# Supporting Information:

# Pd-catalyzed 5-exo-dig cyclization/etherification cascade of *N*-propargyl arylamines for synthesis of polysubstituted furans

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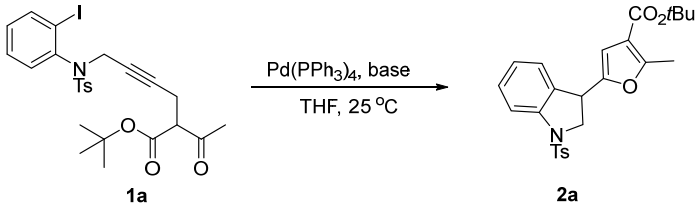
**Contents**

# General information

All reactions were carried out in oven-dried glassware, and monitored by thin layer chromatography (TLC). All reagents and starting materials were reagent grade quality and purchased from commercial sources unless otherwise indicated. All reaction solvents were ultra-dry purchased from commercial sources without purification before use. $^{1}$H NMR spectra were recorded on Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets, td = triplet of doublets), coupling constants (Hz), integration. $^{13}$C NMR data were collected on Bruker Avance III HD 150 or Avance 100 MHz spectrometer. $^{19}$F NMR data were collected on Bruker Avance III HD 565 or Avance 100 MHz spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel IE in comparison with the authentic racemates. Chiral HPLC analysis recorded on Thermo scientific Dionex Ultimate 3000 and Agilent Technologies 1260 Infinity HPLC instruments. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent). Optical rotations recorded on Autopol Automatic Polarimeter. High resolution mass spectra (HRMS) was recorded on a Bruker compact Q-TOF mass spectrometer (ESI). Single-Crystal X-Ray diffraction was recorded at Rigaku oxford diffraction SuperNova.

# Optimization of reaction conditions

**Table S1. Base screening**

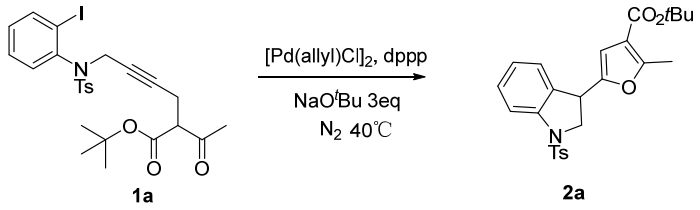



1a 2a

| Entry[a] | Metal | T/°C | Base | Solvent | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 | Pd $(PPh_3)_4$ | 25 | KOH | THF | 19 |
| 2 | Pd $(PPh_3)_4$ | 25 | NaOH | THF | 37 |
| 3 | Pd $(PPh_3)_4$ | 25 | $Cs_2CO_3$ | THF | 10 |
| 4 | Pd $(PPh_3)_4$ | 25 | KO$^t$Bu | THF | 9 |
| 5 | Pd $(PPh_3)_4$ | 25 | NaO$^t$Bu | THF | 45 |
| 6 | Pd $(PPh_3)_4$ | 25 | DBU | THF | 23 |
| 7 | Pd $(PPh_3)_4$ | 25 | EtONa | THF | nr |
| 8 | Pd $(PPh_3)_4$ | 25 | KF | THF | nr |

[a]Unless otherwise noted, the reaction conditions were : Pd $(PPh_3)_4$ (10 mol %), **1a** (0.1 mmol), base (2.0 equiv), in 1 mL of solvent, under $N_2$. [b]The yields of isolated.

**Table S2. Solvent screening**

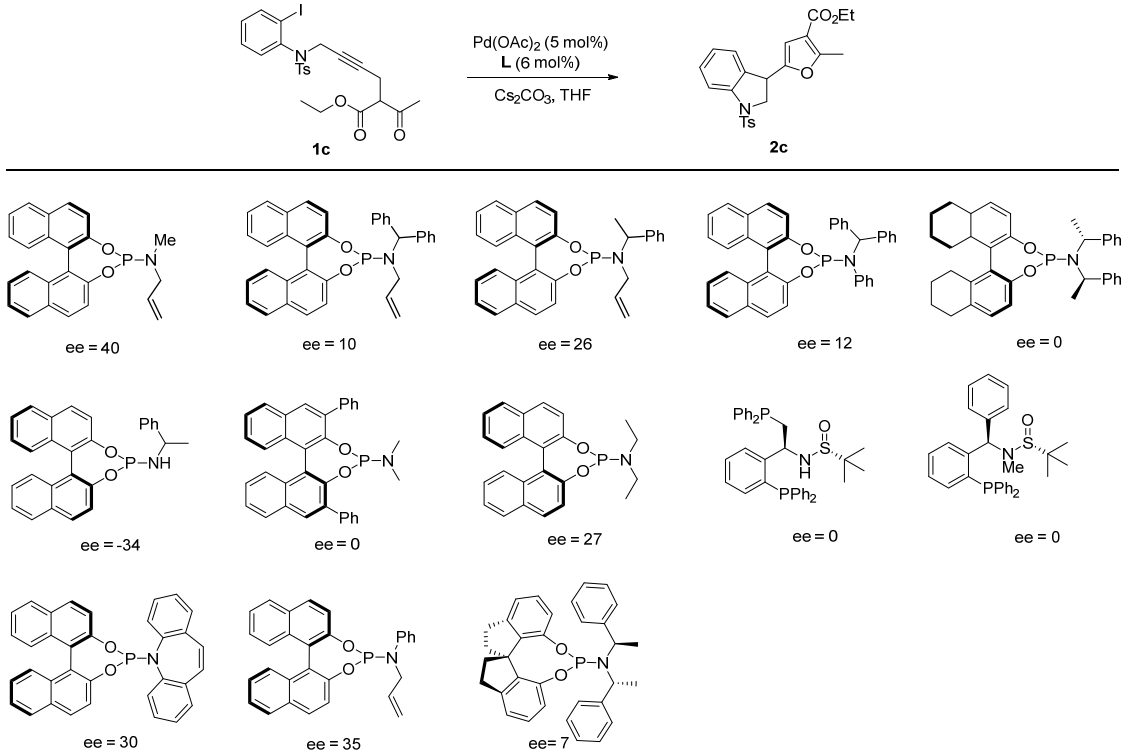



1a 2a

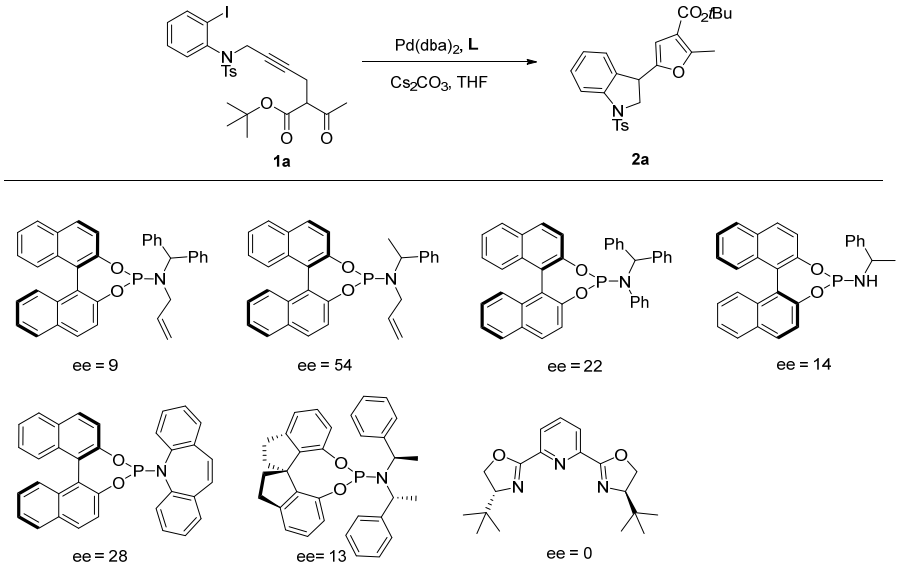
| Entry | Metal | Base | Solvent | *T*/°C | Yield[b] (%) |
|---|---|---|---|---|---|
| 1 | $[Pd(allyl)Cl]_2$ | NaO$^t$Bu | DMF | 40 | nr |
| 2 | $[Pd(allyl)Cl]_2$ | NaO$^t$Bu | DCM | 40 | 10 |
| 3 | $[Pd(allyl)Cl]_2$ | NaO$^t$Bu | PhMe | 40 | trace |
| 4 | $[Pd(allyl)Cl]_2$ | NaO$^t$Bu | PhCl | 40 | trace |
| 5 | $[Pd(allyl)Cl]_2$ | NaO$^t$Bu | DCE | 40 | 6 |
| 6 | $[Pd(allyl)Cl]_2$ | NaO$^t$Bu | EA | 40 | 12 |
| 7 | $[Pd(allyl)Cl]_2$ | NaO$^t$Bu | THF | 40 | 58 |
| 8[c] | $[Pd(allyl)Cl]_2$ | NaO$^t$Bu | THF | 40 | 71 |

[a]Unless otherwise noted, the reaction conditions were : $[Pd(allyl)Cl]_2$ (5 mol %), **L** (11 mol%), **1a** (0.1 mmol), base (3.0 equiv), in 1 mL of solvent, under $N_2$. [b]The yields of isolated. [c]$[Pd(allyl)Cl]_2$ (10 mol %), **L** (22 mol%).

# Enantioselective cyclization/etherification reaction



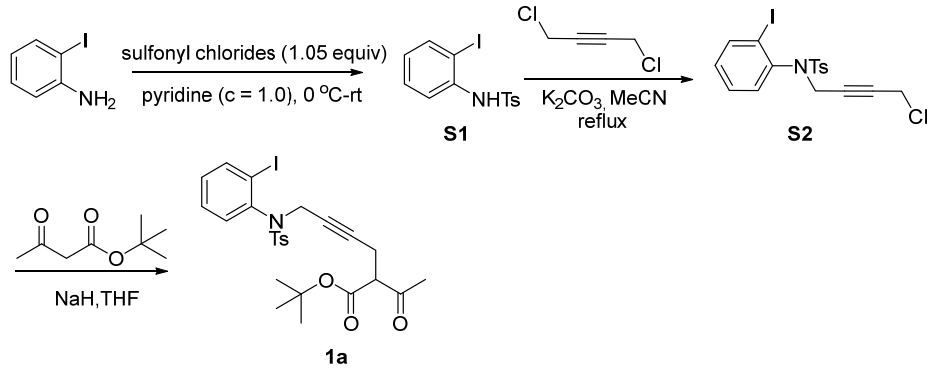

**Scheme S1. Various ligands used in asymmetric reactions for the preparation of 2c**




**Scheme S2. Various ligands used in asymmetric reactions for the preparation of 2a**

# Synthesis of starting materials

Substrates **S1**[1] were prepared according to the reported procedures. Preparation of **1a** was shown as below.

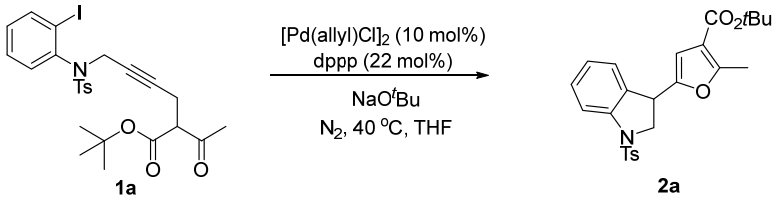



To an oven-dried round flask equipped with a magnetic stir bar, **S1**(3.73 g, 10.0 mmol, 1.0 equiv), 1,4-Dichloro-2-butyne (12 mmol, 1.2 equiv, purchased from commercial sources), and $K_2CO_3$ (6.92 g, 50 mmol, 5.0 equiv) were added in turn and then charged with dry MeCN (70.0 mL) via syringe. The reaction was heated at reflux (oil bath) for 12 h. After the reaction was complete (monitored by TLC), the reaction mixture was diluted with $H_2O$/EtOAc, and the organic layer was washed with brine, dried ($Na_2SO_4$) and concentrated under reduced pressure to give crude **S2** which was purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate = 20/1) to afford pure product **S2** (2.06 g, 45% yield).

To a solution of *tert*-Butyl acetoacetate (3.0 mmol, 1.0 equiv) in dry THF (25.0 mL), NaH (0.1368 g, 3.42 mmol, 60% in mineral oil), was added slowly under stirring at 0 °C. After stirring at room temperature for 0.5 h, the solution was added with **S2** (1.38 g, 3.0 mmol, 1.0 equiv) and tetrabutylammonium iodide (1.66 g, 4.5 mmol, 1.5 equiv). The mixture was then stirred at 25 °C for 12 h. After the reaction was completed, it was quenched with water, then extracted with ethyl acetate for three times. The combined organic layers were dried over $Na_2SO_4$, and concentrated in vacuo to give crude **1a**. which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 15/1) to obtain a colorless oil **1a** (0.97 g, 56% yield) as a mixture of atropisomers or enol isomer. The other substrates were prepared according to the above procedure.

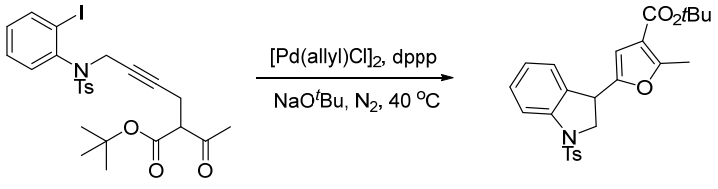
# General Procedures

**General procedure for the synthesis of products (represented by product 2a)**



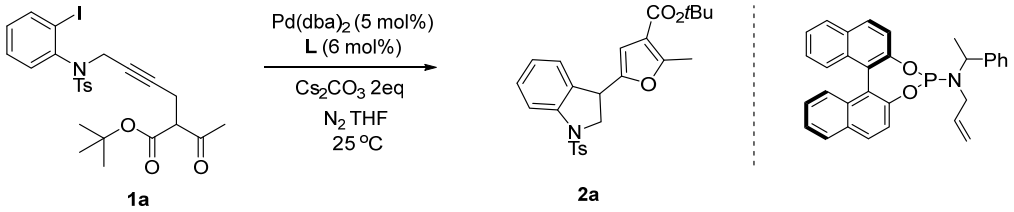

To an oven-dried Schlenk tube equipped with a magnetic stir bar, **1a** (0.1 mmol, 1.0 equiv), and NaO$^t$Bu (0.3 mmol, 3.0 equiv) were added. The tube was sealed with threaded rubber stopper, evacuated and backfilled with $N_2$ (this process was repeated for 3 times). The tube was then charged with a solution of $[Pd(allyl)Cl]_2$ and **L** ($[Pd(allyl)Cl]_2$/**L** = 1:1.1) in dry THF (1.0 mL of 0.001M solution, 10 mol%) via syringe at 25 °C. The complex was stirred at 40 °C for 3 h. After the reaction was complete (monitored by TLC), the reaction mixture was diluted with $CH_2Cl_2$ (about 5 mL) and was filtered over a short silica gel column, washed with $CH_2Cl_2$/MeOH (20:1, 20 mL). The filtrate was concentrated in vacuo to give the crude product, which was then purified by preparative thin layer chromatography (eluent: petroleum ether/ethyl acetate = 25/1) to afford pure product **2a**.

**General procedure for scale-up reaction**



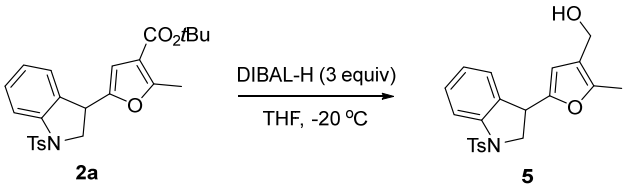

To an oven-dried Schlenk tube equipped with a magnetic stir bar, **1a** (4.0 mmol, 1.0 equiv), and NaO$^t$Bu (12.0 mmol, 3.0 equiv) were added. The tube was sealed with threaded rubber stopper, evacuated and backfilled with $N_2$ (this process was repeated for 3 times). The tube was then charged with a solution of [Pd(allyl)Cl]$_2$ and **L** ([Pd(allyl)Cl]$_2$/**L** = 1:1.1) in dry THF (40.0 mL) via syringe at 25 °C. The complex was stirred at 40 °C for 3 h. After the reaction was complete (monitored by TLC), then extracted with ethyl acetate for three times. The combined organic layers were dried over $Na_2SO_4$, and concentrated in vacuo to give crude **2a**. which was then purified by preparative thin layer chromatography (eluent: petroleum ether/ethyl acetate = 25/1) to afford pure product **2a**.

**General procedure for enantioselective cyclization/etherification reaction**




To an oven-dried Schlenk tube equipped with a magnetic stir bar, **1a** (0.1 mmol, 1.0 equiv), and $Cs_2CO_3$ (0.2 mmol, 2.0 equiv) were added. The tube was sealed with threaded rubber stopper, evacuated and backfilled with $N_2$ (this process was repeated for 3 times). The tube was then charged with a solution of Pd(dba)$_2$ and **L** in dry THF (1.0 mL) via syringe at 25 °C. The complex was stirred at 25 °C. After the reaction was complete (monitored by TLC), the reaction mixture was diluted with $CH_2Cl_2$ (about 5 mL) and was filtered over a short silica gel column, washed with $CH_2Cl_2$/MeOH (20:1, 20 mL). The filtrate was concentrated in vacuo to give the crude product, which was then purified by preparative thin layer chromatography (eluent: petroleum ether/ethyl acetate = 25/1) to afford pure product **2a**.

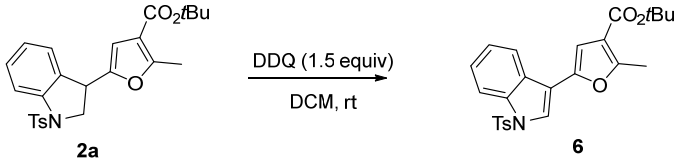
**General procedure for the synthesis of compound 5**[2]




Under nitrogen atmosphere, DIBAL-H (1.1 M in cyclohexane, 3.0 equiv.) was added to a solution of **2a** (45.3 mg, 0.1 mmol) in dry THF (1.0 mL) at -20 °C within 10 minutes. After **2a** was consumed (determined by TLC), the reaction was quenched with saturated aqueous $NH_4Cl$ solution followed by 2N HCl solution. The mixture was extracted with $CH_2Cl_2$ (3 ×3 mL), then the combined organic phases were dried and concentrated. The residue was

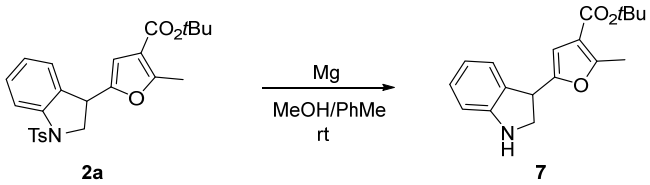
purified by flash chromatography on silica gel (ether/ethyl acetate = 5/1) to afford the product **5** (19.2 mg, 50% yield).

**General procedure for the synthesis of compound 6**



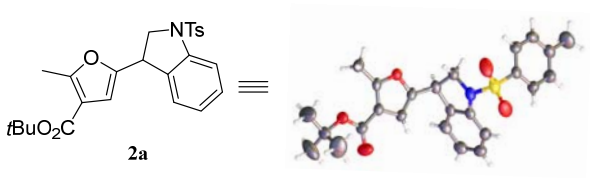

To an oven-dried round flask equipped with a magnetic stir bar, DDQ (34.0 mg, 1.5 mmol) was added to a solution of **2a** (45.3 mg, 0.1 mmol) in dry DCM (1.0 mL). After **2a** was consumed (determined by TLC), the reaction mixture was treated with saturated aqueous $Na_2CO_3$, extracted with dichloromethane, dried over sodium sulfate and concentrated in vacuo. which was then purified by preparative thin layer chromatography (eluent: petroleum ether/ethyl acetate = 20/1) to afford pure product **6** (32.0 mg, 70% yield).

**General procedure for the synthesis of compound 7**[3]




To a suspension of Mg (48mg, 2 mmol) in MeOH (0.5 mL) was added a solution of compound **2a** (0.91g, 0.2 mmol) in toluene (1.0 mL). After **2a** was consumed (determined by TLC), The reaction mixture was then diluted with aqueous $NH_4Cl$ and extracted with ether. The organic layer was dried over $MgSO_4$ and evaporated. which was then purified by preparative thin layer chromatography (eluent: petroleum ether/ethyl acetate = 15/1) to afford pure product **7** (36.0 mg, 61% yield).

# Crystal data of 2a




2a

**Table S4 Crystal data and structure refinement of 2a**

| | |
|---|---|
| Empirical formula | $C_{25}H_{27}NO_5S$ |
| Formula weight | 453.53 |
| Temperature/K | 293(2) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 10.6593(4) |
| b/Å | 11.0723(5) |
| c/Å | 11.3540(5) |
| α/° | 90.428(4) |
| β/° | 111.448(4) |
| γ/° | 105.959(4) |
| Volume/Å$^3$ | 1190.40(10) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.265 |
| μ/mm$^{-1}$ | 1.500 |
| F(000) | 480.0 |
| Crystal size/mm$^3$ | 0.5 × 0.5 × 0.3 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 8.366 to 142.762 |
| Index ranges | -13 ≤ h ≤ 12, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13 |
| Reflections collected | 8739 |
| Independent reflections | 4526 [$R_{int}$ = 0.0205, $R_{sigma}$ = 0.0279] |
| Data/restraints/parameters | 4526/0/294 |
| Goodness-of-fit on F$^2$ | 1.057 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0478, w$R_2$ = 0.1297 |
| Final R indexes [all data] | $R_1$ = 0.0541, w$R_2$ = 0.1349 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.38/-0.40 |

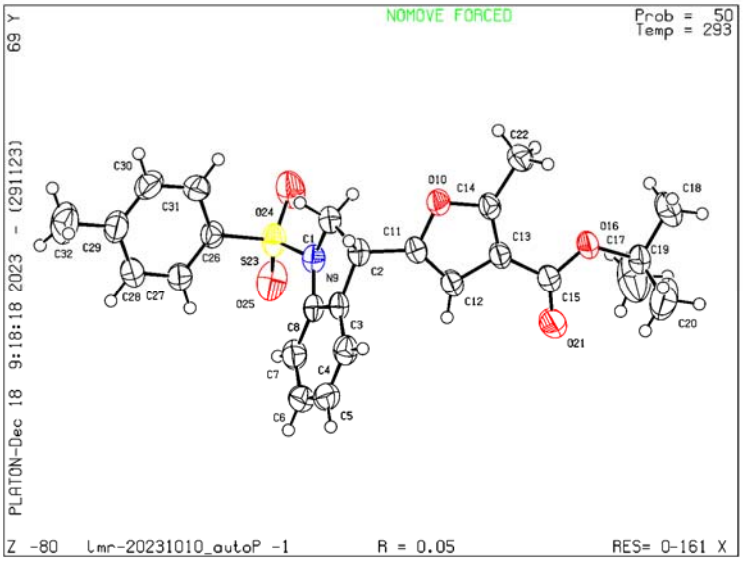
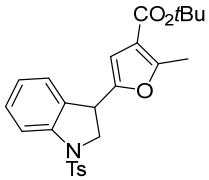



Figure S1 X-ral structure of **2a** with 50% ellipsoid probability

# Characterization data of new compounds

***tert*-Butyl-2-methyl-5(1-tosylindolin-3-yl)furan-3-carboxylate (2a)**



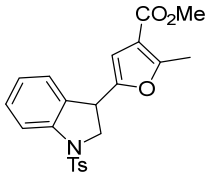

Yellow solid, **m.p.**: 78.9 – 82.5 °C, 63.4 mg, 70% yield.

TCL: Rf = 0.5 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.02 (t, *J* = 7.2 Hz, 1H), 5.97 (s, 1H), 4.31 (dd, *J* = 9.6, 6.6 Hz 1H), 4.22 (t, *J* = 11.4 Hz 1H), 3.97 (dd, *J* = 11.4, 6.6 Hz, 1H), 2.43 (s, 3H), 2.36 (s, 3H), 1.52 (s, 9H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 163.3, 158.2, 151.7, 144.4, 142.0, 134.0, 131.6, 129.7, 129.0, 127.4, 125.6, 124.2, 115.7, 115.6, 107.7, 80.7, 54.9, 39.6, 28.4, 21.7, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{27}NNaO_5S^+$ 476.1502; found 476.1502.

**Methyl-2-methyl-5-(1-tosylindolin-3-yl)furan-3-carboxylate (2b)**



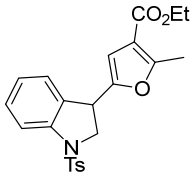
Colorless oil, 24.6mg, 30% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.2 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 5.87 (s, 1H), 4.32 – 4.29 (m, 1H), 4.23 (t, *J* = 10.2 Hz, 1H), 4.01 (q, *J* = 6.0 Hz, 1H), 3.77 (s, 3H), 2.47 (s, 3H), 2.33 (s, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) 164.3, 159.0, 152.3, 144.3, 142.1, 134.1, 131.5, 129.71, 129.1, 127.3, 125.6, 124.4, 115.9, 113.9, 107.4, 55.0, 51.4, 39.6, 29.8, 21.6, 13.8.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{21}NNaO_5S^+$ 434.1033; found 434.1030.

**Ethyl-2-methyl-5-(1-tosylindolin-3-yl)furan-3-carboxylate (2c)**



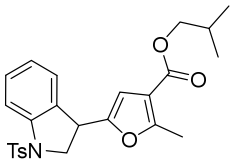

Colorless oil, 36.5 mg, 43% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.03 (t, *J* = 7.6 Hz, 1H), 5.93 (s, 1H), 4.33 – 4.29 (m, 1H), 4.26 – 4.21 (m, 3H), 4.00 (dd, *J* = 10.8, 6.0 Hz, 1H), 2.47 (s, 3H), 2.33 (s, 3H), 1.31 (t, *J* = 8.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.9, 158.9, 152.2, 144.3, 142.1, 134.1, 131.5, 129.7, 129.1, 127.3, 125.6, 124.3, 115.8, 114.2, 107.4, 60.2, 55.0, 39.6, 21.6, 14.5, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{23}NNaO_5S^+$ 448.1189; found 448.1183.

**Isobutyl 2-methyl-5-(1-tosylindolin-3-yl)furan-3-carboxylate (2d)**




Yellow oil, 39.9 mg, 44% yield.

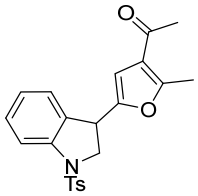
TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.1 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 7.2 Hz, 1H), 5.96 (s, 1H), 4.33 – 4.30 (m, 1H), 4.24 (t, *J* = 10.0 Hz, 1H), 4.01 – 3.97 (m, 3H), 2.47 (s, 3H), 2.33 (s, 3H), 2.01 – 1.97 (m, 1H),

0.97 (d, $J$ = 6.6 Hz, 6H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 164.0, 158.7, 152.2, 144.3, 142.1, 134.1, 131.6, 129.7, 129.1, 127.4, 125.6, 124.3, 115.8, 114.3, 107.5, 70.5, 55.0, 39.6, 27.9, 21.6, 19.4, 14.0.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{27}NNaO_5S^+$ 476.1502; found 476.1501.

**1-(2-Methyl-5-(1-tosylindolin-3-yl)furan-3-yl)ethan-1-one (2e)**



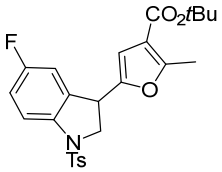

Colorless oil, 34.8 mg, 44% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 2:1).

**$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.72 (d, $J$ = 8.4 Hz, 1H), 7.63 (d, $J$ = 8.4 Hz, 2H), 7.30 (t, $J$ = 7.8 Hz, 1H), 7.18 (d, $J$ = 7.8 Hz, 2H), 7.11 (d, $J$ = 7.2 Hz, 1H), 7.04 (td, $J$ = 7.8, 1.2 Hz, 1H), 5.87 (s, 1H), 4.33 (dd, $J$ = 9.6, 6.0 Hz, 1H), 4.23 (dd, $J$ = 10.8, 9.6 Hz, 1H) , 4.02 (q, $J$ = 6.0 Hz, 1H), 2.49 (s, 3H), 2.34 (s, 3H), 2.27 (s, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 193.9, 158.2, 152.4, 144.3, 142.1, 134.2, 131.4, 129.8, 129.2, 127.4, 125.6, 124.3, 122.1, 115.7, 107.1, 55.0, 39.6, 29.2, 21.7, 14.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{21}NNaO_4S^+$ 418.1083; found 418.1081.

***tert*-Butyl-5-(5-fluoro-1-tosylindolin-3-yl)-2-methylfuran-3-carboxylate (2f)**




Colorless oil, 48.1mg, 51% yield.

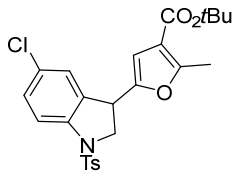
TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.65 (q, $J$ = 4.4 Hz, 1H), 7.60 – 7.58 (m, 2H), 7.19 (d, $J$ = 8.0 Hz, 2H), 6.99 – 6.94 (m, 1H), 6.78 – 6.76 (m, 1H), 5.99 (s, 1H), 4.26 – 4.22 (m, 2H), 4.01 – 3.98 (m, 1H), 2.43 (s, 3H), 2.36 (s, 3H), 1.52 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.2, 160.0 (d, $J_{C-F}$ = 243.4 Hz), 158.4, 150.8, 144.6, 138.1 (d, $J_{C-F}$ = 2.2 Hz), 133.9 (d, $J_{C-F}$ = 8.3 Hz), 133.7, 129.8, 127.4, 117.0 (d, $J_{C-F}$ = 8.5 Hz), 115.8, 115.7 (d, $J_{C-F}$ = 23.4 Hz), 112.7 (d, $J_{C-F}$ = 24.5 Hz), 107.9, 80.9, 55.3, 39.6, 28.4, 21.7, 13.9.

**$^{19}$F NMR** (376 MHz, CDCl3) δ -118.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{26}FNNaO_5S^+$ 494.1408; found 494.1408.

***tert*-Butyl-5-(5-chloro-1-tosylindolin-3-yl)-2-methylfuran-3-carboxylate (2g)**



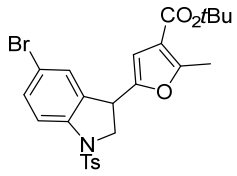

Colorless oil, 59.5 mg, 61% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.4 Hz, 3H), 7.24 – 7.21 (m, 3H), 7.02 (s, 1H), 6.03 (s, 1H), 4.29 – 4.20(m, 2H), 3.96 (dd, *J* = 10.4, 6.4 Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H), 1.52 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.2, 158.4, 150.7, 144.7, 140.8, 133.6, 129.9, 129.5, 129.1, 127.4, 125.67, 116.6, 108.0, 80.9, 55.1, 39.4, 28.5, 21.7, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{26}ClNNaO_5S^+$ 510.1112; found 510.1112.

***tert*-Butyl-5-(5-bromo-1-tosylindolin-3-yl)-2-methylfuran-3-carboxylate (2h)**



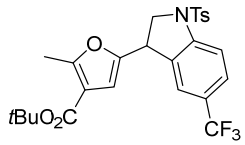

Colorless oil, 56.4 mg, 53% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 5.6 Hz, 2H), 7.57 (d, *J* = 6.0 Hz, 1H), 7.37 (d, *J* = 5.6 Hz, 1H), 7.22 (d, *J* = 5.2 Hz, 2H), 7.16 (s, 1H), 6.03 (s, 1H), 4.31 – 4.29 (m, 1H), 4.22 (t, *J* = 7.2 Hz, 1H), 3.95 (dd, *J* =7.2, 4.4 Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H), 1.52 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.2, 158.4, 150.7, 144.7, 141.2, 133.9, 133.6, 131.9, 129.9, 128.5, 127.4, 116.9, 115.8, 108.0, 80.9, 55.0, 39.3, 28.4, 21.7, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{26}BrNNaO_5S^+$ 554.0607; found 554.0607.

***tert*-Butyl-2-methyl-5-(1-tosyl-5-(trifluoromethyl)indolin-3-yl)furan-3-carboxylae (2i)**




Colorless oil, 49.0 mg, 47% yield.

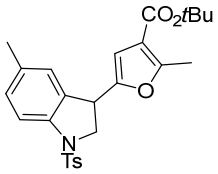
TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.30 (s, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 6.07 (s, 1H), 4.43 – 4.40 (m, 1H), 4.28 (t, *J* = 9.6 Hz, 1H), 4.01 (dd, *J* = 10.8, 7.2 Hz, 1H), 2.43 (s, 3H), 2.39 (s, 3H), 1.53 (s, 9H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 163.2, 158.6, 150.5, 144.9, 133.8, 132.1, 130.0, 126.7 (q, $J_{C–F}$ = 18.0 Hz), 126.3, 126.1, 124.2 (d, $J_{C–F}$ = 271.8 Hz), 122.7 (q, $J_{C–F}$ = 12.0 Hz), 115.8, 114.7, 108.2, 80.9, 55.0, 39.2, 28.4, 21.7, 13.9.

**$^{19}$F NMR** (376 MHz, CDCl3) δ -61.69.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{26}F_3NNaO_5S^+$ 544.1376; found 544.1375.

***tert*-Butyl-2-methyl-5-(5-methyl-1-tosylindolin-3-yl)furan-3-carboxylate (2j)**



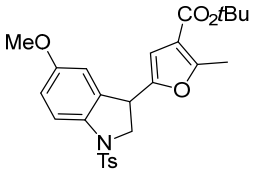

Colorless oil, 55.1 mg, 59% yield.

TCL: Rf = 0.5 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 20.4, 9.0 Hz, 3H), 7.18 (d, *J* =7.8 Hz, 2H), 7.07 (d, *J* =8.4 Hz, 1H), 6.86 (s, 1H), 5.97 (s, 1H), 4.26 – 4.19 (m, 2H), 3.95 – 3.93 (m, 1H), 2.43 (s, 3H), 2.35 (s, 3H), 2.26 (s, 3H), 1.52 (s, 9H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 163.4, 158.1, 151.8, 144.2, 139.7, 134.1, 133.9, 131.9, 129.7, 129.6, 127.4, 126.0, 115.7, 115.6, 107.7, 80.8, 55.1, 39.6, 28.5, 21.7, 21.1, 14.0.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{29}NNaO_5S^+$ 490.1659; found 490.1656.

***tert*-Butyl-5-(5-methoxy-1-tosylindolin-3-yl)-2-methylfuran-3-carboxylate (2k)**



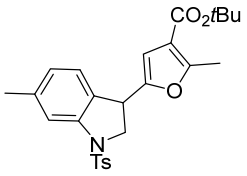

Colorless oil, 60.9 mg, 63% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 20.4, 8.8 Hz, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.81 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.60 (d, *J* = 2.8 Hz, 1H), 5.97 (s, 1H), 4.25 – 4.15 (m, 2H), 3.97 – 3.93 (m, 1H), 3.74 (s, 3H), 2.42 (s, 3H), 2.35 (s, 3H), 1.52 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.3, 158.2, 157.2, 151.4, 144.2, 135.5, 133.8, 133.7, 129.7, 127.5, 117.2, 115.7, 114.1, 111.2, 107.8, 80.8, 55.8, 55.3, 39.9, 28.5, 21.7, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{29}NNaO_6S^+$ 506.1608; found 506.1608.

***tert*-Butyl-2-methyl-5-(6-methyl-1-tosylindolin-3-yl)furan-3-carboxylate (2l)**



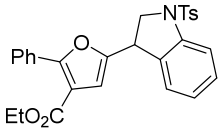

Colorless oil, 46.7 mg, 50% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 2H), 7.53 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 5.96 (s, 1H), 4.25 – 4.18 (m, 2H), 3.97 – 3.93 (m, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 1.51 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.4, 158.1, 152.0, 144.3, 142.2, 139.2, 134.2, 129.7, 128.8, 127.4, 125.2, 125.1, 116.2, 115.6, 107.6, 80.7, 55.2, 39.3, 28.5, 21.8, 21.7, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{29}NNaO_5S^+$ 490.1659; found 490.1659.

**Ethyl-2-phenyl-5-(1-tosylindolin-3-yl)furan-3-carboxylate (4a)**



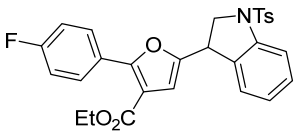

Yellow oil, 54.6 mg, 56% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.87 – 7.85 (m, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.44 – 7.38 (m, 3H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.07 (t, *J* = 8.4 Hz, 1H), 6.11 (s, 1H), 4.42 (dd, *J* = 9.0, 5.4 Hz, 1H), 4.30 (dd, *J* = 11.4, 9.6 Hz, 1H), 4.27 – 4.23 (m, 2H), 4.11 (q, *J* = 6.0 Hz, 1H), 2.30 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 162.4, 156.1, 152.2, 143.3, 141.2, 133.0, 130.3, 128.8, 128.64, 128.55, 128.2, 127.4, 127.2, 126.3, 124.7, 123.5, 115.0, 113.5, 108.7, 59.7, 53.9, 38.7, 20.6, 13.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{25}NNaO_5S^+$ 510.1346; found 510.1345.

**Ethyl-2-(4-fluorophenyl)-5-(1-tosylindolin-3-yl)furan-3-carboxylate (4b)**




Colorless oil, 55.4 mg, 54% yield.

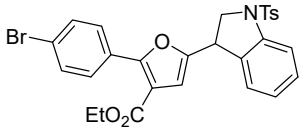
TCL: Rf = 0.6 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ7.89 (dd, *J* = 9.0, 5.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.16 (dd, *J* = 19.2 , 7.8 Hz, 3H), 6.12 (s, 1H), 4.42 (dd, *J* = 9.0, 6.0 Hz, 1H), 4.31 – 4.23 (m, 3H), 4.10 (q, *J* = 6.0 Hz, 1H), 2.31 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.3 (d, $J_{C–F}$ = 250.1 Hz), 163.2, 156.1, 153.0, 144.2, 142.0, 133.9, 131.1, 130.3 (d, $J_{C-F}$ = 7.9 Hz), 129.6, 129.1, 127.2, 125.7 (d, $J_{C–F}$ = 3.8 Hz), 125.5, 124.3, 115.8, 115.2 (d, $J_{C–F}$ = 22.0 Hz), 114.2, 109.6, 60.6, 54.8, 39.5, 21.5, 14.3.

**$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -110.72.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{24}FNNaO_5S^+$ 528.1251; found 528.1251.

**Ethyl-2-(4-bromophenyl)-5-(1-tosylindolin-3-yl)furan-3-carboxylate (4c)**



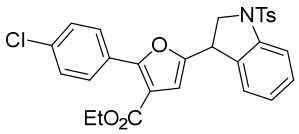

Colorless oil, 55.5 mg, 49% yield.

TCL: Rf = 0.5 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 21.6, 8.4 Hz, 3H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.13 (s, 1H), 4.43 – 4.40 (m, 1H), 4.30 – 4.23 (m, 3H), 4.10 (q, *J* = 6.0 Hz, 1H), 2.31 (s, 3H), 1.31 (t, *J* = 6.6 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 163.2, 155.9, 153.5, 144.4, 142.1, 134.0, 131.5, 131.1, 129.8, 129.8, 129.3, 128.5, 127.3, 125.7, 124.5, 123.9, 115.9, 115.0, 109.9, 60.8, 54.9, 39.7, 21.6, 14.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{24}BrNNaO_5S^+$ 588.0451; found 588.0453.

**Ethyl-2-(4-chlorophenyl)-5-(1-tosylindolin-3-yl)furan-3-carboxylate (4d)**




Colorless oil, 58.4mg, 56% yield.

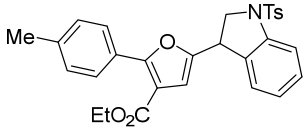
TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.8 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.32 (t ,*J* = 7.6 Hz, 1H), 7.16 (dd, *J* = 14.0 , 7.6 Hz, 3H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.13 (s, 1H), 4.42 (dd, *J* = 9.2 , 6.0 Hz, 1H), 4.31 – 4.23 (m, 3H), 4.10 (dd, *J* = 11.2, 6.0 Hz,

1H), 2.31 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.2, 155.9, 153.5, 144.4, 142.1, 135.5, 134.0, 131.1, 129.8, 129.6, 129.3, 128.5, 128.0, 127.3, 125.7, 124.4, 115.9, 114.9, 109.9, 60.8, 54.9, 39.6, 21.6, 14.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{24}ClNNaO_5S^+$ 544.0956; found 544.0956.

**Ethyl-2-(p-tolyl)-5-(1-tosylindolin-3-yl)furan-3-carboxylate (4e)**



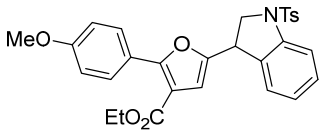

Colorless oil, 53.1 mg, 53% yield.

TCL: Rf = 0.5 (petroleum ether/ethyl acetate = 5:1).

**$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 14.4, 8.4 Hz, 3H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.08 (s, 1H), 4.41 (dd, *J* = 9.0, 6.0 Hz, 1H), 4.30 (dd, *J* = 10.8, 9.0 Hz, 1H), 4.26 – 4.22 (m, 2H), 4.11 (q, *J* = 6.0 Hz, 1H), 2.40 (s, 3H), 2.30 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.5, 157.5, 152.8, 144.3, 142.1, 139.7, 134.0, 131.4, 129.8, 129.2, 128.9, 128.3, 127.3, 126.9, 125.7, 124.4, 116.0, 113.9, 109.6, 60.6, 55.0, 39.7, 21.6, 14.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{29}H_{27}NNaO_5S^+$ 524.1502; found 524.1500.

**Ethyl-2-(4-methoxyphenyl)-5-(1-tosylindolin-3-yl)furan-3-carboxylate (4f)**



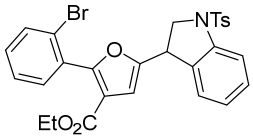

Colorless oil, 55.9 mg, 54% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.08 (s, 1H), 4.41 – 4.39 (m, 1H), 4.29 (t, *J* = 10.8 Hz, 1H), 4.26 – 4.22 (m, 2H), 4.10 (q, *J* = 6.0 Hz, 1H), 3.86 (s, 3H), 2.30 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 163.5, 160.6, 157.4, 152.4, 144.3, 142.1, 134.0, 131.4, 129.9, 129.8, 129.2, 127.3, 125.7, 124.4, 122.3, 115.9, 113.7, 113.2, 109.6, 60.6, 55.5, 55.0, 39.7, 21.6, 14.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{29}H_{27}NNaO_6S^+$ 540.1451; found 540.1451.

**Ethyl-2-(2-bromophenyl)-5-(1-tosylindolin-3-yl)furan-3-carboxylate (4g)**



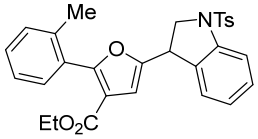

Yellow oil, 44.1mg, 39% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.08 (s, 1H), 4.43 (dd, *J* = 9.6, 6.6 Hz, 1H), 4.31 (t, *J* = 10.8 Hz, 1H), 4.15 – 4.08 (m, 3H), 2.29 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 162.8, 156.1, 154.5, 144.4, 142.2, 134.0, 133.0, 132.5, 131.6, 131.2, 131.1, 129.8, 129.2, 127.4, 126.9, 125.8, 124.4, 124.0, 116.9, 115.9, 108.0, 60.6, 55.2, 39.7, 21.6, 14.1.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{24}BrNNaO_5S^+$ 588.0451; found 588.0450.

**Ethyl-2-(o-tolyl)-5-(1-tosylindolin-3-yl)furan-3-carboxylate (4h)**



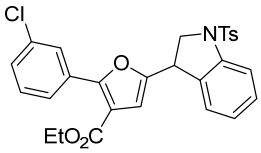

Yellow oil, 55.2 mg, 55% yield.

TCL: Rf = 0.3 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.21 (dd, *J* = 13.8, 7.2 Hz, 2H), 7.12 (t, *J* = 10.2 Hz, 3H), 7.03 (t, *J* = 7.2 Hz, 1H), 6.12 (s, 1H), 4.39 (t, *J* = 8.4 Hz, 1H), 4.26 (t, *J* = 10.2 Hz, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 4.02 (q, *J* = 6.0 Hz, 1H), 2.27 (s, 3H), 2.14 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.1, 158.2, 153.7, 144.4, 142.1, 137.8, 134.0, 131.4, 130.9, 130.1, 129.8, 129.7, 129.2, 127.3, 125.6, 125.2, 124.4, 115.9, 115.8, 108.1, 60.4, 55.0, 39.7, 21.6, 20.2, 14.2.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{29}H_{27}NNaO_5S^+$ 524.1502; found 524.1496.

**Ethyl 2-(3-chlorophenyl)-5-(1-tosylindolin-3-yl)furan-3-carboxylate (4i)**



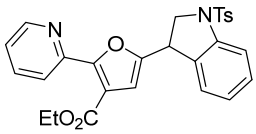

Colorless oil, 51.1 mg, 49% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.80 – 7.77 (m, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.37 – 7.32 (m, 3H), 7.16 (dd, *J* = 10.0, 7.2 Hz, 3H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.13 (s, 1H), 4.42 (dd, *J* = 9.2, 6.0 Hz, 1H), 4.32 – 4.24 (m, 3H), 4.10 (q, *J* = 6.0 Hz, 1H), 2.31 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 163.1, 155.2, 153.8, 144.4, 142.2, 134.2, 134.0, 131.2, 131.1, 129.8, 129.54, 129.46, 129.3, 128.3, 127.3, 126.4, 125.7, 124.5, 116.0, 115.5, 110.0, 60.9, 54.9, 39.7, 21.6, 14.3.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{24}ClNNaO_5S^+$ 544.0956; found 544.0952.

