Supporting Information

Iron-catalyzed Intermolecular Radical Cyclization of Anilines: Strategy for Assembly of 2,2-Disubstituted Indolines

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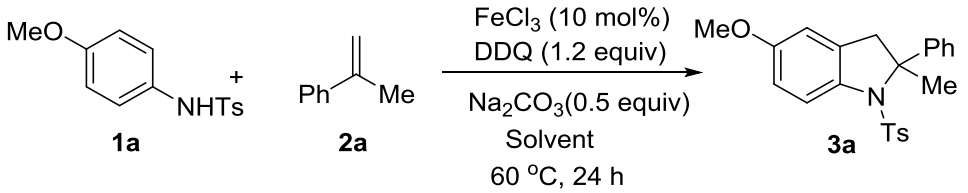
1. General information

Compounds and solvents were purchased from commercial sources and were used as received without further purification unless stated otherwise. All products were purified by flash chromatography on silica gel (200-300 mesh). The chemical yields referred are isolated products. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz or 600 MHz Bruker spectrometers. Chemical shifts are reported in part per million relative to residual solvent of $CDCl_3$ (7.26 ppm for ^{1}H NMR, 77.16 ppm for ^{13}C NMR). Infrared spectra (IR) were recorded on Bruker EQUINAX55 spectrometer. Circular dichrorism (CD) spectra were recorded on a JASCO J-810 spectrometer. Circular polarized luminescence (CPL) spectra were measured on a JASCO CPL-200 spectrometer. The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), quart. (quartet), quint. (quintet), m (multiplet), br (broad). Multiplets which arise from accidental equality of coupling constants of magnetically non-equivalent protons are marked as virtual (virt.). High resolution mass spectra (HRMS) data were measured on a ESI-microTOF Ⅱ. Melting points were measured on a SGW® X-4B and are not corrected. Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates and compounds were visualized with a UV light at 254 nm or 365 nm. Further visualization was achieved by staining with iodine, or $KMnO_4$ followed by heating on a hot plate. Flash column chromatography was performed on silica gel 60 Å, 10–40 μm.

2. Reaction condition optimizations

Table S1. **Solvent screening**[a]

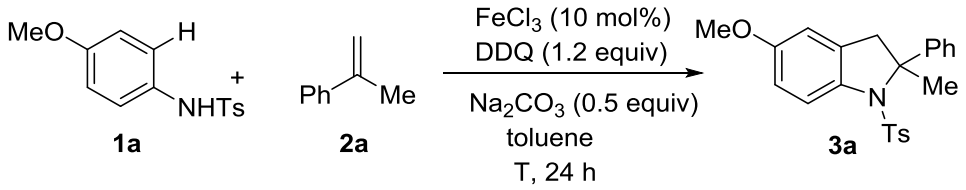


Entry	Solvent(M)	Yield(%)[b]
1	EtOAc	8

2	MeOH	0
3	CH_3CN	29
4	Toluene	69
5	Xylene	34
6	THF	Trace
7	TBME	0
8	DCM	15
9	HFIP	0
10	DCE	54

[a]Reaction conditions: all reactions were performed with **1a** (55.5 mg, 0.2 mmol), **2a** (70.8 mg, 0.6 mmol), $FeCl_3$ (3.3 mg, 0.02 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol) and DDQ (54.2 mg, 0.24 mmol) in 5.0 mL of solvent in Schlenk tube at 60 ^oC for a specific period of time under N_2. [b]Yields are for isolated product after column chromatography.

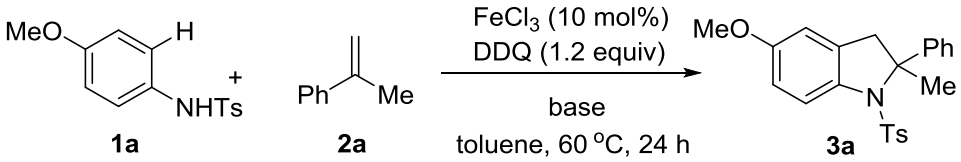
Table S2. **Temperature screening**[a]



entry	T (^oC)	t (h)	yield (%)[b]
1	25	48	38
2	40	48	76
3	50	32	83
4	60	24	87
5	70	24	79
6	80	24	77
7	90	20	77
8	100	12	73
9	125	12	69

[a]Reaction conditions: all reactions were performed with **1a** (55.5 mg, 0.2 mmol), **2a** (70.8 mg, 0.6 mmol), $FeCl_3$ (3.3 mg, 0.02 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol) and DDQ (54.2 mg, 0.24 mmol) in 5.0 mL of solvent in Schlenk tubes at various temperature for a specific period of time under N_2. [b]Yields are for isolated products after column chromatography.

Table S3. **The effect of base**[a]



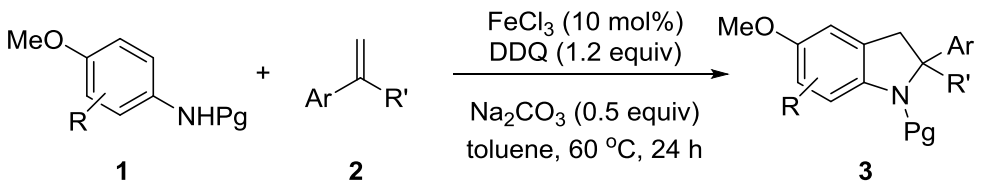
1a **2a** **3a**

entry	base	yield (%)[b]
1	$NaHCO_3$ (0.5 eq)	76
2	Na_2CO_3 (0.5 eq)	87
3	K_2CO_3 (0.5 eq)	trace
4	Li_2CO_3 (0.5 eq)	63
5	Na_2CO_3 (1.0 eq)	83
6	Na_2CO_3 (1.5 eq)	70

[a]Reaction conditions: all reactions were performed with **1a** (55.5 mg, 0.2 mmol), **2a** (70.8 mg, 0.6 mmol), $FeCl_3$ (3.3 mg, 0.02 mmol) and DDQ (54.2 mg, 0.24 mmol) in 5.0 mL of solvent in Schlenk tubes at various temperature for a specific period of time under N_2. [b]Yields are for isolated products after column chromatography.

3. Synthetic procedures

3.1 General procedures for $FeCl_3$-catalyzed intermolecular [3+2] cyclizations between aniline 1 and styrenes 2



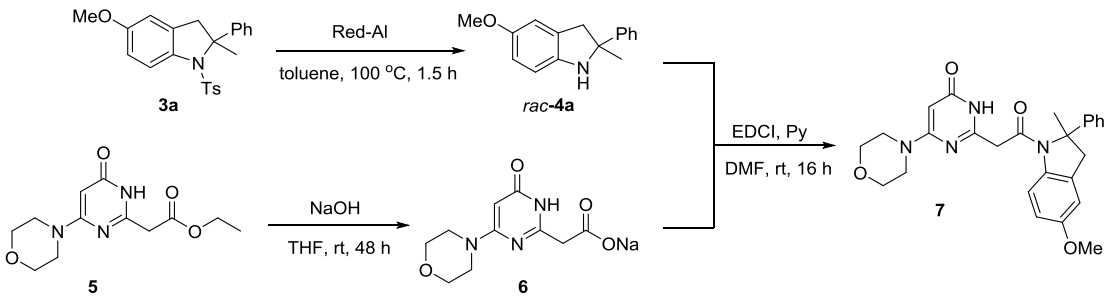
Procedure A:

To an oven dried Schlenk tube equipped with a stir-bar, DDQ (0.24 mmol), $FeCl_3$ (0.02 mmol) and Na_2CO_3 (0.1 mmol) were added. Then the reaction tube was vacuumed and purged with nitrogen for three times. Aniline **1** (0.2 mmol), toluene (5.0 mL) and olefin **2** (0.6 mmol) were added simultaneously under nitrogen. The reaction mixture was stirred at 60 ^{o}C for a specific period of time (see Table 2). Then the mixture was concentrated under vacuum, and the crude product was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (60/1 to 30/1 to 15/1) as an eluent to afford the cyclization product.

Procedure B:

To an oven dried Schlenk tube equipped with a stirring bar, DDQ (0.24 mmol), $FeCl_3$ (0.02 mmol), Na_2CO_3 (0.1 mmol) and aniline **1** (0.2 mmol) were added. Then the reaction tube was vacuumed and purged with nitrogen for three times. Toluene (3.0 mL) was added under nitrogen. The reaction mixture was allowed to stir at 60 ^{o}C. Next, a solution of olefin **2** (0.6 mmol) in 2.0 mL toluene was added dropwise by using a syringe pump (at a rate of 2.0 mL/h).The Schlenk tube was still stirred at 60 ^{o}C for a specific period of time (see Table 2). Then the mixture was concentrated under vacuum, and the crude product was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (60/1 to 30/1 to 15/1) as an eluent to afford the cyclization product.

3.2 Synthesis PI3K ihhibitor analogue 7



Step 1: The deprotection of Ts group was performed according to a known method. [1]To a stirred solution of 5-methoxy-2-methyl-2-phenyl-1-tosylindoline **3a** (393 mg, 1.0 mmol) in dry toluene (10.0 mL), was added sodium bis(2-methoxyethoxy) aluminium hydride (1.51 mL, 5.0 mmol) (70% w/w solution in toluene) under nitrogen and the resulting mixture heated to 100 °C for 1.5 h. The reaction was then cooled, and ethyl acetate was added and the mixture was left to stir for 20 min. The solvent was removed in vacuo to afford a brown oil which was purified by column chromatography on silica gel with petroleum ether ethyl acetate (60/1 to 40/1 to 30/1) to afford indoline *rac*-**4a** as a colourless oil (160.1 mg , 67%).

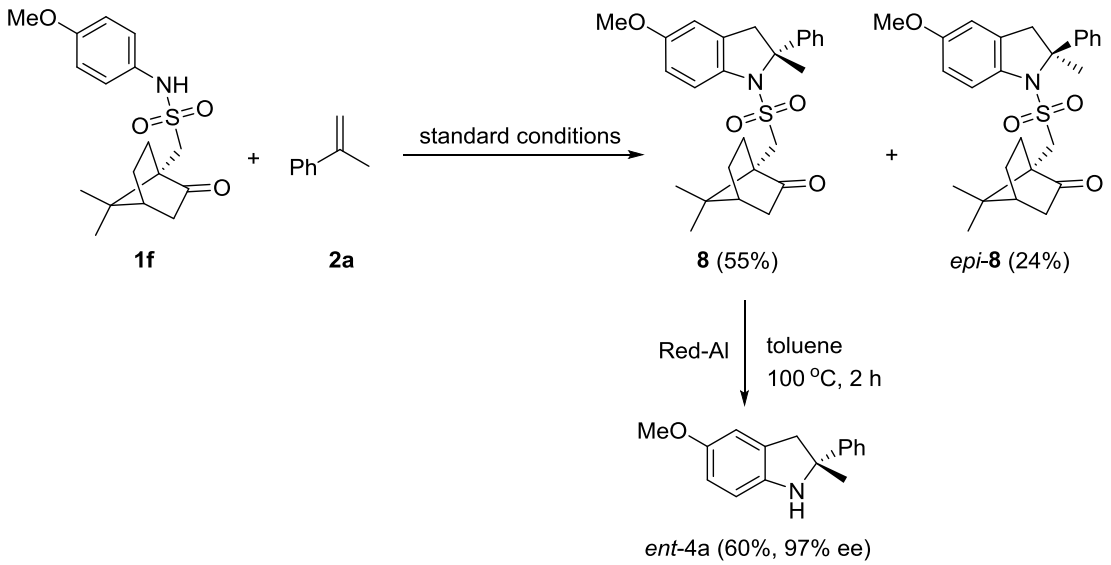
Step 2: Sodium hydroxide (0.19 mL, 0.37 mmol, 2.0 M) were added to a solution of 100 mg (0.37 mmol) of ester **5** in 10 mL of THF. The reaction mixture was stirred for 48h at ambient temperature. The precipitate formed was filtered off through sintered glass, washed with ethyl acetate, and rinsed several times with diethyl ether. The solied was then dried under vacuum to give the product **6** as a white solid (84.0 mg, 87%).[2]

Step 3: To a solution of compound **6** (78.3 mg, 0.3 mmol) in 2 ml of DMF were introduced pyridine (0.084 mL, 0.6 mmol), N-[3-(dimethylamino)propyl]-N'-ethylcarbodiimide hydrochloride (EDCI) (75 mg, 1.3 mmol) and 5-methoxy-2-methyl-2-phenylindoline (143.4 mg, 0.6 mmol). The reaction mixture was stirred at ambient temperature for 16 hours and then concentrated to dryness under reduced pressure. Water and ethyl acetate were added

[1] O. Callaghan, C. Lampard, A. R. Kennedy, J. A. Murphy, *J. Chem. Soc., Perkin Trans.* **1999**, *1,* 995.
[2] V. Certal, J. C. Carry, F. Halley, et al, *J. Med. Chem.* **2014**, *57*, 903.

and the resulting mixture was stirred for 30 minutes. The precipitate formed was filtered off, washed with water, diethylether, petroleum ether and dried to give compound **7** as a white solid (84 mg, 61%).

3.3 Synthesis of chiral indoline *ent*-4a

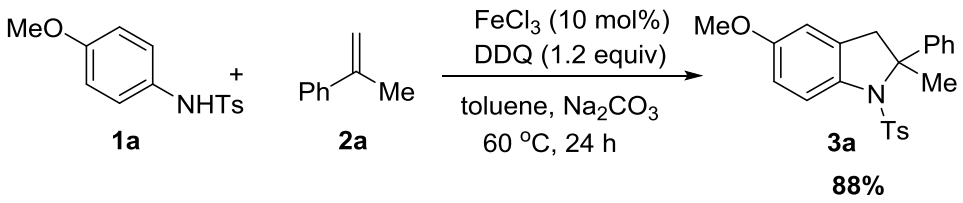


Step 1: To an oven dried Schlenk tube equipped with a stirring bar, DDQ (54.2 mg, 0.24 mmol), $FeCl_3$ (3.3 mg, 0.02 mmol) and Na_2CO_3 (10.6 mg, 0.1 mmol) were added. Then the reaction tube was vacuumed and purged with nitrogen for three times. Aniline **1f** (0.2 mmol), toluene (5.0 mL) and α-methylstyrene **2a** (70.8 mg，0.6 mmol) were added simultaneously under nitrogen. The resulting mixture was stirred at 60 ^{o}C for 20 h. and then concentrated under reduced pressure, The crude mixture was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (60/1 to 30/1 to 15/1) affording compound **8** (49.8 mg, 55%) and *epi*-**8** (21.7 mg, 24%) as white solids.

Step 2: To a stirred solution of compound **8** (the major epimer, 90.6 mg, 0.2 mmol) in dry toluene (2.0 mL) was added sodium bis(2-methoxyethoxy) aluminium hydride (0.30 ml, 1 mmol) (70% w/w solution in toluene) under nitrogen and the resulting mixture was heated to 100 ^{o}C for 2 h. The reaction was then cooled, and ethyl acetate was added. The mixture was left to stir for 20 min. The solvent was then removed in

vacuo to afford a brown oil which was purified by column chromatography on silica gel with petroleum ether ethyl acetate (60/1 to 40/1 to 30/1) to afford *ent*-**4a** (28.7 mg, 60% yield; 97% ee) as a colourless oil.

3.4 Scale up experiment



To an oven dried Schlenk tube equipped with a stirring bar, DDQ (802.8 mg, 3.6 mmol), $FeCl_3$ (48.6 mg, 0.3 mmol) and Na_2CO_3 (159.0 mg, 1.5 mmol) were added. Then the reaction tube was allowed to be vacuumed and purged with nitrogen for three times. Aniline **1a** (832.0 mg, 3.0 mmol), toluene (30.0 mL) and α-methylstyrene **2a** (1.06 g, 9.0 mmol) were added simultaneously under nitrogen. The reaction mixture was stirred at 60 ^oC for 24 h. Water (20.0 ml) was added and the mixture was extracted with CH_2Cl_2 (3 x 20 mL). The organic layers were dried over Na_2SO_4, filtered, concentrated in vacuo and the crude product was obtained by flash chromatography on silica gel with petroleum ether/ethyl acetate (60/1 to 30/1 to 15/1) affording compound **3a** as a white solid (1.03 g, 88%).

4. EPR experiments

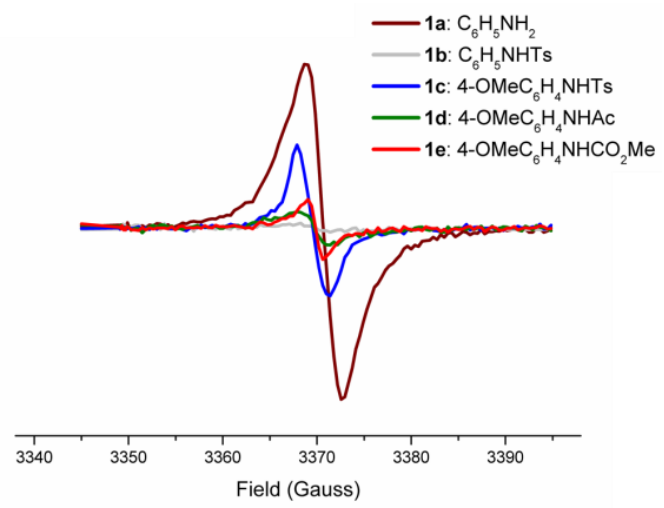


Figure S1. EPR spectra of DDQ and aniline (**1a** – **1e**) mixture in toluene.

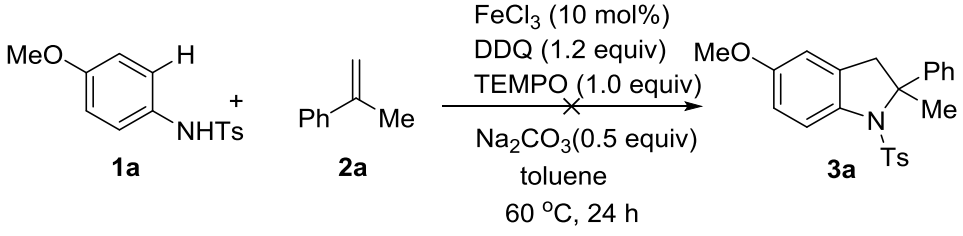
The respective g value of **1a**–**e** are given below: 2.00492, 2.00538, 2.00555, 2.00537, 2.00540.

Procedure for EPR studies of the reaction between DDQ and aniline (1a–e).

To an oven dried Schlenk tube equipped with a stirring bar was added DDQ (27.2 mg, 0.12 mmol) and aniline **1** (0.1 mmol). The reaction tube was vacuumed and purged with nitrogen for three times. Then toluene (2.0 mL) was added under nitrogen and the reaction mixture was stirred at 60 ^{o}C. After 1 hour, 20.0 μL of the reaction mixture was taken out into a small tube and analyzed by EPR at room temperature (Figure S1).

5. Mechanistic studies

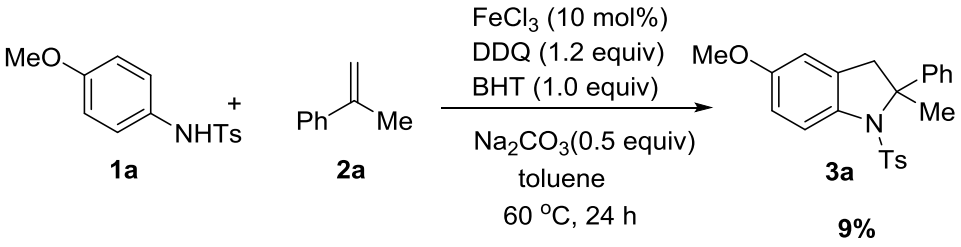
5.1 The radical trapping experiments.



To an oven dried Schlenk tube equipped with a stirring bar, DDQ (54.2 mg, 0.24

mmol)，$FeCl_3$ (3.3 mg, 0.02 mmol) and Na_2CO_3(10.6 mg , 0.1 mmol) were added. Then the reaction tube was vacuumed and purged with nitrogen for three times. TEMPO (31.3 mg, 0.2 mmol), aniline **1a** (55.5 mg, 0.2 mmol), α-methylstyrene **2a** (70.8 mg，0.6 mmol) and toluene (5.0 mL) were added under nitrogen. The Schlenk tube was allowed to stir at 60 ^oC for 24 h.

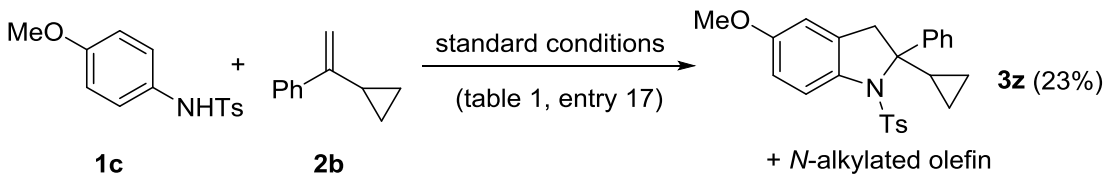
It was found from TLC and crude ^1H NMR that no reaction took place and only starting materials were detected.



To an oven dried Schlenk tube equipped with a stirring bar, DDQ (54.2 mg, 0.24 mmol)，$FeCl_3$ (3.3 mg, 0.02 mmol) and Na_2CO_3 (10.6 mg, 0.1 mmol) were added. Then the reaction tube was vacuumed and purged with nitrogen for three times. BHT (44.1 mg, 0.2 mmol), aniline **1a** (55.5 mg, 0.2 mmol), α-methylstyrene **2a** (70.8 mg，0.6 mmol) and toluene (5.0 mL) were added under nitrogen. The Schlenk tube was allowed to stir at 60℃ for 24 h. Then the mixture was concentrated under vacuum, and the crude product was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (60/1 to 30/1 to 15/1) as an eluent to afford indoline **3a** as a white solid (7 mg, 9%). The majority of starting materials **1a** and **2a** was recovered.

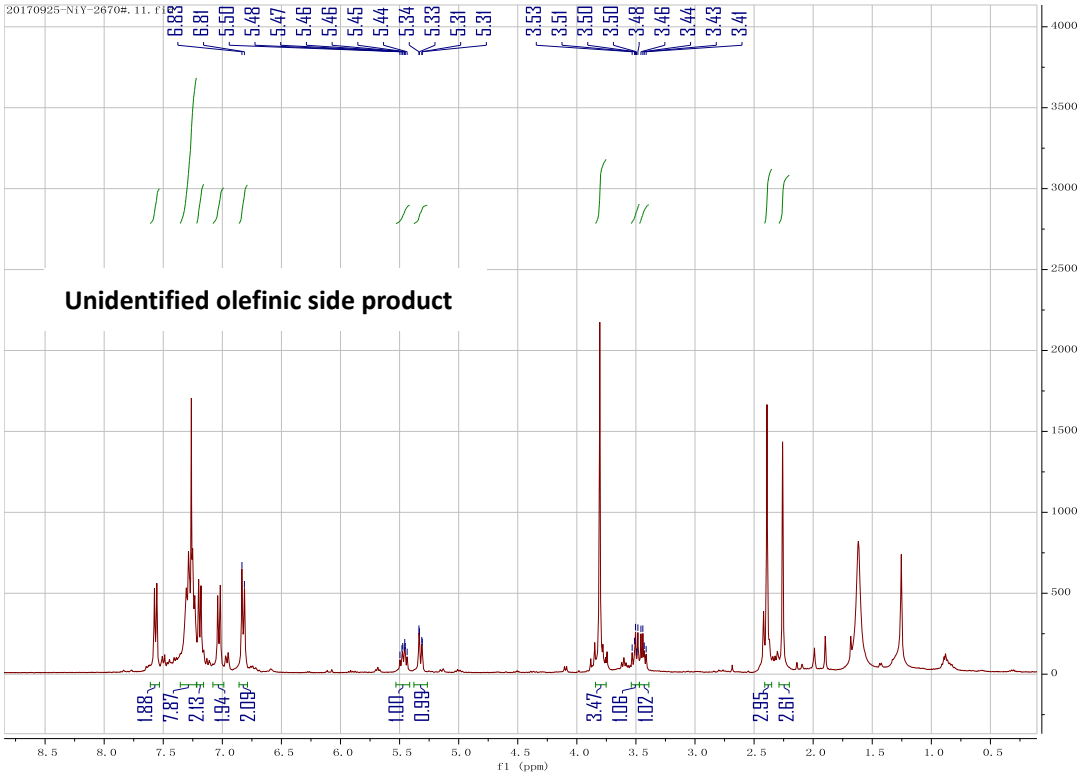
The above radical trapping experiments suggested that a radical mechanism is likely involved in the present $FeCl_3$ catalyzed [3+2] cyclization reaction.

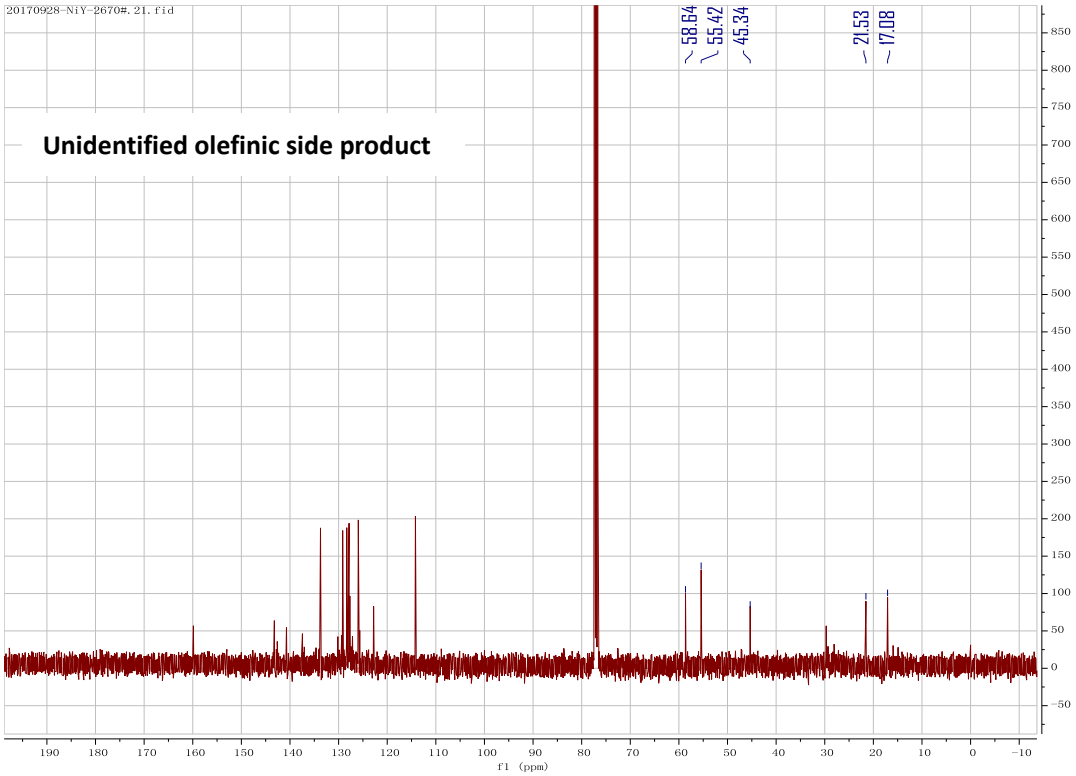
5.2 Experiment with radical clock 2b.



Following the general procedure A, indoline **3z** was isolated and fully characterized

(see data of **3z** in section 6 on Page S30). Meanwhile, after many attempts, we also isolated one of the several side products in very small quantity and its NMR spectra are given below. As shown in the spectra, it is evident this compound bears two olefinic protons (δ 5.25-5.50 ppm). The aromatic proton signals (δ 6.82, m, 2H) suggest the 4-OMeC_6H_4 ring was not functionalized. The aliphatic proton signals (δ 3.52, dd, J = 11.2, 8.1 Hz, 1H and δ 3.44, dd, J = 11.2, 6.4 Hz, 1H) implies the conversion of terminal olefinic protons of **2b** into two alkyl protons of chemical non-equivalence (likely attached to α-carbon of a stereogenic center). Besides, no cyclopropyl motif is present, as also confirmed in the ^{13}C NMR. Due the structural complexity and moderate purity of this side product, we are not able to propose a clear structure at this stage and further efforts are underway to accumulate this compound and derivatize it into a crystalline compound for single X-ray analysis.

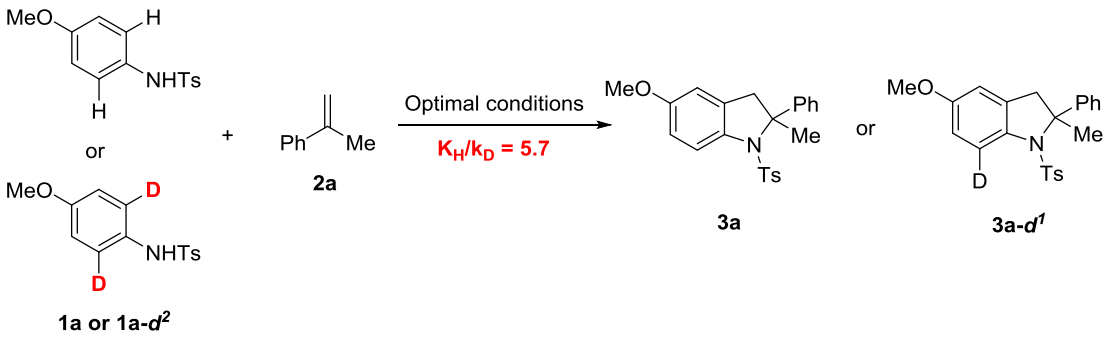


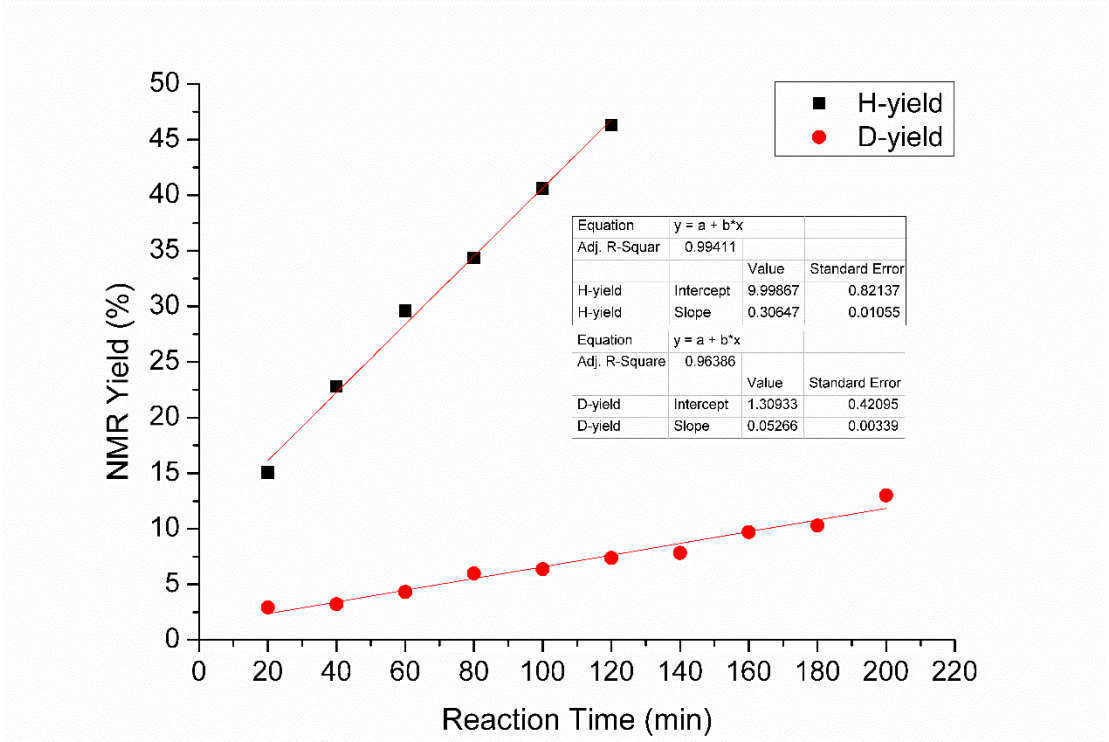


5.3 Kinetic Isotope Effect Experiment.

To an oven dried Schlenk tube equipped with a stirring bar, DDQ (54.2 mg, 0.24 mmol), $FeCl_3$ (3.3 mg, 0.02 mmol), Na_2CO_3 (10.6 mg, 0.1 mmol) and 4,4'-di-tert-butylbiphenyl (53.3 mg, 0.2 mmol) were added. Then the reaction tube was vacuumed and purged with nitrogen for three times. aniline **1a** (55.5 mg, 0.2 mmol), α-methylstyrene **2a** (70.8 mg，0.6 mmol) and toluene (5.0 mL) were added under nitrogen. Subsequently, the Schlenk tube was allowed to stir at 60 ^{o}C. At each time point, a portion (0.2 mL) of the reaction solution was filtered on a short of pad of silica to remove iron catalyst. Then the mixture was concentrated under vacuum and added $CDCl_3$ in NMR tube. They were measured by ^{1}H NMR and the yields were calculated based on 4,4'-di-tert-butylbiphenyl as the internal standard. The same procedure was undertaken for aniline **1a-d^2**.[3]

[3] Aniline **1a-d^2** was synthesized by following a known protocol, see: A. Martins, M. Lautens, *Org. Lett.* **2008**, *10*, 4351.





