Supporting Information

Synthesis of hydroindoles via desymmetric [3+2] cycloadditions of *para*-quinamines with photogenerated ketenes

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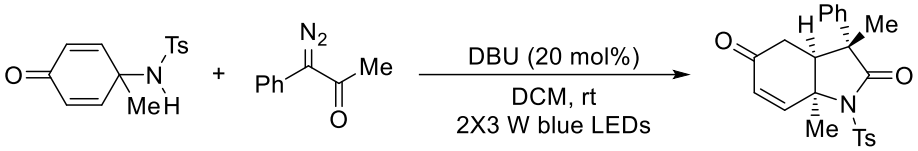
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to standard methods.[1] SepaFlash Column was purchased from Santai Technologies, Inc. Yields referred to isolated compounds through SepaBean® machine T. NMR spectra were recorded on 400 MHz spectrophotometers in $CDCl_3$ solution. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm) for ^1H NMR and chloroform-d (77.0 ppm) for ^{13}C NMR. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. Infrared spectra (IR) spectra were recorded on a Perkin-Elmer 983G instrument. HRMS was recorded on Bruker micrOTOF II. *α*-Diazoketones were synthesized according to the literature.[2-7] The *para*-quinamines **1** were prepared according to previously reported procedure.[8]

2. General Procedures

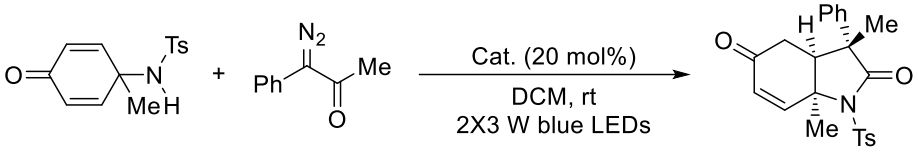


1a **2a** **3aa**

Under argon atmosphere, a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.1 mmol, 22.7 mg), **2a** (0.12 mmol, 19.2 mg) and 1 mL of DCM at room temperature (rt). Then, the catalyst DBU (0.02 mmol, 3 μL) was added through microsyringe in one portion. The resulting solution was stirred under the irradiation of 2x3 W blue LEDs until the reaction was completed, as monitored by TLC analysis (about 7 h). The residue was purified by SepaBean® machine T (petrolether/EtOAc = 5:1) to give the hydroindole product of **3aa** as white solid in 99% yield.

3. Details for Condition Optimization

3.1 The effect of catalyst[a]



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

Entry	Cat.	Yield/%[b]
1	NEt_3	72
2	DIPEA	84
3	DBU	99(99)[c]
4	DABCO	97
5	DMAP	0
6	K_2CO_3	96
7	NaOAc	92

[a] Standard conditions: **1a** (0.1 mmol), **2a** (0.12 mmol) and DBU (0.02 mmol, 20 mol%) in CH_2Cl_2 (1.0 mL) at rt under argon atmosphere and the irradiation of 2x3 W blue LEDs for 7 h. [b] All of the products were obtained with > 95:5 dr; all the yields and dr values were determined by the ^1H NMR analysis of the reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [c] Isolated yield in parentheses.

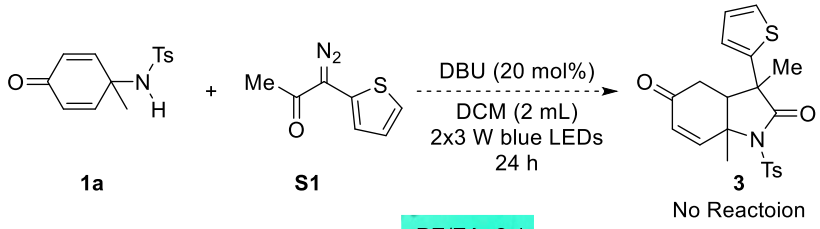
3.2 The effect of solvent[a]

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

Entry	Solvent	Yield/%[b]
1	Toluene	88
2	THF	74
3	CH_3CN	77
4	1,4-dioxane	45

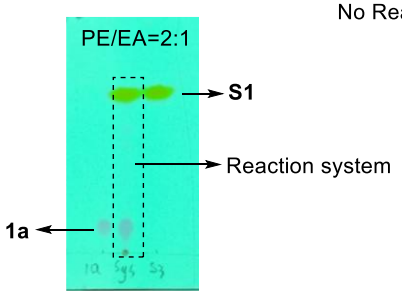
[a] Standard conditions: **1a** (0.1 mmol), **2a** (0.12 mmol) and DBU (0.02 mmol, 20 mol%) in CH_2Cl_2 (1.0 mL) at rt under argon atmosphere and the irradiation of 2x3 W blue LEDs for 7 h. [b] All of the products were obtained with > 95:5 dr; all the yields and dr values were determined by the ^1H NMR analysis of the reaction mixture using 1,3,5-trimethoxybenzene as an internal standard.

3.3 Unsuccessful substrates



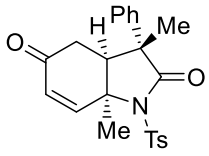
1a S1 3

No Reactoion



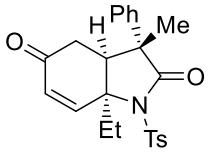
4. Spectral Data of the Products

3,7a-Dimethyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3H)-dione (3aa)



40.5 mg, 99% isolated yield, white solid. M.P.: 161 – 162 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 8.4 Hz, 2H), 7.53 (dd, *J* = 10.5, 1.3 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.26 – 7.21 (m, 1H), 7.09 (d, *J* = 6.9 Hz, 2H), 6.19 (d, *J* = 10.4 Hz, 1H), 2.90 (m, 1H), 2.64 (dd, *J* = 17.7, 7.1 Hz, 1H), 2.52 – 2.47 (m, 1H), 2.46 (s, 3H), 1.90 (s, 3H), 1.34 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 195.4, 176.1, 147.9, 145.4, 141.9, 135.7, 129.5, 129.0, 128.8, 128.7, 127.5, 126.4, 63.2, 52.4, 52.1, 34.1, 27.8, 21.7, 18.8. IR (in KBr): 3553, 3477, 3415, 3232, 2362, 1734, 1685, 1618, 1497, 1396, 1170, 1019, 913, 701 cm^{-1}. HRMS (EI) for $C_{23}H_{23}NO_4SNa$ $[M+Na]^+$: calcd 432.1240, found 432.1237.

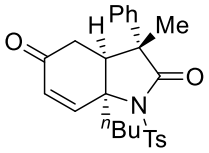
7a-Ethyl-3-methyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione (3ba)



41.9 mg, 99% isolated yield, white solid. M.P.: 162 – 163 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 10.6 Hz, 1H), 7.32 (t, *J* = 8.5 Hz, 4H), 7.27 – 7.23 (m, 1H), 7.14 (d, *J* = 7.1 Hz, 2H), 6.25 (d, *J* = 10.6 Hz, 1H), 3.06 – 3.03 (m, 1H), 2.57 – 2.51 (m, 1H), 2.47 (d, *J* = 3.5 Hz, 1H), 2.44 (s, 3H), 2.42 – 2.34 (m, 1H), 2.12 – 2.03 (m, 1H), 1.24 (s, 3H), 1.10 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 195.8, 176.4, 147.3, 145.4, 141.9, 135.2, 129.9, 129.4, 128.9, 128.8, 127.5, 126.4, 67.1, 52.4, 46.8, 34.5, 31.0, 21.7, 18.5, 8.6. IR (in KBr): 3553, 3476, 3415, 2882, 2362,

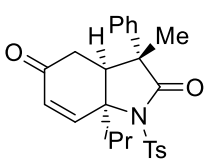
2335, 1733, 1686, 1618, 1395, 1169, 1082, 756, 701 cm^{-1}. HRMS (EI) for $C_{24}H_{25}NO_4SNa$ $[M+Na]^+$: calcd 446.1397, found 446.1397.

7a-Butyl-3-methyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3ca)



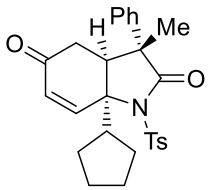
44.7 mg, 99% isolated yield, white solid. M.P.: 159 – 160 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.4 Hz, 2H), 7.50 (dd, *J* = 10.5, 1.3 Hz, 1H), 7.34 – 7.30 (m, 4H), 7.28 – 7.25 (m, 1H), 7.15 – 7.13 (m, 2H), 6.24 (d, *J* = 10.6 Hz, 1H), 3.09 – 3.07 (m, 1H), 2.59 – 2,52 (m, 1H), 2.46 – 2.40 (m, 1H), 2.44 (s, 3H), 2.29 – 2.21 (m, 1H), 2.08 – 2.00 (m, J = 14.1, 12.3, 3.8 Hz, 1H), 1.55 – 1.47 (m, 1H), 1.40 – 1.30 (m, 3H), 1.24 (s, 3H), 0.89 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 195.9, 176.3, 147.5, 145.4, 142.0, 135.3, 129.8, 129.4, 128.9, 128.9, 127.5, 126.4, 66.8, 52.5, 47.2, 38.0, 34.8, 26.3, 22.6, 21.7, 18.9, 13.8. IR (in KBr): 3549, 3475, 3416, 3132, 1837, 1733, 1619, 1395, 1169, 1083, 797, 701 cm^{-1}. HRMS (EI) for $C_{26}H_{29}NO_4SNa$ $[M+Na]^+$: calcd 474.1710, found 474.1709.

7a-Isopropyl-3-methyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*) dione (3da)



42.4 mg, 97% isolated yield, white solid. M.P.: 156 – 157 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 8.4 Hz, 2H), 7.65 (dd, *J* = 10.7, 1.5 Hz, 1H), 7.37 – 7.26 (m, 5H), 7.16 (d, *J* = 7.0 Hz, 2H), 6.39 (d, *J* = 10.7 Hz, 1H), 3.18 – 2.95 (m, 1H), 2.96 (d, *J* = 7.3 Hz, 1H), 2.56 – 2.42 (m, 2H), 2.42 (s, 3H), 1.31 (d, *J* = 6.7 Hz, 3H), 1.16 (s, 3H), 1.03 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 196.0, 176.5, 146.7, 145.3, 141.5, 134.9, 131.1, 129.3, 128.9, 128.8, 127.6, 126.7, 70.5, 52.7, 43.4, 36.2, 35.1, 21.7, 18.1, 17.9, 17.0. IR (in KBr): 3555, 3477, 3415, 3131, 2362, 1836, 1732, 1686, 1395, 1168, 1073, 780, 701, cm^{-1}. HRMS (EI) for $C_{25}H_{27}NO_4SNa$ $[M+Na]^+$: calcd 460.1553, found 460.1556.

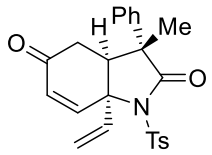
7a-Cyclopentyl-3-methyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3ea)



39.2 mg, 85% isolated yield, white solid. M.P.: 134 – 135 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 10.6 Hz, 1H), 7.36 – 7.26 (m, 5H), 7.20 – 7.18 (m, 2H), 6.31 (d, *J* = 10.6 Hz, 1H), 3.30 – 3.21 (m, 1H), 2.97 (s, 1H), 2.58 – 2.53 (m, 2H), 2.42 (s, 3H), 2.25 – 2.17 (m, 1H), 1.80

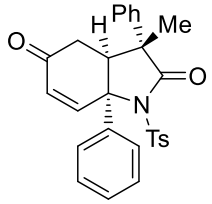
– 1.68 (m, 5H), 1.63 – 1.58 (m, 1H), 1.32 – 1.23 (m, 1H), 1.16 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.9, 176.2, 147.0, 145.3, 141.4, 135.0, 129.9, 129.3, 128.9, 128.8, 127.6, 126.7, 68.5, 52.7, 48.4, 44.5, 36.2, 28.7, 27.4, 25.8, 24.3, 21.6, 18.2. IR (in KBr): 3446, 3129, 2958, 2362, 1732, 1686, 1395, 1168, 1084, 777, 701 cm^{-1}. HRMS (EI) for $C_{27}H_{29}NO_4SNa$ $[M+Na]^+$: calcd 486.1710, found 486.1708.

3-Methyl-3-phenyl-1-tosyl-7a-vinyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3fa)



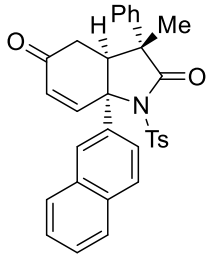
41.7 mg, 99% isolated yield, white solid. M.P.: 143 – 144 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.01 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 10.5 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.24 (m, 3H), 7.12 – 7.10 (m, 2H), 6.41 (d, *J* = 10.5 Hz, 1H), 6.16 (dd, *J* = 17.4, 10.5 Hz, 1H), 5.40 (d, *J* = 10.5 Hz, 1H), 5.28 (d, *J* = 17.4 Hz, 1H), 2.88 (d, *J* = 6.8 Hz, 1H), 2.58 – 2.52 (m, 1H), 2.46 (s, 3H), 2.46 – 2.43 (m, 1H), 1.40 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.5, 176.0, 145.5, 144.5, 141.6, 138.9, 135.6, 131.5, 129.6, 128.8, 128.7, 127.5, 126.4, 116.8, 66.3, 52.2, 51.2, 32.7, 21.7, 18.6. IR (in KBr): 3447, 3130, 2362, 1737, 1687, 1395, 1172, 1088, 754, 701, 624 cm^{-1}. HRMS (EI) for $C_{24}H_{23}NO_4SNa$ $[M+Na]^+$: calcd 444.1240, found 444.1244.

3-Methyl-3,7a-diphenyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3ga)



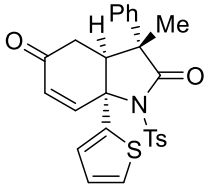
(2 mL DCM as solvent) 46.2 mg, 98% isolated yield, white solid. M.P.: 197 – 198 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.86 (d, *J* = 8.4 Hz, 2H), 7.78 (dd, *J* = 10.6, 1.7 Hz, 1H), 7.46 – 7.37 (m, 5H), 7.33 – 7.28 (m, 4H), 7.24 – 7.22 (m, 1H), 7.20 – 7.18 (m, 2H), 6.57 (d, *J* = 10.6 Hz, 1H), 3.15 – 3.12 (m, 1H), 2.45 (s, 3H), 2.39 (d, *J* = 4.7 Hz, 2H), 1.43 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.7, 176.6, 145.6, 145.3, 141.6, 141.2, 135.2, 131.7, 129.3, 129.2, 129.0, 128.8, 128.5, 127.5, 126.4, 125.4, 68.22, 55.8, 52.7, 32.9, 21.7, 18.6. IR (in KBr): 3445, 3131, 2363, 1737, 1687, 1644, 1395, 1171, 1088, 701, 665, 576 cm^{-1}. HRMS (EI) for $C_{28}H_{25}NO_4SNa$ $[M+Na]^+$: calcd 494.1397, found 494.1394.

3-Methyl-7a-(naphthalen-2-yl)-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole2,5(3*H*)-dione (3ha)



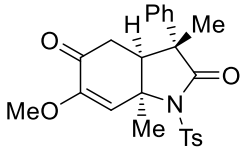
(2 mL DCM as solvent) 52.1 mg, 99% isolated yield, white solid. M.P.: 122 – 123 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 8.7 Hz, 1H), 7.89 – 7.86 (m, 4H), 7.82 – 7.80 (m, 2H), 7.58 – 7.53 (m, 3H), 7.32 – 7.29 (m, 4H), 7.24 – 7.20 (m, 3H), 6.66 (d, *J* = 10.6 Hz, 1H), 3.24 – 3.21 (m,1H), 2.47 (s, 3H), 2.42 – 2.41 (m, 2H), 1.48 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.8, 176.8, 145.6, 145.3, 141.7, 138.2, 135.2, 132.9, 132.7, 131.9, 129.5, 129.4, 129.3, 128.9, 128.3, 127.7, 127.6, 126.9, 126.9, 126.5, 125.0, 122.6, 68.4, 55.3, 52.7, 32.9, 21.8, 18.8. IR (in KBr): 3443, 3130, 2362, 2335, 1735, 1687, 1643, 1395, 1166, 1085, 743, 663 cm^{-1}. HRMS (EI) for $C_{32}H_{27}NO_4SNa$ $[M+Na]^+$: calcd 544.1553, found 544.1546.

3-Methyl-3-phenyl-7a-(thiophen-2-yl)-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3ia)



(2 mL DCM as solvent) 47.3 mg, 99% isolated yield, white solid. M.P.: 115 – 116 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.87 – 7.84 (m, 3H), 7.35 – 7.29 (m, 5H), 7.26 – 7.22 (m, 1H), 7.19 – 7.17 m, 2H), 7.10 – 7.09 (m, 1H), 7.02 – 7.00 (m, 1H), 6.47 (d, *J* = 10.5 Hz, 1H), 3.33 – 3.33 (m, 1H), 2.56 – 2.49 (m, 1H), 2.45– 2.40 (m, 1H), 2.44 (s, 3H), 1.42 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.2, 176.1, 145.5, 145.4, 144.4, 141.3, 135.3, 130.9, 129.3, 129.1, 128.8, 127.6, 127.2, 126.6, 126.5, 126.0, 65.4, 56.9, 52.6, 33.1, 21.7, 18.1. IR (in KBr): 3451, 3122, 2362, 1738, 1689, 1393, 1362, 1259, 1169, 1080, 771, 737, 701 cm^{-1}. HRMS (EI) for $C_{26}H_{23}NO_4S_2Na$ $[M+Na]^+$: calcd 500.0961, found 500.0958.

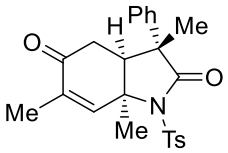
6-Methoxy-3,7a-dimethyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3ja)



(2 mL DCM as solvent) 30.1 mg, 68% isolated yield, white solid. M.P.: 240 – 241 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.26 – 7.22 (m, 1H), 7.09 – 7.06 (m, 2H), 6.41 (s, 1H), 3.76 (s, 3H), 2.89 – 2.86 (m, 1H), 2.75 – 2.69 (m, 1H), 2.61 – 2.55 (m, 1H), 2.47 (s, 3H), 1.88 (s, 3H), 1.35 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 190.5, 176.0, 150.3, 145.4, 142.1, 135.8, 129.5, 128.9, 128.6, 127.5, 126.3, 115.6, 65.0, 55.4, 52.6, 51.5, 35.0, 29.5,

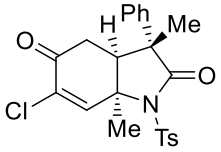
21.7, 19.4. IR (in KBr): 3446, 3134, 2361, 2343, 1400, 1385, 1166, 1090, 881, 736, 669 cm^{-1}. HRMS (EI) for $C_{24}H_{25}NO_5SNa$ $[M+Na]^+$: calcd 462.1346, found 462.1343.

3,6,7a-Trimethyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione (3ka)



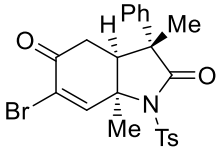
30.2 mg, 71% yield, white solid.**^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.98 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 7.31 – 7.26 (m, 2H), 7.25 – 7.21 (m, 2H), 7.08 – 7.06 (m, 2H), 2.89 – 2.86 (m, 1H), 2.63 (dd, J = 17.4, 6.9 Hz, 1H), 2.49 (dd, J = 17.4, 6.9 Hz, 1H), 2.46 (s, 3H), 1.91 (s, 3H), 1.84 (s, 3H), 1.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 196.0, 176.2, 145.3, 143.2, 142.2, 135.9, 135.7, 129.5, 128.8, 128.6, 127.5, 126.3, 64.0, 52.5, 52.2, 34.4, 27.9, 21.7, 19.1, 15.9. HRMS (EI) for $C_{24}H_{25}NO_4SNa$ $[M+Na]^+$: calcd 446.1397, found 446.1395.

6-Chloro-3,7a-dimethyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione (3la)



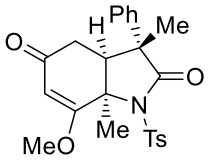
20.2 mg, 45% isolated yield, white solid. M.P.: 188 – 189 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 1.2 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.27 (m, 2H), 7.26 – 7.24 (m, 1H), 7.13 – 7.04 (m, 2H), 2.94 – 2.91 (m, 1H), 2.80 – 2.74 (m, 1H), 2.68 – 2.63 (m, 1H), 2.47 (s, 3H), 1.91 (s, 3H), 1.33 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 187.9, 175.6, 145.7, 143.8, 141.6, 135.4, 133.1, 129.7, 129.90, 128.7, 127.7, 126.3, 64.4, 52.3, 52.0, 34.6, 27.8, 21.7, 19.0. IR (in KBr): 3125, 3061, 3028, 2926, 1736, 1703, 1655, 1618, 1560, 1542, 1459, 1466, 1186, 1170, 906, 814, 702, cm^{-1}. HRMS (EI) for $C_{23}H_{22}ClNO_4SNa$ $[M+Na]^+$: calcd 466.0850, found 466.0848.

6-Bromo-3,7a-dimethyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione (3ma)



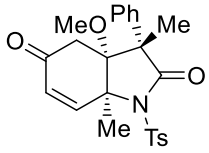
29.8 mg, 62% yield, white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.99 – 7.97 (m, 3H), 7.38 (d, *J* = 8.1 Hz, 1H). 7.32 – 7.27 (m, 3H), 7.09 – 7.07 (m, 2H), 2.94 – 2.92 (m, 1H), 2.78 (dd, *J* = 17.5, 6.7 Hz, 1H), 2.68 (dd, *J* = 17.4, 4.1 Hz, 1H), 2.47 (s, 3H), 1.89 (s, 3H), 1.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 187., 175.62, 148.1, 145.7, 141.6, 135.4, 129.7, 129.0, 128.7, 127.7, 126.3, 125.0, 65.2, 52.3, 52.1, 34.3, 27.6, 21.8, 19.0. HRMS (EI) for $C_{23}H_{22}BrNO_4SNa$ $[M+Na]^+$: calcd 510.0345, found 510.0341.

7-Methoxy-3,7a-dimethyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione (3na)



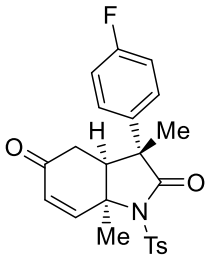
16.4 mg, 41% yield, white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 8.3 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.19 (m, 3H), 6.89 – 6.87 (m, 2H), 5.47 (s, 1H), 3.86 (s, 3H), 2.80 – 2.77 (m, 1H), 2.65 – 2.59 (m, 1H), 2.55 – 2.50 (m, 1H), 2.47 (s, 3H), 2.14 (s, 3H), 1.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 195.1, 177.1, 174.2, 144.9, 143.1, 136.7, 129.2, 129.2, 128.8, 127.4, 126.0, 102.4, 66.0, 56.6, 53.7, 51.3, 32.5, 26.0, 21.7, 17.8. HRMS (EI) for $C_{24}H_{25}NO_5SNa$ $[M+Na]^+$: calcd 462.1346, found 462.1345.

3a-Methoxy-3,7a-dimethyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione (3na')



14.9 mg, 34% yield, white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 10.4 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.24 (m, 3H), 7.15 – 7.12 (m, 2H), 6.21 (d, *J* = 10.4 Hz, 1H), 2.91 (s, 3H), 2.89 (d, *J* = 16.8 Hz, 1H), 2.62 (d, *J* = 16.8 Hz, 1H), 2.47 (s, 3H), 1.57 (s, 3H), 1.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 195.5, 175.0, 149.7, 145.3, 139.0, 135.7, 129.5, 128.7, 128.4, 128.0, 127.9, 127.4, 84.1, 67.3, 57.5, 52.7, 40.2, 22.0, 21.7, 21.5. HRMS (EI) for $C_{24}H_{25}NO_5SNa$ $[M+Na]^+$: calcd 462.1346, found 462.1342.

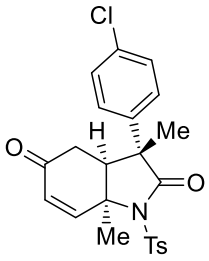
3-(4-Fluorophenyl)-3,7a-dimethyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3ab)



38.8 mg, 91% isolated yield, white solid. M.P.: 195 – 196 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 10.5 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.09 – 7.06 (m, 2H), 7.01 – 6.97 (m, 2H), 6.19 (d, *J* = 10.5 Hz, 1H), 2.86 – 2.84 (m, 1H), 2.68 – 2.62 (m, 1H), 2.50 – 2.45 (m, 1H), 2.46 (s, 3H), 1.93 (s, 3H), 1.33 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.2, 176.0, 161.9 (d, *J* = 247.4 Hz), 147.8, 145.5, 137.6 (d, *J* = 3.4 Hz), 135.6, 129.6, 129.0, 128.7, 128.3 (d, *J* = 8.1 Hz), 115.7 (d, *J* = 21.5 Hz), 63.2, 52.2, 51.9, 33.9, 27.9, 21.8, 19.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = –114.51. IR (in KBr): 3443, 3131, 2362, 2335, 1733, 1686, 1512, 1396,

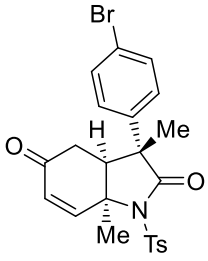
1266, 1169, 1017, 754, 668 cm^{-1}. HRMS (EI) for $C_{23}H_{22}FNO_4SNa$ $[M+Na]^+$: calcd 450.1146, found 450.1142.

3-(4-Chlorophenyl)-3,7a-dimethyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5 (3*H*)-dione (3ac)



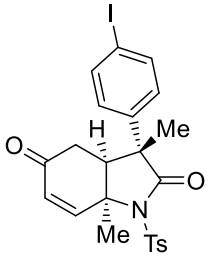
42.8 mg, 96% isolated yield, white solid. M.P.: 181 – 182 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 10.5 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.06 – 7.02 (m, 2H), 6.19 (d, *J* = 10.5 Hz, 1H), 2.86 – 2.83 (m, 1H), 2.68– 2.62 (m, 1H), 2.49 – 2.44 (m, 1H), 2.46 (s, 3H), 1.92 (s, 3H), 1.32 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.1, 175.7, 147.8, 145.5, 140.3, 135.6, 133.6, 129.6, 129.0, 129.0, 128.7, 127.9, 63.2, 52.0, 52.0, 33.9, 27.8, 21.7, 18.8. IR (in KBr): 3416, 3131, 1732, 1684, 1636, 1397, 1170, 1084, 551 cm^{-1}. HRMS (EI) for $C_{23}H_{22}ClNO_4SNa$ $[M+Na]^+$: calcd 466.0850, found 466.0851.

3-(4-Bromophenyl)-3,7a-dimethyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3ad)



47.0 mg, 96% isolated yield, white solid. M.P.: 180 – 181 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* =10.7 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 6.18 (d, *J* = 10.5 Hz, 1H), 2.85 – 2.82 (m, 1H), 2.68– 2.62 (m, 1H), 2.48 – 2.43 (m, 1H), 2.46 (s, 3H), 1.92 (s, 3H), 1.32 (s, 3H).**^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.0, 175.6, 147.7, 145.5, 140.8, 135.5, 131.9, 129.6, 129.0, 128.6, 128.2, 121.7, 63.2, 52.1, 51.9, 33.9, 27.8, 21.7, 18.7. IR (in KBr): 3449, 3128, 2361, 1733, 1686, 1396, 1358, 1171, 1081, 912 cm^{-1}. HRMS (EI) for $C_{23}H_{22}BrNO_4SNa$ $[M+Na]^+$: calcd 510.0345, found 510.0347.

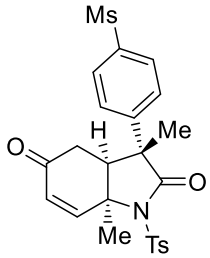
3-(4-Iodophenyl)-3,7a-dimethyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3ae)



53.5 mg, 99% isolated yield, white solid. M.P.: 189 – 190 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 10.5 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.18 (d, *J* = 10.5 Hz, 1H), 2.85 – 2.82 (m, 1H), 2.67– 2.61 (m, 1H), 2.48 – 2.43 (m,

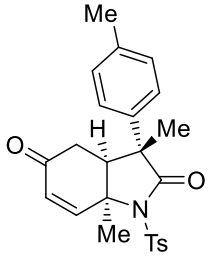
1H), 2.46 (s, 3H), 1.92 (s, 3H), 1.31 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.0, 175.5, 147.7, 145.5, 141.6, 137.8, 135.5, 129.6, 129.0, 128.6, 128.4, 93.2, 63.2, 52.1, 51.8, 33.9, 27.8, 21.7, 18.6. IR (in KBr): 3445, 3128, 2363, 1733, 1685, 1395, 1358, 1172, 1082, 1005, 912, 734 cm^{-1}. HRMS (EI) for $C_{23}H_{22}INO_4SNa$ $[M+Na]^+$: calcd 558.0206, found 558.0206.

3,7a-Dimethyl-3-(4-(methylsulfonyl)phenyl)-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3af)



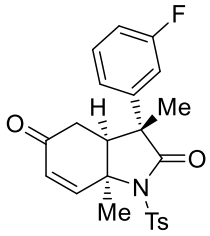
43.6 mg, 89% isolated yield, white solid. M.P.: 180 – 181 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) 7.99 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.56 – 7.53 (m, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 6.21 (d, *J* = 10.5 Hz, 1H), 3.02 (s, 3H), 2.88 – 2.85 (m, 1H), 2.72– 2.66 (m, 1H), 2.50 – 2.45 (m, 1H), 2.47 (s, 3H), 1.97 (s, 3H), 1.40 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 194.6, 175.2, 147.9, 147.6, 145.8, 139.8, 135.4, 129.7, 129.1, 128.7, 128.0, 127.7, 63.5, 52.5, 51.9, 44.4, 33.7, 27.8, 21.8, 18.6. IR (in KBr): 3448, 3128, 2360, 1730, 1685, 1396, 1150, 1081, 738, 666 cm^{-1}. HRMS (EI) for $C_{24}H_{25}NO_6S_2Na$ $[M+Na]^+$: calcd 510.1016, found 510.1014.

3,7a-Dimethyl-3-(p-tolyl)-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3ag)



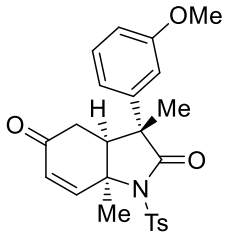
30.8 mg, 73% isolated yield, white solid. M.P.: 200– 201 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.98 (d, J = 8.4 Hz, 2H), 7.52 (dd, *J* = 10.5, 1.3 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 6.17 (d, *J* = 10.5 Hz, 1H), 2.90 – 2.87 (m, 1H), 2.65 – 2.59 (m, 1H), 2.50 – 2.46 (m, 1H), 2.46 (s, 3H), 2.29 (s, 3H), 1.89 (s, 3H), 1.32 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.5, 176.2, 148.0, 145.3, 138.9, 137.3, 135.7, 129.5, 129.5, 128.9, 128.7, 126.2, 63.2, 52.1, 34.1, 27.8, 21.7, 20.9, 18.8. IR (in KBr): 3445, 3130, 2362, 1735, 1685, 1396, 1171, 1018, 810, 741, 708 cm^{-1}. HRMS (EI) for $C_{24}H_{25}NO_4SNa$ $[M+Na]^+$: calcd 446.1397, found 446.1393.

3-(3-Fluorophenyl)-3,7a-dimethyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione (3ah)



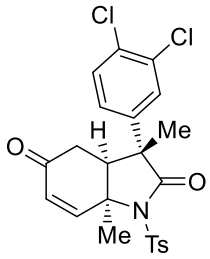
42.4 mg, 99% isolated yield, white solid. M.P.: 155 – 156 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 10.5 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.25 (m, 1H), 6.97 – 6.93 (m, 1H), 6.90 – 6.88 (m, 1H), 6.80 – 6.76 (m, 1H), 6.19 (d, *J* = 10.5 Hz, 1H), 2.89 – 2.86 (m, 1H), 2.69 – 2.63 (m, 1H), 2.51 – 2.46 (m, 1H), 2.46 (s, 3H), 1.92 (s, 3H), 1.34 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.1, 175.5, 162.8 (d, J = 246.9 Hz), 147.8, 145.6, 144.4 (d, *J* = 6.9 Hz), 135.5, 130.4 (d, *J* = 8.3 Hz), 129.6, 129.0, 128.7, 122.1(d, *J* = 3.0 Hz), 114.6 (d, *J* = 20.9 Hz), 113.8 (d, *J* = 22.7 Hz), 63.2, 52.2, 52.2, 51.9, 34.0, 27.7, 21.7, 18.8. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = –111.47. IR (in KBr): 3420, 3130, 2925, 2361, 1685, 1645, 1397, 1292, 1243, 1082, 787, 698 cm^{-1}. HRMS (EI) for $C_{23}H_{22}FNO_4SNa$ $[M+Na]^+$: calcd 450.1146, found 450.1143.

3-(3-methoxyphenyl)-3,7a-dimethyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3ai)



37.0 mg, 84% isolated yield, white solid. M.P.: 187 – 188 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) 7.98 (d, *J* = 8.3 Hz, 2H), 7.50 (d, *J* = 10.5 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.21 (t, *J* = 8.0 Hz, 1H), 6.77 (dd, *J* = 8.1, 2.4 Hz, 1H), 6.66 (d, *J* = 7.7 Hz, 1H), 6.62 – 6.61 (m, 1H), 6.17 (d, *J* = 10.5 Hz, 1H), 3.73 (s, 3H), 2.92 – 2.89 (m, 1H), 2.66 – 2.60 (m, 1H), 2.51 – 2.45 (m, 1H), 2.45 (s, 3H), 1.88 (s, 3H), 1.33 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.4, 175.9, 159.7, 148.0, 145.4, 143.6, 135.7, 129.8, 129.5, 128.9, 128.6, 118.6, 113.0, 112.2, 63.2, 55.2, 52.4, 52.0, 34.2, 27.7, 21.7, 18.9. IR (in KBr): 3421, 3130, 2362, 2335, 1837, 1735, 1396, 1169, 1083, 668, 547 cm^{-1}. HRMS (EI) for $C_{24}H_{25}NO_5SNa$ $[M+Na]^+$: calcd 462.1346, found 462.1344.

