

## Electronic Supplementary Information

### **Rhodium-Catalyzed C-H Activation and Conjugate Addition under Mild Conditions**

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#### **1. General information**

Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) or Sorbent Silica Gel 60 F254 plates. The developed chromatography was analyzed by UV lamp (254 nm). High-resolution mass spectra (HRMS) were obtained from a JEOL JMS-700 instrument (ESI). IR spectra were recorded by a Nexus 670 Avator FTIR spectrometer. Nuclear magnetic resonance (NMR) spectra were recorded on Varian MERCURY plus spectrometer (<sup>1</sup>H 500 MHz, <sup>13</sup>C 125 MHz). NMR yield was calculated based on the integration using mesitylene as an internal standard. Chemical shifts for <sup>1</sup>H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 7.26 ppm). Chemical shifts for <sup>13</sup>C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (CDCl<sub>3</sub>: δ

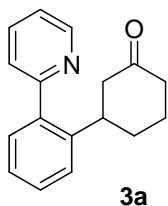
77.23 ppm). Data are reported as following: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, p = quintet, m = multiplet, br = broad signal), coupling constant (Hz), and integration.

**Reagents:** Unless stated otherwise, 2-phenylpyridine analogs **1a-1n** were synthesized starting from 2-bromopyridine (analog) and arylboronic acid following the method reported by Yang *et al.*<sup>1</sup> 1-Phenylpyrazole (**1o**) was synthesized starting from pyrazole and iodobenzene following the method reported by You *et al.*<sup>2</sup> Rhodium catalysts were purchased from Strem Chemicals and used directly without further purification. Substituted cinnaldehydes (**2g-2h**) were synthesized starting from the corresponding aryl iodides or bromides with acrolein diethyl acetal in the presence of Pd(OAc)<sub>2</sub> following the method reported by Cacchi *et al.*<sup>3</sup> Dichloromethane was dried over CaH<sub>2</sub> and used after distillation.

## 2. General experimental procedure for the rhodium-catalyzed C-H activation and conjugate addition

A general experimental procedure is described as following: An oven-dried reaction vessel was charged with (CH<sub>3</sub>CN)<sub>3</sub>Cp\*Rh(SbF<sub>6</sub>)<sub>2</sub> (Rh\*, 8.4 mg, 5 mol%, 0.01 mmol), CH<sub>2</sub>Cl<sub>2</sub> (1 mL, dried over CaH<sub>2</sub>), 2-phenylpyridine (**1a**, 31 mg, 0.2 mmol) and 2-cyclohexenone (**2a**, 0.4 mmol, 38.4 mg, 40.2 μL) under argon. The vessel was sealed and heated at 40 °C (oil bath temperature) for 48 h. The resulting mixture was cooled to room temperature, filtered through a short silica gel pad and transferred to silica gel column directly and eluted with hexanes and ethyl acetate (2:1) to give product **3a** (47.6 mg, 95 % yield).

## 3. Characterization data of product 3a-3v

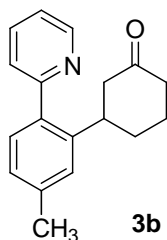


<sup>1</sup> C. Liu, W. Yang, *Chem. Commun.* **2009**, 6267-6269.

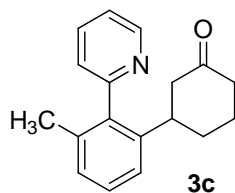
<sup>2</sup> L. Zhu, P. Guo, G. Li, J. Lan, R. Xie, J. You, *J. Org. Chem.* **2007**, 72, 8535-8538.

<sup>3</sup> G. Battistuzzi, S. Cacchi, G. Fabrizi, *Org. Lett.* **2003**, 5, 777-780.

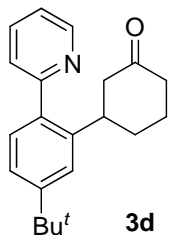
**3a:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.67 (ddd,  $J=1.0, 2.0, 5.0$  Hz, 1H), 7.76 (td,  $J=2.0, 8.0$  Hz, 1H), 7.40-7.44 (m, 2H), 7.26-7.36 (m, 4H), 3.27-3.33 (m, 1H), 2.53 (d,  $J=8.5$  Hz, 2H), 2.30-2.39 (m, 2H), 2.04-2.09 (m, 2H), 1.79-1.87 (m, 1H), 1.53-1.62 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  211.4, 159.8, 149.2, 142.4, 140.0, 136.8, 130.4, 129.0, 126.6, 126.3, 124.4, 122.2, 49.1, 41.4, 40.3, 33.0, 25.7. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{18}\text{ON}$ , 252.1383; found: 252.1376.



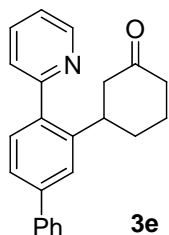
**3b:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.65 (ddd,  $J=1.0, 2.0, 5.0$  Hz, 1H), 7.73 (td,  $J=2.0, 8.0$  Hz, 1H), 7.32 (dt,  $J=1.0, 8.0$  Hz, 1H), 7.23-7.26 (m, 3H), 7.11-7.13 (m, 1H), 3.28-3.34 (m, 1H), 2.52-2.54 (m, 2H), 2.42 (s, 3H), 2.30-2.40 (m, 2H), 2.03-2.10 (m, 2H), 1.78-1.87 (m, 1H), 1.52-1.62 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  211.5, 159.9, 149.3, 142.2, 138.7, 136.7, 130.3, 127.4, 127.0, 124.4, 122.0, 49.1, 41.5, 40.2, 33.0, 25.8, 21.7. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{20}\text{ON}$ , 266.1539; found: 266.1529.



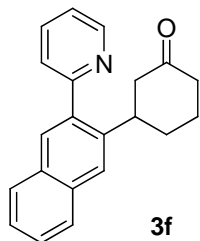
**3c:** a pair of diastereomers.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.68-8.71 (m, 1H), 7.74-7.77 (m, 1H), 7.14-7.33 (m, 4H), 7.14 (d,  $J=7.2$  Hz, 1H), 2.23-2.66 (m, 5H), 1.97-2.03 (m, 5H), 1.69-1.84 (m, 1H), 1.36-1.47 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  211.4, 211.0, 159.3, 150.2, 149.8, 142.2, 140.0, 136.7, 136.5, 136.3, 128.6, 128.4, 124.7, 124.5, 123.3, 123.2, 122.2, 48.9, 48.8, 41.4, 41.3, 41.1, 32.9, 25.7, 25.6, 20.7. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{20}\text{ON}$ , 266.1539; found: 266.1536.



**3d:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.65 (ddd,  $J=1.0, 1.5, 5.0$  Hz, 1H), 7.73 (td,  $J=2.0, 8.0$  Hz, 1H), 7.42 (d,  $J=2.0$  Hz, 1H), 7.35 (dt,  $J=1.0, 6.5$  Hz, 1H), 7.32 (d,  $J=2.0$  Hz, 1H), 7.26-7.28 (m, 1H), 7.24 (ddd,  $J=1.0, 5.0, 7.5$  Hz, 1H), 3.32-3.38 (m, 1H), 2.55 (d,  $J=8.5$  Hz, 2H), 2.32-2.38 (m, 2H), 2.03-2.07 (m, 2H), 1.80-1.88 (m, 1H), 1.58-1.63 (m, 1H), 1.35 (s, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  211.6, 160.0, 151.9, 149.3, 141.8, 137.3, 136.6, 130.1, 124.3, 123.7, 123.0, 122.0, 49.2, 41.5, 40.4, 35.0, 33.0, 31.6, 25.7. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{26}\text{ON}$ , 308.2009; found: 308.1996.