**Ethyl-2-(pyridin-2-yl)-5-(1-tosylindolin-3-yl)furan-3-carboxylate (4j)**



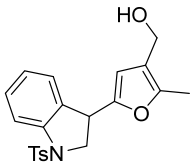

Yellow oil, 34 mg, 35% yield.

TCL: Rf = 0.2 (petroleum ether/ethyl acetate = 2:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.73 (d, *J* = 4.8 Hz, 1H) , 8.11 (d, *J* = 7.8 Hz, 1H), 7.78 (td, *J* = 7.8, 1.8 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.29 (m, 2H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 1H), 6.04 (s, 1H), 4.50 (dd, *J* = 9.6, 6.0 Hz, 1H), 4.30 – 4.23 (m, 3H), 4.12 (dd, *J* = 11.4, 6.0 Hz, 1H), 2.32 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 163.2, 155.4, 154.9, 149.7, 148.1, 144.3, 142.2, 136.3, 134.1, 131.4, 129.8, 129.3, 127.3, 125.8, 124.6, 124.5, 123.7, 117.0, 116.1, 109.4, 61.0, 55.4, 39.7, 21.6, 14.3.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{24}N_2NaO_5S^+$ 511.1298; found 511.1298.

**(2-methyl-5-(1-tosylindolin-3-yl)furan-3-yl)methanol (5)**




Yellow oil, 38.3mg, 50% yield.

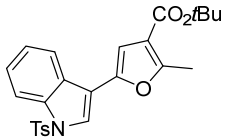
TCL: Rf = 0.3 (petroleum ether/ethyl acetate = 2:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 14.4, 7.8 Hz, 3H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H), 5.75 (s, 1H), 4.36-4.31 (m, 3H), 4.20 (t, *J* = 10.2 Hz, 1H), 3.97 (dd, *J* = 10.8, 7.2 Hz, 1H), 2.36 (s, 3H), 2.18 (s, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ

152.2, 149.0, 144.2, 141.9, 134.1, 132.1, 129.8, 128.8, 127.5, 125.6, 124.1, 119.5, 115.3, 107.7, 56.6, 55.2, 39.8, 21.7, 11.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{21}H_{21}NNaO_4S^+$ 406.1083; found 406.1083.

***tert*-Butyl-2-methyl-5-(1-tosyl-1H-indol-3-yl)furan-3-carboxylate (6)**




Yellow oil, 63.2mg, 70% yield.

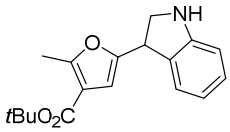
TCL: Rf = 0.6 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.85 – 7.79 (m, 4H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.83 (s, 1H), 2.64 (s, 3H), 2.34 (s, 3H), 1.59 (s, 9H).

**$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 163.4, 157.6, 145.7, 145.3, 135.4, 135.2, 130.1, 127.3, 127.1, 125.3, 123.9, 122.2, 120.9, 116.7, 114.0, 113.7, 107.2, 80.9, 28.5, 21.7, 14.0.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{25}NNaO_5S^+$ 474.1346; found 474.1344.

***tert*-Butyl-5-(indolin-3-yl)-2-methylfuran-3-carboxylate (7)**



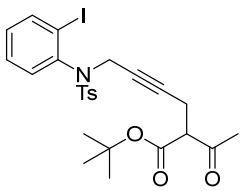

Yellow oil, 36.5mg, 61% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.10 (dd, *J* = 14.0, 7.2 Hz, 2H), 6.75 (t, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.30 (s, 1H), 4.51 (t, *J* = 8.8 Hz, 1H), 3.85 (t, *J* = 9.2 Hz, 1H), 3.63 (t, *J* = 8.4 Hz, 1H), 2.52 (s, 3H), 1.53 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 163.7, 158.0, 153.4, 151.3, 129.1, 128.4, 125.0, 119.2, 115.6, 110.2, 107.0, 80.5, 53.0, 41.6, 28.5, 13.98, 13.95.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{18}H_{21}NNaO_3^+$ 322.1414; found 322.1413.

***tert*-Butyl-2-acetyl-6-((*N*-(2-iodophenyl)-4-methylphenyl)sulfonamido)hex-4-ynoate (1a)**



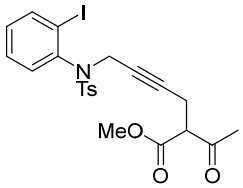

Yellow oil, 73.2 mg, 63% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 9.6 Hz, 3H), 7.02 (d, *J* = 7.6 Hz, 2H), 4.64 (dd, *J* = 18.0, 6.8 Hz, 1H), 4.05 (d, *J* = 18.0 Hz, 1H), 3.39 (t, *J* = 7.6 Hz, 1H), 2.52 – 2.47 (m, 2H), 2.42 (s, 3H), 2.18 (s, 1.5H), 2.16 (s, 1.5H), 1.41 (d, *J* = 2.8 Hz, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 201.2, 166.9, 166.9, 143.8, 140.8, 140.7, 140.0, 136.6, 136.5, 130.9, 130.8, 130.3, 129.3, 128.7, 128.7, 128.2, 102.7, 102.7, 82.6, 82.4, 82.4, 75.3, 75.3, 58.7, 58.8, 41.04, 40.99, 29.3, 27.7, 21.5, 17.3.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{28}INNaO_5S^+$ 604.0625; found 604.0625.

**Methyl-2-acetyl-6-((*N*-(2-iodophenyl)-4-methylphenyl)sulfonamido)hex-4-ynoate (1b)**



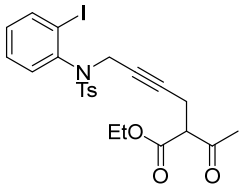

Colorless oil, 65.8 mg, 61% yield, a mixture of atropisomers.

TCL: Rf = 0.3 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 3H), 7.01 – 6.97 (m, 2H), 4.57 (d, *J* = 16.8 Hz, 1H), 4.00 (d, *J* = 18.0 Hz, 1H), 3.65 (s, 1.5 H), 3.64 (s, 1.5 H), 3.44 (t, *J* = 7.6 Hz, 1H), 2.52 – 2.48 (m, 2H), 2.38 (s, 3H), 2.15 (s, 1.5H), 2.12 (s, 1.5H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 200.98, 200.95, 168.5, 144.0, 141.0, 140.9, 140.3, 136.7, 131.2, 130.4, 129.5, 128.9, 128.8, 128.4, 102.8, 82.4, 57.9, 52.9, 41.2, 41.2, 29.7, 29.6, 21.7, 17.7.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{22}INNaO_5S^+$ 562.0156; found 562.0154.

**Ethyl-2-acetyl-6-((*N*-(2-iodophenyl)-4-methylphenyl)sulfonamido)hex-4-ynoate (1c)**




Colorless oil, 71.9 mg, 65% yield.

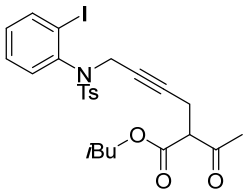
TCL: Rf = 0.5 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.1 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.29 (dd, *J* = 8.1, 6.1 Hz, 3H), 7.05 (dd, *J* = 8.0, 6.6 Hz, 2H), 4.64 (d, *J* = 17.9 Hz, 1H), 4.17 (ddd, *J* = 9.3, 4.3, 2.2 Hz, 2H), 4.07 (d, *J* = 18.0 Hz, 1H), 3.49 (t, *J* = 7.5 Hz, 1H), 2.57 (dt, *J* = 7.6, 2.3 Hz, 2H), 2.45 (s, 3H), 2.22 (s,

1.5H), 2.19 (s, 1.5H), 1.25 (td, *J* = 7.1, 3.4 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 201.08, 201.05, 168.1, 168.0, 144.0, 141.0, 140.9, 140.3, 136.8, 136.7, 131.2, 131.1, 130.4, 129.5, 128.9, 128.8, 128.4, 102.9, 102.8, 82.5, 75.8, 61.9, 58.1, 41.2, 41.2, 29.6, 29.6, 21.7, 17.6, 14.1.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{23}H_{24}INNaO_5S^+$ 576.0312; found 576.0310

**Isobutyl-2-acetyl-6-((*N*-(2-iodophenyl)-4-methylphenyl)sulfonamido)hex-4-ynoate (1d)**



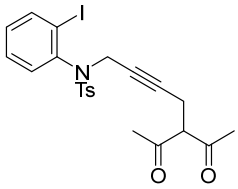

Colorless oil, 75.5 mg, 65% yield.

TCL: Rf = 0.2 (petroleum ether/ethyl acetate = 5:1).

**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 6.8 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 3H), 7.06 – 7.02 (m, 2H), 4.66 – 4.60 (m, 1H), 4.05 (d, *J* = 18.0 Hz, 1H), 3.91 – 3.82 (m, 2H), 3.50 (t, *J* = 7.6 Hz, 1H), 2.59 – 2.53 (m, 2H), 2.43 (s, 3H), 2.21 (s, 1.5H), 2.18 (s, 1.5H), 1.93 – 1.85 (m, 1H), 0.89 (d, *J* = 6.0 Hz, 6H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 201.0, 168.0, 143.9, 140.9, 140.9, 140.2, 136.7, 136.6, 131.1, 131.0, 130.3, 129.5, 128.8, 128.3, 102.82, 102.78, 82.4, 75.7, 71.8, 58.0, 41.2, 29.7, 27.7, 21.7, 19.0, 17.6.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{28}INNaO_5S^+$ 604.0625; found 604.0620.

***N*-(5-acetyl-6-oxohept-2-yn-1-yl)-*N*-(2-iodophenyl)-4-methylbenzenesulfonamide (1e)**




Colorless oil, 20.9 mg, 20% yield, a mixture of enol and atropisomers.

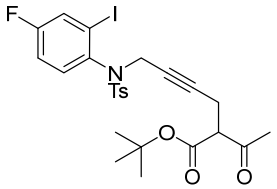
TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 2:1).

**$^{1}$H NMR** (600 MHz, DMSO) δ 16.45 (s, 0.25 H, enol), 7.97 – 7.94 (m, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 1.5 H), 7.40 (d, *J* = 8.1 Hz, 0.5 H), 7.36 (td, *J* = 7.2, 1.2 Hz, 0.78 H), 7.29 (td, *J* = 7.2, 1.2 Hz, 0.25 H), 7.17 – 7.12 (m, 1H), 6.88 (dd, *J* = 7.9, 1.6 Hz, 0.76 H), 6.79 (dd, *J* = 7.9, 1.6 Hz, 0.25 H), 4.53 (d, *J* = 18.6 Hz, 1H), 4.22 (d, *J* = 17.9 Hz, 0.25 H), 4.13 (d, *J* = 17.9 Hz, 0.75 H), 4.23 – 4.12 (m, 1H), 3.81 (t, *J* = 7.2 Hz, 1H), 3.01 (s, 0.5), 2.45 – 2.44 (m, 1.5 H), 2.43 (s, 2H), 2.42 (s, 1H) 2.08 (s, 2H), 2.07 (s, 2.5H), 1.97 (s, 1.5H). **$^{13}$C NMR** (150 MHz, DMSO) δ 202.7, 190.8, 143.9, 140.6,

139.9, 136.1, 130.6, 130.1, 129.7, 128.9, 127.8, 127.7, 106.3, 103.8, 40.8, 39.7, 39.5, 39.4, 29.7, 29.6, 22.8, 21.1, 16.6, 16.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{22}H_{22}INNaO_4S^+$ 546.0206; found 546.0208.

***tert*-Butyl-2-acetyl-6-((*N*-(4-fluoro-2-iodophenyl)-4-methylphenyl)sulfonamido)hex-4-ynoate (1f)**




Colorless oil, 81.5 mg, 68% yield.

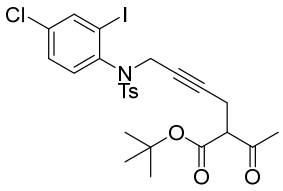
TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, CDCl3) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.02 – 7.00 (m, 2H), 4.64 (dd, *J* = 18.0, 2.4 Hz, 1H), 4.01 (dd, *J* = 18.0, 2.0 Hz, 1H), 3.39 (td, *J* = 7.2, 2.0 Hz, 1H), 2.54 – 2.48 (m, 2H), 2.44 (s, 3H), 2.21 (s, 1.5H), 2.18 (s, 1.5H), 1.42 (d, *J* = 3.6 Hz, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 201.39, 201.36, 167.1, 161.8 (d, $J_{C-F}$ = 254.6 Hz), 144.1, 137.28 (d, $J_{C-F}$ = 8.6 Hz), 137.24 (d, $J_{C-F}$ = 8.6 Hz), 136.6, 136.5, 131.93, 131.85, 131.76, 129.6, 128.4, 127.1 (d, $J_{C-F}$ = 24.6 Hz), 115.9 (d, $J_{C-F}$ = 25.1 Hz), 103.1 (d, $J_{C-F}$ = 8.2 Hz), 103.0 (d, $J_{C-F}$ = 8.2 Hz), 102.9, 82.8, 82.8, 75.44, 75.41, 59.10, 59.09, 41.3, 41.2, 29.4, 27.95, 21.7, 17.5.

**$^{19}$F NMR** (376 MHz, CDCl3) δ-110.45, -110.46.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{27}FINNaO_5S^+$ 622.0531; found 622.0531.

***tert*-Butyl-2-acetyl-6-((*N*-(4-chloro-2-iodophenyl)-4-methylphenyl)sulfonamido)hex-4-ynoate (1g)**



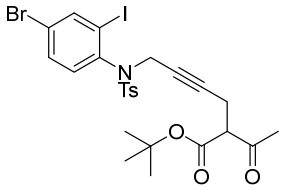

Colorless oil, 73.9 mg, 60% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.0 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 8.4 Hz, 3H), 6.97 (d, *J* = 8.4 Hz, 2H), 4.66 – 4.59 (m, 1H), 4.02 (d, *J* = 17.6 Hz, 1H), 3.38 (t, *J* = 7.6 Hz, 1H), 2.51 – 2.48 (m, 2H), 2.44 (s, 3H), 2.20 (s, 1.5H), 2.17 (s, 1.5H), 1.42 (d, *J* = 3.6 Hz, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 201.3, 167.1, 163.0, 160.5, 144.1, 137.2, 136.5, 131.9, 129.6, 128.4, 127.2, 127.0, 116.0, 115.8, 103.0, 83.0, 82.8, 75.5, 59.1, 41.2, 29.4, 28.0, 21.7, 17.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{27}ClINNaO_5S^+$ 638.0235; found 638.0232.

***tert*-Butyl-2-acetyl-6-((*N*-(4-bromo-2-iodophenyl)-4-methylphenyl)sulfonamido)hex-4-ynoate (1h)**




Yellow oil, 88.4mg, 67% yield.

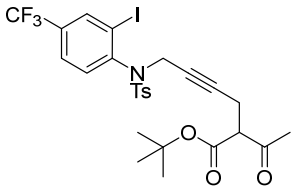
TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.41 (dd, *J* = 8.4 , 2.0 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 8.4 Hz, 1H), 4.60 (dt, *J* = 4.8 , 2.4 Hz, 1H), 3.37 (t, *J* = 7.6 Hz, 1H), 2.50 – 2.47 (m, 2H), 2.42 (s, 3H), 2.19 (s, 1.5H), 2.16 (s, 1.5H), 1.40 (d, *J* = 3.6 Hz, 9H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 201.3, 167.0, 144.2, 142.2, 140.2, 140.1, 136.4, 136.3, 132.09, 132.05, 132.0, 131.9, 129.6, 128.3, 123.5, 103.7, 103.74, 103.66, 83.0, 82.7, 75.2, 75.2, 59.0, 59.0, 41.1, 29.4, 27.9, 21.7, 17.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{25}H_{27}BrINNaO_5S^+$ 681.9730; found 681.9730

***tert*-Butyl 2-acetyl-6-((*N*-(2-iodo-4-(trifluoromethyl)phenyl)-4-methylphenyl)sulfonamido)hex-4-ynoate (1i)**




Colorless oil, 58.4 mg, 45% yield.

TCL: Rf = 0.3 (petroleum ether/ethyl acetate = 5:1).

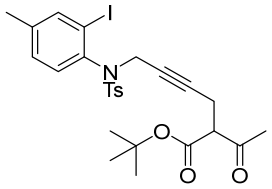
**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.13(s, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 1H), 4.65 (d, *J* = 17.6 Hz, 1H), 4.05 (d, *J* = 18.0 Hz, 1H), 3.37 (t, *J* = 7.2 Hz, 1H), 2.51 – 2.48 (m, 2H), 2.45 (s, 3H), 2.19 (s, 1.5H), 2.16 (s, 1.5H), 1.41 (d, *J* = 4.4 Hz, 9H).

**$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 201.3, 167.1, 144.4, 137.16 (q, $J_{C-F}$ = 4.0 Hz), 136.4, 132.2 (q, $J_{C-F}$ = 33.2 Hz), 131.52, 131.45, 129.7, 128.4, 126.0, 124.64 (q, $J_{C-F}$ = 273.1 Hz), 103.0, 83.3, 82.8, 75.1, 59.1, 41.1, 29.4, 27.9, 21.7, 17.5.

**$^{19}$F NMR** (376 MHz, CDCl3) δ -62.76.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{27}F_3INNaO_5S^+$ 672.0499; found 672.0497.

***tert*-Butyl-2-acetyl-6-((*N*-(2-iodo-4-methylphenyl)-4-methylphenyl)sulfonamido)hex-4-ynoate (1j)**



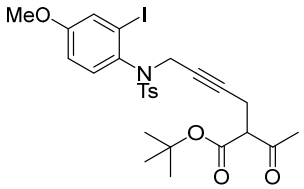
Yellow oil, 77.4mg, 65% yield.

TCL: Rf = 0.5 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.71 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz, 1H), 4.63 (dd, *J* = 18.0, 8.0 Hz, 1H), 4.40 (d, *J* = 19.2 Hz, 1H), 3.40 (t, *J* = 7.6 Hz, 1H), 2.54 – 2.48 (m, 2H), 2.44 (s, 3H), 2.29 (s, 3H), 2.20 (s, 1.5H), 2.17 (s, 1.5H), 1.42 (d, *J* = 2.8 Hz, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 201.3, 167.0, 143.7, 140.7, 140.5, 138.2, 136.7, 130.3, 129.6, 129.3, 128.2, 102.5, 102.4, 82.5, 82.5, 75.5, 58.9, 41.1, 29.3, 27.8, 21.6, 20.5, 17.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{30}INNaO_5S^+$ 618.0782; found 618.0782.

***tert*-Butyl-2-acetyl-6-((*N*-(2-iodo-4-methoxyphenyl)-4-methylphenyl)sulfonamido)hex-4-ynoate (1k)**



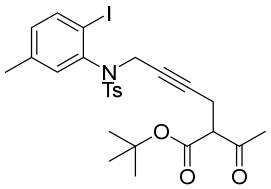
Brown oil, 79.4 mg, 65% yield.

TCL: Rf = 0.3 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.39 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 1H), 6.80 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.68 – 4.61 (m, 1H), 4.03 (dt, *J* = 18.0, 2.0 Hz, 1H), 3.77(s, 3H), 3.41 (t, *J* = 7.2 Hz, 1H), 2.55 – 2.49 (m, 2H), 2.42 (s, 3H), 2.21 (s, 1.5H), 2.18 (s, 1.5H), 1.43 (d, *J* = 3.2 Hz, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 201.35, 167.01, 159.7, 143.7, 136.7, 136.6, 133.5, 133.4, 131.0, 130.9, 129.4, 128.2, 125.0, 114.34, 114.28, 103.2, 82.5, 75.6, 58.9, 55.7, 41.2, 29.4, 27.8, 21.6, 17.4.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{30}INNaO_6S^+$ 634.0731; found 634.0731.

***tert*-Butyl-2-acetyl-6-((*N*-(2-iodo-5-methylphenyl)-4methylphenyl)sulfonamido)hex-4-ynoate (1l)**



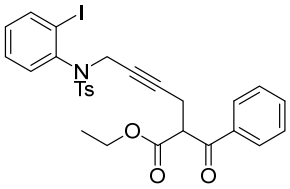
Colorless oil, 79.7 mg, 67% yield.

TCL: Rf = 0.5 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 6.6 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 6.88 (t, *J* = 10.2 Hz, 2H), 4.59 (dd, *J* = 18.0, 11.4 Hz, 1H), 4.06 (dd, *J* = 18.0, 7.8 Hz, 1H), 3.43 (t, *J* = 7.2 Hz, 1H), 2.56 – 2.50 (m, 2H), 2.45 (s, 3H), 2.26 (d, *J* = 5.4 Hz, 3H), 2.22 (s, 1.5H), 2.17 (s, 1.5H), 1.42 (d, *J* = 5.4 Hz, 9H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) 201.4, 167.1, 143.9, 140.7, 140.6, 139.7, 139.2, 136.8, 136.7, 132.1, 131.9, 131.4, 129.4, 128.4, 98.3, 98.1, 82.64, 82.55, 75.7, 75.6, 59.0, 41.2, 41.1, 29.6, 29.5, 27.9, 21.7, 20.9, 17.5.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{26}H_{30}INNaO_5S^+$ 618.0782; found 618.0782.

**Ethyl-2-benzoyl-6-((*N*-(2-iodophenyl)-4-methylphenyl)sulfonamido)hex-4-ynoate (3a)**



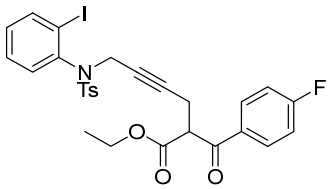
Yellow oil, 80.0 mg, 65% yield.

TCL: Rf = 0.3 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.93 (t, *J* = 9.2 Hz, 2H), 7.87 – 7.82 (m, 1H), 7.67 (dd, *J* = 8.4, 2.8 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.50 – 7.45 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.09 (m 1H), 7.01 – 6.92 (m, 2H), 4.63 (dt, *J* = 18.0, 2.0 Hz, 1H), 4.34 (td, *J* = 7.2, 3.2 Hz, 1H), 4.13 – 3.99 (m, 3H), 2.75 – 2.71 (m, 2H), 2.43 (d, *J* = 3.6 Hz, 3H), 1.11 (td, *J* = 7.2, 5.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 193.2, 168.2, 143.9, 140.9, 140.2, 140.1, 136.8, 135.9, 134.0, 133.9, 131.0, 130.4, 130.3, 129.5, 128.8, 128.7, 128.4, 102.9, 82.8, 77.5, 77.2, 76.8, 75.8, 61.9, 53.1, 41.2, 21.7, 18.5, 14.0.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{26}INNaO_5S^+$ 638.0469; found 638.0468.

**Ethyl-2-(4-fluorobenzoyl)-6-((*N*-(2-iodophenyl)-4-methylphenyl)sulfonamido)hex-4-ynoate (3b)**



Colorless oil, 74.7 mg, 59% yield.

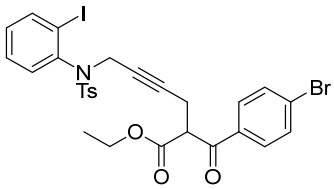
TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 2H), 7.86 – 7.80 (m, 1H), 7.66 (dd, *J* = 8.0, 2.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.11 (m, 3H), 7.02 – 6.94 (m, 2H), 4.61 (dd, *J* = 18.0, 2.4 Hz, 1H), 4.34 (td, *J* = 7.2, 3.6 Hz, 1H), 4.13 – 4.00 (m, 3H), 2.81 – 2.69 (m, 2H), 2.42 (d, *J* = 3.6 Hz, 3H), 1.11 (q, *J* = 6.4 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 191.53, 191.45, 167.9, 165.9 (d, $J_{C\text{-}F}$ = 253.4 Hz), 143.8, 140.7, 140.0, 139.9, 136.51, 136.45, 132.13 (d, $J_{C\text{-}F}$ = 3.1 Hz), 131.53, 131.44, 130.8, 130.7, 130.22, 130.18, 129.3, 128.6, 128.55, 128.2, 115.8 (d, $J_{C\text{-}F}$ = 21.9 Hz), 115.7 (d, $J_{C\text{-}F}$ = 21.9 Hz), 102.73, 102.68, 82.5, 75.7, 61.8, 52.7, 41.0, 21.5, 18.3, 13.8.

$^{19}$F NMR (376 MHz, $CDCl_3$) δ -103.45, -103.55.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{25}FINNaO_5S^+$ 656.0374; found 656.0368.

**Ethyl-2-(4-bromobenzoyl)-6-((*N*-(2-iodophenyl)-4-methylphenyl)sulfonamido)hex-4-ynoate (3c)**



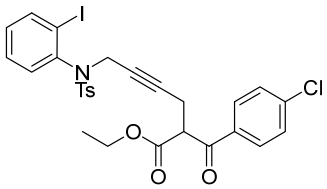
Colorless oil, 84.7 mg,61% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.82 – 7.77 (m, 3H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.60 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.15 (td, *J* = 8.0, 1.6 Hz, 1H), 7.03 – 6.94 (m, 2H), 4.62 – 4.56 (m, 1H), 4.30 (q, *J* = 6.8 Hz, 1H), 4.13 – 3.99 (m, 3H), 2.76 – 2.70 (m, 2H), 2.42 (s, 3H), 1.12 (q, *J* = 6.8 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.4, 167.9, 144.0, 140.9, 140.2, 140.1, 136.7, 134.6, 132.2, 132.1, 131.0, 130.4, 129.5, 129.2, 128.8, 128.7, 128.4, 102.8, 82.5, 76.0, 62.0, 53.0, 41.2, 29.8, 21.7, 18.5, 14.0.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{25}BrINNaO_5S^+$ 715.9574; found 715.9574.

**Ethyl-2-(4-chlorobenzoyl)-6-((*N*-(2-iodophenyl)-4-methylphenyl)sulfonamido)hex-4-ynoate (3d)**



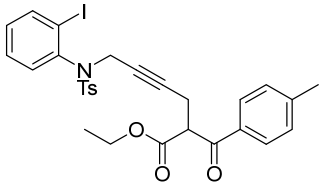
Colorless oil, 87.0 mg, 67% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 3H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.44 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.03 – 6.96 (m, 2H), 4.63 – 4.56 (m, 1H), 4.31 (dd, *J* = 13.2, 7.2 Hz, 1H), 4.14 – 4.00 (m, 3H), 2.76 – 2.71 (m, 2H), 2.44 (s, 3H), 1.13 (q, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.2, 168.0, 144.0, 140.9, 140.6, 140.3, 140.2, 136.8, 134.3, 131.1, 130.3, 129.5, 129.2, 128.8, 128.4, 102.8, 82.6, 76.1, 62.1, 53.1, 41.2, 29.8, 21.8, 18.5, 14.1.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{25}ClINNaO_5S^+$ 672.0079; found 672.0075.

**Ethyl-6-((*N*-(2-iodophenyl)-4-methylphenyl)sulfonamido)-2-(4-methylbenzoyl)hex-4-ynoate (3e)**



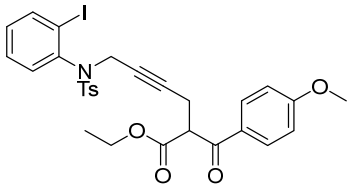
Colorless oil, 75.5 mg, 60% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 3H), 7.68 (dd, *J* = 8.4, 3.6 Hz, 2H), 7.31 – 7.26 (m, 4H), 7.19 – 7.11 (m, 1H), 7.04 – 6.93 (m, 2H), 4.65 (dd, *J* = 18.0, 2.8 Hz, 1H), 4.32 (td, *J* = 7.2, 3.2 Hz, 1H), 4.14 – 3.99 (m, 3H), 2.80 – 2.68 (m, 2H), 2.44 (t, *J* = 4.8 Hz, 6H), 1.13 (dd, *J* = 12.4, 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.7, 192.7, 168.4, 168.3, 145.0, 144.9, 143.9, 140.9, 140.2, 140.1, 136.82, 136.75, 133.3, 131.0, 130.9, 130.3, 130.3, 129.5, 129.5, 129.4, 129.0, 128.8, 128.7, 128.4, 102.93, 102.87, 82.9, 75.7, 61.8, 52.9, 52.8, 41.2, 21.8, 21.7, 18.6, 14.0.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{29}H_{28}INNaO_5S^+$ 652.0625; found 652.0624.

**Ethyl-6-((*N*-(2-iodophenyl)-4-methylphenyl)sulfonamido)-2-(4-methoxybenzoyl)hex-4-ynoate (3f)**



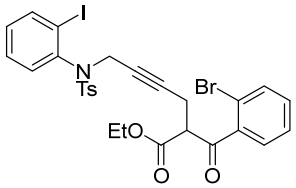
Colorless oil, 82.6 mg, 64% yield.

TCL: Rf = 0.3 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 2H), 7.86 – 7.86 (m, 1H), 7.66 (t, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 7.17 – 7.11 (m, 1H), 7.01 – 6.91 (m, 4H), 4.62 (dd, *J* = 18.0, 2.4 Hz, 1H), 4.29 (t, *J* = 6.0 Hz, 1H), 4.11 – 4.04 (m, 2H), 4.01 (d, *J* = 18.0 Hz, 1H), 3.86 (d, *J* = 3.6 Hz, 3H), 2.74 – 2.66 (m, 2H), 2.42 (d, *J* = 8.4 Hz, 3H), 1.12 (q, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 191.5, 191.4, 168.4, 164.2, 164.1, 143.9, 140.9, 140.2, 140.1, 136.8, 136.7, 131.31, 131.0, 130.9, 130.3, 129.4, 128.8, 128.7, 128.3, 114.0, 113.9, 102.9, 102.8, 83.0, 75.7, 61.8, 61.7, 55.6, 52.7, 52.6, 41.2, 21.7, 18.6, 14.0.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{29}H_{28}INNaO_6S^+$ 668.0574; found 668.0574.

**Ethyl 2-(2-bromobenzoyl)-6-((*N*-(2-iodophenyl)-4-methylphenyl)sulfonamido)hex-4-ynoate (3g)**



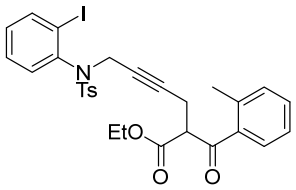

Colorless oil, 83.3 mg, 60% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (400 MHz, $CDCl_3$) δ 12.77 (s, enol, 0.22 H), 7.89 – 7.84 (m, 1H), 7.69 – 7.65 (m, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.39 – 7.19 (m, 6H), 7.05 – 6.98 (m, 2H), 4.66 (d, *J* = 18.0, 1H), 4.33 – 4.26 (m, 1.2H), 4.12 – 4.02 (m, 2.5H), 2.75 – 2.71 (m, 2H), 2.42 (s , 3H), 1.31 (td, *J* = 7.1 Hz, 0.77H), 1.12 – 1.06 (m, 2.3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 196.33, 196.28, 172.3, 170.4, 167.4, 143.9, 140.8, 140.2, 136.7, 133.9, 133.1, 132.3, 131.1, 130.3, 129.5, 129.3, 128.83, 128.75, 128.3, 127.4, 121.3, 119.3, 102.9, 102.7, 82.5, 76.0, 73.39, 61.9, 56.3, 41.2, 21.7, 18.0, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{25}BrINNaO_5S^+$ 715.9574; found 715.9573.

**Ethyl 6-((*N*-(2-iodophenyl)-4-methylphenyl)sulfonamido)-2-(2-methylbenzoyl)hex-4-ynoate (3h)**




Colorless oil, 62.9 mg, 50% yield.

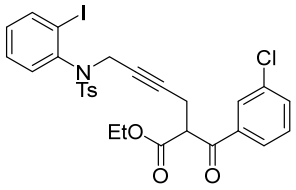
TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 5:1).

**$^1$H NMR** (600 MHz, $CDCl_3$) δ 12.84 (s, enol), 7.88 – 7.81 (m, 1H), 7.66 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.38 (dd, *J* = 13.2, 7.2 Hz, 1H), 7.29 – 7.20 (m, 4H), 7.16 – 7.13 (m, 1H), 7.05 – 6.94 (m,

2H), 4.67 – 4.62 (m, 1H), 4.29 – 4.22 (m, 1.2H), 4.12 – 4.00 (m, 2.6H), 2.77 – 2.65 (m, 2H), 2.43 – 2.37 (m, 5.5H), 2.24 (s, enol, 0.5H), 1.30 (t, *J* = 7.1 Hz, enol, 0.6H), 1.09 – 1.05 (m, 2.4H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 196.54, 196.50, 172.5, 168.14, 168.11, 143.8, 140.9, 140.8, 140.12, 140.08, 140.0, 138.9, 138.8, 136.7, 136.6, 135.8, 133.7, 132.0, 131.94, 131.91, 130.9, 130.8, 130.4, 130.3, 130.2, 129.5, 129.4, 129.3, 128.7, 128.64, 128.61, 128.5, 128.2, 128.1, 127.8, 125.7, 125.5, 102.9, 102.8, 102.7, 98.3, 84.8, 82.74, 82.69, 75.74, 75.69, 73.0, 61.6, 61.0, 55.1, 41.2, 41.2, 21.6, 21.0, 20.9, 19.2, 18.4, 17.2, 14.3, 13.9.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{29}H_{28}INNaO_5S^+$ 652.0625; found 625.0623.

**Ethyl 2-(3-chlorobenzoyl)-6-((*N*-(2-iodophenyl)-4-methylphenyl)sulfonamido)hex-4-ynoate (3i)**



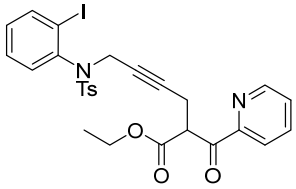

Colorless oil, 58.5 mg, 45% yield.

TCL: Rf = 0.3 (petroleum ether/ethyl acetate = 5:1).

**$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 7.93 – 7.80 (m, 3H), 7.67 (d, *J* = 6.6 Hz, 2H), 7.60 – 7.56 (m, 1H), 7.45 – 7.41 (m, 1H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.14 (m, 1H), 7.03 – 6.95 (m, 2H), 4.63 – 4.59 (m, 1H), 4.31 – 4.26 (m, 1H), 4.14 – 4.01 (m, 3H), 2.74 (s, 2H), 2.45 – 2.43 (m, 3H), 1.16 – 1.12 (m, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 192.0, 167.8, 143.9, 140.9, 140.2, 137.4, 136.6, 135.1, 133.8, 130.9, 130.3, 130.1, 130.0, 128.8, 128.73, 128.65, 128.3, 127.0, 82.5, 76.0, 62.0, 53.0, 41.1, 21.7, 18.4, 14.0.

HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{28}H_{25}ClINNaO_5S^+$ 672.0079; found 672.0077.

**Ethyl-6-((*N*-(2-iodophenyl)-4-methylphenyl)sulfonamido)-2-picolinoylhex-4-ynoate (3j)**




Brown oil, 73.9 mg, 60% yield.

TCL: Rf = 0.4 (petroleum ether/ethyl acetate = 2:1).

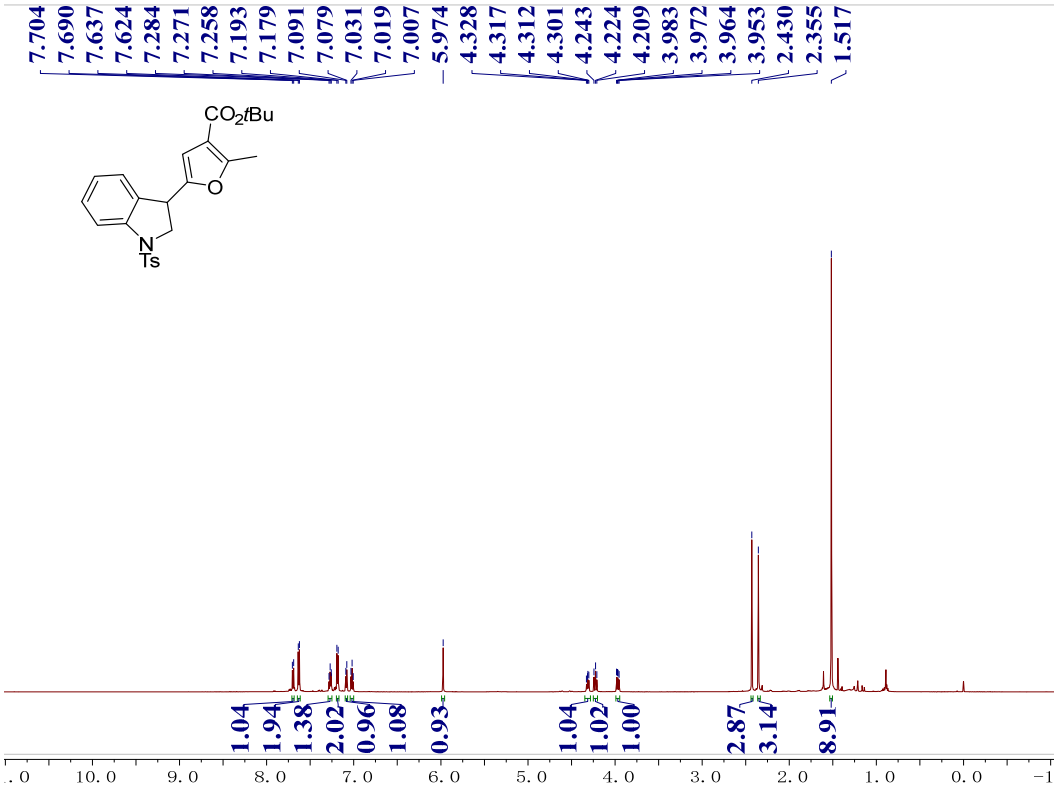
**$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 8.66 (t, *J* = 6.0 Hz, 1H), 8.03 – 7.98 (m, 1H), 7.87 – 7.83 (m, 2H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.50 – 7.48 (m, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 7.20 – 7.12 (m, 1H), 7.00 – 6.95 (m, 2H), 4.74 – 4.64 (m, 2H), 4.10 – 4.05 (m, 2H), 3.98 (d, *J* = 18.0 Hz, 1H), 2.79 – 2.69 (m, 2H), 2.42 (s, 3H), 1.09 (t, *J* = 6.6 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 194.9, 169.1, 152.0, 149.0, 143.9, 141.04,

141.00, 140.19, 140.16, 137.20, 137.16, 137.0, 131.2, 131.1, 130.3, 129.5, 128.8, 128.7, 128.5, 128.4, 127.7, 122.6, 103.0, 103.0, 82.9, 75.6, 61.5, 51.9, 51.7, 41.3, 21.7, 18.2, 14.0.

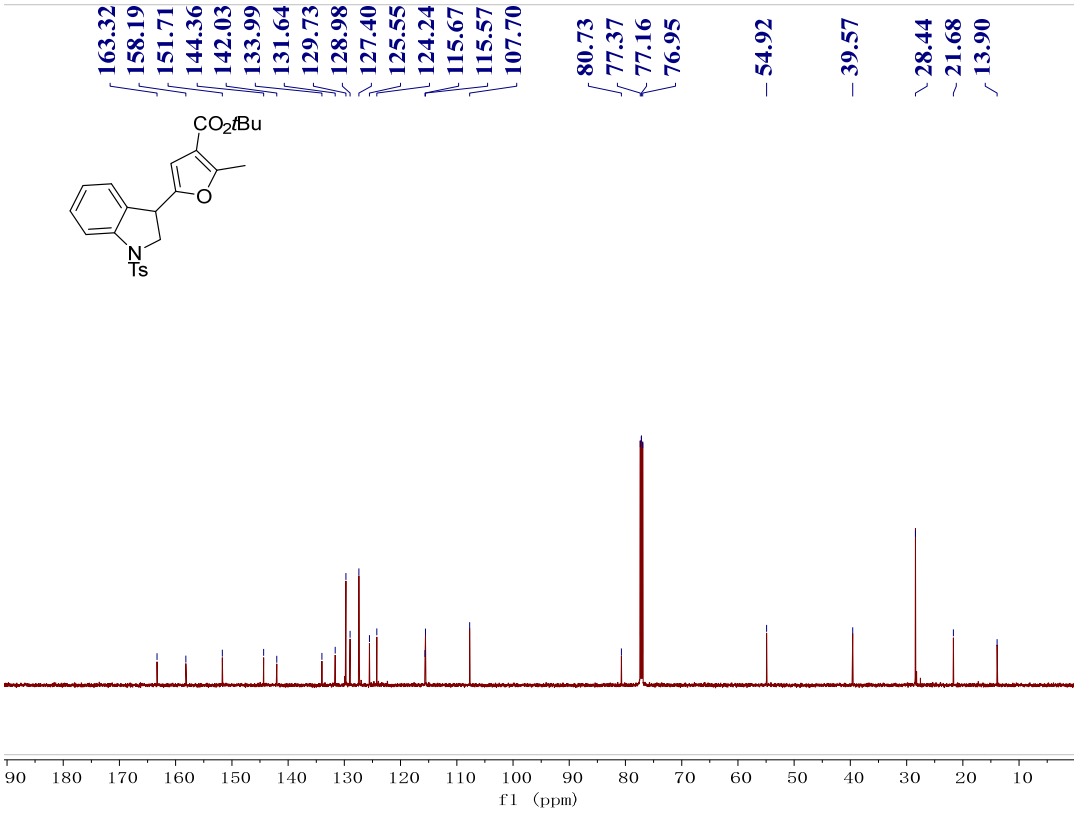
HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{27}H_{25}IN_2NaO_5S^+$ 639.0421; found 639.0419.

