

Supporting Information for:

## Ruthenium-Catalyzed Hydrovinylation of *N*-Acetyl Enamines Leading to Amines with a Quaternary Carbon Center

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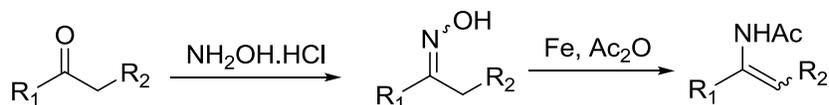
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**General:** All the air or moisture sensitive reactions and manipulations were performed under an nitrogen atmosphere by using standard Schlenk techniques and a Vacuum Atmospheres Drybox (VAC DRI-LAB HE 493). Melting points were measured on a RY-I apparatus and uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV 400 spectrometers or a Varian Mercury Plus 400 spectrometer at 400 MHz ( $^1\text{H}$  NMR) and 100 MHz ( $^{13}\text{C}$  NMR). Chemical shifts were reported in ppm down field from internal  $\text{Me}_4\text{Si}$ . Mass spectra were recorded on IonSpec FT-ICR mass spectrometer with ESI resource. GC analyses were performed using Hewlett Packard Model HP 6890 Series. *N,N*-dimethylformamide and 1,2-dichloroethane were distilled from calcium hydride under nitrogen before use. Toluene and dioxane were distilled under nitrogen from sodium/benzophenone ketyl. Ethylene (99.9%) was purchased from BAPB Gases Industry Company, Ltd., Beijing, China. The *N*-acetyl enamines were prepared from the

corresponding aromatic ketones according to the literature methods, unless otherwise stated.<sup>1</sup> AgX (X = BF<sub>4</sub><sup>-</sup>, OTf<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, PF<sub>6</sub><sup>-</sup> and SbF<sub>6</sub><sup>-</sup>) were purchased from Aldrich Co. and used without further purification. RuHCl(CO)(PCy<sub>3</sub>)<sub>2</sub><sup>2</sup> and NaBARF<sub>3</sub><sup>3</sup> was prepared according to the literature methods.

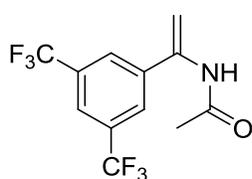
### (A) Preparation of *N*-Acetyl Enamines

The *N*-acetyl enamines were prepared according to the literature procedure.<sup>1</sup>



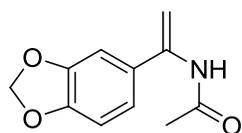
**General procedure:** Acetic anhydride (27.0 g, 264 mmol) and acetic acid (15.9 g, 264 mmol) was added to a solution of ketone oxime (86 mmol) in toluene (250 mL). Fe powder (10.3 g, 185 mmol) was added and the mixture was heated to 75 °C for 5 h. After cooled to room temperature, the reaction mixture was filtered to remove the solid residues which were washed with toluene (2 × 50 mL). The combined filtrate was diluted with toluene (200 mL) and washed with 2 N NaOH (2 × 200 mL). The organic phase was separated, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The obtained residue was chromatographed on a silica gel column eluted with petroleum ether/ethyl acetate (4:1 v/v) to afford the desired enamines as white solids.

#### *N*-Acetyl-1-[3,5-bis(trifluoromethyl)phenyl]-vinylamine (**1l**)



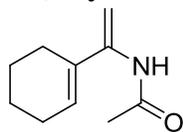
78 % yield, white solid, mp: 134–136 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.07 (s, 3H), 5.18 (s, 1H), 5.69 (s, 1H), 7.42 (brs, 1H), 7.81(m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 24.0, 106.9, 122.1 (m), 123.0 (q, *J* = 271.2 Hz), 126.1, 131.9 (q, *J* = 33.4 Hz), 138.7, 139.9, 169.4. HRMS (ESI) calcd for C<sub>12</sub>H<sub>8</sub>F<sub>6</sub>NO ([M-H]<sup>-</sup>): 296.0516; Found: 296.0522.

#### *N*-Acetyl-1-(3,4-methylenedioxyphenyl)-vinylamine (**1m**)



75 % yield, white solid, mp: 94–96 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 2.12 (s, 3H), 5.01 (s, 1H), 5.74 (s, 1H), 5.98 (s, 2H), 6.78–6.89 (m, 3H), 6.91 (brs, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 23.6, 100.9, 102.2, 106.4, 107.7, 119.5, 132.0, 140.1, 147.3, 147.4, 169.6. HRMS (ESI) calcd for C<sub>11</sub>H<sub>10</sub>NO<sub>3</sub> ([M-H]<sup>-</sup>): 204.0666; Found: 240.0669.

#### *N*-(1-cyclohexenylvinyl)acetamide (**1v**)



70 % yield, white solid, mp: 68–70 °C. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 1.59–1.62 (m, 2H), 1.69–1.71 (m, 2H), 2.05 (s, 3H), 2.16–2.18 (m, 4H) 5.02 (s, 1H), 5.16 (s, 1H), 5.95 (s, 1H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) δ 23.2, 23.3, 23.8, 26.6, 105.2, 126.3, 134.6, 143.0, 172.3. HRMS (ESI) calcd for C<sub>10</sub>H<sub>15</sub>NONa ([M+Na]<sup>+</sup>): 188.1046; Found: 188.1048.

<sup>1</sup> Burk, Mark J.; Casy, Guy; and Johnson, Nicholas B. *J. Org. Chem.* **1998**, *63*, 6084.

<sup>2</sup> Yi, C. S.; Lee, D. W.; Chen, Y. *Organometallics* **1999**, *18*, 2043.

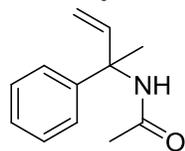
<sup>3</sup> Brookhart, M.; Grant, B.; Jr. Volpe, A. F. *Organometallics*, **1992**, *11*, 3920.

## (B) General Procedure for Hydrovinylation of *N*-Acetyl Enamines



**General procedure:** To a dry Schlenk tube equipped with a stirring bar was added RuHCl(CO)(PCy<sub>3</sub>)<sub>2</sub> (7.3 mg, 0.01 mmol), AgOTf (2.6 mg, 0.01 mmol), enamine (0.2 mmol), 4 Å molecular sieves (100 mg), and degassed anhydrous 1,2-dichloroethane (3 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature for 20 min and a yellow solution was obtained. The nitrogen atmosphere in the Schlenk tube was replaced by ethylene three times and the yellow solution was stirred at 65 °C under 1 atm of ethylene for 0.5–20 h. After removal of molecular sieves by filtration the substrate conversion was determined by GC with a HP-5 column. The product was purified by flash chromatography on a silica gel column with petroleum ether/ethyl acetate, and the yield was determined by measuring the weight of the product.

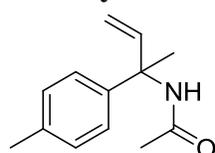
### *N*-Acetyl-1-methyl-1-phenylallylamine (2a)



95 % yield, white solid, mp: 101–103 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.77 (s, 3H), 1.98 (s, 3H), 5.14 (d, *J* = 17.2 Hz, 1H), 5.22 (d, *J* = 10.8 Hz, 1H), 5.92 (brs, 1H), 6.32 (dd, *J* = 17.4, 10.8 Hz, 1H), 7.24–7.26 (m, 1H), 7.31–7.37 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 23.7, 26.3, 59.6, 113.2, 125.3, 126.4, 128.0, 142.0, 144.7, 169.1. HRMS (ESI) calcd for C<sub>12</sub>H<sub>15</sub>NONa ([M+Na]<sup>+</sup>): 212.1046.

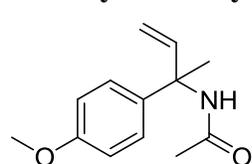
Found: 212.1050.

### *N*-Acetyl-1-methyl-1-(4-methylphenyl)allylamine (2b)



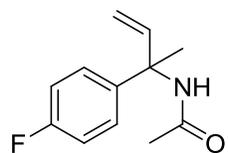
93 % yield, white solid, mp: 77–79 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.63 (s, 3H), 1.82 (s, 3H), 2.22 (s, 3H), 5.02 (d, *J* = 17.6 Hz, 1H), 5.09 (d, *J* = 10.8 Hz, 1H), 6.13 (brs, 1H), 6.23 (dd, *J* = 17.6, 10.8 Hz, 1H), 7.02–7.04 (m, 2H), 7.14–7.16 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 20.8, 23.9, 26.1, 59.6, 113.1, 125.3, 128.9, 136.2, 141.7, 142.2, 169.0. HRMS (ESI) calcd for C<sub>13</sub>H<sub>17</sub>NONa ([M+Na]<sup>+</sup>): 226.1202. Found: 226.1196.

### *N*-Acetyl-1-methyl-1-(4-methoxyphenyl)allylamine (2c)



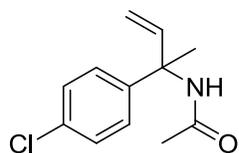
87 % yield, white solid, mp: 83–85 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.76 (s, 3H), 1.96 (s, 3H), 3.78 (s, 3H), 5.10 (d, *J* = 17.6 Hz, 1H), 5.19 (d, *J* = 10.8 Hz, 1H), 5.93 (brs, 1H), 6.29 (dd, *J* = 17.2, 10.8 Hz, 1H), 6.84–6.87 (m, 2H), 7.28–7.30 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 24.2, 26.1, 55.2, 59.5, 113.2, 113.6, 126.7, 136.7, 142.3, 158.3, 168.9. HRMS (ESI) calcd for C<sub>13</sub>H<sub>17</sub>NO<sub>2</sub>Na ([M+Na]<sup>+</sup>): 242.1152. Found: 242.1144.

### *N*-Acetyl-1-methyl-1-(4-fluorophenyl)allylamine (2d)



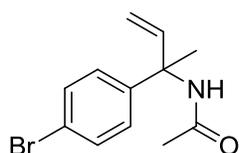
93 % yield, white solid, mp: 108–110 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.59 (s, 3H), 1.82 (s, 3H), 5.02 (d,  $J = 17.2$  Hz, 1H), 5.11 (d,  $J = 10.8$  Hz, 1H), 6.24 (dd,  $J = 17.6, 10.8$  Hz, 1H), 6.32 (brs, 1H), 6.87–6.91 (m, 2H), 7.19–7.23 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  23.8, 26.6, 59.3, 113.5, 114.8 (d,  $J = 21.1$ ), 127.1 (d,  $J = 8.0$ ), 140.4 (d,  $J = 3.1$ ), 141.8, 161.4 (d,  $J = 243.4$ ), 169.1. HRMS (ESI) calcd for  $\text{C}_{12}\text{H}_{14}\text{FNONa}$  ( $[\text{M}+\text{Na}]^+$ ): 230.0952; Found: 230.0958.

#### ***N*-Acetyl-1-methyl-1-(4-chlorophenyl)allylamine (2e)**



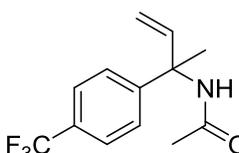
95 % yield, white solid, mp: 107–109 °C,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.62 (s, 3H), 1.87 (s, 3H), 5.04 (d,  $J = 17.6$  Hz, 1H), 5.14 (d,  $J = 10.4$  Hz, 1H), 6.02 (brs, 1H), 6.23 (dd,  $J = 17.6, 10.8$  Hz, 1H), 7.19 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  24.0, 26.5, 59.4, 113.9, 127.0, 128.3, 132.5, 141.7, 143.1, 169.0. HRMS (ESI) calcd for  $\text{C}_{12}\text{H}_{14}\text{ClNONa}$  ( $[\text{M}+\text{Na}]^+$ ): 246.0656. Found: 246.0650.

#### ***N*-Acetyl-1-methyl-1-(4-bromophenyl)allylamine (2f)**



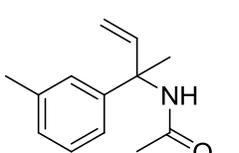
95 % yield, white solid, mp: 114–116 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.56 (s, 3H), 1.82 (s, 3H), 5.02 (d,  $J = 17.2$  Hz, 1H), 5.11 (d,  $J = 10.8$  Hz, 1H), 6.22 (dd,  $J = 17.4, 10.8$  Hz, 1H), 6.31 (brs, 1H), 7.11–7.13 (m, 2H), 7.32–7.34 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  23.8, 26.5, 59.4, 113.8, 120.4, 127.3, 131.1, 141.5, 143.8, 169.1. HRMS (ESI) calcd for  $\text{C}_{12}\text{H}_{14}\text{BrNONa}$  ( $[\text{M}+\text{Na}]^+$ ): 290.0151. Found: 290.0149.

#### ***N*-Acetyl-1-methyl-1-(4-trifluoromethylphenyl)allylamine (2g)**



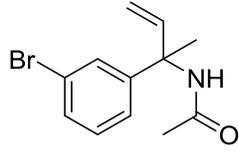
98 % yield, white solid, mp: 82–84 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.55 (s, 3H), 1.81 (s, 3H), 5.04 (d,  $J = 17.2$  Hz, 1H), 5.13 (d,  $J = 10.8$  Hz, 1H), 6.26 (dd,  $J = 17.4, 10.6$  Hz, 1H), 6.41 (brs, 1H), 7.33–7.35 (m, 2H), 7.45–7.47 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  23.6, 26.6, 59.5, 114.2, 124.1 (q,  $J = 270.2$  Hz), 125.1 (q,  $J = 3.6$  Hz), 125.8, 128.6 (q,  $J = 32.1$  Hz), 141.2, 148.8, 169.3. HRMS (ESI) calcd for  $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NONa}$  ( $[\text{M}+\text{Na}]^+$ ): 280.0920. Found: 280.0914.

#### ***N*-Acetyl-1-methyl-1-(3-methylphenyl)allylamine (2h)**



92 % yield, white solid, mp 66–68 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.60 (s, 3H), 1.79 (s, 3H), 2.24 (s, 3H), 5.02 (d,  $J = 17.2$  Hz, 1H), 5.09 (d,  $J = 10.8$  Hz, 1H), 6.24 (dd,  $J = 17.4, 10.6$  Hz, 1H), 6.32 (brs, 1H), 6.92–6.94 (m, 1H), 7.05–7.12 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  21.4, 23.8, 26.2, 59.6, 113.0, 122.3, 126.0, 127.3, 128.0, 137.5, 142.0, 144.7, 169.0. HRMS (ESI) calcd for  $\text{C}_{13}\text{H}_{17}\text{NONa}$  ( $[\text{M}+\text{Na}]^+$ ): 226.1202. Found: 226.1195.

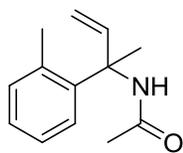
#### ***N*-Acetyl-1-methyl-1-(3-bromophenyl)allylamine (2i)**



94 % yield, white solid, mp 95–97 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.66 (s, 3H), 1.92 (s, 3H), 5.13 (d,  $J = 17.6$  Hz, 1H), 5.22 (d,  $J = 10.8$  Hz, 1H), 6.30 (brs, 1H), 6.31 (dd,  $J = 17.6, 10.8$  Hz, 1H), 7.15–7.19 (m, 1H), 7.25–7.27 (m, 1H), 7.33–7.35 (m, 1H), 7.45–7.46 (m, 1H).  $^{13}\text{C}$  NMR (100

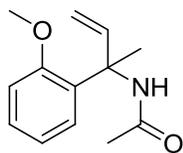
MHz, CDCl<sub>3</sub>) δ 23.8, 26.5, 59.4, 114.0, 122.4, 124.1, 128.7, 129.7, 129.8, 141.4, 147.1, 169.1. HRMS (ESI) calcd for C<sub>12</sub>H<sub>14</sub>BrNONa ([M+Na]<sup>+</sup>): 290.0151. Found: 290.0147.

### ***N*-Acetyl-1-methyl-1-(2-methylphenyl)allylamine (2j)**



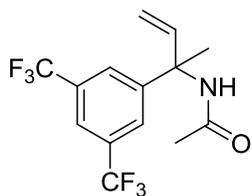
40 % yield, white solid, mp: 103–105 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.86 (s, 3H), 1.92 (s, 3H), 2.37(s, 3H), 4.92 (d, *J* = 17.6 Hz, 1H), 5.12 (d, *J* = 10.4 Hz, 1H), 6.02 (brs, 1H), 6.47 (dd, *J* = 17.6, 10.8 Hz, 1H), 7.12–7.19 (m, 3H), 7.41–7.44 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 22.1, 23.8, 26.0, 60.6, 112.9, 125.7, 126.7, 127.1, 132.4, 135.4, 141.7, 142.7, 168.7. HRMS (ESI) calcd for C<sub>13</sub>H<sub>17</sub>NONa ([M+Na]<sup>+</sup>): 226.1202. Found: 226.1194.

### ***N*-Acetyl-1-methyl-1-(2-methoxyphenyl)allylamine (2k)**



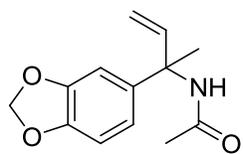
91 % yield, white solid, mp: 94–96 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.79 (s, 3H), 1.85 (s, 3H), 3.74 (s, 3H), 4.98 (d, *J* = 17.2 Hz, 1H), 5.06 (d, *J* = 10.4 Hz, 1H), 6.23 (brs, 1H), 6.29 (dd, *J* = 17.4, 10.6 Hz, 1H), 6.81–6.87 (m, 2H), 7.14–7.18 (m, 1H), 7.27–7.29 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 24.2, 24.3, 55.2, 59.3, 111.8, 112.2, 120.5, 127.6, 128.5, 131.9, 142.9, 156.8, 169.0. HRMS (ESI) calcd for C<sub>13</sub>H<sub>17</sub>NO<sub>2</sub>Na ([M+Na]<sup>+</sup>): 242.1152. Found: 242.1144.

### ***N*-Acetyl-1-methyl-1-[3,5-bis(trifluoromethyl)phenyl]allylamine (2l)**



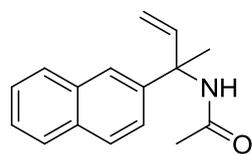
99 % yield, white solid, mp: 120–122 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.65 (s, 3H), 1.92 (s, 3H), 5.17 (d, *J* = 17.6 Hz, 1H), 5.29 (d, *J* = 10.8 Hz, 1H), 6.35 (dd, *J* = 17.4, 10.6 Hz, 1H), 6.44 (brs, 1H), 7.72–7.75 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 23.5, 26.7, 59.3, 115.2, 120.7 (m), 123.4 (q, *J* = 271.0 Hz), 125.8, 131.4(q, *J* = 32.9 Hz), 140.3, 147.6, 169.3. HRMS (ESI) calcd for C<sub>14</sub>H<sub>12</sub>F<sub>6</sub>NO ([M-H]<sup>-</sup>): 324.0829; Found 324.0834.

### ***N*-Acetyl-1-methyl-1-(3,4-methylenedioxyphenyl)allylamine (2m)**



89 % yield, white solid, mp: 84–86 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.69 (s, 3H), 1.94 (s, 3H), 5.10 (d, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 5.91 (s, 1H), 6.09 (brs, 1H), 6.28 (dd, *J* = 17.4, 10.6 Hz, 1H), 6.72–6.74 (m, 1H), 6.80–6.84 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 24.1, 26.4, 59.7, 100.9, 106.4, 107.8, 113.3, 118.6, 138.8, 142.0, 146.2, 147.5, 169.0. HRMS (ESI) calcd for C<sub>13</sub>H<sub>15</sub>NO<sub>3</sub>Na ([M+Na]<sup>+</sup>): 232.0979. Found: 232.0972.

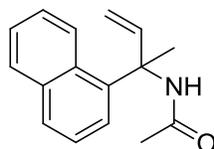
### ***N*-Acetyl-1-methyl-1-(2-naphthalenyl)allylamine (2n)**



96 % yield, white solid, mp: 137–139 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.79 (s, 3H), 1.91 (s, 3H), 5.16 (d, *J* = 17.6 Hz, 1H), 5.25 (d, *J* = 10.8 Hz, 1H), 6.44 (dd, *J* = 17.2, 10.8 Hz, 1H), 6.45 (brs, 1H), 7.47–7.48 (m, 3H), 7.80–7.81(m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 23.8, 26.2, 59.8, 113.5, 123.9, 124.0, 125.6, 125.8, 127.3, 127.9, 128.0, 132.2, 133.0, 141.9, 142.1, 169.1. HRMS (ESI) calcd for C<sub>16</sub>H<sub>17</sub>NONa ([M+Na]<sup>+</sup>): 262.1202; Found: 262.1195.

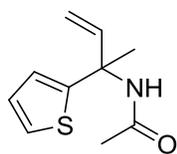
### ***N*-Acetyl-1-methyl-1-(1-naphthalenyl)allylamine (2o)**

74 % yield, white solid, mp: 138–140 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.88 (s, 3H), 2.06 (s,



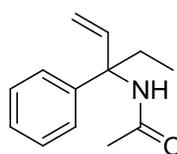
3H), 4.94 (d,  $J = 17.6$  Hz, 1H), 5.17 (d,  $J = 10.4$  Hz, 1H), 6.31 (brs, 1H), 6.77 (dd,  $J = 17.6, 10.4$  Hz, 1H), 7.43–7.48 (m, 3H), 7.65–7.67 (m, 1H), 7.79–7.81 (m, 1H), 7.86–7.89 (m, 1H), 8.29–8.31 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  24.0, 26.4, 61.0, 113.6, 124.8, 124.9, 125.0, 125.1, 126.4, 128.8, 129.3, 130.1, 134.9, 139.4, 143.0, 169.0. HRMS (ESI) calcd for  $\text{C}_{16}\text{H}_{17}\text{NONa}$  ( $[\text{M}+\text{Na}]^+$ ): 262.1202; Found: 262.1195.