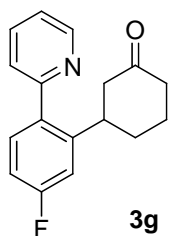


**3e:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.69 (ddd,  $J=1.0, 2.0, 5.0$  Hz, 1H), 7.77 (td,  $J=2.0, 7.5$  Hz, 1H), 7.63-7.65 (m, 3H), 7.53 (dd,  $J=2.0, 8.0$  Hz, 1H), 7.37-7.49 (m, 5H), 7.27 (ddd,  $J=1.0, 4.5, 7.5$  Hz, 1H), 3.38-3.43 (m, 1H), 2.60 (d,  $J=7.0$  Hz, 2H), 2.32-2.39 (m, 2H), 2.07-2.13 (m, 2H), 1.87-1.95 (m, 1H), 1.59-1.63 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  211.2, 159.7, 149.5, 142.8, 141.9, 141.1, 139.1, 136.6, 130.9, 129.0, 127.7, 127.4, 125.4, 125.2, 124.3, 122.2, 49.1, 41.4, 40.4, 33.0, 25.8. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{23}\text{H}_{21}\text{ON}$ , 328.1696; found: 328.1691.

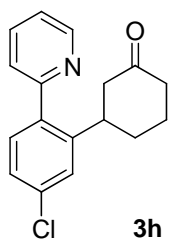


**3f:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.70 (m, 1H), 7.78-7.86 (m, 1H), 7.45-7.47 (m, 5H), 7.49-7.52 (m, 3H), 7.28-7.32 (m, 1H), 3.52-3.58 (m, 1H), 2.60-2.66 (m, 2H), 2.33-2.42 (m, 2H), 2.04-2.16 (m, 2H), 1.84-1.92 (m, 1H), 1.56-1.64 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$

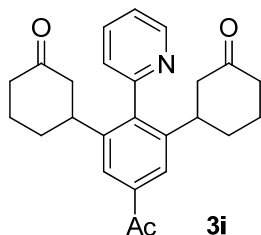
211.5, 160.0, 149.3, 140.7, 138.9, 136.8, 133.5, 132.0, 129.8, 128.0, 127.6, 126.7, 126.3, 125.2, 124.5, 122.2, 49.1, 41.5, 40.1, 33.1, 25.6.



**3g:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.65 (ddd,  $J=1.0, 1.5, 5.0$  Hz, 1H), 7.74 (td,  $J=1.5, 7.5$  Hz, 1H), 7.25-7.32 (m, 3H), 7.11 (dd,  $J=3.0, 10.5$  Hz, 1H), 6.99 (td,  $J=2.5, 8.5$  Hz, 1H), 3.28-3.34 (m, 1H), 2.29-2.54 (m, 4H), 2.03-2.09 (m, 2H), 1.74-1.82 (m, 1H), 1.55-1.61 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  210.8, 164.2, 162.2, 159.0, 149.5, 145.0 (d,  $J=6.9$  Hz), 136.8, 136.2 (d,  $J=3.2$  Hz), 132.1 (d,  $J=8.4$  Hz), 124.3, 122.3, 113.4 (q,  $J=20.9$  Hz), 48.8, 41.3, 40.3, 32.8, 25.6. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{17}\text{ONF}$ , 270.1289; found: 270.1286.

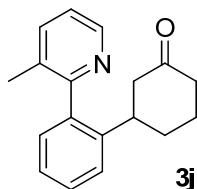


**3h:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.65 (m, 1H), 7.75 (td,  $J=1.5, 7.5$  Hz, 1H), 7.39 (s, 1H), 7.31 (d,  $J=8.0$  Hz, 1H), 7.25-7.28 (m, 3H), 3.27-3.33 (m, 1H), 2.29-2.54 (m, 4H), 2.03-2.09 (m, 2H), 1.76-1.84 (m, 1H), 1.54-1.60 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  210.6, 158.8, 149.5, 144.4, 138.6, 136.8, 134.8, 131.7, 126.8, 126.6, 124.2, 122.4, 48.8, 41.3, 40.2, 32.8, 25.6. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{17}\text{ONCl}$ , 286.0993; found: 286.0986.

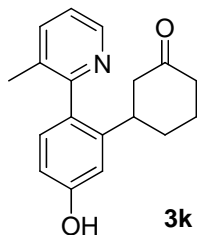


**3i:** two pairs of diastereomers.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.66-8.73 (m, 1H), 7.87-7.88 (m, 2H), 7.72-7.81 (m, 1H), 7.31-7.34 (m, 1H), 7.16 (ddd,  $J=1.0, 2.0, 8.0$  Hz, 1H), 2.66 (s, 3H), 2.26-2.64 (m, 10H), 1.68-2.06 (m, 6H), 1.35-1.45 (m, 2H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$

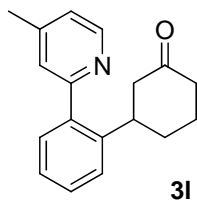
210.59, 210.49, 210.20, 210.17, 157.52, 157.49, 158.58, 150.25, 149.92, 143.95, 143.86, 143.68, 143.61, 143.60, 137.76, 137.08, 136.65, 136.24, 124.52, 124.34, 124.22, 124.16, 124.12, 123.97, 122.99, 122.96, 48.81, 48.73, 48.56, 48.50, 41.46, 41.28, 41.26, 41.19, 32.81, 32.78, 32.76, 26.91, 25.66, 25.64, 25.54. HRMS (ESI)  $m/z$ :  $[M+H]^+$  calcd for  $C_{25}H_{28}O_3N$ , 390.2064; found: 390.2060.



**3j**:  $^1H$  NMR (500 MHz,  $CDCl_3$ , TMS)  $\delta$  8.48 (d,  $J=4.0$  Hz, 1H), 7.57 (dd,  $J=1.0, 8.0$  Hz, 1H), 7.41 (d,  $J=1.0$  Hz, 1H), 7.40 (d,  $J=1.0$  Hz, 1H), 7.27-7.30 (m, 1H), 7.19 (dd,  $J=5.0, 8.0$  Hz, 1H), 7.15 (dt,  $J=1.0, 7.5$  Hz, 1H), 2.73 (br, 1H), 2.57 (br, 1H), 2.26-2.34 (m, 3H), 2.08 (s, 3H), 1.99-2.04 (m, 1H), 1.71 (br, 2H), 1.45-1.50 (m, 1H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ , TMS)  $\delta$  211.4, 159.1, 146.8, 142.1, 139.7, 138.1, 131.7, 129.3, 128.7, 126.6, 126.0, 122.6, 48.5, 41.4, 41.0, 33.1, 25.7, 19.6. HRMS (ESI)  $m/z$ :  $[M+H]^+$  calcd for  $C_{18}H_{19}ON$ , 266.1539; found: 266.1534.

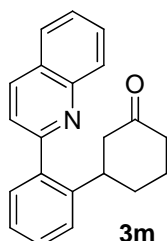


**3k**:  $^1H$  NMR (500 MHz,  $CD_3OD$ , TMS)  $\delta$  8.36 (d,  $J=4.5$  Hz, 1H), 7.77 (dd,  $J=0.5, 7.5$  Hz, 1H), 7.33 (dd,  $J=5.0, 8.0$  Hz, 1H), 6.97 (d,  $J=8.5$  Hz, 1H), 6.93 (d,  $J=2.0$  Hz, 1H), 2.54 (br, 2H), 2.20-2.44 (m, 3H), 2.13 (s, 3H), 2.01-2.04 (m, 2H), 1.80 (br, 1H), 1.35-1.37 (m, 1H);  $^{13}C$  NMR (125 MHz,  $CD_3OD$ , TMS)  $\delta$  211.9, 158.6, 157.8, 145.3, 143.6, 138.8, 133.1, 129.8, 129.7, 122.7, 113.2, 112.6, 112.4, 41.2, 40.3, 32.1, 25.3, 22.7, 18.2. HRMS (ESI)  $m/z$ :  $[M+H]^+$  calcd for  $C_{18}H_{20}O_2N$ , 282.1489; found: 282.1486.

