

# **Supporting Information**

## **Palladium-Catalyzed and Photo-Induced Benzylic C–H Carbonylation/Annulation Under Mild Conditions**

Wei-Wei Ding, Yu Zhou, Shun Song, Zhi-Yong Han\*

*Department of Chemistry, University of Science and Technology of China, Hefei, 230026, China*

*E-mail:* hanzy2014@ustc.edu.cn

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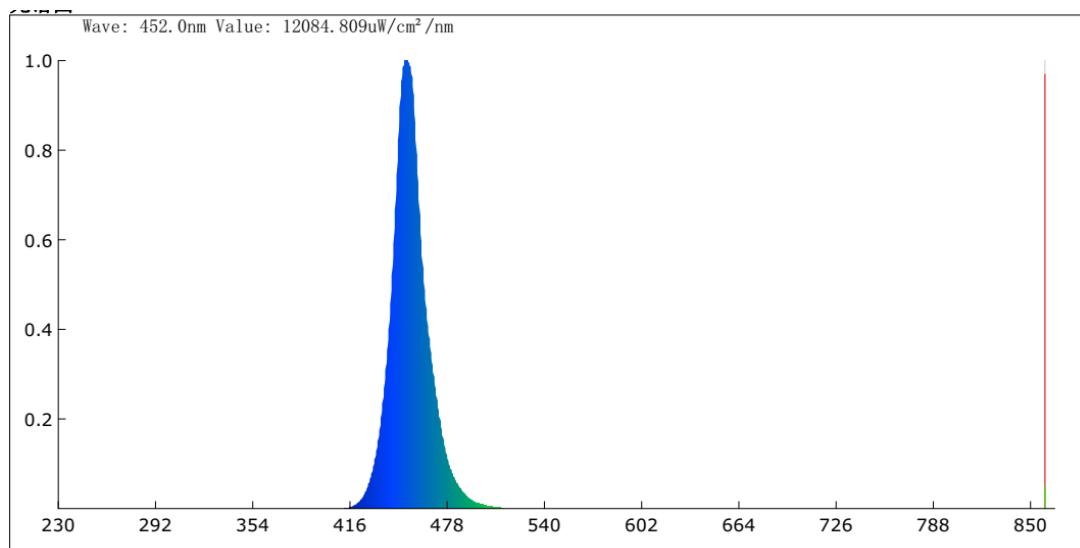
## 1. General Information

### General data:

NMR spectra were recorded on Bruker-400 MHz spectrometer or Bruker-500 MHz spectrometer. Chemical shifts ( $\delta$ ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ( $\text{CDCl}_3$ :  $\delta\text{H} = 7.26$  ppm,  $\delta\text{C} = 77.16$  ppm).

The high resolution mass spectra were recorded on a Thermo LTQ Orbitrap XL (ESI+) or a P-SIMS-Gly of Bruker DaltonicsInc (EI+).

Photocatalytic reactions were performed in 10 mL Schlenk tubes at the indicated temperature under CO and under irradiation with Kessil PR-160L LED (40 W, 456nm) or 10 W 456 nm LED lamp (Figure 1.  $\lambda_{\text{max}} = 455$  nm; commercial supplier: Bibby Scientific Ltd., website: <http://www.rogertech.cn/cpzszong.asp>).



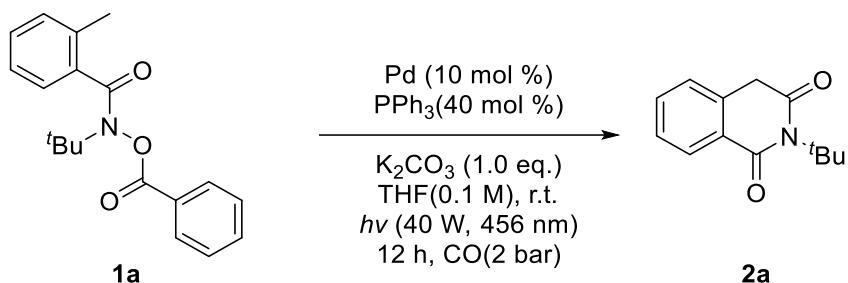
**Figure 1.**Spectrum of the 10 W blue LED

### Materials:

All starting materials, reagents and solvents were purchased from commercial suppliers (Aldrich, Alfa, TCI, Adamas, Energy etc.) and used as supplied unless otherwise stated. Tetrahydrofuran was dried over Na and distilled prior to use.

## 2 . Details for Condition Optimization

**Table S1.** Effect of Pd catalysts on the reaction<sup>[a]</sup>

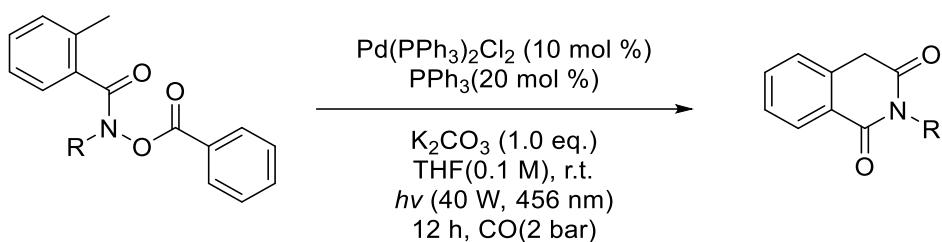


[a] Unless indicated otherwise, the reaction was carried out under CO (2 bar) in the scale of **1a** (0.1

entry	Pd	yield (%) <sup>b</sup>
1	-	n.r.
2	Pd(TFA) <sub>2</sub>	14
3 <sup>c</sup>	Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub>	21
4	Pd(CH <sub>3</sub> CN) <sub>2</sub> Cl <sub>2</sub>	12
5	PdCl <sub>2</sub>	20
6	Pd(acac) <sub>2</sub>	13
7	Pd(OAc) <sub>2</sub>	15
8	Pd(dba) <sub>2</sub>	n.d.

mmol), Pd (10 mol %), PPh<sub>3</sub>(40 mol %), *hν* (40 W, 456 nm) and K<sub>2</sub>CO<sub>3</sub> (1.0 eq.) in THF (1.0 mL) at r.t. for 12h. [b] The yield was determined by <sup>1</sup>H NMR analysis of the crude products based on internal standard. [c] 20 mol% PPh<sub>3</sub> was used.

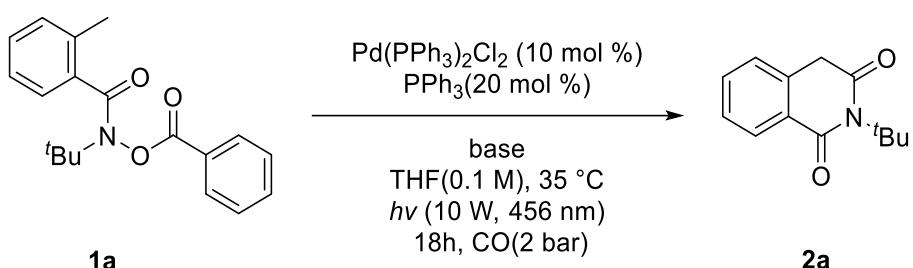
**Table S2.** Effect of the N-protected group on the reaction<sup>[a]</sup>



entry	R	yield (%)
1	'Bu	21
2	Me	n.d.
3	'Pr	trace

[a] Unless indicated otherwise, the reaction was carried out under CO (2 bar) in the scale of sub. (0.1 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>(10 mol %), PPh<sub>3</sub> (20 mol %), *h*v (40 W, 456 nm) and K<sub>2</sub>CO<sub>3</sub> (1.0 eq.) in THF (1.0 mL) at r.t. for 12h. The yield was determined by <sup>1</sup>H NMR analysis of the crude products based on internal standard.

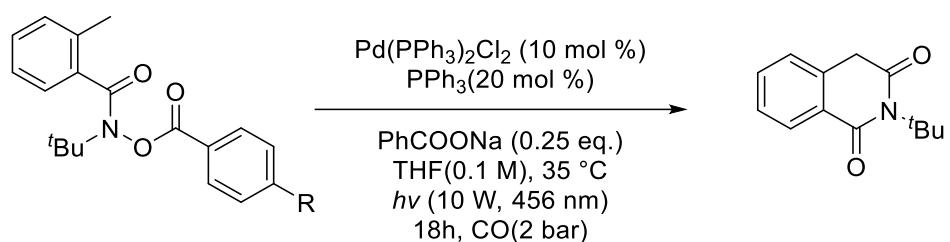
**Table S3.** Effect of base on the reaction<sup>[a]</sup>



entry	base	yield %
1	-	n.r.
2	0.1 eq. K <sub>2</sub> CO <sub>3</sub>	73
3	0.25 eq. K <sub>2</sub> CO <sub>3</sub>	75
4	0.5 eq. K <sub>2</sub> CO <sub>3</sub>	60
5	1.0 eq. K <sub>2</sub> CO <sub>3</sub>	44
6	2.0 eq. K <sub>2</sub> CO <sub>3</sub>	39
7	4.0 eq. K <sub>2</sub> CO <sub>3</sub>	32
8	0.25 eq. Li <sub>2</sub> CO <sub>3</sub>	n.d.
9	0.25 eq. Na <sub>2</sub> CO <sub>3</sub>	78
10	0.25 eq. NaHCO <sub>3</sub>	62
11	0.25 eq. Cs <sub>2</sub> CO <sub>3</sub>	62
12	0.25 eq. K <sub>3</sub> PO <sub>4</sub>	72
13	0.25 eq. PhCOONa	86
15	0.25 eq. PhCOOK	78
16	0.25 eq. DIPEA	19
17	0.25 eq. Et <sub>3</sub> N	30

[a] Unless indicated otherwise, the reaction was carried out under CO (2 bar) in the scale of 1a (0.1 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>(10 mol %), PPh<sub>3</sub> (20 mol %), *hν* (10 W, 456 nm) and base in THF (1.0 mL) at 35 °C for 18h. The yield was determined by <sup>1</sup>H NMR analysis of the crude products based on internal standard.

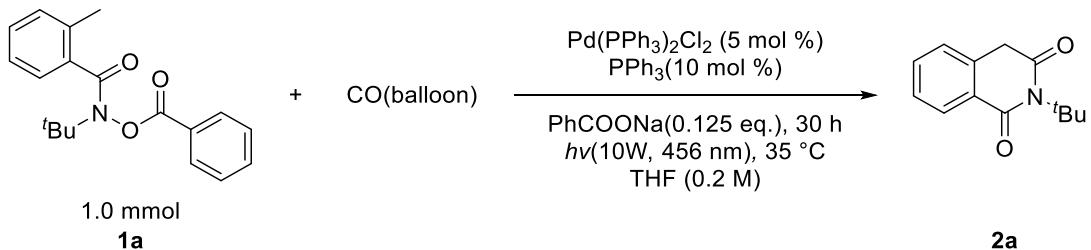
**Table S4.** Effect of the kind of benzoyl on the reaction<sup>[a]</sup>



entry	R	yield (%)
1	H	86
2	CF <sub>3</sub>	77
3	F	78
4	NO <sub>2</sub>	n.d.
5	OMe	44

[a] Unless indicated otherwise, the reaction was carried out under CO (2 bar) in the scale of sub. (0.1 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>(10 mol %), PPh<sub>3</sub> (20 mol %), *hν* (10 W, 456 nm) and PhCOONa (0.25 eq.) in THF (1.0 mL) at 35 °C for 18h. The yield was determined by <sup>1</sup>H NMR analysis of the crude products based on internal standard.

### 3. Big scale reaction:

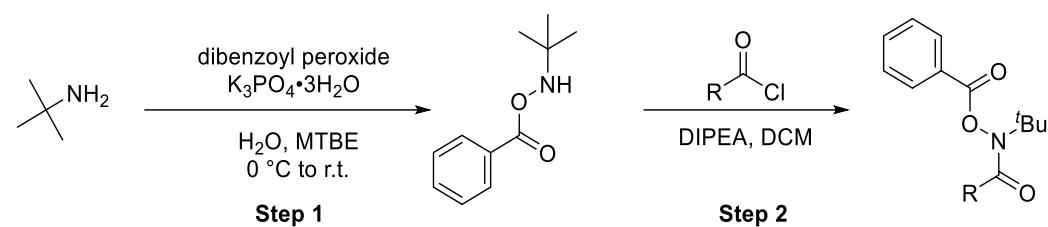


To a flame-dried and  $\text{N}_2$ -purged Schlenk tube (10 mL) was added a stirring bar,  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (0.05 mmol, 35.1 mg),  $\text{PPh}_3$  (0.1 mmol, 26.2 mg),  $\text{PhCOONa}$  (0.125 mmol, 18.0 mg) and N-(benzoyloxy)-N-(tert-butyl)-2-methylbenzamide **1a** (1.0 mmol, 311.4 mg). The vial was sealed with a rubber plug, purged and backfilled with  $\text{N}_2$  three times before adding THF (5.0 mL). The resulting solution was frozen under liquid nitrogen. The nitrogen atmosphere was evacuated from the tube in a Schlenk line and then was pressurized with CO by a CO balloon. The resulting solution was stirred under 456nm 10W LEDs at 35 °C for 30 hours. Then the reaction was taken out of the irradiation system and the excess CO was removed by opening the rubber plug inside a well-ventilated fume hood. The mixture was quenched with water (3.0 mL). The resulting solution was extracted with ethyl acetate (5.0 mL x 3). The combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (toluene: ethyl acetate = 30 : 1) to afford desired products 2-(tert-butyl)isoquinoline-1,3(2H,4H)-dione **2a** (122.1 mg, 56% yield).

## 4. General Procedures

### General procedure for the 2-methylbenzoic acid derivatives (1a-1v):

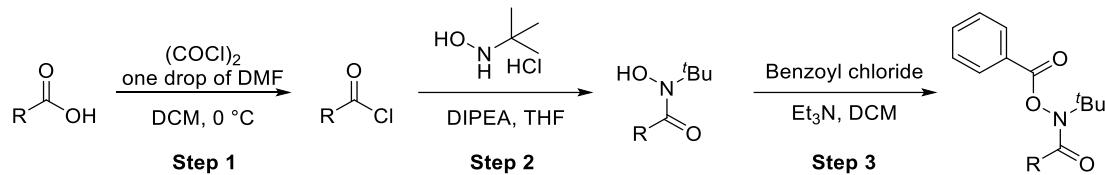
#### Procedure A:



**Step 1<sup>[1]</sup>:**  $K_3PO_4 \cdot 3H_2O$  (31.96 g, 120 mmol) and  $Me_3CNH_2$  (7.30 g, 100 mmol) were added to a two-phase mixture of  $Me_3COMe$  (50 ml) and water (90 ml) in a 500 ml round bottom flask. The mixture was cooled to 0 °C before  $(PhCO_2)_2$  (36.33 g, 105 mmol, wetted with 30% water) was added. The temperature was gradually allowed to rise to r.t., and the reaction mixture was vigorously stirred overnight (17 h). It was then diluted with hexane (100 mL) and water (20 mL); the aqueous layer was extracted with hexane ( $2 \times 50$  mL), and the combined hexane fractions were washed with water ( $2 \times 50$  mL), evaporated under vacuum to furnish a pure compound O-benzoyl-N-(tert-butyl)hydroxylamine as colorless oil in high yield.

**Step 2:** To a solution of O-benzoyl-N-(tert-butyl)hydroxylamine (1.0 equiv.) in  $CH_2Cl_2$  (0.5 M) at 0 °C, DIPEA (1.5 equiv.) was added dropwise. Acyl chloride (1.1 equiv.) was then added dropwise over 5 minutes. The reaction was vigorously stirred at room temperature for 24 h. The solution was evaporated. The residue was purified by column chromatography on alkaline aluminum oxide (petroleum ether: ethyl acetate = 10 : 1) afford desired substrate **1**.

**Procedure B<sup>[2]</sup>:**



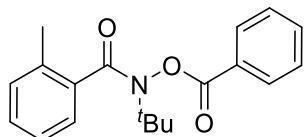
The benzoic acid derivatives for preparing **1t**, **1u** and **1v** were synthetized according to the literature<sup>[3]</sup>.

**Step 1:** To a solution of benzoic acid derivatives (1.0 equiv.) and one drop of anhydrous DMF in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (0.5 M) at 0 °C, oxalyl chloride (1.5 equiv.) was added dropwise over 10 minutes. The reaction was vigorously stirred at room temperature for 2-3 h. The solvent was removed by rotary evaporation. Anhydrous CH<sub>2</sub>Cl<sub>2</sub> was added to remove the residual of oxalyl chloride by evaporation. Then the resulting acyl chloride was redissolved in anhydrous acetonitrile and used directly for the next step without further purification.

**Step 2:** A solution of N-(tert-butyl)hydroxylamine hydrochloride in anhydrous THF (0.4 M) was cooled to 0 °C, treated with DIPEA (2.0 equiv.) and stirred for 15 minutes. The acyl chloride (1.0 equiv.) in anhydrous acetonitrile was added dropwise over 15 minutes and the mixture was allowed to warm to room temperature for 1-2 h. The solution was evaporated. The residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 10 : 1 - 4 : 1) to give the hydroxylamine.

**Step 3:** To a solution of hydroxylamine (1.0 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 M) at 0 °C, Et<sub>3</sub>N (1.5 equiv.) was added dropwise. Benzoyl chloride (1.1 equiv.) was then added dropwise over 5 minutes. The reaction was vigorously stirred at room temperature for 30 min. The solution was evaporated. The residue was purified by column chromatography on alkaline aluminum oxide (petroleum ether: ethyl acetate = 10 : 1) afford desired substrate **1**.

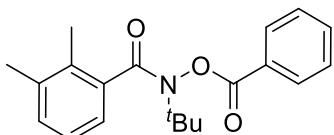
**N-(benzoyloxy)-N-(tert-butyl)-2-methylbenzamide (1a)**



**1a**

Following the general procedure A, O-benzoyl-N-(tert-butyl)hydroxylamine 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1a** as a white solid; 84% yield, 2.61g ; **TLC** (petroleum ether / ethyl acetate = 4/1, v/v): R<sub>f</sub> = 0.6; **<sup>1</sup>H NMR** (**400 MHz**, **CDCl<sub>3</sub>**) δ 7.64 (d, *J* = 7.8 Hz, 2H), 7.55 – 7.46 (m, 1H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 7.4 Hz, 1H), 7.05 (t, *J* = 2.9 Hz, 2H), 7.00 (dt, *J* = 8.3, 4.3 Hz, 1H), 2.42 (s, 3H), 1.62 (s, 9H); **<sup>13</sup>C NMR** (**101 MHz**, **CDCl<sub>3</sub>**) δ 171.5, 165.3, 136.3, 134.3, 133.9, 129.9, 129.4, 128.8, 128.5, 126.7, 125.8, 125.1, 62.9, 27.6, 19.0; **HRMS** (ESI) m/z (M+Na)<sup>+</sup>: calculated for (C<sub>19</sub>H<sub>21</sub>NO<sub>3</sub>Na)<sup>+</sup>: 334.1414, found: 334.1419.

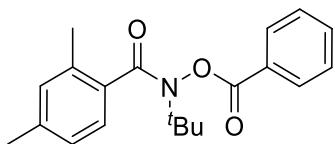
**N-(benzoyloxy)-N-(tert-butyl)-2,3-dimethylbenzamide (1b)**



**1b**

Following the general procedure B, N-(tert-butyl)hydroxylamine hydrochloride 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1b** as a white solid; 35% yield, 1.14 g ; **<sup>1</sup>H NMR** (**400 MHz**, **CDCl<sub>3</sub>**) δ 7.62 (d, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.09 – 7.03 (m, 1H), 6.93 (s, 2H), 2.30 (s, 3H), 2.17 (s, 3H), 1.62 (s, 9H); **<sup>13</sup>C NMR** (**101 MHz**, **CDCl<sub>3</sub>**) δ 172.1, 165.3, 136.7, 133.8, 130.1, 129.4, 128.5, 126.9, 125.1, 123.6, 62.8, 27.6, 20.0, 16.1; **HRMS** (ESI) m/z (M+Na)<sup>+</sup>: calculated for (C<sub>20</sub>H<sub>23</sub>NO<sub>3</sub>Na)<sup>+</sup>: 348.1570, found: 348.1576.

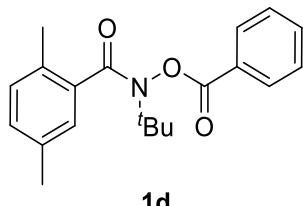
**N-(benzoyloxy)-N-(tert-butyl)-2,4-dimethylbenzamide (1c)**



**1c**

Following the general procedure B, N-(tert-butyl)hydroxylamine hydrochloride 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1c** as a white solid; 22% yield, 716 mg ; **1H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.69 – 7.67 (m, 2H), 7.54 – 7.50 (m, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 1H), 6.87 (s, 1H), 6.81 (d, *J* = 7.7 Hz, 1H), 2.38 (s, 3H), 2.15 (s, 3H), 1.60 (s, 9H). **13C NMR (101 MHz, CDCl<sub>3</sub>)** δ 171.8, 165.4, 138.6, 134.4, 133.8, 133.5, 130.7, 129.5, 128.5, 126.9, 126.0, 125.7, 62.8, 27.7, 21.1, 18.9. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>20</sub>H<sub>23</sub>NO<sub>3</sub>Na)<sup>+</sup>: 348.1570, found: 348.1571.

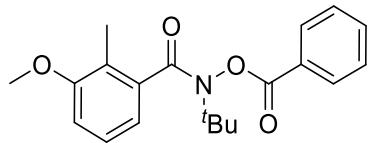
**N-(benzoyloxy)-N-(tert-butyl)-2,5-dimethylbenzamide (1d)**



**1d**

Following the general procedure B, N-(tert-butyl)hydroxylamine hydrochloride 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1d** as a white solid; 41% yield, 1.33 g ; **1H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.65 (d, *J* = 7.7 Hz, 2H), 7.55 – 7.49 (m, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 1.8 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.85 (dd, *J* = 7.8, 1.9 Hz, 1H), 2.37 (s, 3H), 2.15 (s, 3H), 1.61 (s, 9H). **13C NMR (101 MHz, CDCl<sub>3</sub>)** δ 171.8, 165.4, 136.2, 134.7, 133.9, 131.3, 129.9, 129.6, 129.5, 128.6, 127.0, 126.5, 62.9, 27.8, 20.8, 18.6. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>20</sub>H<sub>23</sub>NO<sub>3</sub>Na)<sup>+</sup>: 348.1570, found: 348.1577.

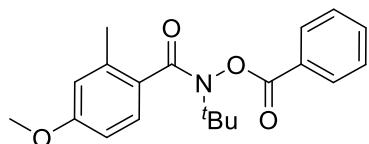
**N-(benzoyloxy)-N-(tert-butyl)-3-methoxy-2-methylbenzamide (1e)**



**1e**

Following the general procedure B, N-(tert-butyl)hydroxylamine hydrochloride 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1e** as a white solid; 32% yield, 1.10 g ; **1H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.64 (d, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 6.99 (t, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 3.72 (s, 3H), 2.26 (s, 3H), 1.62 (s, 9H); **13C NMR (101 MHz, CDCl<sub>3</sub>)** δ 171.3, 165.3, 157.3, 137.7, 133.8, 129.5, 128.5, 126.9, 126.2, 118.0, 110.4, 62.9, 55.5, 27.6, 12.4; **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>20</sub>H<sub>23</sub>NO<sub>4</sub>Na)<sup>+</sup>: 364.1519, found: 364.1526.

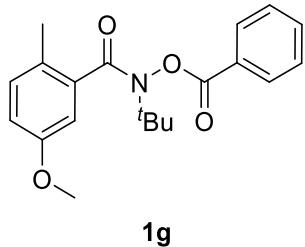
**N-(benzoyloxy)-N-(tert-butyl)-4-methoxy-2-methylbenzamide (1f)**



**1f**

Following the general procedure B, N-(tert-butyl)hydroxylamine hydrochloride 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1f** as a white solid; 28% yield, 956 mg ; **1H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.68 – 7.61 (m, 2H), 7.50 – 7.41 (m, 1H), 7.28 (t, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 2.5 Hz, 1H), 6.47 (dd, *J* = 8.4, 2.6 Hz, 1H), 3.59 (s, 3H), 2.34 (s, 3H), 1.52 (s, 9H); **13C NMR (101 MHz, CDCl<sub>3</sub>)** δ 171.5, 165.4, 159.7, 136.9, 133.9, 129.5, 128.9, 128.6, 127.8, 126.9, 115.5, 110.3, 62.8, 55.1, 27.7, 19.3; **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>20</sub>H<sub>23</sub>NO<sub>4</sub>Na)<sup>+</sup>: 364.1519, found: 364.1516.

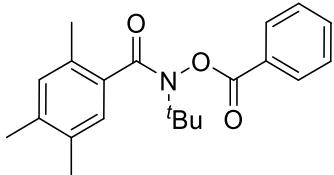
**N-(benzoyloxy)-N-(tert-butyl)-5-methoxy-2-methylbenzamide (1g)**



**1g**

Following the general procedure B, N-(tert-butyl)hydroxylamine hydrochloride 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1g** as a white solid; 32% yield, 1.09 g ; **1H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.67 (d, *J* = 7.7 Hz, 2H), 7.57 – 7.48 (m, 1H), 7.34 (t, *J* = 7.8 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.76 (d, *J* = 2.8 Hz, 1H), 6.62 (dd, *J* = 8.4, 2.8 Hz, 1H), 3.66 (s, 3H), 2.34 (s, 3H), 1.61 (s, 9H); **13C NMR (101 MHz, CDCl<sub>3</sub>)** δ 171.3, 165.4, 157.0, 137.0, 133.9, 131.0, 129.4, 128.6, 126.8, 126.1, 115.4, 110.7, 63.0, 55.4, 27.6, 18.0; **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>20</sub>H<sub>23</sub>NO<sub>4</sub>Na)<sup>+</sup>: 364.1519, found: 364.1519.

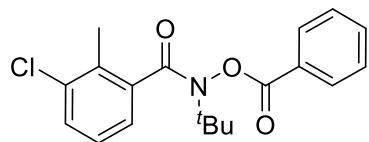
**N-(benzoyloxy)-N-(tert-butyl)-2,4,5-trimethylbenzamide (1h)**



**1h**

Following the general procedure B, N-(tert-butyl)hydroxylamine hydrochloride 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1h** as a white solid; 17% yield, 568 mg **1H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.71 – 7.64 (m, 2H), 7.55 – 7.47 (m, 1H), 7.33 (t, *J* = 7.8 Hz, 2H), 6.99 (s, 1H), 6.81 (s, 1H), 2.34 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 1.60 (s, 9H). **13C NMR (101 MHz, CDCl<sub>3</sub>)** δ 171.8, 165.4, 137.2, 133.7, 133.7, 133.1, 131.7, 131.2, 129.5, 128.5, 127.2, 127.1, 62.8, 27.7, 19.4, 18.9, 18.4. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>21</sub>H<sub>25</sub>NO<sub>3</sub>Na)<sup>+</sup>: 362.1727, found: 362.1736.

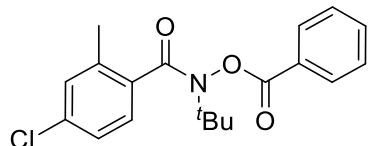
**N-(benzoyloxy)-N-(tert-butyl)-3-chloro-2-methylbenzamide (1i)**



**1i**

Following the general procedure B, N-(tert-butyl)hydroxylamine hydrochloride 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1i** as a white solid; 25% yield, 860 mg. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.65 (d, *J* = 7.7 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.14 (t, *J* = 7.5 Hz, 2H), 6.96 (t, *J* = 7.8 Hz, 1H), 2.44 (s, 3H), 1.62 (s, 9H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.3, 165.2, 138.2, 134.1, 129.6, 129.4, 128.7, 126.4, 124.4, 63.1, 27.5, 16.7. **HRMS (ESI) m/z (M+Na)<sup>+</sup>:** calculated for (C<sub>19</sub>H<sub>20</sub>ClNO<sub>3</sub>Na)<sup>+</sup>: 368.1024, found: 368.1028.

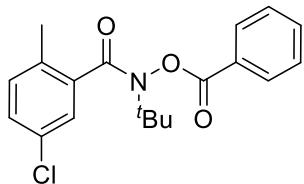
**N-(benzoyloxy)-N-(tert-butyl)-4-chloro-2-methylbenzamide (1j)**



**1j**

Following the general procedure B, N-(tert-butyl)hydroxylamine hydrochloride 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1j** as a white solid; 28% yield, 968 mg ; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.74 – 7.67 (m, 2H), 7.59 – 7.50 (m, 1H), 7.41 – 7.33 (m, 2H), 7.17 (d, *J* = 8.2 Hz, 1H), 7.07 (d, *J* = 2.1 Hz, 1H), 7.00 (dd, *J* = 8.2, 2.1 Hz, 1H), 2.40 (s, 3H), 1.60 (s, 9H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.4, 165.2, 136.8, 134.7, 134.4, 134.2, 130.0, 129.5, 128.7, 127.4, 126.4, 125.3, 63.1, 27.6, 18.9. **HRMS (ESI) m/z (M+Na)<sup>+</sup>:** calculated for (C<sub>19</sub>H<sub>20</sub>ClNO<sub>3</sub>Na)<sup>+</sup>: 368.1024, found: 368.1028.

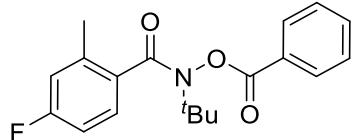
**N-(benzoyloxy)-N-(tert-butyl)-5-chloro-2-methylbenzamide (1k)**



**1k**

Following the general procedure B, N-(tert-butyl)hydroxylamine hydrochloride 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1k** as a white solid; Yield: 9%, 304 mg. **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.71 (d, *J* = 7.7 Hz, 2H), 7.59 – 7.50 (m, 1H), 7.37 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 2.2 Hz, 1H), 7.06 – 6.95 (m, 2H), 2.37 (s, 3H), 1.61 (s, 9H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 169.7, 165.3, 137.6, 134.2, 131.5, 130.9, 129.6, 128.9, 128.8, 126.5, 126.2, 63.2, 27.7, 18.5. **HRMS (ESI) m/z** (M+Na)<sup>+</sup>: calculated for (C<sub>19</sub>H<sub>20</sub>ClNO<sub>3</sub>Na)<sup>+</sup>: 368.1024, found: 368.1027.

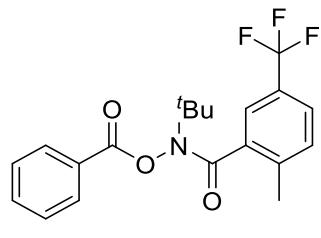
**N-(benzoyloxy)-N-(tert-butyl)-4-fluoro-2-methylbenzamide (1l)**



**1l**

Following the general procedure B, N-(tert-butyl)hydroxylamine hydrochloride 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1l** as a white solid; Yield: 23%, 770 g; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.70 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.58 – 7.50 (m, 1H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.22 (dd, *J* = 8.5, 5.8 Hz, 1H), 6.78 – 6.68 (m, 2H), 2.42 (s, 3H), 1.60 (s, 9H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.6, 165.3, 162.6 (d, *J* = 247.9 Hz), 137.8, 134.2, 132.5 (d, *J* = 3.1 Hz), 129.5, 128.8, 128.1 (d, *J* = 8.8 Hz), 126.6, 116.9 (d, *J* = 21.3 Hz), 112.1 (d, *J* = 21.4 Hz), 63.1, 27.7, 19.2. **HRMS (ESI) m/z** (M+Na)<sup>+</sup>: calculated for (C<sub>19</sub>H<sub>20</sub>FNO<sub>3</sub>Na)<sup>+</sup>: 352.1319, found: 352.1326.

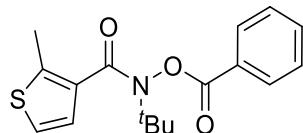
**N-(benzoyloxy)-N-(tert-butyl)-2-methyl-5-(trifluoromethyl)benzamide (1m)**



**1m**

Following the general procedure B, N-(tert-butyl)hydroxylamine hydrochloride 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1m** as a white solid; Yield: 17%, 637 mg; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.62 (d, *J* = 7.5 Hz, 2H), 7.56 – 7.48 (m, 1H), 7.39 (dd, *J* = 10.5, 7.8 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 2H), 7.11 (t, *J* = 7.8 Hz, 1H), 2.55 (s, 3H), 1.63 (s, 9H); **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.2, 165.1, 139.0, 134.2, 132.7, 129.3, 128.6, 126.2, 126.1, 124.2(q, *J* = 272.0 Hz), 63.2, 27.4, 15.6; **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>20</sub>H<sub>20</sub>F<sub>3</sub>NO<sub>3</sub>Na)<sup>+</sup>: 402.1287, found: 402.1289.

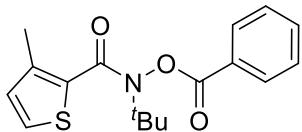
**N-(benzoyloxy)-N-(tert-butyl)-2-methylthiophene-3-carboxamide (1n)**



**1n**

Following the general procedure B, N-(tert-butyl)hydroxylamine hydrochloride 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1n** as a white solid; Yield: 31%, 710 mg; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.84 – 7.82 (m, 2H), 7.58 (ddt, *J* = 8.8, 7.2, 1.3 Hz, 1H), 7.42 – 7.39 (m, 2H), 6.95 (d, *J* = 5.2 Hz, 1H), 6.81 (d, *J* = 5.3 Hz, 1H), 2.55 (s, 3H), 1.58 (s, 9H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 167.6, 165.6, 141.3, 134.0, 133.0, 129.6, 128.7, 126.8, 126.6, 121.5, 63.0, 27.8, 13.9. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>17</sub>H<sub>19</sub>NO<sub>3</sub>SNa)<sup>+</sup>: 340.0978, found: 340.0986.

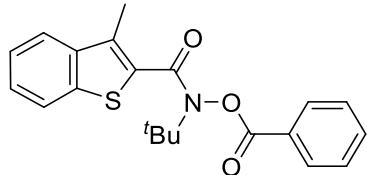
**N-(benzoyloxy)-N-(tert-butyl)-3-methylthiophene-2-carboxamide (1o)**



**1o**

Following the general procedure B, N-(tert-butyl)hydroxylamine hydrochloride 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1o** as a white solid; Yield: 45%, 1.42 g; **1H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.02 – 7.96 (m, 2H), 7.65 – 7.57 (m, 1H), 7.49 – 7.42 (m, 2H), 7.10 (d, *J* = 5.0 Hz, 1H), 6.71 (d, *J* = 5.0 Hz, 1H), 2.43 (s, 3H), 1.59 (s, 9H). **13C NMR (126 MHz, CDCl<sub>3</sub>)** δ 165.5, 165.2, 142.6, 134.2, 130.1, 130.0, 128.8, 128.7, 126.9, 126.8, 63.4, 27.8, 15.7. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>17</sub>H<sub>19</sub>NO<sub>3</sub>SNa)<sup>+</sup>: 340.0978, found: 340.0980.

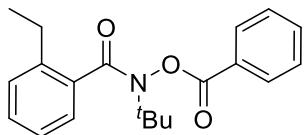
**N-(benzoyloxy)-N-(tert-butyl)-3-methylbenzo[b]thiophene-2-carboxamide (1p)**



**1p**

Following the general procedure B, N-(tert-butyl)hydroxylamine hydrochloride 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1p** as a white solid; Yield: 26%, 960 mg; **1H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.94 – 7.91 (m, 2H), 7.66 (dd, *J* = 8.3, 4.3, 3.3, 2.6 Hz, 2H), 7.56 – 7.49 (m, 1H), 7.41 – 7.36 (m, 2H), 7.33 – 7.28 (m, 2H), 2.57 (s, 3H), 1.63 (s, 9H). **13C NMR (126 MHz, CDCl<sub>3</sub>)** δ 165.5, 139.4, 139.2, 135.0, 134.2, 130.0, 129.9, 128.7, 126.6, 125.6, 124.1, 122.7, 122.3, 63.6, 27.8, 13.0. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>21</sub>H<sub>21</sub>NO<sub>3</sub>SNa)<sup>+</sup>: 390.1134, found: 390.1141.

