Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting information

Pd-catalyzed cascade coupling reaction of cyclopropanols with N-allenyl-2-iodoanilines to construct 3-substituted indole derivatives

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Content

1. General Information.

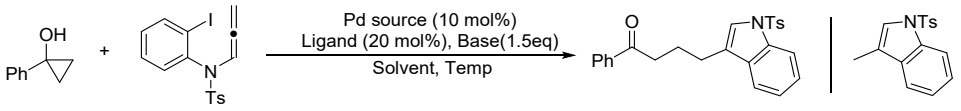
General. All manipulations were carried out in a flame-dried glassware under the nitrogen atmosphere using standard Schlenk techniques. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh).

Structural analysis. Mass spectra were recorded with Agilent 1290-6545XT Ultra-High performance liquid chromatography-quadrupole time-of-flight mass spectrometer using electron spray ionization. ^{1}H NMR spectra were recorded on a Bruker AV-400 spectrometer, a ZK-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d3. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data is being reported as (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet or unresolved, brs = broad singlet, ap= apparent, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer, a ZK-400 spectrometer and a Bruker AV-500 spectrometer in chloroform-d3. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard.

Materials. Commercial reagents, and solvent were purchased from Adamas, J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, TCI and used as received unless otherwise stated. All the starting materials are known compounds. **1a-1l, 1n**, and **2a-2m** were prepared according to literature methods.[1,2] **1m** was purchased from Leyan company.

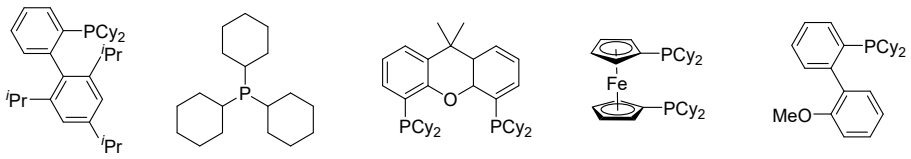
2. More Reaction Condition Study

Table S1. Screening of other parameters for the coupling reactions between 1-phenylcyclopropan-1-ol **1a** with allene **2a**[a, b].



1a 2a 3aa 4 major by-product

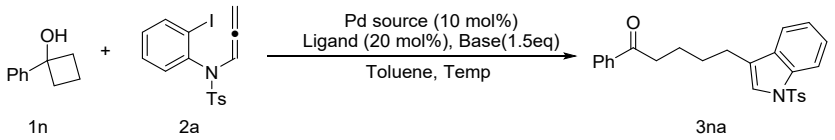
entry	Pd source	Ligand	base	solvent	T (°C)	**3aa** (%)
1	$Pd_2(dba)_3$	L9	Cs_2CO_3	THF	60	nd
2	$Pd_2(dba)_3$	L10	Cs_2CO_3	THF	60	8
3	$Pd_2(dba)_3$	L11	Cs_2CO_3	THF	60	trace
4	$Pd_2(dba)_3$	L12	Cs_2CO_3	THF	60	7
5	$Pd_2(dba)_3$	L6	DABCO	THF	60	nd
6	$Pd_2(dba)_3$	L6	K_2CO_3	THF	60	15
7	$Pd_2(dba)_3$	L6	Na_2CO_3	THF	60	trace
8	$Pd_2(dba)_3$	L6	NaOPiv	THF	60	nd
9	$Pd_2(dba)_3$	L6	Cs_2CO_3	CH_2Cl_2	RT	50
10	$Pd_2(dba)_3$	L6	Cs_2CO_3	Et_2O	RT	28
11	$Pd(acac)_2$	L6	Cs_2CO_3	toluene	RT	47
12	PdI_2	L6	Cs_2CO_3	toluene	RT	17
13	$[Pd(allkyl)Cl]_2$	L6	Cs_2CO_3	toluene	RT	33



L6 (XPhos) L9 L10 L11 L12

[a]Reaction conditions: **1a** (0.15 mmol), **2a** (0.1 mmol), [Pd] (10 mol%), monophosphine ligand (20 mol%), Bisphosphine ligand (10 mol%), base (1.5 eq), solvent (1 mL), 12-48h, N_2 atmosphere. [b]Yields were determined by ^1H NMR spectroscopy using 1,3,5-trimethoxy-benzene as internal standard.

Table S2. Screening of other parameters for the coupling reactions between 1-phenylcyclobutanol -1-ol **1n** with allene **2a**[a, b].



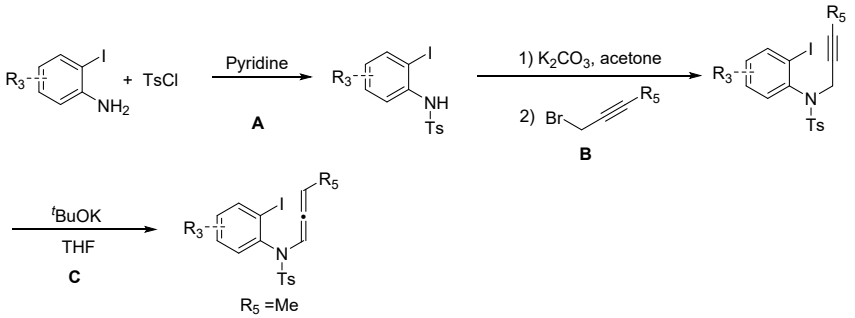
1n 2a 3na

entry	Pd source	Ligand	base	Conv. of **2a**(%)	**3na** (%)
1	$Pd(OAc)_2$	XPhos	Cs_2CO_3	68	nd
2	$Pd(OAc)_2$	SPhos	Cs_2CO_3	100	nd
3	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	100	nd
4	$Pd(OAc)_2$	P(*o*-$MeOC_6H_4$)$_3$	Cs_2CO_3	100	nd
5	$Pd(OAc)_2$	P(*p*-CF_3 C_6H_4)$_3$	Cs_2CO_3	100	nd
6	$Pd(OAc)_2$	Binap	Cs_2CO_3	70	nd
7	$Pd(OAc)_2$	dppe	Cs_2CO_3	67	nd
8	$Pd_2(dba)_3$	XPhos	Cs_2CO_3	100	nd
9	$Pd(OAc)_2$	XPhos	K_3PO_4•$3H_2O$	100	nd
10	$Pd(OAc)_2$	XPhos	NaO^{t}Bu	90	nd
11	$Pd(OAc)_2$	XPhos	Pyridine	100	nd

[a]Reaction conditions: 1n (0.3 mmol), 2a (0.1 mmol), [Pd] (10 mol%), monophosphine ligand (20 mol%), Bisphosphine ligand (10 mol%), base (1.5 eq), solvent (1 mL), 50 - 100 °C，5 - 20 h, N_2 atmosphere. [b]Yields were determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxy-benzene as internal standard.

3. General Experimental procedure

General procedure for the preparation of 2a, 2e-2j, 2m following the reported procedures.[1b,1d]



General procedure A for tosylation using 2a as example:

To a solution of *o*-iodoaniline (2.19 g, 10.0 mmol, 1.0 eq) in pyridine (10 mL) was added *p*-TsCl (2.00 g, 10.5 mmol, 1.05 equiv) at 0°C. The reaction was stirred at rt over night before being quenched with H_2O. The quenched mixture was extracted three times with DCM. The combined organic layers were

first washed with 1 M HCl to remove excess pyridine, and then with sat aq $NaHCO_3$, H_2O, sat aq NaCl, and dried over anhyd $MgSO_4$. The filtrate was concentrated under reduced pressure to give the crude sulfonamide that was used in the next step without further purification.

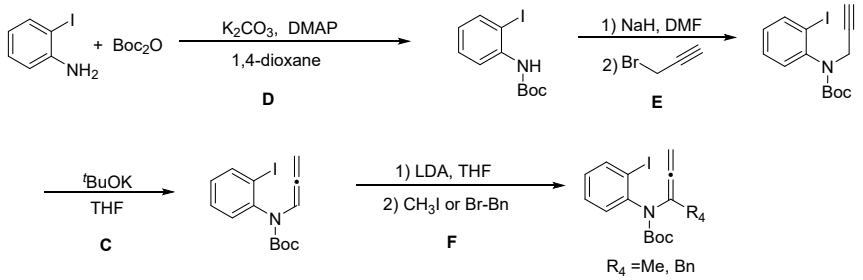
General procedure B for propargylation:

To a solution of the above crude sulfonamide (3.23 g, 8.60 mmol 1.0 eq) in acetone (10 mL) were added K_2CO_3 (5.94 g, 43.0 mmol, 5.0 equiv) and propargyl bromide (1.85 mL, 21.5 mmol, 2.5 equiv). The reaction was heated to reflux for 2-4 h and the reaction progress was monitored using TLC analysis. After the reaction was complete, the mixture was filtered through Celite TM. The filtrate was concentrated under reduced pressure and purified using silica gel flash column chromatography to give the desired propargyl amide.

General procedure C for allenation reaction:

To a solution of the above propargyl amide (2.84 g, 6.91 mmol 1.0 eq) in THF (40 mL) was added ^{t}BuOK (1.0 M solution in THF, 2.07 mL, 2.07 mmol, 0.30 equiv) at 0°C and stirred at rt until the reaction was complete. The mixture was being concentrated under reduced pressure. Subsequently, the residue was suspended in DCM and then filtered through Celite TM. The filtrate was concentrated under reduced pressure and the crude residue was purified using silica gel flash column chromatography to give the desired allenamide **2a**.

General procedure for the preparation of 2c, 2k-2l following the reported procedures.[1a, 1e]



General procedure D:

To a solution of *o*-iodoaniline (2.19 g, 10.0 mmol 1.0 eq) in 1,4-dioxane (40 mL) was added Boc_2O (2.40 g, 11.0 mmol, 1.10 equiv), K_2CO_3 (2.76 g, 20 mmol, 2.0 eq) and DMAP (0.12 g, 1 mmol, 0.1 eq) at 0°C. Then, warmed up to room temperature and stirred overnight. The reaction was quenched with H_2O, aqueous phase was extracted with CH_2Cl_2 (repeated three additional times). The combined organic layers were washed with equal volume of sat aq NaCl and dried over anhyd $MgSO_4$. The filtrate was concentrated under reduced pressure to give the crude Boc-protected aniline that was used in the next step without further purification.

General procedure E:

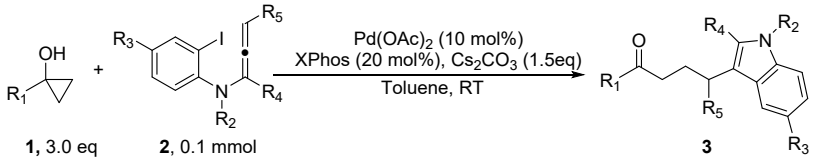
To a solution of above crude N-Boc aniline (2.59 g, 8.12 mmol, 1.0 eq) in anhydrous DMF (50 mL) was added in one portion of sodium hydride (60 % dispersion in oil, 0.49 g, 12.2 mmol, 1.5 eq) at 0 °C and stirred for 10 minutes. Propargyl bromide (0.84 mL, 9.75 mmol, 1.20 equiv) was added

subsequently. After the reaction was complete, the reaction was quenched with sat aq NH_4Cl. The quenched mixture was poured into H_2O and extracted three times with Et_2O. The combined organic layers were washed with equal volume of sat aq NaCl and dried over anhyd $MgSO_4$. After filtration and concentration under reduced pressure, the crude product was purified using silica gel flash column chromatography to give the desired propargyl amide.

General procedure F using 2k as an example:

To a nitrogen protected solution of N-Boc allenamide (0.38 g, 1.0 mmol, 1.0 eq) in anhydrous THF (5mL) was added LDA (2M in THF, 0.6 mL, 1.2 mmol, 1.2 eq) at -78 °C, and stirred for 1 h. To this solution was added dropwise MeI (0.31 mL, 5.0 mmol 5.0 eq). After being stirred at −78 °C for 3.5 h, the reaction was quenched with H_2O and extracted with EtOAc. The organic layer was washed with H_2O and brine, dried over anhyd $MgSO_4$, filtered, and concentrated under reduced pressure. Purification of the residue by flash chromatography gave allenamide **2k** as a colourless oil

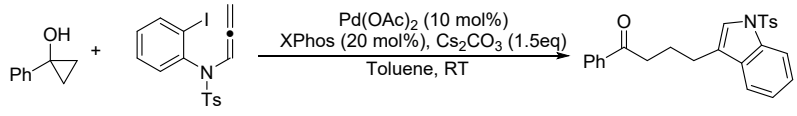
General procedure for the preparation of the products 3



1, 3.0 eq **2**, 0.1 mmol **3**

An oven-dried Schlenk tube under nitrogen atmosphere was charged with cyclopropanols **1** (0.3 mmol, 3.0 equiv), N-allenyl-2-iodoaniline **2** (0.1 mmol, 1.0 equiv), $Pd(OAc)_2$ (2.2mg, 0.01 mmol, 10 mol%), XPhos (9.6 mg, 0.02 mmol, 20 mol%), Cs_2CO_3 (38.9 mg, 0.15 mmol, 1.5 equiv.), toluene (1.0 mL, 0.1 M). The reaction mixture was stirred at room temperature. When the reaction was completed (12-48 h, monitored periodically by TLC), the solvent was removed by vacuum and the crude residue was purified by silica gel column chromatography to afford the corresponding products **3**.

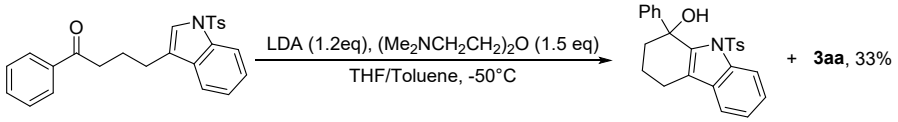
General procedure for the Scale-up experiment



1a, 3.0 eq **2a**, 5 mmol **3aa**, 1.44 g (69%)

An 100 ml oven-dried Schlenk tube under nitrogen atmosphere was charged with 1-phenylcyclopropan-1-ol **1a** (2.01 g, 15.0 mmol, 3.0 equiv), N-(o-iodophenyl)allenamide **2a** (2.06 g, 0.1 mmol, 1.0 equiv), $Pd(OAc)_2$ (112.3 mg, 0.5 mmol, 10 mol%), Xphos (476.7 mg, 1.0 mmol, 20% mol) Cs_2CO_3 (2.44g, 7.5 mmol, 1.5 equiv.), toluene (50 mL, 0.1 M). The reaction mixture was stirred at room temperature. When the reaction was completed (30 h, monitored periodically by TLC), the solvent was removed by vacuum and the crude residue was purified by silica gel column chromatography to afford the corresponding products **3aa**.

General procedure for the Synthetic Applications.

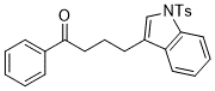


3aa, 0.2 mmol **5**, 51%

An oven-dried Schlenk tube under nitrogen atmosphere was charged with **3aa** (0.2 mmol, 1.0 equiv), bis(N,N′ -dimethylaminoethyl) ether (0.1 mmol, 1.0 equiv), toluene (0.8 mL) and THF (0.2 mL). The solution was cooled to -50 ℃. LDA (1.2 equiv, 2.0 M in THF, Energy) was added. The reaction mixture was stirred at -50 ℃ for 30h. Then, the reaction was quenched with 1 ml H_2O at 0 ℃ and the mixture was extracted with EtOAc. The organic layer was washed with saturated NaCl, dried over Na_2SO_4, and concentrated. The crude residue was purified by silica gel column chromatography to afford the corresponding products **5**.

4. NMR Data of the products

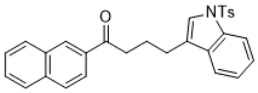
1-phenyl-4-(1-tosyl-1*H*-indol-3-yl)butan-1-one (3aa)



Compound **3aa** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (73%, 30.4 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.2 Hz, 1H), 7.92 - 7.86 (m, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.58 - 7.47 (m, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.35 (s, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.24 - 7.18 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.99 (t, *J* = 7.1 Hz, 2H), 2.76 (t, *J* = 7.5 Hz, 2H), 2.27 (s, 3H), 2.13 (tt, ap p, $J_1 = J_2$ = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.9, 144.8, 137.0, 135.5, 135.3, 133.1, 131.0, 129.8, 128.7, 128.1, 126.8, 124.8, 123.1, 123.0, 122.7, 119.6, 113.9, 37.8, 24.4, 23.4, 21.6. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{25}H_{23}NO_3SNa$: 440.1291, found: 440.1296.

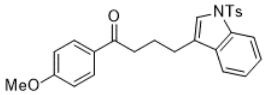
1-(naphthalen-2-yl)-4-(1-tosyl-1*H*-indol-3-yl)butan-1-one (3ba)



compound **3ba** Purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a white solid (74%, 34.5 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 8.04 - 7.94 (m, 2H), 7.90 - 7.81 (m, 3H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.63 - 7.53 (m, 3H), 7.38 (s, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.82 (t, *J* = 7.4 Hz, 2H), 2.25 - 2.15 (m, 5H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.8, 144.7, 135.6, 135.5, 135.2, 134.2, 132.5, 131.0, 129.74, 129.65, 129.6, 128.4, 127.7, 126.74, 126.68, 124.7, 123.8, 123.1, 123.0, 122.6, 119.6, 113.9, 37.8, 24.4, 23.5, 21.4. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{29}H_{25}NO_3SNa$: 490.1447, found: 490.1445.

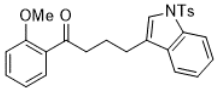
1-(4-methoxyphenyl)-4-(1-tosyl-1*H*-indol-3-yl)butan-1-one (3ca)



Compound **3ca** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (64%, 28.6 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 7.8 Hz, 1H), 7.27 (s, 1H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 3.79 (s, 3H), 2.87 (t, *J* = 7.2 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.22 (s, 3H), 2.04 (tt, ap p, $J_1 = J_2$ = 7.3 Hz, 2H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.5, 163.5, 144.7, 135.5, 135.4, 131.0, 130.3, 130.1, 129.8, 126.8, 124.7, 123.1, 122.9, 122.8, 119.6, 113.84, 113.77, 55.5, 37.4, 24.5, 23.6, 21.6. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{26}H_{25}NO_4SNa$: 470.1397, found: 470.1399.

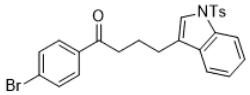
1-(2-methoxyphenyl)-4-(1-tosyl-1*H*-indol-3-yl)butan-1-one (3da)



Compound **3da** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (57%, 25.4 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 - 7.77 (m, 3H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.23 (s, 1H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.87 - 6.81 (m, 2H), 3.73 (s, 3H), 2.92 (t, *J* = 7.1 Hz, 2H), 2.65 (t, *J* = 7.4 Hz, 2H), 2.21 (s, 3H), 2.05 (tt, ap p, $J_1 = J_2$ = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.9, 156.4, 144.7, 137.0, 135.2, 133.1, 132.1, 130.2, 129.8, 128.7, 128.0, 126.7, 123.8, 122.8, 114.8, 113.6, 102.1, 55.7, 37.7, 24.4, 23.2, 21.6. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{26}H_{25}NO_4SNa$: 470.1397, found: 470.1401.

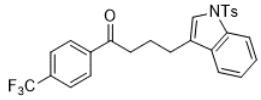
1-(4-bromophenyl)-4-(1-tosyl-1*H*-indol-3-yl)butan-1-one (3ea)



Compound **3ea** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (80%, 39.6 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.3 Hz, 1H), 7.74 - 7.61 (m, 4H), 7.54 - 7.46 (m, 2H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.27 (s, 1H), 7.26 - 7.21 (m, 1H), 7.17 - 7.13 (m, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 2.88 (t, *J* = 7.1 Hz, 2H), 2.69 (t, *J* = 7.2 Hz, 2H), 2.23 (s, 3H), 2.05 (tt, ap p, $J_1 = J_2$ = 7.3 Hz, 2H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.8, 144.8, 135.6, 135.5, 135.4, 132.0, 130.9, 129.8, 129.6, 128.3, 126.8, 124.8, 123.1, 123.0, 122.5, 119.6, 113.9, 37.7, 24.3, 23.3, 21.6. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{25}H_{22}NO_3SBrNa$: 518.0396, found: 518.0392.

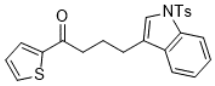
4-(1-tosyl-1*H*-indol-3-yl)-1-(4-(trifluoromethyl)phenyl)butan-1-one (3fa)



Compound **3fa** purified by column chromatography (Eluent: 15% EtOAc in petroleum ether). Isolated as a colorless oil liquid (54%, 26.2 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 - 7.95 (m, 3H), 7.76 - 7.67 (m, 4H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.35 (s, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 3.02 (t, *J* = 7.1 Hz, 2H), 2.78 (t, *J* = 7.4 Hz, 2H), 2.30 (s, 3H), 2.15 (tt, ap p, $J_1 = J_2$ = 7.2 Hz, 2H).^{13}C NMR (125 MHz, Chloroform-*d*) δ 198.8, 144.8, 139.5, 135.4, 135.3, 134.4 (q, *J* = 26.0 Hz), 130.9, 129.8, 128.3, 126.7, 125.7 (q, *J* = 3.0 Hz)124.8, 123.6 (q, *J* = 217.0 Hz), 123.1, 123.0, 122.3, 119.5, 113.8, 38.0, 24.3, 23.1, 21.5. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{26}H_{22}F_3NO_3SNa$: 508.1165, found: 508.1166. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.11.

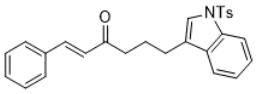
1-(thiophen-2-yl)-4-(1-tosyl-1*H*-indol-3-yl)butan-1-one (3ga)



Compound **3ga** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (62%, 26.2 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.3 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.57 - 7.51 (m, 2H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.27 (s, 1H), 7.26 - 7.19 (m, 1H), 7.17 - 7.11 (m, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 7.04 - 7.00 (m, 1H), 2.85 (t, *J* = 7.2 Hz, 2H), 2.68 (t, *J* = 7.5 Hz, 2H), 2.22 (s, 3H), 2.05 (tt, ap p, $J_1 = J_2$ = 7.3 Hz, 2H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.8, 144.8, 144.3, 135.5, 135.4, 133.6, 131.8, 131,0, 129.9, 128.2, 126.8, 124.8, 123.1, 123.0, 122.6, 119.6, 113.9, 38.5, 24.4, 23.7, 21.6. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{23}H_{21}NO_3S_2Na$: 446.0855, found: 446.0859.

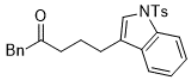
(*E*)-1-phenyl-6-(1-tosyl-1*H*-indol-3-yl)hex-1-en-3-one (3ha)



Compound **3ha** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (72%, 31.9 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.53 - 7.44 (m, 4H), 7.41 - 7.36 (m, 3H), 7.35 (s, 1H), 7.33 - 7.29 (m, 1H), 7.25 - 7.20 (m, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.69 (d, *J* = 16.2 Hz, 1H), 2.78 - 2.66 (m, 4H), 2.28 (s, 3H), 2.07 (tt, ap p, $J_1 = J_2$ = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.9, 144.8, 142.7, 135.5, 135.3, 134.5, 131.0, 130.6, 129.8, 129.0, 128.3, 126.8, 126.2, 124.7, 123.1, 123.0, 122.6, 119.6, 113.9, 40.0, 24.4, 23.4, 21.5. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{27}H_{25}NO_3SNa$: 466.1447, found: 466.1452.