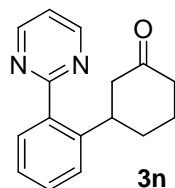


**3l**:  $^1H$  NMR (500 MHz,  $CDCl_3$ , TMS)  $\delta$  8.50 (d,  $J=5.0$  Hz, 1H), 7.38-7.42 (m, 2H), 7.25-7.32 (m, 2H), 7.15 (t,  $J=0.5$  Hz, 1H), 7.08 (ddd,  $J=0.5, 1.5, 5.0$  Hz, 1H), 3.28-3.34 (m, 1H), 2.51-2.54 (m,

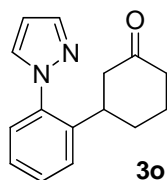
2H), 2.40 (s, 3H), 2.30-2.36 (m, 2H), 2.03-2.09 (m, 2H), 1.78-1.86 (m, 1H), 1.53-1.66 (m, 1H);  
 $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  211.6, 159.8, 149.1, 147.7, 142.4, 140.4, 130.3, 128.8, 126.5,  
126.2, 125.2, 123.2, 49.0, 41.5, 40.2, 33.0, 25.7, 21.4. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  
 $\text{C}_{18}\text{H}_{20}\text{ON}$ , 266.1539; found: 266.1532.



**3m:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.22 (d,  $J=8.0$  Hz, 1H), 8.13 (d,  $J=8.4$  Hz, 1H), 7.87 (d,  $J=8.0$  Hz, 1H), 7.75 (td,  $J=1.6, 8.0$  Hz, 1H), 7.57 (dt,  $J=1.2, 8.4$  Hz, 1H), 7.44-7.51 (m, 4H),  
7.33-7.37 (m, 1H), 3.36-3.44 (m, 1H), 2.67 (dd,  $J=4.0, 6.0$  Hz, 1H), 2.61 (dd,  $J=1.6, 6.0$  Hz, 1H),  
2.32-2.36 (m, 2H), 2.02-2.15 (m, 2H), 1.86 (ddd,  $J=3.6, 12.4, 25.6$  Hz, 1H), 1.47-1.59 (m, 1H);  
 $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  211.2, 159.9, 148.0, 142.7, 140.4, 136.6, 130.4, 130.0, 129.9,  
129.2, 127.7, 126.9, 126.8, 126.75, 126.5, 122.4, 49.2, 41.4, 40.5, 33.2, 25.7. HRMS (ESI)  $m/z$ :  
 $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{20}\text{ON}$ , 302.1539; found: 302.1533.

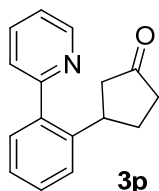


**3n:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.83 (d,  $J=5.0$  Hz, 1H), 7.71 (td,  $J=1.0, 7.5$  Hz, 1H),  
7.45-7.47 (m, 2H), 7.33-7.36 (m, 1H), 7.24 (t,  $J=5.0$  Hz, 1H), 3.68-3.74 (m, 1H), 2.62-2.68 (m,  
1H), 2.53 (dt,  $J=1.0, 7.5$  Hz, 1H), 2.33-2.44 (m, 2H), 2.04-2.13 (m, 2H), 1.82-1.90 (m, 1H),  
1.61-1.70 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  211.6, 167.7, 157.2, 143.2, 138.0, 131.2,  
130.0, 126.7, 126.5, 119.0, 49.2, 41.6, 40.2, 32.9, 25.8. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  
 $\text{C}_{16}\text{H}_{17}\text{ON}_2$ , 253.1335; found: 253.1329.

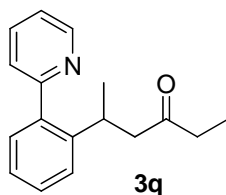


**3o:**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  7.69 (dd,  $J=0.5, 2.0$  Hz, 1H), 7.55 (dd,  $J=0.5, 2.5$  Hz,

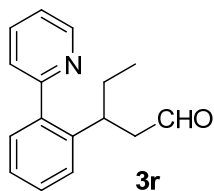
1H), 7.42-7.45 (m, 2H), 7.27-7.34 (m, 2H), 6.43 (t,  $J=2.0$  Hz, 1H), 2.98-3.04 (m, 1H), 2.40-2.52 (m, 2H), 2.28-2.38 (m, 2H), 1.98-2.09 (m, 2H), 1.21-1.80 (m, 1H), 1.57-1.65 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  210.7, 140.9, 140.7, 139.1, 131.1, 129.4, 127.33, 127.3, 127.1, 106.7, 48.4, 41.3, 38.6, 32.7, 25.5. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{15}\text{H}_{17}\text{ON}_2$ , 241.1335; found: 241.1329.



**3p**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.68-8.69 (m, 1H), 7.79 (td,  $J=2.0, 8.0$  Hz, 1H), 7.39-7.43 (m, 3H), 7.28-7.36 (m, 3H), 3.68-3.75 (m, 1H), 2.55 (dd,  $J=8.0, 18.5$  Hz, 1H), 2.41 (dd,  $J=8.0, 18.5$  Hz, 1H), 2.24-2.31 (m, 2H), 2.12-2.20 (m, 1H), 1.98-2.08 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  219.0, 160.1, 149.3, 141.1, 140.8, 136.9, 130.3, 129.1, 126.7, 126.0, 124.4, 122.2, 46.8, 39.1, 38.6, 31.2. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_{16}\text{ON}$ , 238.1226; found: 238.1217.



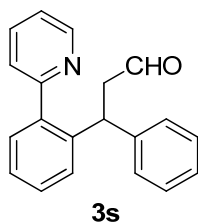
**3q**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  8.67 (ddd,  $J=1.0, 2.0, 5.0$  Hz, 1H), 7.71 (td,  $J=1.0, 7.5$  Hz, 1H), 7.42 (dt,  $J=1.5, 8.0$  Hz, 1H), 7.24-7.39 (m, 5H), 3.55-3.59 (m, 1H), 2.82 (dd,  $J=5.5, 15.5$  Hz, 1H), 2.54 (dd,  $J=9.0, 16.0$  Hz, 1H), 2.26 (q,  $J=7.0$  Hz, 2H), 1.20 (d,  $J=7.0$  Hz, 3H), 0.95 (t,  $J=7.5$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  210.7, 160.2, 149.3, 144.3, 140.2, 136.4, 130.1, 128.8, 126.2, 126.1, 124.5, 122.0, 51.0, 36.2, 30.9, 21.9, 7.9. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{17}\text{H}_{20}\text{ON}$ , 254.1539; found: 254.1534.



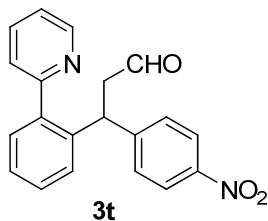
**3r**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  9.64 (dd,  $J=2.0, 3.0$  Hz, 1H), 8.66 (ddd,  $J=1.0, 1.5, 4.5$  Hz, 1H), 7.76 (td,  $J=1.5, 7.5$  Hz, 1H), 7.38-7.42 (m, 2H), 7.25-7.34 (m, 3H), 3.44 (m, 1H), 2.77



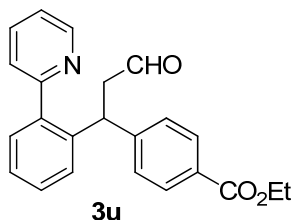
(ddd,  $J=2.5, 7.5, 16.5$  Hz, 1H), 2.63 (ddd,  $J=2.5, 7.5, 16.5$  Hz, 1H), 1.62 (m, 2H), 0.70 (t,  $J=7.5$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  202.9, 160.4, 149.2, 142.0, 141.2, 136.5, 130.1, 129.0, 126.6, 124.6, 122.0, 50.8, 36.7, 29.6, 12.0. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{16}\text{H}_{18}\text{ON}$ , 240.1383; found: 240.1376.



