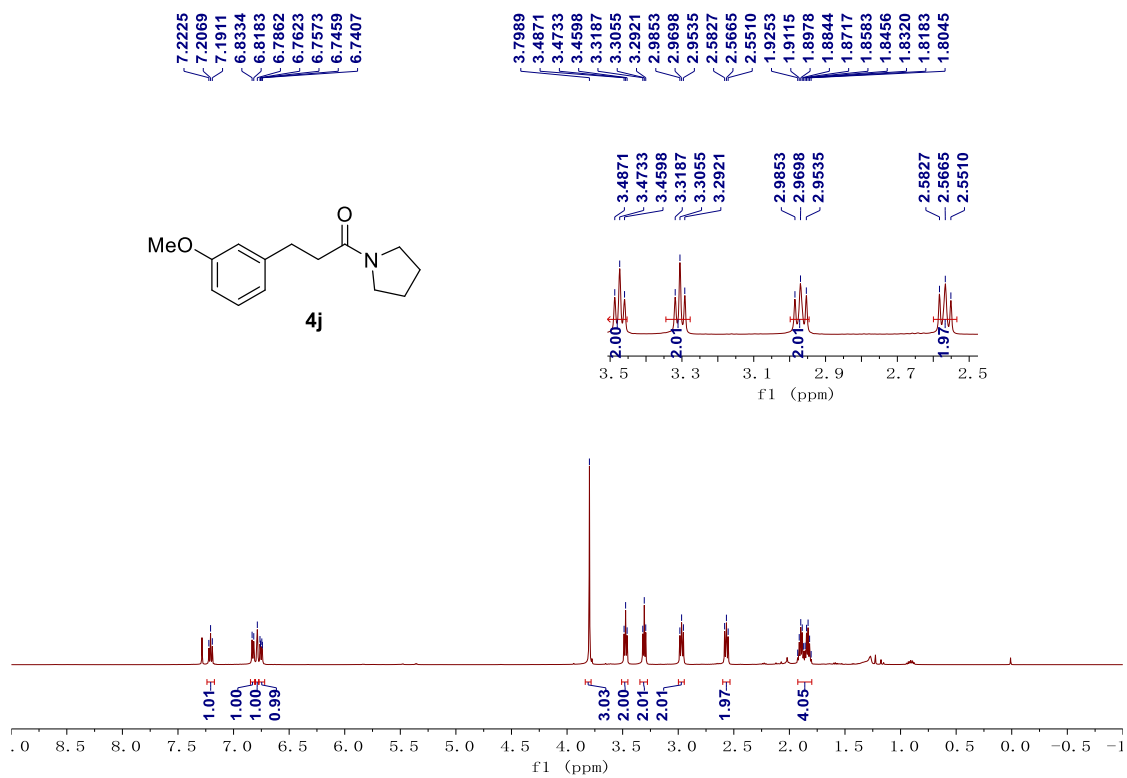


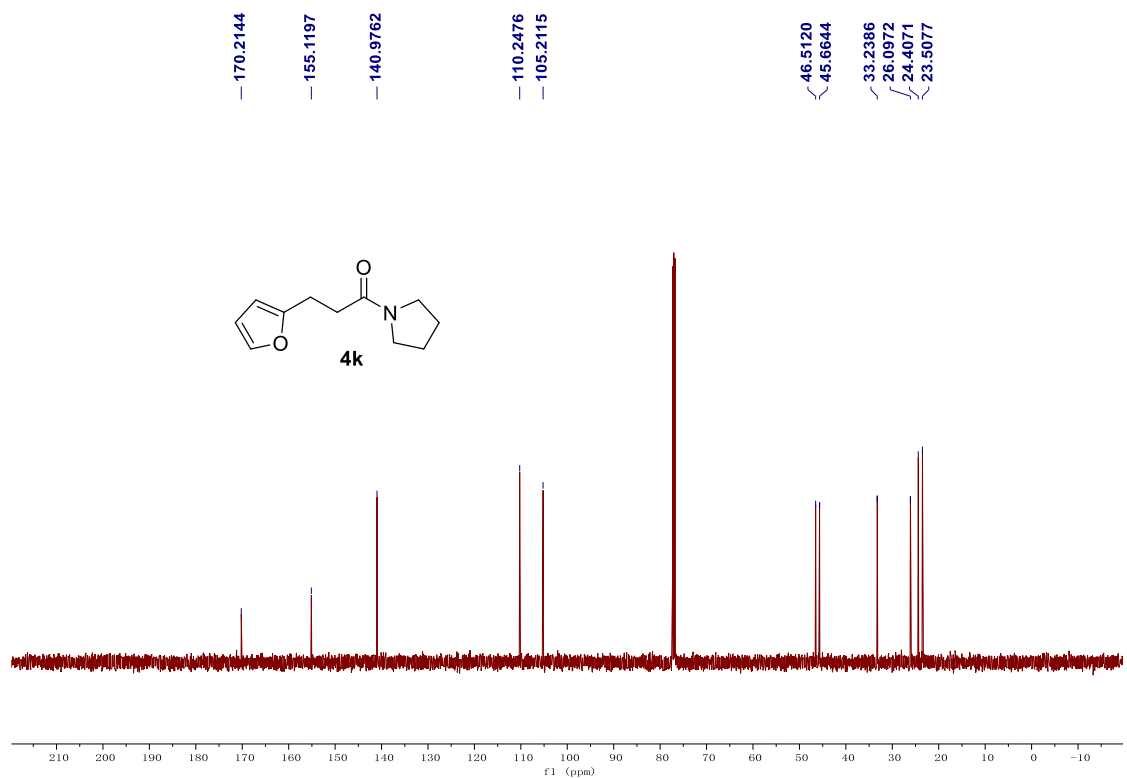
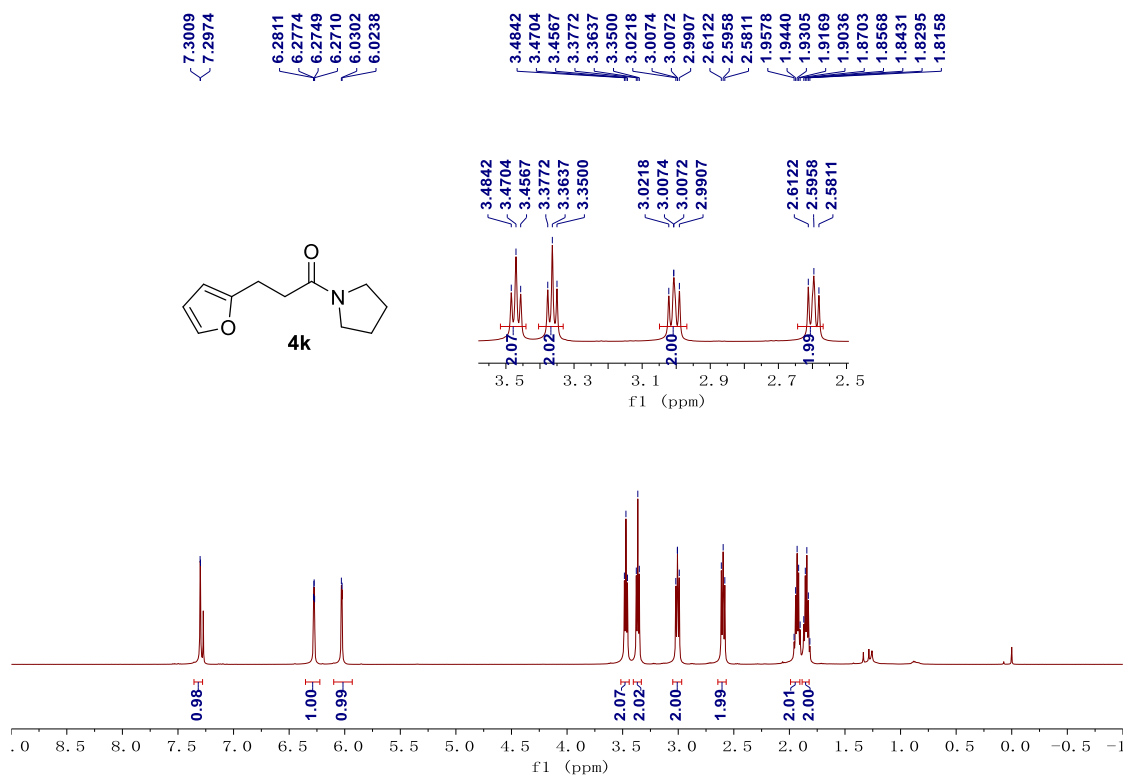


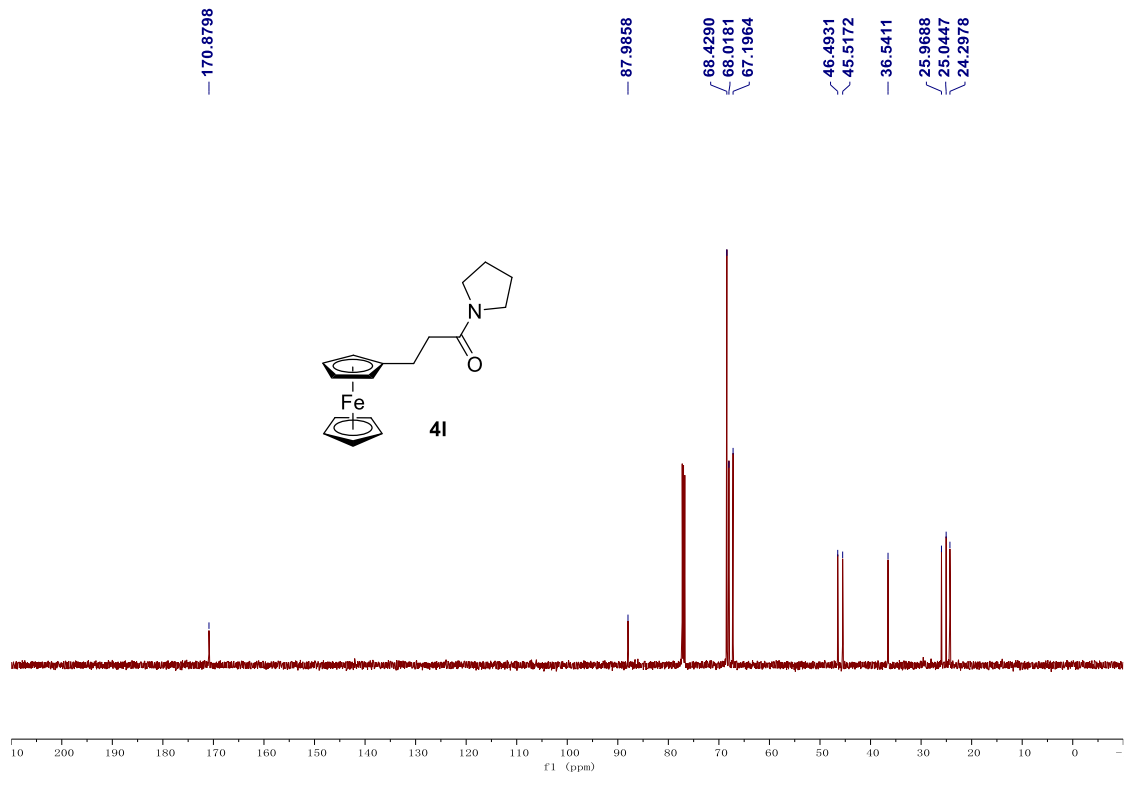
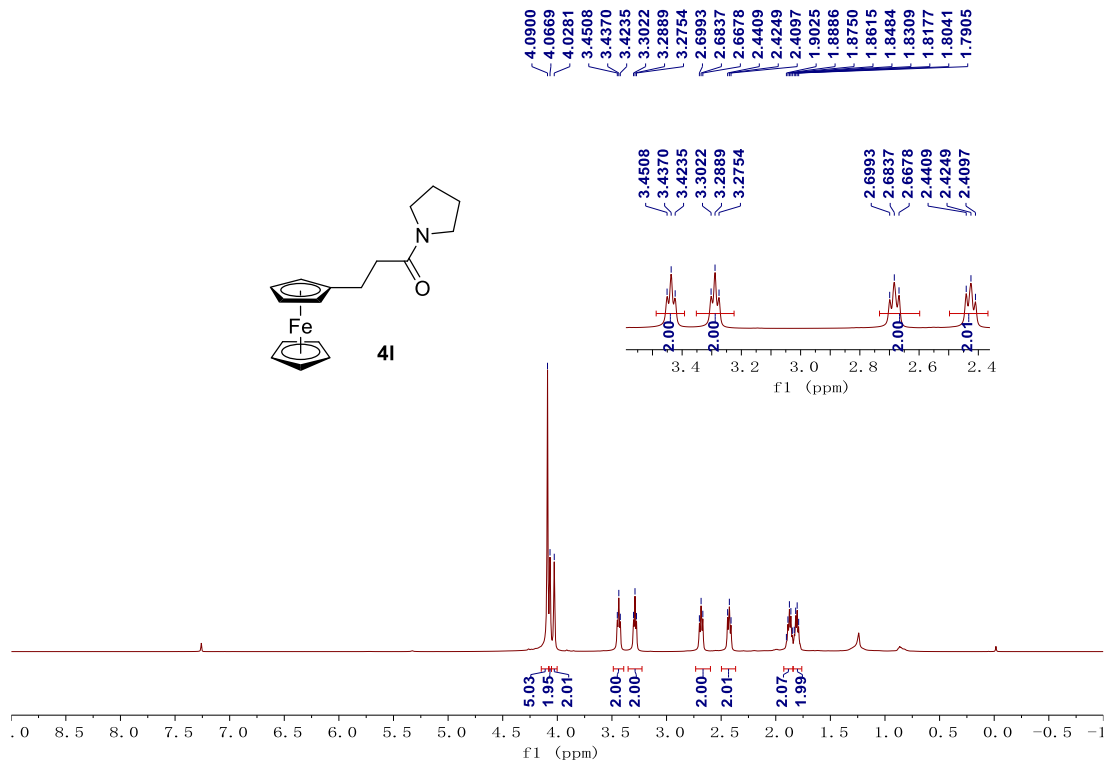


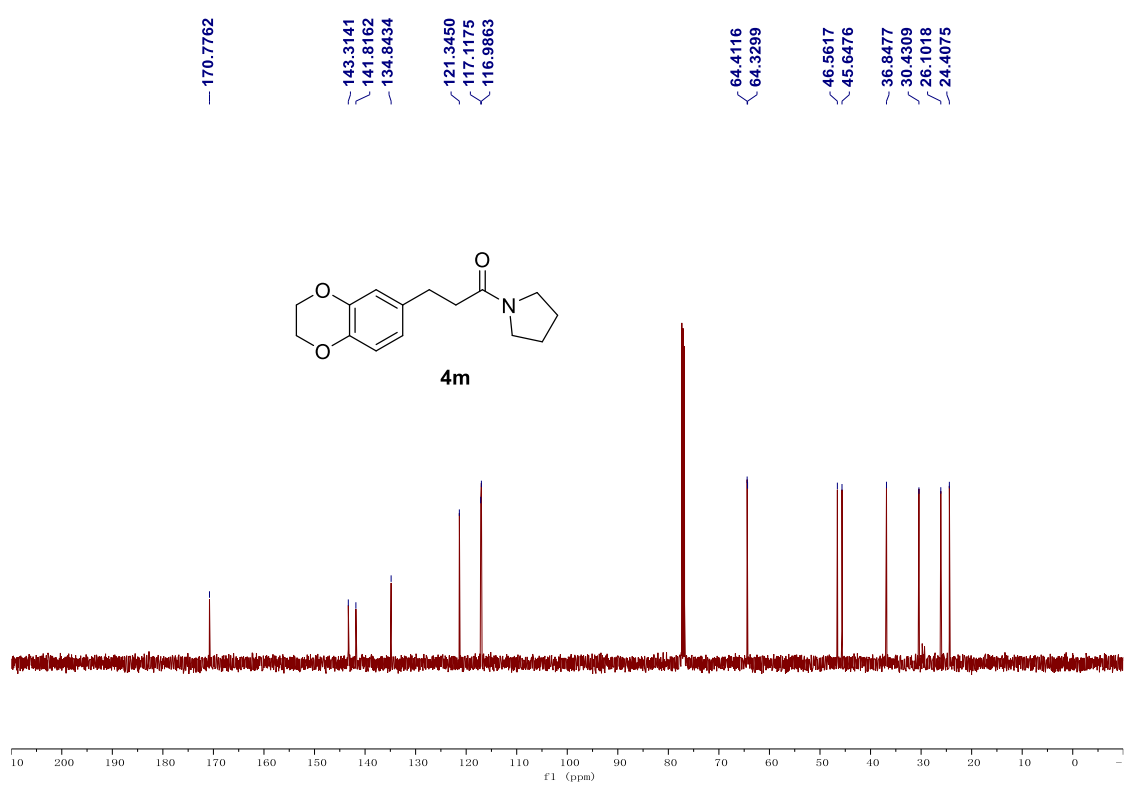
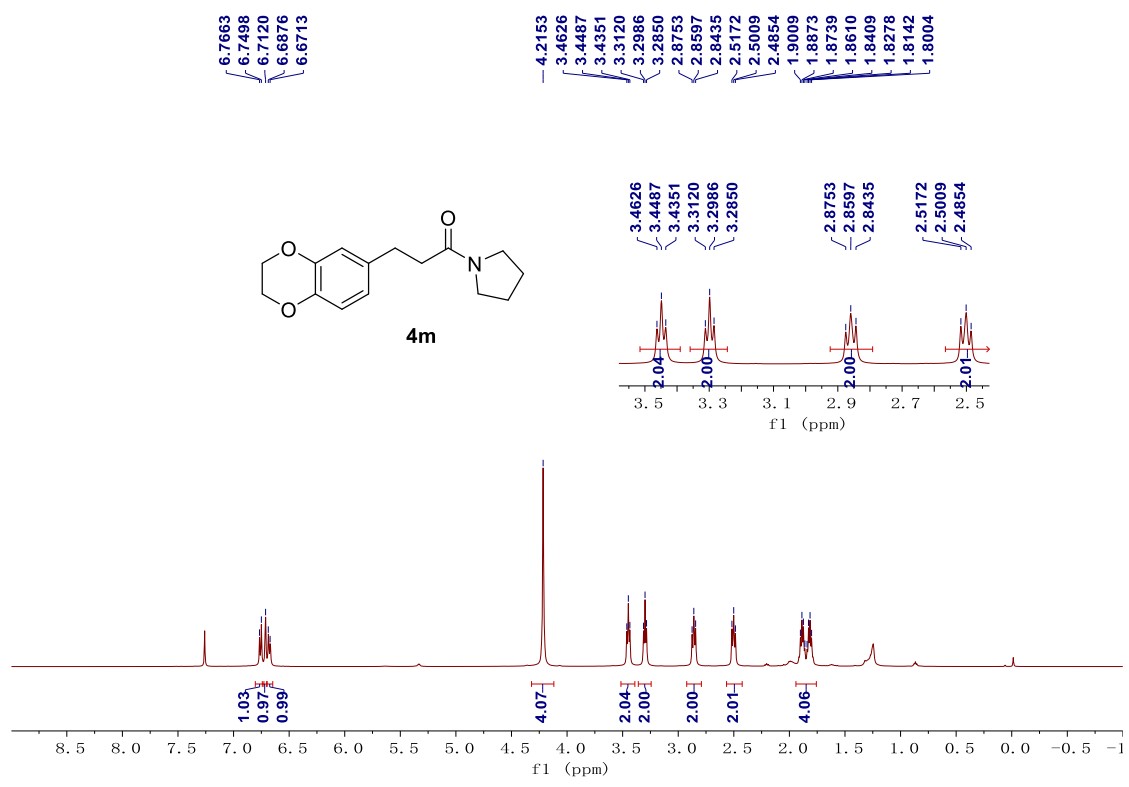