# Copies of $^{1}$H NMR and $^{13}$C NMR spectra

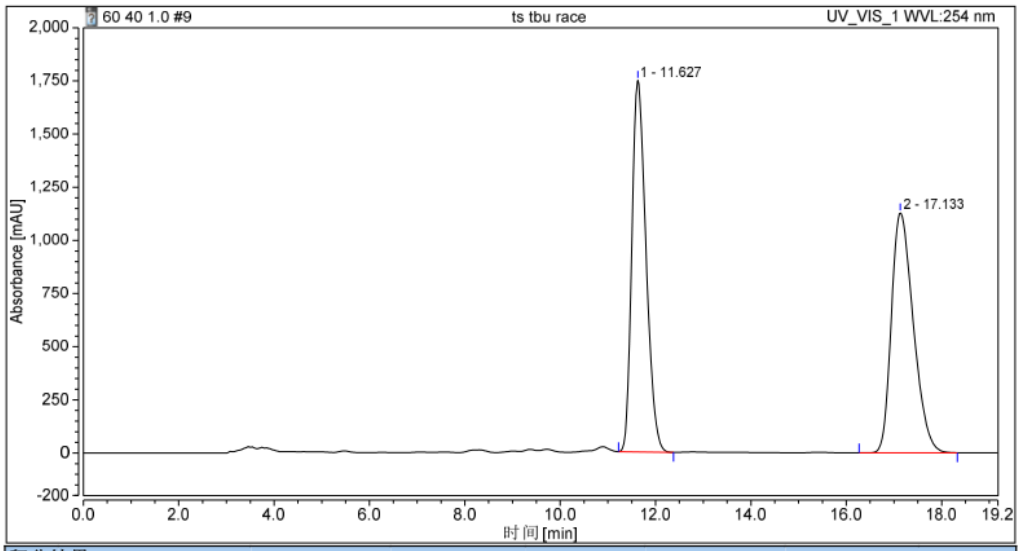
$^{1}$H NMR of **2a** (600 MHz, $CDCl_3$)




$^{13}$C NMR of **2a** (150 MHz, $CDCl_3$)

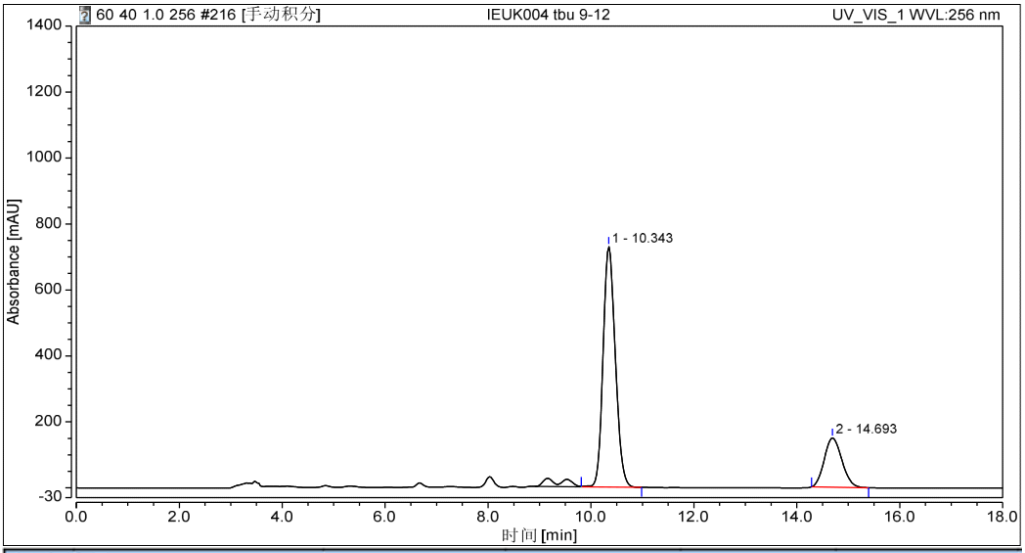


HPLC of **2a**




积分结果

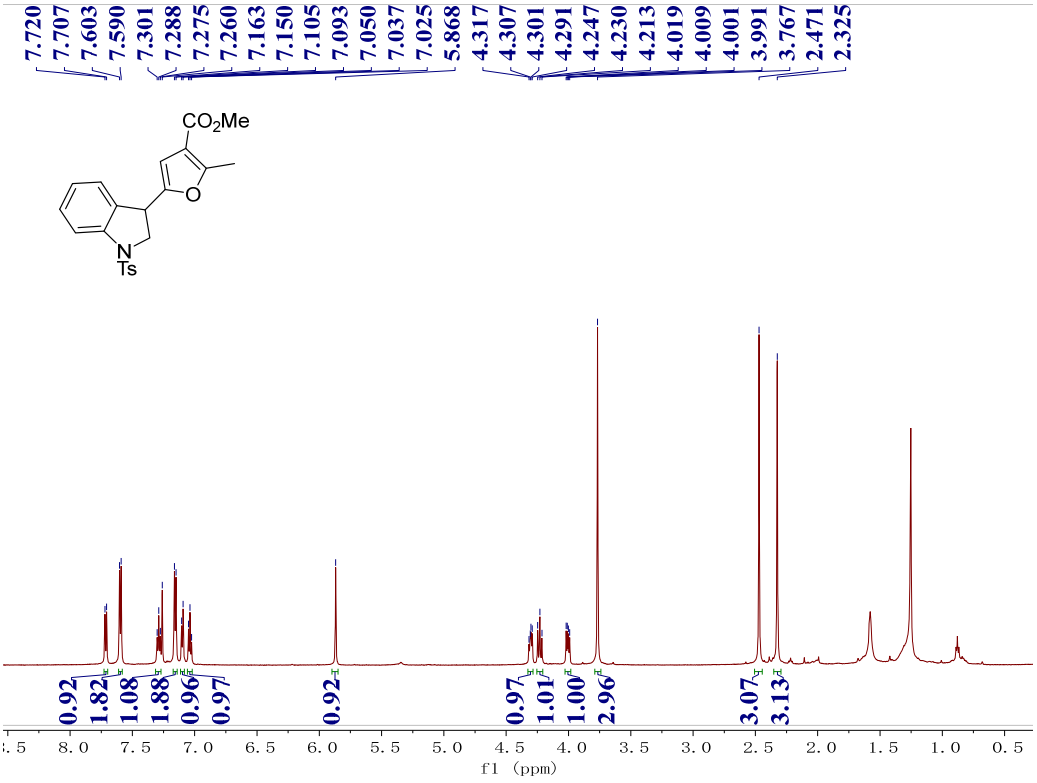
| 序号 | 峰名称 | 保留时间 min | 峰面积 mAU*min | 峰高 mAU | 相对峰面积 % | 相对峰高 % | 样品量 n.a. |
|---|---|---|---|---|---|---|---|
| 1 | | 11.627 | 602.807 | 1748.084 | 50.02 | 60.74 | n.a. |
| 2 | | 17.133 | 602.247 | 1129.818 | 49.98 | 39.26 | n.a. |
| **总和:** | | | **1205.053** | **2877.902** | **100.00** | **100.00** | |



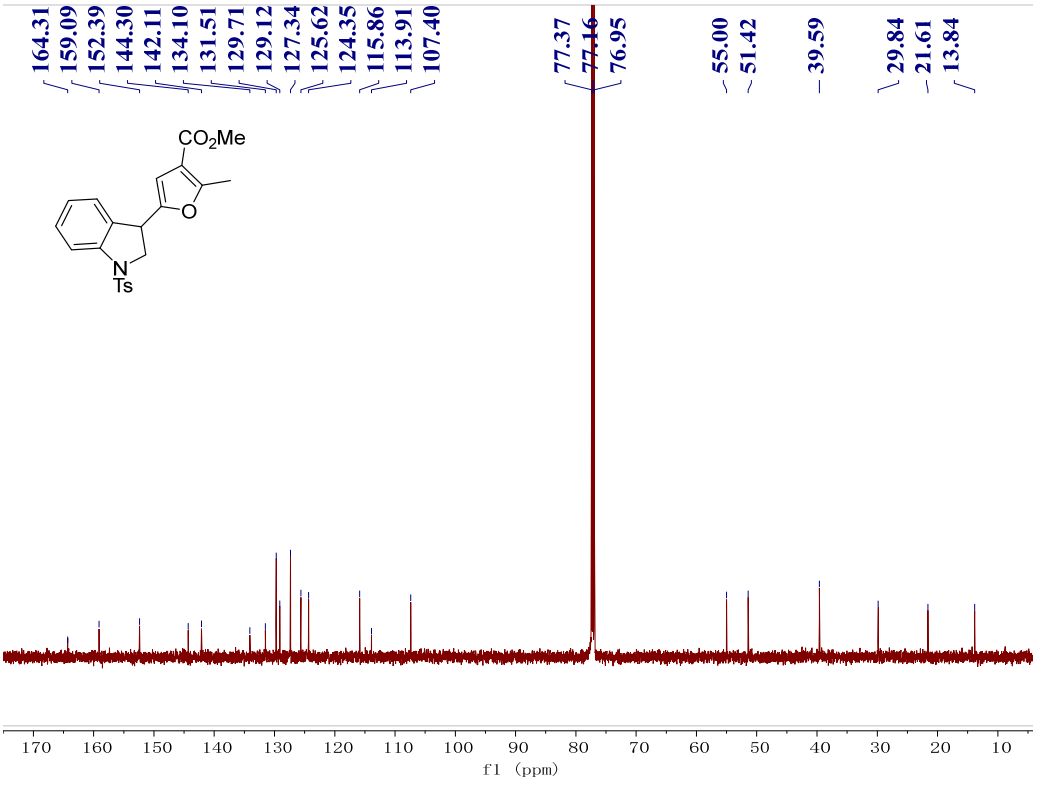

积分结果

| Peak | Retention Time min | Area mAU*min | Height mAU | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 10.343 | 200.764 | 729.613 | 77.20 | 83.01 |
| 2 | 14.693 | 59.284 | 149.374 | 22.80 | 16.99 |
| **Total:** | | **260.048** | **878.987** | **100.00** | **100.00** |

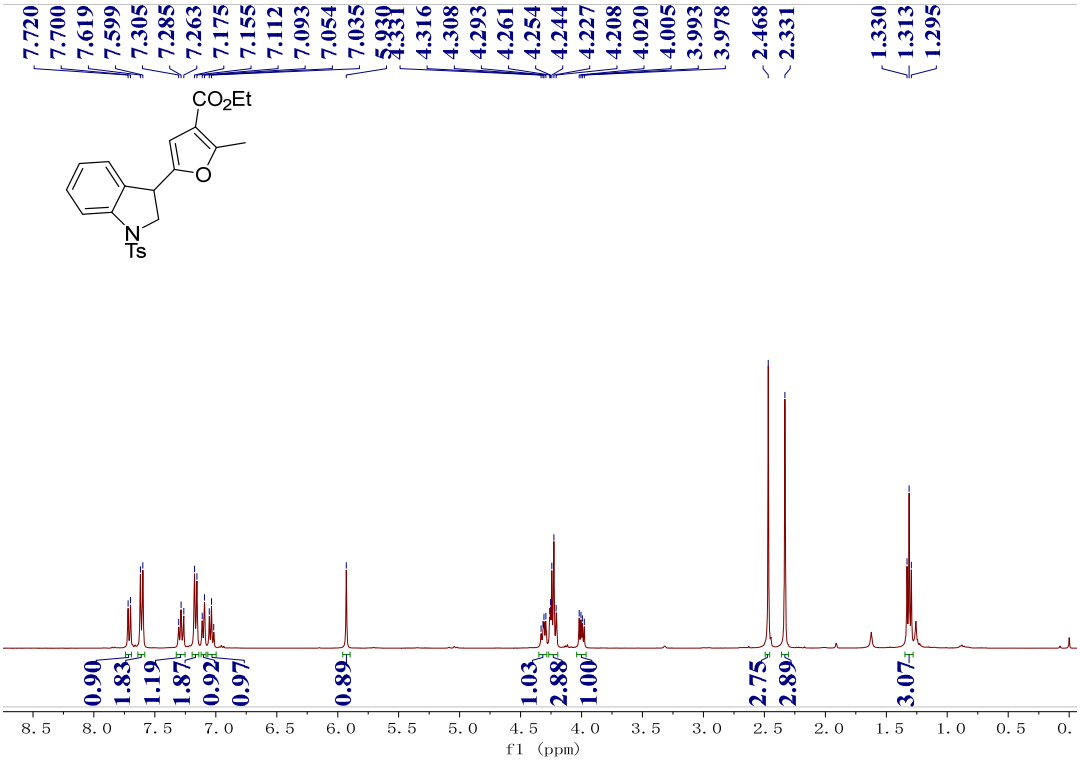
$^{1}$H NMR of **2b** (600 MHz, $CDCl_3$)



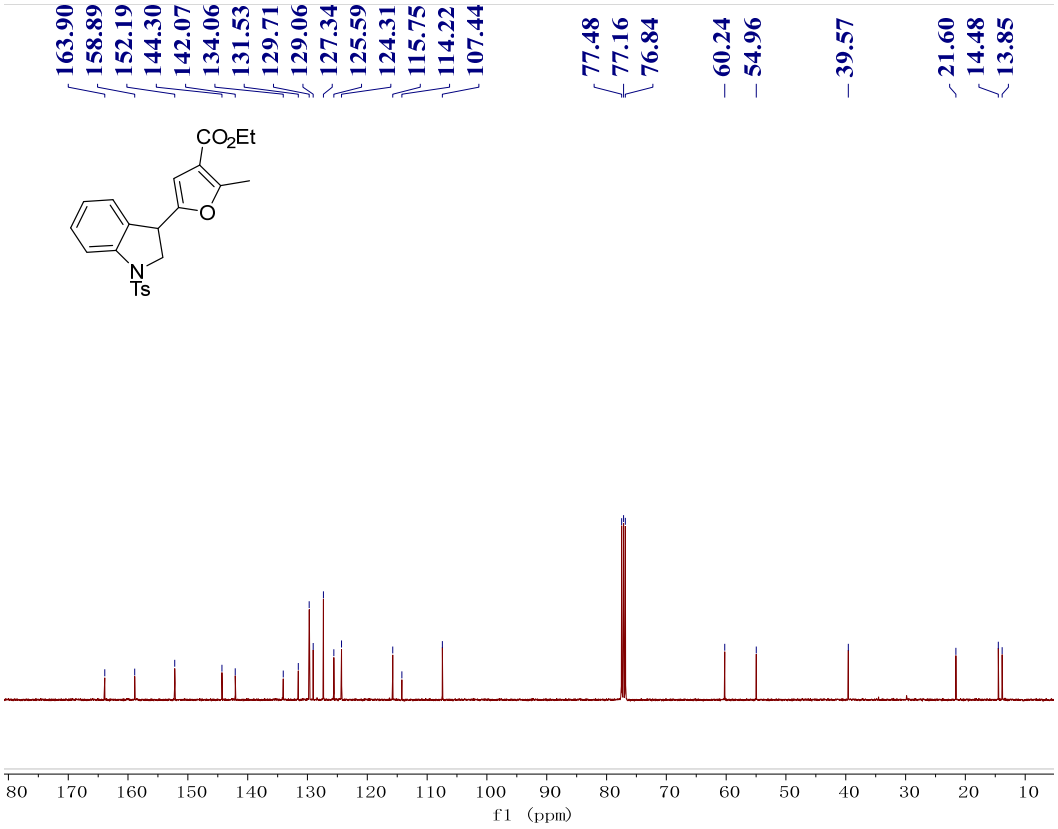

$^{13}$C NMR of **2b** (150 MHz, $CDCl_3$)



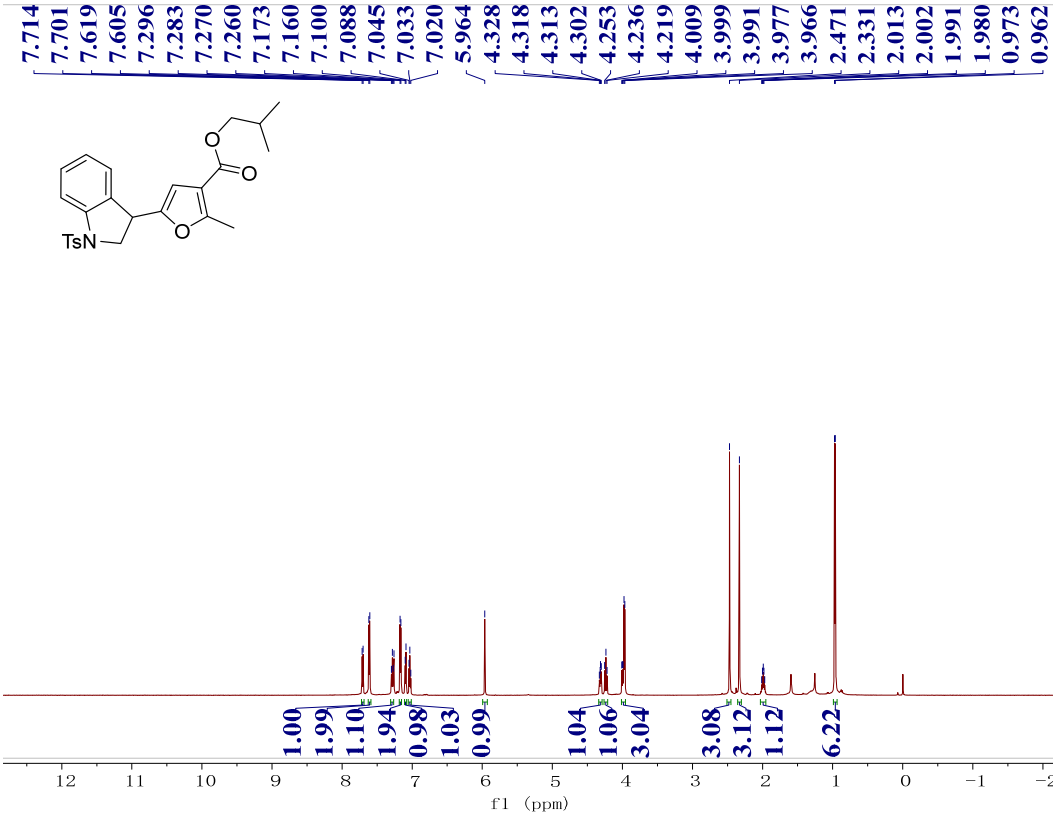
$^{1}$H NMR of **2c** (400 MHz, $CDCl_3$)



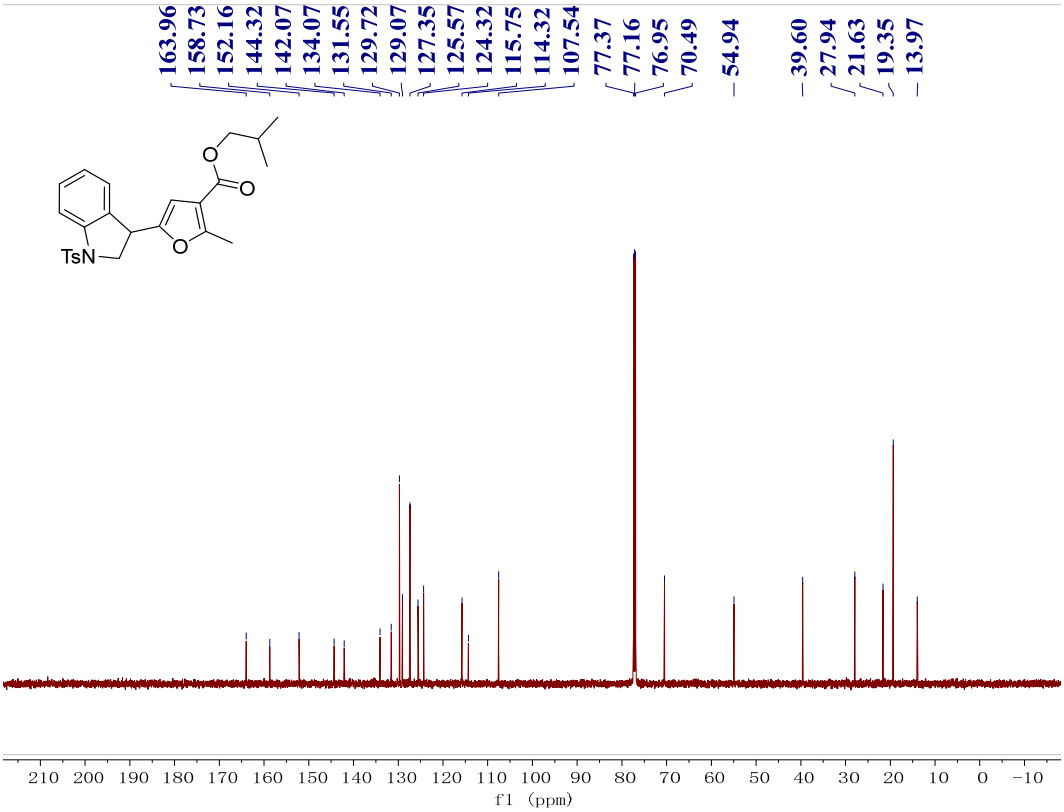

$^{13}$C NMR of **2c** (100 MHz, $CDCl_3$)



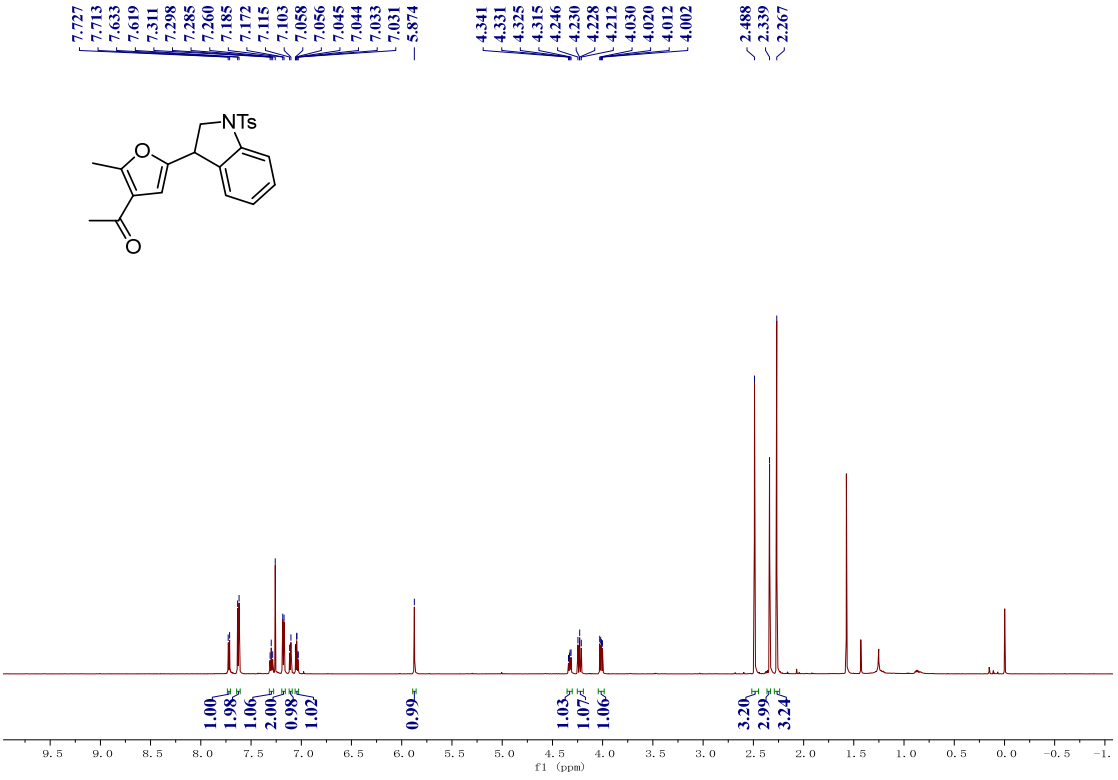
$^{1}$H NMR of **2d** (600 MHz, $CDCl_3$)



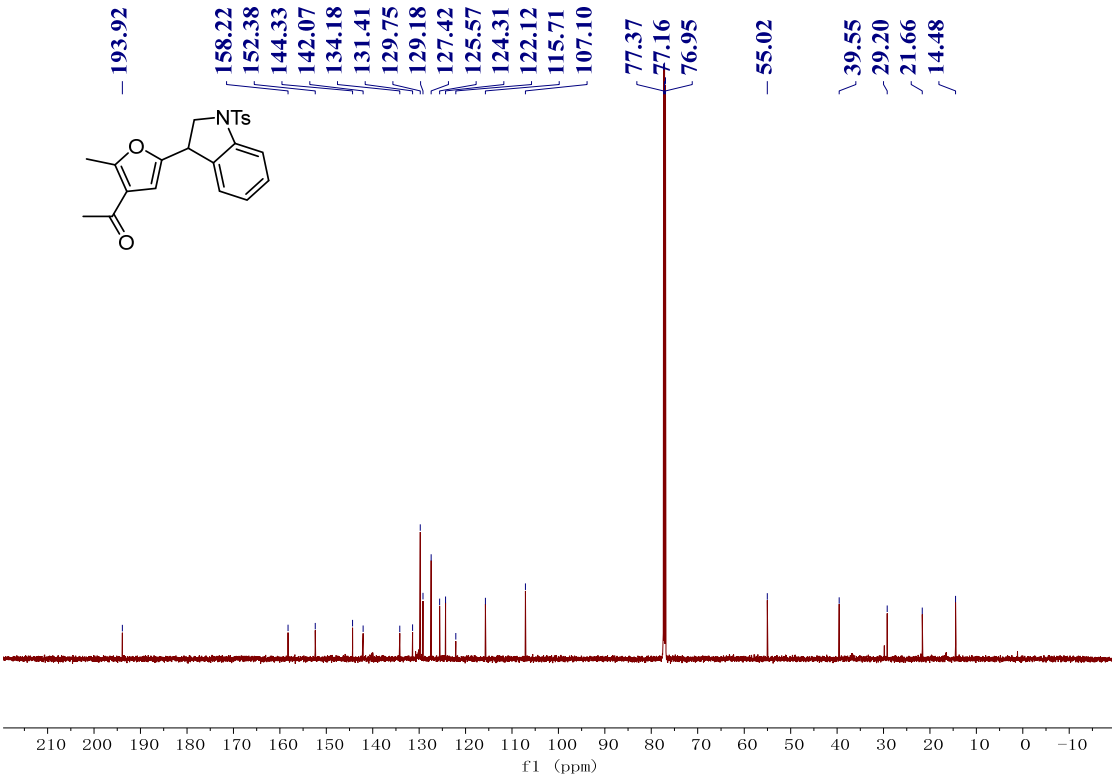

$^{13}$C NMR of **2d** (150 MHz, $CDCl_3$)



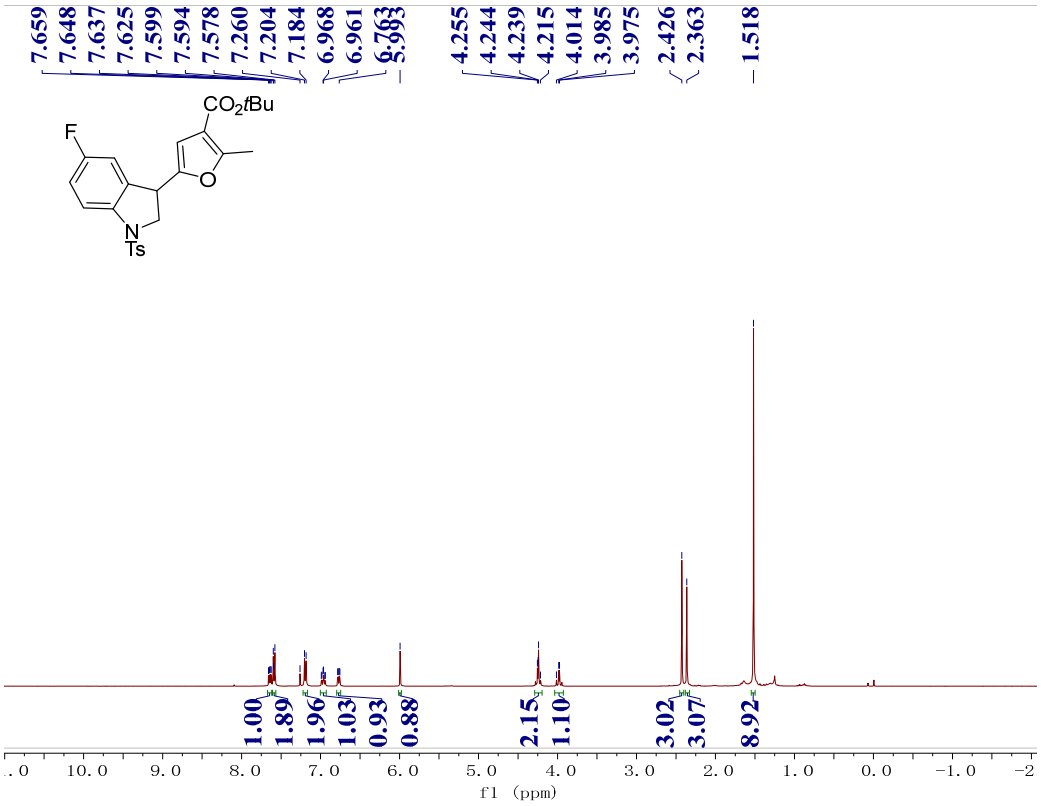
$^{1}$H NMR of **2e** (600 MHz, $CDCl_3$)



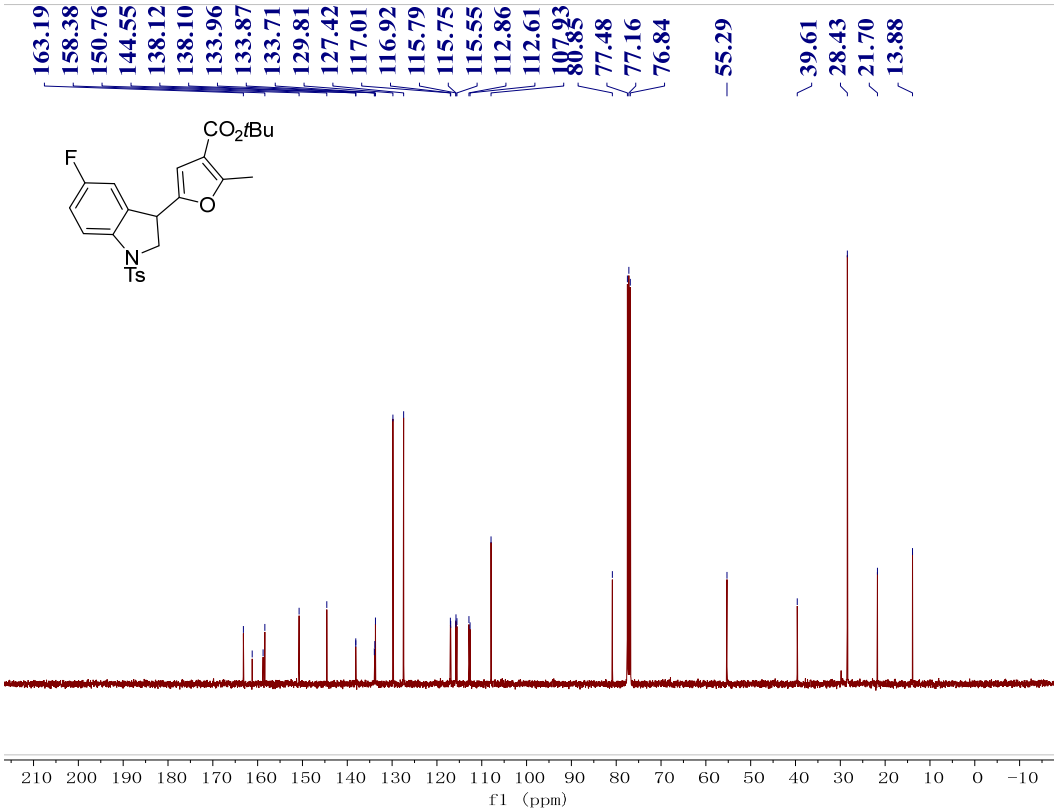

$^{13}$C NMR of **2e** (150 MHz, $CDCl_3$)



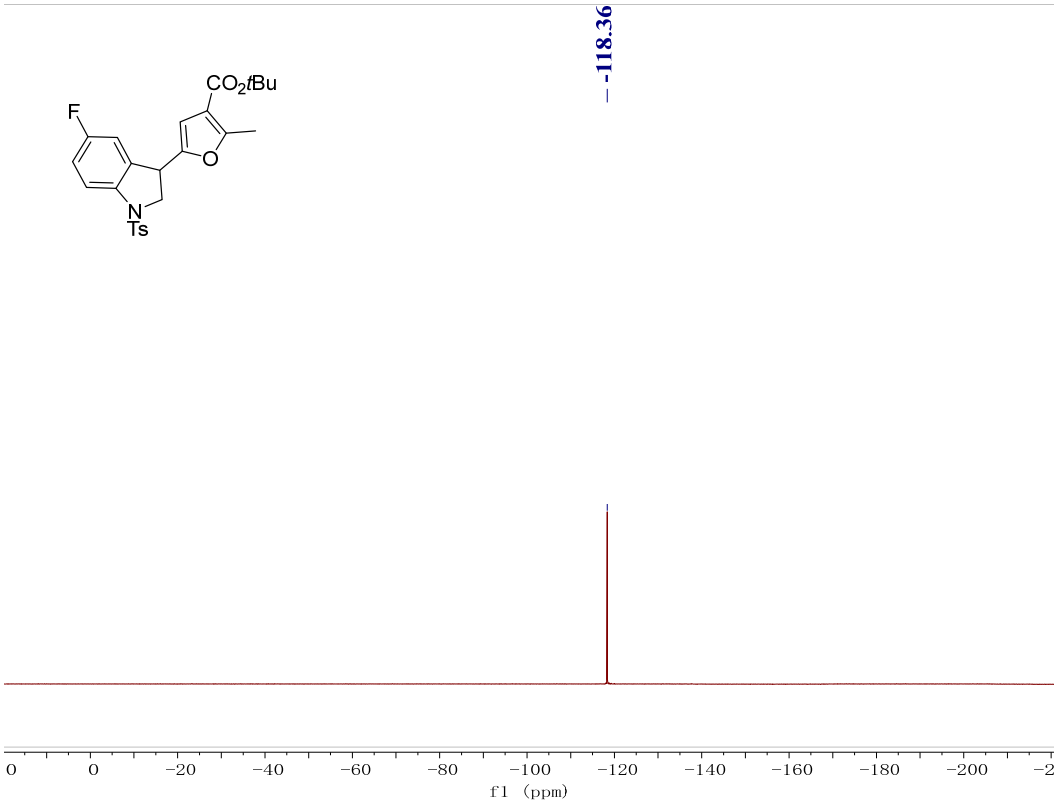
$^{1}$H NMR of **2f** (400 MHz, $CDCl_3$)



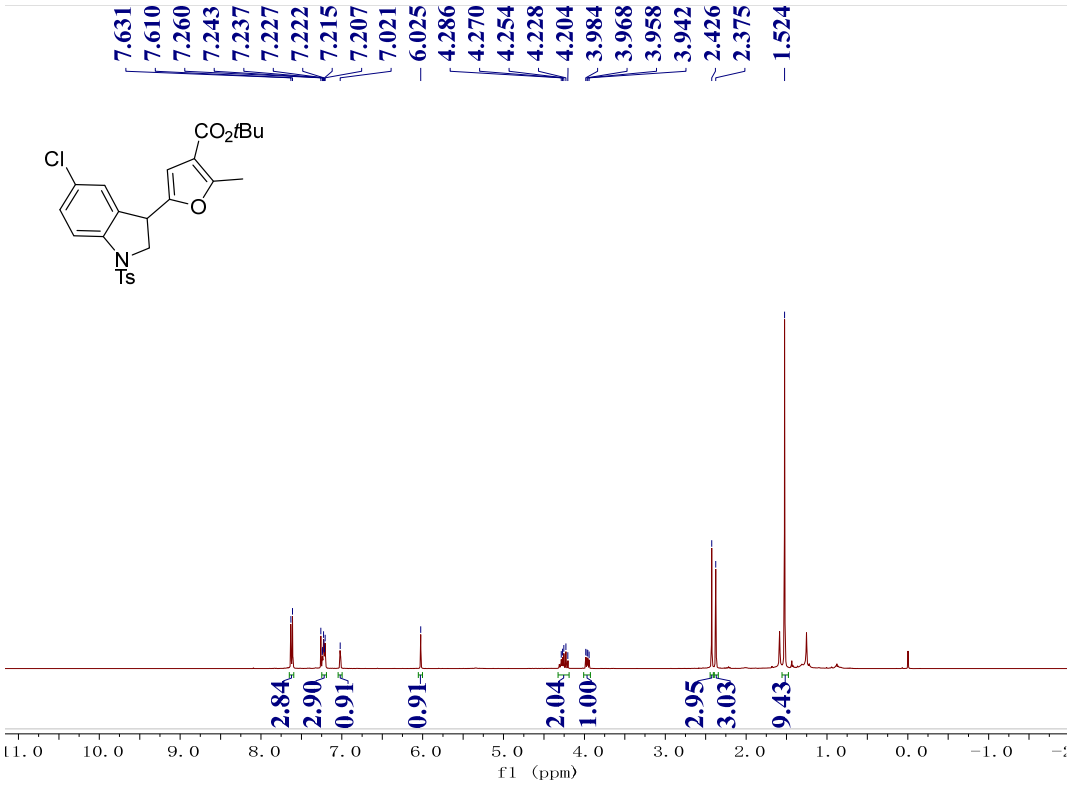

$^{13}$C NMR of **2f** (100 MHz, $CDCl_3$)



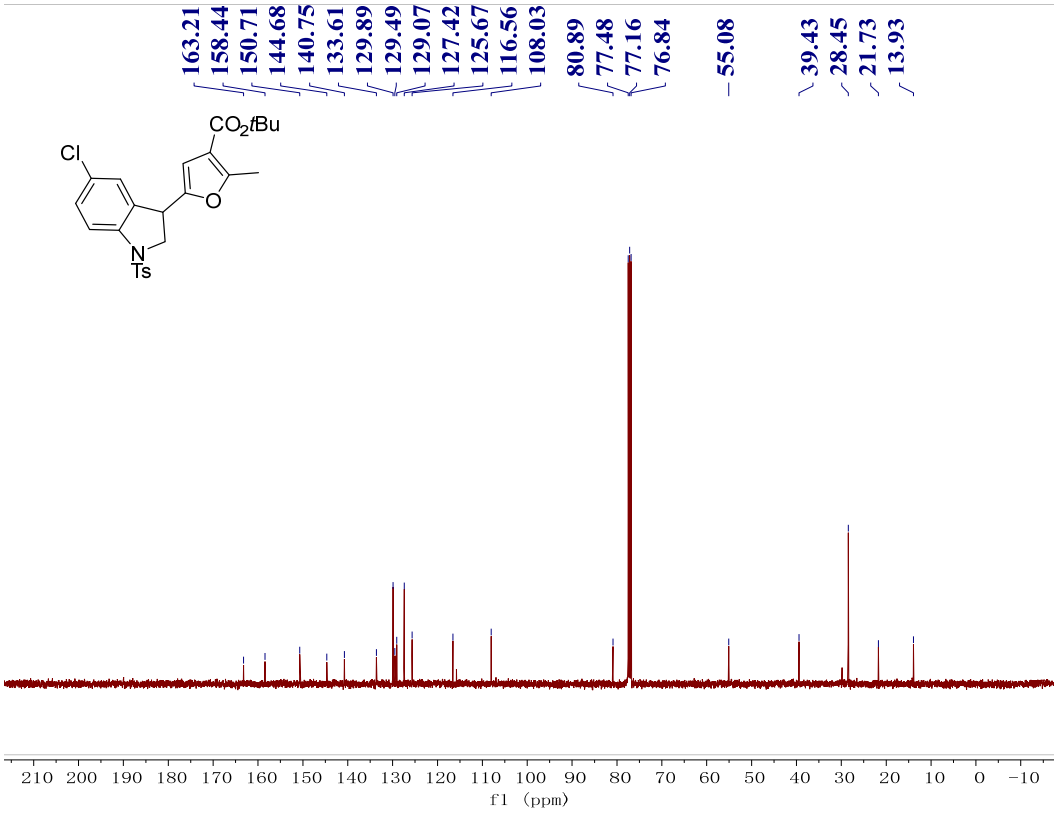
$^{19}$F NMR of **2f** (376 MHz, $CDCl_3$)



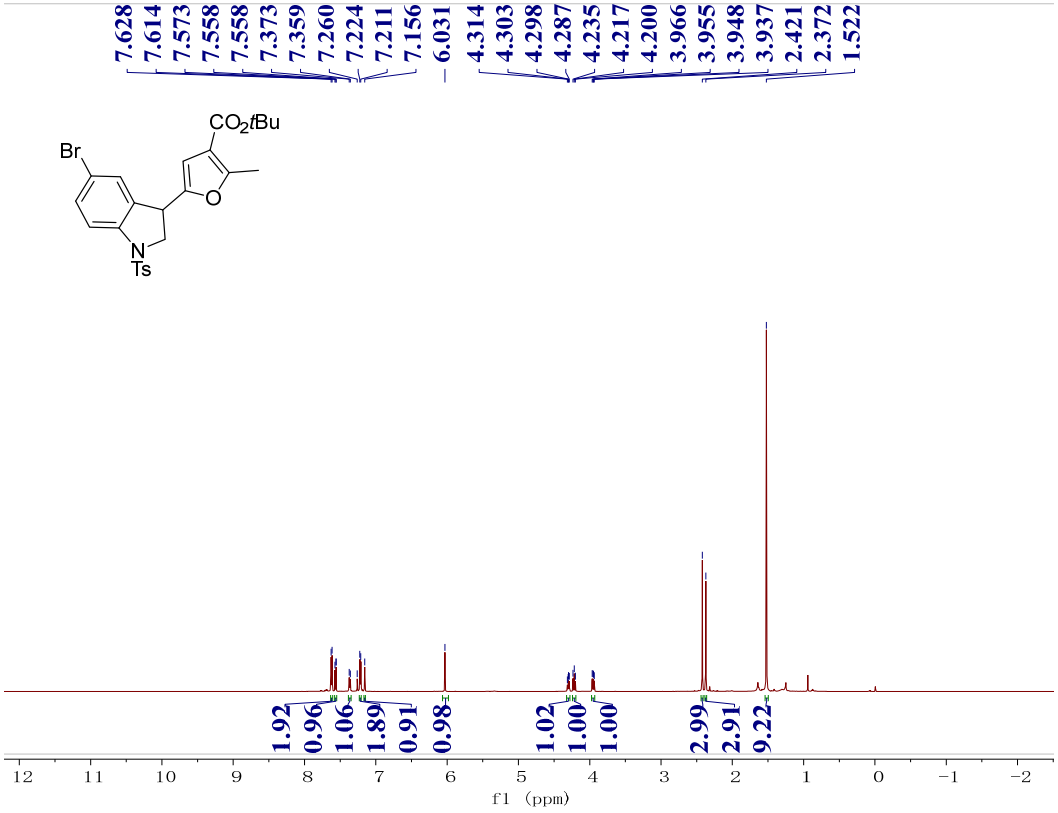

$^{1}$H NMR of **2g** (400 MHz, $CDCl_3$)



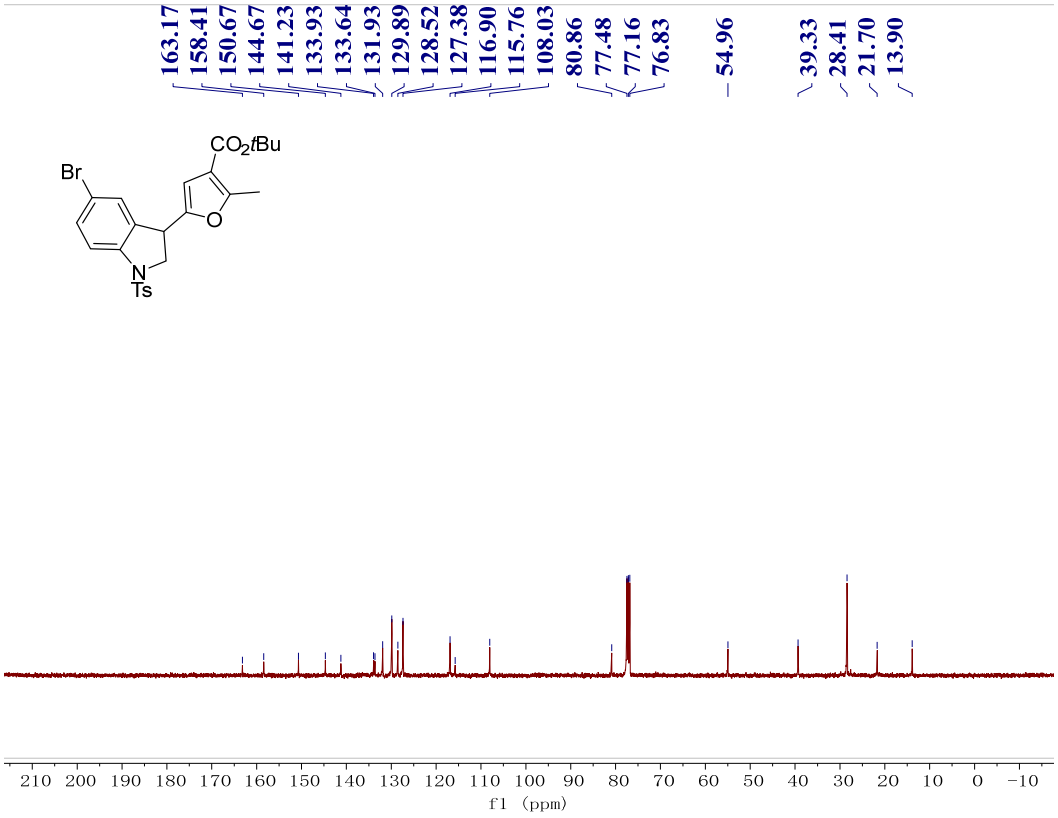
$^{13}$C NMR of **2g** (100 MHz, $CDCl_3$)



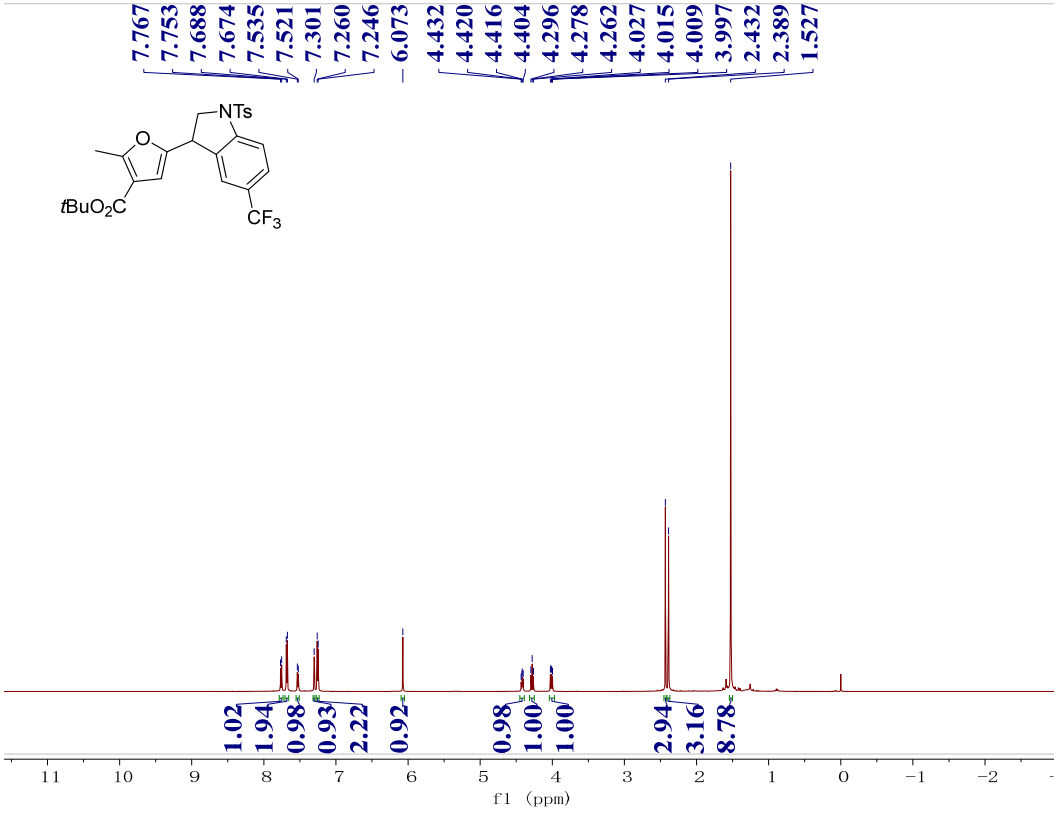

$^{1}$H NMR of **2h** (400 MHz, $CDCl_3$)



