

## Supporting Information

# Synthesis of 2-Acyl Benzofurans and Indoles Based on Nucleophile-Intercepted Meyer-Schuster Rearrangement of *o*-Hydroxyphenyl and *o*-Aminophenyl Propargylic Alcohols

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## General information

All moisture or oxygen-sensitive reactions were carried out in a nitrogen atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. The solvents used were purified by distillation over the drying agents indicated and were transferred under nitrogen: THF (Na), CH<sub>2</sub>Cl<sub>2</sub> (CaH<sub>2</sub>), toluene (Na), ClCH<sub>2</sub>CH<sub>2</sub>Cl (CaH<sub>2</sub>). Reagents were purchased at commercial quality and used without further purification. All reactions were monitored by thin-layer chromatography carried out on 0.25 mm Rushan silica gel plates (GF254) and visualized by exposure to UV light (254 nm) or KMnO<sub>4</sub>. The products were purified by column chromatography on silica gel (200–300 meshes) from Qing Dao Hai Yang Chemical Industry Company in China. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> on a Bruker Advance III 500 MHz instrument (resonance frequencies 500 MHz for <sup>1</sup>H and 125 MHz for <sup>13</sup>C), Bruker Advance III 400 MHz instrument (resonance frequencies 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C), China Qone AS400 MHz instrument (resonance frequencies 400 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C), or Bruker ascend 600 MHz (resonance frequencies 600 MHz for <sup>1</sup>H and 100 MHz for <sup>13</sup>C). Chemical shifts were reported in  $\delta$  value (ppm) relative to CDCl<sub>3</sub> (<sup>1</sup>H NMR: 7.26 ppm, <sup>13</sup>CNMR: 77.00 ppm), DMSO (<sup>1</sup>H NMR: 2.50 ppm, <sup>13</sup>CNMR: 39.5 ppm) or TMS (0.00 ppm). <sup>19</sup>F NMR was recorded on a China Qone AS400 MHz instrument (CFCl<sub>3</sub> as an external standard and low field is positive). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, td = triple doublet, dt = double triplet, m = multiplet. Mass spectrometric data were obtained using a Bruker Solaril X70 high resolution mass spectrometer (samples were dissolved in CH<sub>3</sub>OH and the ion source was ESI). The IR spectra were recorded on a Nicolet iN10.

## Screening of reaction conditions

To a 10 mL Schlenk tube, equipped with a magnetic stir bar, was added *o*-hydroxyphenyl propargylic alcohols **11a** (45 mg, 0.2 mmol) or *o*-aminophenyl propargylic alcohol **12a** (75 mg, 0.2 mmol), pyridine *N*-oxide **18** or isoquinoline *N*-oxide **18a**, and solvent (3 mL) followed by acid catalyst. The reaction mixture was heated in an oil bath at indicated temperature and monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and quenched with saturated aqueous NaHCO<sub>3</sub> solution. The aqueous phase was extracted with EtOAc (10 mL × 3). The organic extracts were combined and washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 3:1 or 3:1) to give the final product.

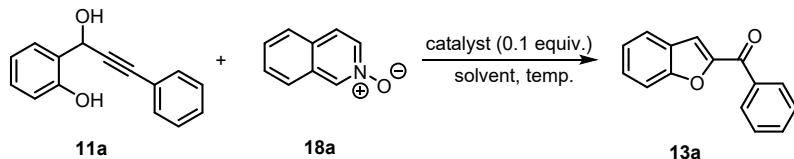
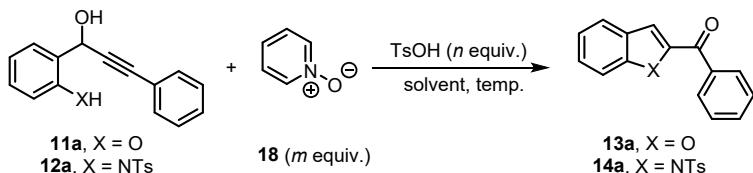


Table S1. Screening of reaction conditions<sup>a</sup>

| entry | solvent | catalyst | temp (°C) | t (h) | yield (%) <sup>b</sup> |
|-------|---------|----------|-----------|-------|------------------------|
| 1     | THF     | TFA      | 50        | 25    | 55                     |
| 2     | THF     | TsOH     | 50        | 24    | 80                     |
| 3     | 1,2-DCE | TsOH     | 50        | 24    | 98                     |

<sup>a</sup>Reaction conditions: compounds **11a** (0.2 mmol) and **18a** (0.3 mmol), solvent (3 mL), catalyst (0.02 mmol); <sup>b</sup>Yield of the isolated product.



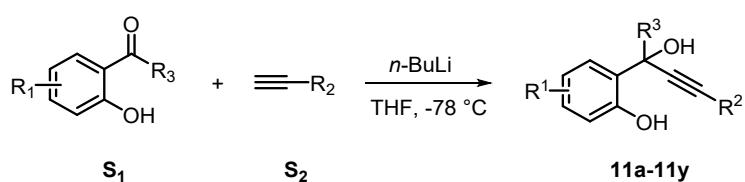
**Table S2. Screening of reaction conditions<sup>a</sup>**

| entry     | X          | solvent            | m          | n          | temp (°C)     | t (h)      | yield (%) <sup>b</sup> |
|-----------|------------|--------------------|------------|------------|---------------|------------|------------------------|
| 1         | O          | 1,2-DCE            | 2.0        | 0.1        | 50            | 24         | 73                     |
| 2         | O          | 1,2-DCE            | 2.0        | 0.1        | 70            | 22         | 80                     |
| 3         | O          | 1,2-DCE            | 2.0        | 0.1        | reflux        | 1          | 98                     |
| 4         | O          | 1,2-DCE            | 1.0        | 0.1        | reflux        | 4          | 93                     |
| <b>5</b>  | <b>O</b>   | <b>1,2-DCE</b>     | <b>1.2</b> | <b>0.1</b> | <b>reflux</b> | <b>1.5</b> | <b>95</b>              |
| 6         | O          | CH <sub>3</sub> CN | 1.2        | 0.1        | reflux        | 3          | 90                     |
| 7         | O          | toluene            | 1.2        | 0.1        | 85            | 3          | 83                     |
| 8         | O          | DMF                | 1.2        | 0.1        | 85            | 2          | 84                     |
| 9         | NTs        | 1,2-DCE            | 1.2        | 0.1        | reflux        | 24         | 50                     |
| 10        | NTs        | 1,2-DCE            | 1.2        | 0.2        | reflux        | 24         | 51                     |
| 11        | NTs        | 1,2-DCE            | 1.2        | 1.0        | reflux        | 24         | 49                     |
| 12        | NTs        | CH <sub>3</sub> CN | 1.2        | 0.2        | reflux        | 14         | 48                     |
| <b>13</b> | <b>NTs</b> | <b>toluene</b>     | <b>1.2</b> | <b>0.2</b> | <b>reflux</b> | <b>12</b>  | <b>91</b>              |
| 14        | NTs        | toluene            | 1.2        | 0.1        | reflux        | 16         | 72                     |

<sup>a</sup>Reaction conditions: compounds **11a** or **12a** (0.2 mmol) and **18** (0.02-0.2 mmol), solvent (3 mL), catalyst; <sup>b</sup>Yield of the isolated product.

#### General procedure for the synthesis of *o*-hydroxyphenyl propargylic alcohols

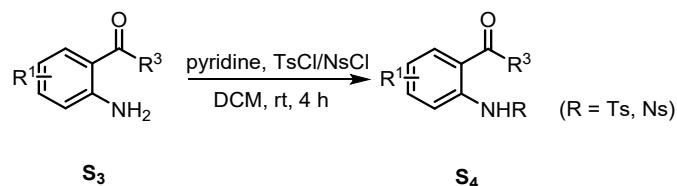
*o*-Hydroxyphenyl propargylic alcohols **11a-11y** were prepared according to the reported literature.<sup>[1]</sup> General synthetic route of propargylic alcohols **11a-11y** is shown below.



To the solution of **S<sub>2</sub>** (22 mmol, 2.2 equiv.) in dry THF (30 mL) was slowly added *n*-BuLi (21 mmol, 2.5 M in THF, 2.1 equiv.) at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at this temperature for 1 h, then a solution of the corresponding salicylaldehyde or *o*-hydroxyphenyl ketone **S<sub>1</sub>** (10 mmol, 1.0 equiv.) in 4 mL of THF was added dropwise via a cannula. The reaction mixture was stirred at -78 °C for another 1-1.5 h until the disappearance of the starting material indicated by TLC (thin-layer chromatography) analysis. Then the reaction mixture was quenched with saturated aqueous NH<sub>4</sub>Cl solution and THF was removed under vacuum. The resulting aqueous phase was extracted with EtOAc (30 mL × 3). The combined organic layers were washed with water (30 mL) and brine (30 mL), dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated under vacuum. The residue was purified by column chromatography (petroleum ether/EtOAc = 10/1) or by crystallization with petroleum ether to give **11a**-

**11y.** The spectral data was in accordance with the reported data.<sup>[1]</sup>

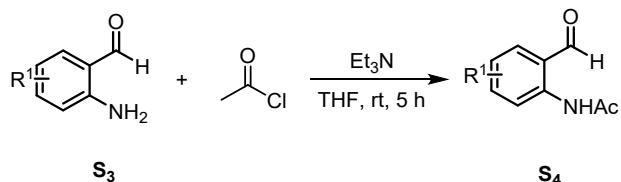
### General procedure for the synthesis of *o*-aminophenyl propargylalcohols



*o*-Aminophenyl propargylalcohols were prepared according to known procedures.<sup>[2]</sup> To an egg-shaped flask was added 2-aminobenzaldehydes or ketones **S<sub>3</sub>** (10 mmol, 1.0 equiv.), DCM (25 mL) and pyridine (13 mmol, 1.3 equiv.). Then TsCl or NsCl (12 mmol, 1.2 equiv.) was added to the above mixture under 0 °C and stirred at room temperature for about 4 h. The reaction was monitored by TLC. Upon completion, the mixture was quenched with water and extracted with DCM (30 mL × 3). The combined organic extracts were washed with water (30 mL) and brine (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1) to afford **S<sub>4</sub>**.

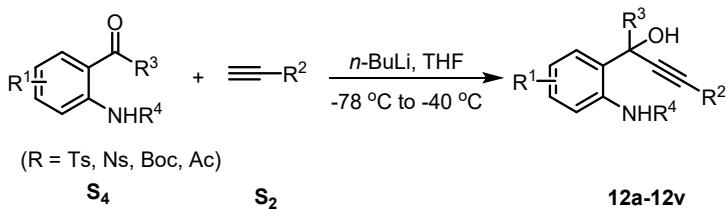


To an egg-shaped flask was added 2-aminobenzaldehydes **S<sub>3</sub>** (10 mmol, 1.0 equiv.), DMF (25 mL) and Et<sub>3</sub>N (30 mmol, 3 equiv.). Then Boc<sub>2</sub>O (12 mmol, 1.2 equiv.) was added to the above mixture under 0 °C and stirred at room temperature for 12 h. The reaction was monitored by TLC. Upon completion, the mixture was quenched with water and extracted with DCM (30 mL × 4). The combined organic extracts were washed with water (30 mL × 3) and brine (30 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5:1) to afford **S<sub>4</sub>**.



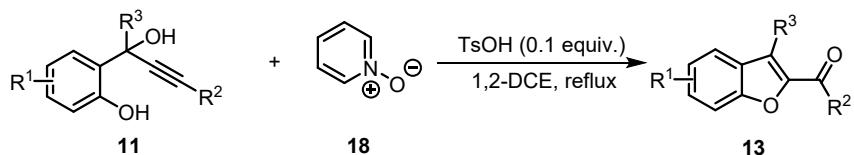
To an egg-shaped flask was added 2-aminobenzaldehydes **S<sub>3</sub>** (10 mmol, 1.0 equiv.), THF (25 mL) and Et<sub>3</sub>N (20 mmol, 2 equiv.). Then acyl chloride (10 mmol, 1.0 equiv.) was added to the above mixture under 0 °C and stirred at room temperature for 5 h. The reaction was monitored by TLC. Upon completion, the mixture was quenched with water and THF was removed under reduced pressure. The resulting aqueous phase was extracted with DCM (30 mL × 3). The combined organic extracts were

washed with water (30 mL) and brine (30 mL), dried over  $\text{Na}_2\text{SO}_4$  and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3:1) to afford **S<sub>4</sub>**.



To a solution of **S<sub>2</sub>** (5.5 mmol, 2.2 equiv.) in THF (5 mL) was added *n*-BuLi dropwise (5.5 mmol, 2.5 M in THF, 2.2 equiv.) at -78 °C under nitrogen atmosphere. Then the mixture was stirred for 10 min at -78 °C. The mixture was warmed to -40 °C and allowed to continue for another 1 h. After that, the system was cooled down to -78 °C and a solution of **S<sub>4</sub>** (2.5 mmol, 1.0 equiv.) in THF (4 mL) was added slowly to the above mixture. The reaction was stirred for 1 h at -78 °C and warmed to room temperature while stirring for another 1 h (monitored by TLC). Upon completion, the reaction mixture was quenched with saturated  $\text{NH}_4\text{Cl}$  solution, and extracted with EtOAc (20 mL × 3) after removal of THF under vacuum. The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 5:1) to afford **12a-12v**. The spectral data was in accordance with the reported data.<sup>[2]</sup>

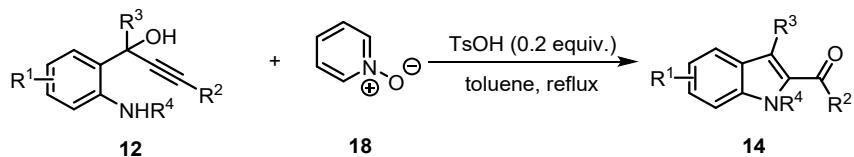
#### General procedure for the synthesis of 2-acyl benzofurans



#### For 0.2 mmol Scale:

To a 10 mL Schlenk tube, equipped with a magnetic stir bar, was added *o*-hydroxyphenyl propargylic alcohols **11** (0.2 mmol), pyridine *N*-oxide **18** (0.24 mmol), and 1,2-DCE (3 mL) followed by TsOH (0.02 mmol). The reaction mixture was stirred at reflux and monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and quenched with saturated aqueous  $\text{NaHCO}_3$  solution. The aqueous phase was extracted with EtOAc (10 mL × 3). The organic extracts were combined and washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and evaporated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 3:1 or 3:1) to give products **13a-y**.

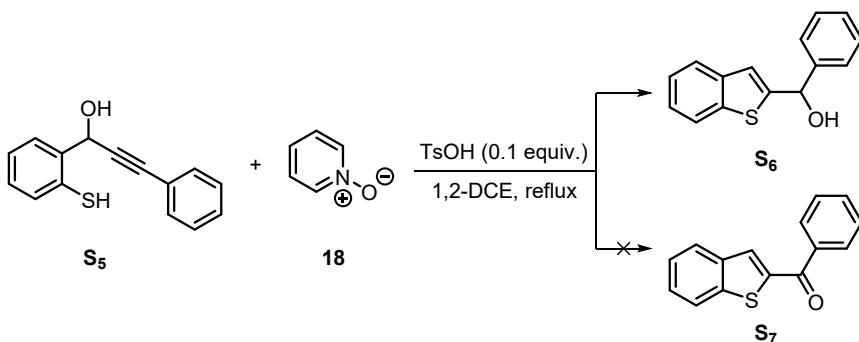
### General procedure for the synthesis of 2-acyl indoles



### For 0.2 mmol Scale:

To a 10 mL Schlenk tube, equipped with a magnetic stir bar, was added *o*-aminophenyl propargylalcohols **12** (0.2 mmol), pyridine *N*-oxide **18** (0.24 mmol), and toluene (3 mL) followed by TsOH (0.04 mmol). The reaction mixture was stirred at reflux and monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and quenched with saturated aqueous NaHCO<sub>3</sub> solution. The aqueous phase was extracted with EtOAc (10 mL × 3). The organic extracts were combined and washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 3:1) to give products **14a-v**.

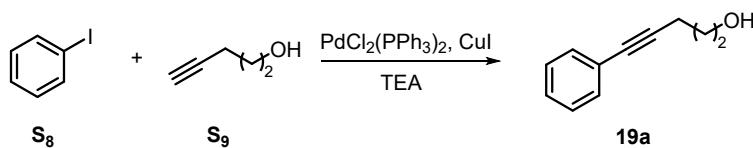
### Attempt to synthesize benzothiophene



To a 10 mL Schlenk tube was added 1-(2-mercaptophenyl)-3-phenylprop-2-yn-1-ol **S<sub>5</sub>**<sup>[3]</sup> (48 mg, 0.2 mmol, 1.0 equiv.), pyridine *N*-oxide **18** (23 mg, 0.24 mmol, 1.2 equiv.) and 1,2-DCE (3 mL) followed by TsOH (4 mg, 0.02 mmol, 0.1 equiv.). The reaction mixture was stirred at reflux and monitored by TLC. No desired product (**S<sub>7</sub>**) was formed according to NMR and mass spectrometry analysis and benzo[*b*]thiophen-2-yl(phenyl)methanol **S<sub>6</sub>** (32 mg, 0.13 mmol) was obtained instead. The spectral data was in accordance with the reported data<sup>[4]</sup>. The investigation of this transformation is underway in our laboratory. Compound **S<sub>6</sub>** (67% yield, white solid, melting point: 80.0 – 82.0 °C): <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.20 (m, 3H), 7.07 (s, 1H), 6.04 (s, 1H), 2.71 (s, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 148.6, 142.5, 139.8, 139.4, 128.6, 128.2, 126.4, 124.2, 124.2, 123.6, 122.4, 121.2, 72.9. IR: ν = 3450, 1620, 1043, 777, 599 cm<sup>-1</sup>; HRMS (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>12</sub>NaOS<sup>+</sup> 263.0502; found: 263.0502.

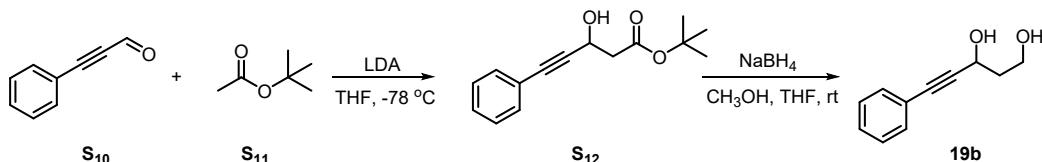
### Control experiments

#### Synthesis of 5-phenylpent-4-yn-1-ol **19a**



$\text{PdCl}_2(\text{PPh}_3)_2$  (70 mg, 0.1 mmol, 0.01 equiv.) and  $\text{CuI}$  (38 mg, 0.2 mmol, 0.02 equiv.) were dissolved in  $\text{Et}_3\text{N}$  (27.80 ml, 200.0 mmol, 20.0 equiv.). 4-Pentyn-1-ol  $\text{S}_9$  (0.93 ml, 10.0 mmol, 1.0 equiv.) and iodobenzene  $\text{S}_8$  (2.24 ml, 20.0 mmol, 2.0 equiv.) were added at the same time to the mixture. The reaction was stirred over night at room temperature and monitored by TLC. The reaction was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  solution and the aqueous layer was extracted with  $\text{EtOAc}$  (30 mL  $\times$  3). The combined organic phase was washed with  $\text{H}_2\text{O}$  and brine and was then dried over  $\text{Na}_2\text{SO}_4$ . After removing the solvent in vacuo, the residue was purified by flash column chromatography (petroleum ether/ $\text{EtOAc}$  = 6:1 to 2:1). The title product **19a** was obtained as a yellowish liquid (1.35 g, 8.4 mmol, 84% yield). The spectra were in accordance with the literature.<sup>[5]</sup>

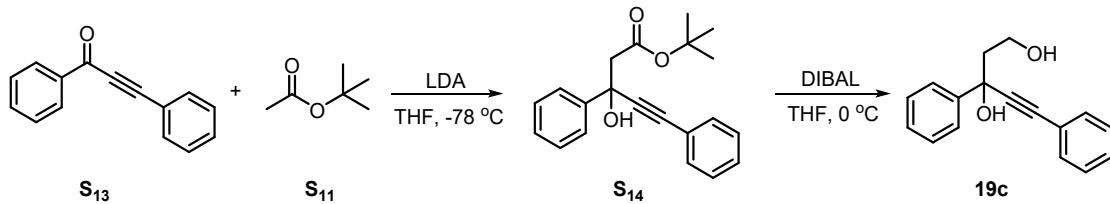
#### Synthesis of 5-phenylpent-4-yne-1,3-diol **19b**



**Step I:** LDA (5.50 ml, 11.0 mmol, 2.0 M in THF, 1.1 equiv.) was added dropwise to a solution of *tert*-butyl acetate  $\text{S}_{11}$  (1.48 ml, 11.0 mmol, 1.1 equiv.) at  $-78^\circ\text{C}$  in THF (25 mL). The reaction mixture was stirred for 1 h and a solution of 3-phenylpropionaldehyde  $\text{S}_{10}$  (1.22 ml, 10.0 mmol, 1.0 equiv.) in THF (20 mL) was slowly added. After 30 minutes, the reaction was quenched with saturated  $\text{NH}_4\text{Cl}$  solution. Most of the organic solvent was evaporated in vacuo. The residue was taken up in ethyl acetate (30 mL) and washed with water (30 mL). The aqueous layer was extracted with  $\text{EtOAc}$  (15 mL  $\times$  2). The organic extracts were combined and dried over  $\text{Na}_2\text{SO}_4$ . Evaporation of the solvent afforded the desired compound as a yellow oil, which was used in the next step without purification.

**Step II:**  $\text{NaBH}_4$  (0.47 g, 12.5 mmol, 2.5 equiv.) was added to a solution of *tert*-butyl-3-hydroxy-5-phenylpent-4-ynoate  $\text{S}_{12}$  (1.23 g, 5.0 mmol, 1.0 equiv.) in THF (20 mL). Methanol (4.05 ml, 100.0 mmol, 20.0 equiv.) was then added. The reaction mixture was allowed to stir at room temperature and monitored by TLC. Upon completion, the reaction was quenched with water. Most of the organic solvent was evaporated in vacuo. The residue was extracted from  $\text{EtOAc}$  (30 mL  $\times$  3). The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated under vacuum. The residue was purified by column chromatography (petroleum ether/ $\text{EtOAc}$  = 10:1) on silica gel to give the title compound **19b** as a yellow oil (0.39 g, 2.3 mmol, 45% yield). All spectra were in accordance with the literature.<sup>[6]</sup>

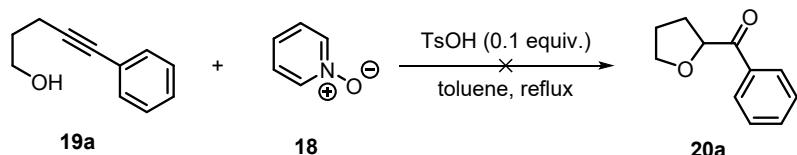
#### Synthesis of 3,5-diphenylpent-4-yne-1,3-diol **19c**<sup>[6]</sup>



**Step I:** LDA (5.50 ml, 11.0 mmol, 2.0 M in THF, 1.1 equiv.) was added dropwise to a solution of *tert*-butyl acetate **S<sub>11</sub> (1.48 ml, 11 mmol, 1.1 equiv.) at -78 °C (20 mL). The reaction mixture was stirred for 1 h and a solution of 1,3-diphenylprop-2-yn-1-one **S<sub>13</sub>** (2.06 g, 10 mmol, 1.0 equiv.) in THF (20 mL) was added slowly. After 30 minutes, the reaction was quenched with a solution of saturated ammonium chloride (25 mL). Most of the organic solvents were evaporated in vacuo. The residue was taken up in ethyl acetate (30 mL) and washed with water (30 mL). The aqueous layer was extracted with ethyl acetate (15 mL × 2). The organic extracts were combined and dried over Na<sub>2</sub>SO<sub>4</sub>. Evaporation of the solvent afforded the desired compound **S<sub>14</sub>** as a yellow oil, which was used in the next step without purification.**

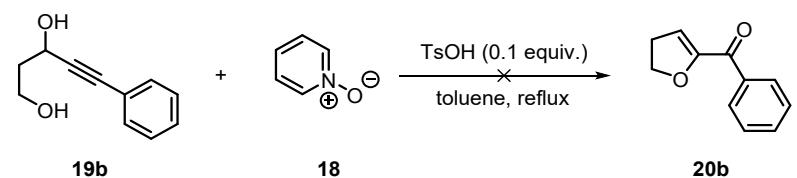
**Step II:** DIBAL (10.00 ml, 20 mmol, 2.0 M in THF, 2.0 equiv.) was added to a solution of *tert*-butyl 3,5-diphenylpent-4-ynoate **S<sub>14</sub>** (3.22 g, 10 mmol, 1.0 equiv.) in THF (30 mL) at 0 °C. The reaction mixture was allowed to stir at 0 °C and monitored by TLC. Upon completion, the reaction was quenched with a 10% NaOH solution and most of the organic solvents were evaporated in vacuo. The residue was extracted with ethyl acetate (30 mL × 3). The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under vacuum. The residue was purified by column chromatography (petroleum ether/EtOAc = 10:1) on silica gel to give the title compound **19c** as a white solid (1.14 g, 4.5 mmol, 45% yield).

#### Control experiment 1:



To a 10 mL Schlenk tube was added 5-phenylpent-4-yn-1-ol **19a** (32 mg, 0.2 mmol, 1.0 equiv.), pyridine *N*-oxide **18** (23 mg, 0.24 mmol, 1.2 equiv.) and toluene (3 mL) followed by TsOH (4 mg, 0.02 mmol, 0.1 equiv.). The reaction mixture was stirred at reflux and monitored by TLC. No desired product was formed according to NMR and mass spectrometry analysis.

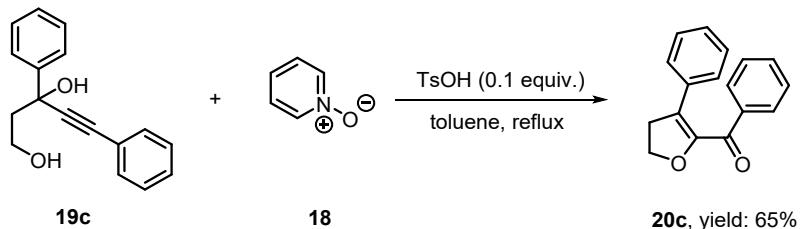
#### Control experiment 2:



To a 10 mL Schlenk tube was added 5-phenylpent-4-yn-1,3-diol **19b** (35 mg, 0.2 mmol, 1.0 equiv.), pyridine *N*-oxide **18** (23 mg, 0.24 mmol, 1.2 equiv.) and toluene (3 mL) followed by TsOH (4 mg, 0.02 mmol, 0.1 equiv.). The reaction mixture was stirred at reflux and monitored by TLC. No desired

product was formed according to NMR and mass spectrometry analysis.

### Control experiment 3:

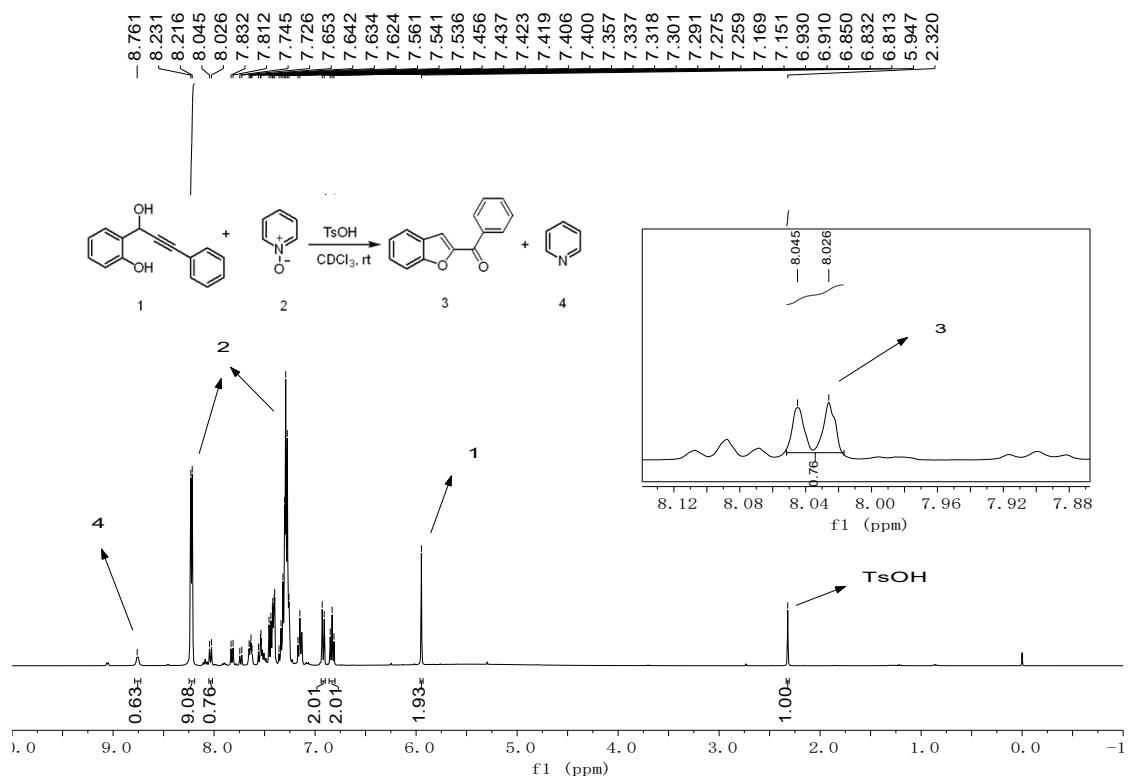


To a 10 mL Schlenk tube was added 3,5-diphenylpent-4-yne-1,3-diol **19c** (50 mg, 0.2 mmol, 1.0 equiv.), pyridine *N*-oxide **18** (23 mg, 0.24 mmol, 1.2 equiv.) and toluene (3 mL) followed by TsOH (4 mg, 0.02 mmol, 0.1 equiv.). The reaction mixture was stirred at reflux and monitored by TLC. The desired product was isolated in 65% yield after work up and column chromatography. Compound **20c** (65% yield, yellow oil): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 – 7.86 (m, 2H), 7.51 – 7.45 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.22 (m, 2H), 7.21 – 7.11 (m, 3H), 4.61 (t, *J* = 10.0 Hz, 2H), 3.30 (t, *J* = 10.0 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 189.4, 147.7, 136.3, 133.3, 133.0, 129.7, 128.2, 128.1, 127.5, 127.3, 121.6, 69.1, 35.2. IR: ν = 3416, 1617, 1400, 1156 cm<sup>-1</sup>; HRMS (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>17</sub>H<sub>14</sub>NaO<sub>2</sub><sup>+</sup> 273.0886; found: 273.0889.

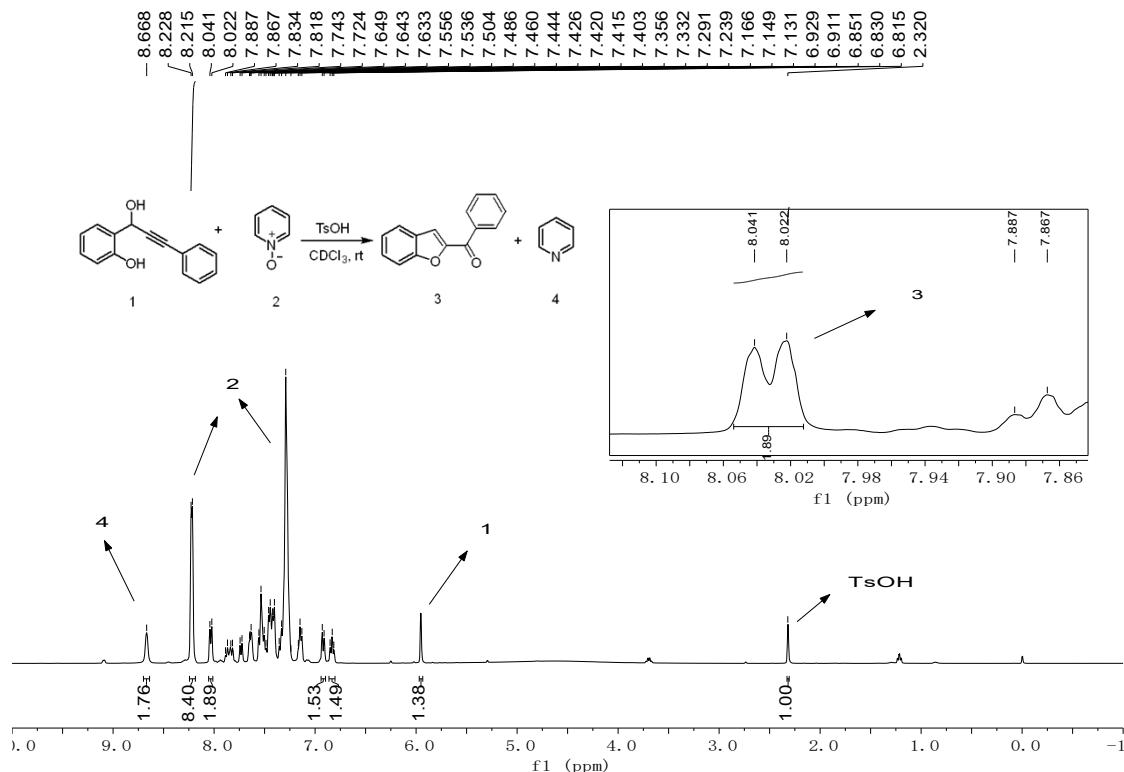
### Control experiment 4:

To probe the probable reaction pathway, we set up an experiment to try to capture the intermediate. To a 10 mL Schlenk tube, equipped with a stir bar, was added *o*-hydroxyphenyl propargylic alcohol **11a** (0.2 mmol, 1.0 equiv.), pyridine *N*-oxide **18** (0.4 mmol, 2 equiv.), and CDCl<sub>3</sub> (3 ml) followed by TsOH (0.02 mmol, 0.1 equiv.). The reaction mixture was then transferred into an NMR tube and subjected to NMR analysis after 0.5 hours and 3 hours. We could observe peaks of product **13a** and pyridine according to NMR analysis, but no useful information of possible intermediate was found.

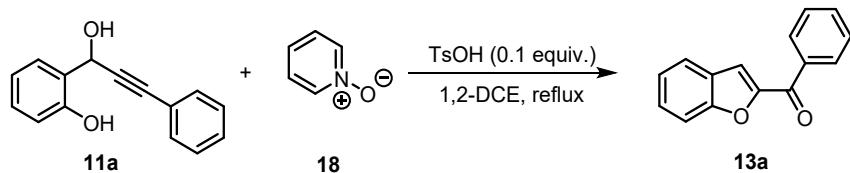
**after 0.5 h**



**after 3 h**

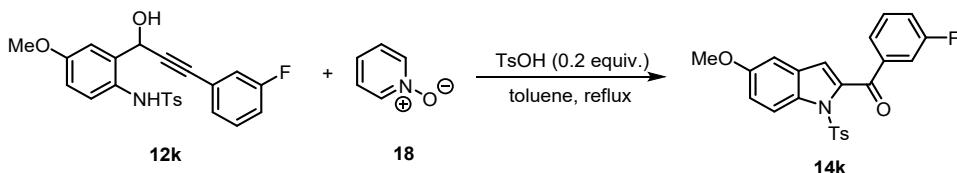


### Scale-up preparation of **13a**

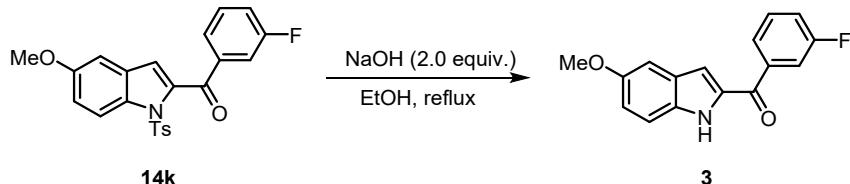


To a 100 mL round-bottom flask, equipped with a stir bar and condenser, was added *o*-hydroxyphenyl propargylic alcohol **11a** (1.121 g, 5.00 mmol, 1.0 equiv.), pyridine *N*-oxide **18** (0.571 g, 6.00 mmol, 1.2 equiv.), and 1,2-DCE (20 ml) followed by TsOH (86 mg, 0.50 mmol, 0.1 equiv.). The reaction mixture was stirred at reflux and monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and quenched with saturated aqueous NaHCO<sub>3</sub> solution. The aqueous phase was extracted with DCM (20 mL × 3). The organic extracts were combined and washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 3:1) to give product **13a** in 92% yield (1.024 g, 4.61 mmol).

### Scale-up preparation and transformation of **14k** and **3**



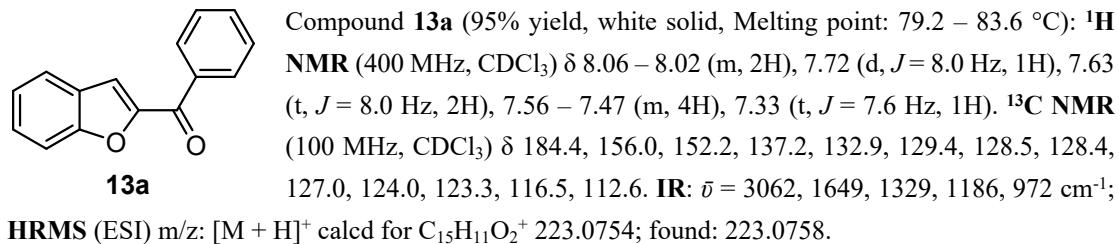
To a 100 mL round-bottom flask, equipped with a stir bar and condenser, was added *o*-aminophenyl propargylalcohol **12k** (1.276 g, 3.00 mmol, 1.0 equiv.), pyridine *N*-oxide **18** (0.342 g, 3.60 mmol, 1.2 equiv.), and toluene (20 mL) followed by TsOH (103 mg, 0.60 mmol, 0.2 equiv.). The reaction mixture was stirred at reflux and monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and quenched with saturated aqueous NaHCO<sub>3</sub> solution. The aqueous phase was extracted with EtOAc (20 mL × 3). The organic extracts were combined and washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1 to 3:1) to give product **14k** in 79% yield (1.010 g, 2.38 mmol).



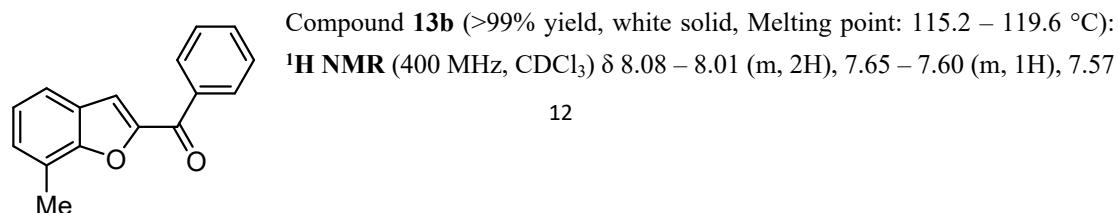
To a 100 mL round-bottom flask, equipped with a stir bar and condenser, was added **14k** (0.999 g, 2.36 mmol, 1.0 equiv.) and EtOH (20 mL) followed by NaOH (0.187 g, 4.72 mmol, 2.0 equiv.). The reaction mixture was stirred at reflux and monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and quenched with saturated aqueous NH<sub>4</sub>Cl solution. The aqueous phase was extracted with EtOAc (20 mL × 3) after removal of CH<sub>3</sub>OH. The organic extracts were combined and washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and evaporated under vacuum. The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to give product **3** in 91% yield (0.577 g, 2.15 mmol).

### Spectra data of compounds **13a**-**13y**, **14a**-**14v**, **14v'**, **19c**, and **3**

#### benzofuran-2-yl(phenyl)methanone (**13a**)

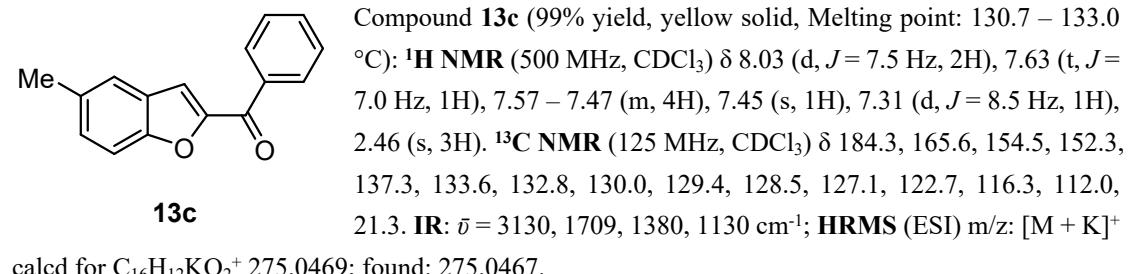


#### (7-methylbenzofuran-2-yl)(phenyl)methanone (**13b**)

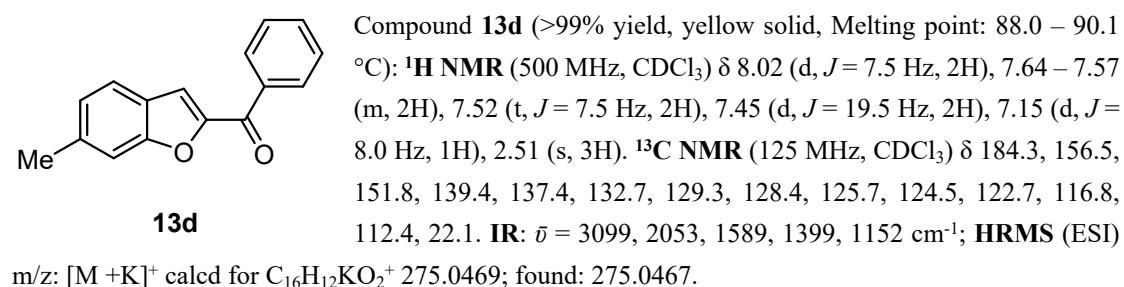


– 7.49 (m, 4H), 7.29 (d,  $J$  = 7.2, 1H), 7.22 (t,  $J$  = 7.6 Hz, 1H), 2.61 (s, 3H).  **$^{13}\text{C}$  NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  184.4, 155.2, 152.0, 137.3, 132.7, 129.4, 129.0, 128.4, 126.4, 124.0, 122.8, 120.6, 117.0, 15.1. **IR:**  $\bar{\nu}$  = 3451, 2065, 1600, 1398, 1156  $\text{cm}^{-1}$ ; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for  $\text{C}_{16}\text{H}_{12}\text{NaO}_2^+$  259.0730; found: 259.0736.

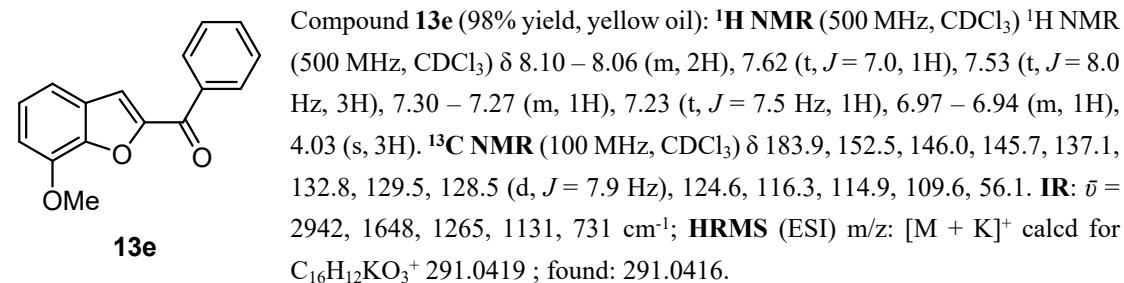
**(5-methylbenzofuran-2-yl)(phenyl)methanone (13c)**



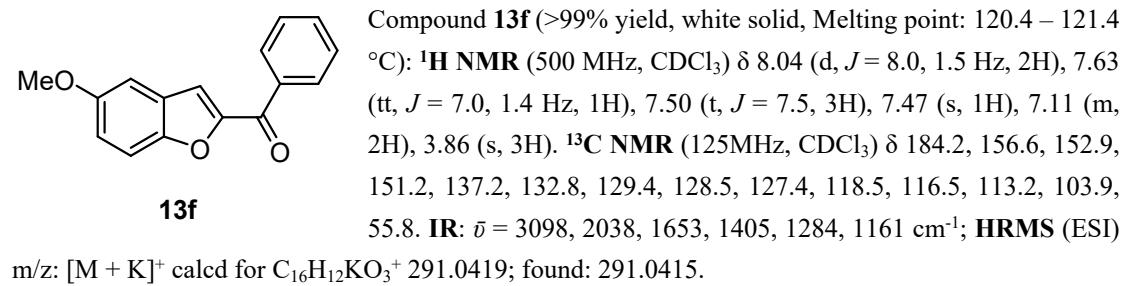
**(6-methylbenzofuran-2-yl)(phenyl)methanone (13d)**



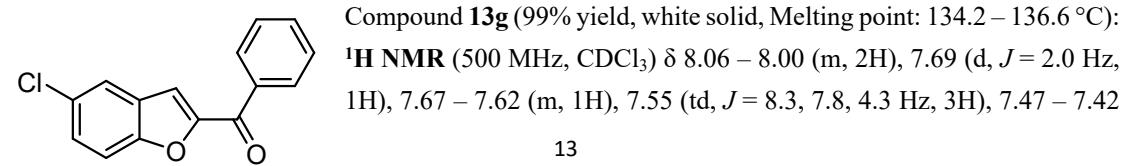
**(7-methoxybenzofuran-2-yl)(phenyl)methanone (13e)**



**(5-methoxybenzofuran-2-yl)(phenyl)methanone (13f)**

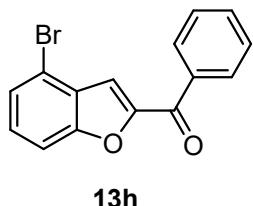


**(6-chlorobenzofuran-2-yl)(phenyl)methanone (13g)**



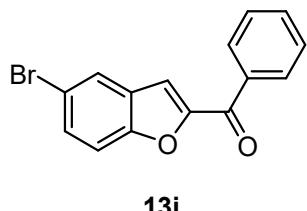
(m, 2H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 184.0, 154.1, 153.2, 136.7, 133.1, 129.5, 129.4, 128.6 (d, *J* = 4.2 Hz), 128.1, 122.5, 115.4, 113.6. **IR:**  $\bar{\nu}$  = 3161, 1719, 1610, 1400, 1130, 770 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>15</sub>H<sub>9</sub>ClKO<sub>2</sub><sup>+</sup> 294.9923 (100%), 296.9894 (32%) found: 294.9921, 296.9893.

#### (7-bromobenzofuran-2-yl)(phenyl)methanone (13h)



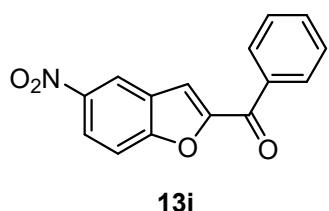
Compound **13h** (98% yield, white solid, Melting point: 114.0 – 115.6 °C): **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.56 (q, *J* = 8.0 Hz, 3H), 7.52 – 7.47 (m, 2H), 7.36 (t, *J* = 8.0 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 184.0, 155.5, 152.1, 136.8, 133.1, 129.4, 129.1, 128.7 (d, *J* = 4.9 Hz), 126.9, 116.3, 116.0, 111.6. **IR:**  $\bar{\nu}$  = 3168, 2060, 1640, 1044, 1150 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>9</sub>BrNaO<sub>2</sub><sup>+</sup> 322.9679 (100%), 324.9658 (98%); found: 322.9680, 324.9658.

#### (5-bromobenzofuran-2-yl)(phenyl)methanone (13i)



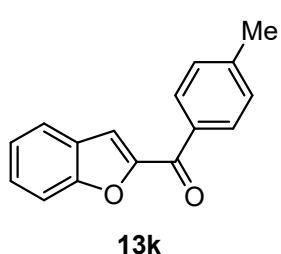
Compound **13i** (99% yield, white solid, Melting point: 135.9 – 136.3 °C): **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 2.5 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.66 – 7.51 (m, 4H), 7.46 (s, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 184.0, 154.6, 153.2, 136.8, 133.1, 131.3, 129.5, 128.8, 128.6, 125.7, 117.0, 115.2, 114.0. **IR:**  $\bar{\nu}$  = 3570, 2296, 1620, 1400, 1160, 546 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>9</sub>BrNaO<sub>2</sub><sup>+</sup> 322.9679 (100%), 324.9658 (98%); found: 322.9679, 324.9657.