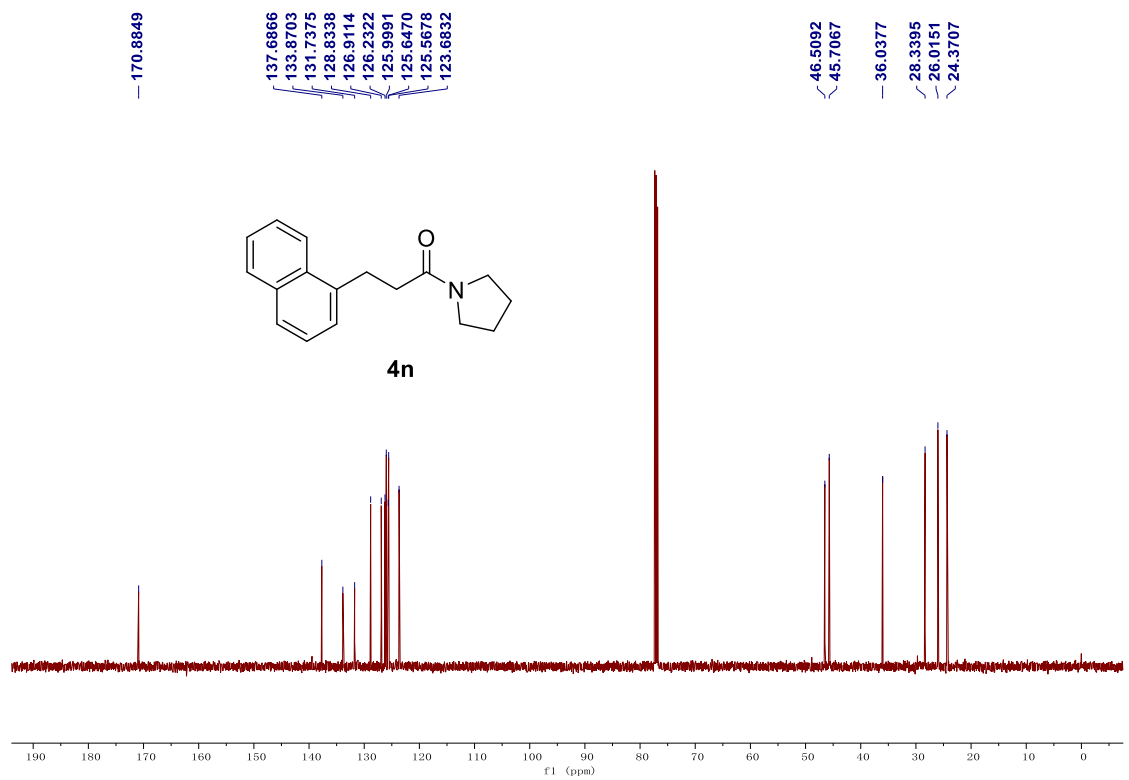
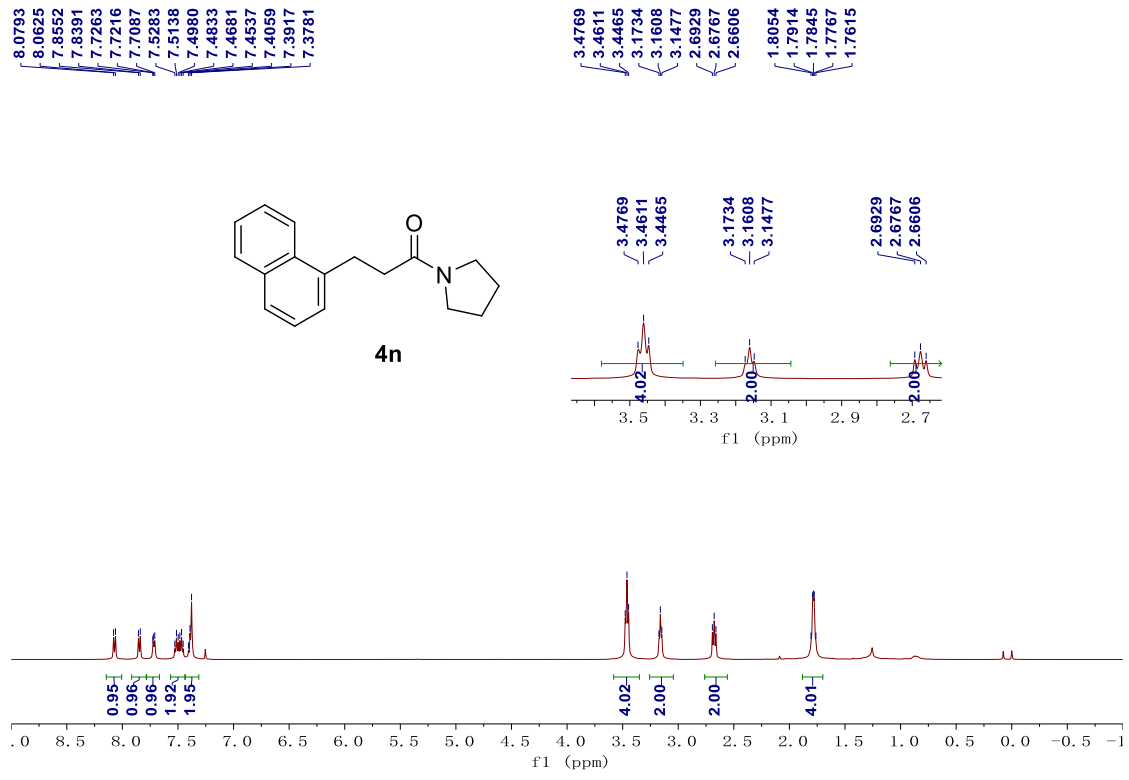


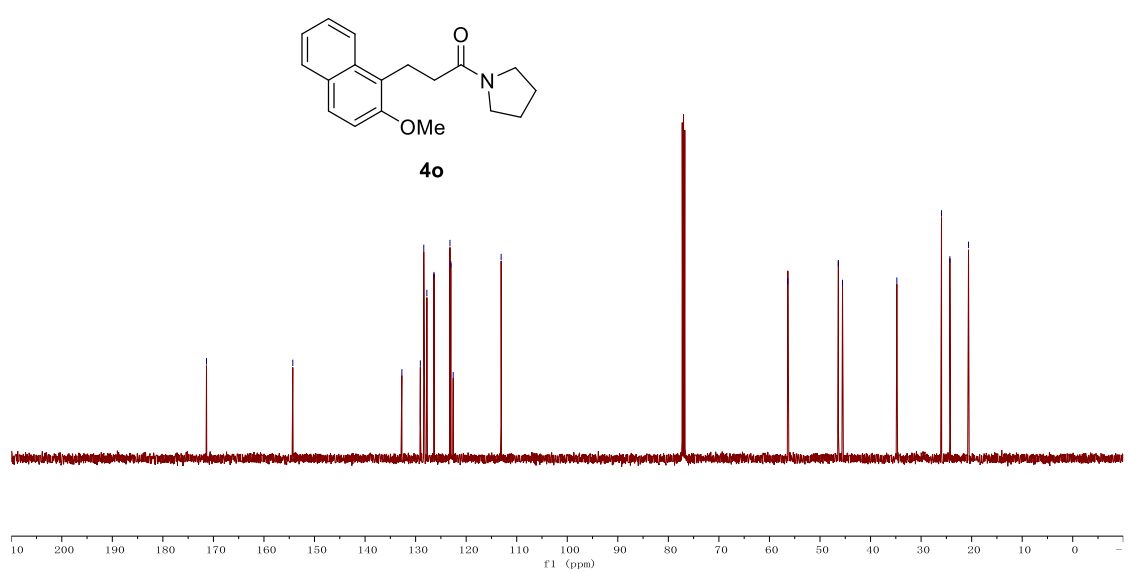
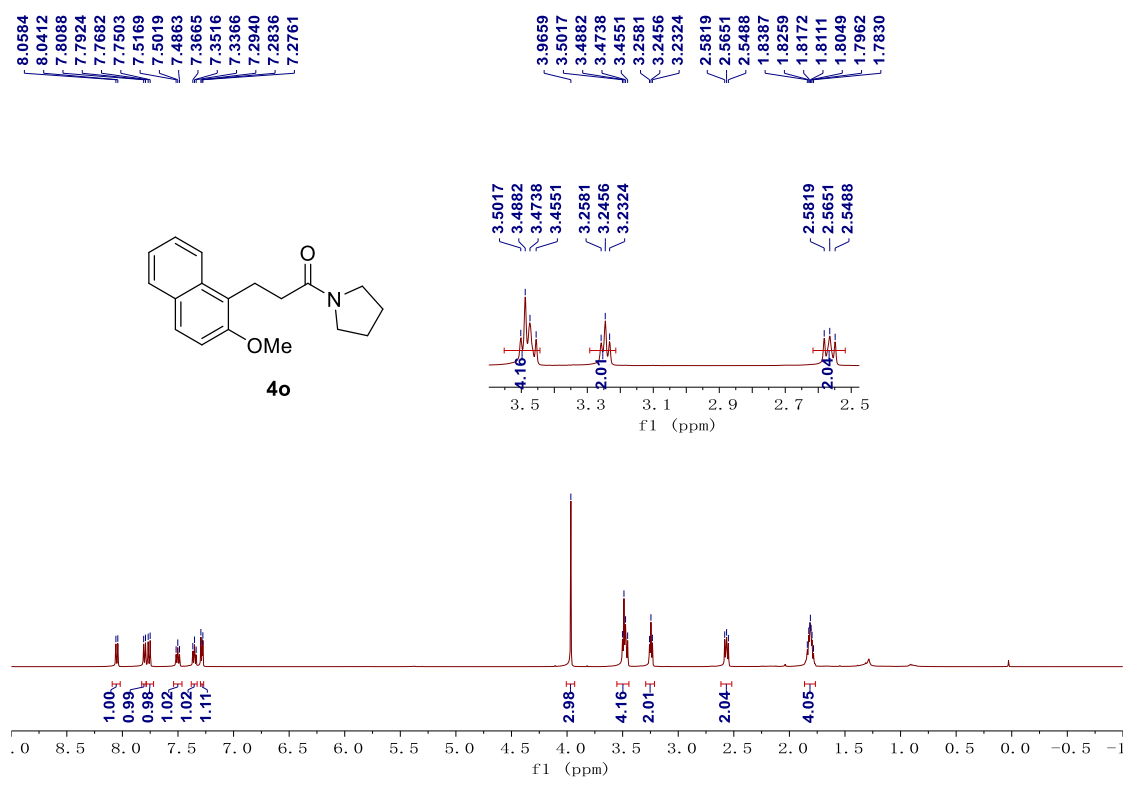




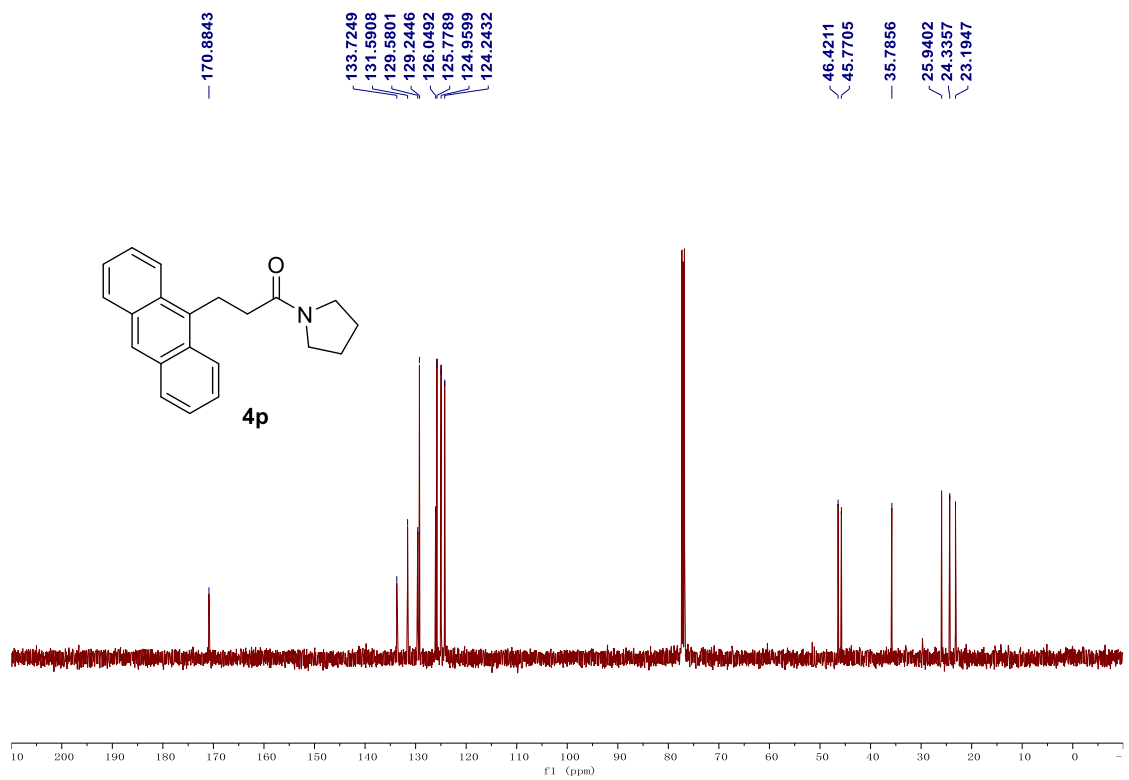
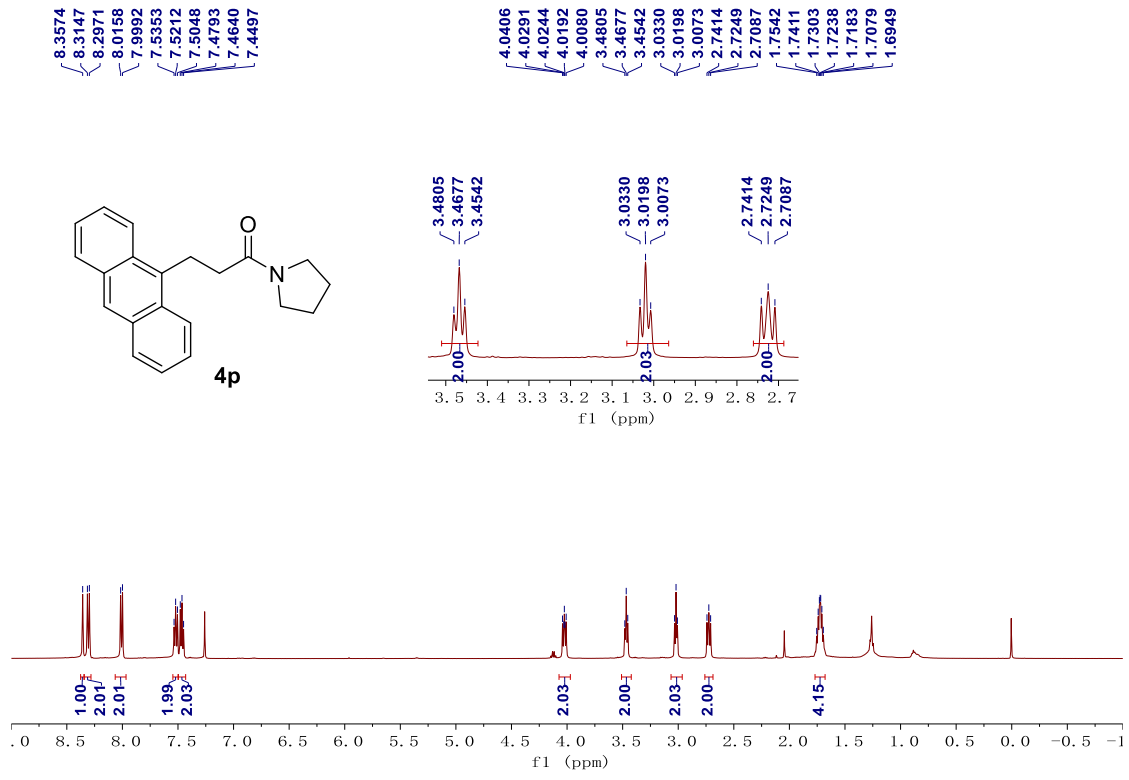


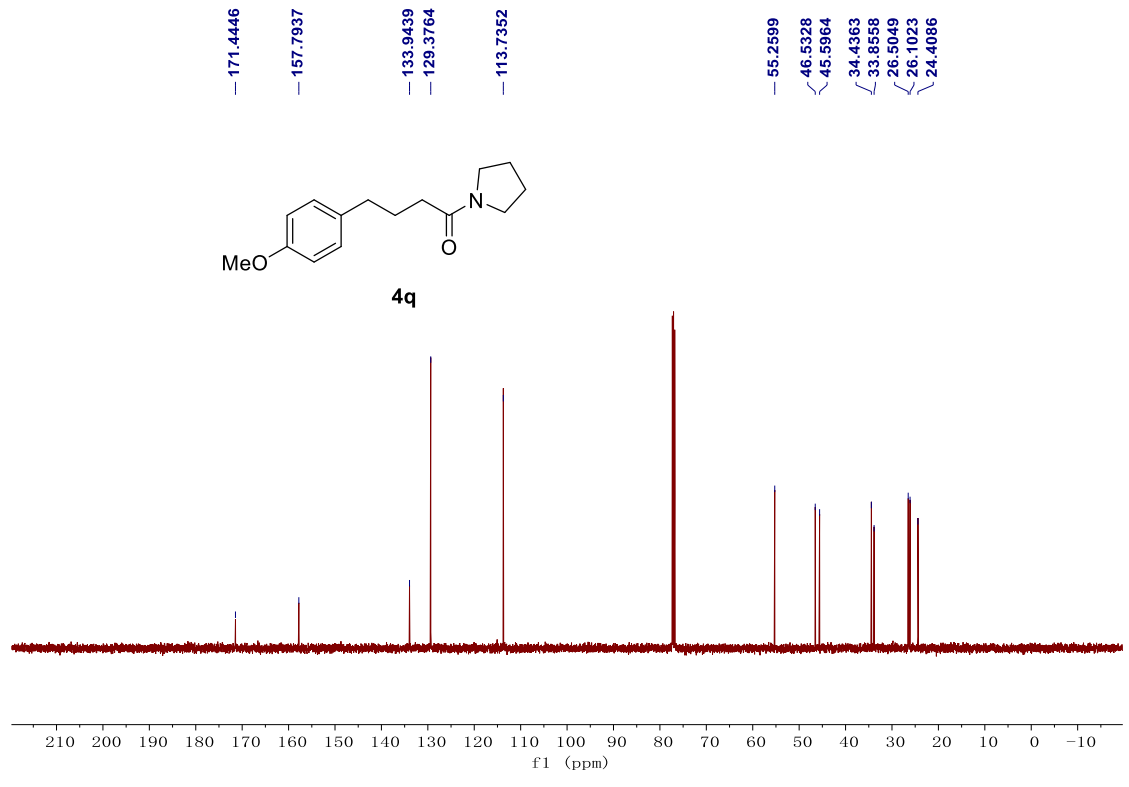
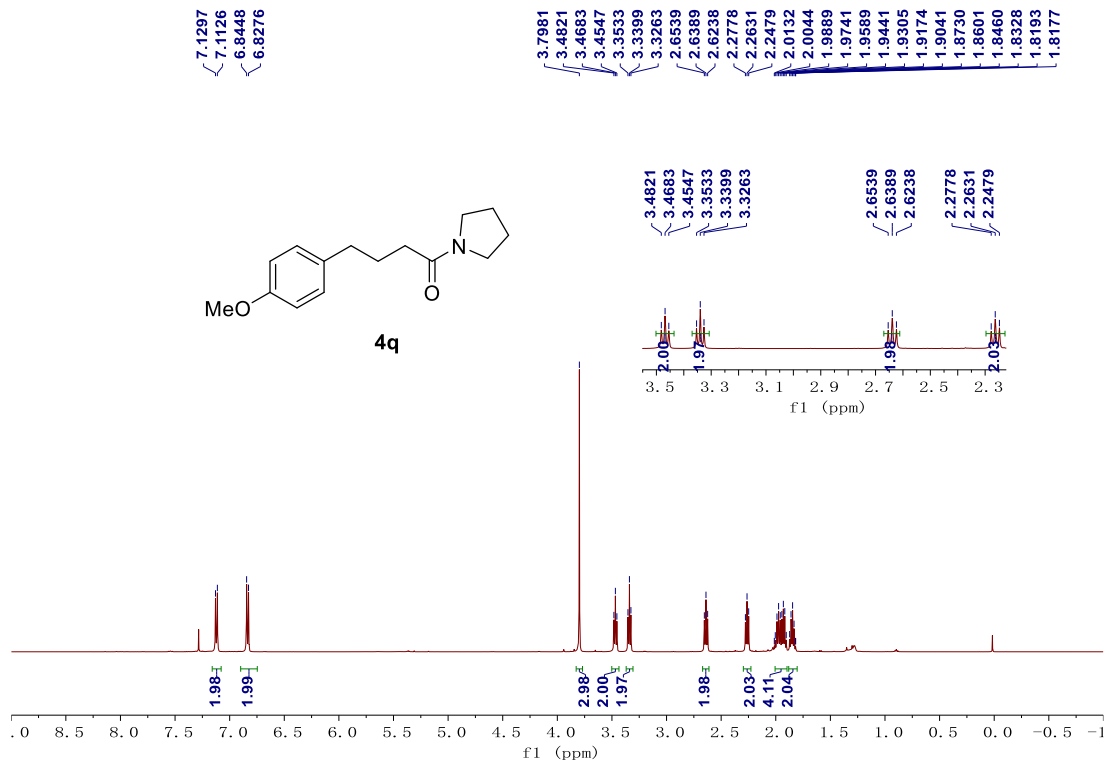