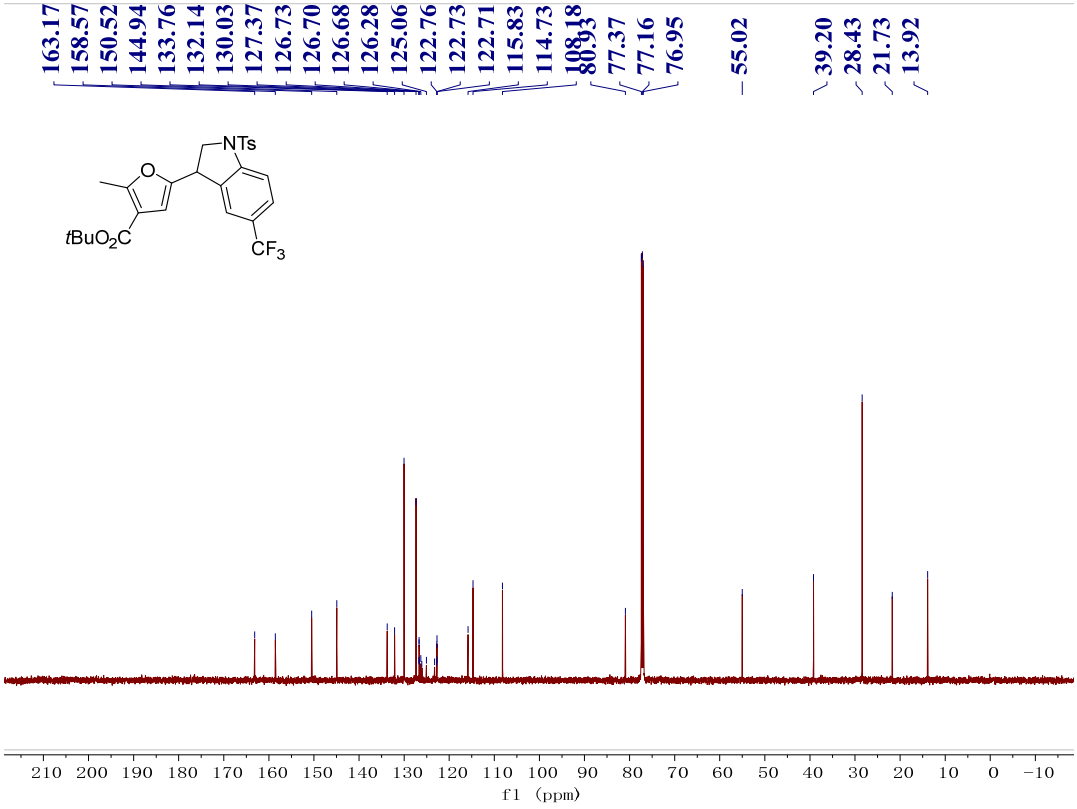
$^{13}$C NMR of **2h** (100 MHz, $CDCl_3$)



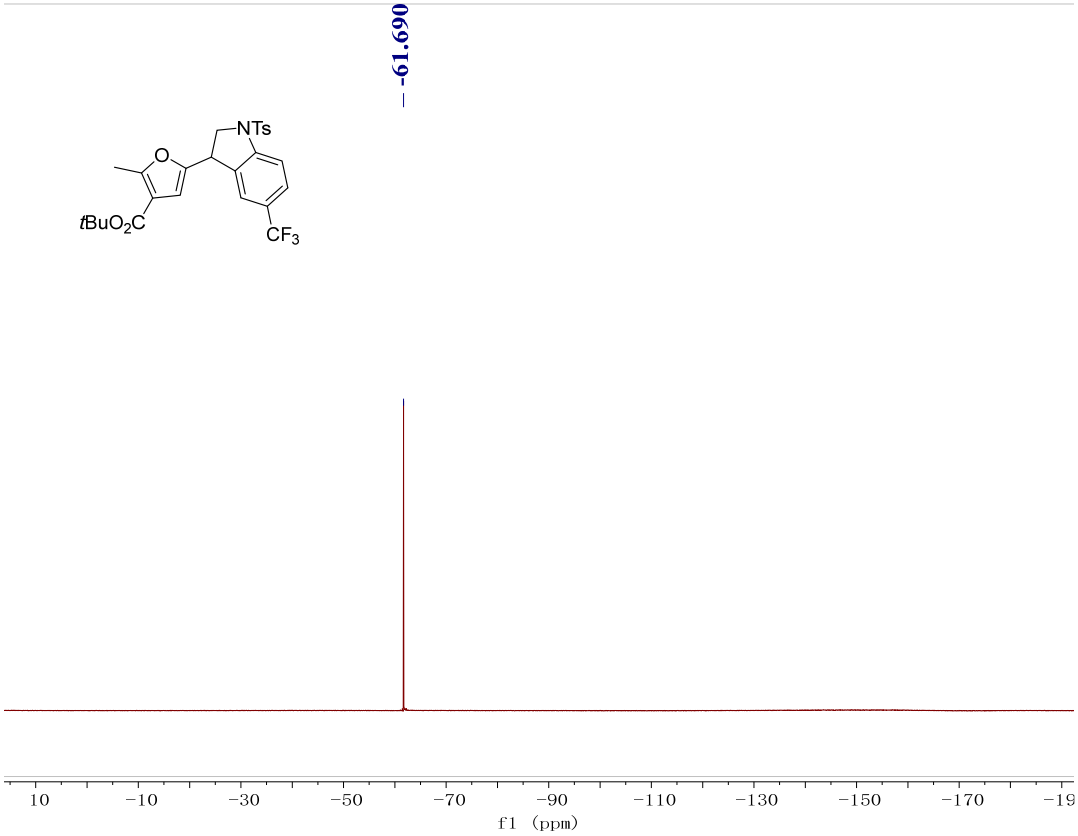

$^{1}$H NMR of **2i** (600 MHz, $CDCl_3$)



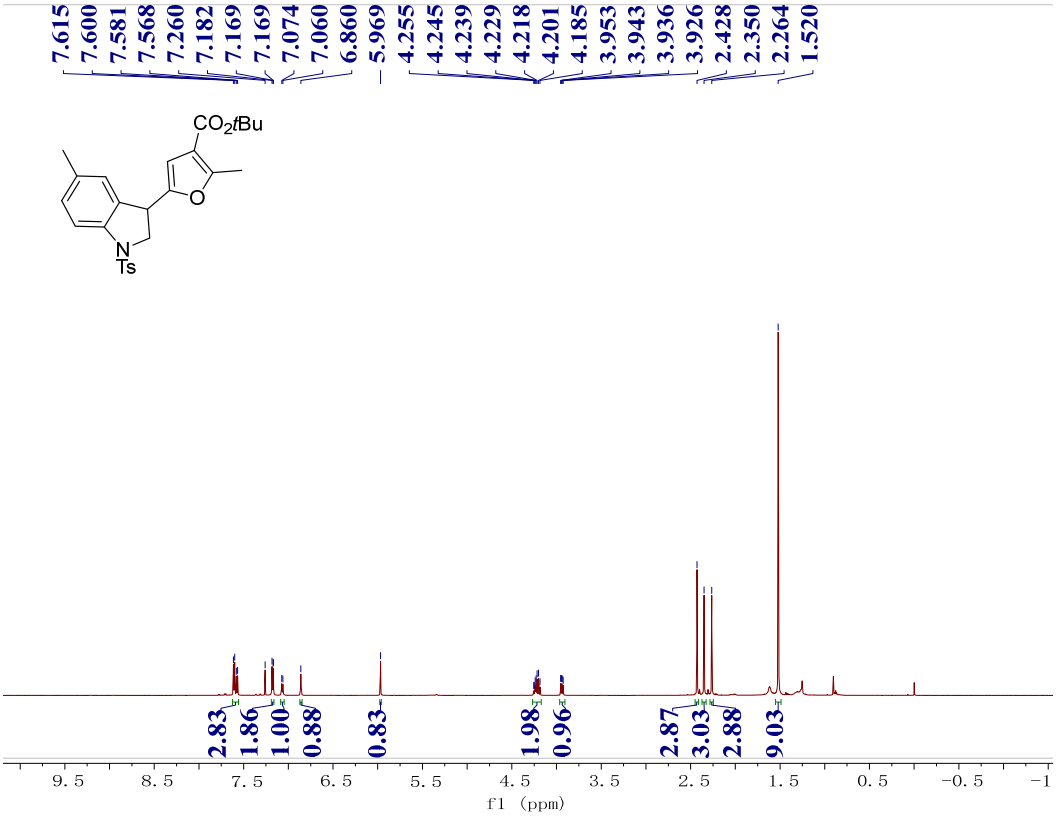
$^{13}$C NMR of **2i** (150 MHz, $CDCl_3$)



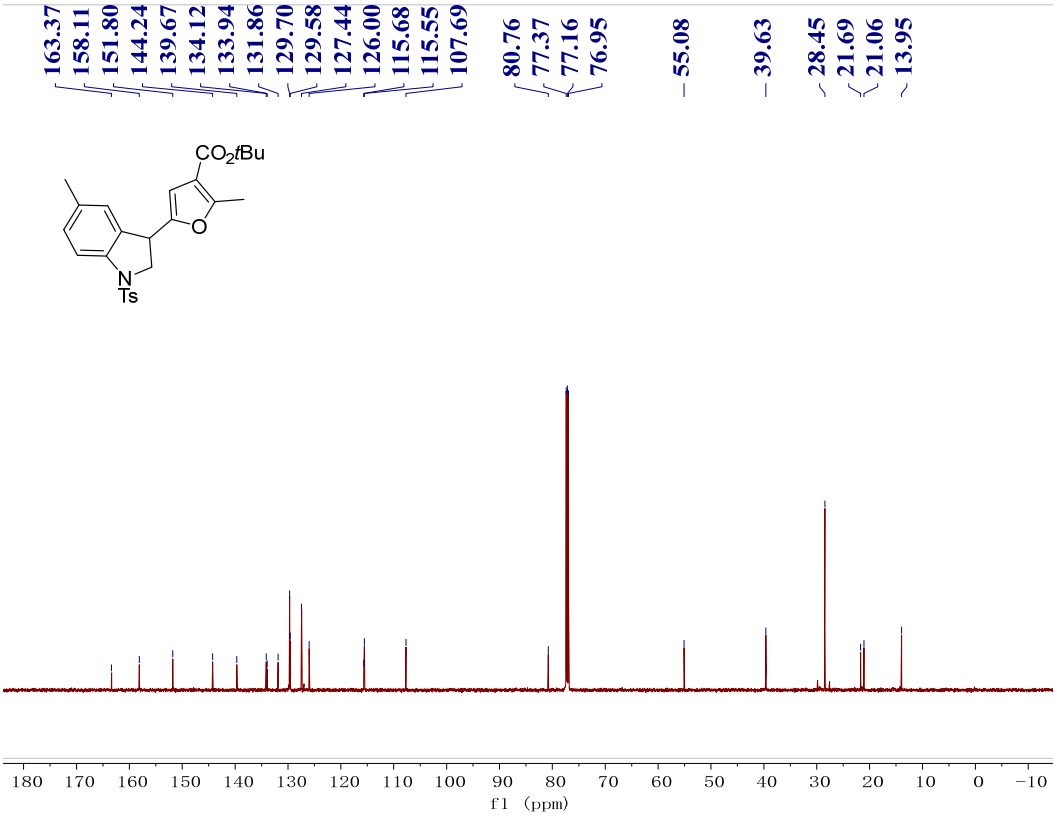

$^{19}$F NMR of **2i** (376 MHz, $CDCl_3$)



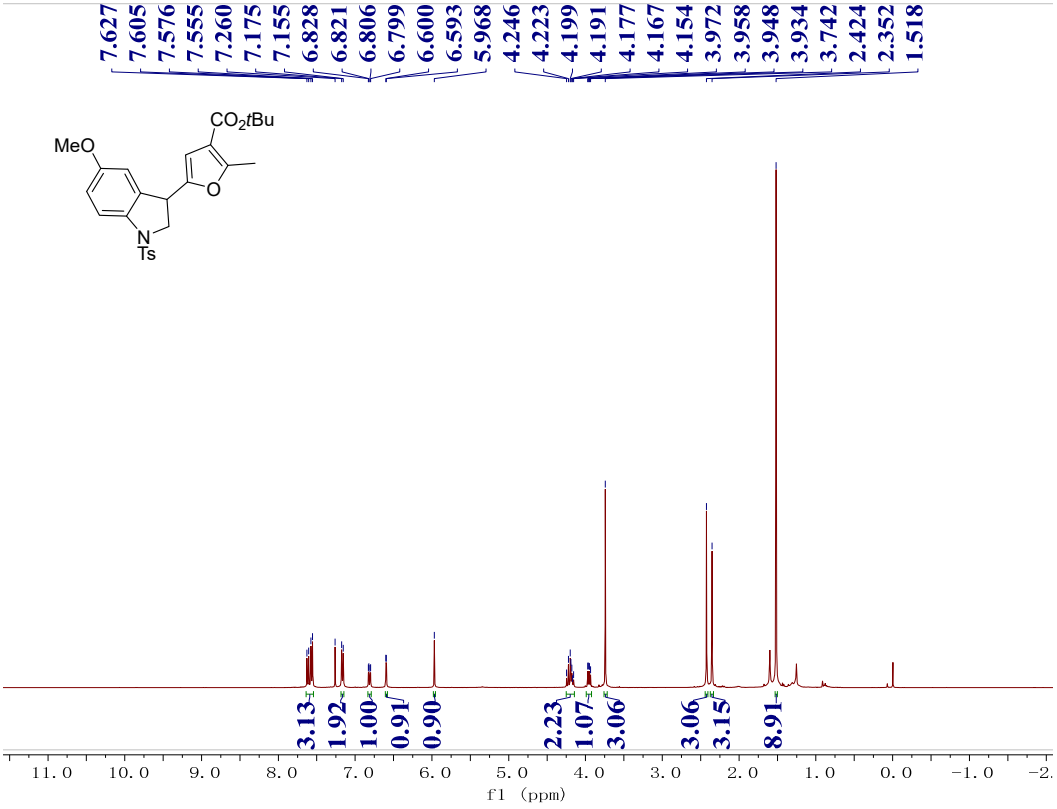
$^{1}$H NMR of **2j** (600 MHz, $CDCl_3$)



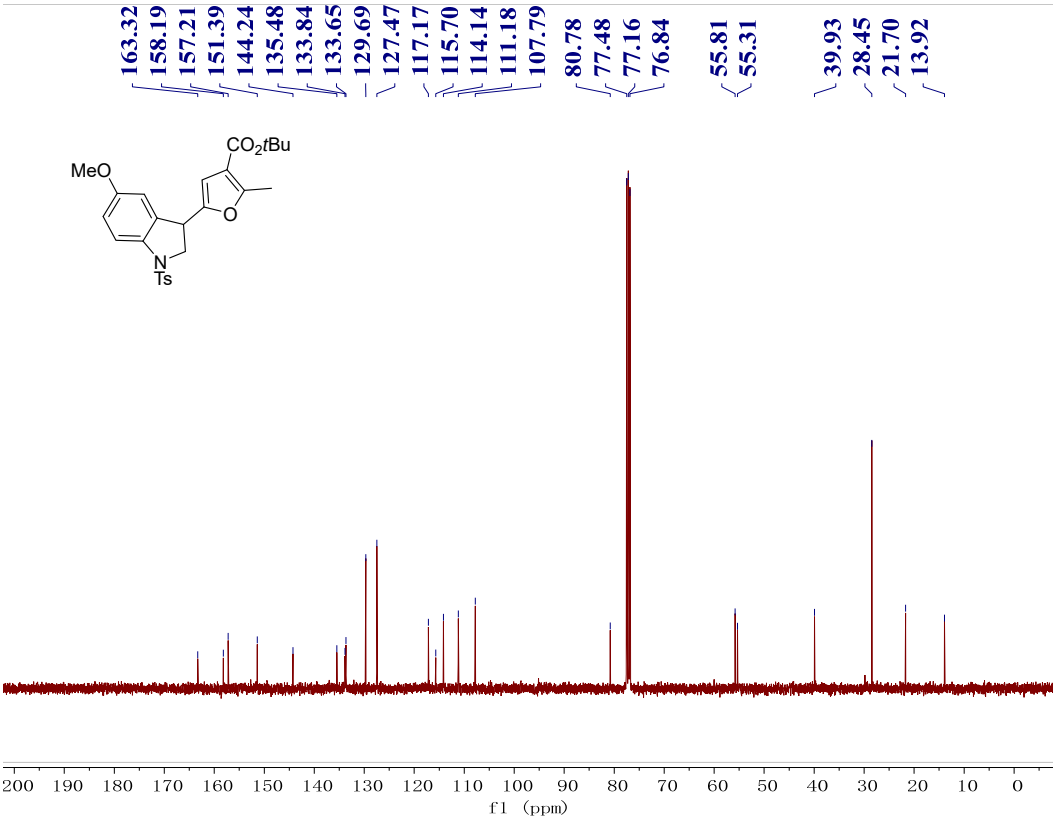

$^{13}$C NMR of **2j** (150 MHz, $CDCl_3$)



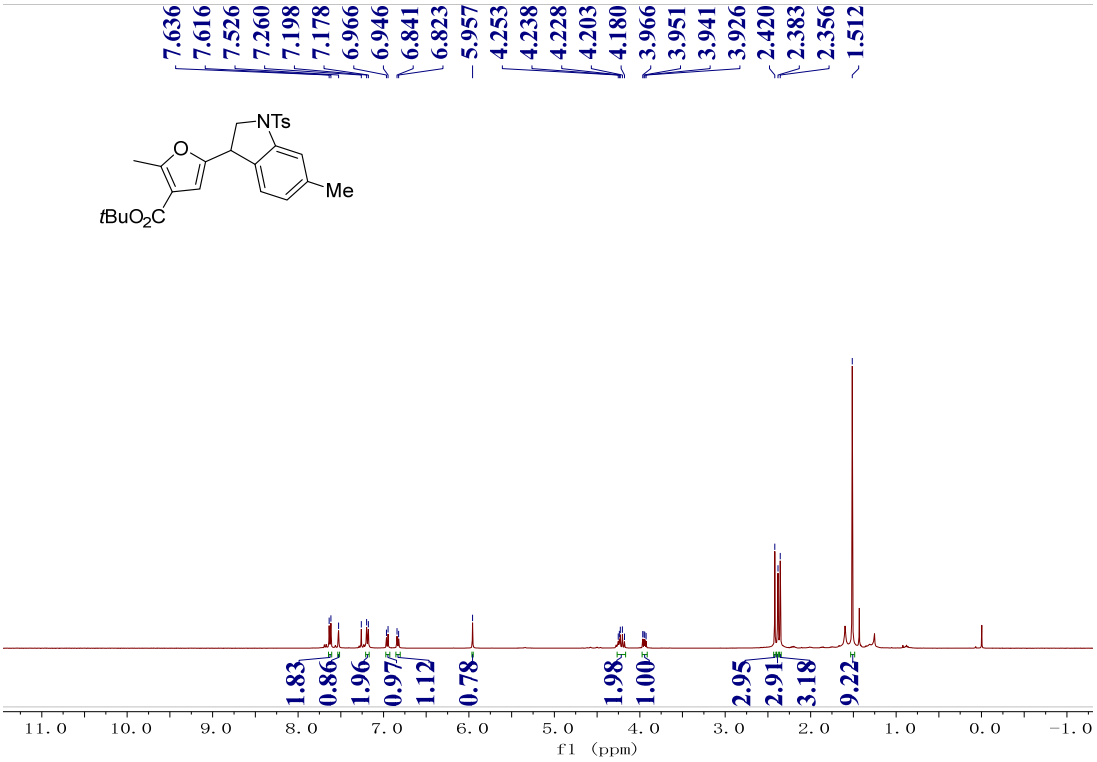
$^{1}$H NMR of **2k** (400 MHz, $CDCl_3$)



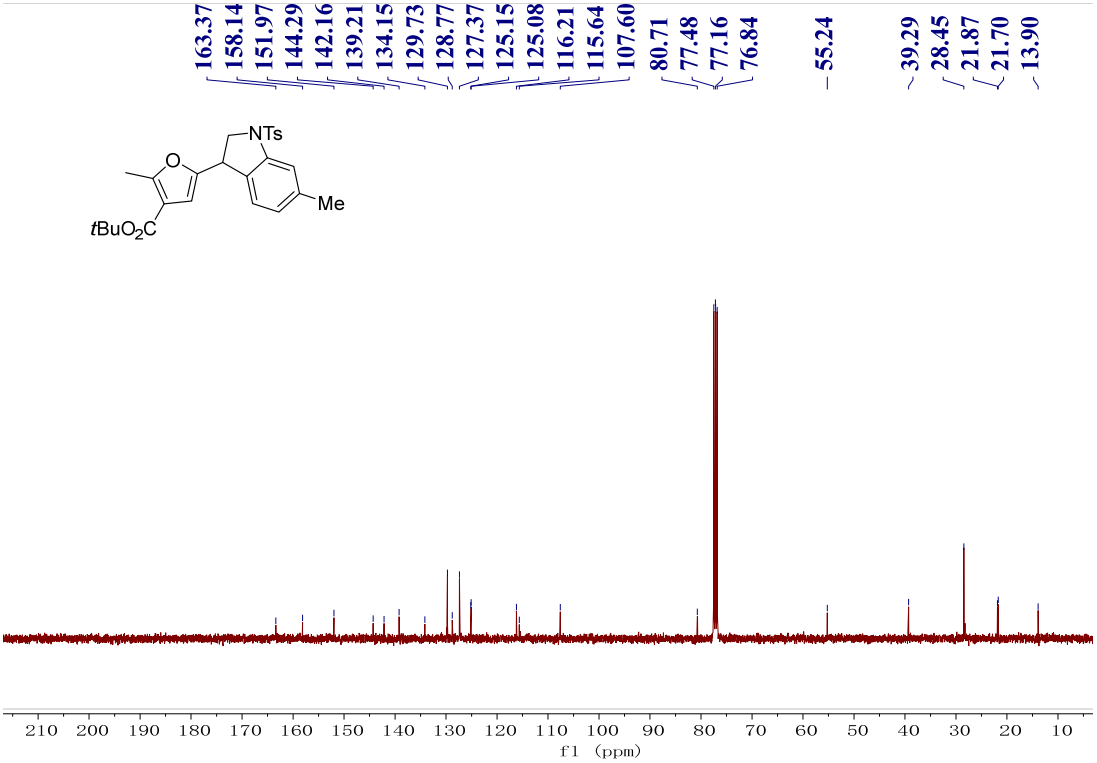

$^{13}$C NMR of **2k** (100 MHz, $CDCl_3$)



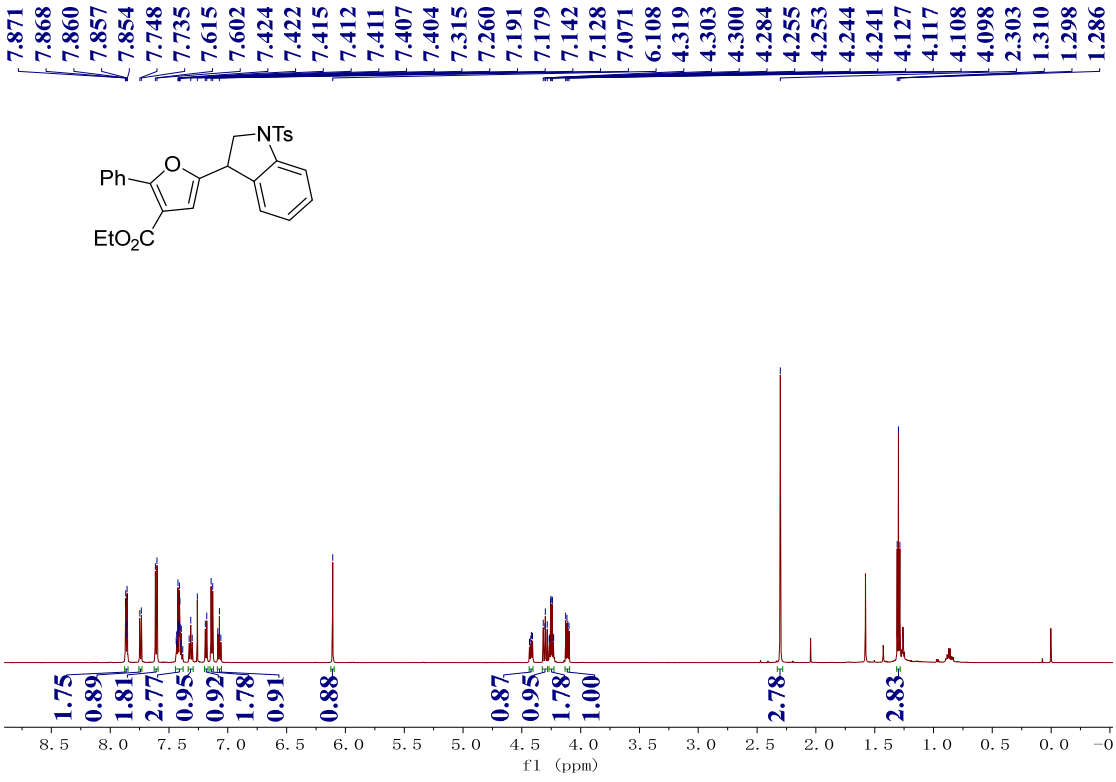
$^{1}$H NMR of **2l** (400 MHz, $CDCl_3$)



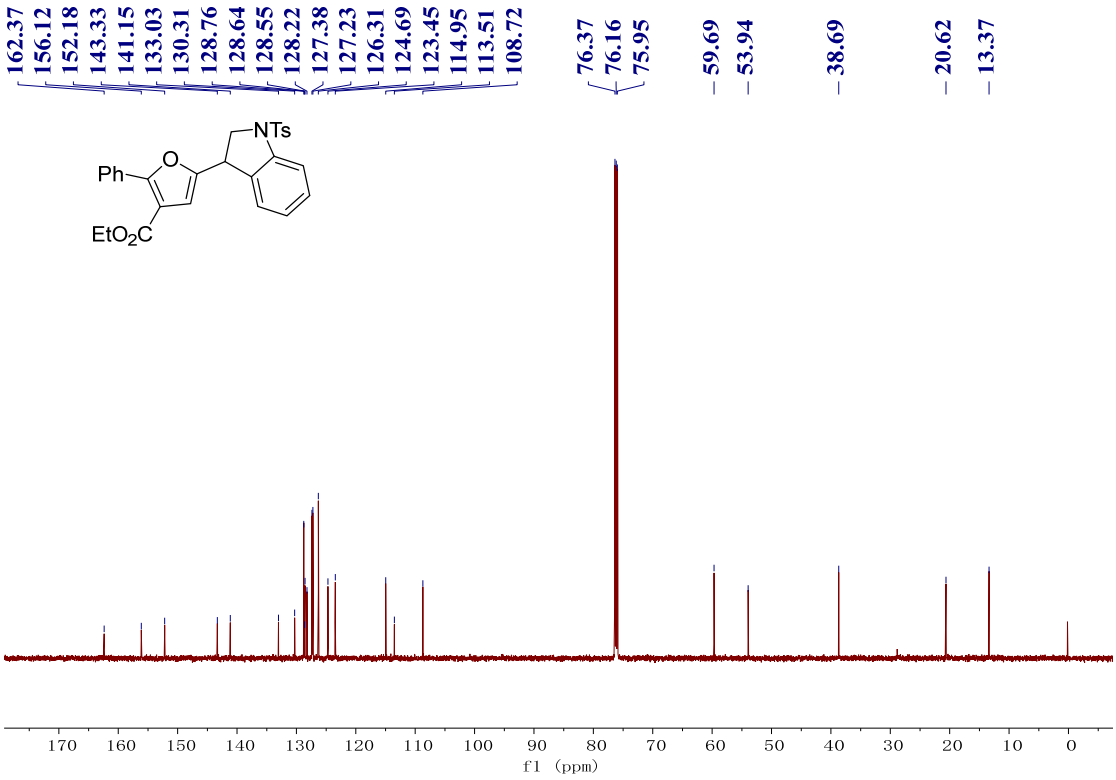

$^{13}$C NMR of **2l** (100 MHz, $CDCl_3$)



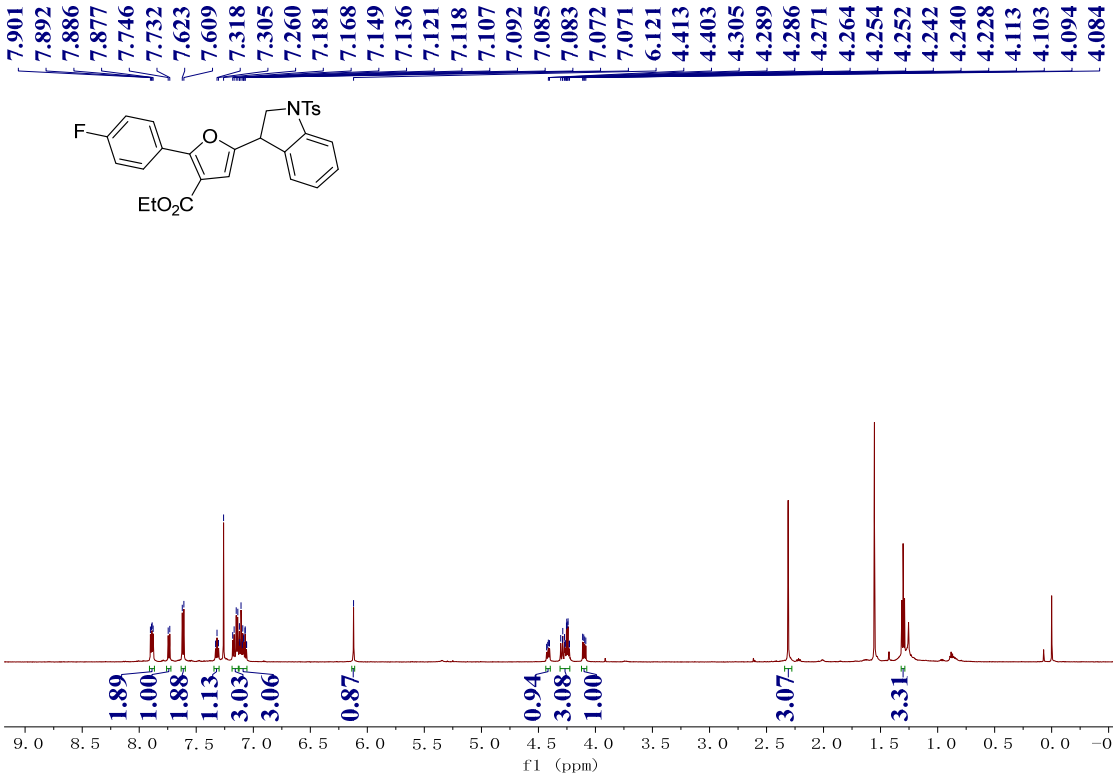
$^{1}$H NMR of **4a** (600 MHz, $CDCl_3$)



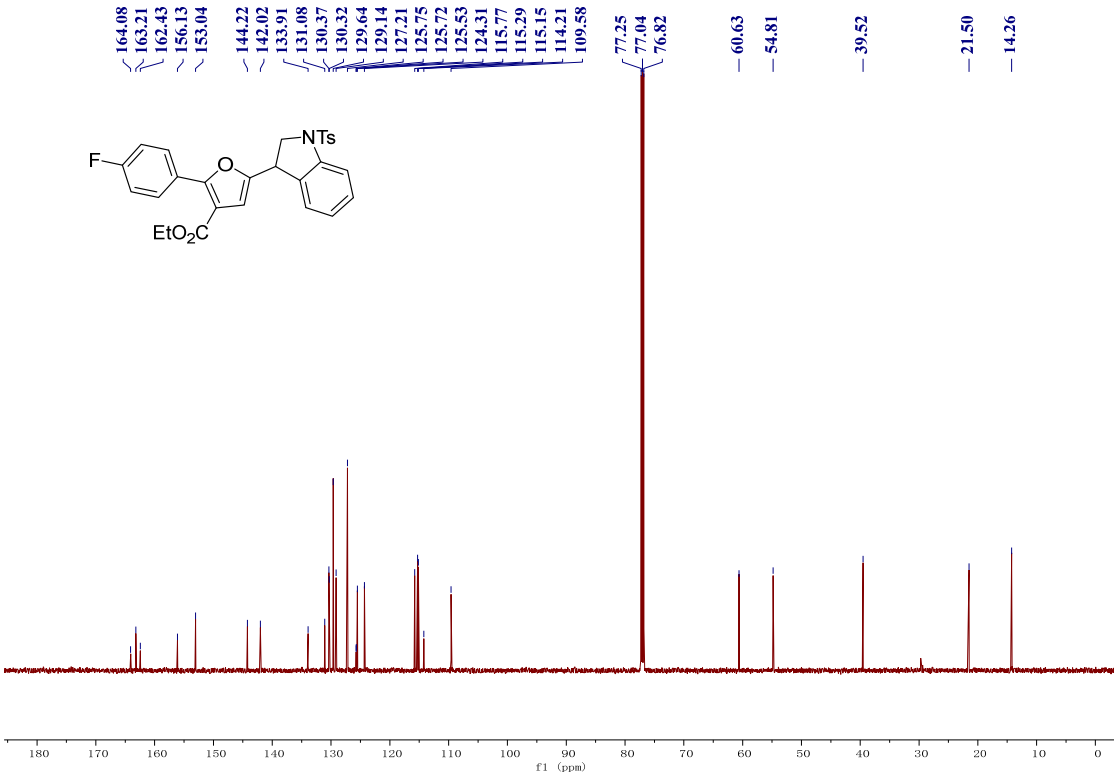

$^{13}$C NMR of **4a** (150 MHz, $CDCl_3$)



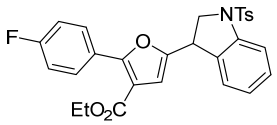
$^{1}$H NMR of **4b** (600 MHz, $CDCl_3$)




$^{13}$C NMR of **4b** (100 MHz, $CDCl_3$)



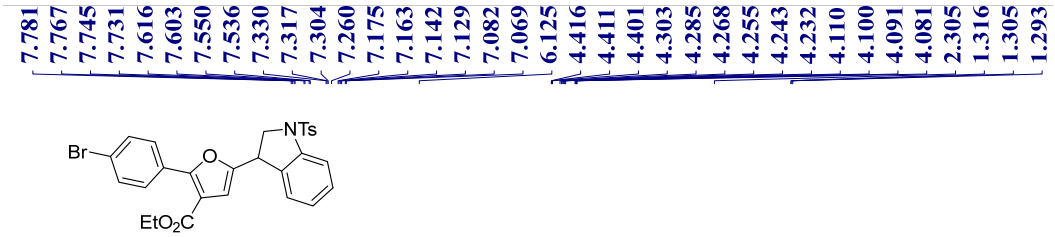
$^{19}$F NMR of **4b** (376 MHz, $CDCl_3$)





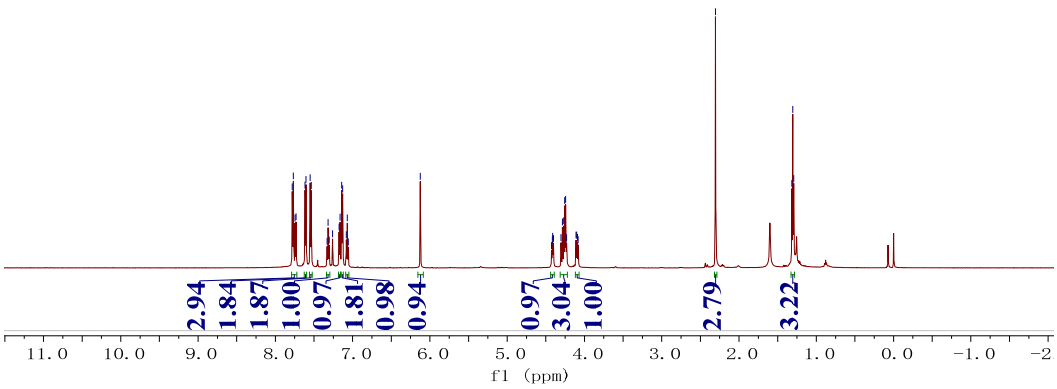


$^{1}$H NMR of **4c** (600 MHz, $CDCl_3$)

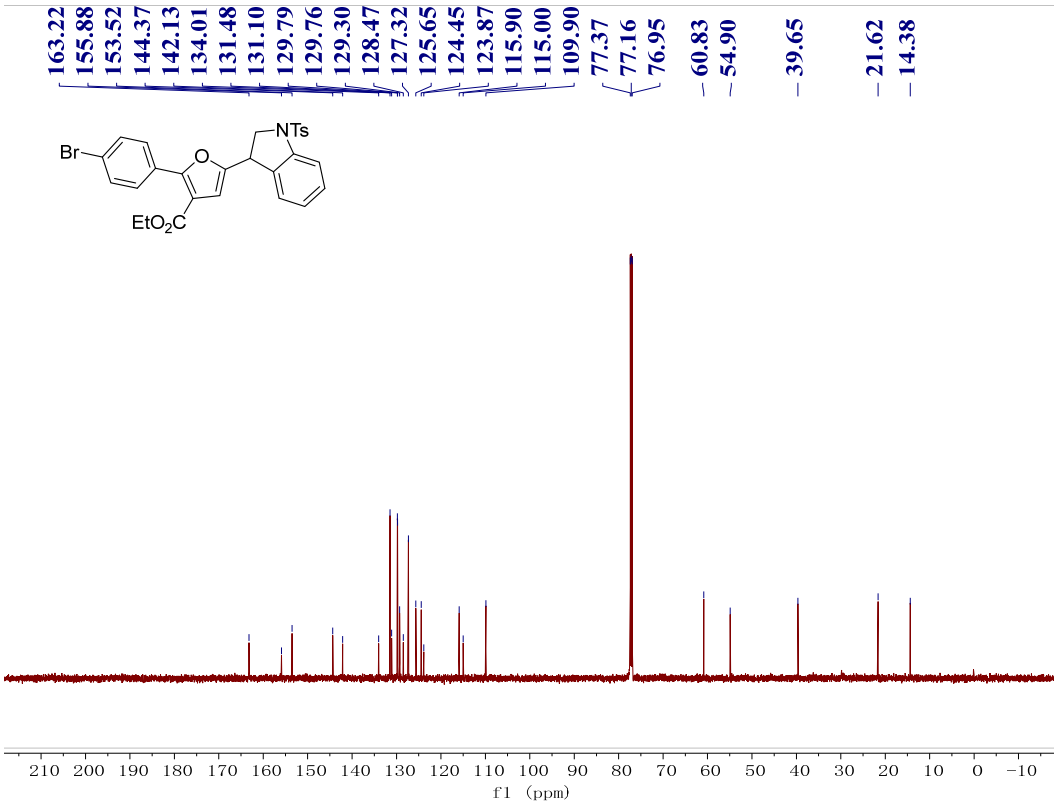




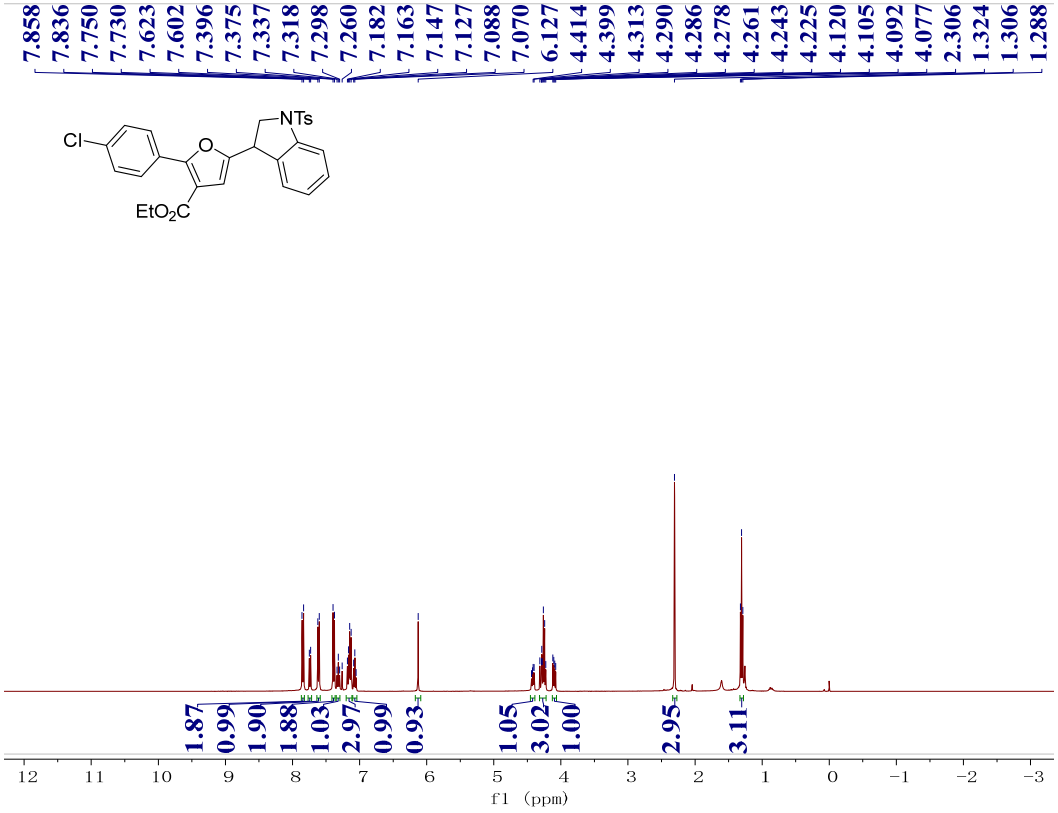




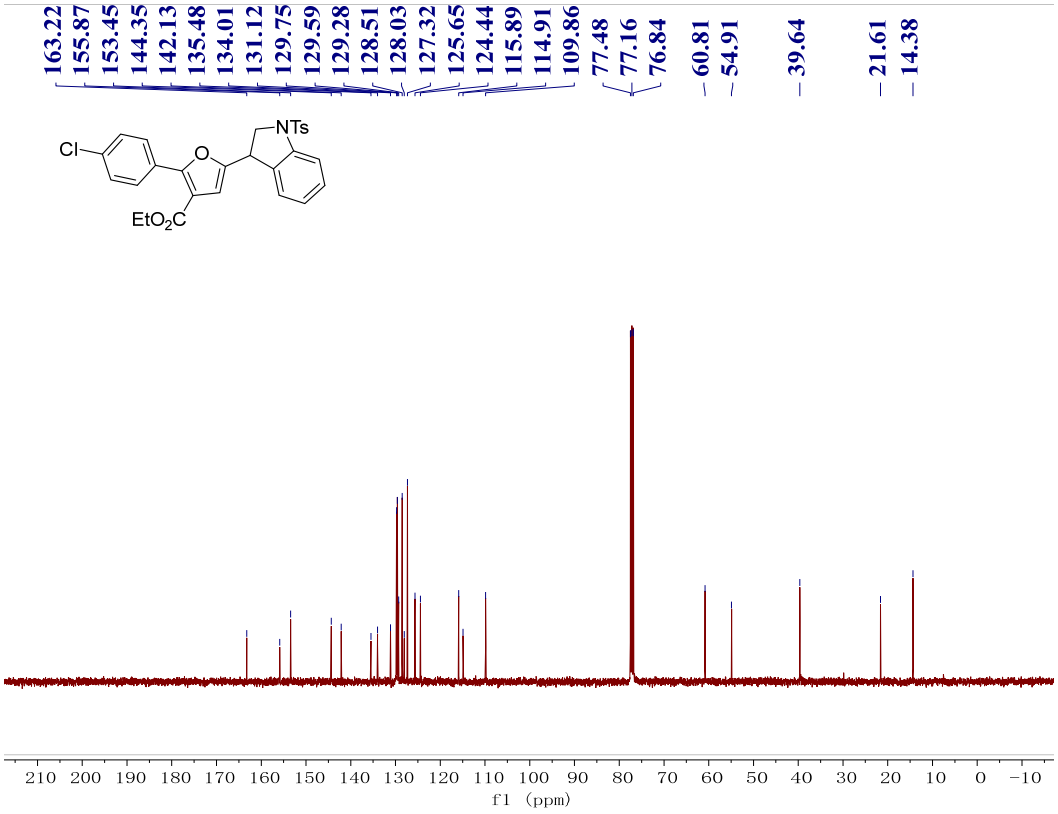
$^{13}$C NMR of **4c** (150 MHz, $CDCl_3$)



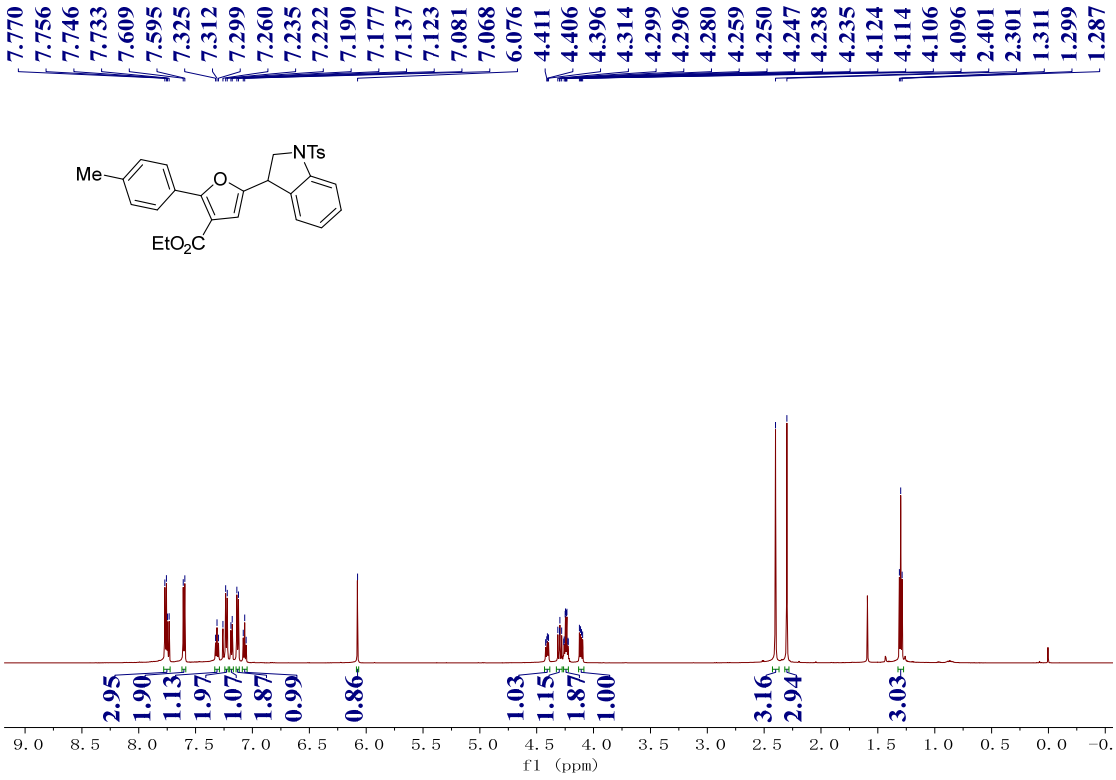

$^{1}$H NMR of **4d** (400 MHz, $CDCl_3$)



