

# Supporting Information

## Synthesis of Dihydropyrazoles Enabled by Pd-Catalyzed Carboamination of Alkenyl Hydrazones with Alkenyl and Aryl Halides

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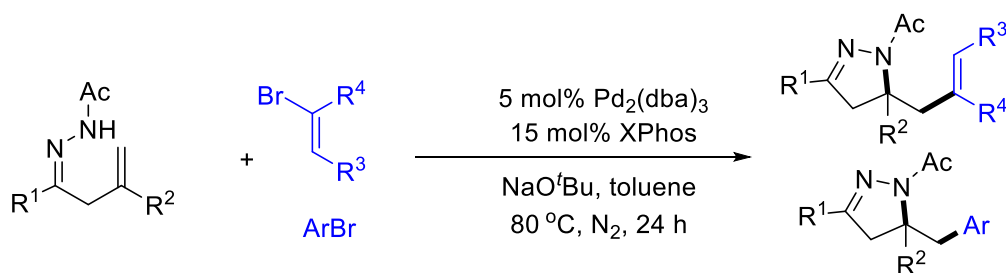
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## 1. General Information:

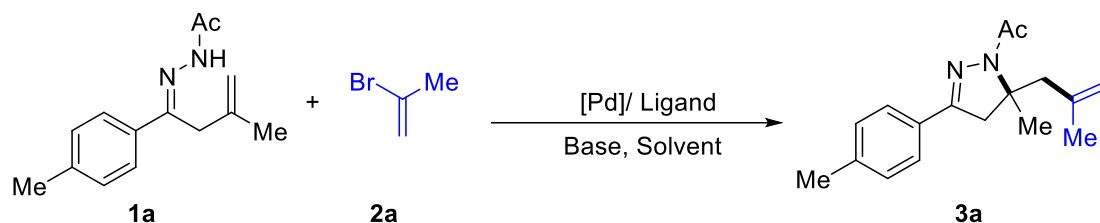
Unless otherwise noted, all reactions were carried out under a air atmosphere; materials obtained from commercial suppliers were used directly without further purification.  $^1\text{H}$  NMR spectra,  $^{13}\text{C}$  NMR spectra, and  $^{19}\text{F}$  NMR spectra were recorded on Agilent 400 or Bruker 400 MHz spectrometer in  $\text{CDCl}_3$ . NMR experiments are reported in  $\delta$  units, parts per million (ppm), and were referenced to  $\text{CDCl}_3$  ( $\delta$  7.26 or 77.0 ppm) as the internal standard. The data is being reported as (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration). All the solvents were used directly without further purification. Reactions were monitored by TLC. Flash column chromatography was performed on silica (particle size 300-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate. Copies of NMR were processed with MestReNova Software. Note,  $\text{Pd}_2(\text{dba})_3$  and Xphos were purchased from energy chemical and  $\text{NaO}^t\text{Bu}$  were purchased from TCI,  $\beta,\gamma$ -unsaturated hydrazones compounds **1** were prepared according to literature procedures.<sup>1-3</sup> Alkenyl bromides were purchased from energy chemical and directly used. Some alkenyl bromides were prepared according to literature procedures<sup>4</sup>.

## 2. General procedure:



A 10 mL sealed tube was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (22.9 mg, 0.025 mmol, 0.05 equiv), Xphos (35.8 mg, 0.075 mmol, 0.15 equiv) and toluene (2.0 mL). After the Pd catalyst/ligand solution was stirred for 10 min at 25 °C.  $\beta$ ,  $\gamma$ -unsaturated hydrazone **1** (0.5 mmol, 1 equiv), vinyl bromides or aryl bromides **2** (1.0 mmol, 2.0 equiv) and NaO<sup>t</sup>Bu (48.1 mg, 0.5 mmol, 1.0 equiv) were added sequentially. Degassed toluene and backfilled with N<sub>2</sub> for 3 times (3  $\times$  1min) at -78 °C. Under nitrogen atmosphere, the reaction mixture was stirred at 80 °C for 24 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product.

## 3. Table S1. Optimization of reaction conditions:

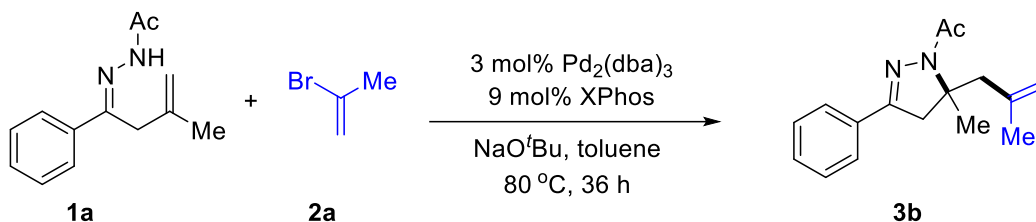


Entry	Pd catalyst	ligand	base	solvent	yield (%) <sup>b</sup>
1	Pd <sub>2</sub> (dba) <sub>3</sub>	PPh <sub>3</sub>	NaO <sup>t</sup> Bu	Toluene	41
2	Pd <sub>2</sub> (dba) <sub>3</sub>	dppf	NaO <sup>t</sup> Bu	Toluene	76
3	Pd <sub>2</sub> (dba) <sub>3</sub>	Xantphos	NaO <sup>t</sup> Bu	Toluene	42
4	Pd <sub>2</sub> (dba) <sub>3</sub>	Dpephos	NaO <sup>t</sup> Bu	Toluene	69
5	Pd <sub>2</sub> (dba) <sub>3</sub>	RuPhos	NaO <sup>t</sup> Bu	Toluene	83
6	Pd <sub>2</sub> (dba) <sub>3</sub>	XPhos	NaO <sup>t</sup> Bu	Toluene	85(79) <sup>d</sup>
7 <sup>c</sup>	Pd <sub>2</sub> (dba) <sub>3</sub>	XPhos	NaO <sup>t</sup> Bu	Toluene	76

8	Pd <sub>2</sub> (dba) <sub>3</sub>	--	NaO <sup>t</sup> Bu	Toluene	trace
9	[Pd(allyl)Cl] <sub>2</sub>	XPhos	NaO <sup>t</sup> Bu	Toluene	73
10 <sup>e</sup>	PdCl <sub>2</sub>	XPhos	NaO <sup>t</sup> Bu	Toluene	<5
11 <sup>e</sup>	Pd(OAc) <sub>2</sub>	XPhos	NaO <sup>t</sup> Bu	Toluene	10
12 <sup>e</sup>	Pd(acac) <sub>2</sub>	XPhos	NaO <sup>t</sup> Bu	Toluene	58
13	Pd <sub>2</sub> (dba) <sub>3</sub>	XPhos	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	67
14	Pd <sub>2</sub> (dba) <sub>3</sub>	XPhos	K <sub>2</sub> CO <sub>3</sub>	Toluene	43
15	Pd <sub>2</sub> (dba) <sub>3</sub>	XPhos	Na <sub>2</sub> CO <sub>3</sub>	Toluene	trace
16	Pd <sub>2</sub> (dba) <sub>3</sub>	XPhos	NaO <sup>t</sup> Bu	THF	68
17	Pd <sub>2</sub> (dba) <sub>3</sub>	XPhos	NaO <sup>t</sup> Bu	1,4-Dioxane	66
18	Pd <sub>2</sub> (dba) <sub>3</sub>	XPhos	NaO <sup>t</sup> Bu	CH <sub>3</sub> CN	71
19	Pd <sub>2</sub> (dba) <sub>3</sub>	XPhos	NaO <sup>t</sup> Bu	DCE	73

<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol, 2 equiv), 5 mol% Pd catalyst, 15 mol% of ligand and base (0.5 mmol, 1.0 equiv) in solvent (2.0 mL) at 80 °C under N<sub>2</sub> for 24 h. <sup>b</sup>Isolated yield. <sup>c</sup>Under air for 24 h. <sup>d</sup>**1a** (0.5 mmol), **2a** (1.0 mmol, 2 equiv), 5 mol% Pd<sub>2</sub>(dba)<sub>3</sub>, 15 mol% ligand and NaO<sup>t</sup>Bu (0.5 mmol, 1.0 equiv) in solvent (2.0 mL) at 80 °C under N<sub>2</sub> for 24 h. <sup>e</sup>Pd catalyst (10 mol%), ligand (15 mol%) was used.

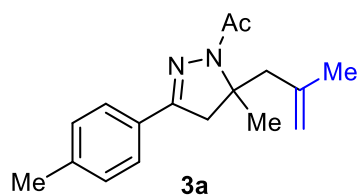
#### 4. Gram-scale synthesis of **3b**:



A 100 mL Schlenk bottom flask was charged with Pd<sub>2</sub>(dba)<sub>3</sub> (274.7 mg, 0.3 mmol, 0.03 equiv), Xphos (429.1 mg, 0.9 mmol, 0.09 equiv) and toluene (40 mL). After the Pd catalyst/ligand solution was stirred for 10 min at 25 °C. β, γ-unsaturated hydrazone **1a** (2.163 g, 10 mmol, 1 equiv), vinyl bromides **2a** (2.420 g, 20 mmol, 2 equiv) and NaO<sup>t</sup>Bu (0.961 g, 10 mmol, 1.0 equiv) were added sequentially. Degassed toluene and backfilled with N<sub>2</sub> for 3 times (3 ×1min) at -78 °C. Under nitrogen atmosphere, the reaction mixture was stirred at 80 °C for 36 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **3b** 1.93 g in 75% yield.



## 5. Characterization data for the product



### 1-(5-methyl-5-(2-methylallyl)-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (**3a**):

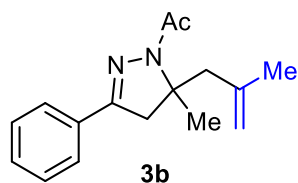
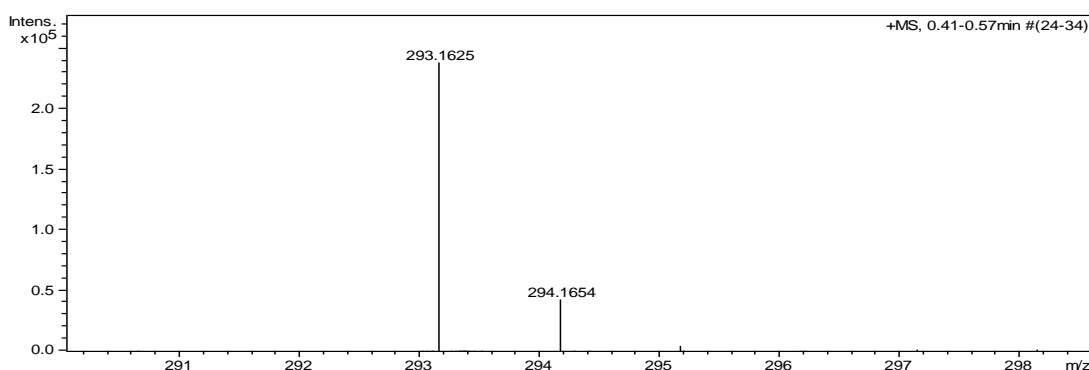
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **3a** (106.7 mg, 79% yield) as a white solid. Mp: 53 - 55 °C.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.84 (s, 1H), 4.71 (s, 1H), 3.47 (d, *J* = 17.6 Hz, 1H), 3.22 (d, *J* = 14.4 Hz, 1H), 2.90 (d, *J* = 17.2 Hz, 1H), 2.43 (d, *J* = 14.0 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 1.69 (s, 3H), 1.67 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 169.8, 152.7, 142.2, 140.2, 129.3, 129.0, 126.2, 115.3, 65.9, 45.2, 44.9, 26.8, 23.5, 23.1, 21.4;

**IR** (KBr)  $\nu$ : 3285, 3071, 2971, 2920, 2303, 1901, 1810, 1653, 1422, 1363, 1327, 1264, 1226, 1182, 1118, 1033, 958, 928, 900, 847, 810, 745, 710, 623, 563, 534, 488, 463, 431 cm<sup>-1</sup>;

**HRMS** Calcd (ESI) *m/z* for C<sub>17</sub>H<sub>22</sub>N<sub>2</sub>NaO [M + Na]<sup>+</sup>: 293.1624, found: 293.1625.



### 1-(5-methyl-5-(2-methylallyl)-3-phenyl-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (**3b**):

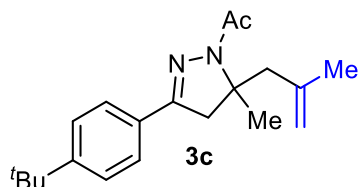
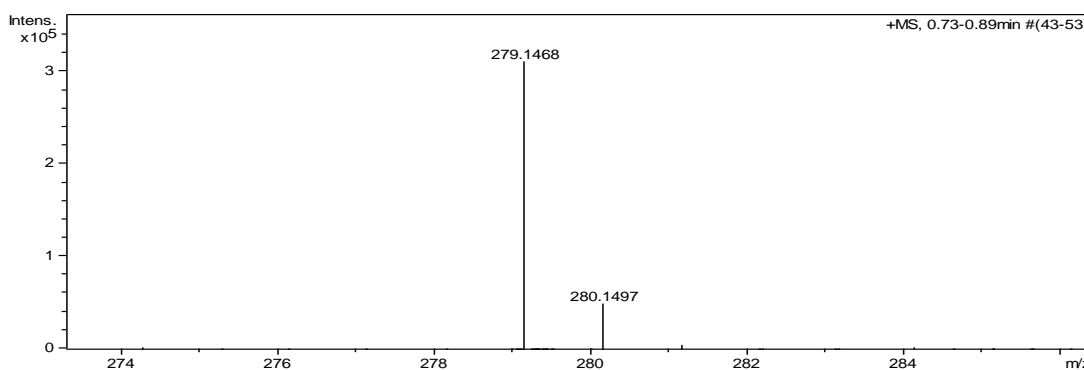
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **3b** (107.6 mg, 84% yield) as a yellow oil.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.70-7.68 (m, 2H), 7.41-7.39 (m, 3H), 4.85 (s, 1H), 4.71 (s, 1H), 3.50 (d, *J* = 17.6 Hz, 1H), 3.23 (d, *J* = 14.0 Hz, 1H), 2.93 (d, *J* = 17.6 Hz, 1H), 2.44 (d, *J* = 14.0 Hz, 1H), 2.35 (s, 3H), 1.70 (s, 3H), 1.67 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 169.9, 152.6, 142.2, 131.8, 129.9, 128.6, 126.3, 115.3, 66.1, 45.1, 44.9, 26.8, 23.5, 23.1;

**IR** (KBr) ν: 2926, 2382, 2349, 2315, 1661, 1411, 1363, 1328, 1261, 1133, 1033, 930, 896, 841, 759, 692, 611, 538, 426 cm<sup>-1</sup>.

**HRMS** Calcd (ESI) *m/z* for C<sub>16</sub>H<sub>20</sub>N<sub>2</sub>NaO [M + Na]<sup>+</sup>: 279.1468, found: 279.1468.



**1-(3-(4-(tert-butyl)phenyl)-5-methyl-5-(2-methylallyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3c):**

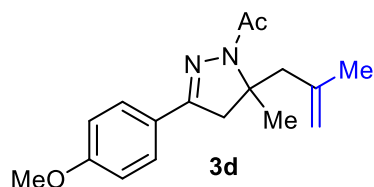
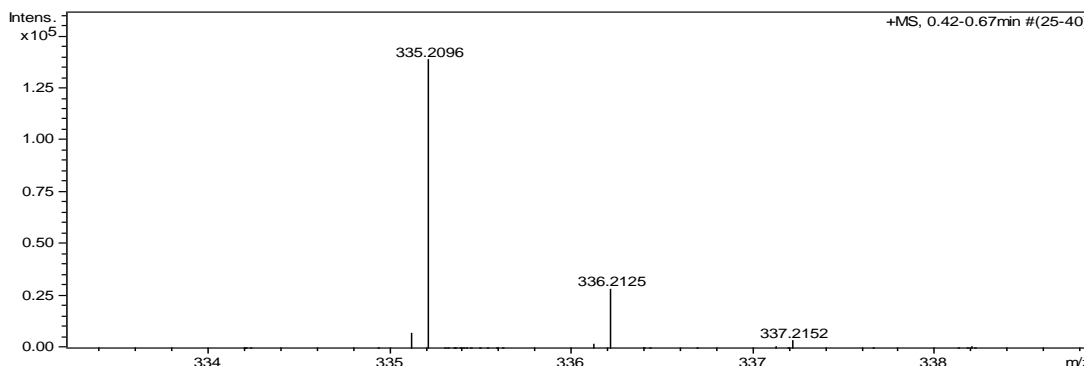
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **3c** (113.5 mg, 73% yield) as a yellow oil.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 4.84 (s, 1H), 4.71 (s, 1H), 3.49 (d, *J* = 17.6 Hz, 1H), 3.24 (d, *J* = 14.0 Hz, 1H), 2.91 (d, *J* = 17.2 Hz, 1H), 2.42 (d, *J* = 14.0 Hz, 1H), 2.35 (s, 3H), 1.69 (s, 3H), 1.67 (s, 3H), 1.34 (s, 9H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 169.8, 153.4, 152.6, 142.2, 129.0, 126.1, 125.5, 115.3, 65.9, 45.2, 44.8, 34.8, 31.1, 26.9, 23.5, 23.1;

**IR** (KBr)  $\nu$ : 3073, 2964, 2870, 2380, 1663, 1602, 1416, 1363, 1327, 1265, 1188, 1116, 1030, 930, 896, 834, 756, 697, 624, 569, 471, 427  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{20}\text{H}_{28}\text{N}_2\text{NaO}$   $[\text{M} + \text{Na}]^+$ : 335.2094, found: 335.2096.



**1-(3-(4-methoxyphenyl)-5-methyl-5-(2-methylallyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3d):**

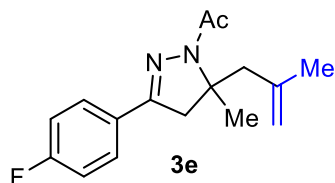
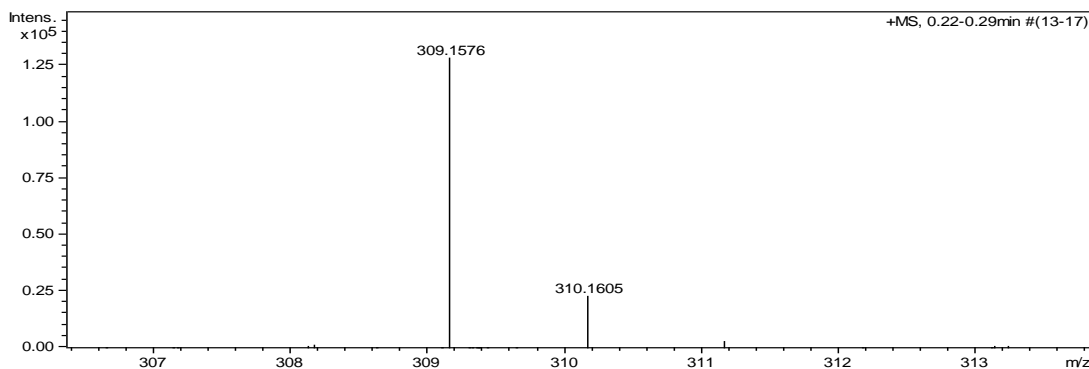
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8) give the product **3d** (114.4 mg, 80% yield) as a yellow solid. Mp: 94 - 97  $^{\circ}\text{C}$ .

$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.62 (d,  $J = 9.2$  Hz, 2H), 6.91 (d,  $J = 8.8$  Hz, 2H), 4.83 (s, 1H), 4.70 (s, 1H), 3.83 (s, 3H), 3.45 (d,  $J = 17.6$  Hz, 1H), 3.21 (d,  $J = 14.0$  Hz, 1H), 2.89 (d,  $J = 17.6$  Hz, 1H), 2.42 (d,  $J = 14.0$  Hz, 1H), 2.33 (s, 3H), 1.69 (s, 3H), 1.66 (s, 3H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  169.6, 161.0, 152.4, 142.2, 127.8, 124.4, 115.2, 114.0, 65.9, 55.3, 45.3, 44.8, 26.8, 23.5, 23.1;

**IR** (KBr)  $\nu$ : 3071, 2974, 2916, 2316, 1652, 1598, 1420, 1398, 1362, 1324, 1263, 1185, 1137, 1090, 1016, 957, 928, 905, 822, 756, 621, 533, 489, 448  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{17}\text{H}_{22}\text{N}_2\text{NaO}_2$   $[\text{M} + \text{Na}]^+$ : 309.1573, found: 309.1576.



**1-(3-(4-fluorophenyl)-5-methyl-5-(2-methylallyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3e):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8) give the product **3e** (113.6 mg, 83% yield) as a yellow solid. Mp: 51 - 53 °C.

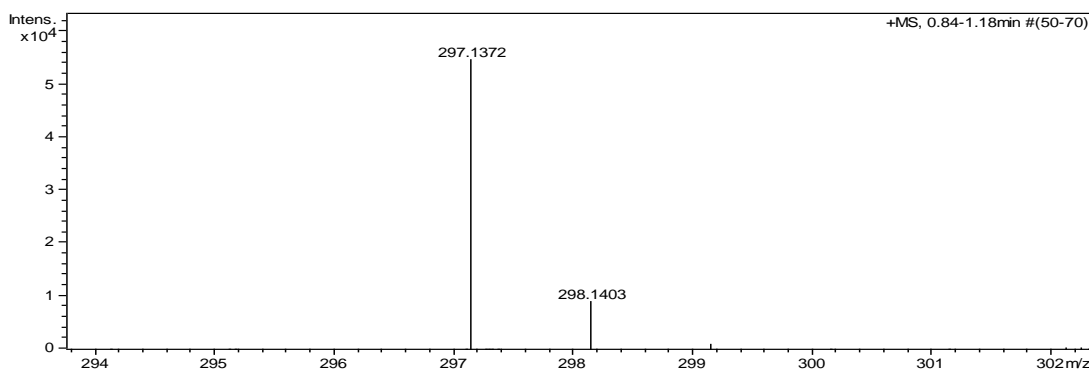
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.68-7.64 (m, 2H), 7.10-7.05 (m, 2H), 4.84 (s, 1H), 4.70 (s, 1H), 3.46 (d, *J* = 17.2 Hz, 1H), 3.21 (d, *J* = 14.0 Hz, 1H), 2.89 (d, *J* = 17.6 Hz, 1H), 2.42 (d, *J* = 14.0 Hz, 1H), 2.32 (s, 3H), 1.68 (s, 3H), 1.66 (s, 3H);

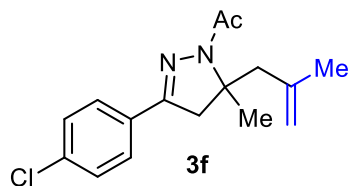
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 169.8, 163.7 (d, *J* = 249.4 Hz), 151.5, 142.1, 128.2 (d, *J* = 8.4 Hz), 128.0 (d, *J* = 3.1 Hz), 115.8, 115.5 (d, *J* = 22.3 Hz), 66.2, 45.2, 44.9, 26.8, 23.5, 23.1;

<sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz) δ -110.14;

IR (KBr) ν: 3076, 2975, 2921, 2319, 1655, 1607, 1514, 1427, 1363, 1327, 1228, 1183, 1155, 1096, 1028, 959, 930, 904, 832, 809, 744, 692, 625, 564, 536, 462 cm<sup>-1</sup>;

HRMS Calcd (ESI)  $m/z$  for C<sub>16</sub>H<sub>19</sub>FN<sub>2</sub>NaO [M + Na]<sup>+</sup>: 297.1374, found: 297.1372.





**1-(3-(4-chlorophenyl)-5-methyl-5-(2-methylallyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3f):**

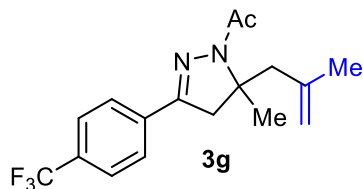
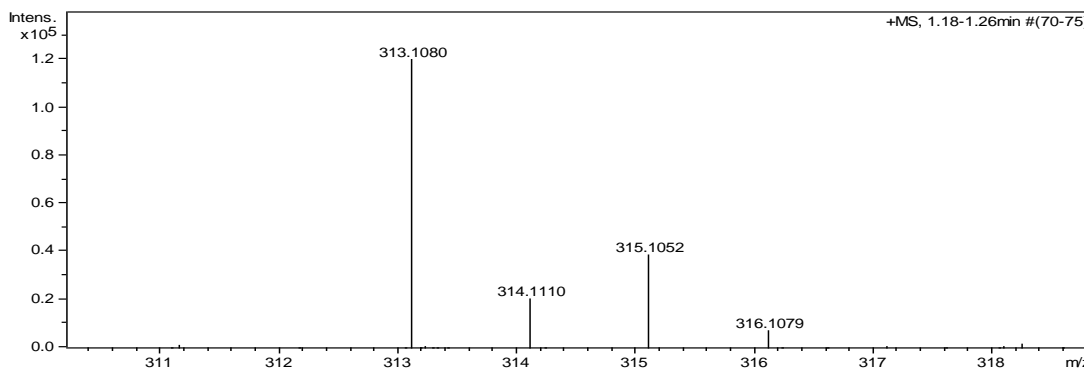
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 6) give the product **3f** (99.2 mg, 68% yield) as a yellow oil.

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.60 (d,  $J = 8.4$  Hz, 2H), 7.36 (d,  $J = 8.4$  Hz, 2H), 4.84 (s, 1H), 4.70 (s, 1H), 3.45 (d,  $J = 17.2$  Hz, 1H), 3.21 (d,  $J = 14.4$  Hz, 1H), 2.89 (d,  $J = 17.6$  Hz, 1H), 2.42 (d,  $J = 14.0$  Hz, 1H), 2.33 (s, 3H), 1.68 (s, 3H), 1.66 (s, 3H);

$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  169.9, 151.4, 142.1, 135.8, 130.3, 128.8, 127.5, 115.4, 66.4, 45.0, 44.9, 26.8, 23.5, 23.1;

**IR** (KBr)  $\nu$ : 3074, 2931, 2841, 2381, 2315, 1659, 1608, 1518, 1410, 1364, 1328, 1254, 1176, 1114, 1036, 931, 898, 833, 630, 578, 545, 457  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{16}\text{H}_{19}\text{ClN}_2\text{NaO}$  [ $\text{M} + \text{Na}$ ] $^+$ : 313.1078, found: 313.1080.



**1-(5-methyl-5-(2-methylallyl)-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3g):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **3g** (119.8 mg, 74% yield) as a white solid. Mp: 85 - 87  $^{\circ}\text{C}$ .

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.78 (d,  $J = 8.4$  Hz, 2H), 7.64 (d,  $J = 8.4$  Hz, 2H), 4.85

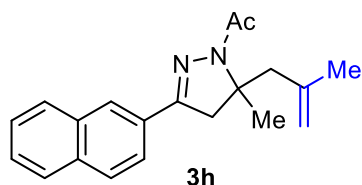
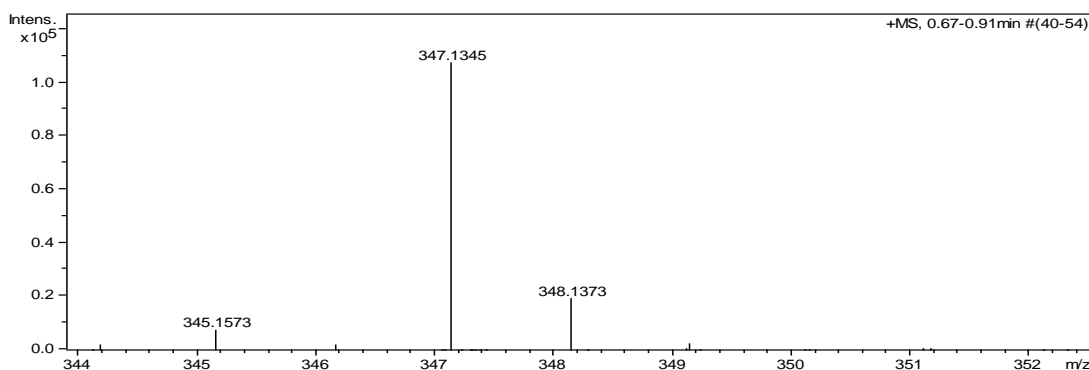
(s, 1H), 4.71 (s, 1H), 3.50 (d,  $J = 17.6$  Hz, 1H), 3.23 (d,  $J = 14.4$  Hz, 1H), 2.93 (d,  $J = 17.6$  Hz, 1H), 2.43 (d,  $J = 14.0$  Hz, 1H), 2.35 (s, 3H), 1.69 (s, 6H (3H\*2));

$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  170.0, 151.1, 142.0, 135.2 (q,  $J = 1.5$  Hz), 131.4 (q,  $J = 32.5$  Hz), 126.5, 125.5 (q,  $J = 3.8$  Hz), 123.8 (q,  $J = 270.8$  Hz), 115.5, 66.6, 44.9 (2C), 26.9, 23.4, 23.1;

$^{19}\text{F}$  NMR (CDCl<sub>3</sub>, 376 MHz)  $\delta$  -62.82;

IR (KBr)  $\nu$ : 3064, 2968, 2913, 2310, 1940, 1818, 1657, 1597, 1525, 1408, 1369, 1329, 1190, 1159, 1114, 1067, 1019, 959, 927, 903, 844, 743, 703, 661, 623, 600, 531, 480, 437 cm<sup>-1</sup>;

HRMS Calcd (ESI)  $m/z$  for C<sub>17</sub>H<sub>19</sub>F<sub>3</sub>N<sub>2</sub>NaO [M + Na]<sup>+</sup>: 347.1342, found: 347.1345.



**1-(5-methyl-5-(2-methylallyl)-3-(naphthalen-2-yl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3h):**

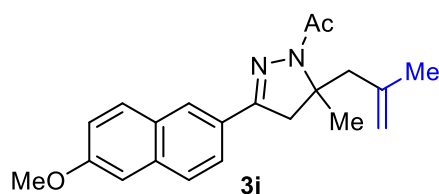
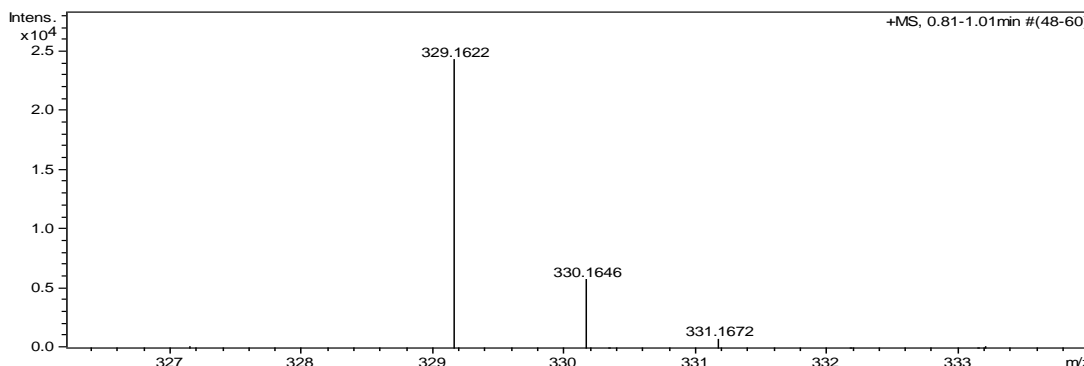
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **3h** (126.8 mg, 83% yield) as a yellow oil.

$^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  8.01 (d,  $J = 8.4$  Hz, 1H), 7.90-7.83 (m, 4H), 7.53-7.51 (m, 2H), 4.87 (s, 1H), 4.76 (s, 1H), 3.62 (d,  $J = 17.2$  Hz, 1H), 3.27 (d,  $J = 14.0$  Hz, 1H), 3.06 (d,  $J = 17.6$  Hz, 1H), 2.49 (d,  $J = 14.0$  Hz, 1H), 2.41 (s, 3H), 1.73 (s, 6H (3H\*2));

$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  169.9, 152.6, 142.1, 134.0, 133.0, 129.4, 128.3 (2C), 127.8, 127.0, 126.6 (2C), 123.1, 115.4, 66.3, 45.1, 45.0, 26.9, 23.6, 23.2;

**IR** (KBr)  $\nu$ : 3060, 2966, 2927, 1662, 1603, 1477, 1413, 1366, 1321, 1264, 1178, 1130, 1018, 930, 897, 858, 818, 747, 632, 558, 475  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{20}\text{H}_{22}\text{N}_2\text{NaO}$   $[\text{M} + \text{Na}]^+$ : 329.1624, found: 329.1622.



**1-(3-(6-methoxynaphthalen-2-yl)-5-methyl-5-(2-methylallyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3i):**

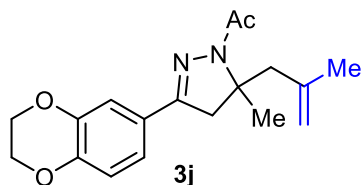
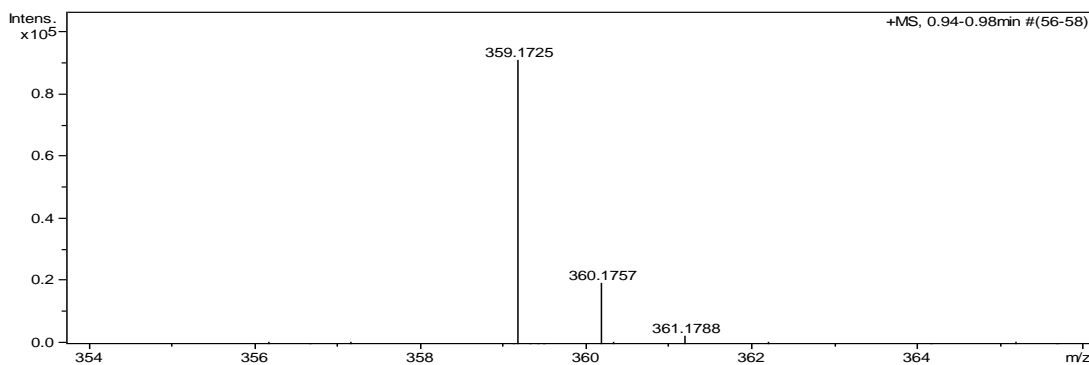
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 6) give the product **3i** (93.4 mg, 56% yield) as a yellow solid. Mp: 79 - 81  $^{\circ}\text{C}$ .

**$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.96 (d,  $J = 8.8$  Hz, 1H), 7.83 (s, 1H), 7.76-7.72 (m, 2H), 7.19-7.14 (m, 2H), 4.86 (s, 1H), 4.75 (s, 1H), 3.93 (s, 3H), 3.59 (d,  $J = 17.2$  Hz, 1H), 3.26 (d,  $J = 14.0$  Hz, 1H), 3.03 (d,  $J = 17.6$  Hz, 1H), 2.48 (d,  $J = 14.0$  Hz, 1H), 2.40 (s, 3H), 1.72 (s, 3H), 1.71 (s, 3H);

**$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  169.8, 158.6, 152.8, 142.2, 135.4, 129.8, 128.3, 127.2, 127.1, 126.4, 123.7, 119.3, 115.3, 106.0, 66.1, 55.3, 45.1, 44.9, 26.8, 23.5, 23.1;

**IR** (KBr)  $\nu$ : 3062, 2950, 2327, 1796, 1675, 1617, 1485, 1381, 1317, 1252, 1203, 1121, 1026, 888, 851, 801, 732, 654, 605, 449  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{21}\text{H}_{24}\text{N}_2\text{NaO}_2$   $[\text{M} + \text{Na}]^+$ : 359.1730, found: 359.1725.



**1-(3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-5-methyl-5-(2-methylallyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3j):**

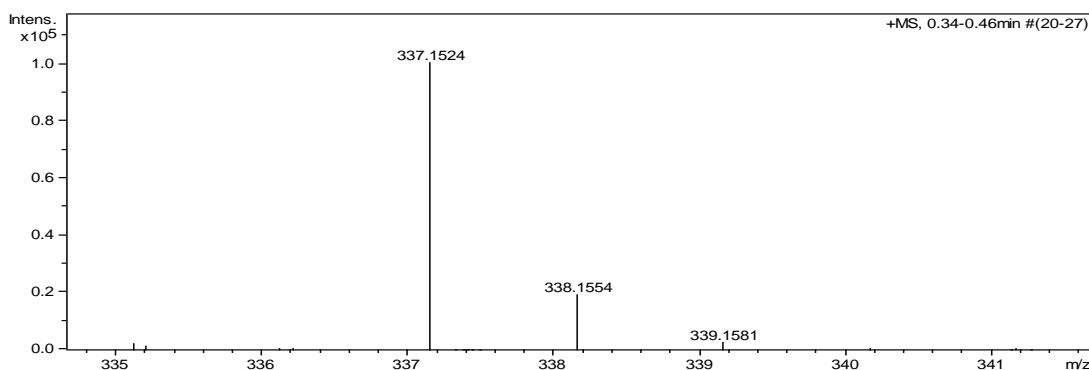
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 6) give the product **3j** (123.3 mg, 78% yield) as a yellow oil.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.20-7.16 (m, 2H), 6.87 (d, *J* = 8.0 Hz, 1H), 4.83 (s, 1H), 4.69 (s, 1H), 4.27 (s, 4H), 3.42 (d, *J* = 17.2 Hz, 1H), 3.20 (d, *J* = 14.0 Hz, 1H), 2.85 (d, *J* = 17.6 Hz, 1H), 2.40 (d, *J* = 14.0 Hz, 1H), 2.31 (s, 3H), 1.68 (s, 3H), 1.65 (s, 3H);

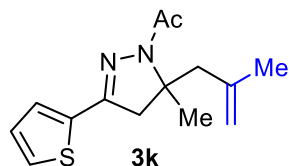
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 169.7, 152.2, 145.3, 143.5, 142.2, 125.4, 119.9, 117.4, 115.3 (2C), 66.0, 64.5, 64.2, 45.3, 44.9, 26.8, 23.5, 23.1;

**IR** (KBr) ν: 3072, 2930, 2312, 1659, 1574, 1513, 1411, 1363, 1317, 1284, 1246, 1183, 1124, 1066, 890, 817, 747, 625, 457 cm<sup>-1</sup>;

**HRMS** Calcd (ESI) *m/z* for C<sub>18</sub>H<sub>22</sub>N<sub>2</sub>NaO<sub>3</sub> [M + Na]<sup>+</sup>: 337.1523, found: 337.1524.







**1-(5-methyl-5-(2-methylallyl)-3-(thiophen-3-yl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3k):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10)

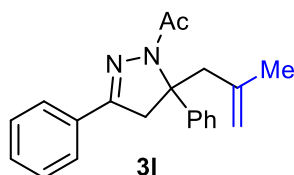
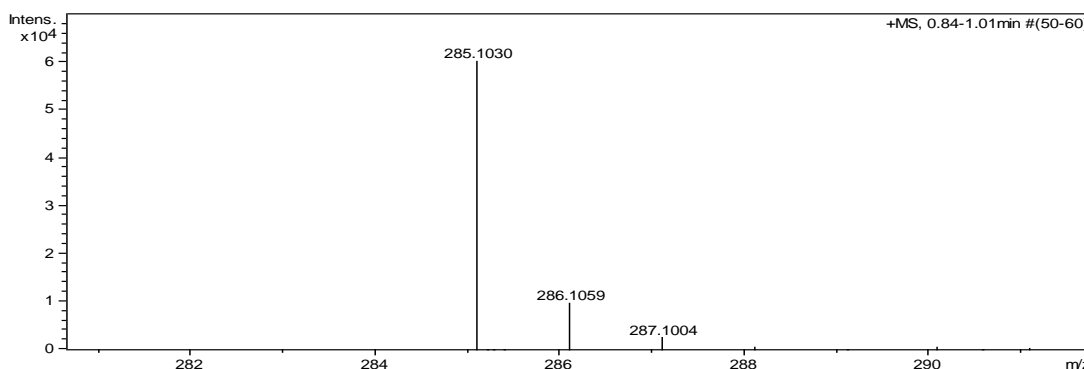
give the product **3k** (83.5 mg, 64% yield) as a yellow solid. Mp: 62 - 64 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.37 (d, *J* = 4.8 Hz, 1H), 7.17 (d, *J* = 3.6 Hz, 1H), 7.04 (dd, *J*<sub>1</sub> = 5.2 Hz, *J*<sub>2</sub> = 3.6 Hz, 1H), 4.85 (s, 1H), 4.70 (s, 1H), 3.48 (d, *J* = 17.6 Hz, 1H), 3.20 (d, *J* = 14.0 Hz, 1H), 2.91 (d, *J* = 17.2 Hz, 1H), 2.42 (d, *J* = 14.4 Hz, 1H), 2.30 (s, 3H), 1.69 (s, 3H), 1.65 (s, 3H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 169.6, 148.3, 142.0, 135.5, 128.1, 128.0, 127.4, 115.4, 66.3, 45.8, 44.8, 26.7, 23.4, 23.1;

IR (KBr) ν: 3083, 2973, 2921, 2314, 1818, 1758, 1657, 1521, 1446, 1402, 1319, 1265, 1221, 1179, 1136, 1083, 1042, 970, 927, 904, 850, 819, 733, 615, 580, 525, 462, 423 cm<sup>-1</sup>;

HRMS Calcd (ESI) *m/z* for C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>NaOS [M + Na]<sup>+</sup>: 285.1032, found: 285.1030.



**1-(5-(2-methylallyl)-3,5-diphenyl-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3l):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8)

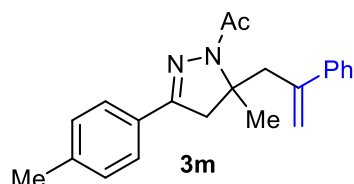
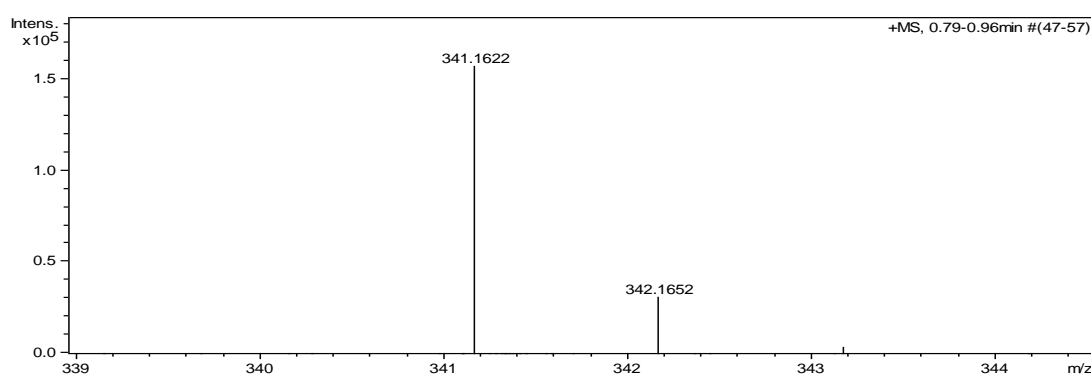
give the product **3l** (67.2 mg, 42% yield) as a yellow solid. Mp: 94 - 96 °C.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.71-7.69 (m, 2H), 7.40-7.38 (m, 3H), 7.32-7.29 (m, 4H), 7.24-7.19 (m, 1H), 4.93 (s, 1H), 4.80 (s, 1H), 3.81 (d, *J* = 18.0 Hz, 1H), 3.71 (d, *J* = 14.4 Hz, 1H), 3.31 (d, *J* = 18.0 Hz, 1H), 2.98 (d, *J* = 14.0 Hz, 1H), 2.40 (s, 3H), 1.76 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 169.2, 152.4, 145.4, 141.7, 131.4, 130.0, 128.6, 128.5, 127.0, 126.4, 124.6, 116.0, 69.8, 48.3, 42.4, 23.4, 23.3;

**IR** (KBr) ν: 3063, 2976, 2314, 1957, 1808, 1666, 1596, 1495, 1407, 1325, 1247, 1178, 1092, 1069, 1035, 991, 924, 898, 763, 693, 629, 591, 541, 468, 445, 421 cm<sup>-1</sup>;

**HRMS** Calcd (ESI) *m/z* for C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>NaO [M + Na]<sup>+</sup>: 341.1624, found: 341.1622.



**1-(5-methyl-5-(2-phenylallyl)-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3m):**

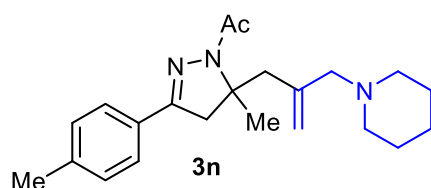
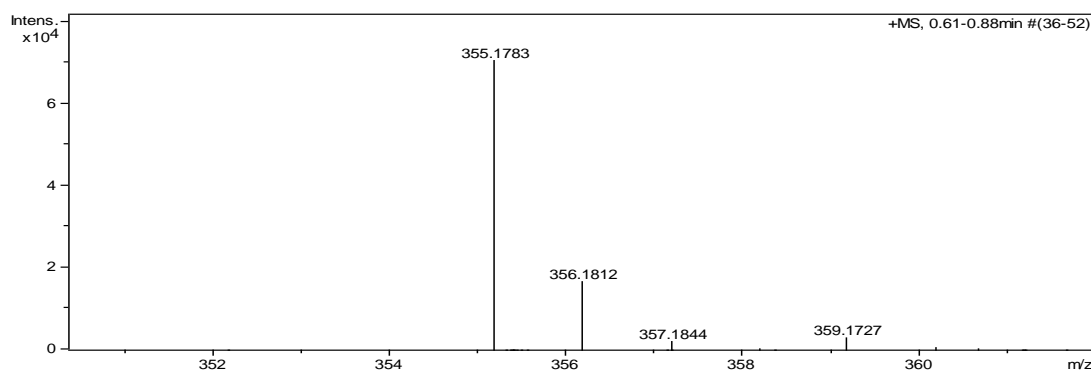
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8) give the product **3m** (125.8 mg, 76% yield) as a yellow solid. Mp: 88 - 91 °C.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.20-7.16 (m, 7H), 5.15 (s, 1H), 5.09 (s, 1H), 3.71 (d, *J* = 13.6 Hz, 1H), 3.31 (d, *J* = 17.6 Hz, 1H), 2.82 (d, *J* = 17.2 Hz, 1H), 2.71 (d, *J* = 14.0 Hz, 1H), 2.38 (s, 3H), 1.91 (s, 3H), 1.72 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 169.9, 152.1, 146.2, 141.6, 139.9, 129.1, 128.9, 127.8, 127.2, 126.7, 126.1, 118.0, 66.1, 45.2, 42.4, 27.0, 23.0, 21.4;

**IR** (KBr) ν: 2983, 2927, 2305, 1651, 1596, 1494, 1439, 1413, 1362, 1328, 1238, 1179, 1129, 1100, 1033, 938, 845, 813, 781, 737, 697, 629, 589, 545, 518, 429 cm<sup>-1</sup>;

**HRMS** Calcd (ESI)  $m/z$  for  $C_{22}H_{24}N_2NaO$   $[M + Na]^+$ : 355.1781, found: 355.1783.



**1-(5-methyl-5-(2-(piperidin-1-ylmethyl)allyl)-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3n):**

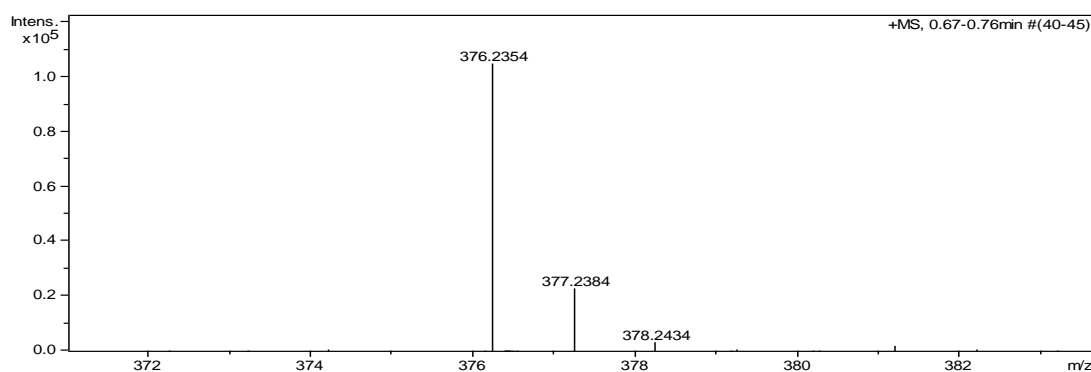
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1 : 2) give the product **3n** (77.5 mg, 44% yield) as a yellow oil.

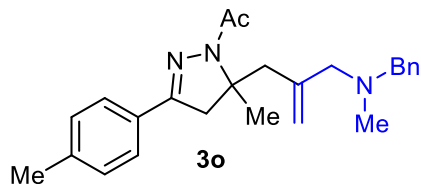
**$^1H$  NMR** ( $CDCl_3$ , 400 MHz)  $\delta$  7.56 (d,  $J = 8.0$  Hz, 2H), 7.20 (d,  $J = 8.0$  Hz, 2H), 5.01 (s, 1H), 4.91 (s, 1H), 3.74 (d,  $J = 17.6$  Hz, 1H), 3.06 (d,  $J = 14.0$  Hz, 1H), 2.91 (d,  $J = 17.6$  Hz, 1H), 2.73 (s, 2H), 2.64 (d,  $J = 14.0$  Hz, 1H), 2.38 (s, 3H), 2.33 (s, 3H), 2.23-2.16 (m, 4H), 1.67 (s, 3H), 1.52-1.48 (m, 4H), 1.41-1.37 (m, 2H);

**$^{13}C$  NMR** ( $CDCl_3$ , 100 MHz)  $\delta$  169.5, 152.8, 143.0, 140.1, 129.3, 129.1, 126.2, 116.6, 66.1, 64.8, 54.3, 45.9, 41.5, 26.7, 26.0, 24.4, 23.5, 21.4;

**IR** (KBr)  $\nu$ : 2933, 2854, 2790, 2752, 2308, 1664, 1407, 1362, 1326, 1272, 1154, 1116, 1036, 997, 931, 859, 816, 792, 743, 711, 624, 595, 545, 511, 429  $cm^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $C_{22}H_{31}N_3NaO$   $[M + Na]^+$ : 376.2359, found: 376.2354.





**1-(5-(2-((benzyl(methyl)amino)methyl)allyl)-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3o):**

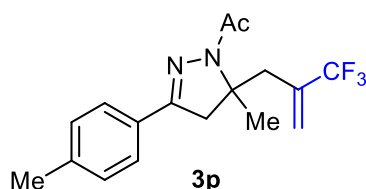
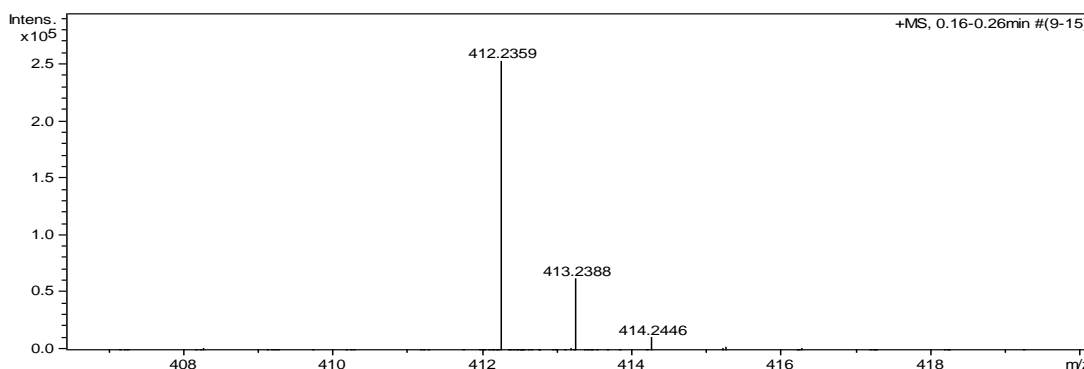
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1 : 5) give the product **3o** (117.8 mg, 60% yield) as a yellow oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.30-7.29 (m, 4H), 7.25-7.21 (m, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.12 (s, 1H), 4.94 (s, 1H), 3.57 (d, *J* = 17.6 Hz, 1H), 3.46 (d, *J* = 13.2 Hz, 1H), 3.33 (d, *J* = 13.2 Hz, 1H), 3.15 (d, *J* = 14.0 Hz, 1H), 2.92-2.81 (m, 3H), 2.68 (d, *J* = 14.4 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 2.04 (s, 3H), 1.69 (s, 3H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 169.6, 152.6, 143.2, 140.1, 139.1, 129.2, 129.0, 128.8, 128.1, 126.8, 126.2, 116.9, 66.2, 63.7, 61.7, 45.8, 41.8, 41.0, 26.8, 23.5, 21.4;

IR (KBr) ν: 3029, 2928, 2785, 2382, 2311, 1660, 1513, 1409, 1362, 1325, 1283, 1181, 1127, 1067, 1028, 930, 816, 743, 700, 623, 426 cm<sup>-1</sup>;

HRMS Calcd (ESI) *m/z* for C<sub>25</sub>H<sub>31</sub>N<sub>3</sub>NaO [M + Na]<sup>+</sup>: 412.2359, found: 412.2359.



**1-(5-methyl-3-(p-tolyl)-5-(2-(trifluoromethyl)allyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3p):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1 : 10)

give the product **3p** (116.0 mg, 72 % yield) as a yellow oil.

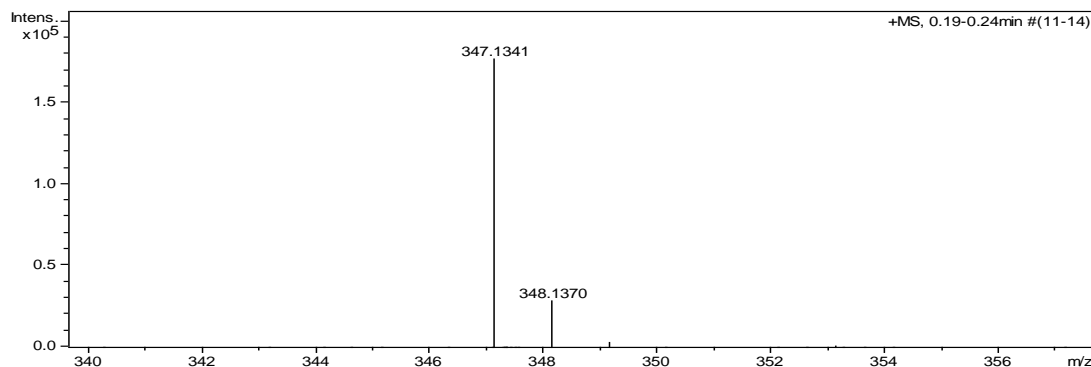
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 5.80 (s, 1H), 5.40 (s, 1H), 3.42-3.33 (m, 2H), 3.00 (d, *J* = 18.0 Hz, 1H), 2.74 (d, *J* = 15.6 Hz, 1H), 2.38 (s, 3H), 2.36 (s, 3H), 1.68 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 169.9, 152.6, 140.5, 134.4 (q, *J* = 29.7 Hz), 129.3, 128.6, 126.3, 123.4 (q, *J* = 272.2 Hz), 122.2 (q, *J* = 5.9 Hz), 65.5, 45.6, 36.0, 26.5, 23.4, 21.4;

**<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 376 MHz) δ -67.40;

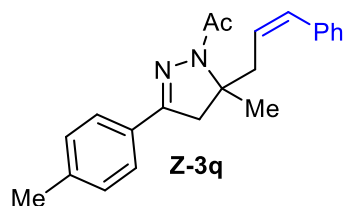
**IR** (KBr) ν: 2931, 2310, 1664, 1608, 1412, 1363, 1326, 1267, 1171, 1123, 1033, 936, 817, 714, 673, 628, 596, 549, 518, 449 cm<sup>-1</sup>;

**HRMS** Calcd (ESI) *m/z* for C<sub>17</sub>H<sub>19</sub>F<sub>3</sub>N<sub>2</sub>NaO [M + Na]<sup>+</sup>: 347.1342, found: 347.1341.



Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1 : 10)

give the product (**Z/E**)-**3q** (111.0 mg, 65% yield) as a yellow oil. According to the analysis of NMR spectroscopy, the **Z/E** configuration ratio is 1 : 4.



**(Z)-1-(5-methyl-5-(3-phenylallyl)-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one ((Z)-3q):**

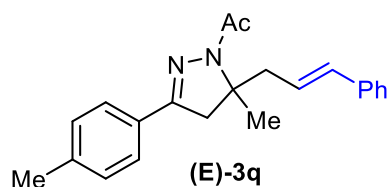
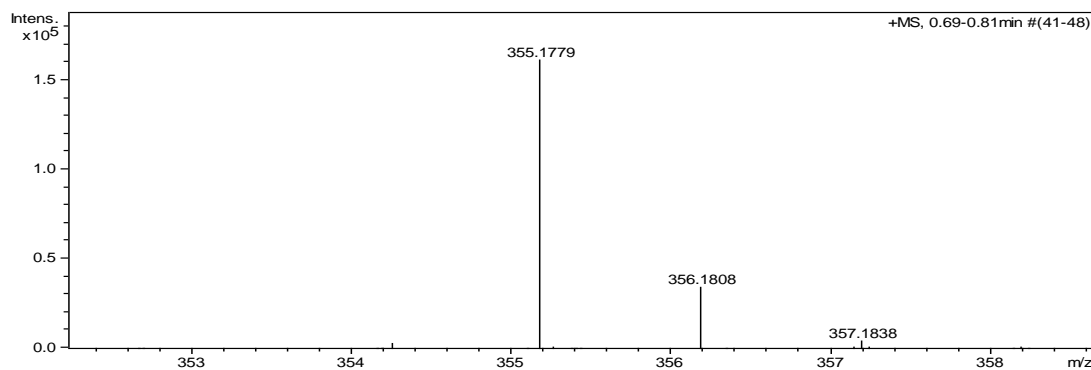
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.35-7.31 (m, 2H), 7.26-7.19 (m, 5H), 6.54 (d, *J* = 12.0 Hz, 1H), 5.53-5.46 (m, 1H), 3.36-3.30 (m, 1H), 3.12 (d, *J* = 17.6 Hz, 1H), 2.97-2.86 (m, 2H), 2.39 (s, 6H (3H\*2)), 1.67 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 169.6, 152.5, 140.3, 137.2, 132.1, 129.3, 128.9, 128.8,

128.2, 126.8, 126.7, 126.3, 66.3, 46.0, 36.4, 25.6, 23.3, 21.5;

**IR** (KBr)  $\nu$ : 2925, 2852, 2383, 2349, 2312, 1658, 1491, 1403, 1326, 1264, 1209, 1164, 1118, 1026, 835, 757, 698, 472, 422  $\text{cm}^{-1}$ .

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{NaO}$   $[\text{M} + \text{Na}]^+$ : 355.1781, found: 355.1779.



**(E)-1-(5-cinnamyl-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one**

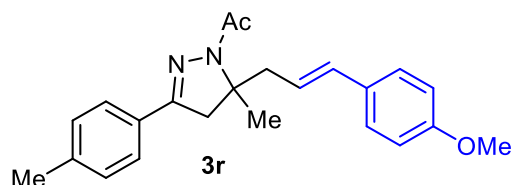
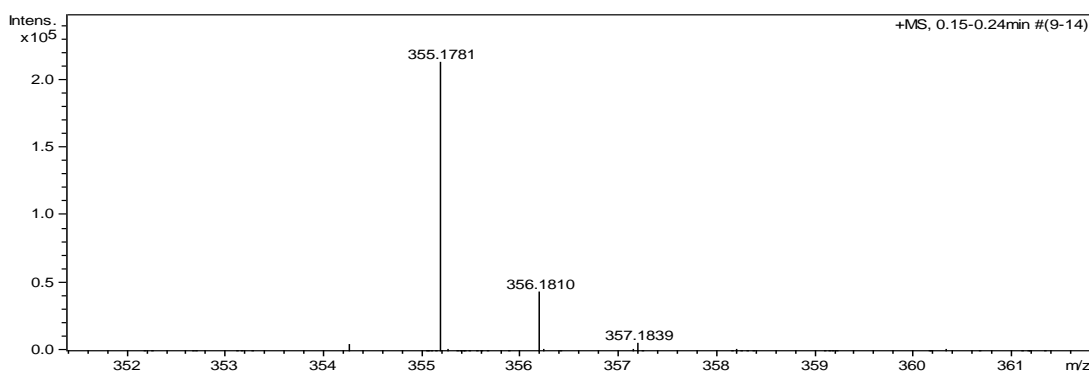
**((E)-3q):**

**$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.56 (d,  $J = 8.4$  Hz, 2H), 7.30-7.23 (m, 4H), 7.20-7.18 (m, 3H), 6.49 (d,  $J = 16.0$  Hz, 1H), 6.08-5.99 (m, 1H), 3.32 (d,  $J = 17.2$  Hz, 1H), 3.17-3.12 (m, 1H), 2.96 (d,  $J = 17.2$  Hz, 1H), 2.79-2.73 (m, 1H), 2.37 (s, 6H (3H\*2)), 1.70 (s, 3H);

**$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  169.8, 152.3, 140.3, 137.2, 134.1, 129.3, 128.9, 128.4, 127.3, 126.3, 126.2, 124.7, 66.5, 45.8, 41.4, 25.5, 23.4, 21.4;

**IR** (KBr)  $\nu$ : 3027, 2925, 2854, 2381, 2311, 1660, 1495, 1408, 1362, 1325, 1179, 1118, 1031, 968, 932, 815, 747, 694, 626, 424  $\text{cm}^{-1}$ .

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{22}\text{H}_{24}\text{N}_2\text{NaO}$   $[\text{M} + \text{Na}]^+$ : 355.1781, found: 355.1781.



**(E)-1-(5-(3-(4-methoxyphenyl)allyl)-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3r):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1 : 7)

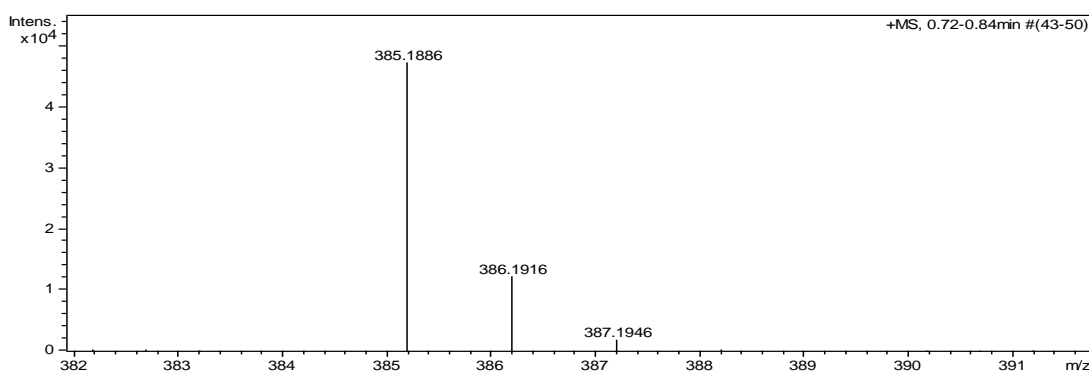
give the product **3r** (121.2 mg, 67% yield) as a yellow oil.