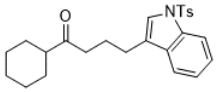
1-phenyl-5-(1-tosyl-1*H*-indol-3-yl)pentan-2-one (3ia)



Compound **3ia** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (73%, 31.4 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.28 - 7.16 (m, 5H), 7.15 - 7.08 (m, 5H), 3.58 (s, 2H), 2.52 (t, *J* = 7.5 Hz, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 1.85 (tt, ap p, $J_1 = J_2$ = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 208.0, 144.8, 135.4, 134.2, 130.9, 129.8, 129.4, 128.8, 127.1, 126.8, 124.7, 123.1, 122.8, 122.5, 119.6, 113.8, 50.3, 41.1, 24.2, 22.9, 21.6. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{26}H_{25}NO_3SNa$: 454.1447, found: 454.1441.

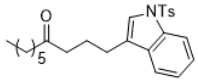
1-cyclohexyl-4-(1-tosyl-1*H*-indol-3-yl)butan-1-one (3ja)



Compound **3ja** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (60%, 25.4 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.33 - 7.27 (m, 2H), 7.24 - 7.16 (m, 3H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.47 (t, *J* = 7.1 Hz, 2H), 2.37 - 2.44 (m, 4H), 1.94 (tt, ap p, $J_1 = J_2$ = 7.3 Hz, 2H), 1.85 - 1.72 (m, 4H), 1.39 - 1.12 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 213.8, 144.8, 135.4, 131.0, 129.8, 126.8, 124.7, 123.1, 122.8, 122.7, 119.6, 113.8, 50.9, 39.8, 28.6, 25.9, 25.7, 24.4, 22.8, 21.6. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{25}H_{29}NO_3SNa$: 446.1760, found: 446.1763.

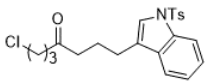
1-(1-tosyl-1*H*-indol-3-yl)decan-4-one (3ka)



Compound **3ka** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (85%, 36.1 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.2 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.34 - 7.27 (m, 2H), 7.24 - 7.16 (m, 3H), 2.66 (t, *J* = 7.4 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.38 - 2.30 (m, 5H), 1.95 (tt, ap p, $J_1 = J_2$ = 7.3 Hz, 2H), 1.62 - 1.50 (m, 2H), 1.35 - 1.38 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 210.9, 144.8, 135.44, 135.40, 131.0, 129.8, 126.8, 124.7, 123.1, 122.8, 122.7, 119.6, 113.8, 43.0, 41.9, 31.6, 29.0, 24.3, 23.9, 23.0, 22.5, 21.6, 14.1. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{25}H_{31}NO_3SNa$: 448.1917, found: 448.1916.

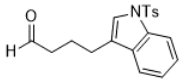
1-chloro-7-(1-tosyl-1*H*-indol-3-yl)heptan-4-one (3la)



Compound **3la** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (68%, 28.3 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.26 - 7.20 (m, 2H), 7.19 - 7.10 (m, 3H), 3.50 (t, *J* = 6.3 Hz, 2H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.50 (t, *J* = 7.0 Hz, 2H), 2.39 (t, *J* = 7.2 Hz, 2H), 2.26 (s, 3H), 2.00 - 1.85 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 209.3, 144.8, 135.44, 135.38, 130.9, 129.9, 126.8, 124.8, 123.1, 122.9, 122.5, 119.5, 113.8, 44.5, 42.1, 39.4, 26.3, 24.3, 22.9, 21.6. HRMS (ESI) m/z: [M + Na]$^+$ Calculated for $C_{22}H_{24}NO_3SClNa$: 440.1058, found: 440.1061.

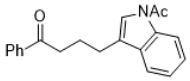
4-(1-tosyl-1*H*-indol-3-yl)butanal (3ma)



Compound **3ma** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (13%, 4.4 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.70 (s, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.26 - 7.21 (m, 2H), 7.19 – 7.16 (m, 1H), 7.15 - 7.11 (m, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.42 (t, *J* = 7.2 Hz, 2H), 2.26 (s, 3H), 1.97 - 1.91 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 201.9, 144.8, 135.5, 135.4, 130.8, 129.9, 126.8, 124.8, 123.1, 123.0, 122.2, 119.5, 113.9, 43.3, 24.2, 21.6, 21.4. HRMS (ESI) m/z: [M + Na]$^+$ Calculated for $C_{19}H_{19}NO_3SNa$: 364.0978, found: 364.0975.

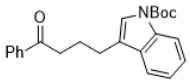
4-(1-acetyl-1*H*-indol-3-yl)-1-phenylbutan-1-one (3ab)



Compound **3ab** purified by column chromatography (Eluent: 15% EtOAc in petroleum ether). Isolated as a colorless oil liquid (71%, 21.6 mg)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.35 (s, 1H), 7.92 - 7.82 (m, 2H), 7.52 - 7.45 (m, 2H), 7.41 - 7.35 (m, 2H), 7.31 - 7.26 (m, 1H), 7.23 - 7.19 (m, 1H), 7.13 (s, 1H), 3.00 (t, *J* = 7.1 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.51 (s, 3H), 2.13 (tt, ap p, $J_1 = J_2$ = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.0, 168.4, 137.0, 136.1, 133.1, 130.7, 128.7, 128.1, 125.3, 123.5, 122.5, 122.1, 119.0, 116.7, 37.9, 24.4, 24.1, 23.6. HRMS (ESI) m/z: [M + Na]$^+$ Calculated for $C_{20}H_{19}NO_2Na$: 328.1308, found: 328.1315.

tert-butyl 3-(4-oxo-4-phenylbutyl)-1*H*-indole-1-carboxylate (3ac)[3]

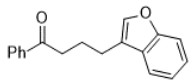


Compound **3ac** purified by column chromatography (Eluent: 5% EtOAc in petroleum ether). Isolated as a colorless oil liquid (78%, 28.3 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (d, *J* = 6.3 Hz, 1H), 7.86 (d, *J* = 7.3 Hz, 2H), 7.48 (t, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.31 (s, 1H), 7.26 - 7.21 (m, 1H), 7.18 - 7.13 (m, 1H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.11 (tt, ap p, $J_1 = J_2$ = 7.3 Hz, 2H), 1.59 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.1, 149.9, 137.1, 133.0, 130.7, 128.6, 128.1, 124.4, 122.6, 122.4, 120.5, 119.1,

115.3, 83.4, 38.0, 28.3, 24.4, 23.7. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{23}H_{25}NO_3Na$: 386.1727, found: 386.1729.

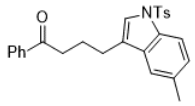
4-(benzofuran-3-yl)-1-phenylbutan-1-one (3ad)



Compound **3ad** purified by column chromatography (Eluent: 5% EtOAc in petroleum ether). Isolated as a colorless oil liquid (80%, 21.1 mg)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.49 - 7.39 (m, 4H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.25 - 7.21 (m, 1H), 3.05 (t, *J* = 7.1 Hz, 2H), 2.79 (t, *J* = 7.4 Hz, 2H), 2.18 (tt, ap p, $J_1 = J_2$ = 7.3 Hz, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 199.9, 155.5, 141.3, 137.0, 133.0, 128.6, 128.1, 128.0, 124.2, 122.3, 119.8, 119.7, 111.5, 37.8, 23.4, 23.0. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{18}H_{16}O_2Na$: 287.1043, found: 287.1046.

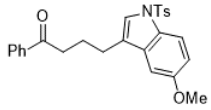
4-(5-methyl-1-tosyl-1*H*-indol-3-yl)-1-phenylbutan-1-one (3ae)



Compound **3ae** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (69%, 29.7 mg)

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.86 - 7.80 (m, 2H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.51 - 7.45 (m, 1H), 7.39 - 7.34 (m, 2H), 7.22 (s, 1H), 7.18 (s, 1H) 7.09 - 7.01 (m, 3H), 2.91 (t, *J* = 7.2 Hz, 2H), 2.66 (t, *J* = 7.4 Hz, 2H), 2.31 (s, 3H), 2.20 (s, 3H), 2.04 (tt, ap p, $J_1 = J_2$ = 7.3 Hz, 2H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 199.9, 144.6, 136.9, 135.3, 133.7, 133.1, 132.7, 131.2, 129.7, 128.6, 128.0, 126.7, 126.1, 123.1, 122.5, 119.5, 113.5, 37.7, 24.3, 23.3, 21.5, 21.4. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{26}H_{25}NO_3SNa$: 454.1447, found: 454.1442.

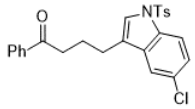
4-(5-methoxy-1-tosyl-1*H*-indol-3-yl)-1-phenylbutan-1-one (3af)



Compound **3af** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (60%, 26.8 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 - 7.77 (m, 3H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.23 (s, 1H), 7.07 (d, *J* = 8.1 Hz, 2H), 6.87 - 6.80 (m, 2H), 3.73 (s, 3H), 2.92 (t, *J* = 7.1 Hz, 2H), 2.65 (t, *J* = 7.4 Hz, 2H), 2.21 (s, 3H), 2.05 (tt, ap p, $J_1 = J_2$ = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.9, 156.4, 144.7, 137.0, 135.2, 133.1, 132.1, 130.2, 129.8, 128.7, 128.0, 126.7, 123.8, 122.8, 114.8, 113.6, 102.1, 55.7, 37.7, 24.4, 23.2, 21.6. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{26}H_{25}NO_4SNa$: 470.1397, found: 470.1395.

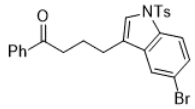
4-(5-chloro-1-tosyl-1*H*-indol-3-yl)-1-phenylbutan-1-one (3ag)



Compound **3ag** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (70%, 31.6 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 7.2 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 1.7 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.32 (m, 1H), 7.27 (s, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 2.93 (t, *J* = 7.1 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.23 (s, 3H), 2.04 (tt, ap p, $J_1 = J_2$ = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.7, 145.1, 136.9, 135.0, 134.2, 133.2, 132.8, 130.0, 128.7, 128.0, 127.6, 126.8, 124.2, 122.5, 122.1, 116.7, 115.3, 37.7, 24.2, 23.3, 21.6. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{25}H_{22}NO_3SClNa$: 474.0901, found: 474.0902.

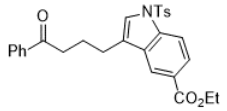
4-(5-bromo-1-tosyl-1*H*-indol-3-yl)-1-phenylbutan-1-one (3ah)



Compound **3ah** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (57%, 28.2 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 - 7.79 (m, 3H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.42 - 7.34 (m, 3H), 7.29 (s, 1H), 7.21 - 7.16 (m 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 2.93 (t, *J* = 7.1 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.23 (s, 3H), 2.04 (tt, ap p, $J_1 = J_2$ = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.7, 145.1, 136.9, 135.1, 133.8, 133.2, 132.3, 129.9, 129.1, 128.7, 128.0, 126.7, 125.0, 124.3, 122.2, 119.4, 114.9, 37.7, 24.3, 23.3, 21.6. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{25}H_{22}NO_3SBrNa$: 518.0396, found:518.0391.

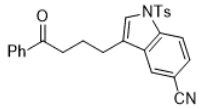
ethyl 3-(4-oxo-4-phenylbutyl)-1-tosyl-1*H*-indole-5-carboxylate (3ai)



Compound **3ai** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil (52%, 25.4 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.96 - 7.91 (m, 2H), 7.87 - 7.83 (m, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 2H), 7.34 (s, 1H), 7.11 (d, *J* = 8.2 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 2.95 (t, *J* = 7.2 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.23 (s, 3H), 2.08 (tt, ap p, $J_1 = J_2$ = 2H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.7, 166.8, 145.2, 138.0, 136.9, 135.1, 133.1, 130.8, 130.0, 128.7, 128.0, 126.8, 126.0, 125.6, 124.1, 123.2, 121.8, 113.5, 61.1, 37.8, 24.3, 23.3, 21.6, 14.5. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{28}H_{27}NO_5SNa$:512.1502, found: 512.1506.

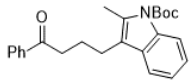
3-(4-oxo-4-phenylbutyl)-1-tosyl-1*H*-indole-5-carbonitrile (3aj)



Compound **3aj** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (60%, 26.5 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 8.6 Hz, 1H), 7.88 - 7.83 (m, 2H), 7.79 - 7.77 (m, 1H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.52 - 7.47 (m, 2H), 7.42 - 7.38 (m, 3H), 7.15 (d, *J* = 8.1 Hz, 2H), 2.97 (t, *J* = 7.0 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.27 (s, 3H), 2.06 (tt, ap p, $J_1 = J_2$ = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.5, 145.6, 137.1, 136.9, 134.9, 133.3, 131.0, 130.2, 128.7, 128.0, 127.8, 126.8, 124.9, 124.7, 122.4, 119.4, 114.6, 106.7, 37.6, 24.2, 23.3, 21.7. HRMS (ESI) m/z: [M + Na]$^+$ Calculated for $C_{26}H_{22}N_2O_3SNa$: 465.1243, found: 465.1247.

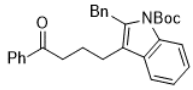
tert-butyl 2-methyl-3-(4-oxo-4-phenylbutyl)-1*H*-indole-1-carboxylate (3ak)



Compound **3ak** purified by column chromatography (Eluent: 5% EtOAc in petroleum ether). Isolated as a colorless oil liquid (67%, 25.2 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 - 7.99 (m, 1H), 7.85 - 7.79 (m, 2H), 7.49 - 7.43 (m, 1H), 7.42 - 7.39 (m, 1H), 7.38 - 7.32 (m, 2H), 7.19 - 7.09 (m, 2H), 2.92 (t, *J* = 7.0 Hz, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.45 (s, 3H), 1.99 (tt, ap p, $J_1 = J_2$ = 7.1 Hz, 2H), 1.60 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.2, 150.9, 137.1, 135.8, 133.4, 133.0, 130.1, 128.6, 128.0, 123.3, 122.4, 118.0, 117.8, 115.4, 83.5, 37.7, 28.4, 24.3, 23.2, 14.0. HRMS (ESI) m/z: [M + Na]$^+$ Calculated for $C_{24}H_{27}NO_3Na$: 400.1883, found: 400.1880.

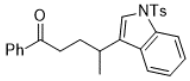
tert-butyl 2-benzyl-3-(4-oxo-4-phenylbutyl)-1*H*-indole-1-carboxylate (3al)



Compound **3al** purified by column chromatography (Eluent: 5% EtOAc in petroleum ether). Isolated as a colorless oil liquid (42%, 19.0 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 (d, *J* = 7.8 Hz, 1H), 7.74 - 7.67 (m, 2H), 7.55 - 7.48 (m, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.24 - 7.19 (m, 1H), 7.18 - 7.10 (m, 3H), 7.07 (t, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 7.3 Hz, 2H), 4.39 (s, 2H), 2.86 (t, *J* = 7.1 Hz, 2H), 2.75 (t, *J* = 7.5 Hz, 2H), 1.99 (tt, ap p, $J_1 = J_2$ = 7.2 Hz, 2H), 1.32 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.0, 150.3, 140.0, 137.0, 136.4, 133.9, 132.9, 129.7, 128.5, 128.3, 128.0, 127.7, 125.9, 123.9, 122.5, 120.0, 118.6, 115.6, 83.6, 37.9, 32.1, 27.9, 24.3, 23.6. HRMS (ESI) m/z: [M + Na]$^+$ Calculated for $C_{30}H_{31}NO_3Na$: 476.2196, found: 476.2191.

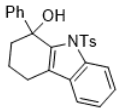
1-phenyl-4-(1-tosyl-1*H*-indol-3-yl)pentan-1-one (3am)



Compound **3am** purified by column chromatography (Eluent: 10% EtOAc in petroleum ether). Isolated as a colorless oil liquid (22%, 9.5 mg)

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 8.3 Hz, 1H), 7.76 - 7.71 (m, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.46 (t, *J* = 8.5 Hz, 2H), 7.35 - 7.29 (m, 2H), 7.27 (s, 1H), 7.25 - 7.20 (m, 1H), 7.13 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 2H), 3.06 - 2.95 (m, 1H), 2.81 (t, *J* = 7.5 Hz, 2H), 2.19 (s, 3H), 2.15 - 1.93 (m, 2H), 1.30 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.1, 144.8, 136.9, 135.7, 135.3, 133.0, 130.4, 129.8, 128.6, 128.0, 126.7, 124.7, 123.1, 122.1, 120.0, 114.0, 36.2, 30.8, 30.3, 21.5, 20.6. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{26}H_{25}NO_3SNa$: 454.1447, found: 454.1446.

1-phenyl-9-tosyl-2,3,4,9-tetrahydro-1*H*-carbazol-1-ol (5)



Compound **5** purified by column chromatography (Eluent: 15% EtOAc in petroleum ether). Isolated as a colorless oil liquid (51%, 42.5 mg)

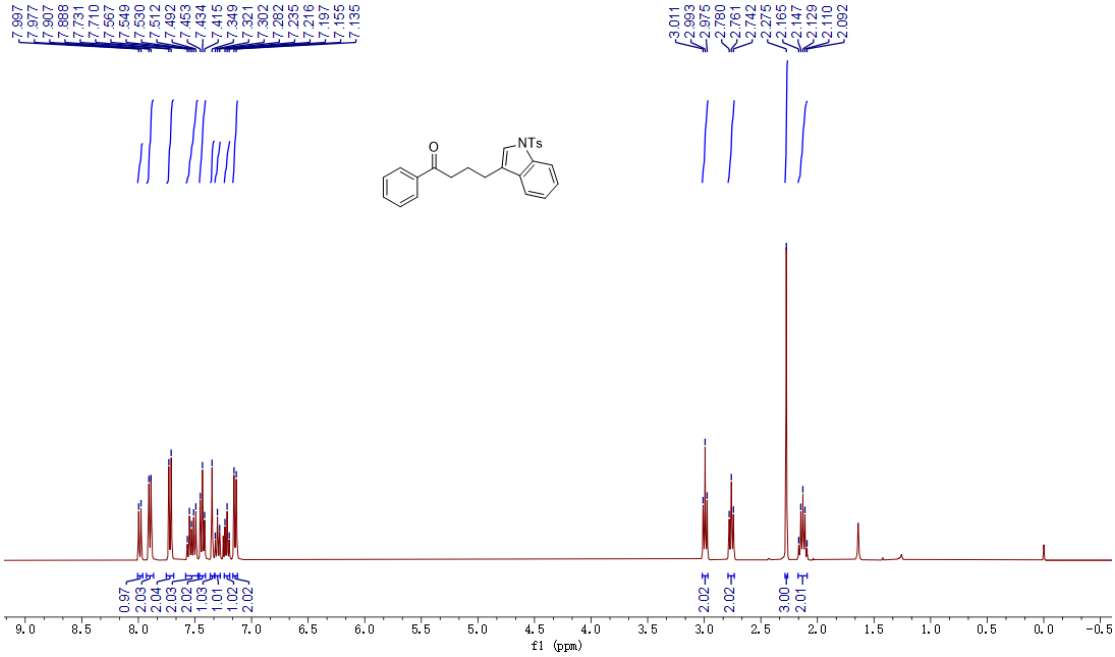
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.2 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.32 - 7.22 (m, 7H), 7.04 (d, *J* = 8.1 Hz, 2H), 5.26 (s, 1H), 2.86 - 2.71 (m, 2H), 2.41 - 2.27 (m, 4H), 2.05 - 1.93 (m, 2H), 1.84 - 1.71 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.8, 144.5, 138.5, 136.9, 135.7, 129.5, 129.4, 128.0, 126.8, 126.7, 125.5, 125.4, 123.72, 123.67, 119.3, 115.1, 73.9, 43.9, 22.2, 21.5, 19.0. HRMS (ESI) m/z: $[M + Na]^+$ Calculated for $C_{25}H_{23}NO_3SNa$: 440.1291, found: 440.1293.

5. References

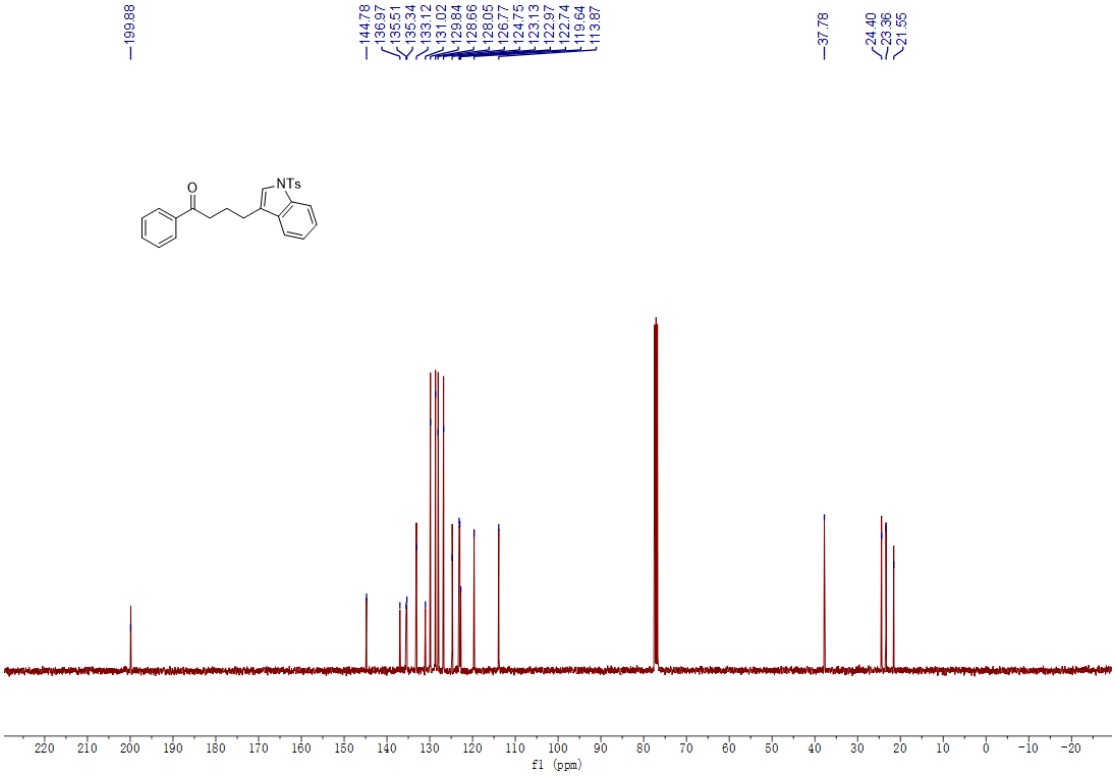
1. a) H. Fuwa, M. Sasaki, *Org. Biomol. Chem.,* 2007, **5**, 2214. b) M.-G. Braun, M. H. Katcher, A. G. Doyle, *Chem. Sci.* 2013, **4**, 1216. c) R. Grigg, J. M. Sansano, V. Santhakumar, V. Sridharan, R. Thangavelanthum, M. Thornton-Pett, D. Wilson, *Tetrahedron.* 1997, 53, 11803. d）D.-C. Wang, P.-P. Cheng, T.-T. Yang, P.-P. Wu, G.-R. Qu, H.-M. Guo, *Org. Lett*. 2021, **23**, 7865. e) J. Hédouin, C. Schneider, I. Gillaizeau, C. Hoarau, *Org. Lett*. 2018, **20**, 6027.
2. O. G. Kulinkovich, *Chem. Rev*., 2003, **103**, 2597.
3. R. O. Torres-Ochoa, A. Leclair, Q. Wang, J. Zhu, *Chem. Eur. J.,* 2019, **25**, 9477.