#### (6-nitrobenzofuran-2-yl)(phenyl)methanone (13j)



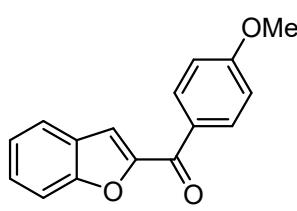
Compound **13j** (91% yield, white solid, Melting point: 195.4 – 198.6 °C): **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.69 (d, *J* = 2.4 Hz, 1H), 8.42 (dd, *J* = 9.4, 2.4 Hz, 1H), 8.06 (d, *J* = 7.6 Hz, 2H), 7.76 (d, *J* = 9.2 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.58 (t, *J* = 7.6 Hz, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 183.7, 158.2, 154.7, 144.9, 136.4, 133.6, 129.5, 128.8, 127.2, 123.5, 119.9, 116.0, 113.2. **IR:**  $\bar{\nu}$  = 3420, 2252, 1631, 1400, 1048 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + H]<sup>+</sup> calcd for C<sub>15</sub>H<sub>10</sub>NO<sub>4</sub><sup>+</sup> 268.0605; found: 268.0606.

#### benzofuran-2-yl(p-tolyl)methanone (13k)



Compound **13k** (97% yield, yellow solid, Melting point: 95.3 – 97.7 °C): **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.00 – 7.94 (m, 2H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.46 (m, 2H), 7.32 (t, *J* = 7.5 Hz, 3H), 2.46 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 184.0, 155.9, 152.4, 143.8, 134.5, 129.6, 129.2, 128.2, 127.0, 123.9, 123.2, 116.1, 112.5, 21.7. **IR:**  $\bar{\nu}$  = 3010, 1737, 1620, 1420, 1172 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>16</sub>H<sub>12</sub>KO<sub>2</sub><sup>+</sup> 275.0469; found: 275.0467.

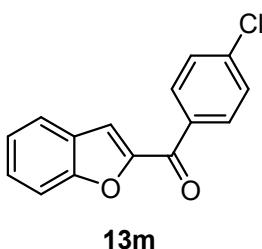
#### benzofuran-2-yl(4-methoxyphenyl)methanone (13l)



Compound **13l** (97% yield, yellow solid, Melting point: 95.7 – 97.7 °C): **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.13 – 8.09 (m, 2H), 7.72 (d, *J* = 10.0 Hz, 1H), 7.63 (d, *J* = 10.0 Hz, 1H), 7.52 (s, 1H), 7.50 – 7.46 (m, 1H), 7.32 (t, *J* = 10.0 Hz, 1H), 7.04 – 7.00 (m, 2H), 3.90 (s, 3H). **<sup>13</sup>C NMR** (125 MHz,

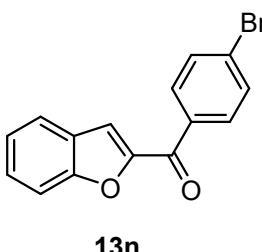
$\text{CDCl}_3$ )  $\delta$  182.8, 163.5, 155.7, 152.6, 131.9, 129.7, 128.0, 127.0, 123.8, 123.1, 115.5, 113.8, 112.4, 55.5. **IR:**  $\bar{\nu}$  = 3102, 2059, 1634, 1394, 1288, 1150  $\text{cm}^{-1}$ ; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>16</sub>H<sub>13</sub>KO<sub>3</sub><sup>+</sup> 291.0419; found: 291.0415.

#### benzofuran-2-yl(4-chlorophenyl)methanone (13m)



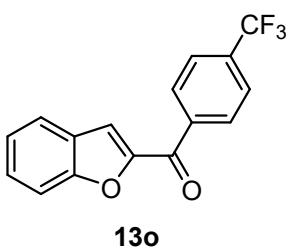
Compound **13m** (98% yield, white solid, Melting point: 148.3 – 148.9 °C): **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J$  = 8.4 Hz, 2H), 7.73 (d,  $J$  = 8.0 Hz, 1H), 7.63 (d,  $J$  = 8.4 Hz, 1H), 7.54 – 7.49 (m, 4H), 7.34 (t,  $J$  = 7.2 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  182.9, 155.9, 152.0, 139.4, 135.3, 130.9, 128.8, 128.5, 126.8, 124.1, 123.3, 116.5, 112.5. **IR:**  $\bar{\nu}$  = 3086, 2077, 1570, 1386, 1154, 672  $\text{cm}^{-1}$ ; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>9</sub>ClNaO<sub>2</sub><sup>+</sup> 279.0184 (100%), 281.0154 (33%); found: 279.0190, 281.0161.

#### benzofuran-2-yl(4-bromophenyl)methanone (13n)



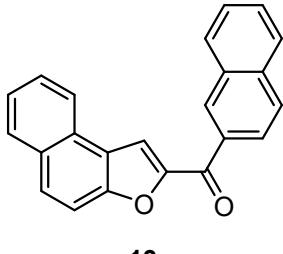
Compound **13n** (93% yield, white solid, Melting point: 135.6 – 137.3 °C): **<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.95 (d,  $J$  = 8.5 Hz, 2H), 7.74 (d,  $J$  = 7.5 Hz, 1H), 7.69 (d,  $J$  = 8.5 Hz, 2H), 7.64 (d,  $J$  = 8.5 Hz, 1H), 7.55 (s, 1H), 7.52 (t,  $J$  = 7.5 Hz, 1H), 7.35 (t,  $J$  = 7.5 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz,  $\text{CDCl}_3$ )  $\delta$  183.1, 156.0, 152.0, 135.8, 131.8, 131.0, 128.6, 128.1, 126.9, 124.1, 123.3, 116.5, 112.5. **IR:**  $\bar{\nu}$  = 3140, 1766, 1288, 1016, 794  $\text{cm}^{-1}$ ; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>15</sub>H<sub>9</sub>BrNaO<sub>2</sub><sup>+</sup> 322.9679 (100%), 324.9658 (98%); found: 322.9679, 324.9657.

#### benzofuran-2-yl(4-(trifluoromethyl)phenyl)methanone (13o)



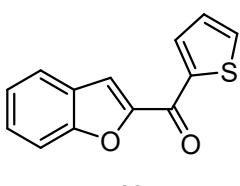
Compound **13o** (89% yield, white solid, Melting point: 149.5 – 158.0 °C): **<sup>1</sup>H NMR** (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.15 (d,  $J$  = 8.0 Hz, 2H), 7.80 (d,  $J$  = 8.0 Hz, 2H), 7.74 (d,  $J$  = 8.0 Hz, 1H), 7.64 (d,  $J$  = 8.4 Hz, 1H), 7.57 (s, 1H), 7.53 (t,  $J$  = 7.6 Hz, 1H) 7.35 (t,  $J$  = 7.6 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz,  $\text{CDCl}_3$ )  $\delta$  183.1, 156.1, 151.8, 140.1, 134.2 (q,  $J$  = 33.2 Hz), 129.7, 128.8, 126.8, 125.5 (q,  $J$  = 4.0 Hz), 123.6 (q,  $J$  = 271.0 Hz), 124.2, 123.5, 117.0, 112.6. **<sup>19</sup>F NMR** (376 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  -61.55. **IR:**  $\bar{\nu}$  = 3060, 1747, 1670, 1335, 1090, 791  $\text{cm}^{-1}$ ; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>16</sub>H<sub>9</sub>F<sub>3</sub>KO<sub>2</sub><sup>+</sup> 329.0187; found: 329.0182.

#### naphthalen-2-yl(naphtho[2,1-b]furan-2-yl)methanone (13p)



Compound **13p** (95% yield, yellow solid, Melting point: 180.2 – 181.8 °C): **<sup>1</sup>H NMR** (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (s, 1H), 8.19 (d,  $J$  = 8.0 Hz, 1H), 8.14 (d,  $J$  = 8.5, 1H), 8.08 (s, 1H), 8.06 – 7.92 (m, 5H), 7.78 (d,  $J$  = 9.0 Hz, 1H), 7.68 – 7.54 (m, 4H). **<sup>13</sup>C NMR** (125 MHz,  $\text{CDCl}_3$ )  $\delta$  183.7, 154.6, 152.1, 135.4, 134.7, 132.4, 131.0, 130.6, 130.1, 129.5, 129.1, 128.5, 128.5, 128.2, 127.9, 127.5, 126.9, 125.6, 125.3, 123.4, 122.9, 115.6, 112.9. **IR:**  $\bar{\nu}$  = 3146, 2063, 1635, 1399, 1161  $\text{cm}^{-1}$ ; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>23</sub>H<sub>14</sub>NaO<sub>2</sub><sup>+</sup> 345.0886; found: 345.0884.

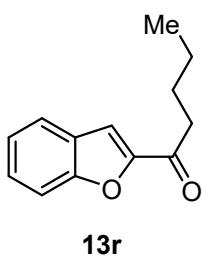
#### benzofuran-2-yl(thiophen-2-yl)methanone (13q)



Compound **13q** (88% yield, yellow solid, Melting point: 69.7 – 71.9 °C): **<sup>1</sup>H**

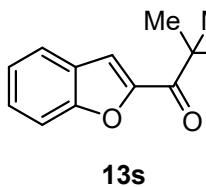
**NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.31 (d, *J* = 3.8 Hz, 1H), 7.77 – 7.69 (m, 3H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 4.0 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 174.9, 155.7, 152.5, 142.2, 134.5, 134.4, 128.3, 128.1, 126.9, 124.0, 123.2, 114.5, 112.3. **IR:**  $\bar{\nu}$  = 3140, 1755, 1326, 1180 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>13</sub>H<sub>8</sub>NaO<sub>2</sub>S<sup>+</sup> 251.0138; found: 251.0144.

#### 1-(benzofuran-2-yl)pentan-1-one (13r)



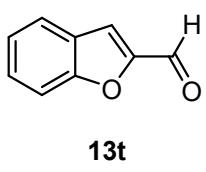
Compound 13r (98% yield, yellow solid, Melting point: 46.1 – 48.4 °C): **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 7.5 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 1H), 2.95 (t, *J* = 7.5 Hz, 2H), 1.76 (m, 2H), 1.44 (m, 2H), 0.97 (t, *J* = 7.0 Hz, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 191.6, 155.5, 152.5, 128.1, 127.0, 123.8, 123.2, 112.6, 112.4, 38.6, 26.3, 22.4, 13.8. **IR:**  $\bar{\nu}$  = 2668, 1702, 1304, 1051, 788, 617 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>13</sub>H<sub>14</sub>KO<sub>2</sub><sup>+</sup> 241.0626; found: 241.0625.

#### 1-(benzofuran-2-yl)-2,2-dimethylpropan-1-one (13s)



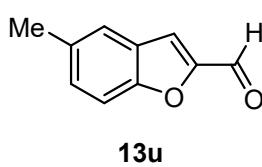
Compound 13s (>99% yield, yellow oil): **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.70 (d, *J* = 7.5 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.46 (t, *J* = 8.0, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 1.43 (s, 9H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 196.7, 155.0, 152.6, 127.7, 126.7, 123.7, 123.0, 113.6, 112.2, 43.5, 26.7. **IR:**  $\bar{\nu}$  = 3150, 1753, 1286, 1027, 783 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>13</sub>H<sub>14</sub>NaO<sub>2</sub><sup>+</sup> 225.0886; found: 225.0888.

#### benzofuran-2-carbaldehyde (13t)



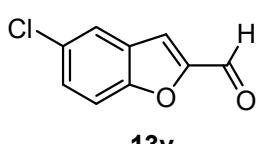
Compound 13t (97% yield, yellow oil): **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 9.88 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.58 (s, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 179.8, 156.2, 152.6, 129.2, 126.6, 124.2, 123.6, 117.9, 112.7. **IR:**  $\bar{\nu}$  = 3420, 1640, 1400, 1150 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + H]<sup>+</sup> calcd for C<sub>9</sub>H<sub>7</sub>O<sub>2</sub><sup>+</sup> 147.0441; found: 147.0444.

#### 5-methylbenzofuran-2-carbaldehyde (13u)



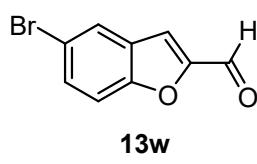
Compound 13u (90% yield, yellow oil): **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.83 (s, 1H), 7.49 (t, *J* = 9.2 Hz, 3H), 7.33 (d, *J* = 8.5 Hz, 1H), 2.46 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 179.7, 154.7, 152.7, 133.8, 130.8, 126.7, 123.0, 117.7, 112.1, 21.2. **IR:**  $\bar{\nu}$  = 3365, 1731, 1457, 1186 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>10</sub>H<sub>8</sub>NaO<sub>2</sub><sup>+</sup> 183.0417; found: 183.0418.

#### 5-chlorobenzofuran-2-carbaldehyde (13v)



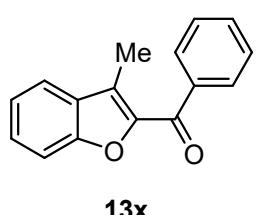
Compound 13v (97% yield, white solid, Melting point: 128.4 – 133.1 °C): **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.88 (s, 1H), 7.72 (s, 1H), 7.53 (d, *J* = 10.1 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 179.6, 154.4, 153.5, 129.8, 129.4, 127.8, 122.9, 116.6, 113.7. **IR:**  $\bar{\nu}$  = 3298, 1649, 1445, 1257, 970 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>9</sub>H<sub>5</sub>ClNaO<sub>2</sub><sup>+</sup> 202.9871 (100%), 204.9841 (32%); found: 202.9870, 204.9843.

#### 5-bromobenzofuran-2-carbaldehyde (13w)



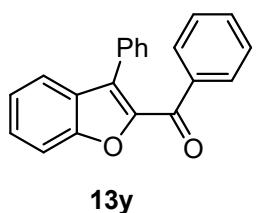
Compound **13w** (93% yield, yellow solid, Melting point: 129.9 – 132.8 °C): **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.86 (s, 1H), 7.87 (s, 1H), 7.58 – 7.57 (m, 1H), 7.49 – 7.46 (m, 2H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 179.6, 154.7, 153.3, 132.1, 128.4, 126.0, 117.2, 116.3, 114.2. **IR:**  $\bar{\nu}$  = 3266, 1643, 1287, 1186 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>9</sub>H<sub>5</sub>BrNaO<sub>2</sub><sup>+</sup> 246.9366 (100%), 248.9345 (98%); found: 246.9361, 248.9342.

#### (3-methylbenzofuran-2-yl)(phenyl)methanone (**13x**)



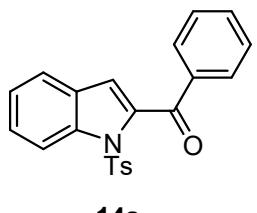
Compound **13x** (99% yield, yellow oil): **1H NMR** (600 MHz, CDCl<sub>3</sub>) δ 8.11 – 8.08 (d, *J* = 7.2 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.56 – 7.48 (m, 5H), 7.34 (t, *J* = 7.8 Hz, 1H), 2.65 (s, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 186.0, 154.2, 148.2, 137.8, 132.6, 129.7, 129.2, 128.3, 128.2, 126.9, 123.3, 121.4, 112.2, 10.0. **IR:**  $\bar{\nu}$  = 3198, 1748, 1672, 1296, 1258, 756 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>16</sub>H<sub>12</sub>NaO<sub>2</sub><sup>+</sup> 259.0730; found: 259.0733.

#### phenyl(3-phenylbenzofuran-2-yl)methanone (**13y**)



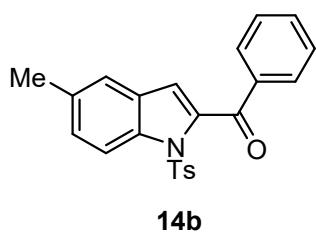
Compound **13y** (>99% yield, yellow oil): **1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 7.87 (d, *J* = 7.5 Hz, 2H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.64 (d, *J* = 8.5 Hz, 1H), 7.54 – 5.45 (m, 4H), 7.38 – 7.32 (m, 6H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 185.7, 154.6, 147.1, 137.2, 132.6, 130.9, 130.0, 129.8, 129.3, 128.3 (d, *J* = 6.3 Hz), 128.2, 128.1 (d, *J* = 6.2 Hz), 123.9, 122.4, 112.4. **IR:**  $\bar{\nu}$  = 3140, 1720, 1660, 1390, 1141 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>21</sub>H<sub>14</sub>NaO<sub>2</sub><sup>+</sup> 321.0886; found: 321.0887.

#### phenyl(1-tosyl-1*H*-indol-2-yl)methanone(**14a**)



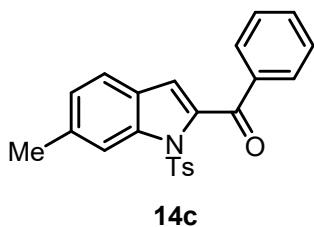
Compound **14a** (91% yield, yellow solid, Melting point: 170.2–172.6 °C): **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.15 – 8.12 (m, 1H), 7.99 – 7.93 (m, 4H), 7.61 (t, *J* = 7.2, 1H), 7.56 (d, *J* = 7.6, 1H), 7.51 – 7.43 (m, 3H), 7.31 – 7.25 (m, 3H), 6.92 (s, 1H), 2.36 (s, 3H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 187.7, 145.2, 138.0, 137.7, 137.6, 135.2, 133.6, 130.1, 129.7, 128.7, 128.6, 127.7, 127.0, 124.3, 122.6, 116.7, 115.2, 77.4, 77.1, 76.8, 21.7. **IR:**  $\bar{\nu}$  = 3138, 3180, 1269, 1044, 788 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + H]<sup>+</sup> calcd for C<sub>22</sub>H<sub>18</sub>NO<sub>3</sub>S<sup>+</sup> 376.1002; found: 376.1000.

#### (5-methyl-1-tosyl-1*H*-indol-2-yl)(phenyl)methanone (**14b**)



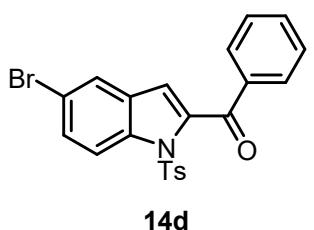
Compound **14b** (88% yield, yellow solid, Melting point: 140.9 – 141.2 °C): **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.91 (d, *J* = 8.4 Hz, 1H), 7.90 – 7.82 (m, 2H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.51 – 7.46 (m, 1H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.22 (s, 1H), 7.17 (d, *J* = 1.7 Hz, 1H), 7.15 – 7.11 (m, 3H), 6.75 (s, 1H), 2.30 (s, 3H), 2.23 (s, 3H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 187.5, 144.9, 137.9, 137.5, 135.9, 135.0, 133.9, 133.4, 129.9, 129.5, 128.8, 128.4, 128.4, 127.4, 122.2, 116.7, 114.7, 21.5, 21.1. **IR:**  $\bar{\nu}$  = 2970, 1807, 1262, 1036, 794 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + H]<sup>+</sup> calcd for C<sub>23</sub>H<sub>20</sub>NO<sub>3</sub>S<sup>+</sup> 390.1159; found: 390.1161.

**(6-methyl-1-tosyl-1*H*-indol-2-yl)(phenyl)methanone (14c)**



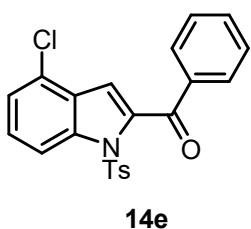
Compound **14c** (76% yield, yellow solid, Melting point: 182.3 – 183.5 °C): **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 7.87 (m, 5H), 7.51 (t, *J* = 7.6 Hz 1H), 7.41 – 7.32 (m, 3H), 7.20 – 7.15 (m, 2H), 7.03 (d, *J* = 8.0, 1H), 6.80 (s, 1H), 2.44 (s, 3H), 2.28 (s, 3H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 187.3, 144.9, 138.3, 137.6, 137.5, 137.4, 135.4, 133.3, 129.9, 129.5, 128.4, 127.4, 126.2, 125.8, 122.1, 117.2, 115.1, 22.2, 21.5. **IR:**  $\bar{\nu}$  = 3410, 1764, 1265, 1035, 805 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>23</sub>H<sub>19</sub>NKO<sub>3</sub>S<sup>+</sup> 428.0718; found: 428.0719.

**(4-bromo-1-tosyl-1*H*-indol-2-yl)(phenyl)methanone (14d)**



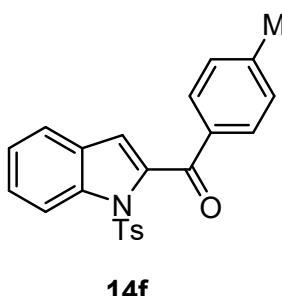
Compound **14d** (93% yield, yellow solid, Melting point: 153.0 – 155.4 °C): **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.01 (d, *J* = 8.8 Hz, 1H), 7.95 (m, *J* = 7.6 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 2.0 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.82 (s, 1H), 2.36 (s, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 187.3, 145.4, 138.7, 137.1, 136.0, 134.7, 133.7, 130.3, 129.9, 129.6 (d, *J* = 14.0 Hz), 128.5, 127.5, 124.9, 117.4, 116.4, 114.7, 21.6. **IR:**  $\bar{\nu}$  = 3174, 1636, 1398, 1156, 762 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>22</sub>H<sub>16</sub>BrNNaO<sub>3</sub>S<sup>+</sup> 475.9927 (100%), 477.9906 (94%); found: 475.9925, 477.9906.

**(5-chloro-1-tosyl-1*H*-indol-2-yl)(phenyl)methanone (14e)**



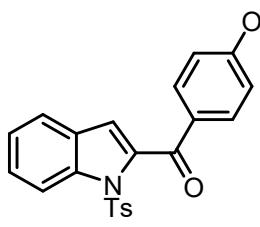
Compound **14e** (91% yield, yellow solid, Melting point: 128.5 – 131.1 °C): **1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.97 (dd, *J* = 11.0, 7.5 Hz, 4H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.29 – 7.27 (m, 3H), 7.01 (s, 1H), 2.36 (s, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 187.3, 145.4, 138.0, 137.9, 137.0, 134.9, 133.7, 130.0, 129.7, 128.5, 127.6, 127.5, 127.5, 127.4, 123.8, 113.5, 113.4, 21.6. **IR:**  $\bar{\nu}$  = 2870, 2184, 1708, 1275, 1080, 736 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>22</sub>H<sub>16</sub>ClNNaO<sub>3</sub>S<sup>+</sup> 432.0432 (100%), 433.0464 (25%); found: 432.0428, 433.0463.

**p-tolyl(1-tosyl-1*H*-indol-2-yl)methanone (14f)**



Compound **14f** (75% yield, yellow solid, Melting point: 165.5 – 167.6 °C): **1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 8.5 Hz, 1H), 7.90 (dd, *J* = 26.5, 7.5 Hz, 4H), 7.53 (d, *J* = 7.5, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.28 – 7.22 (m, 5H), 6.88 (s, 1H), 2.42 (s, 3H), 2.33 (s, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 187.3, 145.0, 144.4, 138.0, 137.4, 135.1, 135.0, 130.1, 129.5, 129.2, 128.6, 127.5, 126.6, 124.1, 122.4, 116.0, 115.0, 21.7, 21.5. **IR:**  $\bar{\nu}$  = 3485, 1605, 1400, 1172 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>23</sub>H<sub>19</sub>NKO<sub>3</sub>S<sup>+</sup> 428.0718; found: 428.0714.

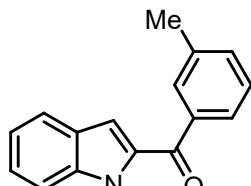
**(4-methoxyphenyl)(1-tosyl-1*H*-indol-2-yl)methanone (14g)**



Compound **14g** (75% yield, yellow solid, Melting point: 158.9 – 159.1 °C): **1H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 8.5 Hz, 1H), 7.95 (dd, *J* = 15.5, 8.5 Hz, 4H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.30 – 7.22 (m, 3H), 6.96 (d, *J* = 9.0 Hz, 2H), 6.87 (s, 1H), 3.87 (s, 3H), 2.34 (s, 3H). **13C NMR** (125 MHz, CDCl<sub>3</sub>) δ 186.4, 164.0, 145.0, 138.0, 137.3,

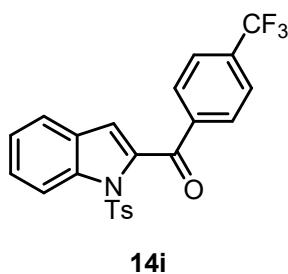
135.1, 132.4, 130.4, 129.5, 128.7, 127.5, 126.5, 124.1, 122.3, 115.4, 115.0, 113.8, 55.5, 21.6. **IR:**  $\bar{\nu}$  = 3421, 1602, 1399, 1294, 1155 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>23</sub>H<sub>19</sub>NKO<sub>4</sub>S<sup>+</sup> 444.0667; found: 444.0668.

**m-tolyl(1-tosyl-1H-indol-2-yl)methanone (14h)**



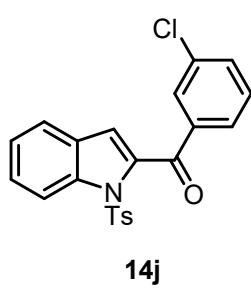
Compound **14h** (90% yield, brown solid, Melting point: 108.8 – 111.7 °C): **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J* = 8.5 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.80 (s, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.38 (m, 2H), 7.35 (t, *J* = 8.0 Hz, 1H), 7.29 – 7.20 (m, 3H), 6.89 (s, 1H), 2.39 (s, 3H), 2.33 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 187.7, 145.0, 138.2, 137.9, 137.5, 137.4, 135.1, 134.3, 130.2, 129.5, 128.5, 128.3, 127.5, 127.4, 126.8, 124.1, 122.4, 116.3, 115.0, 21.5, 21.2. **IR:**  $\bar{\nu}$  = 3440, 1271, 1043, 783 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>23</sub>H<sub>19</sub>NKO<sub>3</sub>S<sup>+</sup> 428.0718; found: 428.0716.

**(1-tosyl-1H-indol-2-yl)(4-(trifluoromethyl)phenyl)methanone (14i)**



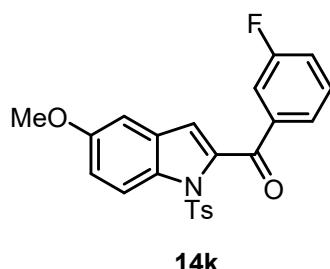
Compound **14i** (83% yield, yellow solid, Melting point: 173.9 – 174.7 °C): **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.13 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.98 (s, 1H), 2.34 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 186.4, 145.3, 140.4, 137.8, 137.4, 134.7, 134.4 (q, *J* = 32.7 Hz), 130.1, 129.6, 128.6, 127.4, 127.3, 125.5 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 272.8 Hz), 124.4, 122.7, 117.5, 115.2, 21.5. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -63.00. **IR:**  $\bar{\nu}$  = 3424, 1661, 1400, 1175 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>23</sub>H<sub>16</sub>F<sub>3</sub>NKO<sub>3</sub>S<sup>+</sup> 482.0435; found: 482.0434.

**(3-chlorophenyl)(1-tosyl-1H-indol-2-yl)methanone (14j)**



Compound **14j** (85% yield, brown solid, Melting point: 134.6 – 136.6 °C): **<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.13 (d, *J* = 8.5 Hz, 1H), 8.00 – 7.78 (m, 4H), 7.61 – 7.37 (m, 4H), 7.34 – 7.21 (m, 3H), 6.95 (s, 1H), 2.35 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 186.2, 145.2, 139.1, 137.7, 137.3, 134.9, 134.8, 133.3, 129.8, 129.6, 129.6, 128.5, 128.1, 127.5, 127.2, 124.3, 122.6, 117.1, 115.2, 21.6. **IR:**  $\bar{\nu}$  = 3397, 1615, 1398, 1156, 614 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>22</sub>H<sub>16</sub>ClNKO<sub>3</sub>S<sup>+</sup> 448.0171 (100%), 449.0204 (25%); found: 448.0177, 449.0210.

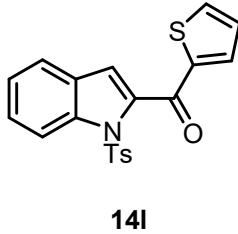
**(3-fluorophenyl)(5-methoxy-1-tosyl-1H-indol-2-yl)methanone (14k)**



Compound **14k** (81% yield, brown solid, Melting point: 151.0 – 152.5 °C): **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.01 (d, *J* = 9.2 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.43 (m, 1H), 7.27 (t, *J* = 8.0, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 1H), 6.96 (s, 1H), 6.89 (s, 1H), 3.79 (s, 3H), 2.32 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 186.2, 162.6 (d, *J* = 246.0 Hz), 157.0, 145.1, 139.6 (d, *J* = 6.5 Hz), 138.1, 134.5, 132.3, 130.1 (d, *J* = 7.7 Hz), 129.7 (d, *J* = 11.9 Hz), 129.6, 127.3, 125.8 (d, *J* = 2.9 Hz), 120.4 (d, *J* = 21.0 Hz), 117.3, 116.7, 116.4, 116.2, 104.1, 55.6, 21.5. **<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) δ -111.88. **IR:**  $\bar{\nu}$  = 3450, 1620, 1035, 787 cm<sup>-1</sup>; **HRMS**

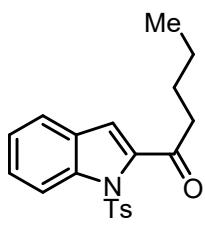
(ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>23</sub>H<sub>18</sub>FNNaO<sub>4</sub>S<sup>+</sup> 446.0833; found: 446.0824.

#### thiophen-2-yl(1-tosyl-1*H*-indol-2-yl)methanone (14l)



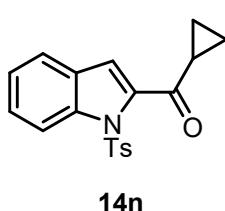
Compound **14l** (78% yield, yellow solid, Melting point: 202.5 – 204.5 °C): <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.14 – 8.11 (m, 1H), 8.00 – 7.98 (m, 2H), 7.78 – 7.74 (m, 2H), 7.58 – 7.56 (m, 1H), 7.47 – 7.43 (m, 1H), 7.31 – 7.26 (m, 3H), 7.18 – 7.15 (m, 1H), 7.05 (s, 1H), 2.35 (s, 3H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>) δ 179.1, 145.1, 144.1, 137.7, 137.2, 135.3, 135.1 (d, *J* = 8.8 Hz), 129.6, 128.3, 128.2, 127.7, 126.9, 124.1, 122.5, 116.3, 115.1, 21.6. **IR**:  $\bar{\nu}$  = 3194, 1637, 1397, 1149 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>20</sub>H<sub>15</sub>NKO<sub>3</sub>S<sub>2</sub><sup>+</sup> 420.0125; found: 420.0128.

#### 1-(1-tosyl-1*H*-indol-2-yl)pentan-1-one (14m)



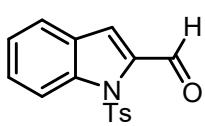
Compound **14m** (68% yield, yellow solid, Melting point: 49.4 – 51.6 °C): <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.84 (t, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.27 – 7.20 (m, 3H), 7.02 (s, 1H), 2.96 (m, *J* = 8.0 Hz, 2H), 2.32 (s, 3H), 1.77 – 1.68 (m, 2H), 1.46 – 1.36 (m, 2H), 0.93 (t, *J* = 7.2, 3H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>) δ 195.4, 144.8, 139.9, 138.4, 135.1, 129.4, 128.5, 127.4, 127.1, 124.2, 122.6, 115.9, 115.5, 42.3, 26.7, 22.3, 21.5, 13.8. **IR**:  $\bar{\nu}$  = 3209, 1752, 1234, 1044, 787, 760 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>20</sub>H<sub>21</sub>NKO<sub>3</sub>S<sup>+</sup> 394.0874; found: 394.0879.

#### cyclopropyl(1-tosyl-1*H*-indol-2-yl)methanone (14n)



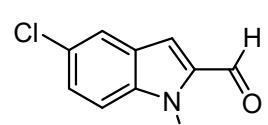
Compound **14n** (74% yield, white solid, Melting point: 112.7 – 114.7 °C): <sup>1</sup>**H NMR** (500 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.27 – 7.19 (m, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 7.13 (s, 1H), 2.62 – 2.57 (m, 1H), 2.32 (s, 3H), 1.32 – 1.29 (m, 2H), 1.12 – 1.08 (m, 2H). <sup>13</sup>**C NMR** (125 MHz, CDCl<sub>3</sub>) δ 194.7, 144.8, 140.5, 138.5, 135.0, 129.4, 128.6, 127.3, 127.2, 124.2, 122.6, 116.5, 115.7, 21.8, 21.5, 12.6. **IR**:  $\bar{\nu}$  = 3413, 1598, 1399, 1156 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>19</sub>H<sub>17</sub>NKO<sub>3</sub>S<sup>+</sup> 378.0561; found: 378.0567.

#### 1-tosyl-1*H*-indole-2-carbaldehyde (14o)



Compound **14o** (78% yield, yellow solid, Melting point: 121.0 – 122.1 °C): <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.44 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.56 (d, *J* = 2.8, 2H), 7.51 (d, *J* = 8.0, 1H), 7.42 (t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 2.8 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 2.21 (s, 3H). <sup>13</sup>**C NMR** (100 MHz, CDCl<sub>3</sub>) δ 183.2, 145.5, 138.3, 137.7, 134.5, 129.9, 128.7, 128.0, 126.5, 124.7, 123.5, 118.8, 115.2, 21.5. **IR**:  $\bar{\nu}$  = 3448, 1674, 1401, 1173 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>16</sub>H<sub>13</sub>NKO<sub>3</sub>S<sup>+</sup> 338.0248; found: 338.0241.

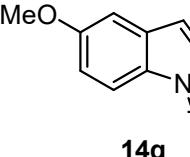
#### 5-chloro-1-tosyl-1*H*-indole-2-carbaldehyde (14p)



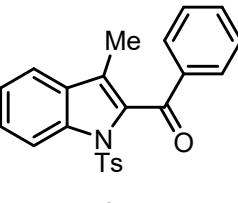
Compound **14p** (91% yield, white solid, Melting point: 129.2 – 130.6 °C): <sup>1</sup>**H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.53 (s, 1H), 8.18 (d, *J* = 9.0 Hz, 1H), 7.64 (d, *J* = 7.7 Hz, 2H), 7.60 (s, 1H), 7.47 (d, *J* = 9.0 Hz, 1H), 7.39 (s, 1H), 7.22 (d, *J*

= 7.8 Hz, 3H), 2.35 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 183.1, 145.9, 138.6, 136.6, 134.3, 130.6, 130.1, 129.2, 129.0, 126.6, 122.9, 117.5, 116.5, 21.6. **IR:**  $\bar{\nu}$  = 3412, 1771, 1429, 1165 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>16</sub>H<sub>12</sub>ClNNaO<sub>3</sub>S<sup>+</sup> 356.0119 (100%), 358.0090 (38%); found: 356.0120, 358.0091.

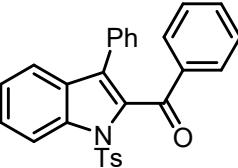
#### 5-methoxy-1-tosyl-1*H*-indole-2-carbaldehyde (**14q**)

  
**14q** Compound **14q** (83% yield, yellow oil): **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.52 (s, 1H), 8.13 (d, *J* = 9.2 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.40 (s, 1H), 7.19 – 7.13 (m, 3H), 6.99 (s, 1H), 3.83 (s, 3H), 2.33 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 183.4, 157.2, 145.5, 138.2, 134.4, 133.2, 129.9, 129.2, 126.5, 119.1, 118.7, 116.4, 104.1, 77.3, 77.0, 76.7, 55.6, 21.6. **IR:**  $\bar{\nu}$  = 3445, 1697, 1386, 1153 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>17</sub>H<sub>15</sub>KNO<sub>4</sub>S<sup>+</sup> 368.0353; found: 368.0358.

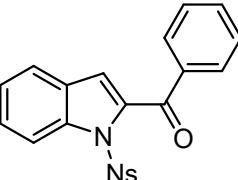
#### (3-methyl-1-tosyl-1*H*-indol-2-yl)(phenyl)methanone (**14r**)

  
**14r** Compound **14r** (71% yield, brown oil): **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.50 – 7.38 (m, 4H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.28 (s, 3H), 2.16 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 189.5, 144.9, 138.4, 136.4, 133.7, 133.6, 133.3, 131.2, 129.5, 128.5, 127.3, 126.6, 124.5, 124.2, 120.3, 115.3, 21.5, 9.3. **IR:**  $\bar{\nu}$  = 3160, 1650, 1036, 1170, 764 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>23</sub>H<sub>19</sub>NNaO<sub>3</sub>S<sup>+</sup> 412.0978; found: 412.0971.

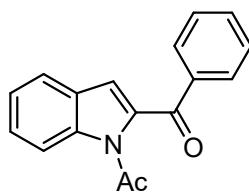
#### phenyl(3-phenyl-1-tosyl-1*H*-indol-2-yl)methanone (**14s**)

  
**14s** Compound **14s** (75% yield, yellow solid, Melting point: 196.7 – 198.5 °C): **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.26 – 8.22 (m, 1H), 7.96 – 7.89 (m, 4H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.53 (td, *J* = 7.6, 6.0 Hz, 2H), 7.44 (dd, *J* = 9.3, 7.5 Hz, 4H), 7.41 – 7.31 (m, 4H), 7.29 (d, *J* = 9.4 Hz, 2H), 2.38 (s, 3H). **<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) δ 189.6, 145.2, 137.9, 135.9, 134.3, 133.4, 132.7, 130.9, 129.7, 129.6, 129.6 (2C), 128.4, 128.4, 128.0, 127.5, 126.8, 126.4, 124.4, 121.2, 114.9, 21.6. **DEPT** (135°)(100 MHz, CDCl<sub>3</sub>) δ 133.5, 129.8, 129.7, 128.6, 128.6, 128.2, 127.6, 126.6, 124.5, 121.3, 115.0, 21.7. **IR:**  $\bar{\nu}$  = 3061, 1646, 1455, 1121, 978, 756, 696 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>28</sub>H<sub>21</sub>NKO<sub>3</sub>S<sup>+</sup> 490.0874; found: 490.0882.

#### (1-((4-nitrophenyl)sulfonyl)-1*H*-indol-2-yl)(phenyl)methanone (**14t**)

  
**14t** Compound **14t** (97% yield, white solid, Melting point: 190.2 – 193.6 °C): **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.32 (q, *J* = 8.9 Hz, 4H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.97 (d, *J* = 7.4 Hz, 2H), 7.67 – 7.57 (m, 3H), 7.55 – 7.47 (m, 3H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.01 (s, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) δ 186.9, 150.5, 144.0, 137.9, 137.6, 136.9, 133.8, 130.0, 128.8, 128.6, 128.3, 127.7, 124.7, 124.1, 123.0, 118.4, 114.8. **IR:**  $\bar{\nu}$  = 3451, 1646, 1372, 1142 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>21</sub>H<sub>14</sub>KN<sub>2</sub>O<sub>5</sub>S<sup>+</sup> 445.0255; found: 445.0254.

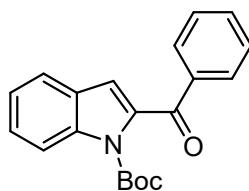
#### 1-(2-benzoyl-1*H*-indol-1-yl)ethan-1-one (**14u**)



**14u**

Compound **14u** (56% yield, white solid, Melting point: 117 – 129 °C): **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.24 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 7.3 Hz, 2H), 7.69 – 7.62 (m, 2H), 7.57 – 7.48 (m, 4H), 7.31 (t, *J* = 7.5 Hz, 1H), 7.07 (s, 1H), 2.56 (s, 3H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 187.1, 170.7, 138.6, 137.2, 137.0, 133.5, 129.7, 128.7, 128.3, 127.3, 124.0, 122.6, 119.9, 115.6, 27.3. **IR:**  $\bar{\nu}$  = 3274, 3069, 1703, 1529, 1276 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>14</sub>NO<sub>2</sub><sup>+</sup> 264.1019; found: 264.1027.

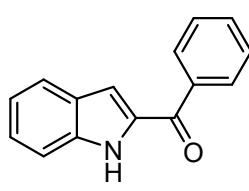
#### **tert-butyl 2-benzoyl-1*H*-indole-1-carboxylate (14v)**



**14v**

Compound **14v** (43% yield, 43% of **14v** and 44% of **14v'** were isolated, yellow solid, Melting point: 123.6 – 129.4 °C): **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 8.22 (d, *J* = 8.4 Hz, 1H), 7.92 (d, *J* = 7.7 Hz, 2H), 7.65 – 7.58 (m, 2H), 7.50 – 7.44 (m, 3H), 7.31 (t, *J* = 7.5 Hz, 1H), 6.94 (s, 1H), 1.36 (s, 9H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 187.7, 149.1, 137.4, 137.3, 137.0, 133.2, 129.5, 128.5, 127.9, 126.6, 123.5, 122.1, 115.1, 114.2, 85.0, 27.5. **IR:**  $\bar{\nu}$  = 3451, 2071, 1620, 1363 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>20</sub>H<sub>19</sub>KNO<sub>3</sub><sup>+</sup> 360.0997; found: 360.1000.

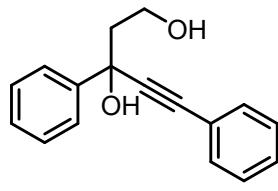
#### **(1*H*-indol-2-yl)(phenyl)methanone (14v')**



**14v'**

Compound **14v'** (44% yield, yellow solid, Melting point: 149.0 – 151.2 °C): **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 10.02 (s, 1H), 8.01 (d, *J* = 7.7 Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 8.9 Hz, 3H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.16 – 7.13 (m, 2H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 187.4, 138.0, 137.8, 134.3, 132.3, 129.2, 128.4, 127.6, 126.4, 123.1, 120.9, 113.0, 112.4. **IR:**  $\bar{\nu}$  = 3444, 3064, 1630, 1524, 1340, 1125 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + K]<sup>+</sup> calcd for C<sub>15</sub>H<sub>11</sub>KNO<sup>+</sup> 260.0473; found: 260.0470.

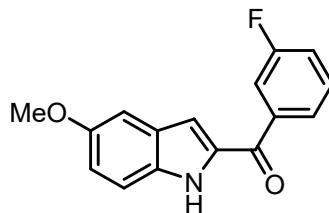
#### **3,5-diphenylpent-4-yne-1,3-diol (19c)**



**19c**

Compound **19c** (45% yield, white solid, Melting point: 138.6 – 141.3 °C): **1H NMR** (500 MHz, DMSO-*d*<sub>6</sub>) δ 7.62 (d, *J* = 7.5 Hz, 2H), 7.47 (dd, *J* = 7.5, 4.0 Hz, 2H), 7.43 – 7.35 (m, 5H), 7.29 (t, *J* = 7.0 Hz, 1H), 6.20 (s, 1H), 4.50 (t, *J* = 5.0 Hz, 1H), 3.68 – 3.68 (m, 1H), 3.57 – 3.51 (m, 1H), 2.17 – 2.03 (m, 2H). **13C NMR** (125 MHz, DMSO-*d*<sub>6</sub>) δ 145.5, 131.3, 128.7, 128.6, 127.9, 127.1, 125.1, 122.3, 93.0, 84.1, 70.5, 57.8, 47.8. **IR:**  $\bar{\nu}$  = 3172, 2910, 1646, 1044, 1160 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>17</sub>H<sub>16</sub>NaO<sub>2</sub><sup>+</sup> 275.1043; found: 275.1045.

#### **(3-fluorophenyl)(5-methoxy-1*H*-indol-2-yl)methanone (3)**



**3**

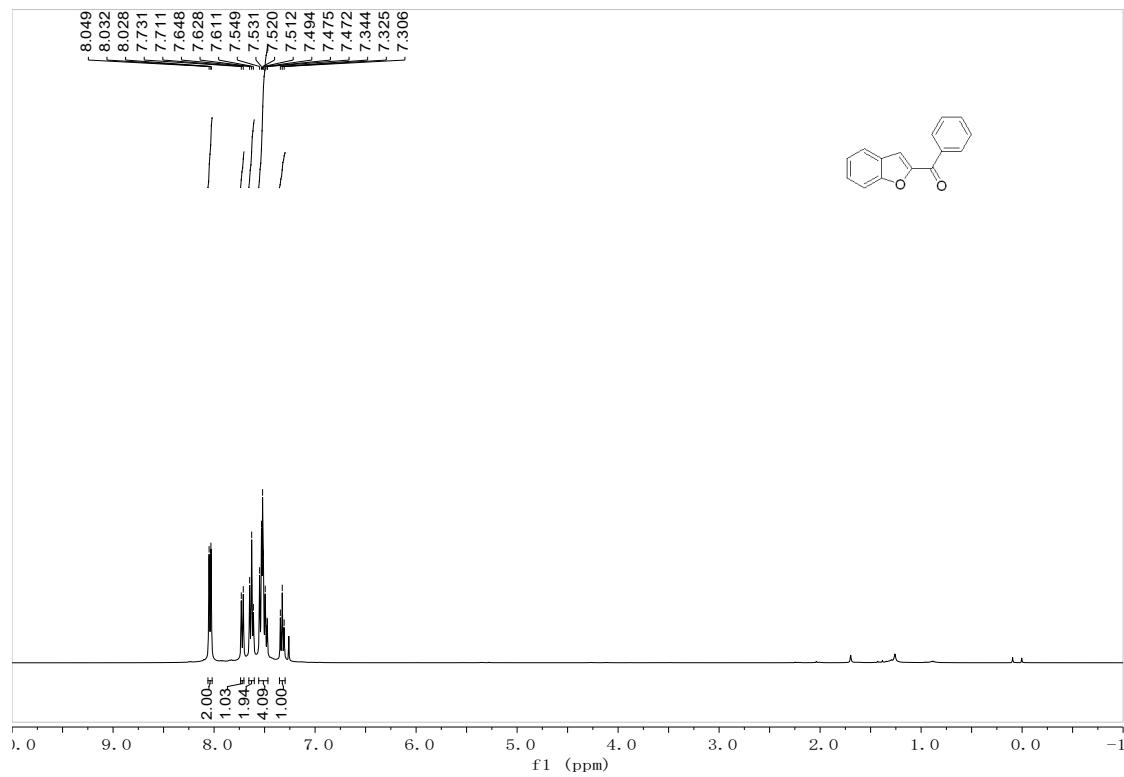
Compound **3** (91% yield, brown oil): **1H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.72 (s, 1H), 7.78 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.69 – 7.66 (m, 1H), 7.50 (td, *J* = 8.0, 5.6 Hz, 1H), 7.41 – 7.37 (m, 1H), 7.31 (td, *J* = 8.4, 2.8 Hz, 1H), 7.10 – 7.05 (m, 3H), 3.84 (s, 3H). **13C NMR** (100 MHz, CDCl<sub>3</sub>) δ 185.5, 162.5 (d, *J* = 246.0 Hz), 154.9, 140.0 (d, *J* = 6.7 Hz), 134.3, 133.4, 130.1 (d, *J* = 7.8 Hz), 127.9, 125.0 (d, *J* = 2.7 Hz), 119.2 (d, *J* = 21.0 Hz), 118.8, 116.1 (d, *J* = 20.0 Hz), 113.3, 112.7, 102.6, 55.6. **19F NMR** (376 MHz, CDCl<sub>3</sub>) δ -111.82 (q, *J* = 8.5 Hz). **IR:**  $\bar{\nu}$  = 3319, 1630, 1519, 1234, 752 cm<sup>-1</sup>; **HRMS** (ESI) m/z: [M + Na]<sup>+</sup> calcd for C<sub>16</sub>H<sub>12</sub>FNNaO<sub>2</sub><sup>+</sup> 292.0745; found: 292.0746.