**3s**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  9.64 (t,  $J=2.0$  Hz, 1H), 8.70 (ddd,  $J=1.0, 1.5, 5.0$  Hz, 1H), 7.70 (td,  $J=1.5, 7.5$  Hz, 1H), 7.12-7.36 (m, 9H), 7.02-7.04 (m, 2H), 5.14 (t,  $J=7.5$  Hz, 1H), 3.17 (ddd,  $J=2.0, 7.0, 17.5$  Hz, 1H), 3.10 (ddd,  $J=2.0, 7.0, 17.5$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  201.8, 160.2, 149.2, 143.4, 141.7, 140.6, 136.7, 130.3, 129.0, 128.6, 128.1, 128.0, 126.8, 126.5, 124.6, 122.2, 49.8, 40.3. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{18}\text{ON}$ , 288.1383; found: 288.1374.

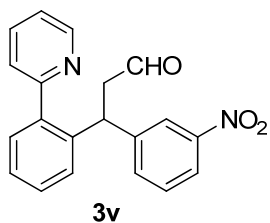


**3t**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  9.68 (s, 1H), 8.68 (d,  $J=4.4$  Hz, 1H), 8.03 (d,  $J=8.8$  Hz, 2H), 7.73 (td,  $J=1.6, 7.6$  Hz, 1H), 7.24-7.42 (m, 6H), 7.19 (d,  $J=7.6$  Hz, 2H), 5.34 (t,  $J=7.6$  Hz, 1H), 3.31 (ddd,  $J=1.6, 6.4, 17.2$  Hz, 1H), 3.16 (ddd,  $J=1.6, 6.4, 17.2$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  200.2, 159.8, 151.3, 149.2, 146.6, 140.6, 140.3, 137.0, 130.7, 129.2, 128.9, 127.9, 127.4, 124.6, 123.8, 122.4, 49.5, 40.0. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{17}\text{O}_3\text{N}_2$ , 333.1234; found: 333.1228.

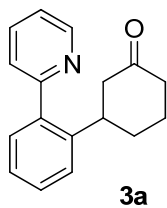


**3u**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  9.66 (s, 1H), 8.69 (d,  $J=4.4$  Hz, 1H), 7.85 (d,  $J=8.4$  Hz, 2H), 7.70 (td,  $J=1.6, 8.0$  Hz, 1H), 7.21-7.39 (m, 5H), 7.08 (d,  $J=8.4$  Hz, 2H), 5.24 (t,  $J=8.0$  Hz,

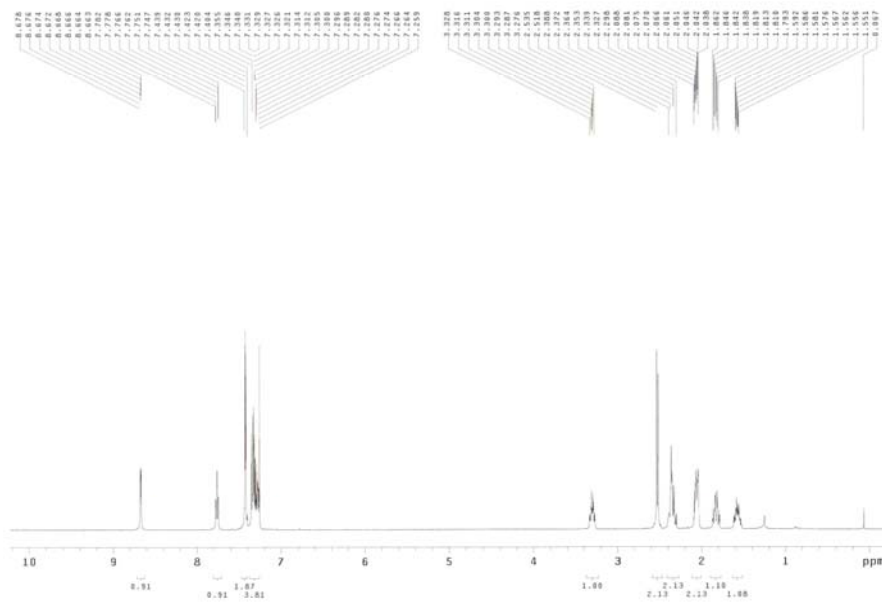
1H), 4.33 (q,  $J=7.2$  Hz, 2H), 3.22 (ddd,  $J=1.6, 7.2, 16.8$  Hz, 1H), 3.12 (ddd,  $J=1.6, 7.2, 16.8$  Hz, 1H), 1.35 (t,  $J=7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  201.1, 166.6, 160.0, 149.2, 148.7, 140.9, 140.6, 136.8, 130.5, 129.9, 129.1, 128.8, 128.0, 127.97, 127.1, 124.6, 122.3, 61.0, 49.6, 40.3, 14.5. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{23}\text{H}_{22}\text{O}_3\text{N}$ , 360.1594; found: 360.1596.



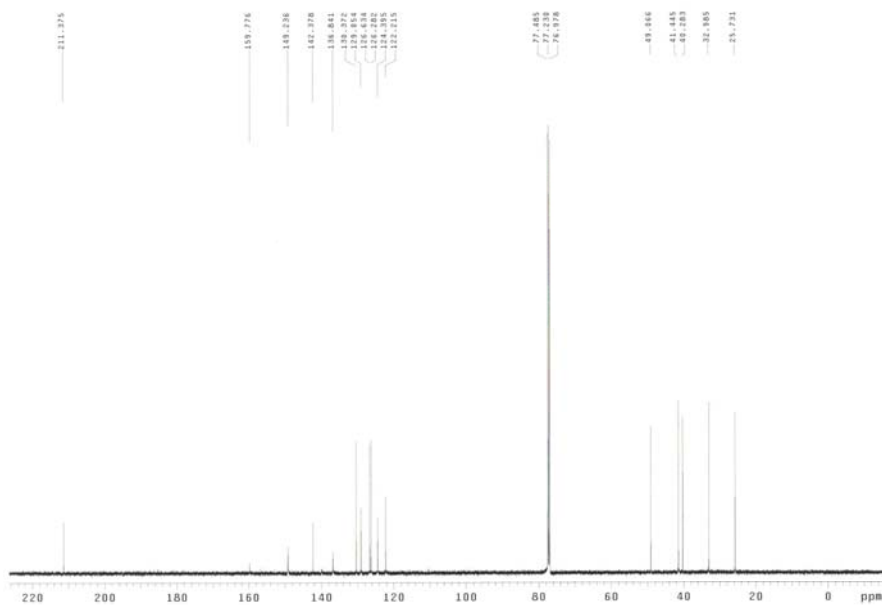
**3v**:  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  9.69 (s, 1H), 8.70 (d,  $J=4.0$  Hz, 1H), 7.97 (d,  $J=8.0$  Hz, 1H), 7.89 (s, 1H), 7.72 (td,  $J=1.5, 7.5$  Hz, 1H), 7.24-7.42 (m, 8H), 5.32 (t,  $J=7.5$  Hz, 2H), 3.32 (ddd,  $J=1.0, 6.5, 17.0$  Hz, 1H), 3.20 (ddd,  $J=1.0, 6.5, 17.0$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS)  $\delta$  200.2, 159.8, 149.2, 148.4, 145.8, 140.6, 140.4, 137.0, 134.5, 130.6, 129.4, 129.2, 127.8, 127.4, 124.5, 12.8, 122.4, 121.6, 49.5, 39.8. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{20}\text{H}_{17}\text{O}_2\text{N}_3$ , 333.1234; found: 333.1236.



