

# **Synthesis of 2,4,6-Trisubstituted Pyridines *via* an Olefin Cross-Metathesis/Heck-Cyclisation-Elimination Sequence**

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**Electronic Supplementary Information**

## General Experimental Details

All solvents and reagents requiring purification were purified using standard laboratory techniques according to methods published by Perrin, Armarego, and Perrin (Pergamon Press, 1966) apart from  $\text{CH}_2\text{Cl}_2$ , THF and Toluene which were dried by filtration through an activated alumina purification column. Petrol refers to petroleum ether in the boiling range 40–60 °C. Flash column chromatography was performed using Merck Kieselgel 60 (40–63  $\mu\text{m}$ ).  $^1\text{H}$  nuclear magnetic resonance spectra (NMR) were recorded at 300 MHz, 400 MHz or 500 MHz.  $^{13}\text{C}$  NMR spectra were recorded at 75 MHz, 101 MHz or 126 MHz as stated. Chemical shifts are reported relative to residual deuterated solvent peaks or tetramethylsilane internal standard. Coupling constants are quoted to the nearest 0.5 Hz for  $^1\text{H}$  NMR and to the nearest 1 Hz for  $^{13}\text{C}$  NMR. Where mixtures of isomers (*e.g.* diastereoisomers) have been characterised together integrals are normalized to the major isomer. Mass spectra under the conditions of electrospray ionisation (ESI) were recorded on a Fisons Platform II. Mass spectra under the conditions of field ionisation (FI) were recorded on a Micromass LCT. Mass spectra under the conditions of chemical ionisation (CI) were recorded on a Fisons Autospec-oeTof. Infrared spectra (IR) were recorded as evaporated films or KBr discs. Melting points were obtained using a Leica VMTG heated-stage microscope and are uncorrected. All materials were purchased from commercial sources where available and used without further purification. Non-commercially available vinyl ketones were synthesised analogous to literature routes either *via* the Weinreb amide formation<sup>1</sup> or  $\alpha$ -methylenation of the corresponding ketones.<sup>2</sup>

**General Procedure A for the cross-metathesis of homoallylic sulfonamide derivatives and enones/acrylates - Step 1** - A re-sealable reaction tube, fitted with a magnetic follower, was charged with Hoveyda-Grubbs 2<sup>nd</sup> generation catalyst (7.5 mol%) and (if solid) the appropriate homoallylic sulfonamide derivative (100 mol%). The tube was then sealed with a rubber septum and purged with argon. Argon sparged  $\text{CH}_2\text{Cl}_2$  (0.25 M with respect to the homoallylic sulfonamide employed), (if liquid) the appropriate homoallylic sulfonamide derivative and the requisite enone (250-500 mol%) were then added sequentially via syringe. The rubber septum was then replaced with a screw cap and the tube was heated at 55 °C (oil bath temperature) for the time stated. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and the crude material was purified directly by flash column chromatography under the conditions noted.

**General Procedure B for tandem Heck arylation/pyridine formation - Step 2 and 3** - A reaction tube, fitted with magnetic follower, was charged with  $\text{Pd}_2(\text{dba})_3$  (5 mol%),  $\text{Pt-Bu}_3\text{HBF}_4$  (20 mol%) and (if solid) the corresponding aryl bromide (250 mol%). The tube was sealed with a septum and purged with argon. The requisite  $\delta$ -sulfonamido enone (100 mol%), the corresponding aryl bromide (if liquid) (250 mol%), anhydrous PhMe (0.1 M with respect to the enone component) and then  $\text{Cy}_2\text{NMe}$  (150 mol%) were added sequentially *via* syringe. The mixture was then heated at 80 °C (oil bath temperature) until TLC analysis indicated full consumption of the  $\delta$ -sulfonamido enone (*ca.* 2-5 h). TFA (100 mol%) was then added and heating was continued until complete condensation of the Heck product was observed by TLC analysis (*ca.* 1-4 h). At this stage, elimination to the final pyridine target was achieved *via* one of two alternative conditions:

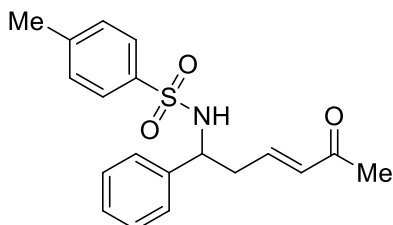
<sup>1</sup> J.-I. Matsuo and Y. Aizawa, *Chem. Commun.* 2005, 2399.

<sup>2</sup> (a) J.-L. Gras, *Tetrahedron Lett.* 1978, **32**, 2955; (b) A. Bugarin, K. D. Jones and B. T. Connell, *Chem. Commun.*, 2010, **46**, 1715.

**Part B - Conditions (i) - Step 4** - DBU (500 mol%) was added to the reaction mixture and heating was continued until complete elimination of the condensation product was observed by TLC analysis (*ca.* 15 minutes – 18 h). The mixture was cooled to room temperature and filtered through a short cartridge of SiO<sub>2</sub> eluting with 33% EtOAc:petrol. The fractions containing the target pyridine were combined and concentrated *in vacuo*. The crude material was purified by flash column chromatography under the conditions noted, affording the corresponding pyridine.

**Part B - Conditions (ii) - Step 4** - The reaction mixture was cooled to room temperature and the mixture was filtered through a short cartridge of SiO<sub>2</sub> eluting with 33% EtOAc:petrol. The fractions containing the Heck condensation product were combined and concentrated *in vacuo*. The crude material was purified by flash column chromatography under the conditions noted, affording pure condensation adduct. Yields and data for this adduct are provided. Next, the condensation adduct (100 mol%) was dissolved in anhydrous PhMe (0.1 M) under an argon atmosphere. KHMDS (0.5 M in PhMe, 120 mol%) was then added *via* syringe and stirring was continued at room temperature until complete conversion to the target pyridine was observed by TLC analysis (*ca.* 0.5-4 h). The mixture was then diluted with brine (*ca.* 50 mL/mmol) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL/mmol). The organic extracts were combined, dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. The crude material was purified by flash column chromatography under the conditions noted, affording the target pyridine.

**(E)-4-Methyl-N-(5-oxo-1-phenylhex-3-en-1-yl)benzenesulfonamide 3a**



**General Procedure A** - **1a** (400 mg, 1.33 mmol) and methylvinylketone (**2a**) (0.27 mL, 3.33 mmol) were employed. Reaction heated for 71 h. The crude material was purified by flash column chromatography eluting with 20% to 50% EtOAc:petrol affording **3a** as a white solid (380 mg, 83%).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.57 (d,  $J$ =8.5 Hz, 2 H), 7.09 - 7.23 (m, 5 H), 7.00 - 7.09 (m, 2 H), 6.54 (dt,  $J$ =16.0, 7.0 Hz, 1 H), 5.99 (d,  $J$ =16.0 Hz, 1 H), 5.75 (d,  $J$ =8.0 Hz, 1 H), 4.44 (q,  $J$ =7.5 Hz, 1 H), 2.76 - 2.55 (m, 2 H), 2.35 (s, 3 H), 2.12 ppm (s, 3 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz):  $\delta$  = 198.3, 143.3, 142.4, 139.7, 137.4, 134.1, 129.4, 128.6, 127.8, 127.0, 126.3, 57.2, 40.3, 26.8, 21.4 ppm

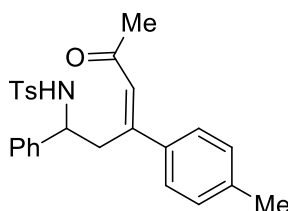
**MS** (ESI<sup>+</sup>) Calculated for C<sub>19</sub>H<sub>21</sub>NNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 366.1134; Found: 366.1143

**FTIR** 3274, 1673, 1495, 1456, 1327, 1257, 1159, 1092 cm<sup>-1</sup>

**MP** 104-106 °C (CH<sub>2</sub>Cl<sub>2</sub>:petrol)

## Isolation of intermediate 5a

### (*E*)-4-Methyl-*N*-(5-oxo-1-phenyl-3-(*p*-tolyl)hex-3-en-1-yl)benzenesulfonamide 5a



A reaction tube, fitted with magnetic follower, was charged with  $\text{Pd}_2(\text{dba})_3$  (24.0 mg, 0.03 mmol, 5 mol%),  $\text{Pt-Bu}_3\text{HBF}_4$  (31.0 mg, 0.11 mmol, 20 mol%), **3a** (180 mg, 0.52 mmol) and 4-bromotoluene (225 mg, 1.32 mmol). The tube was sealed with a septum and purged with argon. Anhydrous PhMe (5.20 mL) and then  $\text{Cy}_2\text{NMe}$  (0.28 mL, 1.31 mmol) were added sequentially *via* syringe and the mixture was then heated at 80 °C for 2.5 h. The mixture was cooled to room temperature and filtered through a short pad of  $\text{SiO}_2$  (eluting with 1:1 petrol-EtOAc). The fractions containing the target were combined, concentrated *in vacuo* and purified by flash column chromatography (10-50% EtOAc:petrol) to afford **5a** as a pale yellow oil (209 mg, 93%).

**$^1\text{H NMR}$**  ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.38 (d,  $J$ =8.0 Hz, 2 H), 7.15 - 7.20 (m, 9 H), 7.01 (d,  $J$ =8.0 Hz, 2 H), 6.85 (d,  $J$ =6.5 Hz, 1 H), 6.50 (s, 1 H), 4.36 (ddd,  $J$ =11.5, 6.5, 3.5 Hz, 1 H), 3.58 (dd,  $J$ =13.5, 11.5 Hz, 1 H), 2.84 (dd,  $J$ =13.5, 3.5 Hz, 1 H), 2.41 (s, 3 H), 2.34 (s, 3 H), 2.32 ppm (s, 3 H)

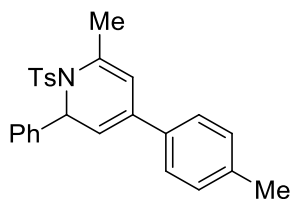
**$^{13}\text{C NMR}$**  ( $\text{CDCl}_3$ , 126 MHz):  $\delta$  = 200.9, 153.5, 142.2, 142.1, 140.0, 138.4, 136.4, 129.5, 128.9, 128.3, 127.2, 127.2, 126.9, 126.8, 126.2, 57.4, 39.0, 31.7, 21.4, 21.3 ppm

**MS** ( $\text{ESI}^+$ ) Calculated for  $\text{C}_{26}\text{H}_{27}\text{NNaO}_3\text{S}$  [ $\text{M}+\text{Na}$ ] $^+$ : 456.1604; Found: 456.1592

**FTIR** 3264, 1667, 1595, 1331, 1159  $\text{cm}^{-1}$

### Isolation of intermediate 6a

#### 6-Methyl-2-phenyl-4-(*p*-tolyl)-1-tosyl-1,2-dihydropyridine 6a



To a solution of **5a** (20 mg, 0.05 mmol) in PhMe (0.50 mL) was added TFA (5  $\mu$ L, 0.05 mmol) and the mixture was heated at 80  $^{\circ}$ C for 1.5 h. The mixture was then filtered directly through SiO<sub>2</sub> 15% EtOAc:petrol to afford condensation adduct **6a** as a pale yellow oil (17 mg, 85%).

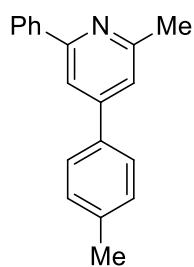
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz):  $\delta$  = 7.68 (d,  $J$ =8.0 Hz, 2 H), 7.46 (d,  $J$ =7.5 Hz, 2 H), 7.26 - 7.35 (m, 3 H), 7.15 (d,  $J$ =8.0 Hz, 2 H), 7.10 (d,  $J$ =8.0 Hz, 2 H), 6.99 (d,  $J$ =8.0 Hz, 2 H), 6.02 (d,  $J$ =6.5 Hz, 1 H), 5.89 (s, 1 H), 5.75 (d,  $J$ =6.5 Hz, 1 H), 2.35 (s, 3 H), 2.30 (s, 3 H), 2.14 ppm (s, 3 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 126 MHz):  $\delta$  = 143.5, 139.3, 137.5, 136.4, 135.7, 135.2, 135.0, 129.2, 129.0, 128.3, 127.8, 127.2, 127.1, 125.6, 117.7, 116.4, 57.4, 23.3, 21.4, 21.1 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>26</sub>H<sub>25</sub>NNaO<sub>2</sub>S [M+Na]<sup>+</sup>: 438.1498; Found: 438.1490

**FTIR** 2922, 1597, 1449, 1348, 1261, 1164 cm<sup>-1</sup>

**2-Methyl-6-phenyl-4-(*p*-tolyl)pyridine 4a**



**General Procedure B - 3a** (100 mg, 0.29 mmol) was employed. The Heck step was conducted for 2.5 h. The condensation step was conducted for 1.5 h. **Part B - Conditions (i)** - The elimination step was conducted for 3 h. The crude material was purified by flash column chromatography eluting with 2% to 4% Et<sub>2</sub>O:petrol affording **4a** as a yellow solid (58 mg, 77%).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ = 8.04 (d, *J*=7.5 Hz, 2 H), 7.72 (s, 1 H), 7.60 (d, *J*=8.0 Hz, 2 H), 7.50 (t, *J*=7.5 Hz, 2 H), 7.43 (t, *J*=7.5 Hz, 1 H), 7.30 - 7.34 (m, 3 H), 2.70 (s, 3 H), 2.44 (s, 3 H)

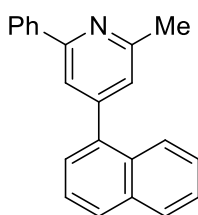
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz): δ = 158.8, 157.6, 149.3, 140.0, 138.9, 135.9, 129.8, 128.7, 128.7, 127.2, 126.9, 119.6, 115.9, 24.9, 21.2 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>19</sub>H<sub>18</sub>N [M+H]<sup>+</sup>: 260.1434; Found: 260.1433

**FTIR** 3032, 2920, 1599, 1547, 1515, 1448 cm<sup>-1</sup>

**MP** 54-56 °C (Et<sub>2</sub>O:petrol)

**2-Methyl-4-(naphthalen-1-yl)-6-phenylpyridine 4b**



**General Procedure B - 3a** (100 mg, 0.29 mmol) was employed. The Heck step was conducted for 3.5 h. The condensation step was conducted for 1 h. **Part B - Conditions (i)** - The elimination step was conducted for 17 h. The crude material was purified by flash column chromatography eluting with 5% EtOAc:petrol affording **4b** as a yellow solid (70 mg, 82%).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ = 8.16 (s, 1 H), 8.12 (d, *J*=7.5 Hz, 2 H), 7.89 - 8.00 (m, 3 H), 7.87 (s, 1 H), 7.80 (dd, *J*=8.5, 2.0 Hz, 1 H), 7.52 - 7.59 (m, 4 H), 7.44 - 7.50 (m, 2 H), 2.77 (s, 3 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz): δ = 158.9, 157.8, 149.4, 139.9, 136.1, 133.5, 133.4, 128.8, 128.8, 128.5, 127.8, 127.2, 126.7, 126.7, 126.4, 124.8, 120.0, 116.3, 24.9 ppm (only 19 signals were observed)

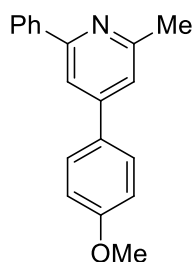
**MS** (ESI<sup>+</sup>) Calculated for C<sub>22</sub>H<sub>18</sub>N [M+H]<sup>+</sup>: 296.1434; Found; 296.1434

**FTIR** 3057, 1596, 1549, 1350 cm<sup>-1</sup>

**MP** 97-99 °C (Et<sub>2</sub>O:petrol)



**4-(4-Methoxyphenyl)-2-methyl-6-phenylpyridine 4c**



**General Procedure B** - **3a** (100 mg, 0.29 mmol) was employed. The Heck step was conducted for 4 h and the condensation step was conducted for 4.5 h. **Part B - Conditions (i)** - The elimination step was conducted for 16 h. The crude material was purified by flash column chromatography eluting with 10% EtOAc:petrol affording **4c** as a yellow oil (62 mg, 78%).

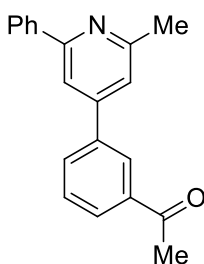
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 8.05 (d,  $J$ =7.0 Hz, 2 H), 7.70 (s, 1 H), 7.65 (d,  $J$ =8.5 Hz, 2 H), 7.50 (t,  $J$ =7.5 Hz, 2 H), 7.43 (t,  $J$ =7.5 Hz, 1 H), 7.30 (s, 1 H), 7.03 (d,  $J$ =8.5 Hz, 2 H), 3.88 (s, 3 H), 2.70 ppm (s, 3 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz):  $\delta$  = 160.4, 158.7, 157.6, 148.9, 140.0, 131.1, 128.7, 128.7, 128.2, 127.1, 119.2, 115.6, 114.5, 55.4, 24.8 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>19</sub>H<sub>18</sub>NO [M+H]<sup>+</sup>: 276.1383; Found: 276.1383

**FTIR** 2958, 1607, 1515, 1252, 1180 cm<sup>-1</sup>

**1-(3-(2-Methyl-6-phenylpyridin-4-yl)phenyl)ethanone 4d**



**General Procedure B - 3a** (100 mg, 0.29 mmol) was employed. The Heck step was conducted for 3 h and the condensation step was conducted for 2 h. **Part B - Conditions (i)** - The elimination step was conducted for 2 h. The crude material was purified by flash column chromatography eluting with 5% EtOAc:PhMe affording **4d** as a yellow oil (58 mg, 70%).

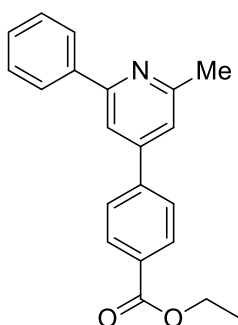
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 8.23 (s, 1 H), 8.05 (d,  $J$ =7.5 Hz, 2 H), 8.02 (d,  $J$ =8.0 Hz, 1 H), 7.86 (d,  $J$ =7.5 Hz, 1 H), 7.73 (s, 1 H), 7.59 (t,  $J$ =8.0 Hz, 1 H), 7.49 (t,  $J$ =7.5 Hz, 2 H), 7.40 - 7.45 (m, 1 H), 7.34 (s, 1 H), 2.71 (s, 3 H), 2.68 ppm (s, 3 H).

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz):  $\delta$  = 197.7, 159.1, 157.8, 148.4, 139.6, 139.4, 137.7, 131.6, 129.4, 128.9, 128.7, 128.7, 127.1, 126.8, 119.8, 116.0, 26.8, 24.9 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>20</sub>H<sub>18</sub>NO [M+H]<sup>+</sup>: 288.1383; Found: 288.1385

**FTIR** 3061, 1685, 1603, 1554, 1436, 1357, 1267 cm<sup>-1</sup>

**Ethyl 4-(2-methyl-6-phenylpyridin-4-yl)benzoate **4e****



**General Procedure B** - **3a** (100 mg, 0.29 mmol), 10 mol% Pd<sub>2</sub>dba<sub>3</sub> and 40 mol% Pt-Bu<sub>3</sub>HBF<sub>4</sub> were employed. The Heck step was conducted for 3 h and the condensation step was conducted for 3 h.  
**Part B - Conditions (i)** - The elimination step was conducted for 14 h. The crude material was purified by flash column chromatography twice eluting with 4% EtOAc:petrol followed by 2% EtOAc:petrol affording **4e** as a colourless oil (61 mg, 68%).

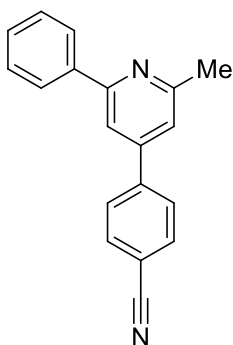
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ = 8.17 (d, *J*=8.0 Hz, 2 H), 8.04 (d, *J*=7.5 Hz, 2 H), 7.73 - 7.77 (m, 3 H), 7.50 (t, *J*=7.5 Hz, 2 H), 7.43 (t, *J*=7.5 Hz, 1 H), 7.34 (d, *J*=1.5 Hz, 1 H), 4.43 (q, *J*=7.0 Hz, 2 H), 2.72 (s, 3 H), 1.44 (t, *J*=7.0 Hz, 3 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz): δ = 166.2, 159.1, 157.9, 148.4, 143.1, 139.6, 130.7, 130.3, 129.0, 128.8, 127.1, 127.1, 119.8, 116.1, 61.2, 24.9, 14.4 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>21</sub>H<sub>20</sub>NO<sub>2</sub> [M+H]<sup>+</sup>: 318.1489; Found: 318.1489

**FTIR** 2981, 1715, 1600, 1547, 1447, 1391, 1368, 1273, 1183, 1104, 1020, 851, 769, 735, 695, 638 cm<sup>-1</sup>

**4-(2-Methyl-6-phenylpyridin-4-yl)benzonitrile 4f**



**General Procedure B** - **3a** (100 mg, 0.29 mmol) was employed. The Heck step was conducted for 3.5 h and the condensation step was conducted for 3 h. **Part B - Conditions (i)** - The elimination step was conducted for 16 h. The crude material was purified by flash column chromatography twice eluting with CH<sub>2</sub>Cl<sub>2</sub> followed by 10% EtOAc:petrol affording **4f** as a colourless solid (57 mg, 73%).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ = 8.01 - 8.06 (m, 2 H), 7.76 - 7.82 (m, 4 H), 7.70 (d, *J*=1.5 Hz, 1 H), 7.50 (t, *J*=7.5 Hz, 2 H), 7.44 (t, *J*=7.5 Hz, 1 H), 7.30 (d, *J*=1.5 Hz, 1 H), 2.72 ppm (s, 3 H)

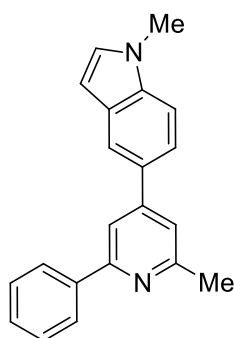
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz): δ = 159.4, 158.1, 147.5, 143.4, 139.4, 132.8, 129.1, 128.8, 127.9, 127.1, 119.7, 118.5, 115.9, 112.6, 24.9 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>19</sub>H<sub>15</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 271.1230; Found: 271.1226

**FTIR** 3062, 2228, 1600, 1573, 1545, 1509, 1449, 1391, 1029, 836, 776, 730, 695, 645 cm<sup>-1</sup>

**MP** 87-89 °C (CH<sub>2</sub>Cl<sub>2</sub>:petrol)

**1-Methyl-5-(2-methyl-6-phenylpyridin-4-yl)-1*H*-indole 4g**



**General Procedure B** - **3a** (100 mg, 0.29 mmol), 10 mol% Pd<sub>2</sub>dba<sub>3</sub> and 40 mol% Pt-Bu<sub>3</sub>HBF<sub>4</sub> were employed. The Heck step was carried out for 2 h. The condensation step was left for 3 h. **Part B - Conditions (i)** - The elimination step was conducted for 17.5 h. The crude material was purified by flash column chromatography twice eluting with CH<sub>2</sub>Cl<sub>2</sub> and then 20% EtOAc:petrol affording **4g** as a yellow oil (56 mg, 65%).

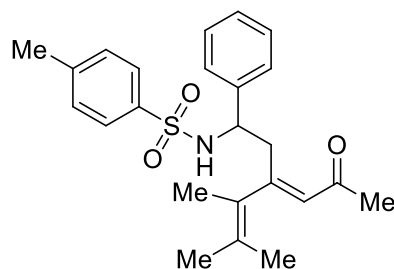
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ = 8.07 (d, *J*=8.5 Hz, 2 H), 7.99 (d, *J*=1.5 Hz, 1 H), 7.82 (s, 1 H), 7.59 (dd, *J*=8.5, 2.0 Hz, 1 H), 7.47 - 7.55 (m, 2 H), 7.45 (s, 1 H), 7.43 (m, 2 H), 7.13 (d, *J*=3.0 Hz, 1 H), 6.59 (d, *J*=3.0 Hz, 1 H), 3.86 (s, 3 H), 2.72 ppm (s, 3 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 75 MHz): δ = 158.6, 157.5, 150.8, 140.3, 137.1, 130.1, 129.9, 129.0, 128.7, 128.6, 127.2, 120.9, 120.0, 119.7, 116.4, 109.8, 101.7, 33.0, 24.9 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>21</sub>H<sub>19</sub>N<sub>2</sub> [M+H]<sup>+</sup>: 299.1543; Found: 299.1539

**FTIR** 2291, 1598, 1551, 1513, 1493, 1448, 1409, 1347, 1327, 1284, 1249, 1080, 1029, 867, 801, 776, 717, 695, 644 cm<sup>-1</sup>

**(E)-4-Methyl-N-(3-(3-methylbut-2-en-2-yl)-5-oxo-1-phenylhex-3-en-1-yl)benzenesulfonamide 5h**



A reaction tube, fitted with magnetic follower, was charged with **3a** (750 mg, 2.18 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (99.8 mg, 0.109 mmol), Pt-Bu<sub>3</sub>HBF<sub>4</sub> (127.7 mg, 0.44 mmol) and 2-bromo-3-methyl-2-butene (0.63 mL, 5.46 mmol). The tube was sealed with a septum and purged with argon. Argon sparged PhMe (22 mL 0.1 M) and then Cy<sub>2</sub>NMe (1.16 mL, 5.46 mmol) were added sequentially *via* syringe. The mixture was then heated to 110 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered through a short pad of SiO<sub>2</sub> eluting with 33% EtOAc:petrol. The fractions containing the target cross coupling product were combined and concentrated *in vacuo*. The crude material was purified by flash column chromatography eluting with 20% EtOAc:petrol affording **5h** as a yellow oil (335 mg, 37%).

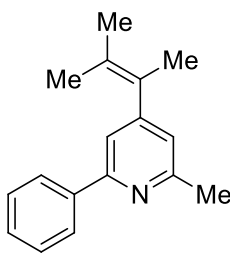
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ = 7.29 (d, *J*=8.0 Hz, 2 H), 7.00 - 7.09 (m, 5 H), 6.90 - 6.98 (m, 3 H), 6.21 (s, 1 H), 4.48 - 4.62 (m, 1 H), 3.30 (t, *J*=12.5 Hz, 1 H), 2.38 (dd, *J*=12.5, 4.0 Hz, 1 H), 2.24 - 2.32 (m, 6 H), 1.74 - 1.83 ppm (m, 9 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz): δ = 201.7, 158.0, 141.9, 141.2, 138.9, 131.1, 129.1, 128.7, 128.4, 128.1, 127.0, 126.6, 126.6, 57.2, 39.4, 31.5, 22.5, 21.3, 20.7, 17.9 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>24</sub>H<sub>30</sub>NO<sub>3</sub>S [M+H]<sup>+</sup>: 412.1941; Found: 412.1927

**FTIR** 2923, 1670, 1597, 1455, 1329, 1157, 1092, 1069, 954, 813, 761, 732, 700, 666 cm<sup>-1</sup>

**2-Methyl-4-(3-methylbut-2-en-2-yl)-6-phenylpyridine 4h**



Compound **5h** (90 mg, 0.22 mmol) was dissolved in anhydrous PhMe (0.1 M) under an argon atmosphere in a flame dried reaction tube sealed with a septum. TFA (16.2  $\mu$ L, 0.22 mmol) was added and the reaction was heated to 80 °C for 3 h. DBU (164  $\mu$ L, 1.09 mmol) was added and stirring continued for 19 h. The crude material was purified by flash column chromatography eluting with 5% Et<sub>2</sub>O:petrol affording **4h** as a colourless oil (17 mg, 33%).