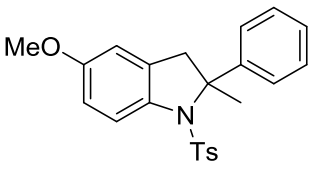
KIE = 0.306/0.053 ≈ 5.7

Figure S2. Plots of the yield against reaction times in the KIE experiments.

The significant kinetic isotope effects ($k_H/k_D \approx 5.7$) implies that the second hydrogen abstract of *ortho*-C–H of aniline **1a** is the rate-determining step.

6. Analytical Data of Products

5-Methoxy-2-methyl-2-phenyl-1-tosylindoline (3a)



3a

Compound **3a** was synthesized following the general procedure A.

A white solid, 69.5 mg, 87% yield.

m.p.: 42 °C – 43 °C.

TLC: R_f = 0.46 (Hexane/EtOAc = 6:1)

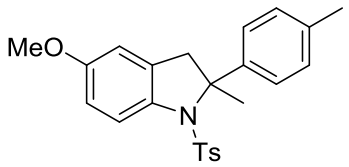
IR (KBr): 2923, 2837, 1599, 1487, 1344, 1223, 1161, 1031, 674, 584, 544 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.55 (d, *J* = 8.9 Hz, 1H), 7.44 – 7.42 (m, 2H), 7.37 (dd, *J* = 6.7, 3.1 Hz, 2H), 7.24 – 7.18 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.75 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.65 (s, 1H), 3.74 (s, 3H), 3.43 – 3.18 (m, 2H), 2.33 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 156.0, 145.3, 143.1, 138.6, 136.1, 129.8, 129.2, 128.2, 127.3, 126.7, 125.8, 114.5, 112.7, 111.0, 72.9, 55.7, 49.1, 27.1, 21.5.

HRMS (ESI): $C_{23}H_{24}NO_3S$ $[M+H]^+$: calcd.: 394.1471; found: 394.1472.

5-Methoxy-2-methyl-2-(p-tolyl)-1-tosylindoline (3b)



3b

Compound **3b** was synthesized following the general procedure A.

A colorless oil, 66.0 mg, 81% yield.

TLC: R_f = 0.43 (Hexane/EtOAc = 6:1).

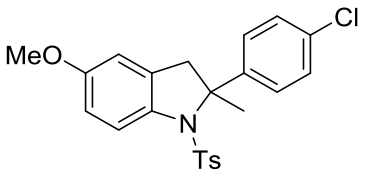
IR (KBr): 2920, 2834, 1618, 1486, 1348, 1224, 1160, 814, 668, 582, 547 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 (d, *J* = 8.9 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.31 – 7.26 (m, 2H), 7.20 – 7.08 (m, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.78 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.69 (d, *J* = 2.6, 1.2 Hz, 1H), 3.79 (s, 3H), 3.43 – 3.23 (m, 2H), 2.38 (s, 3H), 2.34 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 156.0, 143.0, 142.3, 138.7, 136.9, 136.1, 129.8, 129.2, 128.8, 126.7, 125.7, 114.5, 112.6, 111.0, 72.7, 55.7, 49.1, 27.0, 21.5, 21.0.

HRMS (ESI): $C_{24}H_{26}NO_3S$ $[M+H]^+$: calcd.: 408.1628; found: 408.1629.

2-(4-Chlorophenyl)-5-methoxy-2-methyl-1-tosylindoline (3c)



3c

Compound **3c** was synthesized following the general procedure A.

A faint yellow solid, 64.2 mg, 75% yield.

m.p.: 46 °C – 58 °C.

TLC: R_f = 0.41 (Hexane/EtOAc = 6:1).

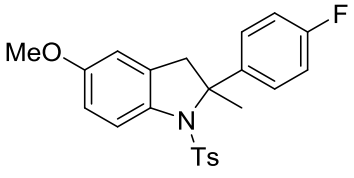
IR (KBr): 2924, 2835, 1599, 1487, 1349, 1223, 1159, 1091, 664, 546 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.60 (d, *J* = 8.9 Hz, 1H), 7.48 – 7.47 (m, 2H), 7.30 (dd, *J* = 8.1, 6.0 Hz, 2H), 7.20 – 7.12 (m, 4H), 6.79 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.68 (d, *J* = 2.6 Hz, 1H), 3.79 (s, 3H), 3.38 – 3.24 (m, 2H), 2.39 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (101 MHz, CDCl3): δ (ppm) 156.2, 143.9, 143.3, 138.6, 136.0, 133.1, 129.4, 129.3, 128.2, 127.2, 126.5, 114.6, 112.9, 111.0, 72.2, 55.7, 49.0, 27.0, 21.5.

HRMS (ESI): $C_{23}H_{23}ClNO_3S$ $[M+H]^+$: calcd.: 428.1082; found: 428.1084.

2-(4-Fluorophenyl)-5-methoxy-2-methyl-1-tosylindoline (3d)



3d

Compound **3d** was synthesized following the general procedure A.

A yellow oil, 70.0 mg, 85% yield.

TLC: R_f = 0.27 (Hexane/EtOAc = 6:1).

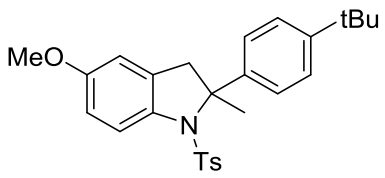
IR (KBr): 2927, 2854, 1600, 1507, 1487, 1346, 1225, 1161, 813, 667, 545 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.57 (d, *J* = 8.9 Hz, 1H), 7.48 – 7.42 (m, 2H), 7.36 – 7.29 (m, 2H), 7.10 (m, 2H), 6.86 (t, *J* = 8.7 Hz, 2H), 6.76 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.66 (d, *J* = 2.5 Hz, 1H), 3.75 (s, 3H), 3.28 (q, *J* = 16.4 Hz, 2H), 2.34 (s, 3H), 2.07 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 161.9 (d, *J* = 246.2 Hz), 156.1, 143.3, 141.2 (d, *J* = 3.2 Hz), 138.6, 136.0, 129.5, 129.3, 127.6, 127.5, 126.6, 114.9, 114.7, 114.6, 111.9 (d, *J* = 182.1 Hz), 72.3, 55.7, 49.1, 27.1, 21.4.

HRMS (ESI): $C_{23}H_{23}FNO_3S$ $[M+H]^+$: calcd.: 412.1377; found: 412.1379.

2-(4-*tert*-Butylphenyl)-5-methoxy-2-methyl-1-tosylindoline (3e)



3e

Compound **3e** was synthesized following the general procedure A.

A colorless oil, 67.4 mg, 75% yield.

TLC: R_f = 0.61 (Hexane/EtOAc = 6:1).

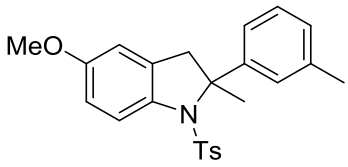
IR (KBr): 2959, 2865, 1600, 1486, 1350, 1223, 1160, 998, 664, 545 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.59 (d, *J* = 8.9 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.27 – 7.22 (m, 2H), 7.18 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.76 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.66 (d, *J* = 2.6 Hz, 1H), 3.76 (s, 3H), 3.49 – 3.16 (m, 2H), 2.32 (s, 3H), 2.10 (s, 3H), 1.29 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 155.9, 150.0, 142.8, 141.7, 138.6, 136.2, 129.8, 129.1, 126.7, 125.6, 124.9, 114.4, 112.6, 110.9, 72.5, 55.7, 49.2, 34.4, 31.4, 27.4, 21.5.

HRMS (ESI): $C_{27}H_{32}NO_3S$ $[M+H]^+$: calcd.: 450.2097; found: 450.2097.

5-Methoxy-2-methyl-2-(m-tolyl)-1-tosylindoline (3f)



3f

Compound **3f** was synthesized following the general procedure A.

A colorless oil, 66.0 mg, 81% yield.

TLC: R_f = 0.40 (Hexane/EtOAc = 6:1).

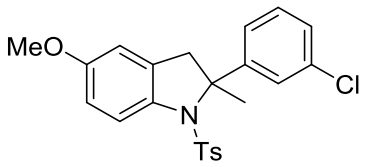
IR (KBr): 2958, 2835, 1745, 1620, 1489, 1351, 1224, 1152, 1033, 1006, 767, 701, 601, 570 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.58 (d, *J* = 8.9 Hz, 1H), 7.39 – 7.37 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.07 (m, 2H), 7.05 – 6.99 (m, 2H), 6.76 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.66 (d, *J* = 2.6 Hz, 1H), 3.77 (s, 3H), 3.46 – 3.18 (m, 2H), 2.34 (s, 3H), 2.18 (s, 3H), 2.08 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 155.9, 144.9, 142.9, 138.6, 137.6, 136.1, 129.8, 129.1, 128.0, 128.0, 126.8, 126.7, 123.0, 114.5, 112.7, 111.0, 72.7, 55.7, 49.3, 27.2, 21.5, 21.4.

HRMS (ESI): $C_{24}H_{26}NO_3S$ $[M+H]^+$: calcd.: 408.1628; found: 408.1627.

2-(3-Chlorophenyl)-5-methoxy-2-methyl-1-tosylindoline (3g)



3g

Compound **3g** was synthesized following the general procedure A.

A colorless oil, 59.1 mg, 69% yield.

TLC: R_f = 0.36 (Hexane/EtOAc = 6:1).

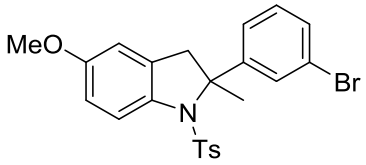
IR (KBr): 2927, 2855, 1593, 1471, 1296, 1146, 1081, 1039, 665, 586 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.89 (d, *J* = 7.9 Hz, 2H), 7.42 – 7.38 (m, 1H), 7.33 (m, 2H), 7.28 – 7.19 (m, 3H), 6.99 (s, 1H), 6.80 (s, 1H), 5.69 (s, 1H), 3.74 (s, 3H), 3.26 – 2.98 (m, 2H), 2.42 (s, 3H), 1.67 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 152.5, 150.1, 144.1, 143.2, 139.0, 134.4, 132.1, 129.8, 129.8, 127.0, 126.9, 125.5, 123.2, 119.5, 118.4, 108.0, 67.0, 56.1, 45.4, 29.3, 21.

HRMS (ESI): $C_{23}H_{23}ClNO_3S$ $[M+H]^+$: calcd.: 428.1082; found: 428.1082.

2-(3-Bromophenyl)-5-methoxy-2-methyl-1-tosylindoline (3h)



3h

Compound **3h** was synthesized following the general procedure B.

A colorless oil, 65.2 mg, 69% yield.

TLC: R_f = 0.33 (Hexane/EtOAc = 6:1).

IR (KBr): 2921, 1596, 1484, 1345, 1222, 1154, 1036, 993, 809, 698, 664, 594, 542 cm^{-1}.

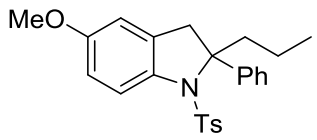
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.51 (d, *J* = 8.9 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.28 (q, *J* = 7.8 Hz, 3H), 7.04 (m, 3H), 6.70 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.59 (d, *J* = 2.6 Hz, 1H), 3.69 (s, 3H), 3.31 – 3.10 (m, 2H), 2.28 (s, 3H), 1.99 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 156.1, 147.4, 143.4, 138.4, 135.9, 130.4, 129.7, 129.4, 129.3, 129.2, 126.5, 124.6, 122.4, 114.6, 112.9, 111.0, 72.2, 55.7, 49.1, 26.9, 21.5.

HRMS (ESI): $C_{23}H_{23}{}^{79}BrNO_3S$ $[M+H]^+$: calcd.: 472.0577; found: 472.0576.

$C_{23}H_{23}{}^{81}BrNO_3S$ $[M+H]^+$: calcd.: 474.0556; found: 474.0555.

5-Methoxy-2-phenyl-2-propyl-1-tosylindoline (3i)



3i

Compound **3i** was synthesized following the general procedure B.

A white solid, 68.3 mg, 81% yield.

m.p.: 168 °C – 170 °C.

TLC: R_f = 0.64 (Hexane/EtOAc = 6:1).

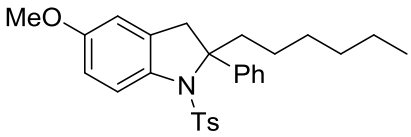
IR (KBr): 2955, 2925, 2867, 1598, 1490, 1350, 1219, 1159, 1038, 811, 701, 659, 595 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.53 (d, *J* = 8.9 Hz, 1H), 7.26 – 7.24 (m, 2H), 7.23 – 7.14 (m, 1H), 7.11 (dd, *J* = 8.1, 5.2 Hz, 4H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.75 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.69 (d, *J* = 2.6 Hz, 1H), 3.77 (s, 3H), 3.41 (s, 2H), 2.88 (td, *J* = 12.9, 4.5 Hz, 1H), 2.30 (s, 3H), 2.18 (td, *J* = 12.7, 3.9 Hz, 1H), 1.44 – 1.22 (m, 2H), 1.03 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 155.7, 144.1, 142.7, 138.0, 136.7, 130.1, 128.9, 128.0, 127.3, 126.8, 126.7, 113.9, 112.6, 110.5, 74.8, 55.7, 46.4, 41.2, 21.4, 17.3, 14.4.

HRMS (ESI): $C_{25}H_{28}NO_3S$ $[M+H]^+$: calcd.: 422.1784; found: 422.1784.

2-Hexyl-5-methoxy-2-phenyl-1-tosylindoline (3j)



3j

Compound **3j** was synthesized following the general procedure A.

A white solid, 67.6 mg, 73% yield.

m.p.: 124 °C – 126 °C.

TLC: R_f = 0.57 (Hexane/EtOAc = 6:1).

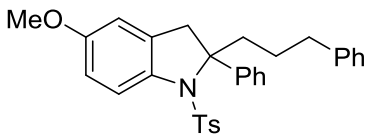
IR (KBr): 2946, 2918, 1599, 1488, 1342, 1216, 1157, 1032, 992, 704, 661, 601, 538 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.57 (d, *J* = 8.8 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.23 – 7.19 (m, 1H), 7.15 – 7.12 (m, 4H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.79 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.73 (d, *J* = 2.7 Hz, 1H), 3.81 (s, 3H), 3.43 (s, 2H), 2.96 – 2.82 (m, 1H), 2.33 (s, 3H), 2.27 (ddd, *J* = 13.3, 12.0, 3.8 Hz, 1H), 1.54 (ddt, *J* = 12.2, 7.5, 3.6 Hz, 1H), 1.49 – 1.40 (m, 2H), 1.37 – 1.30 (m, 5H), 0.91 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 155.7, 144.2, 142.7, 138.1, 136.7, 130.2, 128.9, 128.0, 127.3, 126.7, 126.7, 114.0, 112.6, 110.6, 74.9, 55.7, 46.2, 38.9, 31.8, 29.7, 23.9, 22.7 , 21.4, 14.1.

HRMS (ESI): $C_{28}H_{34}NO_3S$ $[M+H]^+$: calcd.: 464.2254; found: 464.2254.

5-Methoxy-2-phenyl-2-(3-phenylpropyl)-1-tosylindoline (3k)



3k

Compound **3k** was synthesized following the general procedure A.

A white solid, 90.6 mg, 91% yield.

m.p.: 137 °C – 139 °C.

TLC: R_f = 0.43 (Hexane/EtOAc = 6:1).

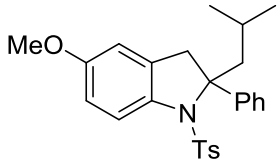
IR (KBr): 3007, 2939, 2879, 1601, 1488, 1455, 1343, 1214, 1158, 1032, 996, 701, 662, 600, 555 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.59 (d, *J* = 8.9 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.26 – 7.21 (m, 4H), 7.17 – 7.13 (m, 4H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.80 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.73 (d, *J* = 2.6 Hz, 1H), 3.81 (s, 3H), 3.40 (q, *J* = 17.0 Hz, 2H), 3.01 – 2.94 (m, 1H), 2.86 (ddd, *J* = 14.2, 8.6, 6.0 Hz, 1H), 2.78 – 2.71 (m, 1H), 2.34 (s, 3H), 2.31 (d, *J* = 3.8 Hz, 1H), 2.03 – 1.92 (m, 1H), 1.70 (td, *J* = 7.6, 7.0, 3.4 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 155.8, 144.0, 142.7, 142.1, 138.0, 136.6, 130.1, 129.0, 128.6, 128.4, 128.0, 127.4, 126.7, 126.6, 125.9, 114.1, 112.7, 110.6, 74.7, 55.7, 46.2, 38.4, 36.1, 25.8, 21.4.

HRMS (ESI): $C_{31}H_{32}NO_3S$ $[M+H]^+$: calcd.: 498.2097; found: 498.2097.

2-Isobutyl-5-methoxy-2-phenyl-1-tosylindoline (3l)



3l

Compound **3l** was synthesized following the general procedure A.

A white solid, 66.2 mg, 76% yield.

m.p.: 129 °C – 131 °C.

TLC: R_f = 0.56 (Hexane/EtOAc = 6:1).

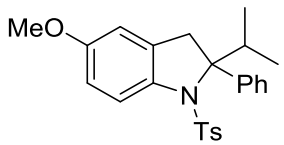
IR (KBr): 2963, 2920, 1489, 1439, 1347, 1216, 1157, 1090, 1038, 993, 808, 660, 595, 543 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.66 (d, *J* = 8.9 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.20 – 7.15 (m, 1H), 7.10 – 7.02 (m, 4H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.80 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.75 (d, *J* = 1.4 Hz, 1H), 3.82 (s, 3H), 3.49 (s, 2H), 2.94 (dd, *J* = 13.9, 6.3 Hz, 1H), 2.32 (s, 3H), 2.17 (dd, *J* = 13.9, 4.5 Hz, 1H), 1.95 – 1.87 (m, 1H), 1.18 (d, *J* = 6.6 Hz, 3H), 0.99 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 155.9, 144.2, 142.5, 138.2, 136.8, 130.6, 128.8, 127.8, 127.3, 126.9, 126.6, 114.6, 112.7, 110.5, 74.6, 55.7, 47.0, 46.0, 25.5, 24.6, 24.4, 21.4.

HRMS (ESI): $C_{26}H_{30}NO_3S$ $[M+H]^+$: calcd.: 436.1941; found: 436.1941.

2-Isopropyl-5-methoxy-2-phenyl-1-tosylindoline (3m)



3m

Compound **3m** was synthesized following the general procedure A.

A white solid, 56.5 mg, 67% yield.

m.p.: 82 °C – 84 °C.

TLC: R_f = 0.46 (Hexane/EtOAc = 6:1).

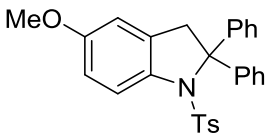
IR (KBr): 2956, 2921, 2951, 1645, 1626, 1486, 1348, 1160, 571, 545 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44 (d, *J* = 8.8 Hz, 1H), 7.31 – 7.29 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 2H), 6.85 – 6.77 (m, 4H), 6.74 (dd, *J* = 11.3, 5.5 Hz, 2H), 3.78 (s, 3H), 3.74 (s, 1H), 3.28 –3.60 (m, 2H), 2.24 (s, 3H), 1.21 (d, *J* = 6.6 Hz, 3H), 1.02 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 155.5, 142.3, 141.8, 137.3, 136.2, 130.4, 128.7, 128.1, 127.9, 127.5, 126.8, 113.8, 112.6, 110.3, 78.5, 55.7, 40.4, 32.2, 21.3, 18.4, 17.3.

HRMS (ESI): $C_{25}H_{28}NO_3S$ $[M+H]^+$: calcd.: 422.1784; found: 422.1784.

5-Methoxy-2,2-diphenyl-1-tosylindoline (3n)



3n

Compound **3n** was synthesized following the general procedure A.

A white solid, 56.5 mg, 62% yield.

m.p.: 78 °C – 80 °C.

TLC: R_f = 0.43 (Hexane/EtOAc = 6:1).

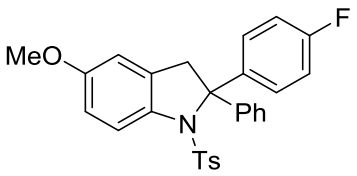
IR (KBr): 2920, 2836, 1596, 1488, 1446, 1347, 1212, 1158, 1030, 701, 547 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77 (d, *J* = 9.0 Hz, 1H), 7.45 – 7.38 (m, 4H), 7.28 – 7.22 (m, 6H), 6.94 – 6.84 (m, 4H), 6.80 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.62 (d, *J* = 2.6 Hz, 1H), 3.81 (s, 2H), 3.75 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 156.1, 143.5, 142.8, 137.8, 135.8, 129.3, 129.1, 128.8, 127.7, 127.2, 126.6, 114.9, 113.0, 110.5, 78.9, 55.7, 52.0, 21.4.

HRMS (ESI): $C_{28}H_{26}NO_3S$ $[M+H]^+$: calcd.: 456.1628; found: 456.1627.

2-(4-Fluorophenyl)-5-methoxy-2-phenyl-1-tosylindolin (3o)



3o

Compound **3o** was synthesized following the general procedure A.

A white solid, 65.4 mg, 69% yield.

m.p.: 174 °C – 176 °C.

TLC: R_f = 0.41(Hexane/EtOAc = 6:1).

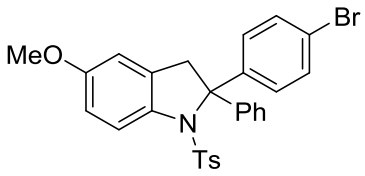
IR (KBr): 2944, 2919, 1601, 1505, 1489, 1355, 1242, 1219, 1161, 1037, 828, 671, 551 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.82 (d, *J* = 8.9 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.41 – 7.37 (m, 2H), 7.29 (dd, *J* = 4.8, 2.3 Hz, 3H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.95 – 6.90 (m, 4H), 6.84 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.66 (d, *J* = 2.7 Hz, 1H), 3.81 (s, 2H), 3.79 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 161.9 (d, *J* = 247.3 Hz), 156.3, 143.5, 144.0, 139.1, 137.9, 131.1 (d, *J* = 8.1 Hz), 129.1, 128.9, 128.8, 127.8, 127.4, 126.5, 115.1, 114.4, 114.3, 113.1, 110.5, 78.4, 55.7, 51.9, 21.4.

HRMS (ESI): $C_{28}H_{25}FNO_3S$ $[M+H]^+$: calcd.: 474.1534; found: 474.1532.

2-(4-Bromophenyl)-5-methoxy-2-phenyl-1-tosylindoline (3p)



3p

Compound **3p** was synthesized following the general procedure A.

A white solid, 66.3 mg, 62% yield.

m.p.:165 °C – 167 °C.

TLC: R_f = 0.35 (Hexane/EtOAc = 6:1).

IR (KBr): 2919, 1596, 1488, 1351, 1217, 1158, 1038, 1003, 816, 700, 666, 548 cm^{-1}

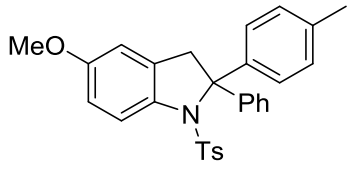
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83 (d, *J* = 8.9 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.32 – 7.23 (m, 5H), 7.00 – 6.90 (m, 4H), 6.85 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.66 (d, *J* = 2.6 Hz, 1H), 3.86 – 3.75 (m, 2H), 3.79 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 156.3, 143.0, 134.0, 142.6, 137.8, 135.8, 130.9, 130.7, 129.0, 128.8, 127.8, 127.5, 126.4, 121.6, 115.1, 113.2, 110.5, 78.3, 55.7, 51.9, 21.5.

HRMS (ESI): $C_{28}H_{25}{}^{79}BrNO_3S$ $[M+H]^+$: calcd.: 534.0733; found: 534.0730.

$C_{28}H_{25}{}^{81}BrNO_3S$ $[M+H]^+$: calcd.: 536.0713; found: 536.0710.

5-Methoxy-2-phenyl-2-(p-tolyl)-1-tosylindoline (3q)



3q

Compound **3q** was synthesized following the general procedure A.

A white solid, 65.7 mg, 70% yield.

m.p.: 191 °C – 193 °C.

TLC: R_f = 0.44 (Hexane/EtOAc = 6:1).

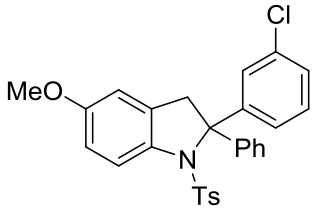
IR (KBr): 2939, 2919, 1598, 1488, 1356, 1247, 1219, 1161, 1033, 1006, 964, 813, 671, 550 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.82 (d, *J* = 8.9 Hz, 1H), 7.47 – 7.46 (m, 2H), 7.34 – 7.26 (m, 5H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.97 – 6.90 (m, 4H), 6.83 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.66 (d, *J* = 1.5 Hz, 1H), 3.89 – 3.80 (m, 2H), 3.79 (s, 3H), 2.38 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 156.2 , 143.8 , 142.7 , 140.4 , 138.0 , 137.0 , 136.0 , 129.4 , 129.2 , 129.0 , 128.7 , 128.3 , 127.7 , 127.2 , 126.6 , 115.0 , 113.0 , 110.5 , 78.8 , 55.7 , 51.8 , 21.4 , 21.0.

HRMS (ESI): $C_{29}H_{28}NO_3S$ $[M+H]^+$: calcd.: 470.1784; found: 470.1783.

2-(3-Chlorophenyl)-5-methoxy-2-phenyl-1-tosylindoline (3r)



3r

Compound **3r** was synthesized following the general procedure A.

A white solid, 58.8 mg, 60% yield.

m.p.: 165 °C – 167 °C.

IR (KBr): 2967, 2941, 1596, 1486, 1355, 1215, 1162, 1015, 703, 668, 548 cm^{-1}.

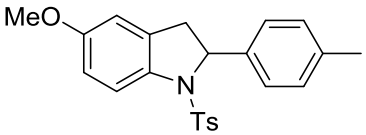
TLC: R_f = 0.47 (Hexane/EtOAc = 6:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.85 (d, *J* = 8.9 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.38 – 7.34 (m, 1H), 7.33 – 7.27 (m, 4H), 7.27 – 7.20 (m, 2H), 6.99 – 6.92 (m, 4H), 6.85 (dd, *J* = 9.0, 2.7 Hz, 1H), 6.66 (d, *J* = 2.7 Hz, 1H), 3.81 (s, 2H), 3.79 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 156.3 , 145.5 , 143.1 , 142.9 , 137.8 , 135.8 , 133.7 , 129.1 , 129.0 , 128.9 , 128.9 , 127.9 , 127.8 , 127.5 , 127.5 , 126.3 , 115.1 , 113.2 , 110.5 , 78.3 , 55.7 , 51.9 , 21.4 .

HRMS (ESI): $C_{28}H_{25}ClNO_3S$ $[M+H]^+$: calcd.: 490.1238; found: 490.1239.

5-Methoxy-2-(p-tolyl)-1-tosylindoline (3s)



3s

Compound **3s** was synthesized following the general procedure A.

A colorless oil, 69.3 mg, 88% yield.

TLC: R_f = 0.63 (Hexane/EtOAc = 6:1).

IR (KBr): 3003, 2924, 2862, 1603, 1508, 1347, 1248, 1162, 1091, 813, 550 cm^{-1}.

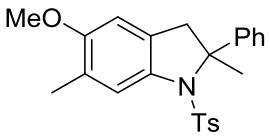
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.62 (d, *J* = 8.8 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.24 – 7.13 (m, 4H), 7.09 (d, *J* = 7.8 Hz, 2H), 6.78 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.58 (d, *J*

= 2.6 Hz, 1H), 5.24 (dd, *J* = 9.6, 2.6 Hz, 1H), 3.75 (s, 3H), 3.06 (dd, *J* = 16.2, 9.7 Hz, 1H), 2.76 (dd, *J* = 16.2, 2.7 Hz, 1H), 2.36 (s, 3H), 2.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 157.5, 143.7, 139.6, 137.3, 135.2, 135.1, 133.5, 129.5, 129.3, 127.2, 125.9, 118.2, 112.9, 110.8, 64.9, 55.6, 37.8, 21.6, 21.1.

HRMS (ESI): $C_{23}H_{24}NO_3S$ $[M+H]^+$: calcd.: 394.1471; found: 394.1472.

5-Methoxy-2,6-dimethyl-2-phenyl-1-tosylindoline (3t)



3t

Compound **3t** was synthesized following the general procedure A.

A white solid, 70.1 mg, 86% yield.

m.p.: 92 °C – 94 °C.

TLC: R_f = 0.62 (Hexane/EtOAc = 6:1).