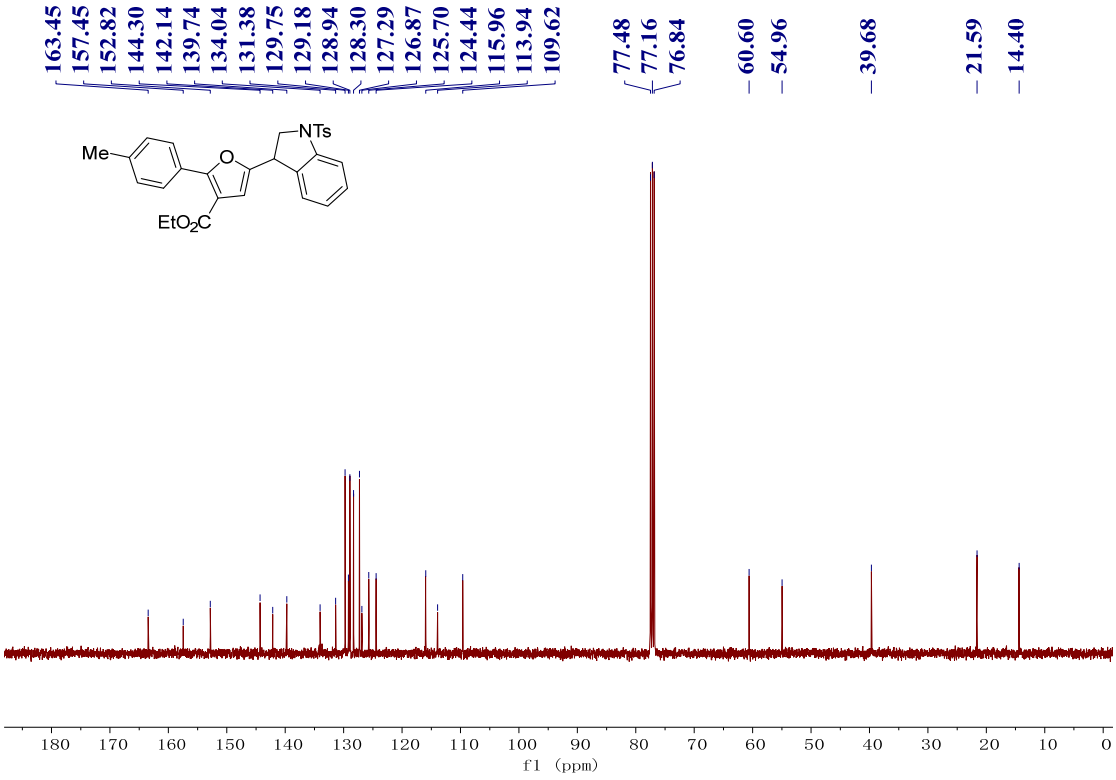
$^{13}$C NMR of **4d** (100 MHz, $CDCl_3$)



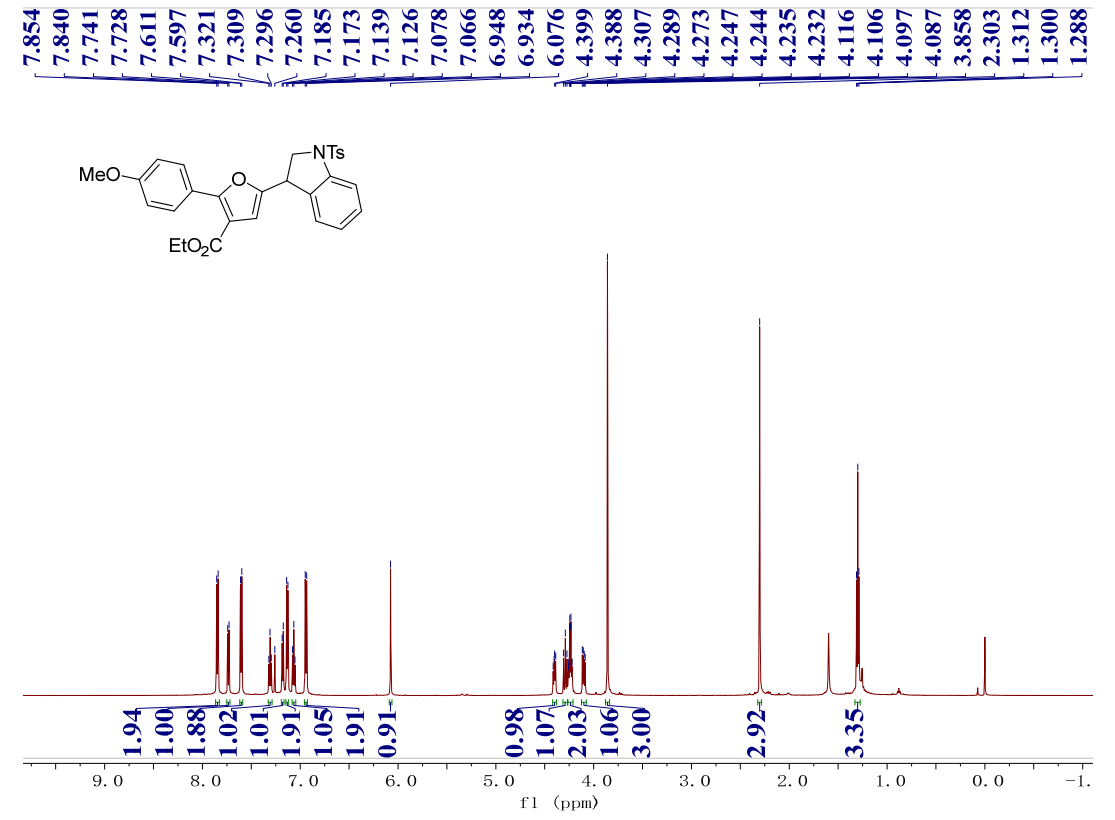

$^{1}$H NMR of **4e** (600 MHz, $CDCl_3$)



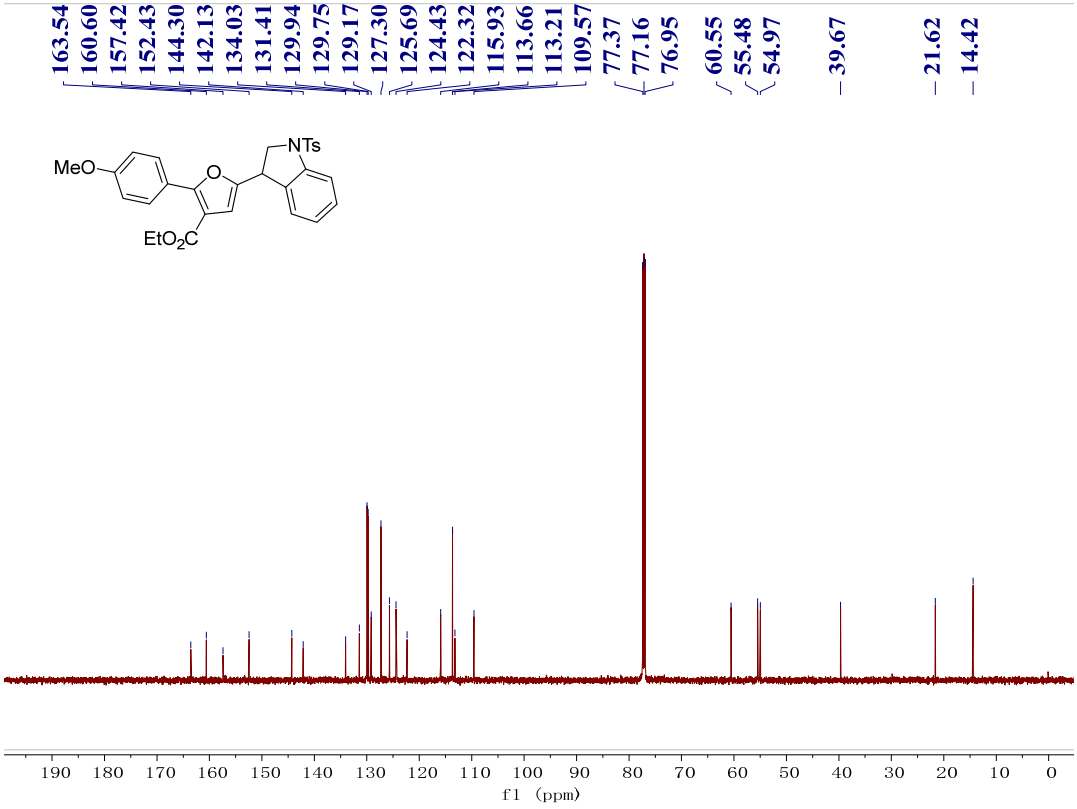
$^{13}$C NMR of **4e** (100 MHz, $CDCl_3$)



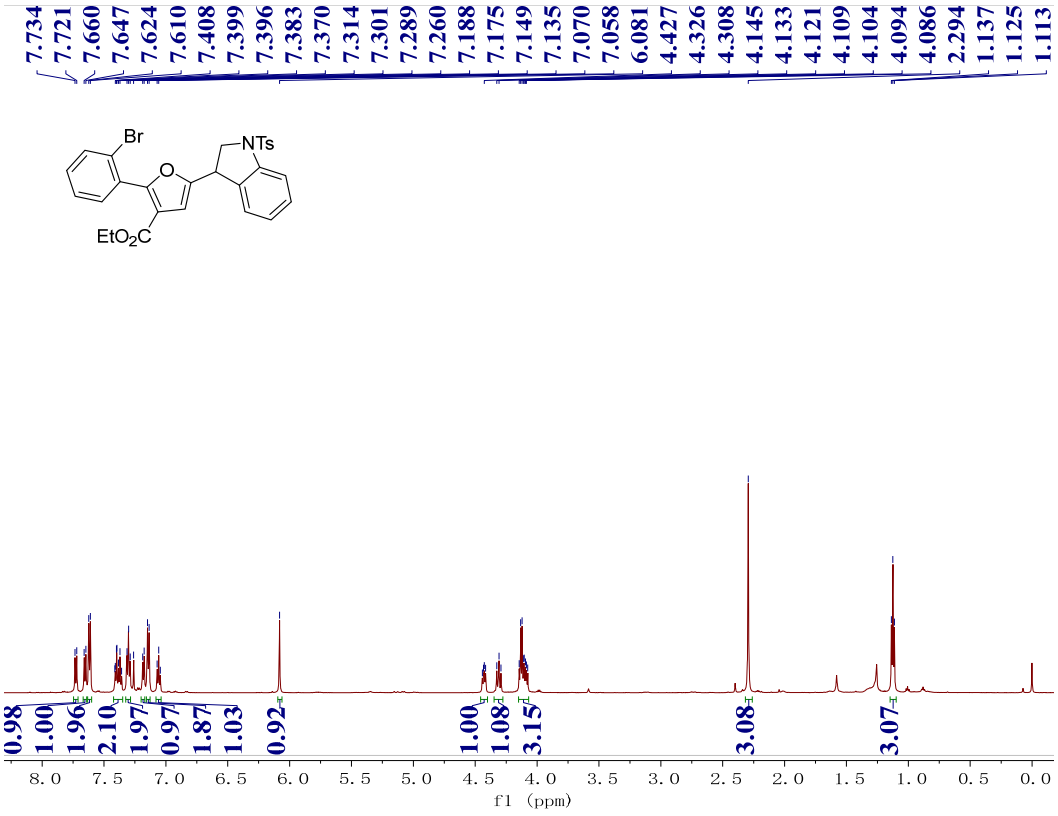

$^{1}$H NMR of **4f** (600 MHz, $CDCl_3$)



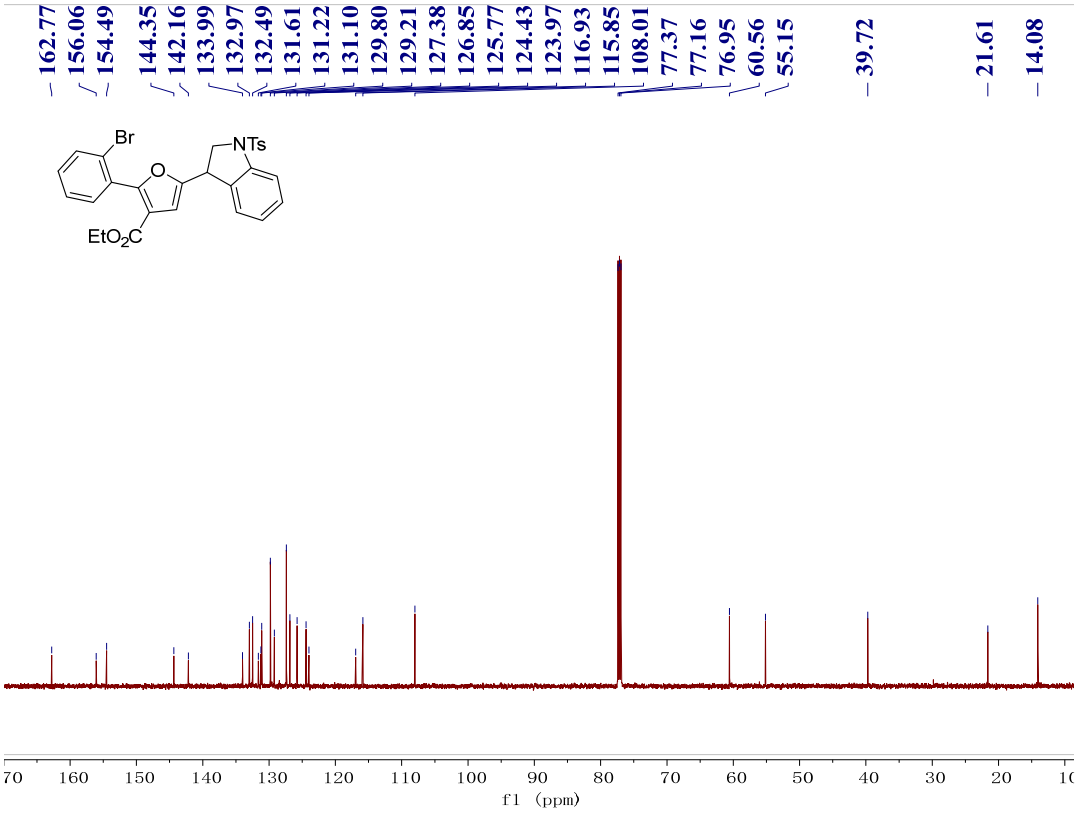
$^{13}$C NMR of **4f** (150 MHz, $CDCl_3$)



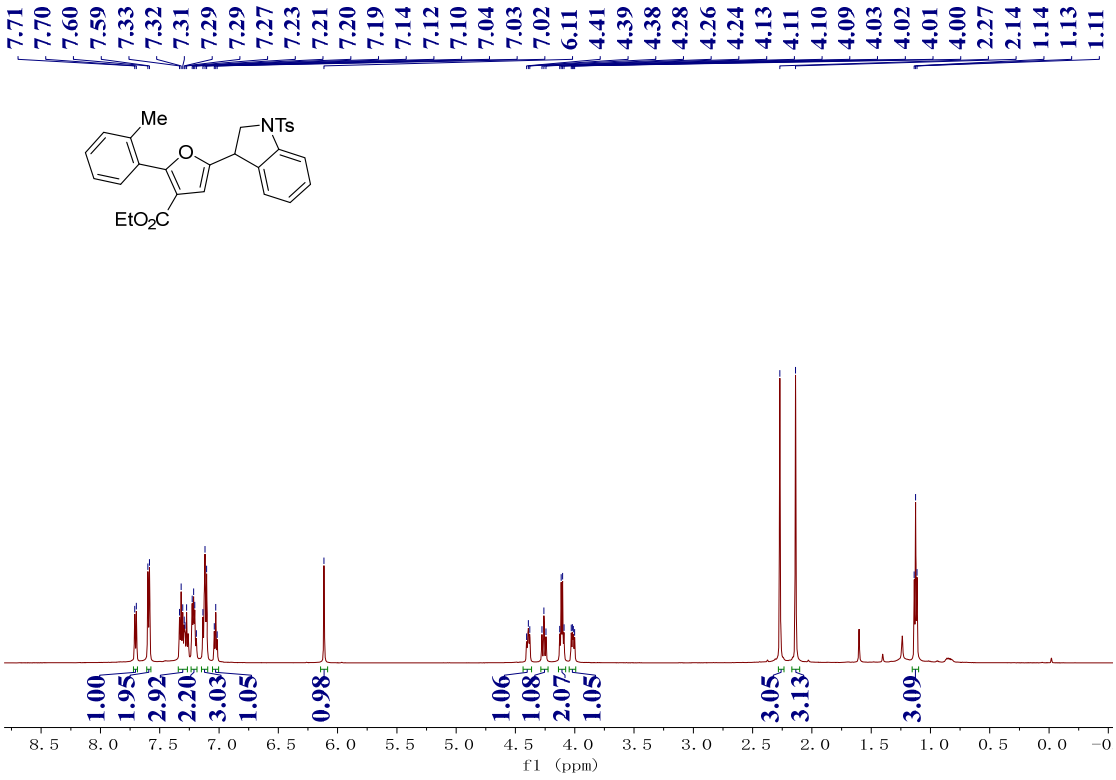

$^{1}$H NMR of **4g** (600 MHz, $CDCl_3$)



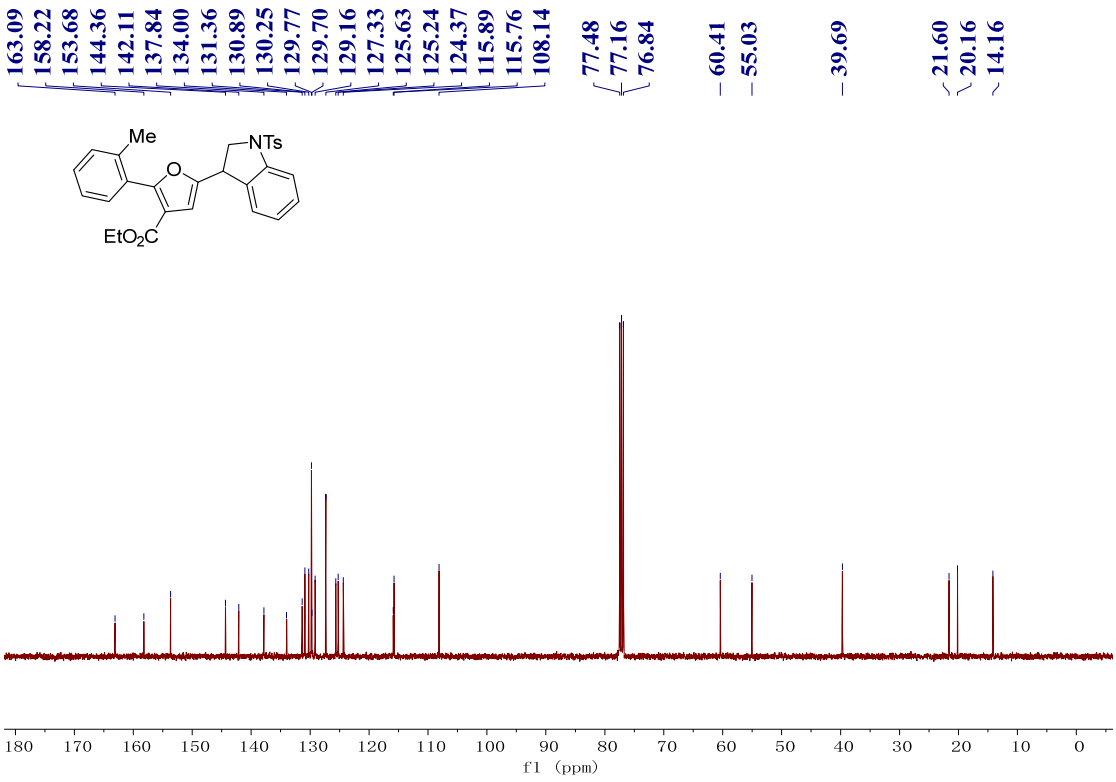
$^{13}$C NMR of **4g** (150 MHz, $CDCl_3$)



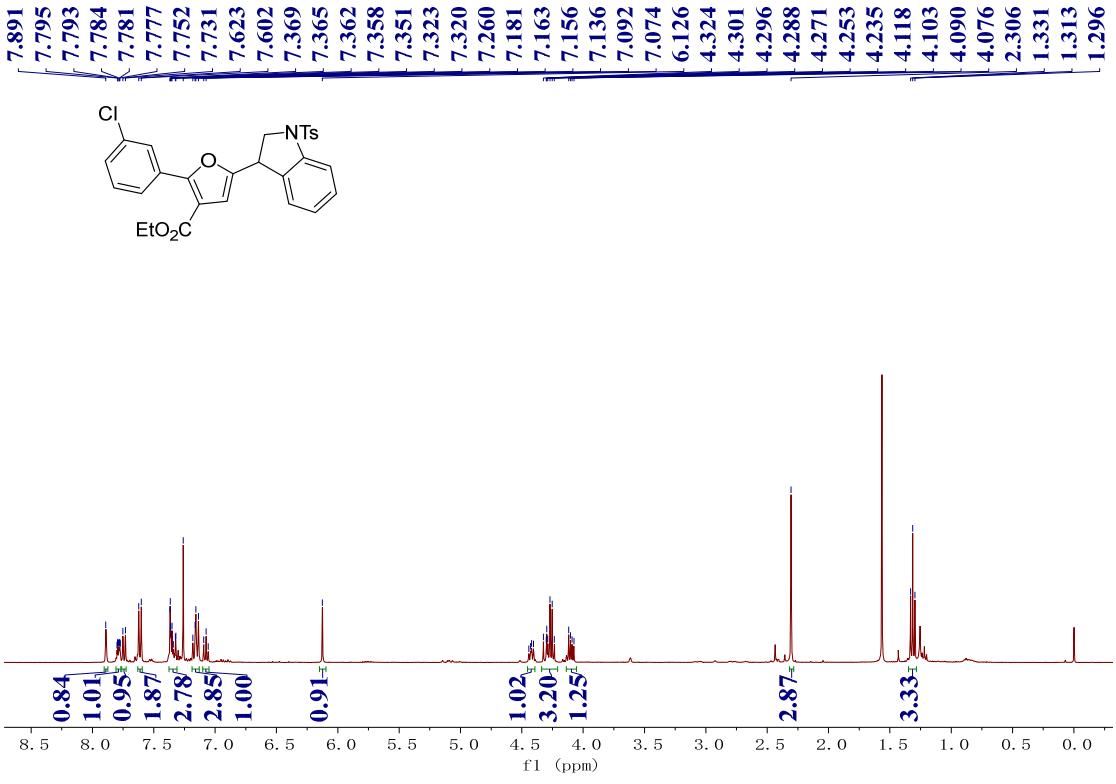

$^{1}$H NMR of **4h** (600 MHz, $CDCl_3$)



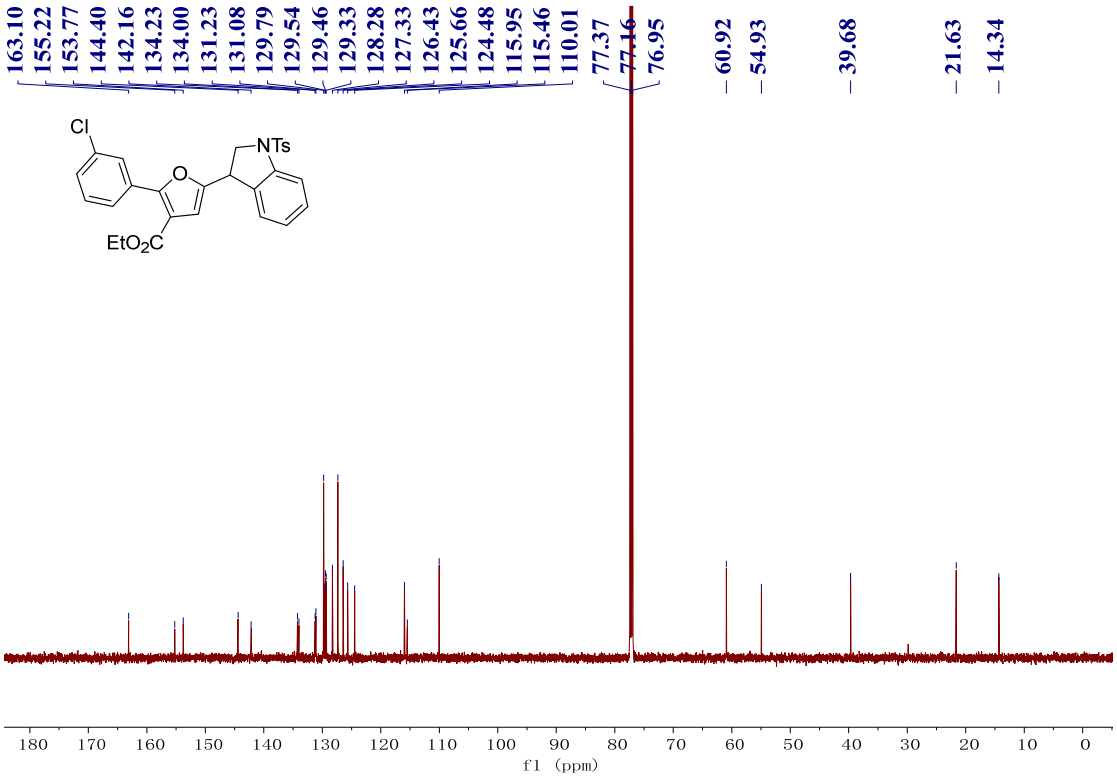
$^{13}$C NMR of **4h** (100 MHz, $CDCl_3$)



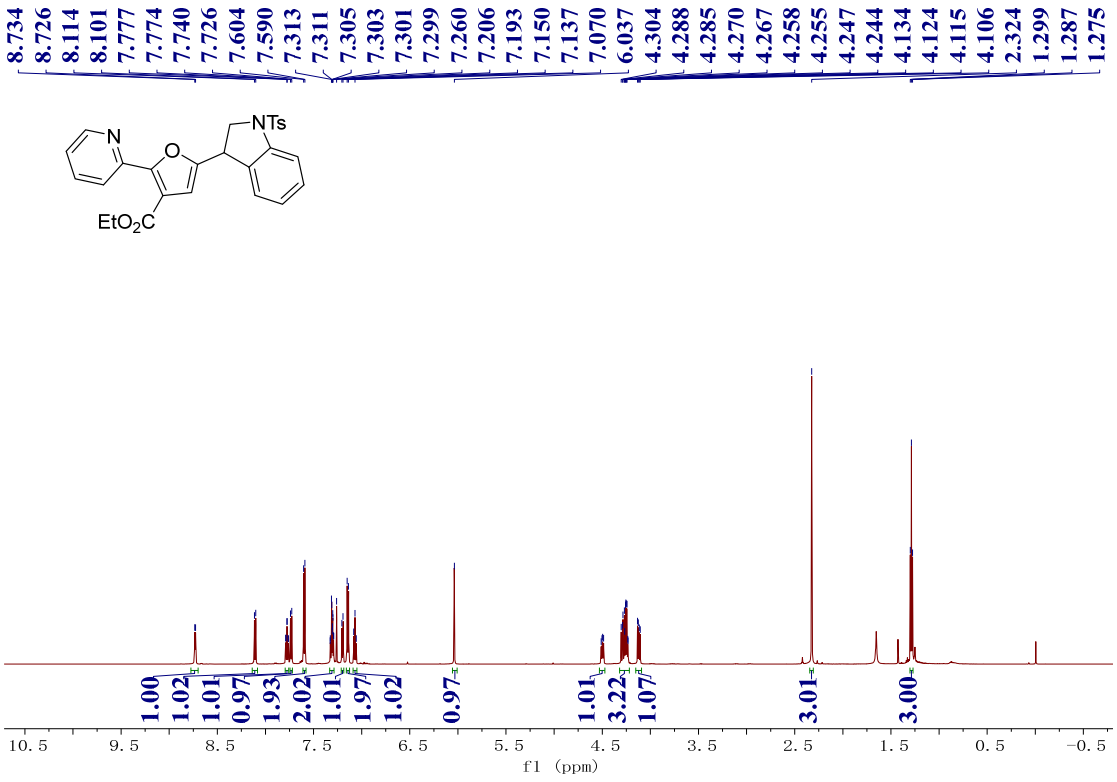

$^{1}$H NMR of **4i** (400 MHz, $CDCl_3$)



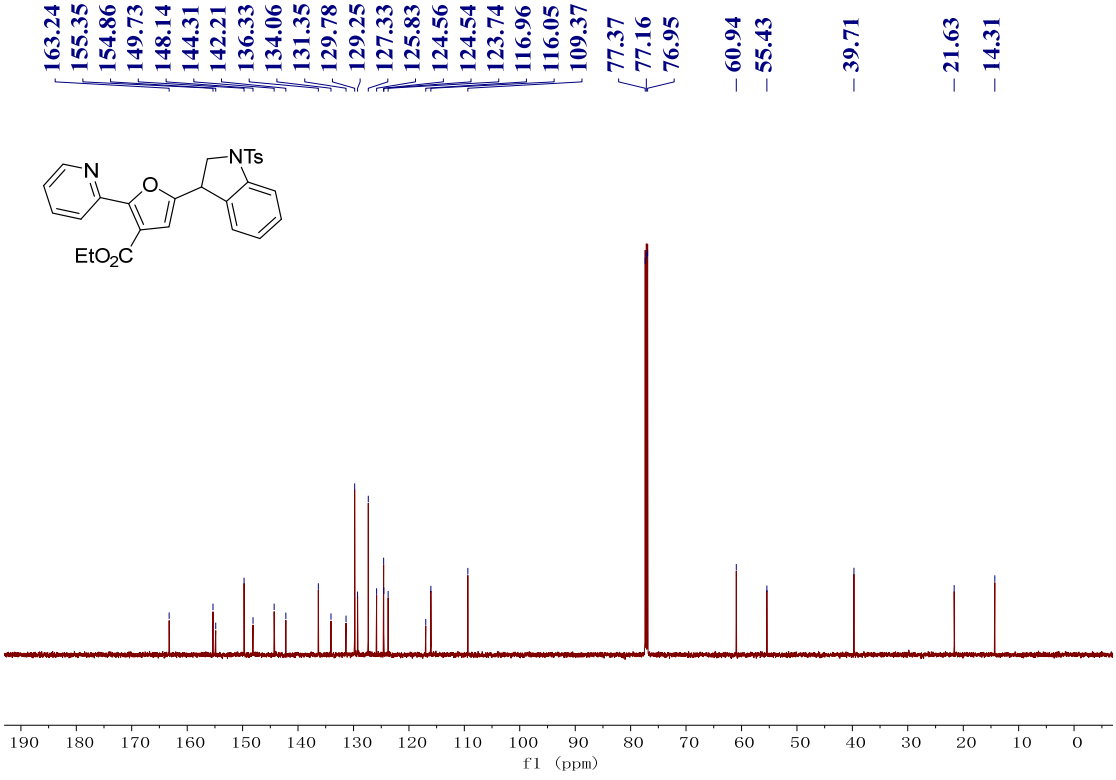
$^{13}$C NMR of **4i** (150 MHz, $CDCl_3$)



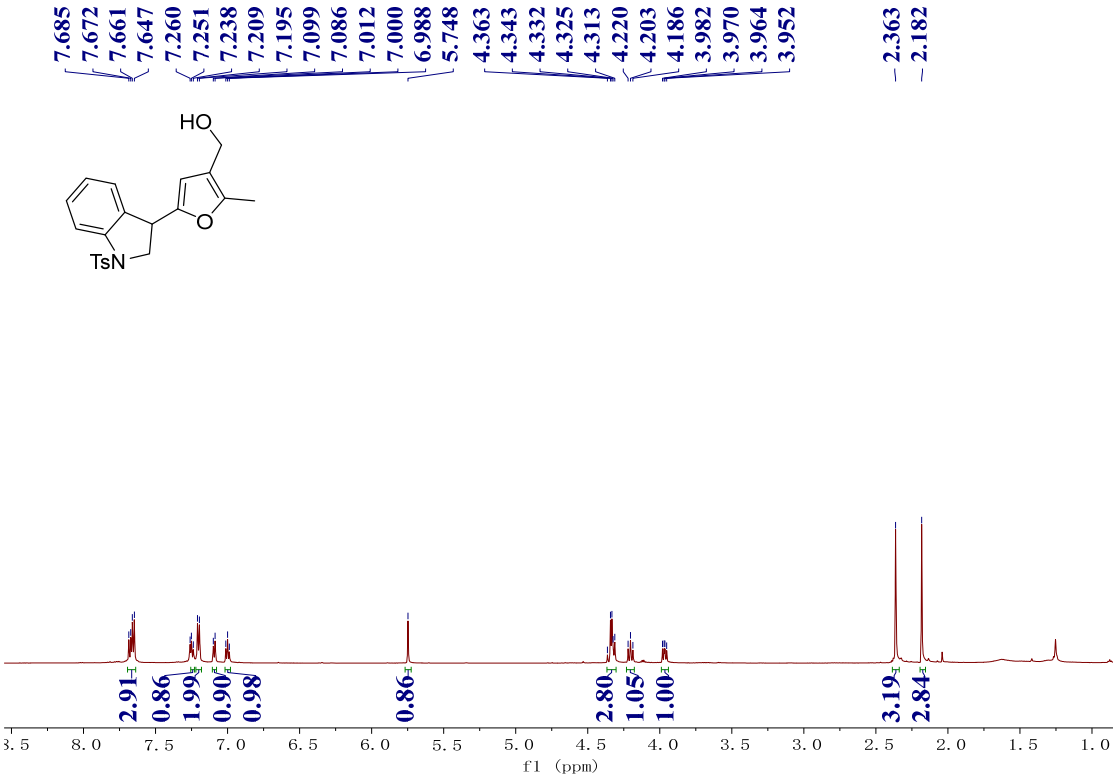

$^{1}$H NMR of **4j** (600 MHz, $CDCl_3$)



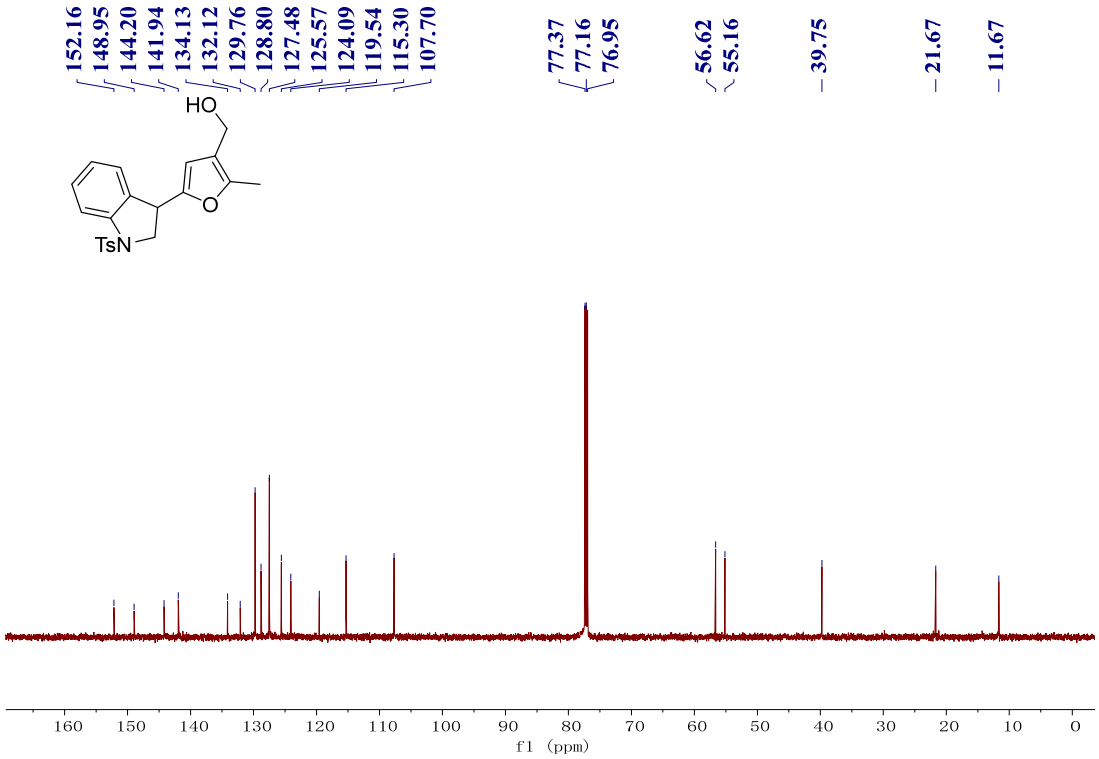
$^{13}$C NMR of **4j** (150 MHz, $CDCl_3$)



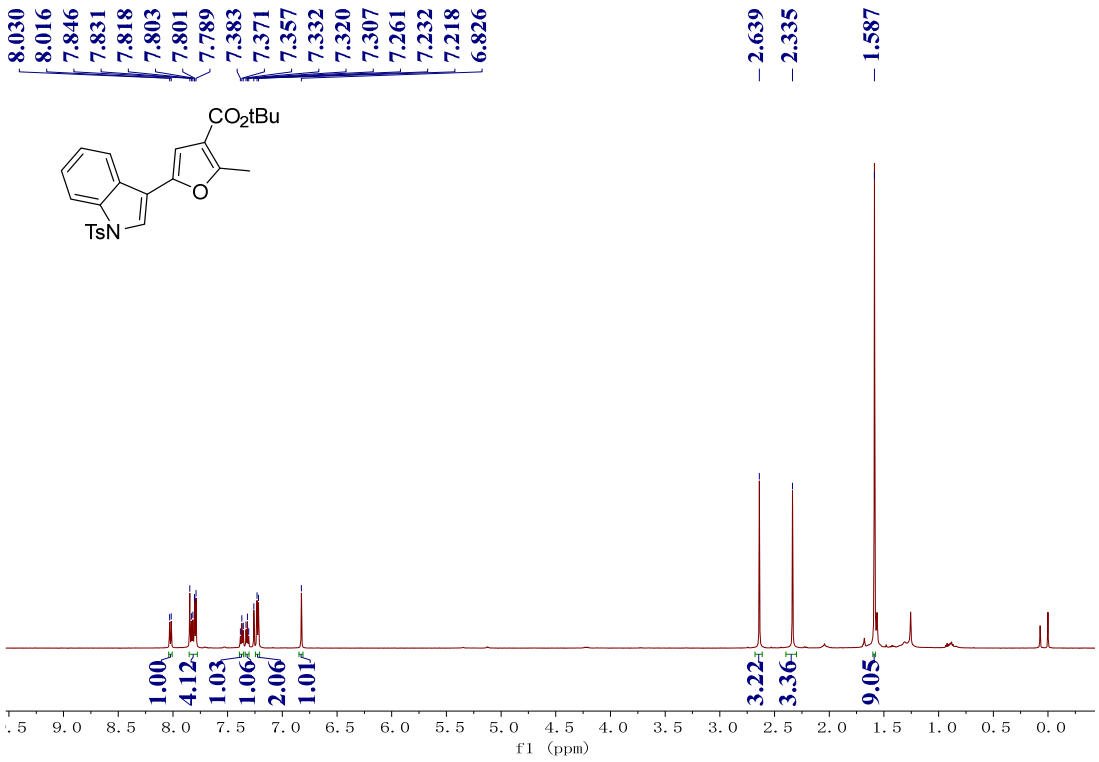

$^{1}$H NMR of **5** (600 MHz, $CDCl_3$)



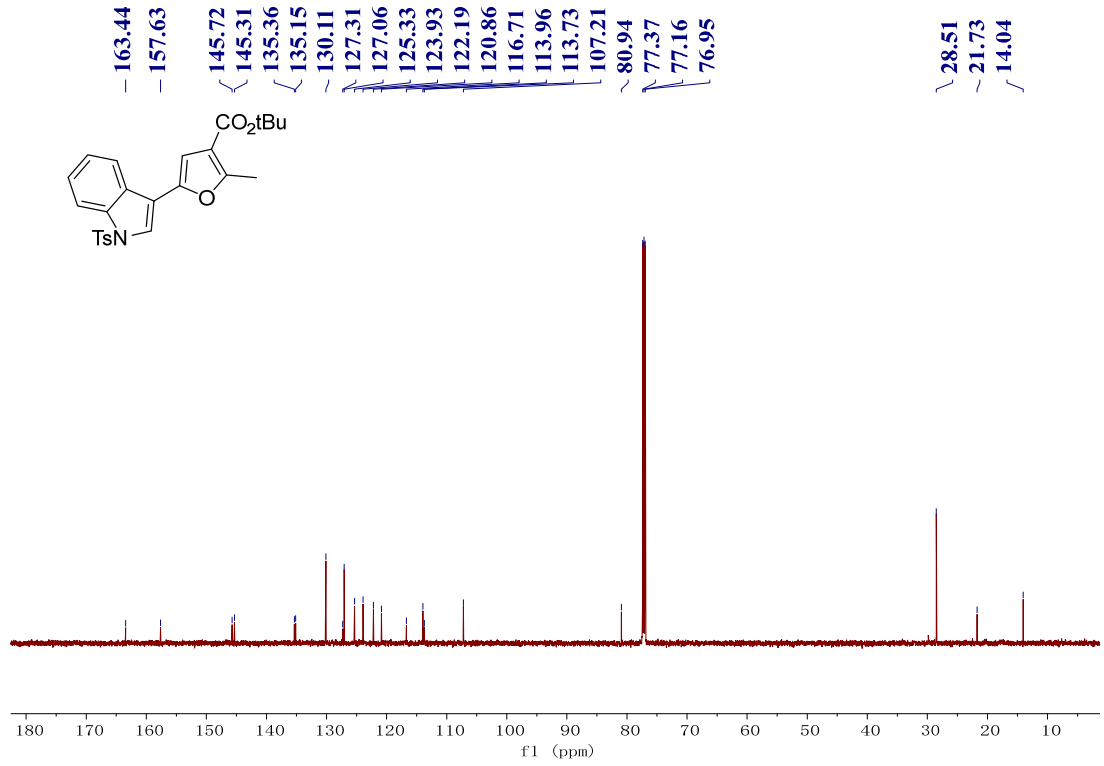
$^{13}$C NMR of **5** (150 MHz, $CDCl_3$)



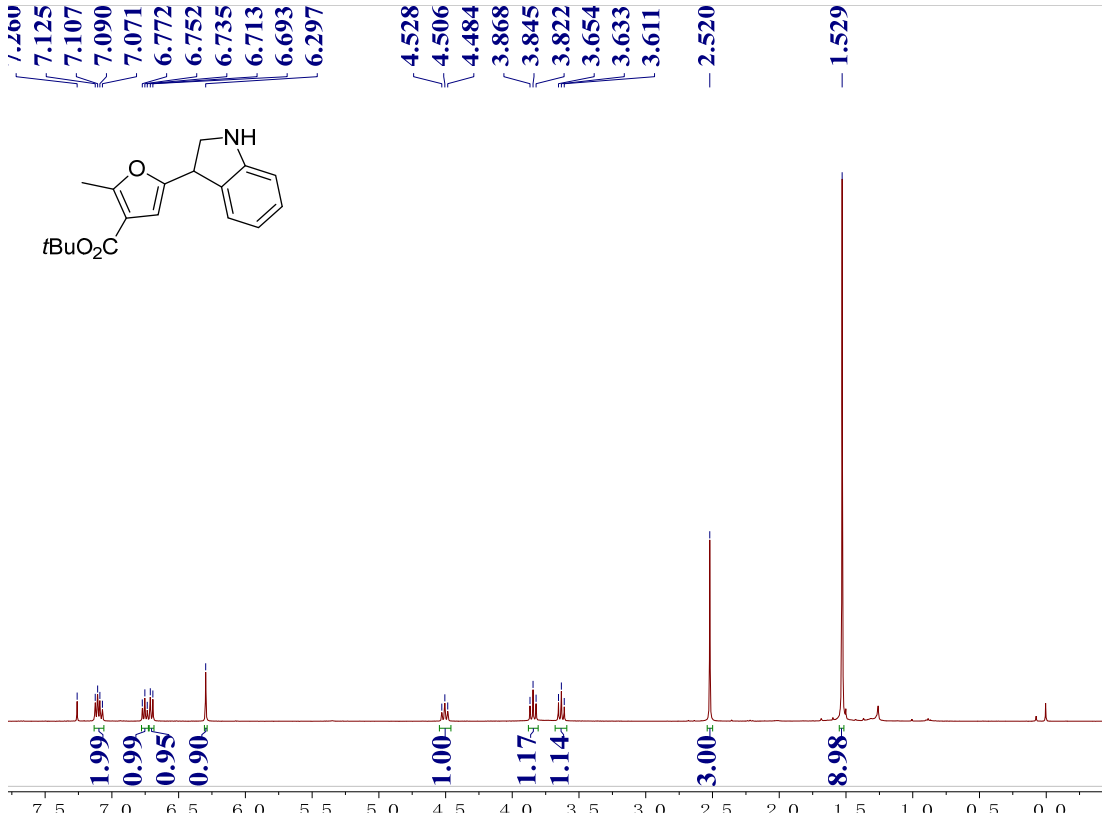

$^{1}$H NMR of **6** (600 MHz, $CDCl_3$)