1370 3a



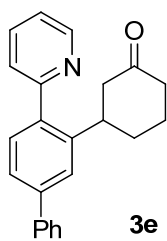
1370 3a



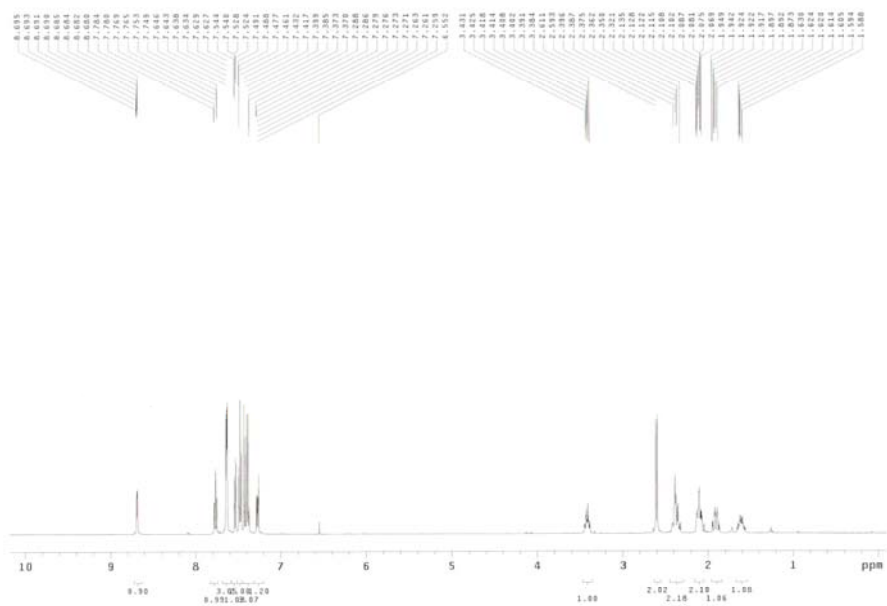




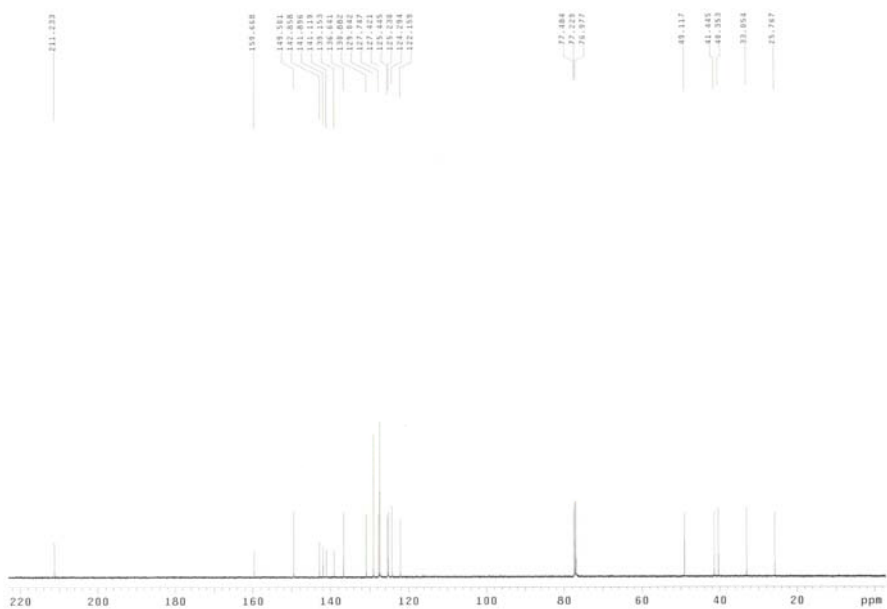




1637-169 3e



1637-169 3e



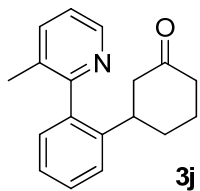




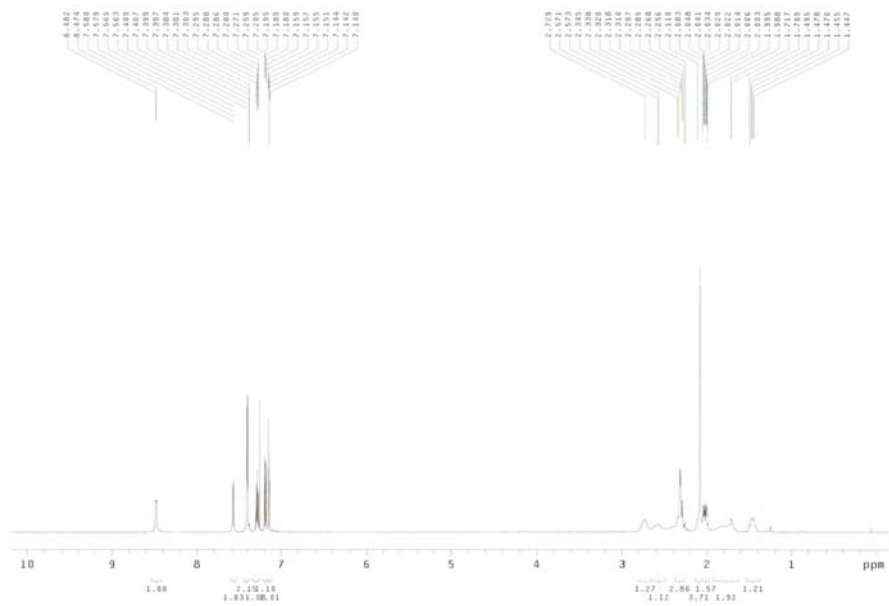




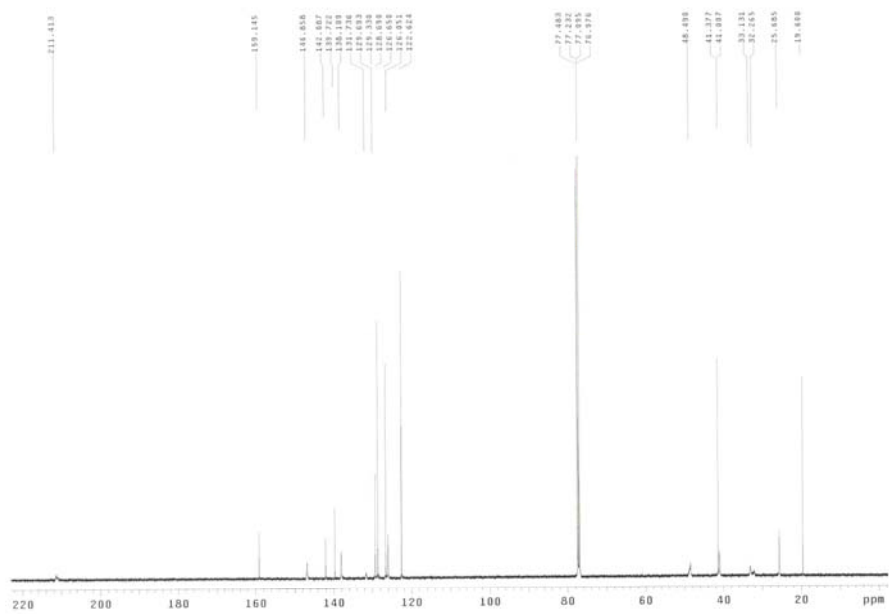




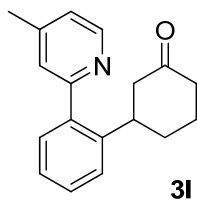
(400L - 500MHz) 3j