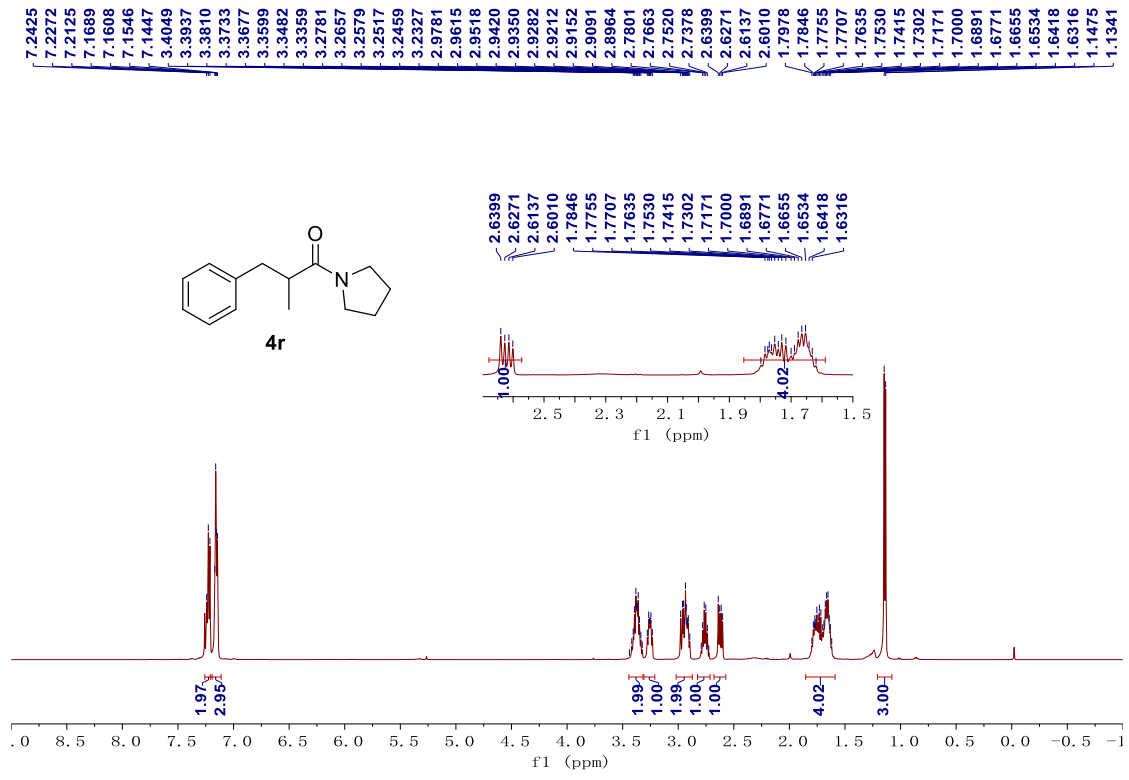


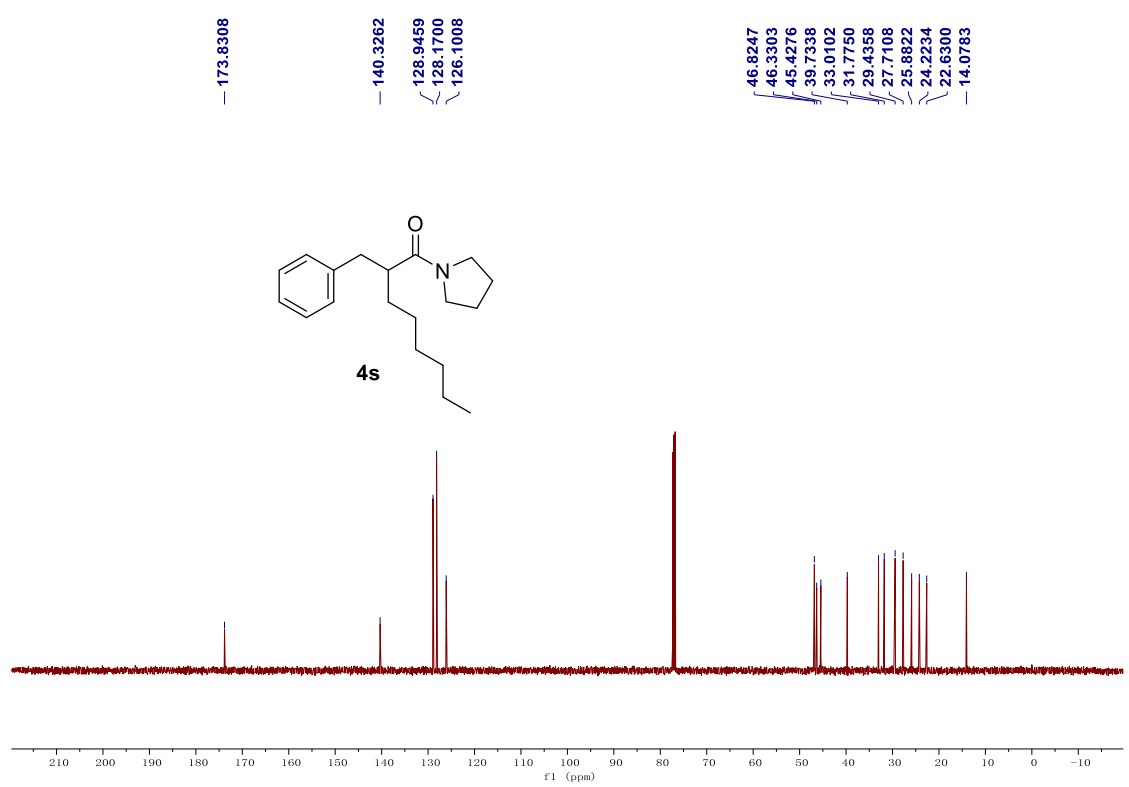
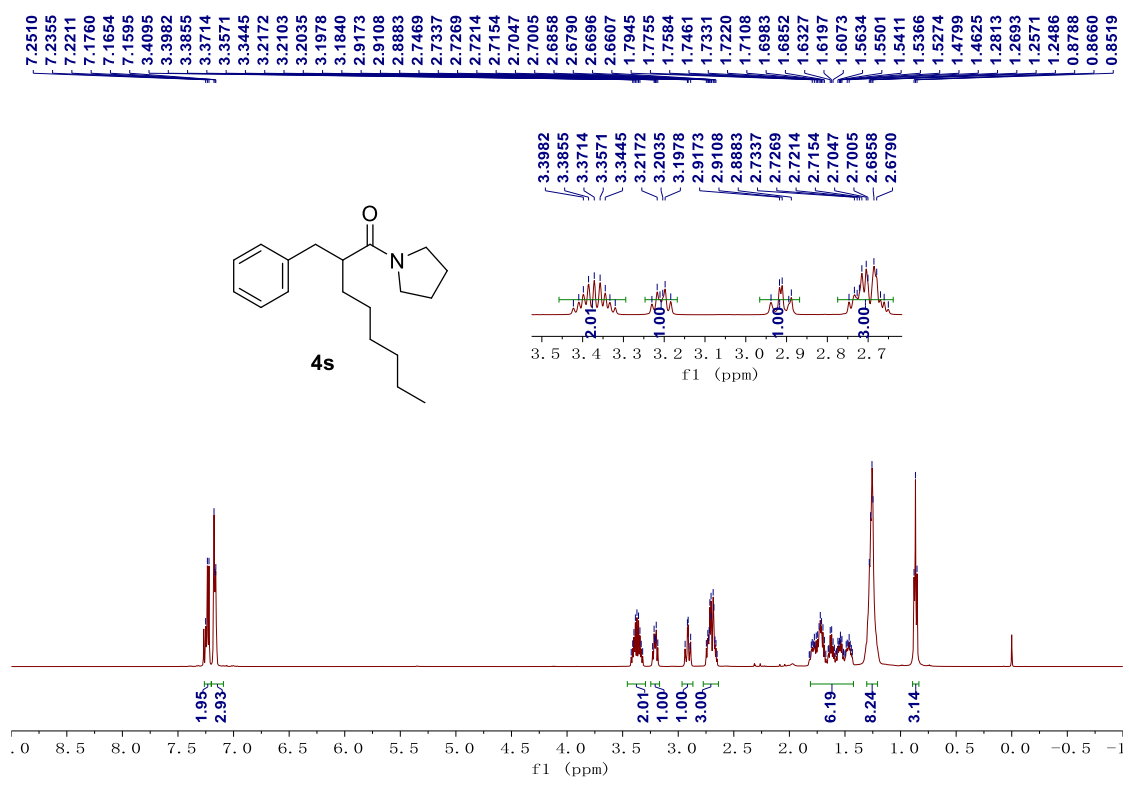


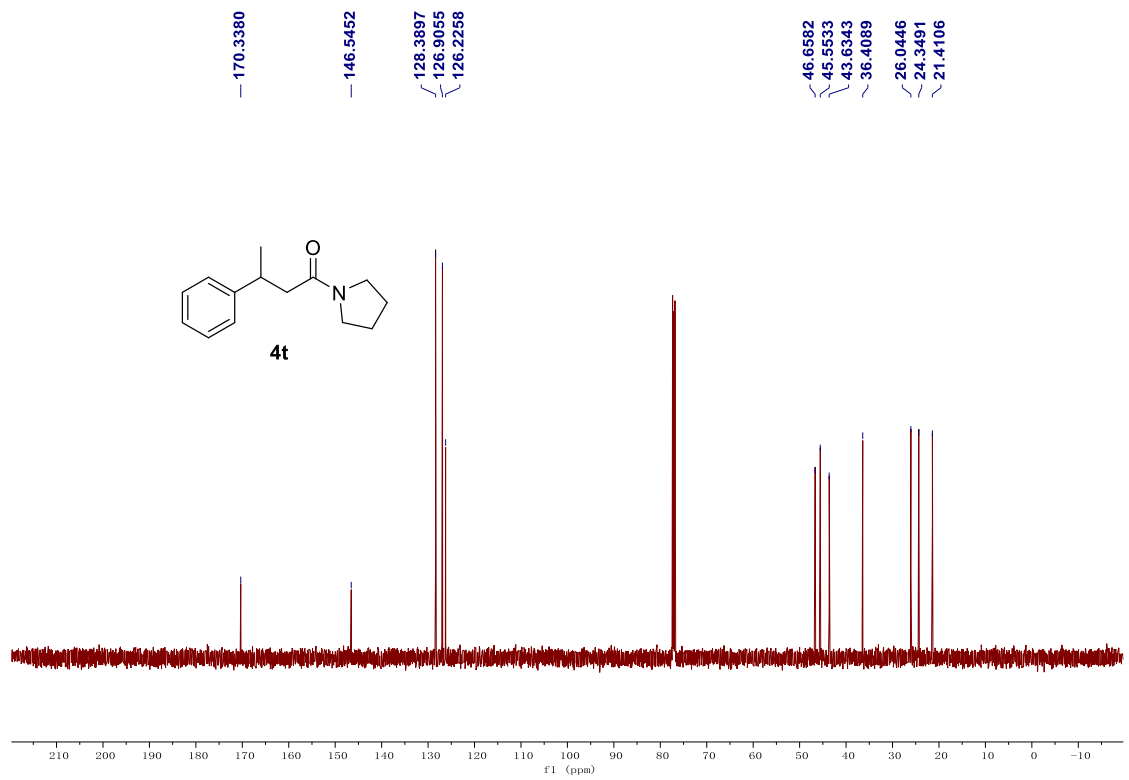
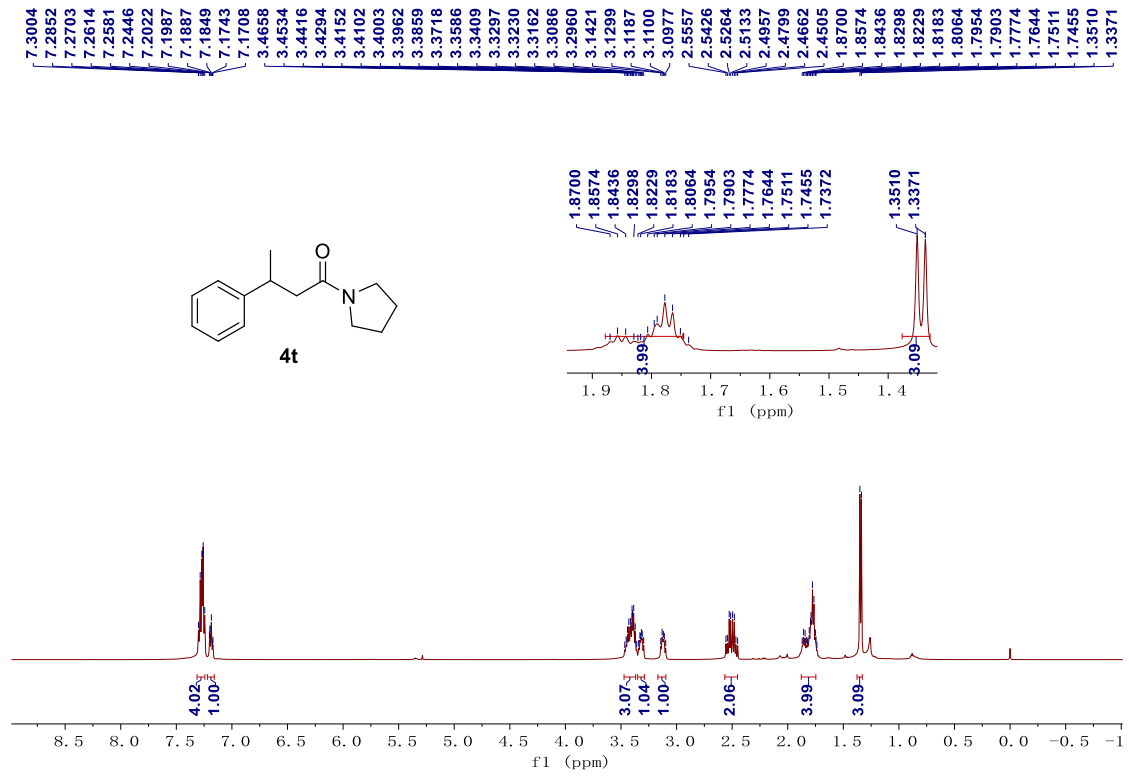


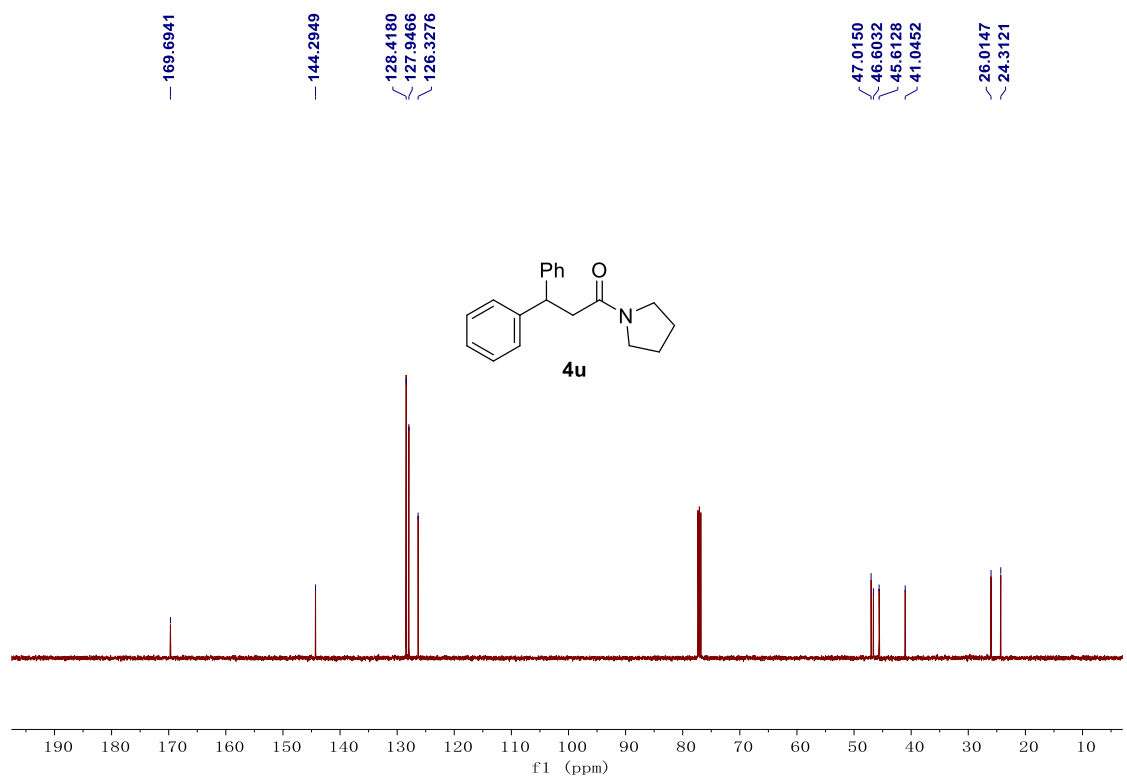
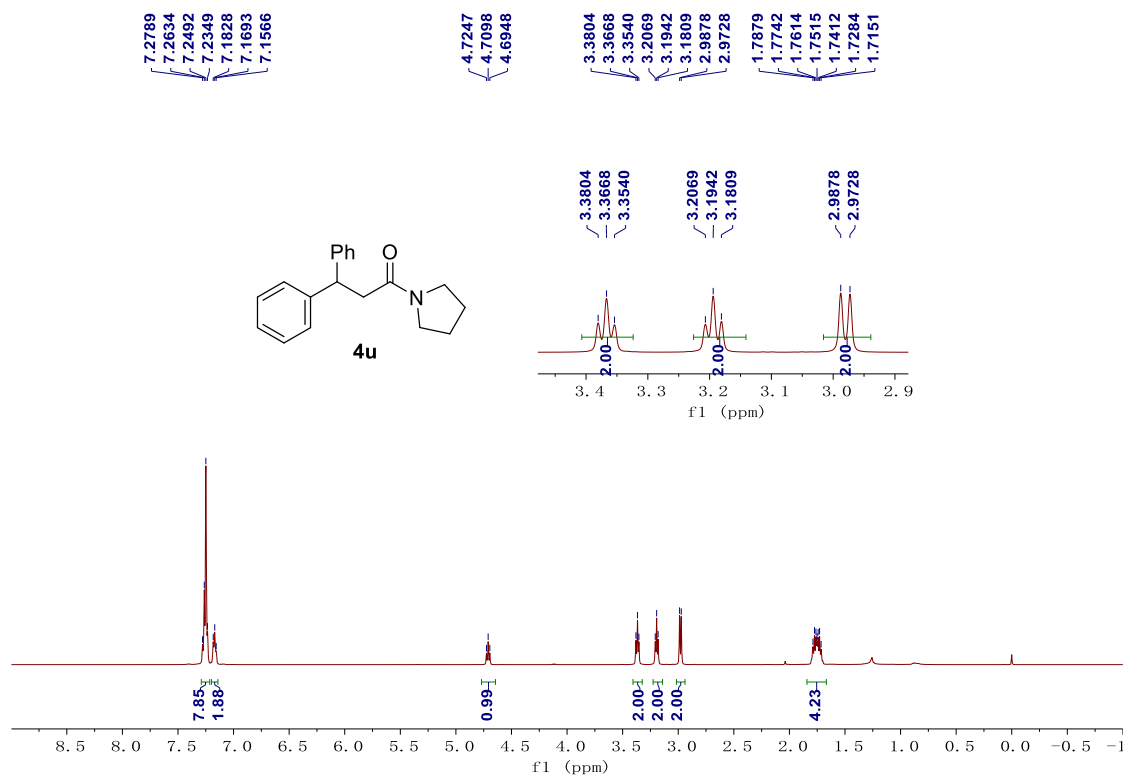


