Supporting Information

Facile synthesis of 2-vinylindolines *via* a phosphine-mediated *α*-umpolung/Wittig olefination/cyclization cascade process

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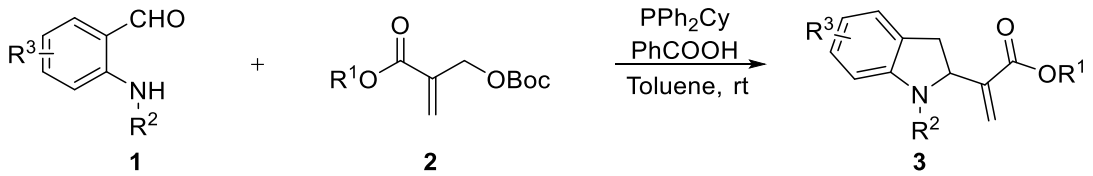
I. General Information

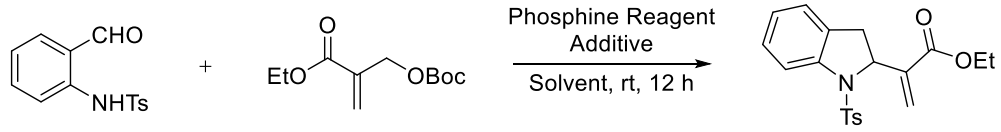
Unless otherwise specified, **all reactions** were carried out under a nitrogen atmosphere at room temperature. **All solvents** were purified according to the standard procedures. **All chemicals** which are commercially available were employed without further purification. **Thin-layer chromatography (TLC)** was performed on silica gel plates (GF254) using UV-light (254 and 365 nm). **Flash chromatography** was conducted on silica gel (200–300 mesh). **^{1}H and ^{13}C{^{1}H} NMR spectra** were recorded on a Bruker 400 MHz spectrometer. **Chemical shifts** were reported in parts per million (ppm). The **^{1}H NMR (400 MHz)** chemical shifts were measured relative to residual non-deuterated solvent resonance ($CDCl_3$: δ = 7.260 ppm, $(CD_3)_2CO$: δ = 2.050 ppm). The **^{13}C{^{1}H} NMR (100 MHz)** chemical shifts were given using $CDCl_3$ or $(CD_3)_2CO$ as the internal standard ($CDCl_3$: δ = 77.00 ppm, $(CD_3)_2CO$: δ = 29.84 ppm). **All high-resolution mass spectra (HR-MS)** were obtained on a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer solariX (Bruker Daltonik GmbH, Bremen, Germany). **Crystal measurement** was performed by Bruker D8 Venture X-ray diffractionmeter.

II. Representative Procedure of the Reaction



To a stirred solution of *o*-aminobenzaldehyde **1** (0.1 mmol, 1.0 equiv) and allyl carbonate **2** (0.15 mmol, 1.5 equiv) in toluene (2.0 mL) was added PPh_2Cy (0.12 mmol, 1.2 equiv) and benzoic acid (20 mol %) at room temperature. After the reaction of the raw material, the reaction mixture was purified without concentration via flash chromatography on silica gel (PE:EtOAc:DCM = 19:1:6) to afford compounds **3**.

Table S1. Optimization of the reaction conditions.[a]

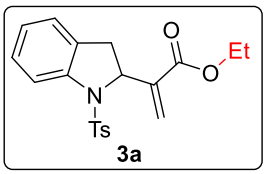


Entry	Phosphine	Solvent	Additive	Yield [%][b]
1	PPh_3	toluene	-	N.D.
2	$(2\text{-}MeC_6H_4)_3P$	toluene	-	N.R.
3	Ph_2MeP	toluene	-	trace
4	Ph_2PrP	toluene	-	trace
5	Ph_2CyP	toluene	-	30
6	$PhMe_2P$	toluene	-	N.D.
7	$PhCy_2P$	toluene		N.D.
8	PBu_3	toluene	-	trace
9	$(MeO)_3P$	toluene	-	N.D.
10	$(EtO)_3P$	toluene	-	N.D.
11	PPh_2Cy	DCM	-	20
12	PPh_2Cy	THF	-	trace
13	PPh_2Cy	MeCN	-	N.R.
14	PPh_2Cy	toluene	C_6H_5OH	28
15	PPh_2Cy	toluene	$4\text{-}NO_2C_6H_4OH$	41
16	***PPh_2Cy***	***toluene***	***$PhCO_2H$***	***88***
17	PPh_2Cy	toluene	CH_3CO_2H	53
18	PPh_2Cy	toluene	CH_3CO_2Na	26
19	PPh_2Cy	toluene	$PhCO_2Na$	31
20	PPh_2Cy	toluene	$NaHCO_3$	17
21	PPh_2Cy	toluene	$KHCO_3$	22
22[c]	PPh_2Cy	toluene	$PhCO_2H$	58
23[d]	PPh_2Cy	toluene	$PhCO_2H$	49

[a]Unless otherwise stated, all reactions were performed with **1a** (0.1 mmol), **2a** (0.15 mmol), the phosphine reagent (0.12 mmol) and the additive (20 mol%) in the solvent specified (2.0 mL) at room temperature. [b]Isolated yield. [c]The additive (10 mol%) in the solvent specified (2.0 mL). [d]The additive (30 mol%) in the solvent specified (2.0 mL).

III. Analytical Data

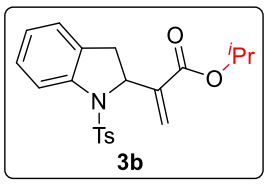
Ethyl 2-(1-tosylindolin-2-yl)acrylate (3a)



3a

The **3a** was prepared according to the general procedure described above using **1a** (27.5 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (32.5 mg, 88% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (d, J = 8.1 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.25 – 7.20 (m, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.05 – 6.97 (m, 2H), 6.34 (s, 1H), 6.04 (s, 1H), 5.16 – 5.11 (m, 1H), 4.30 – 4.16 (m, 2H), 3.10 (dd, J = 16.5, 10.2 Hz, 1H), 2.61 (dd, J = 16.5, 3.0 Hz, 1H), 2.36 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.8, 144.1, 141.6, 140.1, 134.7, 131.1, 129.7, 127.9, 127.1, 125.7, 125.2, 124.9, 117.0, 61.3, 61.0, 36.2, 21.5, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{20}H_{21}NO_4SNa^+$ $[M+Na]^+$: 394.1083, found 394.1098.

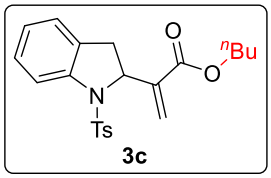
Isopropyl 2-(1-tosylindolin-2-yl)acrylate (3b)



3b

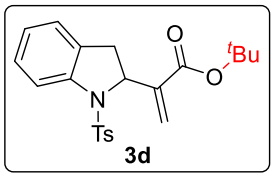
The **3b** was prepared according to the general procedure described above using **1a** (27.5 mg, 0.1 mmol), **2b** (36.6 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (32.4 mg, 84% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.72 (d, J = 8.1 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.26 – 7.20 (m, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.05 – 6.98 (m, 2H), 6.31 (s, 1H), 6.01 (s, 1H), 5.16 – 5.11 (m, 1H), 5.11 – 5.03 (m, 1H), 3.09 (dd, J = 16.5, 10.2 Hz, 1H), 2.61 (dd, J = 16.5, 3.1 Hz, 1H), 2.36 (s, 3H), 1.26 (dd, J = 6.3, 2.9 Hz, 6H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.3, 144.0, 141.6, 140.4, 134.8, 131.2, 129.6, 127.8, 127.1, 125.4, 125.2, 124.9, 117.0, 68.5, 61.4, 36.2, 21.78, 21.75, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{21}H_{23}NO_4SNa^+$ $[M+Na]^+$: 408.1240, found 408.1234.

Butyl 2-(1-tosylindolin-2-yl)acrylate (3c)



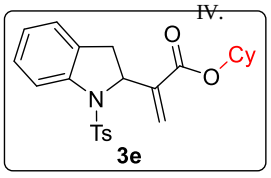
The **3c** was prepared according to the general procedure described above using **1a** (27.5 mg, 0.1 mmol), **2c** (38.7 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (33.7 mg, 85% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73 (d, J = 8.1 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.26 – 7.21 (m, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.06 – 6.98 (m, 2H), 6.33 (s, 1H), 6.03 (s, 1H), 5.17 – 5.11 (m, 1H), 4.23 – 4.12 (m, 2H), 3.09 (dd, J = 16.6, 10.2 Hz, 1H), 2.61 (dd, J = 16.6, 3.1 Hz, 1H), 2.36 (s, 3H), 1.69 – 1.62 (m, 2H), 1.43 – 1.37 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.8, 144.1, 141.6, 140.1, 134.6, 131.1, 129.6, 127.8, 127.1, 125.6, 125.2, 124.9, 117.0, 64.8, 61.3, 36.2, 30.6, 21.5, 19.2, 13.7. **HRMS (ESI)** m/z: calcd. for $C_{22}H_{25}NO_4SNa^+$ $[M+Na]^+$: 422.1397, found 422.1381.

Tert-Butyl 2-(1-tosylindolin-2-yl)acrylate (3d)



The **3d** was prepared according to the general procedure described above using **1a** (27.5 mg, 0.1 mmol), **2d** (38.7 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (34.7 mg, 87% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). **^{1}H NMR (400 MHz, CDCl3)** δ 7.72 (d, J = 8.2 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.25 – 7.20 (m, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.05 – 6.97 (m, 2H), 6.22 (s, 1H), 5.96 (s, 1H), 5.16 – 5.08 (m, 1H), 3.05 (dd, J = 16.6, 10.2 Hz, 1H), 2.59 (dd, J = 16.6, 3.0 Hz, 1H), 2.35 (s, 3H), 1.48 (s, 9H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.0, 144.0, 141.6, 141.3, 134.7, 131.3, 129.6, 127.8, 127.1, 125.2, 124.9, 124.8, 117.1, 81.4, 61.4, 36.2, 28.1, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{22}H_{25}NO_4SNa^+$ $[M+Na]^+$: 422.1397, found 422.1409.

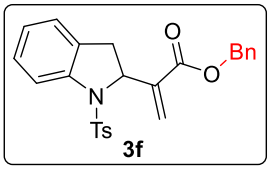
Cyclohexyl 2-(1-tosylindolin-2-yl)acrylate (3e)



The **3e** was prepared according to the general procedure described above using **1a** (27.5 mg, 0.1 mmol), **2e** (42.6 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (22.4 mg, 53% yield) after flash column

chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). **^{1}H NMR (400 MHz, CDCl3)** δ 7.73 (d, J = 8.1 Hz, 1H), 7.62 – 7.53 (m, 2H), 7.25 – 7.20 (m, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.07 – 6.96 (m, 2H), 6.32 (s, 1H), 6.01 (s, 1H), 5.20 – 5.08 (m, 1H), 4.93 – 4.81 (m, 1H), 3.08 (dd, J = 16.6, 10.2 Hz, 1H), 2.62 (dd, J = 16.6, 3.1 Hz, 1H), 2.36 (s, 3H), 1.89 – 1.68 (m, 4H), 1.56 – 1.36 (m, 6H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.1, 144.0, 141.6, 140.5, 134.7, 131.2, 129.6, 127.8, 127.1, 125.4, 125.2, 124.9, 117.0, 73.2, 61.4, 36.2, 31.5, 25.4, 23.6, 21.6. **HRMS (ESI)** m/z: calcd. for $C_{24}H_{27}NO_4SNa^+$ $[M+Na]^+$: 448.1553, found 448.1551.

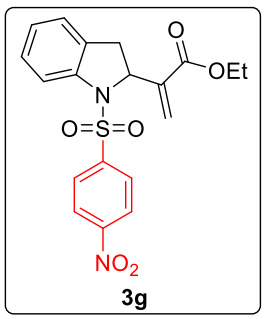
Benzyl 2-(1-tosylindolin-2-yl)acrylate (3f)



3f

The **3f** was prepared according to the general procedure described above using **1a** (27.5 mg, 0.1 mmol), **2f** (43.9 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (20.2 mg, 46% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.74 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.44 – 7.30 (m, 5H), 7.26 – 7.20 (m, 1H), 7.17 (d, J = 8.1 Hz, 2H), 7.05 – 6.97 (m, 2H), 6.40 (s, 1H), 6.08 (s, 1H), 5.22 (d, J = 3.0 Hz, 2H), 5.19 – 5.14 (m, 1H), 3.09 (dd, J = 16.6, 10.2 Hz, 1H), 2.62 (dd, J = 16.6, 3.1 Hz, 1H), 2.36 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.6, 144.1, 141.5, 139.9, 135.6, 134.6, 131.0, 129.6, 128.6, 128.3, 128.1, 127.8, 127.1, 126.2, 125.2, 124.9, 117.0, 66.7, 61.2, 36.2, 21.5. **HRMS (ESI)** m/z: calcd. for $C_{25}H_{23}NO_4SNa^+$ $[M+Na]^+$: 456.1240, found 456.1241.

Ethyl 2-(1-((4-nitrophenyl)sulfonyl)indolin-2-yl)acrylate (3g)

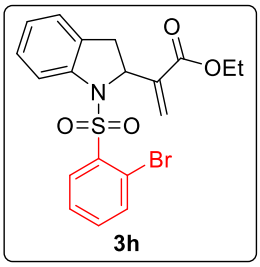


3g

The **3g** was prepared according to the general procedure described above using **1b** (30.6 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (25.2 mg, 63% yield) after flash column chromatography on silica gel

(PE:EtOAc:DCM = 19:1:6). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.25 (d, J = 8.7 Hz, 2H), 7.90 (d, J = 8.7 Hz, 2H), 7.74 (d, J = 8.1 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.11 – 7.01 (m, 2H), 6.36 (s, 1H), 6.01 (s, 1H), 5.16 (d, J = 7.8 Hz, 1H), 4.32 – 4.15 (m, 2H), 3.12 (dd, J = 16.7, 10.2 Hz, 1H), 2.68 (dd, J = 16.7, 3.0 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.5, 150.4, 143.2, 140.6, 139.7, 130.9, 128.3, 128.2, 125.8, 125.67, 125.65, 124.3, 116.6, 61.6, 61.2, 36.2, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{19}H_{18}N_2O_6SNa^+$ $[M+Na]^+$: 425.0778, found 425.0787.

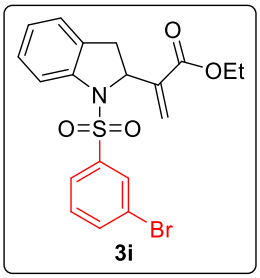
Ethyl 2-(1-((2-bromophenyl)sulfonyl)indolin-2-yl)acrylate (3h)



3h

The **3h** was prepared according to the general procedure described above using **1c** (33.9 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (23.9 mg, 55% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 121.0 – 122.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.22 (dd, J = 7.9, 1.7 Hz, 1H), 7.66 (d, J = 7.7 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.39 – 7.33 (m, 1H), 7.28 (s, 1H), 7.12 – 7.04 (m, 2H), 6.97 – 6.91 (m, 1H), 6.32 (s, 1H), 6.02 (d, J = 1.4 Hz, 1H), 5.75 (d, J = 10.0 Hz, 1H), 4.32 – 4.17 (m, 2H), 3.62 (dd, J = 16.3, 10.0 Hz, 1H), 2.81 (dd, J = 16.3, 2.0 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.6, 140.7, 139.8, 138.0, 135.7, 134.0, 133.3, 129.9, 127.5, 127.4, 125.6, 125.3, 123.9, 120.1, 114.2, 63.1, 61.0, 36.0, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{19}H_{18}BrNO_4SNa^+$ $[M+Na]^+$: 458.0032, found 458.0038.

Ethyl 2-(1-((3-bromophenyl)sulfonyl)indolin-2-yl)acrylate (3i)

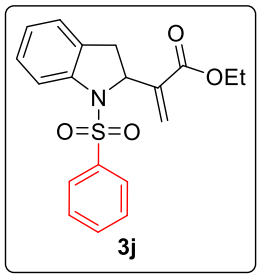


3i

The **3i** was prepared according to the general procedure described above using **1d** (33.9 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (24.0 mg, 55% yield) after flash column chromatography on silica gel

(PE:EtOAc:DCM = 19:1:6). m.p.: 33.8 – 34.5 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (t, J = 1.8 Hz, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.28 (d, J = 7.9 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.09 – 7.01 (m, 2H), 6.34 (s, 1H), 6.01 (s, 1H), 5.18 – 5.12 (m, 1H), 4.31 – 4.16 (m, 2H), 3.16 (dd, J = 16.6, 10.2 Hz, 1H), 2.67 (dd, J = 16.7, 3.0 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.6, 141.0, 139.9, 139.5, 136.2, 130.9, 130.5, 130.0, 128.0, 125.7, 125.5, 125.4, 125.3, 123.0, 116.6, 61.5, 61.0, 36.2, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{19}H_{18}BrNO_4SNa^+$ $[M+Na]^+$: 458.0032, found 458.0031.

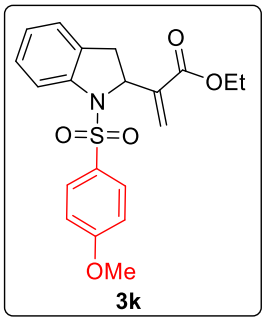
Ethyl 2-(1-(phenylsulfonyl)indolin-2-yl)acrylate (3j)



3j

The **3j** was prepared according to the general procedure described above using **1e** (26.1 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (23.6 mg, 66% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 128.0 – 131.0 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.75 (d, J = 8.1 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.57 – 7.50 (m, 1H), 7.44 – 7.37 (m, 2H), 7.25 – 7.19 (m, 1H), 7.08 – 7.01 (m, 1H), 7.01 – 6.96 (m, 1H), 6.34 (s, 1H), 6.03 (s, 1H), 5.21 – 5.10 (m, 1H), 4.30 – 4.16 (m, 2H), 3.08 (dd, J = 16.6, 10.2 Hz, 1H), 2.62 (dd, J = 16.6, 3.0 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.7, 141.4, 140.0, 137.6, 133.2, 131.1, 129.0, 127.9, 127.0, 125.7, 125.3, 125.0, 116.9, 61.3, 61.0, 36.2, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{19}H_{19}NO_4SNa^+$ $[M+Na]^+$: 380.0927, found 380.0935.

Ethyl 2-(1-((4-methoxyphenyl)sulfonyl)indolin-2-yl)acrylate (3k)

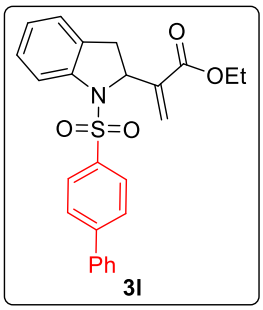


3k

The **3k** was prepared according to the general procedure described above using **1f** (29.1 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (34.4 mg, 89% yield) after flash column chromatography on silica gel

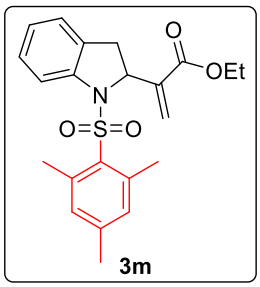
(PE:EtOAc:DCM = 19:1:6). **^{1}H NMR (400 MHz, $CDCl_3$)** δ7.73 (d, J = 8.1 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.25 – 7.20 (m, 1H), 7.06 – 6.97 (m, 2H), 6.88 – 6.81 (m, 2H), 6.33 (s, 1H), 6.04 (s, 1H), 5.16 – 5.09 (m, 1H), 4.30 – 4.15 (m, 2H), 3.81 (s, 3H), 3.11 (dd, J = 16.6, 10.2 Hz, 1H), 2.62 (dd, J = 16.6, 3.0 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ. 165.8, 163.2, 141.6, 140.2, 131.1, 129.24, 129.16, 127.8, 125.6, 125.2, 124.9, 117.0, 114.2, 61.2, 60.9, 55.5, 36.2, 14.1 **HRMS (ESI)** m/z: calcd. for $C_{20}H_{21}NO_5SNa^+$ $[M+Na]^+$: 410.1033, found 410.1025.

Ethyl 2-(1-([1,1'-biphenyl]-4-ylsulfonyl)indolin-2-yl)acrylate (3l)



The **3l** was prepared according to the general procedure described above using **1g** (33.7 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (22.3 mg, 51% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 122.0 – 123.8 ^{o}C. **^{1}H NMR (400 MHz, CDCl3)** δ 7.82 – 7.74 (m, 3H), 7.60 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.3 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.04 (q, J = 7.6 Hz, 2H), 6.36 (s, 1H), 6.07 (s, 1H), 5.28 – 5.16 (m, 1H), 4.33 – 4.17 (m, 2H), 3.16 (dd, J = 16.6, 10.2 Hz, 1H), 2.66 (dd, J = 16.6, 2.9 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.7, 145.9, 141.4, 140.1, 138.9, 136.1, 131.1, 129.0, 128.5, 127.9, 127.6, 127.5, 127.2, 125.7, 125.3, 125.0, 116.9, 61.3, 61.0, 36.2, 14.1. **HRMS (ESI)** m/z: alcd. for $C_{25}H_{23}NO_4SNa^+$ $[M+Na]^+$: 456.1240, found 456.1240.

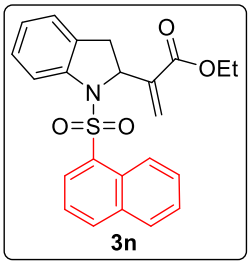
Ethyl 2-(1-(mesitylsulfonyl)indolin-2-yl)acrylate (3m)



The **3m** was prepared according to the general procedure described above using **1h** (30.3 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (27.9 mg, 70% yield) after flash column chromatography on silica gel

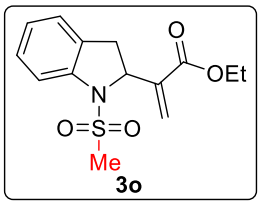
(PE:EtOAc:DCM = 19:1:6). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.21 (d, J = 7.6 Hz, 1H), 7.13 – 7.08 (m, 2H), 6.99 – 6.94 (m, 1H), 6.92 (s, 2H), 6.19 (s, 1H), 5.86 (s, 1H), 5.30 – 5.25 (m, 1H), 4.25 – 4.12 (m, 2H), 3.51 (dd, J = 16.3, 10.0 Hz, 1H), 2.75 (dd, J = 16.4, 2.4 Hz, 1H), 2.57 (s, 6H), 2.28 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.6, 143.0, 142.4, 140.4, 139.5, 132.9, 132.2, 130.9, 127.6, 125.4, 123.8, 115.2, 61.0, 60.9, 36.5, 23.0, 21.0, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{22}H_{25}NO_4SNa^+$ $[M+Na]^+$: 422.1397, found 422.1387.

Ethyl 2-(1-(naphthalen-1-ylsulfonyl)indolin-2-yl)acrylate (3n)



The **3n** was prepared according to the general procedure described above using **1i** (31.1 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (24.9 mg, 62% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 80.5 – 82.1 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.56 (d, J = 8.4 Hz, 1H), 8.26 – 8.19 (m 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.88 – 7.83 (m 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.24 – 7.16 (m 1H), 7.02 – 6.91 (m, 2H), 6.27 (s, 1H), 5.99 (d, J = 1.4 Hz, 1H), 5.36 – 5.29 (m 1H), 4.26 – 4.13 (m, 2H), 3.01 (dd, J = 16.4, 9.9 Hz, 1H), 2.60 (dd, J = 16.3, 2.2 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.6, 141.6, 139.5, 134.6, 134.3, 133.8, 130.7, 130.4, 128.8, 128.7, 128.0, 127.6, 126.9, 125.7, 125.3, 124.7, 124.0, 116.6, 61.6, 60.9, 36.1, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{23}H_{21}NO_4SNa^+$ $[M+Na]^+$: 430.1083, found 430.1087.

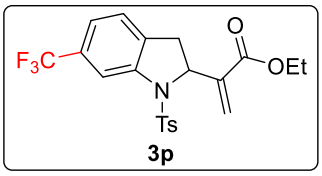
Ethyl 2-(1-(methylsulfonyl)indolin-2-yl)acrylate (3o)



The **3o** was prepared according to the general procedure described above using **1j** (19.9 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (18.2 mg, 62%

yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 (d, J = 8.0 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.17 (d, J = 7.4 Hz, 1H), 7.11 – 7.04 (m, 1H), 6.34 (s, 1H), 5.98 (s, 1H), 5.29 – 5.17 (m, 1H), 4.33 – 4.17 (m, 2H), 3.69 (dd, J = 16.7, 10.4 Hz, 1H), 2.87 (m, 4H), 1.30 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.7, 141.4, 140.4, 130.2, 128.2, 125.5, 124.8, 115.5, 61.6, 61.0, 36.6, 36.1, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{14}H_{17}NO_4SNa^+$ $[M+Na]^+$: 318.0770, found 318.0770.

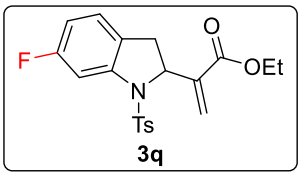
Ethyl 2-(1-tosyl-6-(trifluoromethyl)indolin-2-yl)acrylate (3p)



3p

The **3p** was prepared according to the general procedure described above using **1k** (34.3 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a reddish brown oily liquid (24.9 mg, 57% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.97 (s, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 7.8 Hz, 1H), 7.22 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.8 Hz, 1H), 6.37 (s, 1H), 6.03 (s, 1H), 5.26 – 5.13 (m, 1H), 4.33 – 4.16 (m, 2H), 3.19 (dd, J = 17.1, 10.4 Hz, 1H), 2.72 (dd, J = 17.1, 3.0 Hz, 1H), 2.37 (s, 3H), 1.30 (d, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ165.5, 144.6, 142.3, 139.9, 135.0, 134.4, 130.5 (q, J = 33 Hz), 129.9, 127.1, 126.0, 125.5, 123.9 (d, J = 270 Hz), 121.7 (q, J = 4 Hz), 113.4 (q, J = 33 Hz), 61.7, 61.1, 36.2, 21.6, 14.1. **^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$)** δ -62.2. **HRMS (ESI)** m/z: calcd. for $C_{21}H_{20}F_3NO_4SNa^+$ $[M+Na]^+$: 462.0957, found 462.0967.

Ethyl 2-(6-fluoro-1-tosylindolin-2-yl)acrylate (3q)

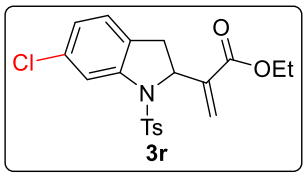


3q

The **3q** was prepared according to the general procedure described above using **1l** (29.3 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a white solid (19.7 mg, 51% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 79.2 – 80.2 ^{o}C. **^{1}H**

NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.2 Hz, 2H), 7.50 – 7.44 (m, 1H), 7.22 (d, J = 8.0 Hz, 2H), 6.95 – 6.89 (m, 1H), 6.75 – 6.67 (m, 1H), 6.35 (s, 1H), 6.01 (s, 1H), 5.20 – 5.14 (m, 1H), 4.30 – 4.16 (m, 2H), 3.09 (dd, J = 16.3, 10.4 Hz, 1H), 2.60 (dd, J = 16.3, 3.2 Hz, 1H), 2.38 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 165.6, 163.6 (d, J = 242 Hz), 144.4, 142.9 (d, J = 11 Hz), 140.0, 134.6, 129.8, 127.1, 126.2 (d, J = 3 Hz), 125.8, 125.8 (d, J = 3 Hz), 111.5 (d, J = 23 Hz), 104.7 (d, J = 28 Hz), 62.2, 61.0, 35.6, 21.6, 14.1. **$^{19}F\{^1H\}$ NMR (376 MHz, $CDCl_3$)** δ -113.6. **HRMS (ESI)** m/z: calcd. for $C_{20}H_{20}FNO_4SNa^+$ $[M+Na]^+$: 412.0989, found 412.0989.

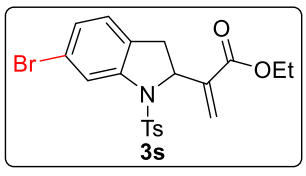
Ethyl 2-(6-chloro-1-tosylindolin-2-yl)acrylate (3r)



3r

The **3r** was prepared according to the general procedure described above using **1m** (30.9 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (19.5 mg, 48% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 87.2 – 88.3 ^oC. **^1H NMR (400 MHz, $CDCl_3$)** δ 7.74 (d, J = 1.9 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.99 (dd, J = 8.0, 1.9 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.35 (s, 1H), 6.01 (s, 1H), 5.18 – 5.11 (m, 1H), 4.30 – 4.15 (m, 2H), 3.08 (dd, J = 16.7, 10.4 Hz, 1H), 2.60 (dd, J = 16.7, 3.2 Hz, 1H), 2.38 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 165.6, 144.4, 142.8, 139.9, 134.5, 133.5, 129.9, 129.5, 127.1, 125.9, 125.8, 124.9, 117.0, 61.9, 61.1, 35.8, 21.6, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{20}H_{20}ClNO_4SH^+$ $[M+H]^+$: 406.0874, found 406.0863.

Ethyl 2-(6-bromo-1-tosylindolin-2-yl)acrylate (3s)

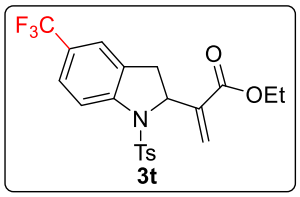


3s

The **3s** was prepared according to the general procedure described above using **1n** (35.3 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (22.3 mg, 50% yield) after flash

column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 95.2 – 96.8 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.89 (d, J = 1.7 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.14 (dd, J = 7.9, 1.8 Hz, 1H), 6.86 (d, J = 7.9 Hz, 1H), 6.35 (s, 1H), 6.01 (s, 1H), 5.16 – 5.11 (m, 1H), 4.30 – 4.16 (m, 2H), 3.05 (dd, J = 16.9, 10.3 Hz, 1H), 2.59 (dd, J = 16.8, 3.2 Hz, 1H), 2.38 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.6, 144.4, 143.0, 139.8, 134.4, 130.1, 129.8, 127.8, 127.1, 126.4, 125.8, 121.1, 119.8, 61.8, 61.0, 35.8, 21.6, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{20}H_{20}BrNO_4SNa^+$ $[M+Na]^+$: 472.0189, found 472.0185.

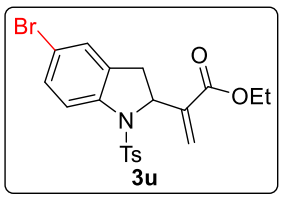
Ethyl 2-(1-tosyl-5-(trifluoromethyl)indolin-2-yl)acrylate (3t)



3t

The **3t** was prepared according to the general procedure described above using **1o** (34.3 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (23.3 mg, 53% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (d, J = 8.5 Hz, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.4 Hz, 1H), 7.26 – 7.20 (m, 3H), 6.36 (s, 1H), 6.00 (s, 1H), 5.20 (dd, J = 10.4, 3.3 Hz, 1H), 4.30 – 4.16 (m, 2H), 3.22 (dd, J = 16.8, 10.5 Hz, 1H), 2.73 (dd, J = 16.9, 3.4 Hz, 1H), 2.38 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.5, 144.7, 144.6, 139.9, 134.6, 131.5, 129.9, 127.0, 126.7 (q, J = 32 Hz), 126.0, 125.5 (q, J = 4 Hz), 122.7, 122.4 (q, J = 4 Hz), 116.0, 61.8, 61.1, 36.0, 21.5, 14.1. **^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$)** δ -61.9. **HRMS (ESI)** m/z: calcd. for $C_{21}H_{20}F_3NO_4SNa^+$ $[M+Na]^+$: 462.0957, found 462.0962.

Ethyl 2-(5-bromo-1-tosylindolin-2-yl)acrylate (3u)

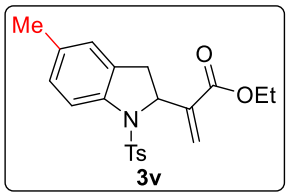


3u

The **3u** was prepared according to the general procedure described above using **1p** (35.3 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (21.2 mg, 47% yield)

after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 113.7 – 115.0 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (d, J = 8.5 Hz, 1H), 7.57 (d, J = 8.1 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.21 (d, J = 8.0 Hz, 2H), 7.12 (s, 1H), 6.34 (s, 1H), 6.01 (s, 1H), 5.17 – 5.08 (m, 1H), 4.30-4.16 (m, 2H), 3.08 (dd, J = 16.8, 10.3 Hz, 1H), 2.61 (dd, J = 16.9, 3.1 Hz, 1H), 2.38 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.6, 144.4, 140.9, 139.8, 134.4, 133.5, 130.8, 129.8, 128.3, 127.1, 125.9, 118.2, 117.7, 61.6, 61.1, 36.0, 21.6, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{20}H_{20}BrNO_4SNa^+$ $[M+Na]^+$: 472.0189, found 472.0193.

