

## **Supporting information**

### **Synthesis of 3-Pyrrolin-2-ones by Rhodium-Catalyzed Transannulation of 1-Sulfonyl-1,2,3-triazole with Ketene Silyl Acetal**

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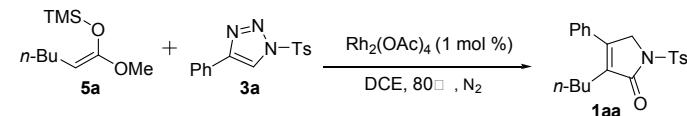
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## 1. General

Analytical thin layer chromatography (TLC) was performed using Silica Gel HSGF<sub>254</sub> pre-coated plates. Flash column chromatography was performed using 200-300 Mesh Silica Gel. Proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were recorded using Brucker Avance II DMX 400MHz spectrometers. Chemical shift ( $\delta$ ) is reported in parts per million (ppm) downfield relative to tetramethylsilane (TMS, 0.0 ppm) or CDCl<sub>3</sub> (7.26 ppm). Coupling constants ( $J$ ) are reported in Hz. Multiplicities are reported using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; Carbon-13 nuclear magnetic resonance (<sup>13</sup>C-NMR) spectra were recorded using a Brucker Avance II DMX 400 spectrometer at 100 MHz. Chemical shift is reported in ppm relative to the carbon resonance of CDCl<sub>3</sub> (77.00 ppm). Infrared spectra were obtained on a Nicolet Avartar 370 IR spectrometer and are reported in wavenumbers. High resolution mass spectra (HRMS) were obtained by Mass Spectrometry Core Laboratory of Zhejiang University, and are reported as m/e (relative ratio). Accurate masses are reported for the molecular ion (M<sup>+</sup>) or a suitable fragment ion.

## 2. Optimization of reaction conditions

**Table S1** Optimization of Reaction Conditions <sup>[a]</sup>



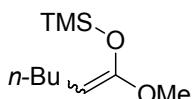
Entry	Ketene silyl acetals	Time [h]	Yield [%] <sup>[b]</sup>
1	1.0 (equiv)	7	59.5
2	0.7 (equiv)	11	28.3
3	1.3 (equiv)	11	69.8
4	1.5 (equiv)	8	86
5	1.8 (equiv)	7	93
6	2.0 (equiv)	8	91.5

[a] 0.2 mmol of triazole **3a** and ketene silyl acetal **5a** were used; the reaction was carried out in 2 mL of DCE under N<sub>2</sub>, DCE = 1,2-dichloroethane. [b] Yield of isolated products.

### 3. Synthetic procedures and Spectra data of ketene silyl acetals.

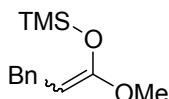
#### General Procedure for Preparation of Silyl Ketene Acetals.<sup>[1]</sup>

A solution of *n*-butyllithium (2.4 M in hexane, 7.05 mL, 19.9 mmol) was added dropwise to a solution of diisopropylamine (2.85 mL, 20.3 mmol) in THF (30 mL) at 0 °C. After being stirred 30 min at 0°C, the reaction mixture was cooled to -78 °C, and then appropriate ester (15 mmol) in THF (8 mL) was added dropwise. The reaction mixture was stirred at -78 °C for 1 h, and then trimethylsilyl chloride (2.25 mL, 18.0 mmol) in THF (8 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred overnight. The solvent was evaporated, and cold hexane (50 mL) was added under a nitrogen atmosphere. The resulting suspension was filtered through a short pad of celite. The filtrate was concentrated under reduced pressure. The **5a**, **5b**, **5c**, **5d**, **5f** was purified by distillation to give a silyl ketene acetal. The compound **5e** was not further purified. The spectroscopic data of **5a**, **5b**, **5c**, **5f** are identical to that reported in the literature.<sup>[1-2]</sup>



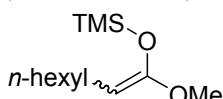
**5a**

**1-Methoxy-1-trimethylsiloxy-1-hexene (5a):** 78%; Colorless oil, bp 65–70 °C/1 mmHg; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 3.68 (t, *J* = 8.0 Hz, 1H), 3.51 (s, 3H), 1.97 – 1.92 (m, 2H), 1.29 (m, 4H), 0.88 (t, *J* = 7.3 Hz, 3H), 0.23 (s, 9H).



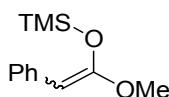
**5b**

**1-Methoxy-1-trimethylsiloxy-3-phenylpropene (5b):** 45%. Colorless oil, bp 115 °C/1mmHg; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.34 – 7.21 (m, 5H), 3.95 (t, *J*=7.2 Hz, 1H), 3.59 (s, 3H), 3.37 (d, *J*=7.2 Hz, 2H), 0.28 (s, 9H).



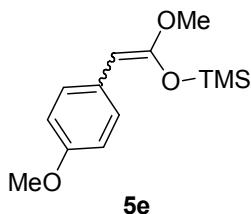
**5c**

**1-Methoxy-1-trimethylsiloxy-1-octylene (5c):** 82%. Colorless oil, bp 75 °C/1mmHg; IR (film): 2926, 2854, 1745, 1681, 1170 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 3.67 (t, *J*=7.2 Hz, 1H), 3.51 (s, 3H), 1.96 – 1.91 (m, 2H), 1.29 – 1.25 (m, 8H), 0.87 (t, *J*=6.0 Hz, 3H), 0.23 (s, 9H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 153.5, 85.5, 54.9, 31.9, 30.7, 28.9, 24.4, 22.7, 14.1, -0.25;

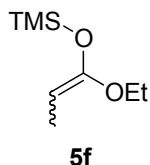


**5d**

**1-Methoxy-1-trimethylsiloxy-1-phenylethylene (5d):** 74%. Colorless oil, bp 100-102 °C/1mmHg; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.44 – 7.37 (m, 2H), 7.28 – 7.19 (t, *J* = 8.0 Hz, 2H), 7.06 – 6.98 (m, 1H), 4.67 (s, 1H), 3.69 (s, 3 H), 0.32 (s, 9H).



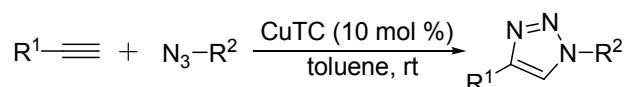
**(1-methoxy-2-(4-methoxyphenyl)vinyloxy)trimethylsilane (5e):** Yellow oil, yield: 64%;  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  7.34 (d,  $J = 8.0$  Hz, 2H), 6.81 (d,  $J = 8.0$  Hz, 2H), 4.65 (s, 1H), 3.78 (s, 3H), 3.67 (s, 3H), 0.31 (s, 9H).



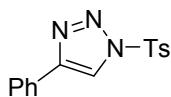
**1-methoxy-1-trimethylsiloxy-3-propene (5f):** Colorless oil, Yield: 46%; bp 60-64 °C/1mmHg;  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  3.83 (q,  $J = 7.2$  Hz, 2H), 3.74 (q,  $J = 8.0$  Hz, 1H), 1.51 (d,  $J = 8.0$  Hz, 3H), 1.23 (t,  $J = 7.2$  Hz, 3H), 0.21 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-d)  $\delta$  153.0, 80.3, 62.9, 14.8, 9.5, -0.3.

#### 4. Synthetic procedures and Spectra data of 1-Sulfonyl-1,2,3-triazoles.

**General procedure for preparation of 1-sulfonyl-1,2,3-triazoles:**<sup>[3]</sup>



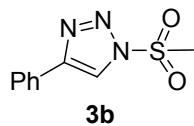
A flask was charged with copper (I) thiophene-2-carboxylate (CuTC, 0.095 g, 0.5 mmol, 0.1 equiv in regards to alkyne), toluene (20 mL), and the alkyne (5.0 mmol, 1 equiv). The reaction mixture was cooled in an ice-water bath. Subsequently, the sulfonyl azide (5.0 mmol, 1 equiv) was added slowly as the limiting reagent to avoid a run-away exotherm, and the reaction mixture allowed to warm to room temperature and stirred overnight. The reaction was diluted with saturated aq NH<sub>4</sub>Cl and extracted into DCM (2 × 20 mL). The combined organics were dried (Na<sub>2</sub>SO<sub>4</sub>) and filtered through celite. The eluent was concentrated in vacuo. The obtained crude product was purified by SiO<sub>2</sub>-column chromatography (PE: EA = 30:1) to give the desired product. The compound **3a**, **3b**, **3c**, **3d**, **3e**, **3f**, **3g**, **3h**, **3i**, **3j**, **3k**, **3l**, **3n**, **3p** were reported in the literature.<sup>[3-10]</sup> The spectra data of **3m** and **3o** as follows.



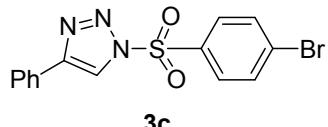
**3a**

**4-phenyl-1-tosyl-1H-1,2,3-triazole (3a):** White solid, yield: 95.0%;  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  8.32 (s, 1H), 8.02 (d,  $J = 8.0$  Hz, 2H), 7.82 (d,  $J = 8.0$  Hz, 2H), 7.48 – 7.34 (m,

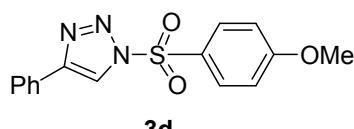
5H), 2.44 (s, 3H).



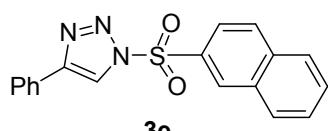
**1-(methylsulfonyl)-4-phenyl-1*H*-1,2,3-triazole (3b):** White solid, yield: 86%;  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  8.32 (s, 1H), 7.88 (d,  $J = 8.0$  Hz, 2H), 7.53 – 7.44 (m, 2H), 7.46 – 7.39 (m, 1H), 3.58 (s, 3H).



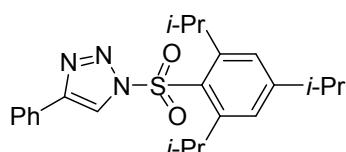
**1-(4-bromophenylsulfonyl)-4-phenyl-1*H*-1,2,3-triazole (3c):** White solid, yield: 87.5%;  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  8.32 (s, 1H), 8.02 (d,  $J = 8.0$  Hz, 2H), 7.83 (d,  $J = 8.0$  Hz, 2H), 7.76 (d,  $J = 8.0$  Hz, 2H), 7.49 – 7.36 (m, 3H).



**1-(4-methoxyphenylsulfonyl)-4-phenyl-1*H*-1,2,3-triazole (3d):** White solid, yield: 55.0%;  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  8.31 (s, 1H), 8.09 (d,  $J = 8.0$  Hz, 2H), 7.83 (d,  $J = 8.0$  Hz, 2H), 7.48 – 7.39 (m, 2H), 7.42 – 7.33 (m, 1H), 7.04 (d,  $J = 8.0$  Hz, 2H), 3.89 (s, 3H).

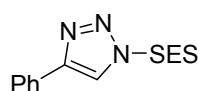


**1-(naphthalen-2-ylsulfonyl)-4-phenyl-1*H*-1,2,3-triazole (3e):** White solid, yield: 42.0%;  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  8.78 (s, 1H), 8.37 (s, 1H), 8.06 – 8.00 (m, 3H), 7.93 (d,  $J = 8.0$  Hz, 1H), 7.84 – 7.80 (d,  $J = 8.0$  Hz, 2H), 7.77 – 7.63 (m, 2H), 7.47 – 7.38 (m, 2H), 7.39 – 7.34 (m, 1H).

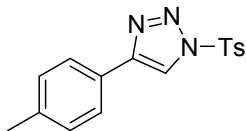


**3f**

**4-phenyl-1-(2,4,6-triisopropylphenylsulfonyl)-1*H*-1,2,3-triazole (3f):** White solid, yield: 55%;  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  8.40 (s, 1H), 7.87 (d,  $J = 8.0$  Hz, 2H), 7.50 – 7.42 (m, 2H), 7.43 – 7.35 (m, 1H), 7.25 (s, 2H), 4.24 – 4.12 (m, 2H), 2.98 – 2.88 (m, 1H), 1.26 (d,  $J = 6.8$  Hz, 6H), 1.23 (d,  $J = 6.8$  Hz, 12H).

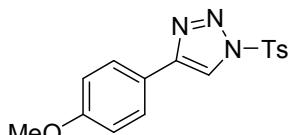


**4-phenyl-1-(2-(trimethylsilyl)ethylsulfonyl)-1*H*-1,2,3-triazole (3g):** White solid, yield: 84%; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.29 (s, 1H), 7.89 (d, *J*=8.0 Hz, 2H), 7.52 – 7.43 (m, 2H), 7.45 – 7.37 (m, 1H), 3.79 – 3.46 (m, 2H), 1.01 – 0.96 (m, 2H), 0.06 (s, 9H).



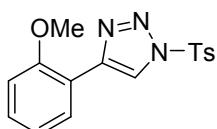
**3h**

**4-p-tolyl-1-tosyl-1*H*-1,2,3-triazole (3h):** White solid, yield: 80.0%; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.27 (s, 1H), 8.02 (d, *J*=8.4 Hz, 2H), 7.71 (d, *J*=8.4 Hz, 2H), 7.39 (d, *J*=8.4 Hz, 2H), 7.24 (d, *J*=8.4 Hz, 2H), 2.45 (s, 3H), 2.38 (s, 3H).



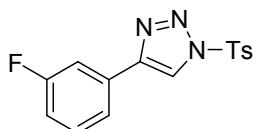
**3i**

**4-(4-methoxyphenyl)-1-tosyl-1*H*-1,2,3-triazole (3i):** White solid, yield: 85%; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.22 (s, 1H), 8.01 (d, *J*=8.2 Hz, 2H), 7.75 (d, *J*=8.2 Hz, 2H), 7.37 (d, *J*=8.2 Hz, 2H), 6.95 (d, *J*=8.2 Hz, 2H), 3.83 (s, 3H), 2.43 (s, 3H).



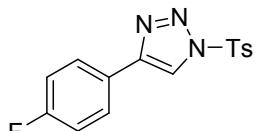
**3j**

**4-(2-methoxyphenyl)-1-tosyl-1*H*-1,2,3-triazole (3j):** Yellow solid, yield: 69%; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.57 (s, 1H), 8.32 (dd, *J*=8.0, 4.0 Hz, 1H), 8.02 (d, *J*=8.0 Hz, 2H), 7.39 – 7.31 (m, 3H), 7.10 – 7.02 (t, *J*=8.0 Hz, 1H), 6.98 (d, *J*=8.0 Hz, 1H), 3.97 (s, 3H), 2.43 (s, 3H). HRMS (EI) calcd for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub>O<sub>3</sub>S<sup>+</sup> 329.0834, found 329.0844.



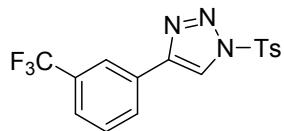
**3k**

**4-(3-fluorophenyl)-1-tosyl-1*H*-1,2,3-triazole (3k):** White solid, yield: 30%; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.32 (s, 1H), 8.03 (d, *J*=8.0 Hz, 2H), 7.57 (t, *J*=12.0 Hz, 2H), 7.44 – 7.35 (m, 3H), 7.07 (t, *J*=8.0 Hz, 1H), 2.46 (s, 3H).



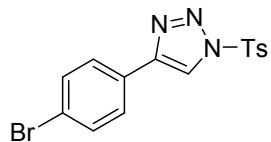
**3l**

**4-(4-fluorophenyl)-1-tosyl-1*H*-1,2,3-triazole (3l):** White solid, yield: 52%; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.28 (s, 1H), 8.04 (d, *J* = 12.0 Hz, 2H), 7.81 (t, *J* = 12.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 8.0 Hz, 2H), 2.46 (s, 3H).



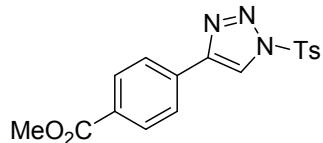
**3m**

**1-tosyl-4-(3-(trifluoromethyl)phenyl)-1*H*-1,2,3-triazole (3m):** White solid, yield: 40%; mp 115.1 – 117.5 °C; IR (KBr): 3147, 1594, 1397, 1175, 803, 671 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.40 (s, 1H), 8.11 – 8.00 (m, 4H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 12.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 147.6, 145.9, 132.7, 131.4 (q, *J* = 69.7 Hz), 130.5, 129.7, 129.5, 129.2, 128.7, 125.5 (d, *J* = 3.7 Hz), 124.0 (q, *J* = 543.5 Hz), 122.8 (d, *J* = 3.8 Hz), 119.6, 21.7. HRMS (EI) calcd for C<sub>16</sub>H<sub>12</sub>F<sub>3</sub>N<sub>3</sub>O<sub>2</sub>S<sup>+</sup> 367.0602, found 367.0608.



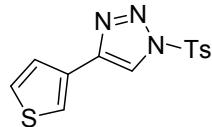
**3n**

**4-(4-bromophenyl)-1-tosyl-1*H*-1,2,3-triazole (3n):** White solid, yield: 21.8%; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.32 (s, 1H), 8.03 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H).



**3o**

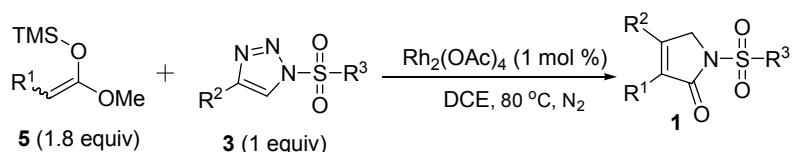
**methyl 4-(1-tosyl-1*H*-1,2,3-triazol-4-yl)benzoate (3o):** White solid, yield: 76.8%; mp 176.8 – 179.9 °C; IR (KBr): 3124, 1719, 1392, 1176, 774, 696 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.40 (s, 1H), 8.11 (d, *J* = 8.2 Hz, 2H), 8.04 (d, *J* = 8.2 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 3.94 (s, 3H), 2.46 (s, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 166.5, 147.6, 146.3, 133.1, 132.9, 130.5, 130.3, 128.8, 125.9, 119.8, 52.2, 21.9. HRMS (EI) calcd for C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O<sub>4</sub>S<sup>+</sup> 357.0783, found 357.0780.



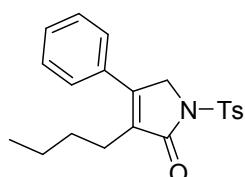
**3p**

**4-(thiophen-3-yl)-1-tosyl-1*H*-1,2,3-triazole (3p):** White solid, yield: 27%; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.21 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.77 (s, 1H), 7.44 – 7.36 (m, 4H), 2.45 (s, 3H).

## 5. Reaction scope.

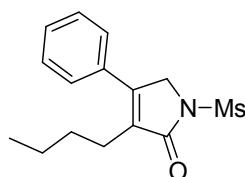


**General procedure:** Under a nitrogen atmosphere, DCE (0.5 mL) was added to reaction flask charged with  $\text{Rh}_2(\text{OAc})_4$  (0.9 mg, 1 mol %), 1-sulfonyl-1,2,3-triazoles **3** (0.2 mmol). Then a solution of silyl ketene acetals **5** (0.36 mmol) in DCE (1.5 mL) was added dropwise. The reaction was stirred at 80°C, until TLC analysis showed that intermediate **6** was completely consumed. The reaction mixture was filtered through a short plug of silica gel. The solution of mixture was concentrated and then purified by flash chromatography to give the corresponding product **1**.



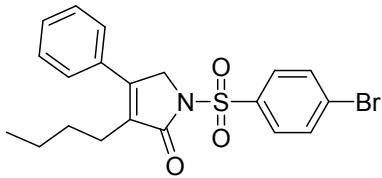
**1aa**

**3-butyl-4-phenyl-1-tosyl-1*H*-pyrrol-2(*5H*)-one (**1aa**):** White solid, yield: 93%; mp 110.1 – 112.7 °C; IR (KBr): 2956, 2870, 1716, 1361, 1169, 814, 667 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.43 – 7.32 (m, 4H), 4.65 (s, 2H), 2.44 (s, 3H), 2.39 (t, *J* = 8.0 Hz, 2H), 1.54 – 1.43 (m, 2H), 1.37 – 1.26 (m, 2H), 0.87 (t, *J* = 6.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 169.4, 150.0, 145.0, 135.4, 133.2, 132.3, 129.9, 129.7, 129.0, 128.0, 127.2, 51.5, 29.9, 24.2, 22.8, 21.7, 13.7; HRMS (EI) calcd for  $\text{C}_{21}\text{H}_{23}\text{NO}_3\text{S}^+$  369.1399, found 369.1397.



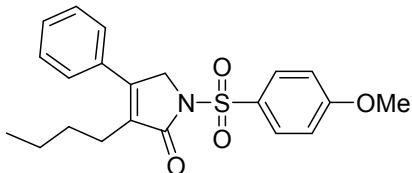
**1ab**

**3-butyl-1-(methylsulfonyl)-4-phenyl-1*H*-pyrrol-2(*5H*)-one (**1ab**):** White solid, yield: 56.0%; mp 135.3 – 136.0 °C; IR (KBr): 2946, 2927, 2871, 1715, 1346, 1172, 766, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.52 – 7.44 (m, 3H), 7.44 – 7.39 (m, 2H), 4.64 (s, 2H), 3.39 (s, 3H), 2.49 (t, *J* = 8.0 Hz, 2H), 1.63 – 1.50 (m, 2H), 1.47 – 1.29 (m, 2H), 1.02 – 0.87 (t, *J* = 8.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 170.4, 150.7, 133.0, 132.2, 130.1, 129.1, 127.3, 50.9, 41.0, 30.1, 24.2, 22.8, 13.7; HRMS (EI) calcd for  $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{S}^+$  293.1086, found 293.1089.



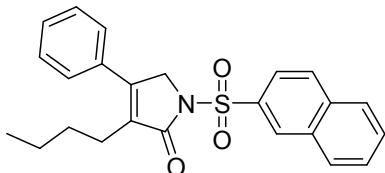
**1ac**

**1-(4-bromophenylsulfonyl)-3-butyl-4-phenyl-1*H*-pyrrol-2(*5H*)-one (1ac):** White solid, yield: 55.0%; mp 152.6 – 153.1 °C; IR (KBr): 2952, 2925, 2856, 1732, 1363, 1159, 760, 689 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.43 – 7.36 (d, *J* = 8.0 Hz, 2H), 4.65 (s, 2H), 2.40 (t, *J* = 8.0 Hz, 1H), 1.56 – 1.43 (m, 2H), 1.40 – 1.26 (m, 2H), 0.87 (t, *J* = 6.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 169.4, 150.4, 137.3, 133.0, 132.4, 132.1, 130.1, 129.6, 129.3, 129.1, 127.3, 51.5, 29.9, 24.2, 22.8, 13.7. HRMS (EI) calcd for C<sub>20</sub>H<sub>20</sub>BrNO<sub>3</sub>S<sup>+</sup> 433.0347, found 433.0347.