## References

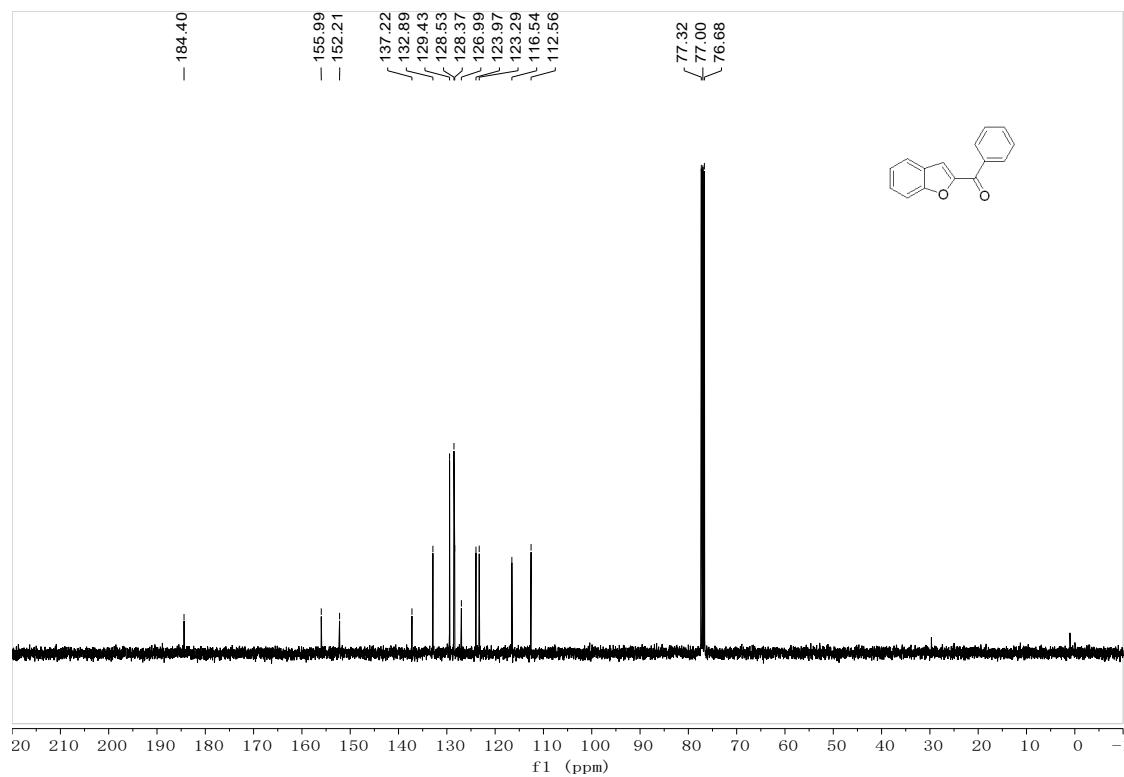
- [1] (a) Li, Y.; Xue, J.; Li, X.; Chen, R. *Synlett* **2012**, *23*, 1043-1046. (b) Ranjith Kumar, G.; Kiran Kumar, Y.; Kant, R.; Sridhar Reddy, M. *Org. Biomol. Chem.* **2016**, *14*, 4077-4088. (c) Saha, S.; Schneider, C. *Org. Lett.* **2015**, *17*, 648-651. (d) Yoshida, M.; Fujino, Y.; Doi, T. *Org. Lett.* **2011**, *13*, 4526-4529. (e) Zhang, M.; Yang, J.; Xu, Q.; Dong, C.; Han, L.-B.; Shen, R. *Adv. Synth. Catal.* **2018**, *360*, 334-345.
- [2] (a) Susanti, D.; Koh, F.; Kusuma, J. A.; Kothandaraman, P.; Chan, P. W. *J. Org. Chem.* **2012**, *77*, 7166-7175. (b) Ueda, J. I.; Enomoto, Y.; Seki, M.; Konishi, T.; Ogasawara, M.; Yoshida, K. *J. Org. Chem.* **2020**, *85*, 6420-6428. (c) Wang, A.; Hu, X.; Xie, X.; Liu, Y. *Adv. Synth. Catal.* **2021**, *363*, 3769-3774.
- [3] Yang, L.; Zhou, S.; Zhao, J. Q.; You, Y.; Wang, Z. H.; Zhou, M. Q.; Yuan, W. C. *Org. Biomol. Chem.* **2021**, *19*, 3678-3686.
- [4] Sangeetha, S.; Sekar, G. *Org. Lett.* **2017**, *19*, 1670-1673.
- [5] Geffers, F. J.; Kurth, F. R.; Jones, P. G.; Werz, D. B. *Chemistry* **2021**, *27*, 14846-14850.
- [6] Allart, E. A.; Christie, S. D.; Pritchard, G. J.; Elsegood, M. R. *Chem. Commun.* **2009**, 7339-7341.

### Copies of NMR spectra

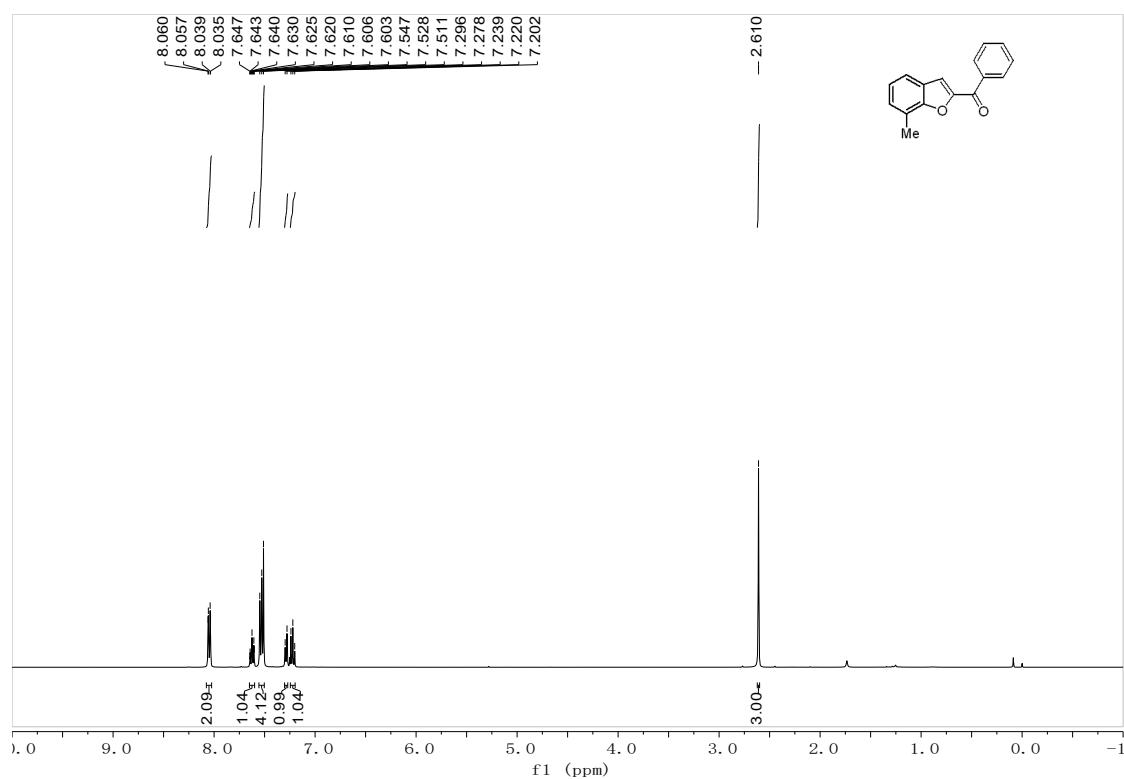
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectroscopy of **13a**



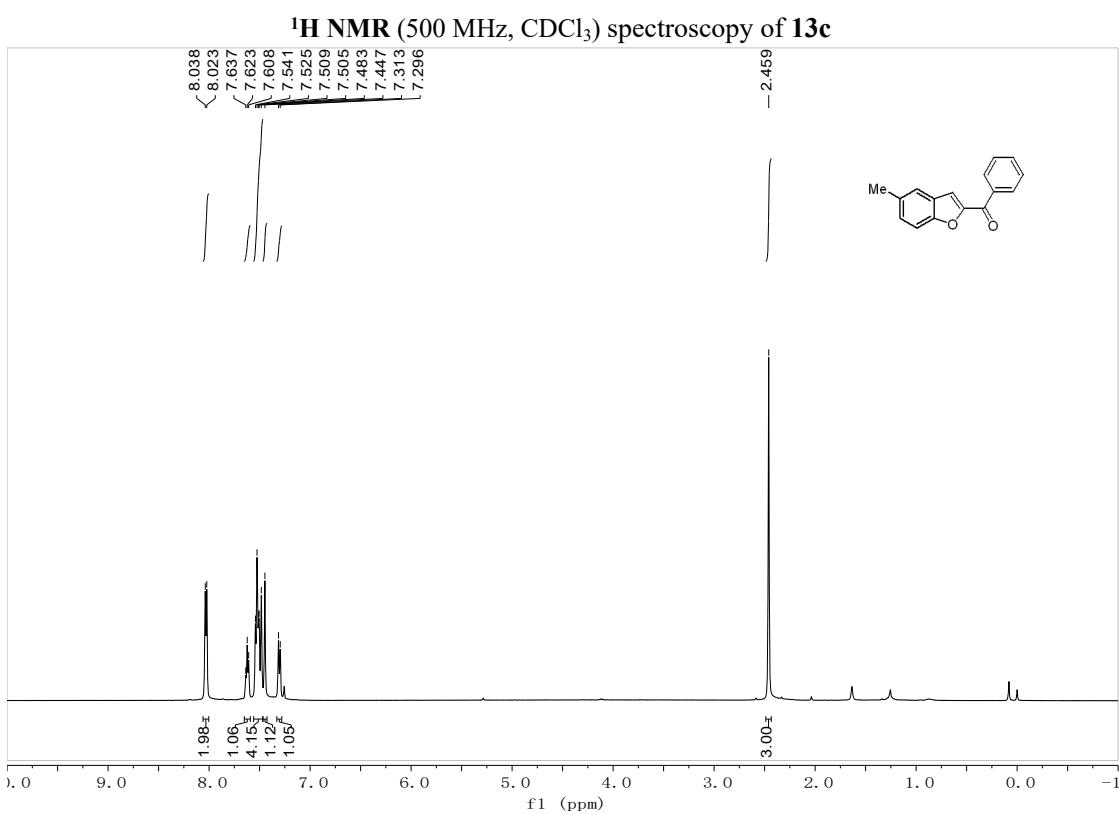
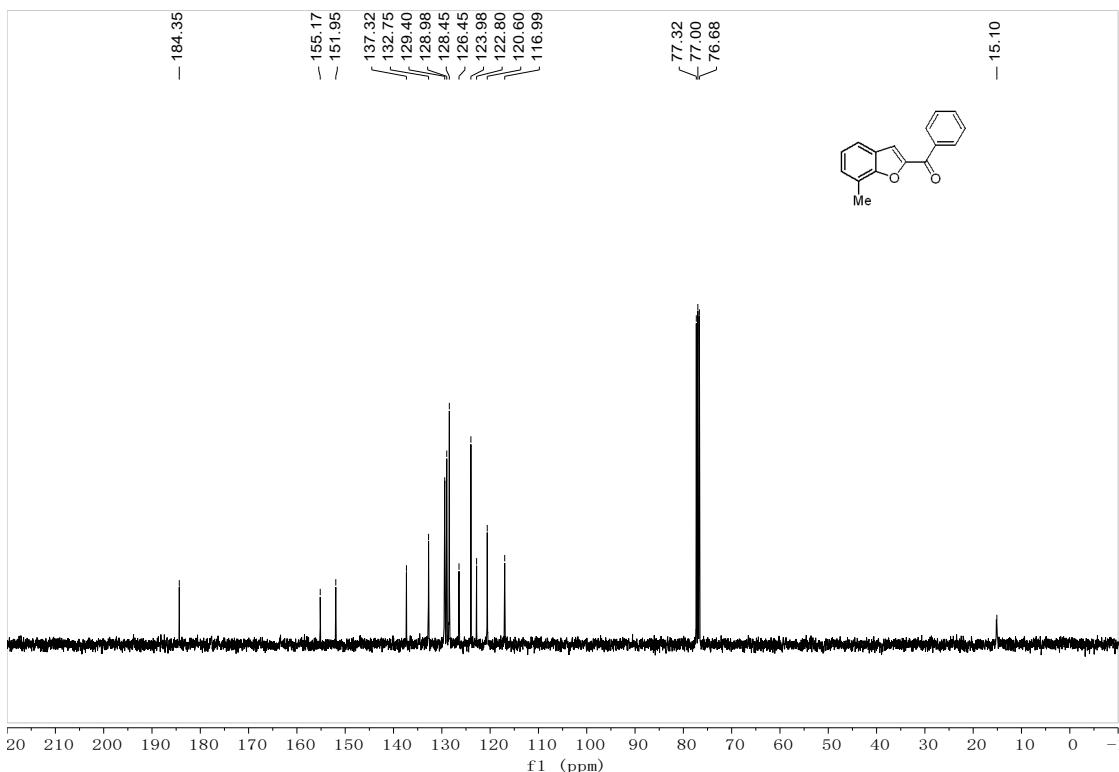
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectroscopy of **13a**



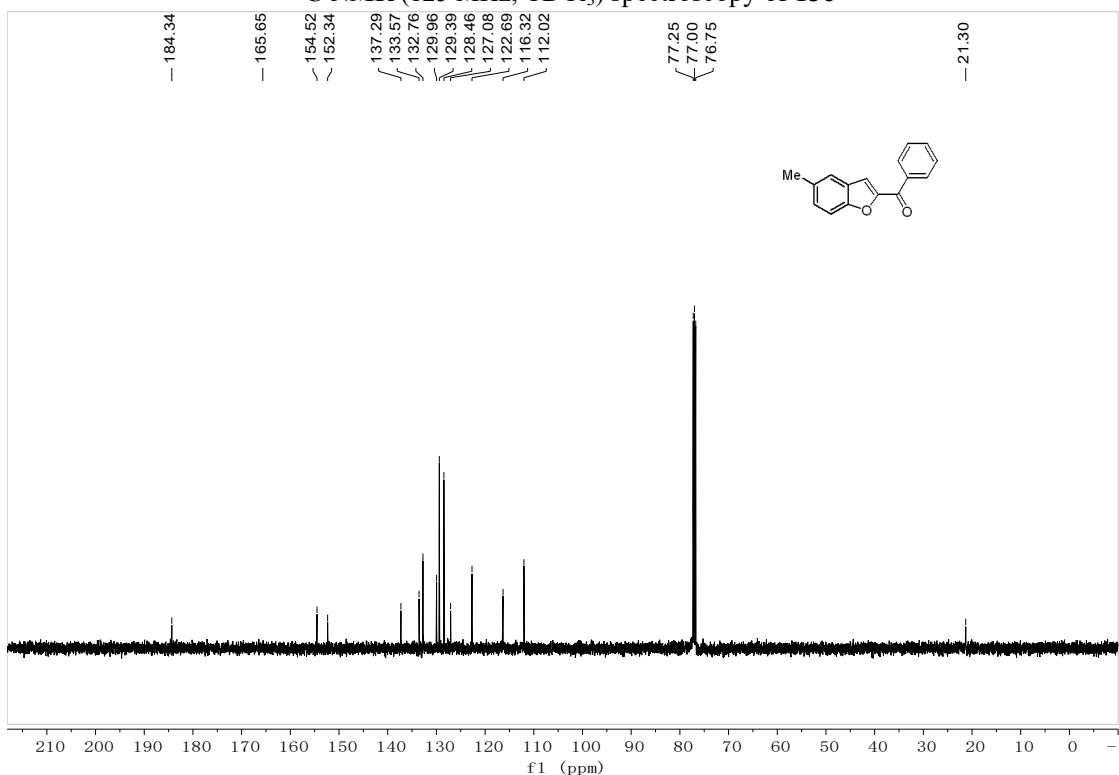
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) spectroscopy of **13b**



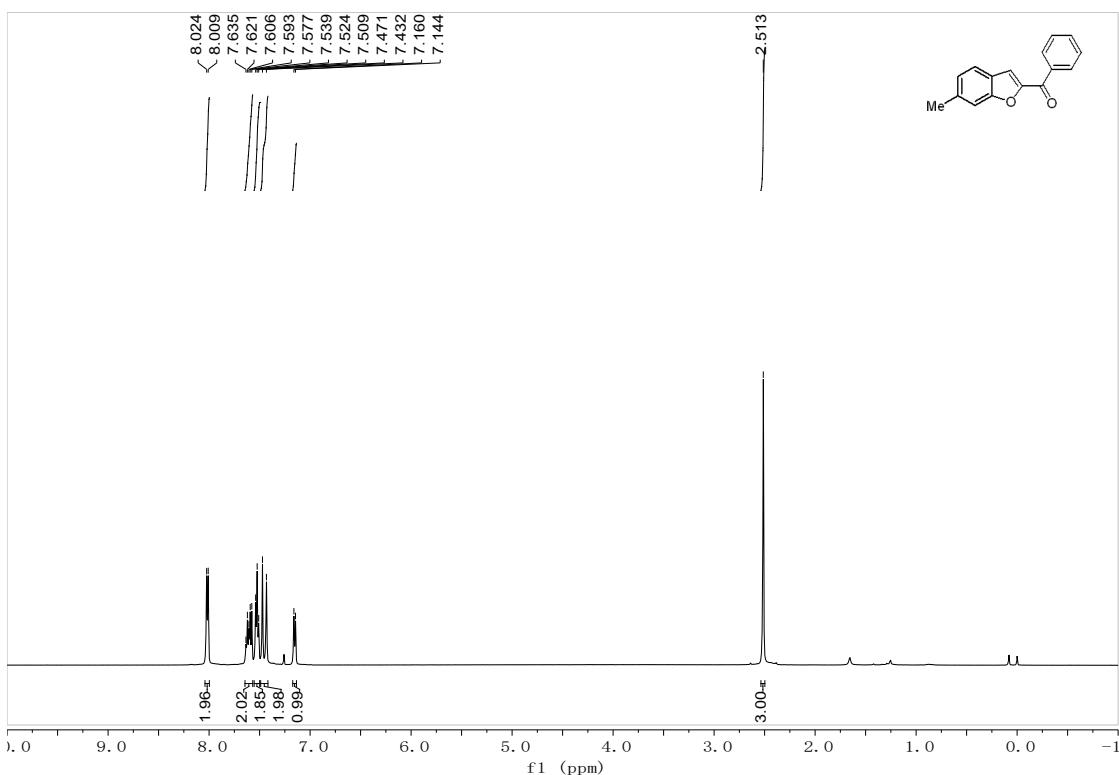
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) spectroscopy of **13b**



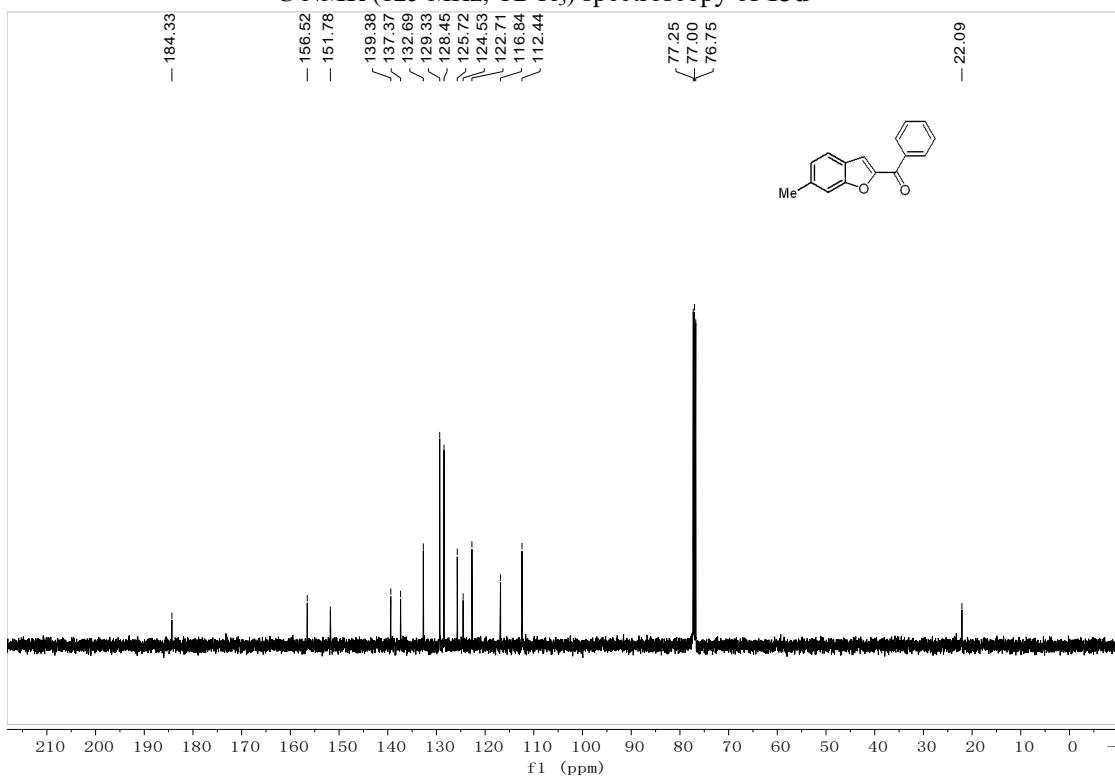
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectroscopy of 13c



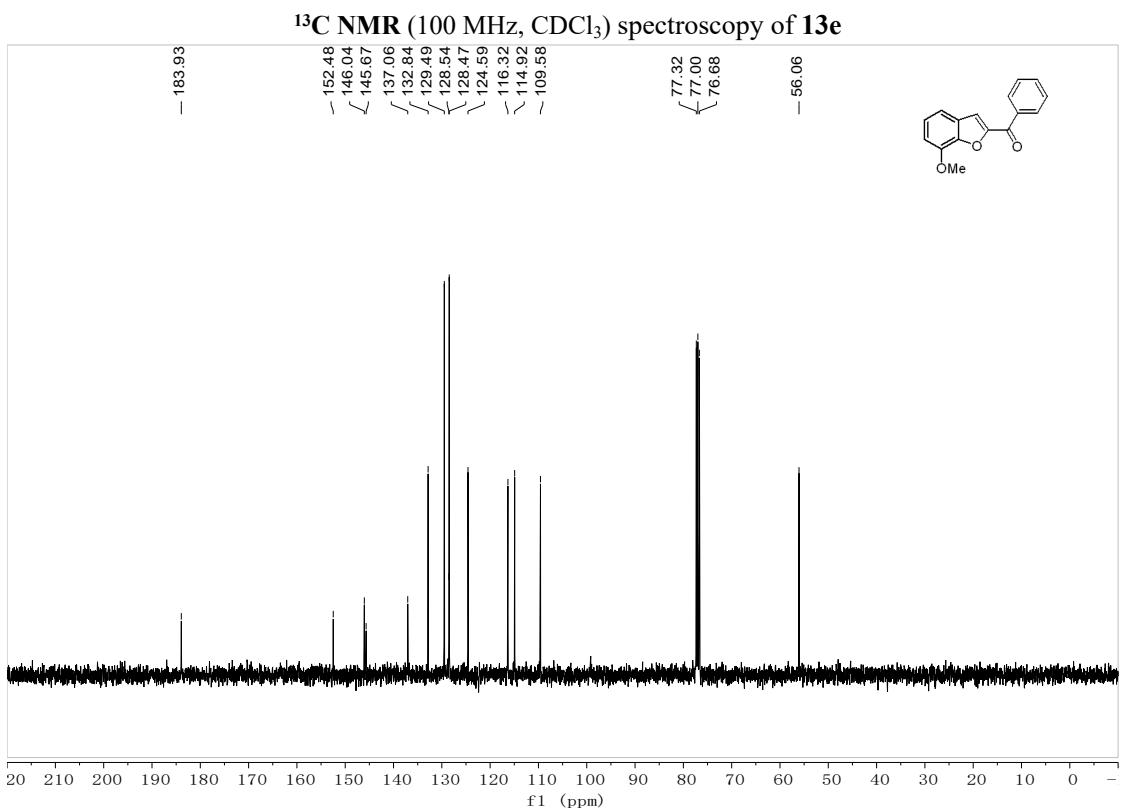
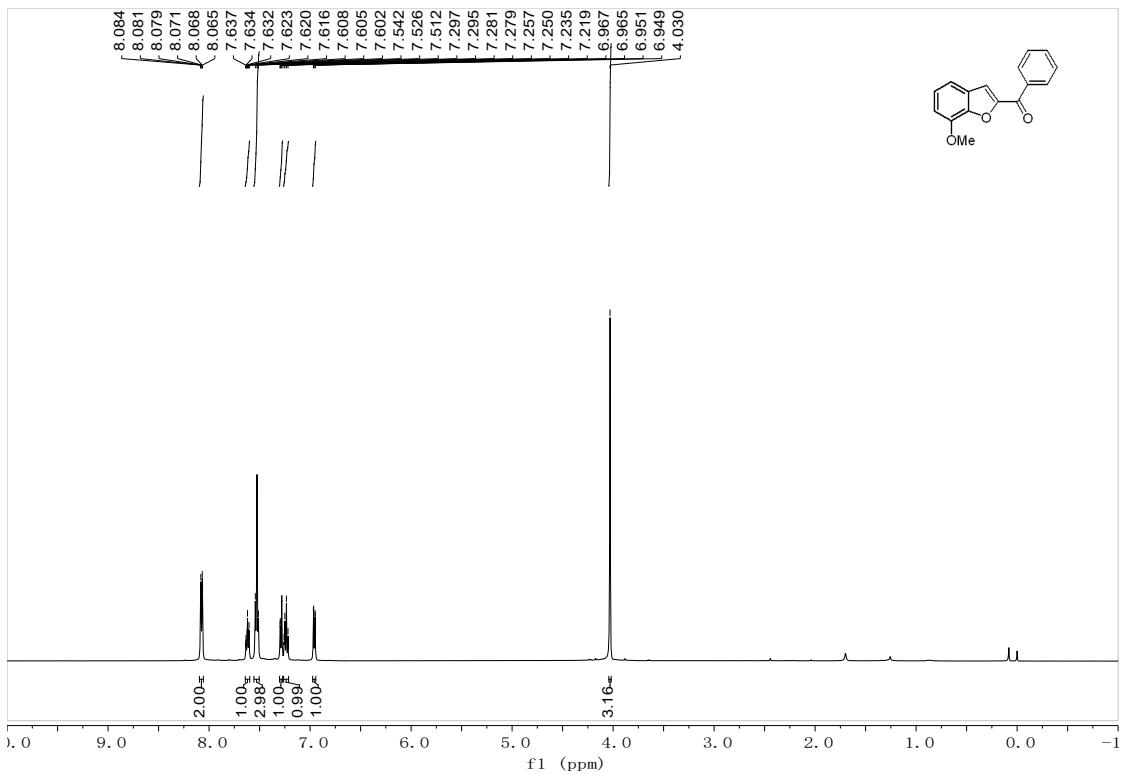
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectroscopy of 13d



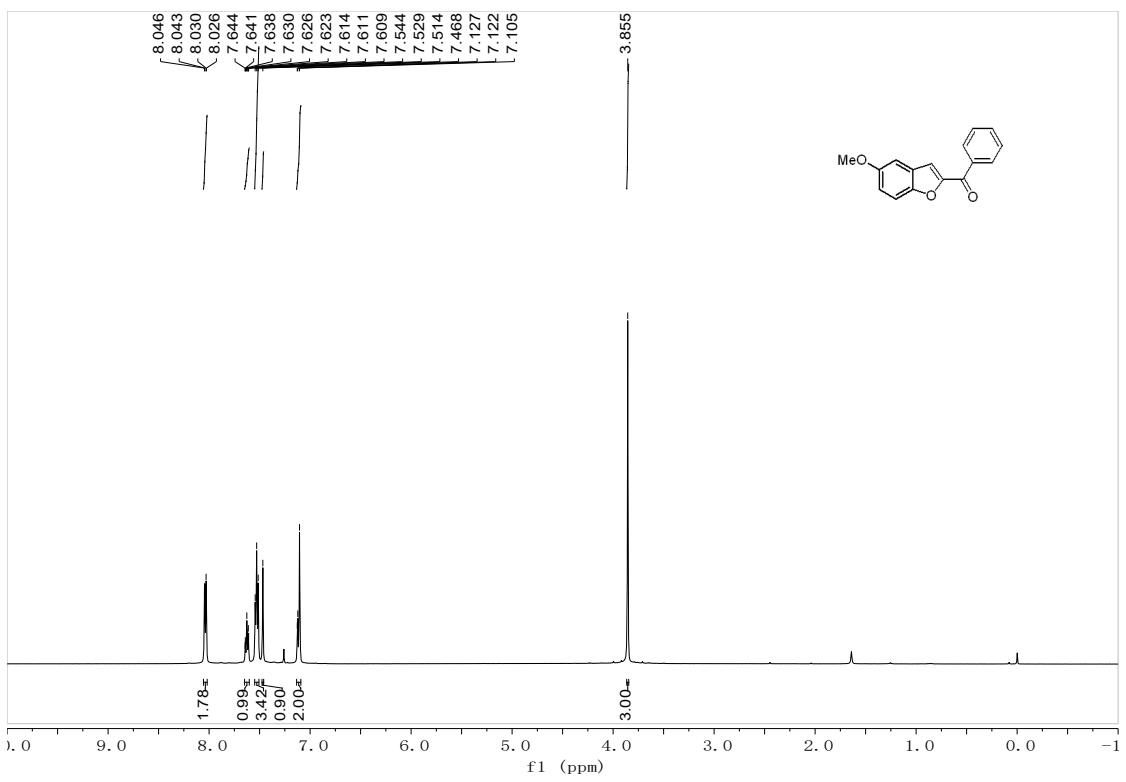
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectroscopy of **13d**



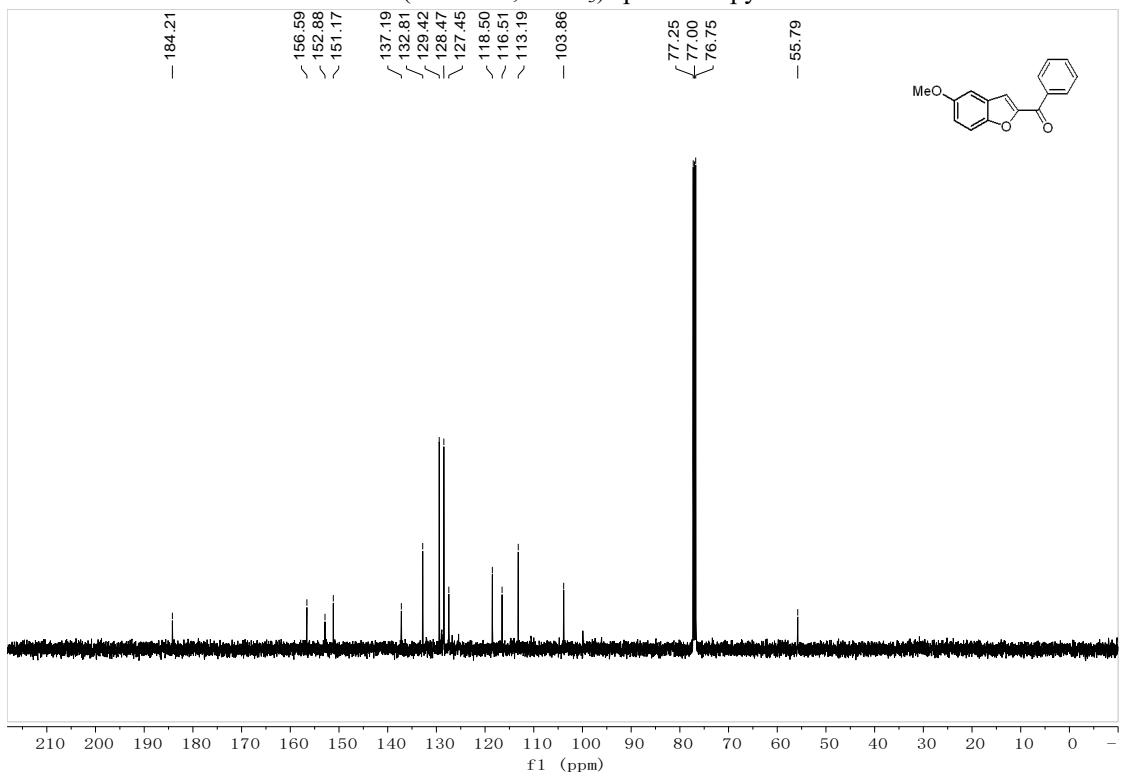
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectroscopy of **13e**



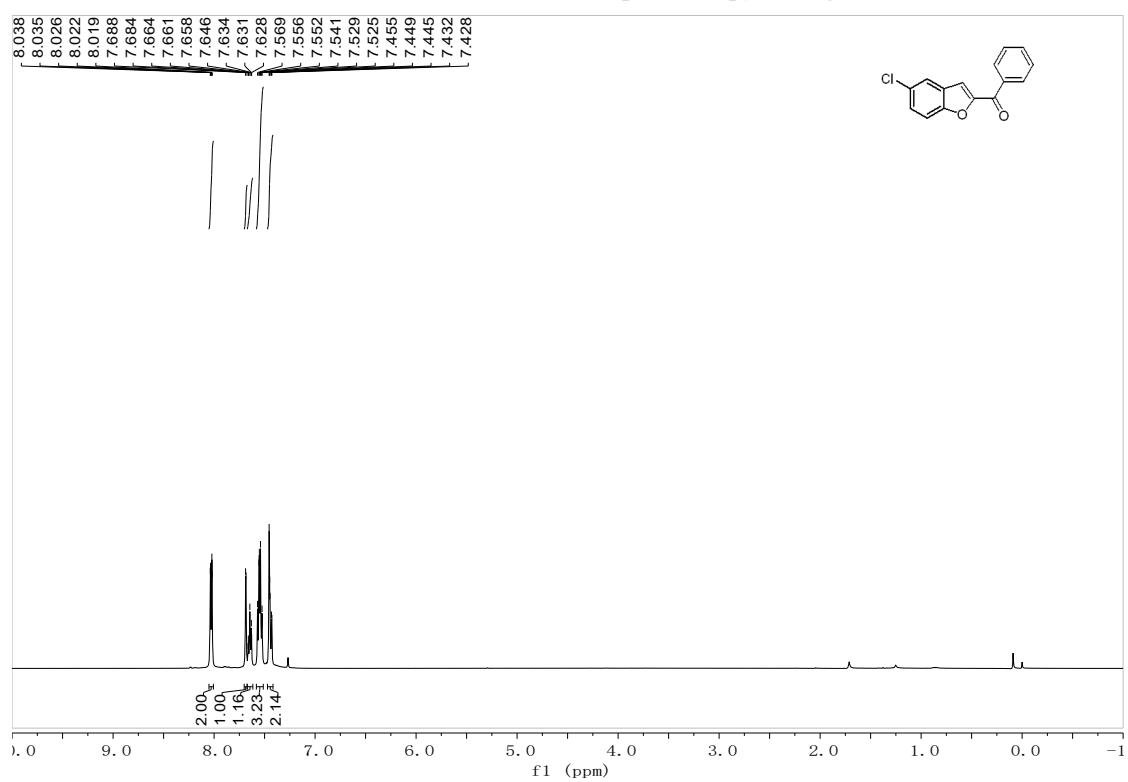
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectroscopy of **13f**



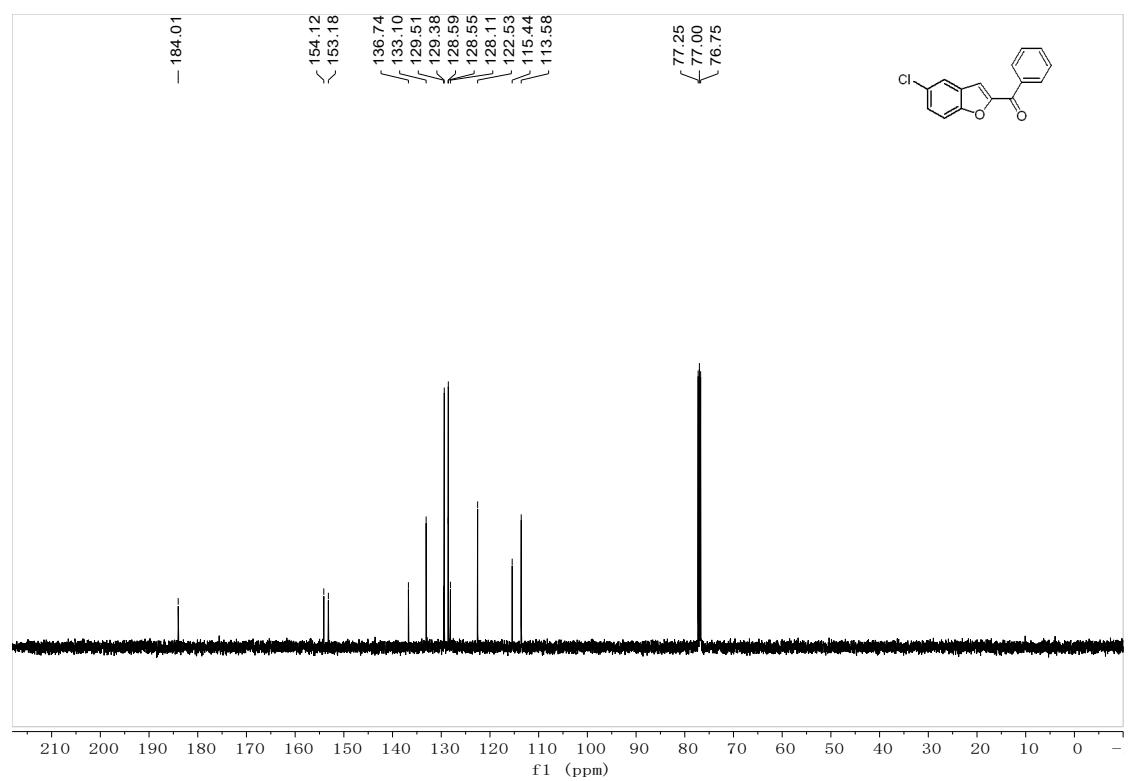
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) spectroscopy of **13f**



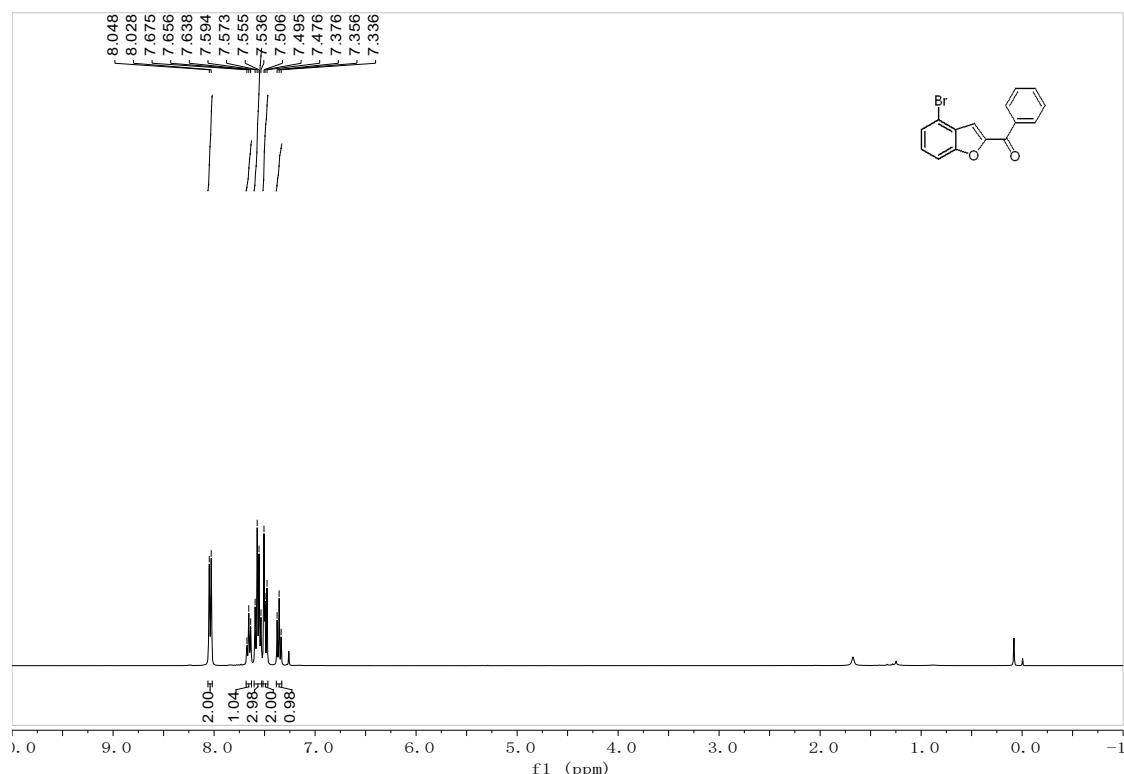
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectroscopy of 13g**



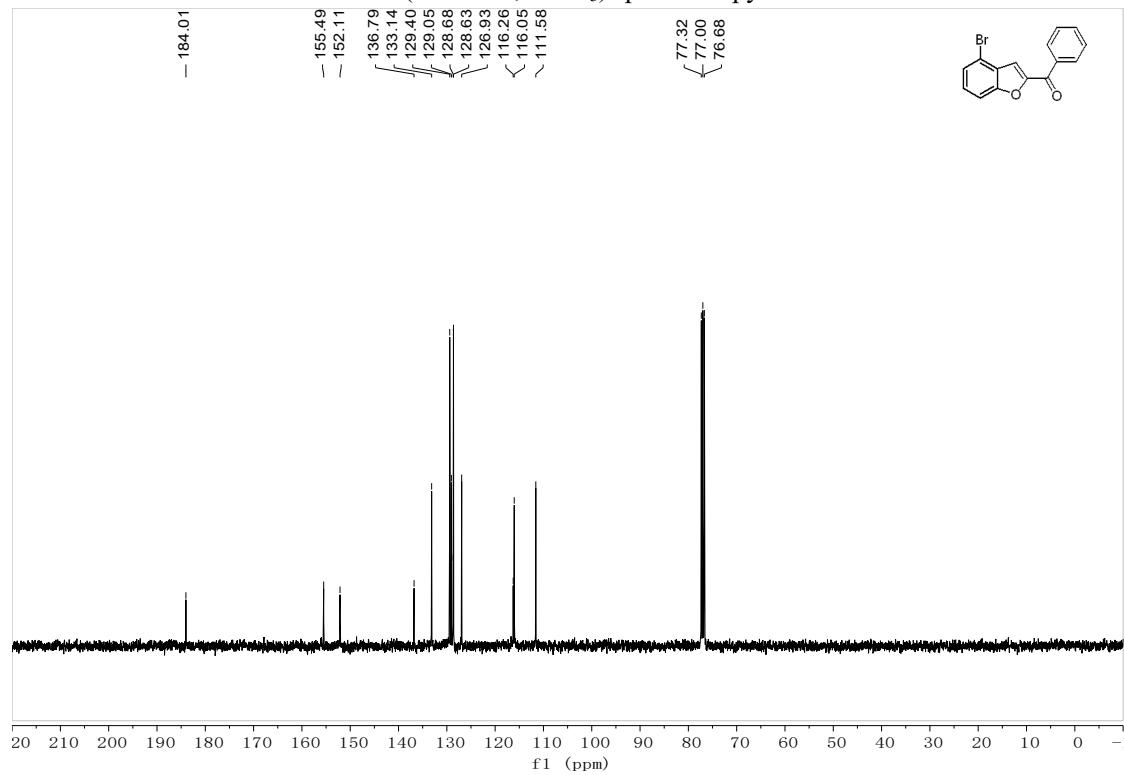
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectroscopy of 13g**



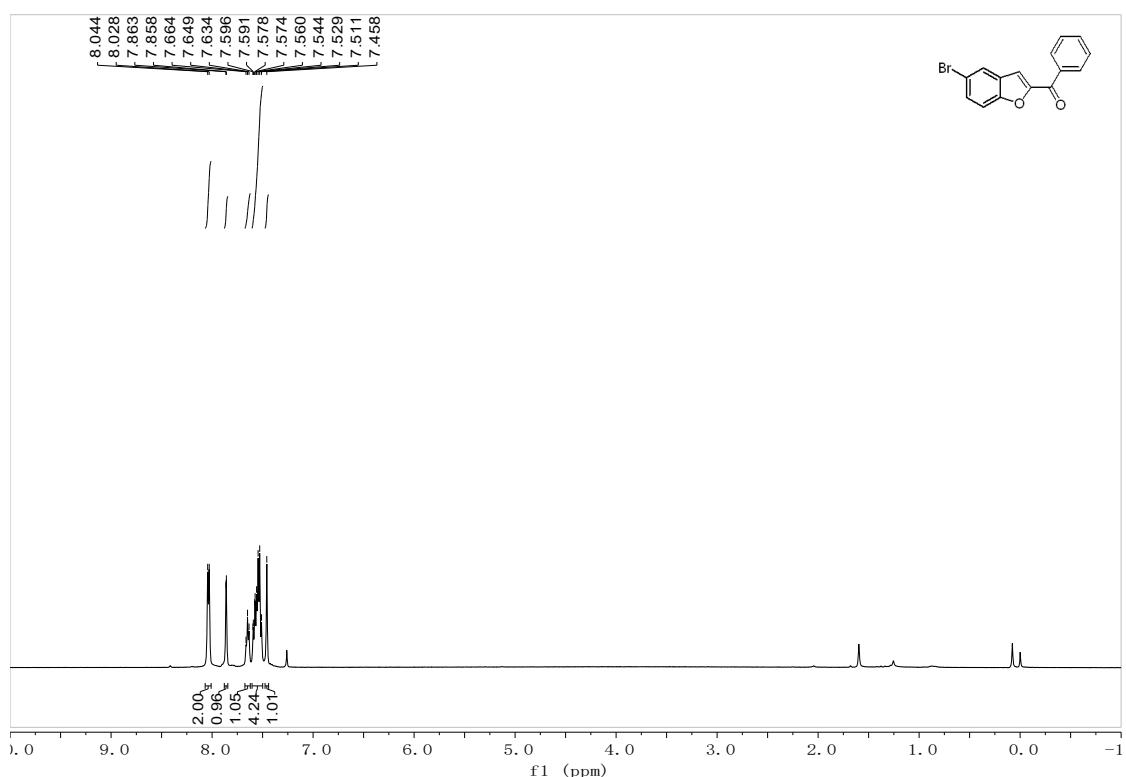
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectroscopy of 13h**



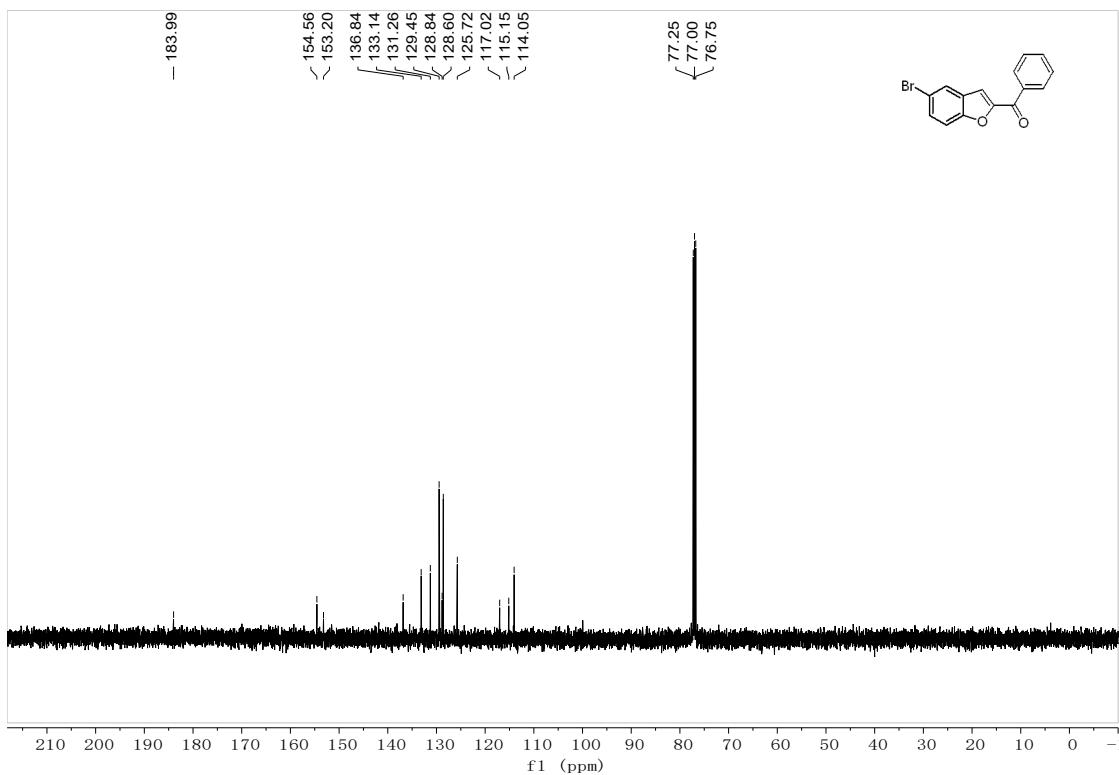
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectroscopy of 13h**



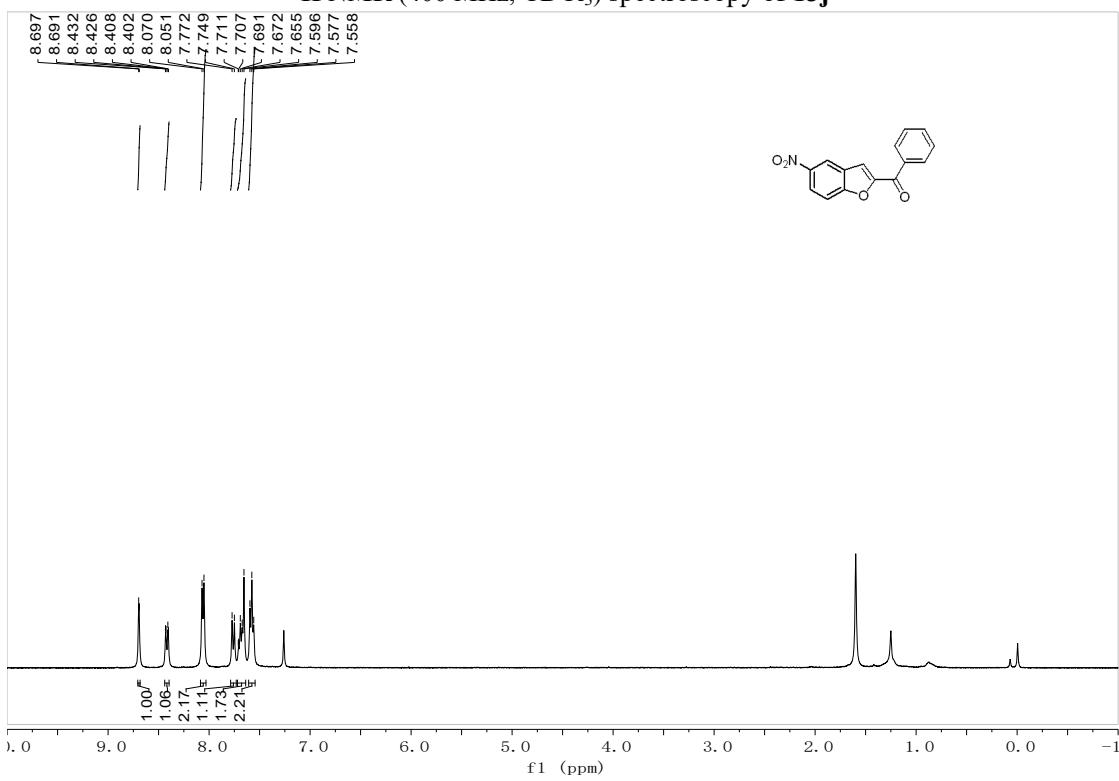
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectroscopy of **13i**