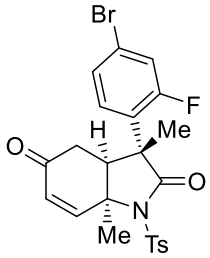
3-(3,4-Dichlorophenyl)-3,7a-dimethyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3aj)



42.3 mg, 88% isolated yield, white solid. M.P.: 170 – 171 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 10.7 Hz, 1H), 7.37 (dd, *J* = 8.3, 3.0 Hz, 3H), 7.16 (d, *J* = 2.3 Hz, 1H), 6.96 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.19 (d, *J* = 10.5 Hz, 1H), 2.85 – 2.82 (m, 1H), 2.71– 2.65 (m, 1H), 2.50

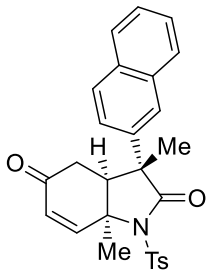
– 2.45 (m, 1H), 2.46 (s, 3H), 1.94 (s, 3H), 1.32 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 194.8, 175.1, 147.6, 145.7, 141.9, 135.3, 132.9, 131.9, 130.7, 129.6, 129.0, 128.6, 126.0, 63.3, 51.8, 51.6, 33.8, 27.8, 21.7, 18.8. IR (in KBr): 3442, 3128, 2359, 1733, 1686, 1470, 1393, 1359, 1171, 1083, 814, 737, 702 cm^{-1}. HRMS (EI) for $C_{23}H_{21}Cl_2NO_4SNa$ $[M+Na]^+$: calcd 500.0461, found 500.0462.

3-(4-Bromo-2-fluorophenyl)-3,7a-dimethyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3ak)



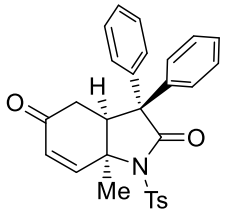
36.0 mg, 71% isolated yield, white solid. M.P.: 238 – 239 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 8.3 Hz, 2H), 7.53 (dd, *J* = 10.5, 1.5 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.28 – 7.25 (m, 1H), 7.16 (dd, *J* = 11.0, 2.0 Hz, 1H), 7.06 (t, *J* = 8.4 Hz, 1H), 6.17 (d, *J* = 10.5 Hz, 1H), 2.91 – 2.89 (m, 1H), 2.65 – 2.59 (m, 1H), 2.46 (s, 3H), 2.38 – 2.33 (m, 1H), 1.98 (s, 3H), 1.38 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.0, 174.8, 159.5 (d, *J* = 251.6 Hz), 148.4, 145.3, 135.7, 129.5, 129.3 (d, *J* = 4.3 Hz), 128.7, 128.5, 128.1 (d, *J* = 11.1 Hz), 127.6 (d, *J* = 3.4 Hz), 122.5(d, *J* = 10.2 Hz), 120.1 (d, *J* = 25.4 Hz), 63.4, 49.6, 49.6, 49.4, 49.3, 33.6, 27.0, 21.7, 17.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ = –107.56. IR (in KBr): 3346, 3134, 2363, 1793, 1773, 1718,1400, 1385, 1152, 1083, 711 cm^{-1}. HRMS (EI) for $C_{23}H_{21}BrFNO_4SNa$ $[M+Na]^+$: calcd 528.0251, found 528.0253.

3,7a-Dimethyl-3-(naphthalen-2-yl)-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione (3al)



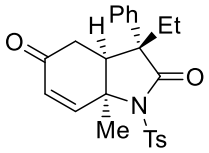
30.6 mg, 66% isolated yield, white solid. M.P.: 187 – 188 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.01 (d, *J* = 8.4 Hz, 2H), 7.78 – 7.76 (m, 2H), 7.72 – 7.70 (m, 1H), 7.55 – 7.51 (m, 2H), 7.49 – 7.45 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.13 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.20 (d, *J* = 10.5 Hz, 1H), 3.02 – 2.99 (m, 1H), 2.67– 2.61 (m, 1H), 2.54 – 2.49 (m, 1H), 2.47 (s, 3H), 1.89 (s, 3H), 1.45 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.5, 176.0, 148.0, 145.4, 139.1, 135.6, 132.9, 132.3, 129.6, 129.0, 128.9, 128.7, 128.0, 127.4, 126.5, 126.4, 125.3, 124.3, 63.4, 52.6, 51.7, 34.2, 27.8, 21.7, 18.8. IR (in KBr): 3134, 2363, 2345, 1734, 1684, 1399, 1385, 1294, 1172, 1107, 736, 703, cm^{-1}. HRMS (EI) for $C_{23}H_{21}BrFNO_4SNa$ $[M+Na]^+$: calcd 482.1397, found 482.1395.

7a-Methyl-3,3-diphenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione (3am)



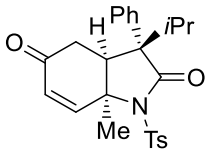
42.9 mg, 91% isolated yield, white solid. M.P.: 135 – 136 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.33 – 7.22 (m, 6H), 7.17 – 7.13 (m, 1H), 7.09 – 7.05 (m, 2H), 6.75 (d, *J* = 8.1 Hz, 2H), 5.48 (d, *J* = 10.5 Hz, 1H), 3.72 – 3.69 (m, 1H), 2.99– 2.85 (m, 2H), 2.45 (s, 3H), 2.03 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 192.6, 173.9, 146.6, 145.6, 140.1, 139.9, 135.6, 129.9, 129.6, 129.1, 128.4, 128.3, 128.2, 128.0, 127.7, 127.6, 63.2, 58.9, 47.7, 34.5, 27.4, 21.7. IR (in KBr): 3134, 2361, 1733, 1718, 1684, 1663, 1446, 1186 782, 701 cm^{-1}. HRMS (EI) for $C_{28}H_{25}NO_4SNa$ $[M+Na]^+$: calcd 494.1397, found 494.1394.

3-Ethyl-7a-methyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3an)



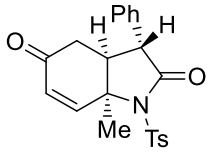
38.7 mg, 91% isolated yield, white solid. M.P.: 117 – 118 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 10.5 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.29 ((m, 2H), 7.27 – 7.23 (m, 1H), 7.10 – 7.07 (m, 2H), 6.19 (d, *J* = 10.5 Hz, 1H), 3.82– 2.79 (m, 1H), 2.62– 2.50 (m, 2H), 2.46 (s, 3H), 1.94– 1,85 (m, 1H), 1.80 (s, 3H), 1.77 – 1.70 (m, 2H), 0.60 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.7, 174.6, 148.6, 145.3, 139.2, 135.77, 129.4, 129.0, 128.9, 128.6, 127.3, 127.0, 62.7, 56.1, 52.8, 34.0, 27.9, 24.0, 21.7, 8.3. IR (in KBr): 3128, 1733, 1684, 1399, 1170, 1085, 669, 573 cm^{-1}. HRMS (EI) for $C_{24}H_{25}NO_4SNa$ $[M+Na]^+$: calcd 446.1397, found 446.1391.

3-Isopropyl-7a-methyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione (3ao)



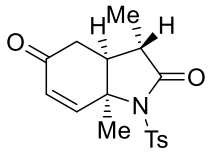
36.0 mg, 82% isolated yield, white solid. M.P.: 208 – 209 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.19 – 7.08 (m, 4H), 6.82 (d, *J* = 7.1 Hz, 2H), 5.44 (d, *J* = 10.5 Hz, 1H), 3.04 – 3.03 (m, 1H), 2.72 – 2.08 (m, 2H), 2.49 (s, 3H), 2.30 – 2.20 (m, 1H), 1.97 (s, 3H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 192.7, 175.1, 146.3, 145.4, 136.7, 136.1, 129.5, 129.3, 128.8, 128.2, 128.1, 127.4, 63.4, 57.8, 48.6, 34.4, 32.8, 27.0, 21.7, 17.9. HRMS (EI) for $C_{25}H_{27}NO_4SNa$ $[M+Na]^+$: calcd 460.1553, found 460.1552.

7a-Methyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3ap)



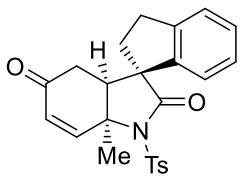
(0.2 mmol *α*-diazoketone) 39.2 mg, 99% isolated yield, white solid. M.P.: 106 – 107 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.27 (m, 6H), 7.04 – 7.02 (m, 2H), 6.16 (d, *J* = 10.4, 1H), 3.40 (d, *J* = 12.2 Hz, 1H), 2.71 – 2.64 (m, 2H), 2.49 – 2.44 (m, 1H), 2.44 (s, 3H), 2.04 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 194.5, 172.0, 146.7, 145.4, 135.9, 133.7, 129.6, 128.9, 128.8, 128.7, 128.5, 128.1, 64.5, 51.6, 48.8, 35.2, 25.0, 21.7. IR (in KBr): 3128, 2361, 1740, 1684, 1399, 1357, 1169, 1132, 1086 cm^{-1}. HRMS (EI) for $C_{22}H_{21}NO_4SNa$ $[M+Na]^+$: calcd 418.1083, found 418.1082.

3,7a-Dimethyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3aq)



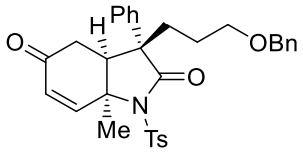
(0.5 mmol *α*-diazoketone), 32.0 mg, 96% isolated yield, white solid. M.P.: 99 – 100 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.29 (m, 1H), 6.08 (d, *J* = 10.4 Hz, 1H), 2.80 – 2.75 (m, 1H), 2.61 – 2.56 (m, 1H), 2.45 (s, 3H), 2.32 – 2.24 (m, 1H), 2.23 – 2.17 (m, 1H), 1.95 (s, 3H), 1.11 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 194.6, 174.2, 147.2, 145.3, 136.1, 129.6, 128.5, 128.2, 64.7, 48.2, 39.6, 35.6, 24.8, 21.7, 12.1. IR (in KBr): 3129, 1735, 1685, 1651, 1400, 1171, 1087, 736, 671 cm^{-1}. HRMS (EI) for $C_{17}H_{19}NO_4SNa$ $[M+Na]^+$: calcd 356.0927, found 356.0922.

7a'-Methyl-1'-tosyl-1',2,3,3a',4',7a'-hexahydrospiro[indene-1,3'-indole]-2',5'-dione (3ar)



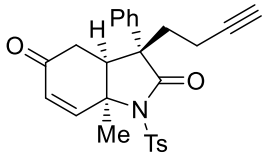
32.5 mg, 77% isolated yield, white solid. M.P.: 194 – 195 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 8.4 Hz, 2H), 7.55 (dd, *J* = 10.5, 1.8 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.23 – 7.19 (m, 2H), 7.17 – 7.13 (m, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.16 – 6.13 (m, 1H), 3.06 – 2.94 (m, 2H), 2.84 – 2.77 (m, 1H), 2.74 – 2.67 (m, 1H), 2.42 (s, 3H), 2.37(d, *J* = 18.4 Hz, 1H), 2.05 (s, 3H), 2.03 – 1.94 (m, 2H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 194.8, 174.8, 148.4, 145.2, 145.2, 140.5, 135.9, 129.5, 128.6, 128.6, 128.5, 126.8, 124.9, 122.5, 63.6, 59.7, 48.5, 33.4, 33.4, 30.7, 26.7, 21.6. IR (in KBr): 1734, 1684, 1394, 1358, 1269, 1211, 1171, 1087, 912 cm^{-1}. HRMS (EI) for $C_{24}H_{23}NO_4SNa$ $[M+Na]^+$: calcd 444.1240, found 444.1241.

3-(3-(Benzyloxy)propyl)-7a-methyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (3as)



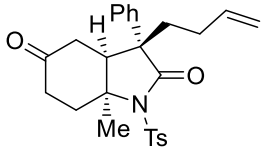
47.9 mg, 65% isolated yield, white solid. M.P.: 184 – 185 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 10.5 Hz, 1H), 7.37 – 7.21 (m, 10H), 7.10 – 7.08 (m, 2H), 6.19 (d, *J* = 10.5 Hz, 1H), 4.38 – 4.31 (m, 2H), 3.22 – 3.11 (m, 2H), 2.84 – 2.81 (m, 1H), 2.63 – 2.50 (m, 2H), 2.42 (s, 3H), 2.04 – 1.92(m, 1H), 1.78 – 1.70 (m, 1H), 1.76 (s, 3H), 1.36 – 1.22 (m, 2H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.5, 174.7, 148.4, 145.2, 139.5, 138.5, 135.7, 129.4, 129.0, 128.9, 128.6, 128.3, 127.4, 127.4, 126.9, 72.5, 69.5, 62.8, 55.7, 52.7, 34.0, 28.0, 28.0, 24.2, 21.6. IR (in KBr): 3128, 2361, 1733, 1685, 1399, 1359, 1170, 1086, 736 cm^{-1}. HRMS (EI) for $C_{32}H_{33}NO_5SNa$ $[M+Na]^+$: 566.1972, found 566.1969.

3-(But-3-yn-1-yl)-7a-methyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione (3at)



(0.5 mmol *α*-diazoketone), 43.1 mg, 96% isolated yield, white solid. M.P.: 113 – 114 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 10.5, 1H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.25 (m, 3H), 7.09 – 7.07 (m, 2H), 6.22 (d, *J* = 10.5 Hz, 1H), 2.84 (t, *J* = 6.1 Hz, 1H), 2.68 – 2.62 (m, 1H), 2.52 – 2.47 (m, 1H), 2.47 (s, 3H), 2.11 – 1.92 (m, 3H), 1.85 (t, *J* = 2.5 Hz, 1H), 1.77 – 1.70 (m, 1H). 1.72 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 195.3, 174.2, 148.3, 145.5, 138.8, 135.5, 129.6, 129.2, 129.1, 128.1, 127.8, 126.7, 83.1, 68.8, 62.9, 55.5, 52.4, 34.3, 30.5, 27.9, 21.7, 13.6. IR (in KBr): 3128, 2362, 1684, 1651, 1559, 1541, 1400, 1168, cm^{-1}. HRMS (EI) for $C_{26}H_{25}NO_4SNa$ $[M+Na]^+$: calcd 470.1397, found 470.1394.

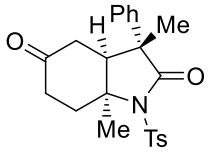
3-(But-3-en-1-yl)-7a-methyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione (3au)



41.4 mg, 92% yield, white solid, **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 8.3 Hz, 2H), 7.56 (d, *J* = 10.4 Hz, 1H), 7.37 – 7.35 (m, 2H), 7.33 – 7.29 (m, 2H), 7.27 – 7.24 (m, 1H), 7.09 (d, *J* = 7.4 Hz, 2H), 6.20 (d, *J* = 10.5 Hz, 1H), 5.54 – 5.44 (m, 1H), 4.80 (d, *J* = 10.2 Hz, 1H), 4.72 (d, *J* = 17.0 Hz, 1H). 4.89 –

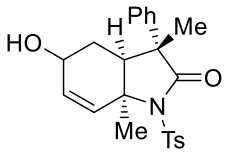
4.66 (m, 2H), 2.81 (t, *J* = 5.8 Hz, 1H), 2.63 – 2.51 (m, 2H), 2.46 (s, 3H), 1.92 – 1.86 (m, 1H), 1.80 (s, 3H), 1.74 – 1.64 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 195.6, 174.5, 148.4, 145.3, 139.2, 137.2, 135.5, 129.5, 129.1, 129.0, 128.7, 127.5, 126.9, 114.8, 62.8, 55.8, 52.8, 34.0, 30.1, 28.1, 28.0, 21.7. HRMS (EI) for $C_{26}H_{29}NO_4SNa$ $[M+Na]^+$: calcd 474.1710, found 474.1713.

3,7a-Dimethyl-3-phenyl-1-tosylhexahydro-2*H*-indole-2,5(3*H*)-dione (5)



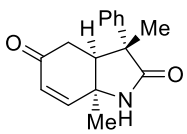
80.5 mg, 98% isolated yield, white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.99 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.13 (m, 3H), 6.81 – 6.78 (m, 2H), 2.77 – 2.69 (m, 2H), 2.56 – 2.40 (m, 7H), 2.35 – 2.24 (m, 1H), 1.39 (s, 3H), 1.29 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 210.1, 175.5, 145.3, 145.0, 135.6, 129.3, 129.3, 129.0, 127.2, 125.4, 65.6, 52.1, 49.9, 39.1, 35.4, 34.3, 25.5, 22.2, 21.7. IR (in KBr): 3129, 2361, 1700, 1651, 1558, 1541, 1508, 1400, 1164 cm^{-1}. HRMS (EI) for $C_{23}H_{25}NO_4SNa$ $[M+Na]^+$: calcd 434.1397, found 434.1394.

5-Hydroxy-3,7a-dimethyl-3-phenyl-1-tosyl-1,3,3a,4,5,7a-hexahydro-2*H*-indol-2-one (6)



40.7 mg, 99% isolated yield, white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.25 – 7.20 (m, 3H), 7.02 – 6.99 (m, 2H), 6.40 (dd, *J* = 10.2, 2.0 Hz, 1H), 5.97 (d, *J* = 10.2, 1H), 4.35 – 4.31 (m, 1H), 2.68 – 2.63 (m, 1H), 2.46 (s, 3H), 2.22 – 2.16 (m, 1H), 2.04 – 1.90 (m, 1H), 1.28 (s, 3H), 1.26 – 1.13 (m, 1H), 1.15 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 175.5, 145.3, 144.8, 136.0, 134.5, 130.7, 129.3, 129.0, 128.8, 127.1, 125.5, 66.4, 64.4, 53.2, 48.9, 33.4, 27.7, 22.7, 21.7. IR (in KBr): 1728, 1597, 1495, 1400, 1355, 1277, 1207, 1171, 1020 cm^{-1}. HRMS (EI) for $C_{23}H_{25}NO_4SNa$ $[M+Na]^+$: calcd 434.1397, found 434.1398.

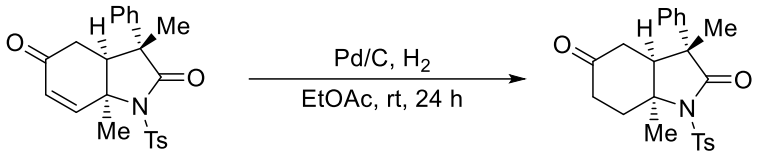
3,7a-Dimethyl-3-phenyl-1,3a,4,7a-tetrahydro-2*H*-indole-2,5(3*H*)-dione (7)



25.9 mg, 51% isolated yield, white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.84 (s, 1H), 7.40 – 7.36 (m, 2H), 7.33 – 7.26 (m, 3H), 6.64 (d, *J* = 10.3 Hz, 1H), 6.04 (d, *J* = 10.3 Hz, 1H), 2.88 – 2.85 (m, 1H), 2.65 – 2.55 (m, 2H), 1.55 (s,

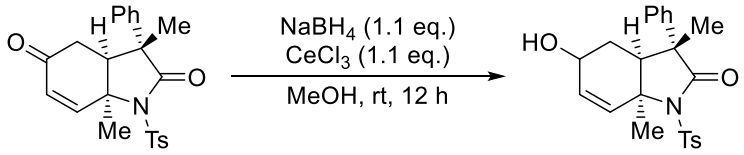
3H), 1.47 (s, 3H). **^{13}C NMR (**100 MHz, $CDCl_3$) δ = 196.4, 180.2, 150.2, 143.8, 128.7, 127.6, 127.1, 126.4, 54.6, 53.6, 53.2, 33.7, 27.4, 17.7. IR (in KBr): 3128, 2361, 1680, 1540, 1400, 1163, 739, cm^{-1}. HRMS (EI) for $C_{16}H_{17}NNaO_2$ $[M+Na]^+$: calcd 278.1151, found 278.1152.

5. Demonstration of the Synthetic Utility



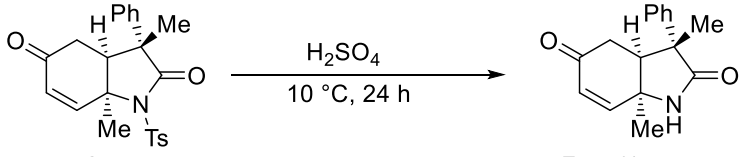
3aa **5:** 95% yield

Pd/C (8 mg, 10% mass concentration) was added to a solution of compound **3aa** (0.2 mmol, 81.9 mg) in 2 mL of ethyl acetate. The mixture was placed under H_2 atmosphere. After the reaction was left to stir at room temperature for 24 h, the mixture was filtered over Celite and washed with dichloromethane. The crude was purified by SepaBean® machine T (petroleum ether/ EtOAc = 5:1) to afford the desired product **5** as a white solid (79 mg, 95% yield).



3aa **6:** 99% yield

A solution of **3aa** (41 mg, 0.1 mmol) and $CeCl_3$ (0.11 mmol) in MeOH (1.0 mL) was stirred at room temperature for 30 min. Then, $NaBH_4$ (0.11 mmol) was added at 0 °C and then the mixture was stirred for 12 h at room temperature. Reaction was quenched by 1M HCl aq. (1.0 mL). Organic layer was extracted with EtOAc (1.0 mL, three times), and dried over Na_2SO_4. Reaction mixture was dried in vacuo and purified by SepaBean® machine T (petroleum ether/EtOAc = 1:1) as an eluent to form pure product **6** as a white solid (40.6 mg, 99% yield, > 95:5 dr).

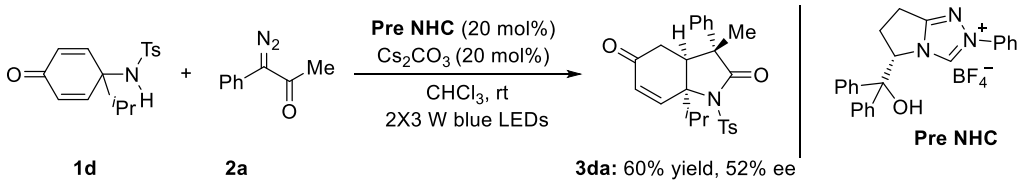


3aa **7:** 51% yield

3aa (41 mg, 0.1 mmol) and concentrated H_2SO_4 (1 mL) were added to a pressure tube. The reaction mixture was stirred at 10℃ for 24 h. Then the solution was added dropwise into Et_2O

with stirring, and ice-water was added to the solution. The aqueous layer was made alkaline by addition of NaOH(aq.) and was then extracted with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by SepaBean® machine T (petroleum ether/EtOAc, 1:1) to afford the pure product **7** in 55% yield (13.1 mg).

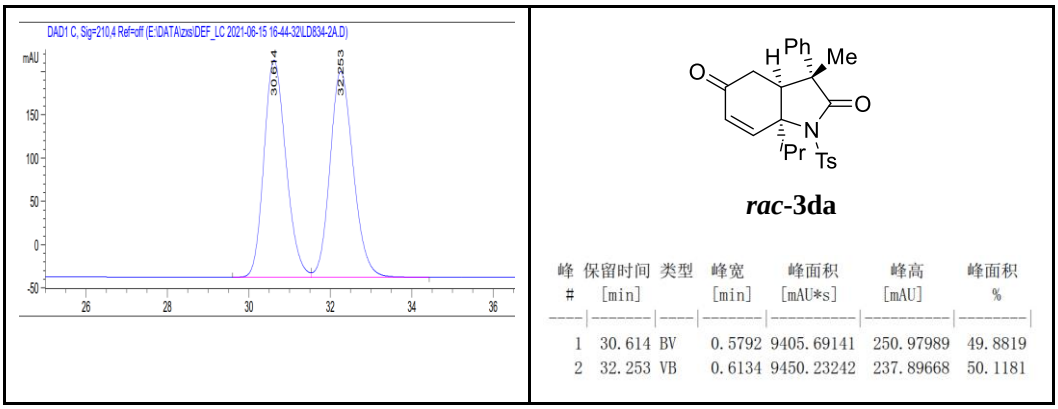
6. Preliminary Results on the Asymmetric [3+2] Cycloaddition



Under an argon atmosphere, a flame-dried 10 mL Schlenk tube equipped with a magnetic stir bar was charged with **Pre NHC** (20 mol%, 9.1 mg), Cs_2CO_3 (20 mol%, 6.52 mg) and 1 mL of $CHCl_3$, the solution was stirred for 30 mins at room temperature. Then **1d** (0.1 mmol, 30.5 mg) and **2a** (0.2 mmol, 32.06 mg) were added in one portion. The resulting solution was stirred under the irradiation of 2x3 W blue LEDs. Then the reaction mixture was stirred at this temperature. And the reaction was monitored by TLC.

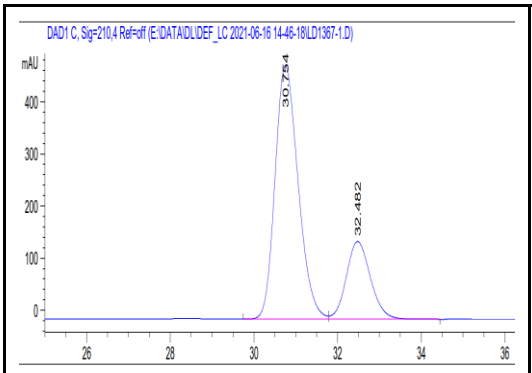
7a-Isopropyl-3-methyl-3-phenyl-1-tosyl-1,3a,4,7a-tetrahydro-2H-indole-2,5(3H)-dione (chiral 3da)

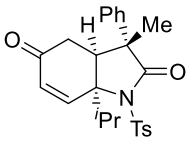
15 mg, 34% isolated yield, white solid; $[\alpha]$ ^{25}D = -3.4 (*c* = 1.0, $CHCl_3$); ee = 52%; determined by HPLC (Chiralpak AD column, hexane/*i*-PrOH, 90:10 v/v, flow rate 0.5 mL/min, λ = 210 nm, 25 ^oC). t_R (major) = 30.754 min, t_R (minor) = 32.482 min.



***rac*-3da**

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	30.614	BV	0.5792	9405.69141	250.97989	49.8819
2	32.253	VB	0.6134	9450.23242	237.89668	50.1181





***chiral*-3da**

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	30.754	BV	0.5933	1.86436e4	486.23584	75.7150
2	32.482	VB	0.6221	5979.77930	149.03690	24.2850

7. References

[1] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals, 4th ed.*; Pergamon Press: Oxford, **1997**.

[2] Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* 1978, **43**, 2923.

[3] J. J. Douglas, G. Churchill, A. M. Z. Slawin, D. J. Fox and A. D. Smith, *Chem. – Eur. J.*, 2015, **21**, 16354.

[4] B. L. Hodous, G. C. Fu, *J. Am. Chem. Soc.*, 2002, **124**, 10006.

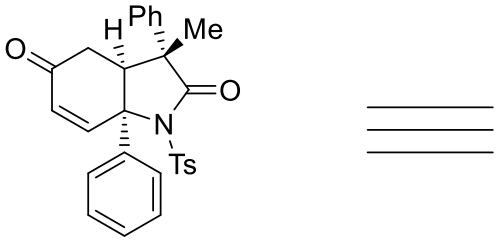
[5] P.-L. Shao, X.-Y. Chen, L.-H. Sun, *Tetrahedron Lett.*, 2010, **51**, 2316.

[6] L.-M. Baigrie, H.-R. Seiklay, T.T. Tidwell, *J. Am. Chem. Soc.*, 1985, **107**, 5391.

[7] M. Schmittel, H.-V. Seggern, *J. Am. Chem. Soc.*, 1993, **115**, 2165.

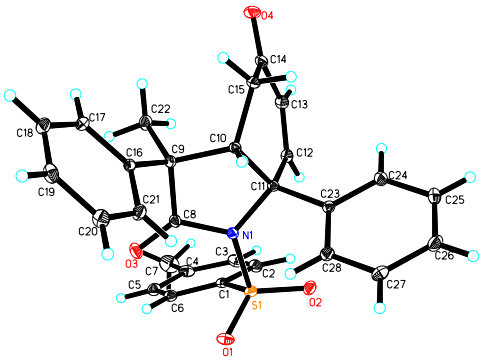
[8] Jin, H.; Zhang, Q. Li, E. Jia, P. Li, N. Huang, Y. *Org. Biomol. Chem.*, 2017, **15**, 7097.

8. X-Ray Structure of Product 3ga



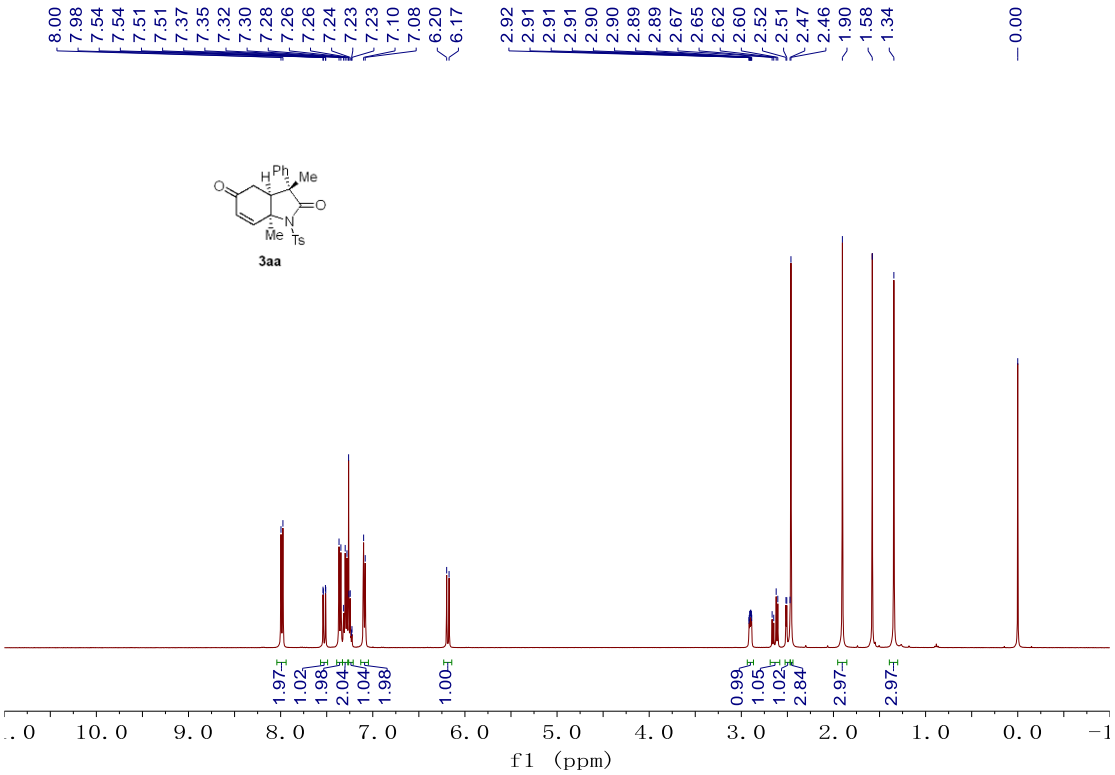
3ga

CCDC: 2061598

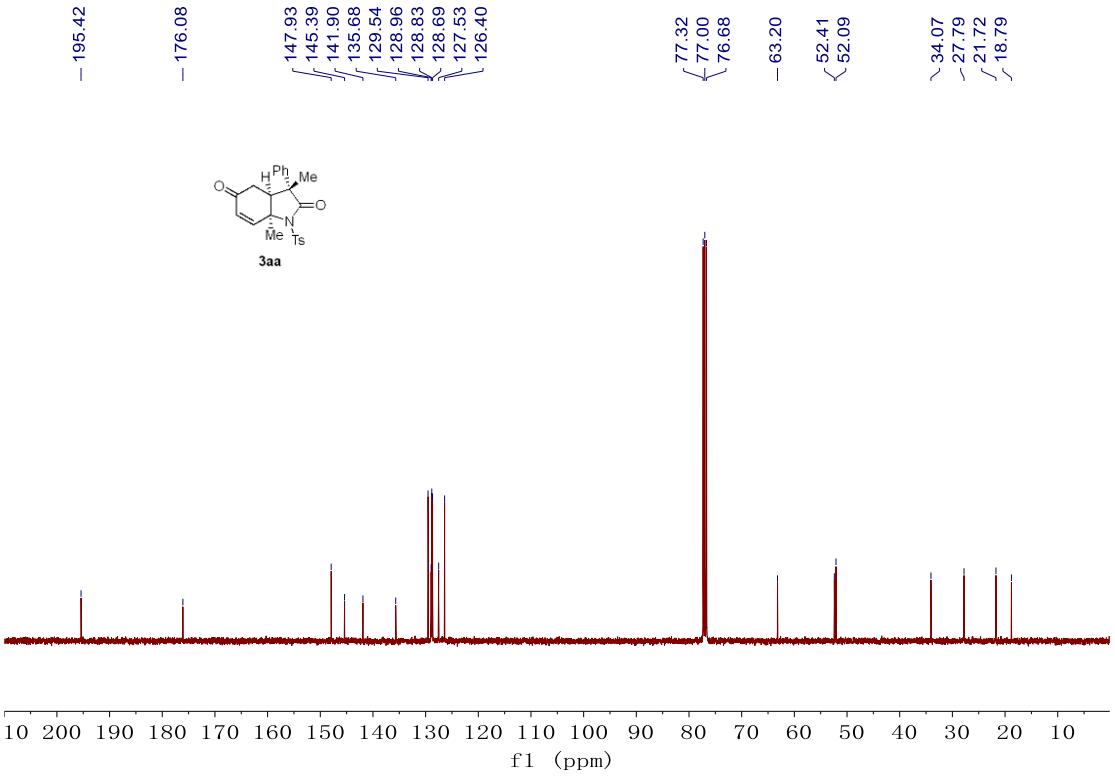


9. Copies of NMR Spectra of Products

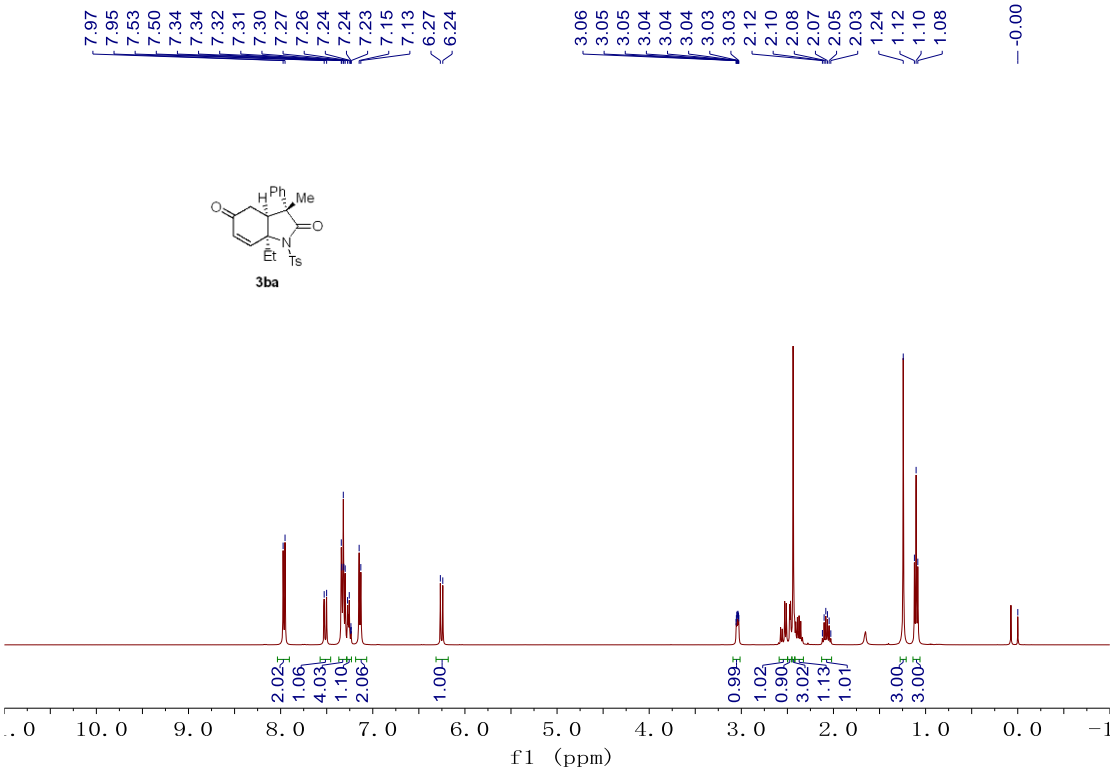
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aa**