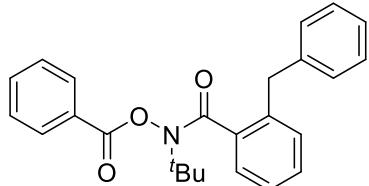
**N-(benzoyloxy)-N-(tert-butyl)-2-ethylbenzamide (1q)**



**1q**

Following the general procedure A, O-benzoyl-N-(tert-butyl)hydroxylamine 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1q** as a white solid; Yield: 65%, 2.11 g; **1H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.61 (d, *J* = 7.7 Hz, 2H), 7.55 – 7.44 (m, 1H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.23 – 7.17 (m, 1H), 7.17 – 7.06 (m, 2H), 7.00 (td, *J* = 7.1, 2.0 Hz, 1H), 2.86 – 2.66 (m, 2H), 1.62 (s, 9H), 1.29 (t, *J* = 7.6 Hz, 3H). **13C NMR (101 MHz, CDCl<sub>3</sub>)** δ 171.7, 165.4, 135.9, 133.8, 129.4, 129.0, 128.5, 128.2, 126.8, 125.2, 62.9, 27.5, 25.8, 15.2. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>20</sub>H<sub>23</sub>NO<sub>3</sub>Na)<sup>+</sup>: 348.1570, found: 348.1576.

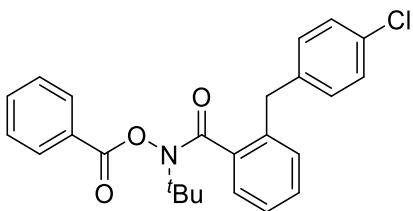
**N-(benzoyloxy)-2-benzyl-N-(tert-butyl)benzamide (1r)**



**1r**

Following the general procedure A, O-benzoyl-N-(tert-butyl)hydroxylamine 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1r** as a white solid; Yield: 74%, 2.87 g; **1H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.65 (d, *J* = 7.7 Hz, 2H), 7.52 (dd, *J* = 8.3, 6.6 Hz, 1H), 7.37 – 7.17 (m, 8H), 7.04 (tt, *J* = 7.5, 3.8 Hz, 2H), 6.94 (d, *J* = 7.4 Hz, 1H), 4.19 – 4.06 (m, 2H), 1.60 (s, 9H). **13C NMR (101 MHz, CDCl<sub>3</sub>)** δ 171.6, 165.4, 140.4, 136.1, 133.9, 129.7, 129.5, 129.5, 129.0, 128.6, 128.4, 126.7, 126.2, 126.0, 125.5, 63.1, 38.3, 27.6. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>25</sub>H<sub>25</sub>NO<sub>3</sub>Na)<sup>+</sup>: 410.1727, found: 410.1731.

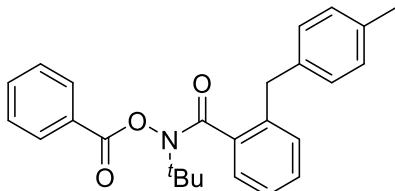
**N-(benzoyloxy)-N-(tert-butyl)-2-(4-chlorobenzyl)benzamide (1s)**



**1s**

Following the general procedure A, O-benzoyl-N-(tert-butyl)hydroxylamine 10.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1s** as a white solid; Yield: 53%, 2.24 g; **1H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.65 (d, *J* = 7.7 Hz, 2H), 7.56 – 7.48 (m, 1H), 7.37 – 7.26 (m, 5H), 7.25 – 7.19 (m, 2H), 7.05 (pd, *J* = 7.4, 1.7 Hz, 2H), 6.94 (d, *J* = 7.3 Hz, 1H), 4.12 (q, *J* = 15.6 Hz, 2H), 1.60 (s, 9H). **13C NMR (101 MHz, CDCl<sub>3</sub>)** δ 165.5, 140.5, 134.0, 129.8, 129.6, 129.6, 129.1, 128.6, 128.5, 126.8, 126.3, 126.1, 125.6, 63.2, 38.4, 27.7. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>25</sub>H<sub>24</sub>ClNO<sub>3</sub>Na)<sup>+</sup>: 444.1337, found: 444.1333.

**N-(benzoyloxy)-N-(tert-butyl)-2-(4-methylbenzyl)benzamide (1t)**

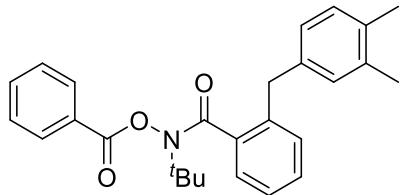


**1t**

Following the general procedure B, N-(tert-butyl)hydroxylamine hydrochloride 5.0 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1t** as a white solid; Yield: 30%, 580 mg **1H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.64 (d, *J* = 7.4 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.34 (t, *J* = 7.7 Hz, 2H), 7.28 (dd, *J* = 7.3, 1.8 Hz, 1H), 7.13 (q, *J* = 8.0 Hz, 4H), 7.05 (dtd, *J* = 13.9, 7.6, 4.0 Hz, 2H), 6.95 (d, *J* = 7.5 Hz, 1H), 4.18 – 4.03 (m, 2H), 2.34 (s, 3H), 1.61 (s, 9H). **13C NMR (126 MHz, CDCl<sub>3</sub>)** δ 172.4, 165.4,

137.3, 136.1, 135.6, 133.9, 129.6, 129.5 129.3, 129.1, 129.0, 128.5, 126.8, 125.9, 125.5, 63.0, 37.9, 27.6, 21.1. **HRMS** (ESI) m/z (M+Na)<sup>+</sup>: calculated for (C<sub>26</sub>H<sub>27</sub>NO<sub>3</sub>Na)<sup>+</sup>: 424.1883, found: 424.1888.

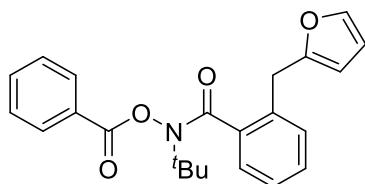
**N-(benzoyloxy)-N-(tert-butyl)-2-(3,4-dimethylbenzyl)benzamide (1u)**



**1u**

**Following the general procedure B,** N-(tert-butyl)hydroxylamine hydrochloride 4.2 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **1u** as a white solid; Yield: 43%, 0.75 g; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.64 (d, *J* = 7.7 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 1H), 7.10 – 6.91 (m, 6H), 4.11 – 4.00 (m, 2H), 2.25 (s, 3H), 2.23 (s, 3H), 1.62 (s, 9H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 171.6, 165.4, 137.7, 136.5, 136.1, 134.3, 133.9, 130.8, 129.7, 129.6, 129.5, 129.0, 128.5, 126.9, 126.8, 125.9, 125.4, 63.0, 37.8, 27.6, 19.8, 19.4. **HRMS (ESI) m/z (M+Na)<sup>+</sup>:** calculated for (C<sub>27</sub>H<sub>29</sub>NO<sub>3</sub>Na)<sup>+</sup>: 438.2040, found: 438.2040.

**N-(benzoyloxy)-N-(tert-butyl)-2-(furan-2-ylmethyl)benzamide (1v)**



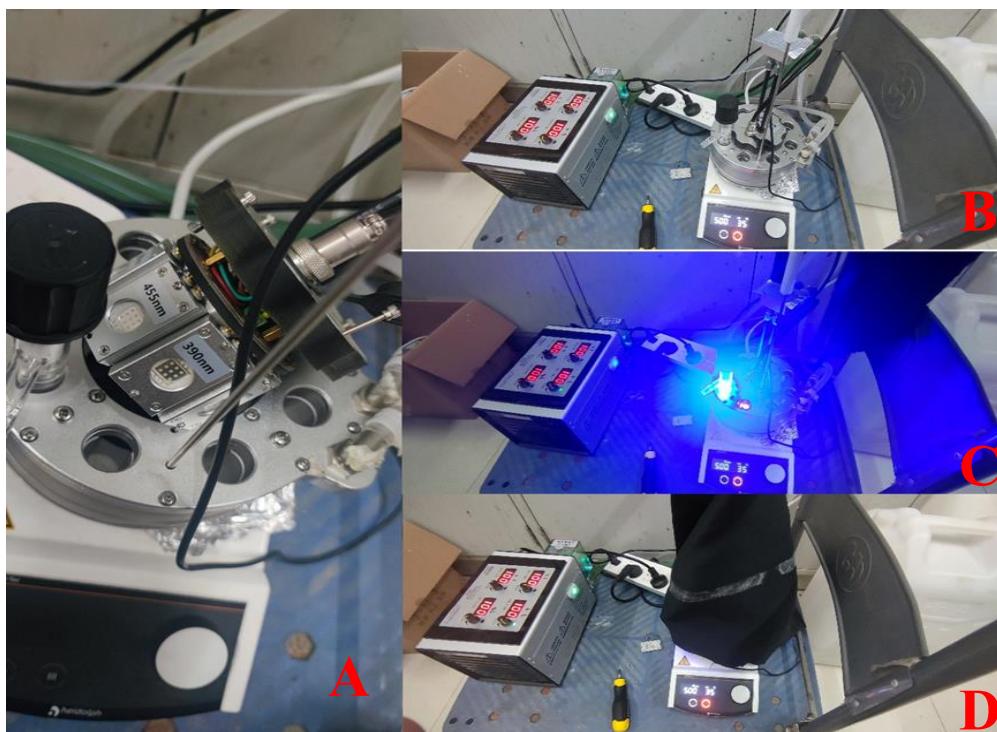
**1v**

**Following the general procedure B,** N-(tert-butyl)hydroxylamine hydrochloride 7.2 mmol was used. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 4:1, v/v) to afford **1v** as a white solid; Yield: 45%, 1.20 g; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.63 (d, *J* = 7.8 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.17 (dd, *J* = 5.2, 1.2 Hz,

1H), 7.14 – 7.07 (m, 2H), 7.07 – 7.01 (m, 1H), 6.95 (dd,  $J = 5.2, 3.4$  Hz, 1H), 6.86 (d,  $J = 3.4$  Hz, 1H), 4.37 – 4.23 (m, 2H), 1.60 (s, 9H).  **$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )**  $\delta$  171.3, 165.5, 142.9, 135.8, 134.0, 129.7, 129.4, 129.3, 128.6, 126.9, 126.7, 126.1, 126.0, 124.2, 63.2, 32.6, 27.7. **HRMS** (ESI) m/z ( $\text{M}+\text{H})^+$ : calculated for  $(\text{C}_{23}\text{H}_{24}\text{NO}_4)^+$ : 378.1700, found: 378.1691.

### General procedure for the Products:

To a flame-dried and N<sub>2</sub>-purged Schlenk tube (10 mL) was added a stirring bar, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.005 mmol, 3.5 mg), PPh<sub>3</sub> (0.01 mmol, 2.6 mg), PhCOONa (0.0125 mmol, 1.8 mg) and **1** (0.1 mmol). Then the tube was purged and backfilled with N<sub>2</sub> three times before adding THF (1.0 mL). The resulting solution was frozen under liquid nitrogen. The nitrogen atmosphere was evacuated from the tube in a Schlenk line and then was pressurized with 2 bar CO. The resulting solution was stirred under 456 nm 10W LEDs at 35 °C for 18 hours (**Figure 2.**). Then the reaction was taken out of the irradiation system. The excess CO was removed by opening the cap inside a well-ventilated fume hood. The mixture was quenched with water (1.0 mL). The resulting solution was extracted with ethyl acetate (2.0 mL x 3). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford desired product **2**.



**Figure 2.** Photographs of photocatalysis and heating device

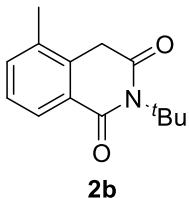
**2-(tert-butyl)isoquinoline-1,3(2H,4H)-dione (2a)**



**2a**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2a** as a white solid; **Yield:** 85%, 18.6 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.5; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.11 (dd, J = 7.9, 1.4 Hz, 1H), 7.52 (td, J = 7.5, 1.4 Hz, 1H), 7.44 - 7.35 (m, 1H), 7.21 (d, J = 7.6 Hz, 1H), 3.94 (s, 2H), 1.67 (s, 9H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.1, 166.3, 133.4, 133.0, 128.7, 128.0, 127.5, 126.5, 60.6, 39.8, 29.4. **HRMS (ESI) m/z (M+Na)<sup>+</sup>:** calculated for (C<sub>13</sub>H<sub>15</sub>NO<sub>2</sub>Na)<sup>+</sup>: 240.0995, found: 240.0999.

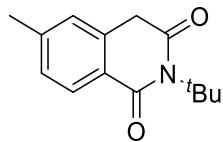
**2-(tert-butyl)-5-methylisoquinoline-1,3(2H,4H)-dione (2b)**



**2b**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2b** as a white solid; **Yield:** 82%, 19.0 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.5; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.99 – 7.97 (m, 1H), 7.37 (d, J = 7.4 Hz, 1H), 7.31 (t, J = 7.7 Hz, 1H), 3.80 (s, 2H), 2.27 (s, 3H), 1.67 (s, 9H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.0, 166.6, 134.7, 134.1, 132.0, 128.1, 127.3, 126.5, 60.5, 38.1, 29.4, 18.4. **HRMS (ESI) m/z (M+Na)<sup>+</sup>:** calculated for (C<sub>14</sub>H<sub>17</sub>NO<sub>2</sub>Na)<sup>+</sup>: 254.1151, found: 254.1151.

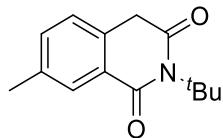
**2-(tert-butyl)-6-methylisoquinoline-1,3(2H,4H)-dione (2c)**



**2c**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2c** as a white solid; **Yield:** 84%, 19.4 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.5; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.99 (d, *J* = 8.1 Hz, 1H), 7.21 – 7.18 (m, 1H), 7.01 (d, *J* = 1.8 Hz, 1H), 3.89 (s, 2H), 2.40 (s, 3H), 1.66 (s, 9H); **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.3, 166.4, 143.9, 133.4, 128.8, 128.5, 126.9, 125.4, 60.5, 39.8, 29.5, 21.6. **HRMS (ESI)** m/z (M+Na)<sup>+</sup>: calculated for (C<sub>14</sub>H<sub>17</sub>NO<sub>2</sub>Na)<sup>+</sup>: 254.1151, found: 254.1152.

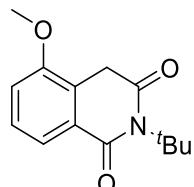
#### **2-(tert-butyl)-7-methylisoquinoline-1,3(2H,4H)-dione (2d)**



**2d**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2d** as a white solid; **Yield:** 74%, 17.1 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.4; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.91 (s, 1H), 7.32 (dd, *J* = 7.8, 1.9 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 1H), 3.88 (s, 2H), 2.39 (s, 3H), 1.66 (s, 9H); **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 172.4, 166.6, 137.3, 134.0, 130.4, 128.9, 127.7, 126.5, 60.5, 39.5, 29.4, 21.1. **HRMS (ESI)** m/z (M+Na)<sup>+</sup>: calculated for (C<sub>14</sub>H<sub>17</sub>NO<sub>2</sub>Na)<sup>+</sup>: 254.1151, found: 254.1149.

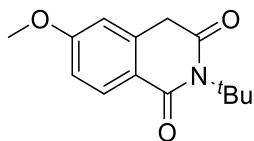
#### **2-(tert-butyl)-5-methoxyisoquinoline-1,3(2H,4H)-dione(2e)**



**2e**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2e** as a white solid; **Yield:** 92%, 22.7 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.4; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.70 (dd, J = 7.9, 1.0 Hz, 1H), 7.39 – 7.31 (m, 1H), 7.02 (dd, J = 8.2, 1.1 Hz, 1H), 3.87 (s, 3H), 3.80 (s, 2H), 1.66 (s, 9H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.2, 166.4, 155.4, 129.0, 128.0, 122.6, 120.1, 113.5, 60.4, 55.7, 35.1, 29.4. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>14</sub>H<sub>17</sub>NO<sub>3</sub>Na)<sup>+</sup>: 270.1101, found: 270.1101.

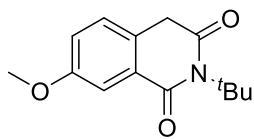
### 2-(tert-butyl)-6-methoxyisoquinoline-1,3(2H,4H)-dione (**2f**)



**2f**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 5:1, v/v) to afford **2f** as a white solid; **Yield:** 96%, 23.8 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.3; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.04 (d, J = 8.8 Hz, 1H), 6.90 (dd, J = 8.8, 2.5 Hz, 1H), 6.64 (dd, J = 2.4, 1.2 Hz, 1H), 3.88 (s, 2H), 3.85 (s, 3H), 1.65 (s, 9H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 172.1, 166.0, 163.3, 135.6, 130.9, 120.8, 114.1, 110.5, 60.4, 55.6, 40.2, 29.5. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>14</sub>H<sub>17</sub>NO<sub>3</sub>Na)<sup>+</sup>: 270.1101, found: 270.1103.

### 2-(tert-butyl)-7-methoxyisoquinoline-1,3(2H,4H)-dione (**2g**)

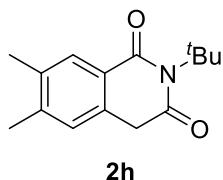


**2g**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2g** as a white solid; **Yield:** 75%, 18.5 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.4; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.61 – 7.60 (m, 1H), 7.13 – 7.08 (m, 2H), 3.87 (s, 2H), 3.86 (s, 3H), 1.67 (s, 9H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.5, 166.3, 159.0, 128.8, 127.8,

125.6, 121.5, 110.9, 60.6, 55.6, 39.2, 29.4. **HRMS** (ESI) m/z (M+Na)<sup>+</sup>: calculated for (C<sub>14</sub>H<sub>17</sub>NO<sub>3</sub>Na)<sup>+</sup>: 270.1101, found: 270.1099.

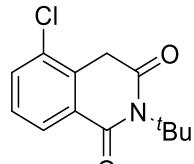
### **2-(tert-butyl)-6,7-dimethylisoquinoline-1,3(2H,4H)-dione (2h)**



**2h**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2h** as a white solid; **Yield:** 90%, 22.1 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.4; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.86 (s, 1H), 6.96 (s, 1H), 3.85 (s, 2H), 2.30 (s, 6H), 1.66 (s, 9H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.5, 166.6, 142.8, 136.2, 130.8, 129.3, 127.5, 125.6, 60.4, 39.5, 29.5, 20.0, 19.5. **HRMS** (ESI) m/z (M+Na)<sup>+</sup>: calculated for (C<sub>15</sub>H<sub>19</sub>NO<sub>2</sub>Na)<sup>+</sup>: 268.1308, found: 268.1314

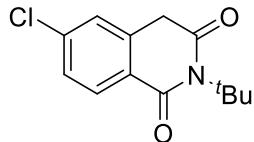
### **2-(tert-butyl)-5-chloroisoquinoline-1,3(2H,4H)-dione (2i)**



**2i**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 20:1, v/v) to afford **2i** as a white solid; **Yield:** 79%, 20.0 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.6; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.06 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.40 – 7.35 (m, 1H), 3.93 (s, 2H), 1.67 (s, 9H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.8, 165.3, 133.2, 132.2, 131.7, 129.8, 128.4, 127.3, 60.9, 38.1, 29.3. **HRMS** (ESI) m/z (M+Na)<sup>+</sup>: calculated for (C<sub>13</sub>H<sub>14</sub>ClNO<sub>2</sub>Na)<sup>+</sup>: 274.0605, found: 274.0595.

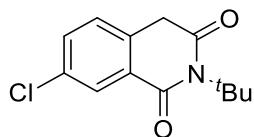
### **2-(tert-butyl)-6-chloroisoquinoline-1,3(2H,4H)-dione (2j)**



**2j**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2j** as a white solid; **Yield:** 51%, 12.8 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.5; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.05 (d, *J* = 8.4 Hz, 1H), 7.37 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.22 (dt, *J* = 2.2, 1.1 Hz, 1H), 3.91 (s, 2H), 1.66 (s, 9H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 171.3, 165.4, 139.4, 134.9, 130.4, 128.1, 126.5, 126.4, 60.9, 39.5, 29.4. **HRMS (ESI)** m/z (M+Na)<sup>+</sup>: calculated for (C<sub>13</sub>H<sub>14</sub>ClNO<sub>2</sub>Na)<sup>+</sup>: 274.0605, found: 274.0601.

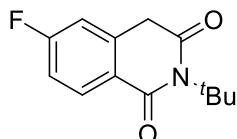
### 2-(tert-butyl)-7-chloroisoquinoline-1,3(2H,4H)-dione (**2k**)



**2k**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2k** as a white solid; **Yield:** 60%, 15.1 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.5; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.09 (d, *J* = 2.3 Hz, 1H), 7.48 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.17 – 7.13 (m, 1H), 3.90 (d, *J* = 1.0 Hz, 2H), 1.66 (s, 9H) **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 171.5, 165.1, 133.7, 133.1, 131.6, 129.4, 128.6, 128.0, 61.0, 39.3, 29.4. **HRMS (ESI)** m/z (M+Na)<sup>+</sup>: calculated for (C<sub>13</sub>H<sub>14</sub>ClNO<sub>2</sub>Na)<sup>+</sup>: 274.0605, found: 274.0605.

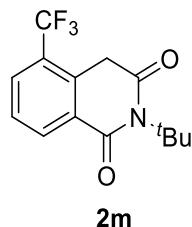
### 2-(tert-butyl)-6-fluoroisoquinoline-1,3(2H,4H)-dione (**2l**)



**2l**

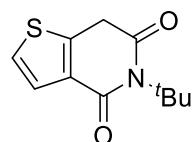
The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2l** as a white solid; **Yield:** 82%, 19.3 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.4; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.14 (dd, J = 8.8, 5.7 Hz, 1H), 7.09 (td, J = 8.5, 2.5 Hz, 1H), 6.91 (ddt, J = 8.5, 2.4, 1.0 Hz, 1H), 3.93 (s, 2H), 1.66 (s, 9H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 171.4, 165.4 (d, J = 254.6 Hz), 165.3, 136.1 (d, J = 9.6 Hz), 131.8 (d, J = 9.6 Hz), 124.3 (d, J = 2.8 Hz), 115.3 (d, J = 22.1 Hz), 113.1 (d, J = 22.7 Hz), 60.8, 39.8, 29.4. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>13</sub>H<sub>14</sub>FNO<sub>2</sub>Na)<sup>+</sup>: 258.0901, found: 258.0903.

### 2-(tert-butyl)-5-(trifluoromethyl)isoquinoline-1,3(2H,4H)-dione (**2m**)



The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2m** as a white solid; **Yield:** 56%, 16.0 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.6; **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.36 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.55 – 7.51 (m, 1H), 4.12 (s, 2H), 1.67 (s, 9H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.4, 165.1, 132.6, 131.9, 130.2 (q, J = 5.2 Hz), 129.7, 127.5, 126.3(q, J = 272.0 Hz), 61.1, 37.3, 29.3. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>14</sub>H<sub>14</sub>F<sub>3</sub>NO<sub>2</sub>Na)<sup>+</sup>: 308.0869, found: 308.0879.

### 5-(tert-butyl)thieno[3,2-c]pyridine-4,6(5H,7H)-dione (**2n**)

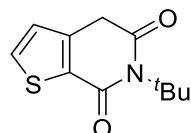


**2n**

The crude reaction mixture was purified by column chromatography on silica gel

(eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2n** as a white solid; **Yield:** 31%, 6.9 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.4, **<sup>1</sup>H NMR** (**400 MHz, CDCl<sub>3</sub>**) δ 7.42 (d, *J* = 5.3 Hz, 1H), 7.20 (d, *J* = 5.2 Hz, 1H), 4.00 (s, 2H), 1.66 (s, 9H) **<sup>13</sup>C NMR** (**101 MHz, CDCl<sub>3</sub>**) δ 171.5, 162.5, 141.2, 129.6, 125.9, 124.8, 60.6, 37.2, 29.6. **HRMS** (ESI) m/z (M+Na)<sup>+</sup>: calculated for (C<sub>11</sub>H<sub>13</sub>NO<sub>2</sub>SNa)<sup>+</sup>: 246.0559, found: 246.0558.

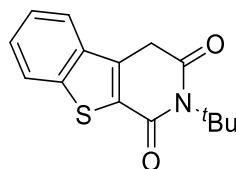
### 6-(tert-butyl)thieno[2,3-c]pyridine-5,7(4H,6H)-dione (**2o**)



**2o**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2o** as a white solid; **Yield:** 45%, 10.0 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.3, **<sup>1</sup>H NMR** (**500 MHz, CDCl<sub>3</sub>**) δ 7.59 (d, *J* = 5.0 Hz, 1H), 6.94 (d, *J* = 5.0 Hz, 1H), 3.86 (s, 2H), 1.67 (s, 9H). **<sup>13</sup>C NMR** (**126 MHz, CDCl<sub>3</sub>**) δ 172.9, 162.3, 139.0, 133.2, 131.8, 125.8, 61.0, 38.1, 29.7. **HRMS** (ESI) m/z (M+Na)<sup>+</sup>: calculated for (C<sub>11</sub>H<sub>13</sub>NO<sub>2</sub>SNa)<sup>+</sup>: 246.0559, found: 246.0559.

### 2-(tert-butyl)benzo[4,5]thieno[2,3-c]pyridine-1,3(2H,4H)-dione (**2p**)

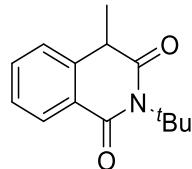


**2p**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2p** as a white solid; **Yield:** 31%, 8.5 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.5, **<sup>1</sup>H NMR** (**500 MHz, CDCl<sub>3</sub>**) δ 7.91 (dt, *J* = 8.0, 0.9 Hz, 1H), 7.75 – 7.68 (m, 1H), 7.48 (dd, *J*

= 24.7, 8.1, 7.2, 1.2 Hz, 2H), 4.02 (s, 2H), 1.71 (s, 9H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 172.3, 162.9, 141.7, 136.2, 134.4, 131.5, 127.7, 125.2, 123.5, 123.0, 61.3, 36.5, 29.6. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>15</sub>H<sub>15</sub>NO<sub>2</sub>SNa)<sup>+</sup>: 296.0716, found: 296.0726.

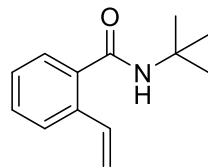
### 2-(tert-butyl)-4-methylisoquinoline-1,3(2H,4H)-dione (2q)



**2q**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 20:1, v/v) to afford **2q** as a white solid; **Yield:** 28%, 6.5 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.65; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.13 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.55 (td, *J* = 7.5, 1.4 Hz, 1H), 7.40 (td, *J* = 7.7, 1.2 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 1H), 3.79 (q, *J* = 7.2 Hz, 1H), 1.66 (s, 9H), 1.59 (d, *J* = 7.2 Hz, 3H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 177.0, 165.7, 139.5, 133.2, 128.8, 127.4, 126.9, 125.9, 60.0, 44.4, 29.3, 21.0. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>14</sub>H<sub>17</sub>NO<sub>2</sub>Na)<sup>+</sup>: 254.1151, found: 254.1160.

### N-(tert-butyl)-2-vinylbenzamide (2q')

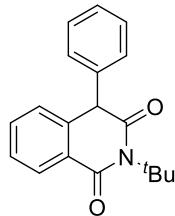


**2q'**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 5:1, v/v) to afford **2q'** as a white solid; **Yield:** 50 %, 10.2 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.3; **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.57 – 7.51 (m, 1H), 7.42 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.37 (td, *J* = 7.7, 1.5 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.02 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.72 (dd, *J* = 17.5, 1.2 Hz, 1H), 5.60 (s, 1H), 5.35 (dd, *J* = 11.0, 1.1 Hz, 1H), 1.46 (s, 9H) **<sup>13</sup>C NMR**

**(126 MHz, CDCl<sub>3</sub>)** δ 168.9, 136.7, 135.5, 134.6, 129.8, 127.7, 127.3, 126.2, 116.5, 52.0, 28.8. **HRMS** (ESI) m/z (M+Na)<sup>+</sup>: calculated for (C<sub>13</sub>H<sub>17</sub>NONa)<sup>+</sup>: 226.1202, found: 226.1210.

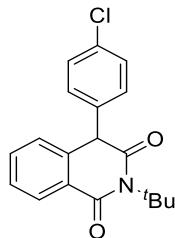
### 2-(tert-butyl)-4-phenylisoquinoline-1,3(2H,4H)-dione (2r)



**2r**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2r** as a white solid; **Yield:** 89%, 26.1 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.6, **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.24 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.53 (td, *J* = 7.4, 1.5 Hz, 1H), 7.46 (td, *J* = 7.6, 1.4 Hz, 1H), 7.36 – 7.24 (m, 3H), 7.12 (ddd, *J* = 7.3, 5.7, 1.8 Hz, 3H), 4.97 (s, 1H), 1.46 (s, 9H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 174.1, 165.5, 137.6, 137.0, 133.5, 129.0, 128.7, 128.1, 128.0, 127.9, 127.6, 60.0, 56.2, 28.8. **HRMS** (ESI) m/z (M+Na)<sup>+</sup>: calculated for (C<sub>19</sub>H<sub>19</sub>NO<sub>2</sub>Na)<sup>+</sup>: 316.1308, found: 316.1310.

### 2-(tert-butyl)-4-(4-chlorophenyl)isoquinoline-1,3(2H,4H)-dione (2s)

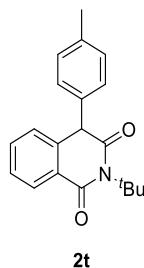


**2s**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2s** as a white solid; **Yield:** 78%, 25.6 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.5, **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.24 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.52 (td, *J* = 7.5, 1.5 Hz, 1H), 7.46 (td, *J* = 7.6, 1.3 Hz, 1H), 7.36 – 7.24 (m, 2H), 7.18 – 7.08 (m, 3H), 4.97 (s, 1H), 1.46 (s, 9H) **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 174.1, 165.5, 137.6, 137.0, 133.5, 129.0,

128.7, 128.1, 128.0, 127.6, 60.0, 56.3, 28.8. **HRMS** (ESI) m/z (M+Na)<sup>+</sup>: calculated for (C<sub>19</sub>H<sub>18</sub>ClNO<sub>2</sub>Na)<sup>+</sup>: 350.0918, found: 350.0920.

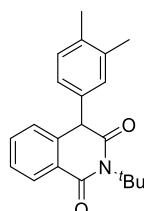
### 2-(tert-butyl)-4-(p-tolyl)isoquinoline-1,3(2H,4H)-dione (**2t**)



**2t**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2t** as a white solid; **Yield:** 86%, 26.3 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.6, **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.22 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.51 (td, *J* = 7.5, 1.5 Hz, 1H), 7.44 (td, *J* = 7.6, 1.3 Hz, 1H), 7.13 – 7.07 (m, 3H), 7.04 – 6.98 (m, 2H), 4.93 (s, 1H), 2.31 (s, 3H), 1.47 (s, 9H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 174.2, 165.5, 137.9, 137.3, 134.7, 133.4, 129.6, 128.7, 127.9, 127.9, 127.6, 59.9, 55.9, 28.9, 21.1. **HRMS** (ESI) m/z (M+Na)<sup>+</sup>: calculated for (C<sub>20</sub>H<sub>21</sub>NO<sub>2</sub>Na)<sup>+</sup>: 330.1465, found: 330.1467.

### 2-(tert-butyl)-4-(3,4-dimethylphenyl)isoquinoline-1,3(2H,4H)-dione (**2u**)

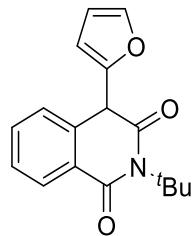


**2u**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2u** as a white solid; **Yield:** 88%, 28.3 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.6, **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.22 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.50 (td, *J* = 7.4, 1.5 Hz, 1H), 7.43 (td, *J* = 7.7, 1.3 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 2.1 Hz, 1H), 6.82 (dd, *J* = 7.8, 2.1 Hz, 1H), 4.89 (s, 1H), 2.22 (s, 3H), 2.20 (s, 3H), 1.49

(s, 9H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 174.3, 165.6, 137.5, 137.2, 136.5, 135.1, 133.4, 130.2, 129.3, 128.6, 127.8, 127.8, 127.6, 125.3, 59.9, 55.9, 28.9, 19.8, 19.4. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>21</sub>H<sub>23</sub>NO<sub>2</sub>Na)<sup>+</sup>: 344.1621, found: 344.1626.

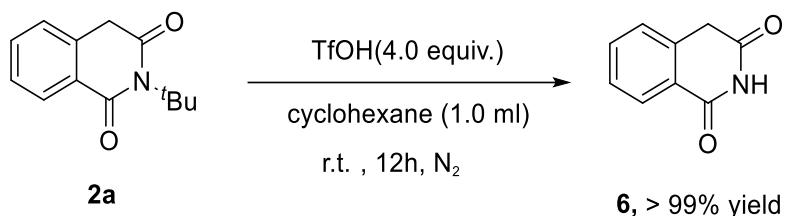
**2-(tert-butyl)-4-(furan-2-yl)isoquinoline-1,3(2H,4H)-dione (2v)**



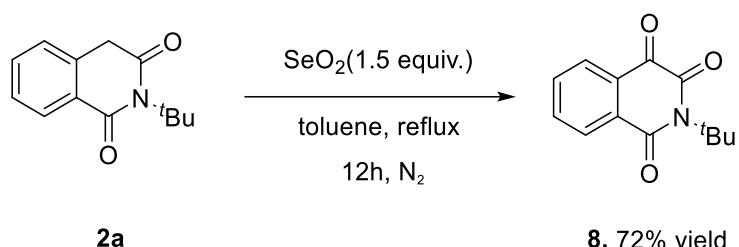
**2v**

The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate 10:1, v/v) to afford **2v** as a white solid; **Yield:** 24%, 6.8 mg; **TLC** (petroleum ether / ethyl acetate = 10/1, v/v): R<sub>f</sub> = 0.5, **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.21 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.55 (td, *J* = 7.5, 1.4 Hz, 1H), 7.47 (td, *J* = 7.7, 1.3 Hz, 1H), 7.27 – 7.20 (m, 2H), 6.95 (dd, *J* = 5.2, 3.5 Hz, 1H), 6.85 (dt, *J* = 3.5, 1.1 Hz, 1H), 5.20 (s, 1H), 1.53 (s, 9H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 173.0, 165.1, 140.4, 136.6, 133.5, 129.0, 128.3, 127.5, 127.3, 127.1, 126.5, 125.9, 60.3, 51.4, 28.9. **HRMS (ESI) m/z (M+Na)<sup>+</sup>**: calculated for (C<sub>17</sub>H<sub>17</sub>NO<sub>3</sub>Na)<sup>+</sup>: 306.1101, found: 306.1089.

## 5. Synthetic Applications

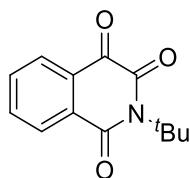


To a flame-dried and N<sub>2</sub>-purged Schlenk tube (10 mL) was added a stirring bar, **2a** (21.7 mg, 0.1 mmol). Then the tube was purged and backfilled with N<sub>2</sub> three times before adding anhydrous cyclohexane (1.0 mL). TfOH (60.0 mg, 0.4 mmol) was added to the solution under N<sub>2</sub>. The resulting solution was frozen under liquid nitrogen and pump away the trace oxygen in the solution, then the tube was backfilled with N<sub>2</sub>. After the solution was stirred at r.t. for 12 hours. The mixture was filtered and the yellow solid was washed by methanol (1.0 ml x 3), diethyl ether (1.0 ml x 2) and dried in vacuum to afford desired product **3** (16.0 mg, > 99% yield, yellow solid).



