Supporting Information

Palladium-Catalyzed Oxidative Cyclization of Aniline-Tethered Alkylidenecyclopropanes with O_2: a Facile Protocol to Selectively Synthesize 2- and 3-Vinylindoles

Bo Cao,[a] Marwan Simaan,[c] Ilan Marek,[c] Yin Wei,[b,] and Min Shi[a,b,]**

[a]Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, 130 Mei Long Road, Shanghai 200237, China.

[b]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032 China.

weiyin@mail.sioc.ac.cn. Mshi@mail.sioc.ac.cn. Fax 86-21-64166128

[c]The Mallat Family Laboratory of Organic Chemistry, Schulich Faculty of Chemistry and Lise Meitner-Minerva Center for Computational Quantum Chemistry, Technion-Israel Institute of Technology, Technion City, Haifa 32000 Israel.

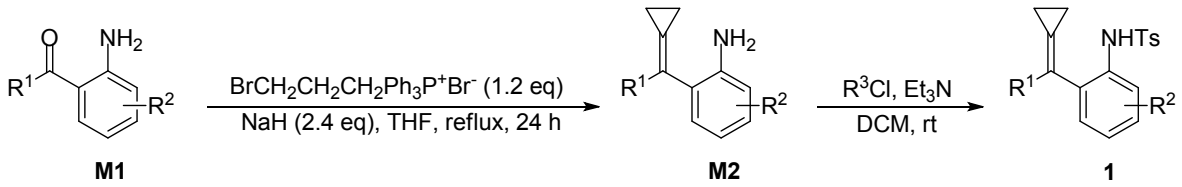
CONTENTS

1. General Remarks.

^{1}H NMR spectrum were recorded on a Bruker AM-400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; J-values are in Hz. ^{13}C NMR spectrum were recorded at 100 MHz. ^{19}F NMR spectrum were recorded at 376 MHz. Data for ^{1}H, ^{13}C, ^{19}F NMR were recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, br = broad). Mass spectrum were recorded with a HP-5989 instrument. All of the compounds reported in this paper gave satisfactory HRMS analytic data. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Infrared spectrum were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. THF, toluene and 1,4-dioxane were distilled from sodium (Na) under argon (Ar) atmosphere. DMF and dichloromethane were distilled from CaH_2 under argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

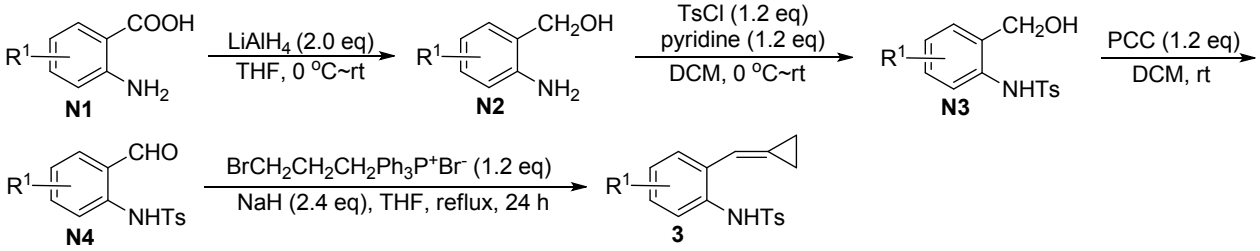
Compounds **M1**, **M2**, **1** and **3**[1], [2] were prepared according to the previous literatures.

2. General procedure for synthesis of ACPs 1 and 3



Under argon atmosphere, a solution of 3-bromopropyltriphenylphosphonium bromide (5.5 g, 12 mmol) and NaH (576 mg, 24 mmol) in THF (10 mL) was stirred at 70 °C for 12 h. Afterwards **M1** (10 mmol) in THF (5 mL) was added and the reaction solution was stirred at 70 °C for another 12 h. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 50 / 1) to afford the product **M2** in moderate yield.

To a solution of **M2** (2 mmol) and Et_3N (556 μL, 4 mmol) in DCM (5 mL) was added R_3Cl (3 mmol) at 0 °C. Afterwards the mixture was stirred at room temperature overnight. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 50 / 1) to afford the product **1** in high yield.



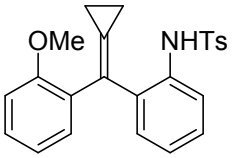
To a solution of **N1** (30 mmol, 1.0 eq) in dry THF was added dropwise into a solution of $LiAlH_4$ (60 mmol, 2.0 eq) in THF while the temperature was maintained at 0 °C. The resulting mixture was allowed to warm to room temperature and was stirred for 2 hours. Then the mixture was hydrolyzed by addition of H_2O (2.5 mL) and 5% NaOH (7.5 mL). The resulting suspension was filtered, and the precipitate was washed with ethyl acetate. Next, the combined organic collection was evaporated. The residue was recrystallized from ethyl acetate and petroleum eher,

affording the corresponding alcohols **N2** quantitatively as a white or yellow soild.

To a solution of **N2** (10.0mmol) and pyridine (1.0 mL, 12.0 mmol) in DCM (30 mL) was added a solution of *p*-TsCl (2.3 g, 12.0 mmol) in DCM (10 mL), and the mixture was stirred at rt for 3 hours. Upon completion monitored by TLC, 10 mL of saturated sodium bicarbonate was added to the reaction mixture. The aqueous phase was extracted with CH_2Cl_2 (3×15 mL), and the combined organic phases washed with H_2O (1×20 mL), and brine (1×20 mL) respectively. The organic phase was separated and dried over Na_2SO_4. After concentration, the resulting solid was added to a suspension of PCC (3.3 g, 12.0 mmol) in DCM (30 mL). After being stirred at rt for 2 h, the mixture was filtered and concentrated. The residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 8 / 1) to afford the product **N4** in moderate yield as colorless solid.

A solution of 3-bromopropyltriphenylphosphonium bromide (1.4 g, 3 mmol), NaH (168 mg, 7 mmol) and **N4** (2 mmol) in THF (8 mL) was stirred at 70 ^{o}C for 12 h. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 50 / 1) to afford the product **3** in moderate yield.

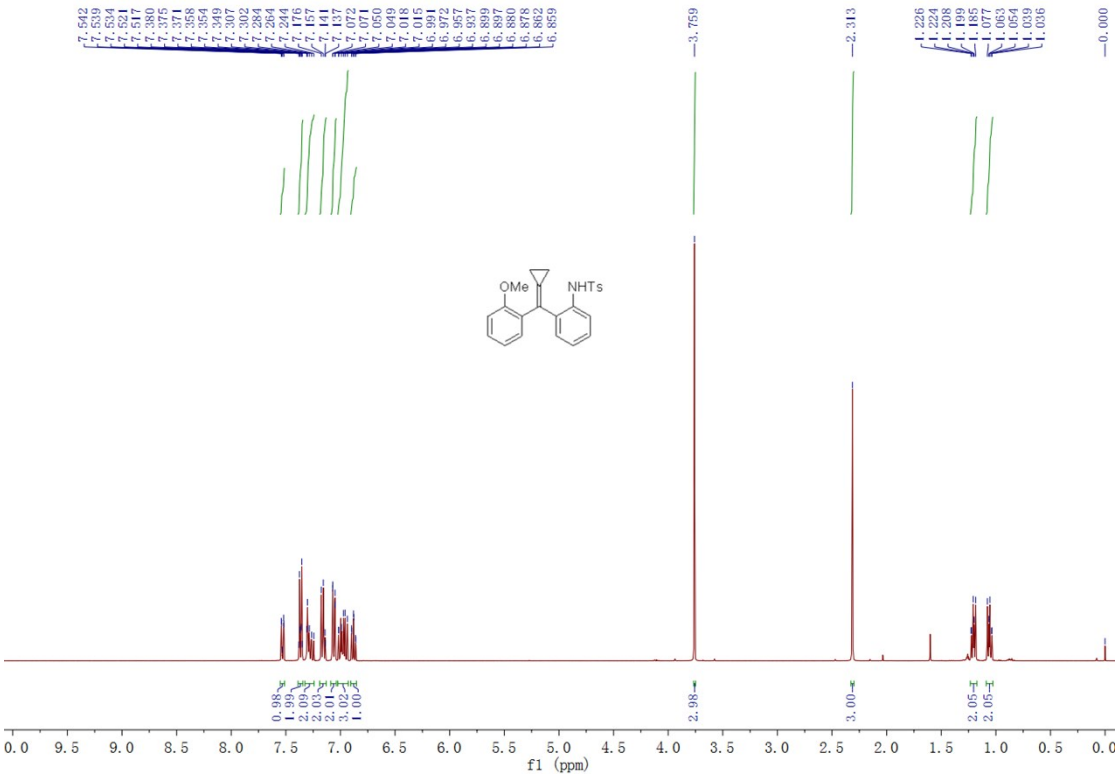
3. Characterization and spectra charts for ACPs 1 and 3



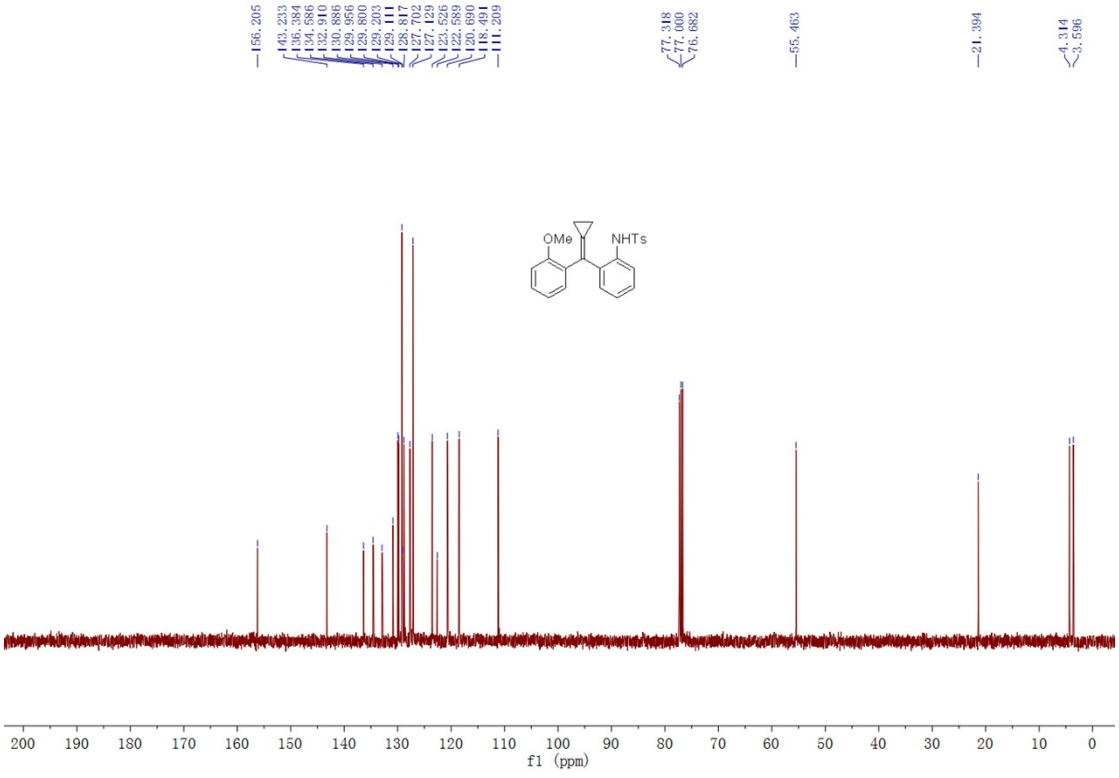
***N*-(2-(cyclopropylidene(2-methoxyphenyl)methyl)phenyl)-4-methylbenzenesulfonamide 1b**

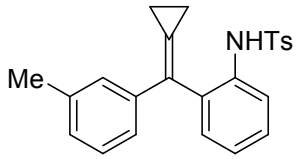
A faint yellow solid, 54% yield (378 mg). M.p.: 142-144 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.03-1.08 (m, 2H), 1.18-1.23 (m, 2H), 2.31 (s, 3H), 3.76 (s, 3H), 6.85-6.90 (m, 1H), 6.93-7.20 (m, 3H), 7.06 (dd, J = 0.4 Hz, 8.8 Hz, 2H), 7.13-7.18 (m, 2H), 7.24-7.31 (m, 2H), 7.34-7.38 (m, 2H), 7.51-7.55 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 3.6, 4.3, 21.4, 55.5, 111.2, 118.5, 120.7, 122.6, 123.5, 127.1, 127.7, 128.8, 129.1, 129.2, 129.8, 130.0, 130.9, 132.9, 134.6, 136.4, 143.2, 156.2. IR (neat) $\bar{\nu}$ 3267, 3065, 3053, 2970, 2920, 2845, 1599, 1577, 1489, 1328, 1241, 1166, 1112, 1088, 1019, 918, 887, 751, 653 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{27}N_2O_3S^{+1}(M+NH_4)^+$ requires: 423.1737, Found: 423.1739.

^{1}H NMR spectrum of 1b:



^{13}C NMR spectrum of 1b:

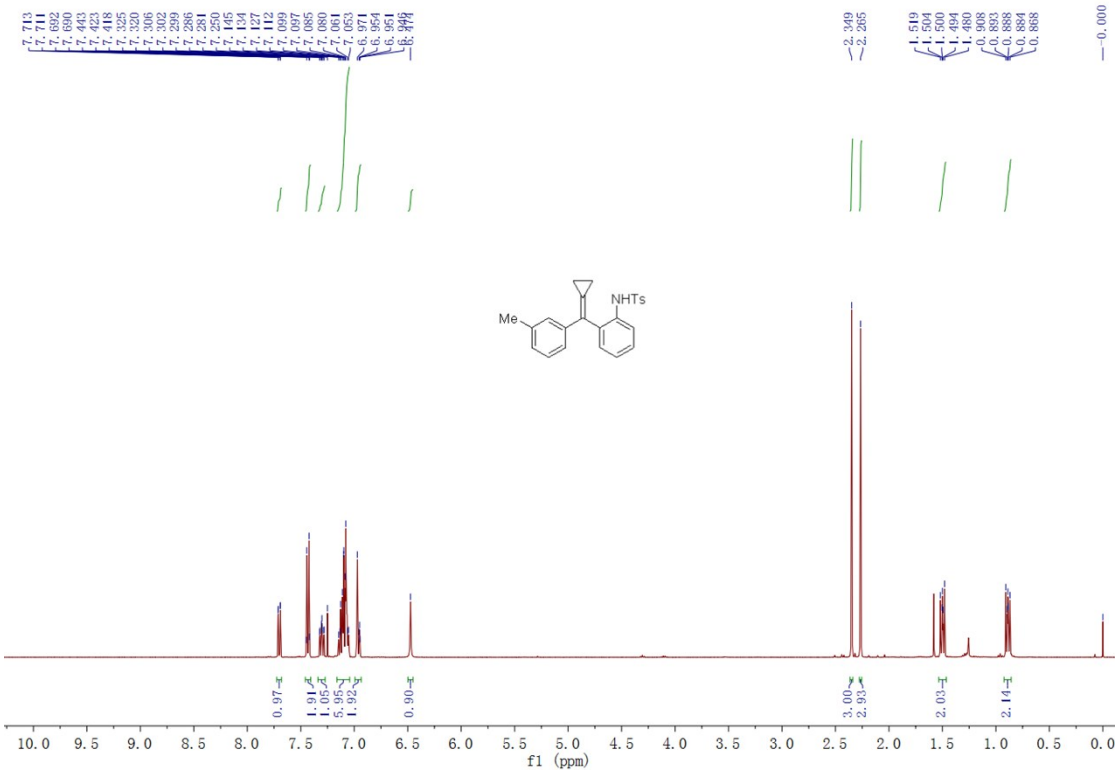




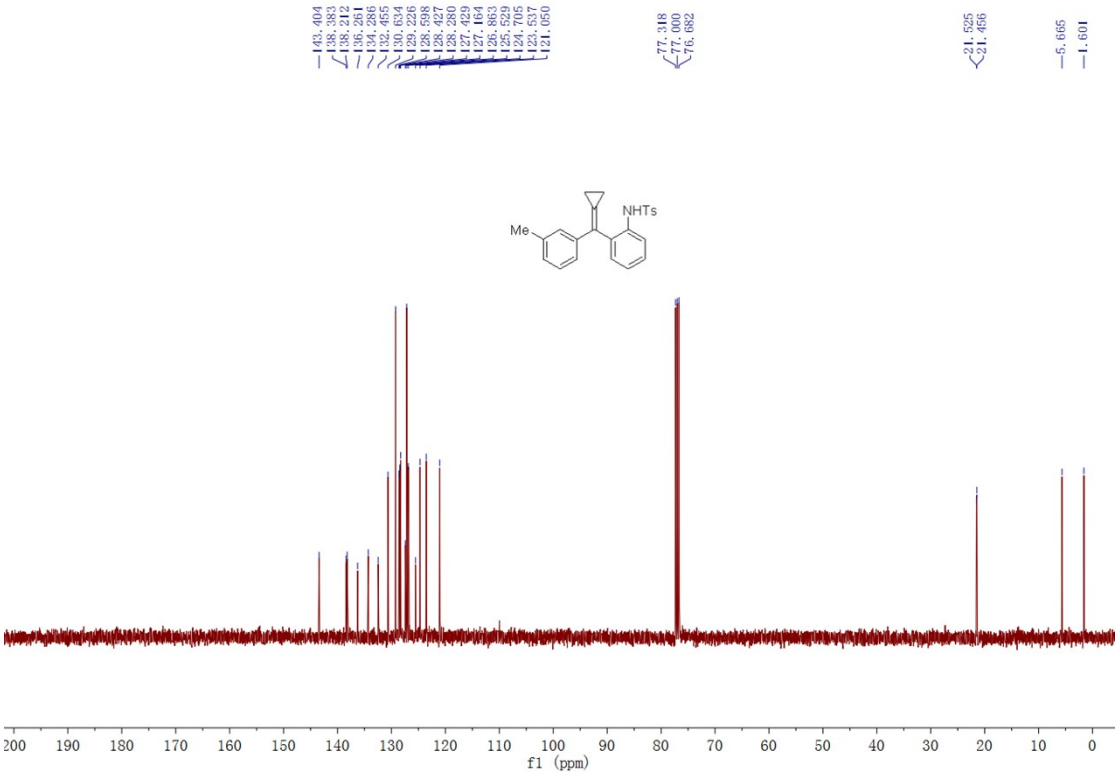
***N*-(2-(cyclopropylidene(*m*-tolyl)methyl)phenyl)-4-methylbenzenesulfonamide 1c**

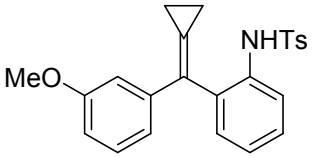
A white solid, 58% yield (312 mg). M.p.: 114-117 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.86-0.91 (m, 2H), 1.48-1.52 (m, 2H), 2.27 (s, 3H), 2.35 (s, 3H), 6.47 (s, 1H), 6.94-6.98 (m, 2H), 7.05-7.15 (m, 6H), 7.28-7.33 (m, 1H), 7.41-7.45 (m, 2H), 7.70 (dd, J = 0.8 Hz, 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.6, 5.7, 21.46, 21.53, 121.1, 123.5, 124.7, 125.5, 126.9, 127.2, 127.4, 128.3, 128.4, 128.6, 129.2, 130.6, 132.5, 134.3, 136.3, 138.2, 138.4, 143.4. IR (neat) $\bar{\nu}$ 3255, 3048, 3015, 2967, 2920, 2848, 1724, 1596, 1577, 1493, 1452, 1395, 1334, 1279, 1169, 1092, 913, 856, 809, 787, 749, 698, 667 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{27}N_2O_2S^{+1}(M+NH_4)^+$ requires: 407.1788, Found: 407.1790.