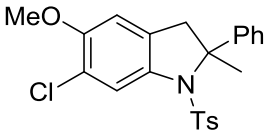
IR (KBr): 2920, 2964, 1599, 1497, 1463, 1411, 1344, 1215, 1155, 1088, 1028, 657, 596 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49 (s, 1H), 7.43 – 7.41 (m, 2H), 7.40 – 7.32 (m, 2H), 7.24 – 7.17 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.58 (s, 1H), 3.75 (s, 3H), 3.41 – 3.16 (m, 2H), 2.33 (s, 3H), 2.24 (s, 3H), 2.08 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 154.1, 145.5, 142.9, 138.8, 135.5, 129.2, 128.1, 127.2, 126.6, 126.2, 126.0, 125.8, 116.4, 107.1, 72.8, 55.7, 49.3, 27.1, 21.5, 16.9.

HRMS (ESI): $C_{24}H_{26}NO_3S$ $[M+H]^+$: calcd.: 408.1628; found: 408.1629.

6-Chloro-5-methoxy-2-methyl-2-phenyl-1-tosylindoline (3u)



3u

Compound **3u** was synthesized following the general procedure A.

A white solid, 58.2 mg, 68% yield.

m.p.: 147 °C – 149 °C.

TLC: R_f = 0.36 (Hexane/EtOAc = 6:1).

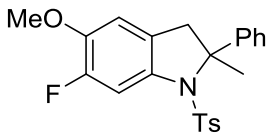
IR (KBr): 2922, 2867, 1600, 1486, 1344, 1159, 1056, 998, 697, 594, 560, 537 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73 (s, 1H), 7.41 – 7.39 (m, 2H), 7.34 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.22 (dd, *J* = 5.2, 1.8 Hz, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.69 (s, 1H), 3.83 (s, 3H), 3.44 – 3.13 (m, 2H), 2.36 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 151.3, 144.8, 143.3, 138.3, 136.3, 129.3, 128.2, 127.7, 127.4, 126.7, 125.8, 121.6, 115.8, 109.3, 73.3, 56.6, 49.0, 27.0, 21.5.

HRMS (ESI): $C_{23}H_{23}ClNO_3S$ $[M+H]^+$: calcd.: 428.1082; found: 428.1084.

6-Fluoro-5-methoxy-2-methyl-2-phenyl-1-tosylindoline (3v)



3v

Compound **3v** was synthesized following the general procedure A.

A white solid, 52.7 mg, 64% yield.

m.p.: 117 °C – 119 °C.

TLC: R_f = 0.55 (Hexane/EtOAc = 6:1).

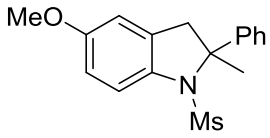
IR (KBr): 2960, 2928, 2855, 1599, 1502, 1349, 1223, 1157, 1088, 1021, 989, 701, 597 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.48 (d, *J* = 12.5 Hz, 1H), 7.41 – 7.39 (m, 2H), 7.35 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.25 – 7.19 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.71 (d, *J* = 8.3 Hz, 1H), 3.82 (s, 3H), 3.45 – 3.14 (m, 2H), 2.35 (s, 3H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 152.1 (d, *J* = 243.1 Hz), 144.9, 143.6 (d, *J* = 11.7 Hz), 143.3, 138.3, 135.8 (d, *J* = 10.0 Hz), 129.3, 128.2, 127.4, 126.7, 125.8, 123.0, 110.7 (d, *J* = 2.9 Hz), 103.5 (d, *J* = 25.9 Hz), 73.4, 57.0, 48.9, 27.0, 21.5.

HRMS (ESI): $C_{23}H_{23}FNO_3S$ $[M+H]^+$: calcd.: 412.1377; found: 412.1378.

5-Methoxy-2-methyl-1-(methylsulfonyl)-2-phenylindoline (3w)



3w

Compound **3w** was synthesized following the general procedure A.

A colorless oil, 54.6 mg, 86% yield.

TLC: R_f = 0.44 (Hexane/EtOAc = 6:1).

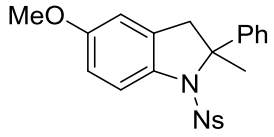
IR (KBr): 2922, 2850, 1600, 1488, 1345, 1225, 1153, 1033, 1008, 763, 530 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.51 – 7.43 (m, 2H), 7.36 – 7.24 (m, 4H), 6.82 – 6.73 (m, 2H), 3.80 (s, 3H), 3.59 – 3.27 (m, 2H), 2.56 (s, 3H), 2.11 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 156.1, 144.5, 135.7, 129.7, 128.4, 127.8, 125.7, 113.5, 112.8, 111.3, 72.3, 55.8, 49.0, 38.7, 26.6.

HRMS (ESI): $C_{17}H_{20}NO_3S$ $[M+H]^+$: calcd.: 318.1158; found: 318.1162.

5-Methoxy-2-methyl-1-((4-nitrophenyl) sulfonyl)-2-phenylindoline (3x)



3x

Compound **3x** was synthesized following the general procedure A.

A yellow solid, 66.2 mg, 78% yield.

m.p.: 97 °C – 99 °C.

TLC: R_f = 0.32 (Hexane/EtOAc = 6:1).

IR (KBr): 3119, 2923, 2851, 1608, 1529, 1490, 1352, 1312, 1224, 1159, 1025, 996, 740, 607 cm^{-1}.

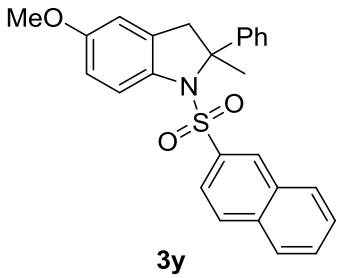
^{1}H NMR (400 MHz, CDCl3): δ (ppm) 8.04 (d, *J* = 8.6 Hz, 2H), 7.67 (d, *J* = 8.9 Hz, 1H), 7.53 – 7.51 (m, 2H), 7.29 – 7.18 (m, 3H), 7.12 (t, *J* = 7.5 Hz, 2H), 6.82 (dd, *J* =

9.0, 2.6 Hz, 1H), 6.71 (d, *J* = 2.6 Hz, 1H), 3.79 (s, 3H), 3.54 – 3.25 (m, 2H), 2.13 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 156.6, 149.5, 146.6, 143.8, 135.2, 129.9, 128.2, 127.8, 127.5, 126.2, 123.7, 114.5, 113.1, 111.16, 72.9, 55.7, 49.2, 27.5.

HRMS (ESI): $C_{22}H_{21}N_2O_5S$ $[M+H]^+$: calcd.: 425.1166; found: 425.1166.

5-Methoxy-2-methyl-1-(naphthalen-2-yl)-2-phenylindoline (3y)



3y

Compound **3y** was synthesized following the general procedure A.

A yellow solid, 73.0 mg, 85% yield.

m.p.: 126 °C – 128 °C.

TLC: R_f = 0.35 (Hexane/EtOAc = 6:1).

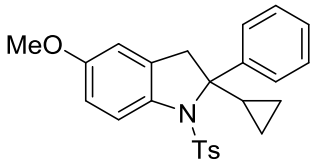
IR (KBr): 2922, 2867, 1600, 1486, 1344, 1159, 1056, 998, 697, 594, 560, 537 cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.63 – 8.53 (m, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.75 (d, *J* = 7.4 Hz, 1H), 7.52 (ddd, *J* = 10.0, 7.7, 4.6 Hz, 3H), 7.40 (dt, *J* = 7.3, 2.1 Hz, 2H), 7.32 – 7.23 (m, 1H), 7.15 (dd, *J* = 5.2, 2.3 Hz, 3H), 6.72 (d, *J* = 7.6 Hz, 2H), 3.76 (d, *J* = 1.8 Hz, 3H), 3.47 – 3.23 (m, 2H), 2.06 (d, *J* = 2.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 156.2, 144.8, 138.3, 137.1, 134.3, 133.3, 129.5, 128.7, 128.4, 128.1, 128.0, 127.3, 126.8, 126.7, 125.8, 125.1, 124.0, 115.5, 112.7, 111.3, 73.8, 55.7, 48.7, 26.3.

HRMS (ESI): $C_{26}H_{24}NO_3S$ $[M+H]^+$: calcd.: 430.1471; found: 430.1475.

2-Cyclopropyl-5-methoxy-2-phenyl-1-tosylindoline (3z)



3z

Compound **3z** was synthesized following the general procedure A.

A colorless oil, 19.3 mg, 23% yield.

TLC: R_f = 0.34 (Hexane/EtOAc = 6:1).

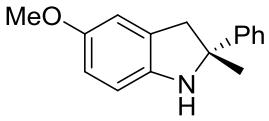
IR (KBr): 3005, 2922, 2837, 1599, 1488, 1347, 1212, 1160, 1090, 1032, 911, 731, 673, 547 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.66 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 3H), 7.31 – 7.28 (m, 2H), 7.26 (d, *J* = 7.1 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.77 (dd, *J* = 8.9, 2.7 Hz, 1H), 6.62 (d, *J* = 3.0 Hz, 1H), 3.77 (s, 3H), 2.88 – 2.72 (m, 2H), 2.40 (s, 3H), 2.35 – 2.26 (m, 1H), 0.98 – 0.81 (m, 1H), 0.66 – 0.55 (m, 1H), 0.34 (q, *J* = 7.7, 7.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 154.1, 145.4, 141.2, 137.7, 134.9, 127.4, 127.1, 126.5, 125.4, 125.0, 124.1, 112.1, 110.9, 109.3, 75.7, 53.9, 37.8, 19.7, 14.7, 2.6, 0.0.

HRMS (ESI): $C_{25}H_{27}NO_3S$ $[M+H]^+$: calcd.: 420.1628; found: 420.1633.

(*R*)-5-Methoxy-2-methyl-2-phenylindoline (*ent*-4a)



ent-**4a**

A colorless oil, 28.7 mg, 60% yield.

$[\alpha]_D^{20}$ = -30.1° (*c* = 1.00, $CHCl_3$);

TLC: R_f = 0.72 (Hexane/EtOAc = 3:1).

IR (KBr): 3348, 3026, 2961, 1492, 1436, 1237, 1143, 1032, 765, 701 cm^{-1}

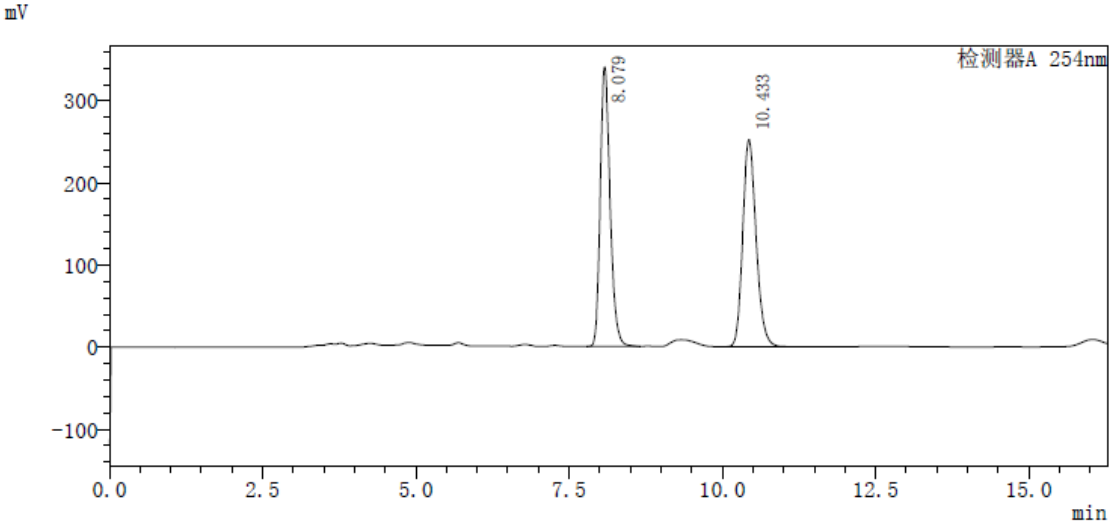
^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.54 (dt, *J* = 8.1, 1.4 Hz, 2H), 7.38 (td, *J* = 7.8, 1.5 Hz, 2H), 7.30 – 7.27 (m, 1H), 6.77 – 6.74 (m, 1H), 6.71 – 6.64 (m, 2H), 3.79 (d, *J* = 1.2 Hz, 3H), 3.29 – 3.18 (m, 2H), 1.68 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 153.5, 148.8, 143.9, 129.3, 128.4, 126.5, 125.2, 112.4, 111.8, 109.9, 66.7, 56.0, 46.2, 29.5.

HRMS (ESI): $C_{16}H_{19}NO$ $[M+H]^+$: calcd.: 240.1383; found: 240.1385.

Chiral HPLC: Chiralcel IC-H, λ= 254 nm, 10% ^{i}PrOH/hexanes, flow rate = 1.0 L/min. t_R: 8.15 min, 10.54 min; ee = 97%.

<色谱图>



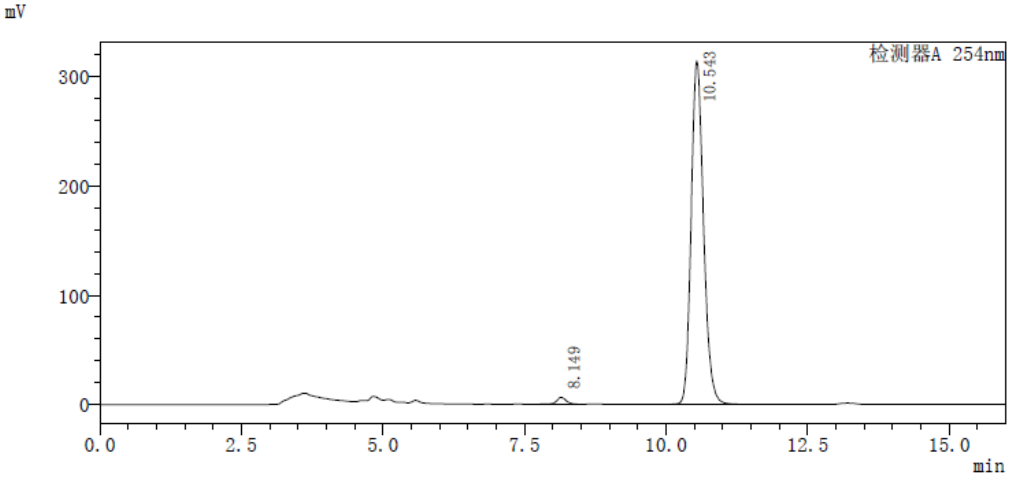
<峰表>

检测器A 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.079	3808578	340124	49.826	%		RT:8.079
2	10.433	3835183	252506	50.174	%		RT:10.433
总计		7643761	592629				

peak	Retention time	area	height	concentration	Unit of concentration
1	8.079	3808578	340124	49.826	%
2	10.433	3835183	252506	50.174	%
total		7643761	592629	100	%

〈色谱图〉



〈峰表〉

检测器A 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.149	73108	6274	1.506	%		RT:8.149
2	10.543	4782407	313498	98.494	%		RT:10.543
总计		4855515	319771				

peak	Retention time	area	height	concentration	Unit of concentration
1	8.149	73108	6274	1.506	%
2	10.543	4782407	313498	98.494	%
total		4855515	319771	100	%

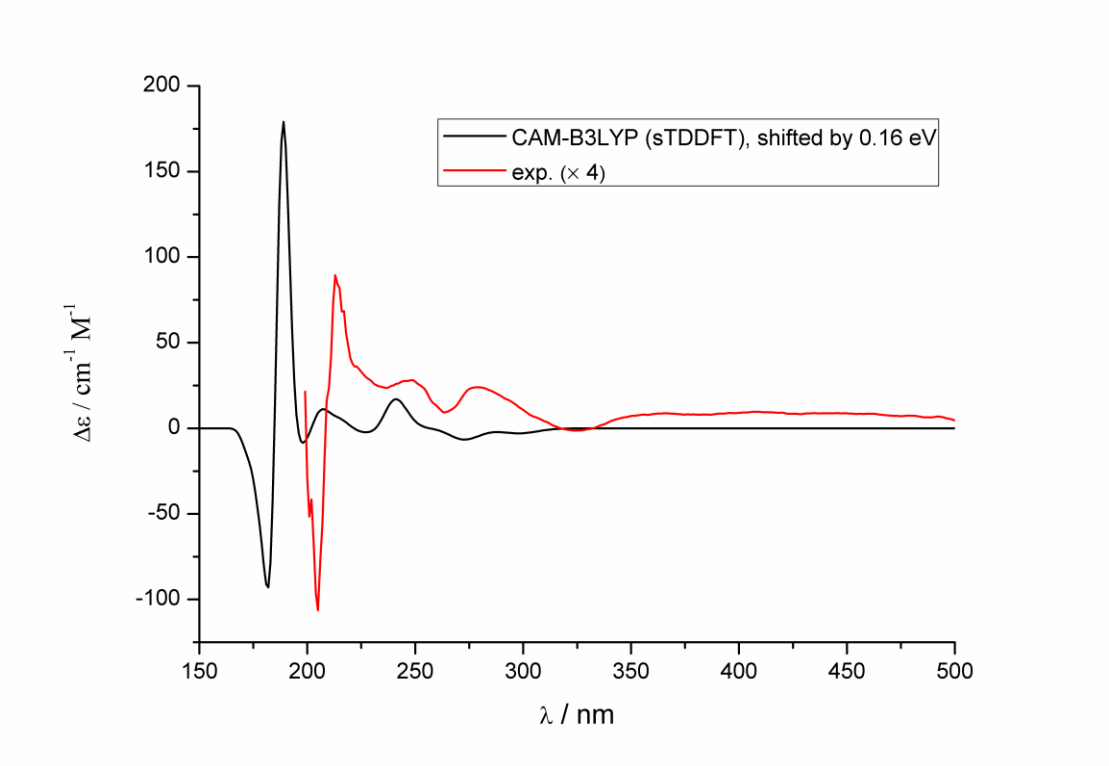
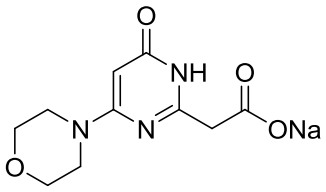


Figure S3: Calculated and measured ECD spectra of *ent*-**4a**. For better comparison, the intensities of the experimental spectrum are multiplied by four.

Sodium 2-(4-morpholino-6-oxo-1,6-dihydropyrimidin-2-yl)acetate (6)



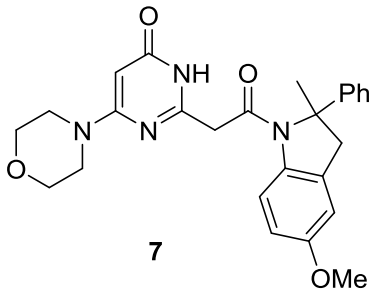
6

A yellow solid, 84.0 mg, 61% yield.

TLC: R_f = 0.19 (DCM/MeOH = 20:1).

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 13.42 (s, 1H), 5.34 (s, 1H), 3.75 (t, J = 4.9 Hz, 4H), 3.67 (s, 2H), 3.54 (t, J = 4.9 Hz, 4H).

2-[2-(5-Methoxy-2-methyl-2-phenylindolin-1-yl)-2-oxoethyl]-6-morpholinopyrimidin-4(3H)-one (7)



7

A yellow solid, 84 mg, 61% yield.

TLC: R_f = 0.22 (DCM/MeOH = 20:1).

m.p.: 118 °C – 120 °C.

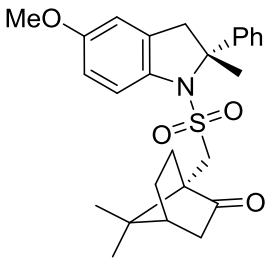
IR (KBr): 3449, 2922, 2853, 1645, 1561, 1486, 1381, 1238, 1117, 1031, 806, 701 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.92 (s, 1H), 8.36 (d, *J* = 9.0 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 4H), 7.27 (d, *J* = 7.8 Hz, 2H), 6.81 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.69 (d, *J* = 2.6 Hz, 1H), 5.20 (s, 1H), 3.80 (s, 3H), 3.70 (t, *J* = 4.8 Hz, 4H), 3.47 – 3.34 (m, 5H), 3.34 – 3.24 (m, 2H), 3.08 (d, *J* = 15.7 Hz, 1H), 2.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ (ppm) 166.3, 163.8, 162.4, 157.3, 154.1, 146.2, 136.3, 129.5, 129.3, 127.7, 124.7, 119.1, 112.5, 110.1, 85.0, 68.9, 66.4, 55.6, 50.5, 44.6, 41.9, 26.3.

HRMS (ESI): $C_{26}H_{29}N_4O_4$ $[M+H]^+$: calcd.: 461.2183; found: 461.2185.

Compound (8)



8

Compound **8** was synthesized following the general procedure A.

A white solid, 49.8 mg, 55% yield.

m.p.: 172 °C – 174 °C.

TLC: R_f = 0.28 (Hexane/EtOAc = 6:1).

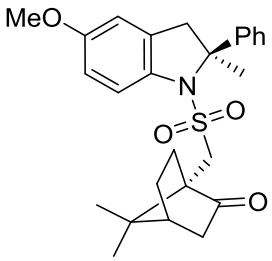
IR (KBr): 2962, 2932, 1745, 1489, 1357, 1229, 1155, 1012, 769, 705, 603, 553 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.52 (d, *J* = 8.7 Hz, 3H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.28 (td, *J* = 7.1, 1.2 Hz, 1H), 6.85 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.78 – 6.72 (m, 1H), 3.82 (s, 3H), 3.52 – 3.34 (m, 2H), 3.25 (d, *J* = 14.6 Hz, 1H), 2.86 (d, *J* = 14.6 Hz, 1H), 2.52 – 2.42 (m, 1H), 2.37 (dt, *J* = 18.4, 4.0 Hz, 1H), 2.13 (s, 3H), 2.08 (t, *J* = 4.5 Hz, 1H), 2.06 – 1.98 (m, 1H), 1.91 (d, *J* = 18.4 Hz, 1H), 1.56 (ddd, *J* = 14.1, 9.4, 4.8 Hz, 1H), 1.39 (td, *J* = 9.2, 4.7 Hz, 1H), 1.12 (s, 3H), 0.88 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 215.0, 156.0, 145.8, 135.9, 129.1, 128.4, 127.4, 125.4, 113.8, 112.9, 111.4, 72.3, 58.6, 55.8, 49.2, 48.9, 47.6, 43.1, 42.6, 26.8, 26.4, 25.6, 20.1, 19.9.

HRMS (ESI): $C_{26}H_{32}NO_4S$ $[M+H]^+$: calcd.: 454.2047; found: 454.2046.

Compound (*epi*-8)



epi-**8**

Compound *epi*-**8** was synthesized following the general procedure A.

A white solid, 21.7 mg, 24% yield.

m.p.: 156 °C –158 °C.

TLC: R_f = 0.30 (Hexane/EtOAc = 6:1).

IR (KBr): 2963, 2931, 1743, 1492, 1351, 1230, 1155, 1012, 818, 767, 704, 601, 508 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.57 – 7.50 (m, 3H), 7.34 (td, *J* = 7.1, 6.0, 1.5 Hz, 2H), 7.32 – 7.28 (m, 1H), 6.86 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.81 (d, *J* = 2.8 Hz, 1H), 3.83 (s, 3H), 3.61 – 3.42 (m, 2H), 3.33 (d, *J* = 14.5 Hz, 1H), 2.41 (ddd, *J* = 14.9, 11.7, 3.9 Hz, 1H), 2.29 (dt, *J* = 18.4, 4.0 Hz, 1H), 2.18 (s, 3H), 2.05 – 2.00 (m, 1H),

1.97 (d, *J* = 4.0 Hz, 1H), 1.89 (d, *J* = 18.4 Hz, 1H), 1.80 (s, 1H), 1.69 (ddd, *J* = 14.1, 9.4, 4.7 Hz, 1H), 1.39 (ddd, *J* = 13.0, 9.4, 3.9 Hz, 1H), 0.82 (s, 3H), 0.56 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 214.8, 155.9, 144.4, 136.0, 129.6, 128.3, 127.9, 126.2, 114.1, 112.9, 111.2, 72.0, 57.9, 55.8, 48.9, 47.8, 47.2, 42.5, 42.4, 27.3, 27.0, 24.8, 19.5, 19.5.

HRMS (ESI): $C_{26}H_{32}NO_4S$ $[M+H]^+$: calcd.: 454.2047; found: 454.2046.

7. X-Ray Crystallographic Analysis of 3y

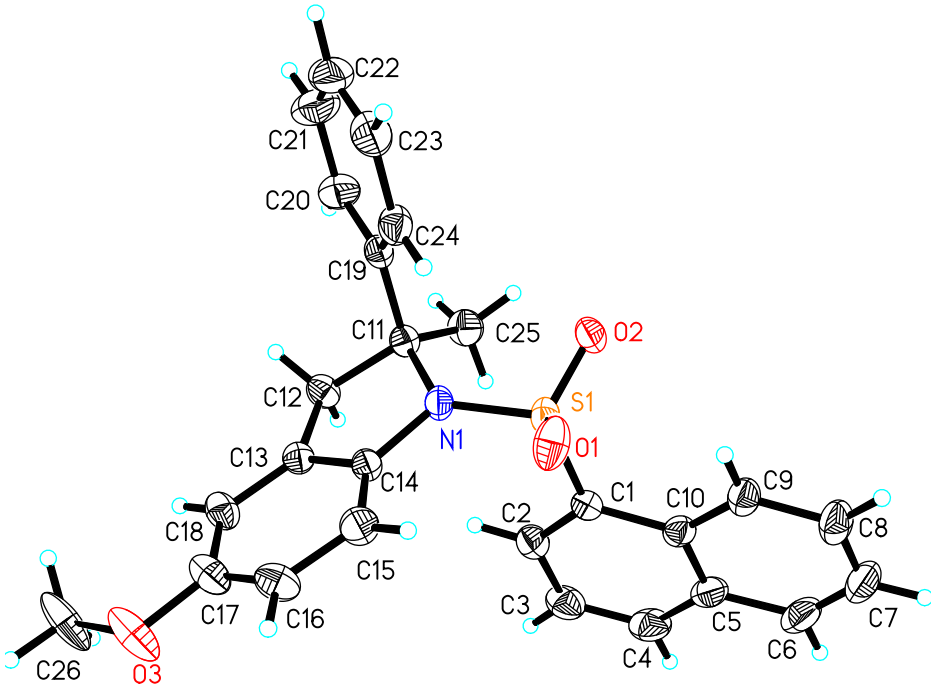
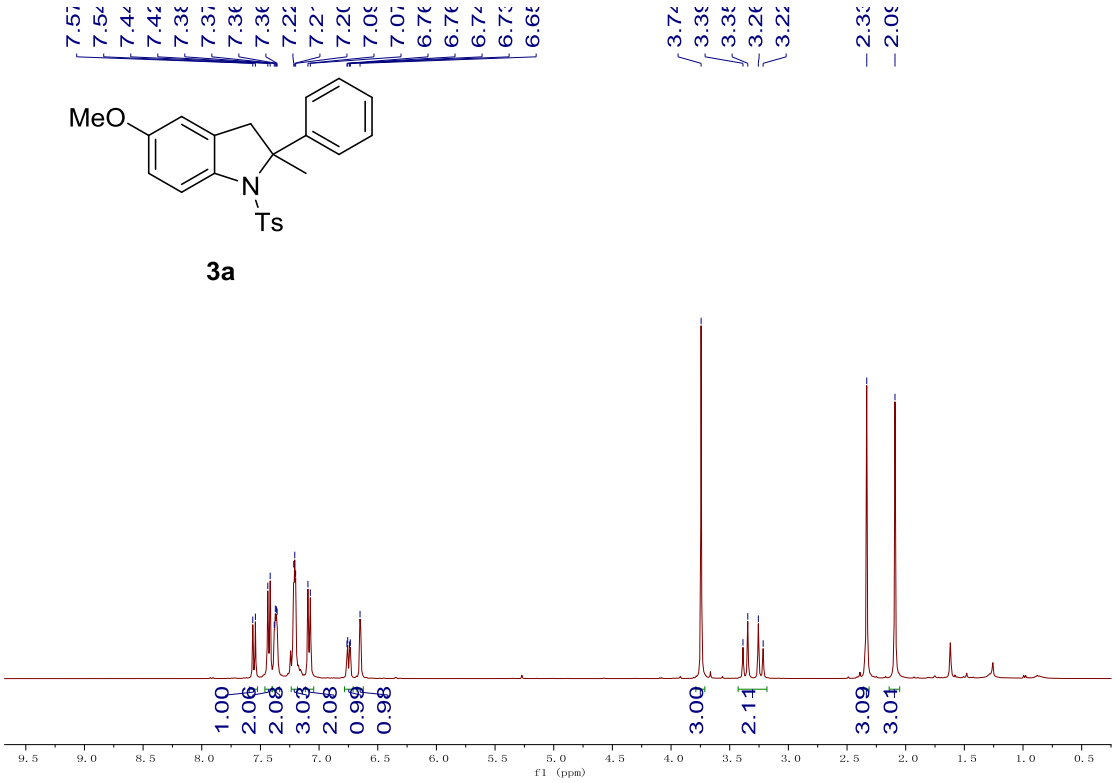


Table S2 Crystallographic data and structural refinement for compound **3y**

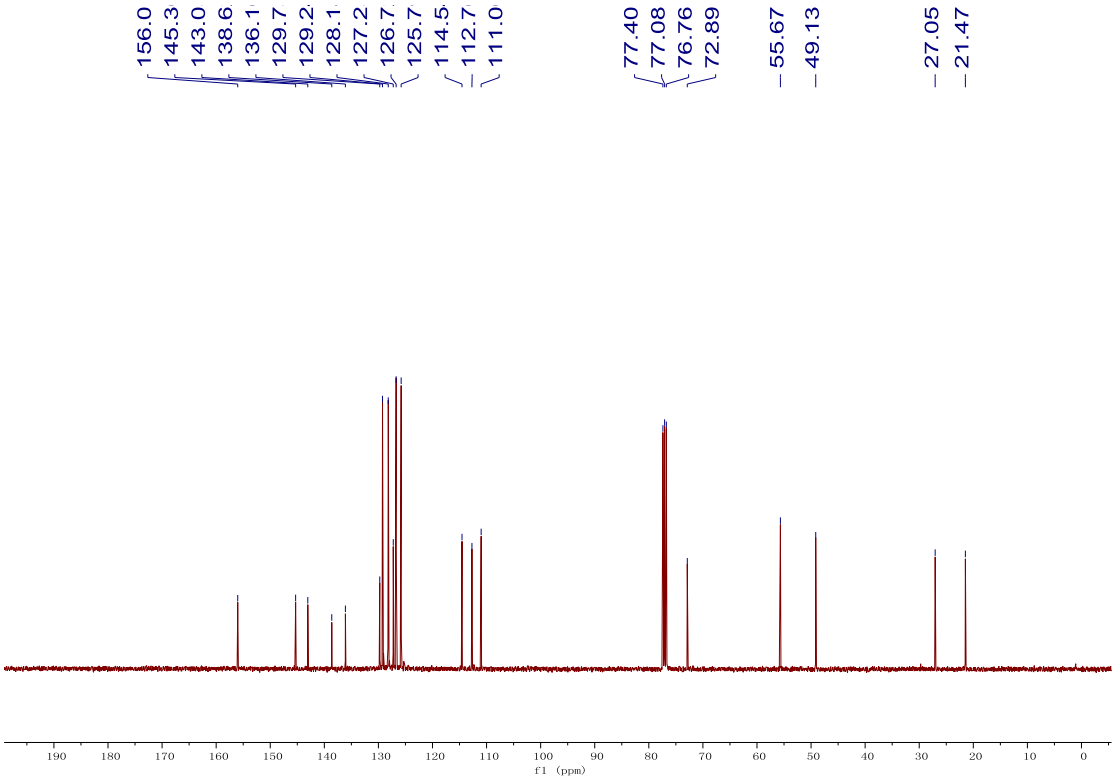
Complex	**Compound 1**
Formula	$C_{26}H_{23}NO_3S$
Formula weight	429.51
Temp (K)	273.15
λ (Mo, Kα), Å	0.71073
Crystal system	orthorhombic
Space group	*Pna2$_1$*
a (Å)	11.3867(14)

b (Å)	17.839(2)
c (Å)	10.6699(13)
α (deg)	90
β (deg)	90
γ (deg)	90
V ($Å^3$)	2167.3(5)
Z	4
$\rho_{calc}g/cm^3$	1.316
Absorption coefficient	0.178
F(000)	904.0
Crystal size/mm^3	0.15 × 0.12 × 0.1
Index ranges	-16 ≤ h ≤ 16, -25 ≤ k ≤ 25, -15 ≤ l ≤ 14
Reflections collected	23067
Independent reflections	7009 [R_{int} = 0.0361, R_{sigma} = 0.0414]
Data/restraints/parameters	7009/1/282
Largest diff. peak/hole / e $Å^{-3}$	0.24/-0.20
Flack parameter	0.01(3)
2θ range for data collection (deg)	4.244–64.418
Final R1a, wR2b	0.0698, 0.1215
Goodness-of-fit on F2	1.045