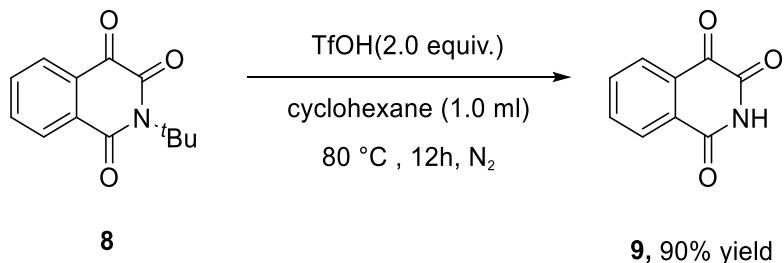
To a flame-dried and N<sub>2</sub>-purged Schlenk tube (10 mL) was added a stirring bar, **2a** (43.5 mg, 0.2 mmol), SeO<sub>2</sub> (33.3 mg, 0.3 mmol) and toluene (2.0 mL). After the solution was stirred at 110 °C for 12 hours. The mixture was filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether: ethyl acetate = 4 : 1) to afford desired product **4** (33.4 mg, 72% yield, white solid). The spectral data are consistent with previous literature reports.

**2-(tert-butyl)isoquinoline-1,3,4(2H)-trione(**8**)**



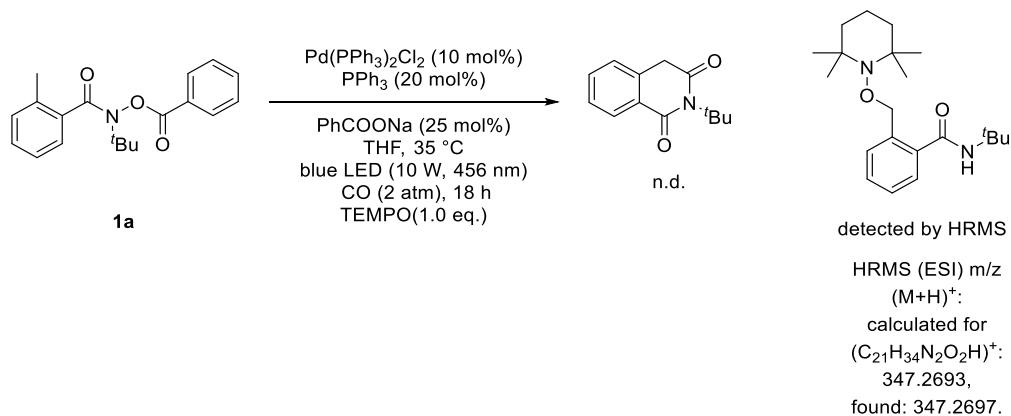
**8**

White solid, 33.4 mg, 72% yield, **TLC** (petroleum ether / ethyl acetate = 10/1, v/v):  
**Rf** = 0.3, **1H NMR** (**400 MHz, CDCl<sub>3</sub>**)  $\delta$  8.26 (dd, *J* = 7.8, 1.2 Hz, 1H), 8.13 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.87 (td, *J* = 7.6, 1.3 Hz, 1H), 7.78 (td, *J* = 7.6, 1.2 Hz, 1H), 1.72 (s, 9H). **13C NMR** (**101 MHz, CDCl<sub>3</sub>**)  $\delta$  176.6, 163.7, 159.7, 136.0, 133.9, 132.7, 130.1, 129.5, 127.0, 62.4, 29.3. **HRMS** (ESI) m/z (M+Na)<sup>+</sup>: calculated for (C<sub>13</sub>H<sub>13</sub>NO<sub>3</sub>Na)<sup>+</sup>: 254.0788, found: 254.0791.

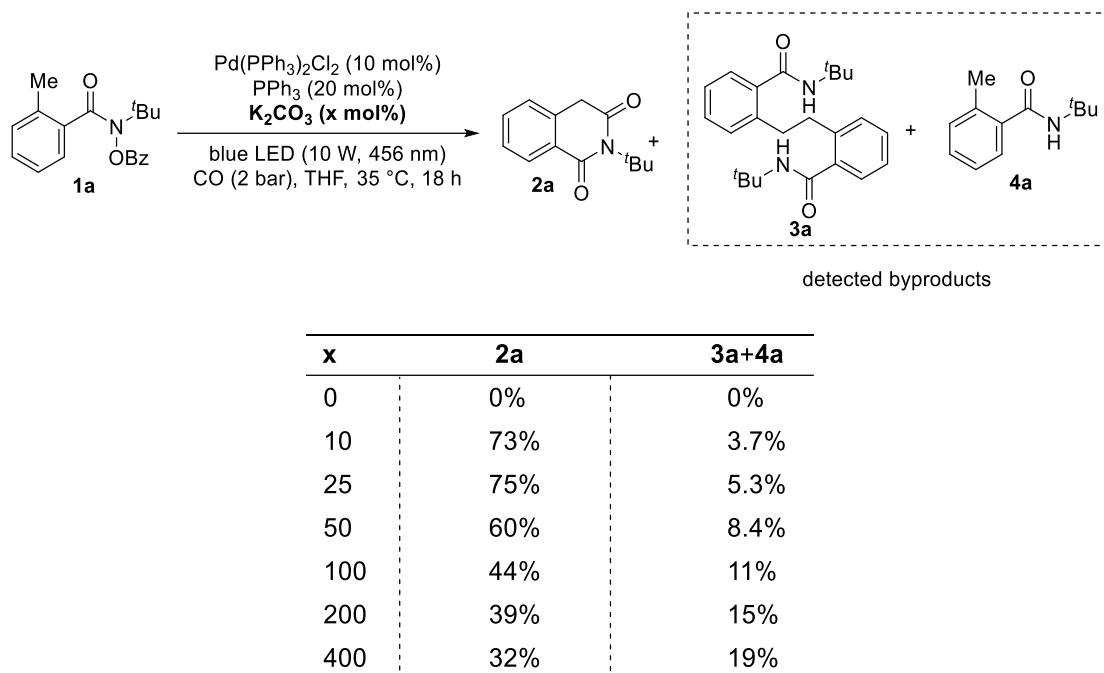


To a flame-dried and N<sub>2</sub>-purged Schlenk tube (10 mL) was added a stirring bar, **8** (8.4 mg, 0.036 mmol). Then the tube was purged and backfilled with N<sub>2</sub> three times before adding anhydrous cyclohexane (1.0 mL). TfOH (10.8 mg, 0.072 mmol) was added to the solution under N<sub>2</sub>. After the solution was stirred at 80 °C for 12 hours. The mixture was filtered and the dark red solid was washed by methanol (1.0 ml x 3), diethyl ether (1.0 ml x 2) and dried in vacuum to afford desired product **5** (90% yield, brown solid). The spectral data are consistent with previous literature reports.

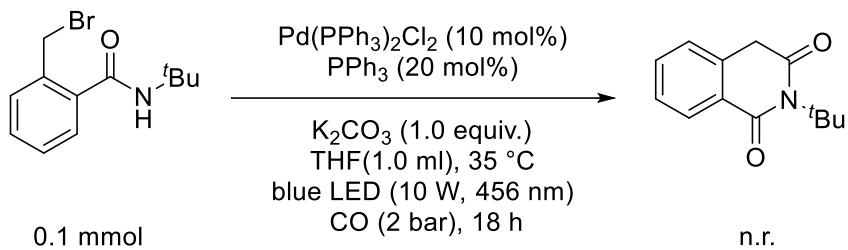
## 6. Mechanistic Investigations



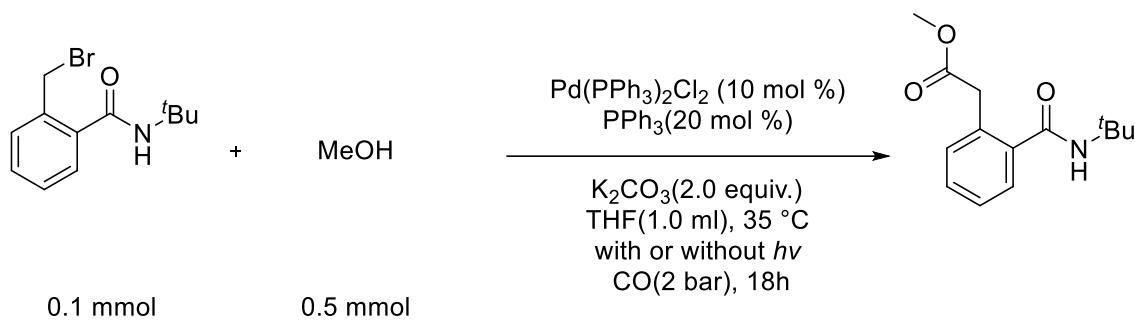
To a flame-dried and N<sub>2</sub>-purged Schlenk tube (10 mL) was added a stirring bar, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.01mmol, 7.0mg), PPh<sub>3</sub> (0.02 mmol, 5.3 mg), PhCOONa (0.025 mmol, 3.6 mg), **1a** (0.1 mmol), and TEMPO (0.1 mmol). Then the tube was purged and backfilled with N<sub>2</sub> three times before adding THF (1.0 mL). The resulting solution was frozen under liquid nitrogen. The nitrogen atmosphere was evacuated from the tube in a Schlenk line and then was pressurized with 2 bar CO. The resulting solution was stirred under 456nm 10W LEDs at 35 °C for 18 hours. Then the reaction was taken out of the irradiation system. The excess CO was removed by opening the cap inside a well-ventilated fume hood.



To a flame-dried and N<sub>2</sub>-purged Schlenk tube (10 mL) was added a stirring bar, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.01mmol, 7.0mg), PPh<sub>3</sub> (0.02 mmol, 5.3 mg) and K<sub>2</sub>CO<sub>3</sub>. Then the tube was purged and backfilled with N<sub>2</sub> three times before adding THF (1.0 mL). The resulting solution was frozen under liquid nitrogen. The nitrogen atmosphere was evacuated from the tube in a Schlenk line and then was pressurized with 2 bar CO. The resulting solution was stirred under 456nm 10W LEDs at 35 °C for 18 hours. Then the reaction was taken out of the irradiation system. The excess CO was removed by opening the cap inside a well-ventilated fume hood.



To a flame-dried and N<sub>2</sub>-purged Schlenk tube (10 mL) was added a stirring bar, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.01mmol, 7.0mg), PPh<sub>3</sub> (0.02 mmol, 5.3 mg), K<sub>2</sub>CO<sub>3</sub> (0.1mmol, 13.8mg) , 2-(bromomethyl)-N-(tert-butyl)benzamide (0.1 mmol). Then the tube was purged and backfilled with N<sub>2</sub> three times before adding THF (1.0 mL). The resulting solution was frozen under liquid nitrogen. The nitrogen atmosphere was evacuated from the tube in a Schlenk line and then was pressurized with 2 bar CO. The resulting solution was stirred under 456nm 10W LEDs at 35 °C for 18 hours. Then the reaction was taken out of the irradiation system. The excess CO was removed by opening the cap inside a well-ventilated fume hood.



To a flame-dried and N<sub>2</sub>-purged Schlenk tube (10 mL) was added a stirring bar, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.01mmol, 7.0mg), PPh<sub>3</sub> (0.02 mmol, 5.3 mg), K<sub>2</sub>CO<sub>3</sub> (0.2mmol) , 2-(bromomethyl)-N-(tert-butyl)benzamide (0.1 mmol). Then the tube was purged and backfilled with N<sub>2</sub> three times before adding THF (1.0 mL). The resulting solution was frozen under liquid nitrogen. The nitrogen atmosphere was evacuated from the tube in a Schlenk line and then was pressurized with 2 bar CO. The resulting solution was stirred under 456nm 10W LEDs (or dark) at 35 °C for 18 hours. Then the reaction was taken out of the irradiation system. The excess CO was removed by opening the cap inside a well-ventilated fume hood.

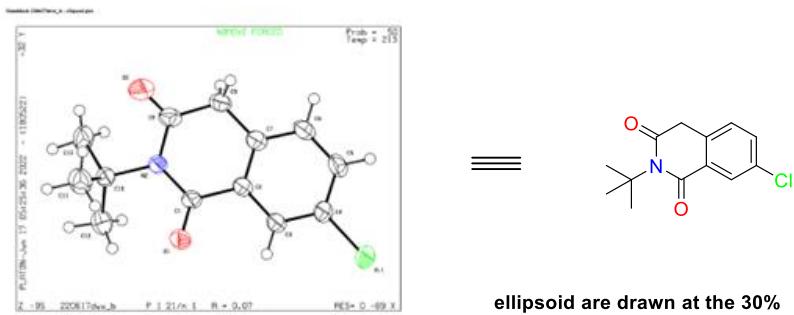
## 7. References:

- [1] S. K. Quek, I. M. Lyapkalo and H. V. Huynh, *Synthesis* **2006**, 2006, 1423-1426.
- [2] H. Chen, W. Jin and S. Yu, *Organic Letters* **2020**, 22, 5910-5914.
- [3] X. Ren, L. Zhu, Y. Yu, Z.-X. Wang and X. Huang, *Organic Letters* **2020**, 22, 3251-3257.

## 8. X-Ray single crystal data for **2k**.

For single crystal of **2k** (grew from dichloromethane/petroleum ether), a suitable crystal was selected and measured on a 'Bruker D8 Venture' diffractometer. The crystal was kept at 213.00 K during data collection.

**CCDC Number: 2179790**

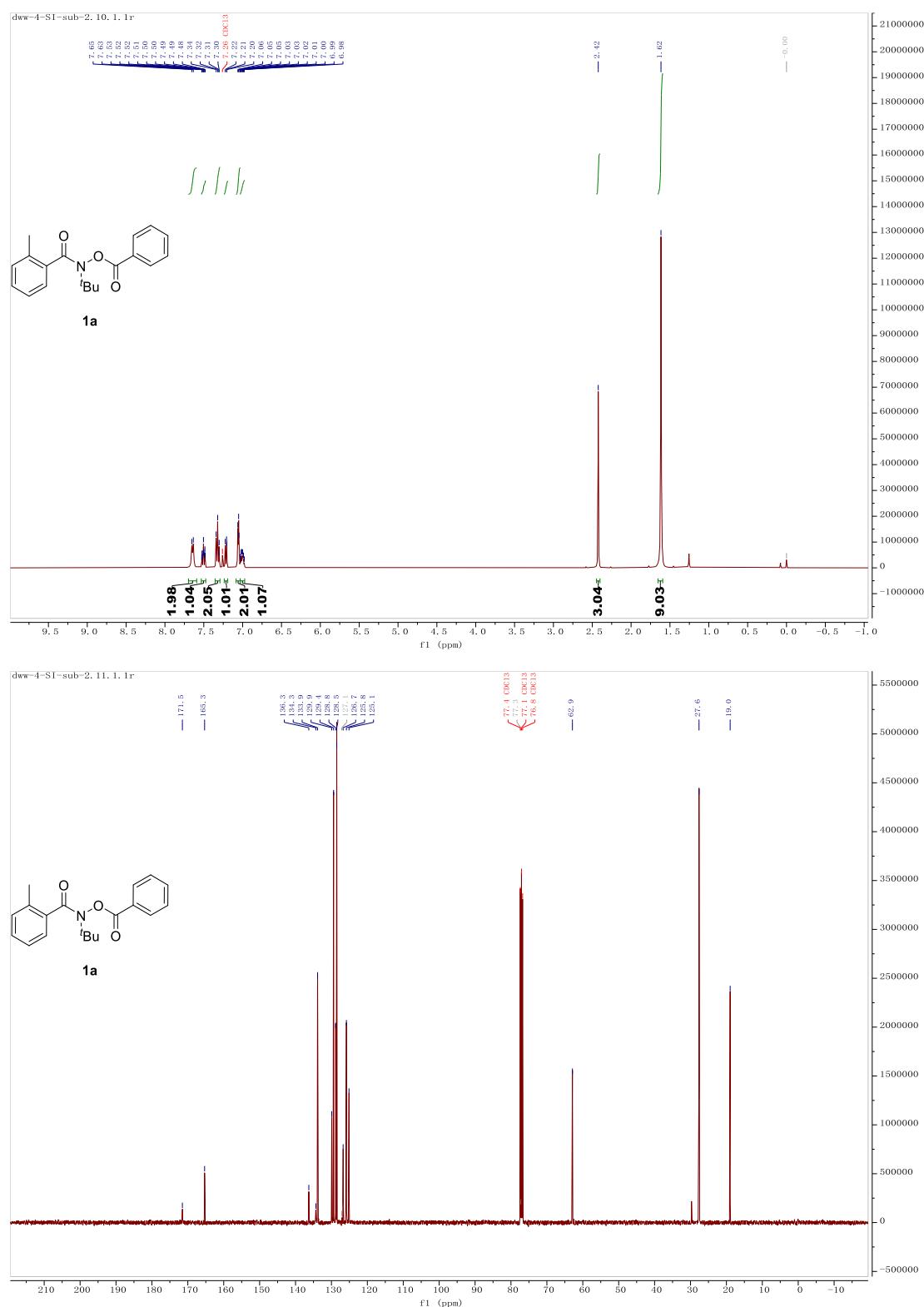


ellipsoids are drawn at the 30%

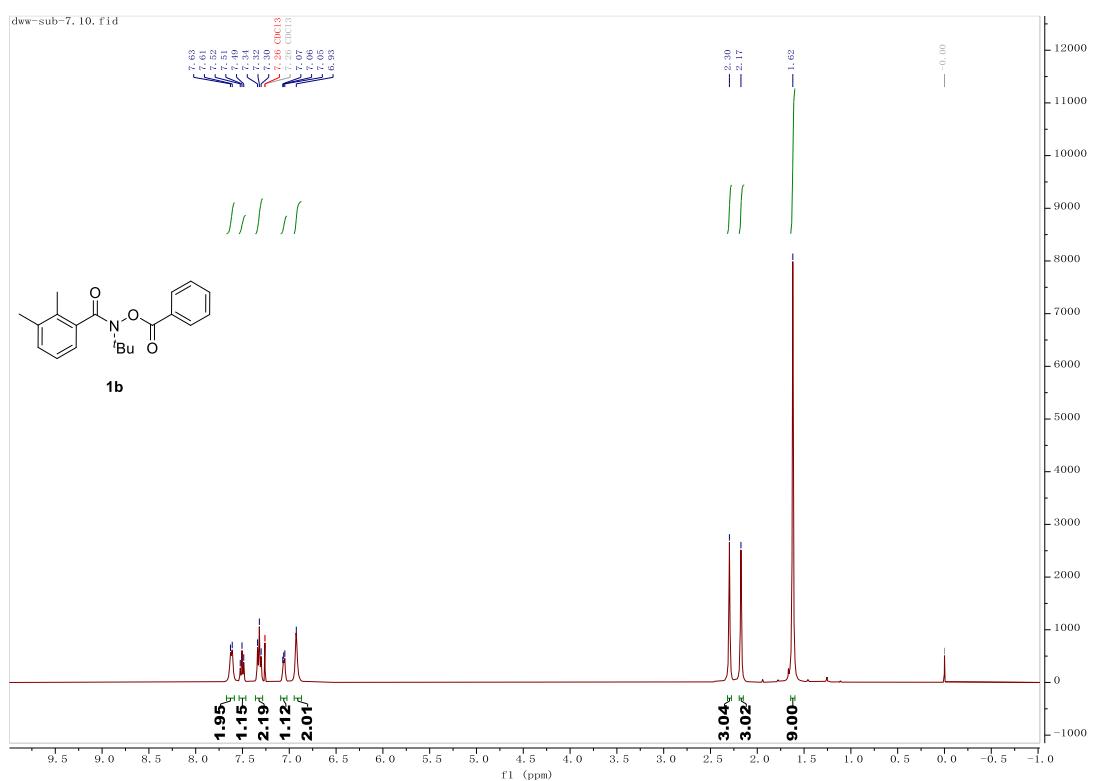
Identification code	220617dww_b
Empirical formula	C26 H28 Cl2 N2 O4
Formula weight	503.40
Temperature	213.00 K
Wavelength	1.34139 Å
Crystal system	Monoclinic
Space group	P 1 21/n 1
Unit cell dimensions	a = 6.1485(3) Å b = 9.6385(4) Å c = 20.3370(9) Å
	α= 90 ° β= 90.053(3) °. γ = 90 °
Volume	1205.22(9) Å <sup>3</sup>
Z	2
Density (calculated)	1.387 Mg/m <sup>3</sup>
Absorption coefficient	1.795 mm <sup>-1</sup>
F(000)	528
Crystal size	0.07 x 0.07 x 0.05 mm <sup>3</sup>
Theta range for data collection	3.782 to 54.966 °
Index ranges	-7<=h<=7, -10<=k<=11, -24<=l<=24
Reflections collected	10591
Independent reflections	2287 [R(int) = 0.0883]
Completeness to theta = 53.594 °	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.2377
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	2287 / 0 / 157
Goodness-of-fit on F <sup>2</sup>	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0731, wR2 = 0.2014
R indices (all data)	R1 = 0.0923, wR2 = 0.2204
Extinction coefficient	n/a
Largest diff. peak and hole	0.512 and -0.701 e.Å <sup>-3</sup>

## 9. NMR Spectra

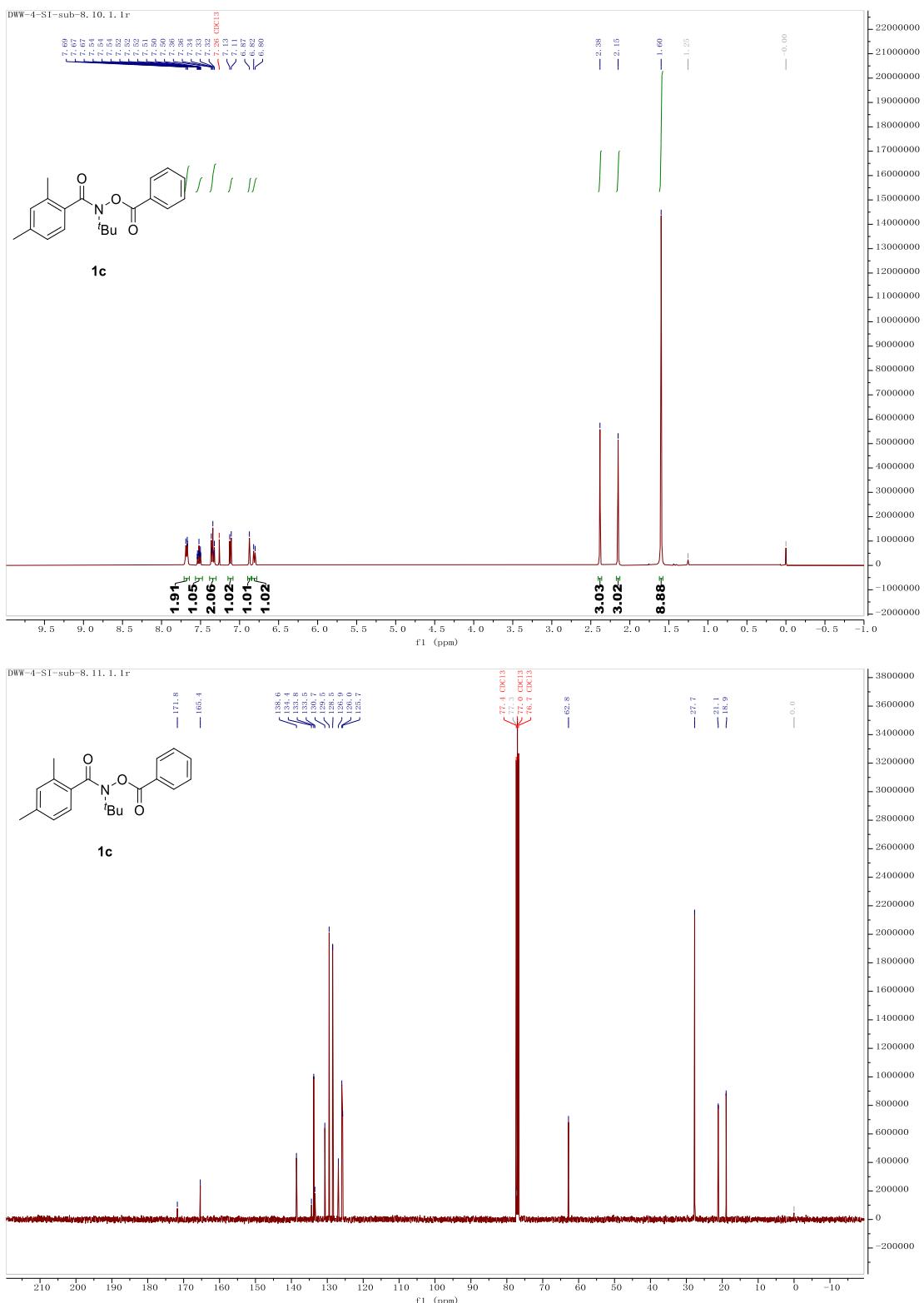
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 1a**



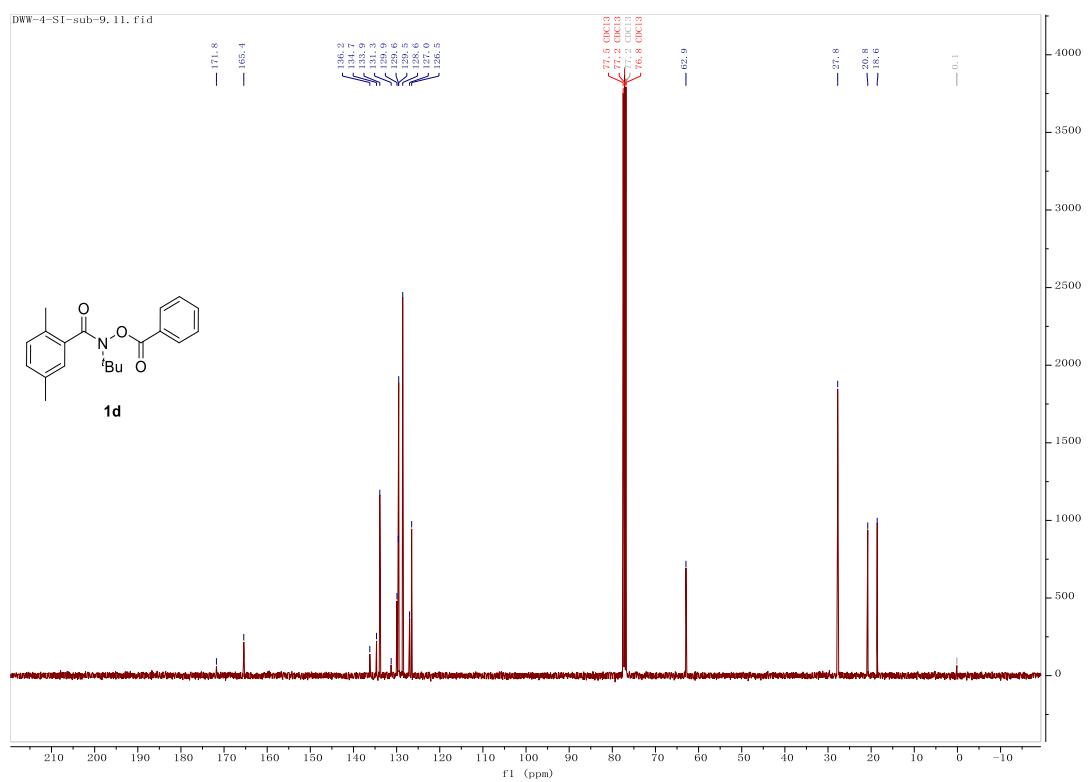
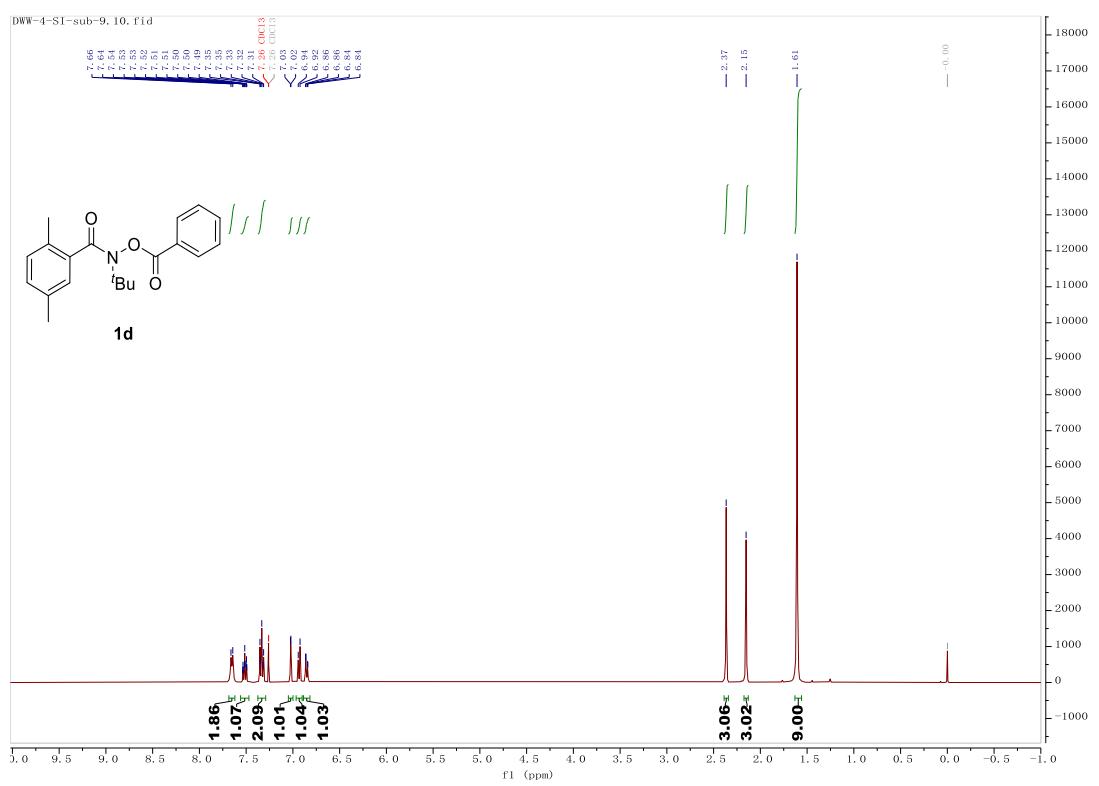
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 1b**



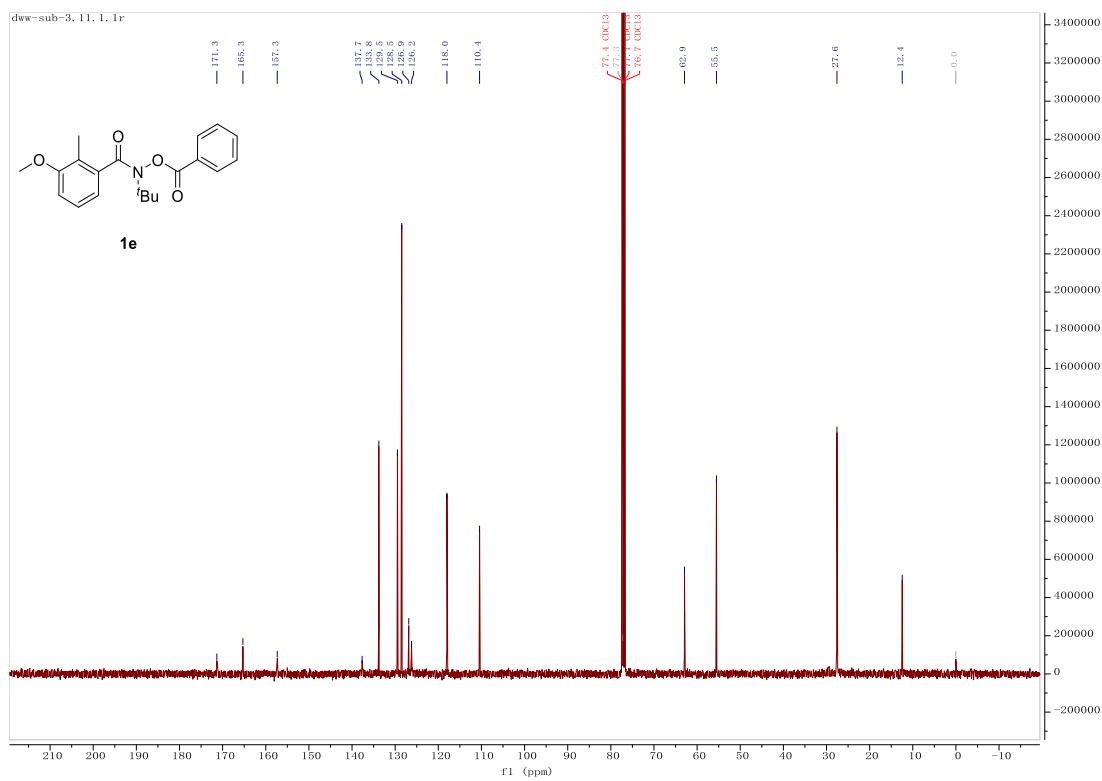
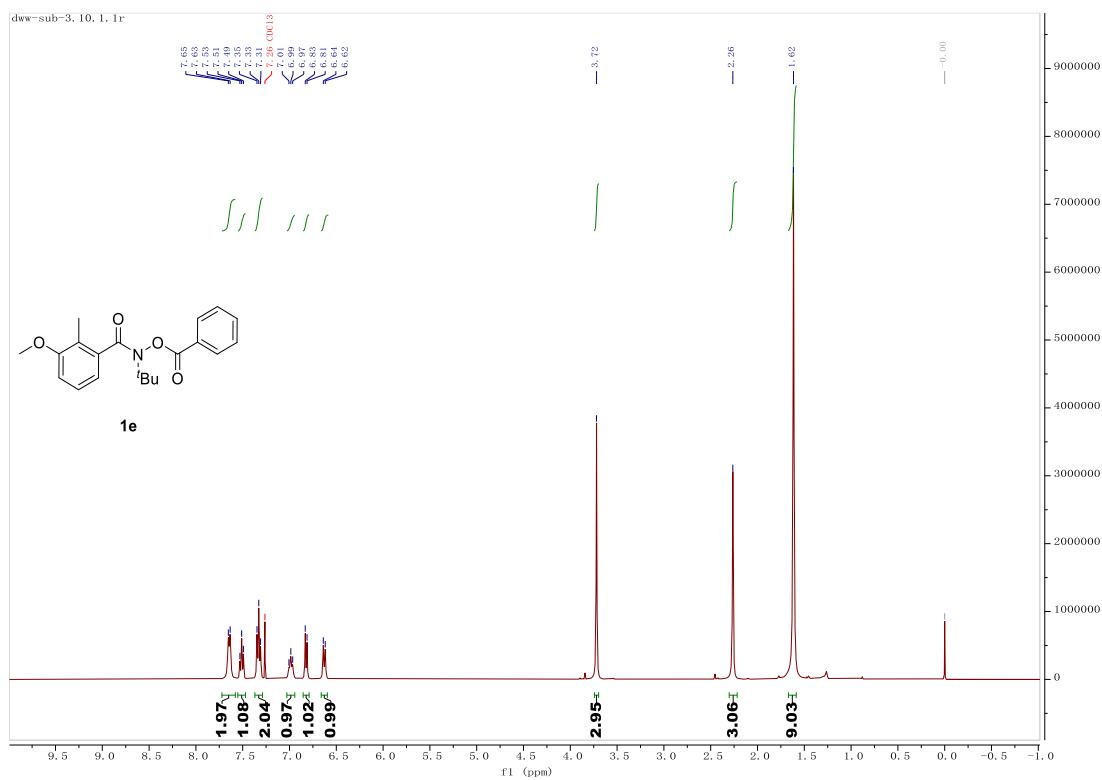
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 1c**