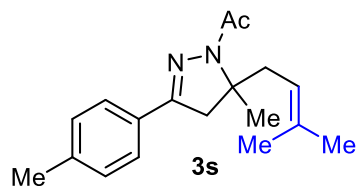
$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.57 (d,  $J = 8.0$  Hz, 2H), 7.22 (d,  $J = 8.8$  Hz, 2H), 7.19 (d,  $J = 8.0$  Hz, 2H), 6.80 (d,  $J = 8.8$  Hz, 2H), 6.44 (d,  $J = 15.6$  Hz, 1H), 5.95-5.87 (m, 1H), 3.78 (s, 3H), 3.32 (d,  $J = 17.2$  Hz, 1H), 3.12 (dd,  $J_1 = 14.0$ ,  $J_2 = 7.2$  Hz, 1H), 2.95 (d,  $J = 17.2$  Hz, 1H), 2.74 (dd,  $J_1 = 14.0$ ,  $J_2 = 7.6$  Hz, 1H), 2.38 (s, 3H\*2), 1.70 (s, 3H);

$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  169.7, 158.9, 152.3, 140.2, 133.4, 130.1, 129.2, 128.9, 127.2, 126.2, 122.4, 113.8, 66.6, 55.2, 45.8, 41.3, 25.4, 23.3, 21.4;

**IR** (KBr)  $\nu$ : 2929, 2838, 2389, 2314, 1660, 1606, 1511, 1417, 1362, 1326, 1300, 1249, 1176, 1110, 1033, 969, 933, 816, 631, 550, 516  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{23}\text{H}_{26}\text{N}_2\text{NaO}_2$   $[\text{M} + \text{Na}]^+$ : 385.1886, found: 385.1886.





**1-(5-methyl-5-(3-methylbut-2-en-1-yl)-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3s):**

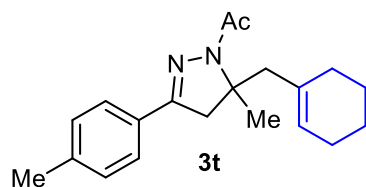
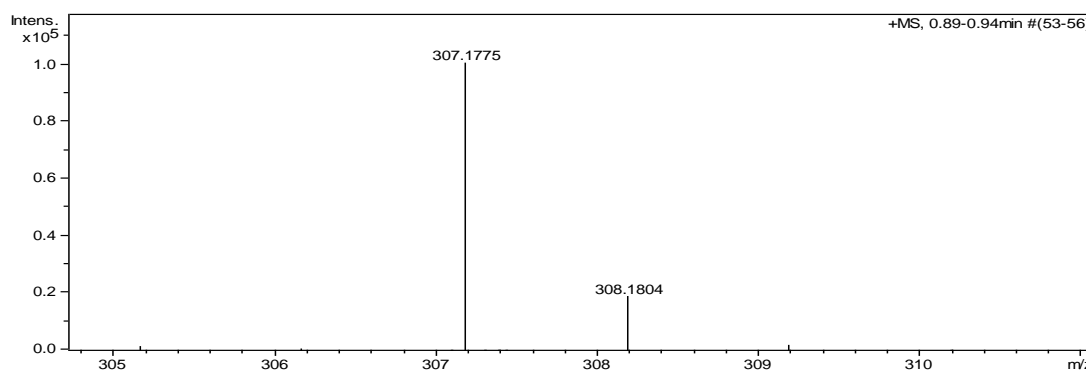
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **3s** (64.6 mg, 45% yield) as a yellow solid. Mp: 60 - 62 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.02-4.98 (m, 1H), 3.18 (d, *J* = 17.2 Hz, 1H), 2.92-2.84 (m, 2H), 2.61 (dd, *J*<sub>1</sub> = 14.8 Hz, *J*<sub>2</sub> = 8.0 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H), 1.66 (s, 3H), 1.64 (s, 3H), 1.62 (s, 3H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 169.5, 152.3, 140.0, 135.2, 129.2, 129.0, 126.2, 118.7, 66.8, 45.8, 36.1, 25.9, 25.2, 23.3, 21.4, 18.1;

IR (KBr) ν: 2993, 2967, 2927, 1648, 1409, 1359, 1326, 1264, 1230, 1159, 1115, 1030, 968, 939, 919, 888, 841, 816, 713, 637, 604, 547, 501, 439 cm<sup>-1</sup>;

HRMS Calcd (ESI) *m/z* for C<sub>18</sub>H<sub>24</sub>N<sub>2</sub>NaO [M + Na]<sup>+</sup>: 307.1781, found: 307.1775.



**1-(5-(cyclohex-1-en-1-ylmethyl)-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3t):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **3t** (107.9 mg, 70% yield) as a yellow solid. Mp: 74 - 76 °C.

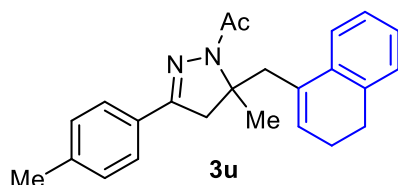
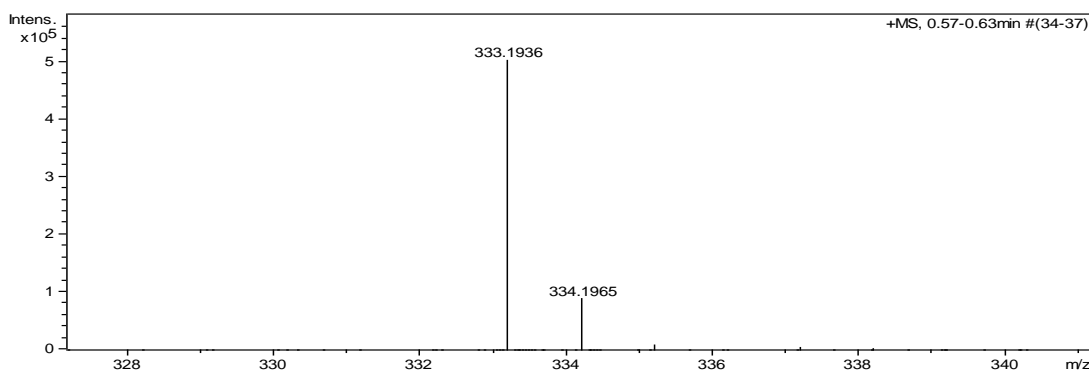


**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 5.43 (s, 1H), 3.43 (d, *J* = 17.6 Hz, 1H), 3.07 (d, *J* = 14.0 Hz, 1H), 2.87 (d, *J* = 17.2 Hz, 1H), 2.38 (s, 3H), 2.33 (s, 3H), 2.30 (d, *J* = 14.0 Hz, 1H), 1.93-1.88 (m, 4H), 1.65 (s, 3H), 1.50-1.33 (m, 4H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 169.7, 152.7, 140.0, 134.4, 129.2, 129.1, 126.5, 126.2, 66.5, 45.6, 45.4, 29.2, 26.7, 25.4, 23.5, 23.0, 22.1, 21.4;

**IR** (KBr) ν: 3066, 3034, 2992, 2928, 2855, 2389, 2303, 1931, 1656, 1410, 1362, 1327, 1259, 1229, 1184, 1137, 1099, 1031, 940, 884, 822, 707, 625, 601, 540, 458, 421 cm<sup>-1</sup>.

**HRMS** Calcd (ESI) *m/z* for C<sub>20</sub>H<sub>26</sub>N<sub>2</sub>NaO [M + Na]<sup>+</sup>: 333.1937, found: 333.1936.



**1-(5-((3,4-dihydronaphthalen-1-yl)methyl)-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3u):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1 : 8) give the product **3u** (159.3 mg, 89% yield) as a yellow oil.

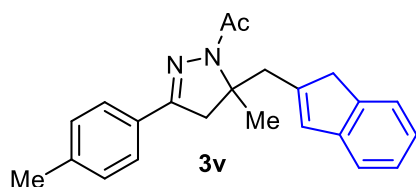
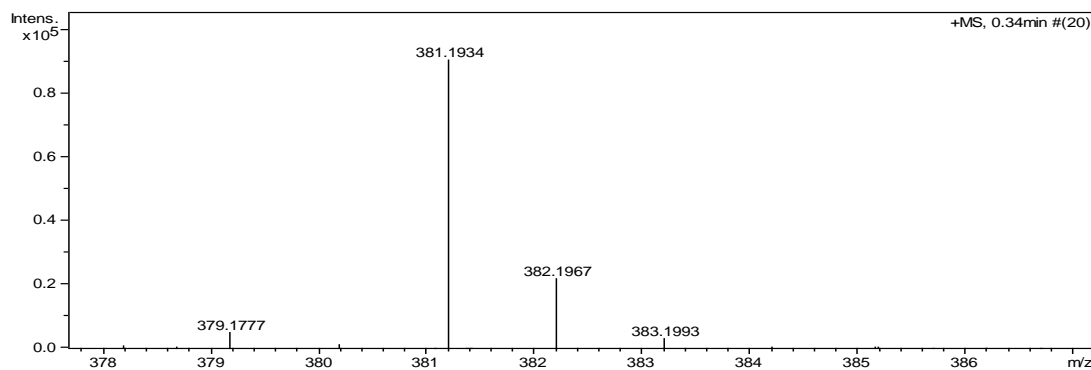
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.41 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 5.89 (t, *J* = 4.8 Hz, 1H), 3.42 (d, *J* = 17.6 Hz, 1H), 3.37 (d, *J* = 14.0 Hz, 1H), 2.93 (d, *J* = 14.4 Hz, 1H), 2.80 (d, *J* = 17.6 Hz, 1H), 2.51-2.38 (m, 2H), 2.36 (s, 3H), 2.22 (s, 3H), 2.12-2.06 (m, 2H), 1.77 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 170.1, 152.5, 139.9, 136.7, 135.1, 133.2, 129.4, 129.1,

128.8, 127.3, 126.5, 126.0, 123.0, 67.3, 45.6, 38.5, 28.2, 26.5, 23.5, 23.2, 21.4;

**IR** (KBr)  $\nu$ : 2928, 2387, 2311, 1660, 1409, 1362, 1326, 1181, 1110, 1030, 938, 815, 771, 742, 626, 593, 548  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{24}\text{H}_{26}\text{N}_2\text{NaO}$   $[\text{M} + \text{Na}]^+$ : 381.1937, found: 381.1934.



**1-(5-((1H-inden-2-yl)methyl)-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (3v):**

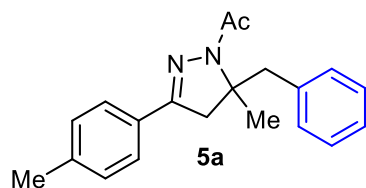
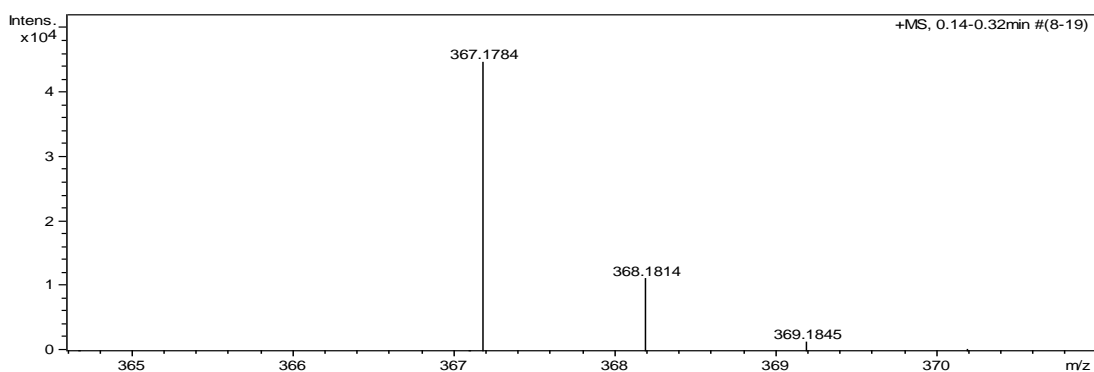
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8) give the product **3v** (155.9 mg, 91% yield) as a yellow solid. Mp: 101 - 103 °C.

**$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.55 (d,  $J = 8.4$  Hz, 2H), 7.36 (d,  $J = 7.6$  Hz, 1H), 7.29-7.27 (m, 1H), 7.23-7.18 (m, 3H), 7.14-7.10 (m, 1H), 6.61 (s, 1H), 3.67 (d,  $J = 14.8$  Hz, 1H), 3.45 (d,  $J = 17.2$  Hz, 1H), 3.33 (s, 2H), 3.06-2.98 (m, 2H), 2.43 (s, 3H), 2.38 (s, 3H), 1.73 (s, 3H);

**$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  169.9, 152.5, 145.2, 144.7, 143.5, 140.3, 130.4, 129.2, 128.7, 126.2, 126.1, 124.0, 123.3, 120.2, 66.2, 45.8, 41.6, 39.1, 26.3, 23.6, 21.4;

**IR** (KBr)  $\nu$ : 3059, 3016, 2958, 2924, 1648, 1603, 1406, 1361, 1326, 1262, 1174, 1117, 1092, 1029, 930, 907, 842, 816, 753, 715, 629, 594, 550, 503, 465, 422  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{23}\text{H}_{24}\text{N}_2\text{NaO}$   $[\text{M} + \text{Na}]^+$ : 367.1781, found: 367.1784.



**1-(5-benzyl-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one(5a):**

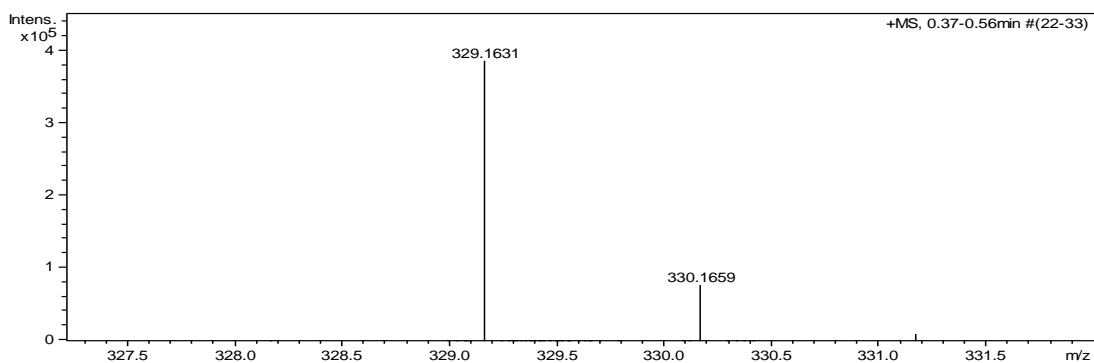
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **5a** (150.8 mg, 98% yield) as a yellow solid. Mp: 88 - 92 °C.

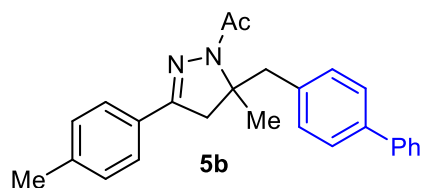
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.24-7.20 (m, 2H), 7.17-7.12 (m, 5H), 3.55 (d, *J* = 13.6 Hz, 1H), 3.37 (d, *J* = 17.6 Hz, 1H), 3.11 (d, *J* = 13.2 Hz, 1H), 2.83 (d, *J* = 17.6 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 1.74 (s, 3H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 170.0, 152.2, 140.1, 136.9, 130.1, 129.1, 128.8, 128.2, 126.6, 126.1, 67.1, 45.0, 42.7, 25.8, 23.6, 21.4;

IR (KBr) ν: 3068, 3026, 2962, 2921, 2310, 1933, 1653, 1603, 1494, 1430, 1362, 1328, 1263, 1228, 1176, 1115, 1072, 1029, 965, 931, 889, 822, 757, 704, 622, 589, 544, 513, 482, 427 cm<sup>-1</sup>;

HRMS Calcd (ESI) m/z for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>NaO [M + Na]<sup>+</sup>: 329.1624, found: 329.1631.





**1-(5-([1,1'-biphenyl]-4-ylmethyl)-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5b):**

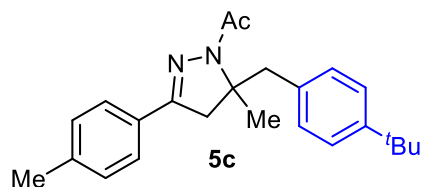
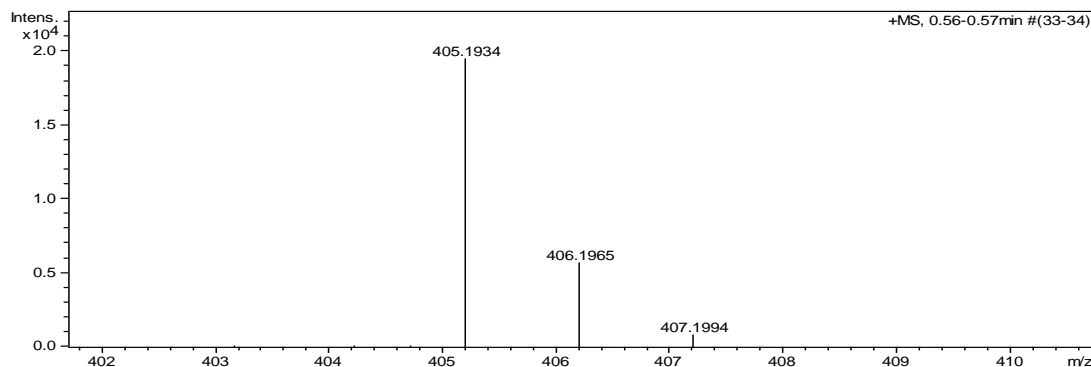
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8) give the product **5b** (182.6 mg, 95% yield) as a yellow solid. Mp: 126 - 128 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.53-7.50 (m, 2H), 7.47-7.44 (m, 4H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.31-7.27 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 3.59 (d, *J* = 13.2 Hz, 1H), 3.40 (d, *J* = 17.6 Hz, 1H), 3.16 (d, *J* = 13.6 Hz, 1H), 2.86 (d, *J* = 17.6 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H), 1.76 (s, 3H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 170.1, 152.2, 140.7, 140.1, 139.3, 136.1, 130.6, 129.2, 128.8, 128.6, 127.1, 126.9 (2C), 126.1, 67.2, 45.1, 42.4, 25.8, 23.6, 21.4;

IR (KBr) ν: 3024, 2933, 1796, 1637, 1486, 1409, 1362, 1323, 1160, 1119, 1031, 918, 814, 768, 739, 691, 608, 547, 507, 446 cm<sup>-1</sup>;

HRMS Calcd (ESI) *m/z* for C<sub>26</sub>H<sub>26</sub>N<sub>2</sub>NaO [M + Na]<sup>+</sup>: 405.1937, found: 405.1934.



**1-(5-(4-(tert-butyl)benzyl)-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5c):**

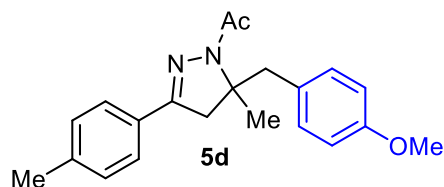
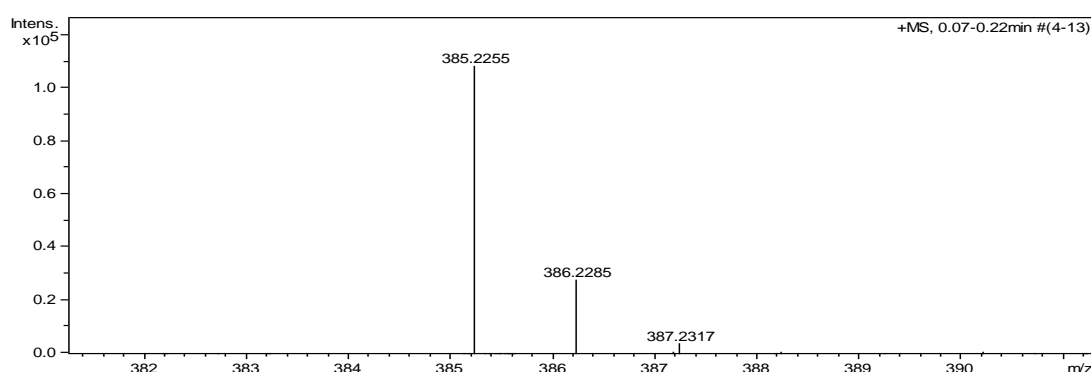
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **5c** (164.3 mg, 91% yield) as a yellow solid. Mp: 98 - 100 °C.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 3.44 (d, *J* = 13.6 Hz, 1H), 3.36 (d, *J* = 17.6 Hz, 1H), 3.15 (d, *J* = 13.6 Hz, 1H), 2.81 (d, *J* = 17.2 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H), 1.73 (s, 3H), 1.25 (s, 9H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 170.0, 152.3, 149.3, 140.0, 133.8, 129.9, 129.1, 128.9, 126.1, 125.1, 67.3, 45.1, 42.1, 34.3, 31.2, 25.6, 23.6, 21.4;

**IR** (KBr) ν: 2957, 2868, 1913, 1639, 1517, 1434, 1408, 1363, 1327, 1268, 1241, 1166, 1114, 1029, 944, 837, 814, 686, 629, 552, 503, 457 cm<sup>-1</sup>;

**HRMS** Calcd (ESI) *m/z* for C<sub>24</sub>H<sub>30</sub>N<sub>2</sub>NaO [M + Na]<sup>+</sup>: 385.2250, found: 385.2255.



**1-(5-(4-methoxybenzyl)-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5d):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 6) give the product **5d** (149.6 mg, 89% yield) as a yellow solid. Mp: 88 - 91 °C.

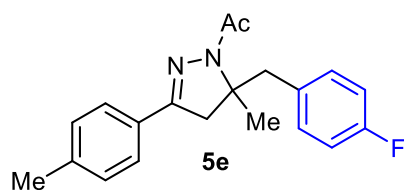
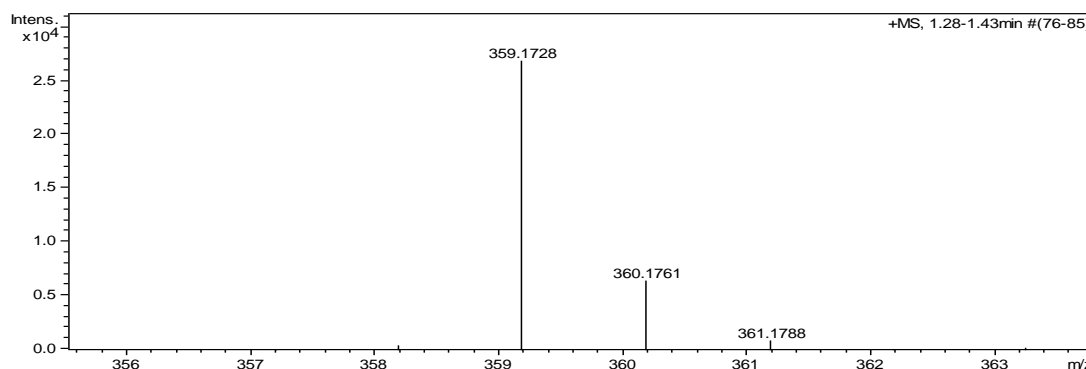
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.77 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 3.51 (d, *J* = 13.6 Hz, 1H), 3.36 (d, *J* = 17.6 Hz, 1H), 3.05 (d, *J* = 13.6 Hz, 1H), 2.84 (d, *J* = 17.2 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H), 1.73 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 170.0, 158.2, 152.2, 140.0, 131.1, 129.1, 129.0, 128.8, 126.1, 113.6, 67.2, 55.0, 45.0, 41.8, 25.8, 23.6, 21.4;

**IR** (KBr) ν: 2993, 2967, 2928, 2833, 2311, 1901, 1648, 1611, 1515, 1404, 1364, 1327,

1254, 1158, 1113, 1082, 1039, 937, 839, 814, 763, 706, 635, 598, 528, 449  $\text{cm}^{-1}$ .

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{21}\text{H}_{24}\text{N}_2\text{NaO}_2$   $[\text{M} + \text{Na}]^+$ : 359.1730, found: 359.1728.



**1-(5-(4-fluorobenzyl)-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5e):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8) give the product **5e** (151.9 mg, 94% yield) as a yellow solid. Mp: 95 - 96  $^{\circ}\text{C}$ .

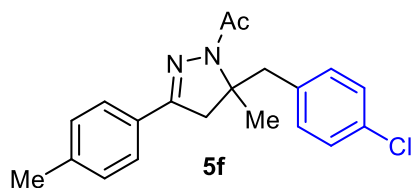
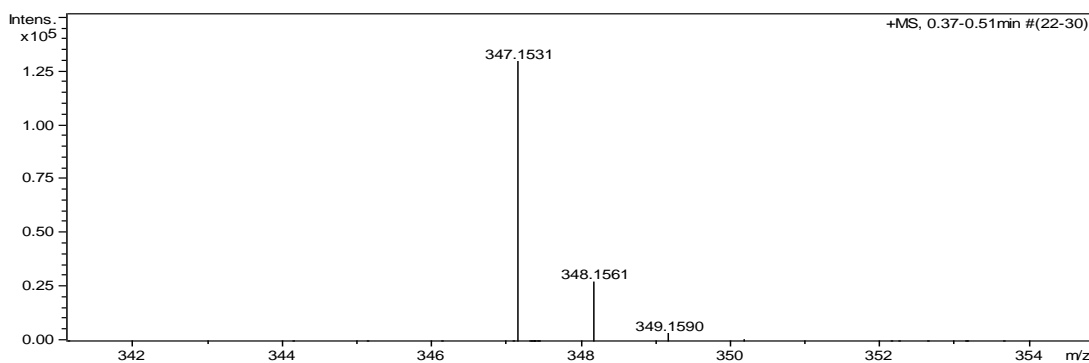
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.44 (d,  $J = 8.0$  Hz, 2H), 7.16-7.11 (m, 4H), 6.91 (t,  $J = 8.4$  Hz, 2H), 3.60 (d,  $J = 14.0$  Hz, 1H), 3.32 (d,  $J = 17.6$  Hz, 1H), 3.01 (d,  $J = 13.6$  Hz, 1H), 2.88 (d,  $J = 17.2$  Hz, 1H), 2.37 (s, 3H), 2.35 (s, 3H), 1.74 (s, 3H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  170.1, 161.7 (d,  $J = 243.6$  Hz), 152.1, 140.2, 132.7 (d,  $J = 3.3$  Hz), 131.5 (d,  $J = 7.8$  Hz), 129.2, 128.6, 126.1, 115.0 (d,  $J = 21.0$  Hz), 67.0 (d,  $J = 1.3$  Hz), 45.1, 41.9, 25.9, 23.6, 21.4;

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , 376 MHz)  $\delta$  -116.35;

**IR** (KBr)  $\nu$ : 2965, 2929, 1899, 1645, 1603, 1512, 1407, 1364, 1325, 1227, 1156, 1113, 1031, 939, 816, 770, 634, 602, 516, 449  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{20}\text{H}_{21}\text{FN}_2\text{NaO}$   $[\text{M} + \text{Na}]^+$ : 347.1530, found: 347.1531.



**1-(5-(4-chlorobenzyl)-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5f):**

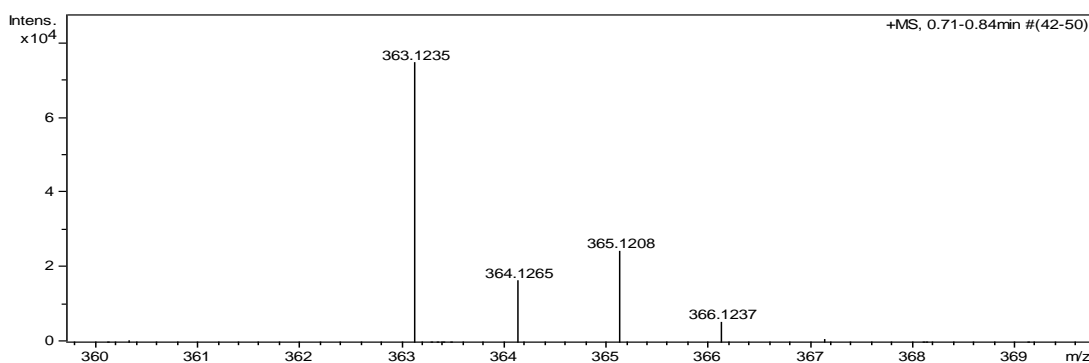
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8) give the product **5f** (145.4 mg, 85% yield) as a white solid. Mp: 121 - 123 °C.

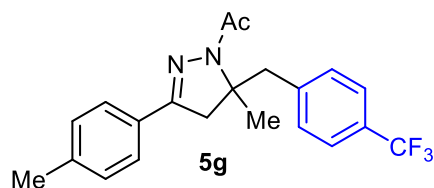
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 3.60 (d, *J* = 13.6 Hz, 1H), 3.31 (d, *J* = 17.2 Hz, 1H), 3.03 (d, *J* = 13.6 Hz, 1H), 2.88 (d, *J* = 17.2 Hz, 1H), 2.37 (s, 3H), 2.35 (s, 3H), 1.74 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 170.1, 152.1, 140.2, 135.4, 132.5, 131.4, 129.2, 128.6, 128.4, 126.1, 66.9, 45.1, 42.0, 25.9, 23.6, 21.4;

**IR** (KBr) ν: 2965, 2927, 2863, 1903, 1645, 1494, 1407, 1324, 1254, 1158, 1089, 1027, 933, 805, 626, 551, 512, 446 cm<sup>-1</sup>;

**HRMS** Calcd (ESI) *m/z* for C<sub>20</sub>H<sub>21</sub>ClN<sub>2</sub>NaO [M + Na]<sup>+</sup>: 363.1235, found: 363.1235.





**1-(5-methyl-3-(p-tolyl)-5-(4-(trifluoromethyl)benzyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5g):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **5g** (182.7 mg, 98% yield) as a yellow solid. Mp: 86 - 88 °C.

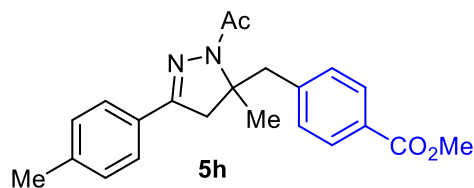
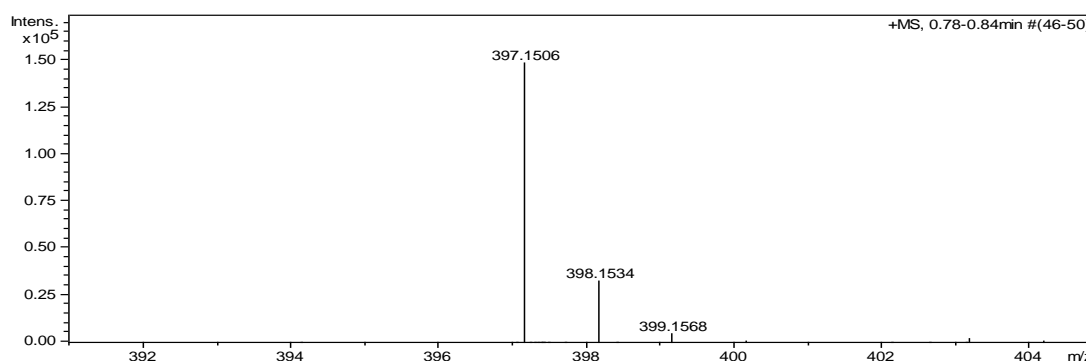
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.49 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 3.69 (d, *J* = 13.6 Hz, 1H), 3.31 (d, *J* = 17.2 Hz, 1H), 3.14 (d, *J* = 13.6 Hz, 1H), 2.91 (d, *J* = 17.6 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H), 1.76 (s, 3H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 170.2, 152.1, 141.1 (q, *J* = 1.4 Hz), 140.3, 130.4, 129.2, 128.8 (q, *J* = 32.2 Hz), 128.5, 126.1, 125.1 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 270.6 Hz), 66.8, 45.1, 42.5, 25.9, 23.5, 21.3;

<sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz) δ -62.47;

IR (KBr) ν: 2971, 2932, 1641, 1414, 1365, 1323, 1169, 1133, 1065, 1020, 918, 849, 815, 744, 708, 653, 614, 554, 503, 451 cm<sup>-1</sup>;

HRMS Calcd (ESI) *m/z* for C<sub>21</sub>H<sub>21</sub>F<sub>3</sub>N<sub>2</sub>NaO [M + Na]<sup>+</sup>: 397.1498, found: 397.1506.



**Methyl 4-((1-acetyl-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-5-yl)methyl)benzoate (5h):**



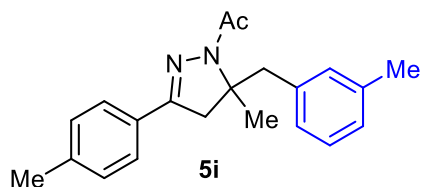
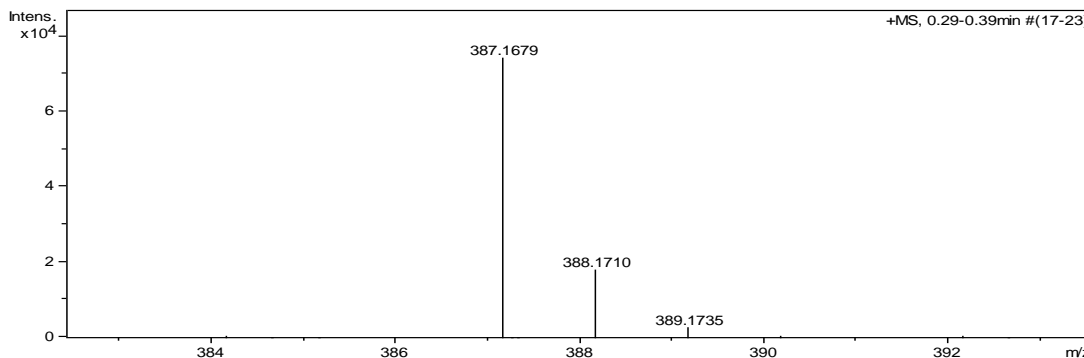
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 7) give the product **5h** (152.8 mg, 84% yield) as a yellow solid. Mp: 145 - 147 °C.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.88 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.83 (s, 3H), 3.69 (d, *J* = 13.6 Hz, 1H), 3.31 (d, *J* = 17.6 Hz, 1H), 3.08 (d, *J* = 13.6 Hz, 1H), 2.87 (d, *J* = 17.6 Hz, 1H), 2.35 (s, 3H), 2.31 (s, 3H), 1.74 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 170.0, 166.7, 152.0, 142.3, 140.1, 130.0, 129.4, 129.1, 128.4, 126.0, 66.8, 51.8, 45.1, 42.6, 26.0, 23.5, 21.3;

**IR** (KBr) ν: 2937, 1715, 1650, 1605, 1441, 1408, 1361, 1323, 1284, 1179, 1108, 1027, 968, 934, 843, 810, 765, 713, 628, 539, 488, 427 cm<sup>-1</sup>;

**HRMS** Calcd (ESI) *m/z* for C<sub>22</sub>H<sub>24</sub>N<sub>2</sub>NaO<sub>3</sub> [M + Na]<sup>+</sup>: 387.1679, found: 387.1679.



**1-(5-methyl-5-(3-methylbenzyl)-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5i):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **5i** (148.1 mg, 92% yield) as a yellow solid. Mp: 67 - 69 °C.

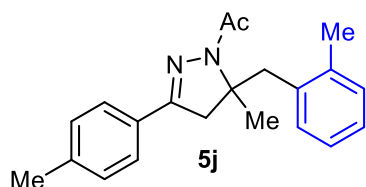
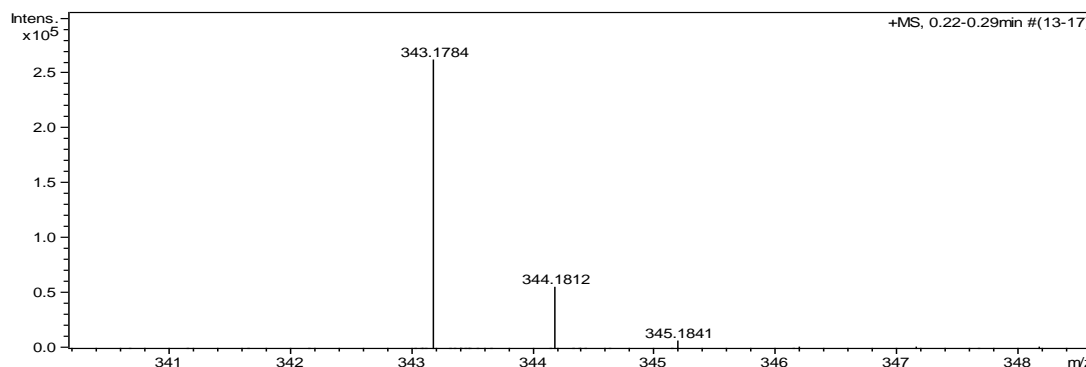
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.00-6.97 (m, 3H), 3.51 (d, *J* = 13.6 Hz, 1H), 3.39 (d, *J* = 17.6 Hz, 1H), 3.11 (d, *J* = 13.6 Hz, 1H), 2.84 (d, *J* = 17.2 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H), 2.28 (s, 3H), 1.75 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 170.0, 152.2, 140.0, 137.6, 136.9, 131.0, 129.1, 128.9,

128.0, 127.3, 127.2, 126.1, 67.2, 45.1, 42.6, 25.8, 23.6, 21.4, 21.3;

**IR** (KBr)  $\nu$ : 2924, 2381, 2311, 1660, 1606, 1409, 1362, 1326, 1179, 1114, 1031, 933, 816, 789, 746, 698, 622, 592, 430  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{21}\text{H}_{24}\text{N}_2\text{NaO}$   $[\text{M} + \text{Na}]^+$ : 343.1781, found: 343.1784.



**1-(5-methyl-5-(2-methylbenzyl)-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5j):**

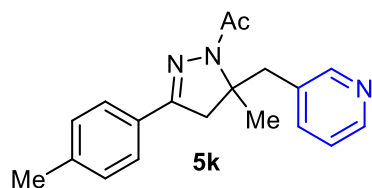
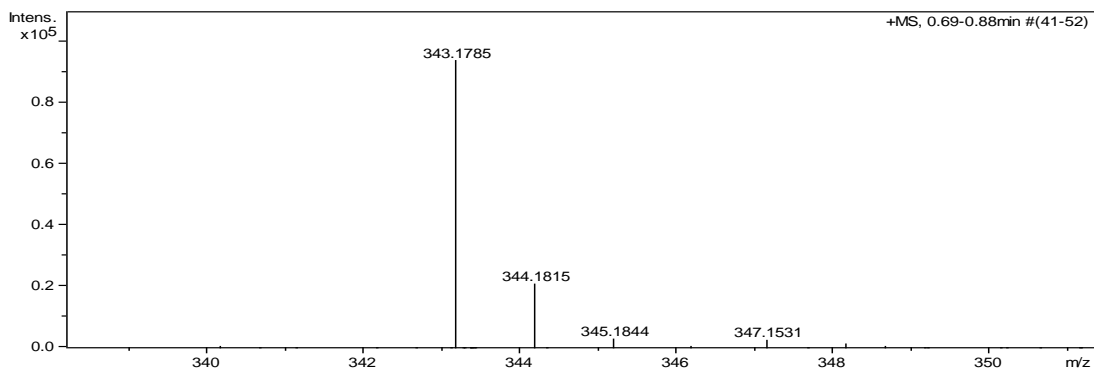
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **5j** (121.6 mg, 76% yield) as a yellow solid. Mp: 76 - 78  $^{\circ}\text{C}$ .

**$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.52 (d,  $J = 8.0$  Hz, 2H), 7.19-7.10 (m, 6H), 3.50-3.41, (m, 2H), 3.26 (d,  $J = 17.2$  Hz, 1H), 2.81 (d,  $J = 17.2$  Hz, 1H), 2.44 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 1.74 (s, 3H);

**$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  170.0, 152.4, 140.1, 136.9, 135.4, 130.5, 130.4, 129.2, 128.8, 126.6, 126.1, 125.8, 67.7, 44.8, 38.2, 25.6, 23.7, 21.4, 20.3;

**IR** (KBr)  $\nu$ : 3065, 3020, 2966, 2930, 2387, 2312, 1925, 1813, 1650, 1492, 1412, 1361, 1327, 1261, 1227, 1178, 1095, 1030, 964, 927, 818, 748, 622, 595, 542, 507, 450  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{21}\text{H}_{24}\text{N}_2\text{NaO}$   $[\text{M} + \text{Na}]^+$ : 343.1781, found: 343.1785.



**1-(5-methyl-5-(pyridin-3-ylmethyl)-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (**5k**):**

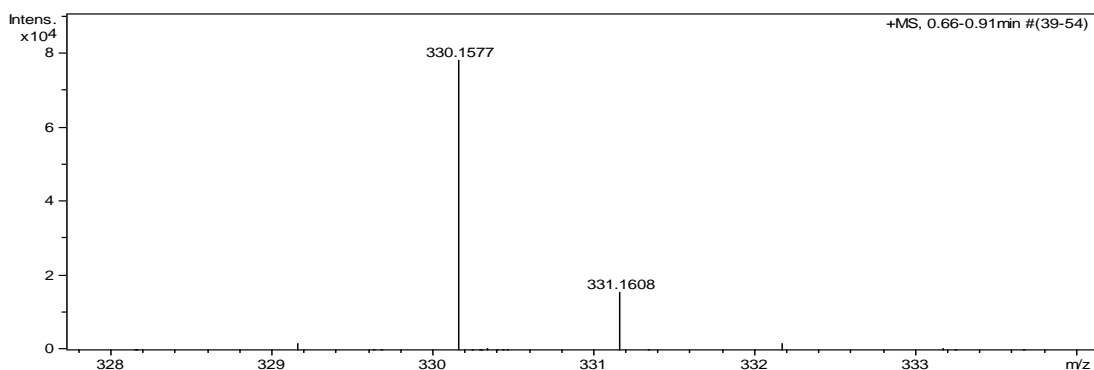
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 2) give the product **5k** (137.2 mg, 89% yield) as a yellow oil.

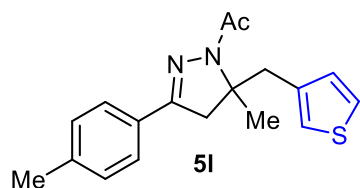
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 8.40-8.38 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.15-7.10 (m, 3H), 3.65 (d, *J* = 13.6 Hz, 1H), 3.26 (d, *J* = 17.2 Hz, 1H), 3.01 (d, *J* = 14.0 Hz, 1H), 2.90 (d, *J* = 17.6 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H), 1.74 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 170.1, 152.1, 150.9, 148.0, 140.3, 137.4, 132.4, 129.2, 128.3, 126.1, 123.2, 66.7, 45.1, 39.9, 25.9, 23.5, 21.3;

**IR** (KBr) ν: 2927, 2379, 2313, 1659, 1421, 1363, 1327, 1264, 1110, 1029, 933, 817, 719, 624, 546, 516, 431 cm<sup>-1</sup>;

**HRMS** Calcd (ESI) m/z for C<sub>19</sub>H<sub>21</sub>N<sub>3</sub>NaO [M + Na]<sup>+</sup>: 330.1577, found: 330.1577.





**1-(5-methyl-5-(thiophen-3-ylmethyl)-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5l):**

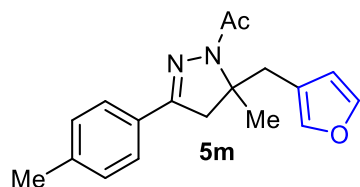
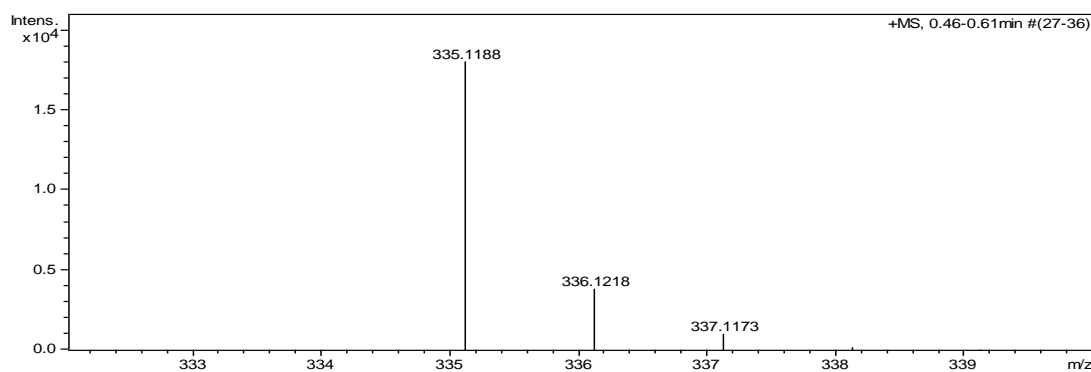
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8) give the product **5l** (136.4 mg, 87% yield) as a yellow solid. Mp: 93 - 94 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.19-7.15 (m, 3H), 6.99 (d, *J* = 3.2 Hz, 1H), 6.91 (d, *J* = 4.8 Hz, 1H), 3.64 (d, *J* = 14.4 Hz, 1H), 3.35 (d, *J* = 17.2 Hz, 1H), 3.13 (d, *J* = 14.0 Hz, 1H), 2.91 (d, *J* = 17.2 Hz, 1H), 2.37 (s, 3H), 2.36 (s, 3H), 1.73 (s, 3H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.9, 152.2, 140.1, 137.1, 129.2, 129.0, 128.8, 126.1, 125.2, 122.9, 66.7, 45.7, 37.6, 25.7, 23.5, 21.4;

IR (KBr) ν: 3097, 2977, 1637, 1435, 1412, 1362, 1329, 1270, 1240, 1161, 1114, 1031, 935, 859, 810, 736, 699, 628, 591, 550, 500, 446 cm<sup>-1</sup>;

HRMS Calcd (ESI) *m/z* for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>NaOS [M + Na]<sup>+</sup>: 335.1189, found: 335.1188.



**1-(5-(furan-3-ylmethyl)-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5m):**

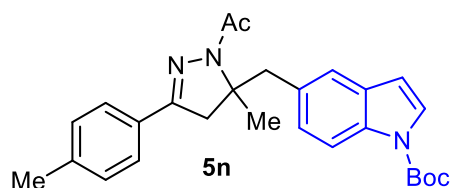
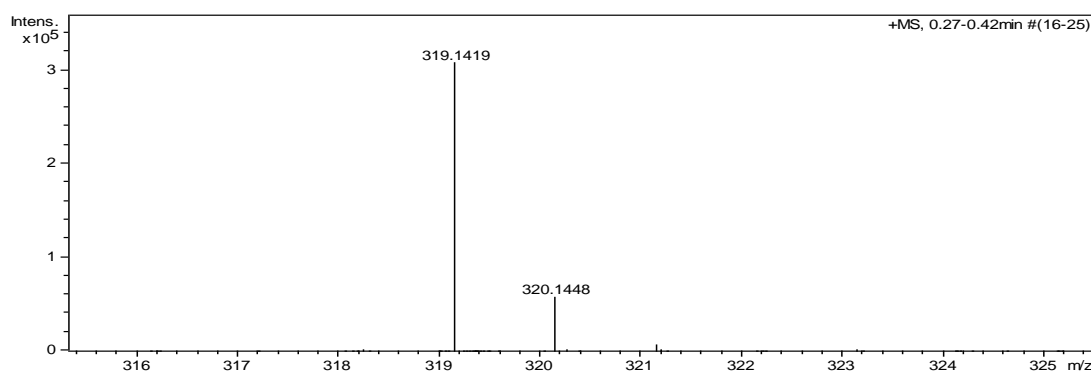
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 7) give the product **5m** (135.3 mg, 91% yield) as a yellow solid. Mp: 78 - 80 °C.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.28-7.22 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.22 (s, 1H), 3.48 (d, *J* = 14.4 Hz, 1H), 3.28 (d, *J* = 17.2 Hz, 1H), 2.95-2.87 (m, 2H), 2.36 (s, 6H (3H\*2)), 1.71 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 169.8, 152.2, 142.9, 140.5, 140.2, 129.2, 128.8, 126.2, 119.9, 111.7, 66.5, 45.9, 32.9, 25.7, 23.5, 21.4;

**IR** (KBr) ν: 3132, 2971, 2931, 2313, 1640, 1500, 1438, 1410, 1362, 1330, 1255, 1152, 1115, 1023, 938, 871, 847, 816, 739, 630, 601, 549, 501, 450 cm<sup>-1</sup>;

**HRMS** Calcd (ESI) *m/z* for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>2</sub> [M + Na]<sup>+</sup>: 319.1417, found: 319.1419.



**tert-butyl-5-((1-acetyl-5-methyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-5-yl)methyl)-1H-indole-1-carboxylate (5n):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 7) give the product **5n** (215.8 mg, 97% yield) as a yellow solid. Mp: 62 - 65 °C.

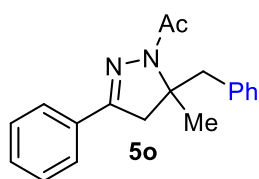
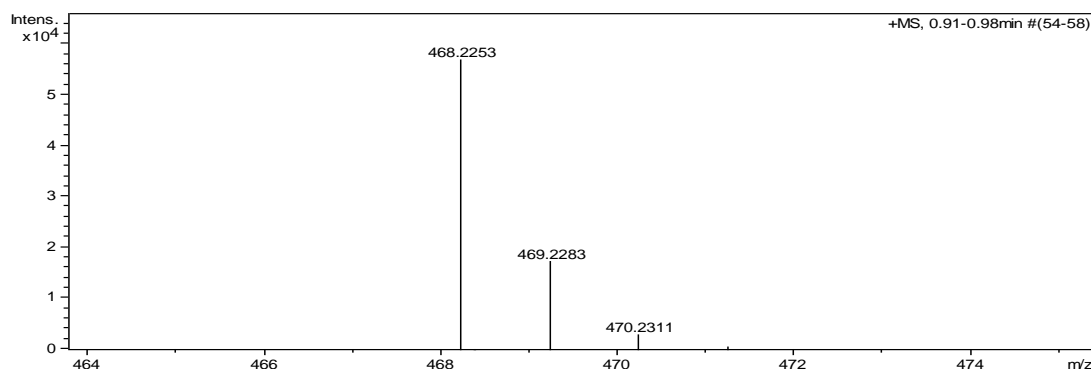
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 3.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.37 (s, 1H), 7.14-7.12 (m, 3H), 6.49 (d, *J* = 4.0 Hz, 1H), 3.64 (d, *J* = 13.6 Hz, 1H), 3.45 (d, *J* = 17.2 Hz, 1H), 3.26 (d, *J* = 13.6 Hz, 1H), 2.82 (d, *J* = 17.6 Hz, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 1.75 (s, 3H), 1.65 (s, 9H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 170.1, 152.2, 149.6, 140.0, 134.0, 131.2, 130.6, 129.1, 128.8, 126.5, 126.1, 125.9, 122.4, 114.7, 107.1, 83.5, 67.3, 45.0, 42.5, 28.1, 25.8, 23.6, 21.3;

**IR** (KBr) ν: 3132, 2971, 2931, 2313, 1640, 1500, 1438, 1410, 1362, 1330, 1255, 1152,

1115, 1023, 938, 871, 847, 816, 739, 630, 601, 549, 501, 450  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{27}\text{H}_{31}\text{N}_3\text{NaO}_3$   $[\text{M} + \text{Na}]^+$ : 468.2258, found: 468.2253.



**1-(5-benzyl-5-methyl-3-phenyl-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5o):**

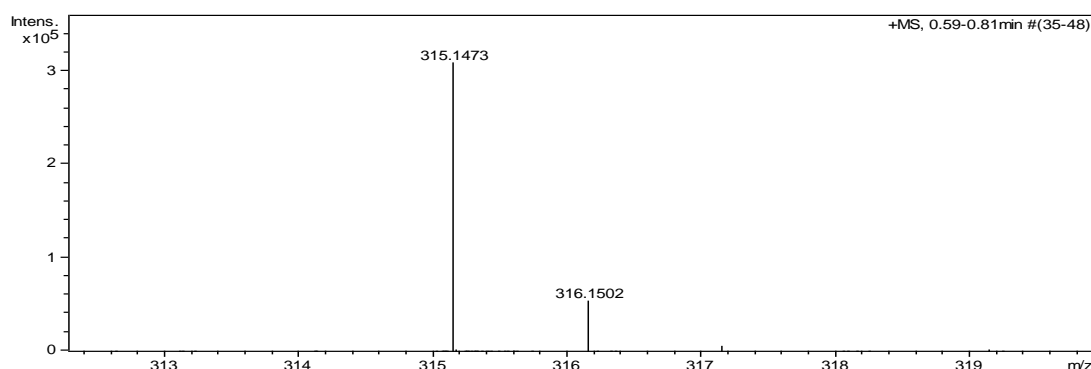
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **5o** (129.9 mg, 89% yield) as a yellow solid. Mp: 58 - 60  $^{\circ}\text{C}$ .

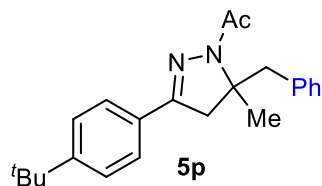
$^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.56-7.54 (m, 2H), 7.35-7.33 (m, 3H), 7.25-7.21 (m, 2H), 7.19-7.16 (m, 3H), 3.57 (d,  $J = 13.6$  Hz, 1H), 3.40 (d,  $J = 17.6$  Hz, 1H), 3.12 (d,  $J = 13.6$  Hz, 1H), 2.86 (d,  $J = 17.2$  Hz, 1H), 2.38 (s, 3H), 1.76 (s, 3H);

$^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  170.2, 152.1, 136.9, 131.6, 130.2, 129.8, 128.5, 128.2, 126.6, 126.2, 67.3, 45.0, 42.7, 25.9, 23.6;

**IR** (KBr)  $\nu$ : 3078, 3022, 2969, 2921, 2847, 1965, 1896, 1651, 1598, 1495, 1433, 1409, 1365, 1330, 1231, 1158, 1127, 1074, 1030, 934, 843, 762, 697, 647, 613, 545, 514, 483, 419  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{19}\text{H}_{20}\text{N}_2\text{NaO}$   $[\text{M} + \text{Na}]^+$ : 315.1468, found: 315.1473.





**1-(5-benzyl-3-(4-(tert-butyl)phenyl)-5-methyl-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5p):**

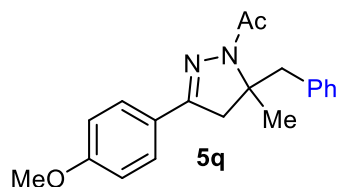
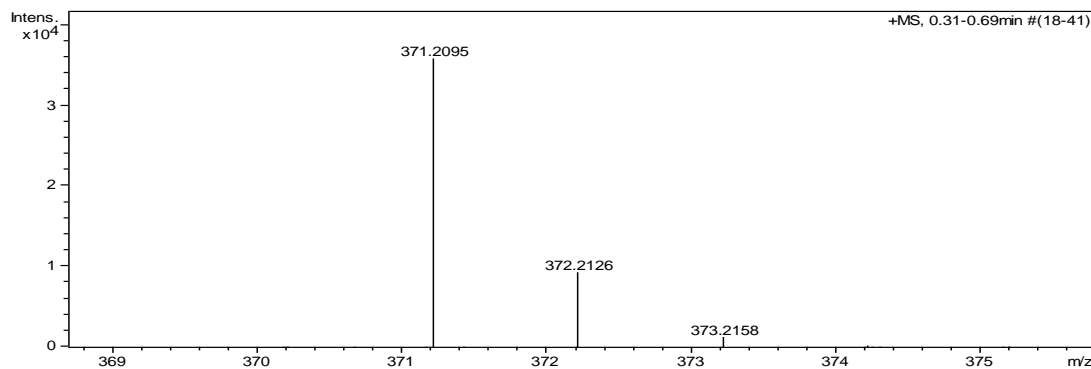
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **5p** (146.4 mg, 84% yield) as a yellow solid. Mp: 73 - 75 °C.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.25-7.22 (m, 2H), 7.19-7.17 (m, 3H), 3.58 (d, *J* = 13.6 Hz, 1H), 3.39 (d, *J* = 17.6 Hz, 1H), 3.13 (d, *J* = 13.6 Hz, 1H), 2.85 (d, *J* = 17.2 Hz, 1H), 2.39 (s, 3H), 1.74 (s, 3H), 1.31 (s, 9H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 170.1, 153.2, 152.1, 137.0, 130.2, 128.8, 128.2, 126.6, 126.0, 125.4, 67.1, 45.0, 42.7, 34.7, 31.1, 25.9, 23.6;

**IR** (KBr) ν: 2962, 2384, 2312, 1660, 1603, 1411, 1362, 1326, 1266, 1169, 1117, 1030, 932, 834, 740, 704, 622, 568, 421 cm<sup>-1</sup>;

**HRMS** Calcd (ESI) *m/z* for C<sub>23</sub>H<sub>28</sub>N<sub>2</sub>NaO [M + Na]<sup>+</sup>: 371.2094, found: 371.2095.



**1-(5-benzyl-3-(4-methoxyphenyl)-5-methyl-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5q):**

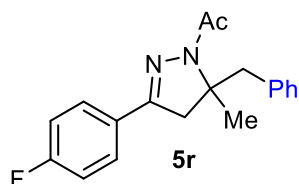
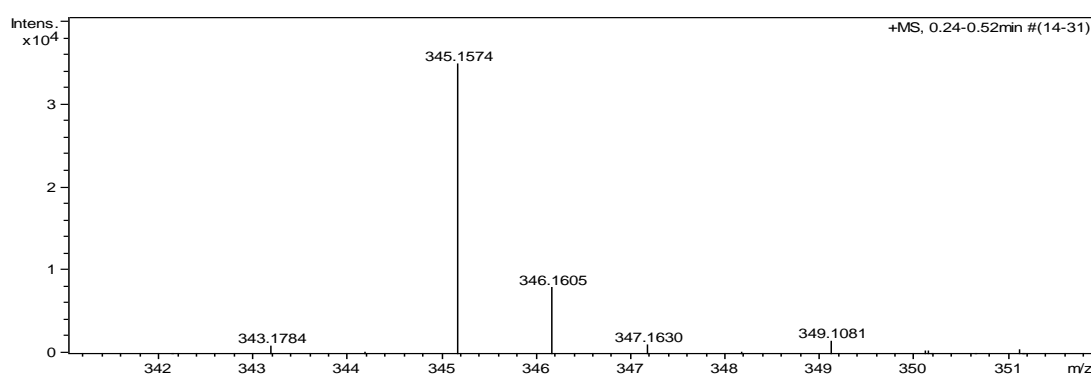
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **5q** (126.8 mg, 79% yield) as a yellow solid. Mp: 64 - 67 °C.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.49 (d, *J* = 9.2 Hz, 2H), 7.25-7.21 (m, 2H), 7.18-7.15 (m, 3H), 6.85 (d, *J* = 9.2 Hz, 2H), 3.80 (s, 3H), 3.55 (d, *J* = 13.6 Hz, 1H), 3.36 (d, *J* = 17.2 Hz, 1H), 3.12 (d, *J* = 13.6 Hz, 1H), 2.83 (d, *J* = 17.6 Hz, 1H), 2.37 (s, 3H), 1.74 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 169.9, 160.9, 151.9, 137.0, 130.2, 128.2, 127.7, 126.6, 124.3, 113.9, 67.1, 55.3, 45.2, 42.7, 25.9, 23.6;

**IR** (KBr) ν: 2931, 2844, 2307, 2041, 1967, 1887, 1637, 1517, 1417, 1369, 1333, 1251, 1170, 1112, 1026, 933, 824, 758, 711, 628, 581, 532 cm<sup>-1</sup>;

**HRMS** Calcd (ESI) *m/z* for C<sub>20</sub>H<sub>22</sub>N<sub>2</sub>NaO<sub>2</sub> [M + Na]<sup>+</sup>: 345.1573, found: 345.1574.



**1-(5-benzyl-3-(4-fluorophenyl)-5-methyl-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5r):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8) give the product **5r** (142.3 mg, 92% yield) as a yellow solid. Mp: 78 - 80 °C.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.54-7.51 (m, 2H), 7.26-7.21 (m, 2H), 7.19-7.15 (m, 3H), 7.02 (t, *J* = 8.8 Hz, 2H), 3.58 (d, *J* = 13.6 Hz, 1H), 3.37 (d, *J* = 17.6 Hz, 1H), 3.09 (d, *J* = 13.6 Hz, 1H), 2.85 (d, *J* = 17.2 Hz, 1H), 2.37 (s, 3H), 1.76 (s, 3H);

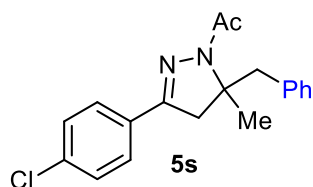
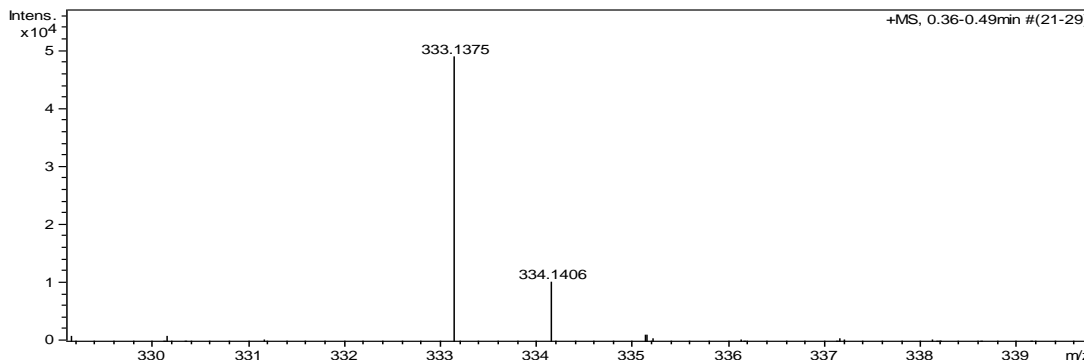
**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 170.1, 163.6 (d, *J* = 249.3 Hz), 151.1, 136.8, 130.1, 128.2, 128.1 (d, *J* = 8.4 Hz), 127.8 (d, *J* = 3.3 Hz), 126.6, 115.6 (d, *J* = 21.9 Hz), 67.5, 45.1, 42.7, 26.0, 23.6;

**<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 376 MHz) δ -110.2;



**IR** (KBr)  $\nu$ : 3063, 3032, 2997, 2961, 2920, 2385, 2311, 1912, 1655, 1604, 1516, 1434, 1362, 1325, 1224, 1158, 1131, 1098, 1074, 1026, 965, 937, 900, 839, 808, 759, 707, 624, 591, 568, 541, 517, 491, 439  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{19}\text{H}_{19}\text{FN}_2\text{NaO}$   $[\text{M} + \text{Na}]^+$ : 333.1374, found: 333.1375.