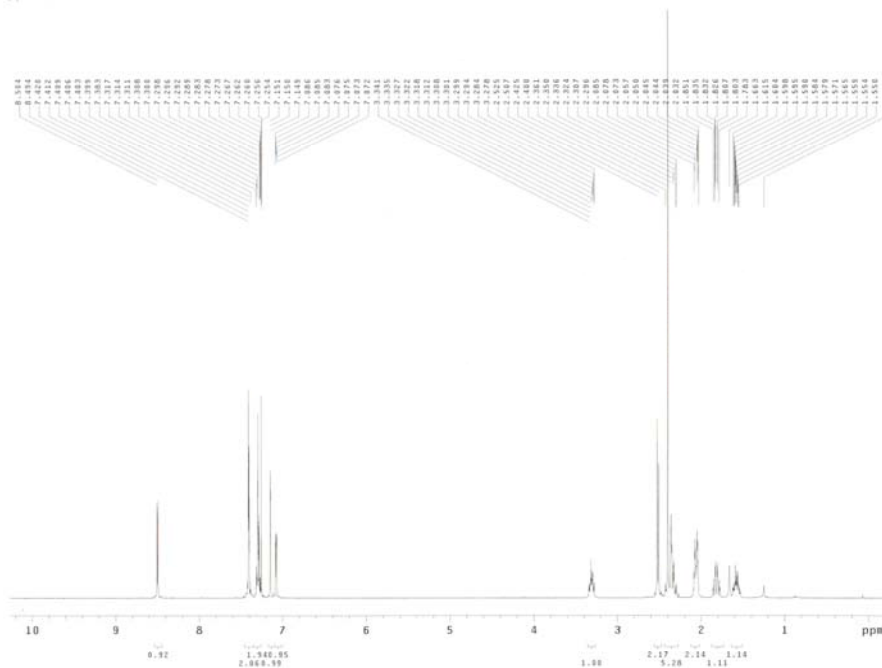
(400L - 500MHz) 3j







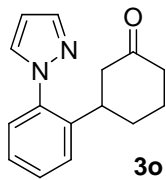
MS-31



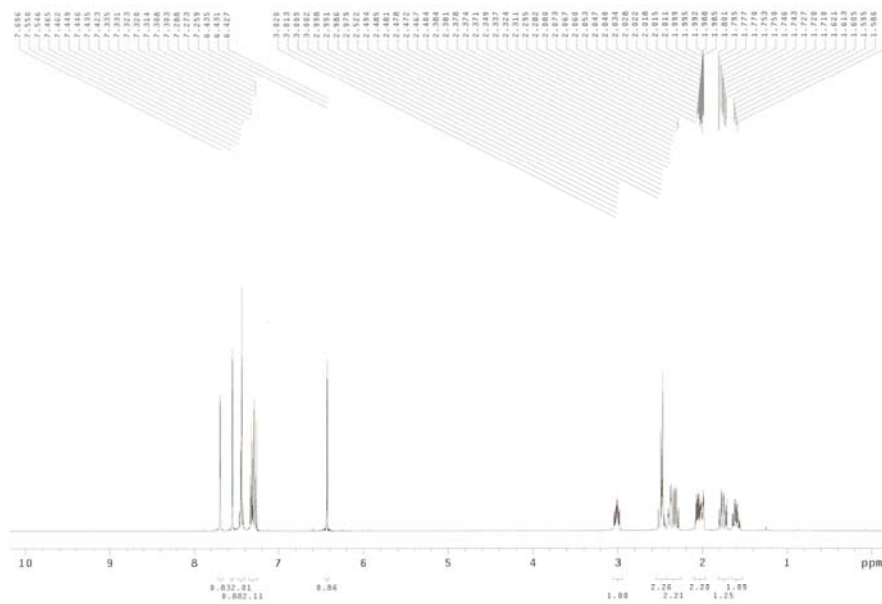




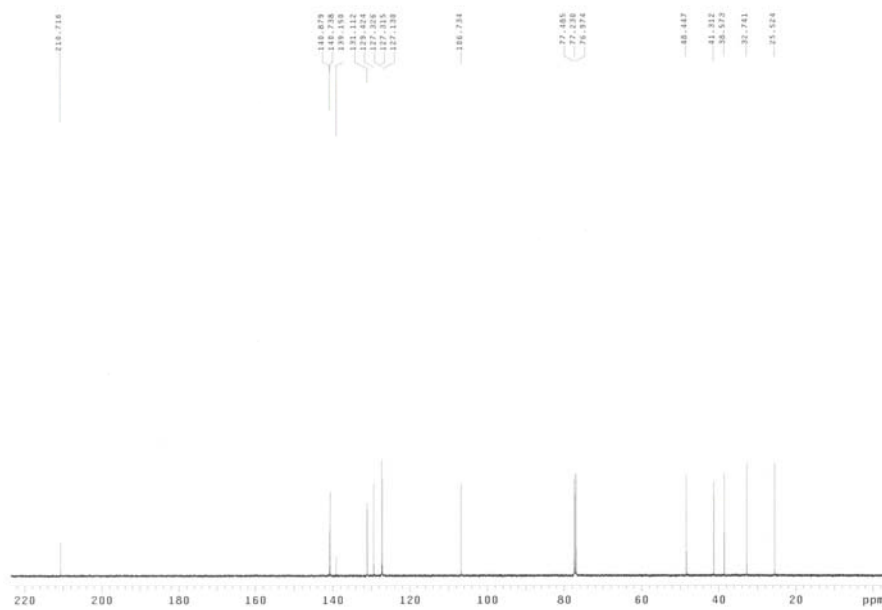


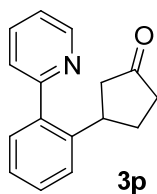


1H NMR 30

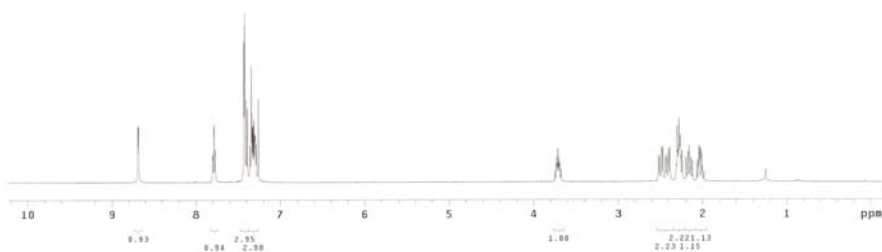


13C NMR 30

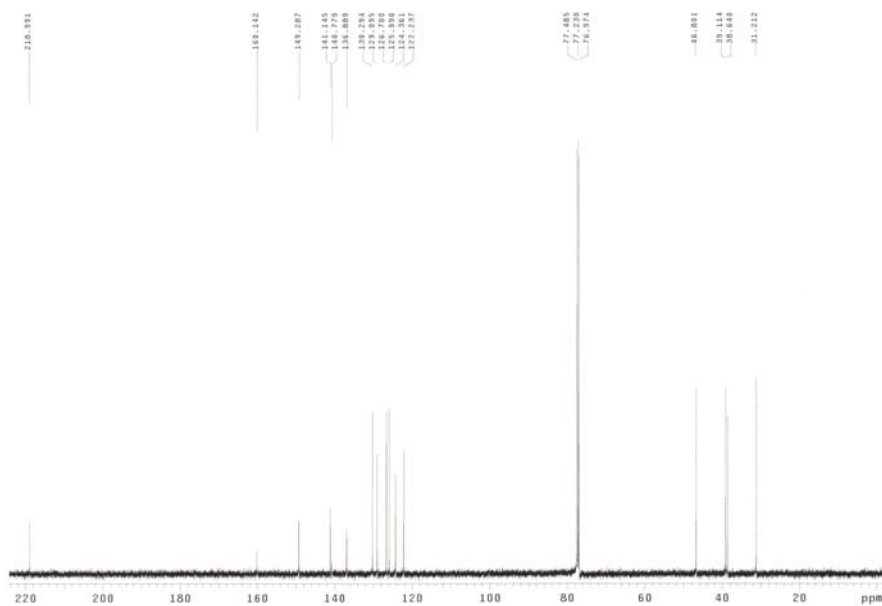


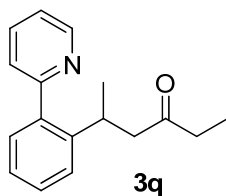