8. NMR spectra of products



3a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143.0
138.6
136.1
129.7
129.2
128.1
127.2
126.7
125.7
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112.7
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77.08
76.76
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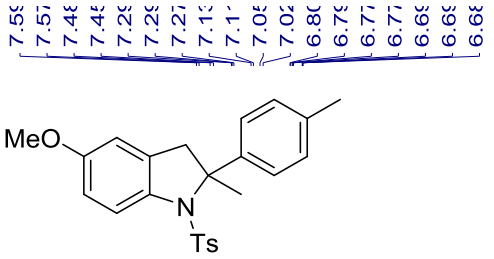
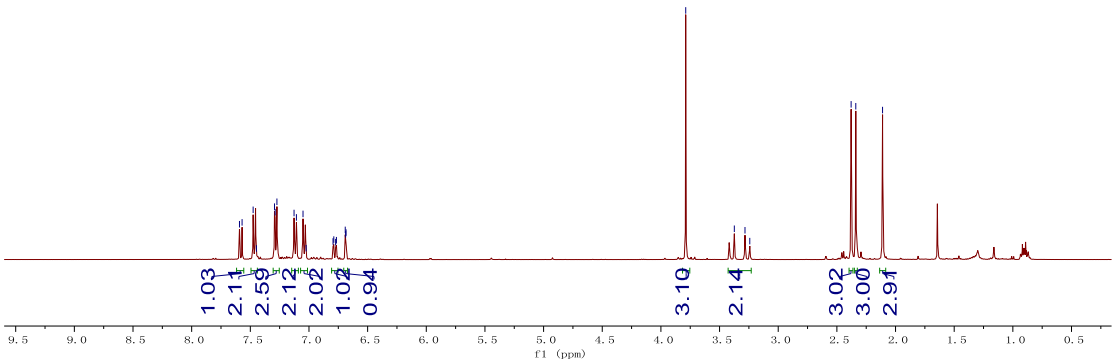
55.67
49.13
27.05
21.47
f1 (ppm)


MeO
N
Ts

3b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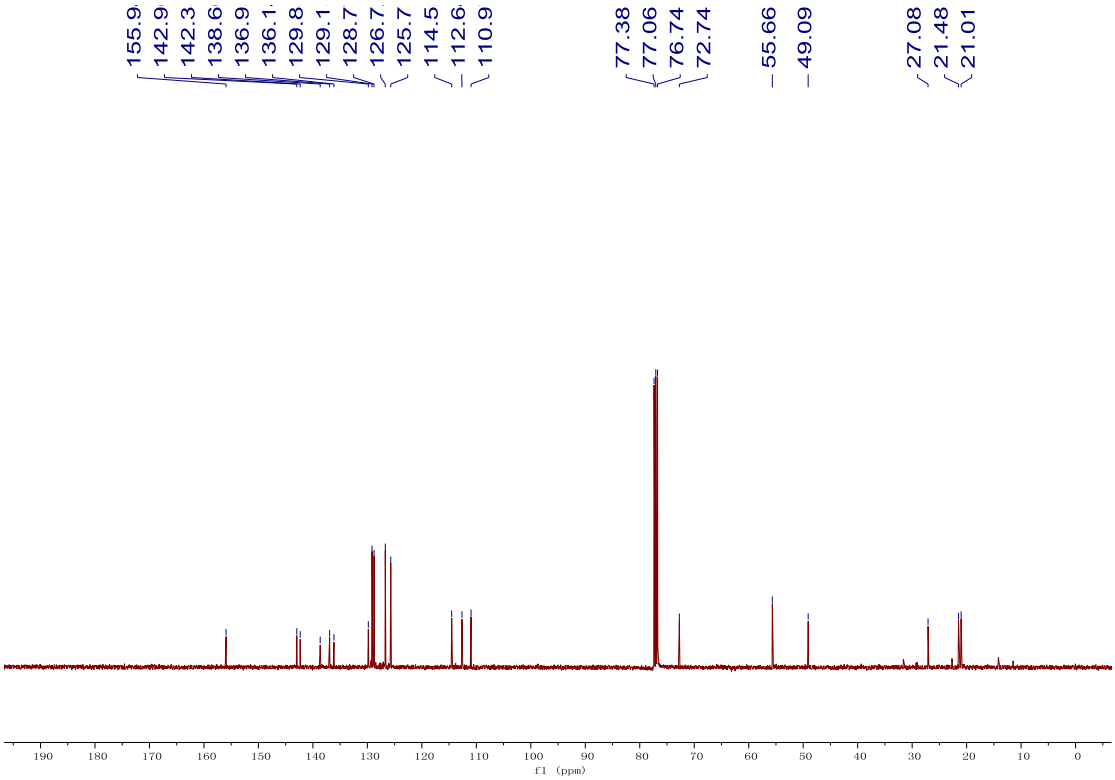
0.94
3.10
2.14
3.02
3.00
2.91
f1 (ppm)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136.9
136.1
129.8
129.1
128.7
126.7
125.7
114.5
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77.06
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72.74
55.66
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27.08
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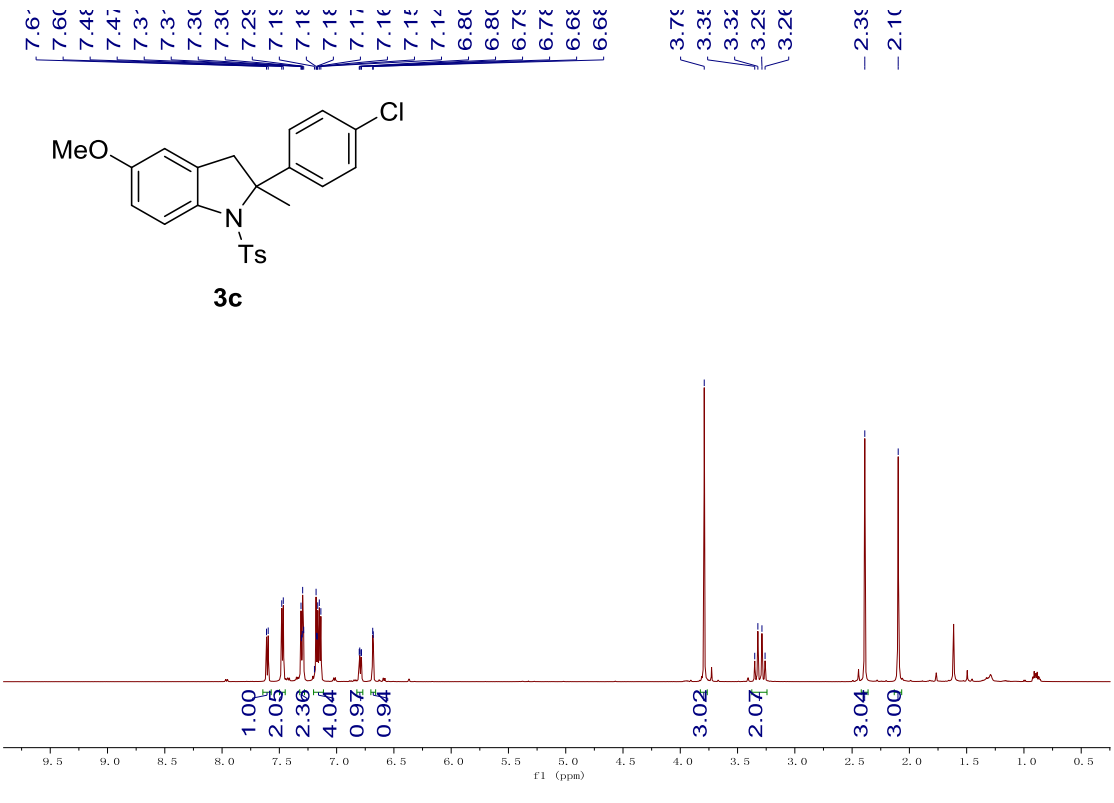
21.01
f1 (ppm)


MeO
Cl
N
Ts
3c
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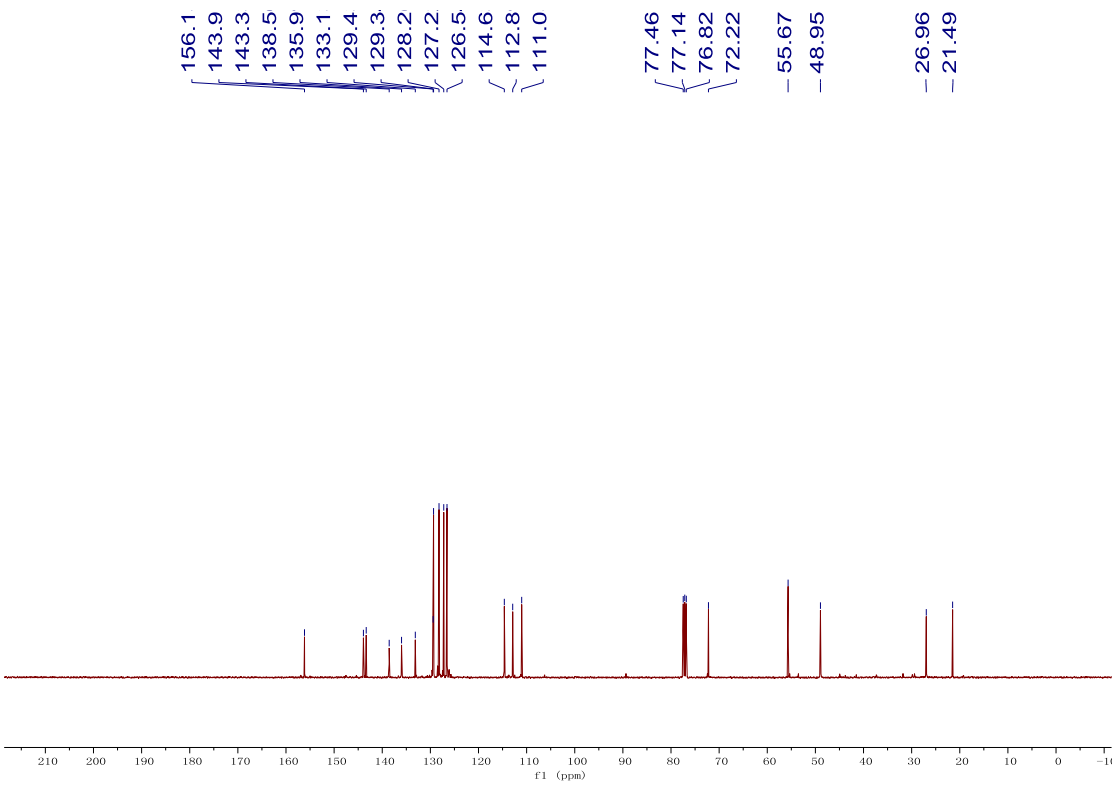
2.07
3.04
3.00
f1 (ppm)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143.9
143.3
138.5
135.9
133.1
129.4
129.3
128.2
127.2
126.5
114.6
112.8
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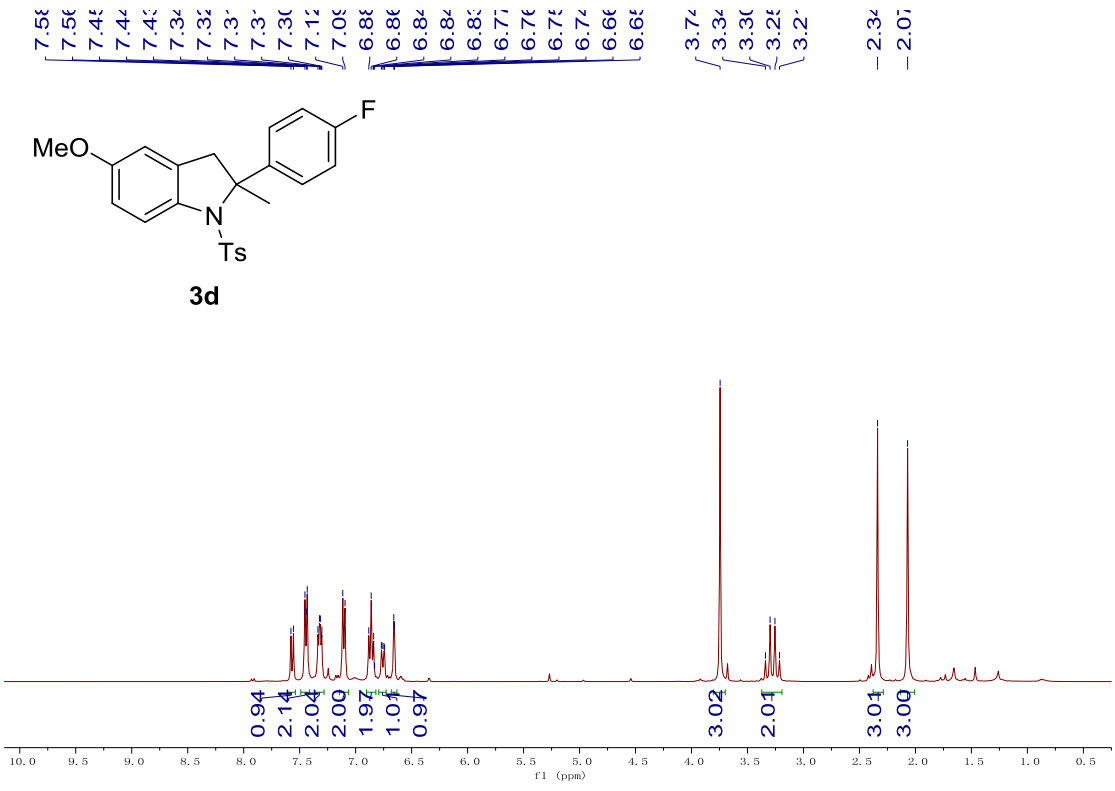
77.14
76.82
72.22
55.67
48.95
26.96
21.49
f1 (ppm)


MeO
F
N
Ts
3d
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1.01
0.97
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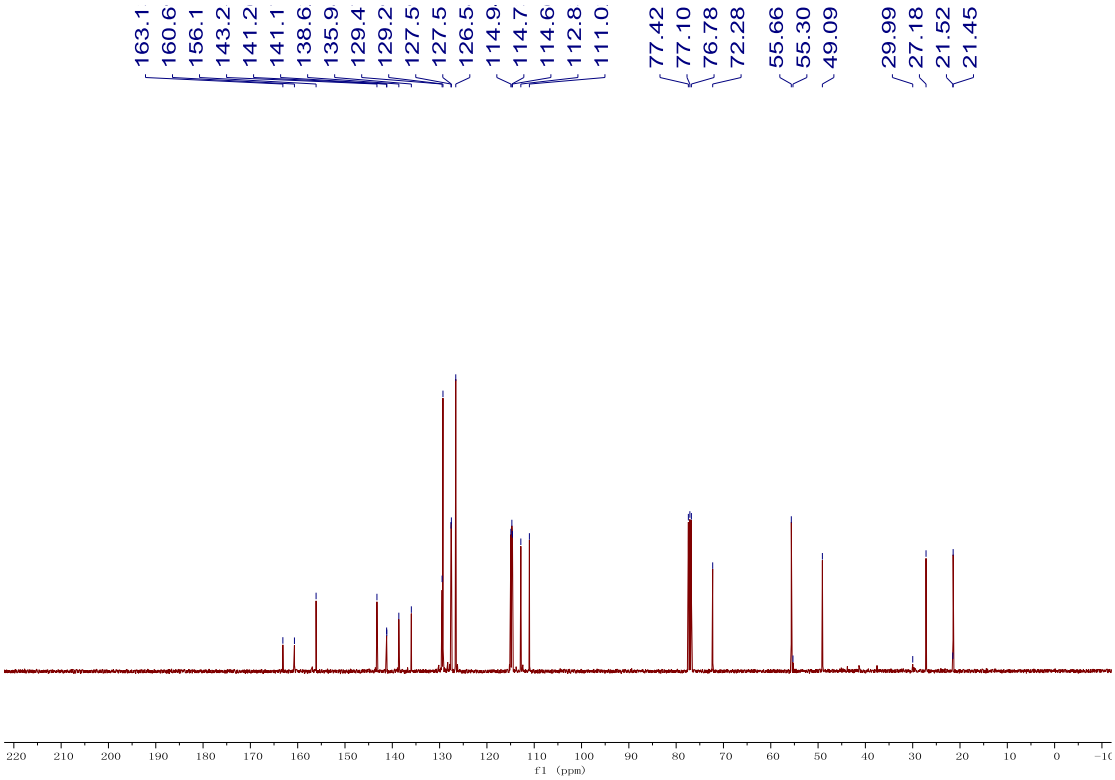
2.01
3.01
3.00
f1 (ppm)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156.1
143.2
141.2
141.1
138.6
135.9
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127.5
126.5
114.9
114.7
114.6
112.8
111.0
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27.18
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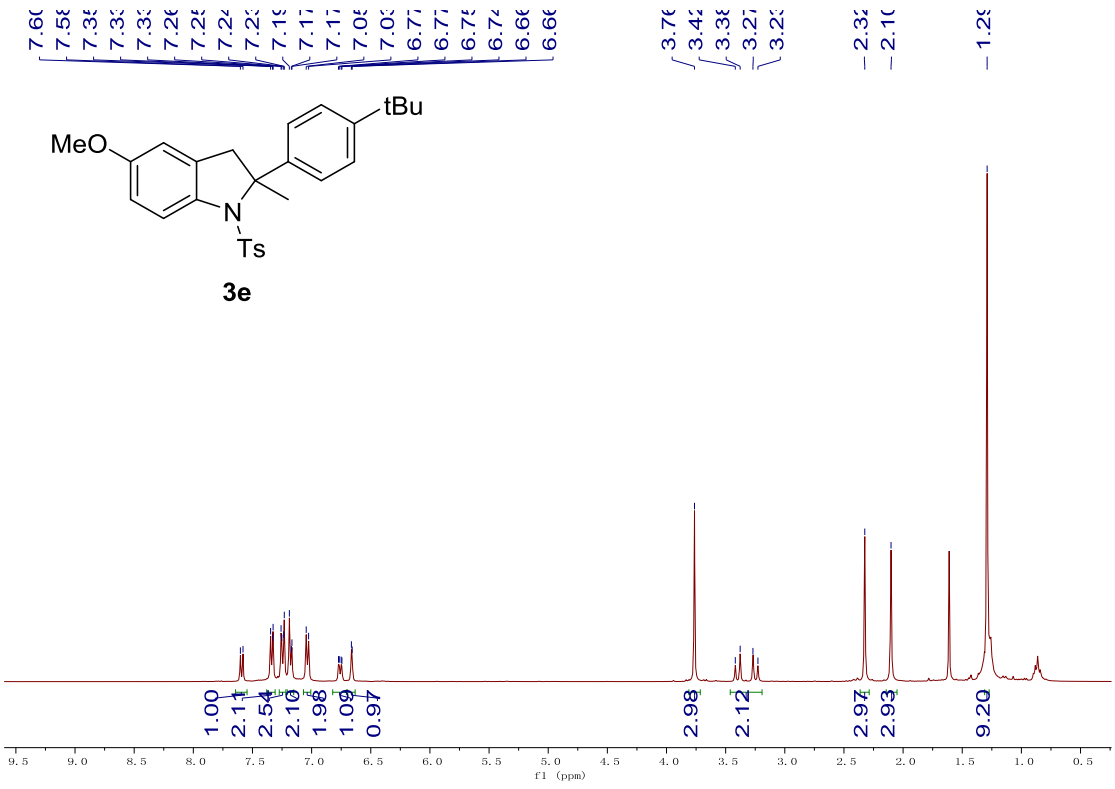
f1 (ppm)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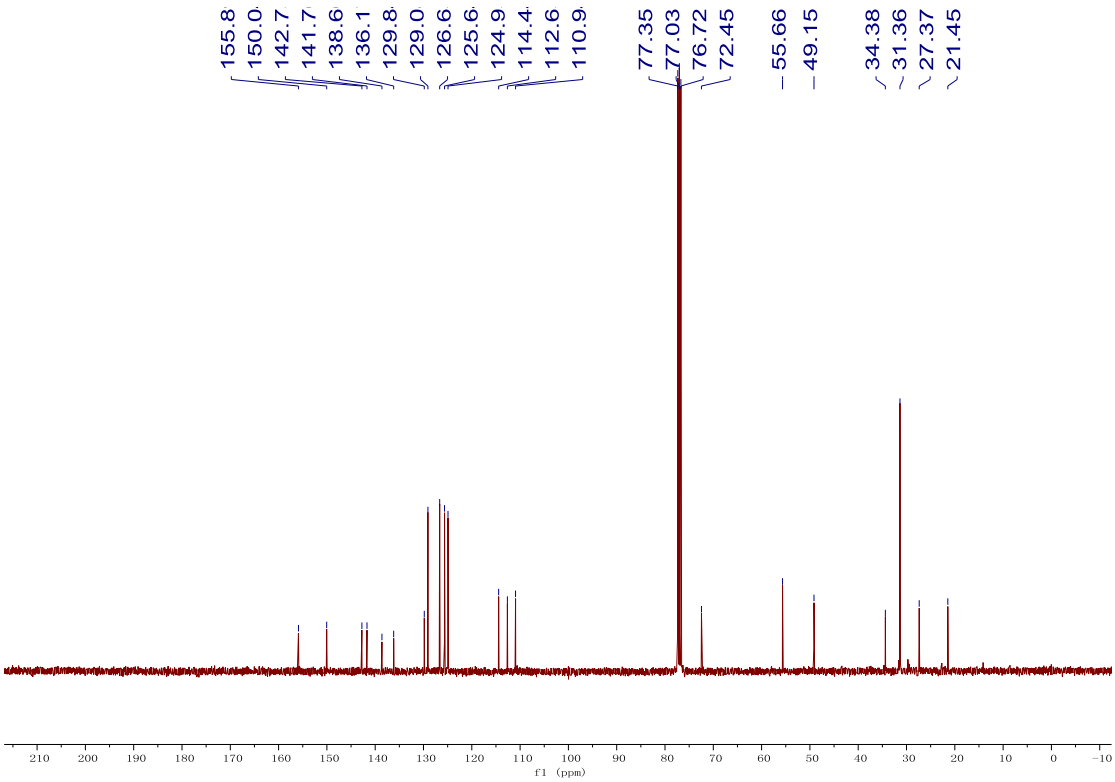
tBu
N
Ts
3e
f1 (ppm)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125.6
124.9
114.4
112.6
110.9
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55.66
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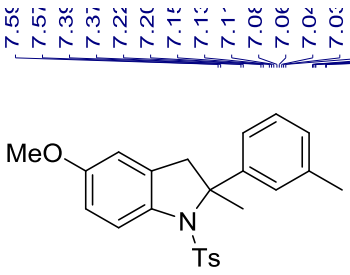
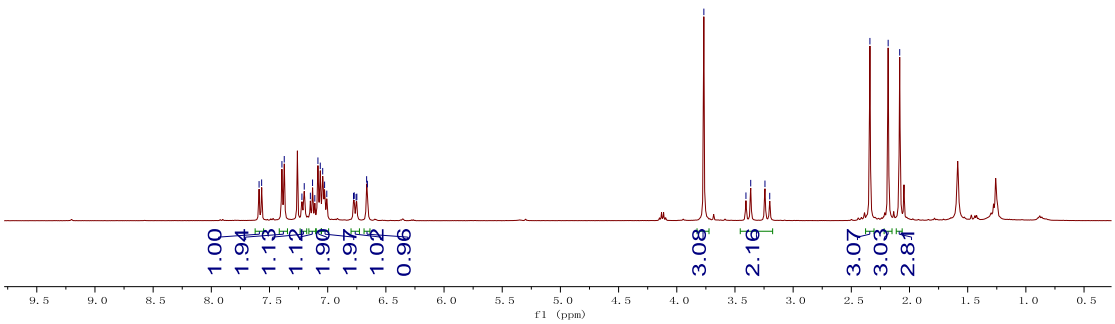
34.38
31.36
27.37
21.45
f1 (ppm)


MeO
N
Ts

3f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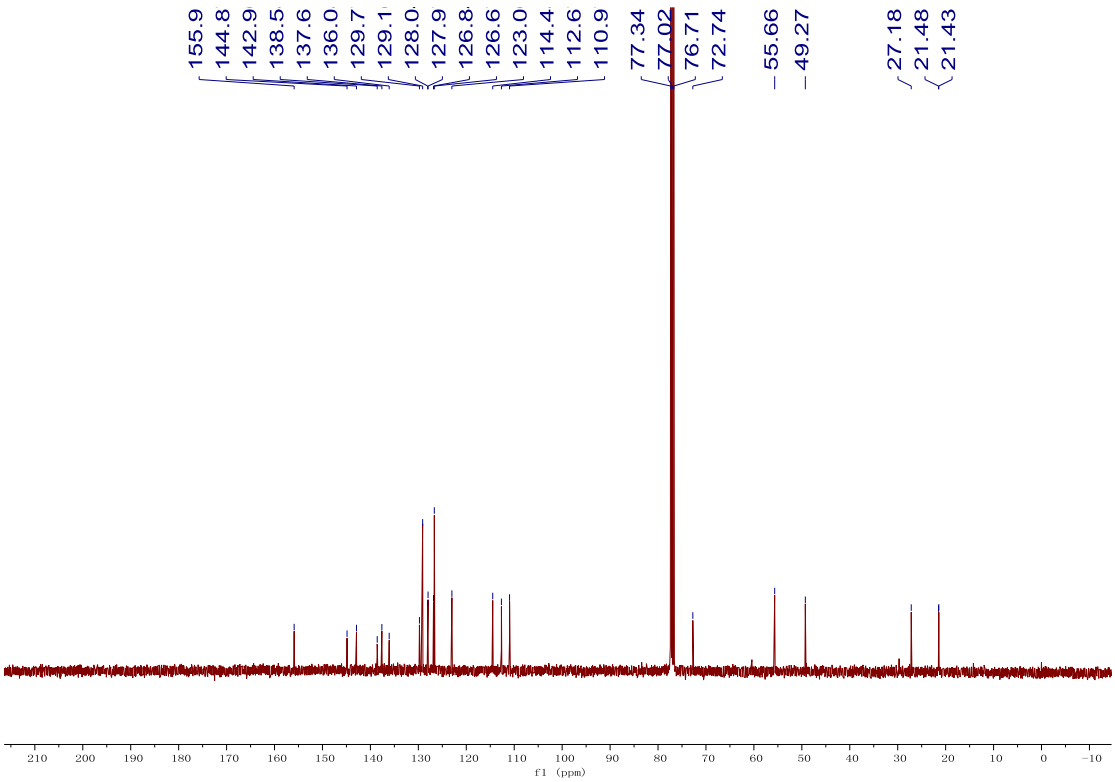
2.16
3.07
3.03
2.84
f1 (ppm)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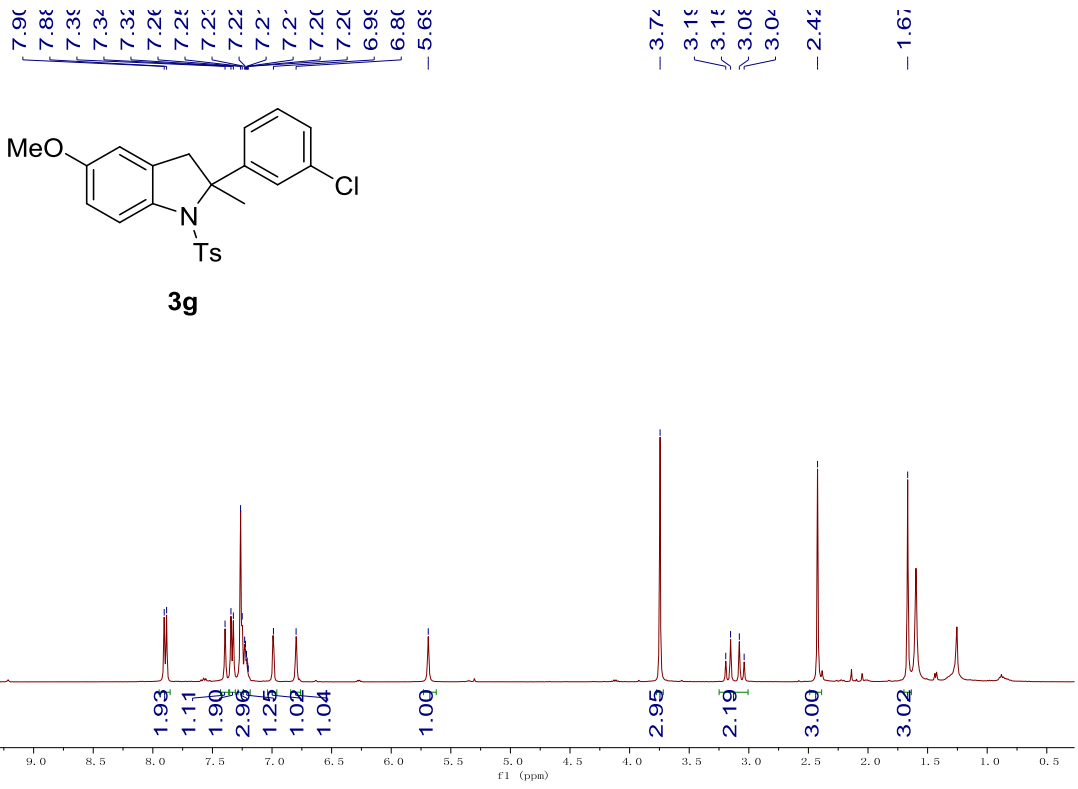
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3.04
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MeO
Cl
N
Ts
1.93
1.11
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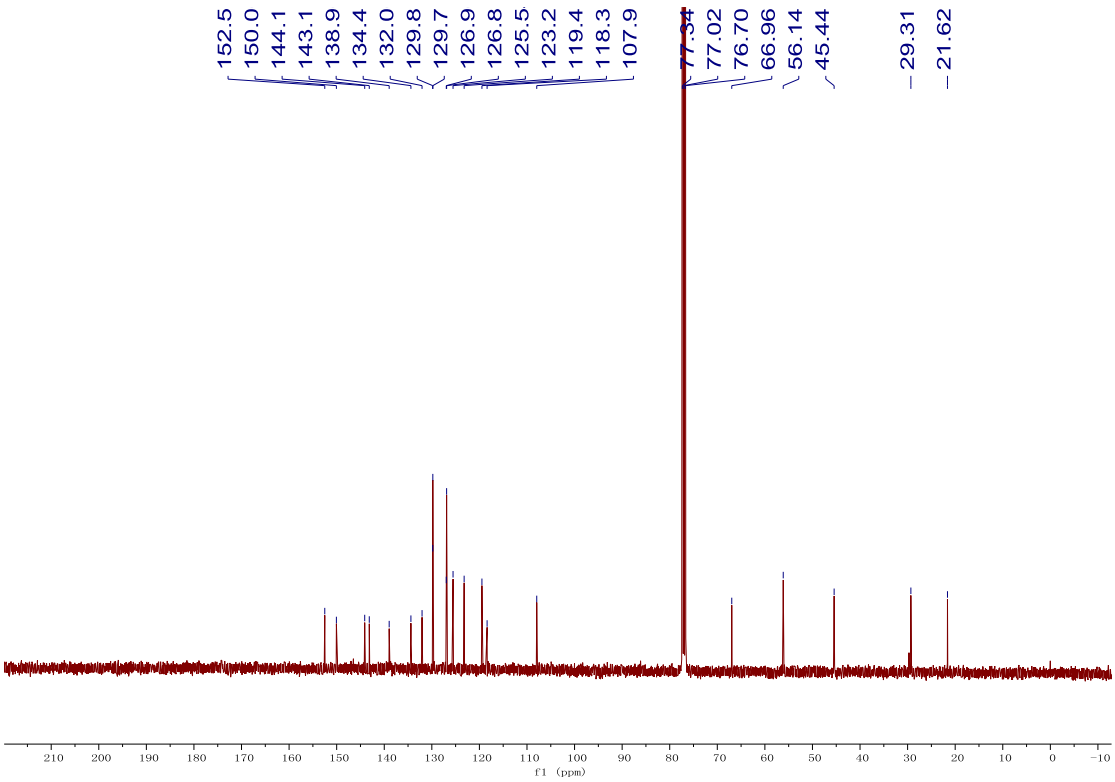
1.02
1.04
1.00
2.95
2.19
3.00
3.02
f1 (ppm)