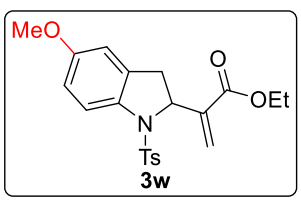
Ethyl 2-(5-methyl-1-tosylindolin-2-yl)acrylate (3v)



3v

The **3v** was prepared according to the general procedure described above using **1q** (28.9 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (23.6 mg, 61% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 165.0 – 165.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.60 (d, J = 8.2 Hz, 1H), 7.58 – 7.53 (m, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.02 (dd, J = 8.2, 1.6 Hz, 1H), 6.80 (s, 1H), 6.32 (s, 1H), 6.03 (s, 1H), 5.14 – 5.08 (m, 1H), 4.30 – 4.16 (m, 2H), 3.02 (dd, J = 16.5, 10.1 Hz, 1H), 2.55 (dd, J = 16.5, 3.0 Hz, 1H), 2.35 (s, 3H), 2.25 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.8, 144.0, 140.2, 139.2, 134.8, 134.7, 131.2, 129.6, 128.4, 127.1, 125.8, 125.5, 116.8, 61.4, 60.9, 36.1, 21.5, 20.9, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{21}H_{23}NO_4SNa^+$ $[M+Na]^+$: 408.1240, found 408.1243.

Ethyl 2-(5-methoxy-1-tosylindolin-2-yl)acrylate (3w)

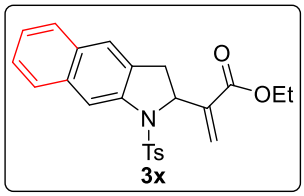


3w

The **3w** was prepared according to the general procedure described above using **1r** (30.5 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (25.6 mg, 64%

yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 148.0 – 149.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, J = 8.8 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.17 (d, J = 8.1 Hz, 2H), 6.76 (dd, J = 8.8, 2.7 Hz, 1H), 6.53 (d, J = 2.6 Hz, 1H), 6.31 (s, 1H), 6.04 (s, 1H), 5.14 – 5.06 (m, 1H), 4.30 – 4.13 (m, 2H), 3.73 (s, 3H), 2.95 (dd, J = 16.6, 10.0 Hz, 1H), 2.52 (dd, J = 16.7, 2.8 Hz, 1H), 2.35 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.7, 157.6, 143.9, 139.8, 134.8, 134.4, 133.1, 129.6, 127.1, 125.6, 118.3, 112.9, 110.8, 61.6, 60.9, 55.5, 36.3, 21.5, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{21}H_{23}NO_5SNa^+$ $[M+Na]^+$: 424.1189, found 424.1182.

Ethyl 2-(1-tosyl-2,3-dihydro-1H-benzo[f]indol-2-yl)acrylate (3x)

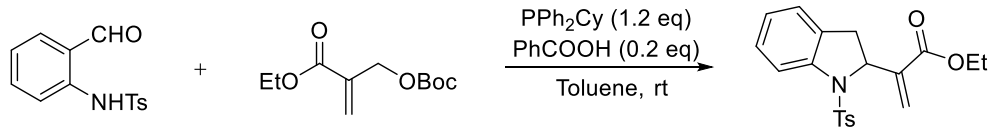


3x

The **3x** was prepared according to the general procedure described above using **1s** (32.5 mg, 0.1 mmol), **2a** (34.5 mg, 0.15 mmol), PPh_2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (30.3 mg, 72% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.11 (s, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.68 – 7.62 (m, 3H), 7.48 – 7.42 (m, 2H), 7.37 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H), 7.16 (d, J = 8.0 Hz, 2H), 6.33 (s, 1H), 6.09 – 6.01 (m, 1H), 5.32 – 5.23 (m, 1H), 4.31 – 4.17 (m, 2H), 3.26 (ddd, J = 16.8, 10.0, 1.8 Hz, 1H), 2.82 (dd, J = 16.8, 1.8 Hz, 1H), 2.33 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.7, 144.1, 140.1, 140.0, 135.1, 133.5, 131.40, 131.38, 129.7, 127.9, 127.3, 127.0, 126.0, 125.7, 125.0, 124.0, 113.1, 61.7, 61.0, 35.8, 21.5, 14.1. **HRMS (ESI)** m/z: calcd. for $C_{24}H_{23}NO_4SNa^+$ $[M+Na]^+$: 444.1240, found 444.1249.

IV. Gram-Scale and Synthetic Manipulations

(a) Synthesis of 3a on gram-scale.

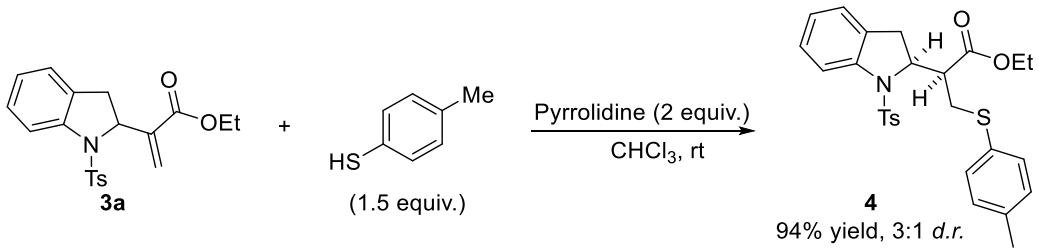


1a **2a** (1.5 equiv.) **3a**, 78% yield

To a stirred solution of *o*-aminobenzaldehyde **1a** (4.0 mmol, 1.0 eqvuiv) and allyl carbonate **2a** (6 mmol, 1.5 equiv) were added to toluene (80.0 mL) with PPh_2Cy (1.2 equiv) and PhCOOH (20 mol %), and stirred at room temperature. The reaction mixture was purified by flash chromatography on silica gel (PE:EtOAc:DCM = 19:1:6) with a yield of 78%.

(b) Synthetic manipulations of 3a.

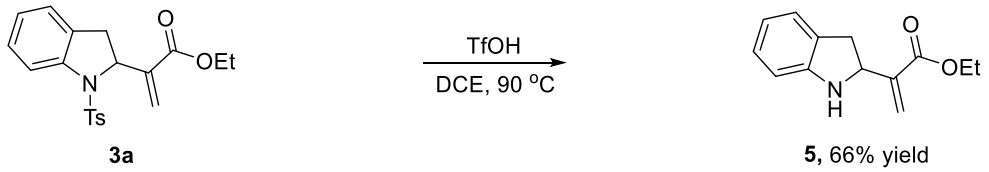
Ethyl 3-(p-tolylthio)-2-(1-tosylindolin-2-yl)propanoate (4)



According to the known procedure.[1] *p*-Toluenethiol (18.6 mg, 0.15 mmol) and Pyrrolidine (16 μL, 0.2 mmol) were added to a solution of **3a** (37.1 mg, 0.1 mmol) in $CHCl_3$ (4.0 mL) at room temperature. The resulting reaction mixture was stirred at rt for 12 hours. The reaction was quenched with saturated NH_4Cl and the mixture was extracted with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column on silica gel (PE:EtOAc:DCM = 5:2:1) to afford a white solid **4** (46.6 mg, 94% yield, 3:1 *d.r.*). m.p.: 99.5 – 101.0 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.2 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 7.24 – 7.18 (m, 1H), 7.16 – 7.08 (m, 4H), 7.03 (t, J = 7.3 Hz, 1H), 6.99 (d, J = 7.3 Hz, 1H), 4.55 (ddd, J = 9.7, 4.2, 2.4 Hz, 1H), 3.87 (q, J = 7.1 Hz, 2H), 3.17 (d, J = 6.9 Hz, 2H), 3.03 (ddd, J = 8.0, 6.3, 4.1 Hz,

1H), 2.81 (dd, *J* = 16.5, 2.3 Hz, 1H), 2.63 (dd, *J* = 16.5, 9.7 Hz, 1H), 2.34 (s, 3H), 2.31 (s, 3H), 1.10 (t, *J* = 7.1 Hz, 3H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 171.1, 144.1, 141.8, 136.5, 134.5, 132.4, 131.8, 130.5, 129.8, 129.6, 127.9 127.1, 125.3, 124.7, 118.2, 62.4, 61.0, 51.3, 31.8, 31.6, 21.5, 21.0, 13.9. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{29}NO_4S_2Na^+$ $[M+Na]^+$: 518.1430, found 518.1430.

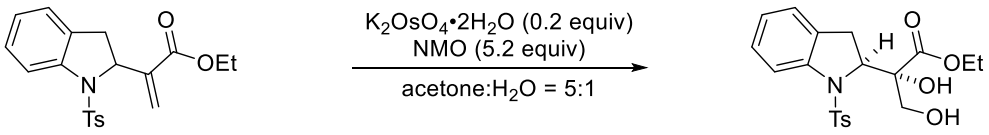
Ethyl 2-(indolin-2-yl)acrylate (5)



3a **5,** 66% yield

According to the known procedure.[2] TfOH (30.0 mg, 0.2 mmol) was added to a solution of **3a** (37.1 mg, 0.1 mmol) in DCE (2.0 mL) at room temperature. The resulting reaction mixture was heated at 90 °C and stirred by reflux for 4 hours. The reaction was quenched with saturated $NaHCO_3$ and the mixture was extracted with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column on silica gel (PE:EtOAc:DCM = 5:1:1) to afford a brown oil **5** (14.3 mg, 66% yield). **^1H NMR (400 MHz, $CDCl_3$)** δ 7.12 – 7.00 (m, 2H), 6.73 – 6.68 (m, 1H), 6.65 (d, *J* = 7.7 Hz, 1H), 6.29 (t, *J* = 1.2 Hz, 1H), 5.95 (t, *J* = 1.4 Hz, 1H), 4.78 (t, *J* = 9.0, 1H), 4.31 – 4.19 (m, 2H), 4.07 (s, 1H), 3.40 (dd, *J* = 15.6, 9.1 Hz, 1H), 2.84 (dd, *J* = 15.5, 8.9 Hz, 1H), 1.33 (t, *J* = 7.1 Hz, 3H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 166.6, 150.4, 142.5, 127.8, 127.4, 124.6, 123.9, 118.9, 109.1, 60.8, 59.0, 36.5, 14.2. **HRMS (ESI)** m/z: calcd. for $C_{13}H_{15}NO_2Na^+$ $[M+Na]^+$: 240.0995, found 240.0994.

Ethyl 2,3-dihydroxy-2-(1-tosylindolin-2-yl)propanoate (6)

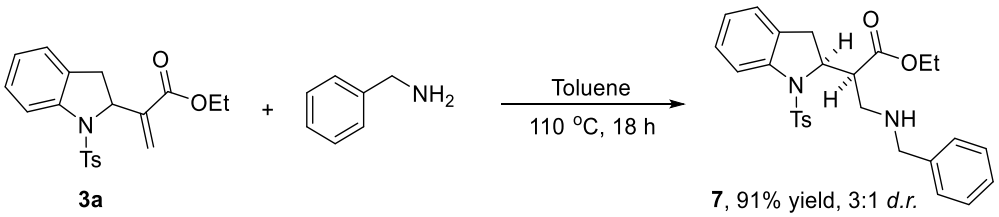


3a **6,** 71% yield, 1.4:1 *d.r.*

According to the known procedure.[3] Potassium osmiate dihydrate (7.3 mg, 0.02 mmol) and 4-methylmorpholine N-oxide (0.05 mL, 0.52 mmol) were added to a solution of **3a** (37.1 mg, 0.1 mmol) in acetone:H_2O = 5:1 (4.0 mL) at room temperature. The resulting reaction mixture was stirred at rt for 12 h. The reaction was

quenched with saturated Na_2SO_3 and the mixture was extracted with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column on silica gel (PE:EtOAc:DCM = 5:2:1) to afford a white solid **6** (28.6 mg, 71% yield, 1.4:1 *d.r.*). m.p.: 109.2 – 110.9 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, J = 8.0 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.25 – 7.18 (m, 1H), 7.13 (d, J = 8.0 Hz, 2H), 7.08 – 7.02 (m, 1H), 7.00 – 6.95 (m, 1H), 4.61 (dd, J = 8.9, 2.5 Hz, 1H), 4.16 – 4.09 (m, 2H), 4.09 – 4.04 (m, 1H), 3.88 (dd, J = 11.9, 6.6 Hz, 1H), 3.50 (s, 1H), 2.70 (t, J = 7.2 Hz, 1H), 2.62 (dd, J = 16.5, 2.5 Hz, 1H), 2.54 (dd, J = 16.4, 8.9 Hz, 1H), 2.34 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 172.7, 144.3, 141.9, 133.8, 133.7, 129.6, 127.6, 127.2, 125.8, 124.2, 118.9, 80.5, 64.8, 64.1, 62.5, 30.6, 21.5, 14.0. **HRMS (ESI)** m/z: calcd. for $C_{20}H_{23}NO_6SNa^+$ $[M+Na]^+$: 428.1138, found 428.1146.

Ethyl 3-(benzylamino)-2-(1-tosylindolin-2-yl)propanoate (7)

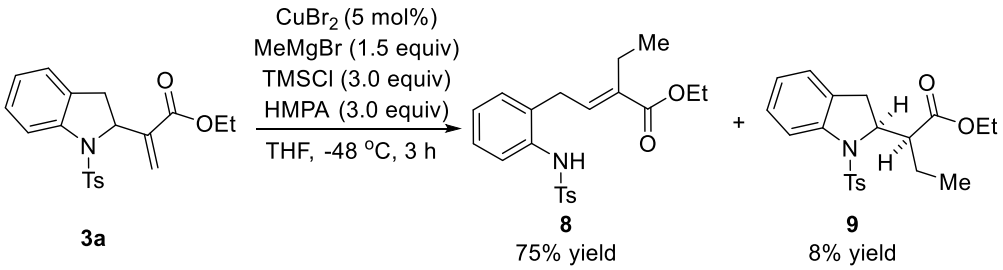


3a **7**, 91% yield, 3:1 *d.r.*

Benzylamine (53.6 mg, 0.5 mmol) was added to a solution of **3a** (37.1 mg, 0.1 mmol) in Toluene (2.0 mL) at room temperature. The resulting reaction mixture was heated at 110 °C and stirred by reflux for 18 hours. The reaction was quenched with saturated $NaHCO_3$ and the mixture was extracted with CH_2Cl_2. The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column on silica gel (PE:EtOAc:DCM = 10:5:1) to afford a brown oil **7** (43.6 mg, 91% yield, 3:1 *d.r.*). **^{1}H NMR (400 MHz, $(CD_3)_2CO$)** δ 7.58 – 7.51 (m, 3H), 7.31 – 7.28 (m, 3H), 7.27 – 7.25 (m, 3H), 7.25 – 7.18 (m, 2H), 7.10 – 7.02 (m, 2H), 7.78 – 7.71 (m, 1H), 3.99 – 3.90 (m, 2H), 3.76 – 3.63 (m, 2H), 3.03 – 2.97 (m, 1H), 2.93 – 2.90 (m, 1H), 2.88 – 2.87 (m, 1H), 2.86 – 2.83 (m, 1H), 2.71 (dd, J = 16.6, 9.7 Hz, 1H), 2.34 (s, 3H), 1.13 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$)** δ 172.4, 145.1, 142.8, 141.7, 135.8, 134.1, 130.5, 128.9, 128.8, 128.3, 128.0, 127.4,

126.0, 125.8, 118.6, 62.8, 61.0, 54.3, 52.1, 46.9, 32.8, 21.4, 14.3. **HRMS (ESI)** m/z: calcd. for $C_{27}H_{30}N_2O_4SH^+$ $[M+H]^+$: 479.1999, found 479.2005.

Ethyl (Z)-2-ethyl-4-(2-((4-methylphenyl)sulfonamido)phenyl)but-2-enoate (8)



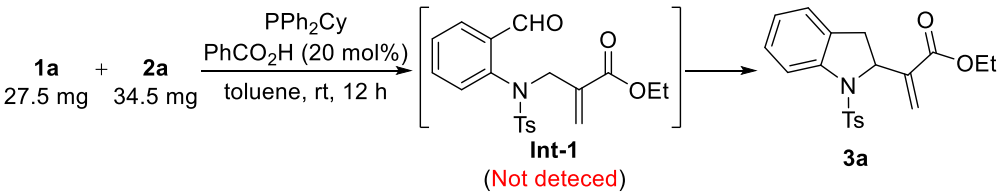
3a **8** 75% yield **9** 8% yield

The **3a** (37.1 mg, 0.1 mmol) and $CuBr_2$ (11.2 mg, 0.05 mmol)was added to an reaction tube. Vacuum for 15 minutes and inject nitrogen. Then, THF (1 mL), Me_3SiCl (31.1 mg, 0.3 mmol) and HMPA (53.6 mg, 0.3 mmol) were added at -48 °C and MeMgBr (0.15 mL, 0.15 mmol) was added drop by drop for 1 hours. The reaction was quenched with saturated NH_4Cl and the mixture was extracted with EtOAc. The combined organic phases were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column on silica gel (PE:EtOAc = 5:2) to afford a white solid **8** (29.1 mg, 75% yield) and **9** (2.9 mg, 8% yield). Compound data of **8**: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 7.20 – 7.13 (m, 3H), 7.12 – 7.05 (m, 1H), 6.57 (dd, J = 15.4, 8.0 Hz, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.29 (d, J = 7.5 Hz, 2H), 2.40 (s, 3H), 2.31 (q, J = 7.5 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H), 1.00 (t, J = 7.5 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.3, 143.9, 137.6, 136.5, 135.8, 134.4, 134.1, 129.8, 129.6, 127.5, 127.19, 127.15, 126.2, 60.6, 29.9, 21.5, 20.1, 14.2, 13.7. **HRMS (ESI)** m/z: calcd. for $C_{21}H_{25}NO_4SNa^+$ $[M+Na]^+$: 410.1397, found 410.1407.

Compound data of **9**: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.3 Hz, 2H), 7.24 – 7.18 (m, 1H), 7.12 (d, J = 8.1 Hz, 2H), 7.07 – 6.98 (m, 2H), 4.41 (td, J = 8.1, 2.9 Hz, 1H), 4.11 – 3.98 (m, 2H), 2.59 – 2.49 (m, 3H), 2.33 (s, 3H), 1.97 – 1.76 (m, 2H), 1.15 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 173.6, 143.9, 143.8, 141.4, 135.2, 133.1, 129.5, 127.6, 127.1, 125.4, 125.0, 118.9, 63.6, 60.5, 52.5, 32.8, 22.6, 21.5, 14.2, 11.6. **HRMS (ESI)** m/z: calcd. for $C_{21}H_{25}NO_4SNa^+$ $[M+Na]^+$: 410.1397, found 410.1402.

V. Mechanistic Studies

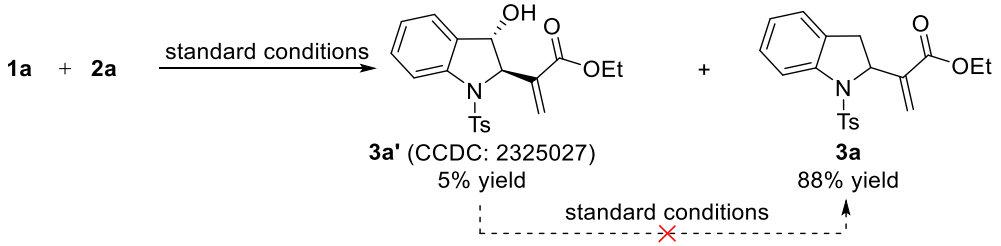
(a) Control Experiments of 1a and 2a.



PPh_2Cy	0.2 equiv	0.5 equiv	0.8 equiv	1.0 equiv	1.2 equiv
3a (%)	2.2 mg (6%)	9.0 mg (24%)	16.1 mg (43%)	23.4 mg (63%)	32.5 mg (88%)
1a (%)	24.1 mg (88%)	18.4 mg (67%)	9.6 mg (35%)	3.3 mg (12%)	0.0 mg (0%)

To a stirred solution of *o*-aminobenzaldehyde **1a** (27.5 mg, 0.1 mmol) and allyl carbonate **2a** (34.5 mg, 0.15 mmol, 1.5 equiv) in toluene (2.0 mL) was added PPh_2Cy (0.2-1.2 equiv) and benzoic acid (2.4 mg, 20 mol%) at room temperature for 12 h. The reaction mixture was purified without concentration via flash chromatography on silica gel (PE:EtOAc:DCM = 19:1:6) to afford compounds **3a** and **1a**.

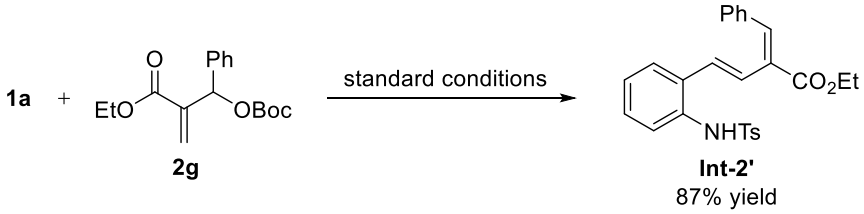
(b) Transformation Experiment of 3a'



To a stirred solution of *o*-aminobenzaldehyde **1a** (27.5 mg, 0.1 mmol) and allyl carbonate **2a** (34.5 mg, 0.15 mmol, 1.5 equiv) in toluene (2.0 mL) was added PPh_2Cy (32.2 mg, 0.12 mmol, 1.2 equiv) and benzoic acid (2.4 mg, 20 mol%) at room temperature for 12 h. The reaction mixture was purified without concentration via flash chromatography on silica gel (PE:EtOAc:DCM = 19:1:6) to afford compounds **3a'** (1.9 mg, 5% yield). Compound data of **3a'**: **^{1}H NMR (400 MHz, $(CD_3)_2CO$)** δ 7.73 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.2 Hz, 1H), 7.38 – 7.25 (m, 4H), 7.10 – 7.04 (m, 1H), 6.26 (s, 1H), 5.86 (s, 1H), 4.99 (s, 1H), 4.85– 4.79 (m, 2H), 4.21 (qd, J = 7.1, 4.6 Hz, 2H), 2.35 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz,**

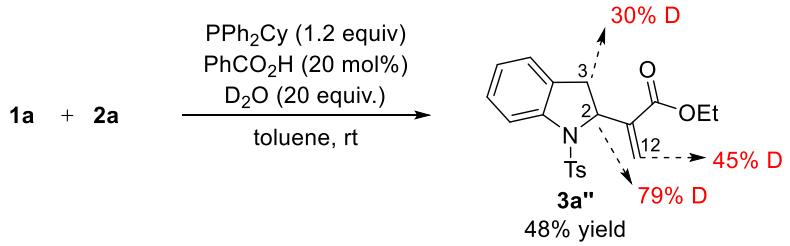
(CD_3)$_2$CO) δ 166.0, 145.1, 142.9, 139.8, 135.9, 133.6, 130.5, 130.4, 128.4, 127.3, 126.2, 125.0, 115.9, 76.7, 72.8, 61.5, 21.4, 14.3. **HRMS (ESI)** m/z: calcd. for $C_{20}H_{21}NO_5SNa^+$ $[M+Na]^+$: 410.1033, found 410.1038.

(c) Control Experiment of 1a and 2g



To a stirred solution of *o*-aminobenzaldehyde **1a** (27.5 mg, 0.1 mmol) and allyl carbonate **2g** (46.0 mg, 0.15 mmol, 1.5 equiv) in toluene (2.0 mL) was added PPh_2Cy (32.2 mg, 0.12 mmol, 1.2 equiv) and benzoic acid (2.4 mg, 20 mol%) at room temperature for 12 h. The reaction mixture was purified without concentration via flash chromatography on silica gel (PE:EtOAc:DCM = 20:3:1) to afford compounds **Int-2'** (38.9 mg, 87% yield). Compound data of **Int-2'**: **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 – 7.55 (m, 3H), 7.46 – 7.34 (m, 6H), 7.30 – 7.27 (m, 1H), 7.23 – 7.20 (m, 1H), 7.18 – 7.14 (m, 2H), 7.03 (d, J = 16.2 Hz, 1H), 6.70 (d, J = 16.3 Hz, 1H), 6.57 (s, 1H), 4.38 (q, J = 7.1 Hz, 2H), 2.30 (s, 3H), 1.44 (t, J = 7.1 Hz, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.0, 143.8, 139.9, 136.4, 135.3, 133.6, 132.4, 130.0, 129.51, 129.48, 129.0, 128.8, 128.7, 128.6, 127.3, 126.5, 126.3, 125.5, 125.3, 61.2, 21.5, 14.4. **HRMS (ESI)** m/z: calcd. for $C_{26}H_{25}NO_4SNa^+$ $[M+Na]^+$: 470.1397, found 470.1404.

(d) The Deuterium Labeling Experiment



To a stirred solution of *o*-aminobenzaldehyde **1a** (27.5 mg, 0.1 mmol), allyl carbonate **2a** (34.5 mg, 0.15 mmol, 1.5 equiv), D_2O (40.0 mg, 20.0 equiv), PPh_2Cy (32.2 mg,

0.12 mmol, 1.2 equiv), benzoic acid (2.4 mg, 20 mol%) and 2.0 mL of toluene. The resulting reaction mixture was stirred at room temperature for 12 h. The reaction mixture was concentrated and the residue was purified by silica gel flash column chromatography (PE:EtOAc:DCM = 19:1:6) to afford corresponding product d-**3a''** as a yellow oily liquid (18.1 mg, 48% yield).

VI. References

1. (a) Patil, D. V.; Phun, L. H.; France, S. Indium-Catalyzed Homo-Nazarov Cyclizations of Alkenyl Cyclopropyl Ketones. *Org. Lett.* **2010**, *12*, 5684–5687. (b) Cabrera, S.; Alemán, J.; Bolze, P.; Bertelsen, S.; Jørgensen, K. A. An Unexpected Organocatalytic Asymmetric Tandem Michael/Morita–Baylis–Hillman Reaction. *Angew. Chem. Int. Ed.* **2008**, *47*, 121–125.

2. Javorskis, T.; Orentas, E. Chemoselective Deprotection of Sulfonamides Under Acidic Conditions: Scope, Sulfonyl Group Migration, and Synthetic Applications. *J. Org. Chem.* **2017**, *82*, 13423–13439.

3. Gao, J.; Li, Y.; Wang, N.; Li, Z.; Huang, N.; Yao, H. One-Pot Stereoselective Synthesis of 2, 3, 4-Unprotected *β*-N-Glycopyranosides from Glycals and Amines. *Adv. Synth. Catal*. **2023**, *365*, 2350–2355.

VII. X-Ray Crystallographic Analysis

Crystal Growth Method: 20 mg of **3j** was added in a HPLC vial and dissolved by 1.0 mL DCM, closed the lid. Then put it in a large bottle, added PE to the same level of the liquid in the HPLC vial, tighten the lid, put it in a fumehood and waited for growth.

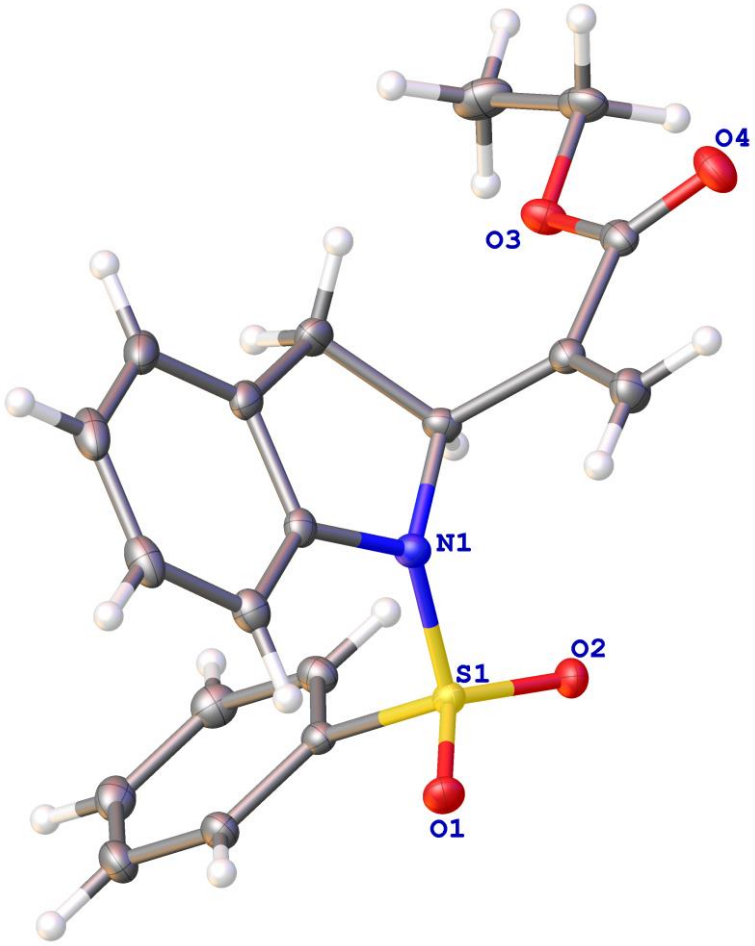


Figure S1. X-ray structure of **3j** (ellipsoid contour at 50% probability CCDC 2287281)

Crystal Growth Method: 15 mg of **4** was added in a HPLC vial and dissolved by 1.0 mL DCM, closed the lid. Then put it in a large bottle, added PE to the same level of the liquid in the HPLC vial, tighten the lid, put it in a fumehood and waited for growth.

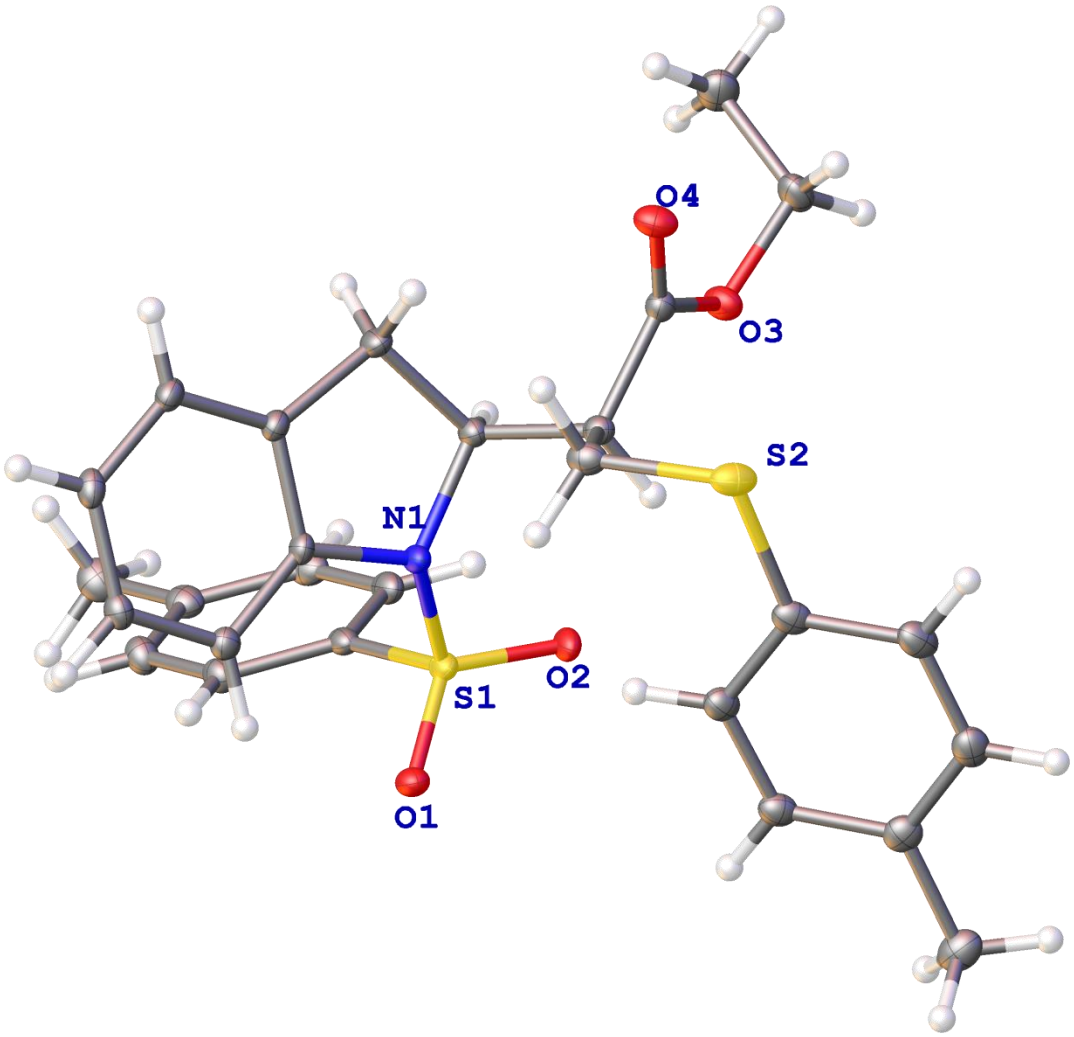


Figure S2. X-ray structure of **4** (ellipsoid contour at 50% probability CCDC 2293949)

Crystal Growth Method: 5 mg of **3a'** was added in a HPLC vial and dissolved by 1.0 mL DCM, closed the lid. Then put it in a large bottle, added PE to the same level of the liquid in the HPLC vial, tighten the lid, put it in a fumehood and waited for growth.