^{1}H NMR spectrum of 1c:



^{13}C NMR spectrum of 1c:

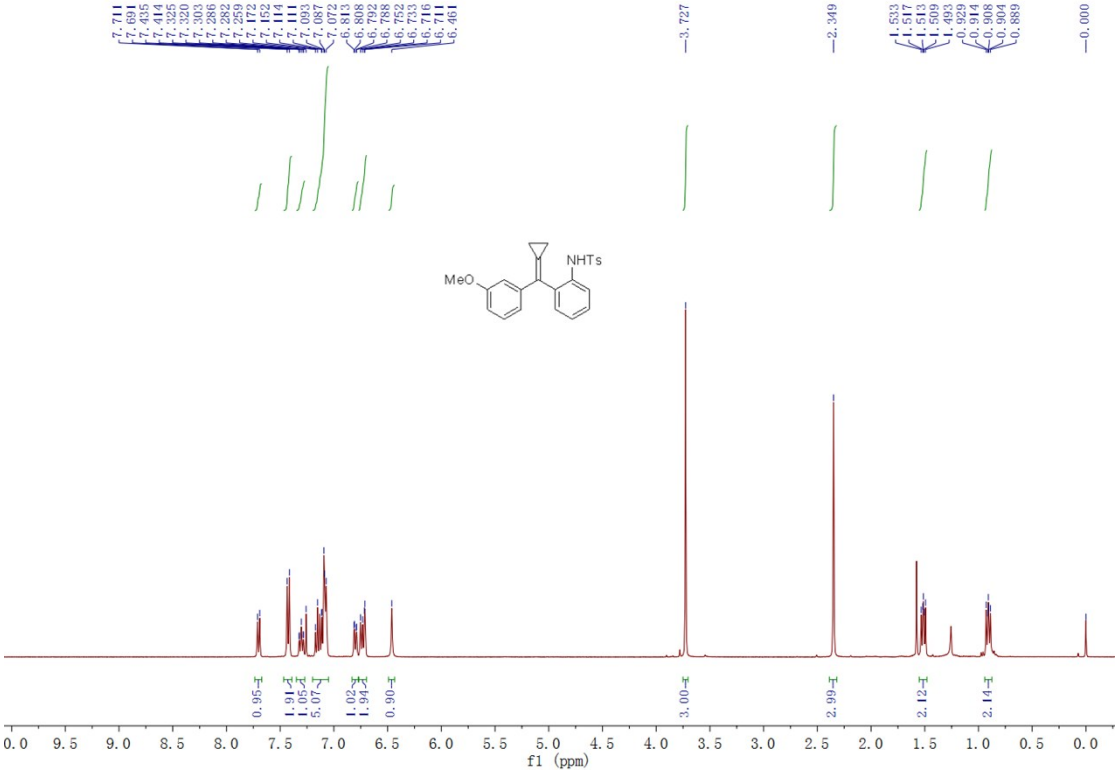




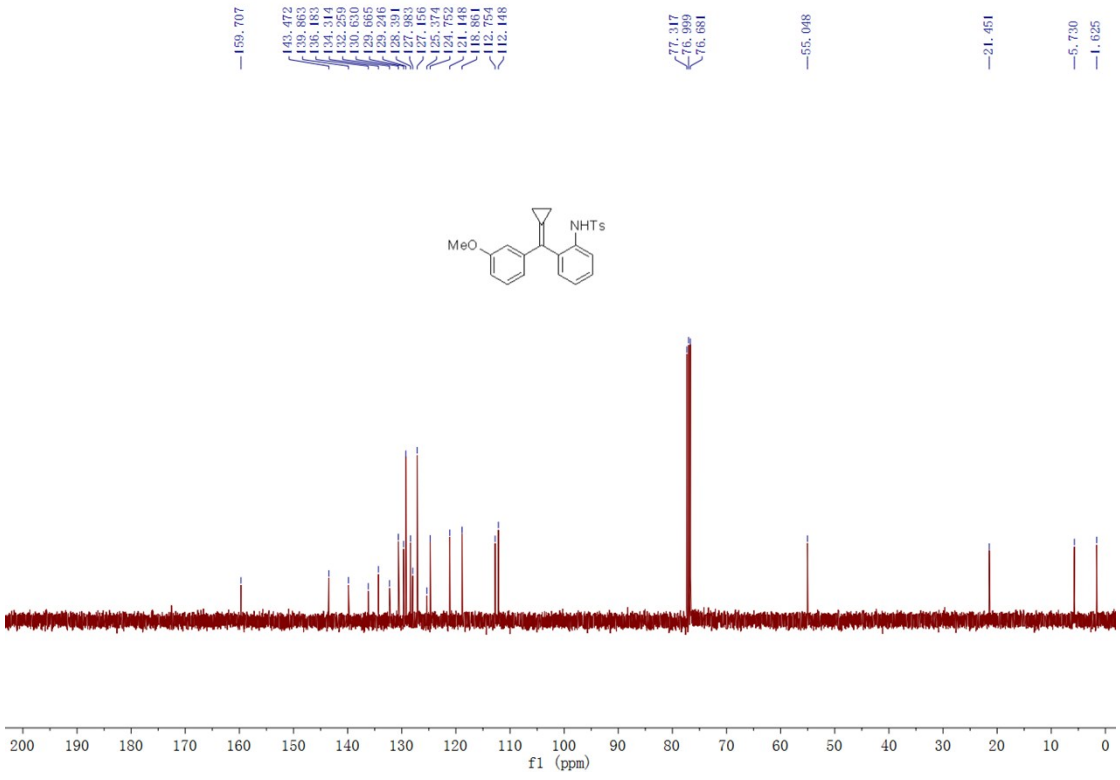
***N*-(2-(cyclopropylidene(3-methoxyphenyl)methyl)phenyl)-4-methylbenzenesulfonamide 1d**

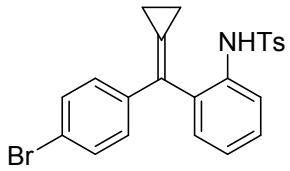
A faint yellow solid, 42% yield (270 mg). M.p.: 148-150 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.88-0.93 (m, 2H), 1.49-1.54 (m, 2H), 2.35 (s, 3H), 3.73 (s, 3H), 6.46 (s, 1H), 6.71-6.76 (m, 2H), 6.80 (dd, *J* = 1.6 Hz, 8.0 Hz, 1H), 7.07-7.18 (m, 5H), 7.28-7.33 (m, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.6, 5.7, 21.5, 55.0, 112.1, 112.8, 118.9, 121.1, 124.8, 125.4, 127.2, 128.0, 128.4, 129.2, 129.7, 130.6, 132.3, 134.3, 136.2, 139.9, 143.5, 159.7. IR (neat) $\bar{\nu}$ 3254, 3087, 3054, 3023, 2967, 2951, 2915, 2851, 2829, 1603, 1578, 1485, 1446, 1431, 1396, 1334, 1285, 1205, 1168, 1159, 1092, 1044, 911, 855, 814, 776, 694, 665 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{27}N_2O_3S^{+1}(M+NH_4)^+$ requires: 423.1737, Found: 423.1739.

^{1}H NMR spectrum of 1d:



^{13}C NMR spectrum of 1d:

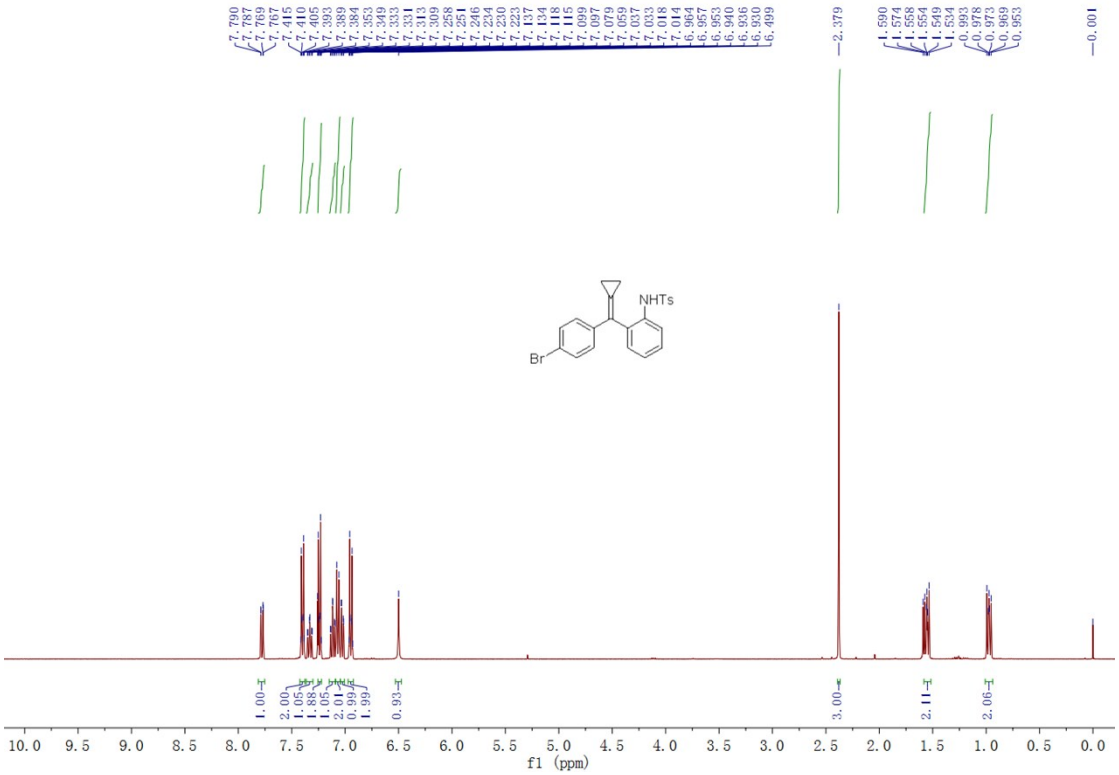




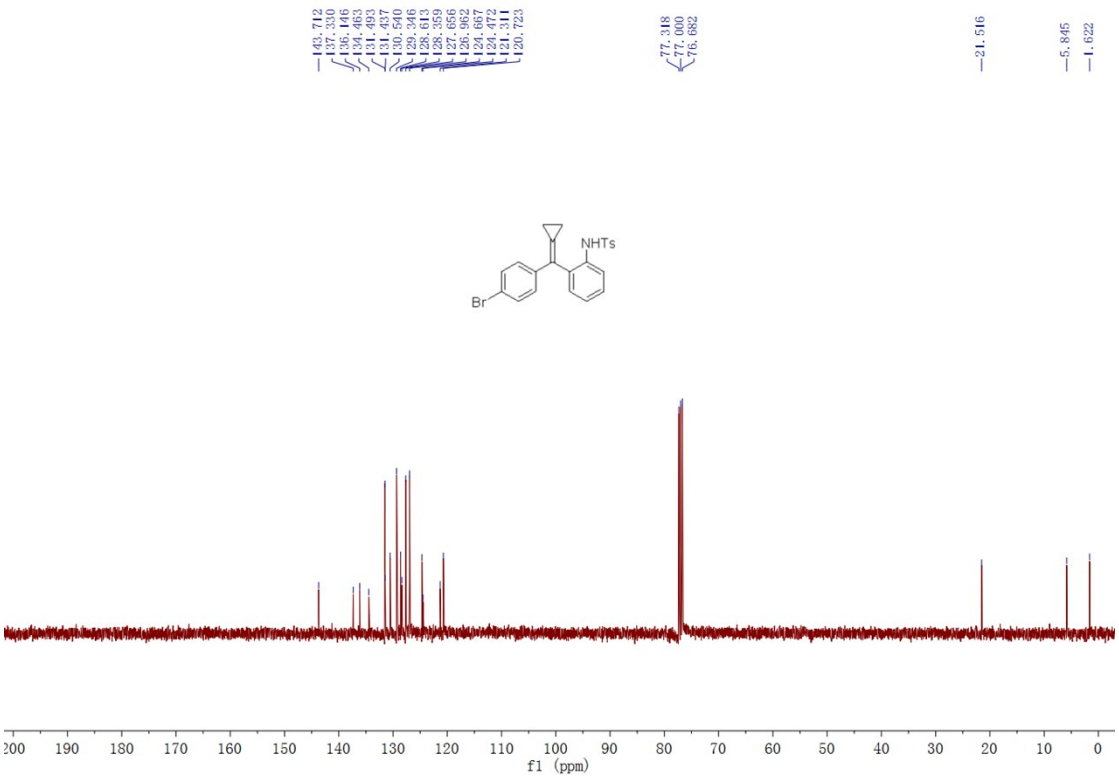
***N*-(2-((4-bromophenyl)(cyclopropylidene)methyl)phenyl)-4-methylbenzenesulfonamide 1f**

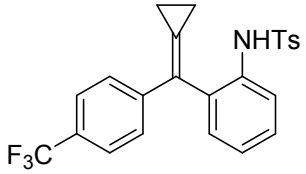
A faint yellow solid, 74% yield (399 mg). M.p.: 167-169 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.95-1.00 (m, 2H), 1.53-1.59 (m, 2H), 2.38 (s, 3H), 6.50 (s, 1H), 6.93-6.97 (m, 2H), 7.03 (dd, J = 1.6 Hz, 7.6 Hz, 1H), 7.07 (d, J = 8.0 Hz, 2H), 7.12 (ddd, J = 0.8 Hz, 7.2 Hz, 7.2 Hz, 1H), 7.22-7.26 (m, 2H), 7.30-7.36 (m, 2H), 7.38-7.42 (m, 2H), 7.78 (dd, J = 0.8 Hz, 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.6, 5.8, 21.5, 120.7, 121.3, 124.5, 124.7, 127.0, 127.7, 128.4, 128.6, 129.3, 130.5, 131.4, 131.5, 134.5, 136.1, 137.3, 143.7. IR (neat) $\bar{\nu}$ 3255, 3067, 3042, 2973, 2918, 1602, 1580, 1486, 1399, 1336, 1092, 924, 893, 812, 748, 706, 664 cm^{-1}. HRMS (APCI) Calcd. for $C_{23}H_{21}BrNO_2S^{+1}(M+H)^+$ requires: 454.0471, Found: 454.0456.

^{1}H NMR spectrum of 1f:



^{13}C NMR spectrum of 1f:

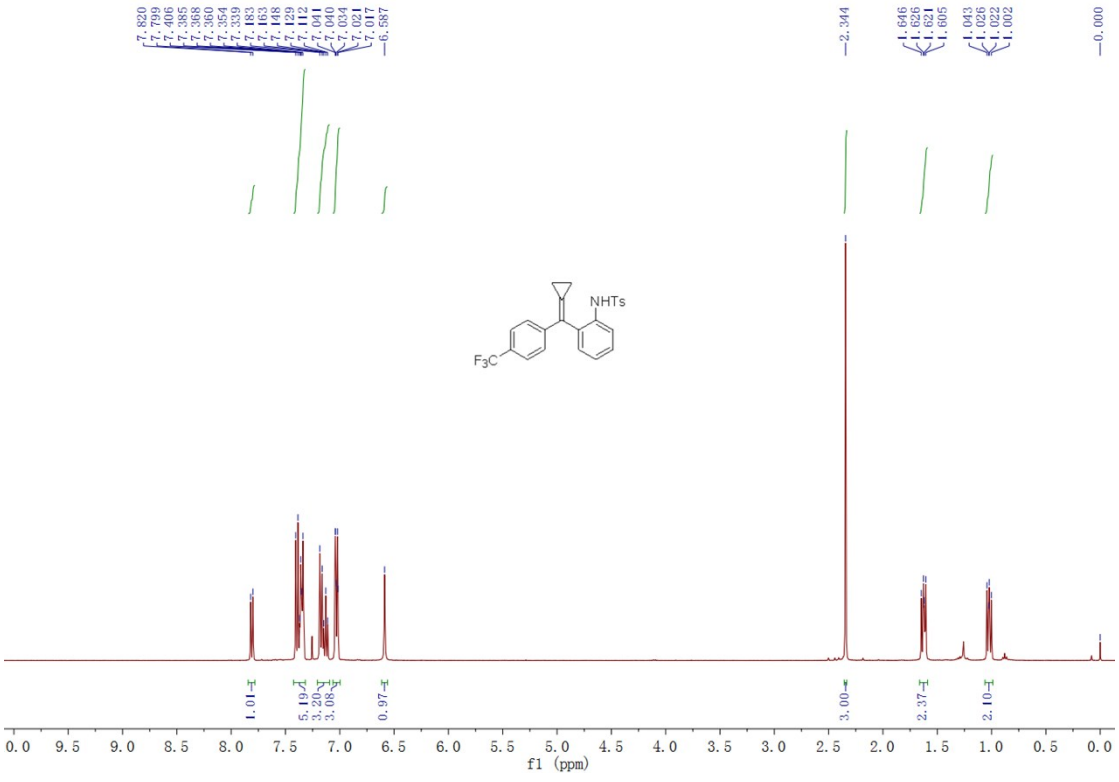




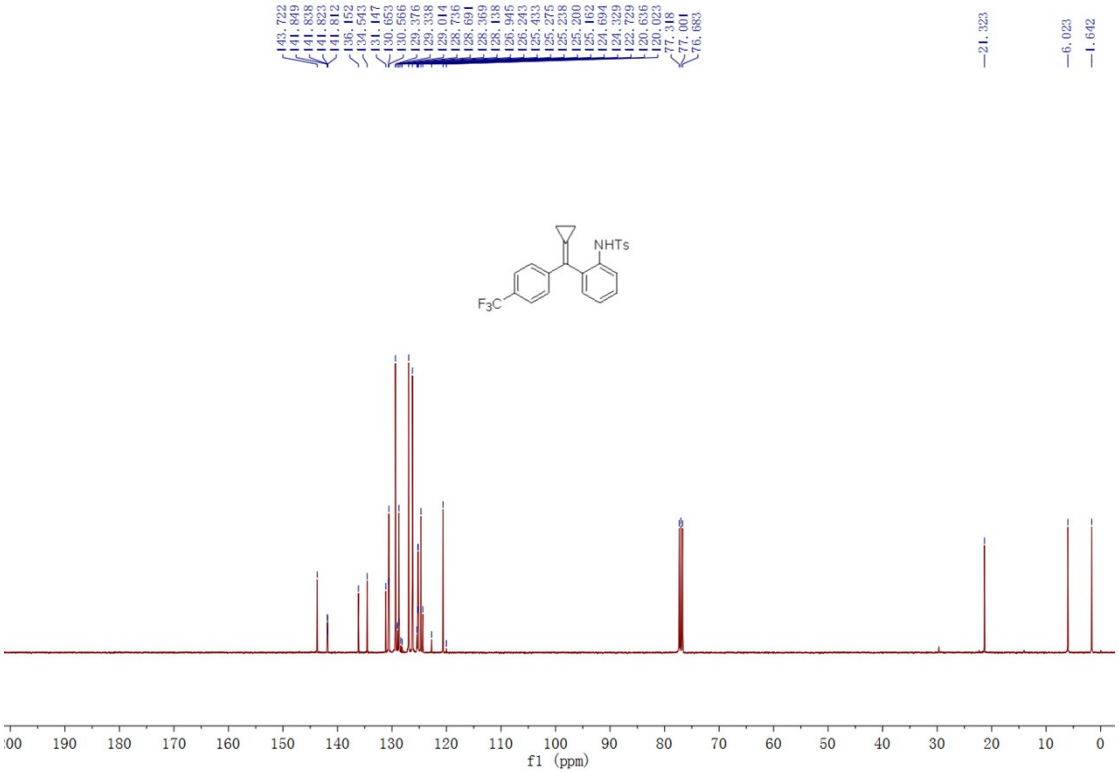
***N*-(2-(cyclopropylidene(4-(trifluoromethyl)phenyl)methyl)phenyl)-4-methylbenzenesulfonamide 1h**

A faint yellow solid, 55% yield (336 mg). M.p.: 143-145 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.00-1.04 (m, 2H), 1.60-1.65 (m, 2H), 2.34 (s, 3H), 6.59 (s, 1H), 7.00-7.03 (m, 3H), 7.11-7.19 (m, 3H), 7.33-7.41 (m, 5H), 7.81 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.6, 6.0, 21.3, 120.6, 124.1 (q, J = 270.6 Hz), 124.3, 124.7, 125.2 (q, J = 3.8 Hz), 126.2, 126.9, 128.7, 128.9 (q, J = 32.2 Hz), 129.4, 130.6, 130.7, 131.1, 134.5, 136.2, 141.8 (q, J = 1.1 Hz), 143.7. ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -62.5. IR (neat) $\bar{\nu}$ 3284, 3264, 3062, 3037, 1613, 1491, 1395, 1338, 1325, 1117, 1093, 1070, 1042, 934, 811, 760, 738, 660 cm^{-1}. HRMS (ESI) Calcd. for $C_{24}H_{24}F_3N_2O_2S^{+1}(M+NH_4)^+$ requires: 461.1505, Found: 461.1508.

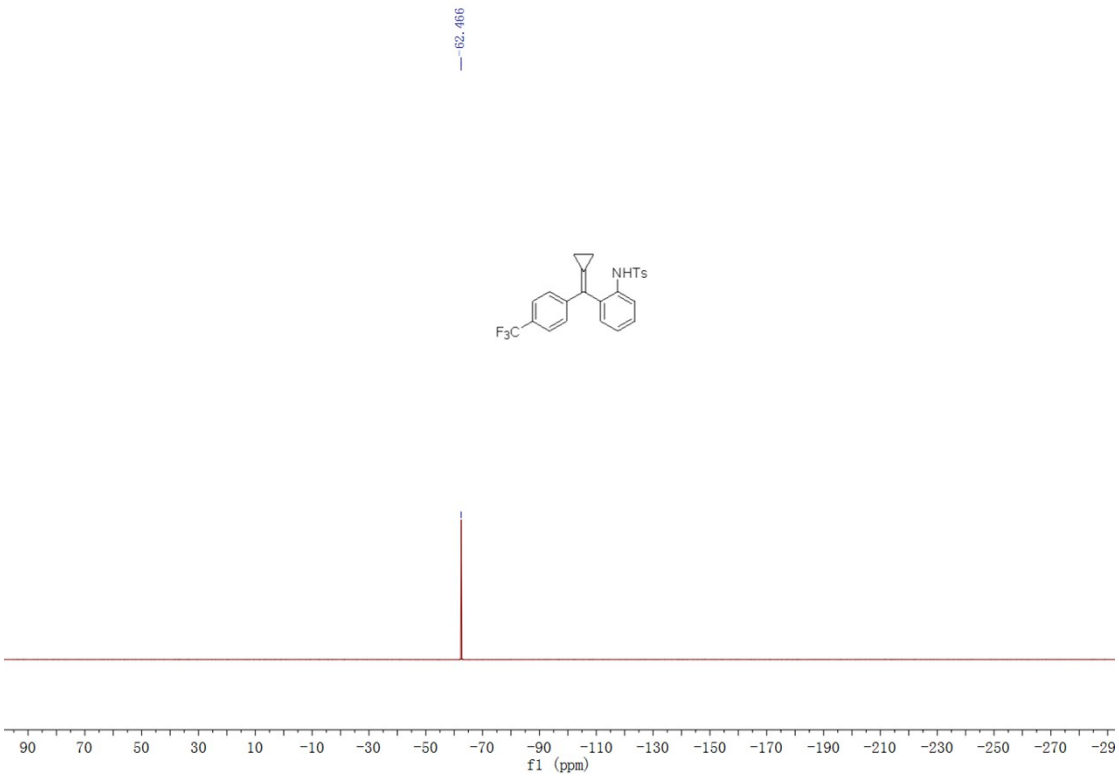
^{1}H NMR spectrum of 1h:

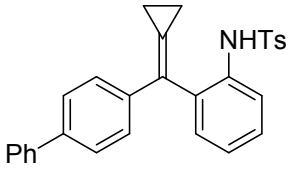


^{13}C NMR spectrum of 1h:



^{19}F NMR spectrum of 1h:

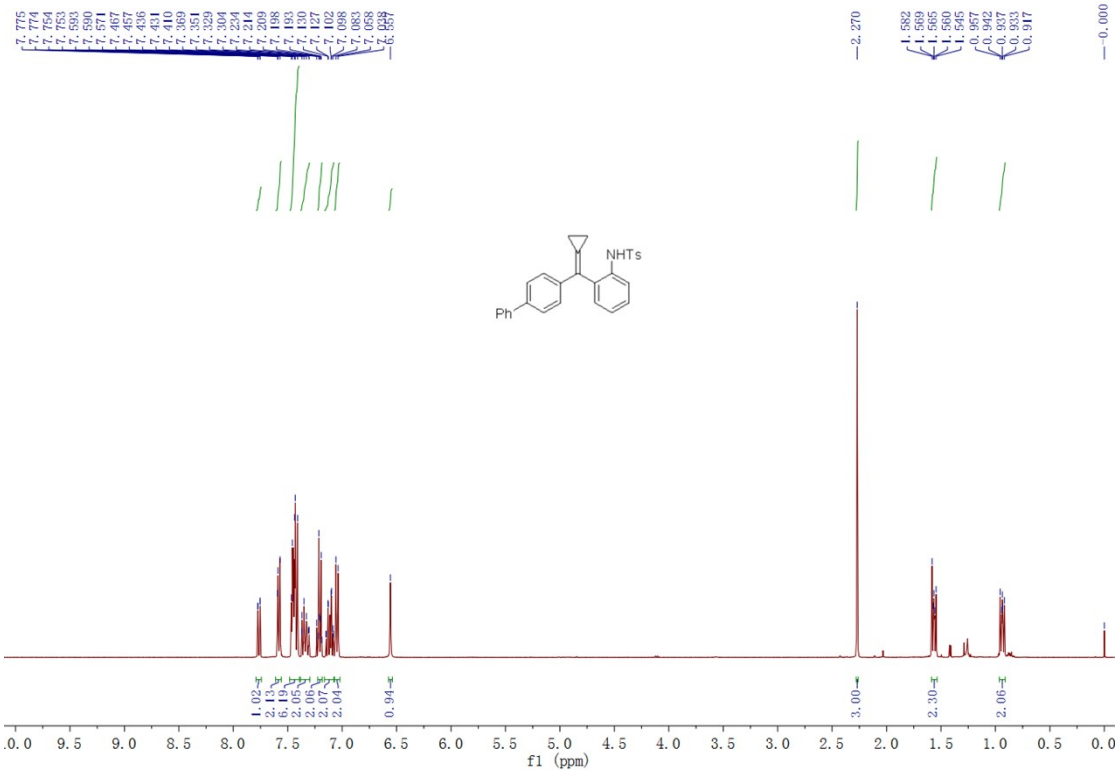




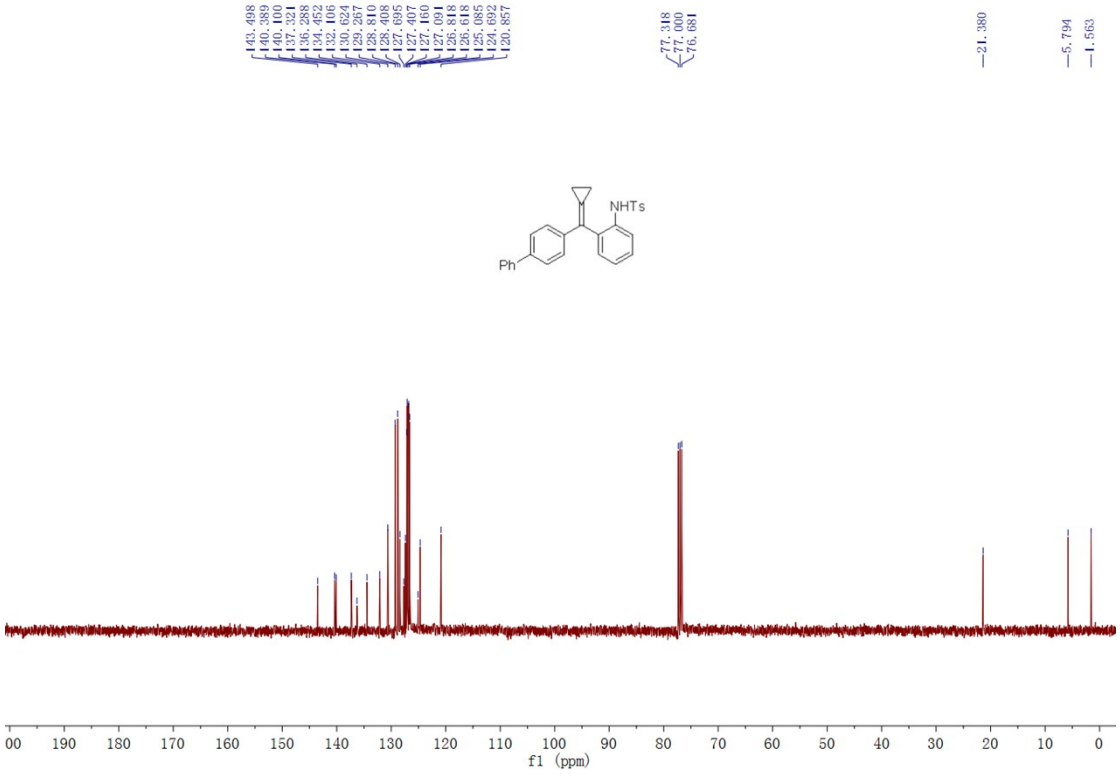
***N*-(2-([1,1'-biphenyl]-4-yl(cyclopropylidene)methyl)phenyl)-4-methylbenzenesulfonamide 1i**

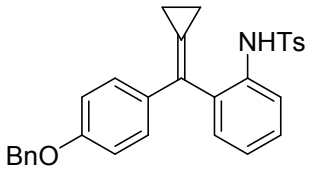
A white solid, 67% yield (301 mg). M.p.: 161-163 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.91-0.96 (m, 2H), 1.54-1.59 (m, 2H), 2.27 (s, 3H), 6.56 (s, 1H), 7.05 (d, J = 8.0 Hz, 2H), 7.07-7.15 (m, 2H), 7.18-7.22 (m, 2H), 7.30-7.38 (m, 2H), 7.41-7.47 (m, 6H), 7.57-7.60 (m, 2H), 7.76 (dd, J = 0.4 Hz, 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.6, 5.8, 21.4, 120.9, 124.7, 125.1, 126.6, 126.8, 127.1, 127.2, 127.4, 127.7, 128.4, 128.8, 129.3, 130.6, 132.1, 134.5, 136.3, 137.3, 140.1, 140.4, 143.5. IR (neat) $\bar{\nu}$ 3356, 3337, 3314, 3254, 3067, 3026, 2976, 1599, 1580, 1488, 1449, 1412, 1384, 1333, 1274, 1166, 1091, 921, 895, 847, 812, 766, 730, 701, 664 cm^{-1}. HRMS (ESI) Calcd. for $C_{29}H_{29}N_2O_2S^{+1}(M+NH_4)^+$ requires: 469.1944, Found: 469.1938.

^{1}H NMR spectrum of 1i:



^{13}C NMR spectrum of 1i:

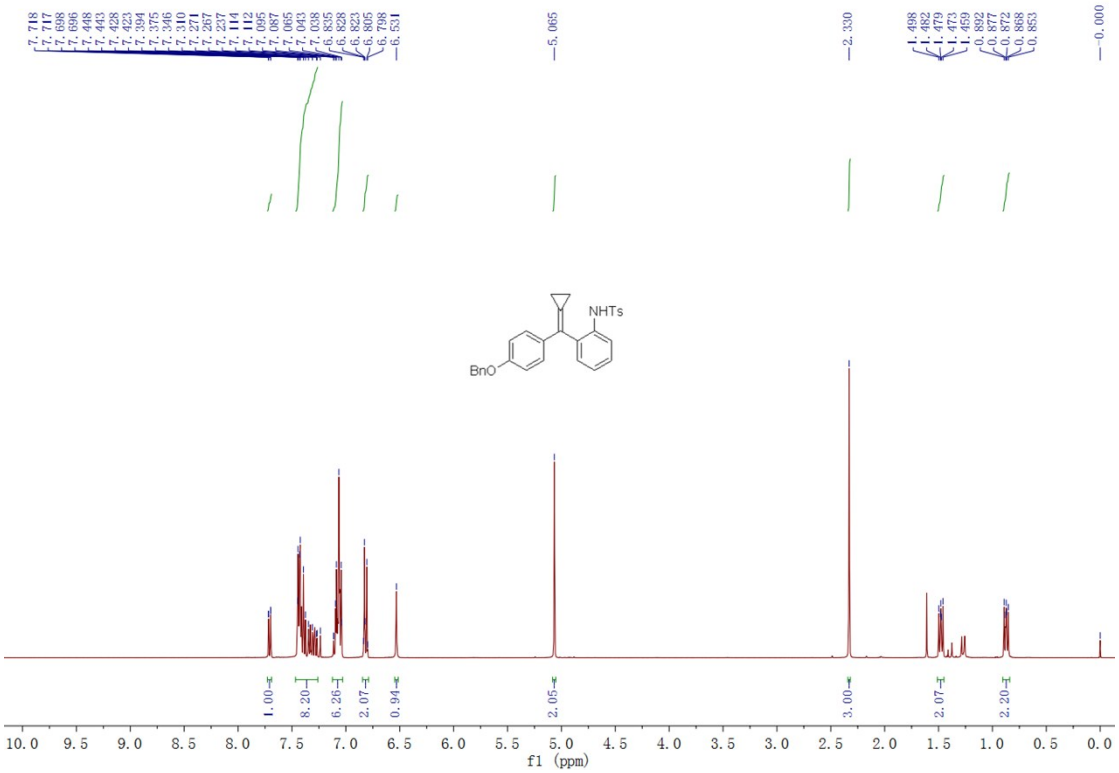




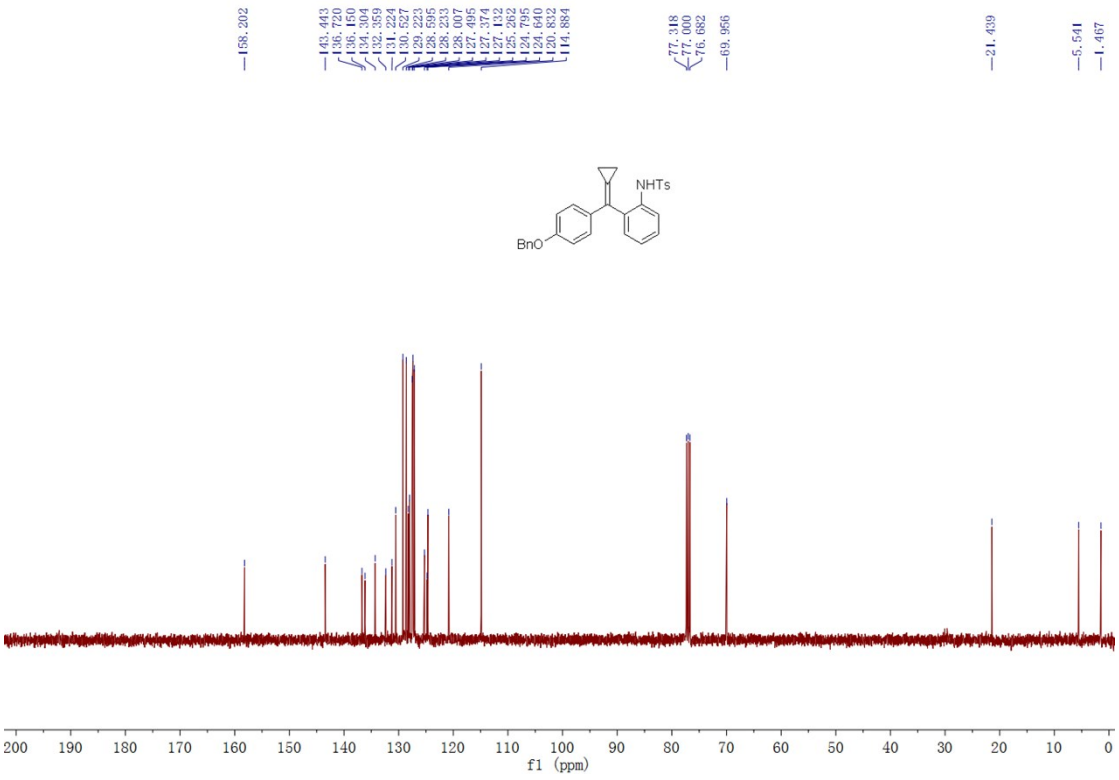
***N*-(2-((4-(benzyloxy)phenyl)(cyclopropylidene)methyl)phenyl)-4-methylbenzenesulfonamide 1j**

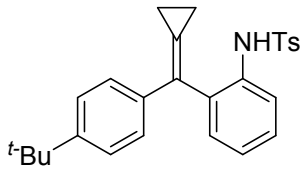
A white solid, 78% yield (374 mg). M.p.: 128-130 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.85-0.90 (m, 2H), 1.45-1.50 (m, 2H), 2.33 (s, 3H), 5.01 (s, 2H), 6.53 (s, 1H), 6.79-6.84 (m, 2H), 7.03-7.12 (m, 6H), 7.23-7.45 (m, 8H), 7.71 (dd, J = 0.8 Hz, 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.5, 5.5, 21.4, 70.0, 114.9, 120.8, 124.6, 124.8, 125.3, 127.1, 127.4, 127.5, 128.0, 128.2, 128.6, 129.2, 130.5, 131.2, 132.4, 134.3, 136.2, 136.7, 143.4, 158.2. IR (neat) $\bar{\nu}$ 3262, 3065, 3031, 2967, 2959, 2856, 1603, 1576, 1508, 1489, 1381, 1333, 1243, 1164, 1092, 1039, 921, 833, 814, 757, 740, 688, 667 cm^{-1}. HRMS (ESI) Calcd. for $C_{30}H_{31}N_2O_3S^{+1}(M+NH_4)^+$ requires: 499.2050, Found: 499.2044.

^{1}H NMR spectrum of 1j:



^{13}C NMR spectrum of 1j:

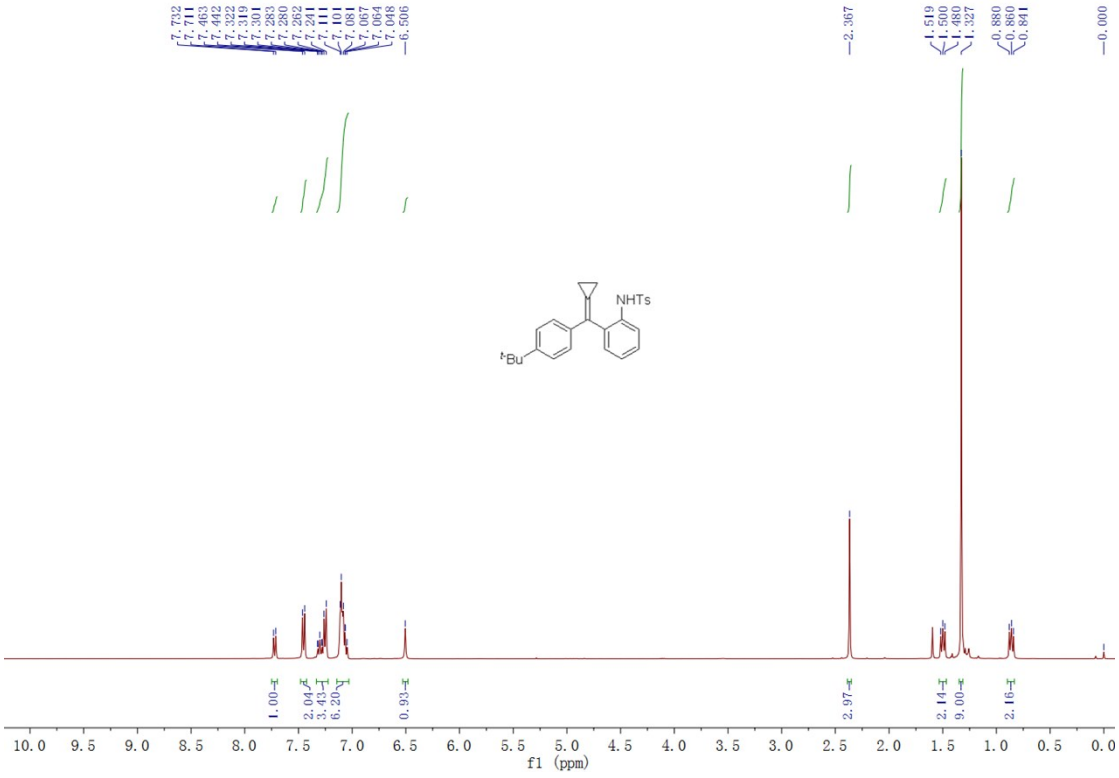




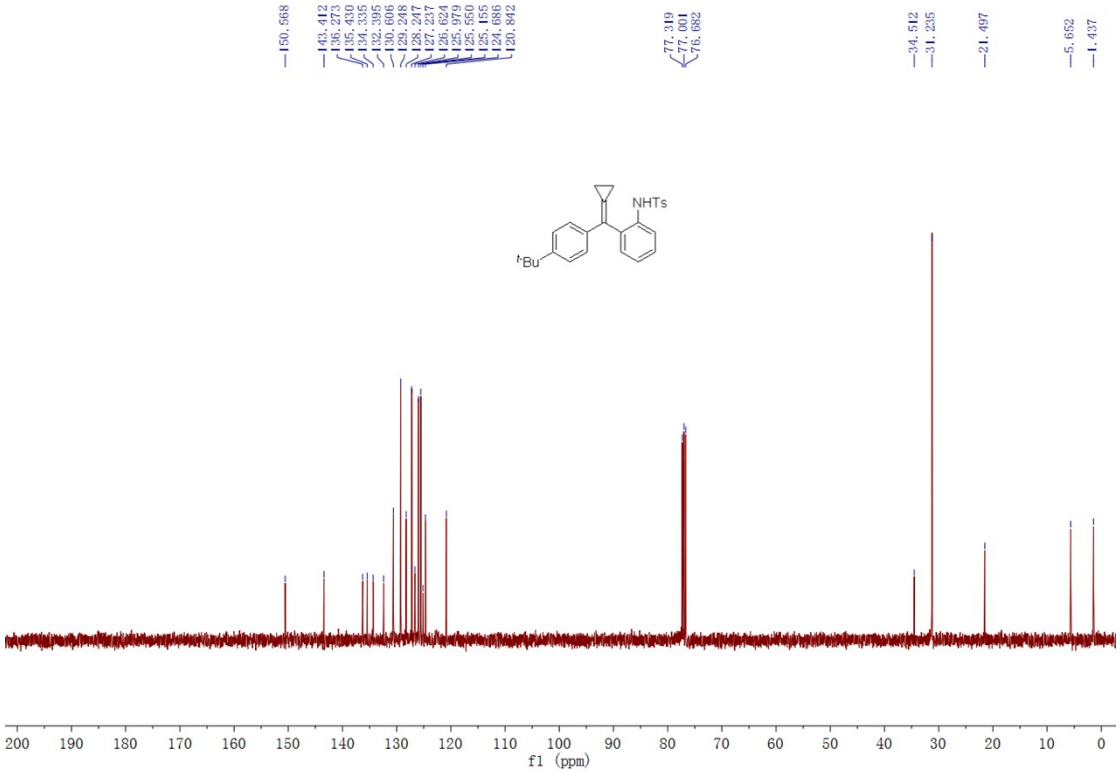
***N*-(2-((4-(*tert*-butyl)phenyl)(cyclopropylidene)methyl)phenyl)-4-methylbenzenesulfonamide 1k**

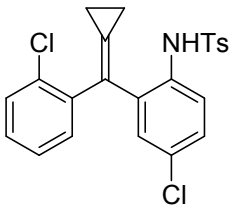
An orange solid, 99% yield (595 mg). M.p.: 104-107 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.84-0.88 (m, 2H), 1.33 (s, 9H), 1.48-1.52 (m, 2H), 2.37 (s, 3H), 6.51 (s, 1H), 7.04-7.12 (m, 6H), 7.24-7.33 (m, 3H), 7.45 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.4, 5.7, 21.5, 31.2, 34.5, 120.8, 124.7, 125.2, 125.6, 126.0, 126.7, 127.2, 128.2, 129.2, 130.6, 132.4, 134.3, 135.4, 136.3, 143.4, 150.6. IR (neat) $\bar{\nu}$ 3258, 2962, 2954, 2926, 2868, 1599, 1577, 1337, 1269, 1165, 1105, 1091, 1016, 923, 895, 831, 812, 755, 662 cm^{-1}. HRMS (APCI) Calcd. for $C_{27}H_{30}NO_2S^{+1}(M+H)^+$ requires: 432.1992, Found: 432.2004.