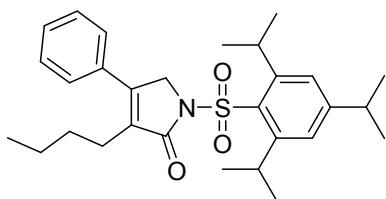
**1ad**

**3-butyl-1-(4-methoxyphenylsulfonyl)-4-phenyl-1*H*-pyrrol-2(*5H*)-one (1ad):** White solid, yield: 78.0%; mp 100.2 – 102.1 °C; IR (KBr): 2956, 2929, 2860, 1715, 1360, 1163, 764, 696 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.08 – 8.05 (m, 2H), 7.49 – 7.41 (m, 3H), 7.42 – 7.37 (m, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 4.65 (s, 2H), 3.87 (s, 3H), 2.39 (t, *J* = 8.0 Hz, 2H), 1.56 – 1.43 (m, 2H), 1.39 – 1.26 (m, 2H), 0.87 (t, *J* = 6.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 169.4, 163.8, 149.9, 133.1, 132.2, 130.3, 129.9, 129.8, 129.0, 127.2, 114.2, 55.6, 51.5, 29.9, 24.2, 22.8, 13.6; HRMS (EI) calcd for C<sub>20</sub>H<sub>23</sub>NO<sub>4</sub>S<sup>+</sup> 385.1348, found 385.1347.



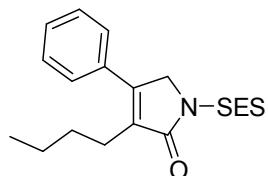
**1ae**

**3-butyl-1-(naphthalen-2-ylsulfonyl)-4-phenyl-1*H*-pyrrol-2(*5H*)-one (1ae):** White solid, yield: 85.0%; mp 138.3 – 140.0°C; IR (KBr): 2956, 2928, 2860, 1716, 1352, 1170, 763, 662 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.70 (s, 1H), 8.09 (d, *J* = 12.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 12.0 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.48 – 7.41 (m, 5H), 7.38 (d, *J* = 7.9 Hz, 2H), 4.70 (s, 2H), 2.42 – 2.33 (t, *J* = 8.0 Hz, 2H), 1.53 – 1.42 (m, 2H), 1.36 – 1.26 (m, 2H), 0.84 (t, *J* = 6.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 169.4, 150.2, 135.4, 135.3, 133.1, 132.2, 131.9, 129.9, 129.8, 129.6, 129.4, 129.3, 129.0, 127.9, 127.6, 127.2, 122.6, 51.6, 29.9, 24.2, 22.7, 13.6; HRMS (EI) calcd for C<sub>24</sub>H<sub>23</sub>NO<sub>3</sub>S<sup>+</sup> 405.1399, found 405.1397.



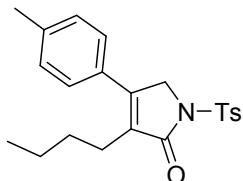
**1af**

**3-butyl-4-phenyl-1-(2,4,6-triisopropylphenylsulfonyl)-1*H*-pyrrol-2(*5H*)-one (1af):** Pale yellow oil, yield: 61.0%; IR (film): 2958, 2929, 2869, 1719, 1364, 1170, 763, 696 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.49 – 7.42 (m, 5H), 7.21 (s, 2H), 4.68 (s, 2H), 4.22 – 4.15 (m, 2H), 2.95 – 2.88 (m, 1H), 2.40 (t, *J* = 7.8 Hz, 2H), 1.48 – 1.42 (m, 2H), 1.29–1.25 (m, 2H), 1.27 (d, *J* = 6.9 Hz, 18H), 0.84 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 169.7, 153.9, 151.4, 149.7, 133.2, 132.5, 131.7, 129.8, 129.1, 127.3, 123.9, 50.4, 34.2, 30.0, 29.4, 24.5, 24.0, 23.5, 22.7, 13.6; HRMS (EI) calcd for C<sub>29</sub>H<sub>39</sub>NO<sub>3</sub>S<sup>+</sup> 481.2651, found 481.2655.



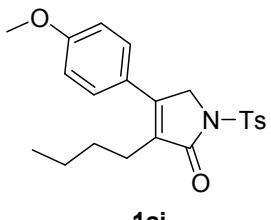
**1ag**

**3-butyl-4-phenyl-1-(2-(trimethylsilyl)ethylsulfonyl)-1*H*-pyrrol-2(*5H*)-one (1ag):** Pale yellow oil, yield: 55.0%; IR (film): 2956, 2929, 2871, 1713, 1351, 1153, 763, 696 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.47 – 7.37 (m, 3H), 7.39 – 7.35 (d, *J*=8.0 Hz, 2H), 4.58 (s, 2H), 3.49 – 3.41 (m, 2H), 2.45 (t, *J* = 8.0 Hz, 2H), 1.54 – 1.46 (m, 2H), 1.36 – 1.28 (m, 2H), 1.01 – 0.95 (m, 2H), 0.85 (t, *J* = 6.0 Hz, 3H), 0.02 (s, 9H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 170.5, 150.6, 133.0, 132.3, 130.0, 129.1, 127.3, 51.7, 49.9, 30.1, 24.2, 22.8, 13.7, 9.6, 2.0; HRMS (EI) calcd for C<sub>19</sub>H<sub>29</sub>NO<sub>3</sub>SSi<sup>+</sup> 379.1637, found 379.1636.



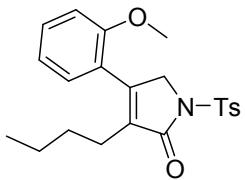
**1ah**

**3-butyl-4-p-tolyl-1-tosyl-1*H*-pyrrol-2(*5H*)-one (1ah):** White solid, yield: 68.0%; mp 135.2 – 137.0 °C; IR (KBr): 2923, 2855, 1729, 1362, 1159, 815, 669 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.22 (m, 4H), 4.63 (s, 2H), 2.43 (s, 3H), 2.44 – 2.35 (m, 5H), 1.55 – 1.44 (m, 2H), 1.37 – 1.28 (m, 2H), 0.87 (t, *J* = 8.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 169.6, 150.0, 144.9 140.3, 135.5, 132.3, 129.7, 129.6, 129.4, 128.0, 127.1, 51.4, 29.9, 24.2, 22.8, 21.6, 21.3, 13.7. HRMS (EI) calcd for C<sub>22</sub>H<sub>25</sub>NO<sub>3</sub>S<sup>+</sup> 383.1555, found 383.1557.



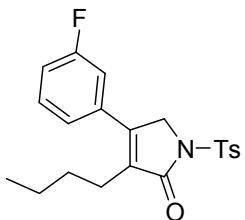
**1ai**

**3-butyl-4-(4-methoxyphenyl)-1-tosyl-1H-pyrrol-2(5H)-one (1ai):** White solid, yield: 87.0%; mp 130.0 – 132.2 °C; IR (KBr): 2956, 2928, 2859, 1716, 1362, 1168, 814, 667 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.31 (m, 4H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.63 (s, 2H), 3.85 (s, 3H), 2.43 (s, 3H), 2.43 – 2.35 (m, 2H), 1.53 – 1.44 (m, 2H), 1.40 – 1.28 (m, 2H), 0.88 (t, *J* = 8.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 169.7, 160.8, 149.5, 144.9, 135.5, 131.2, 129.6, 128.7, 127.9, 124.6, 114.4, 55.3, 51.3, 29.8, 24.2, 22.8, 21.6, 13.7; HRMS (EI) calcd for C<sub>22</sub>H<sub>25</sub>NO<sub>4</sub>S<sup>+</sup> 399.1504, found 399.1501.



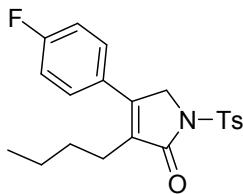
**1aj**

**3-butyl-4-(2-methoxyphenyl)-1-tosyl-1H-pyrrol-2(5H)-one (1aj):** Pale yellow oil, yield: 64.0%; IR (film): 2956, 2928, 2870, 1720, 1362, 1169, 814, 667 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.00 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.34 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 4.65 (s, 2H), 3.82 (s, 3H), 2.44 (s, 3H), 2.18 (t, *J* = 7.9 Hz, 2H), 1.47 – 1.35 (m, 2H), 1.22 – 1.15 (m, 2H), 0.78 (t, *J* = 6.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 169.4, 156.6, 150.4, 144.8, 135.7, 134.2, 130.9, 129.7, 129.6, 128.1, 121.4, 120.6, 111.1, 55.4, 52.3, 29.7, 24.2, 22.5, 21.6, 13.6; HRMS (EI) calcd for C<sub>22</sub>H<sub>25</sub>NO<sub>4</sub>S<sup>+</sup> 399.1504, found 399.1500.



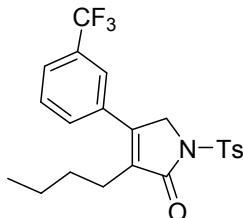
**1ak**

**3-butyl-4-(3-fluorophenyl)-1-tosyl-1H-pyrrol-2(5H)-one (1ak):** White solid, yield: 75.0%; mp 105.1 – 106.6 °C; IR (KBr): 2957, 2928, 2870, 1720, 1362, 1169, 814, 667 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.01 (d, *J* = 8.0 Hz, 2H), 7.50 – 7.39 (m, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.20 – 7.07 (m, 3H), 4.63 (s, 2H), 2.44 (s, 3H), 2.39 (t, *J* = 8.0 Hz, 2H), 1.53 – 1.43 (m, 2H), 1.36 – 1.27 (m, 2H), 0.87 (t, *J* = 8.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 169.0, 164.0, 161.5, 148.4 (d, *J* = 3.0 Hz), 145.1, 135.2, 134.2 (t, *J* = 4.5 Hz), 130.7 (d, *J* = 8.0 Hz), 129.7, 128.0, 123.0 (d, *J* = 3.0 Hz), 115.7 (t, *J* = 5.2 Hz), 115.5 (t, *J* = 5.4 Hz), 51.4, 29.8, 24.1, 22.7, 21.6, 13.6; HRMS (EI) calcd for C<sub>21</sub>H<sub>22</sub>FNO<sub>3</sub>S<sup>+</sup> 387.1304, found 387.1304.



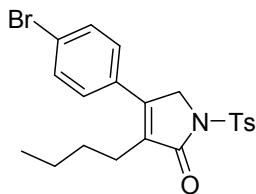
**1al**

**3-butyl-4-(4-fluorophenyl)-1-tosyl-1H-pyrrol-2(5H)-one (1al):** White solid, yield: 81.0%; mp 127.6 – 129.0 °C; IR (KBr): 2957, 2928, 2870, 1720, 1361, 1169, 814, 667 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.01 (d, *J*=8.0 Hz, 2H), 7.42 – 7.33 (m, 4H), 7.16 (t, *J*=8.0 Hz, 2H), 4.63 (s, 2H), 2.44 (s, 3H), 2.37 (t, *J*=8.0 Hz, 2H), 1.50 – 1.43 (m, 2H), 1.38 – 1.26 (m, 2H), 0.87 (t, *J*=6.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 169.3, 164.6, 162.1, 148.8, 145.1, 135.3, 133.1, 129.7, 129.2 (d, *J*=8.0 Hz), 128.0, 116.3 (d, *J*=21.0 Hz), 51.5, 29.9, 24.2, 22.8, 21.7, 13.7; HRMS (EI) calcd for C<sub>21</sub>H<sub>22</sub>FNO<sub>3</sub>S<sup>+</sup> 387.1304, found 387.1310.



**1am**

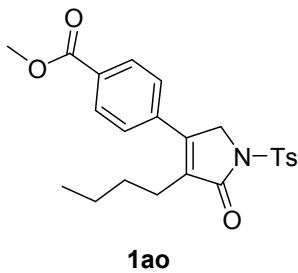
**3-butyl-1-tosyl-4-(3-(trifluoromethyl)phenyl)-1H-pyrrol-2(5H)-one (1am):** White solid, yield: 78.0%; mp 121.4 – 123.0 °C; IR (KBr): 2959, 2930, 2872, 1721, 1362, 1168, 811, 670 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.02 (d, *J*=8.0 Hz, 2H), 7.70 (d, *J*=8.0 Hz, 1H), 7.65 – 7.56 (m, 3H), 7.37 (d, *J*=8.0 Hz, 2H), 4.67 (s, 2H), 2.45 (s, 3H), 2.38 (t, *J*=8.0 Hz, 2H), 1.56 – 1.43 (m, 2H), 1.38 – 1.27 (m, 2H), 0.87 (t, *J*=8.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 168.8, 148.1, 145.2, 135.3, 134.9, 133.1, 131.6, 130.5 (q, *J*=65.1 Hz), 129.8, 129.7, 128.1, 126.4, 124.1 (q, *J*=3.8 Hz), 124.1 (q, *J*=544.3 Hz), 51.4, 29.9, 24.2, 22.7, 21.6, 13.5; HRMS (EI) calcd for C<sub>22</sub>H<sub>22</sub>F<sub>3</sub>NO<sub>3</sub>S<sup>+</sup> 437.1272, found 437.1274.



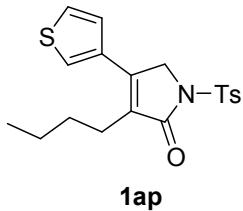
**1an**

**4-(4-bromophenyl)-3-butyl-1-tosyl-1H-pyrrol-2(5H)-one (1an):** White solid, yield: 91.0%; mp 147.5 – 150.8 °C; IR (KBr): 2956, 2926, 2870, 1720, 1361, 1168, 814, 666 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.00 (d, *J*=8.0 Hz, 2H), 7.59 (d, *J*=8.0 Hz, 2H), 7.35 (d, *J*=8.0 Hz, 2H), 7.26 (d, *J*=8.0 Hz, 2H), 4.61 (s, 2H), 2.43 (s, 3H), 2.36 (t, *J*=8.0 Hz, 2H), 1.50 – 1.43 (m, 2H), 1.36 – 1.25 (m, 2H), 0.86 (t, *J*=8.0 Hz, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 169.0, 148.6, 145.0, 135.3, 133.8, 132.3, 131.1, 129.7, 128.7, 128.0, 124.2, 51.3, 29.8, 24.2, 22.7, 21.6, 13.6;

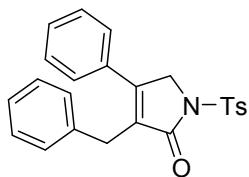
HRMS (EI) calcd for  $C_{21}H_{22}BrNO_3S^+$  447.0504, found 447.0504.



**methyl 4-(4-butyl-5-oxo-1-tosyl-2,5-dihydro-1*H*-pyrrol-3-yl)benzoate (1ao):** White solid, yield: 78.0%; mp 122.9 – 123.8 °C; IR (KBr): 2955, 2928, 2870, 1720, 1169, 814, 666  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  8.12 (d,  $J=8.0$  Hz, 2H), 8.01 (d,  $J=8.0$  Hz, 2H), 7.46 (d,  $J=8.0$  Hz, 2H), 7.36 (d,  $J=8.0$  Hz, 2H), 4.66 (s, 2H), 3.95 (s, 3H), 2.44 (s, 3H), 2.41 – 2.37 (t,  $J=8.0$  Hz, 2H), 1.54 – 1.43 (m, 2H), 1.34 – 1.27 (m, 2H), 0.86 (t,  $J=6.0$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-d)  $\delta$  168.9, 166.1, 148.7, 145.1, 136.6, 135.3, 134.9, 131.2, 130.2, 129.8, 128.1, 127.3, 52.4, 51.4, 29.9, 24.3, 22.7, 21.7, 13.6; HRMS (EI) calcd for  $C_{23}H_{25}NO_5S^+$  427.1453, found 427.1448.

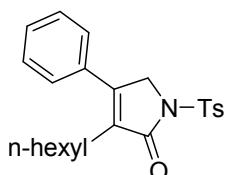


**3-butyl-4-(thiophen-3-yl)-1-tosyl-1*H*-pyrrol-2(5*H*)-one (1ap):** Pale yellow oil, yield: 72.0%; IR (film): 2956, 2928, 2870, 1716, 1367, 1168, 812, 666  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  7.99 (d,  $J=8.0$  Hz, 2H), 7.53 (s, 1H), 7.49 – 7.42 (m, 1H), 7.34 (d,  $J=8.0$  Hz, 2H), 7.26 (d,  $J=4.0$  Hz, 1H), 4.66 (s, 2H), 2.47 – 2.40 (m, 5H), 1.52 – 1.43 (m, 2H), 1.41 – 1.31 (m, 2H), 0.90 (t,  $J=8.0$  Hz, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-d)  $\delta$  169.7, 144.9, 144.2, 135.4, 133.3, 131.2, 129.7, 127.9, 127.1, 125.9, 125.6, 51.2, 29.7, 24.3, 22.8, 21.6, 13.7; HRMS (EI) calcd for  $C_{19}H_{21}NO_3S_2^+$  375.0963, found 375.0966.



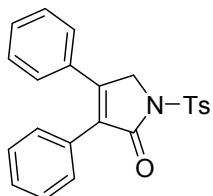
**1ba**

**3-benzyl-4-phenyl-1-tosyl-1*H*-pyrrol-2(5*H*)-one (1ba):** White solid, yield: 66.0%; mp 154.9 – 156.8 °C; IR (KBr): 3060, 3027, 2924, 2853, 1716, 1361, 1171, 815, 667  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz, Chloroform-d)  $\delta$  8.01 (d,  $J=8.0$  Hz, 2H), 7.43 – 7.33 (m, 7H), 7.24 – 7.09 (m, 5H), 4.72 (s, 2H), 3.75 (s, 2H), 2.44 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz, Chloroform-d)  $\delta$  169.3, 152.0, 145.0, 137.6, 135.4, 131.8, 131.2, 130.2, 129.7, 129.0, 128.6, 128.2, 128.0, 127.4, 126.4, 51.8, 30.0, 21.6; HRMS (EI) calcd for  $C_{24}H_{21}NO_3S^+$  403.1242, found 403.1250.



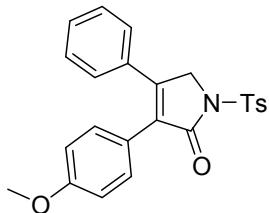
**1ca**

**3-hexyl-4-phenyl-1-tosyl-1*H*-pyrrol-2(5*H*)-one (1ca):** Light yellow solid, yield: 87.0%; mp 161.5 – 163.4 °C; IR (KBr): 2284, 1685, 1362, 1116, 769, 689 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.40 (m, 3H), 7.40 – 7.37 (m, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 4.64 (s, 2H), 2.43 (s, 3H), 2.43 – 2.34 (t, *J* = 8.0 Hz, 2H), 1.56 – 1.43 (m, 2H), 1.31 – 1.18 (m, 6H), 0.83 (t, *J* = 6.7 Hz, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 169.4, 150.0, 145.0, 135.4, 133.2, 132.3, 129.9, 129.7, 129.0, 128.0, 127.2, 51.5, 31.3, 29.3, 27.7, 24.4, 22.4, 21.6, 14.0; HRMS (EI) calcd for C<sub>23</sub>H<sub>27</sub>NO<sub>3</sub>S<sup>+</sup> 397.1712, found 397.1714.



**1da**

**3,4-diphenyl-1-tosyl-1*H*-pyrrol-2(5*H*)-one (1da):** Yellow solid, yield: 52.0%; mp 177.2 – 178.8 °C; IR (KBr): 2359, 2341, 1715, 1356, 1166, 811, 669 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.22 (m, 12H), 4.80 (s, 2H), 2.43 (s, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 168.0, 150.7, 145.2, 135.1, 131.6, 131.1, 130.3, 130.0, 129.7, 129.3, 128.8, 128.7, 128.5, 128.2, 127.7, 51.3, 21.7; HRMS (EI) calcd for C<sub>23</sub>H<sub>19</sub>NO<sub>3</sub>S<sup>+</sup> 389.1086, found 389.1087.



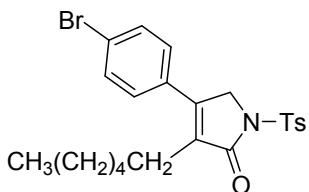
**1ea**

**3-(4-methoxyphenyl)-4-phenyl-1-tosyl-1*H*-pyrrol-2(5*H*)-one (1ea):** Yellow solid, yield: 58.0%; mp 176.1 – 178.8 °C; IR (KBr): 2925, 1720, 1359, 1164, 814, 667 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.32 (m, 6H), 7.24 (d, *J* = 8.0 Hz, 3H), 6.82 (d, *J* = 8.0 Hz, 2H), 4.76 (s, 2H), 3.78 (s, 3H), 2.42 (s, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 168.3, 159.9, 149.5, 145.1, 135.4, 132.1, 130.7, 130.1, 129.7, 129.1, 128.8, 128.2, 127.6, 122.3, 114.0, 55.2, 51.3, 21.6; HRMS (EI) calcd for C<sub>24</sub>H<sub>21</sub>NO<sub>4</sub>S<sup>+</sup> 419.1191, found 419.1193.



**1fa**

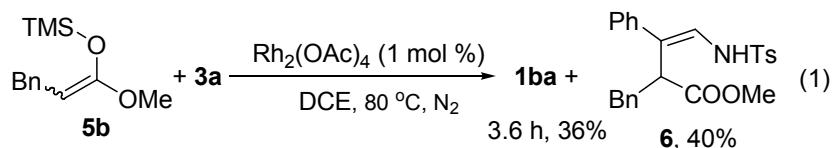
**3-methyl-4-phenyl-1-tosyl-1H-pyrrol-2(5H)-one (1fa):** White solid, yield: 83.0%; mp 160.8 – 163.4 °C; IR (KBr): 2925, 1715, 1353, 1171, 811, 667 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.93 (d, *J*=8.0 Hz, 2H), 7.42 – 7.31 (m, 5H), 7.26 (d, *J*=8.0 Hz, 2H), 4.59 (s, 2H), 2.35 (s, 3H), 1.92 (s, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 169.6, 149.8, 145.0, 135.4, 132.1, 129.9, 129.7, 129.0, 128.3, 128.0, 127.3, 51.2, 21.6, 10.2; HRMS (EI) calcd for C<sub>18</sub>H<sub>17</sub>NO<sub>3</sub>S<sup>+</sup> 327.0929, found 327.0936.