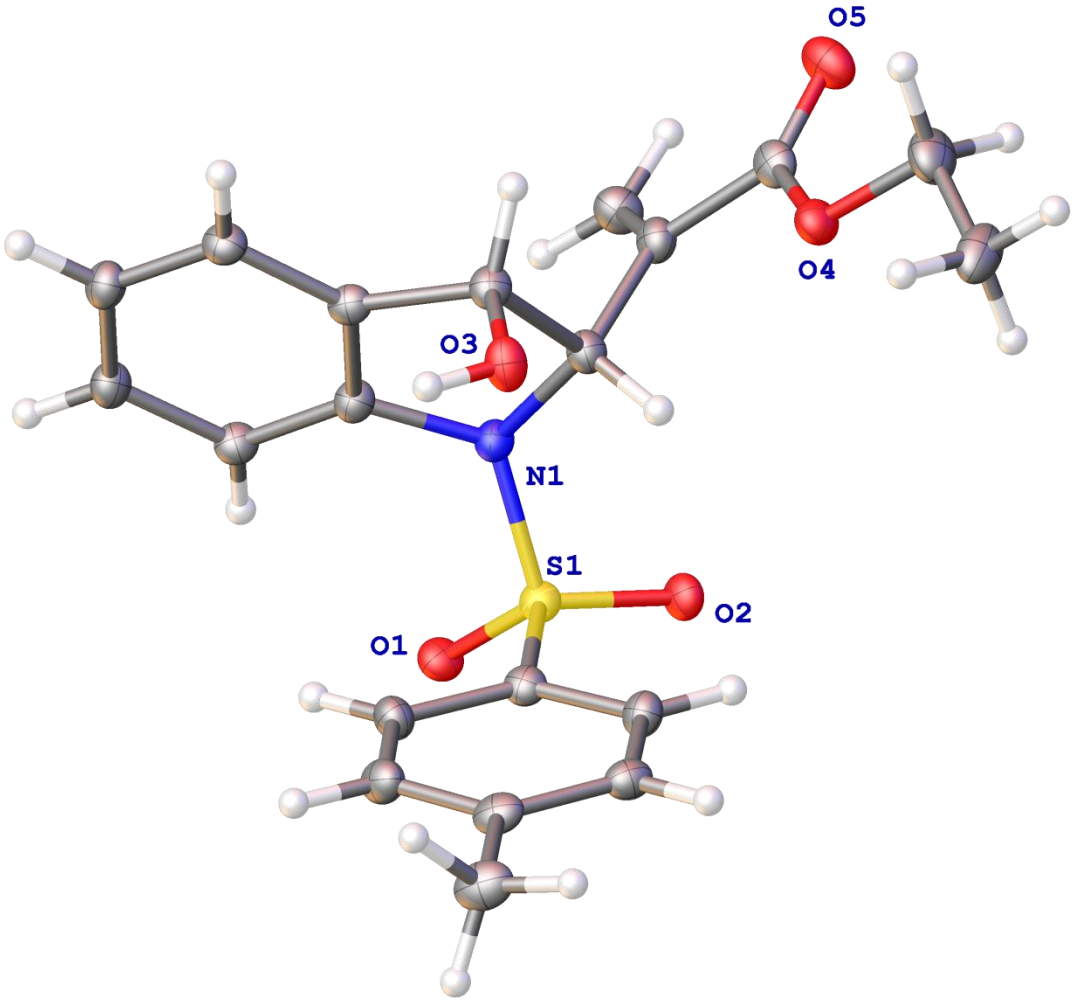
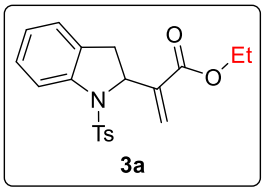


Figure S3. X-ray structure of **3a'** (ellipsoid contour at 50% probability CCDC 2325027)

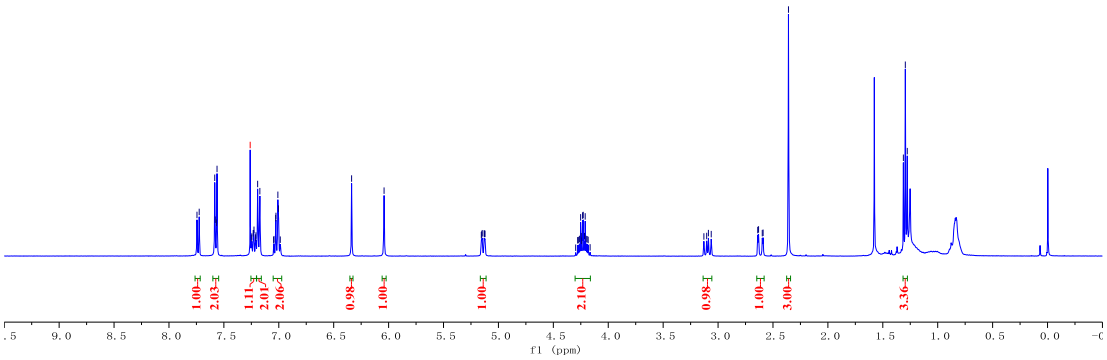
Table S1. Crystal data and structure refinement for **3j**, **4**, and **3a'**.

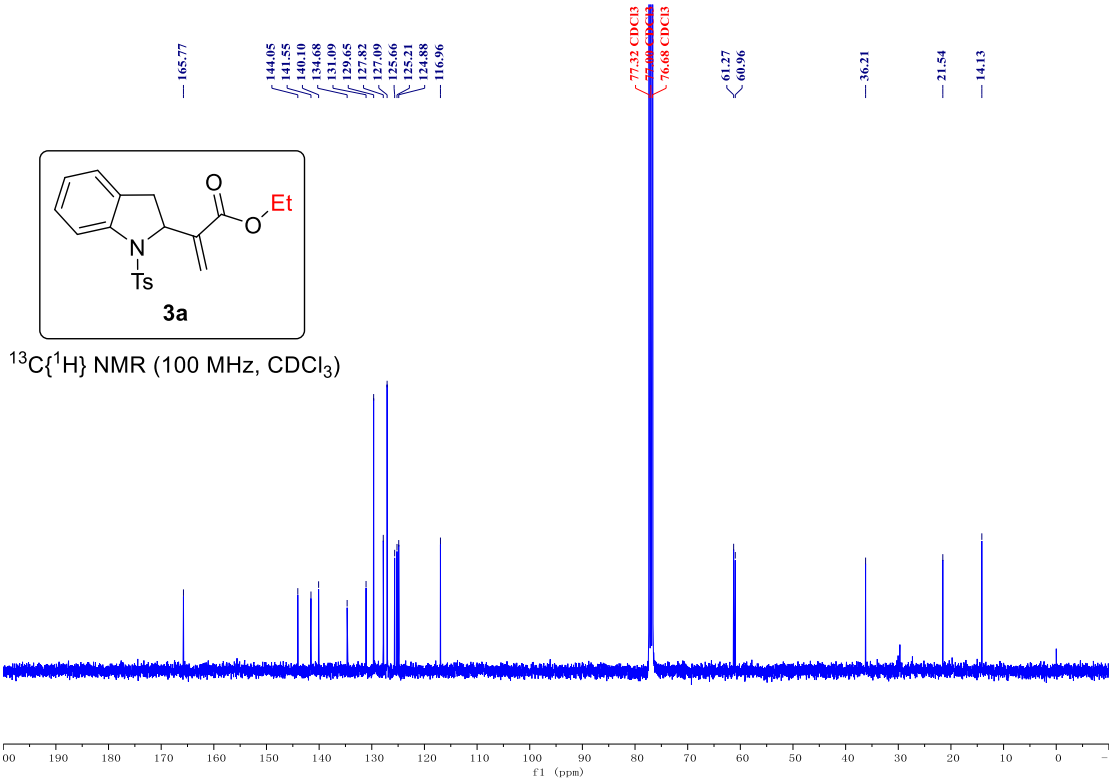
Identification code	**3j**	**4**	**3a'**
Empirical formula	$C_{19}H_{19}NO_4S$	$C_{27}H_{29}NO_4S_2$	$C_{20}H_{21}NO_5S$
Formula weight	357.41	495.63	387.44
Temperature/K	150.00(10)	100.0(6)	99.97(15)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	P-1
a/Å	8.30100(10)	9.24180(10)	8.0093(9)
b/Å	11.06510(10)	19.5215(3)	9.9303(10)
c/Å	18.7113(2)	14.0366(2)	13.0524(6)
α/°	90	90	92.274(6)
β/°	93.4680(10)	99.178(2)	107.728(8)
γ/°	90	90	106.033(10)
Volume/Å^3	1715.51(3)	2499.98(6)	941.63(16)
Z	4	4	2
Pcalc(g/cm^3)	1.384	1.317	1.366
μ/mm $^{-1}$	1.884	2.204	1.800
F(000)	752.0	1048.0	408.0
Crystal size/mm^3	0.15 × 0.12 × 0.1	0.16 × 0.14 × 0.12	0.15 × 0.14 × 0.1
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.29 to 148.79	7.824 to 148.864	7.176 to 150.146
Index ranges	-10 ≤ h ≤ 9, -13 ≤ k ≤ 13, -22 ≤ l ≤ 22	-9 ≤ h ≤ 11, -22 ≤ k ≤ 23, -17 ≤ l ≤ 14	-6 ≤ h ≤ 9, -12 ≤ k ≤ 12, -15 ≤ l ≤ 16
Reflections collected	18184	13621	7837
Independent reflections	3454 [R_{int} = 0.0211, R_{sigma} = 0.0120]	4968 [R_{int} = 0.0430, R_{sigma} = 0.0514]	3580 [Rint = 0.0590, R_{sigma}= 0.0619]
Data/restraints/parameters	3454/0/228	4968/0/310	3580/0/255
Goodness-of-fit on F^2	1.033	1.096	1.162
Final R indexes [I>=2σ (I)]	R_1 = 0.0297, wR_2 = 0.0770	R_1 = 0.0453, wR_2 = 0.1197	R1 = 0.0793, wR2 = 0.2277
Final R indexes [all data]	R_1 = 0.0301, wR_2 = 0.0772	R_1 = 0.0548, wR_2 = 0.1248	R1 = 0.0908, wR2 = 0.2536
Largest diff. peak/hole / e Å^{-3}	0.28/-0.37	0.38/-0.49	1.02/-1.27

VIII. Copies of ^{1}H and $^{13}C\{^{1}H\}$ NMR Spectra

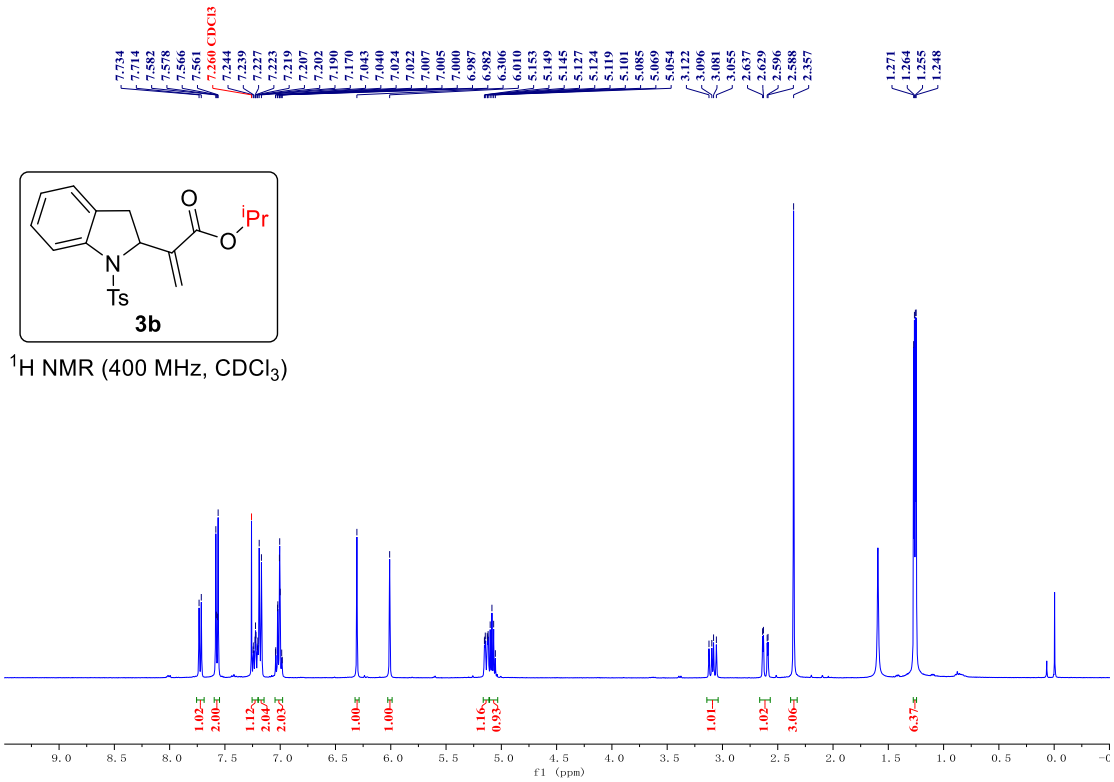


^{1}H NMR (400 MHz, $CDCl_3$)





$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)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7.582
7.578
7.566
7.561
7.260 CDCl3
7.244
7.239
7.227
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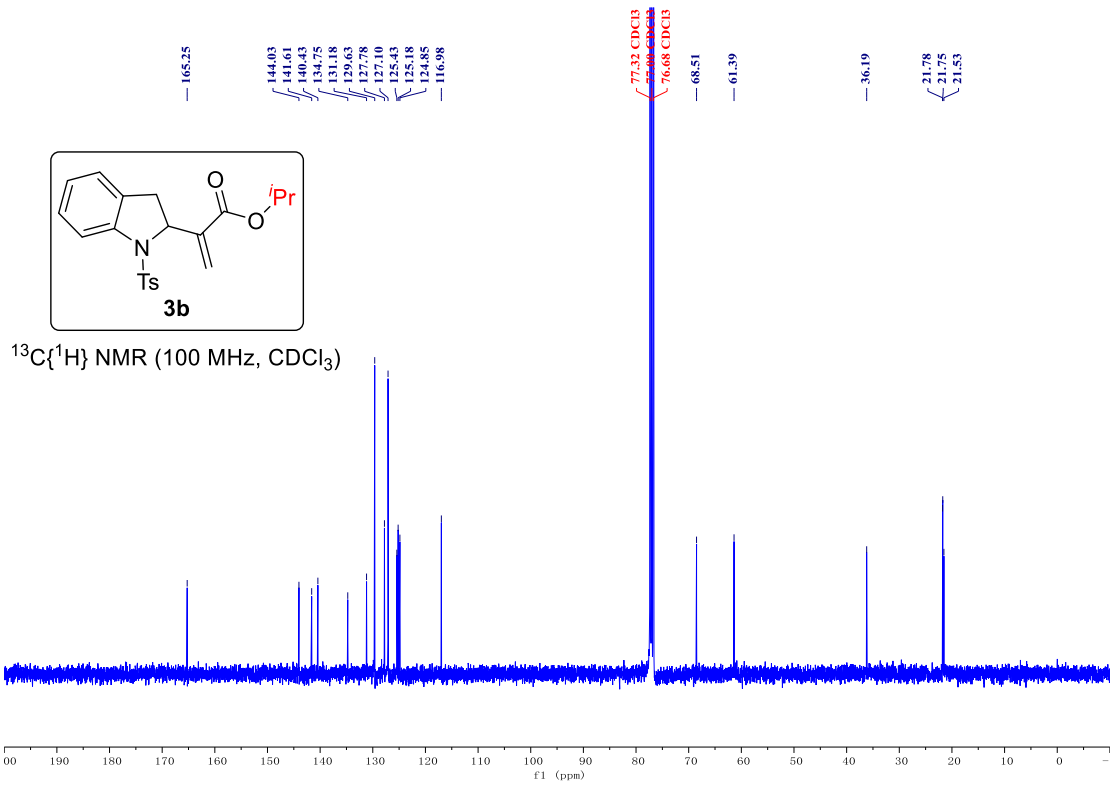
7.219
7.207
7.202
7.190
7.170
7.043
7.040
7.024
7.022
7.007
7.005
7.000
6.987
6.982
6.306
6.010
5.153
5.149
5.145
5.127
5.124
5.119
5.101
5.085
5.069
5.054
3.122
3.096
3.081
3.055
2.637
2.629
2.596
2.588
2.357
1.271
1.264
1.255
1.248
O
iPr
O
N
Ts
3b
1H NMR (400 MHz, CDCl3)
1.02
2.00
1.12
2.04
2.03
1.00
1.00
1.16
0.93
1.01
1.02
3.06
6.37
f1 (ppm)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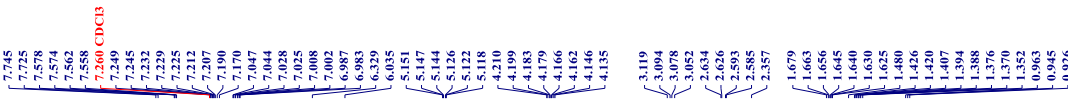
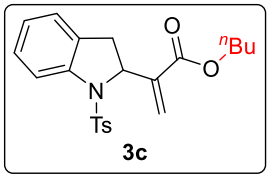
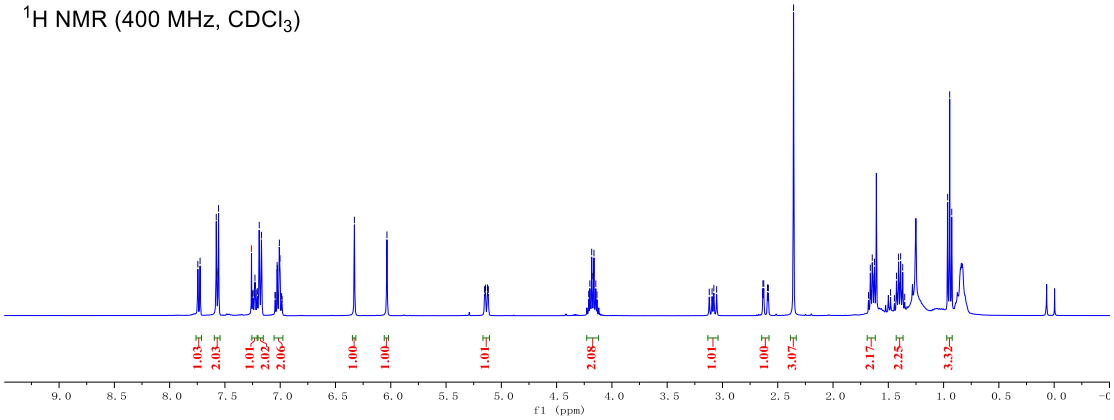
144.03
141.61
140.43
134.75
131.18
129.63
127.78
127.10
125.43
125.18
124.85
116.98
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
68.51
61.39
36.19
21.78
21.75
21.53
O
iPr
O
N
Ts
3b
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

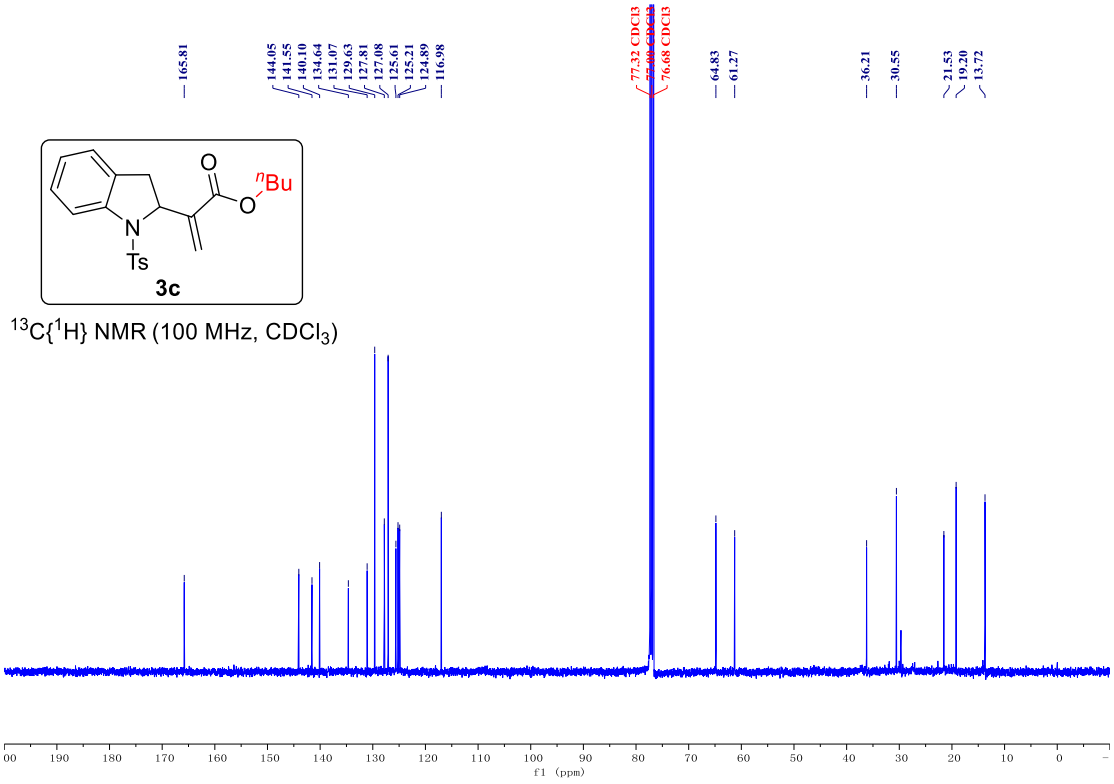




3c

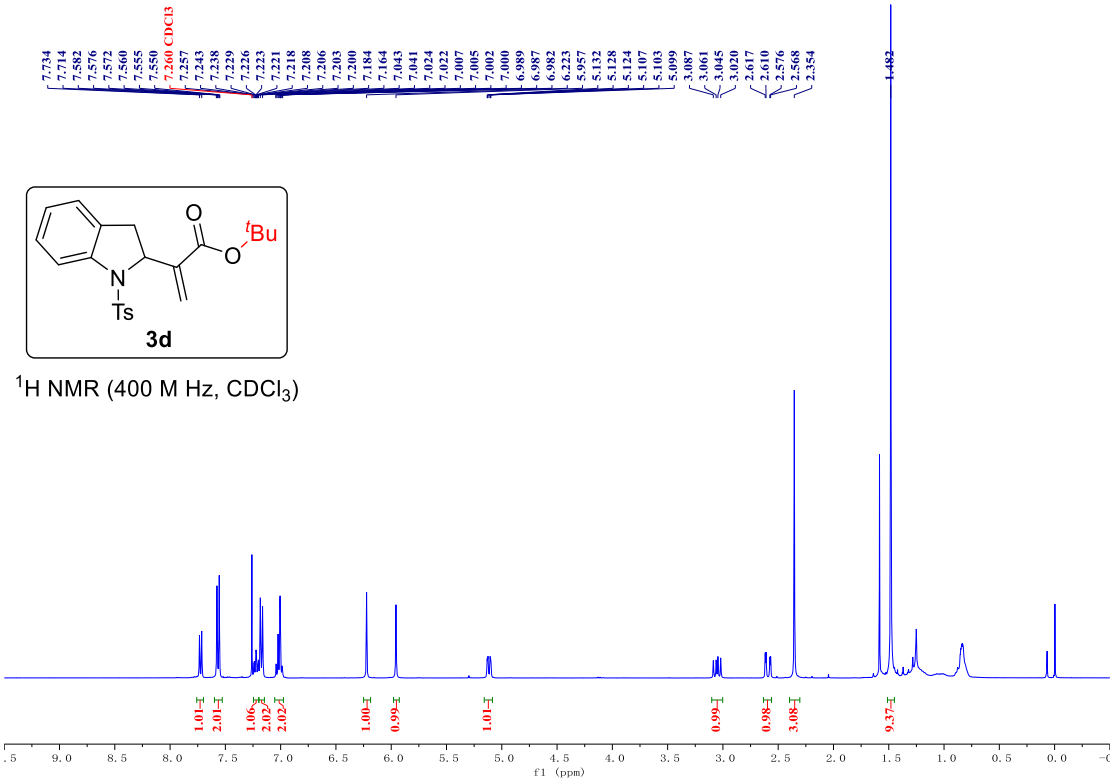
^{1}H NMR (400 MHz, $CDCl_3$)



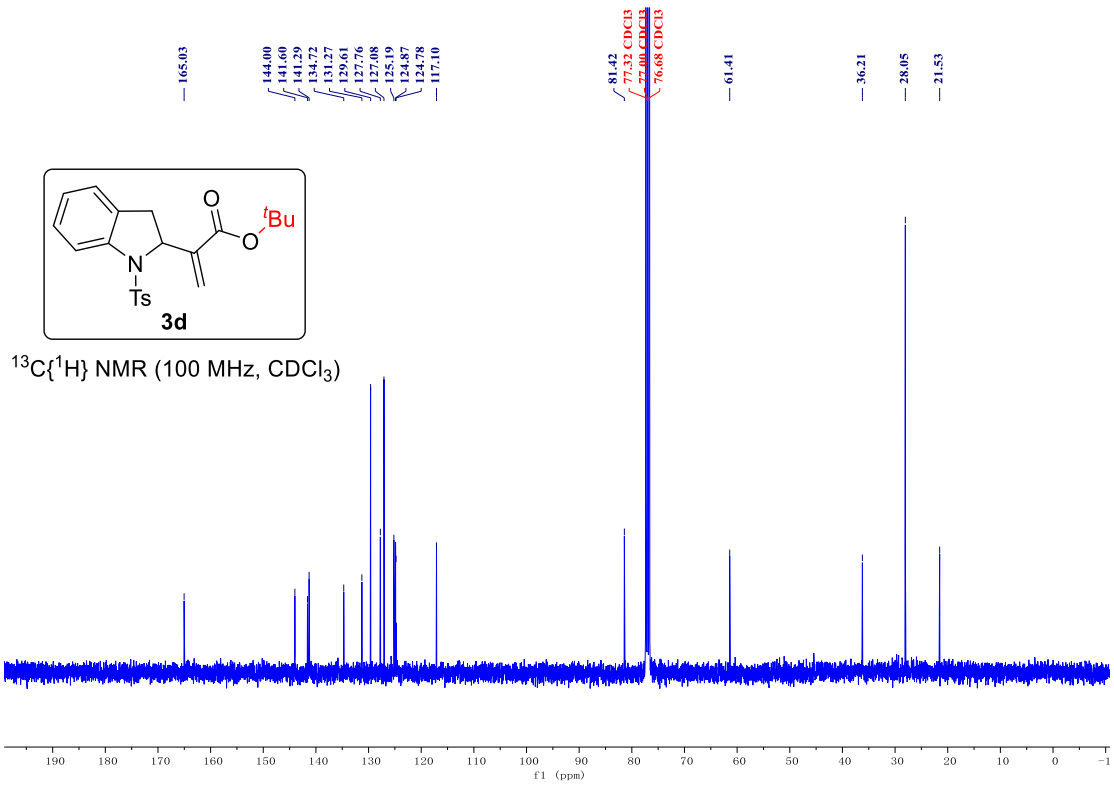


3c

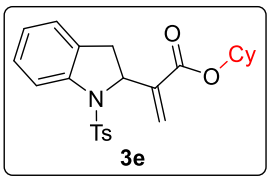
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 M Hz, $CDCl_3$)

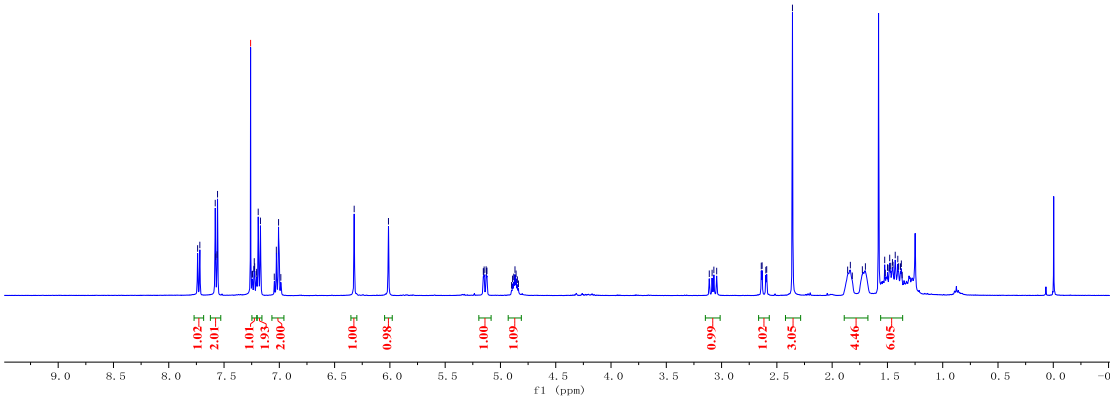


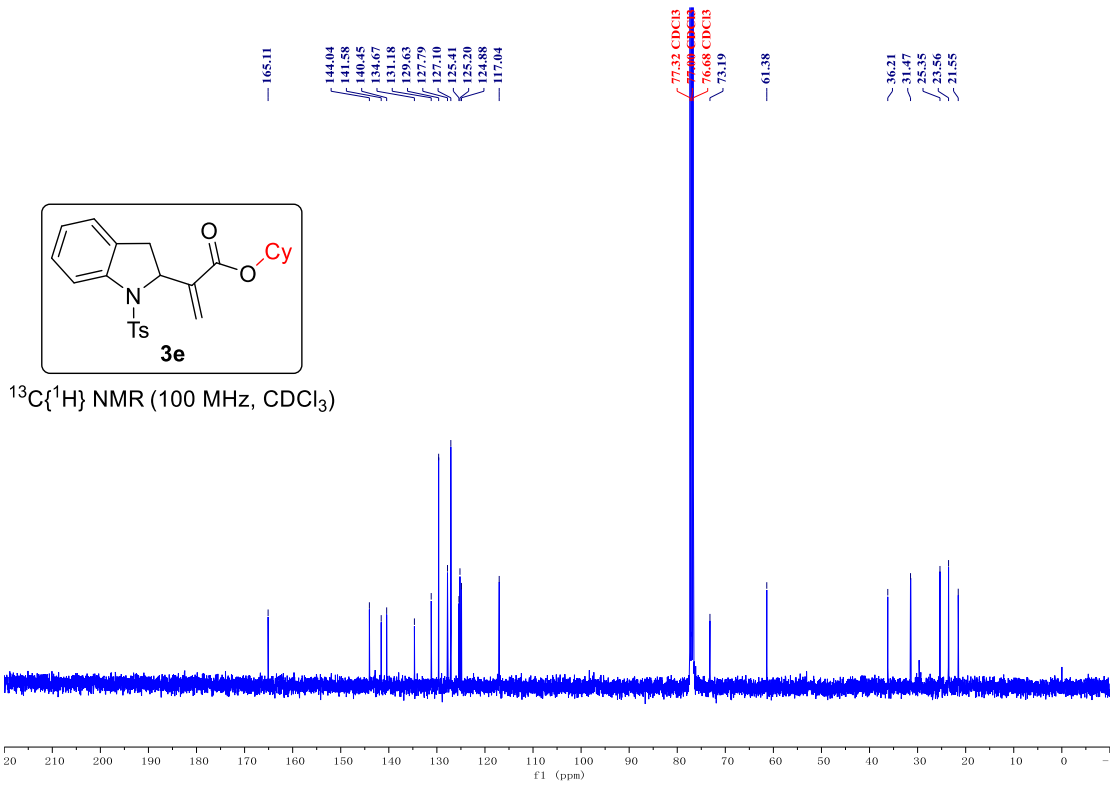
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