6. Copies of NMR spectra of the products.

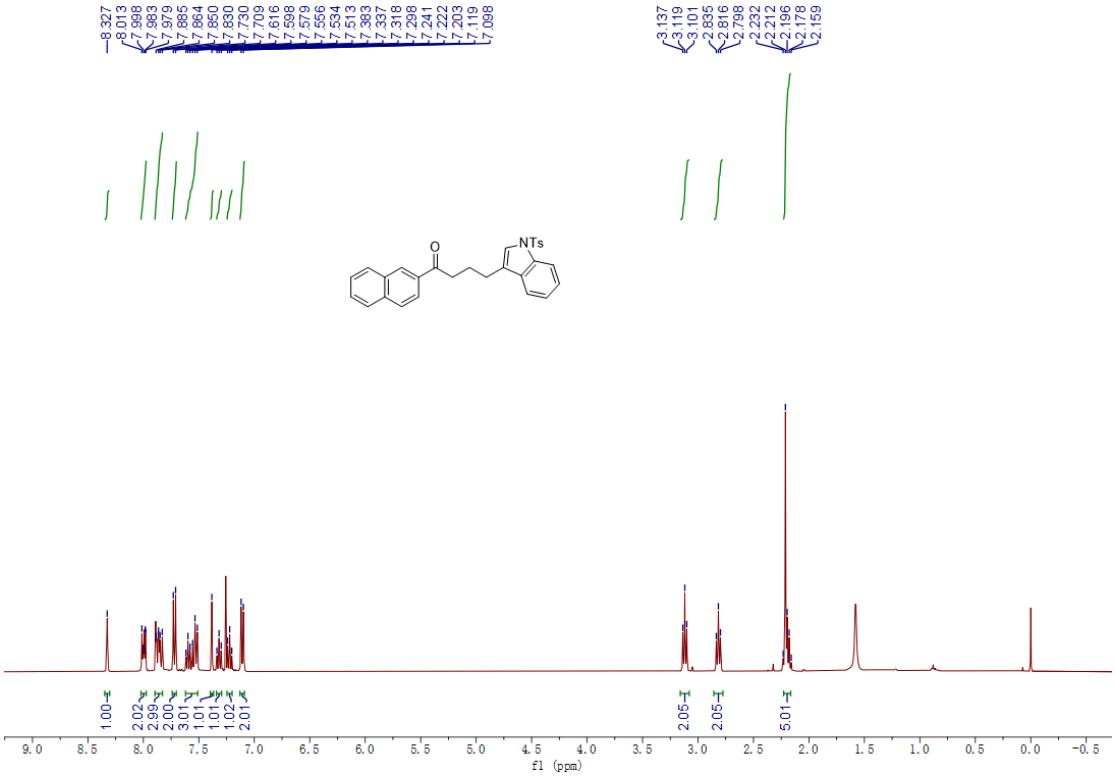
^{1}H NMR of **3aa** (400 MHz, $CDCl_3$)



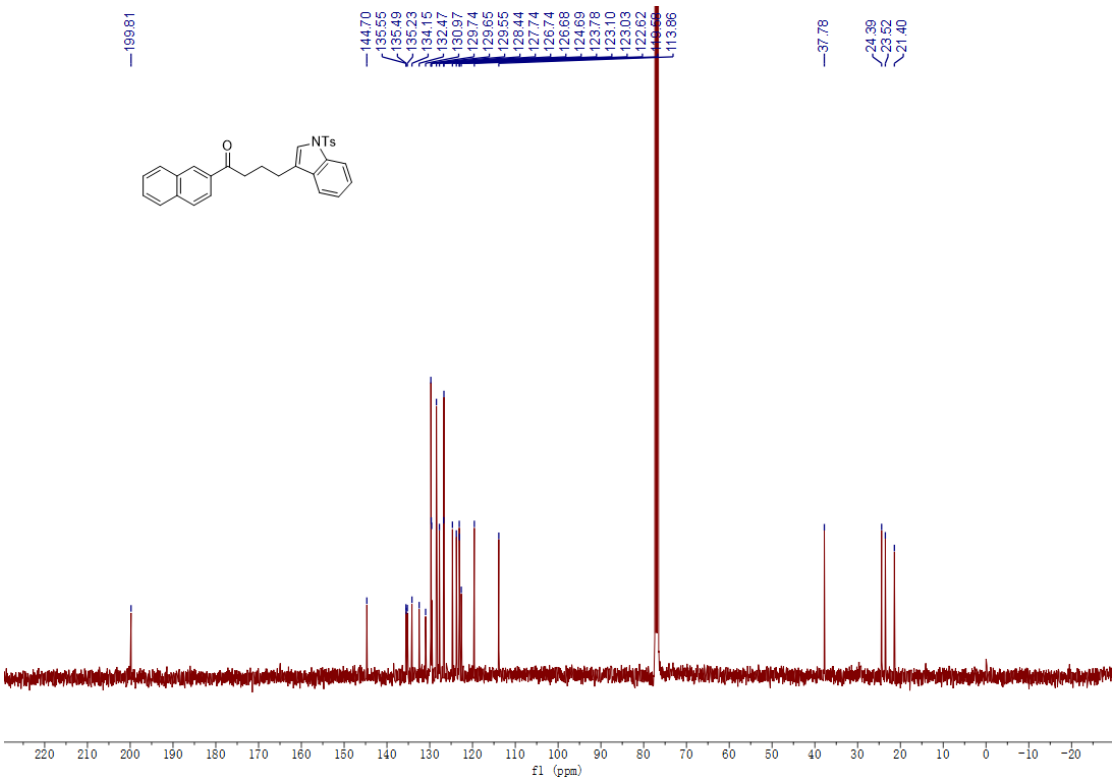
^{13}C NMR of **3aa** (100 MHz, $CDCl_3$)



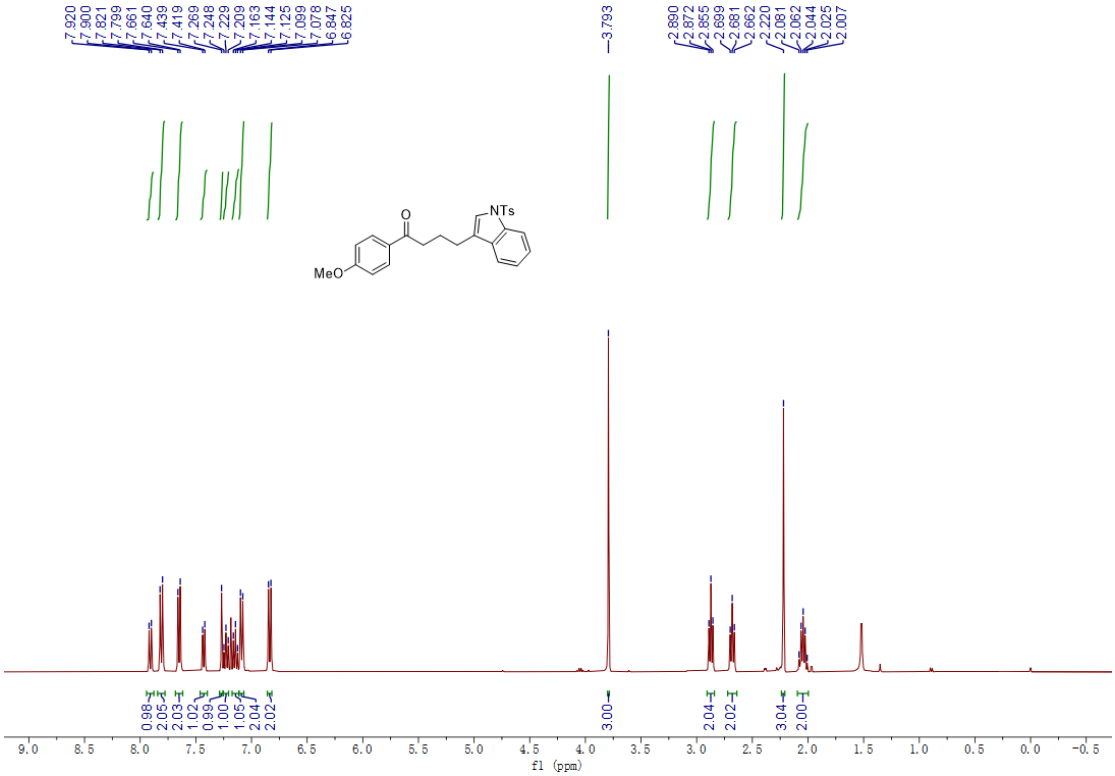
^{1}H NMR of **3ba** (400 MHz, $CDCl_3$)



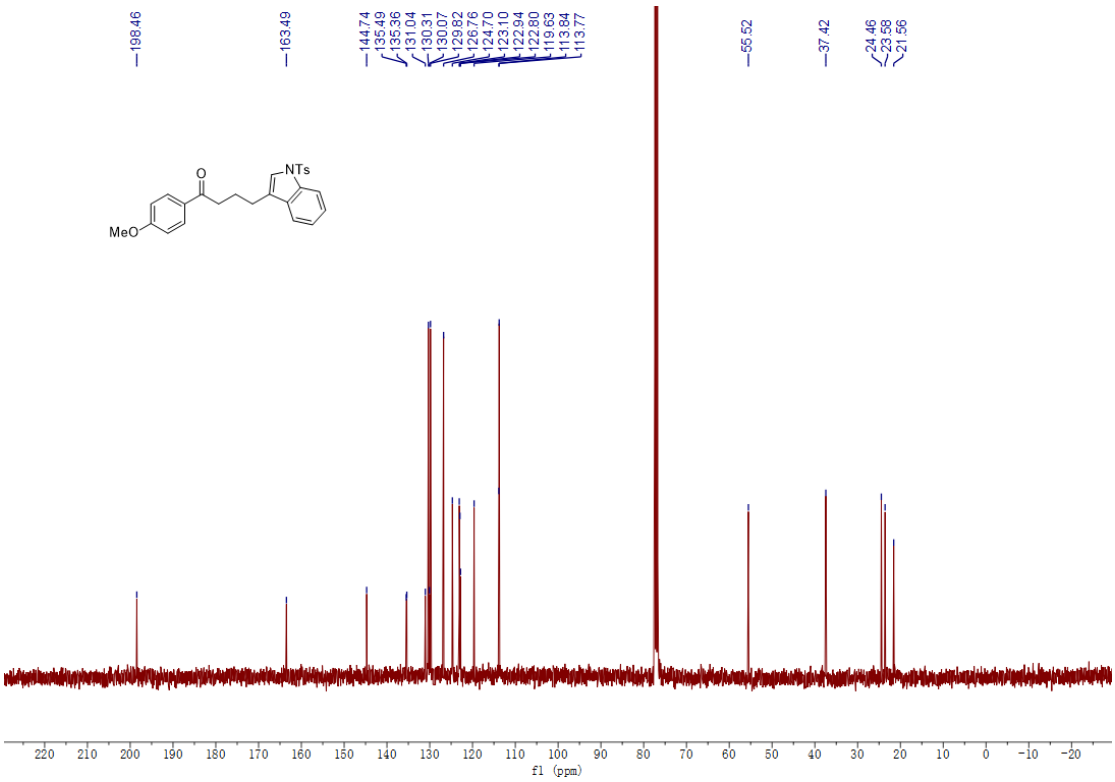
^{13}C NMR of **3ba** (100 MHz, $CDCl_3$)



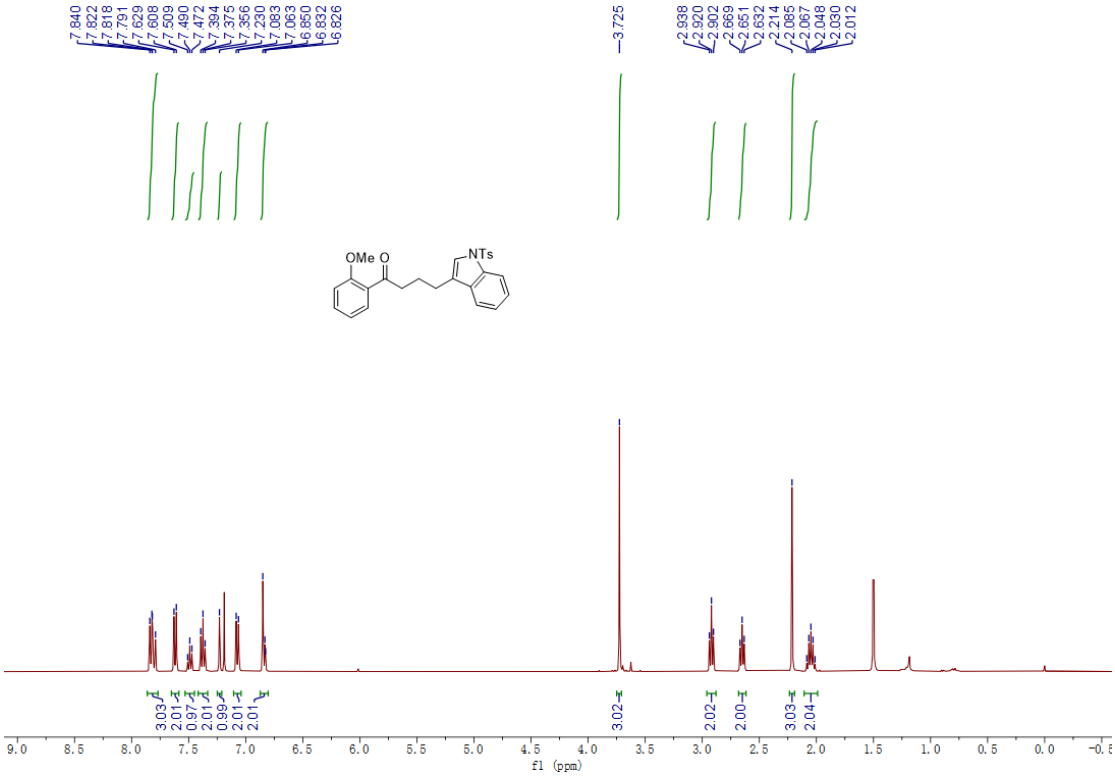
^{1}H NMR of **3ca** (400 MHz, $CDCl_3$)



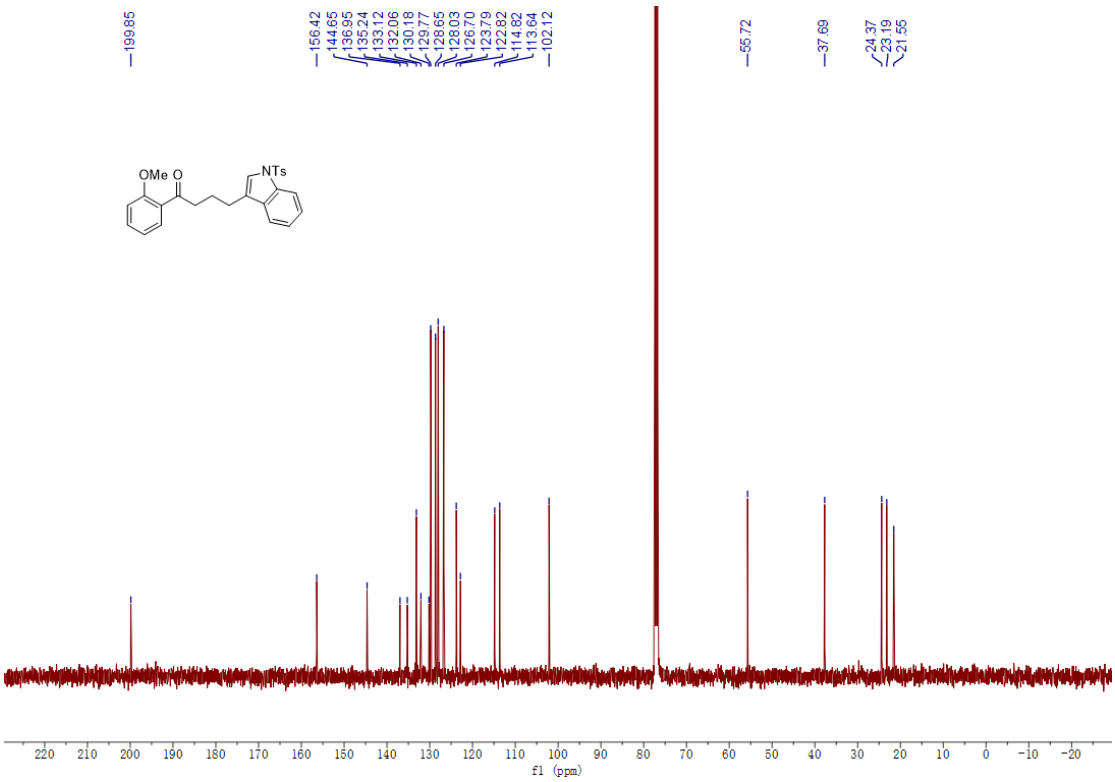
^{13}C NMR of **3ca** (100 MHz, $CDCl_3$)



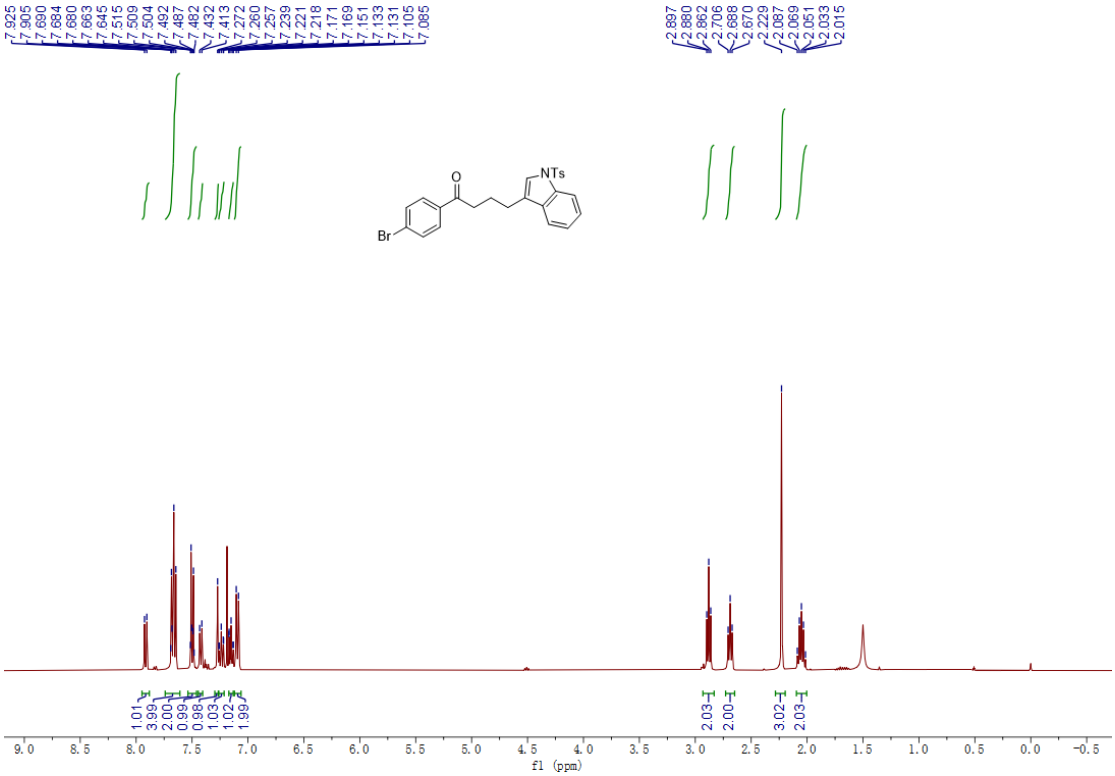
^{1}H NMR of **3da** (400 MHz, $CDCl_3$)



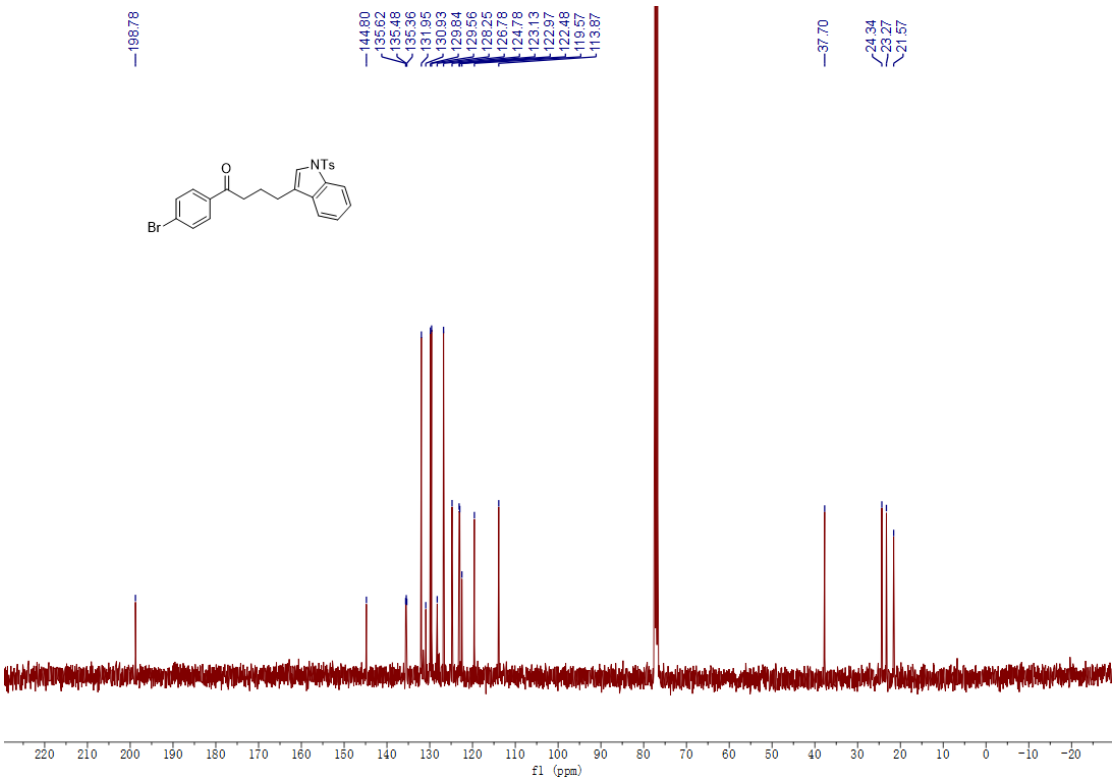
^{13}C NMR of **3da** (100 MHz, $CDCl_3$)