**1cn**

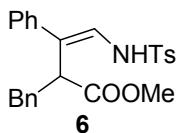
**4-(4-bromophenyl)-3-hexyl-1-tosyl-1H-pyrrol-2(5H)-one (1cn):** White solid, yield: 95.0%; mp 103.6 – 104.2 °C; IR (KBr): 2926, 2856, 1719, 1588, 1361, 1169, 815 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 4.61 (s, 2H), 2.44 (s, 3H), 2.38 – 2.33 (m, 2H), 1.53 – 1.41 (m, 2H), 1.35 – 1.16 (m, 6H), 0.84 (t, *J* = 6.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 169.1, 148.6, 145.1, 135.4, 133.9, 132.3, 131.2, 129.8, 128.7, 128.1, 124.3, 51.3, 31.3, 29.3, 27.7, 24.5, 22.5, 21.7, 14.0. HRMS (EI) calcd for C<sub>23</sub>H<sub>26</sub>BrNO<sub>3</sub>S<sup>+</sup> 475.0817, found 475.0815.

## 6. Mechanistic studies.



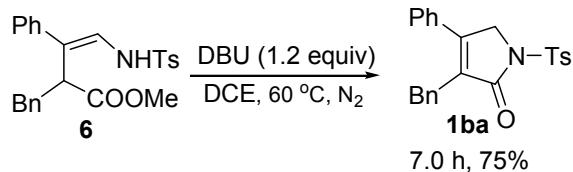
### Synthesis of 6:

DCE (5.0 mL) was added to reaction flask charged with Rh<sub>2</sub>(OAc)<sub>4</sub> (2.7 mg, 1 mol%), 1-sulfonyl-1,2,3-triazoles **3a** (0.6 mmol). Then a solution of silyl ketene acetals **5** (1.08 mmol) in DCE (5.0 mL) was added dropwise. The reaction was stirred at 80°C for 3.6 h (TLC analysis showed that triazole was completely consumed). The reaction mixture was filtered through a short plug of silica gel. The solution of mixture was concentrated and then purified by flash chromatography to give the corresponding product **6** and **1ba**.



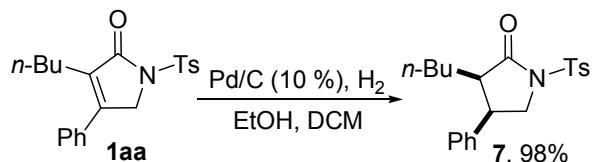
**(E)-methyl 2-benzyl-4-(4-methylphenylsulfonamido)-3-phenylbut-3-enoate (6):** Pale yellow oil, yield: 40.0%; IR (film): 3290, 3061, 3029, 2924, 2853, 1735, 1343, 1162, 813, 699 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.60 (d, *J*=8.0 Hz, 1H), 7.80 (d, *J*=8.0 Hz, 2H), 7.32 (d, *J*=8.0 Hz, 2H), 7.23 – 7.14 (m, 6H), 7.02 (d, *J*=8.0 Hz, 2H), 6.96 (d, *J*=8.2 Hz, 2H), 6.49 (d, *J*=8.2 Hz, 1H), 3.69 (t, *J*=8.0 Hz, 1H), 3.56 (s, 3H), 3.20 – 3.09 (m, 1H), 2.92 – 2.82 (m, 1H), 2.41 (s, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 174.9, 143.8, 140.8, 138.1, 137.5, 129.8, 128.8, 128.4, 128.3, 126.9, 126.8, 126.7, 126.6, 125.2, 119.0, 52.6, 50.3, 35.3, 21.5; HRMS (EI) calcd for C<sub>25</sub>H<sub>25</sub>NO<sub>4</sub>S<sup>+</sup> 435.1504, found 435.1036.

#### Synthesis of 1ba by DBU:



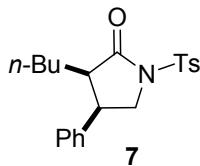
DCE (2.0 mL) was added to reaction flask charged with **6** (0.1 mmol). Then a solution of DBU (0.12 mmol) in DCE (0.5 ml) was added dropwise. The reaction was stirred at 60°C for 7.0 h, until TLC analysis showed that starting material was completely consumed. The solution of mixture was concentrated and then purified by flash chromatography to give the corresponding product **1ba**.

#### 7. Synthetic derivatization of 3-pyrrolin-2-one



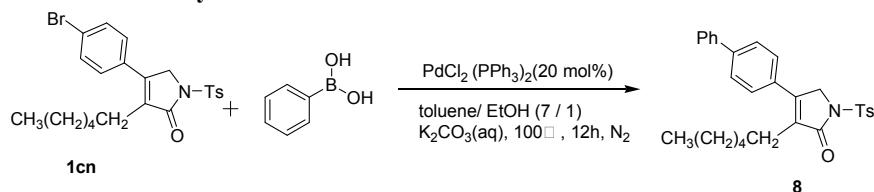
#### Synthesis of 7:<sup>[11]</sup>

A room temperature stirred mixture of **1aa** (140 mg, 0.38 mmol) and palladium on carbon (10%, 40.4 mg, 0.38 mmol) in ethanol (5 mL) and DCM (1 ml) was charged with hydrogen gas (6 atm). The mixture was stirred for 20 h during which time the hydrogen gas was replenished. The reaction mixture was then filtered through celite with the aid of ethanol. Removal of the solvent in vacuo gave a crude yellow oil. Purification of the crude material by flash chromatography (gradient: EtOAc to 1:20 MeOH/EtOAc) gave the product **7** as a yellow oil (98% yield).

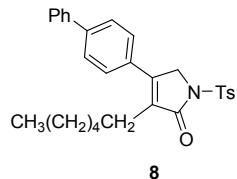


**3-butyl-4-phenyl-1-tosylpyrrolidin-2-one (7):** yellow oil, yield: 98%; IR (film): 2956, 2931, 2861, 1736, 1361, 1167, 814, 662 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.24 – 7.12 (m, 3H), 6.87 (d, *J* = 8.0 Hz, 2H), 4.22 – 4.13 (m, 1H), 4.03 – 3.95 (m, 1H), 3.56 – 3.52 (m, 1H), 2.81 – 2.70 (m, 1H), 2.47 (s, 3H), 1.28 – 0.85 (m, 6H), 0.73 – 0.64 (t, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 174.5, 145.1, 138.8, 135.0, 129.6, 128.6, 128.0, 127.3, 127.2, 52.0, 47.8, 40.8, 29.0, 25.0, 22.2, 21.6, 13.5; HRMS (EI) calcd for C<sub>21</sub>H<sub>25</sub>NO<sub>3</sub>S<sup>+</sup> 371.1555, found 371.1552.

**General Procedure for Synthesis of 8:**<sup>[13]</sup>

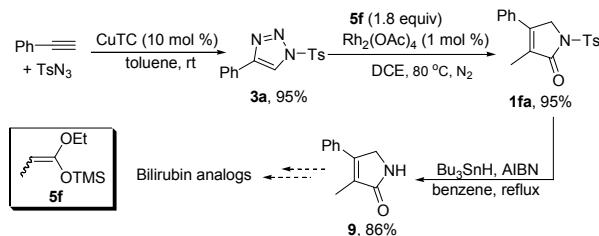


A mixture of phenylboronic acid (26.8 mg, 0.22 mmol), bis(-triphenylphosphine) palladium(II) chloride (12.6 mg, 0.02 mmol), **1cn** (0.1 mmol), toluene (3.5 mL), ethanol (0.5 mL) and saturated solution of K<sub>2</sub>CO<sub>3</sub> (0.5 mL) were heated at 100 °C with magnetic stirring under nitrogen atmosphere. Some solid began to appear after 2 h and heating was continued for another 10 h. The reaction mixture was filtered through a short plug of silica gel. The solution of mixture was concentrated and then purified by flash chromatography to give the corresponding product **8**.



**4-(4-phenyl)-3-hexyl-1-tosyl-1H-pyrrol-2(5H)-one (8):** yellow oil, yield: 75%; IR (film): 2953, 2925, 2855, 1717, 1633, 766 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.47 (dd, *J* = 8.0, 4.8 Hz, 4H), 7.40 (d, *J* = 7.2 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 2H), 4.66 (s, 2H), 2.46 – 2.40 (m, 5H), 1.57 – 1.48 (m, 2H), 1.29 (m, 6H), 0.84 (t, *J* = 6.8 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.5, 149.4, 145.0, 142.7, 139.8, 135.8, 133.2, 131.1, 129.7, 129.0, 128.1, 128.0, 127.7, 127.6, 127.0, 51.5, 31.4, 29.3, 27.8, 24.6, 22.5, 21.6, 14.0. HRMS (EI) calcd for C<sub>29</sub>H<sub>31</sub>NO<sub>3</sub>S<sup>+</sup> 473.2025, found 473.2022.

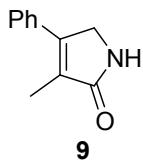
**Synthesis of 9:**<sup>[12]</sup>



A flask was charged with copper (I) thiophene-2-carboxylate (CuTC, 0.1 equiv in regards to alkyne), toluene (20 mL), and the phenylacetylene (1 equiv). The reaction mixture was cooled in an ice-water bath. Subsequently, the TsN<sub>3</sub> (1 equiv) was added slowly as the limiting reagent to avoid a run-away exotherm, and the reaction mixture allowed to warm to room temperature and stirred overnight. The reaction was diluted with saturated aq NH<sub>4</sub>Cl and extracted into DCM (2 × 20 mL). The combined organics were dried (Na<sub>2</sub>SO<sub>4</sub>) and filtered through celite. The eluent was concentrated in vacuo. The obtained crude product was purified by SiO<sub>2</sub>-column chromatography (PE: EA = 30:1) to give the desired product **3a**.

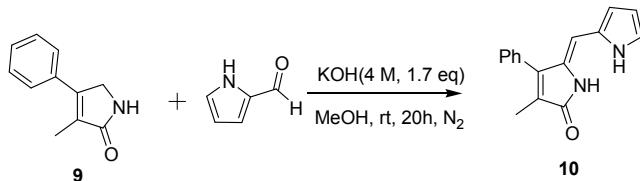
DCE (3.0 mL) was added to reaction flask charged with Rh<sub>2</sub>(OAc)<sub>4</sub> (4.5 mg, 1 mol %), 4-phenyl-1-tosyl-1H-1,2,3-triazole **3a** (1.0 mmol). Then a solution of silyl ketene acetals **5f** (1.8 mmol) in DCE (4.0 mL) was added dropwise. The reaction was stirred at 80 °C for 10 h. The reaction mixture was filtered through a short plug of silica gel. The solution of mixture was concentrated and then purified by flash chromatography to give the corresponding product **1fa**.

The solution of **1fa** (0.074 g, 0.20 mmol) in dry benzene (7 mL) was heated to reflux under nitrogen atmosphere, and Bu<sub>3</sub>SnH (0.12 mL, 0.43 mmol) and AIBN (0.007g, 0.04 mmol) in dry benzene (5 mL) were added as a solution. The reaction was stirred at 95 °C until TLC analysis showed that starting material was completely consumed. Then the solvent was removed in vacuo to afford a colorless oil liquid. Diethyl ether (20 mL), saturated KF (5 mL), and water (20 mL) were added, and the resulting mixture was stirred overnight. The water layer was extracted with benzene. The combined organic layer was dried (Na<sub>2</sub>SO<sub>4</sub>), and the solution of mixture was concentrated and then purified by flash chromatography to give the corresponding product **9**.

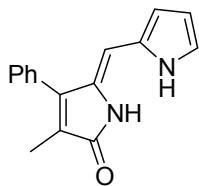


**3-methyl-4-phenyl-1*H*-pyrrol-2(*5H*)-one(9):** White solid, yield: 86%; mp 155.3 – 156.4 °C; IR (KBr): 3430, 2925, 2855, 2283, 1716, 1362, 1169, 763, 696 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.99 – 7.86 (br, 1H), 7.40 – 7.34 (m, 4H), 7.36 – 7.27 (m, 1H), 4.20 (s, 2H), 2.03 (s, 3H). <sup>13</sup>C NMR (100 MHz, Chloroform-d) δ 176.2, 149.0, 133.8, 129.2, 128.8, 128.7, 127.3, 48.1, 10.1.

#### Synthesis of **10**:<sup>[14]</sup>



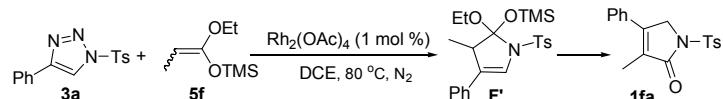
3-methyl-4-phenyl-1*H*-pyrrol-2(*5H*)-one (34.6 mg, 0.2 mmol) and pyrrole-2-carbaldehyde (23.8 mg, 0.25 mmol) were dissolved in methanol (2 mL) under nitrogen atmosphere. To the mixture was added 4 M potassium hydroxide (0.85 mL), and the reaction mixture was stirred at room temperature for 20 h. The yellow precipitate obtained was collected by vacuum filtration and washed with cold methanol (5 mL). The crude product was recrystallized from methanol and water and dried in vacuo to give product **10**.



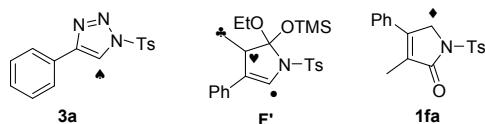
**10**

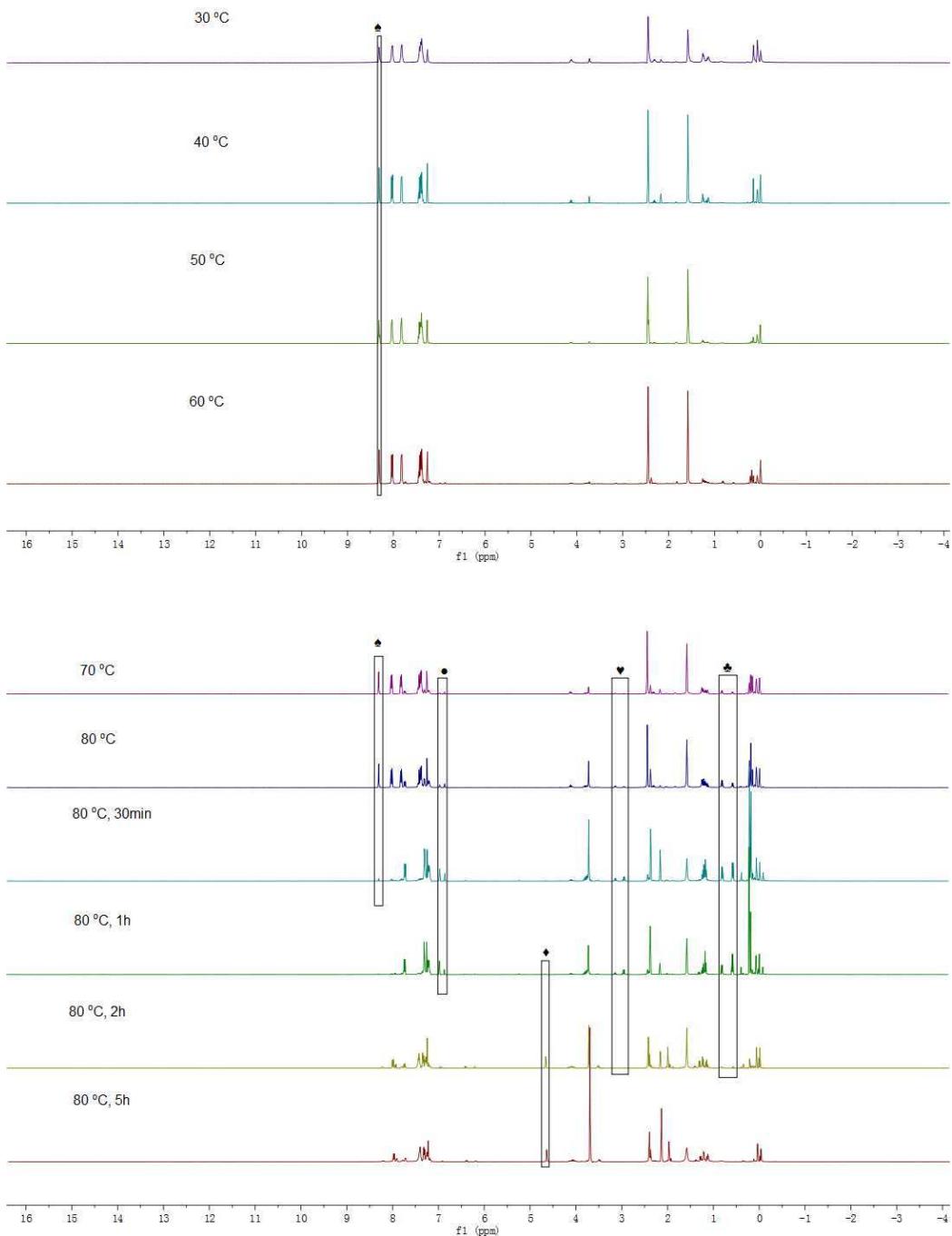
**2-methyl-3-phenyl-(10*H*)-dipyrrin-1-one (**10**):** Yellow solid, yield: 45%; mp 202.5 – 205.4 °C; IR (KBr): 3444, 3344, 2923, 1669, 1634, 1160, 788, 686 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 11.40 (br, 1H), 10.84 (br, 1H), 7.54 – 7.43 (m, 3H), 7.35 (d, *J* = 7.2 Hz, 2H), 7.10 – 7.08 (m, 1H), 6.42 – 6.36 (m, 1H), 6.28 – 6.25 (m, 1H), 6.05 (s, 1H), 2.01 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.6, 146.8, 132.2, 129.8, 129.7, 128.5, 128.4, 127.6, 125.4, 123.8, 116.8, 110.2, 107.3, 8.9. HRMS (EI) calcd for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sup>+</sup> 250.1106, found 250.1103.

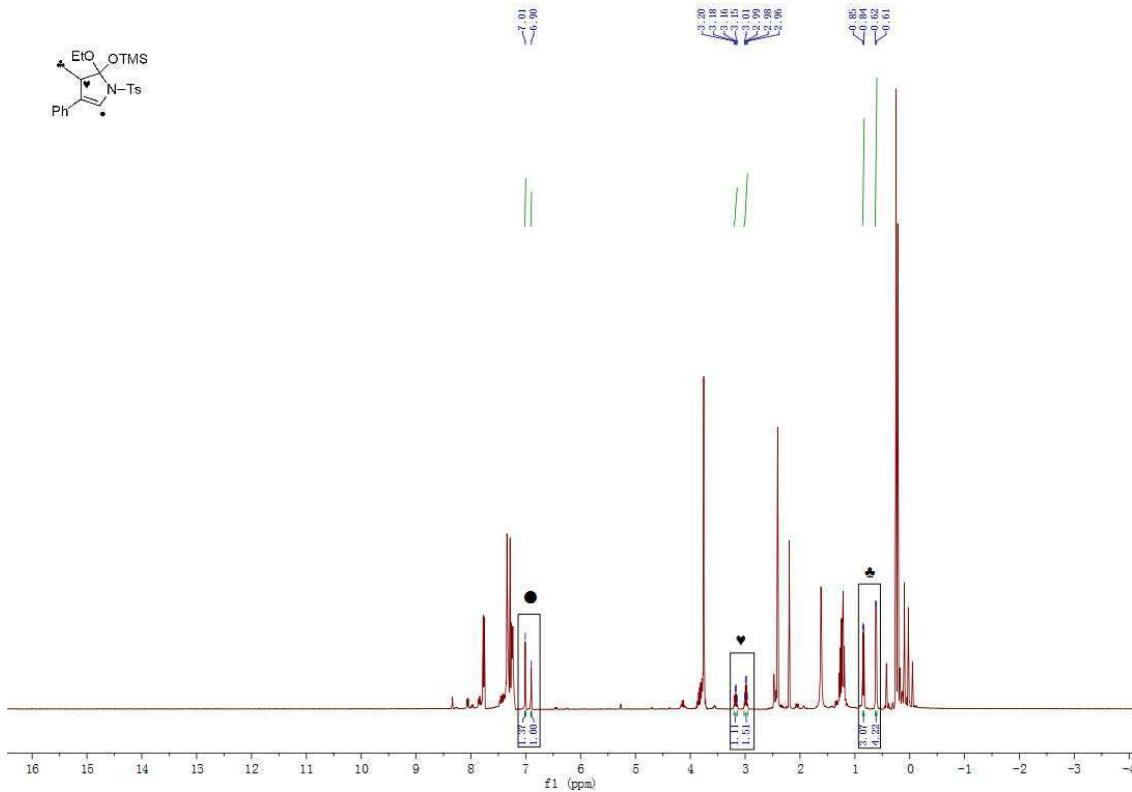
## 8. NMR studies



**The procedure of Rh<sub>2</sub>(OAc)<sub>4</sub>-catalyzed reaction of **3a** with **5f** was monitored by <sup>1</sup>H NMR (400 MHz) in DCE:** Under a nitrogen atmosphere, DCE (3.0 mL) was added to reaction flask charged with Rh<sub>2</sub>(OAc)<sub>4</sub> (1.8 mg, 1 mol %), 1-sulfonyl-1,2,3-triazoles **3** (0.4 mmol). Then a solution of silyl ketene acetals **5f** (0.72 mmol) in DCE (2.0 mL) was added dropwise. The reaction was stirred at 30°C, 40°C, 50°C, 60°C, 70°C, 80°C. The sample of the reaction mixture was obtained by injection syringe, concentrated in vacuo and then monitored by <sup>1</sup>H NMR in CDCl<sub>3</sub>.