### ***N*-(2-(thiophen-2-yl)but-3-en-2-yl)acetamide (2p)**



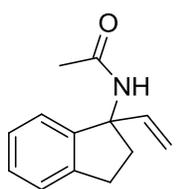
68 % yield, yellow oil, solidified to a light yellow solid after standing at room temperature.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.91 (s, 3H), 1.96 (s, 3H), 5.16 (d,  $J = 17.2$  Hz, 1H), 5.21 (d,  $J = 10.4$  Hz, 1H), 5.97 (brs, 1H), 6.27 (dd,  $J = 17.2, 10.4$  Hz, 1H), 6.92–6.97 (m, 2H), 7.19–7.21 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  24.2, 26.9, 58.2, 113.6, 124.0, 124.4, 126.7, 141.8, 150.0, 169.0. HRMS (ESI) calcd for  $\text{C}_{10}\text{H}_{13}\text{NOSNa}$  ( $[\text{M}+\text{Na}]^+$ ): 218.0610; Found: 218.0616

### ***N*-Acetyl-1-ethyl-1-phenylallylamine (2q)**



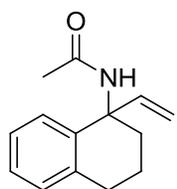
45 % yield, colorless oil, solidified to a white solid after standing at room temperature.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  0.71 (t,  $J = 7.2$  Hz, 3H), 1.92 (s, 3H), 1.90–1.98 (m, 1H), 2.09–2.18 (m, 1H), 5.05 (d,  $J = 17.6$  Hz, 1H), 5.13 (d,  $J = 10.8$  Hz, 1H), 6.28 (dd,  $J = 17.6, 10.8$  Hz, 1H), 7.10–7.13 (m, 1H), 7.20–7.26 (m, 4H), 8.00 (brs, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_3\text{OD}$ )  $\delta$  8.7, 23.3, 33.1, 64.4, 114.2, 127.3, 127.4, 129.0, 142.1, 145.1, 172.4. HRMS (ESI) calcd for  $\text{C}_{13}\text{H}_{16}\text{NO}$  ( $[\text{M}-\text{H}]^-$ ): 202.1237; Found: 202.1240.

### ***N*-Acetyl-1-vinylindan-1-amine (2r)**



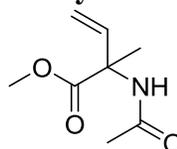
55 % yield, white solid, mp: 70–72 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.90 (s, 3H), 2.33–2.40 (m, 1H), 2.65–2.71 (m, 1H), 2.78–2.85 (m, 1H), 2.88–2.97 (m, 1H), 4.91 (d,  $J = 17.2$  Hz, 1H), 5.07 (d,  $J = 10.4$  Hz, 1H), 5.64 (brs, 1H), 6.09 (dd,  $J = 17.2, 10.4$  Hz, 1H), 7.16–7.20 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  24.0, 29.9, 38.2, 68.4, 112.9, 123.6, 125.0, 126.7, 128.3, 140.0, 143.9, 144.8, 169.3. HRMS (ESI) calcd for  $\text{C}_{13}\text{H}_{14}\text{NO}$  ( $[\text{M}-\text{H}]^-$ ): 200.1081. Found: 200.1084.

### ***N*-Acetyl-1-vinyltetrahydronaphthyl-1-amine (2s)**



43 % yield, white solid, mp: 103–105 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.79–1.83 (m, 2H), 1.91–1.99 (m, 1H), 1.96 (s, 3H), 2.73–2.90 (m, 3H), 4.91 (d,  $J = 17.2$  Hz, 1H), 5.23 (d,  $J = 10.8$  Hz, 1H), 5.62 (brs, 1H), 6.12 (dd,  $J = 17.2, 10.8$  Hz, 1H), 7.10–7.12 (m, 1H), 7.17–7.19 (m, 2H), 7.30–7.32 (m, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  19.0, 24.5, 29.6, 32.4, 60.4, 114.9, 126.2, 127.4, 127.8, 129.3, 137.7, 138.3, 142.1, 168.7. HRMS (ESI) calcd for  $\text{C}_{14}\text{H}_{16}\text{NO}$  ( $[\text{M}-\text{H}]^-$ ): 214.1237; Found: 214.1240.

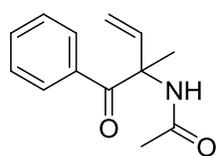
### **Methyl 2-acetamido-2-methylbut-3-enoate (2t)**



67 % yield, colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.62 (s, 3H), 1.99 (s, 3H), 3.72 (s, 3H), 5.20 (d,  $J = 10.4$  Hz, 1H), 5.23 (d,  $J = 17.6$  Hz, 1H), 6.07 (dd,  $J = 17.6, 10.8$  Hz, 1H), 6.43 (brs, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  22.6, 23.3, 52.8, 60.4, 115.3, 137.3, 169.3, 173.0. HRMS (ESI) calcd for  $\text{C}_8\text{H}_{13}\text{NO}_3\text{Na}$

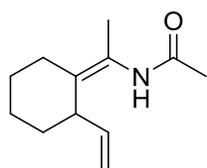
([M+Na]<sup>+</sup>): 194.0788; Found: 194.0795.

### ***N*-Acetyl-1-methyl-1-benzoylallylamine (2u)**



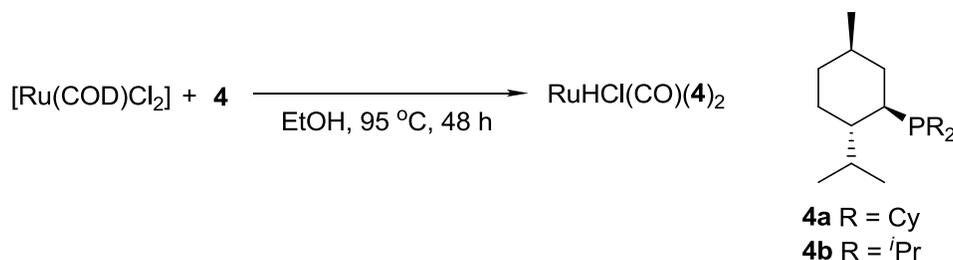
72 % yield, colorless oil, solidified to a white solid after standing at room temperature. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 1.77 (s, 3H), 1.90 (s, 3H), 5.29 (d, *J* = 17.2 Hz, 1H), 5.31 (d, *J* = 10.8 Hz, 1H), 6.32 (dd, *J* = 17.6, 10.8 Hz, 1H), 7.14 (brs, 1H), 7.36–7.39 (m, 2H), 7.46–7.50 (m, 1H), 7.90–7.92 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 23.5, 23.7, 64.7, 116.6, 128.0, 129.2, 132.2, 134.7, 138.6, 168.8, 198.7. HRMS (ESI) calcd for C<sub>13</sub>H<sub>15</sub>NO<sub>2</sub>Na ([M+Na]<sup>+</sup>): 240.0995; Found: 240.0990.

### ***N*-(1-(2-vinylcyclohexylidene)ethyl)acetamide (3)**



64 % yield, colorless oil, solidified to a white solid after standing at room temperature. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 1.28–1.38 (m, 1H), 1.52–1.63 (m, 4H), 1.77–1.81 (m, 2H), 1.85 (s, 3H), 1.97 (s, 3H), 2.45 (m, 1H), 3.39 (m, 1H), 4.97 (d, *J* = 17.2 Hz, 1H), 5.02 (d, *J* = 10.8 Hz, 1H), 5.87 (dq, *J* = 17.2, 10.4, 4.8 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) δ 17.4, 22.5, 22.6, 26.8, 28.4, 32.7, 41.3, 115.2, 124.2, 136.2, 141.6, 172.3. HRMS (ESI) calcd for C<sub>12</sub>H<sub>19</sub>NONa ([M+Na]<sup>+</sup>): 216.1359; Found: 216.1367.

## **(C) General Procedure for the Preparation of Chiral Ruthenium Catalysts<sup>2</sup>**



**General procedure:** To a dry Parr autoclave equipped with a stirring bar was added [RuCl<sub>2</sub>(COD)]<sub>n</sub> (0.193 g, 0.560 mmol) and chiral phosphine ligand **4** (1.4 mmol) and anhydrous EtOH (6 mL) under nitrogen atmosphere. Then, the Parr autoclave was sealed and heated to 90 °C for 48 h. After cooled to room temperature, the yellowish crude product was filtered off and washed extensively with EtOH, then Et<sub>2</sub>O, and dried under vacuum to yield RuHCl(CO)(**4**)<sub>2</sub> complex as a light yellow powder.

### **RuHCl(CO)(**4a**)<sub>2</sub> (R = Cy)**

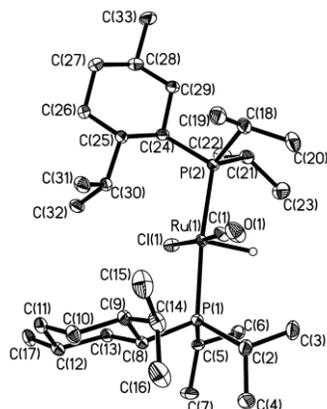
46 % yield, yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ -24.07 (s, 1H), 0.73–2.52 (m, 82H). <sup>31</sup>P NMR (133 MHz, CDCl<sub>3</sub>) δ 41.75 (s).

### **RuHCl(CO)(**4b**)<sub>2</sub> (R = *i*Pr)**

51 % yield, yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ -23.31 (t, *J* = 18 Hz, 1H), 0.76–3.19 (m, 66 H). <sup>31</sup>P NMR (133 MHz, CDCl<sub>3</sub>) δ 51.55 (s).

The structure of the chiral ruthenium catalyst RuHCl(CO)(**4**)<sub>2</sub> was determined by the crystal

structure of RuHCl(CO)(**4b**)<sub>2</sub> (Figure 1), which was obtained by evaporation of the complex solution in EtOH at room temperature.



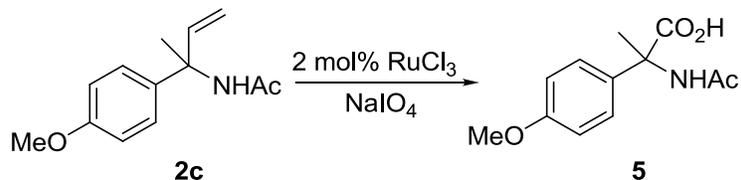
**Figure 1**

**Table 1.** Crystal data and structure refinement for RuHCl(CO)(**4b**)<sub>2</sub>

Empirical formula	C <sub>33</sub> H <sub>64</sub> ClOP <sub>2</sub> Ru
Formula weight	675.3
Temperature	113(2) K
Wavelength	0.7107 Å
Crystal system, space group	monoclinic, P 1 21 1
Unit cell dimensions	a = 9.9660(1) Å      α = 90.00 deg. b = 13.8450(17) Å    β = 92.71 deg. c = 13.0720(15) Å    γ = 90.00 deg.
Volume	1801.6(4) Å <sup>3</sup>
Z, Calculated density	2, 1.2447 Mg/m <sup>3</sup>
Absorption coefficient	0.621 mm <sup>-1</sup>
F(000)	722
Crystal size	0.24 × 0.22 × 0.20 mm
Theta range for data collection	1.50 to 28.30 deg.
Limiting indices	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -17 ≤ l ≤ 17
Reflections collected / unique	23160 / 8512 [R(int) = 0.0448]

Completeness to theta = 25.01	99.8 %
Absorption correction	multi-scan
Max. and min. transmission	0.8859 and 0.8654
Refinement method	CrystalClear (Rigaku/MSI Inc., 2005)
Data / restraints / parameters	8512 / 2 / 359
Goodness-of-fit on F <sup>2</sup>	1.064
Final R indices [I > 2σ(I)]	R1 = 0.0383, wR2 = 0.0826
R indices (all data)	R1 = 0.0416, wR2 = 0.0841
Absolute structure parameter	-0.01(2)
Largest diff. peak and hole	1.781 and -0.547 e. Å <sup>3</sup>

#### (D) Synthesis of $\alpha$ -Amino Acid 5<sup>4</sup>



Compound **2c** (219 mg, 1 mmol), RuCl<sub>3</sub>·3H<sub>2</sub>O (5.8 mg, 0.022 mmol) and NaIO<sub>4</sub> (960 mg, 4.5 mmol) were added to a mixed solvent of MeCN, CCl<sub>4</sub> and H<sub>2</sub>O (20 mL, 2:2:3 v/v), and the resulting mixture was stirred at room temperature for 2 h. The solid residues were removed by filtration, and the filtrate was extracted with ethyl acetate (2 × 200 mL). The organic phases were combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under vacuum to give crude product. Recrystallization of crude product with petroleum ether/ethyl acetate afforded pure product (213 mg, 90% yield) as a white solid, mp: 204–206 °C. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 1.81 (s, 3H), 1.90 (s, 1H), 3.70 (s, 3H), 6.81–6.84 (m, 2H), 7.36–7.38 (m, 2H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) δ 22.9, 23.3, 55.8, 62.7, 114.7, 128.6, 133.8, 160.8, 172.7, 176.0. HRMS (ESI) calcd for C<sub>12</sub>H<sub>14</sub>NO<sub>4</sub> ([M-H]<sup>-</sup>): 236.0928; Found: 236.0922.

#### (E) Comparison of Reaction Rates for the Hydrovinylation of 1a, 1c and 1f

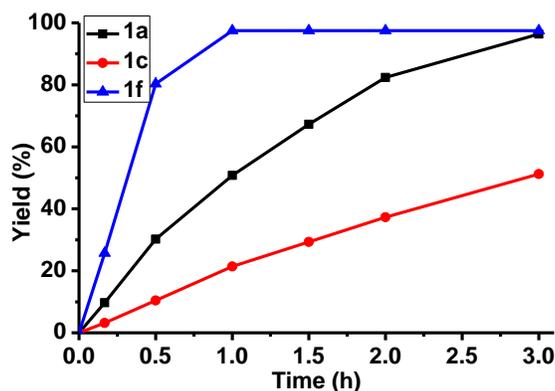
<sup>4</sup> Singh, O. V.; Han, H. *Tetrahedron Lett.* **2007**, 48, 7094.

**General procedure for the hydrovinylation of 1a, 1c and 1f, separately:** To a dry Schlenk tube equipped with a stirring bar was added RuHCl(CO)(PCy<sub>3</sub>)<sub>2</sub> (7.3 mg, 0.01 mmol), AgOTf (2.6 mg, 0.01 mmol), enamine (0.2 mmol), 4Å molecular sieves (100 mg), tetradecane (16 µL, as internal standard, which was added to calibrate the yields of the products.) and degassed anhydrous 1,2-dichloroethane (3 mL) under an nitrogen atmosphere. The mixture was stirred at room temperature for 20 min. The nitrogen atmosphere in the Schlenk tube was replaced by ethylene three times and the yellow solution was stirred at 65 °C under 1 atm of ethylene. Samples of the reaction solution were taken at interval of 10 min or 30 min and subjected to GC analyses [HP–5 column, 30 m; carrier gas, N<sub>2</sub> (1.0 mL/min); inject temperature, 230 °C; initial temperature, 175 °C (standing); final temperature, 175 °C]. **For hydrovinylation of 1a:** *t*<sub>R</sub> 5.65 min (product **2a**), *t*<sub>R</sub> 4.79 min (**1a**), *t*<sub>R</sub> 3.90 min (internal standard: tetradecane.). **For hydrovinylation of 1c:** *t*<sub>R</sub> 11.86 min (product **2c**), *t*<sub>R</sub> 9.70 min (**1c**), *t*<sub>R</sub> 3.90 min (internal standard: tetradecane). **For hydrovinylation of 1f:** *t*<sub>R</sub> 13.72 min (product **2f**), *t*<sub>R</sub> 10.47 min (**1f**), *t*<sub>R</sub> 3.90 min (internal standard: tetradecane).

The results are listed in Table 2 and the plot of yield against time see Figure 2.

**Table 2.** Hydrovinylation of *N*-acetyl enamines **1a**, **1c**, and **1f** (respective individual).

Time (h)	Yield of <b>2a</b> (%)	Yield of <b>2c</b> (%)	Yield of <b>2f</b> (%)
0.167	9.7	3.2	25.7
0.5	30.2	10.4	80.3
1	50.8	21.4	97.5
1.5	67.3	29.3	97.5
2	82.4	37.3	97.5
3	96.4	51.2	97.5



**Figure 2.**

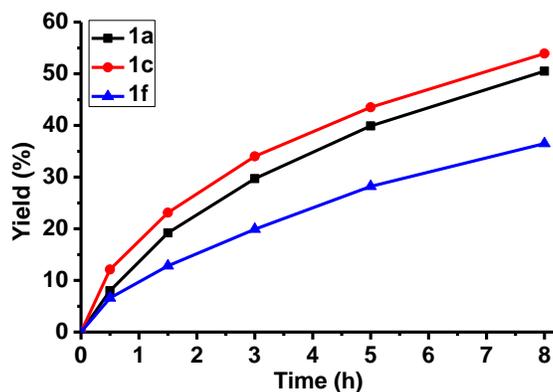
**Hydrovinylation of 1a, 1c and 1f in one reaction:** To a dry Schlenk tube equipped with a stirring bar was added RuHCl(CO)(PCy<sub>3</sub>)<sub>2</sub> (7.3 mg, 0.01 mmol), AgOTf (2.6 mg, 0.01 mmol), **1a** (32.2 mg, 0.2 mmol), **1c** (38.2 mg, 0.2 mmol), **1f** (48.0 mg, 0.2 mmol), 4Å molecular sieves (100 mg), tetradecane (16 µL, as internal standard, which was added to calibrate the yields of the products.) and degassed anhydrous 1,2-dichloroethane (3 mL) under an nitrogen atmosphere. The mixture was stirred at room temperature for 20 min and the nitrogen atmosphere in the Schlenk tube was replaced by ethylene three times, and then was stirred at 65 °C under 1 atm of ethylene. Samples of the reaction solution were taken at interval of 0.5, 1.0, 1.5, 2 or 3 h and

subjected to GC analyses [HP-5 column, 30 m; carrier gas, N<sub>2</sub> (1.0 mL/min); inject temperature, 230 °C; initial temperature, 175 °C (standing); final temperature, 175 °C]. **For hydrovinylation of 1a, 1c and 1f, competitively:**  $t_R$  3.90 min (internal standard: tetradecane),  $t_R$  5.65 min (product 2a),  $t_R$  4.79 min (1a),  $t_R$  11.86 min (product 2c),  $t_R$  9.70 min (1c),  $t_R$  13.72 min (product 2f),  $t_R$  10.47 min (1f). The reaction was repeated 5 times and the average yields were used.

The results are listed in Table 3 and the plot of yield against time see Figure 3.

**Table 3.** Hydrovinylation of *N*-acetyl enamines **1a**, **1c**, and **1f** (competitive).

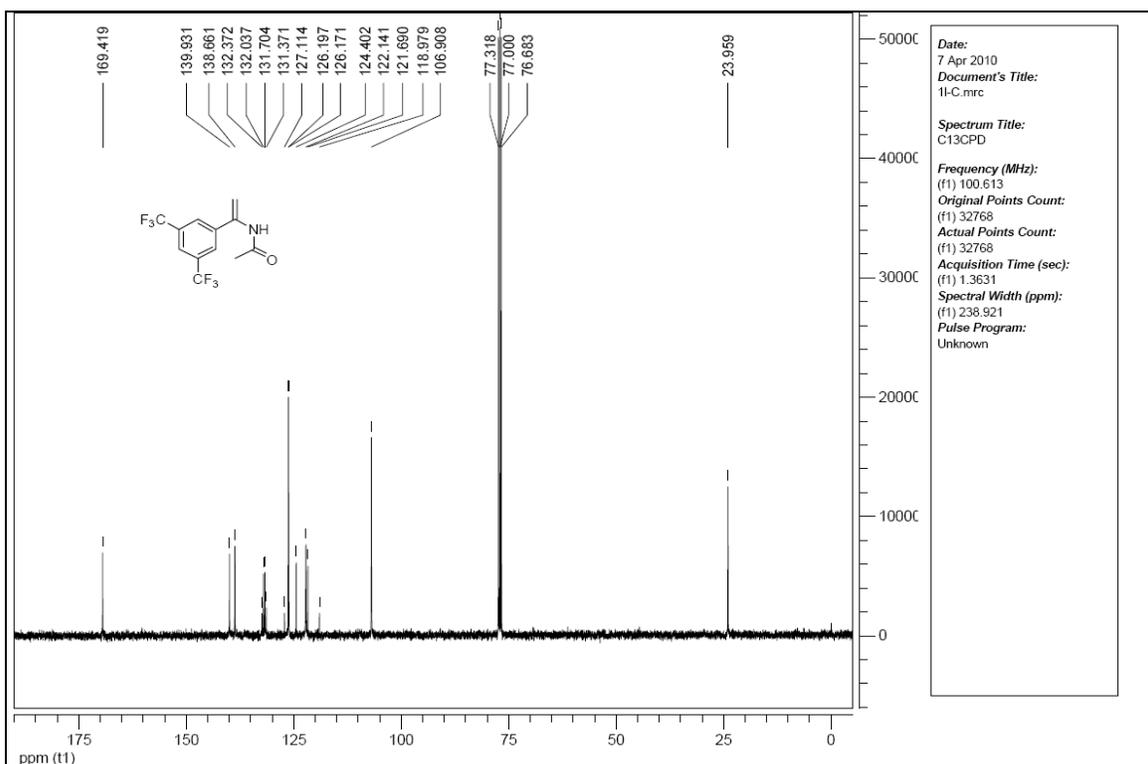
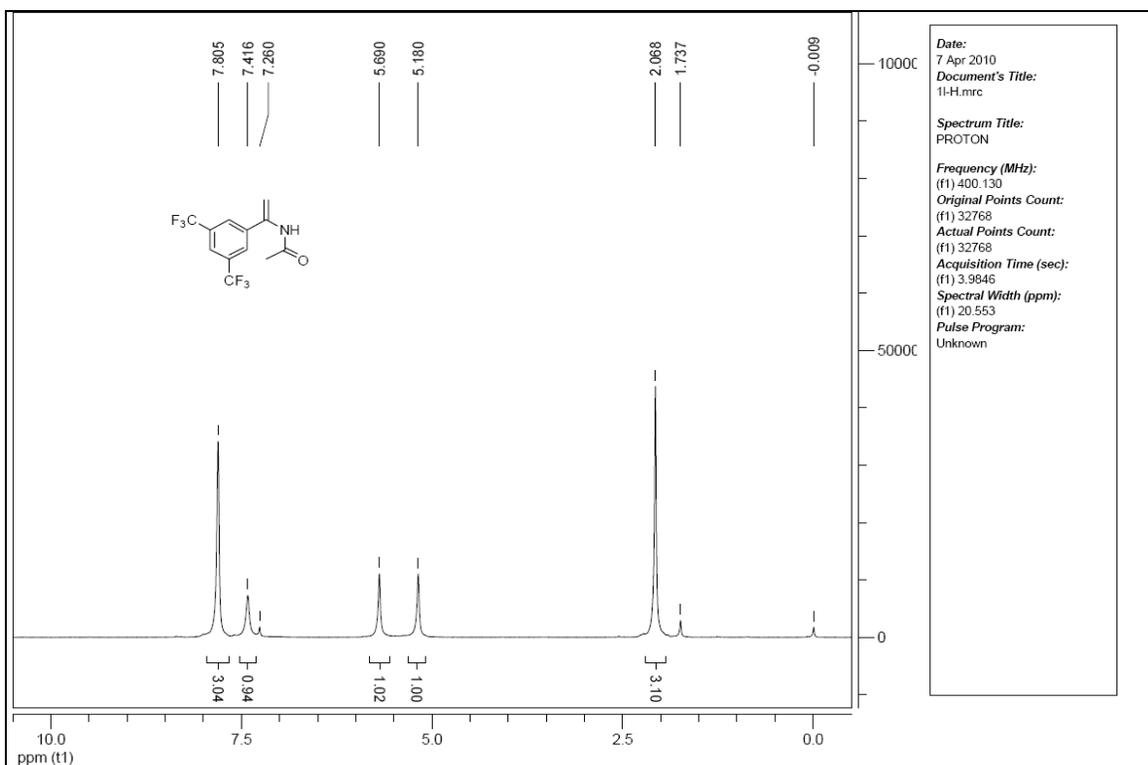
Time (h)	Yield of <b>2a</b> (%)	Yield of <b>2c</b> (%)	Yield of <b>2f</b> (%)
0.5	8.0	12.1	6.6
1.5	19.2	23.1	12.8
3	29.7	34.0	19.9
5	39.9	43.5	28.2
8	50.5	53.9	36.5