3e

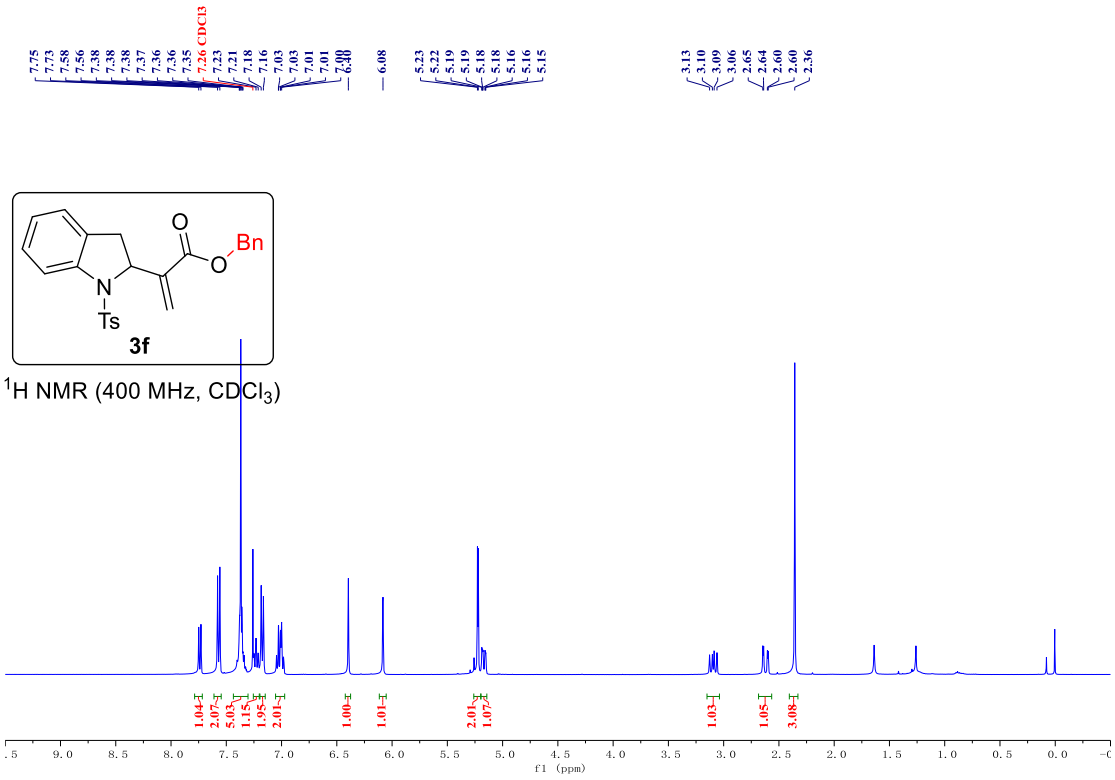
^{1}H NMR (400 MHz, $CDCl_3$)



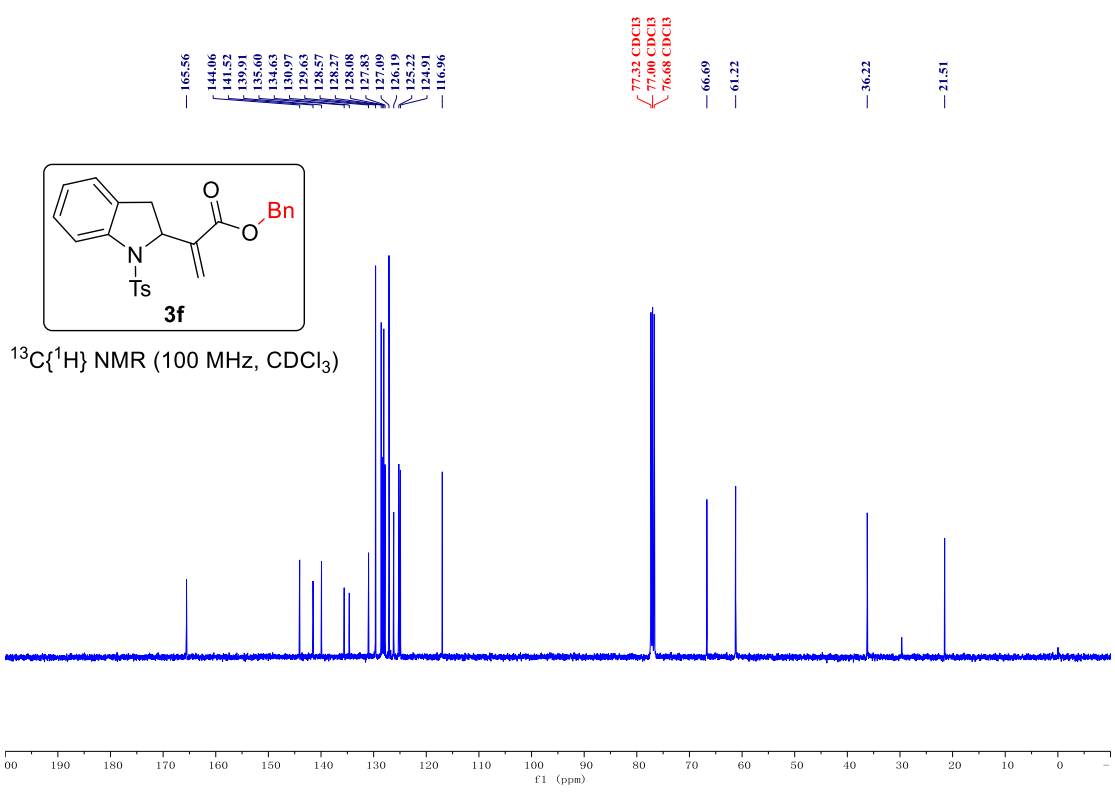


3e

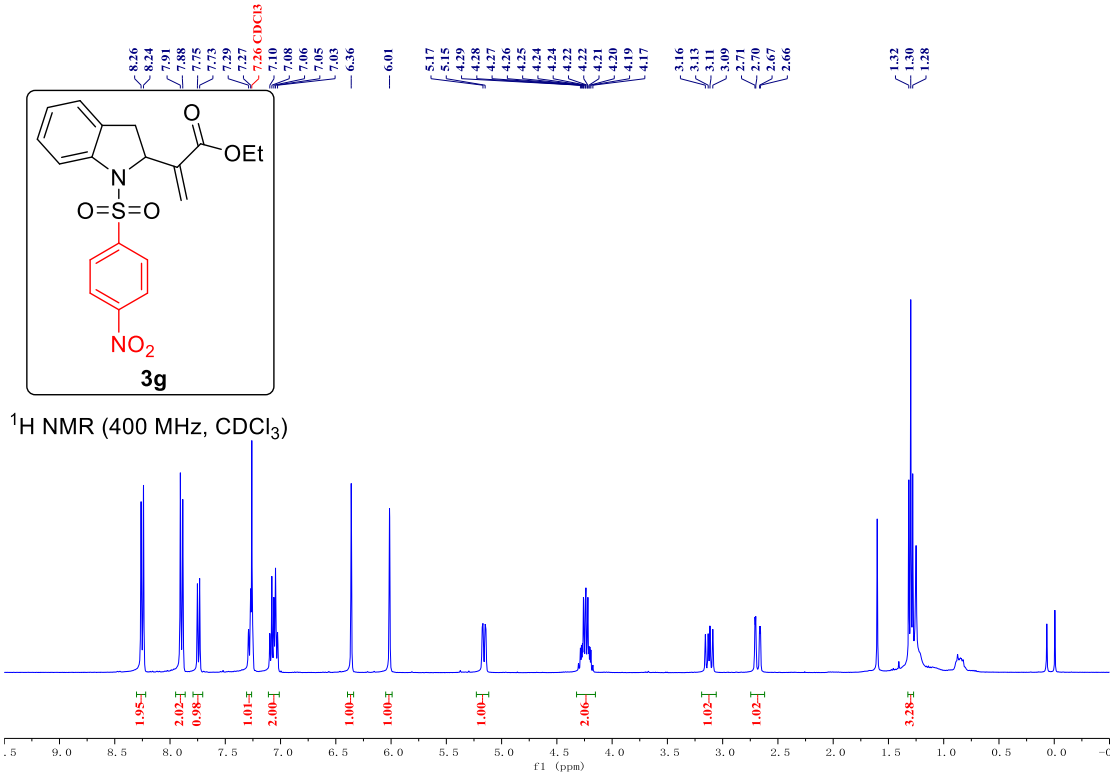
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)



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



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)


8.26
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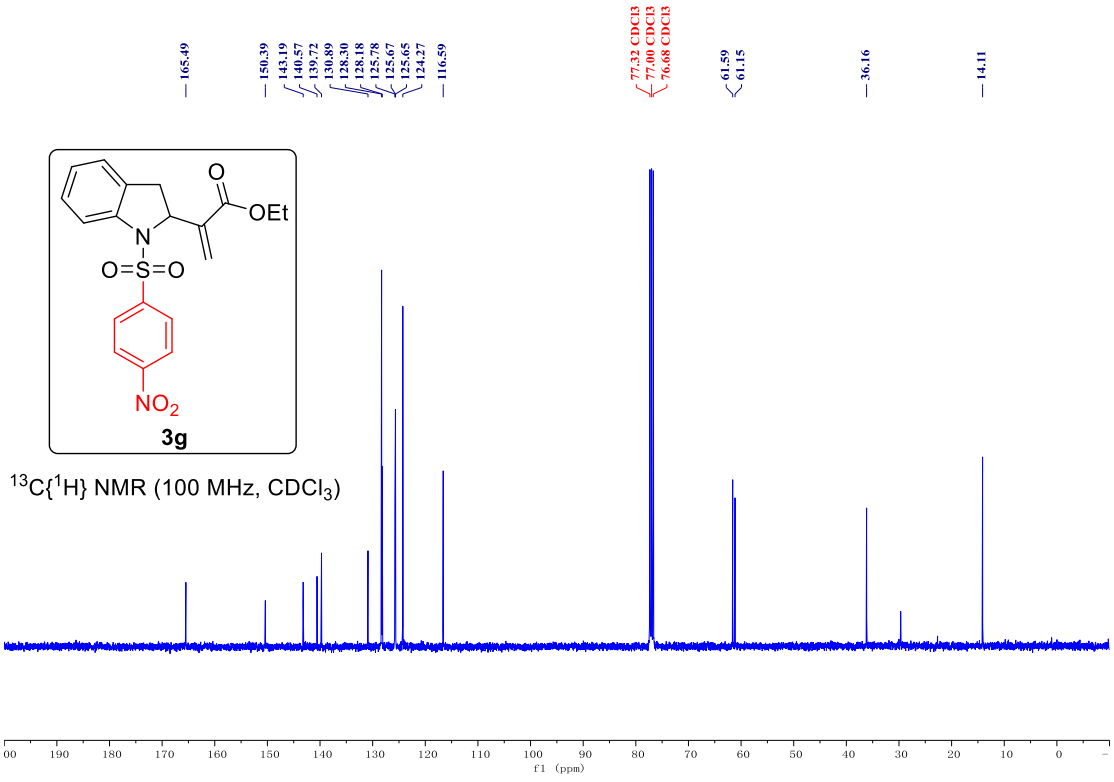
7.88
7.75
7.73
7.29
7.27
7.26 CDCl3
7.10
7.08
7.06
7.05
7.03
6.36
6.01
5.17
5.15
4.29
4.28
4.27
4.26
4.25
4.24
4.24
4.22
4.22
4.21
4.20
4.19
4.17
3.16
3.13
3.11
3.09
2.71
2.70
2.67
2.66
1.32
1.30
1.28
O
OEt
N
O=S=O
NO2
3g
1H NMR (400 MHz, CDCl3)
1.95
2.02
0.98
1.01
2.00
1.00
1.00
1.00
2.06
1.02
1.02
3.28
f1 (ppm)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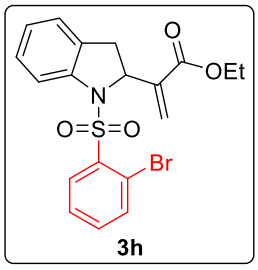
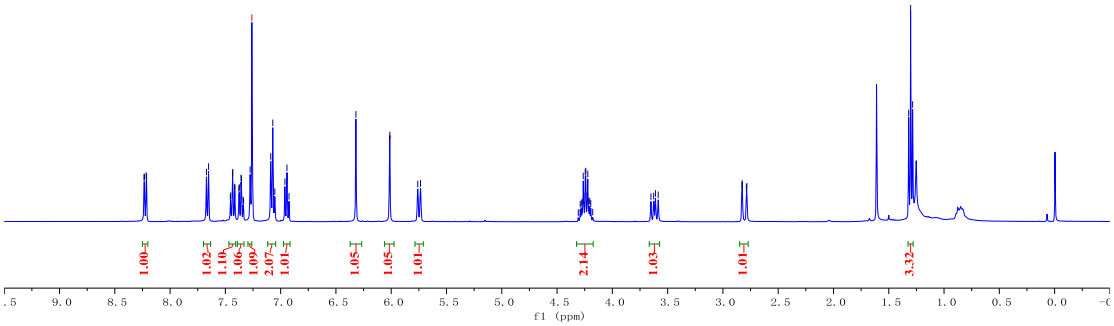
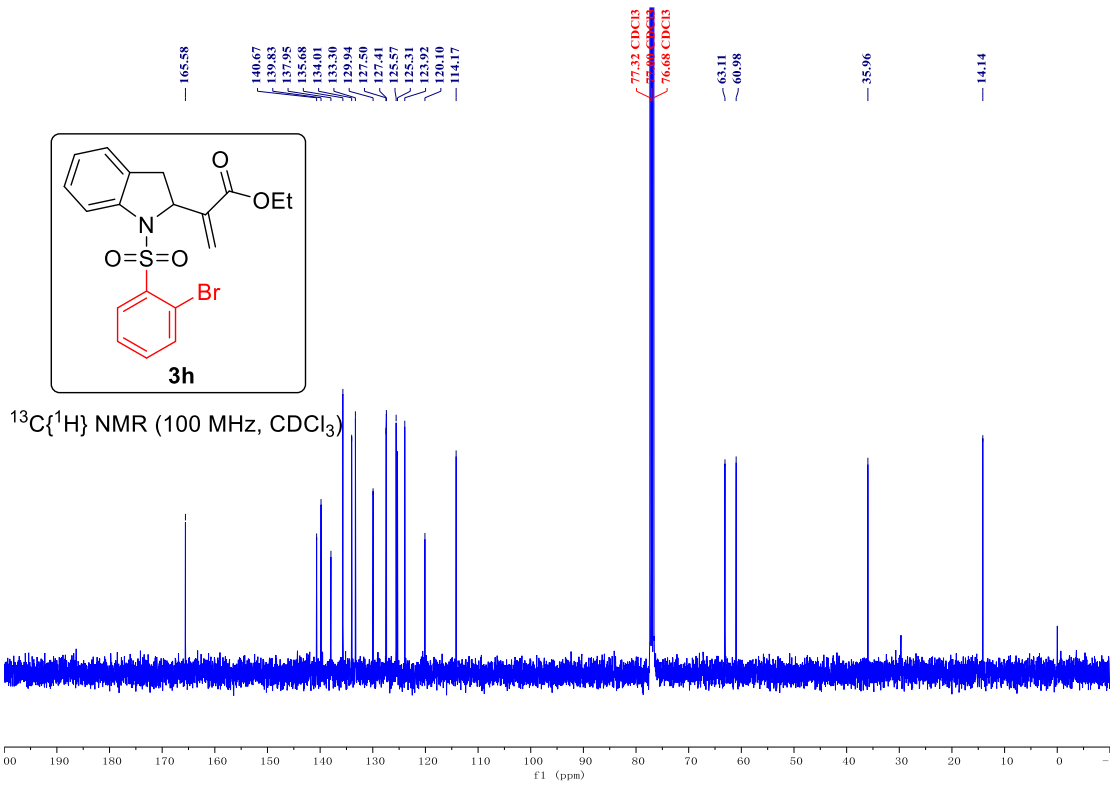
150.39
143.19
140.57
139.72
130.89
128.30
128.18
125.78
125.67
125.65
124.27
116.59
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
61.59
61.15
36.16
14.11
O
OEt
N
O=S=O
NO2
3g
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)



3h

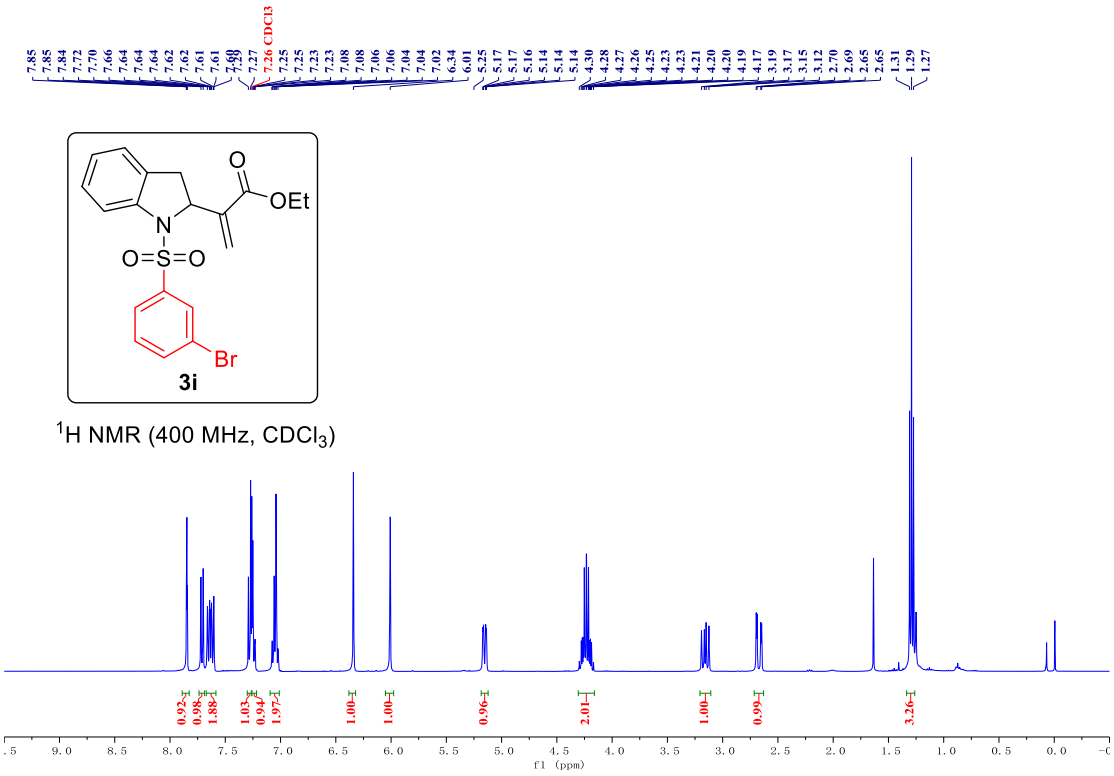
^{1}H NMR (400 MHz, $CDCl_3$)

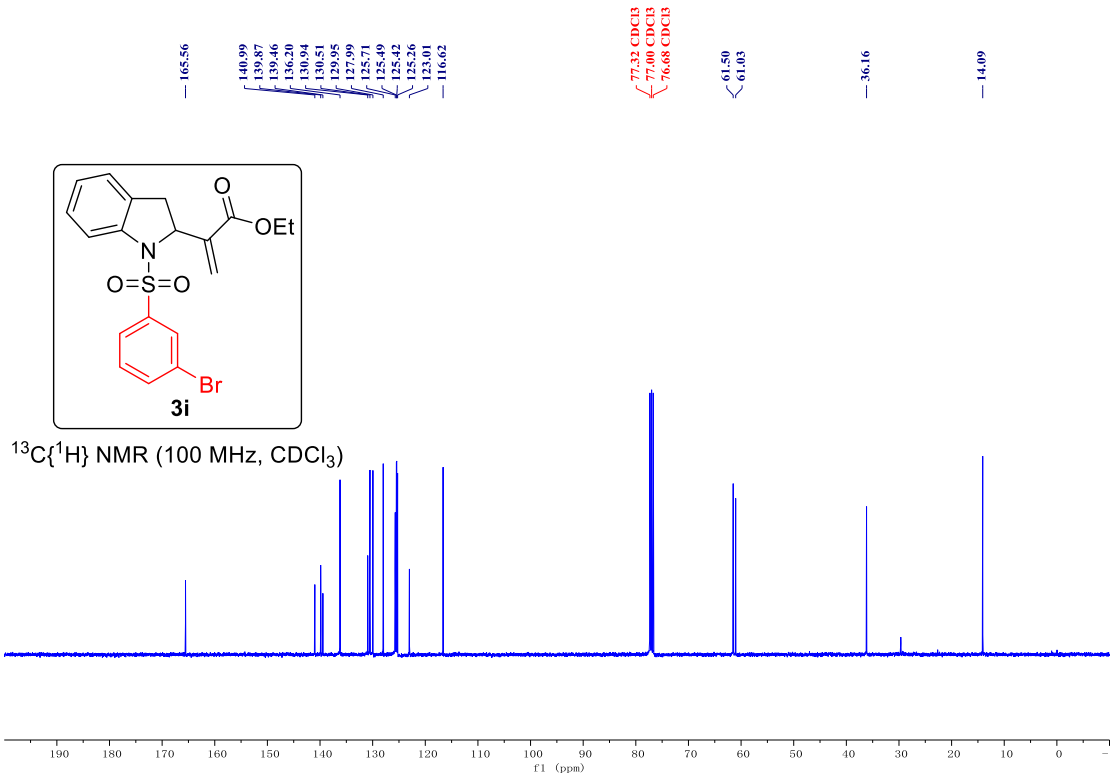




3h

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)