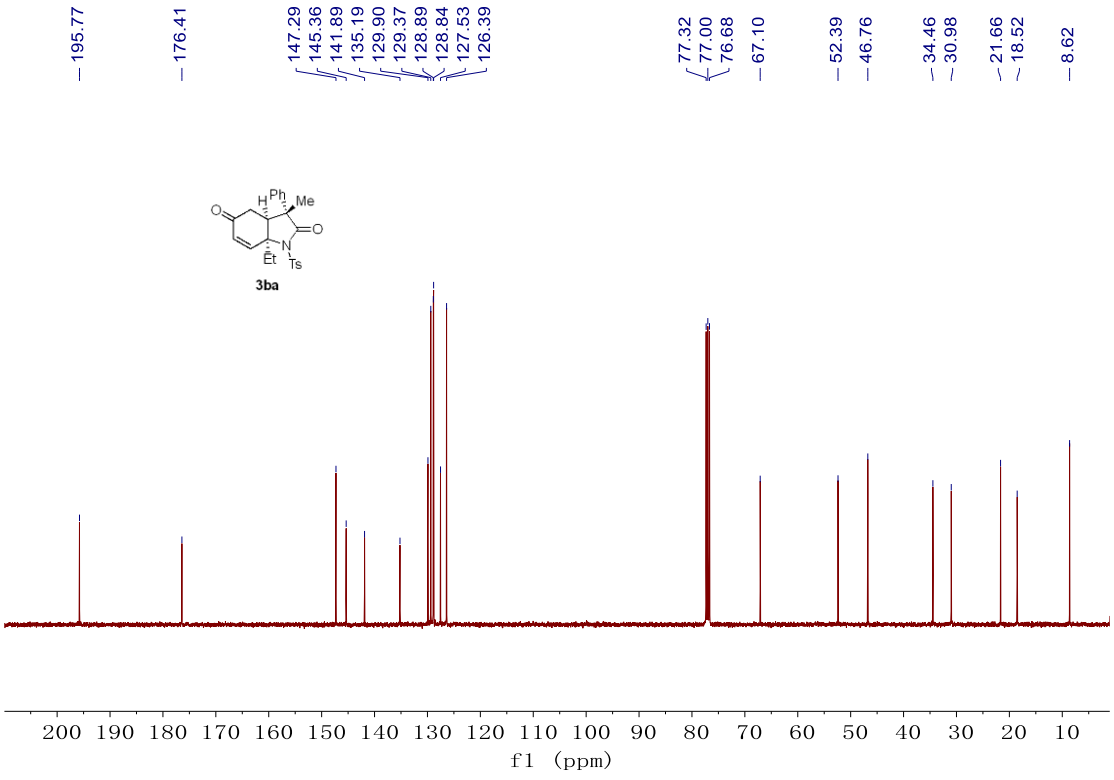
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3aa**



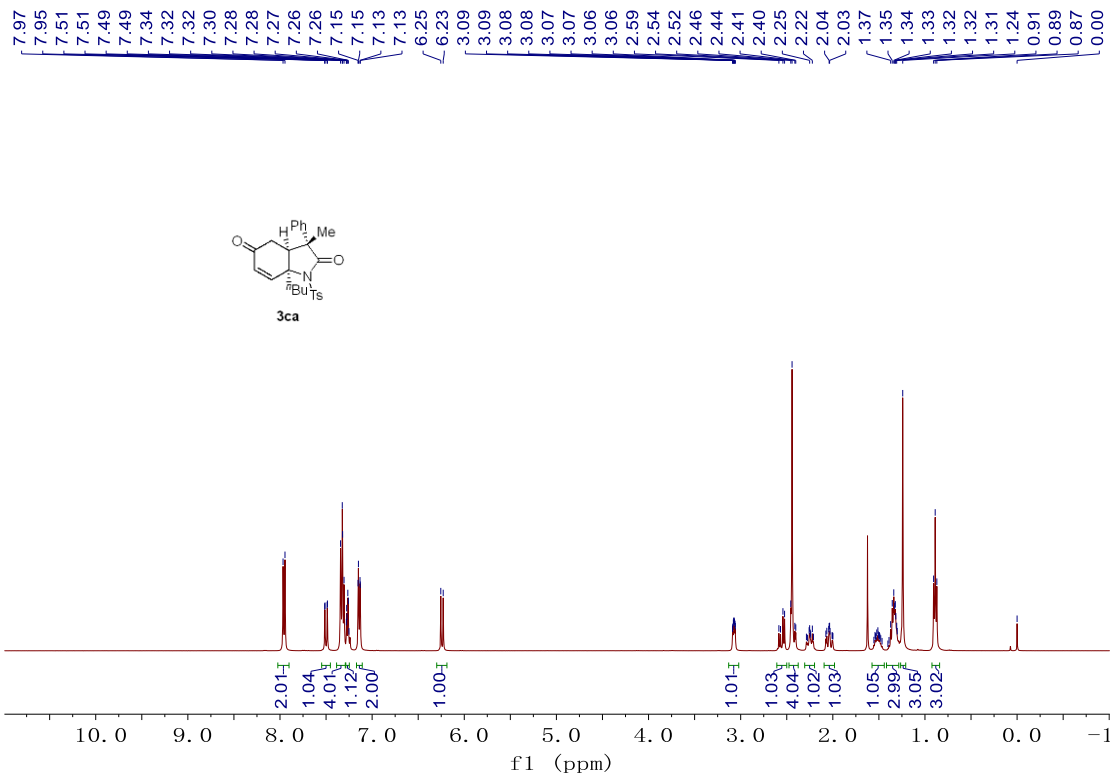
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ba**



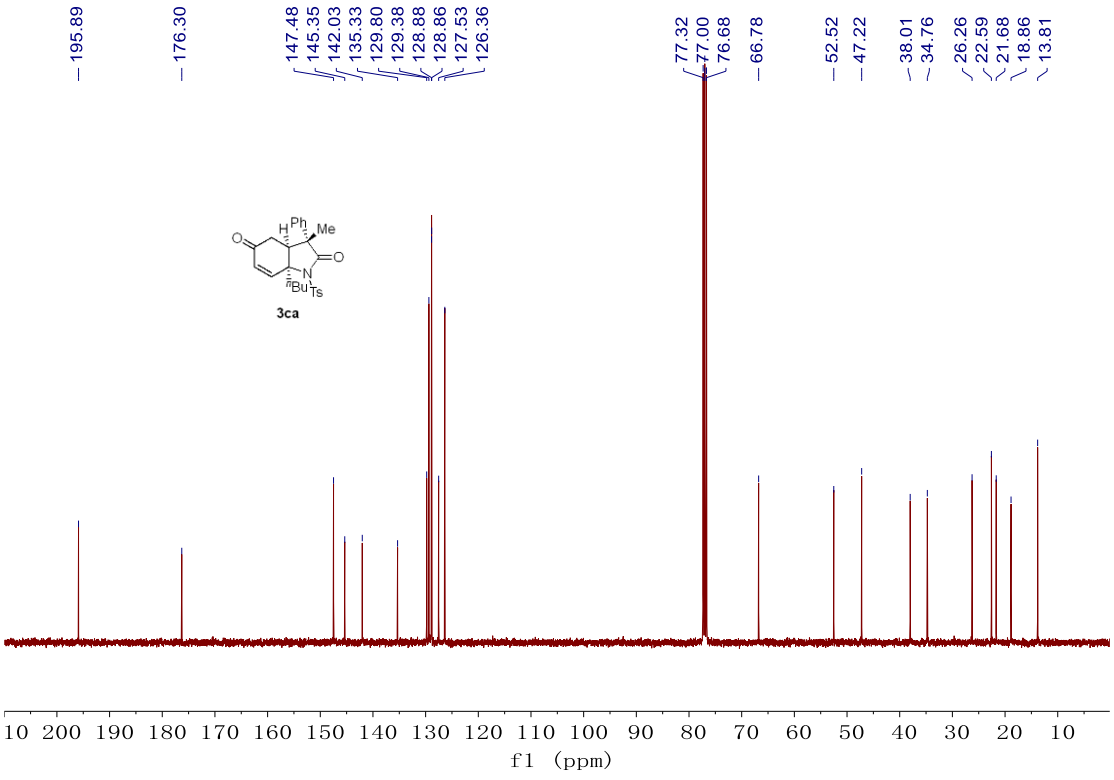
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ba**



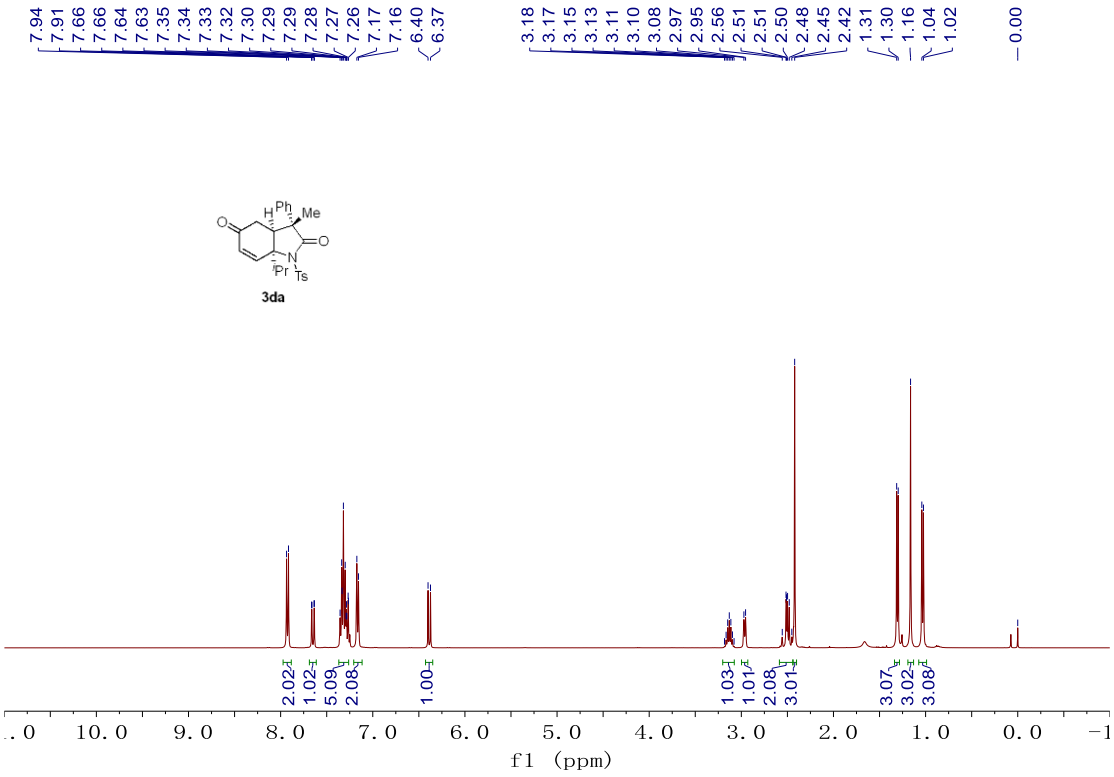
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ca**



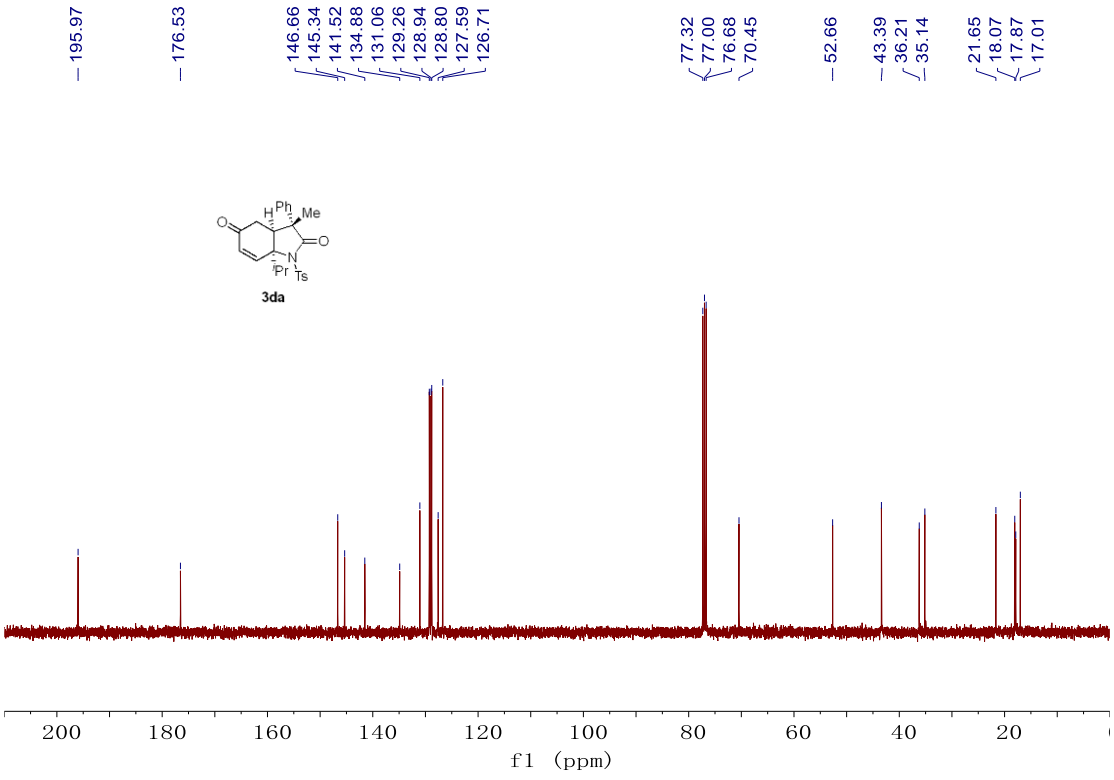
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ca**



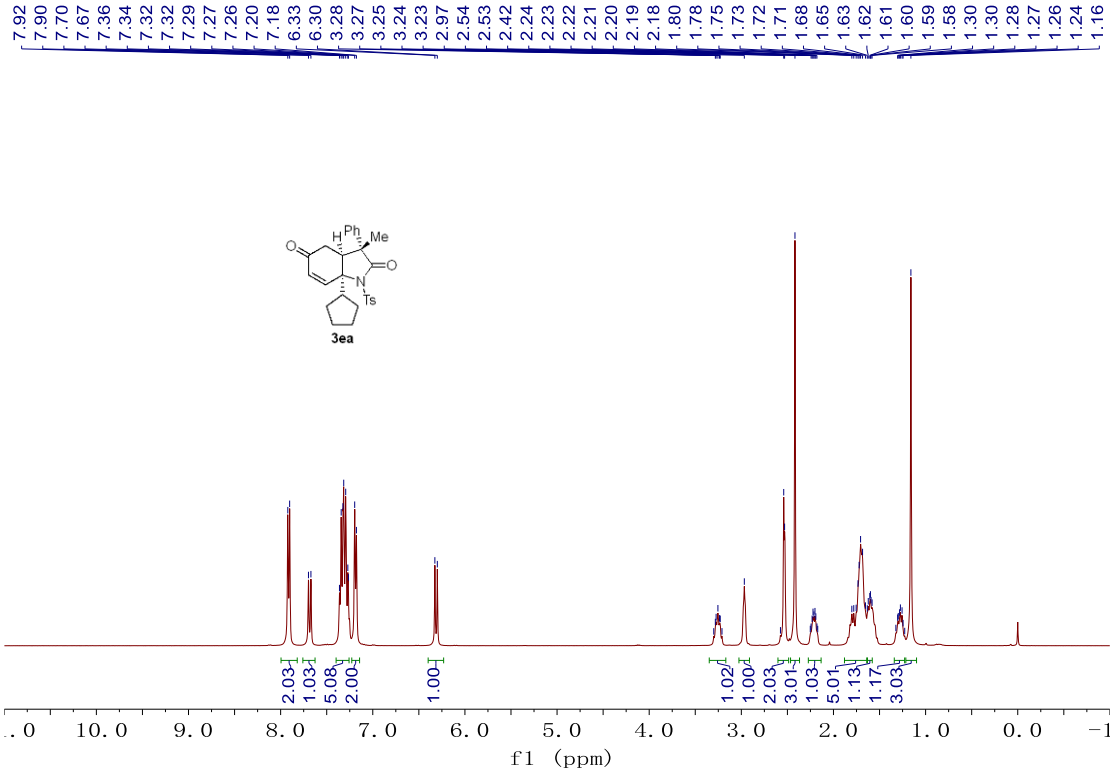
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3da**



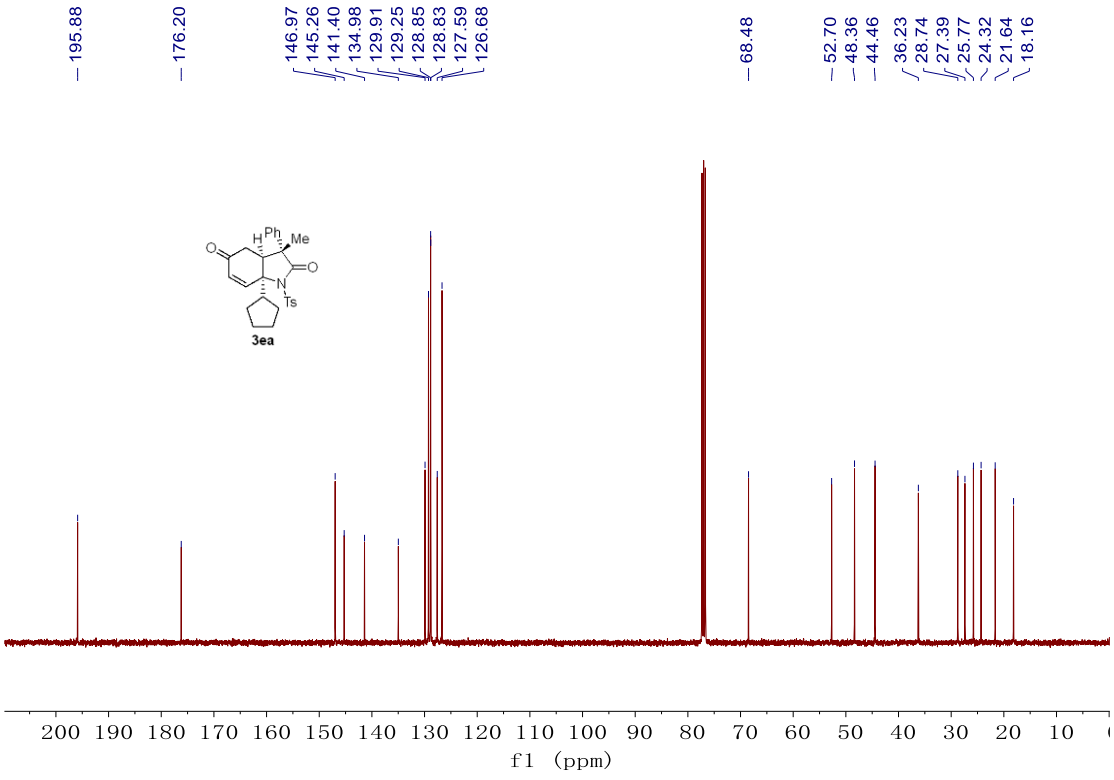
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3da**



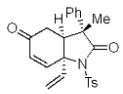
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ea**

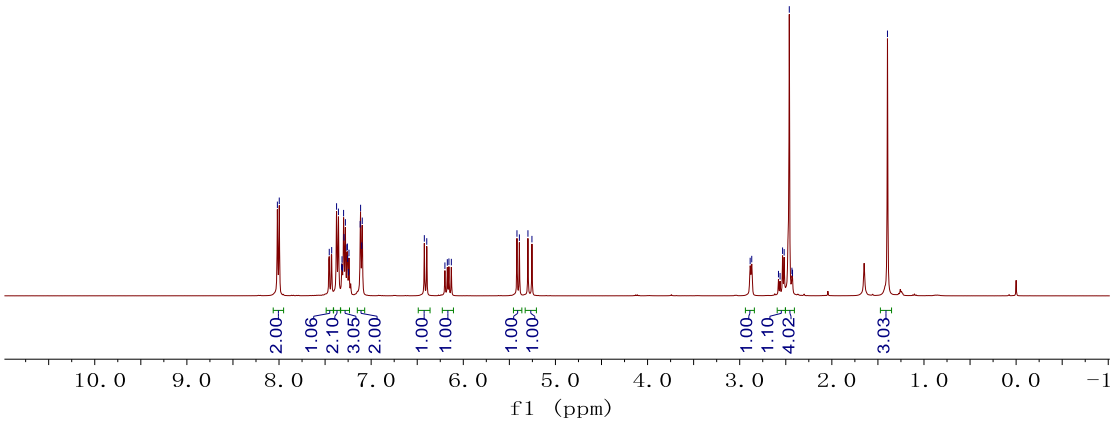


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ea**

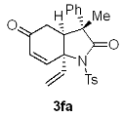


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3fa**

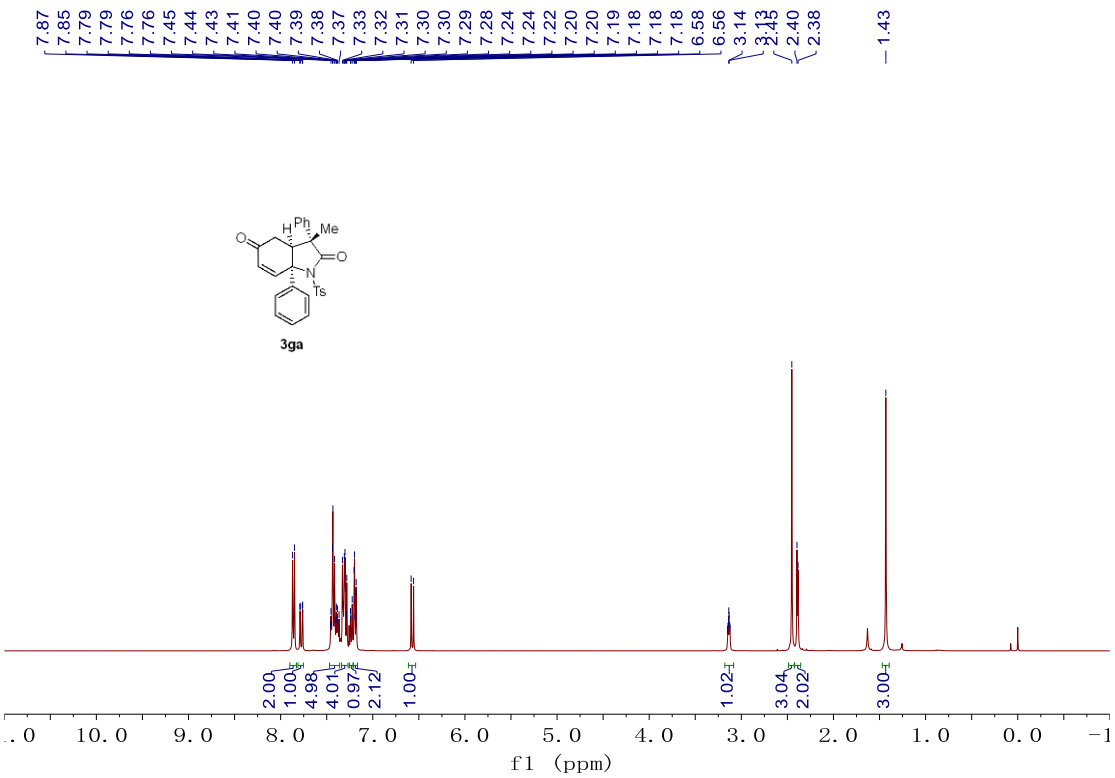




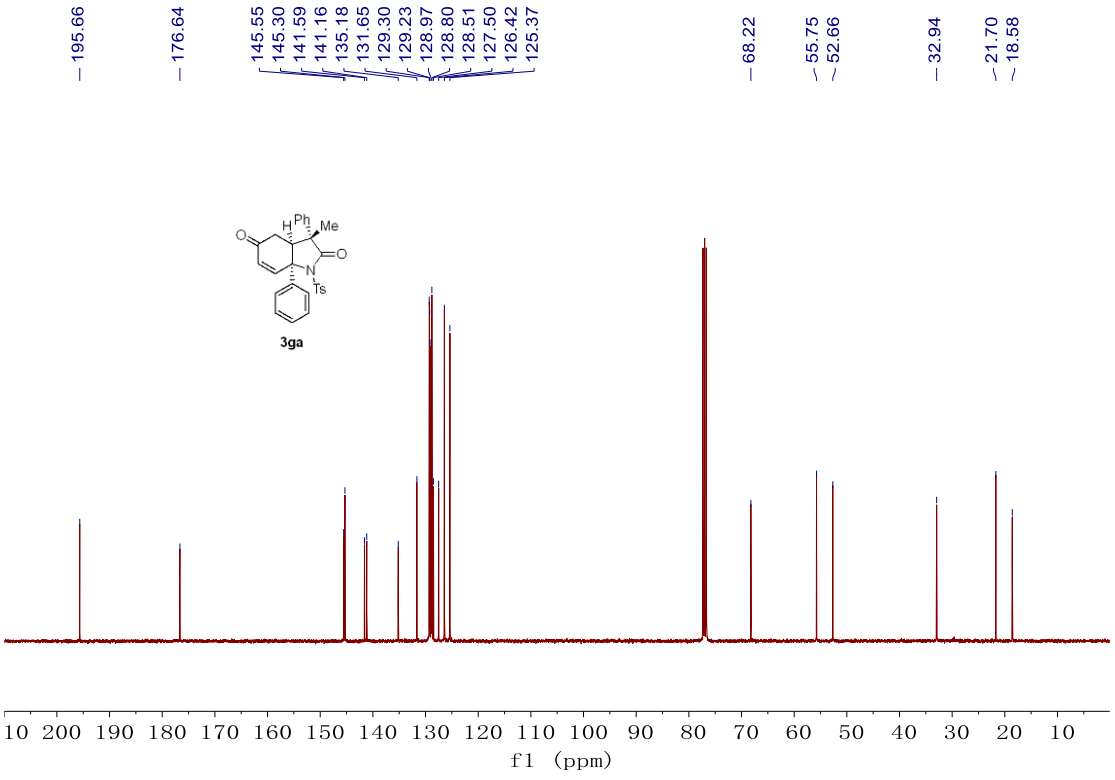
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3fa**



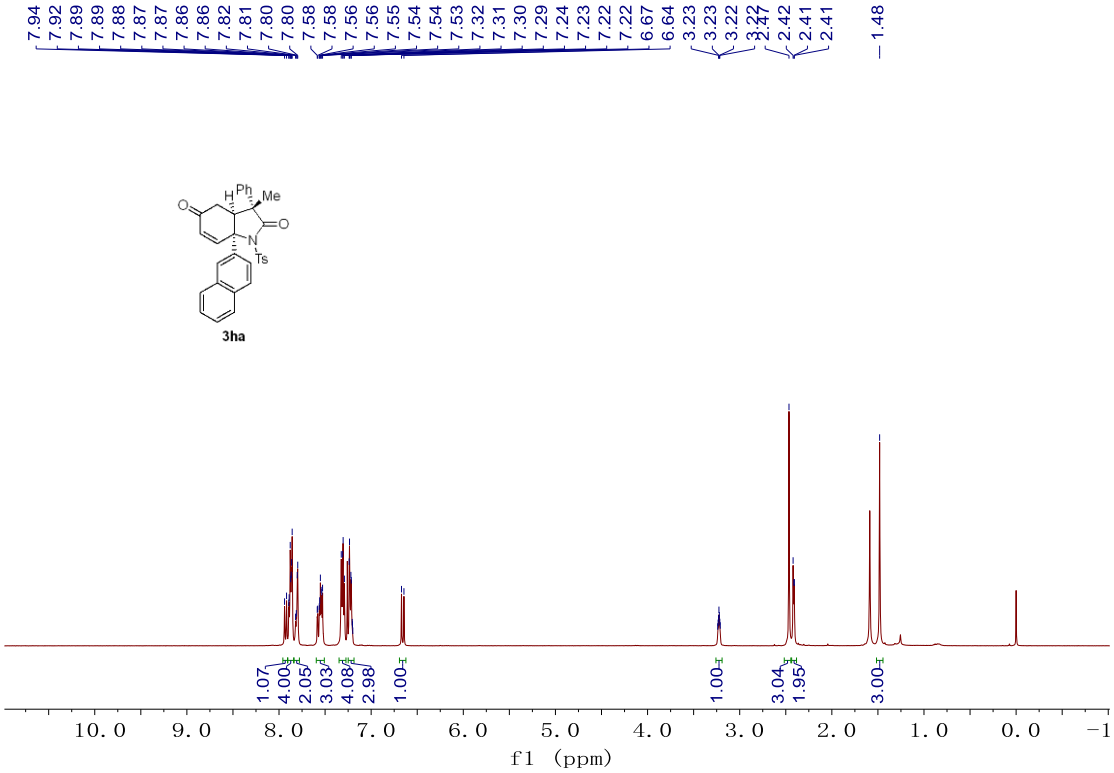
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ga**



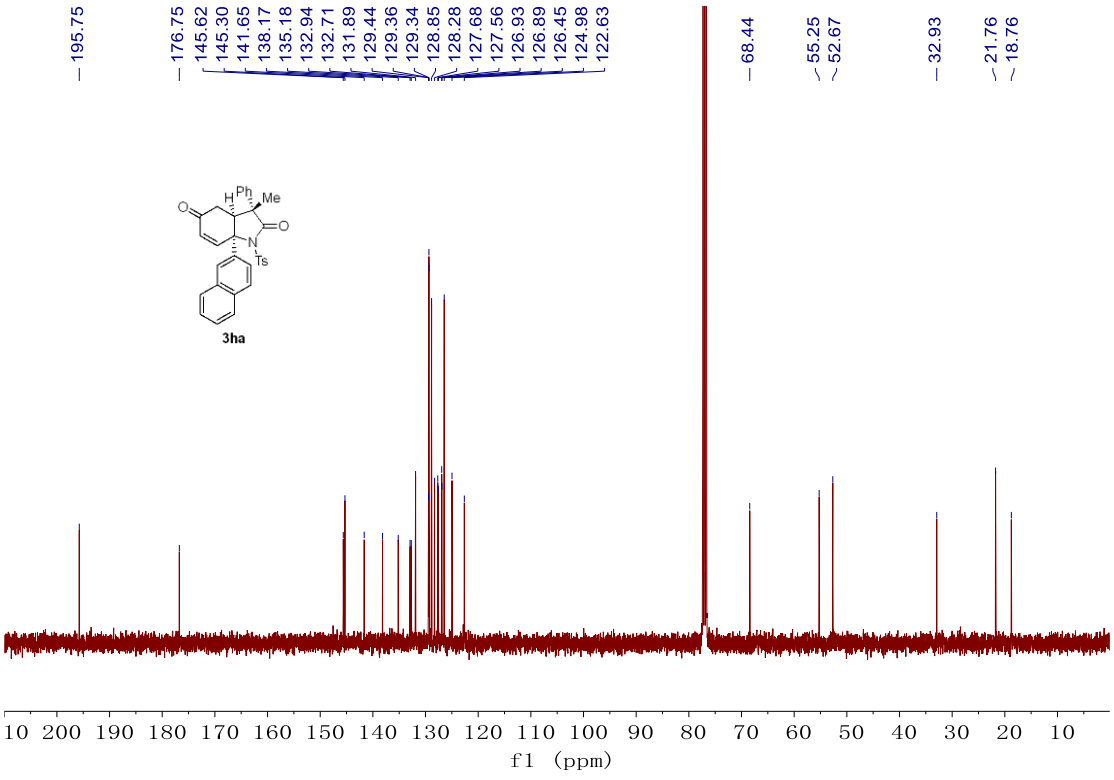
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ga**