^{1}H NMR spectrum of 1k:



^{13}C NMR spectrum of 1k:

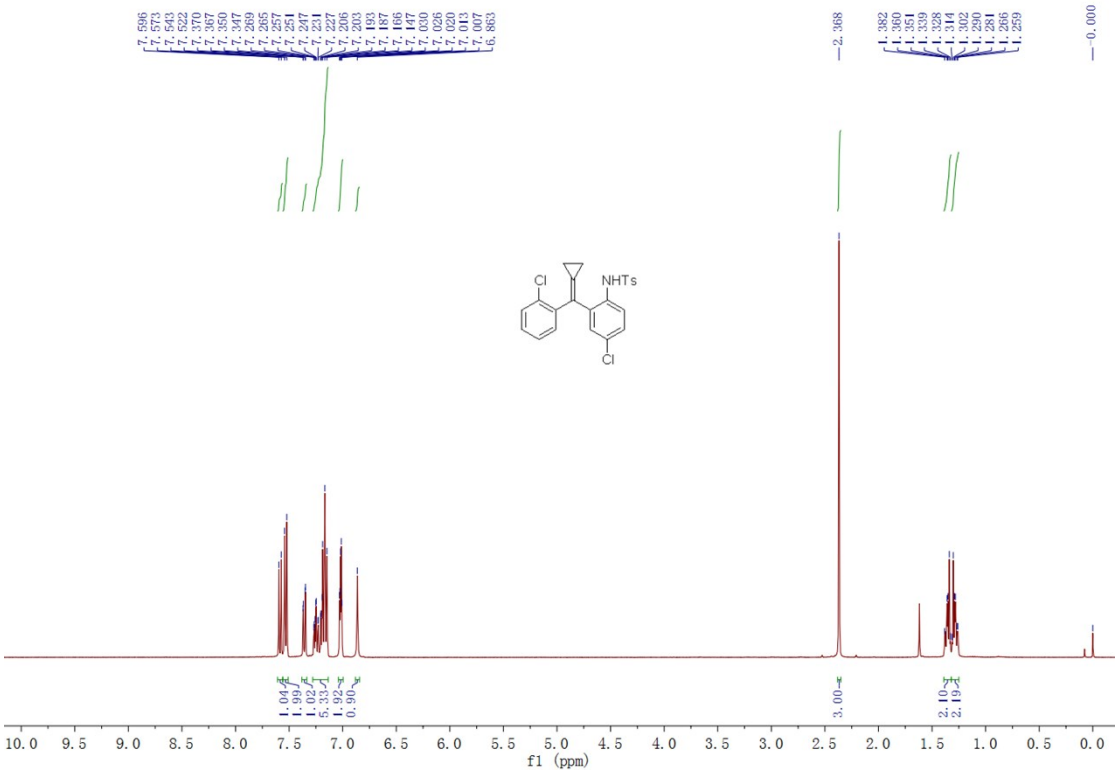




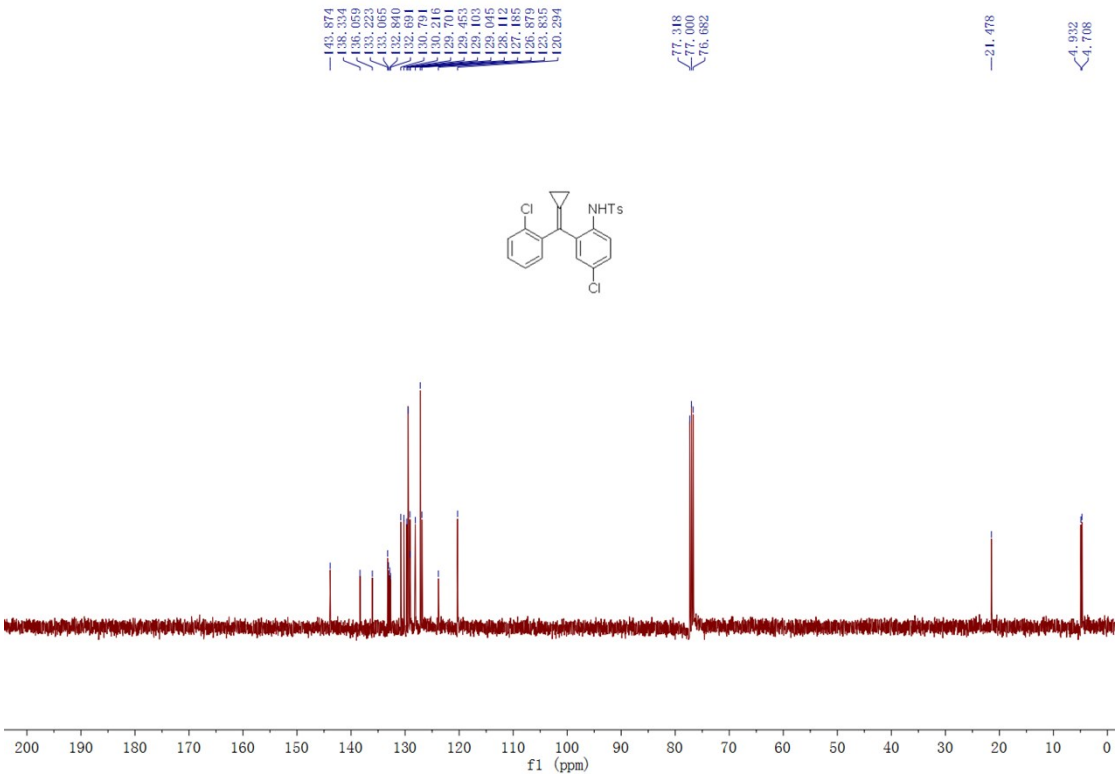
***N*-(4-chloro-2-((2-chlorophenyl)(cyclopropylidene)methyl)phenyl)-4-methylbenzenesulfonamide 1m**

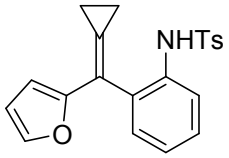
A brown solid, 59% yield (361 mg). M.p.: 115-118 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.25-1.31 (m, 2H), 1.32-1.39 (m, 2H), 2.37 (s, 3H), 6.86 (s, 1H), 7.00-7.03 (m, 2H), 7.14-7.27 (m, 5H), 7.36 (dd, J = 1.2 Hz, 8.0 Hz, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 9.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 4.7, 4.9, 21.5, 120.3, 123.8, 126.9, 127.2, 128.1, 129.0, 129.1, 129.5, 129.7, 130.2, 130.8, 132.7, 132.8, 133.1, 133.2, 136.1, 138.3, 143.9. IR (neat) $\bar{\nu}$ 3334, 3257, 2959, 2929, 2851, 1594, 1482, 1471, 1380, 1338, 1263, 1165, 1116, 1089, 1019, 922, 883, 833, 818, 750, 704, 673, 658 cm^{-1}. HRMS (APCI) Calcd. for $C_{23}H_{20}Cl_2NO_2S^{+1}(M+NH_4)^+$ requires: 444.0586, Found: 444.0588.

^{1}H NMR spectrum of 1m:



^{13}C NMR spectrum of 1m:

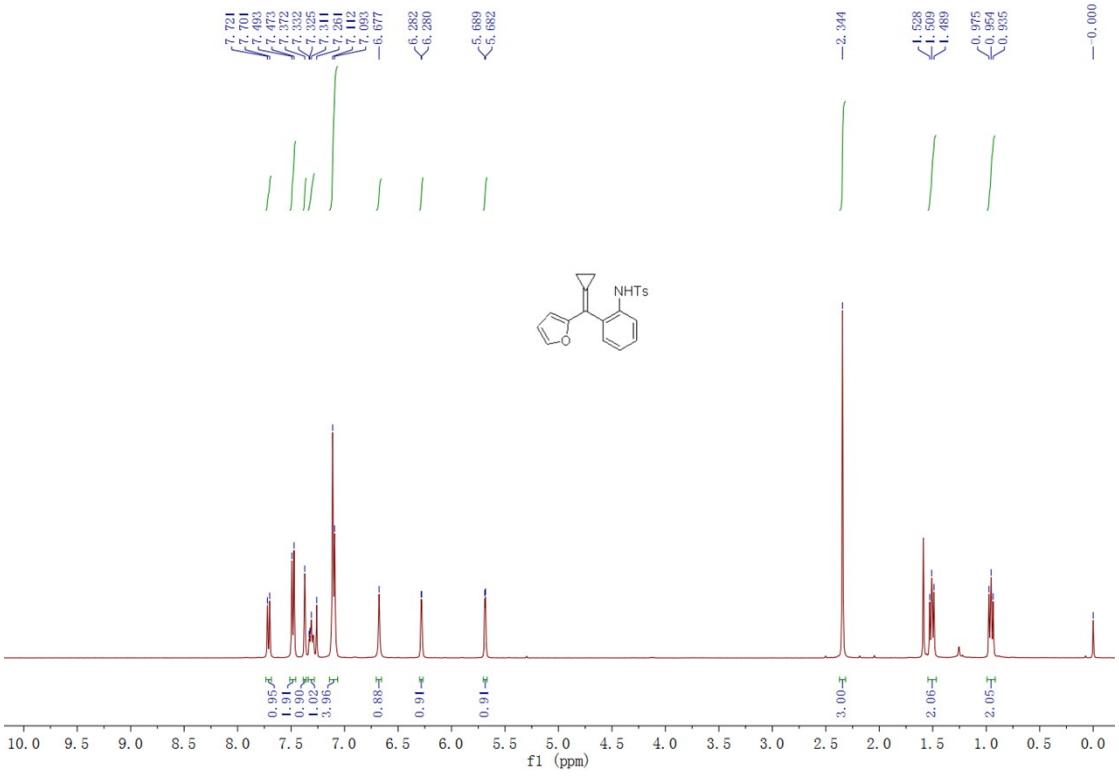




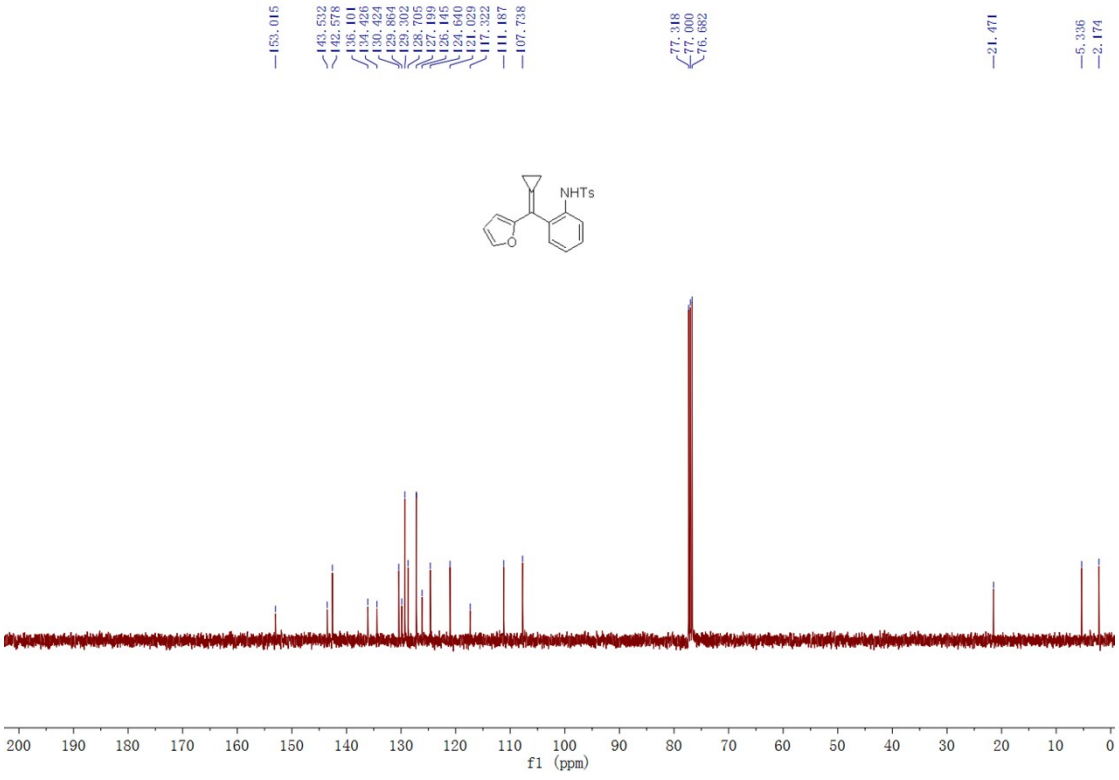
***N*-(2-(cyclopropylidene(furan-2-yl)methyl)phenyl)-4-methylbenzenesulfonamide 1n**

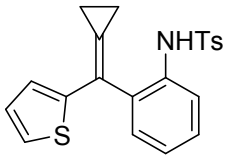
A faint yellow solid, 11% yield (122 mg). M.p.: 129-131 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.93-0.98 (m, 2H), 1.48-1.53 (m, 2H), 2.34 (s, 3H), 5.69 (d, *J* = 2.8 Hz, 1H), 6.28 (dd, *J* = 2.0 Hz, 2.8 Hz, 1H), 6.68 (s, 1H), 7.07-7.13 (m, 4H), 7.29-7.34 (m, 1H), 7.37 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.2, 5.3, 21.5, 107.7, 111.2, 117.3, 121.0, 124.6, 126.1, 127.2, 128.7, 129.3, 129.9, 130.4, 134.4, 136.1, 142.6, 143.5, 153.0. IR (neat) $\bar{\nu}$ 3269, 3062, 3034, 2990, 2970, 2923, 2851, 1599, 1580, 1488, 1382, 1333, 1169, 1148, 1093, 1009, 941, 910, 860, 816, 808, 751, 740, 728, 707, 693, 681 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{20}NO_3S^{+1}(M+H)^+$ requires: 366.1158, Found: 366.1160.

^{1}H NMR spectrum of 1n:



^{13}C NMR spectrum of 1n:

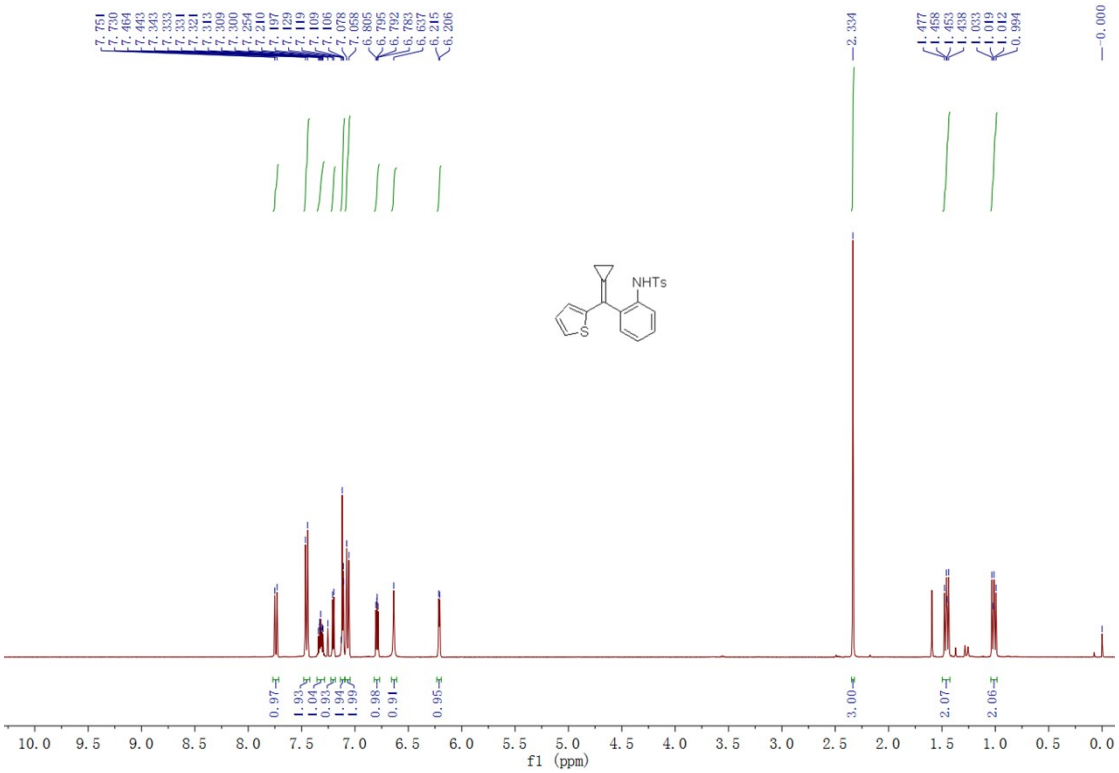




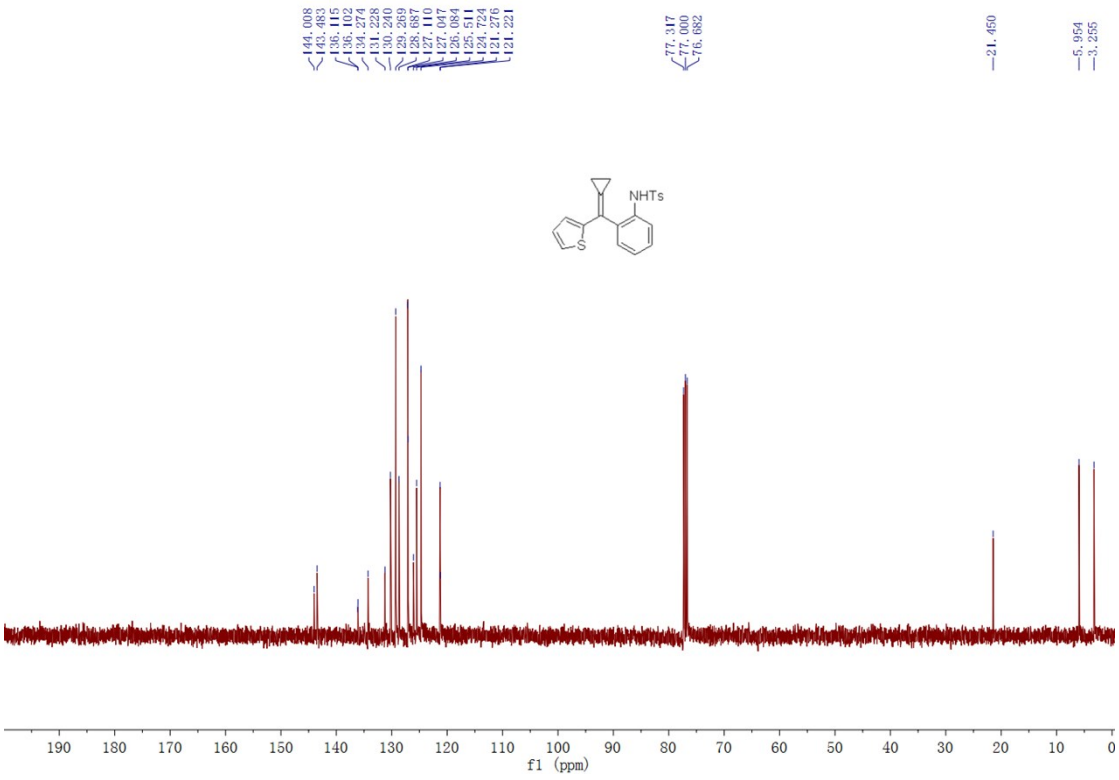
***N*-(2-(cyclopropylidene(thiophen-2-yl)methyl)phenyl)-4-methylbenzenesulfonamide 1o**

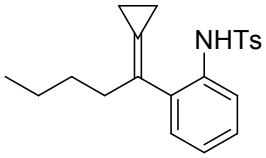
A faint yellow solid, 85% yield (449 mg). M.p.: 165-167 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.99-1.04 (m, 2H), 1.43-1.48 (m, 2H), 2.33 (s, 3H), 6.21 (d, J = 3.6 Hz, 1H), 6.64 (s, 1H), 6.79 (dd, J = 3.6 Hz, 4.8 Hz, 1H), 7.07 (d, J = 8.0 Hz, 2H), 7.10-7.13 (m, 2H), 7.20 (d, J = 5.2 Hz, 1H), 7.30-7.35 (m, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 3.3, 6.0, 21.5, 121.2, 121.3, 124.7, 125.5, 126.1, 127.0, 127.1, 128.7, 129.3, 130.2, 131.2, 134.3, 136.10, 136.12, 143.5, 144.0. IR (neat) $\bar{\nu}$ 3264, 3101, 3067, 3042, 2965, 1600, 1582, 1492, 1455, 1393, 1335, 1297, 1278, 1162, 1092, 914, 838, 820, 813, 702, 670, 653 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{20}NO_2S_2^{+1}(M+H)^+$ requires: 382.0930, Found: 382.0932.

^{1}H NMR spectrum of 1o:



^{13}C NMR spectrum of 1o:

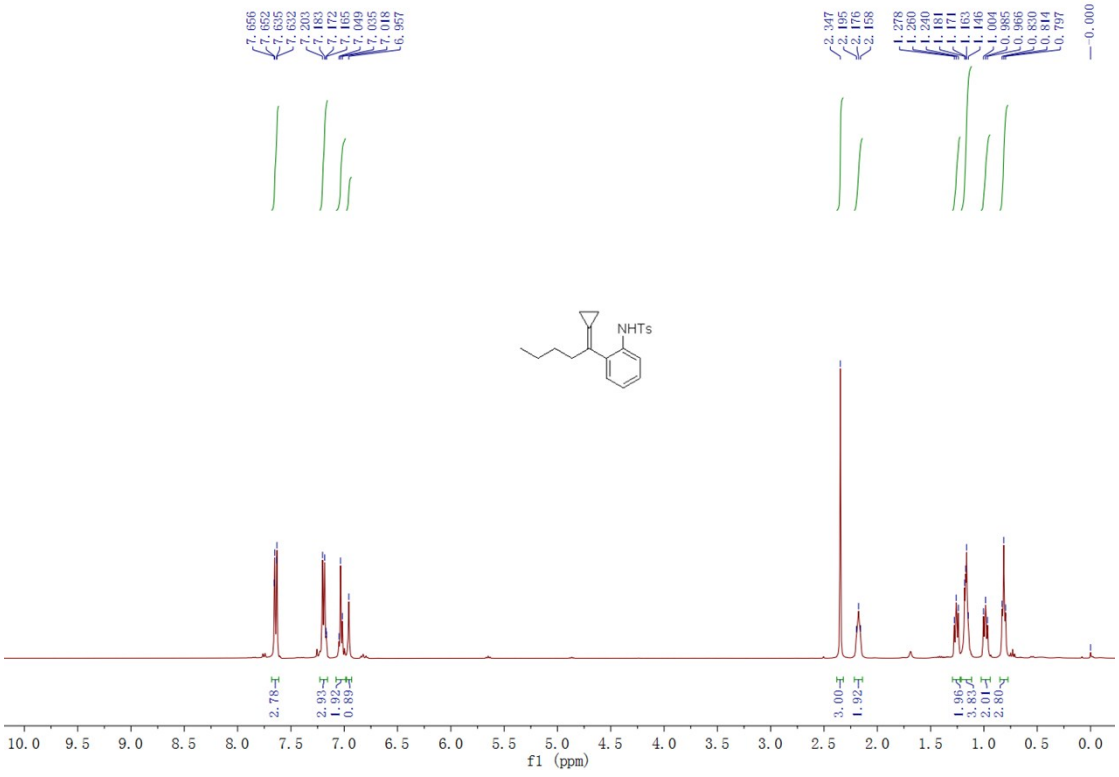




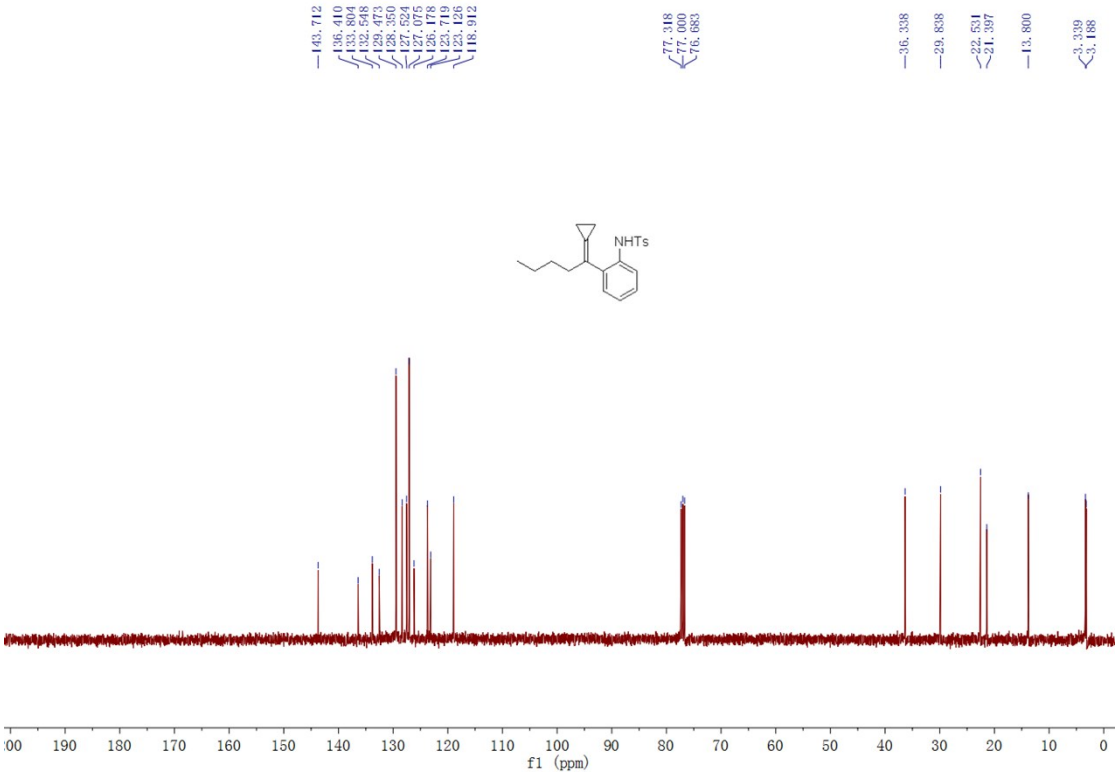
***N*-(2-(1-cyclopropylidenepentyl)phenyl)-4-methylbenzenesulfonamide 1q**

A yellow solid, 60% yield (486 mg). M.p.: 74-77 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.81, (t, J = 6.8 Hz, 3H), 0.96-1.01 (m, 2H), 1.14-1.19 (m, 4H), 1.24-1.28 (m, 2H), 2.18, (t, J = 7.2 Hz, 2H), 2.35 (s, 3H), 6.96 (s, 1H), 7.01-7.05 (m, 2H), 7.16-7.21 (m, 3H), 7.63-7.66 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 3.2, 3.3, 13.8, 21.4, 22.5, 29.8, 36.3, 118.9, 123.1, 123.7, 126.2, 127.1, 127.5, 128.4, 129.5, 132.5, 133.8, 136.4, 143.7. IR (neat) $\bar{\nu}$ 3279, 3253, 3067, 3034, 2956, 2926, 2873, 2851, 1599, 1574, 1489, 1452, 1381, 1328, 1289, 1260, 1169, 1159, 1092, 910, 816, 809, 759, 750, 709, 693, 659 cm^{-1}. HRMS (ESI) Calcd. for $C_{21}H_{29}N_2O_2S^{+1}(M+NH_4)^+$ requires: 373.1944, Found: 373.1943.