7.85
7.85
7.84
7.72
7.70
7.66
7.64
7.64
7.64
7.62
7.62
7.61
7.61
7.60
7.27
7.26 CDCl3
7.25
7.25
7.23
7.23
7.08
7.08
7.06
7.06
7.04
7.04
7.02
6.34
6.01
5.25
5.17
5.17
5.16
5.14
5.14
5.14
4.30
4.28
4.27
4.26
4.25
4.23
4.23
4.21
4.20
4.20
4.19
4.17
3.19
3.17
3.15
3.12
2.70
2.69
2.65
2.65
1.31
1.29
1.27
O
OEt
N
O=S=O
Br
3i
1H NMR (400 MHz, CDCl3)
0.92
0.98
1.88
1.03
0.94
1.97
1.00
1.00
0.96
2.01
1.00
0.99
3.26
f1 (ppm)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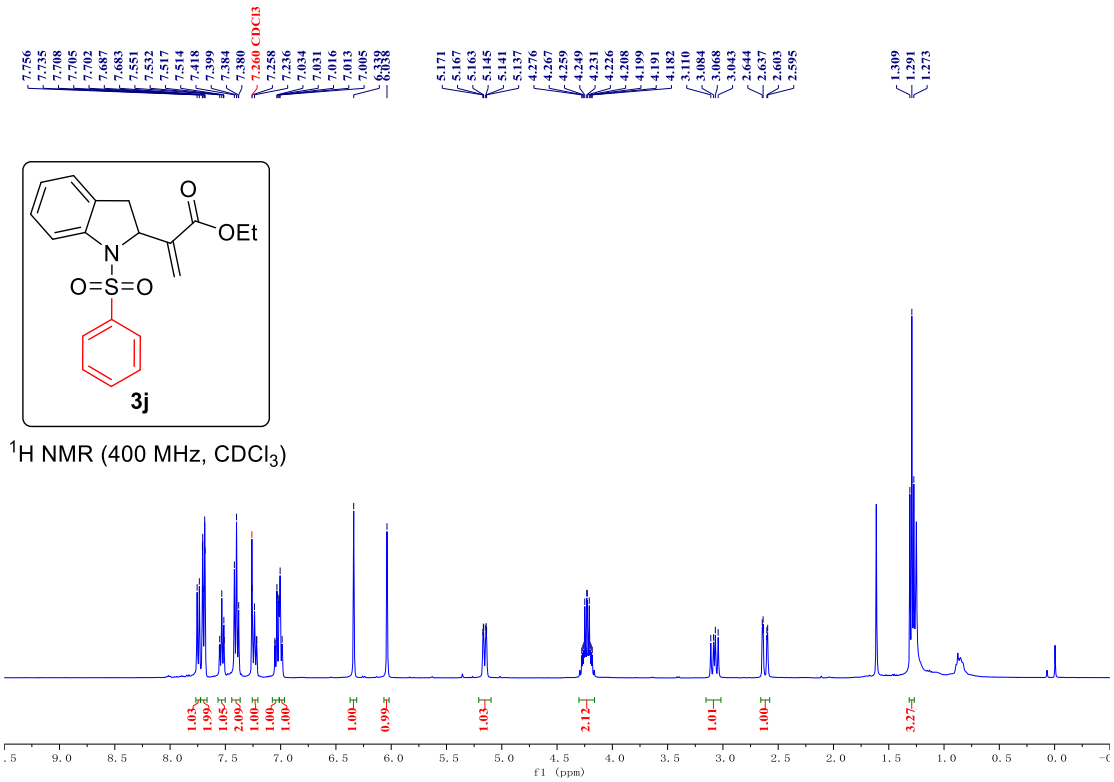
140.99
139.87
139.46
136.20
130.94
130.51
129.95
127.99
125.71
125.49
125.42
125.26
123.01
116.62
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
61.50
61.03
36.16
14.09
O
OEt
N
O=S=O
Br
3i
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)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7.708
7.705
7.702
7.687
7.683
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7.514
7.418
7.399
7.384
7.380
7.260 CDCl3
7.258
7.236
7.034
7.031
7.016
7.013
7.005
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6.038
5.171
5.167
5.163
5.145
5.141
5.137
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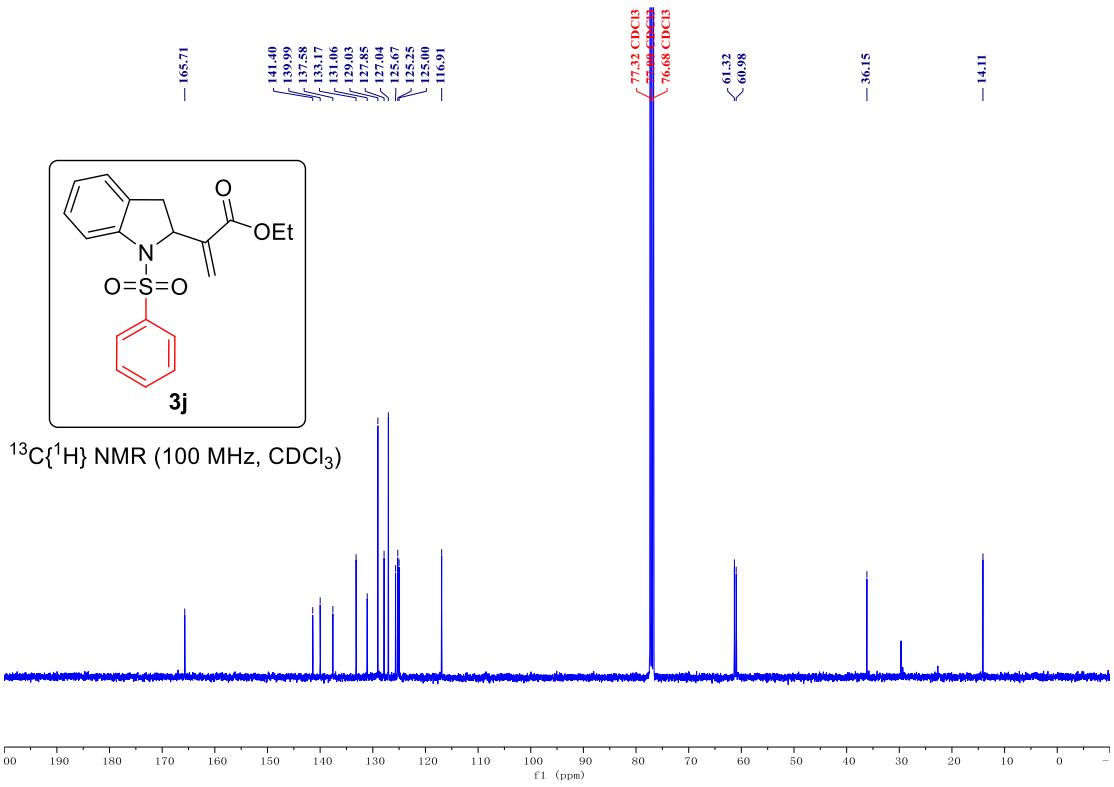
4.267
4.259
4.249
4.231
4.226
4.208
4.199
4.191
4.182
3.110
3.084
3.068
3.043
2.644
2.637
2.603
2.595
1.309
1.291
1.273
O
OEt
N
O=S=O
3j
1H NMR (400 MHz, CDCl3)
1.03
1.99
1.05
2.09
1.00
1.00
1.00
0.99
1.03
2.12
1.01
1.00
3.27
f1 (ppm)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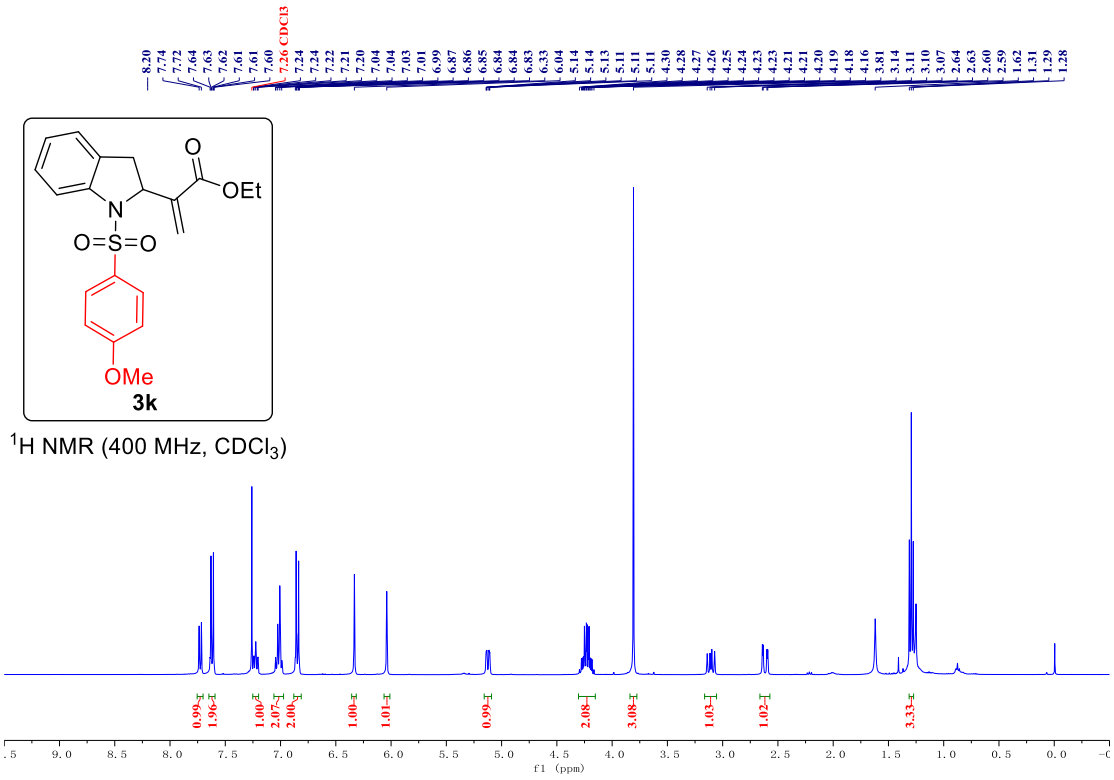
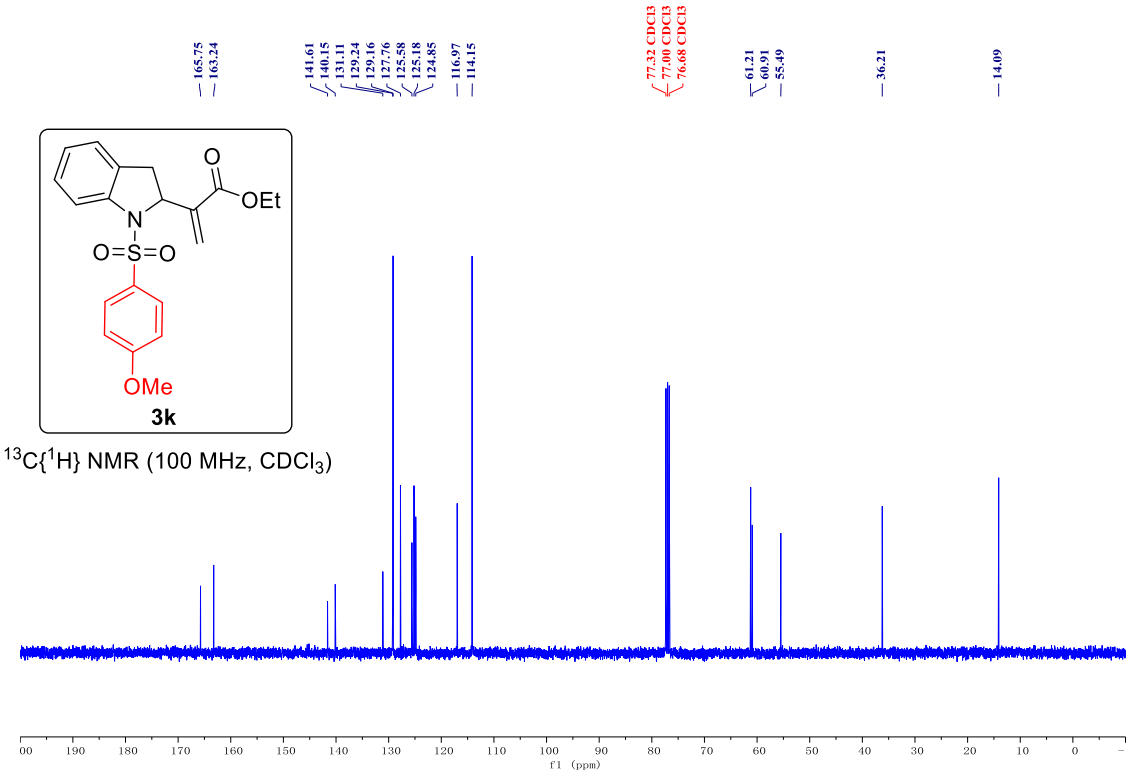
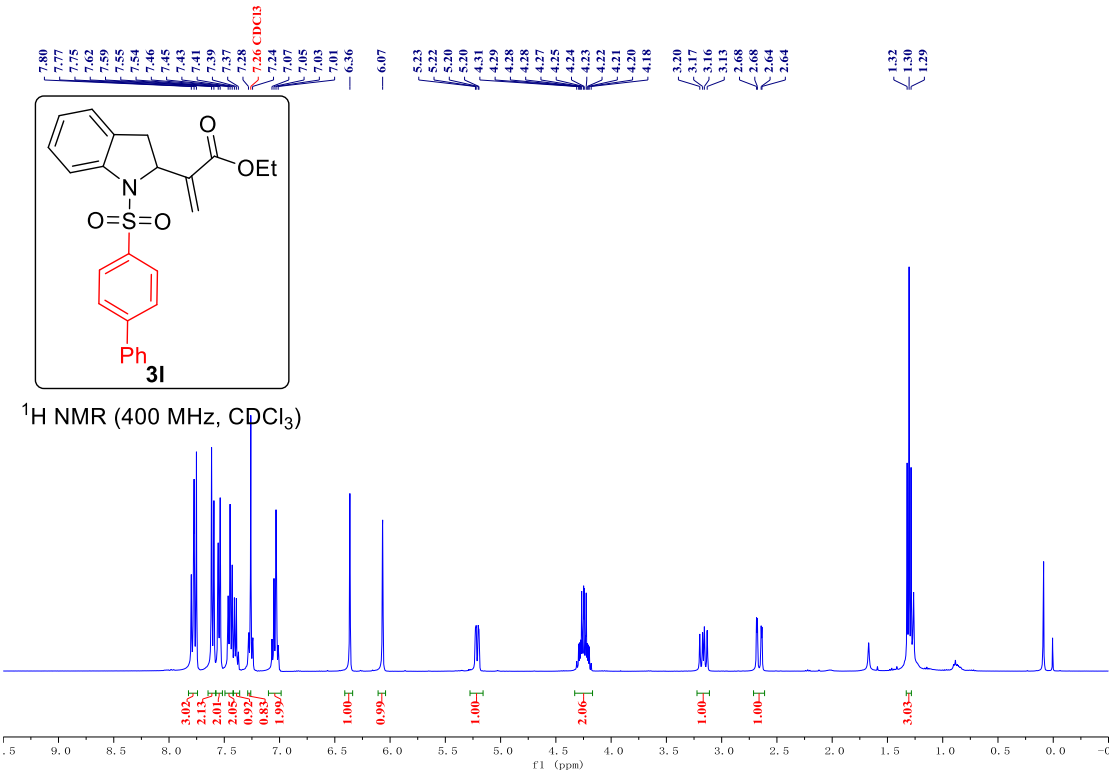
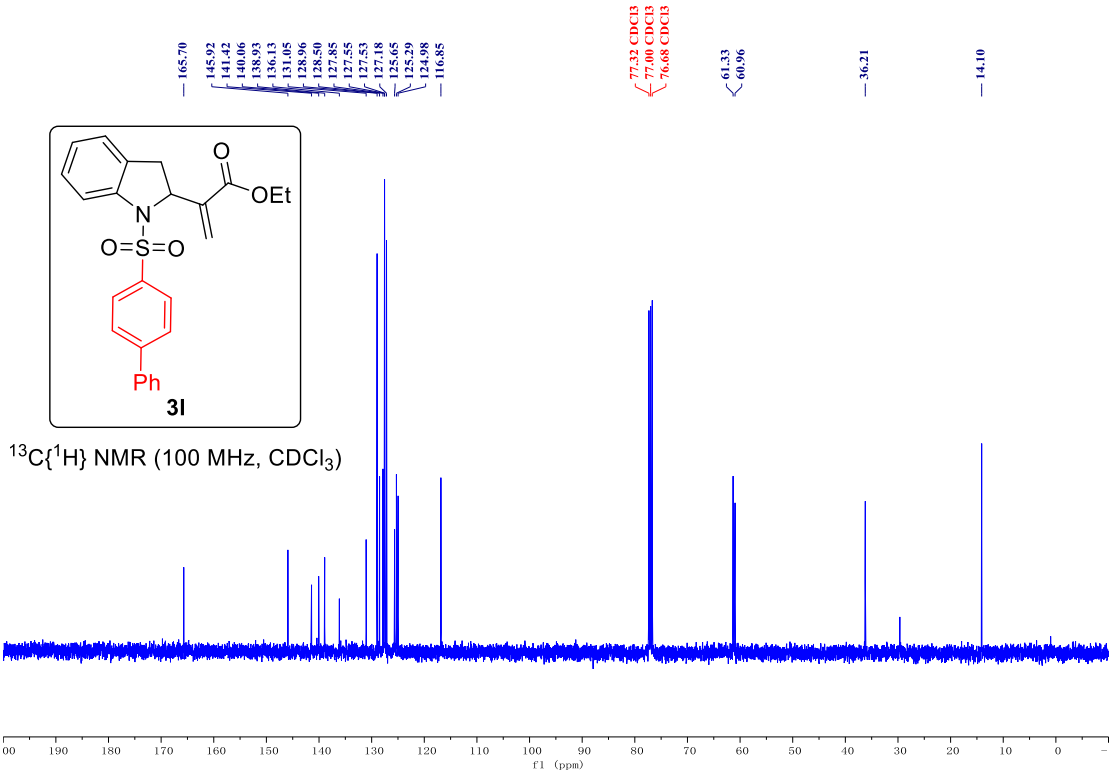
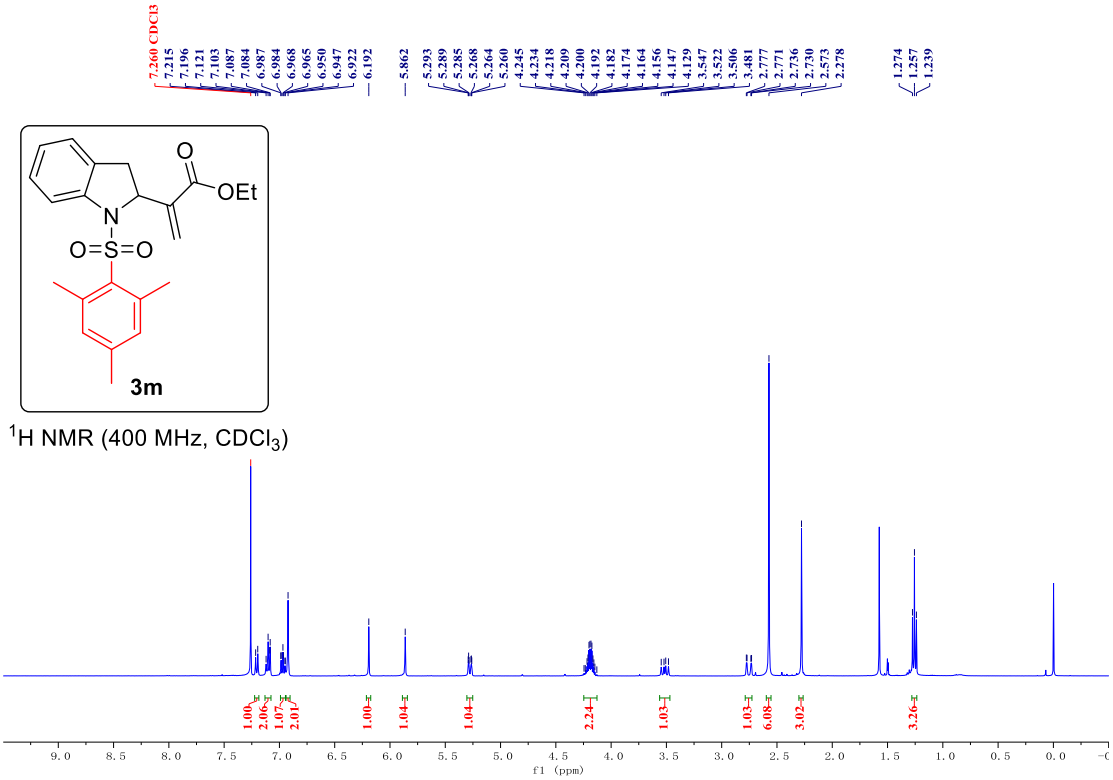
139.99
137.58
133.17
131.06
129.03
127.85
127.04
125.67
125.25
125.00
116.91
77.32 CDCl3
76.68 CDCl3
61.32
60.98
36.15
14.11
O
OEt
N
O=S=O
3j
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)


O
OEt
N
O=S=O
OMe
3k
1H NMR (400 MHz, CDCl3)
f1 (ppm)

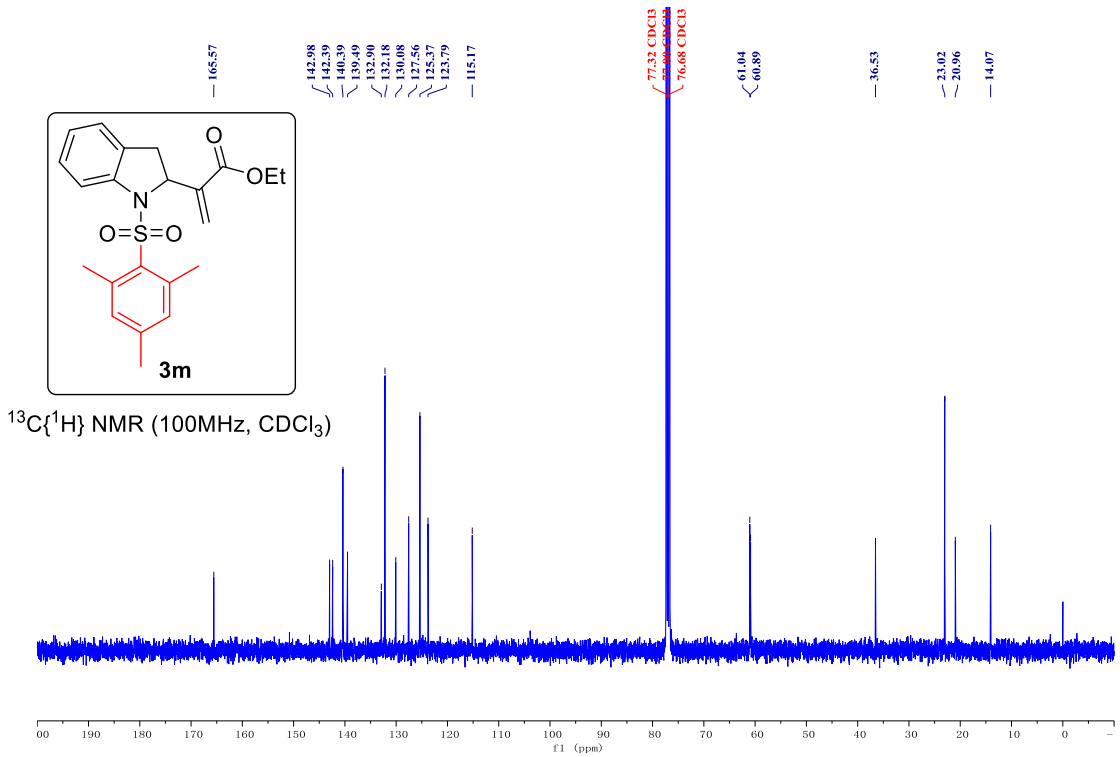

O
OEt
N
O=S=O
OMe
3k
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)


7.80
7.77
7.75
7.62
7.59
7.55
7.54
7.46
7.45
7.43
7.41
7.39
7.37
7.28
7.26 CDCl3
7.24
7.07
7.05
7.03
7.01
6.36
6.07
5.23
5.22
5.20
5.20
4.31
4.29
4.28
4.28
4.27
4.25
4.24
4.23
4.22
4.21
4.20
4.18
3.20
3.17
3.16
3.13
2.68
2.64
2.64
1.32
1.30
1.29
O
OEt
N
O=S=O
Ph
3l
1H NMR (400 MHz, CDCl3)
3.02
2.13
2.01
2.05
0.92
0.83
1.99
1.00
0.99
1.00
2.06
1.00
1.00
3.03
f1 (ppm)

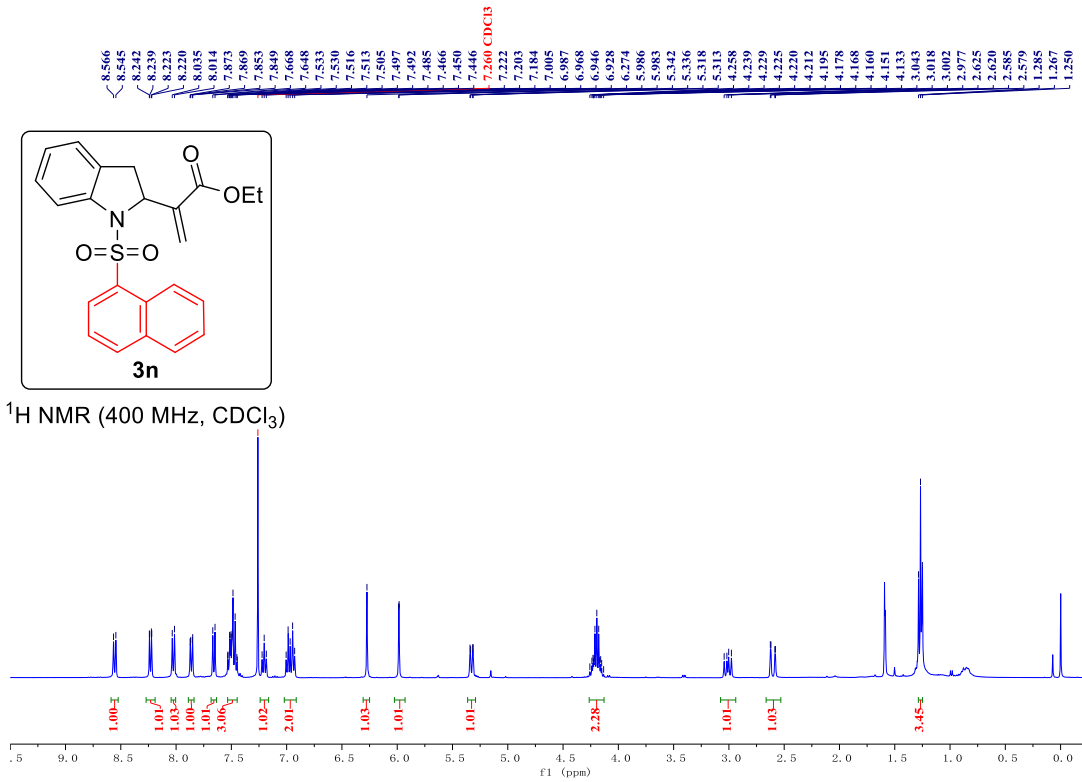

165.70
145.92
141.42
140.06
138.93
136.13
131.05
128.96
128.50
127.85
127.55
127.53
127.18
125.65
125.29
124.98
116.85
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
61.33
60.96
36.21
14.10
O
OEt
N
O=S=O
Ph
3l
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

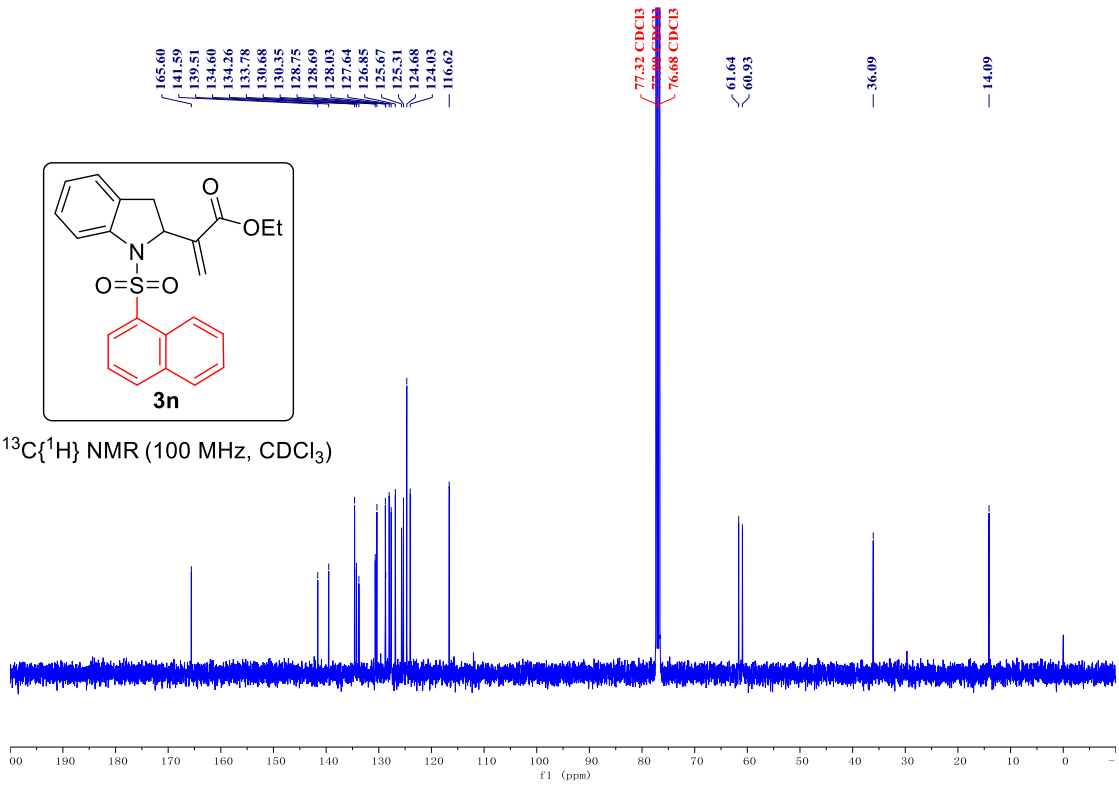


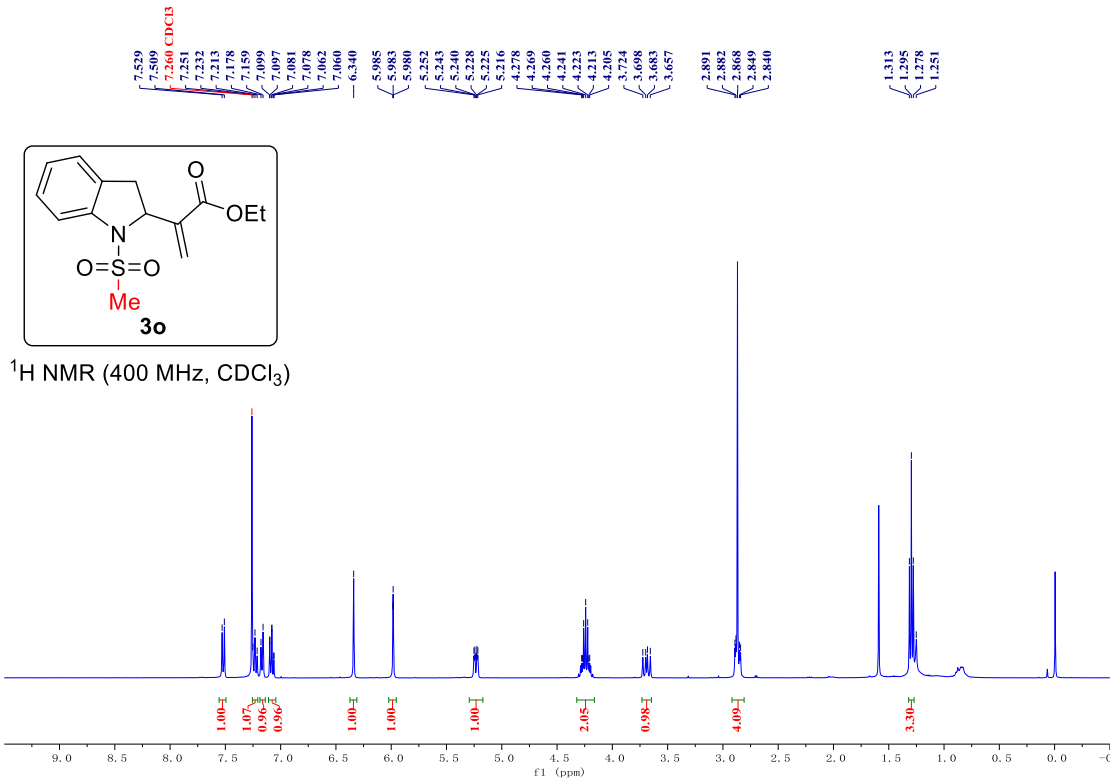
^{1}H NMR (400 MHz, $CDCl_3$)



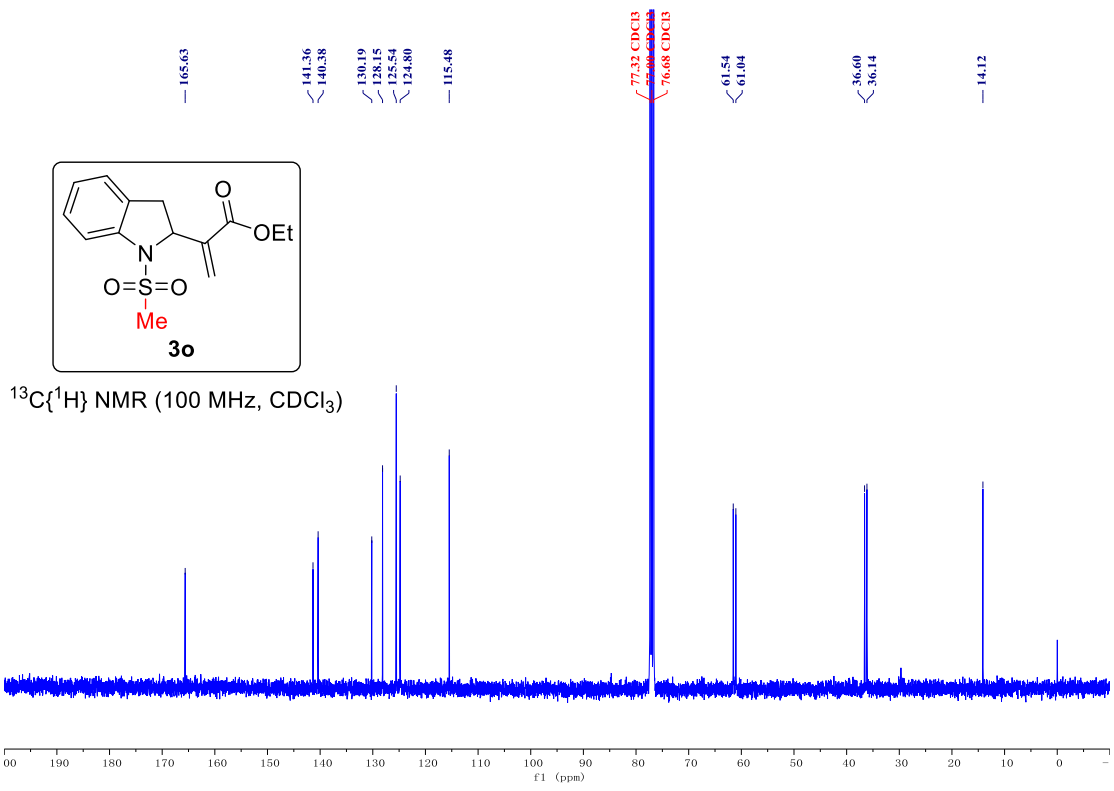
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)


3n
1H NMR (400 MHz, CDCl3)
f1 (ppm)

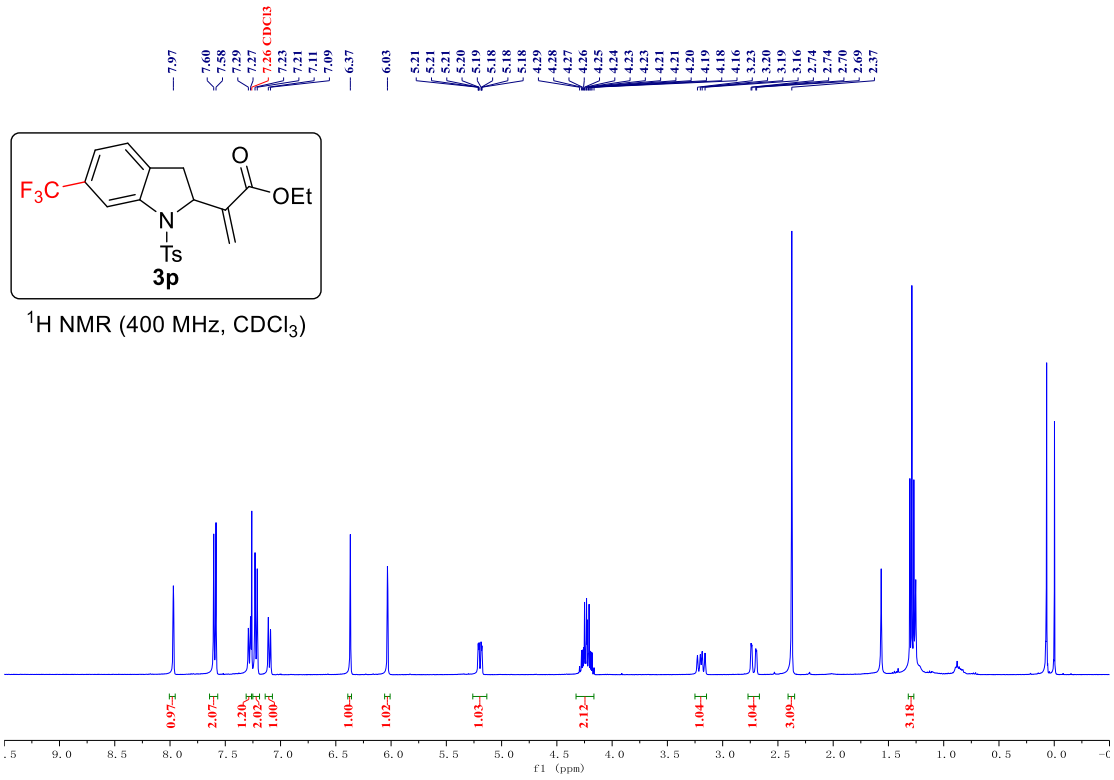

3n
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

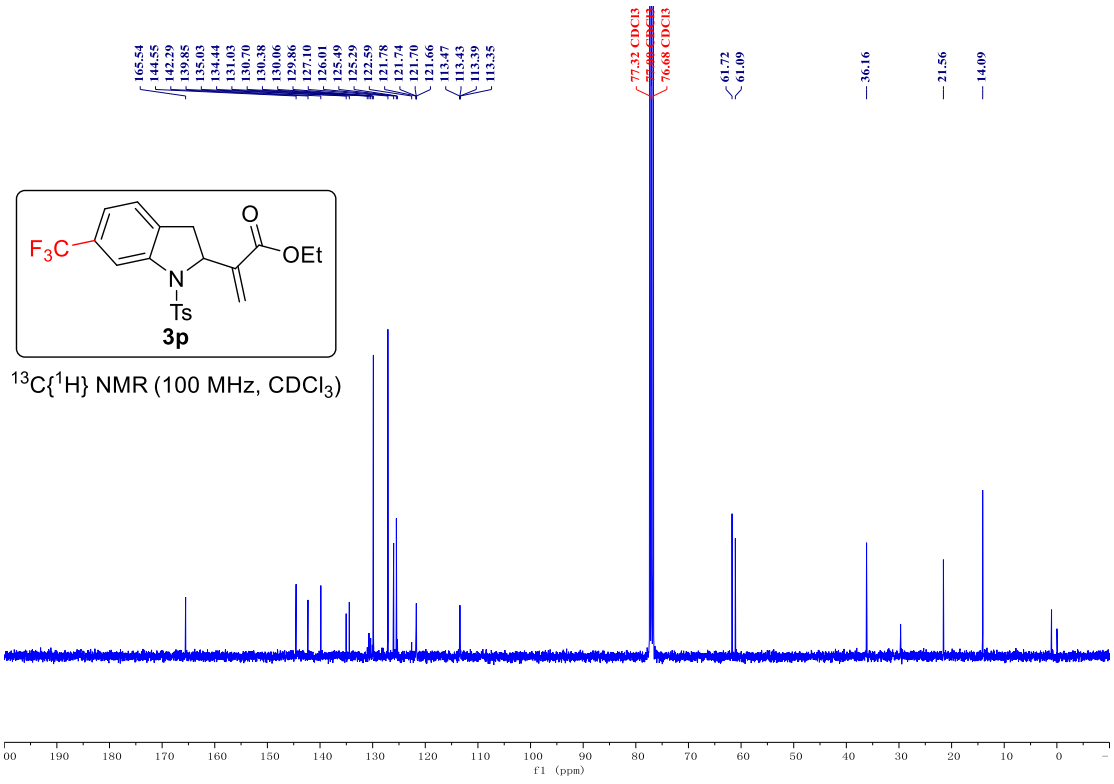


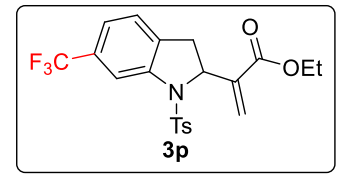
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