**1-(5-benzyl-3-(4-chlorophenyl)-5-methyl-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5s):**

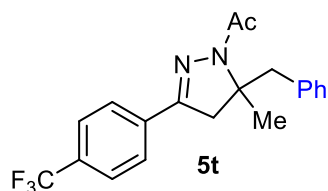
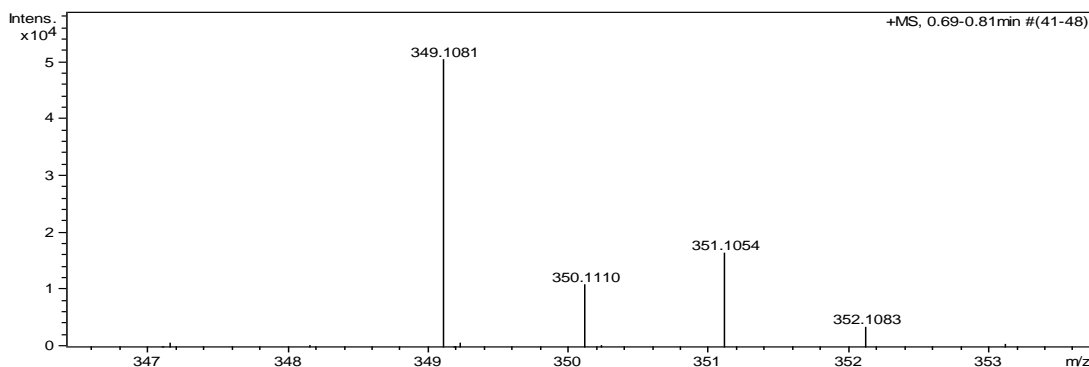
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8) give the product **5s** (131.1 mg, 80% yield) as a yellow solid. Mp: 96 - 98 °C.

**$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.46 (d,  $J = 8.8$  Hz, 2H), 7.30 (d,  $J = 8.4$  Hz, 2H), 7.25-7.21 (m, 2H), 7.19-7.14 (m, 3H), 3.58 (d,  $J = 13.6$  Hz, 1H), 3.36 (d,  $J = 17.2$  Hz, 1H), 3.08 (d,  $J = 13.6$  Hz, 1H), 2.84 (d,  $J = 17.6$  Hz, 1H), 2.37 (s, 3H), 1.77 (s, 3H);

**$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  170.2, 151.0, 136.8, 135.7, 130.1 (2C), 128.7, 128.2, 127.4, 126.7, 67.6, 45.0, 42.8, 26.0, 23.6;

**IR** (KBr)  $\nu$ : 3030, 2920, 2302, 1764, 1655, 1598, 1495, 1423, 1323, 1259, 1181, 1134, 1086, 1024, 929, 830, 761, 701, 618, 522, 468, 424  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{19}\text{H}_{19}\text{ClN}_2\text{NaO}$   $[\text{M} + \text{Na}]^+$ : 349.1078, found: 349.1081.



**1-(5-benzyl-5-methyl-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5t):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **5t** (178.7 mg, 99% yield) as a yellow solid. Mp: 86 - 88 °C.

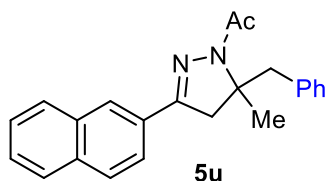
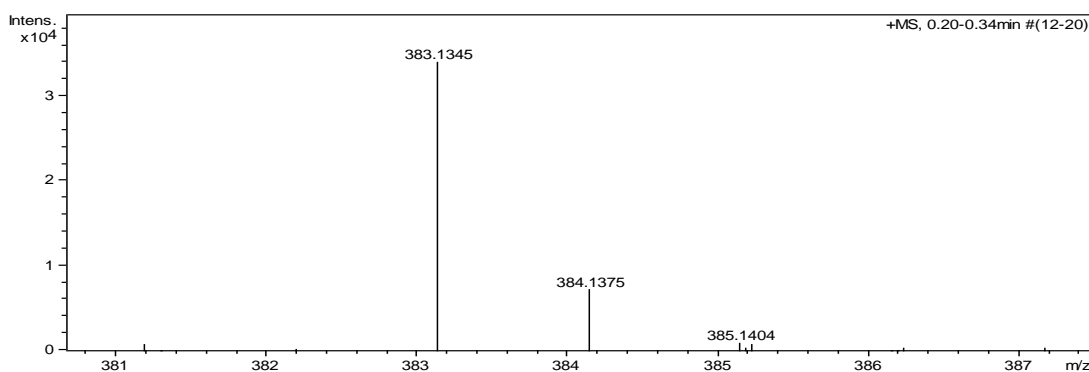
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.63 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.25-7.22 (m, 2H), 7.19-7.15 (m, 3H), 3.61 (d, *J* = 13.6 Hz, 1H), 3.40 (d, *J* = 17.6 Hz, 1H), 3.07 (d, *J* = 13.6 Hz, 1H), 2.89 (d, *J* = 17.6 Hz, 1H), 2.39 (s, 3H), 1.79 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 170.4, 150.6, 136.7, 135.0 (q, *J* = 1.6 Hz), 131.3 (q, *J* = 32.4 Hz), 130.1, 128.3, 126.7, 126.3, 125.4 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 270.8 Hz), 67.9, 44.9, 42.8, 26.1, 23.5;

**<sup>19</sup>F NMR** (CDCl<sub>3</sub>, 376 MHz) δ -62.82;

**IR** (KBr) ν: 3294, 3060, 2967, 2918, 2307, 1947, 1817, 1656, 1598, 1525, 1496, 1430, 1406, 1369, 1326, 1187, 1156, 1116, 1067, 1026, 967, 922, 875, 844, 757, 699, 665, 599, 514, 447 cm<sup>-1</sup>.

**HRMS** Calcd (ESI) m/z for C<sub>20</sub>H<sub>19</sub>F<sub>3</sub>N<sub>2</sub>NaO [M + Na]<sup>+</sup>: 383.1342, found: 383.1345.



**1-(5-benzyl-5-methyl-3-(naphthalen-2-yl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5u):**

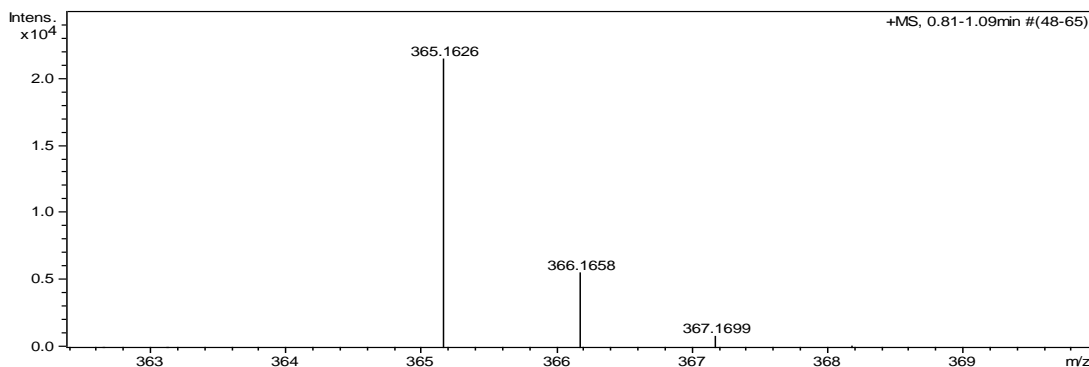
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8) give the product **5u** (131.5 mg, 77% yield) as a yellow solid. Mp: 124 - 126 °C.

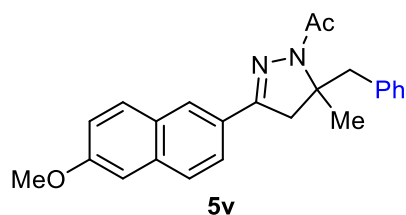
$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.85-7.74 (m, 5H), 7.49-7.47 (m, 2H), 7.24-7.13 (m, 5H), 3.59 (d,  $J = 13.6$  Hz, 1H), 3.50 (d,  $J = 17.2$  Hz, 1H), 3.15 (d,  $J = 13.6$  Hz, 1H), 2.97 (d,  $J = 17.2$  Hz, 1H), 2.43 (s, 3H), 1.79 (s, 3H);

$^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  170.2, 152.1, 136.9, 133.9, 132.9, 130.2, 129.2, 128.2 (2C), 128.1, 127.8, 126.9, 126.6 (2C), 126.5, 123.0, 67.5, 45.0, 42.8, 26.0, 23.7;

**IR** (KBr)  $\nu$ : 3056, 3023, 2972, 2928, 1769, 1650, 1475, 1436, 1410, 1364, 1319, 1240, 1157, 1125, 1069, 1015, 930, 854, 820, 751, 706, 643, 613, 547, 516, 478  $\text{cm}^{-1}$ .

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{23}\text{H}_{22}\text{N}_2\text{NaO}$  [ $\text{M} + \text{Na}$ ] $^+$ : 365.1624, found: 365.1626.





**1-(5-benzyl-3-(6-methoxynaphthalen-2-yl)-5-methyl-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5v):**

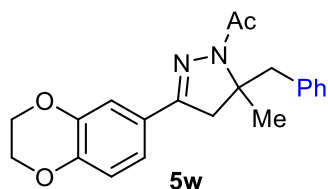
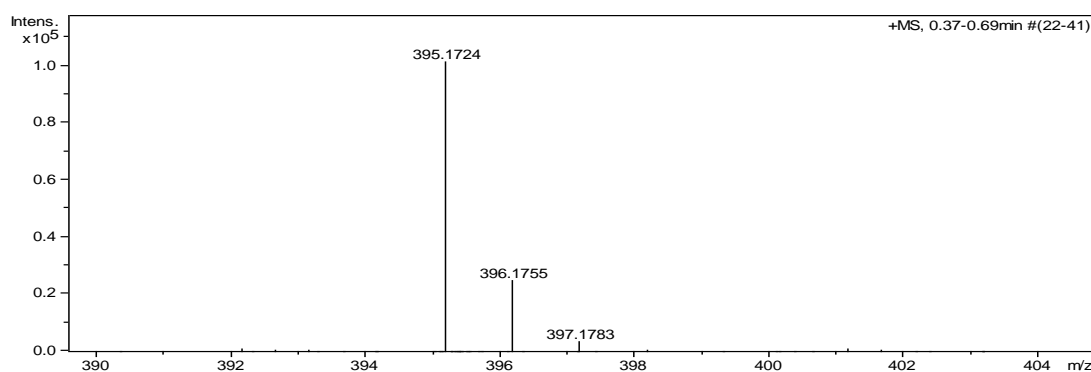
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **5v** (147.8 mg, 79% yield) as a yellow solid. Mp: 100 - 102 °C.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.81 (d, *J* = 8.8 Hz, 1H), 7.71-7.64 (m, 3H), 7.25-7.13 (m, 6H), 7.10 (s, 1H), 3.90 (s, 3H), 3.58 (d, *J* = 13.6 Hz, 1H), 3.48 (d, *J* = 17.6 Hz, 1H), 3.15 (d, *J* = 13.6 Hz, 1H), 2.95 (d, *J* = 17.6 Hz, 1H), 2.42 (s, 3H), 1.78 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 170.1, 158.5, 152.4 (2C), 137.0, 135.3, 130.2, 129.8, 128.2, 127.0 (2C), 126.6, 126.3, 123.6, 119.3, 106.0, 67.3, 55.3, 45.0, 42.8, 25.9, 23.6;

**IR** (KBr) ν: 2919, 1947, 1659, 1614, 1490, 1439, 1382, 1322, 1255, 1206, 1163, 1119, 1024, 918, 888, 856, 821, 757, 700, 634, 521, 467 cm<sup>-1</sup>

**HRMS** Calcd (ESI) *m/z* for C<sub>24</sub>H<sub>24</sub>N<sub>2</sub>NaO<sub>2</sub> [M + Na]<sup>+</sup>: 395.1730, found: 395.1724.



**1-(5-benzyl-3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-5-methyl-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5w):**

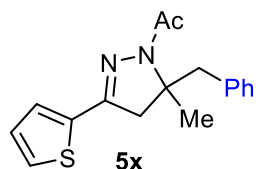
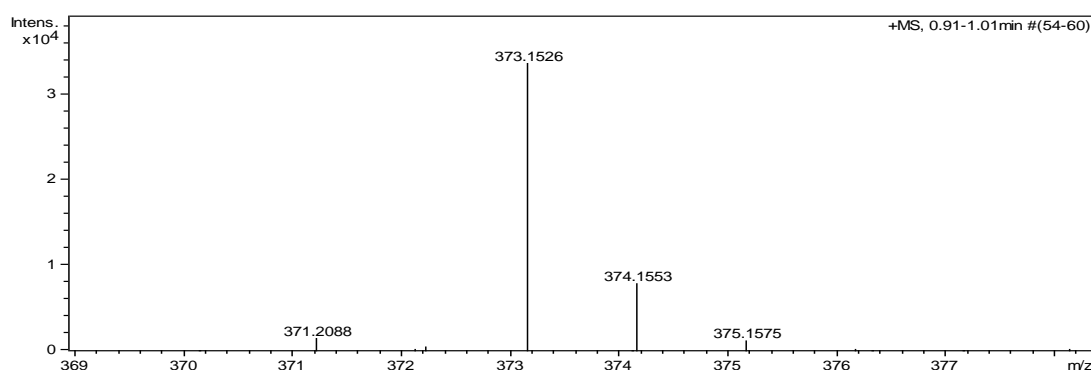
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 4) give the product **5w** (155.1 mg, 89% yield) as a yellow oil.

**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.26-7.21 (m, 2H), 7.19-7.15 (m, 3H), 7.08-7.04 (m, 2H), 6.82 (d, *J* = 8.4 Hz, 1H), 4.25 (s, 4H), 3.54 (d, *J* = 13.6 Hz, 1H), 3.33 (d, *J* = 17.2 Hz, 1H), 3.11 (d, *J* = 13.6 Hz, 1H), 2.79 (d, *J* = 17.2 Hz, 1H), 2.35 (s, 3H), 1.73 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 170.0, 151.7, 145.2, 143.4, 137.0, 130.2, 128.2, 126.6, 125.2, 119.8, 117.3, 115.2, 67.2, 64.5, 64.2, 45.1, 42.7, 25.9, 23.6;

**IR** (KBr) ν: 3028, 2972, 2930, 2878, 1954, 1658, 1605, 1575, 1513, 1412, 1363, 1317, 1284, 1246, 1183, 1125, 1066, 932, 889, 818, 751, 708, 623, 591, 490, 453 cm<sup>-1</sup>.

**HRMS** Calcd (ESI) *m/z* for C<sub>21</sub>H<sub>22</sub>N<sub>2</sub>NaO<sub>3</sub> [M + Na]<sup>+</sup>: 373.1523, found: 373.1526.



**1-(5-benzyl-5-methyl-3-(thiophen-2-yl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5x):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8) give the product **5x** (137.1 mg, 92% yield) as a yellow solid. Mp: 100 - 103 °C.

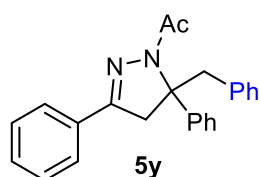
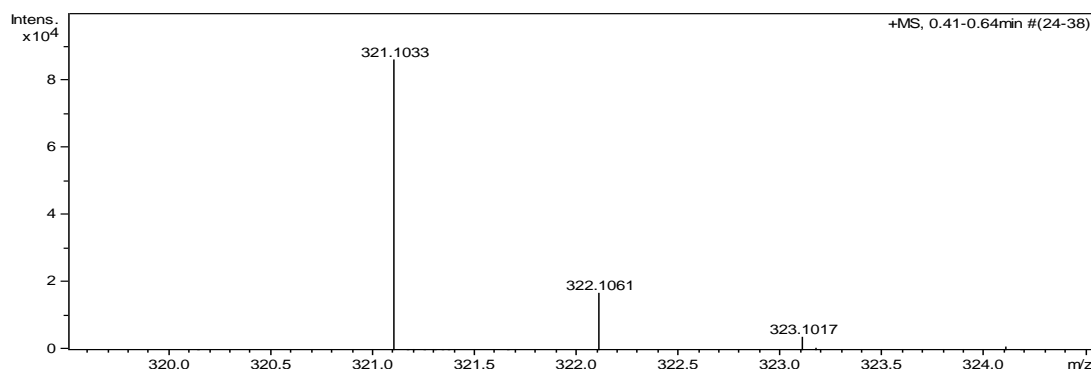
**<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ 7.32 (d, *J* = 4.8 Hz, 1H), 7.25-7.22 (m, 2H), 7.20-7.15 (m, 3H), 7.08-7.07 (m, 1H), 6.99 (dd, *J*<sub>1</sub> = 5.2 Hz, *J*<sub>2</sub> = 3.6 Hz, 1H), 3.54 (d, *J* = 13.6 Hz, 1H), 3.38 (d, *J* = 17.2 Hz, 1H), 3.13 (d, *J* = 13.6 Hz, 1H), 2.84 (d, *J* = 17.2 Hz, 1H), 2.34 (s, 3H), 1.74 (s, 3H);

**<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ 170.0, 147.8, 136.8, 135.3, 130.2, 128.3, 128.1, 127.9, 127.3, 126.7, 67.5, 45.7, 42.7, 25.8, 23.5;

**IR** (KBr) ν: 3107, 3074, 3026, 2987, 2933, 1793, 1647, 1526, 1494, 1450, 1405, 1364,

1318, 1263, 1226, 1134, 1078, 1032, 972, 929, 853, 820, 759, 707, 614, 480  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{17}\text{H}_{18}\text{N}_2\text{NaOS}$   $[\text{M} + \text{Na}]^+$ : 321.1032, found: 321.1033.



**1-(5-benzyl-3,5-diphenyl-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5y):**

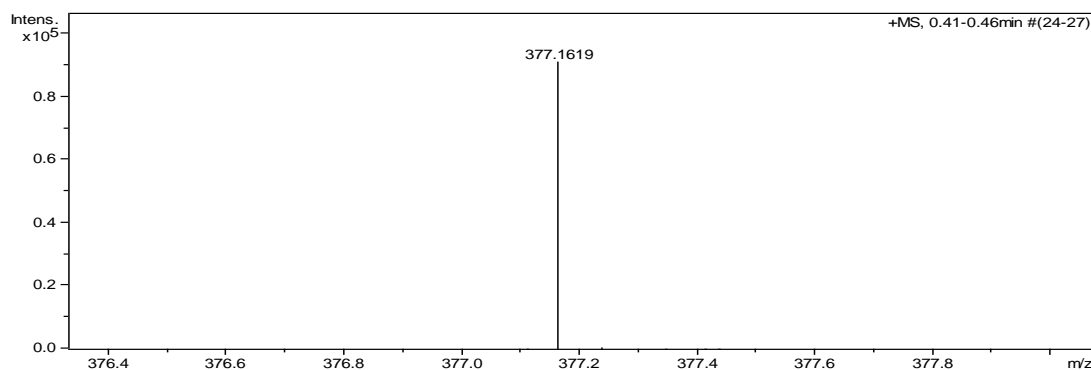
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8) give the product **5y** (123.8 mg, 70% yield) as a yellow solid. Mp: 135 - 137 °C.

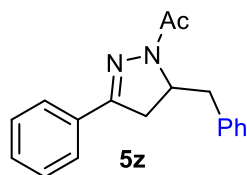
<sup>1</sup>H NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  7.53-7.50 (m, 2H), 7.45-7.38 (m, 4H), 7.34-7.30 (m, 4H), 7.28-7.23 (m, 4H), 7.21-7.17 (m, 1H), 4.35 (d,  $J = 13.6$  Hz, 1H), 3.76 (d,  $J = 17.6$  Hz, 1H), 3.44-3.35 (m, 2H), 2.45 (s, 3H);

<sup>13</sup>C NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  169.6, 151.7, 145.3, 136.2, 131.2, 130.3, 129.8, 128.7, 128.4, 128.2, 127.1, 126.8, 126.2, 124.7, 71.2, 48.5, 40.1, 23.5;

**IR** (KBr)  $\nu$ : 3060, 3026, 2927, 2386, 2314, 1963, 1804, 1663, 1596, 1495, 1414, 1359, 1324, 1229, 1155, 1063, 1029, 982, 926, 846, 802, 760, 722, 694, 624, 599, 537, 462, 422  $\text{cm}^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $\text{C}_{24}\text{H}_{22}\text{N}_2\text{NaO}$   $[\text{M} + \text{Na}]^+$ : 377.1624, found: 377.1619.





**1-(5-benzyl-3-phenyl-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5z):**

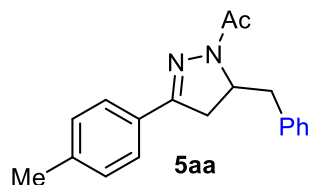
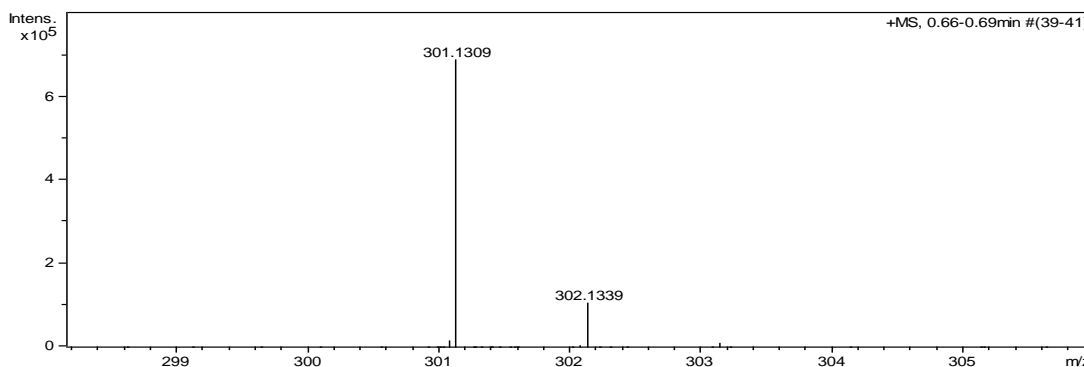
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8) give the product **5z** (103.1 mg, 74% yield) as a yellow solid. Mp: 79 - 82 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.65-7.63 (m, 2H), 7.38-7.36 (m, 3H), 7.31-7.28 (m, 2H), 7.23-7.20 (m, 3H), 4.91-4.84 (m, 1H), 3.49 (dd, *J*<sub>1</sub> = 13.2 Hz, *J*<sub>2</sub> = 2.8 Hz, 1H), 3.15 (dd, *J*<sub>1</sub> = 17.6 Hz, *J*<sub>2</sub> = 10.8 Hz, 1H), 2.95 (dd, *J*<sub>1</sub> = 17.6 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 2.65 (dd, *J*<sub>1</sub> = 13.2 Hz, *J*<sub>2</sub> = 10.0 Hz, 1H), 2.41 (s, 3H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 169.1, 154.3, 137.0, 131.5, 130.1, 129.4, 128.6, 128.5, 126.6, 126.4, 57.8, 38.5, 37.1, 22.0;

IR (KBr) ν: 2964, 2870, 1663, 1602, 1418, 1363, 1327, 1266, 1117, 1031, 930, 896, 835, 754, 625, 569, 472, 426 cm<sup>-1</sup>;

HRMS Calcd (ESI) m/z for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>NaO [M + Na]<sup>+</sup>: 301.1311, found: 301.1309.



**1-(5-benzyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5aa):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 10) give the product **5aa** (105.3 mg, 72% yield) as a yellow solid. Mp: 112 - 115 °C.

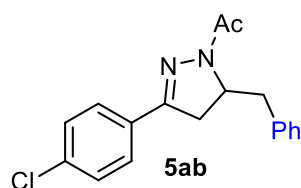
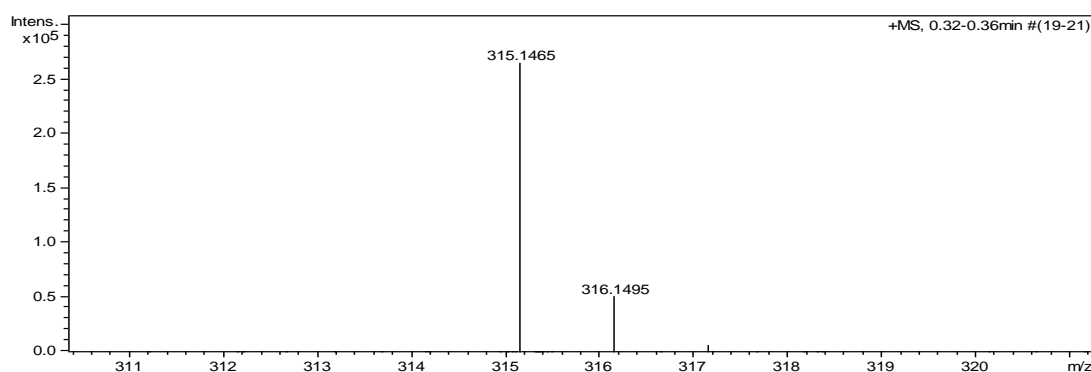
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.54 (d, *J* = 7.6 Hz, 2H), 7.31-7.28 (m, 2H), 7.25-7.17 (m, 5H), 4.90-4.82 (m, 1H), 3.49 (dd, *J*<sub>1</sub> = 13.2 Hz, *J*<sub>2</sub> = 3.6 Hz, 1H), 3.14 (dd, *J*<sub>1</sub> =

17.6 Hz,  $J_2 = 11.2$  Hz, 1H), 2.93 (dd,  $J_1 = 17.6$  Hz,  $J_2 = 3.2$  Hz, 1H), 2.63 (dd,  $J_1 = 12.8$  Hz,  $J_2 = 10.8$  Hz, 1H), 2.41 (s, 3H), 2.37 (s, 3H);

$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  169.0, 154.4, 140.4, 137.1, 129.5, 129.3, 128.7, 128.5, 126.6, 126.3, 57.7, 38.5, 37.1, 22.0, 21.4;

IR (KBr)  $\nu$ : 3059, 3029, 2924, 1904, 1650, 1494, 1439, 1358, 1330, 1250, 1221, 1153, 1079, 1029, 959, 889, 863, 813, 745, 705, 620, 587, 549, 509, 477, 428 cm<sup>-1</sup>;

HRMS Calcd (ESI)  $m/z$  for C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>NaO [M + Na]<sup>+</sup>: 315.1468, found: 315.1465.



**1-(5-benzyl-3-(4-chlorophenyl)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one (5ab):**

Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 6) give the product **5ab** (99.8 mg, 64% yield) as a yellow solid. Mp: 121 - 124 °C.

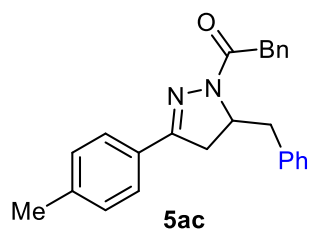
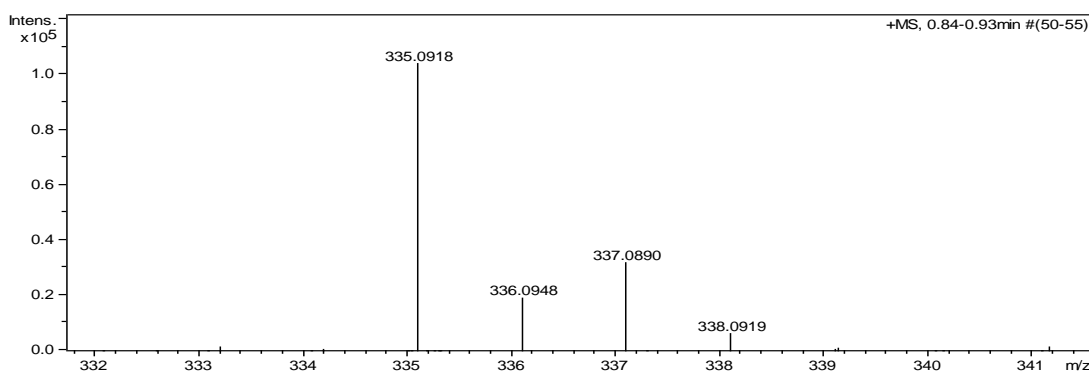
$^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.56 (d,  $J = 8.4$  Hz, 2H), 7.34-7.27 (m, 4H), 7.23-7.20 (m, 3H), 4.92-4.84 (m, 1H), 3.46 (dd,  $J_1 = 13.6$  Hz,  $J_2 = 3.2$  Hz, 1H), 3.13 (dd,  $J_1 = 17.6$  Hz,  $J_2 = 10.8$  Hz, 1H), 2.91 (dd,  $J_1 = 17.6$  Hz,  $J_2 = 4.0$  Hz, 1H), 2.67 (dd,  $J_1 = 13.2$  Hz,  $J_2 = 9.6$  Hz, 1H), 2.40 (s, 3H);

$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  169.1, 153.1, 136.8, 136.0, 130.0, 129.4, 128.8, 128.5, 127.6, 126.7, 57.9, 38.4, 37.0, 22.0;

IR (KBr)  $\nu$ : 3060, 3031, 2927, 2312, 1892, 1655, 1593, 1494, 1426, 1358, 1327, 1247, 1155, 1089, 1019, 959, 922, 890, 862, 826, 745, 704, 620, 587, 547, 512, 478, 436 cm<sup>-1</sup>;

HRMS Calcd (ESI)  $m/z$  for C<sub>18</sub>H<sub>17</sub>ClN<sub>2</sub>NaO [M + Na]<sup>+</sup>: 335.0922, found: 335.0918.





**1-(5-benzyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-1-yl)-2-phenylethan-1-one (5ac):**

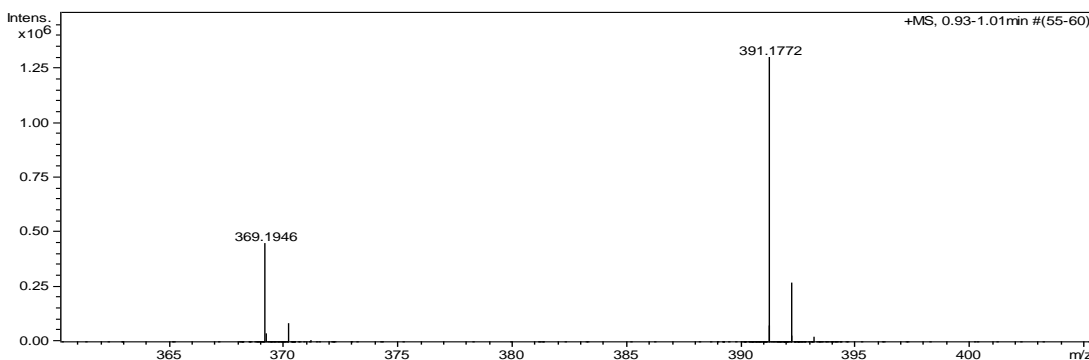
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 8) give the product **5ac** (153.5 mg, 83% yield) as a yellow solid. Mp: 114 - 116 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.25-7.13 (m, 8H), 4.86-4.79 (m, 1H), 4.15-4.07 (m, 2H), 3.44 (dd, *J*<sub>1</sub> = 13.2 Hz, *J*<sub>2</sub> = 2.4 Hz, 1H), 3.11 (dd, *J*<sub>1</sub> = 17.6 Hz, *J*<sub>2</sub> = 10.8 Hz, 1H), 2.91 (dd, *J*<sub>1</sub> = 17.6 Hz, *J*<sub>2</sub> = 4.0 Hz, 1H), 2.63 (d, *J*<sub>1</sub> = 12.0 Hz, *J*<sub>2</sub> = 10.8, 1H), 2.37 (s, 3H);

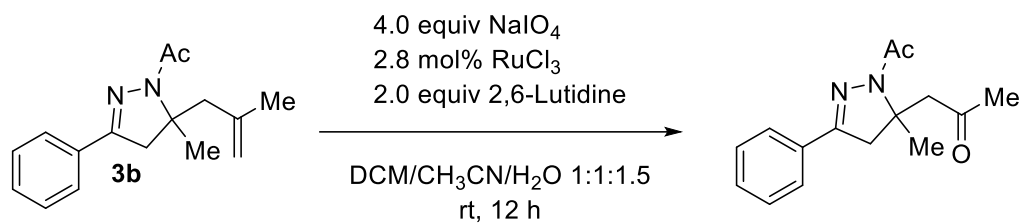
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz) δ 169.3, 154.6, 140.5, 136.9, 135.6, 129.5, 129.4, 129.3, 128.7, 128.5, 128.3, 126.5, 126.4, 57.9, 41.2, 38.3, 37.0, 21.4;

IR (KBr) ν: 3279, 3065, 3027, 2942, 2870, 1957, 1896, 1811, 1648, 1598, 1582, 1494, 1454, 1358, 1336, 1316, 1255, 1151, 1082, 1037, 921, 864, 818, 746, 715, 707, 615, 524, 476 cm<sup>-1</sup>;

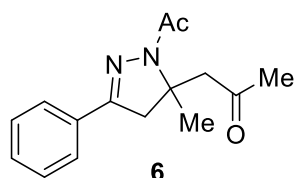
HRMS Calcd (ESI) m/z for C<sub>25</sub>H<sub>24</sub>N<sub>2</sub>NaO [M + Na]<sup>+</sup>: 391.1781, found: 391.1772.



**5. Experimental procedure for synthesis of 6**



An oven-dried Schlenk tube (25 mL) equipped with a magnetic stir bar was charged with **3b** (128.2 mg, 0.5 mmol, 1.0 equiv) and DCM: CH<sub>3</sub>CN (1/1) 6.0 mL, followed 2,6-Lutidine (107.2 mg, 1.0 mmol, 2.0 equiv), water (4.5 mL) and sodium periodate (427.8 mg, 2.0 mmol, 4.0 equiv) were then added sequentially. To the resulting mixture a stock solution of ruthenium(III) chloride trihydrate (0.028 M in water) (0.5 mL, 0.014 mmol, 2.8 mol %) was added dropwise via a syringe forming a brown suspension. The reaction was stirred vigorously at room temperature 12 h. The reaction was diluted with water (10 mL) then extracted with DCM (3 x 10 mL). The organic extracts were combined then washed with brine (10 mL), The organic layer was separated, dried over anhydrous NaSO<sub>4</sub>, filtered and evaporated under reduced pressure. The resulting residue was purified by flash silica chromatography using PE/EA (5:1) as an eluent to obtain the ketone compound **6** (80.2 mg, 62% yield).



**1-(1-acetyl-5-methyl-3-phenyl-4,5-dihydro-1H-pyrazol-5-yl)propan-2-one (6) :**

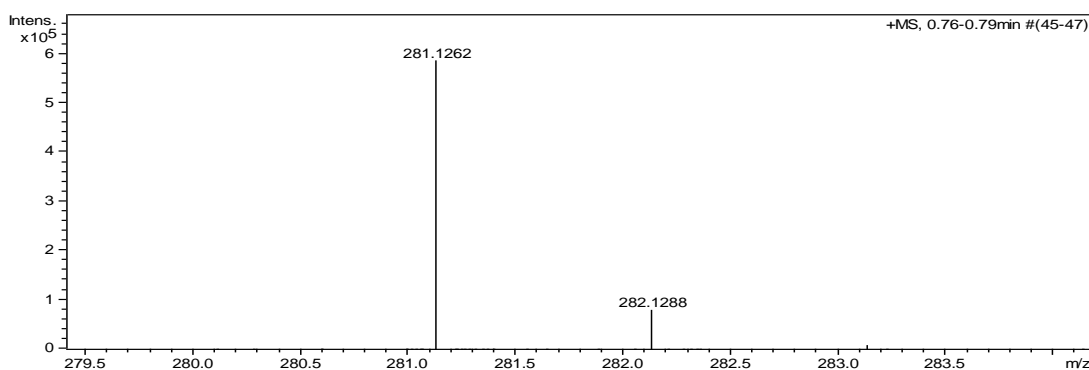
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **6** (80.2 mg, 62 % yield) as a yellow oil.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.70-7.66 (m, 2H), 7.40-7.37 (m, 3H), 3.47 (d, *J* = 18.0 Hz, 1H), 3.41 (d, *J* = 17.6 Hz, 1H), 3.33 (d, *J* = 17.6 Hz, 1H), 3.16 (d, *J* = 18.0 Hz, 1H), 2.34 (s, 3H), 2.12 (s, 3H), 1.59 (s, 3H);

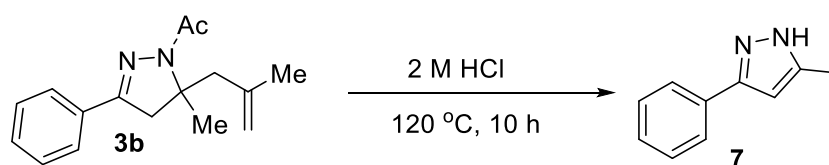
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 206.4, 169.8, 153.2, 131.6, 130.0, 128.5, 126.4, 63.7, 50.3, 46.7, 30.8, 24.9, 23.2.

IR (KBr) ν: 3301, 3059, 2931, 2394, 2297, 2060, 1965, 1896, 1716, 1658, 1416, 1173, 1035, 948, 856, 761, 691, 605, 551, 508, 428 cm<sup>-1</sup>;

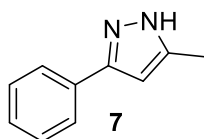
**HRMS** Calcd (ESI)  $m/z$  for  $C_{15}H_{18}N_2NaO_2$   $[M + Na]^+$ : 281.1260, found: 281.1262.



### Experimental procedure for synthesis of **7**



A sealed tube was charged with **3b** (128.2 mg, 0.5 mmol, 1 equiv) and 2 mL 2 M HCl. The reaction mixture was stirred at 120 °C for 10 h. After completion of the reaction (monitored by TLC), neutralize basicity by triethylamine, the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product **7** (47.9 mg in 61% yield).



### 5-methyl-3-phenyl-1H-pyrazole (**7**)<sup>5</sup>:

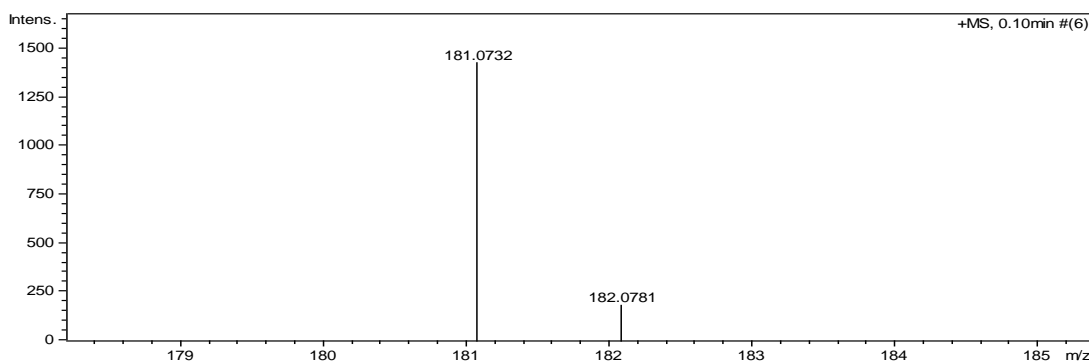
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 2) give the product **7** (47.9 mg, 61% yield) as a yellow solid. Mp: 118 - 120 °C.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  9.22 (s, 1H), 7.71-7.68 (m, 2H), 7.36-7.31 (m, 2H), 7.29-7.24 (m, 1H), 6.32 (s, 1H), 2.24 (s, 3H);

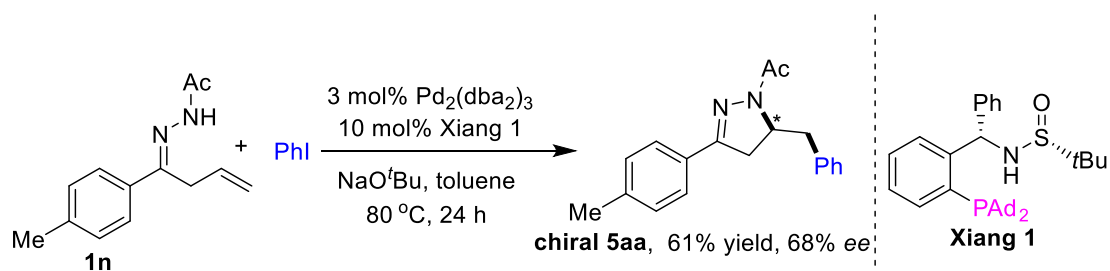
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  149.8, 143.1, 132.5, 128.6, 127.7, 125.7, 102.0, 11.6.

IR (KBr)  $\nu$ : 3060, 3031, 2927, 2312, 1892, 1655, 1593, 1494, 1426, 1358, 1327, 1247, 1155, 1089, 1019, 959, 922, 890, 862, 826, 745, 704, 620, 587, 547, 512, 478, 436  $cm^{-1}$ ;

**HRMS** Calcd (ESI)  $m/z$  for  $C_{10}H_{10}N_2Na$   $[M + Na]^+$ : 181.0736, found: 181.0732.



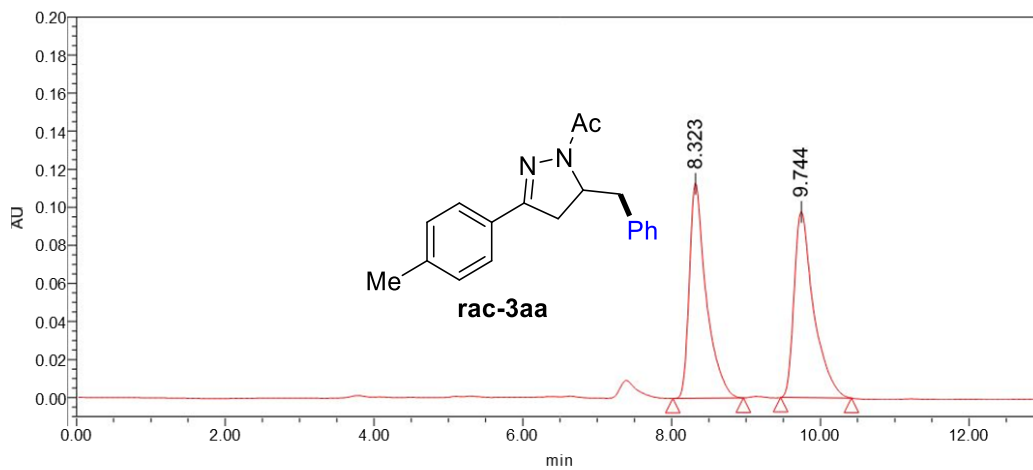
## 6. Enantioselective synthesis of **5aa**



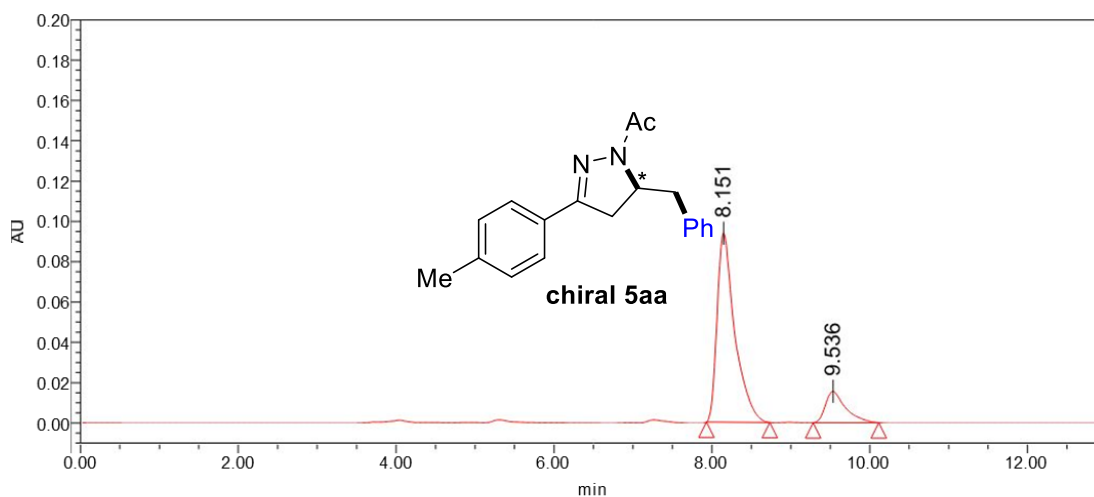
A sealed tube was charged with  $\text{Pd}_2(\text{dba})_3$  (5.5 mg, 0.006 mmol, 0.03 equiv) and Xiang **1** (11.8 mg, 0.02 mmol, 0.1 equiv) and toluene (2.0 mL). After the catalyst/ligand solution was stirred for 30 min at 25 °C.  $\beta$ ,  $\gamma$ -unsaturated hydrazone **1n** (0.2 mmol, 1 equiv), iodobenzene (0.4 mmol, 2 equiv) and  $\text{NaO}^t\text{Bu}$  (19.2 mg, 0.2 mmol, 1.0 equiv) were added sequentially. Degassed toluene and backfilled with  $\text{N}_2$  for 3 times ( $3 \times 1\text{min}$ ) at -78 °C. Under nitrogen atmosphere, the reaction mixture was stirred at 80 °C for 24 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired chiral product chiral **5aa** 35.9 mg in 61% yield with 68% ee.

HPLC traces of chiral **5aa**. HPLC conditions: chiralpak AD-H column, hexanes/*i*-PrOH = 90/10, 1.0 mL/min,  $t$  (major) = 8.152 min;  $t$  (minor) = 9.536 min.

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR data match **5aa**

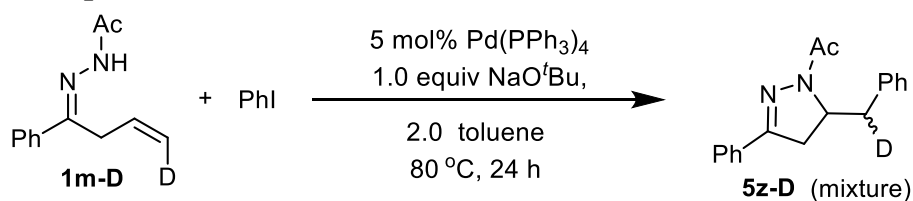


	RetTime (min)	Height	Area	Area %
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2	9.744	97875	1784226	50.03



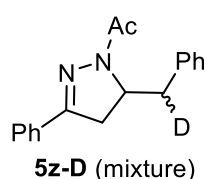
	RetTime (min)	Height	Area	Area %
1	8.151	93876	1455495	84.07
2	9.536	15652	275758	15.93

## 6. Control experiment of 1m-D:



A 10 mL sealed tube was charged with  $\text{Pd}(\text{PPh}_3)_4$  (11.5 mg, 0.01 mmol, 0.05 equiv),

and toluene (2.0 mL).  $\beta$ ,  $\gamma$ -unsaturated hydrazone **1m-D** (40.7 mg, 0.2 mmol, 1 equiv), iodobenzene (0.4 mmol, 2 equiv) and NaO<sup>t</sup>Bu (19.2 mg, 0.2 mmol, 1.0 equiv) were added sequentially. Degassed toluene and backfilled with N<sub>2</sub> for 3 times (3 × 1min) at -78 °C. Under nitrogen atmosphere, the reaction mixture was stirred at 80 °C for 24 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired chiral product chiral **5z-D** 36.2 mg in 65% yield, *d.r.* = 1:1



**1-(3-phenyl-5-(phenylmethyl-d)-4,5-dihydro-1H-pyrazol-1-yl)ethan-1-one D-5z (mixture):**

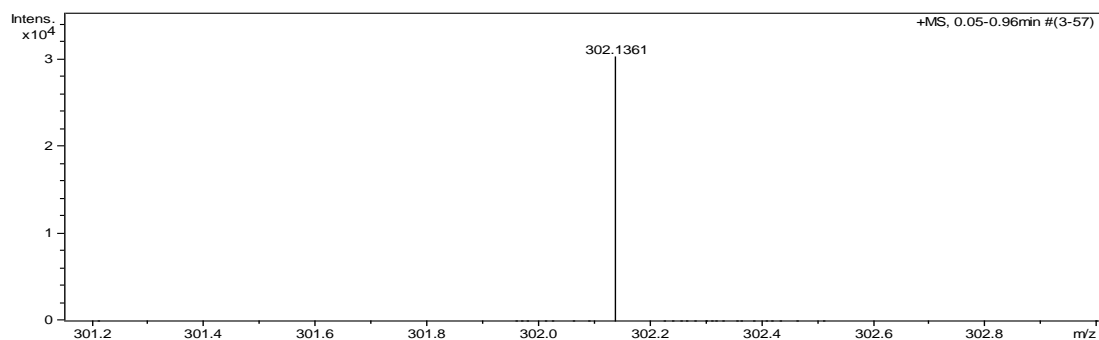
Flash column chromatography on a silica gel (ethyl acetate: petroleum ether, 1: 5) give the product **D-5z** (36.2 mg, 65% yield) as a yellow as a white solid.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.67-7.64 (m, 2H), 7.41-7.38 (m, 3H), 7.23-7.29 (m, 2H), 7.25-7.23 (m, 3H), 4.91-4.85 (m, 1H), 3.48 (d, *J* = 3.6 Hz, 0.5H), 3.17 (dd, *J*<sub>1</sub> = 17.6 Hz, *J*<sub>2</sub> = 10.8 Hz, 1H), 2.96 (dd, *J*<sub>1</sub> = 17.6 Hz, *J*<sub>2</sub> = 4.4 Hz, 1H), 2.63 (d, *J* = 10.0 Hz, 0.5H), 2.43 (s, 3H);

<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz)  $\delta$  169.2, 154.4, 136.93, 131.5, 130.1, 129.5, 129.4 (2C), 128.6(2C), 126.6, 126.4, 57.7(2C), 38.4, 38.3, 38.2, 38.1, 38.0, 37.9, 37.0, 22.0.

IR (KBr)  $\nu$ : 3060, 3027, 2930, 1656, 1595, 1496, 1417, 1361, 1335, 759, 692, 609 cm<sup>-1</sup>;

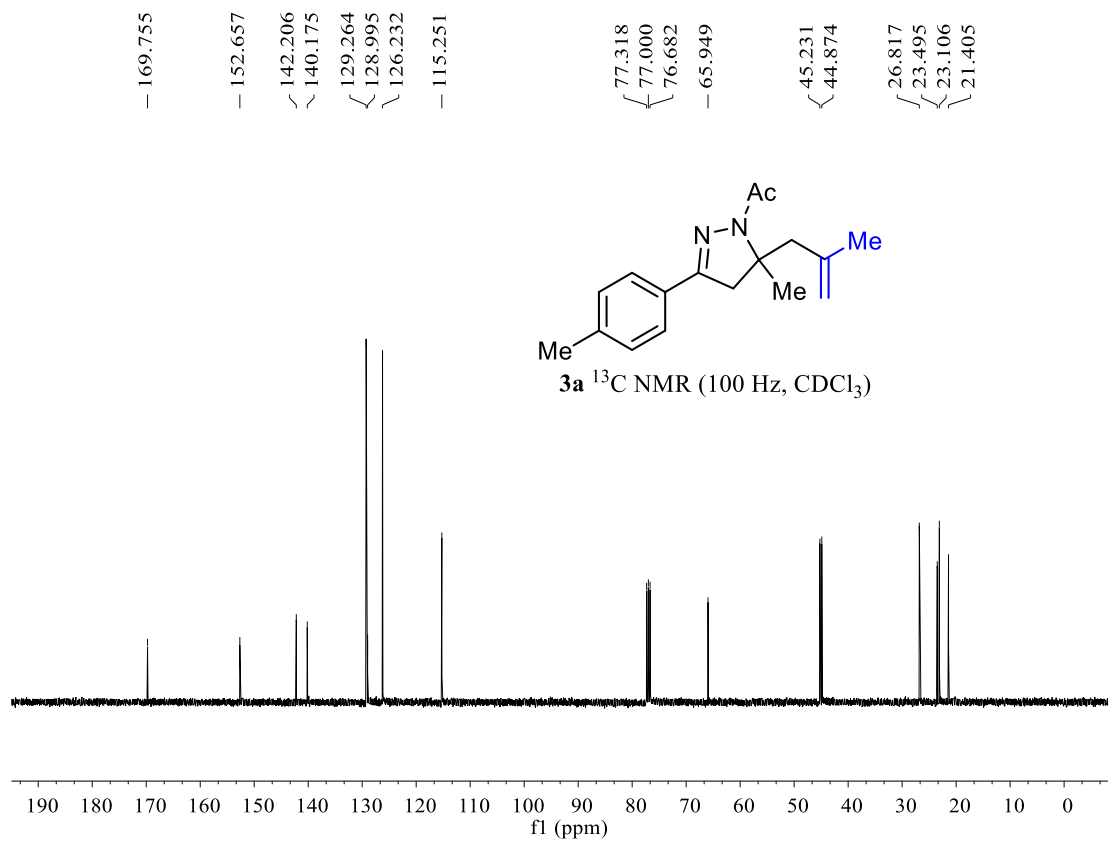
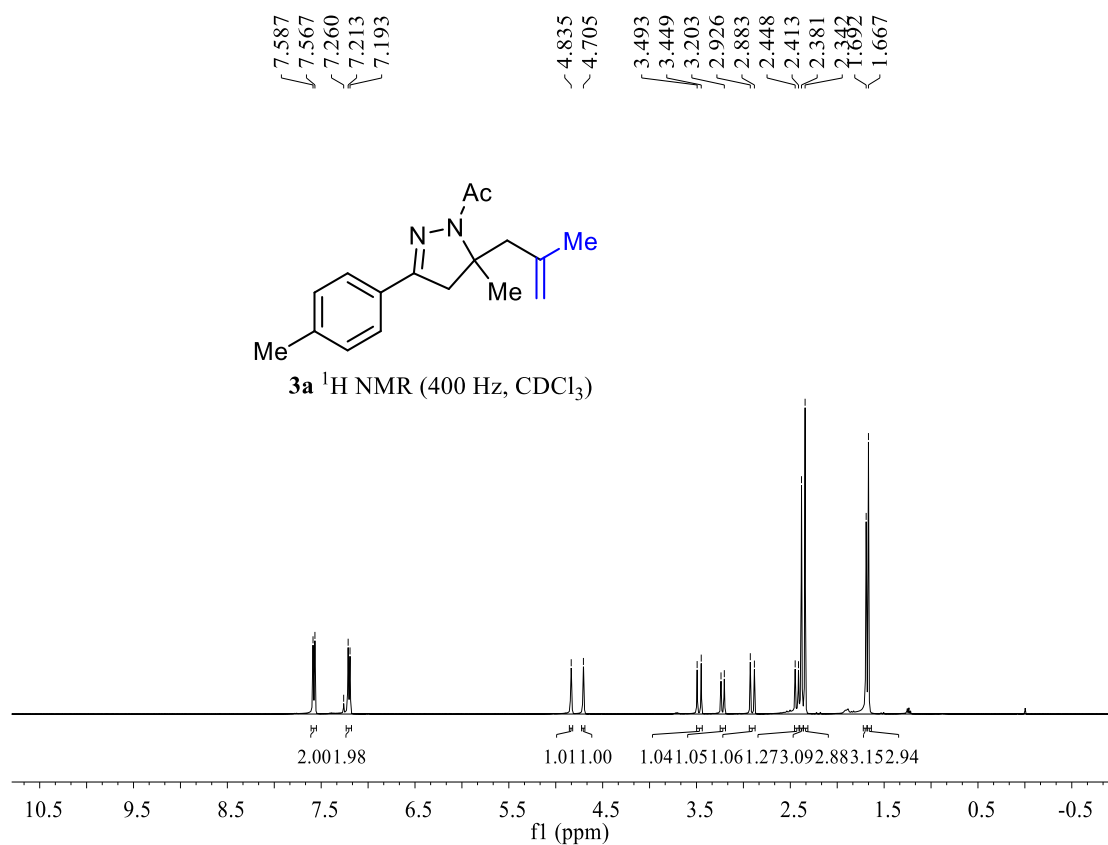
HRMS Calcd (ESI) *m/z* for C<sub>18</sub>H<sub>17</sub>DN<sub>2</sub>NaO [M + Na]<sup>+</sup>: 302.1374, found: 302.1361.



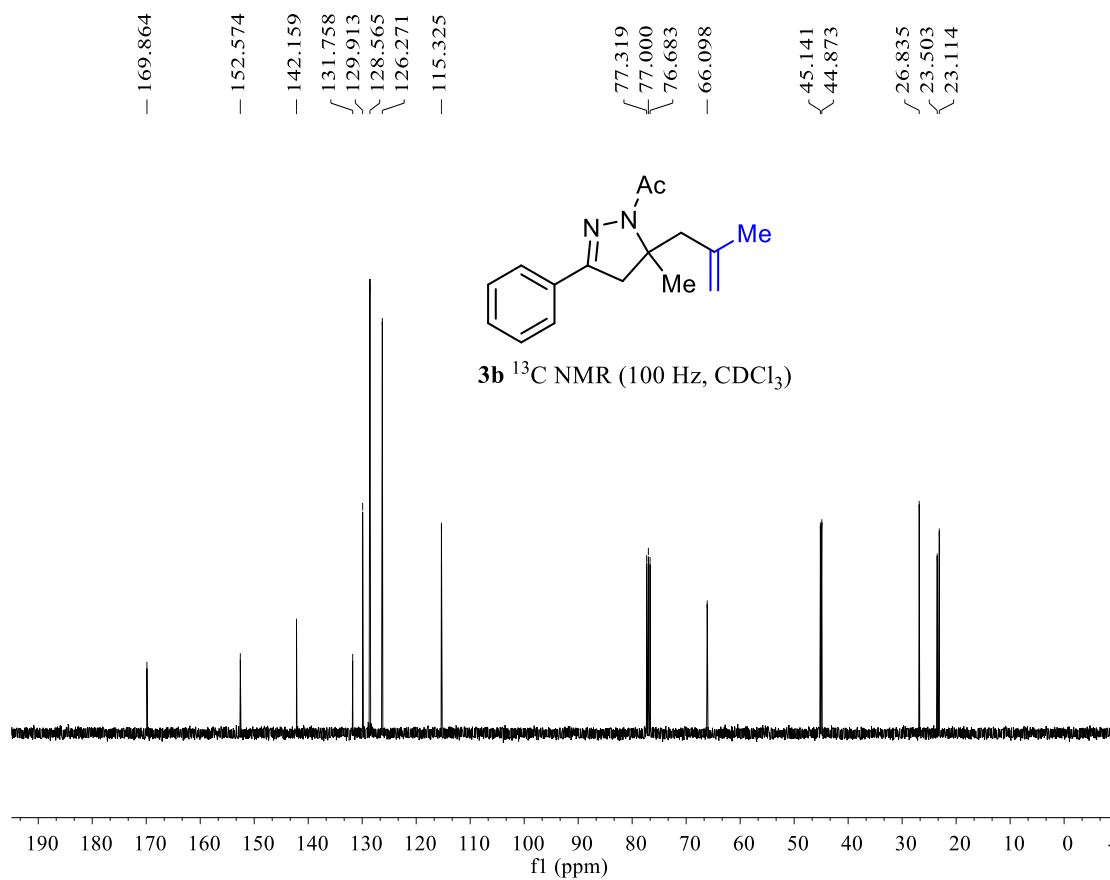
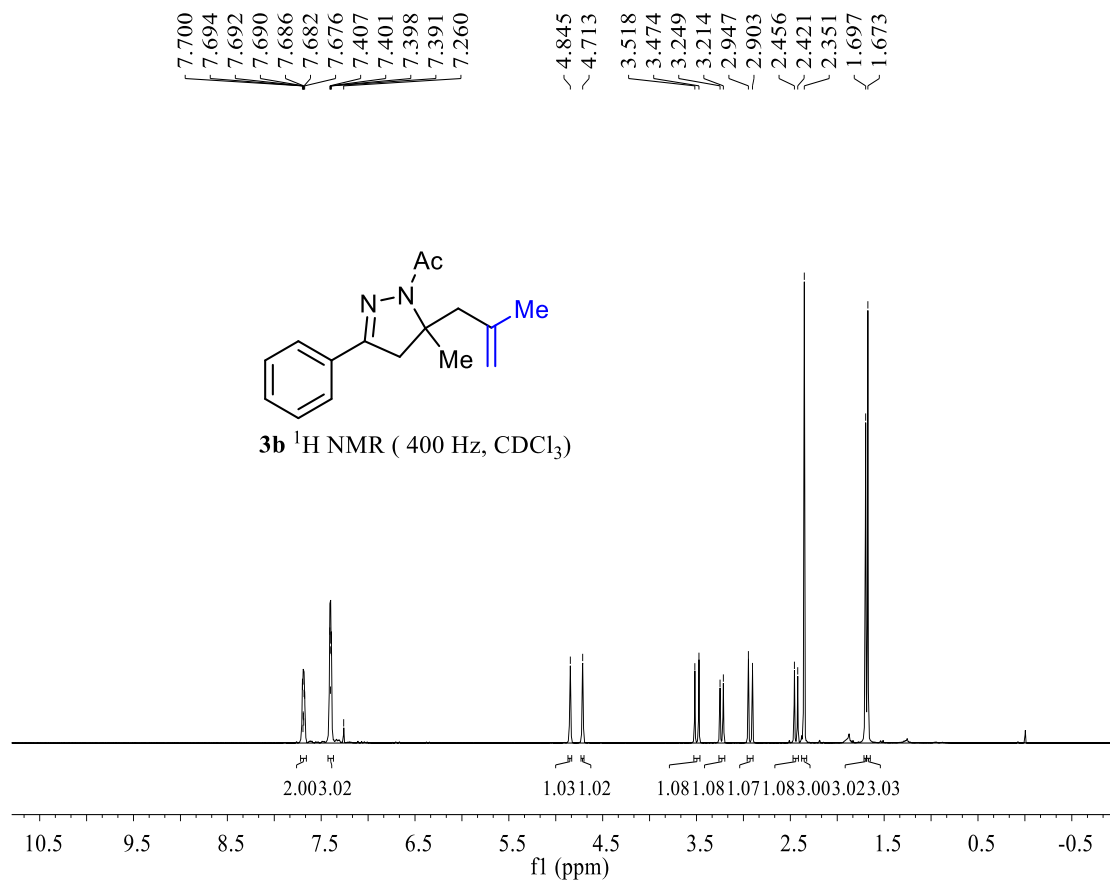
## 7. References:

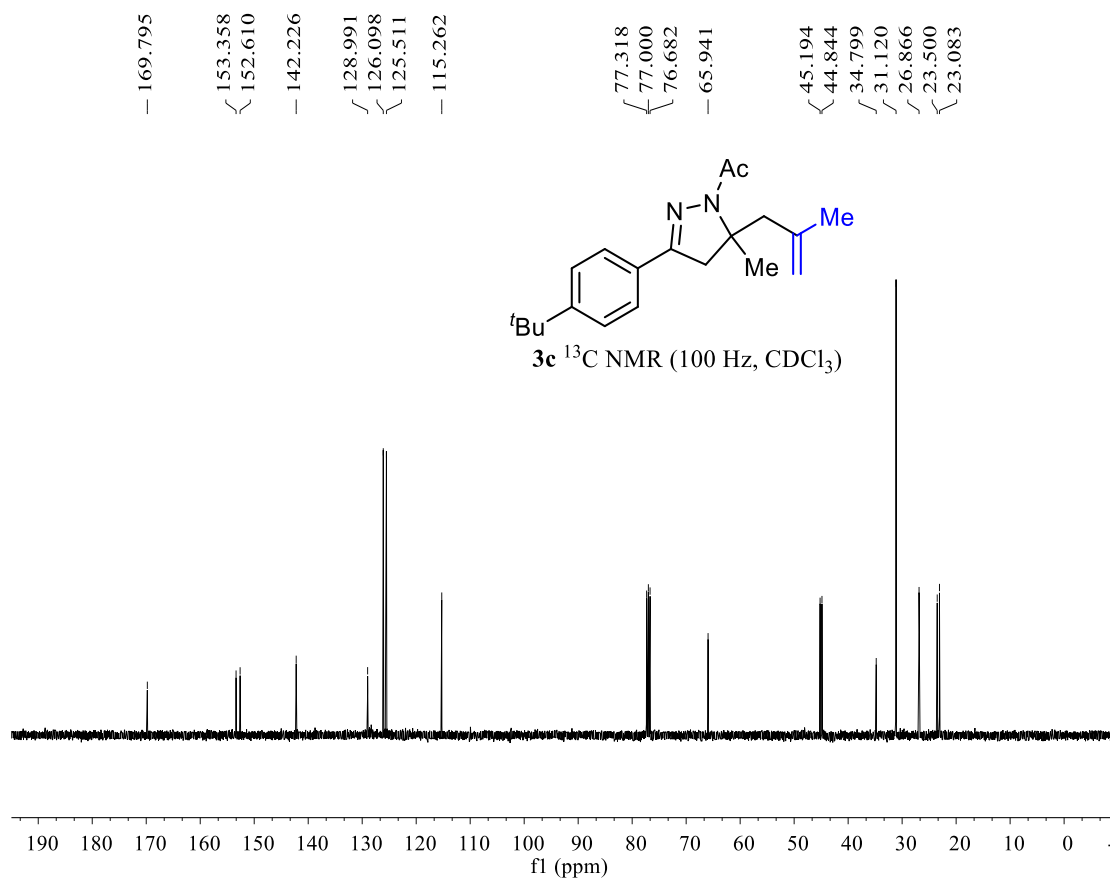
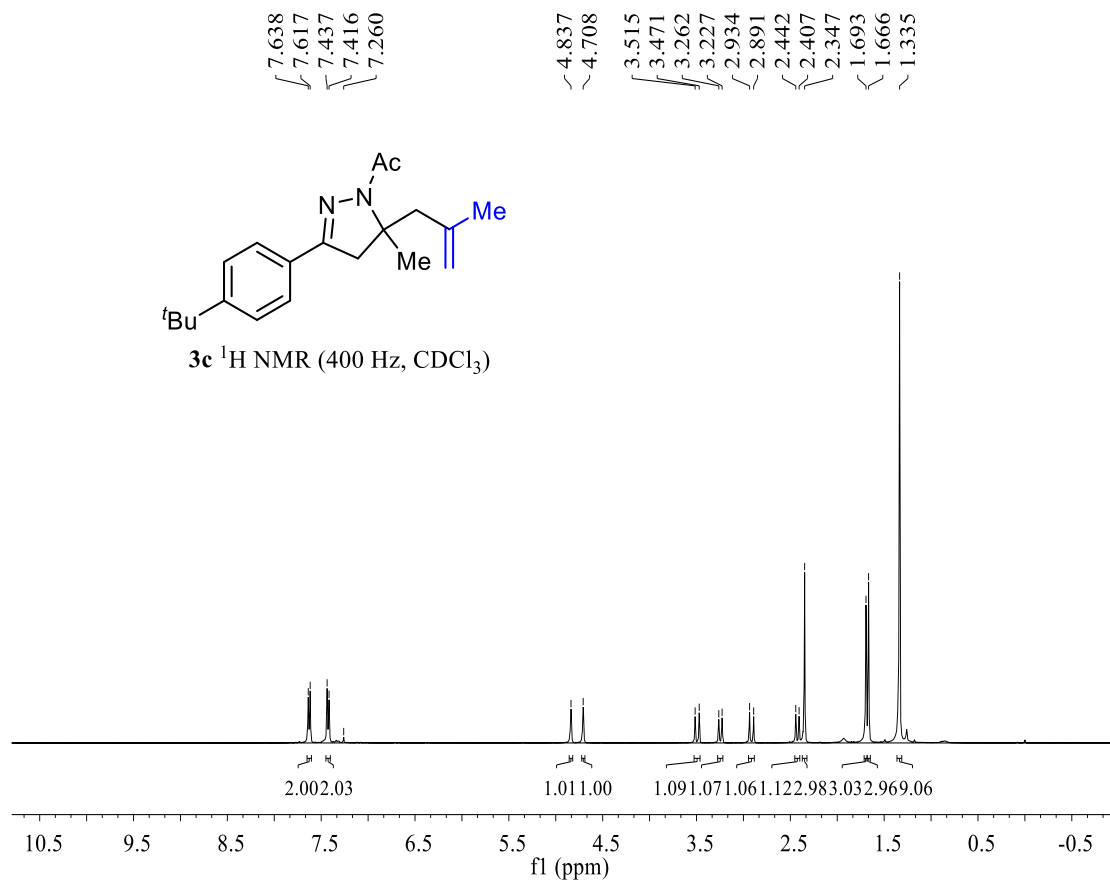
1. Z. Fan, Z. Pan, L. Huang and J. Cheng, *J. Org. Chem.* 2019, **84**, 4236.
2. Y.-Q. Guo, M.-N. Zhao, Z.-H. Ren and Z.-H. Guan, *Org. Lett.* 2018, **20**, 3337.
3. M.-N. Yang, D.-M. Yan, Q.-Q. Zhao, J.-R. Chen and W.-J. Xiao, *Org. Lett.*, 2017, **19**, 5208.
4. S. Duan, G. Deng, Y. Zi, X. Wu, X. Tian, Z. Liu, M. Li, H. Zhang, X. Yang and P. Walsh, *Chem. Sci.* 2021, **12**, 6406.
5. J. Wen, Y. Fu, R.-Y. Zhang, J. Zhang, S.-Y. Chen and X.-Q. Yu. Zhang, *Tetrahedron* 2011, **67** 9618.