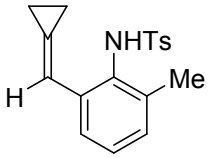
^{1}H NMR spectrum of 1q:



^{13}C NMR spectrum of 1q:



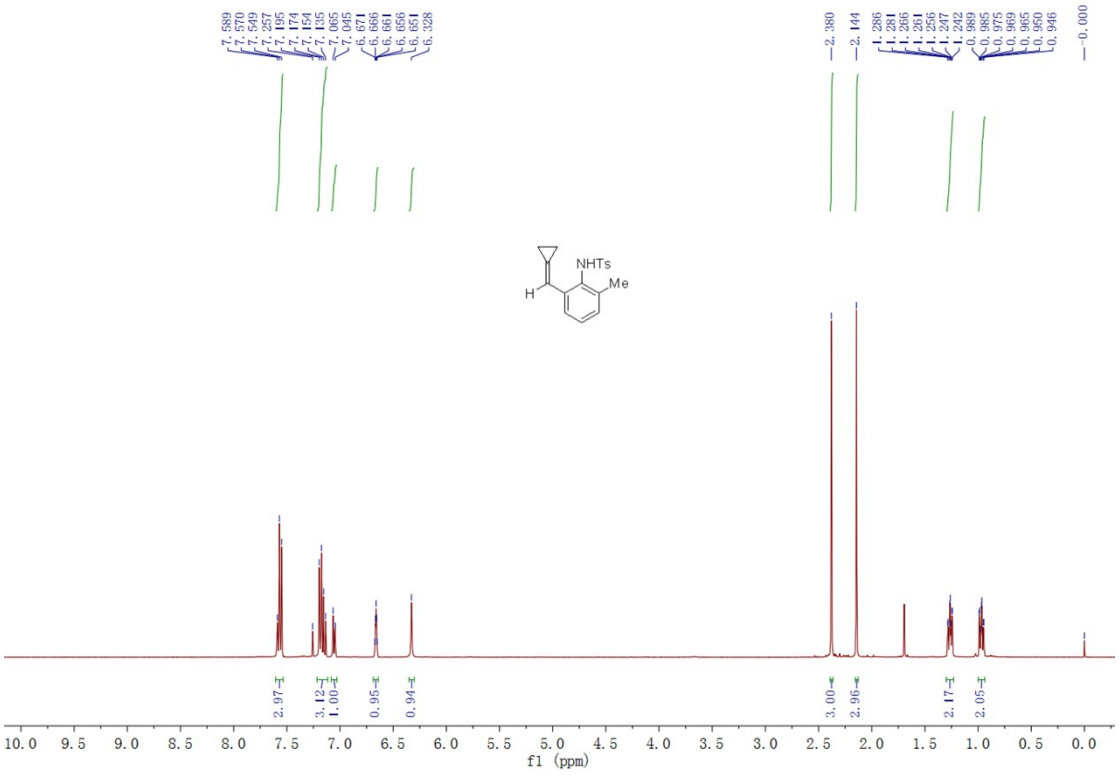
Characterization and spectra charts for 3



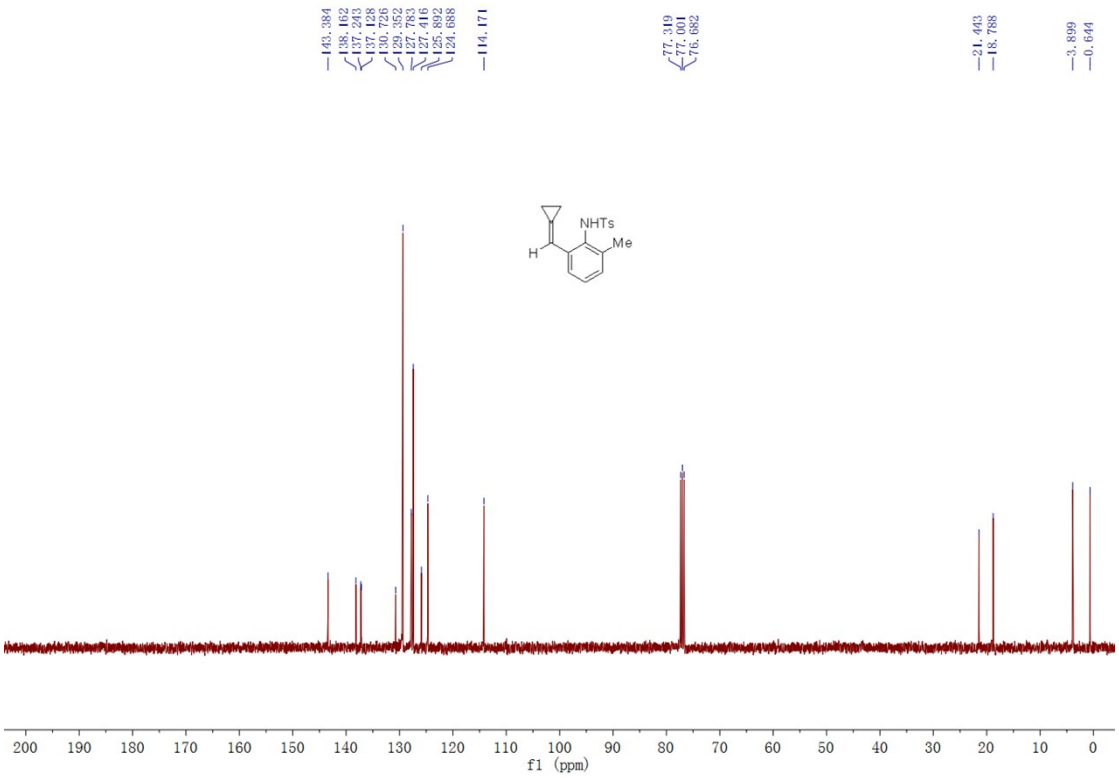
***N*-(2-(cyclopropylidenemethyl)-6-methylphenyl)-4-methylbenzenesulfonamide 3b**

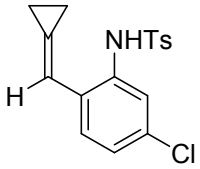
A white solid, 73% yield (690 mg). M.p.: 159-161 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.94-0.99 (m, 2H), 1.24-1.29 (m, 2H), 2.14 (s, 3H), 2.38 (s, 3H), 6.33 (s, 1H), 6.65-6.68 (m, 1H), 7.06 (d, J = 8.0 Hz, 1H), 7.13-7.20 (m, 3H), 7.54-7.59 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.6, 3.9, 18.8, 21.4, 114.2, 124.7, 125.9, 127.4, 127.8, 129.4, 130.7, 137.1, 137.2, 138.2, 143.4. IR (neat) $\bar{\nu}$ 3239, 3037, 2979, 2934, 2815, 1595, 1582, 1465, 1406, 1325, 1196, 1183, 1157, 1090, 977, 918, 807, 765, 716, 664 cm^{-1}. HRMS (APCI) Calcd. for $C_{18}H_{20}NO_2S^{+1}(M+1H)^+$ requires: 314.1209, Found: 314.1214.

^{1}H NMR spectrum of 3b:



^{13}C NMR spectrum of 3b:

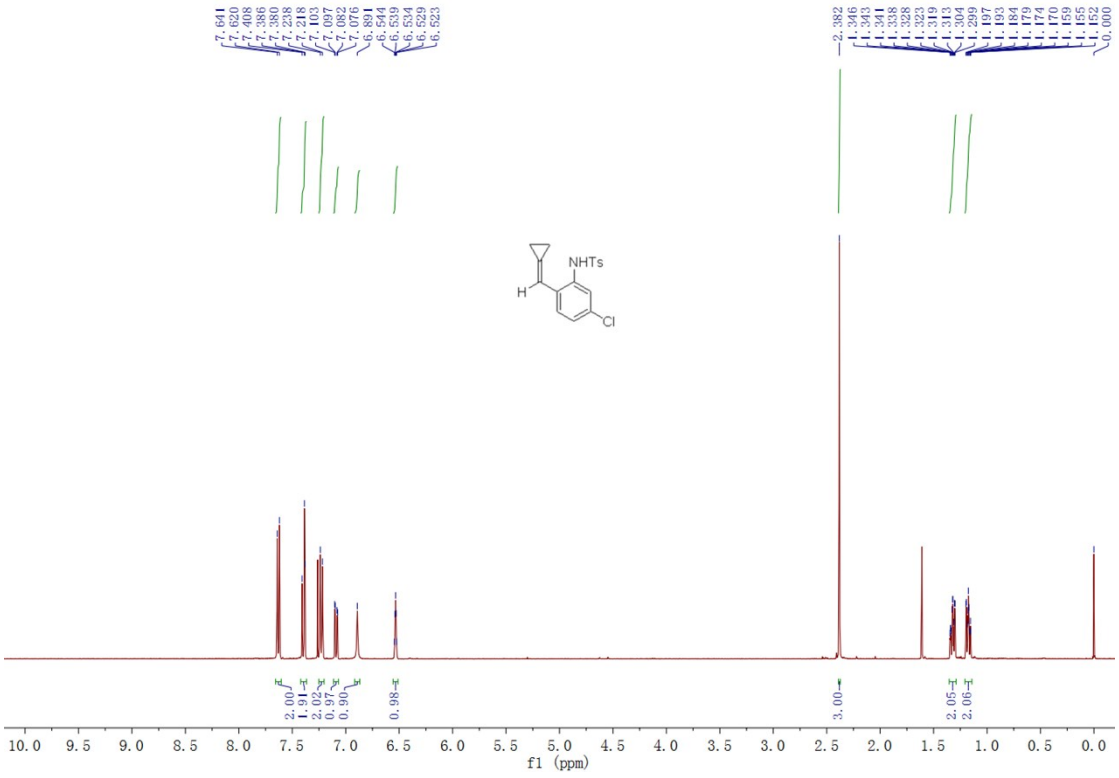




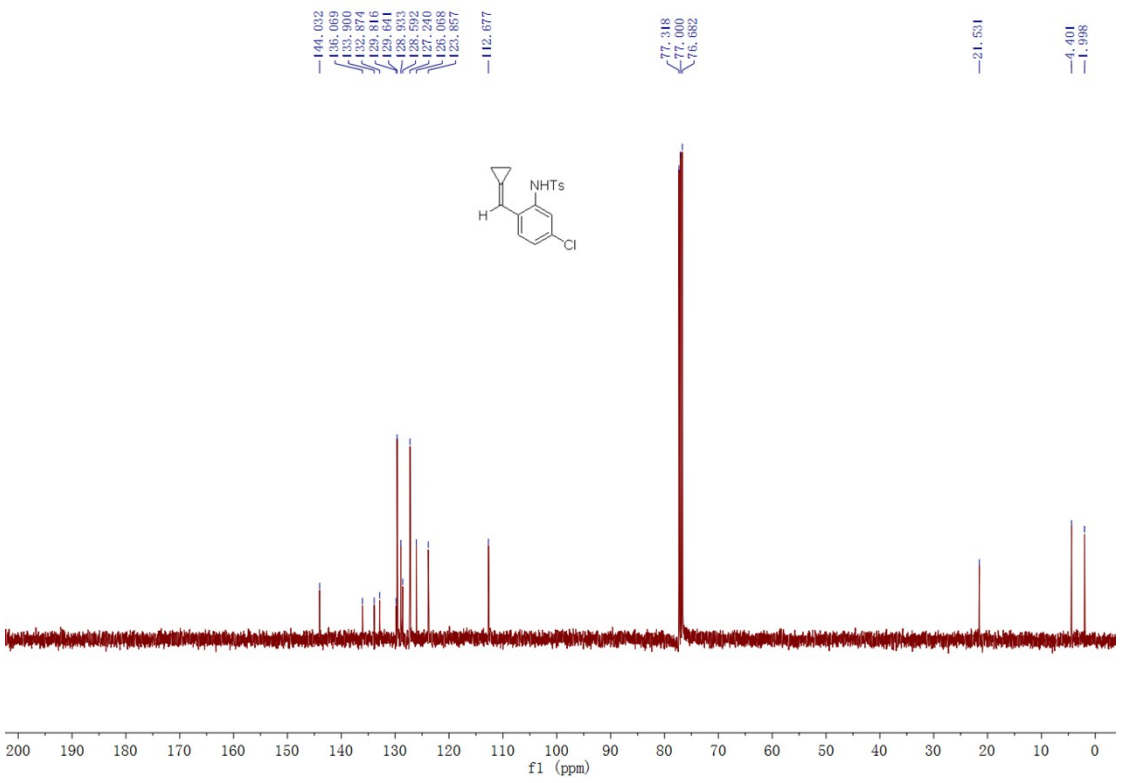
***N*-(5-chloro-2-(cyclopropylidenemethyl)phenyl)-4-methylbenzenesulfonamide 3c**

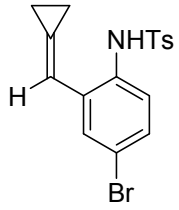
A white solid, 49% yield (492 mg). M.p.: 167-169 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.15-1.20 (m, 2H), 1.29-1.35 (m, 2H), 2.38 (s, 3H), 6.52-6.55 (m, 1H), 6.89 (s, 1H), 7.09 (dd, J = 2.4 Hz, 8.4 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.38-7.41 (m, 2H), 7.61-7.65 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 2.0, 4.4, 21.5, 112.7, 123.9, 126.1, 127.2, 128.6, 128.9, 129.6, 129.8, 132.9, 133.9, 136.1, 144.0. IR (neat) $\bar{\nu}$ 3273, 3070, 3040, 2979, 2959, 2920, 1595, 1557, 1483, 1388, 1330, 1307, 1159, 1121, 1089, 1011, 978, 926, 834, 816, 726, 704, 678, 669 cm^{-1}. HRMS (ESI) Calcd. for $C_{17}H_{20}ClN_2O_2S^{+1}(M+NH_4)^+$ requires 351.0929, Found: 351.0928.

^{1}H NMR spectrum of 3c:



^{13}C NMR spectrum of 3c:

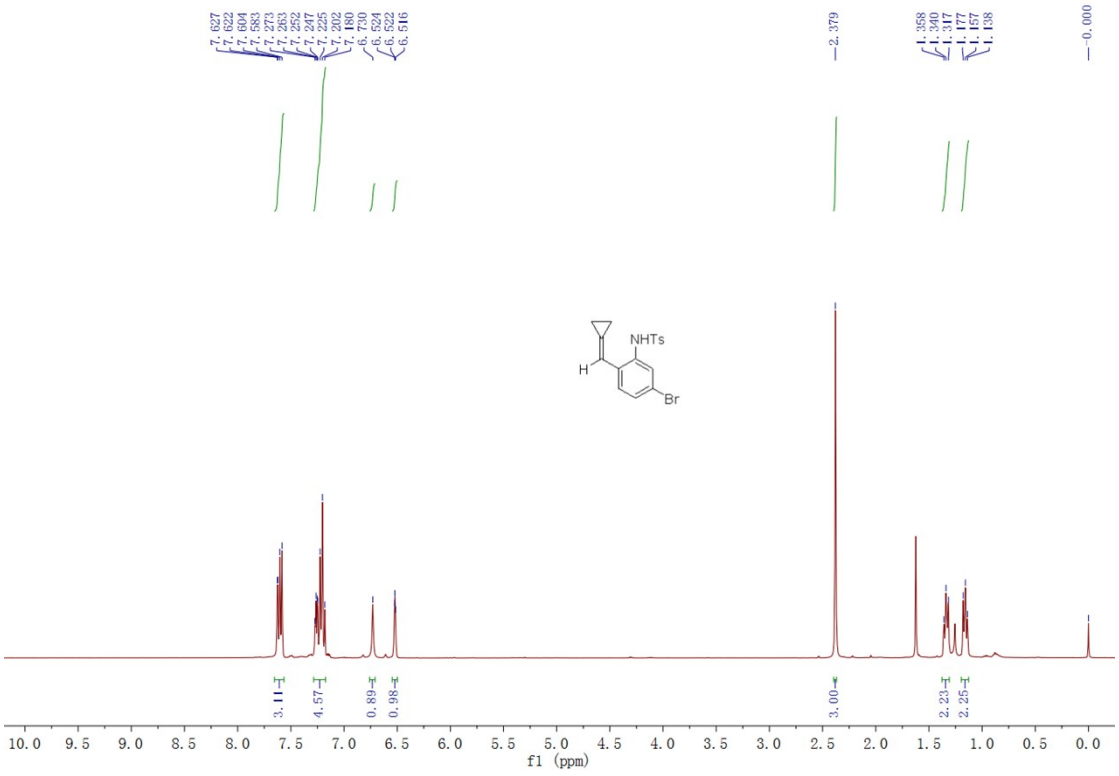




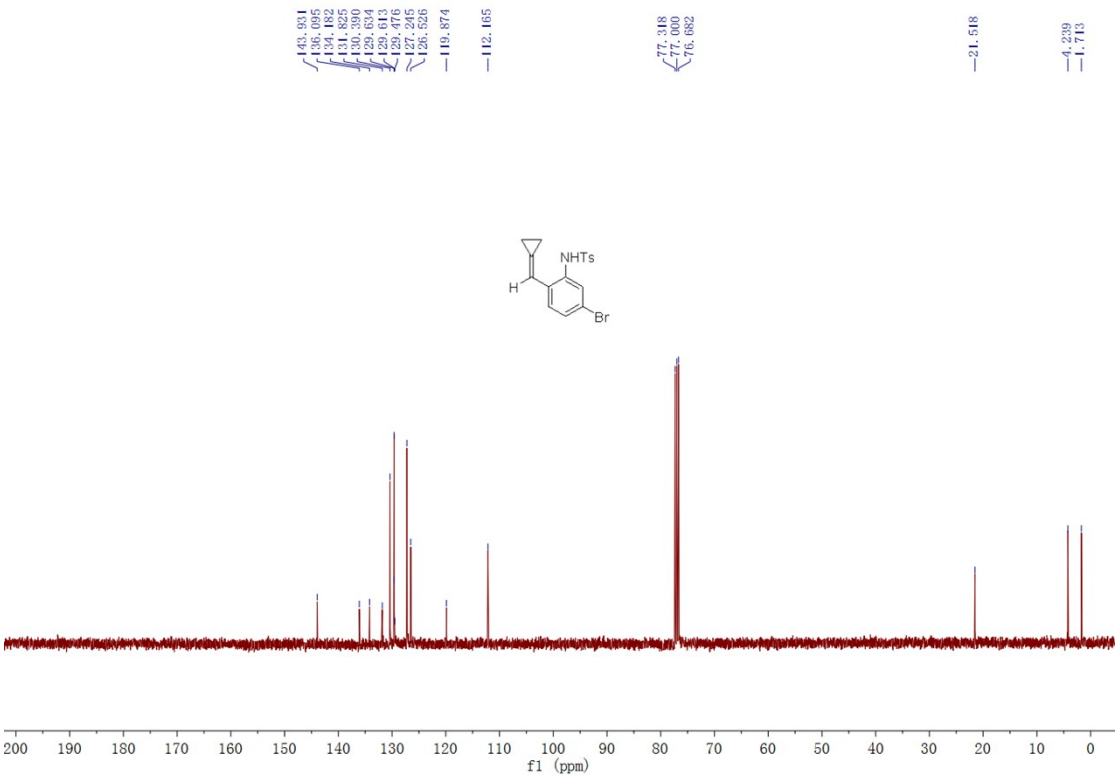
***N*-(4-bromo-2-(cyclopropylidenemethyl)phenyl)-4-methylbenzenesulfonamide 3d**

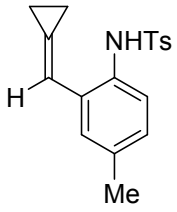
A faint yellow solid, 59% yield (1.209 g). M.p.: 187-188 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.13-1.18 (m, 2H), 1.31-1.36 (m, 2H), 2.38 (s, 3H), 6.51-6.53 (m, 1H), 6.73 (s, 1H), 7.18-7.28 (m, 4H), 7.58-7.63 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.7, 4.2, 21.5, 112.2, 119.9, 126.5, 127.2, 129.5, 129.61, 129.63, 130.4, 131.8, 134.2, 136.1, 143.9. IR (neat) $\bar{\nu}$ 3272, 2962, 2918, 1596, 1585, 1476, 1385, 1329, 1307, 1158, 1088, 976, 867, 818, 800, 768, 719, 675, 657 cm^{-1}. HRMS (APCI) Calcd. for $C_{17}H_{17}BrNO_2S^{+1}(M+H)^+$ requires: 378.0158, Found: 378.0149.