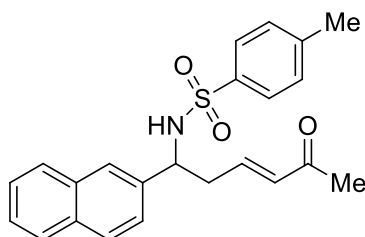
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz):  $\delta$  = 7.95 - 7.99 (m, 2 H), 7.46 (t,  $J$ =7.5 Hz, 2 H), 7.39 (t,  $J$ =7.5 Hz, 1 H), 7.29 (s, 1 H), 6.88 (s, 1 H), 2.62 (s, 3 H), 1.98 (s, 3 H), 1.84 (s, 3 H), 1.66 ppm (d,  $J$ =1.5 Hz, 3 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 126 MHz):  $\delta$  = 158.0, 156.8, 154.2, 140.1, 129.1, 128.6, 128.5, 128.2, 127.0, 121.6, 117.9, 24.7, 22.1, 20.6, 20.1 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>17</sub>H<sub>20</sub>N [M+H]<sup>+</sup>: 238.1590; Found: 238.1592

**FTIR** 2921, 1599, 1547, 1497, 1449, 1401, 1374, 1225, 1164, 1030, 873, 776, 742, 695, 660, 645 cm<sup>-1</sup>

**(E)-4-Methyl-N-(1-(naphthalen-2-yl)-5-oxohex-3-en-1-yl)benzenesulfonamide 3i**



**General Procedure A** – **1b** (200 mg, 0.57 mmol) and methylvinylketone (**2a**) (0.12 mL, 1.43 mmol) were employed. Reaction heated for 48 h. The crude material was purified by flash column chromatography eluting with petrol:EtOAc (3:1) affording **3i** as a white solid (182 mg, 81%).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 300 MHz): δ = 7.75 - 7.71 (m, 1 H), 7.64 - 7.59 (m, 2 H), 7.52 (d, *J*=8.5 Hz, 2 H), 7.45 - 7.39 (m, 3 H), 7.18 (dd, *J*=8.5, 1.5 Hz, 1 H), 6.91 (d, 2H, *J*=8.0 Hz, 2 H), 6.57 (dt, *J*=16.0, 7.0 Hz, 1 H), 6.08 - 5.95 (m, 2 H), 4.62 (q, *J*=7.5 Hz, 1 H), 2.83 - 2.63 (m, 2 H), 2.15 (s, 3 H), 2.00 ppm (s, 3 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 75 MHz): δ = 198.3, 143.2, 142.3, 137.2, 136.6, 134.0, 134.0, 132.9, 132.6, 129.2, 128.6, 127.8, 127.4, 126.9, 126.1, 126.0, 125.7, 123.8, 57.4, 39.9, 26.7, 21.1 ppm

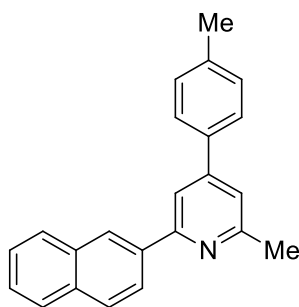
**MS** (ESI<sup>+</sup>) Calculated for C<sub>23</sub>H<sub>23</sub>NNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 416.1291; Found: 416.1289

**FTIR** 1672, 1329, 1156, 815, 668 cm<sup>-1</sup>

**MP** 114-115 °C (CH<sub>2</sub>Cl<sub>2</sub>)



**2-Methyl-6-(naphthalen-2-yl)-4-(p-tolyl)pyridine 4i**



**General Procedure B – 3i** (100 mg, 0.26 mmol) was employed. The Heck step was conducted for 4.5 h. The condensation step was conducted for 1.5 h. **Part B - Conditions (i)** - The elimination step was conducted for 8 h. The crude material was purified by flash column chromatography twice eluting with Et<sub>2</sub>O:petrol (1:20) and CH<sub>2</sub>Cl<sub>2</sub>:petrol (1:2) affording **4i** as a yellow solid (45 mg, 55%).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 300 MHz): δ = 8.52 (s, 1 H), 8.18 (dd, *J*=8.5, 1.5 Hz, 1 H), 7.99 - 7.93 (m, 2 H), 7.90 - 7.84 (m, 2 H), 7.62 (d, *J*=8.0 Hz, 2 H), 7.52 - 7.49 (m, 2 H), 7.35 - 7.31 (m, 3 H), 2.73 (s, 3 H), 2.44 ppm (s, 3 H)

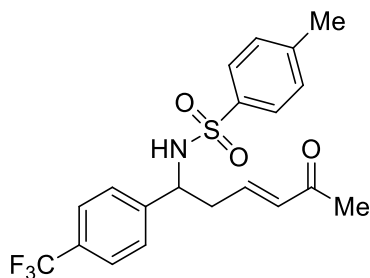
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 75 MHz): δ = 158.9, 157.4, 149.4, 139.0, 137.2, 135.9, 133.6, 133.5, 129.8, 128.7, 128.4, 127.6, 126.9, 126.4, 126.3, 126.2, 124.9, 119.6, 116.2, 24.9, 21.2 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>23</sub>H<sub>20</sub>N [M+H]<sup>+</sup>: 310.1590; Found: 310.1585

**FTIR** 2363, 2341, 1601, 1547, 814 cm<sup>-1</sup>

**MP** 99 °C (CH<sub>2</sub>Cl<sub>2</sub>)

**(E)-4-Methyl-N-(5-oxo-1-(4-(trifluoromethyl)phenyl)hex-3-en-1-yl)benzenesulfonamide 3j**



**General Procedure A** - **1c** (500 mg 1.35 mmol) and methylvinylketone (**2a**) (0.55 mL, 6.77 mmol) were employed. Reaction heated for 72 h. The crude material was purified by flash column chromatography eluting with 30% to 50% EtOAc:petrol affording **3j** as a white solid (490 mg, 88%).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ = 7.50 (d, *J*=8.0 Hz, 2 H), 7.39 (d, *J*=8.0 Hz, 2 H), 7.17 (d, *J*=8.0 Hz, 2 H), 7.09 (d, *J*=8.0 Hz, 2 H), 6.53 (dt, *J*=16.0, 8.0 Hz, 1 H), 6.05 (d, *J*=16.0 Hz, 1 H), 5.85 (d, *J*=8.0 Hz, 1 H), 4.55 (q, *J*=7.5 Hz, 1 H), 2.57 - 2.73 (m, 2 H), 2.36 (s, 3 H), 2.15 ppm (s, 3 H)

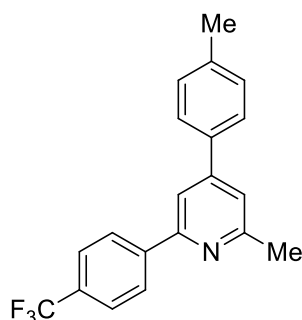
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 126 MHz): δ = 198.1, 143.7, 143.6, 141.2, 137.0, 134.4, 129.9 (q, *J*<sub>C-F</sub>=33.0 Hz), 129.5, 127.0, 126.9, 125.5 (q, *J*<sub>C-F</sub>=4.0 Hz), 123.8 (q, *J*<sub>C-F</sub>=273.0 Hz) 56.8, 39.9, 27.0, 21.3 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>20</sub>H<sub>20</sub>F<sub>3</sub>NNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 434.1008; Found: 434.1008

**FTIR** 3272, 1675, 1424, 1326, 1160, 1120, 1068, 1018, 815, 670 cm<sup>-1</sup>

**MP** 132-134 °C (CH<sub>2</sub>Cl<sub>2</sub>:petrol)

**2-Methyl-4-(*p*-tolyl)-6-(4-(trifluoromethyl)phenyl)pyridine 4j**



**General Procedure B** - **3j** (100 mg, 0.243 mmol) was employed. 10 mol% Pd<sub>2</sub>dba<sub>3</sub> and 40 mol% Pt-Bu<sub>3</sub>HBF<sub>4</sub> were employed. The Heck step was carried out for 3 h. The condensation step was left for 3 h. **Part B - Conditions (i)** - The elimination step was conducted for 15 h. The crude material was purified by flash column chromatography twice eluting with 4% EtOAc:petrol followed by 2% EtOAc:petrol affording **4j** as a white solid (57 mg, 72%).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ = 8.16 (d, *J*=8.0 Hz, 2 H), 7.72 - 7.77 (m, 3 H), 7.60 (d, *J*=8.0 Hz, 2 H), 7.37 (d, *J*=1.5 Hz, 1 H), 7.33 (d, *J*=8.0 Hz, 2 H), 2.71 (s, 3 H), 2.45 ppm (s, 3 H)

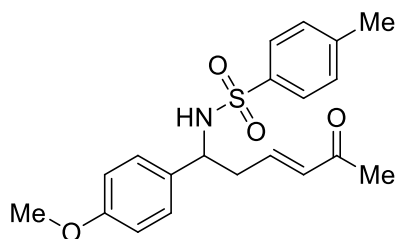
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 75 MHz): δ = 159.2, 156.0, 149.7, 143.3, 139.2, 135.6, 130.5 (q, *J*<sub>C-F</sub>=32.0 Hz), 129.8, 127.4, 126.9, 125.5 (q, *J*<sub>C-F</sub>=4.0 Hz), 124.2 (q, *J*<sub>C-F</sub>=272.0 Hz), 120.4, 116.2, 24.8, 21.2 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>20</sub>H<sub>17</sub>F<sub>3</sub>N [M+H]<sup>+</sup>: 328.1308; Found: 328.1299

**FTIR** 1602, 1548, 1390, 1324, 1165, 1124, 1064, 1017, 848, 814 cm<sup>-1</sup>

**MP** 75-77 °C (CH<sub>2</sub>Cl<sub>2</sub>:petrol)

**(E)-N-(1-(4-Methoxyphenyl)-5-oxohex-3-en-1-yl)-4-methylbenzenesulfonamide 3k**



**General Procedure A** – **1c** (150 mg, 0.45 mmol) and methylvinylketone (**2a**) (92  $\mu$ L, 1.13 mmol) were employed. Reaction heated for 71 h. The crude material was purified by flash column chromatography eluting with petrol:EtOAc (3:1 grading to 2:1), affording **3k** as a white solid (160 mg, 95%).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 7.54 (d,  $J$ =8.5 Hz, 2 H), 7.12 (d,  $J$ =8.0 Hz, 2 H), 6.94 (d,  $J$ =8.5 Hz, 2 H), 6.66 (d,  $J$ =8.5 Hz, 2 H), 6.51 (dt,  $J$ =16.0, 7.0 Hz, 1 H), 5.95 (d,  $J$ =16.0, 1 H), 5.75 (d,  $J$ =7.5 Hz, 1 H), 4.36 (q,  $J$ =7.0 Hz, 1 H), 3.71 (s, 3 H), 2.74 - 2.53 (m, 2 H), 2.35 (s, 3 H), 2.10 ppm (s, 3 H)

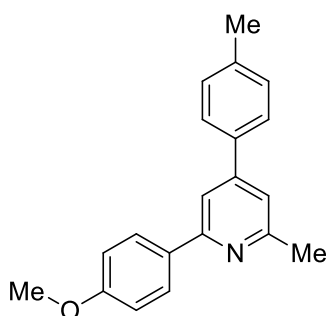
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 75 MHz):  $\delta$  = 198.3, 159.0, 143.1, 142.6, 137.4, 133.8, 131.7, 129.3, 127.5, 126.9, 113.9, 56.6, 55.1, 40.1, 26.7, 21.3 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>20</sub>H<sub>23</sub>NNaO<sub>4</sub>S [M+Na]<sup>+</sup>: 396.1240; Found: 396.1241

**FTIR** 1673, 1514, 1251, 1158 cm<sup>-1</sup>

**MP** 115 °C (CH<sub>2</sub>Cl<sub>2</sub>)

**2-(4-Methoxyphenyl)-6-methyl-4-(*p*-tolyl)pyridine 4k**



**General Procedure B** – **3k** (58 mg, 0.16 mmol) was employed. The Heck step was conducted for 3 h. The condensation step was conducted for 2 h. **Part B - Conditions (i)** - The elimination step was conducted for 7 h. The crude material was purified by flash column chromatography eluting twice with Et<sub>2</sub>O:petrol (1:20) and CH<sub>2</sub>Cl<sub>2</sub>:petrol (1:2) affording **4k** as an amorphous solid (23 mg, 50%).

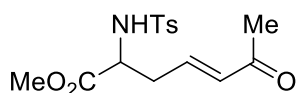
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 300 MHz): δ = 8.04 - 7.97 (m, 2 H), 7.65 (d, *J*=0.5 Hz, 1 H), 7.57 (d, *J*=8.0 Hz, 2 H), 7.30 (d, *J*=8.0 Hz, 2 H), 7.26 - 7.22 (m, 1 H), 7.04 - 6.97 (m, 2 H), 3.87 (s, 3 H), 2.66 (s, 3 H), 2.42 ppm (s, 3 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz): δ = 160.3, 158.6, 157.2, 149.3, 138.8, 136.1, 132.6, 129.7, 128.4, 126.9, 118.9, 115.2, 114.1, 55.4, 24.8, 21.2 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>20</sub>H<sub>20</sub>NO [M+H]<sup>+</sup>: 290.1539; Found: 290.1534

**FTIR** 2361, 2341, 1601, 1513, 1248, 1175, 1034, 814 cm<sup>-1</sup>

**(E)-Methyl 2-(4-methylphenylsulfonamido)-6-oxohept-4-enoate 3I**



**General Procedure A** - **1e** (250 mg, 0.88 mmol) and methylvinylketone (**2a**) (180  $\mu$ L, 2.22 mmol) were employed. The mixture was heated for 91 h. The crude material was purified by flash column chromatography eluting with 50% EtOAc:petrol affording **3I** as a colourless solid (269 mg, 94%).

**<sup>1</sup>H NMR** ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 7.72 (d,  $J$ =8.0 Hz, 2 H), 7.30 (d,  $J$ =8.0 Hz, 2 H), 6.60 (dt,  $J$ =16.0, 7.5 Hz, 1 H), 6.04 (d,  $J$ =16.0 Hz, 1 H), 5.47 (d,  $J$ =8.5 Hz, 1 H), 4.07 (ddd,  $J$ =8.5, 7.0, 6.0 Hz, 1 H), 3.56 (s, 3 H), 2.65 - 2.69 (m, 1 H), 2.54 - 2.62 (m, 1 H), 2.42 (s, 3 H), 2.20 ppm (s, 3 H)

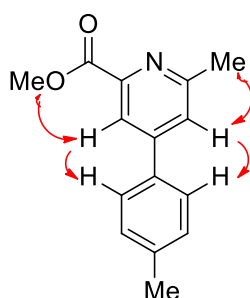
**<sup>13</sup>C NMR** ( $\text{CDCl}_3$ , 101 MHz):  $\delta$  = 198.0, 170.8, 144.0, 140.2, 136.5, 134.6, 129.8, 127.2, 54.7, 52.8, 36.1, 26.8, 21.5 ppm

**MS** ( $\text{ESI}^+$ ) Calculated for  $\text{C}_{15}\text{H}_{19}\text{NNaO}_5\text{S}$   $[\text{M}+\text{Na}]^+$ : 348.0876; Found: 348.0879

**FTIR** 3265, 1744, 1674, 1435, 1339, 1161  $\text{cm}^{-1}$

**MP** 92-94  $^{\circ}\text{C}$  ( $\text{CH}_2\text{Cl}_2$ :petrol)

**Methyl 6-methyl-4-(*p*-tolyl)picolinate **4l****



**General Procedure B** - **3l** (95 mg, 0.29 mmol) was employed. The Heck step was conducted for 4 h and the condensation step was conducted for 5 h. **Part B - Conditions (i)** - The elimination step was conducted for 10 mins. The crude material was purified by flash column chromatography eluting with 25% EtOAc:petrol affording **4l** as a pale yellow solid (41 mg, 59%).

*Characteristic nOe correlations associated with **4l** are represented on the compound structure by red arrows.*

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ = 8.19 (d, *J*=1.5 Hz, 1 H), 7.58 (d, *J*=8.0 Hz, 2 H), 7.53 (d, *J*=1.5 Hz, 1 H), 7.29 (d, *J*=8.0 Hz, 2 H), 4.02 (s, 3 H), 2.70 (s, 3 H), 2.41 ppm (s, 3 H)

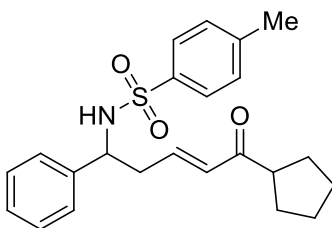
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz): δ = 166.2, 159.4, 149.6, 148.0, 139.6, 134.4, 129.9, 126.9, 124.2, 120.4, 52.9, 24.7, 21.2 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>15</sub>H<sub>15</sub>NNaO<sub>2</sub> [M+Na]<sup>+</sup>: 264.0995; Found: 264.1004

**FTIR** 2951, 1742, 1719, 1604, 1441, 1345, 1254, 1146 cm<sup>-1</sup>

**MP** 67-69 °C (Et<sub>2</sub>O:petrol)

**(E)-N-(5-Cyclopentyl-5-oxo-1-phenylpent-3-en-1-yl)-4-methylbenzenesulfonamide **3m****



**General Procedure A** - **1a** (500 mg, 1.66 mmol) and cyclopentylvinylketone (**2b**) (515 mg mL, 4.15 mmol) were employed. Reaction heated for 48 h. The crude material was purified by flash column chromatography eluting with petrol:EtOAc (4:1) affording **3m** as a white solid (504 mg, 76%).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.52 (d,  $J$ =8.5 Hz, 2 H), 7.12 - 7.01 (m, 7 H), 6.54 (dt,  $J$ =16.0, 7.0 Hz, 1 H), 6.19 (d,  $J$ =8.0 Hz, 1 H), 6.01 (d,  $J$ =16.0 Hz, 1 H), 4.42 (q,  $J$ =7.0 Hz, 1 H), 2.90 (qn,  $J$ =8.0 Hz, 1 H), 2.65 (m, 1 H), 2.55 (m, 1 H), 2.30 (s, 3 H), 1.72 - 1.45 ppm (m, 8 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz):  $\delta$  = 202.1, 142.8, 140.9, 139.6, 137.3, 132.3, 129.1, 128.2, 127.3, 126.7, 126.3, 57.1, 48.3, 40.1, 28.8, 28.8, 25.9, 21.2 ppm

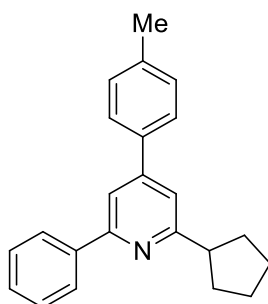
**MS** (ESI<sup>+</sup>) Calculated for C<sub>23</sub>H<sub>27</sub>NNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 420.1604; Found: 420.1603

**FTIR** 2953, 2360, 1663, 1327, 1158, 668 cm<sup>-1</sup>

**MP** 97-99 °C (CH<sub>2</sub>Cl<sub>2</sub>)



**2-Cyclopentyl-6-phenyl-4-(*p*-tolyl)pyridine 4m**



**General Procedure B – 3m** (50 mg, 0.13 mmol) was employed. The Heck step was conducted for 7 h. The condensation step was conducted for 1.5 h. **Part B - Conditions (i)** - The elimination step was conducted for 3 h. The crude material was purified by flash column chromatography twice eluting with Et<sub>2</sub>O:petrol (1:20) and CH<sub>2</sub>Cl<sub>2</sub>:petrol (1:2) affording **4m** as a colourless oil (16 mg, 41%).

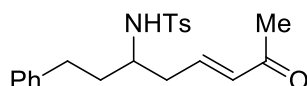
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 300 MHz): δ = 8.12 - 8.07 (m, 2 H), 7.71 (d, *J*=1.5 Hz, 1 H), 7.62 - 7.57 (m, 2 H), 7.51 - 7.36 (m, 3 H), 7.33 - 7.28 (m, 3 H), 3.31 (qn, *J*=8.5 Hz, 1 H), 2.43 (s, 3 H), 2.20 - 2.07 (m, 2 H), 1.99 - 1.68 ppm (m, 6 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 75 MHz): δ = 166.1, 160.0, 149.2, 140.1, 138.7, 136.3, 129.7, 128.6, 128.6, 127.1, 127.0, 118.0, 115.8, 48.2, 33.7, 25.9, 21.2 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>23</sub>H<sub>23</sub>NNa [M+Na]<sup>+</sup>: 314.1903; Found: 314.1907

**FTIR** 2360, 2342, 1598, 1547, 816, 775, 693, 669 cm<sup>-1</sup>

**(E)-4-Methyl-N-(7-oxo-1-phenyloct-5-en-3-yl)benzenesulfonamide 3n**



**General Procedure A** - **1f** (300 mg, 0.91 mmol) and methylvinylketone (**2a**) (185  $\mu$ L, 2.28 mmol) were employed. The mixture was heated for 65 h. The crude material was purified by flash column chromatography eluting with 25% - 33% EtOAc affording **3n** as a colourless solid (268 mg, 79%).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.74 (d,  $J$ =8.0 Hz, 2 H), 7.31 (d,  $J$ =8.0 Hz, 2 H), 7.24 (dd,  $J$ =7.5, 7.0 Hz, 2 H), 7.19 (t,  $J$ =7.5 Hz, 1 H), 7.00 (d,  $J$ =7.0 Hz, 2 H), 6.59 (dt,  $J$ =16.0, 7.5 Hz, 1 H), 5.98 (d,  $J$ =16.0 Hz, 1 H), 4.73 (d,  $J$ =8.5 Hz, 1 H), 3.37 - 3.47 (m, 1 H), 2.57 (ddd,  $J$ =14.0, 9.5, 6.5 Hz, 1 H), 2.37 - 2.51 (m, 5 H), 2.28 - 2.37 (m, 1 H), 2.16 (s, 3 H), 1.62 - 1.81 ppm (m, 2 H)

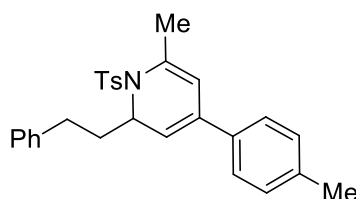
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 198.1, 143.7, 142.4, 140.6, 137.8, 134.1, 129.8, 128.5, 128.2, 127.0, 126.2, 52.8, 38.2, 36.7, 31.7, 27.0, 21.5 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>21</sub>H<sub>25</sub>NNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 394.1447; Found: 394.1445

**FTIR** 3276, 1672, 1453, 1326, 1158, 1091 cm<sup>-1</sup>

**MP** 107.5-108.5 °C (CH<sub>2</sub>Cl<sub>2</sub>:petrol)

**6-Methyl-2-phenethyl-4-(*p*-tolyl)-1-tosyl-1,2-dihydropyridine 6n**



**General Procedure B - 3n** (108 mg, 0.29 mmol) was employed. The Heck step was conducted for 3.5 h and the condensation step was conducted for 2 h. **Part B - Conditions (ii)** - The crude material was purified by flash column chromatography eluting with 15% petrol:PhMe affording **6n** as a yellow oil (90 mg, 70%).

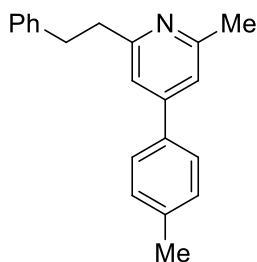
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz): δ = 7.62 (dt, *J*=8.0, 1.5 Hz, 2 H), 7.28 - 7.33 (m, 2 H), 7.22 - 7.26 (m, 2 H), 7.17 - 7.23 (m, 1 H), 7.11 (d, *J*=8.0 Hz, 2 H), 7.05 (d, *J*=8.0 Hz, 2 H), 6.85 (dt, *J*=8.0, 1.5 Hz, 2 H), 5.91 (dq, *J*=1.5, 1.0 Hz, 1 H), 5.46 (d, *J*=6.0 Hz, 1 H), 4.87 (dt, *J*=9.0, 5.5 Hz, 1 H), 2.87 (ddd, *J*=14.0, 10.0, 5.5 Hz, 1 H), 2.75 (ddd, *J*=14.0, 10.0, 6.0 Hz, 1 H), 2.32 (s, 3 H), 2.28 (s, 3 H), 2.27 (s, 3 H), 1.91 (dddd, *J*=14.0, 10.0, 9.0, 5.0 Hz, 1 H), 1.79 ppm (dddd, *J*=14.0, 10.0, 6.0, 5.5 Hz, 1 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 126 MHz): δ = 143.3, 141.9, 137.2, 136.3, 135.4, 134.1, 134.0, 129.0, 128.9, 128.5, 128.4, 127.1, 125.8, 125.5, 118.8, 117.4, 55.8, 33.9, 31.2, 23.3, 21.4, 21.0 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>28</sub>H<sub>29</sub>NNaO<sub>2</sub>S [M+Na]<sup>+</sup>: 466.1811; Found: 466.1815

**FTIR** 2929, 1598, 1454, 1341, 1160, 1028 cm<sup>-1</sup>

**2-Methyl-6-phenethyl-4-(*p*-tolyl)pyridine 4n**



**General Procedure B - Part B - Conditions (ii) - 6n** (52 mg, 0.12 mmol) was employed. The reaction was carried out for 0.5 h. The crude material was purified by flash column chromatography eluting with 15% petrol:PhMe affording **4n** as a colourless oil (25 mg, 75%)

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.49 (d,  $J$ =8.0 Hz, 2 H), 7.19 - 7.33 (m, 8 H), 7.10 (s, 1 H), 3.07 - 3.18 (m, 4 H), 2.64 (s, 3 H), 2.42 ppm (s, 3 H)

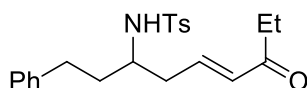
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz):  $\delta$  = 161.1, 158.3, 148.9, 141.7, 138.8, 135.8, 129.7, 128.5, 128.3, 126.9, 125.9, 118.6, 117.9, 40.4, 36.4, 24.7, 21.2 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>21</sub>H<sub>22</sub>N [M+H]<sup>+</sup>: 288.1747; Found: 288.1743

**FTIR** 3026, 2922, 1603, 1551, 1516, 1453 cm<sup>-1</sup>

**MP** 48-51 °C (Et<sub>2</sub>O:petrol)

**(E)-4-Methyl-N-(7-oxo-1-phenylnon-5-en-3-yl)benzenesulfonamide 3o**



**General Procedure A** - **1f** (145 mg, 0.44 mmol) and ethylvinylketone (**3c**) (110  $\mu$ L, 1.10 mmol) were employed. The mixture was heated for 72 h. The crude material was purified by flash column chromatography eluting with 25% EtOAc:petrol affording **3o** as a colourless, crystalline solid (120 mg, 71%).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.75 (d,  $J$ =8.0 Hz, 2 H), 7.30 (d,  $J$ =8.0 Hz, 2 H), 7.14 - 7.28 (m, 3 H), 7.00 (d,  $J$ =7.5 Hz, 2 H), 6.62 (dt,  $J$ =16.0, 7.5 Hz, 1 H), 6.01 (d,  $J$ =16.0 Hz, 1 H), 5.12 (d,  $J$ =8.5 Hz, 1 H), 3.36 - 3.46 (m, 1 H), 2.58 (ddd,  $J$ =14.0, 9.5, 6.5 Hz, 1 H), 2.27 - 2.50 (m, 8 H), 1.62 - 1.80 (m, 2 H), 1.05 ppm (t,  $J$ =7.0 Hz, 3 H)

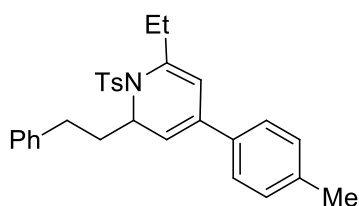
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz):  $\delta$  = 200.6, 143.6, 141.1, 140.8, 137.9, 133.0, 129.8, 128.5, 128.3, 127.0, 126.1, 52.8, 38.1, 36.6, 33.2, 31.7, 21.5, 7.9 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>22</sub>H<sub>27</sub>NNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 408.1604; Found: 408.1597

**FTIR** 3277, 2937, 1670, 1326, 1158, 1091 cm<sup>-1</sup>

**MP** 95-96.5 °C (CH<sub>2</sub>Cl<sub>2</sub>:petrol)

**6-Ethyl-2-phenethyl-4-(*p*-tolyl)-1-tosyl-1,2-dihydropyridine 6o**



**General Procedure B - 3o** (71 mg, 0.18 mmol) was employed. The Heck step was conducted for 3.5 h and the condensation step was conducted for 36 h. **Part B - Conditions (ii)** - The crude material was purified by flash column chromatography eluting with 8% EtOAc:petrol affording **6o** as a yellow oil (53 mg, 65%).

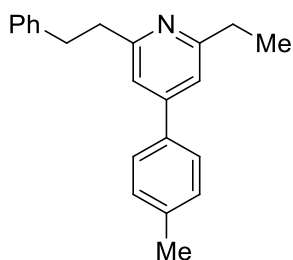
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.62 (d,  $J$ =8.5 Hz, 2 H), 7.20 - 7.34 (m, 5 H), 7.09 (d,  $J$ =8.5 Hz, 2 H), 7.04 (d,  $J$ =8.0 Hz, 2 H), 6.81 (d,  $J$ =8.0 Hz, 2 H), 5.94 (s, 1 H), 5.42 (d,  $J$ =6.0 Hz, 1 H), 4.86 (ddd,  $J$ =9.5, 6.0, 6.0 Hz, 1 H), 2.85 - 2.95 (m, 2 H), 2.76 (ddd,  $J$ =14.0, 10.0, 6.5 Hz, 1 H), 2.54 (dq,  $J$ =15.5, 7.5 Hz, 1 H), 2.32 (s, 3 H), 2.27 (s, 3 H), 1.88 - 1.98 (m, 1 H), 1.69 - 1.79 (m, 1 H), 1.26 ppm (t,  $J$ =7.5 Hz, 3 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz):  $\delta$  = 143.3, 141.8, 139.8, 137.2, 136.2, 135.5, 133.8, 129.0, 128.8, 128.5, 128.4, 127.2, 125.9, 125.5, 119.4, 116.6, 55.7, 33.6, 31.5, 29.4, 21.4, 21.1, 12.9 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>29</sub>H<sub>31</sub>NNaO<sub>2</sub>S [M+Na]<sup>+</sup>: 480.1968; Found: 480.1960

**FTIR** 2931, 1597, 1453, 1344, 1160, 1036 cm<sup>-1</sup>

**2-Ethyl-6-phenethyl-4-(*p*-tolyl)pyridine 4o**



**General Procedure B - Part B - Conditions (ii) - 6o** (28 mg, 0.06 mmol) was employed. The reaction was carried out for 1 h. The crude material was purified by flash column chromatography eluting with 5% EtOAc:petrol affording **4o** as a colourless oil (12 mg, 65%).

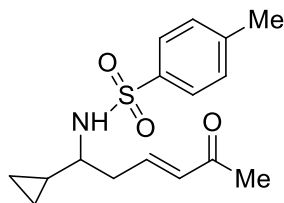
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ = 7.49 (d, *J*=8.0 Hz, 2 H), 7.18 - 7.32 (m, 8 H), 7.09-7.11 (m, 1 H), 3.06 - 3.18 (m, 4 H), 2.89 (q, *J*=7.5 Hz, 2 H), 2.42 (s, 3 H), 1.37 ppm (t, *J*=7.5 Hz, 3 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz): δ = 163.6, 161.0, 149.0, 141.8, 138.7, 136.0, 129.6, 128.5, 128.3, 126.9, 125.9, 118.1, 117.2, 40.3, 36.3, 31.6, 21.2, 14.3 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>22</sub>H<sub>24</sub>N [M+H]<sup>+</sup>: 302.1903; Found: 302.1903

**FTIR** 2925, 1601, 1550, 1453 cm<sup>-1</sup>

**(E)-N-(1-Cyclopropyl-5-oxohex-3-en-1-yl)-4-methylbenzenesulfonamide 3p**



**General Procedure A** - **1g** (400 mg, 1.51 mmol) and methylvinylketone (**2a**) (0.31 mL, 3.77 mmol) were employed. Reaction heated for 72 h. The crude material was purified by flash column chromatography eluting with 25% EtOAc:petrol affording **3p** as a brown oil (436 mg, 94%).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 300 MHz): δ = 7.62 (d, *J*=8.0 Hz, 2 H), 7.17 (d, *J*=8.0 Hz, 2 H), 6.61 (qn, *J*=7.5 Hz, 1 H), 5.88 (d, *J*=16.0 Hz, 1 H), 5.18 - 5.05 (m, 1 H), 2.58 - 2.26 (m, 6 H), 2.05 (s, 3 H), 0.74 - 0.60 (m, 1 H), 0.43 - 0.31 (m, 1 H), 0.23 - 0.14 (m, 1 H), 0.04 - 0.07 (m, 1 H), 0.18 - 0.26 ppm (m, 1 H)

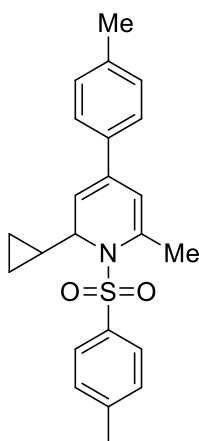
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 75 MHz): δ = 198.4, 143.4, 143.2, 137.8, 133.8, 129.6, 127.0, 58.2, 38.8, 26.7, 21.5, 16.1, 4.1, 3.6 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>16</sub>H<sub>21</sub>NNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 330.1134; Found: 330.1141

**FTIR** 1361, 1670, 1326, 1156, 1093, 981, 816, 665 cm<sup>-1</sup>



**2-Cyclopropyl-6-methyl-4-(*p*-tolyl)-1-tosyl-1,2-dihydropyridine 6p**



**General Procedure B – 3m** (47 mg, 0.15 mmol) was employed. The Heck step was conducted for 4 h. The condensation step was conducted for 1.5 h. The crude reaction mixture was directly purified by flash column chromatography eluting with Et<sub>2</sub>O:petrol (1:10) affording **6p** as a colourless oil (38 mg, 66%).