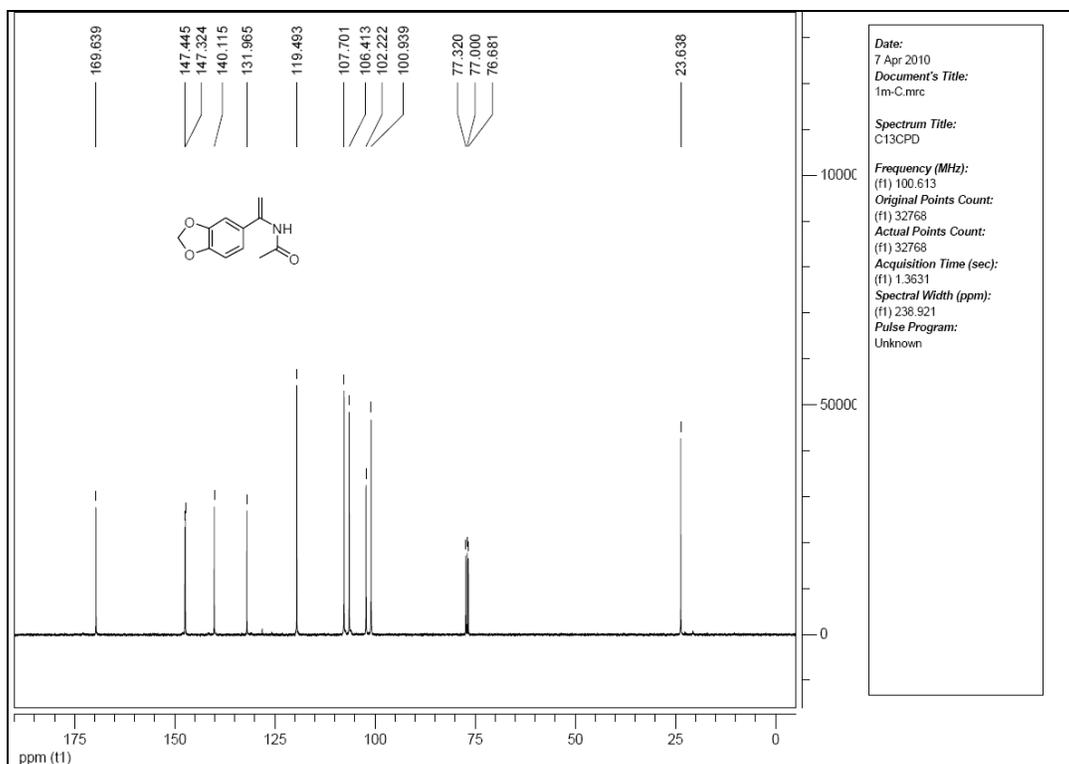
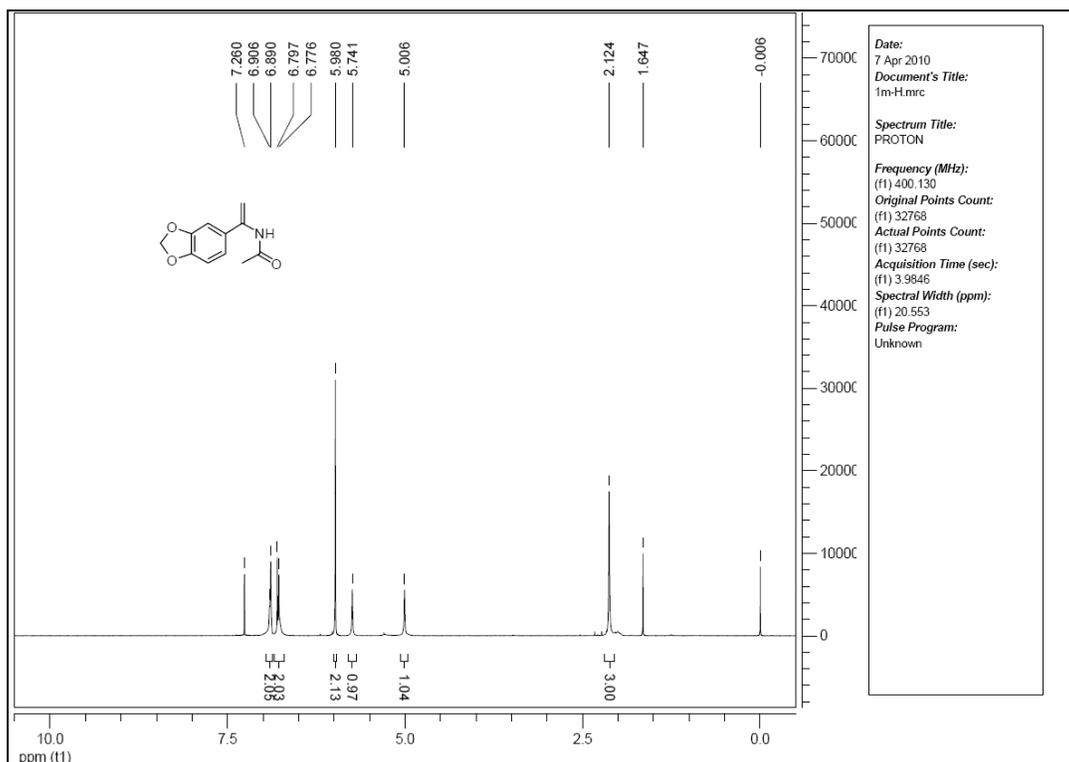
**Figure 3.**

## (F) NMR Spectrum of the New Substrates and Products

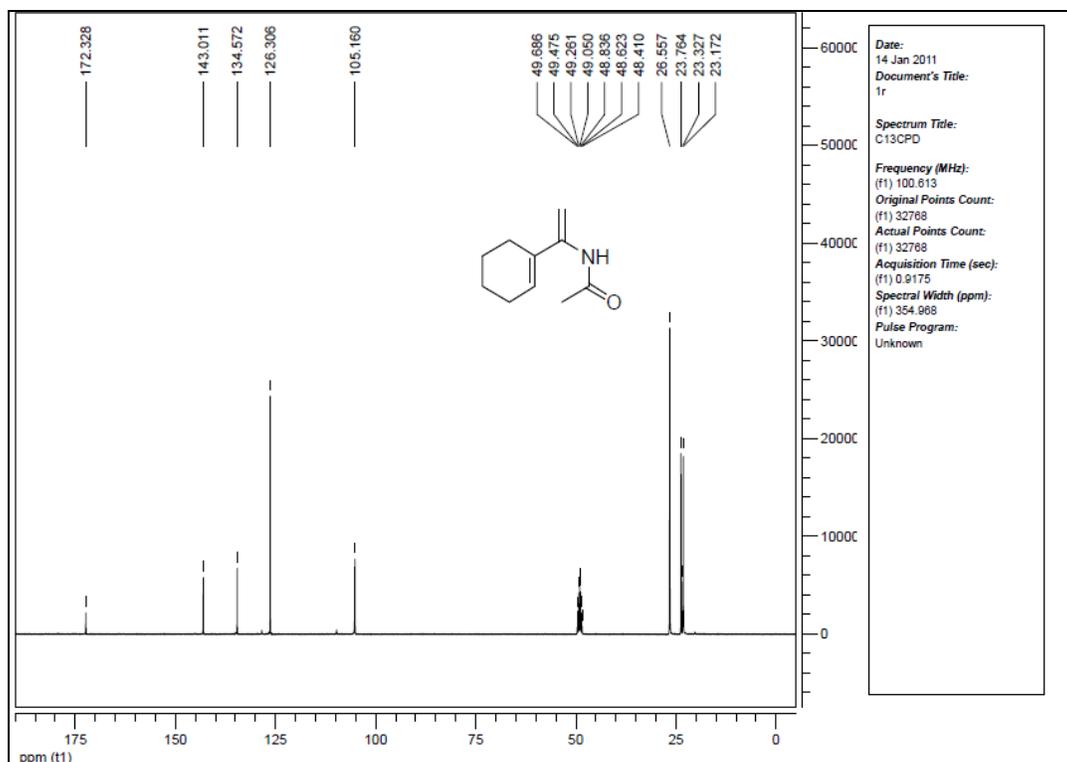
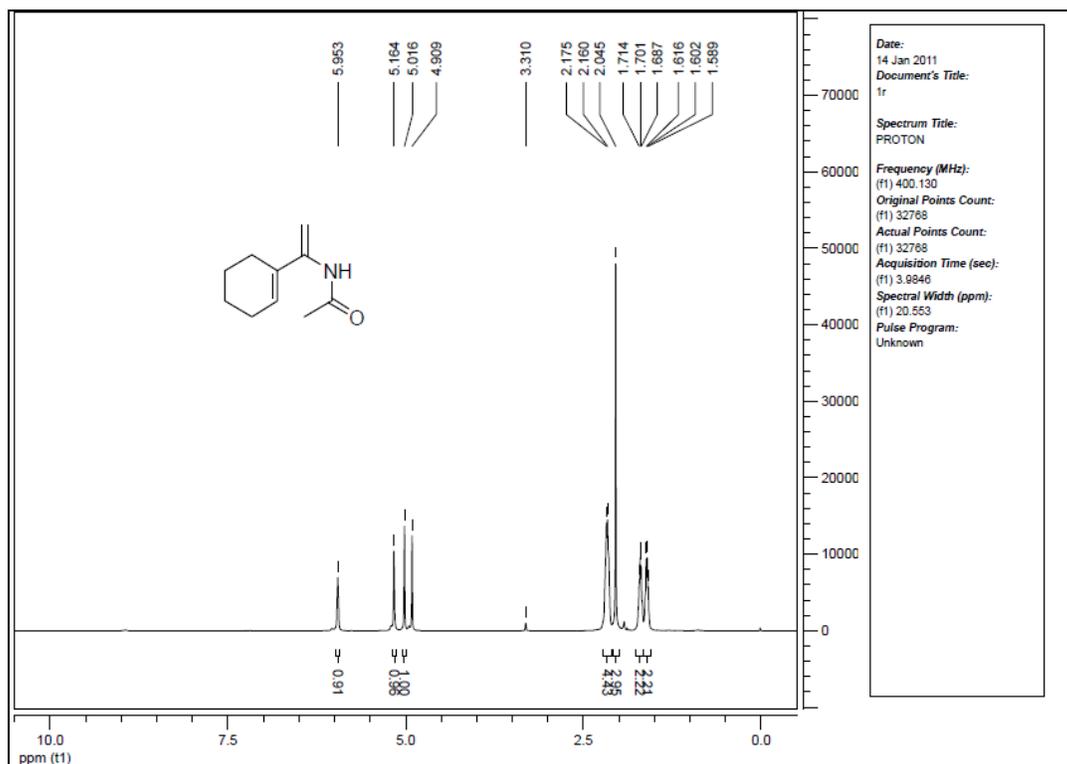
### *N*-Acetyl-1-[3,5-bis(trifluoromethyl)phenyl]vinylamine (11)



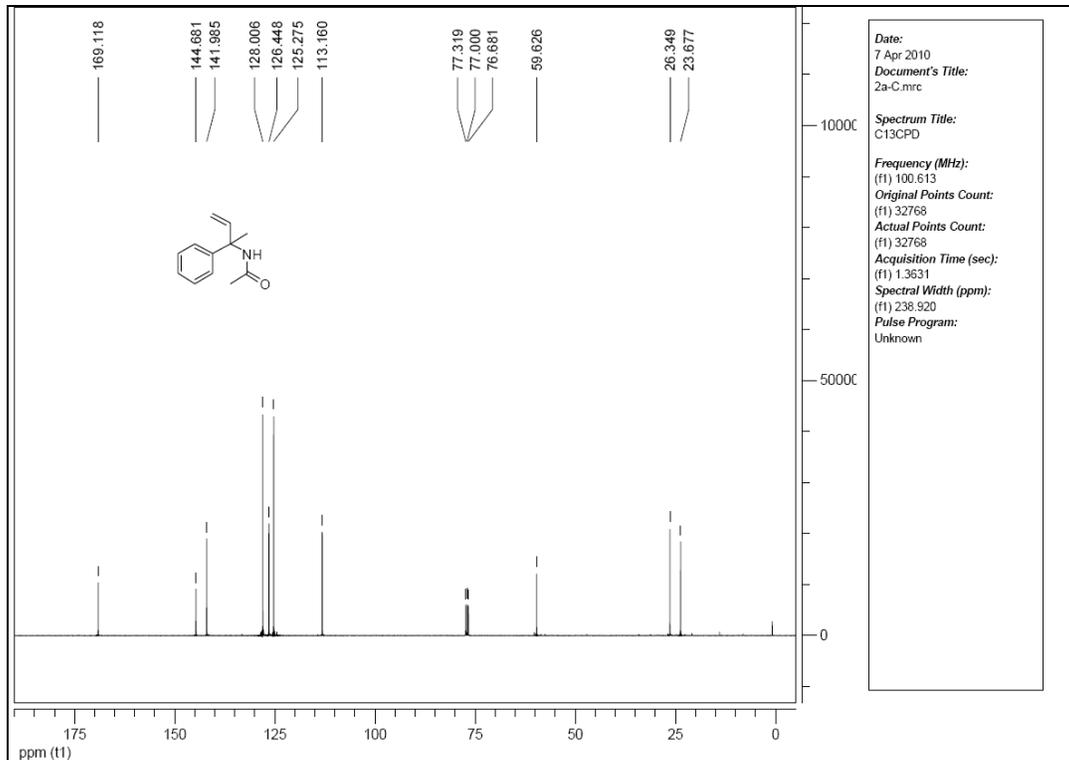
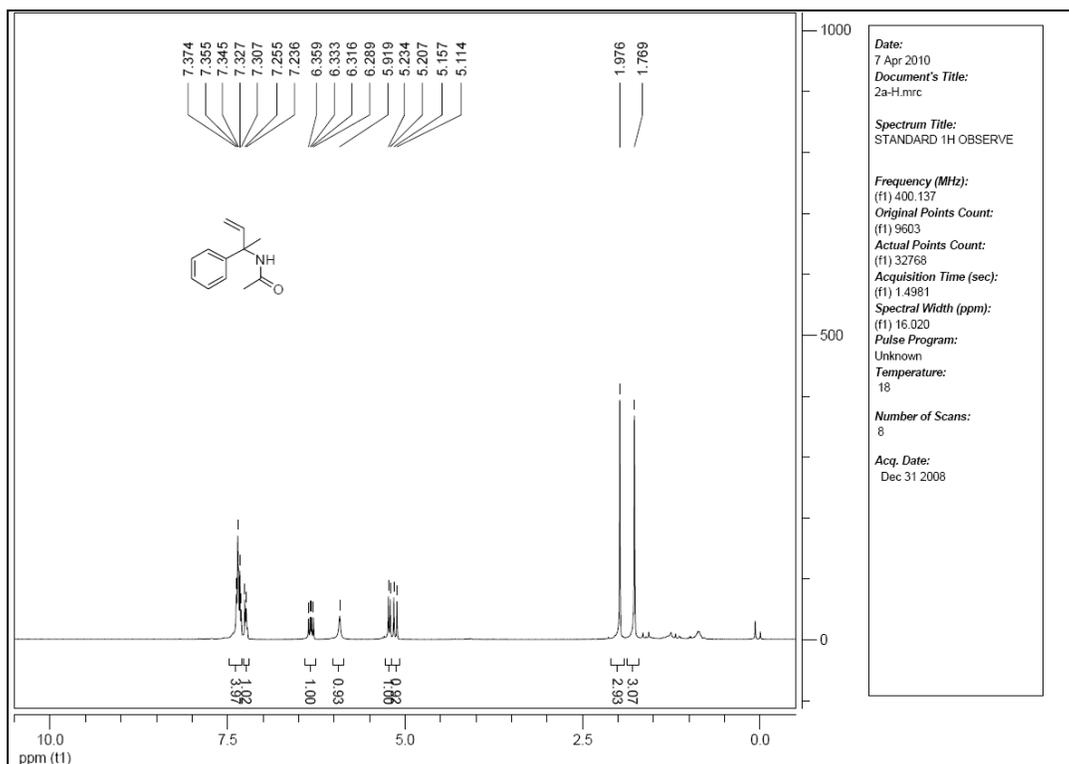
# N-Acetyl-1-(3,4-methylenedioxyphenyl)vinylamine (1m)



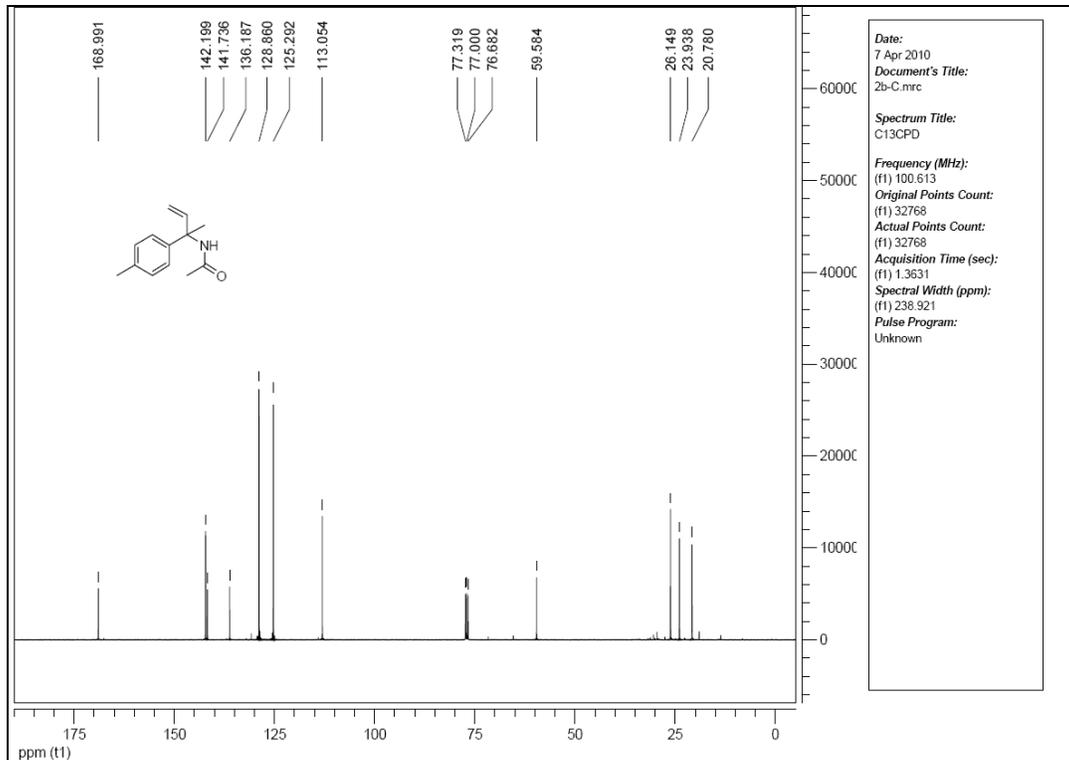
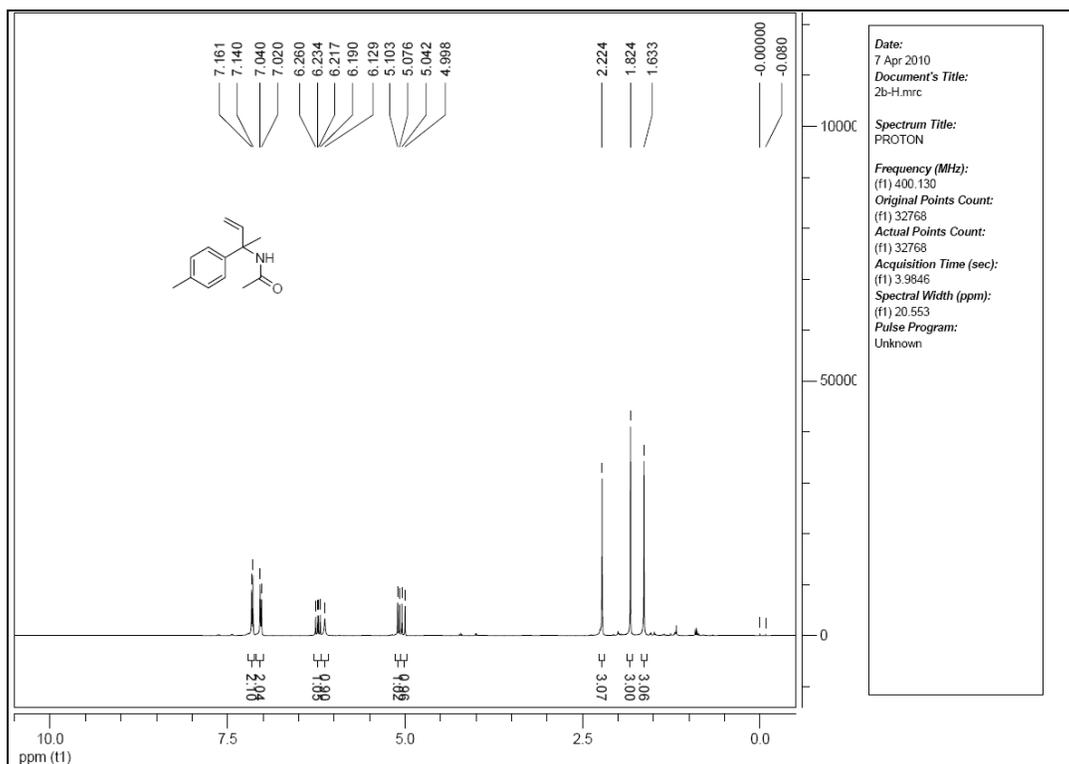
# N-(1-cyclohexenylvinyl)acetamide (1v)