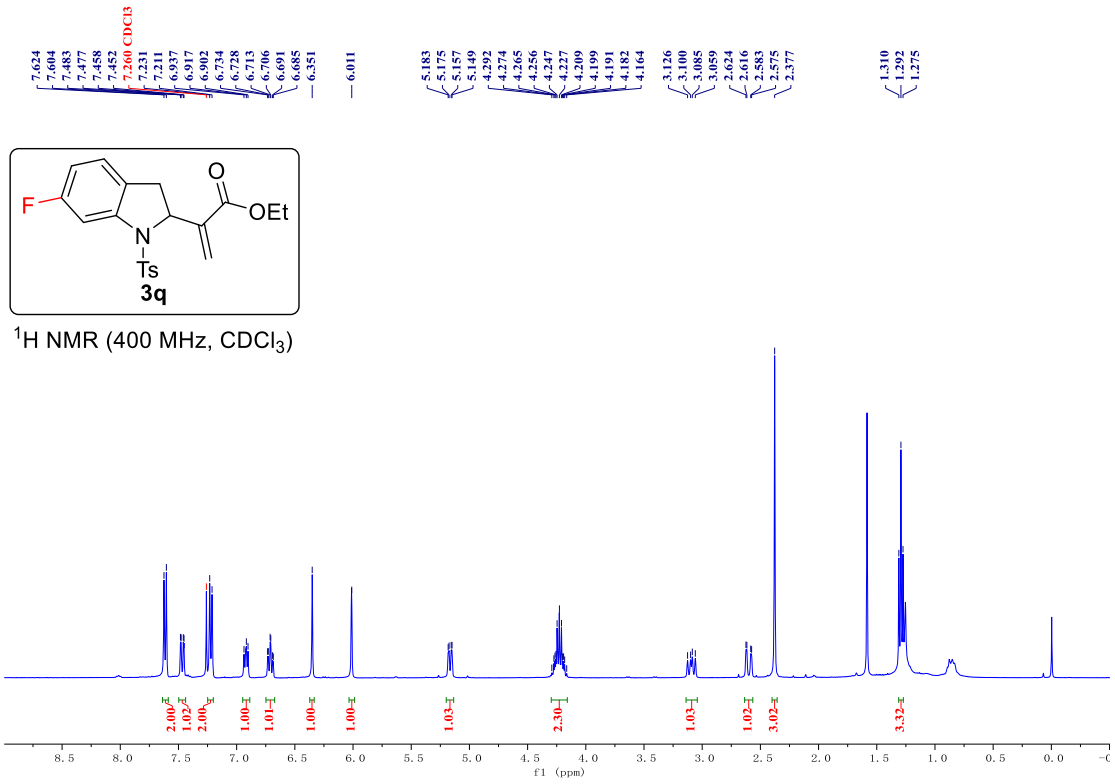

7.97
7.60
7.58
7.29
7.27
7.26 CDCl3
7.23
7.21
7.11
7.09
6.37
6.03
5.21
5.21
5.21
5.20
5.19
5.18
5.18
5.18
4.29
4.28
4.27
4.26
4.25
4.24
4.23
4.23
4.21
4.21
4.20
4.19
4.18
4.16
3.23
3.20
3.19
3.16
2.74
2.74
2.70
2.69
2.37
F3C
O
OEt
N
Ts
3p
1H NMR (400 MHz, CDCl3)
0.97
2.07
1.20
2.02
1.00
1.00
1.02
1.03
2.12
1.04
1.04
3.09
3.18
f1 (ppm)

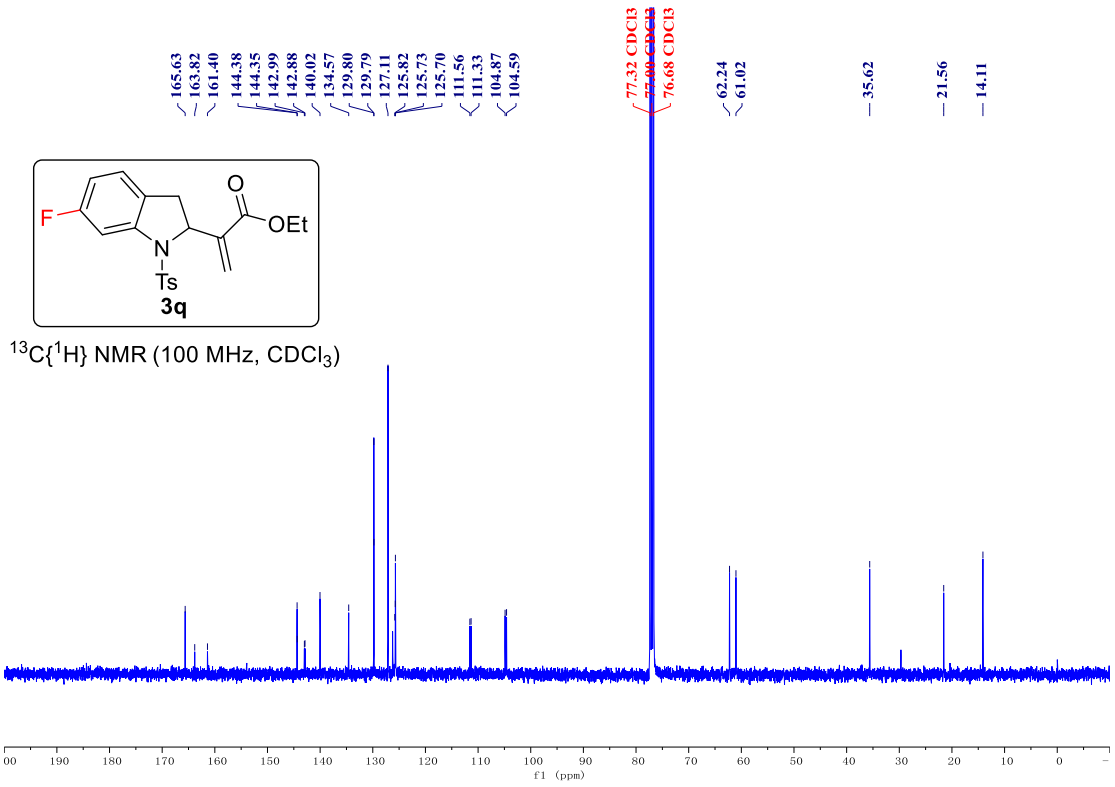

165.54
144.55
142.29
139.85
135.03
134.44
131.03
130.70
130.38
130.06
129.86
127.10
126.01
125.49
125.29
122.59
121.78
121.74
121.70
121.66
113.47
113.43
113.39
113.35
77.32 CDCl3
76.68 CDCl3
61.72
61.09
36.16
21.56
14.09
F3C
O
OEt
N
Ts
3p
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

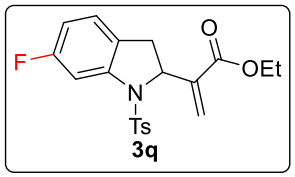


3p

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

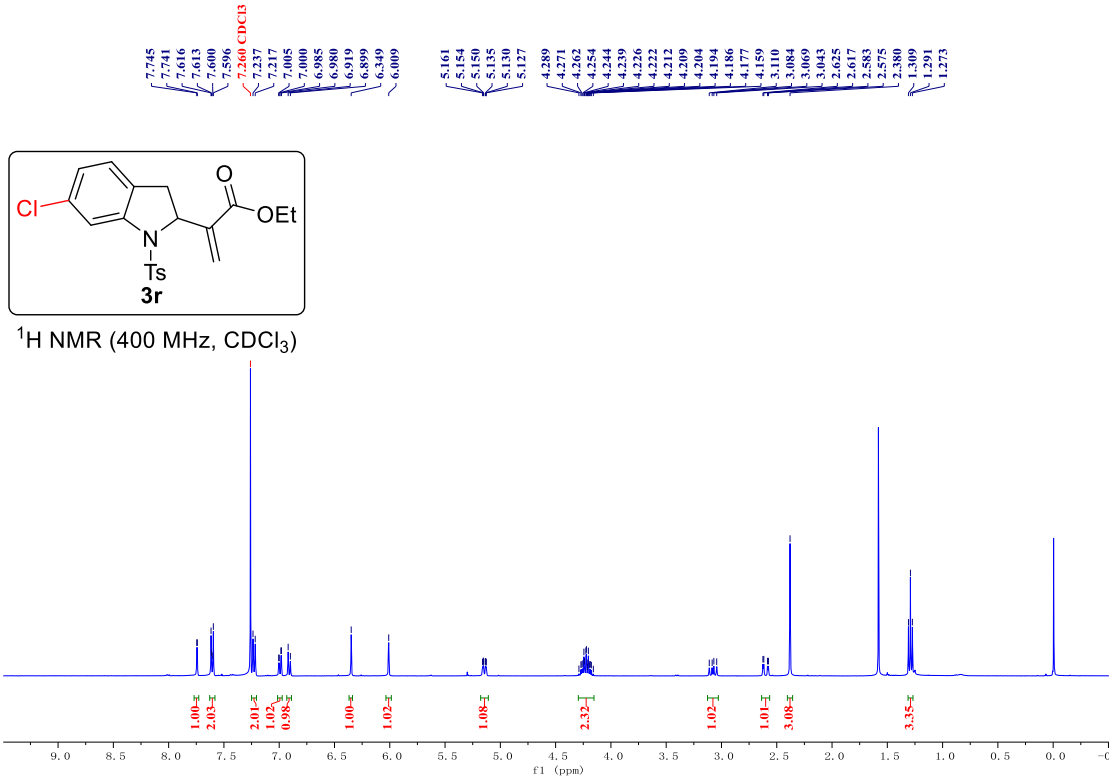

7.624
7.604
7.483
7.477
7.458
7.452
7.260 CDCl3
7.231
7.211
6.937
6.917
6.902
6.734
6.728
6.713
6.706
6.691
6.685
6.351
6.011
5.183
5.175
5.157
5.149
4.292
4.274
4.265
4.256
4.247
4.227
4.209
4.199
4.191
4.182
4.164
3.126
3.100
3.085
3.059
2.624
2.616
2.583
2.575
2.377
1.310
1.292
1.275
F
O
OEt
N
Ts
3q
1H NMR (400 MHz, CDCl3)
2.00
1.02
2.00
1.00
1.01
1.00
1.00
1.03
2.30
1.03
1.02
3.02
3.32
f1 (ppm)

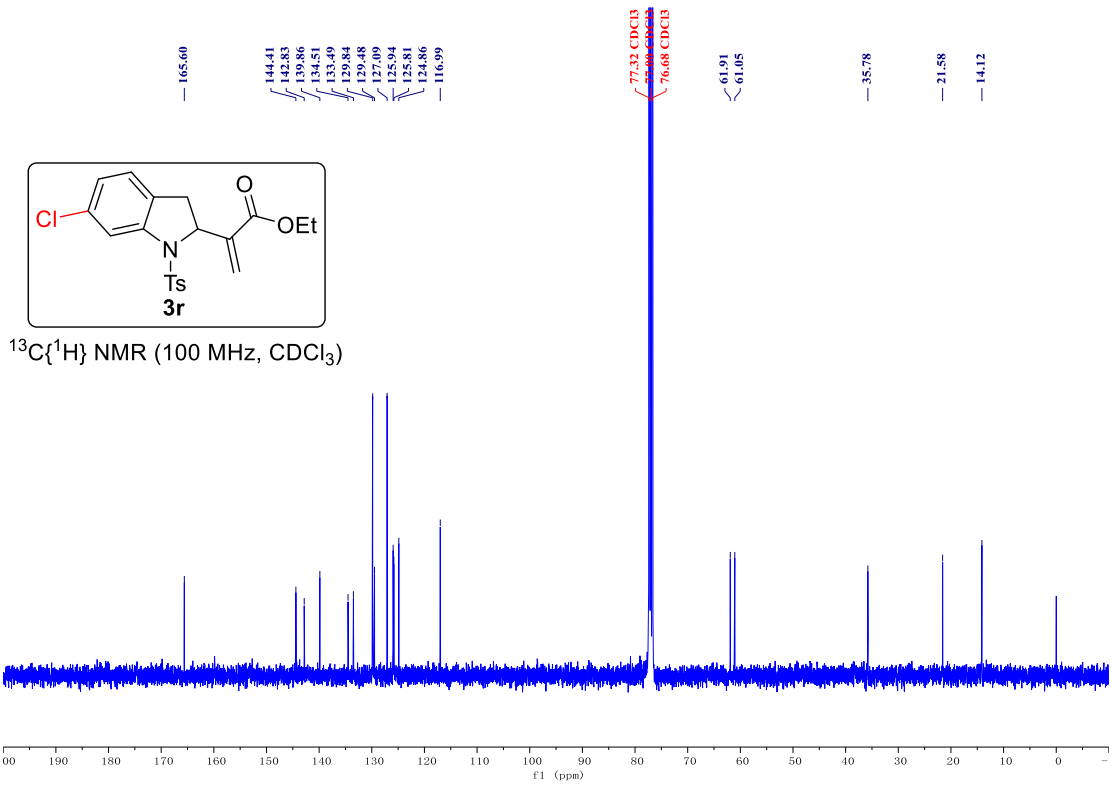

165.63
163.82
161.40
144.38
144.35
142.99
142.88
140.02
134.57
129.80
129.79
127.11
125.82
125.73
125.70
111.56
111.33
104.87
104.59
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
62.24
61.02
35.62
21.56
14.11
F
O
OEt
N
Ts
3q
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

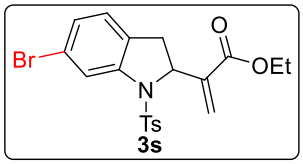


3q

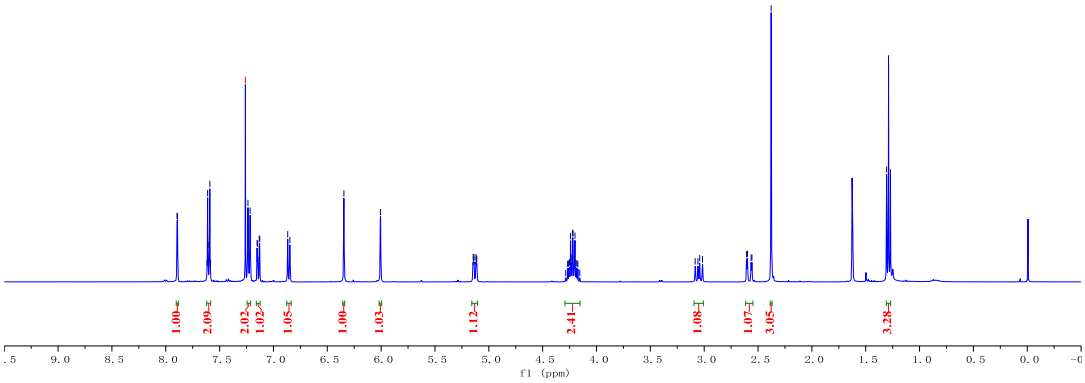
$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

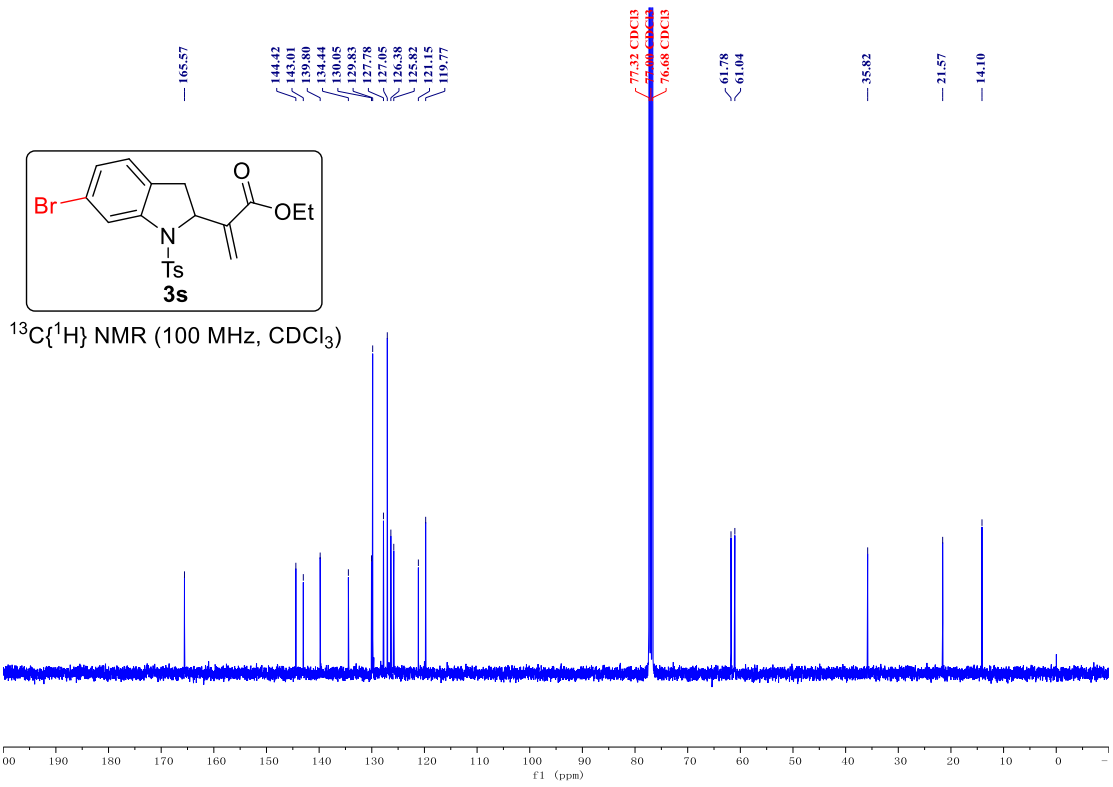

7.745
7.741
7.616
7.613
7.600
7.596
7.260 CDCl3
7.237
7.217
7.005
7.000
6.985
6.980
6.919
6.899
6.349
6.009
5.161
5.154
5.150
5.135
5.130
5.127
4.289
4.271
4.262
4.254
4.244
4.239
4.226
4.222
4.212
4.209
4.204
4.194
4.186
4.177
4.159
3.110
3.084
3.069
3.043
2.625
2.617
2.583
2.575
2.380
1.309
1.291
1.273
Cl
O
OEt
N
Ts
3r
1H NMR (400 MHz, CDCl3)
1.00
2.03
2.01
1.02
0.98
1.00
1.02
1.08
2.32
1.02
1.01
3.08
3.35
f1 (ppm)


165.60
144.41
142.83
139.86
134.51
133.49
129.84
129.48
127.09
125.94
125.81
124.86
116.99
77.32 CDCl3
76.68 CDCl3
61.91
61.05
35.78
21.58
14.12
Cl
O
OEt
N
Ts
3r
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

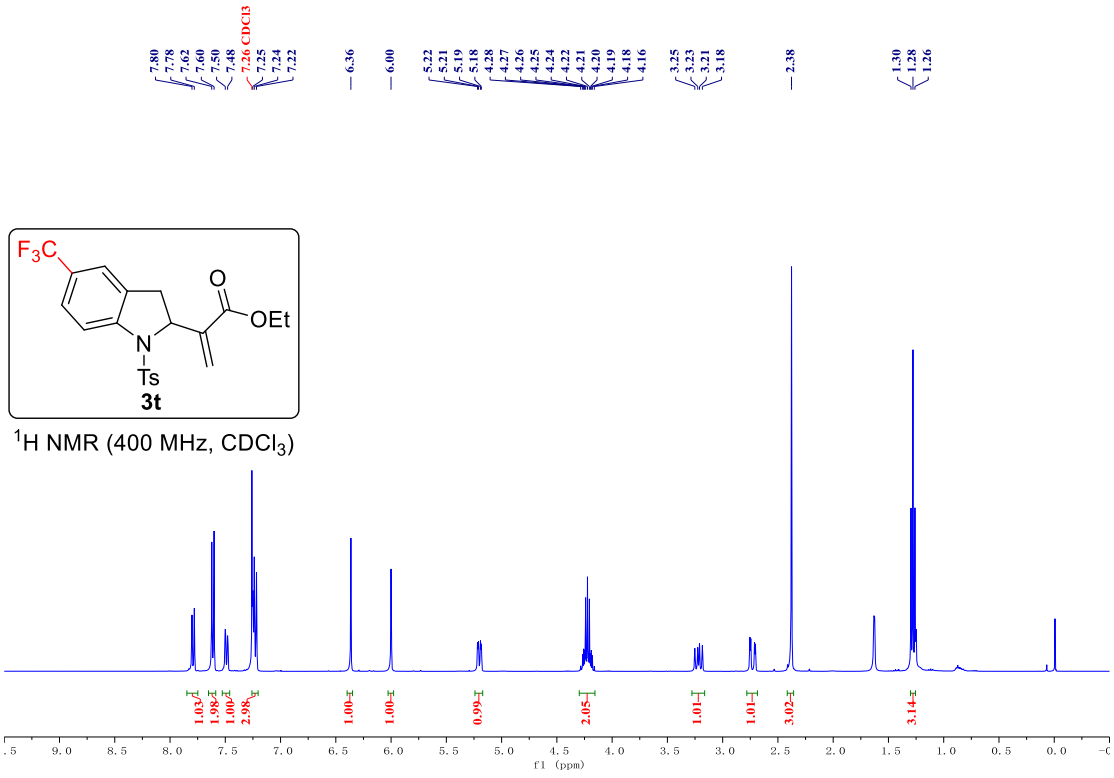


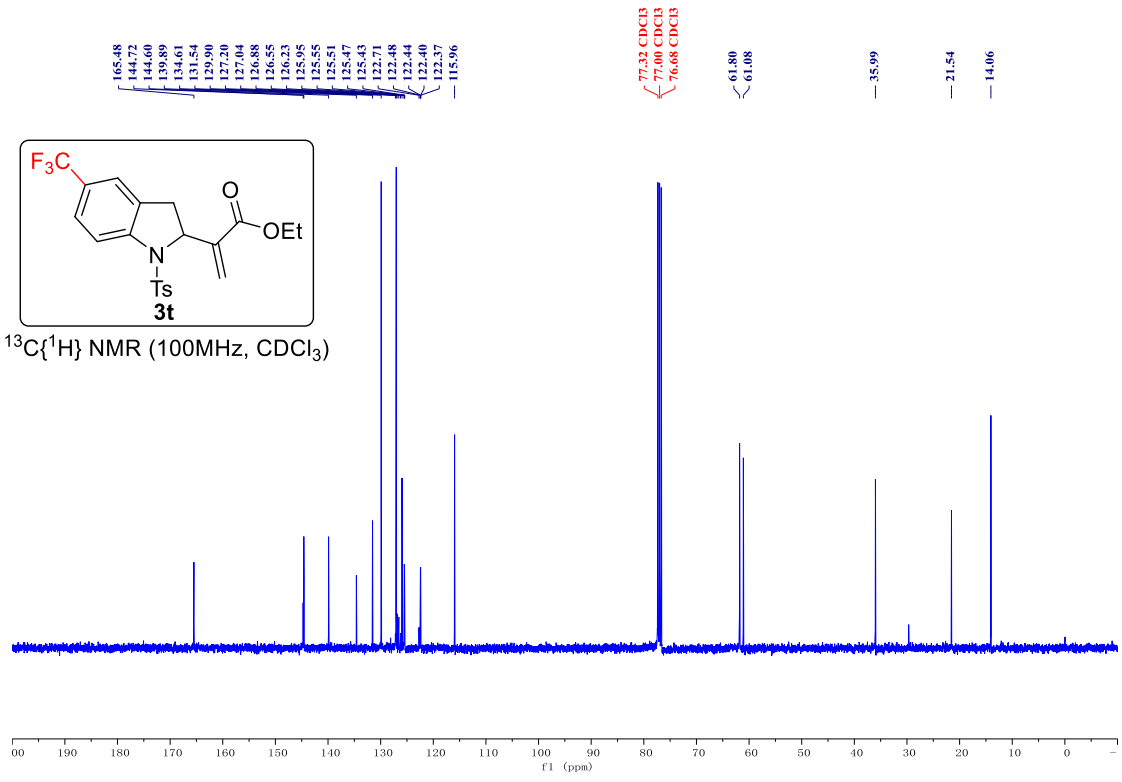
^{1}H NMR (400 MHz, $CDCl_3$)

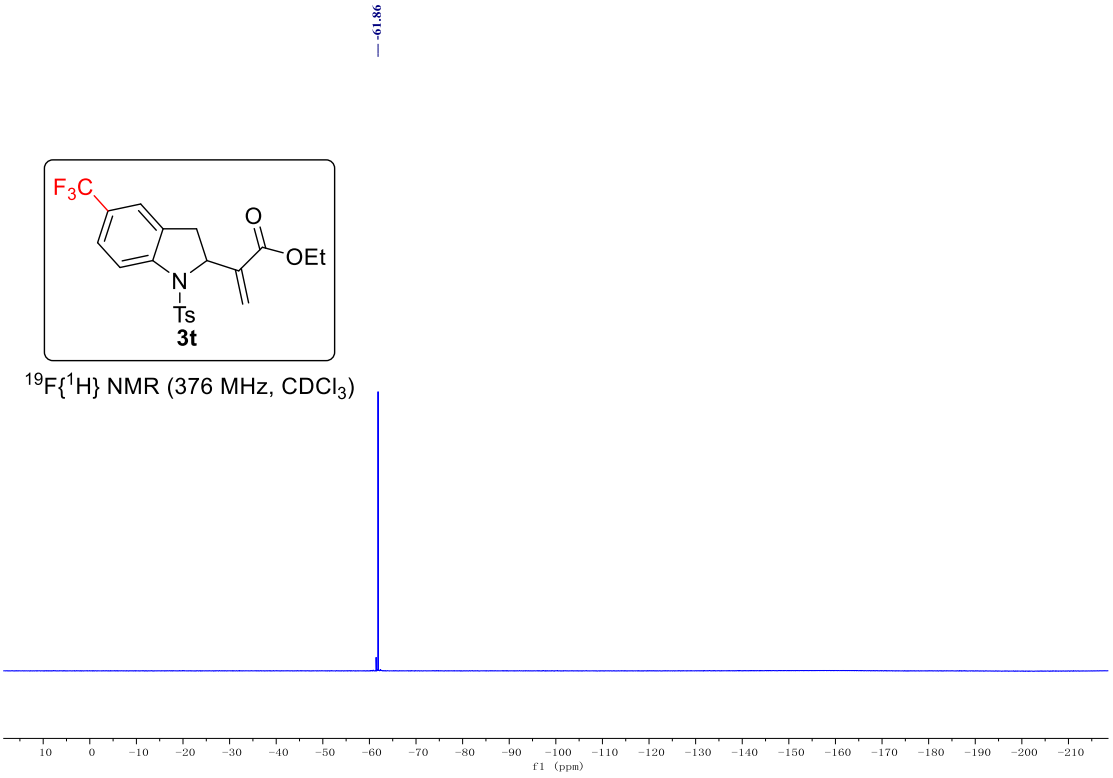




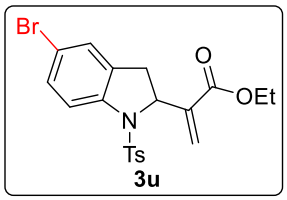
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)


7.80
7.78
7.62
7.60
7.50
7.48
7.26 CDCl3
7.25
7.24
7.22
6.36
6.00
5.22
5.21
5.19
5.18
4.28
4.27
4.26
4.25
4.24
4.22
4.21
4.20
4.19
4.18
4.16
3.25
3.23
3.21
3.18
2.38
1.30
1.28
1.26
F3C
O
OEt
N
Ts
3t
1H NMR (400 MHz, CDCl3)
1.03
1.98
1.00
2.98
1.00
1.00
0.99
2.05
1.01
1.01
3.02
3.14
f1 (ppm)

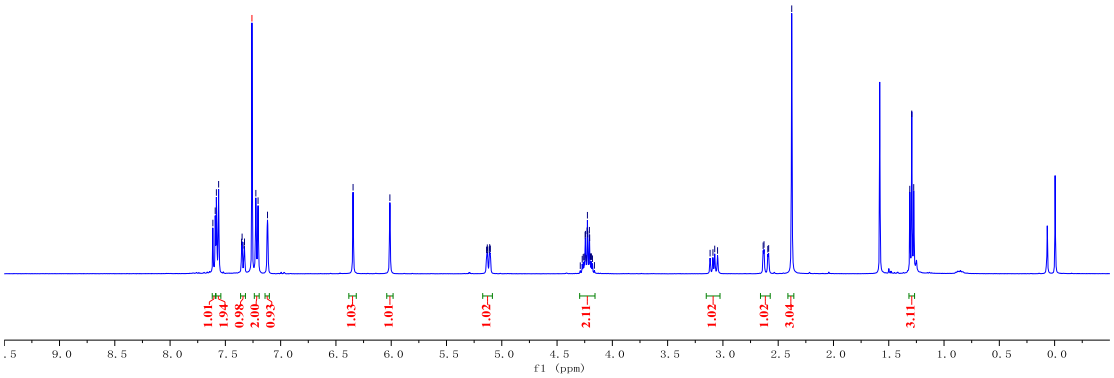

165.48
144.72
144.60
139.89
134.61
131.54
129.90
127.20
127.04
126.88
126.55
126.23
125.95
125.55
125.51
125.47
125.43
122.71
122.48
122.44
122.40
122.37
115.96
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
61.80
61.08
35.99
21.54
14.06
F3C
O
OEt
N
Ts
3t
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)

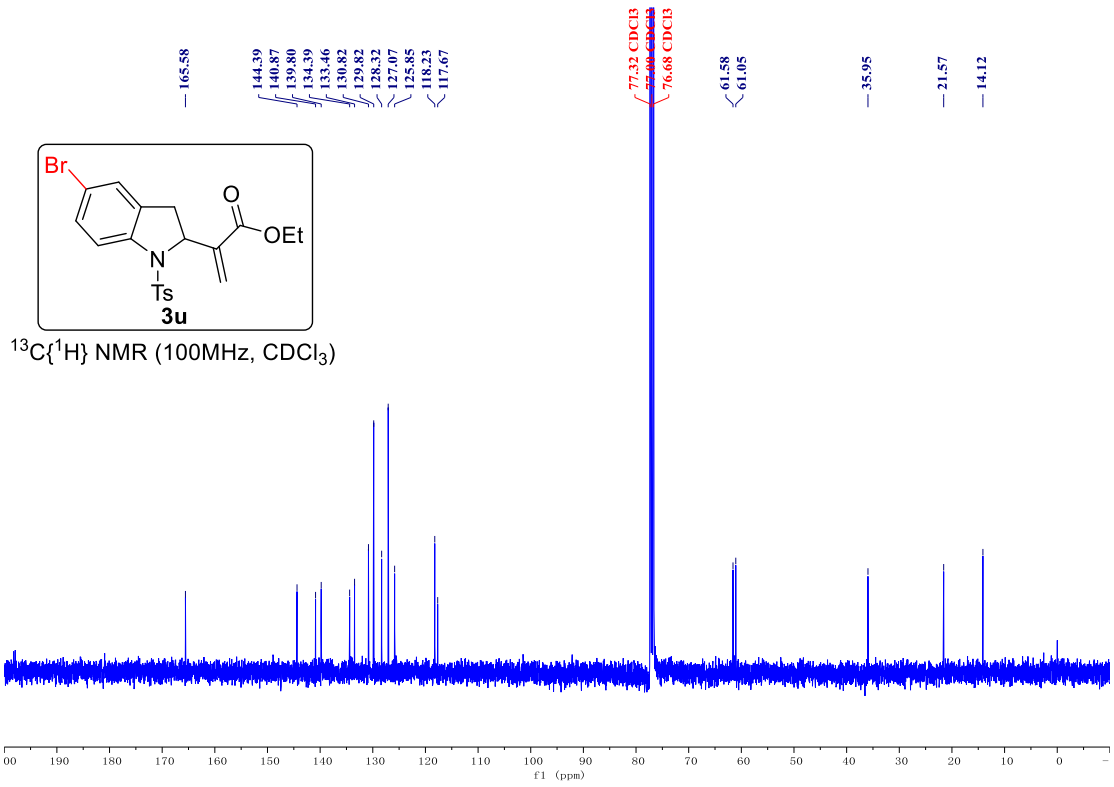


$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$)