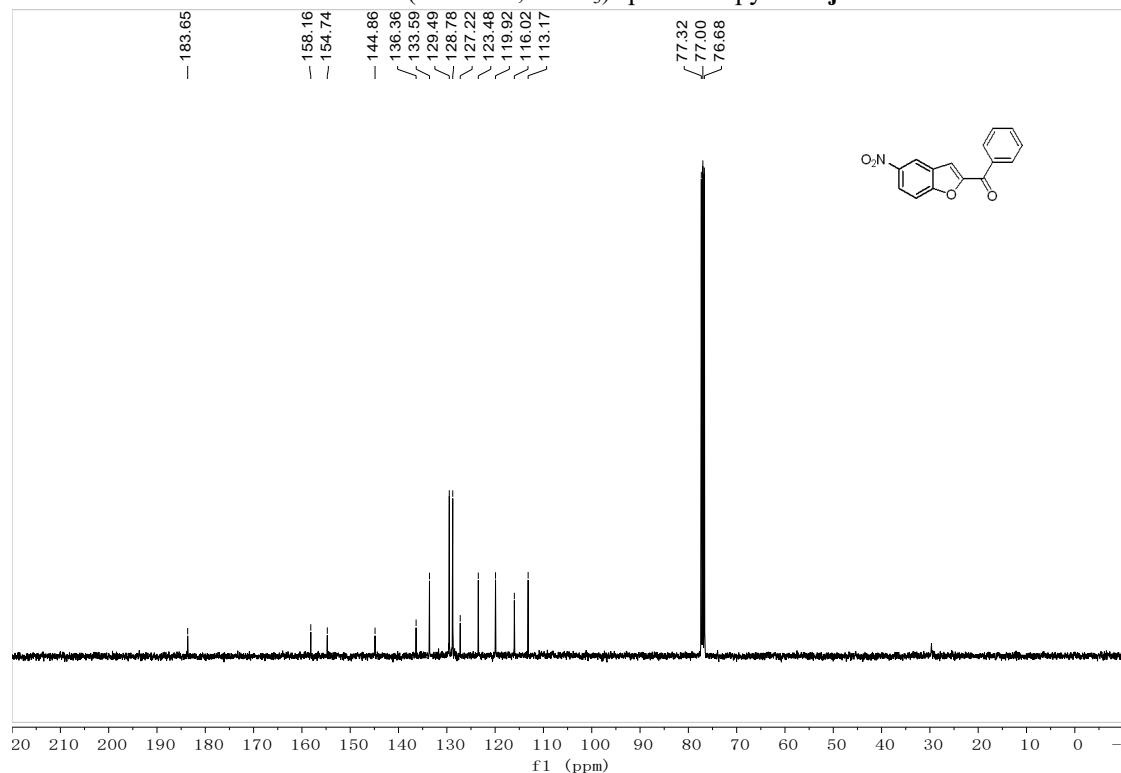
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectroscopy of **13i**



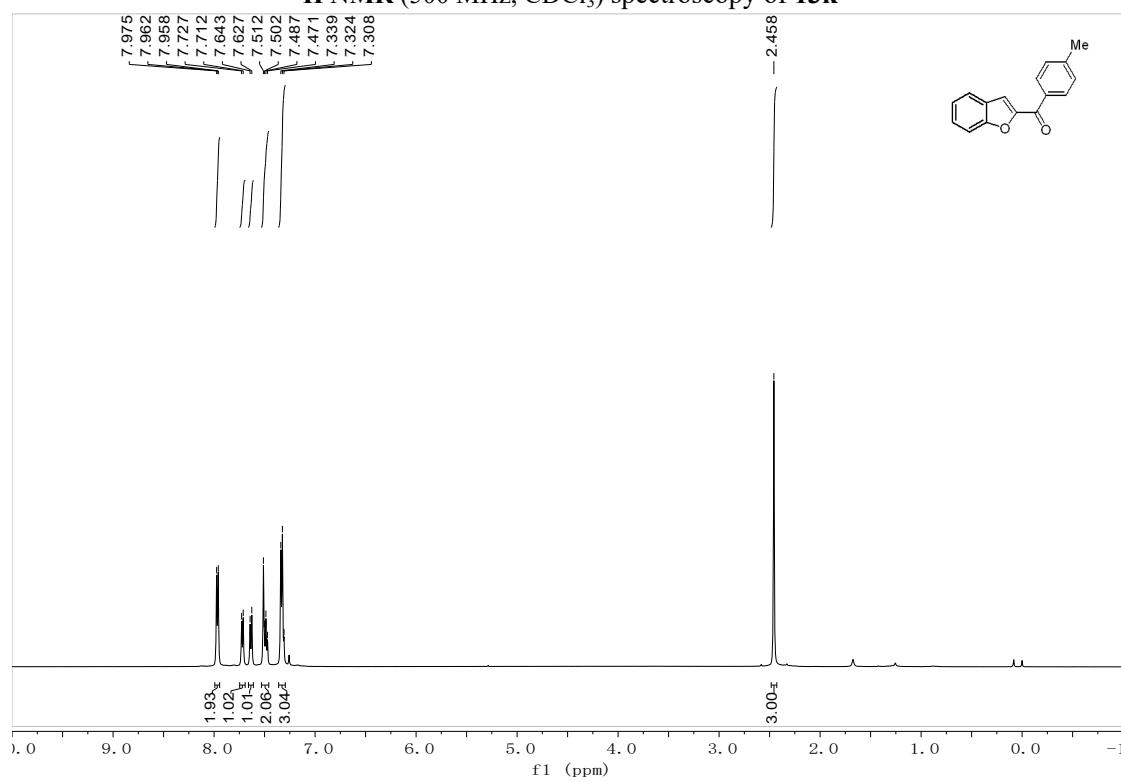
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) spectroscopy of **13j**



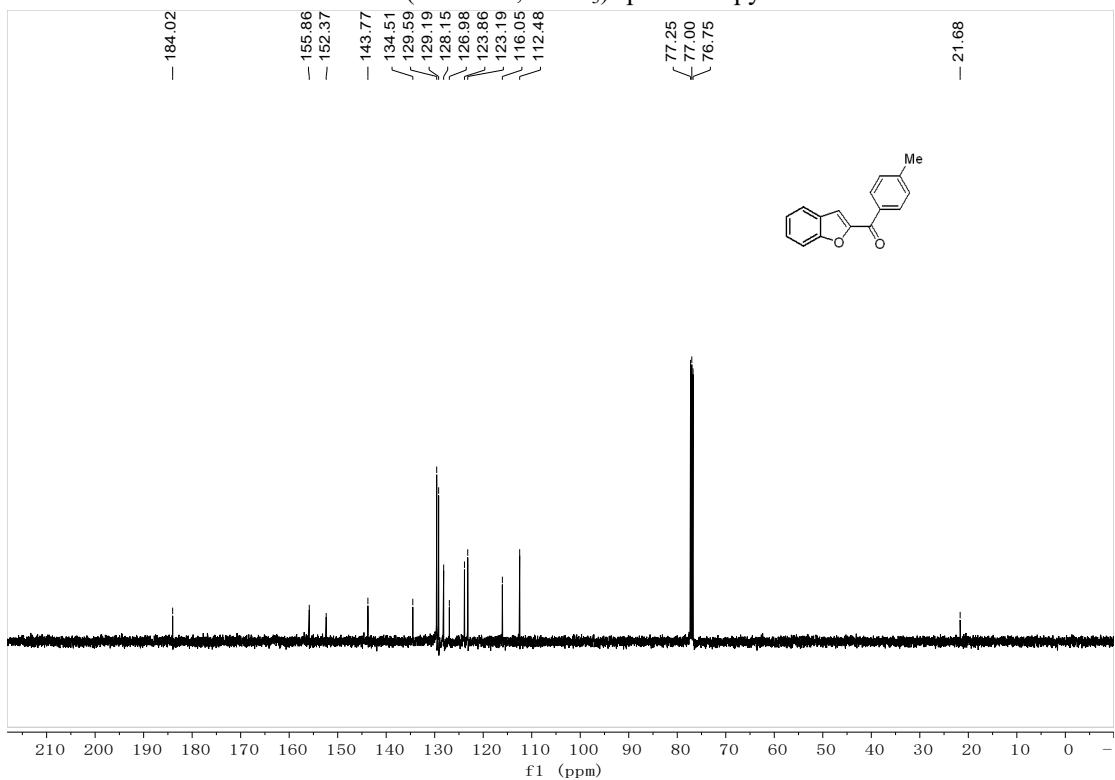
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectroscopy of **13j**



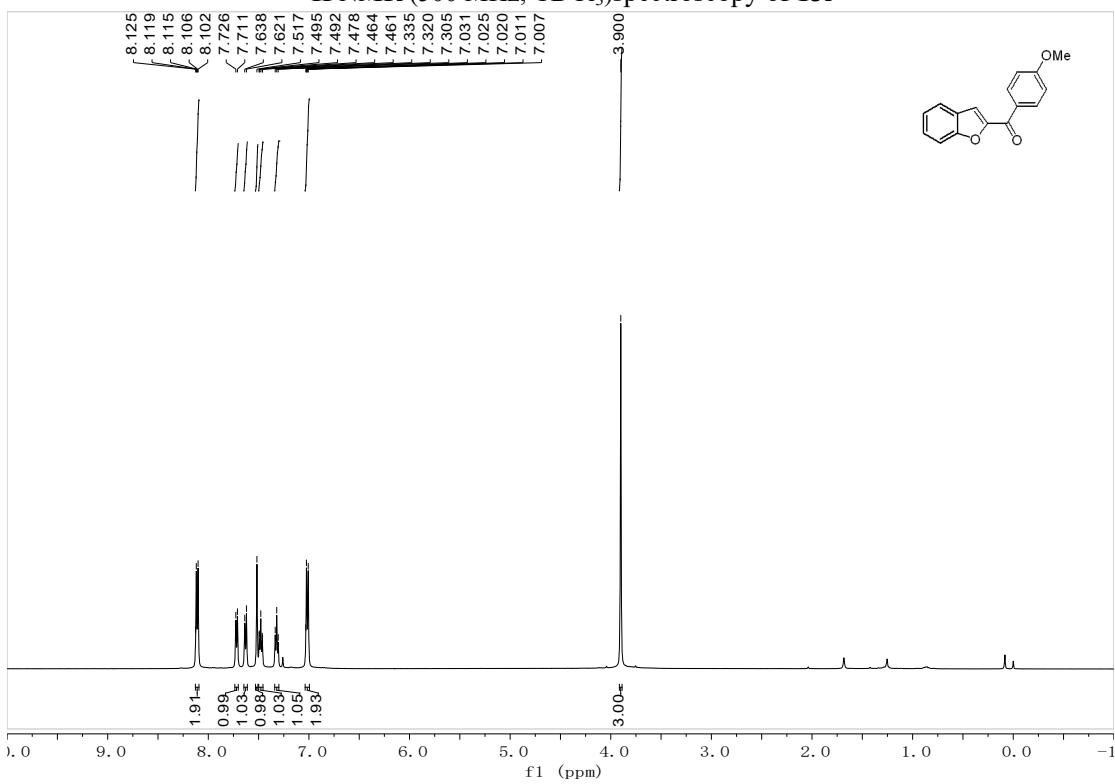
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectroscopy of **13k**



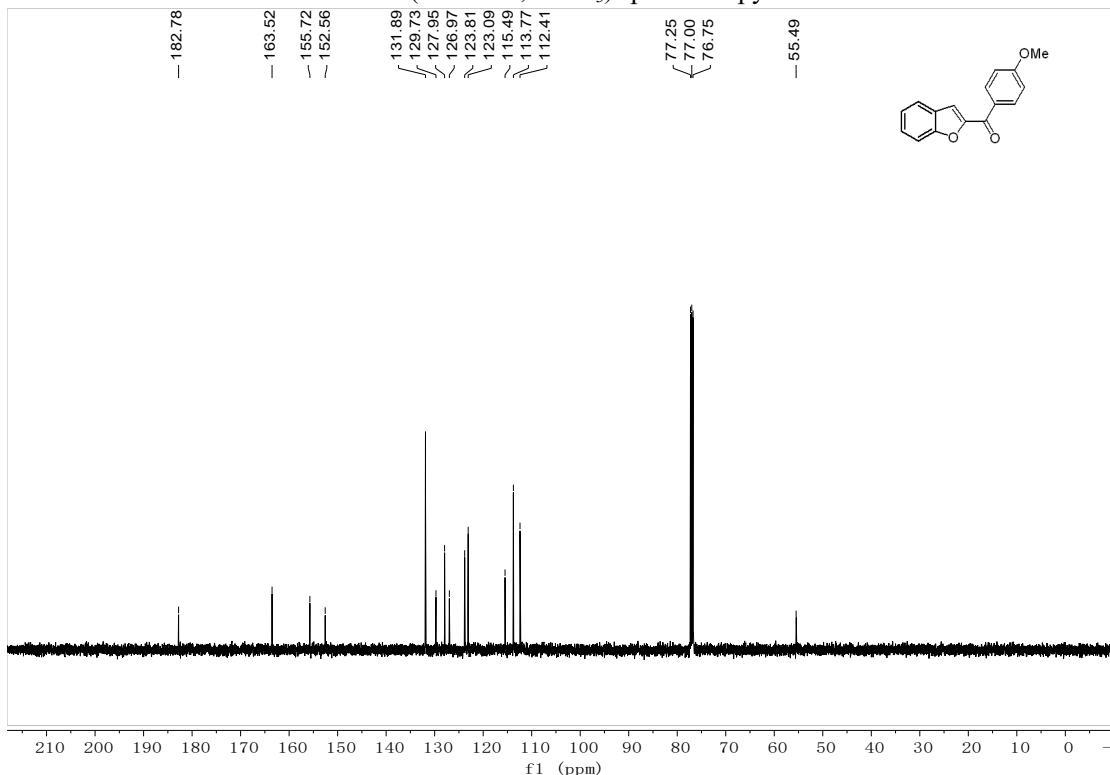
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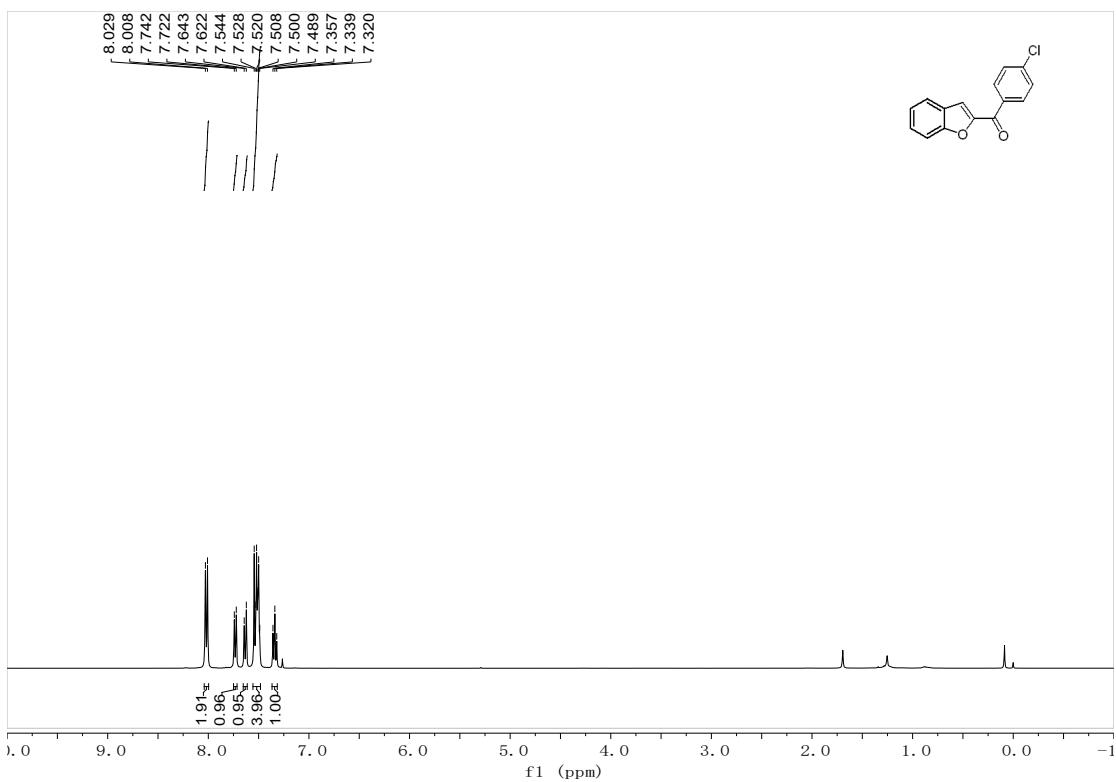
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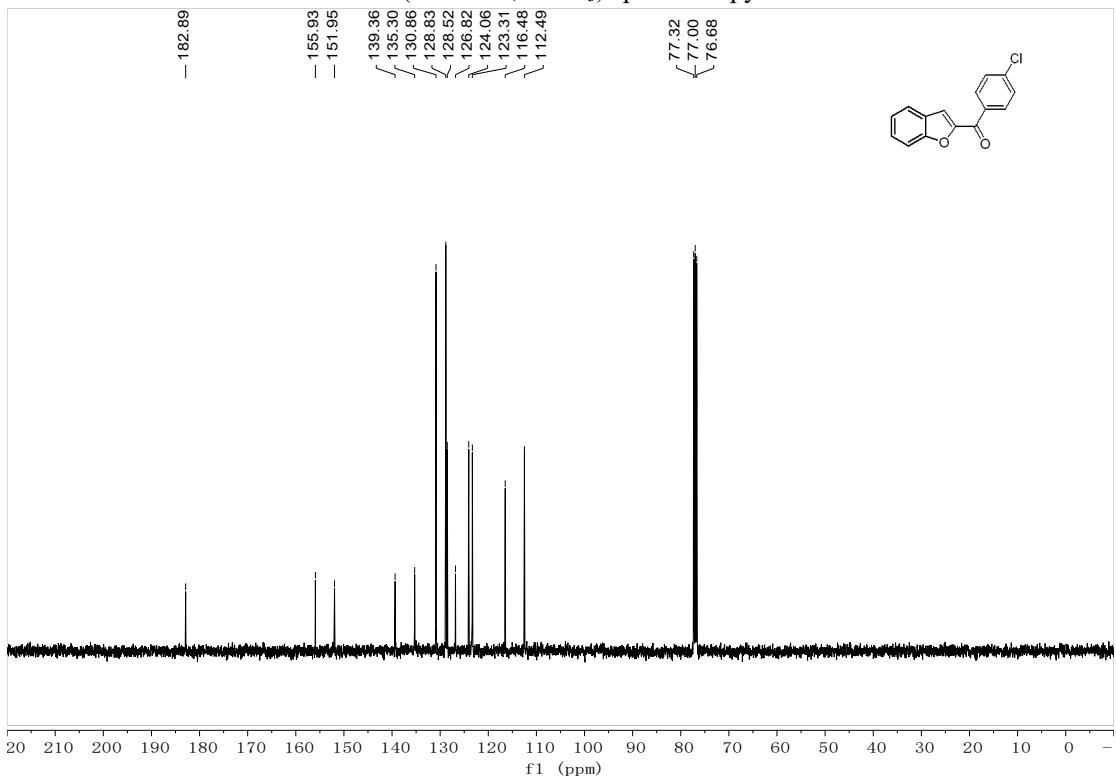
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectroscopy of 13l**



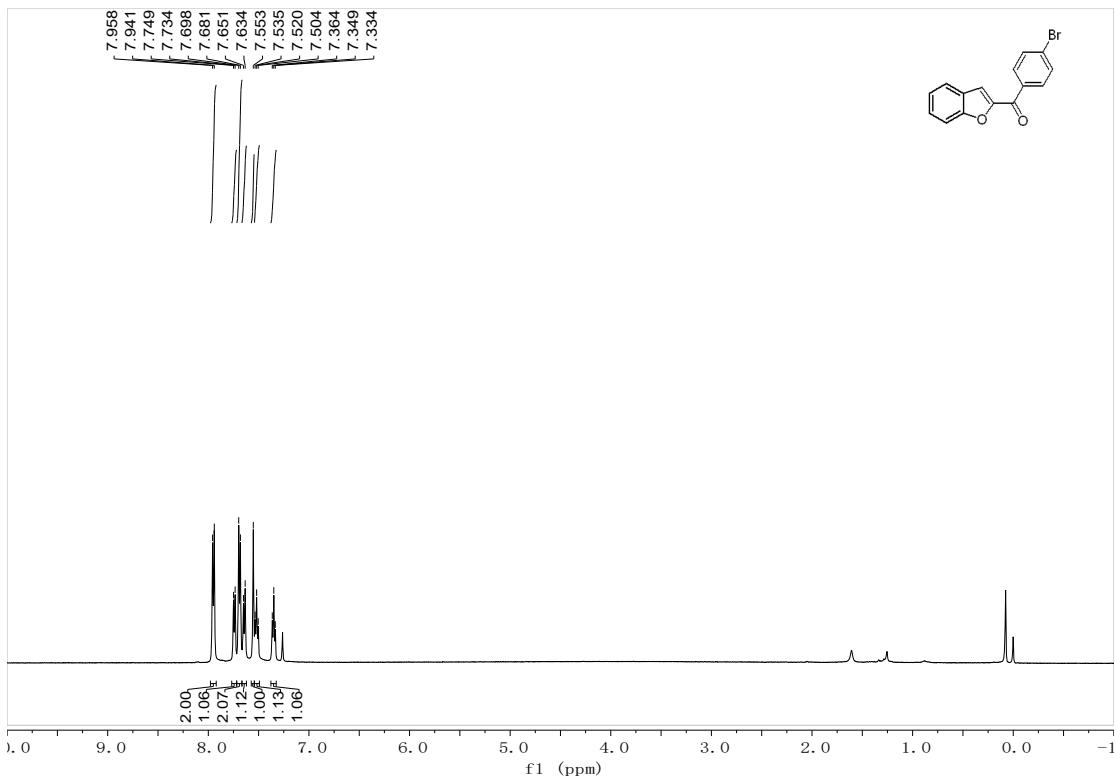
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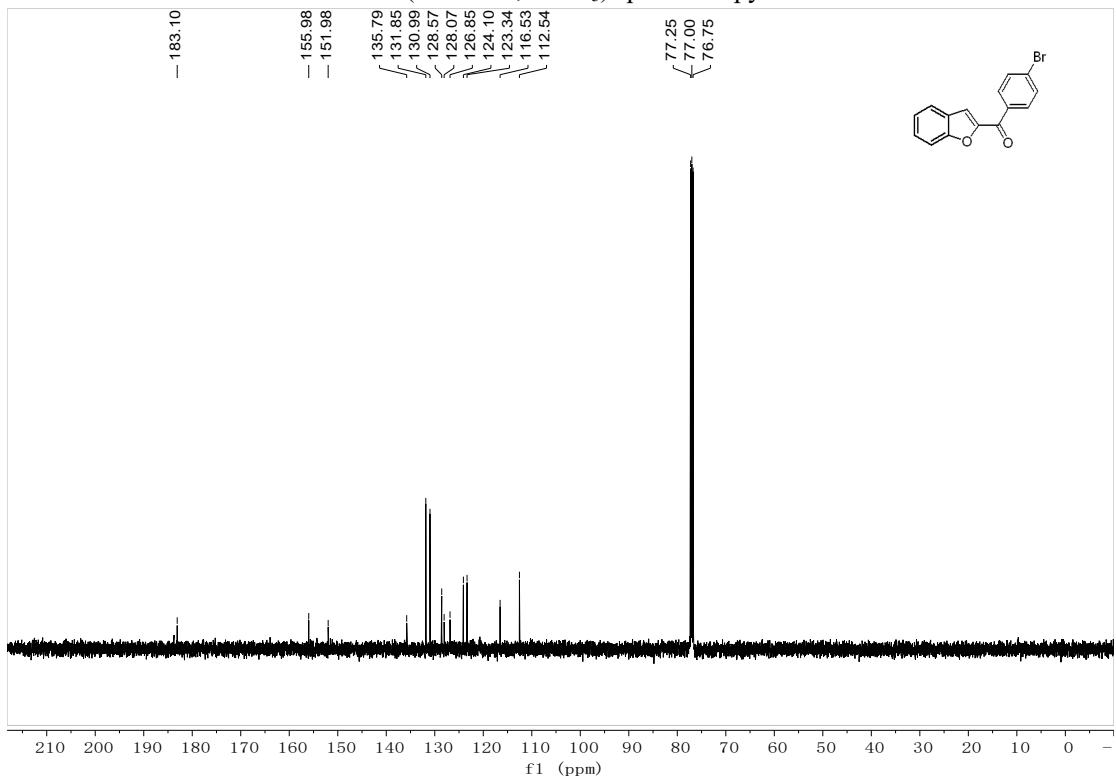
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) spectroscopy of **13m**



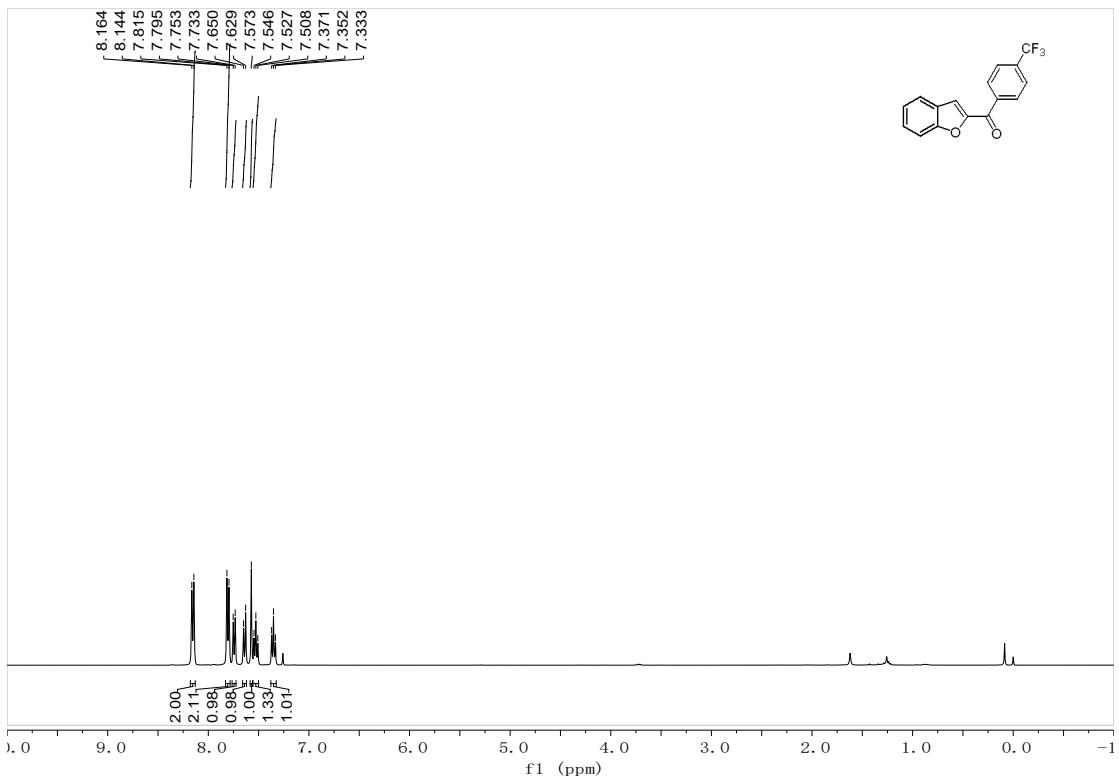
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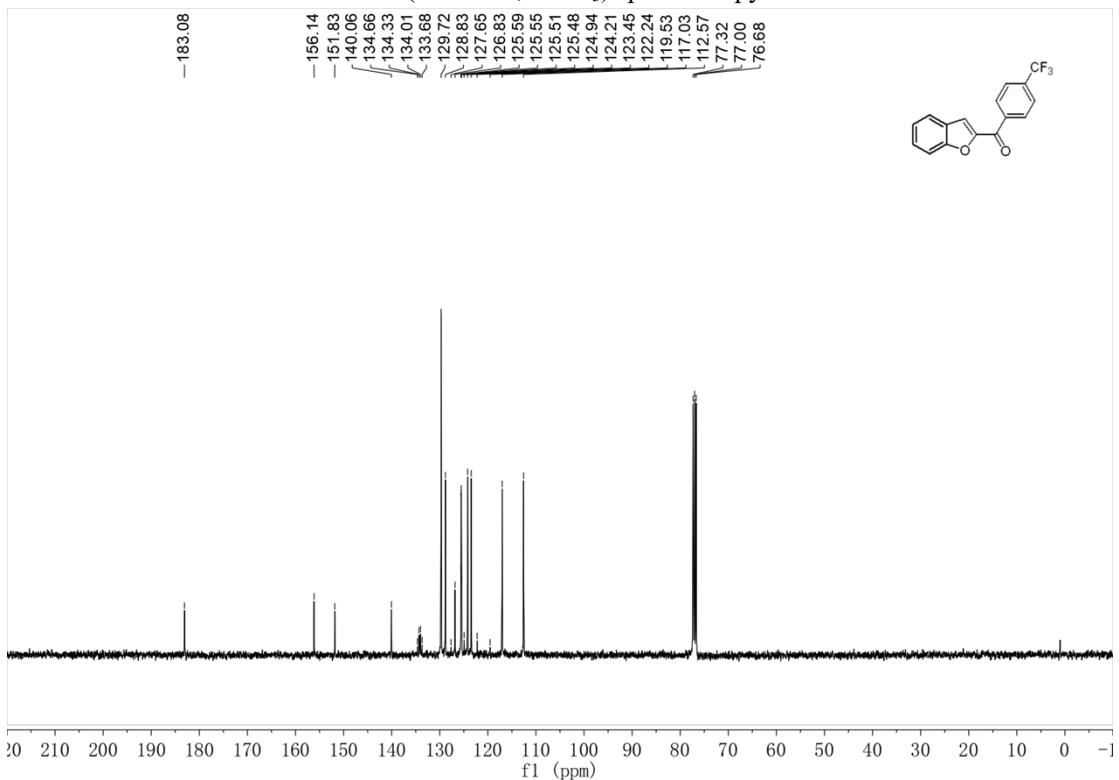
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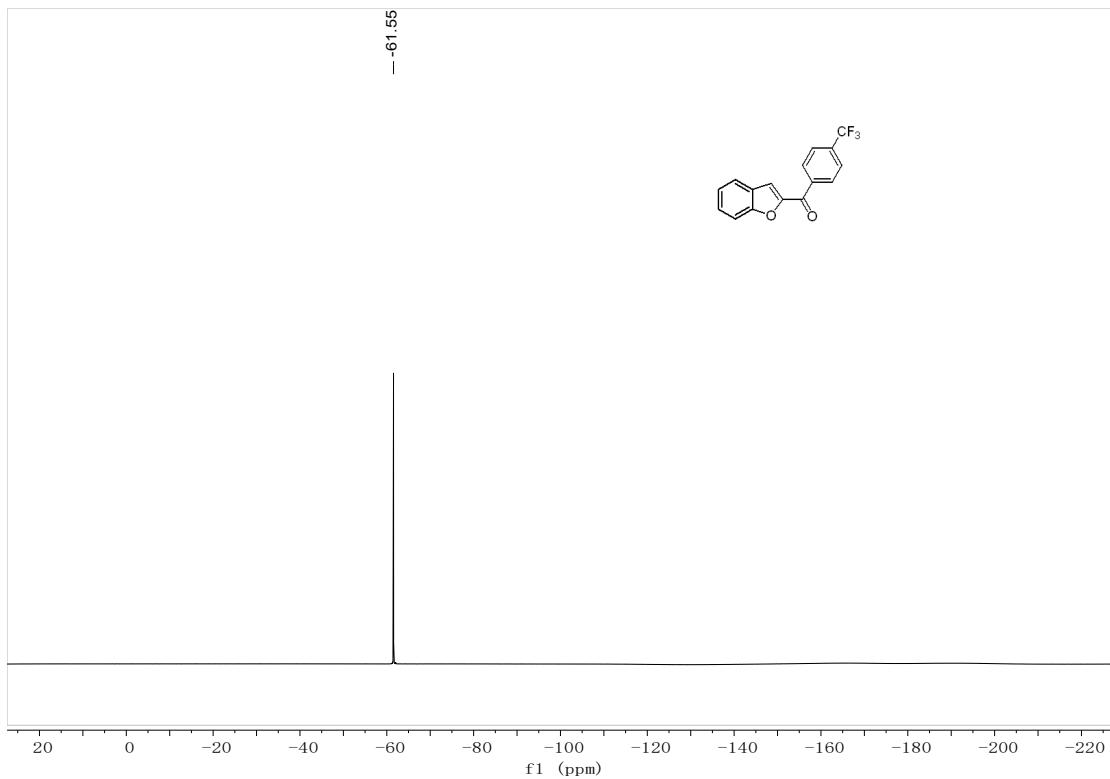
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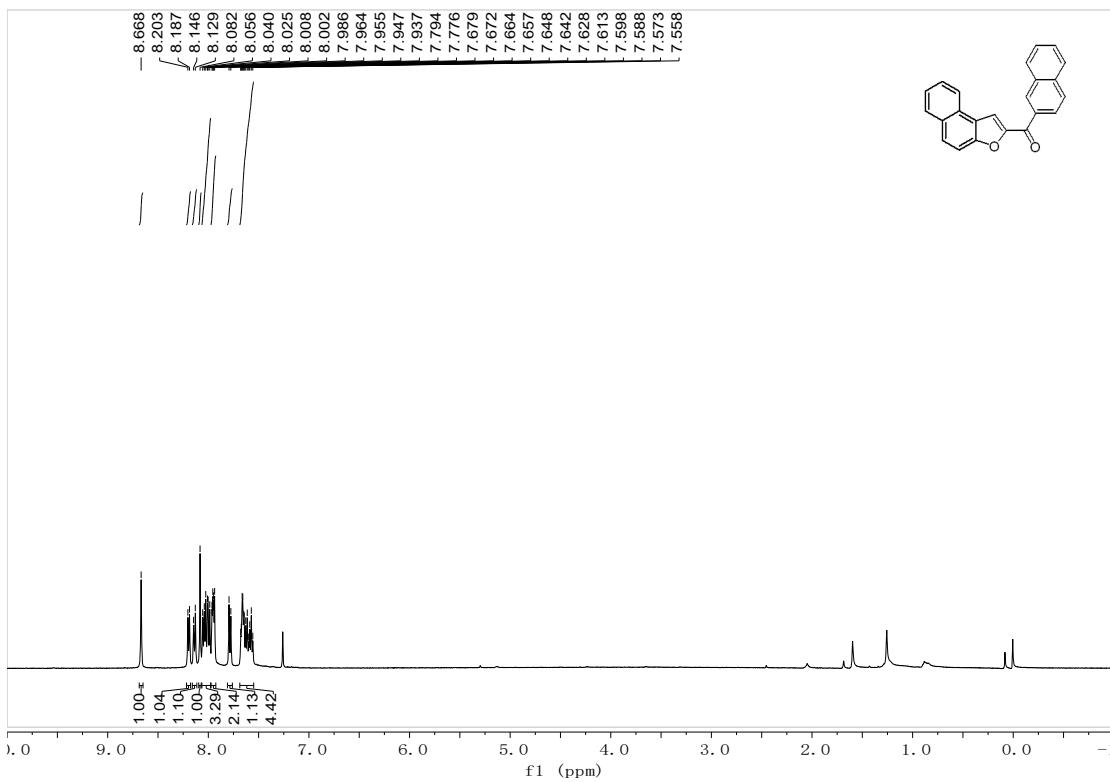
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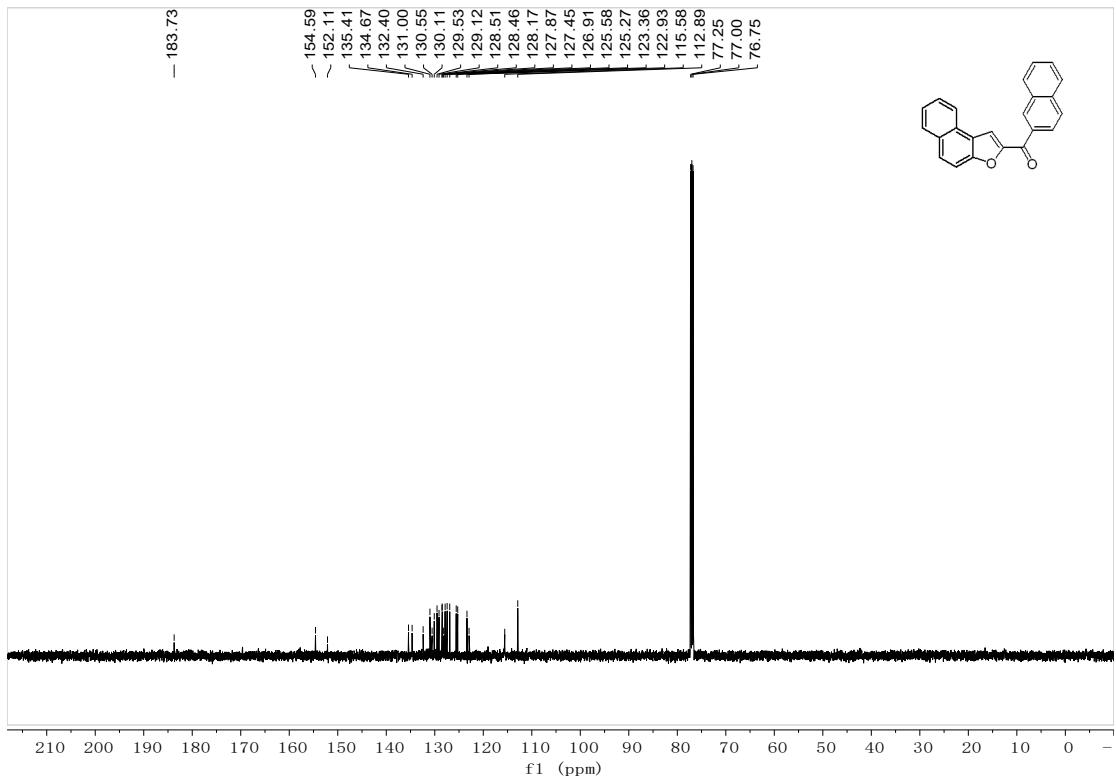
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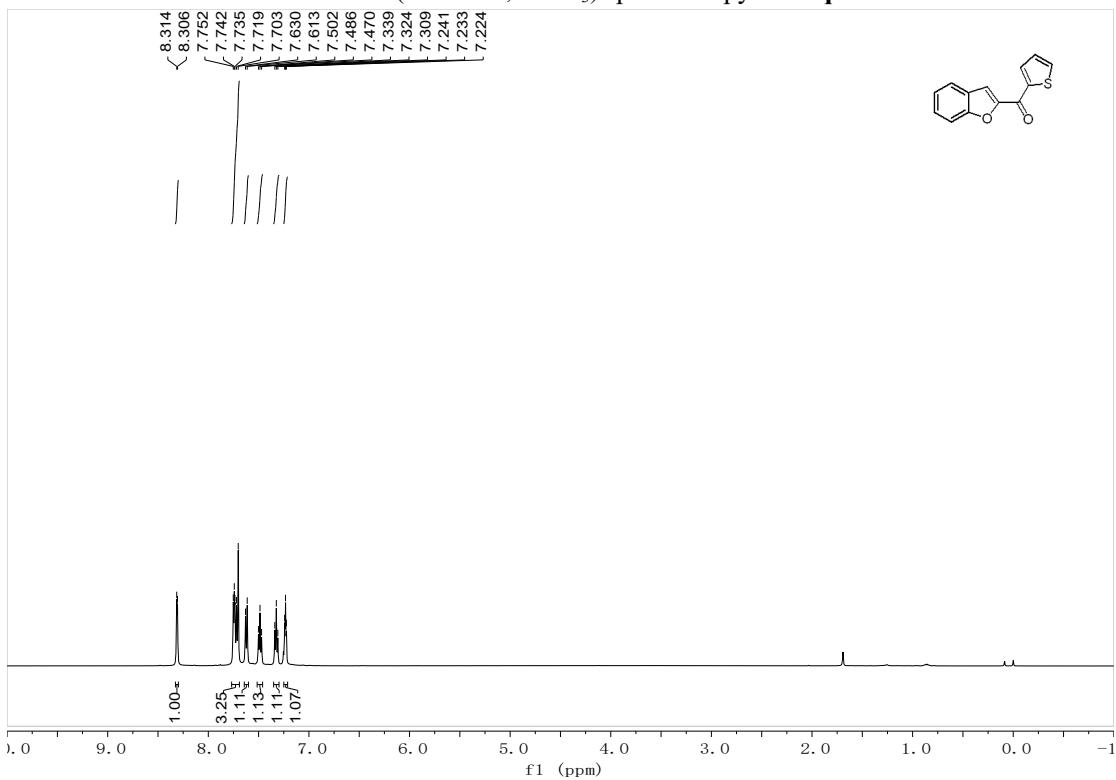
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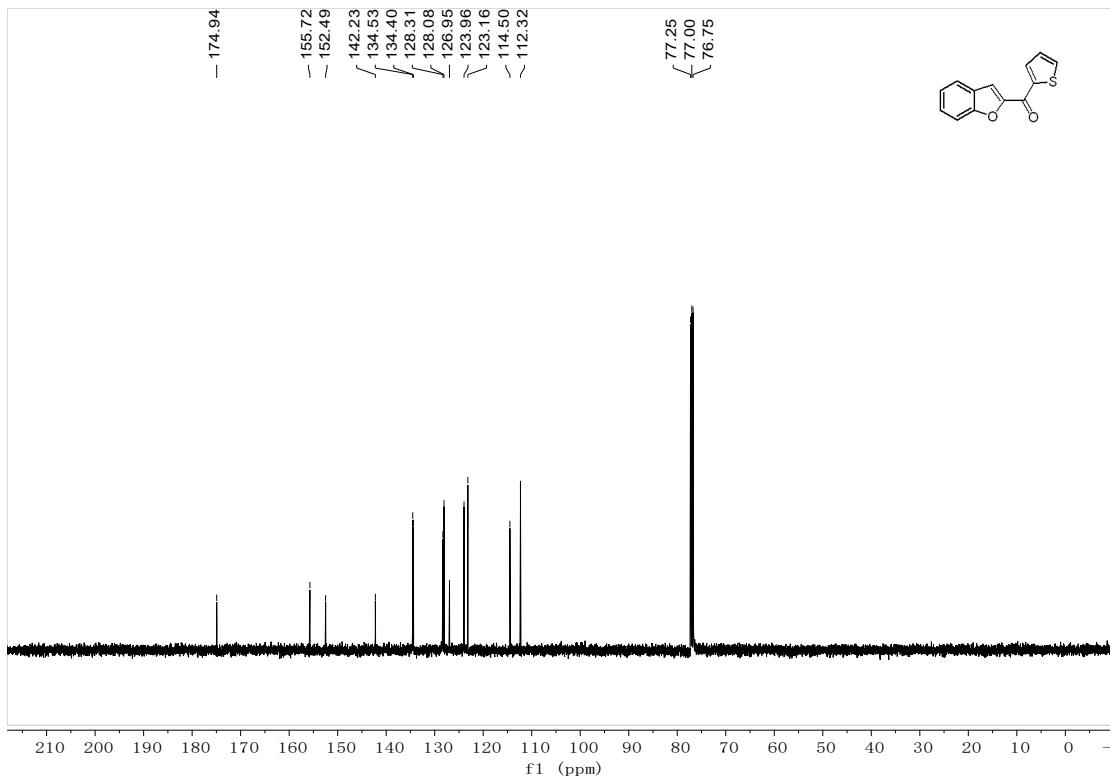
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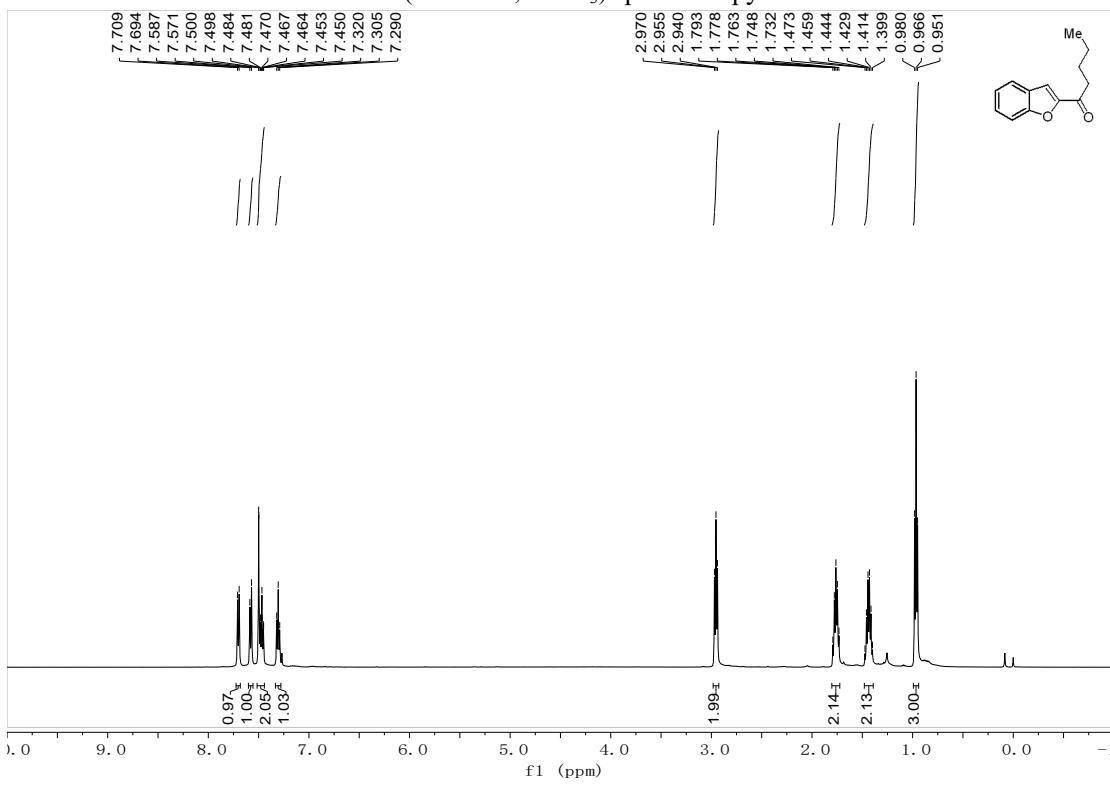
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) spectroscopy of **13q**