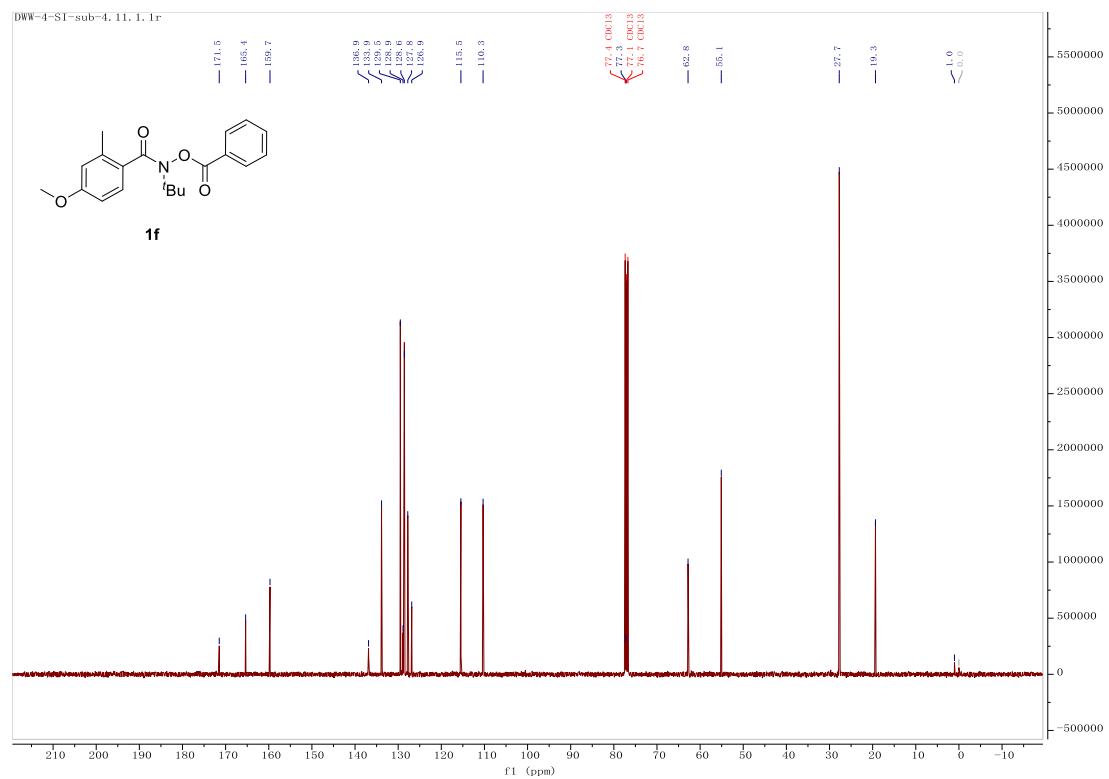
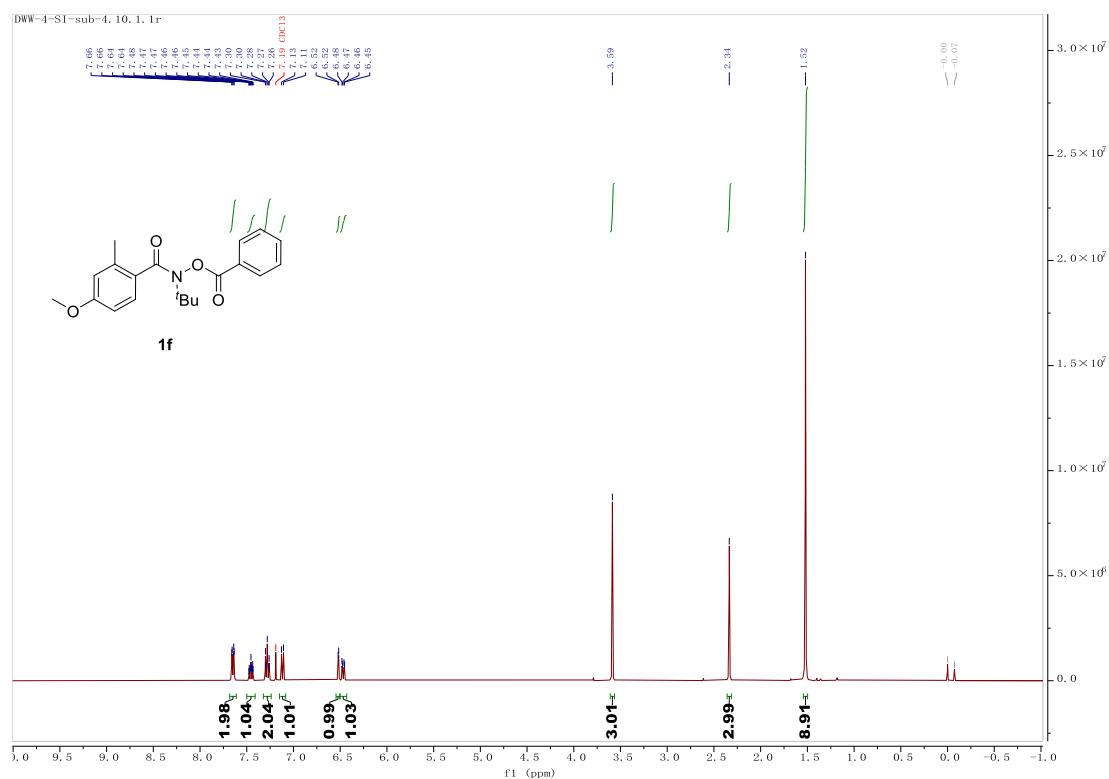
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 1d



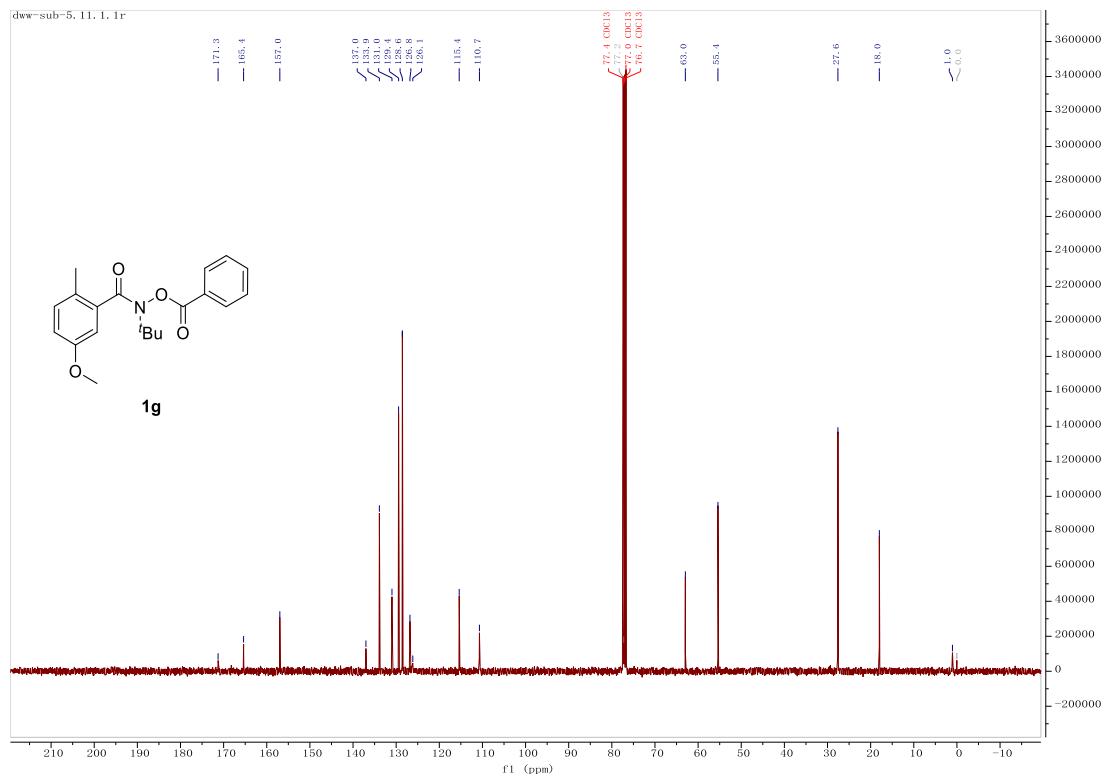
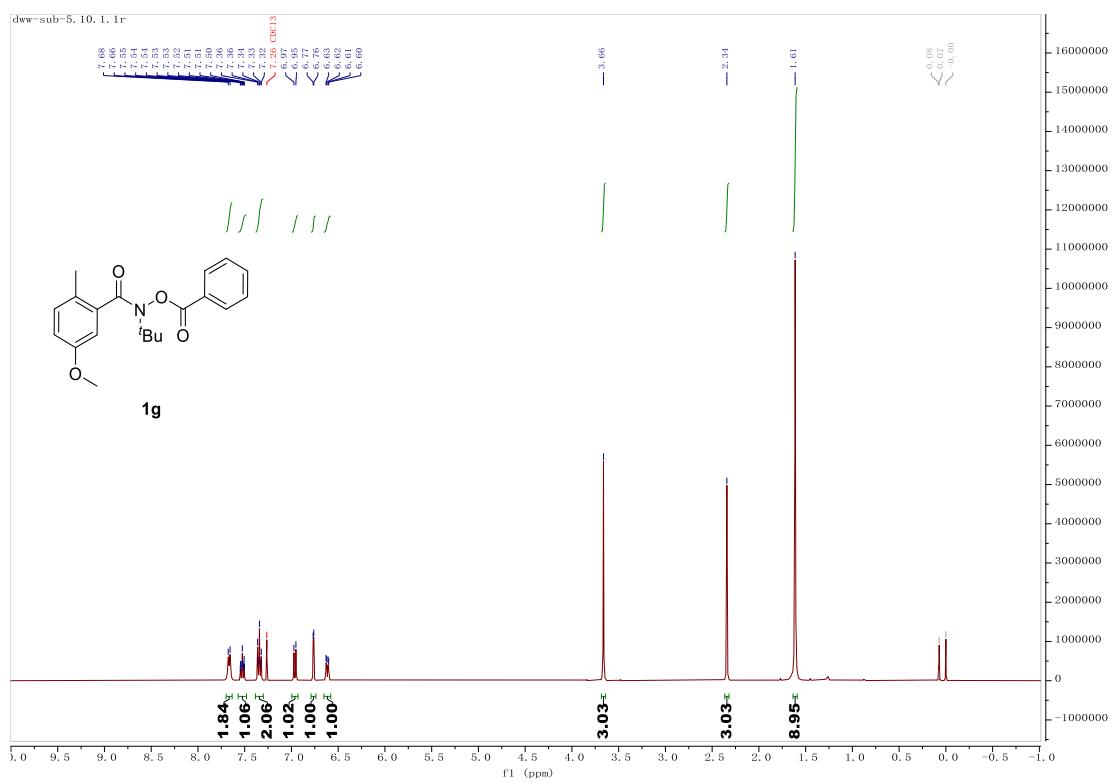
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 1e**



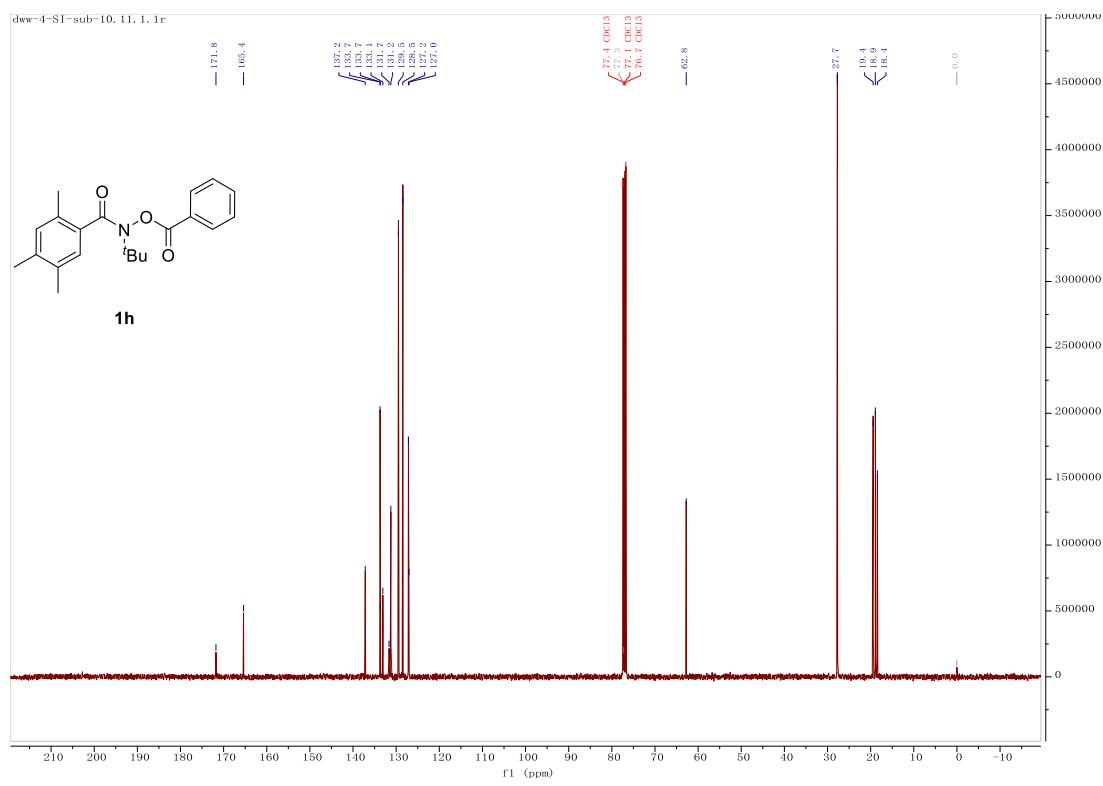
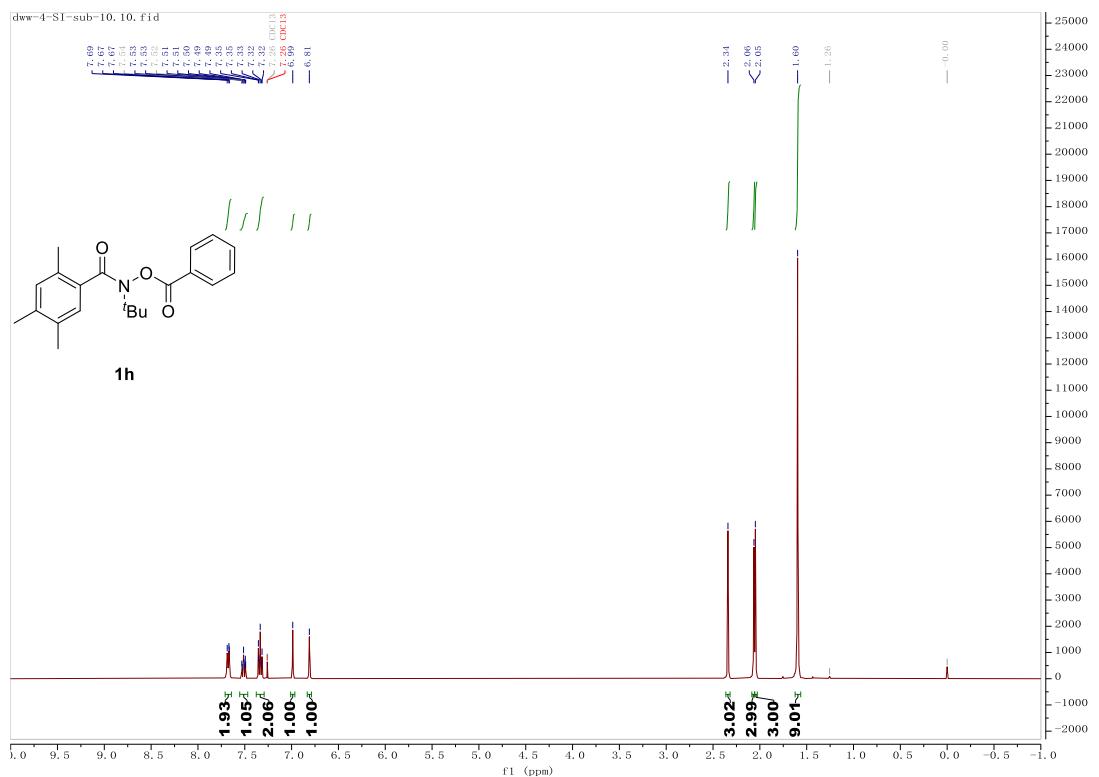
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for **1f****



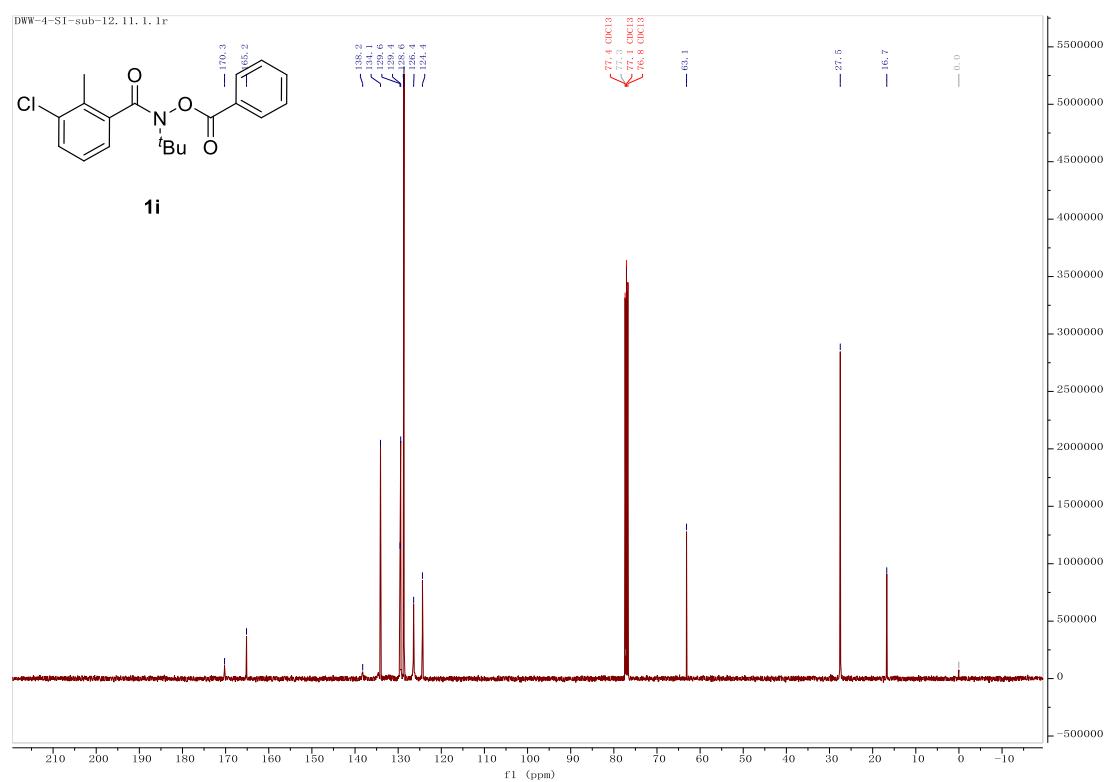
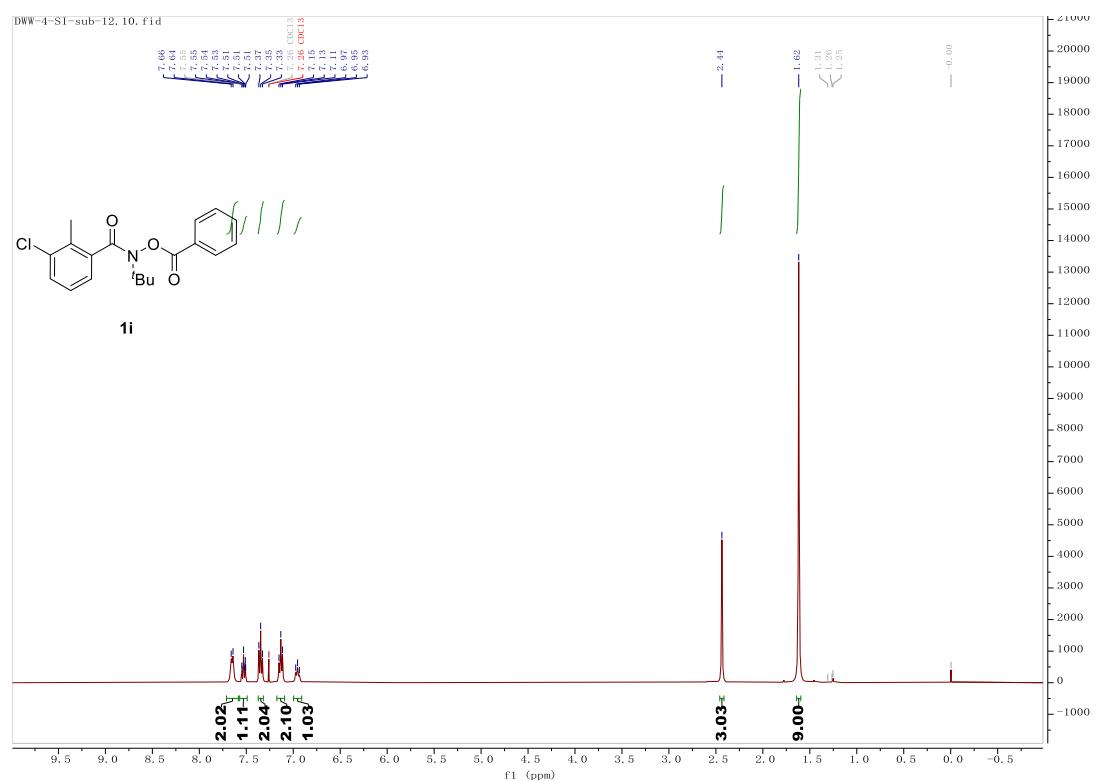
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 1g



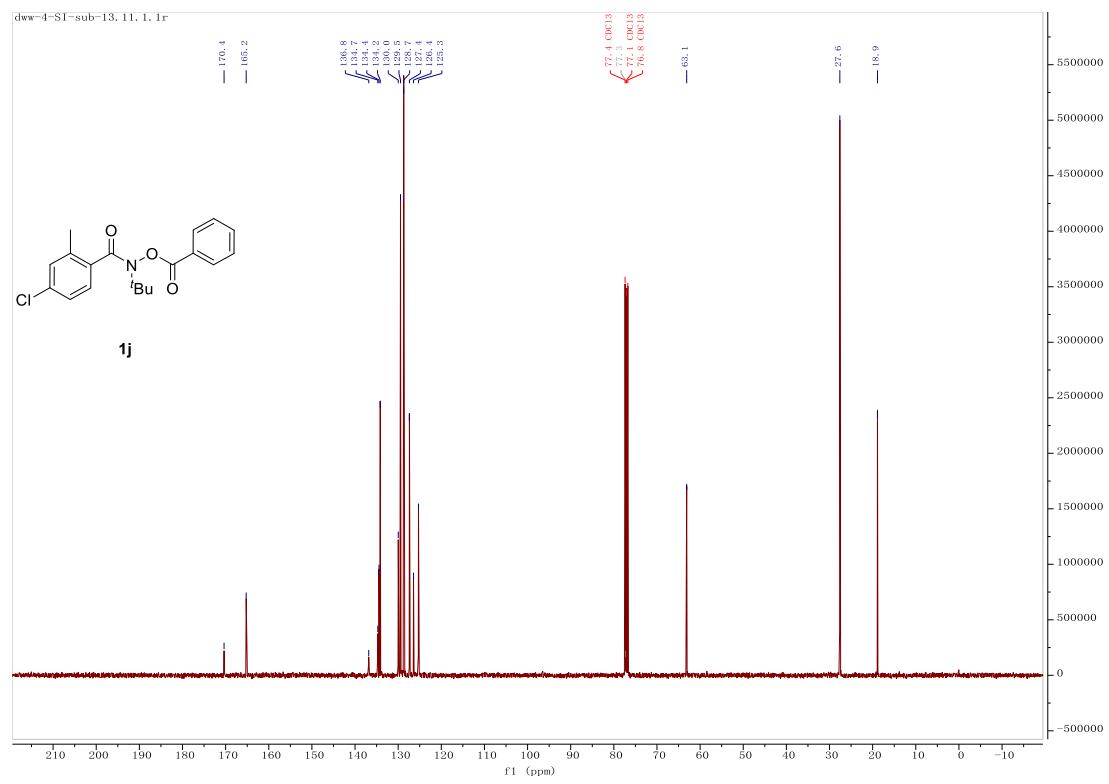
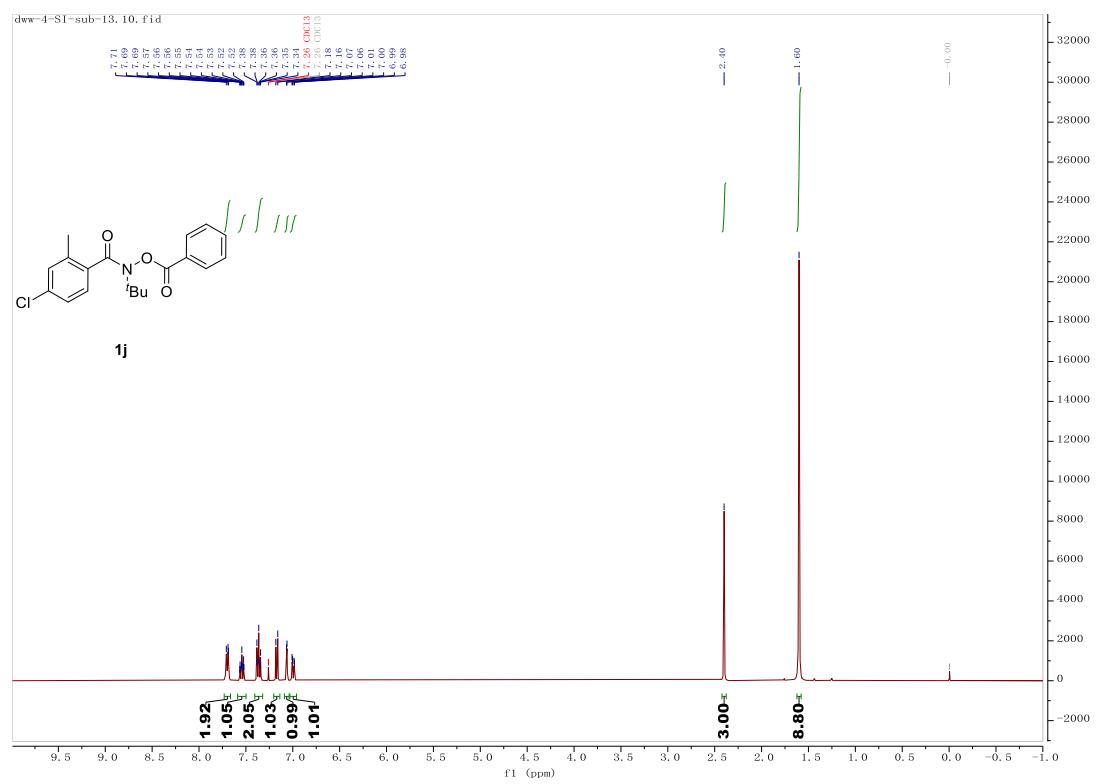
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 1h



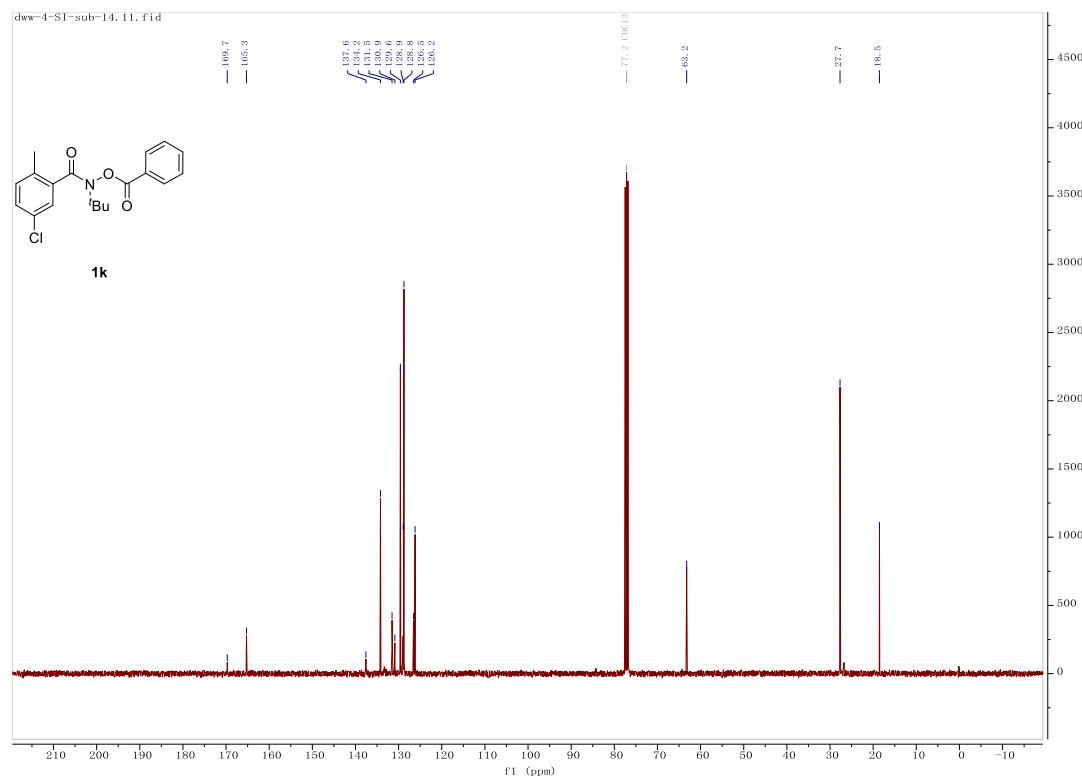
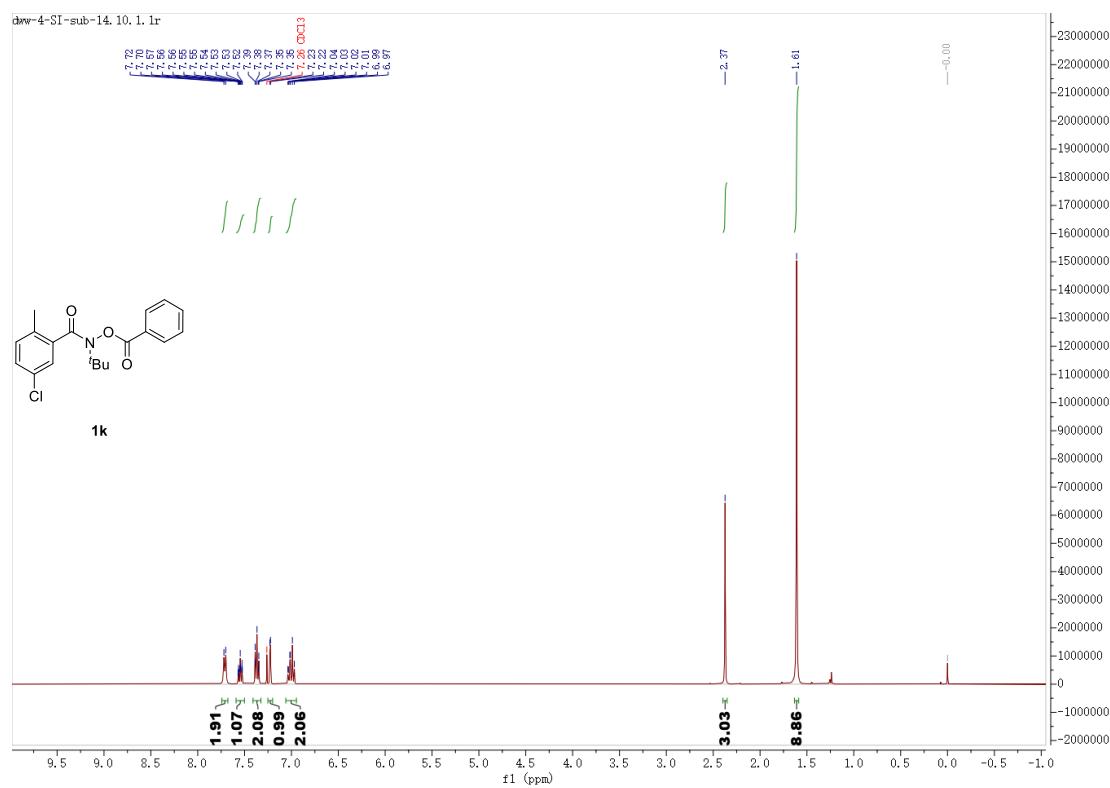
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 1i**