^{1}H NMR spectrum of 3d:



^{13}C NMR spectrum of 3d:

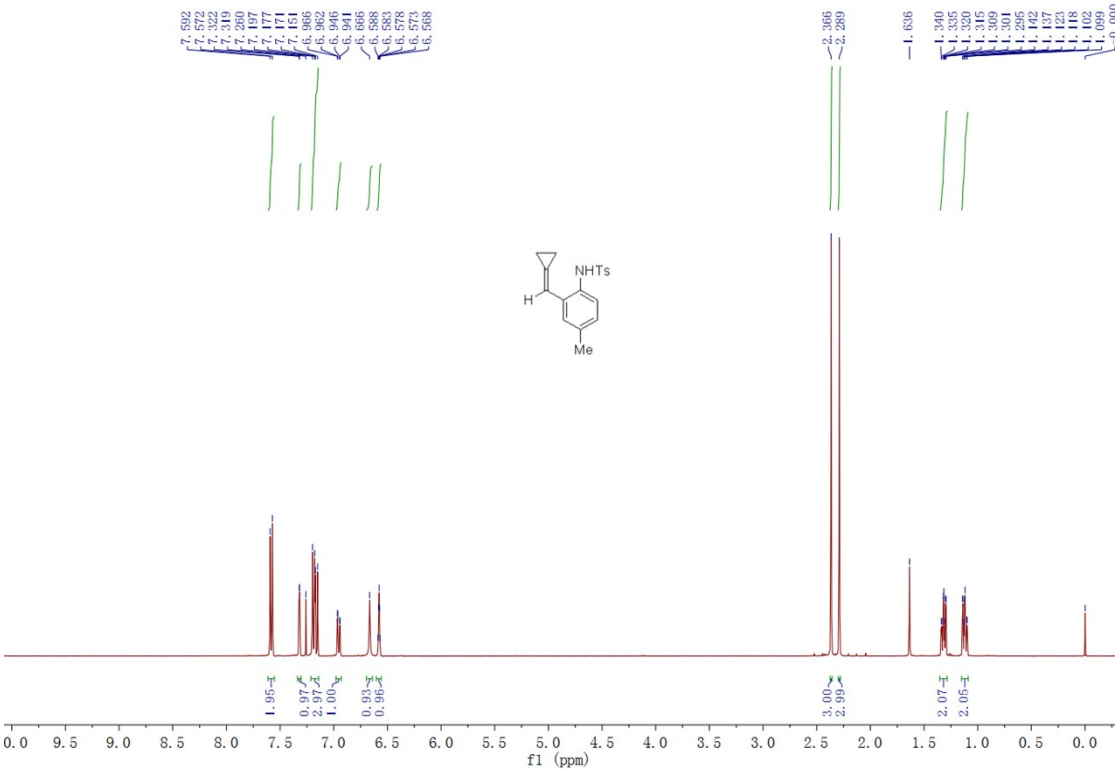




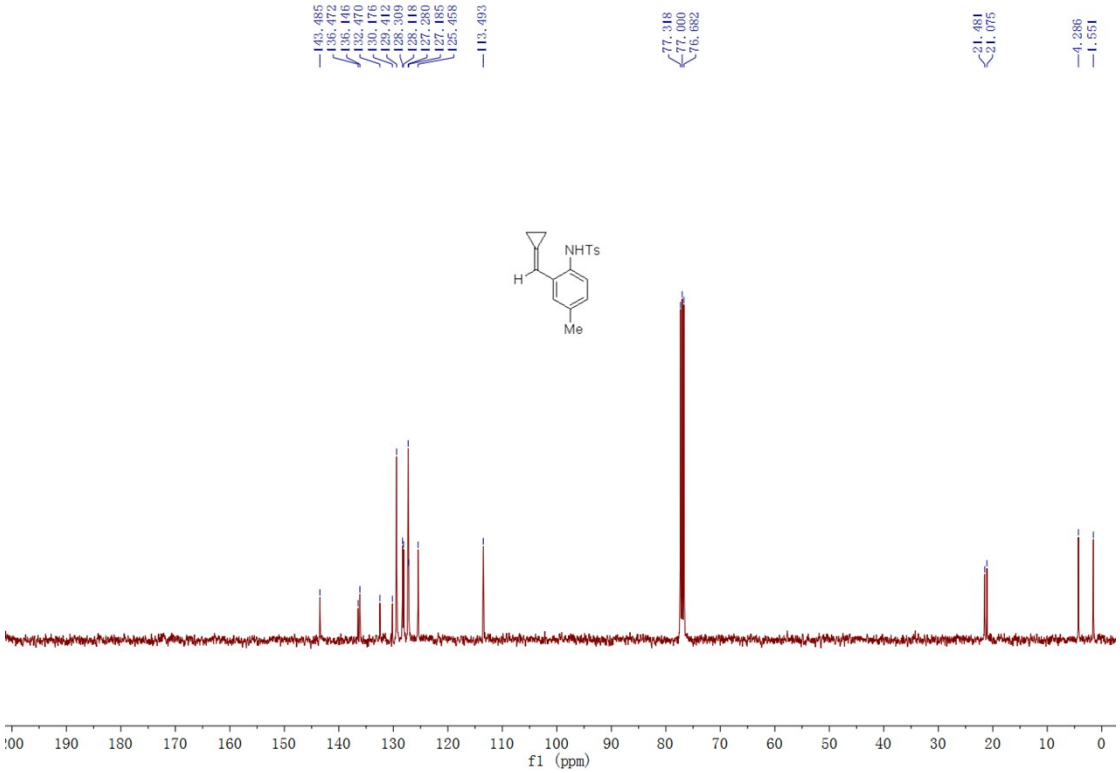
***N*-(2-(cyclopropylidenemethyl)-4-methylphenyl)-4-methylbenzenesulfonamide 3e**

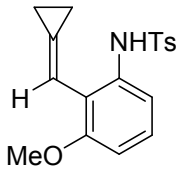
A white solid, 61% yield (577 mg). M.p.: 155-158 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.09-1.15 (m, 2H), 1.29-1.34 (m, 2H), 2.29 (s, 3H), 2.37 (s, 3H), 6.56-6.59 (m, 1H), 6.67 (s, 1H), 6.95 (dd, J = 2.0 Hz, 8.4 Hz, 1H), 7.15-7.20 (m, 3H), 7.32 (d, J = 1.2 Hz, 1H), 7.56-7.60 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.6, 4.3, 21.1, 21.5, 113.5, 125.5, 127.2, 127.3, 128.1, 128.3, 129.4, 130.2, 132.5, 136.1, 136.5, 143.5. IR (neat) $\bar{\nu}$ 3271, 3054, 3037, 2981, 2970, 2915, 1594, 1571, 1494, 1410, 1382, 1324, 1159, 1090, 895, 884, 814, 704, 680 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{20}NO_2S^{+1}(M+H)^+$ requires 314.1209, Found: 314.1208.

^{1}H NMR spectrum of 3e:



^{13}C NMR spectrum of 3e:

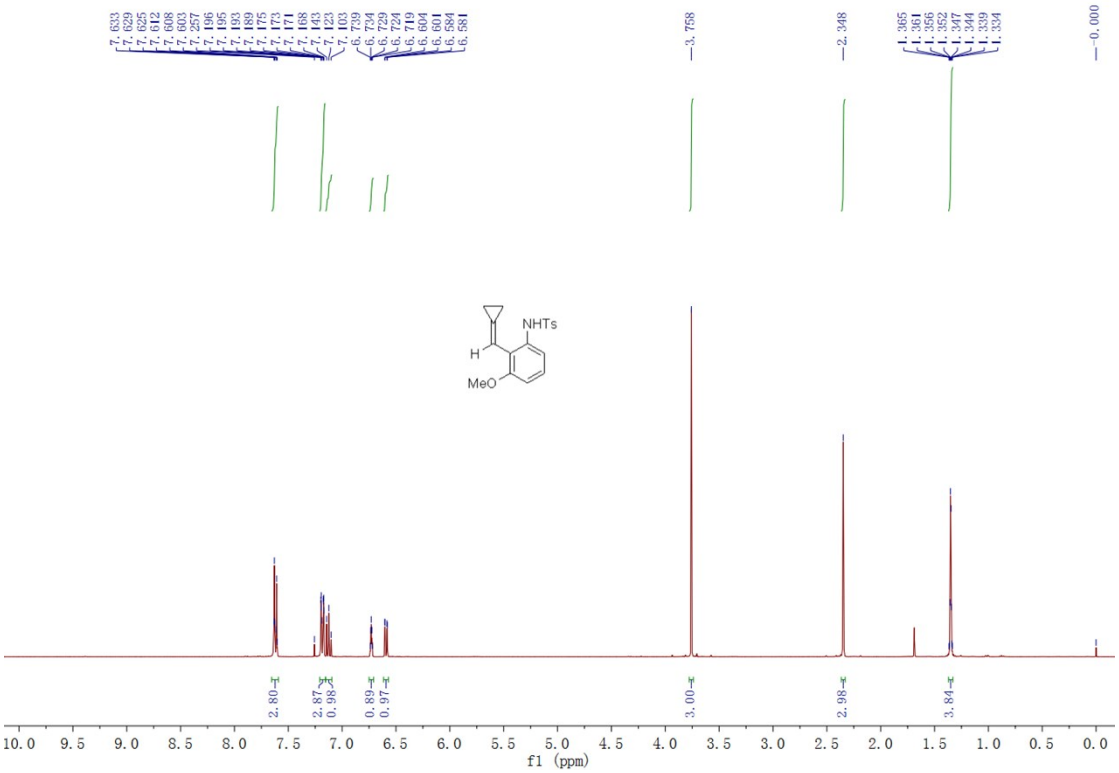




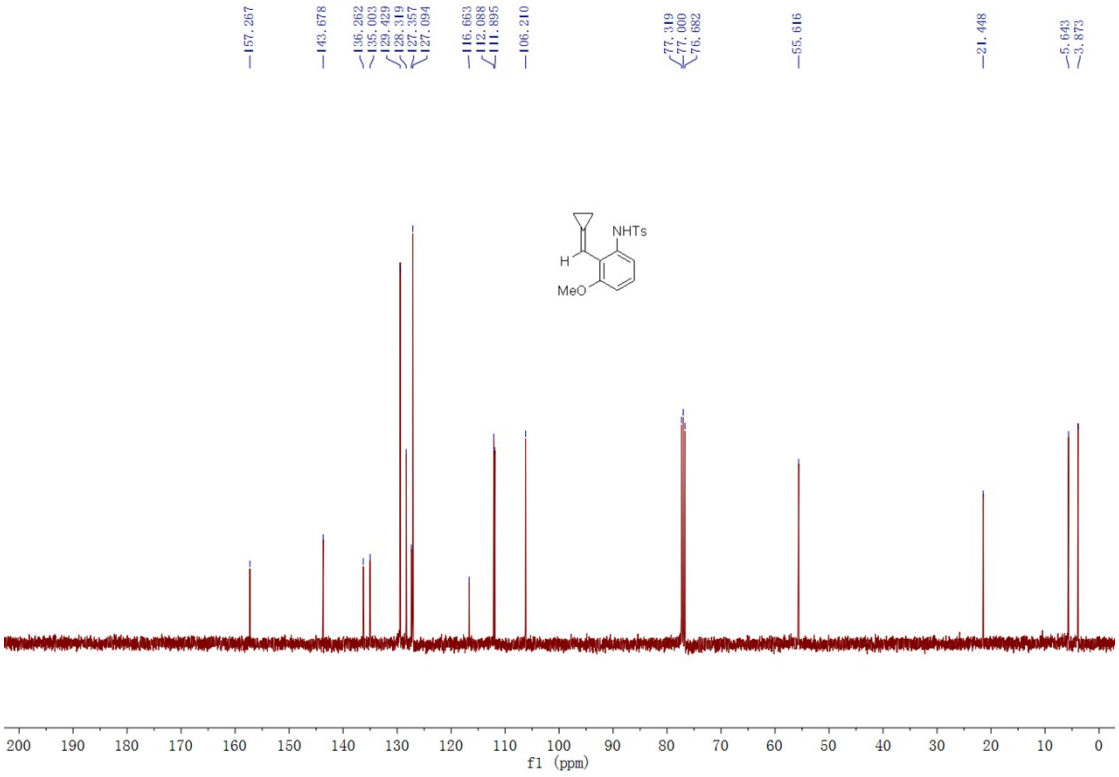
***N*-(2-(cyclopropylidenemethyl)-3-methoxyphenyl)-4-methylbenzenesulfonamide 3f**

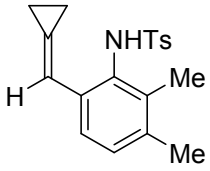
A yellow solid, 39% yield (385 mg). M.p.: 113-116 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.33-1.37 (m, 4H), 2.35 (s, 3H), 3.76 (s, 3H), 6.59 (dd, J = 1.2 Hz, 8.0 Hz, 1H), 6.72-6.74 (m, 1H), 7.10-7.20 (m, 4H), 7.60-7.64 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 3.9, 5.6, 21.4, 55.6, 106.2, 111.9, 112.1, 116.7, 127.1, 127.4, 128.3, 129.4, 135.0, 136.3, 143.7, 157.3. IR (neat) $\bar{\nu}$ 3316, 3001, 2967, 2940, 2918, 2840, 1598, 1587, 1471, 1388, 1306, 1293, 1254, 1155, 1086, 982, 815, 775, 658 cm^{-1}. HRMS (ESI) Calcd. for $C_{18}H_{20}NO_3S^{+1}(M+H)^+$ requires: 330.1158, Found: 330.1157.

^{1}H NMR spectrum of 3f:



^{13}C NMR spectrum of 3f:

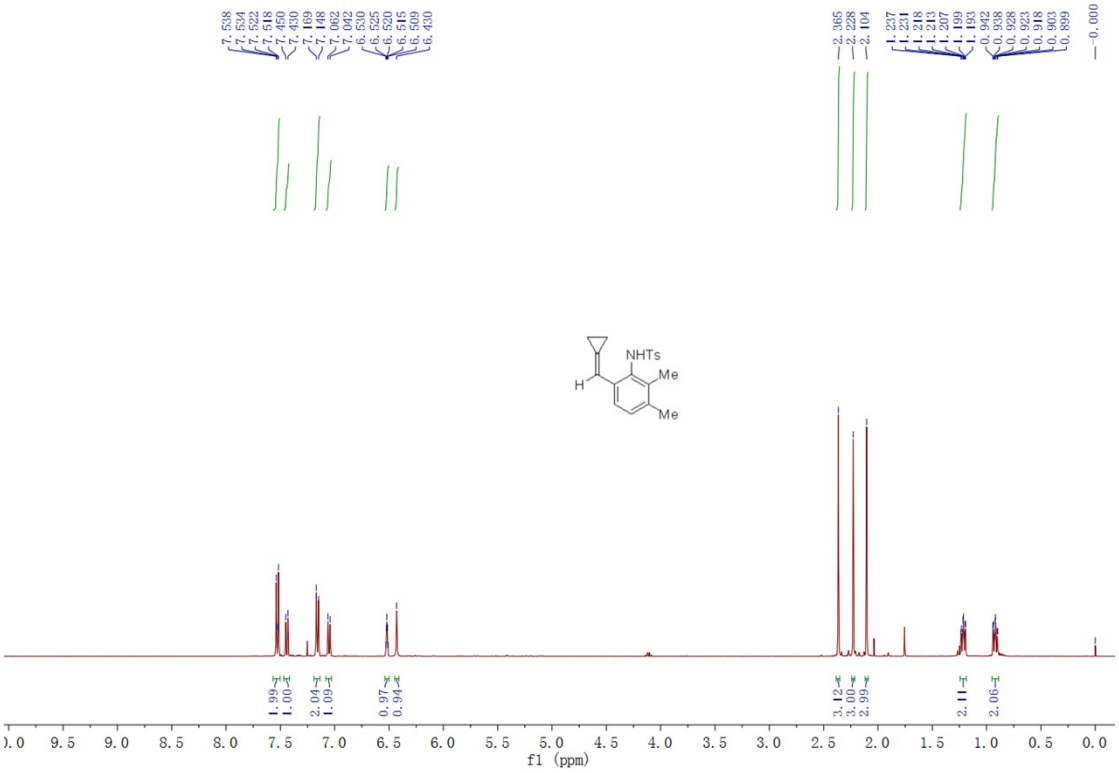




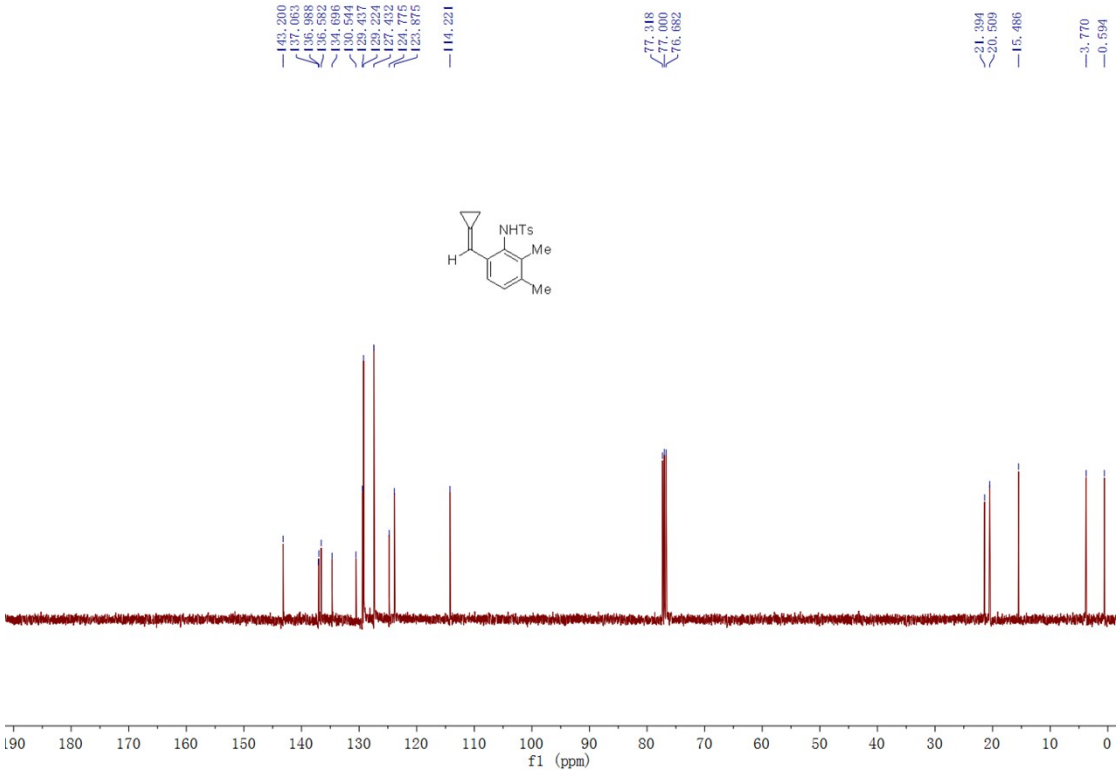
***N*-(6-(cyclopropylidenemethyl)-2,3-dimethylphenyl)-4-methylbenzenesulfonamide 3g**

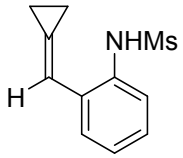
A white solid, 73% yield (713 mg). M.p.: 169-171 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.90-0.95 (m, 2H), 1.19-1.24 (m, 2H), 2.10 (s, 3H), 2.23 (s, 3H), 2.37 (s, 1H), 6.43 (s, 1H), 6.50-6.53 (m, 1H), 7.05 (d, J = 8.0 Hz, 1H), 7.16 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.0 Hz, 1H), 7.51-7.55 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 0.6, 3.8, 15.5, 20.5, 21.4, 114.2, 123.9, 124.8, 127.4, 129.2, 129.4, 130.5, 134.7, 136.6, 137.0, 137.1, 143.2. IR (neat) $\bar{\nu}$ 3272, 3067, 3040, 2970, 2920, 1597, 1482, 1455, 1402, 1378, 1326, 1159, 1082, 1003, 956, 834, 813, 753, 704, 666 cm^{-1}. HRMS (ESI) Calcd. for $C_{19}H_{22}NO_2S^{+1}(M+H)^+$ requires: 328.1366, Found: 328.1366.