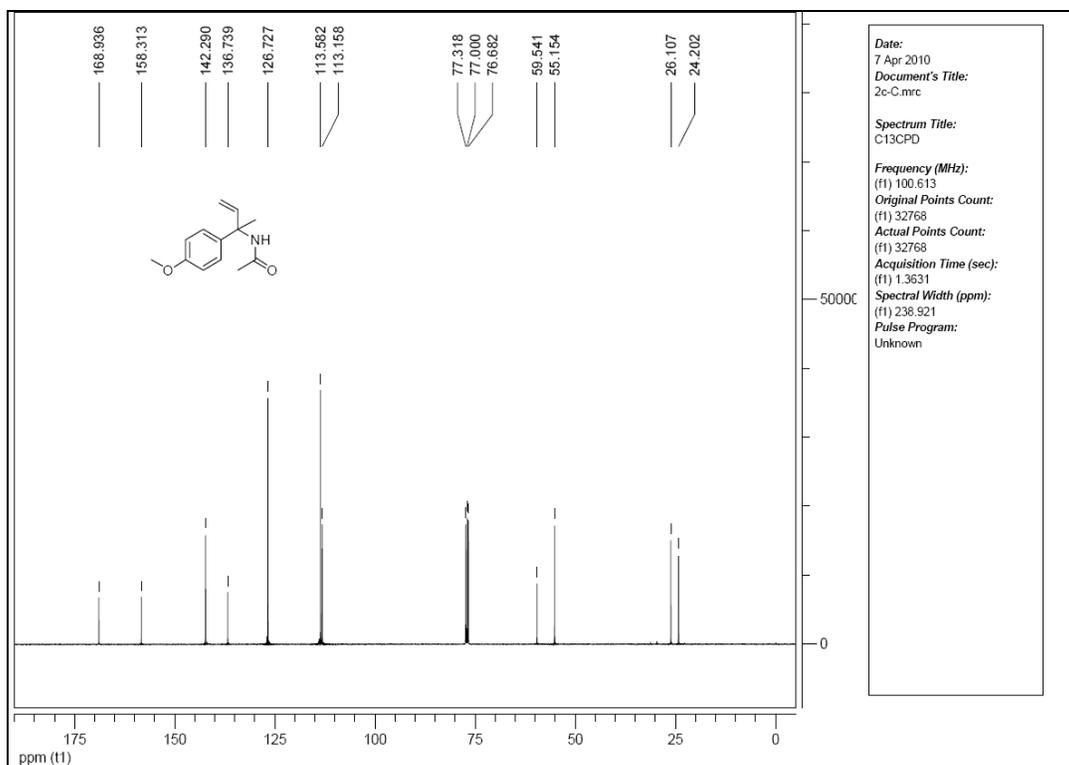
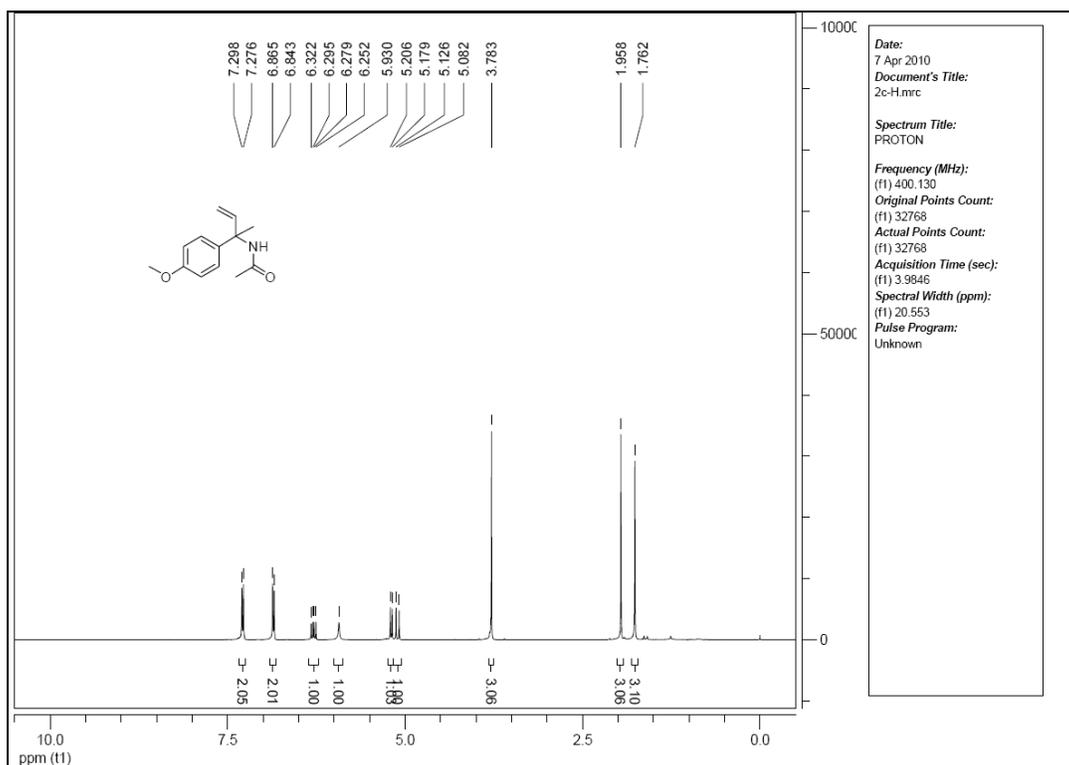
# N-Acetyl-1-methyl-1-phenylallylamine (2a)



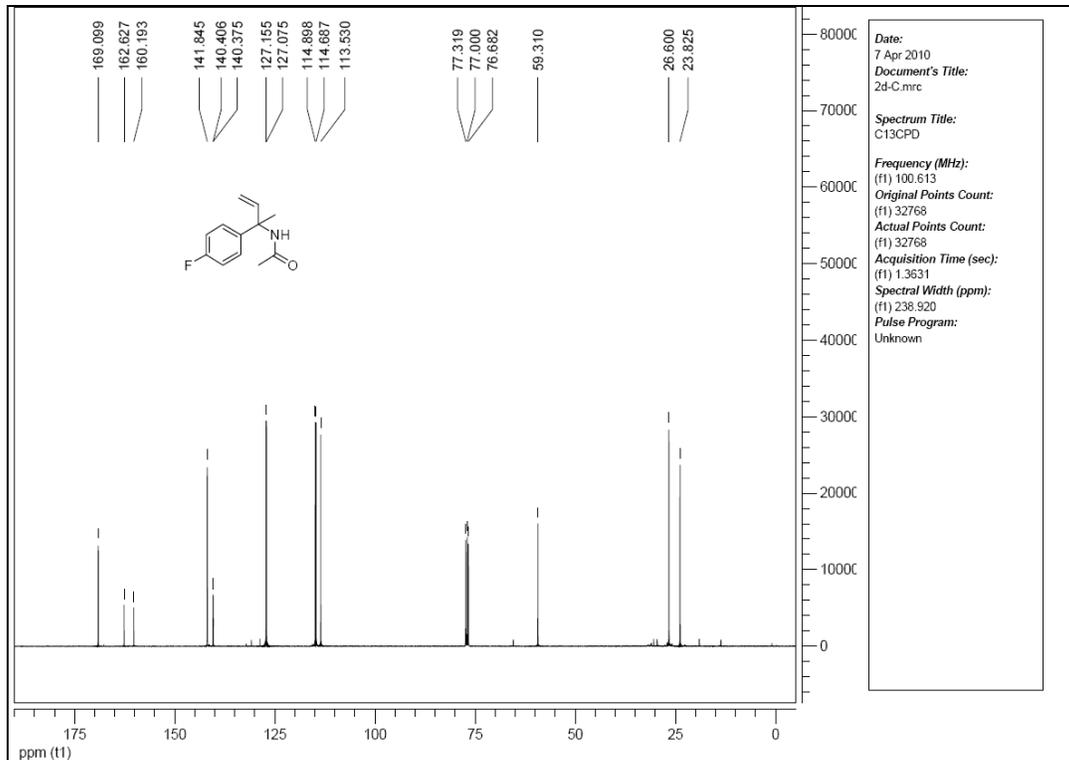
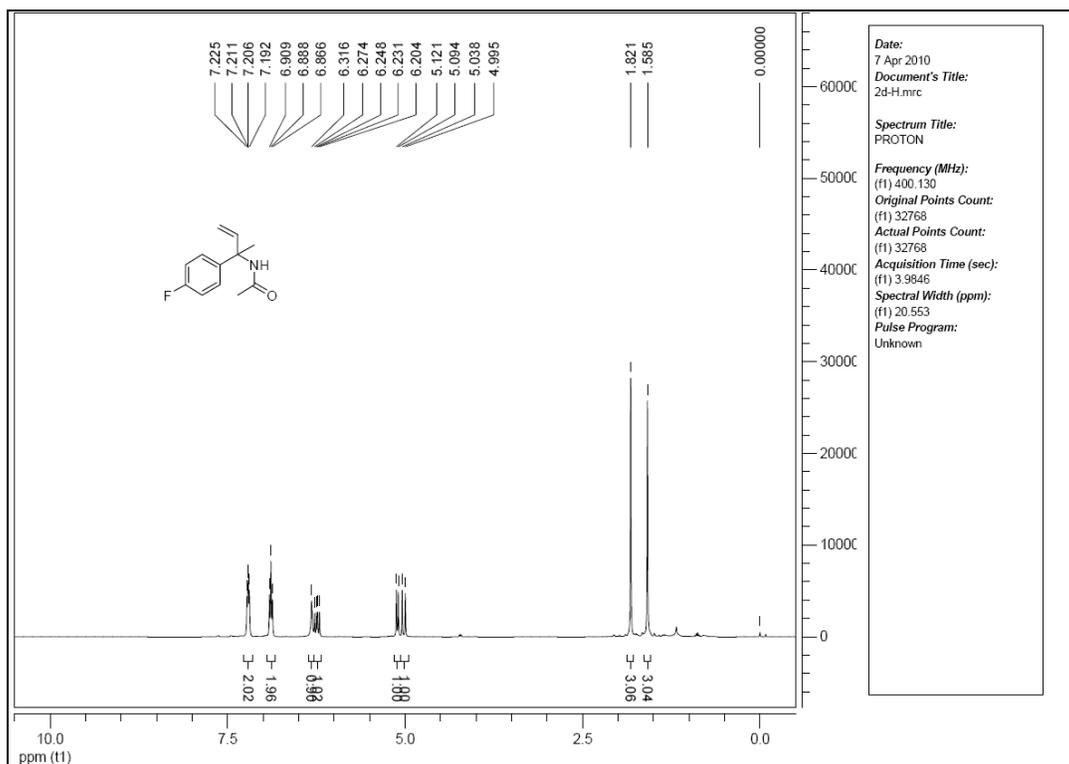
# N-Acetyl-1-methyl-1-(4-methylphenyl)allylamine (2b)



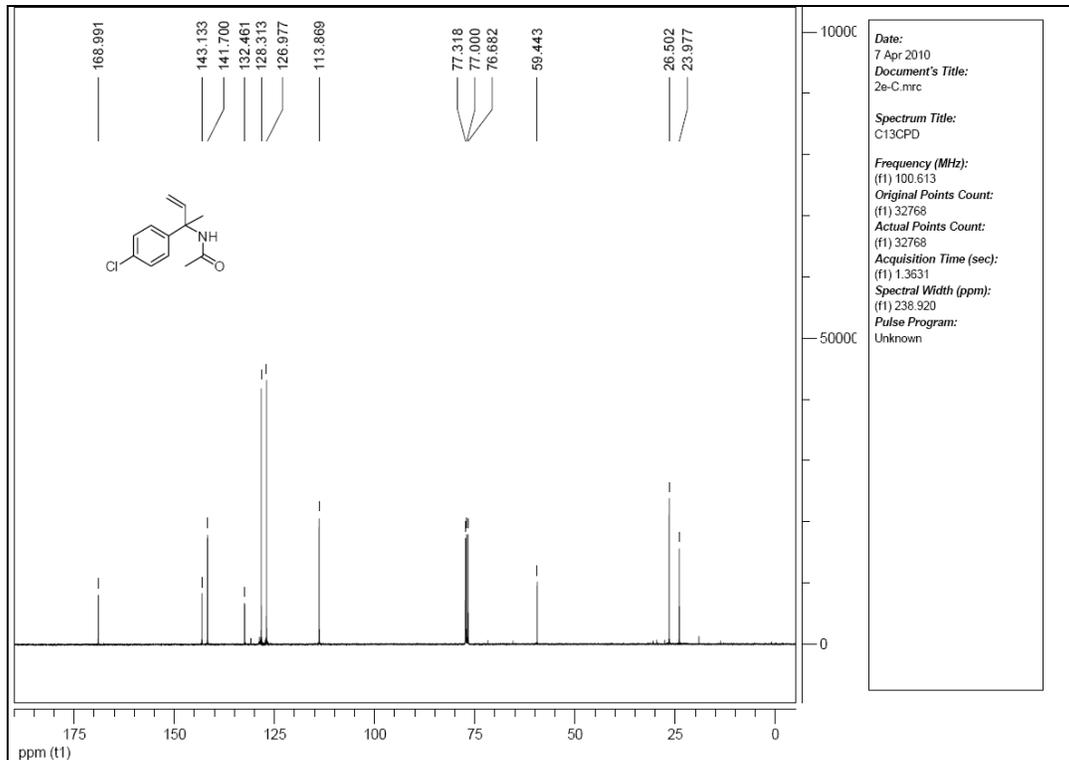
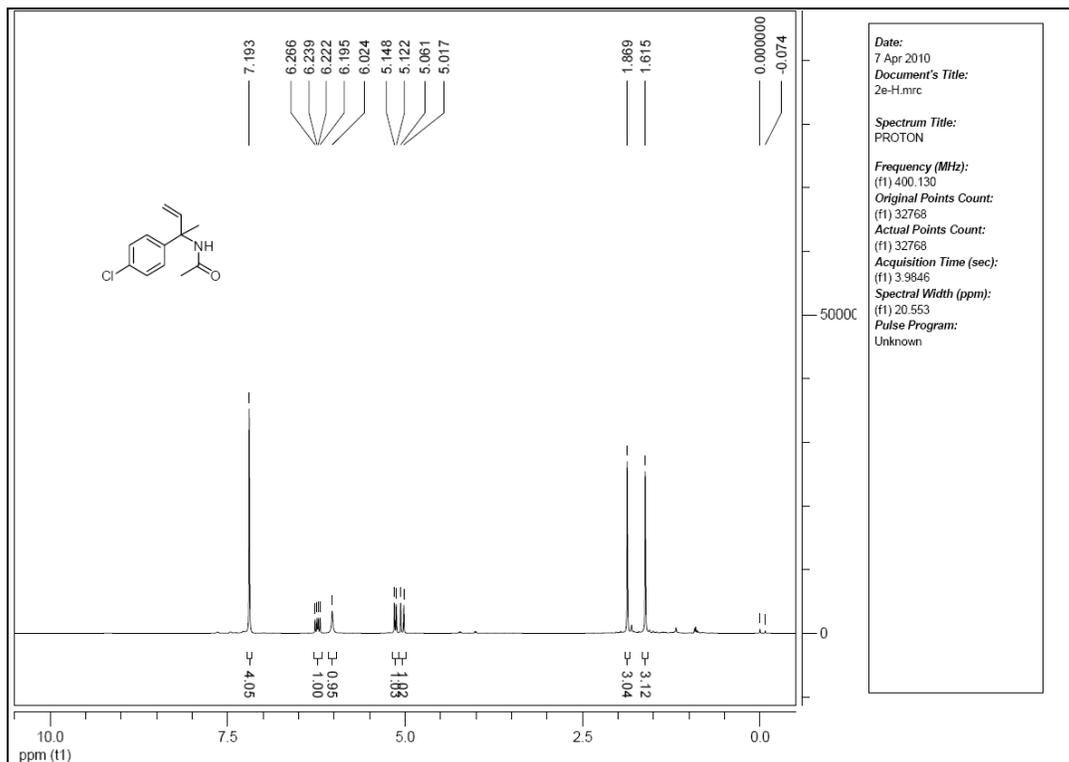
# N-Acetyl-1-methyl-1-(4-methoxyphenyl)allylamine (2c)



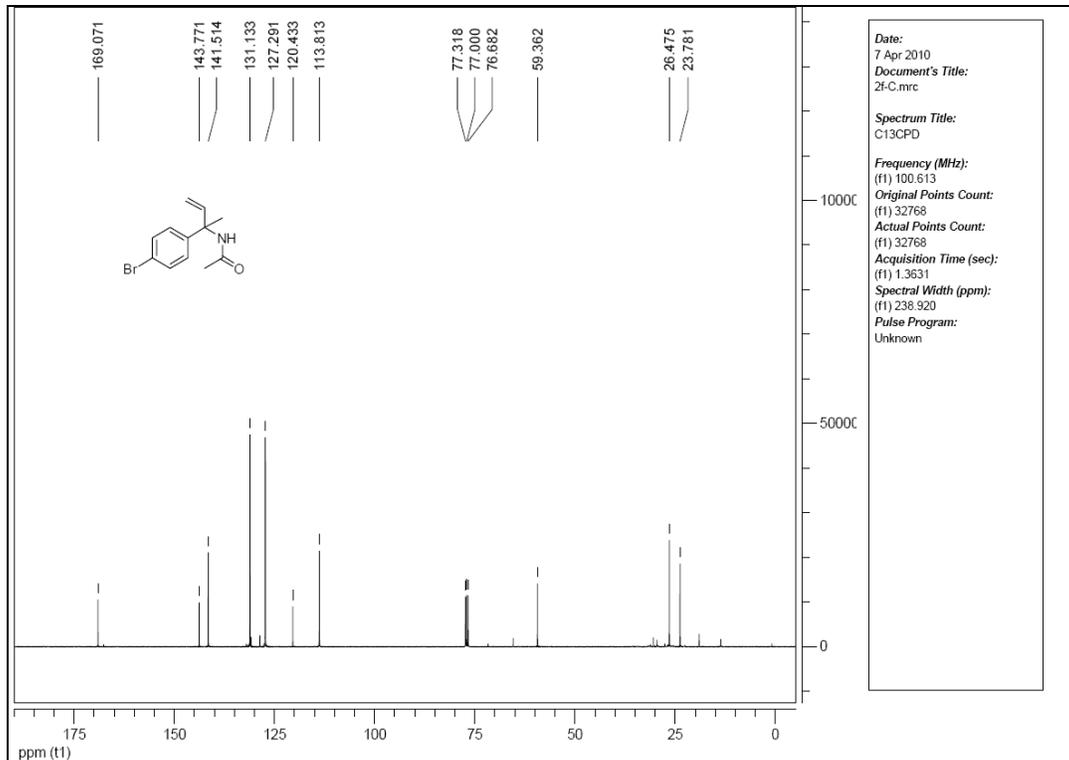
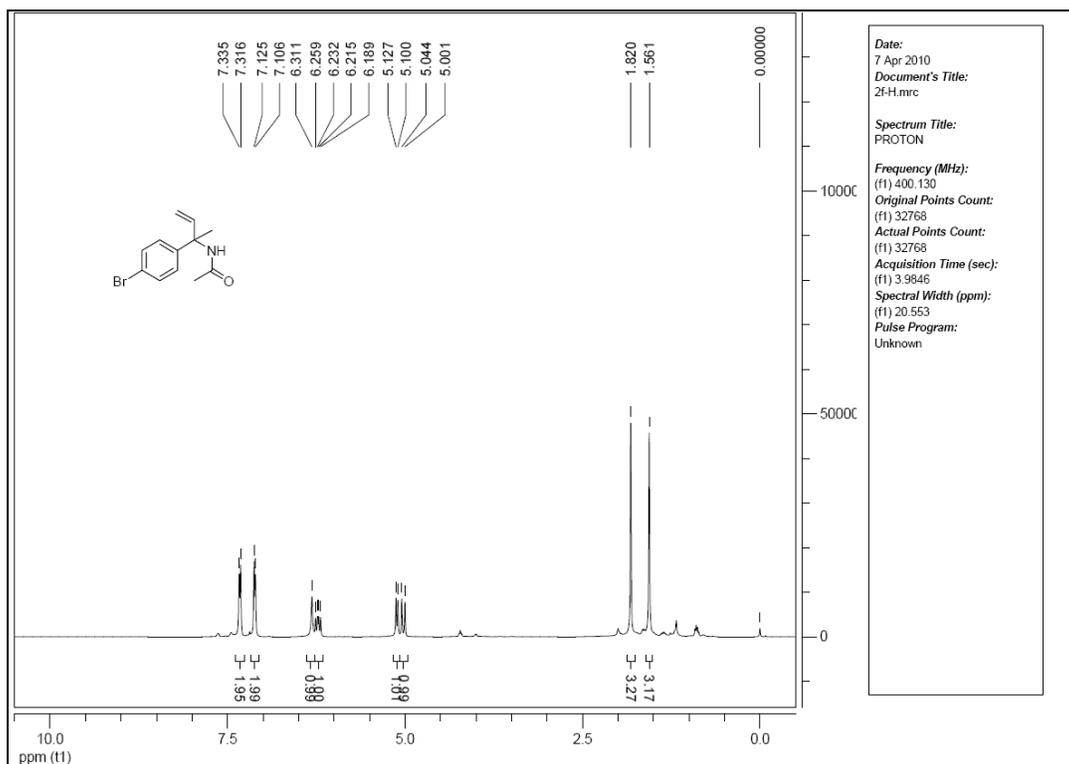
# N-Acetyl-1-methyl-1-(4-fluorophenyl)allylamine (2d)