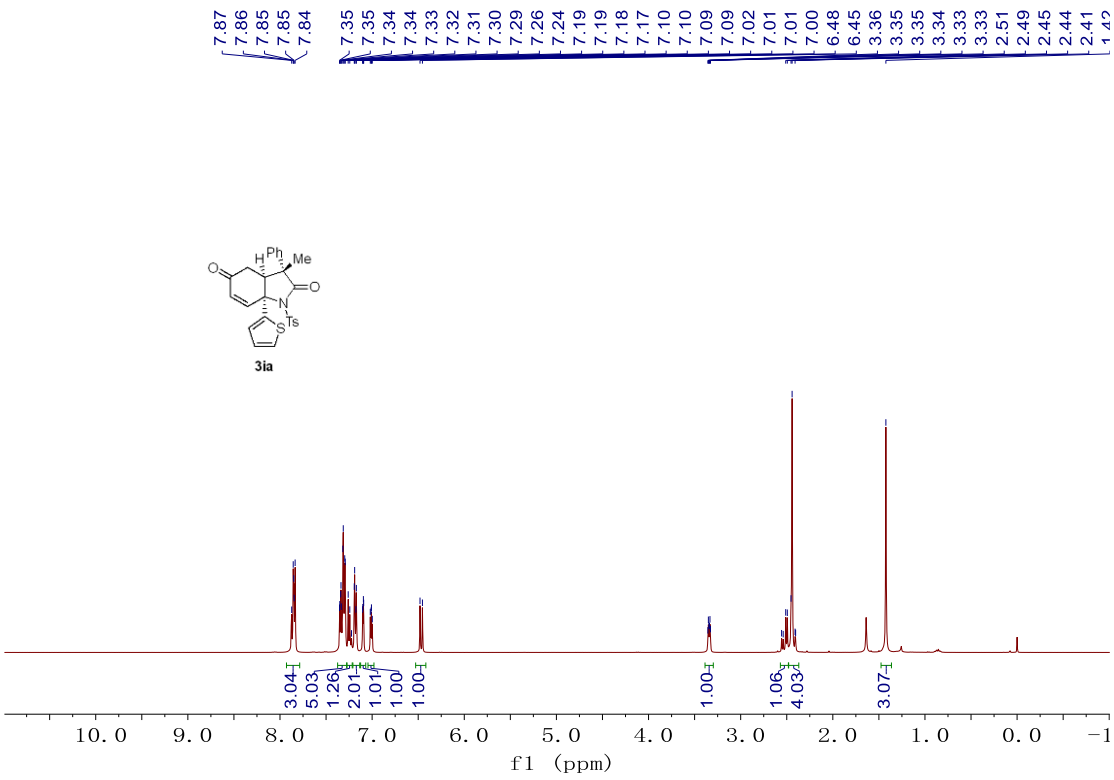
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ha**



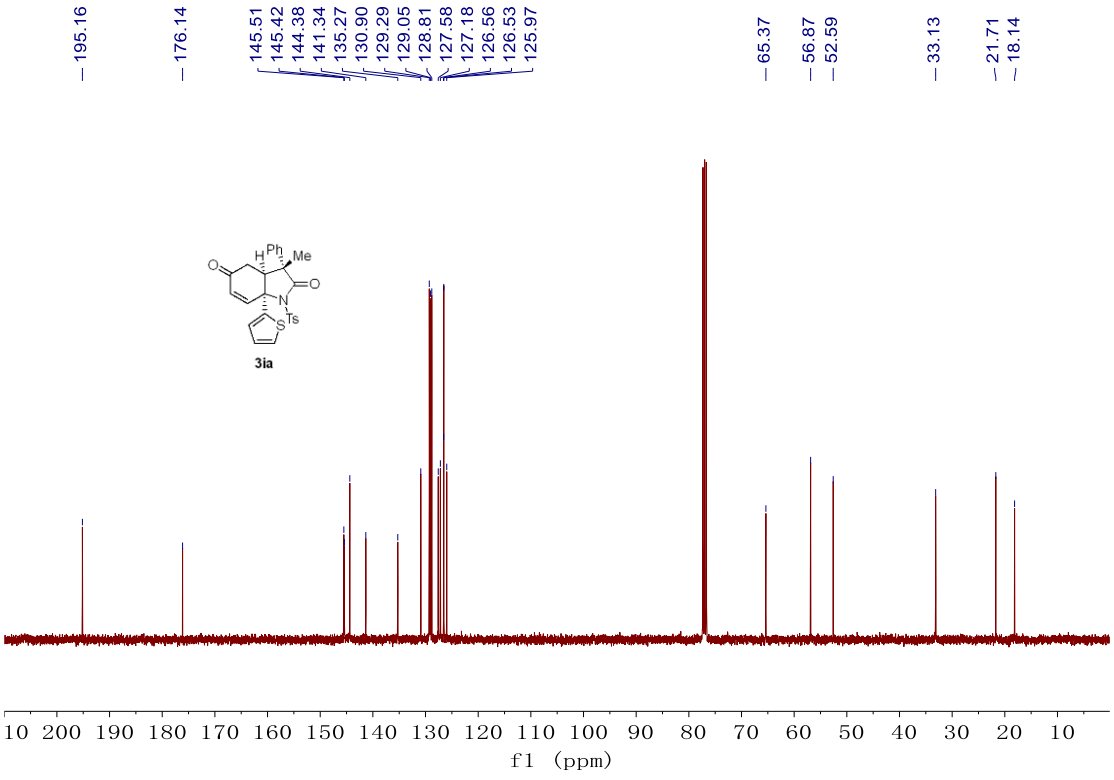
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ha**



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



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



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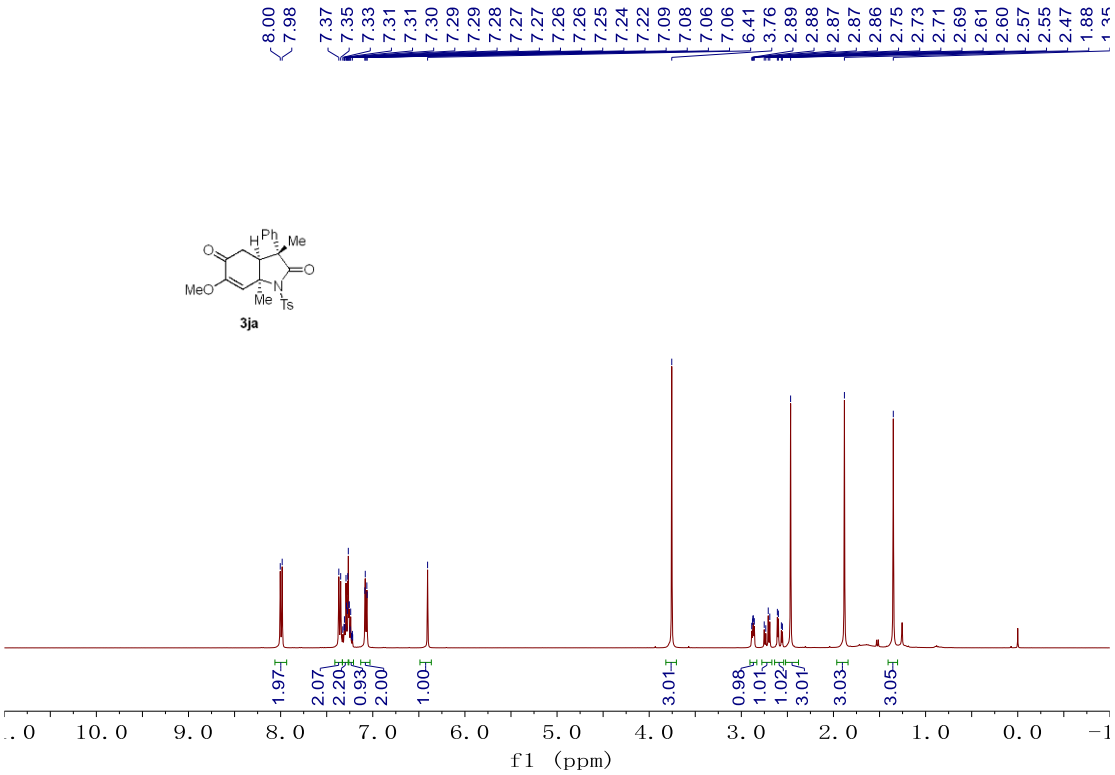
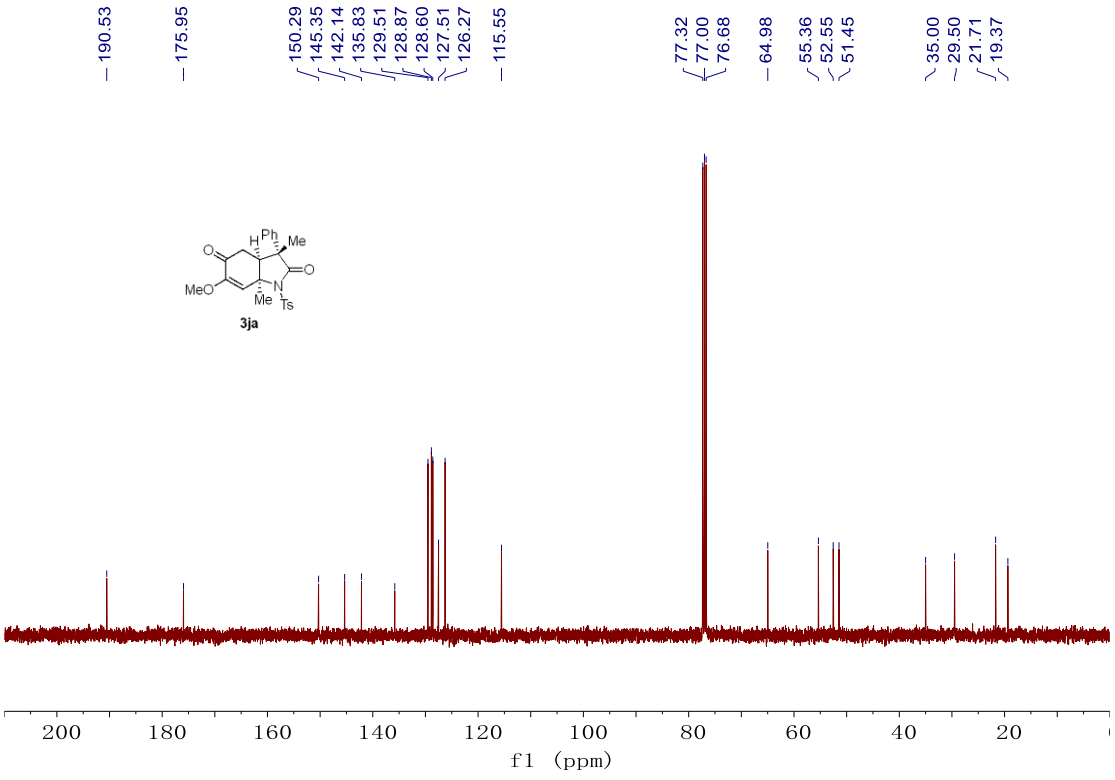
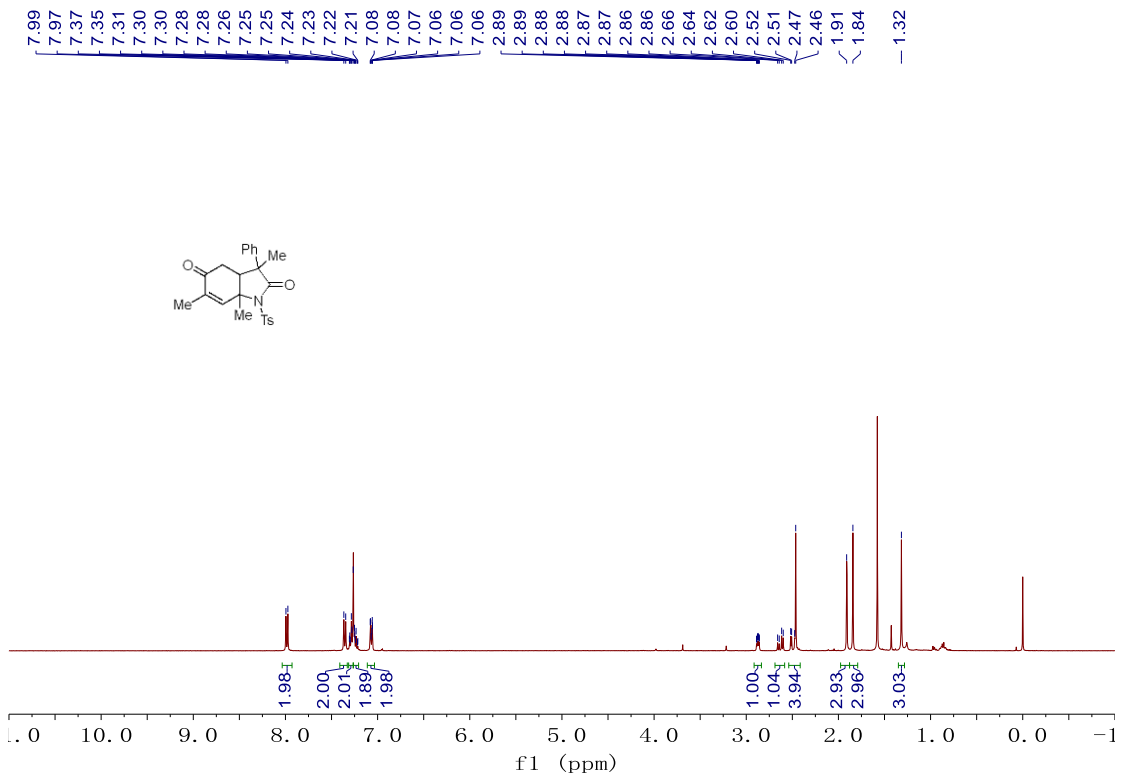


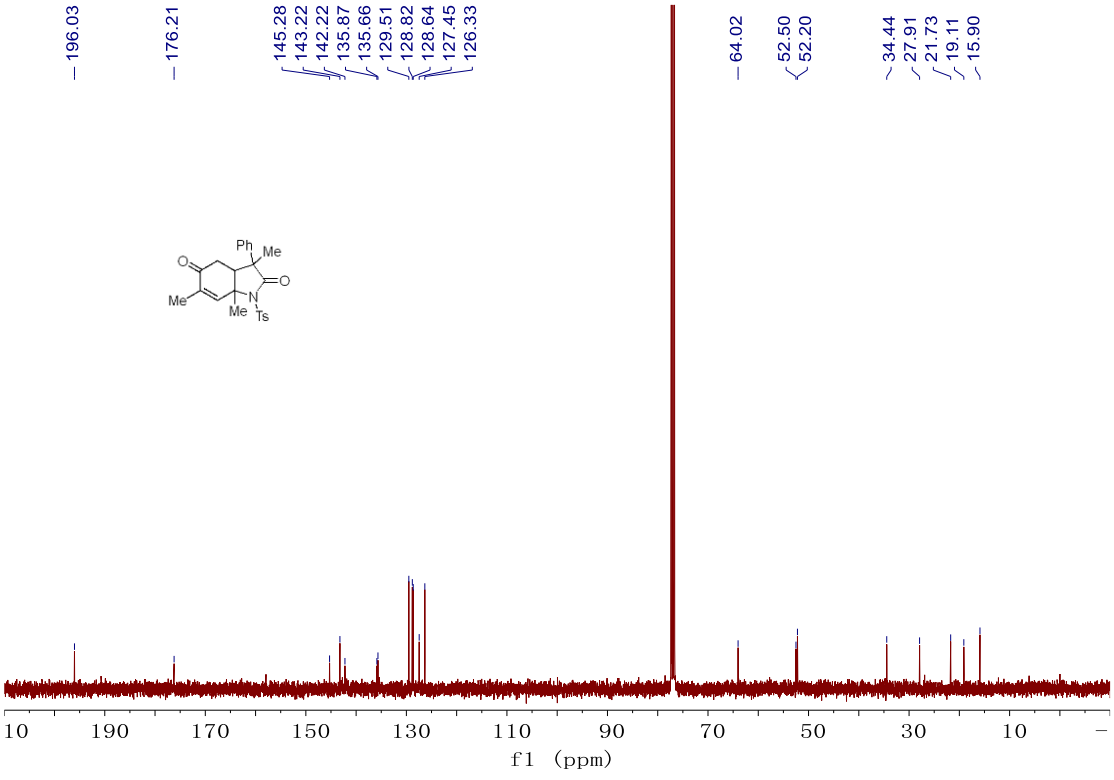
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ja**



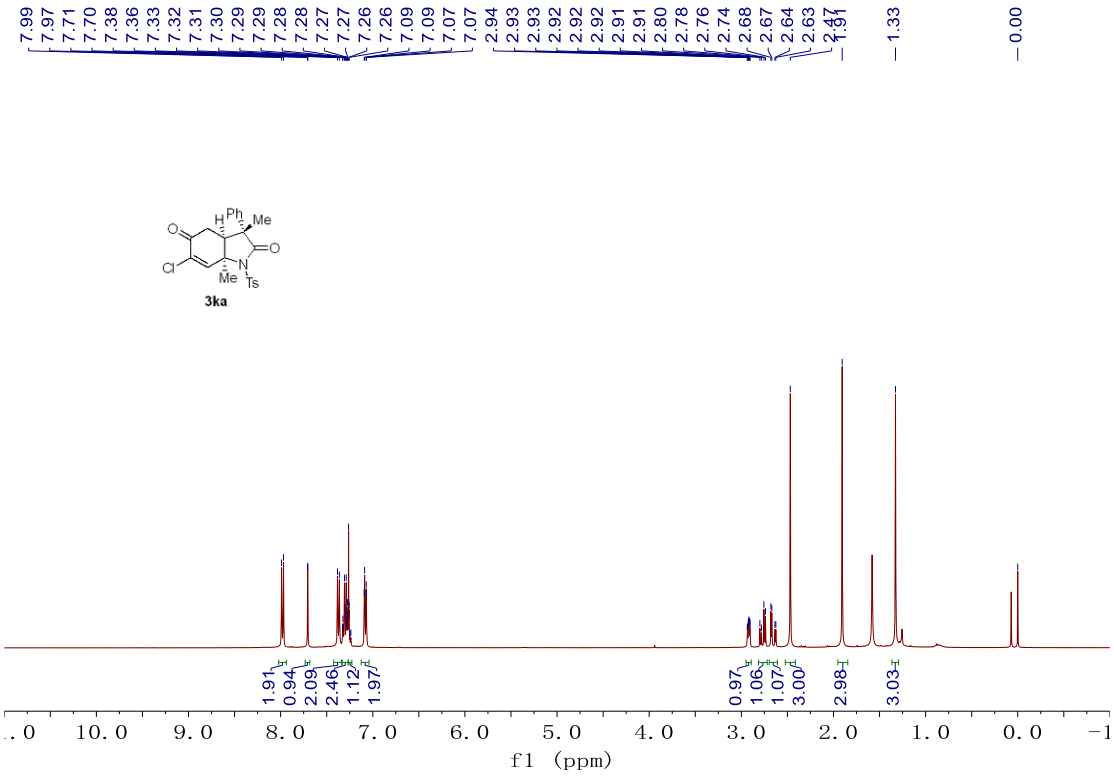
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ka**



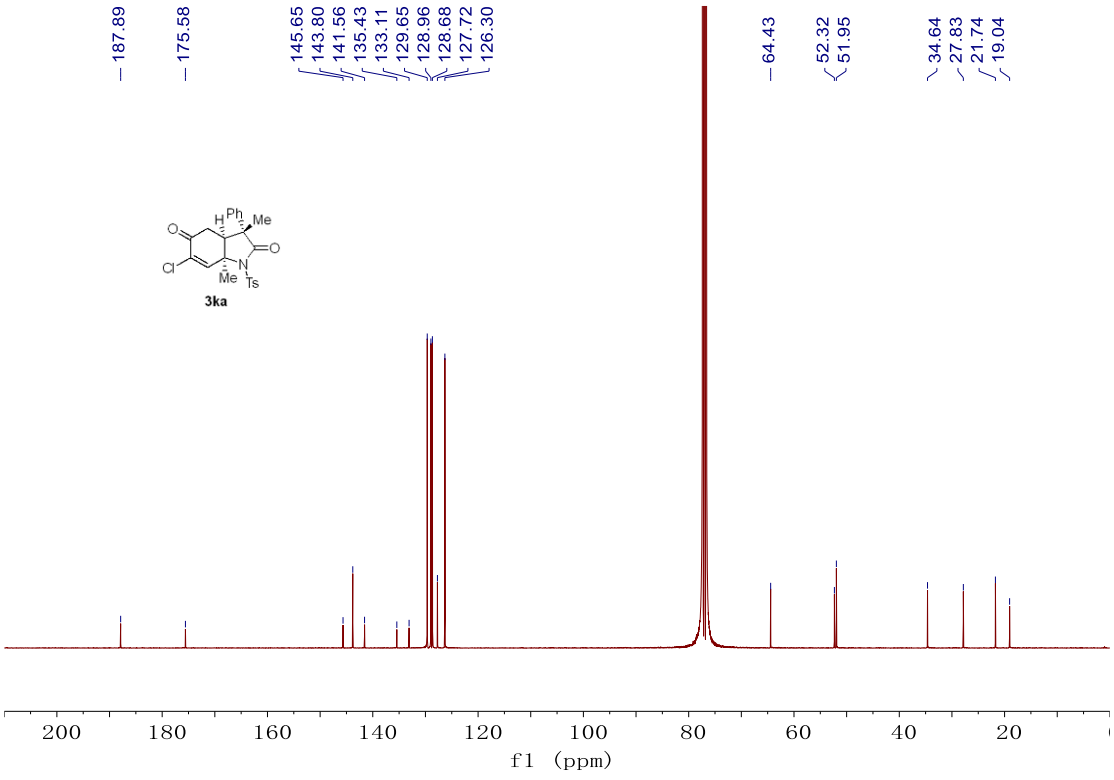
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ka**



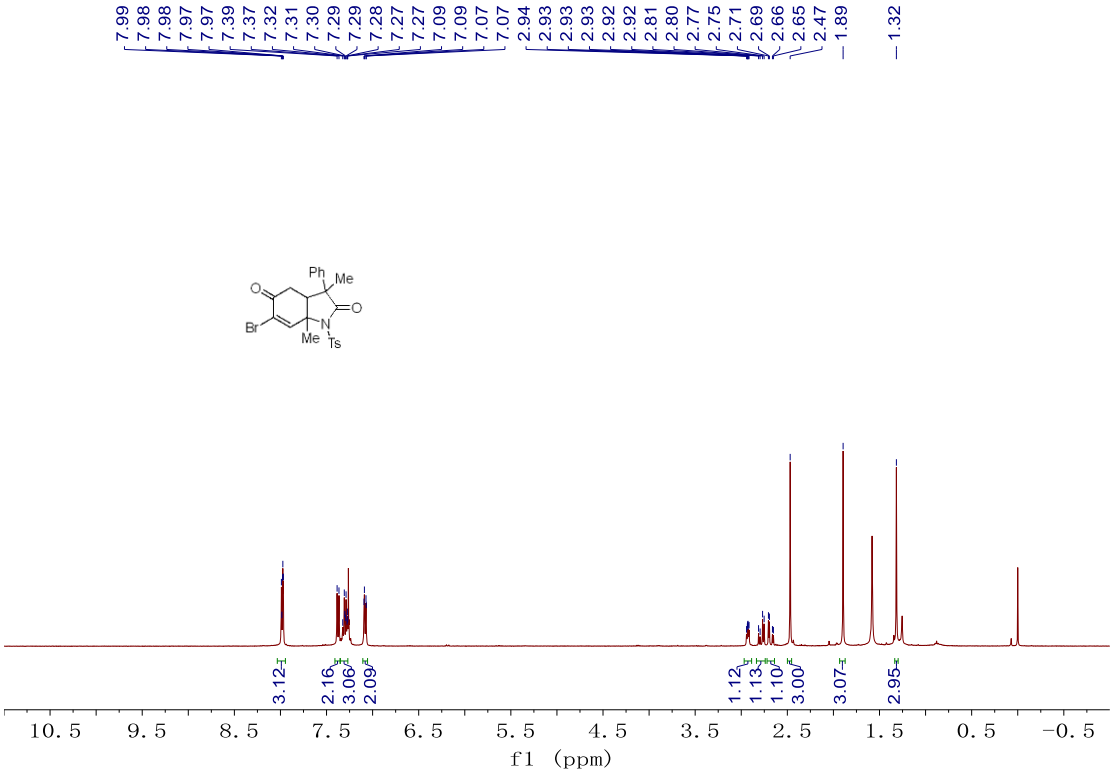
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3la**



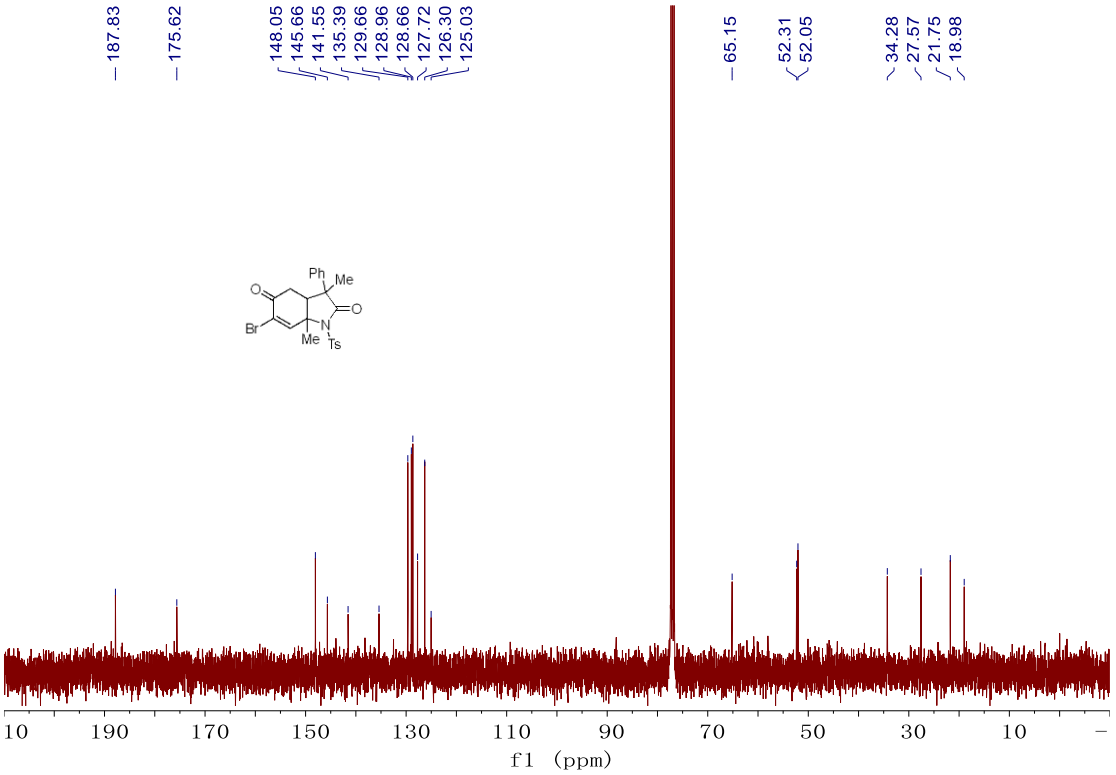
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3la**



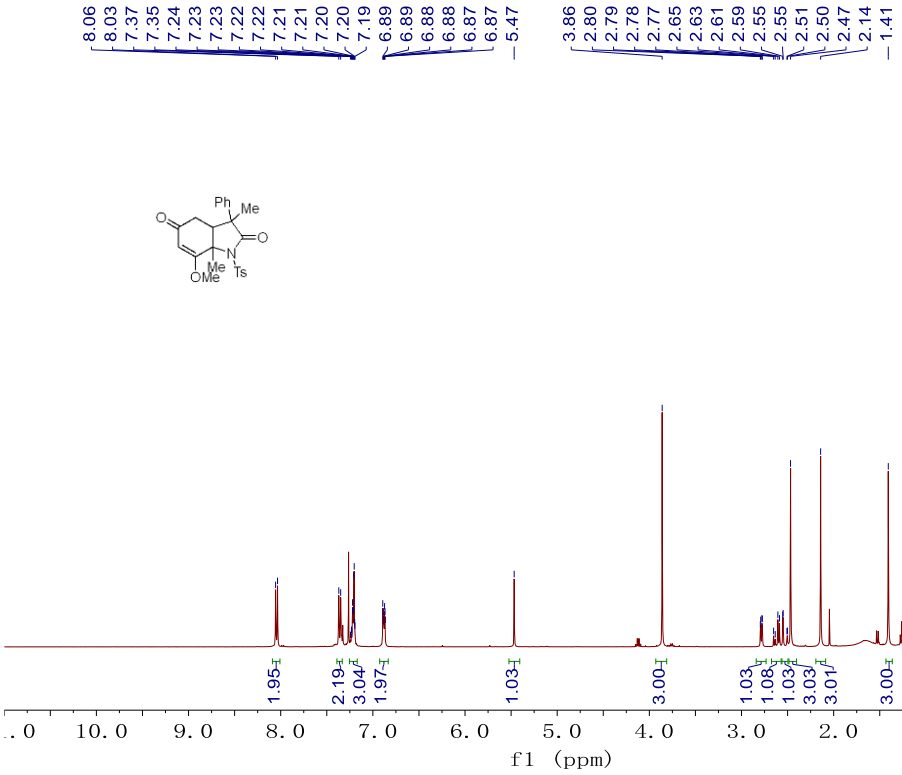
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ma**



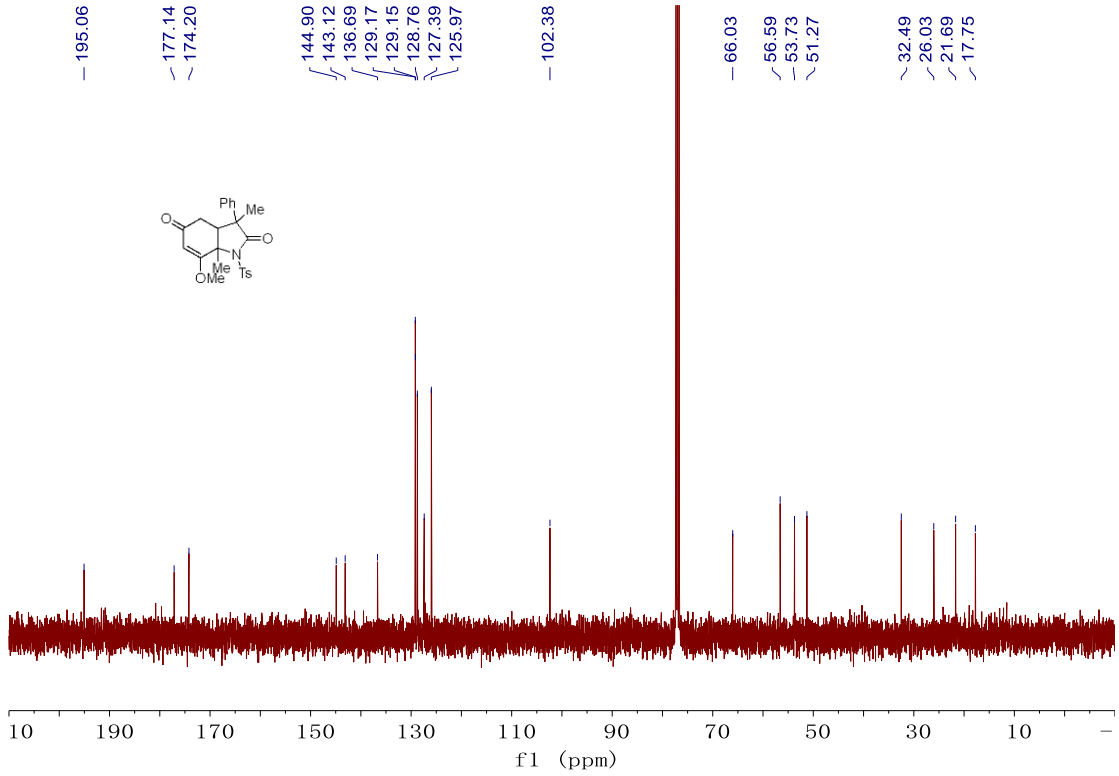
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ma**