^{1}H NMR spectrum of 3g:



^{13}C NMR spectrum of 3g:

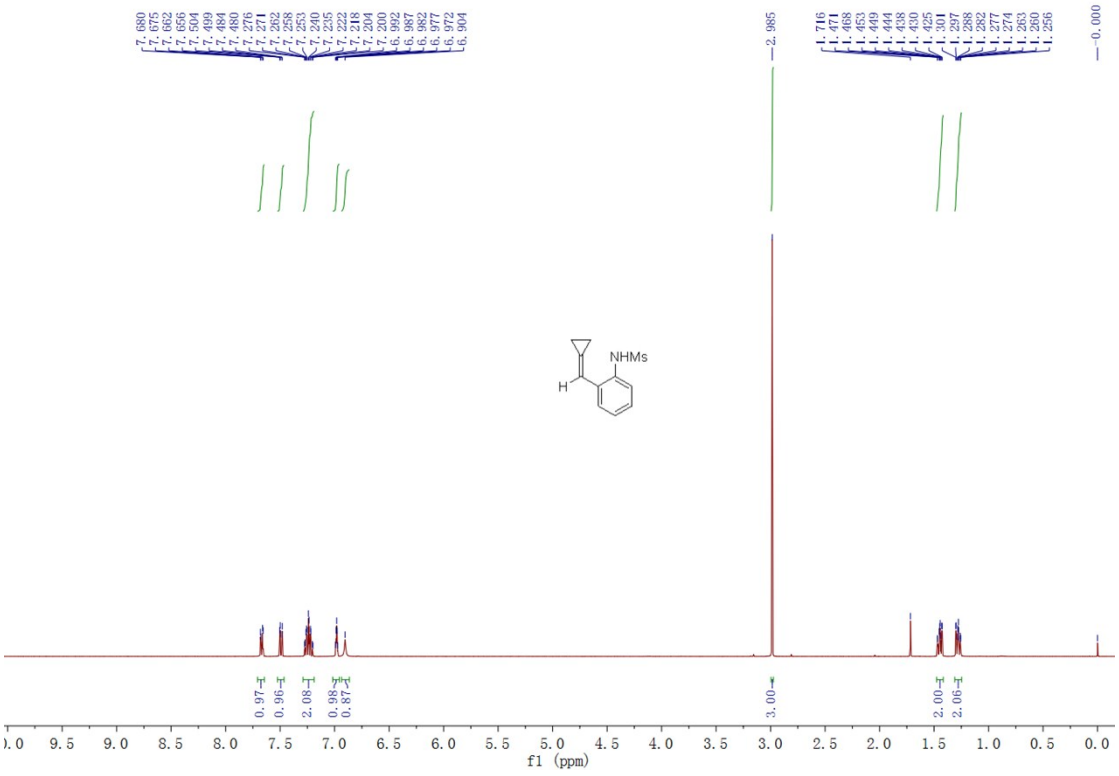




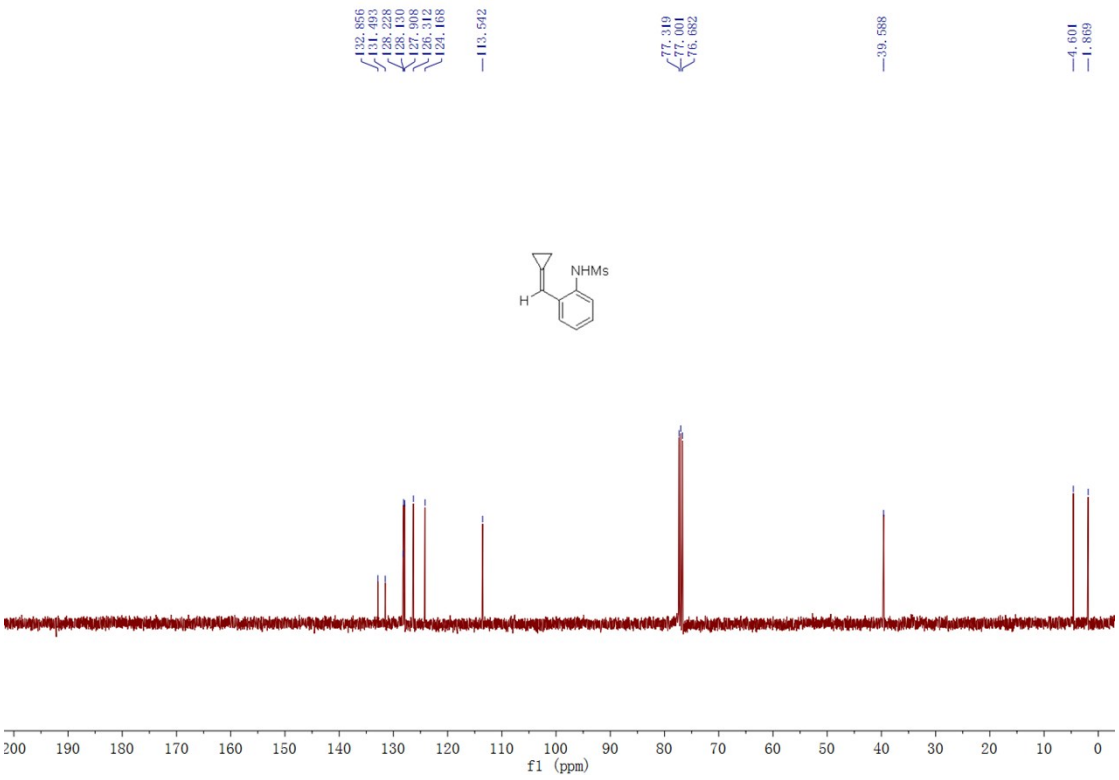
***N*-(2-(cyclopropylidenemethyl)phenyl)methanesulfonamide 3h**

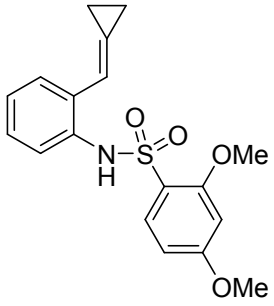
A faint yellow solid, 48% yield (215 mg). M.p.: 115-117 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.25-1.31 (m, 2H), 1.42-1.48 (m, 2H), 2.99 (s, 3H), 6.90 (s, 1H), 6.97-7.00 (m, 1H), 7.20-7.28 (m, 2H), 7.49 (dd, J = 1.6 Hz, 7.6 Hz, 1H), 7.67 (dd, J = 2.0 Hz, 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.9, 4.6, 39.6, 113.5, 124.2, 126.3, 127.9, 128.1, 128.2, 131.5, 132.9. IR (neat) $\bar{\nu}$ 3279, 3078, 3067, 3034, 2970, 2926, 2845, 1599, 1569, 1488, 1393, 1321, 1272, 1101, 1046, 972, 912, 832, 796, 769, 749 cm^{-1}. HRMS (APCI) Calcd. for $C_{11}H_{14}NO_2S^{+1}(M+H)^+$ requires: 224.0740, Found: 224.0742.

^{1}H NMR spectrum of 3h:



^{13}C NMR spectrum of 3h:

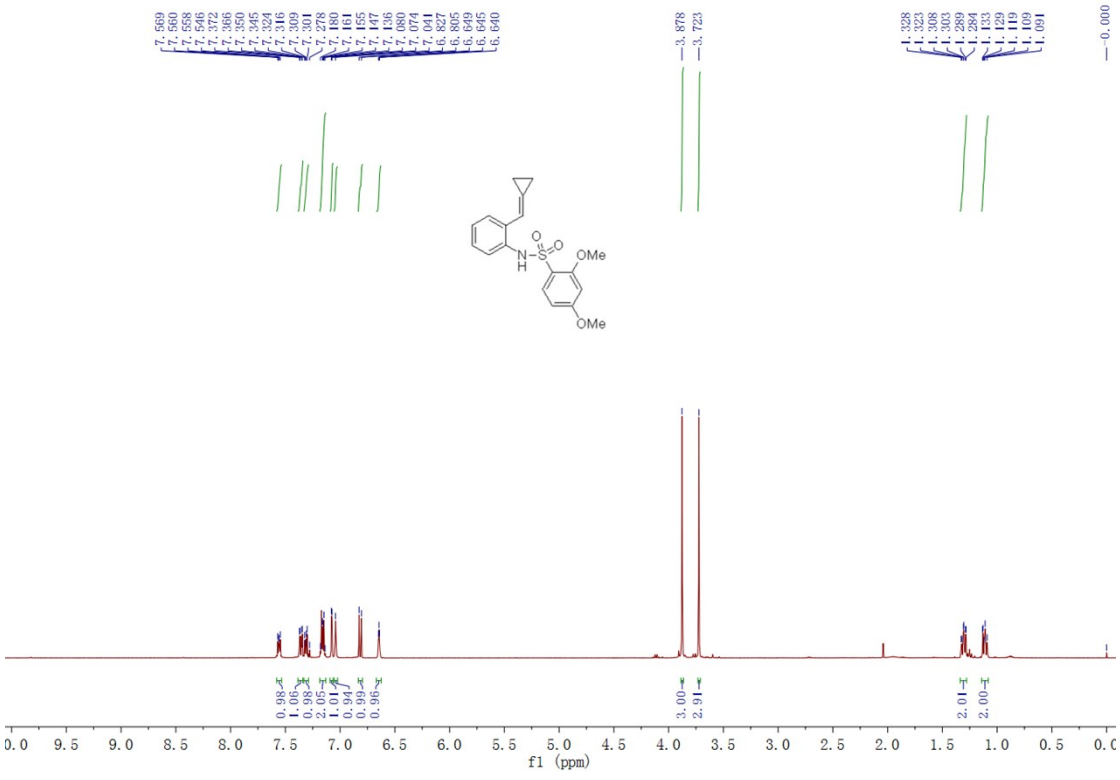




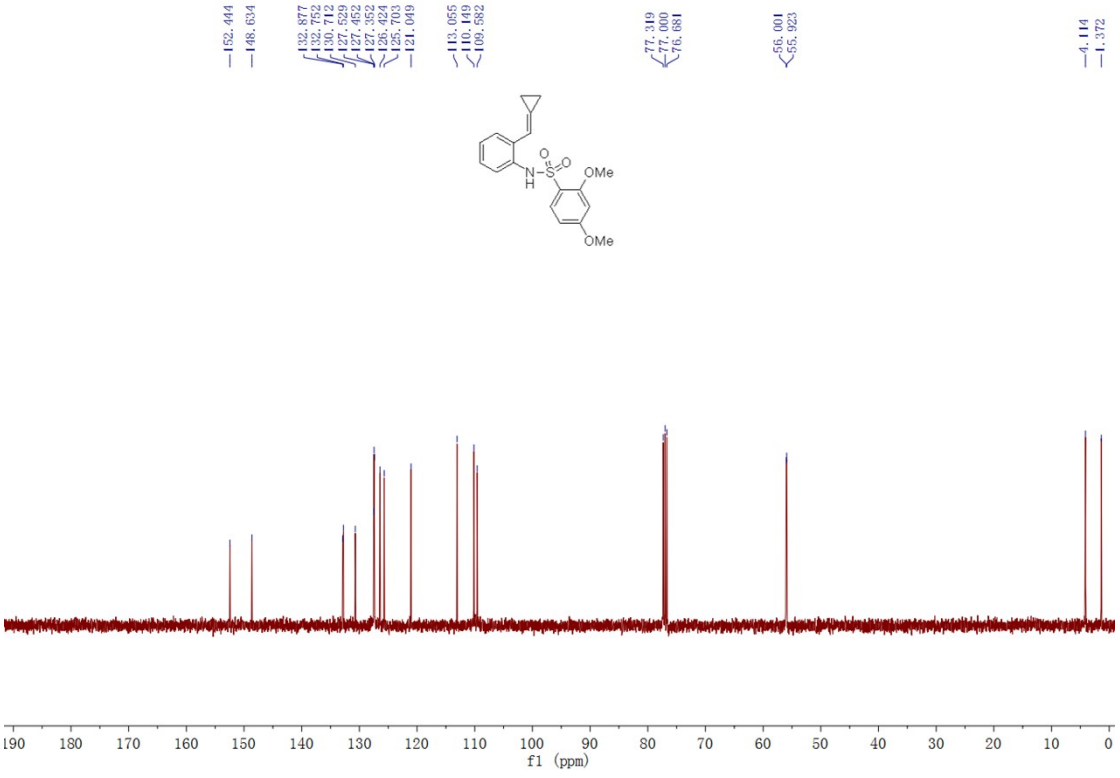
***N*-(2-(cyclopropylidenemethyl)phenyl)-2,4-dimethoxybenzenesulfonamide 3j**

A faint yellow solid, 47% yield (678 mg). M.p.: 113-115 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.09-1.14 (m, 2H), 1.28-1.33 (m, 2H), 3.72 (s, 3H), 3.88 (s, 3H), 6.63-6.66 (m, 1H), 6.82 (d, J = 8.8 Hz, 1H), 7.04 (s, 1H), 7.08 (d, J = 2.4 Hz, 1H), 7.13-7.18 (m, 2H), 7.27-7.33 (m, 1H), 7.36 (dd, J = 2.0 Hz, 8.4 Hz, 1H), 7.54-7.57 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 1.4, 4.1, 55.9, 56.0, 109.6, 110.1, 113.1, 121.0, 125.7, 126.4, 127.4, 127.45, 127.53, 130.7, 132.8, 132.9, 148.6, 152.4. IR (neat) $\bar{\nu}$ 3259, 3040, 3009, 2973, 2937, 2901, 2840, 1587, 1509, 1455, 1389, 1328, 1264, 1236, 1185, 1152, 1135, 1026, 1016, 907, 843, 806, 750, 688 cm^{-1}. HRMS (APCI) Calcd. for $C_{18}H_{20}NO_4S^{+1}(M+H)^+$ requires 346.1108, Found: 346.1105.

^{1}H NMR spectrum of 3j:

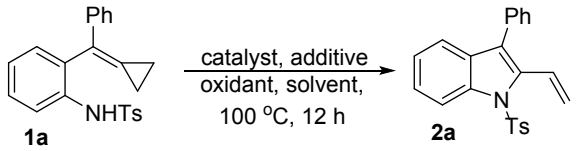


^{13}C NMR spectrum of 3j:



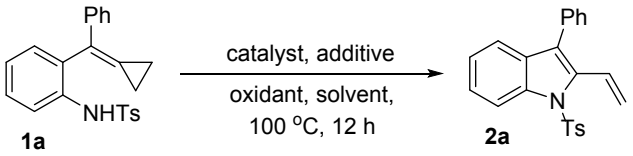
4. Optimization of the reaction conditions

Table SI-1. Optimization of Conditions for Pd-Catalyzed Oxidative Cyclization of Substrate **1a**



Entry[a]	Catalyst	Additive (equiv.)	Solvent	Oxidant	Yield (%)[b]
1	$Pd(CH_3CN)_4(OTf)_2$	none	dioxane	air	trace
2	$Pd(dppp)(H_2O)_2(OTf)_2$	none	dioxane	air	trace
3	$Pd(OAc)_2$/bpy	K_2CO_3 (2.0)	toluene	air	trace
4	$Pd(PPh_3)_4$	K_2CO_3 (2.0)	toluene	air	27
5	$Pd(TFA)_2$	K_2CO_3 (2.0)	toluene	air	32
6	$Pd(dppf)Cl_2$	K_2CO_3 (2.0)	toluene	air	38
7	$Pd(PPh_3)_2Cl_2$	K_2CO_3 (2.0)	toluene	air	45
8[d]	$Pd(PPh_3)_2Cl_2$	K_2CO_3 (2.0)	toluene	BQ	19
9[e]	$Pd(PPh_3)_2Cl_2$	K_2CO_3 (2.0)	toluene	$CuCl_2$	13
10[f]	$Pd(PPh_3)_2Cl_2$	K_2CO_3 (2.0)	toluene	AgOAc	13
11	$Pd(OAc)_2$	K_2CO_3 (2.0)	toluene	O_2	28 (24)[c]
12	$Pd_2(dba)_3 \cdot CHCl_3$	K_2CO_3 (2.0)	toluene	O_2	8
13	$Pd(dppb)Cl_2$	K_2CO_3 (2.0)	toluene	O_2	12
14	$Pd(PhCN)_2Cl_2$	K_2CO_3 (2.0)	toluene	O_2	13
15	$Pd(PPh_3)_2Cl_2$	K_2CO_3 (2.0)	toluene	O_2	39[c]
16	$Pd(dppf)Cl_2$	K_2CO_3 (2.0)	toluene	O_2	17
17	$PdCl_2$	K_2CO_3 (2.0)	toluene	O_2	0
18	$Pd(PPh_3)_2Cl_2$	K_2CO_3 (1.0)	toluene	O_2	34
19	$Pd(PPh_3)_2Cl_2$	K_2CO_3 (0.5)	toluene	O_2	43
20	$Pd(PPh_3)_2Cl_2$	K_2CO_3 (0.25)	toluene	O_2	50
21	$Pd(PPh_3)_2Cl_2$	K_2CO_3 (0.1)	toluene	O_2	48
22	$Pd(PPh_3)_2Cl_2$	Cs_2CO_3 (0.25)	toluene	O_2	43
23	$Pd(PPh_3)_2Cl_2$	Na_2CO_3 (0.75)	toluene	O_2	48
24	$Pd(PPh_3)_2Cl_2$	^{t}BuONa (0.5)	toluene	O_2	33
25	$Pd(PPh_3)_2Cl_2$	NaOH (1.0)	toluene	O_2	7
26	$Pd(PPh_3)_2Cl_2$	$NaHCO_3$ (1.0)	toluene	O_2	52
27	$Pd(PPh_3)_2Cl_2$	EtONa (1.0)	toluene	O_2	46
28	$Pd(PPh_3)_2Cl_2$	NaOAc (1.0)	toluene	O_2	43
29	$Pd(PPh_3)_2Cl_2$	$Na(COO)_2$ (1.0)	toluene	O_2	0
30	$Pd(PPh_3)_2Cl_2$	Na_3PO_4 (1.0)	toluene	O_2	51
31	$Pd(PPh_3)_2Cl_2$	EtOK (1.0)	toluene	O_2	13
32	$Pd(PPh_3)_2Cl_2$	$KHCO_3$ (0.1)	toluene	O_2	55
33	$Pd(PPh_3)_2Cl_2$	$K_3PO_4 \cdot H_2O$ (1.0)	toluene	O_2	22
34	$Pd(PPh_3)_2Cl_2$	K_3PO_4 (1.0)	toluene	O_2	34
35	$Pd(PPh_3)_2Cl_2$	^{t}BuOLi (1.0)	toluene	O_2	46
36	$Pd(PPh_3)_2Cl_2$	NH_4HCO_3 (1.0)	toluene	O_2	0
37	$Pd(PPh_3)_2Cl_2$	Et_3N (2.0)	toluene	O_2	0
38	$Pd(PPh_3)_2Cl_2$	DBU (1.0)	toluene	O_2	trace
39	$Pd(PPh_3)_2Cl_2$	DABCO (1.0)	toluene	O_2	trace
40	$Pd(PPh_3)_2Cl_2$	DMAP (1.0)	toluene	O_2	0

[a] Reactions were performed with **1a** (0.2 mmol), additive and 10 mol % of catalyst in solvent (2.0 mL) under O_2 (1.0 atm; balloon) at 100 °C in 12 h. [b] Yields are determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c] Yield of the isolated products. [d] Using 2.0 equiv. BQ under Ar. [e] Using 2.0 equiv. $CuCl_2$ under Ar. [f] Using 2.0 equiv. AgOAc under Ar. [g] The reaction was performed in air.

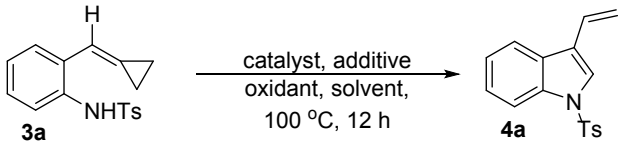


1a **2a**

Entry[a]	Catalyst	Additive (equiv.)	Solvent	Oxidant	Yield (%)[b]
41	$Pd[P(4\text{-}MeOC_6H_4)_3]_2Cl_2$	$KHCO_3$ (1.0)	toluene	O_2	52
42	$PdIPrCl_2$	$KHCO_3$ (1.0)	toluene	O_2	38
43	$Pd[P(4\text{-}FC_6H_4)_3]_2Cl_2$	$KHCO_3$ (1.0)	toluene	O_2	64
44	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	$KHCO_3$ (1.0)	toluene	O_2	74 (63)[c]
45	$Pd[(C_6F_5)_3P]_2Cl_2$	$KHCO_3$ (1.0)	toluene	O_2	8
46	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	K_2CO_3 (1.0)	toluene	O_2	43
47	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	Na_2CO_3 (1.0)	toluene	O_2	53
48	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	$NaHCO_3$ (1.0)	toluene	O_2	61
49	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	Na_3PO_4 (1.0)	toluene	O_2	49
50	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	CH_3COONa (1.0)	toluene	O_2	60
51	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	$KHCO_3$ (1.5)	toluene	O_2	49
52	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	$KHCO_3$ (2.0)	toluene	O_2	51
53	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	$KHCO_3$ (3.0)	toluene	O_2	49
54	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$ (0.05 eq)	$KHCO_3$ (1.0)	toluene	O_2	62
55	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$ (0.15 eq)	$KHCO_3$ (1.0)	toluene	O_2	49
56	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$ (0.20 eq)	$KHCO_3$ (1.0)	toluene	O_2	52
57	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	$KHCO_3$ (1.0)	$CF_3C_6H_5$	O_2	39
58	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	$KHCO_3$ (1.0)	$MeOC_6H_5$	O_2	70
59	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	$KHCO_3$ (1.0)	p-xylene	O_2	72
60	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	$KHCO_3$ (1.0)	o-xylene	O_2	69
61	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	$KHCO_3$ (1.0)	BrC_6H_5	O_2	trace
62	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	$KHCO_3$ (1.0)	ClC_6H_5	O_2	64
63	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	$KHCO_3$ (1.0)	DMSO	O_2	28
64	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	$KHCO_3$ (1.0)	DMF	O_2	27
65[g]	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	$KHCO_3$ (1.0)	toluene	air	50

[a] Reactions were performed with **1a** (0.2 mmol), additive and 10 mol % of catalyst in solvent (2.0 mL) under O_2 (1.0 atm; balloon) at 100 °C in 12 h. [b] Yields are determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c] Yield of the isolated products. [d] Using 2.0 equiv. BQ under Ar. [e] Using 2.0 equiv. $CuCl_2$ under Ar. [f] Using 2.0 equiv. AgOAc under Ar. [g] The reaction was performed in air.

Table SI-2. Optimization of Conditions for Pd-Catalyzed Oxidative Cyclization of Substrate **3a**



Entry[a]	Catalyst	Additive (1.0 equiv.)	Solvent	Oxidant	Yield (%)[b]
1	$Pd(PPh_3)_2Cl_2$	$KHCO_3$	toluene	O_2	41
2	$Pd[P(4\text{-}MeOC_6H_4)_3]_2Cl_2$	$KHCO_3$	toluene	O_2	60 (58)[c]
3	$PdIPrCl_2$	$KHCO_3$	toluene	O_2	24
4	$Pd[P(4\text{-}FC_6H_4)_3]_2Cl_2$	$KHCO_3$	toluene	O_2	56
5	$Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$	$KHCO_3$	toluene	O_2	48
6	$Pd[P(C_6F_5)_3]_2Cl_2$	$KHCO_3$	toluene	O_2	17
7	$Pd[P(4\text{-}MeOC_6H_4)_3]_2Cl_2$	$NaHCO_3$	toluene	O_2	39
8	$Pd[P(4\text{-}MeOC_6H_4)_3]_2Cl_2$	Na_3PO_4	toluene	O_2	50
9	$Pd[P(4\text{-}MeOC_6H_4)_3]_2Cl_2$	NaOAc	toluene	O_2	8
10[d]	$Pd[P(4\text{-}MeOC_6H_4)_3]_2Cl_2$	$KHCO_3$	toluene	O_2	45

[a] Reactions were performed with **1a** (0.2 mmol), additive and 10 mol % of catalyst in solvent (2.0 mL) under O_2 (1.0 atm; balloon) at 100 °C in 12 h. [b] Yields are determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c] Yield of the isolated products. [d] Using 2.0 equiv. $KHCO_3$.