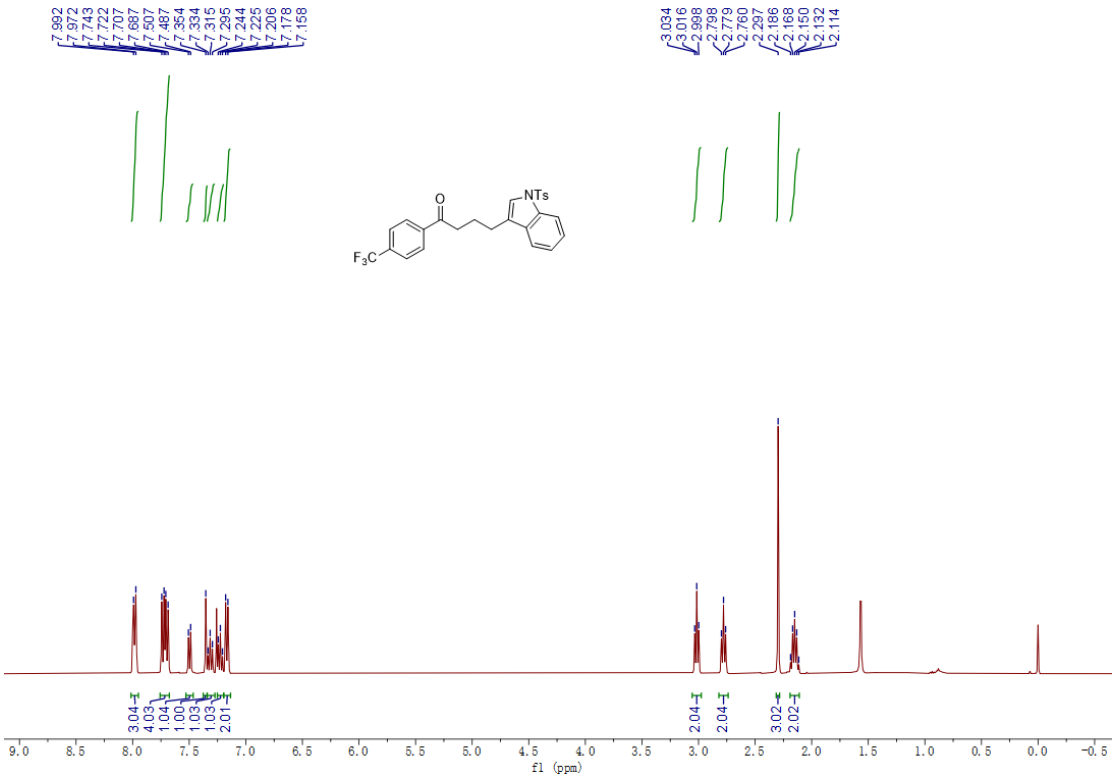
^{1}H NMR of **3ea** (400 MHz, $CDCl_3$)



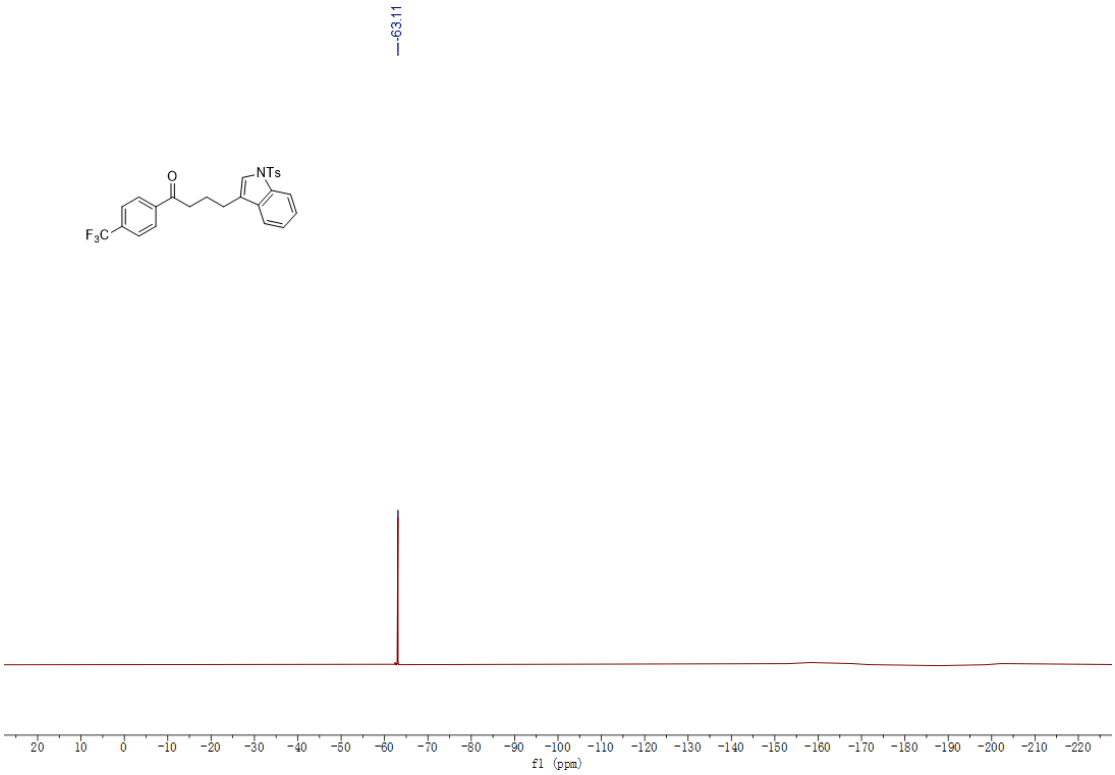
^{13}C NMR of **3ea** (100 MHz, $CDCl_3$)



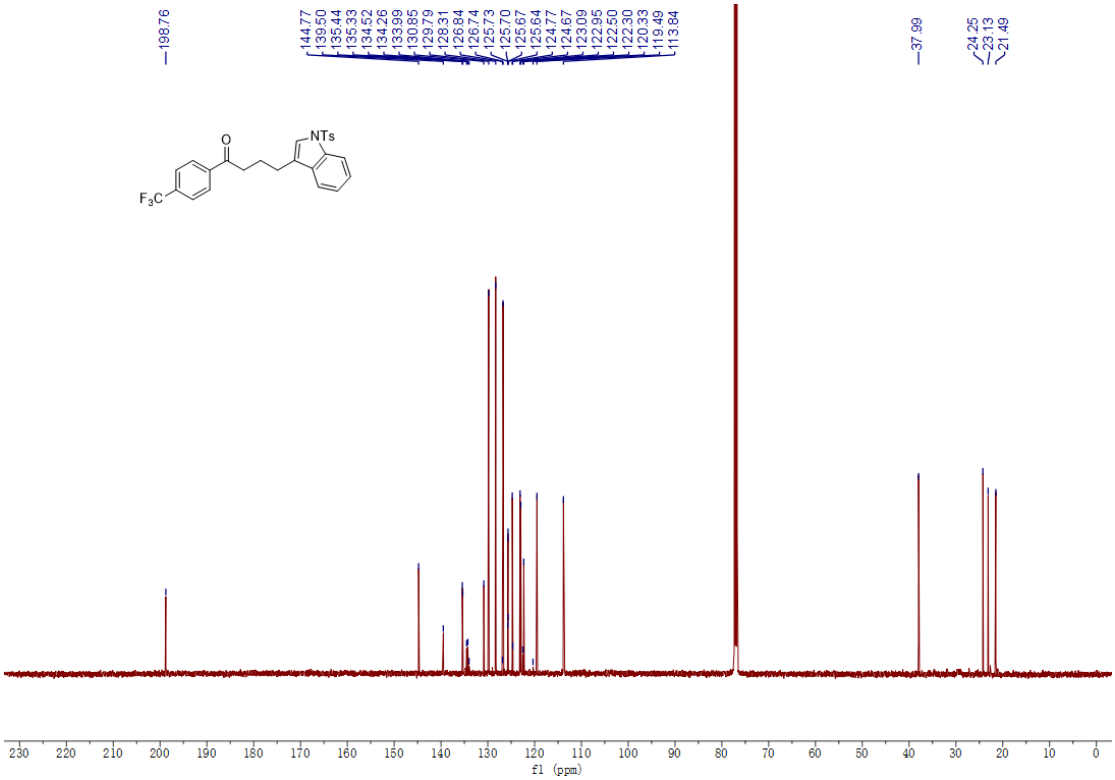
^{1}H NMR of **3fa** (400 MHz, $CDCl_3$)



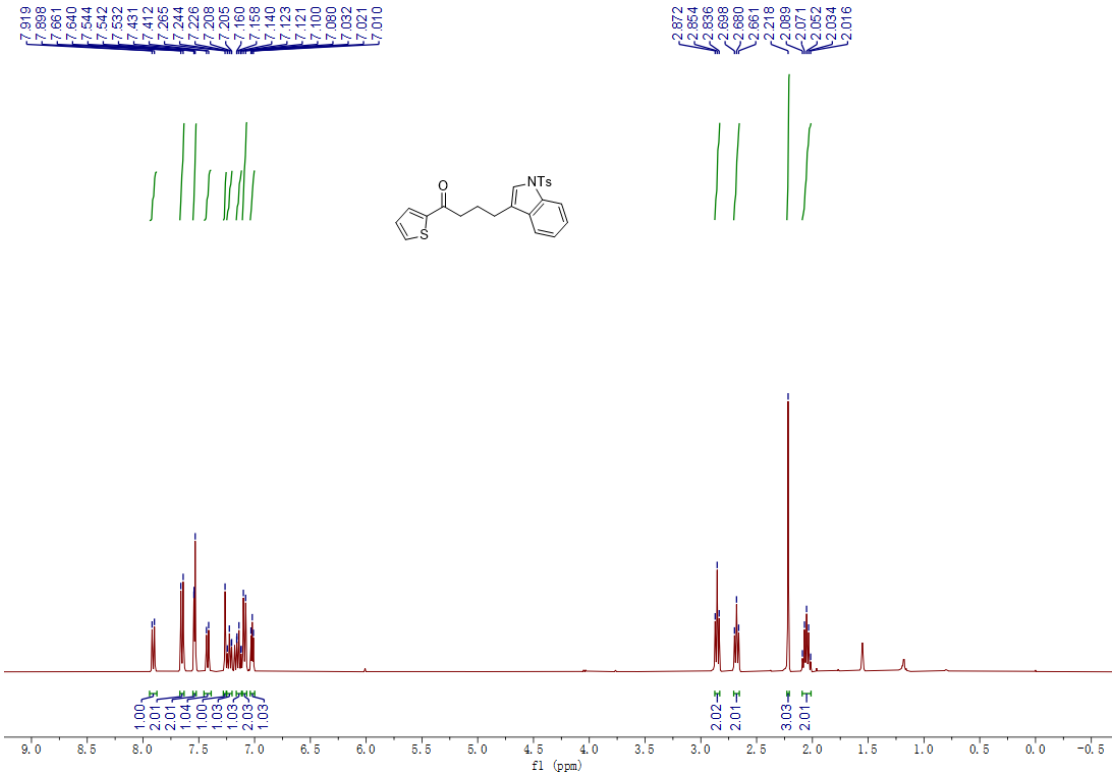
^{19}F NMR of **3fa** (376 MHz, $CDCl_3$)



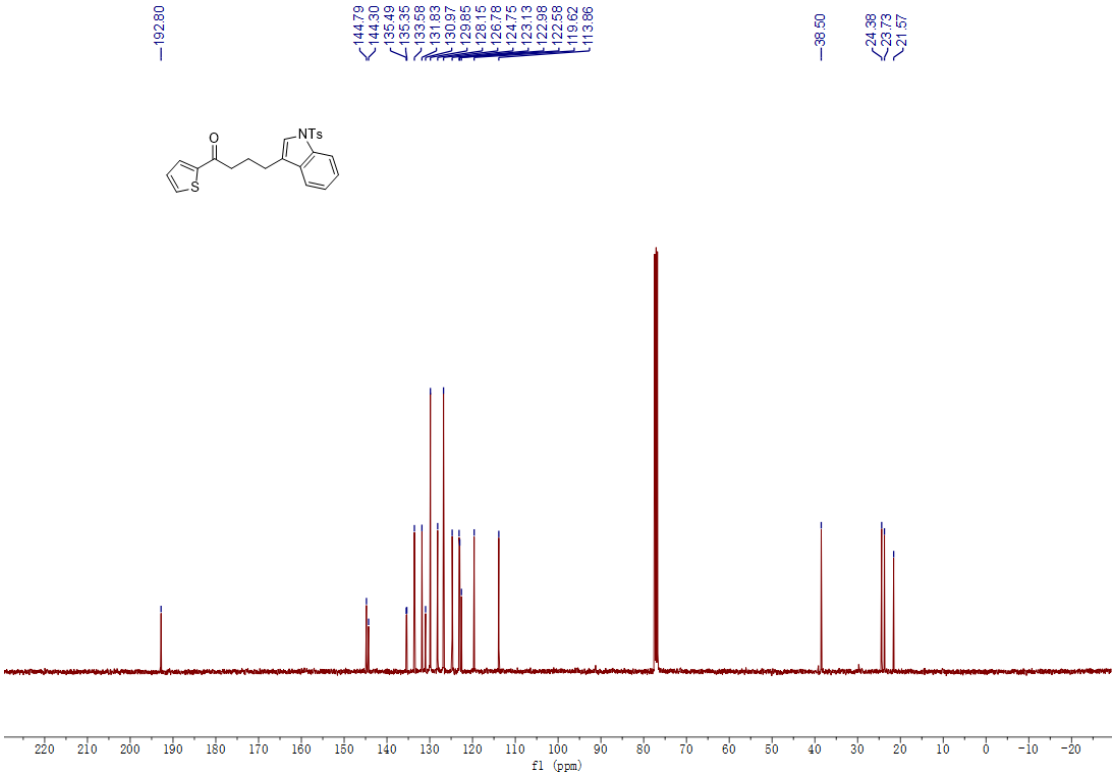
^{13}C NMR of **3fa** (125 MHz, $CDCl_3$)



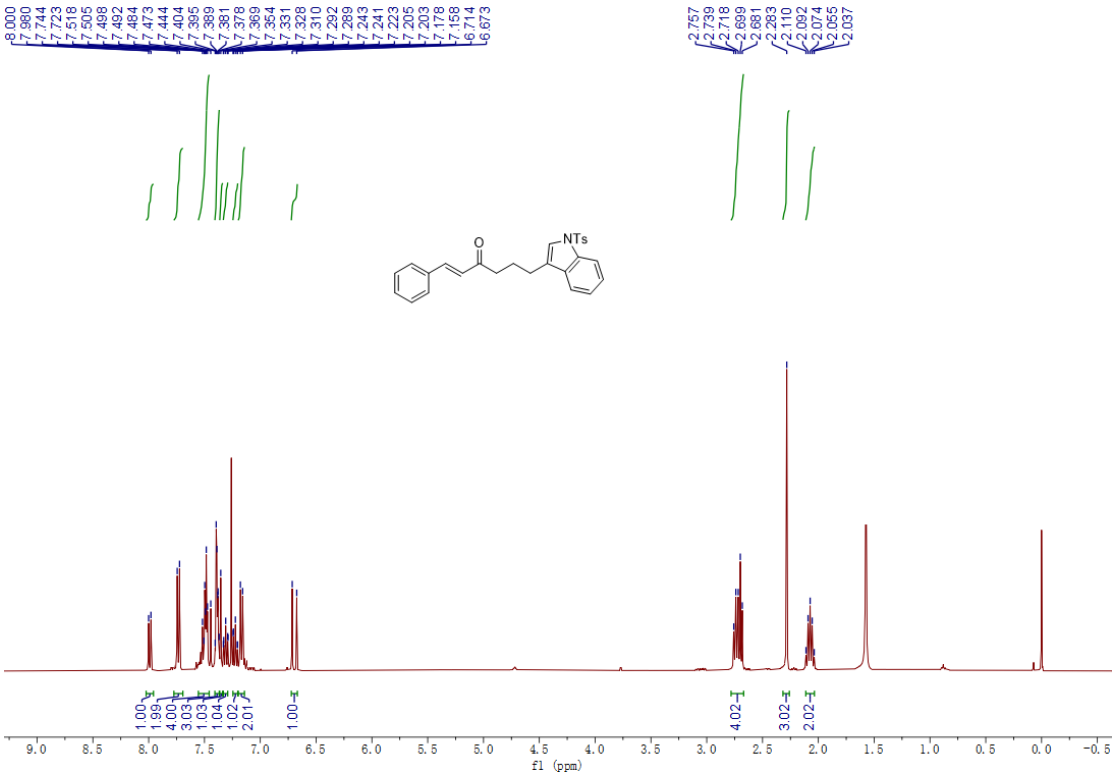
^{1}H NMR of **3ga** (400 MHz, $CDCl_3$)



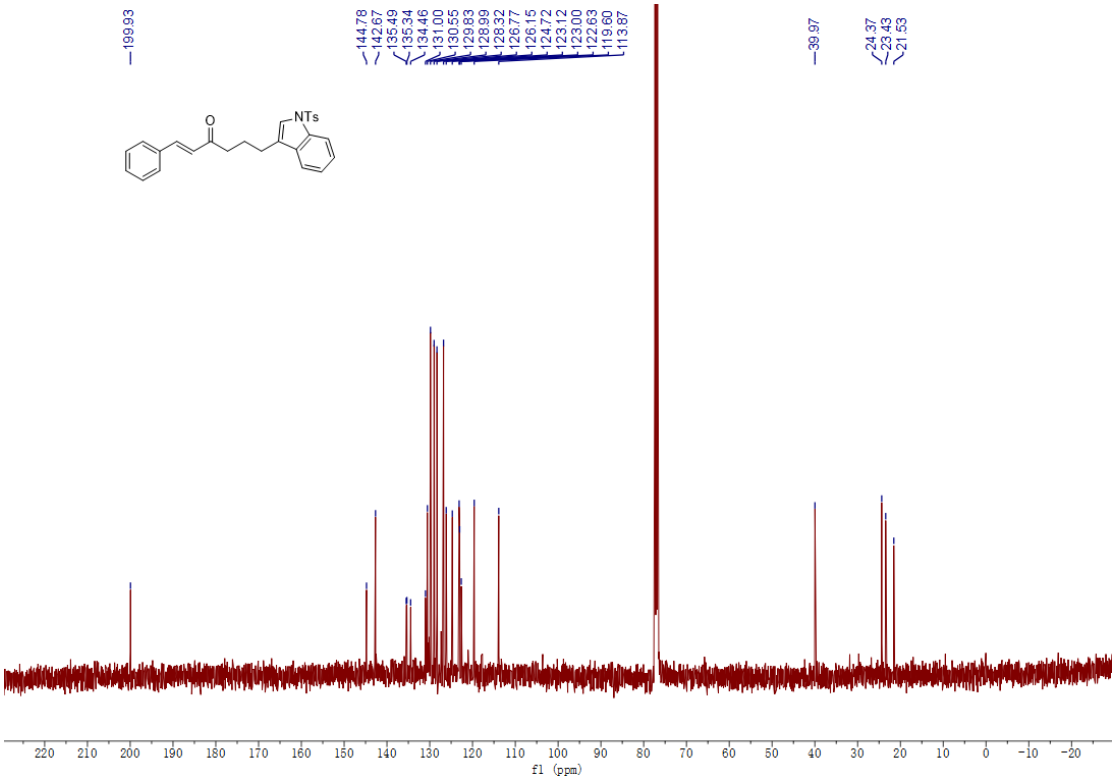
^{13}C NMR of **3ga** (100 MHz, $CDCl_3$)



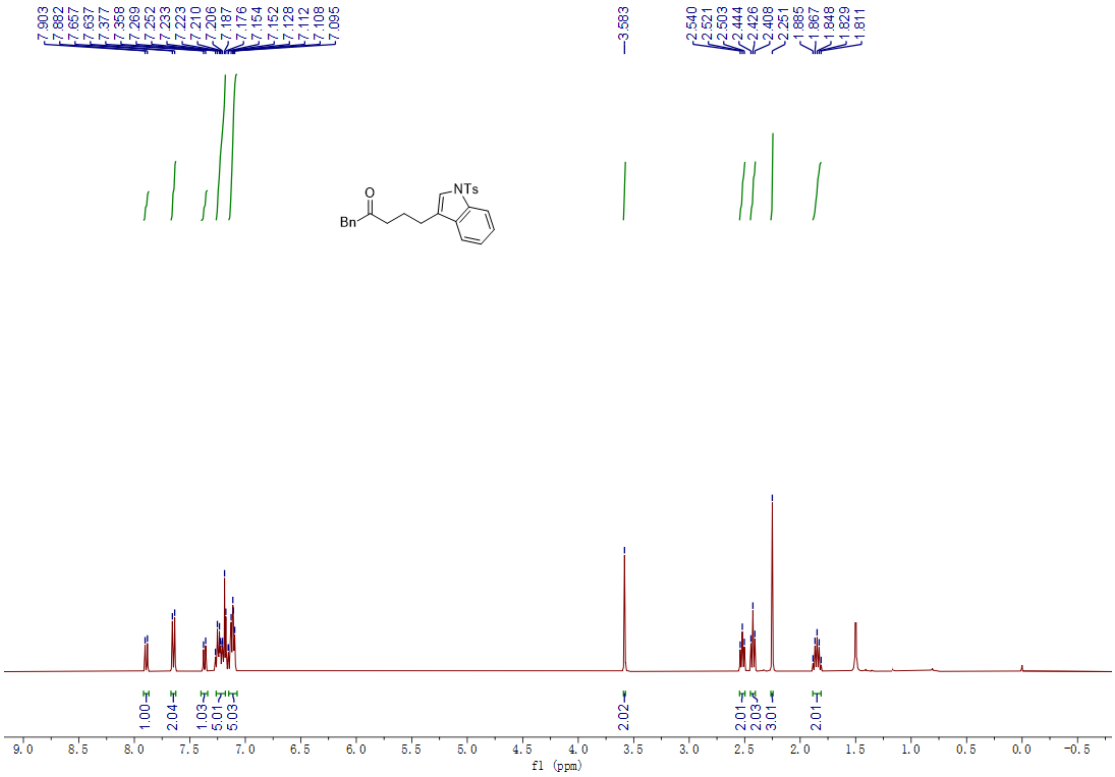
^{1}H NMR of **3ha** (400 MHz, $CDCl_3$)



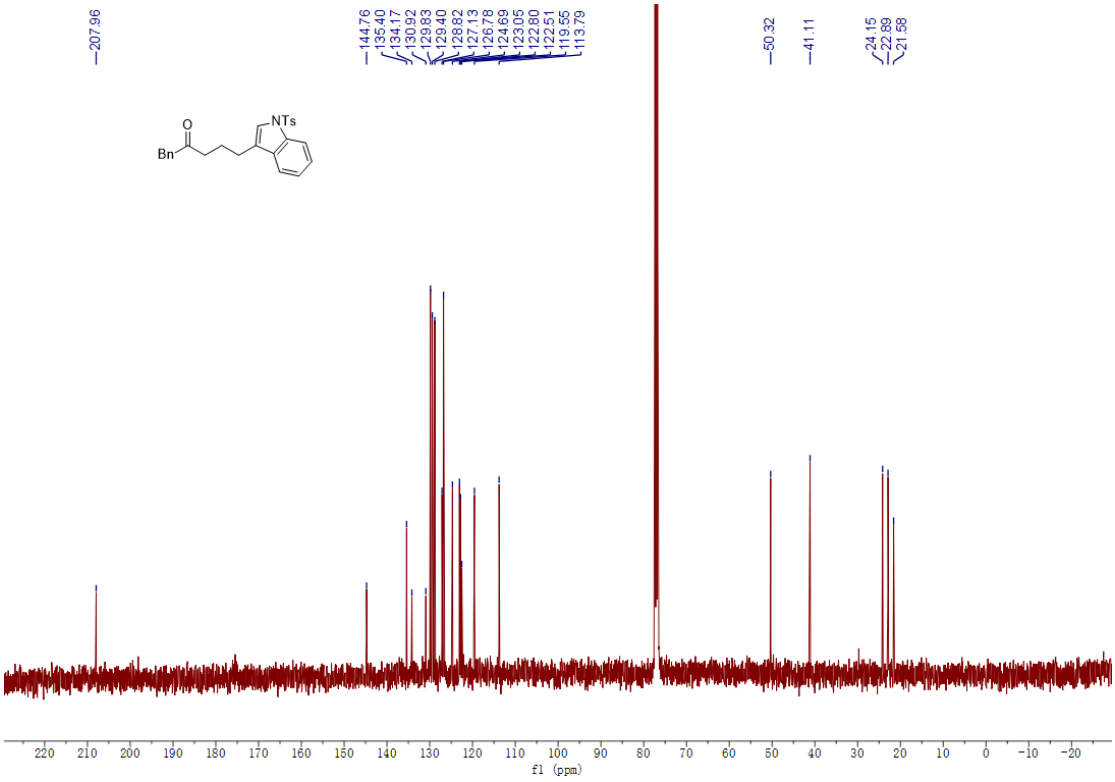
^{13}C NMR of **3ha** (100 MHz, $CDCl_3$)