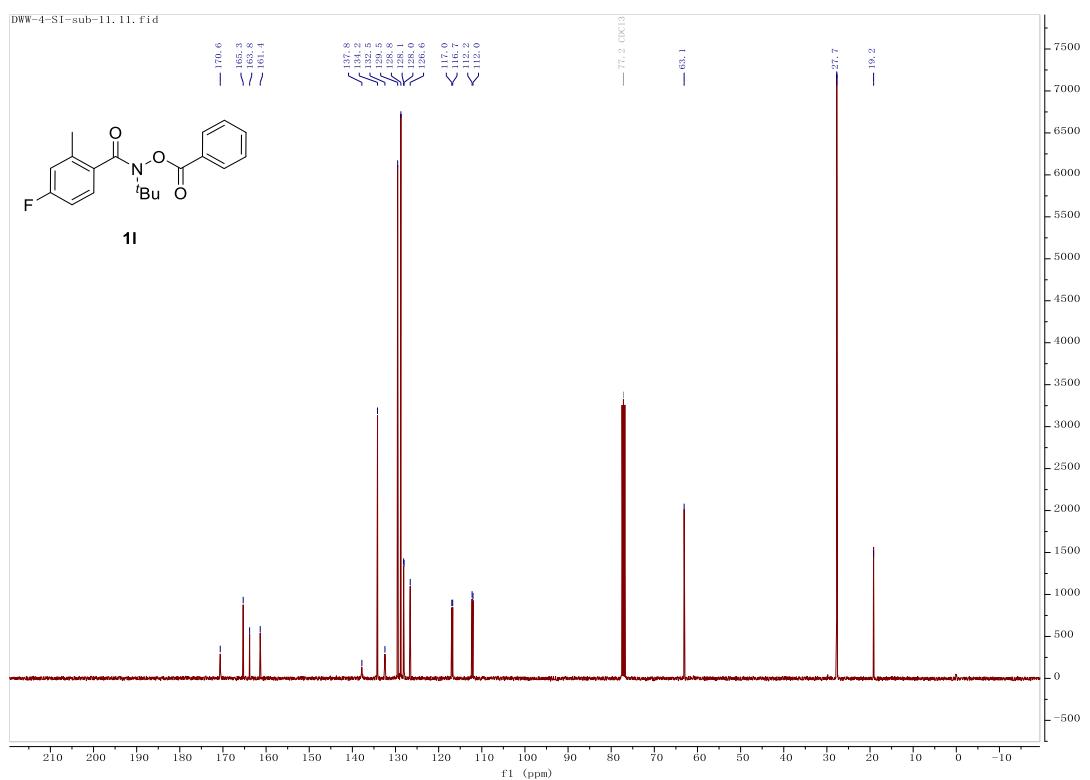
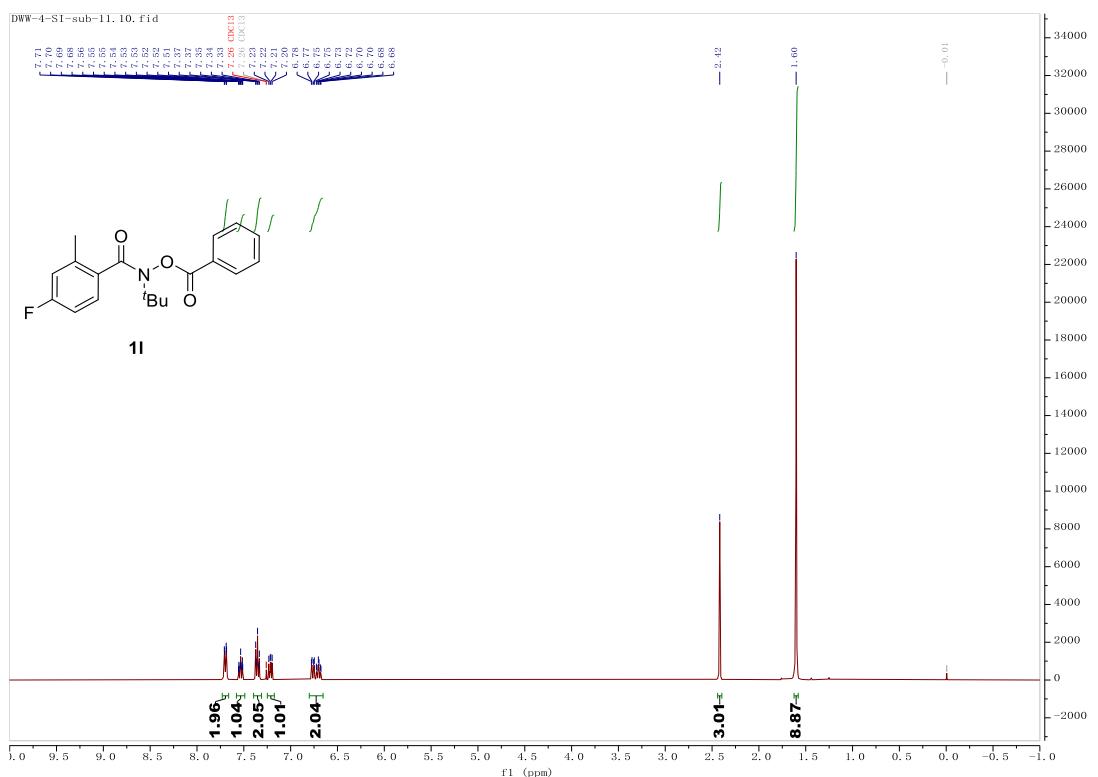
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 1j**



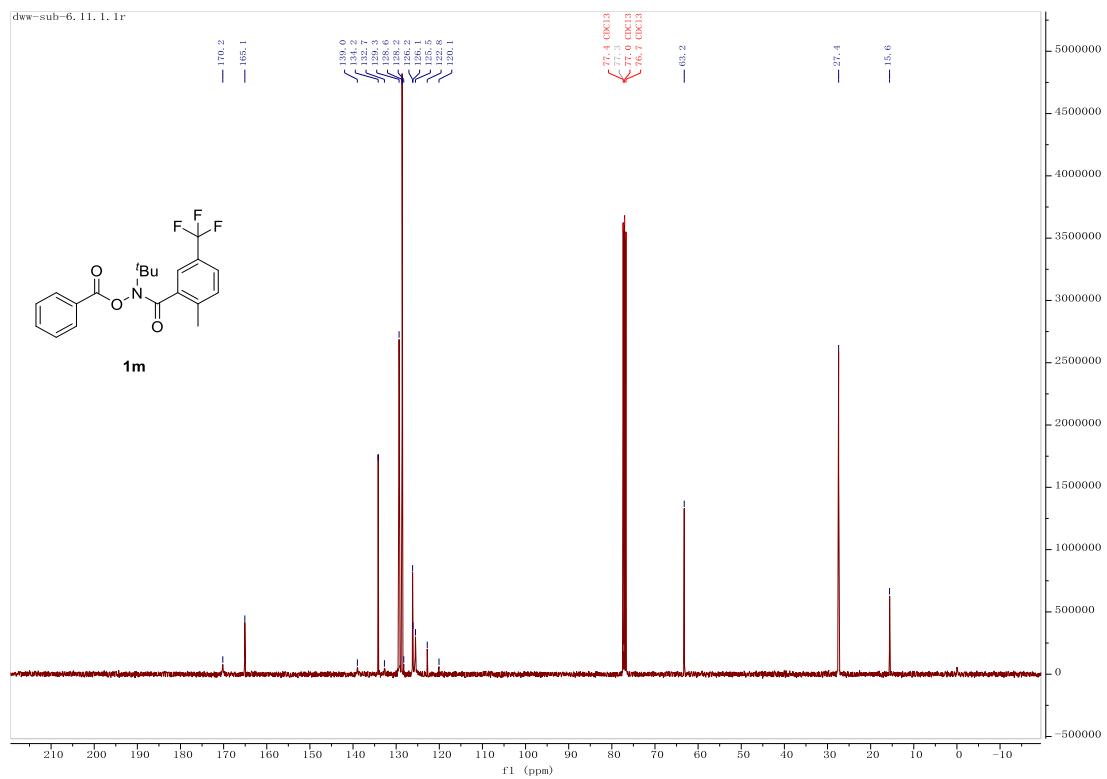
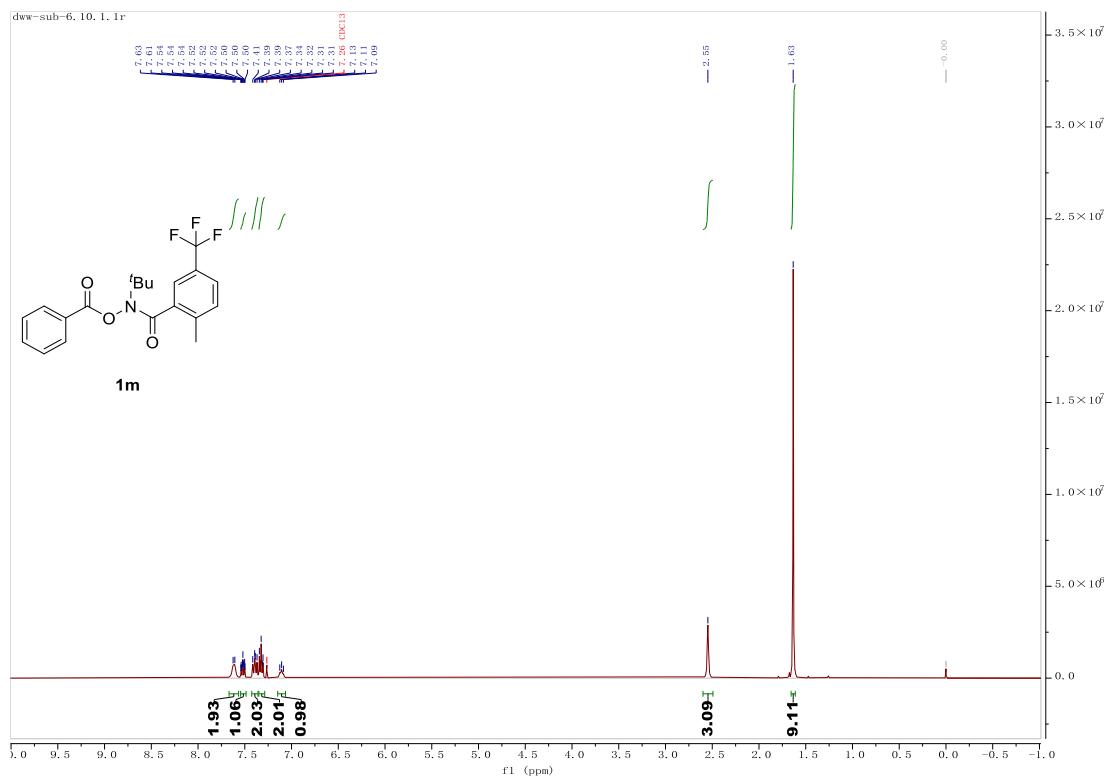
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 1k**



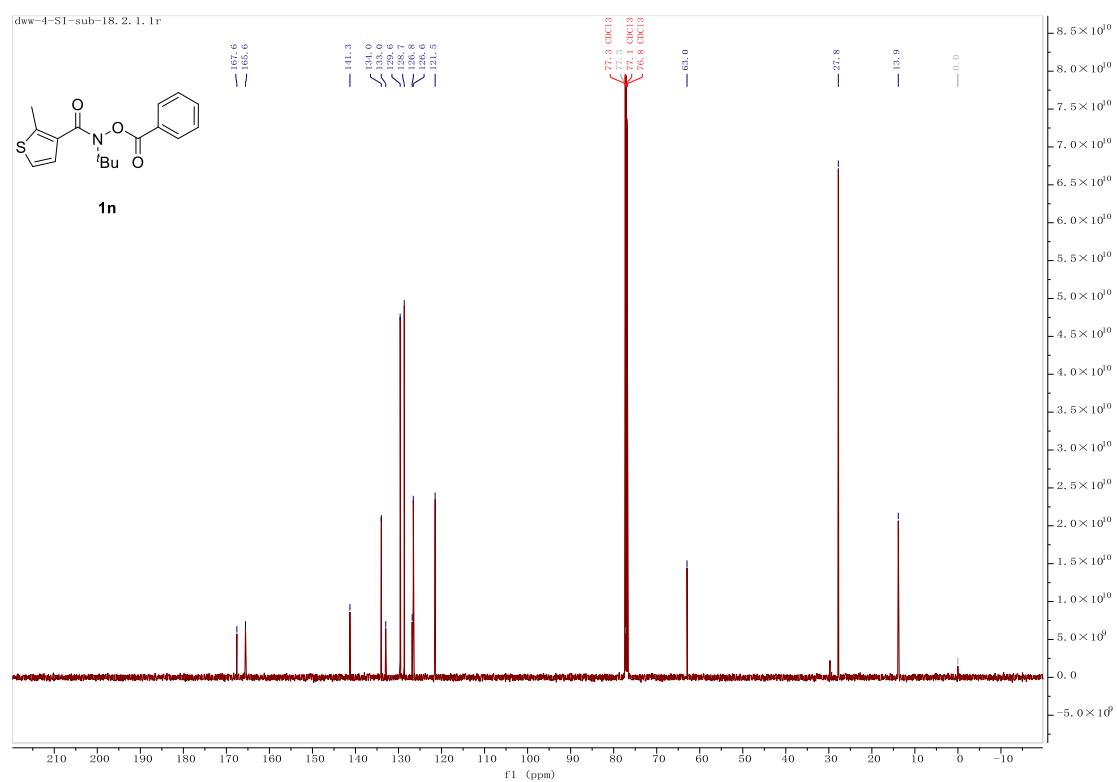
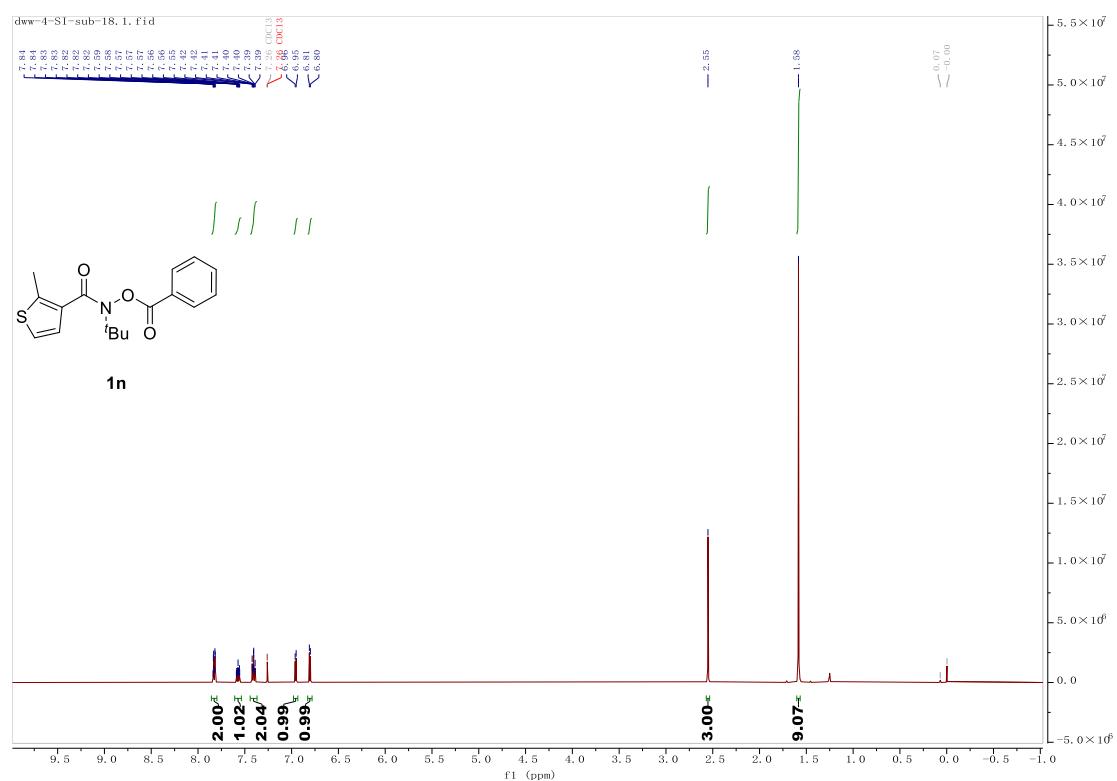
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 11**



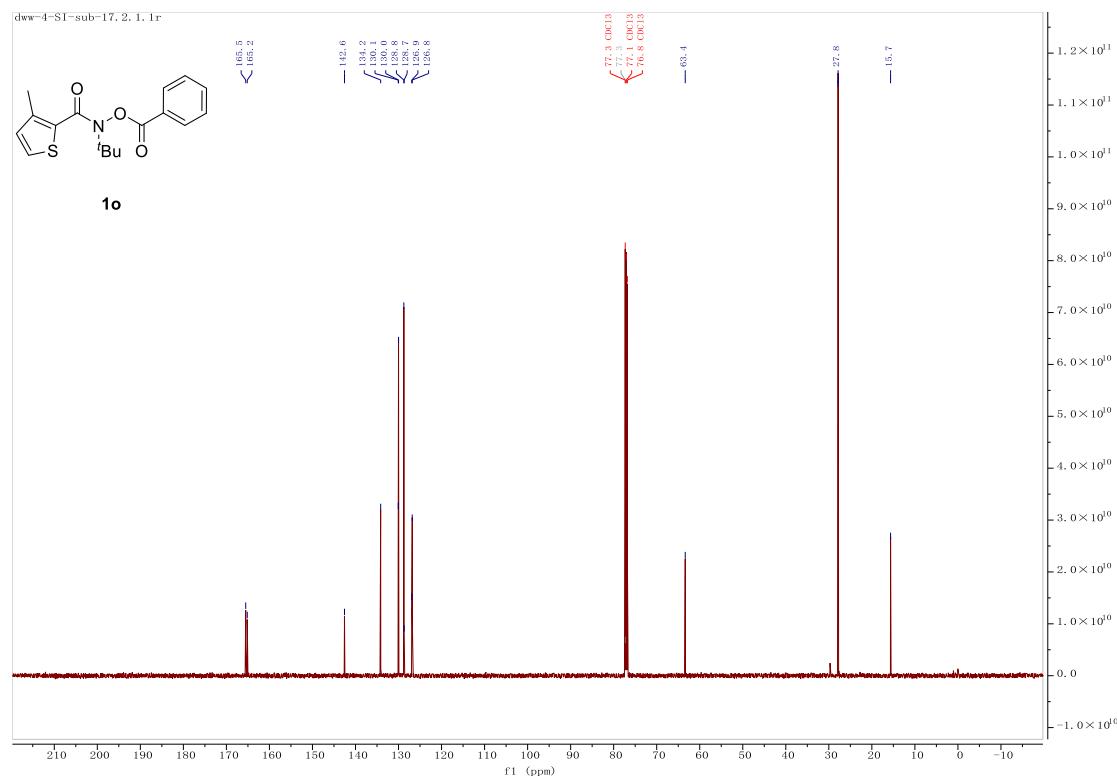
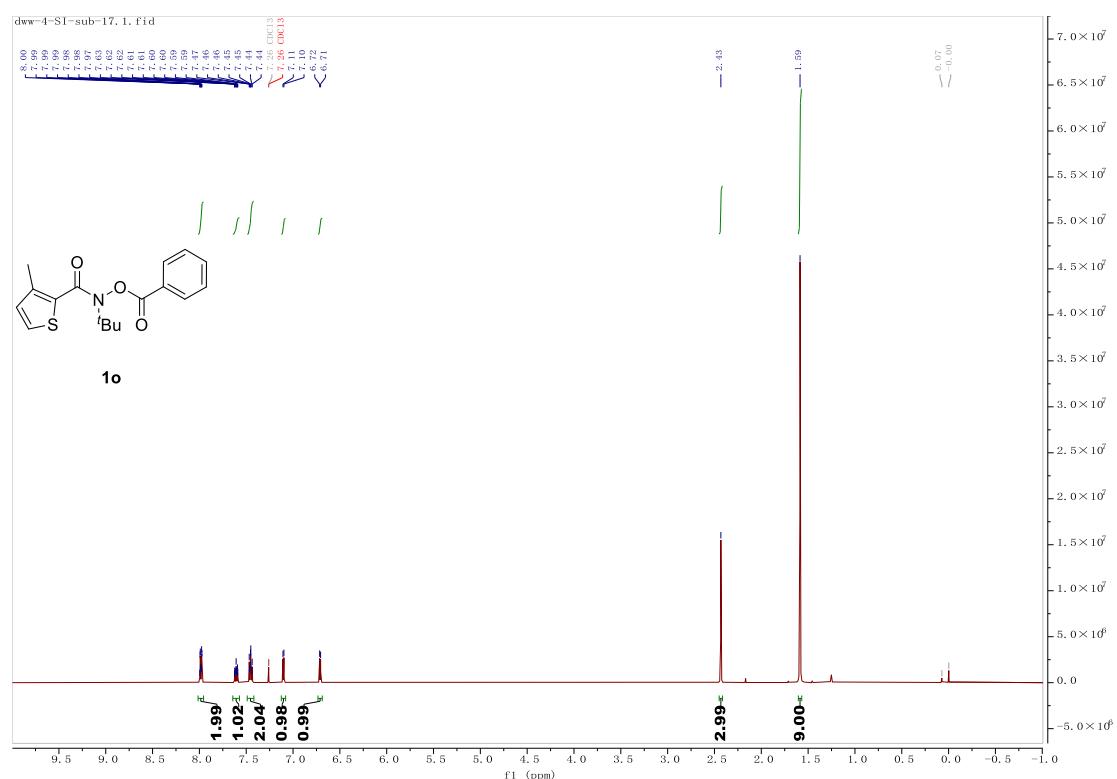
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for **1m****



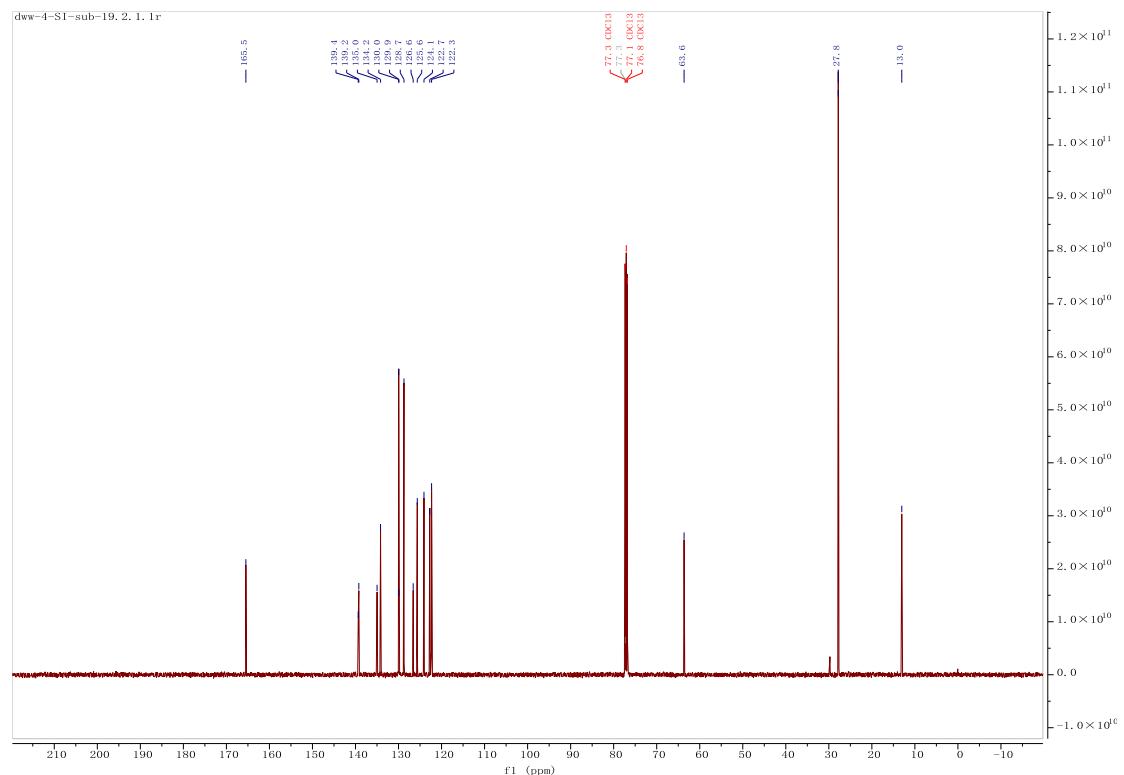
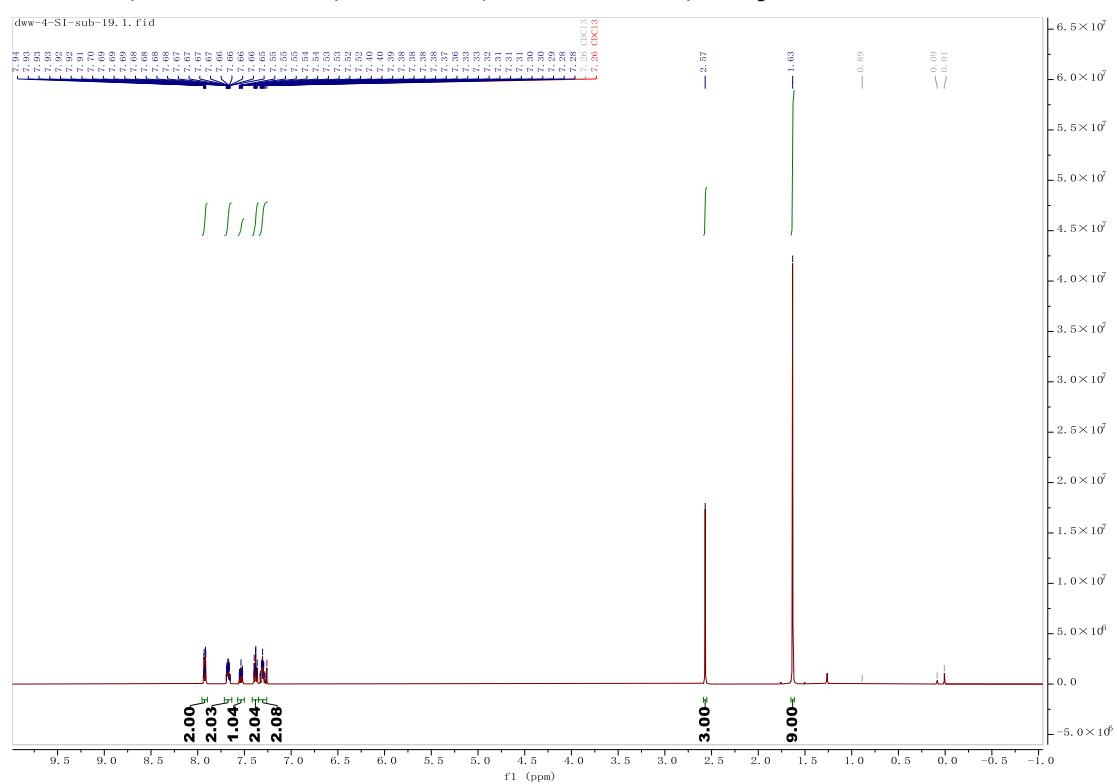
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) for 1n**



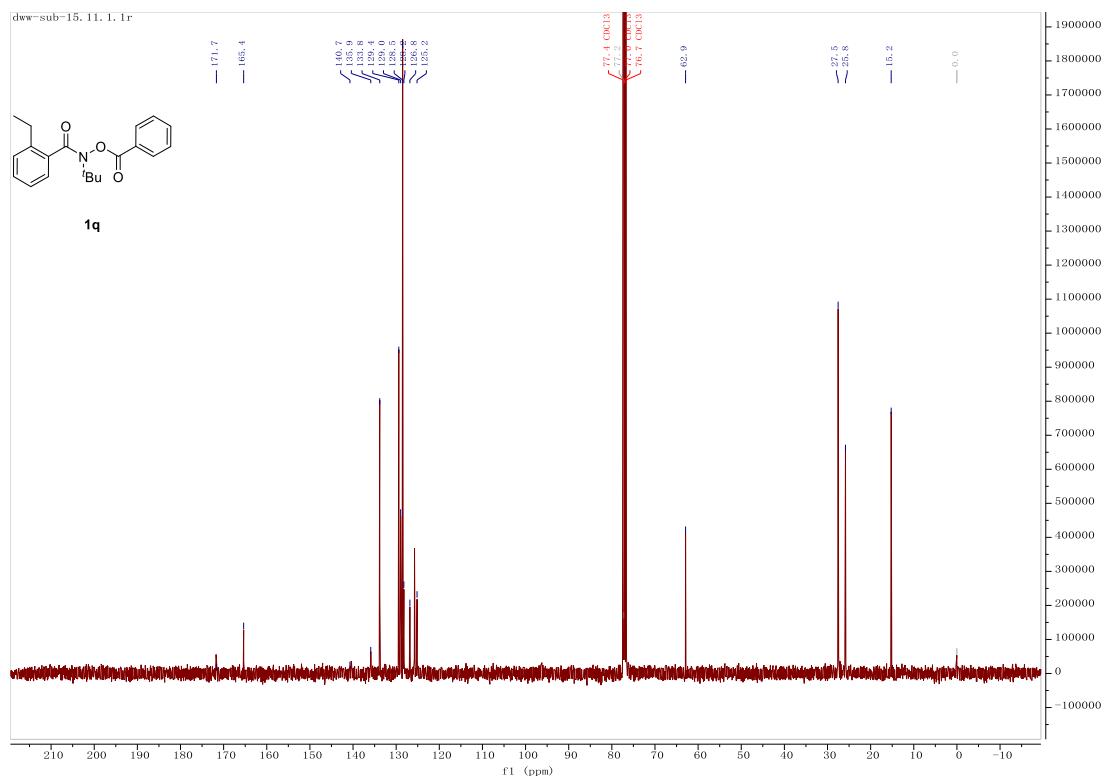
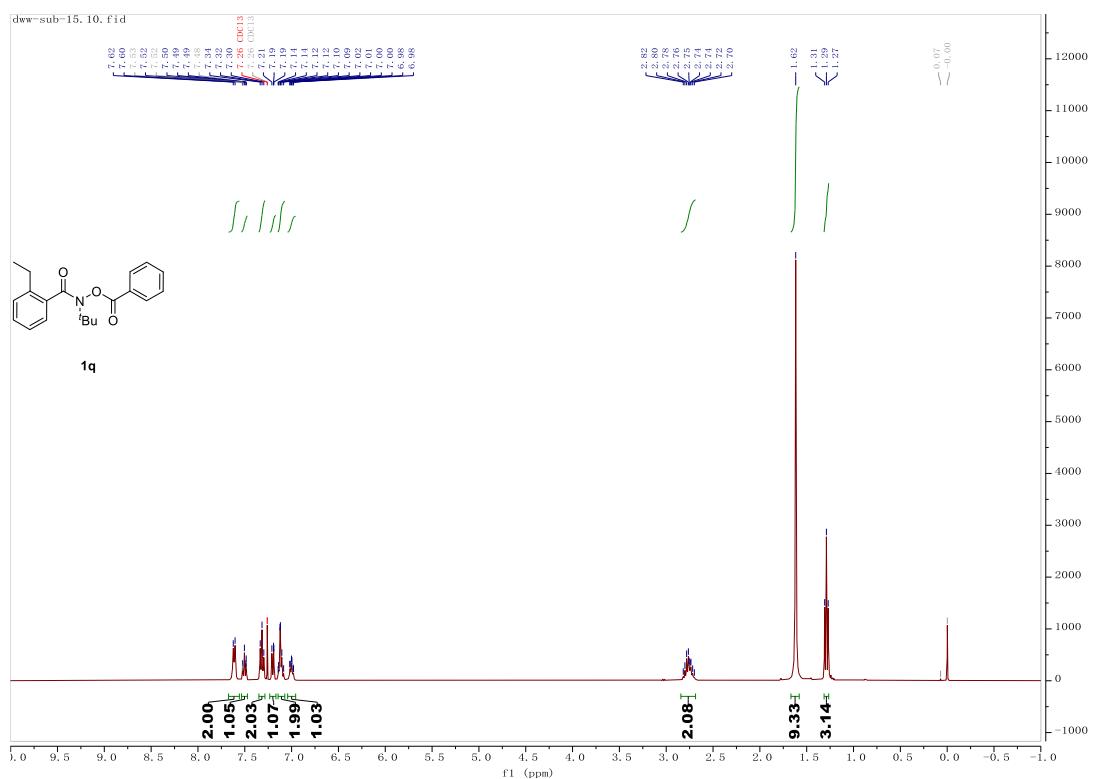
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) for **1o****



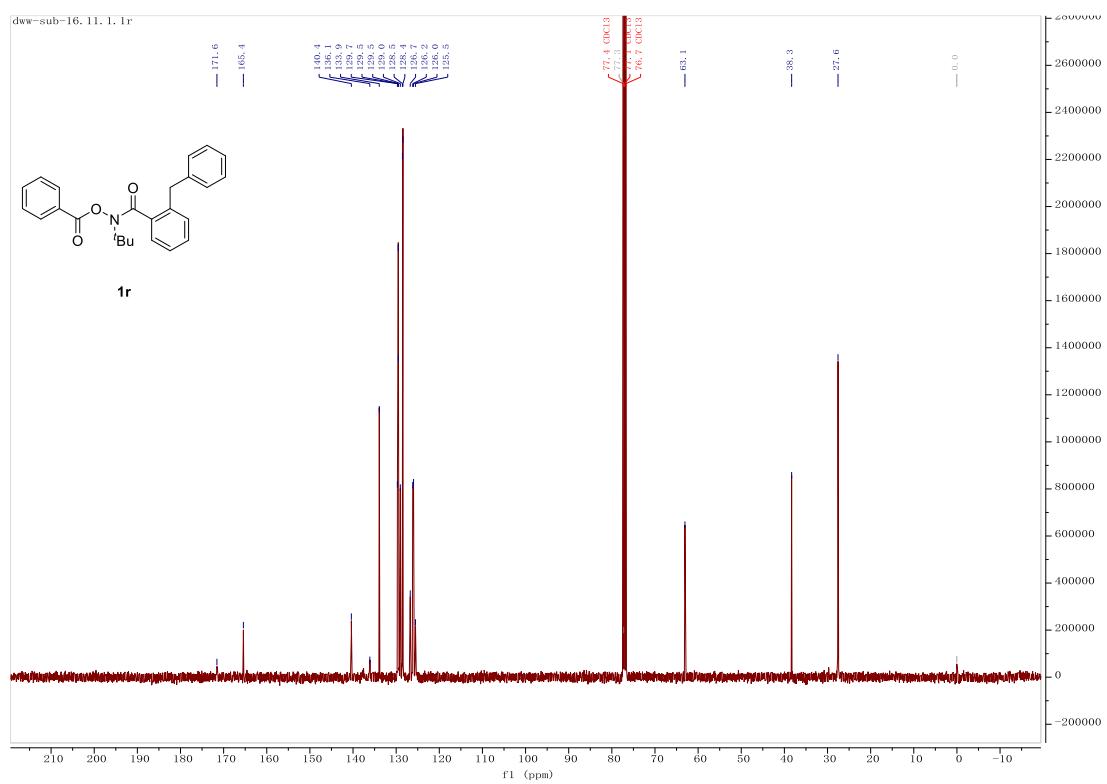
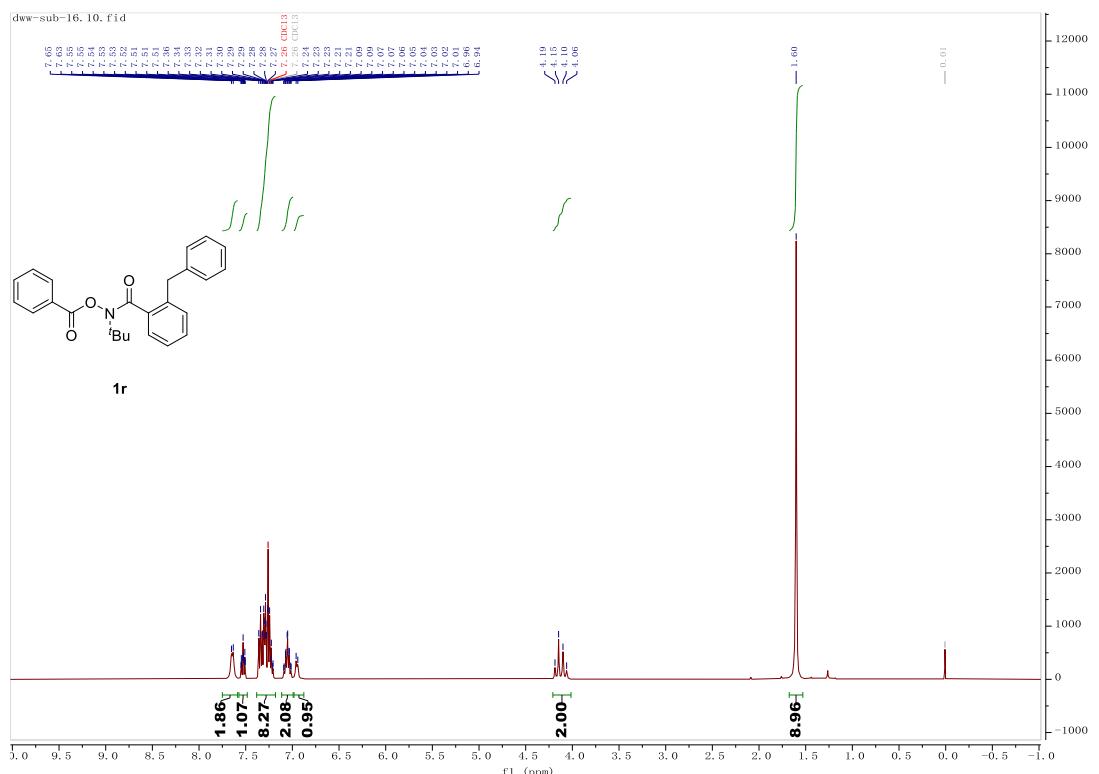
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) for 1p**