3g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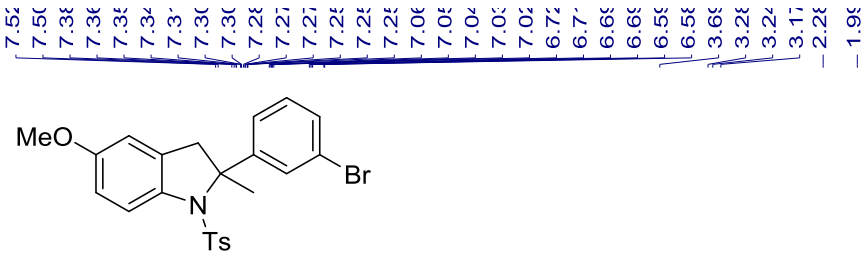
f1 (ppm)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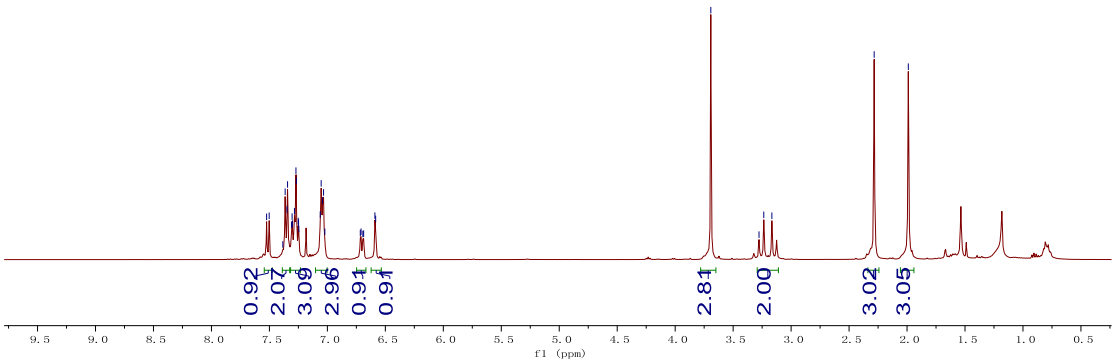
Br
N
Ts

3h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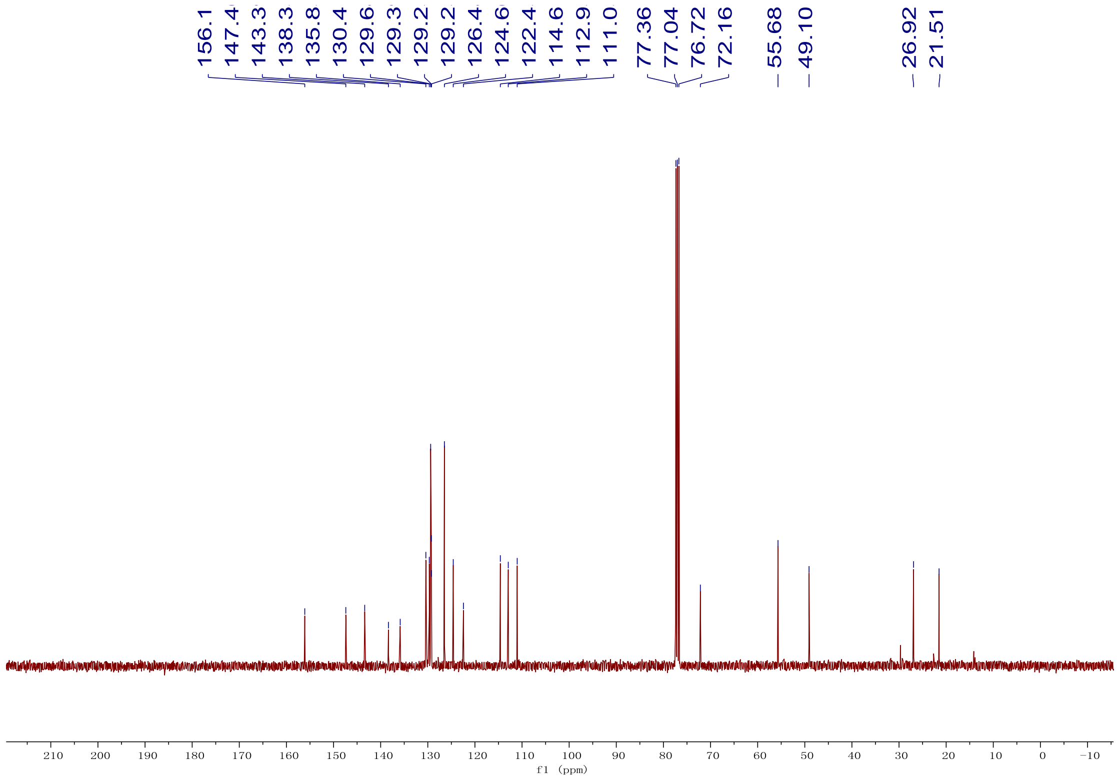
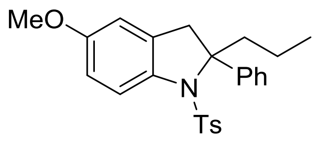
f1 (ppm)





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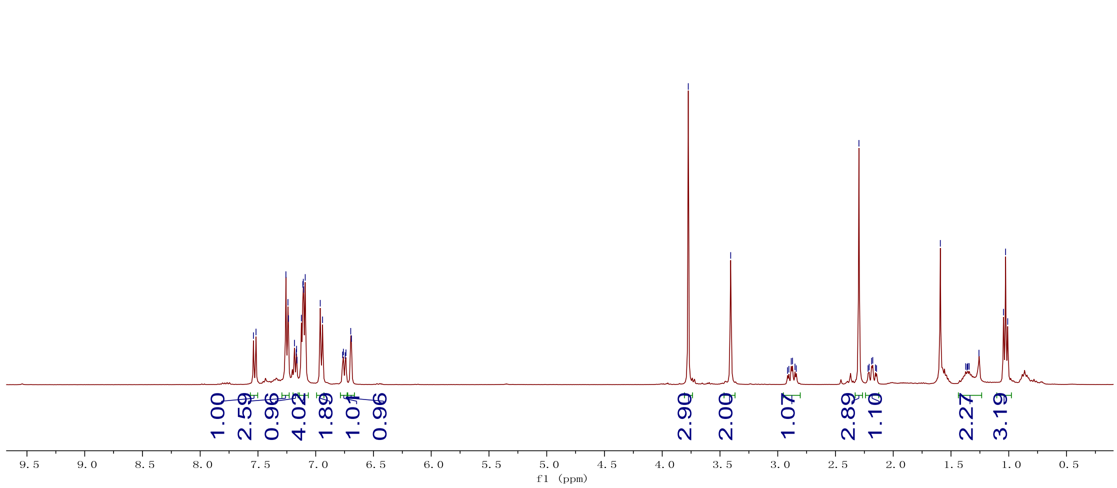

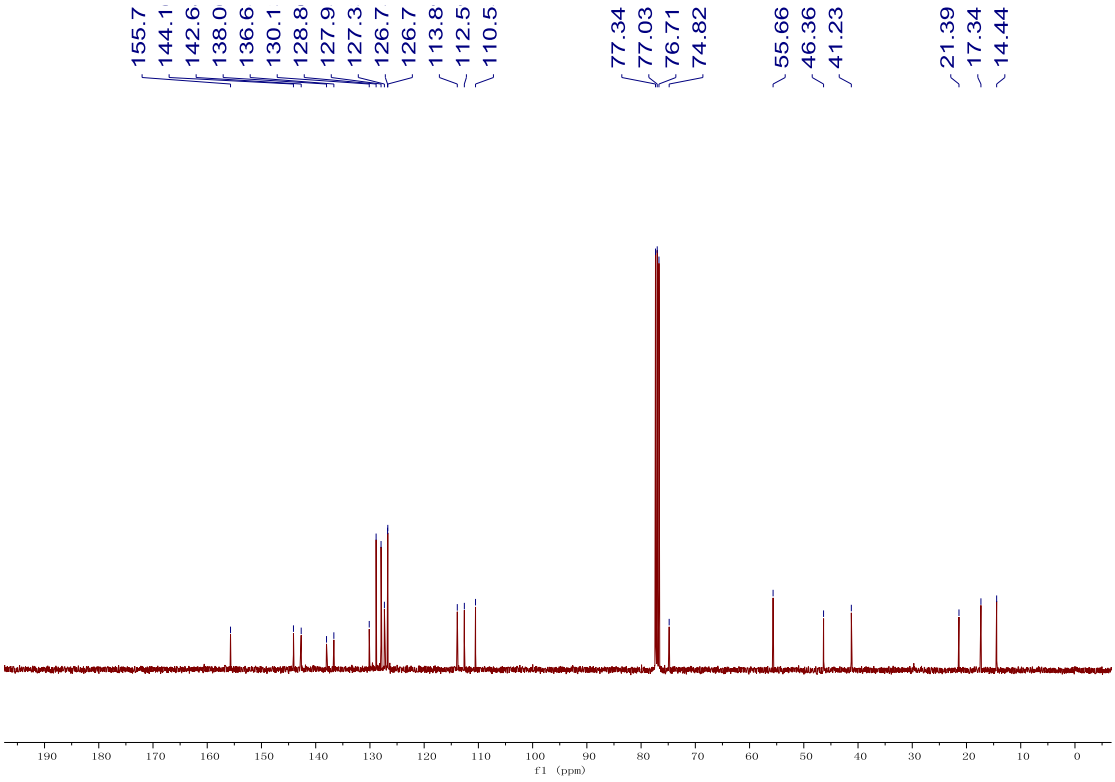
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21.39
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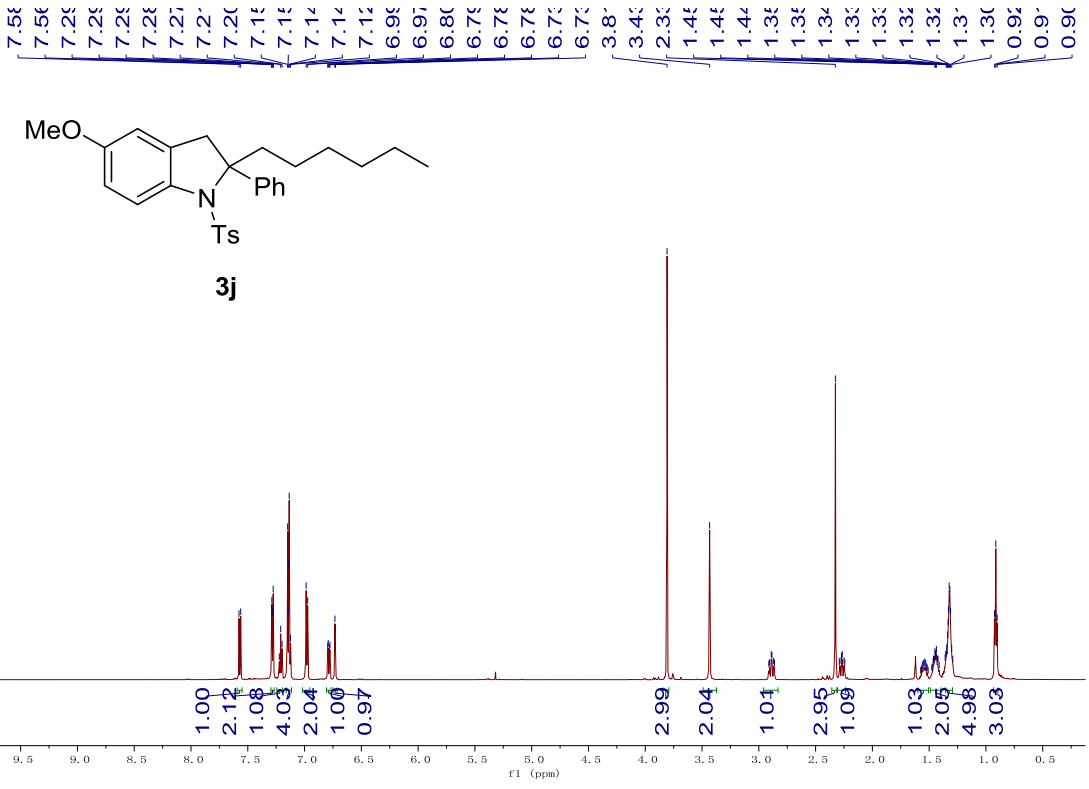
14.44
f1 (ppm)


MeO
Ph
N
Ts
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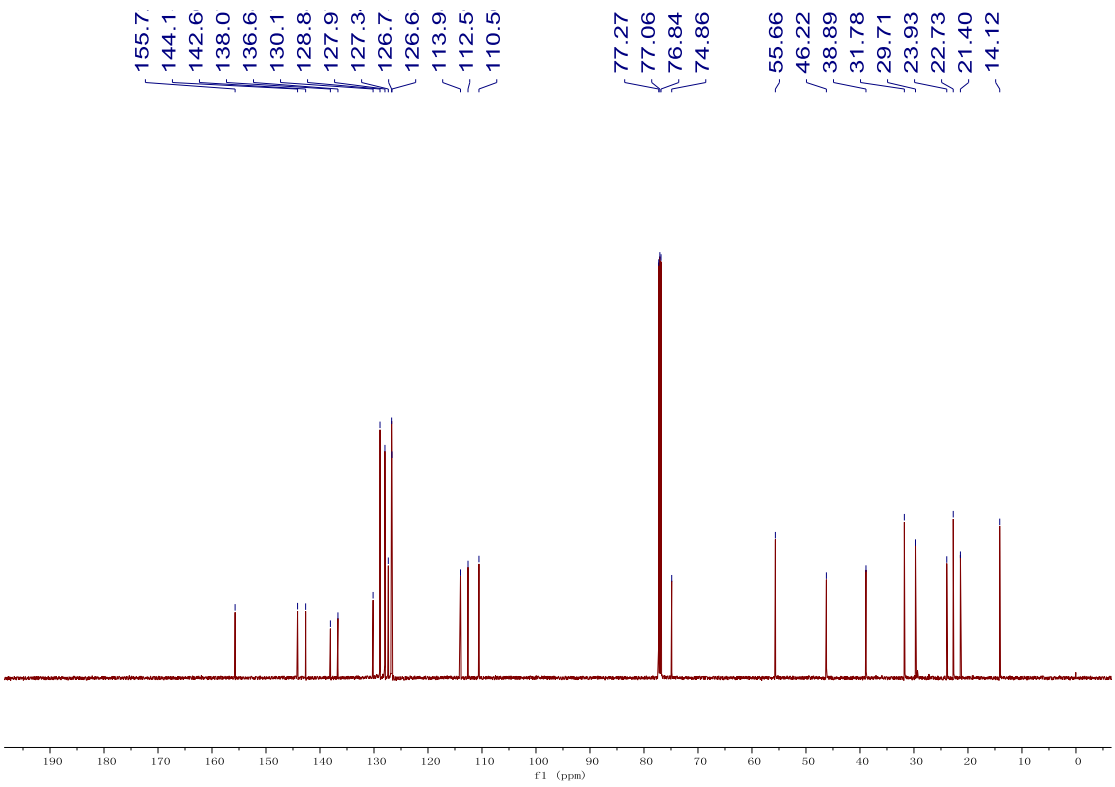
f1 (ppm)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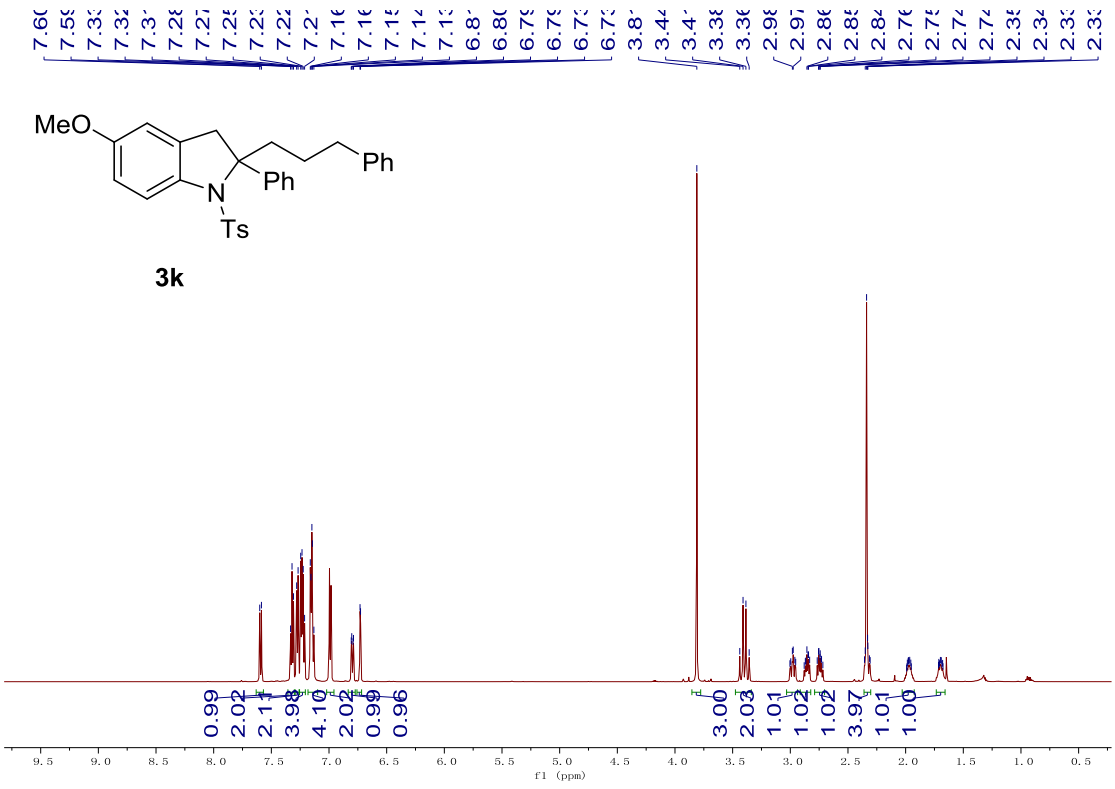
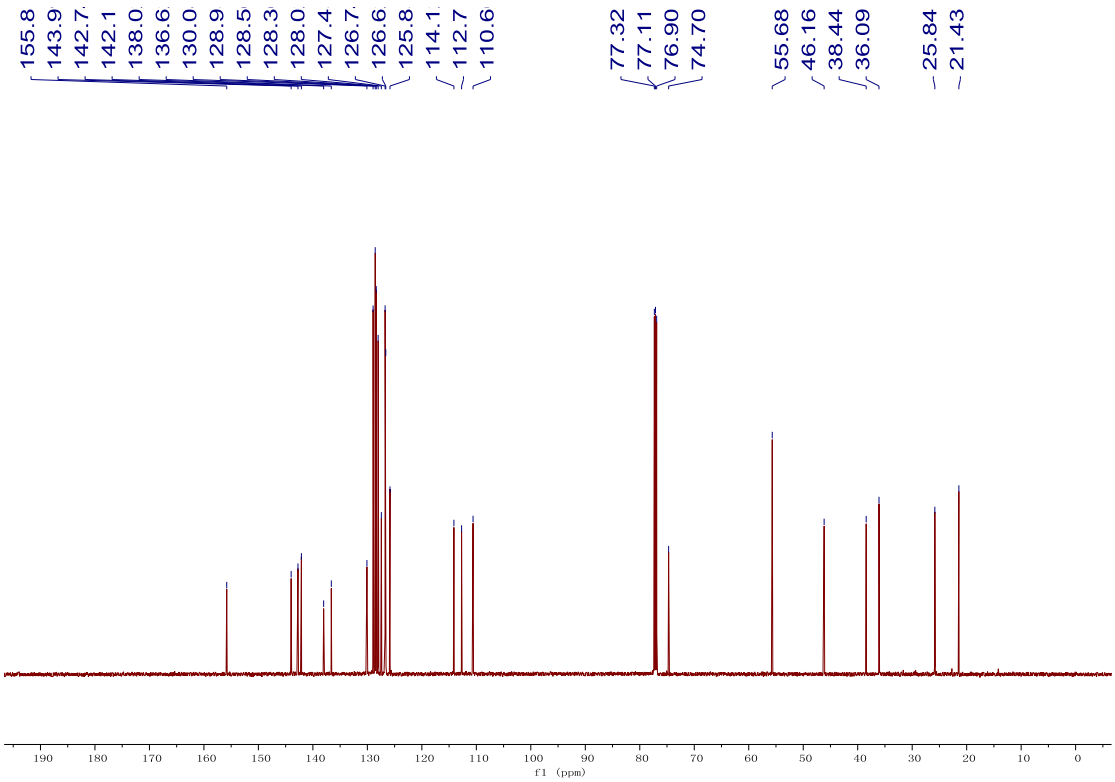
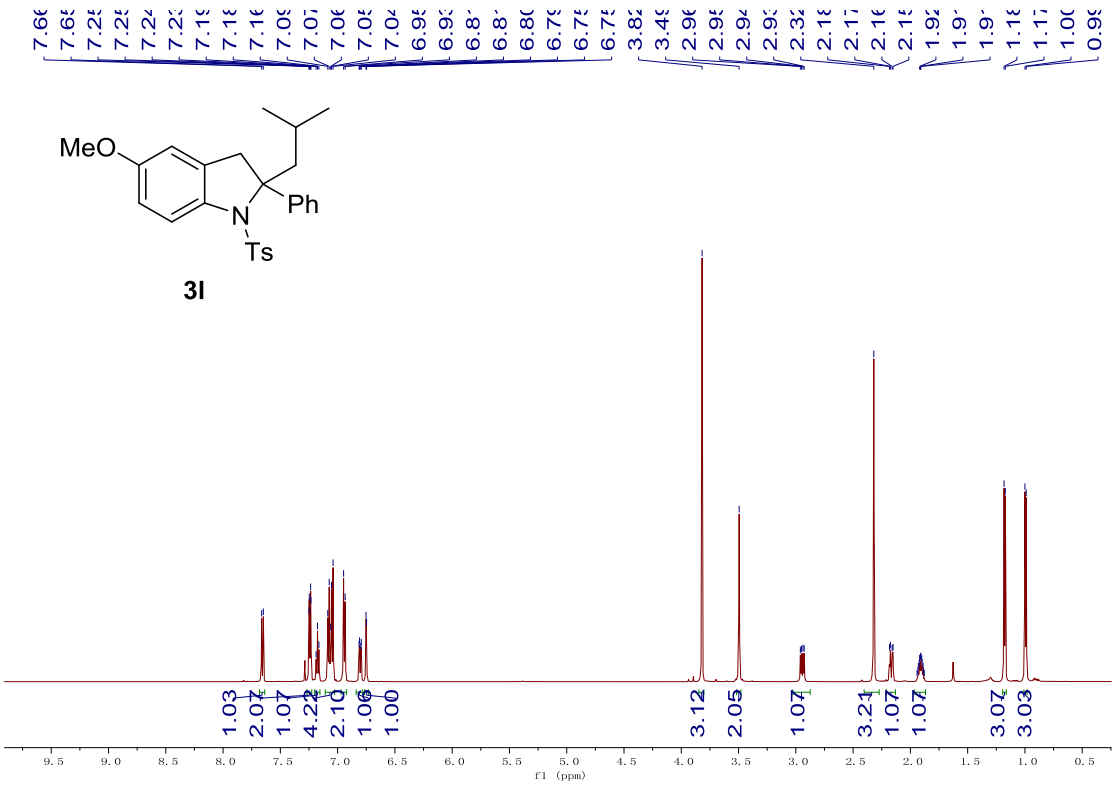
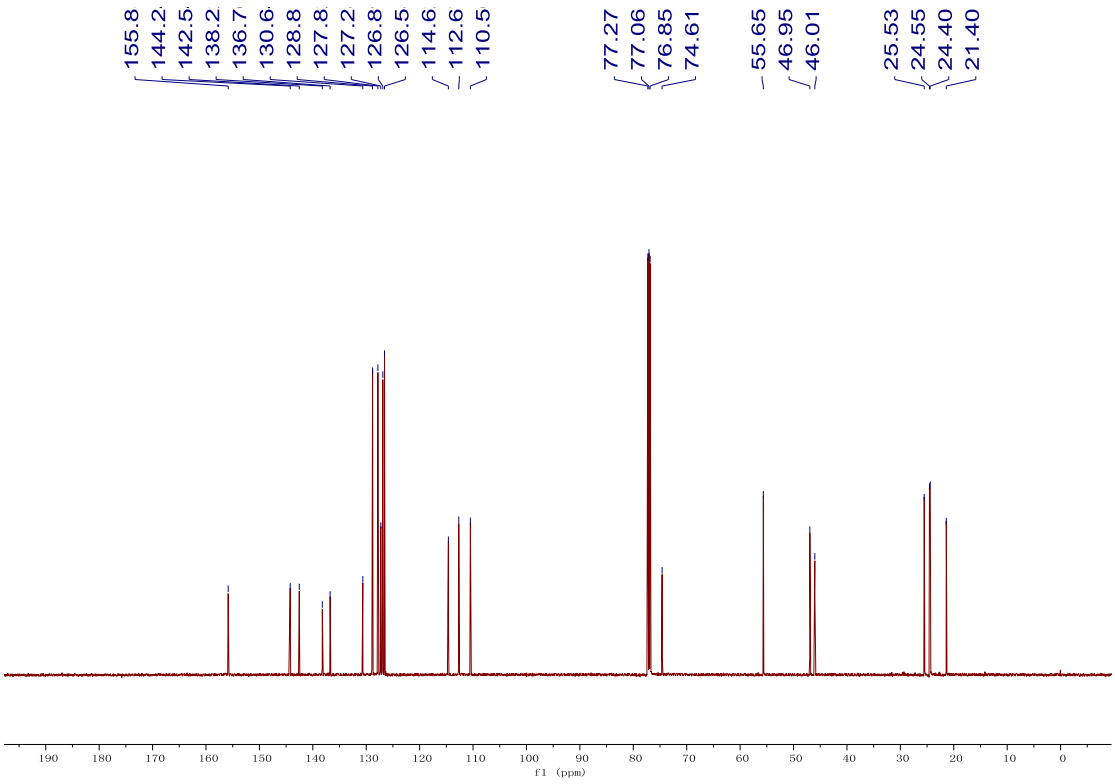
77.06
76.84
74.86
55.66
46.22
38.89
31.78
29.71
23.93
22.73
21.40
14.12
f1 (ppm)

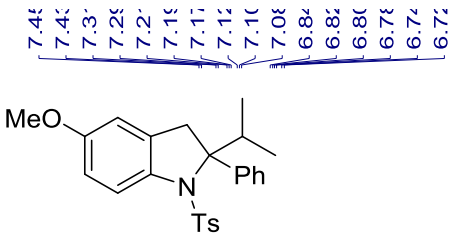

MeO
Ph
Ph
N
Ts
3k
f1 (ppm)


155.8
143.9
142.7
142.1
138.0
136.6
130.0
128.9
128.5
128.3
128.0
127.4
126.7
126.6
125.8
114.1
112.7
110.6
77.32
77.11
76.90
74.70
55.68
46.16
38.44
36.09
25.84
21.43
f1 (ppm)

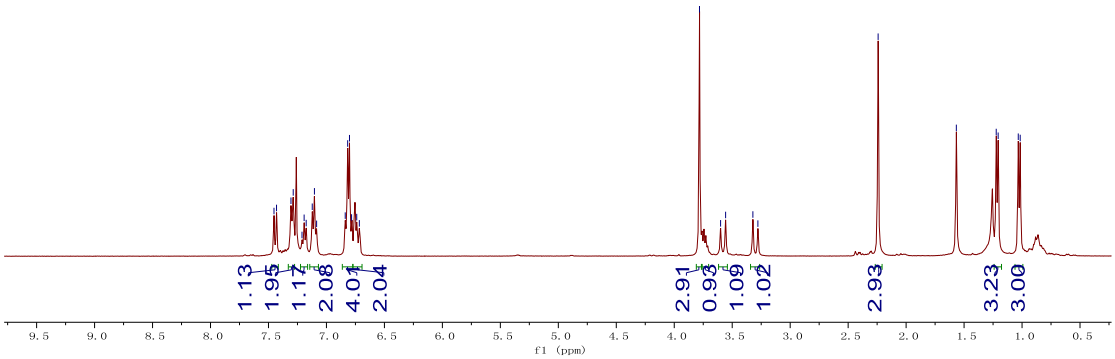

MeO
Ph
N
Ts
1.03
2.07
1.07
4.22
2.10
1.08
1.00
3.12
2.05
1.07
3.21
1.07
1.07
3.07
3.03
f1 (ppm)