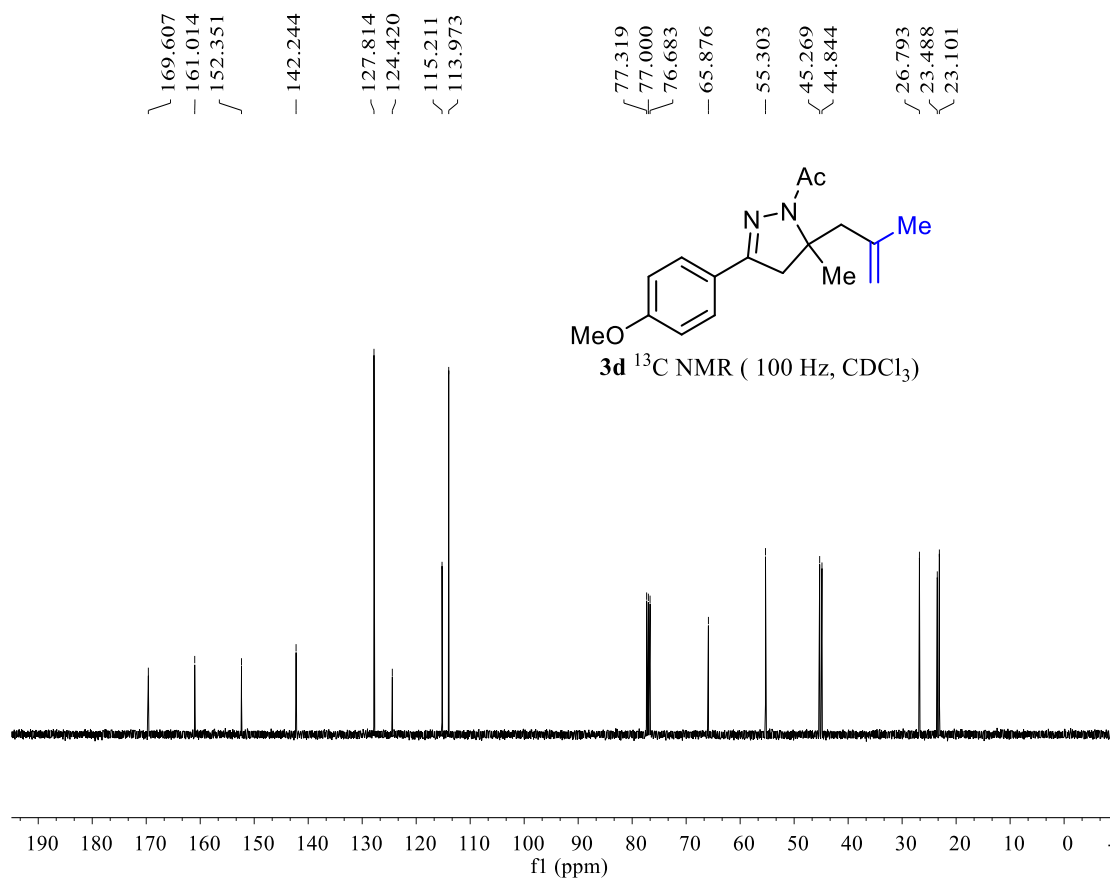
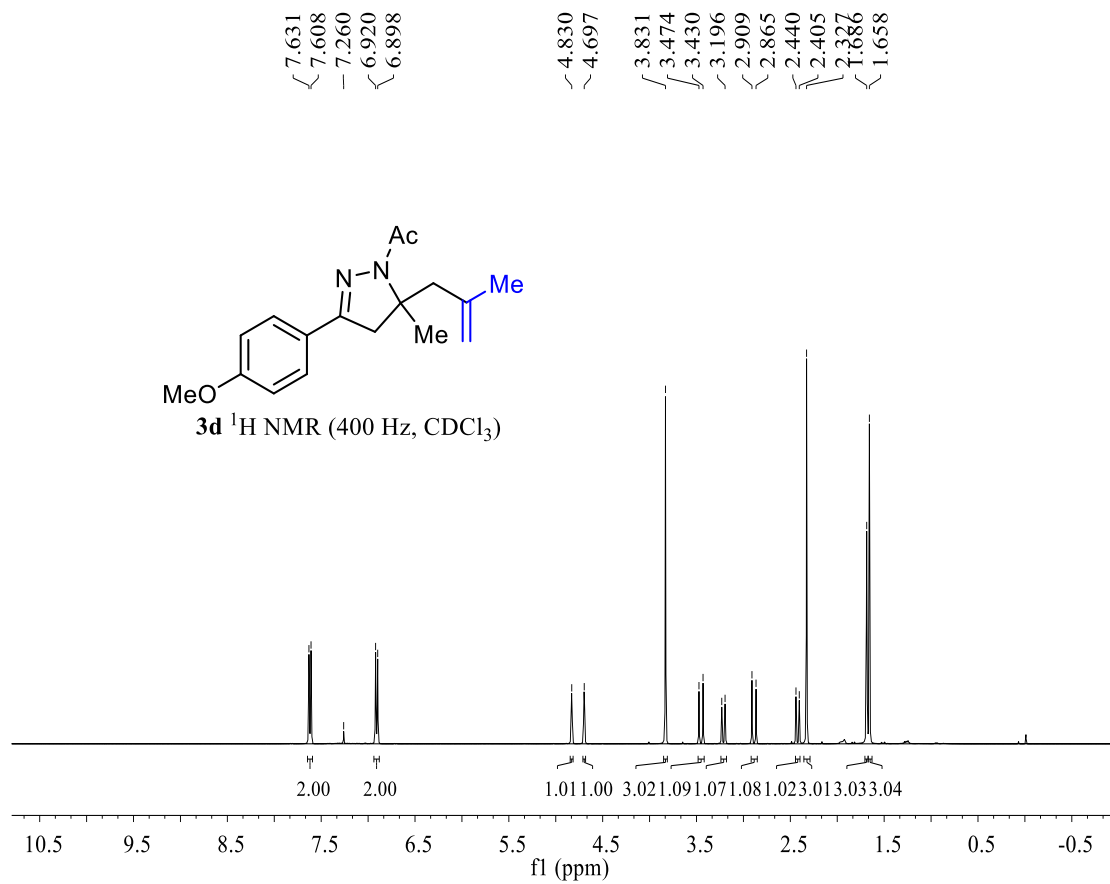
## 8. Copies of NMR spectra for new compounds

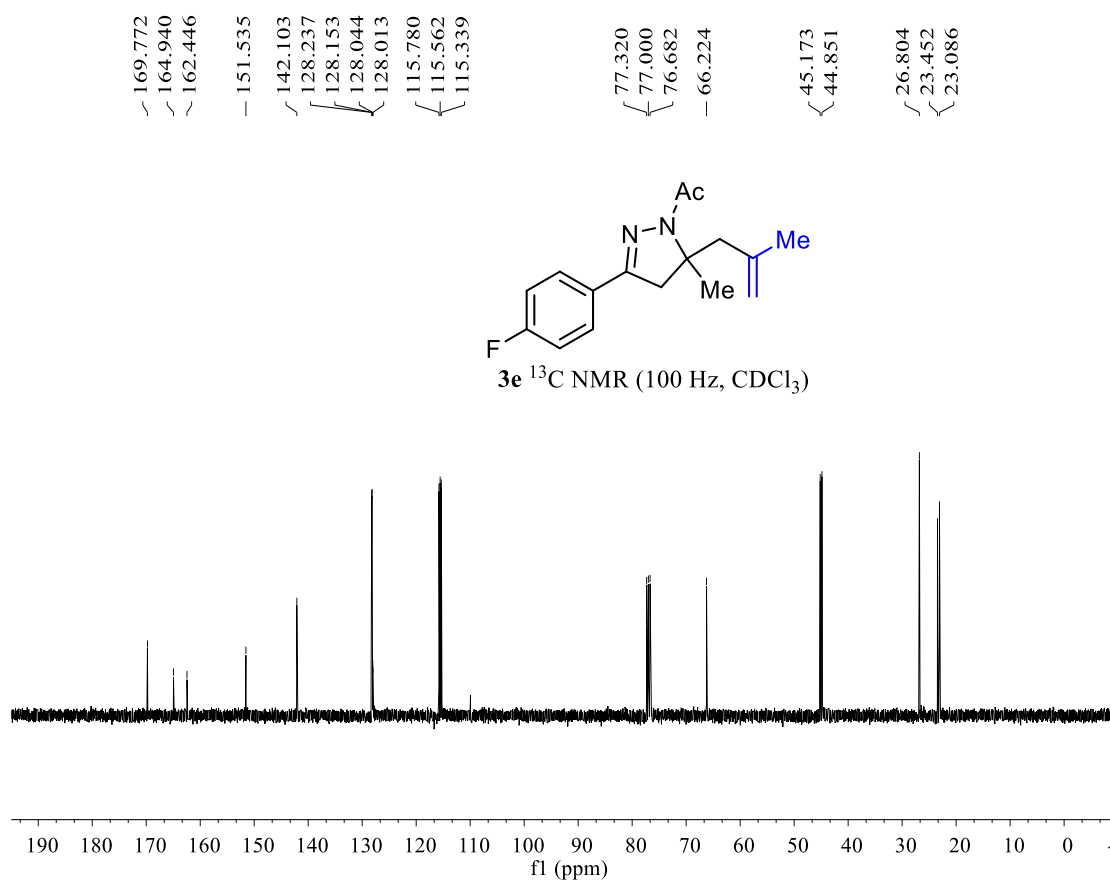
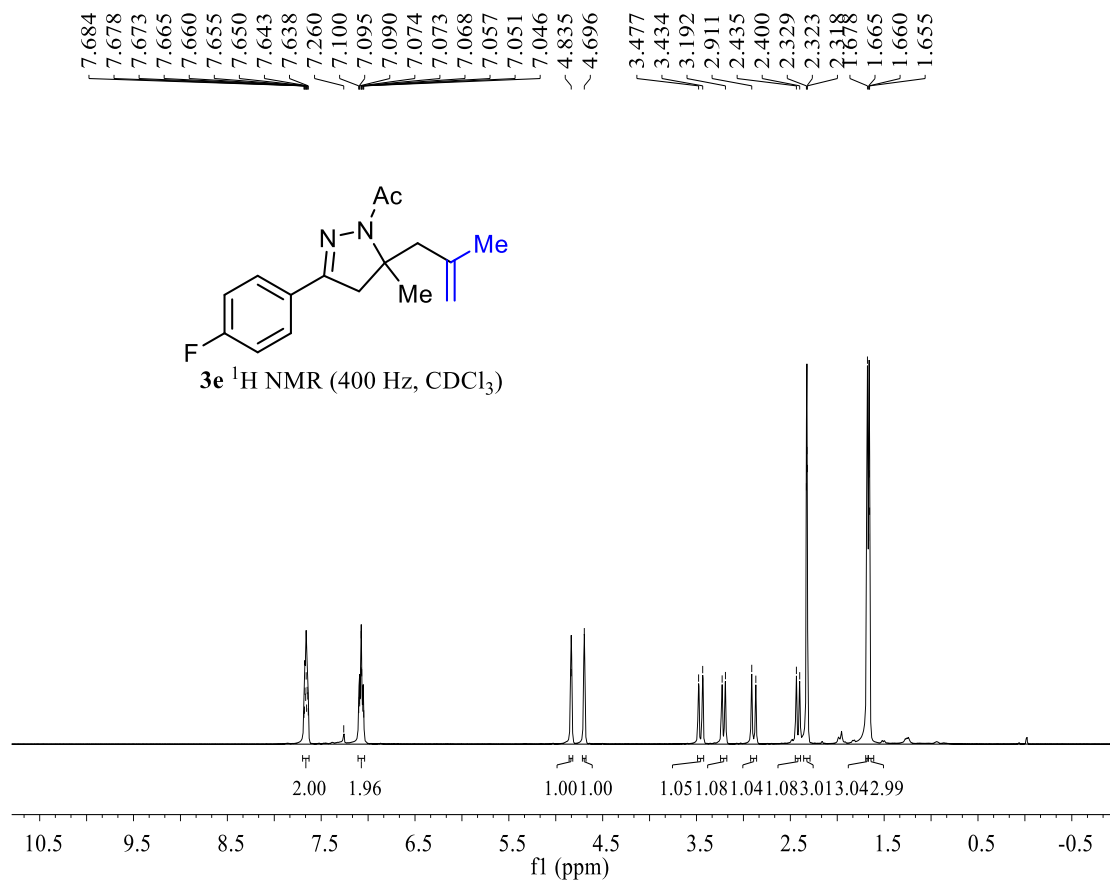


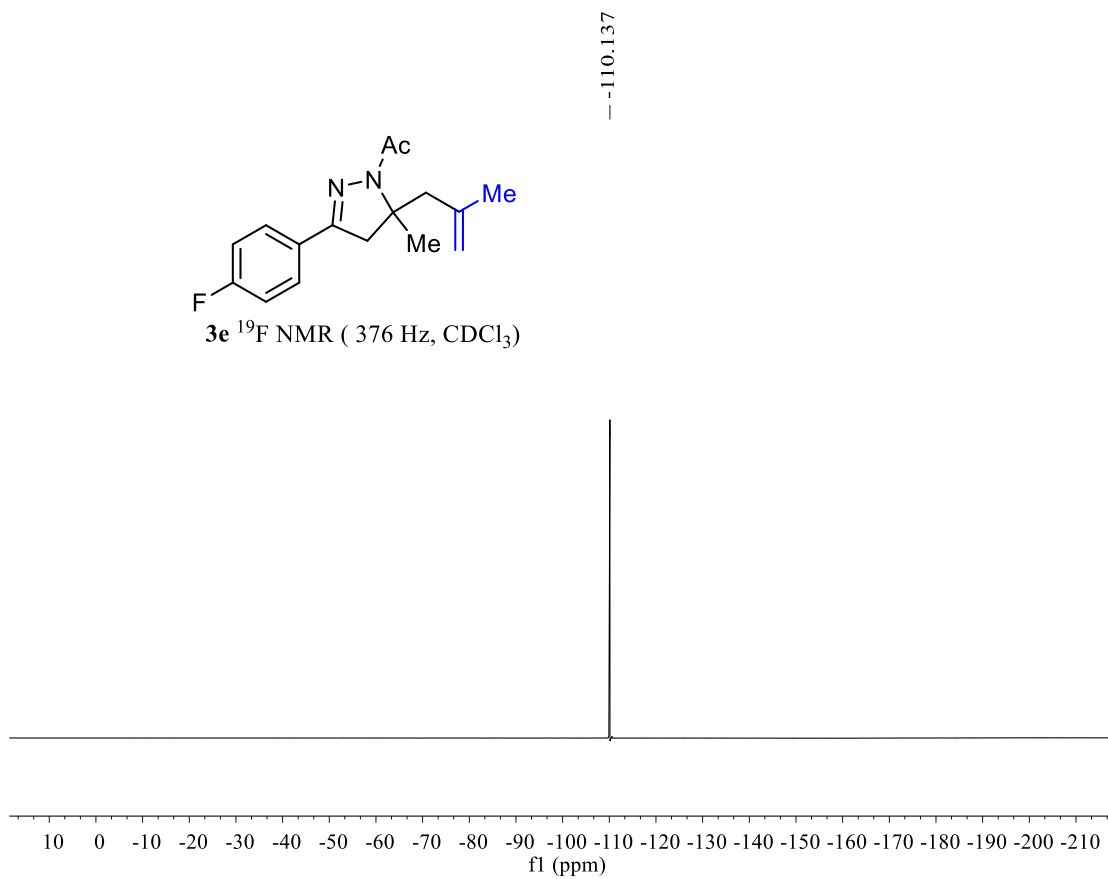
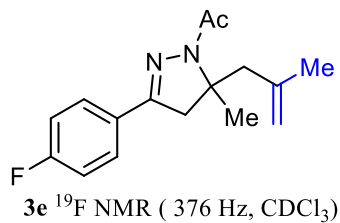








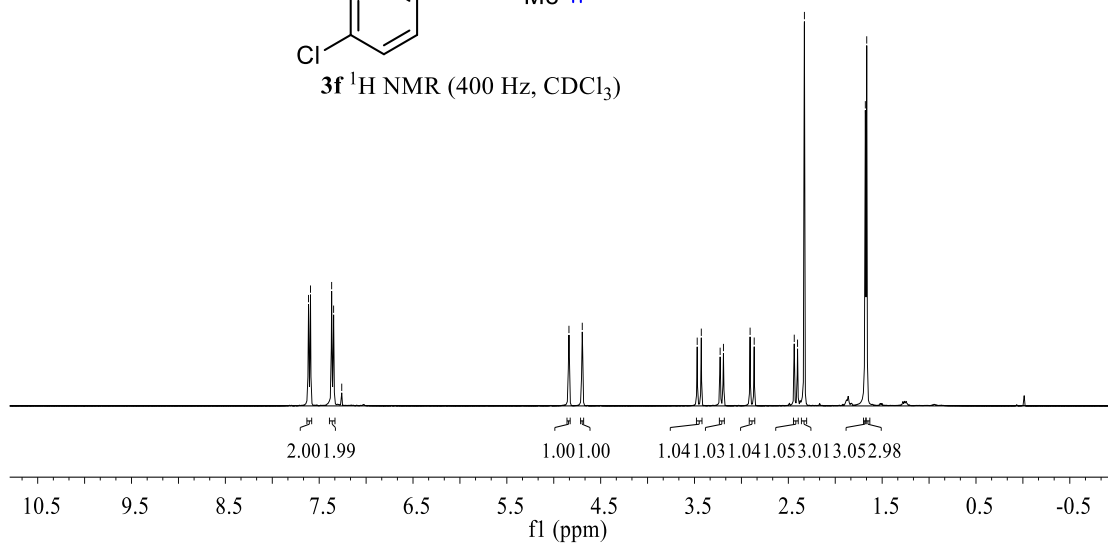
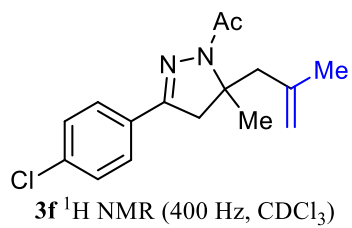


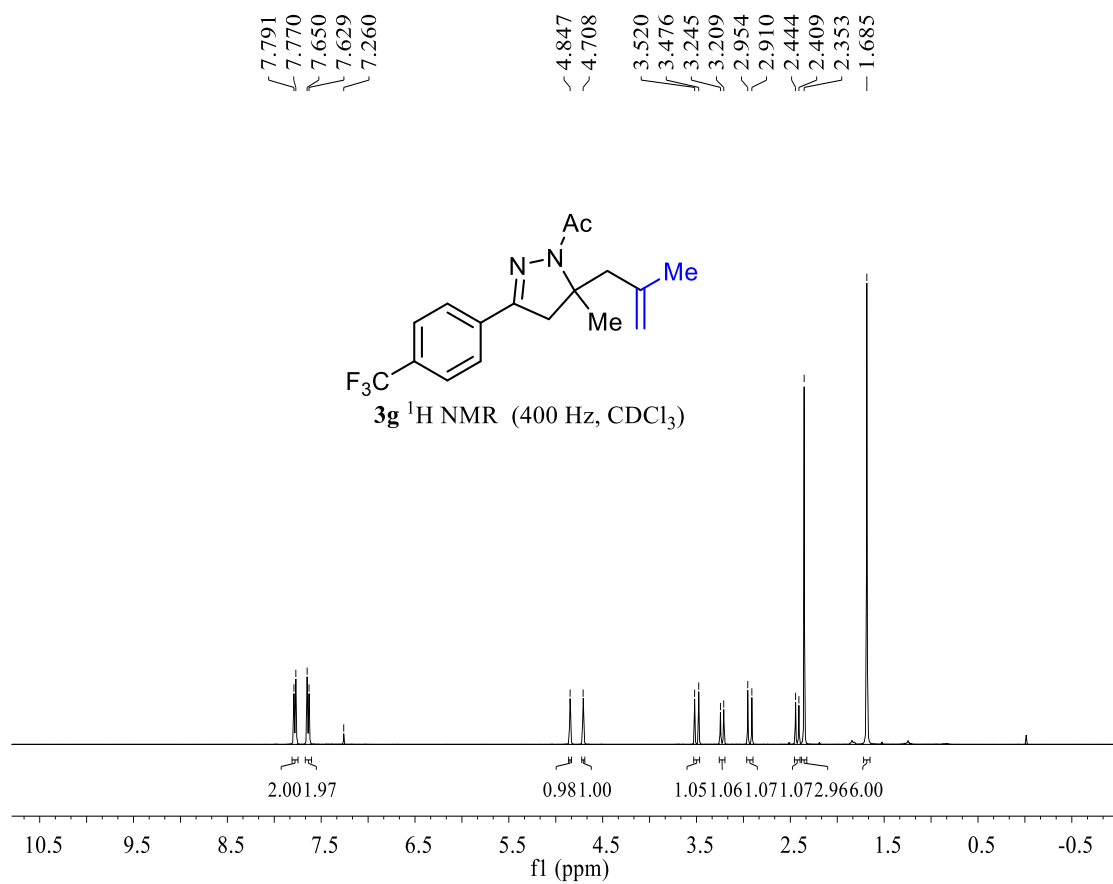
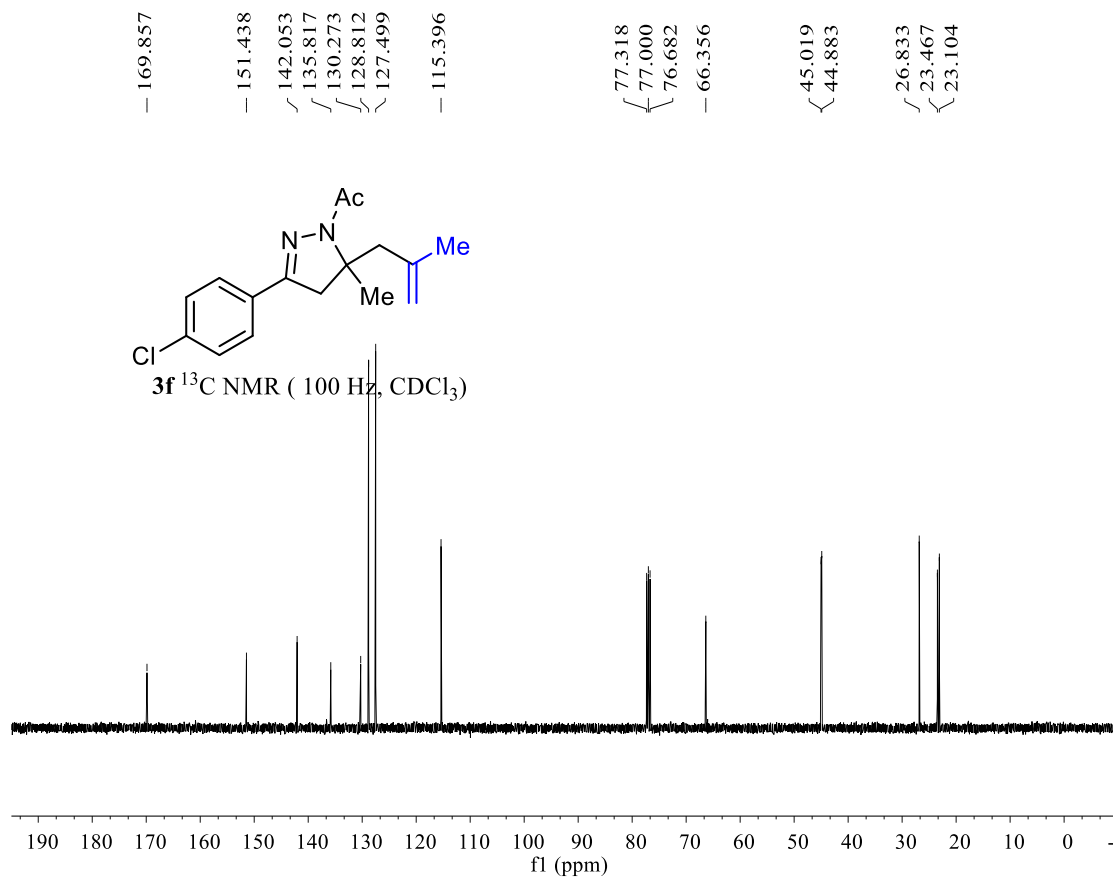


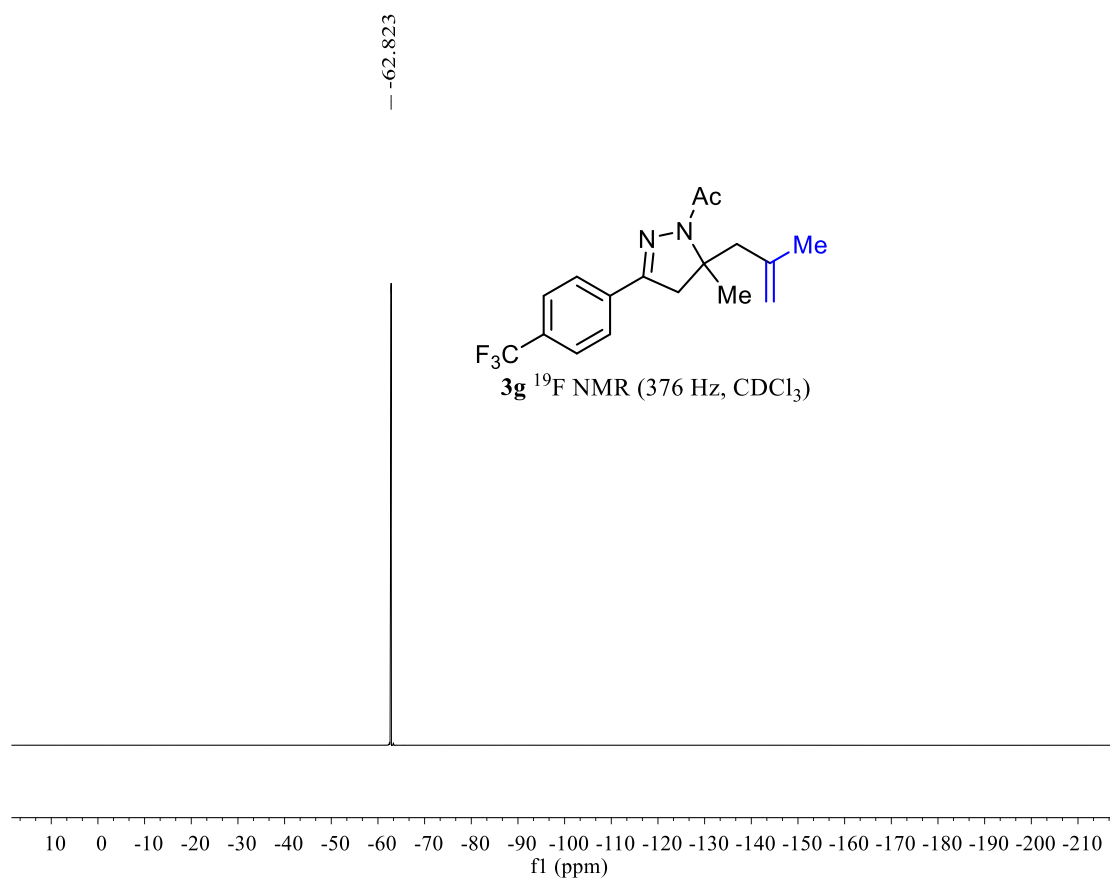
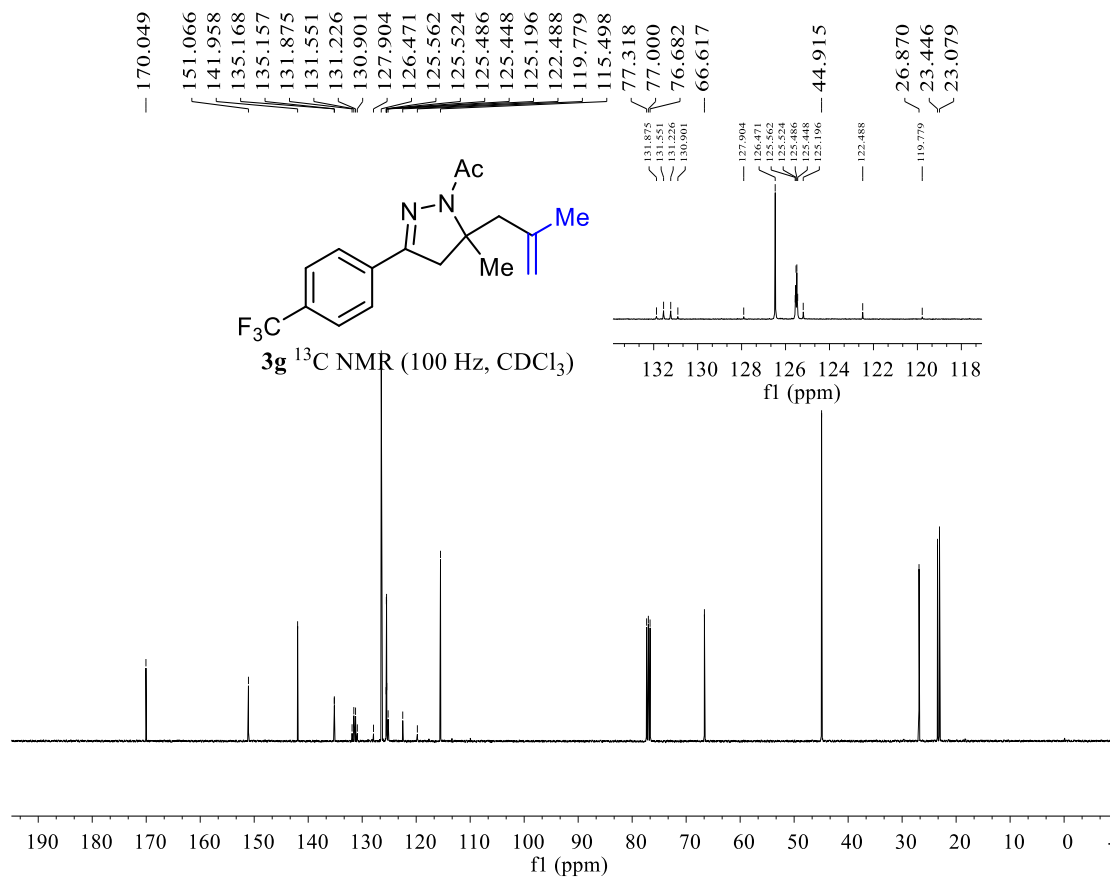
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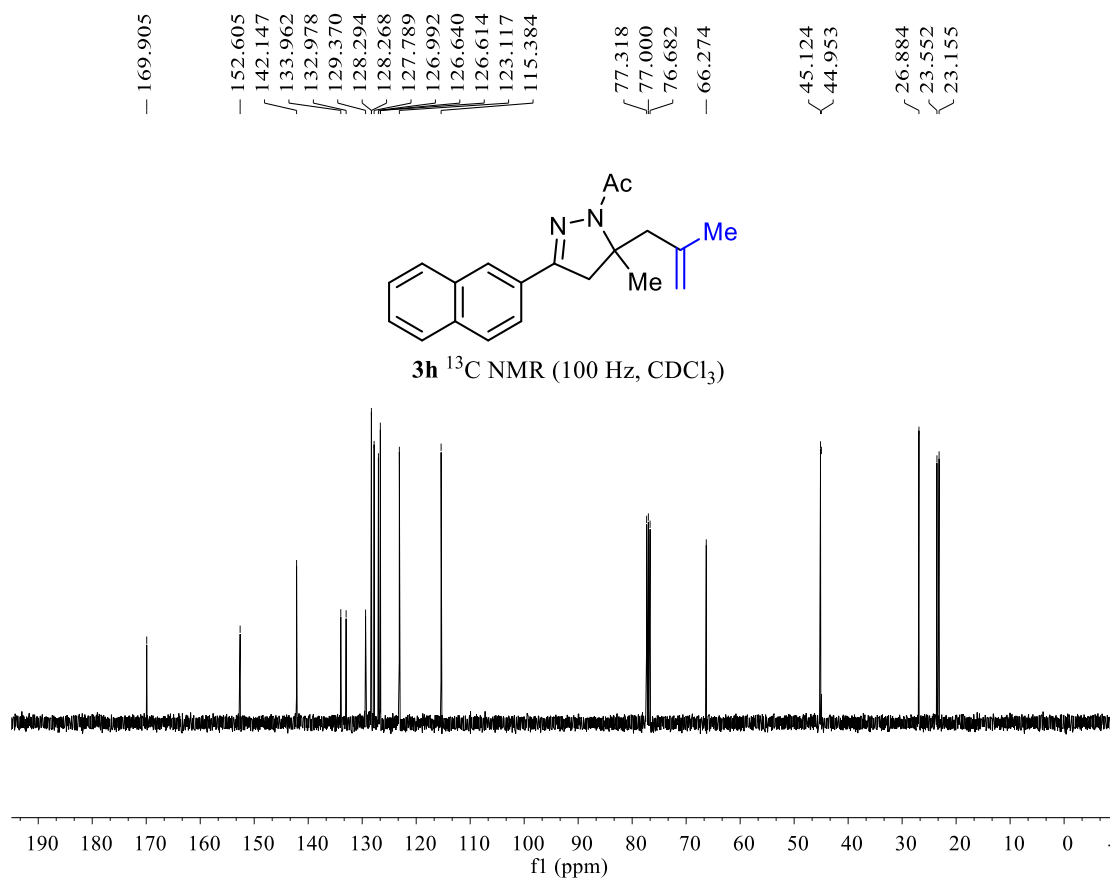
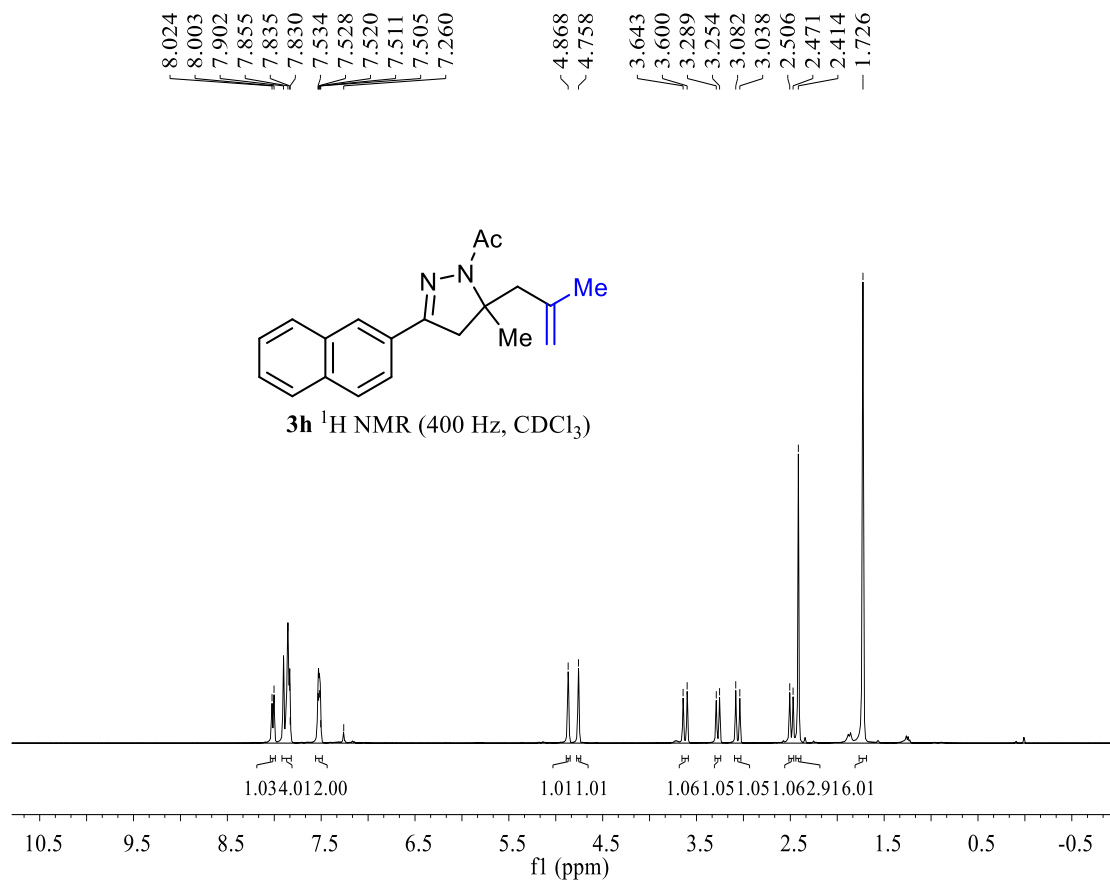
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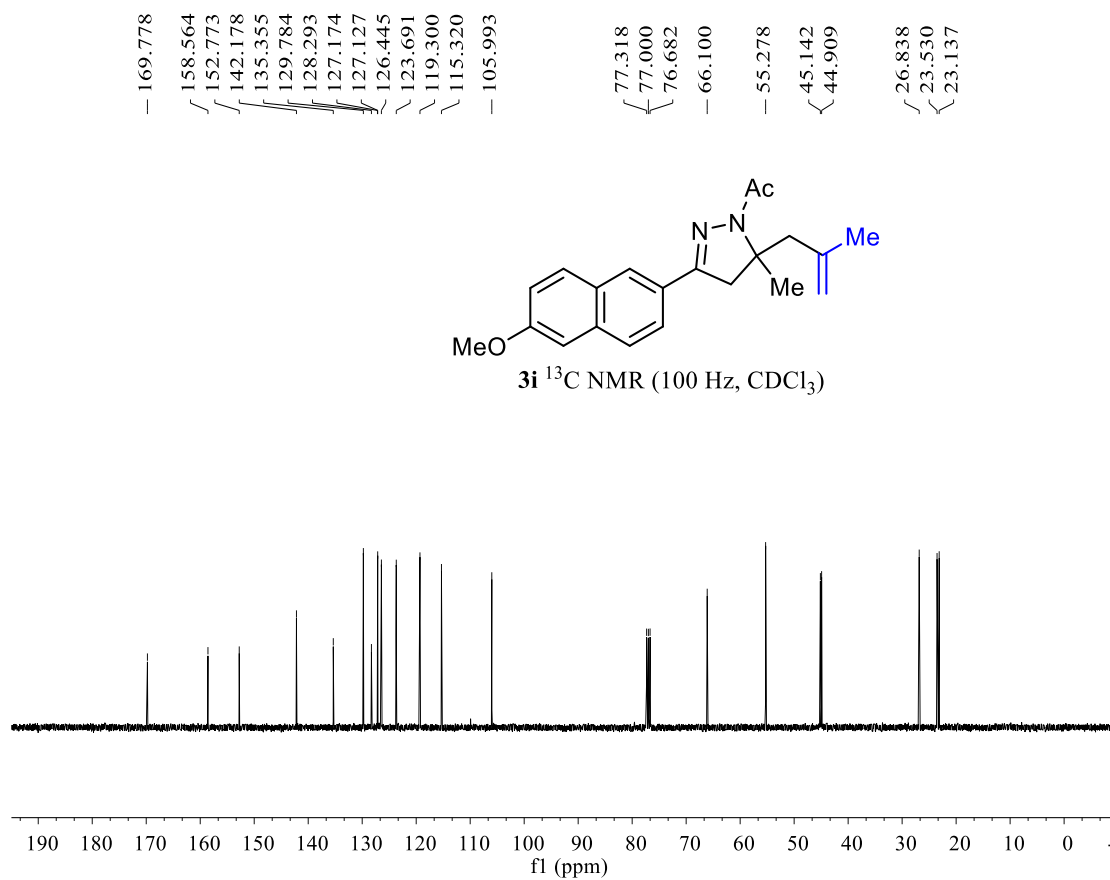
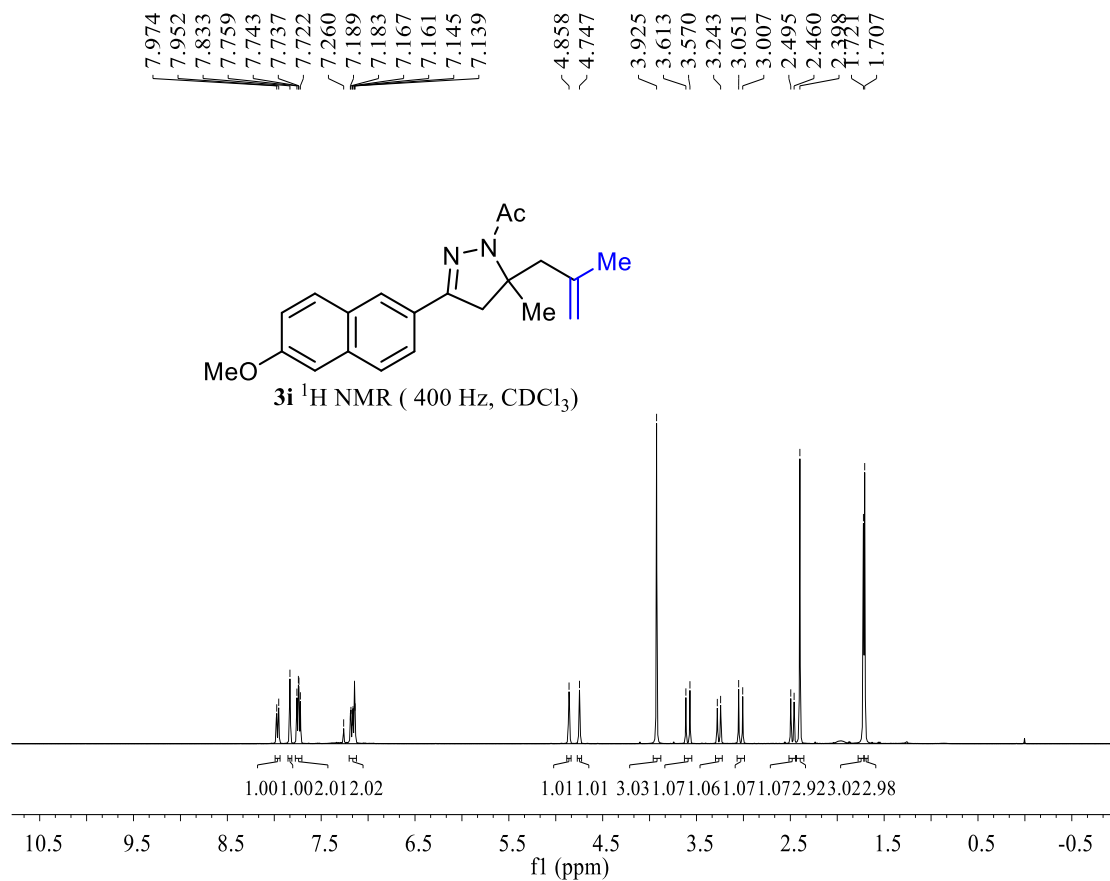




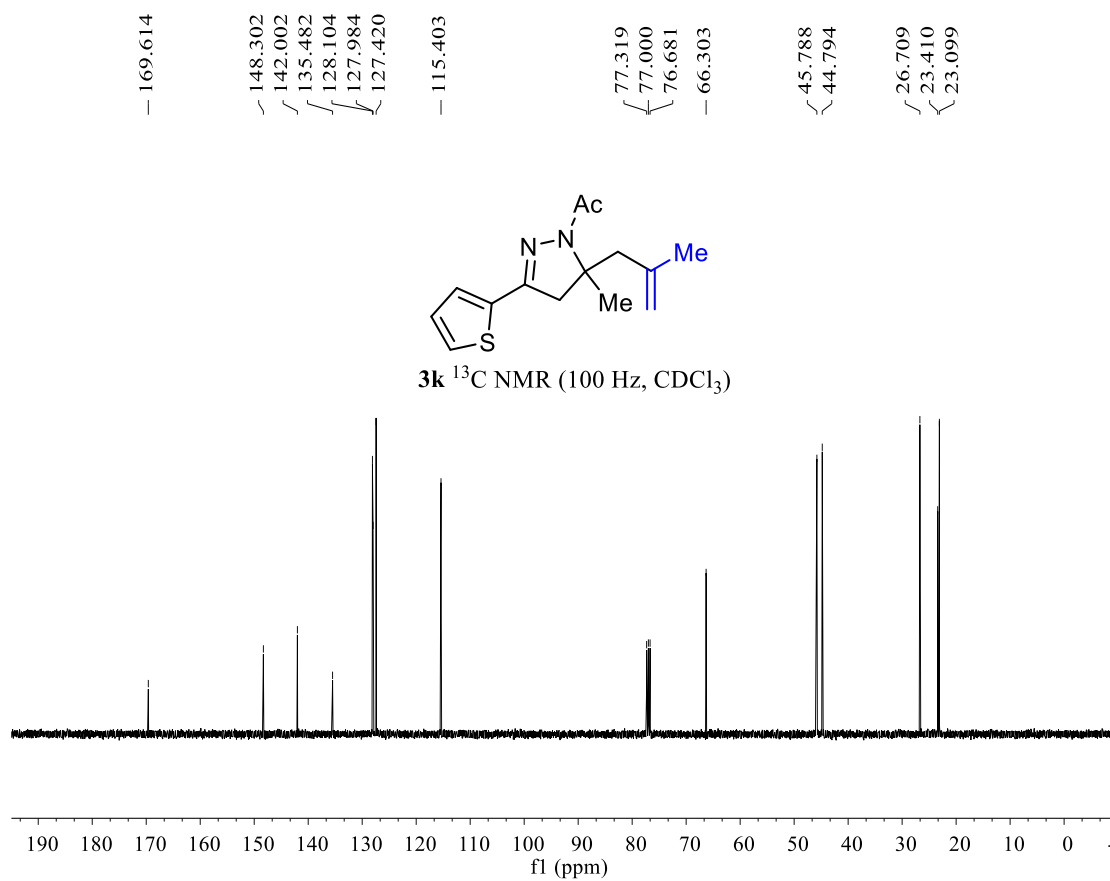
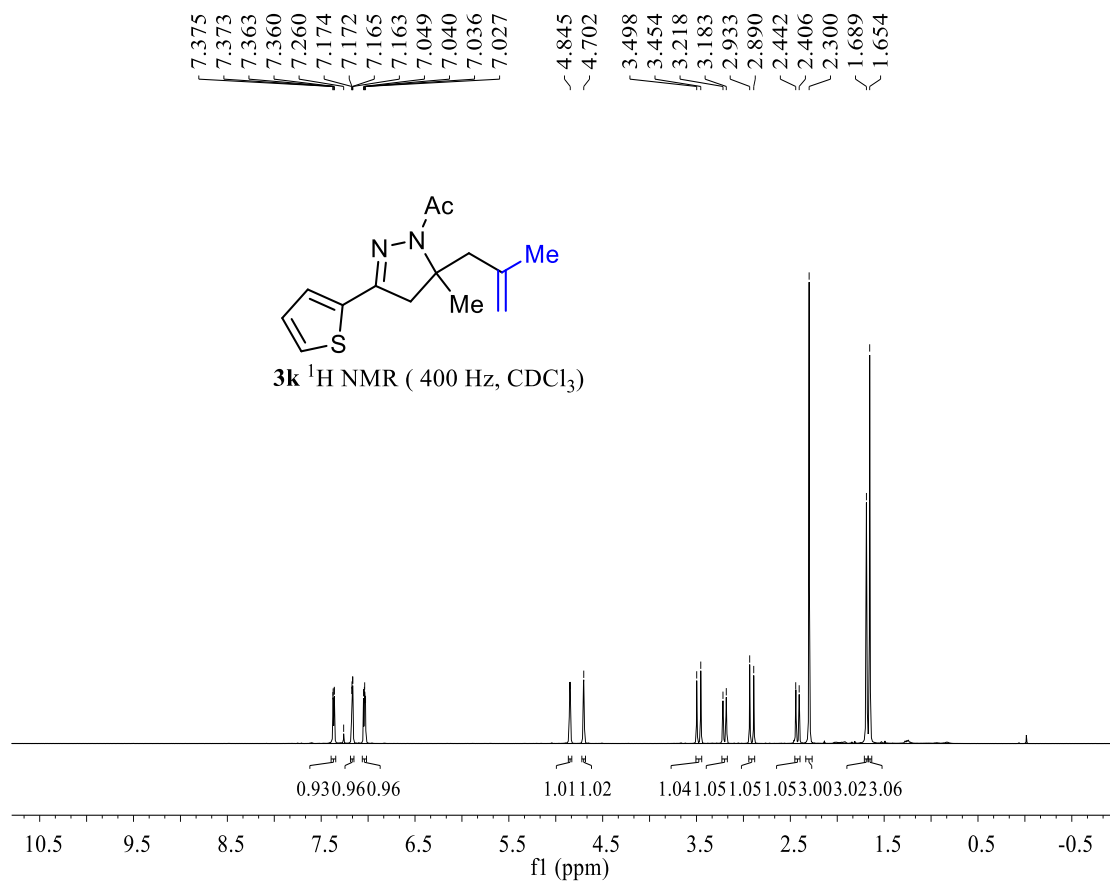


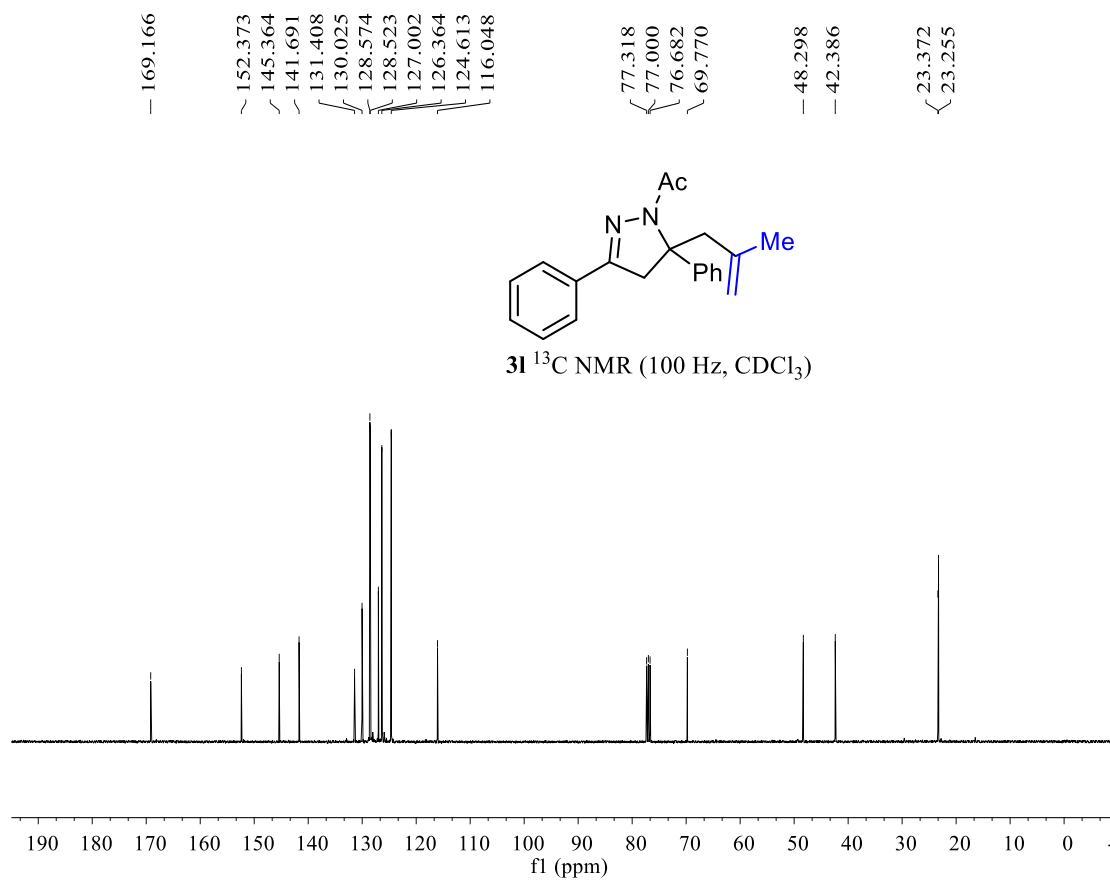
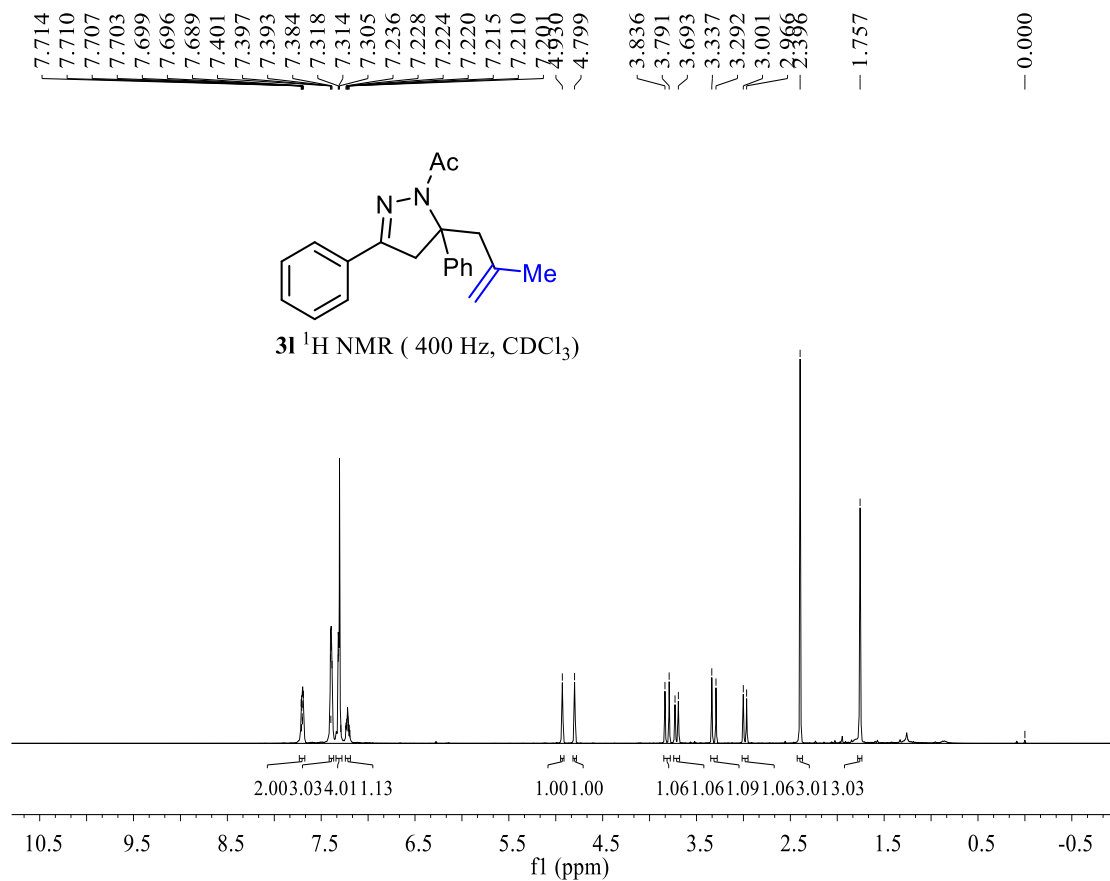