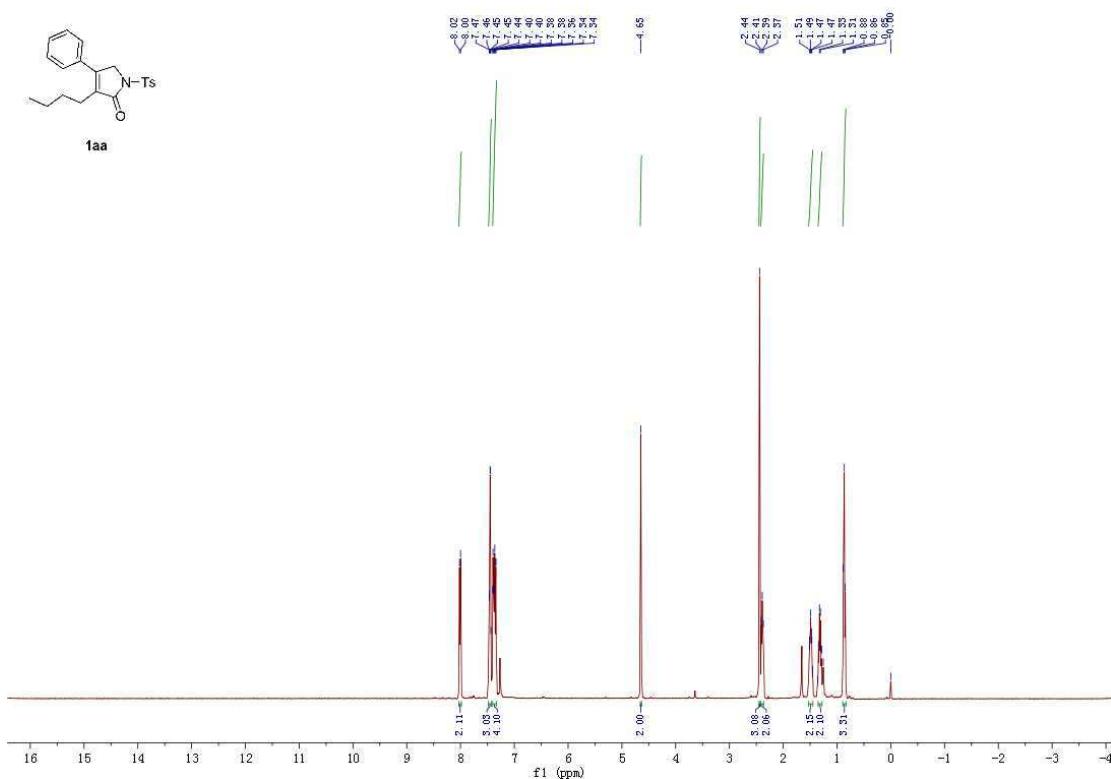


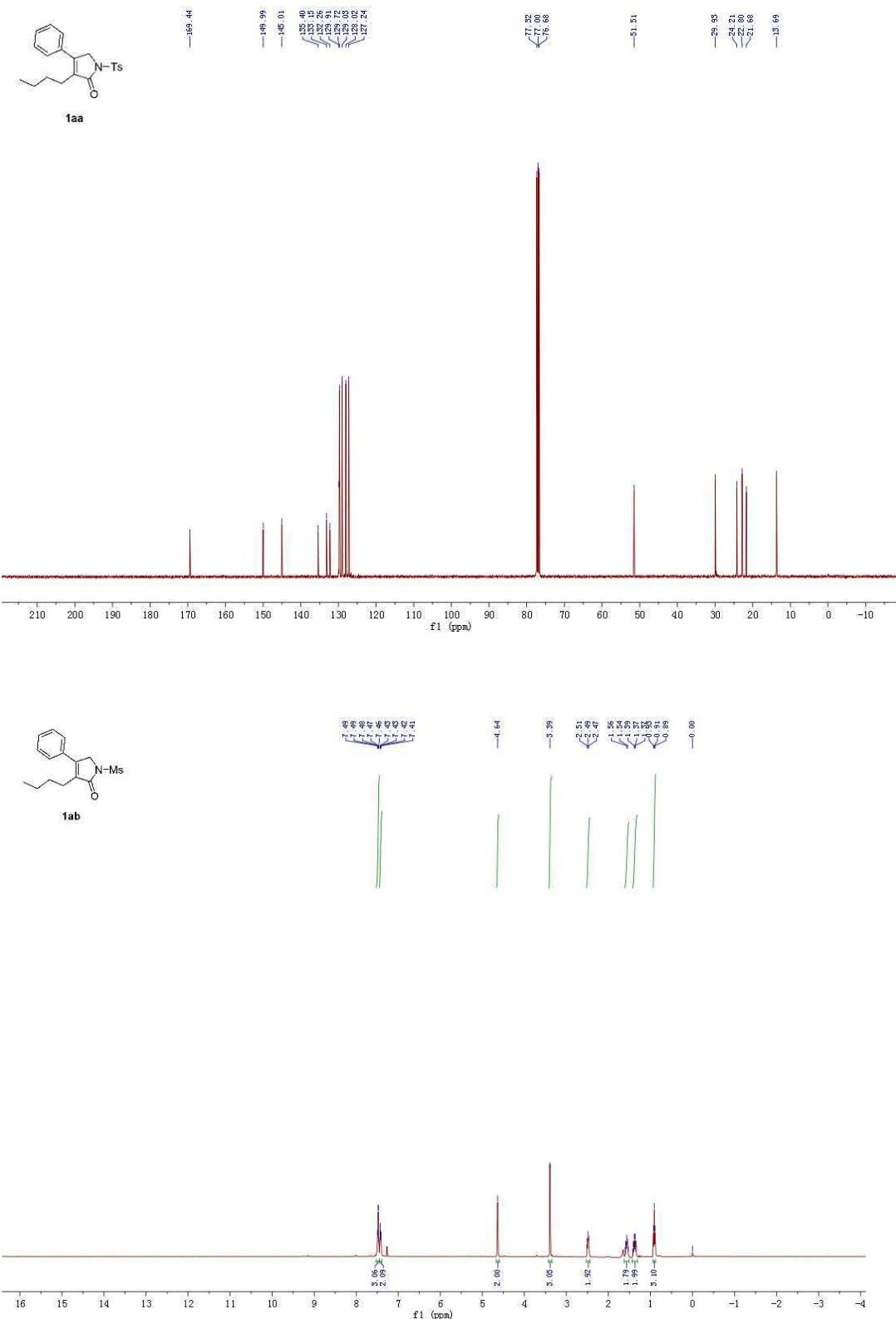
## 9. References

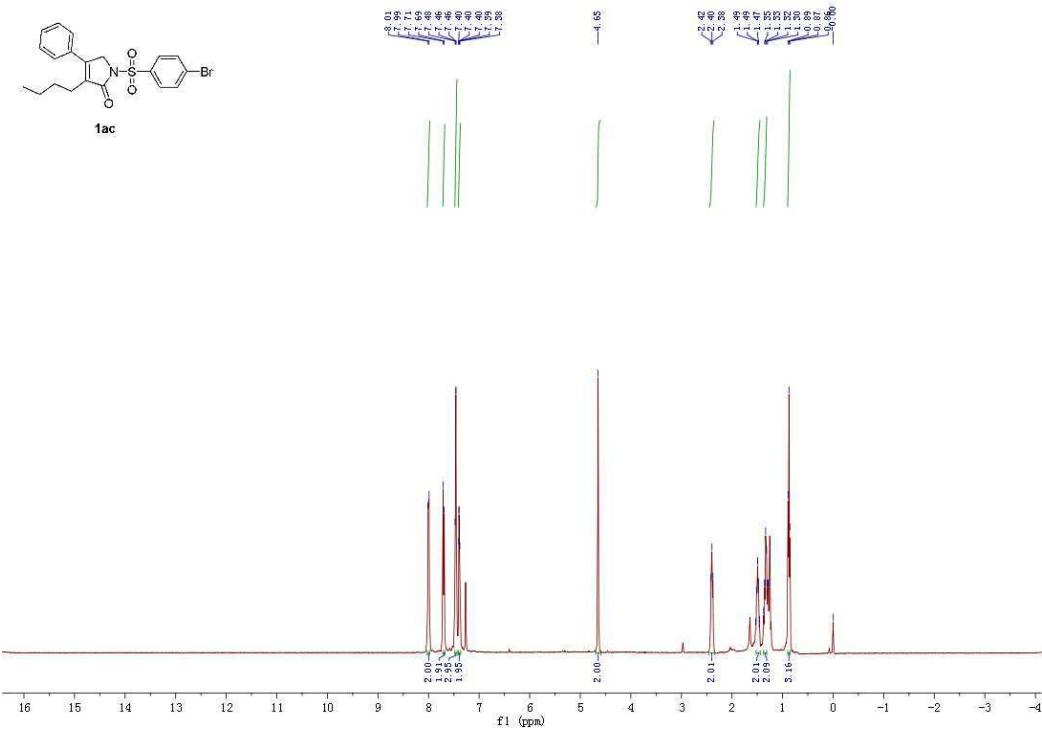
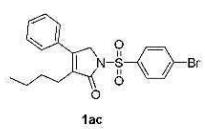
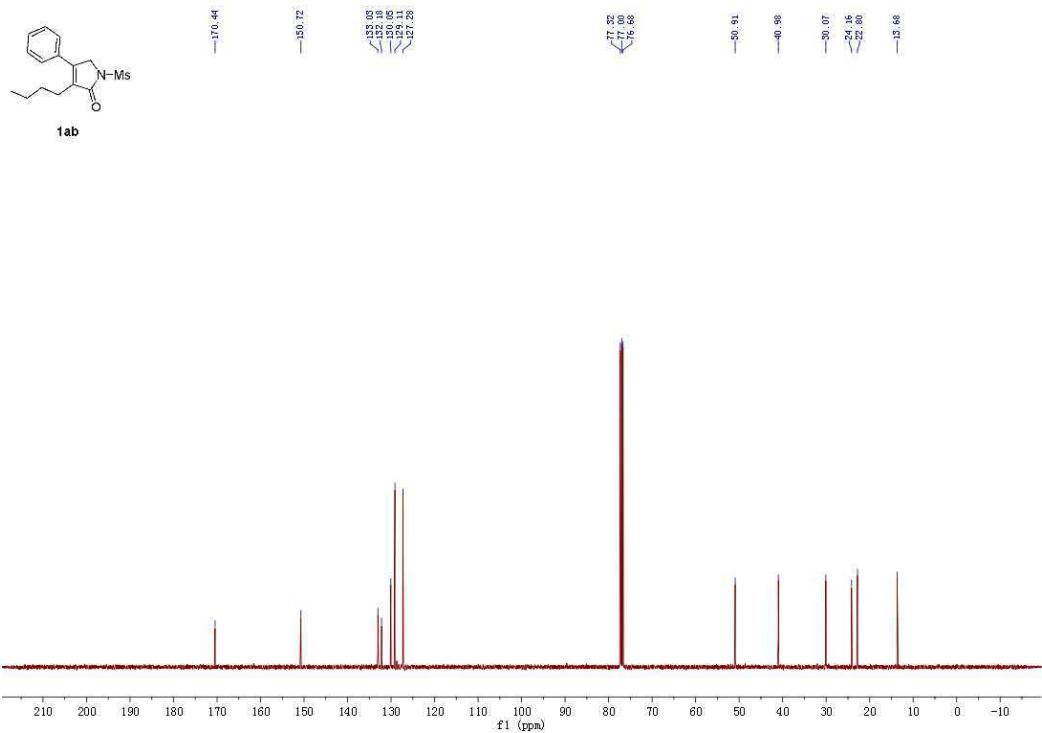
- [1] Miura, T.; Morimoto, M.; Murakami, M. *Org. Lett.* **2006**, *8*, 5215.
- [2] Oisaki, K.; Suto, Y.; Kanai, M.; Shibasaki, M. *J. Am. Chem. Soc.* **2003**, *125*, 5644.
- [3] Raushel, J.; Fokin, V. V. *Org. Lett.* **2010**, *12*, 4952.
- [4] Chuprakov, S.; Kwok, S. W.; Zhang, L.; Lercher, L.; Fokin, V. V. *J. Am. Chem. Soc.* **2009**, *131*, 18034.
- [5] Miura, T.; Biyajima, T.; Fujii, T.; Murakami, M. *J. Am. Chem. Soc.* **2012**, *134*, 194.
- [6] Horneff, T.; Chuprakov, S.; Chernyak, N.; Gevorgyan, V.; Fokin, V. V. *J. Am. Chem. Soc.* **2008**, *130*, 14972.
- [7] Wang, F.; Fu, H.; Jiang, Y.; Zhao, Y. *Adv. Synth. Catal.* **2008**, *350*, 1830.
- [8] Parr, B. T.; Green, S. A.; Davies, H. M. L. *J. Am. Chem. Soc.* **2013**, *135*, 4716.
- [9] Chuprakov, S.; Worrell, B. T.; Selander, N.; Sit, R. K.; Fokin, V. V. *J. Am. Chem. Soc.* **2014**, *136*, 195.

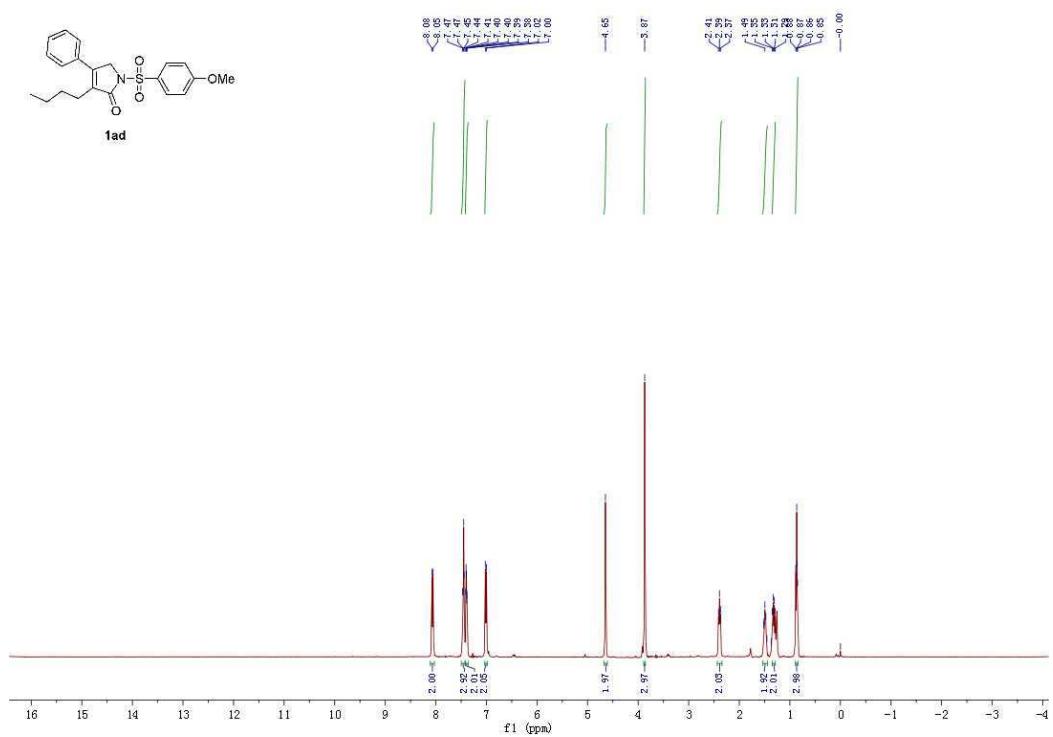
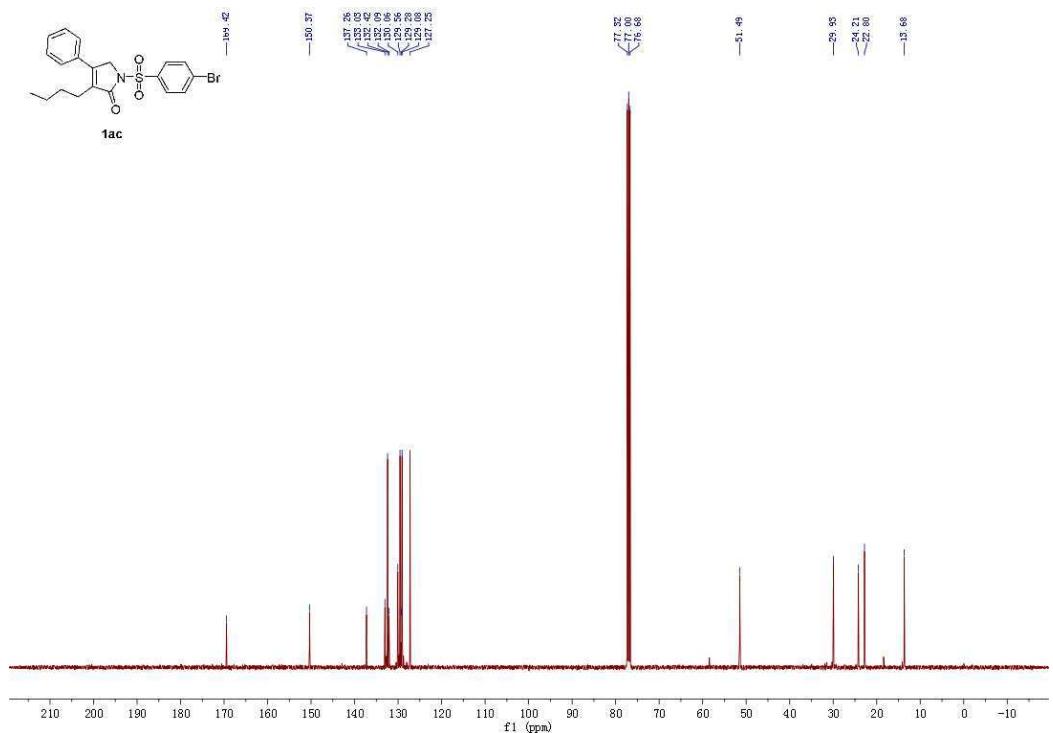
- [10] Liu, R.; Zhang, M.; Winston, M. G.; Tang, W. *Chem. Commun.*, **2013**, 49, 4376.
- [11] Sarah J. P.; Opalka, Y. S.; Pelkey, E. T. *Tetrahedron Lett.* **2007**, 48, 827.
- [12] Xu, Z.; Lu, X. *J. Org. Chem.* **1998**, 63, 5031.
- [13] Wan, W.; Du, H.; Wang, J.; Le, Y.; Jiang, H.; Chen, H.; Hao, S. Z. *Dyes and Pigments*. **2013**, 96, 642.
- [14] Huggins, M. T.; Musto, C.; Munro, L.; Catalano, V. J. *Tetrahedron* **2007**, 63, 12994.

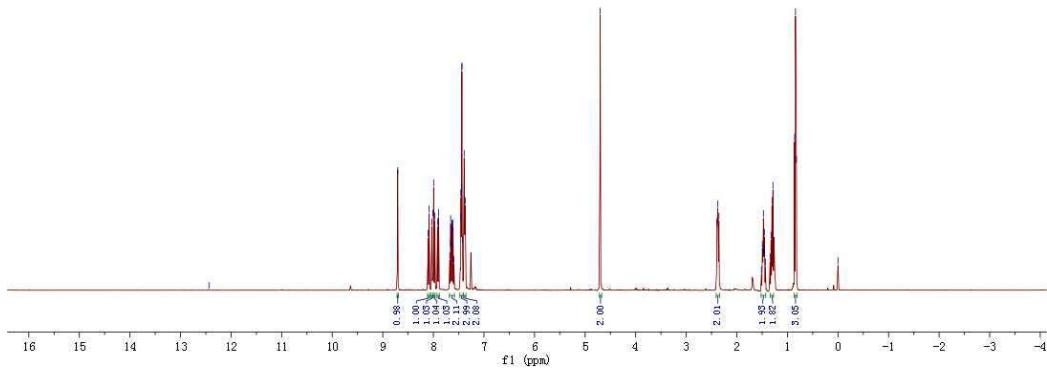
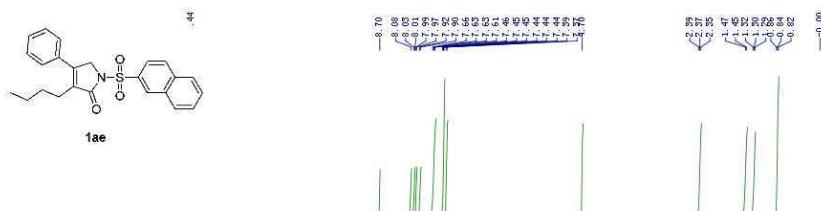
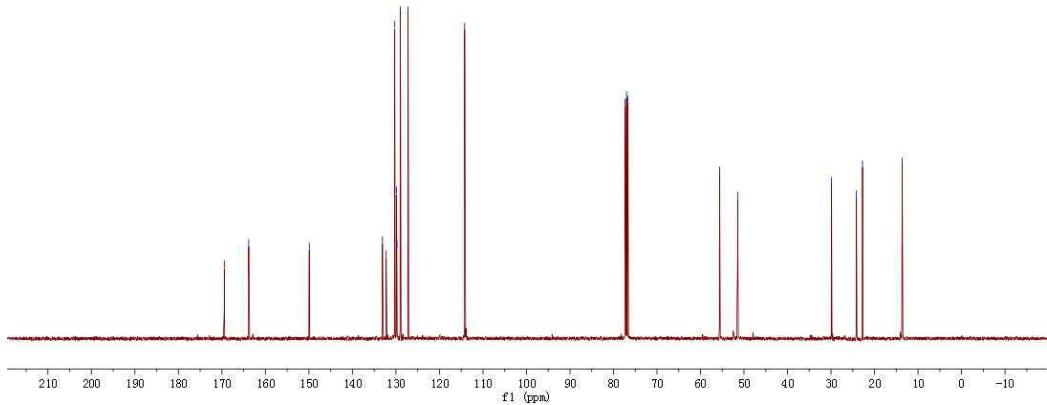
## 9. $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra for New Compounds