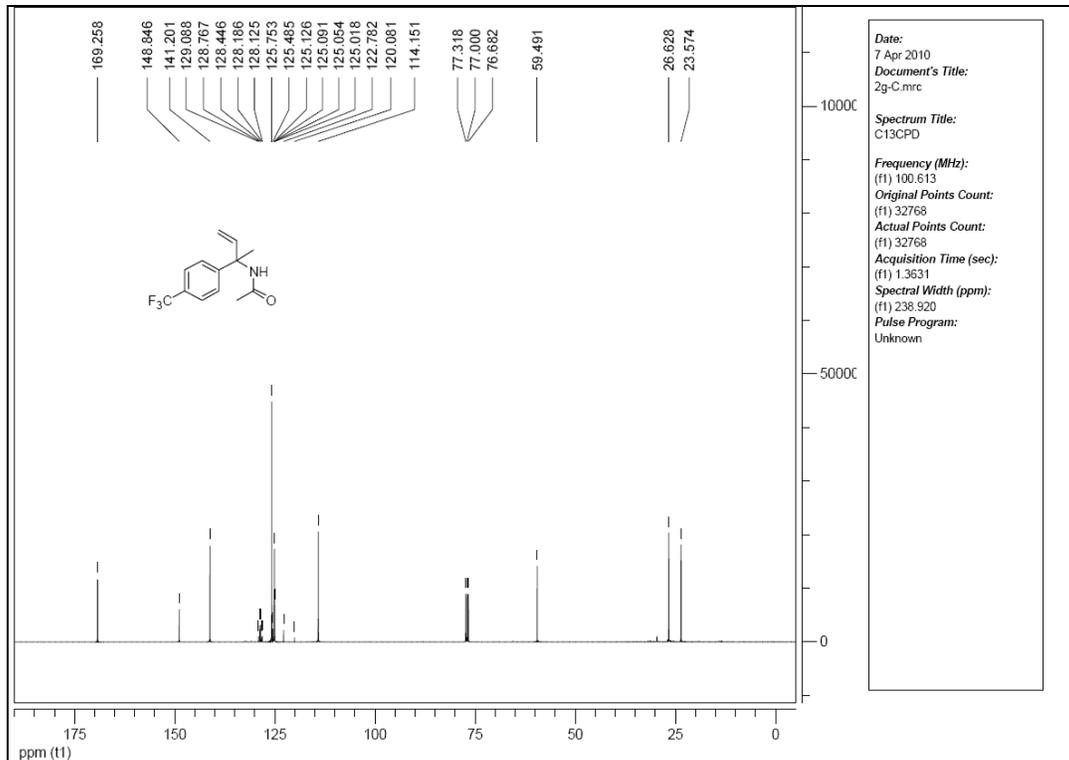
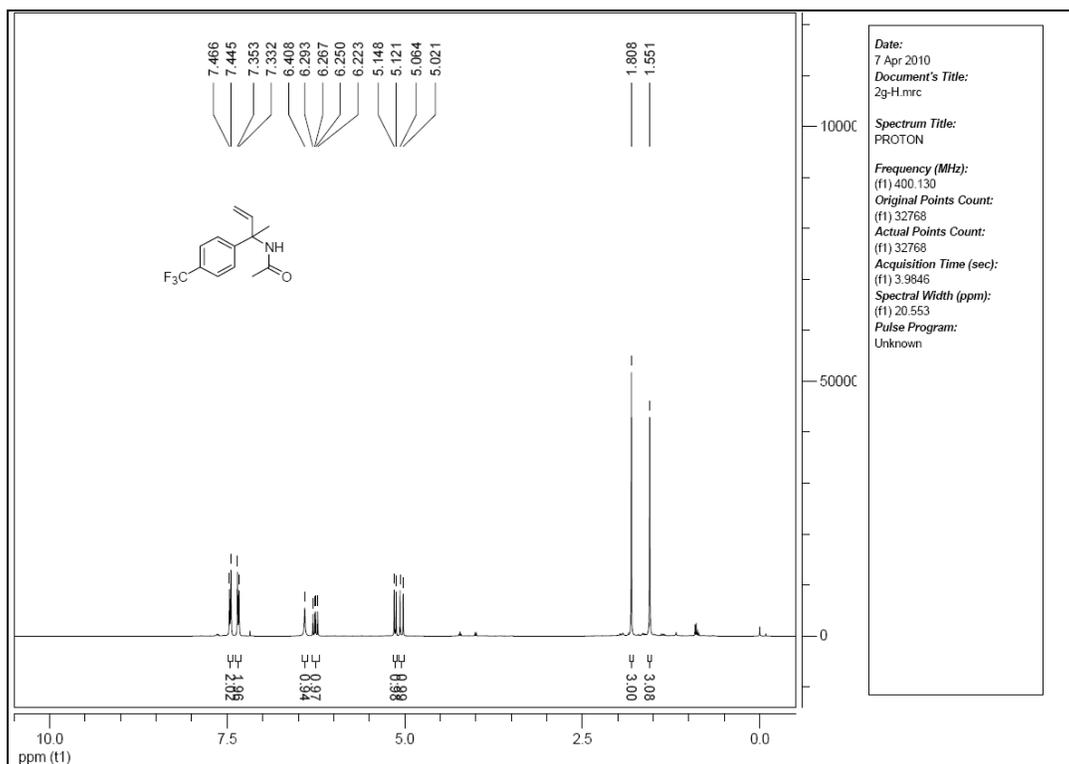
**N-Acetyl-1-methyl-1-(4-chlorophenyl)allylamine (2e)**



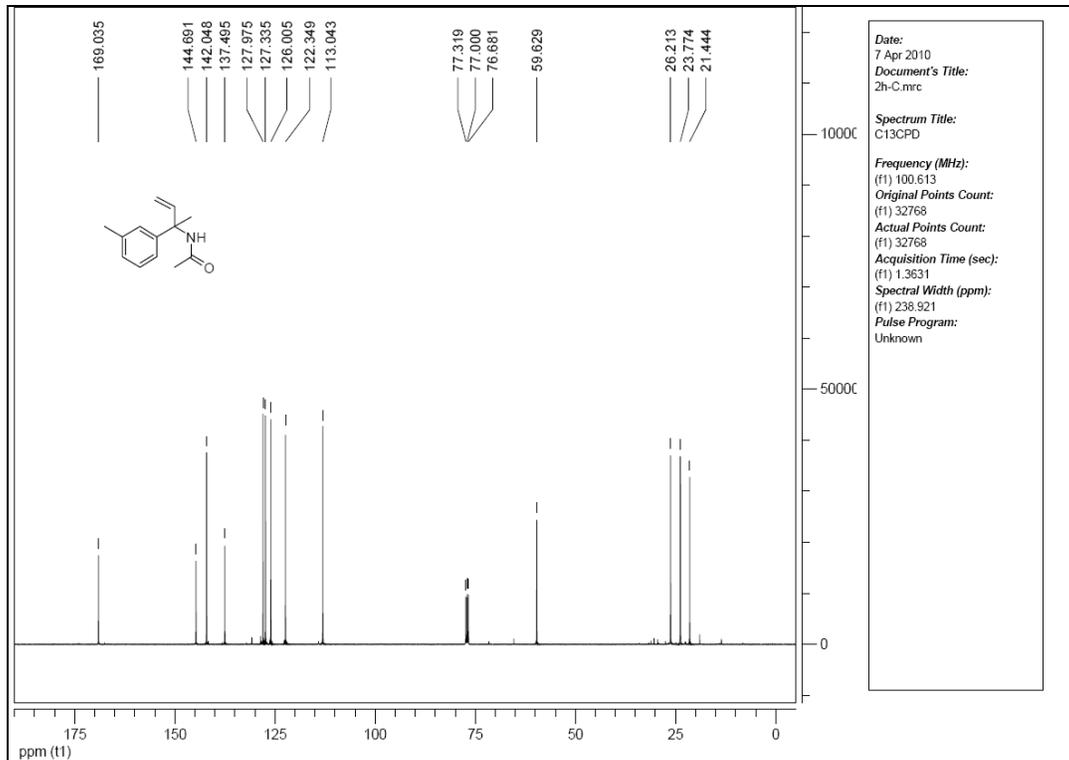
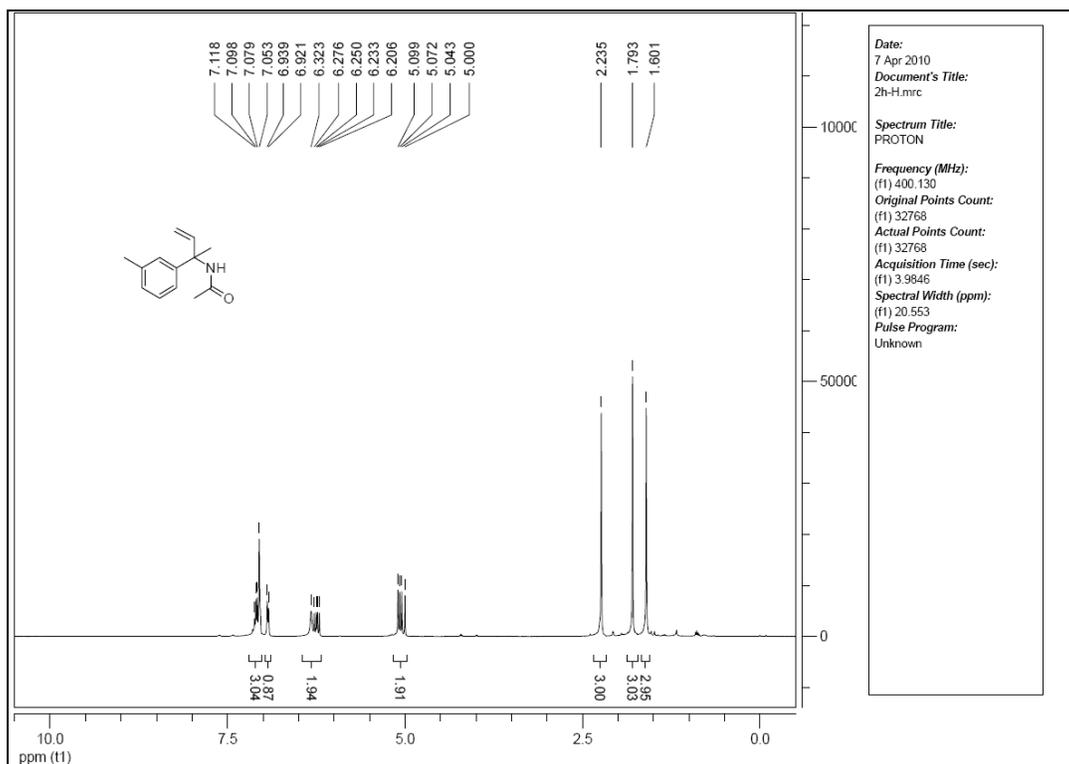
**N-Acetyl-1-methyl-1-(4-bromophenyl)allylamine (2f)**



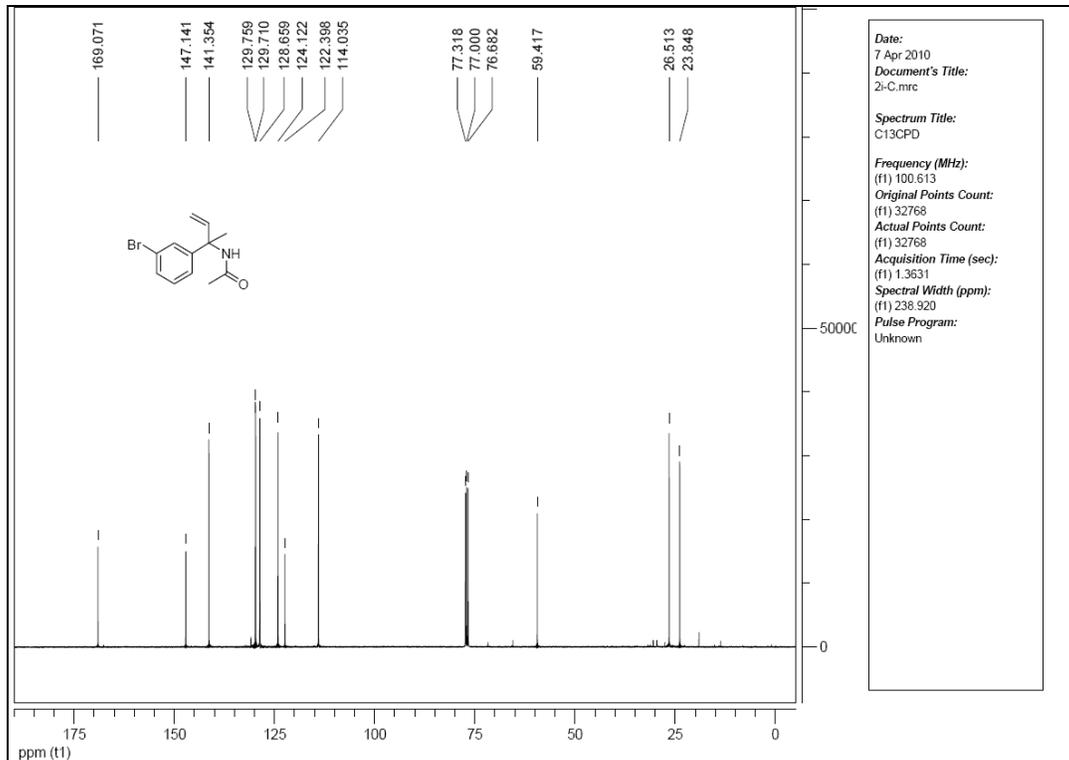
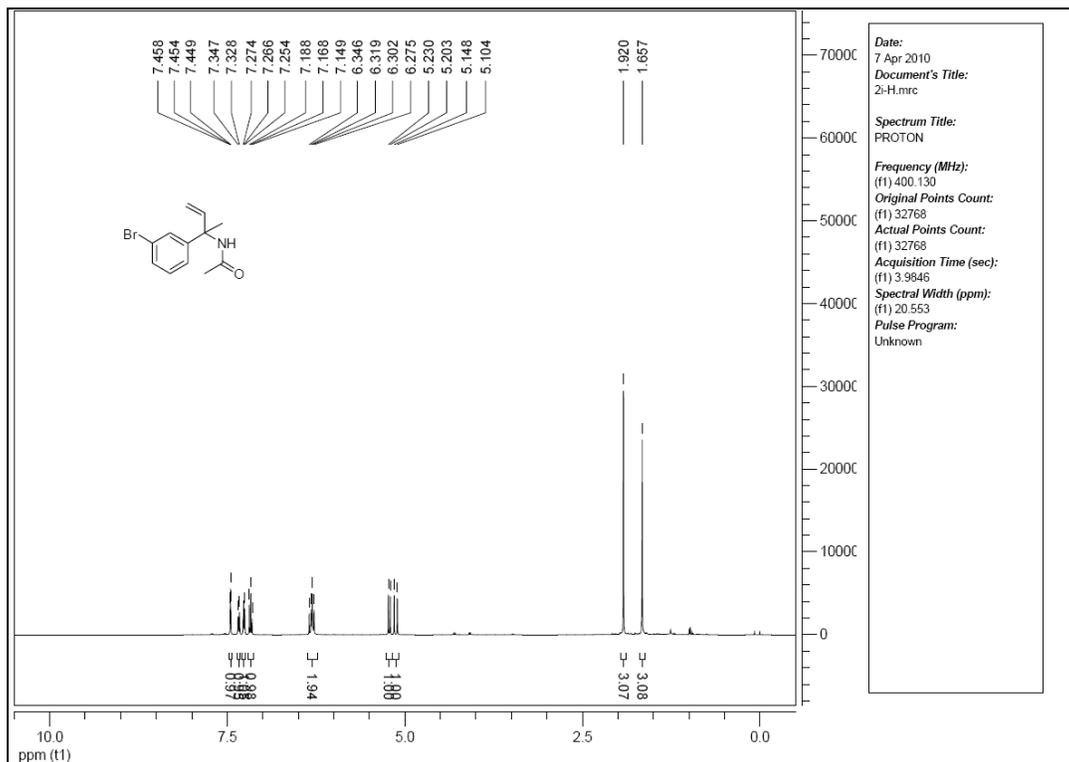
# N-Acetyl-1-methyl-1-(4-trifluoromethylphenyl)allylamine (2g)



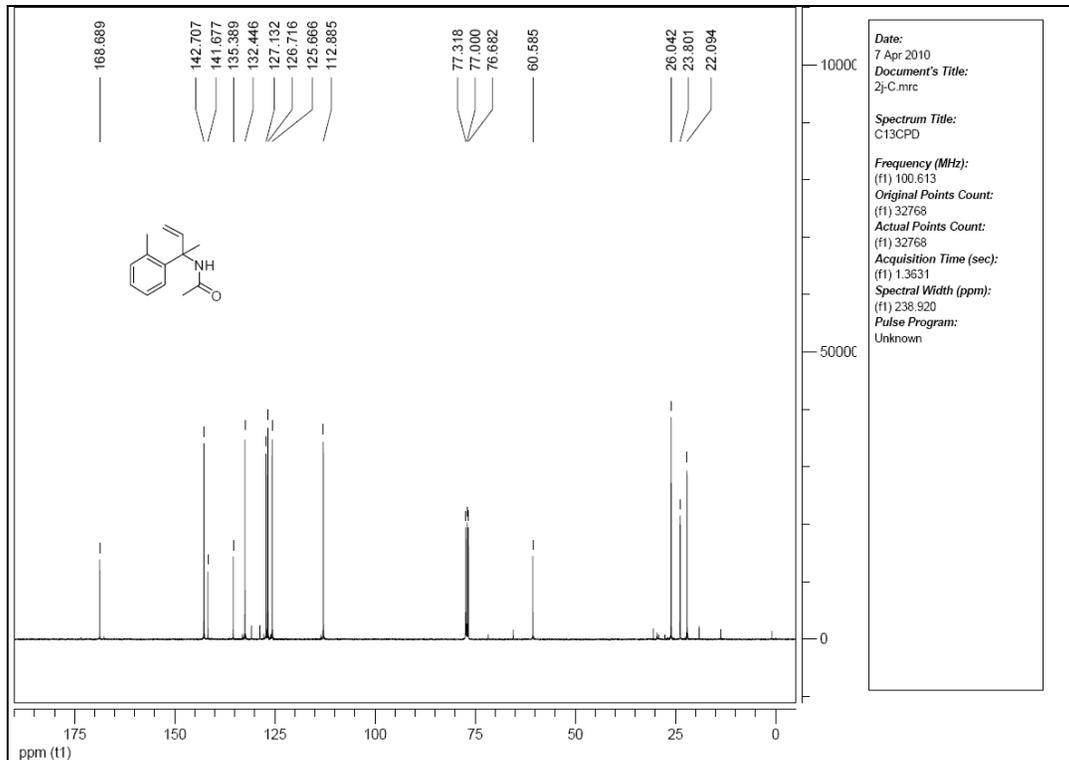
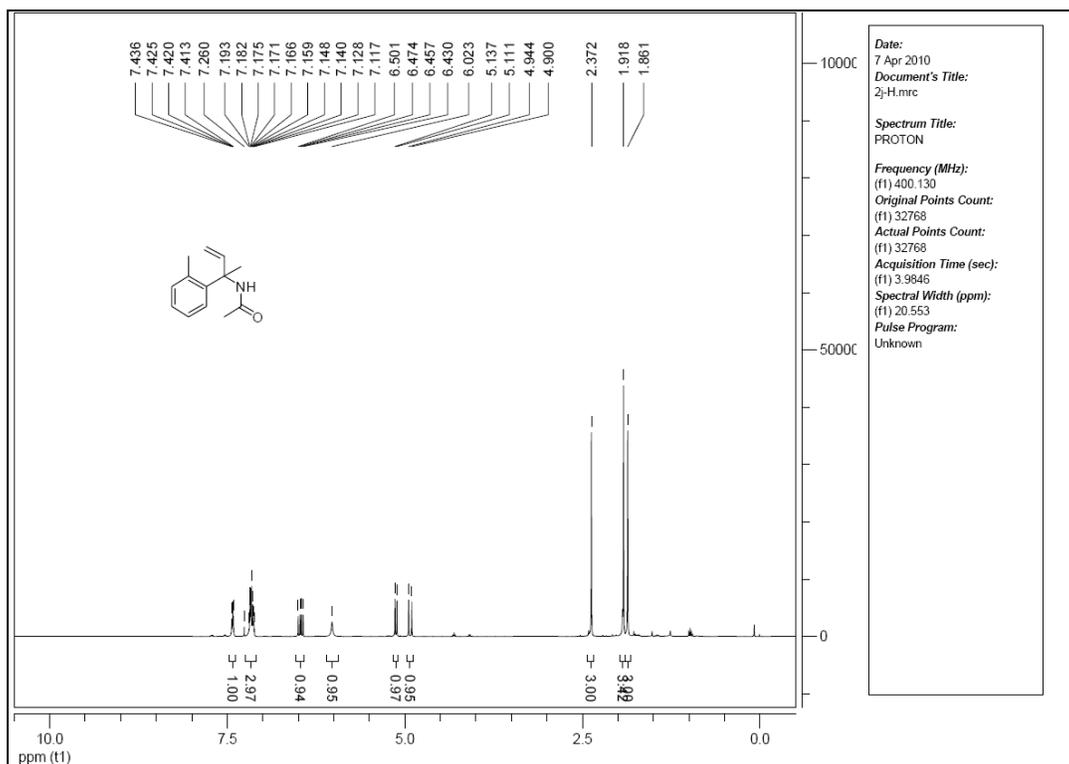
# N-Acetyl-1-methyl-1-(3-methylphenyl)allylamine (2h)