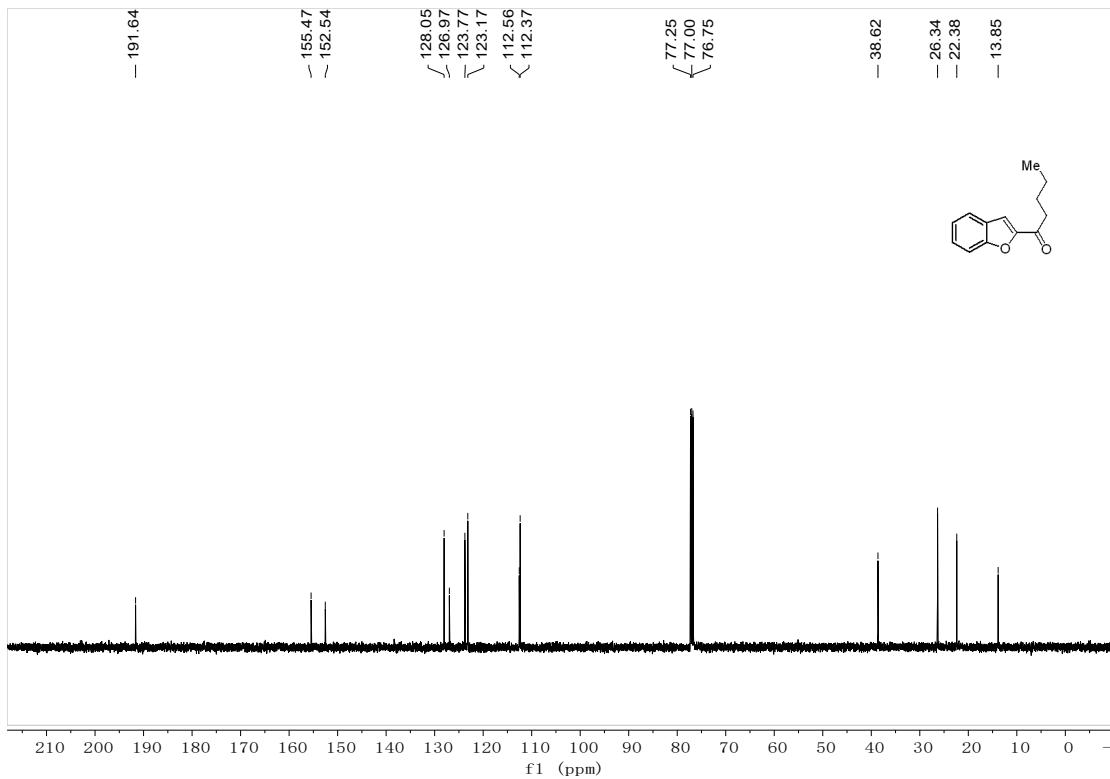
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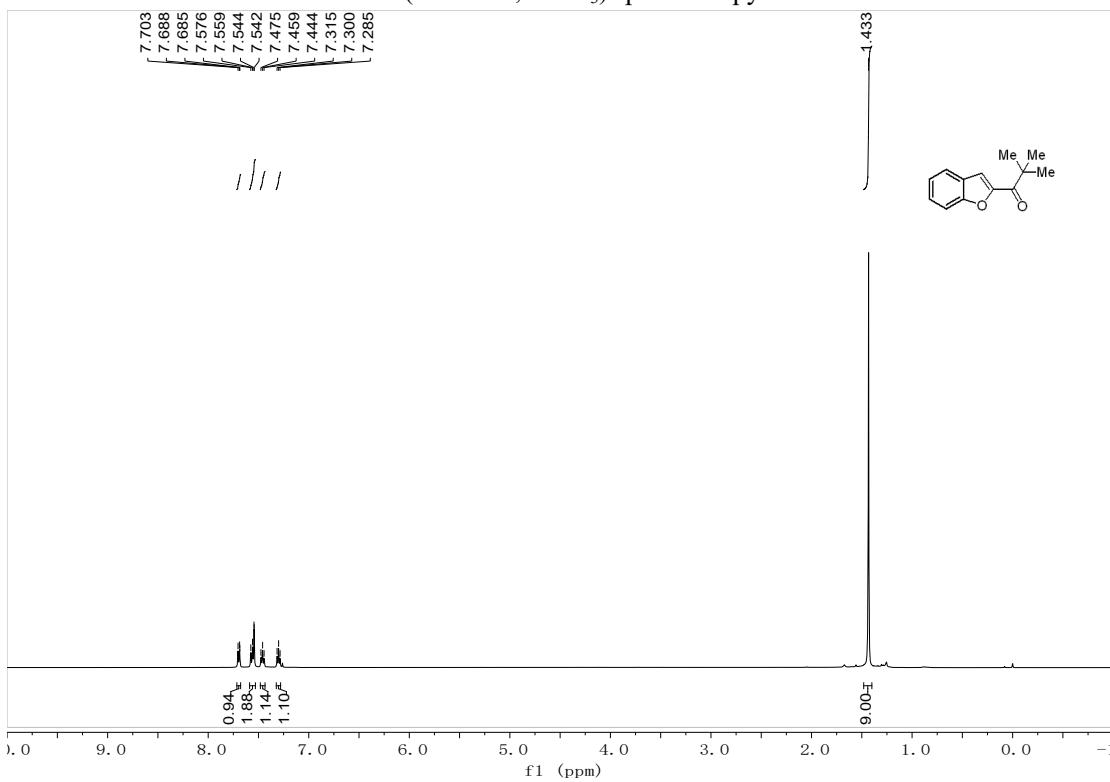
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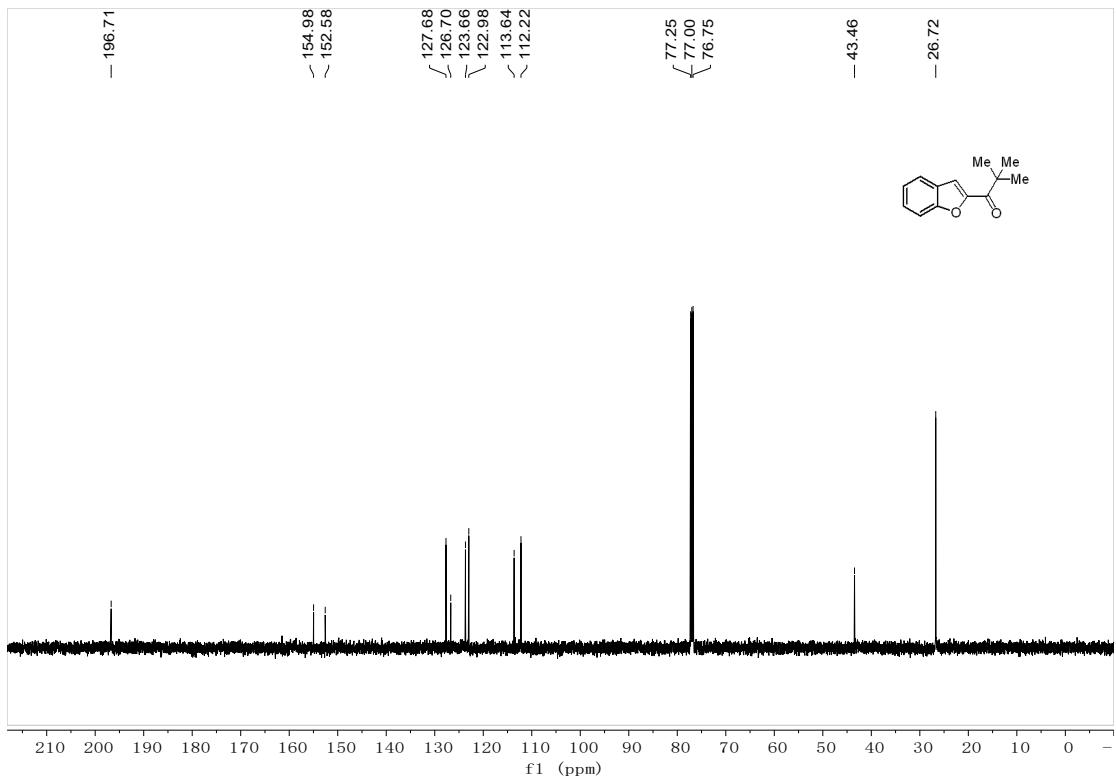
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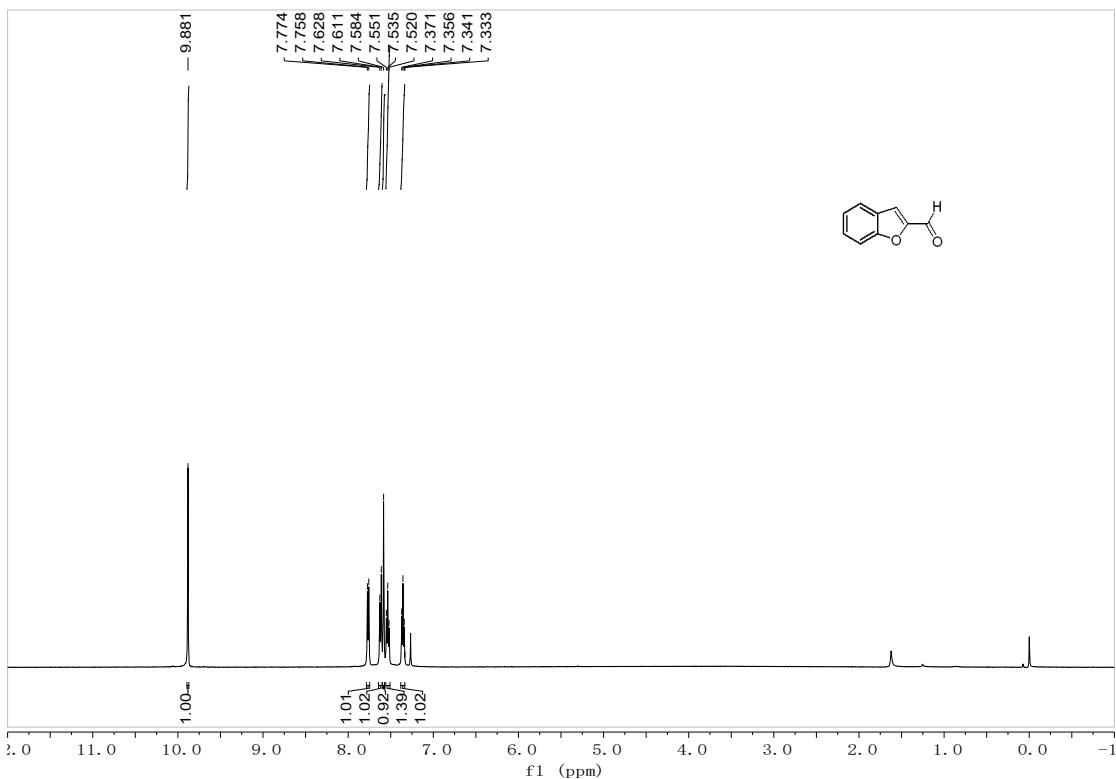
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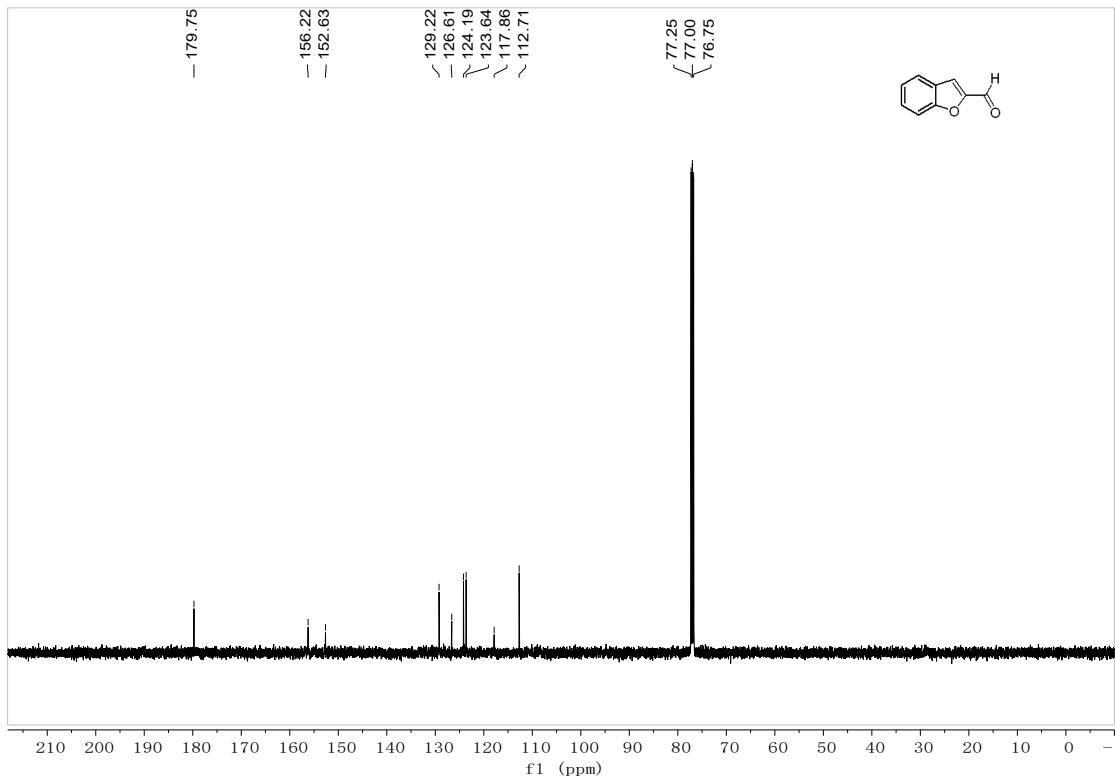
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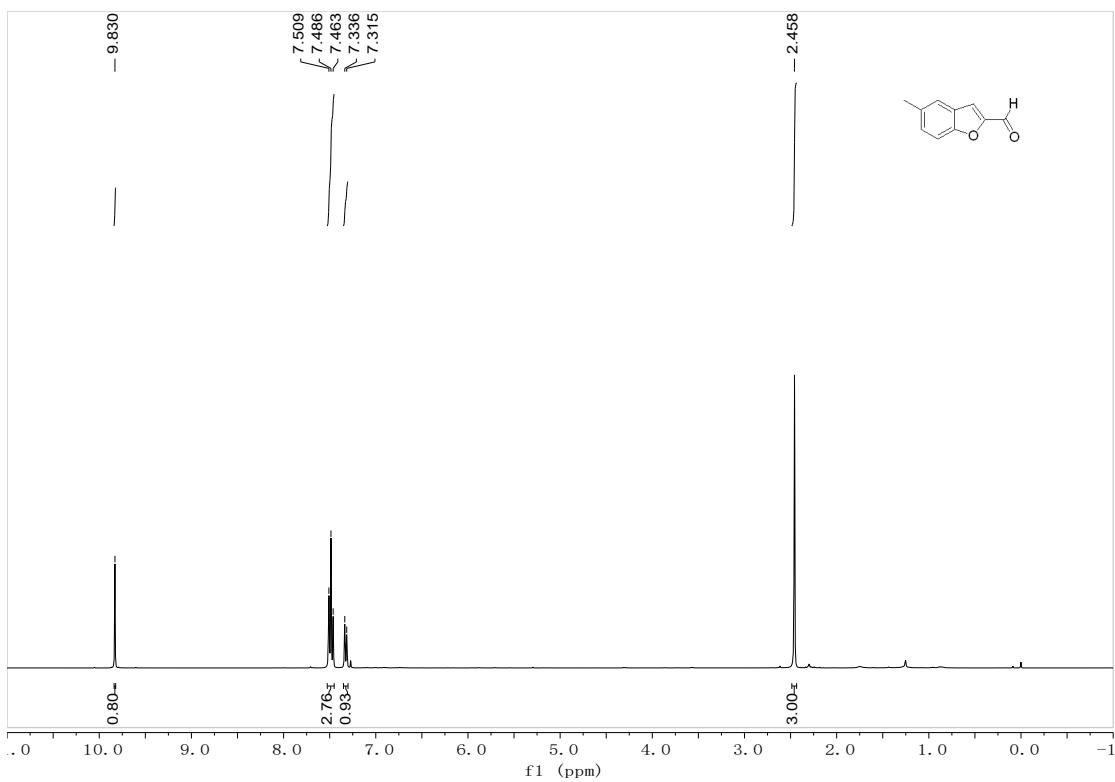
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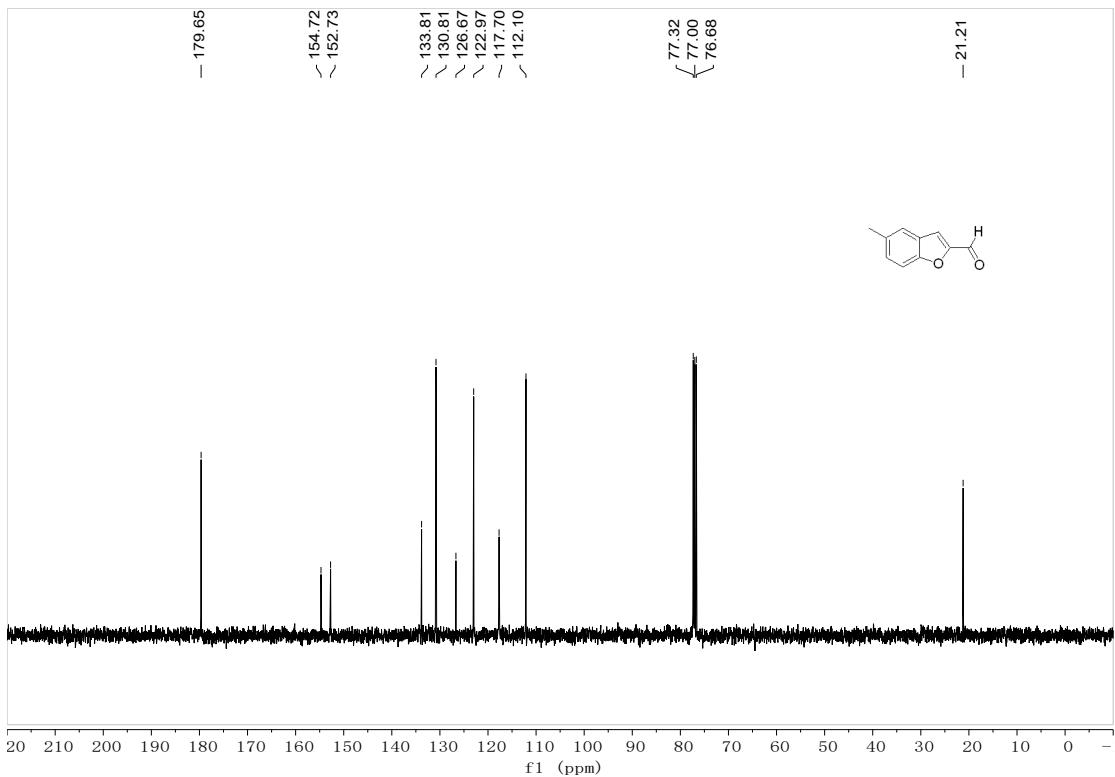
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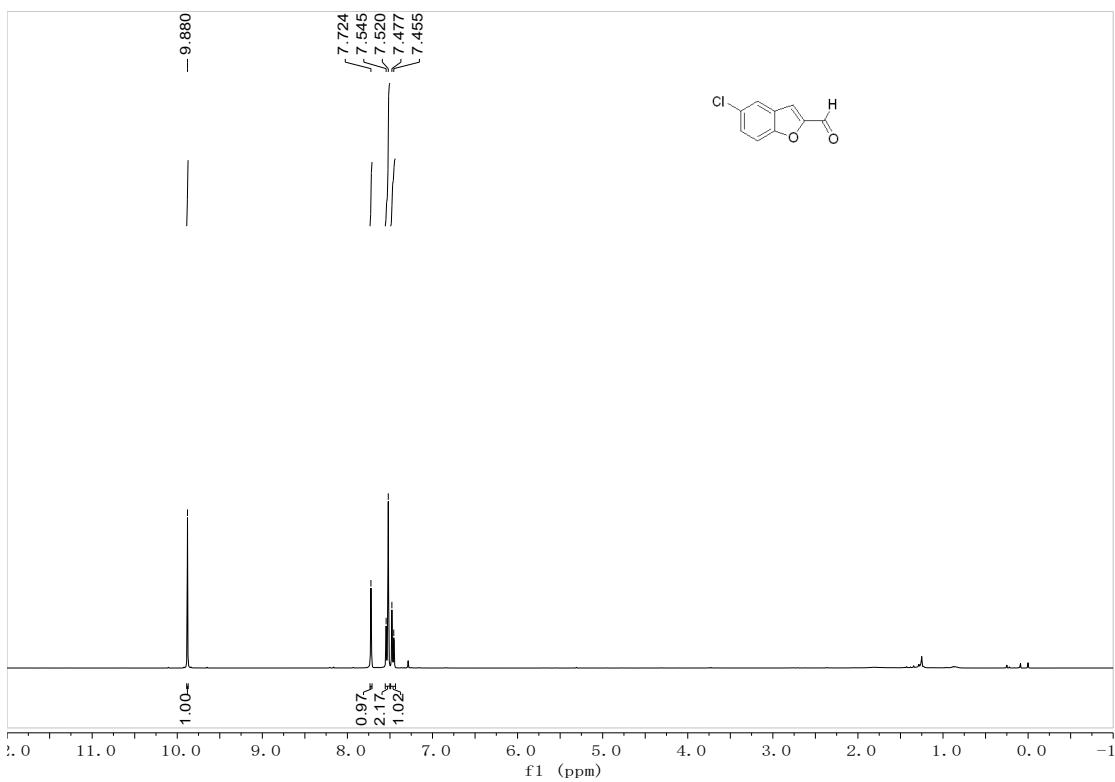
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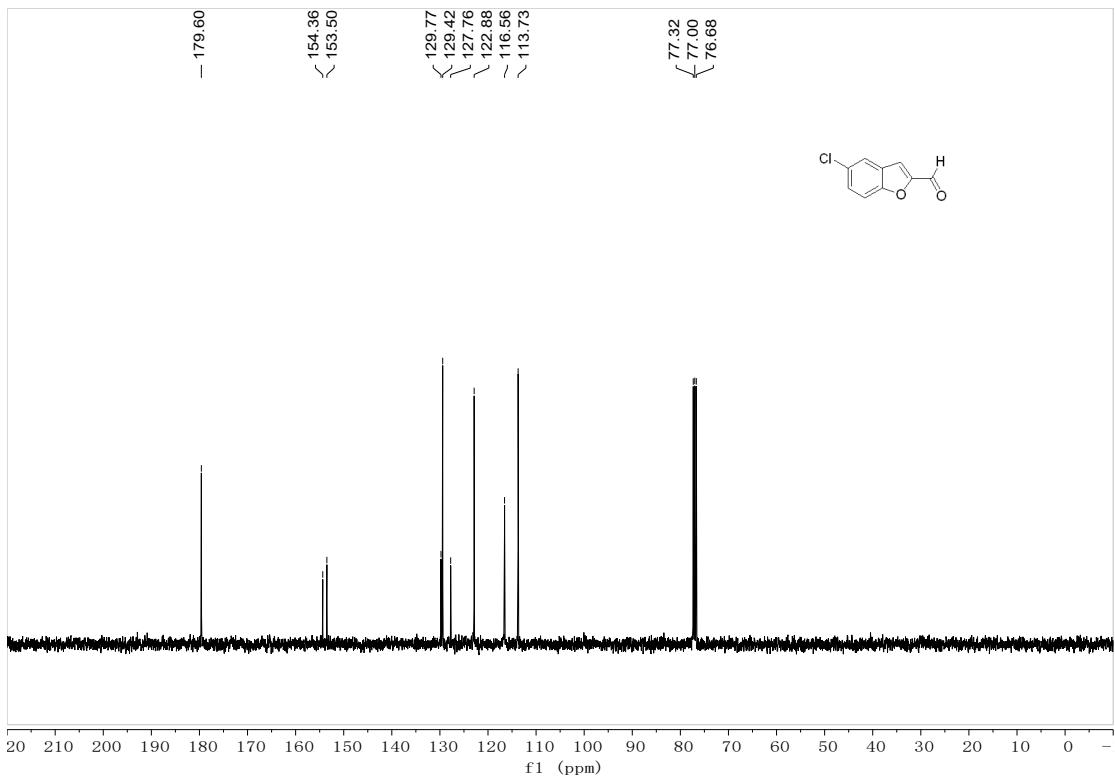
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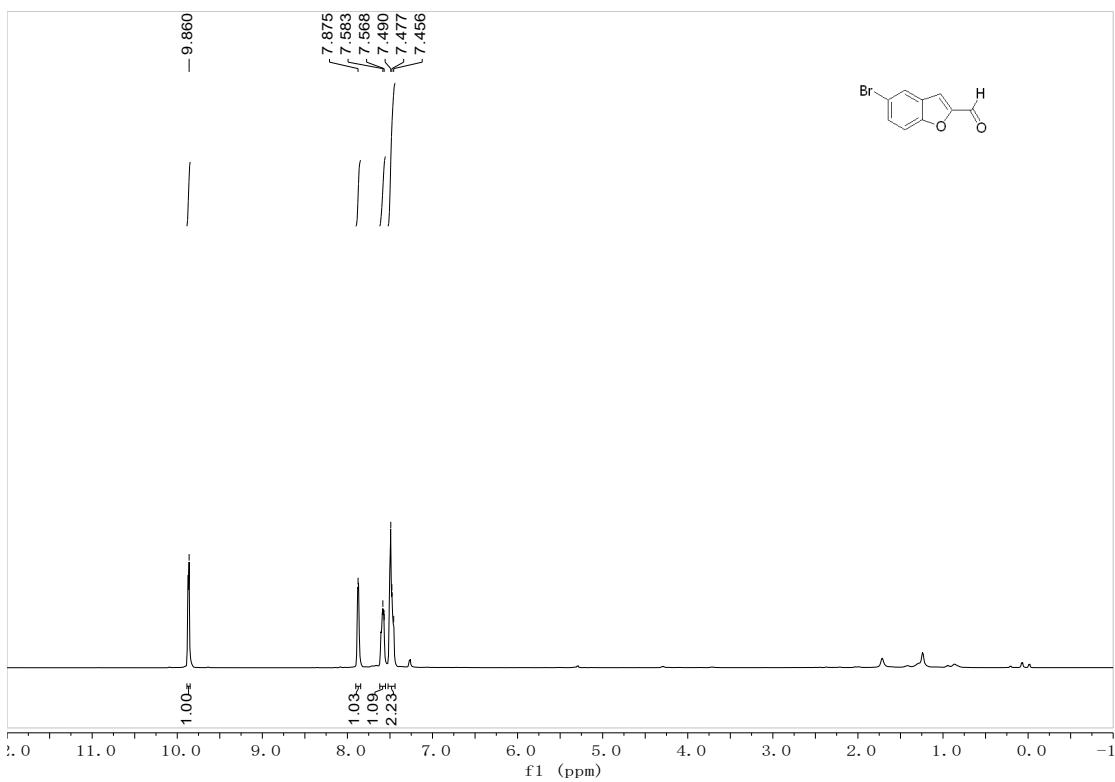
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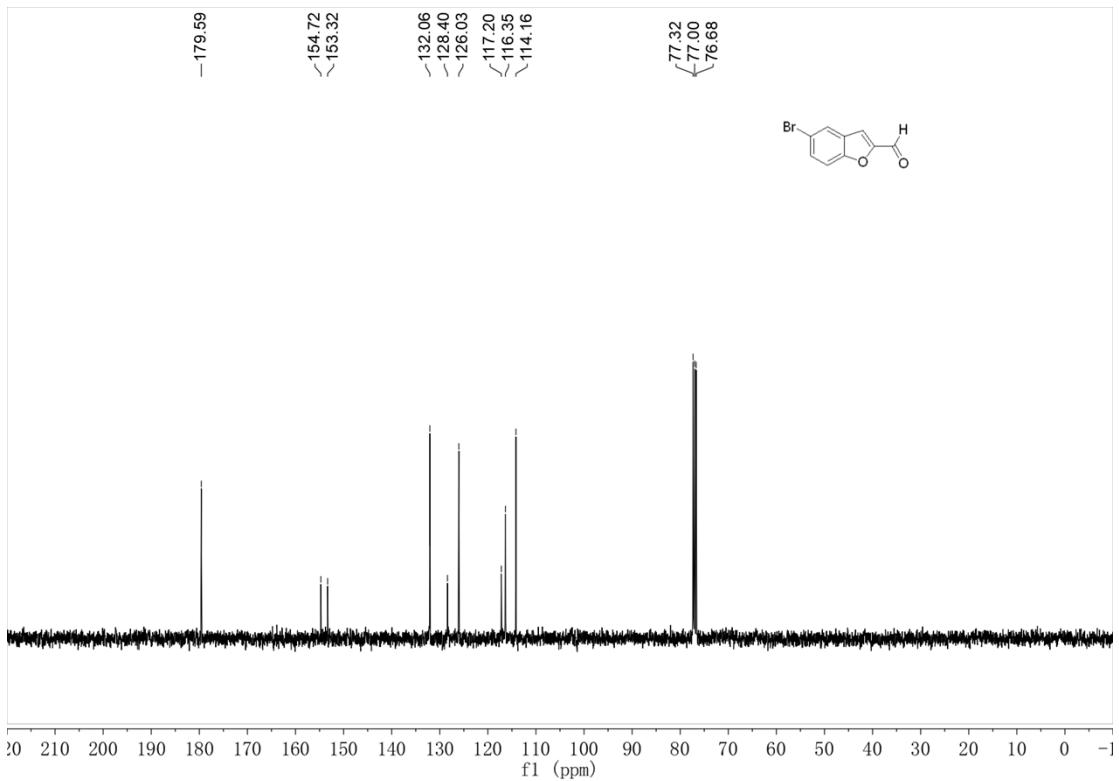
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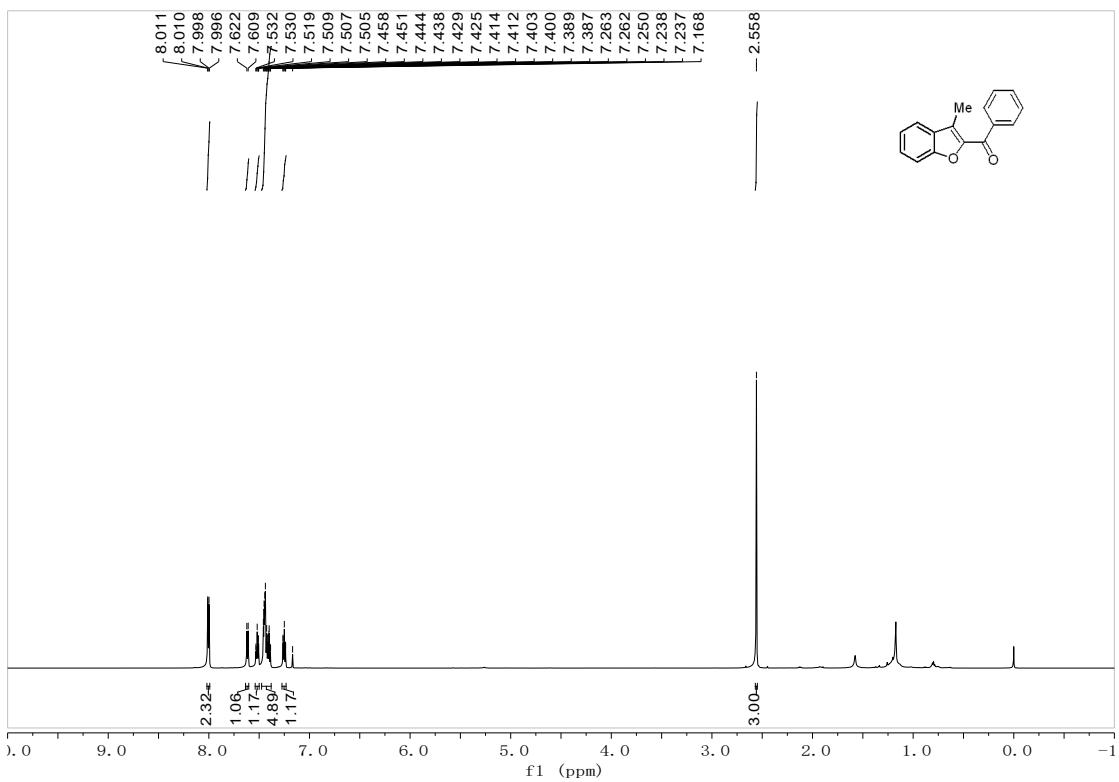
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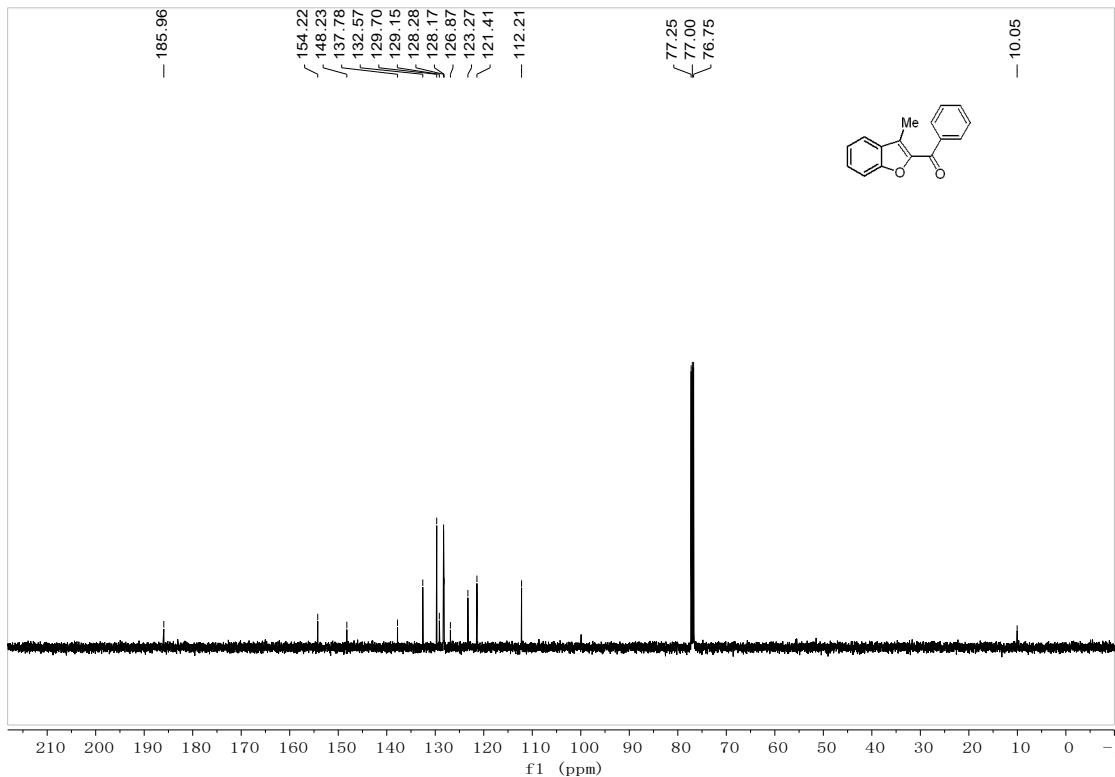
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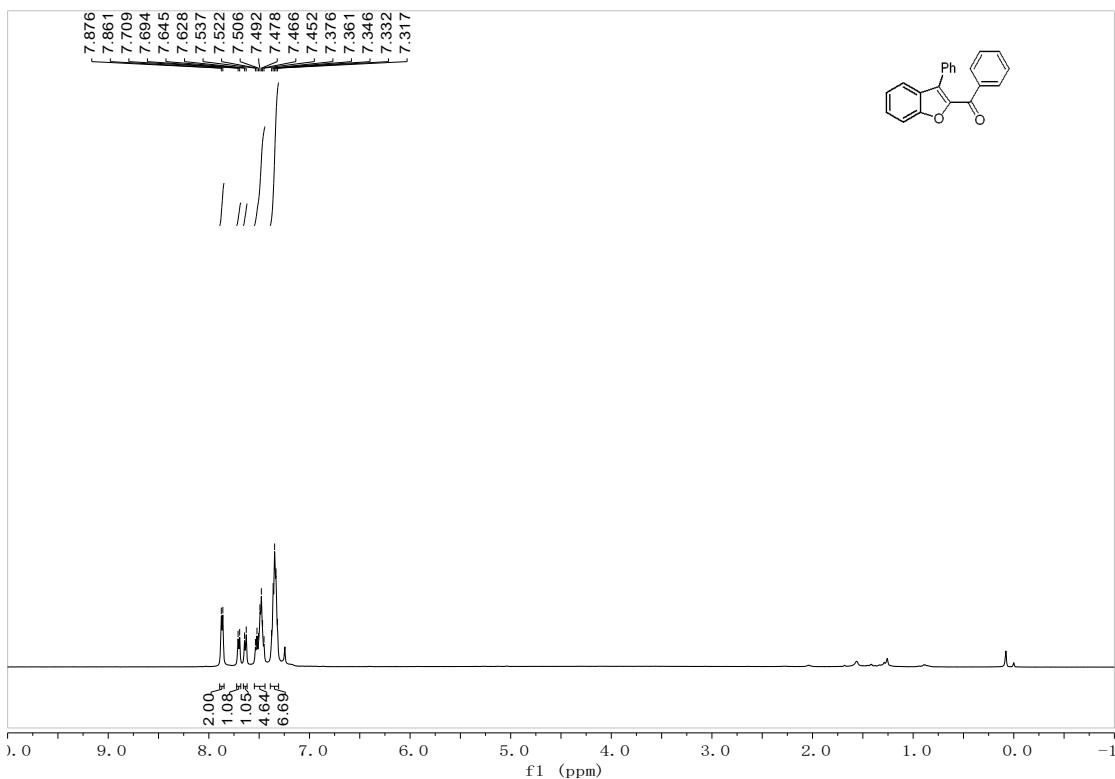
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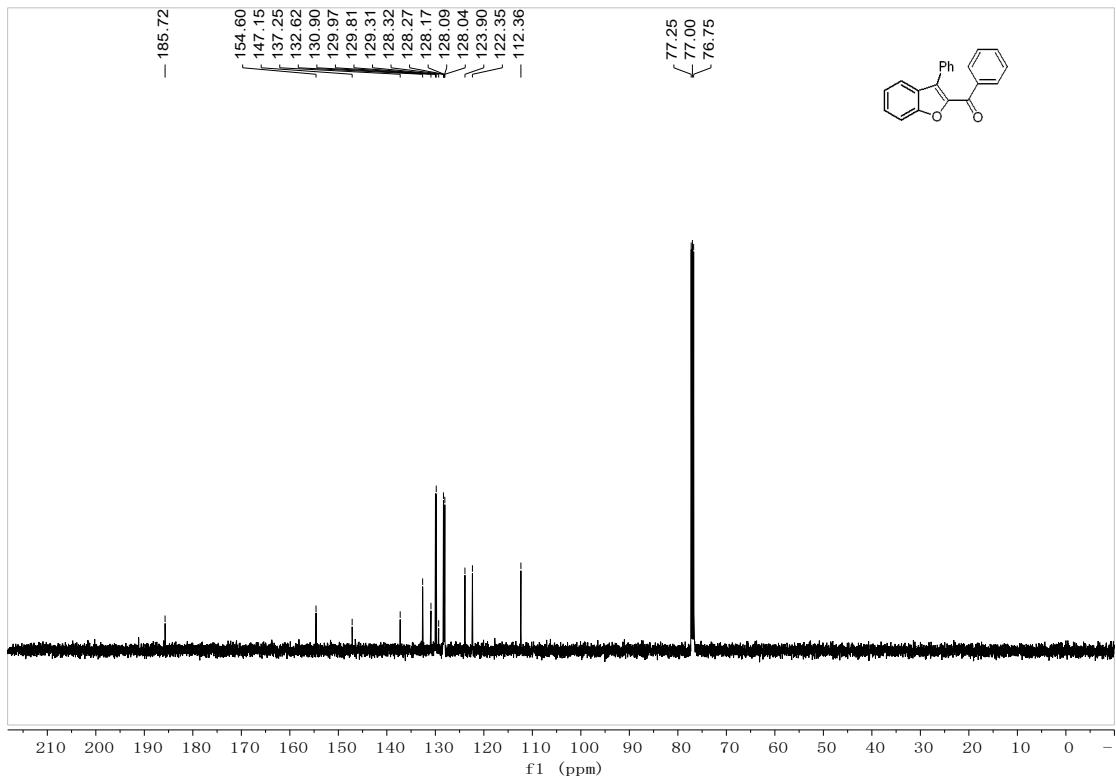
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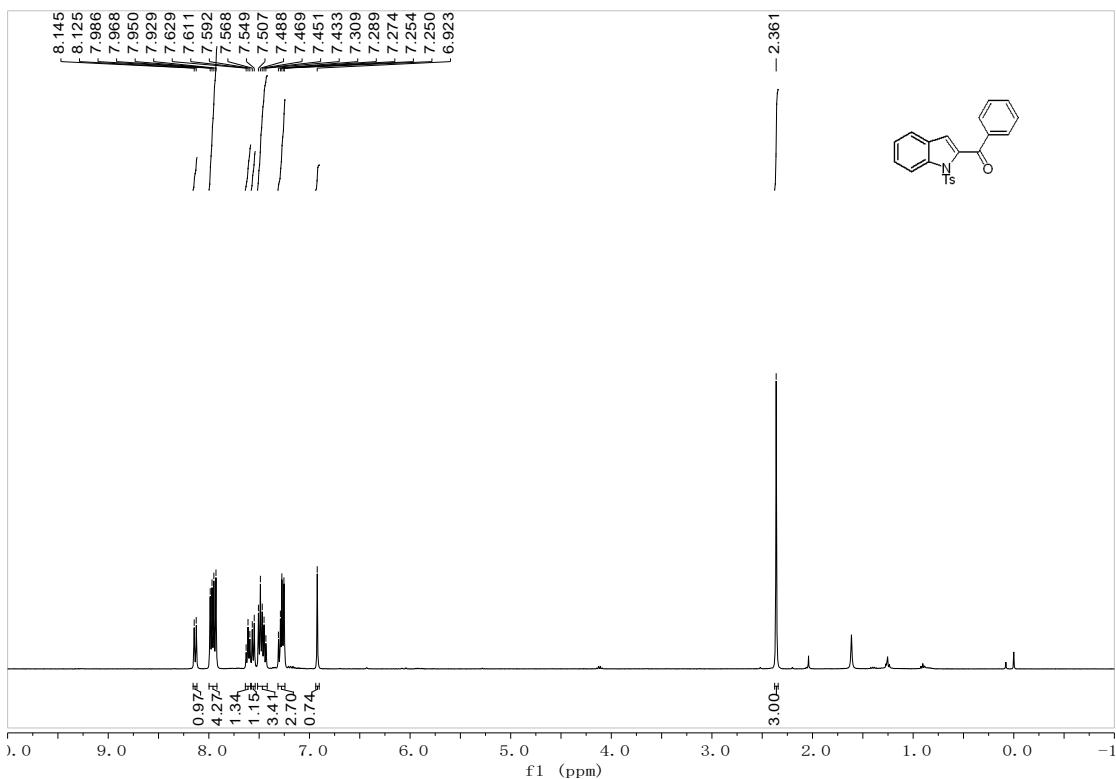
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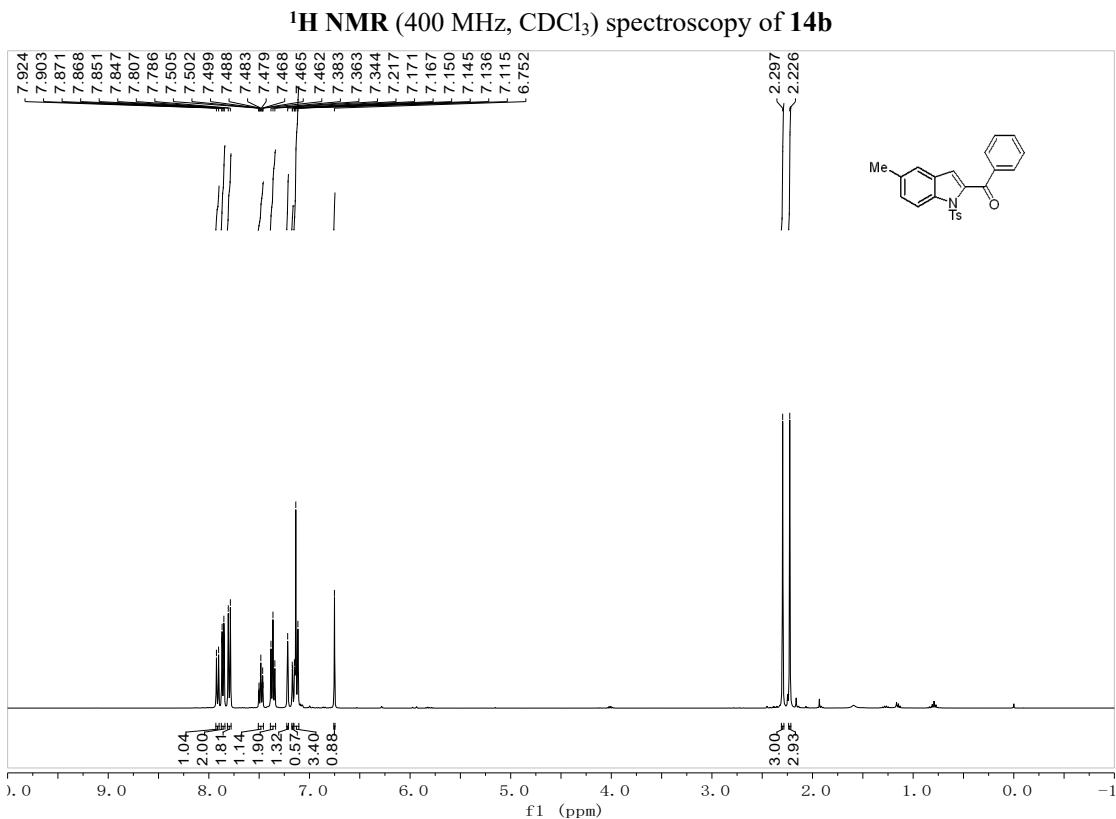
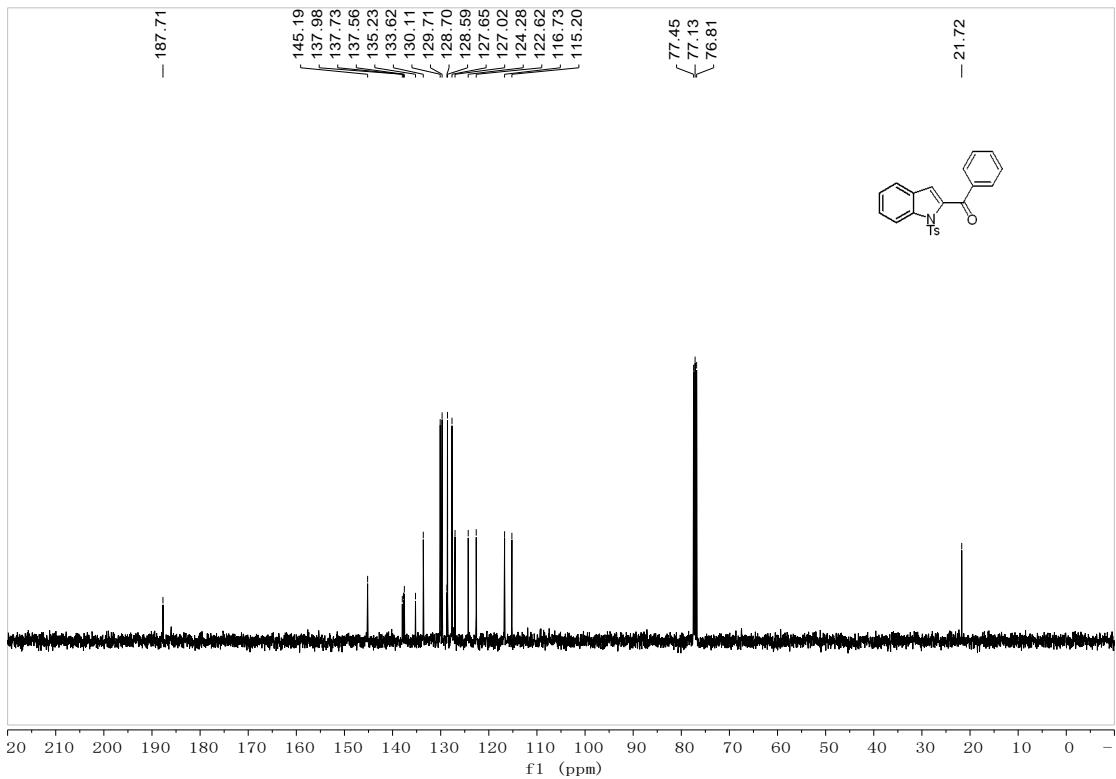
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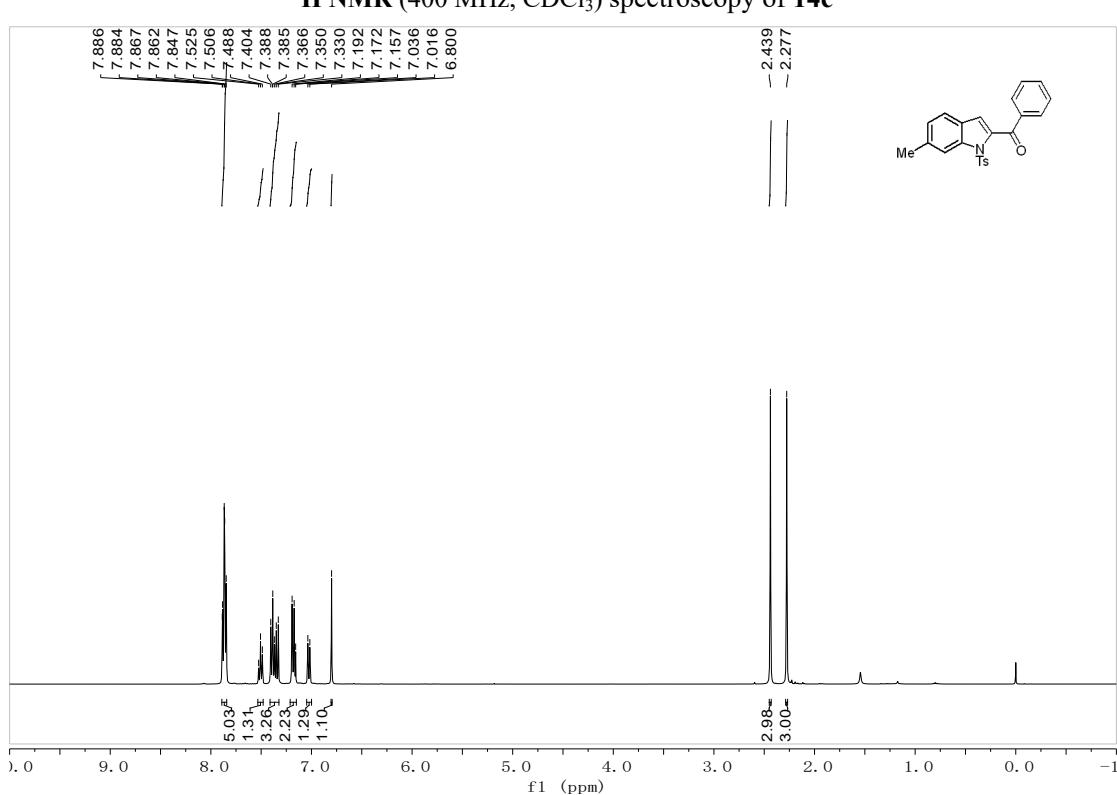
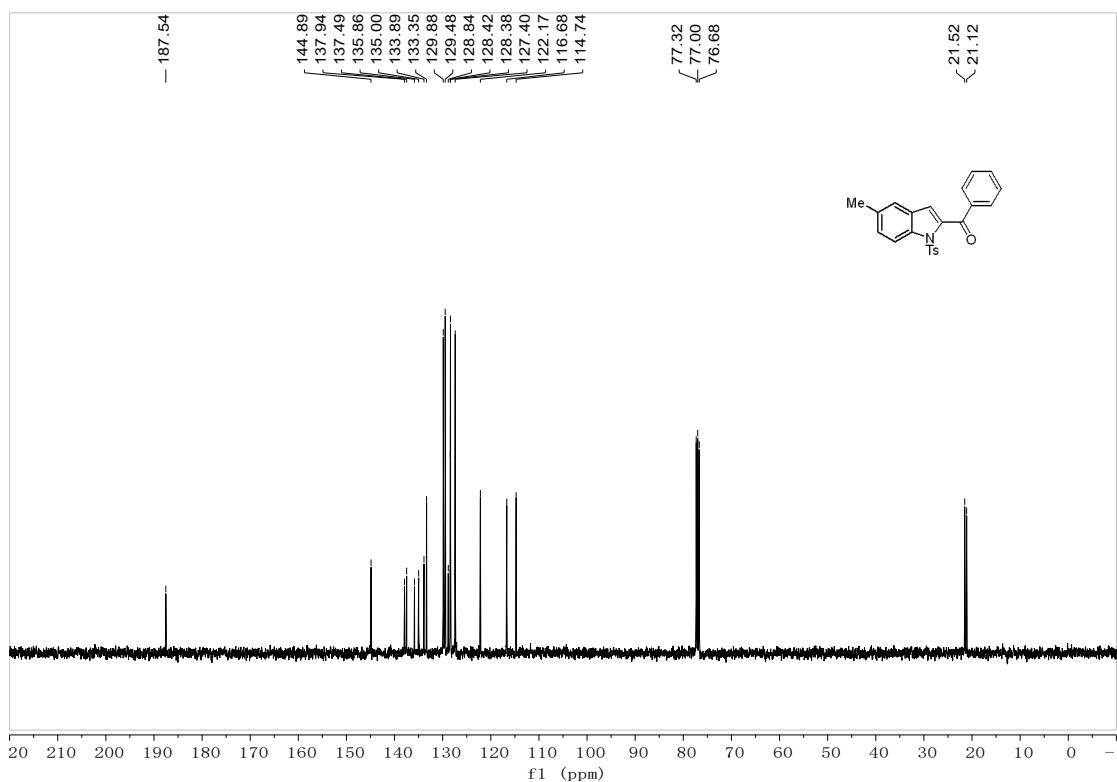
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectroscopy of **14a**