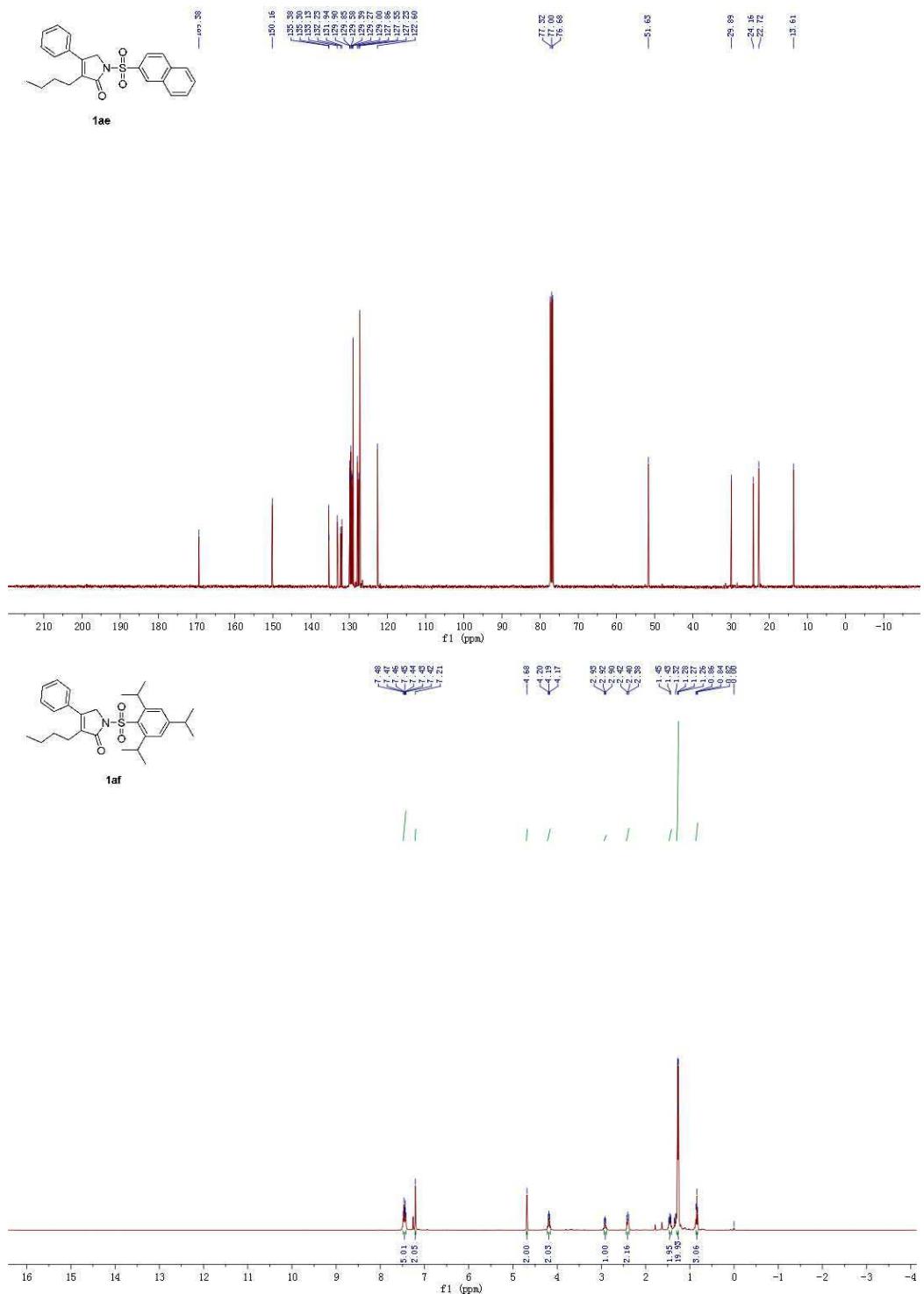


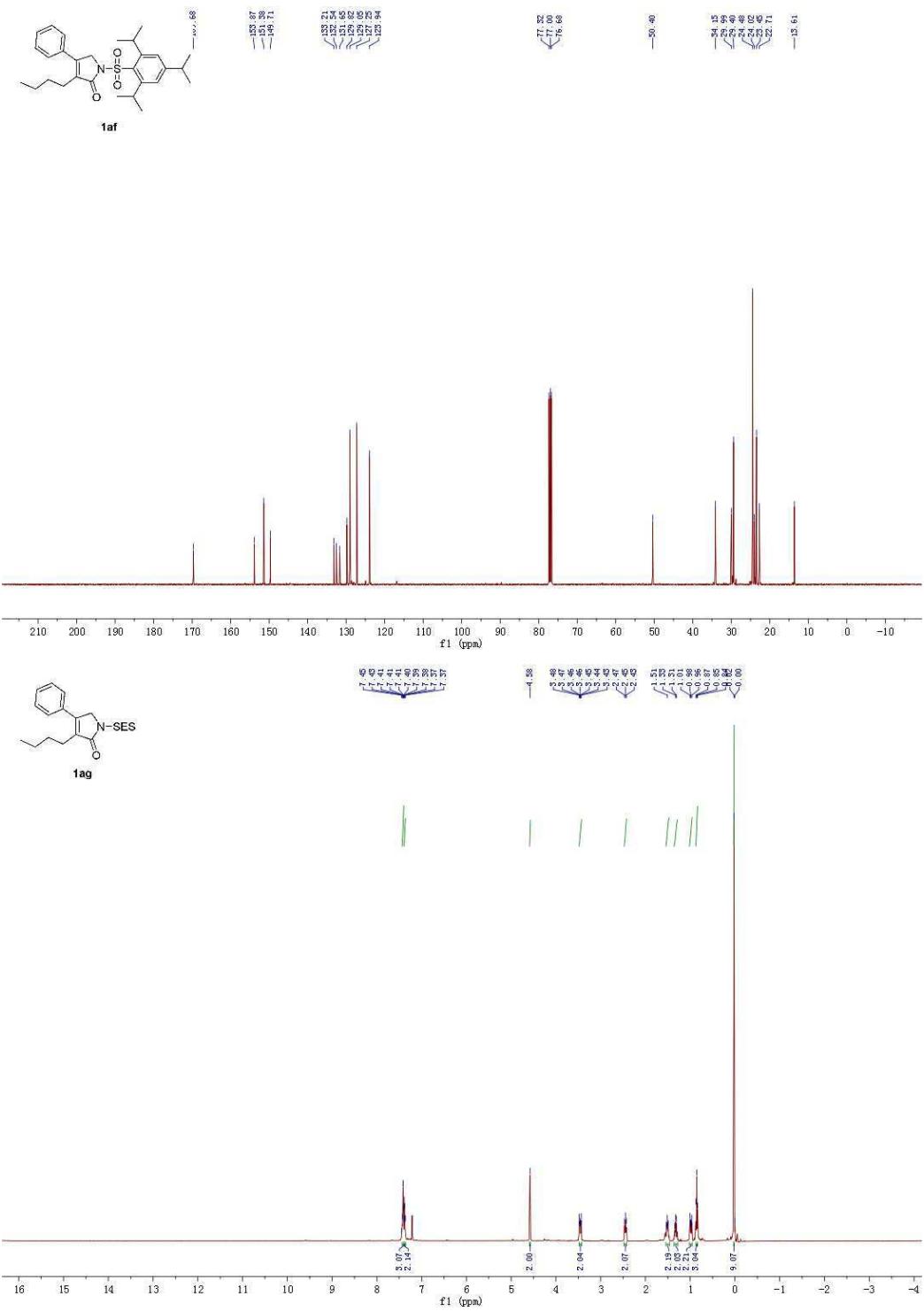


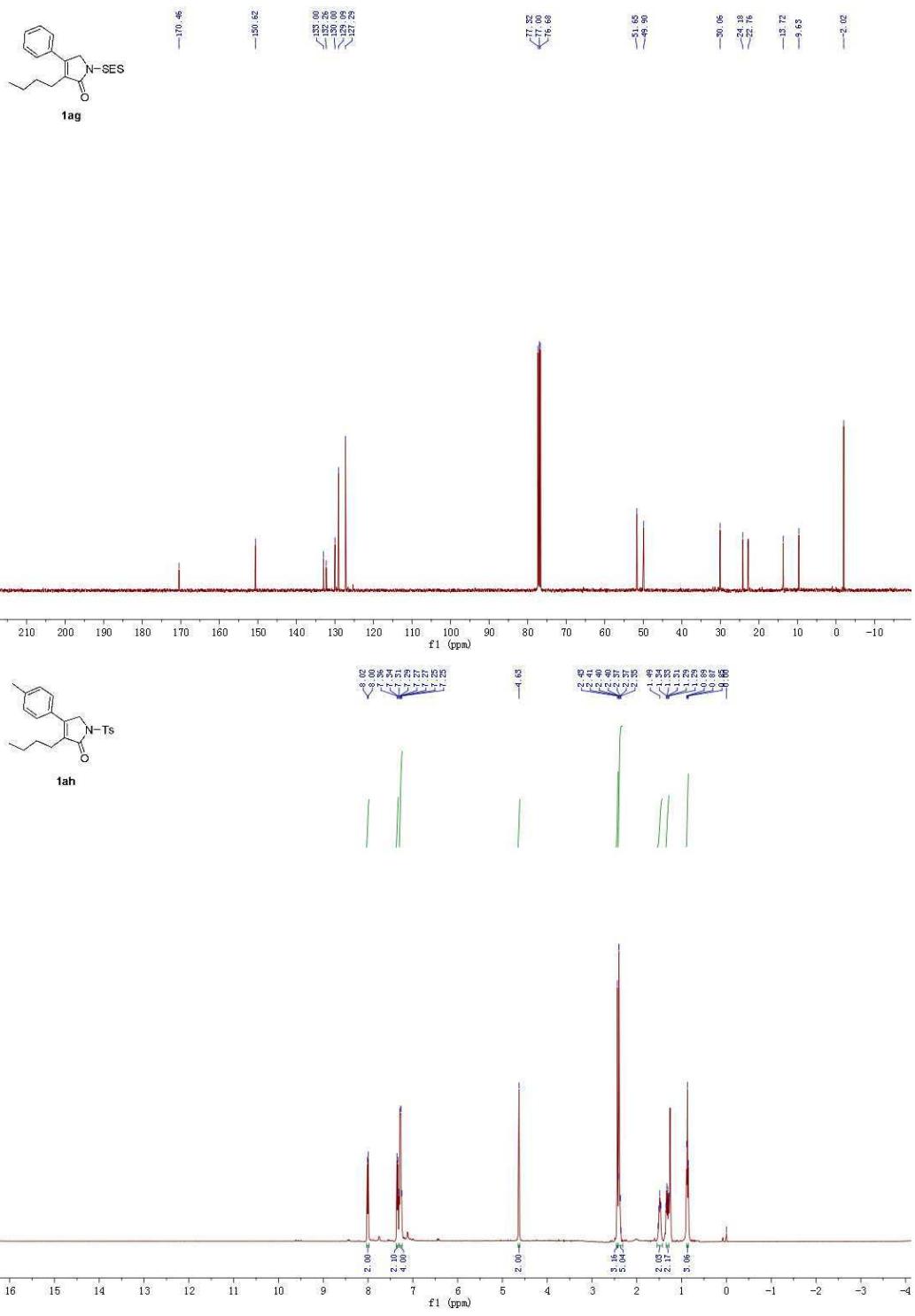


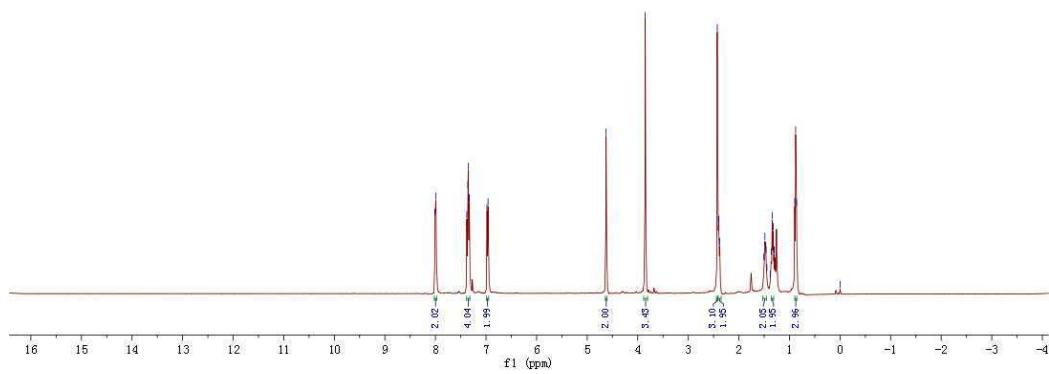
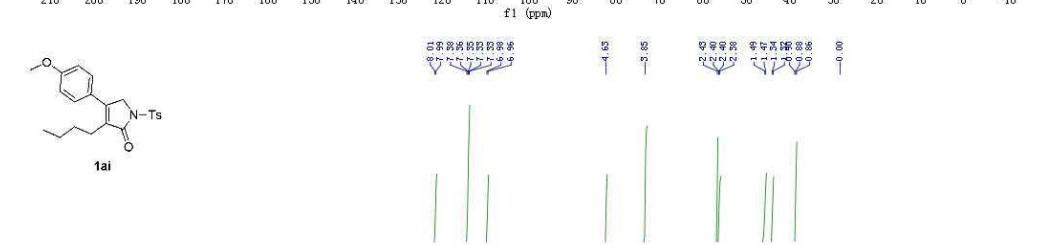
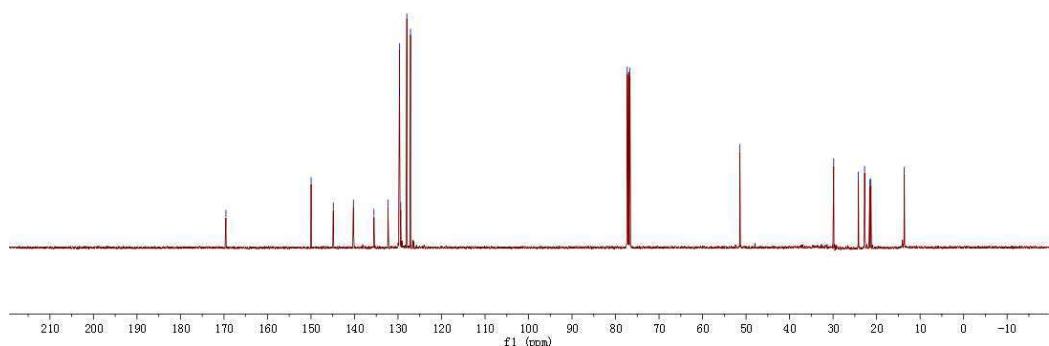


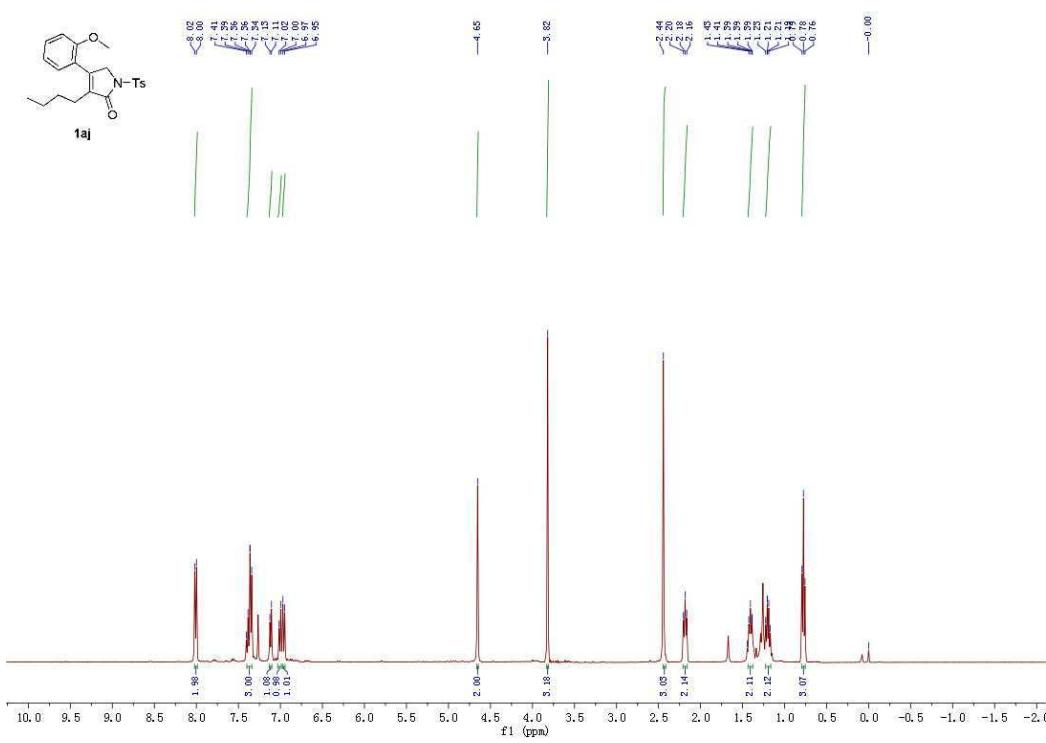
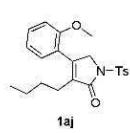
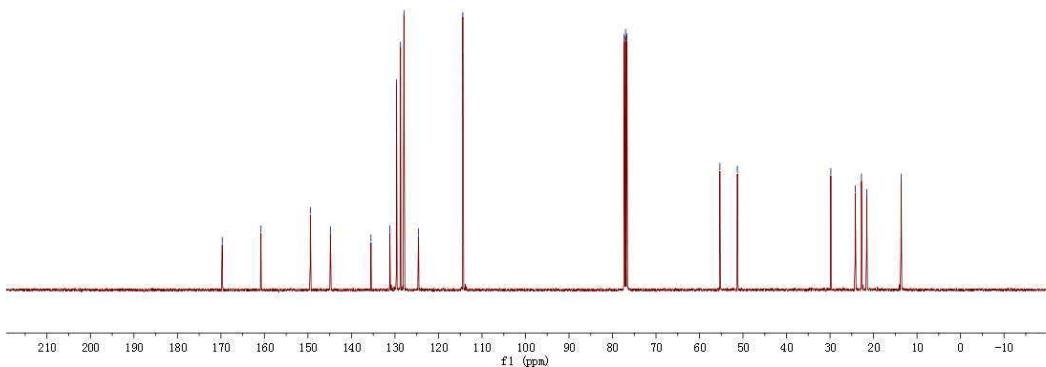
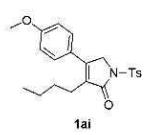


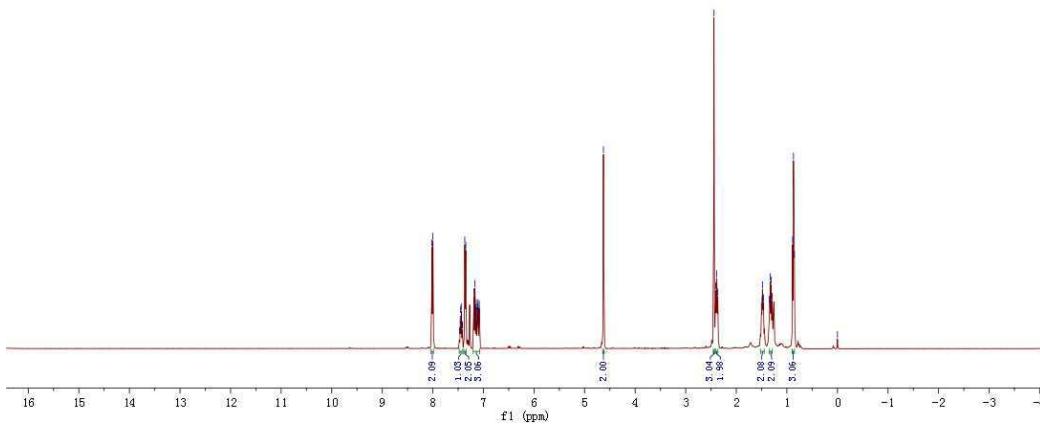
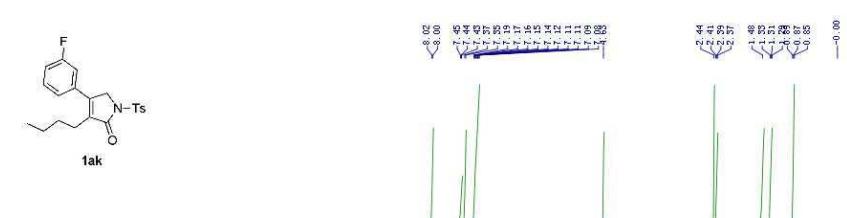
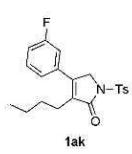
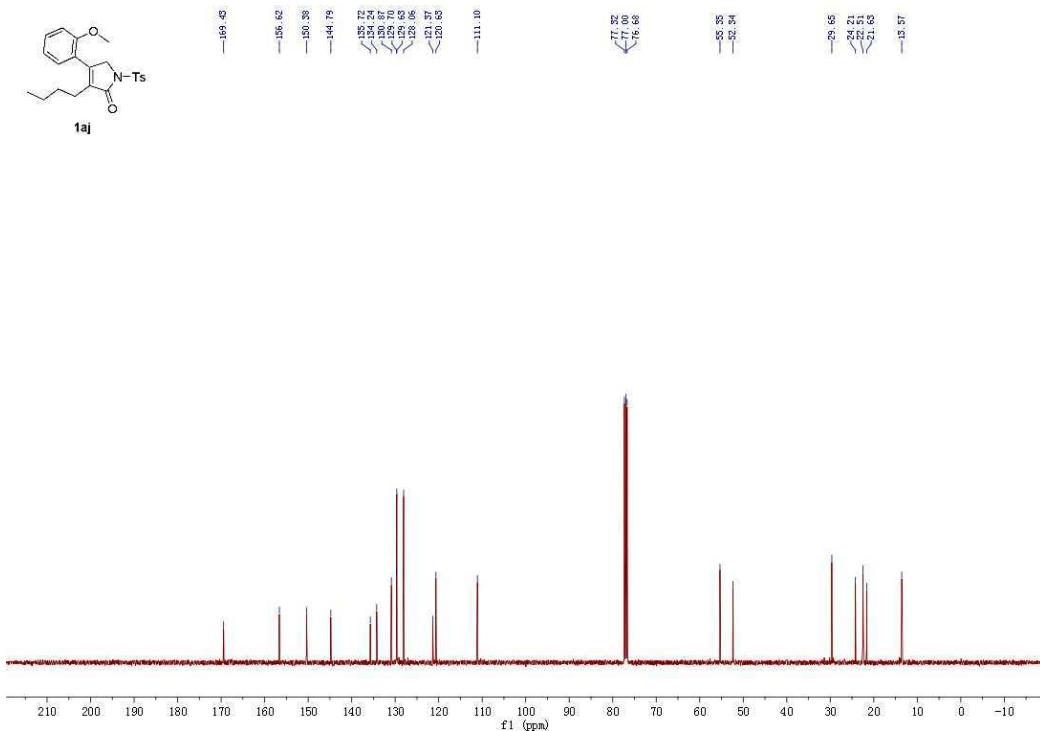
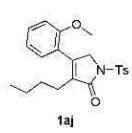


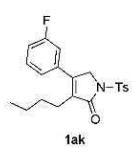




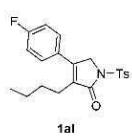
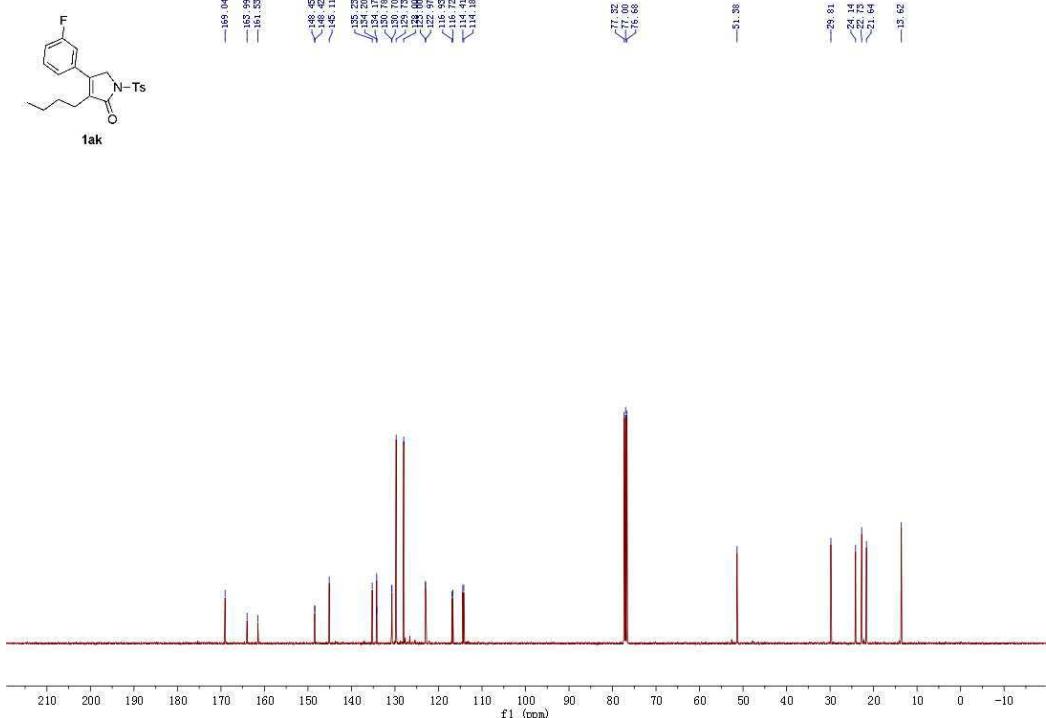