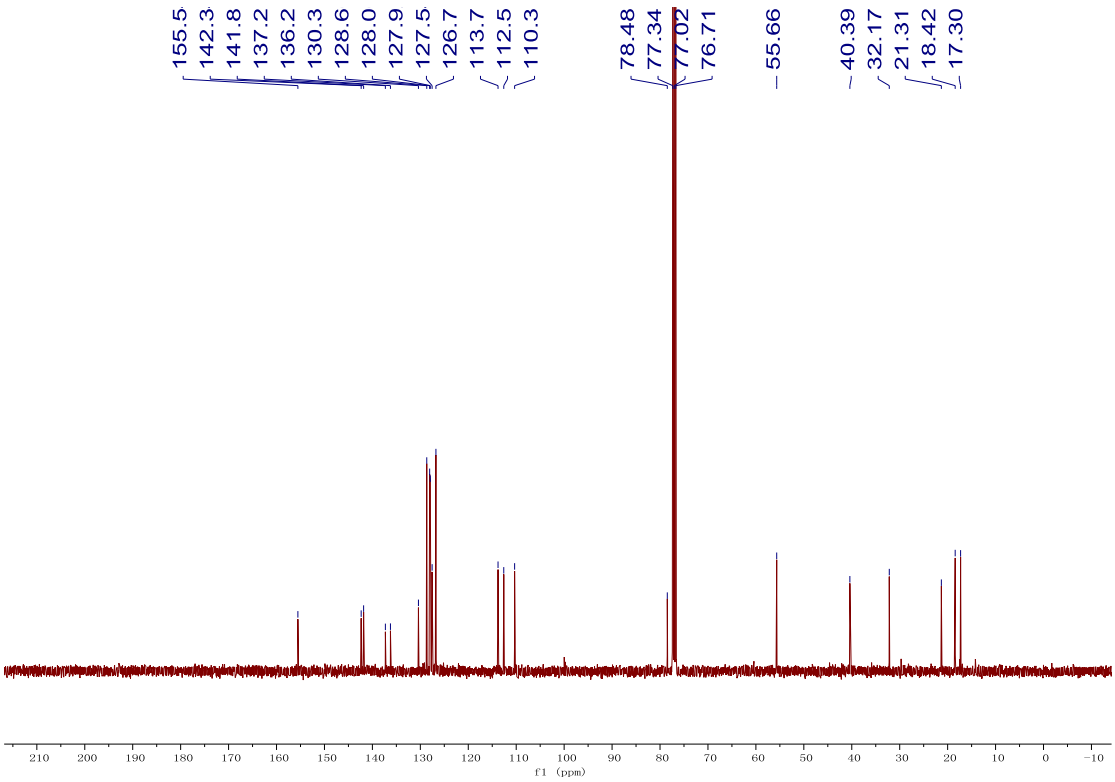
3l

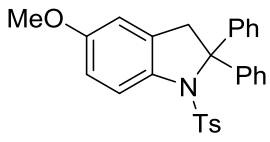

155.8
144.2
142.5
138.2
136.7
130.6
128.8
127.8
127.2
126.8
126.5
114.6
112.6
110.5
77.27
77.06
76.85
74.61
55.65
46.95
46.01
25.53
24.55
24.40
21.40
f1 (ppm)


MeO
Ph
N
Ts

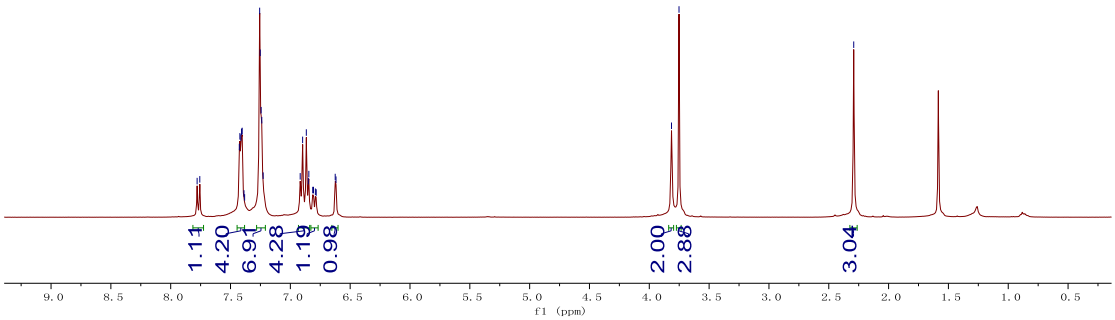
3m

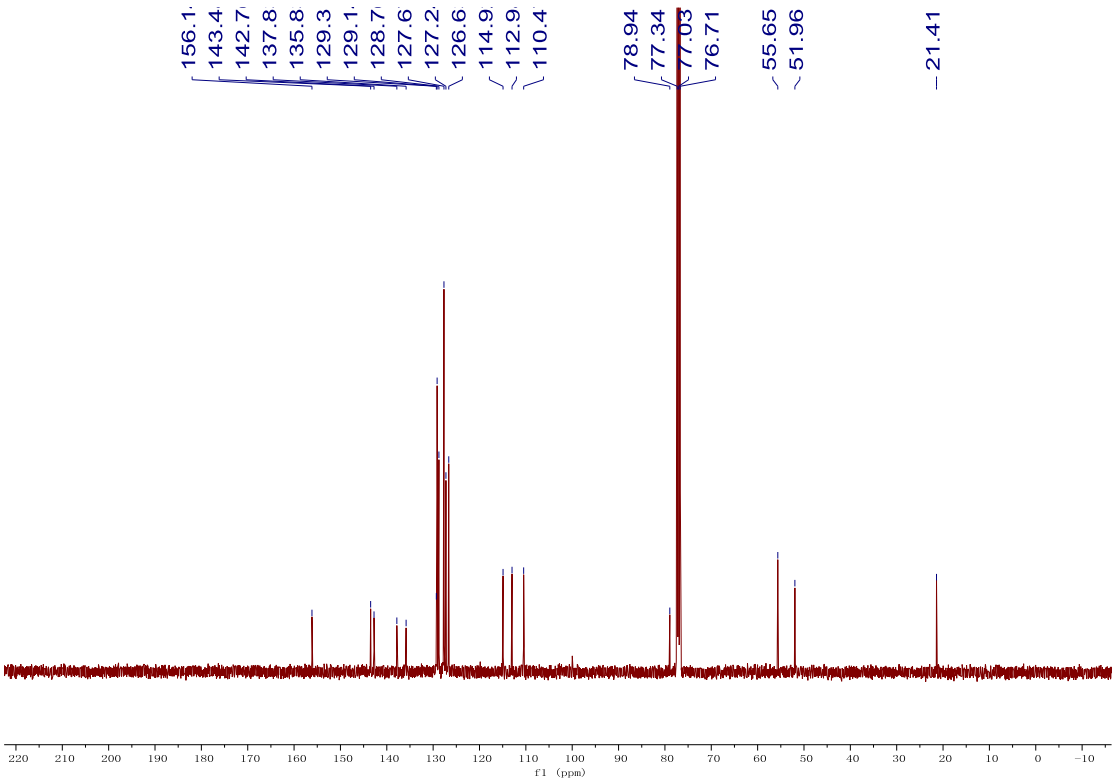

1.13
1.95
1.17
2.08
4.03
2.04
2.91
0.93
1.09
1.02
2.93
3.23
3.00
f1 (ppm)


155.5
142.3
141.8
137.2
136.2
130.3
128.6
128.0
127.9
127.5
126.7
113.7
112.5
110.3
78.48
77.34
77.02
76.71
55.66
40.39
32.17
21.31
18.42
17.30
f1 (ppm)


MeO
Ph
Ph
N
Ts

3n


1.11
4.20
6.91
4.28
1.19
0.98
2.00
2.88
3.04
f1 (ppm)


156.1
143.4
142.7
137.8
135.8
129.3
129.1
128.7
127.6
127.2
126.6
114.9
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110.4
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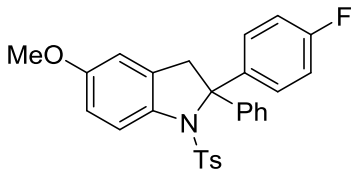
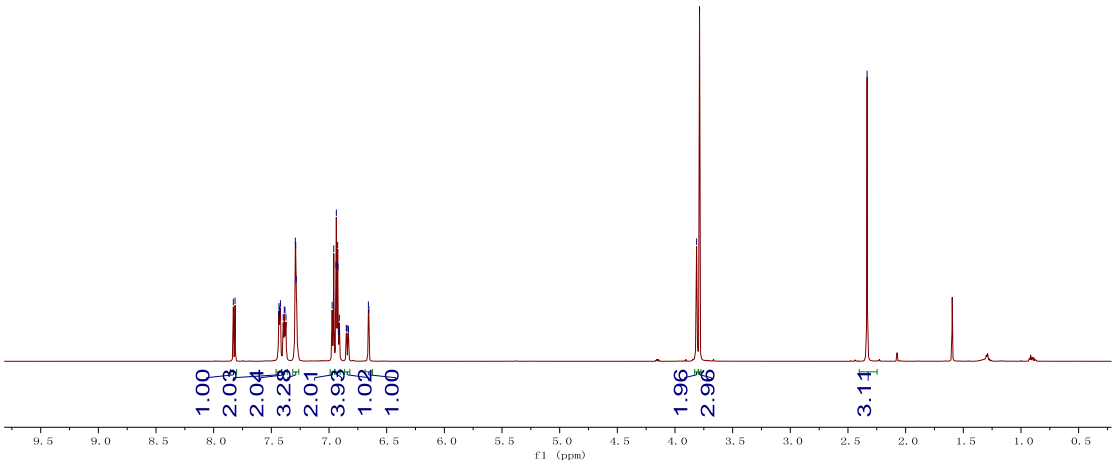
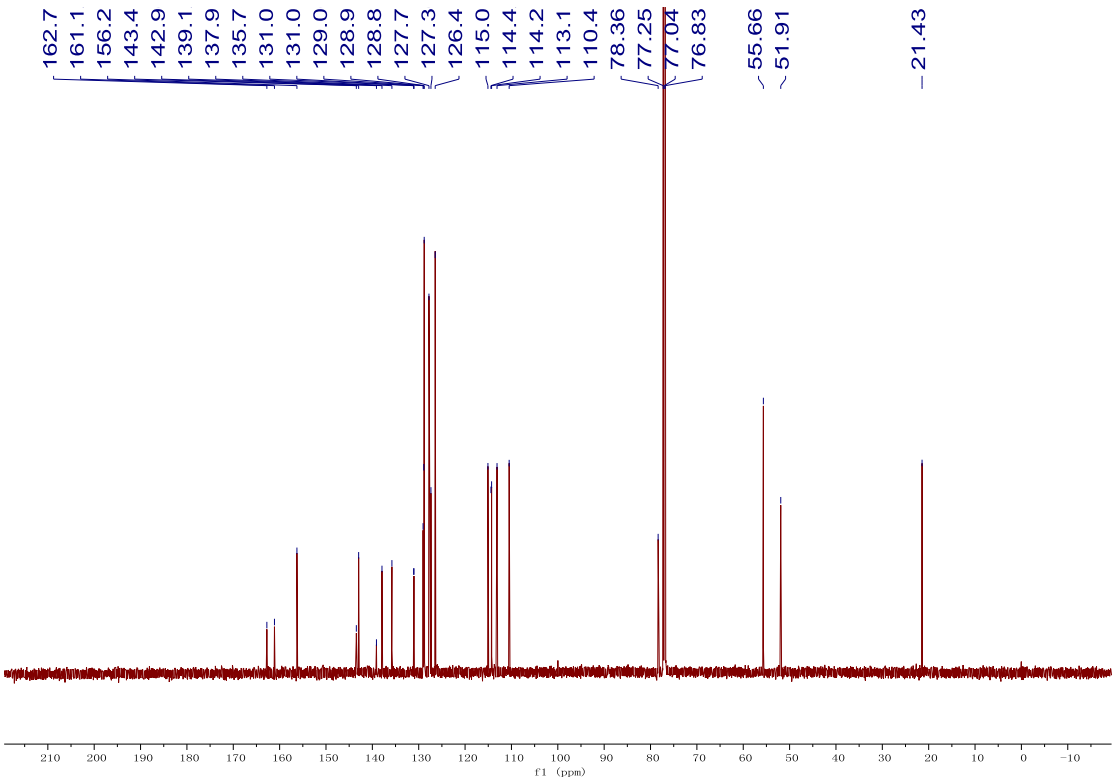
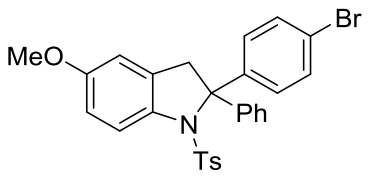
77.03
76.71
55.65
51.96
21.41
f1 (ppm)


F
MeO
Ph
N
Ts

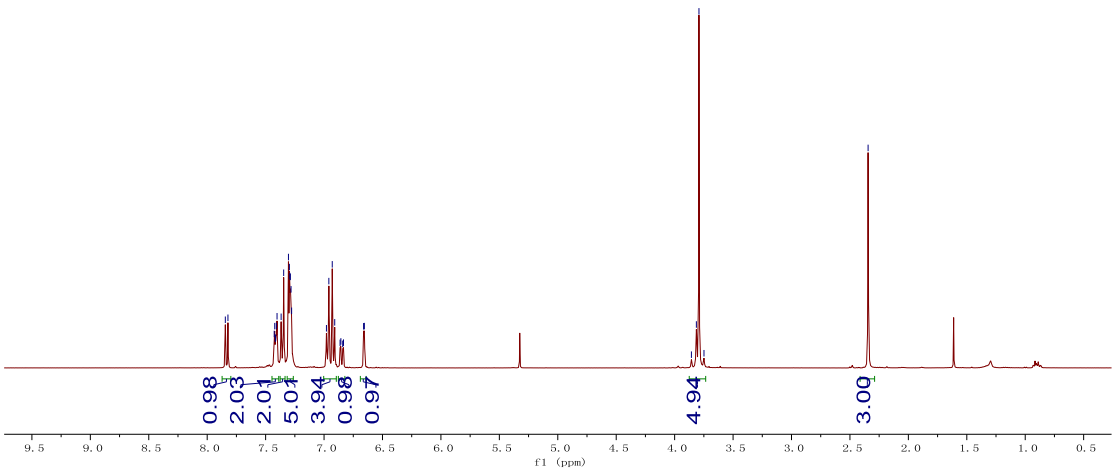
3o

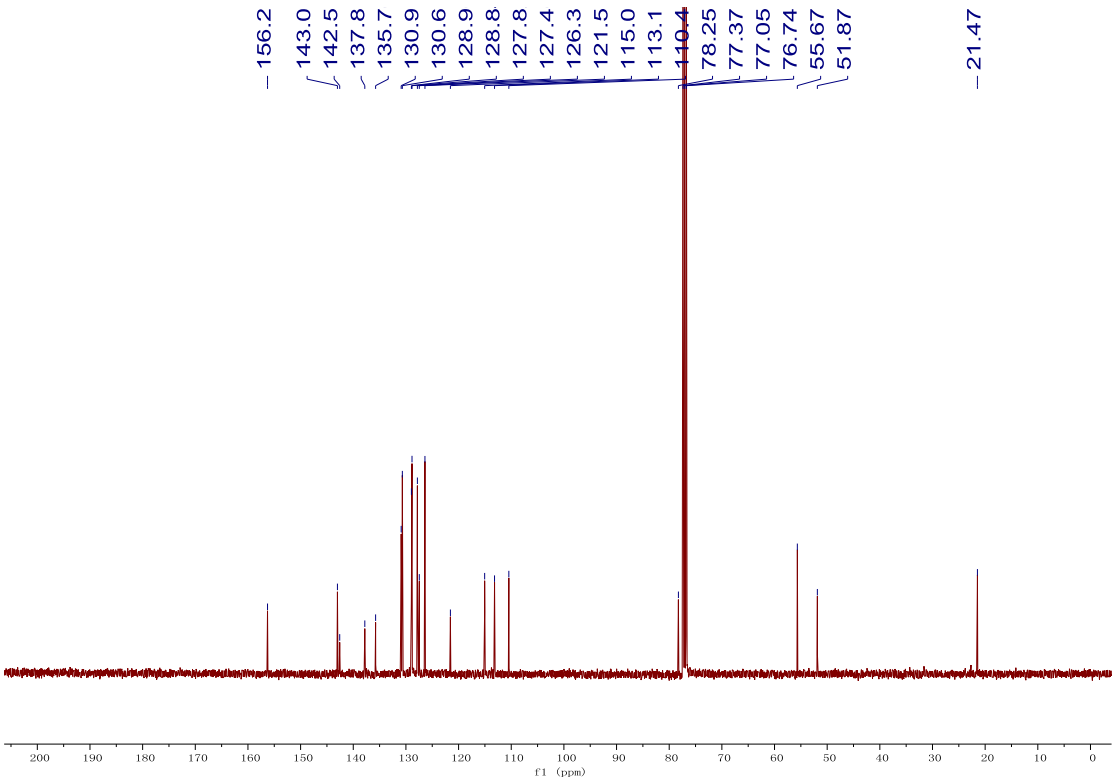

1.00
2.03
2.04
3.28
2.01
3.93
1.02
1.00
1.96
2.96
3.11
f1 (ppm)

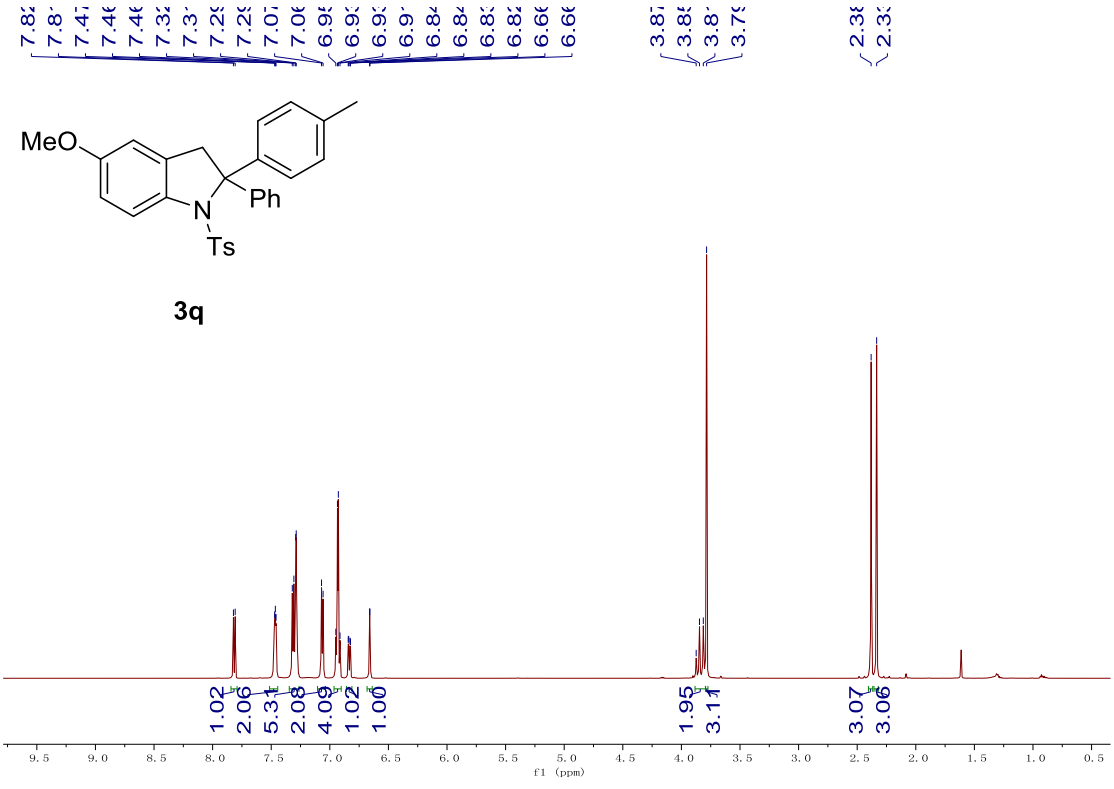

162.7
161.1
156.2
143.4
142.9
139.1
137.9
135.7
131.0
131.0
129.0
128.9
128.8
127.7
127.3
126.4
115.0
114.4
114.2
113.1
110.4
78.36
77.25
77.04
76.83
55.66
51.91
21.43
f1 (ppm)

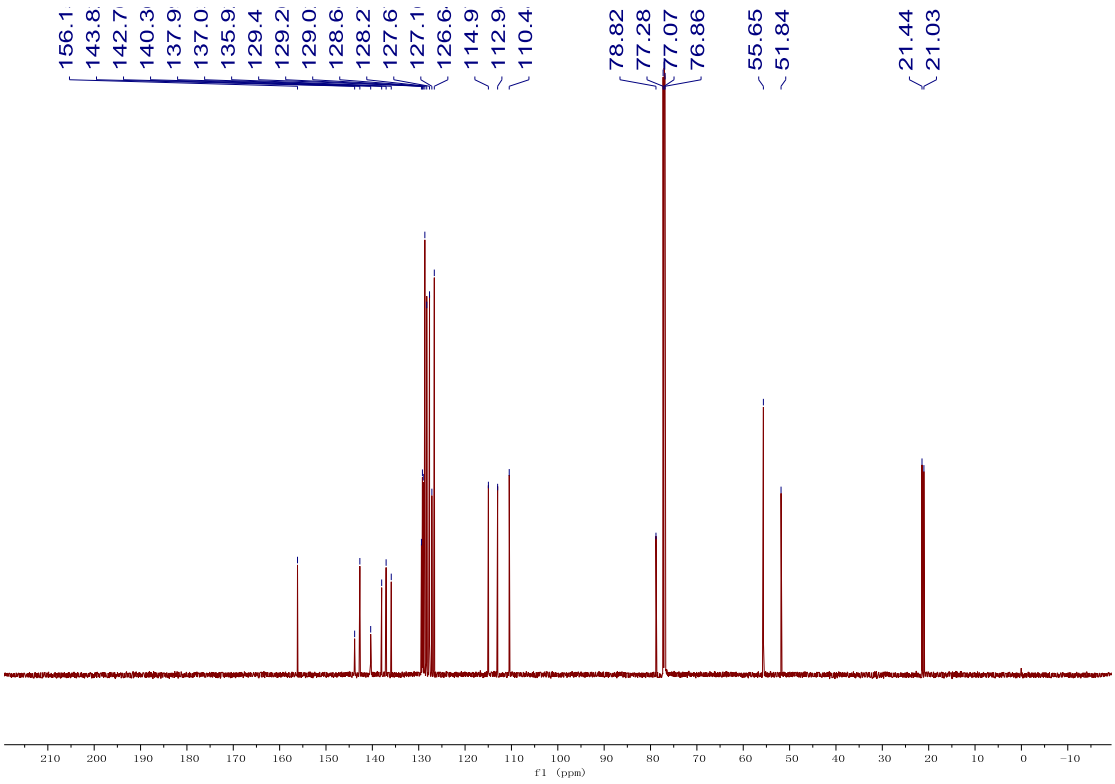

Br
MeO
Ph
N
Ts

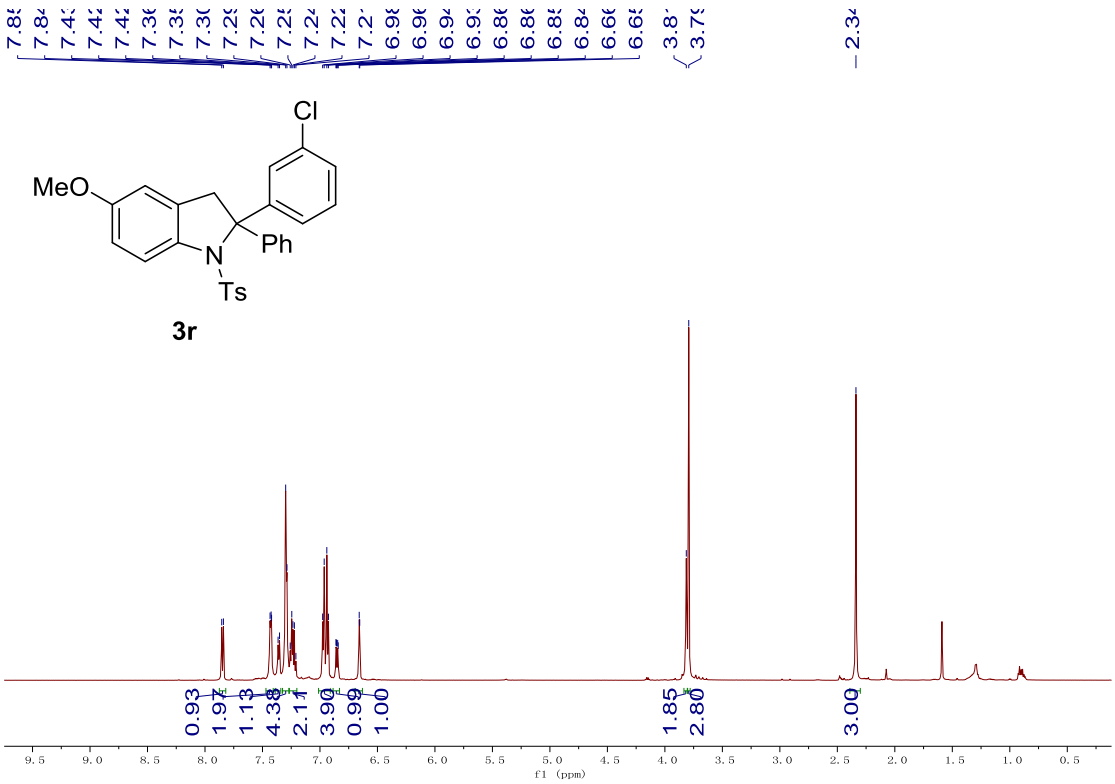
3p

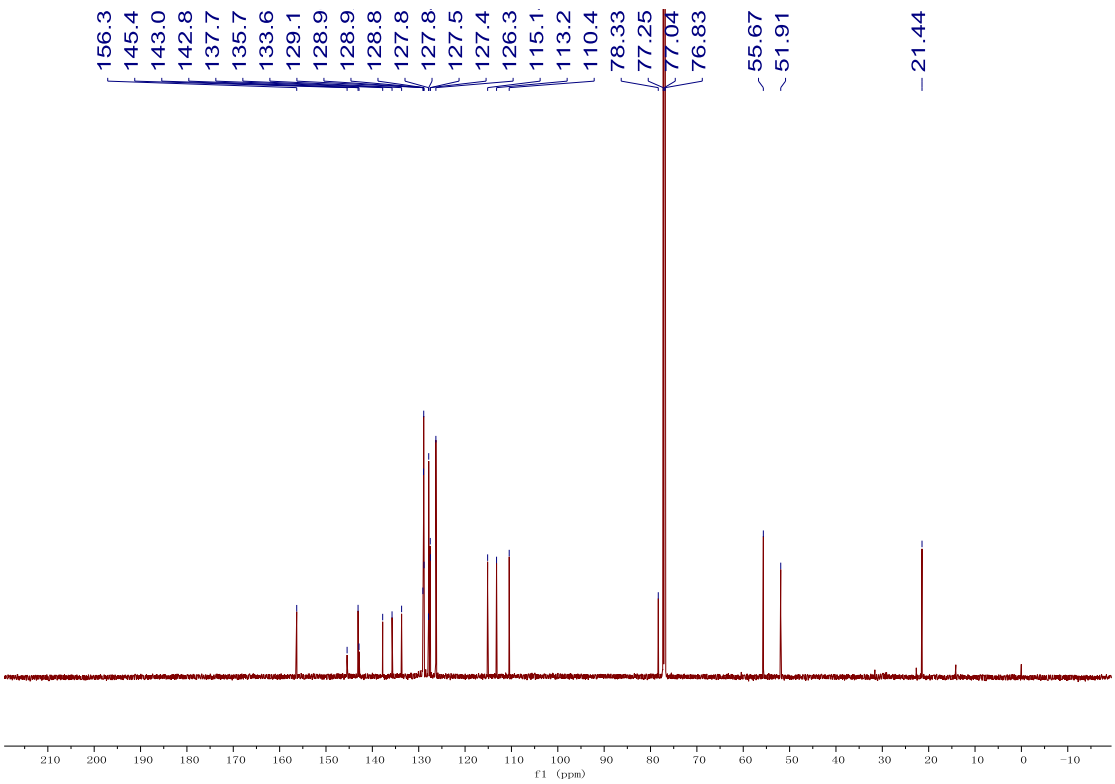

0.98
2.03
2.01
5.01
3.94
0.98
0.97
4.94
3.00
f1 (ppm)

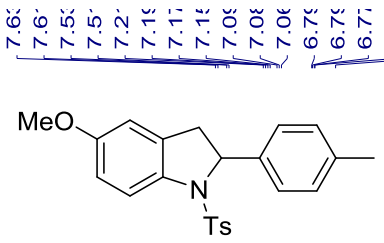

156.2
143.0
142.5
137.8
135.7
130.9
130.6
128.9
128.8
127.8
127.4
126.3
121.5
115.0
113.1
110.4
78.25
77.37
77.05
76.74
55.67
51.87
21.47
f1 (ppm)


MeO
Ph
N
Ts
3q
1.02
2.06
5.31
2.08
4.05
1.02
1.00
1.95
3.14
3.07
3.06
f1 (ppm)

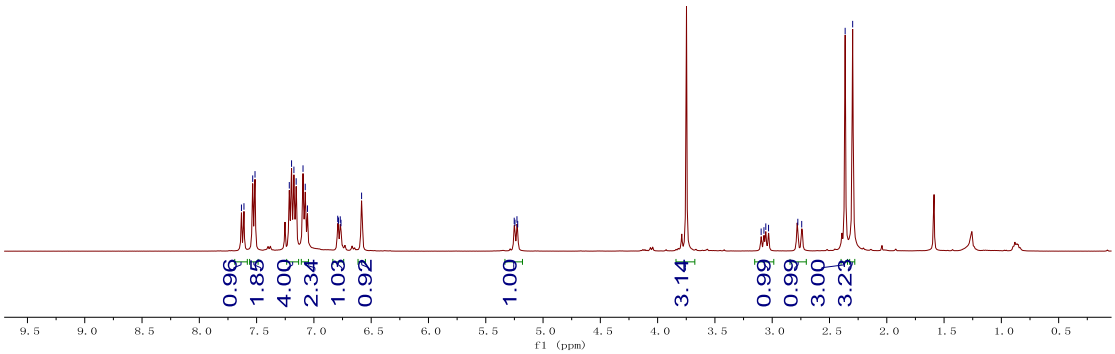

156.1
143.8
142.7
140.3
137.9
137.0
135.9
129.4
129.2
129.0
128.6
128.2
127.6
127.1
126.6
114.9
112.9
110.4
78.82
77.28
77.07
76.86
55.65
51.84
21.44
21.03
f1 (ppm)