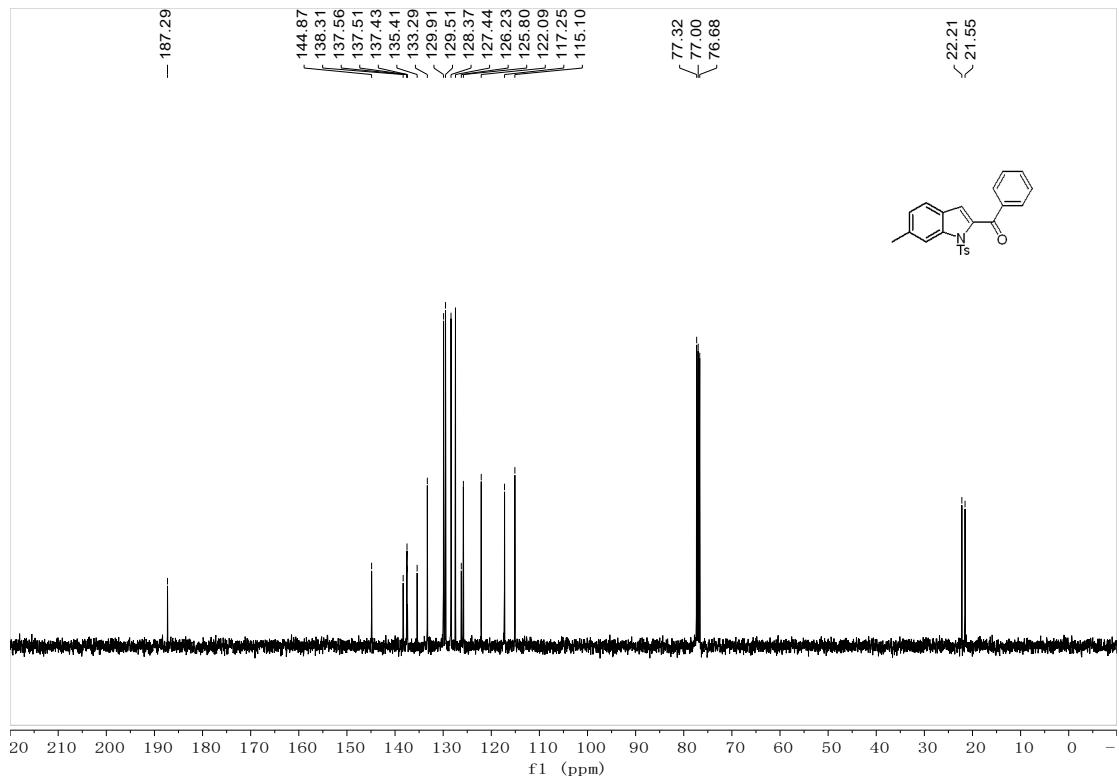
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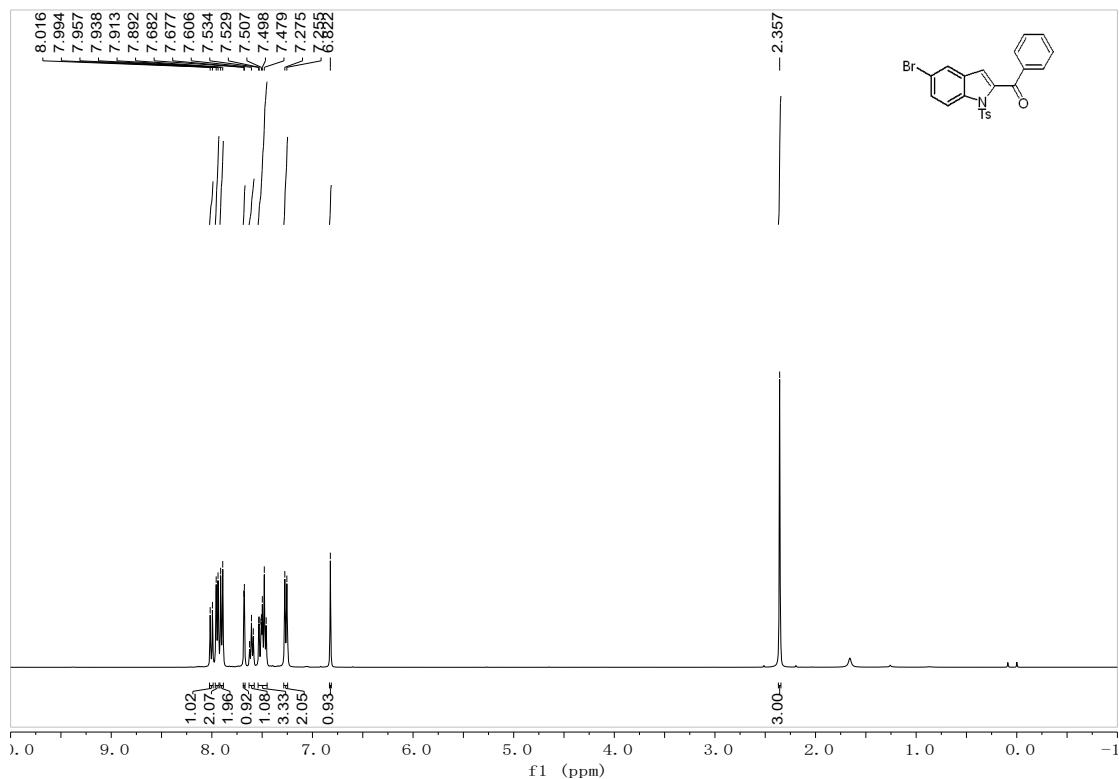
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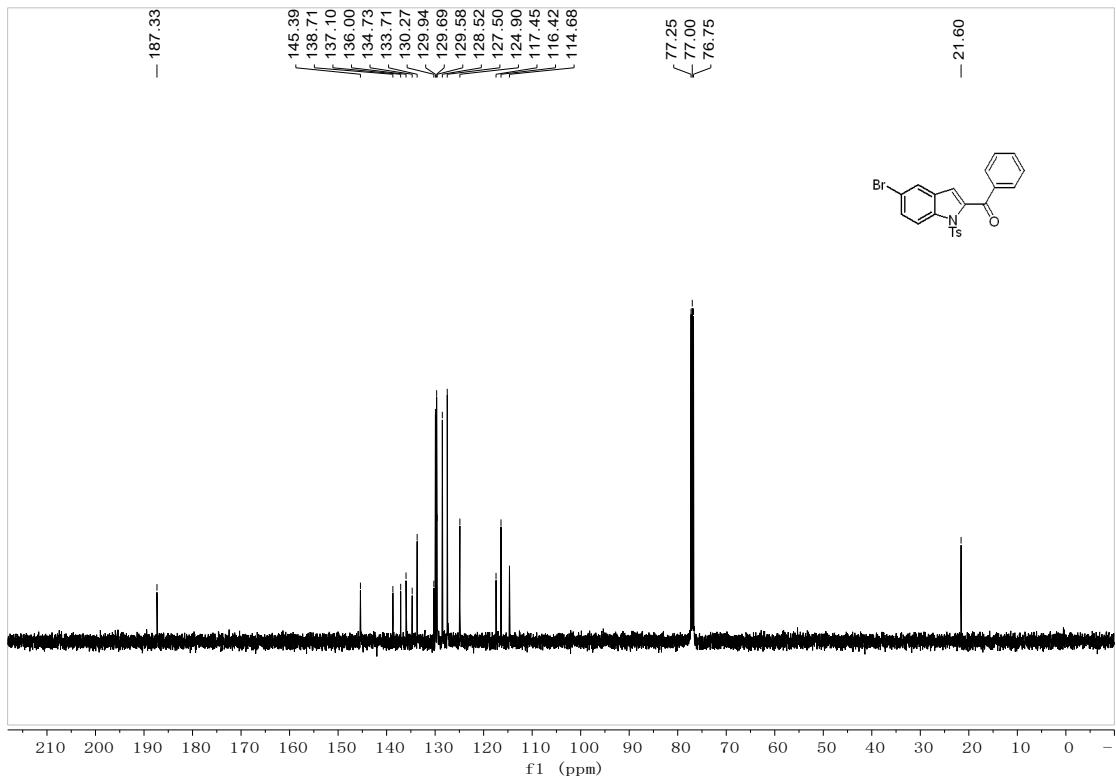
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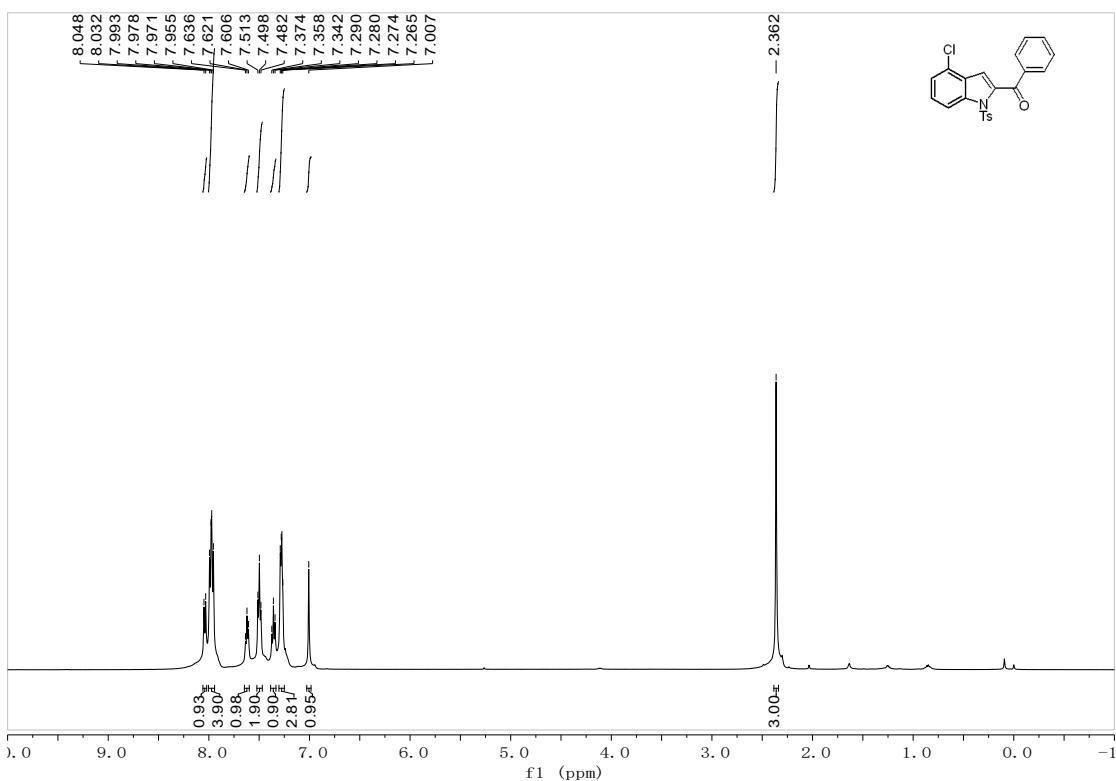
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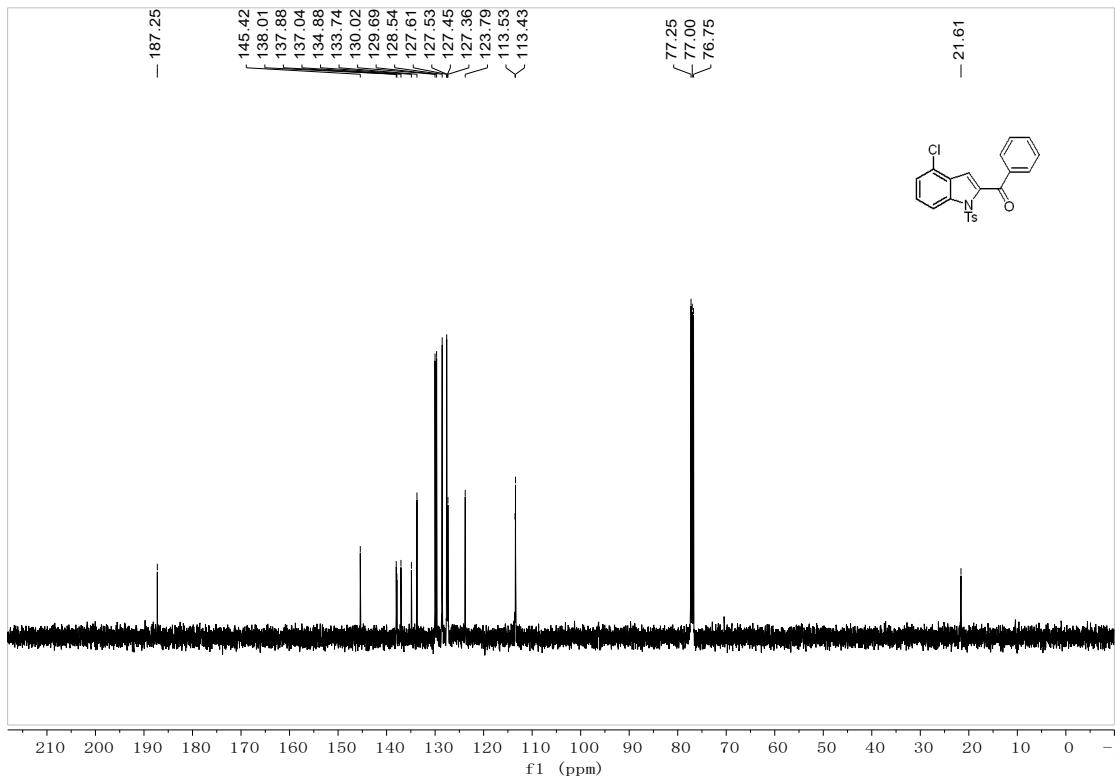
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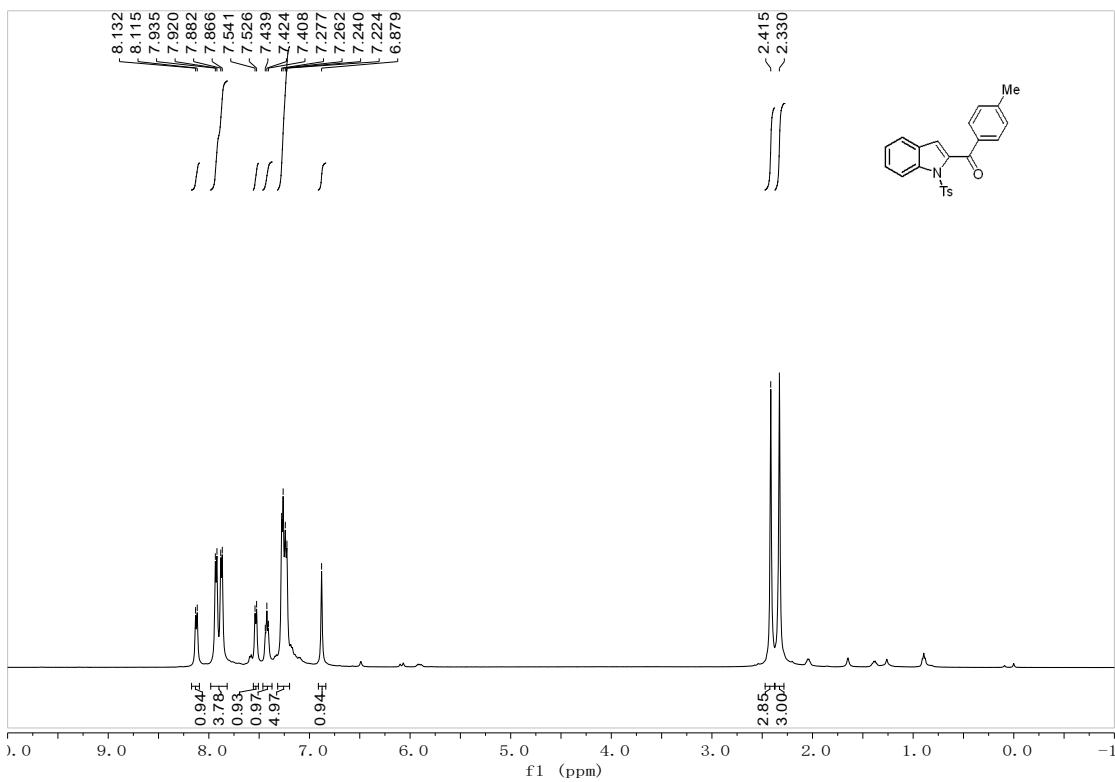
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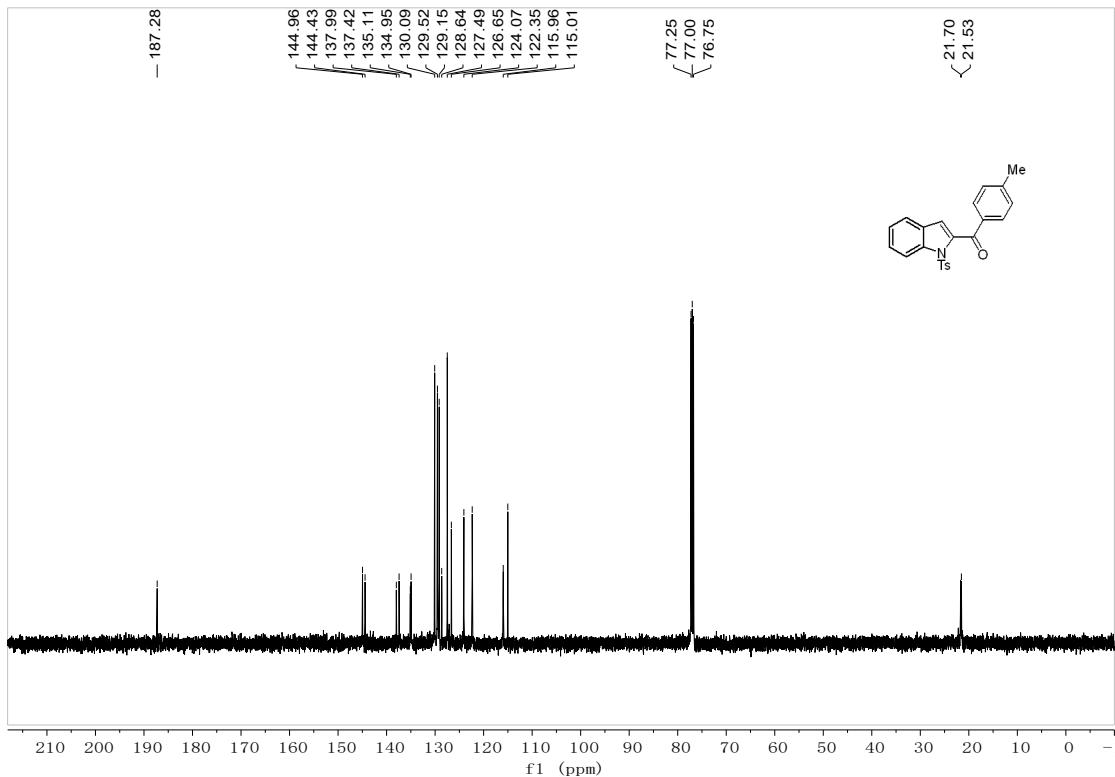
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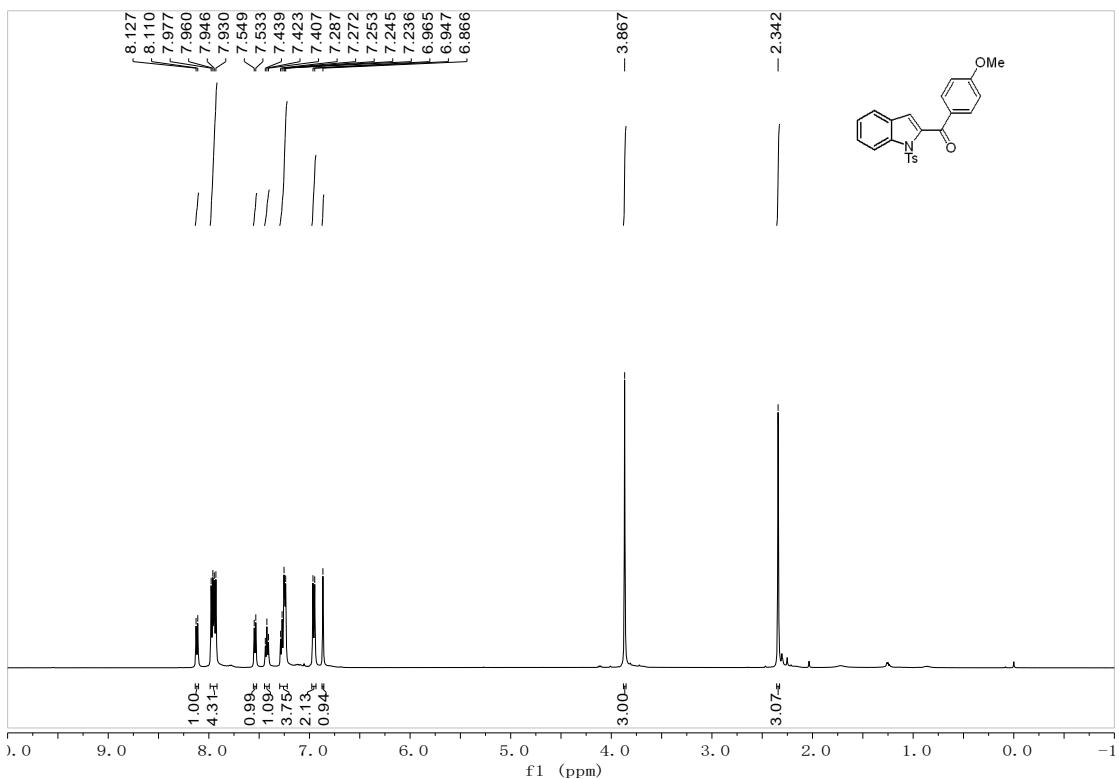
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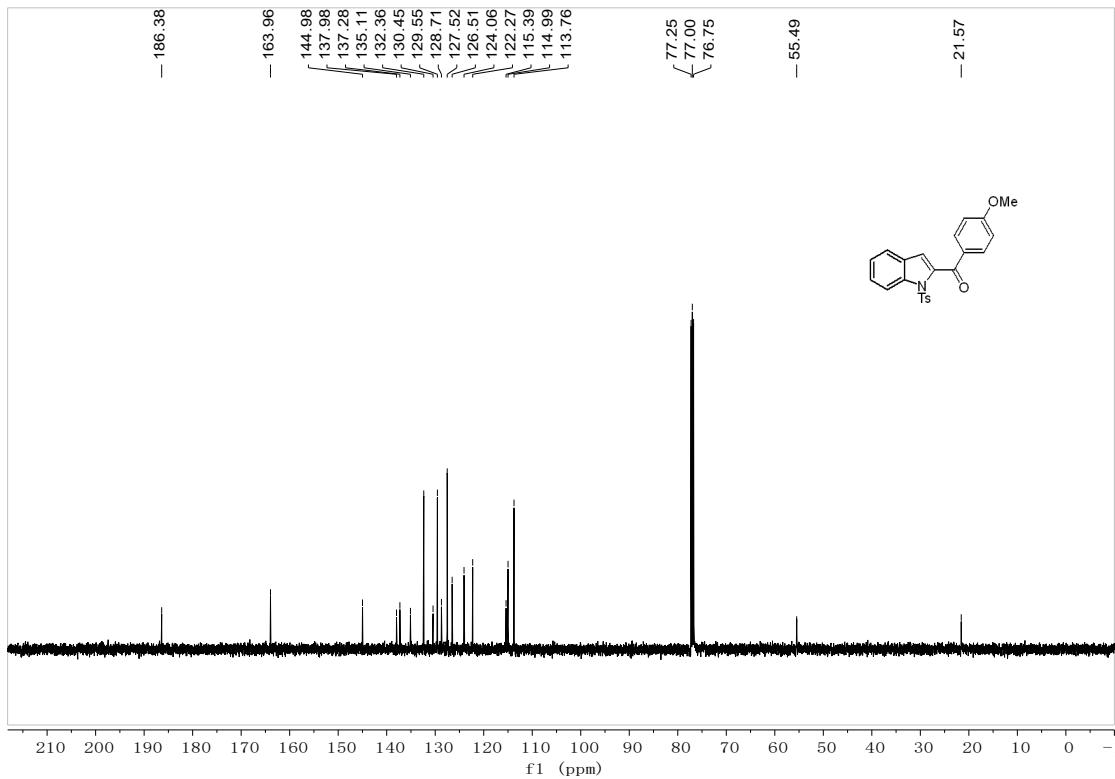
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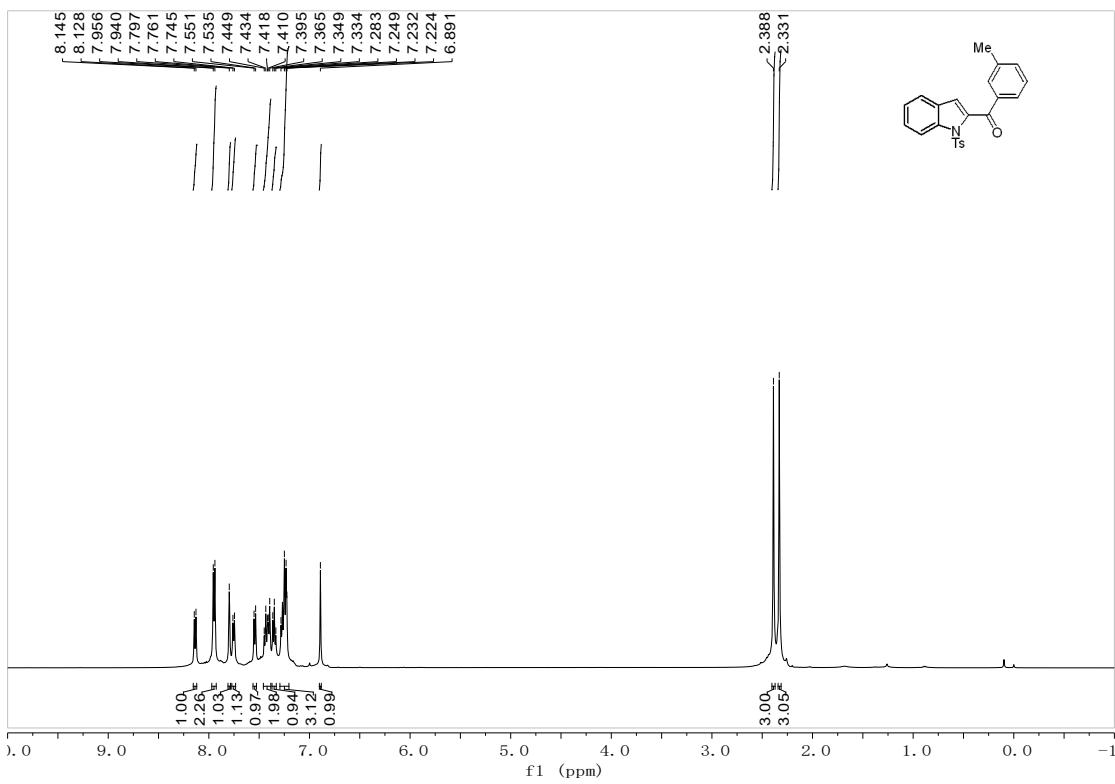
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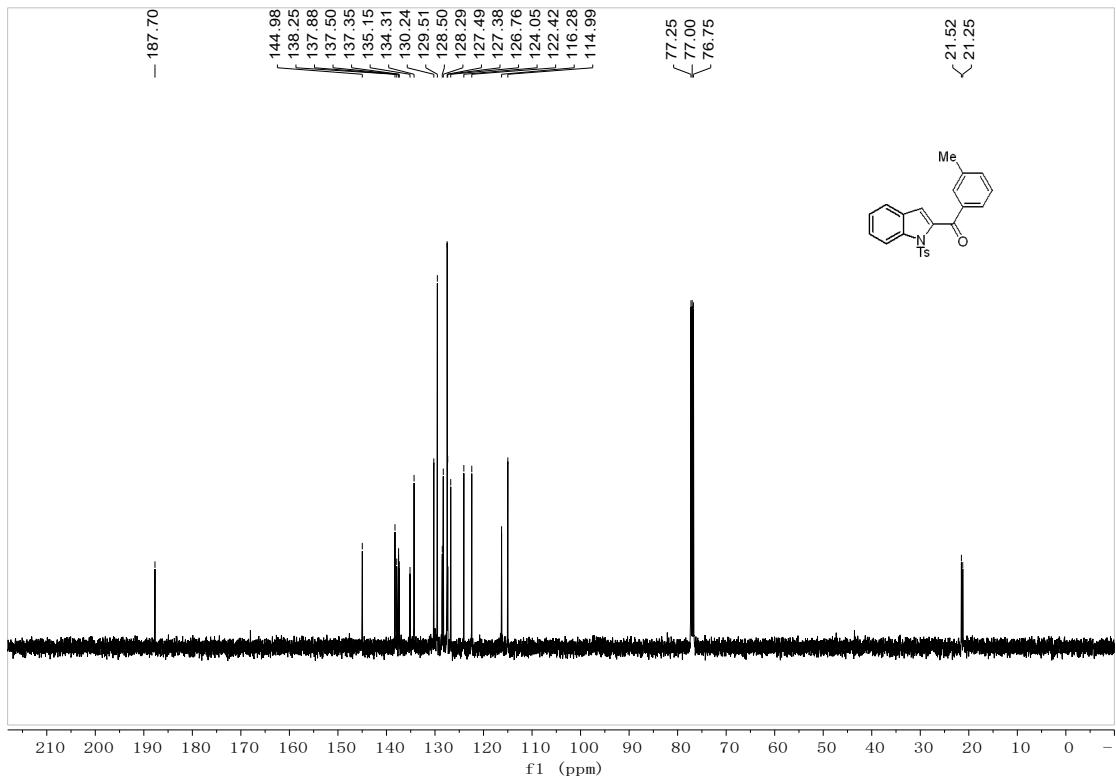
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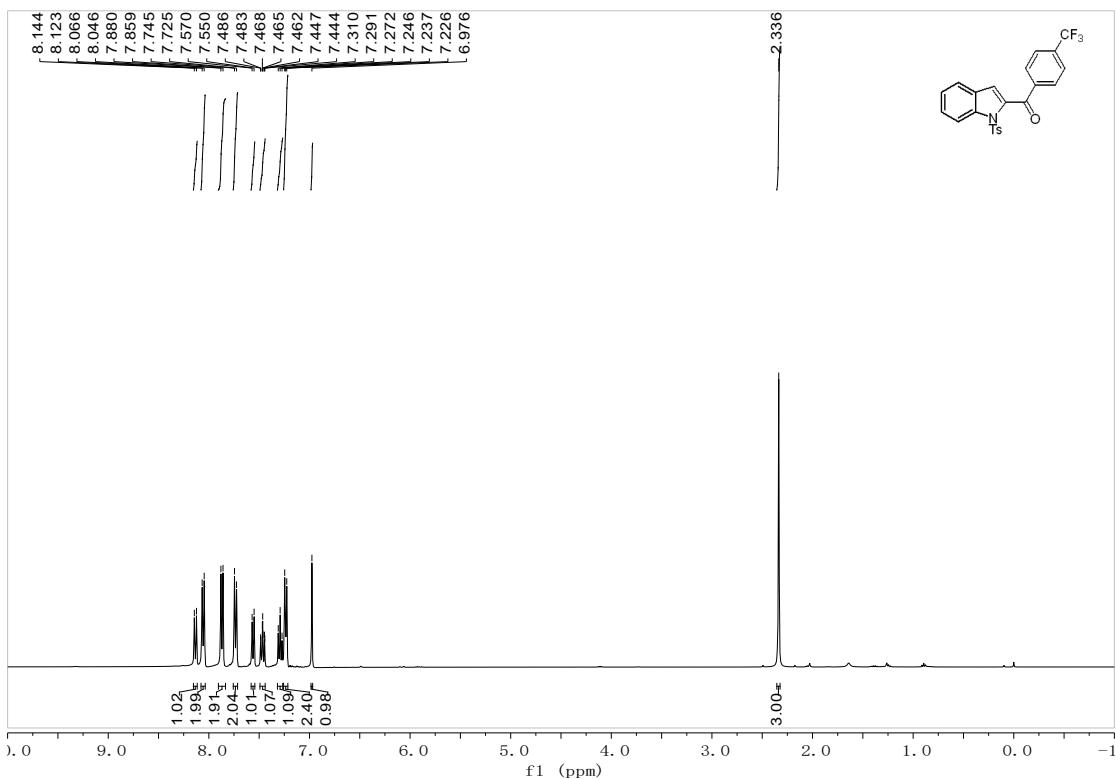
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectroscopy of **14h**



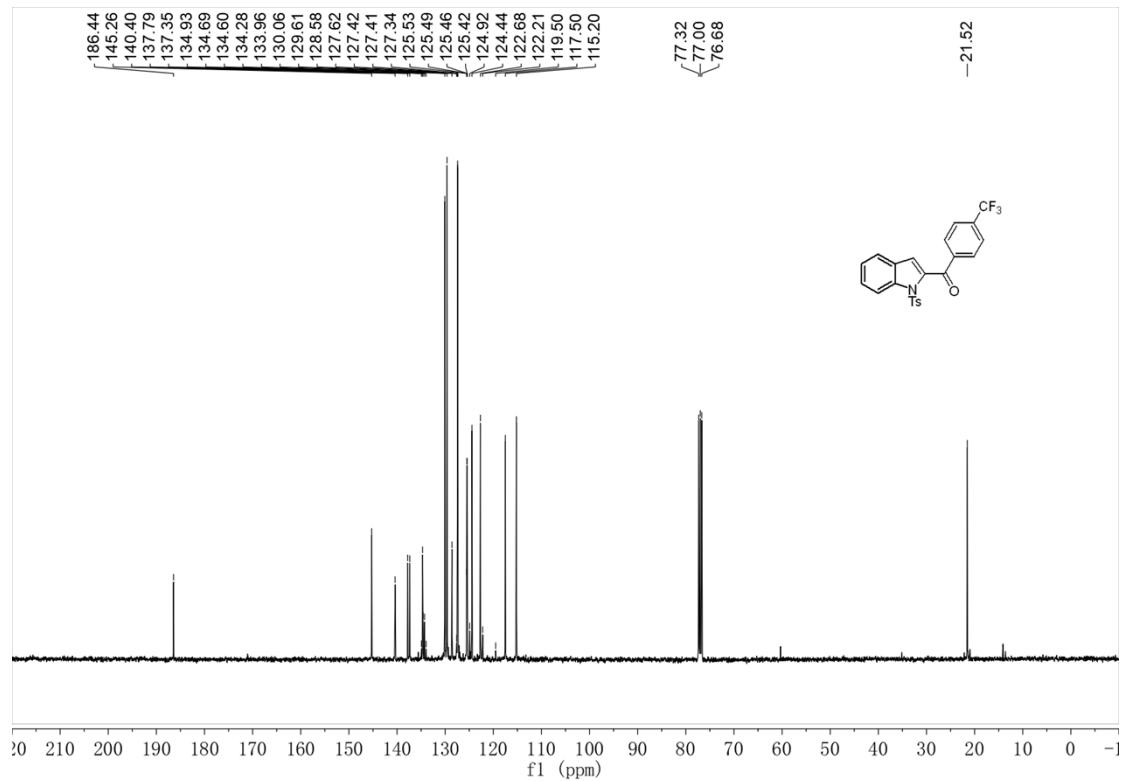
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectroscopy of **14h**



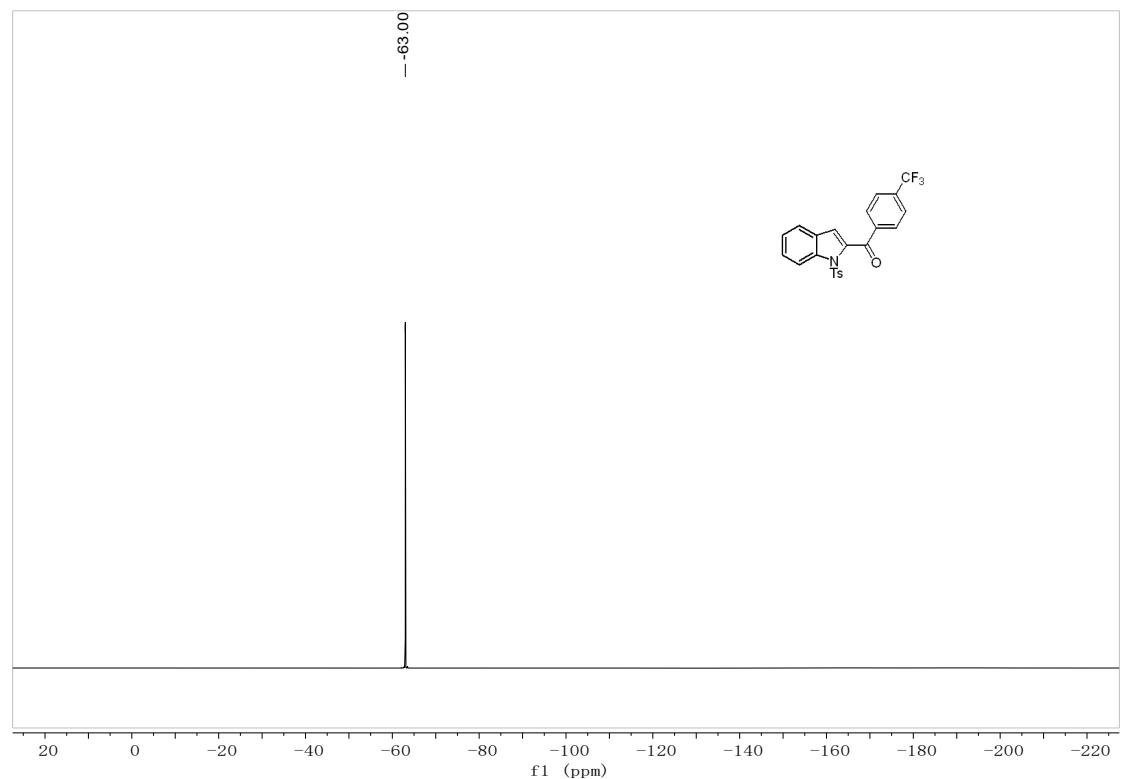
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectroscopy of **14i**



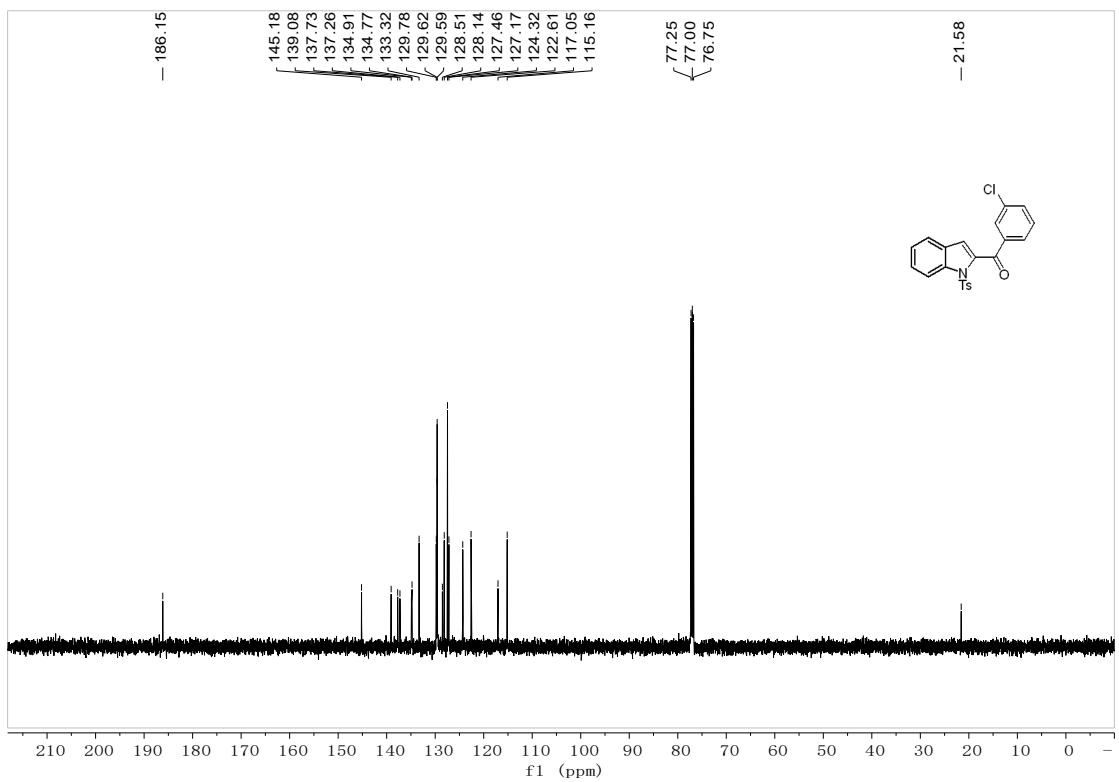
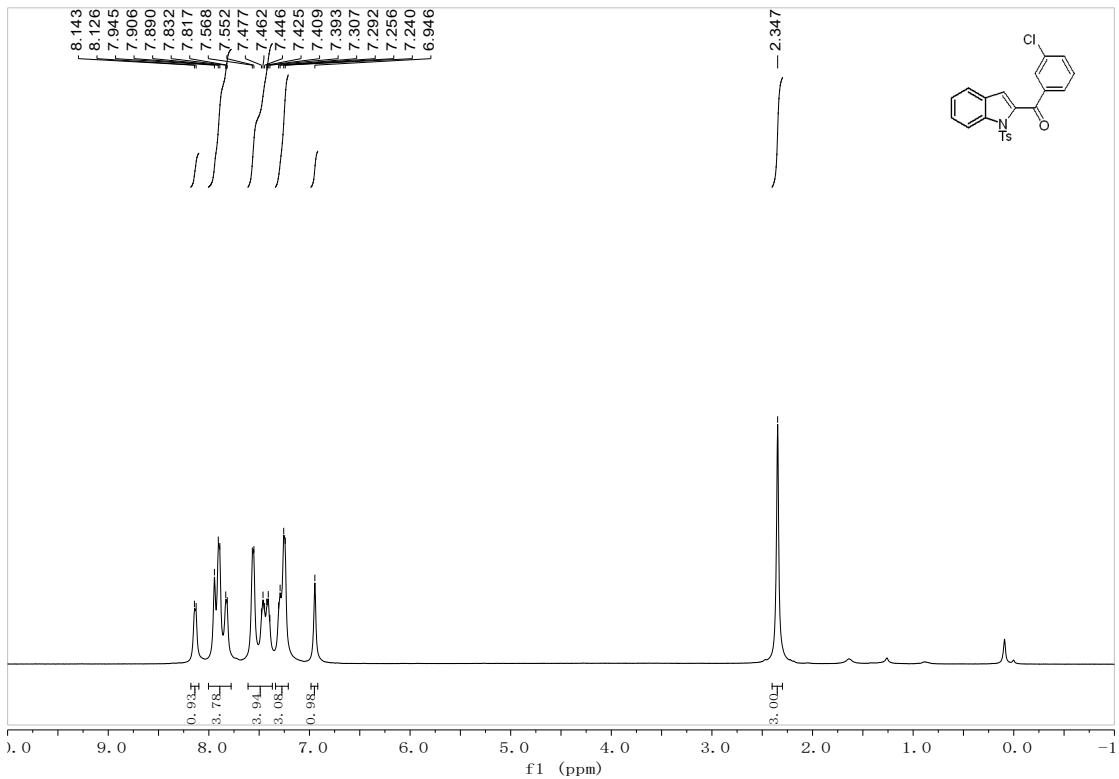
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectroscopy of **14i**



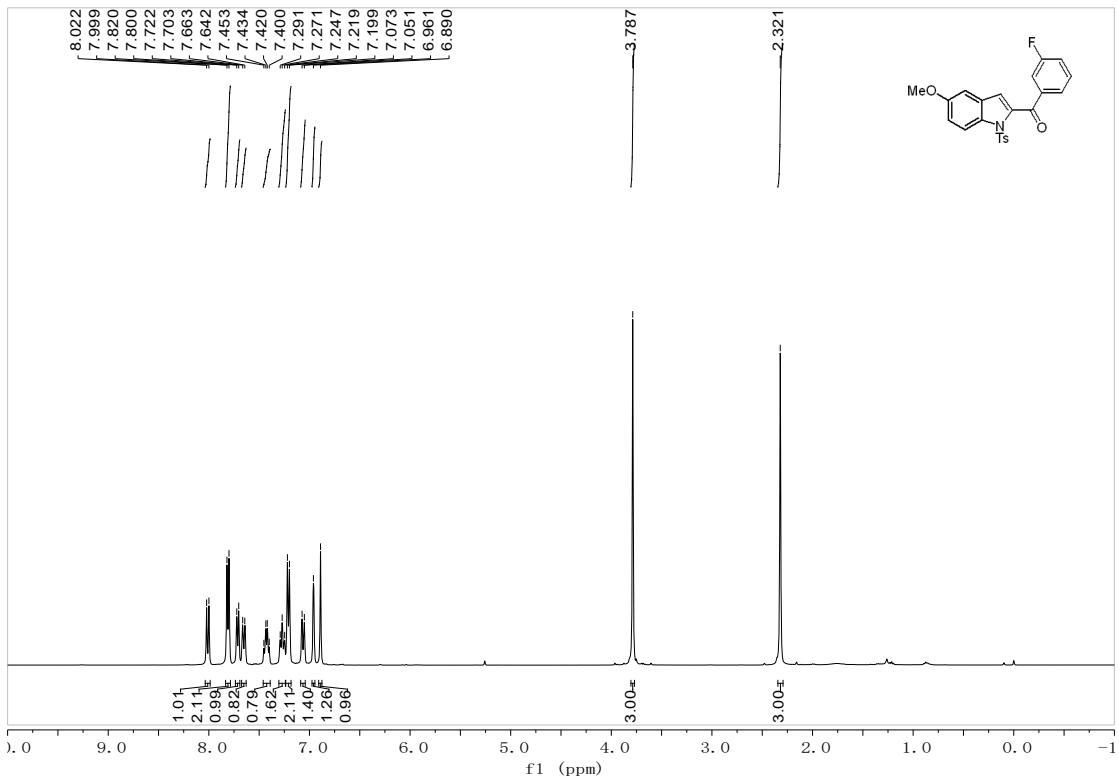
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) spectroscopy of **14i**