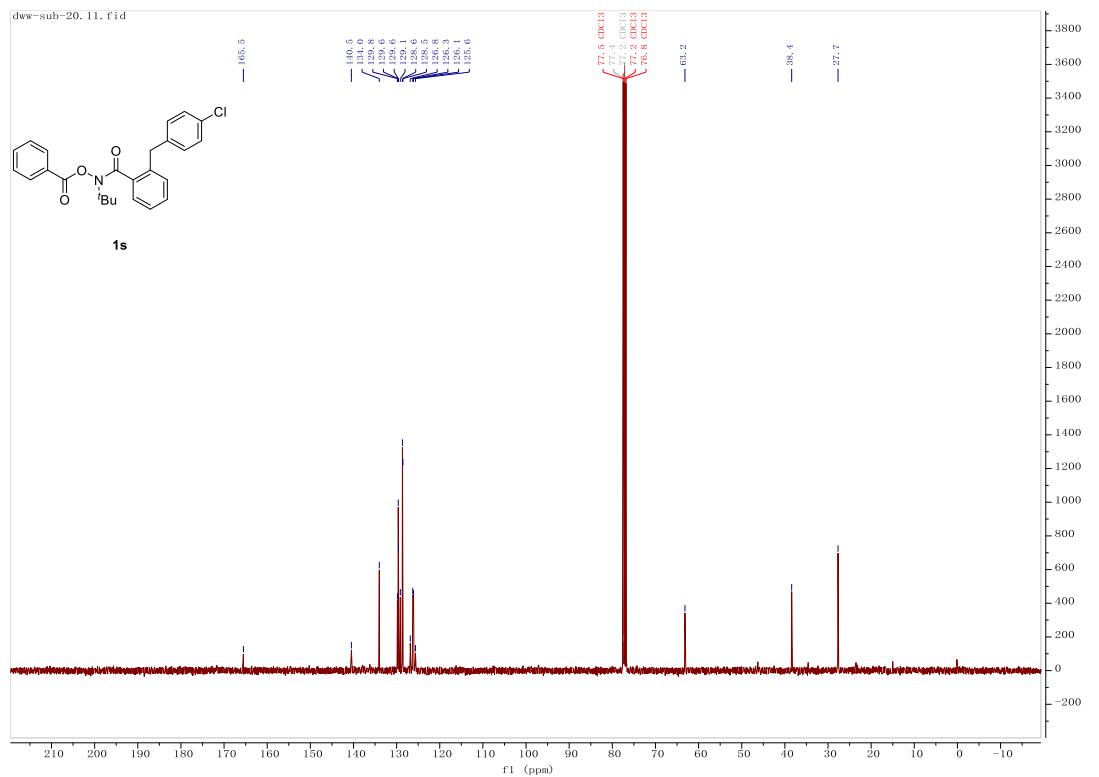
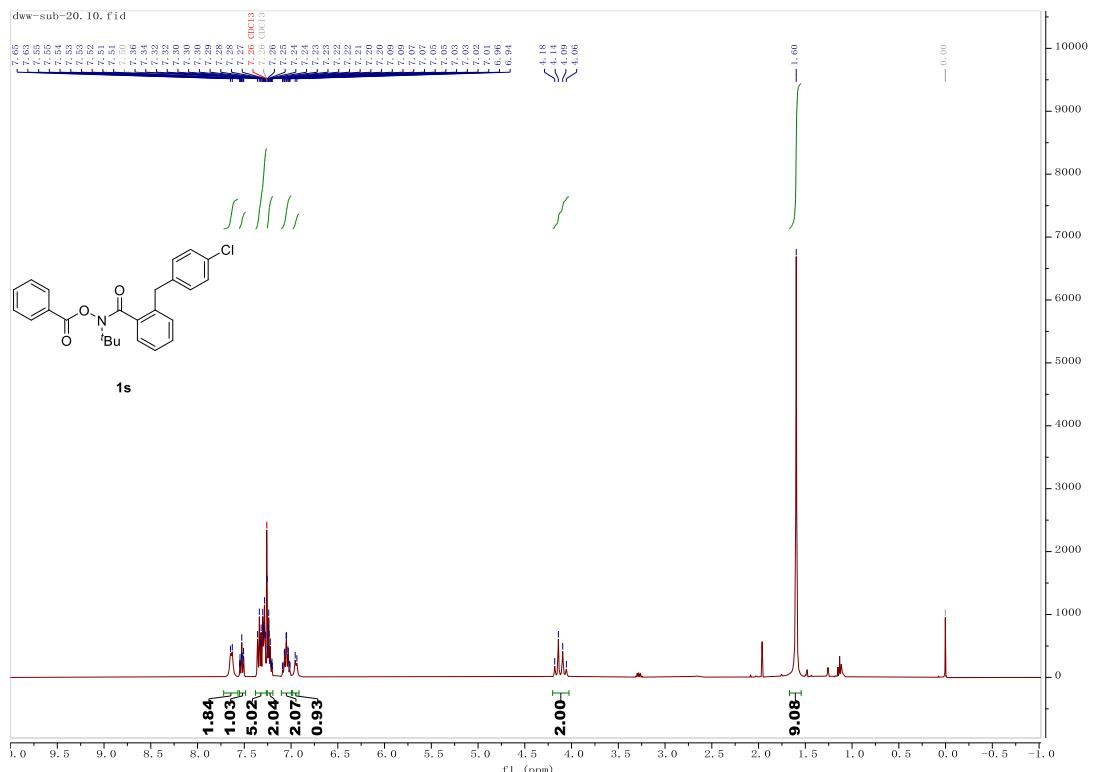
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 1q**



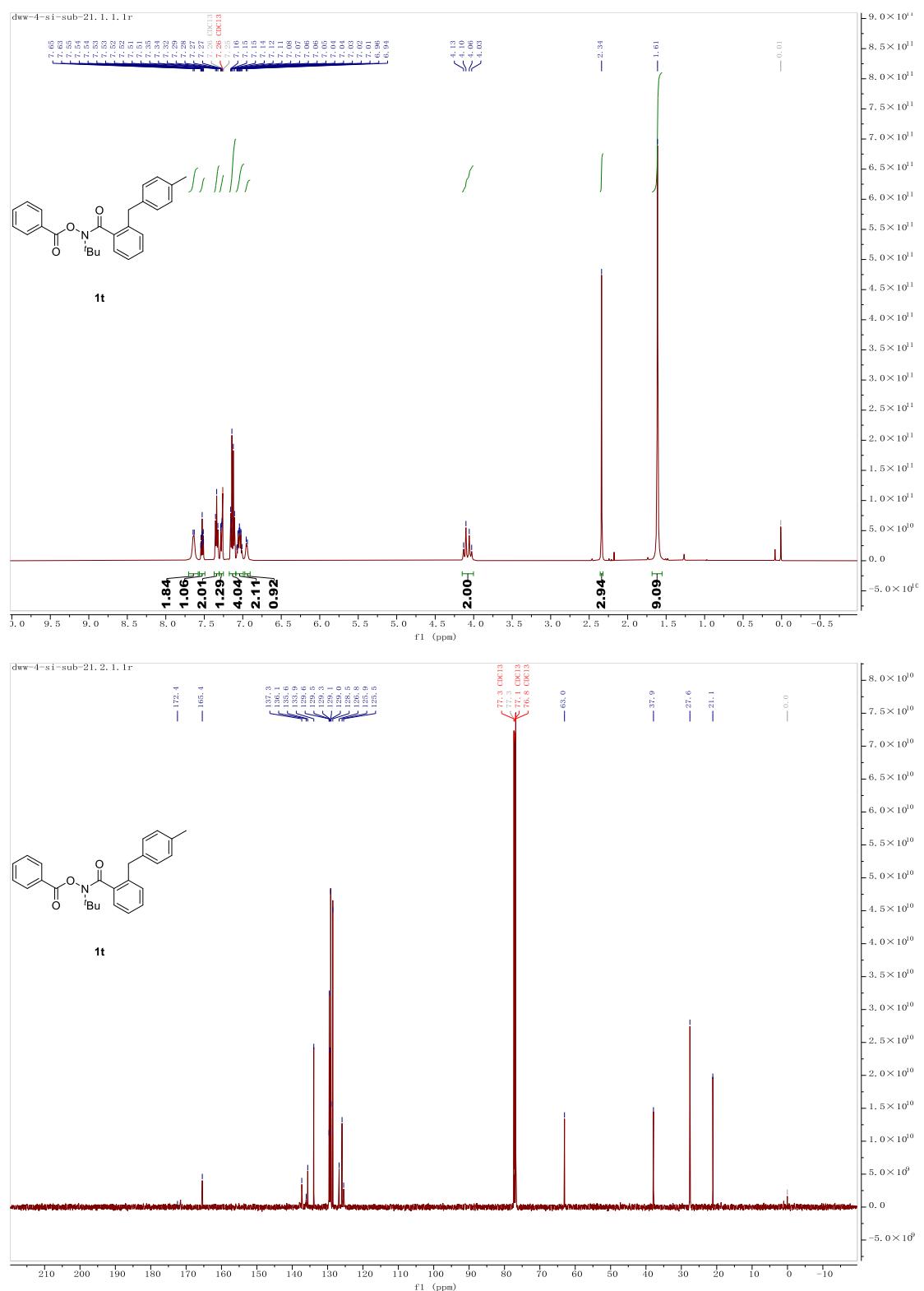
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 1r



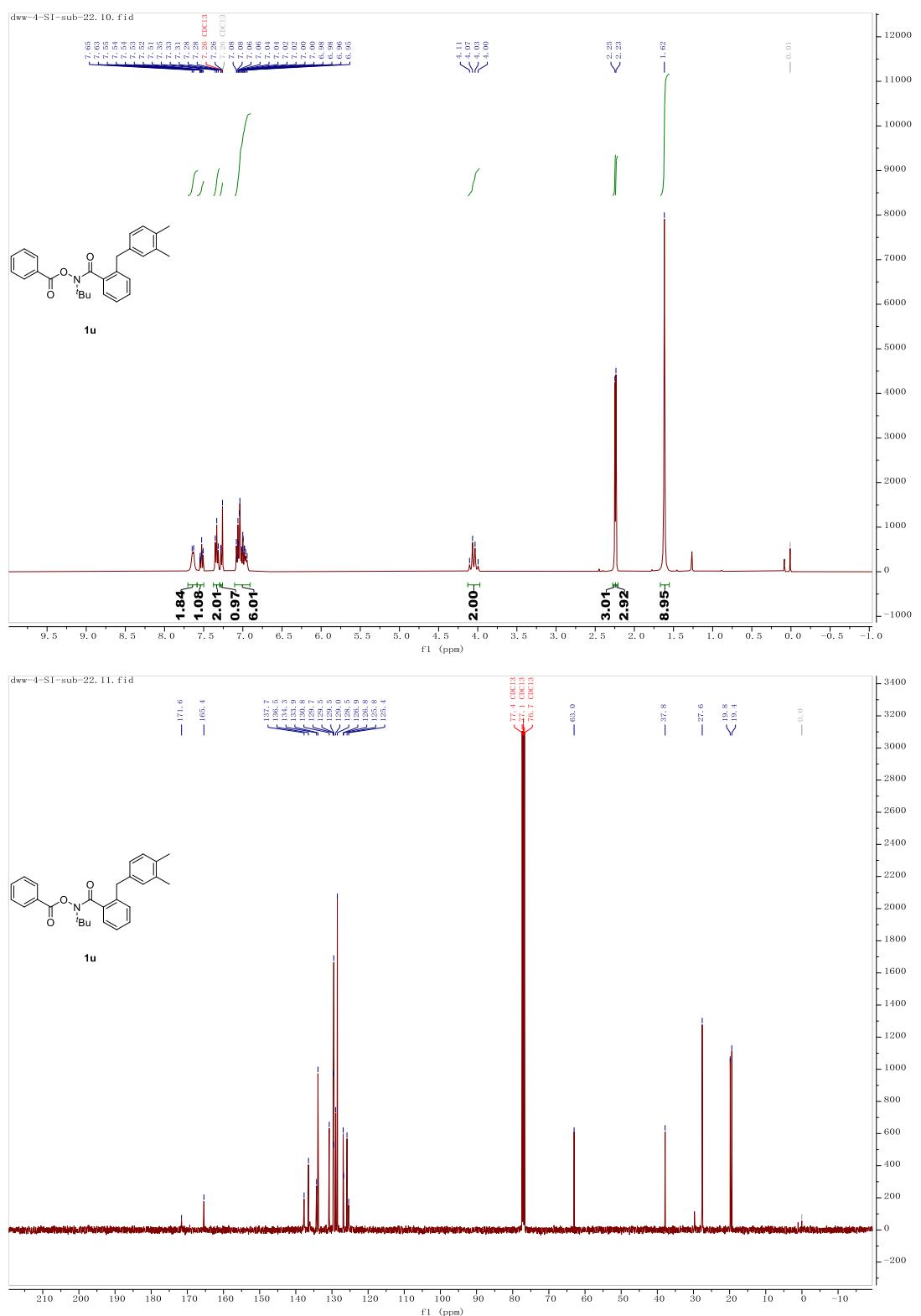
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 1s**



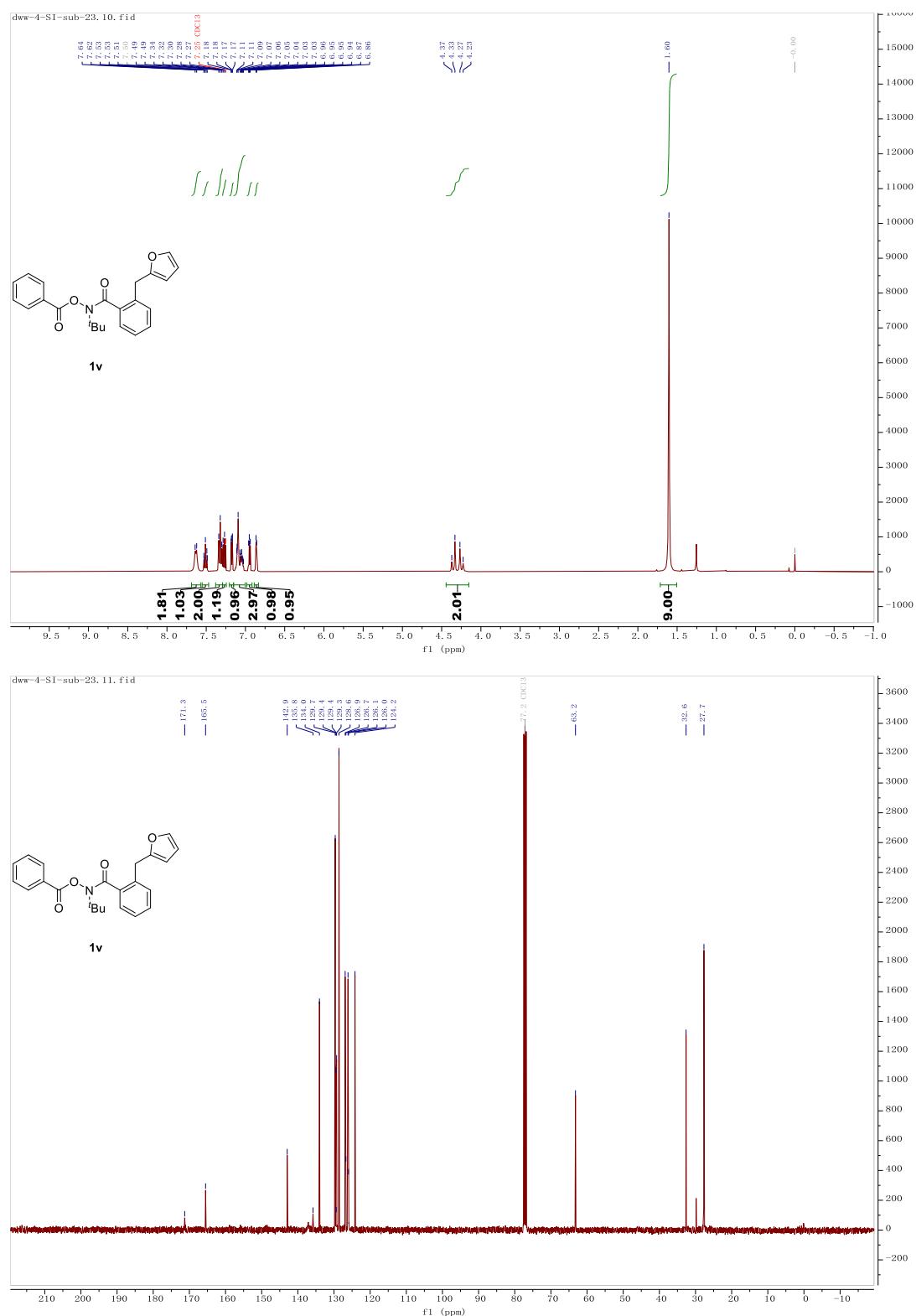
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) for **1t****



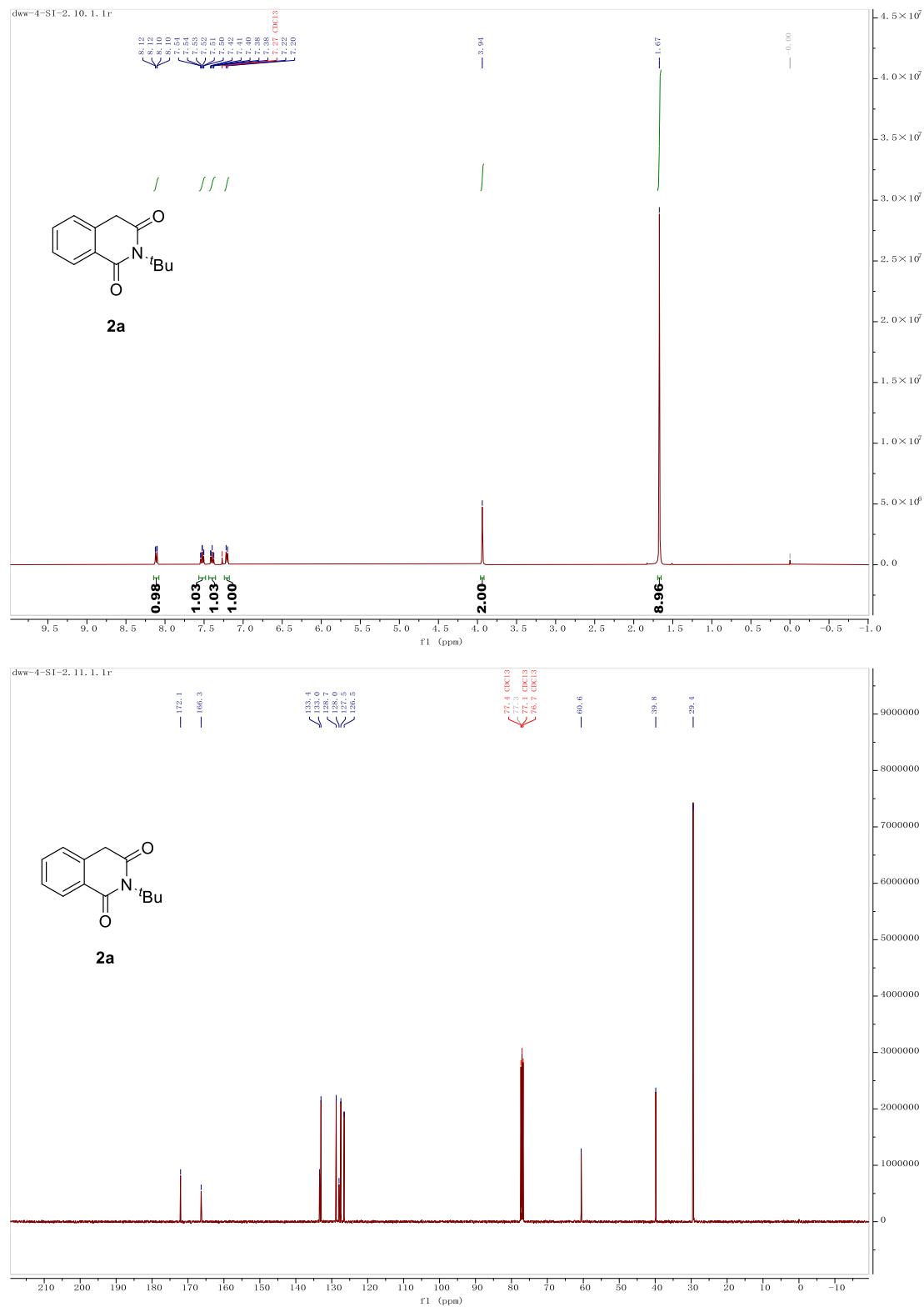
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 1u**



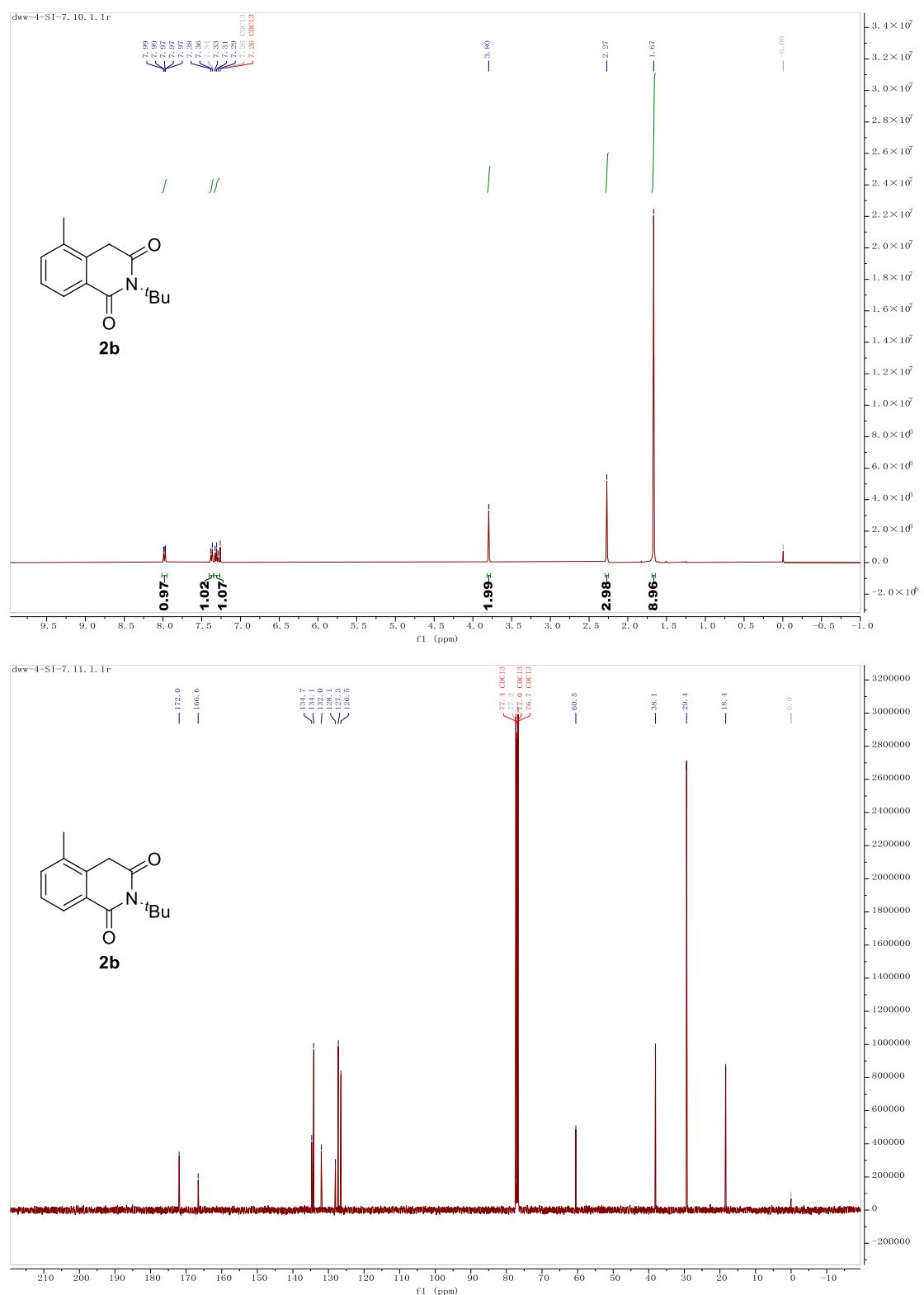
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 1v**



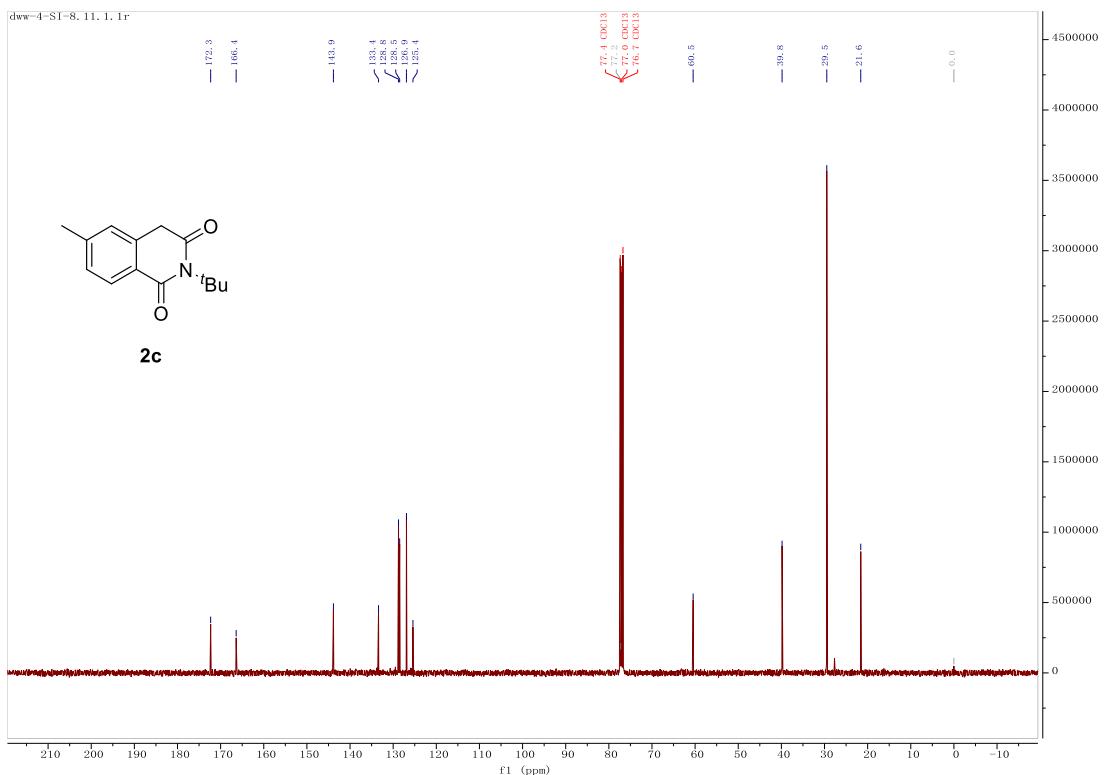
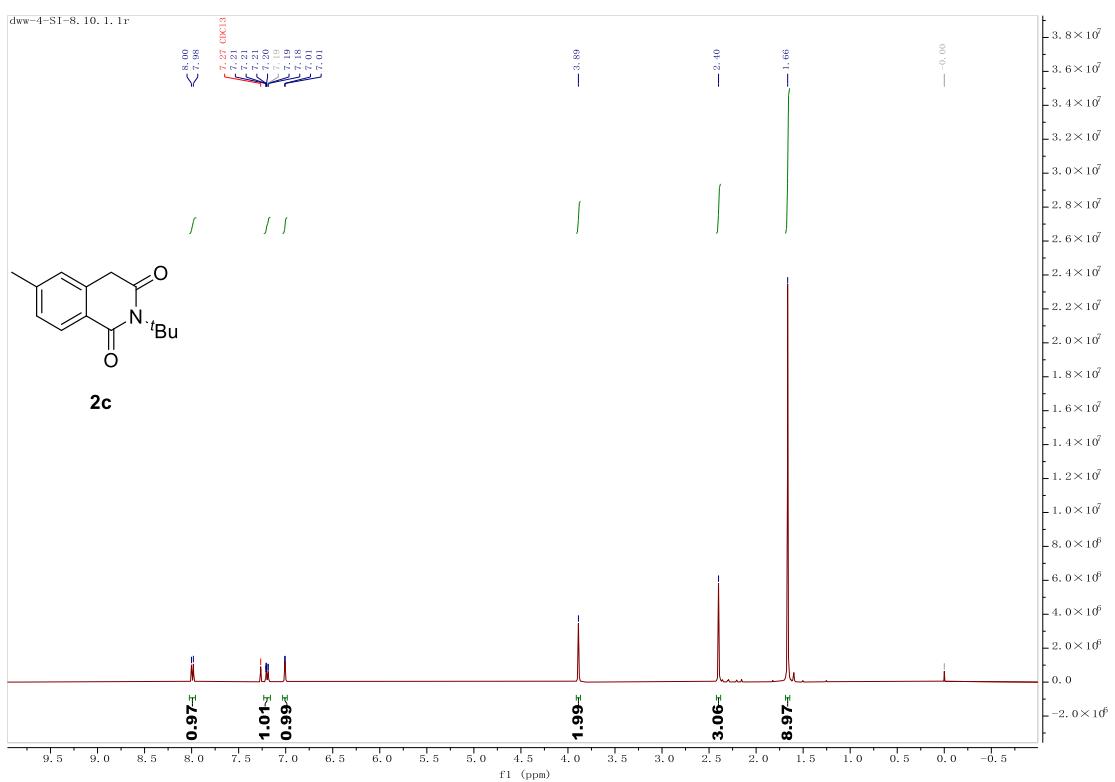
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 2a**



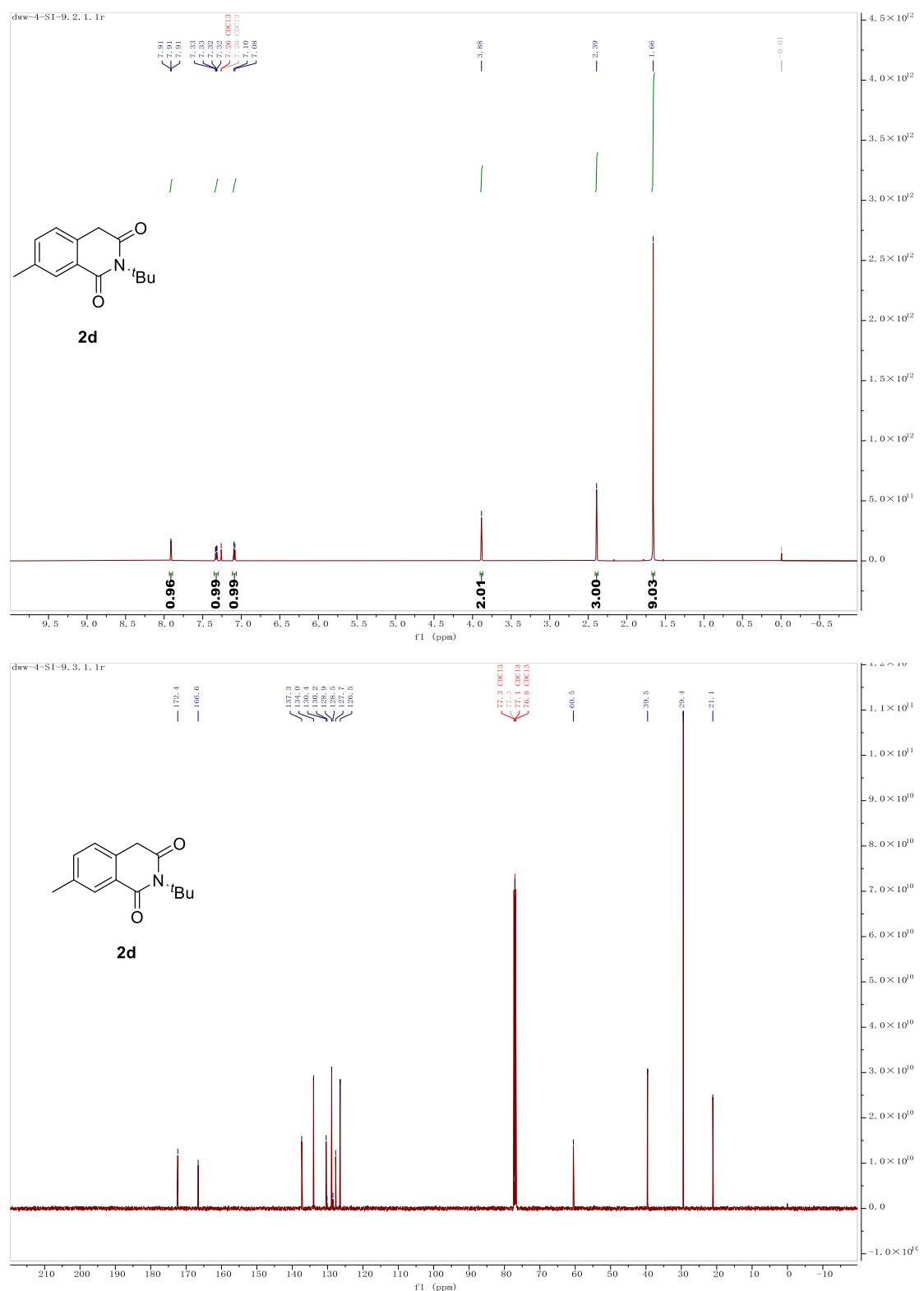
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 2b**



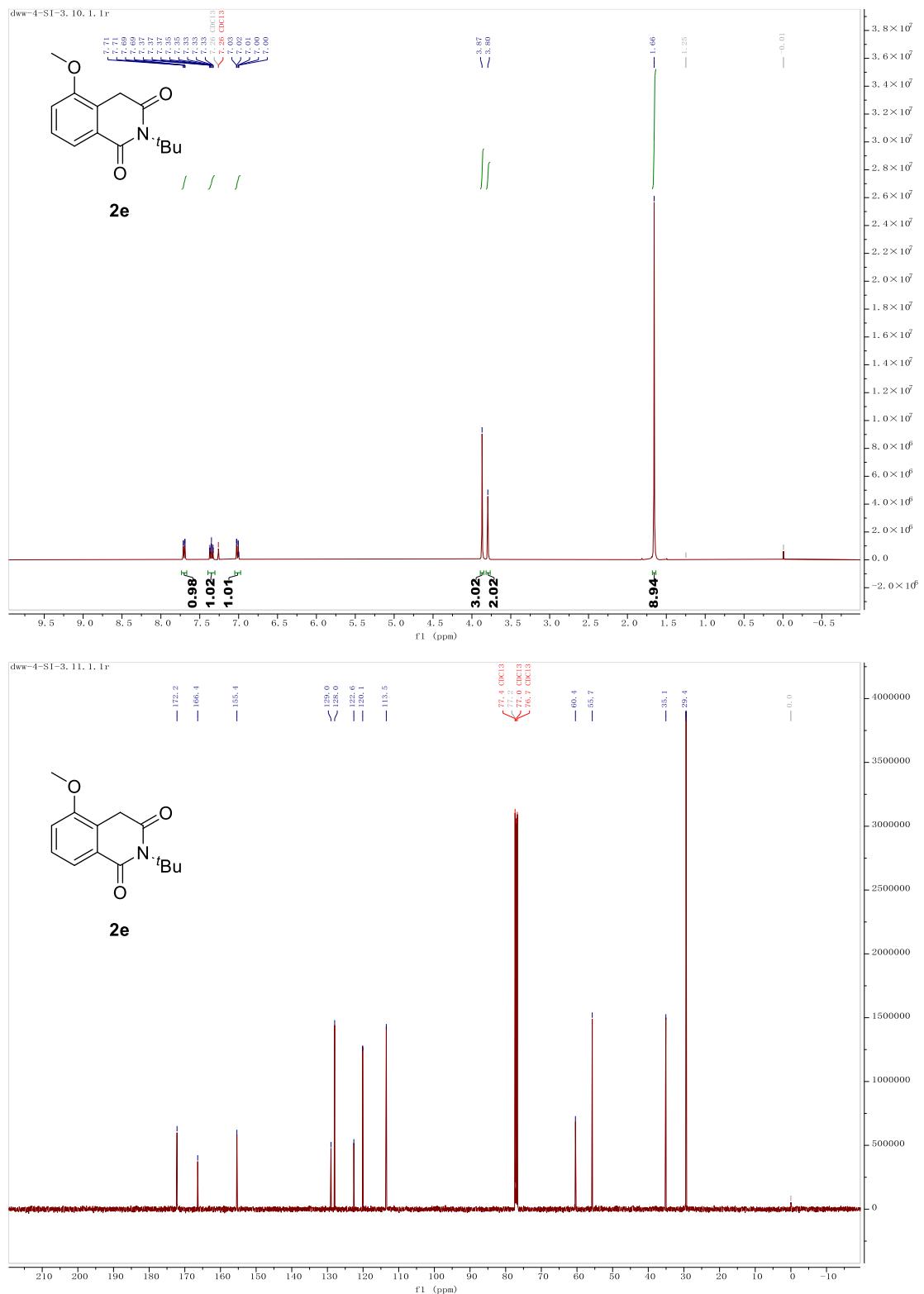
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 2c