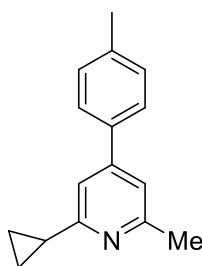
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ = 7.57 (d, *J*=7.5 Hz, 2 H), 7.09 (d, *J*=8.0 Hz, 2 H), 7.05 (d, *J*=8.0 Hz, 2 H), 6.92 (d, *J*=7.5 Hz, 2 H), 5.87 (s, 1 H), 5.52 (d, *J*=6.0 Hz, 1 H), 4.13 (dd, *J*=8.0, 6.5 Hz, 1 H), 2.32 (s, 3 H), 2.28 (s, 3 H), 2.27 (s, 3 H), 1.14 - 1.05 (m, 1 H), 0.55 - 0.32 ppm (m, 4 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 75 MHz): δ = 143.2, 137.2, 136.5, 135.5, 135.1, 134.2, 129.1, 128.9, 127.0, 125.6, 117.1, 116.7, 60.5, 23.3, 21.4, 21.1, 14.3, 3.1, 2.3 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>23</sub>H<sub>25</sub>NNaO<sub>2</sub>S [M+Na]<sup>+</sup>: 420.1498; Found: 402.1492

**FTIR** 2361, 2342, 1161, 669 cm<sup>-1</sup>

**2-Cyclopropyl-6-methyl-4-(*p*-tolyl)pyridine 4p**



Compound **6p** (9.0 mg, 0.02 mmol) was added to a solution of KOH (20 mg in 1 mL of EtOH) and heated to 90 °C in a sealed tube for 3 h. The reaction was allowed to cool to rt and was diluted with water and extracted with EtOAc (x3). The combined organic layers were dried with MgSO<sub>4</sub>, filtered and concentrated. Flash column chromatography eluting with Et<sub>2</sub>O:petrol (1:20) affording **4p** as a colourless oil (4.2 mg, 80%).

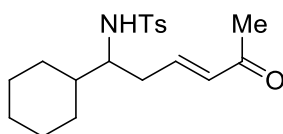
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 500 MHz): δ = 7.51 (d, *J*=8.0 Hz, 2 H), 7.26 (m, 2 H), 7.11, (s, 1 H), 7.05 (s, 1 H), 2.54 (s, 3 H), 2.41 (s, 3 H), 2.10 (m, 1 H), 1.03 - 0.97 ppm (m, 4 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 126 MHz): δ = 162.4, 158.1, 148.6, 138.6, 136.0, 129.6, 126.8, 118.0, 115.2, 24.6, 21.2, 17.4, 9.5 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>16</sub>H<sub>18</sub>N [M+H]<sup>+</sup>: 224.1434; Found: 224.1430

**FTIR** 2361, 2341, 1602, 1550, 814, 669 cm<sup>-1</sup>

**(E)-N-(1-Cyclohexyl-5-oxohex-3-en-1-yl)-4-methylbenzenesulfonamide 3q**



**General Procedure A** - **1h** (270 mg, 0.88 mmol) and methylvinylketone (**2a**) (180  $\mu$ L, 2.22 mmol) were employed. The mixture was heated for 48 h. The crude material was purified by flash column chromatography eluting with 25-33% EtOAc:petrol affording **3q** as a pale brown solid (232 mg, 76%).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.73 (d,  $J$ =8.0 Hz, 2 H), 7.27 (d,  $J$ =8.0 Hz, 2 H), 6.54 (dt,  $J$  = 16.0, 7.5 Hz, 1 H), 5.93 (d,  $J$ =16.0 Hz, 1 H), 5.15 (d,  $J$ =9.0 Hz, 1 H), 3.16 - 3.24 (m, 1 H), 2.40 (s, 3 H), 2.19 - 2.38 (m, 2 H), 2.11 (s, 3 H), 1.48 - 1.76 (m, 5 H), 1.27 - 1.38 (m, 1 H), 0.76 - 1.18 ppm (m, 5 H)

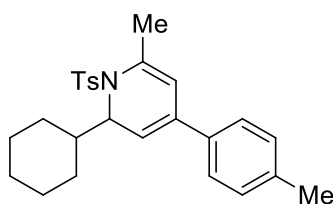
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz):  $\delta$  = 198.3, 143.7, 143.4, 138.2, 133.7, 129.6, 127.0, 58.0, 41.5, 35.2, 28.9, 28.4, 26.7, 26.1, 26.0, 21.5 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>19</sub>H<sub>27</sub>NNaO<sub>3</sub>S [M+Na]<sup>+</sup>: 372.1604; Found: 372.1599

**FTIR** 3281, 2927, 1672, 1448, 1328, 1158 cm<sup>-1</sup>

**MP** 111.5-112.5 °C (CH<sub>2</sub>Cl<sub>2</sub>:petrol)

**2-Cyclohexyl-6-methyl-4-(*p*-tolyl)-1-tosyl-1,2-dihydropyridine 6q**



**General Procedure B - 3q** (100 mg, 0.29 mmol) was employed. The Heck step was conducted for 3.5 h and the condensation step was conducted for 3.5 h. **Part B - Conditions (ii)** - The crude material was purified by flash column chromatography eluting with 5% EtOAc:petrol affording **6q** as a colourless oil (92 mg, 75%).

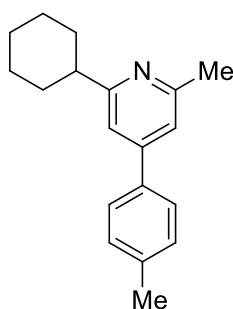
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.60 (d,  $J$ =8.5 Hz, 2 H), 7.10 (d,  $J$ =8.0 Hz, 2 H), 7.05 (d,  $J$ =8.0 Hz, 2 H), 6.89 (d,  $J$ =8.5 Hz, 2 H), 5.86 - 5.88 (m, 1 H), 5.54 (d,  $J$ =6.0 Hz, 1 H), 4.51 (dd,  $J$ =9.0, 6.0 Hz, 1 H), 2.32 (s, 3 H), 2.27 (s, 3 H), 2.25 (s, 3 H), 1.99 - 2.06 (m, 1 H), 1.71 - 1.86 (m, 3 H), 1.52 - 1.70 (m, 2 H), 1.04 - 1.26 ppm (m, 5 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz):  $\delta$  = 143.2, 137.1, 136.5, 135.6, 134.7, 133.8, 129.0, 128.9, 127.1, 125.6, 118.2, 117.5, 60.8, 40.2, 29.3, 29.1, 26.6, 26.0, 25.8, 23.2, 21.4, 21.1 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>26</sub>H<sub>31</sub>NNaO<sub>2</sub>S [M+Na]<sup>+</sup>: 444.1968; Found: 444.1967

**FTIR** 2924, 1448, 1343, 1164 cm<sup>-1</sup>

**2-Cyclohexyl-6-methyl-4-(*p*-tolyl)pyridine 4q**



**General Procedure B - Part B - Conditions (ii) - 6q** (41 mg, 0.09 mmol) was employed. The reaction was carried out for 1.25 h. The crude material was purified by flash column chromatography eluting with 15% EtOAc:petrol affording **4q** as a colourless oil (15 mg, 61%).

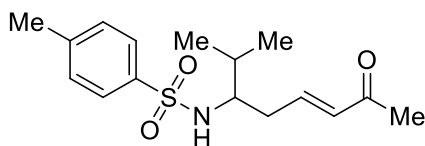
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ = 7.53 (d, *J*=8.0 Hz, 2 H), 7.28 (d, *J*=8.0 Hz, 2 H), 7.16 - 7.18 (m, 2 H), 2.75 (tt, *J*=11.5, 3.0 Hz, 1 H), 2.59 (s, 3 H), 2.41 (s, 3 H), 1.99 - 2.05 (m, 2 H), 1.84 - 1.90 (m, 2 H), 1.74 - 1.81 (m, 1 H), 1.39 - 1.60 (m, 4 H), 1.24 - 1.36 ppm (m, 1 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz): δ = 166.6, 157.8, 148.9, 138.6, 136.2, 129.6, 126.9, 118.6, 115.4, 46.9, 33.2, 26.6, 26.1, 24.7, 21.2 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>19</sub>H<sub>24</sub>N [M+H]<sup>+</sup>: 266.1903; Found: 266.1905

**FTIR** 2924, 2851, 1602, 1550, 1515, 1448 cm<sup>-1</sup>

**(E)-4-Methyl-N-(2-methyl-7-oxooct-5-en-3-yl)benzenesulfonamide 3r**



**General Procedure A** - **1i** (200 mg, 0.75 mmol) and methylvinylketone (**2a**) (0.30 mL, 3.74 mmol) were employed. Reaction heated for 71 h. The crude material was purified by flash column chromatography eluting with 20% EtOAc:petrol affording **3r** as a white solid (197 mg, 85%).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ = 7.75 (d, *J*=8.5 Hz, 2 H), 7.29 (d, *J*=8.0 Hz, 2 H), 6.56 (dt, *J*=16.0, 7.0 Hz, 1 H), 5.97 (d, *J*=16.0 Hz, 1 H), 4.82 (d, *J*=9.0 Hz, 1 H), 3.16 - 3.28 (m, 1 H), 2.42 (s, 3 H), 2.21 - 2.40 (m, 2 H), 2.14 (s, 3 H), 1.73 (m, 1 H), 0.81 ppm (d, *J*=7.0 Hz, 6 H)

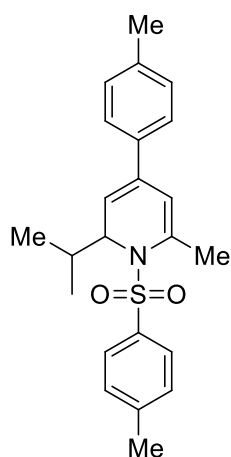
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz): δ = 198.2, 143.5, 138.0, 133.7, 129.7, 127.0, 58.4, 35.4, 31.5, 26.7, 21.5, 18.5, 17.7 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>16</sub>H<sub>24</sub>NO<sub>3</sub>S [M+H]<sup>+</sup>: 310.1471; Found: 310.1472

**FTIR** 3282, 3005, 2964, 2876, 1673, 1627, 1599, 1495, 1427, 1391, 1362, 1325, 1305, 1276, 1260, 1159, 1094, 1038, 981, 862, 816, 764, 750, 707 cm<sup>-1</sup>

**MP** 85-87 °C (CH<sub>2</sub>Cl<sub>2</sub>:petrol)

**2-Isopropyl-6-methyl-4-(*p*-tolyl)-1-tosyl-1,2-dihydropyridine 6r**



**General Procedure B - 3r** (100 mg, 0.32 mmol) was employed. The Heck step was carried out for 4 h. The cyclisation step was carried out for 2.5 h. **Part B - Conditions (ii)** - The crude material was purified by flash column chromatography eluting with 50% CH<sub>2</sub>Cl<sub>2</sub>:petrol affording **6r** as a yellow oil (82 mg, 71%).

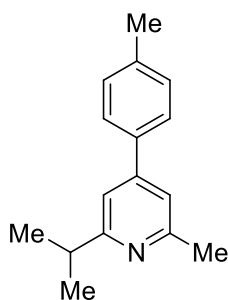
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 300 MHz): δ = 7.52 (d, *J*=8.0 Hz, 2 H), 6.94 - 7.06 (m, 4 H), 6.79 (d, *J*=8.0 Hz, 2 H), 5.79 (s, 1 H), 5.47 (d, *J*=6.0 Hz, 1 H), 4.29 (dd, *J*=9.0, 6.0 Hz, 1 H), 2.24 (s, 3 H), 2.14 - 2.21 (m, 6 H), 1.71 - 1.80 (m, 1 H), 0.96 (d, *J*=6.5 Hz, 3 H), 0.90 ppm (d, *J*=6.5 Hz, 3 H)

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 75 MHz): δ = 143.2, 137.2, 136.5, 135.6, 134.6, 133.9, 129.0, 128.9, 127.1, 125.6, 118.3, 117.6, 61.9, 30.9, 23.2, 21.4, 21.1, 19.0, 18.8 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>23</sub>H<sub>28</sub>NO<sub>2</sub>S [M+H]<sup>+</sup>: 382.1835; Found: 382.1828

**FTIR** 2960, 1597, 1514, 1449, 1342, 1166, 1087, 971, 871, 800, 736, 705, 674, 629 cm<sup>-1</sup>

**2-Isopropyl-6-methyl-4-(*p*-tolyl)pyridine 4r**



**General Procedure B - Part B - Conditions (ii) - 6r** (34 mg, mmol) was employed. The aromatisation step was carried out for 3 h. The crude material was purified by flash column chromatography eluting with 5% EtOAc:petrol affording **4r** as a yellow oil (14 mg, 61%).

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz):  $\delta$  = 7.53 (d,  $J$ =8.0 Hz, 2 H), 7.25 - 7.33 (m, 2 H), 7.18 (s, 2 H), 3.10 (spt,  $J$ =7.0 Hz, 1 H), 2.60 (s, 3 H), 2.42 (s, 3 H), 1.35 ppm (d,  $J$ =7.0 Hz, 6 H)

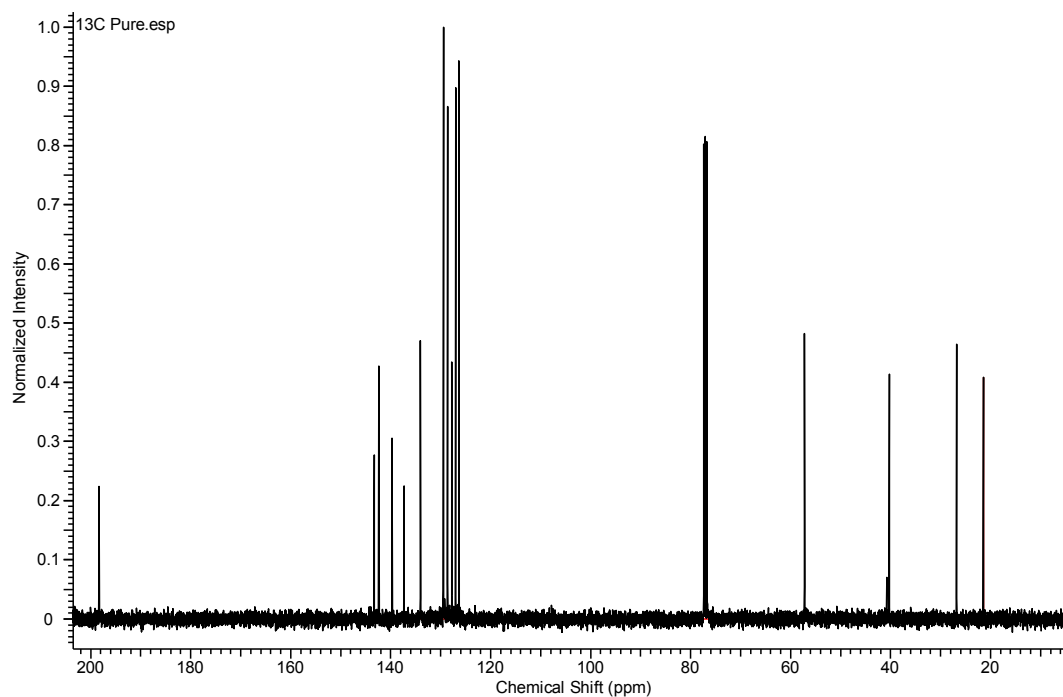
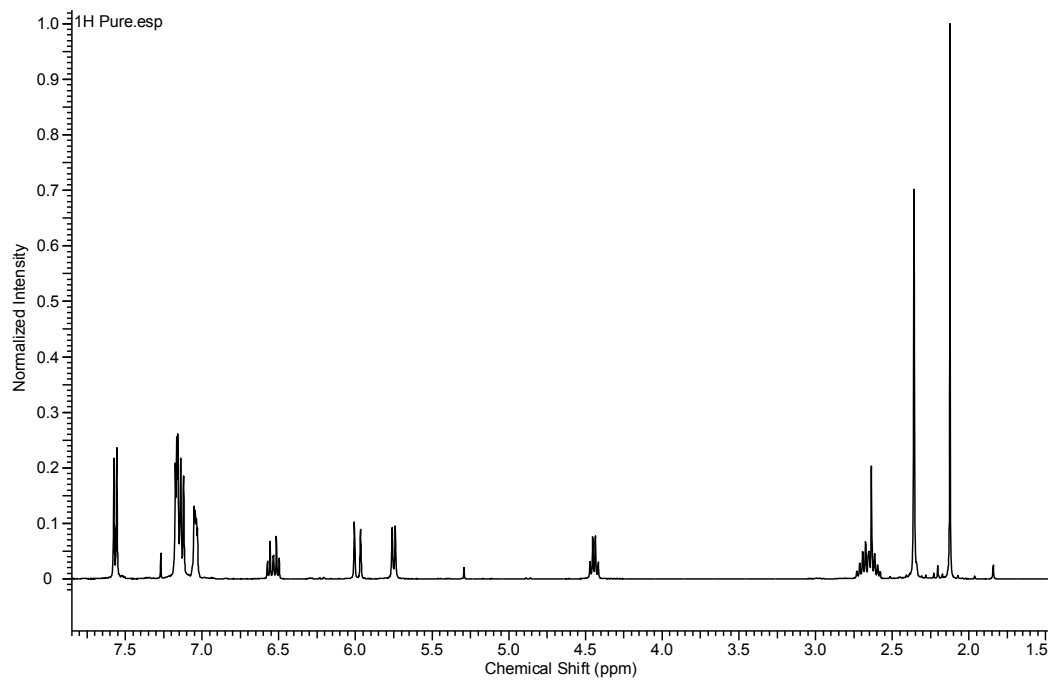
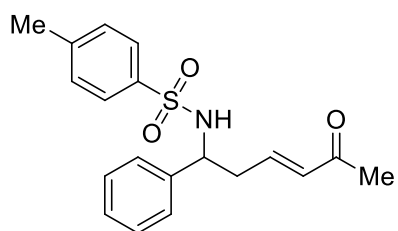
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 101 MHz):  $\delta$  = 167.4, 157.8, 149.0, 138.7, 136.2, 129.6, 126.9, 118.6, 115.0, 36.6, 24.7, 22.8, 21.2 ppm

**MS** (ESI<sup>+</sup>) Calculated for C<sub>16</sub>H<sub>20</sub>N [M+H]<sup>+</sup>: 226.1590; Found: 226.1588

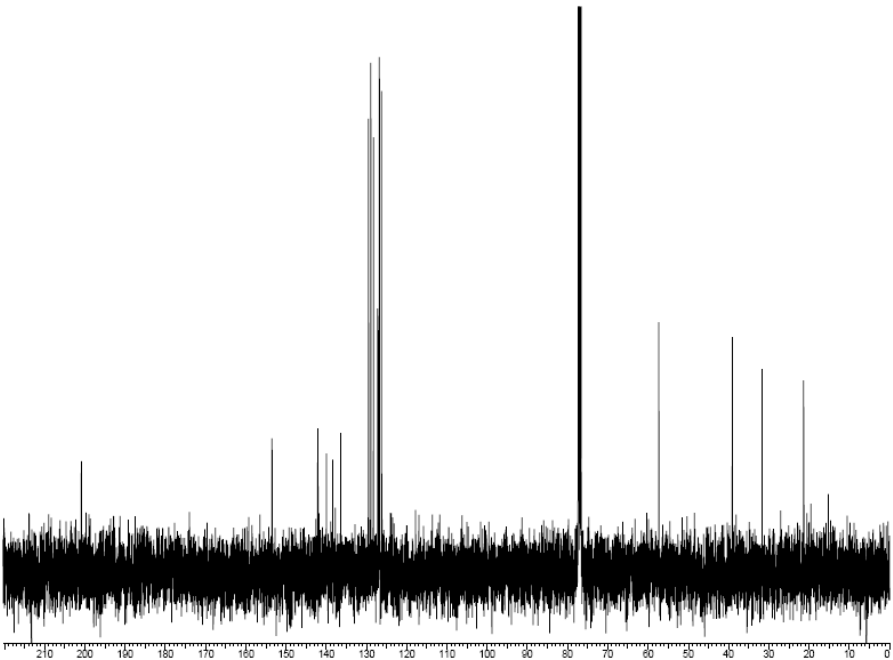
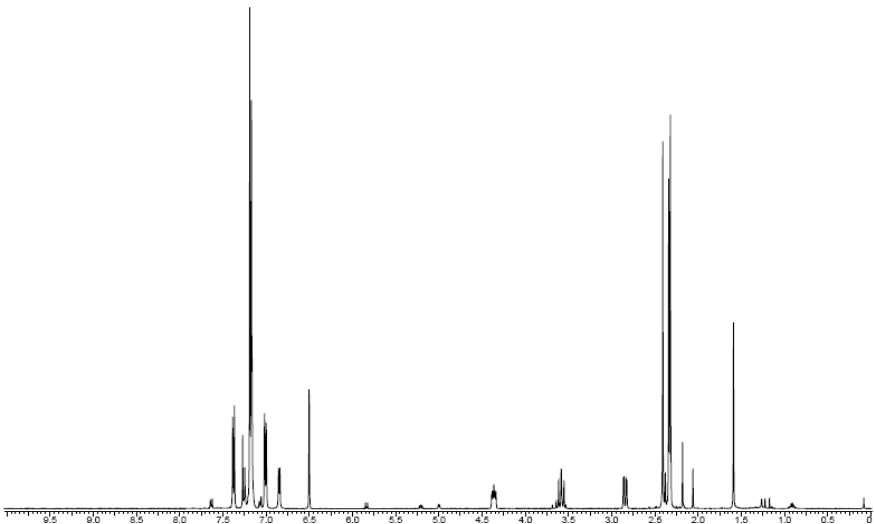
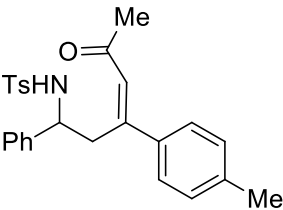
**FTIR** 2961, 1602, 1552, 1516, 1457, 1094, 872, 814 cm<sup>-1</sup>



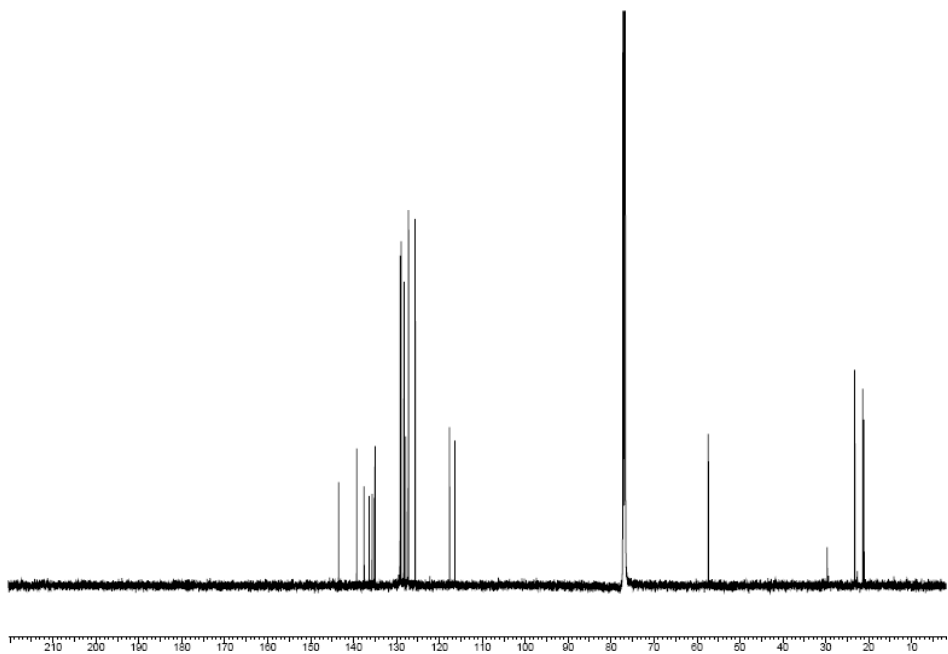
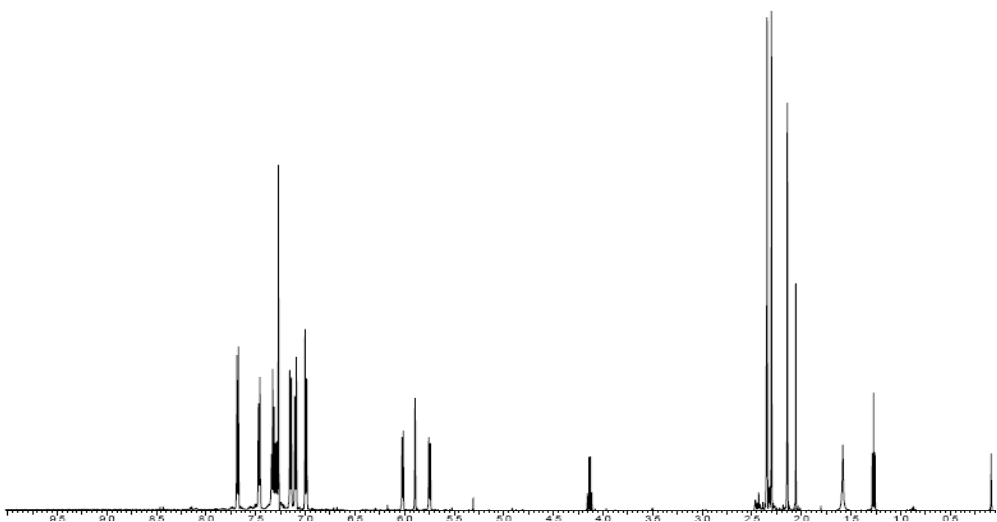
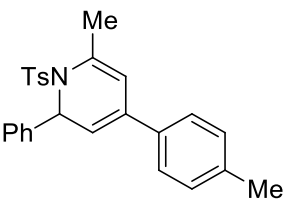
**(E)-4-Methyl-N-(5-oxo-1-phenylhex-3-en-1-yl)benzenesulfonamide 3a**



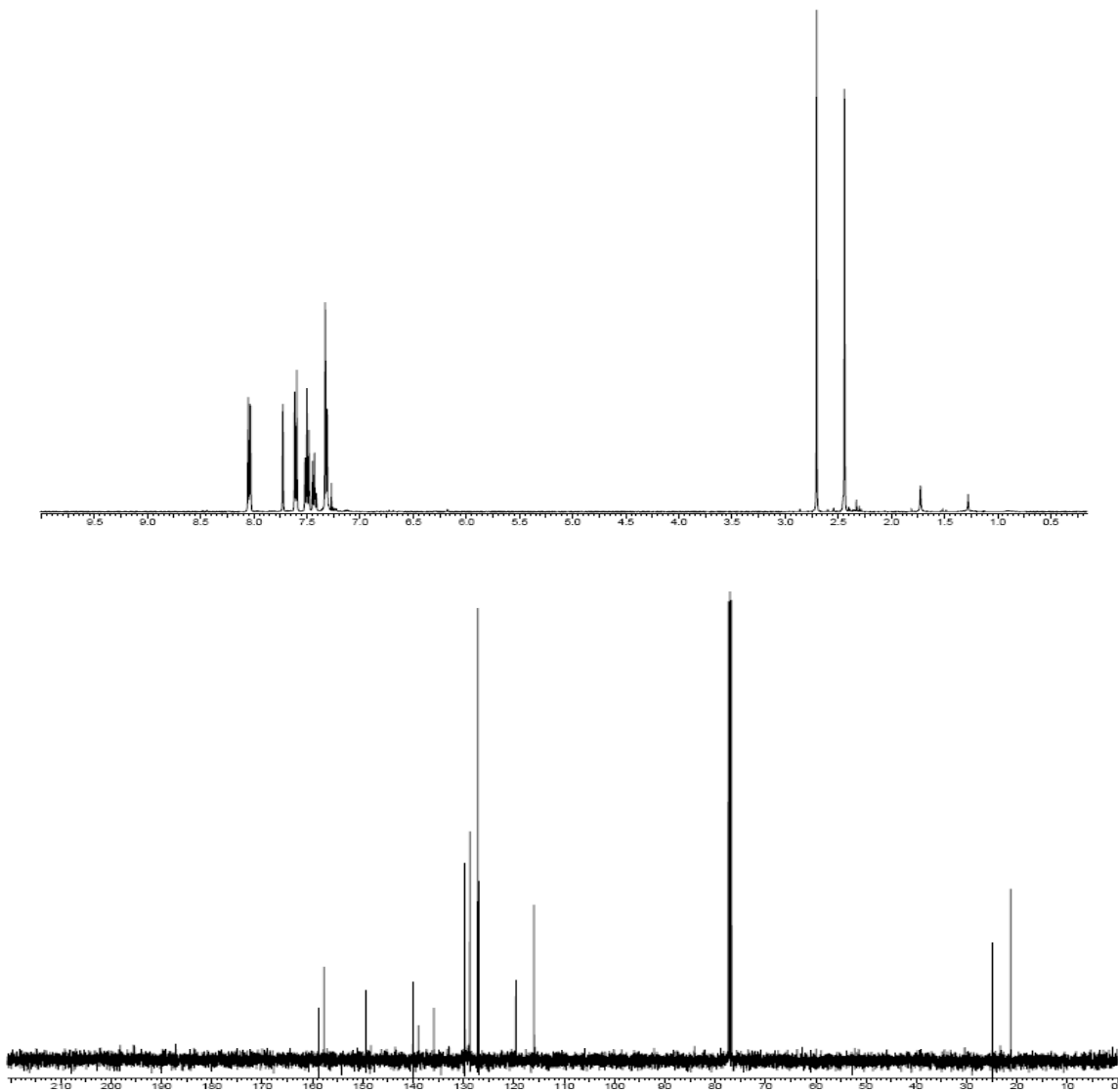
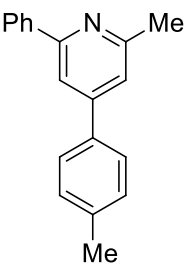
**(E)-4-Methyl-N-(5-oxo-1-phenyl-3-(p-tolyl)hex-3-en-1-yl)benzenesulfonamide 5a**