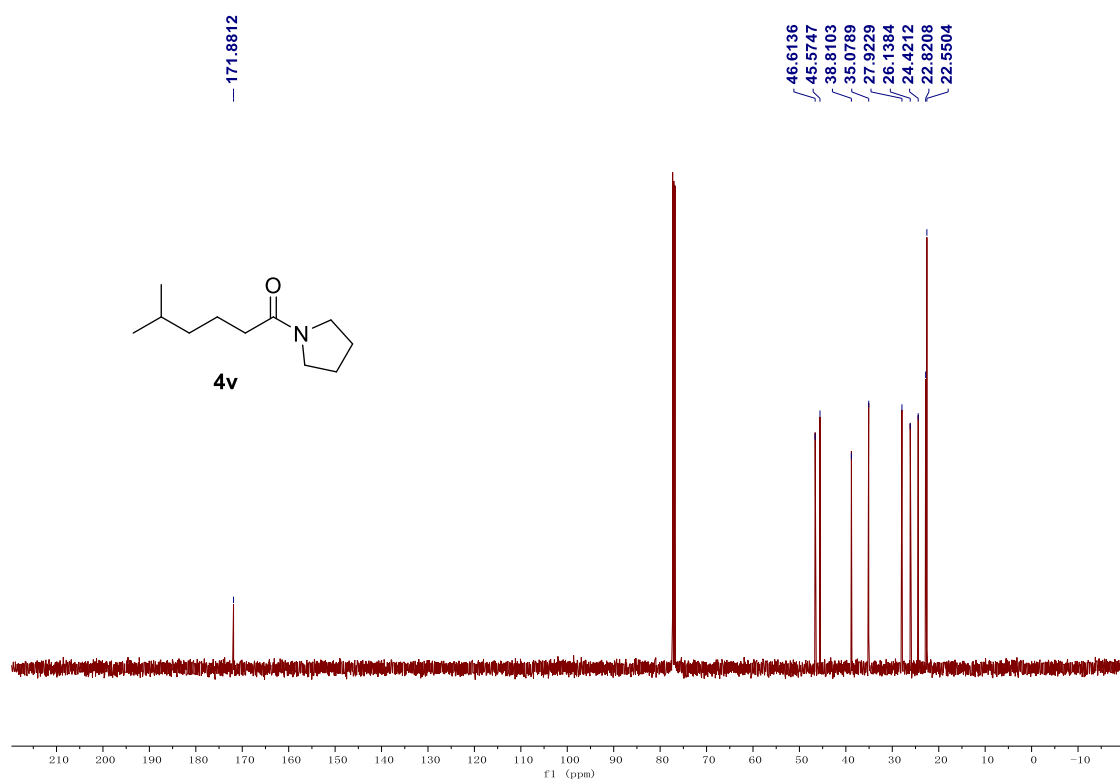
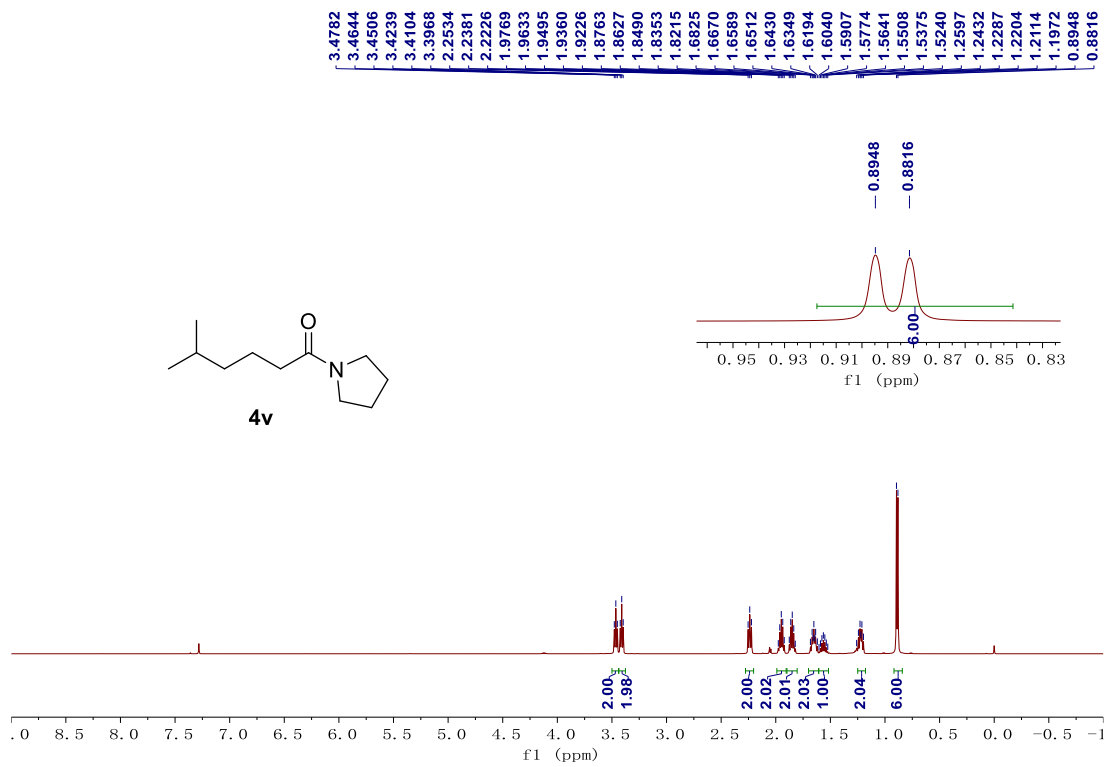


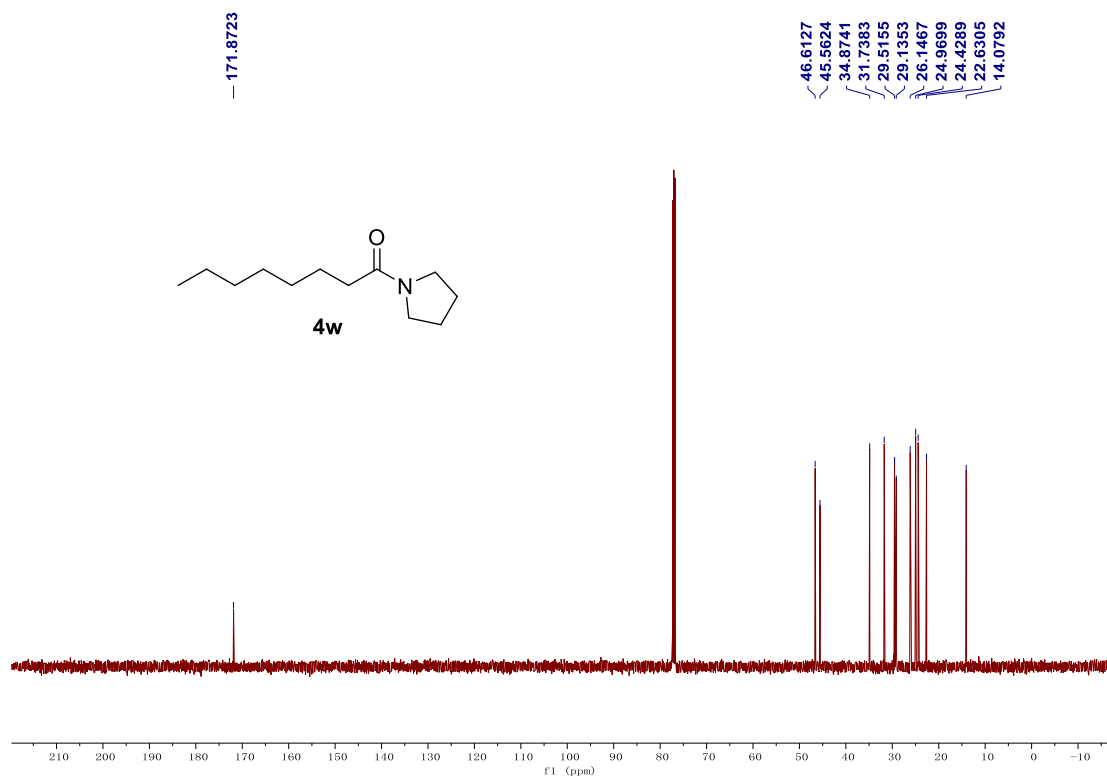
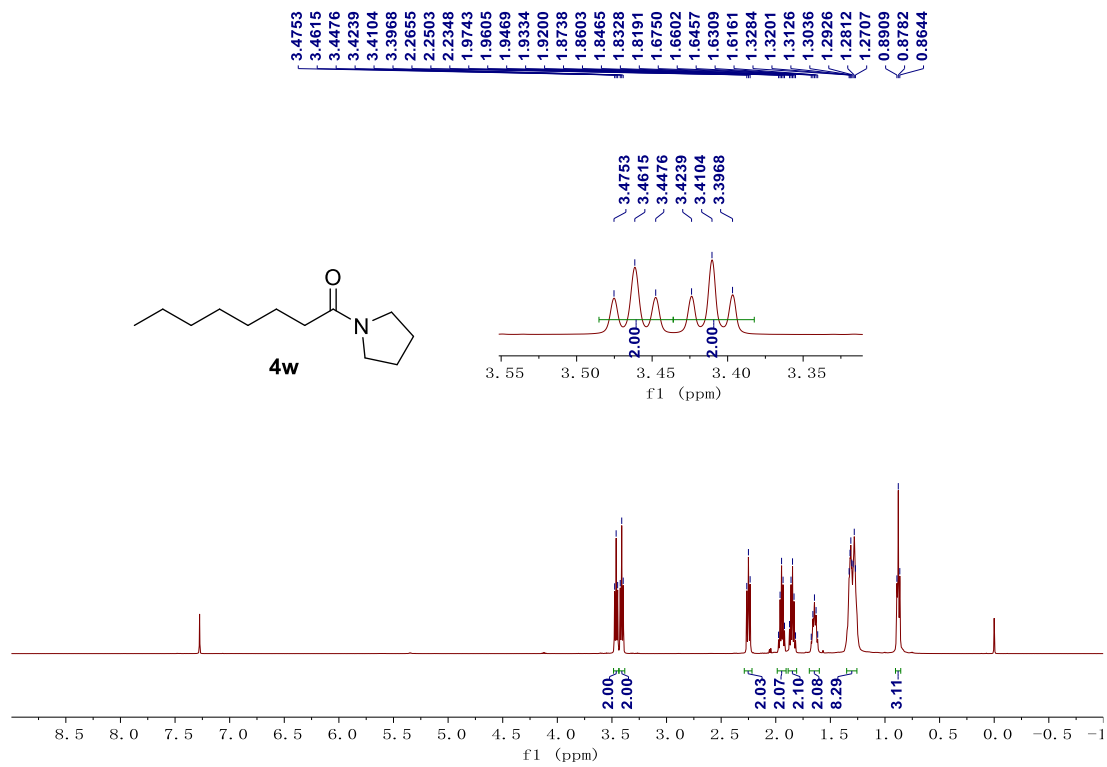




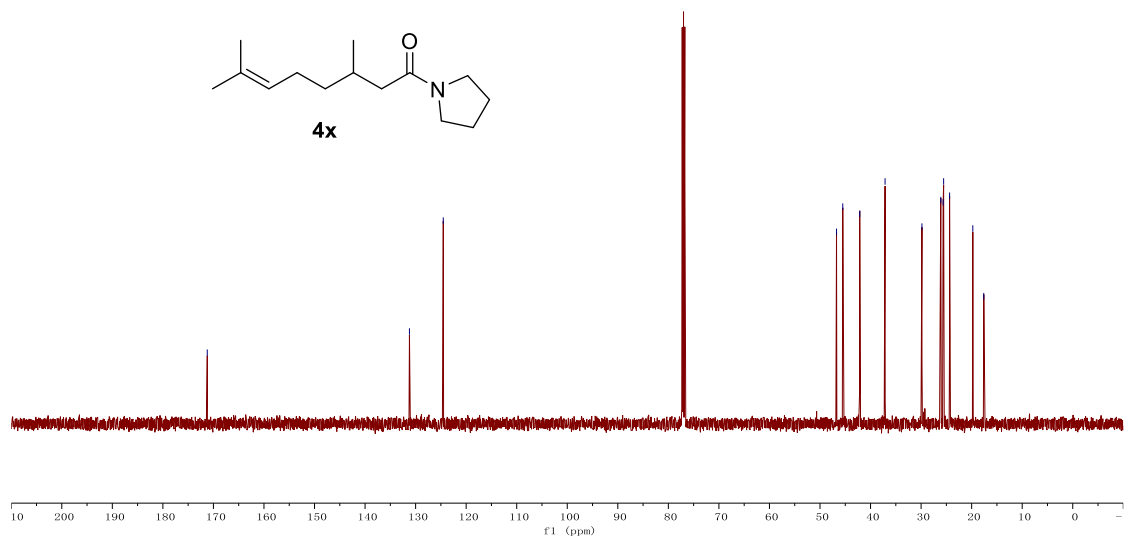
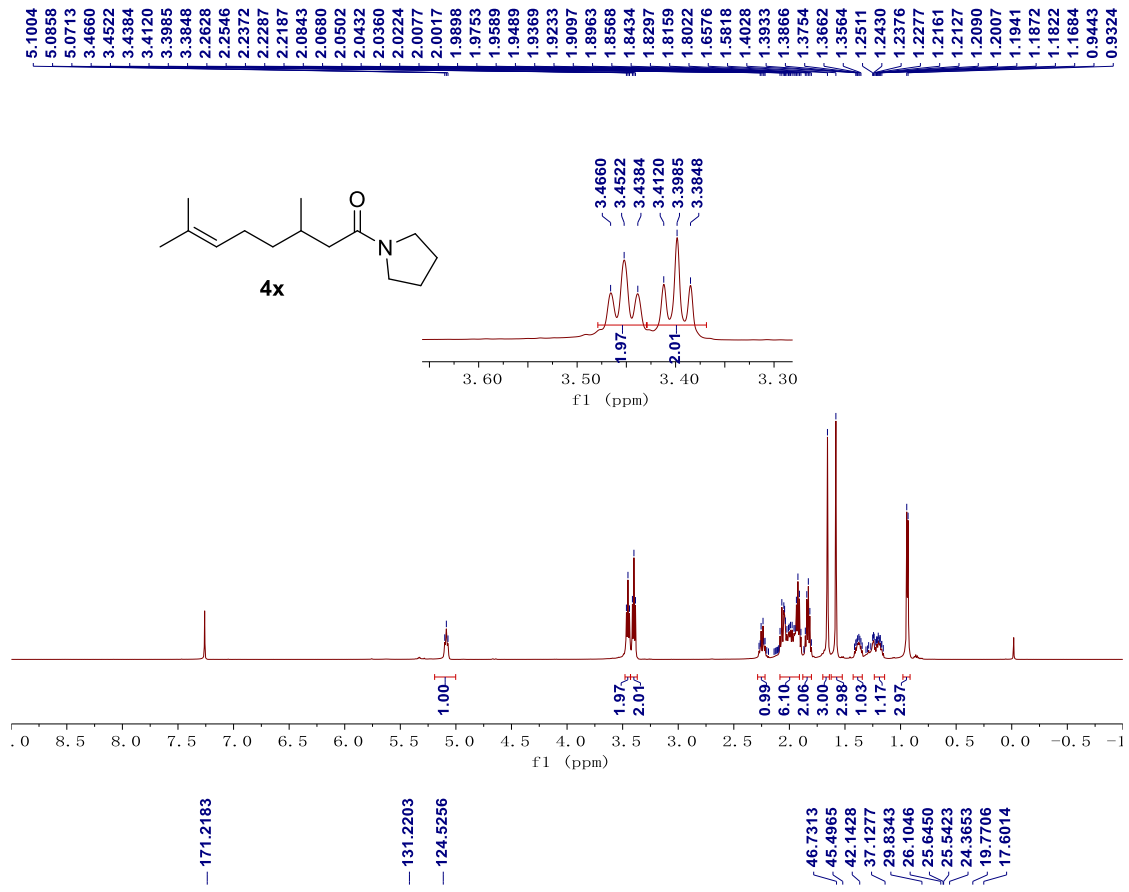


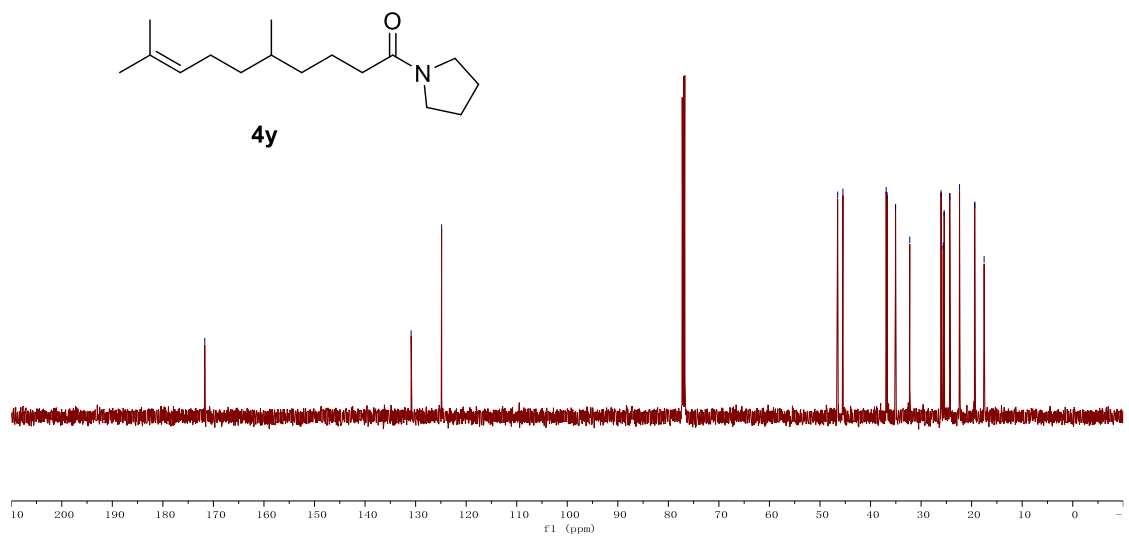
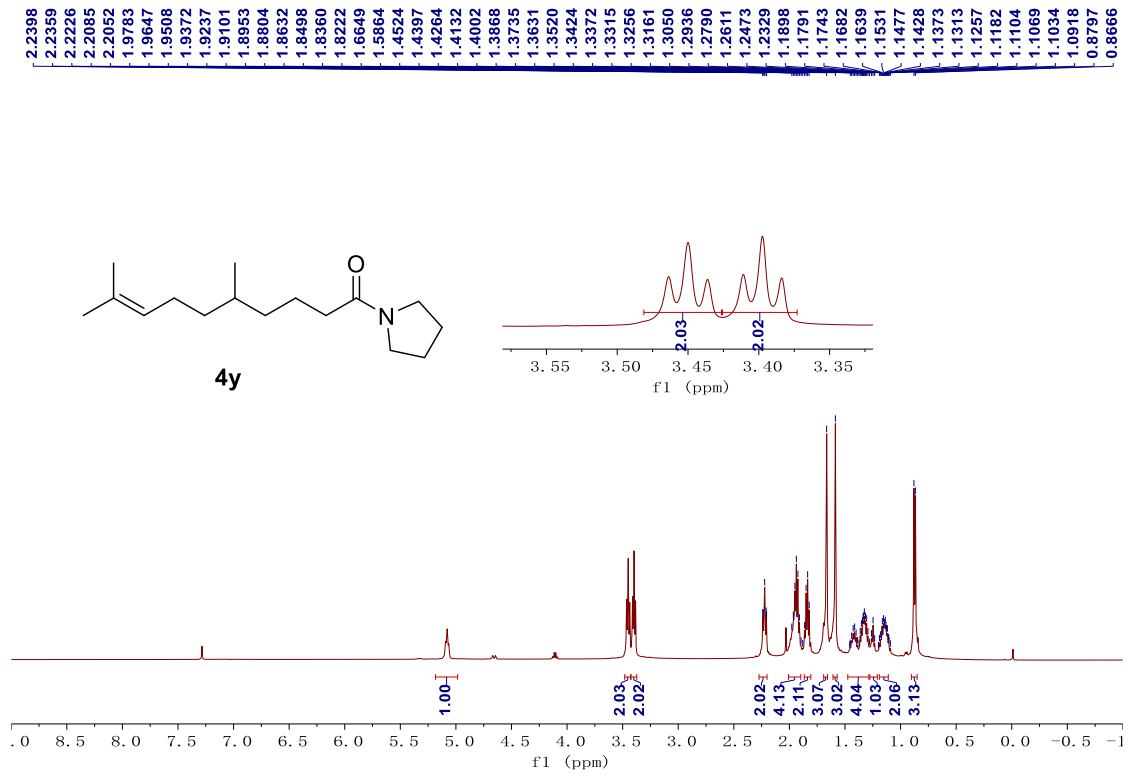