**N-Acetyl-1-methyl-1-(3-bromophenyl)allylamine (2i)**

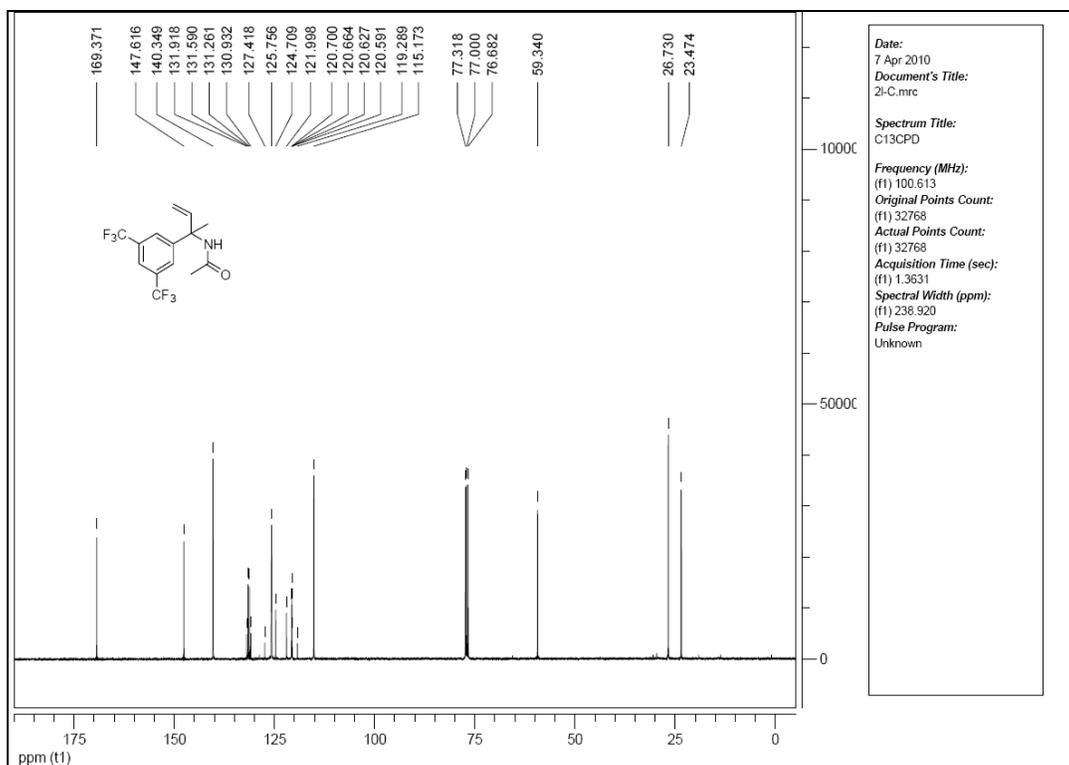
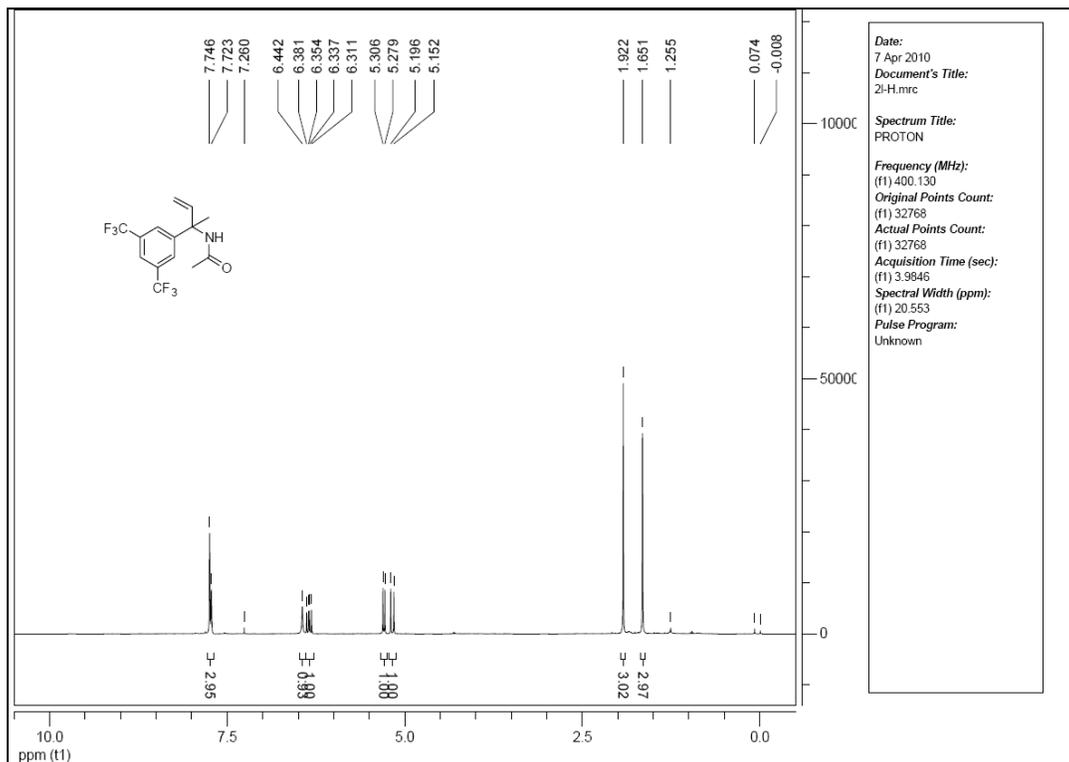


# N-Acetyl-1-methyl-1-(2-methylphenyl)allylamine (2j)

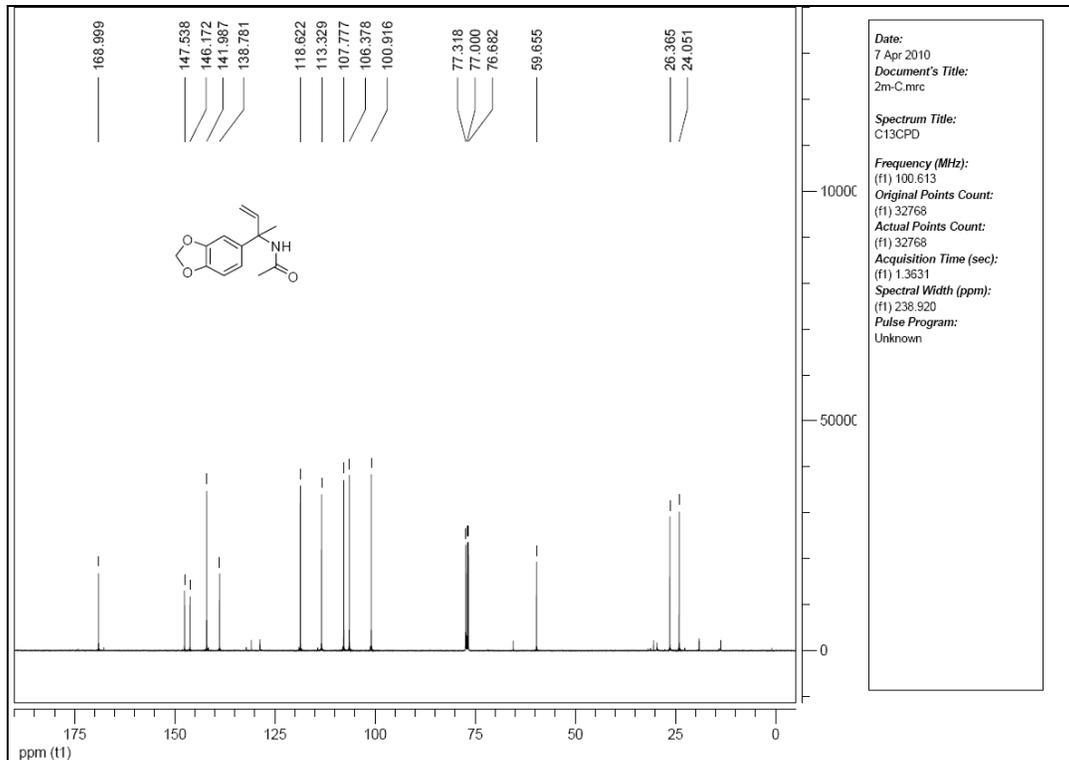
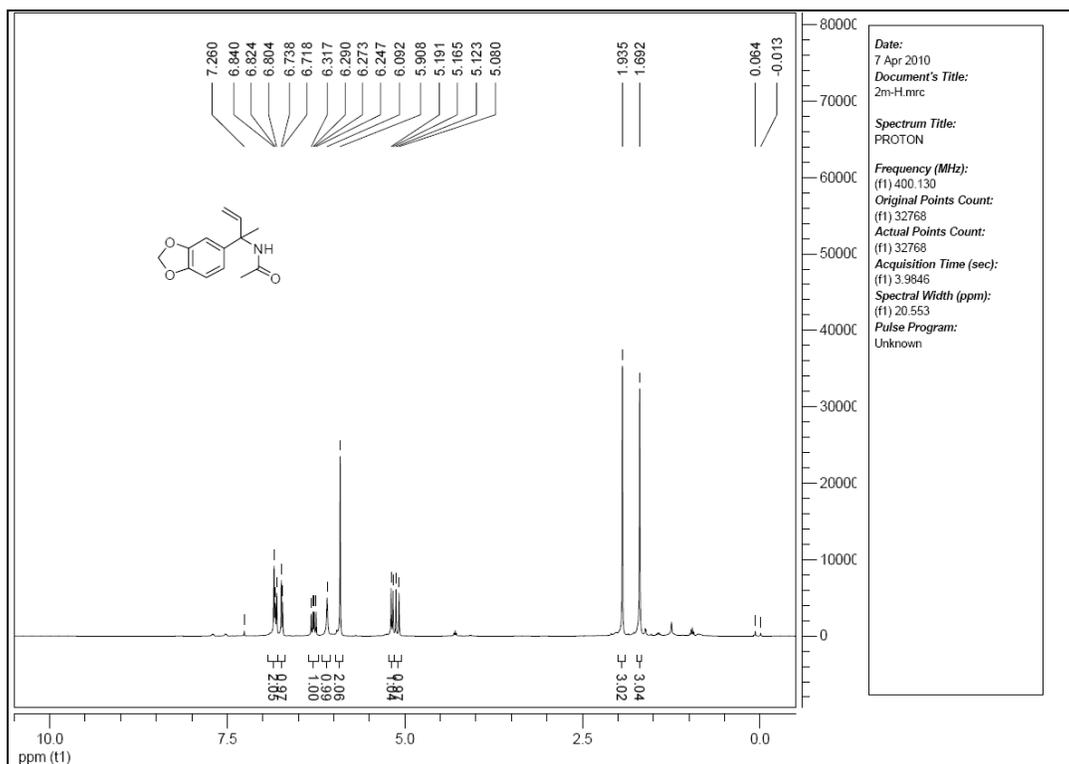




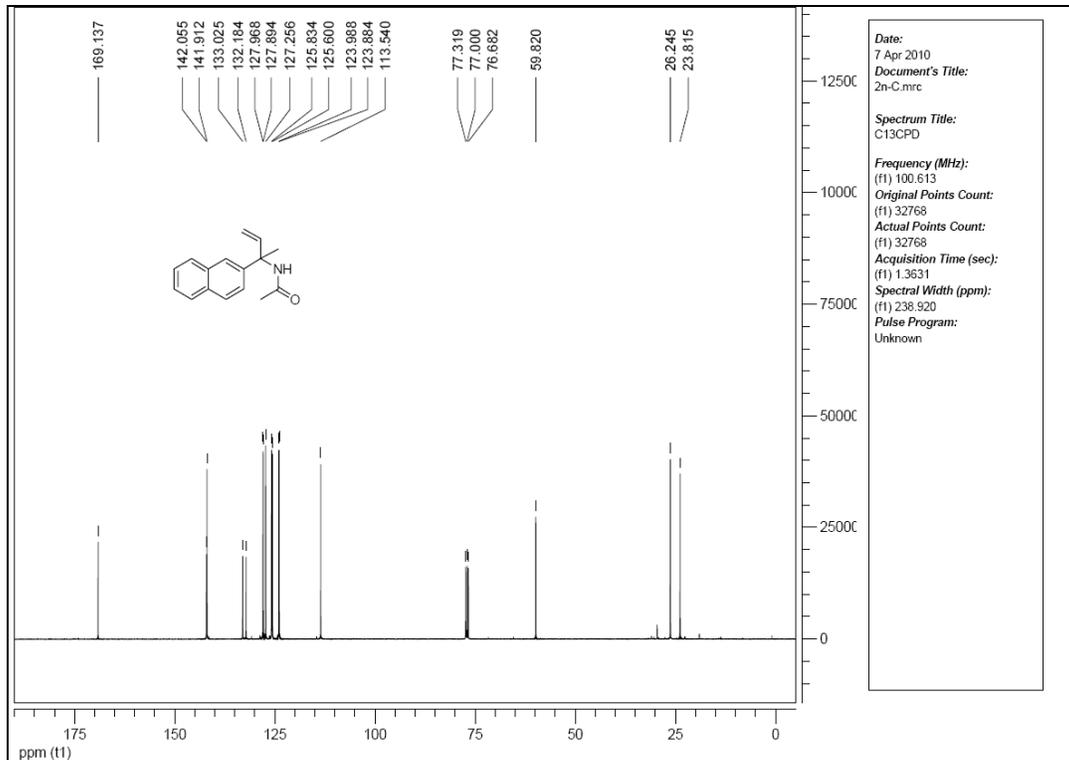
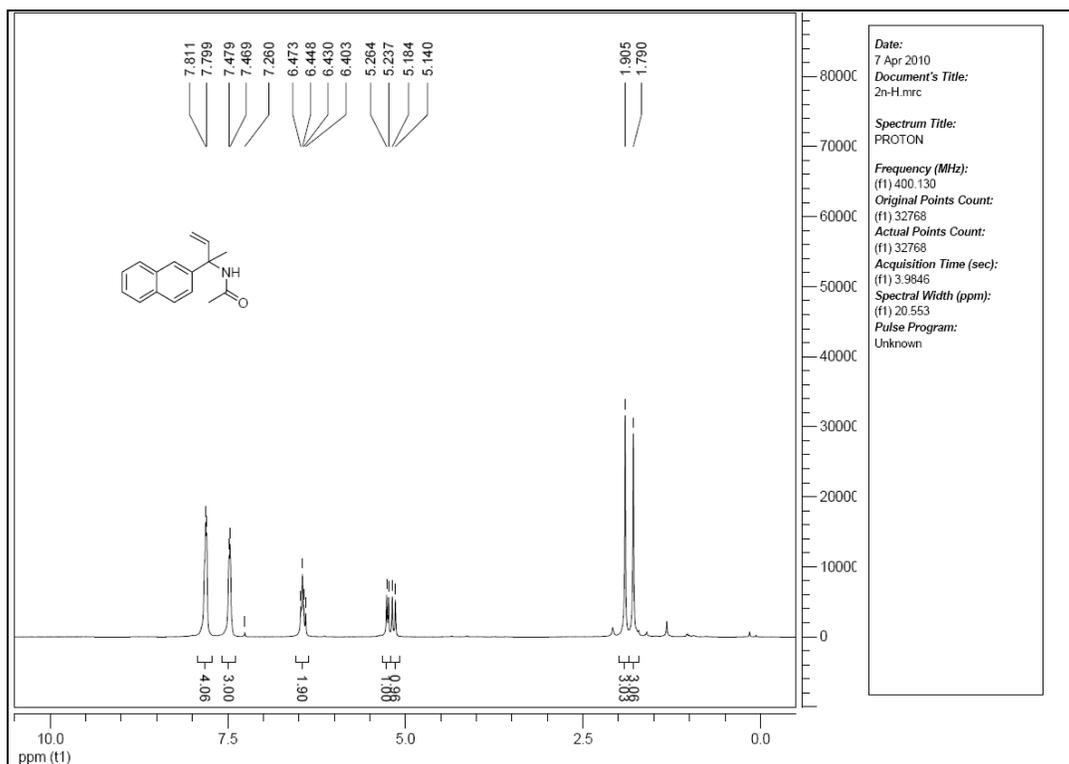
**N-Acetyl-1-methyl-1-[3,5-bis(trifluoromethyl)phenyl]allylamine (2l)**



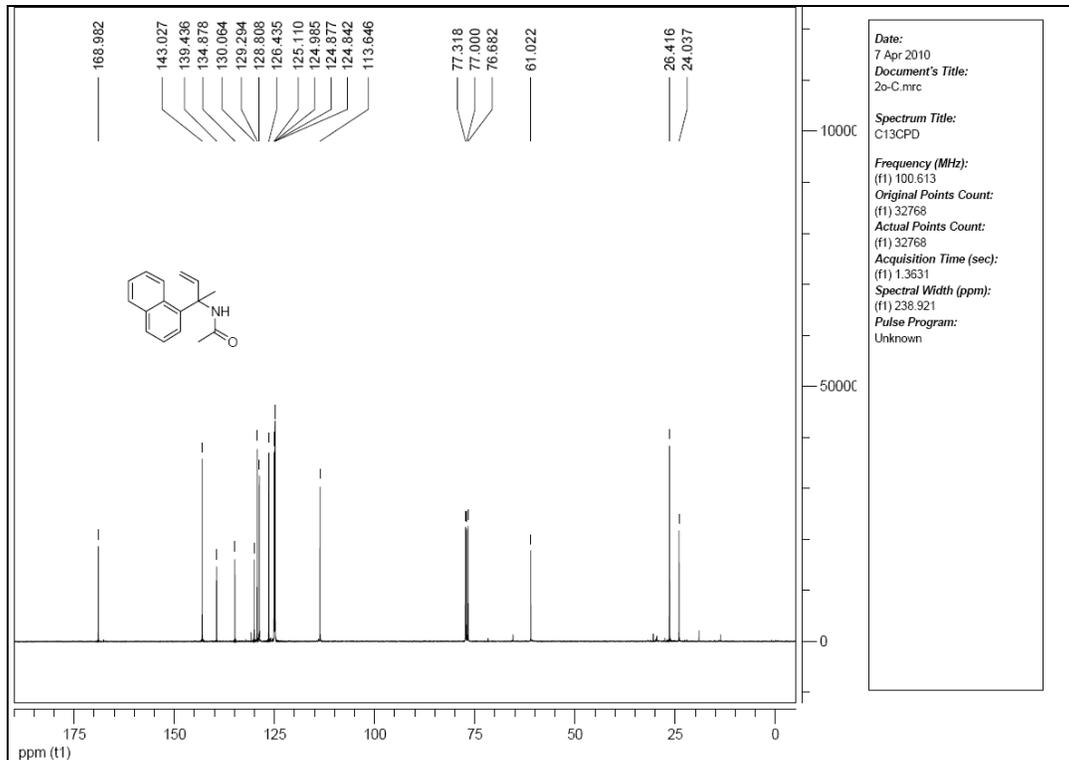
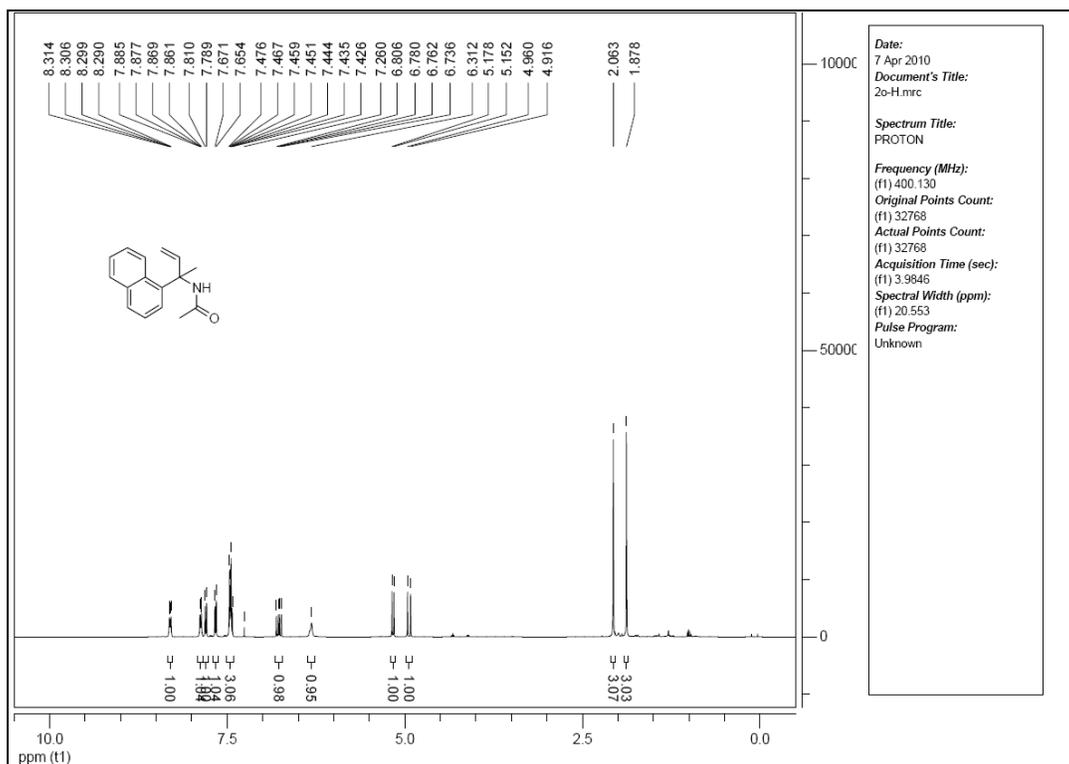
**N-Acetyl-1-methyl-1-(3,4-methylenedioxyphenyl)allylamine (2m)**