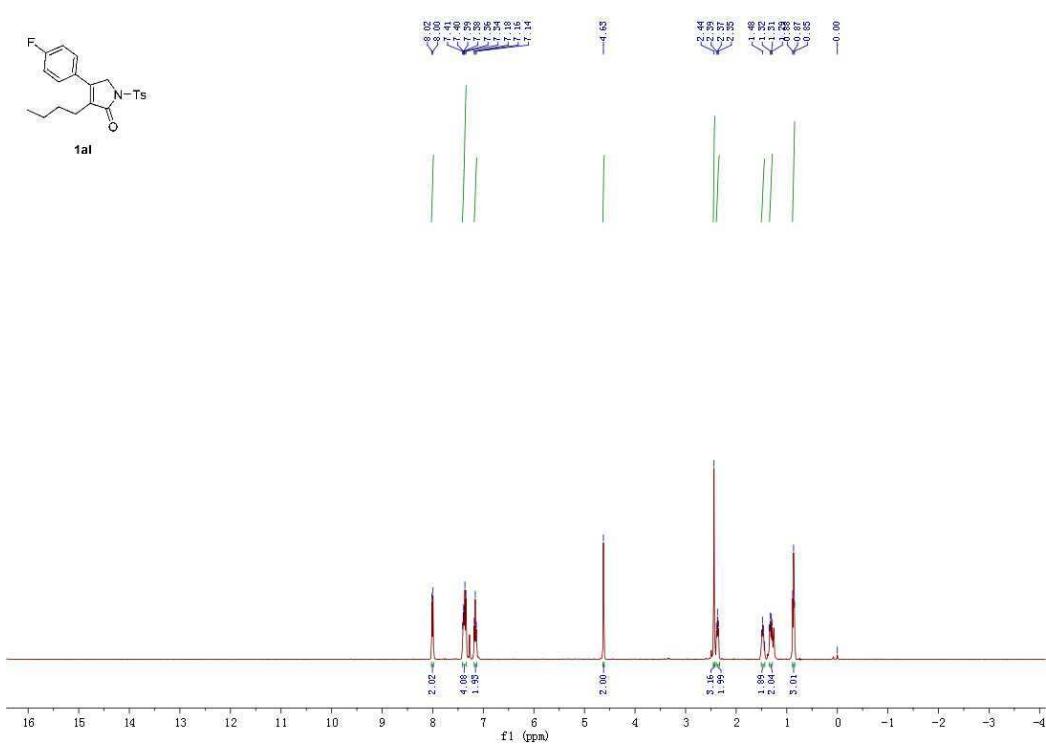


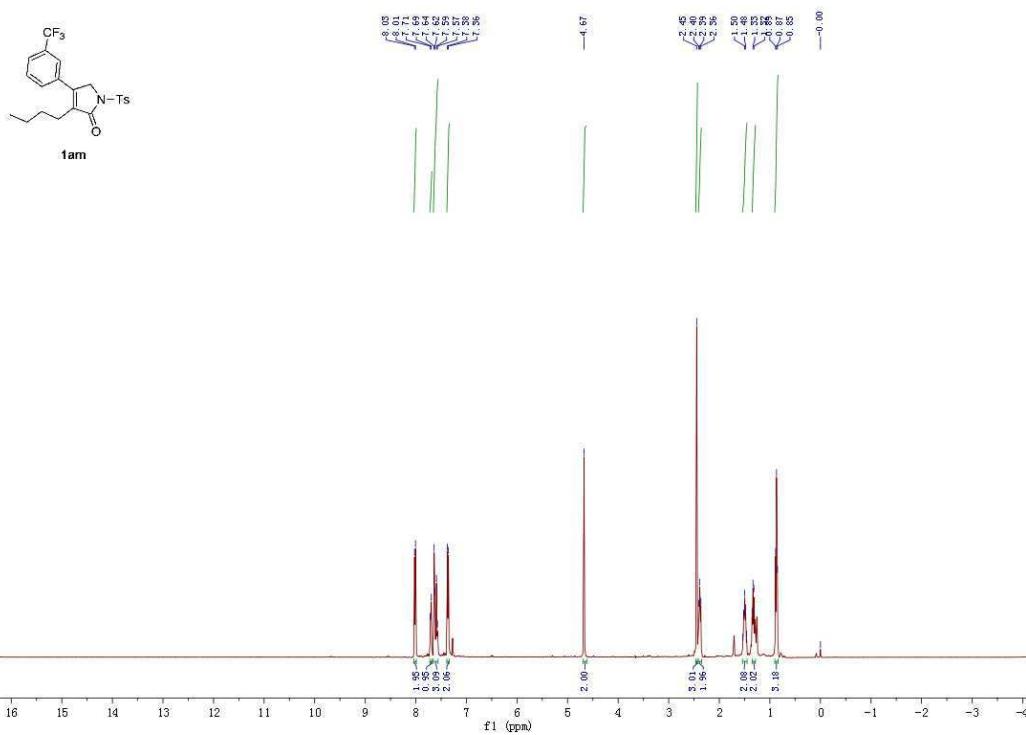
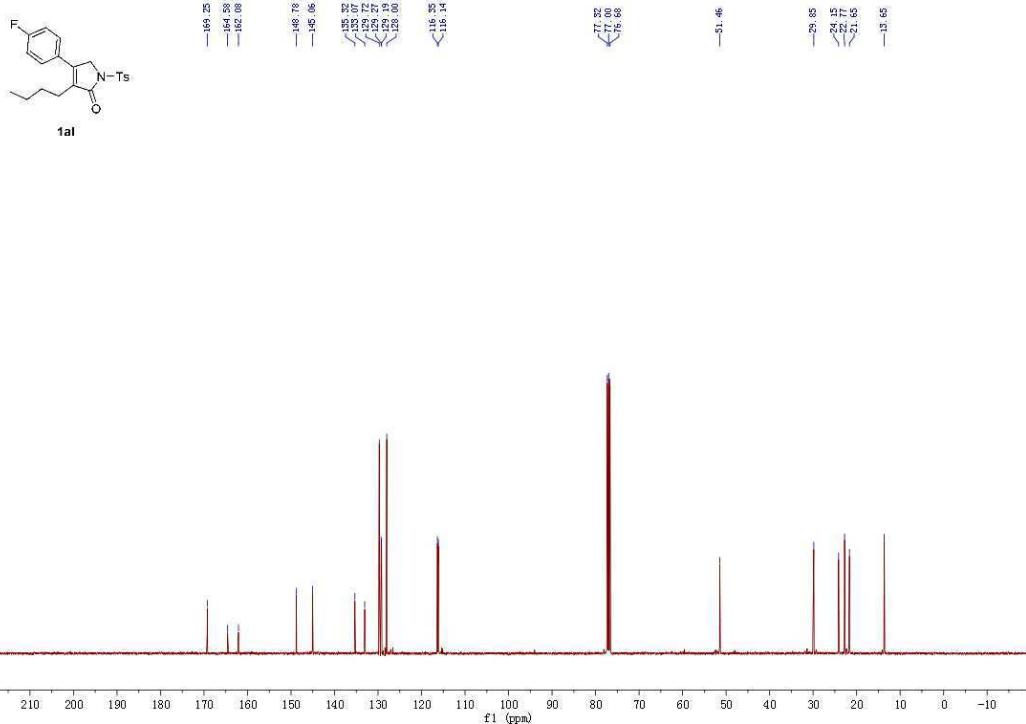


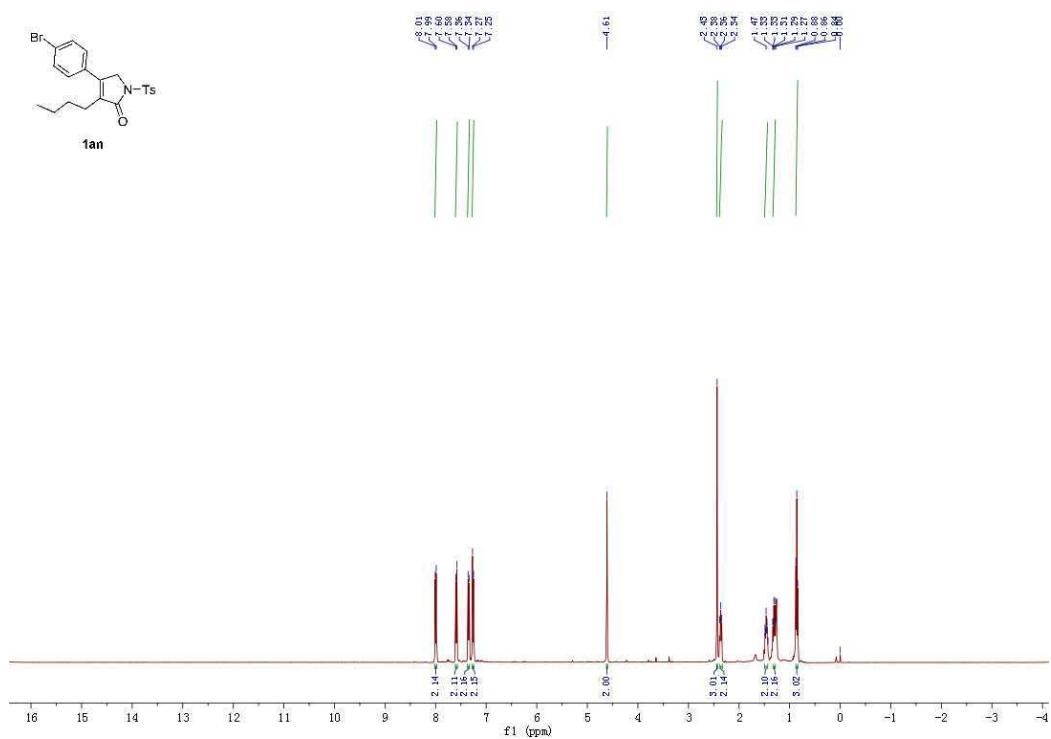
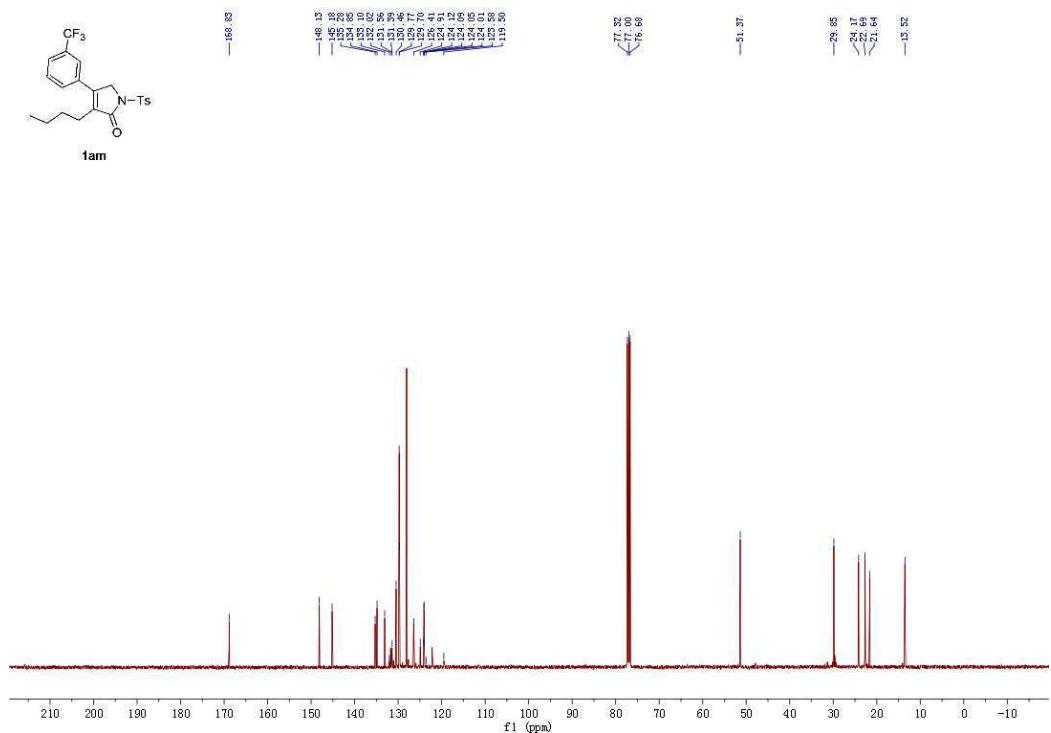
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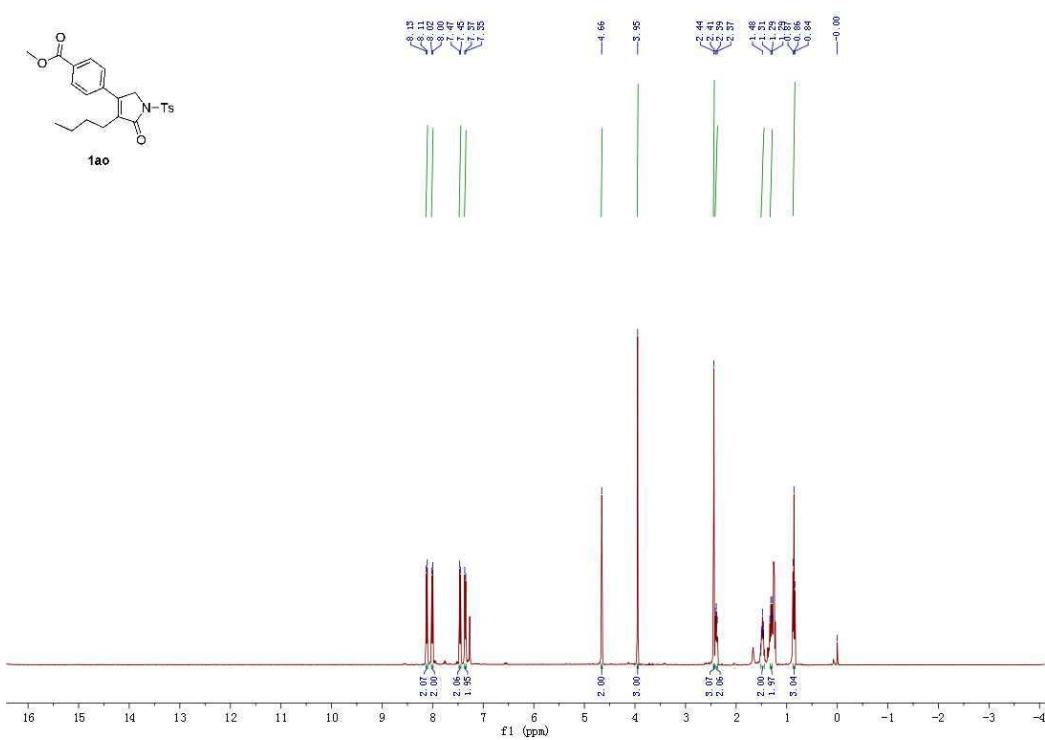
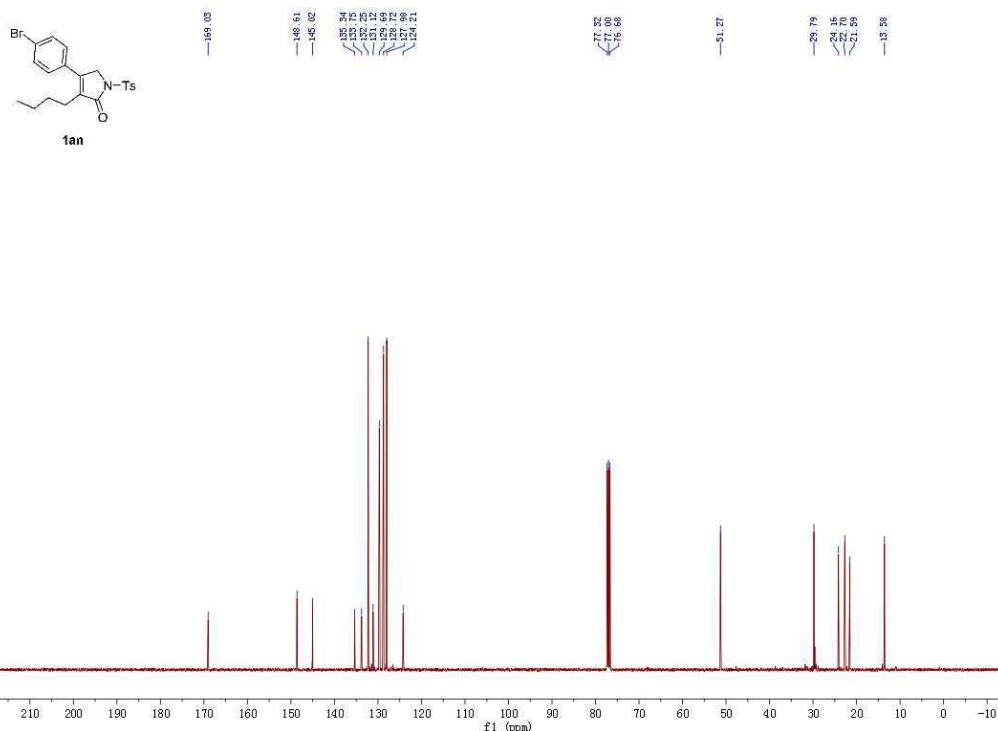


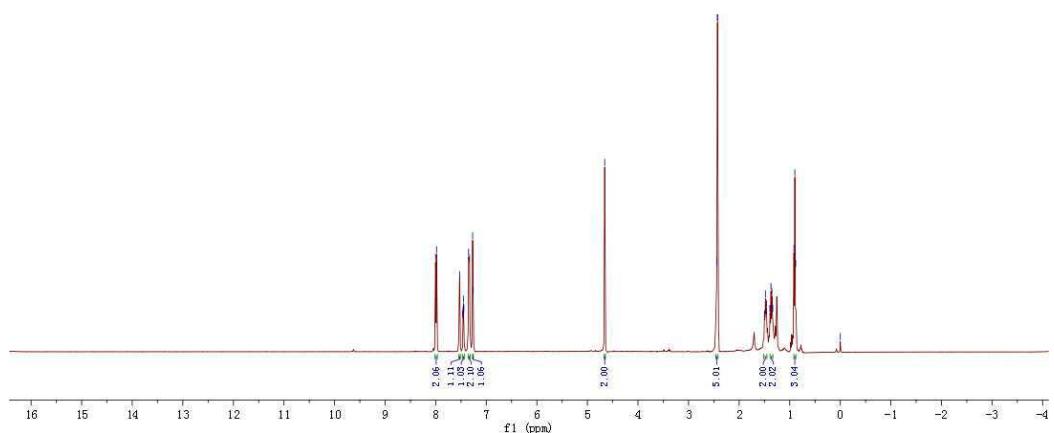
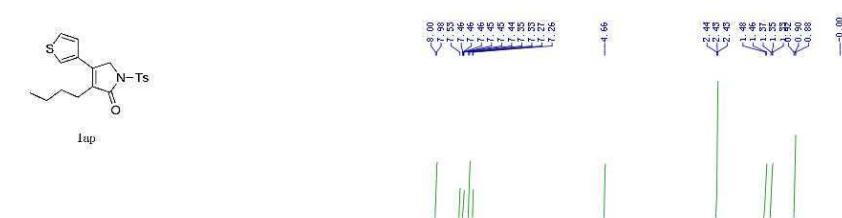
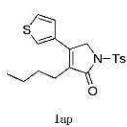
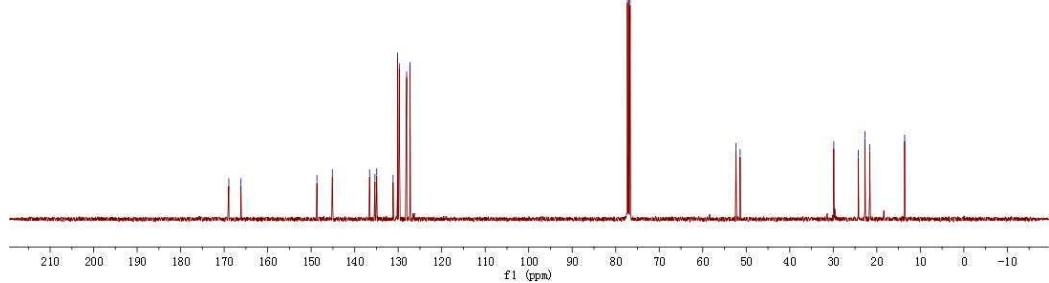
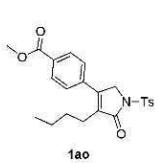
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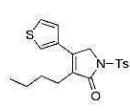




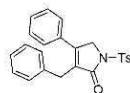
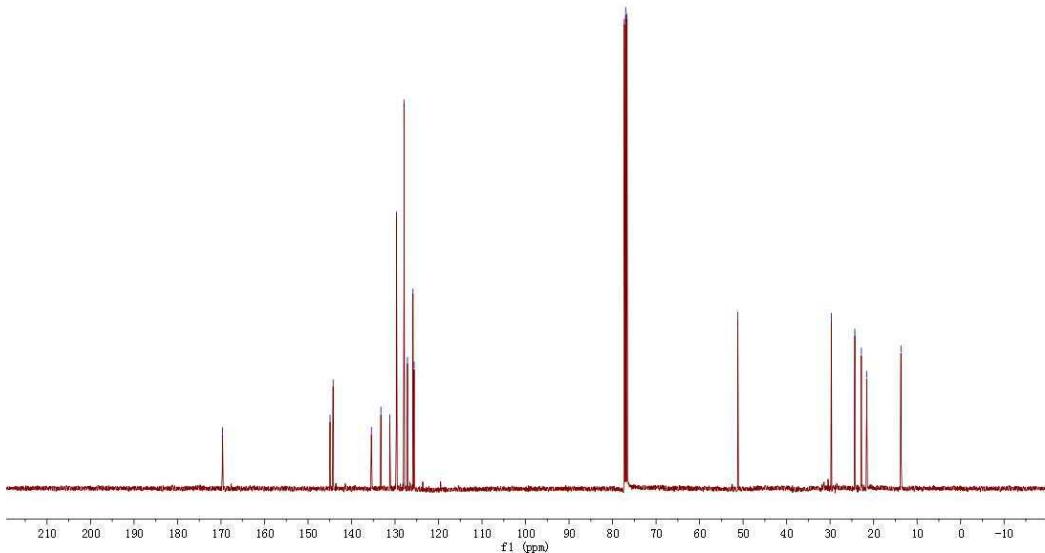