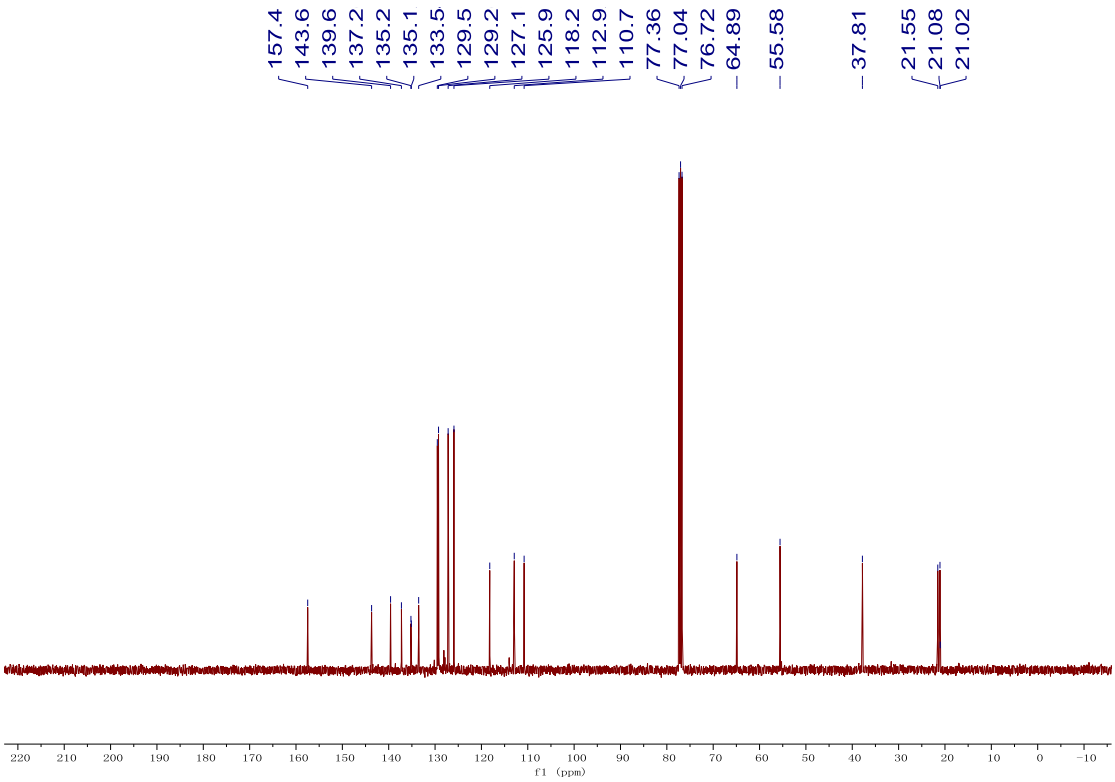

Cl
MeO
Ph
N
Ts
3r
f1 (ppm)

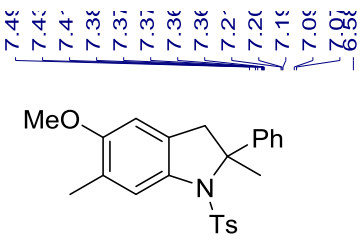

156.3
145.4
143.0
142.8
137.7
135.7
133.6
129.1
128.9
128.9
128.8
127.8
127.8
127.5
127.4
126.3
115.1
113.2
110.4
78.33
77.25
77.04
76.83
55.67
51.91
21.44
f1 (ppm)


MeO
N
Ts

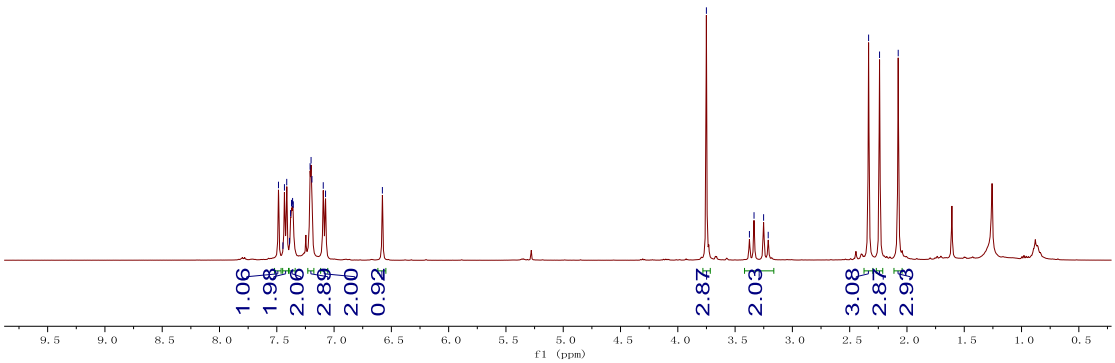
3s

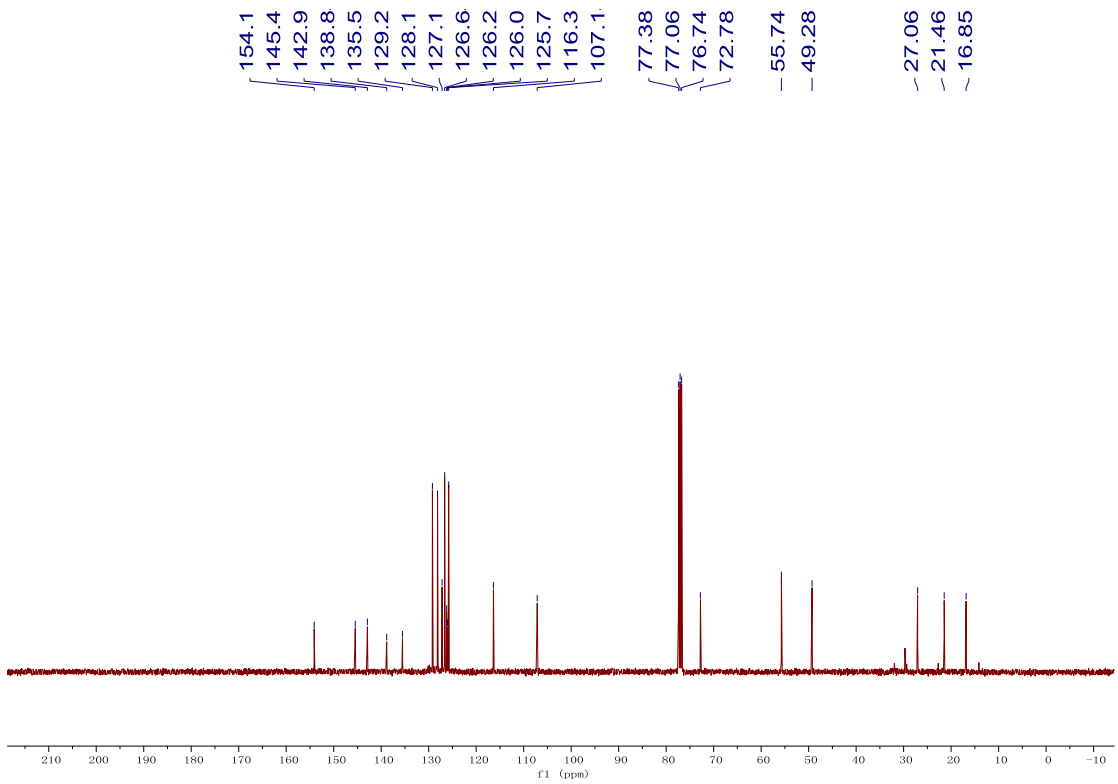

0.96
1.85
4.00
2.34
1.03
0.92
1.00
3.14
0.99
0.99
3.00
3.22
f1 (ppm)

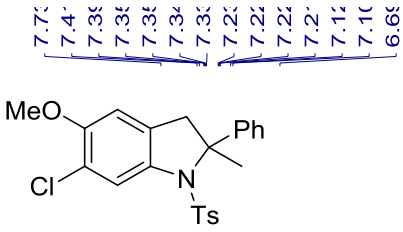

157.4
143.6
139.6
137.2
135.2
135.1
133.5
129.5
129.2
127.1
125.9
118.2
112.9
110.7
77.36
77.04
76.72
64.89
55.58
37.81
21.55
21.08
21.02
f1 (ppm)


MeO
Ph
N
Ts

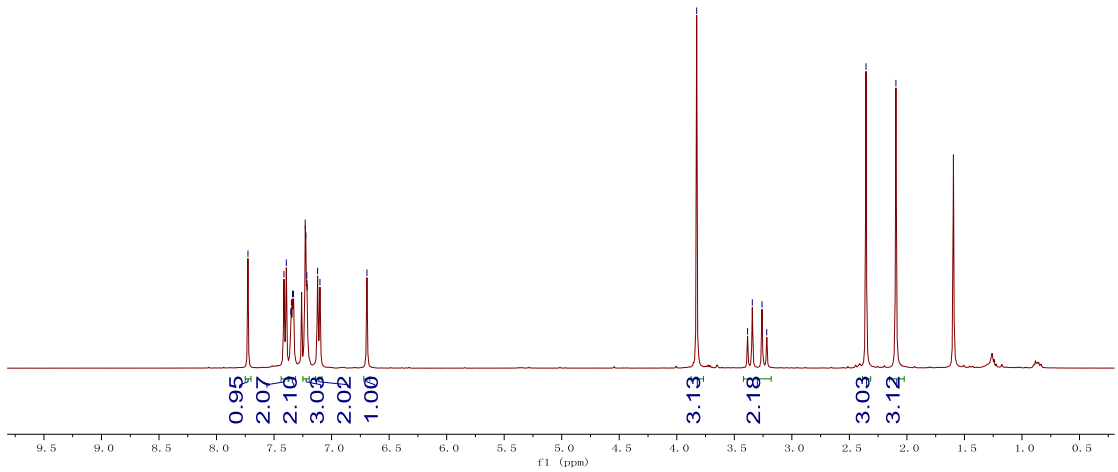
3t

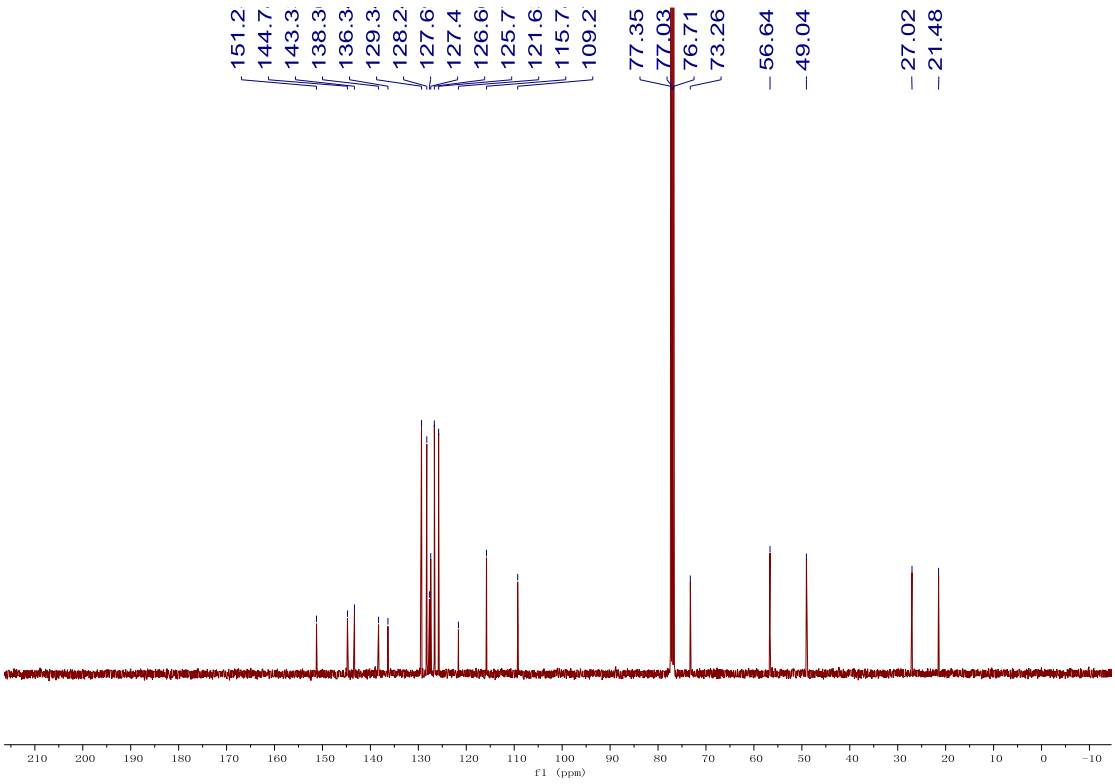

1.06
1.90
2.08
2.85
2.00
0.92
2.87
2.03
3.08
2.87
2.93
f1 (ppm)

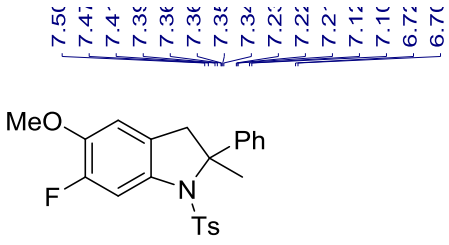

154.1
145.4
142.9
138.8
135.5
129.2
128.1
127.1
126.6
126.2
126.0
125.7
116.3
107.1
77.38
77.06
76.74
72.78
55.74
49.28
27.06
21.46
16.85
f1 (ppm)


MeO
Cl
Ph
N
Ts

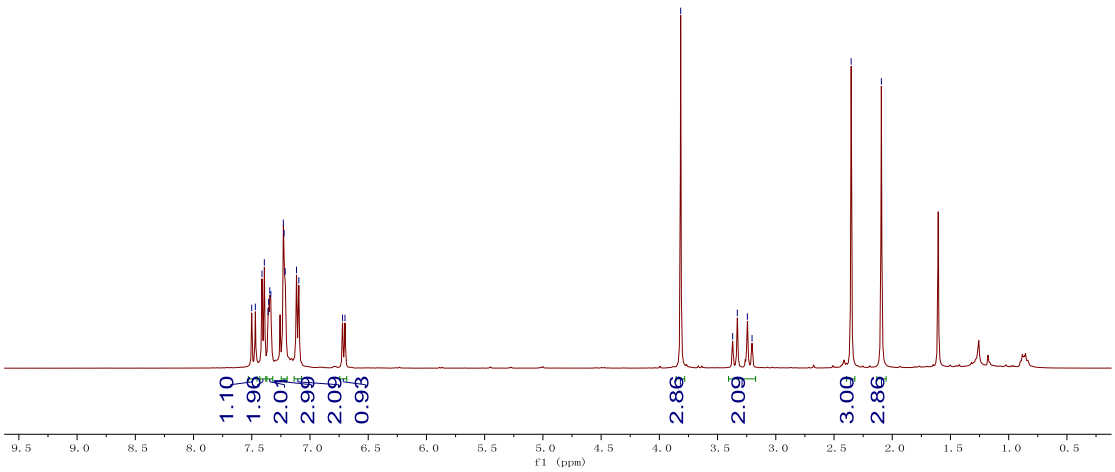
3u

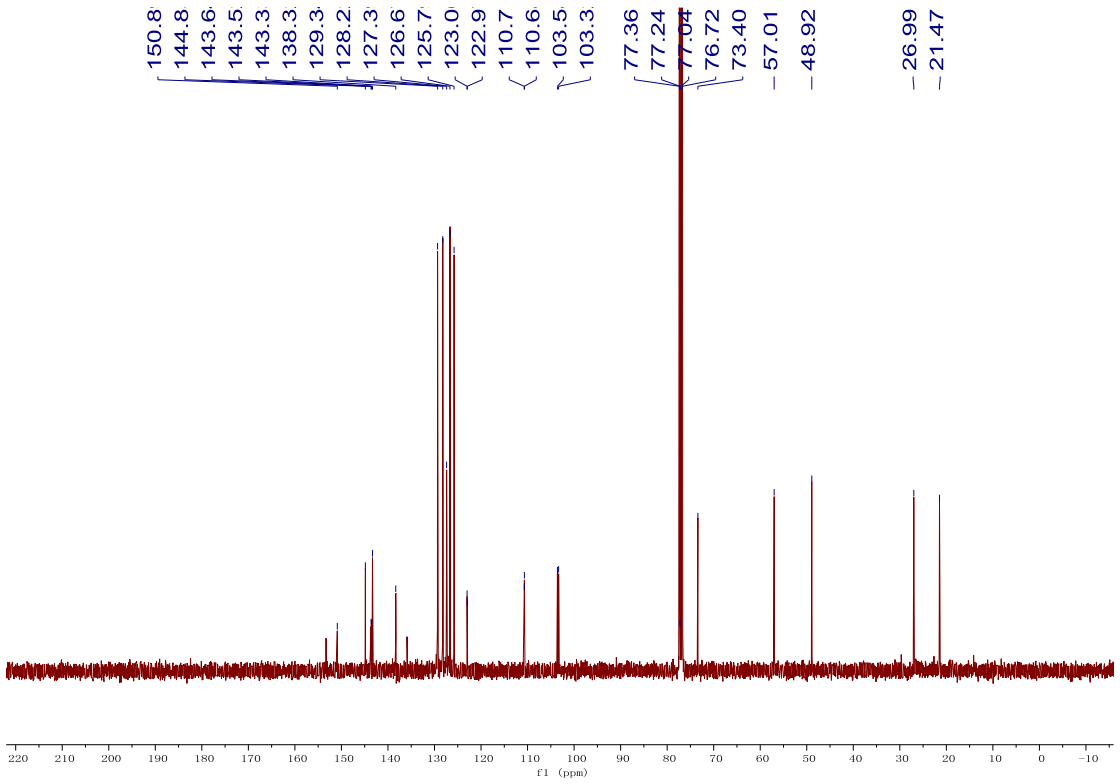

0.95
2.07
2.10
3.05
2.02
1.00
3.13
2.18
3.03
3.12
f1 (ppm)

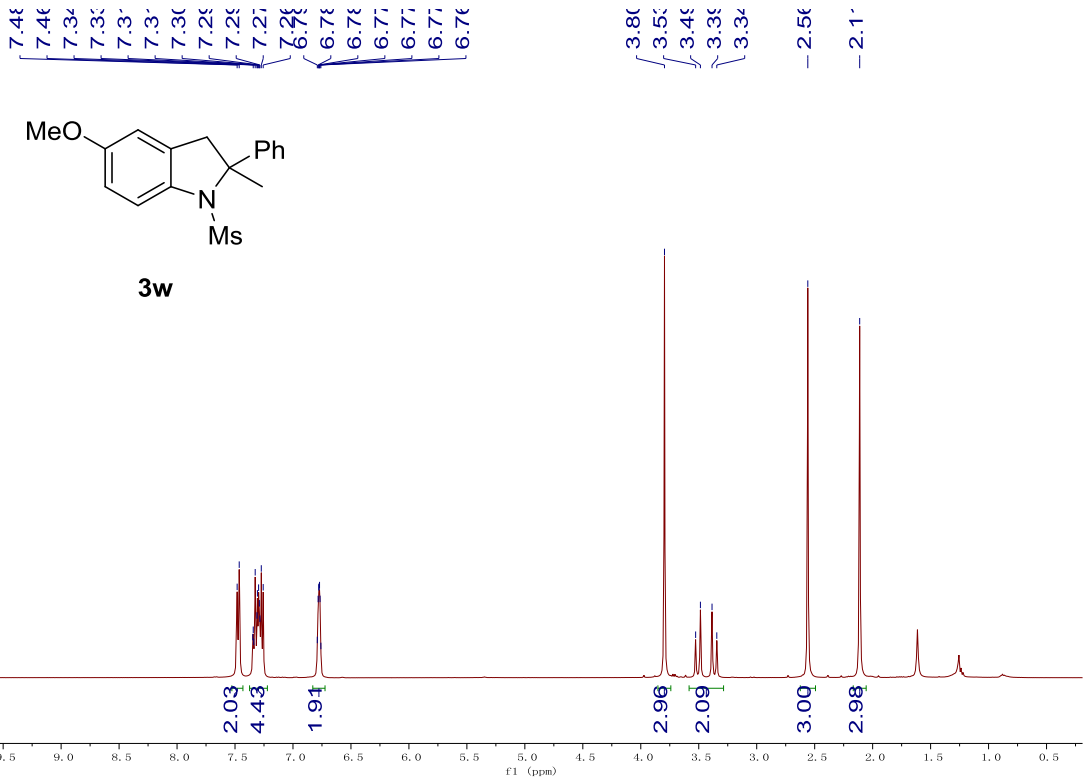

151.2
144.7
143.3
138.3
136.3
129.3
128.2
127.6
127.4
126.6
125.7
121.6
115.7
109.2
77.35
77.03
76.71
73.26
56.64
49.04
27.02
21.48
f1 (ppm)

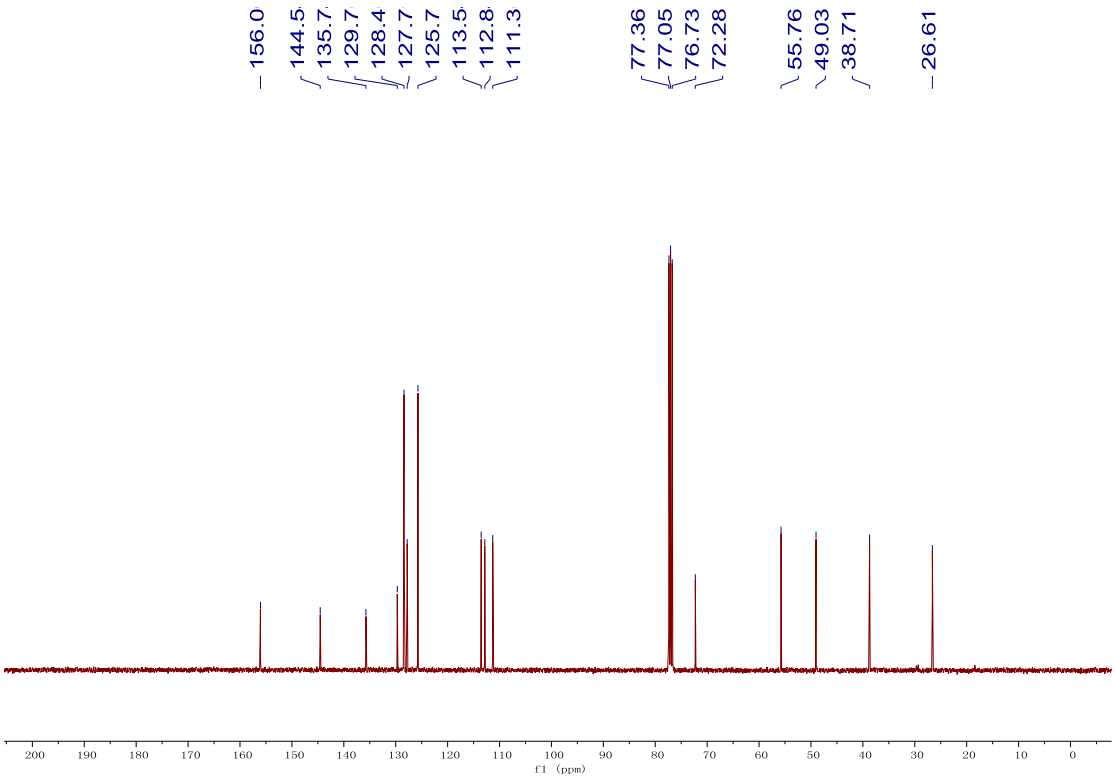

MeO
Ph
F
N
Ts

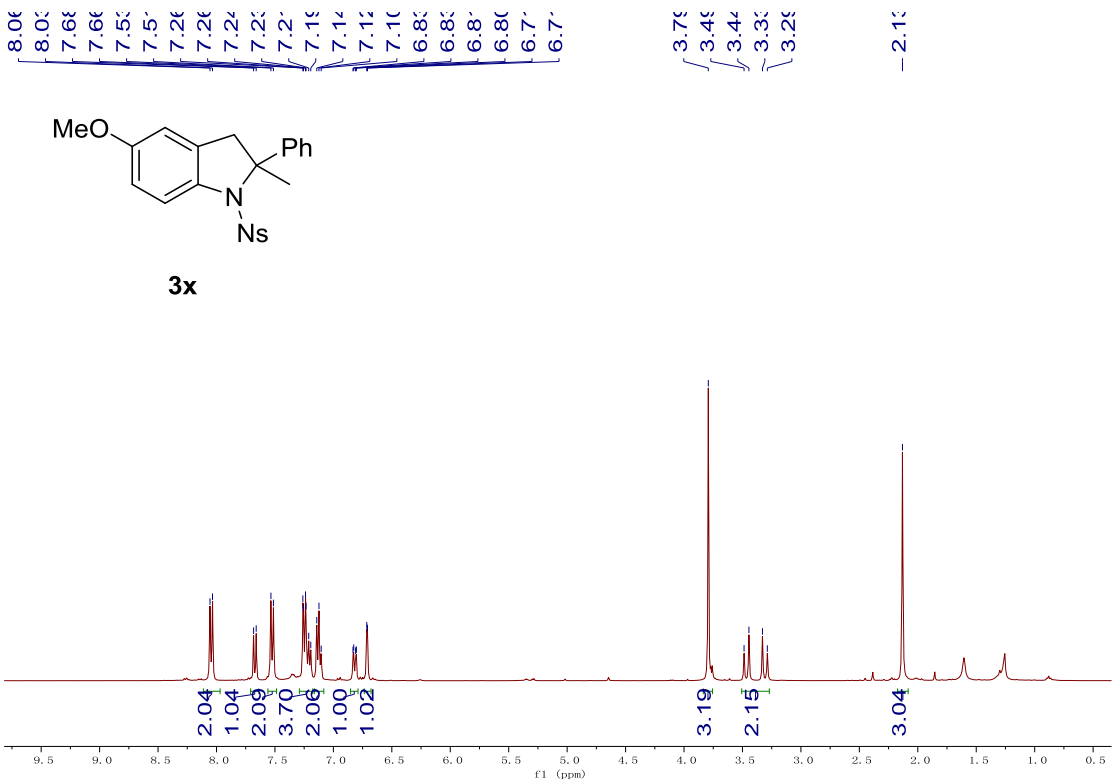
3v


1.10
1.90
2.03
2.99
2.09
0.93
2.86
2.09
3.00
2.86
f1 (ppm)

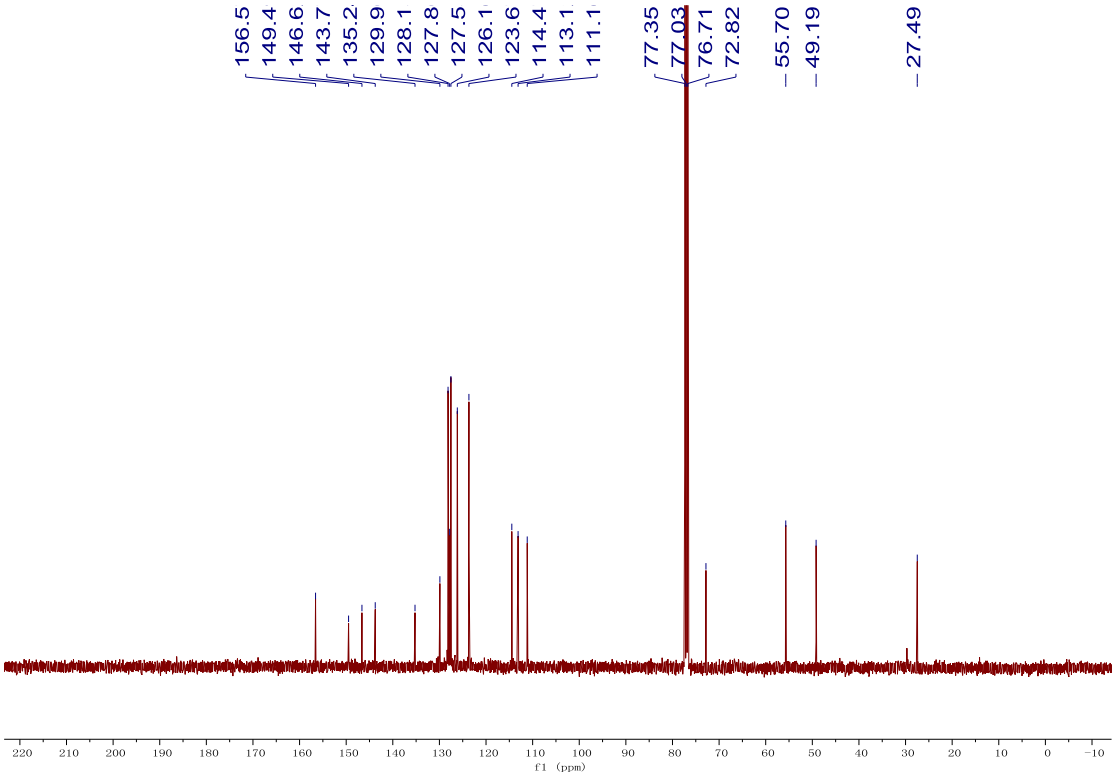

150.8
144.8
143.6
143.5
143.3
138.3
129.3
128.2
127.3
126.6
125.7
123.0
122.9
110.7
110.6
103.5
103.3
77.36
77.24
77.04
76.72
73.40
57.01
48.92
26.99
21.47
f1 (ppm)

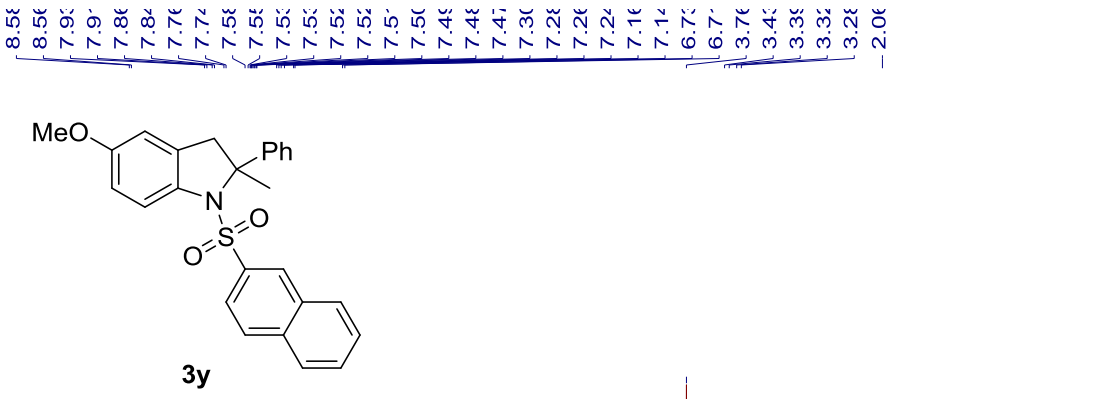

MeO
Ph
N
Ms
3w
2.03
4.43
1.91
2.96
2.09
3.00
2.98
f1 (ppm)