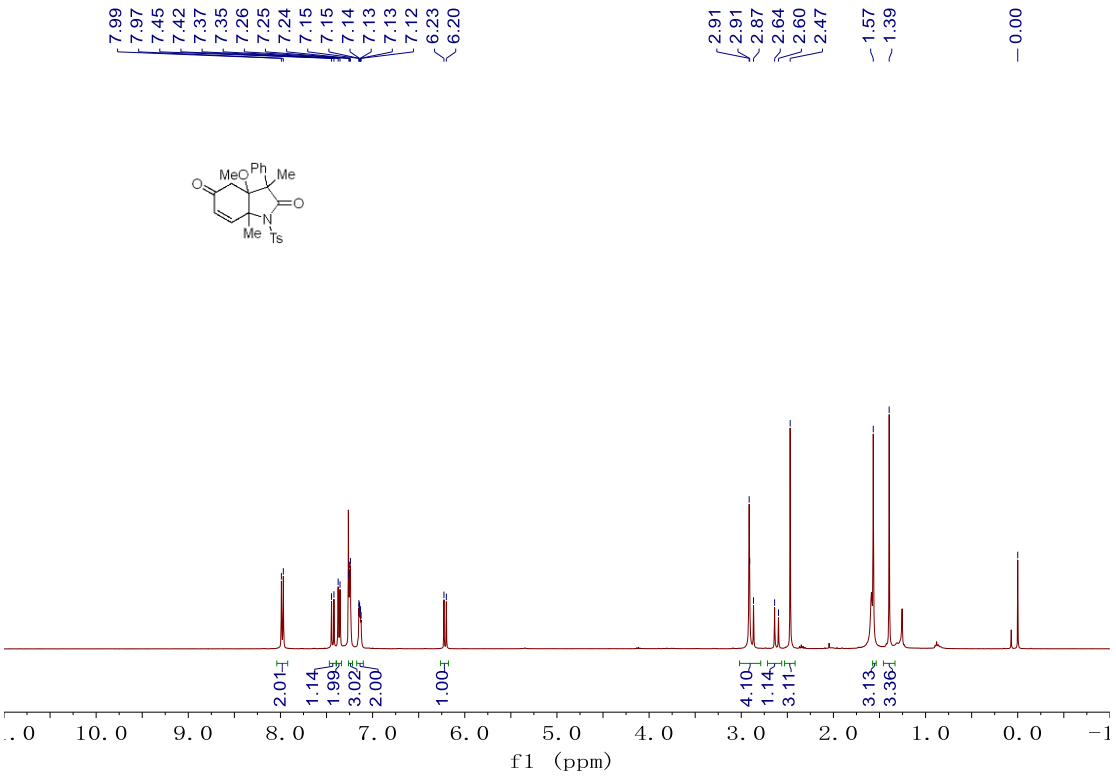
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3na**



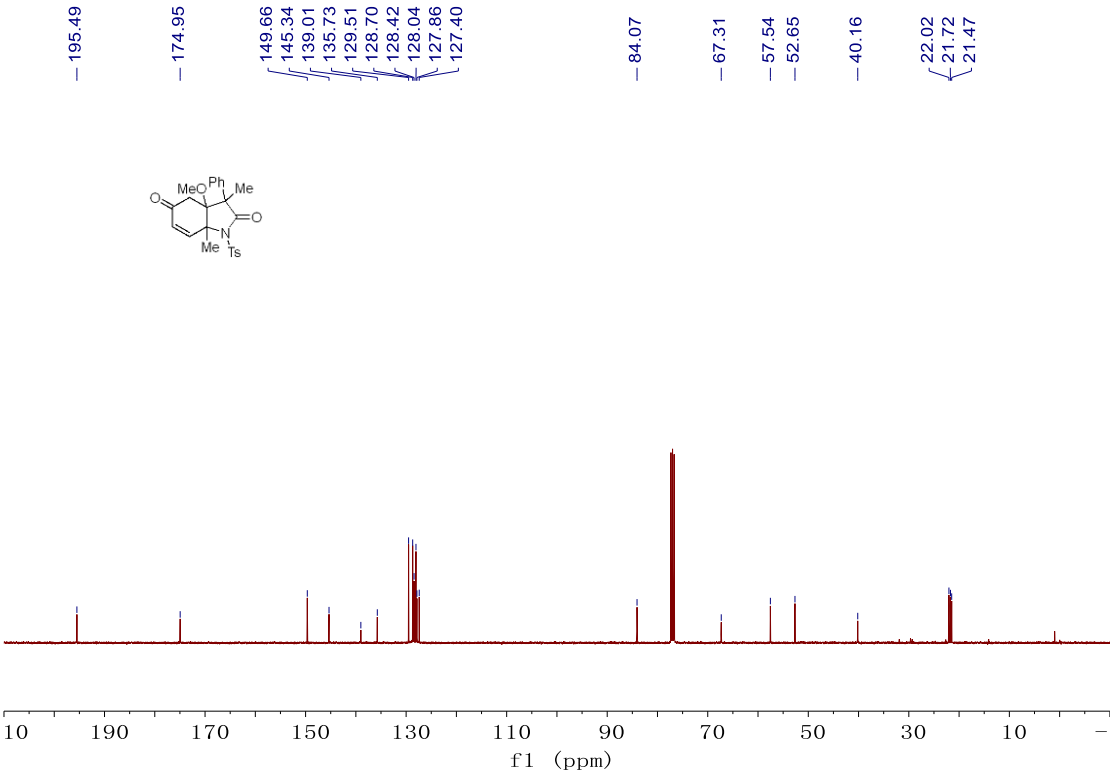
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3na**



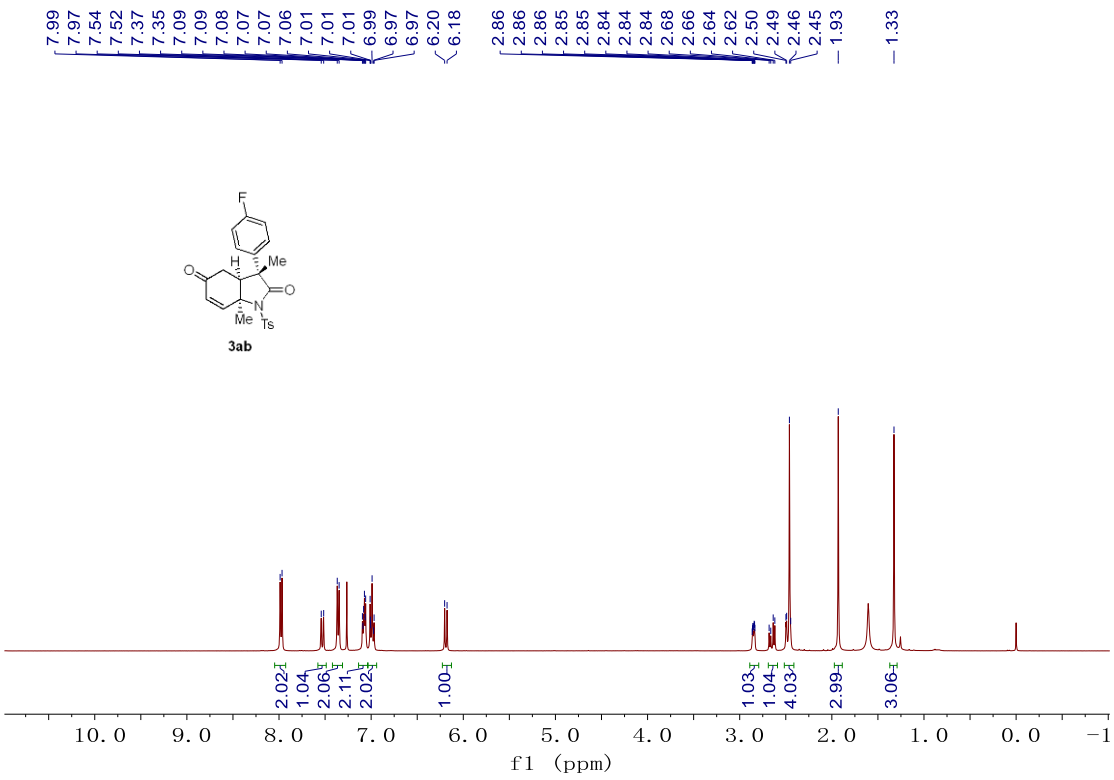
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3na'**



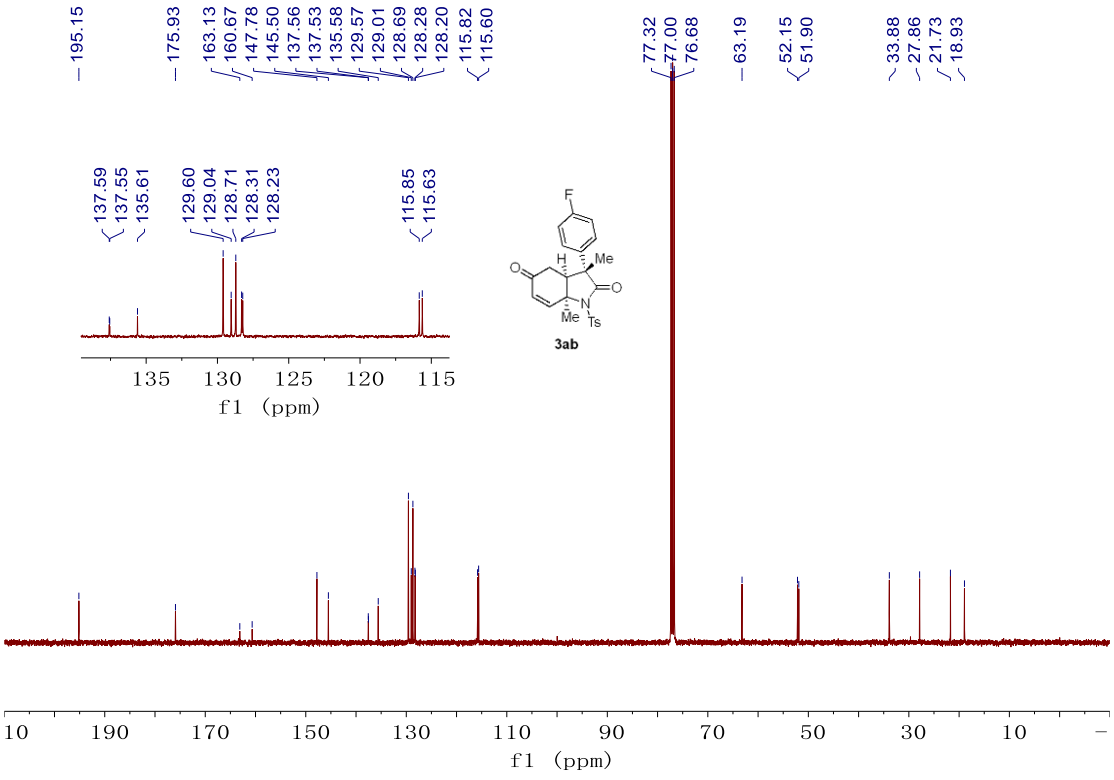
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3na'**



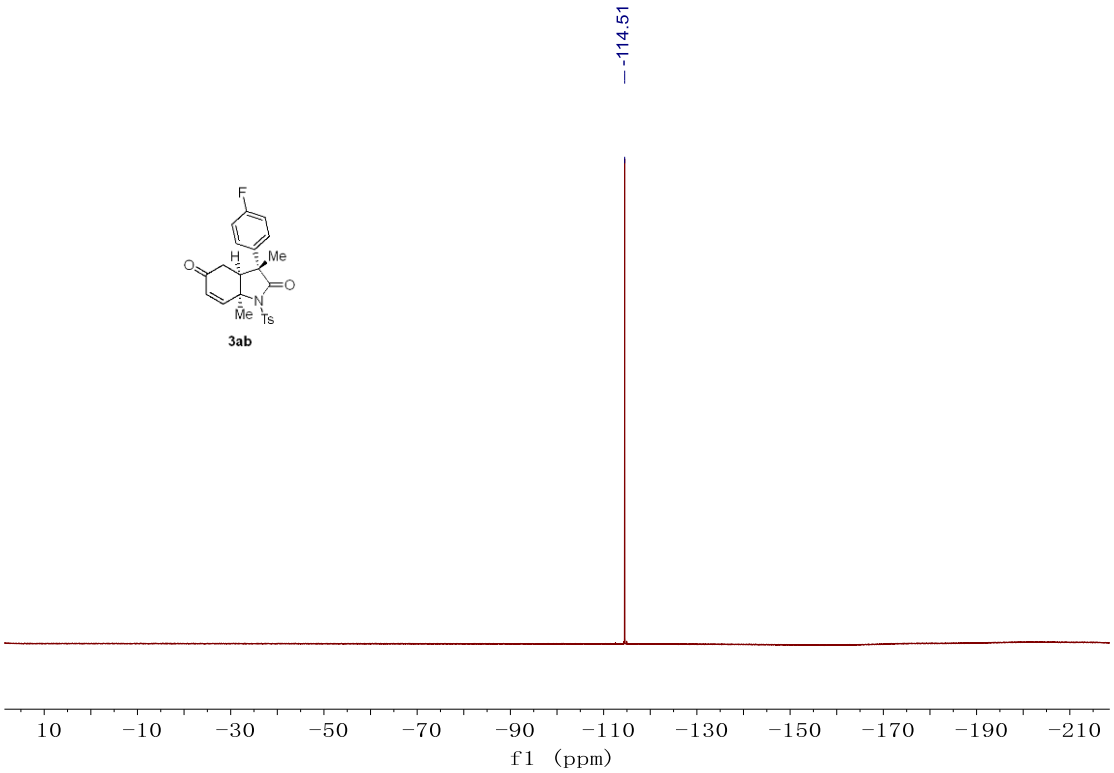
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ab**



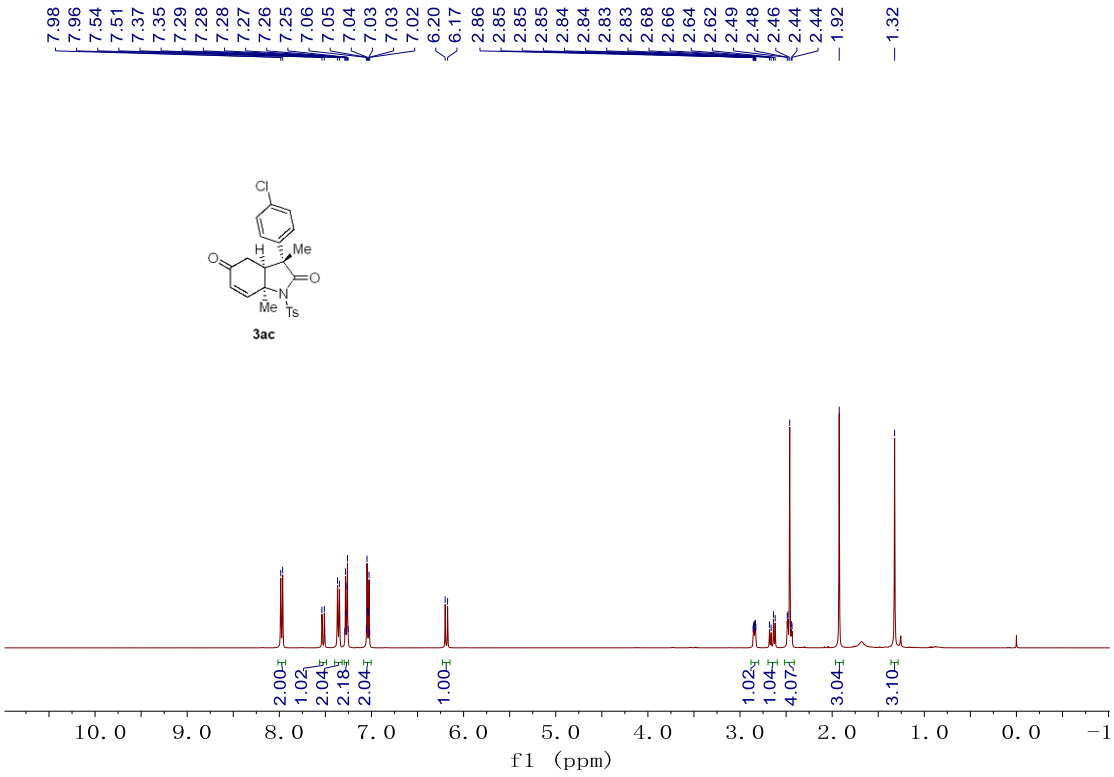
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ab**



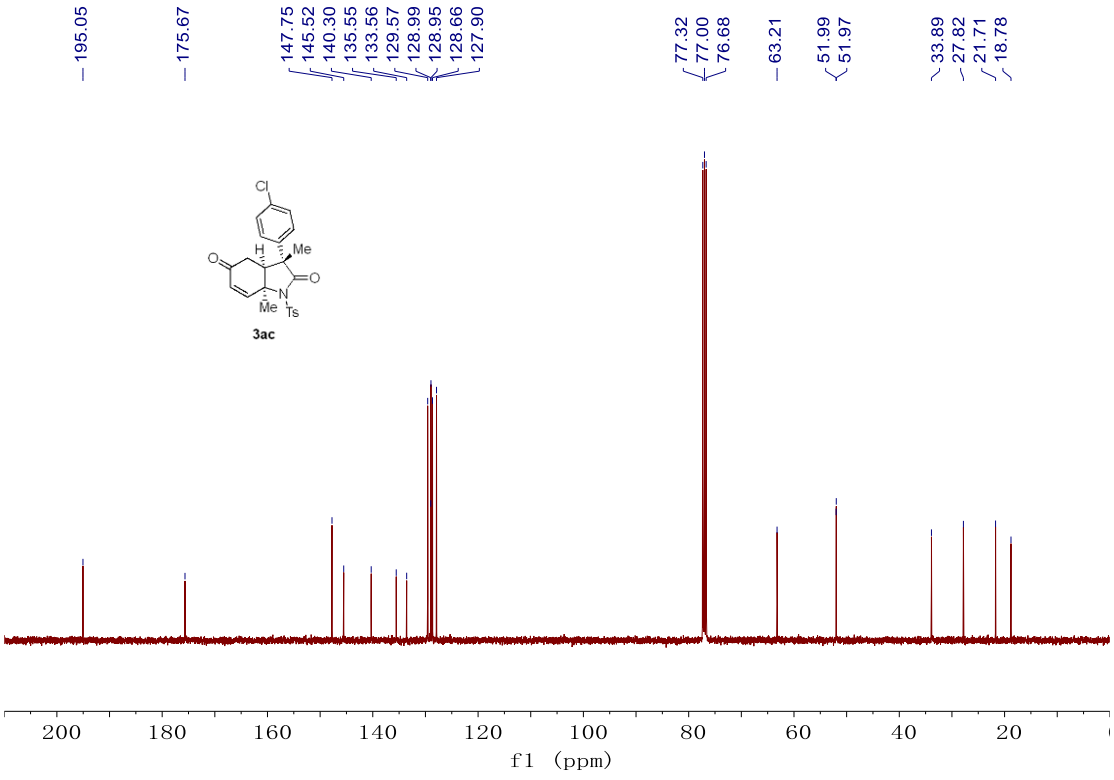
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **3ab**



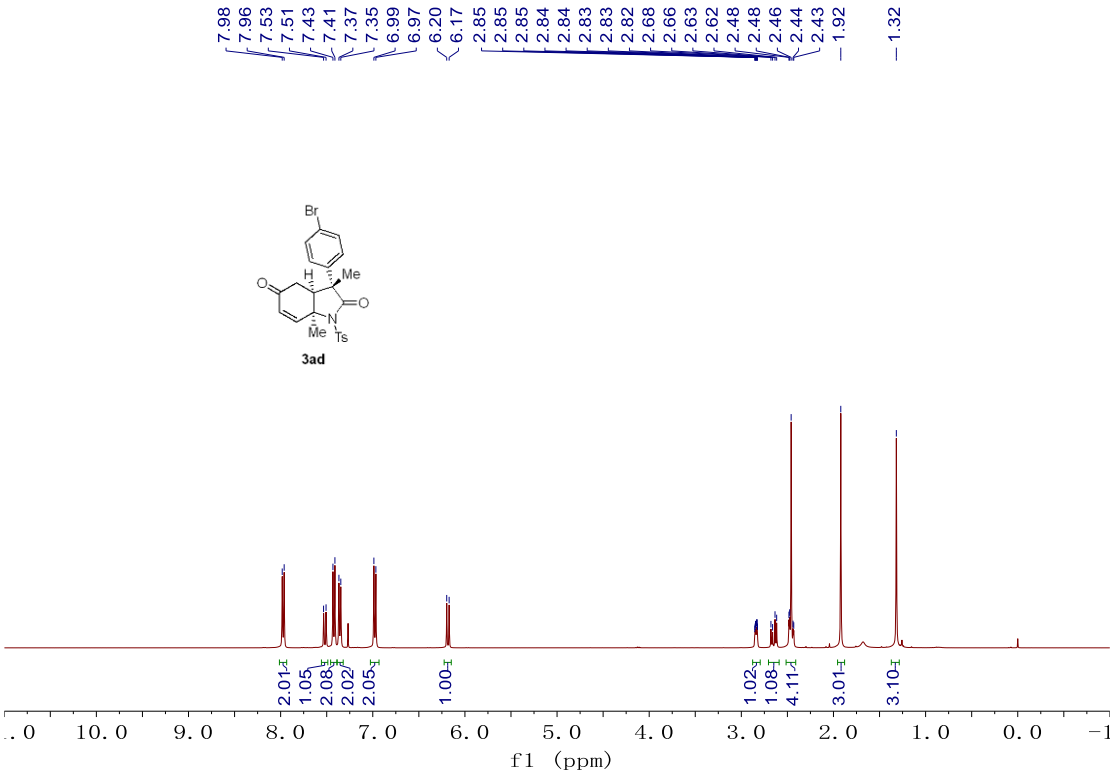
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ac**



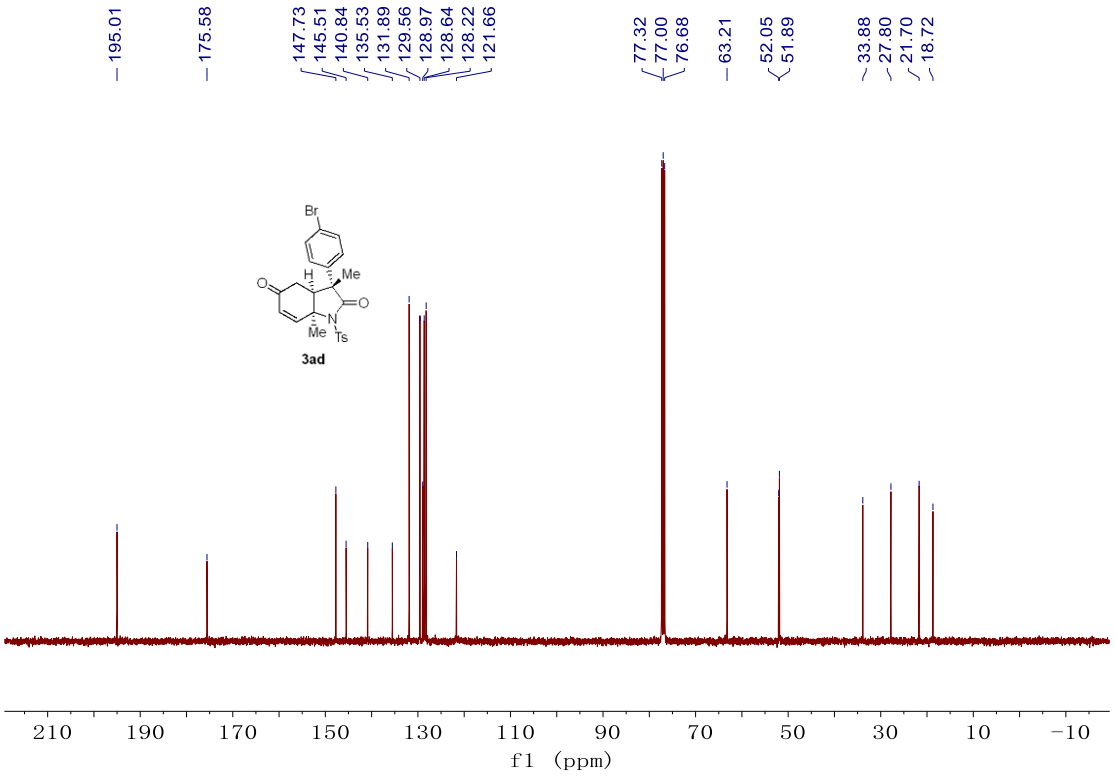
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ac**



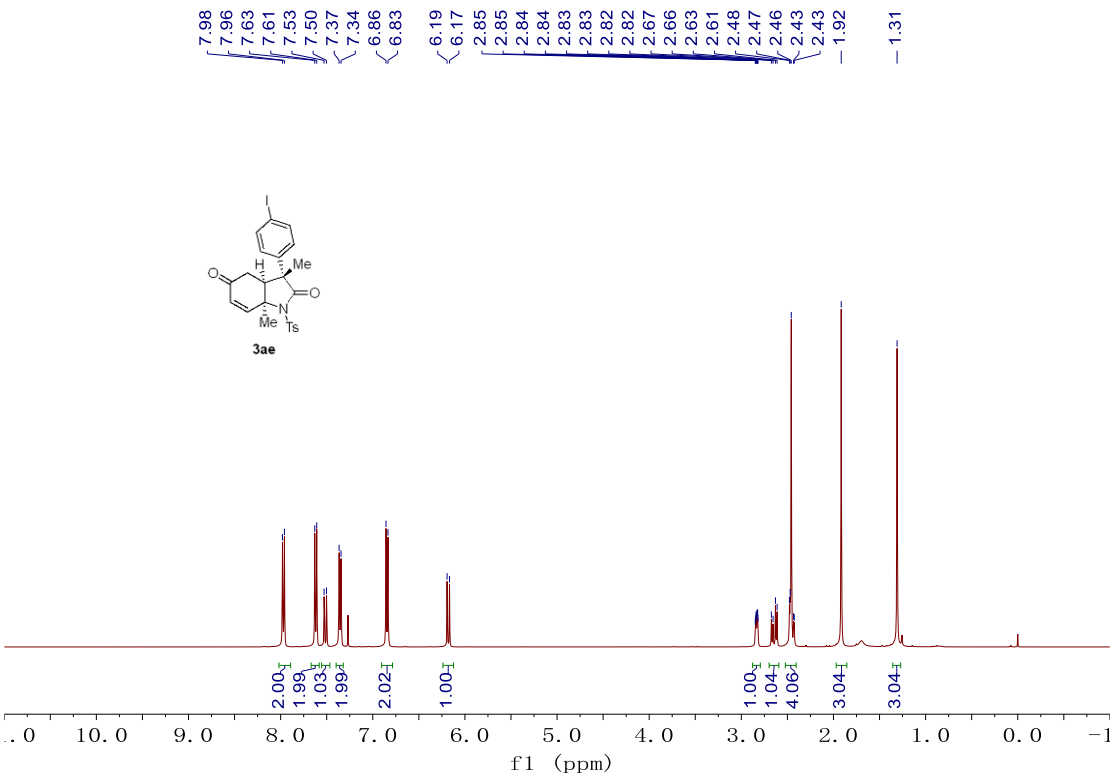
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ad**



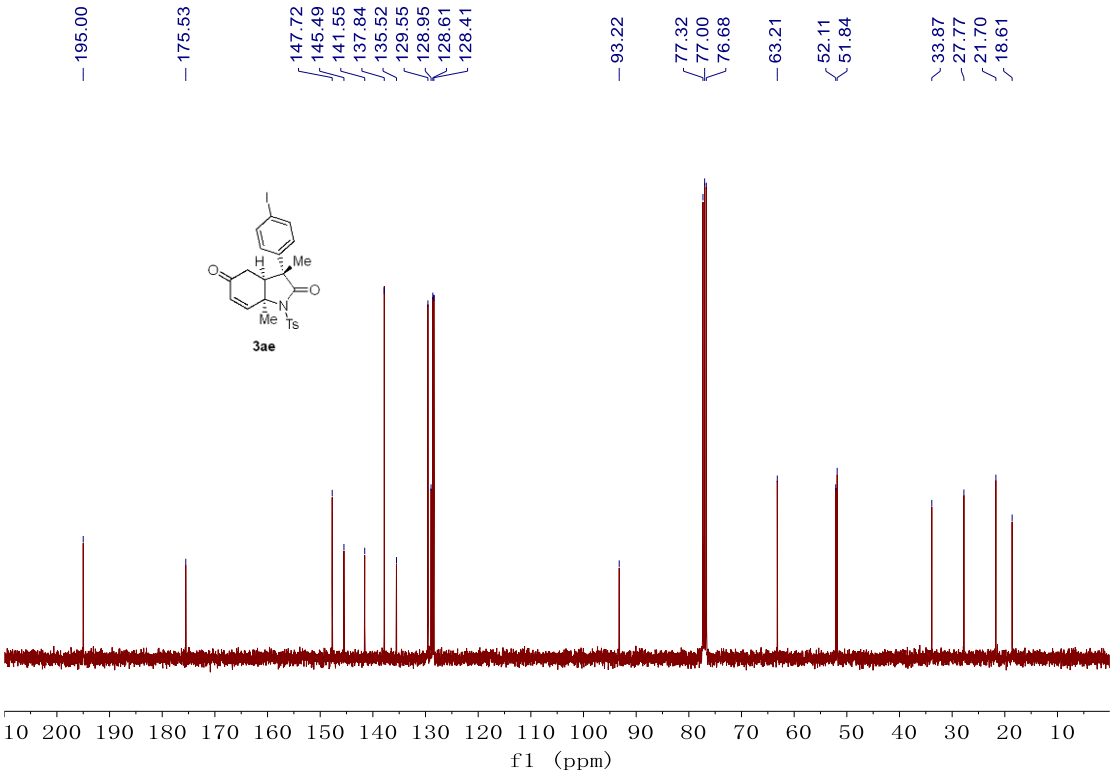
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ad**



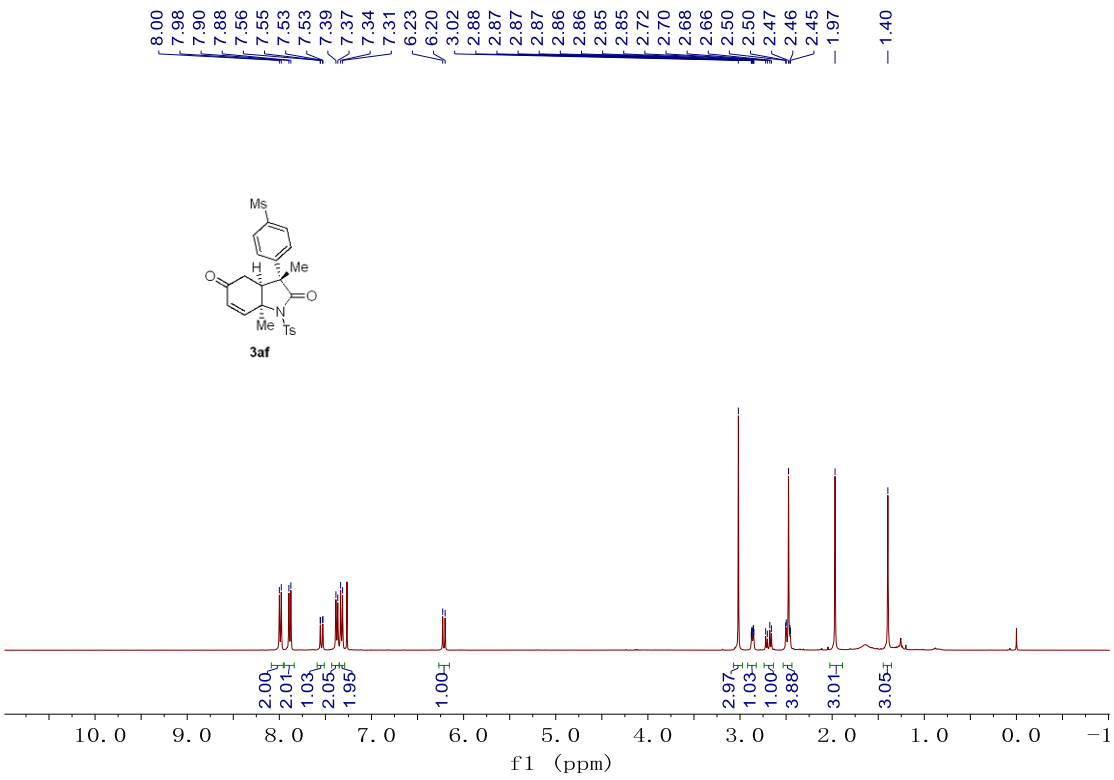
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ae**



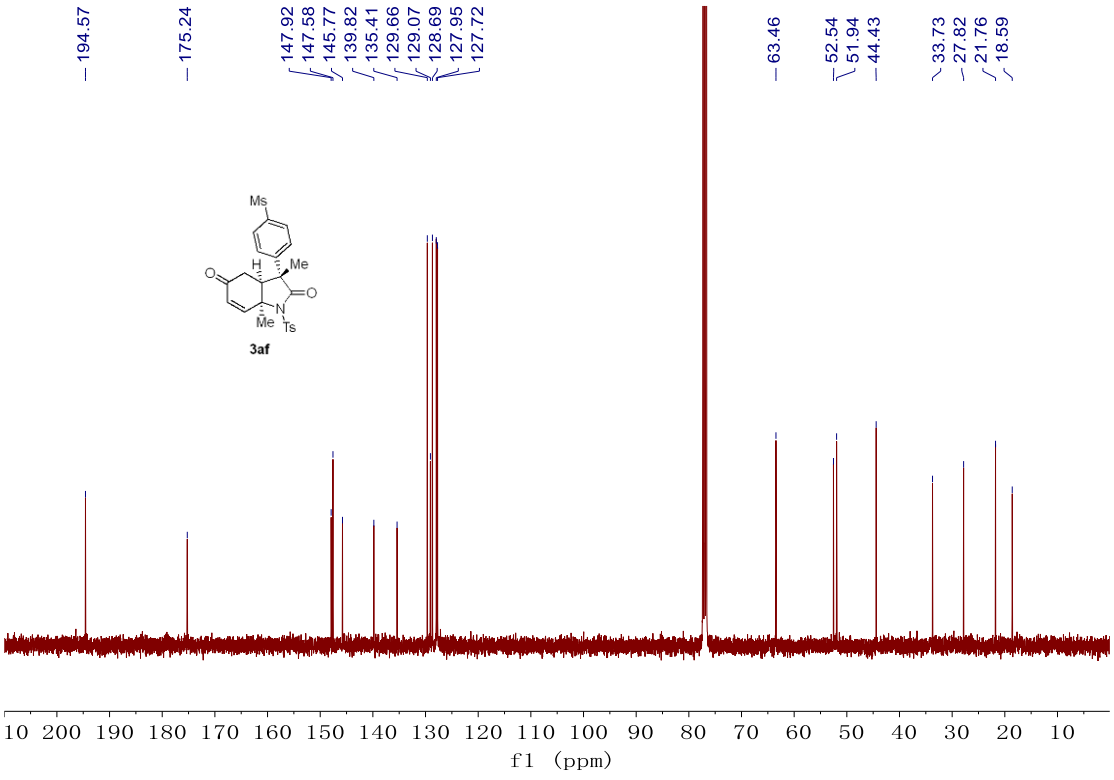
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ae**