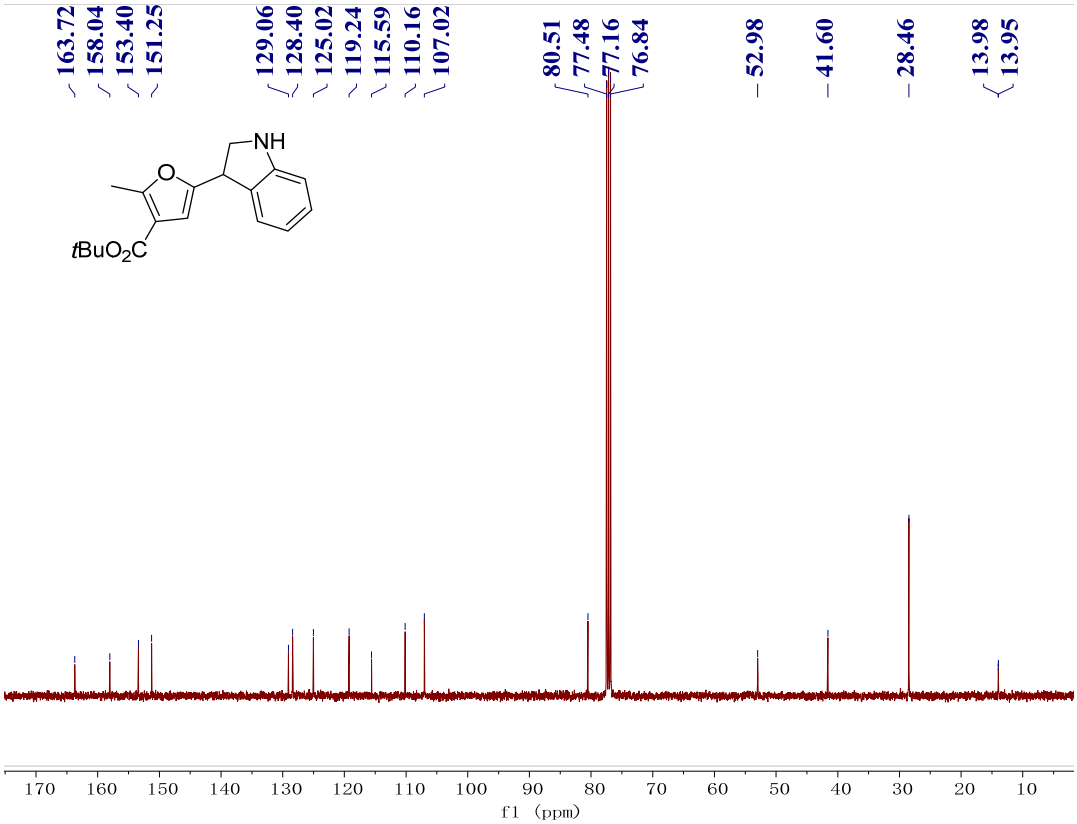
$^{13}$C NMR of **6** (150 MHz, $CDCl_3$)



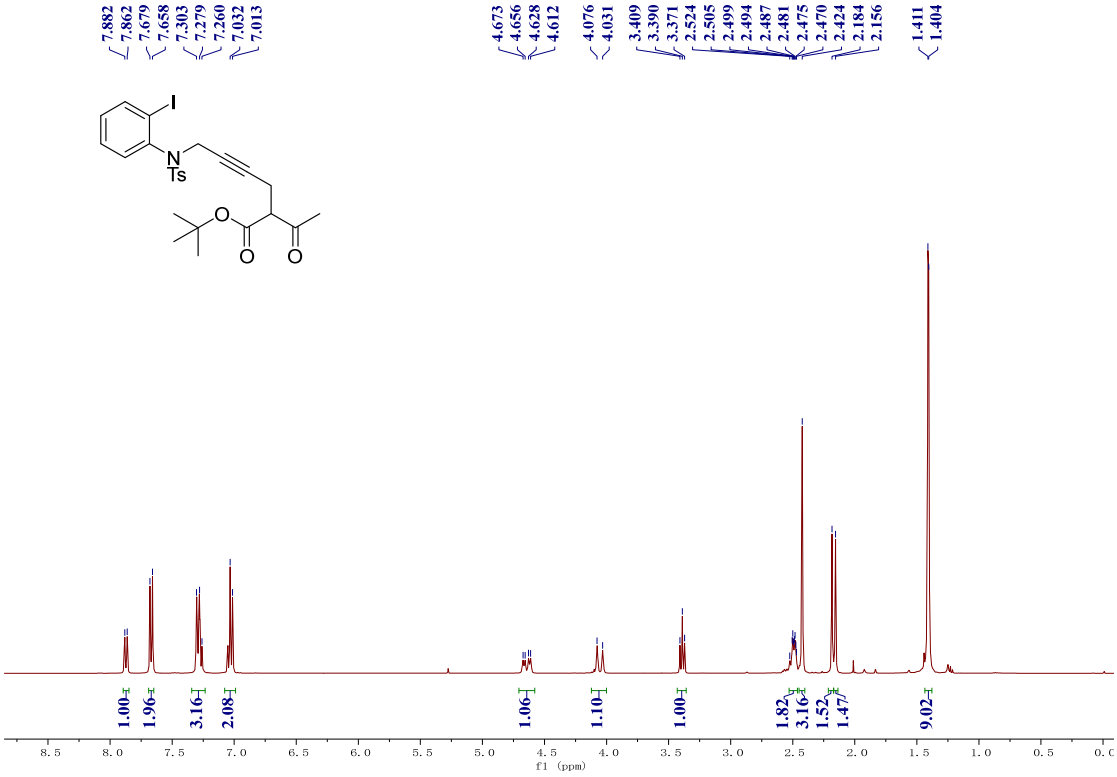

$^{1}$H NMR of **7** (400 MHz, $CDCl_3$)



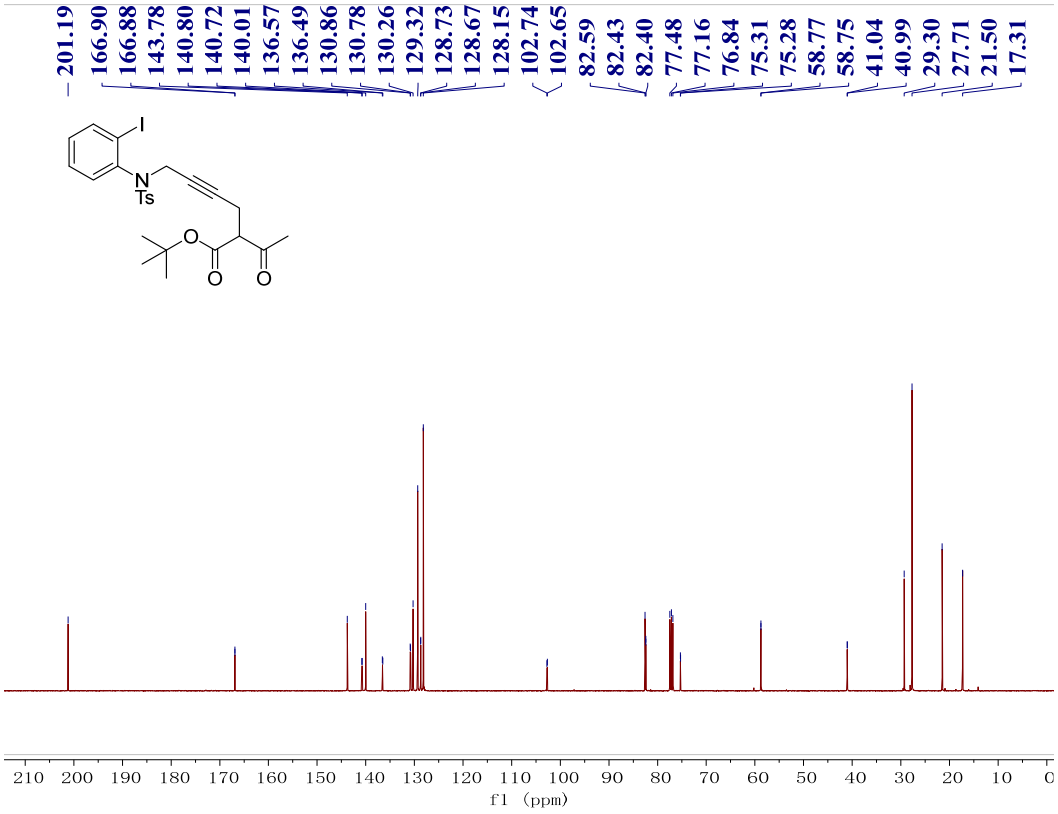
$^{13}$C NMR of **7** (100 MHz, $CDCl_3$)



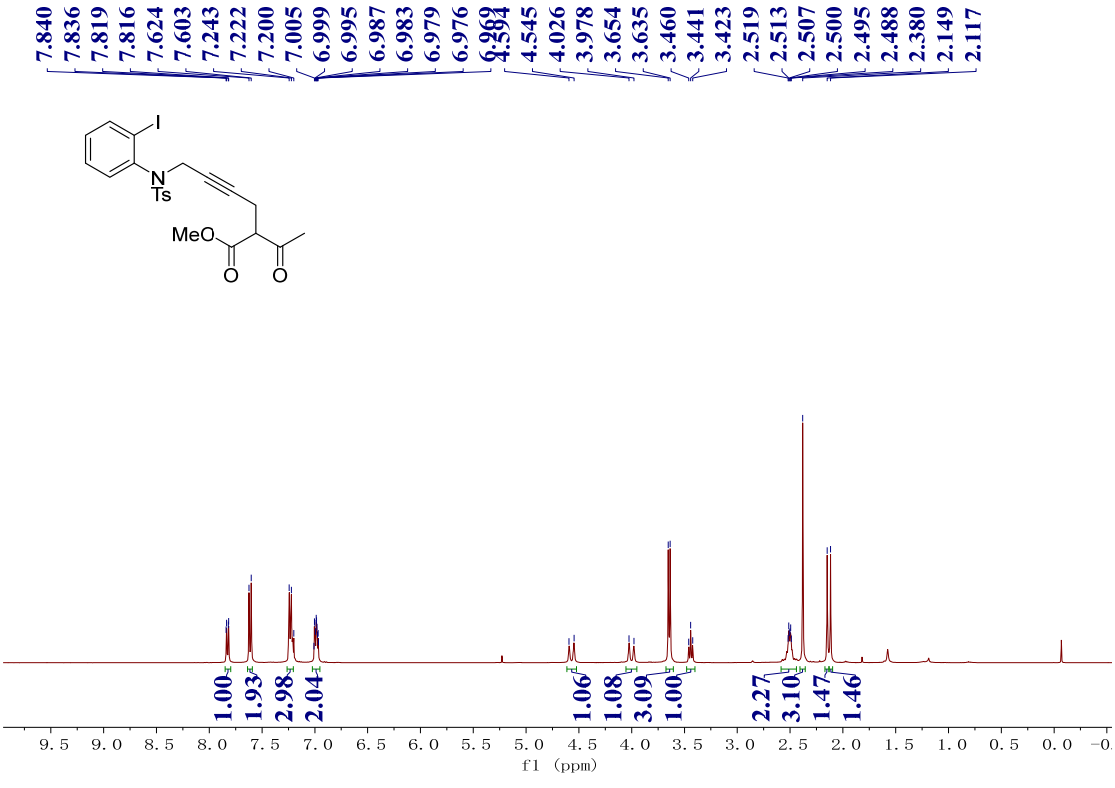

$^{1}$H NMR of **1a** (400 MHz, $CDCl_3$)



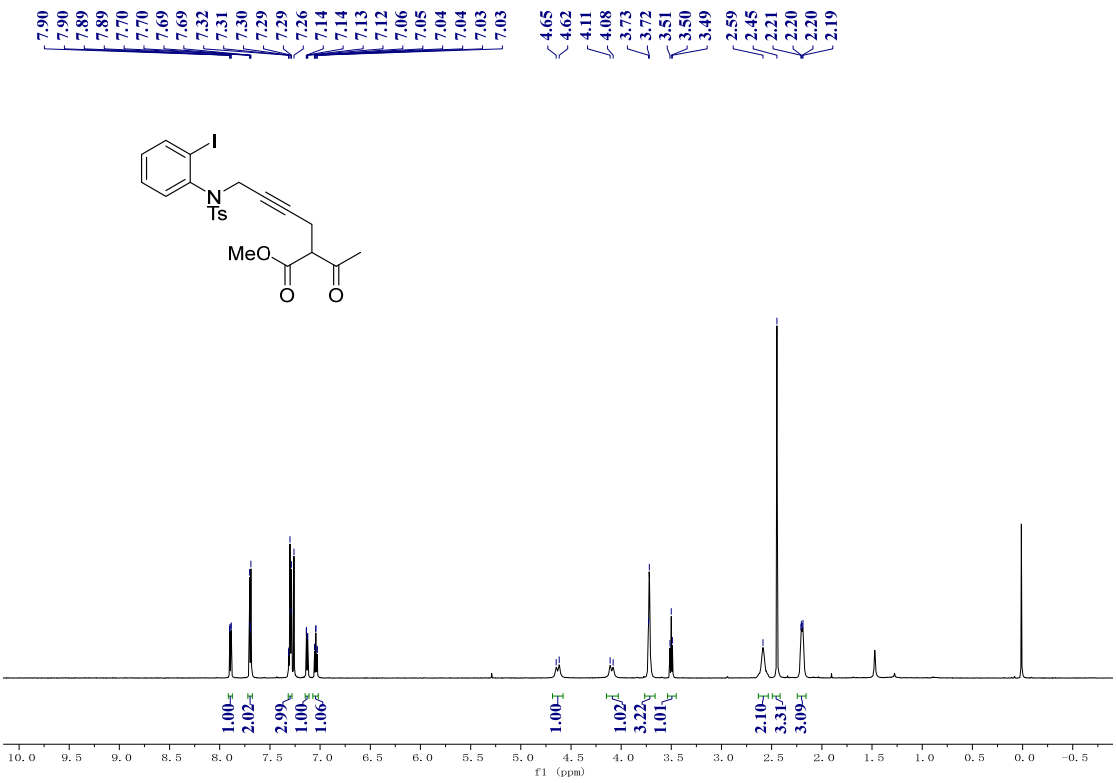
$^{13}C$ NMR of **1a** (100 MHz, $CDCl_3$)



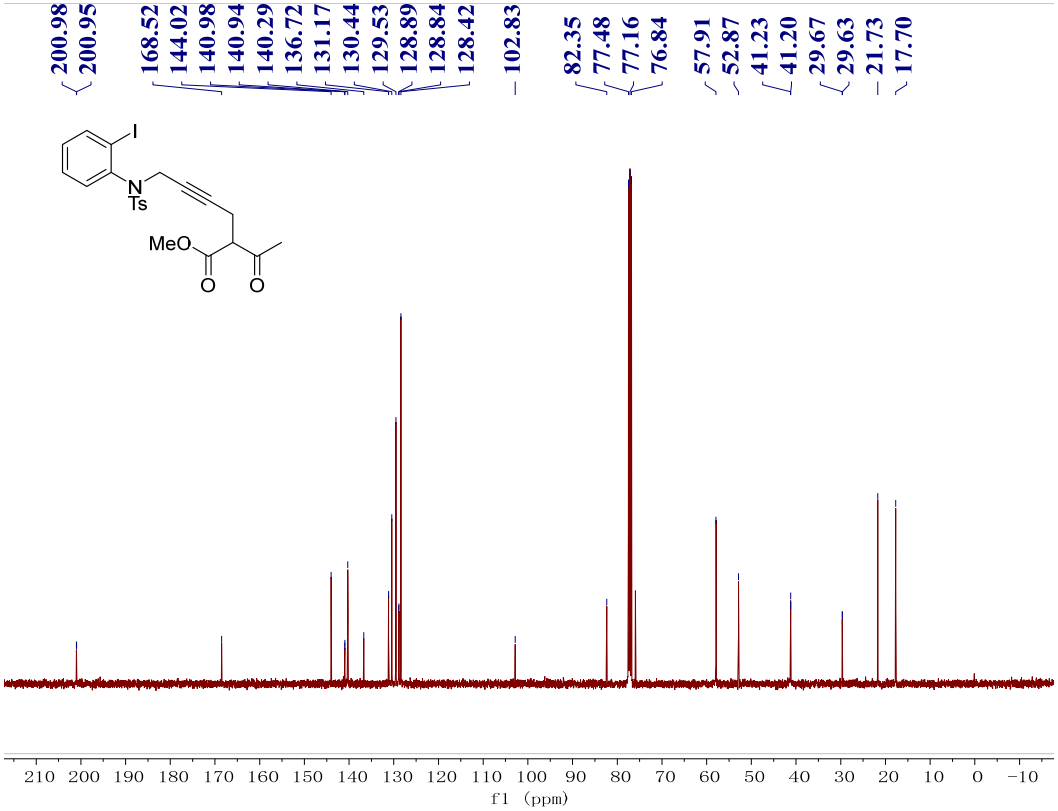

$^{1}H$ NMR of **1b** (400 MHz, $CDCl_3$)



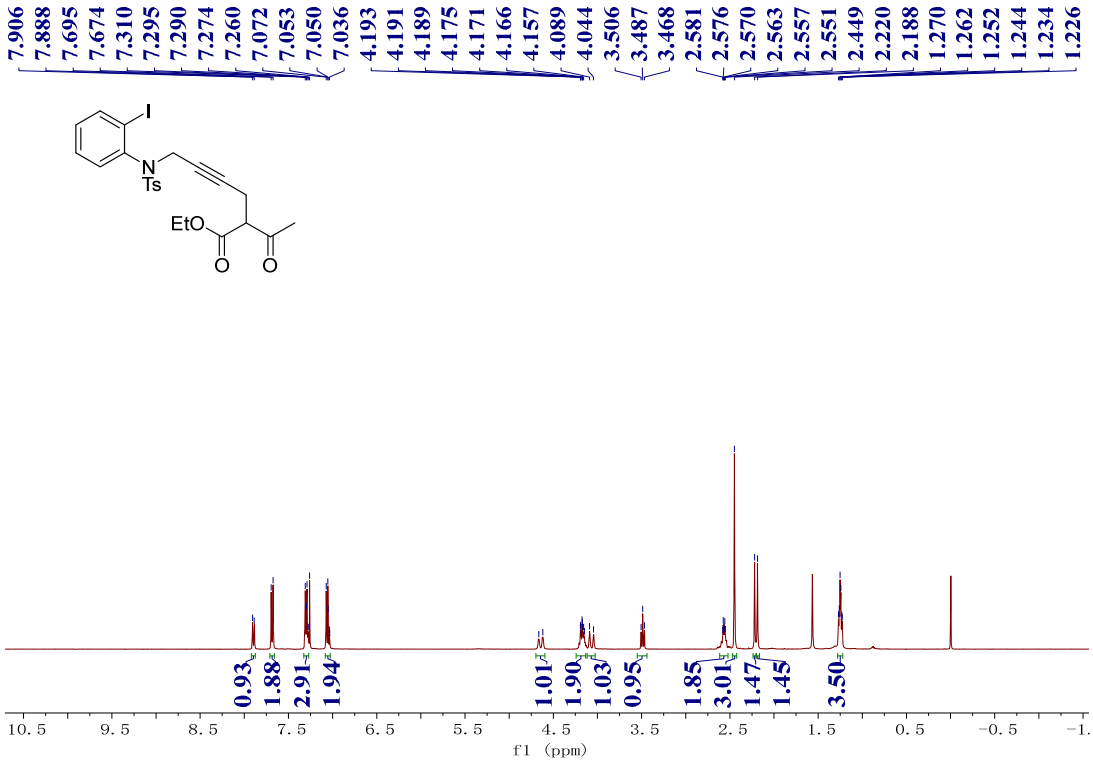
$^{1}$H NMR of **1b** (600 MHz, $CDCl_3$, 55 °C)



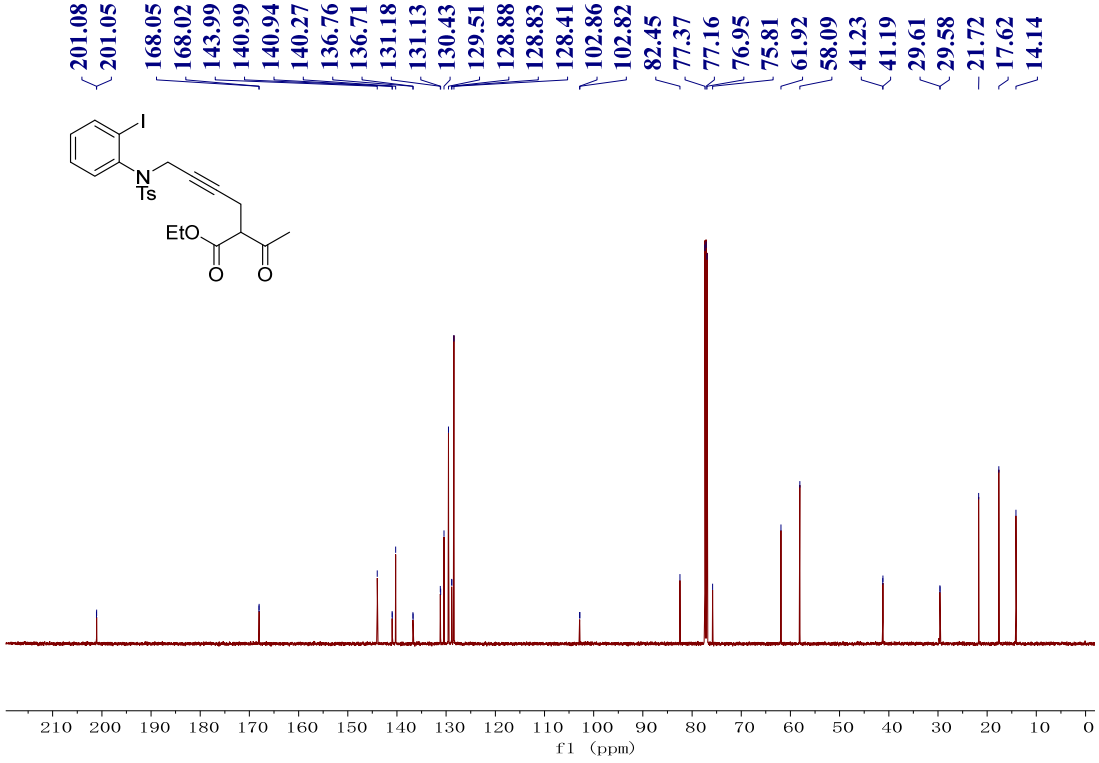

$^{13}$C NMR of **1b** (100 MHz, $CDCl_3$)



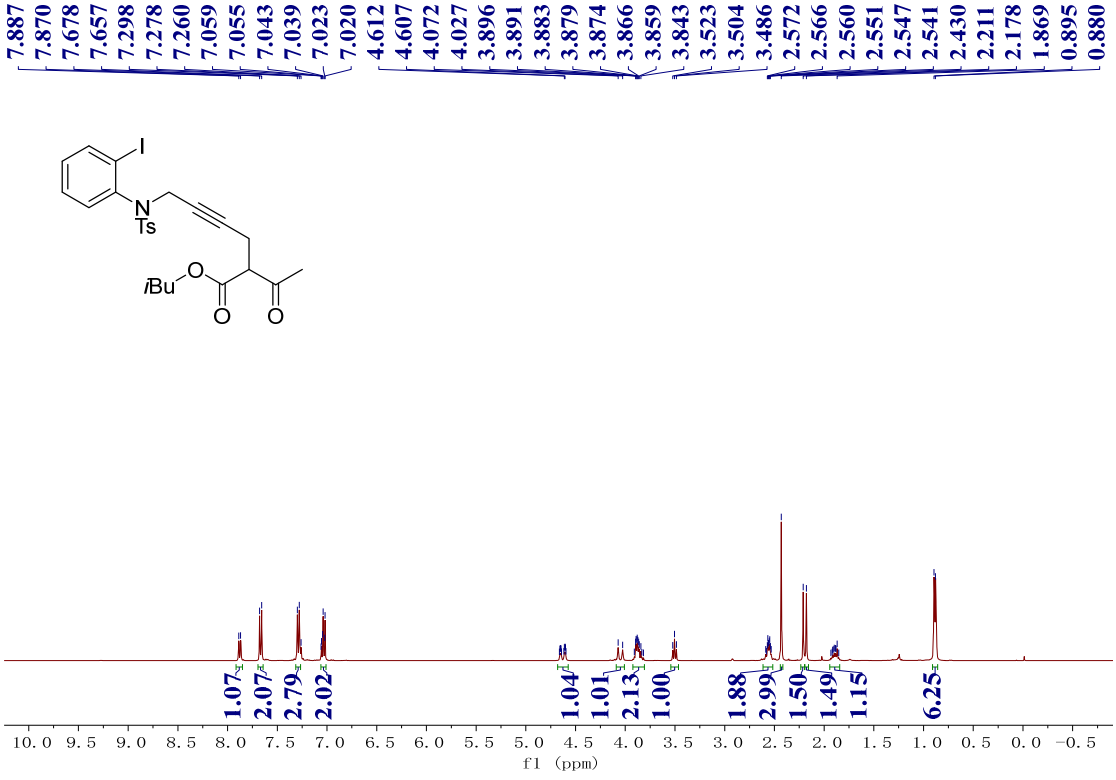
$^{1}$H NMR of **1c** (400 MHz, $CDCl_3$)



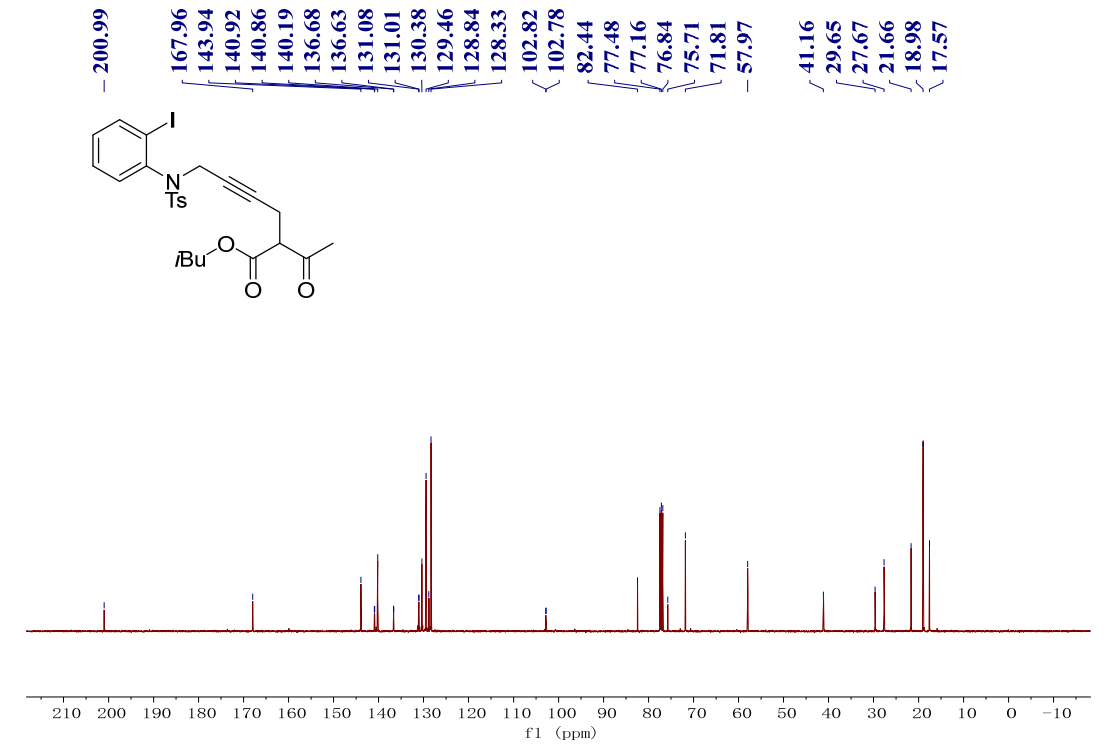

$^{13}$C NMR of **1c** (100 MHz, $CDCl_3$)



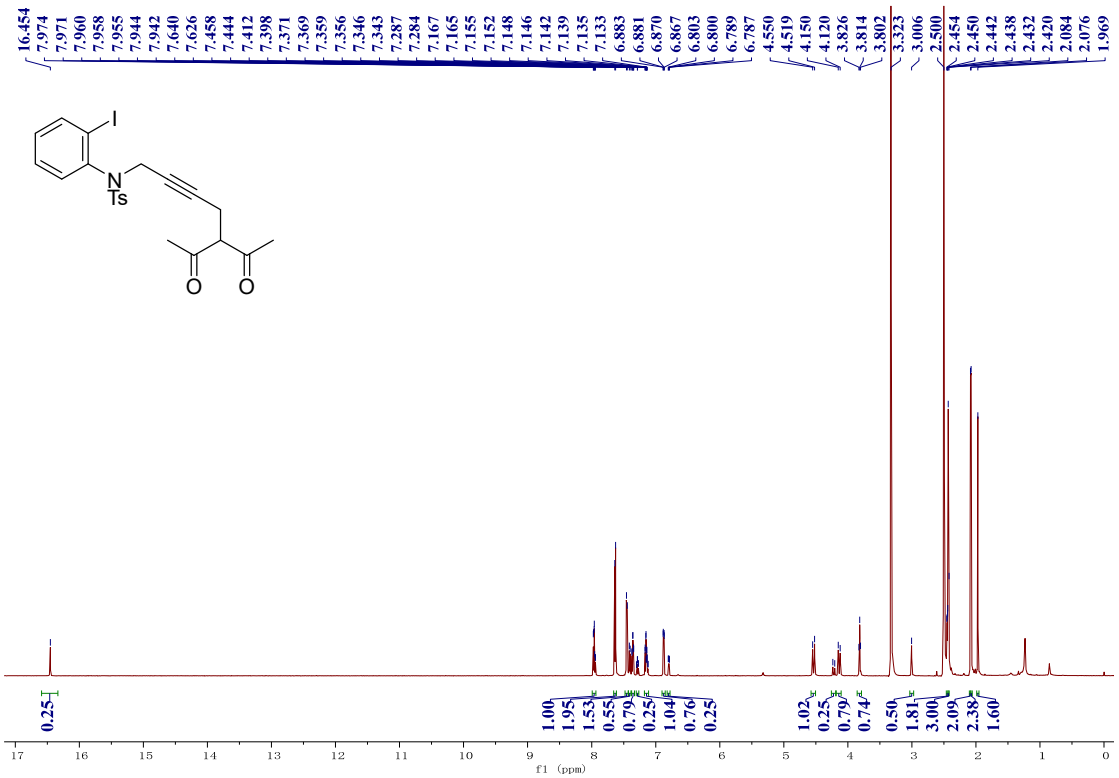
$^{1}$H NMR of **1d** (400 MHz, $CDCl_3$)



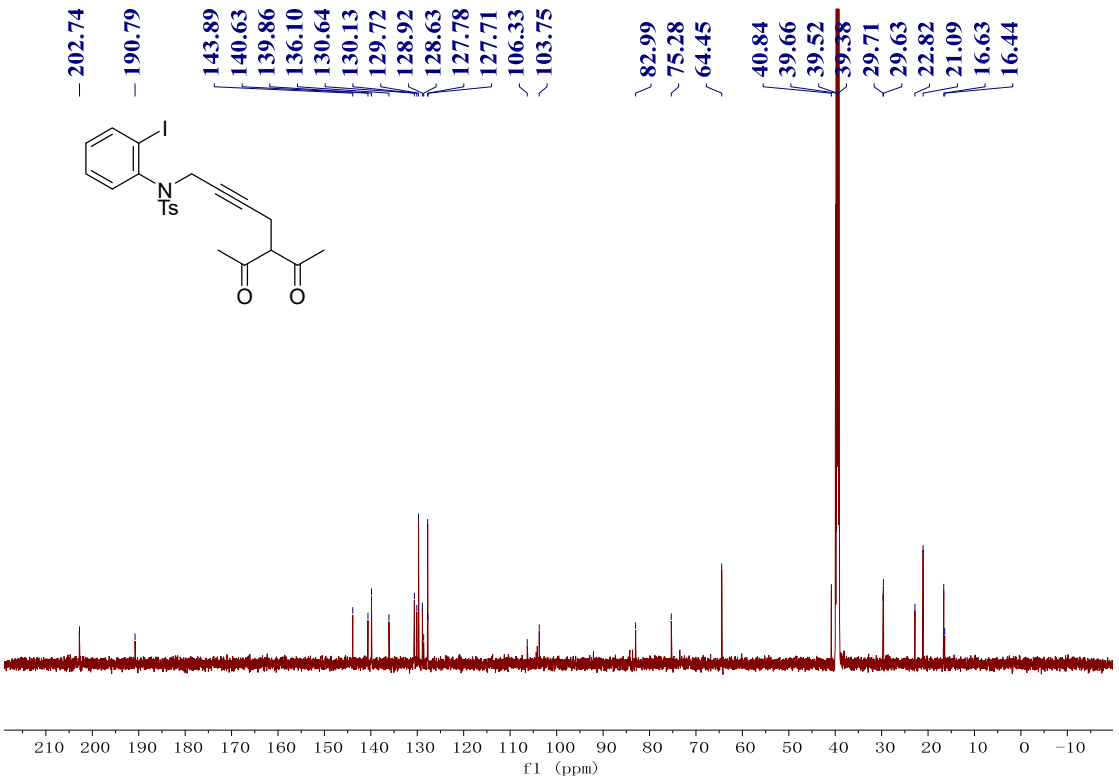

$^{13}$C NMR of **1d** (100 MHz, $CDCl_3$)



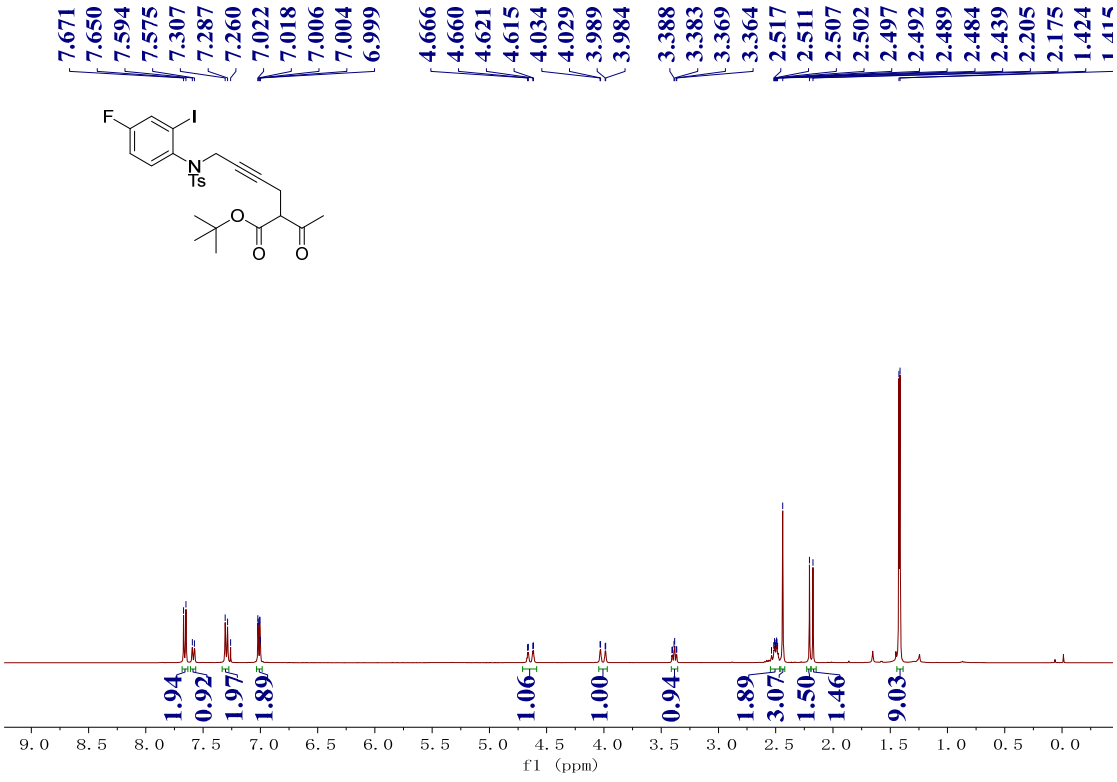
$^{1}$H NMR of **1e** (600 MHz, DMSO)



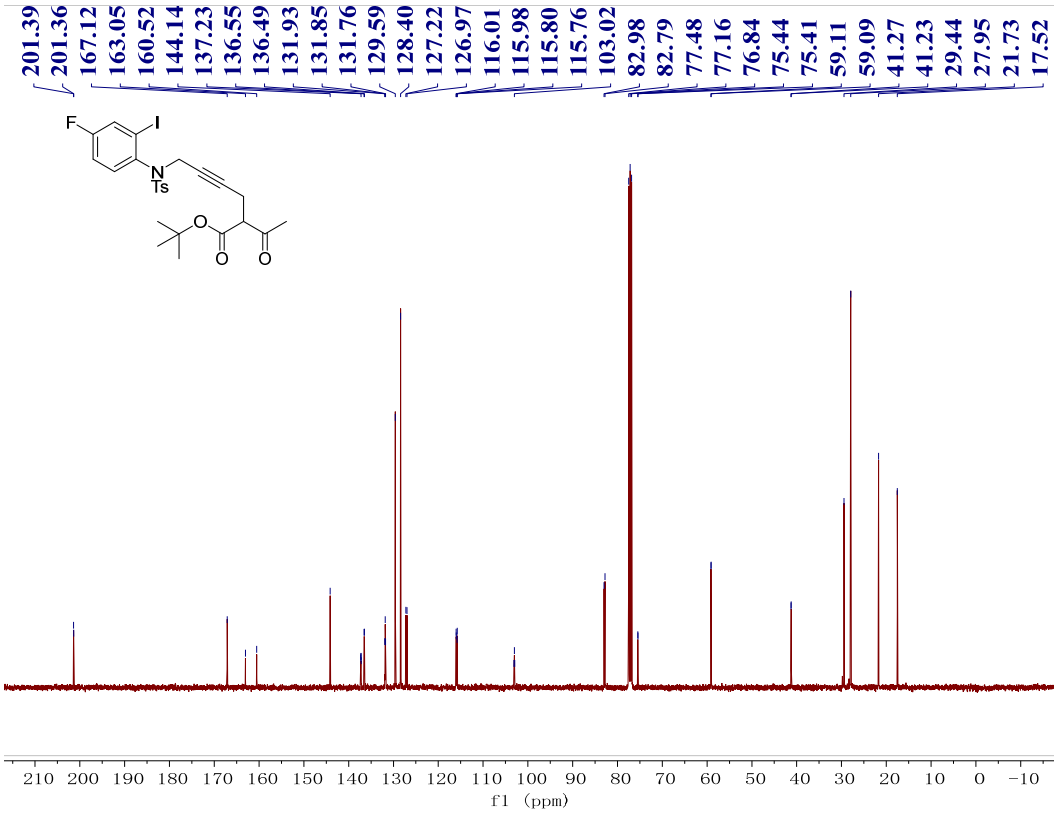

$^{13}$C NMR of **1e** (150 MHz, DMSO)



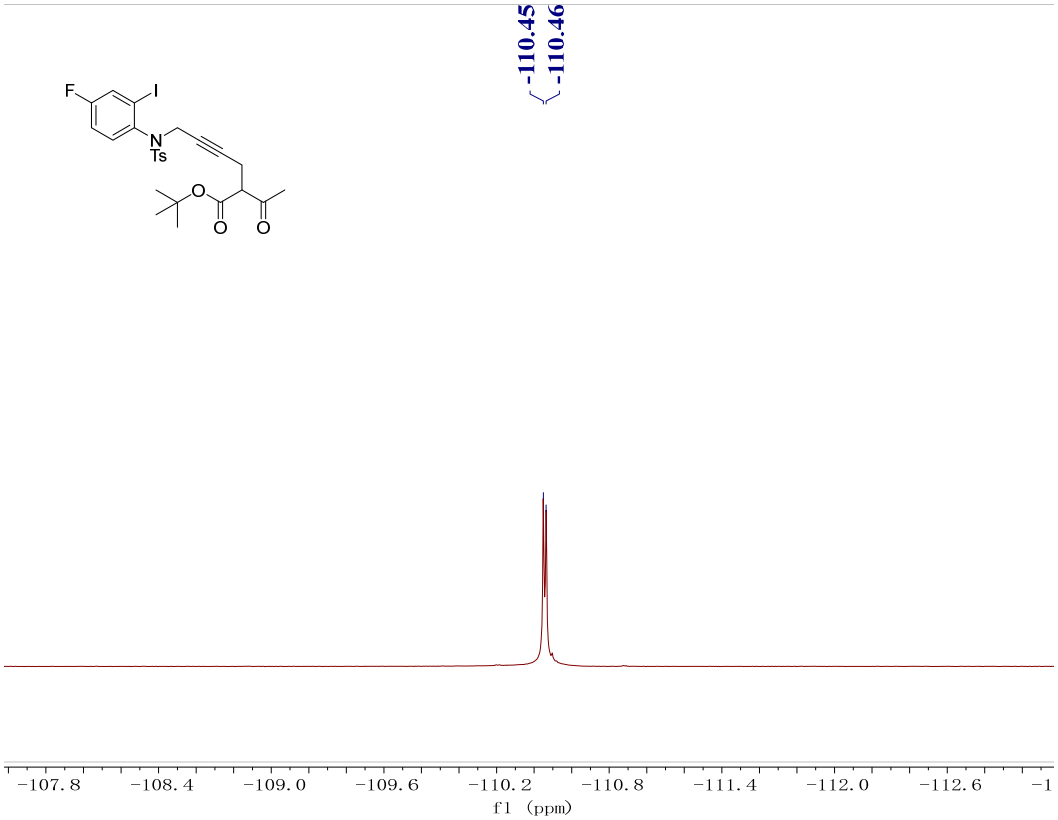
$^{1}$H NMR of **1f** (400 MHz, $CDCl_3$)



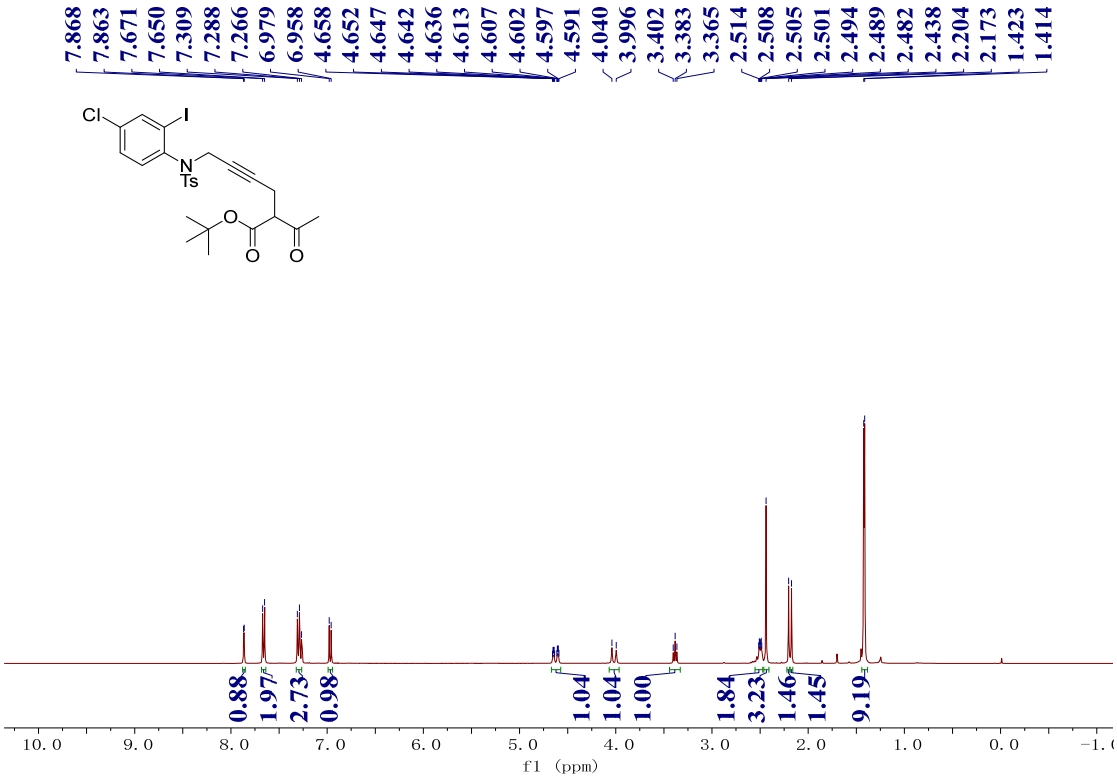

$^{13}$C NMR of **1f** (100 MHz, $CDCl_3$)