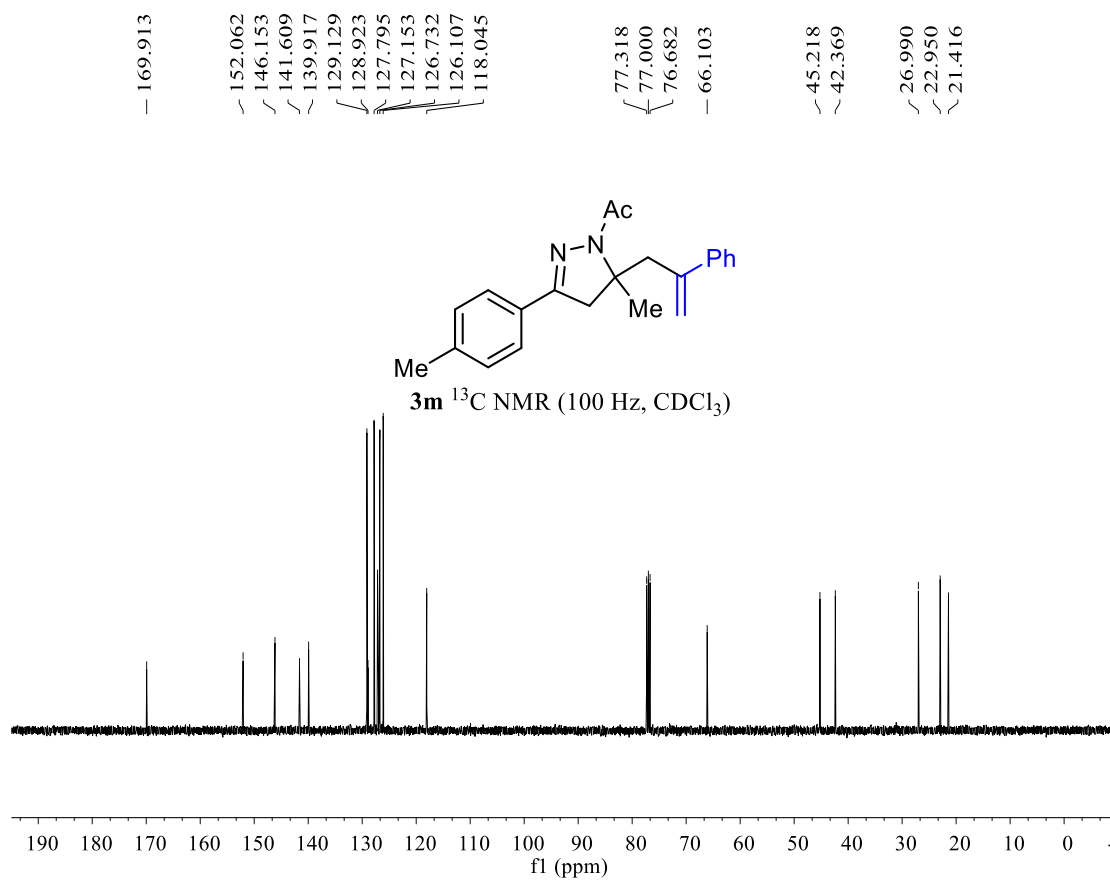
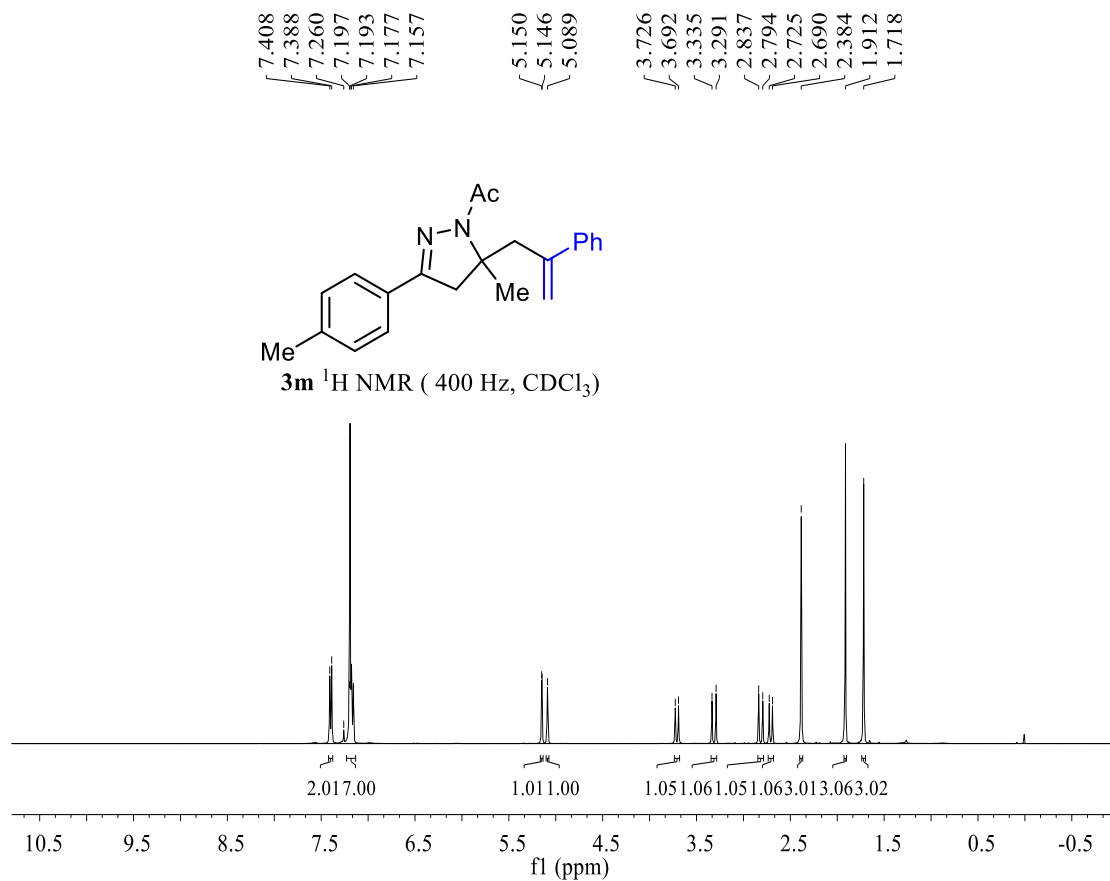


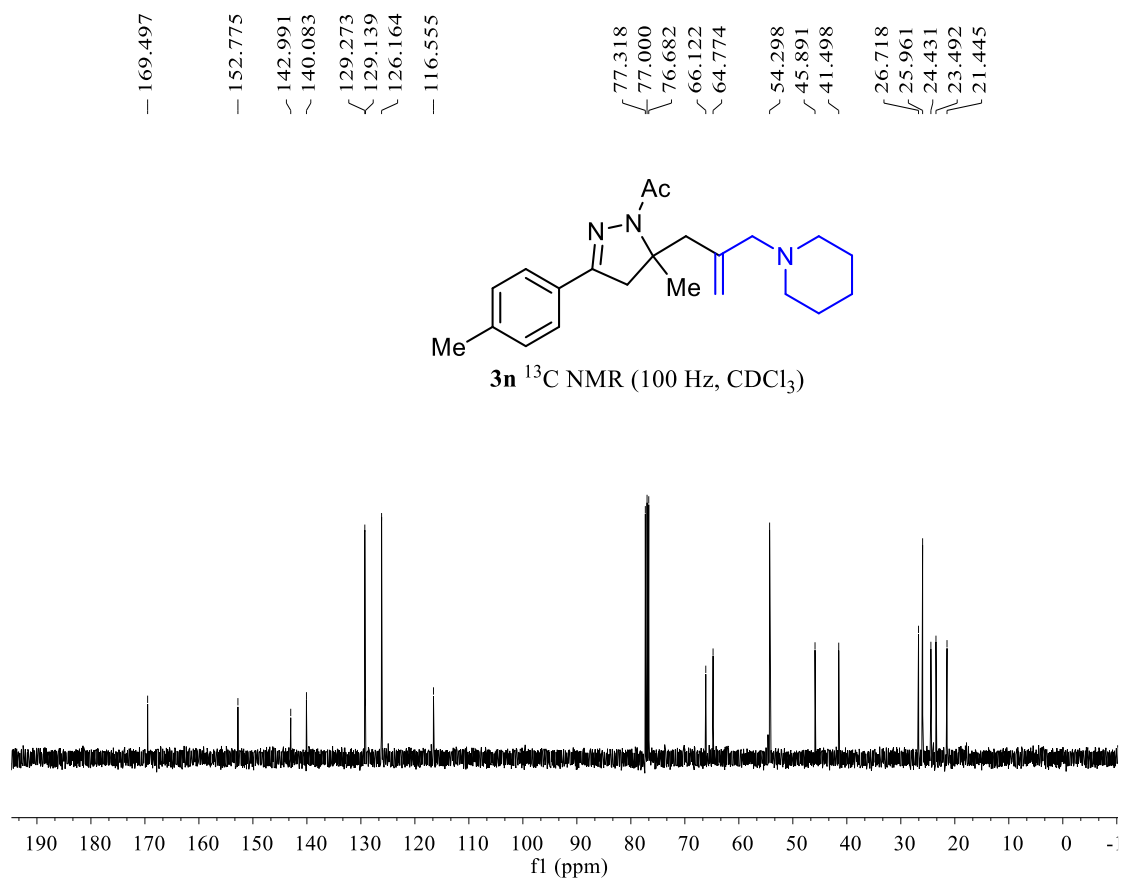
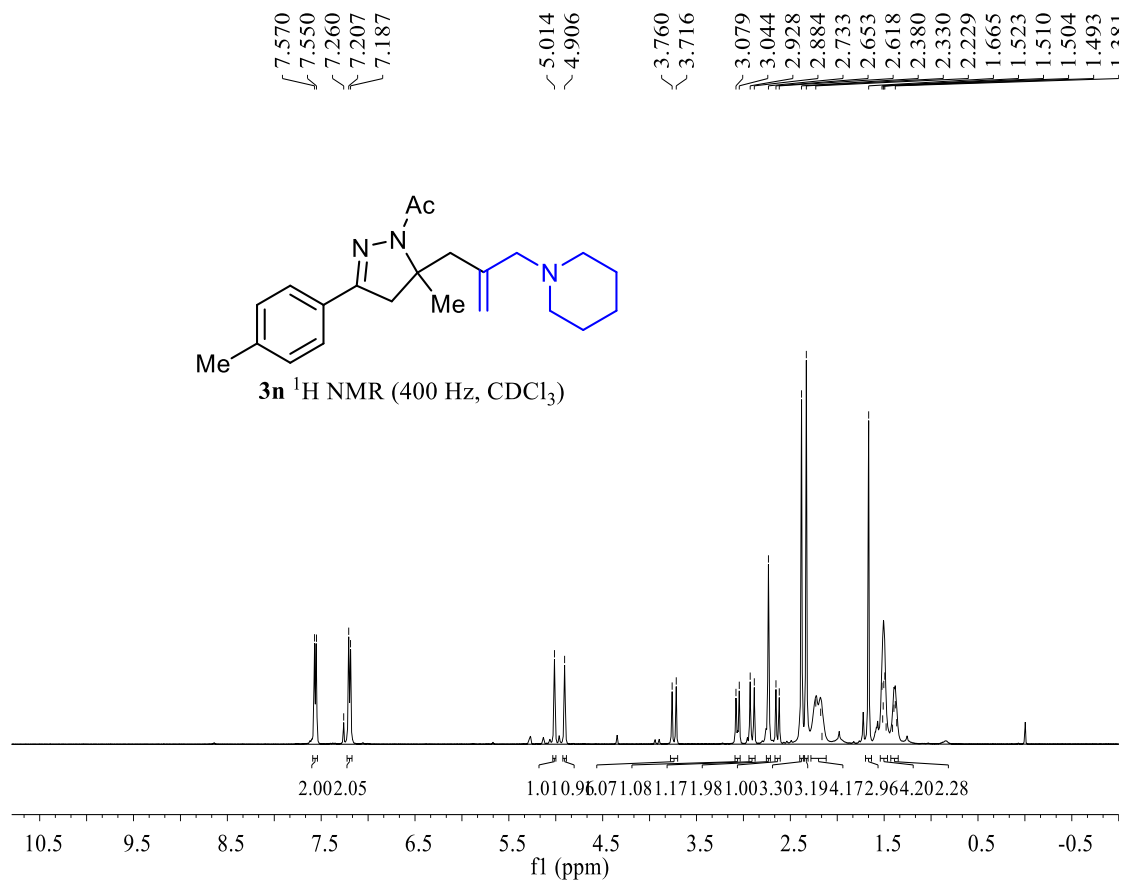






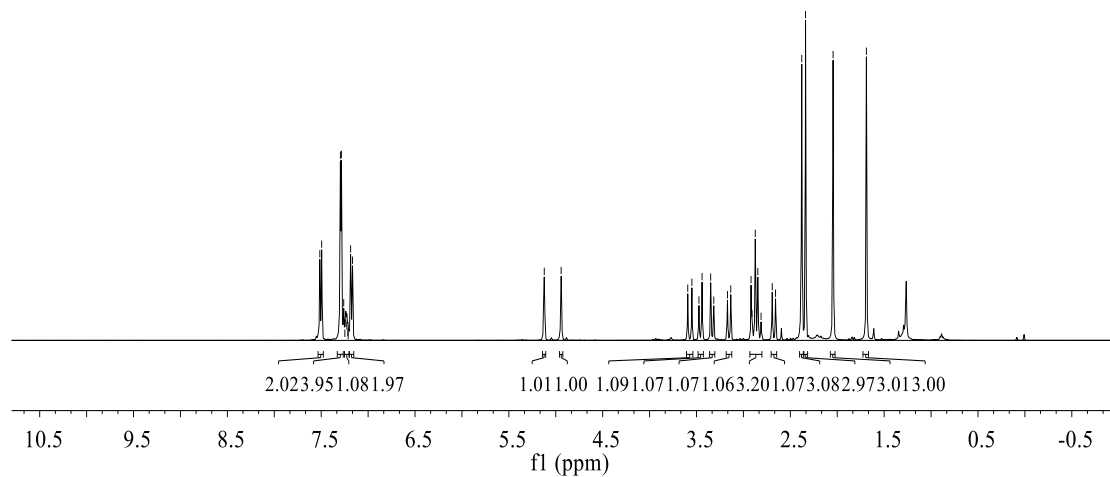
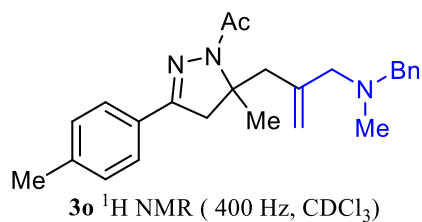






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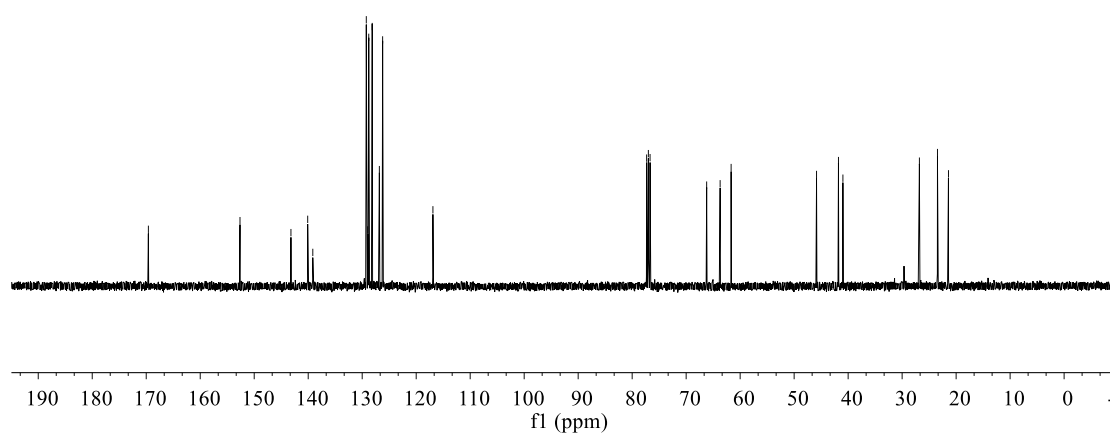
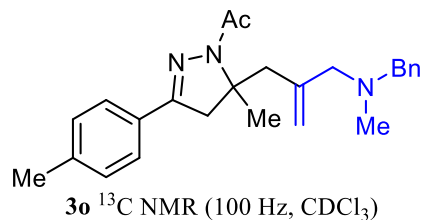
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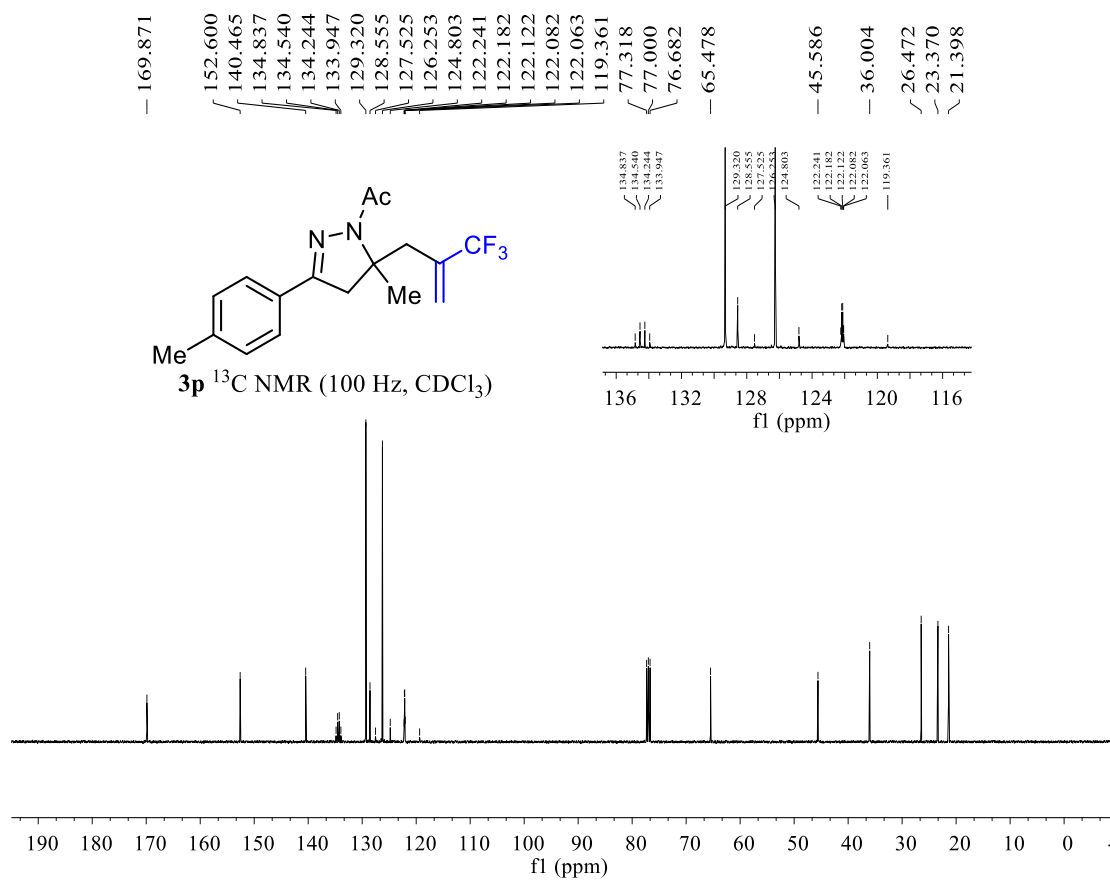
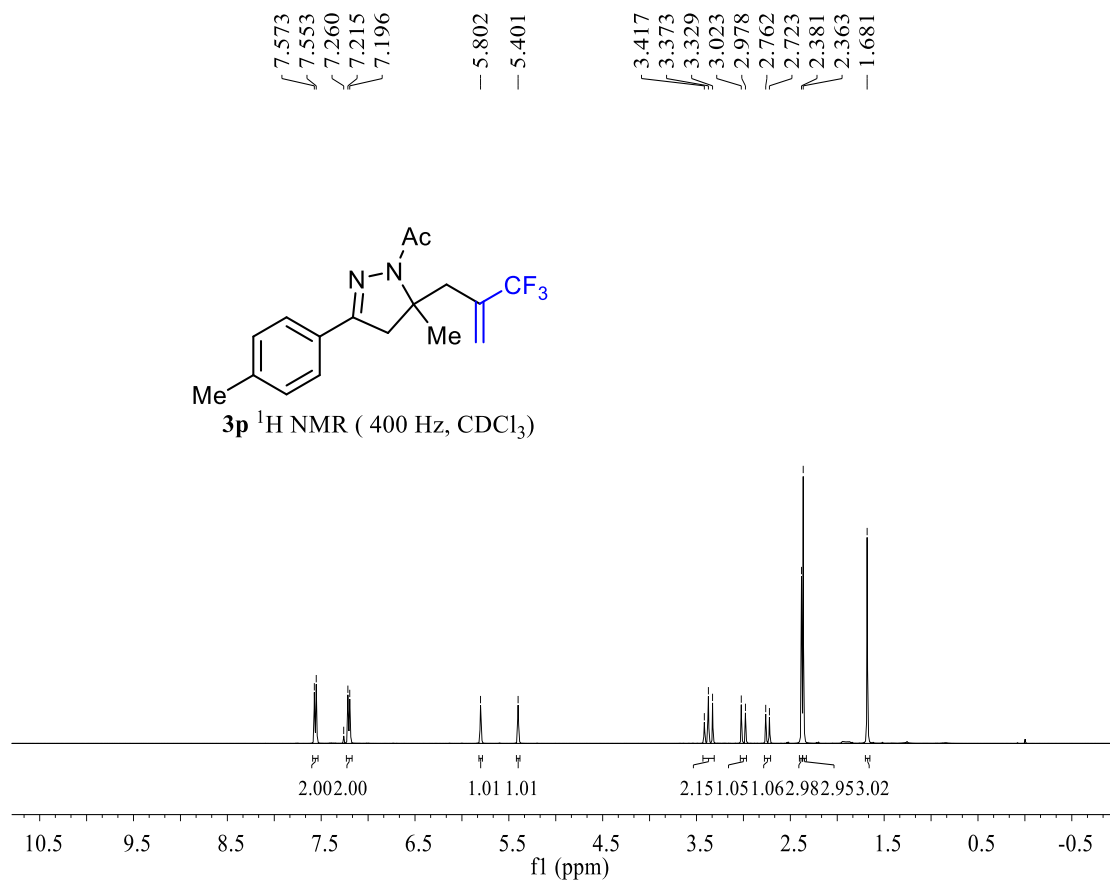
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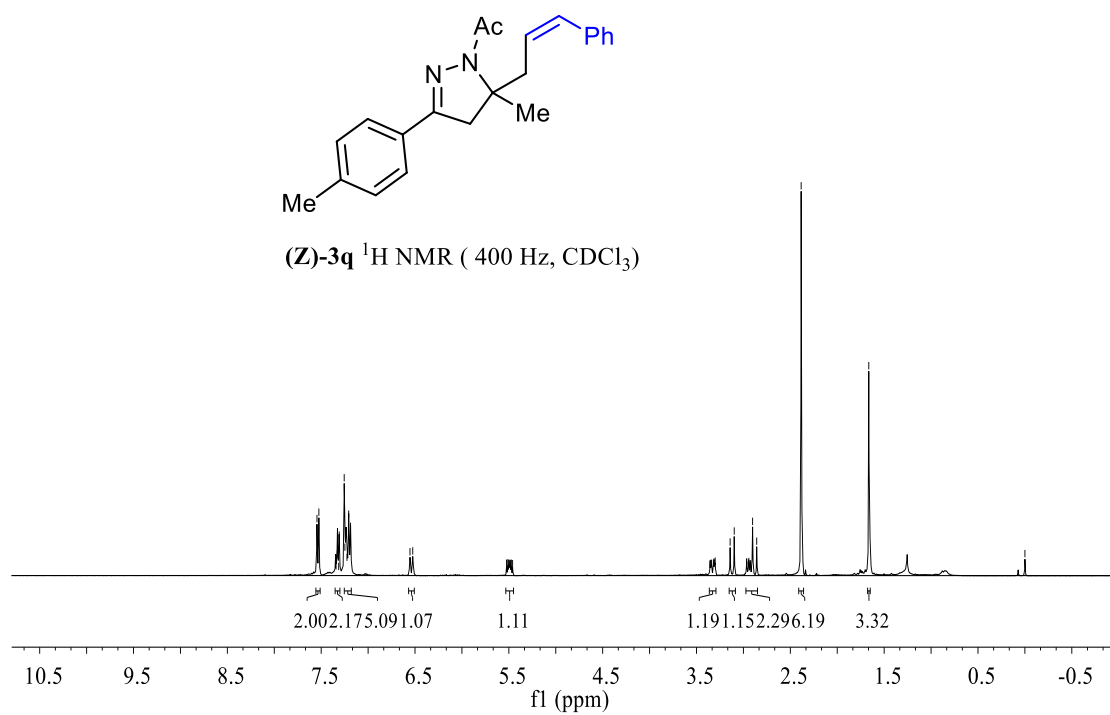
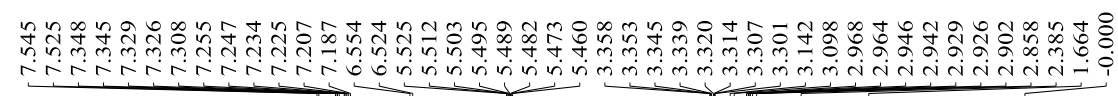
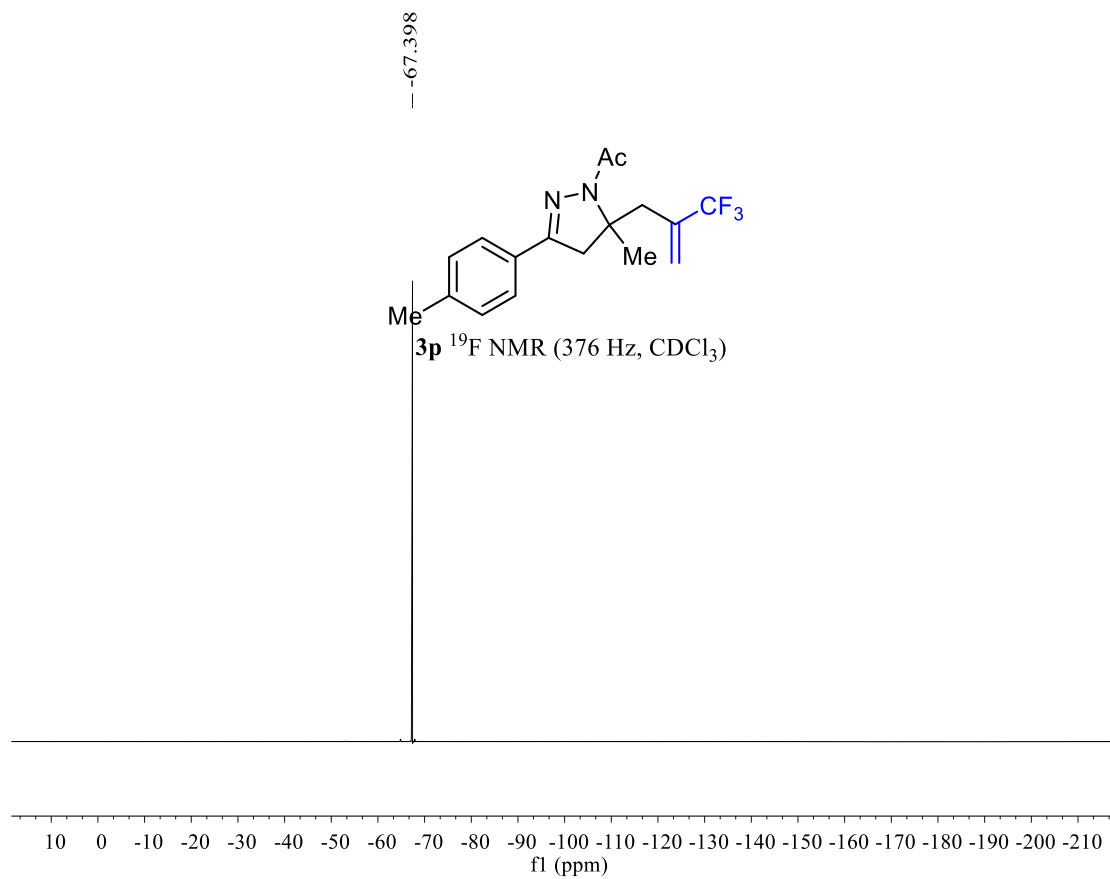
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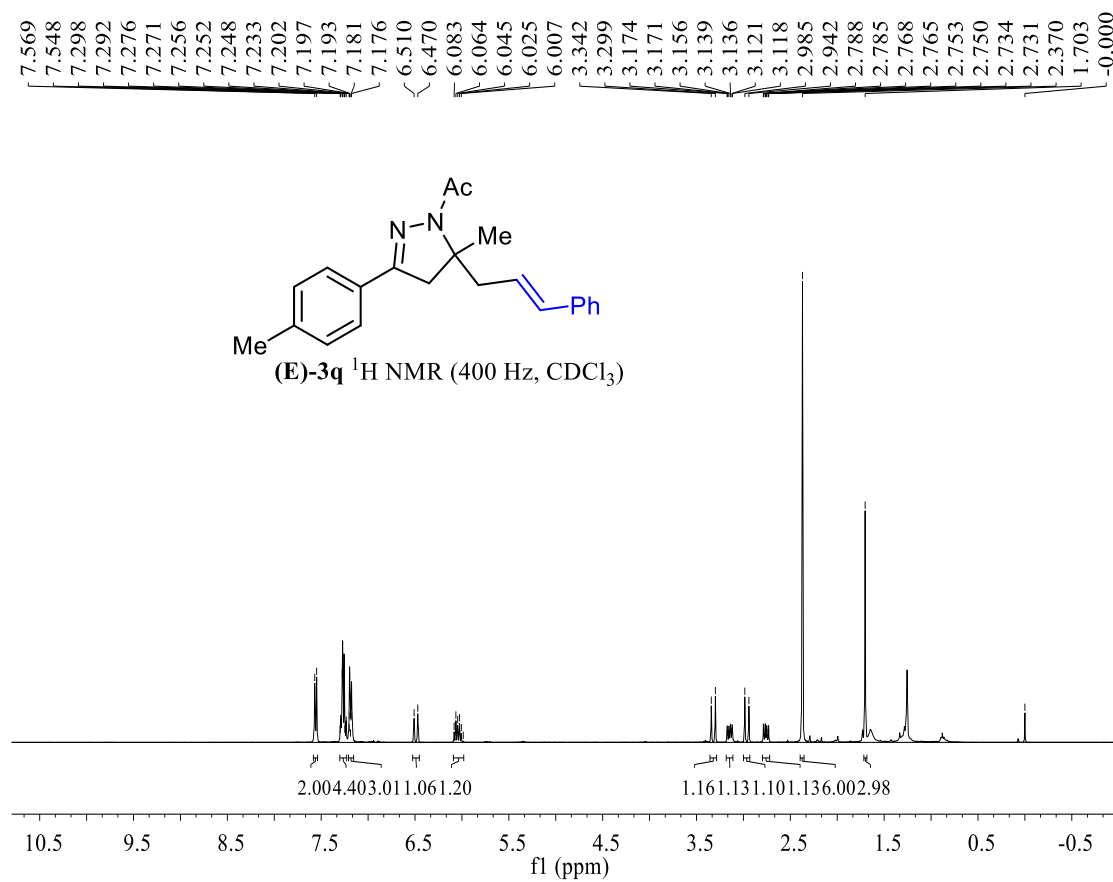
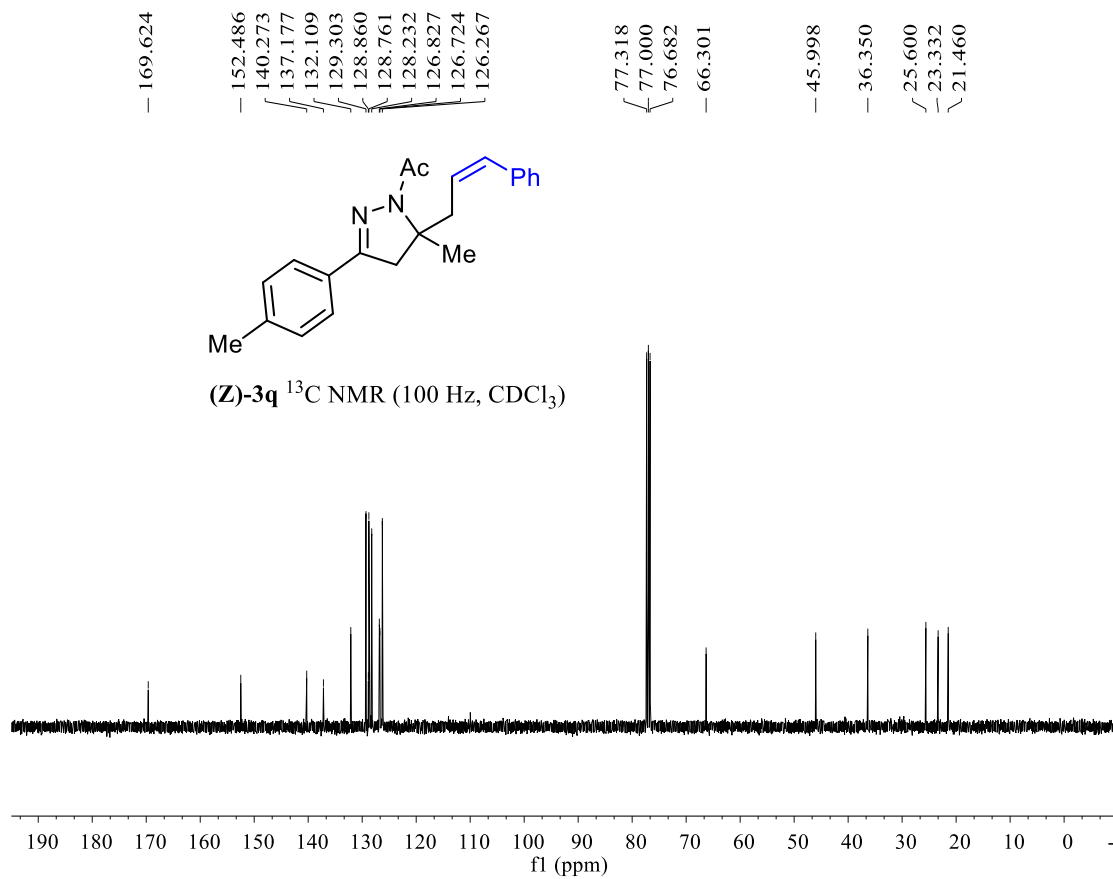
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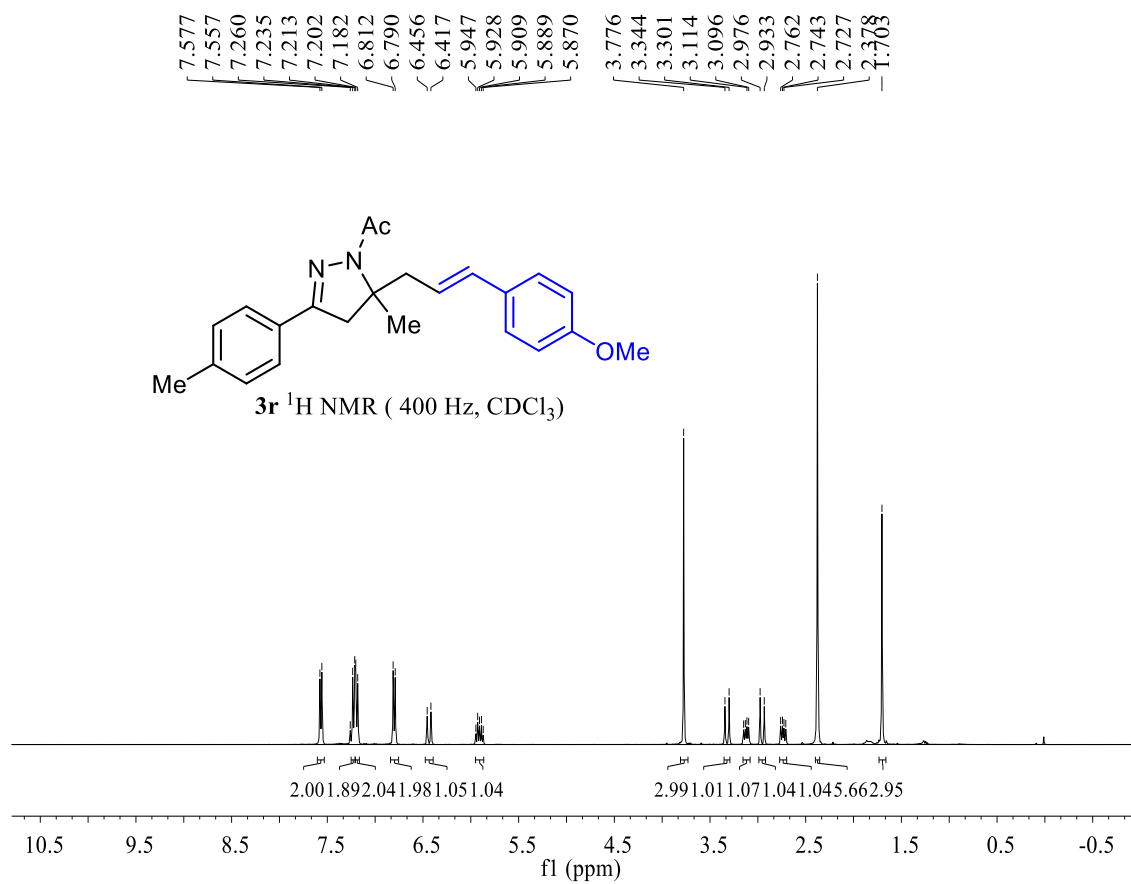
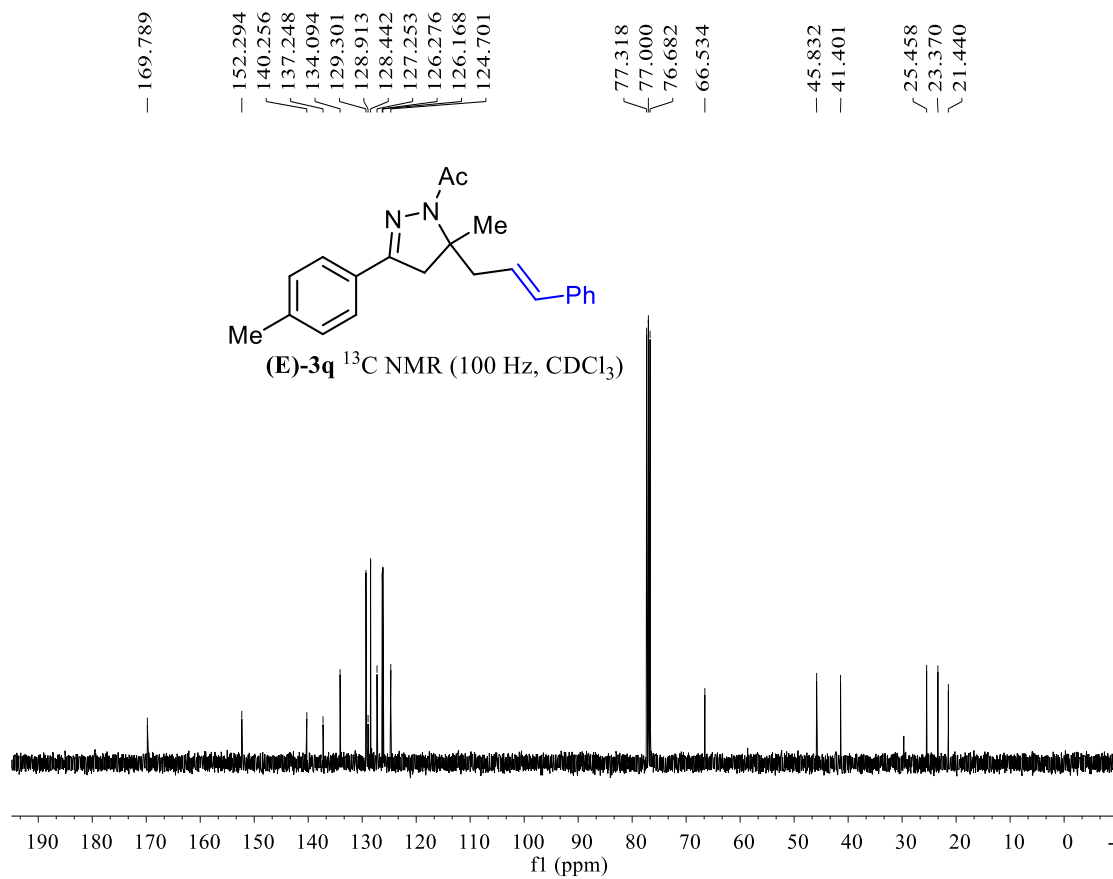


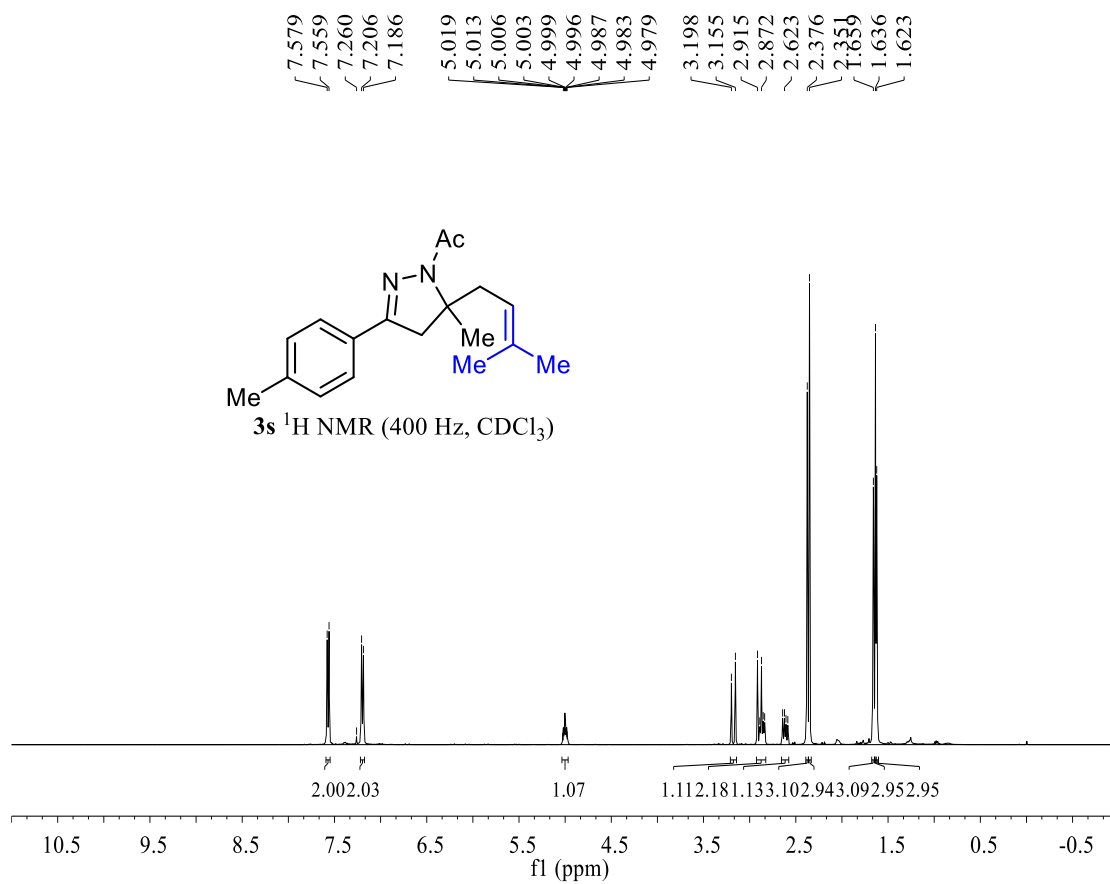
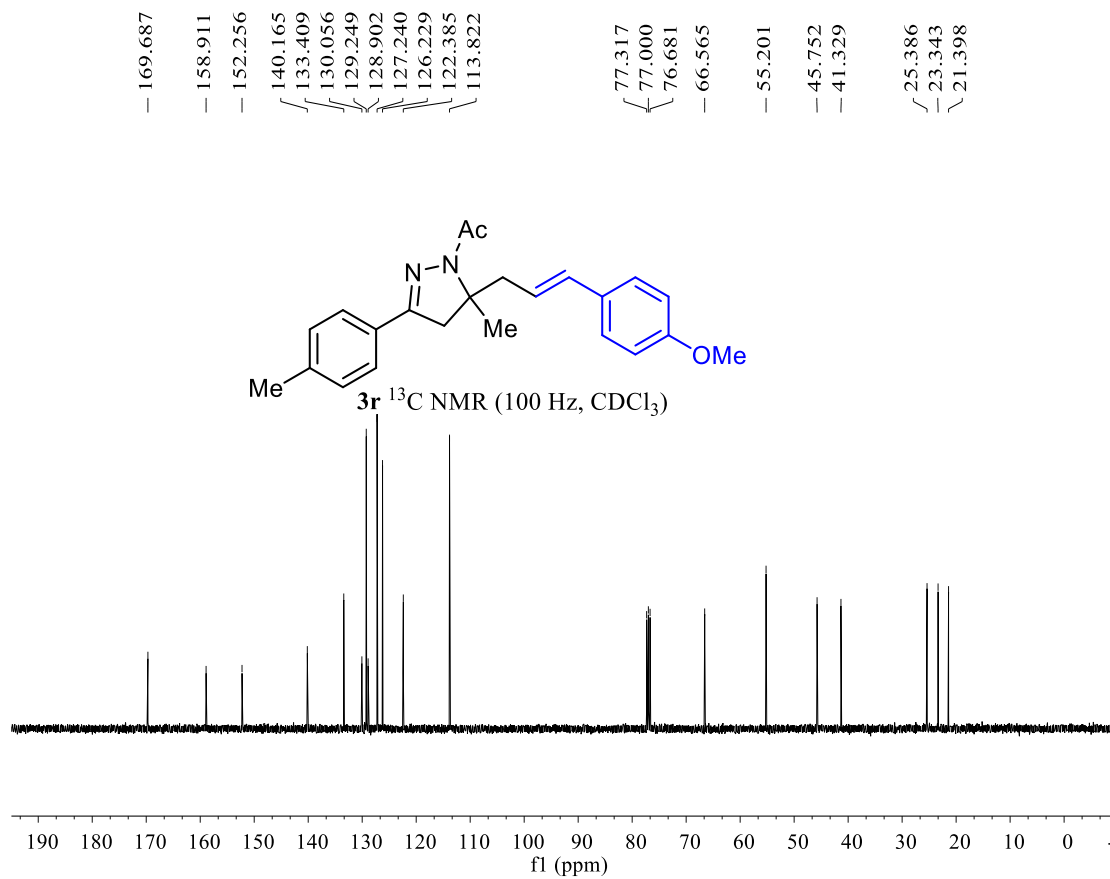


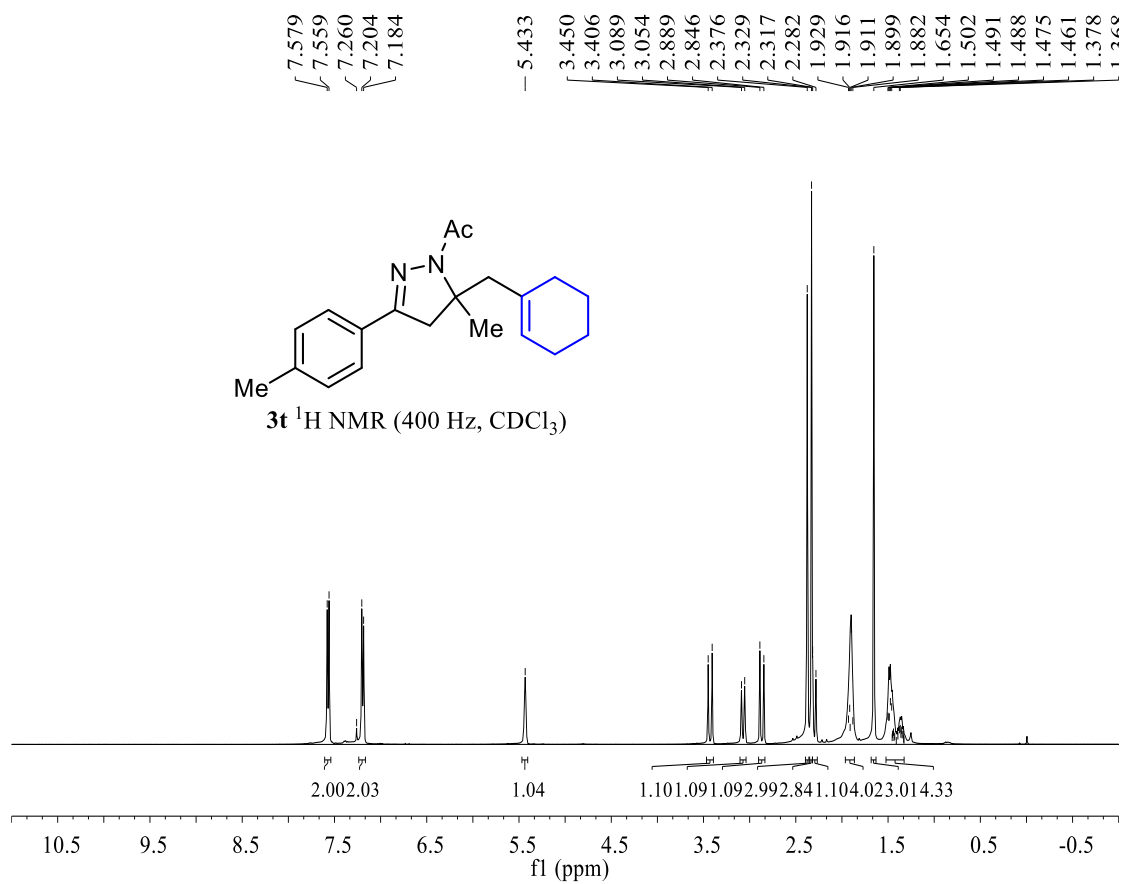
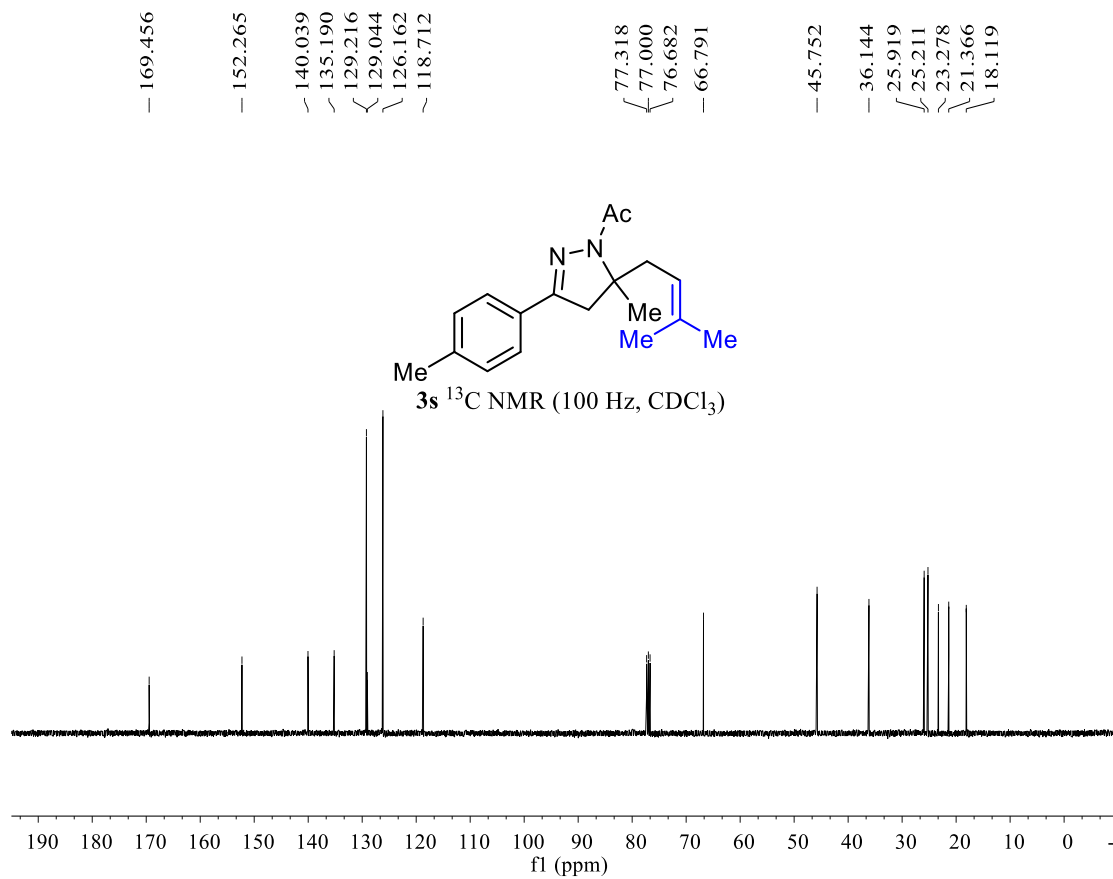


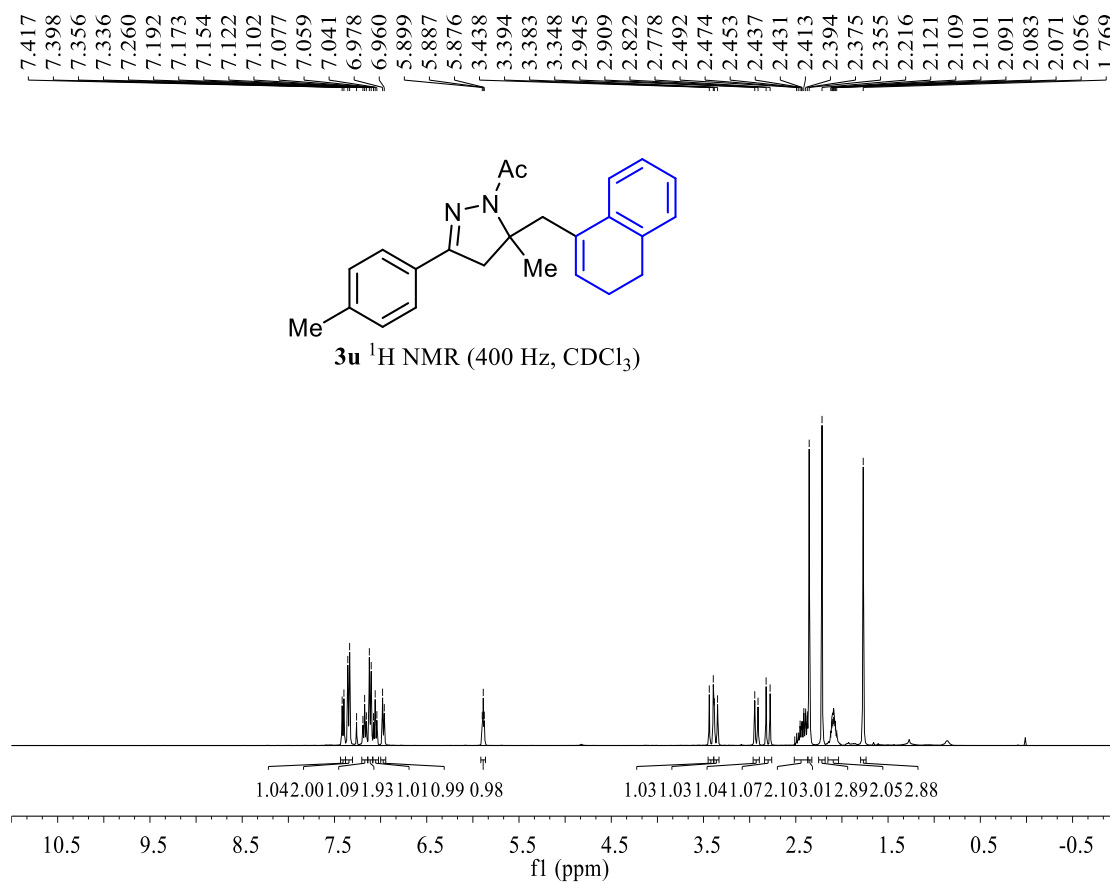
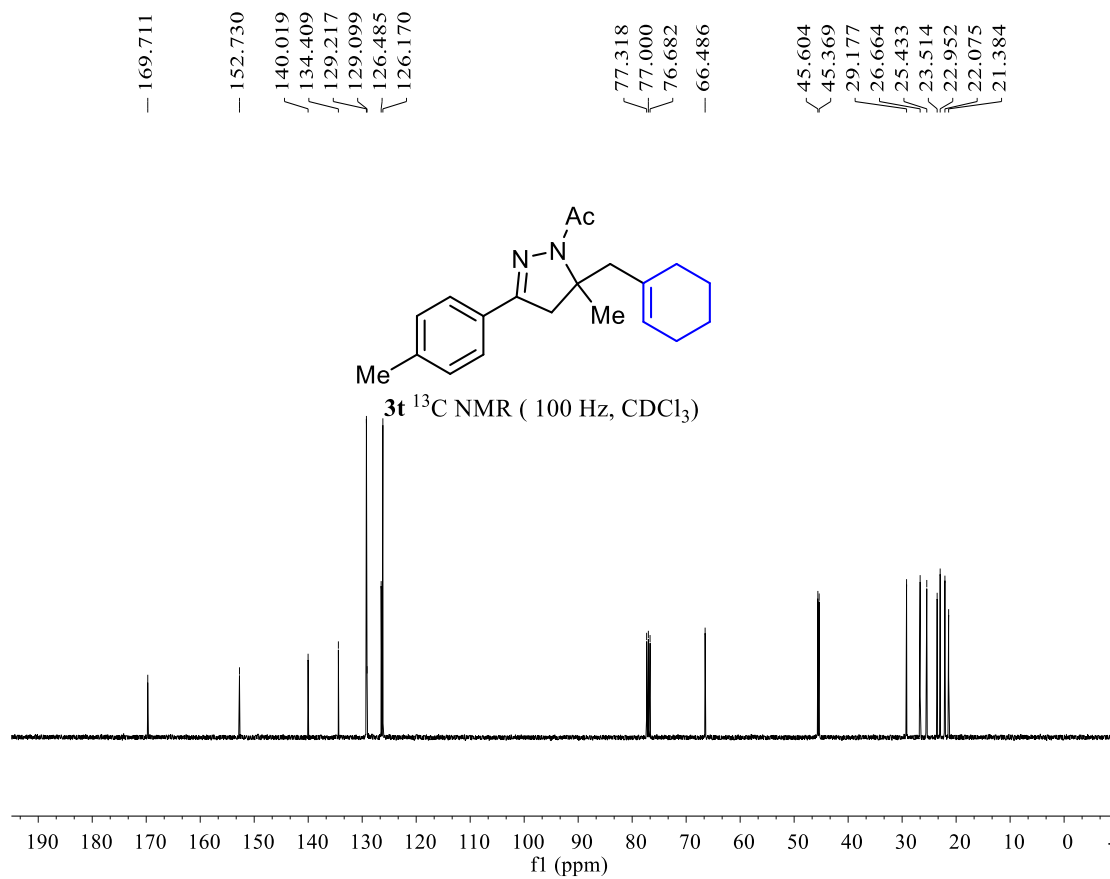




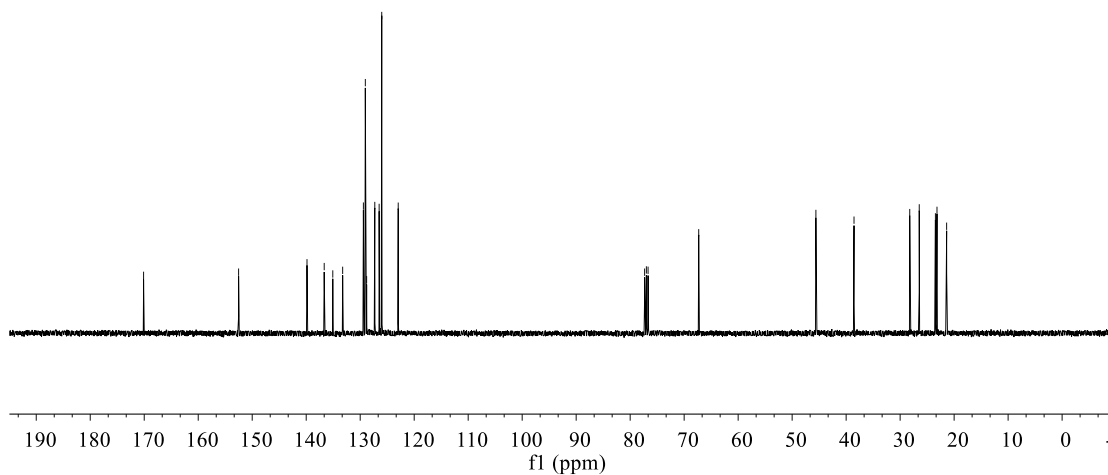
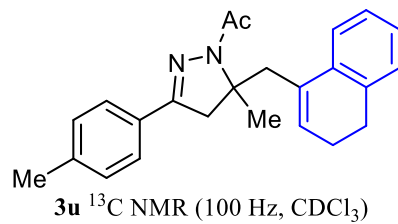




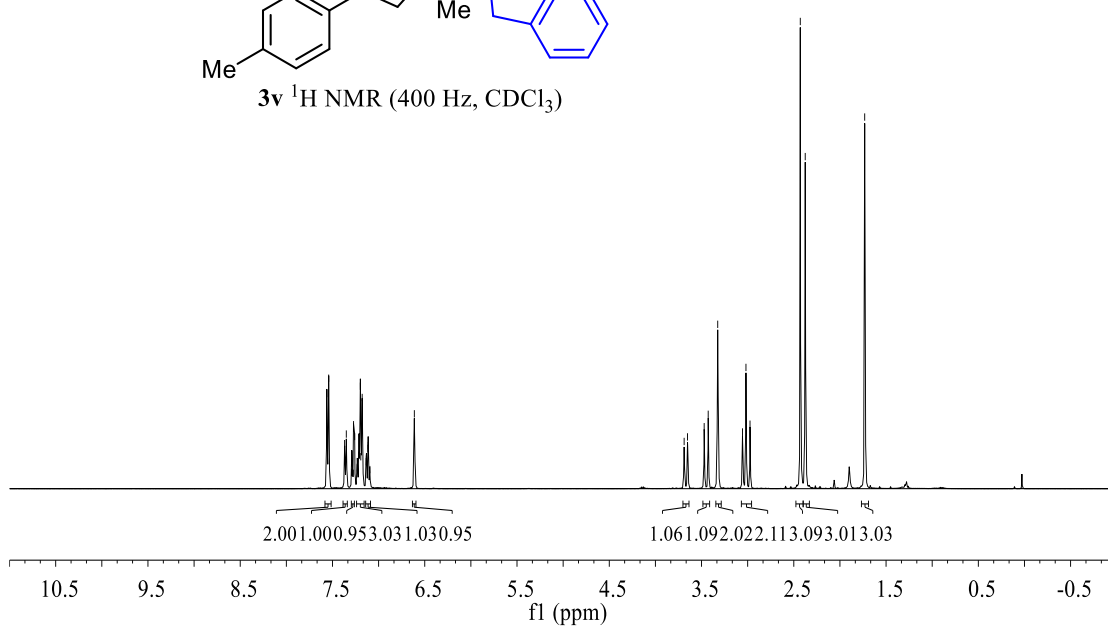
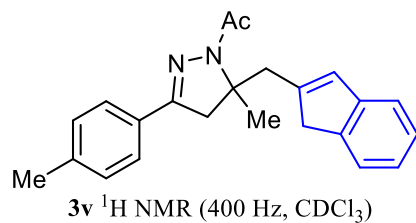