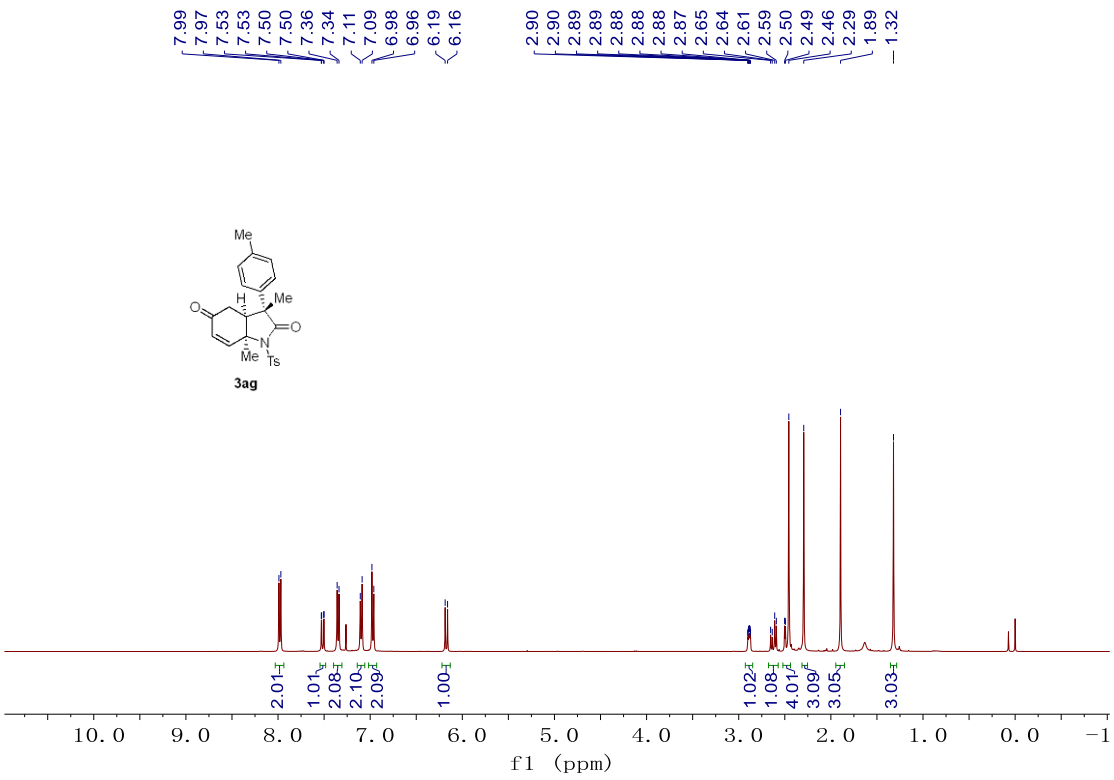
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3af**



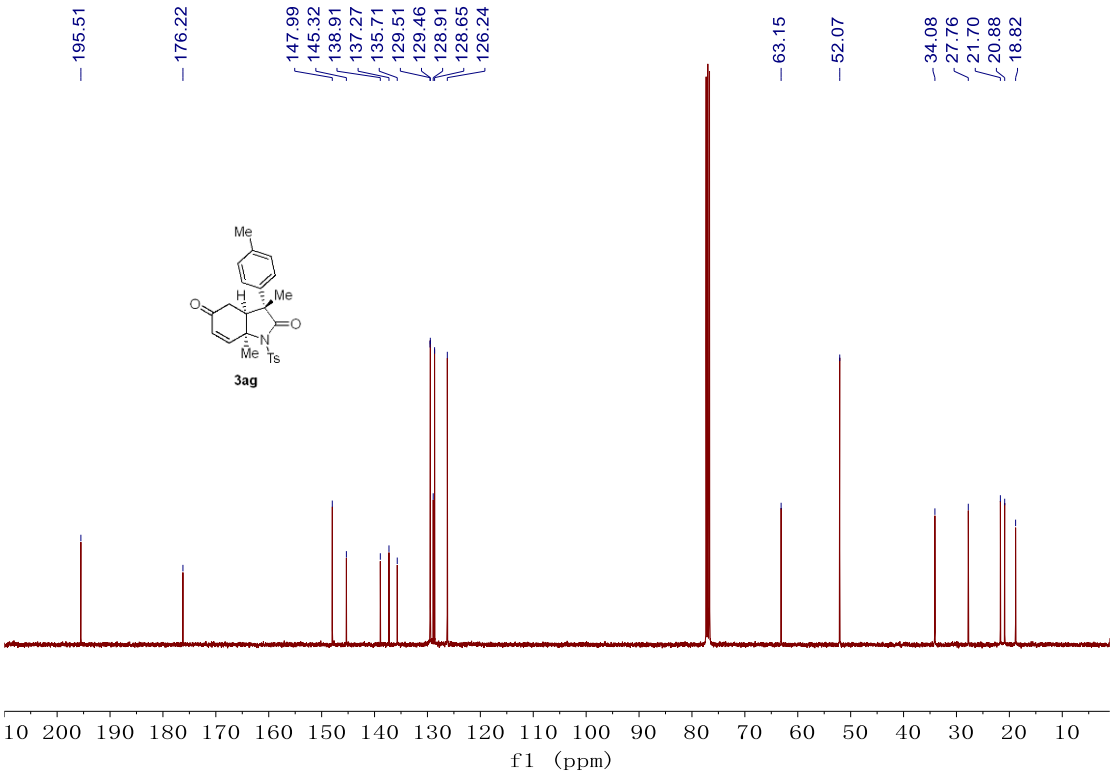
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3af**



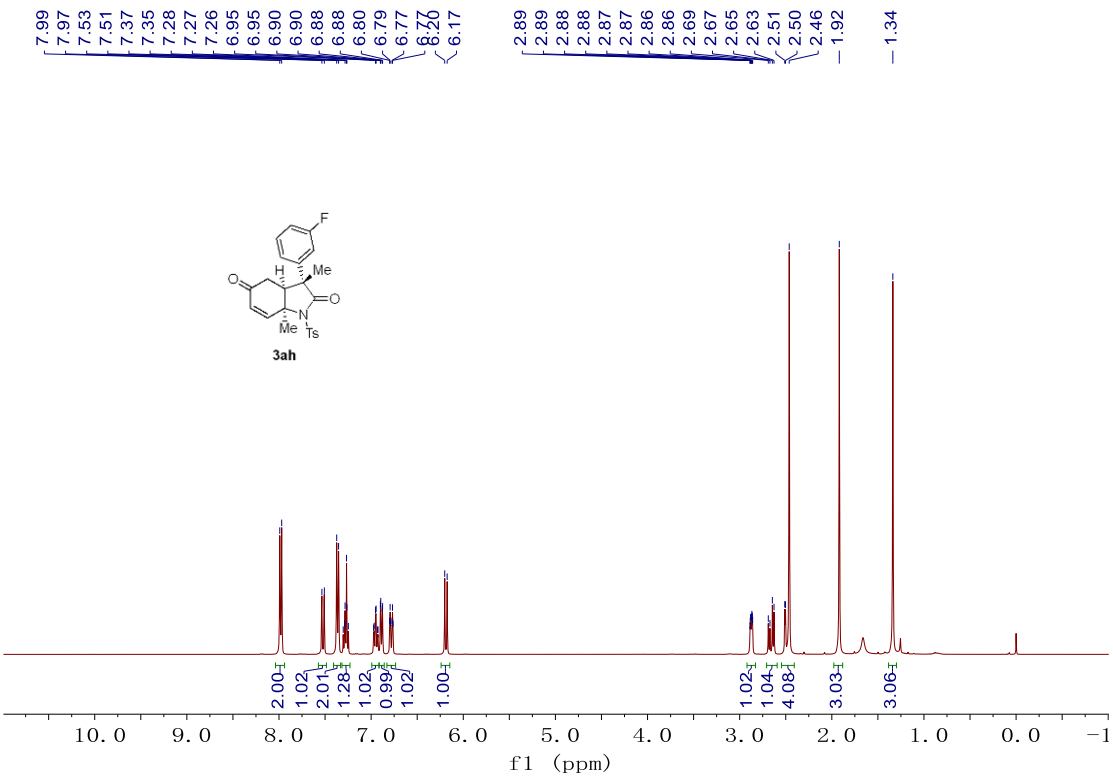
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ag**



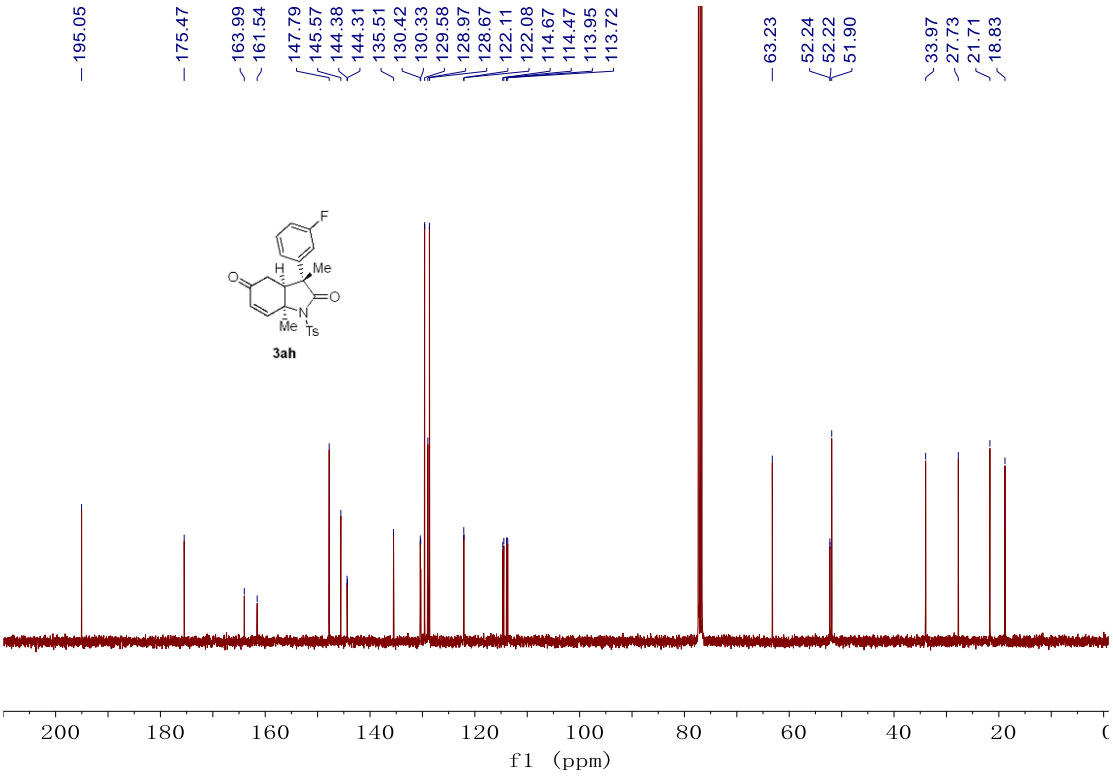
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ag**



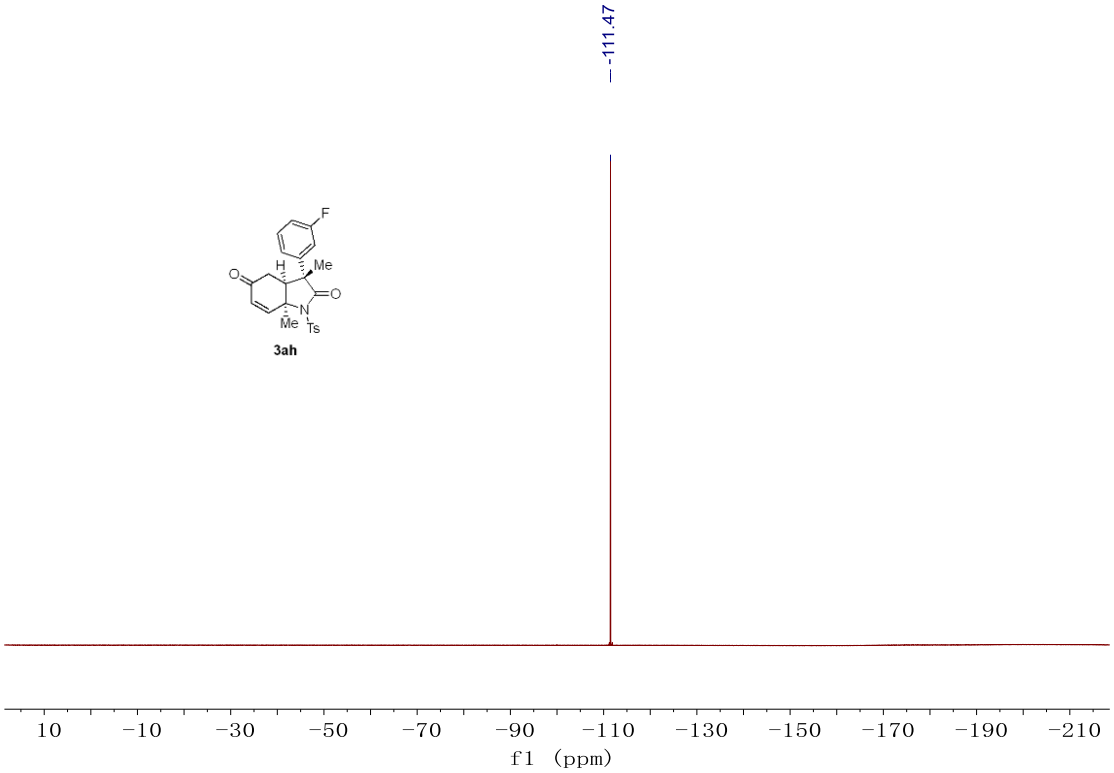
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ah**



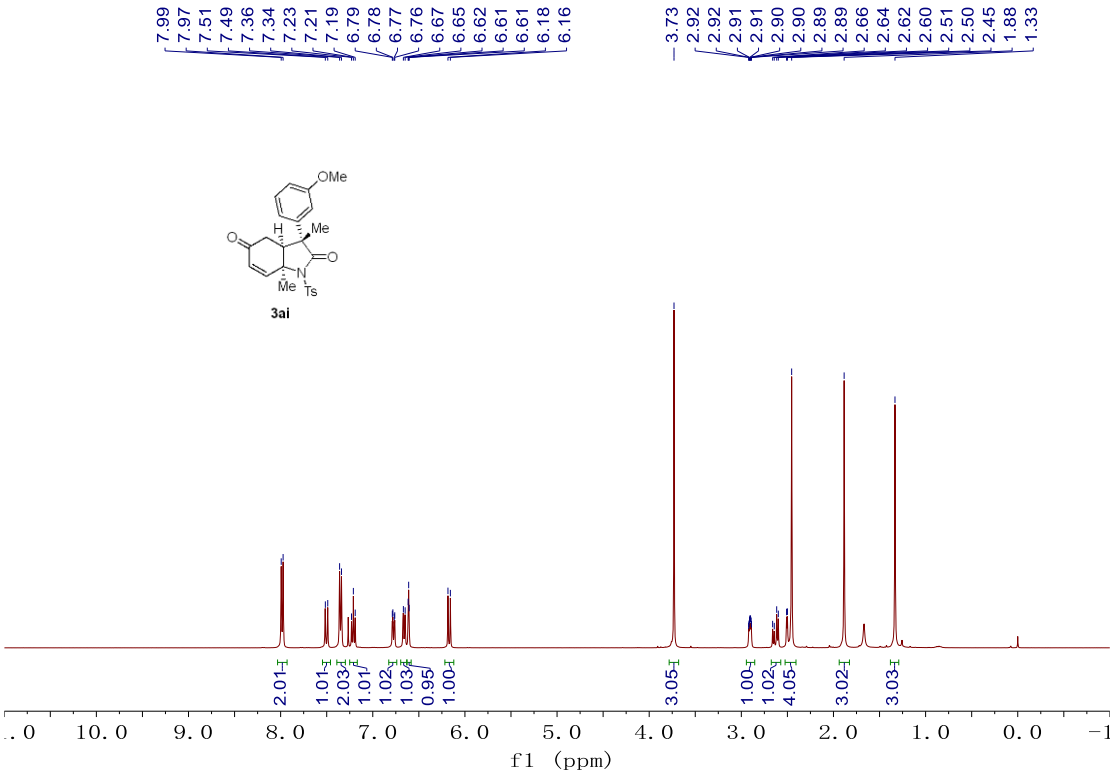
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ah**



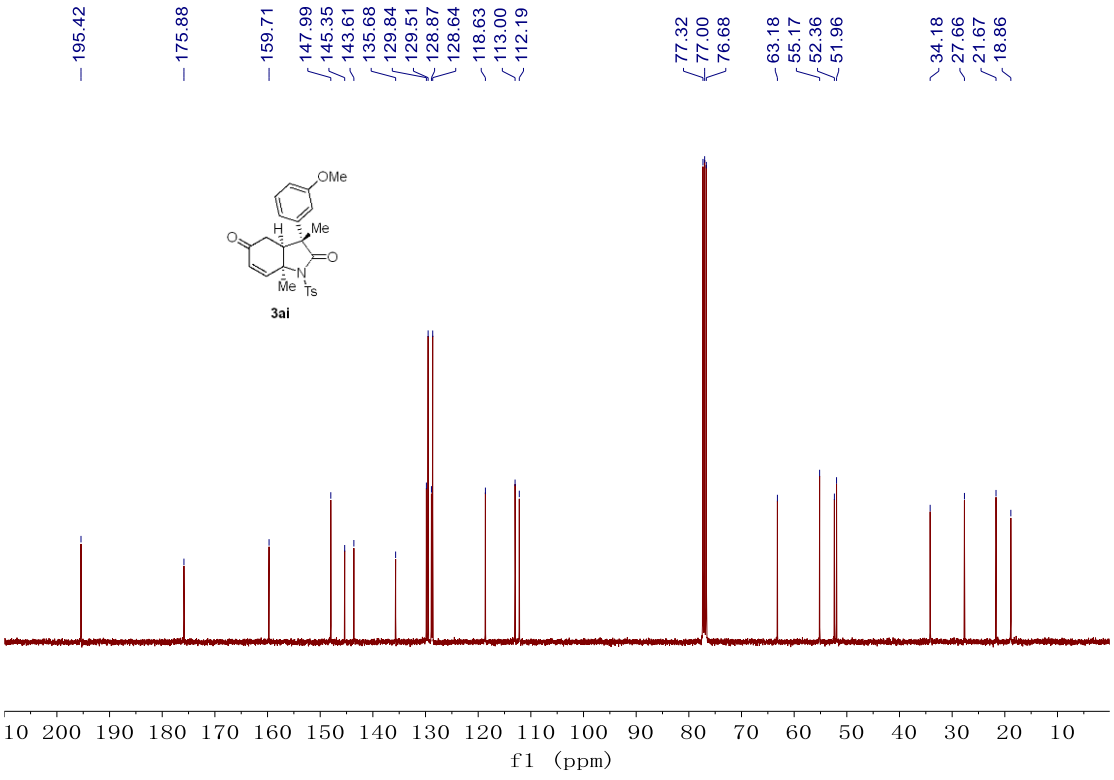
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **3ah**



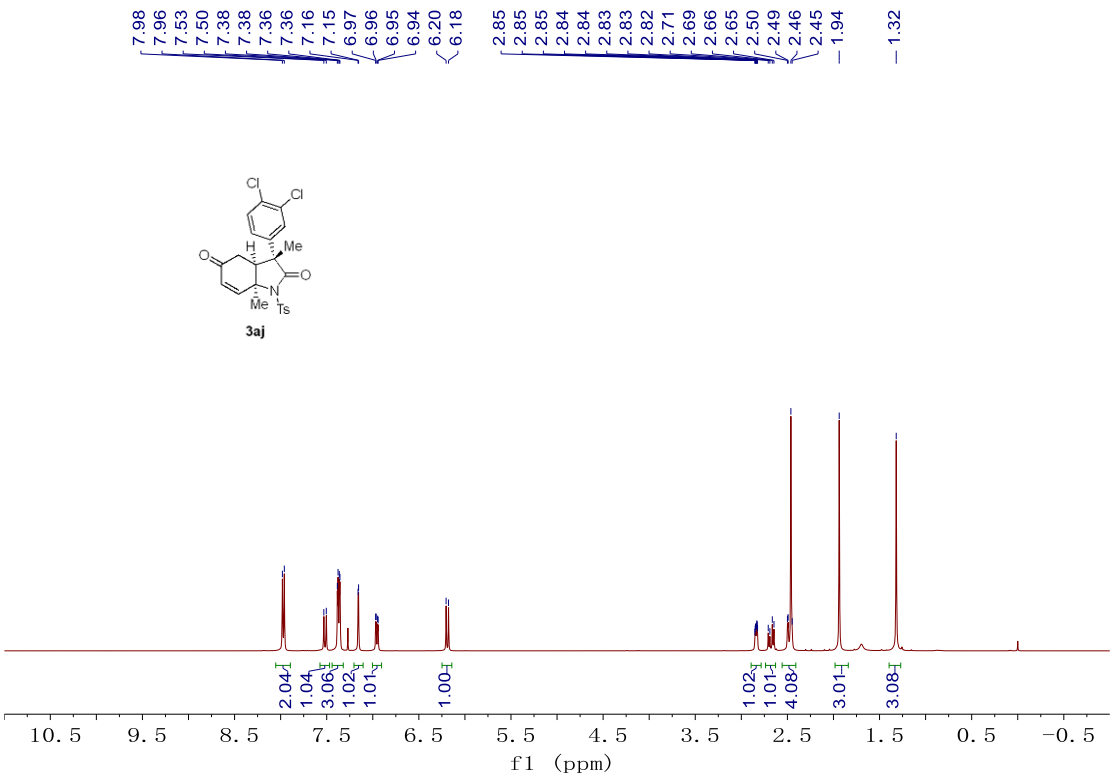
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ai**



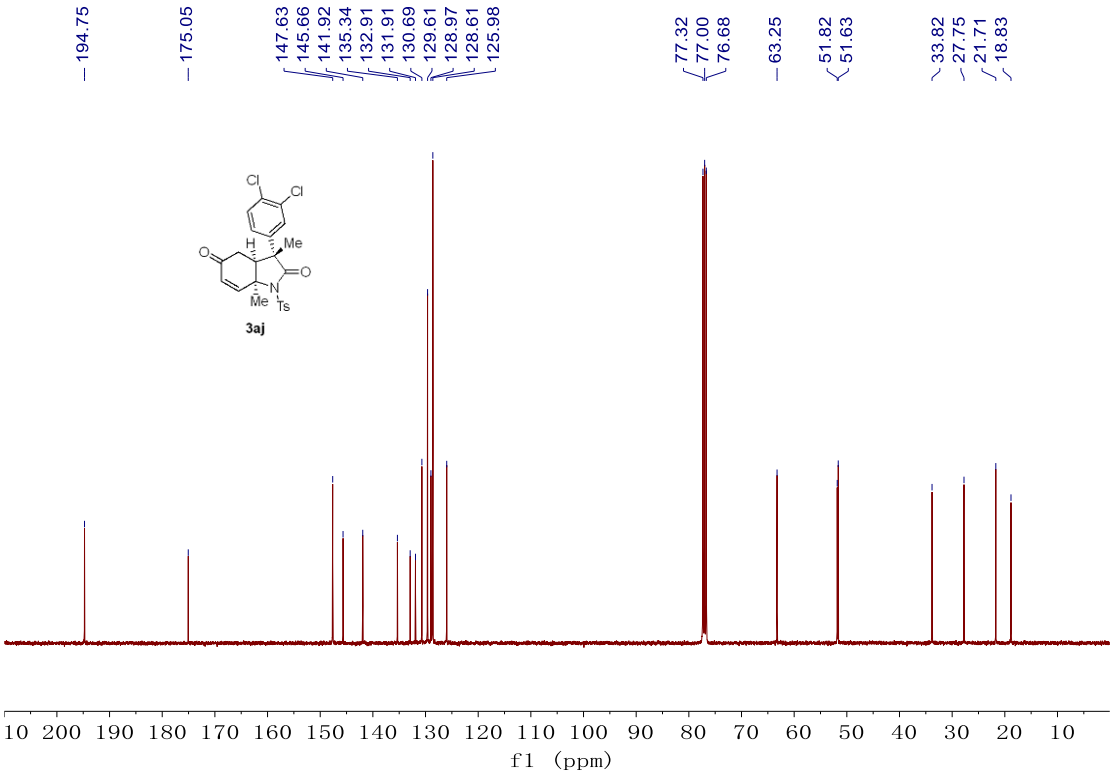
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ai**



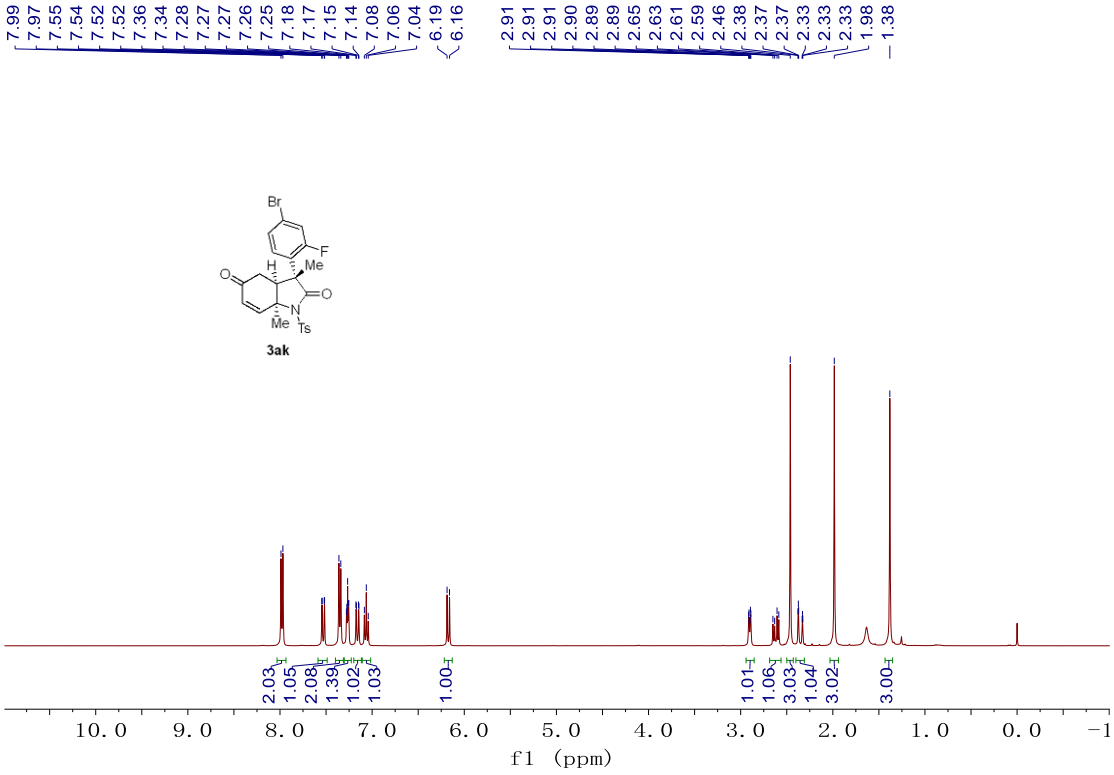
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aj**



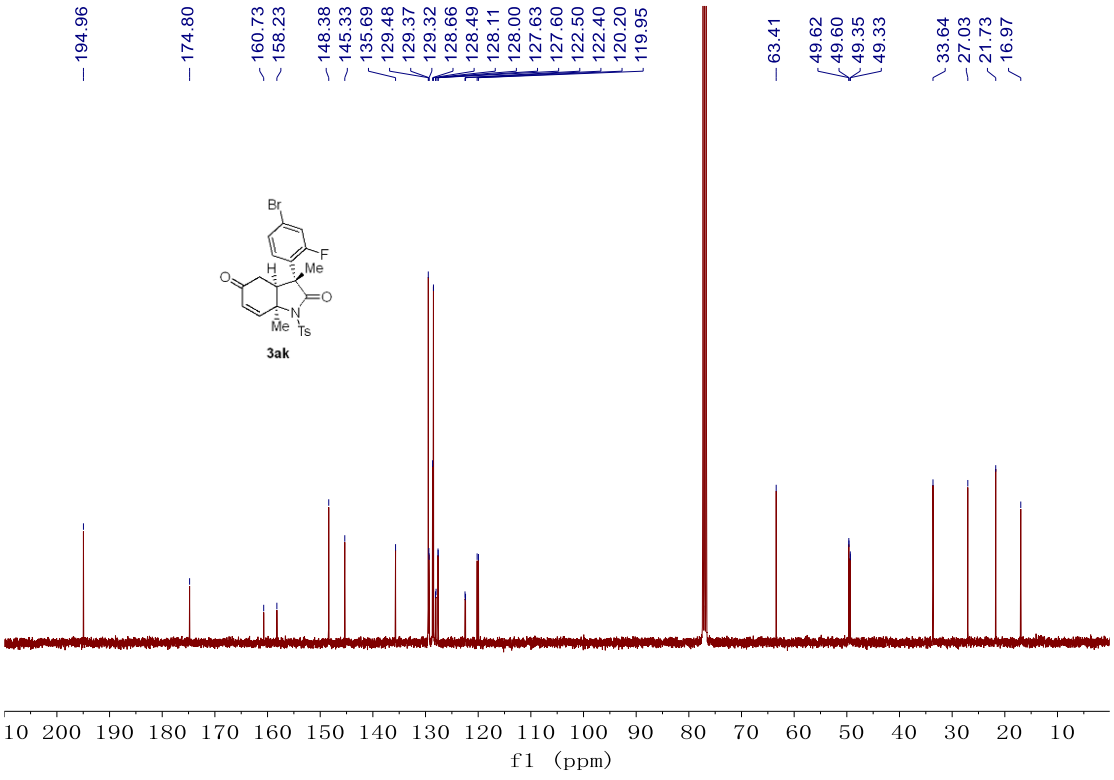
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3aj**



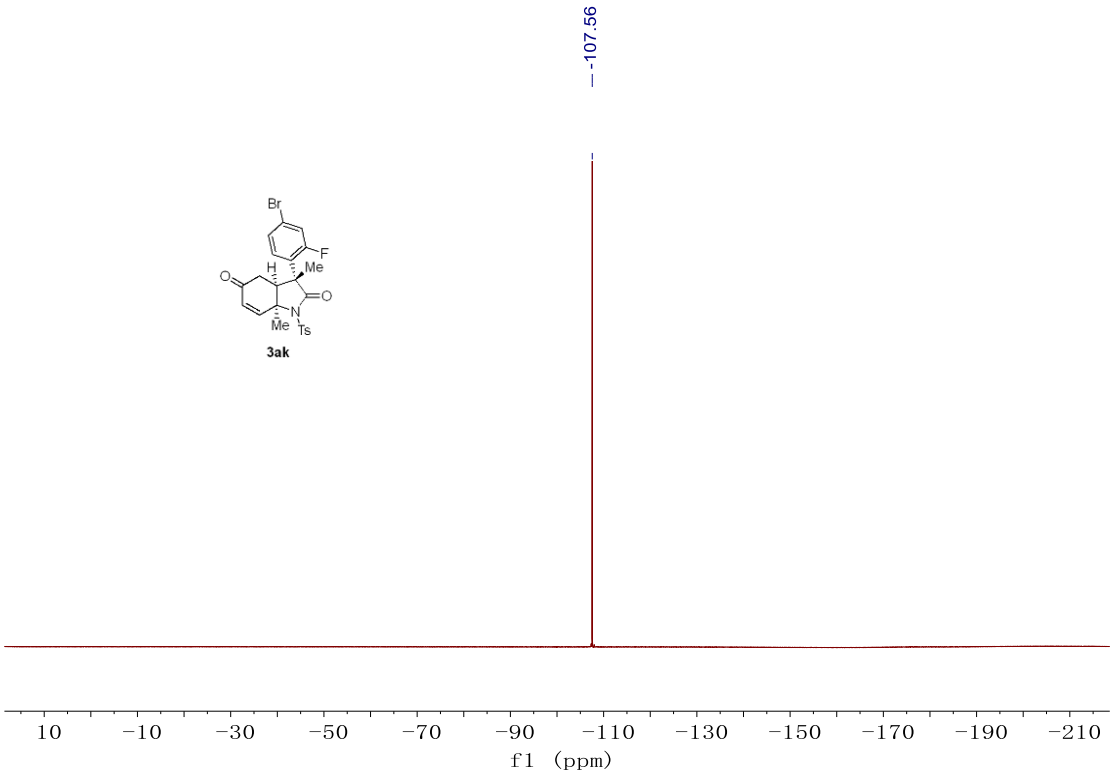
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ak**