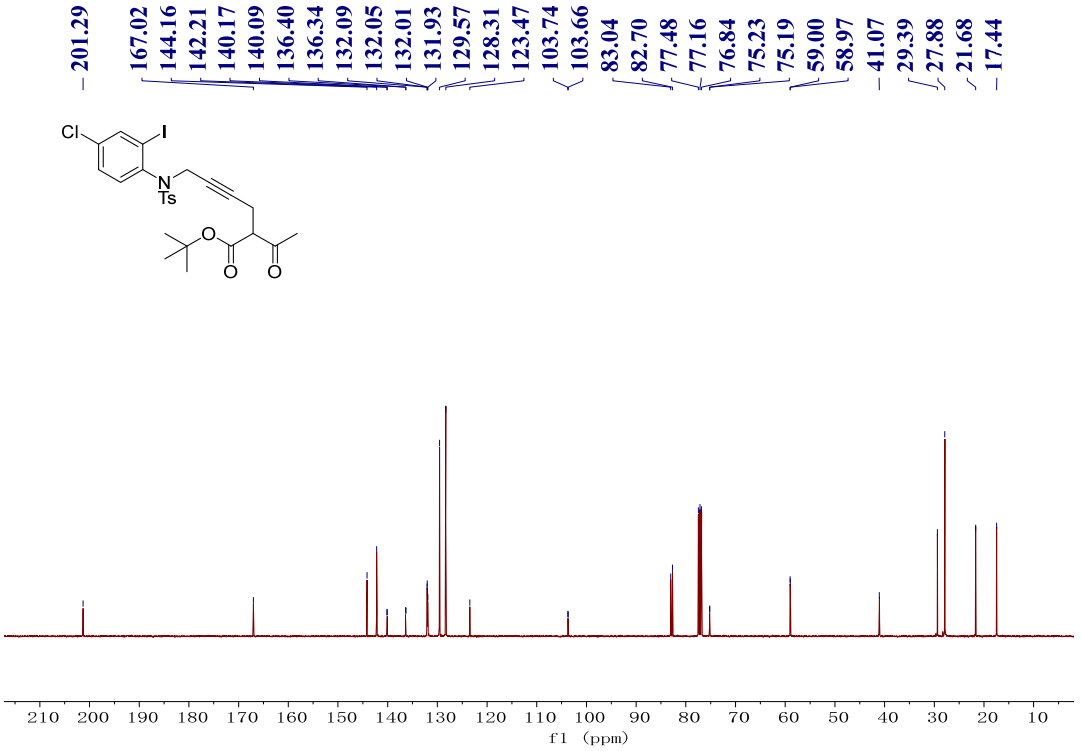
$^{19}$F NMR of **1f** (376 MHz, $CDCl_3$)



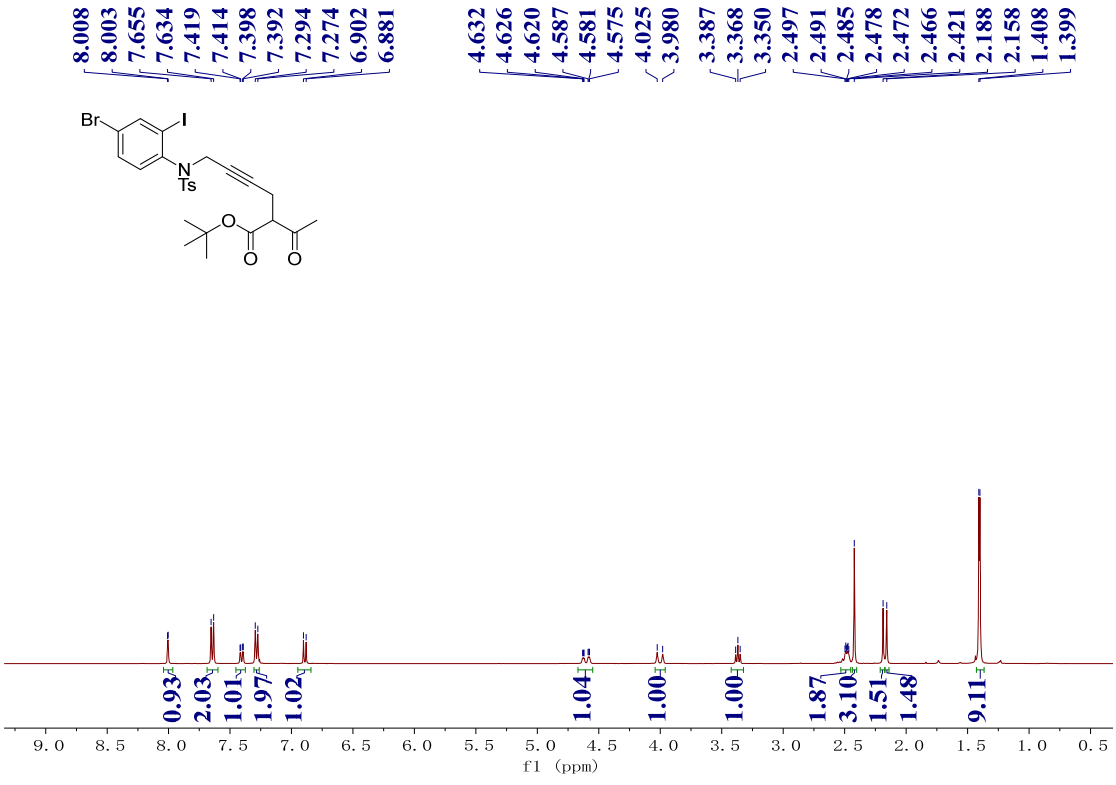

$^{1}$H NMR of **1g** (400 MHz, $CDCl_3$)



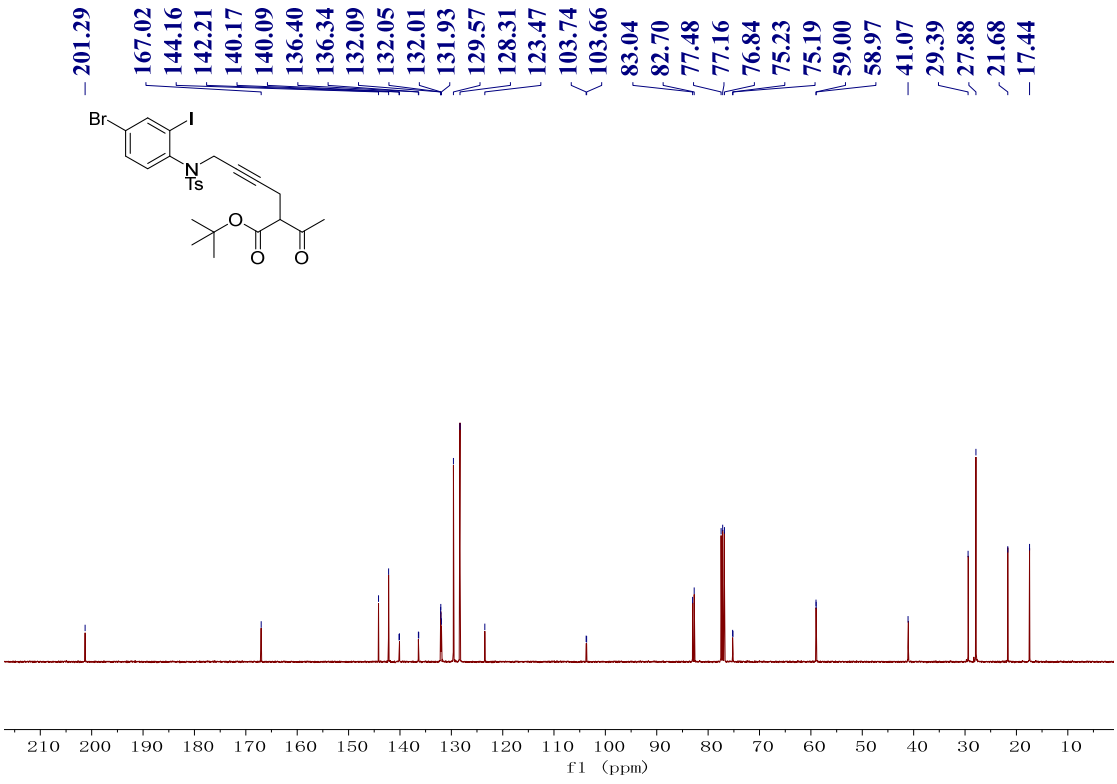
$^{13}$C NMR of **1g** (100 MHz, $CDCl_3$)



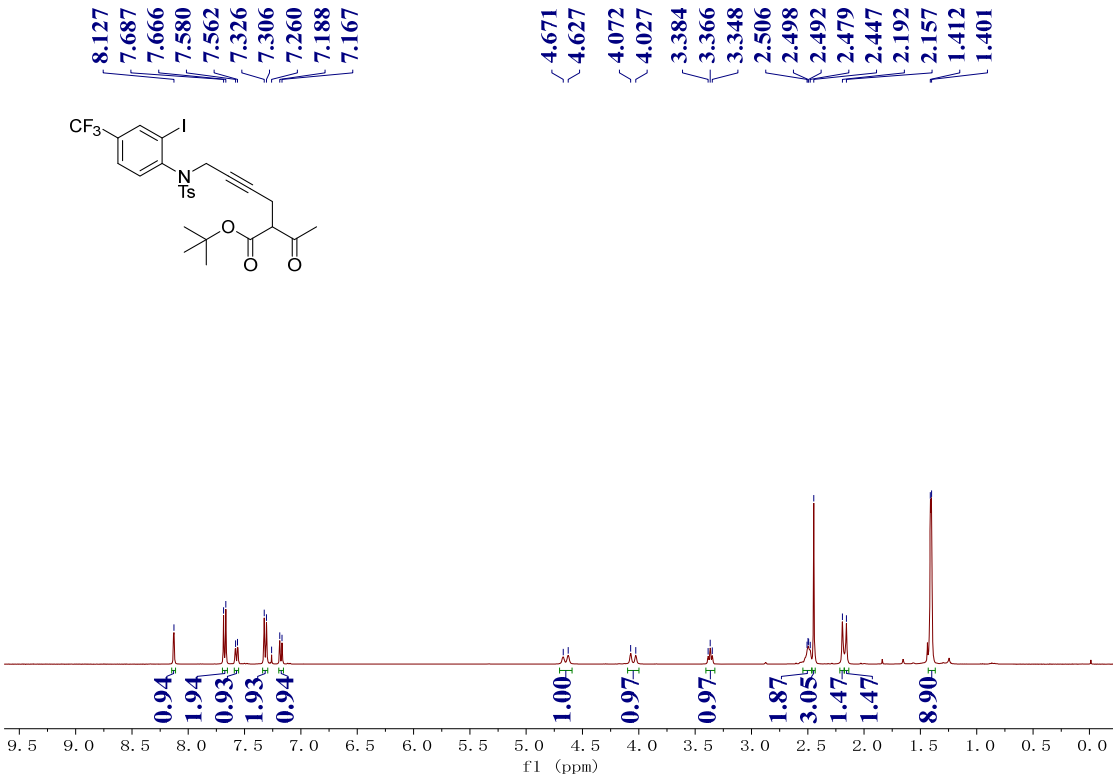

$^{1}$H NMR of **1h** (400 MHz, $CDCl_3$)



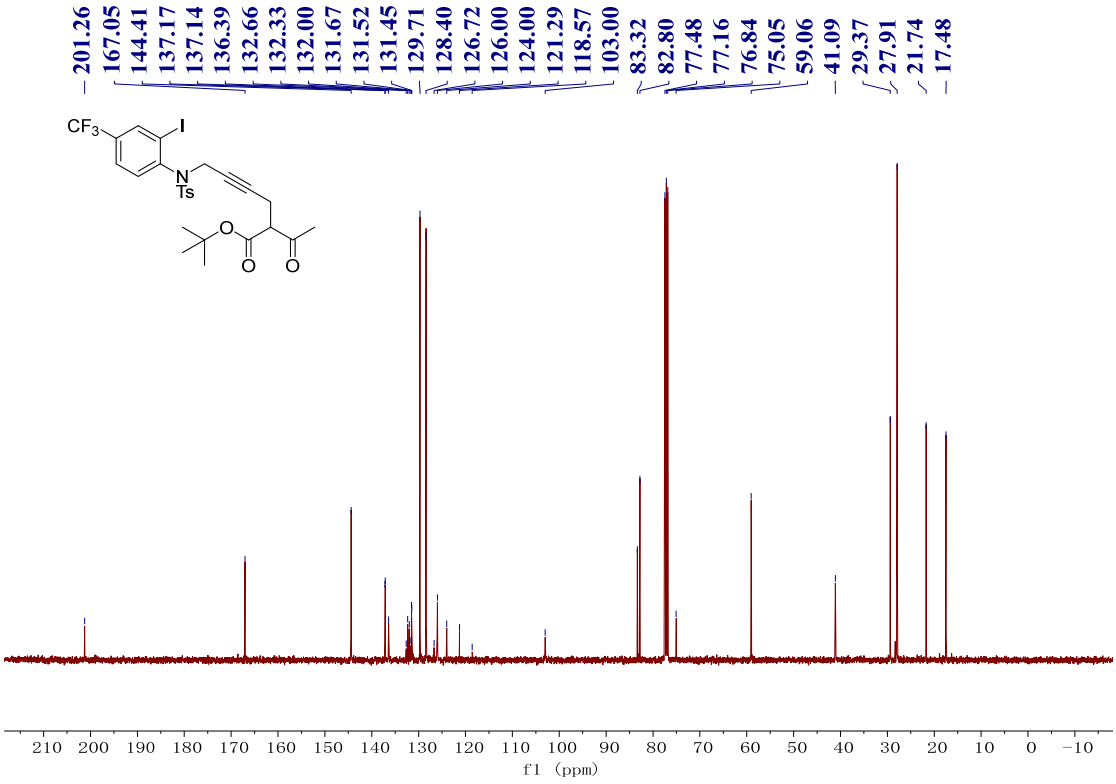
$^{13}$C NMR of **1h** (100 MHz, $CDCl_3$)



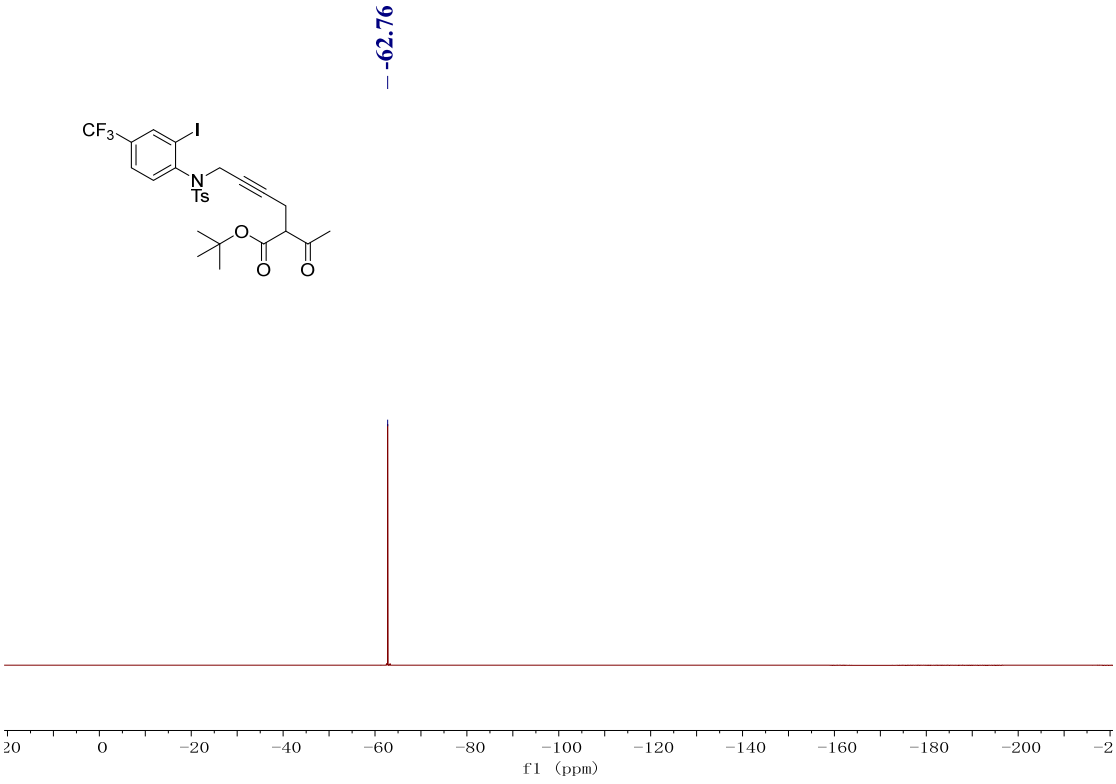

$^{1}$H NMR of **1i** (400 MHz, $CDCl_3$)



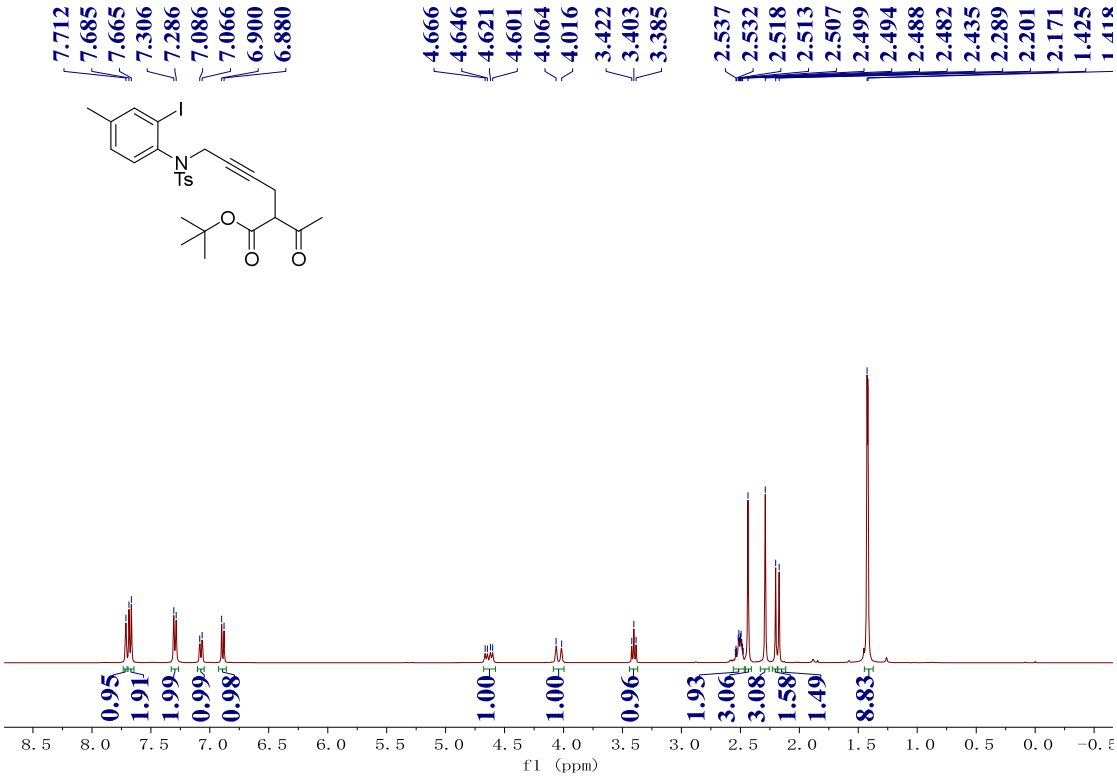
$^{13}$C NMR of **1i** (100 MHz, $CDCl_3$)



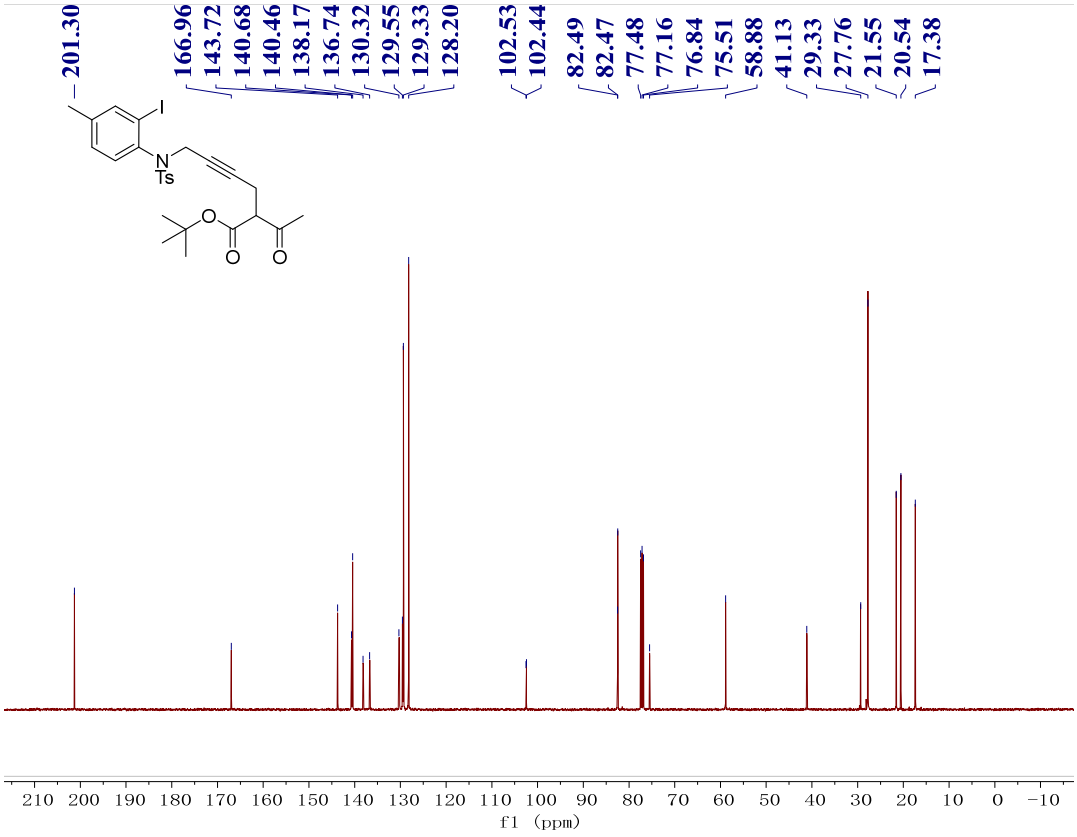

$^{19}$F NMR of **1i** (376 MHz, $CDCl_3$)



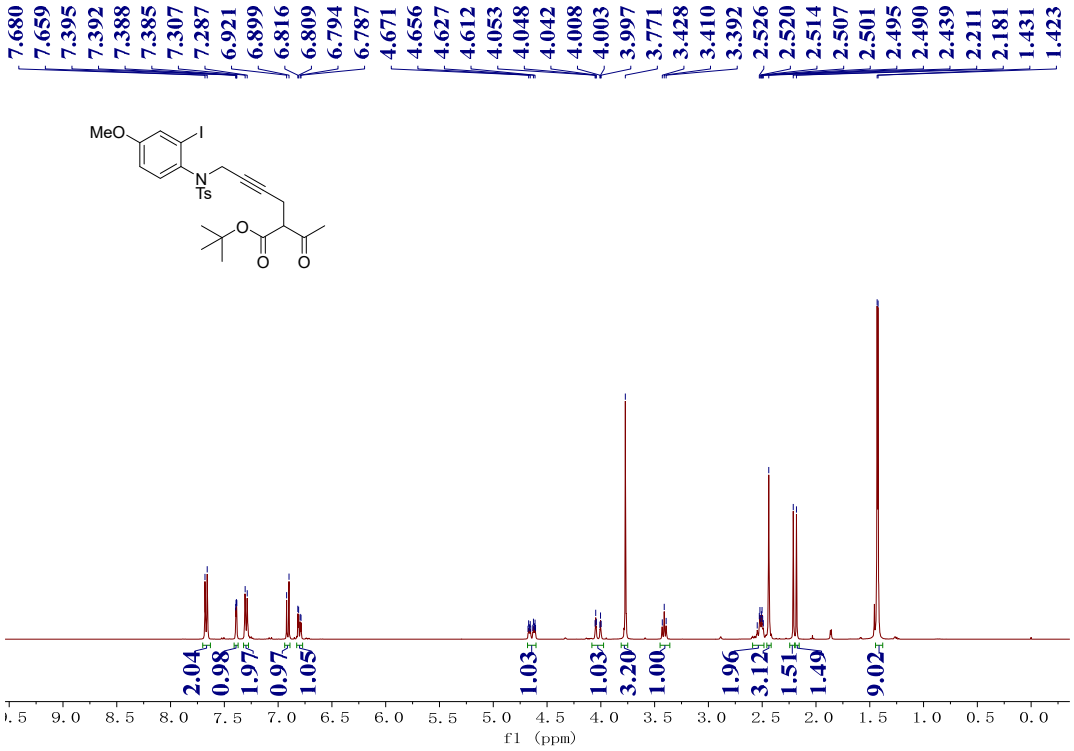
$^{1}$H NMR of **1j** (400 MHz, $CDCl_3$)



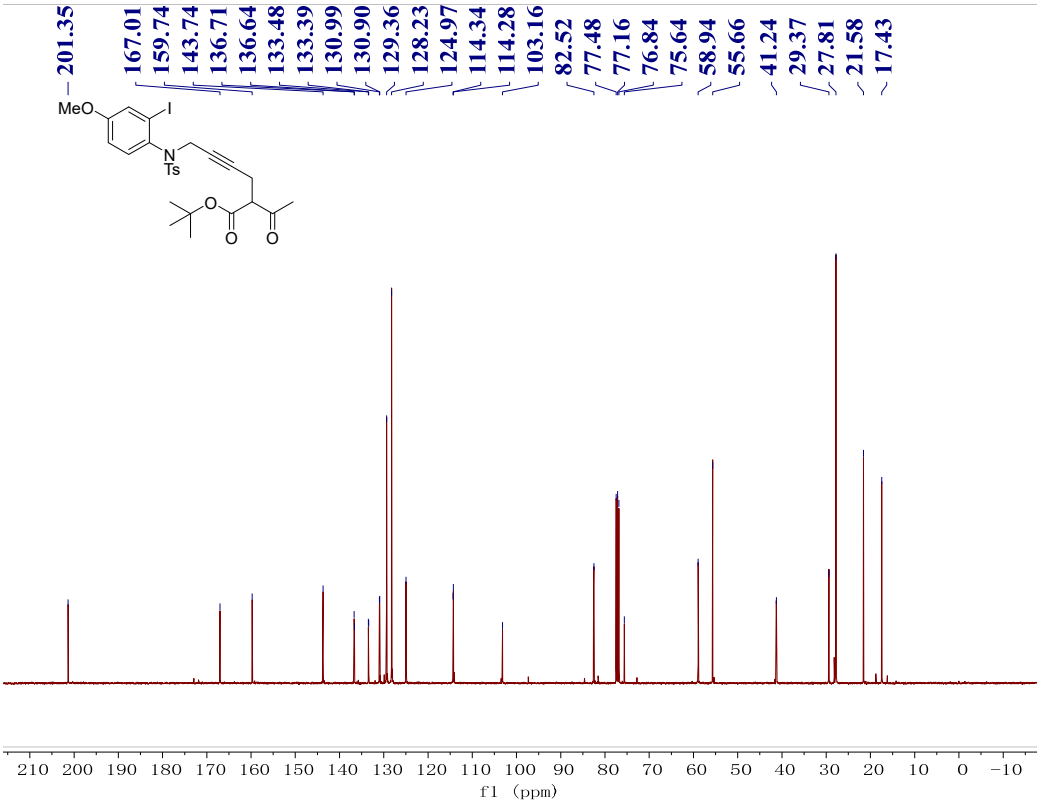

$^{13}$C NMR of **1j** (100 MHz, $CDCl_3$)



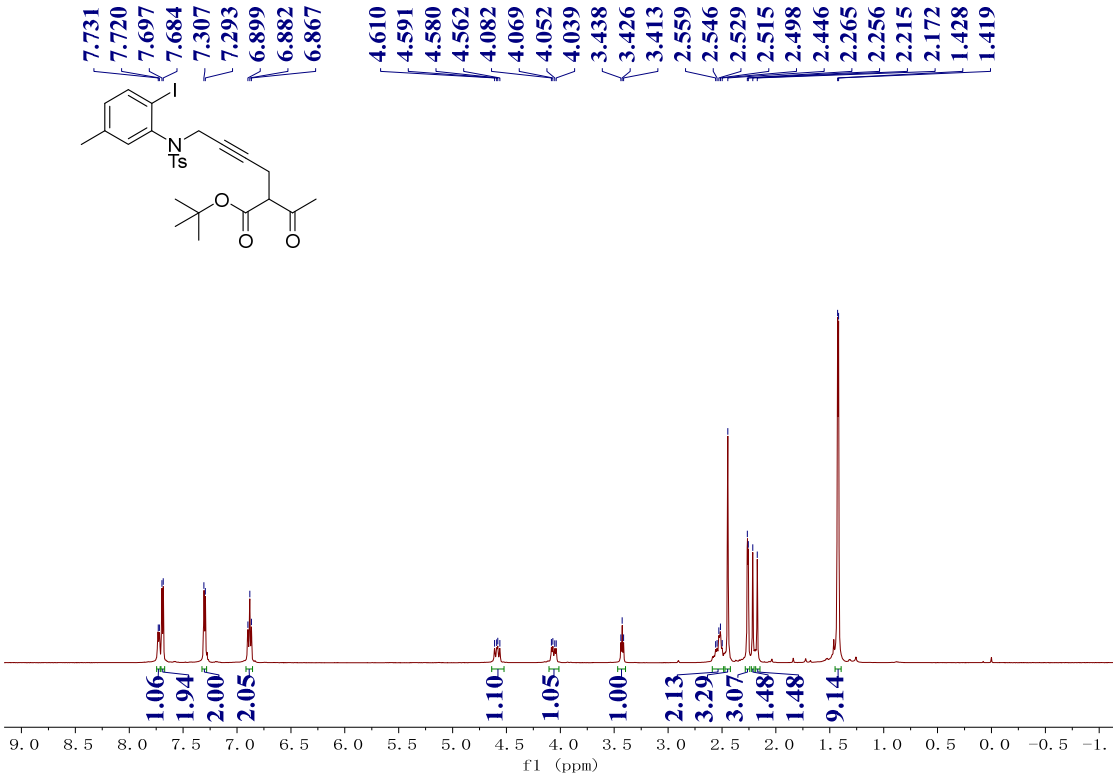
$^{1}$H NMR of **1k** (400 MHz, $CDCl_3$)



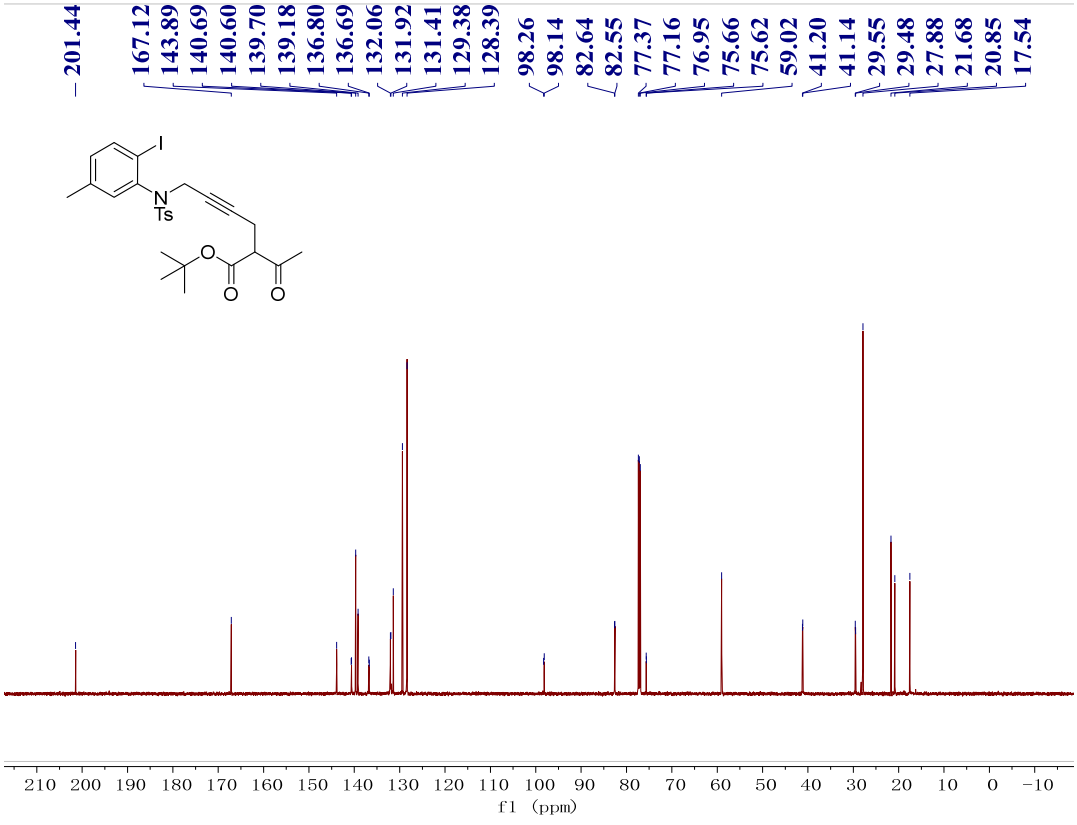

$^{13}$C NMR of **1k** (100 MHz, $CDCl_3$)



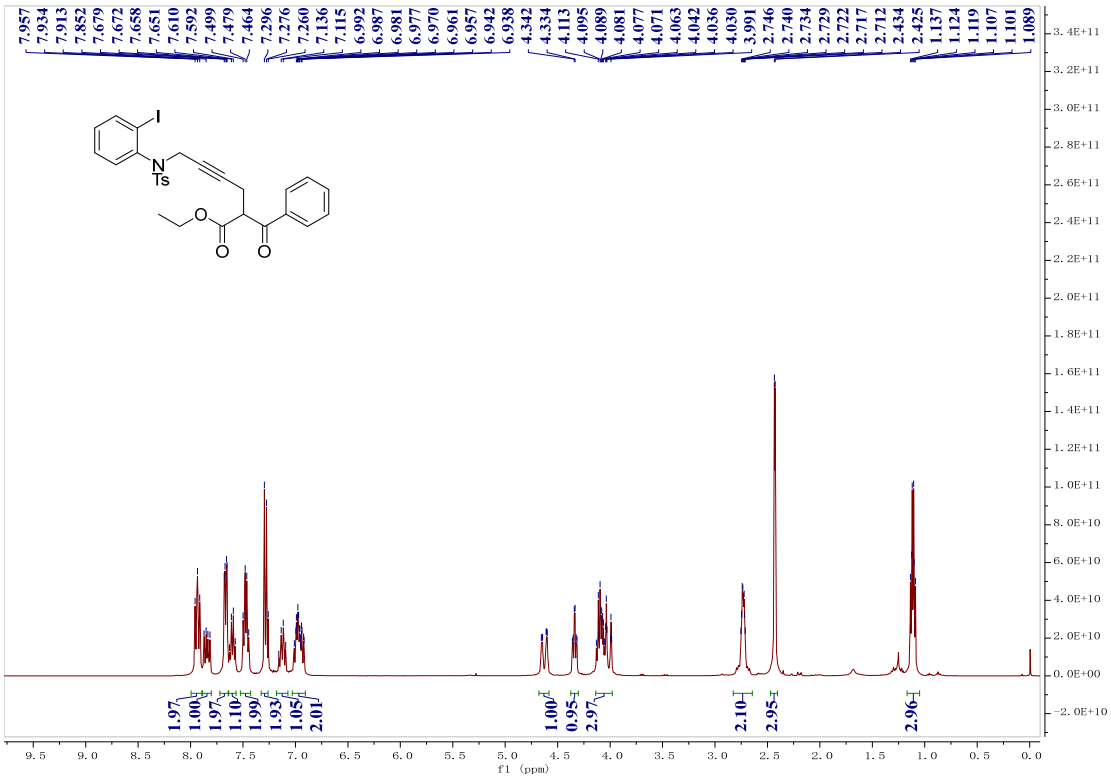
$^{1}$H NMR of **1l** (600 MHz, $CDCl_3$)



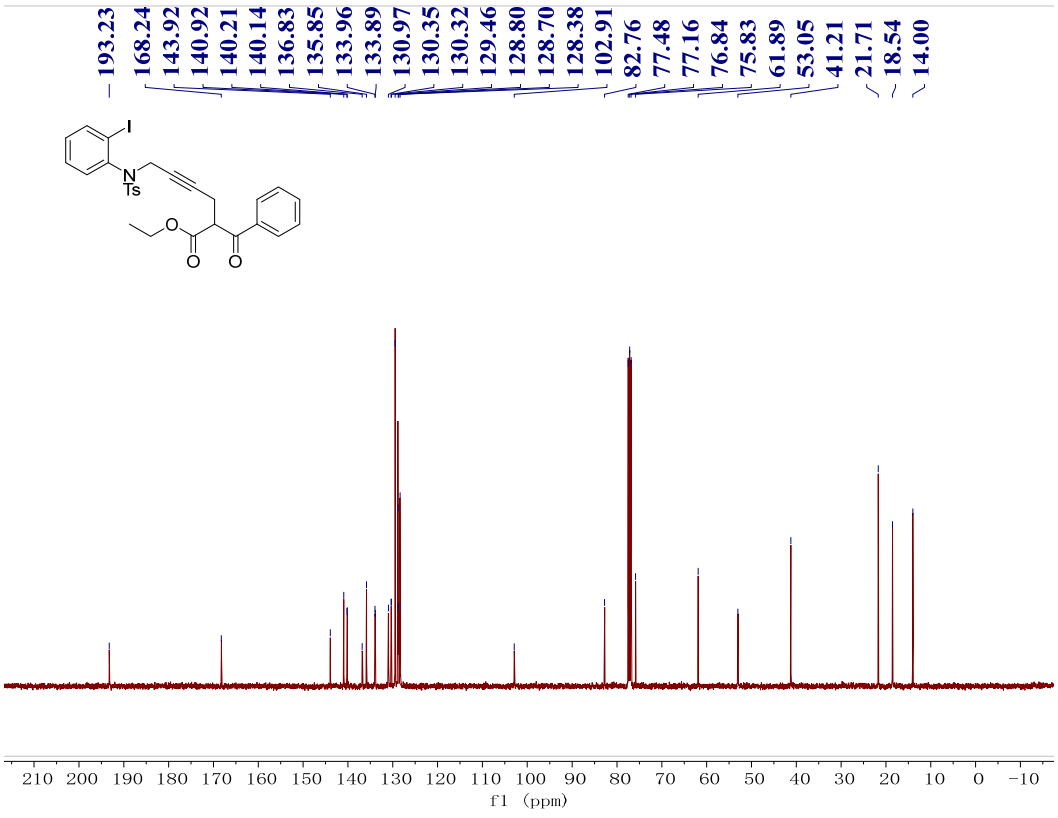

$^{13}$C NMR of **1l** (150 MHz, $CDCl_3$)



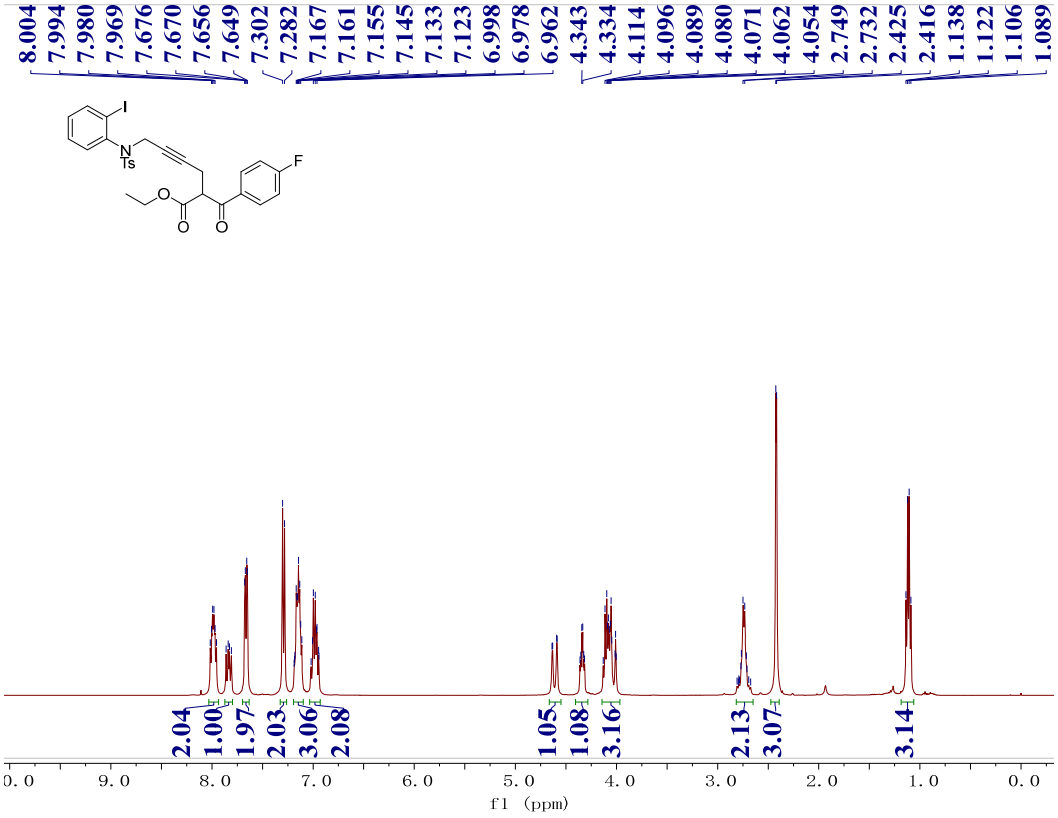
$^{1}$H NMR of **3a** (400 MHz, $CDCl_3$)



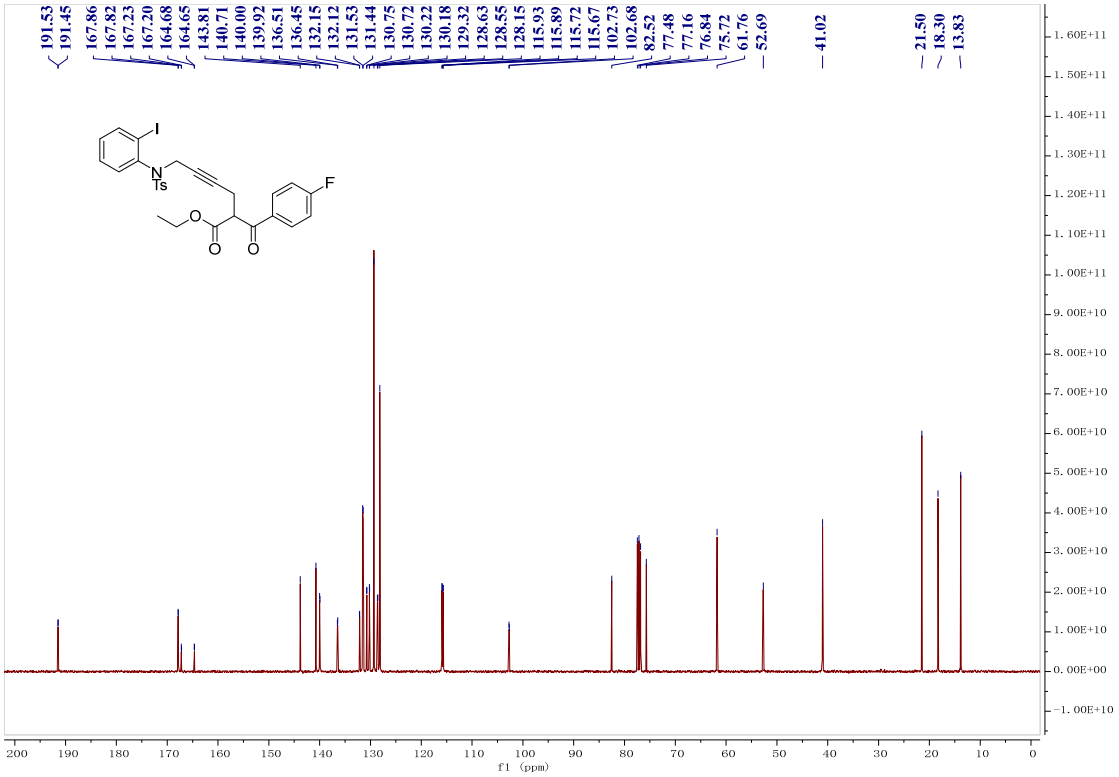

$^{13}$C NMR of **3a** (100 MHz, $CDCl_3$)



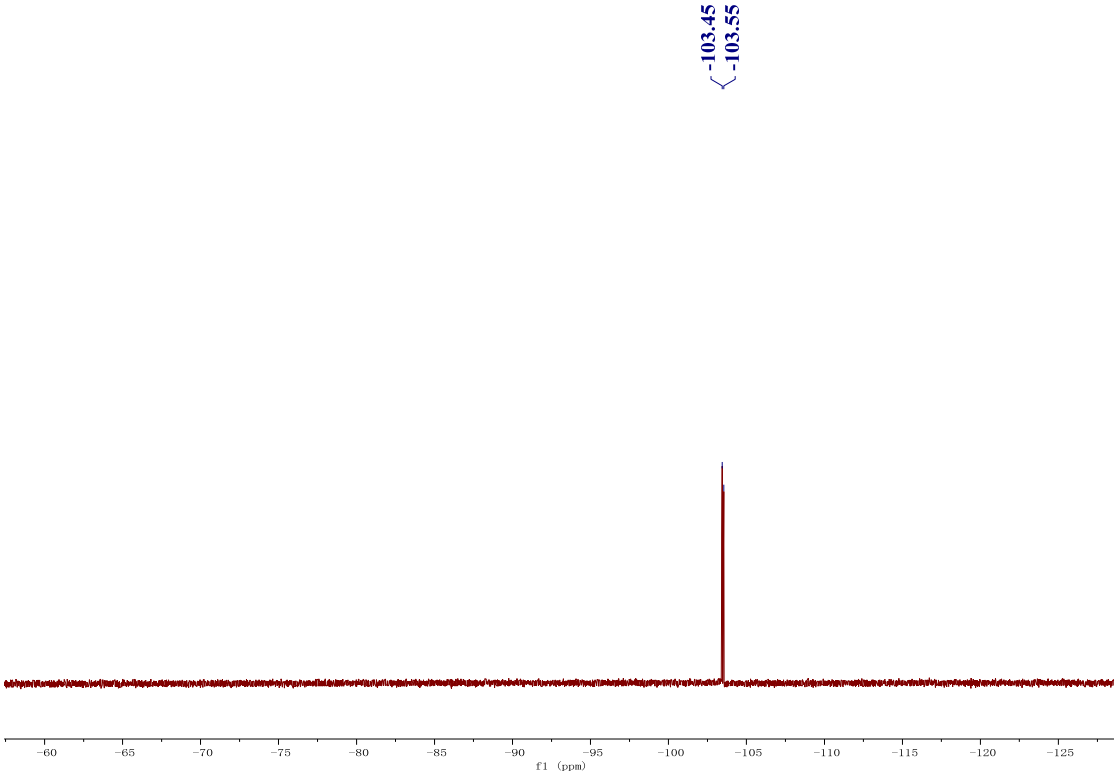
$^{1}$H NMR of **3b** (400 MHz, $CDCl_3$)