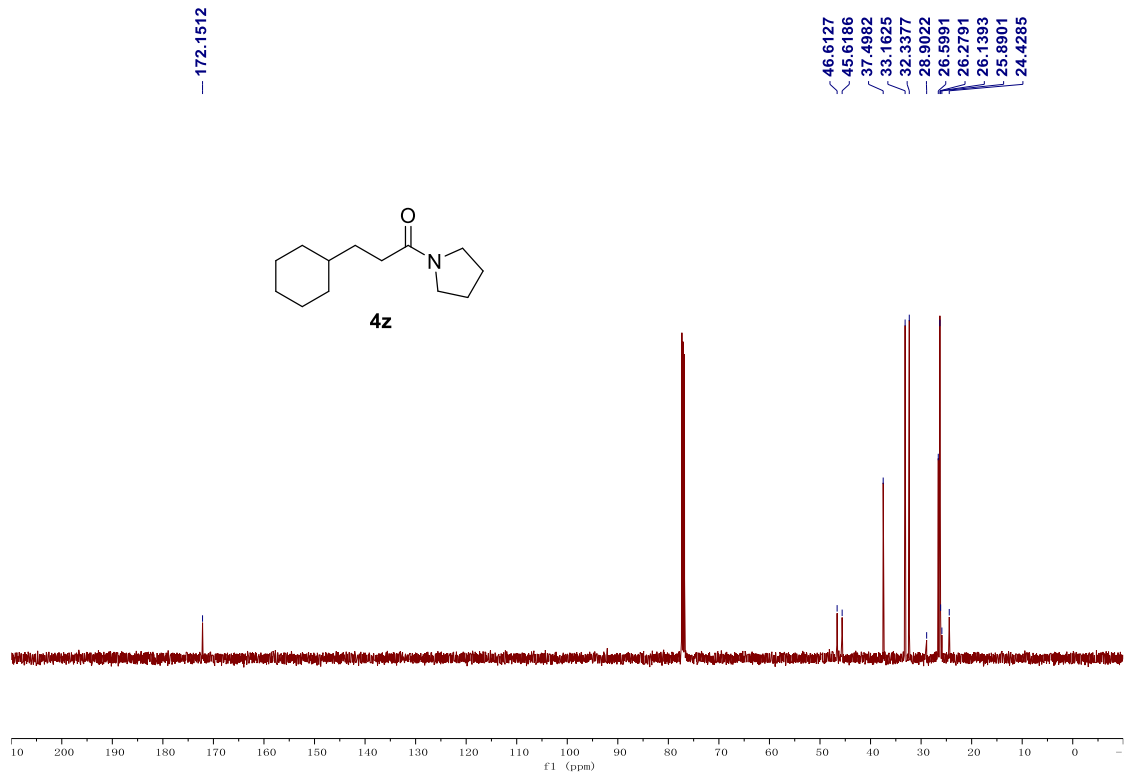
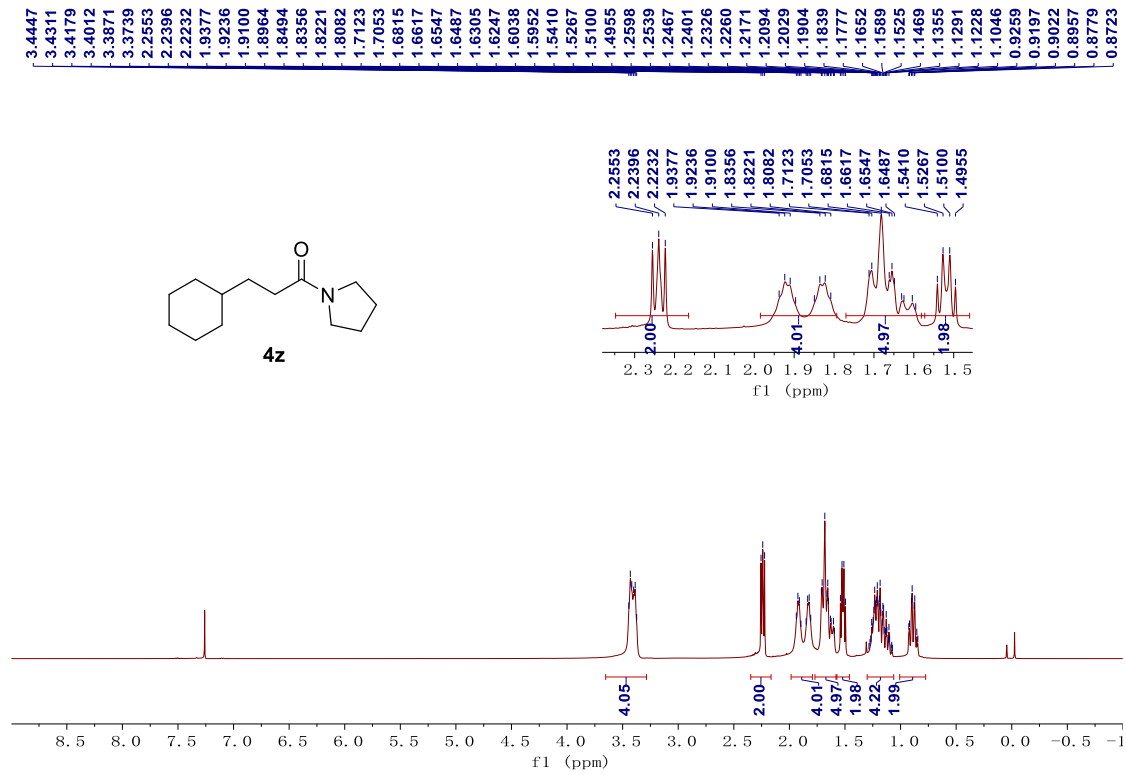


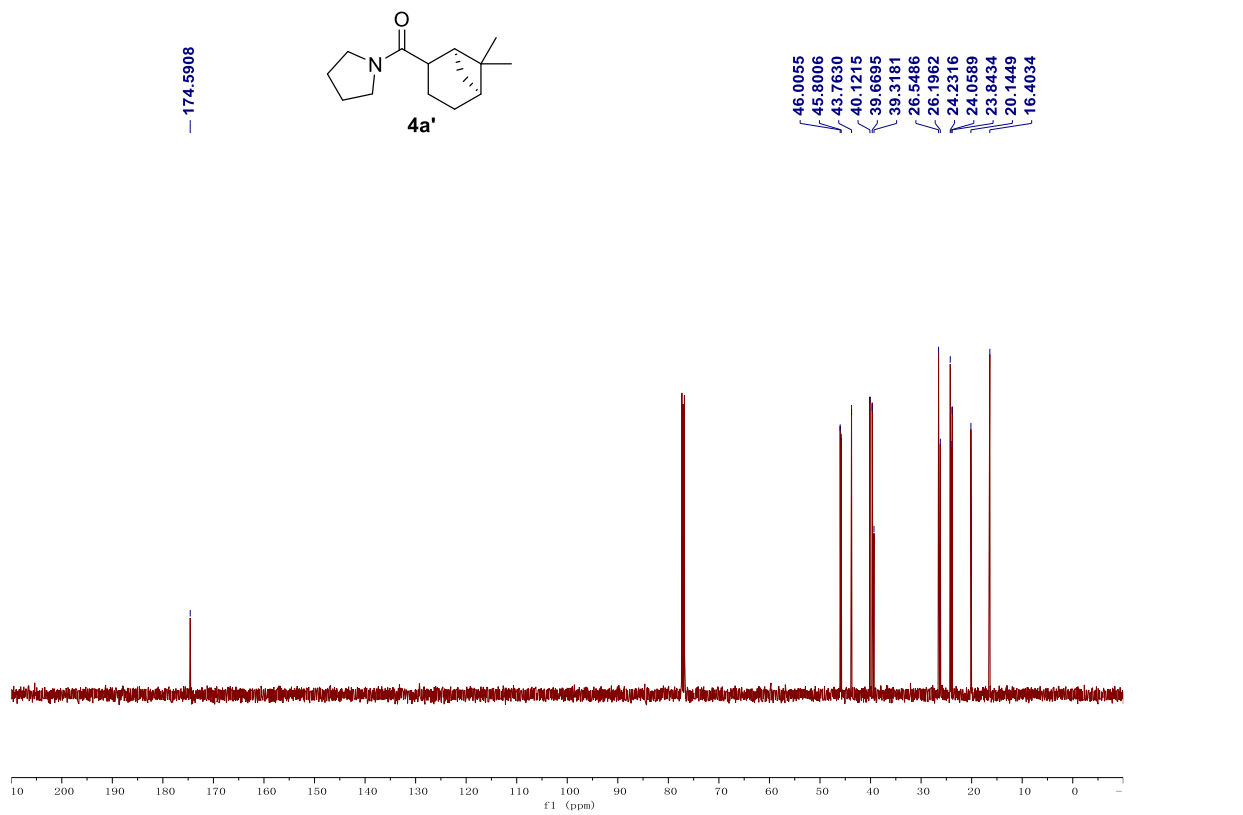
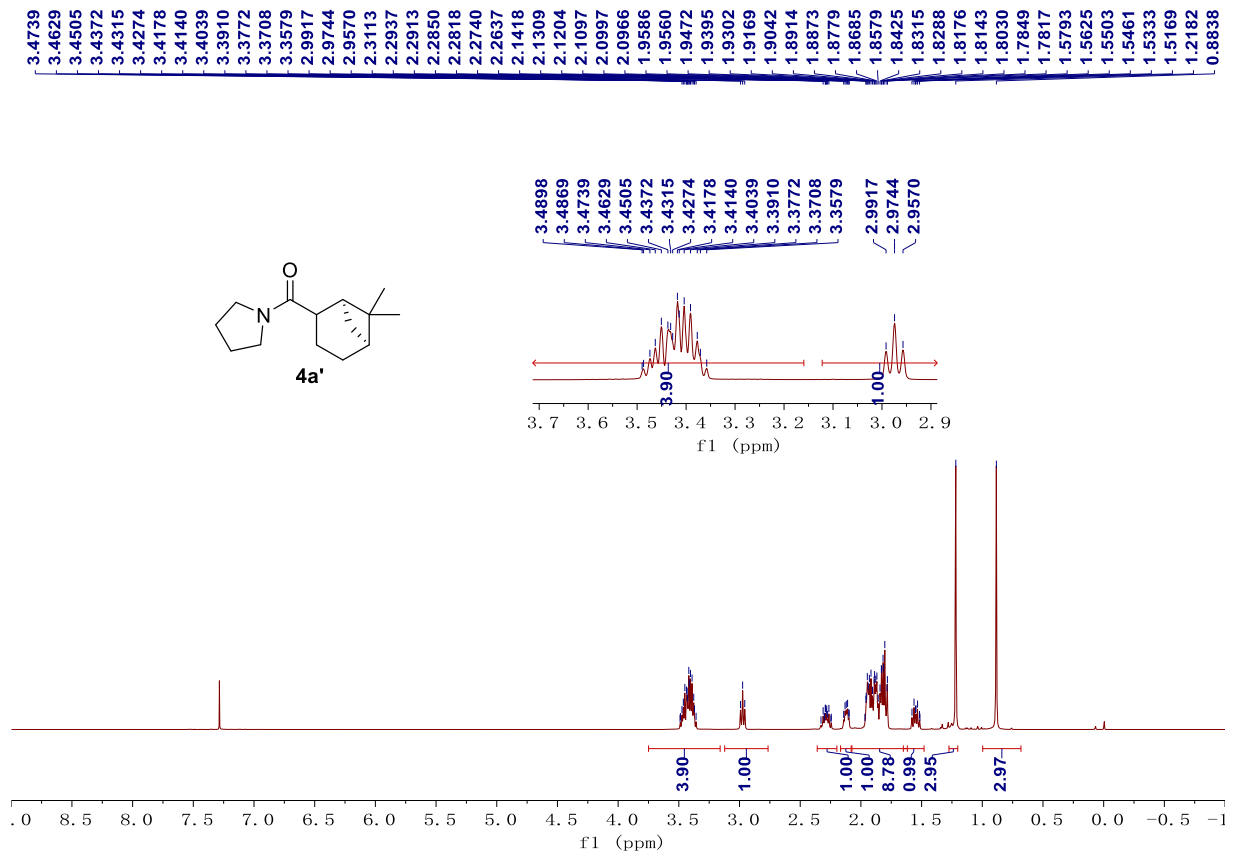


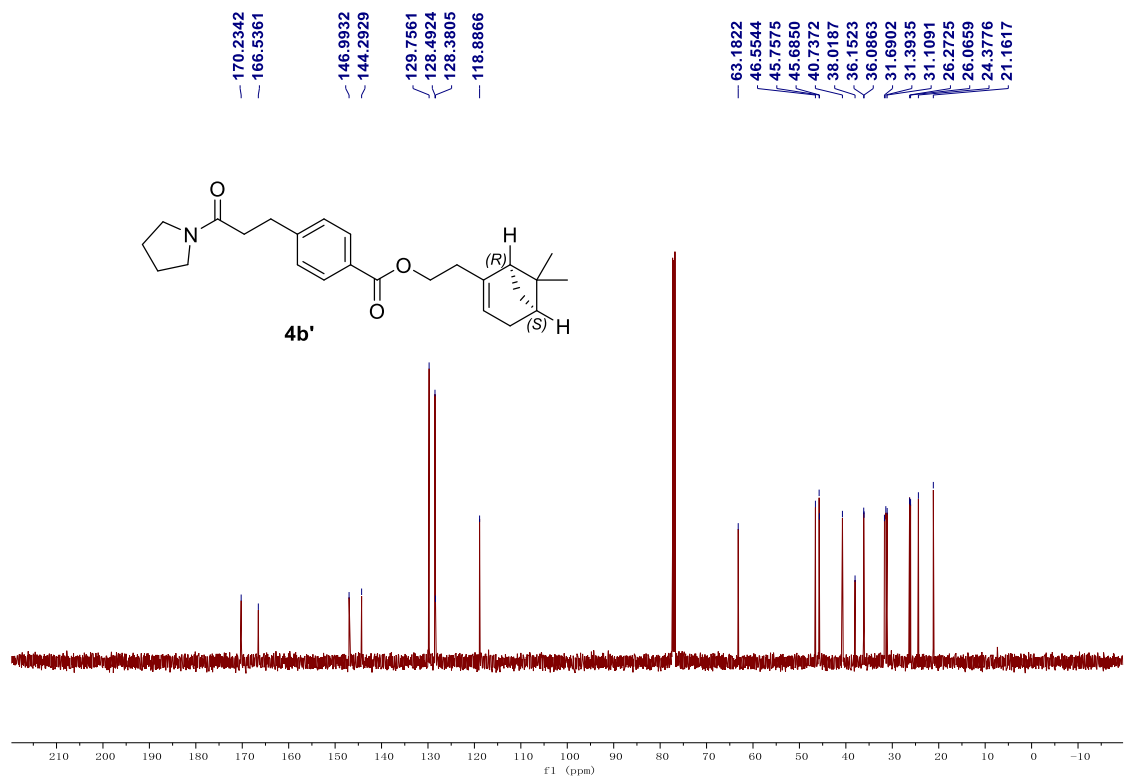
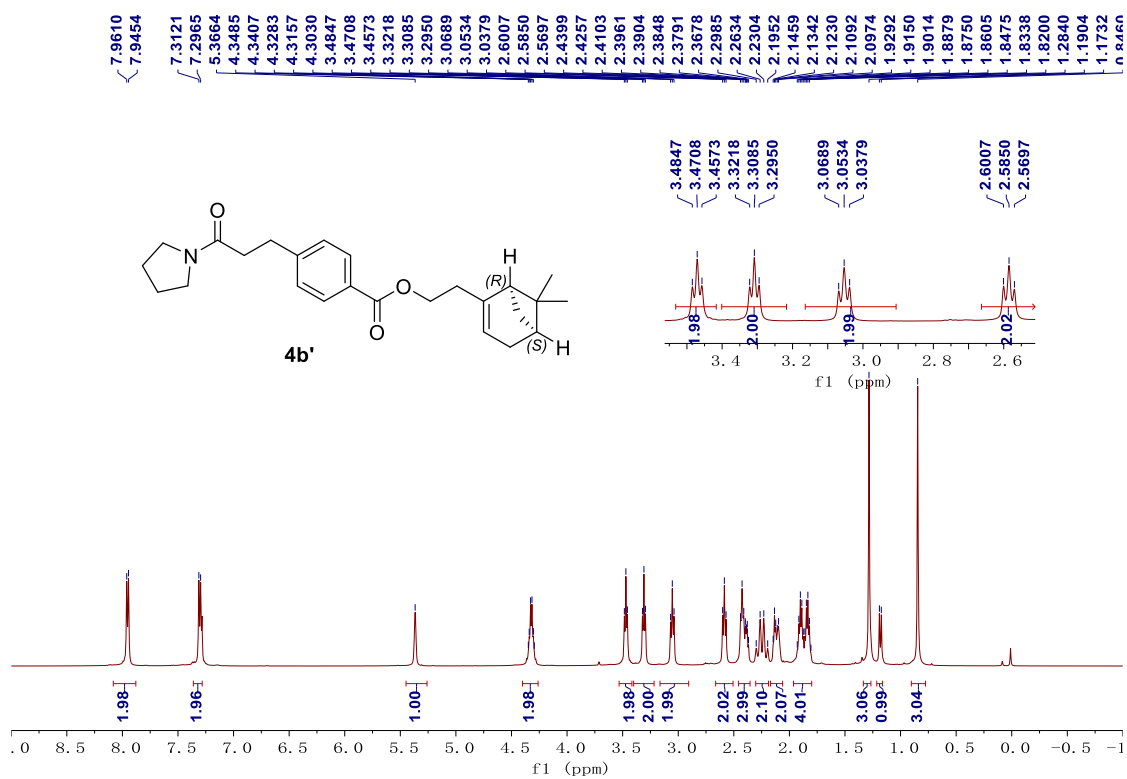


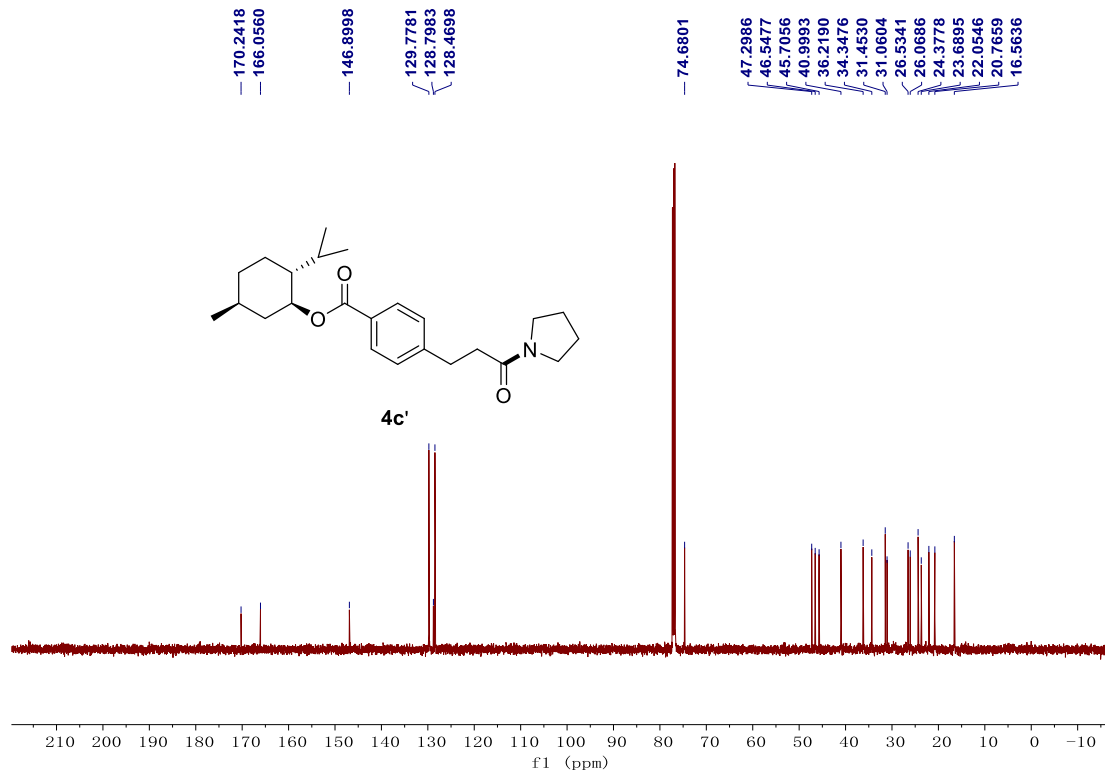
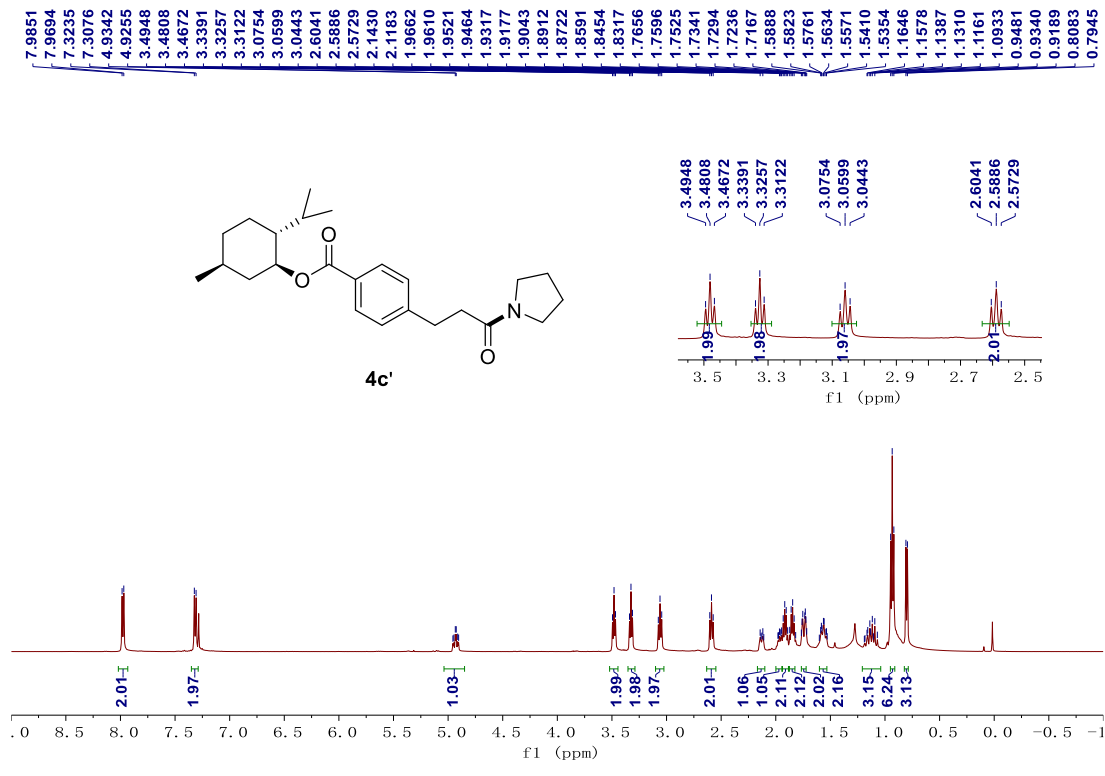