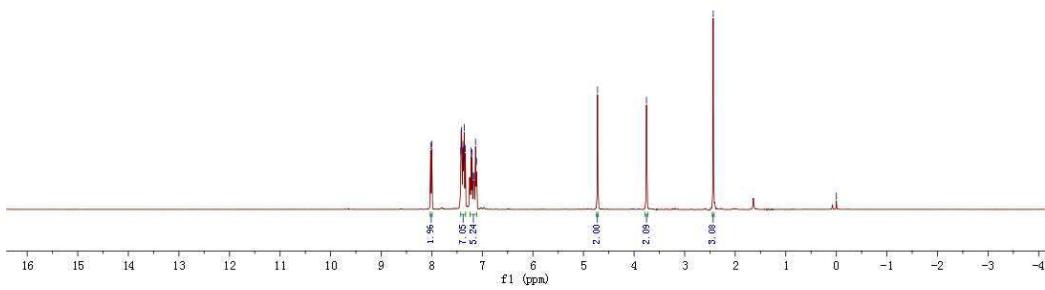
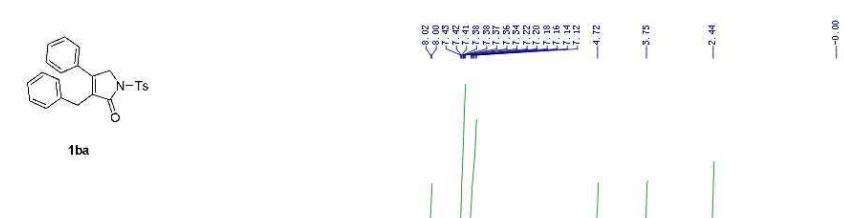


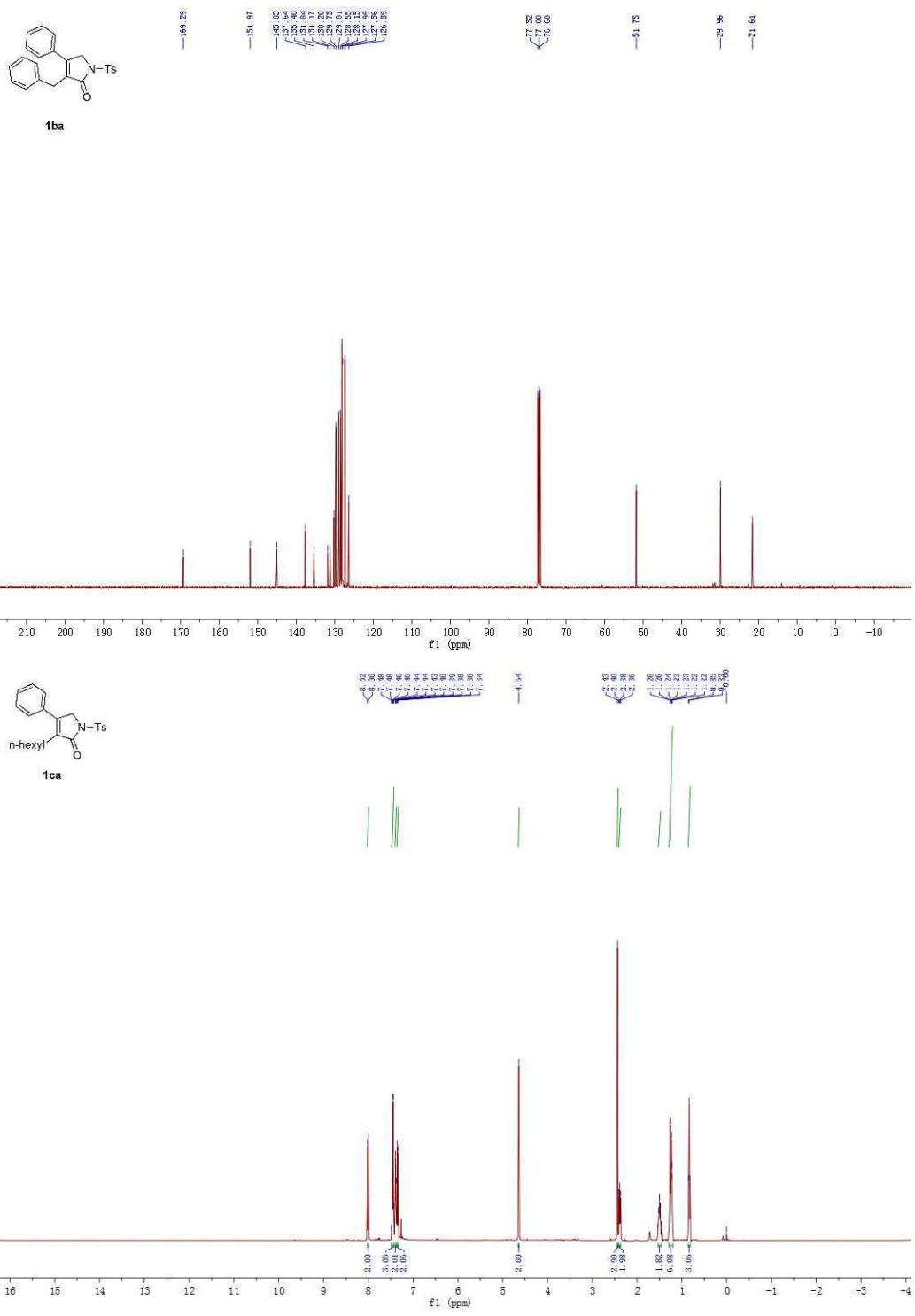


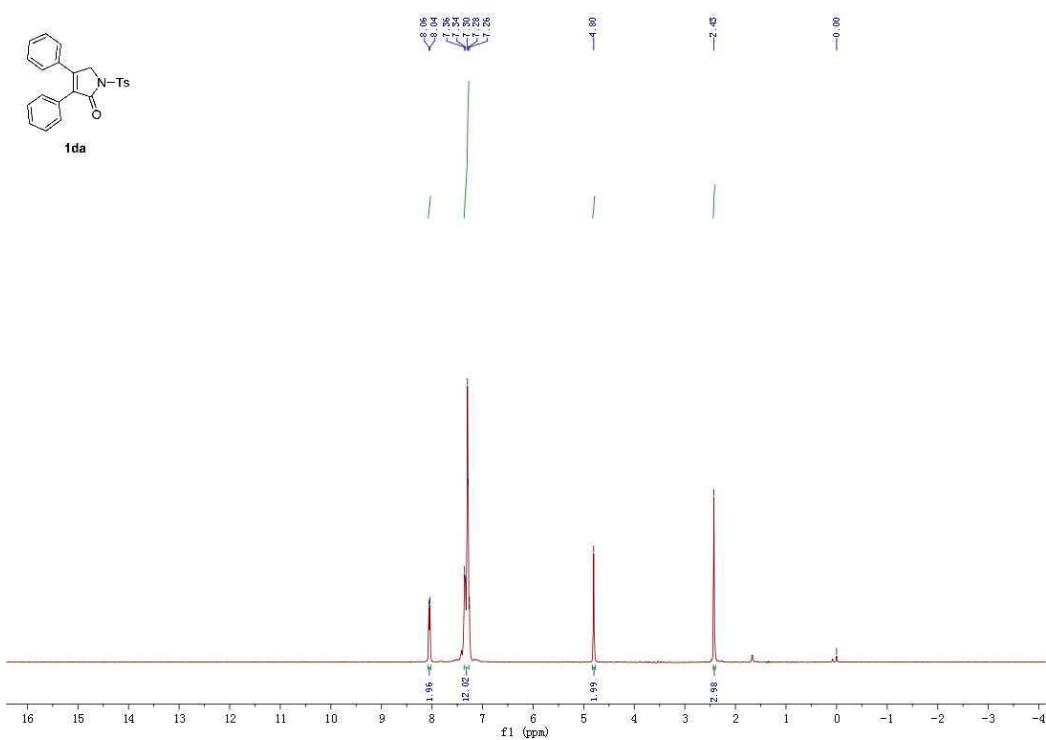
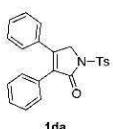
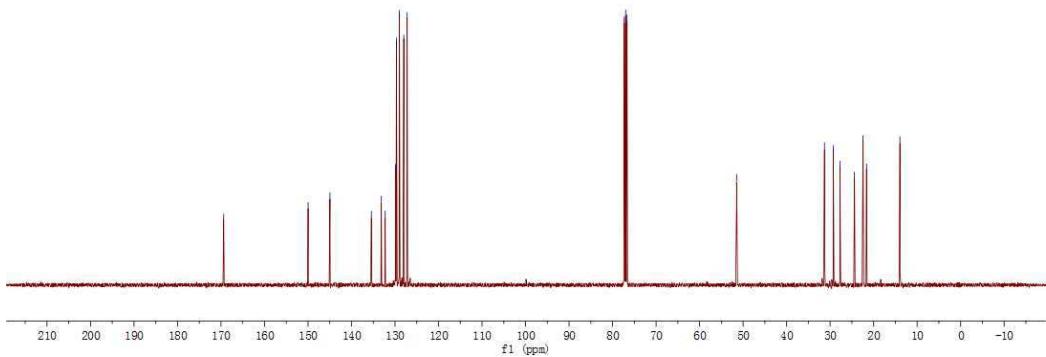
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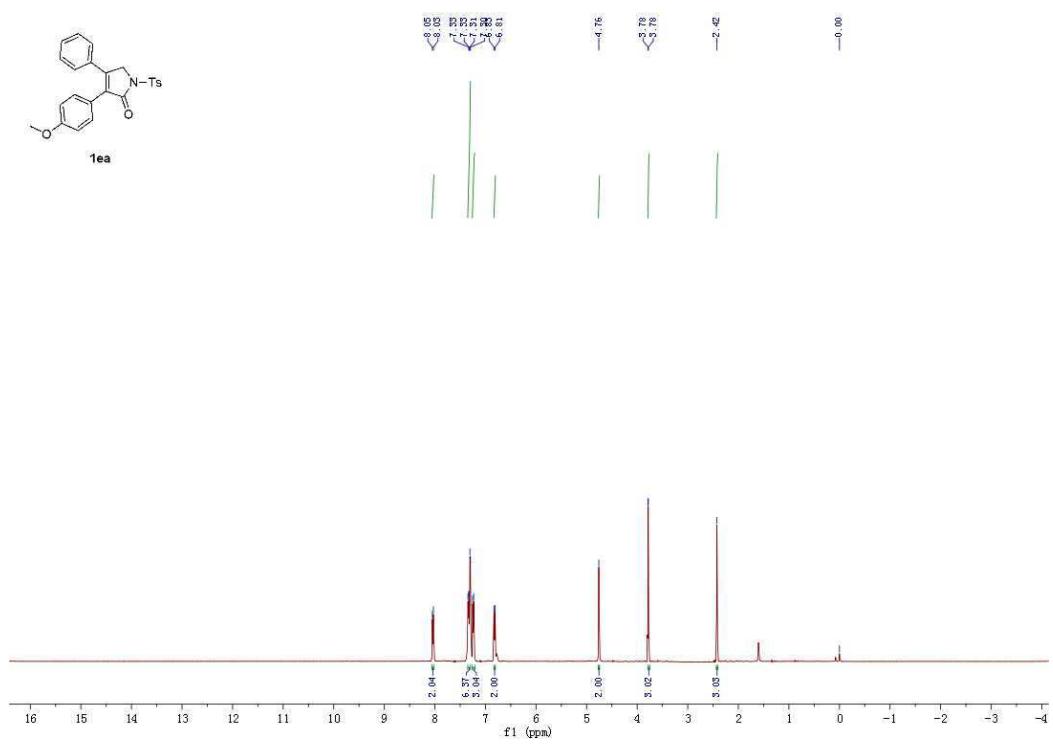
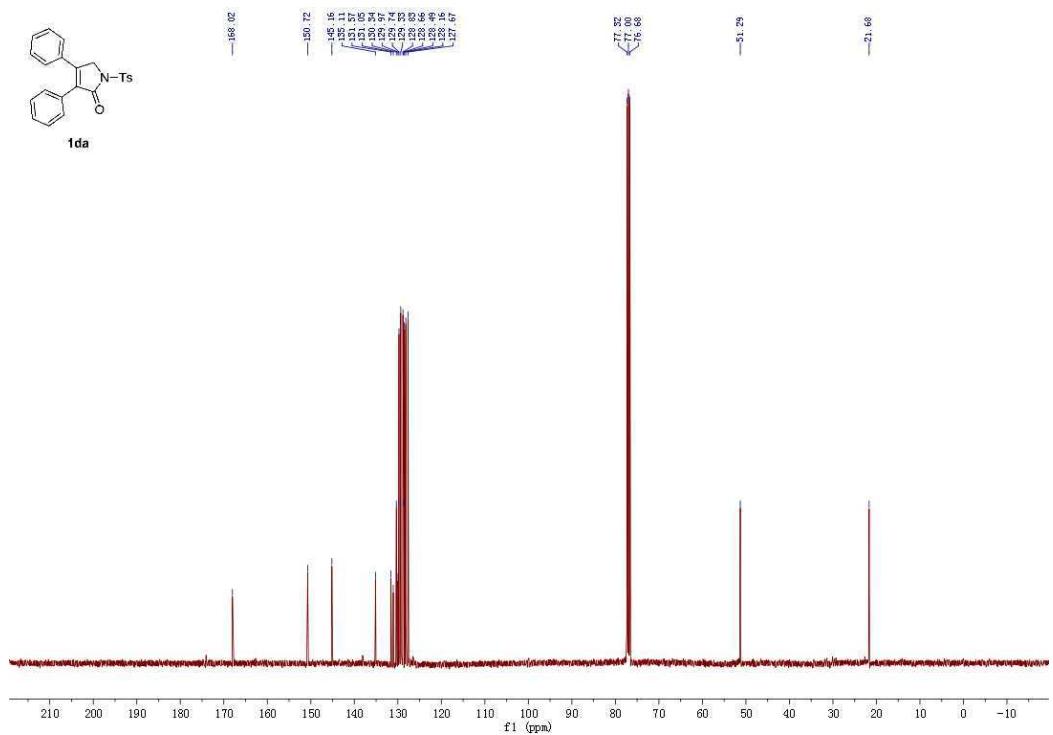


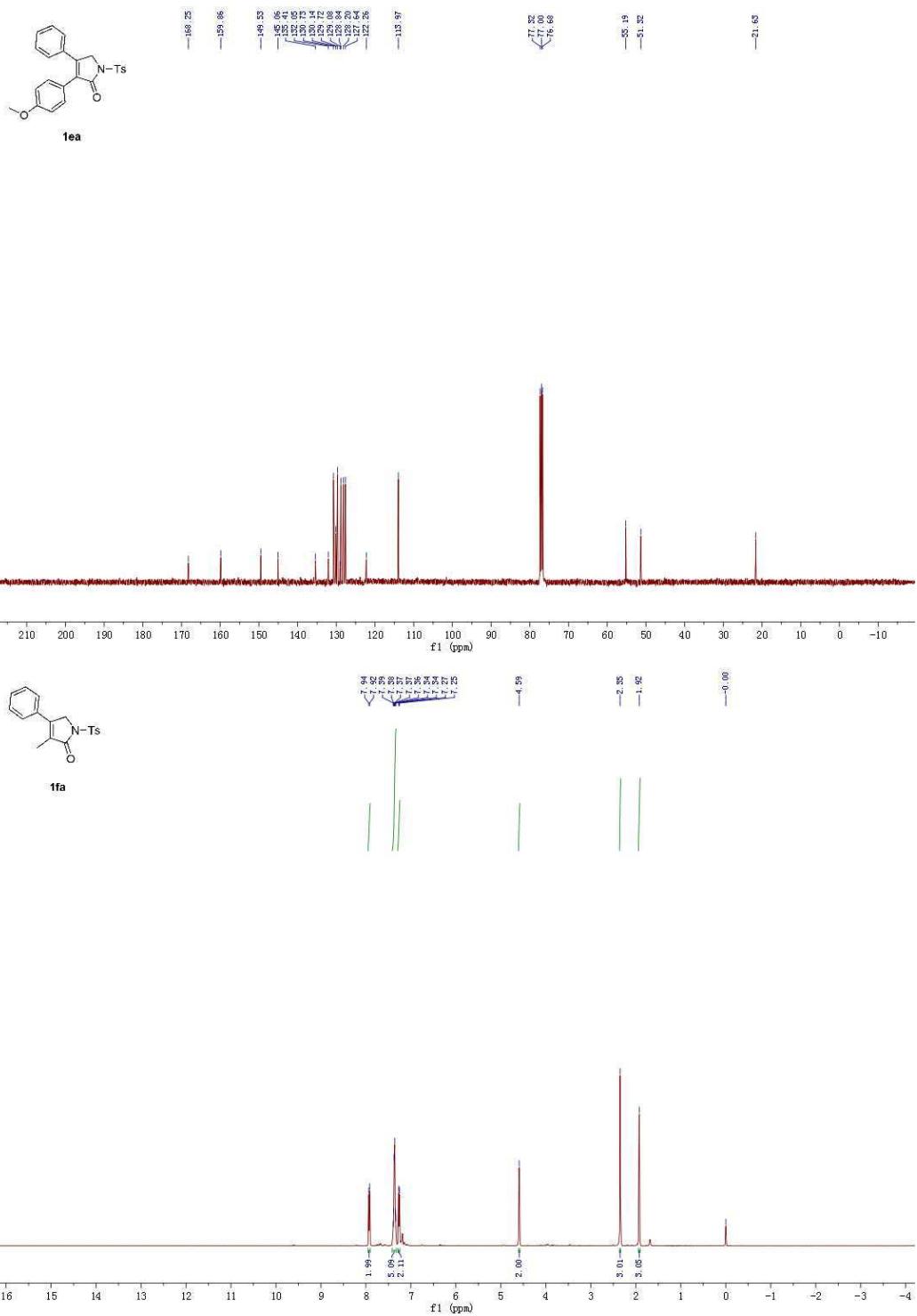
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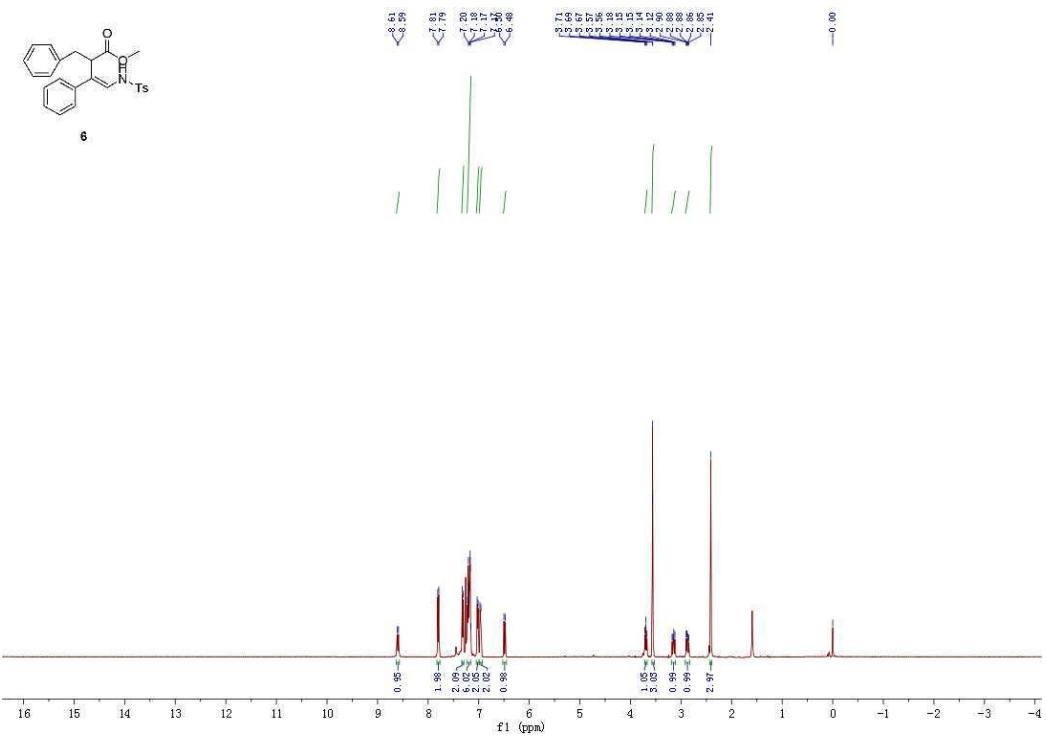
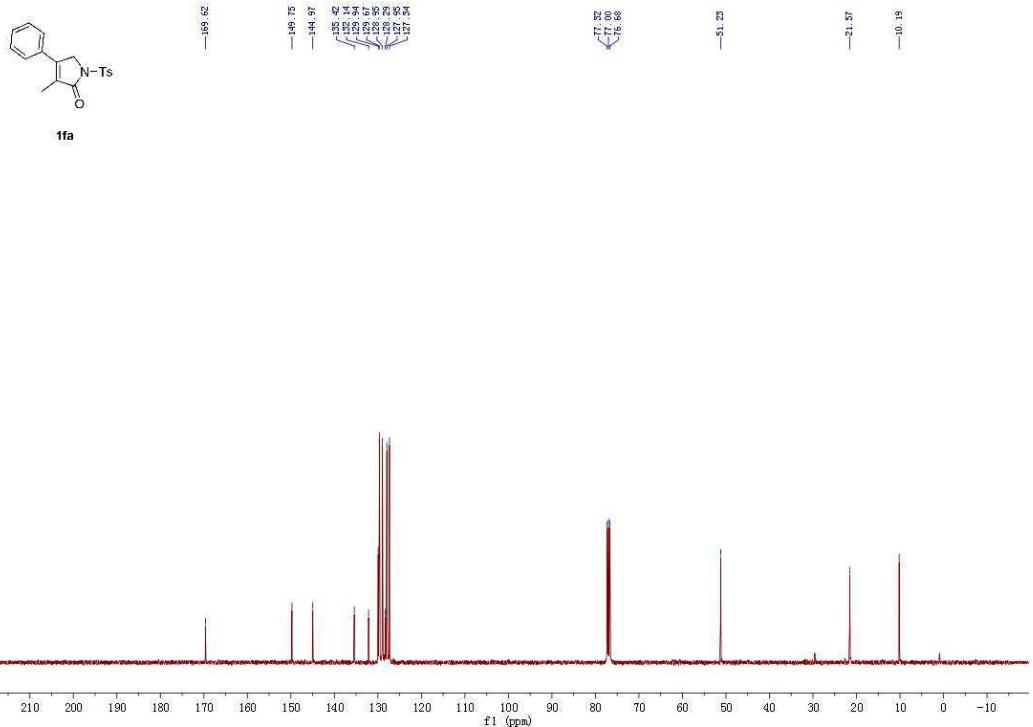