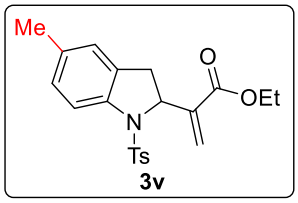


^{1}H NMR (400 MHz, $CDCl_3$)

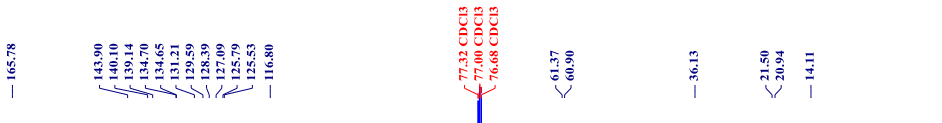


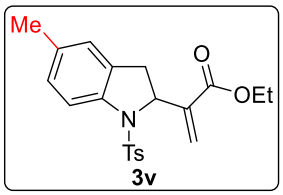


^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)

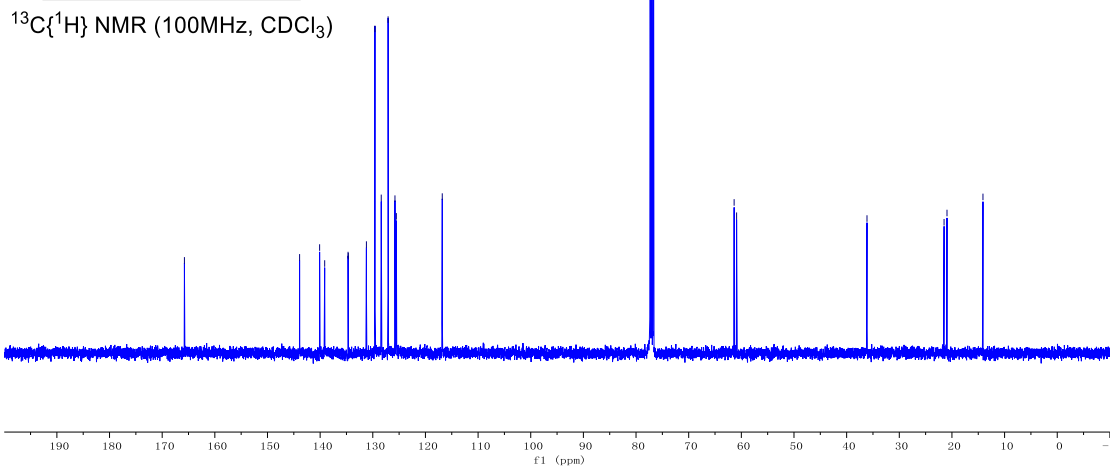


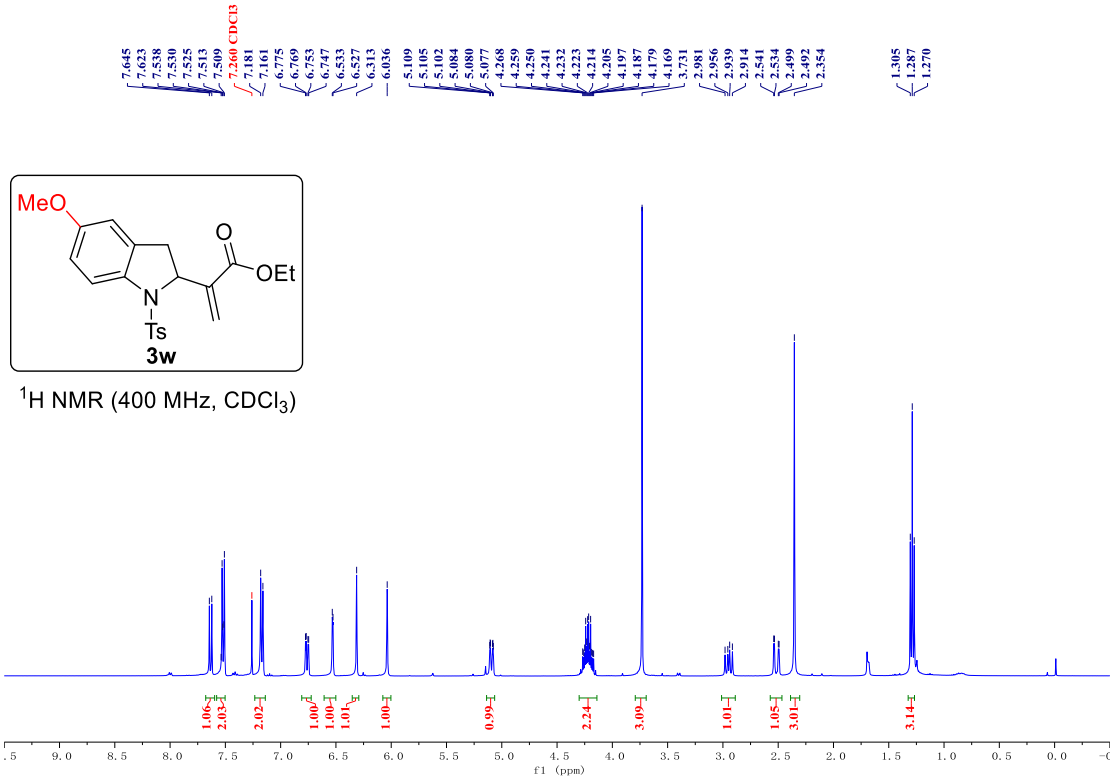
^{1}H NMR (400 MHz, $CDCl_3$)

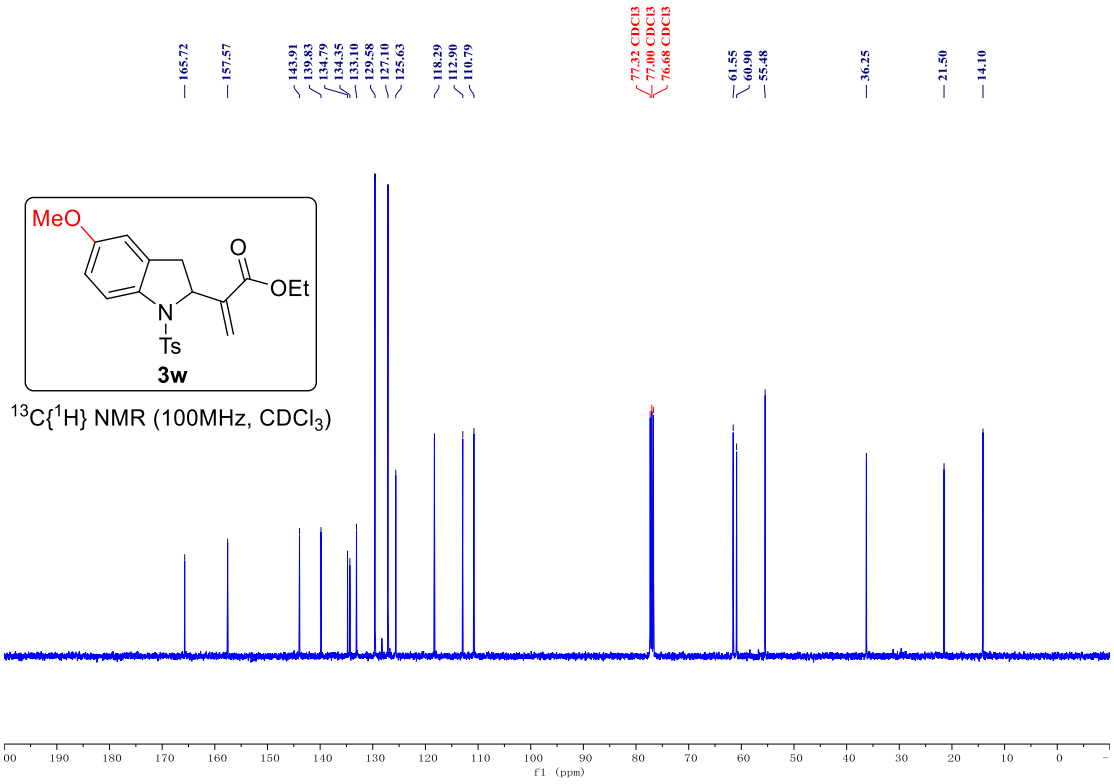


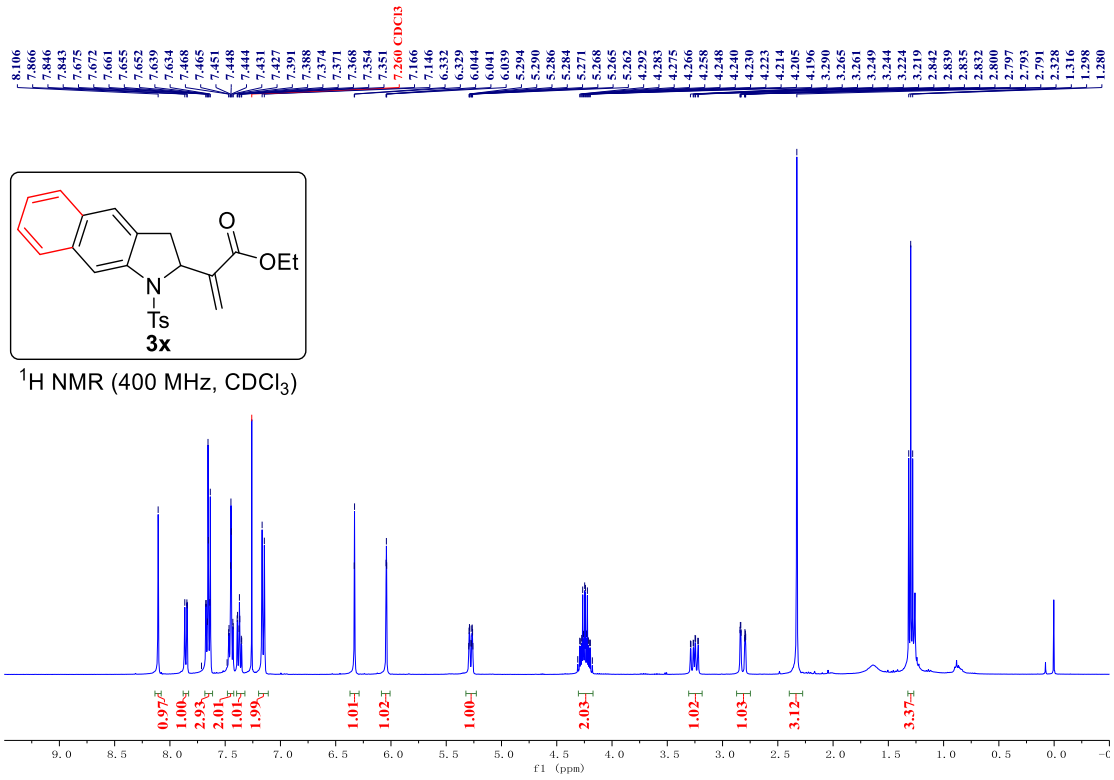


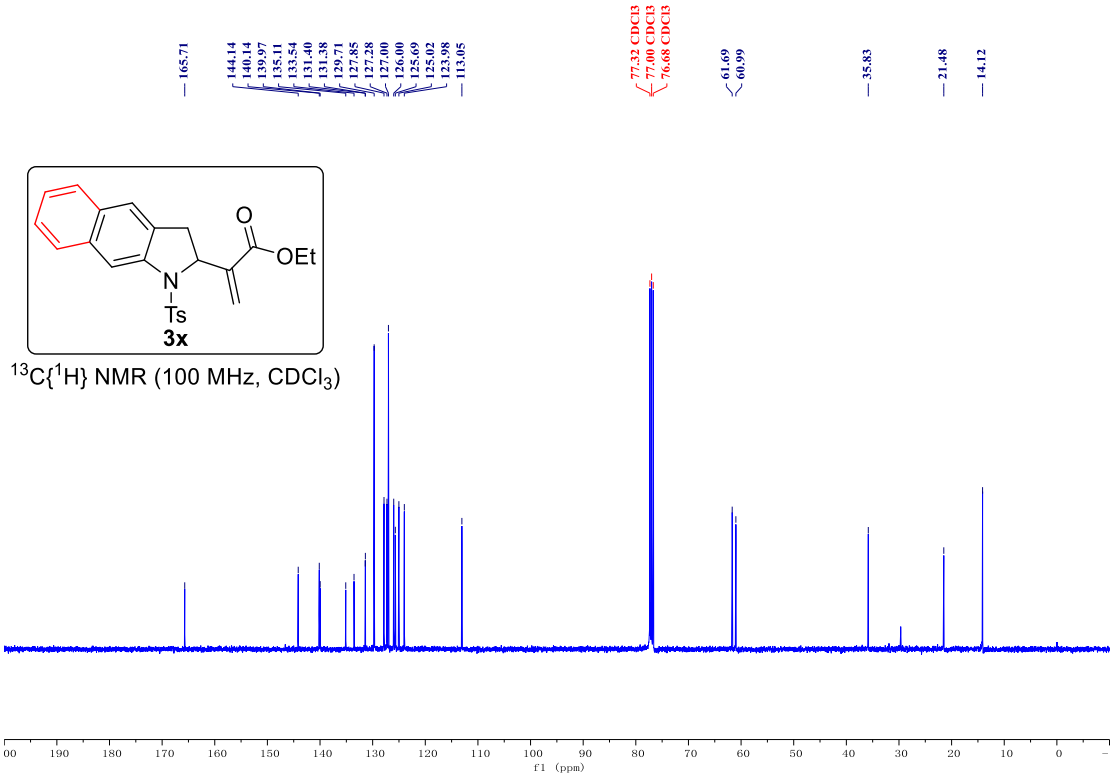
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$)

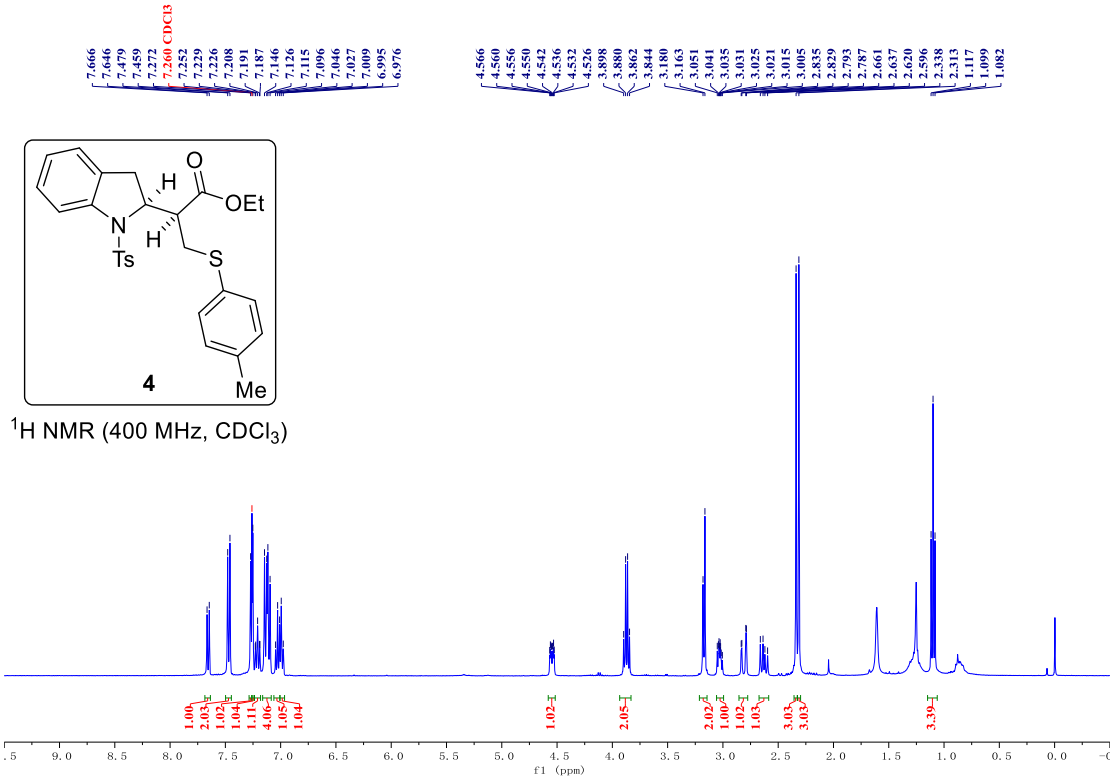



7.645
7.623
7.538
7.530
7.525
7.513
7.509
7.260 CDCl3
7.181
7.161
6.775
6.769
6.753
6.747
6.533
6.527
6.313
6.036
5.109
5.105
5.102
5.084
5.080
5.077
4.268
4.259
4.250
4.241
4.232
4.223
4.214
4.205
4.197
4.187
4.179
4.169
3.731
2.981
2.956
2.939
2.914
2.541
2.534
2.499
2.492
2.354
1.305
1.287
1.270
MeO
O
OEt
N
Ts
3w
1H NMR (400 MHz, CDCl3)
1.06
2.03
2.02
1.00
1.00
1.01
1.00
0.99
2.24
3.09
1.01
1.05
3.01
3.14
f1 (ppm)

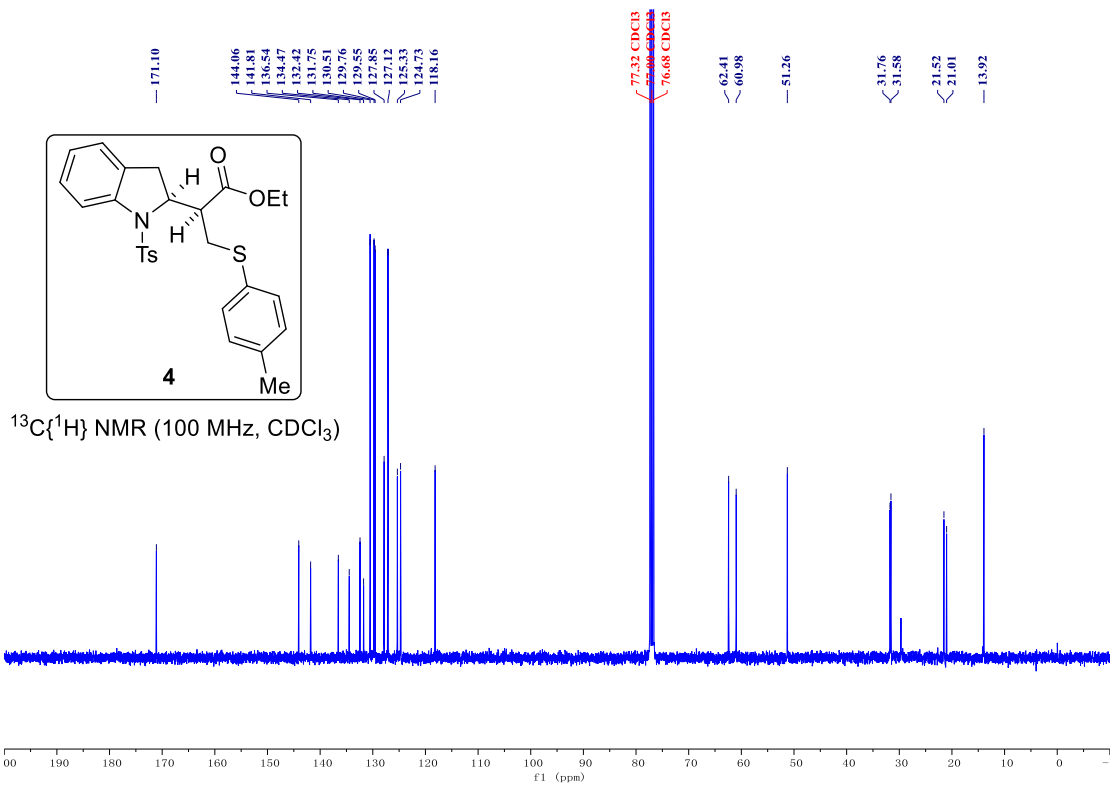

165.72
157.57
143.91
139.83
134.79
134.35
133.10
129.58
127.10
125.63
118.29
112.90
110.79
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
61.55
60.90
55.48
36.25
21.50
14.10
MeO
O
OEt
N
Ts
3w
13C{1H} NMR (100MHz, CDCl3)
f1 (ppm)


8.106
7.866
7.846
7.843
7.675
7.672
7.661
7.655
7.652
7.639
7.634
7.468
7.465
7.451
7.448
7.444
7.431
7.427
7.391
7.388
7.374
7.371
7.368
7.354
7.351
7.260 CDCl3
7.166
7.146
6.332
6.329
6.044
6.041
6.039
5.294
5.290
5.286
5.284
5.271
5.268
5.265
5.262
4.292
4.283
4.275
4.266
4.258
4.248
4.240
4.230
4.223
4.214
4.205
4.196
3.290
3.265
3.261
3.249
3.244
3.224
3.219
2.842
2.839
2.835
2.832
2.800
2.797
2.793
2.791
2.328
1.316
1.298
1.280
O
OEt
N
Ts
3x
1H NMR (400 MHz, CDCl3)
0.97
1.00
2.93
2.01
1.01
1.99
1.01
1.02
1.00
2.03
1.02
1.03
3.12
3.37
f1 (ppm)

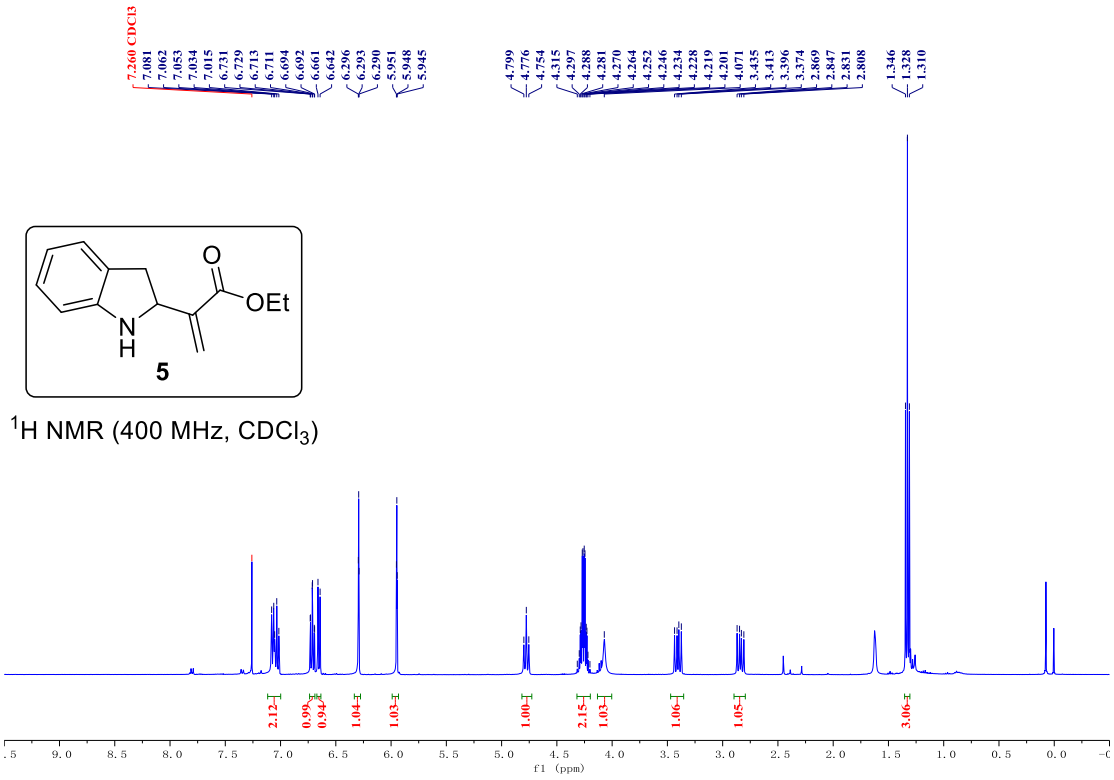

165.71
144.14
140.14
139.97
135.11
133.54
131.40
131.38
129.71
127.85
127.28
127.00
126.00
125.69
125.02
123.98
113.05
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
61.69
60.99
35.83
21.48
14.12
O
OEt
N
Ts
3x
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)



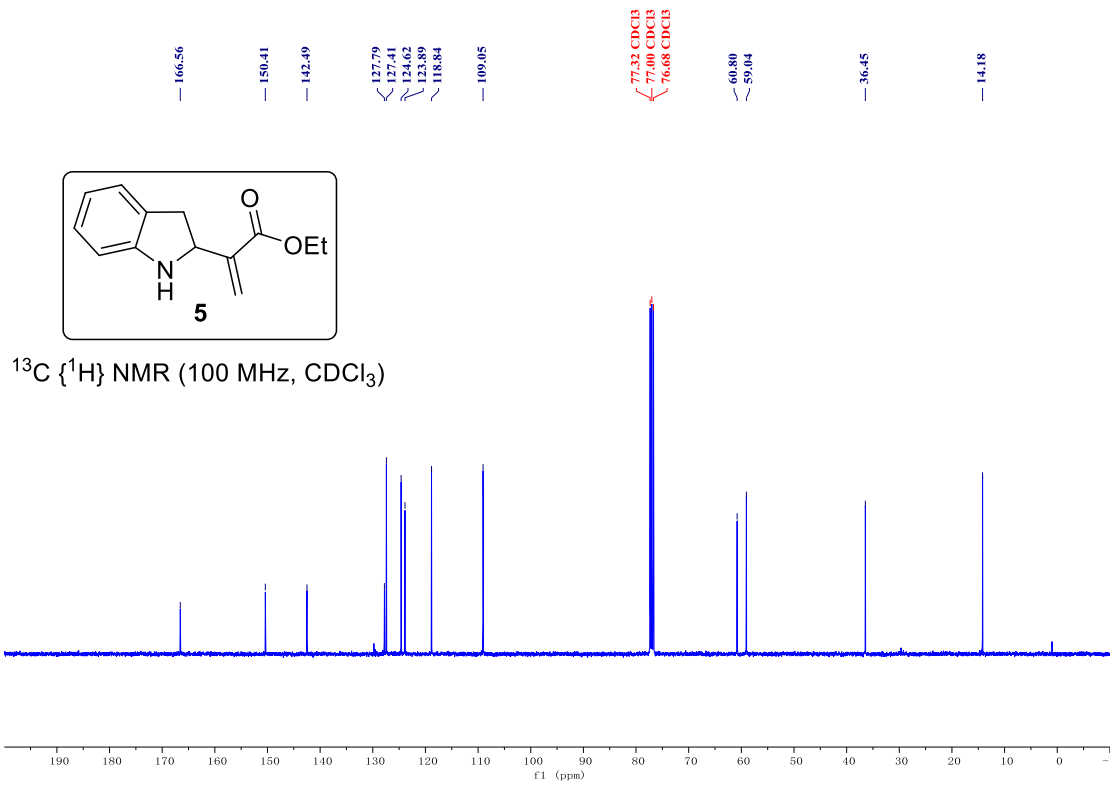
^{1}H NMR (400 MHz, $CDCl_3$)



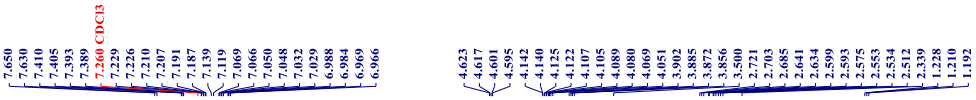
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)

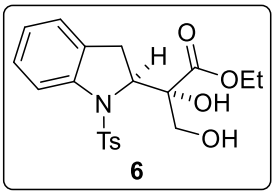


^{1}H NMR (400 MHz, $CDCl_3$)



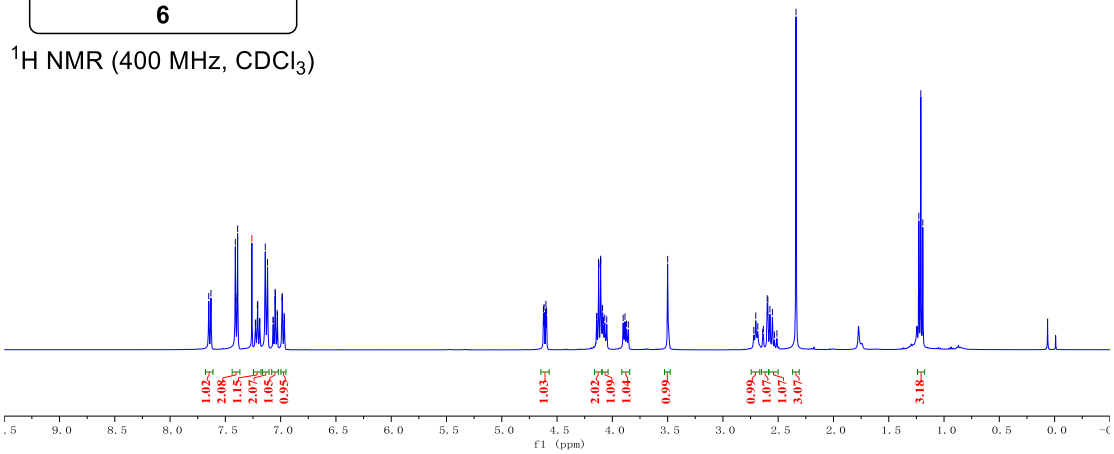
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)