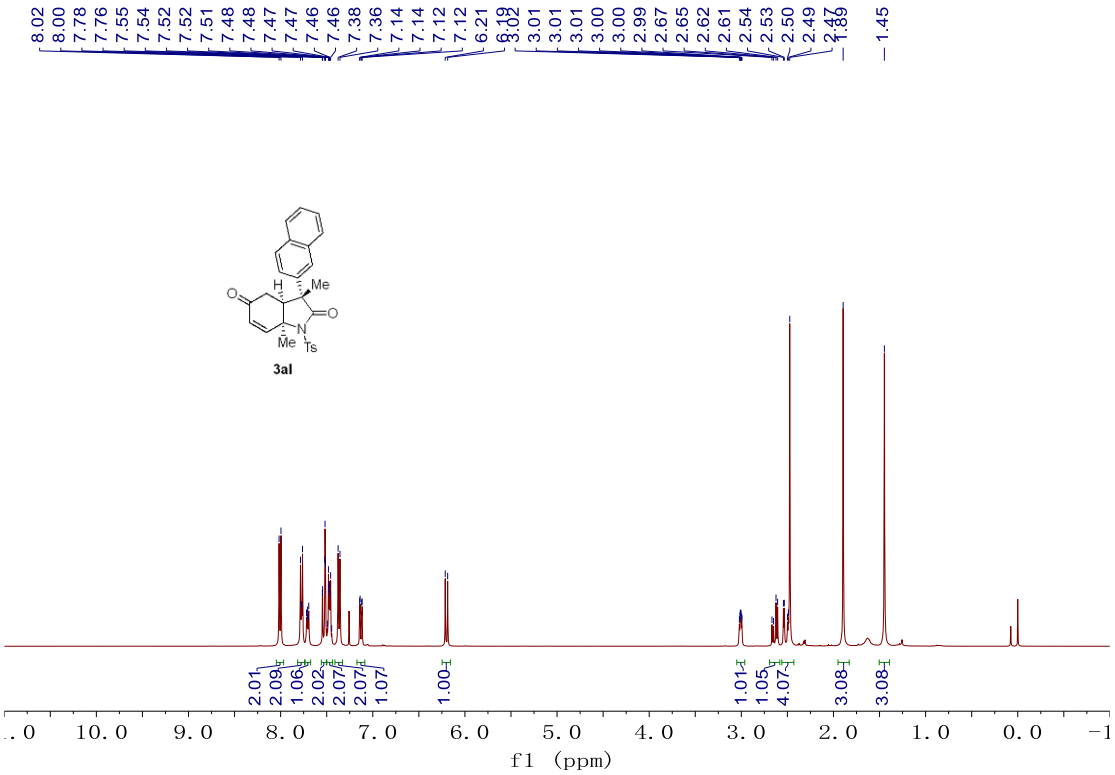
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ak**



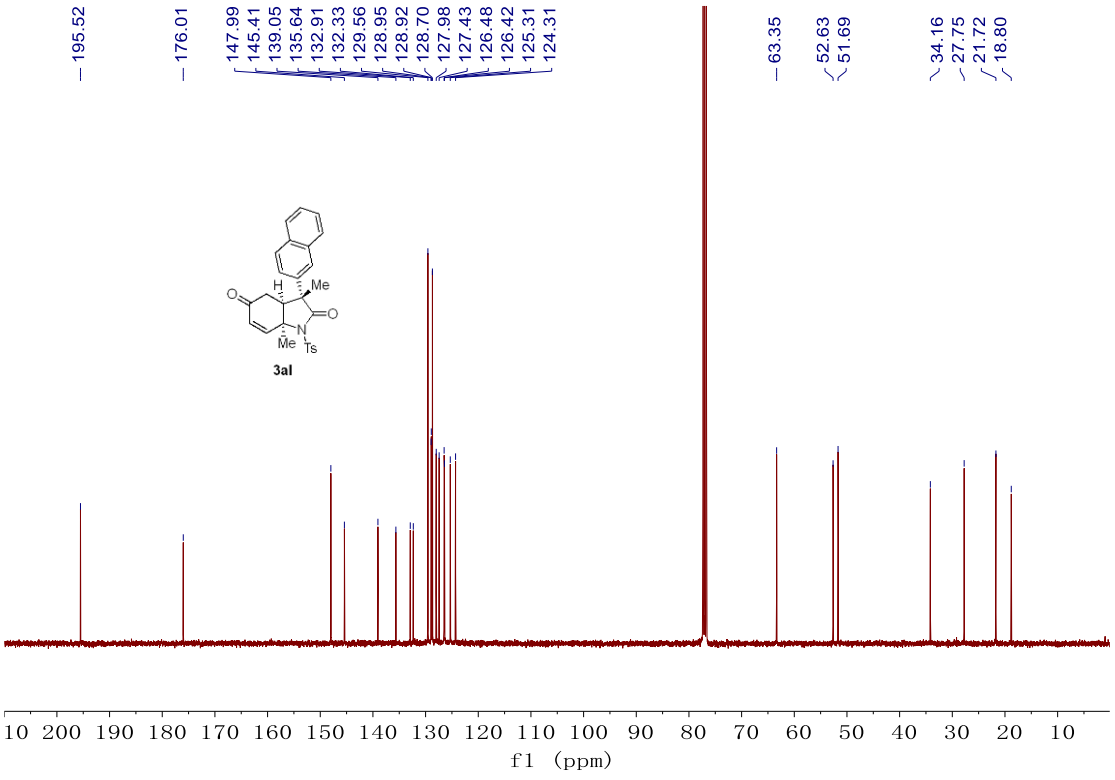
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of **3ak**



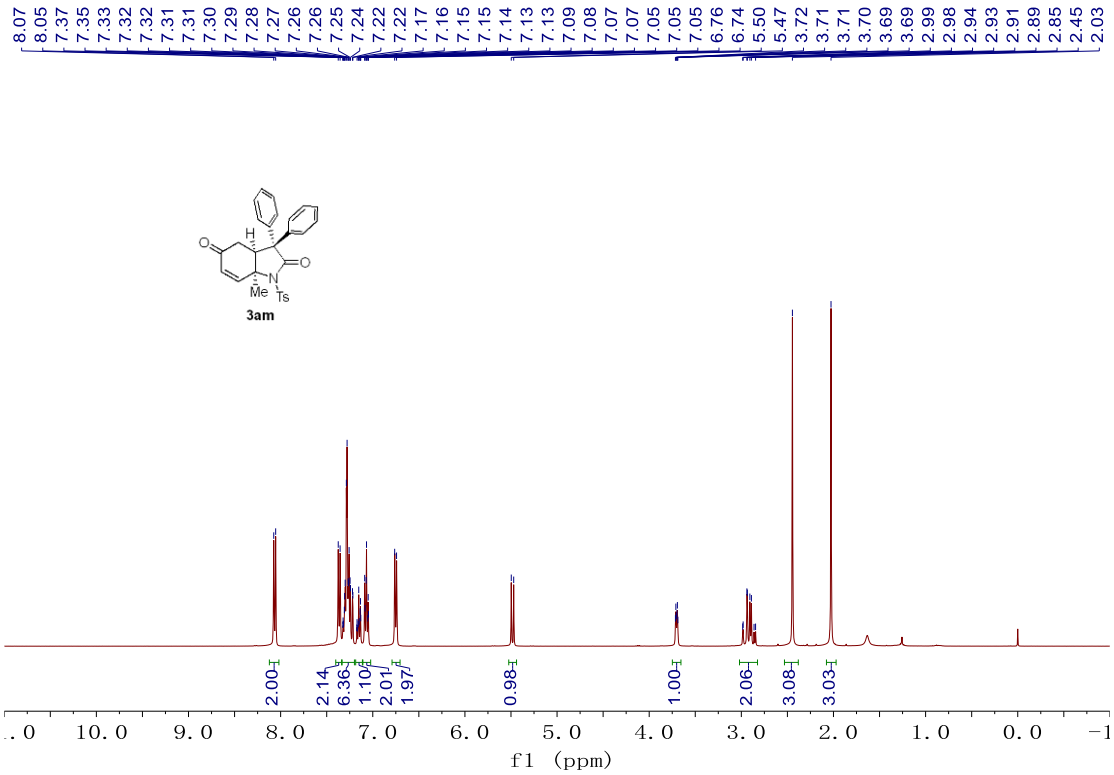
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3al**



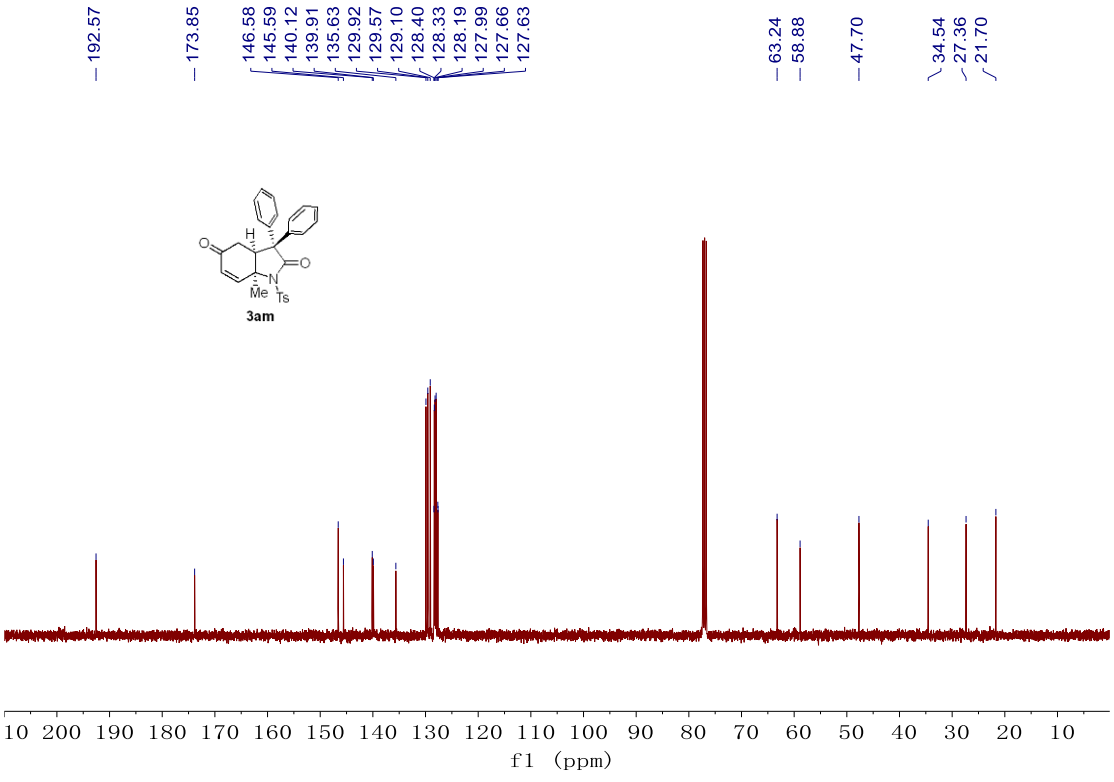
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3al**



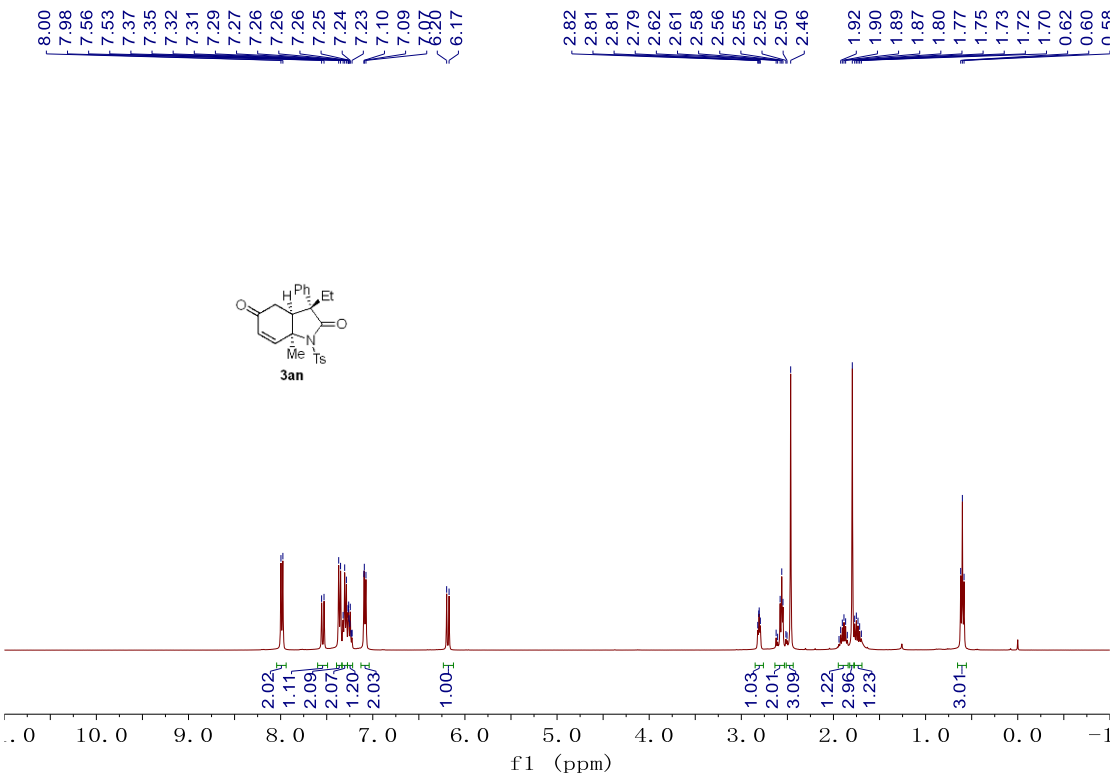
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3am**



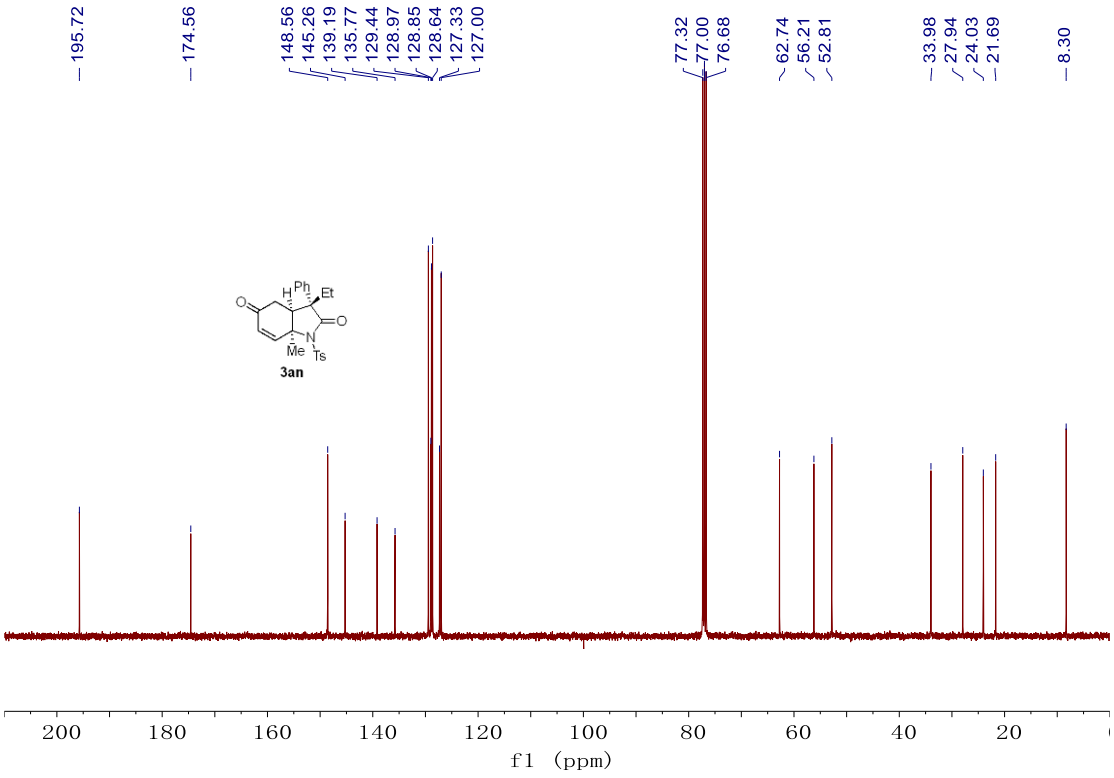
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3am**



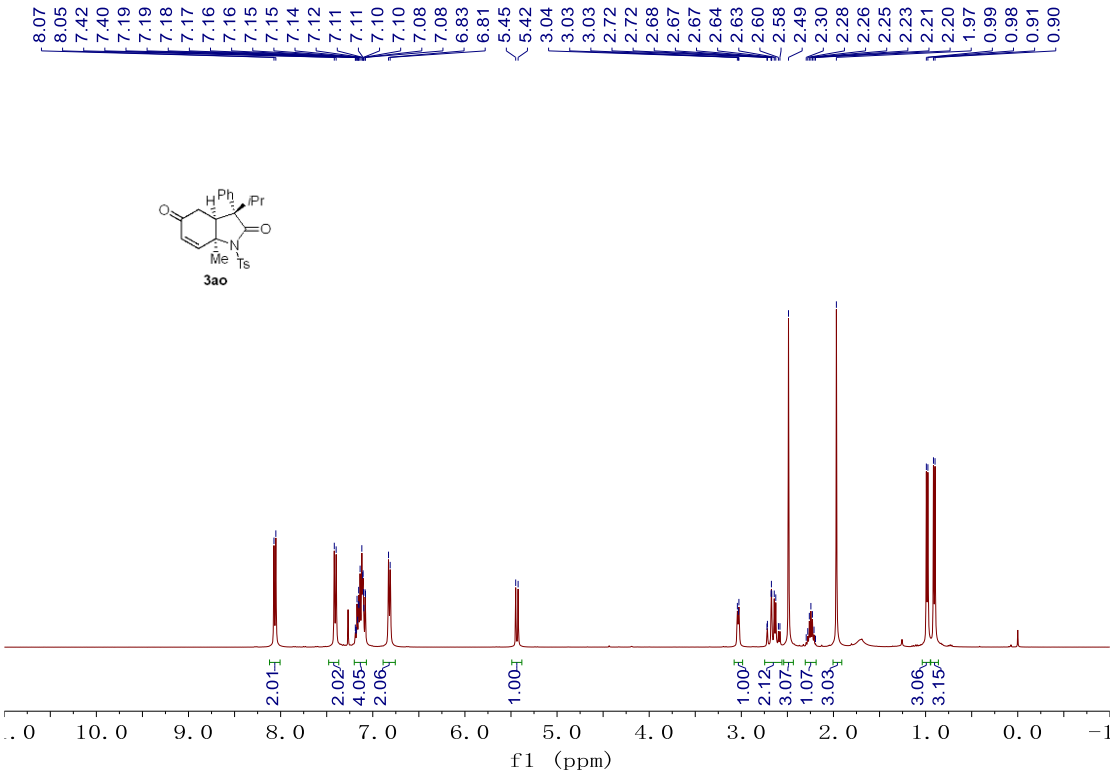
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3an**



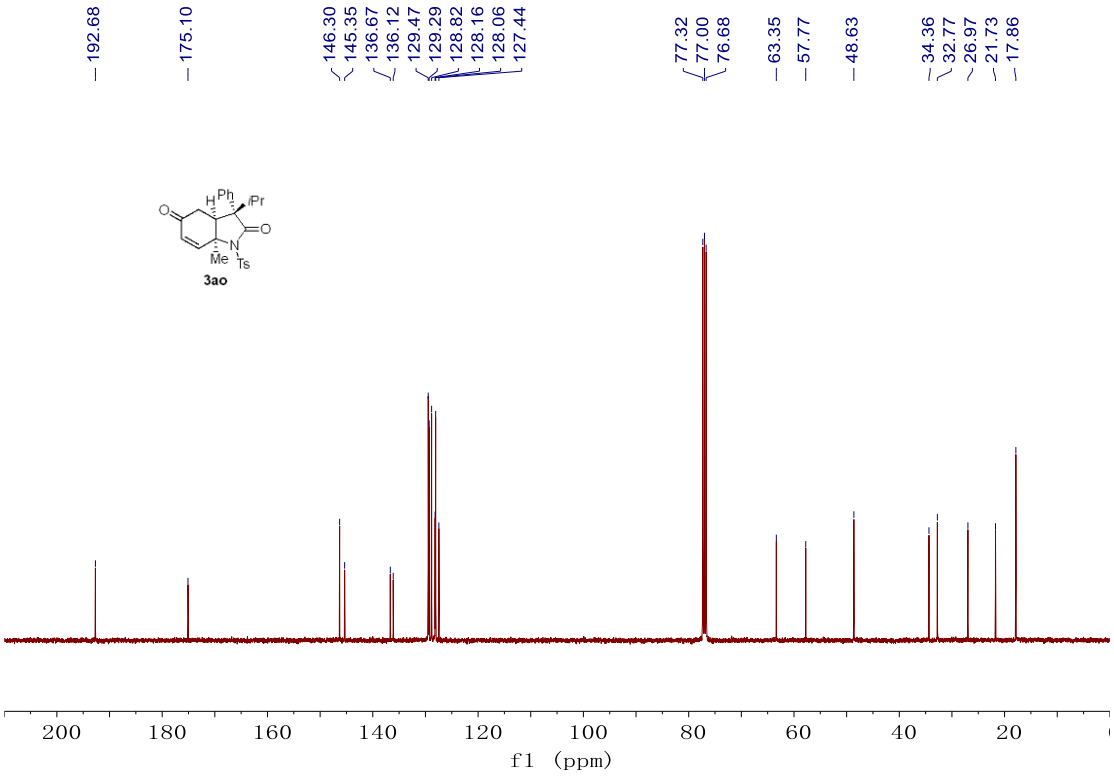
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3an**



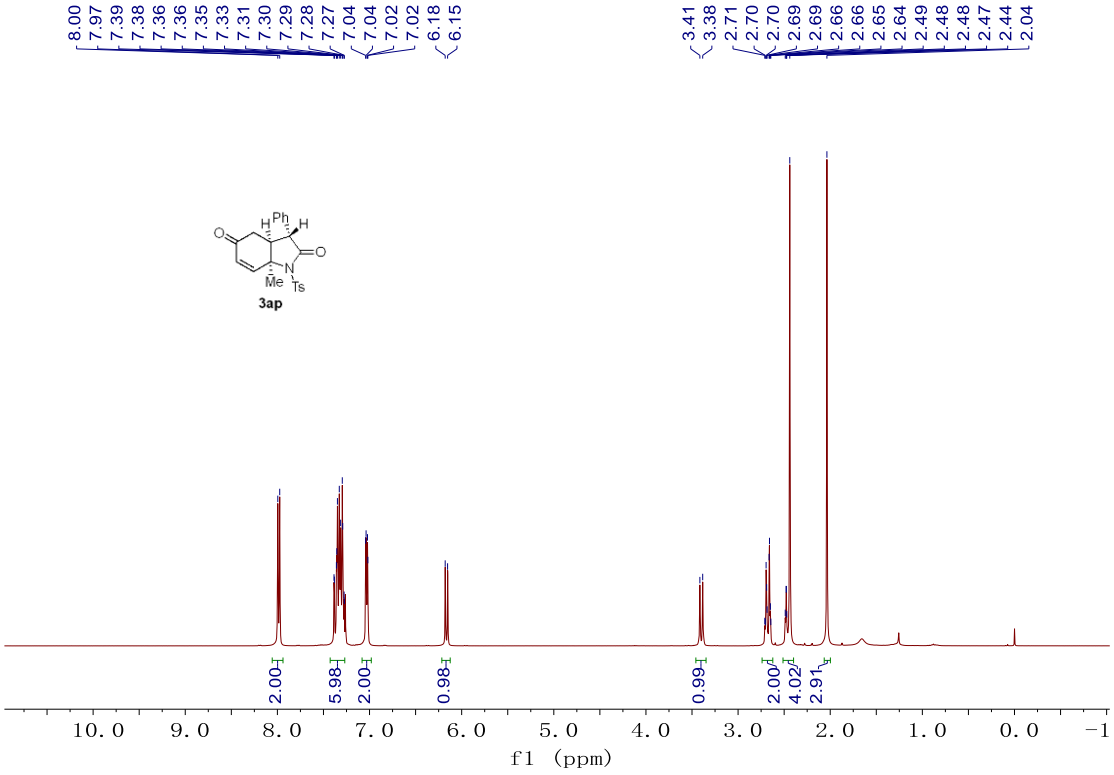
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ao**



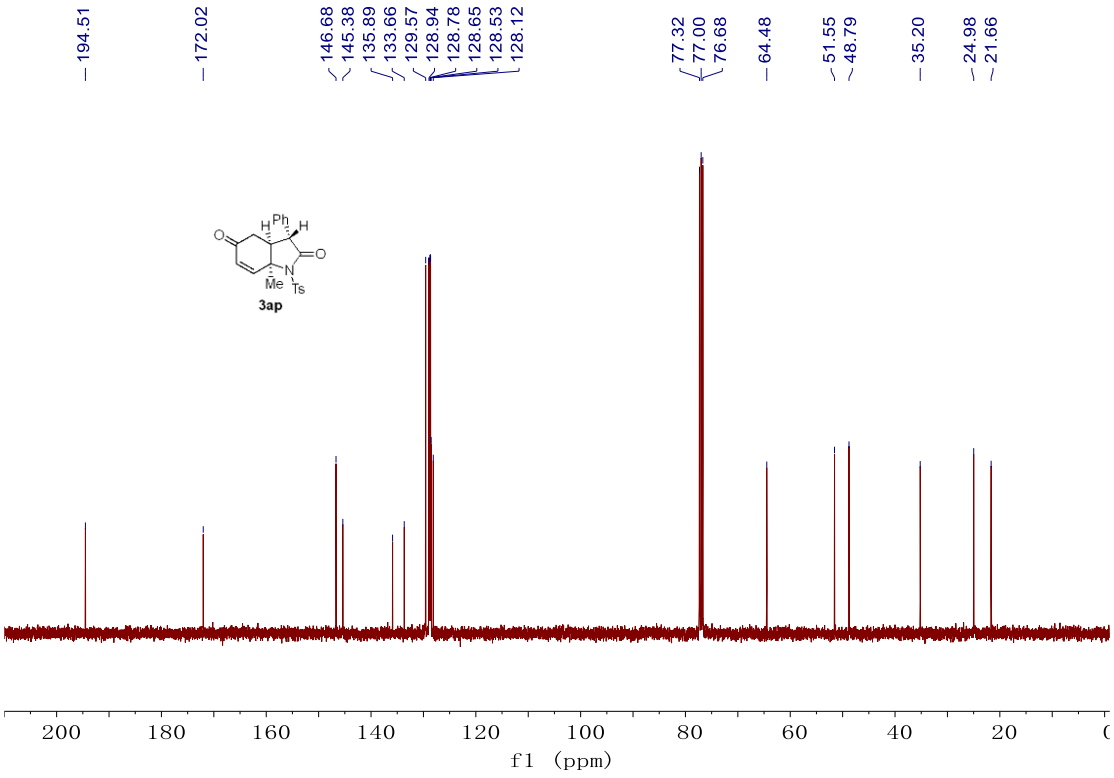
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ao**



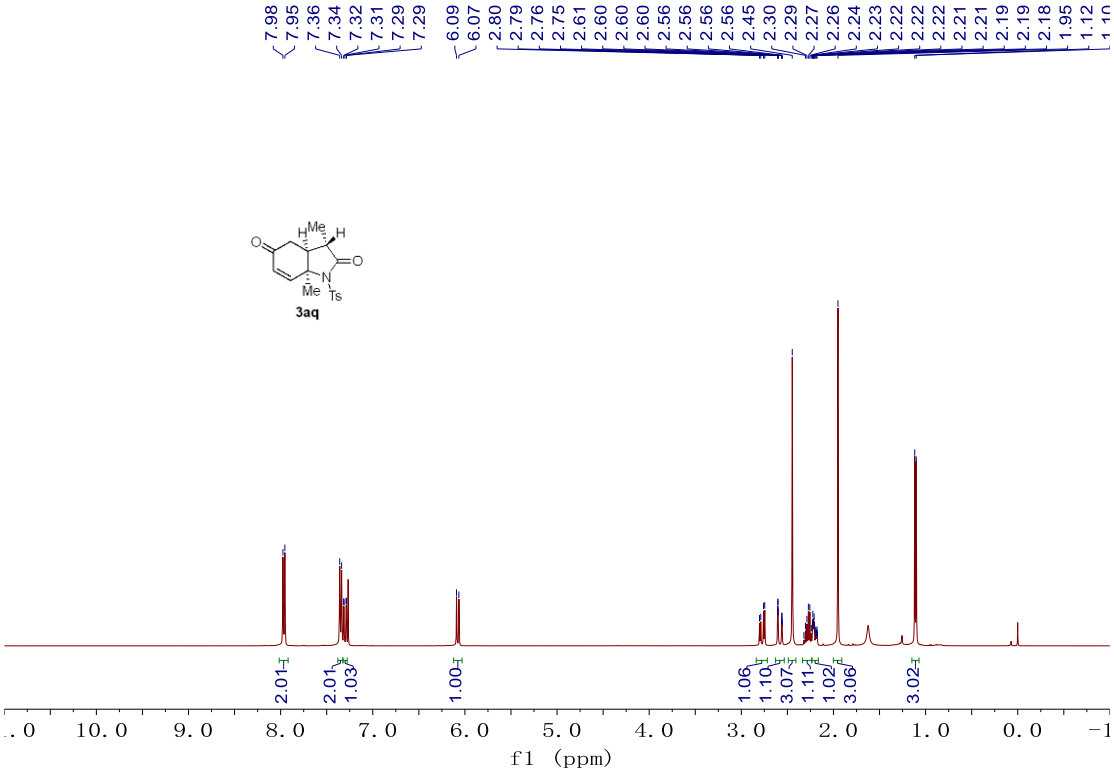
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ap**



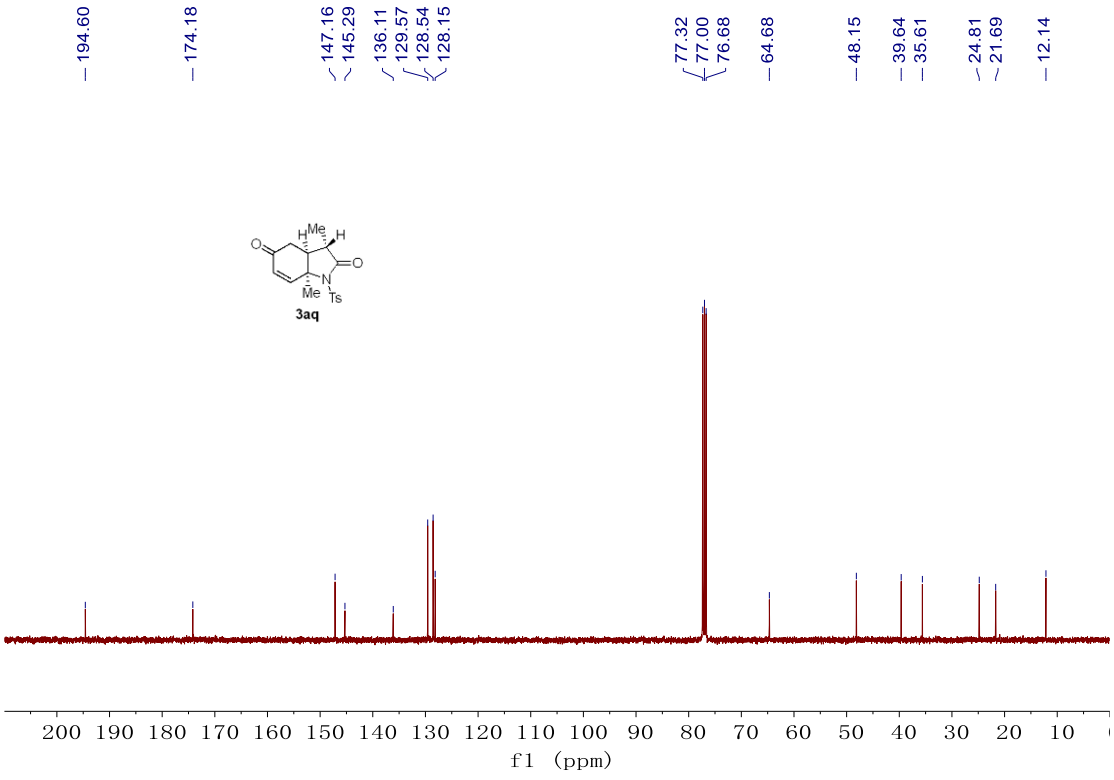
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ap**



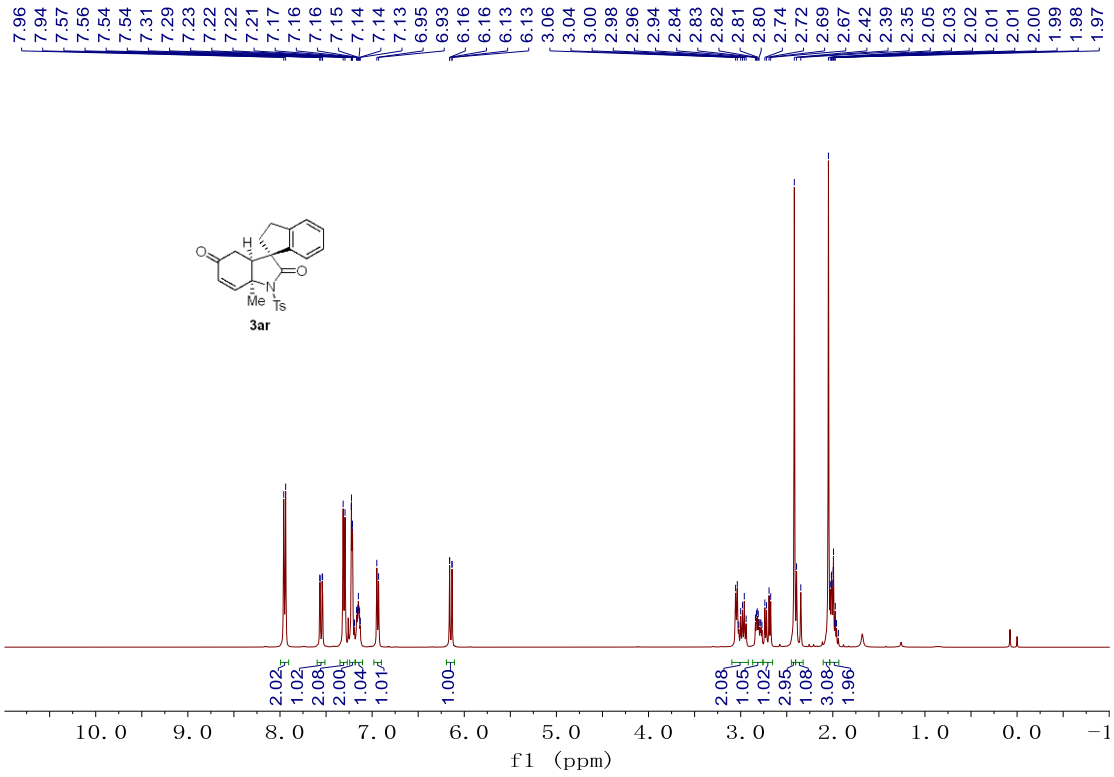
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3aq**