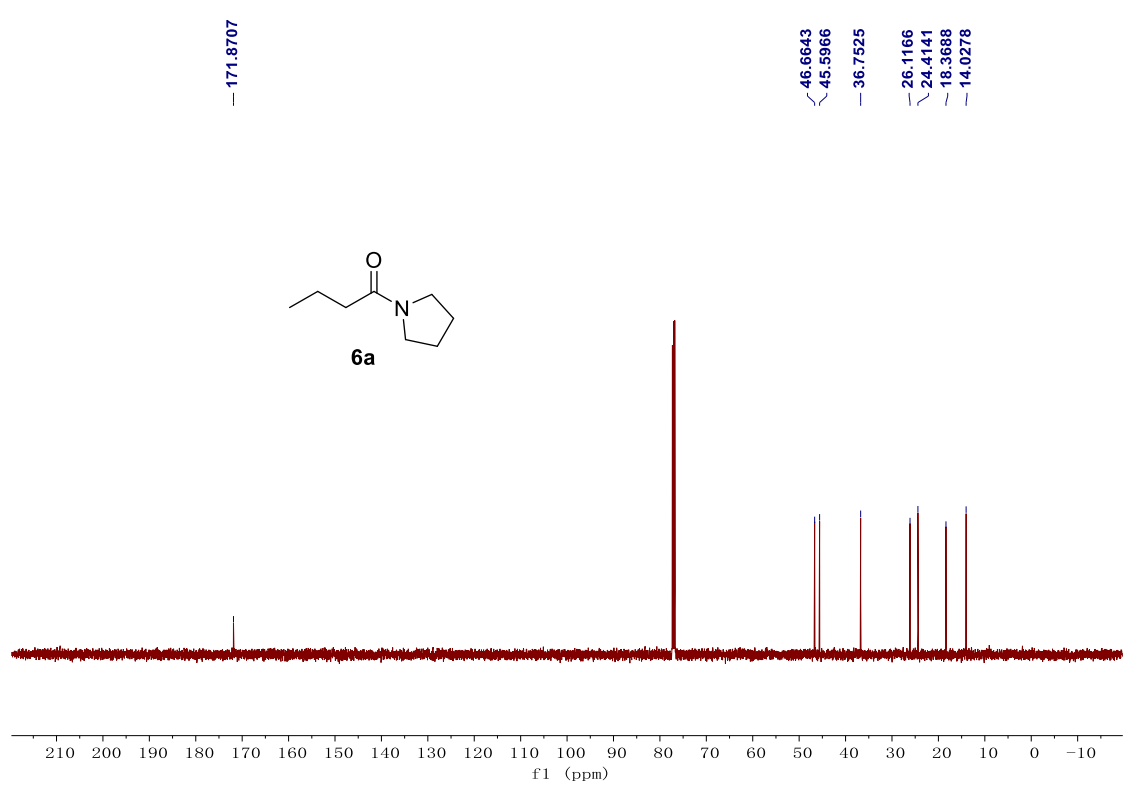
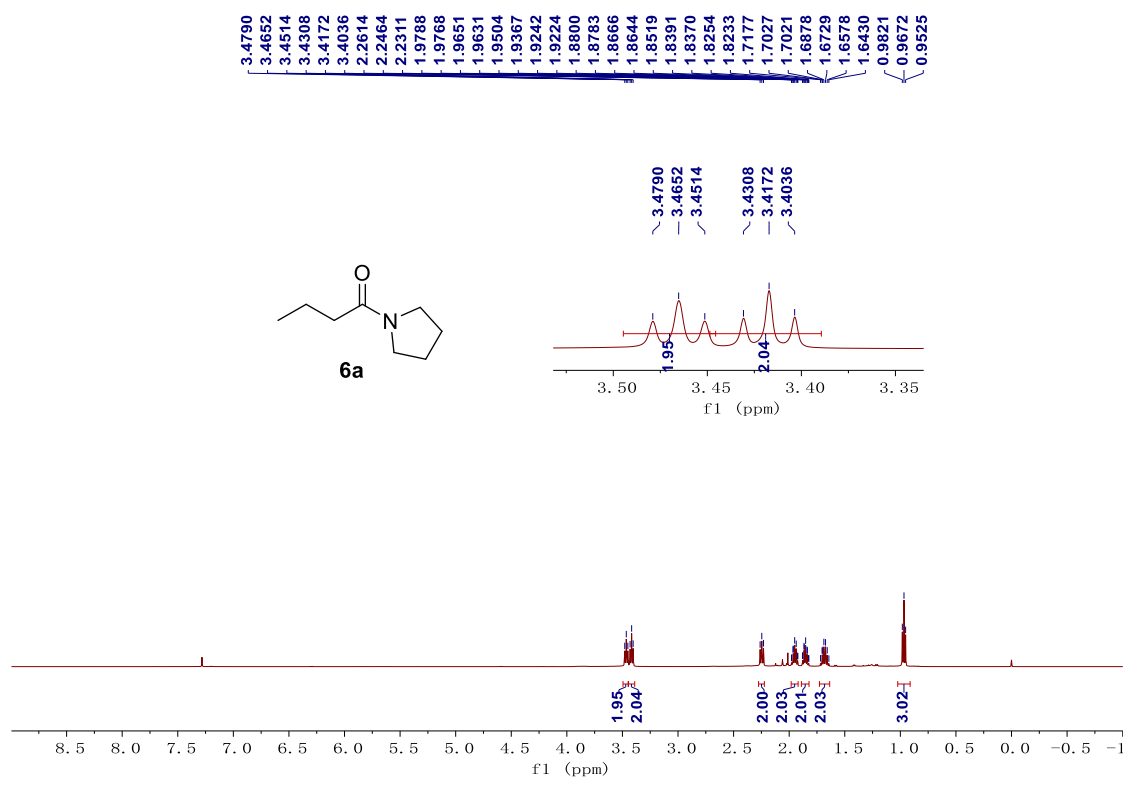


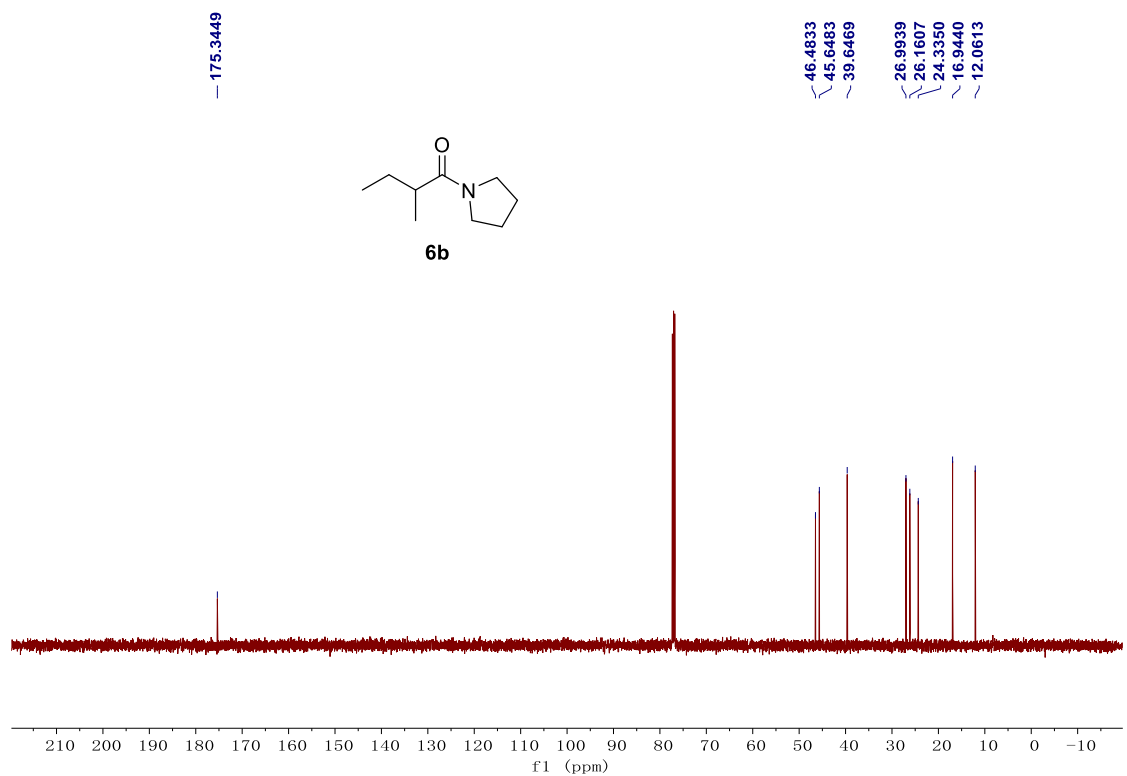
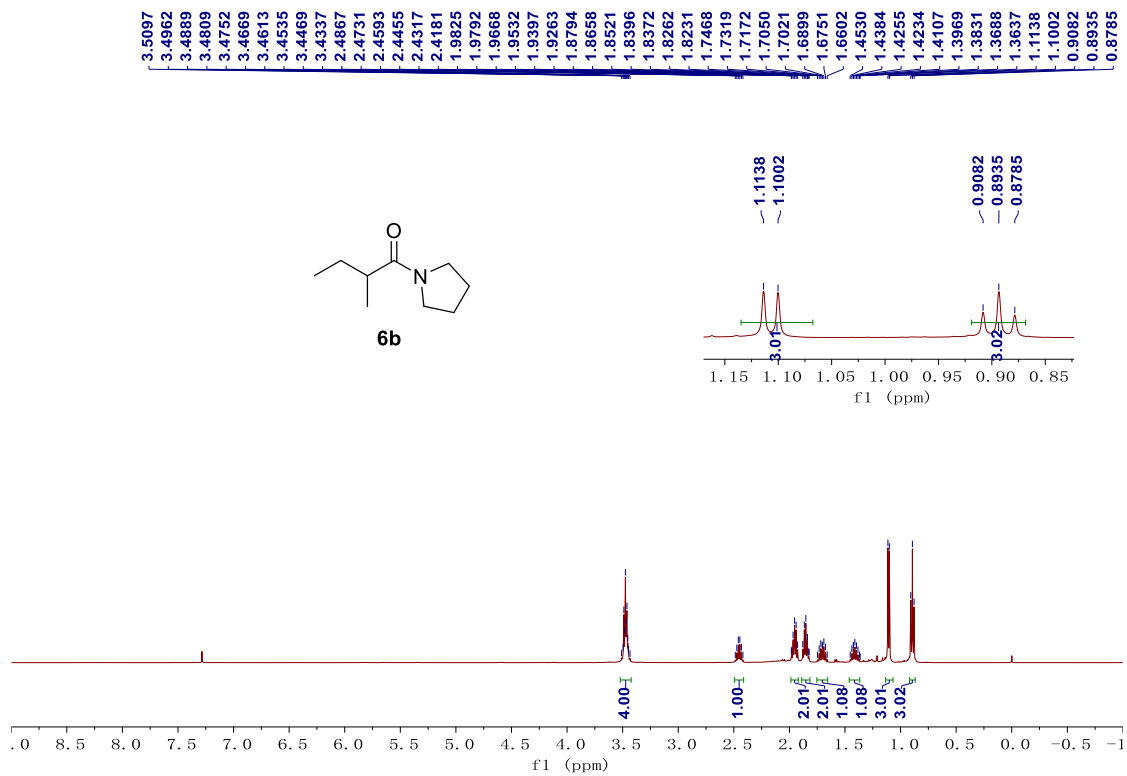




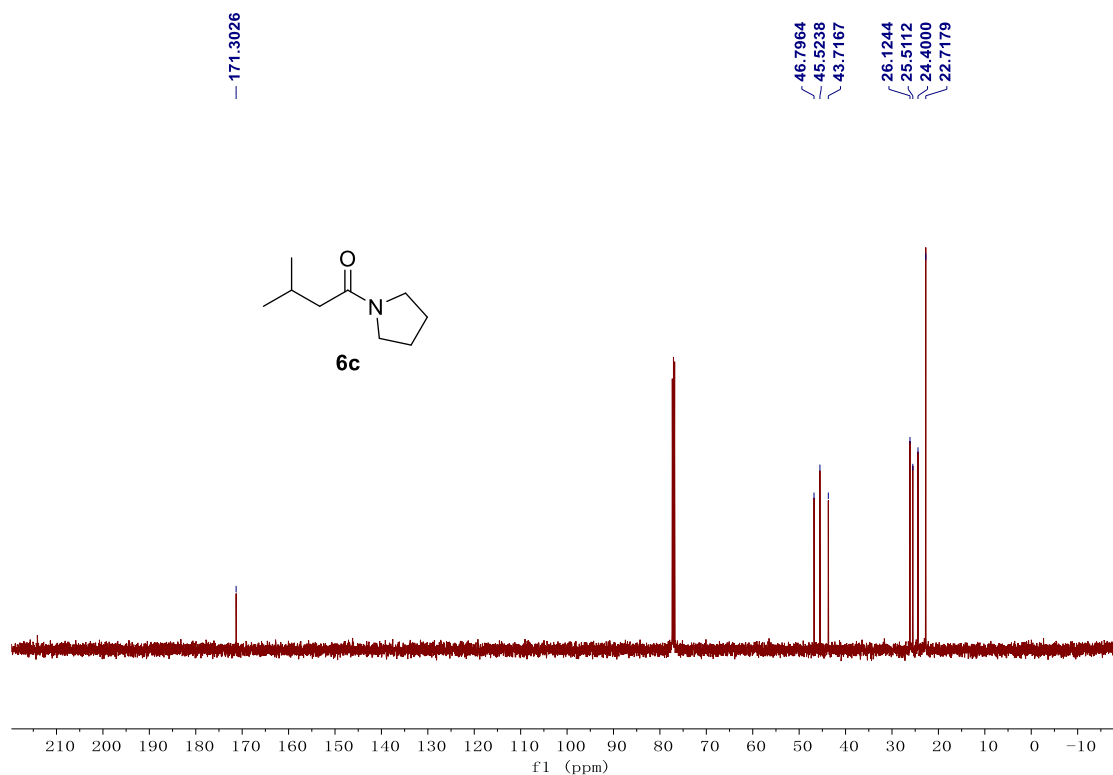
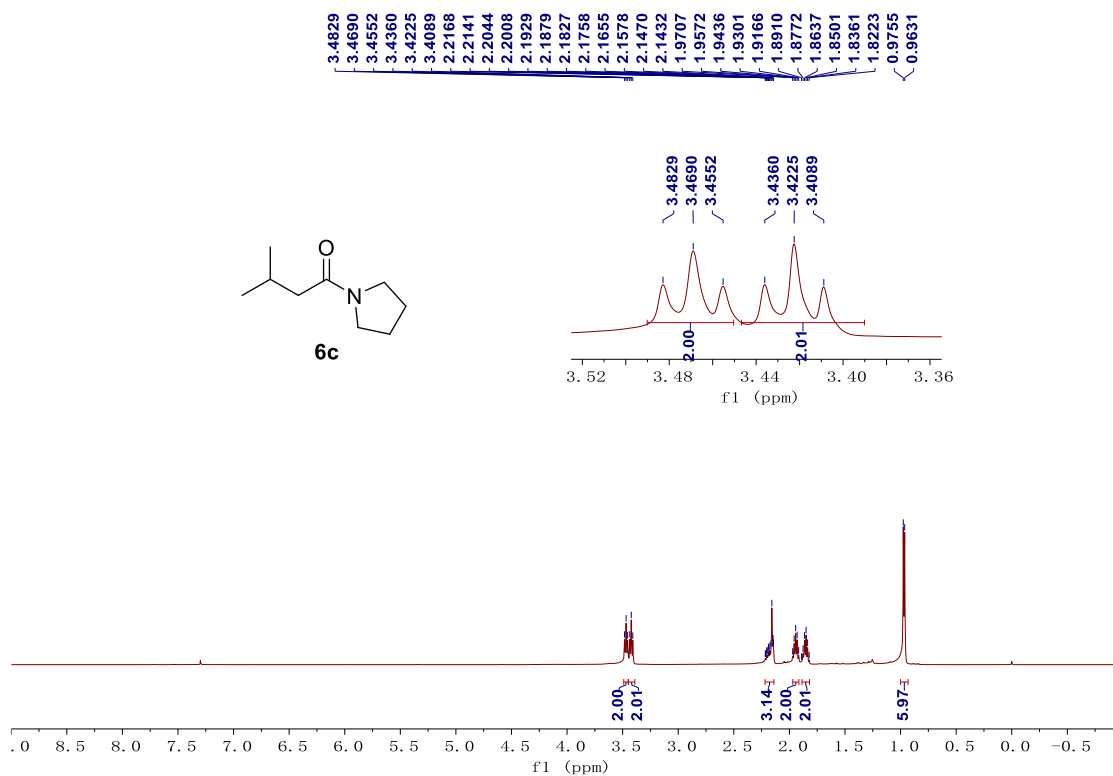


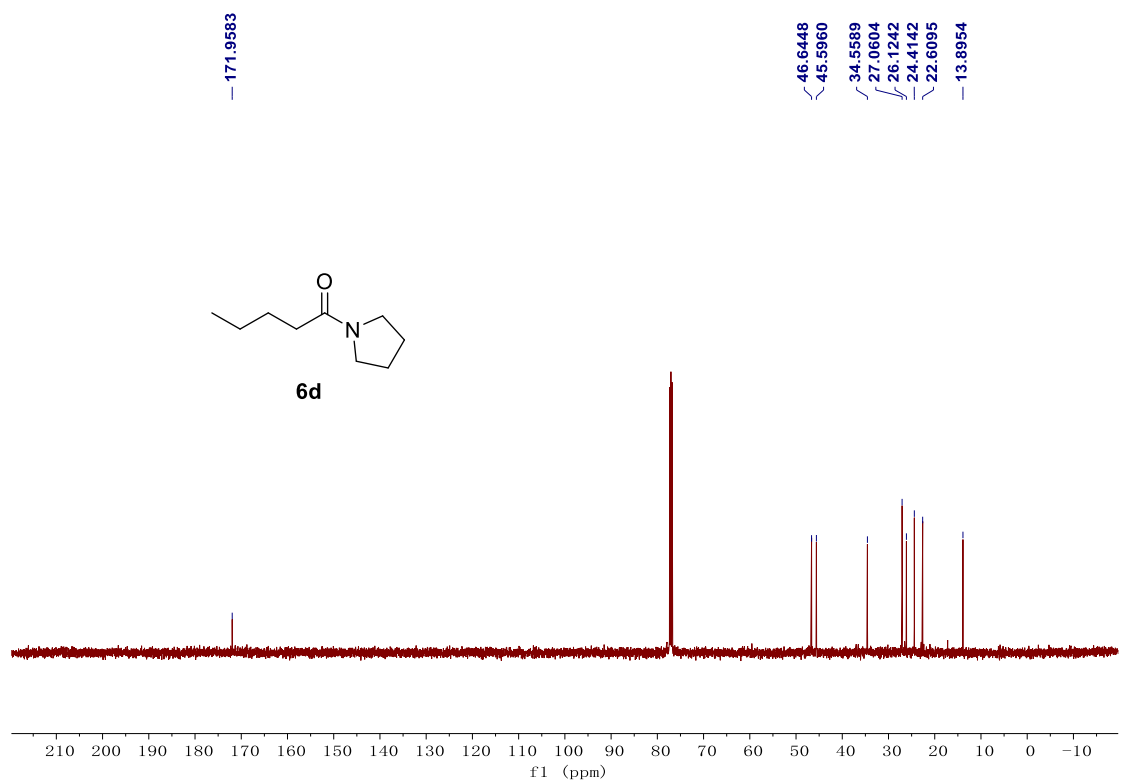
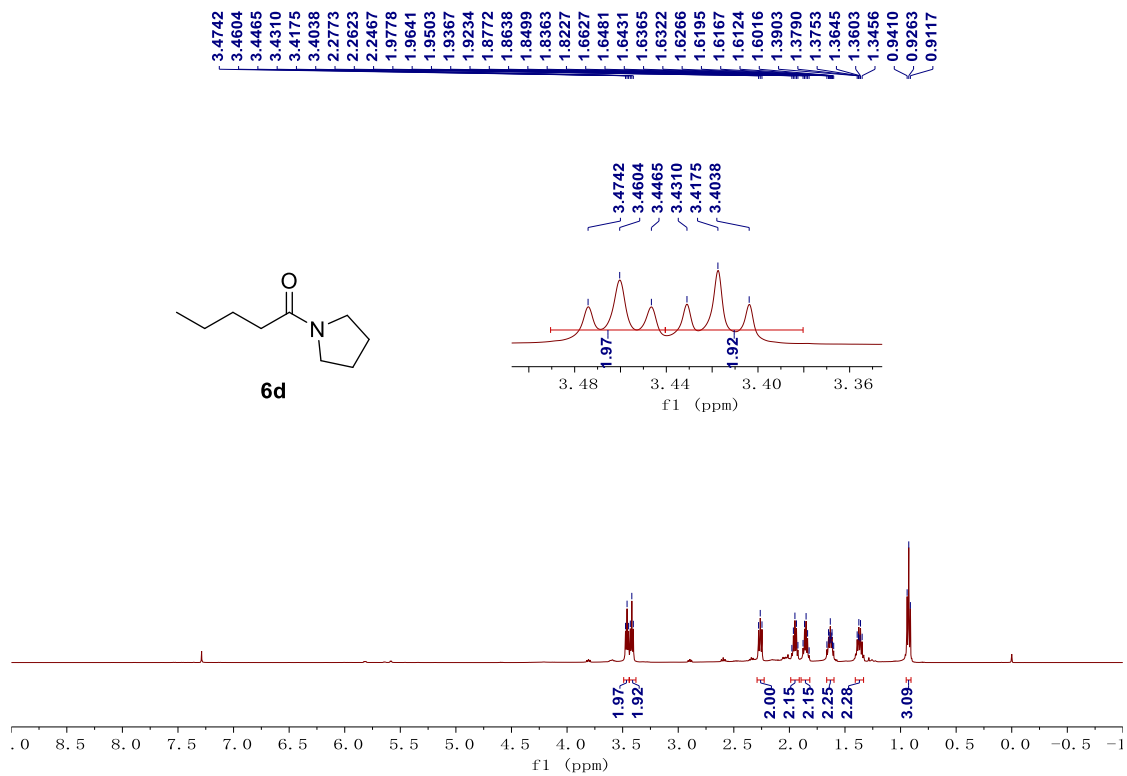