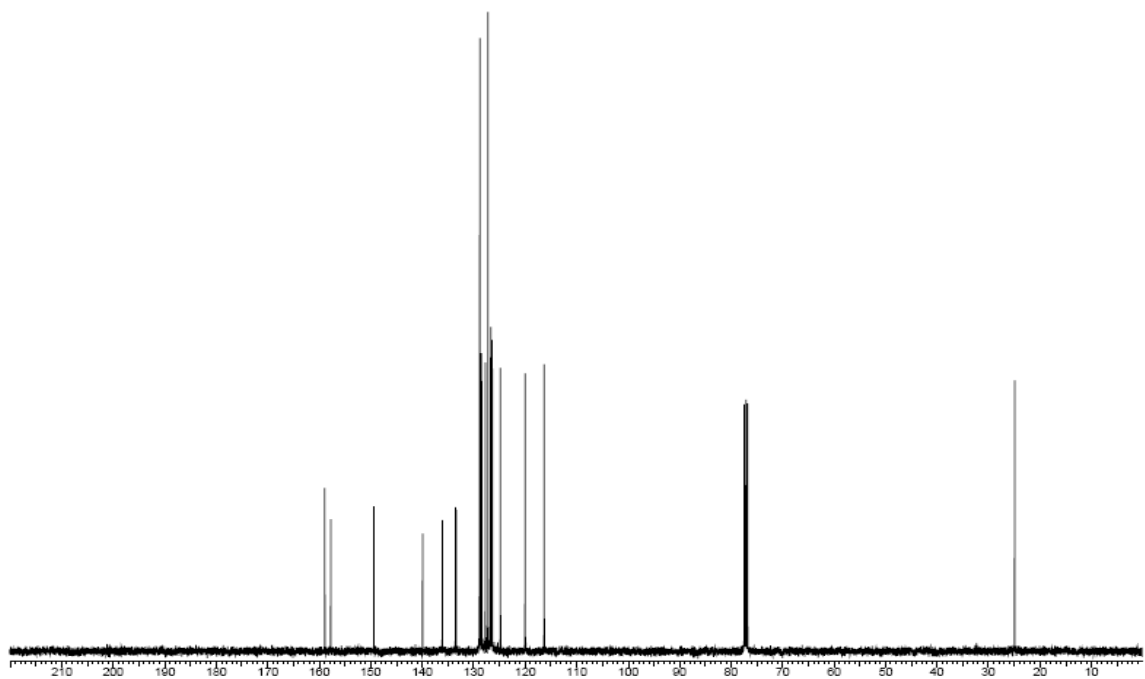
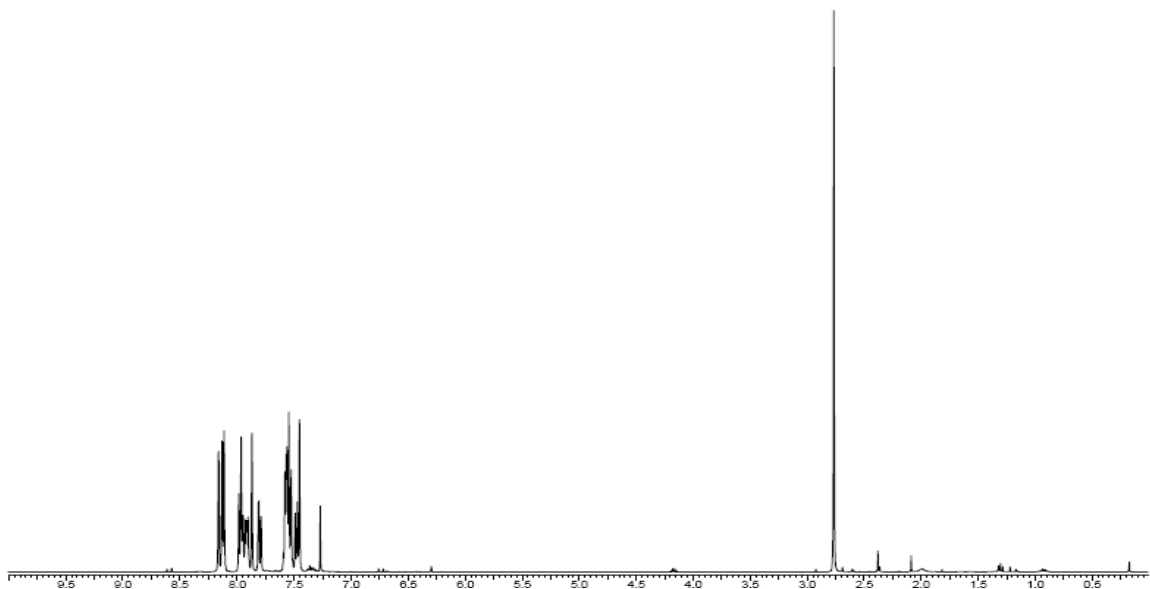
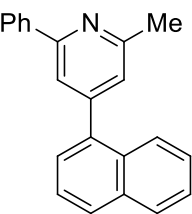
6-Methyl-2-phenyl-4-(*p*-tolyl)-1-tosyl-1,2-dihydropyridine 6a



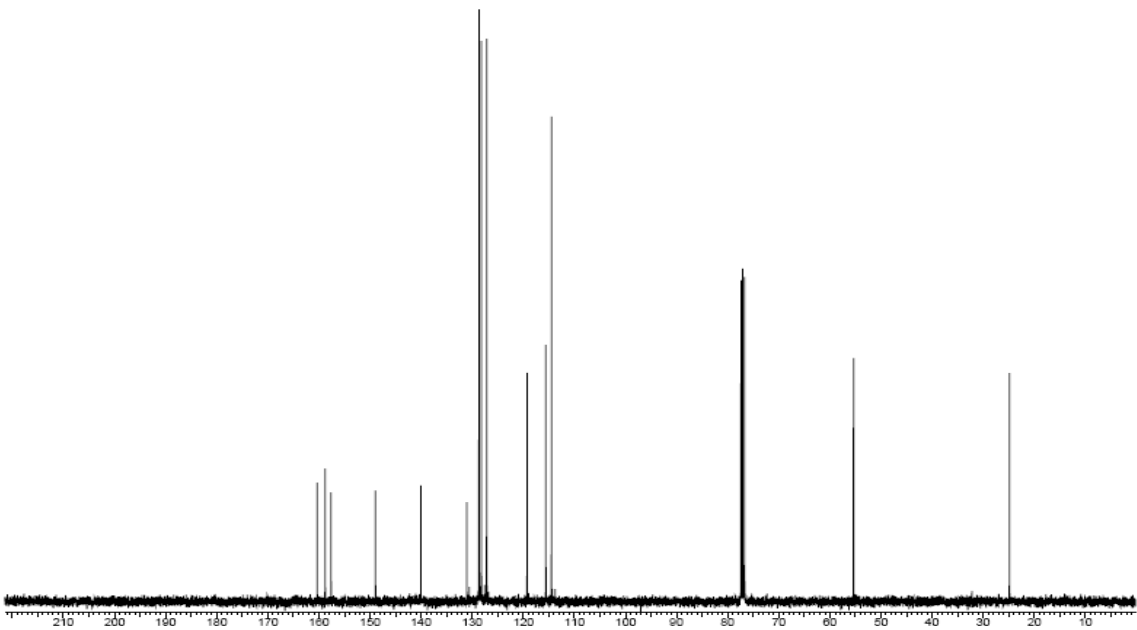
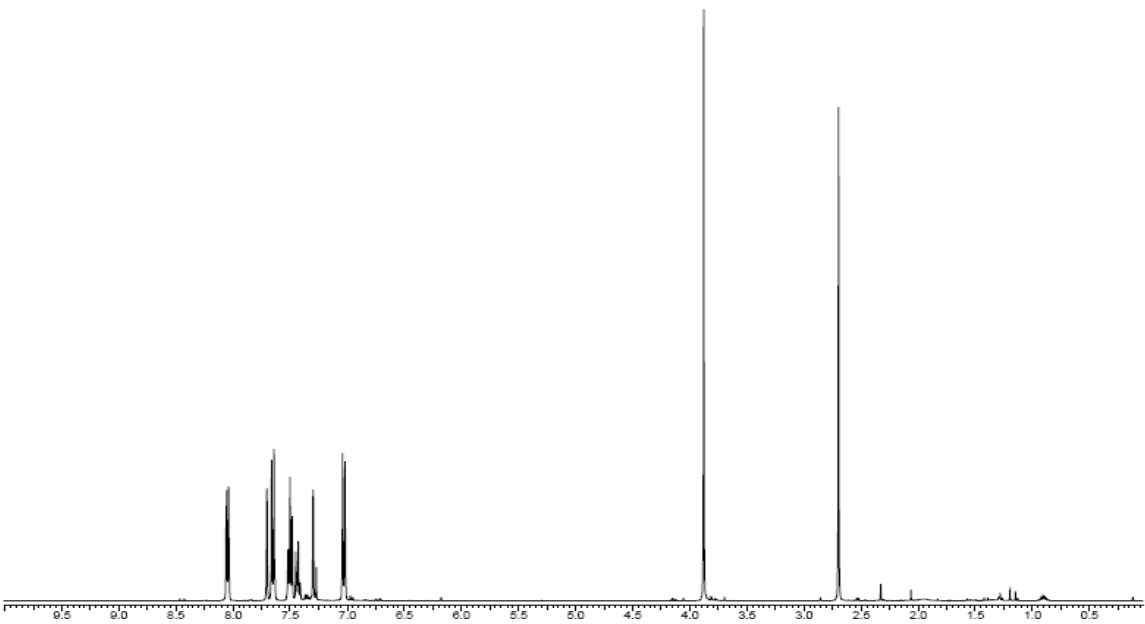
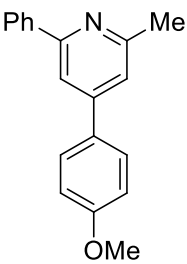
2-Methyl-6-phenyl-4-(*p*-tolyl)pyridine 4a



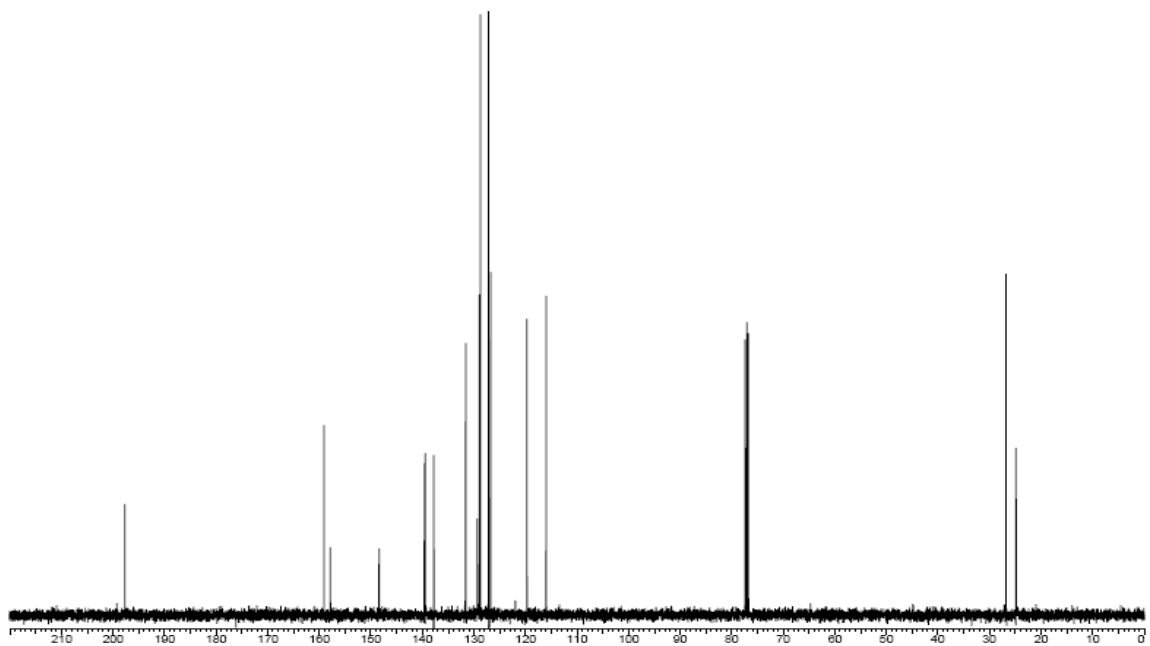
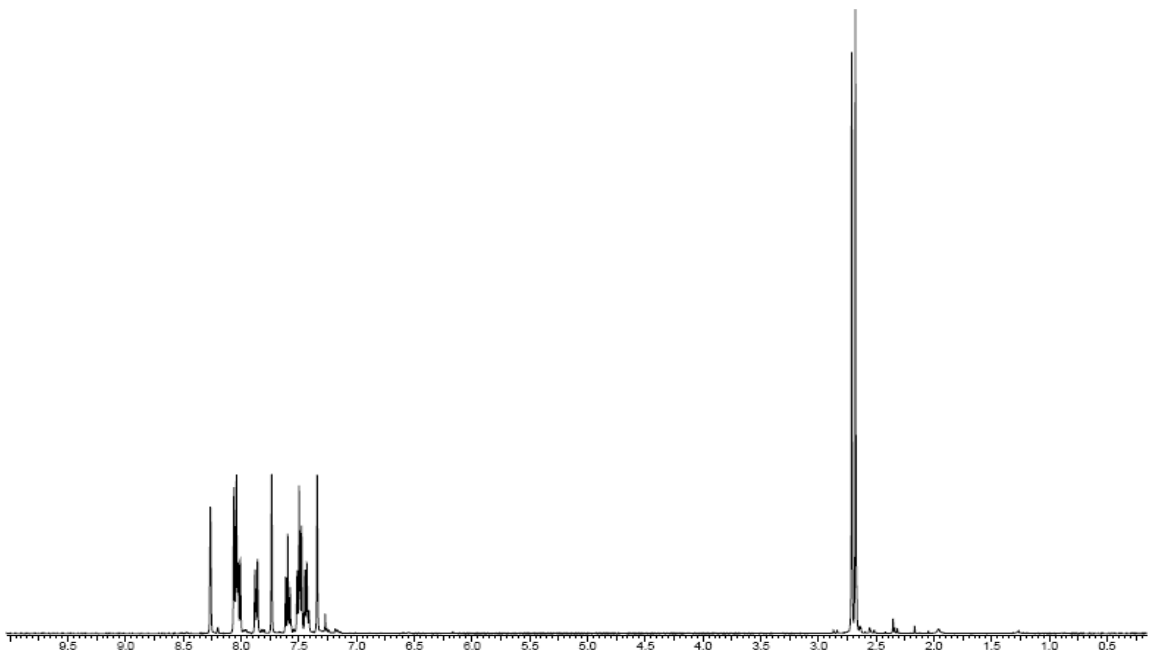
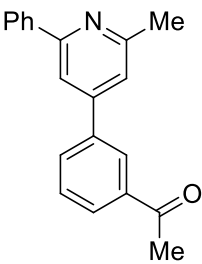
2-Methyl-4-(naphthalen-1-yl)-6-phenylpyridine 4b



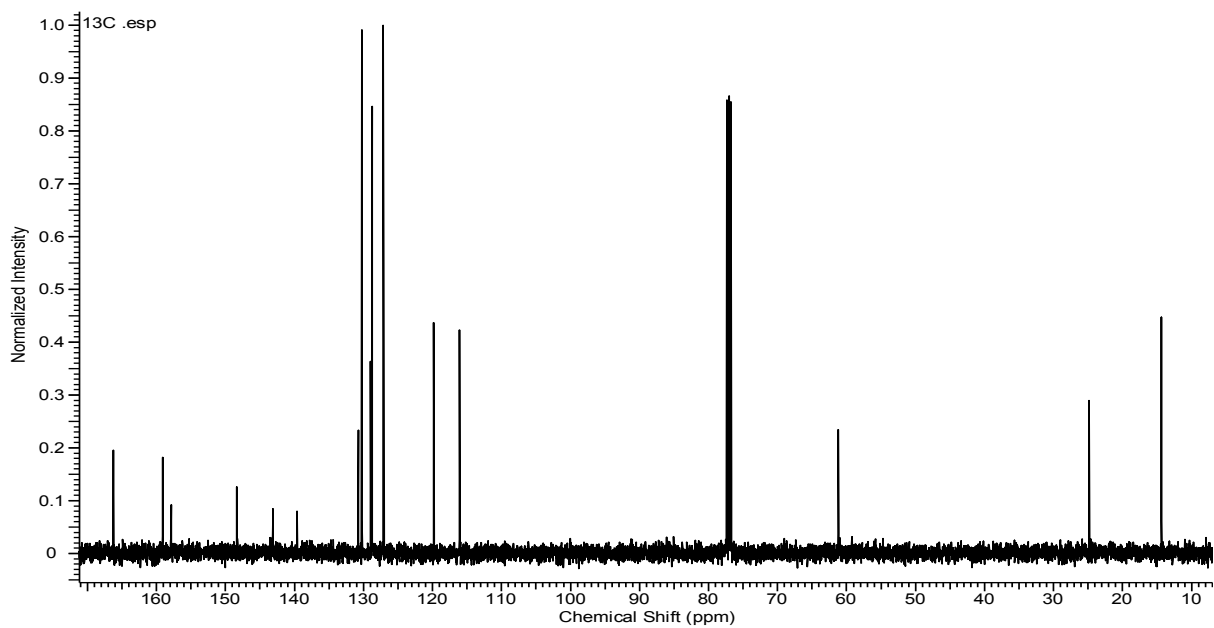
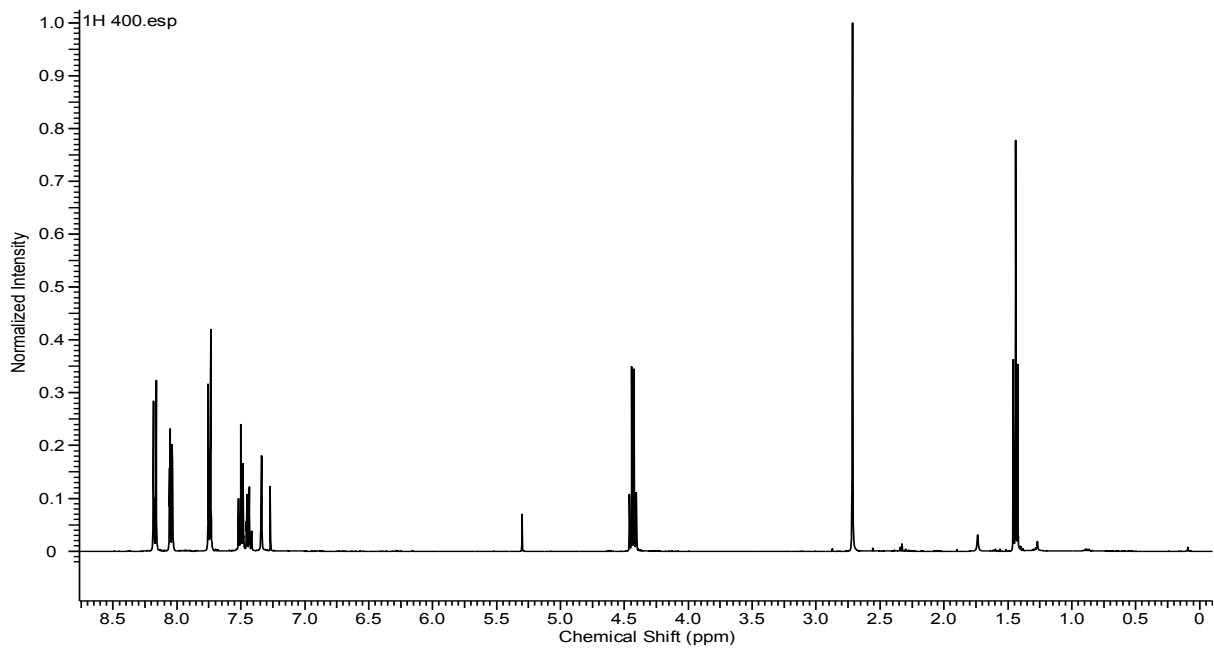
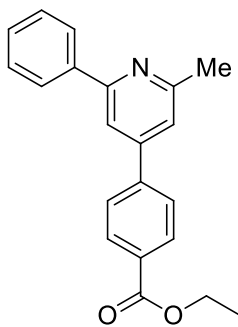
**4-(4-Methoxyphenyl)-2-methyl-6  
phenylpyridine 4c**



1-(3-(2-Methyl-6-phenylpyridin-4-yl)phenyl)ethanone 4d

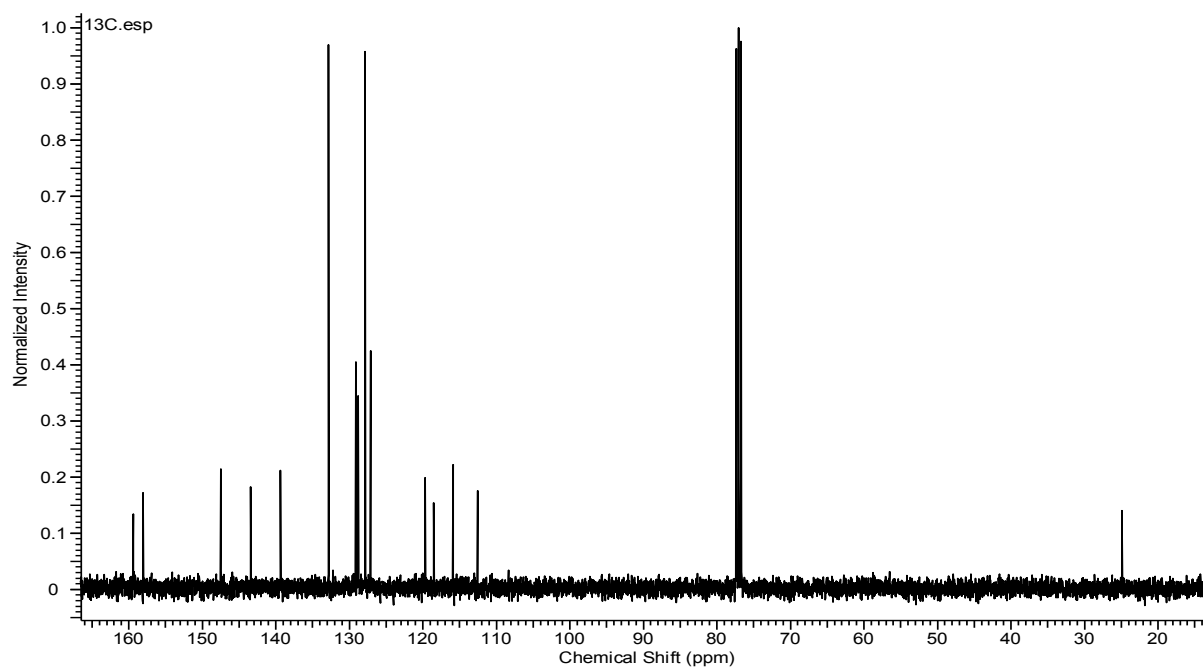
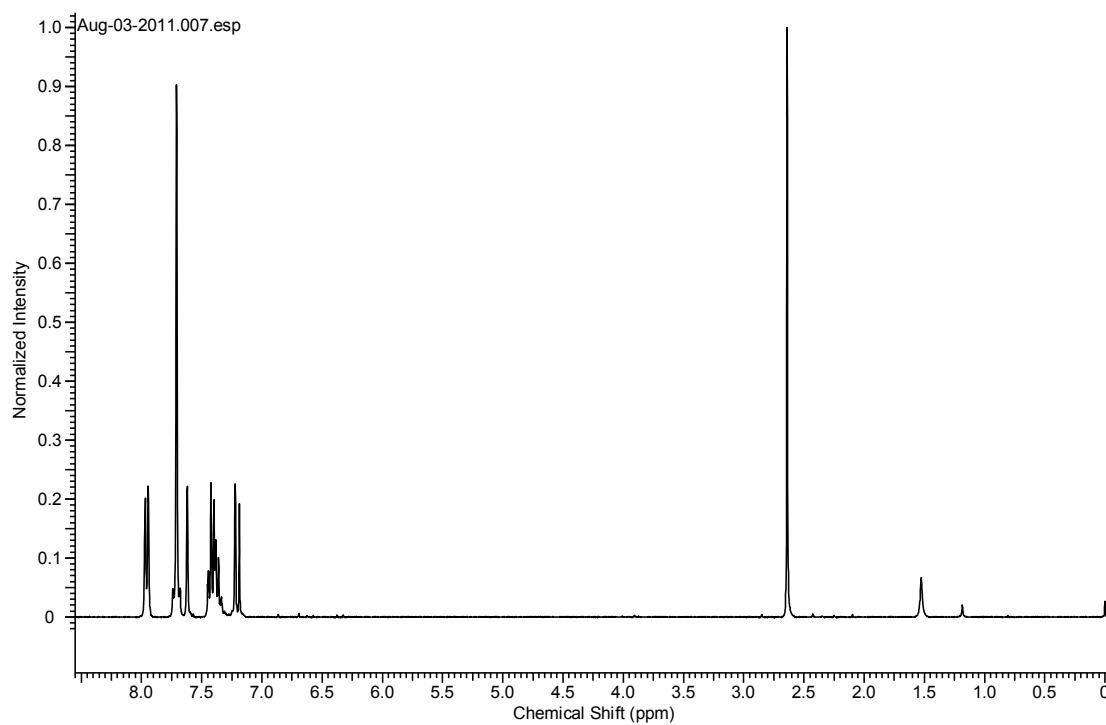
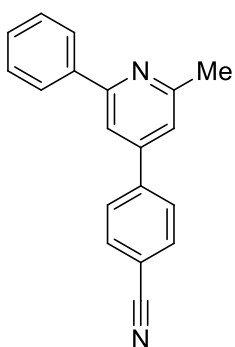


Ethyl 4-(2-methyl-6-phenylpyridin-4-yl)benzoate 4e

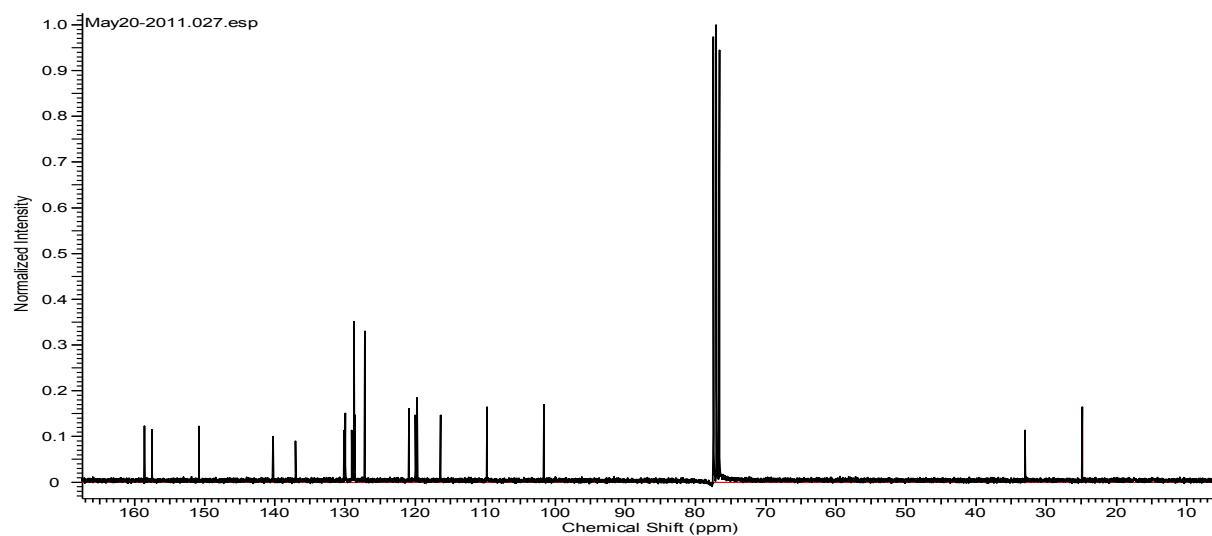
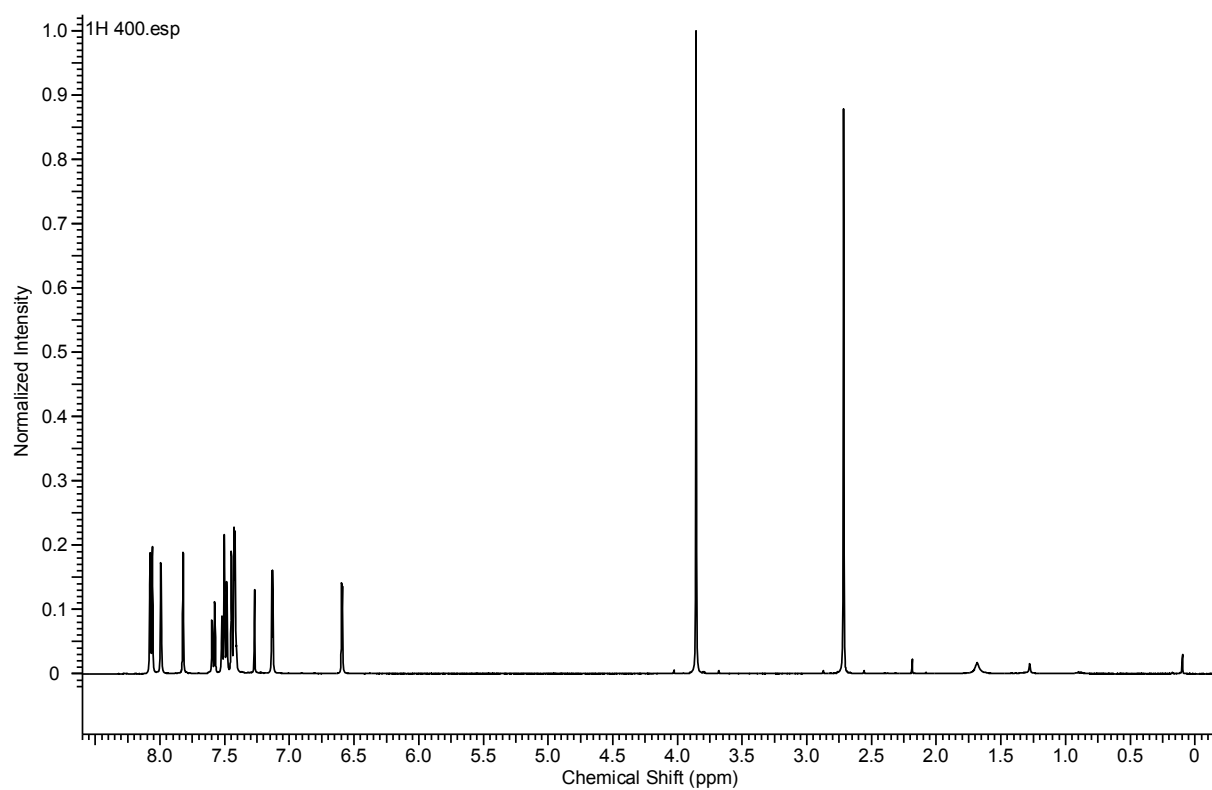
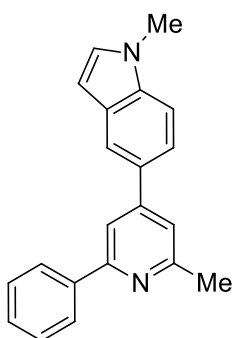