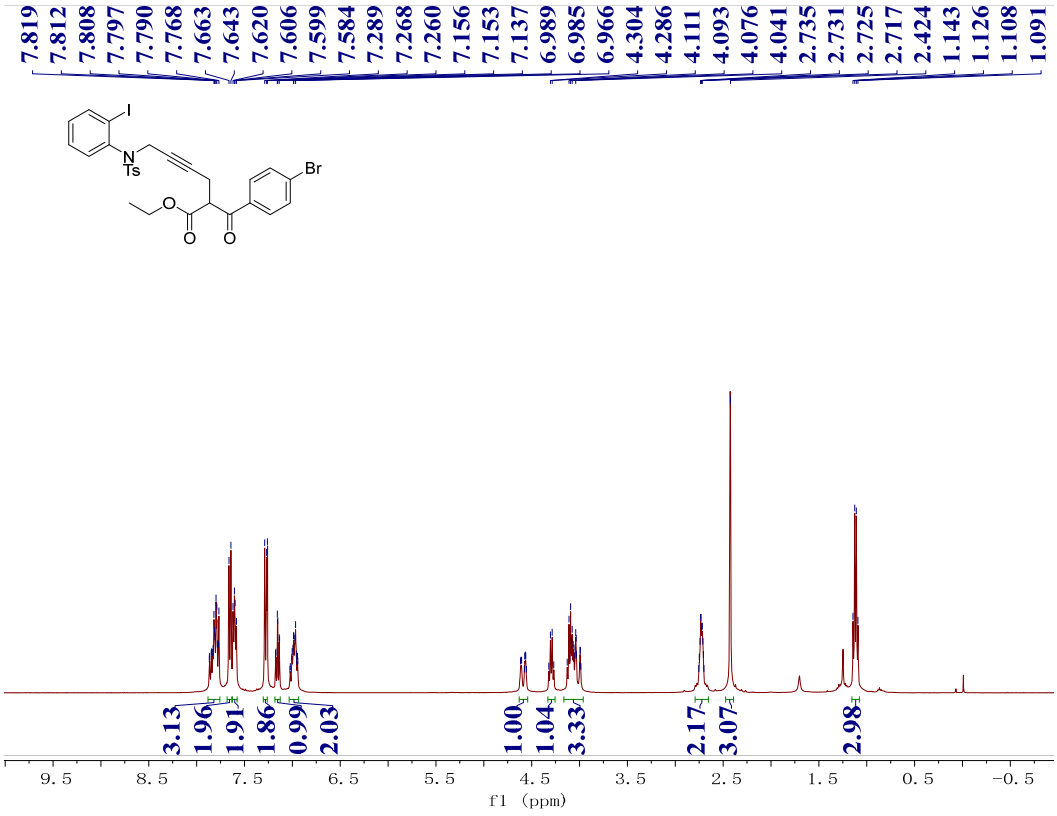

$^{13}$C NMR of **3b** (100 MHz, $CDCl_3$)



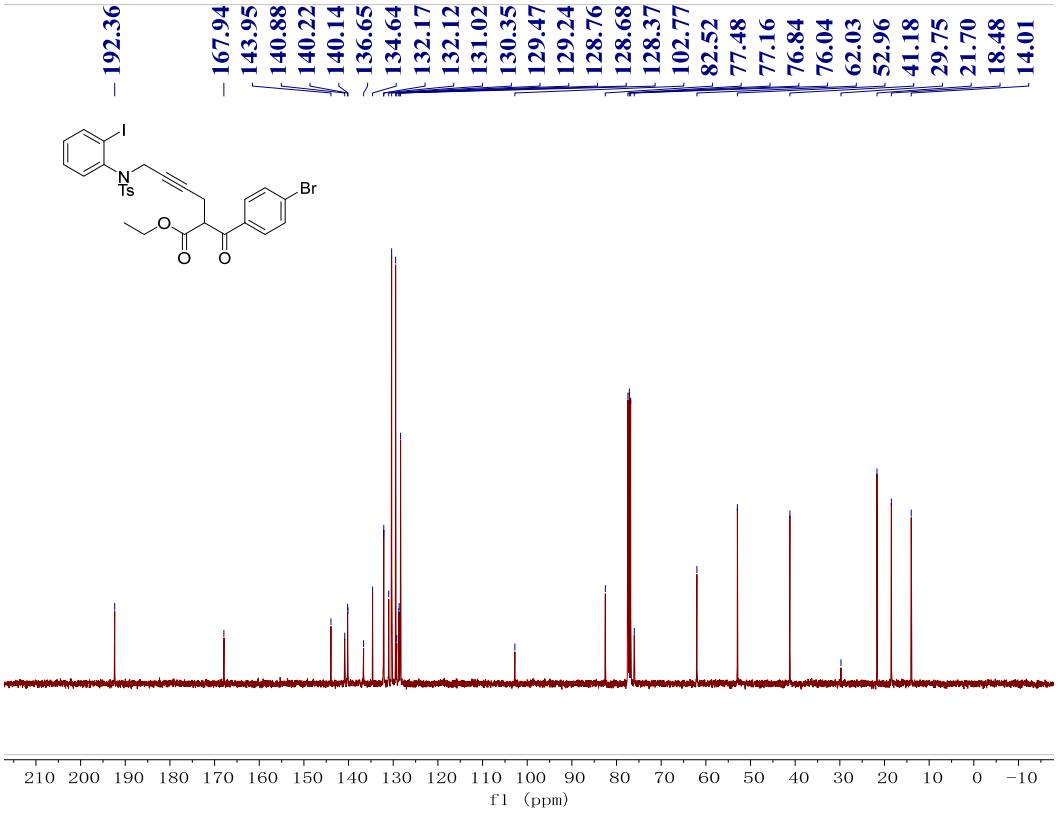
$^{19}$F NMR of **3b** (376 MHz, $CDCl_3$)



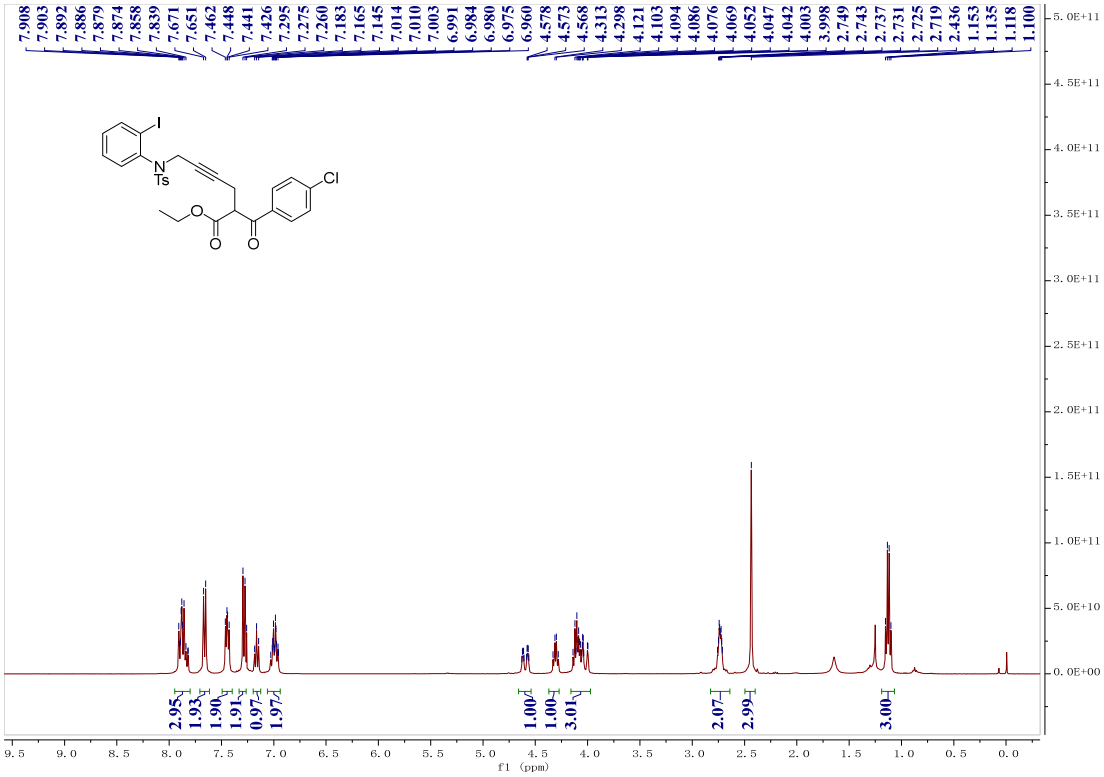

$^{1}$H NMR of **3c** (400 MHz, $CDCl_3$)



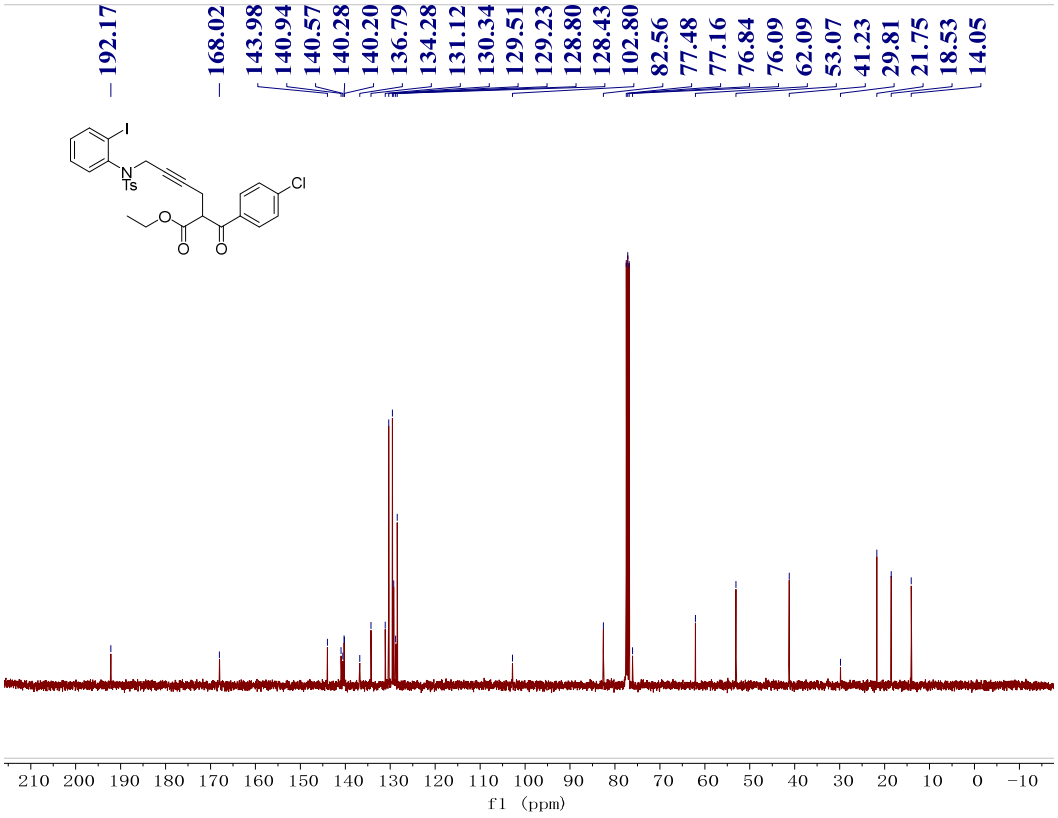
$^{13}$C NMR of **3c** (100 MHz, $CDCl_3$)



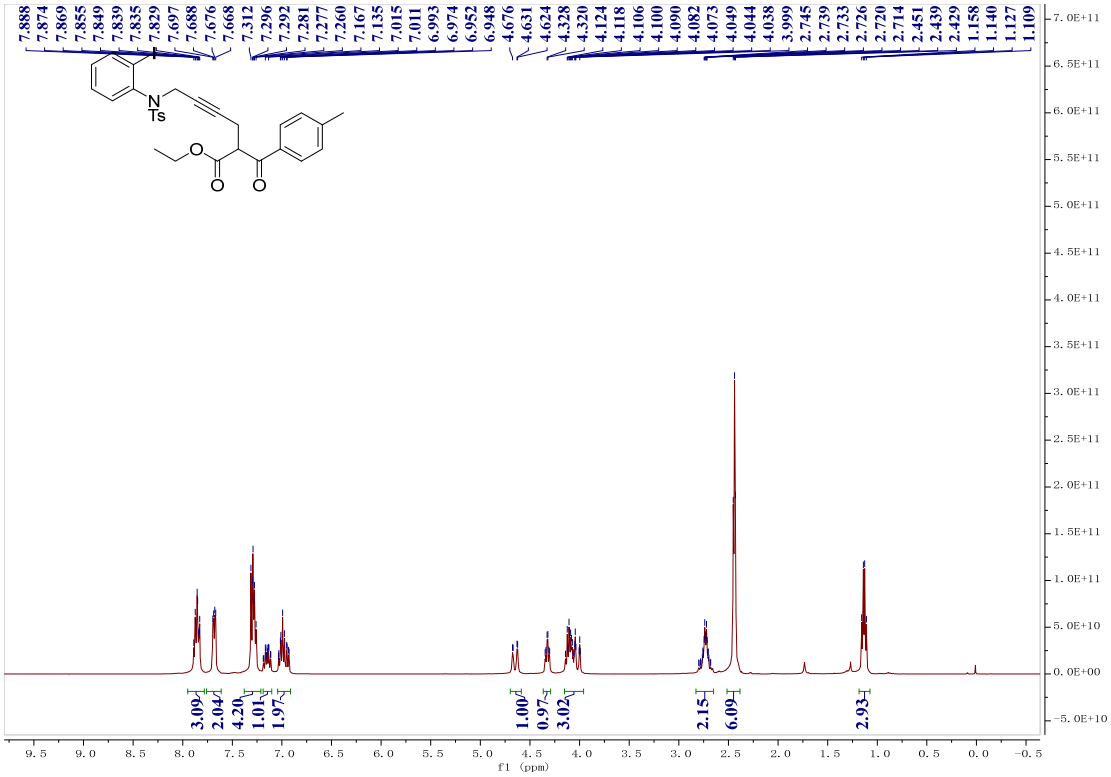

$^{1}$H NMR of **3d** (400 MHz, $CDCl_3$)



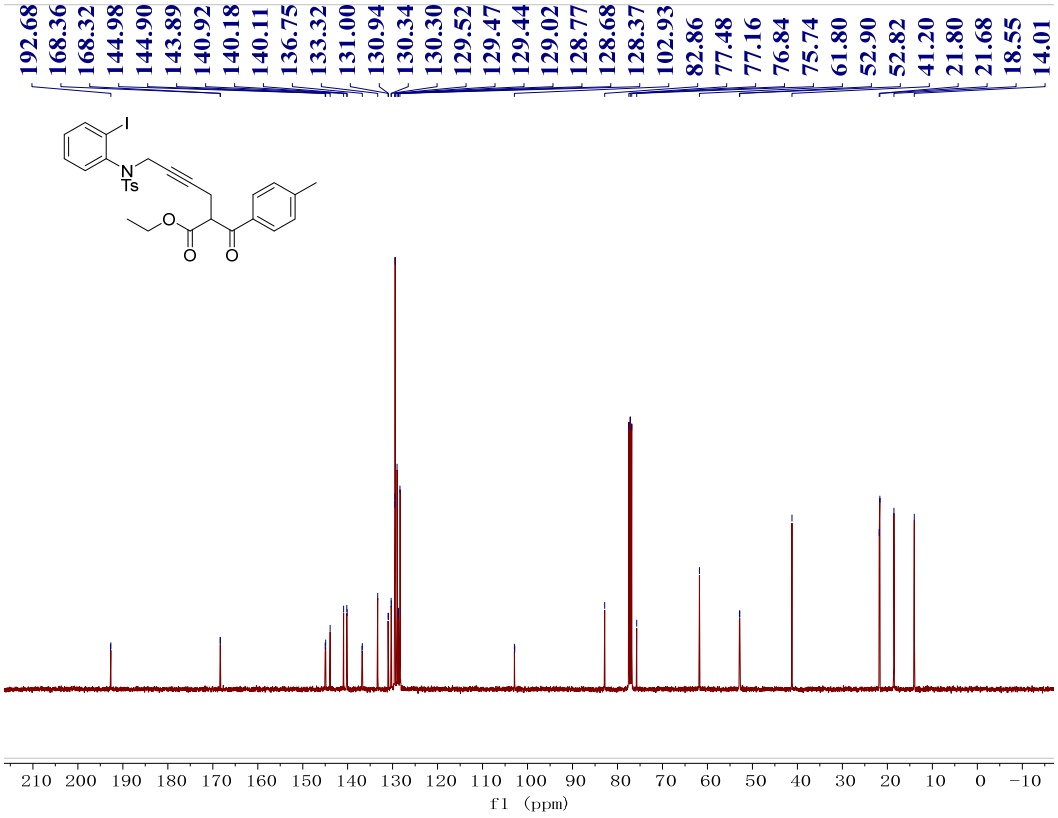
$^{13}$C NMR of **3d** (100 MHz, $CDCl_3$)



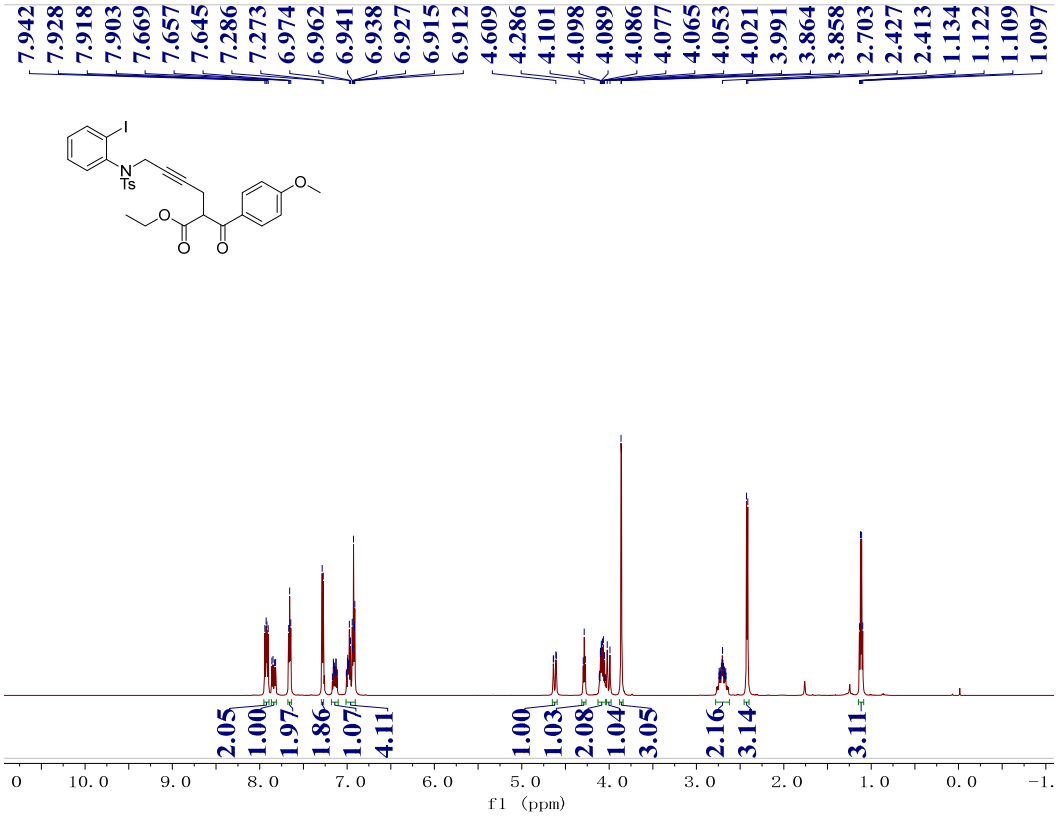

$^{1}$H NMR of **3e** (400 MHz, $CDCl_3$)



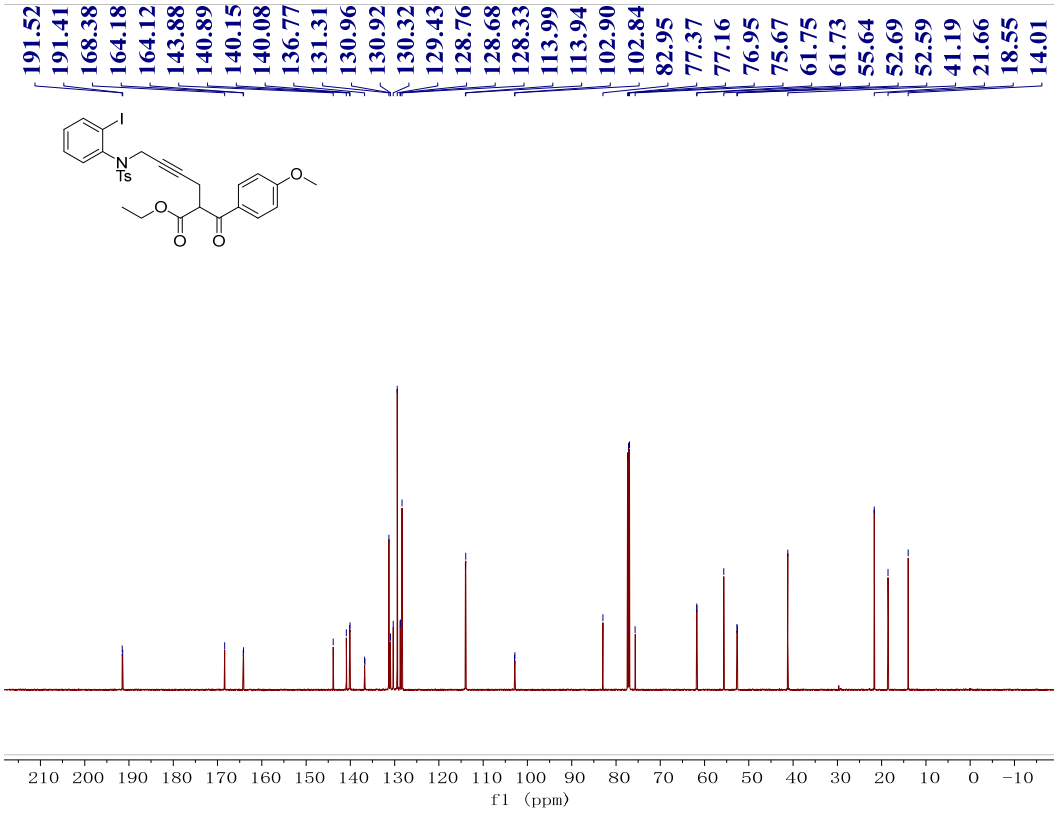
$^{13}$C NMR of **3e** (100 MHz, $CDCl_3$)



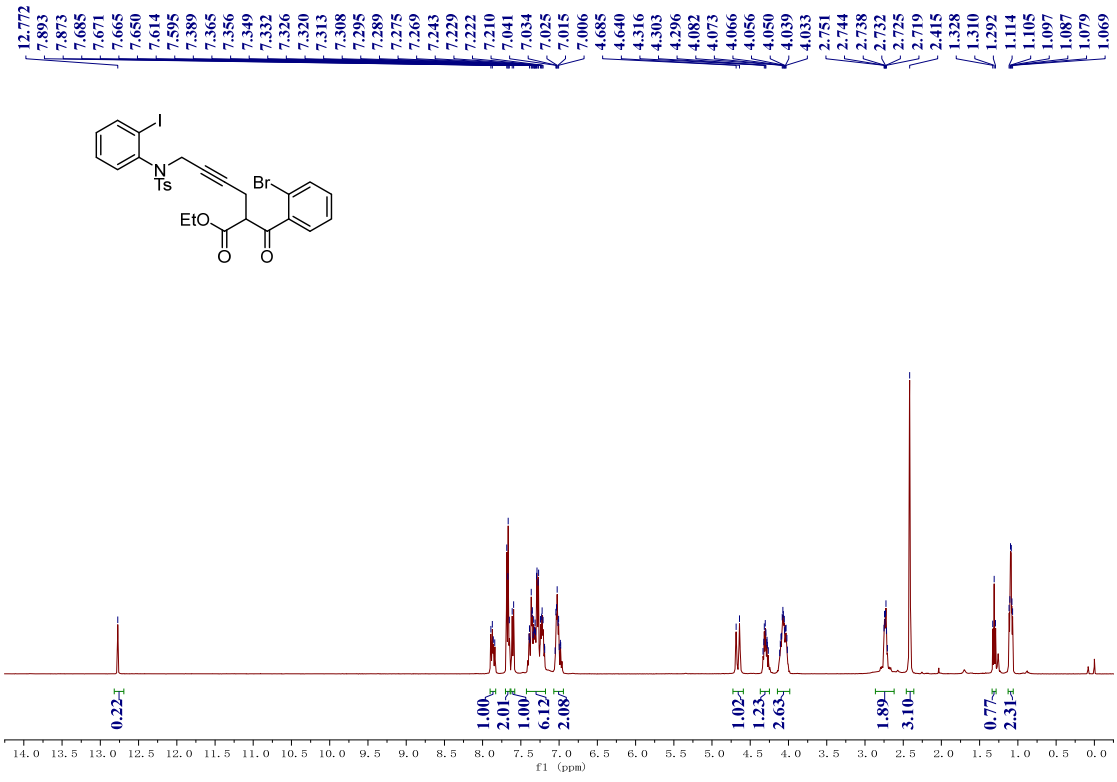

$^{1}$H NMR of **3f** (600 MHz, $CDCl_3$)



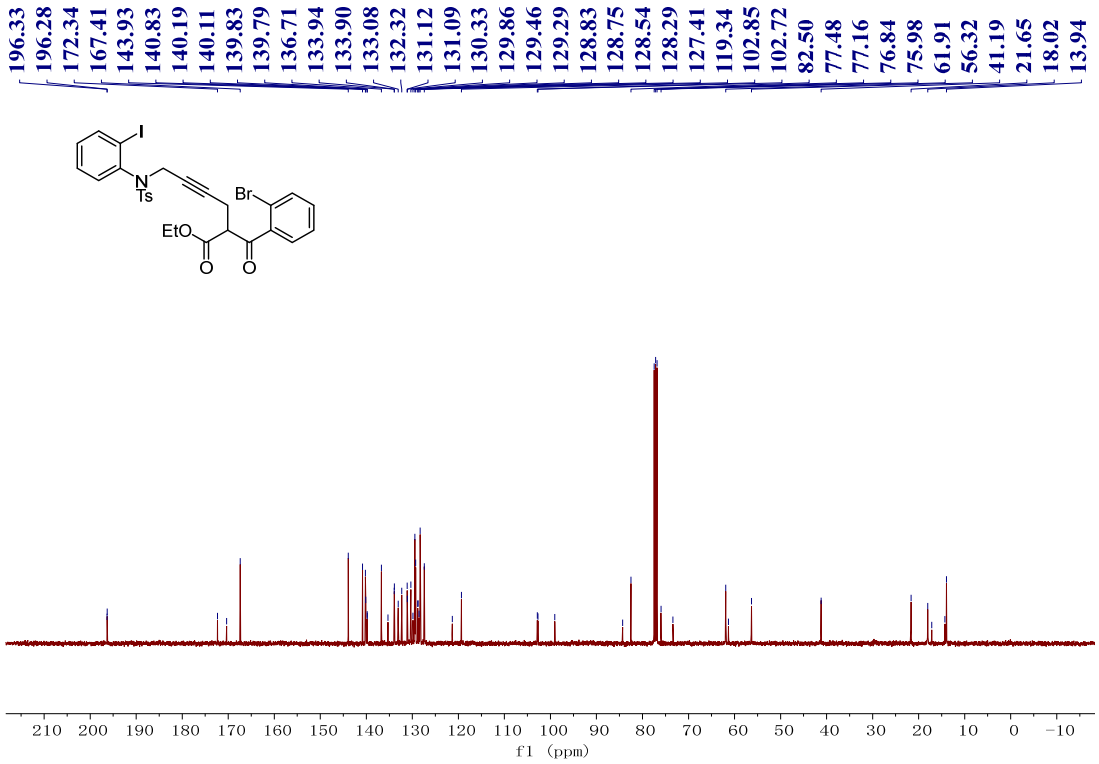
$^{13}$C NMR of **3f** (100 MHz, $CDCl_3$)



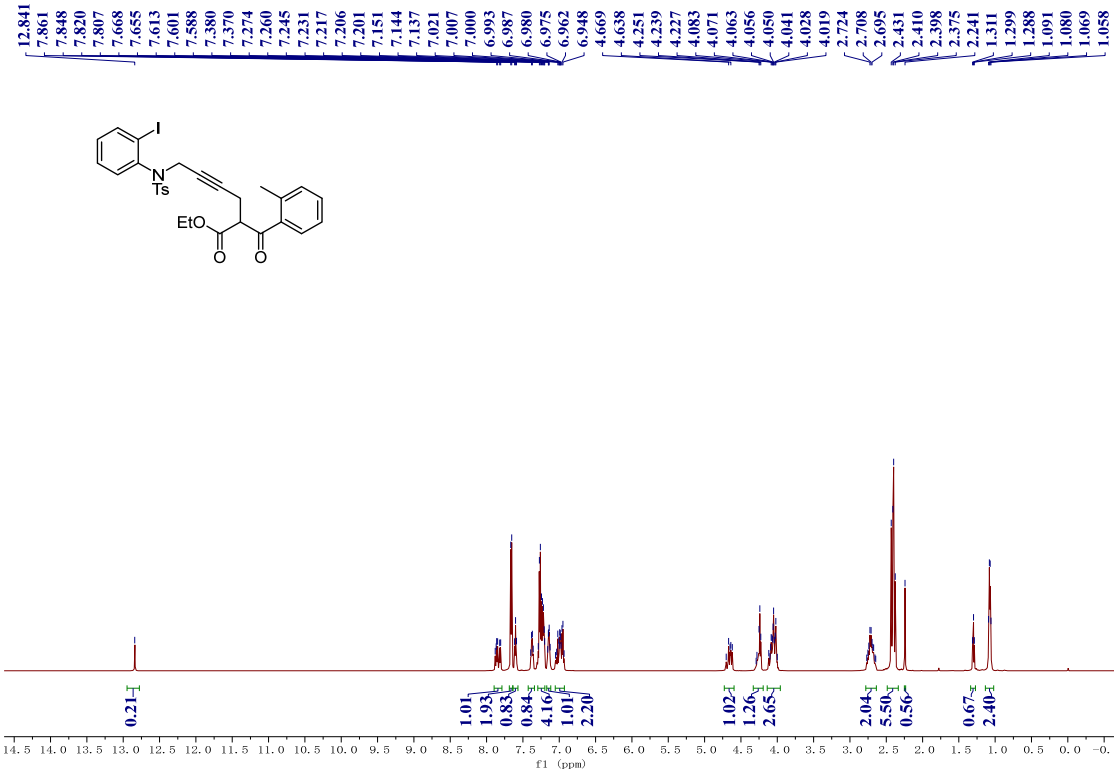

$^{1}$H NMR of **3g** (400 MHz, $CDCl_3$)



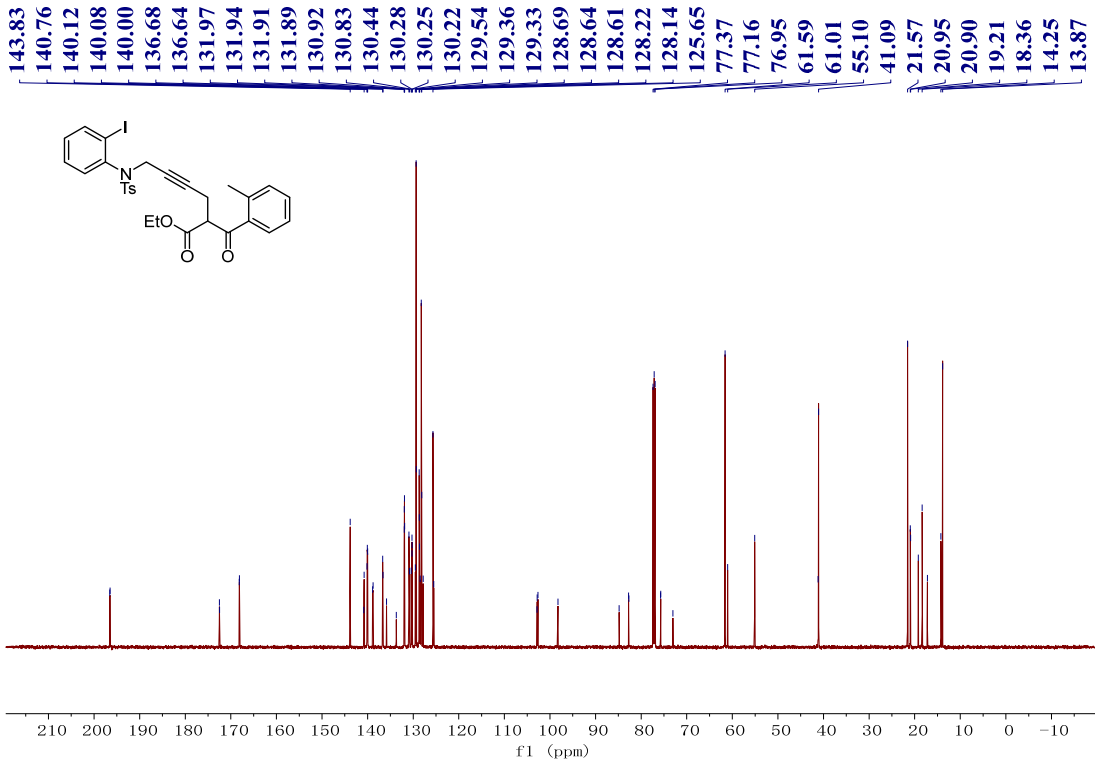
$^{13}$C NMR of **3g** (100 MHz, $CDCl_3$)



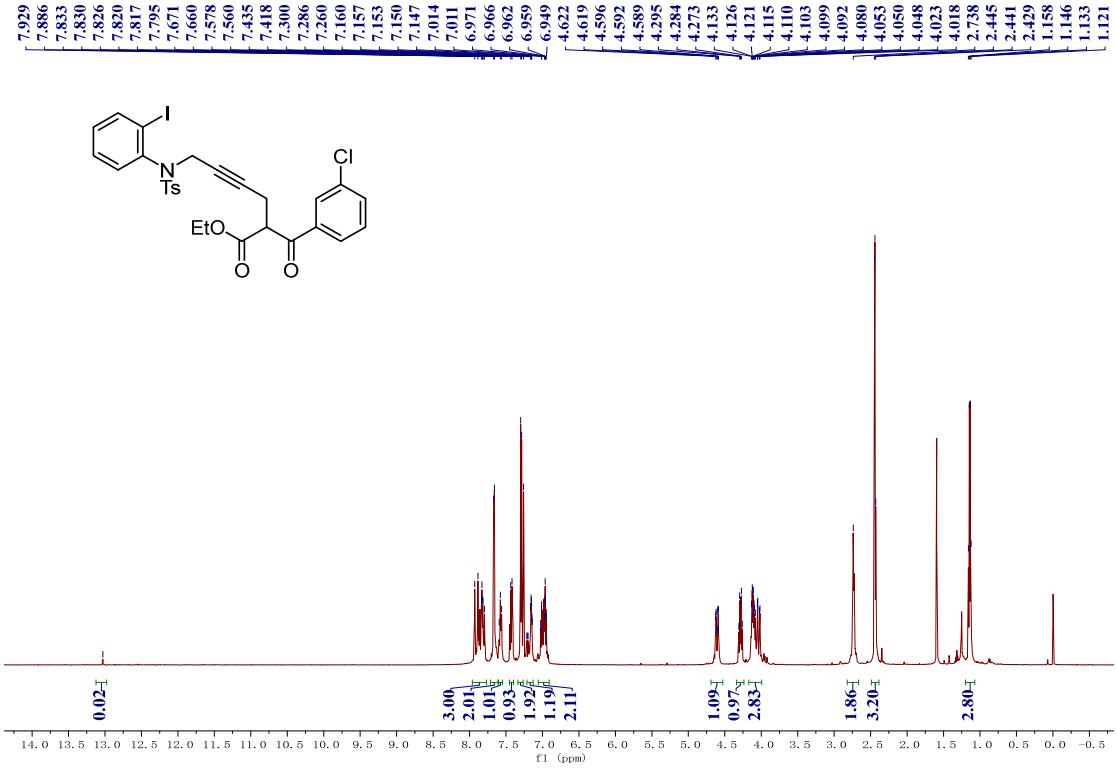

$^{1}$H NMR of **3h** (600 MHz, $CDCl_3$)



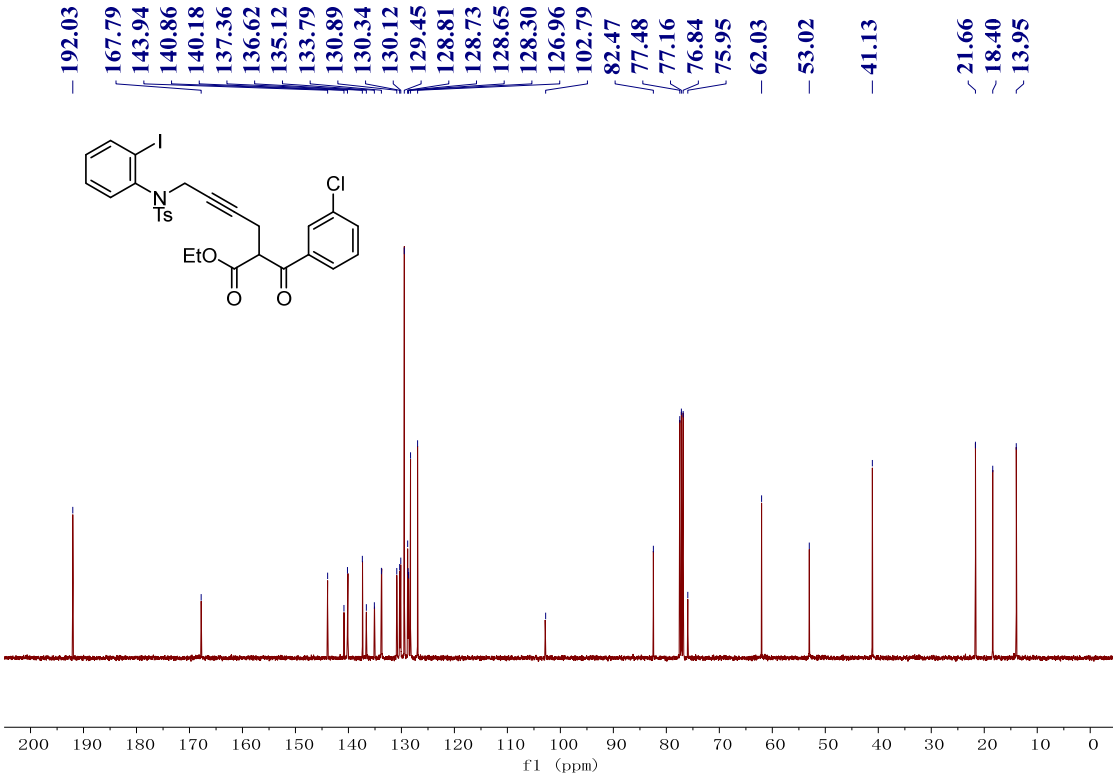
$^{13}$C NMR of **3h** (150 MHz, $CDCl_3$)



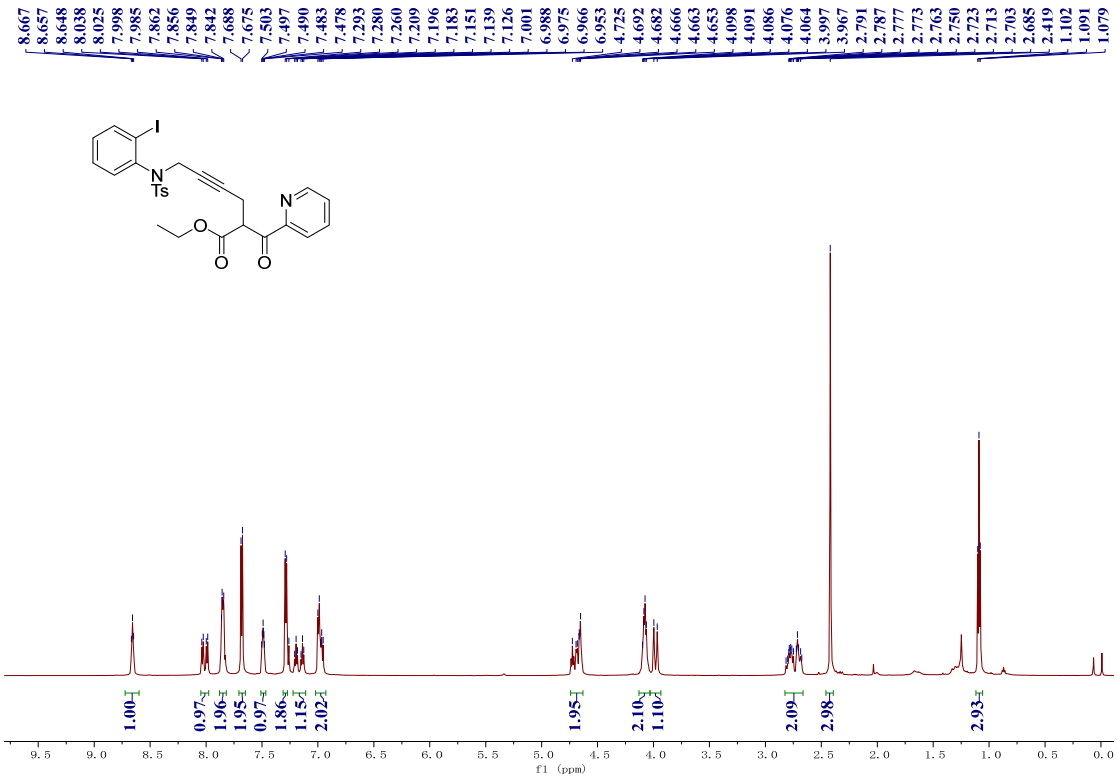

$^{1}$H NMR of **3i** (600 MHz, $CDCl_3$)



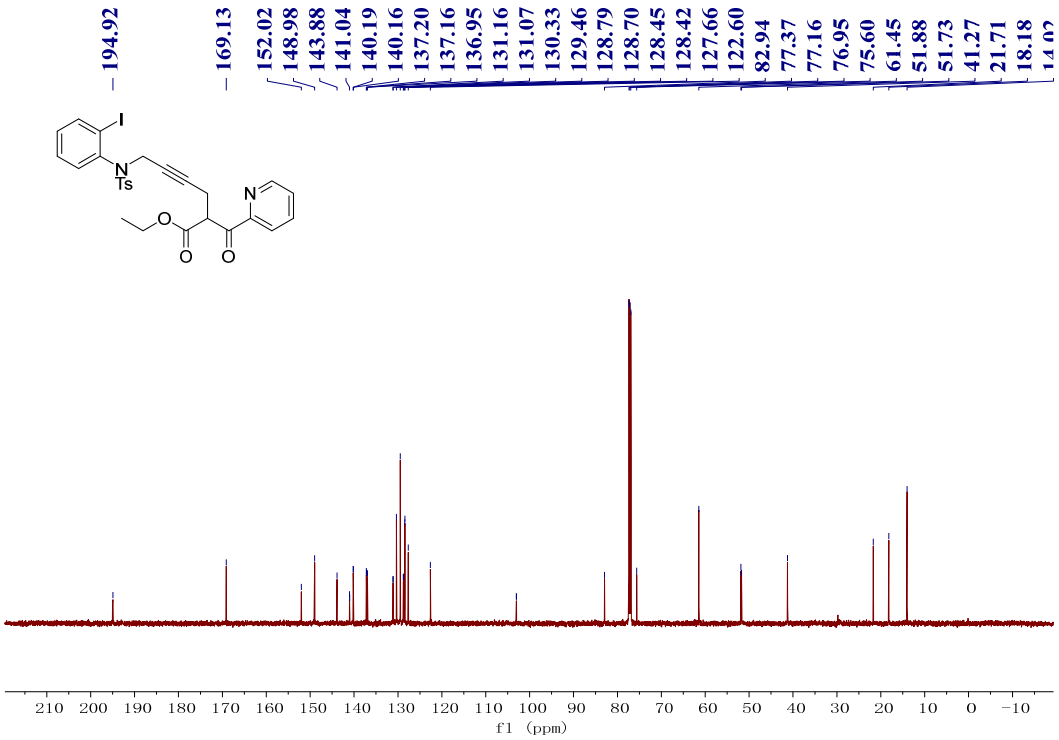
$^{13}$C NMR of **3i** (100 MHz, $CDCl_3$)




$^{1}$H NMR of **3j** (400 MHz, $CDCl_3$)



$^{13}$C NMR of **3j** (100 MHz, $CDCl_3$)

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