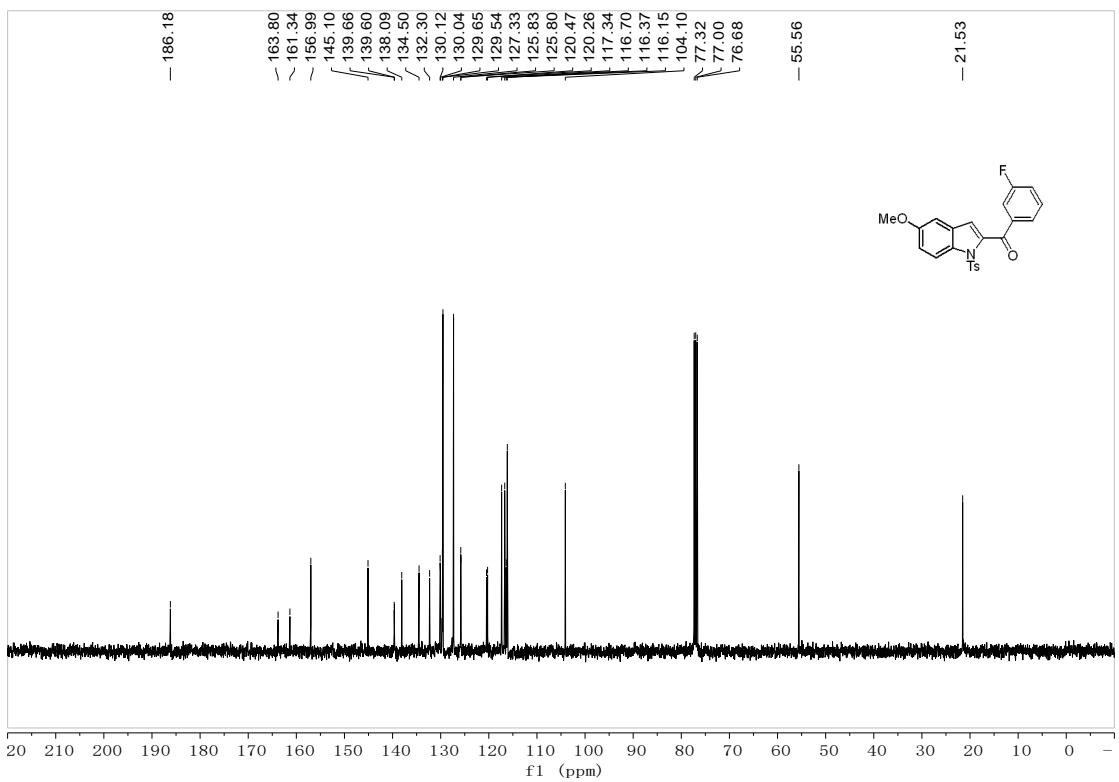
**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>) spectroscopy of **14j**



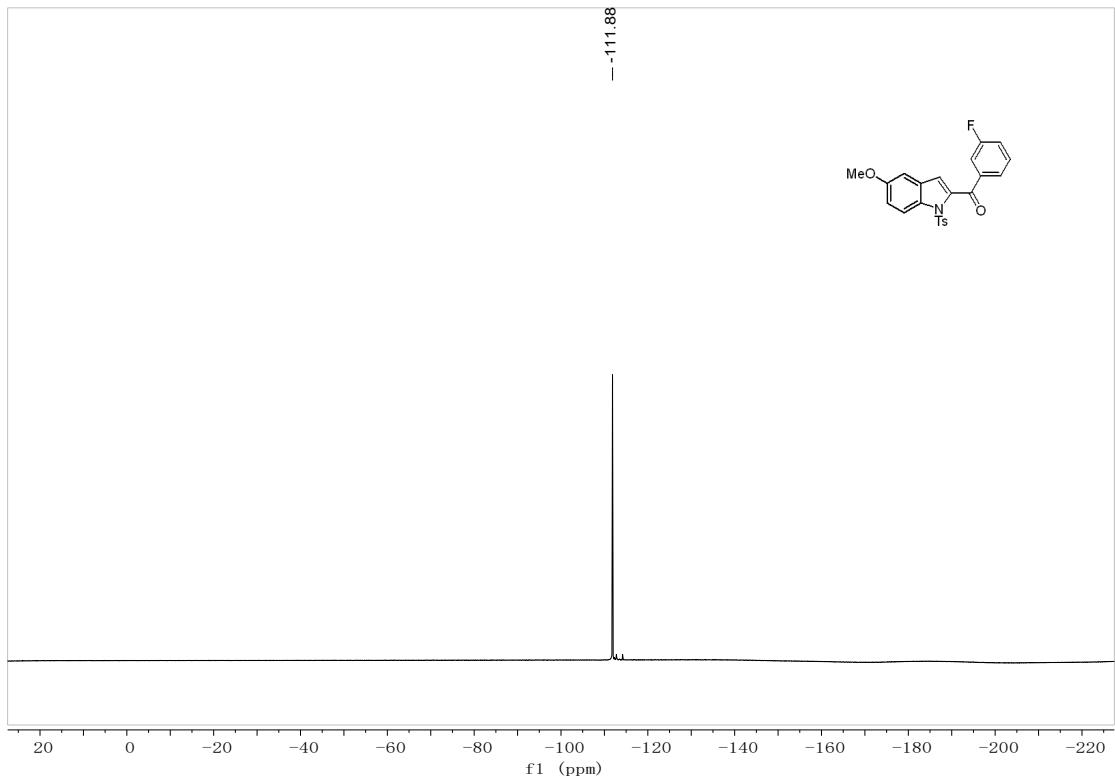
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectroscopy of **14k**



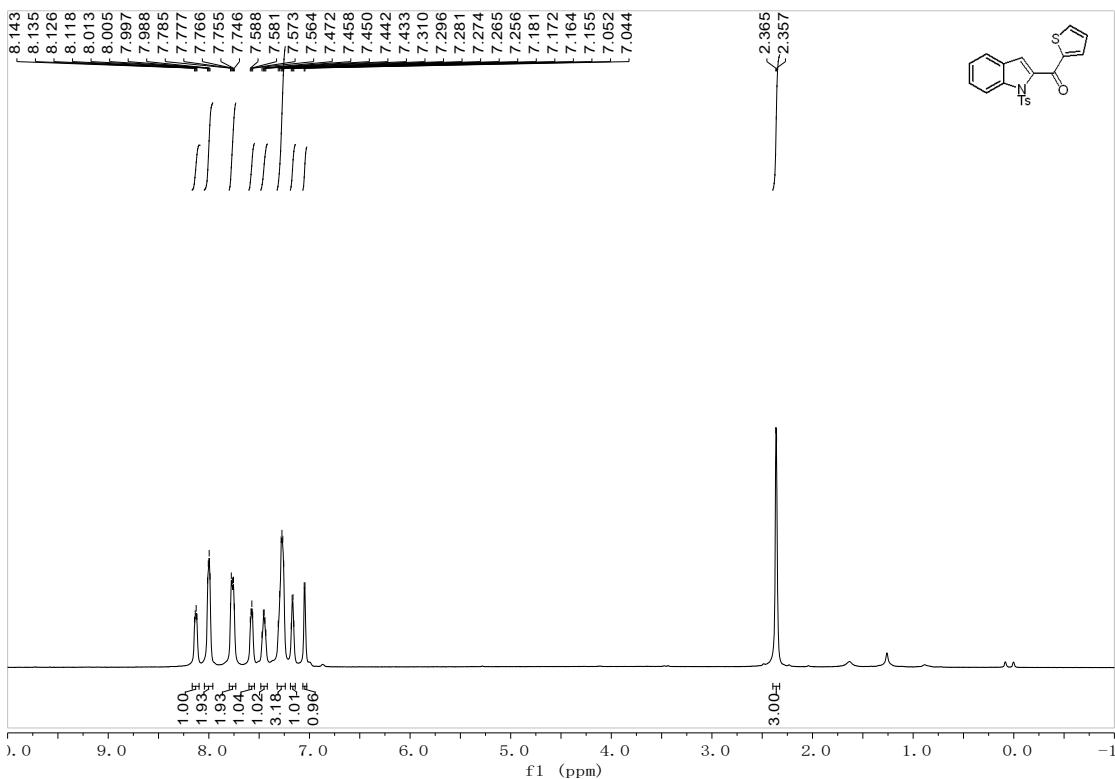
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) spectroscopy of **14k**



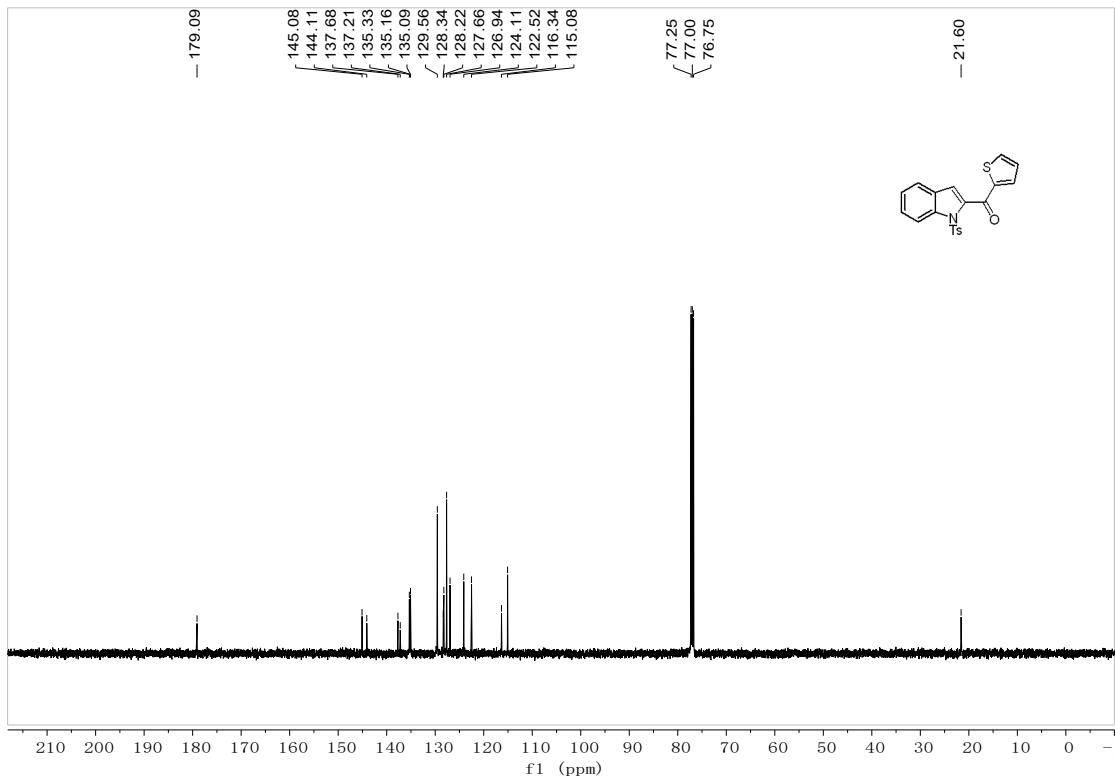
**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>) spectroscopy of **14k**



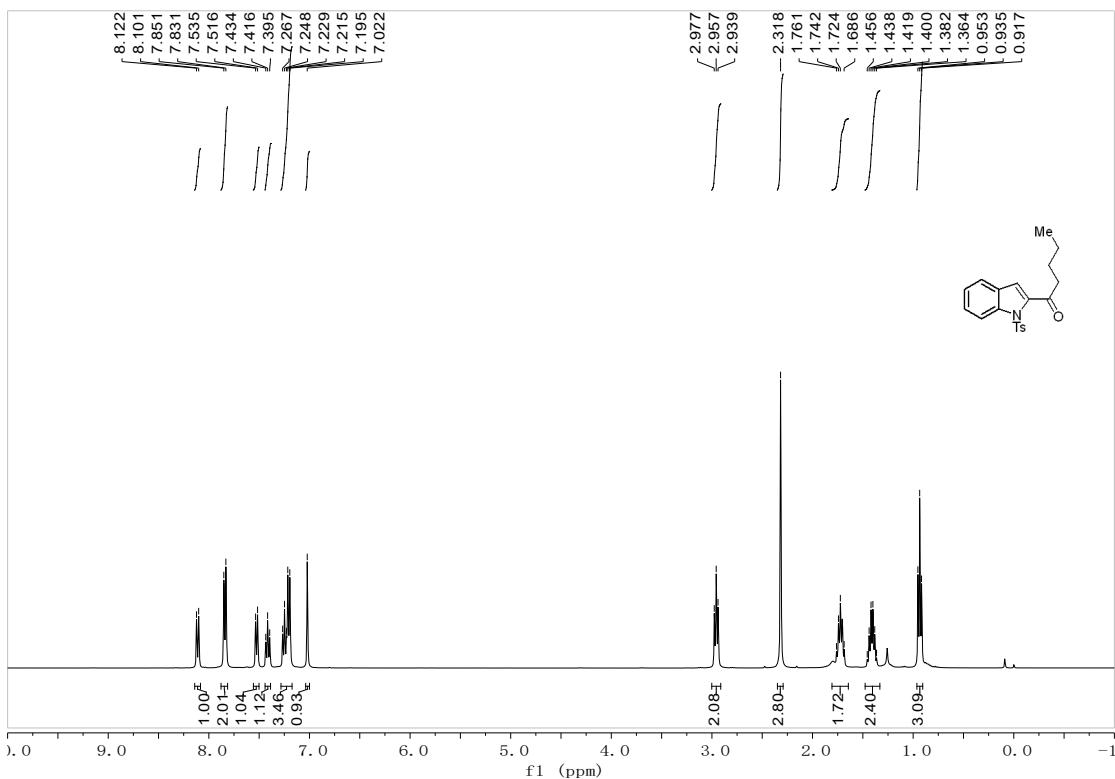
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectroscopy of 14l**



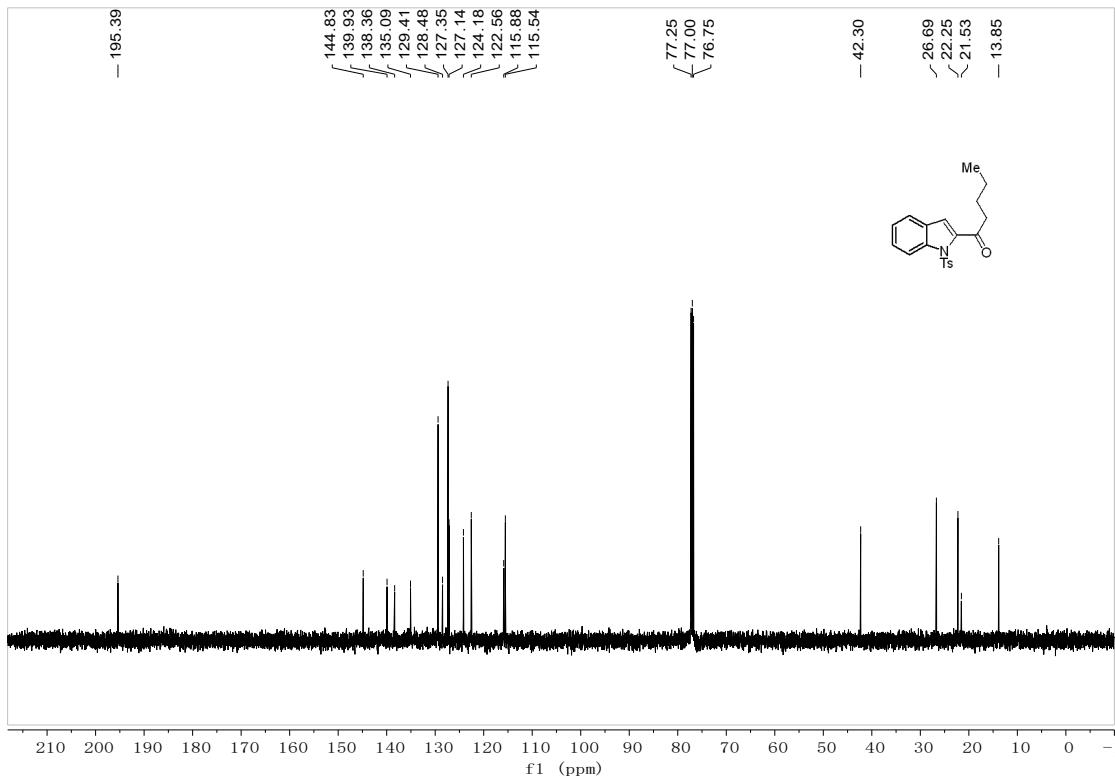
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectroscopy of 14l**



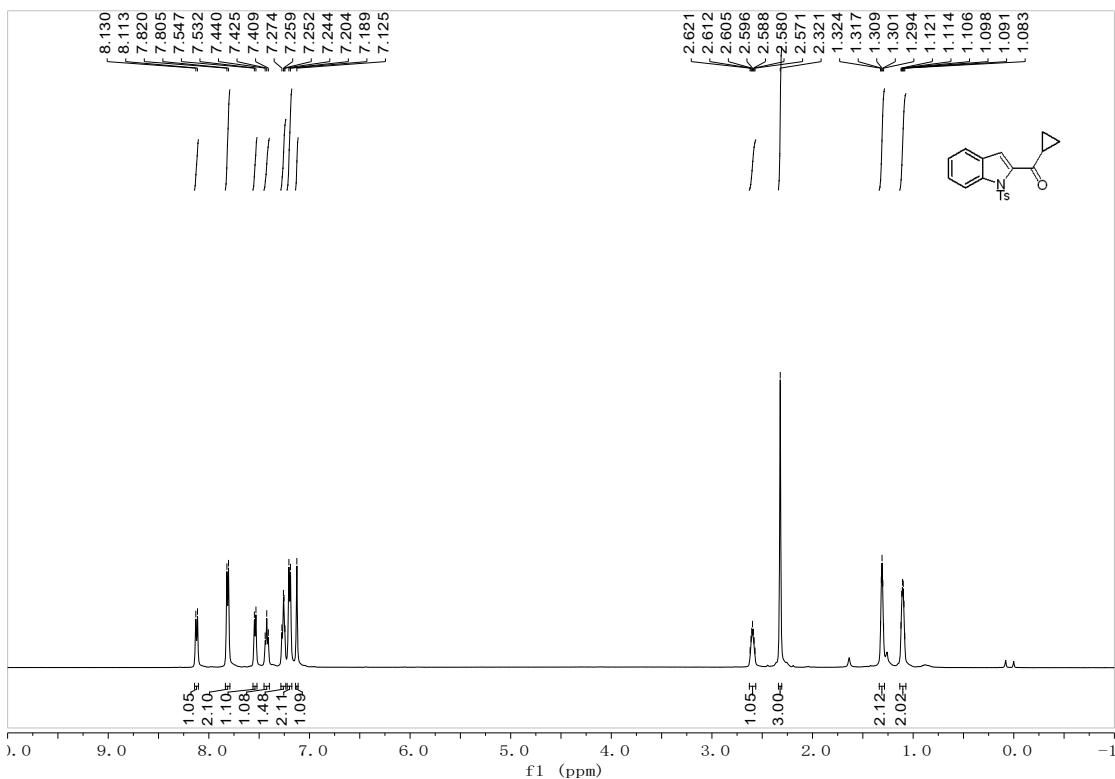
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) spectroscopy of **14m**



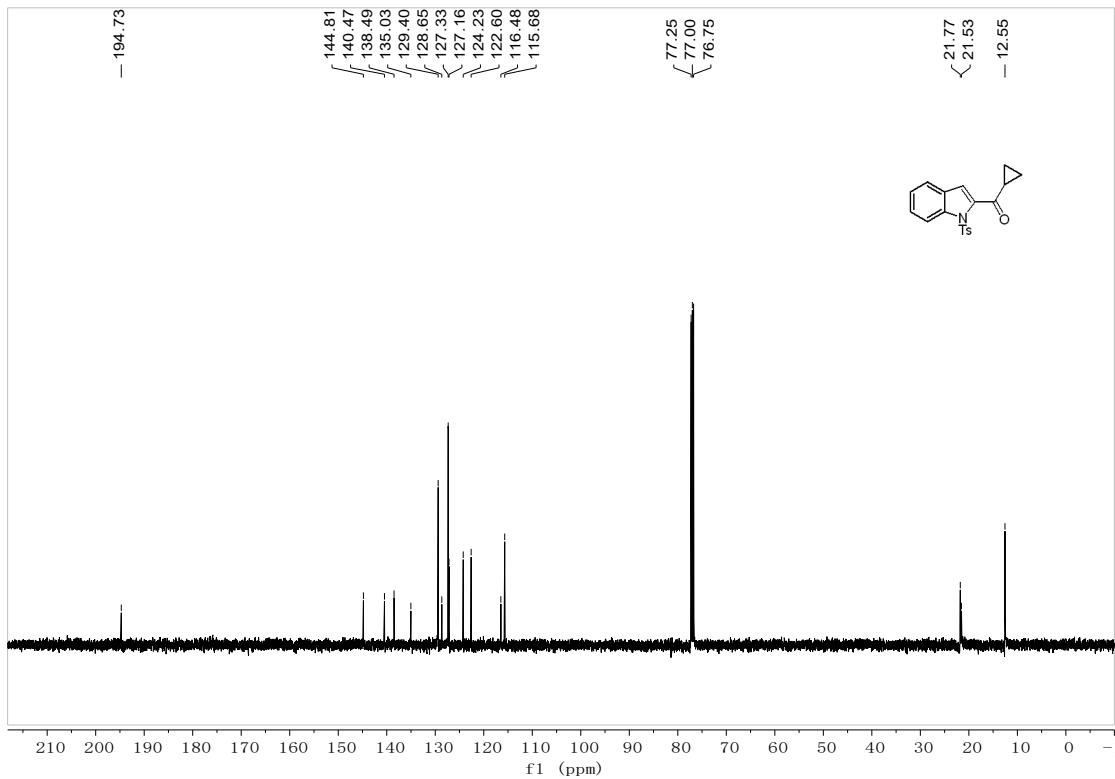
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>) spectroscopy of **14m**



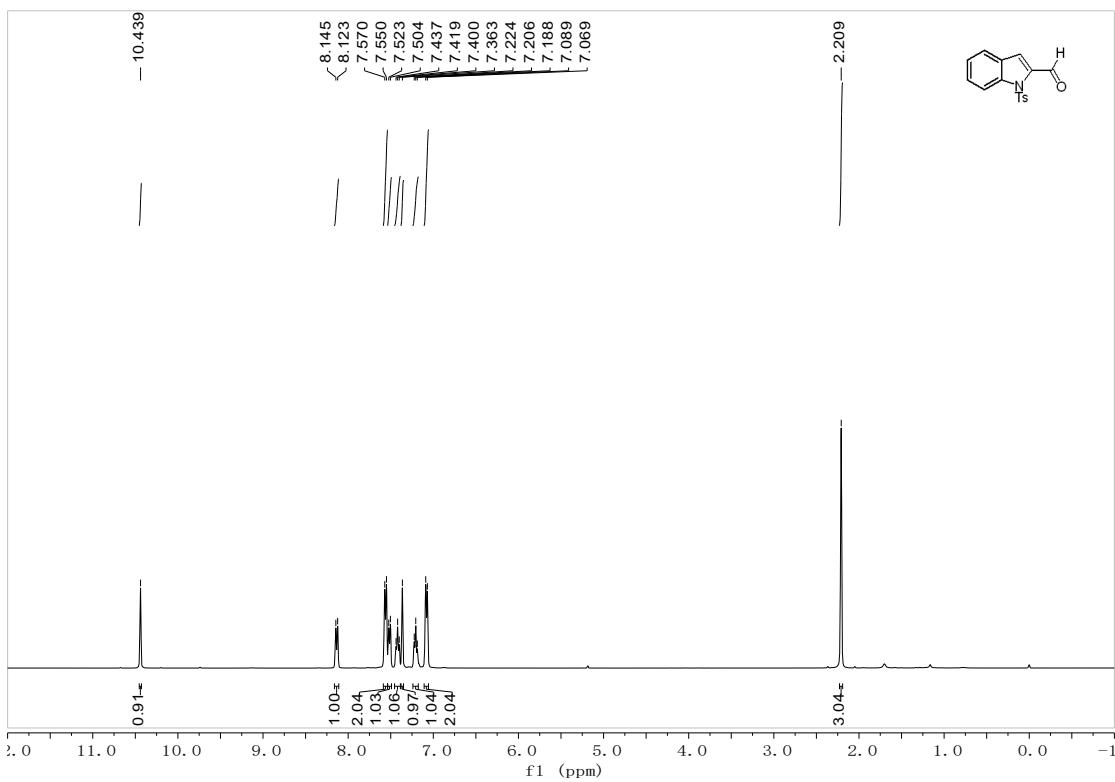
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectroscopy of **14n**



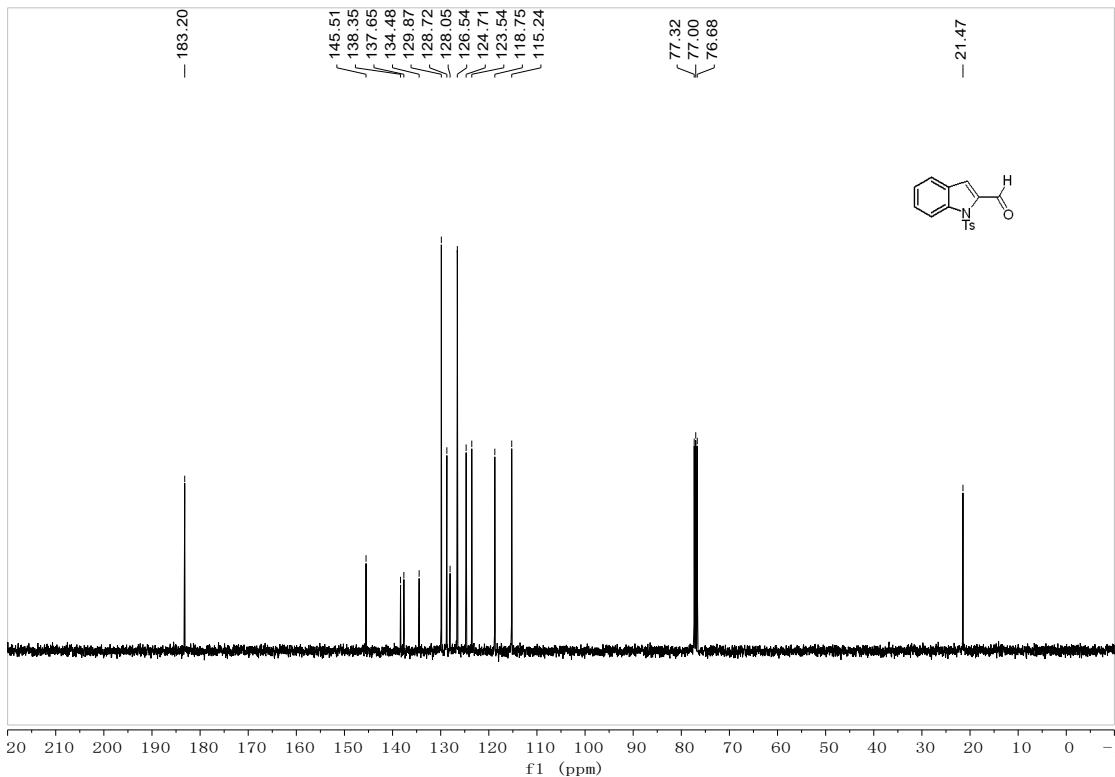
$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ) spectroscopy of **14n**



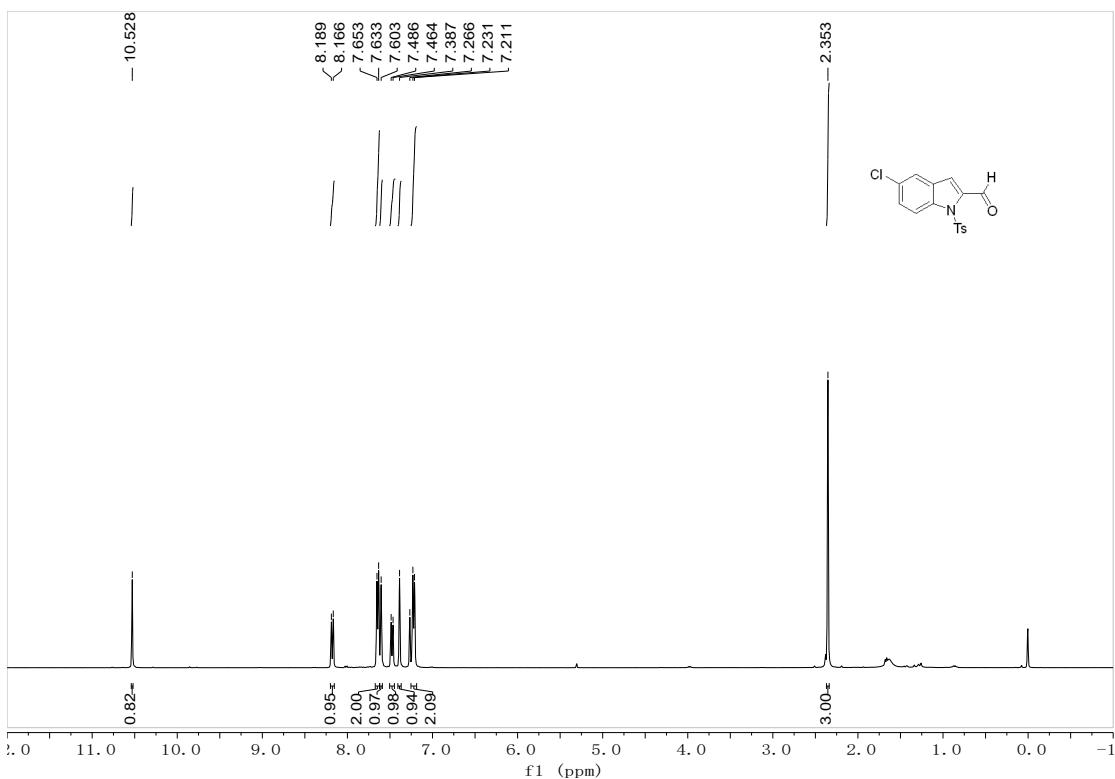
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectroscopy of **14o****



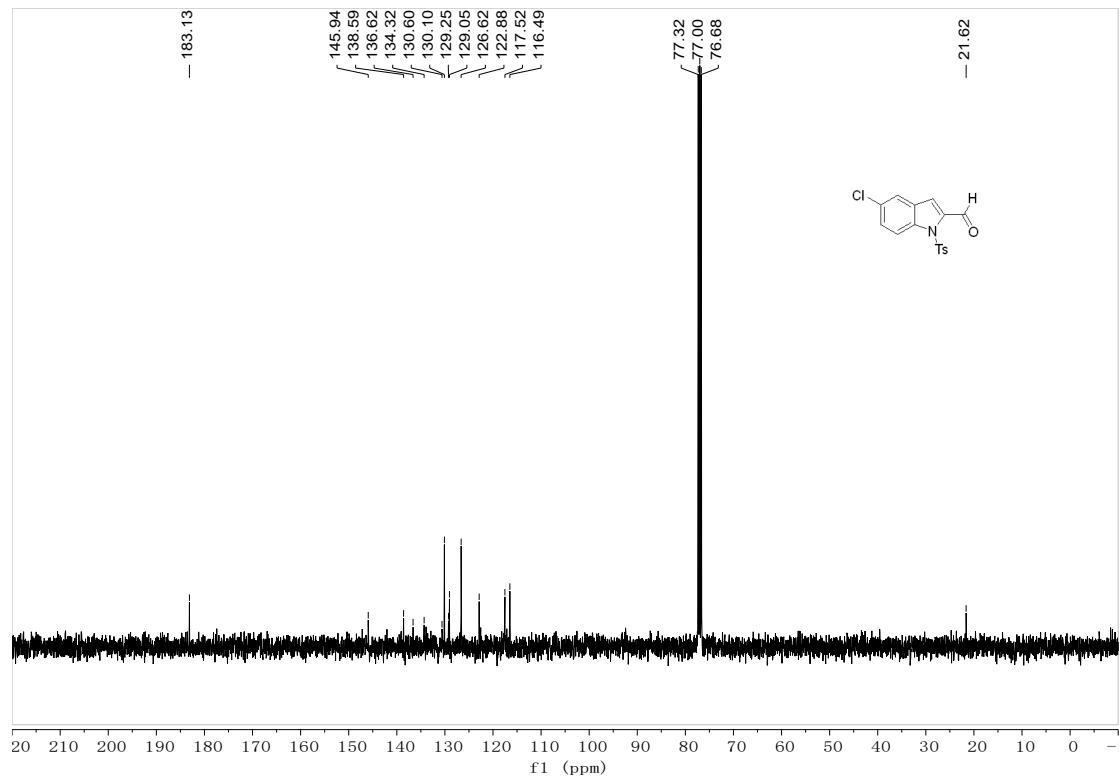
**$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectroscopy of **14o****



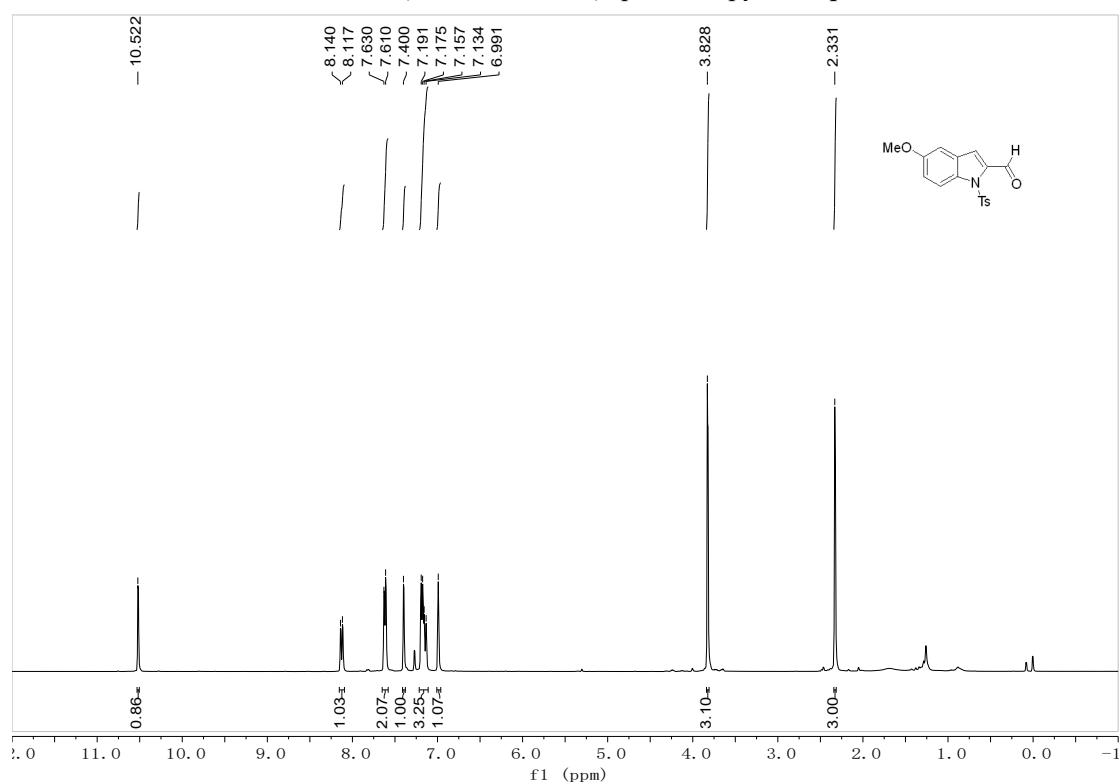
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectroscopy of **14p**



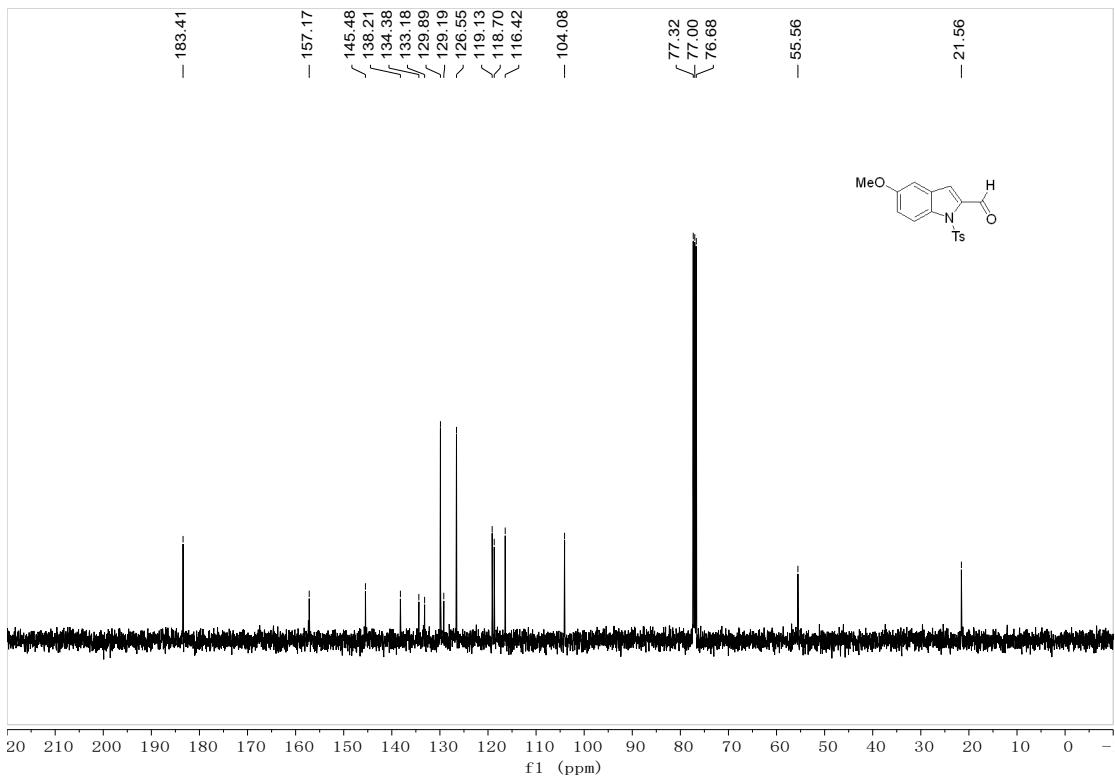
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectroscopy of **14p**



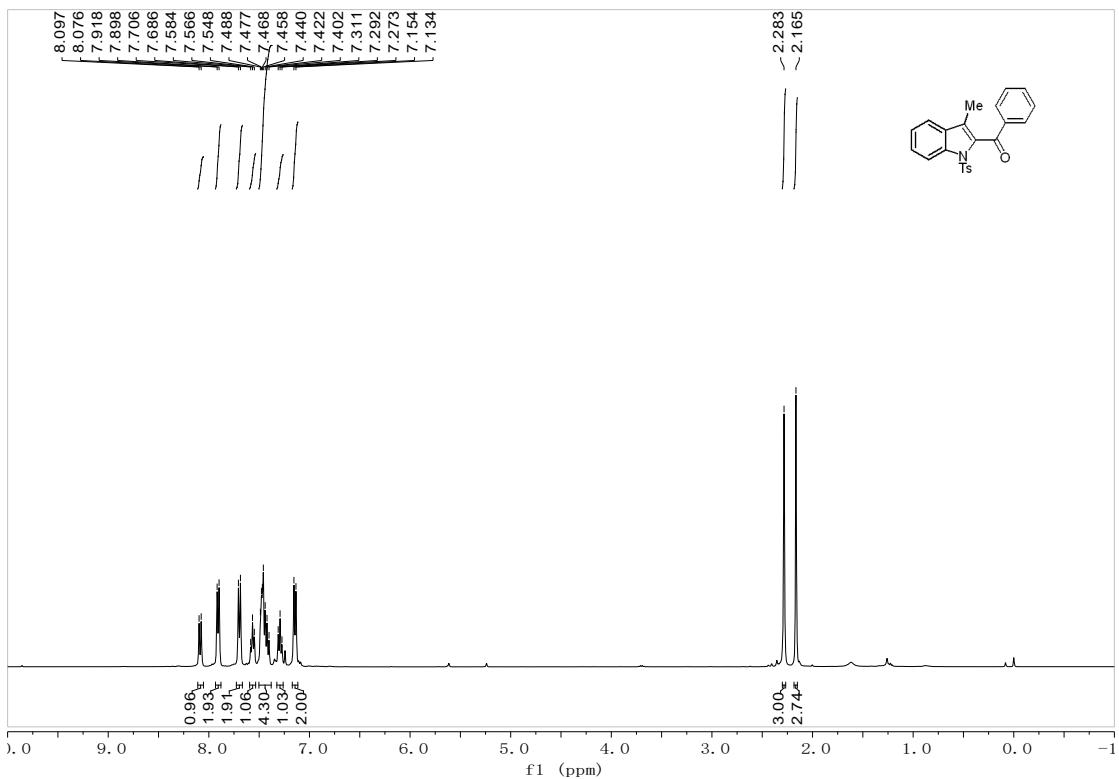
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectroscopy of **14q**



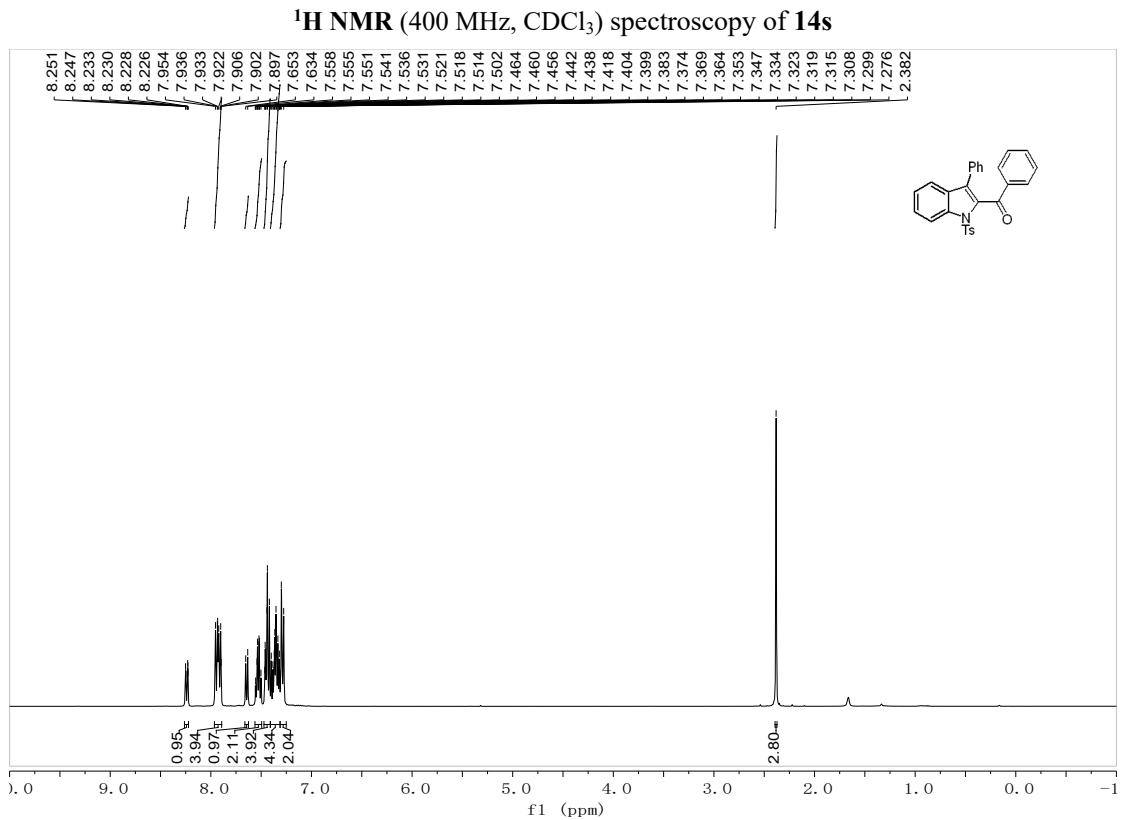
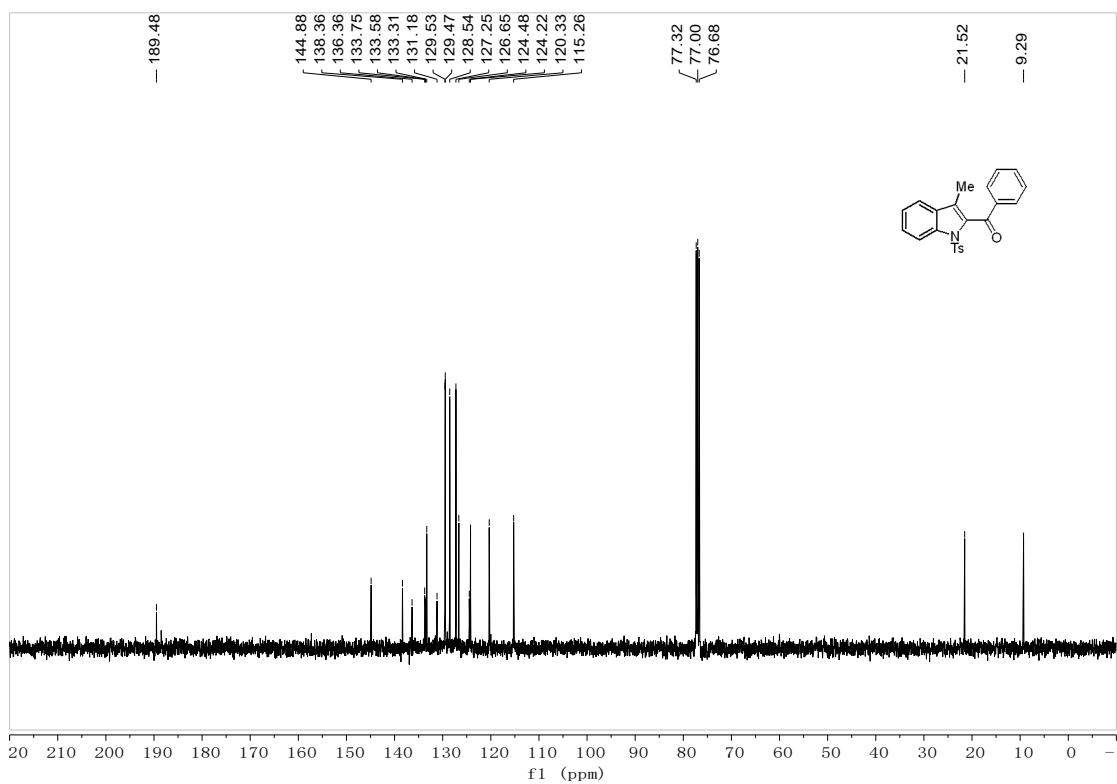
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectroscopy of **14q**