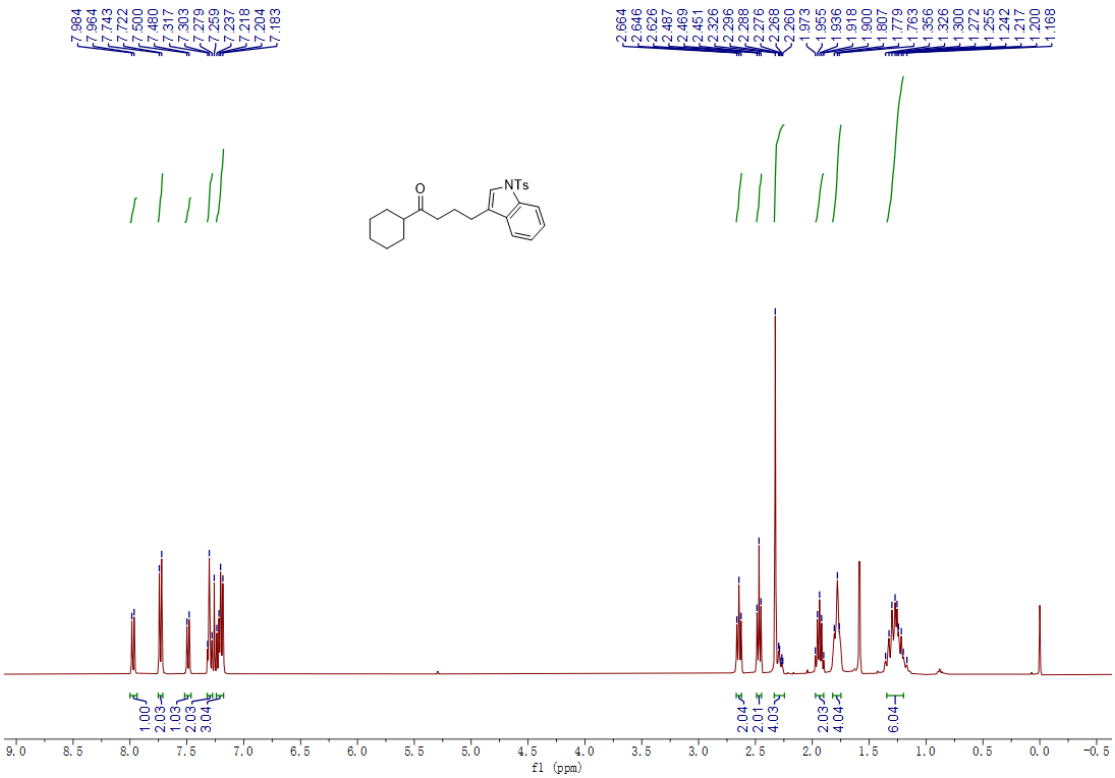
^{1}H NMR of **3ia** (400 MHz, $CDCl_3$)



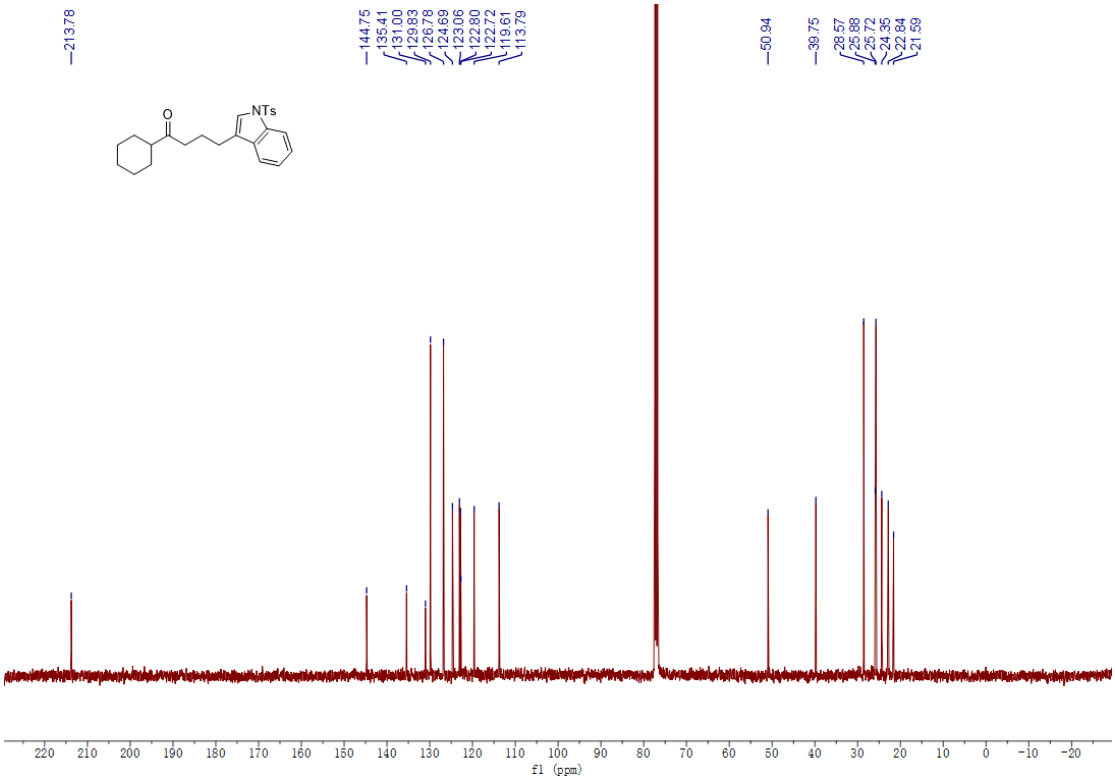
^{13}C NMR of **3ia** (100 MHz, $CDCl_3$)



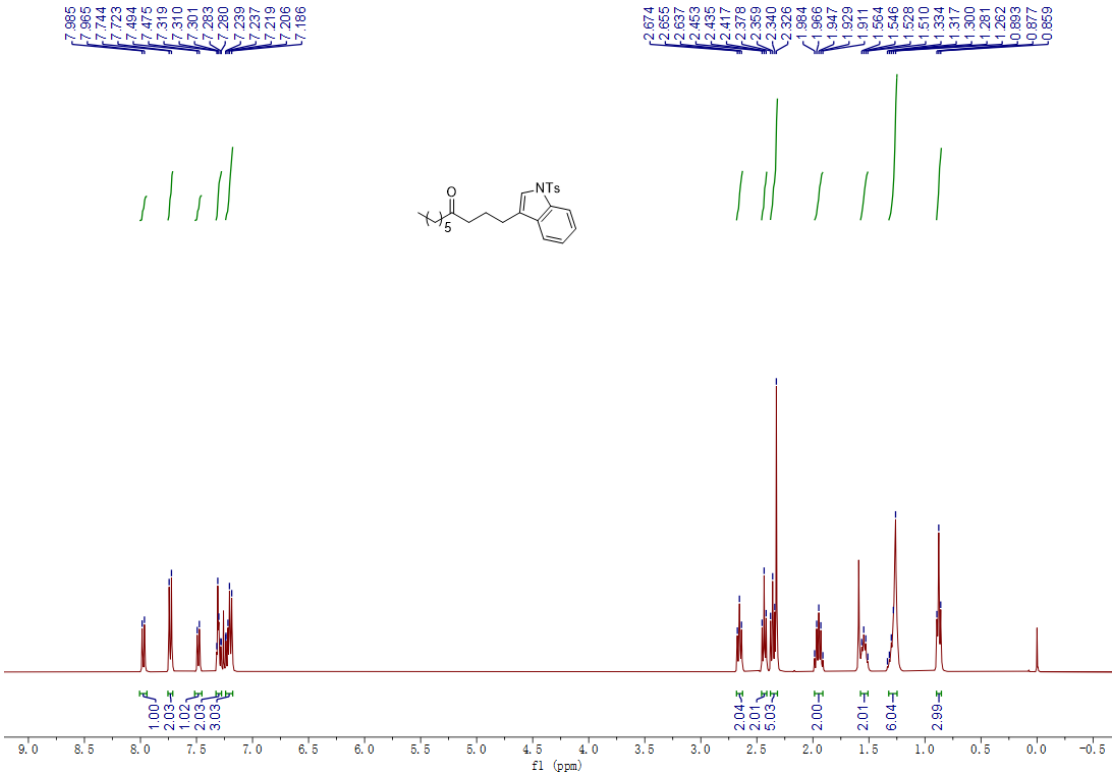
^{1}H NMR of **3ja** (400 MHz, $CDCl_3$)



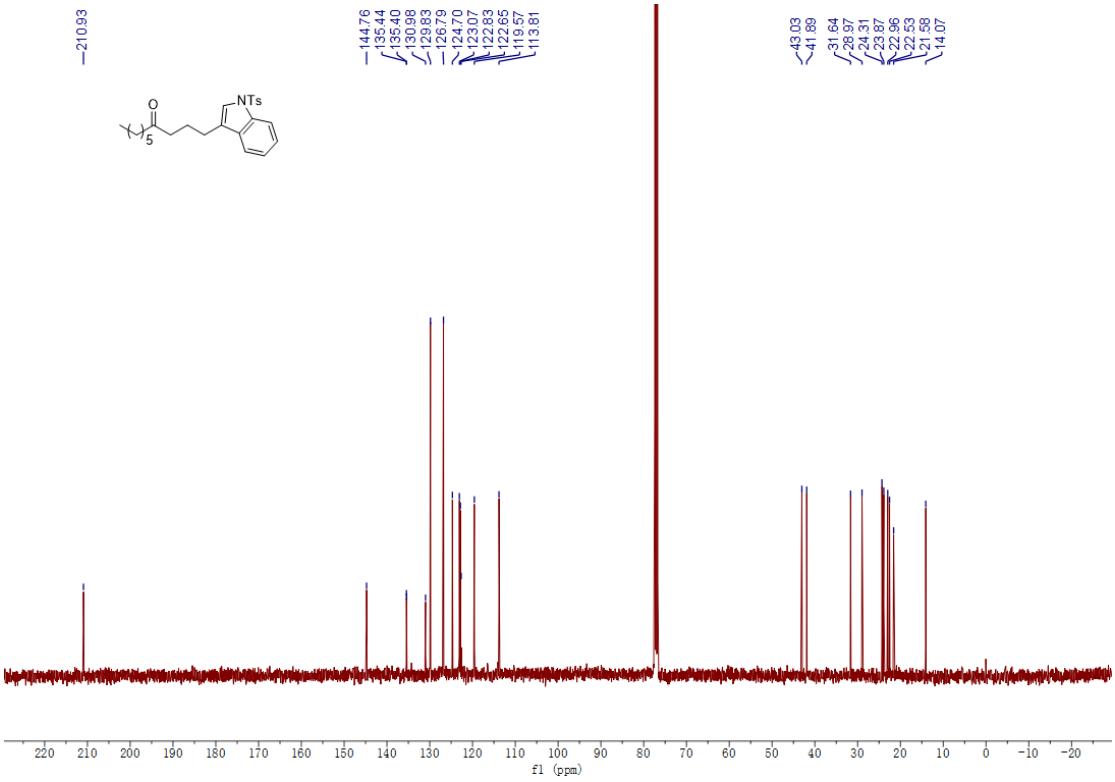
^{13}C NMR of **3ja** (100 MHz, $CDCl_3$)



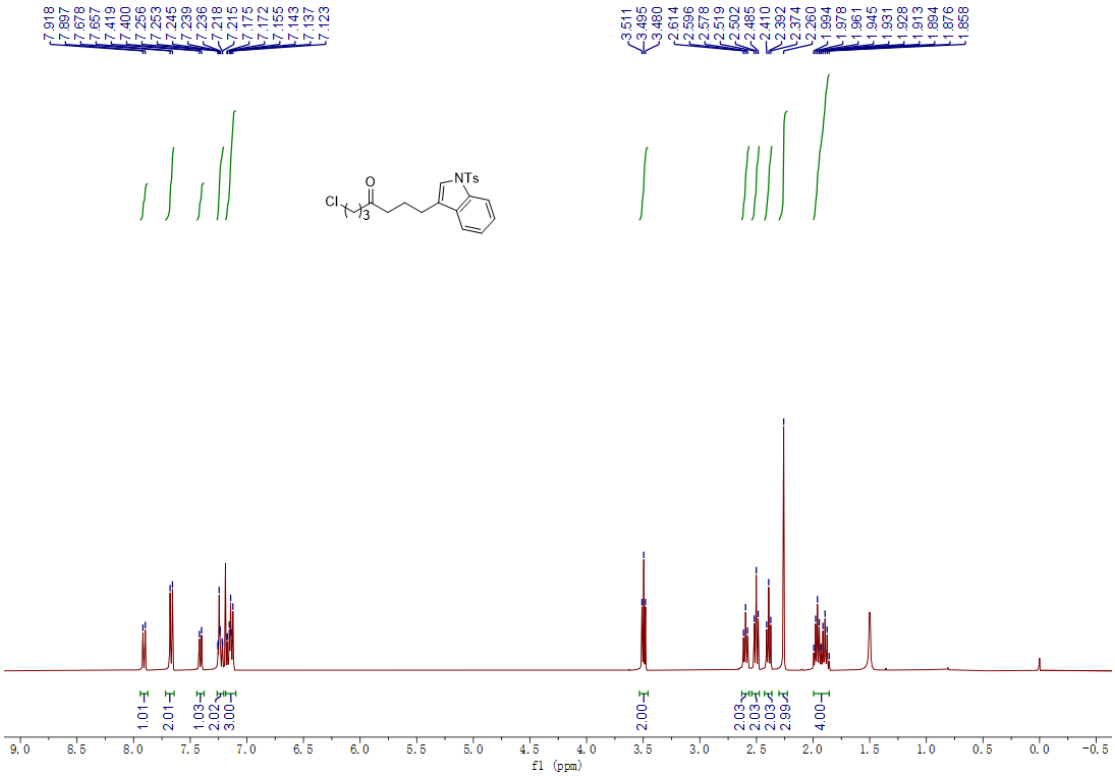
^{1}H NMR of **3ka** (400 MHz, $CDCl_3$)



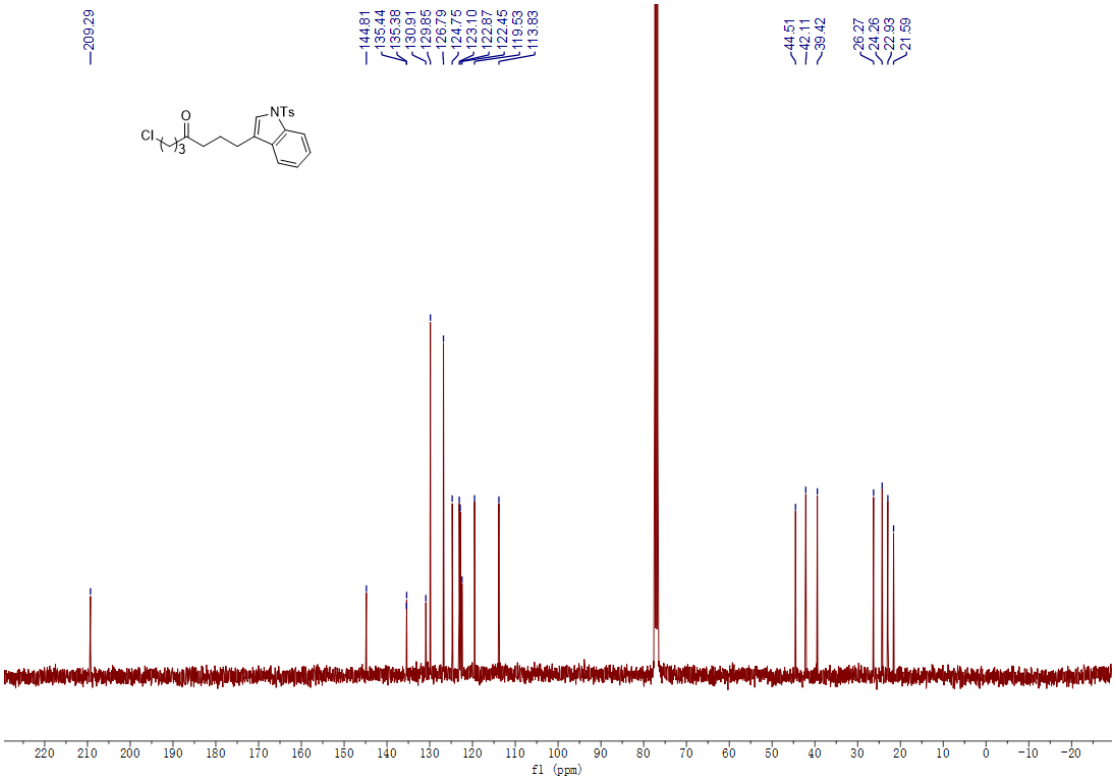
^{13}C NMR of **3ka** (100 MHz, $CDCl_3$)



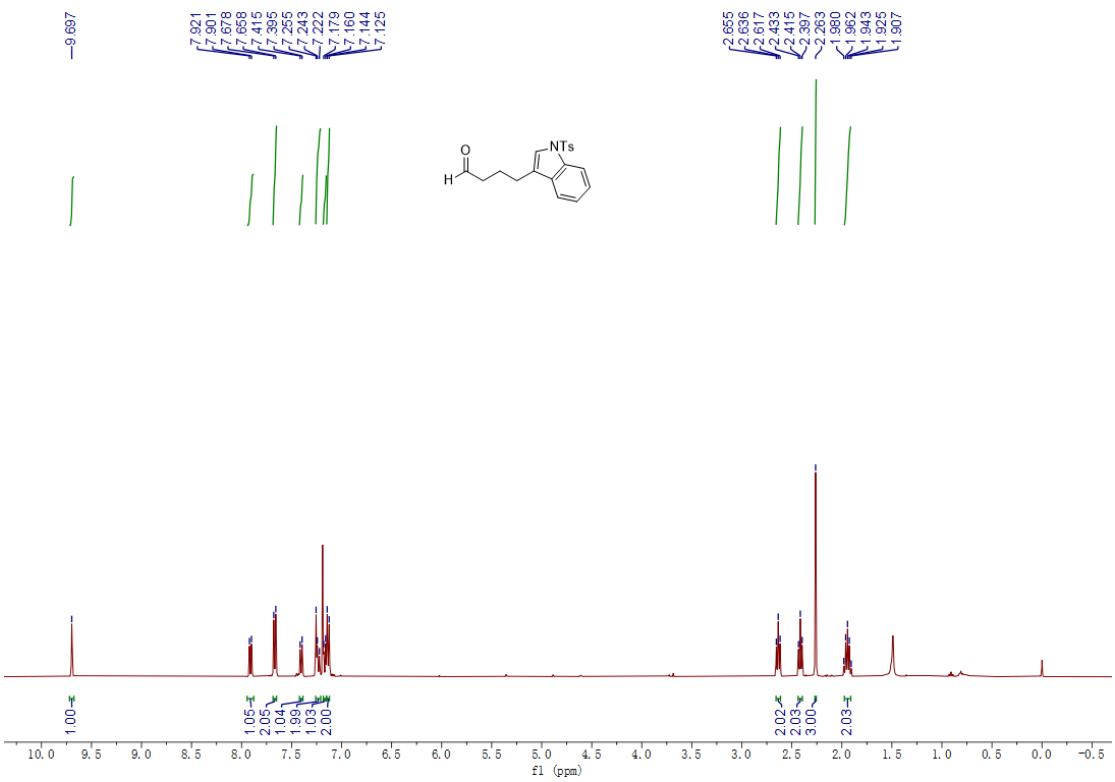
^{1}H NMR of **3la** (400 MHz, $CDCl_3$)



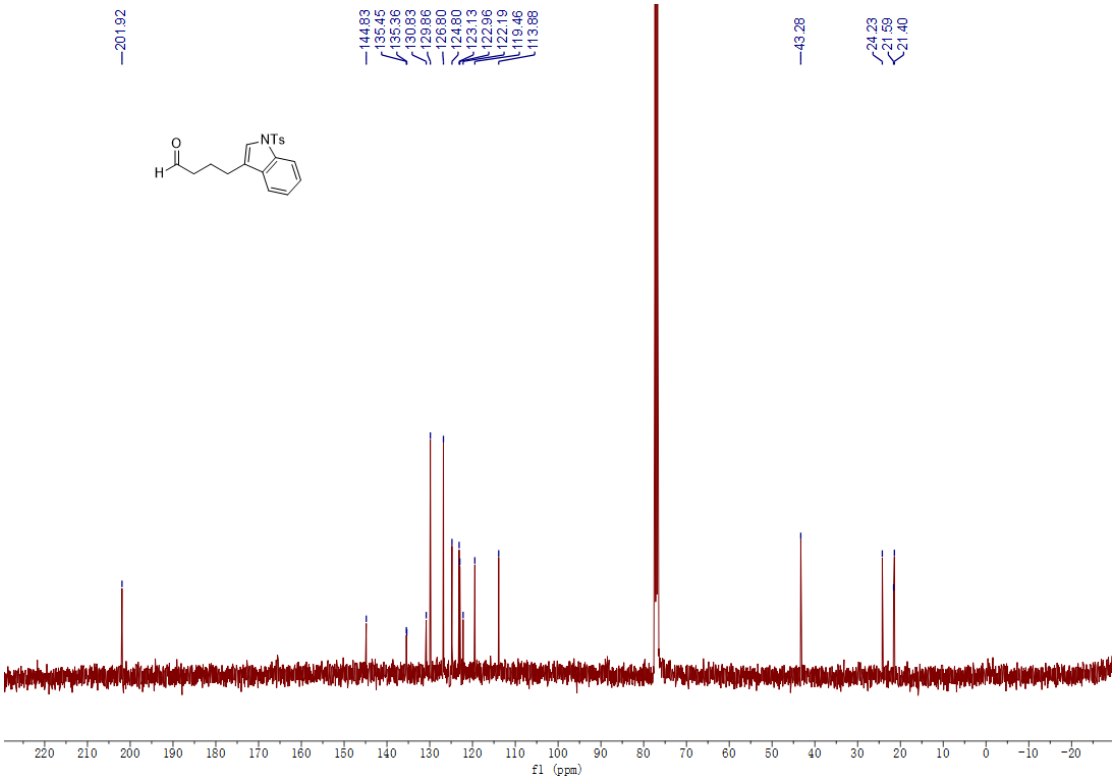
^{13}C NMR of **3la** (100 MHz, $CDCl_3$)