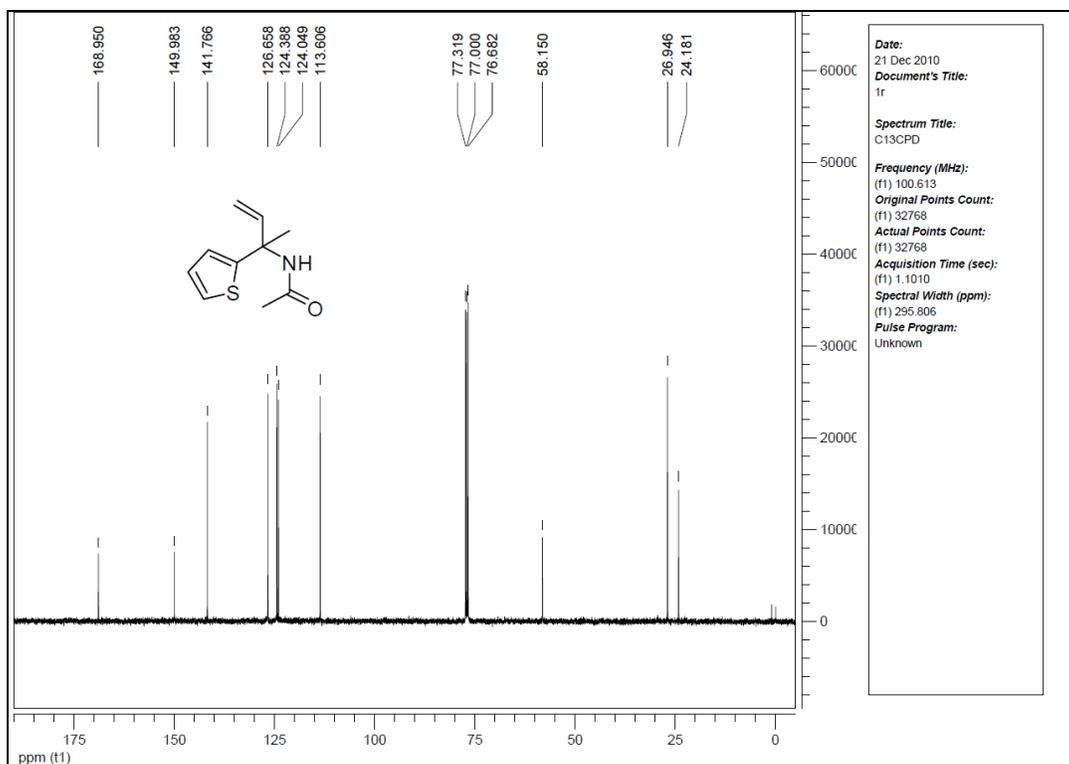
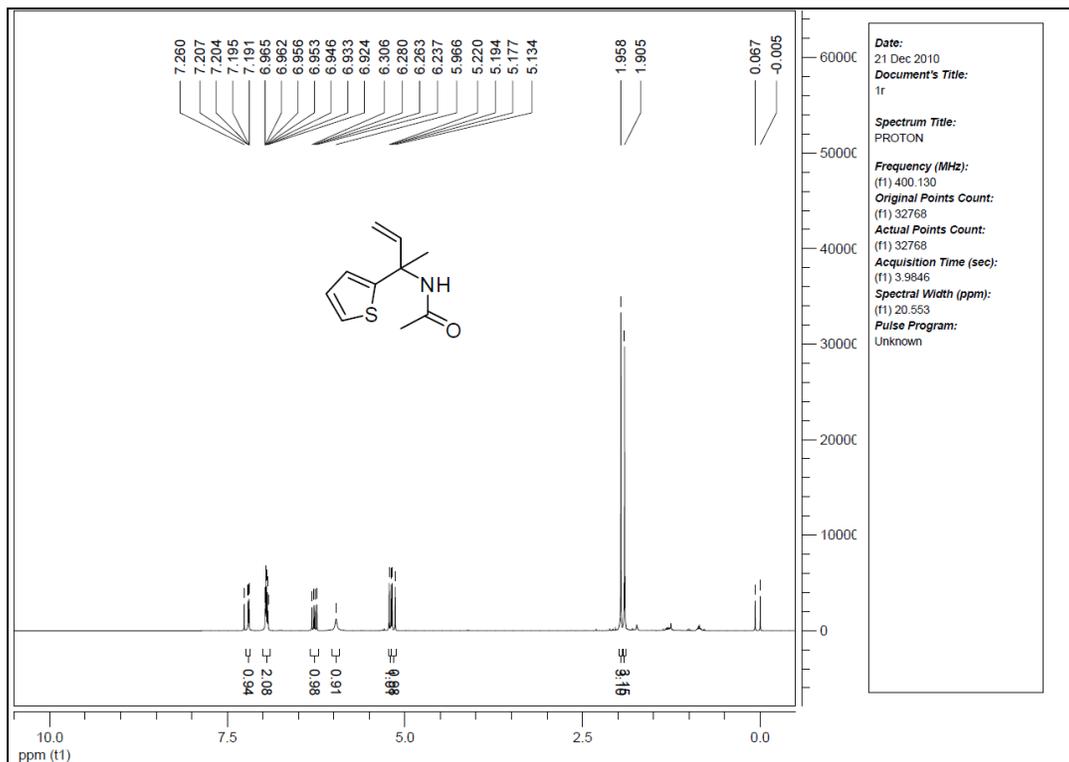
# N-Acetyl-1-methyl-1-(2-naphthalenyl)allylamine (2n)



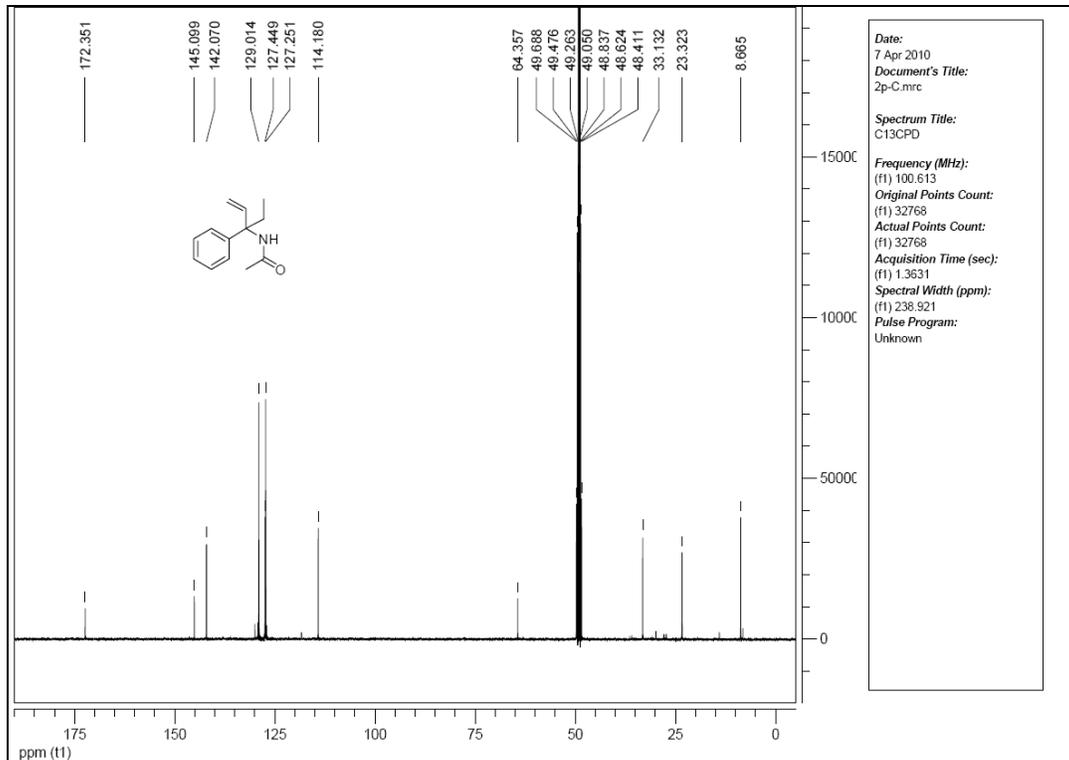
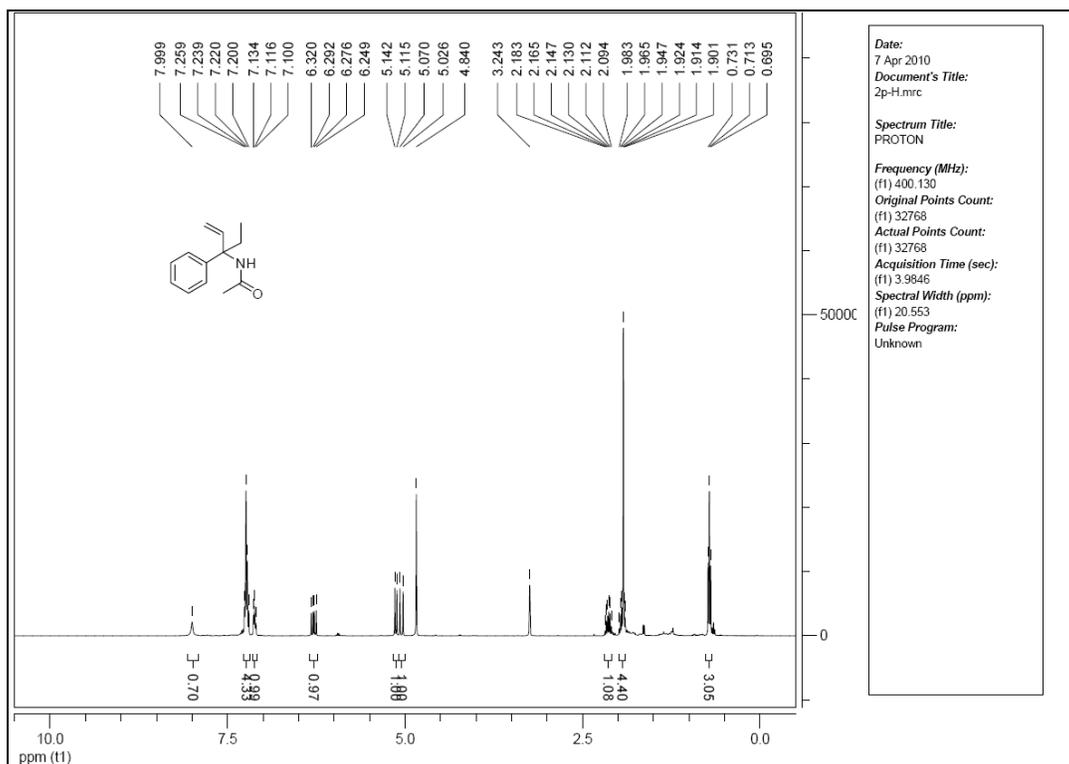
# N-Acetyl-1-methyl-1-(1-naphthalenyl)allylamine (2o)



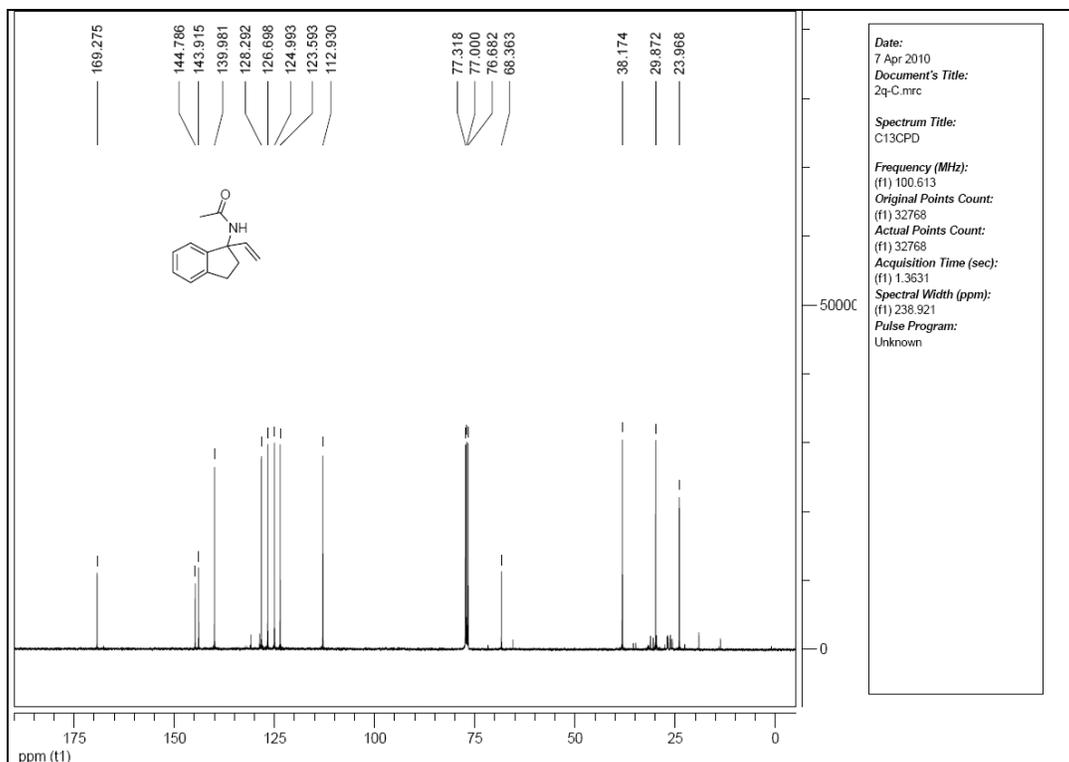
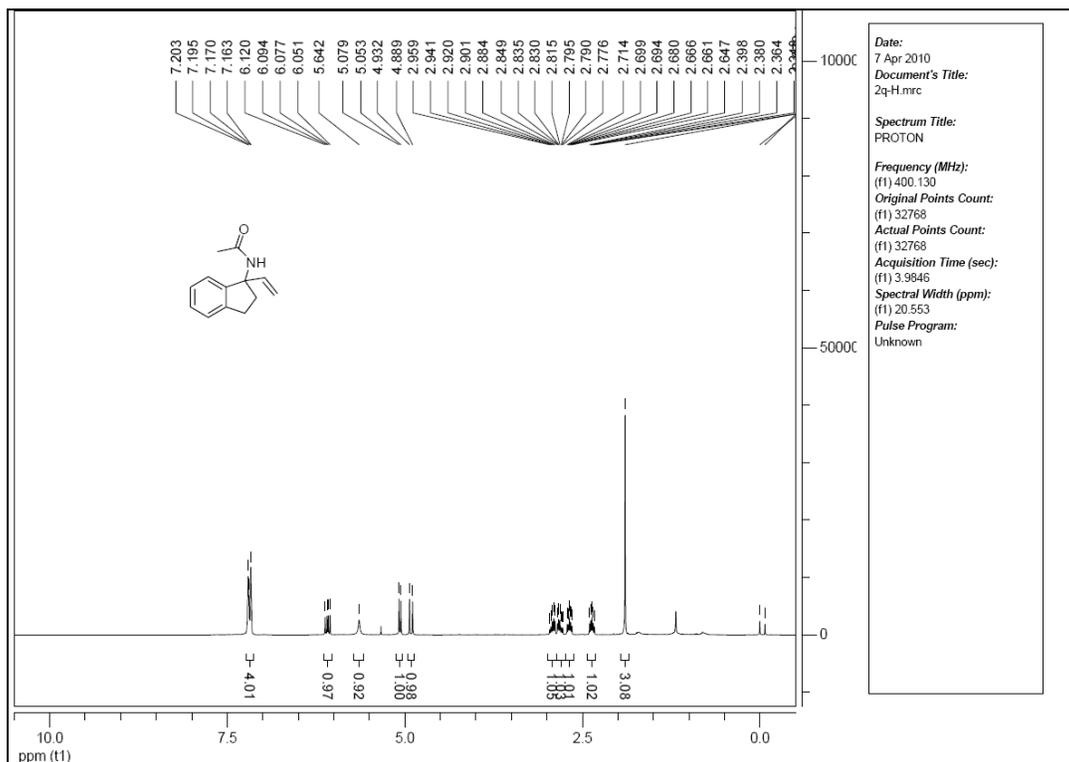
**N-(2-(thiophen-2-yl)but-3-en-2-yl)acetamide (2p)**



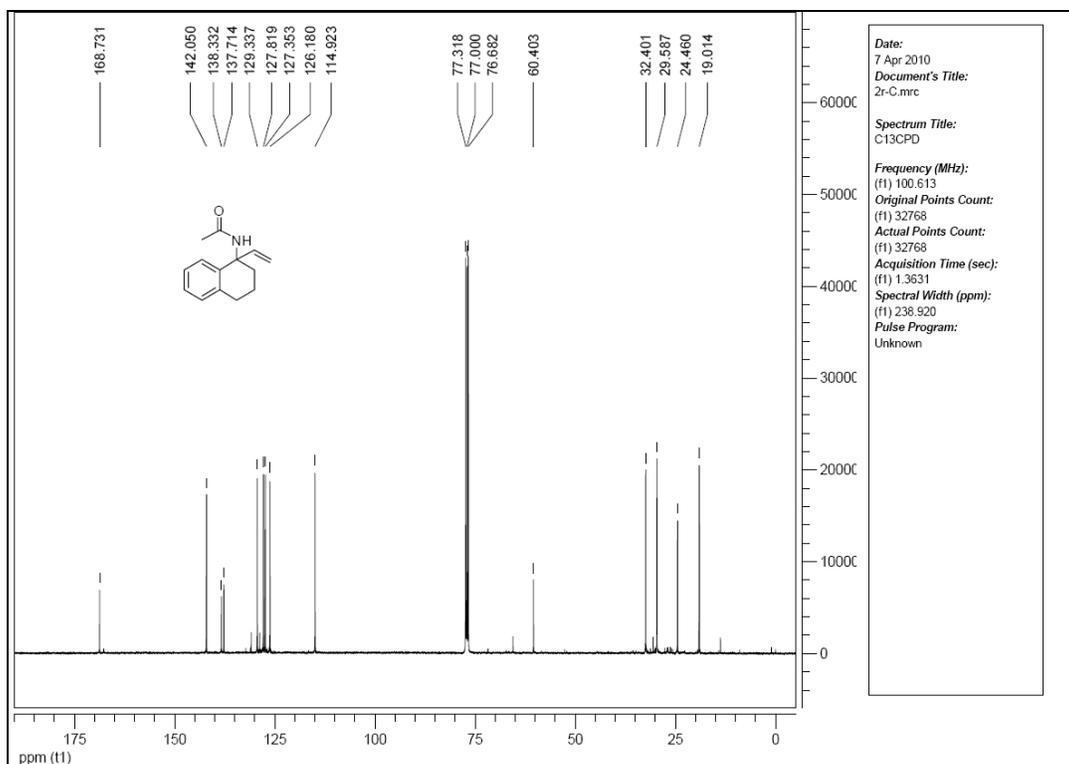
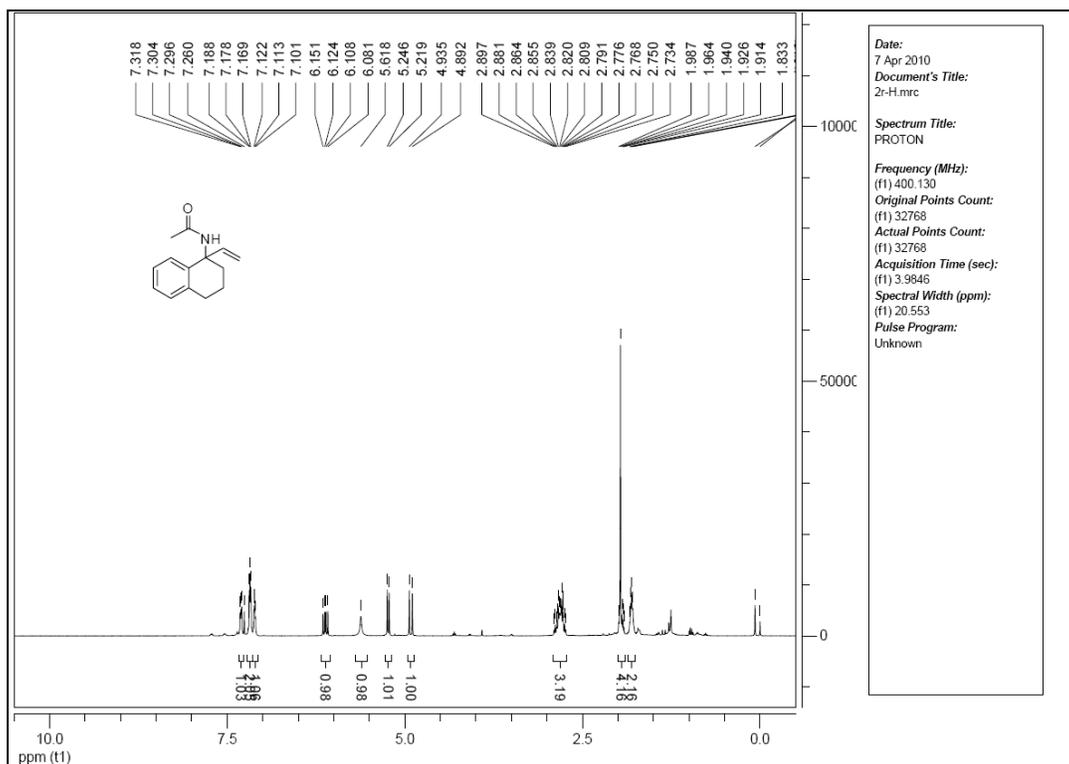
# N-Acetyl-1-ethyl-1-phenylallylamine (2q)