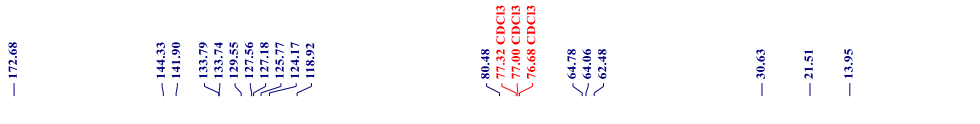


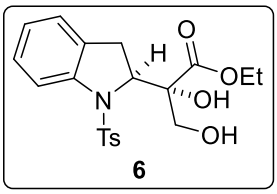


6

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

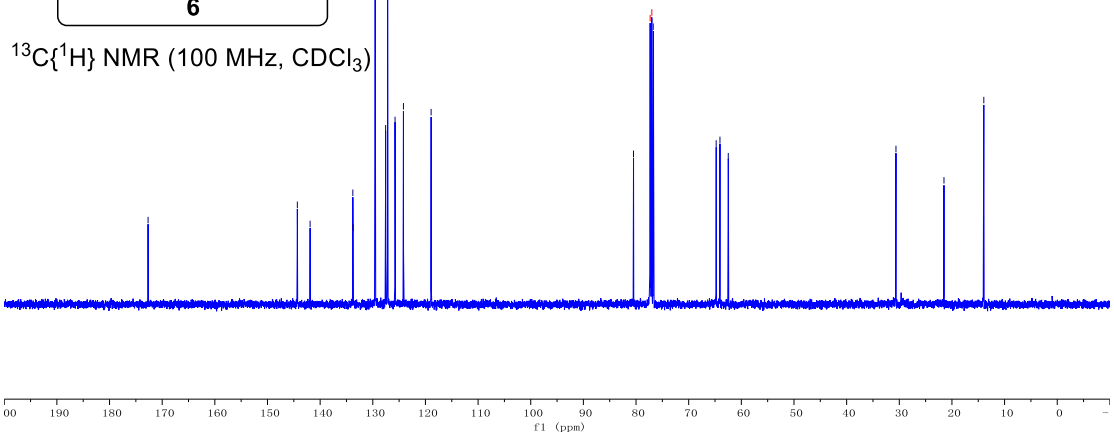


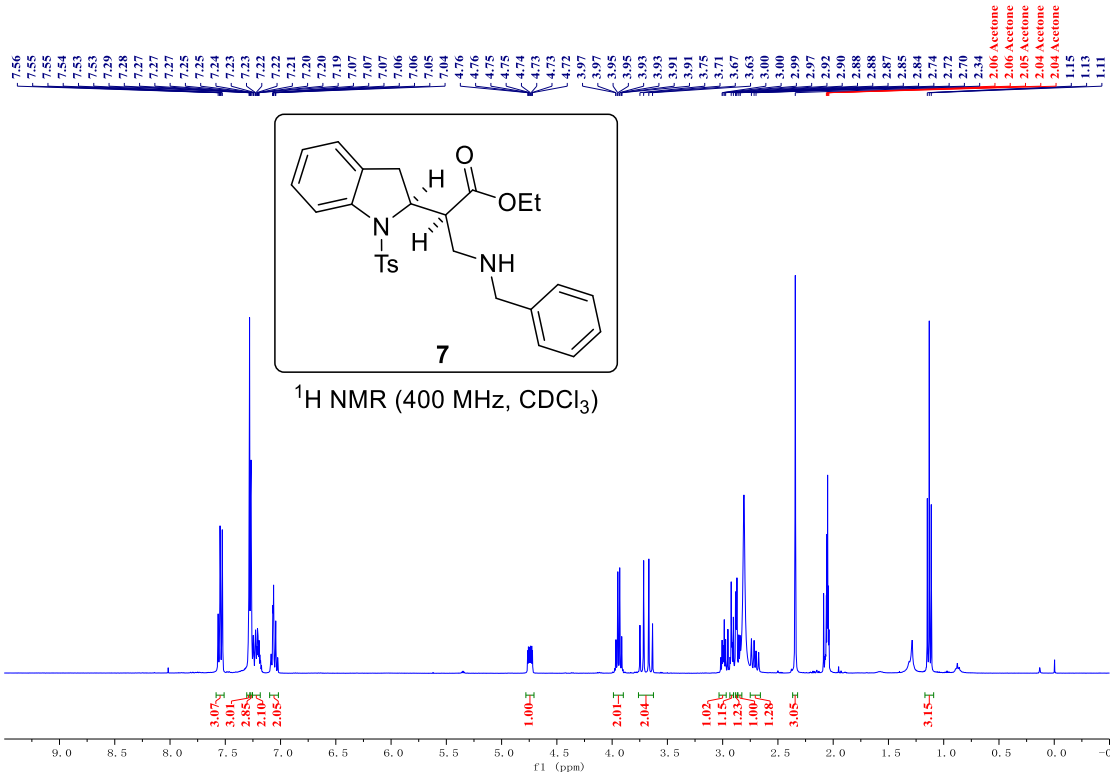


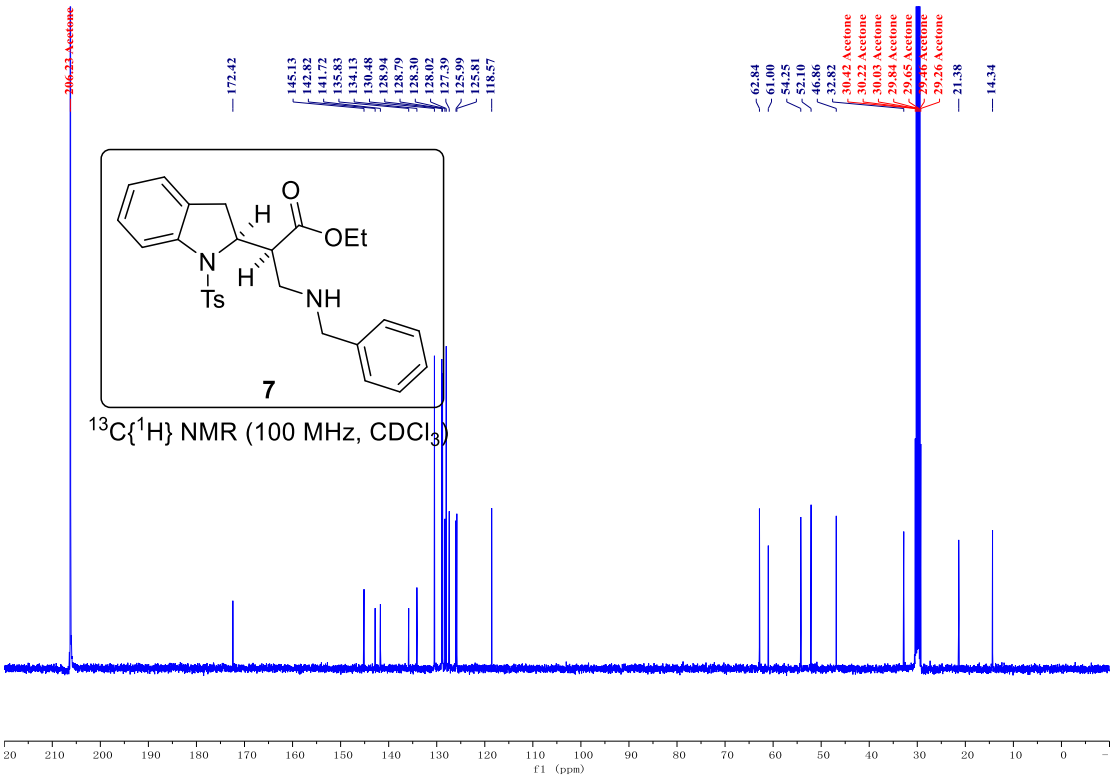


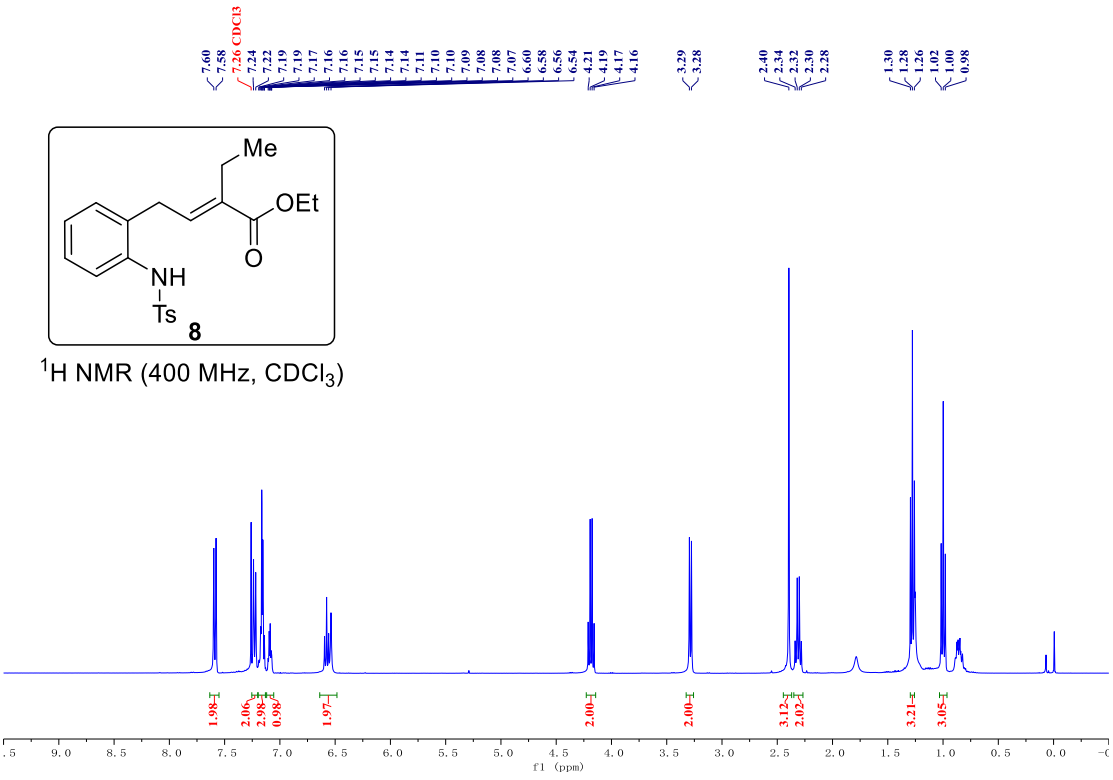
6

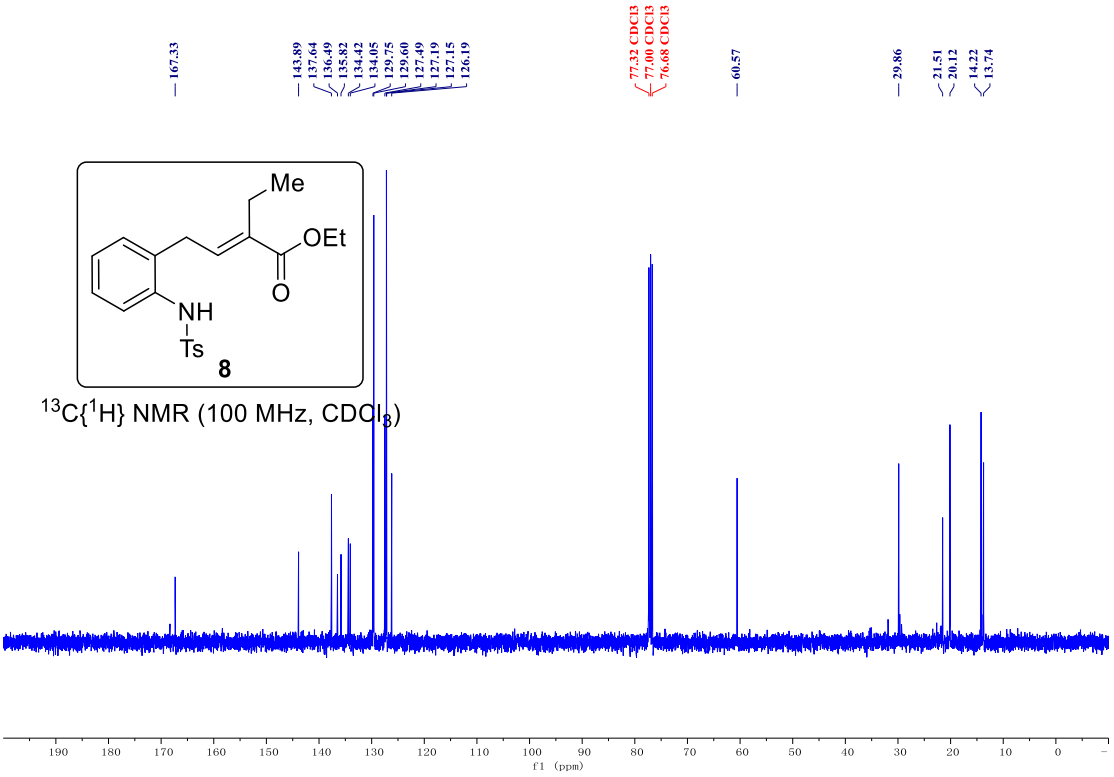
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

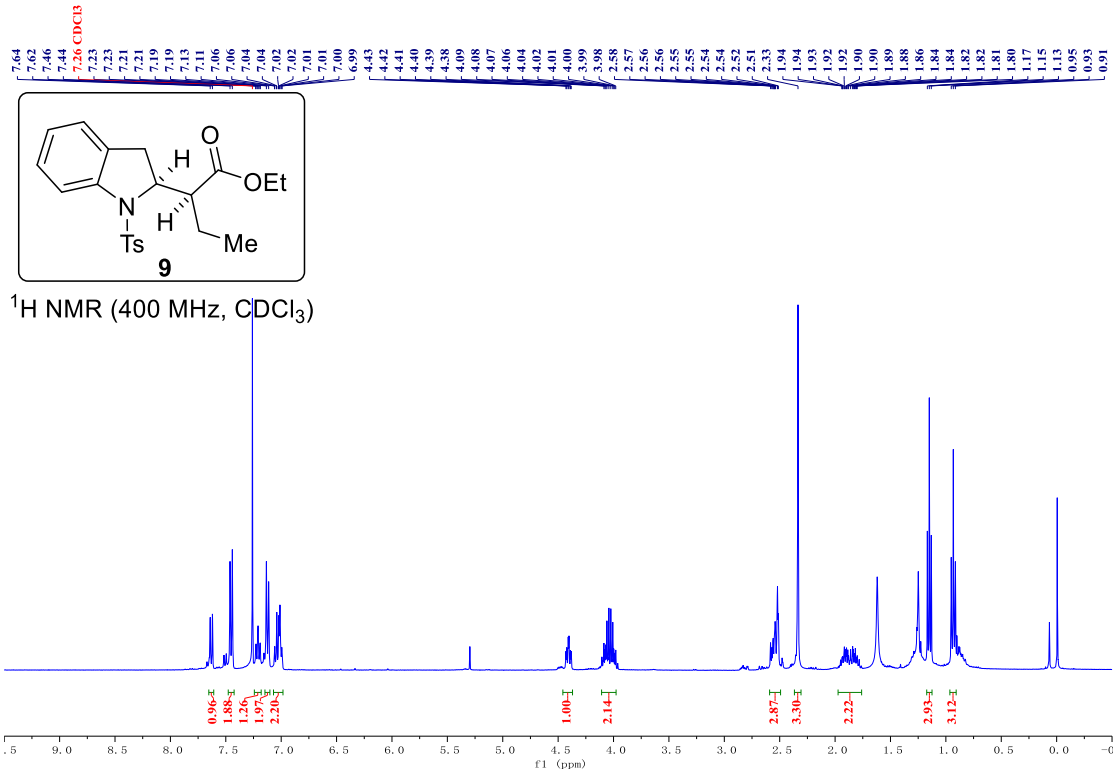


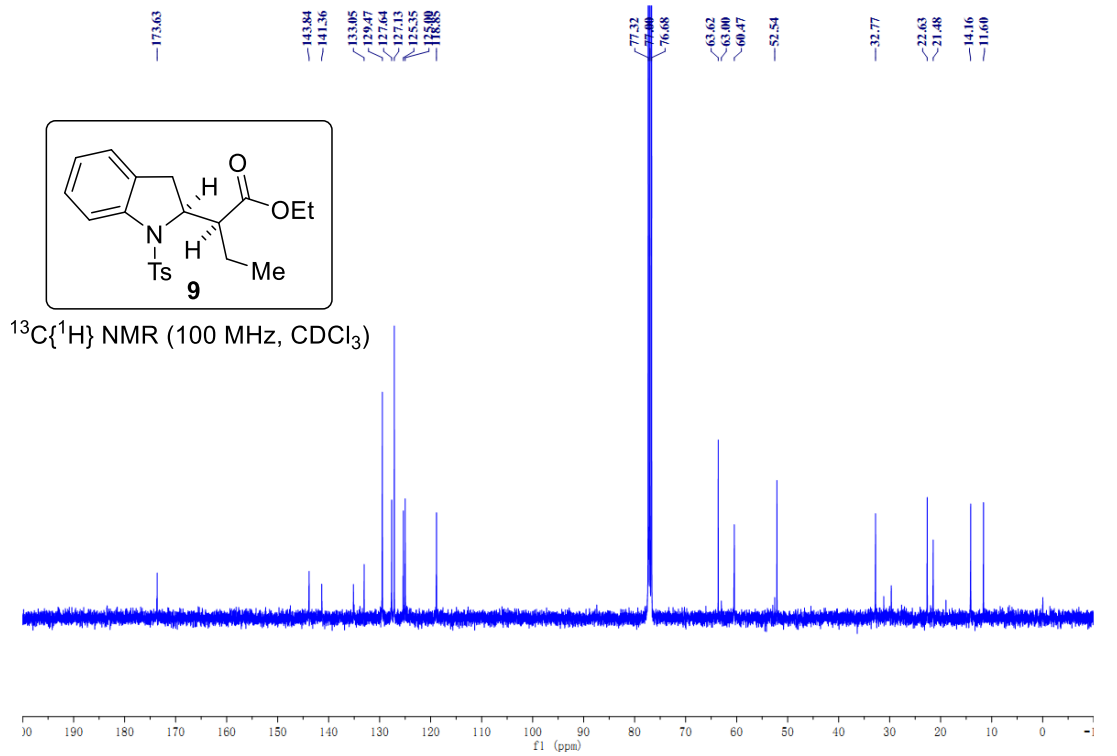

O
H
OEt
N
H
Ts
NH
7
1H NMR (400 MHz, CDCl3)
f1 (ppm)

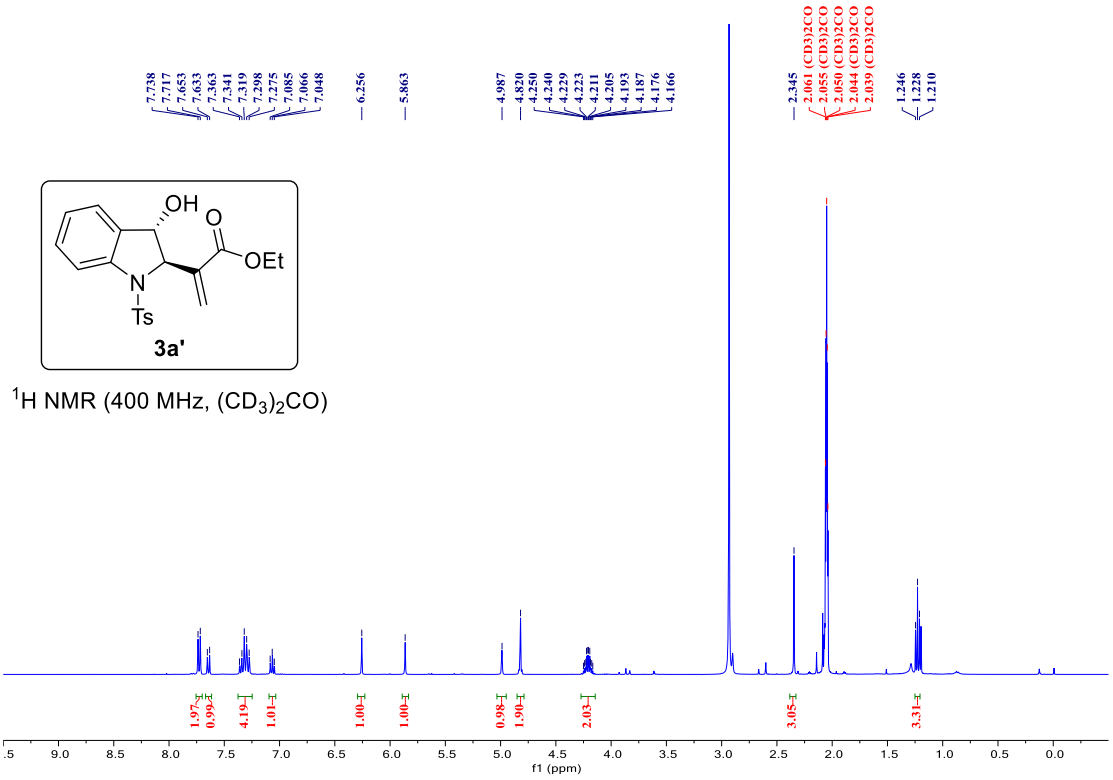

O
H
OEt
N
H
Ts
NH
7
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)


7.60
7.58
7.26 CDCl3
7.24
7.22
7.19
7.17
7.16
7.16
7.15
7.15
7.14
7.14
7.11
7.10
7.10
7.09
7.08
7.08
7.07
6.60
6.58
6.56
6.54
4.21
4.19
4.17
4.16
3.29
3.28
2.40
2.34
2.32
2.30
2.28
1.30
1.28
1.26
1.02
1.00
0.98
Me
OEt
O
NH
Ts
8
1H NMR (400 MHz, CDCl3)
1.99
2.06
2.98
0.98
1.97
2.00
2.00
3.12
2.02
3.21
3.05
f1 (ppm)

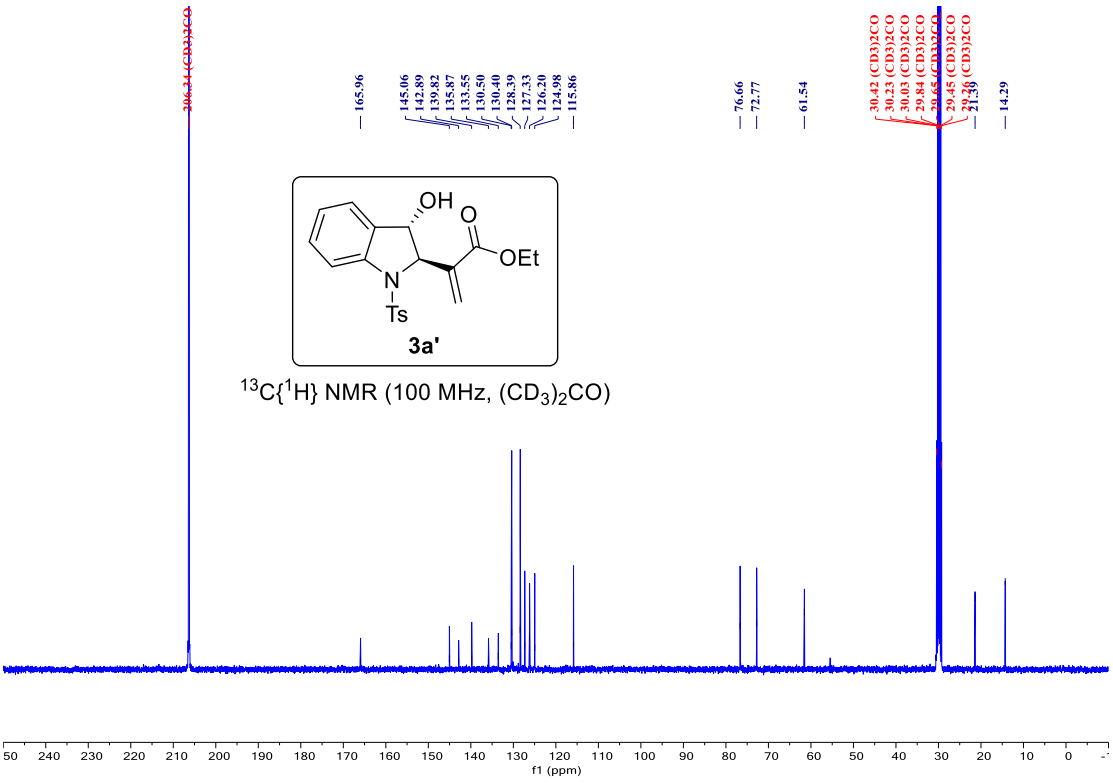

167.33
143.89
137.64
136.49
135.82
134.42
134.05
129.75
129.60
127.49
127.19
127.15
126.19
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
60.57
29.86
21.51
20.12
14.22
13.74
Me
OEt
O
NH
Ts
8
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)


O
H
OEt
N
H
Ts
Me
9
1H NMR (400 MHz, CDCl3)
f1 (ppm)

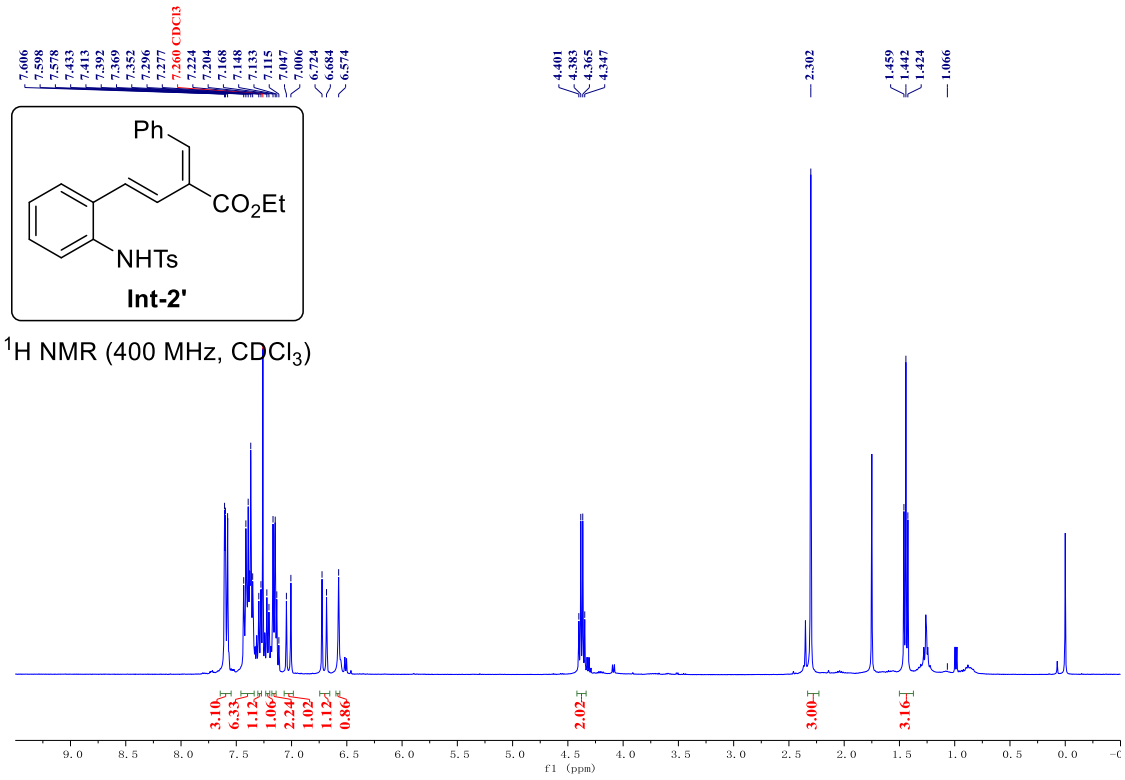

O
H
OEt
N
H
Ts
Me
9
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)

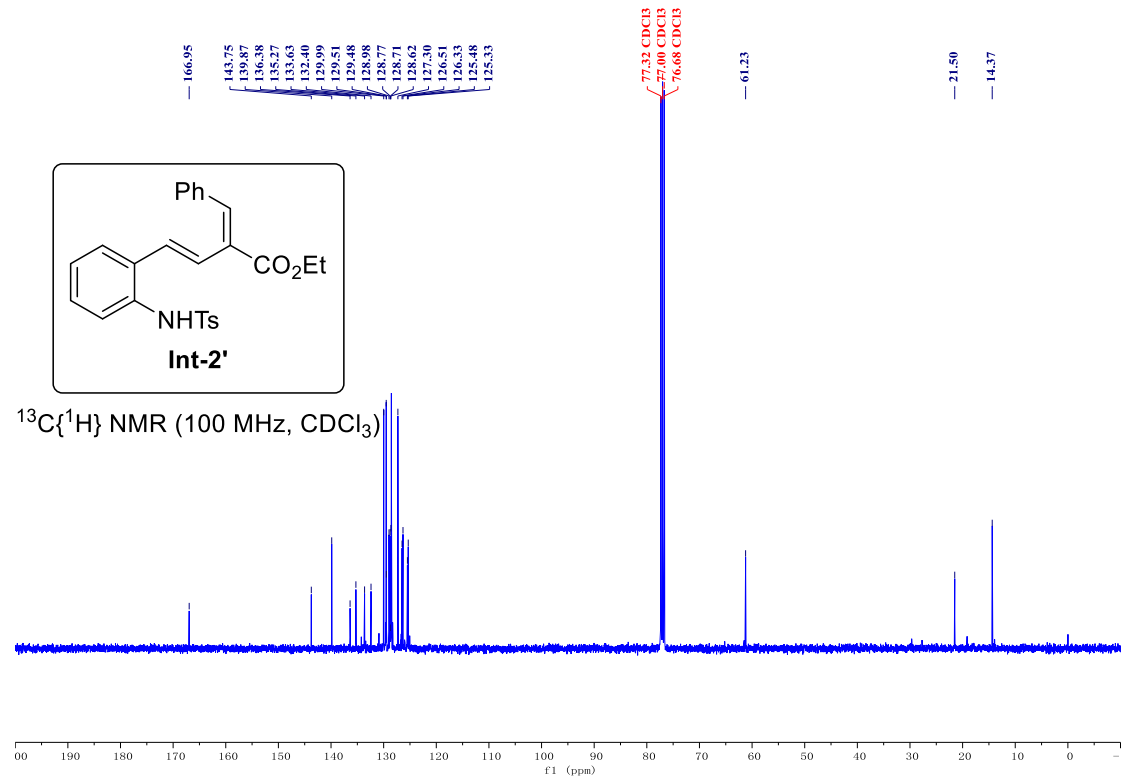


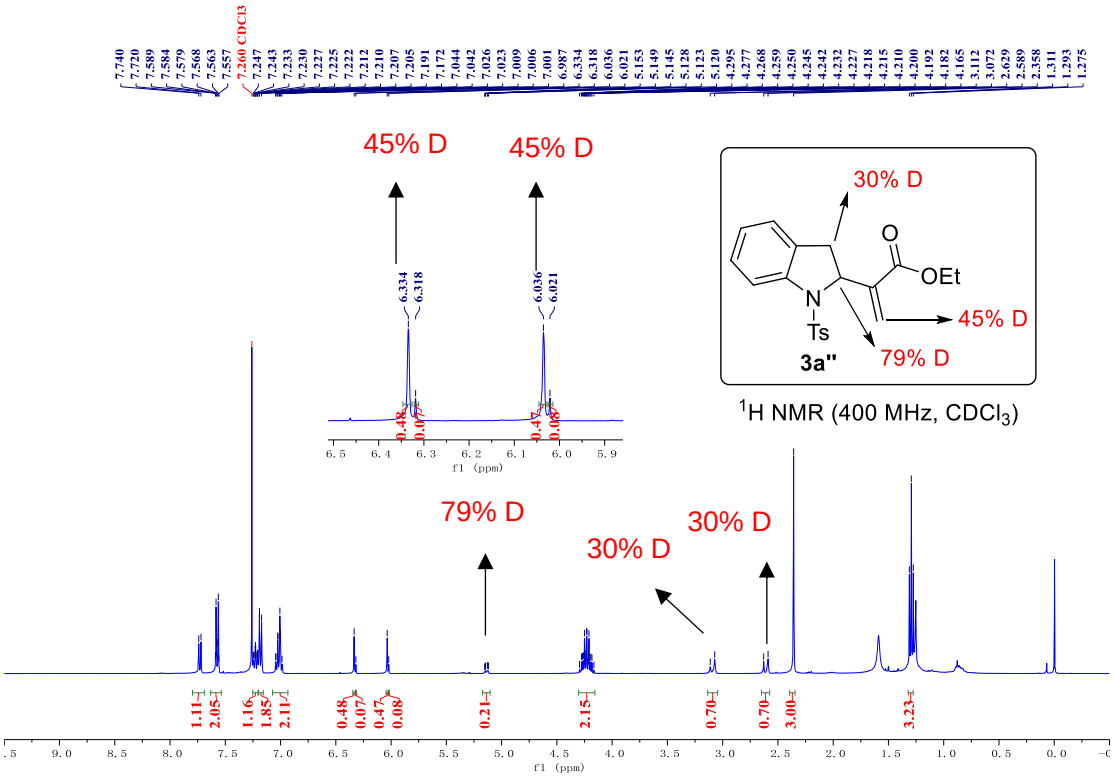
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



^{13}C{^{1}H} NMR (100 MHz, $(CD_3)_2CO$)


Ph
CO2Et
NHTs
Int-2'
1H NMR (400 MHz, CDCl3)
7.606
7.598
7.578
7.433
7.413
7.392
7.369
7.352
7.296
7.277
7.260 CDCl3
7.224
7.204
7.168
7.148
7.133
7.115
7.047
7.006
6.724
6.684
6.574
4.401
4.383
4.365
4.347
2.302
1.459
1.442
1.424
1.066
3.10
6.33
1.12
1.06
2.24
1.02
1.12
0.86
2.02
3.00
3.16
f1 (ppm)


Ph
CO2Et
NHTs
Int-2'
13C{1H} NMR (100 MHz, CDCl3)
166.95
143.75
139.87
136.38
135.27
133.63
132.40
129.99
129.51
129.48
128.98
128.77
128.71
128.62
127.30
126.51
126.33
125.48
125.33
77.32 CDCl3
77.00 CDCl3
76.68 CDCl3
61.23
21.50
14.37
f1 (ppm)


7.740
7.720
7.589
7.584
7.579
7.568
7.563
7.557
7.260 CDCl3
7.247
7.243
7.233
7.230
7.227
7.225
7.222
7.212
7.210
7.207
7.205
7.191
7.172
7.044
7.042
7.026
7.023
7.009
7.006
7.001
6.987
6.334
6.318
6.036
6.021
5.153
5.149
5.145
5.128
5.123
5.120
4.295
4.277
4.268
4.259
4.250
4.245
4.242
4.232
4.227
4.218
4.215
4.210
4.200
4.192
4.182
4.165
3.112
3.072
2.629
2.589
2.358
1.311
1.293
1.275
45% D
45% D
6.334
6.318
6.036
6.021
0.48
0.07
0.47
0.08
6.5 6.4 6.3 6.2 6.1 6.0 5.9
f1 (ppm)
30% D
O
OEt
N
Ts
45% D
3a''
79% D
1H NMR (400 MHz, CDCl3)
79% D
30% D
30% D
1.11
2.05
1.16
1.85
2.11
0.48
0.07
0.47
0.08
0.21
2.15
0.70
0.70
3.00
3.23
f1 (ppm)