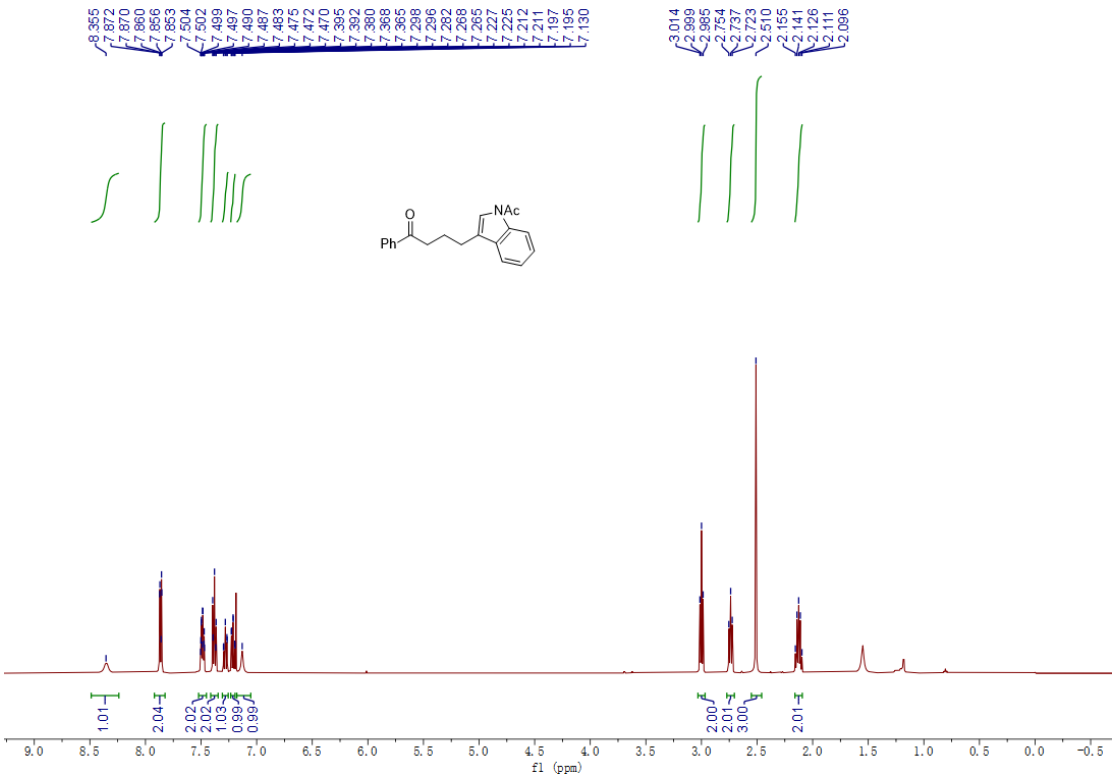
^{1}H NMR of **3ma** (400 MHz, $CDCl_3$)



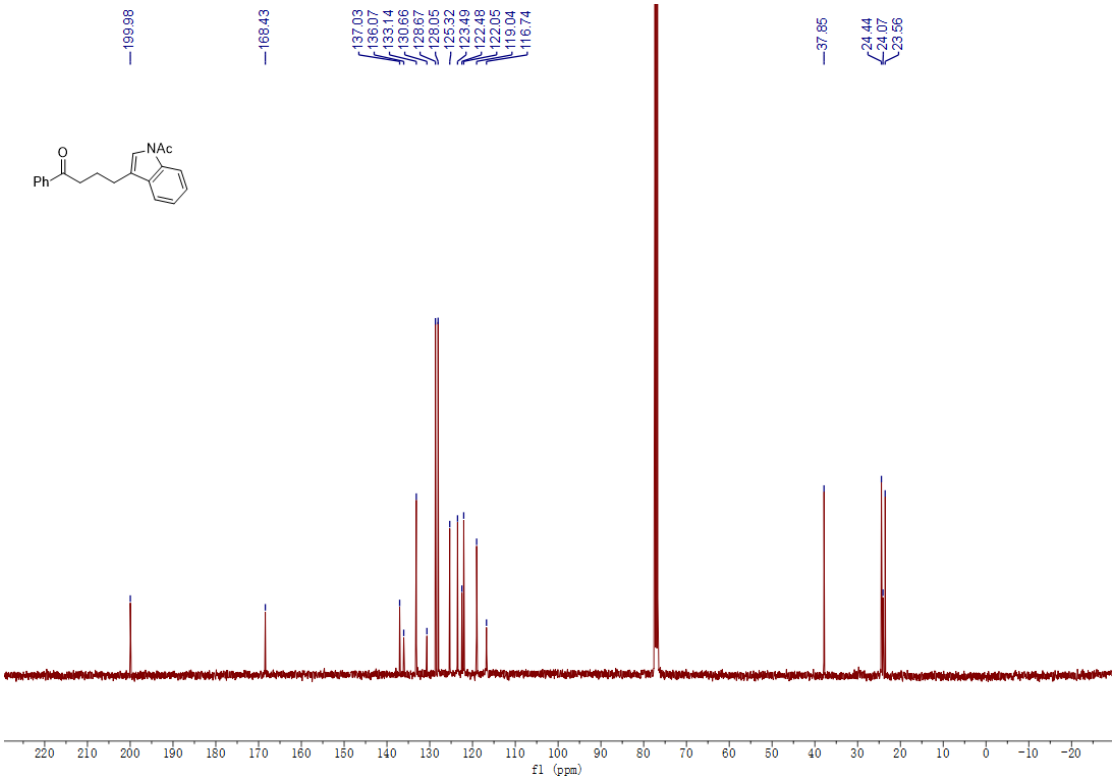
^{13}C NMR of **3ma** (100 MHz, $CDCl_3$)



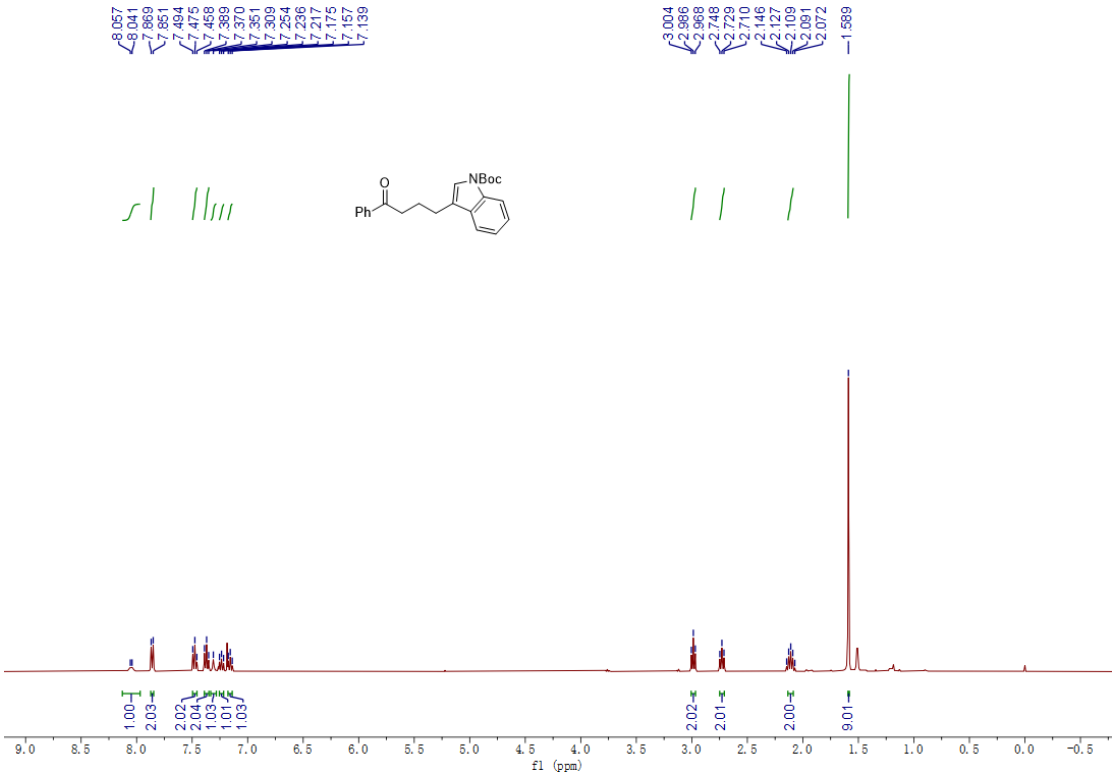
^{1}H NMR of **3ab** (400 MHz, $CDCl_3$)



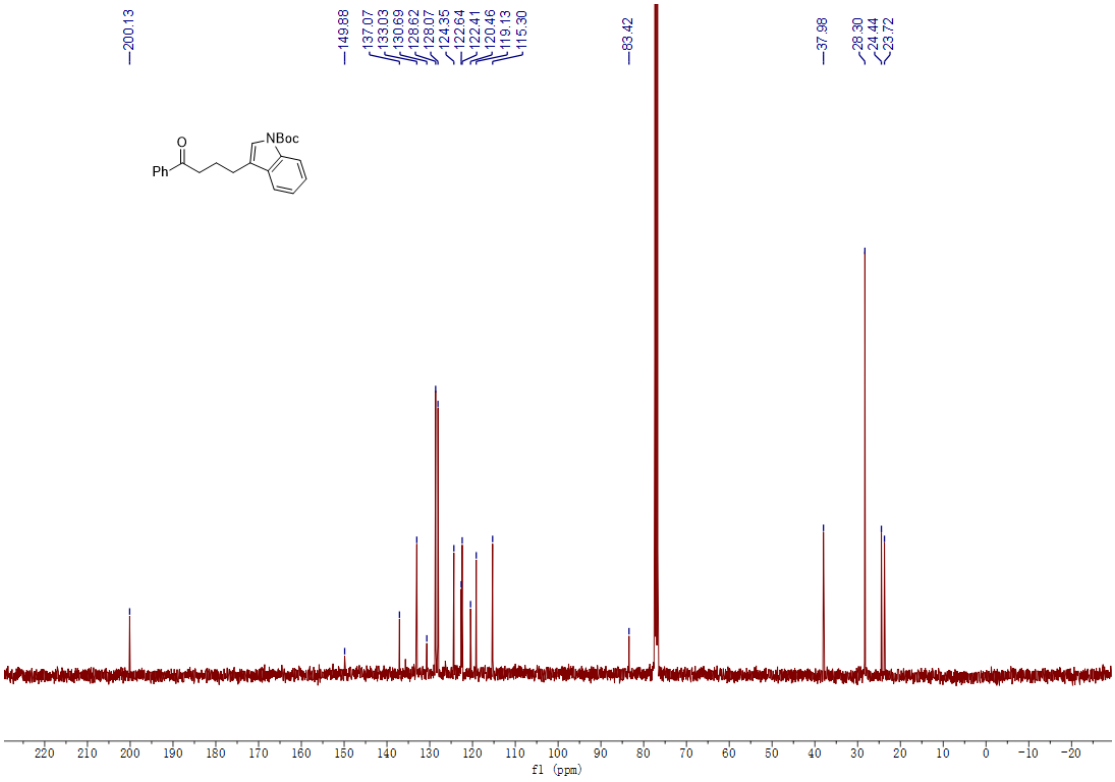
^{13}C NMR of **3ab** (100 MHz, $CDCl_3$)



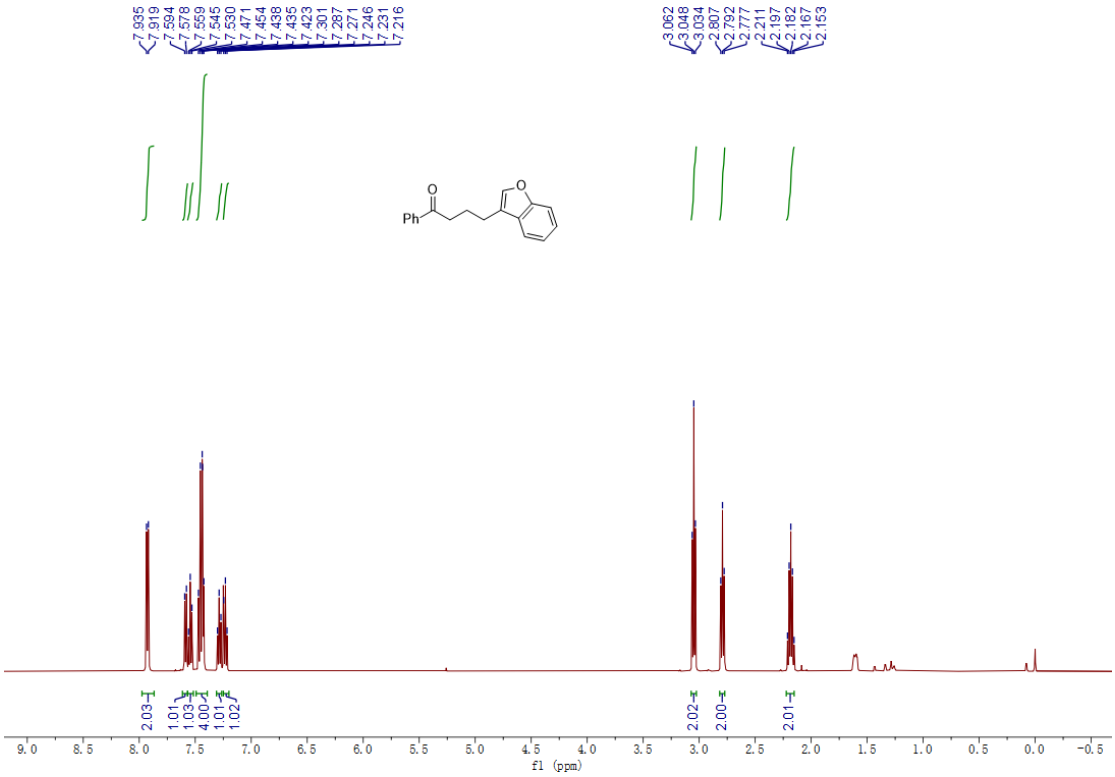
^{1}H NMR of **3ac** (400 MHz, $CDCl_3$)



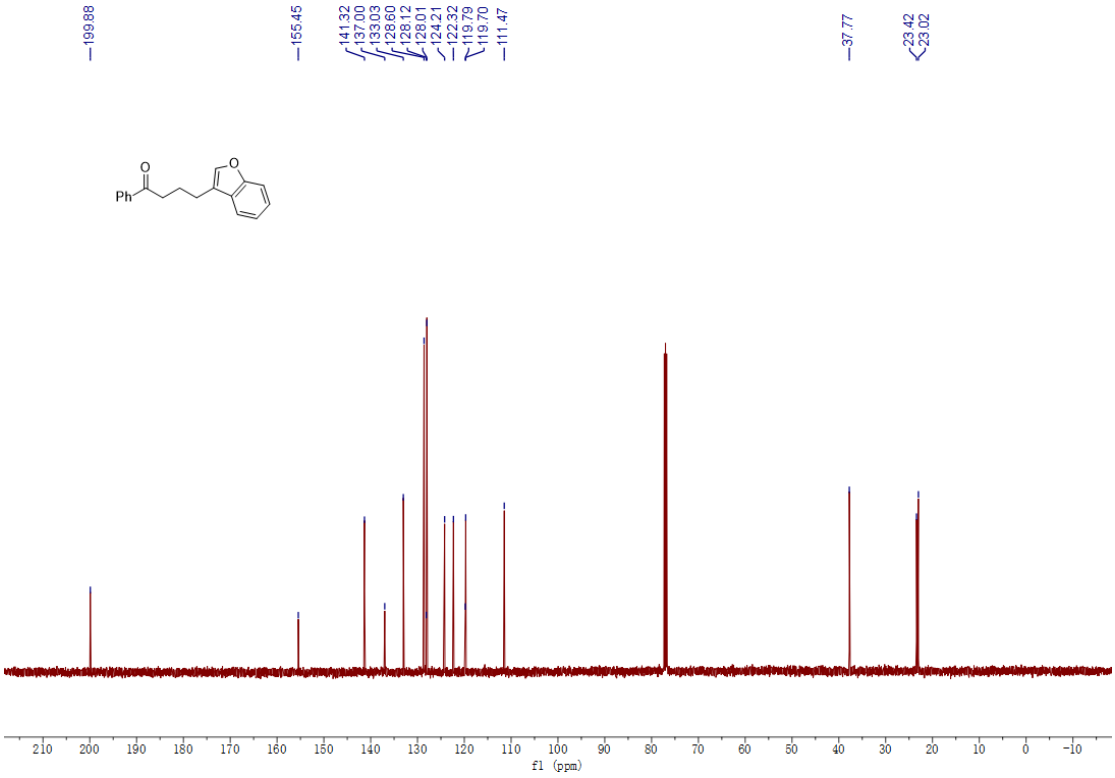
^{13}C NMR of **3ac** (100 MHz, $CDCl_3$)



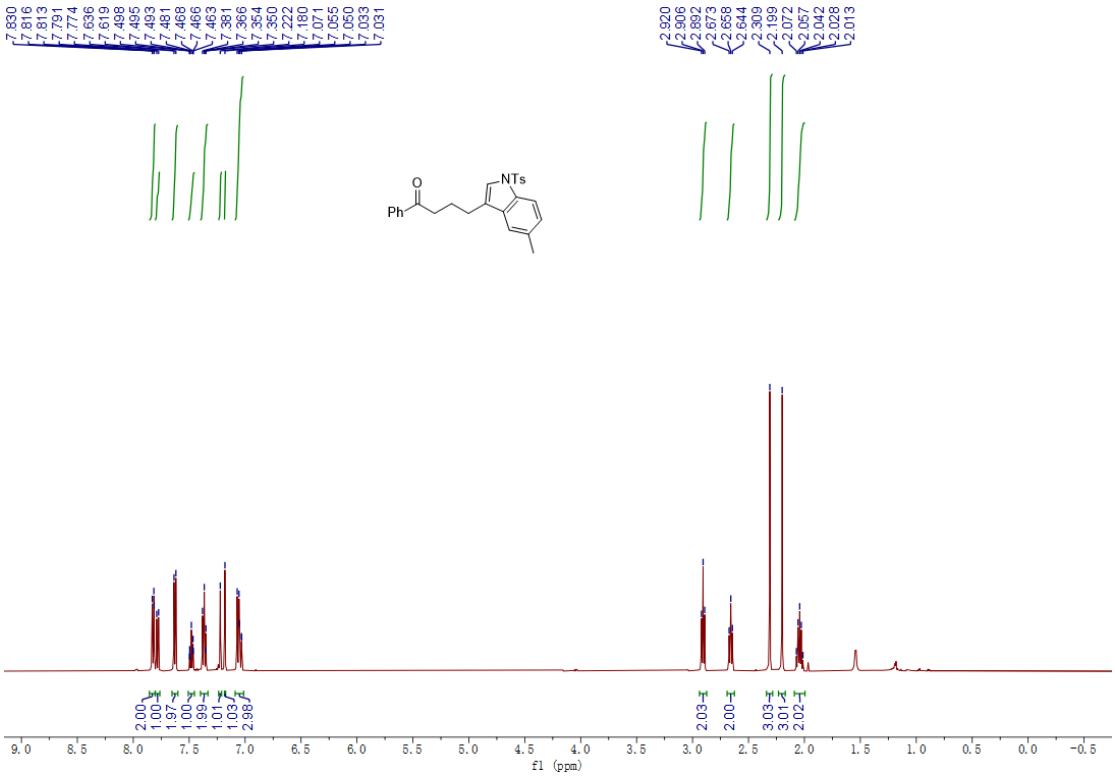
^{1}H NMR of **3ad** (500 MHz, $CDCl_3$)



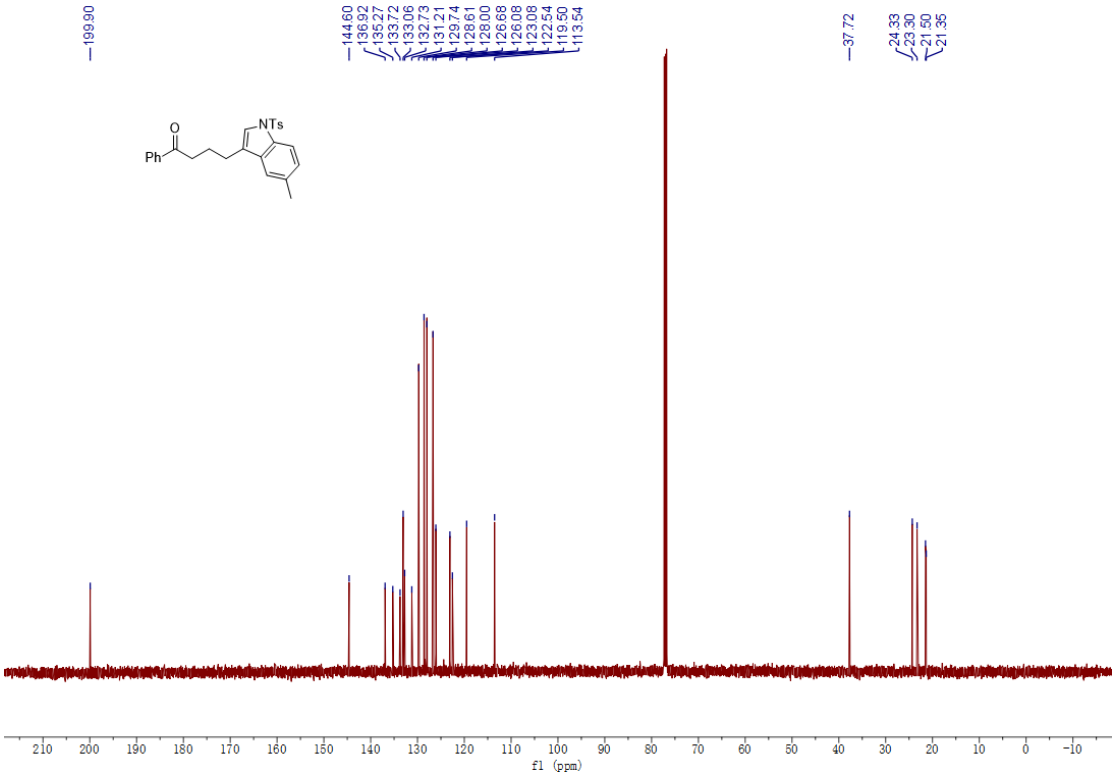
^{13}C NMR of **3ad** (125 MHz, $CDCl_3$)