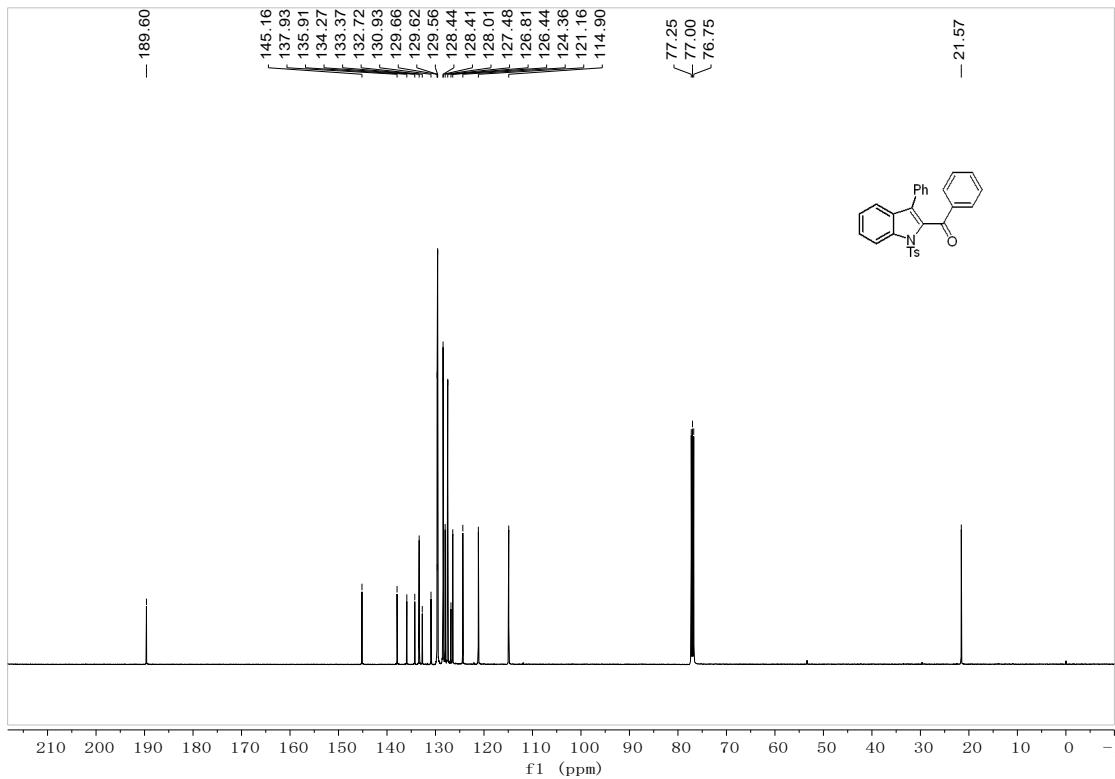
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectroscopy of 14r



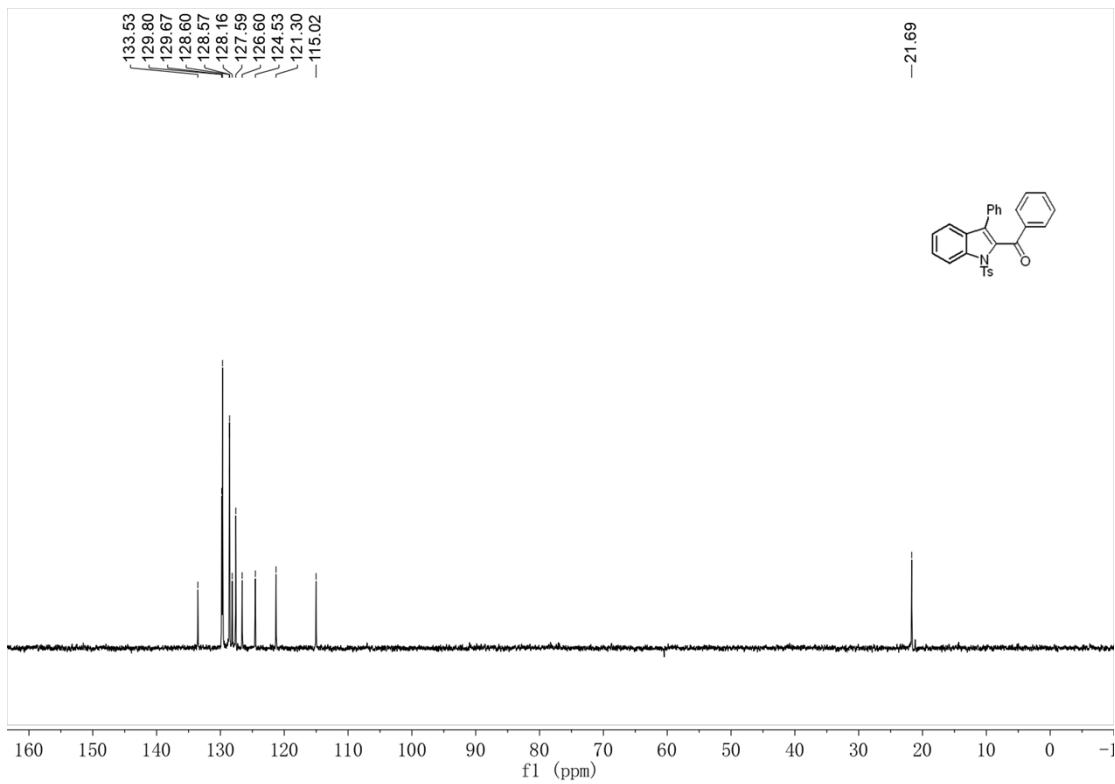
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectroscopy of 14r



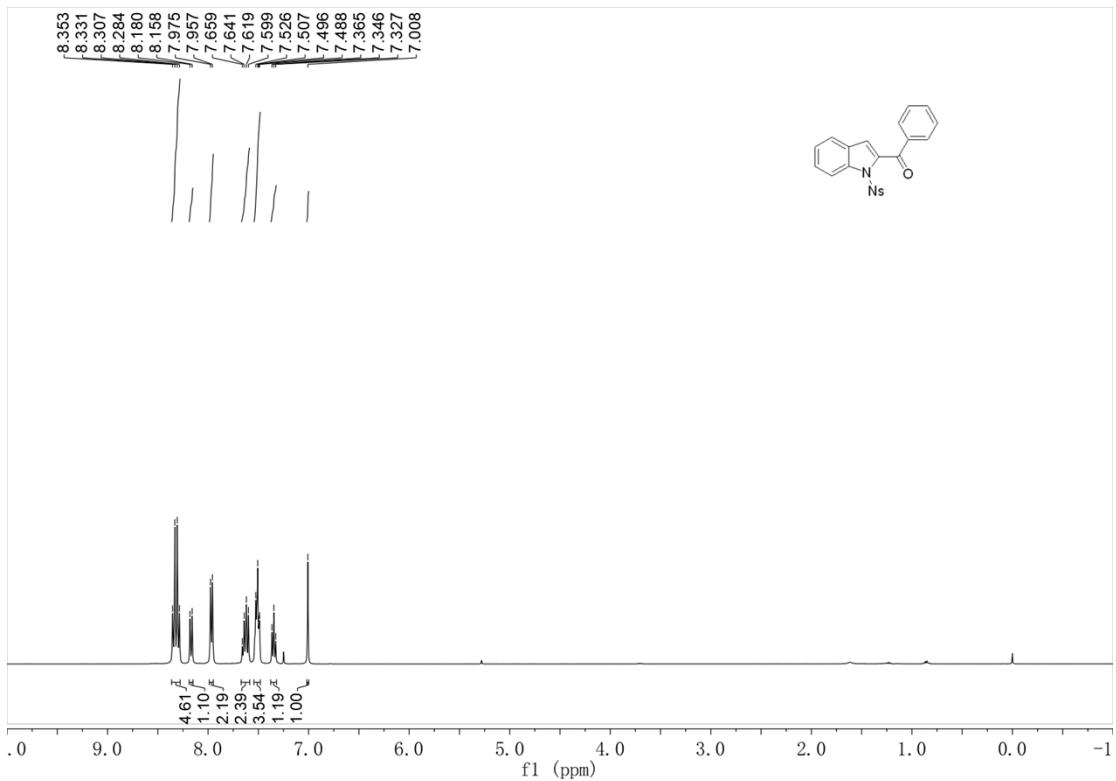
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectrum of **14s**



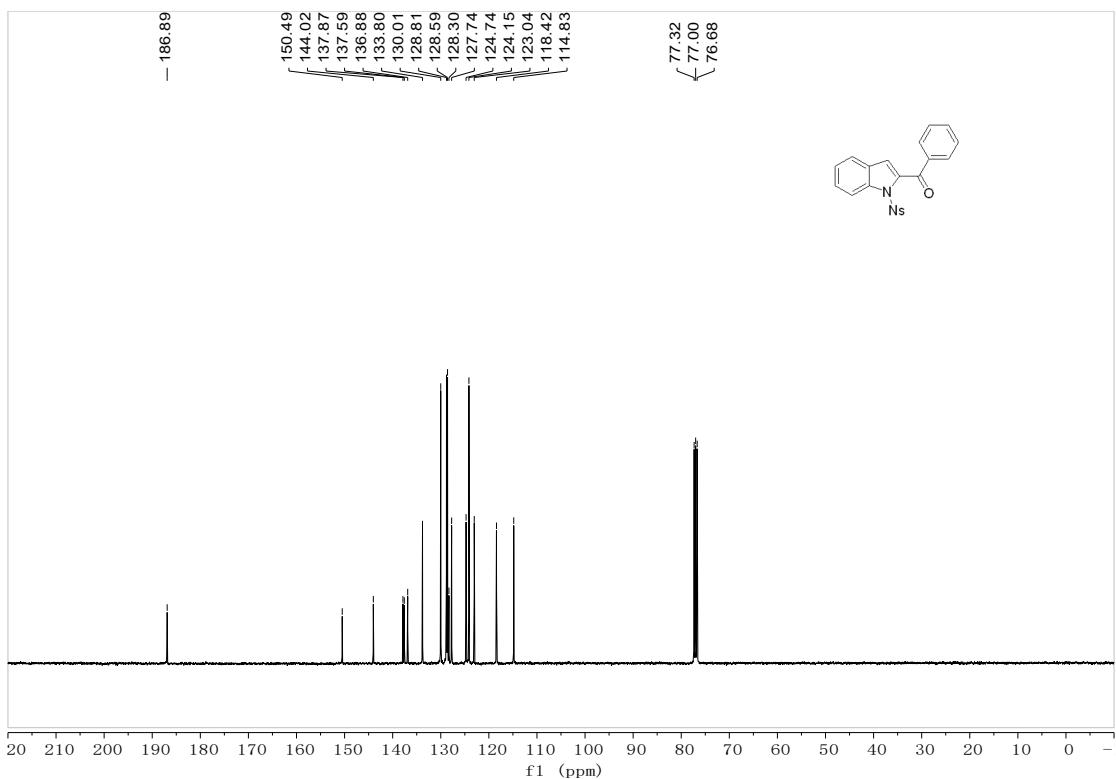
**DEPT ( $\theta = 135^\circ$ , 100 MHz,  $\text{CDCl}_3$ ) spectroscopy of **14s****



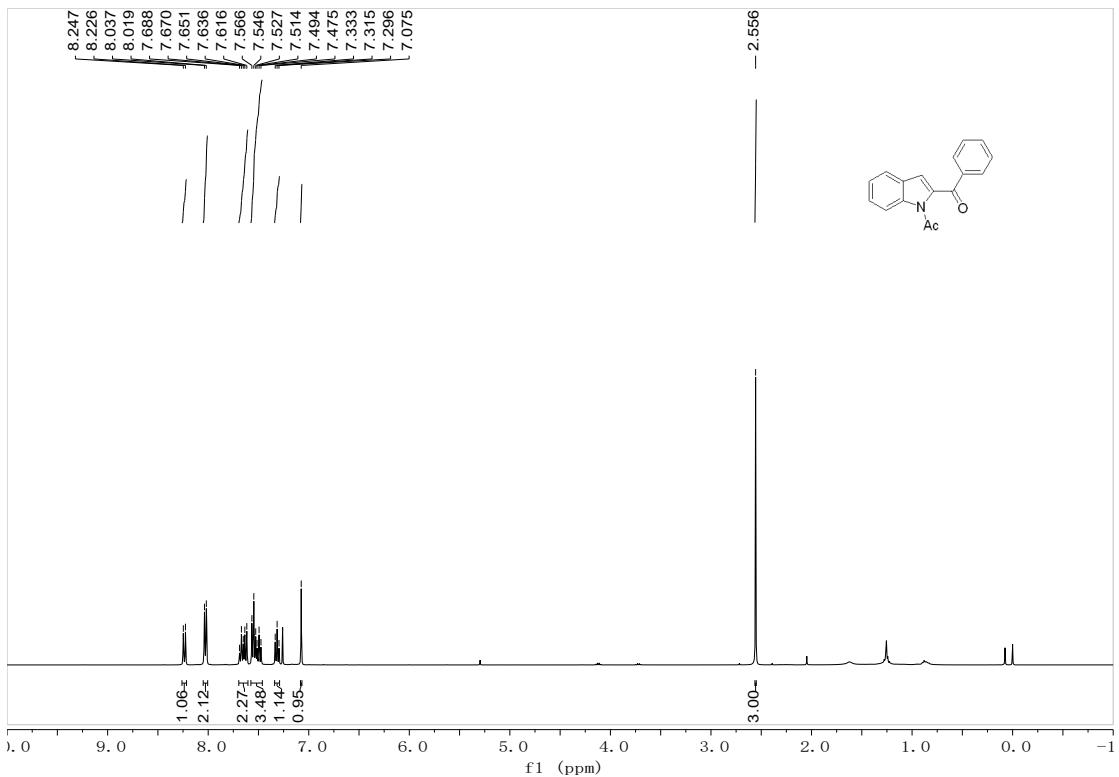
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) spectroscopy of **14t****



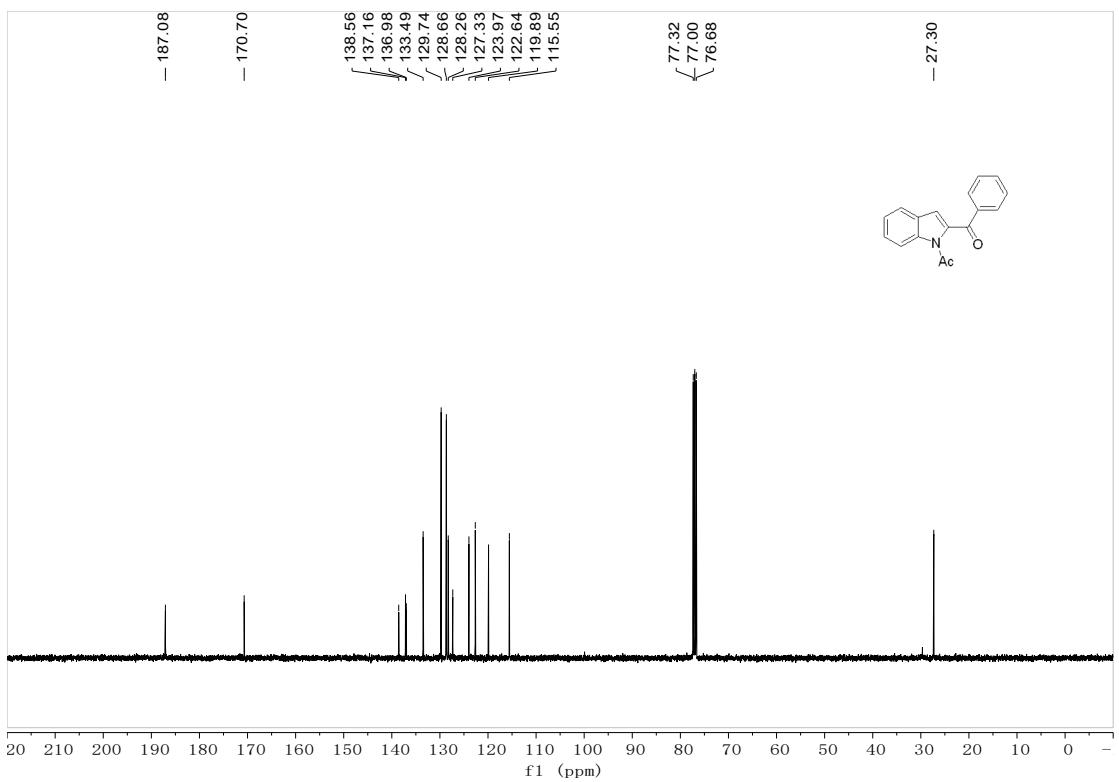
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectroscopy of **14t**



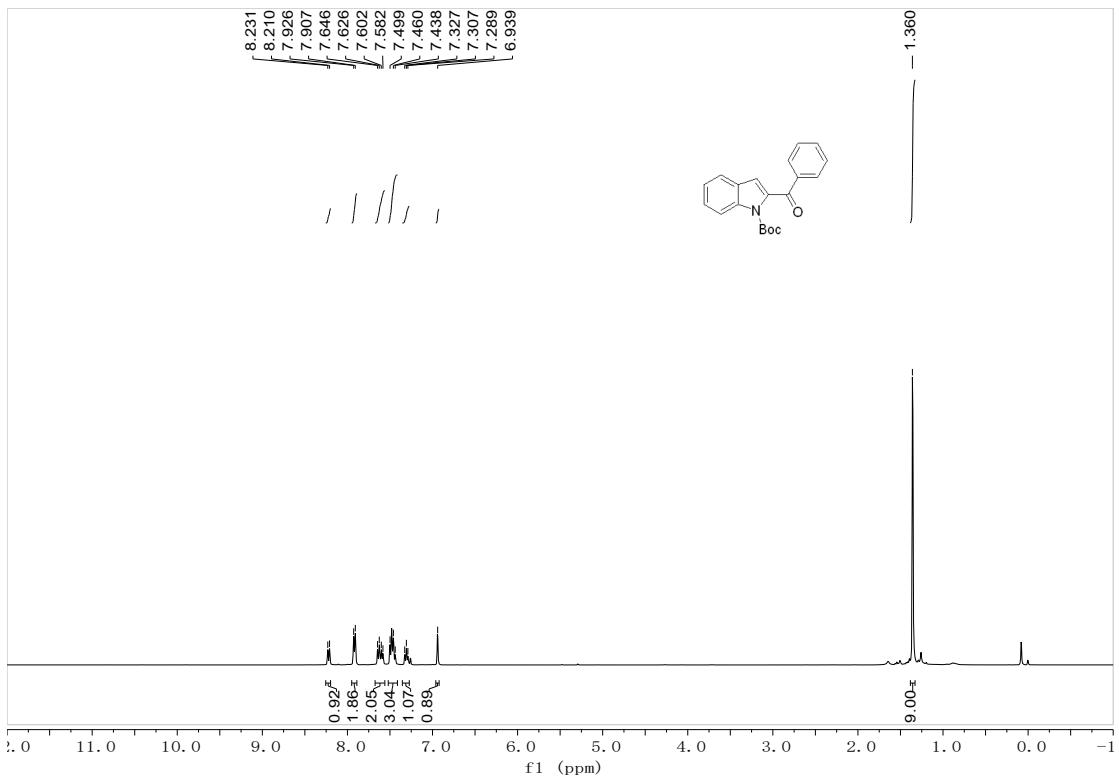
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectroscopy of **14u**



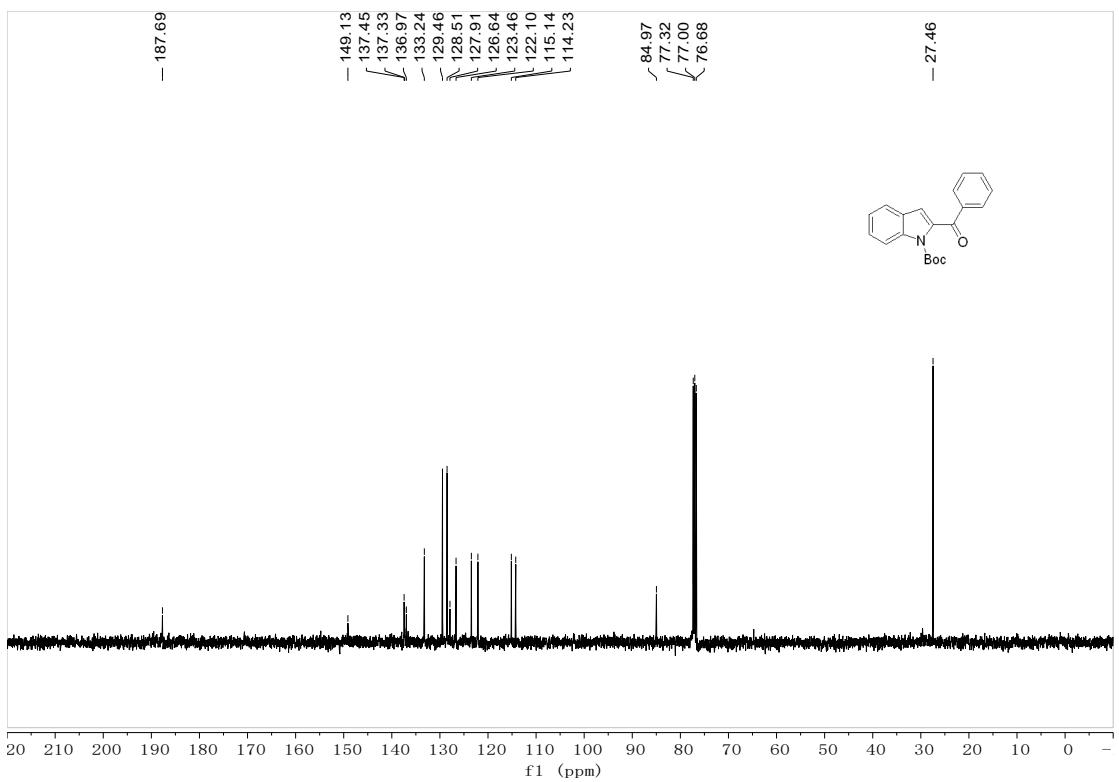
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectroscopy of **14u**



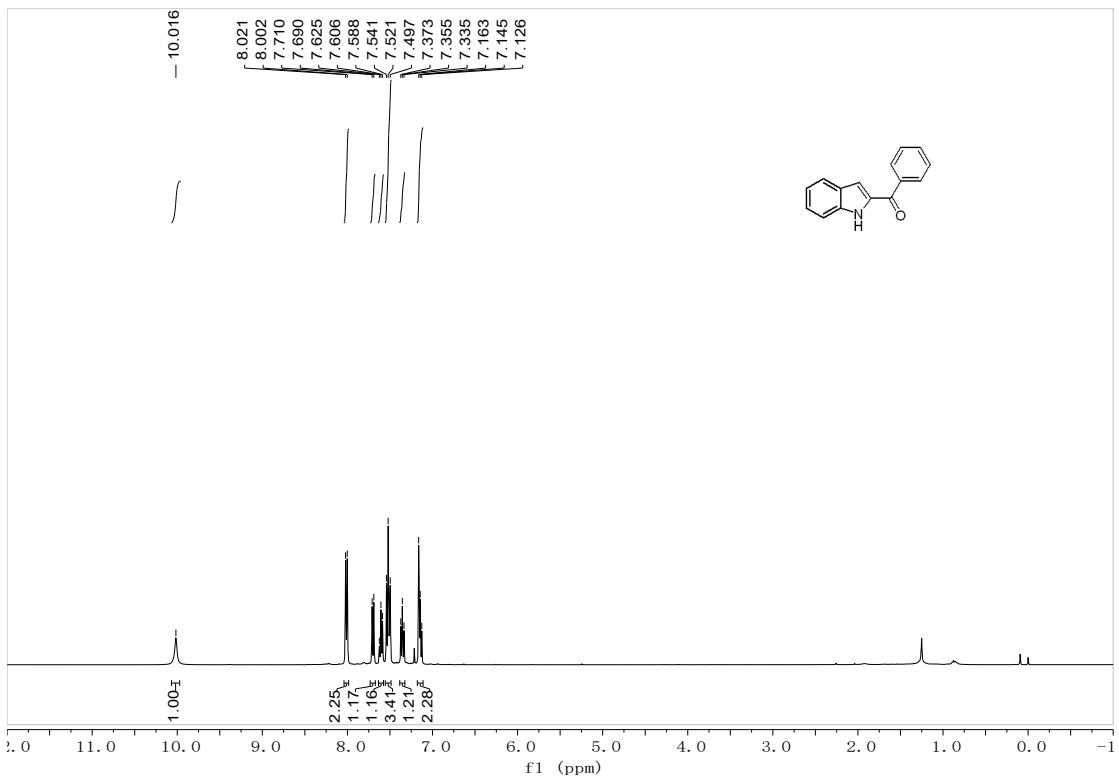
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectroscopy of **14v**



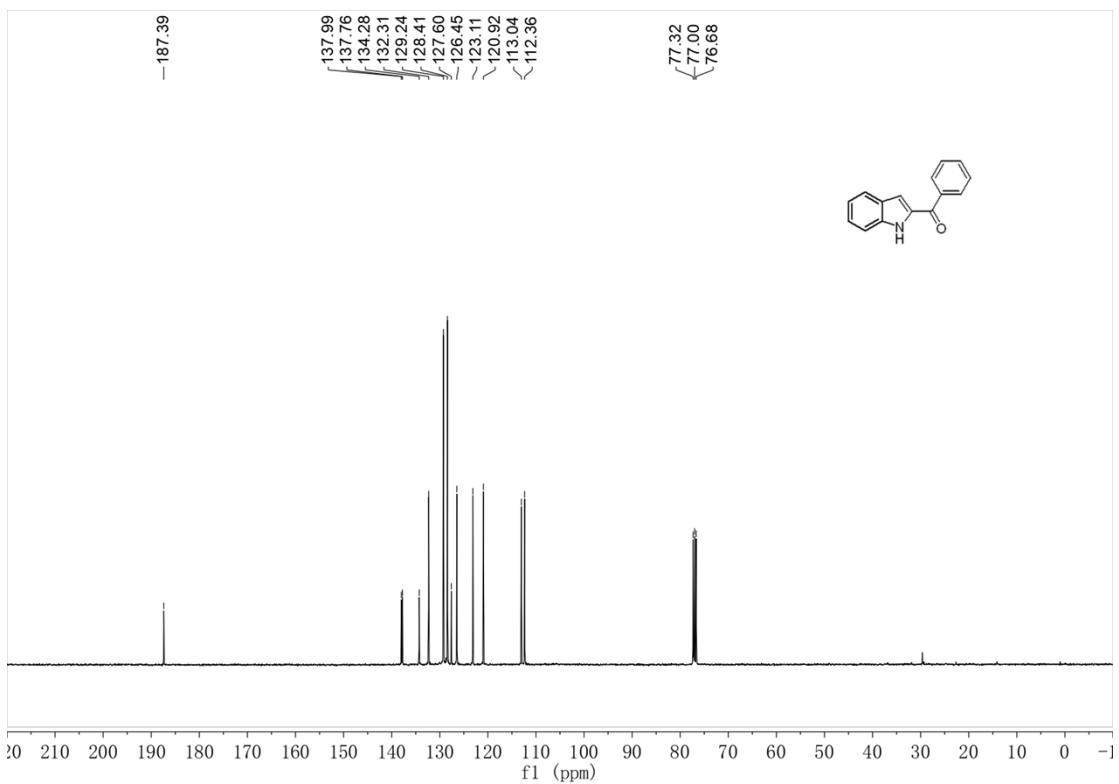
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectroscopy of **14v****



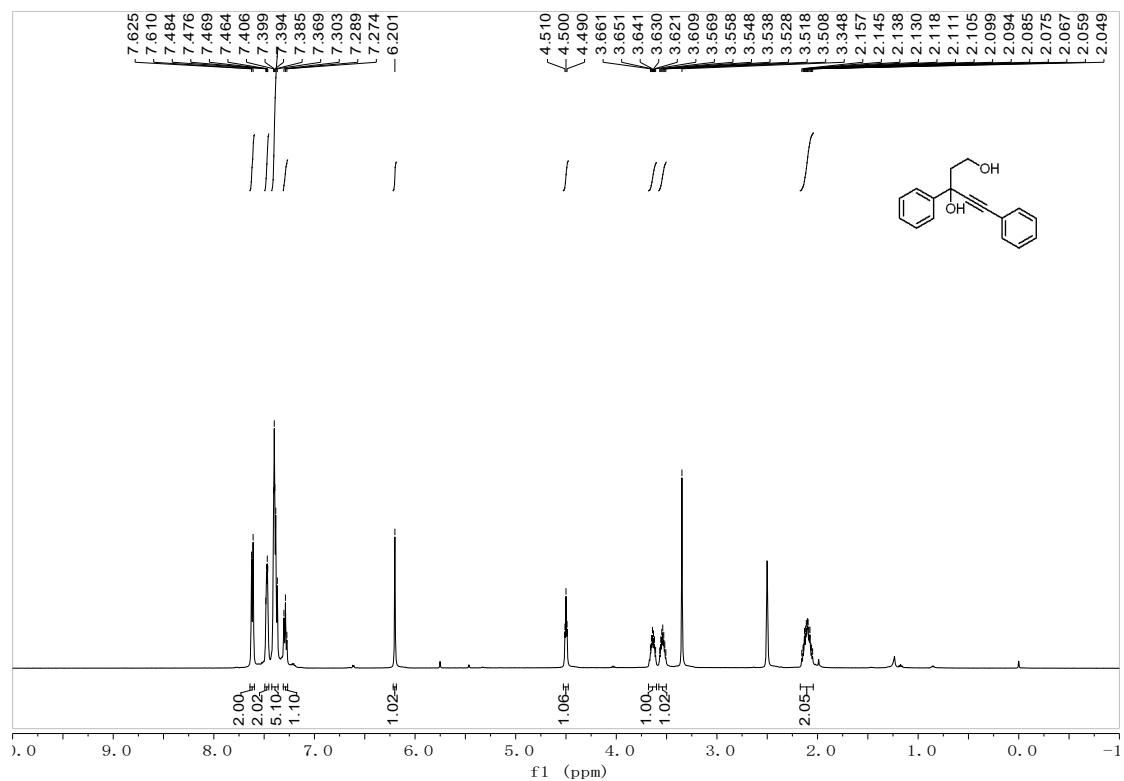
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectroscopy of **14v'****



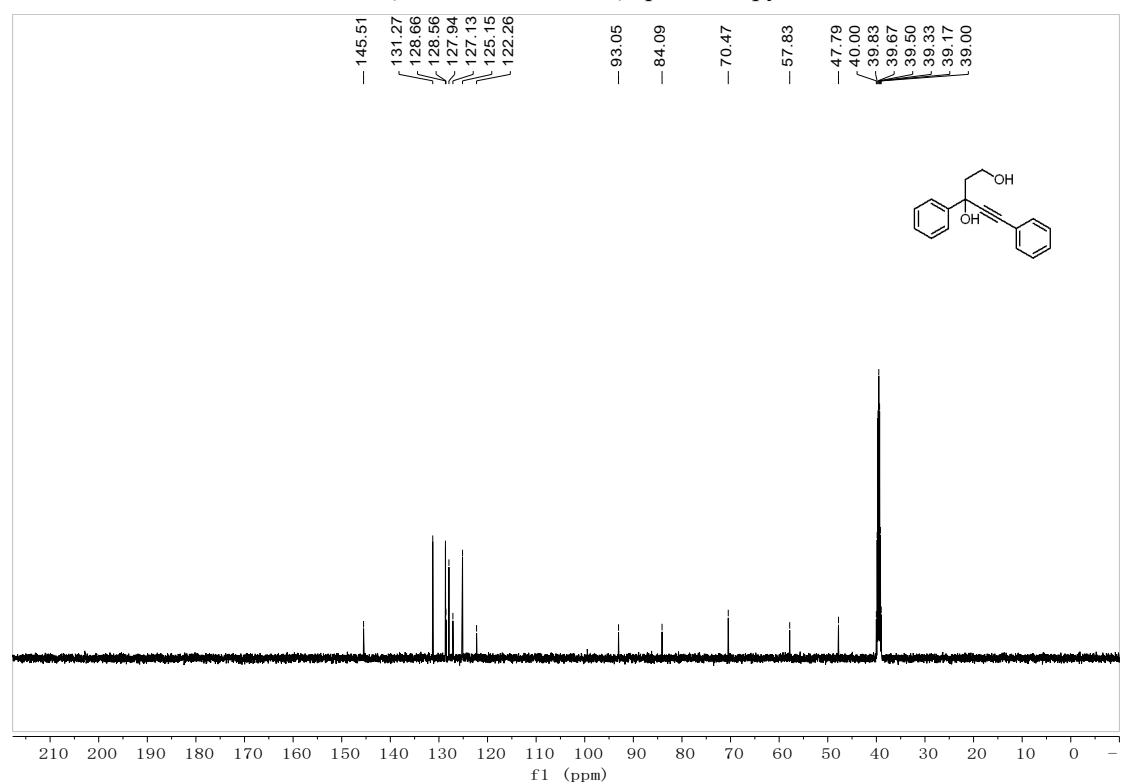
**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>) spectroscopy of **14v'**



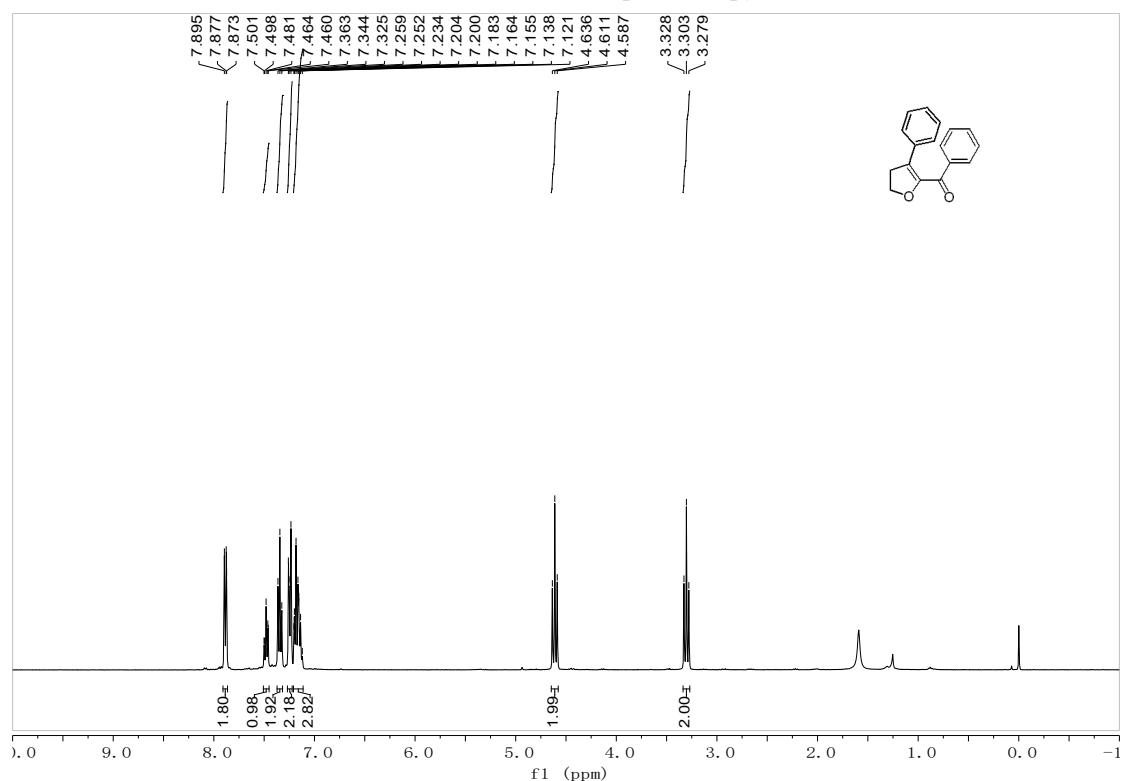
**<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) spectroscopy of 19c**



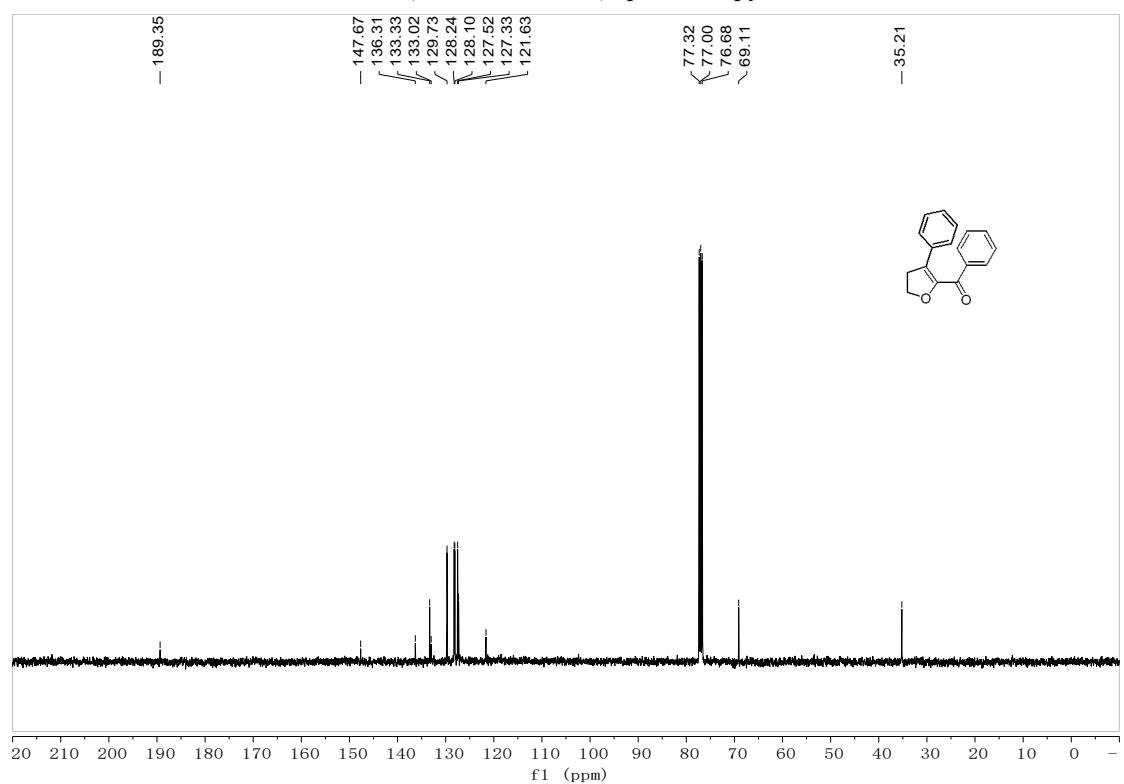
**<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) spectroscopy of 19c**



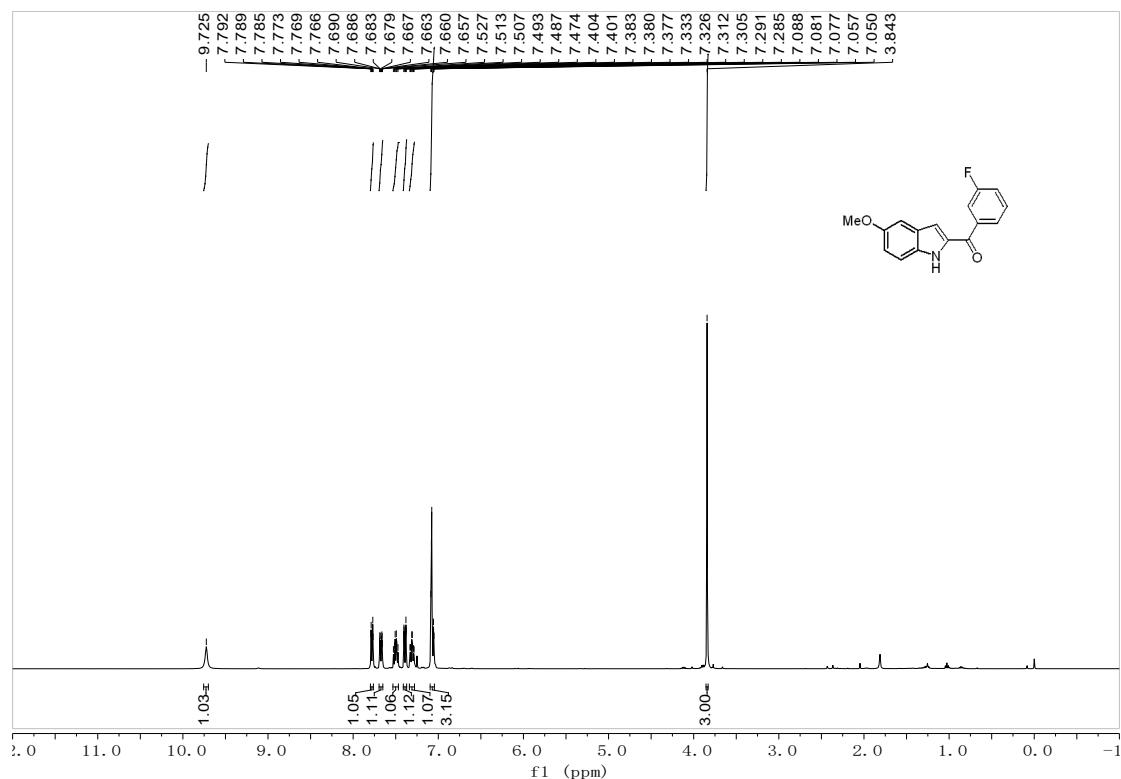
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectroscopy of 20c



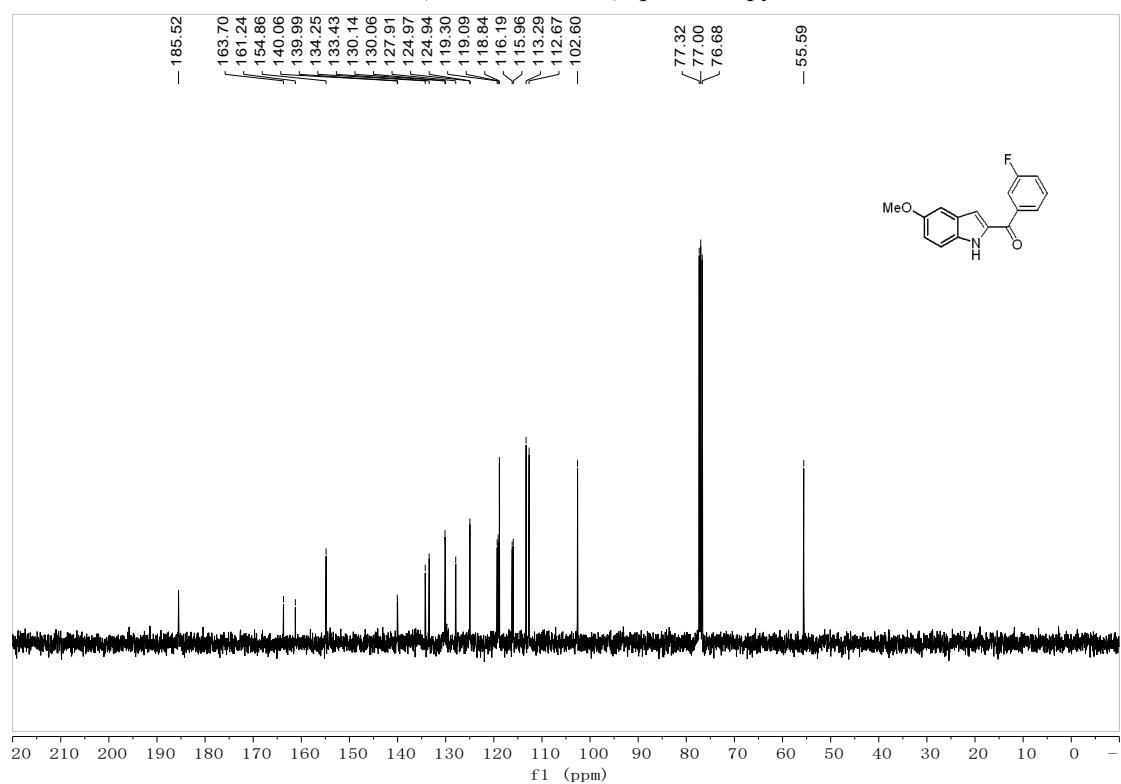
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectroscopy of 20c



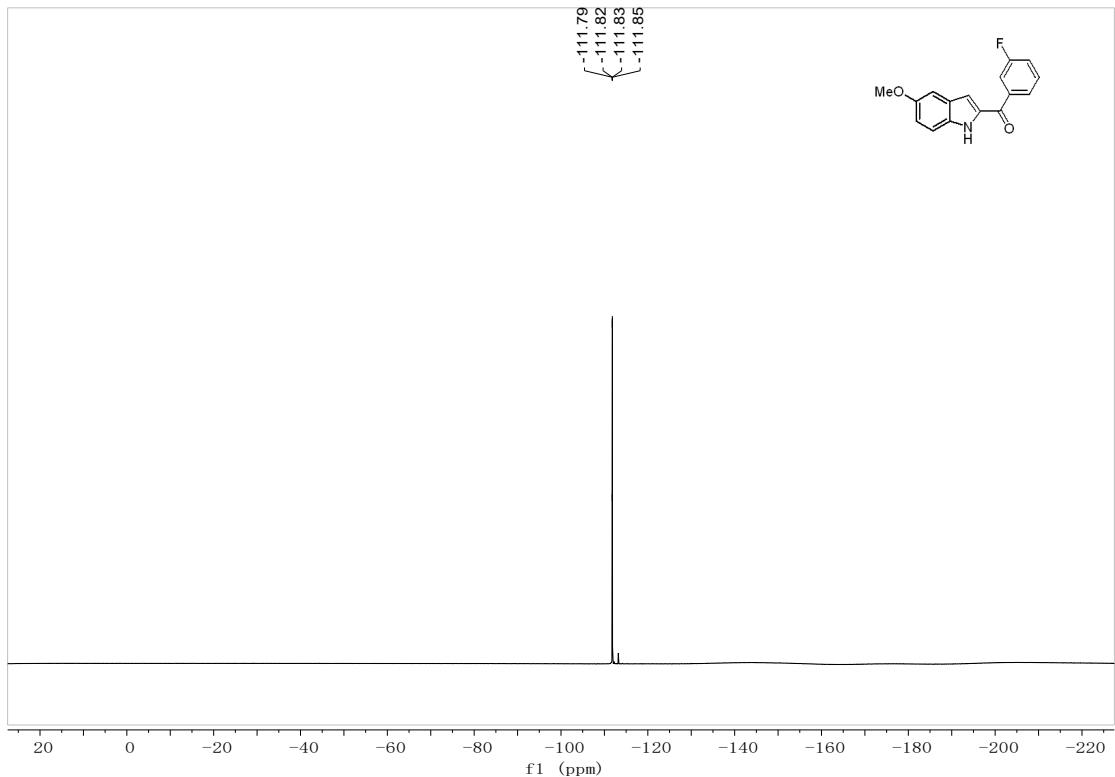
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) spectroscopy of **3****



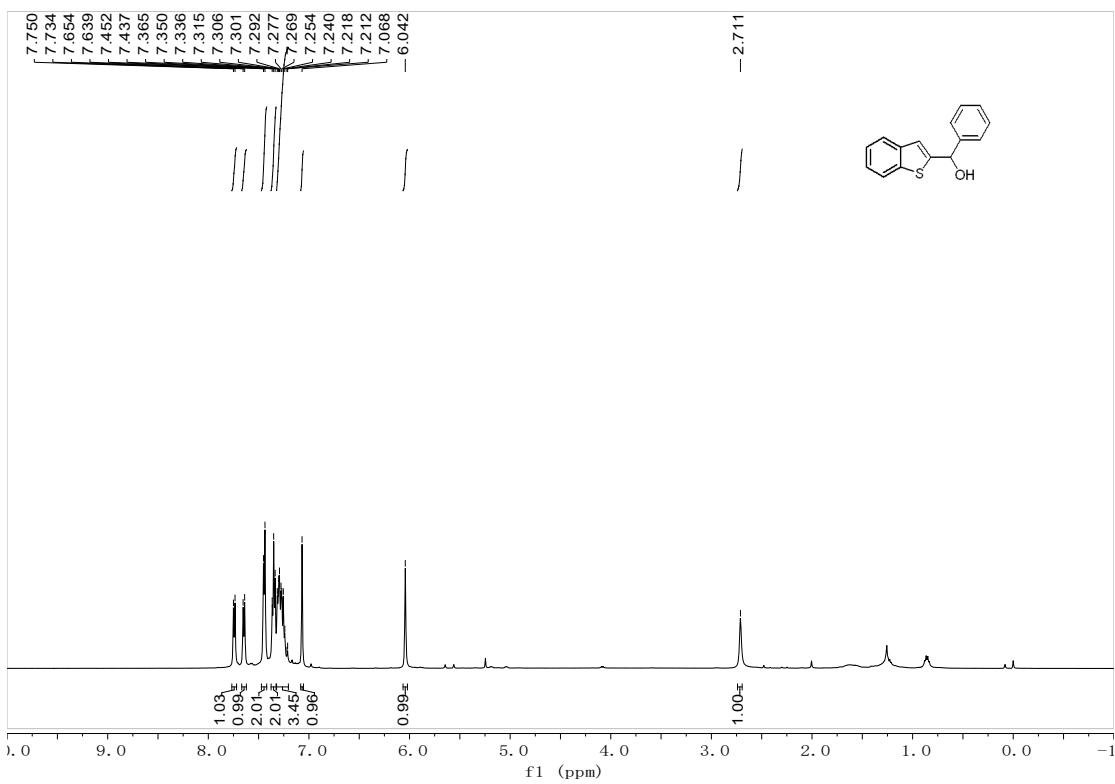
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) spectroscopy of **3****



**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectroscopy of **3****



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) spectroscopy of **S<sub>6</sub>**



<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) spectroscopy of **S<sub>6</sub>**