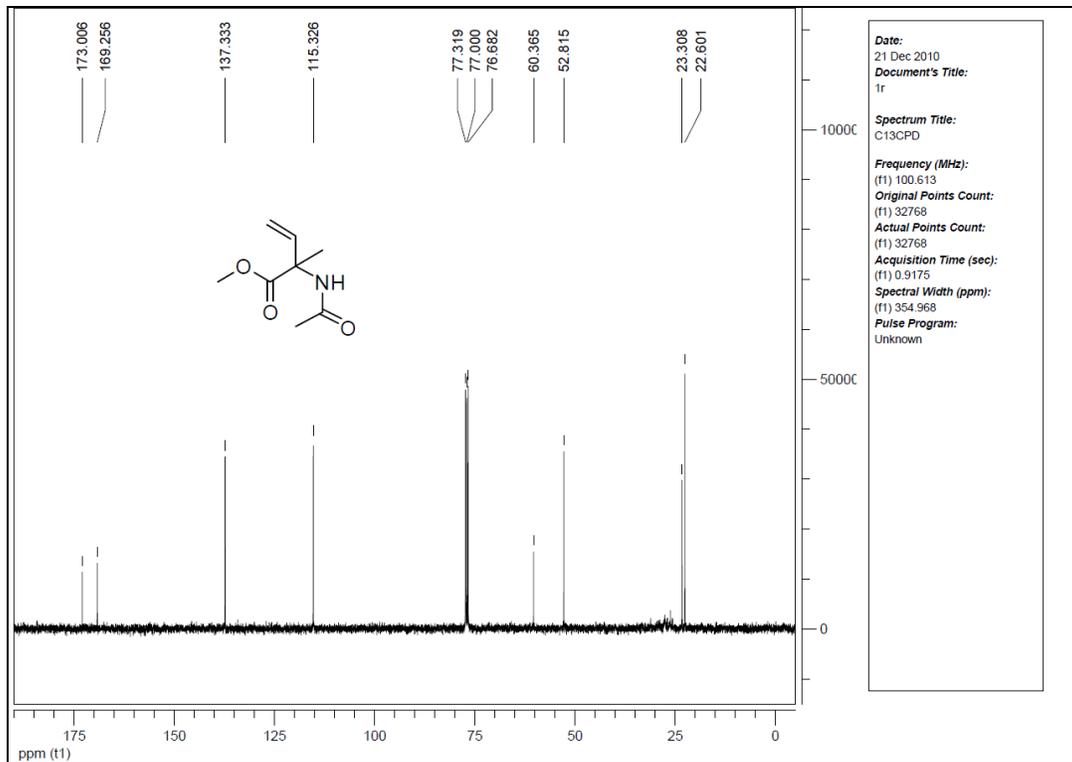
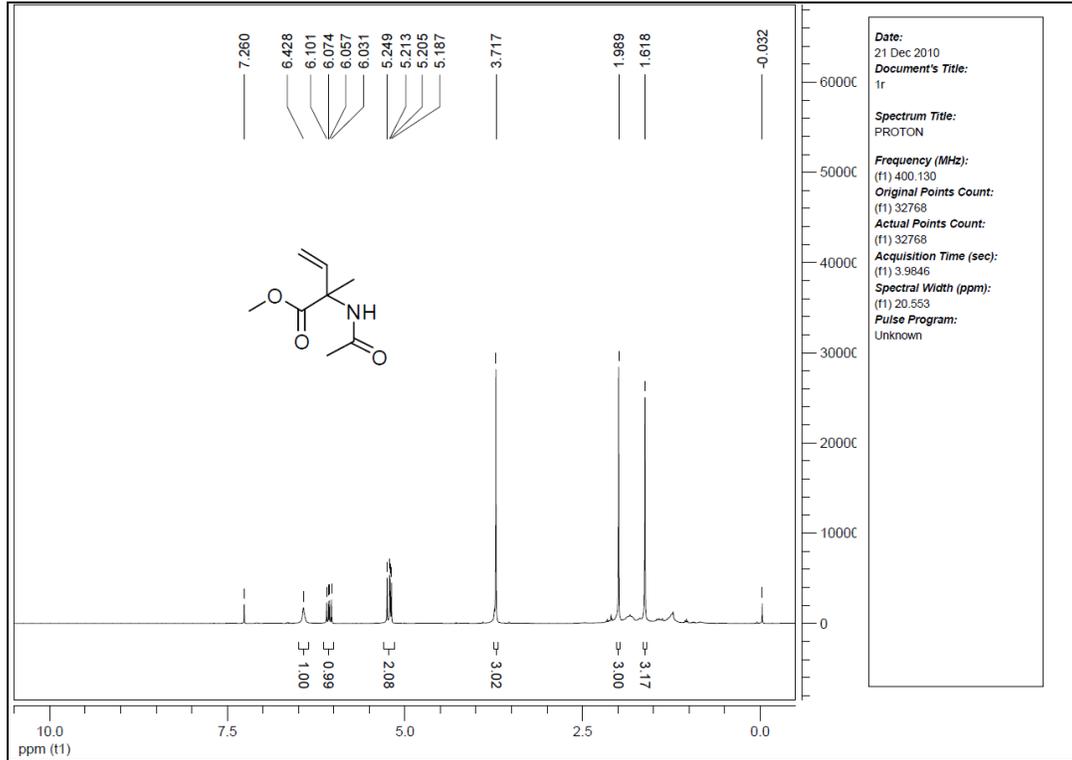
# N-Acetyl-1-vinylindan-1-amine (2r)



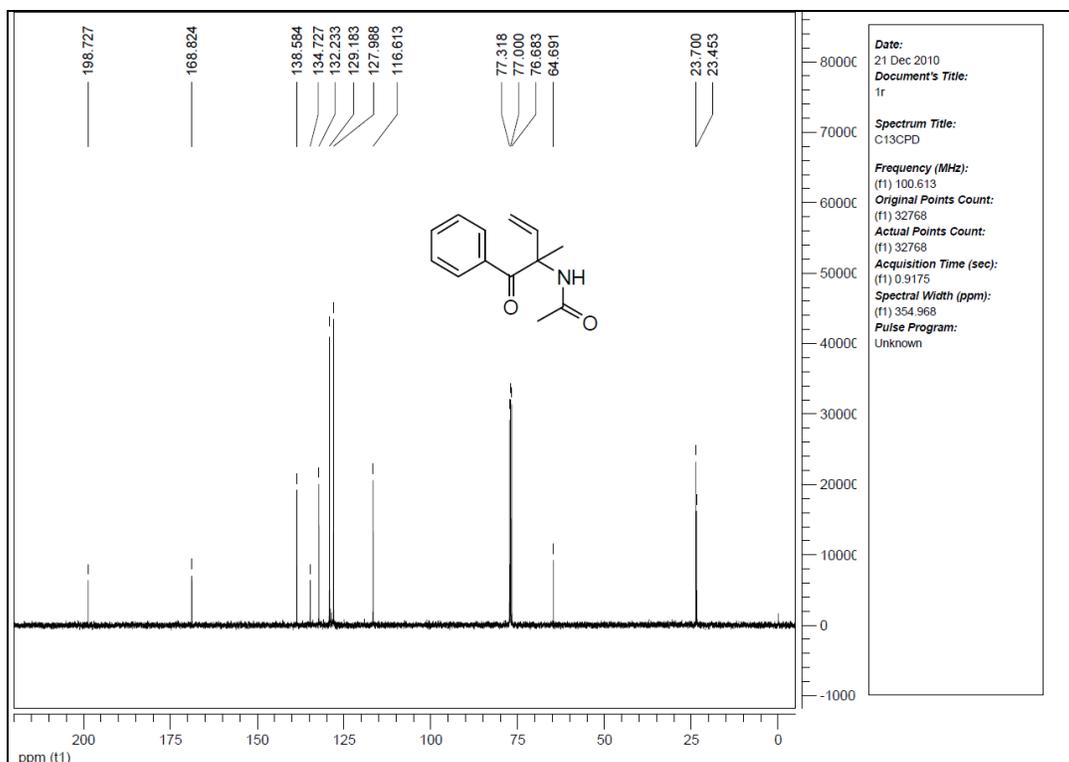
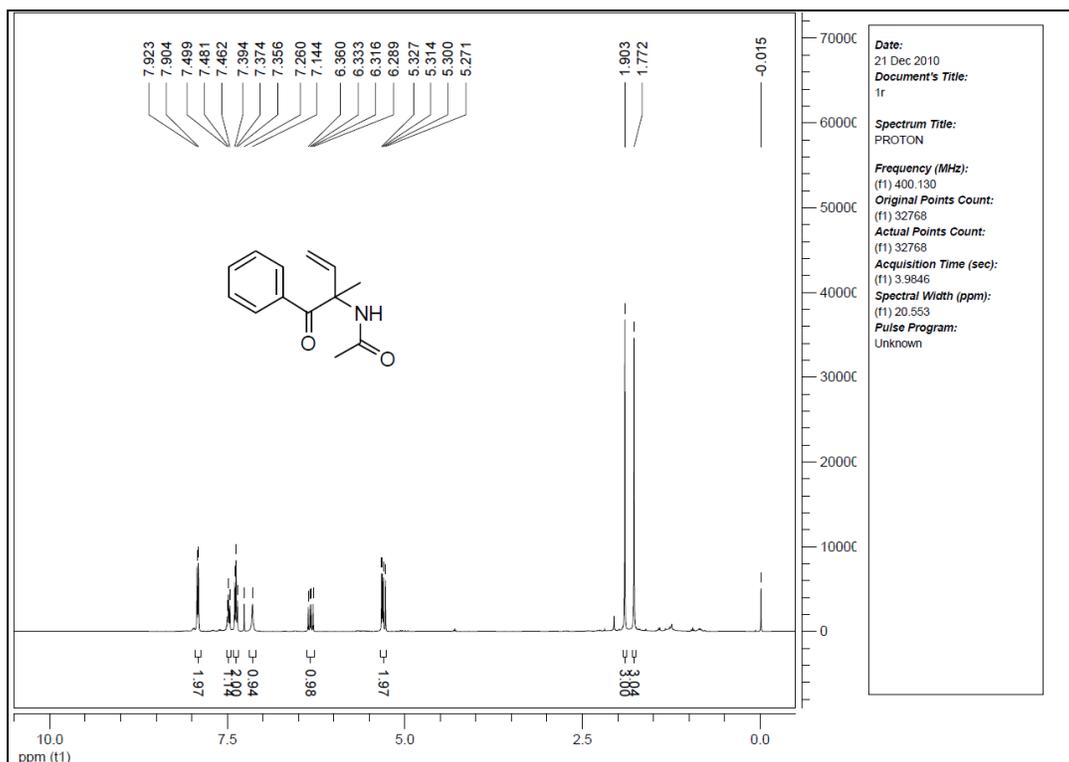
# N-Acetyl-1-vinyltetrahydronaphthyl-1-amine (2s)



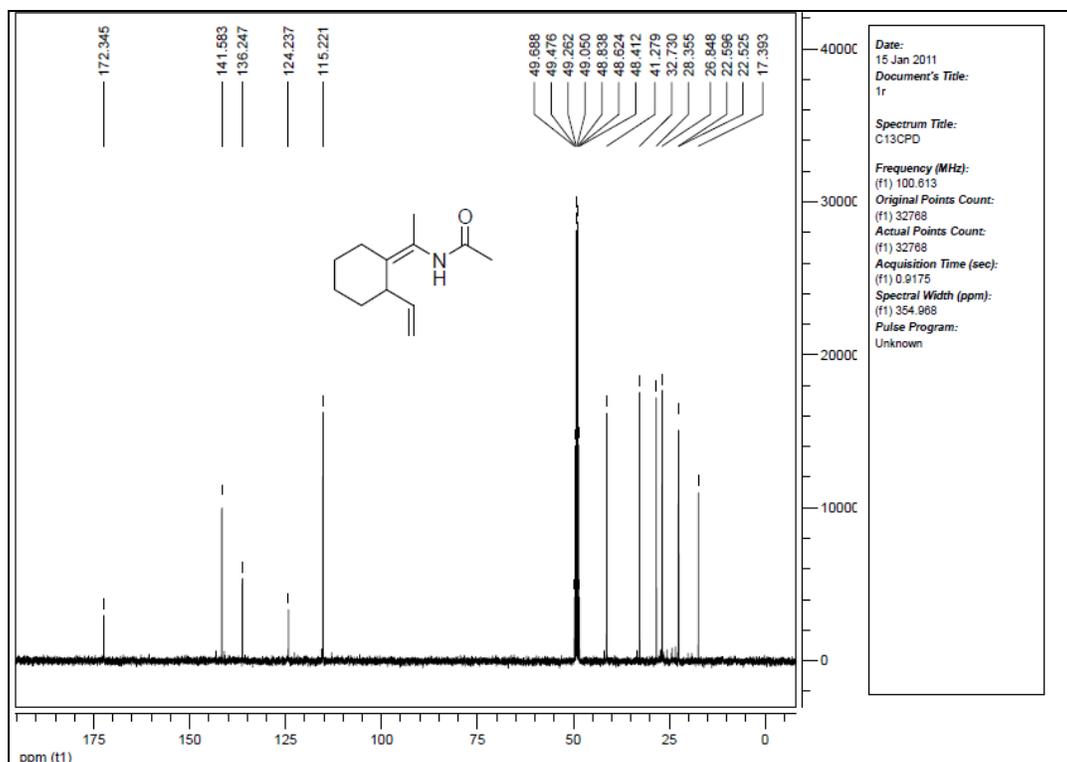
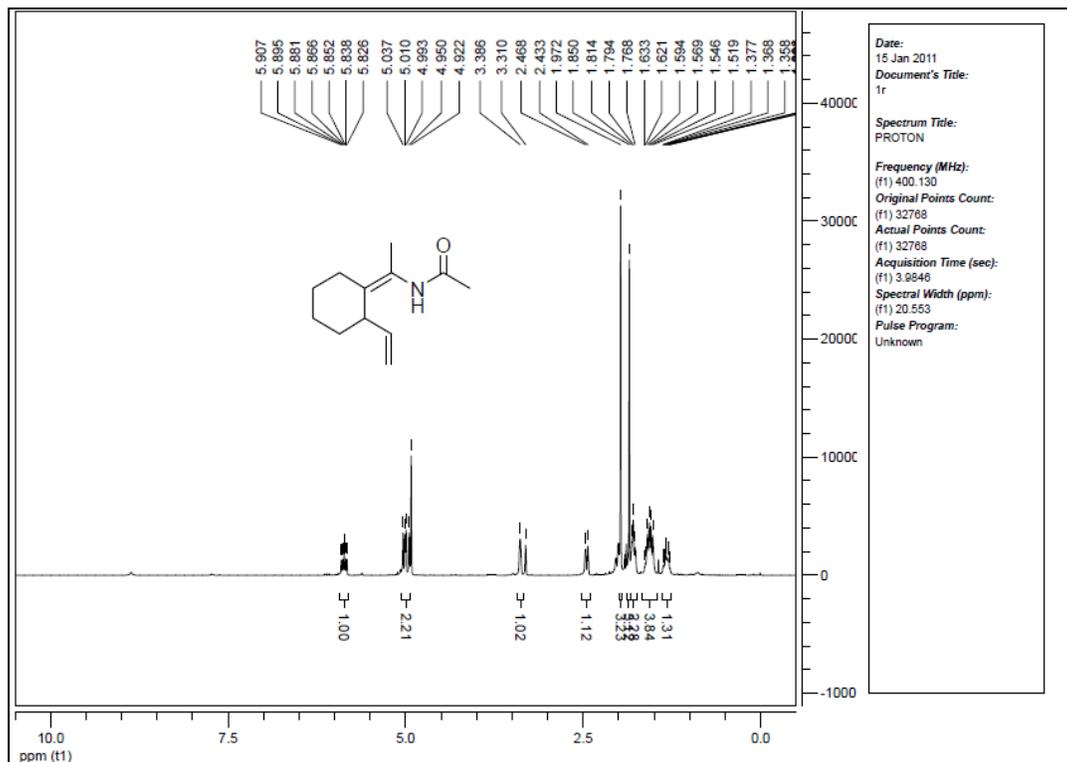
# Methyl 2-acetamido-2-methylbut-3-enoate (2t)



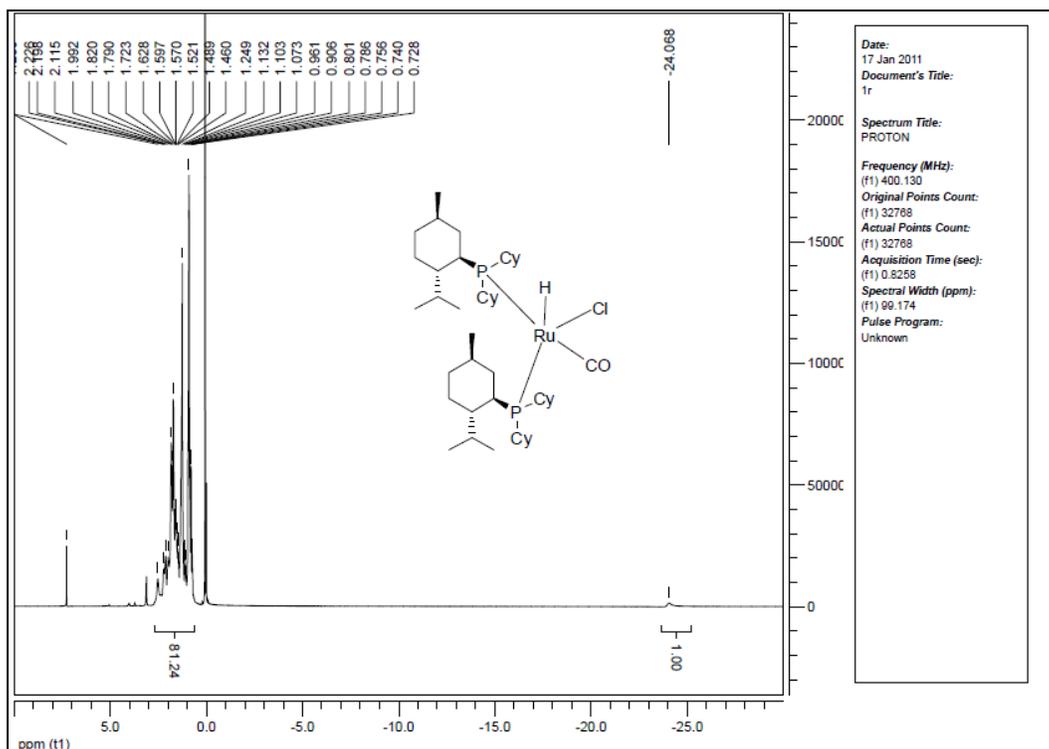
**N-Acetyl-1-methyl-1-benzoylallylamine (2u)**



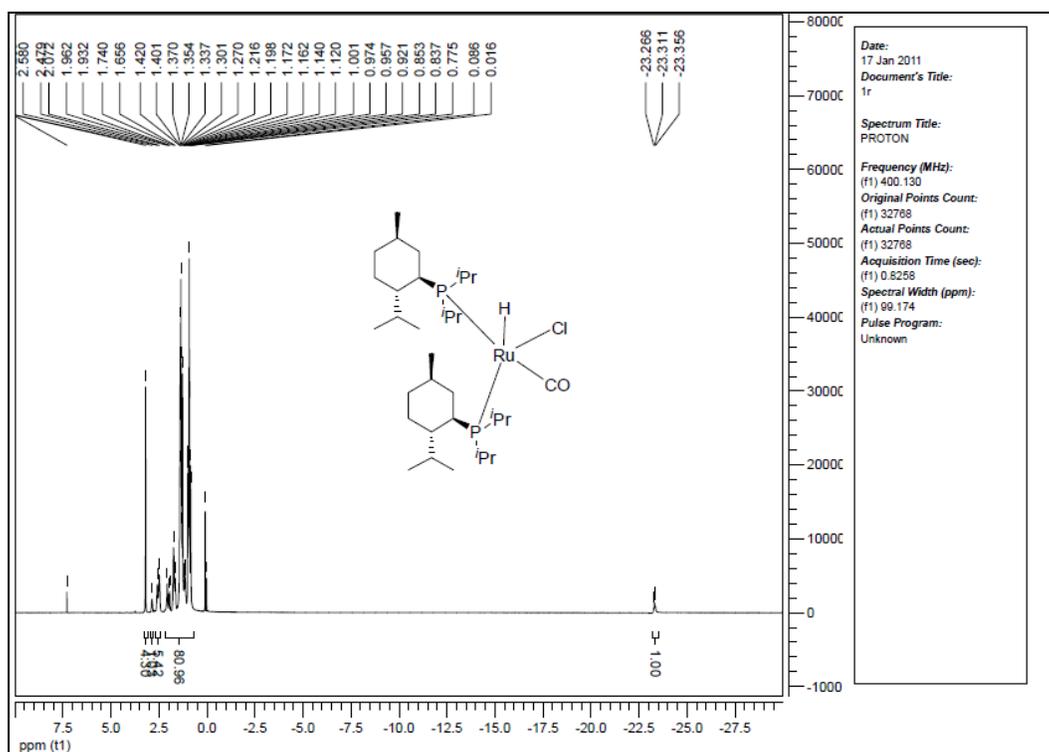
**N-(1-(2-vinylcyclohexylidene)ethyl)acetamide (3)**



**RuHCl(CO)(4a)<sub>2</sub> (4a R=Cy)**



**RuHCl(CO)(4b)<sub>2</sub> (4b R=<sup>i</sup>Pr)**



## 2-Acetamido-2-(4-methoxyphenyl)propanoic acid (5)