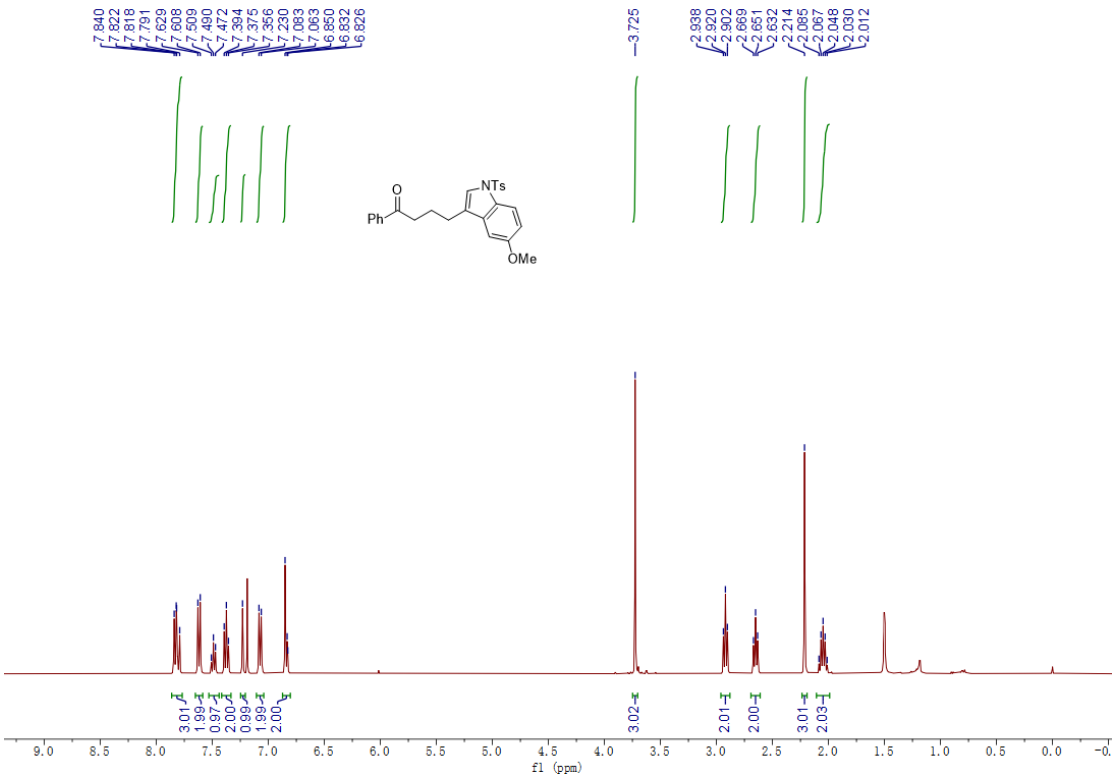
^{1}H NMR of **3ae** (500 MHz, $CDCl_3$)



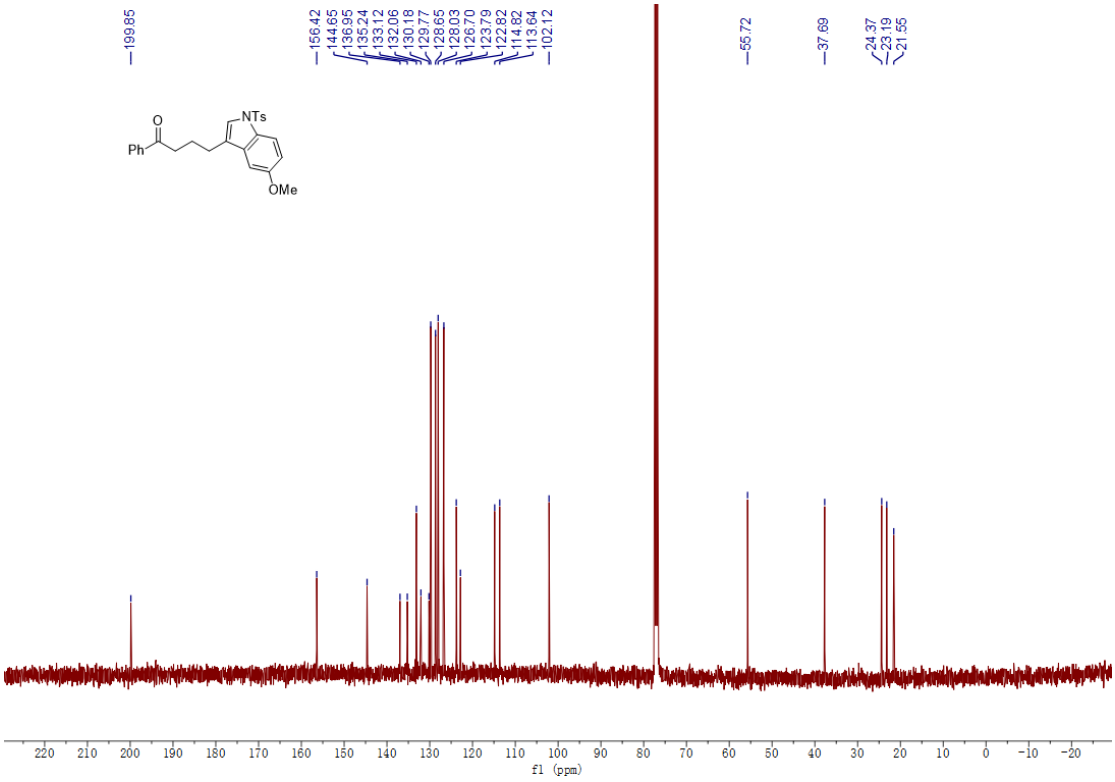
^{13}C NMR of **3ae** (125 MHz, $CDCl_3$)



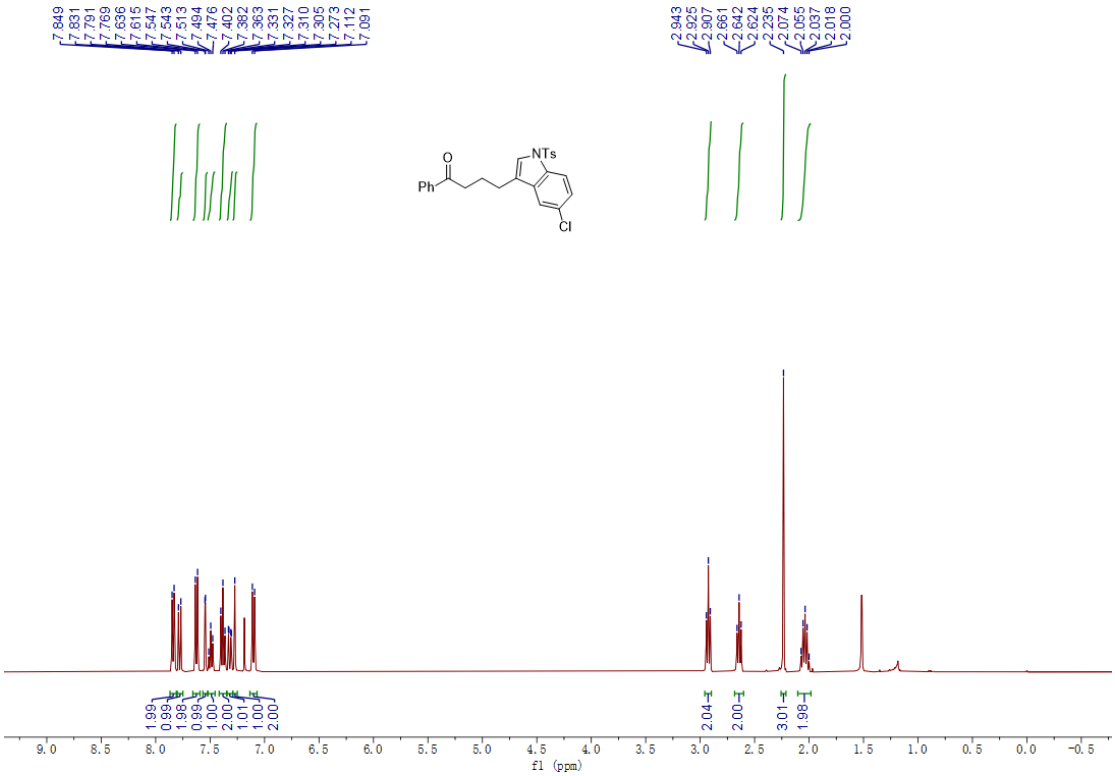
^{1}H NMR of **3af**(400 MHz, $CDCl_3$)



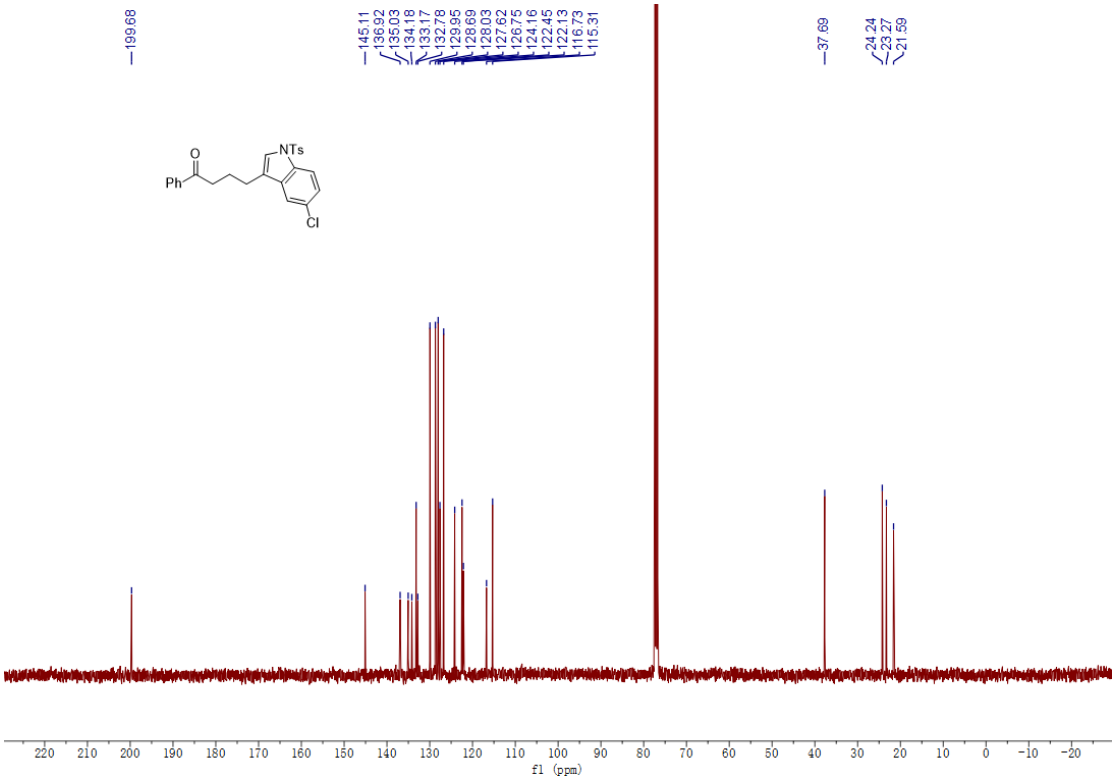
^{13}C NMR of **3af** (100 MHz, $CDCl_3$)



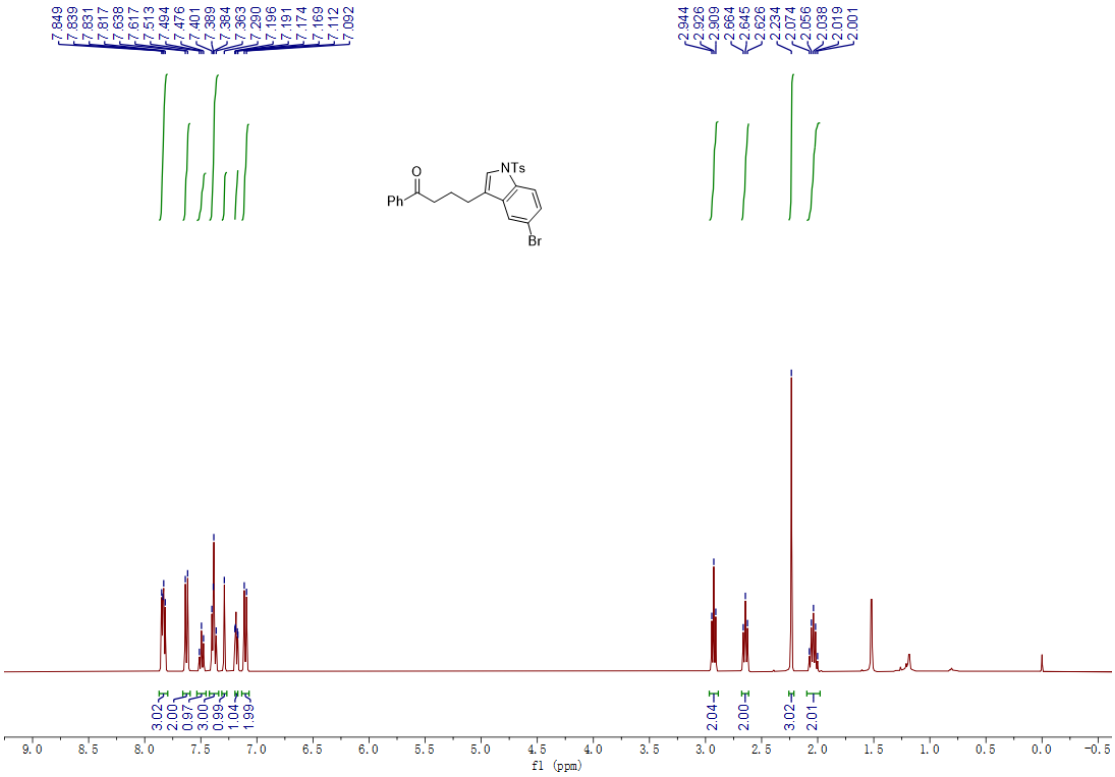
^{1}H NMR of **3ag** (400 MHz, $CDCl_3$)



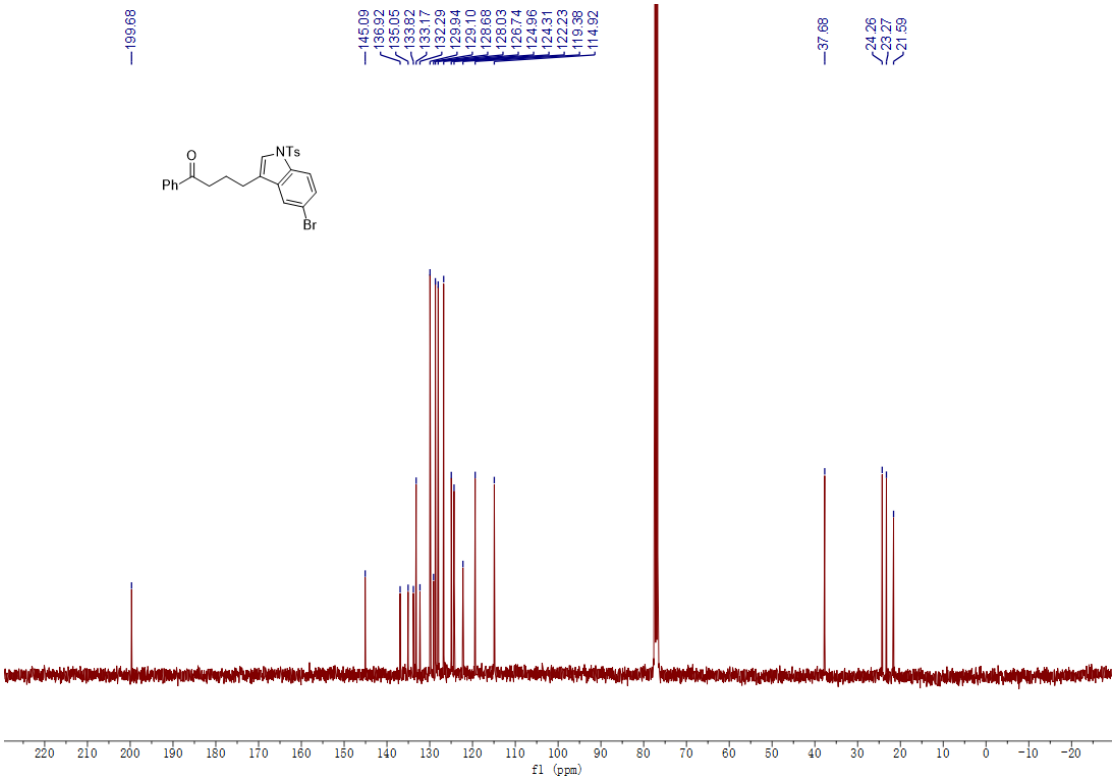
^{13}C NMR of **3ag** (100 MHz, $CDCl_3$)



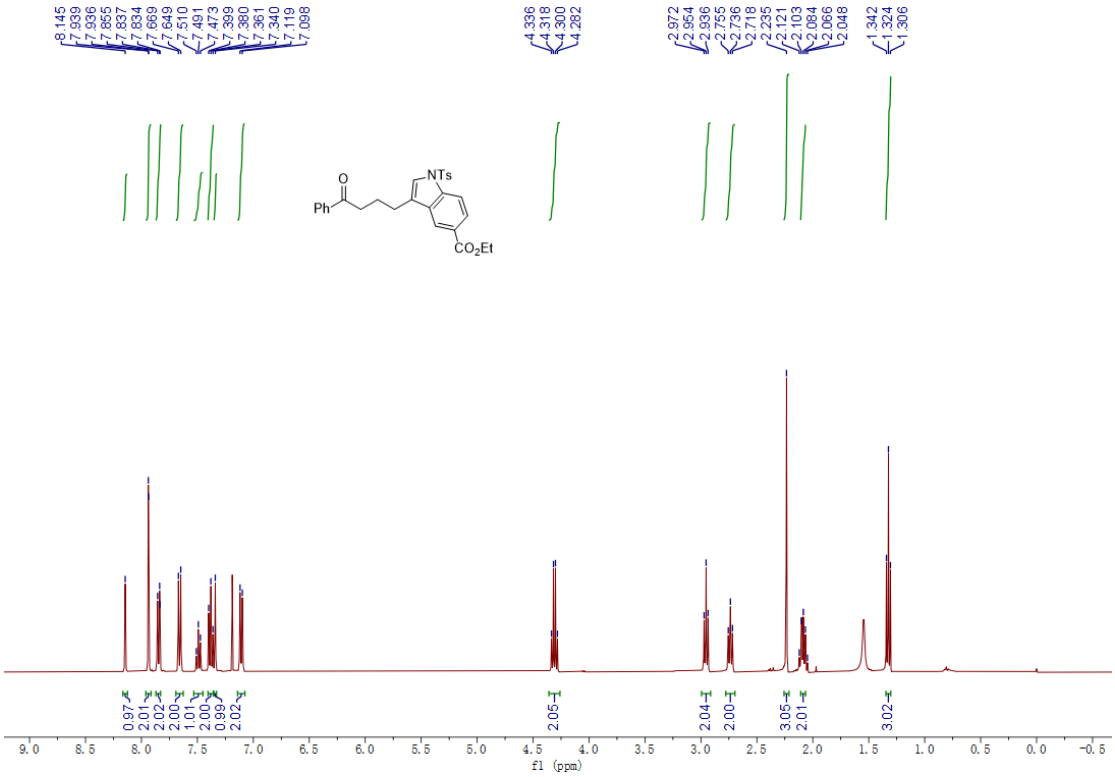
^{1}H NMR of **3ah** (400 MHz, $CDCl_3$)



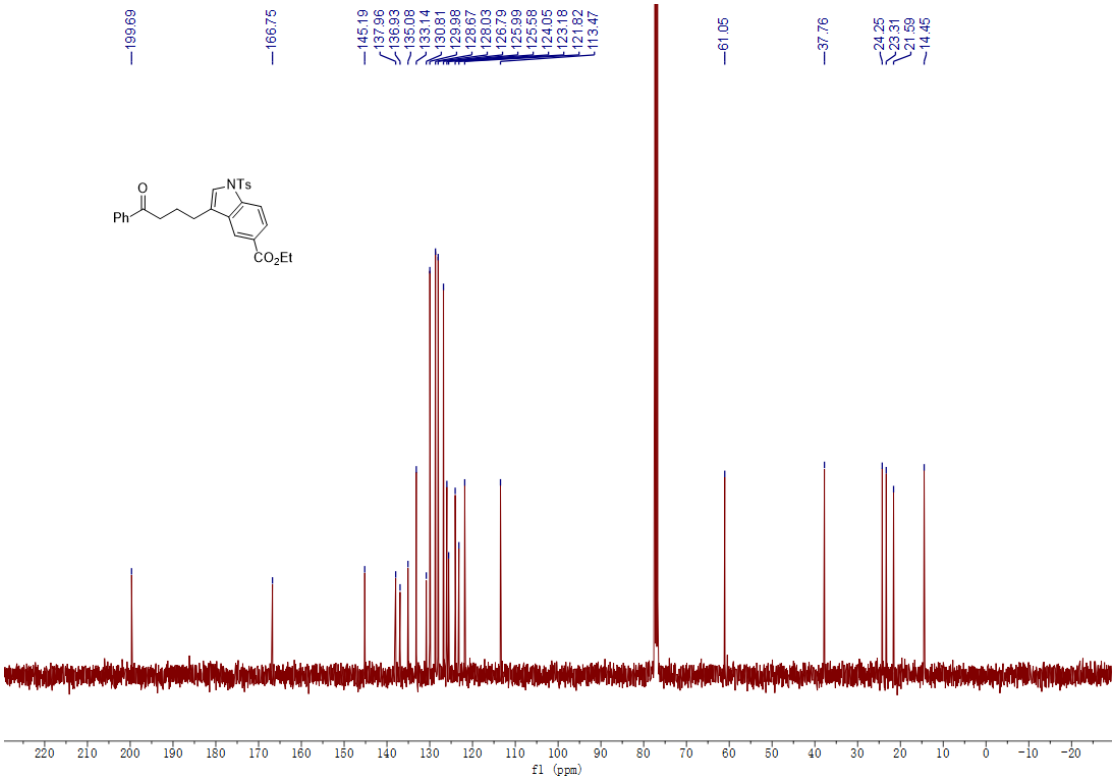
^{13}C NMR of **3ah** (100 MHz, $CDCl_3$)



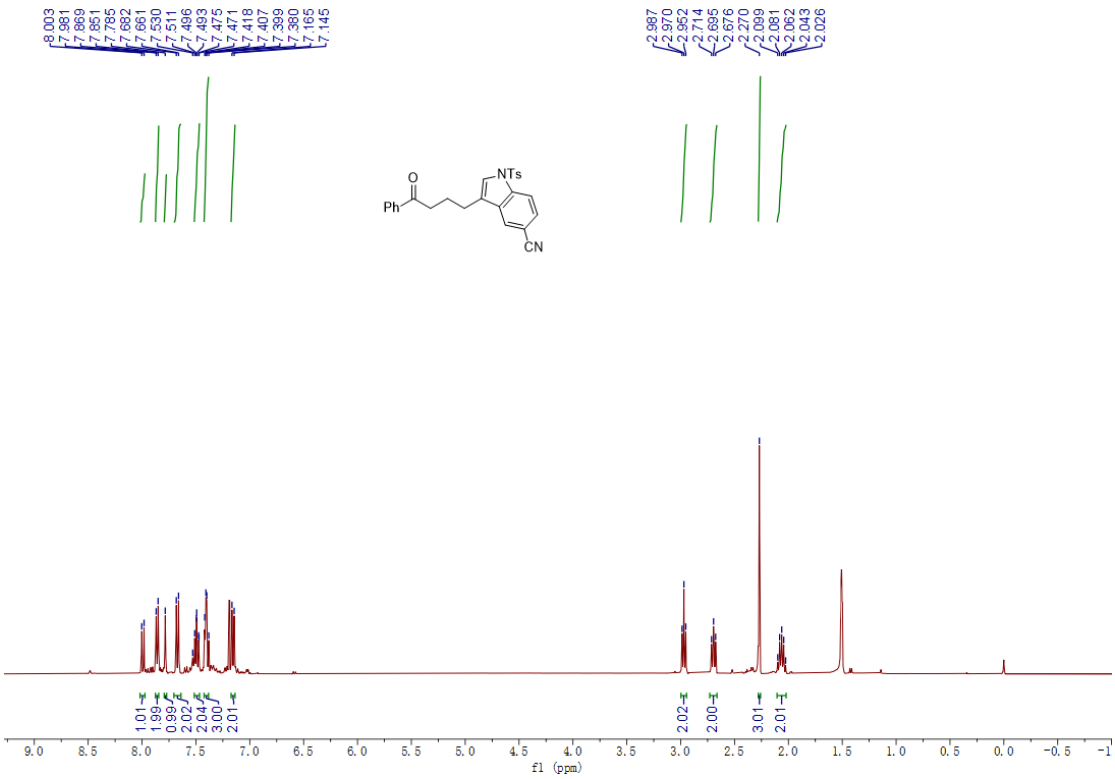
^{1}H NMR of **3ai** (400 MHz, $CDCl_3$)