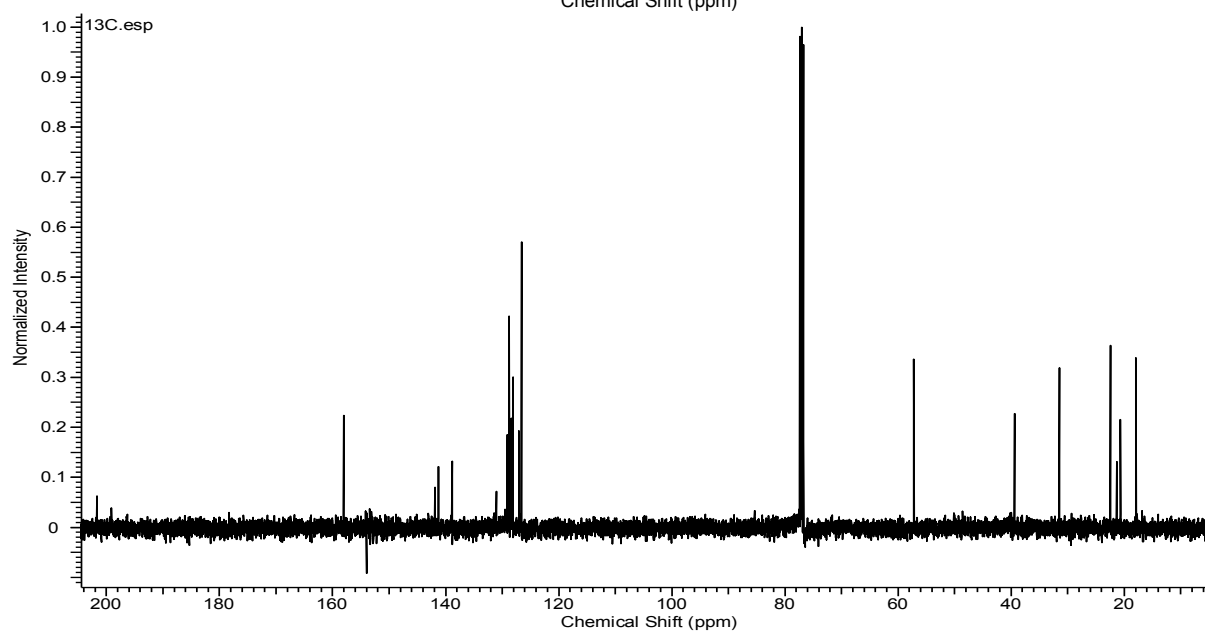
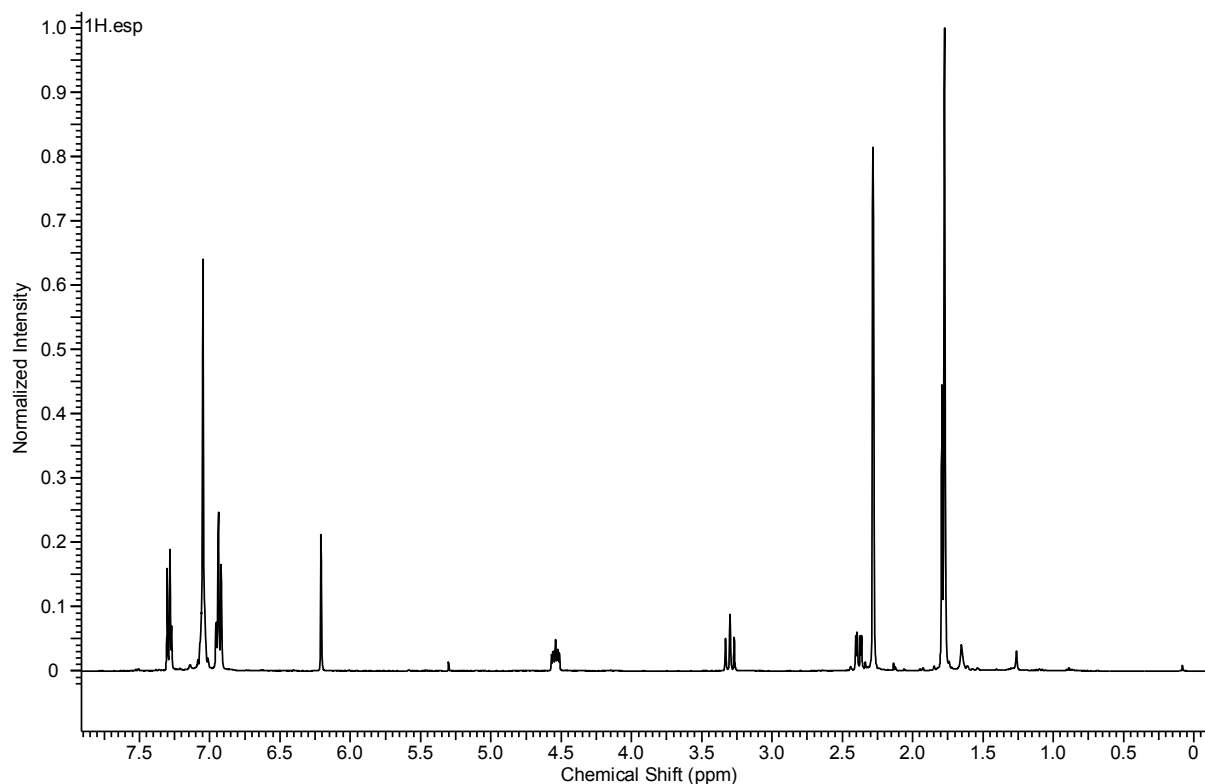
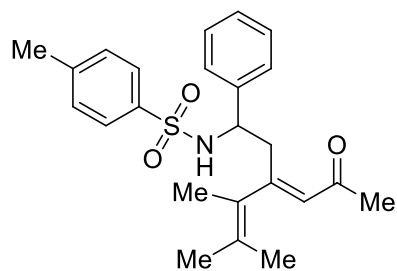
**4-(2-Methyl-6-phenylpyridin-4-yl)benzonitrile 4f**



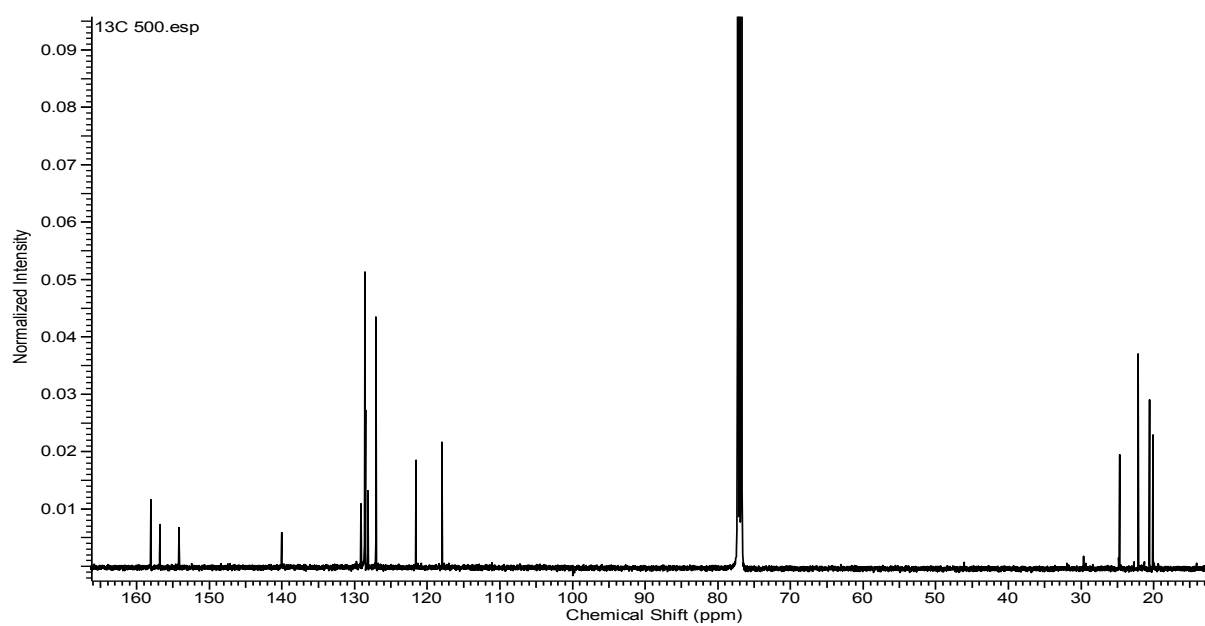
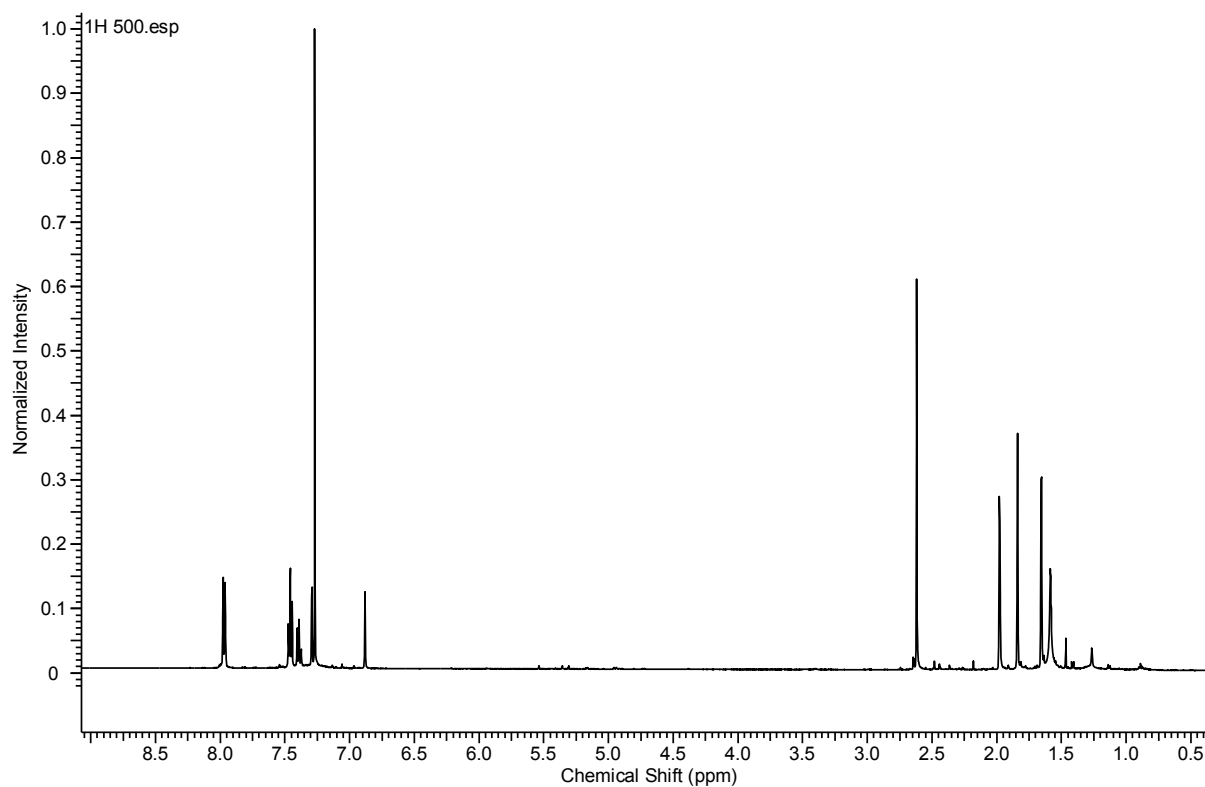
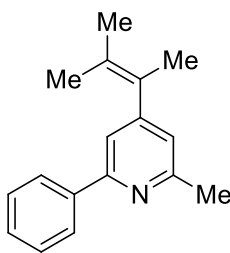
**1-Methyl-5-(2-methyl-6-phenylpyridin-4-yl)-1*H*-indole 4g**



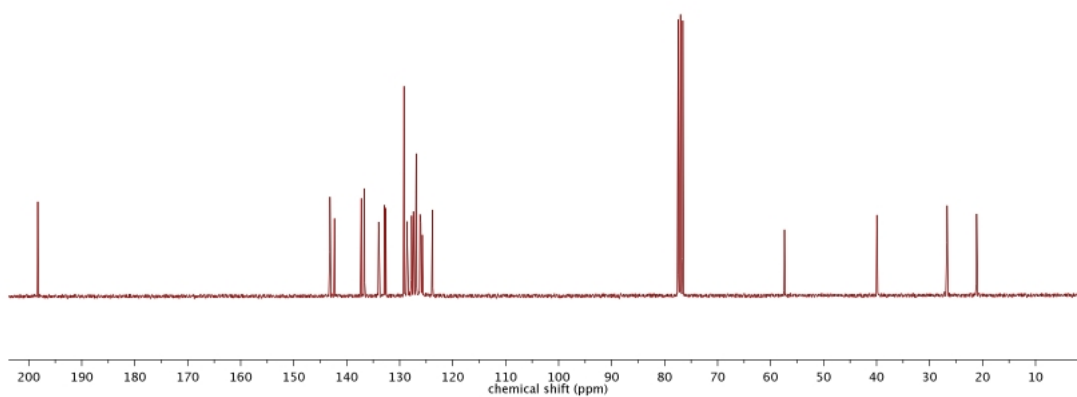
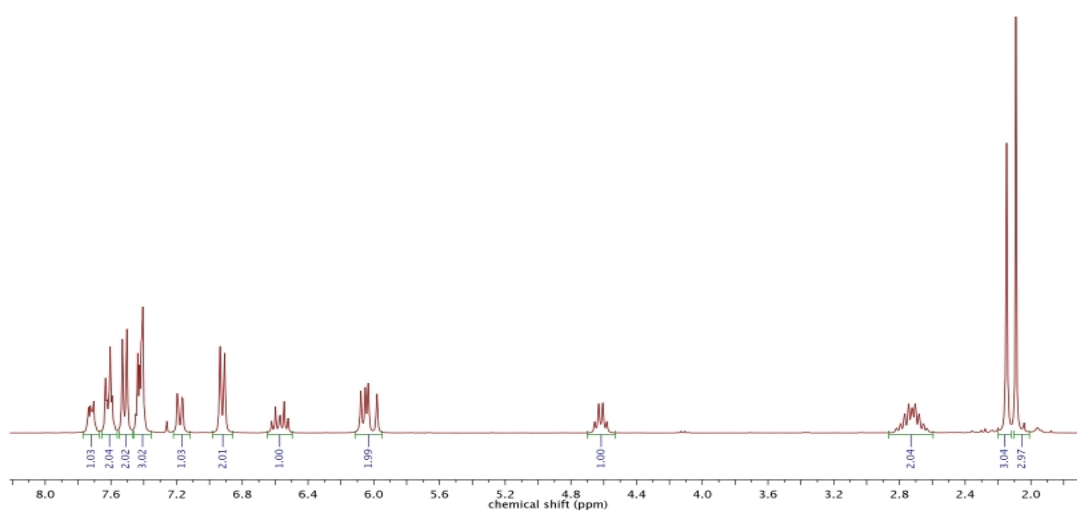
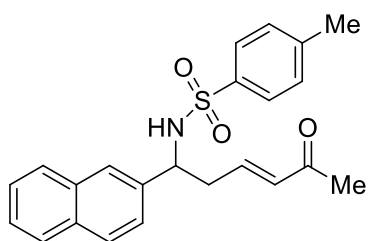
**(*E*)-4-Methyl-*N*-(3-(3-methylbut-2-en-2-yl)-5-oxo-1-phenylhex-3-en-1-yl)benzenesulfonamide 5h**



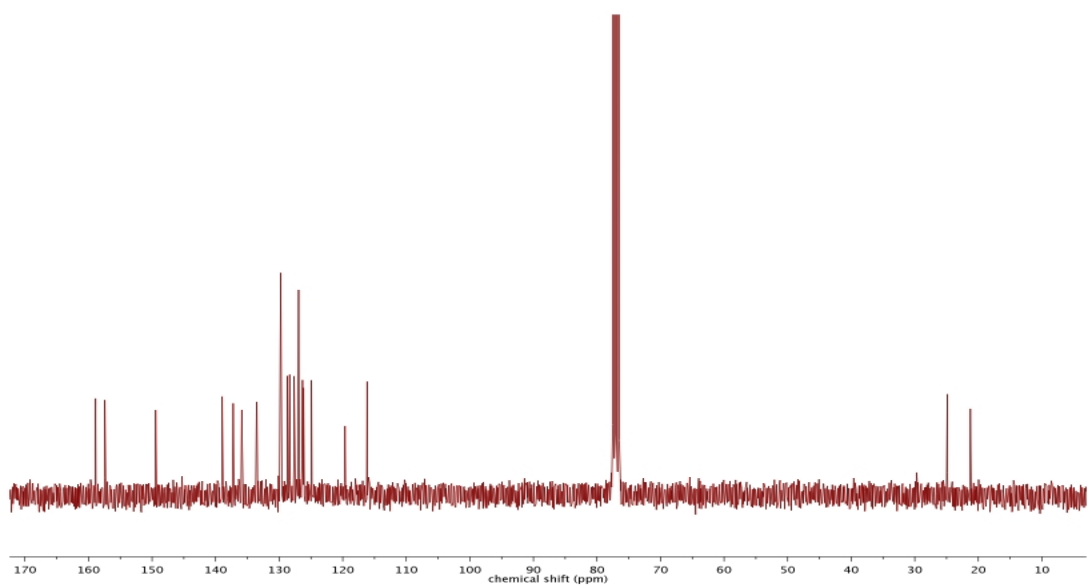
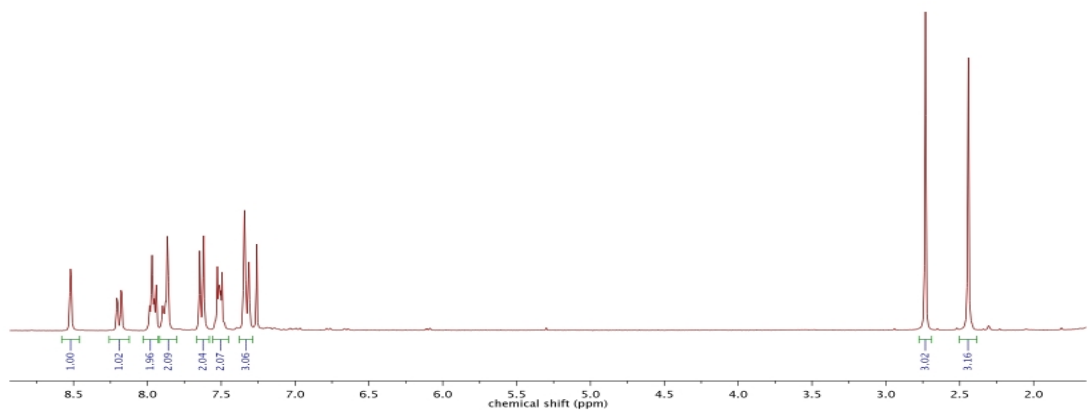
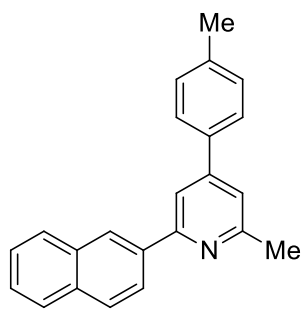
**2-Methyl-4-(3-methylbut-2-en-2-yl)-6-phenylpyridine 4h**



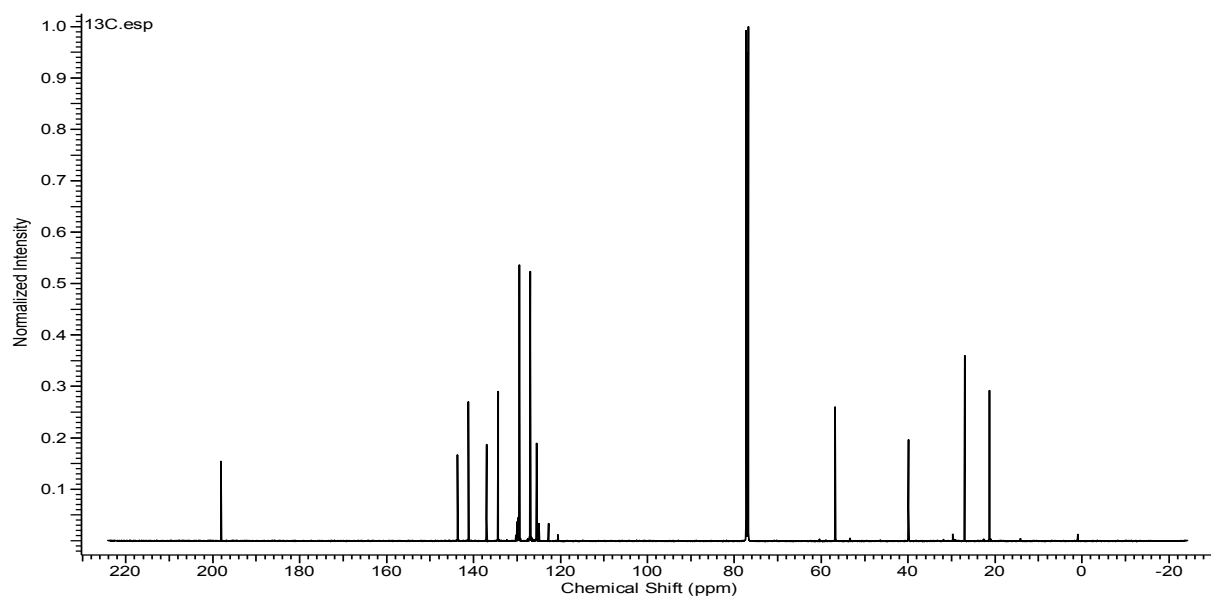
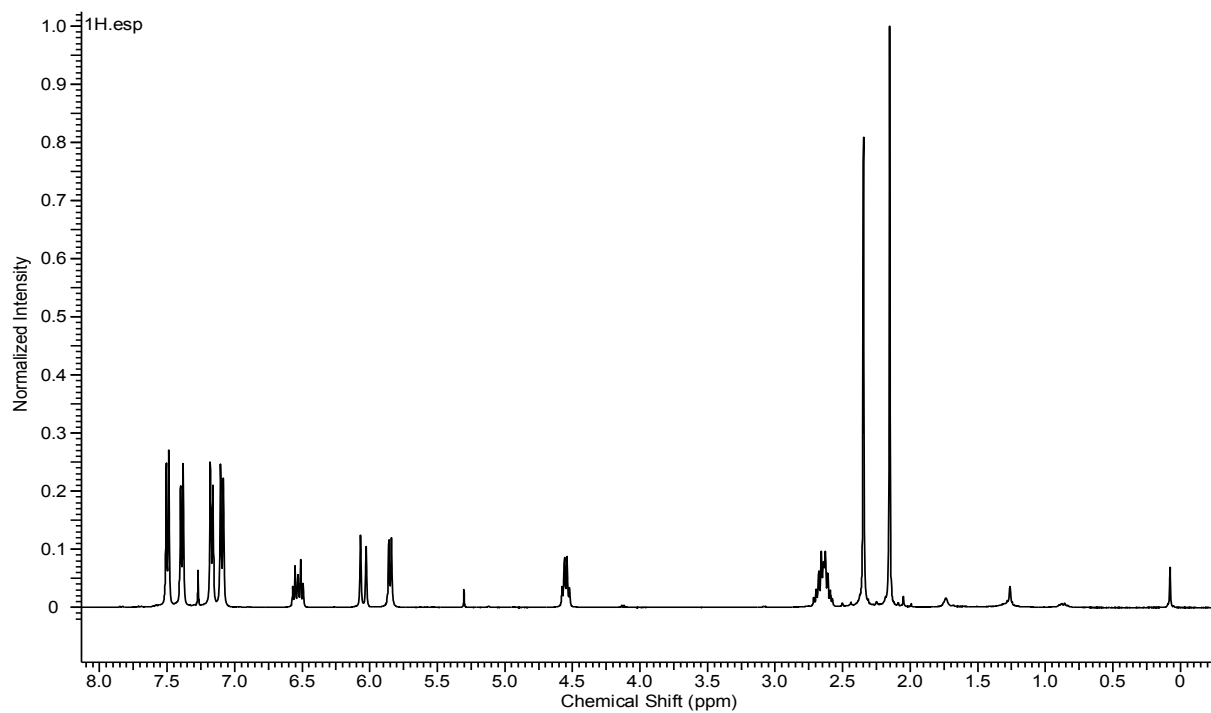
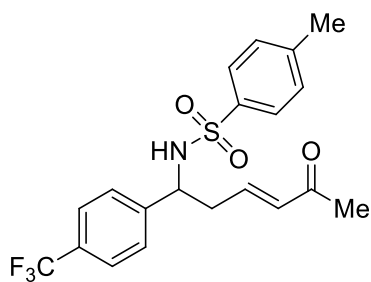
**(E)-4-Methyl-N-(1-(naphthalen-2-yl)-5-oxohex-3-en-1-yl)benzenesulfonamide 3i**



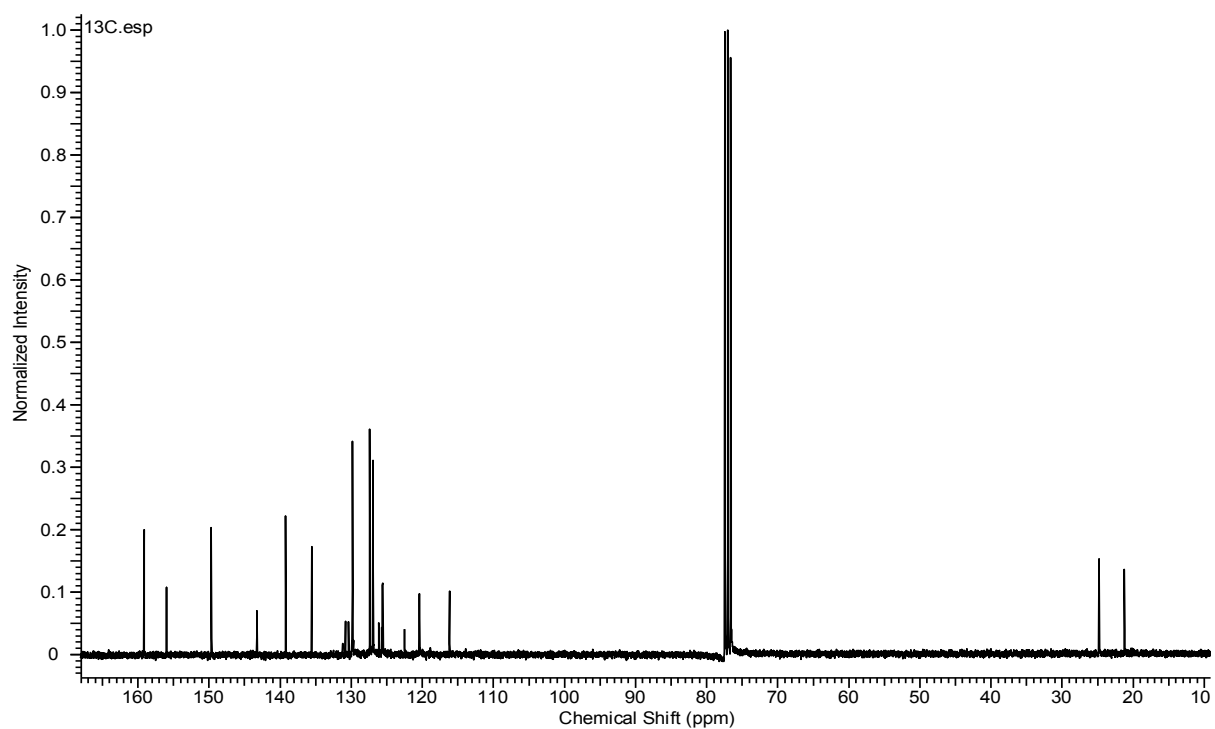
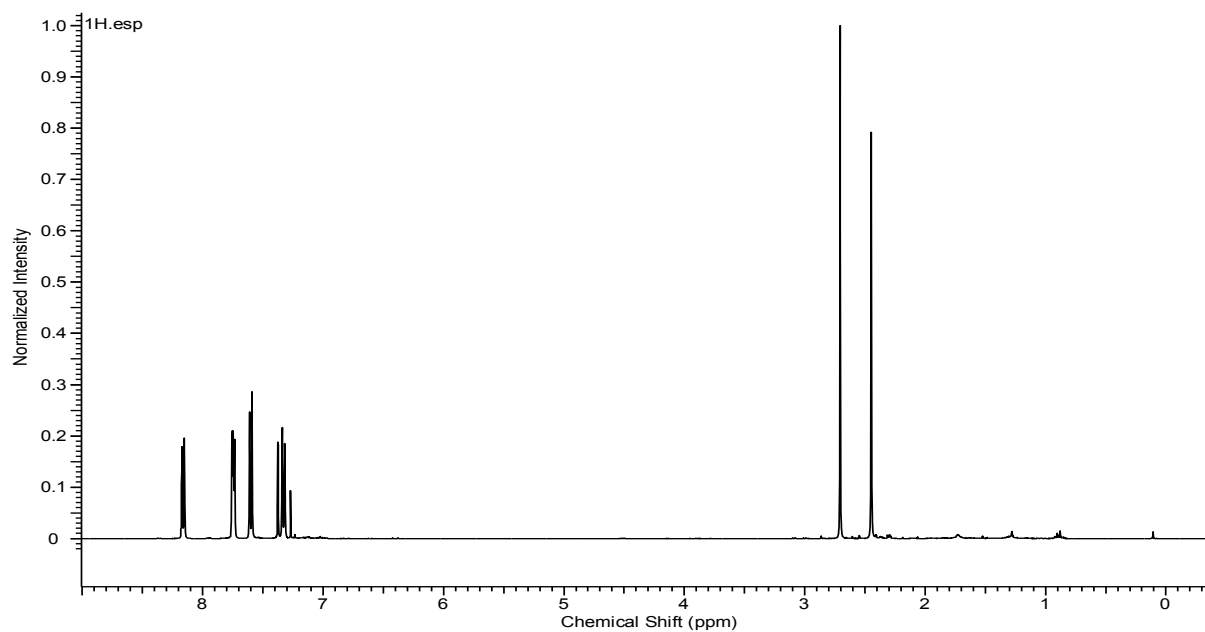
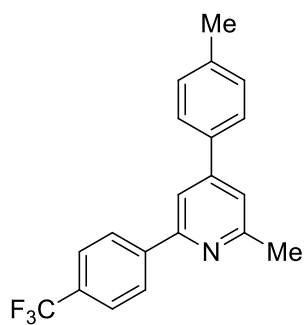
2-Methyl-6-(naphthalen-2-yl)-4-(*p*-tolyl)pyridine 4i