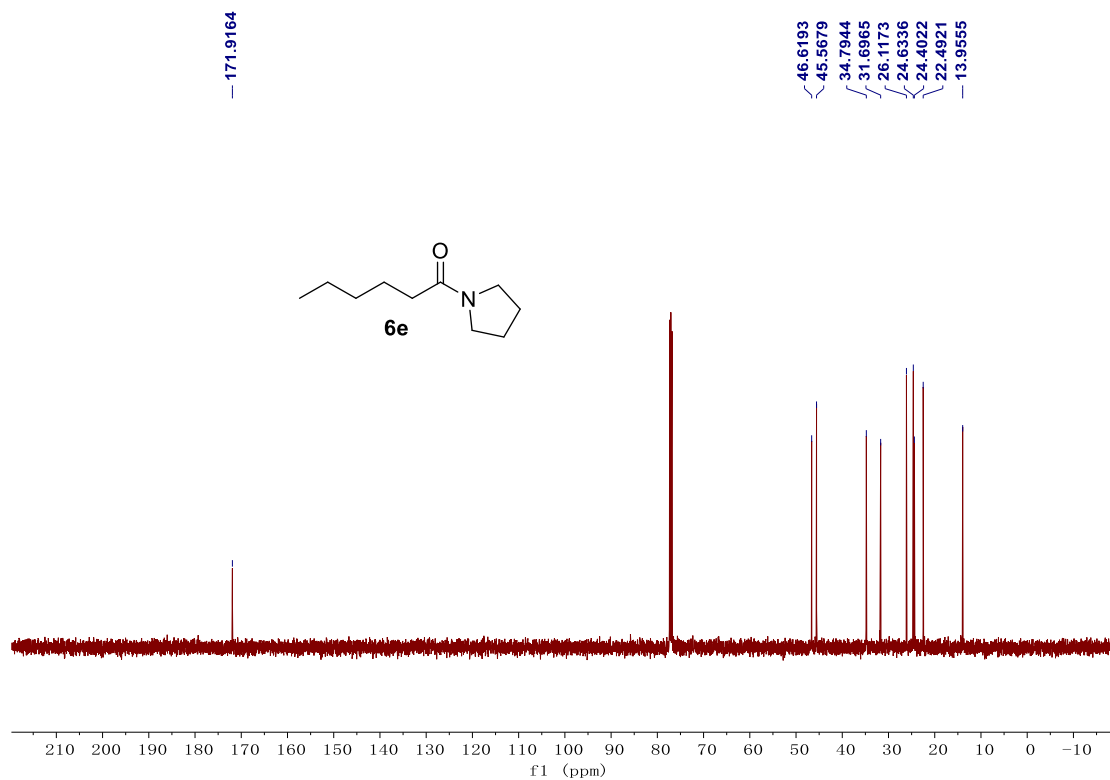
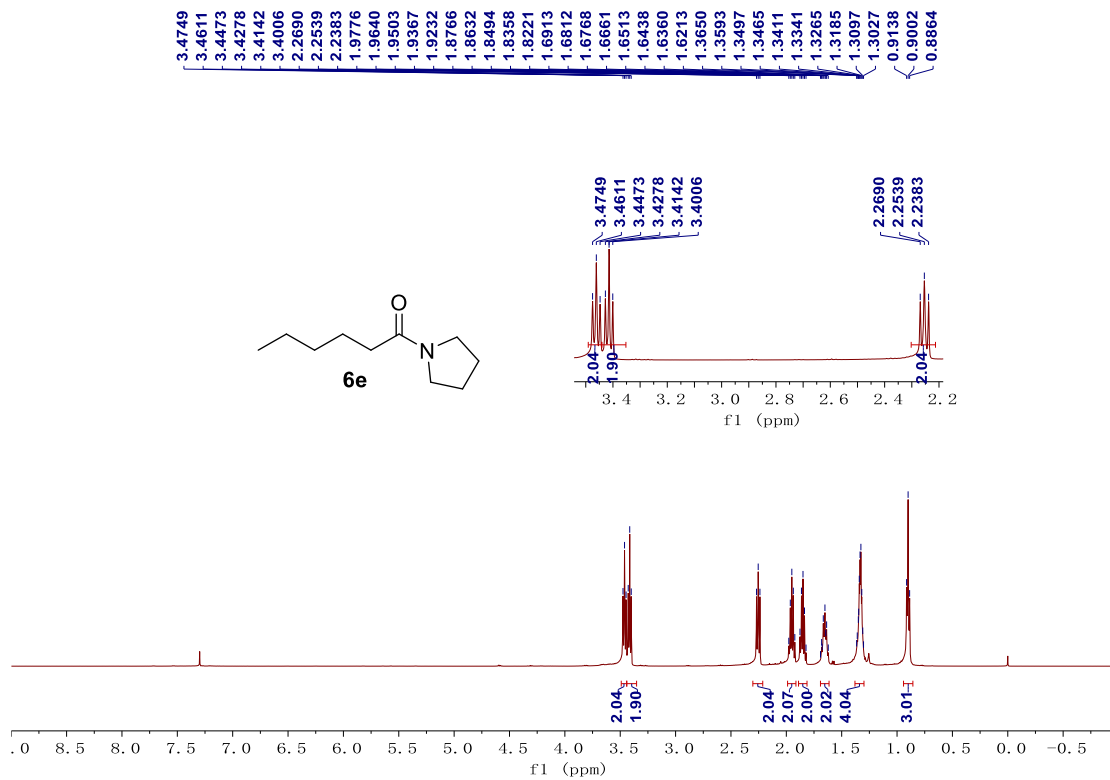


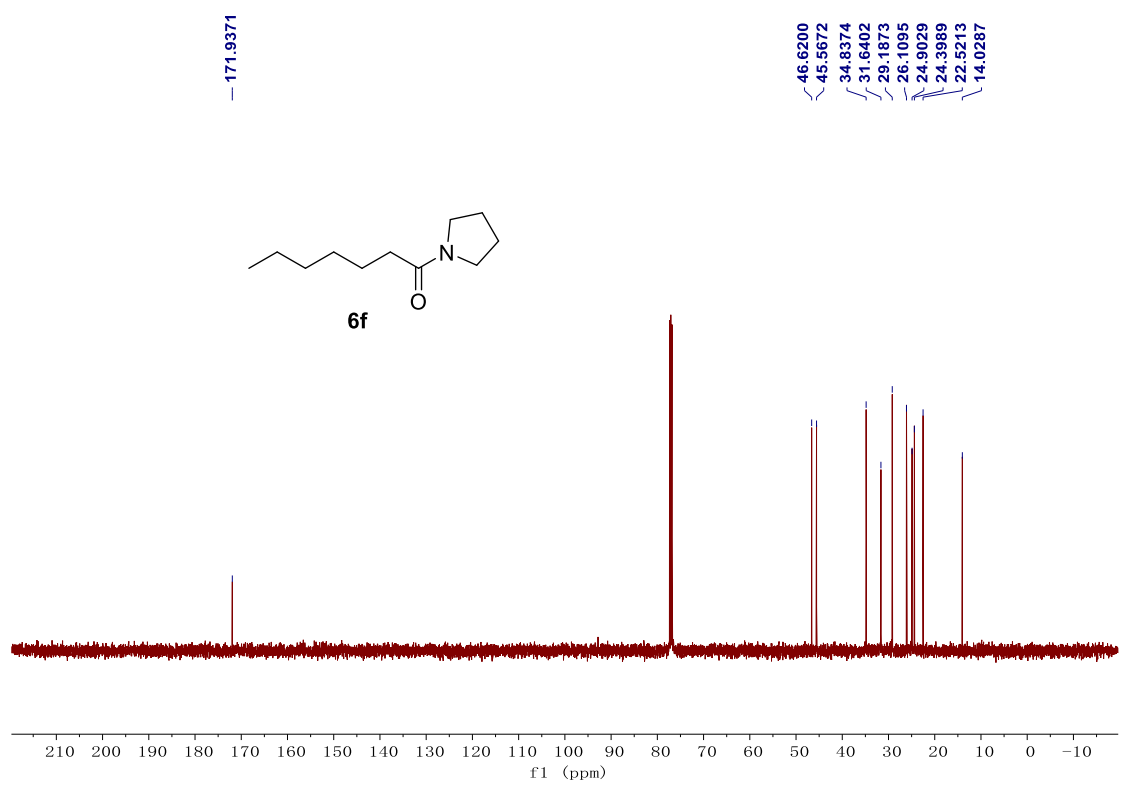
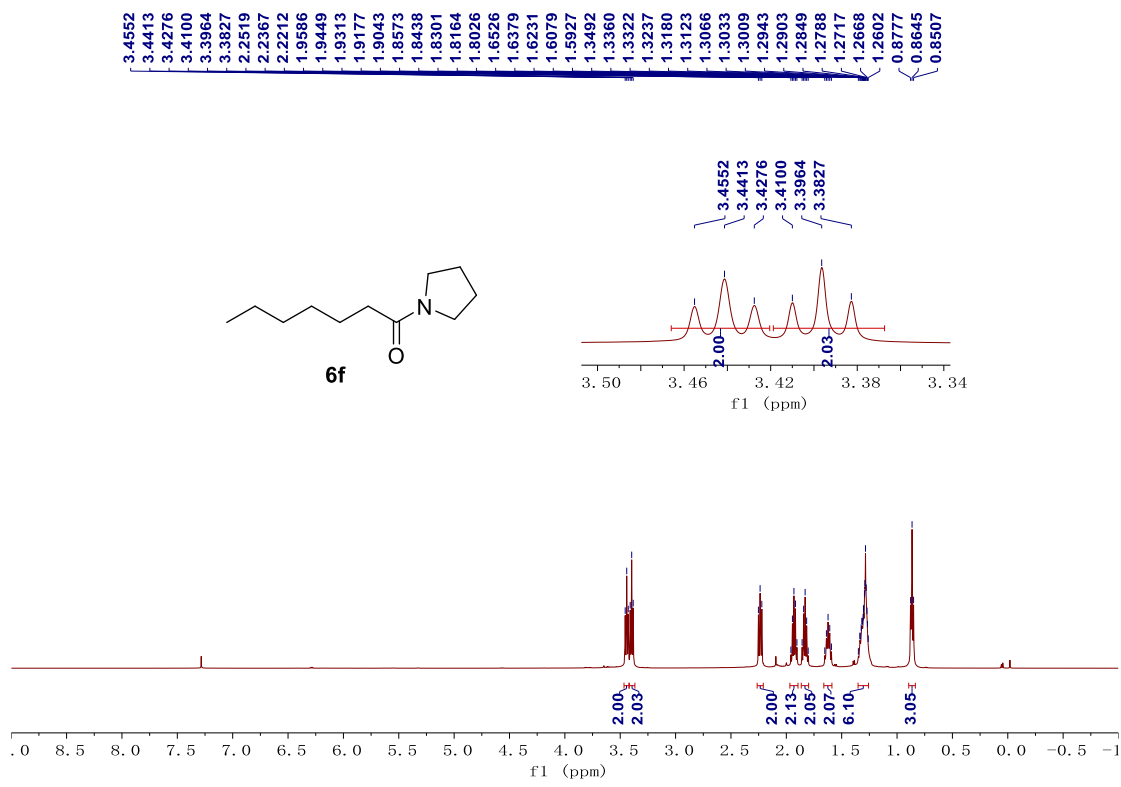


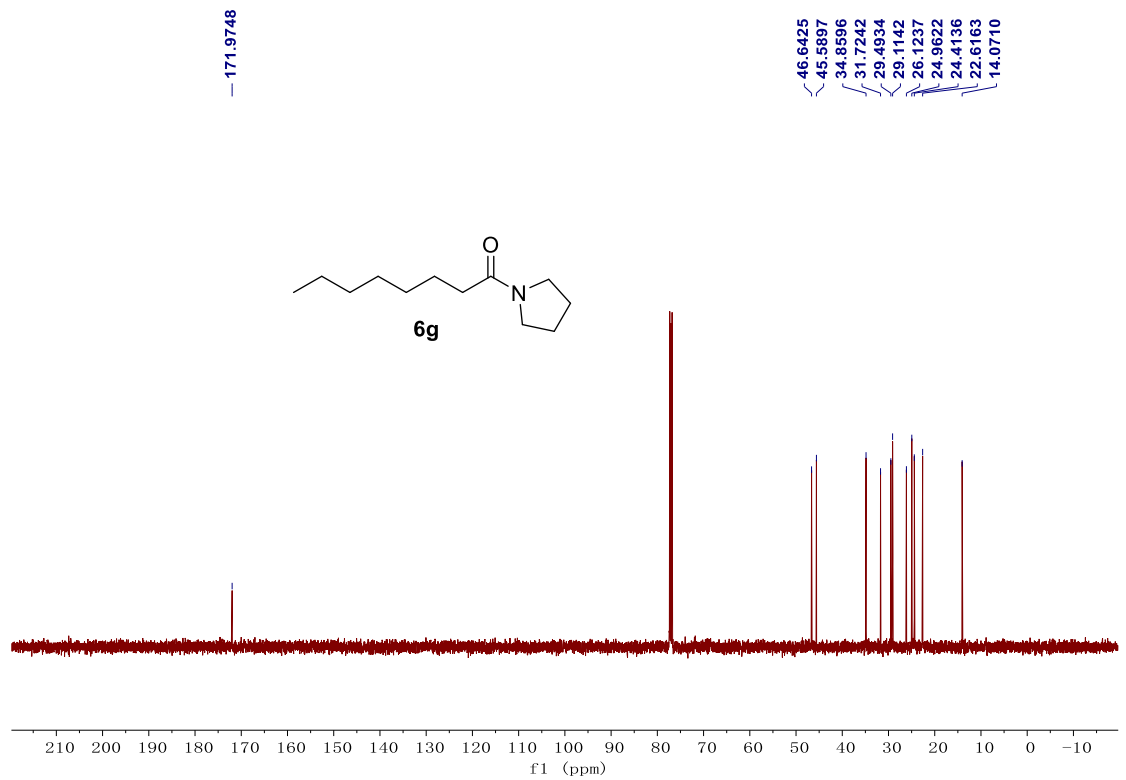
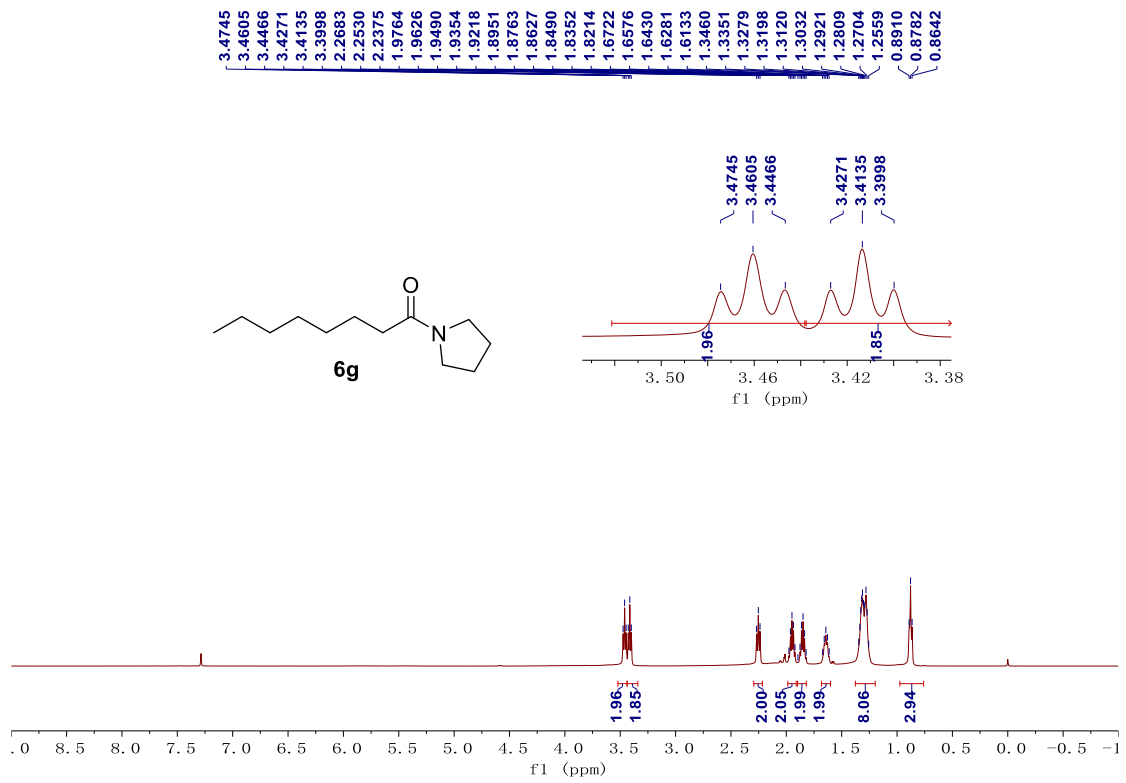