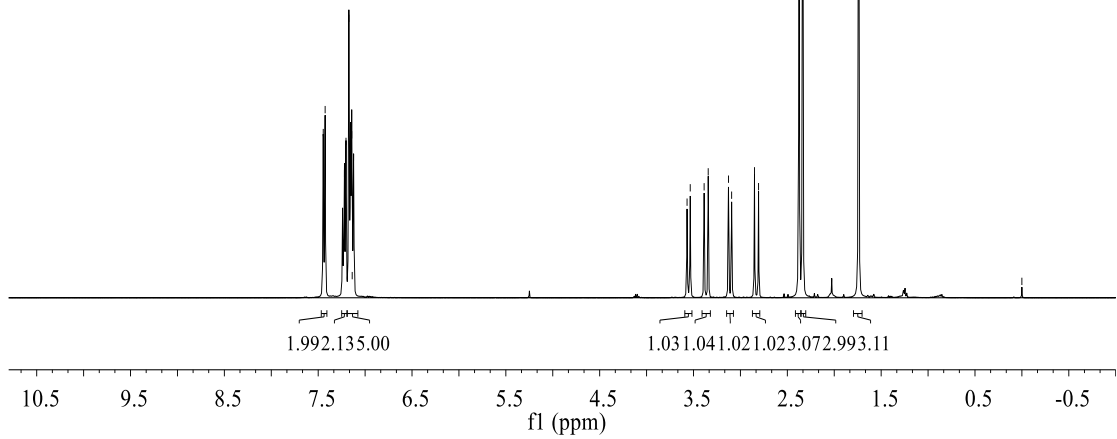
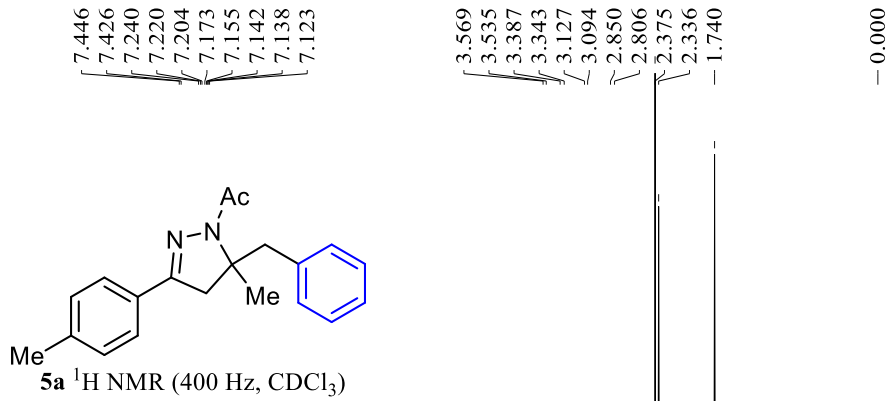
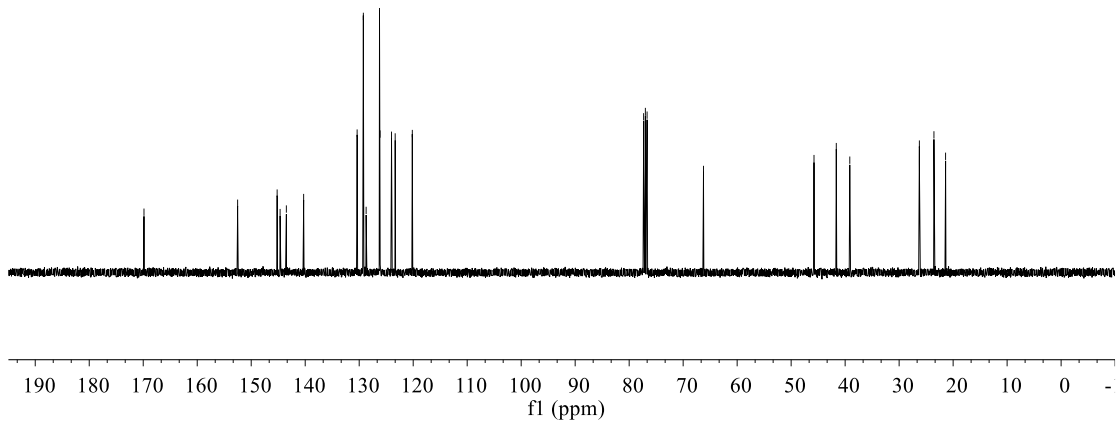
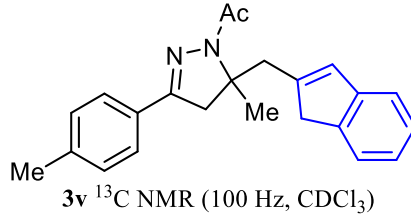
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 128.802  
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 126.492  
 126.006  
 122.958  
 77.318  
 77.000  
 76.684  
 67.300  
 45.599  
 38.539  
 28.217  
 26.460  
 23.467  
 23.172  
 21.383



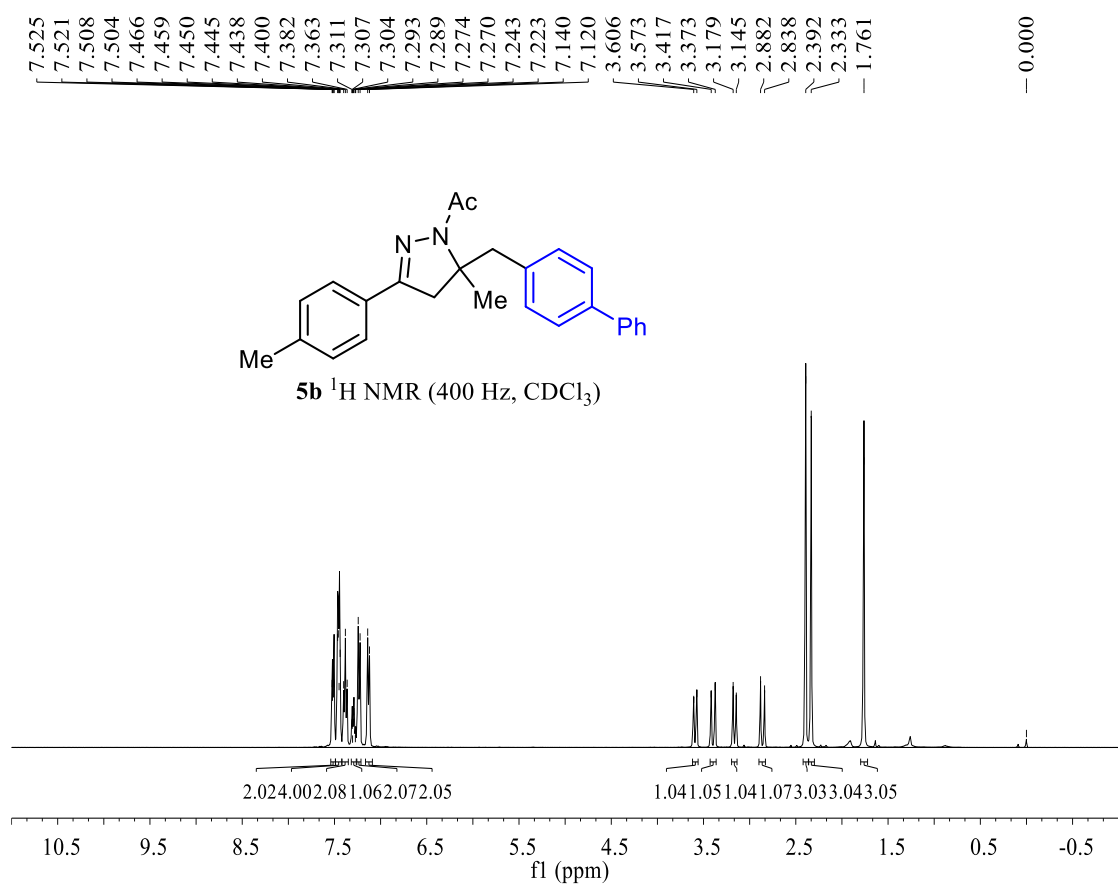
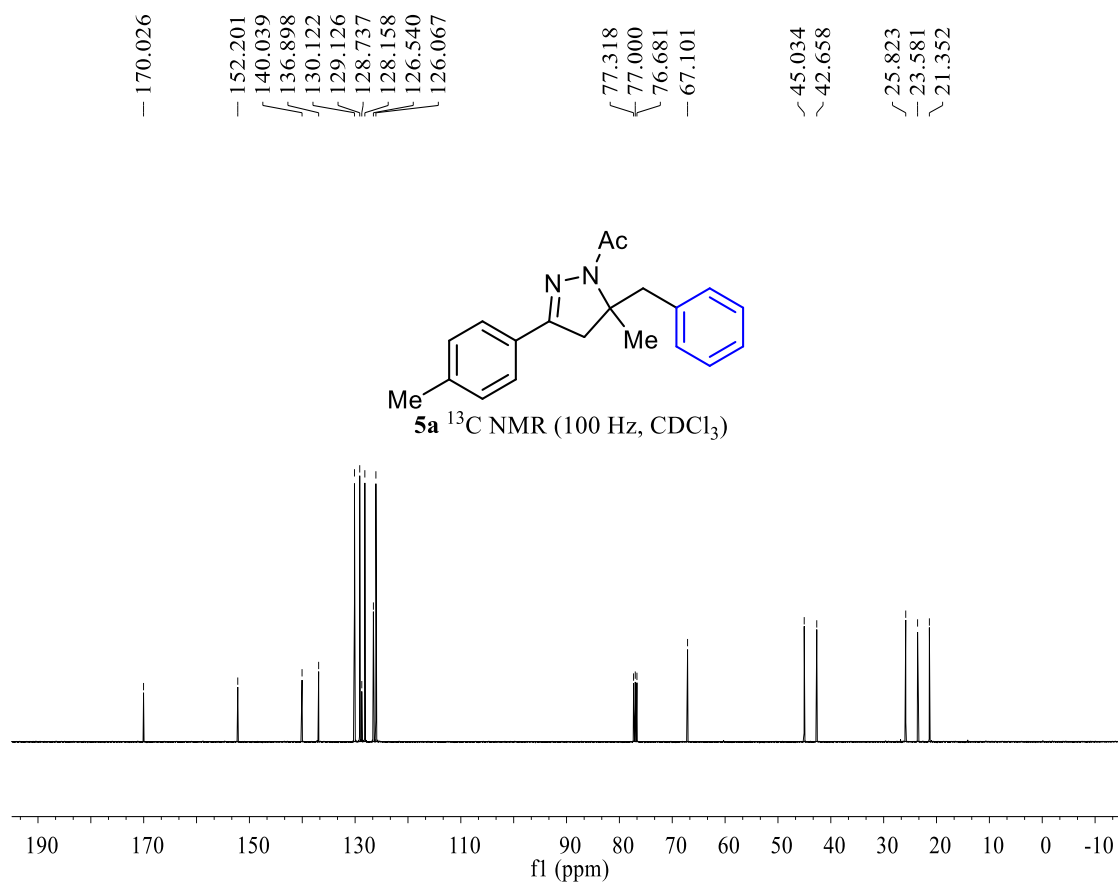
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 7.369  
 7.350  
 7.291  
 7.288  
 7.271  
 7.260  
 7.233  
 7.230  
 7.214  
 7.211  
 7.198  
 7.193  
 7.178  
 7.135  
 7.131  
 7.116  
 7.113  
 7.098  
 7.095  
 6.613  
 6.689  
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 3.471  
 3.428  
 3.325  
 3.056  
 3.019  
 2.975  
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 2.376  
 1.732

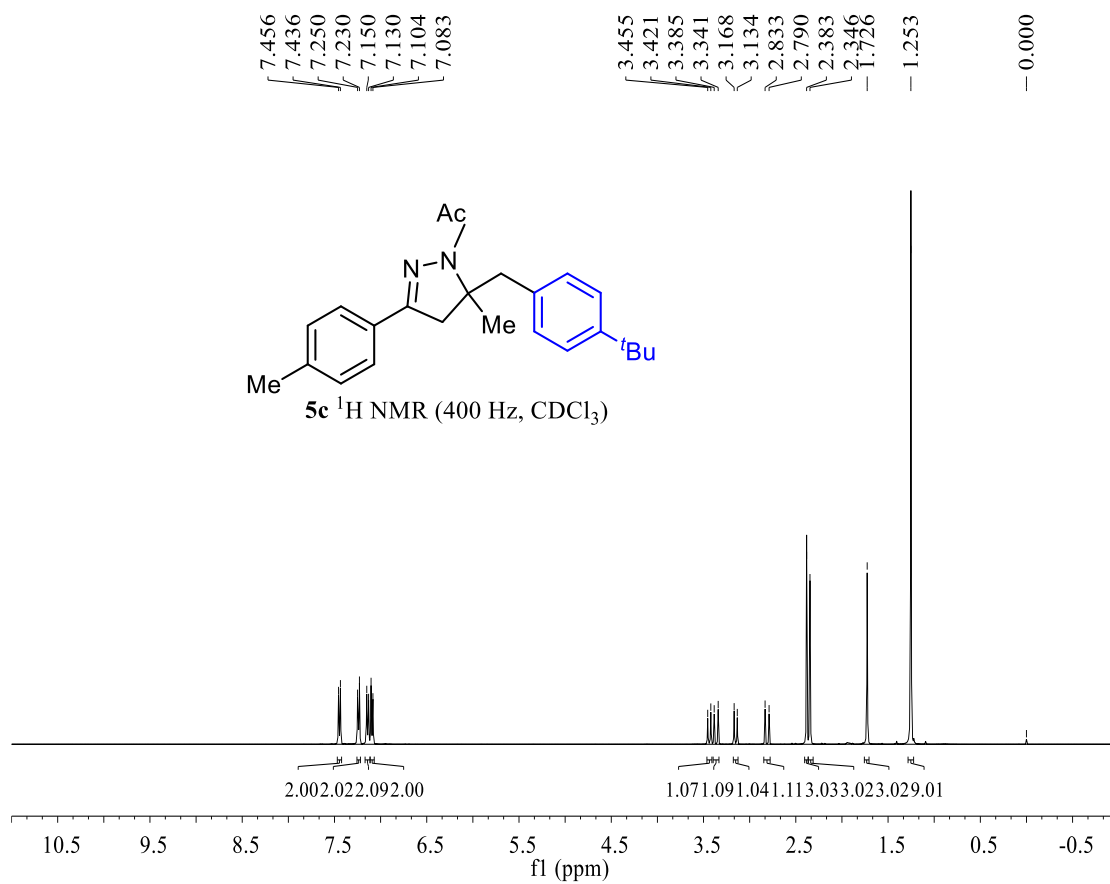
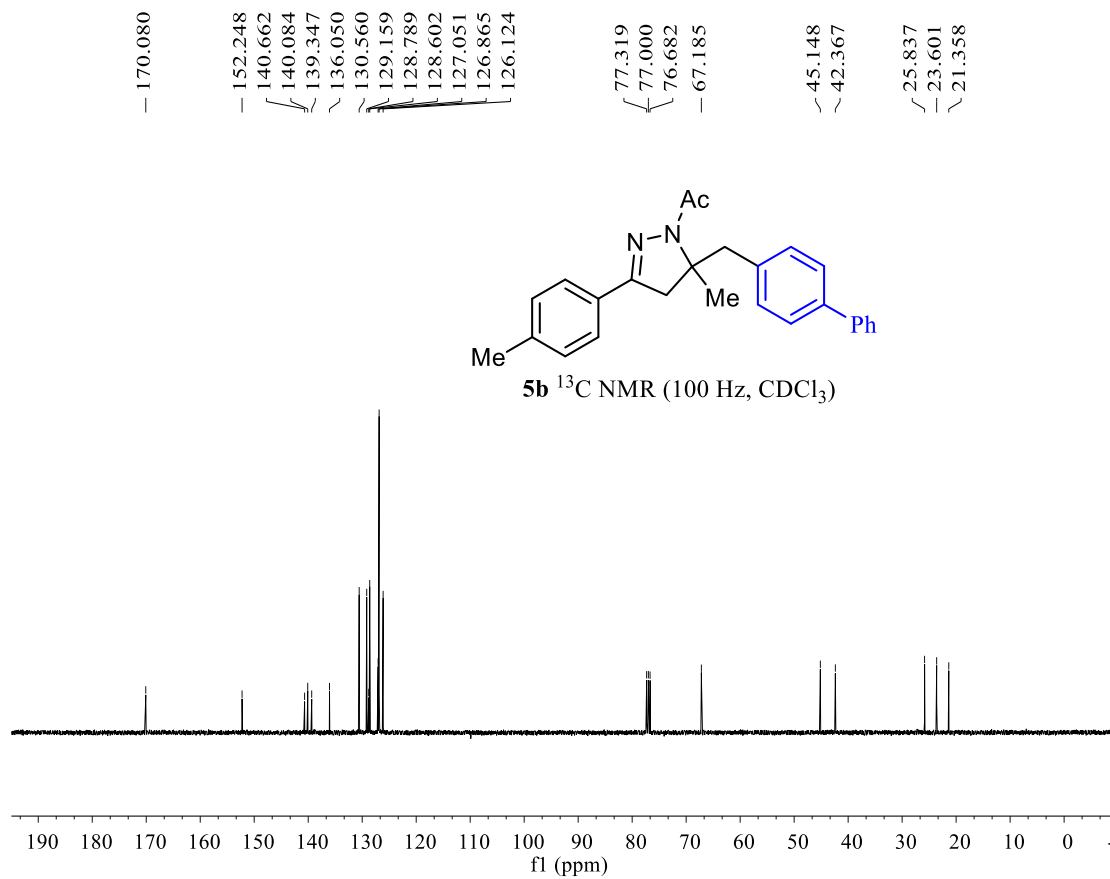


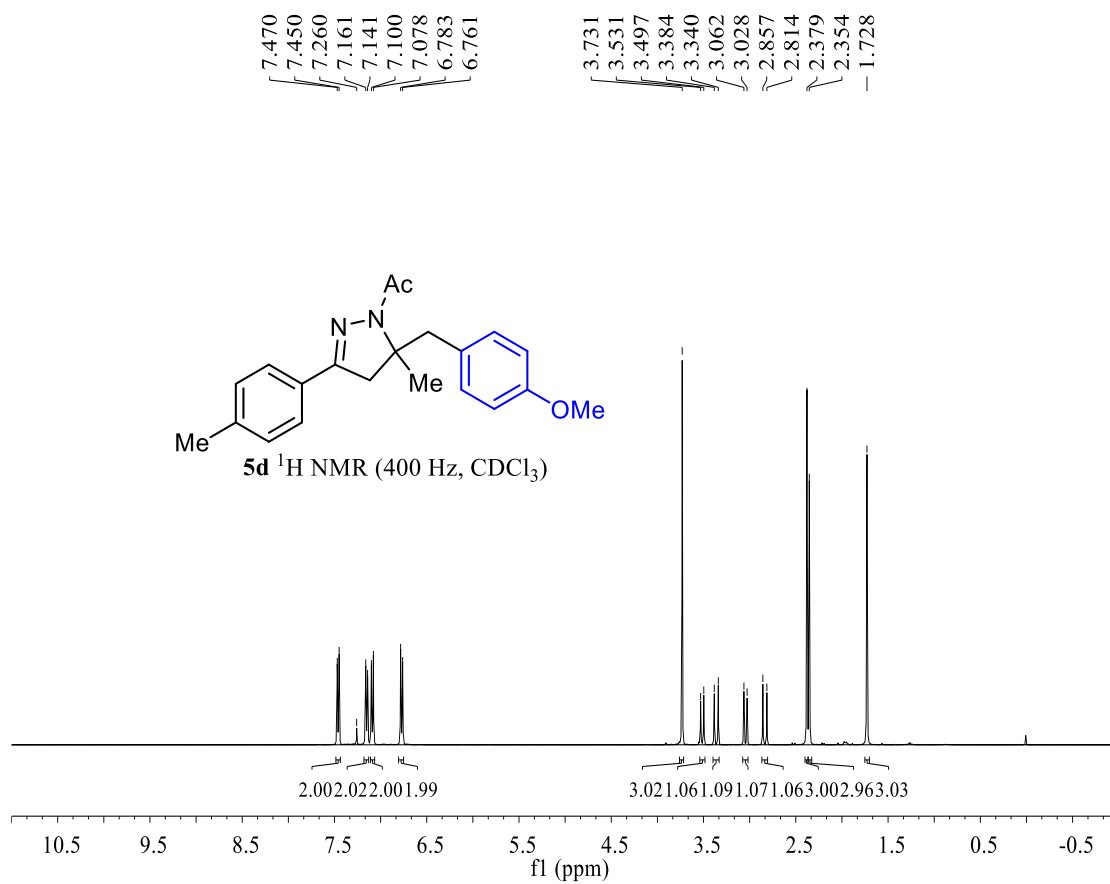
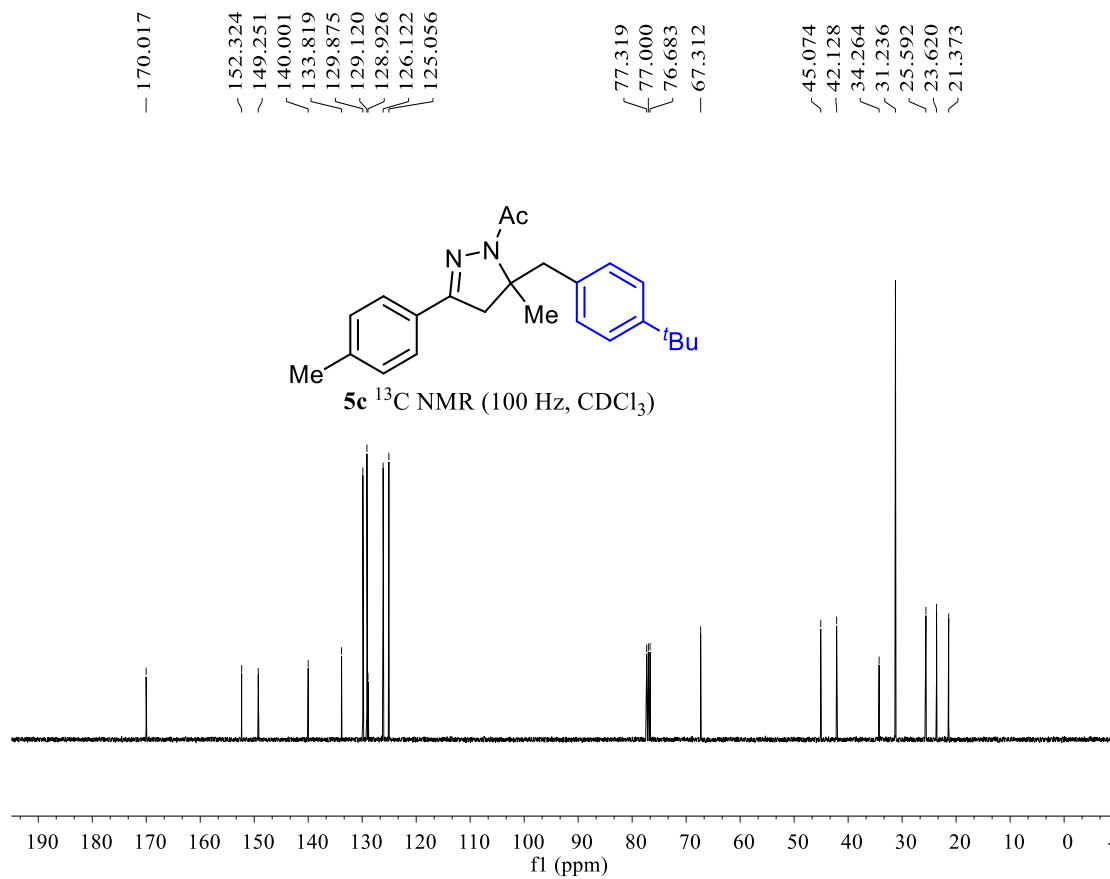
169.857  
 152.513  
 145.196  
 144.650  
 143.491  
 140.286  
 130.381  
 129.232  
 128.714  
 126.237  
 126.134  
 124.008  
 123.335  
 120.163  
 77.318  
 77.000  
 76.682  
 66.236  
 45.764  
 41.639  
 39.136  
 26.252  
 23.551  
 21.393

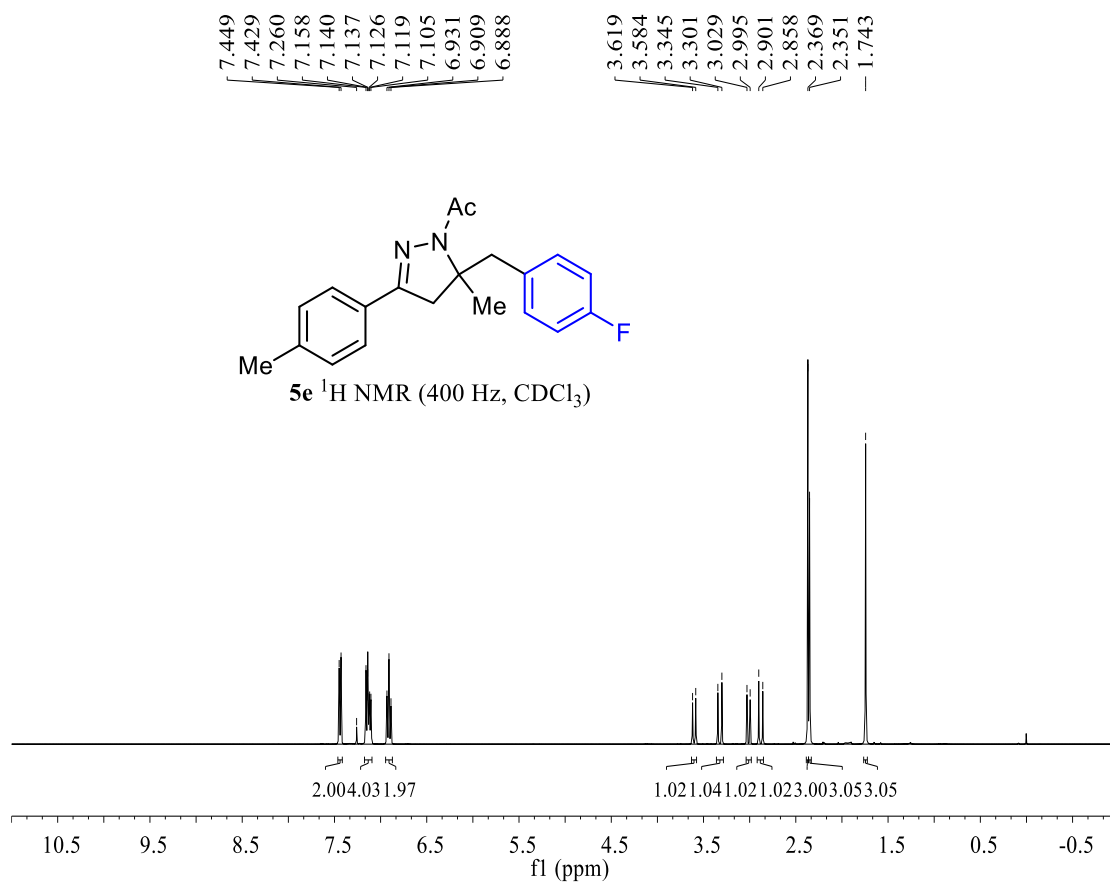
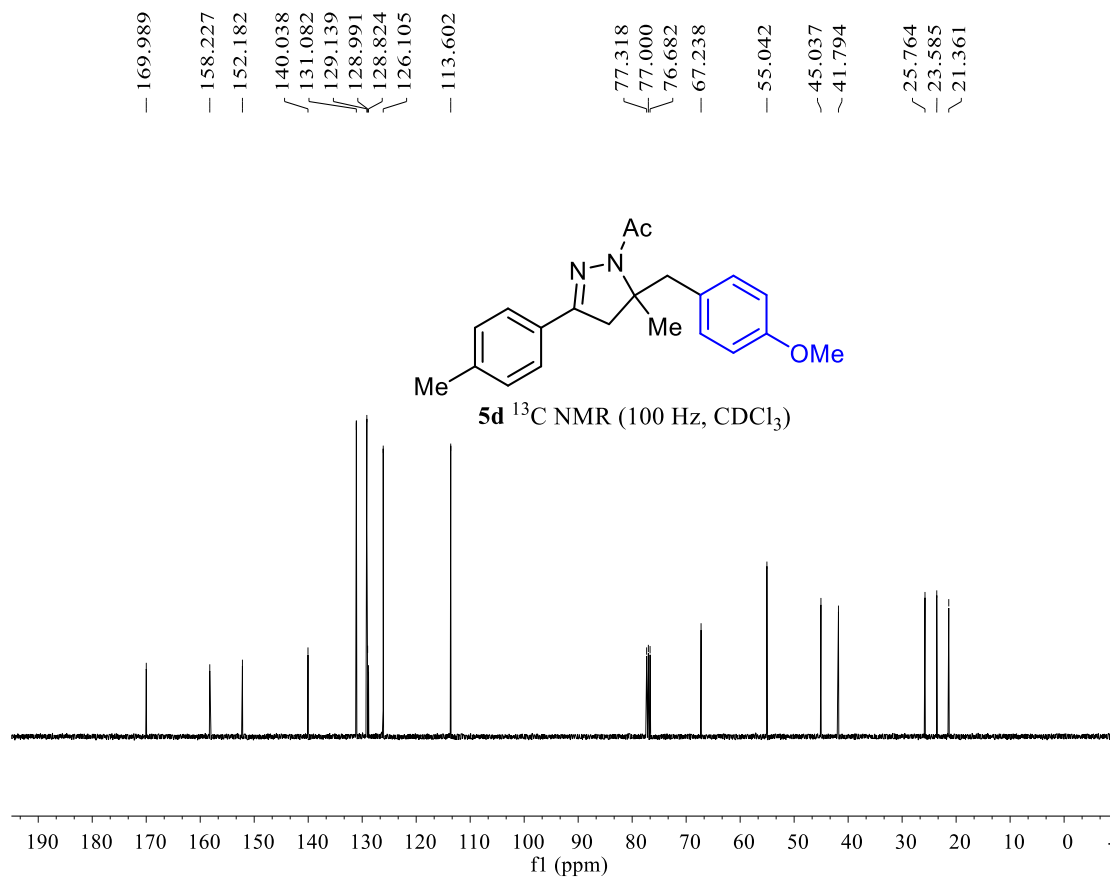










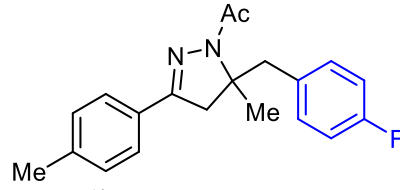


170.097  
162.919  
160.483  
152.131  
140.192  
132.671  
132.638  
131.512  
131.434  
129.192  
128.639  
126.078  
115.146  
114.936

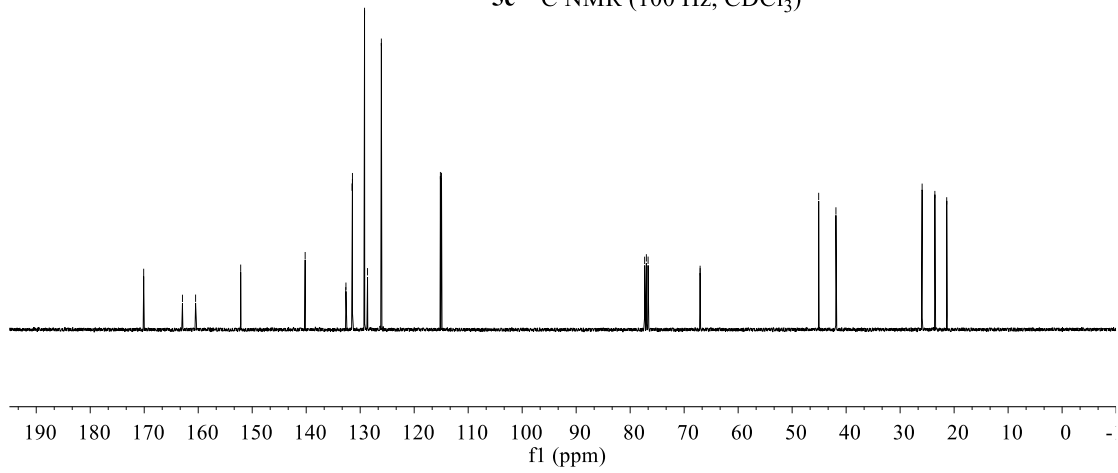
77.317  
77.000  
76.681  
67.044  
67.031

45.083  
41.888

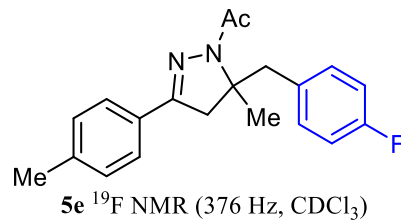
25.925  
23.567  
21.370



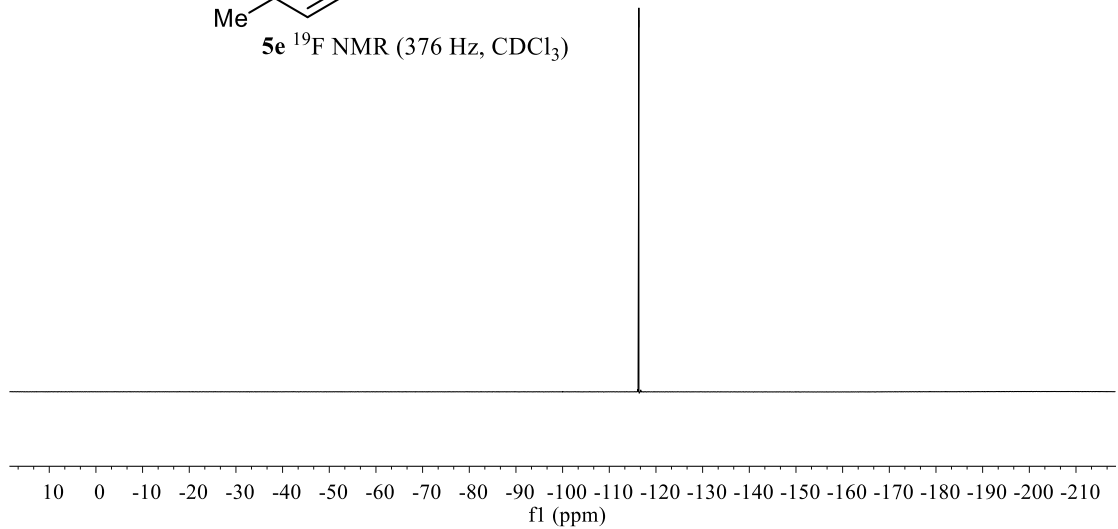
5e <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>)

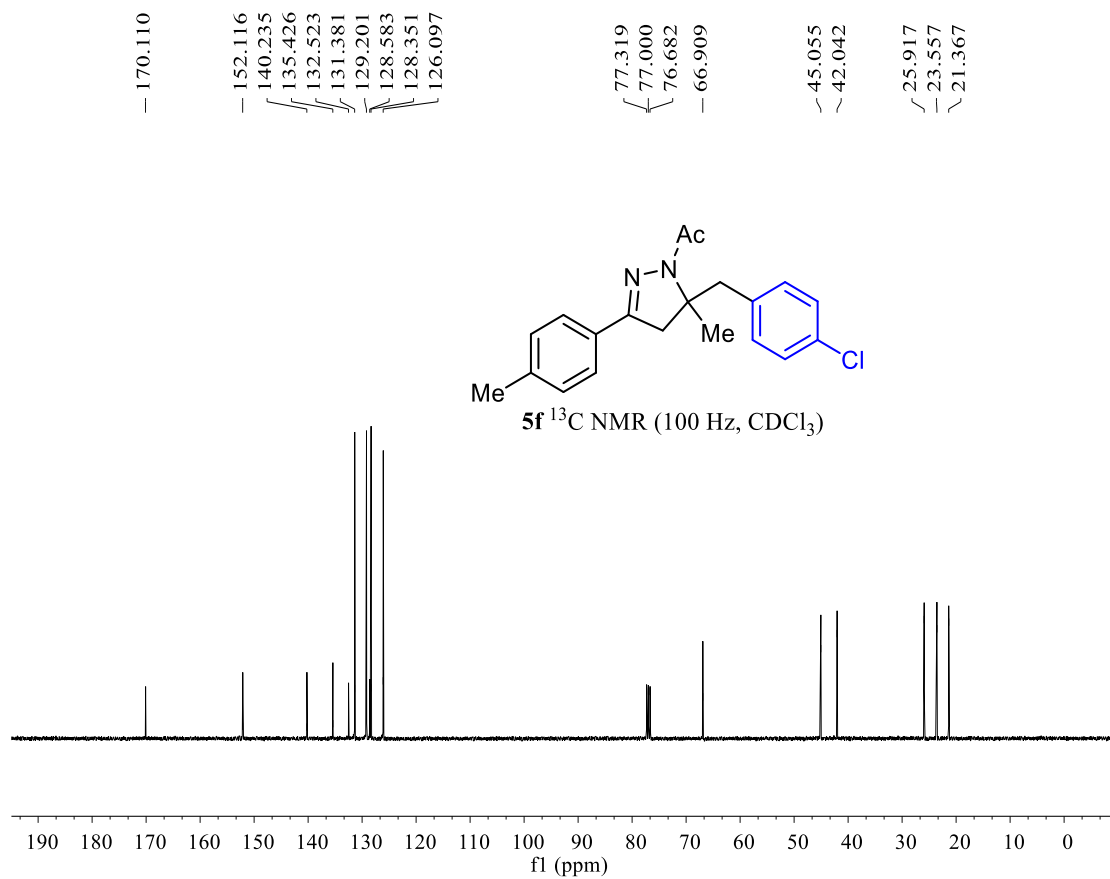
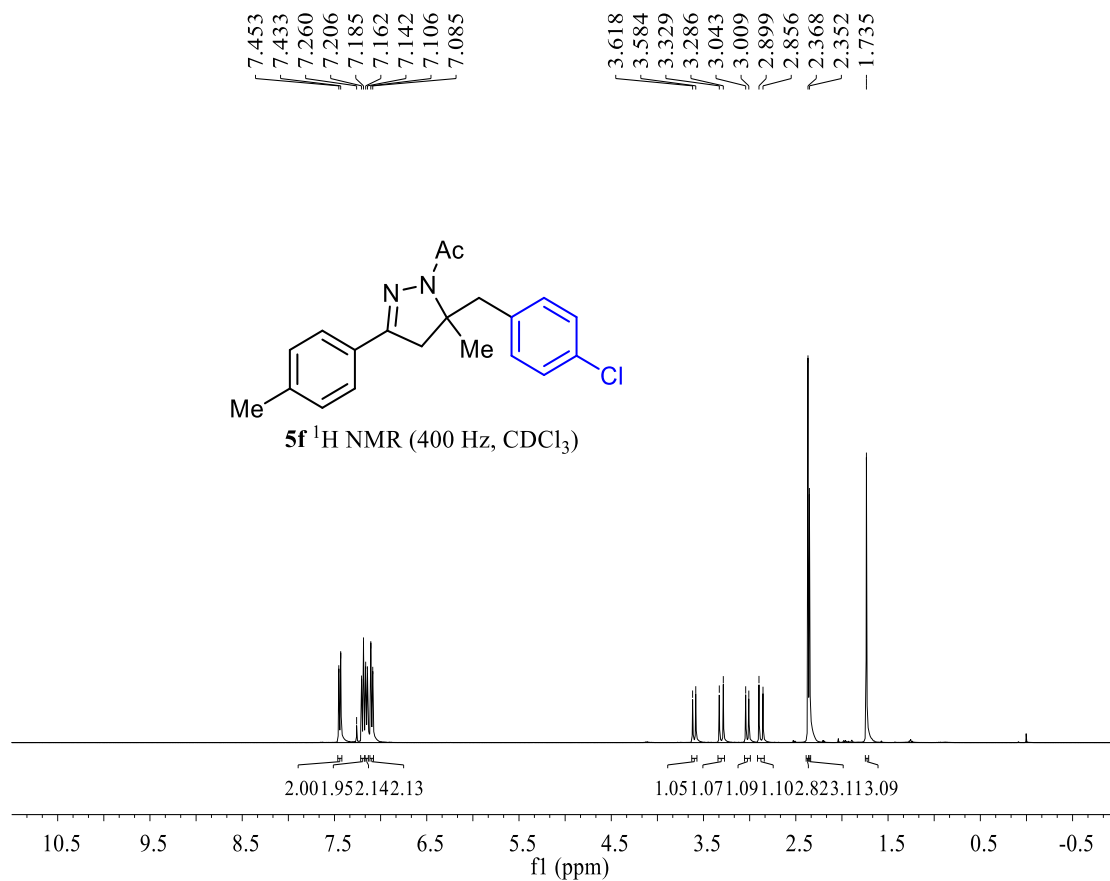


-116.347



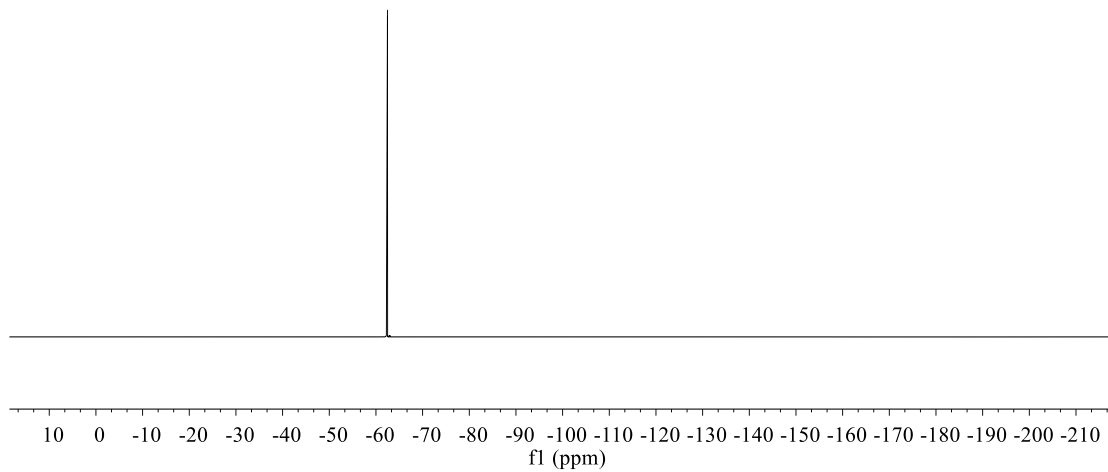
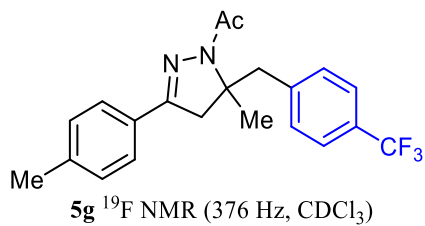
5e <sup>19</sup>F NMR (376 Hz, CDCl<sub>3</sub>)



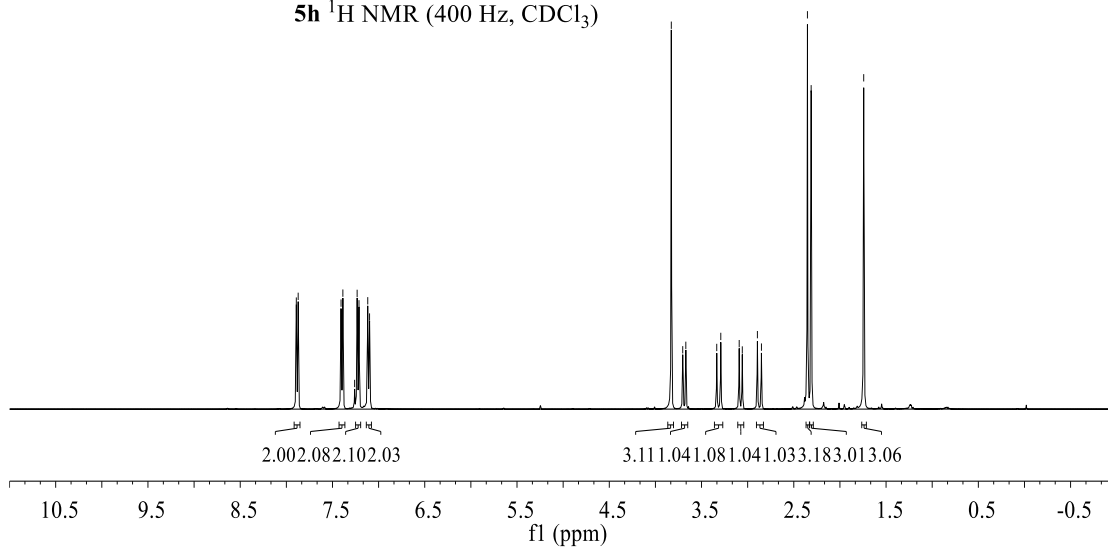
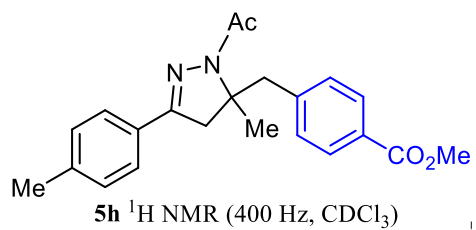




--62.467

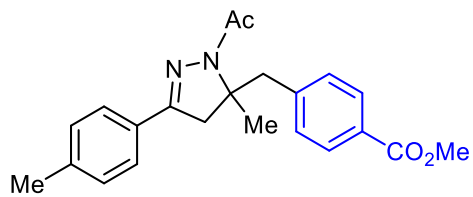


7.892 7.872 7.407 7.387 7.260 7.233 7.213 7.118 7.098 3.828 3.704 3.670 3.335 3.291 3.092 3.058 2.895 2.851 2.352 2.312 -1.742

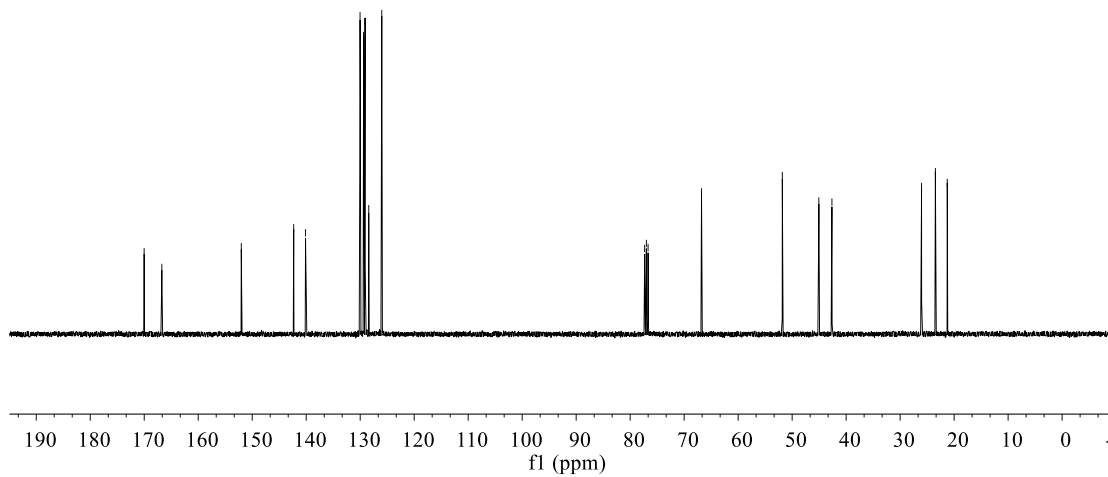




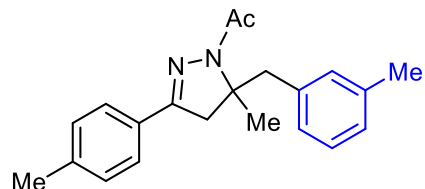
~ 170.016  
 ~ 166.735  
 — 152.023  
 ~ 142.310  
 ~ 140.124  
 { 130.024  
 { 129.374  
 { 129.095  
 { 128.411  
 { 125.998  
 { 77.318  
 { 77.000  
 { 76.681  
 — 66.782  
 — 51.819  
 / 45.051  
 — 42.628  
 / 26.031  
 — 23.471  
 ~ 21.270



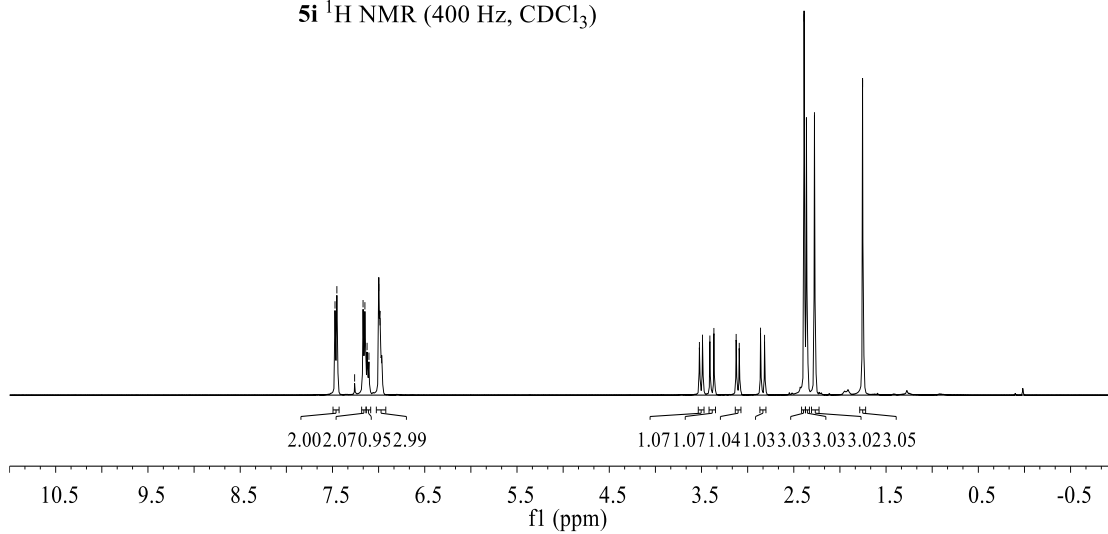
**5h**  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ )



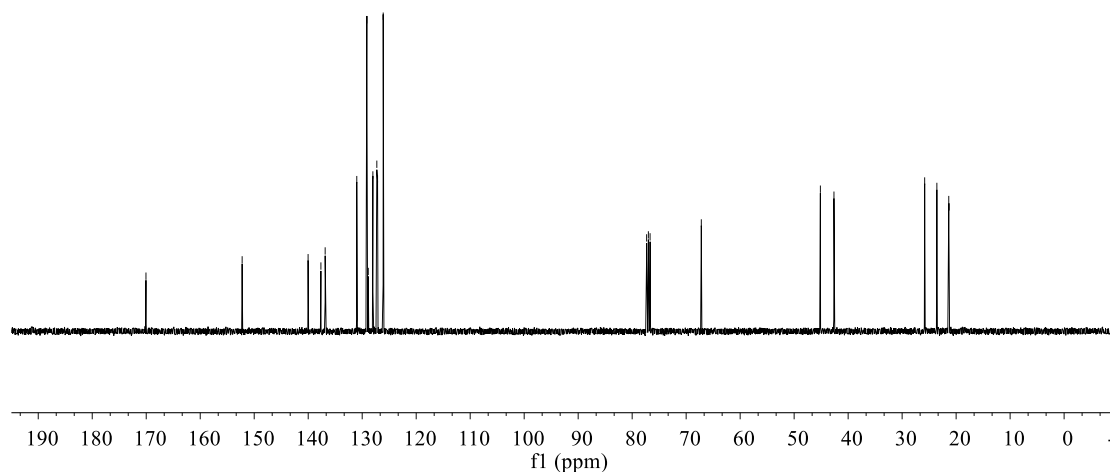
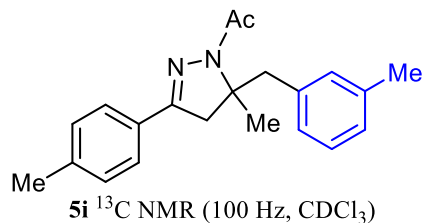
{ 7.473  
 { 7.452  
 { 7.260  
 { 7.169  
 { 7.149  
 { 7.125  
 { 7.105  
 { 6.998  
 { 6.985  
 { 6.967  
 { 3.523  
 { 3.489  
 { 3.410  
 { 3.366  
 { 3.125  
 { 3.091  
 { 2.860  
 { 2.817  
 { 2.389  
 { 2.363  
 { 2.276  
 { 1.754



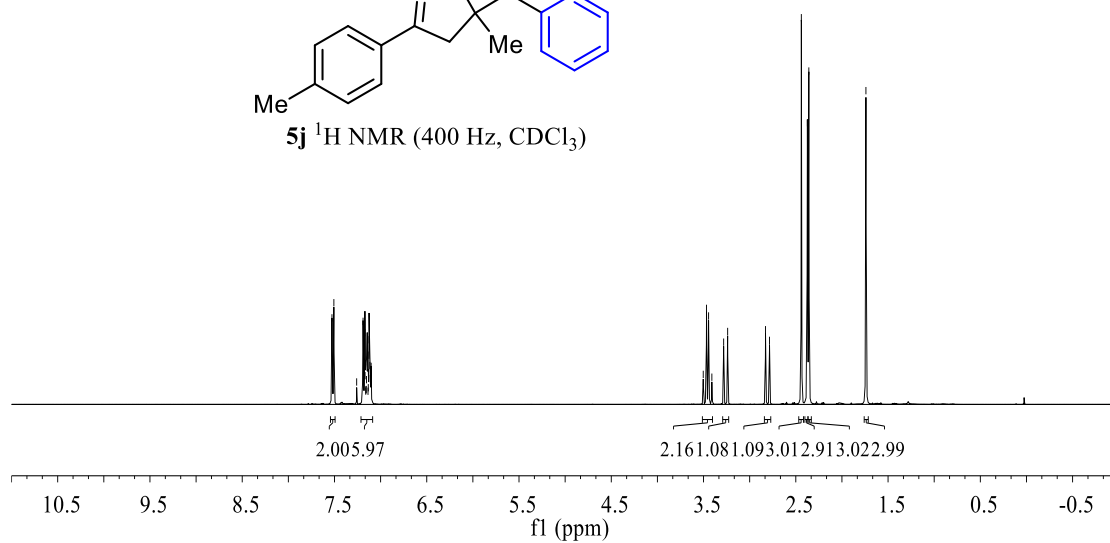
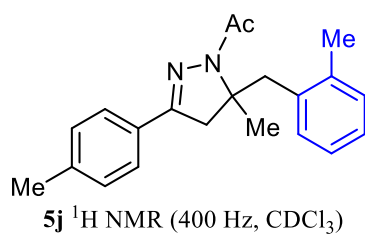
**5i**  $^1\text{H}$  NMR (400 Hz,  $\text{CDCl}_3$ )

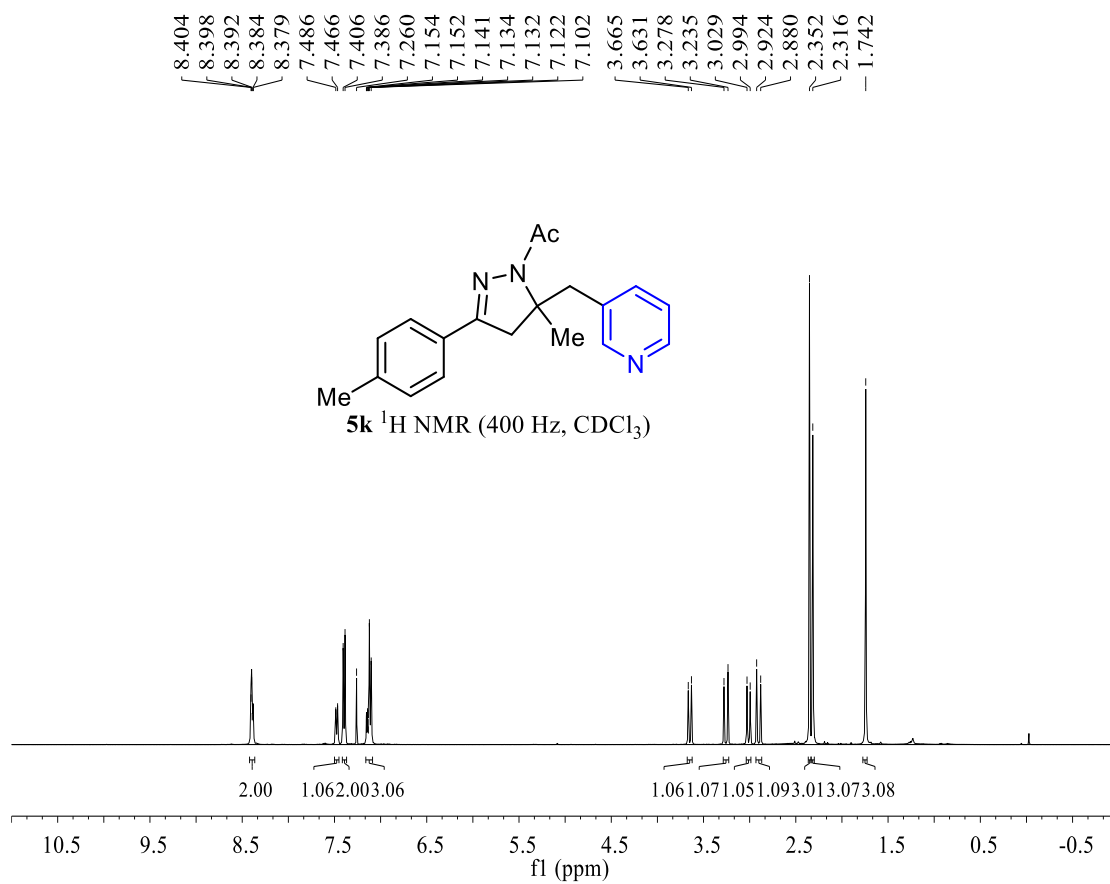
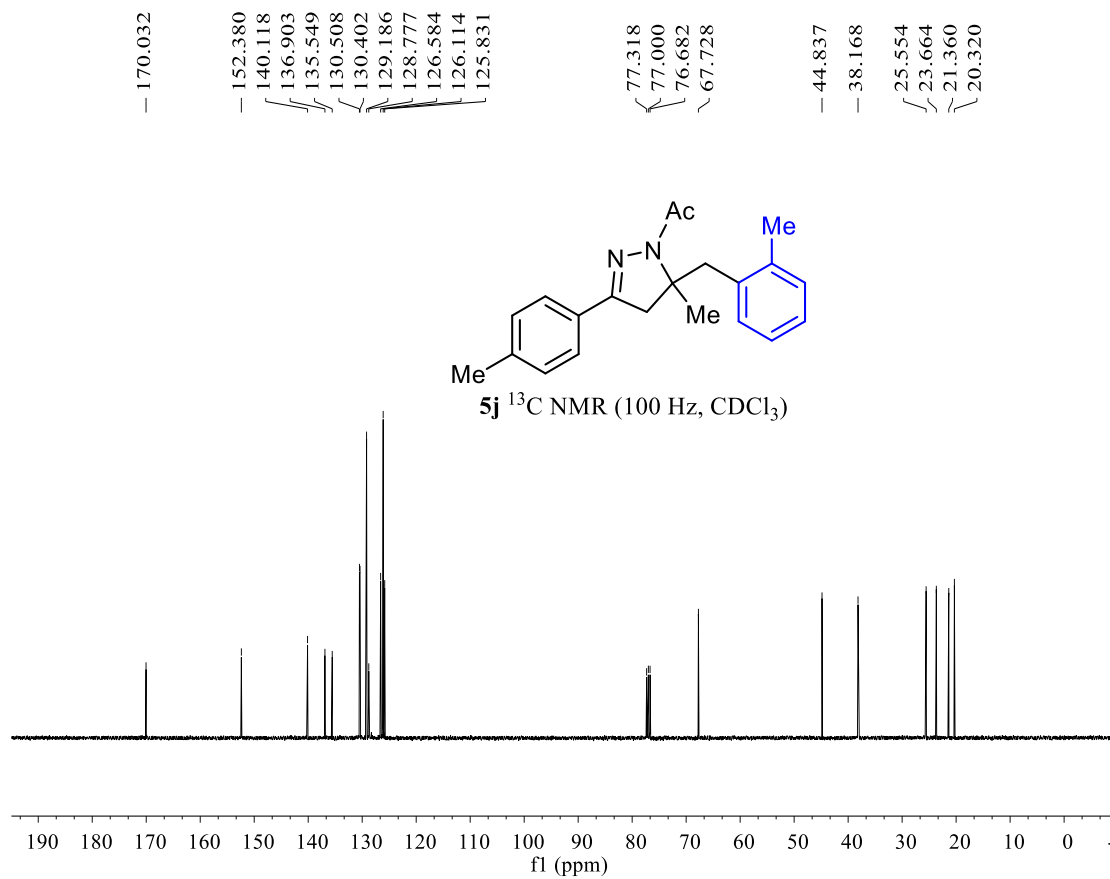


170.046  
 152.234  
 140.018  
 137.645  
 136.858  
 131.001  
 129.138  
 128.873  
 128.022  
 127.286  
 127.150  
 126.109  
 77.317  
 77.000  
 76.681  
 67.193  
 45.142  
 42.625  
 25.823  
 23.564  
 21.362  
 21.291

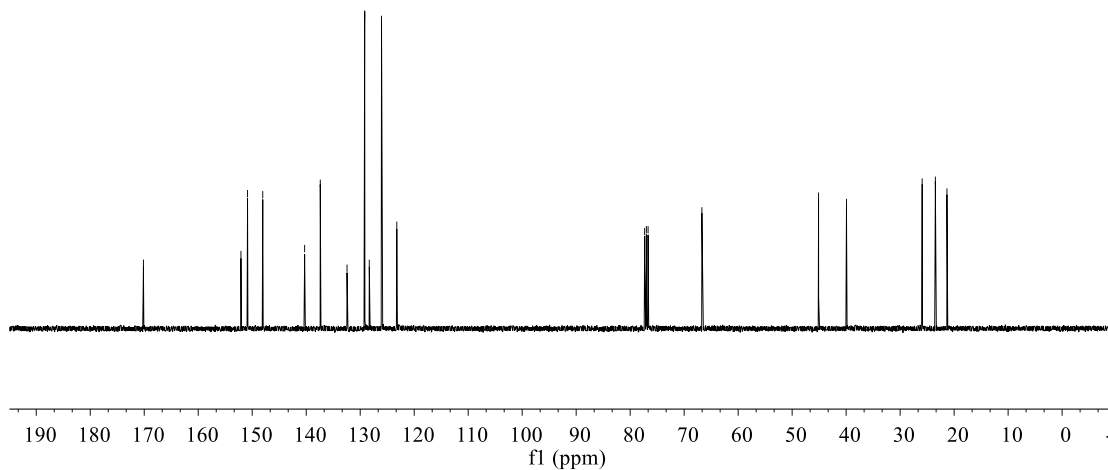
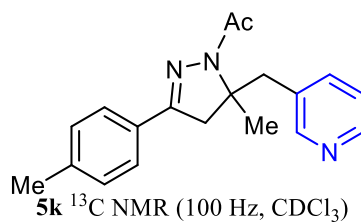


7.527  
 7.507  
 7.260  
 7.190  
 7.170  
 7.168  
 7.161  
 7.159  
 7.156  
 7.153  
 7.147  
 7.144  
 7.137  
 7.134  
 7.127  
 7.125  
 7.117  
 7.113  
 7.110  
 7.103  
 3.503  
 3.468  
 3.445  
 3.410  
 3.282  
 3.239  
 2.828  
 2.785  
 2.440  
 2.375  
 2.359  
 1.740

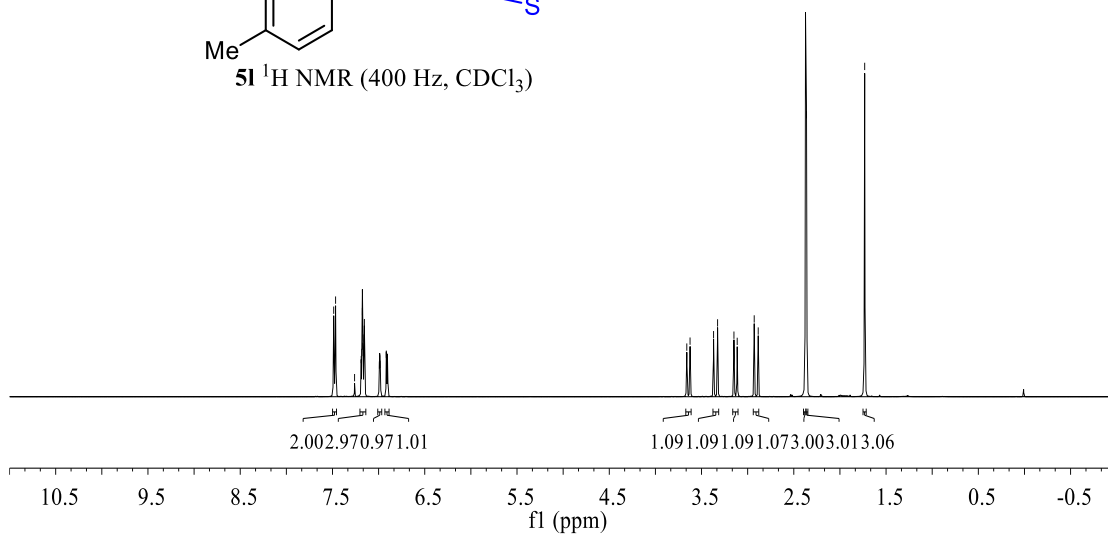
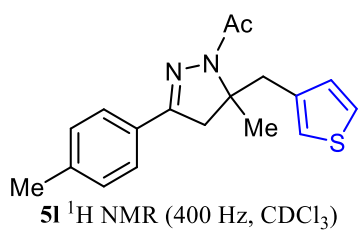