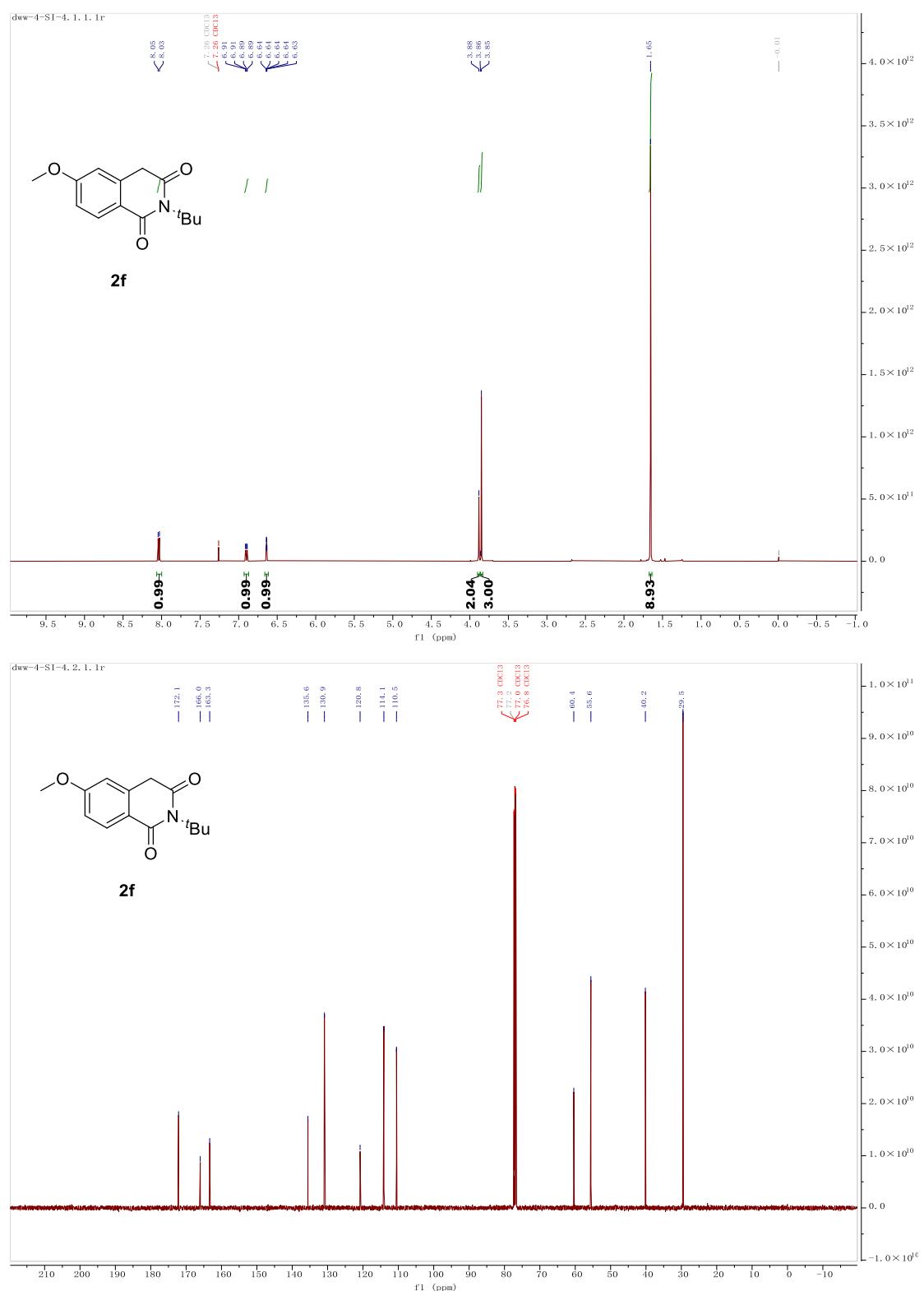
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) for 2d**



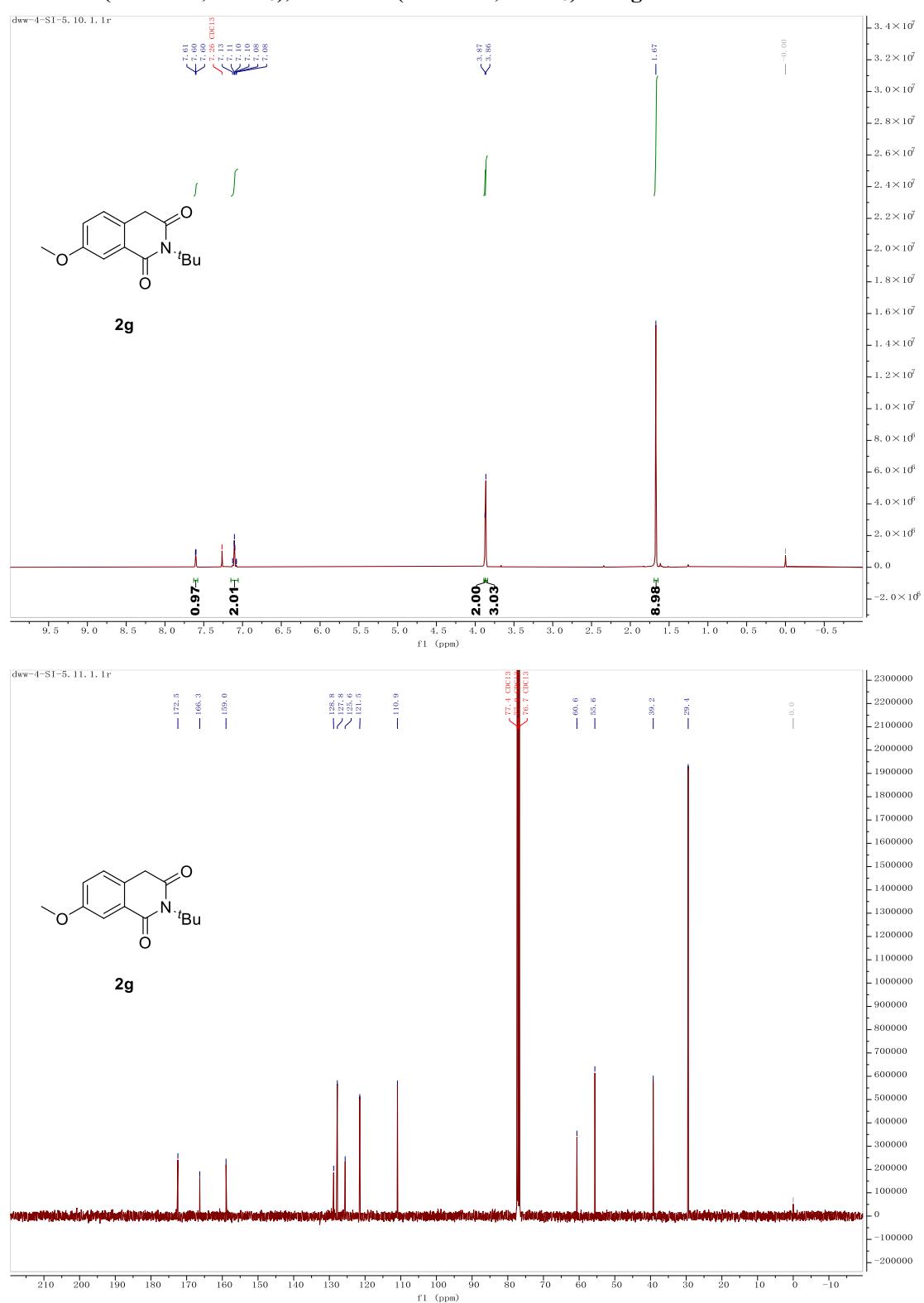
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 2e**



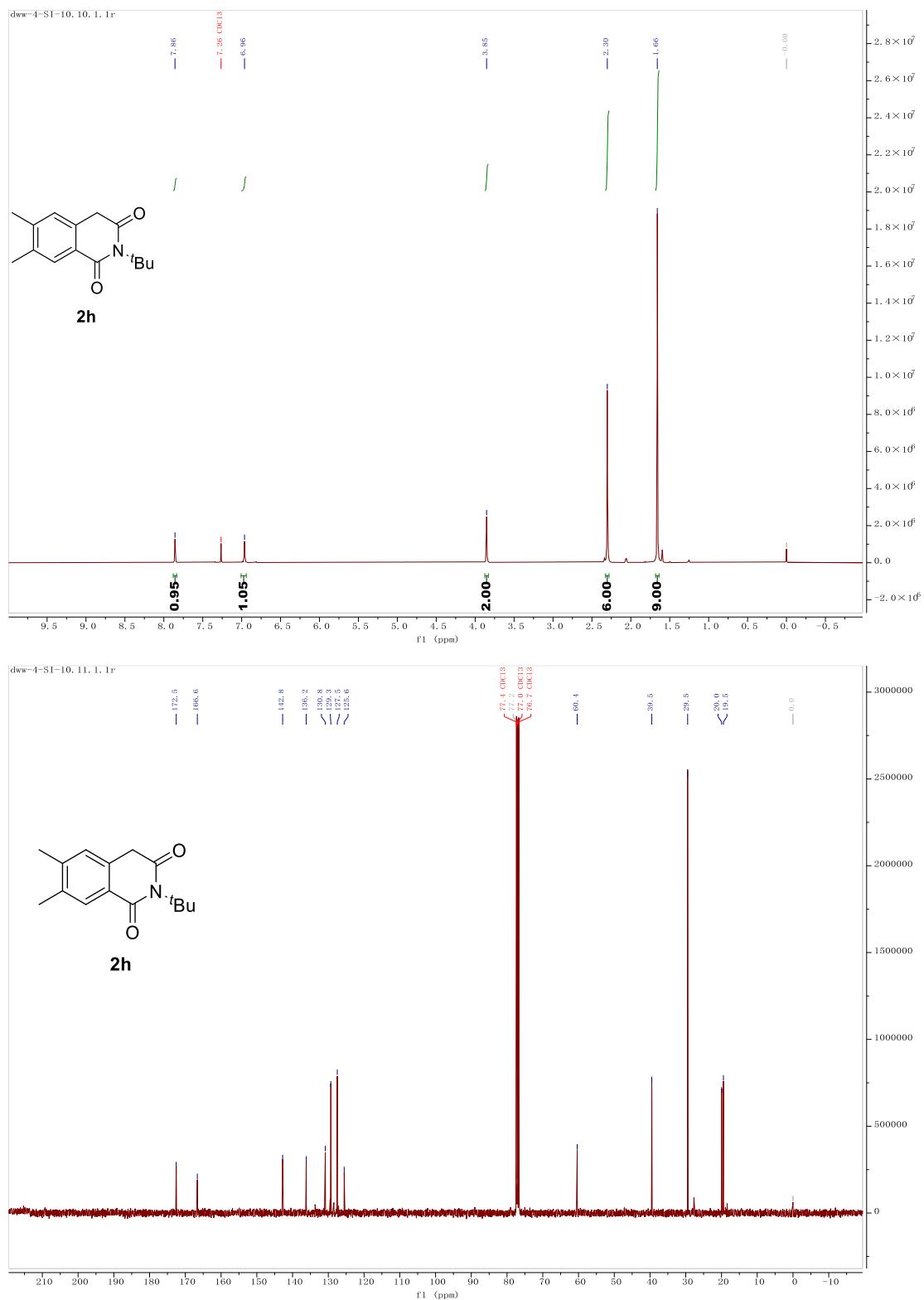
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) for 2f**



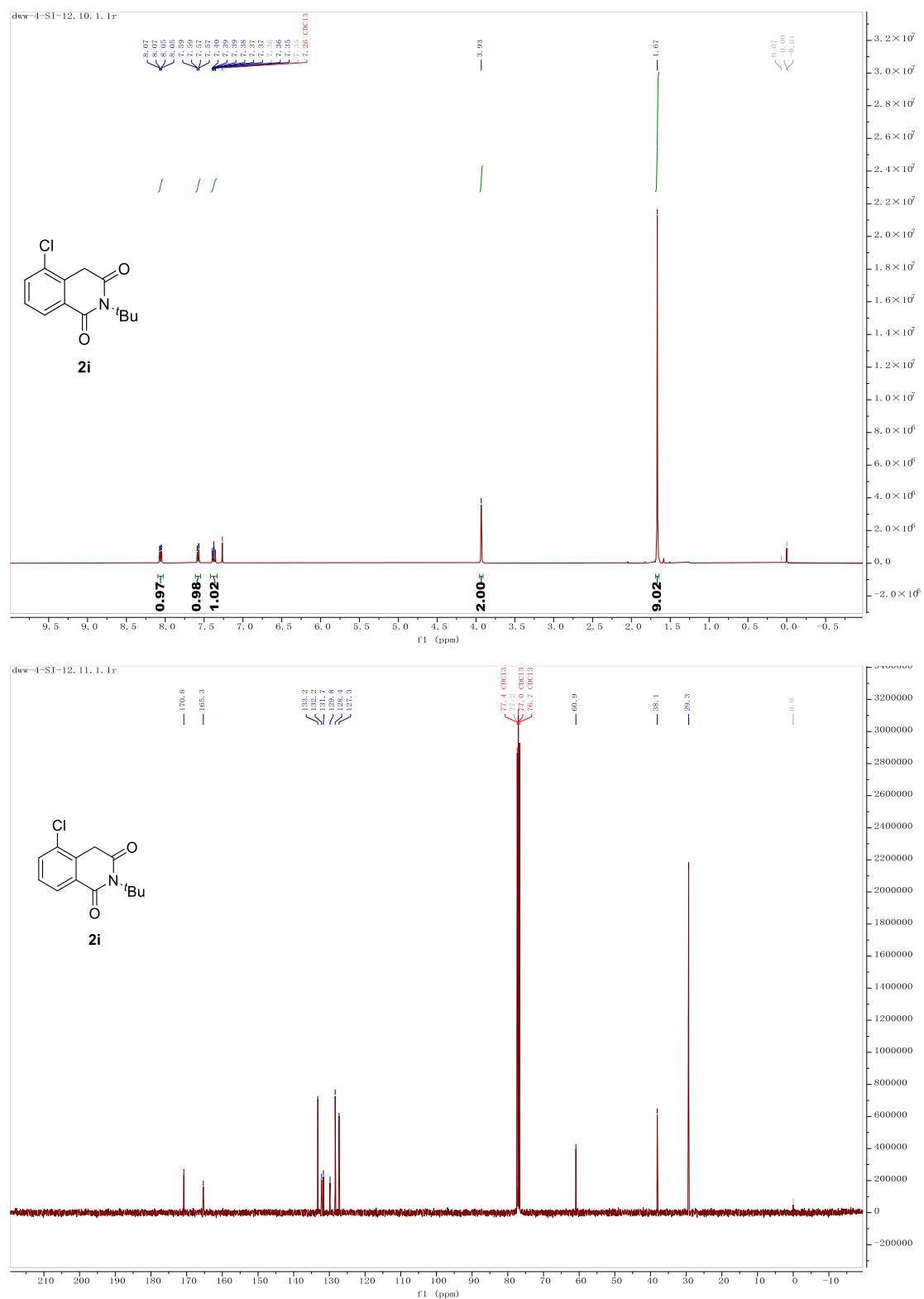
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 2g**



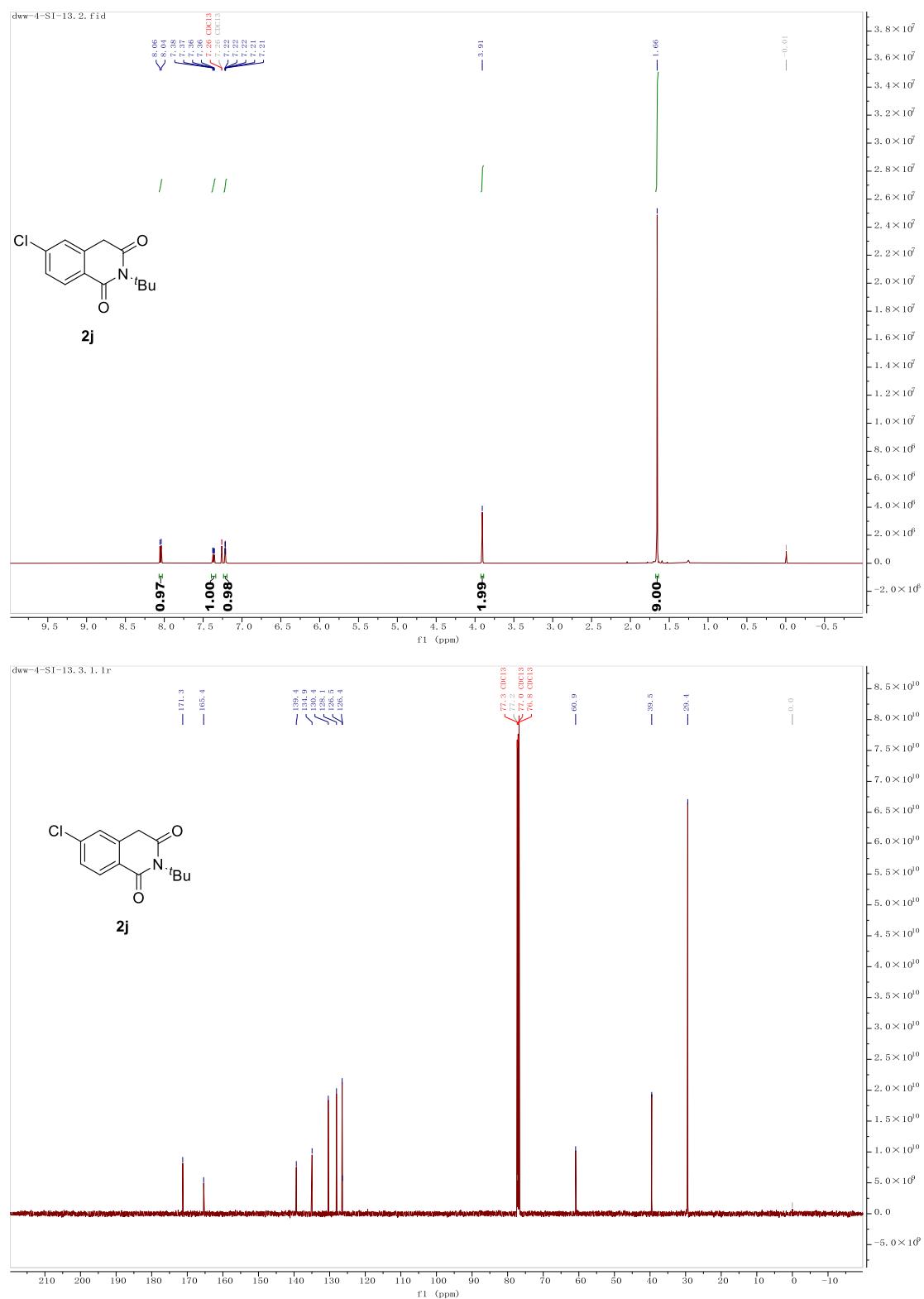
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 2h**



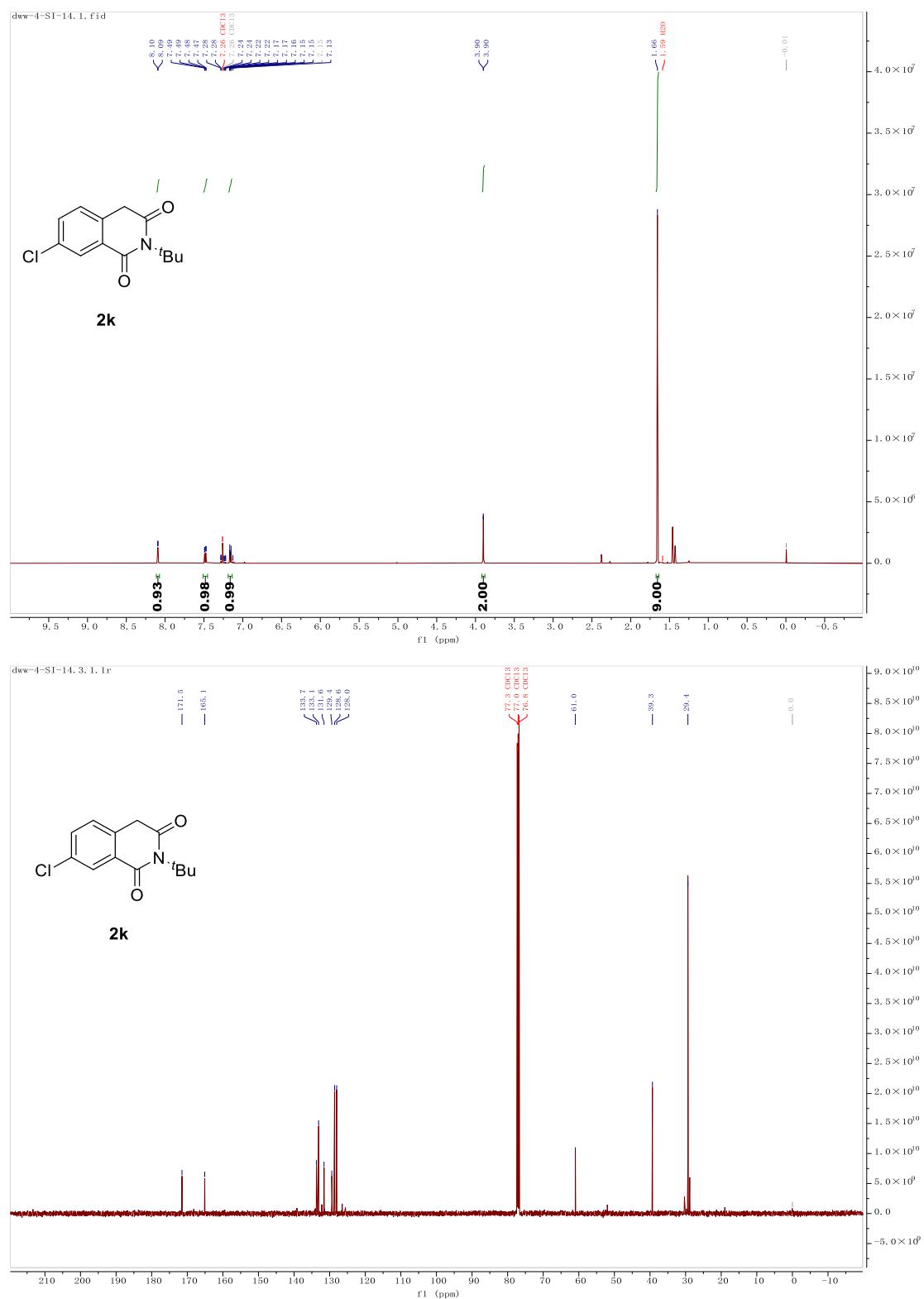
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 2i**



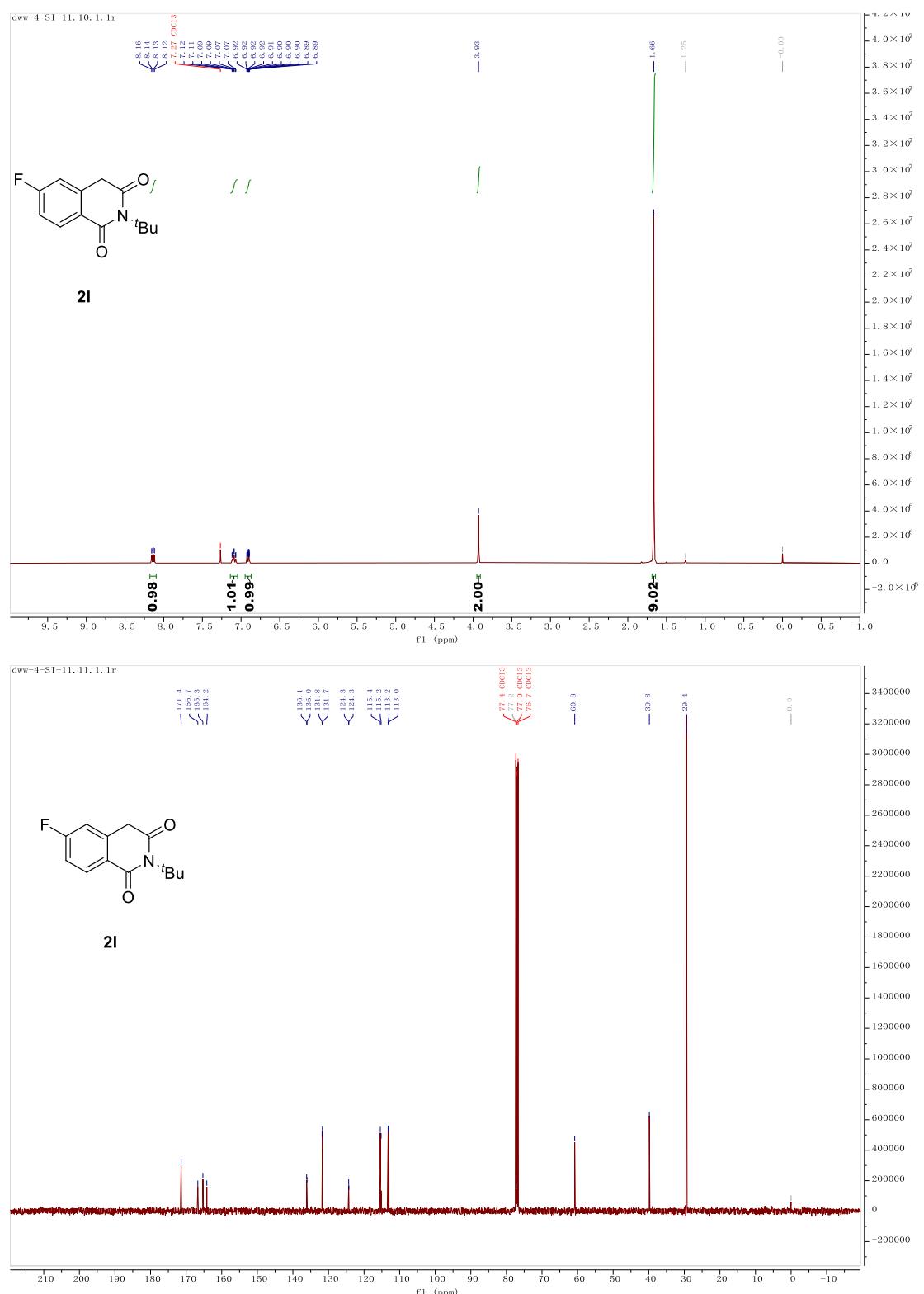
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) for 2j**



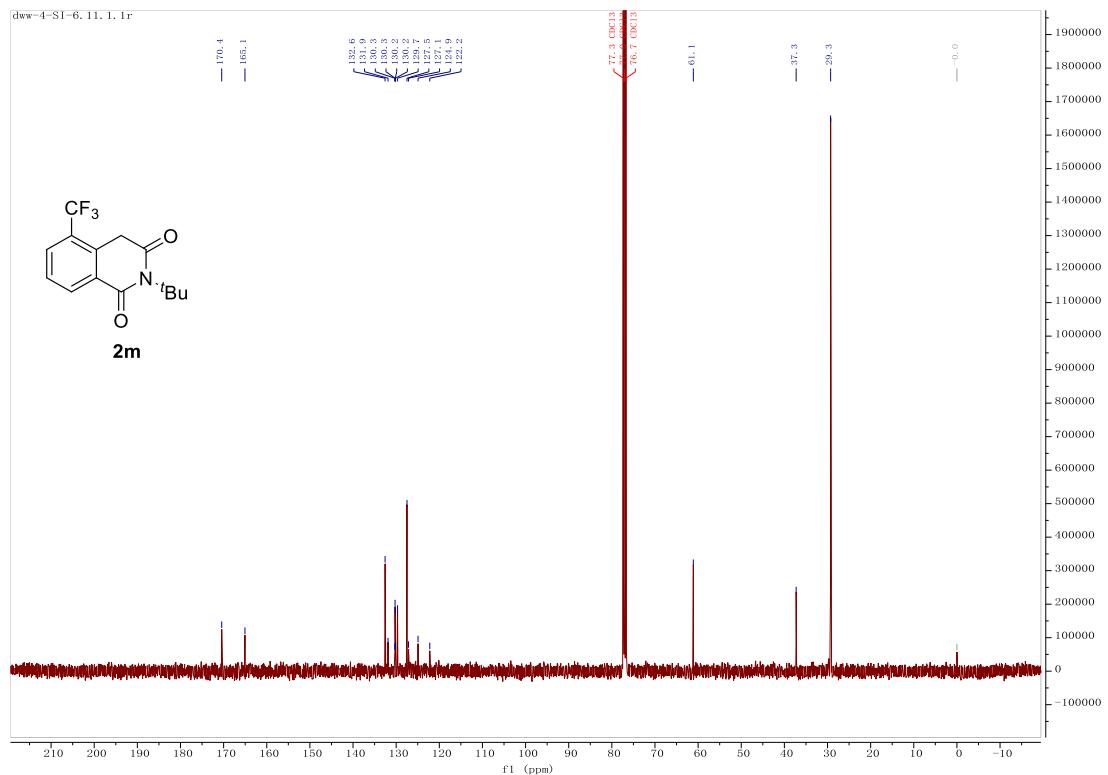
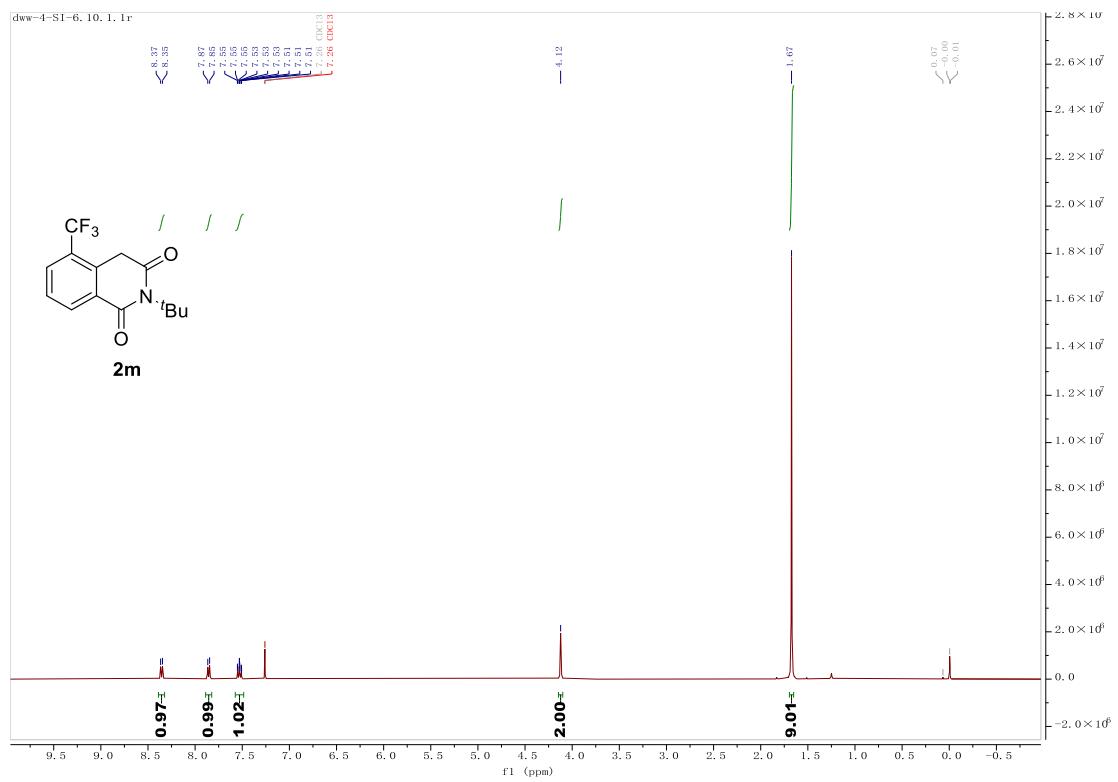
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) for 2k**



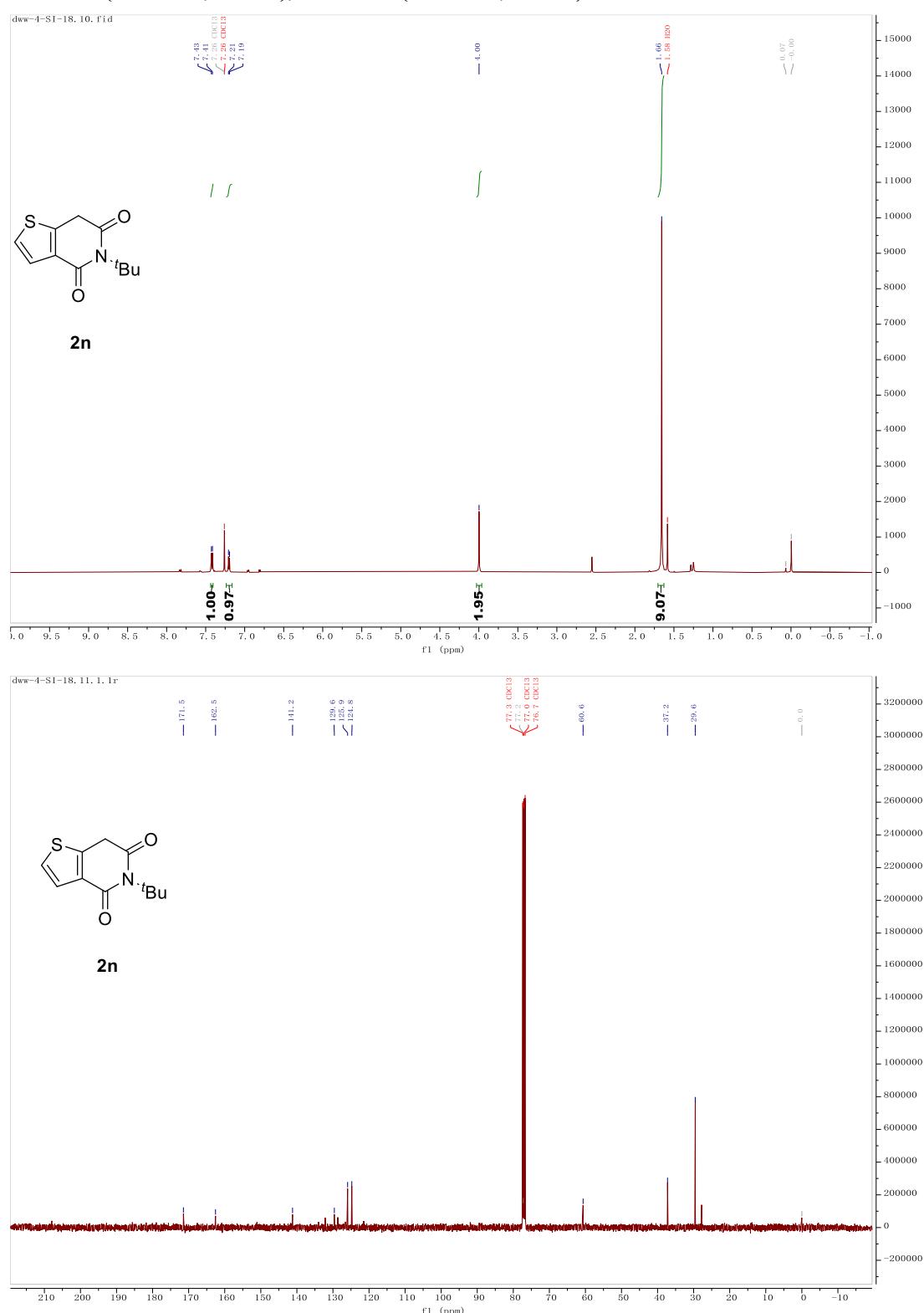
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 2l**