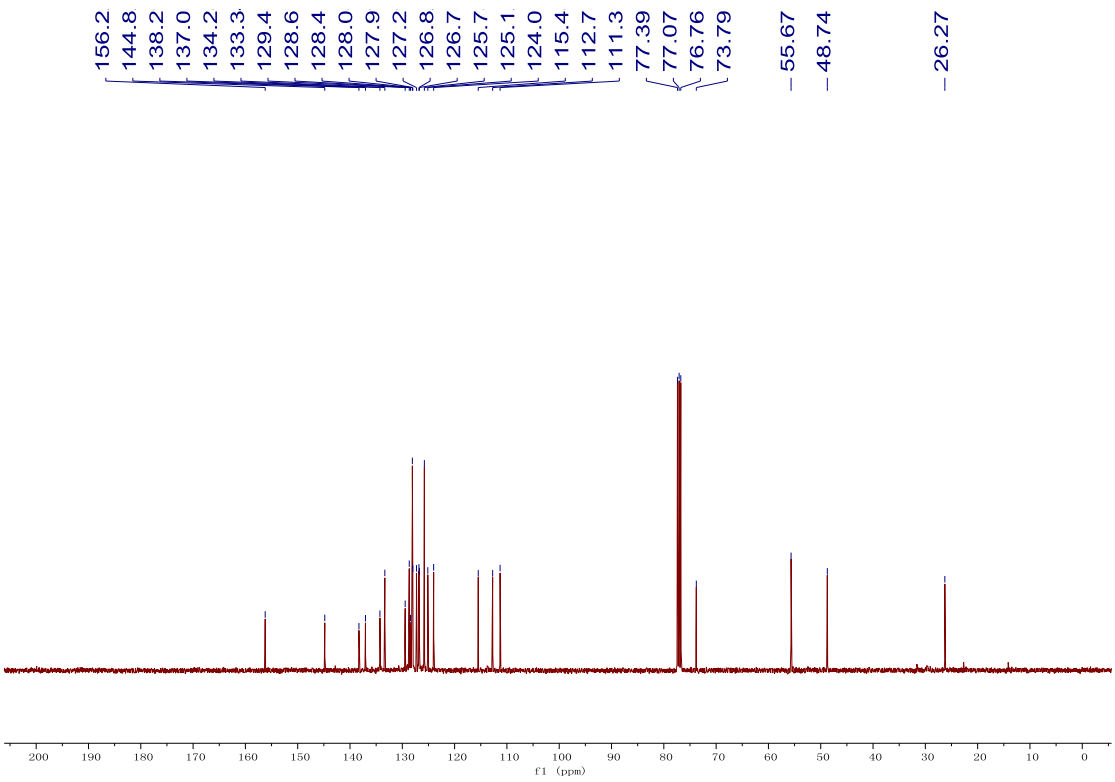

156.0
144.5
135.7
129.7
128.4
127.7
125.7
113.5
112.8
111.3
77.36
77.05
76.73
72.28
55.76
49.03
38.71
26.61
f1 (ppm)

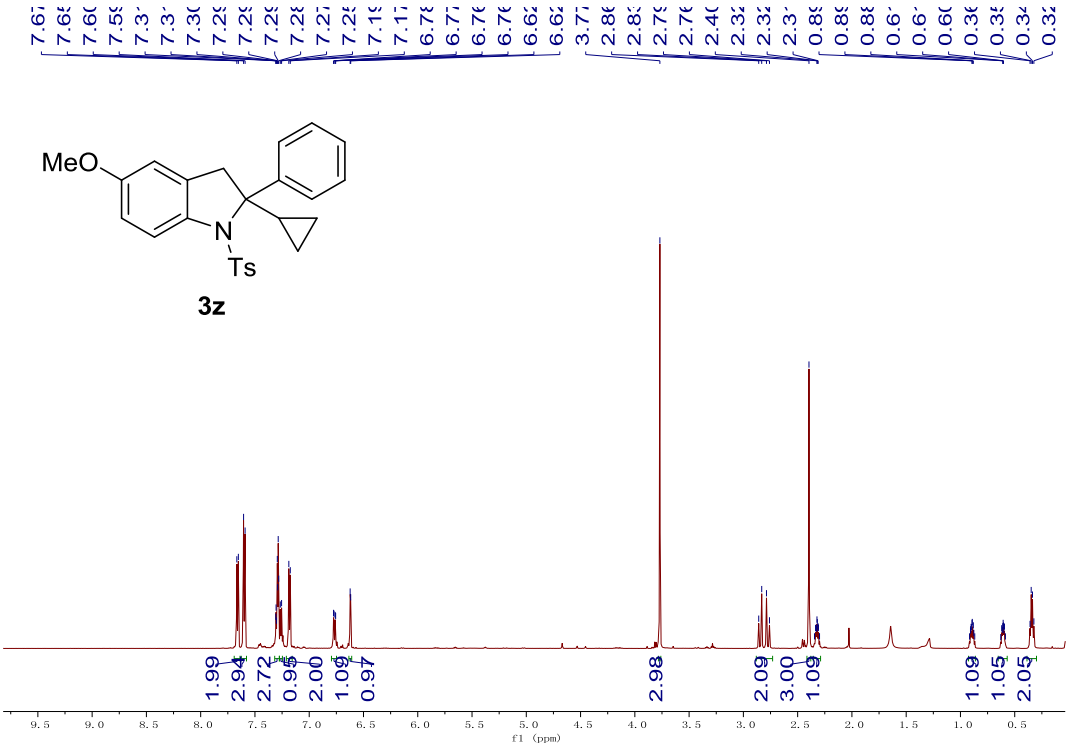

MeO
Ph
N
Ns
f1 (ppm)

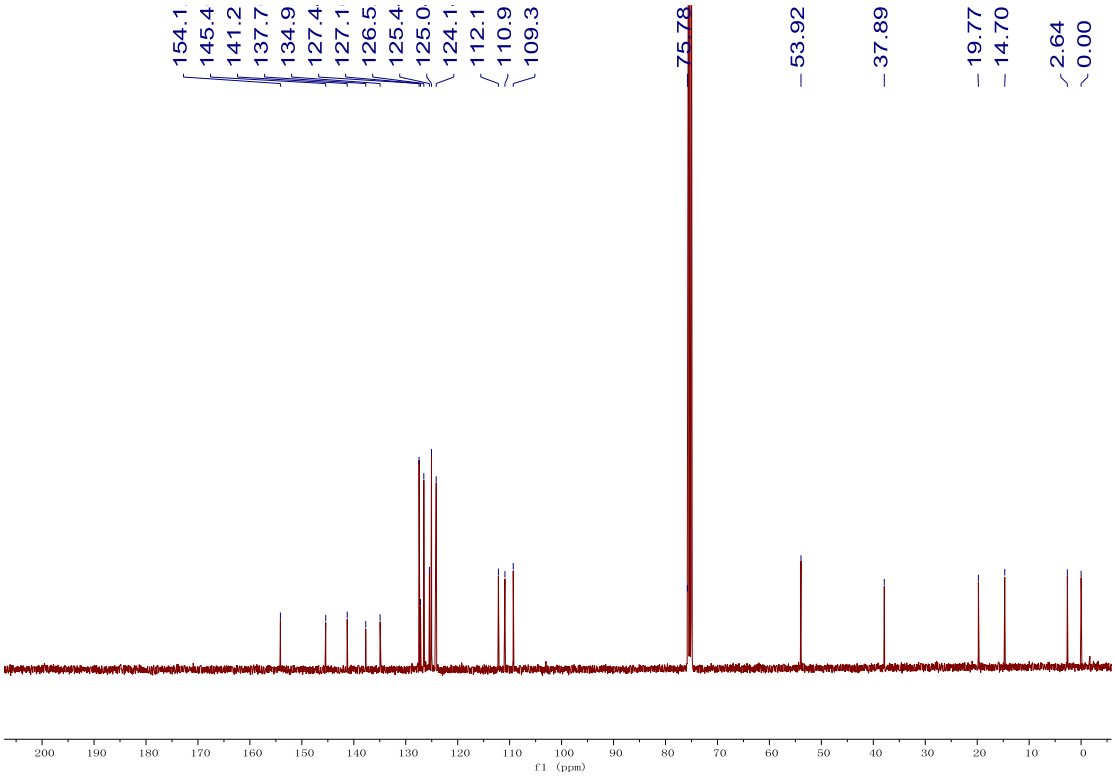
3x

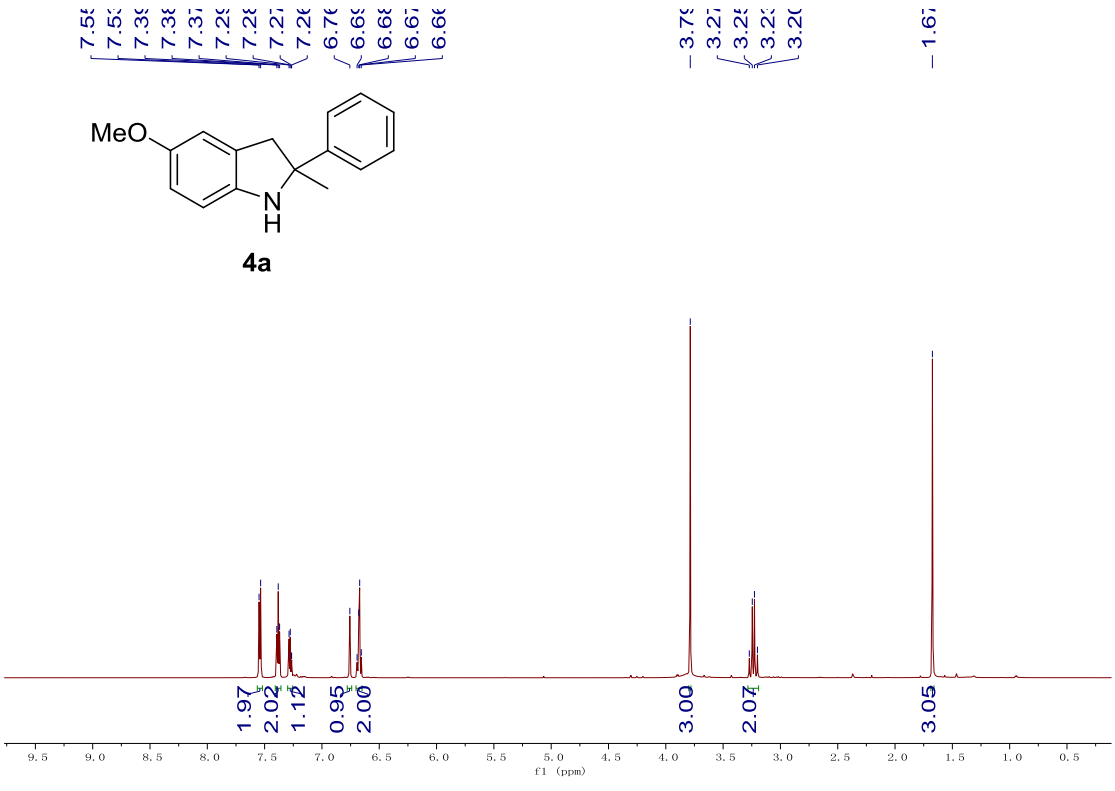

156.5
149.4
146.6
143.7
135.2
129.9
128.1
127.8
127.5
126.1
123.6
114.4
113.1
111.1
77.35
77.03
76.71
72.82
55.70
49.19
27.49
f1 (ppm)

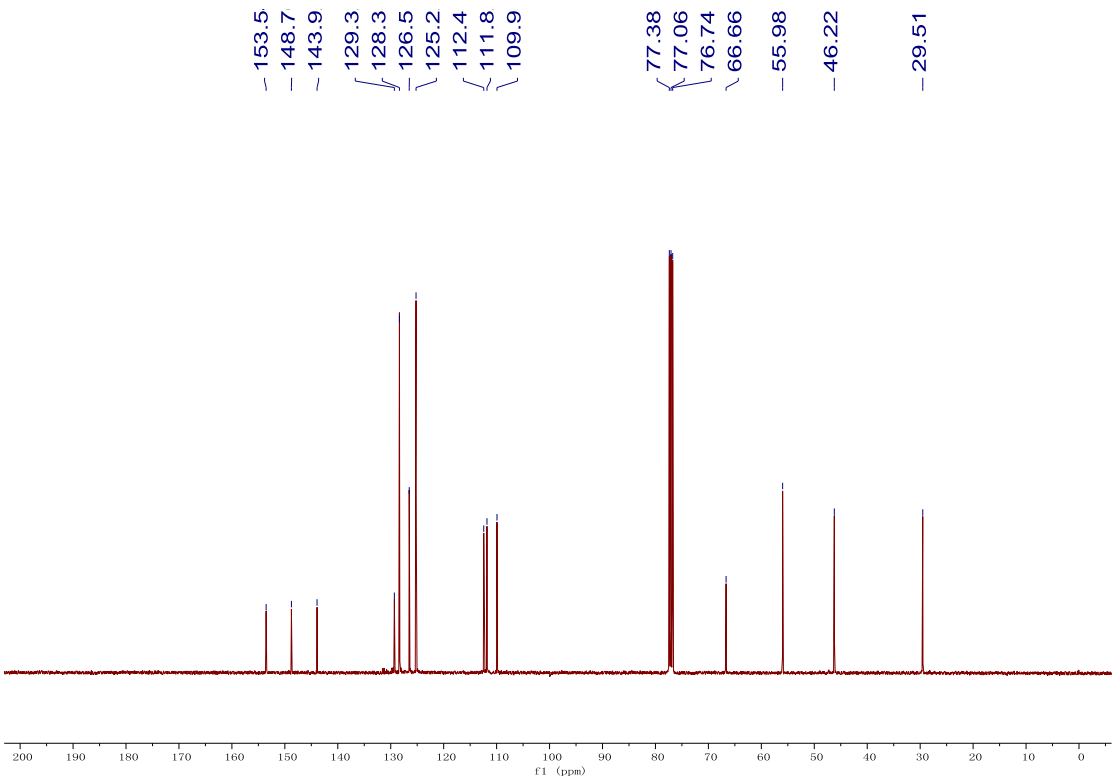

MeO
Ph
N
O
S
O
O
3y
1.00
0.99
1.05
0.97
3.04
2.11
1.59
2.99
1.87
3.00
2.00
2.92
f1 (ppm)

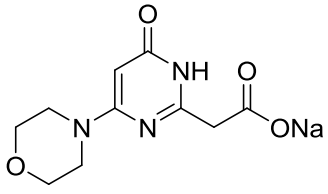

156.2
144.8
138.2
137.0
134.2
133.3
129.4
128.6
128.4
128.0
127.9
127.2
126.8
126.7
125.7
125.1
124.0
115.4
112.7
111.3
77.39
77.07
76.76
73.79
55.67
48.74
26.27
f1 (ppm)


MeO
N
Ts
3z
1.99
2.94
2.72
0.95
2.00
1.09
0.97
2.98
2.09
3.00
1.09
1.09
1.05
2.05
f1 (ppm)


154.1
145.4
141.2
137.7
134.9
127.4
127.1
126.5
125.4
125.0
124.1
112.1
110.9
109.3
75.78
53.92
37.89
19.77
14.70
2.64
0.00
f1 (ppm)

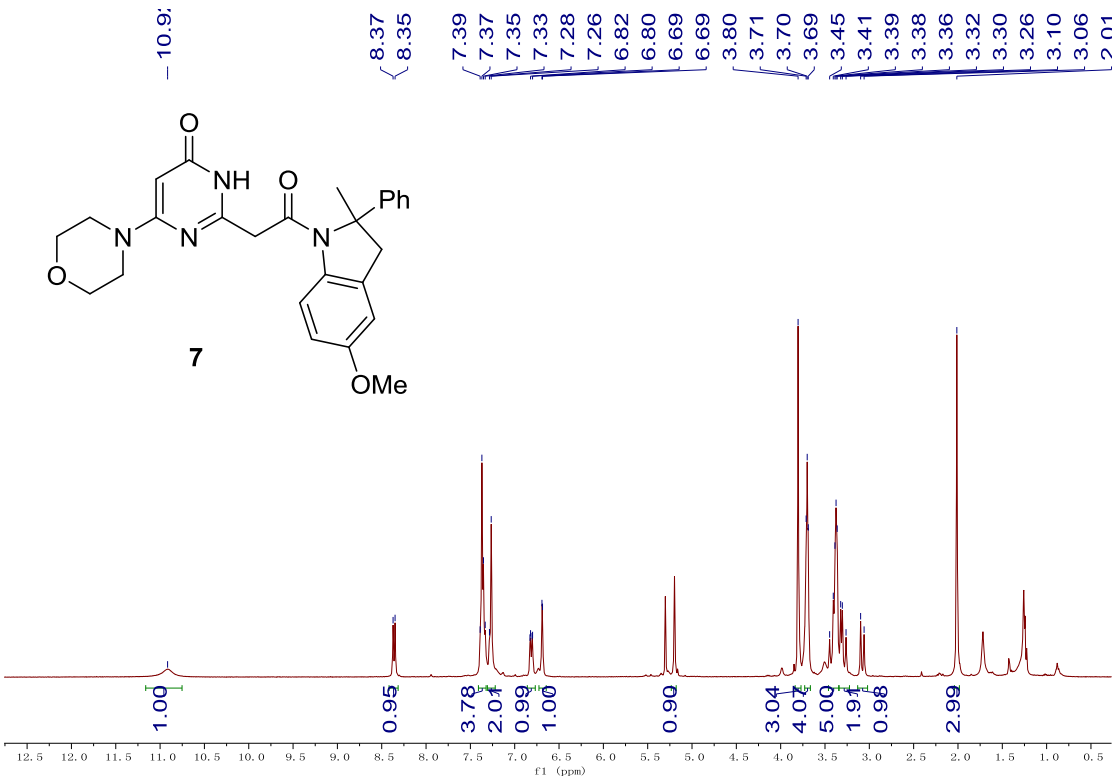

MeO
N
H
4a
1.97
2.02
1.12
0.95
2.00
3.00
2.07
3.05
f1 (ppm)

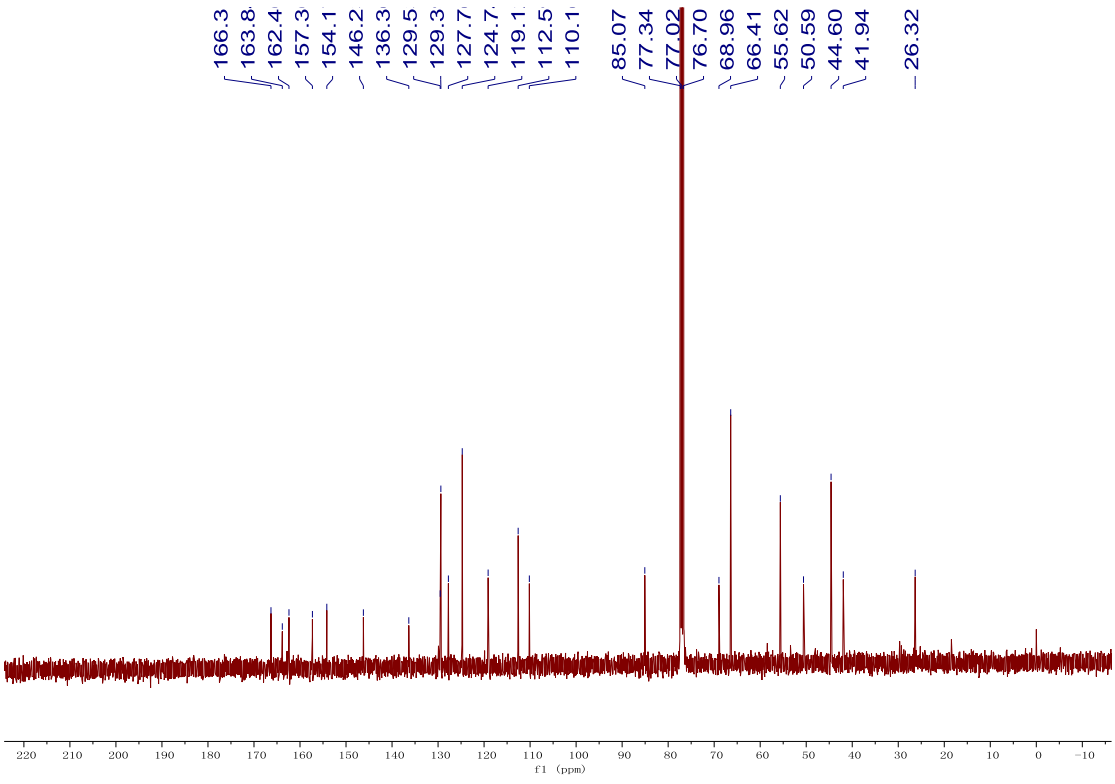

153.5
148.7
143.9
129.3
128.3
126.5
125.2
112.4
111.8
109.9
77.38
77.06
76.74
66.66
55.98
46.22
29.51
f1 (ppm)

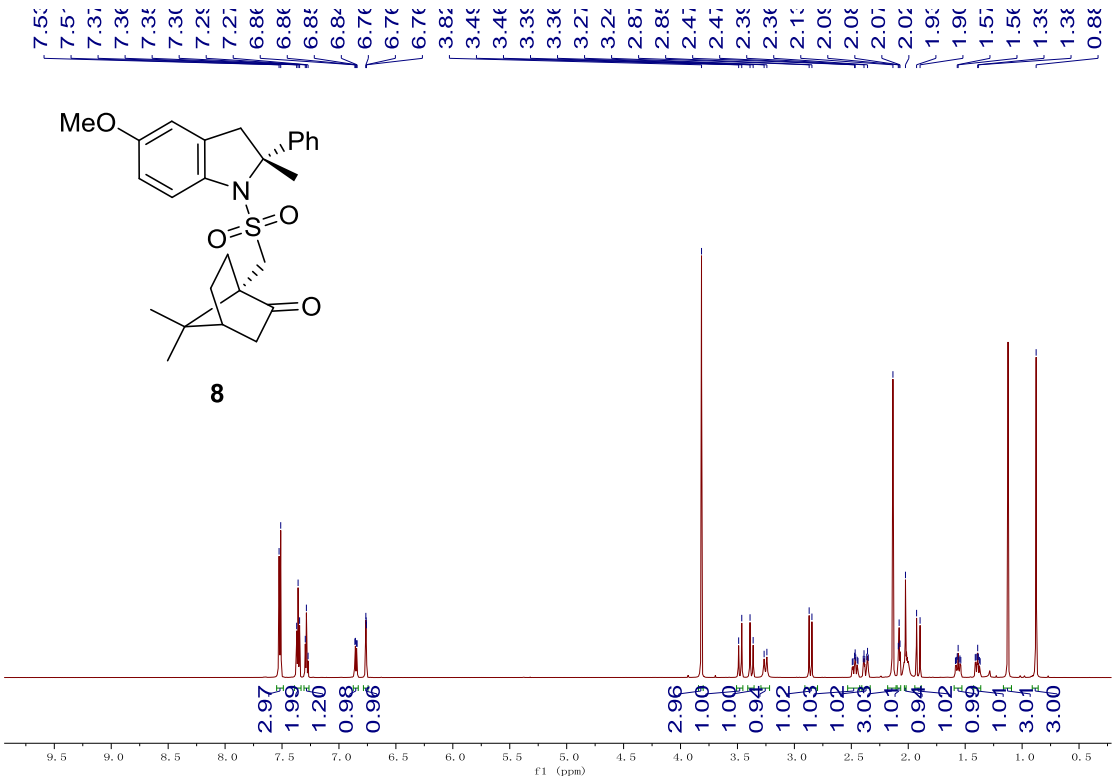

O
NH
O
N
N
ONa
O

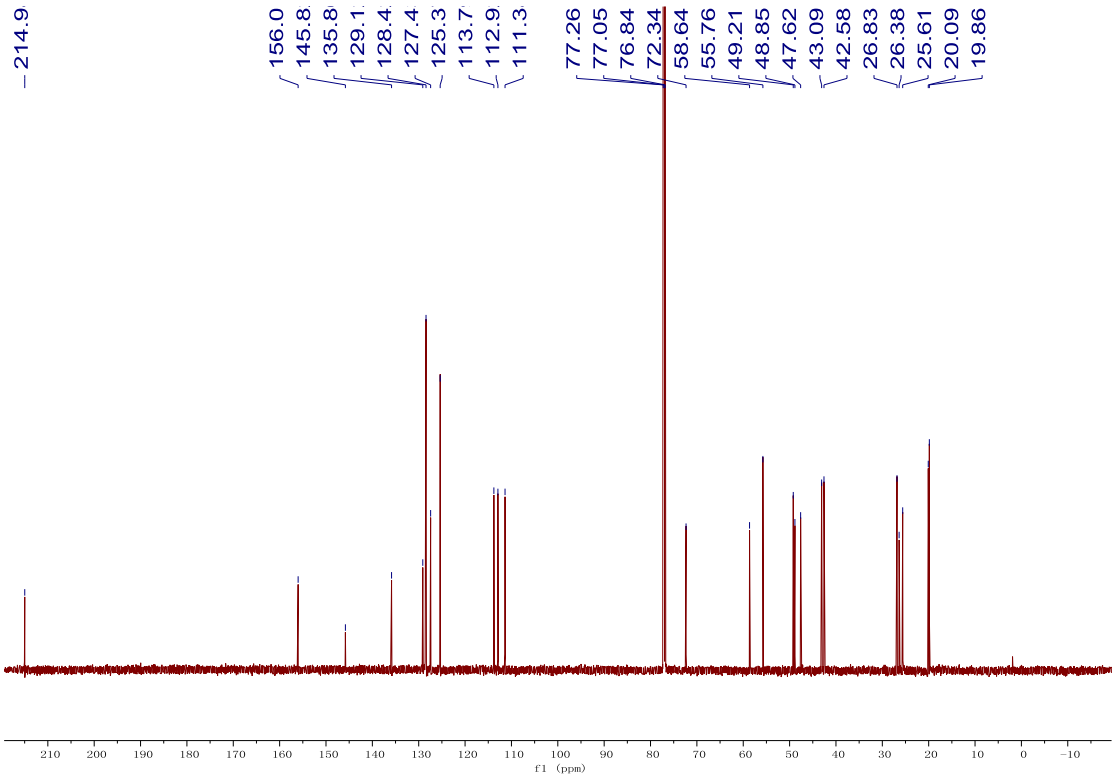
6

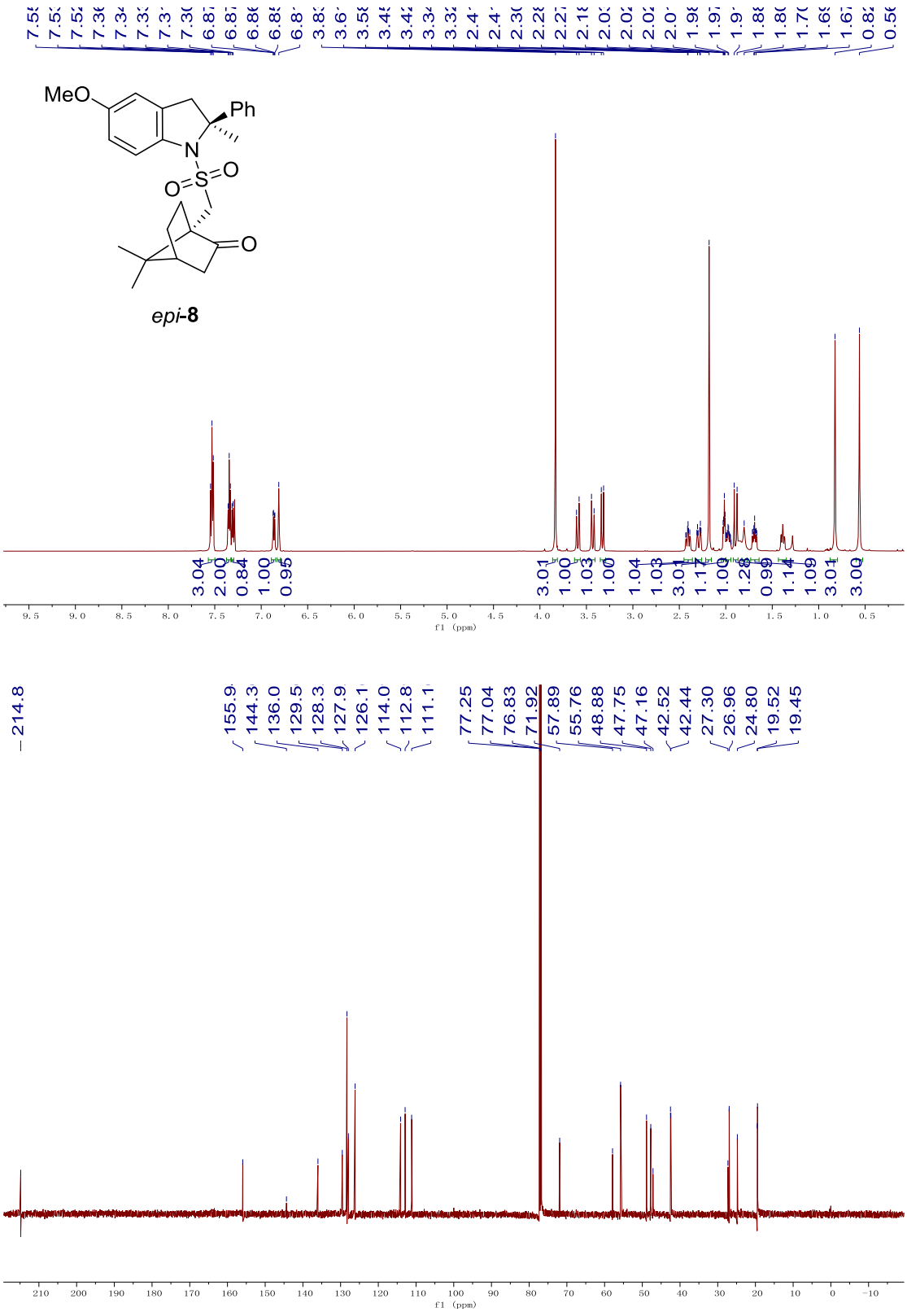
13.4
5.34
3.76
3.75
3.74
3.67
3.55
3.54
3.54
1.02
0.92
4.10
2.00
4.00
f1 (ppm)


10.9
8.37
8.35
7.39
7.37
7.35
7.33
7.28
7.26
6.82
6.80
6.69
6.69
3.80
3.71
3.70
3.69
3.45
3.41
3.39
3.38
3.36
3.32
3.30
3.26
3.10
3.06
O
NH
O
Ph
N
N
N
O
7
OMe
1.00
0.95
3.78
2.04
0.99
1.00
0.90
3.04
4.07
5.00
1.91
0.98
2.99
f1 (ppm)


166.3
163.8
162.4
157.3
154.1
146.2
136.3
129.5
129.3
127.7
124.7
119.1
112.5
110.1
85.07
77.34
77.02
76.70
68.96
66.41
55.62
50.59
44.60
41.94
26.32
f1 (ppm)


MeO
Ph
N
O
S
O
O
8
f1 (ppm)


214.9
156.0
145.8
135.8
129.1
128.4
127.4
125.3
113.7
112.9
111.3
77.26
77.05
76.84
72.34
58.64
55.76
49.21
48.85
47.62
43.09
42.58
26.83
26.38
25.61
20.09
19.86
f1 (ppm)


MeO
Ph
N
O
S
O
O
epi-8
f1 (ppm)