131 3p

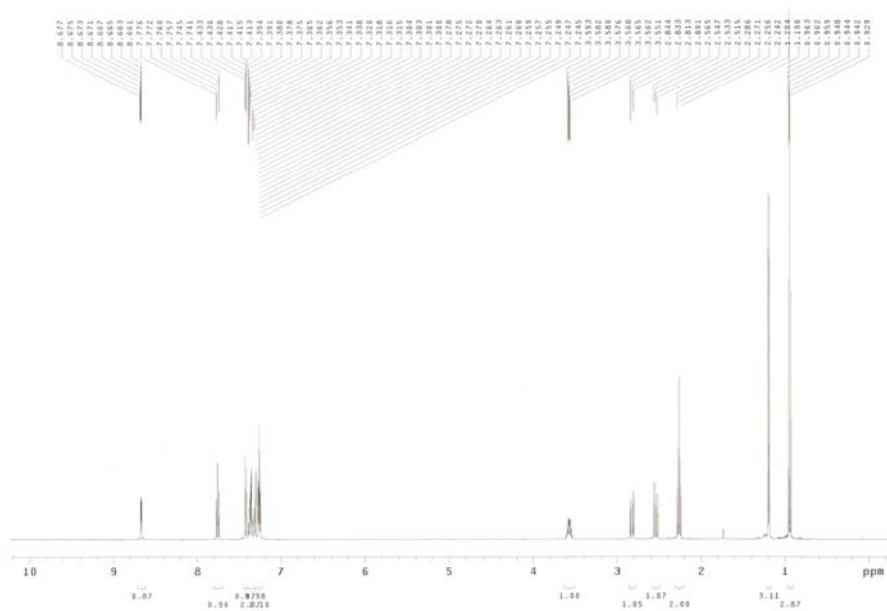


591 3p

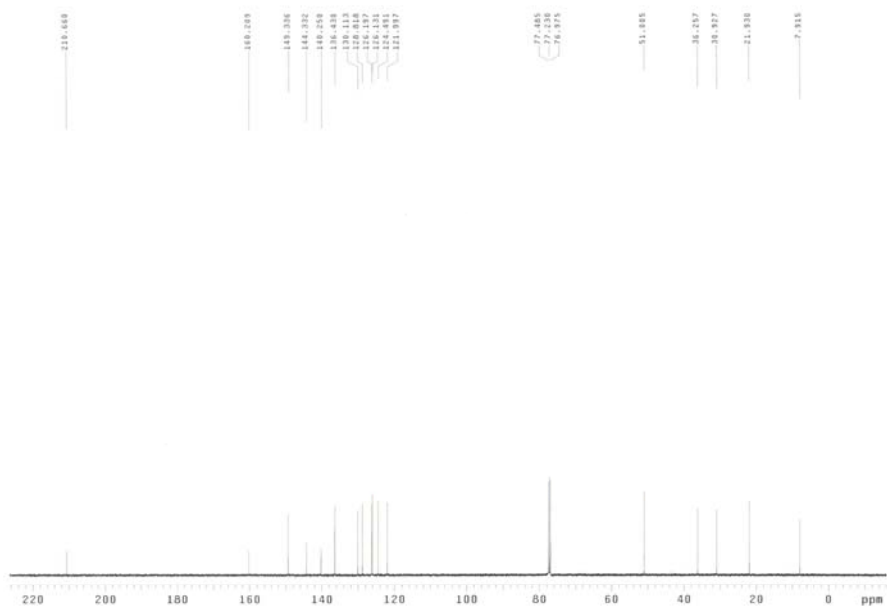


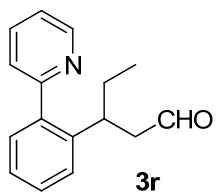


1466 3q

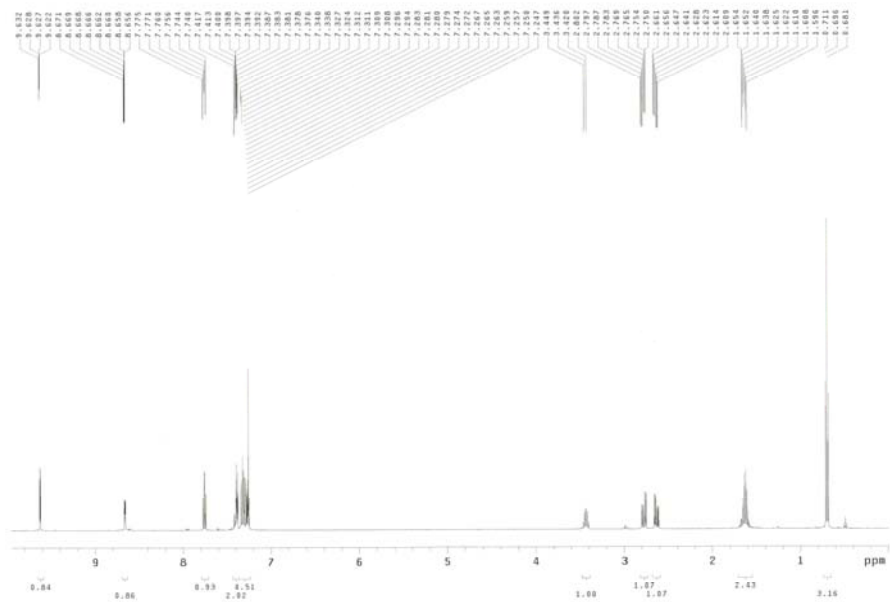


1466 3q

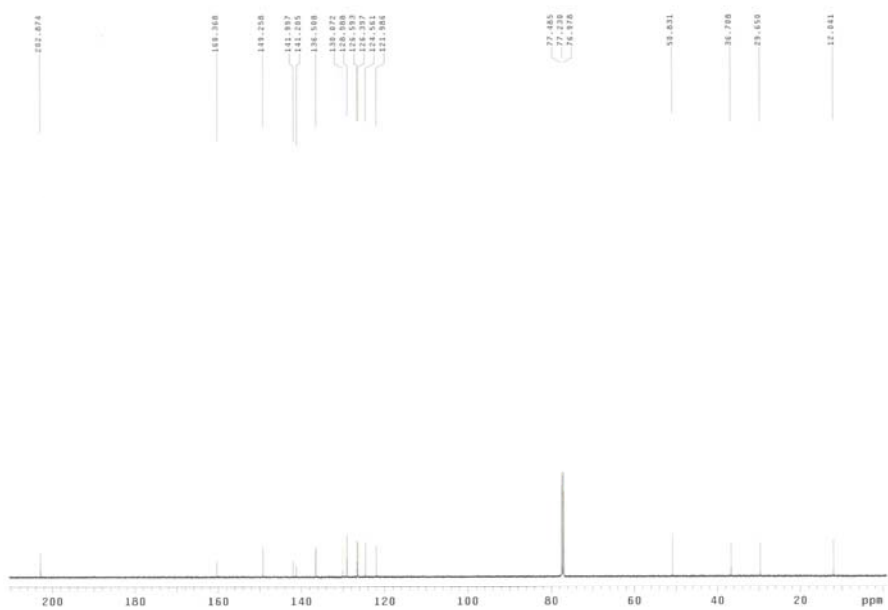


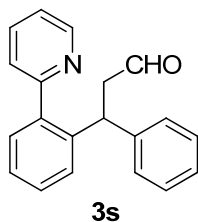


1441-5000 3r

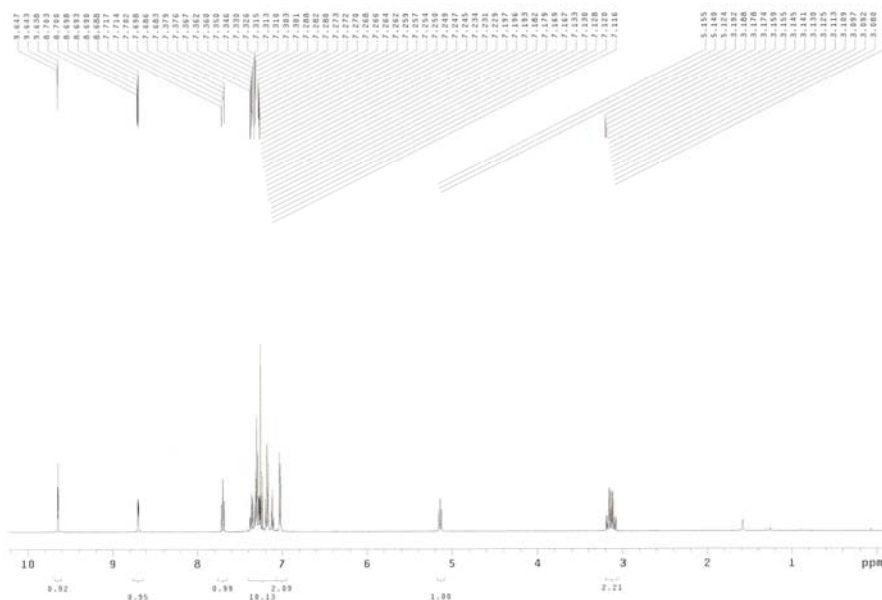


1446-5000 3r

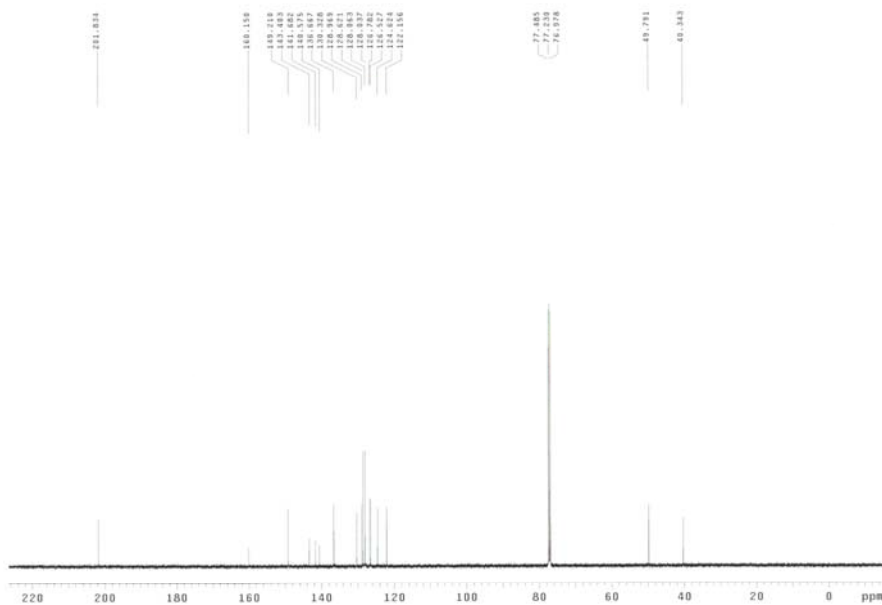