**(*E*)-4-Methyl-*N*-(5-oxo-1-(4-(trifluoromethyl)phenyl)hex-3-en-1-yl)benzenesulfonamide 3j**

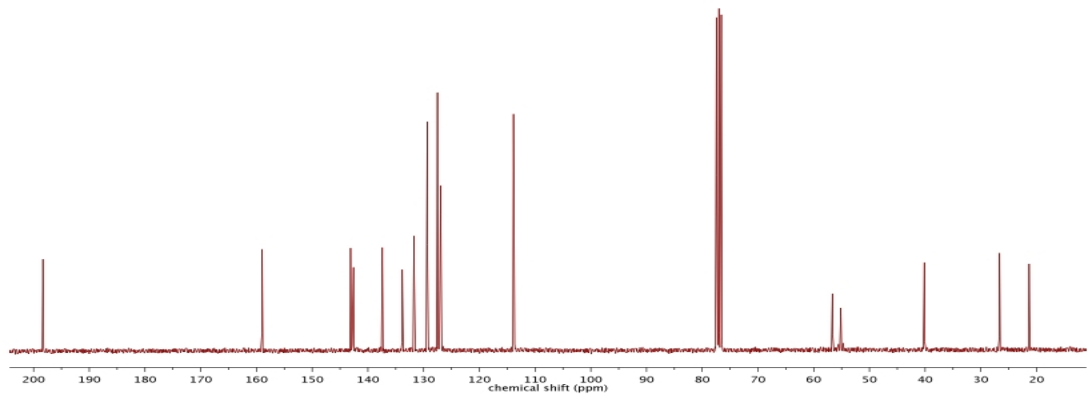
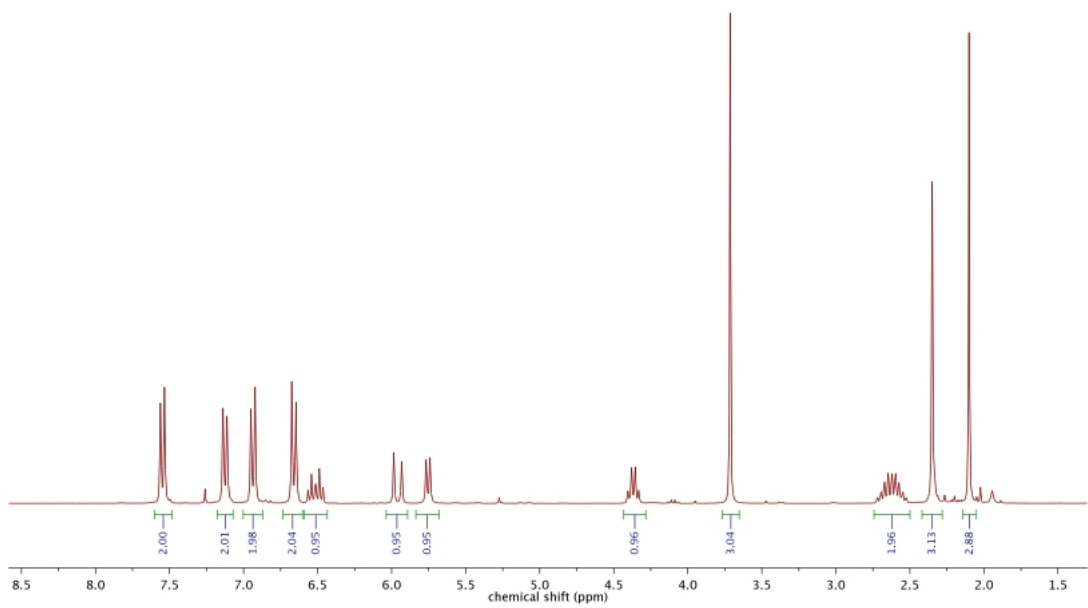
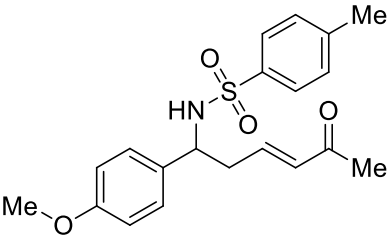


**2-Methyl-4-(*p*-tolyl)-6-(4-(trifluoromethyl)phenyl)pyridine 4j**

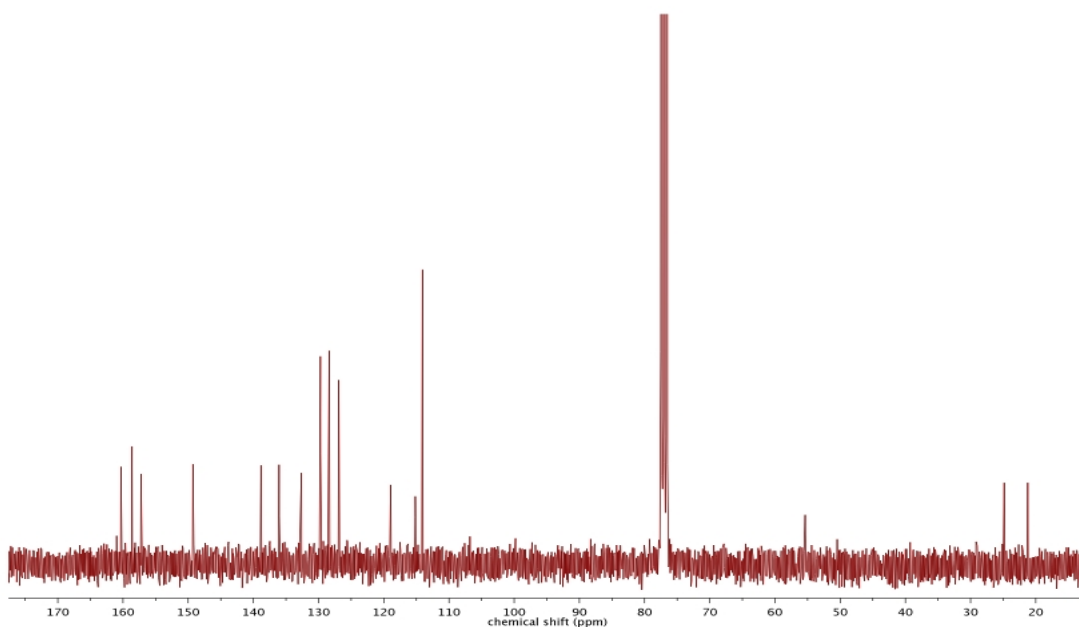
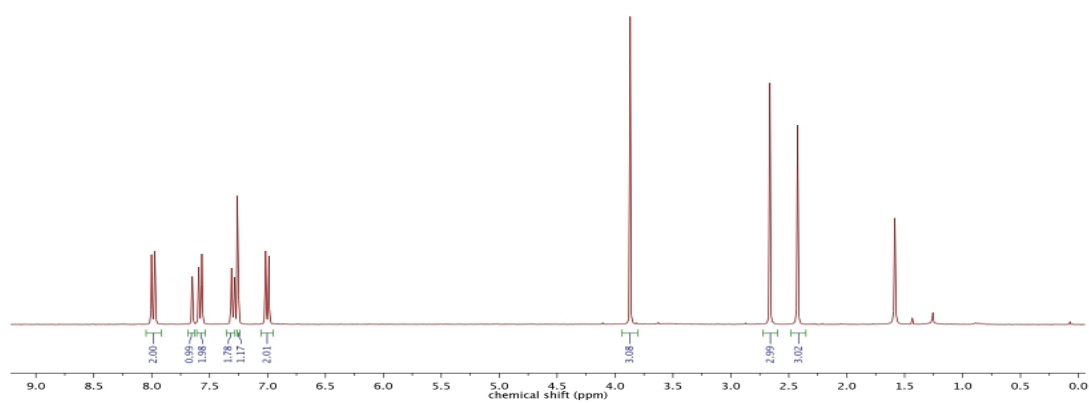
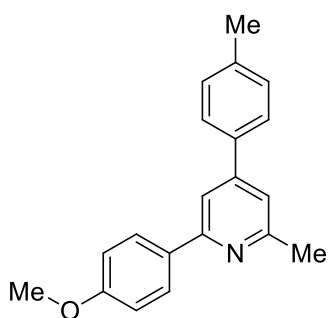




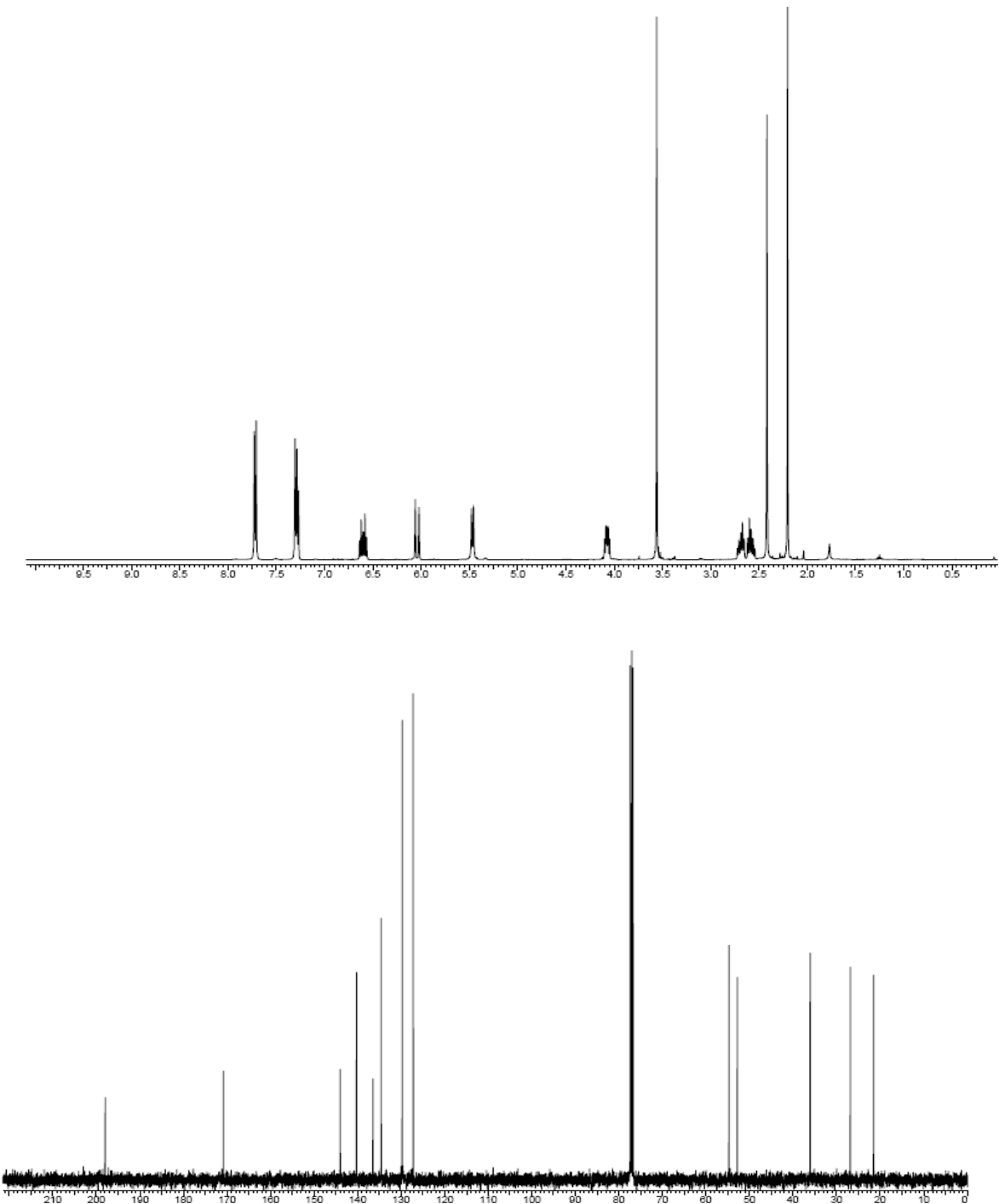
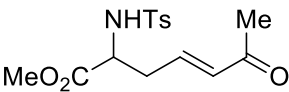
**(E)-N-(1-(4-Methoxyphenyl)-5-oxohex-3-en-1-yl)-4-methylbenzenesulfonamide 3k**



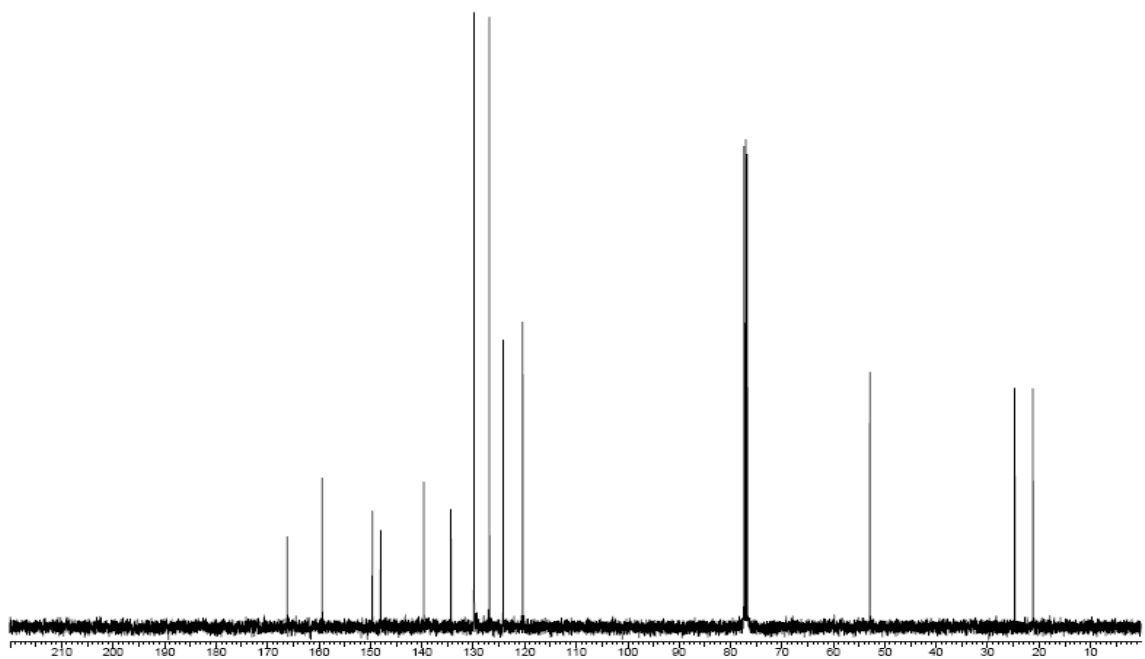
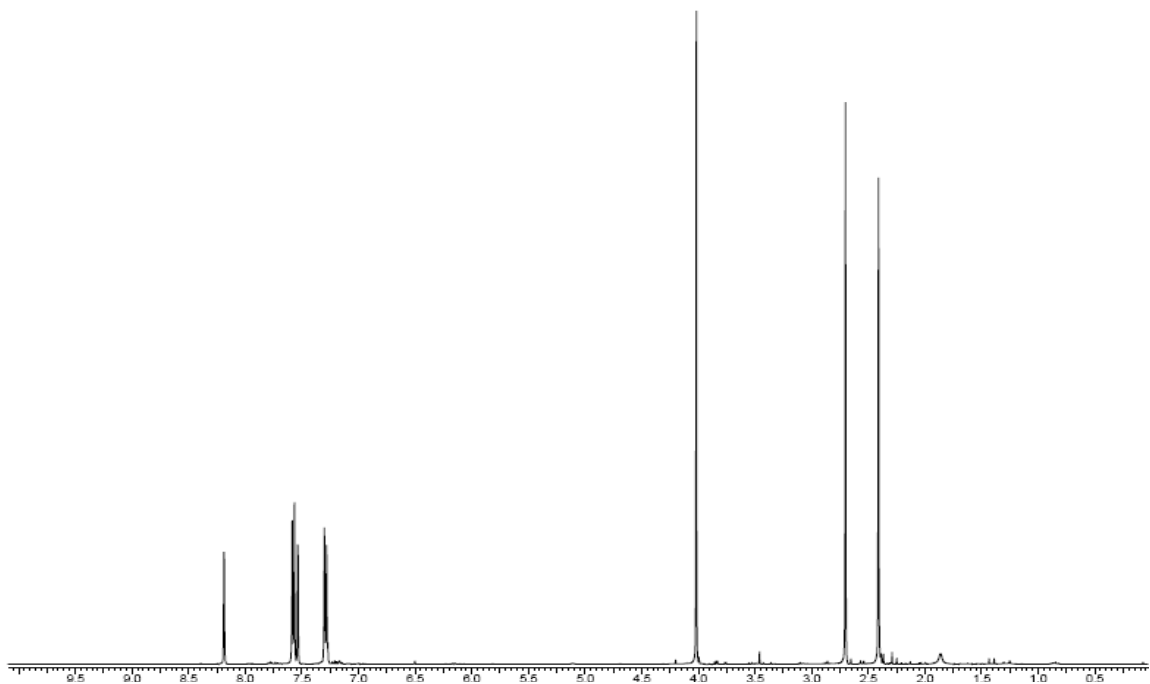
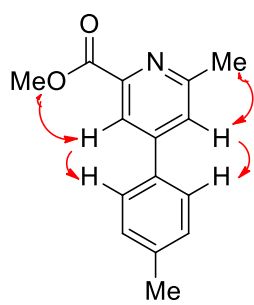
**2-(4-Methoxyphenyl)-6-methyl-4-(*p*-tolyl)pyridine 4k**



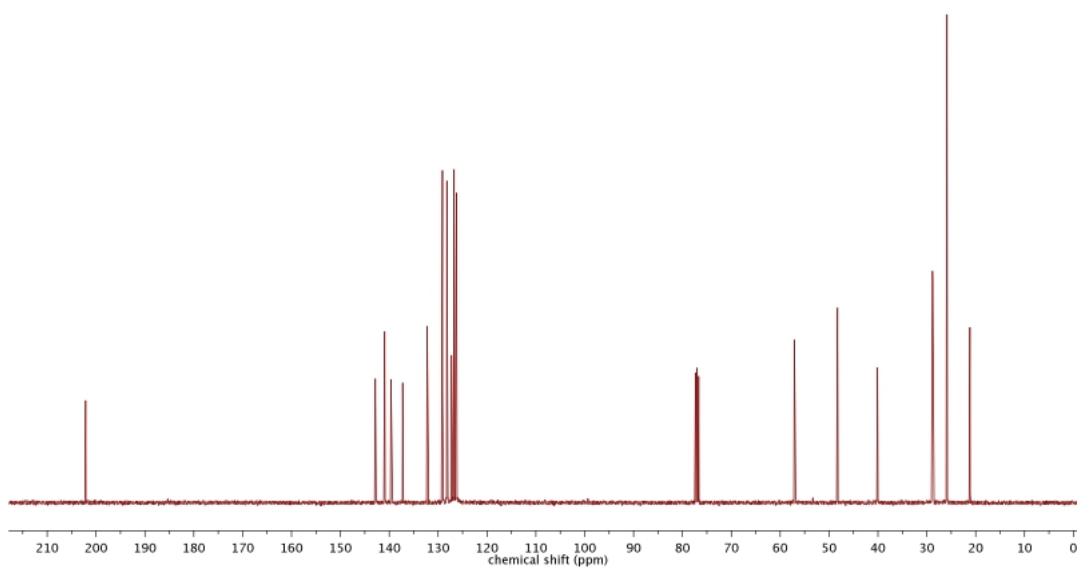
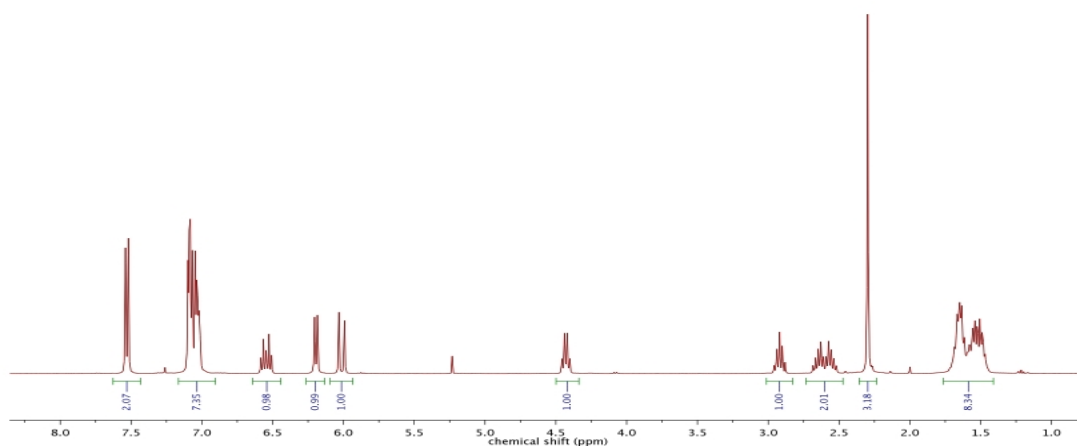
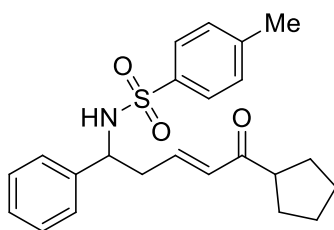
**(E)-Methyl 2-(4-methylphenylsulfonamido)-6-oxohept-4-enoate 3l**



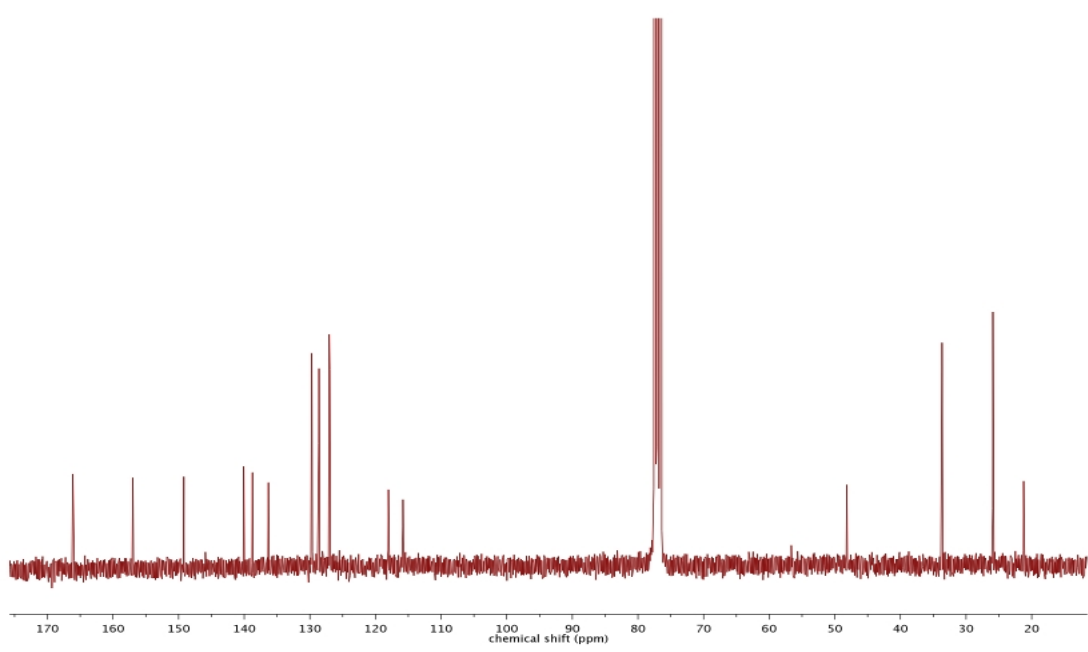
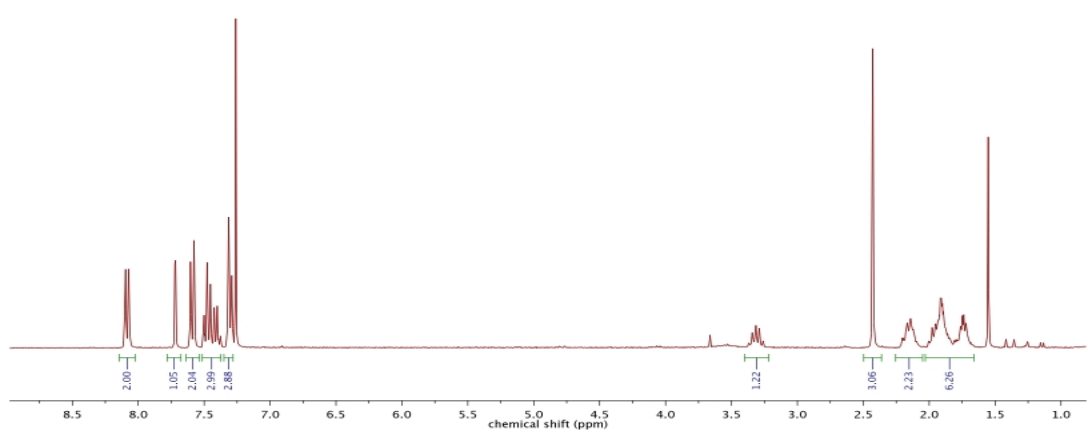
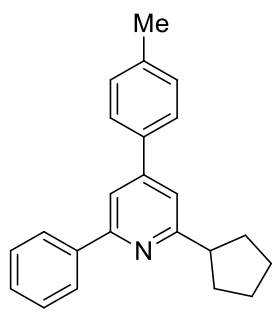
Methyl 6-methyl-4-(*p*-tolyl)picolinate 4l



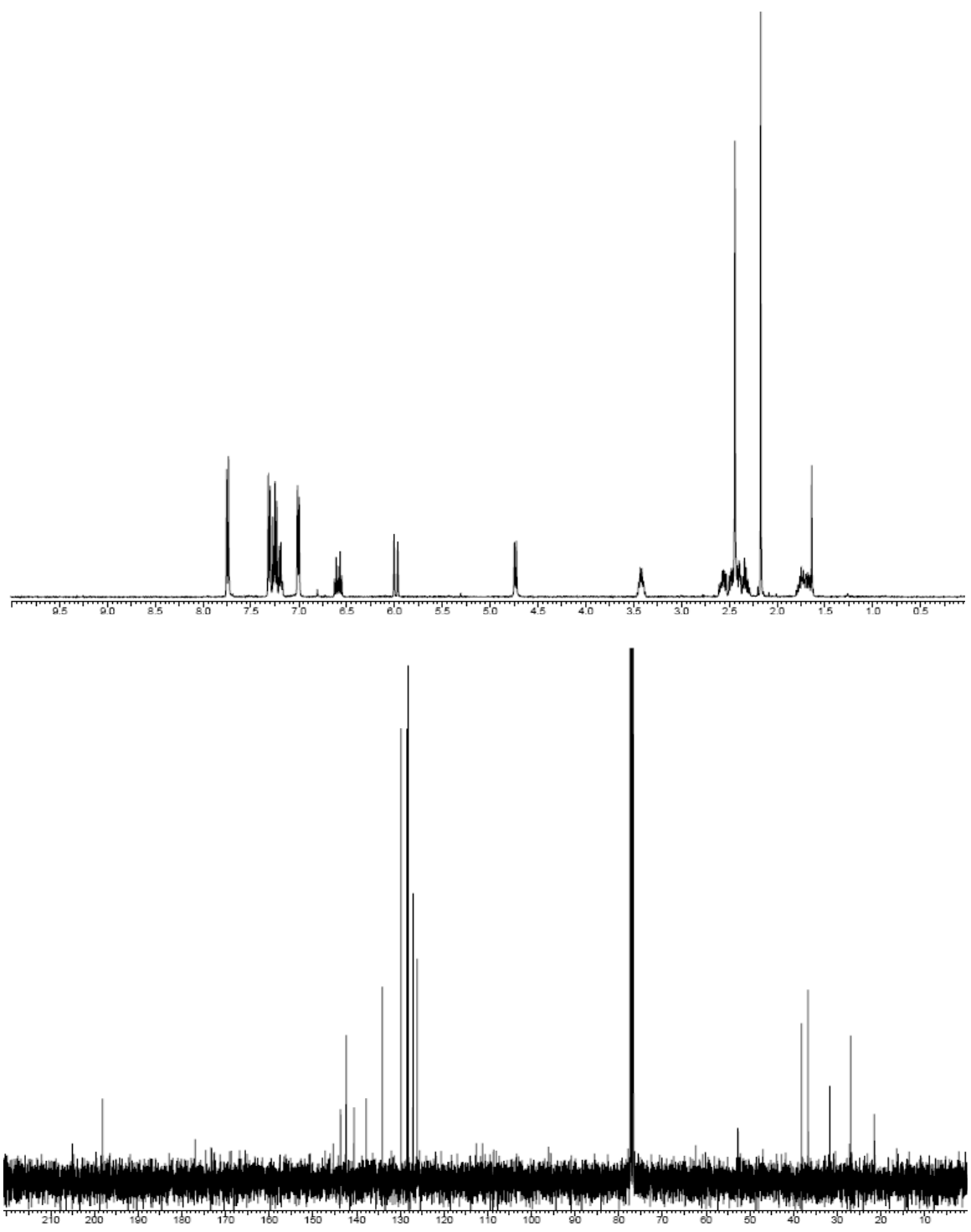
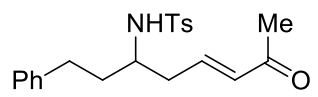
**(E)-N-(5-Cyclopentyl-5-oxo-1-phenylpent-3-en-1-yl)-4-methylbenzenesulfonamide 3m**