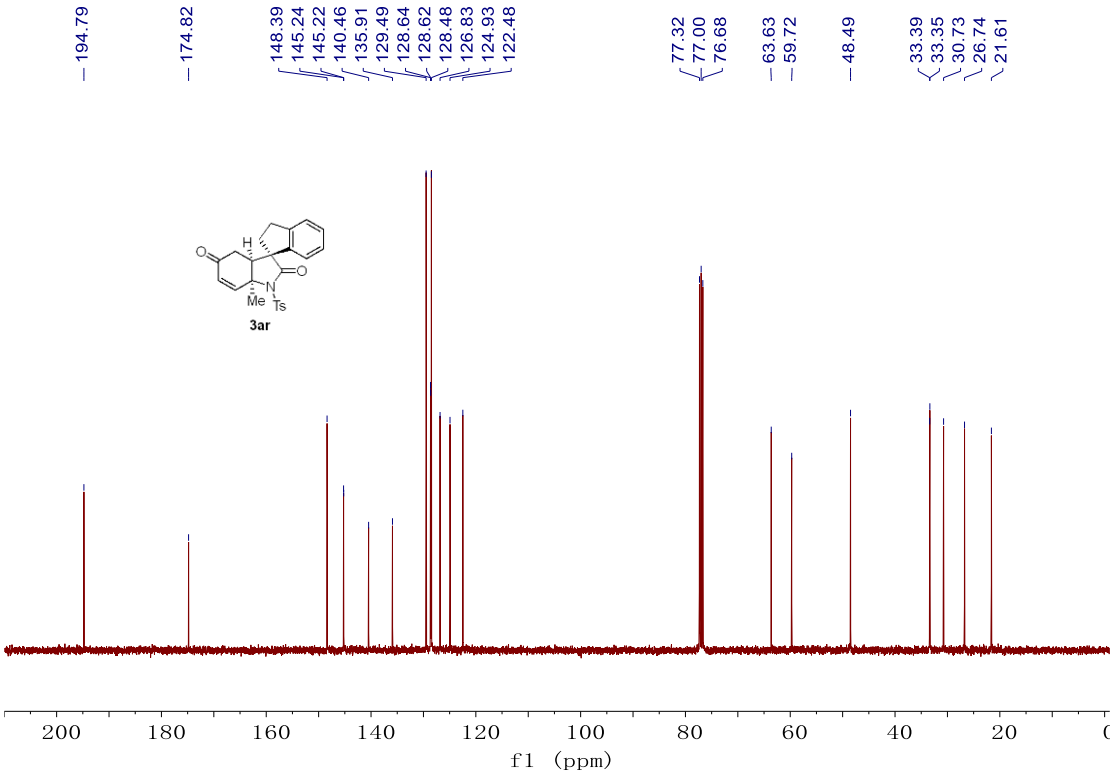
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3aq**



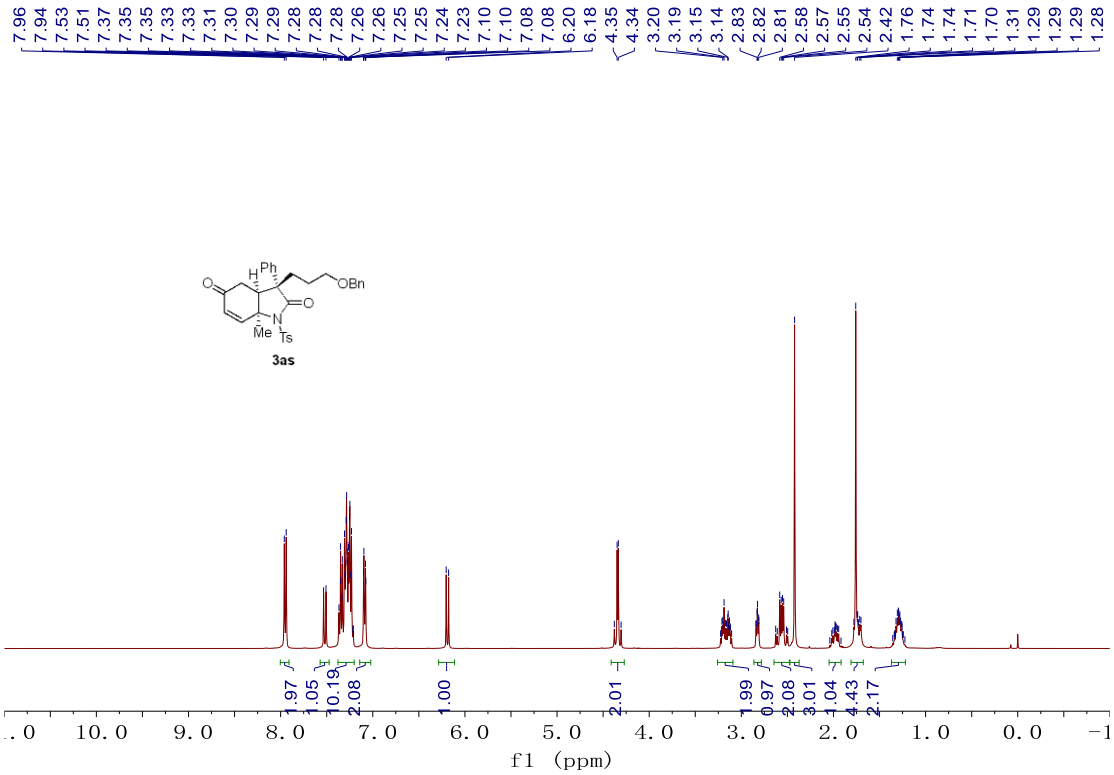
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3ar**



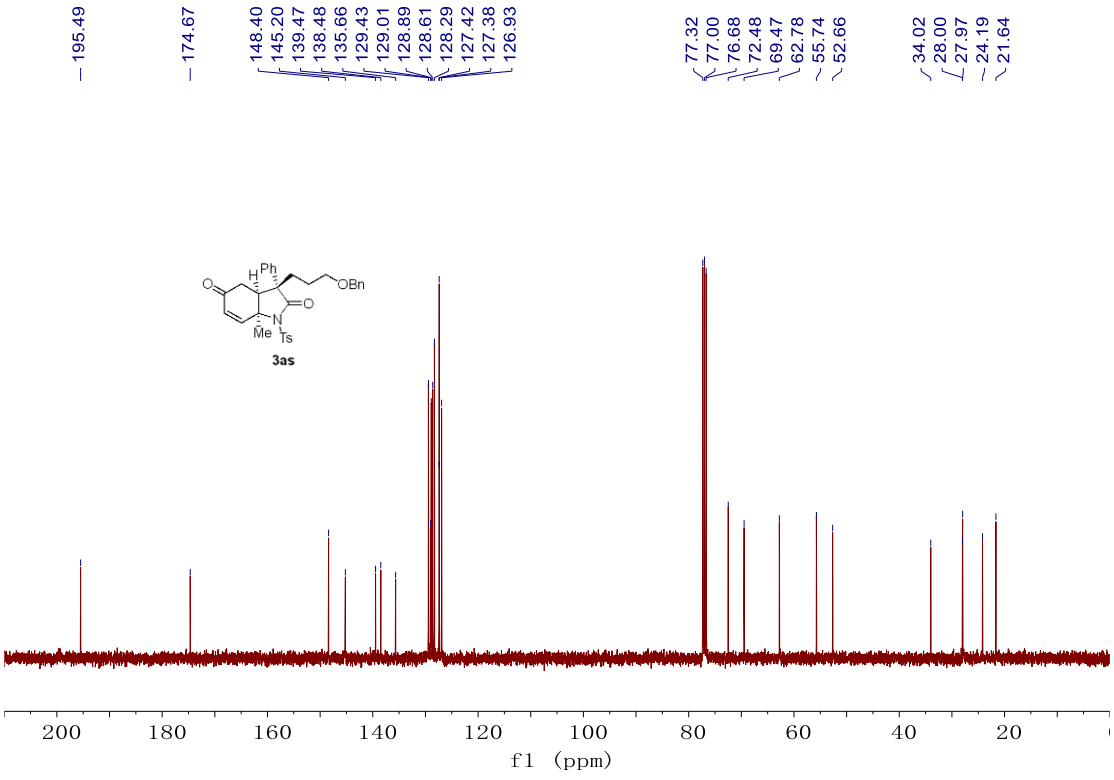
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3ar**



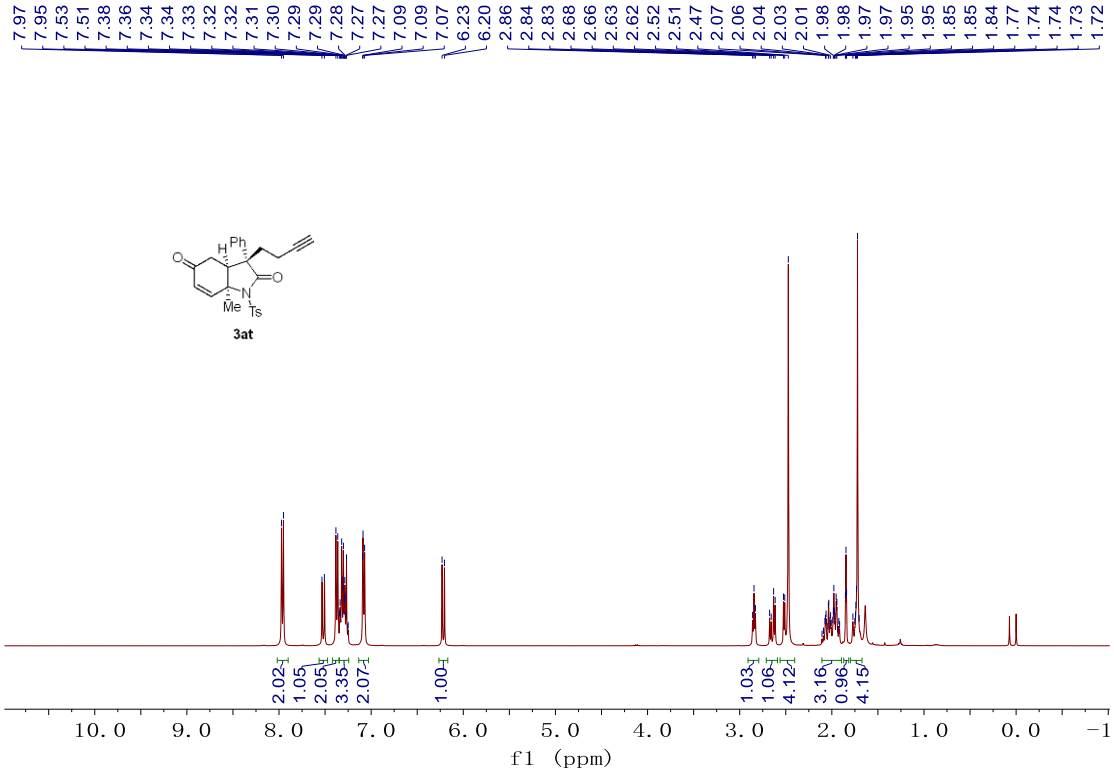
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3as**



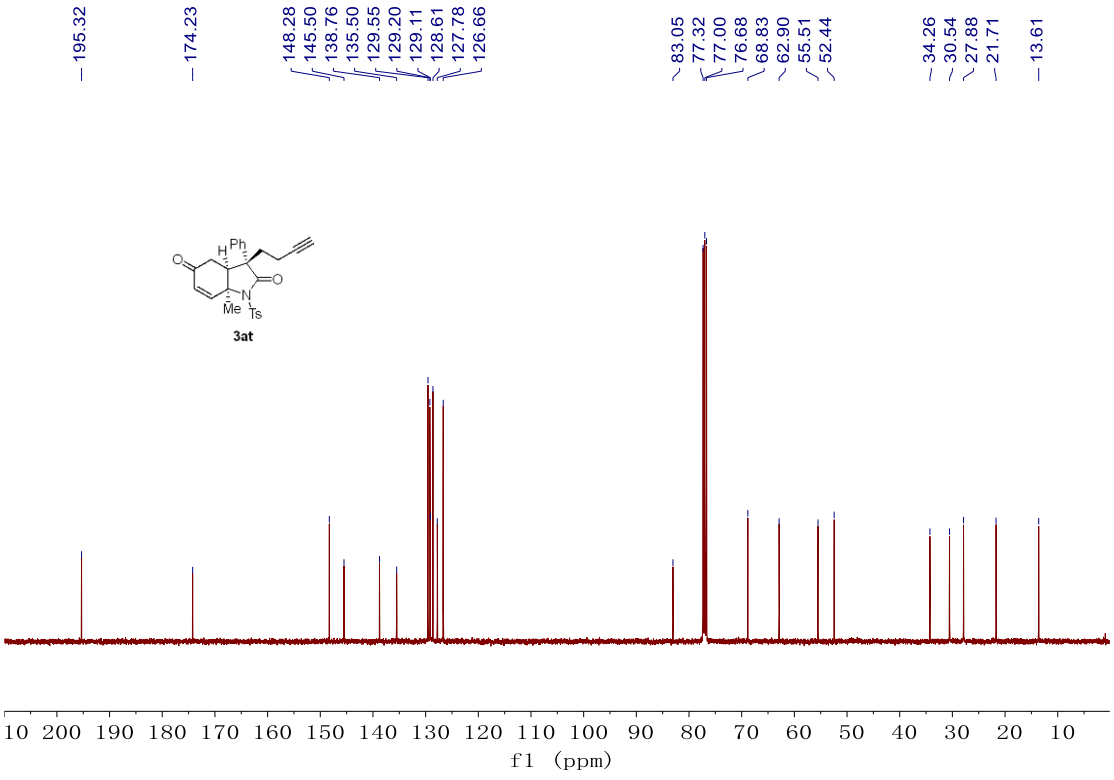
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3as**



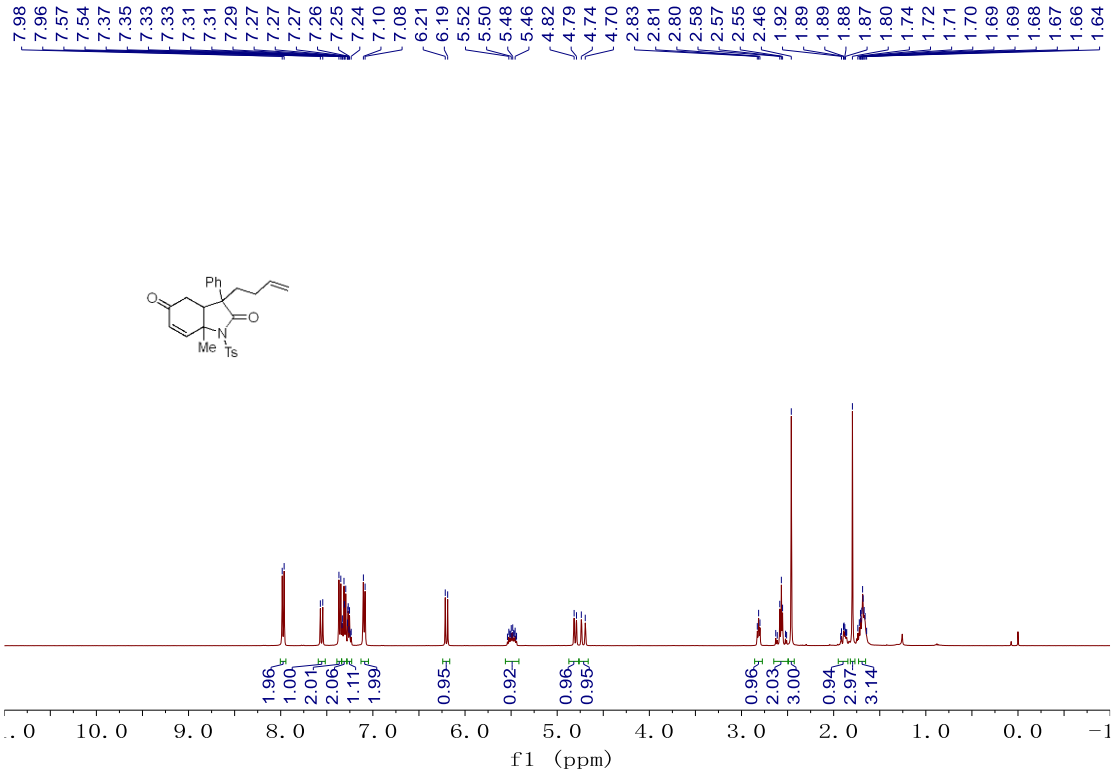
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3at**



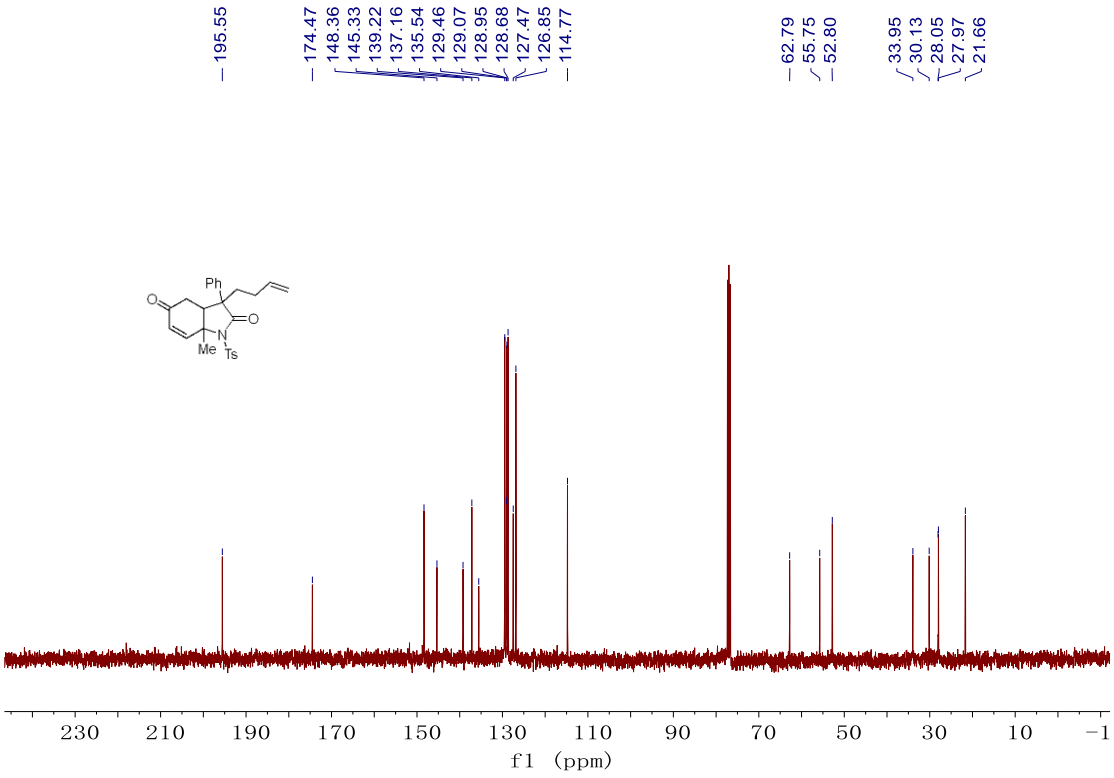
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3at**



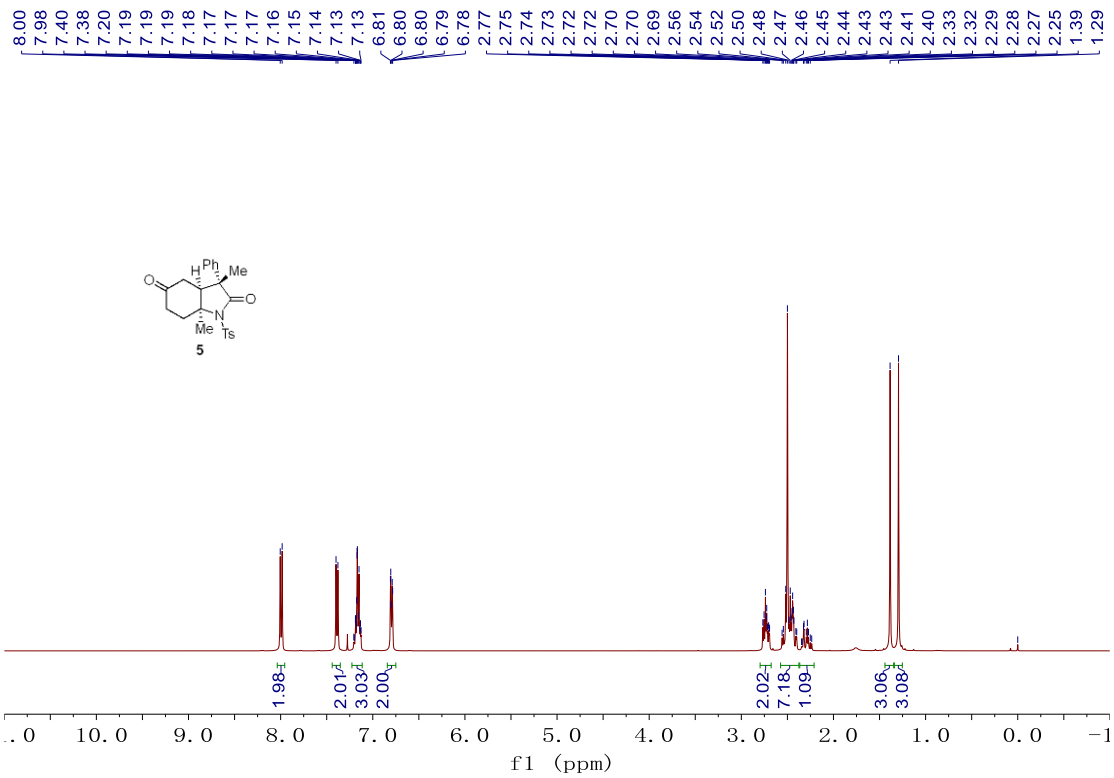
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3au**



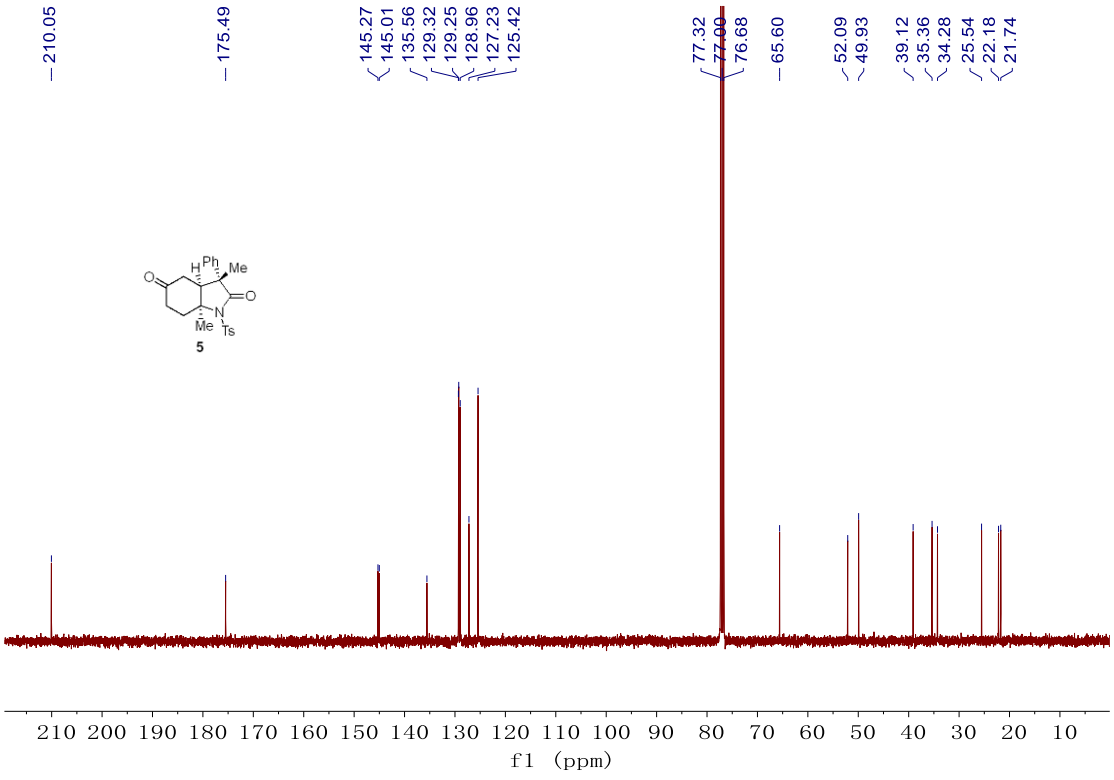
^{13}C NMR (100 MHz, $CDCl_3$) spectrum **3au**



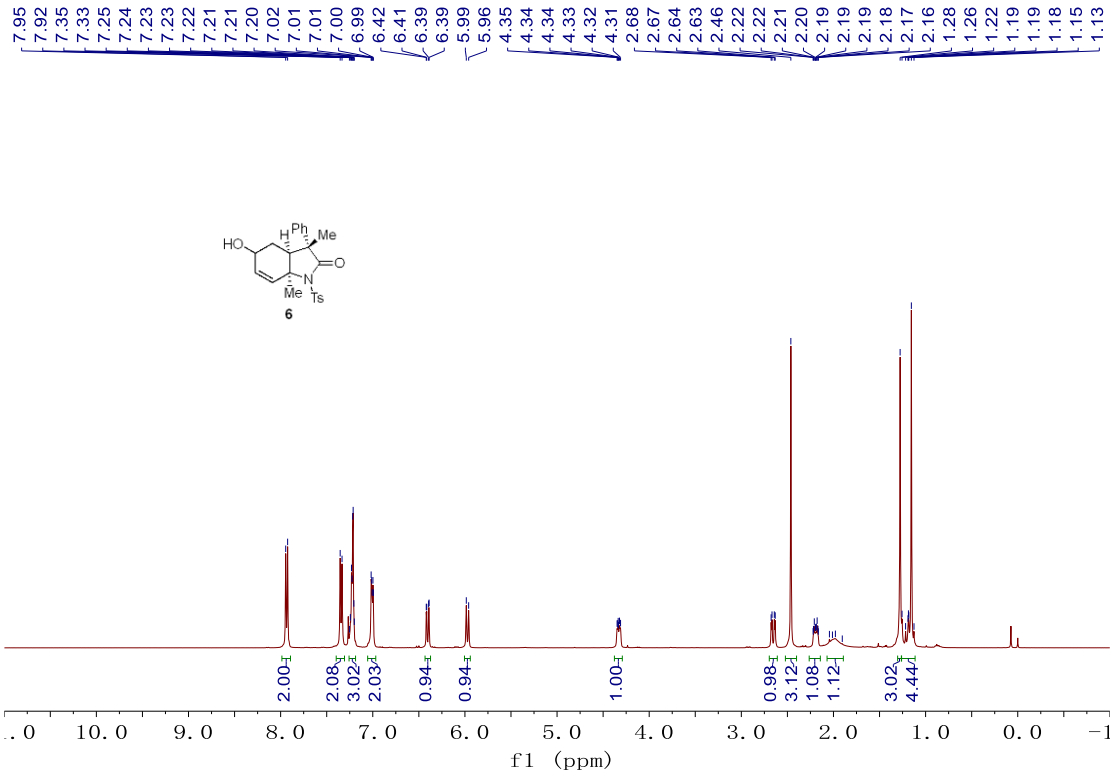
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5**



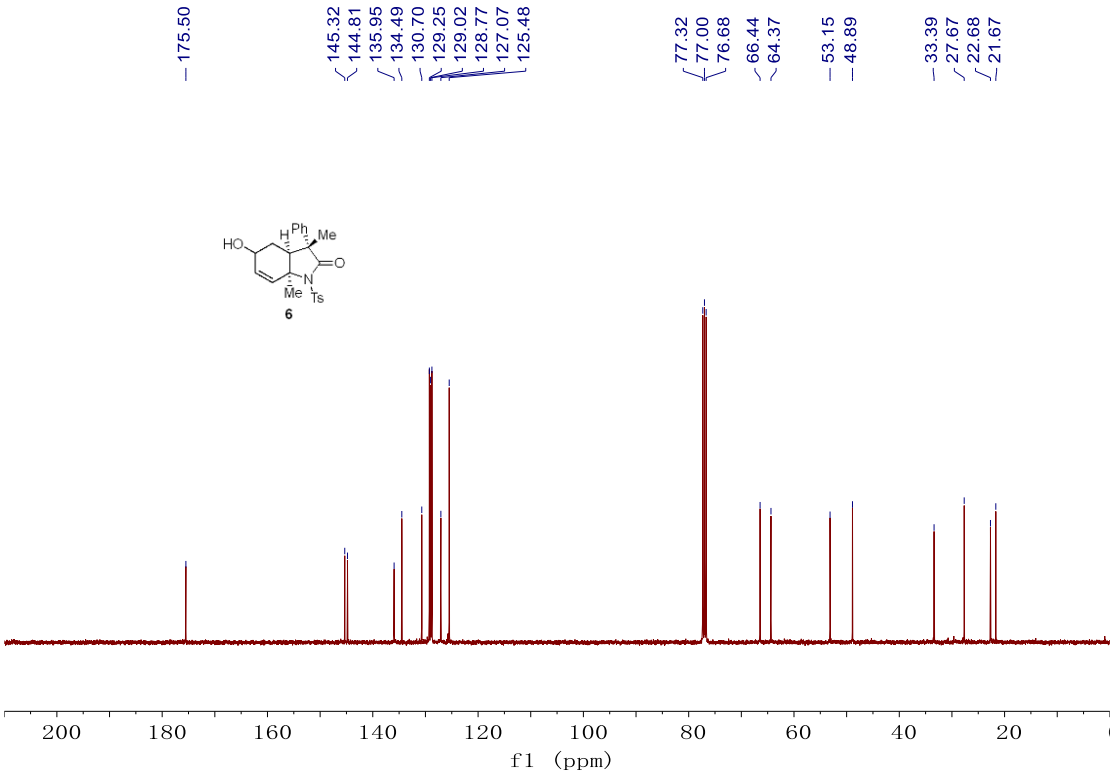
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **5**



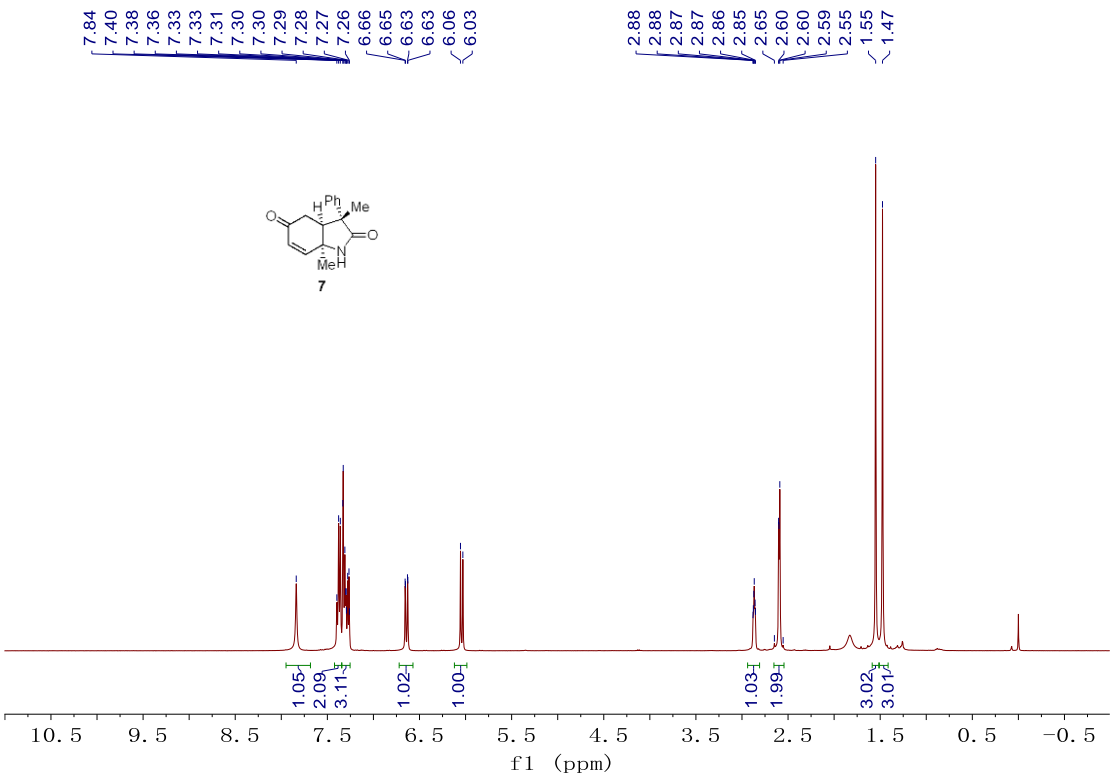
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6**



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



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