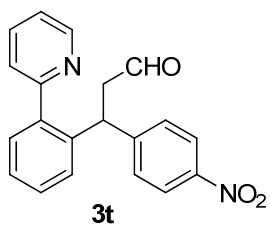


163-1000-35

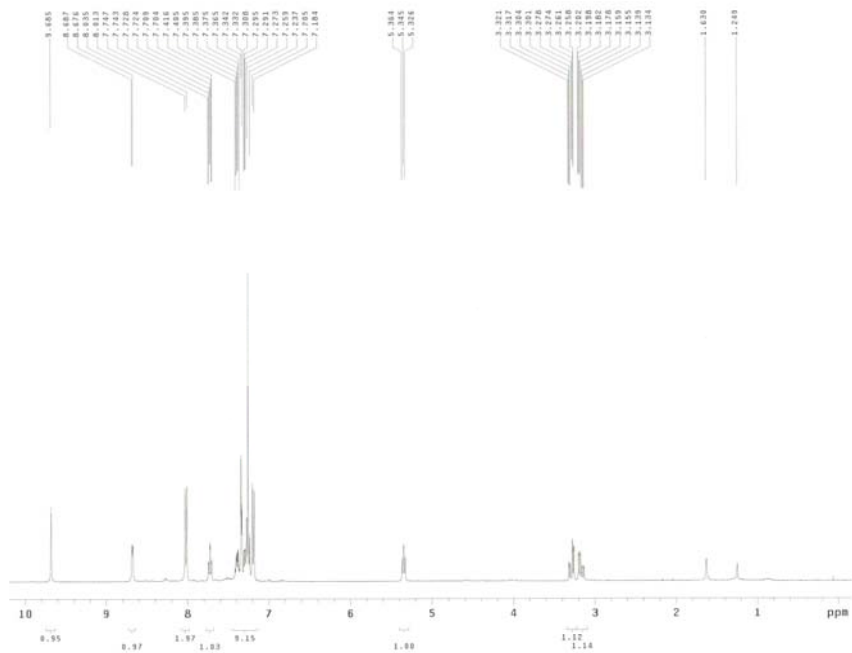


163-1000-35

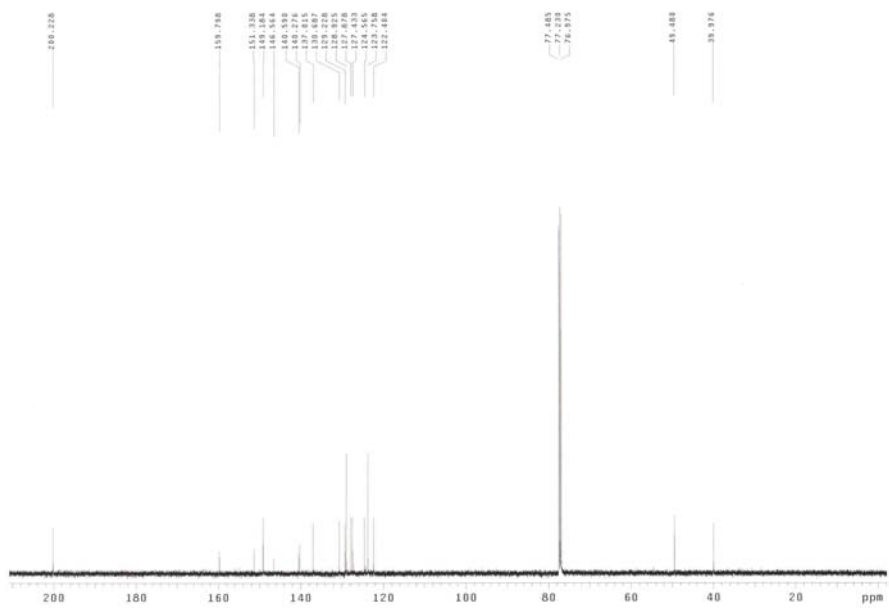




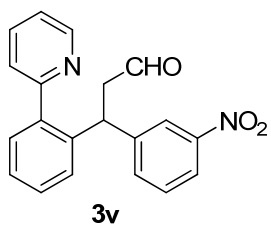
300 - 400M 3t



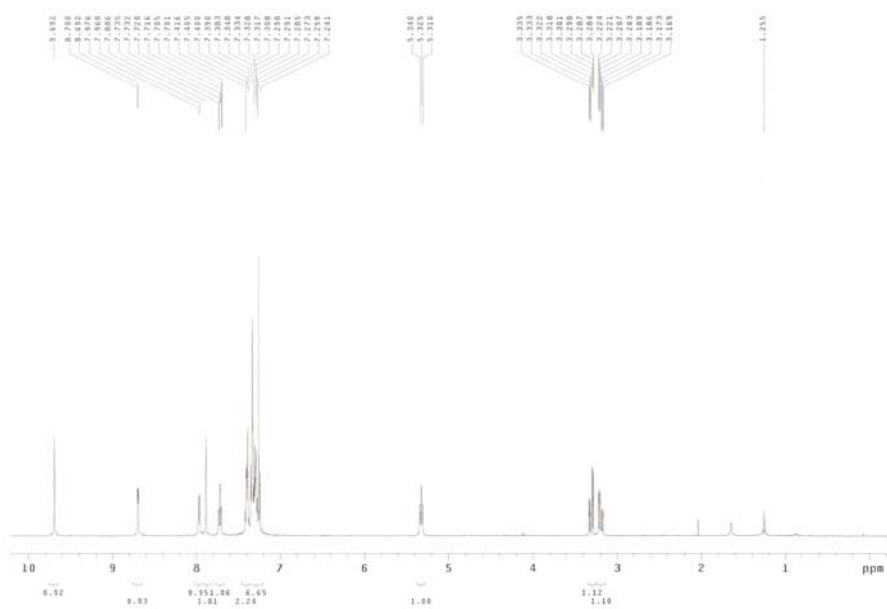
1304 - 500M 3t







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



<sup>13</sup>C NMR (CDCl<sub>3</sub>) 3V