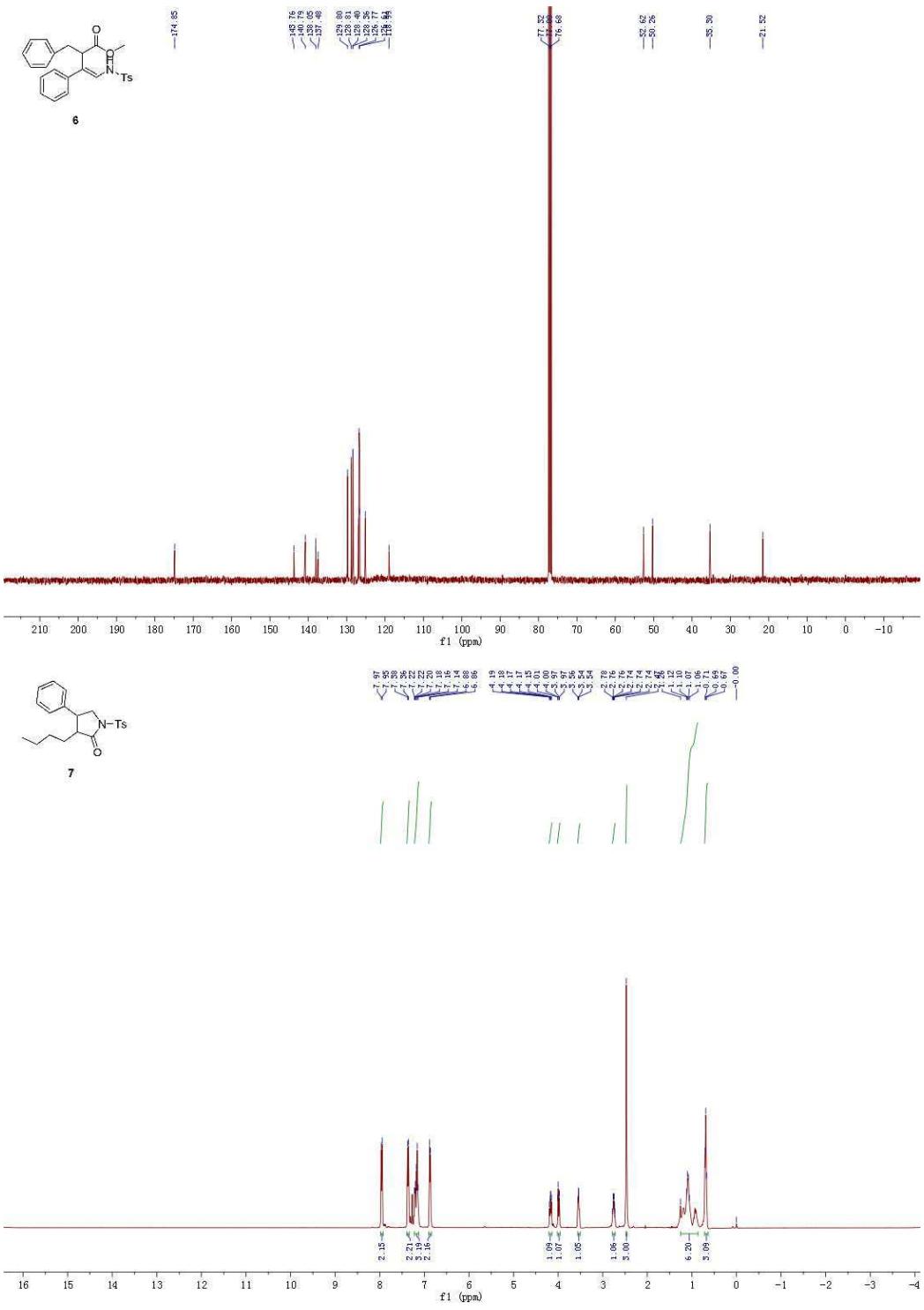


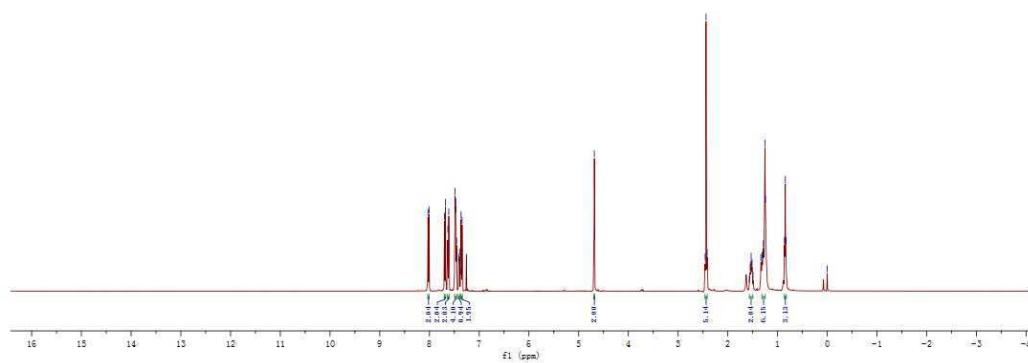
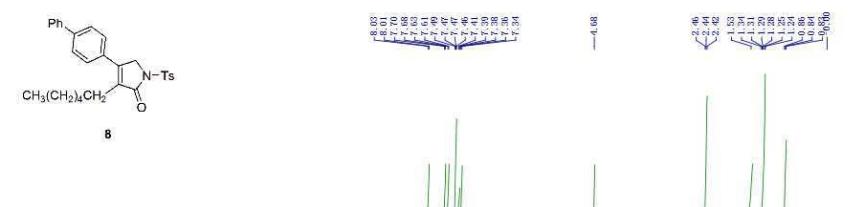
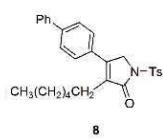
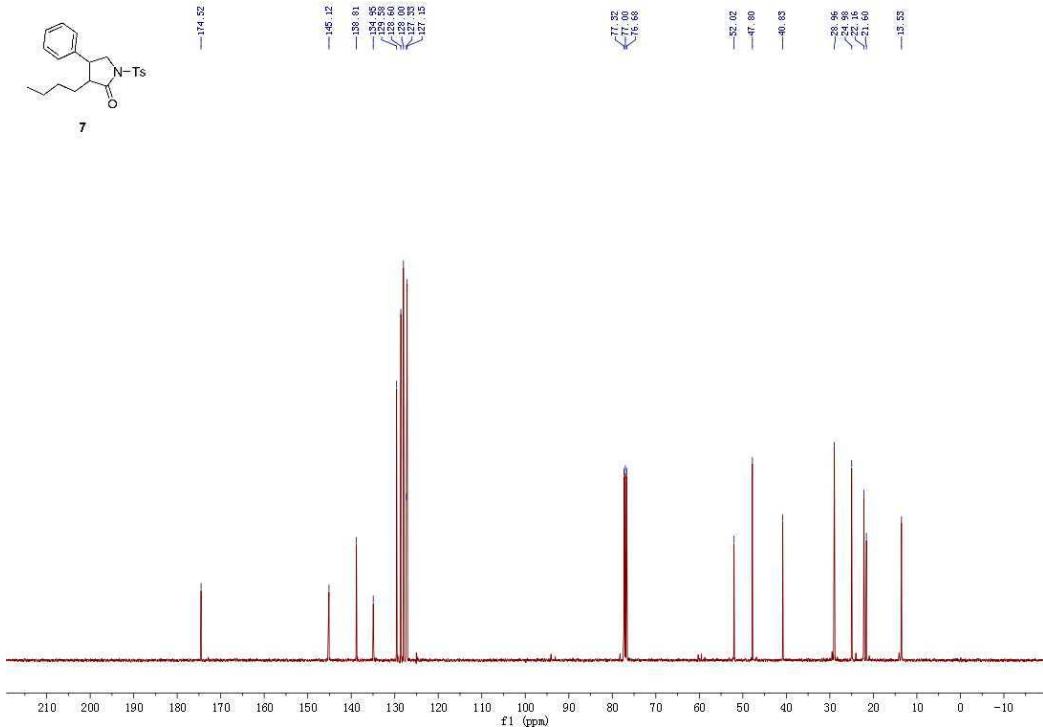
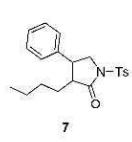


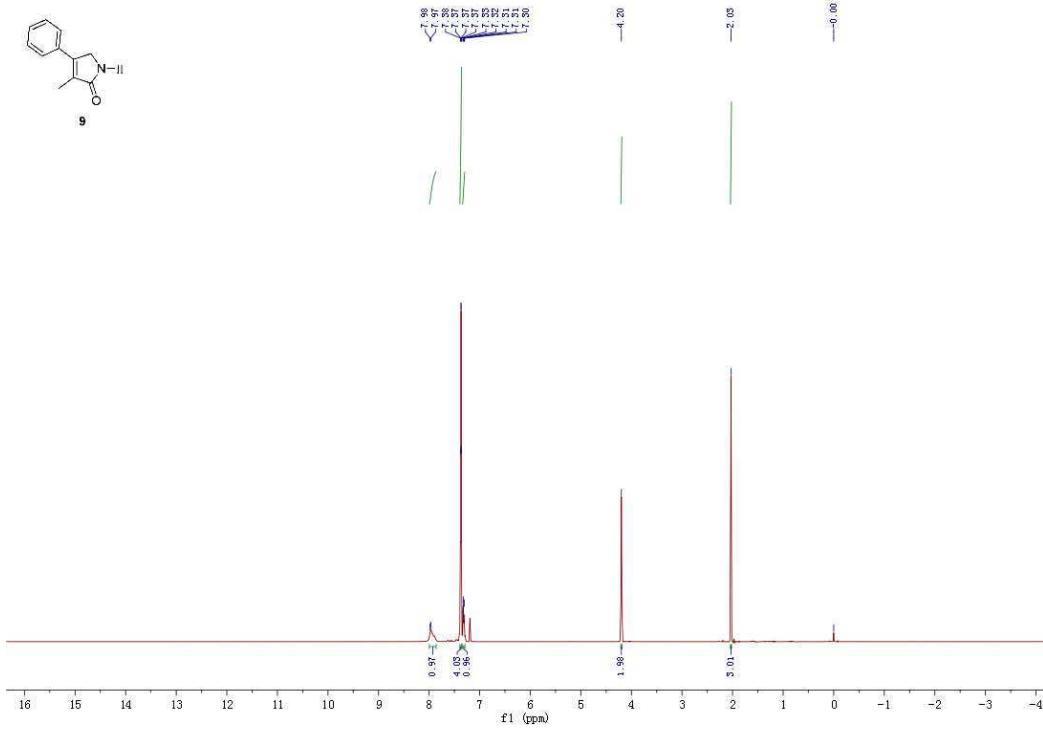
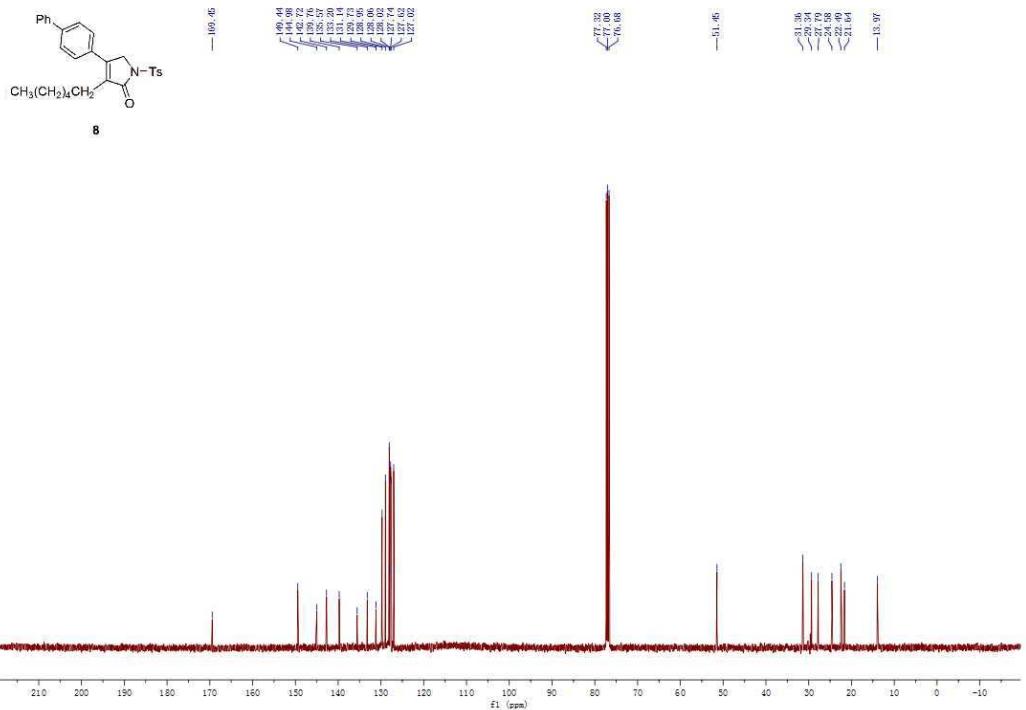


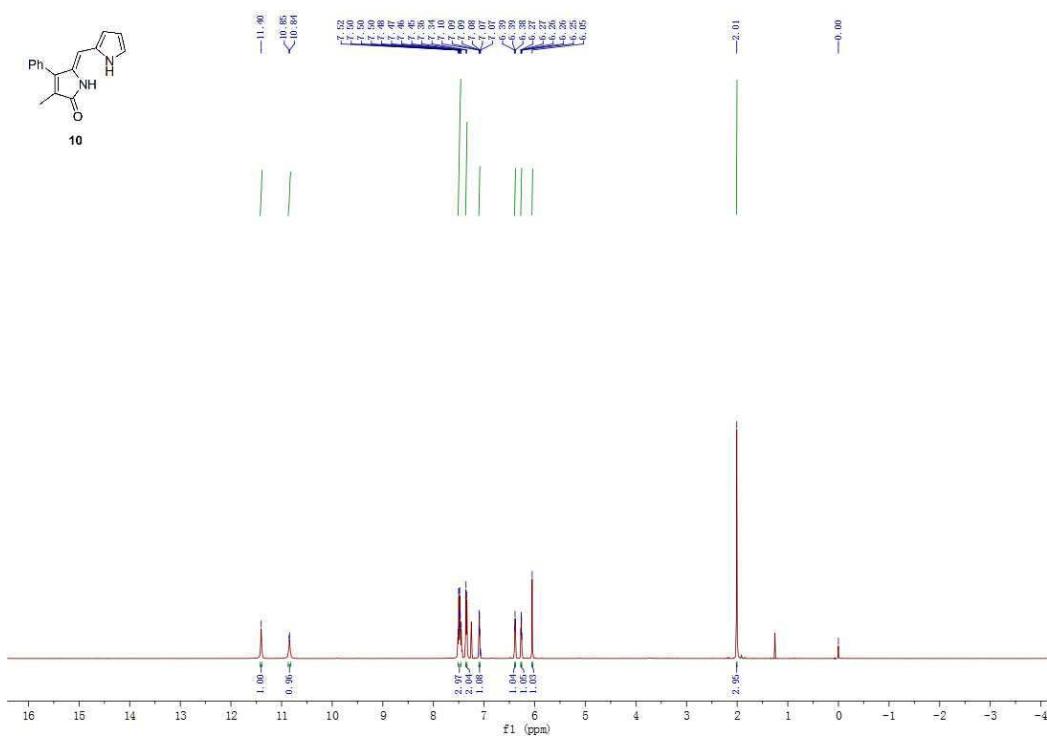
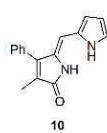
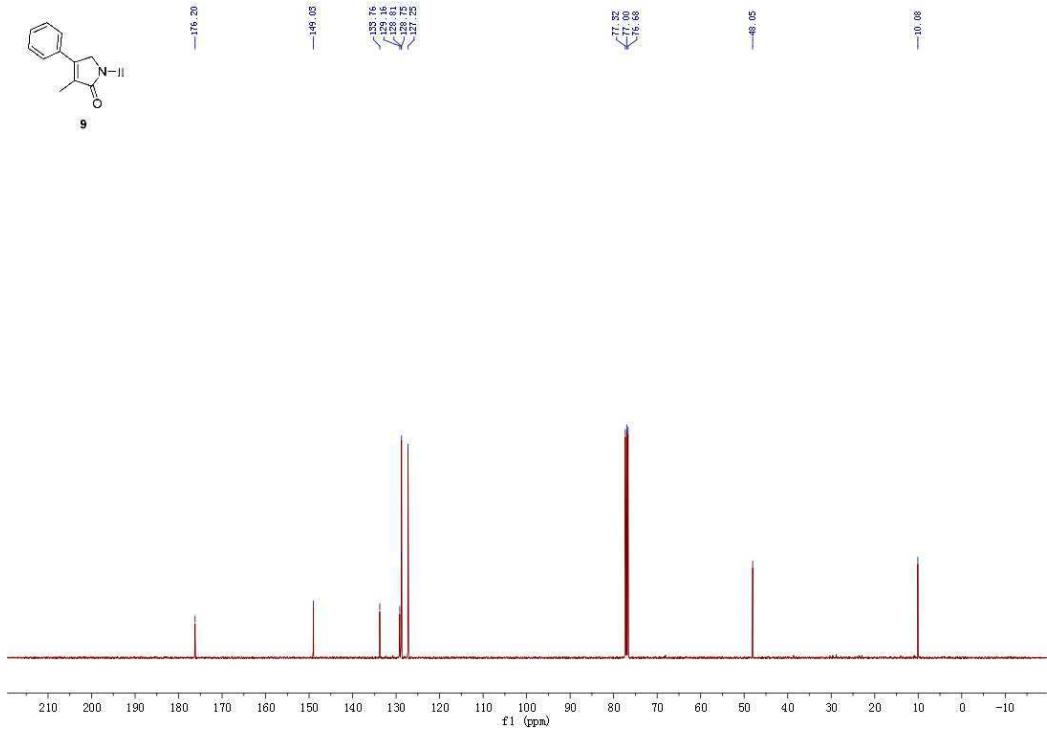
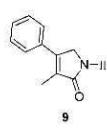


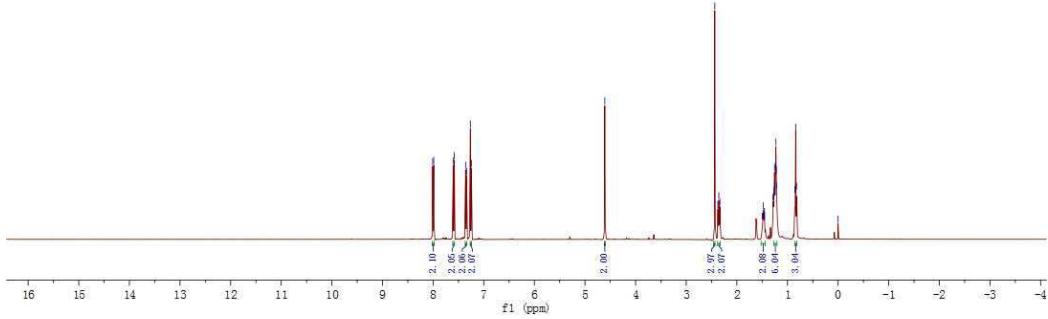
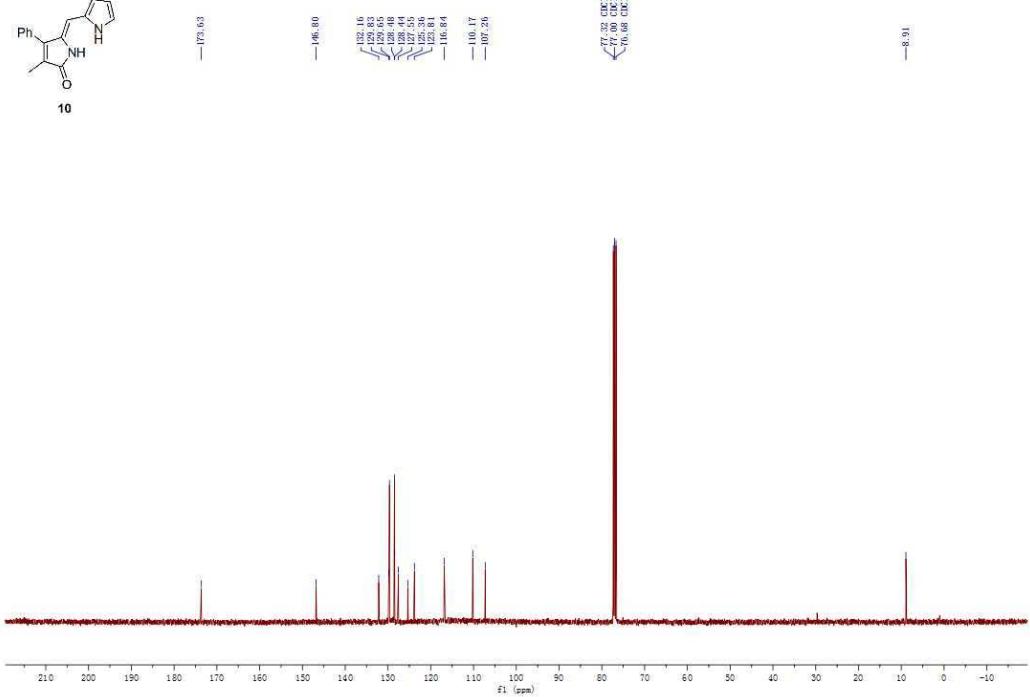
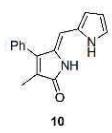






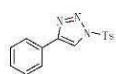
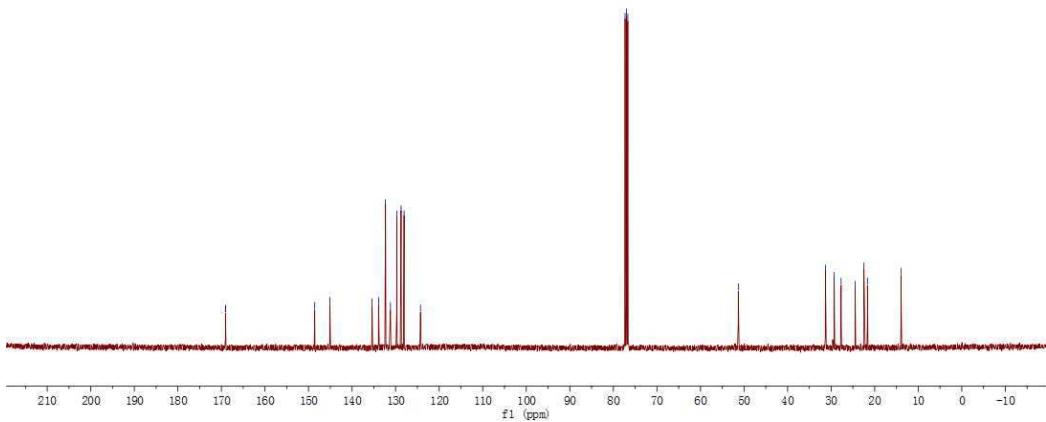








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