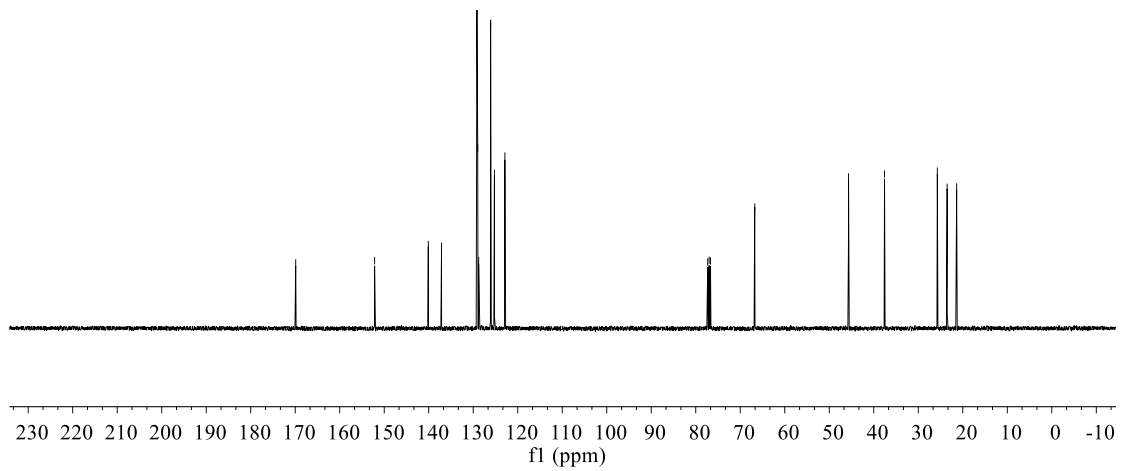
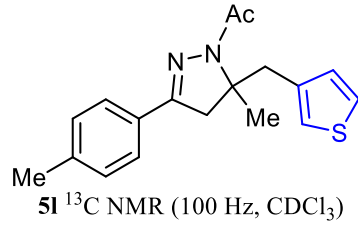
170.145  
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 150.862  
 148.042  
 140.291  
 137.393  
 132.437  
 129.166  
 128.316  
 126.050  
 123.215  
 77.318  
 77.000  
 76.681  
 66.712  
 45.105  
 39.936  
 25.917  
 23.475  
 21.328



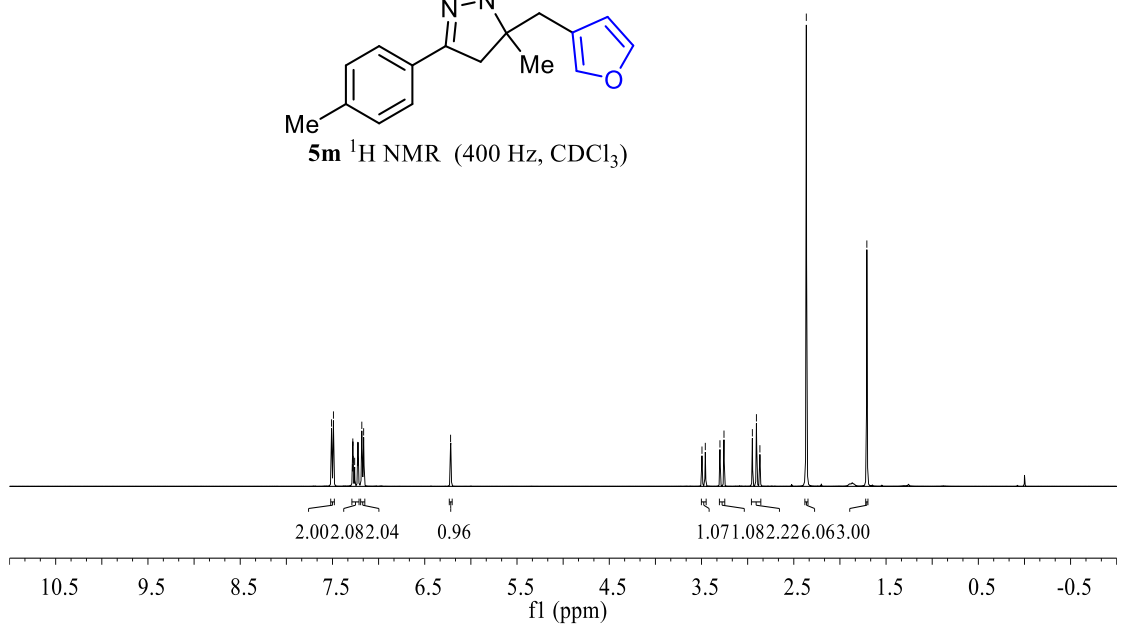
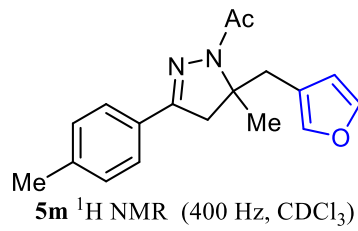
7.487  
 7.466  
 7.260  
 7.189  
 7.181  
 7.176  
 7.174  
 7.169  
 7.154  
 6.992  
 6.984  
 6.917  
 6.905  
 3.660  
 3.624  
 3.369  
 3.326  
 3.149  
 3.114  
 2.929  
 2.886  
 2.373  
 2.362  
 1.732

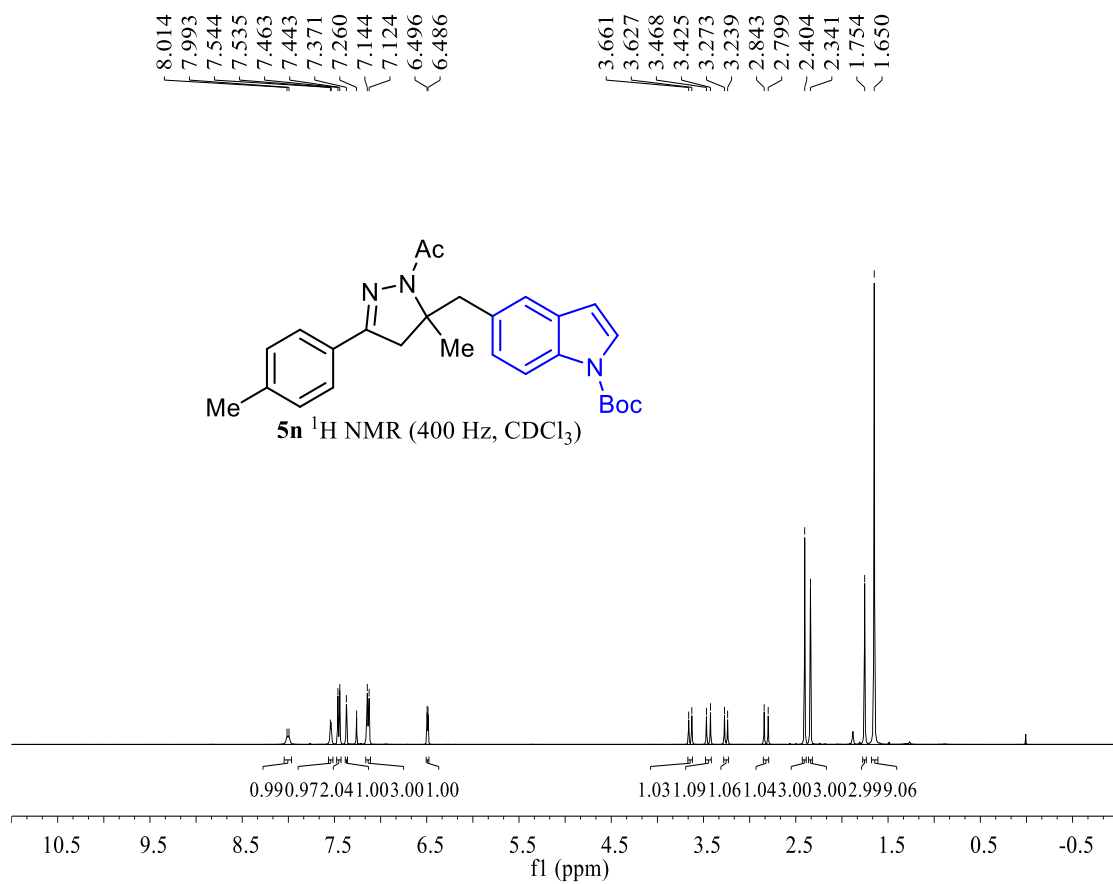
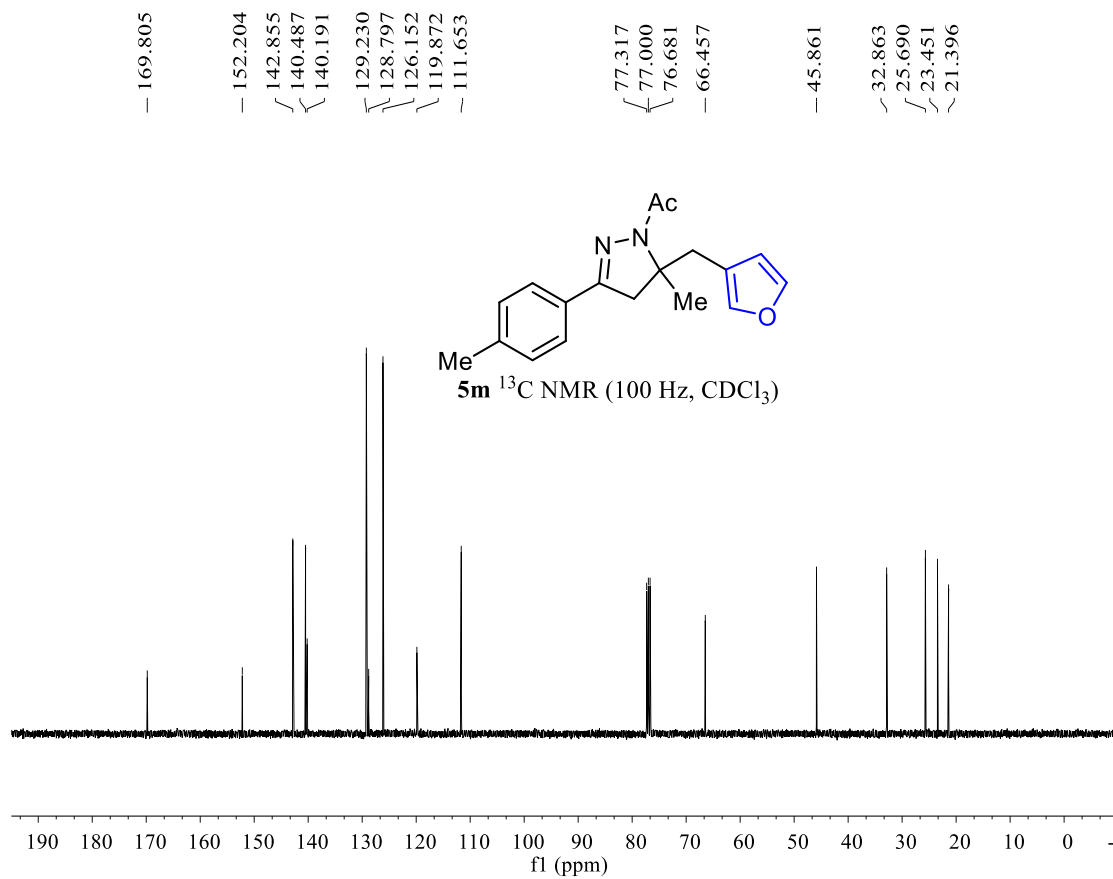


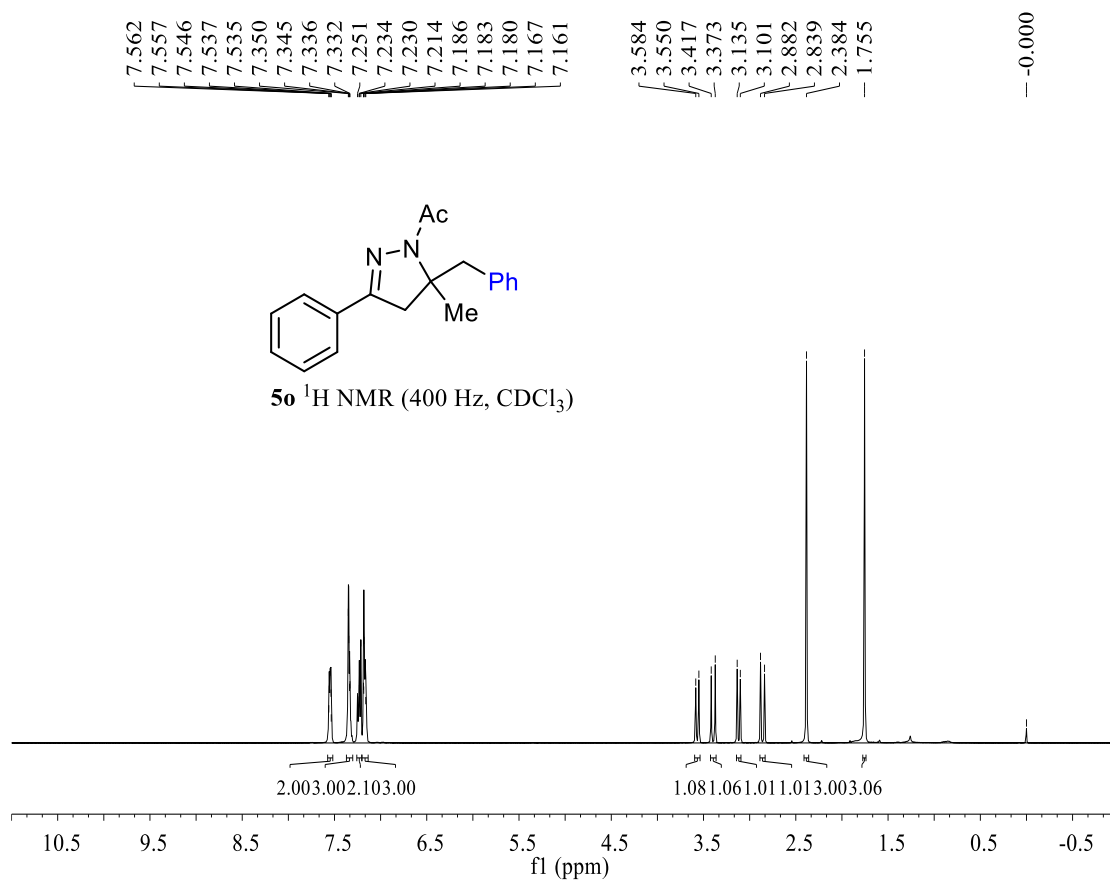
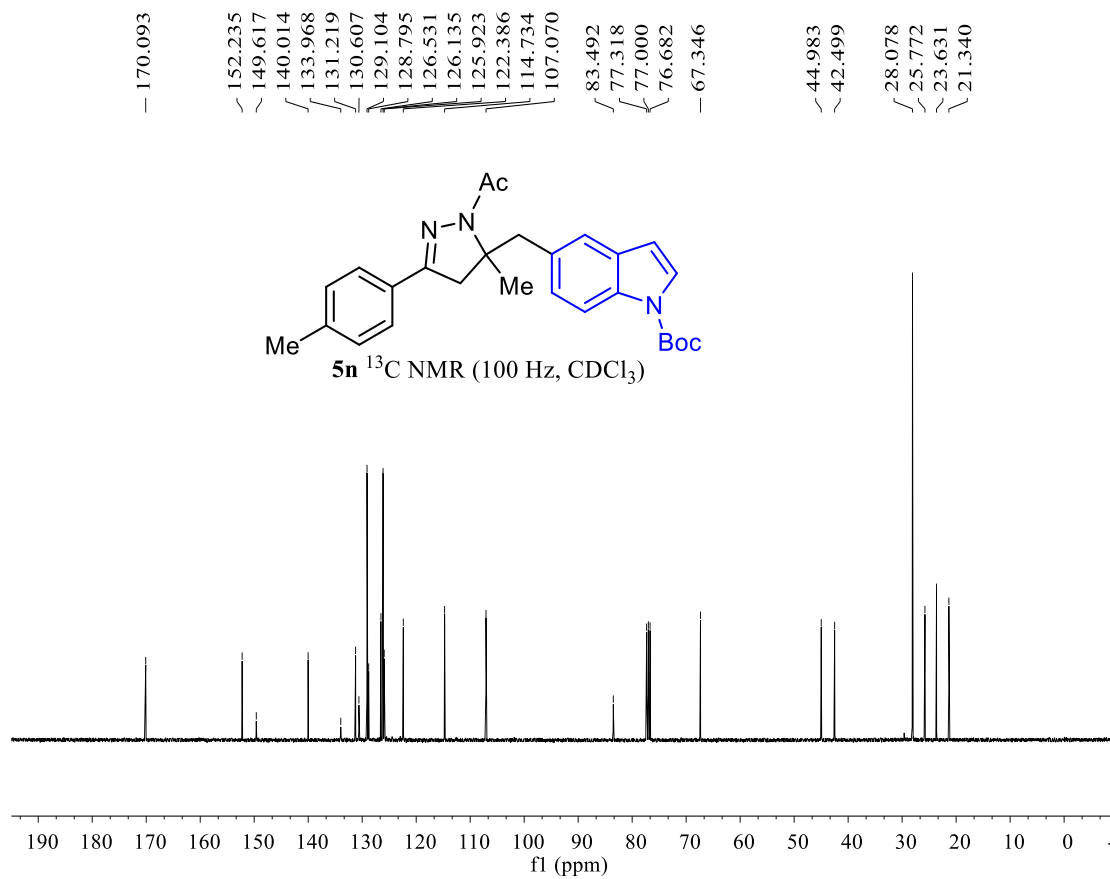
- 169.889  
 - 152.162  
 - 140.096  
 - 137.128  
 - 129.170  
 - 128.992  
 - 128.772  
 - 126.094  
 - 125.241  
 - 122.890  
 - 77.317  
 - 77.000  
 - 76.681  
 - 66.749  
 - 45.664  
 - 37.582  
 - 25.716  
 - 23.505  
 - 21.373

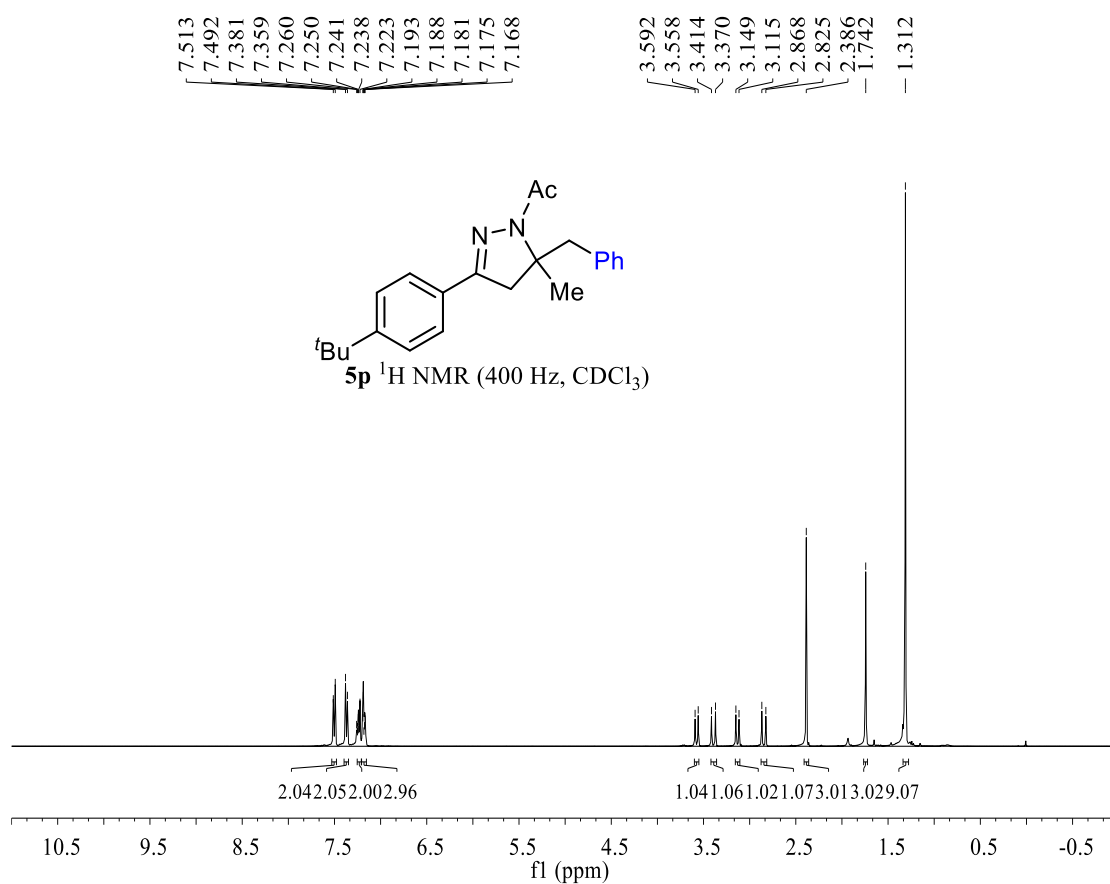
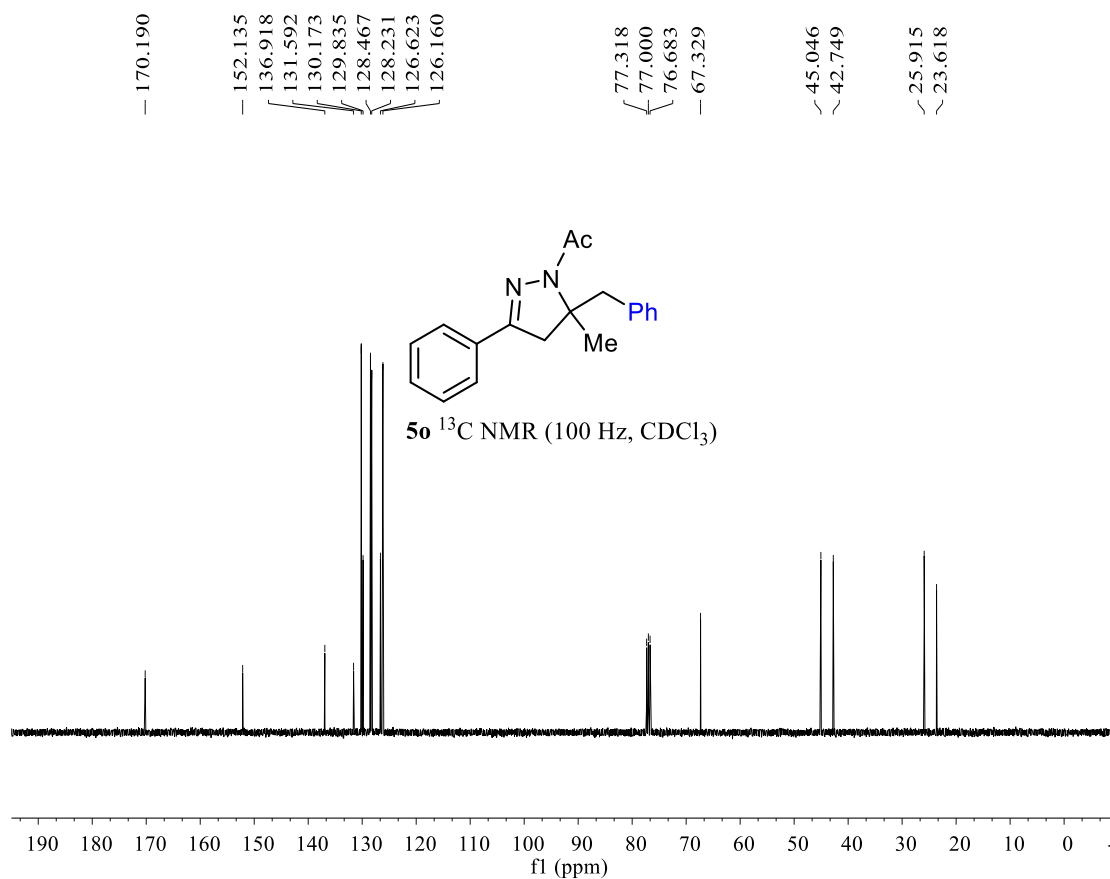


7.510  
 7.490  
 7.284  
 7.279  
 7.275  
 7.260  
 7.227  
 7.225  
 7.223  
 7.220  
 7.182  
 7.162  
 - 6.220  
 3.495  
 3.459  
 3.300  
 3.257  
 2.949  
 2.905  
 2.867  
 2.364  
 - 1.708

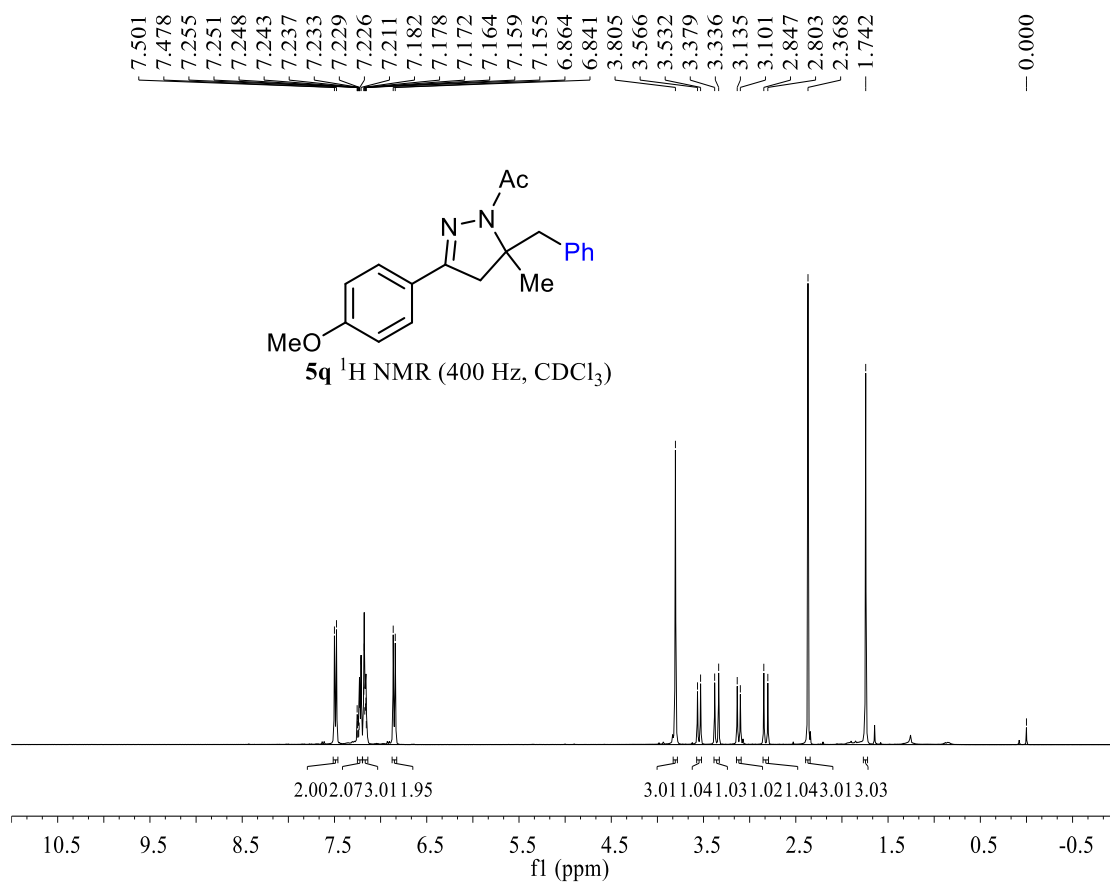
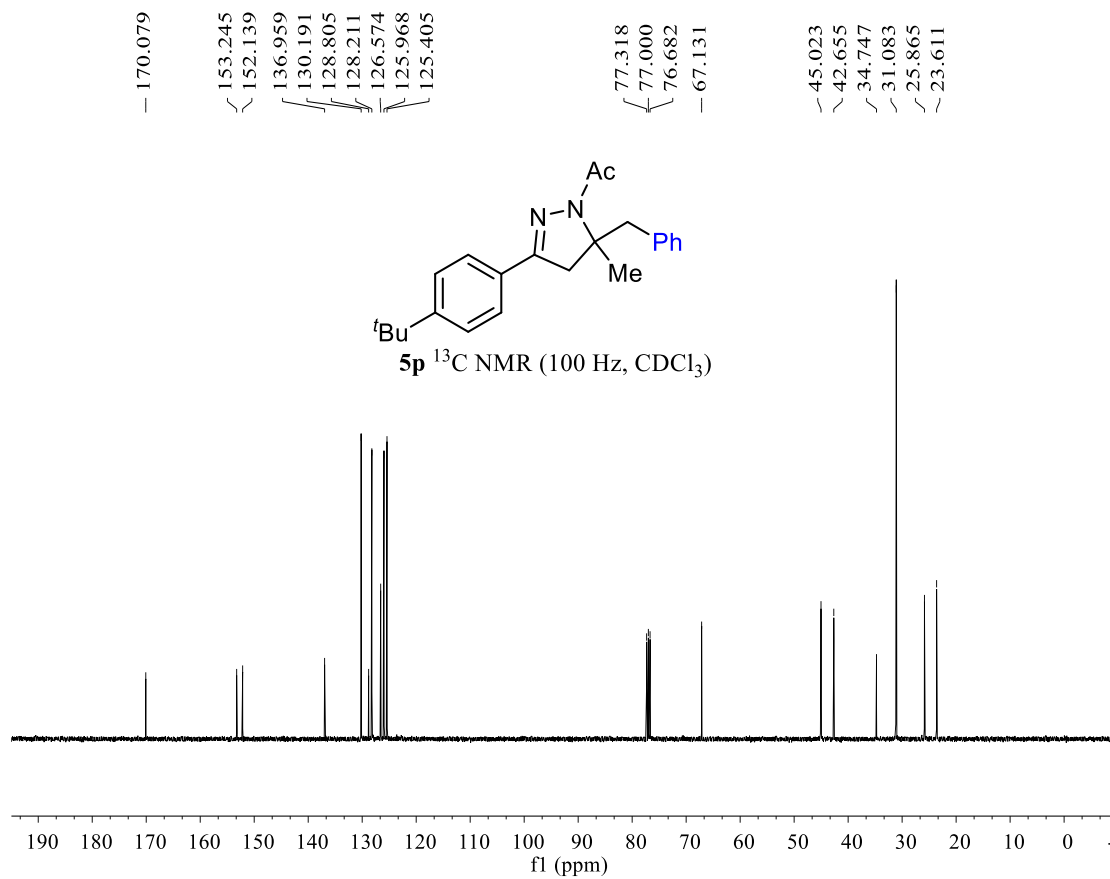


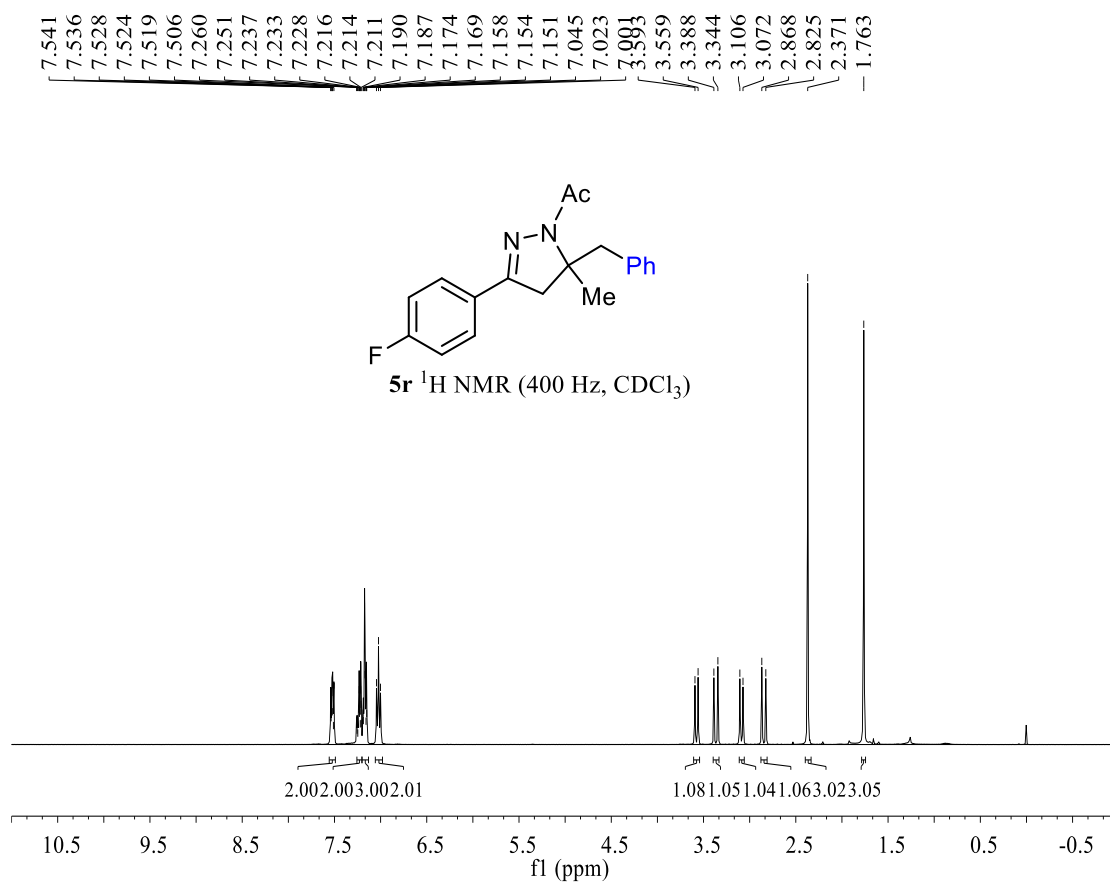
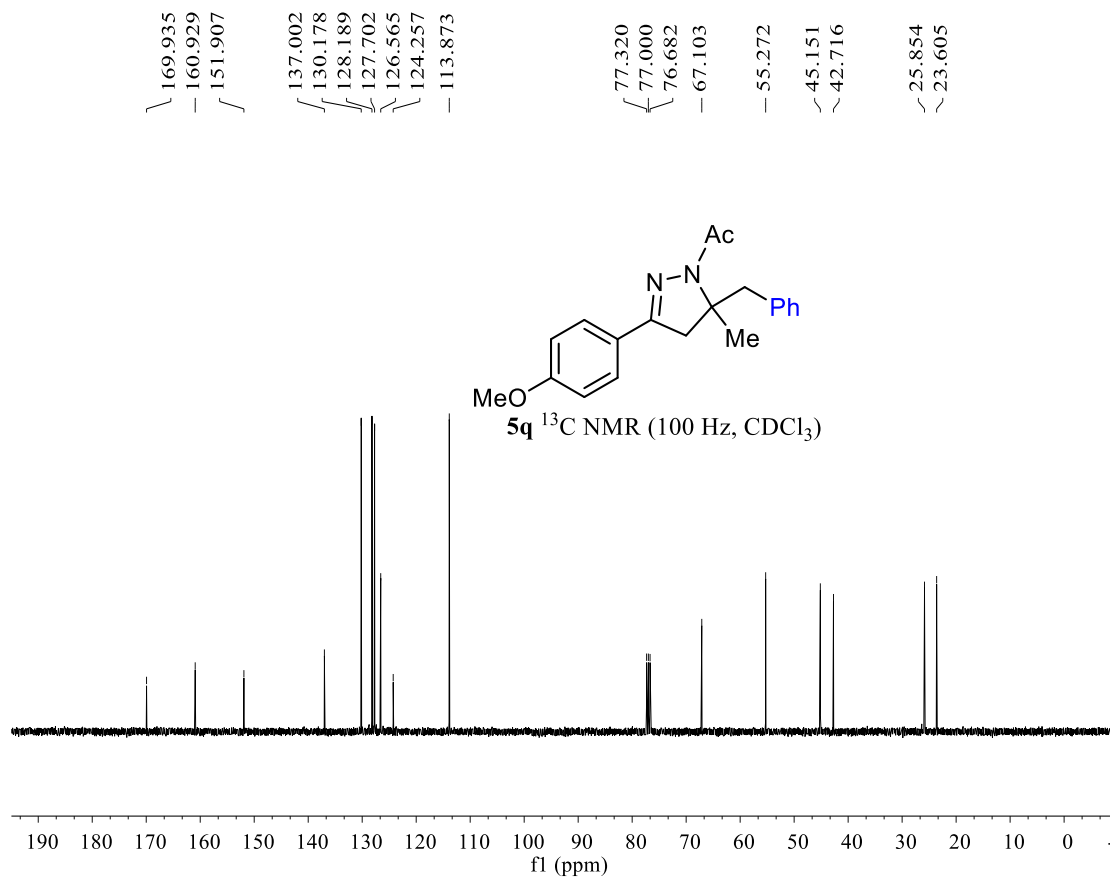












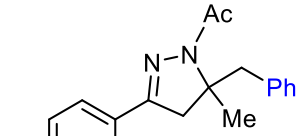
~ 170.146  
~ 164.887  
~ 162.394

~ 151.115  
136.865  
130.138  
128.248  
128.132  
128.048  
127.888  
127.855  
126.665  
115.707  
115.488

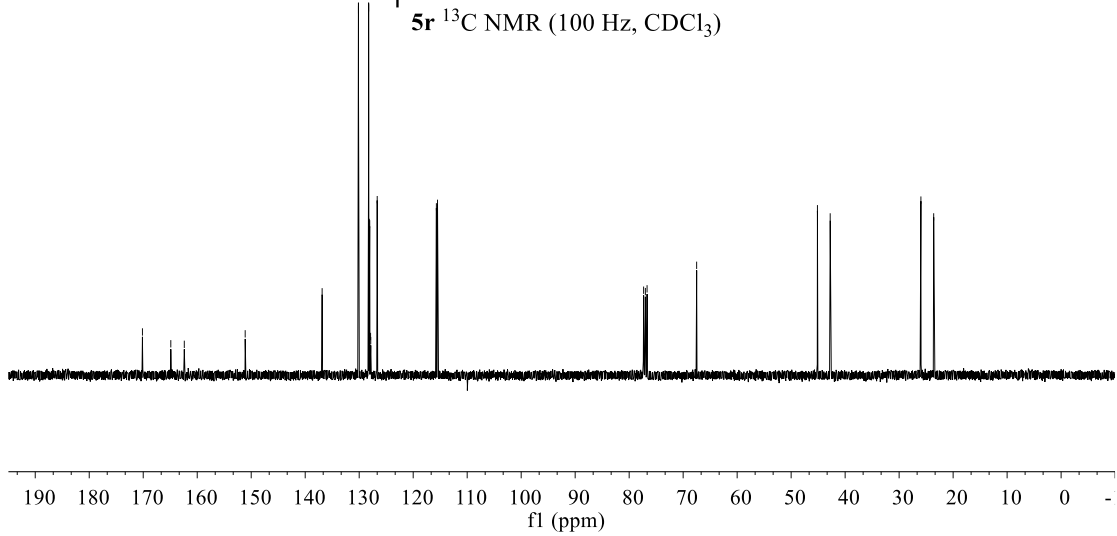
77.318  
77.000  
76.683  
- 67.497

~ 45.131  
~ 42.768

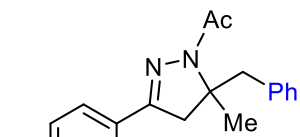
~ 25.966  
~ 23.595



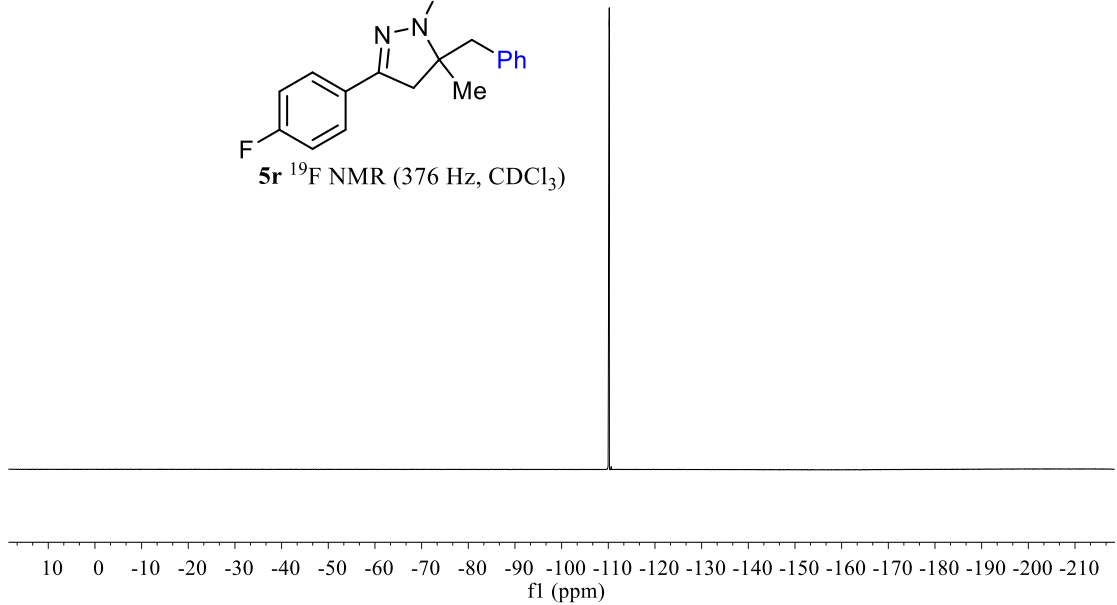
**5r** <sup>13</sup>C NMR (100 Hz, CDCl<sub>3</sub>)

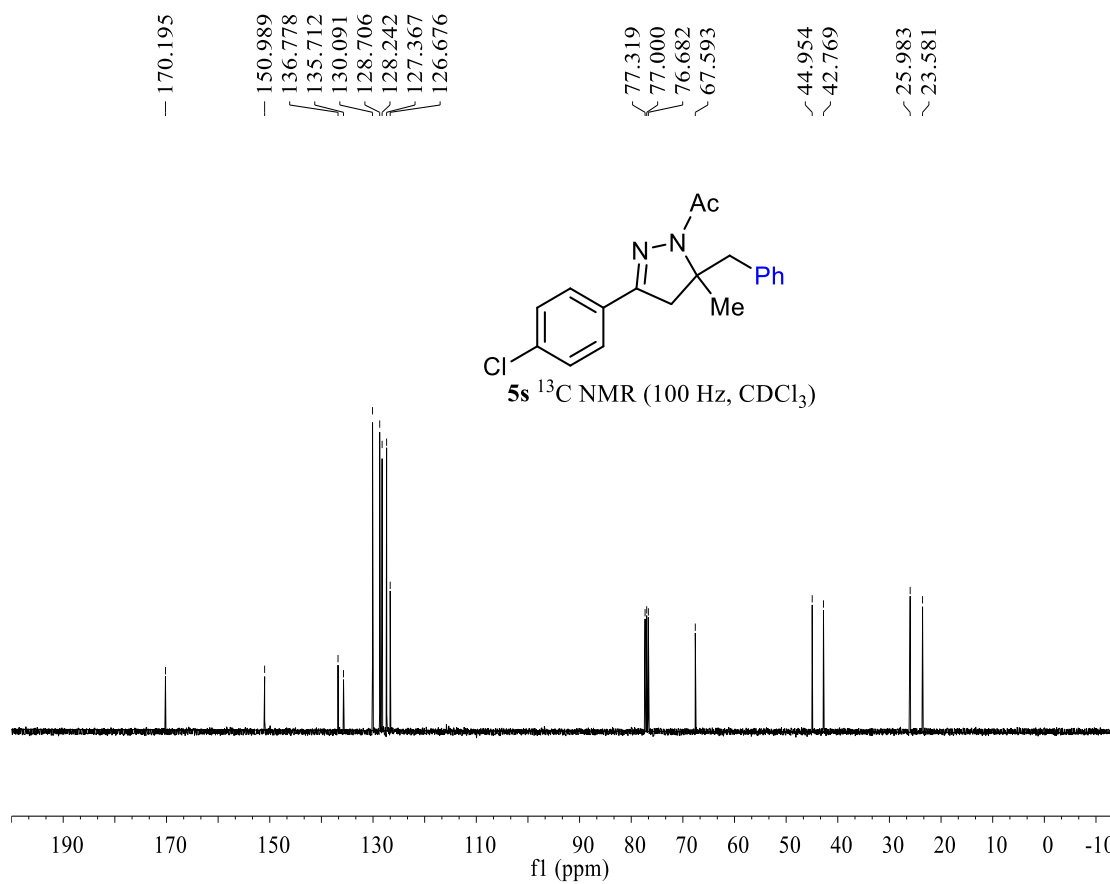
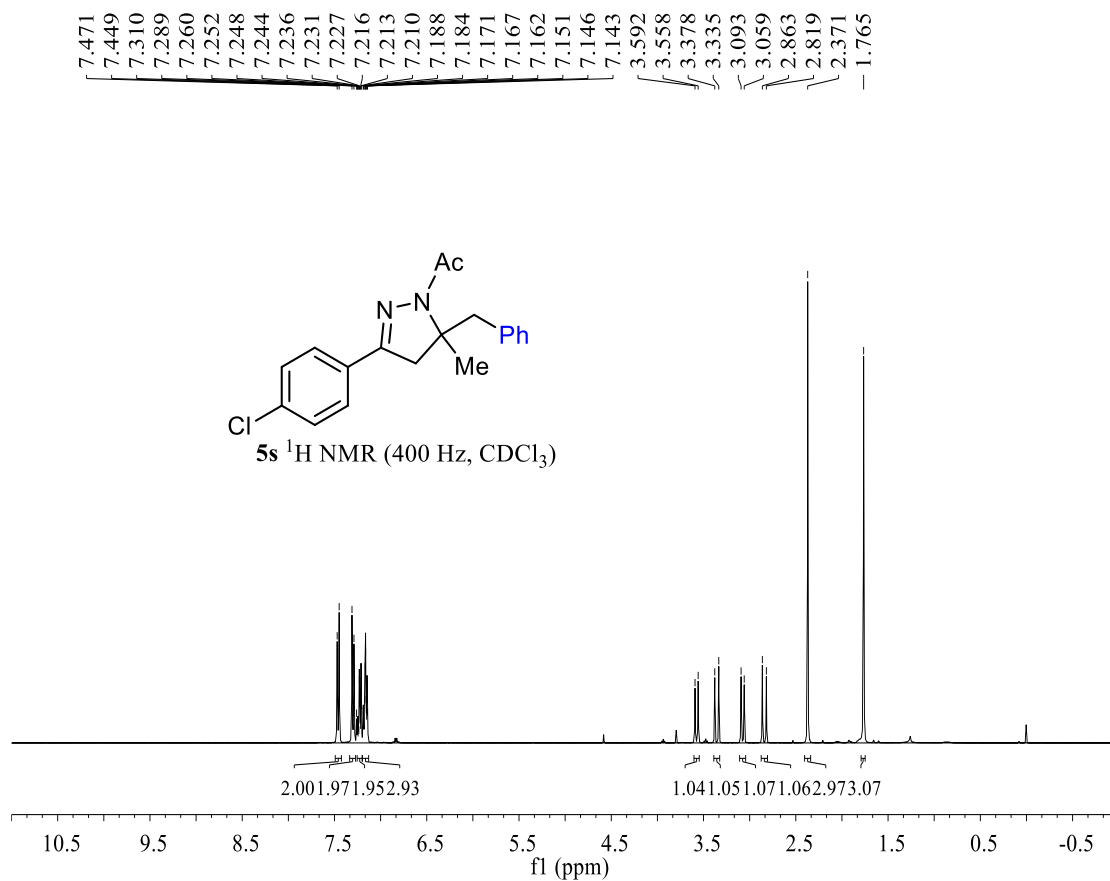


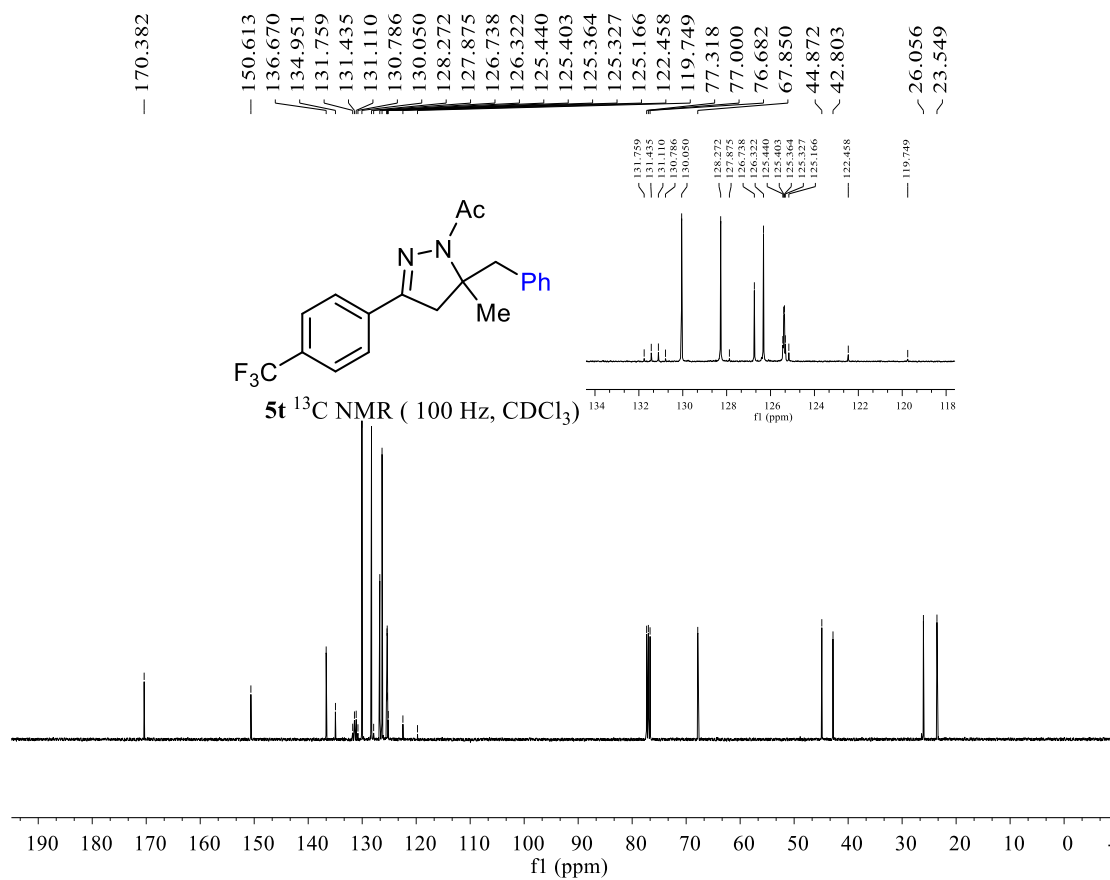
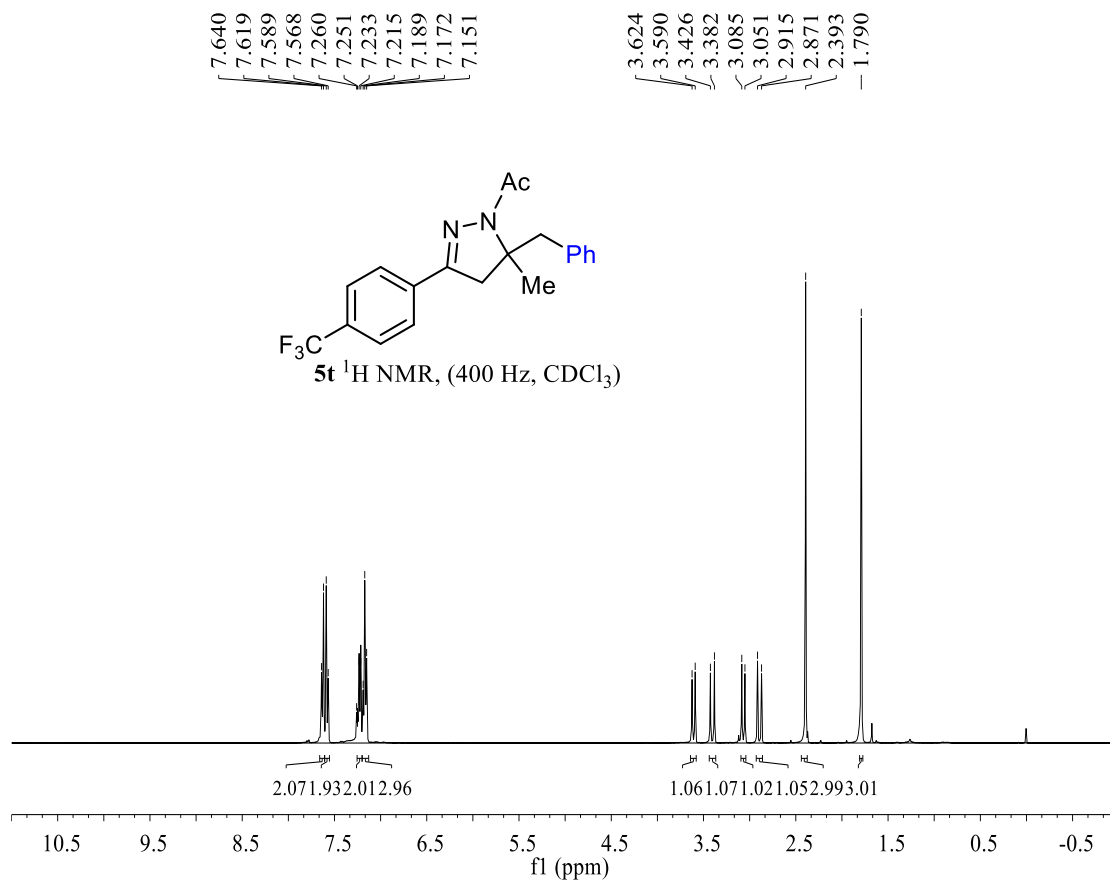
-110.205



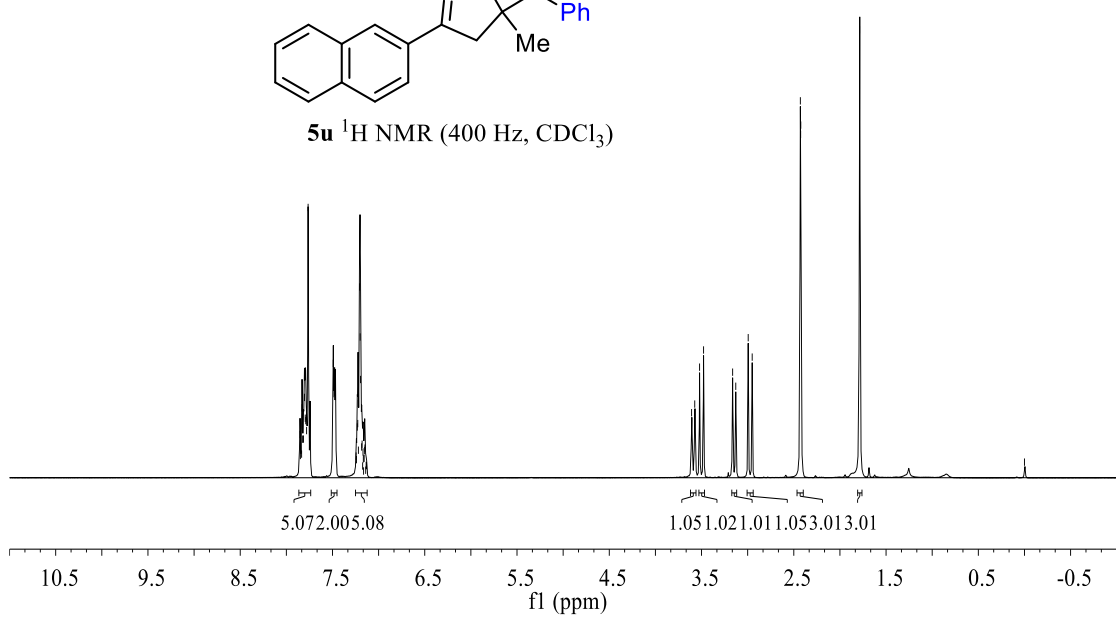
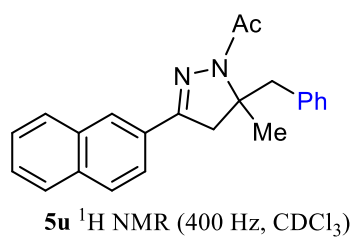
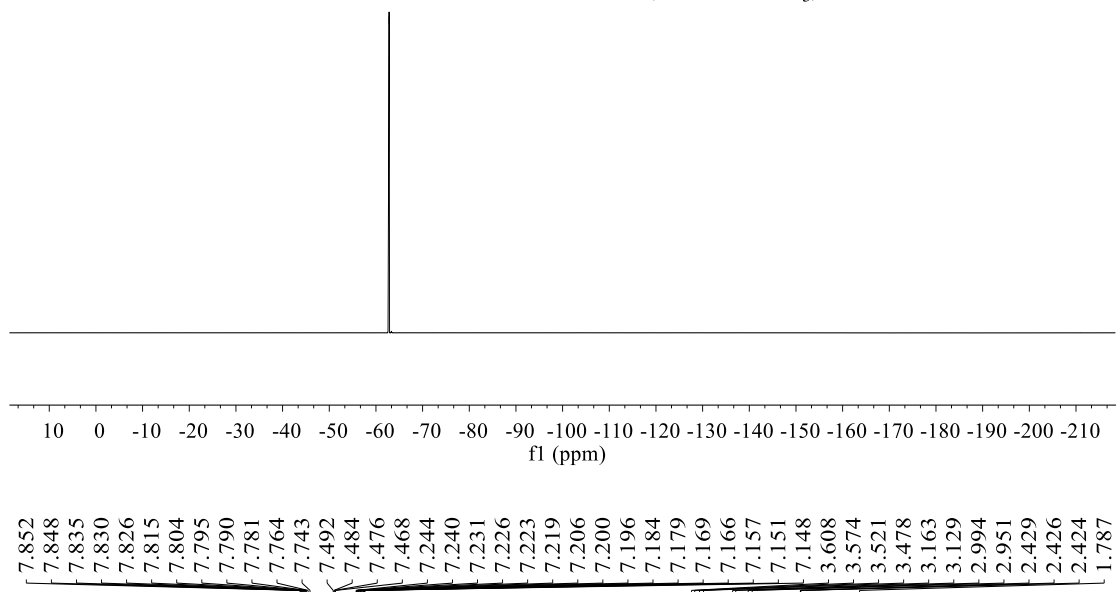
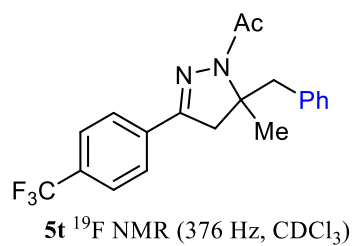
**5r** <sup>19</sup>F NMR (376 Hz, CDCl<sub>3</sub>)

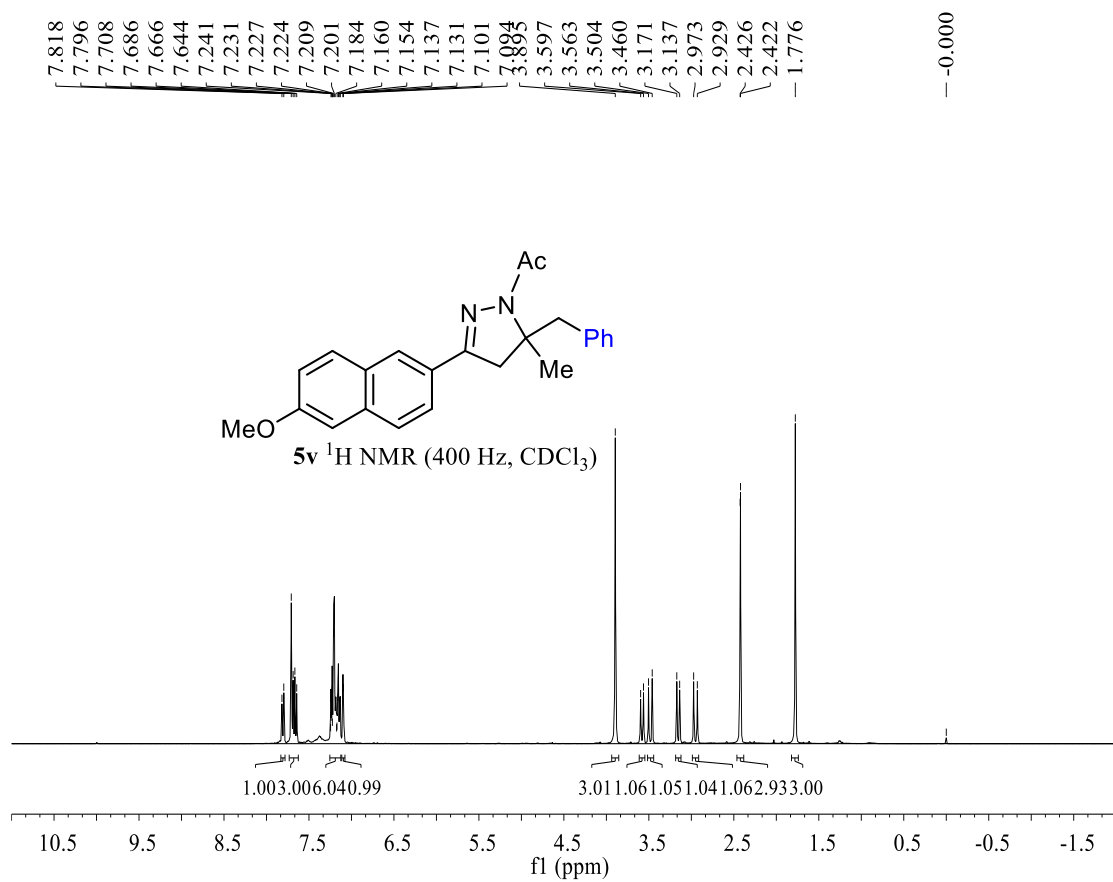
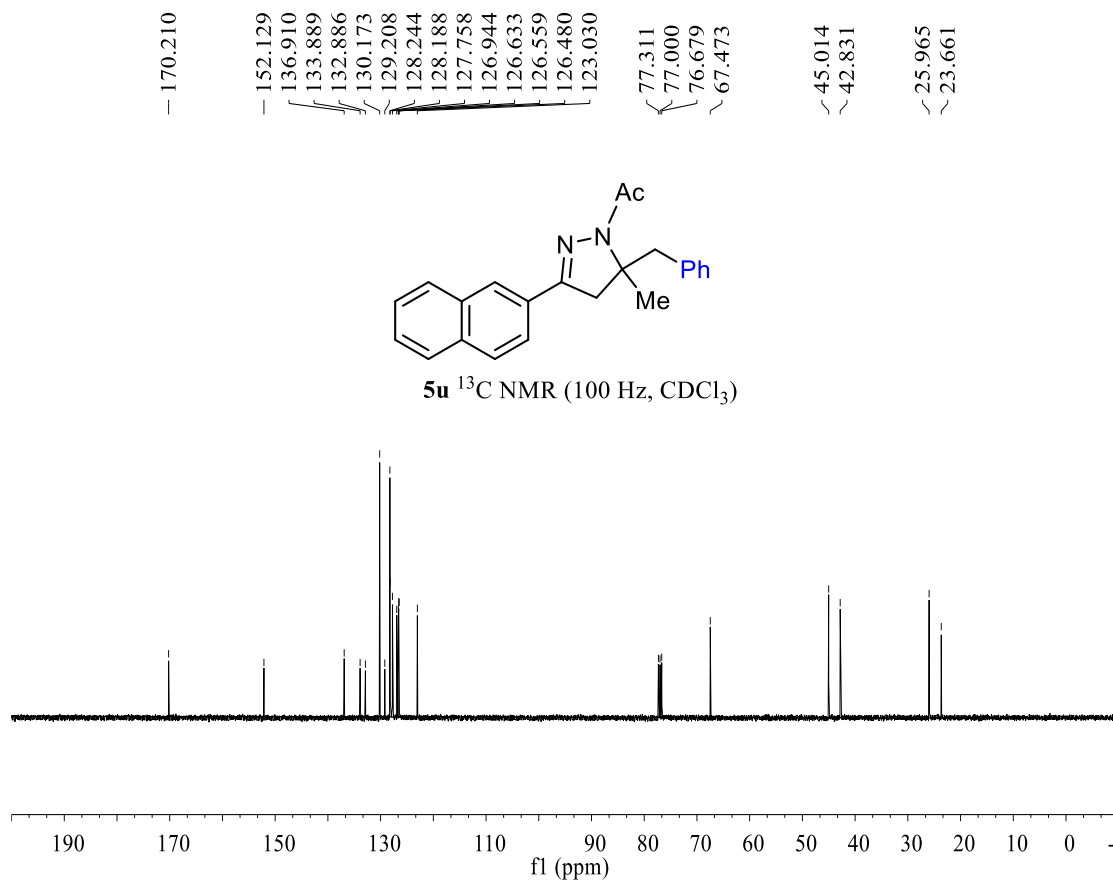