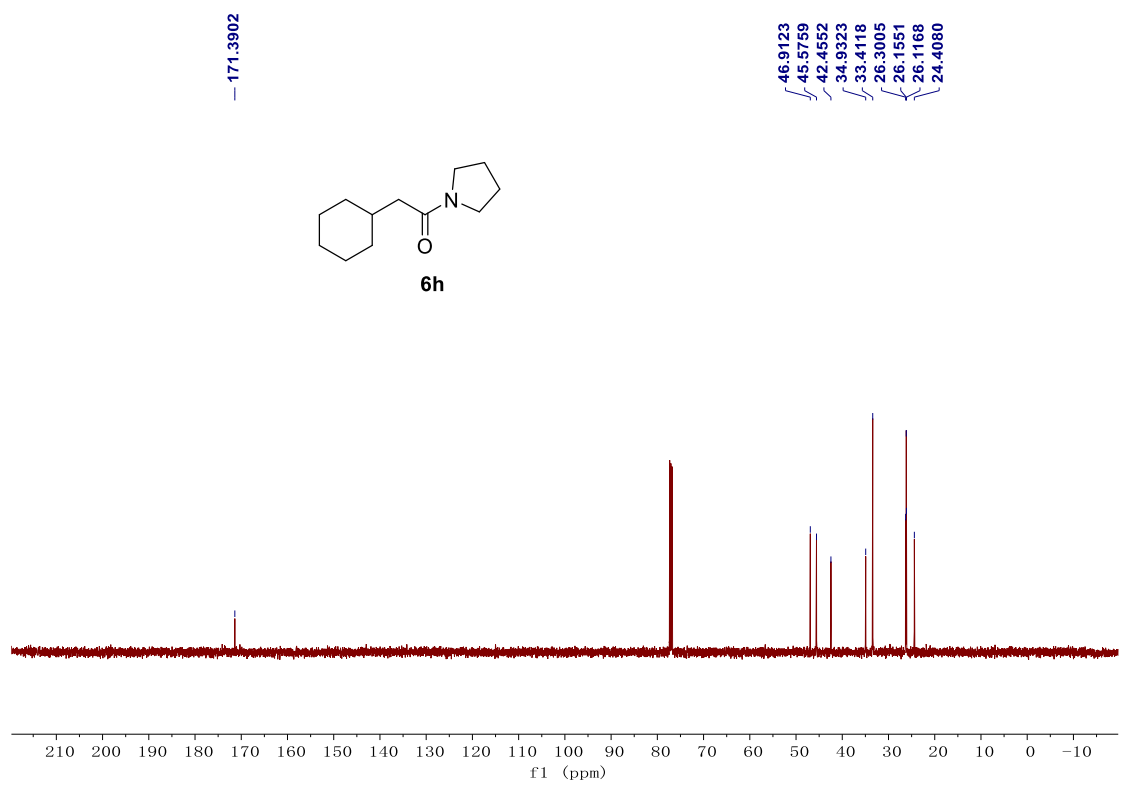
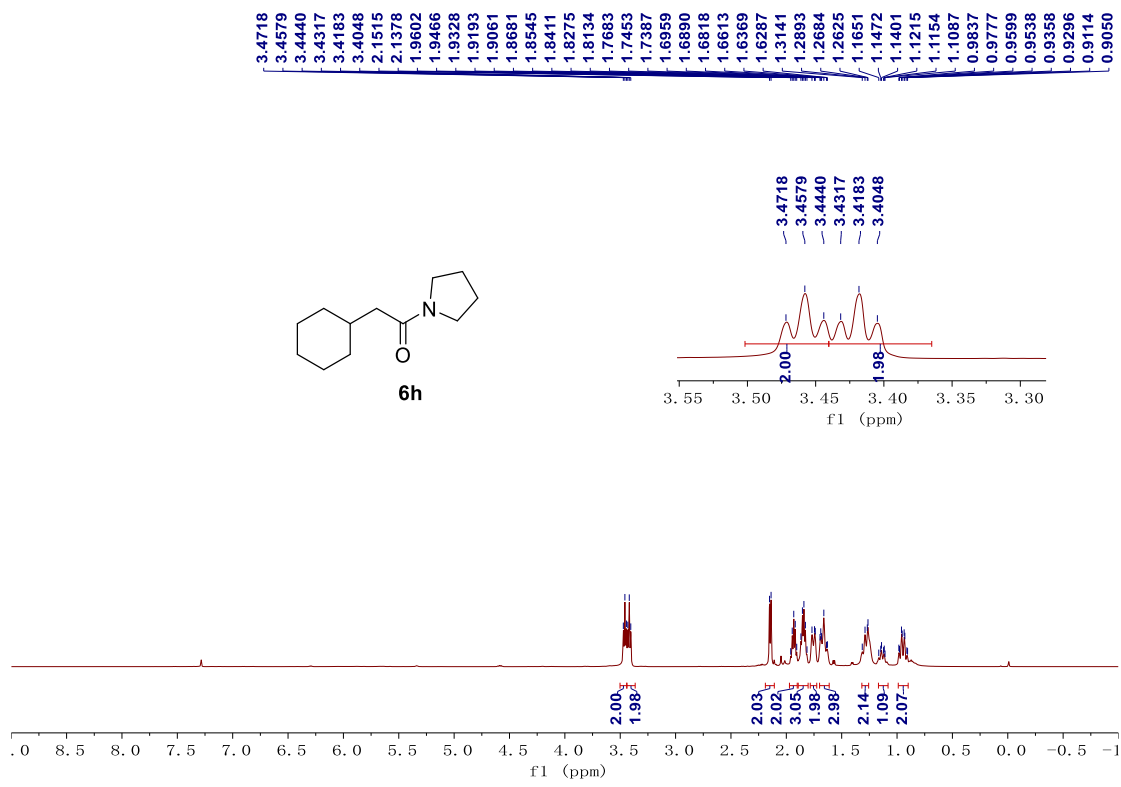


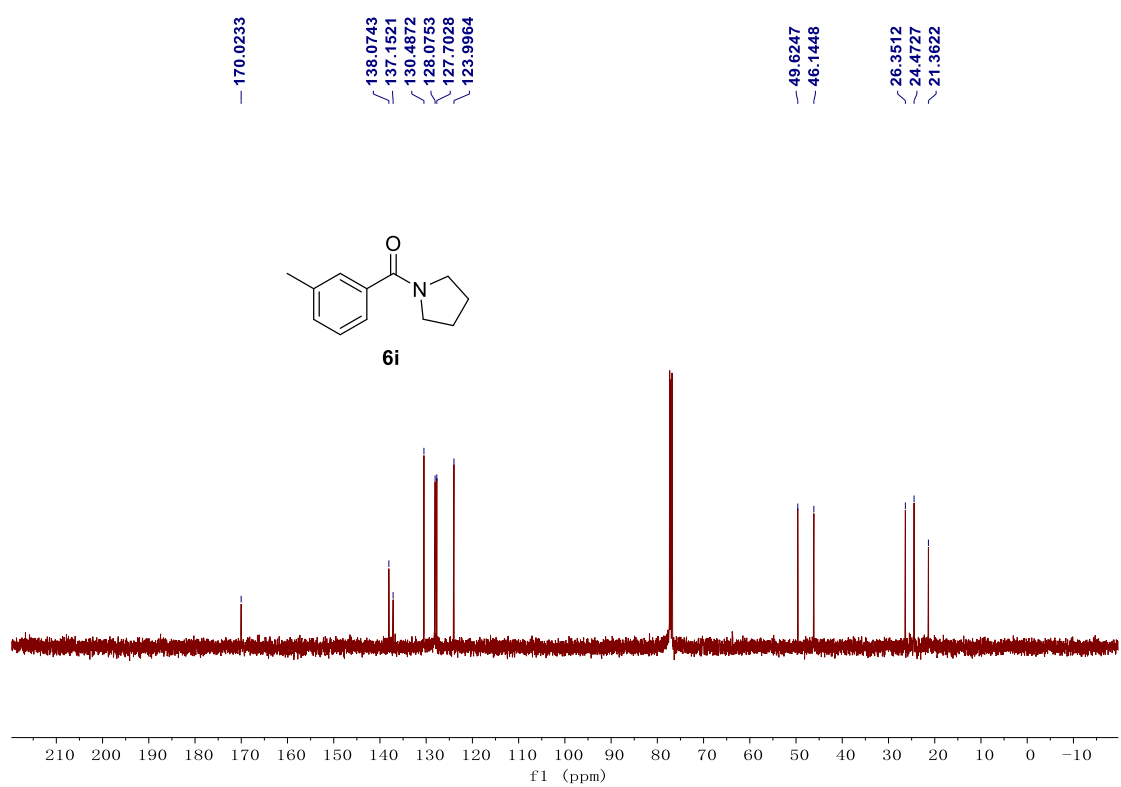
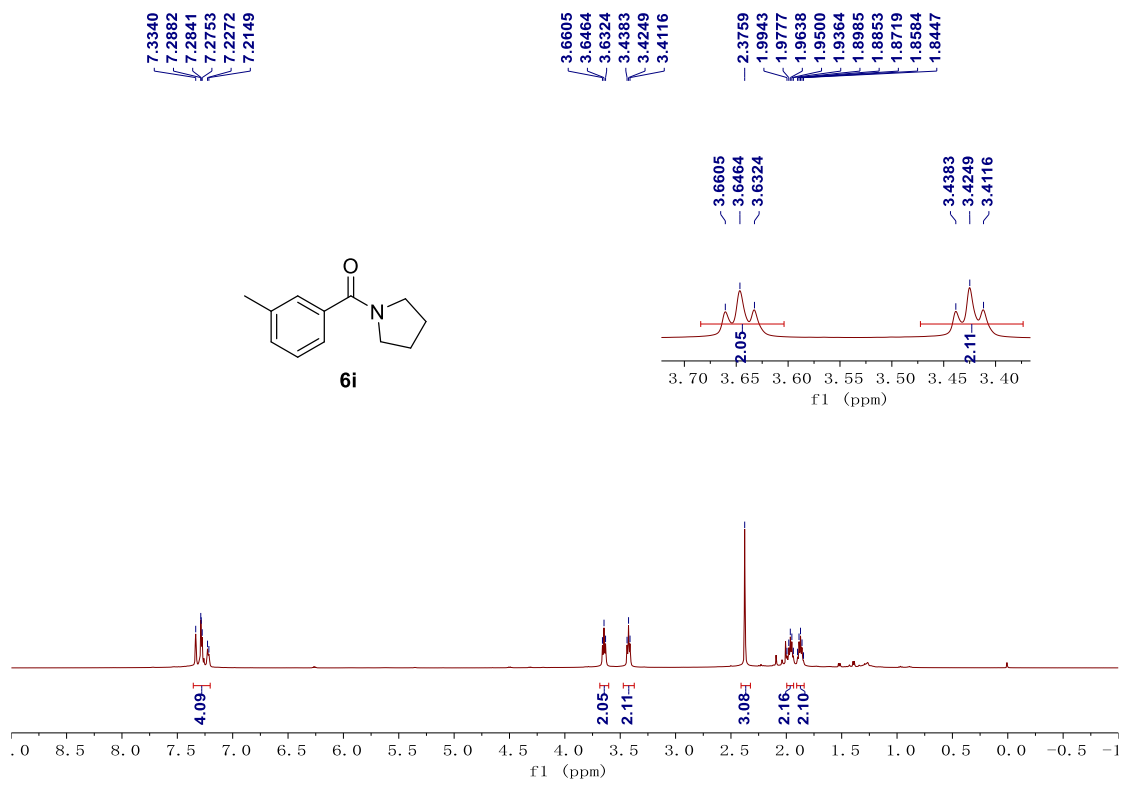


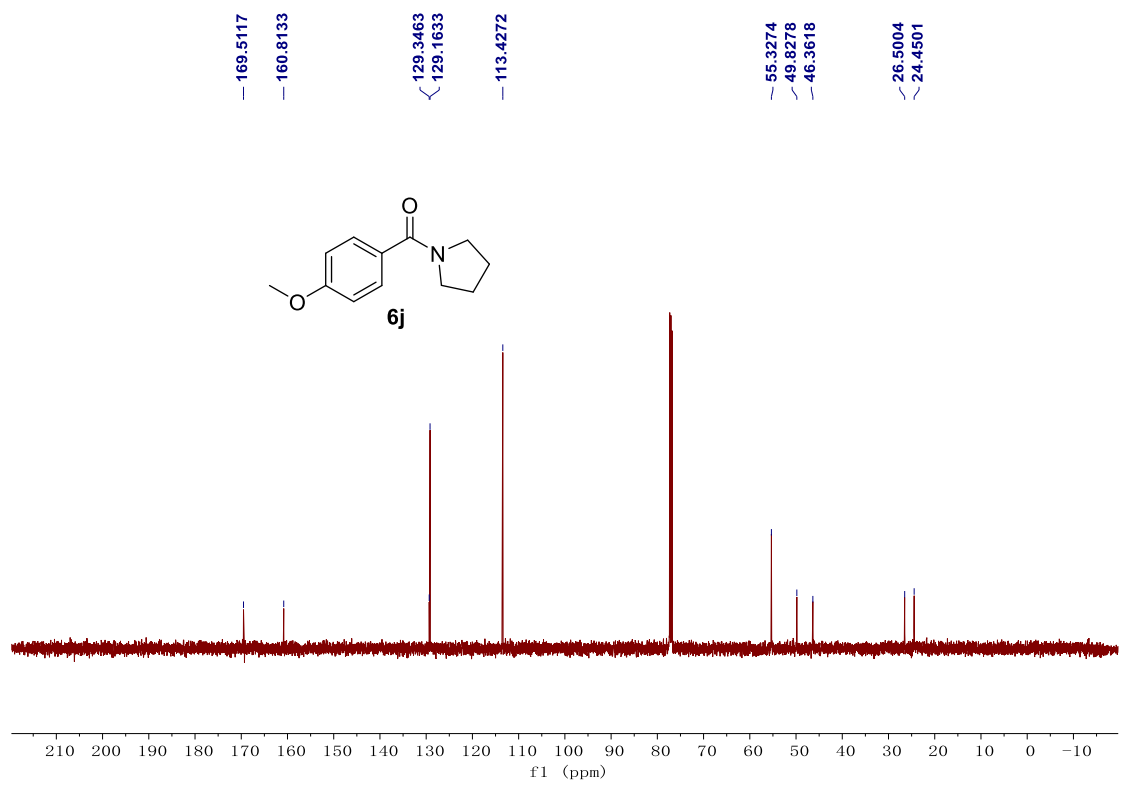
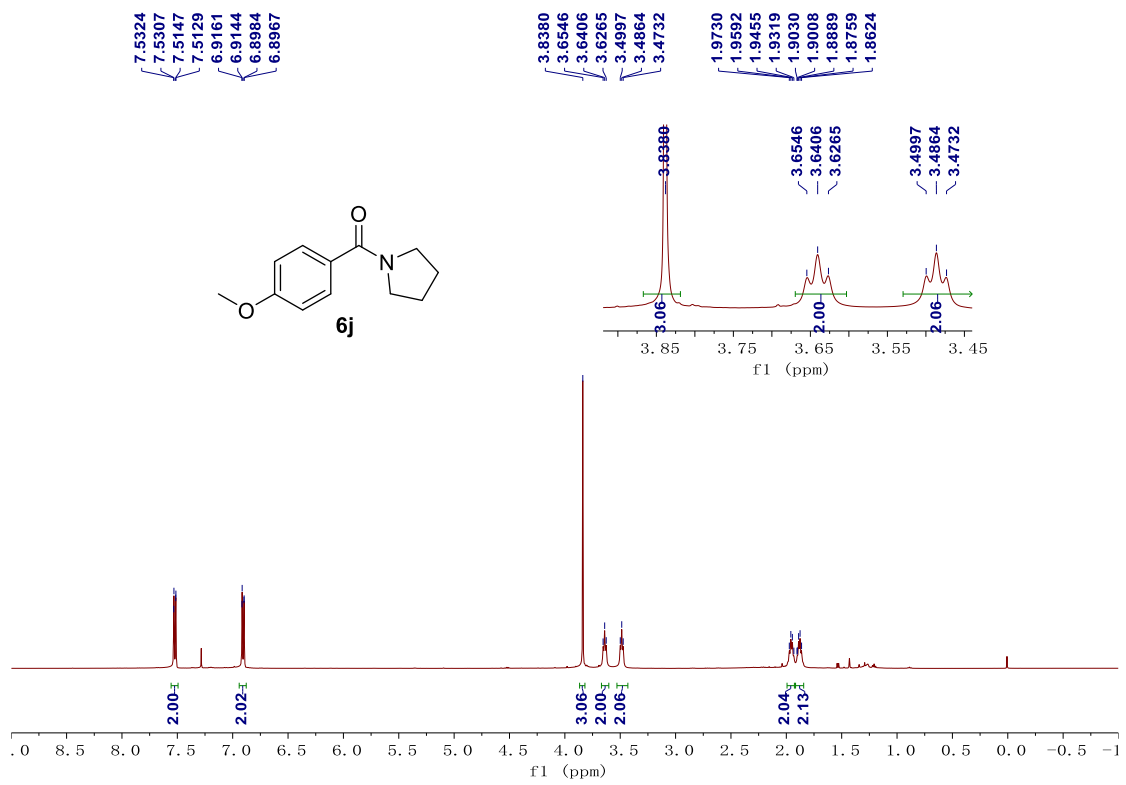




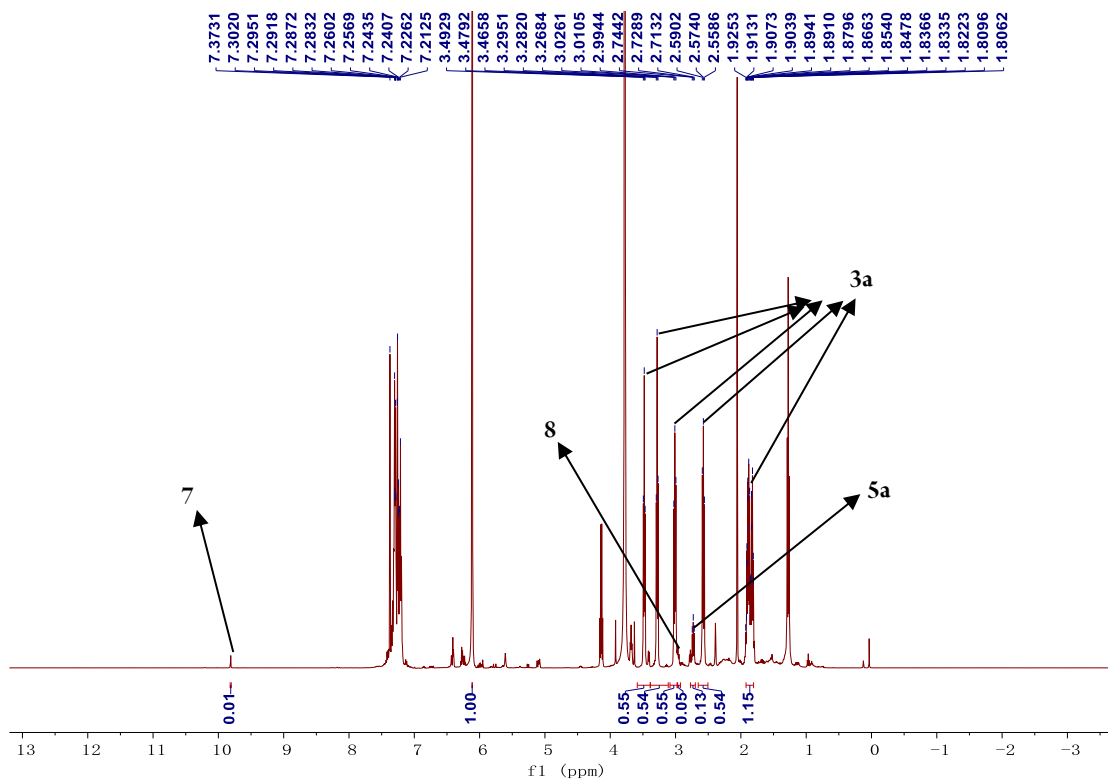
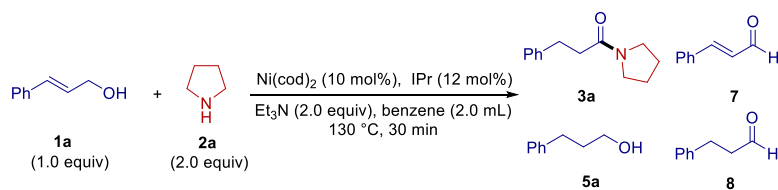
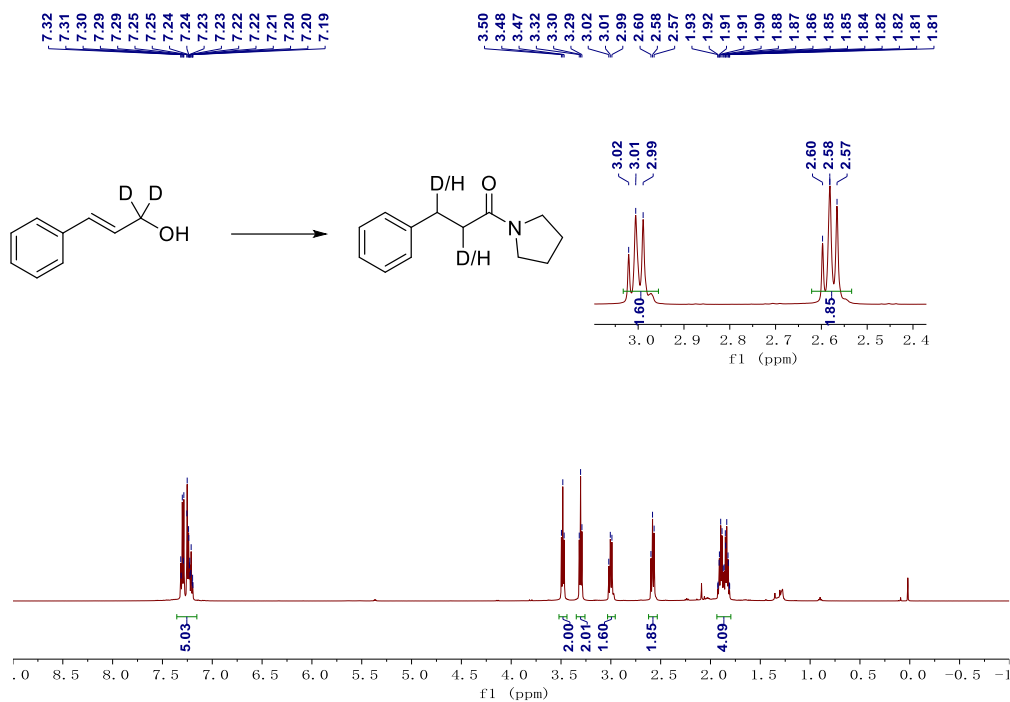












$^1\text{H}$  NMR spectra of the intermediates.