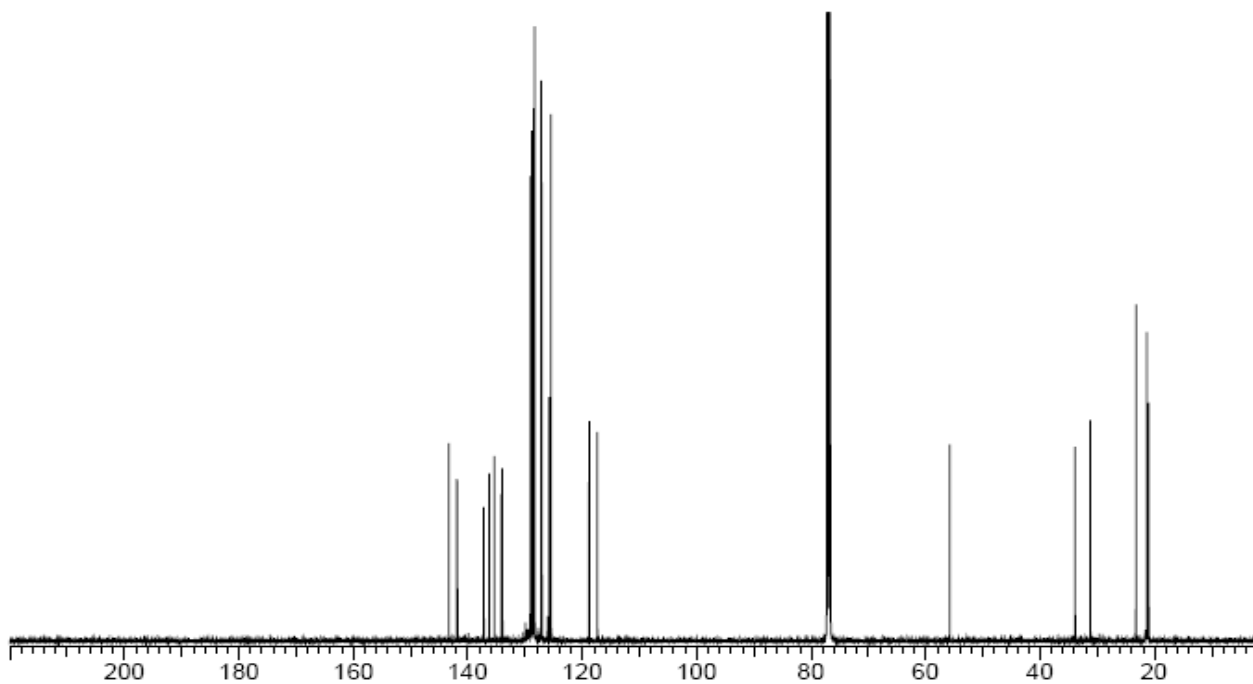
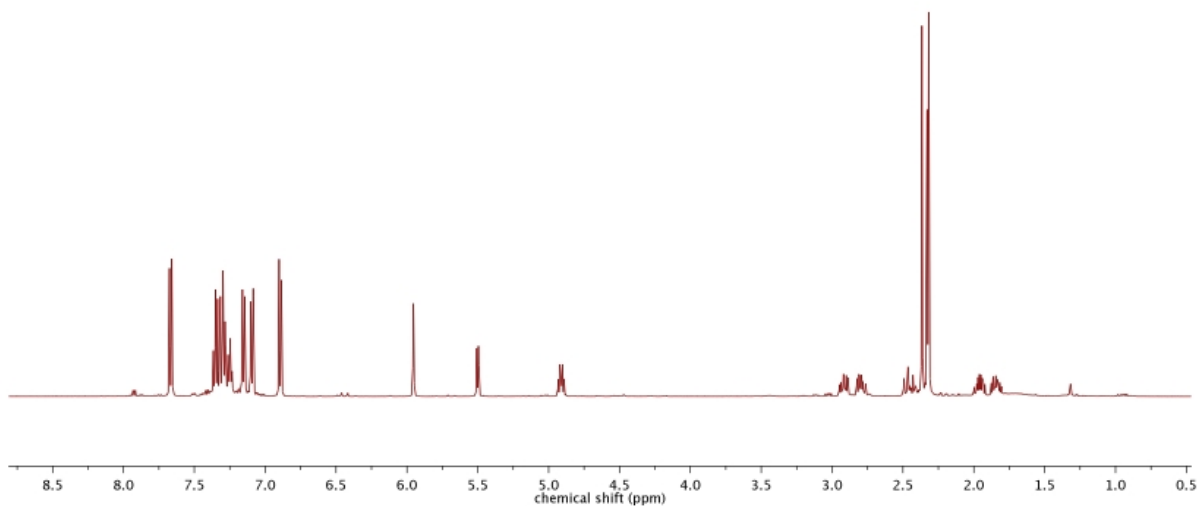
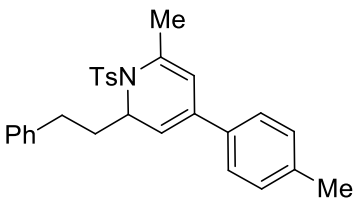
2-Cyclopentyl-6-phenyl-4-(*p*-tolyl)pyridine 4m



**(E)-4-Methyl-N-(7-oxo-1-phenyloct-5-en-3-yl)benzenesulfonamide 3n**

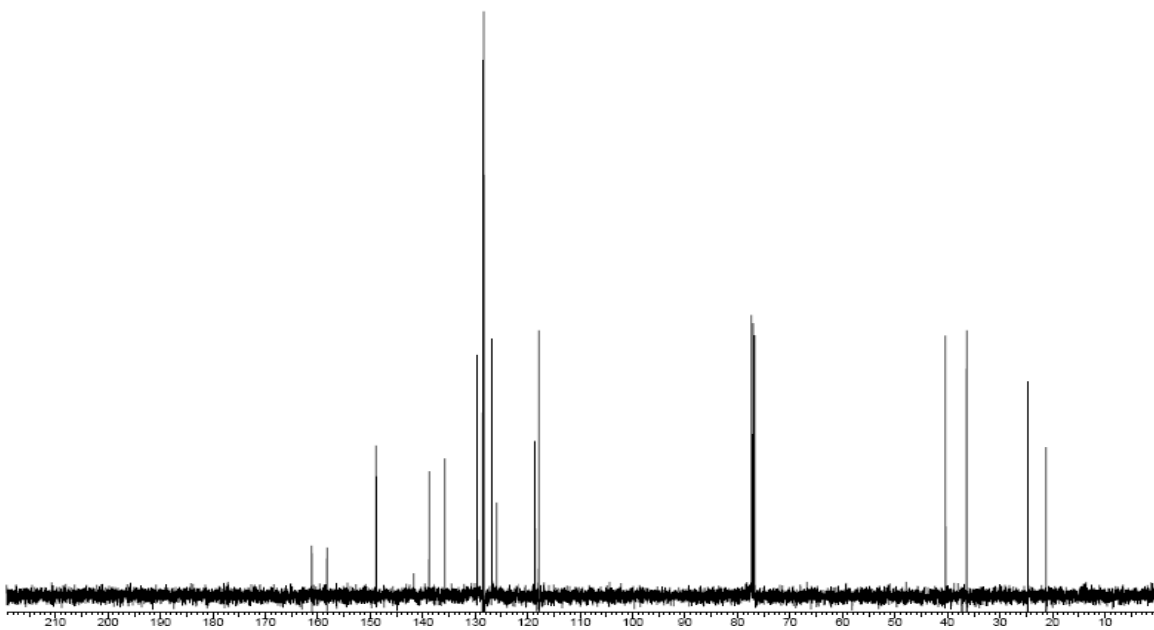
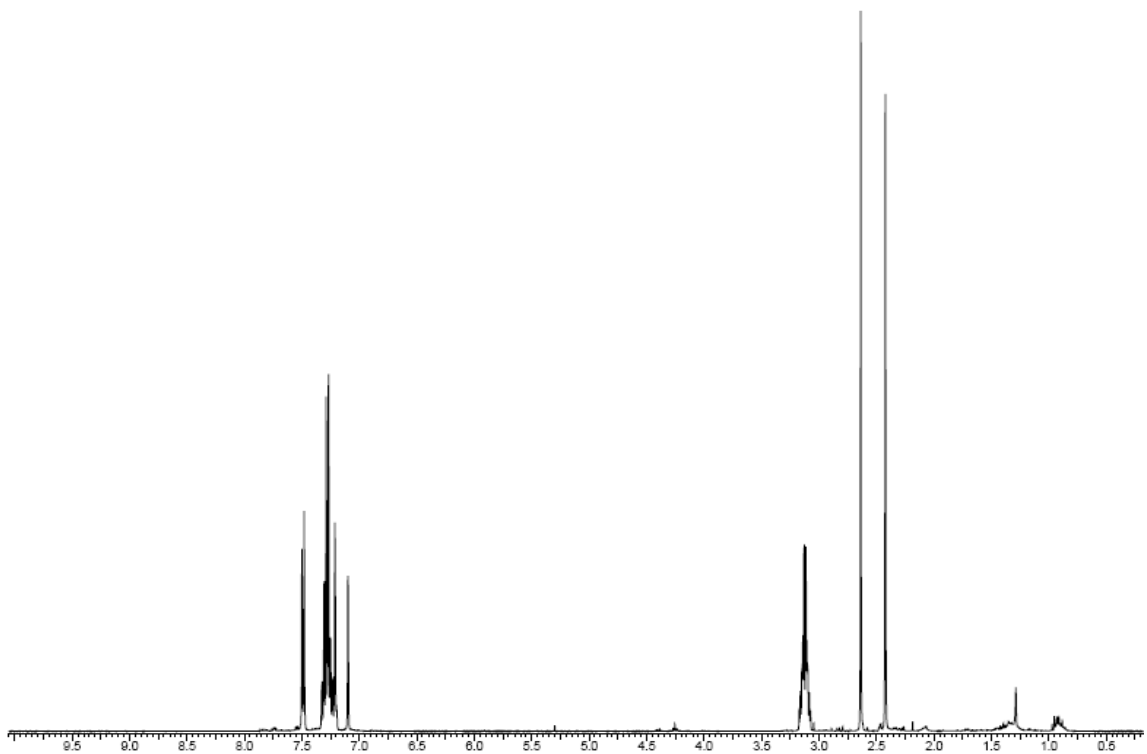
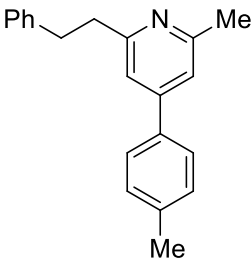


6-Methyl-2-phenethyl-4-(*p*-tolyl)-1-tosyl-1,2-dihydropyridine 6n

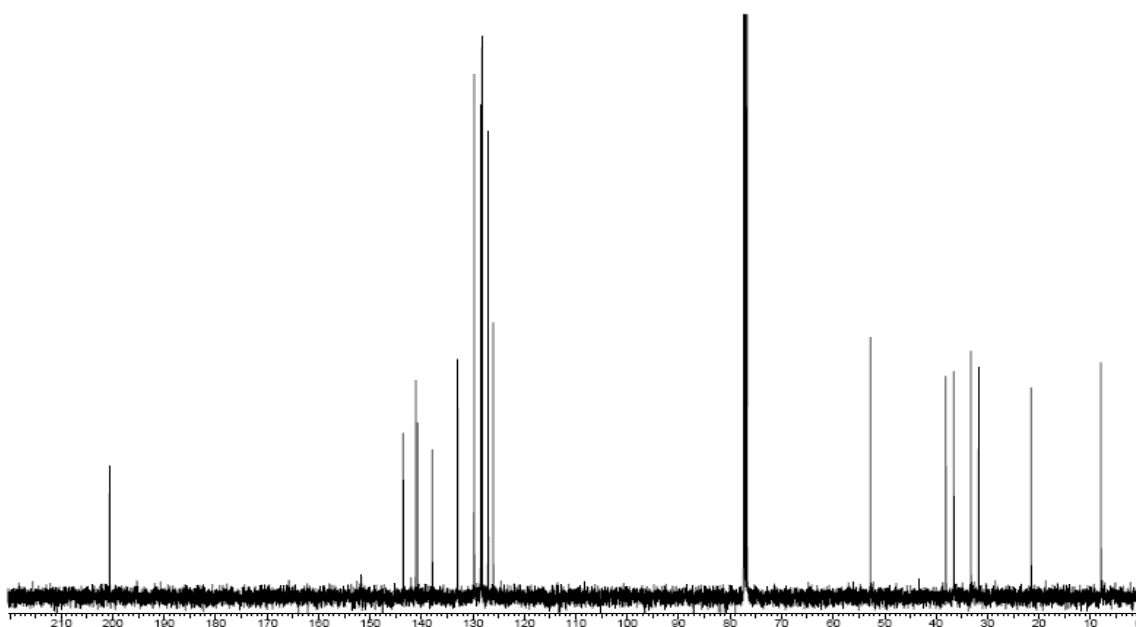
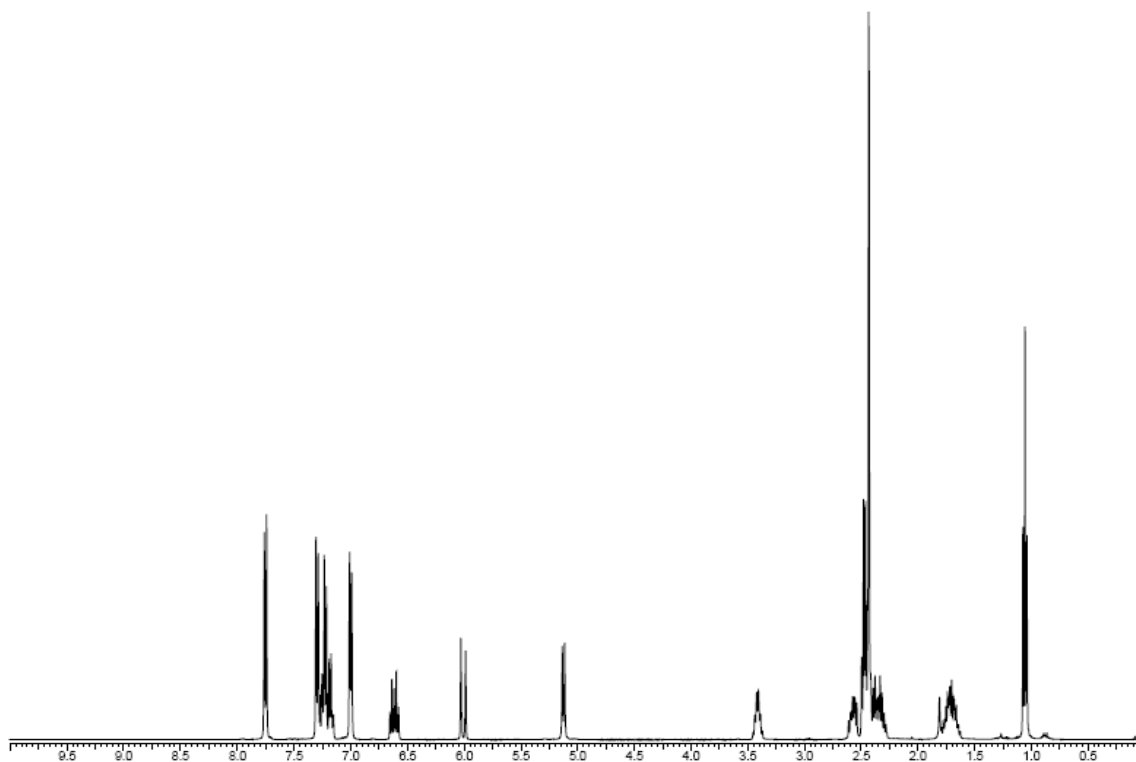
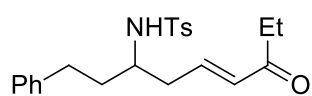




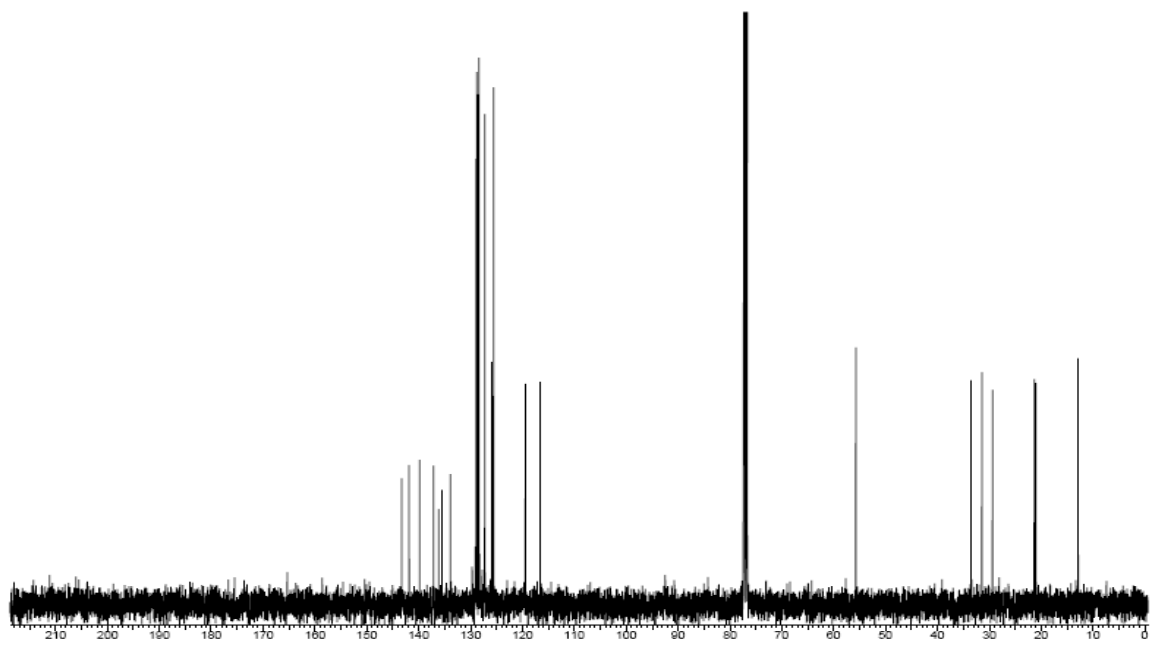
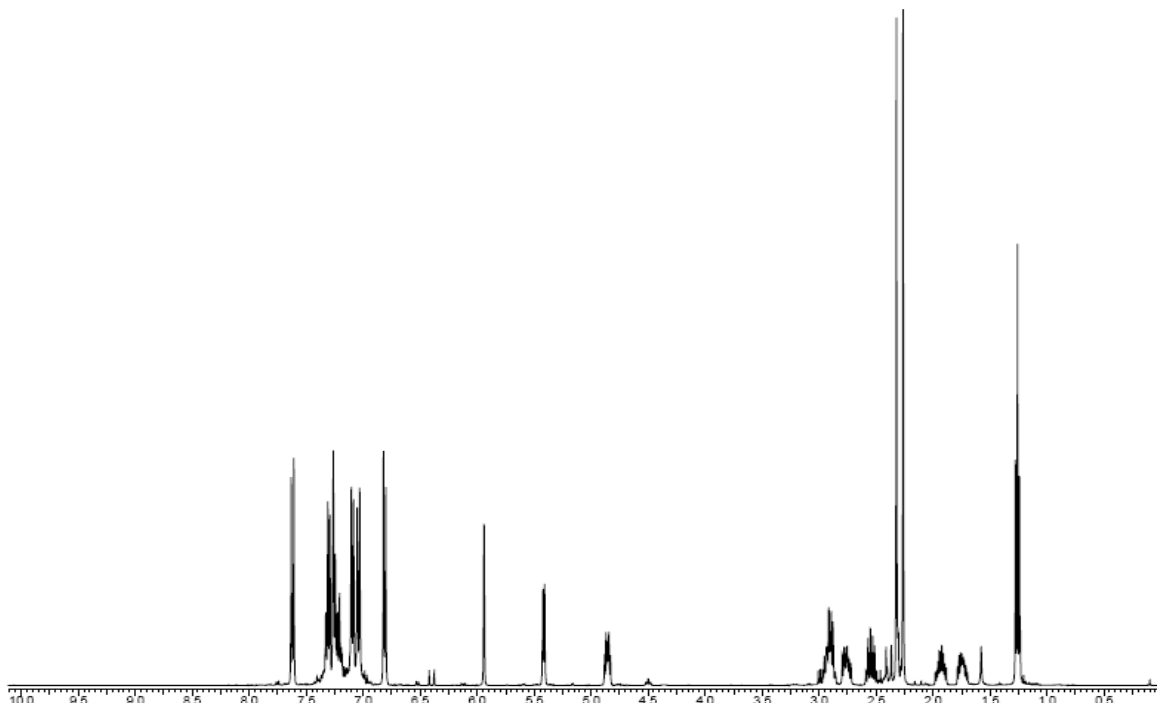
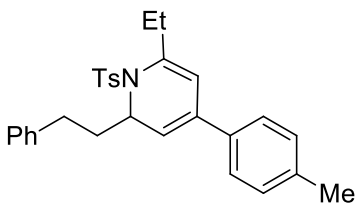
2-Methyl-6-phenethyl-4-(*p*-tolyl)pyridine 4n



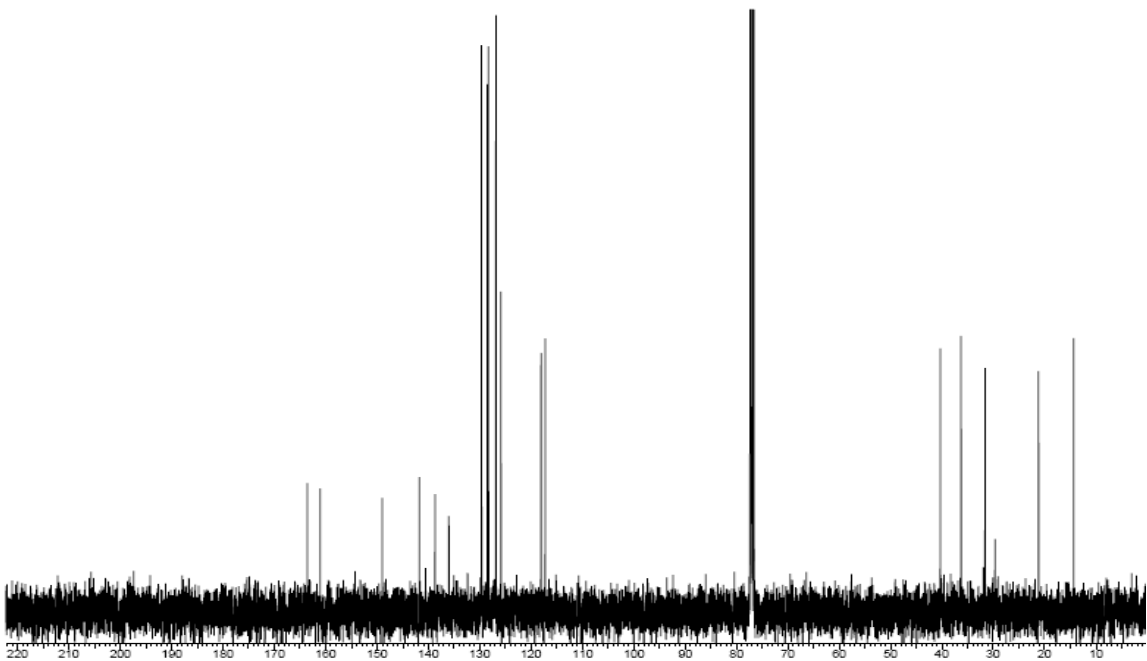
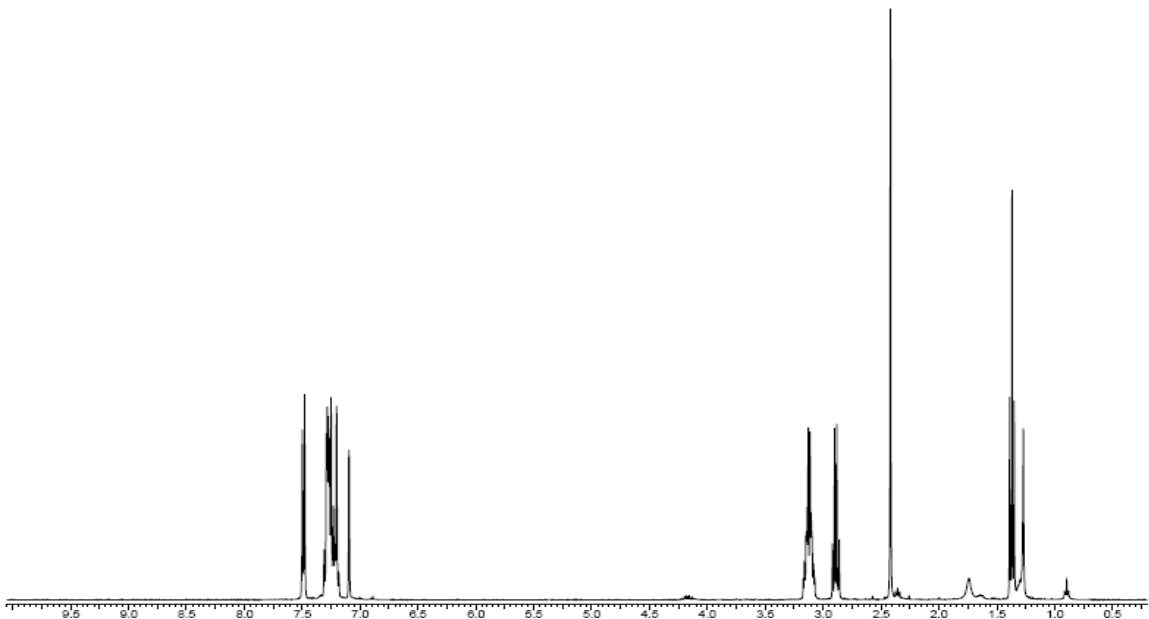
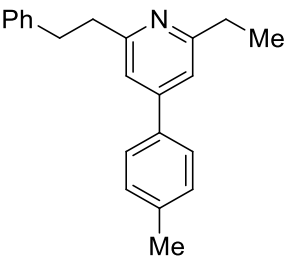
**(E)-4-Methyl-N-(7-oxo-1-phenylnon-5-en-3-yl)benzenesulfonamide 3o**



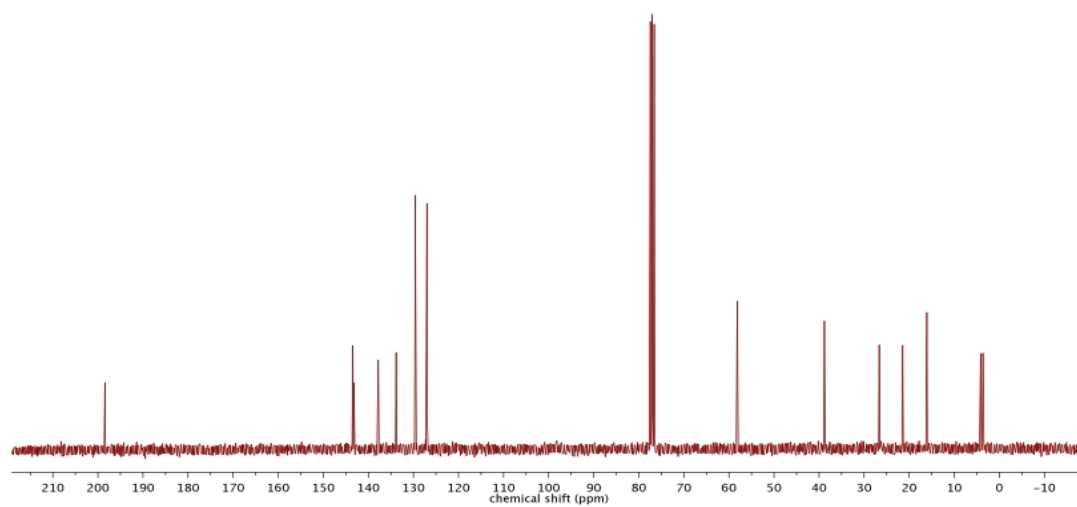
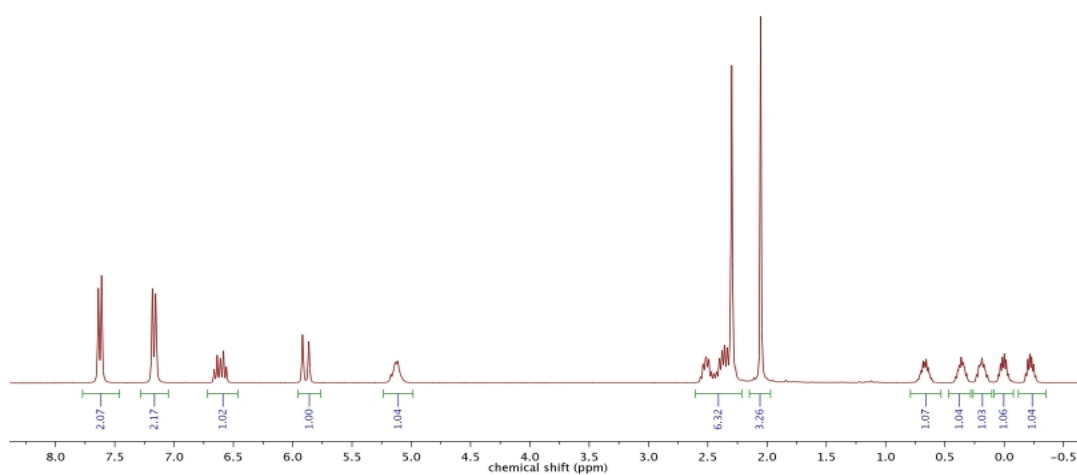
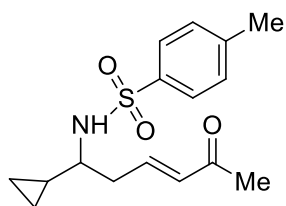
6-Ethyl-2-phenethyl-4-(*p*-tolyl)-1-tosyl-1,2-dihydropyridine 6o



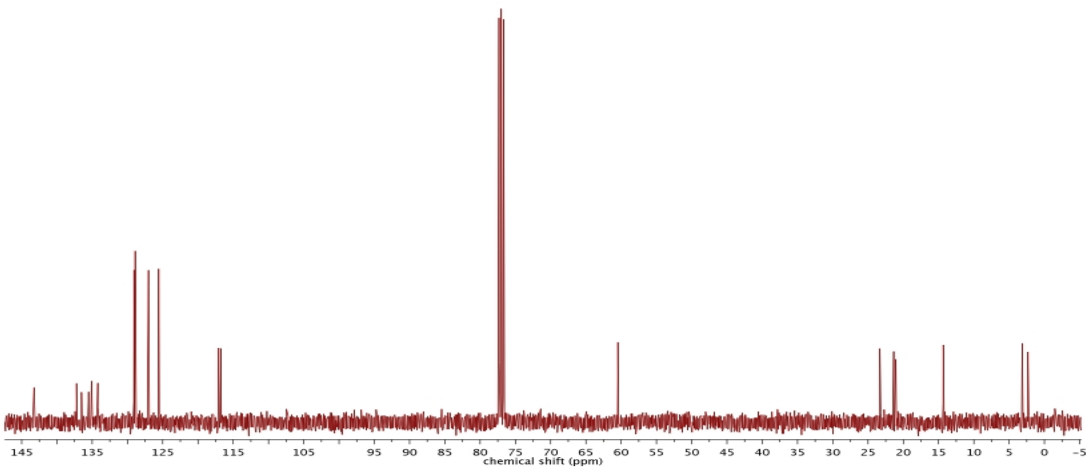
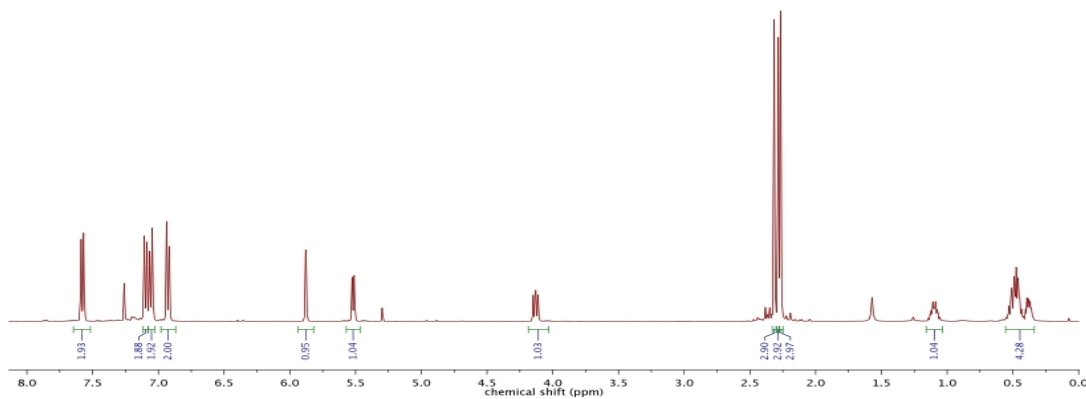
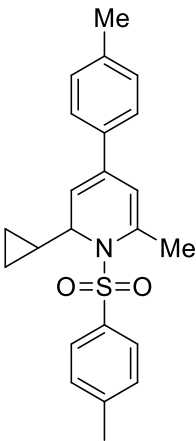
2-Ethyl-6-phenethyl-4-(*p*-tolyl)pyridine 4o