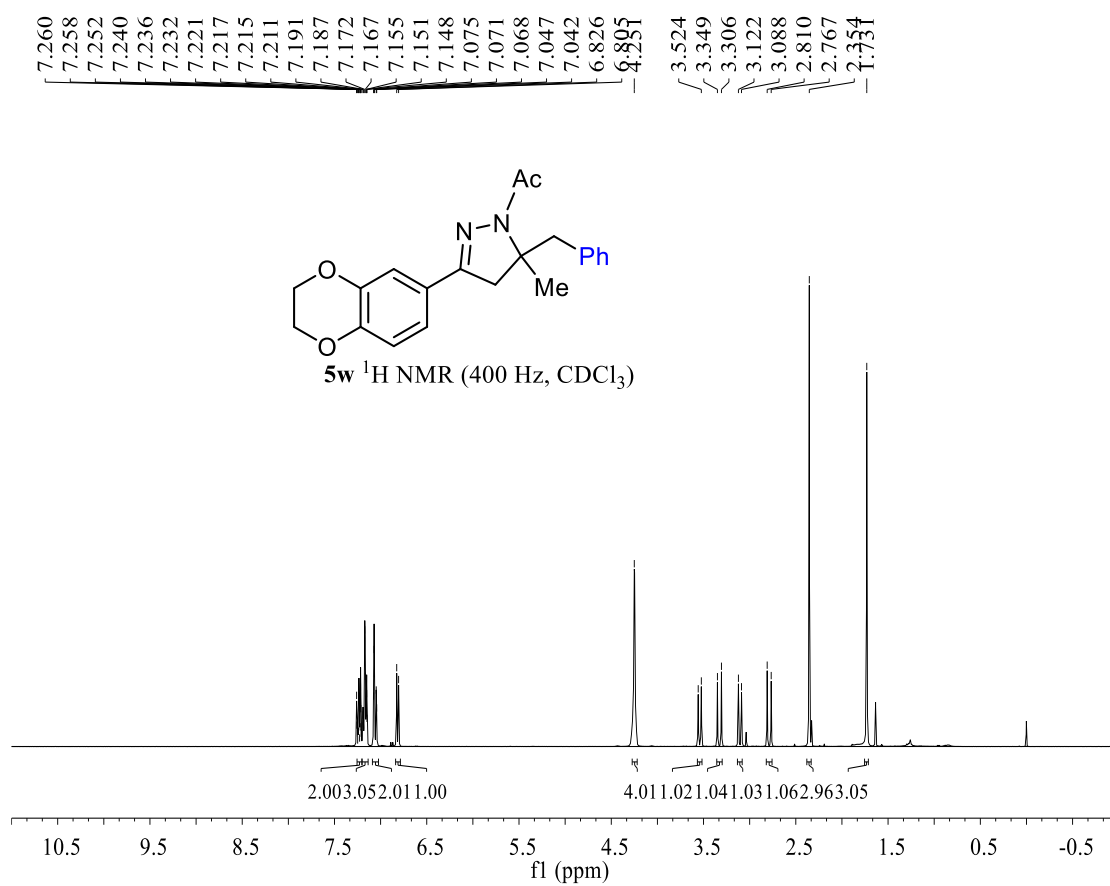
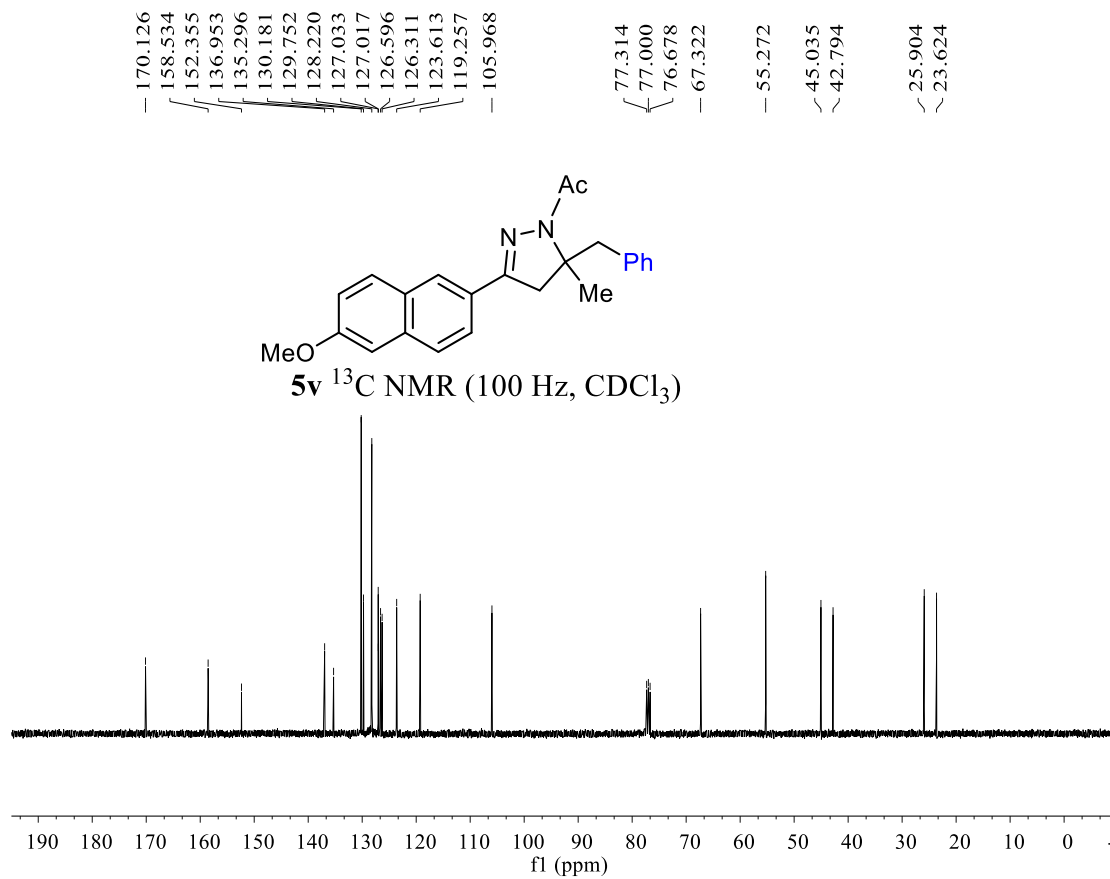




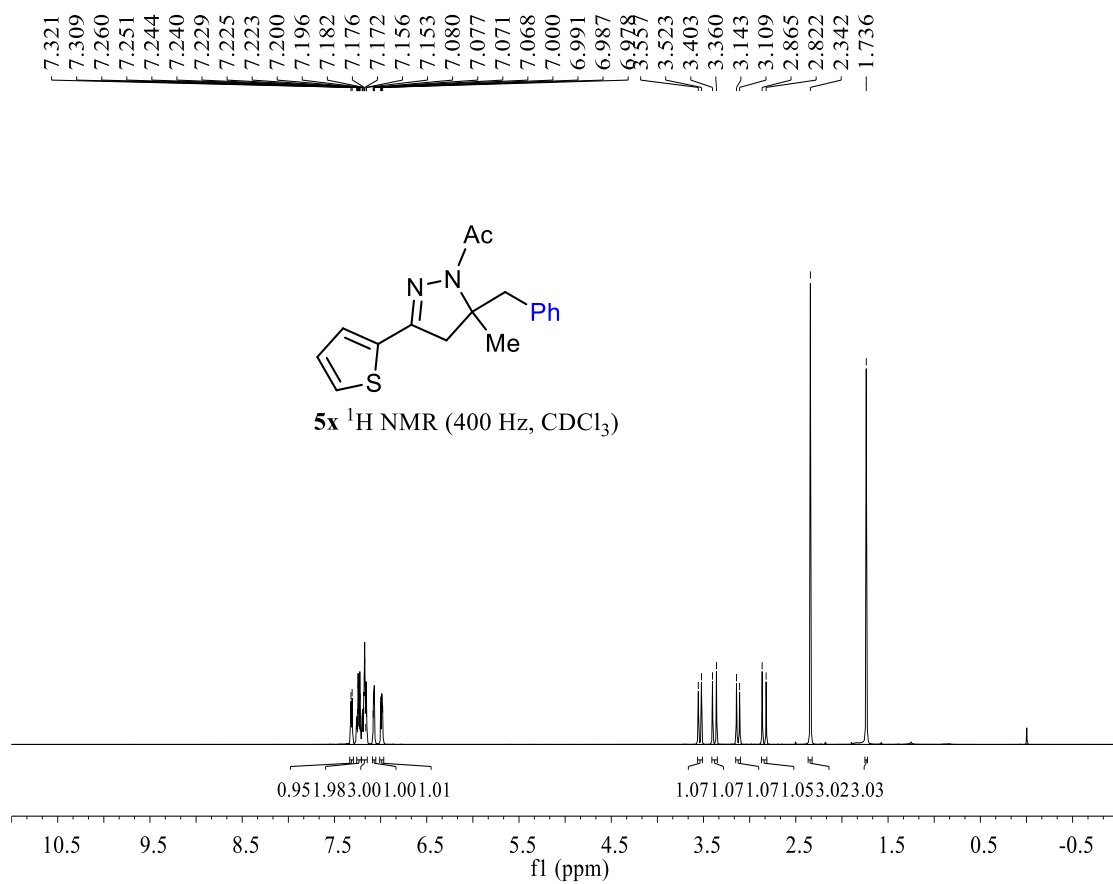
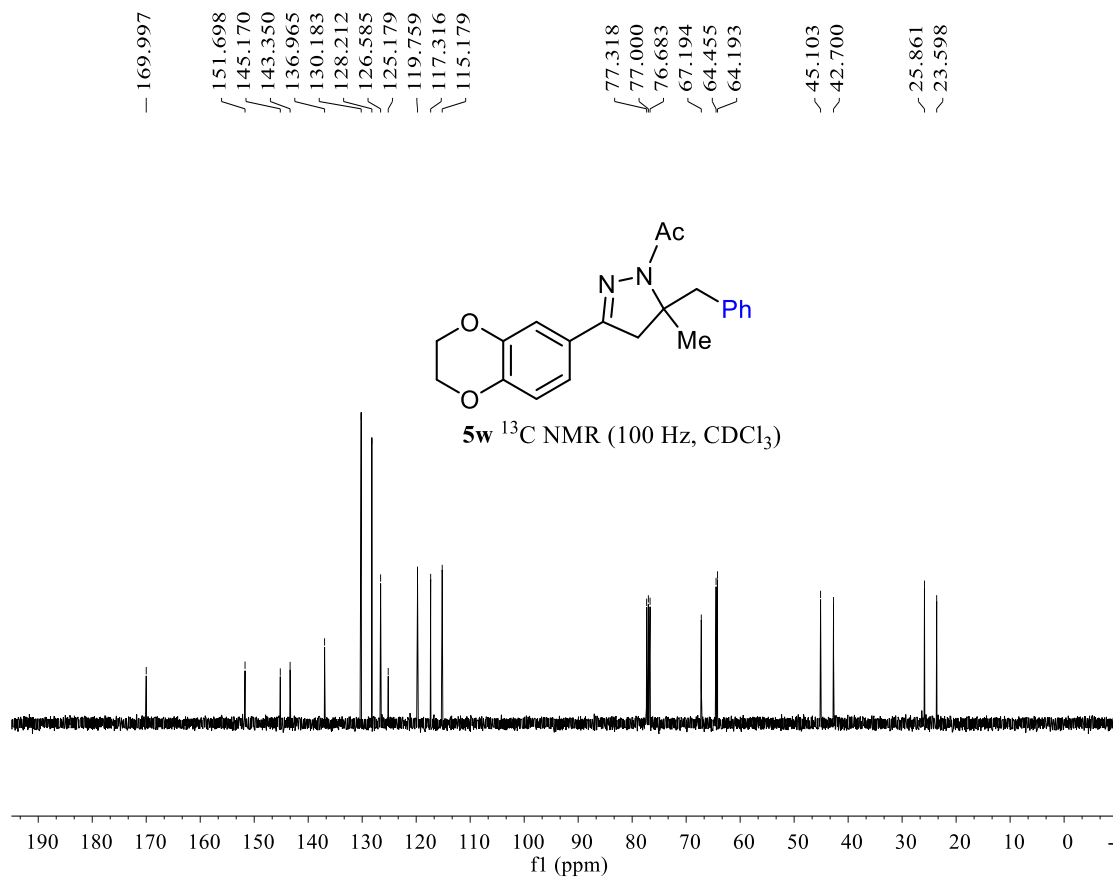
--62.822

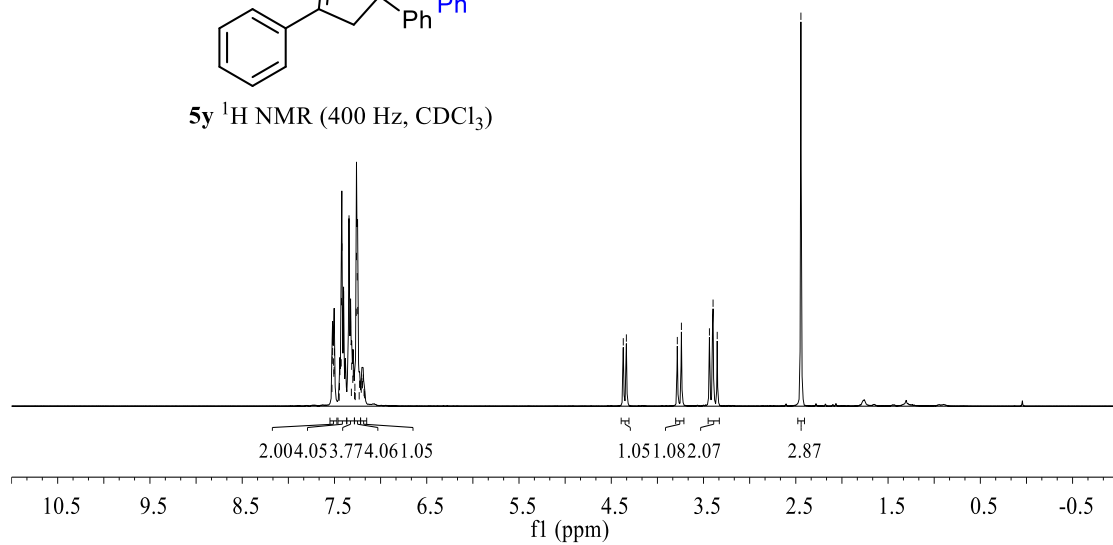
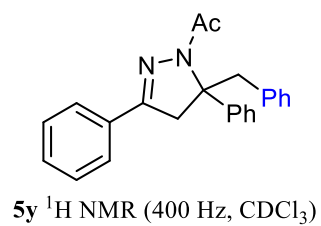
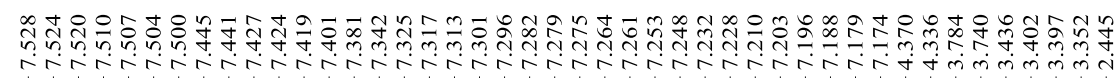
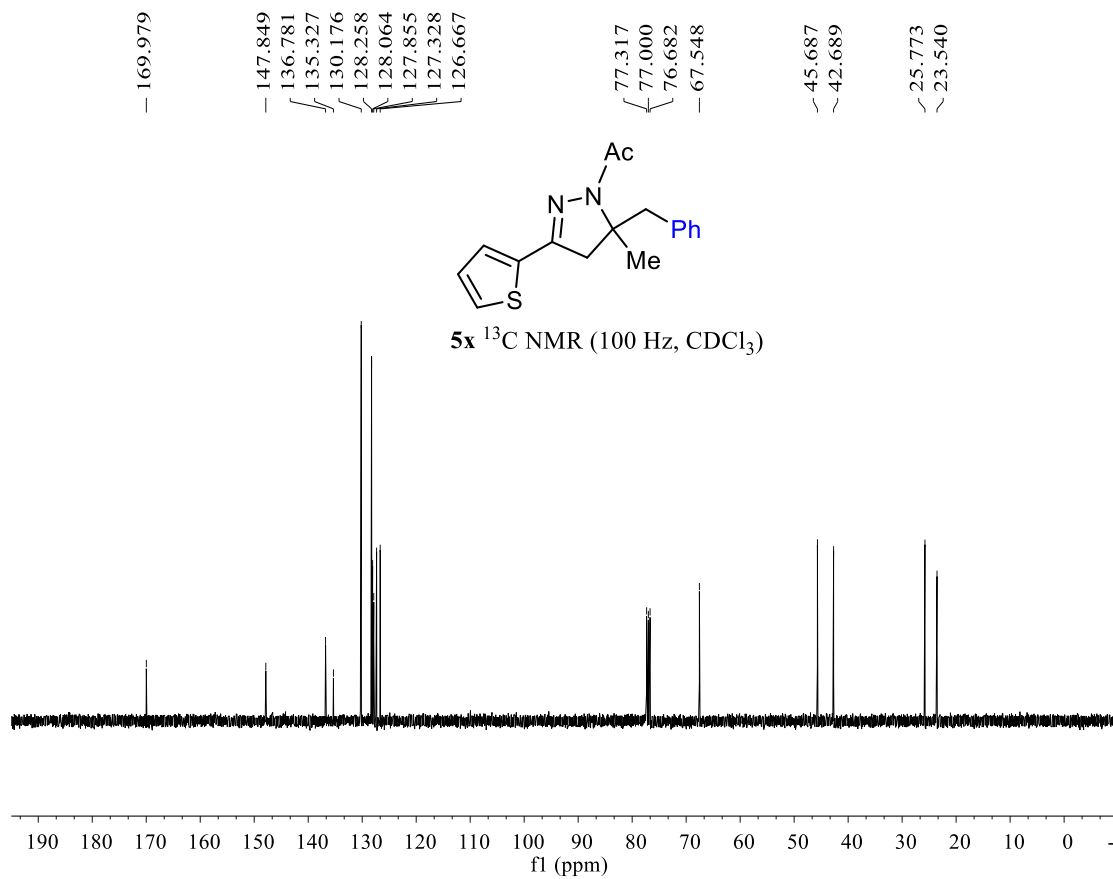












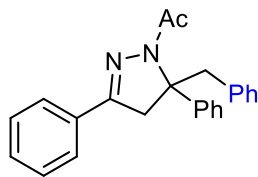
169.595  
151.707  
145.250  
136.235  
131.165  
130.308  
129.841  
128.697  
128.389  
128.249  
127.102  
126.795  
126.165  
124.670

77.316  
77.000  
76.681  
71.210

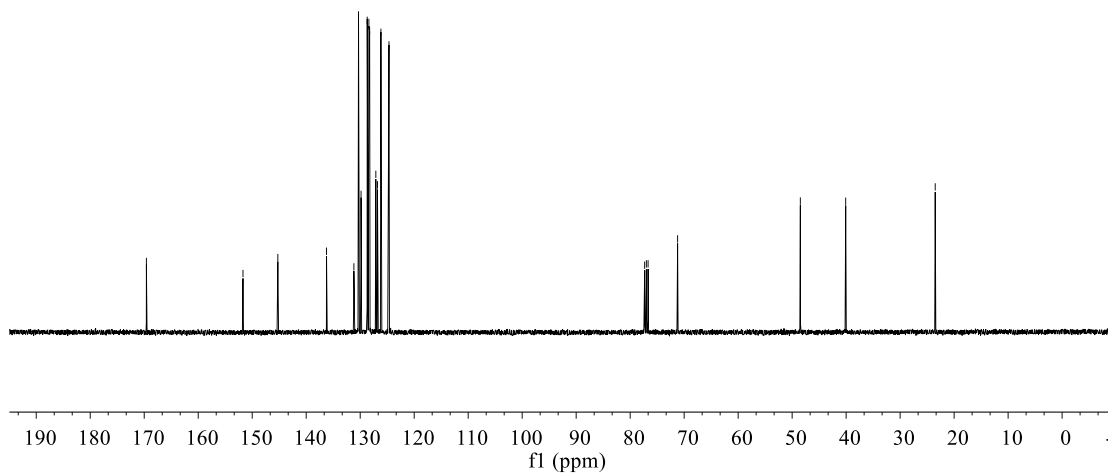
48.483

40.079

23.501



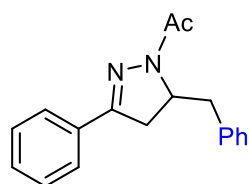
**5y**  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ )



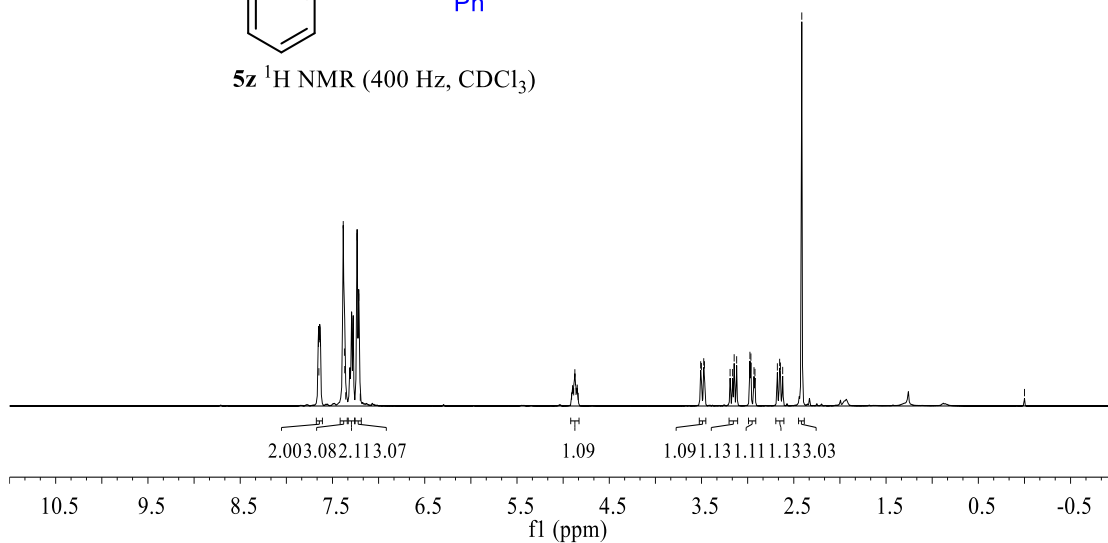
7.652  
7.647  
7.638  
7.630  
7.383  
7.371  
7.367  
7.356  
7.313  
7.293  
7.275  
7.233  
7.215  
7.199

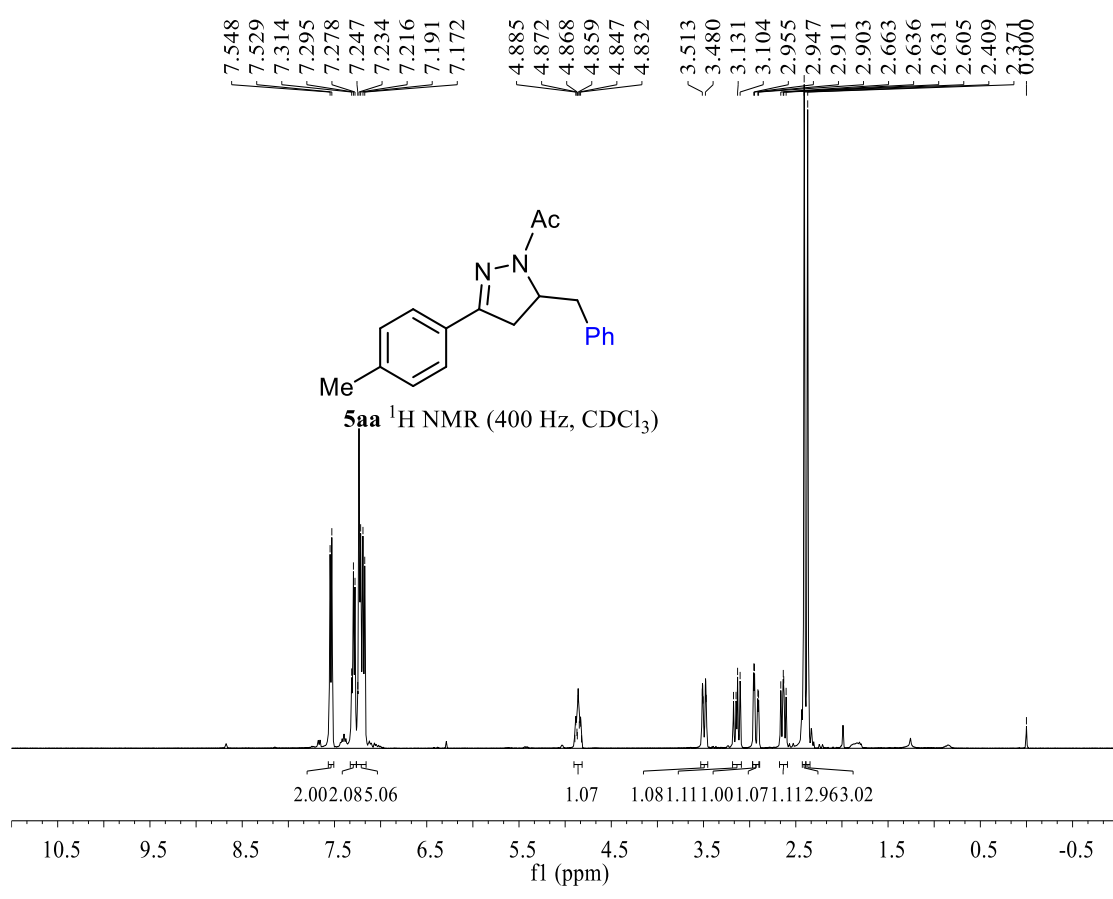
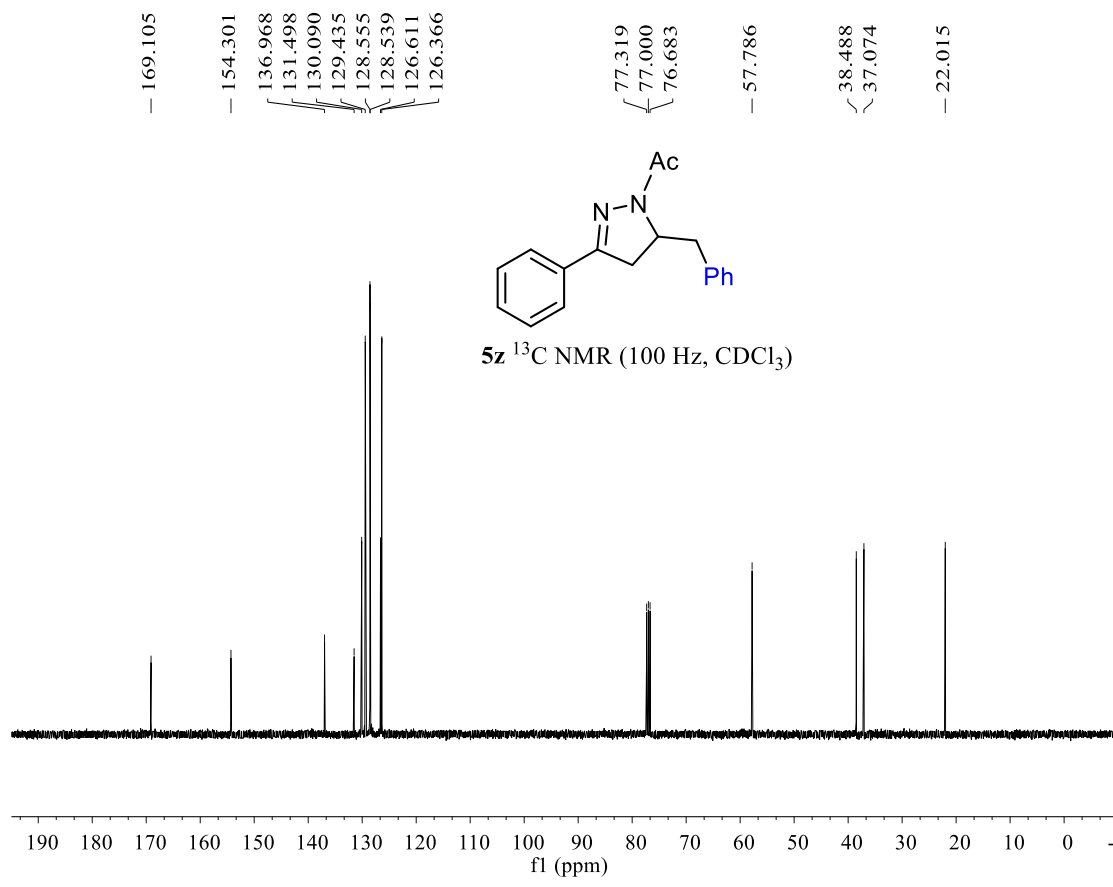
4.908  
4.899  
4.885  
4.873  
4.860  
4.847

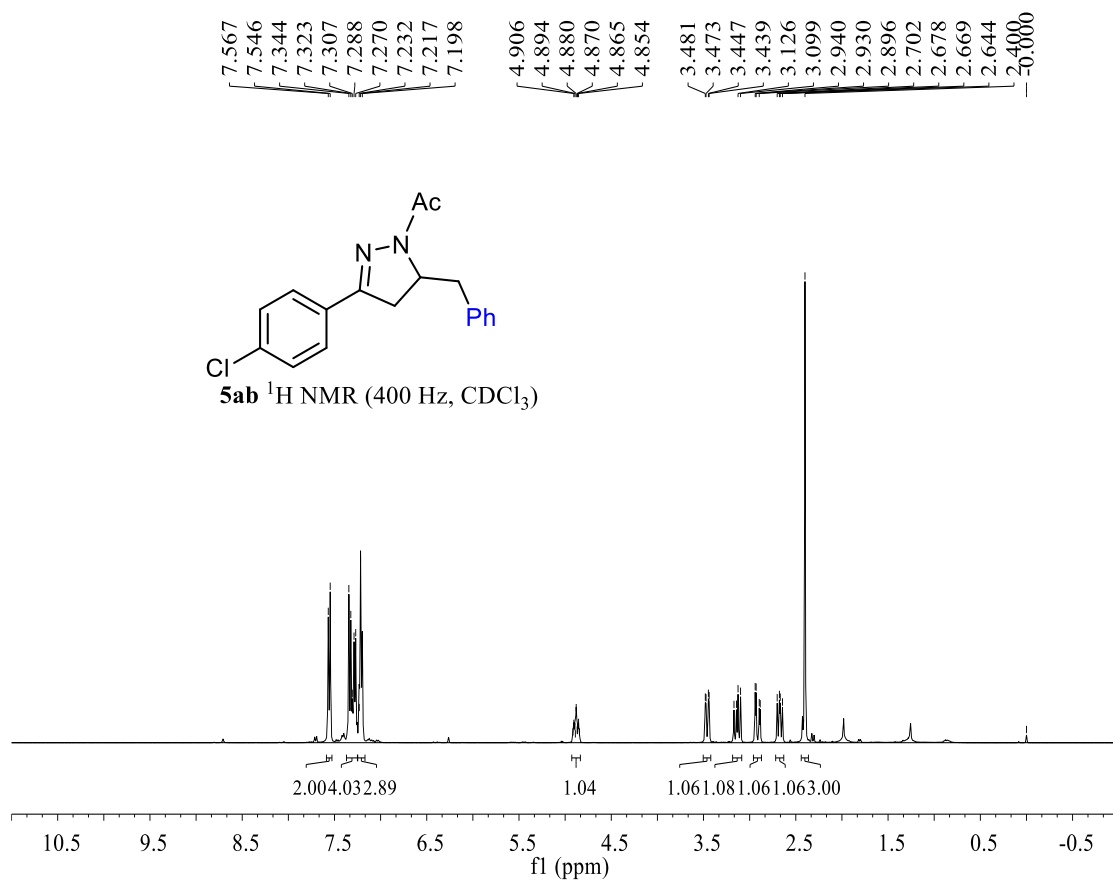
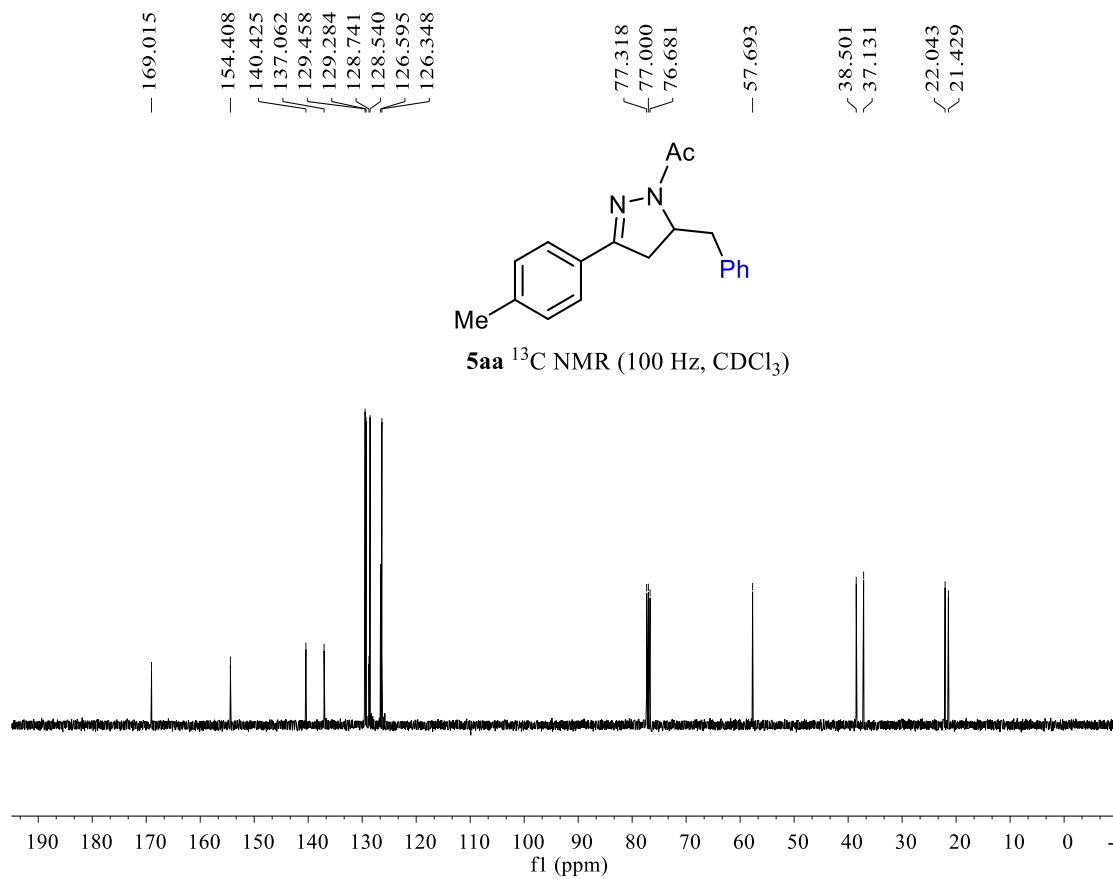
3.509  
3.502  
3.476  
3.468  
3.146  
3.119  
2.975  
2.965  
2.931  
2.678  
2.653  
2.645  
2.620  
2.413  
-0.000

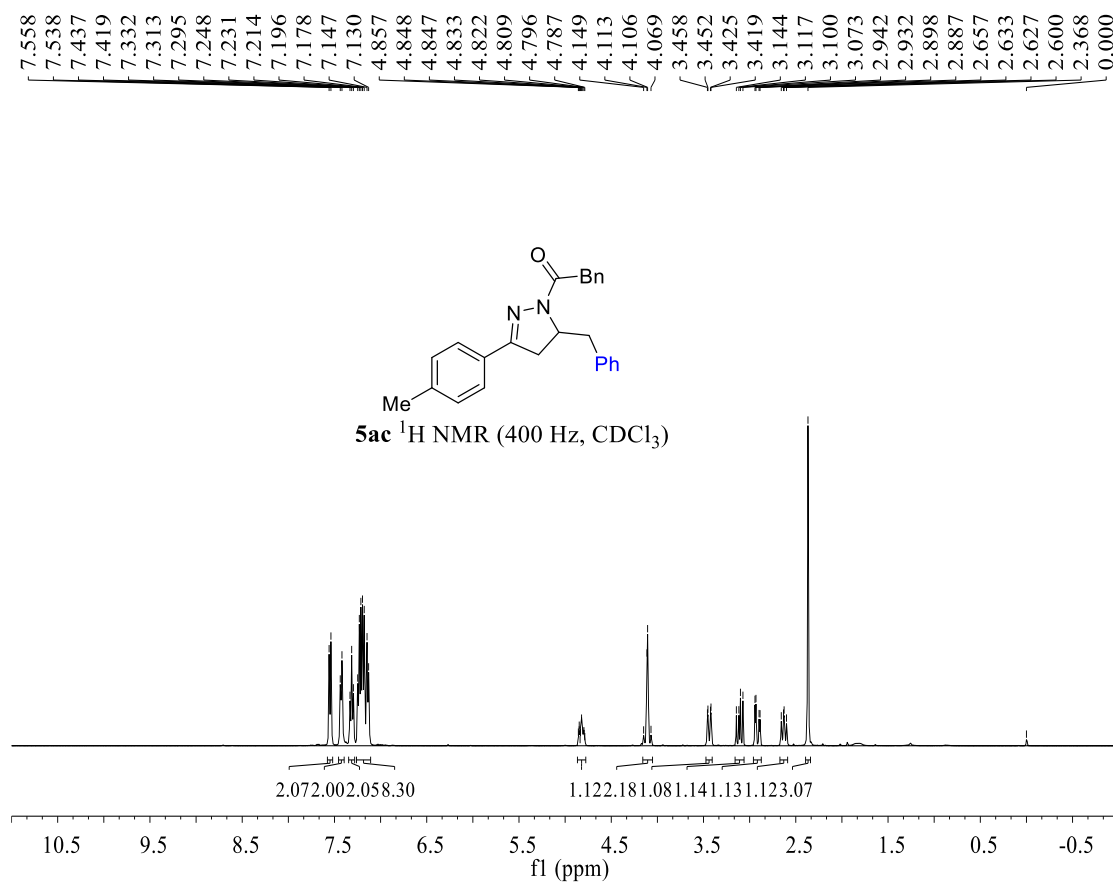
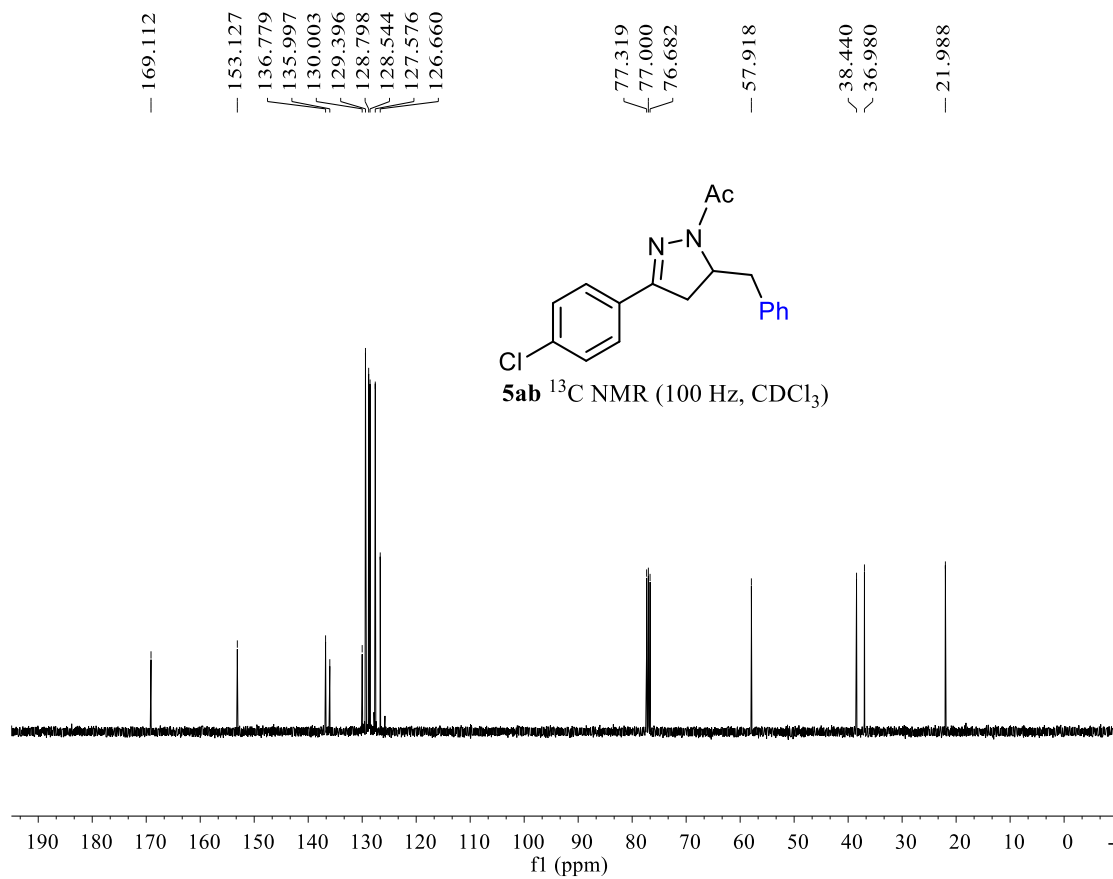


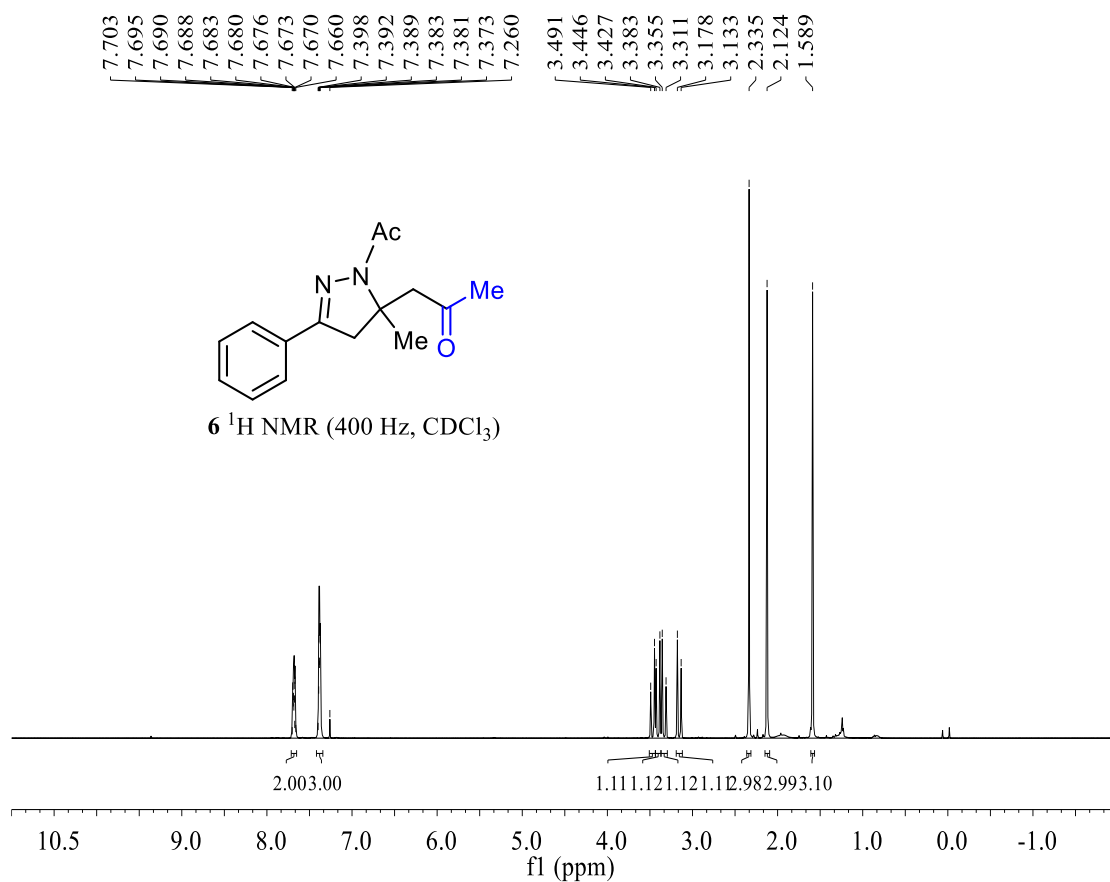
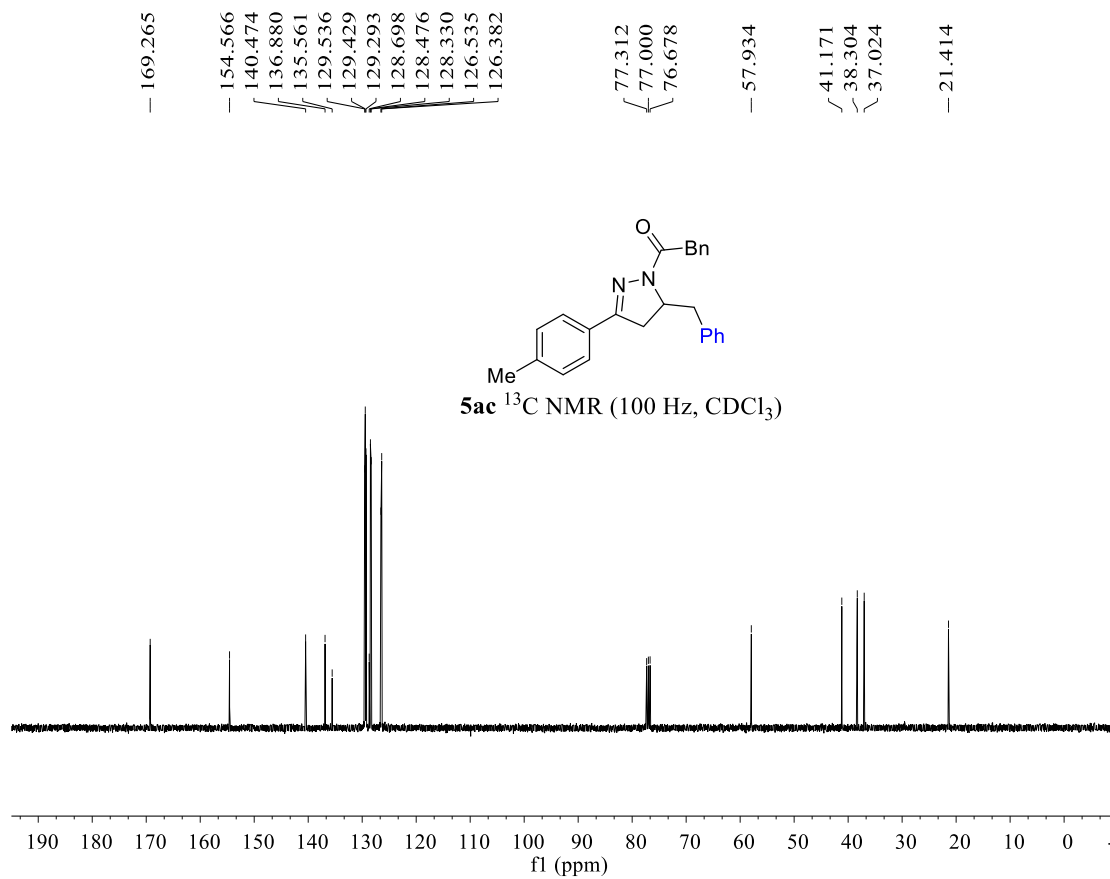
**5z**  $^1\text{H}$  NMR (400 Hz,  $\text{CDCl}_3$ )

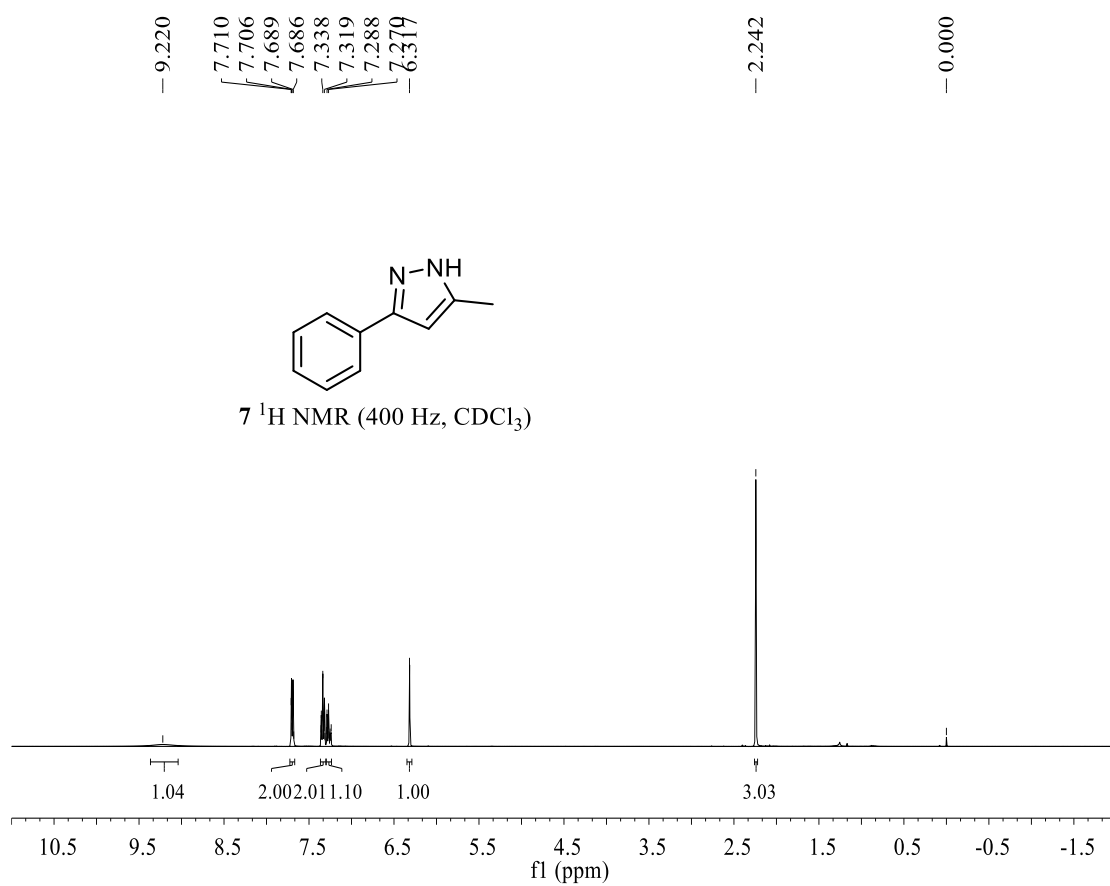
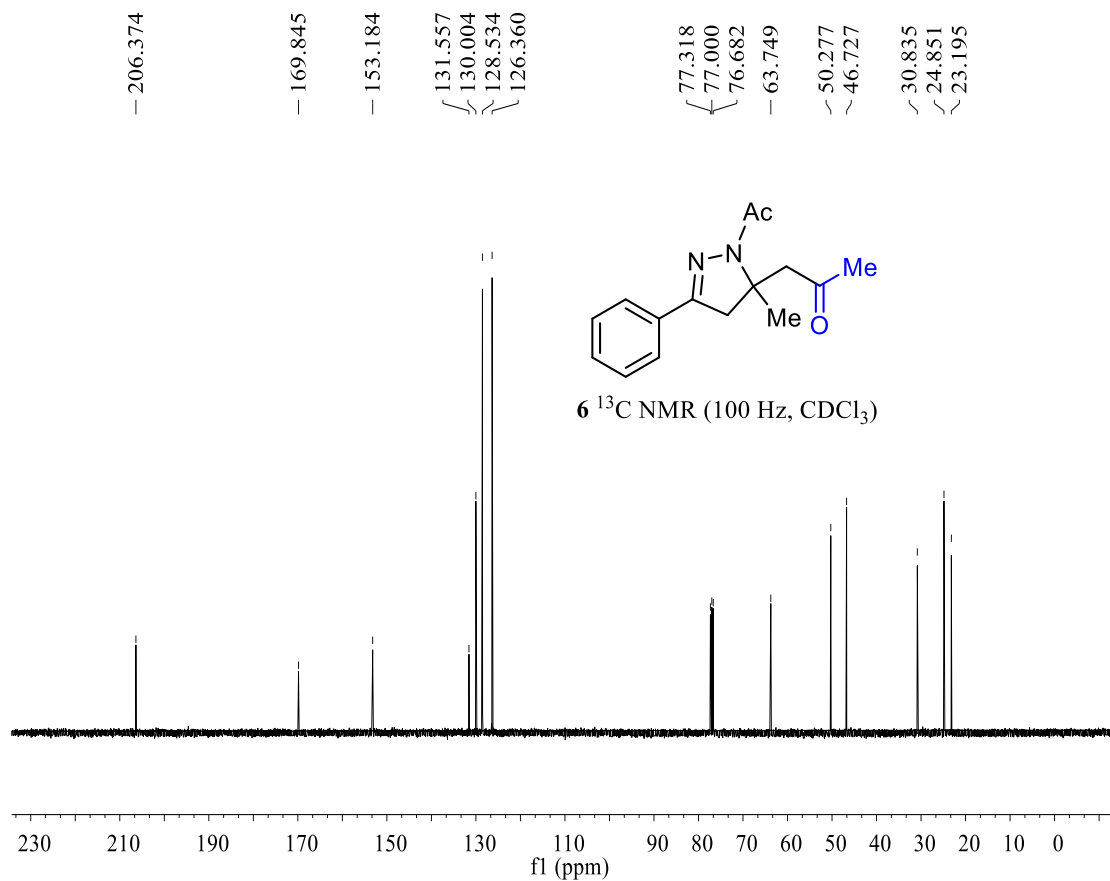




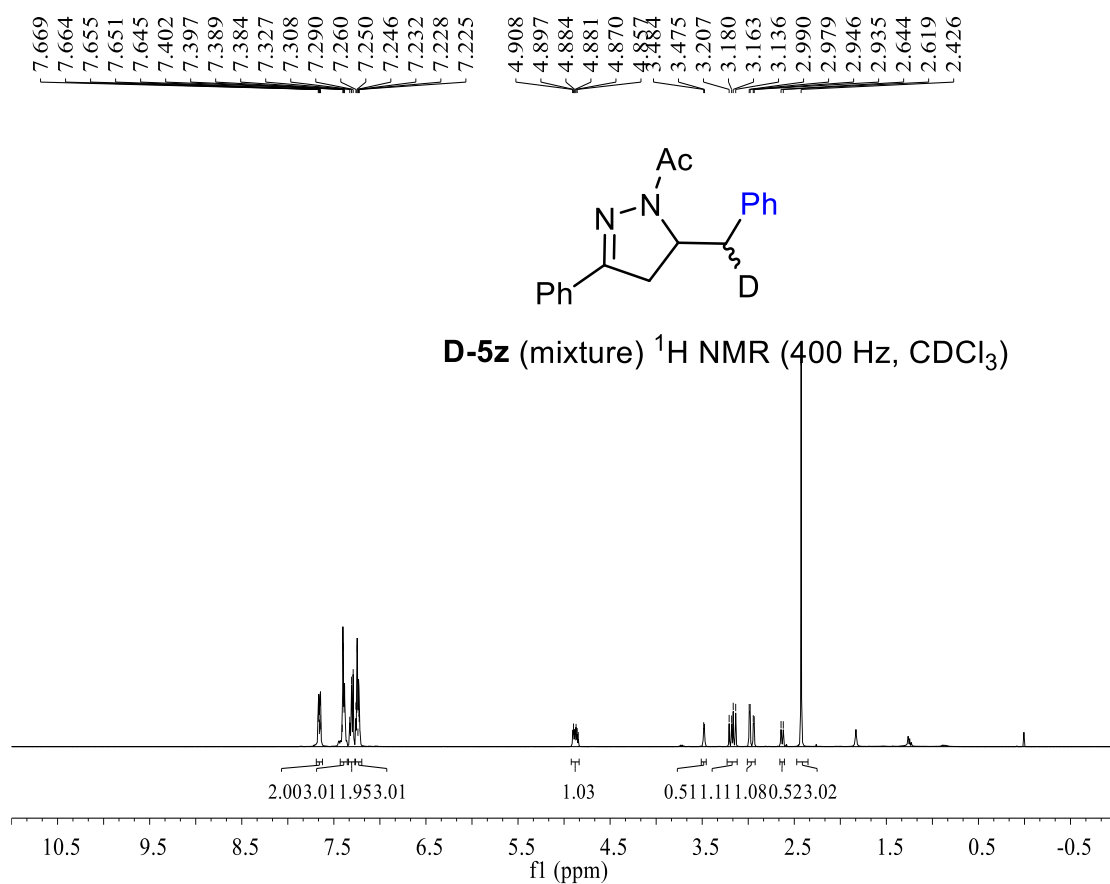
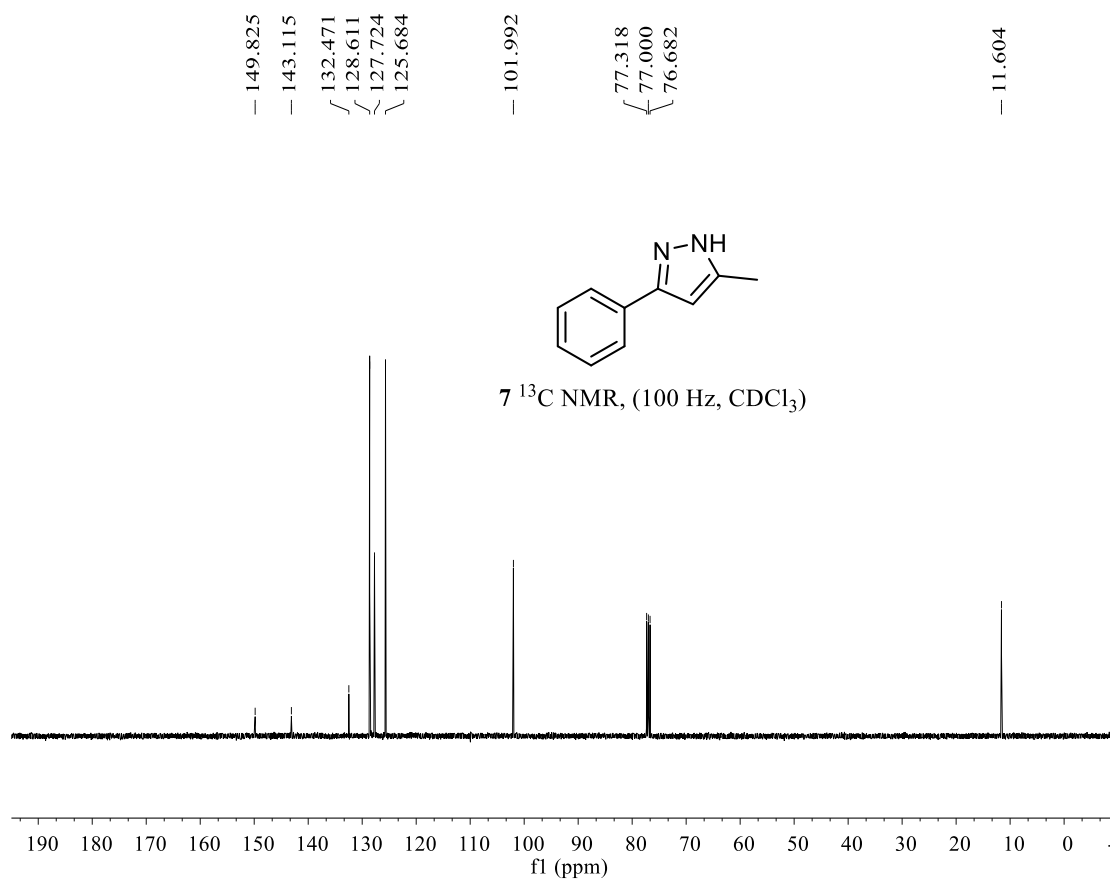




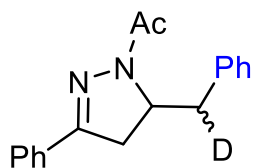








- 169.153  
 - 154.360  
 136.927  
 131.492  
 130.127  
 129.459  
 129.446  
 128.582  
 128.564  
 126.639  
 126.387  
 77.318  
 77.000  
 76.682  
 57.756  
 57.728  
 38.176  
 38.121  
 37.984  
 37.049



**D-5z** (mixture)  $^{13}\text{C}$  NMR (100 Hz,  $\text{CDCl}_3$ )