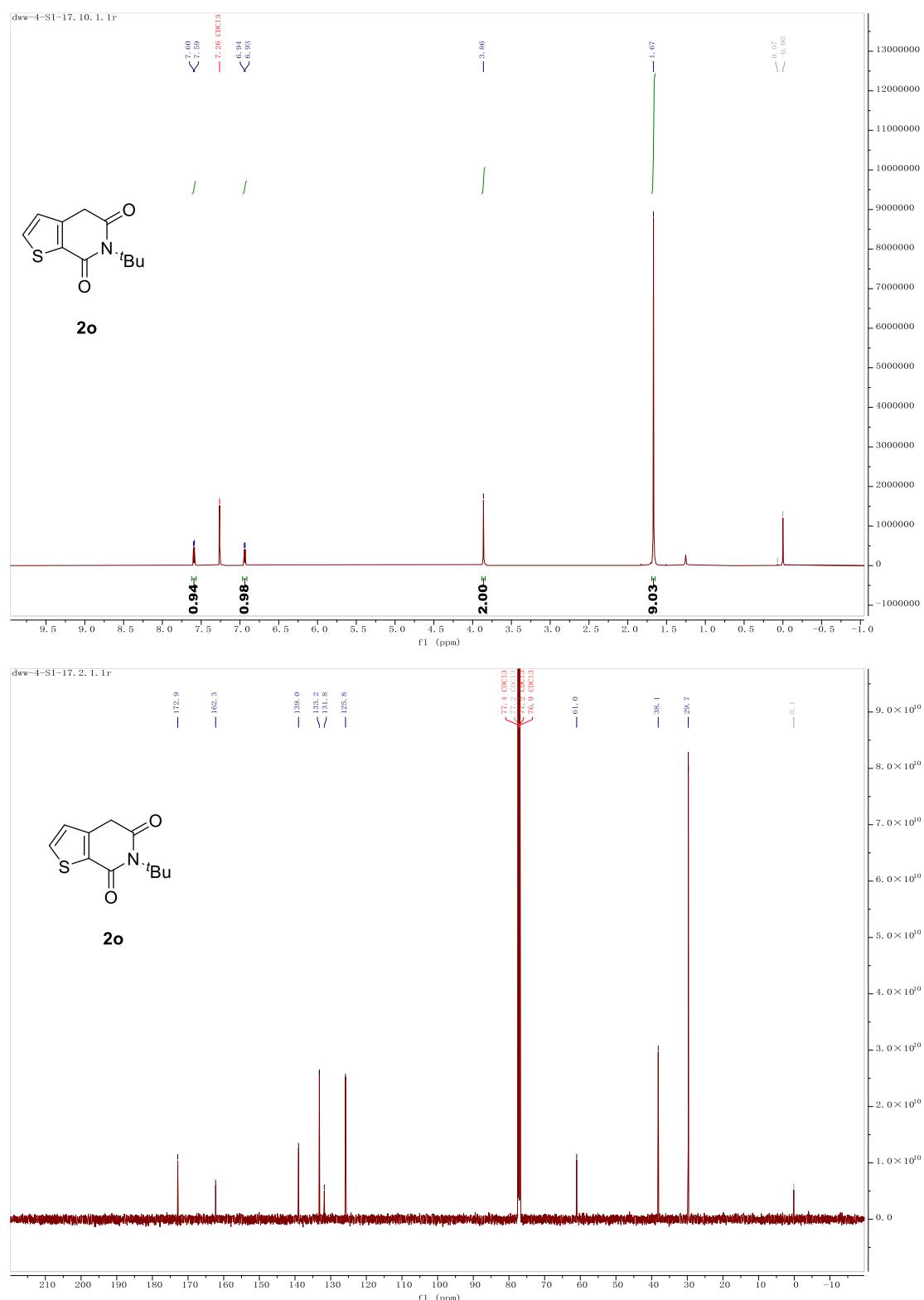
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 2m



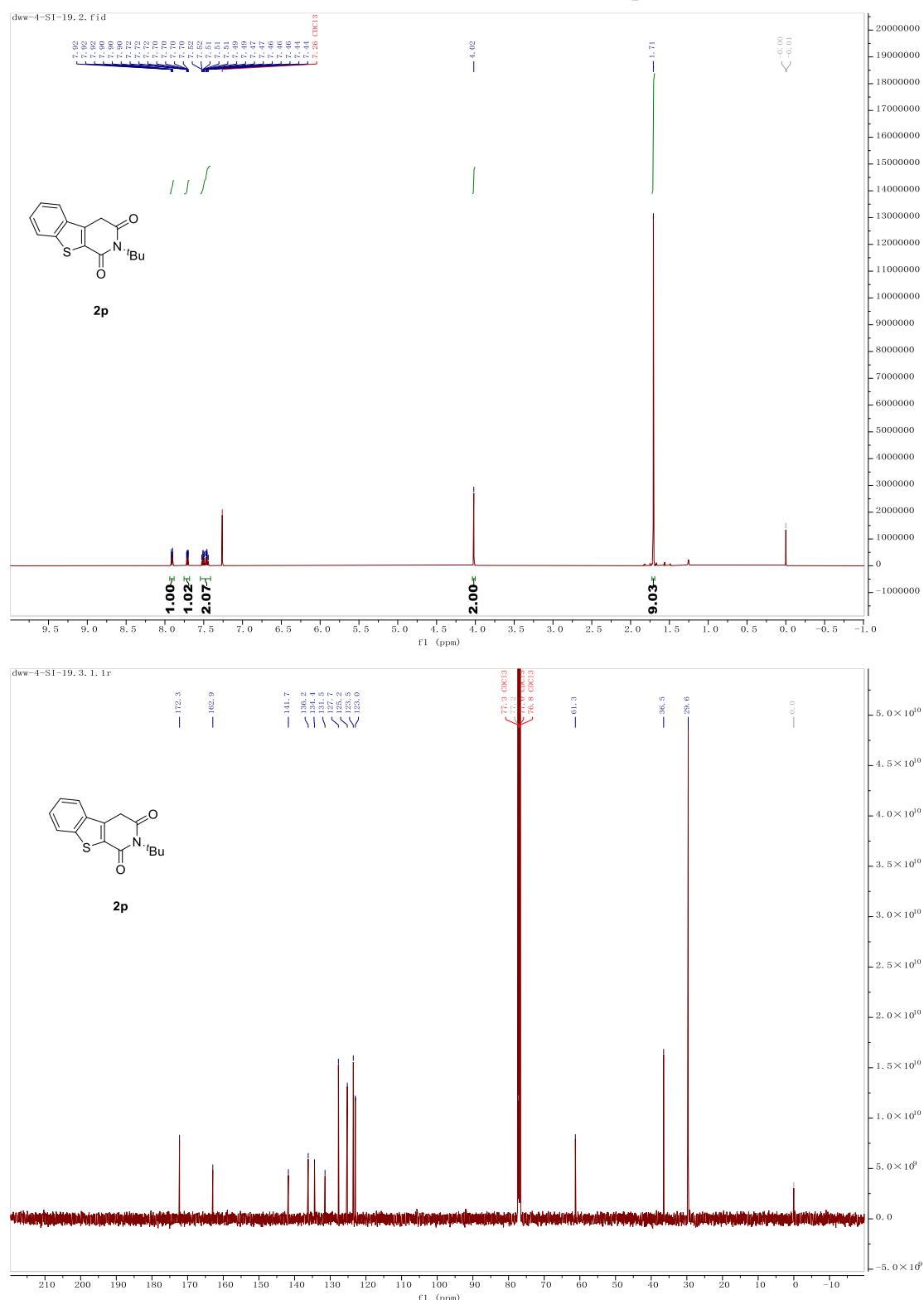
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 2n**



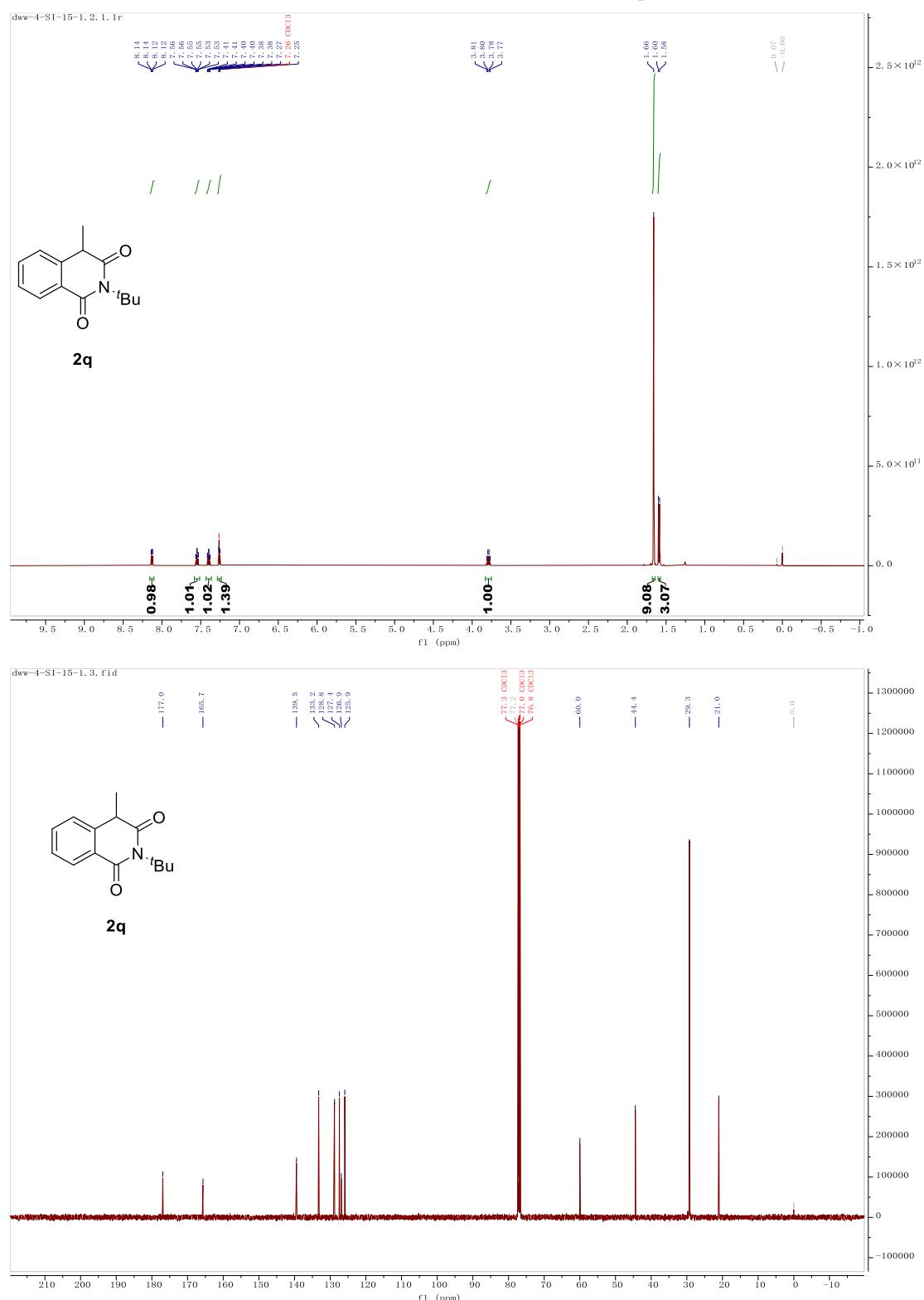
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) for 2o**



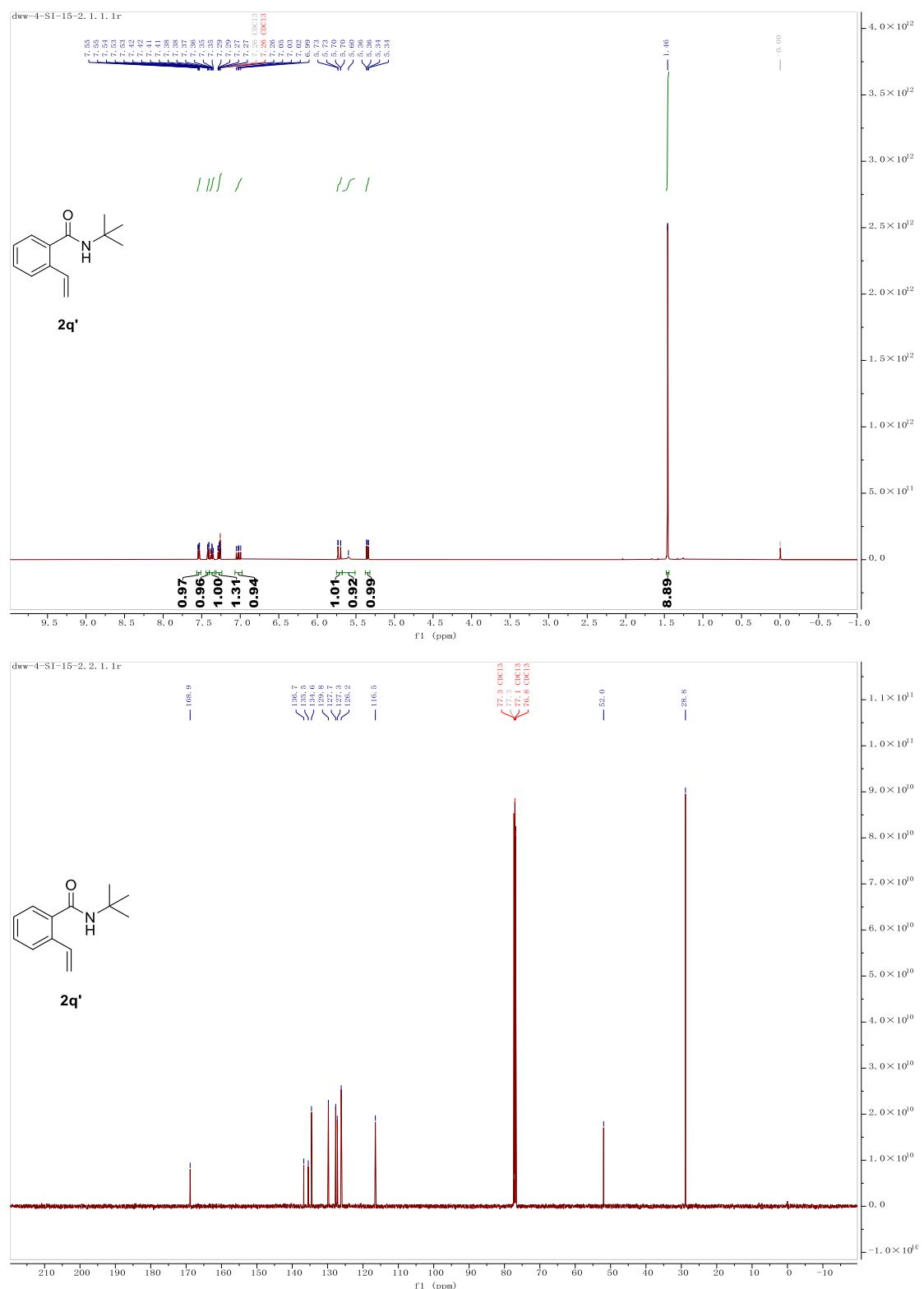
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) for 2p**



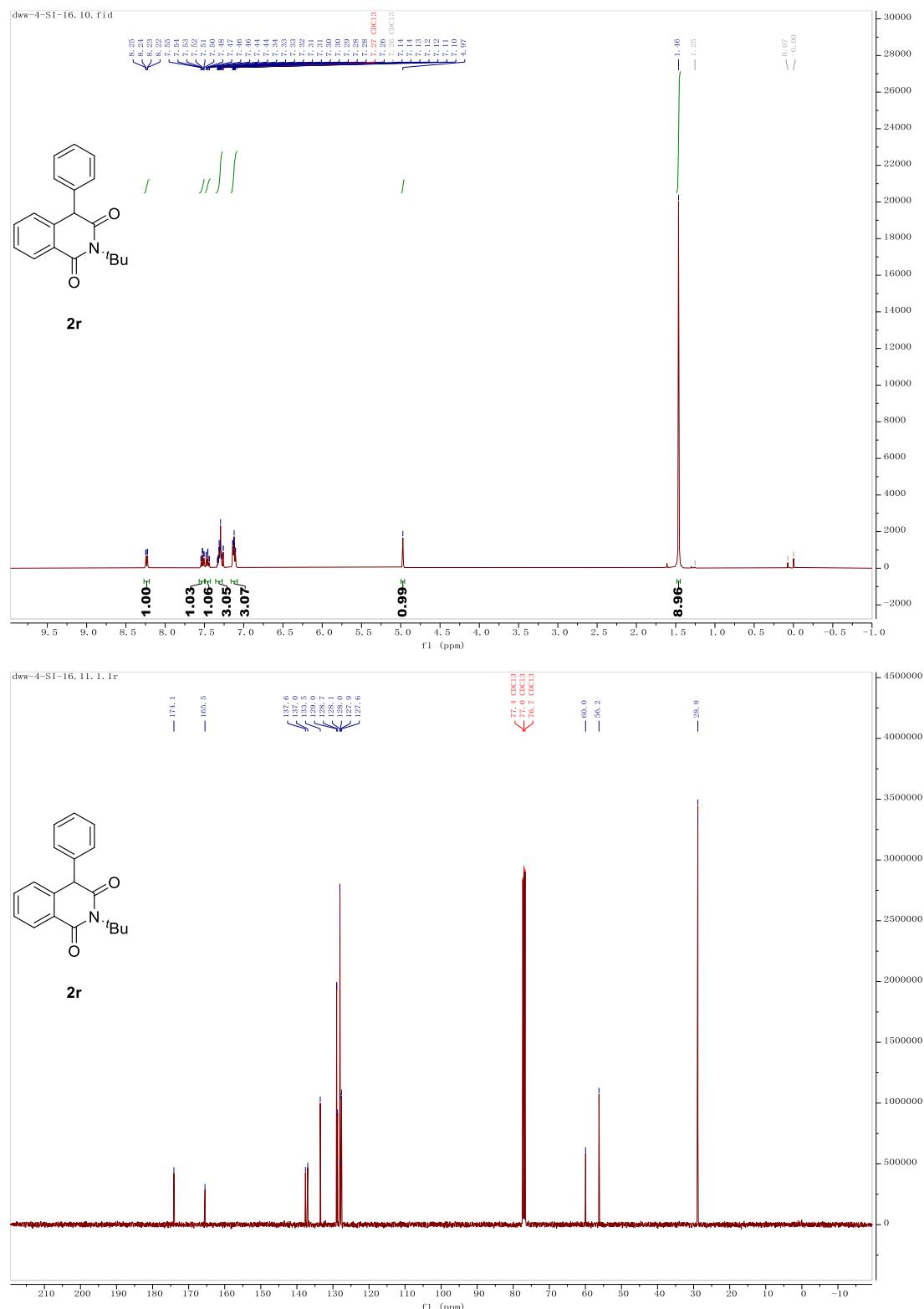
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) for 2q**

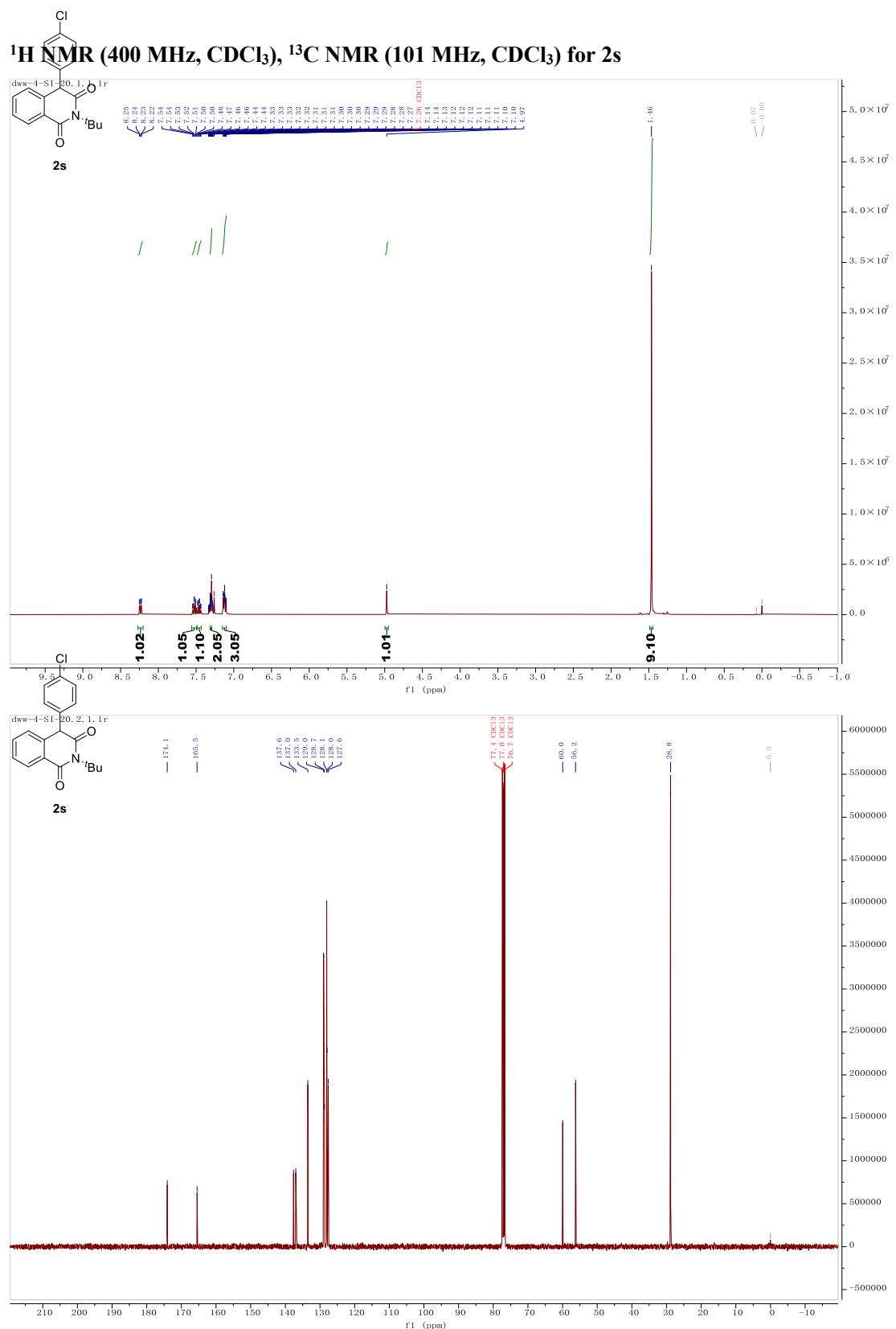


**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) for 2q'**

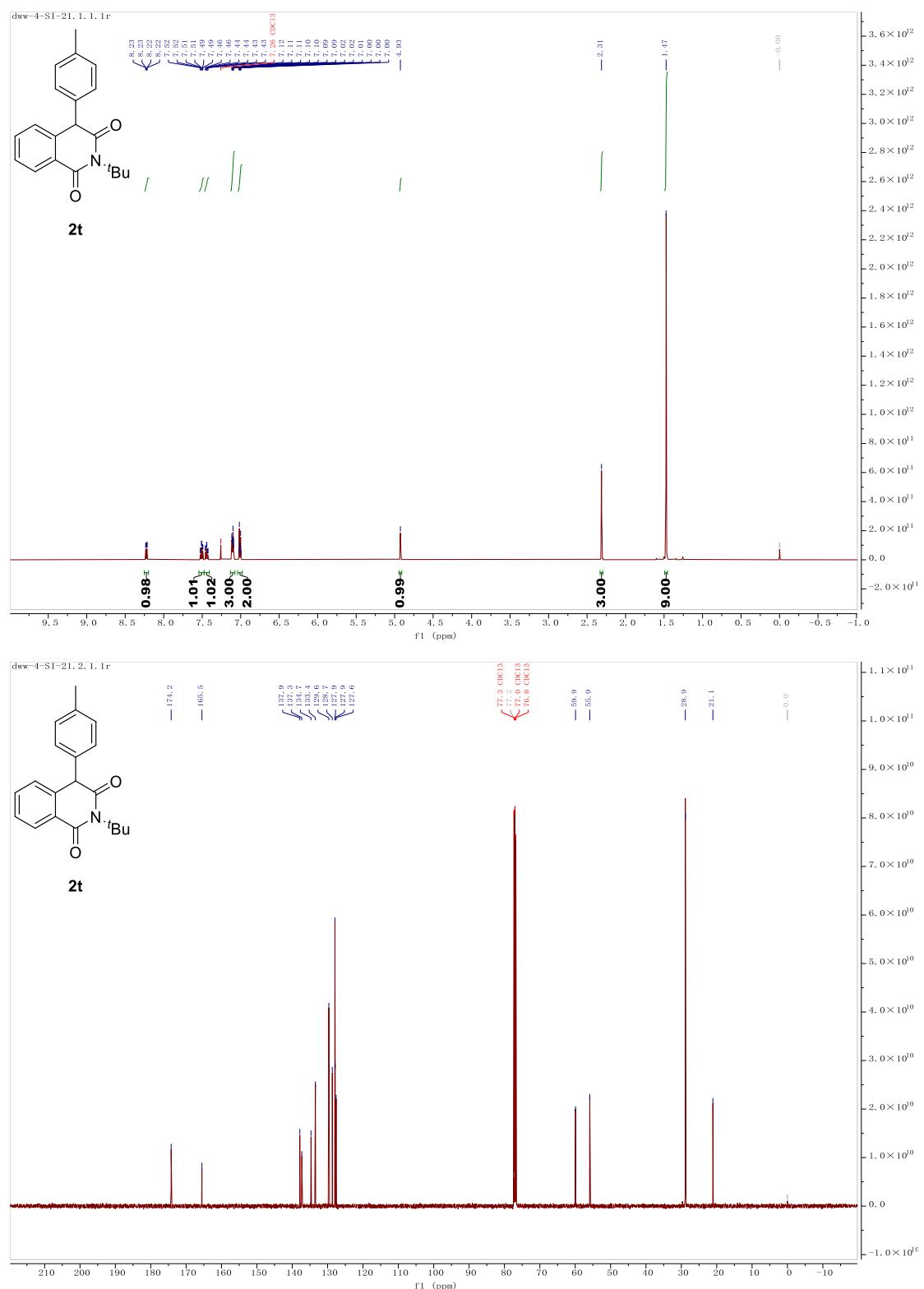


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 2r**

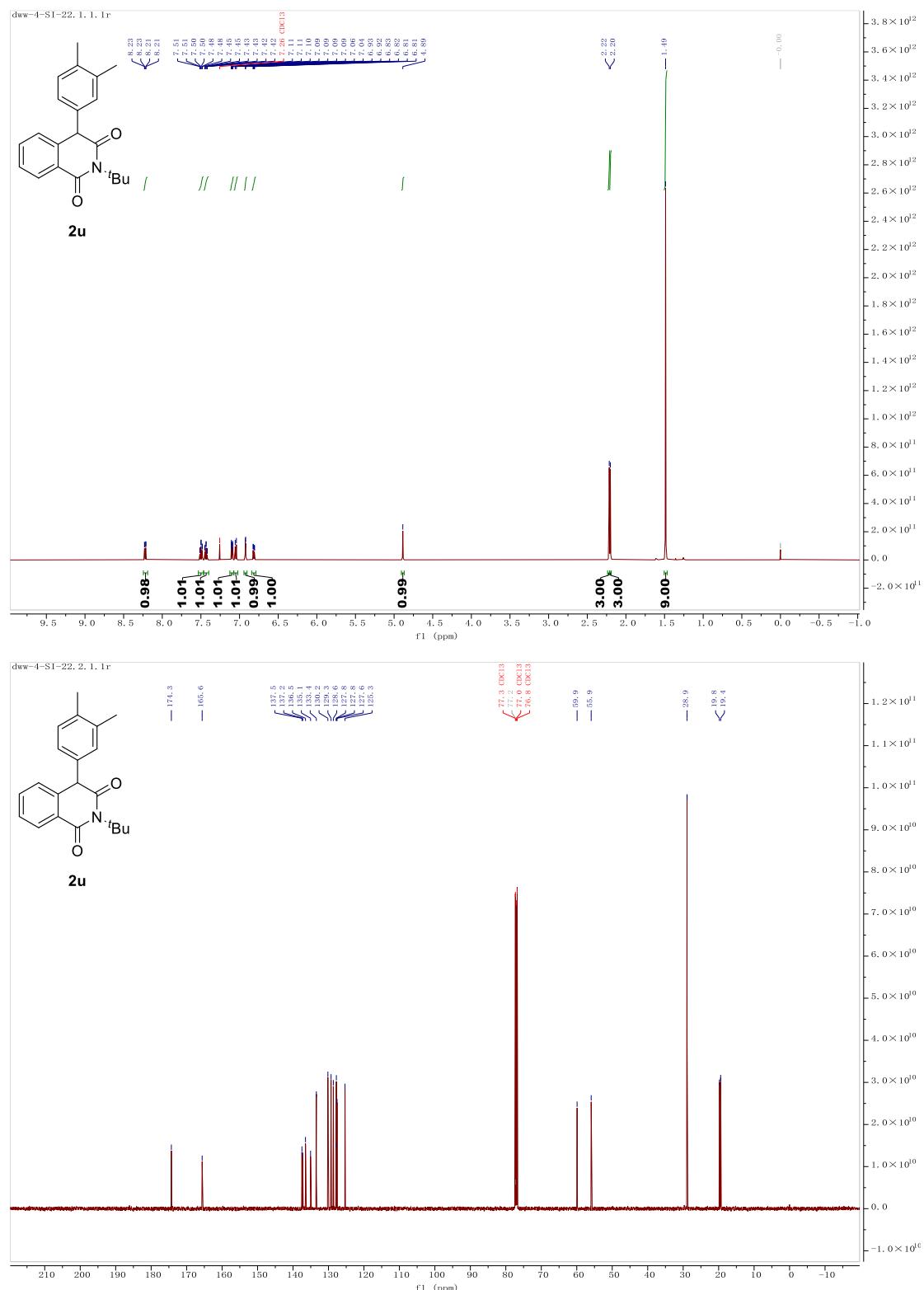




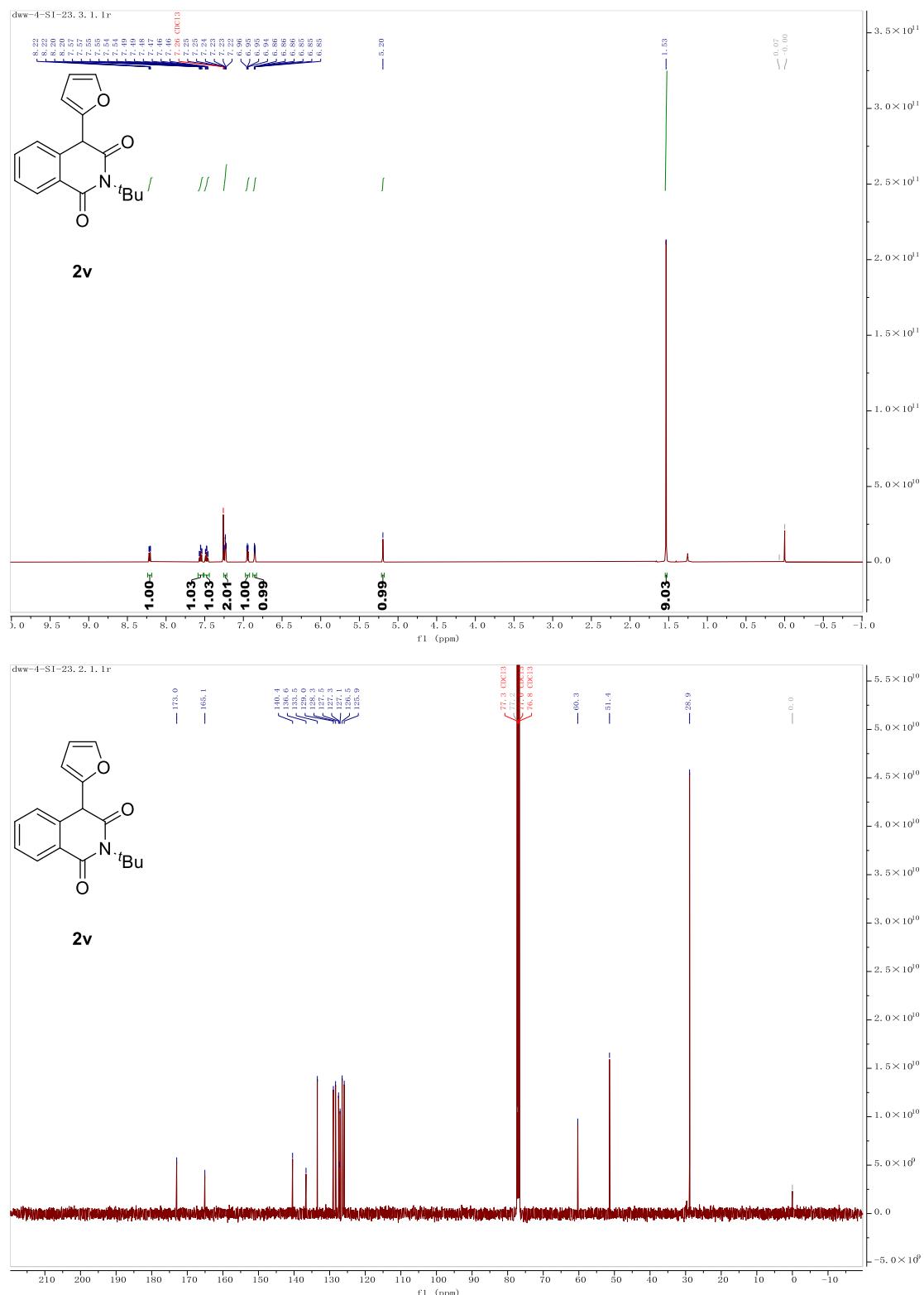
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) for 2t**



**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) for 2u**



**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) for 2v**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) for 8**