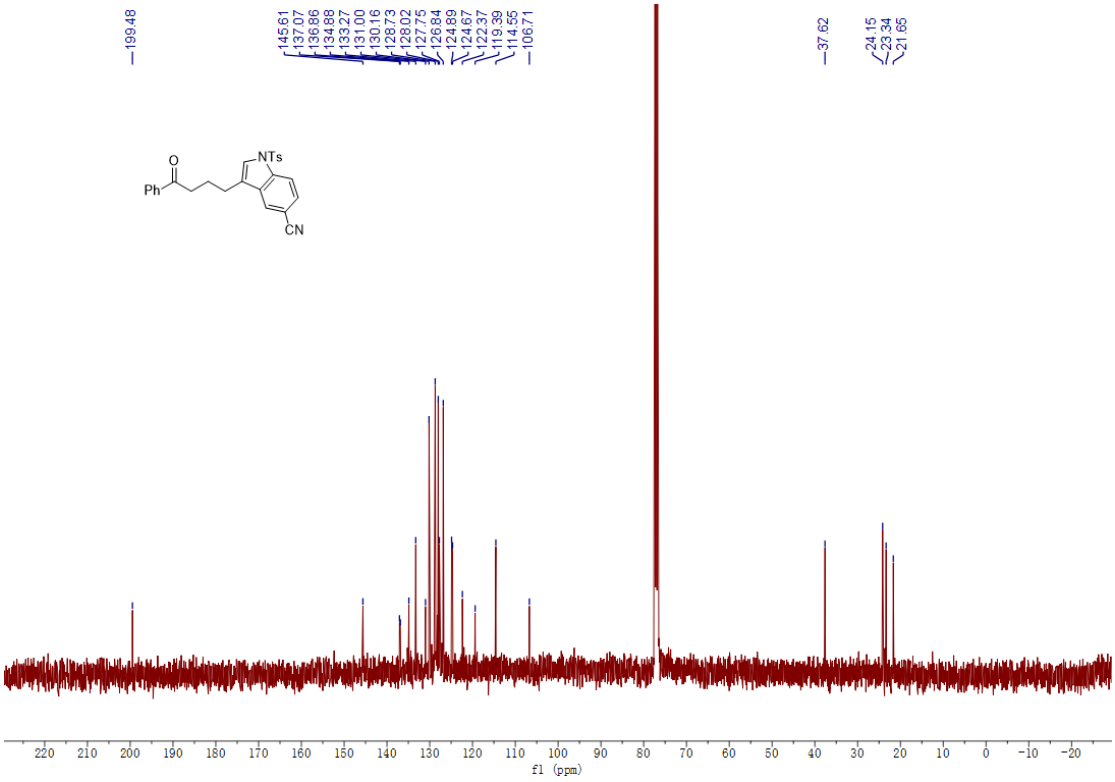
^{13}C NMR of **3ai** (100 MHz, $CDCl_3$)



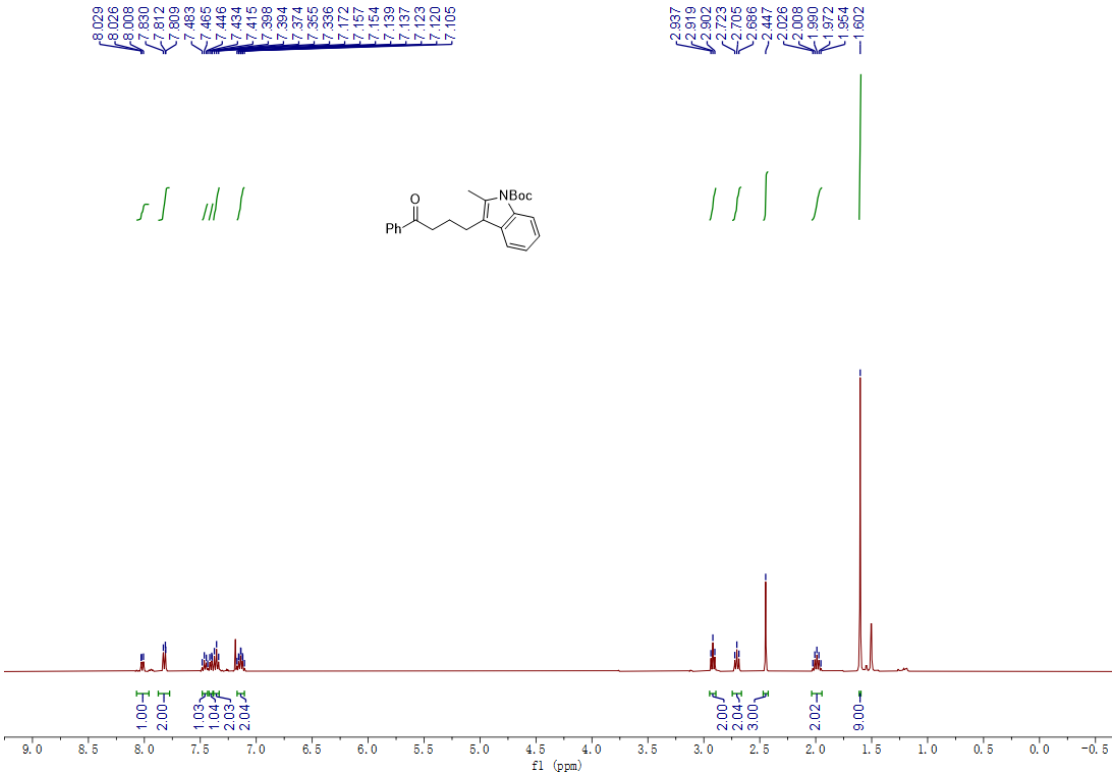
^{1}H NMR of **3aj** (400 MHz, $CDCl_3$)



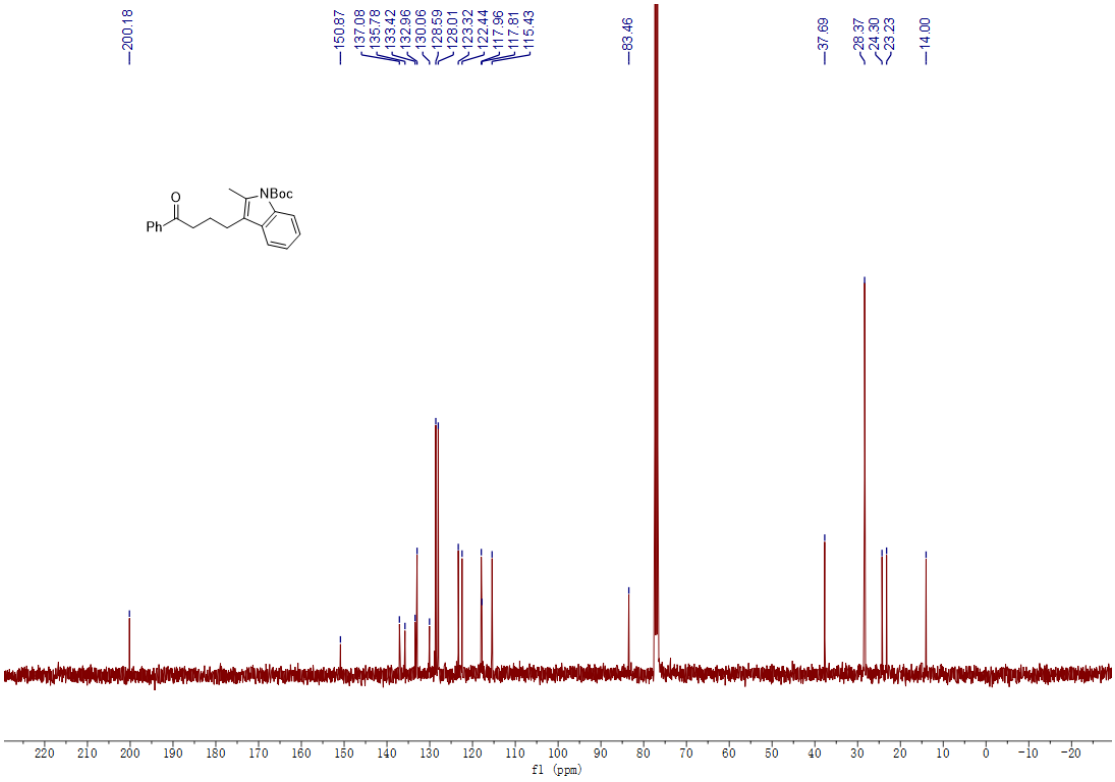
^{13}C NMR of **3aj** (100 MHz, $CDCl_3$)



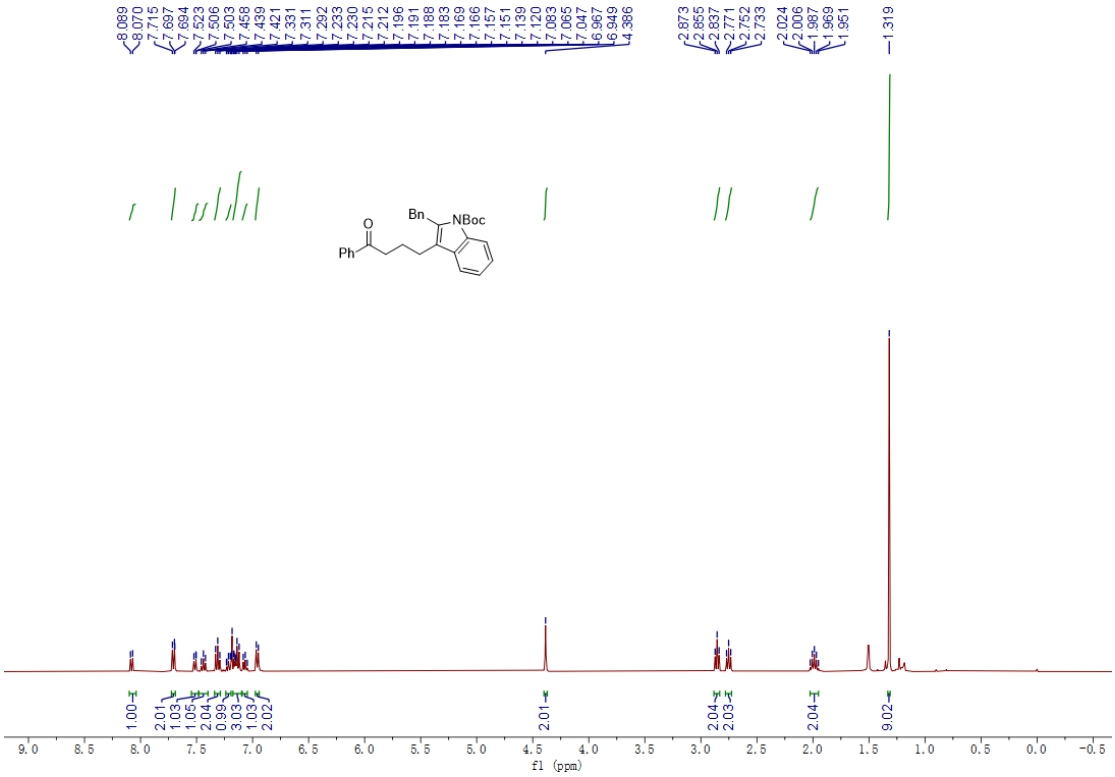
^{1}H NMR of **3ak** (400 MHz, $CDCl_3$)



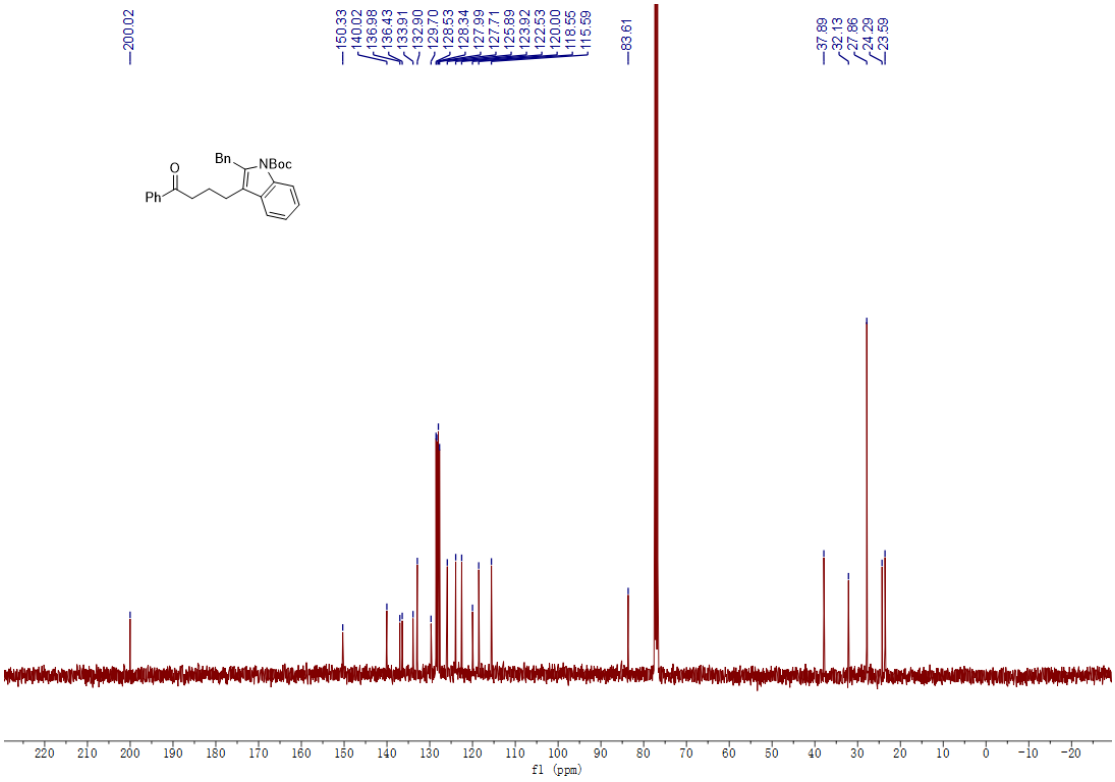
^{13}C NMR of **3ak** (100 MHz, $CDCl_3$)



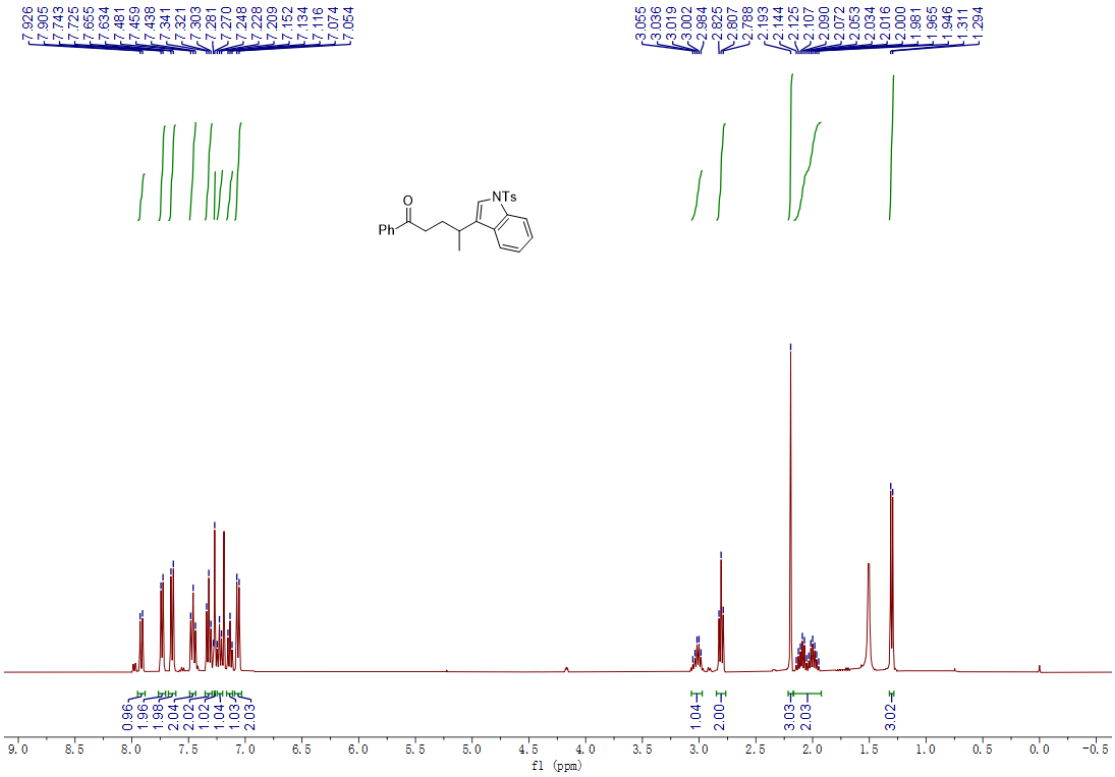
^{1}H NMR of **3al** (400 MHz, $CDCl_3$)



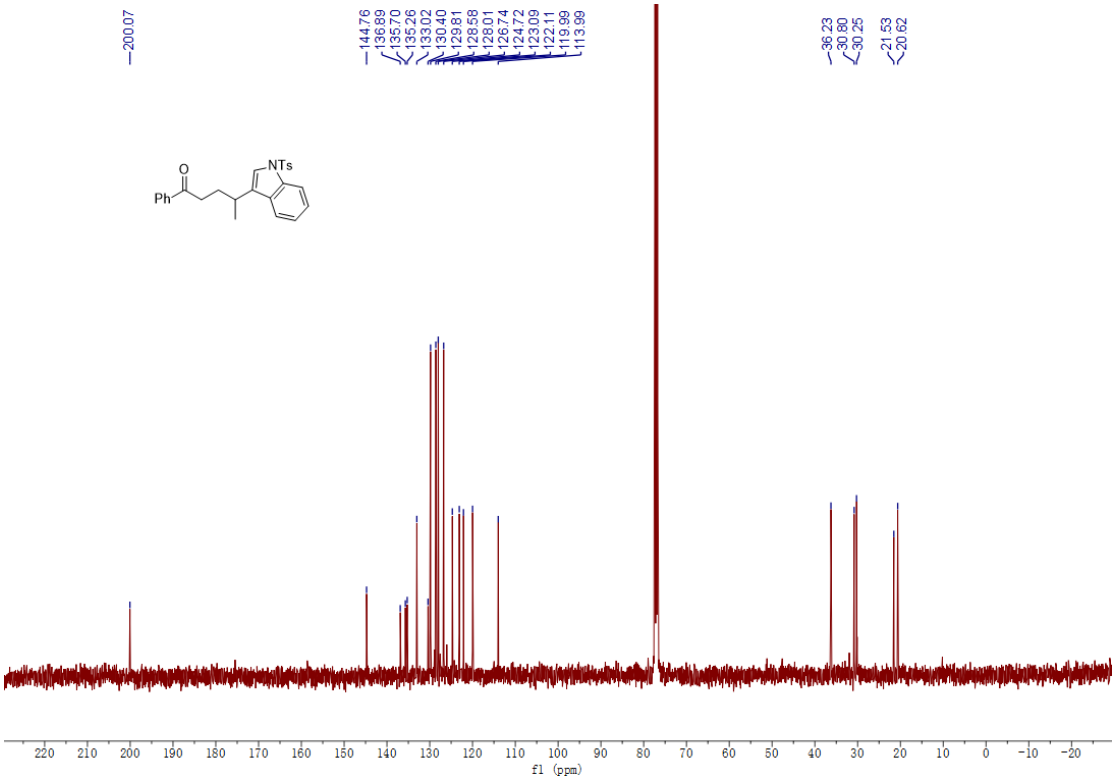
^{13}C NMR of **3al** (100 MHz, $CDCl_3$)



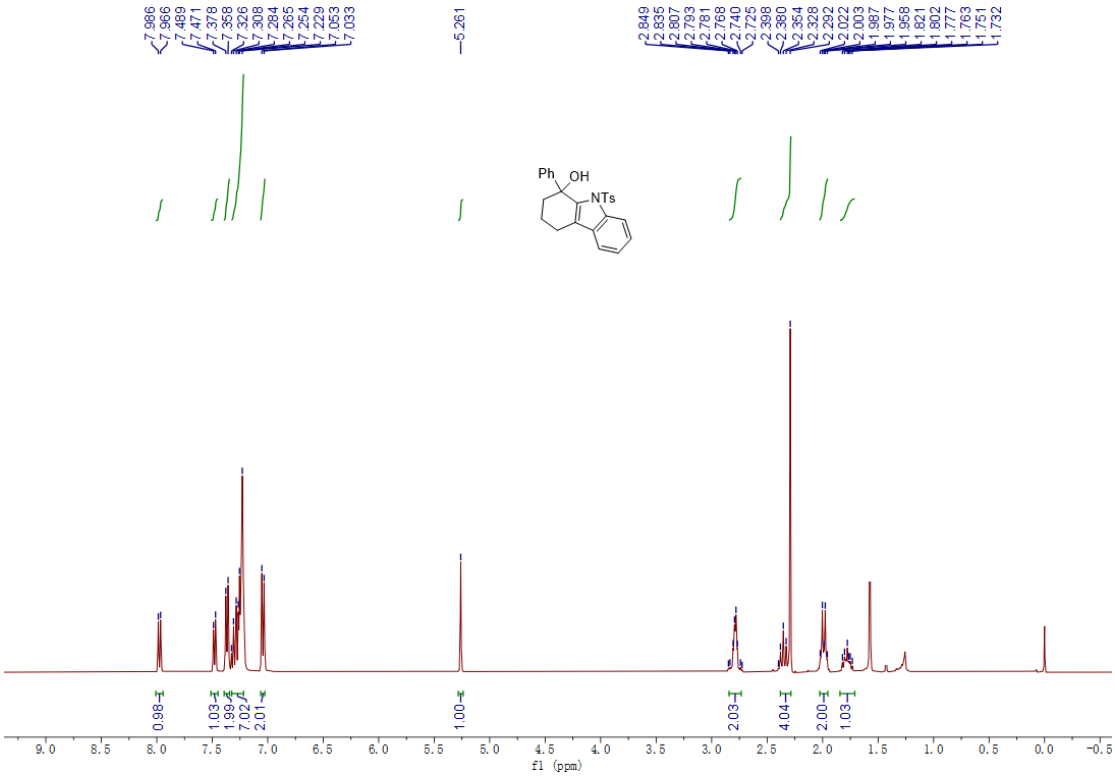
^{1}H NMR of **3am** (400 MHz, $CDCl_3$)



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



^{1}H NMR of **5** (400 MHz, $CDCl_3$)



^{13}C NMR of **5** (100 MHz, $CDCl_3$)