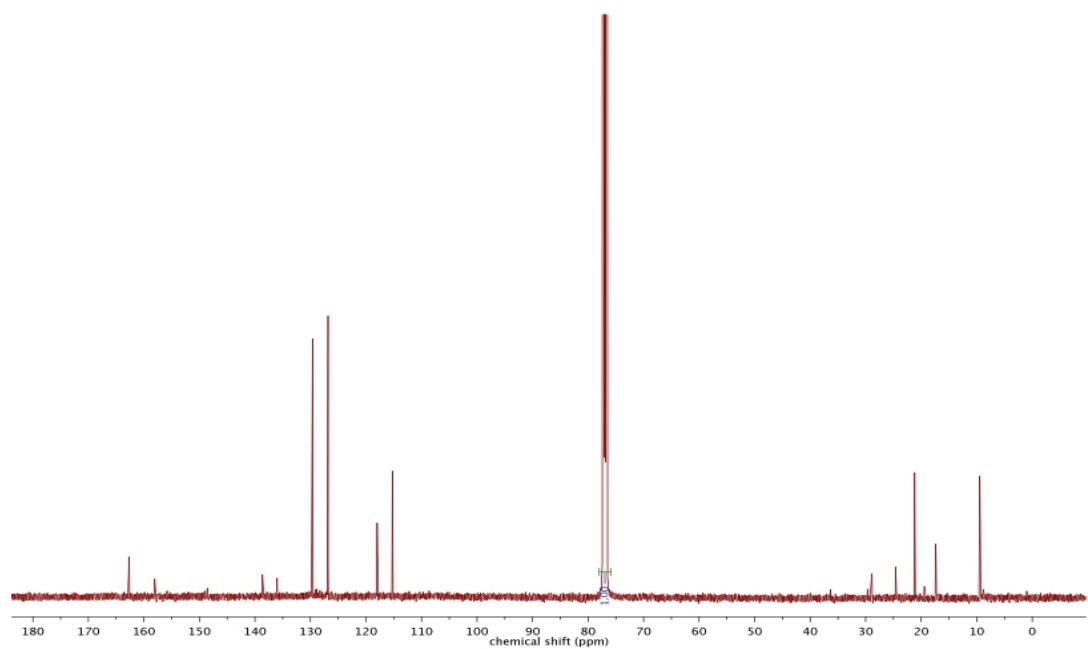
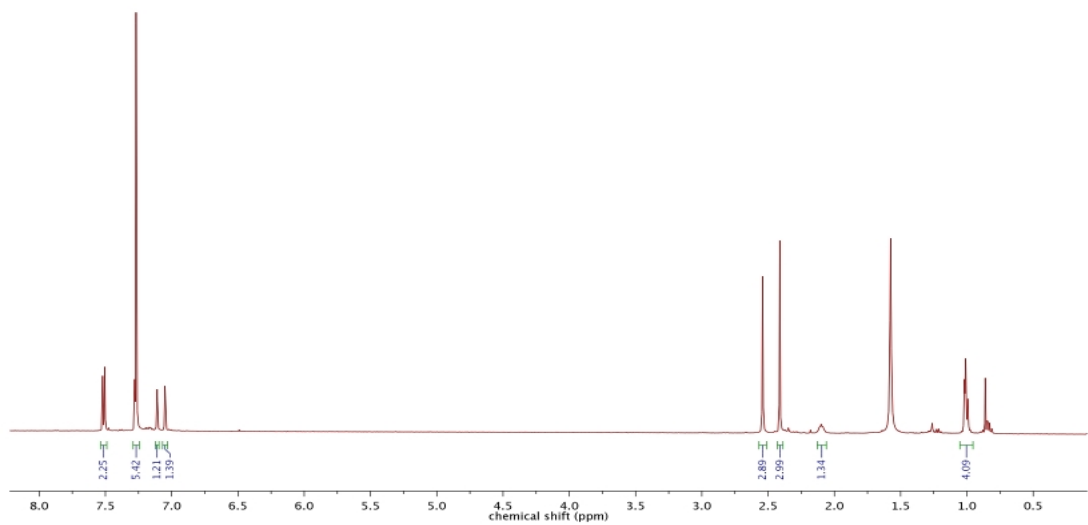
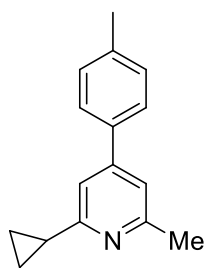
**(*E*)-*N*-(1-Cyclopropyl-5-oxohex-3-en-1-yl)-4-methylbenzenesulfonamide 3p**



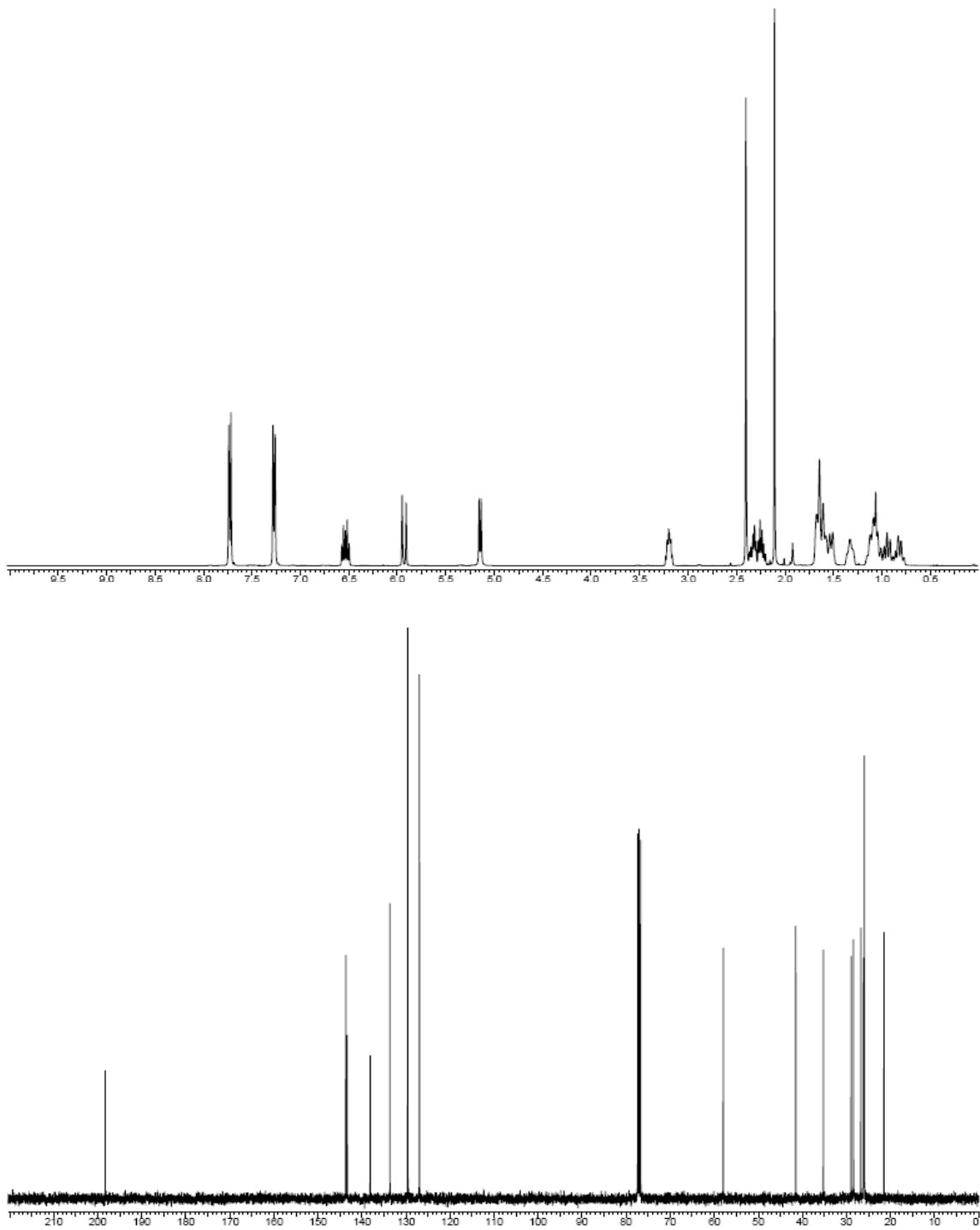
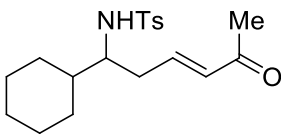
2-Cyclopropyl-6-methyl-4-(*p*-tolyl)-1-tosyl-1,2-dihydropyridine 6p



2-Cyclopropyl-6-methyl-4-(*p*-tolyl)pyridine 4p

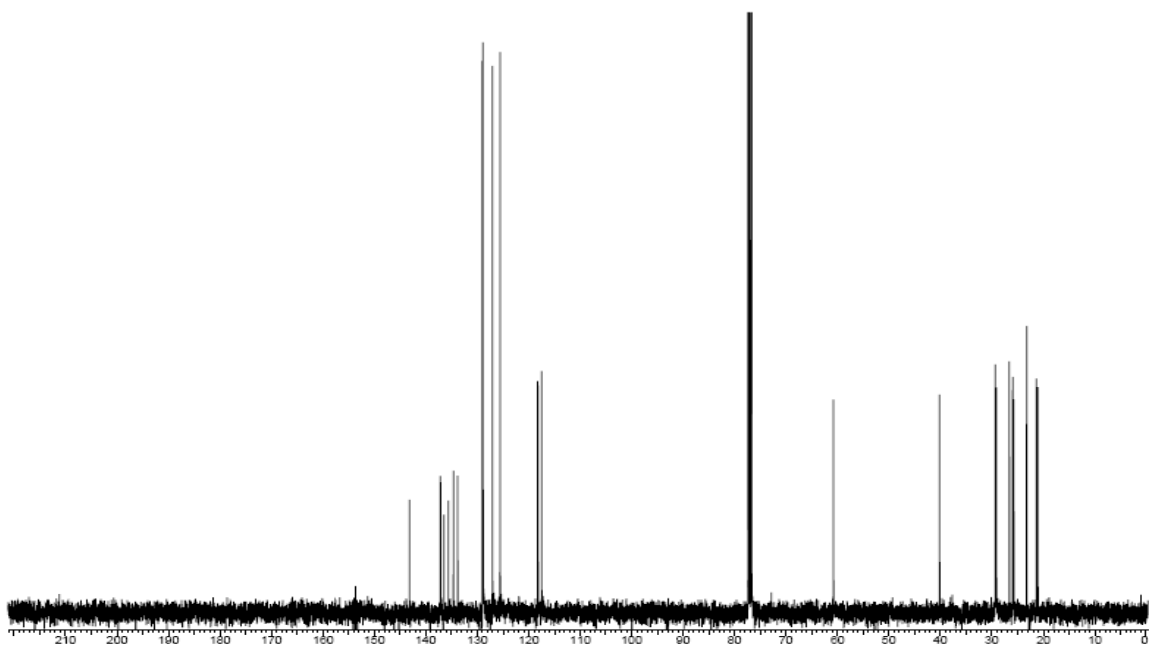
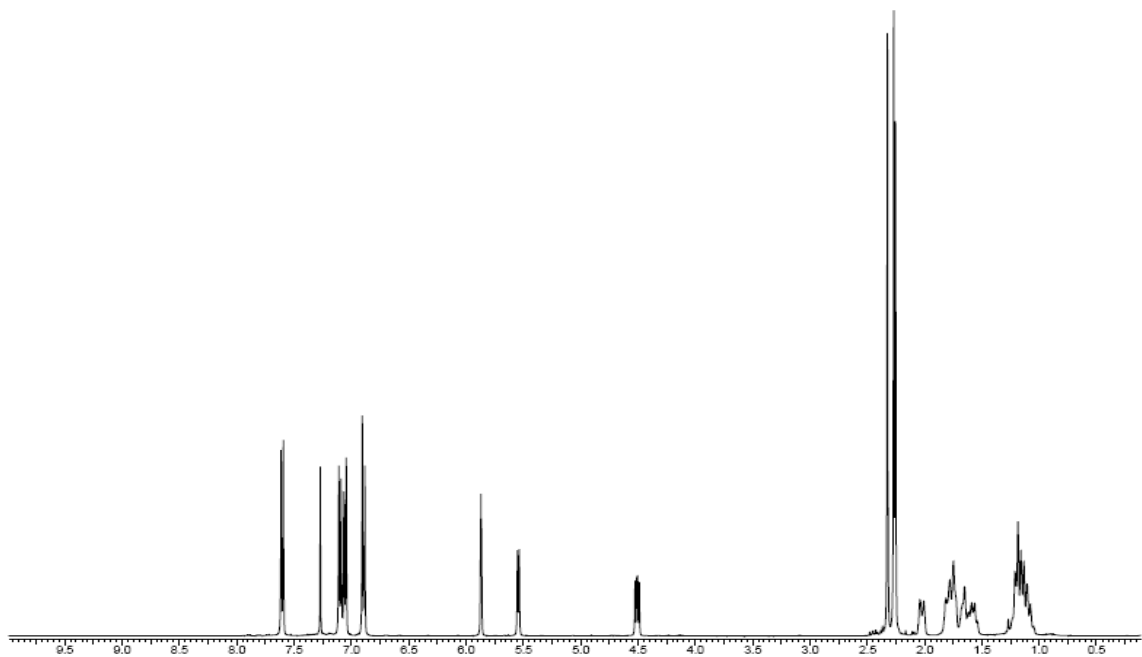
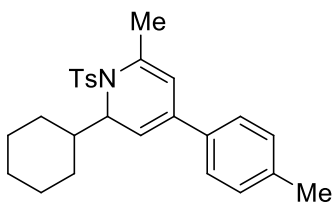


**(E)-N-(1-Cyclohexyl-5-oxohex-3-en-1-yl)-4-methylbenzenesulfonamide 3q**

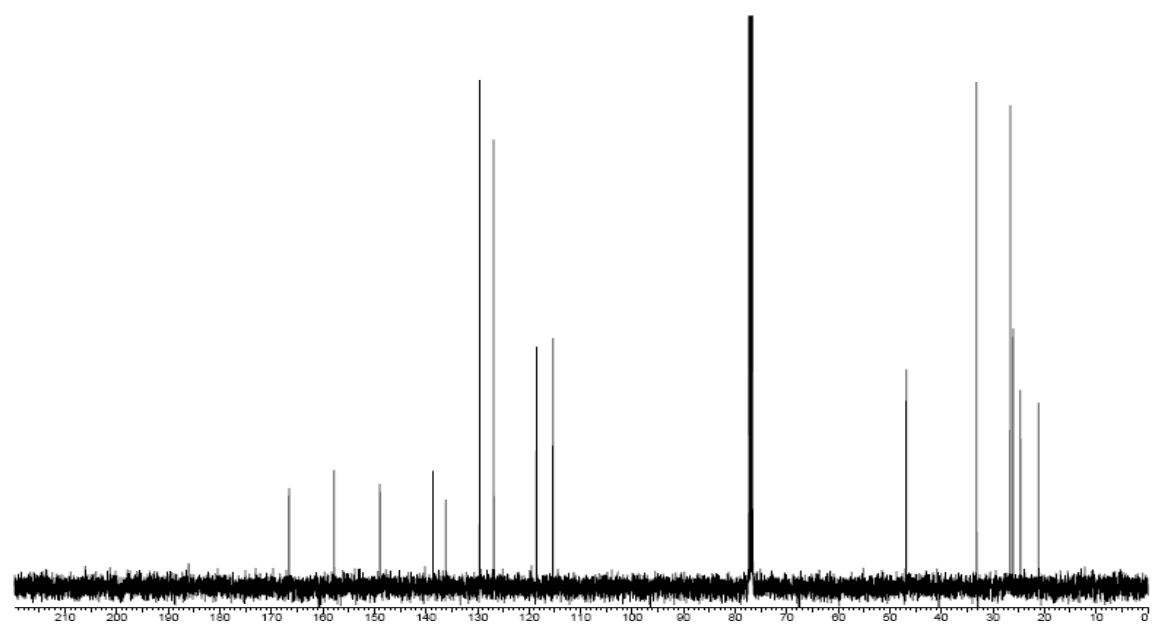
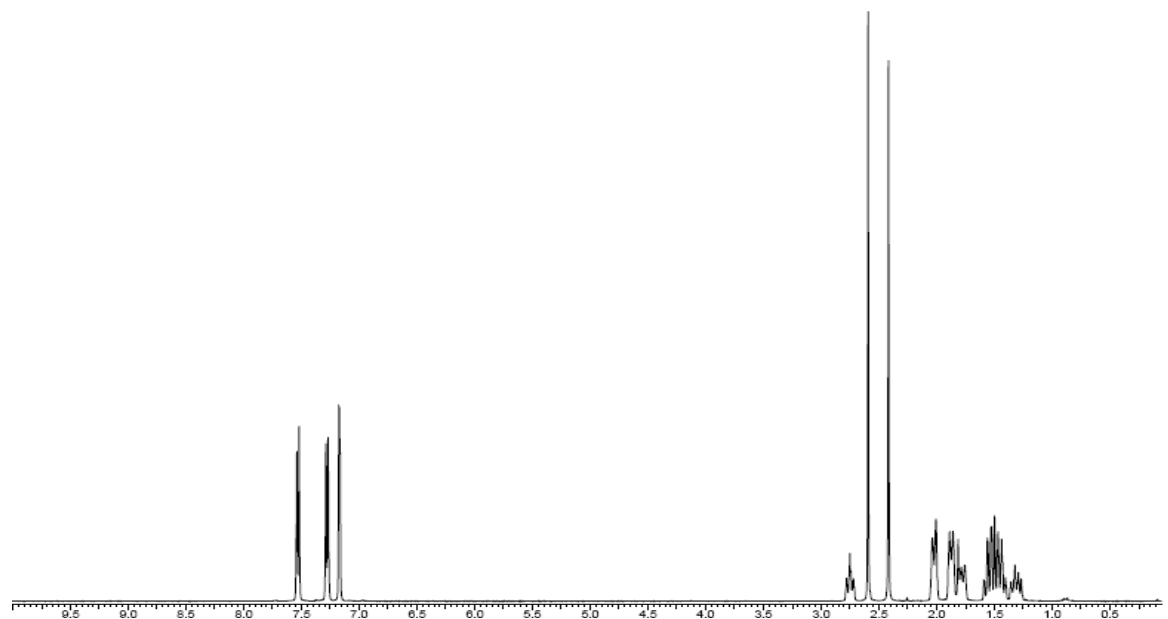
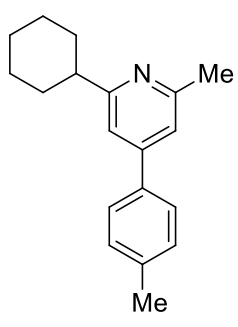




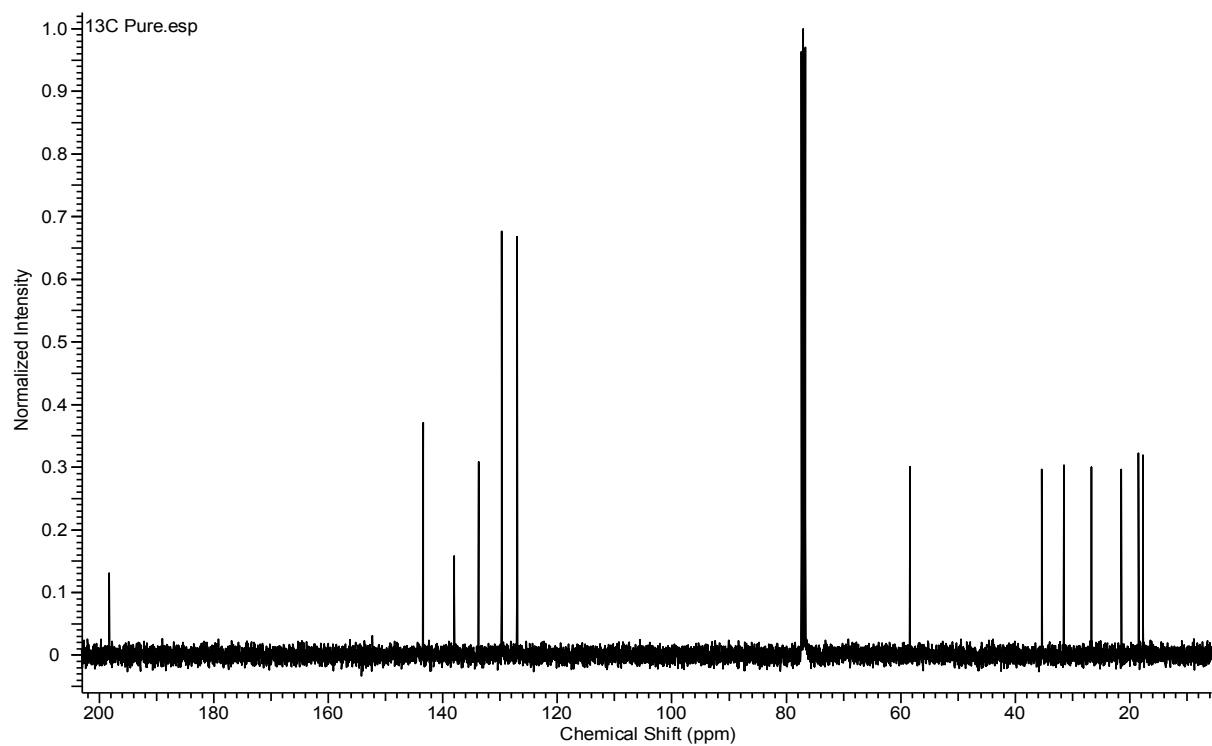
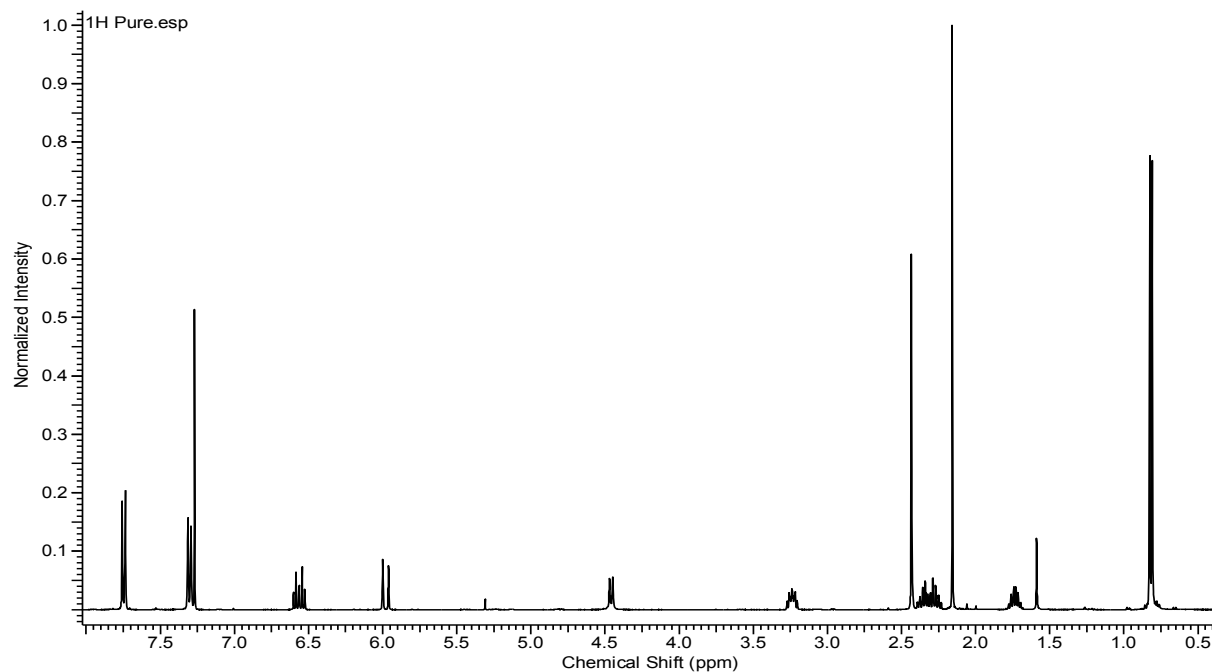
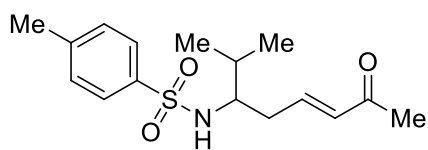
2-Cyclohexyl-6-methyl-4-(*p*-tolyl)-1-tosyl-1,2-dihydropyridine 6q



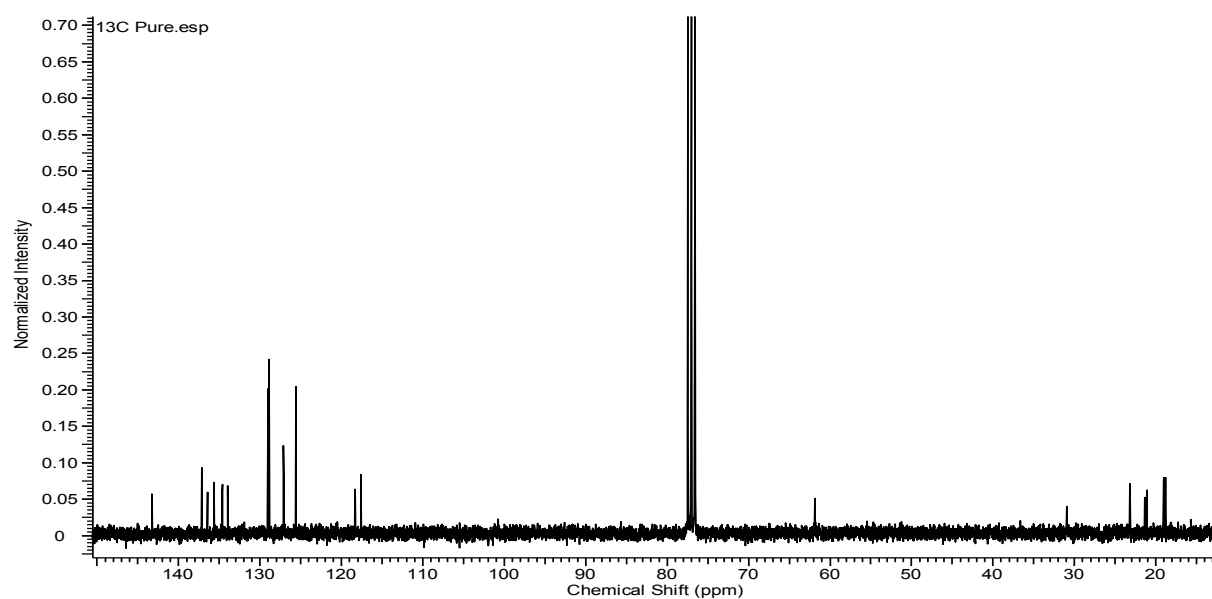
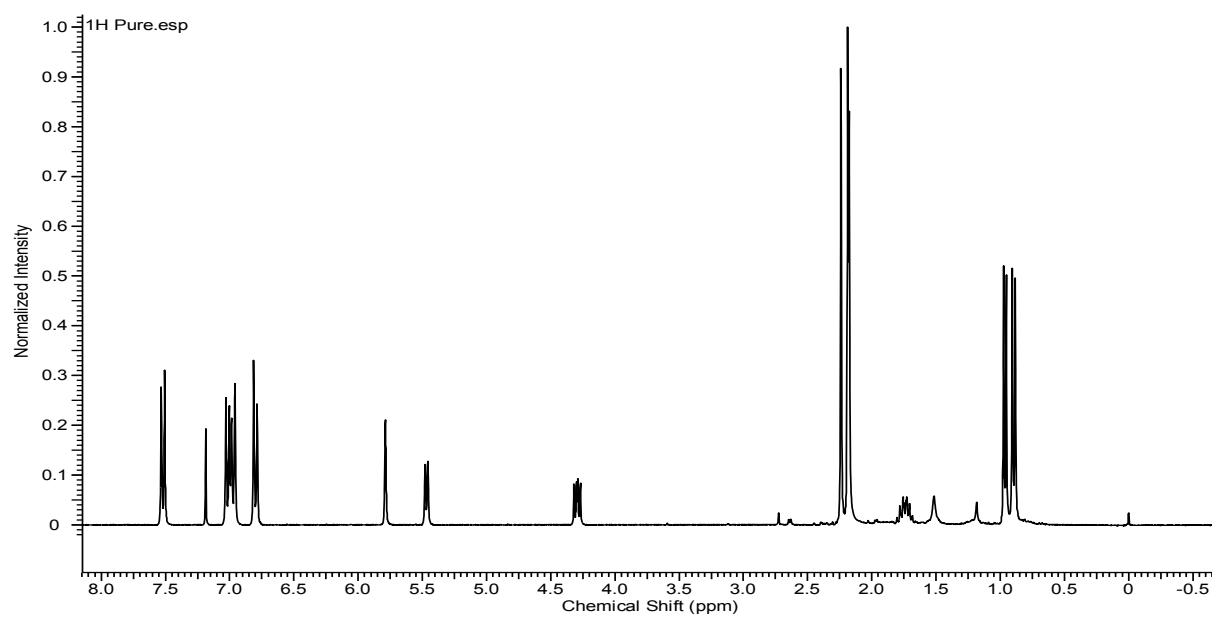
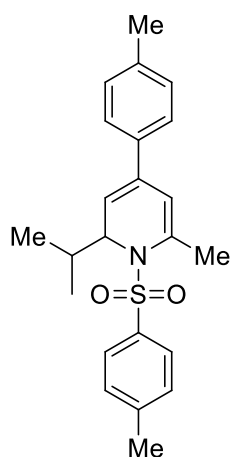
2-Cyclohexyl-6-methyl-4-(*p*-tolyl)pyridine 4q



**(*E*)-4-Methyl-*N*-(2-methyl-7-oxooct-5-en-3-yl)benzenesulfonamide 3r**



**2-Isopropyl-6-methyl-4-(*p*-tolyl)-1-tosyl-1,2-dihydropyridine 6r**



**2-Isopropyl-6-methyl-4-(*p*-tolyl)pyridine 4r**