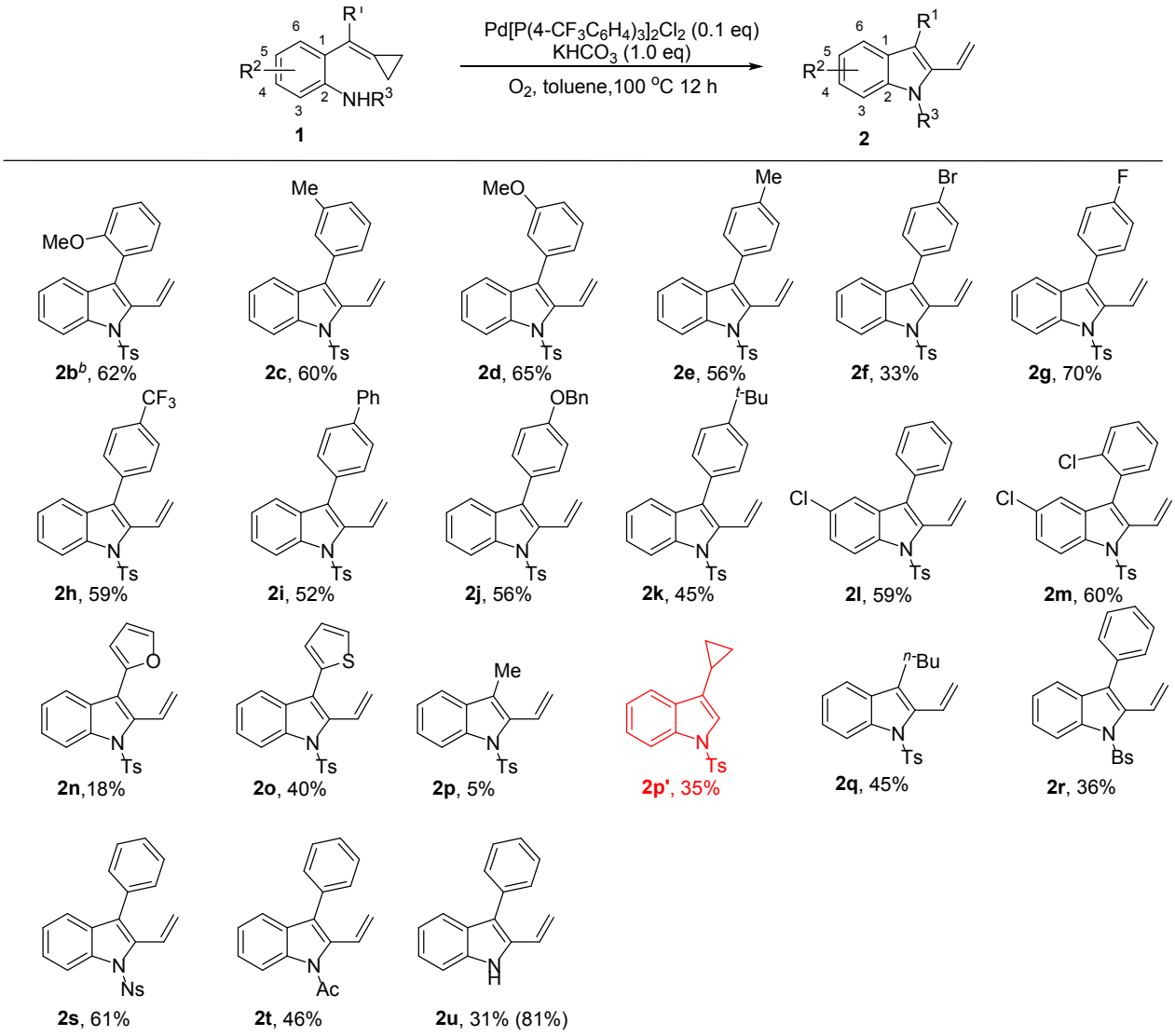
5. General procedure for synthesis of products 2 and 4

To a flame dried Schlenk tube was added ACPs **1** (0.2 mmol), $Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$ (10 mol%), $KHCO_3$ (1.0 mmol). Then, the tube was evacuated and backfilled with O_2 for 3 times, and inserted an O_2 balloon. The anhydrous solvent toluene (2.0 mL) was added under O_2. Next, the resulting solution was allowed to stir at 100 °C for 12 h. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel to give the desired products **2** (eluent: petroleum ether / ethyl acetate = 20 / 1).

To a flame dried Schlenk tube was added ACPs **3** (0.2 mmol), $Pd[P(4\text{-}MeOC_6H_4)_3]_2Cl_2$ (10 mol%), $KHCO_3$ (1.0 mmol). Then, the tube was evacuated and backfilled with O_2 for 3 times, and inserted an O_2 balloon. The anhydrous solvent toluene (2.0 mL) was added under O_2. Next, the resulting solution was allowed to stir at 100 °C for 12 h. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography on silica gel to give the desired products **4** (eluent: petroleum ether / ethyl acetate = 30 / 1).

6. Substrate scope for synthesis of 2 and 4

Scheme SI-1. Substrate Scope for the Synthesis of 2-Vinylindole **2**[a]

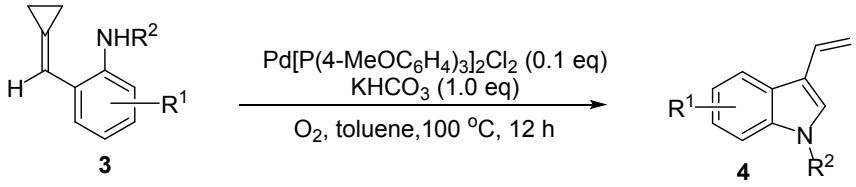


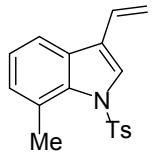
[a] The reaction was conducted with **1** (0.2 mmol), $PdCl_2[P(4\text{-}CF_3C_6H_4)_3]_2$ (0.2 mmol) and $KHCO_3$ (0.2 mmol) in toluene (2.0 mL) for 12 h at 100 °C with an O_2 balloon. [b] Yield of the isolated products. c Yield of detosylation from **2a** (Reaction condition: 10 equiv. KOH, MeOH/THF=1:10, reflux for 3 h).

Having determined the viability of the Pd-catalyzed oxidative cycloaddition of ACPs, different substrates **1** were examined in the presence of $Pd[P(4\text{-}CF_3C_6H_4)_3]_2Cl_2$ and $KHCO_3$ in toluene at 100 °C under O_2 and the results are summarized in Scheme SI-1. We first examined the substituent position effect at benzene ring: as for substrates **1b-1e**, the reactions could all proceed smoothly to furnish the corresponding 2-vinylindols **2b-2e** in the yields ranging from 56% to 65% regardless of whether they have substituents at the *ortho*-, *meta*-, or *para*-position. Then, the electronic effect at the *para*-position of the benzene ring was examined. Substrates with both

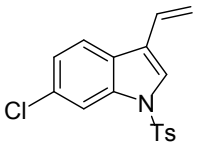
electron-donating and electron-withdrawing groups can afford the desired products **2f-2k** in yields from 33% to 70%. When substrates **1l** (R^1 = Ph, R^2 = 5-Cl) and **1m** (R^1 = 2-ClC_6H_4, R^2 = 5-Cl) were employed as the substrate, the corresponding products **2l** and **2m** were obtained in 59% and 60% yield. To further investigate this reaction, we attempted substrates with a heteroaromatic (furan **1n** and thiophene **1o**) or alkyl group (methyl group **1p** and *n*-butyl group **1q**). The experimental results showed that **1o** and **1q** were suitable under the current reaction conditions, giving the corresponding products **2o** and **2q** in 40% and 45% yields. However the yield of **2n** and **2p** are low, which is probably due to the byproducts. The byproduct **2p'** was main product and the byproduct of **1n** cannot be determined. Other N-sulfonyl protecting groups such as 4-bromobenzene sulfonyl (Bs) **1r**, 4-nitrobenzene sulfonyl (Ns) **1s** and N-carbonyl protecting group (Ac) **1t** were compatible in this reaction. To our delight, N without protecting group also worked smoothly, giving the desired product **2u** albeit in 31% yield. Also we got **2u** through detosylation of **2a** in yield 81%.

Scheme SI-2. Substrate Scope for the Synthesis of 3-Vinylindole **4**[a]

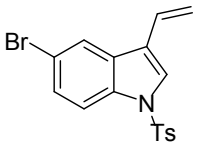




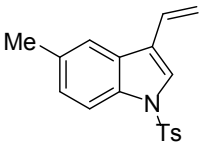
4b[b], 51%



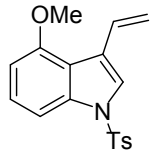
4c, 46%



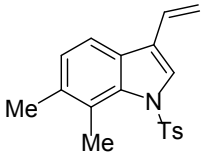
4d, 39%



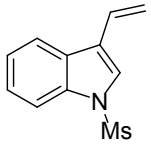
4e, 58%



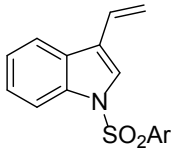
4f, 40%



4g, 42%



4h, 55%

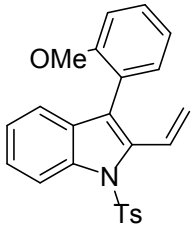


4i, 48%
Ar = (2,4-$MeO_2C_6H_3$)

[a] The reaction was conducted with **3** (0.2 mmol), $PdCl_2[P(4\text{-}MeOC_6H_4)_3]_2$ (0.2 mmol) and $KHCO_3$ (0.2 mmol) in toluene (2.0 mL) for 12 h at 100 °C with an O_2 balloon. [b] Yield of the isolated products.

With the optimized reaction conditions in hand, the substrate scope for **3** was explored and the results are shown in Scheme SI-1. The substrates of type **3** having both electron-donating and electron-withdrawing substituents (R^1) at different positions of benzene ring were tolerated, providing the 3-vinylindoles (**4b**-**4g**) in moderate yields from 39% to 58%. Also, when methyl sulfonyl and 2,4-dimethoxybenzene sulfonyl were used as N-protecting groups, the reaction took place efficiently to afford the corresponding 3-vinylindoles **4h** and **4i** in yields of 55% and 48%.

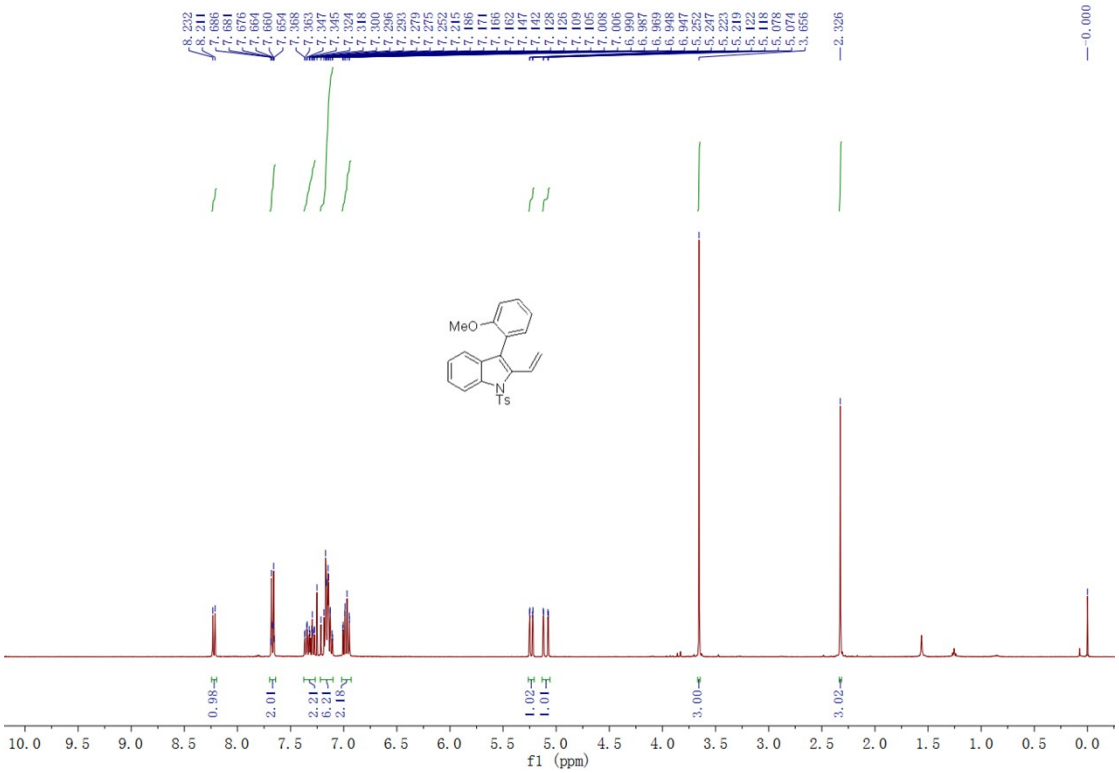
7. Characterization and spectra charts for vinylindoles 2 and 4



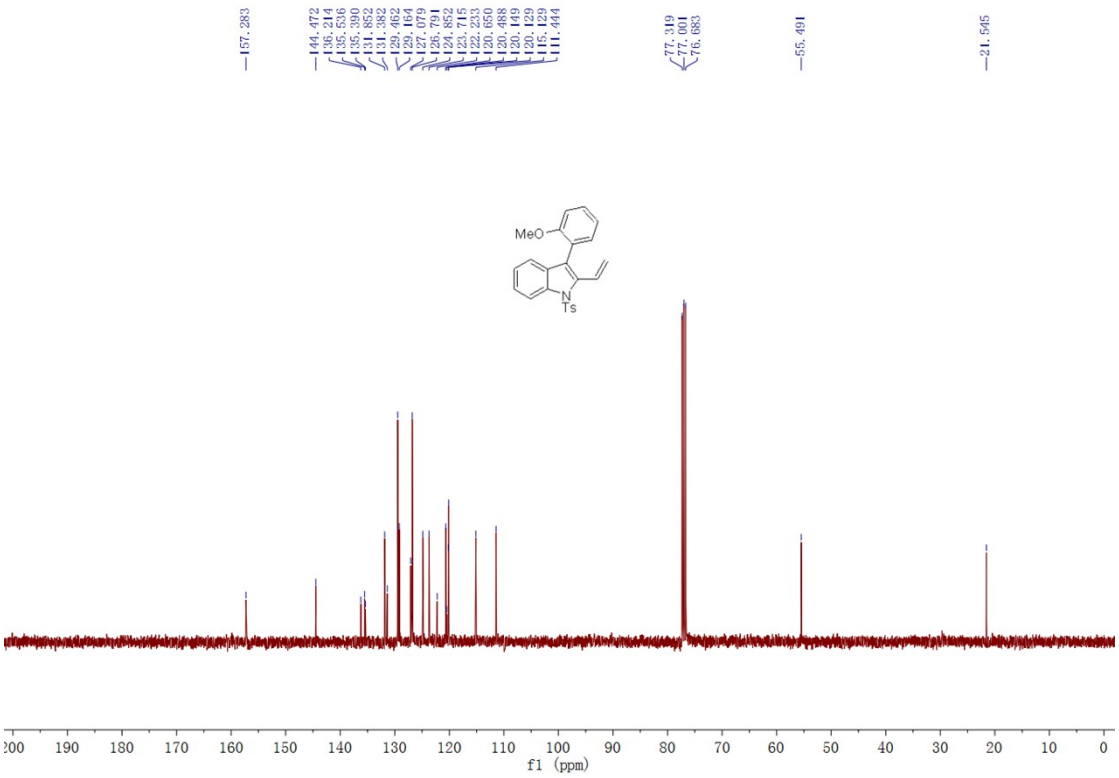
3-(2-methoxyphenyl)-1-tosyl-2-vinyl-1*H*-indole 2b

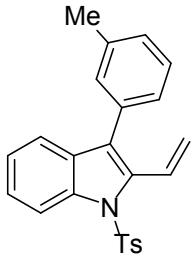
A faint yellow solid, 62% yield (60 mg). M.p.: 62-65 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.33 (s, 3H), 3.66 (s, 3H), 5.10 (dd, *J* = 1.6 Hz, 17.6 Hz, 1H), 5.24 (dd, *J* = 1.6 Hz, 10.4 Hz, 1H), 6.94-7.01 (m, 2H), 7.10-7.22 (m, 6H), 7.27-7.37 (m, 2H), 7.65-7.69 (m, 2H), 8.22 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 55.5, 111.4, 115.1, 120.13, 120.15, 120.5, 120.7, 122.2, 123.7, 124.9, 126.8, 127.1, 129.2, 129.5, 131.4, 131.9, 135.4, 135.5, 136.2, 144.5, 157.3. IR (neat) $\bar{\nu}$ 3070, 3048, 3031, 3004, 2959, 2929, 2834, 1616, 1597, 1577, 1493, 1449, 1372, 1246, 1173, 1148, 1090, 1022, 1014, 932, 812, 749, 667 cm^{-1}. HRMS (APCI) Calcd. for $C_{24}H_{22}NO_3S^{+1}(M+H)^+$ requires: 404.1315, Found: 404.1309.

^{1}H NMR spectrum of 2b:



^{13}C NMR spectrum of 2b:

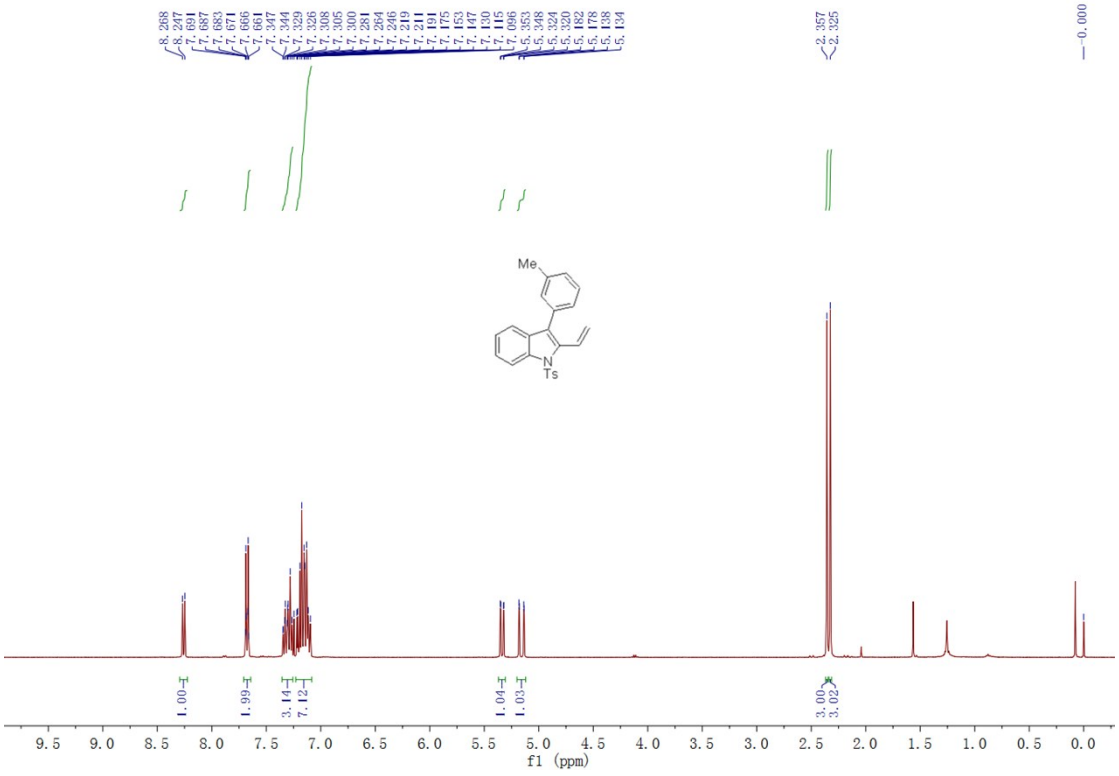




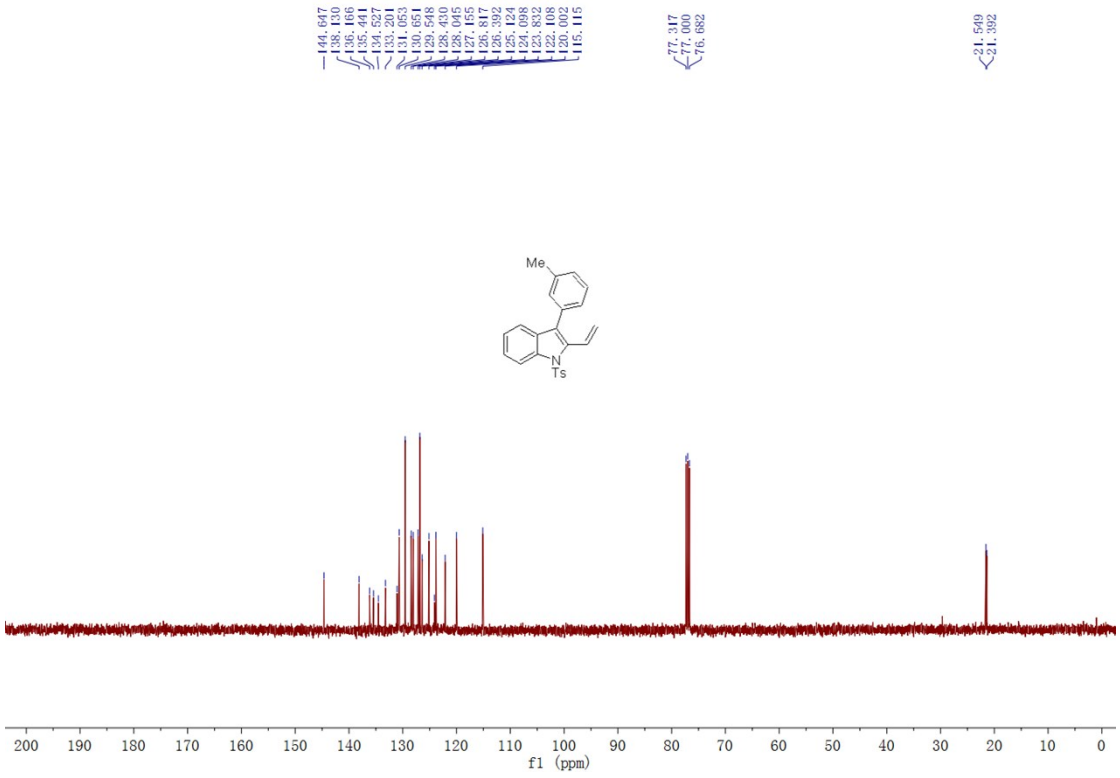
3-(*m*-tolyl)-1-tosyl-2-vinyl-1*H*-indole 2c

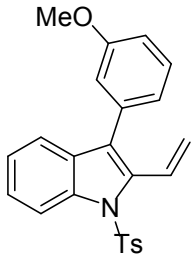
An orange solid, 60% yield (47 mg). M.p.: 71-73 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.33 (s, 3H), 3.66 (s, 3H), 5.16 (dd, *J* = 1.6 Hz, 17.6 Hz, 1H), 5.34 (dd, *J* = 1.6 Hz, 11.2 Hz, 1H), 7.09-7.22 (m, 7H), 7.26-7.35 (m, 3H), 7.66-7.70 (m, 2H), 8.26 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 21.5, 115.1, 120.0, 122.1, 123.8, 124.1, 125.1, 126.4, 126.8, 127.2, 128.0, 128.4, 129.5, 130.7, 131.1, 133.2, 134.5, 135.4, 136.2, 138.1, 144.6. IR (neat) $\bar{\nu}$ 3067, 3029, 3048, 2965, 2920, 2859, 1610, 1598, 1540, 1491, 1449, 1374, 1261, 1228, 1187, 1174, 1148, 1090, 1035, 924, 812, 791, 747, 705, 683, 668 cm^{-1}. HRMS (APCI) Calcd. for $C_{24}H_{22}NO_2S^{+1}(M+H)^+$ requires: 388.1366, Found: 388.1366.

^{1}H NMR spectrum of 2c:



^{13}C NMR spectrum of 2c:

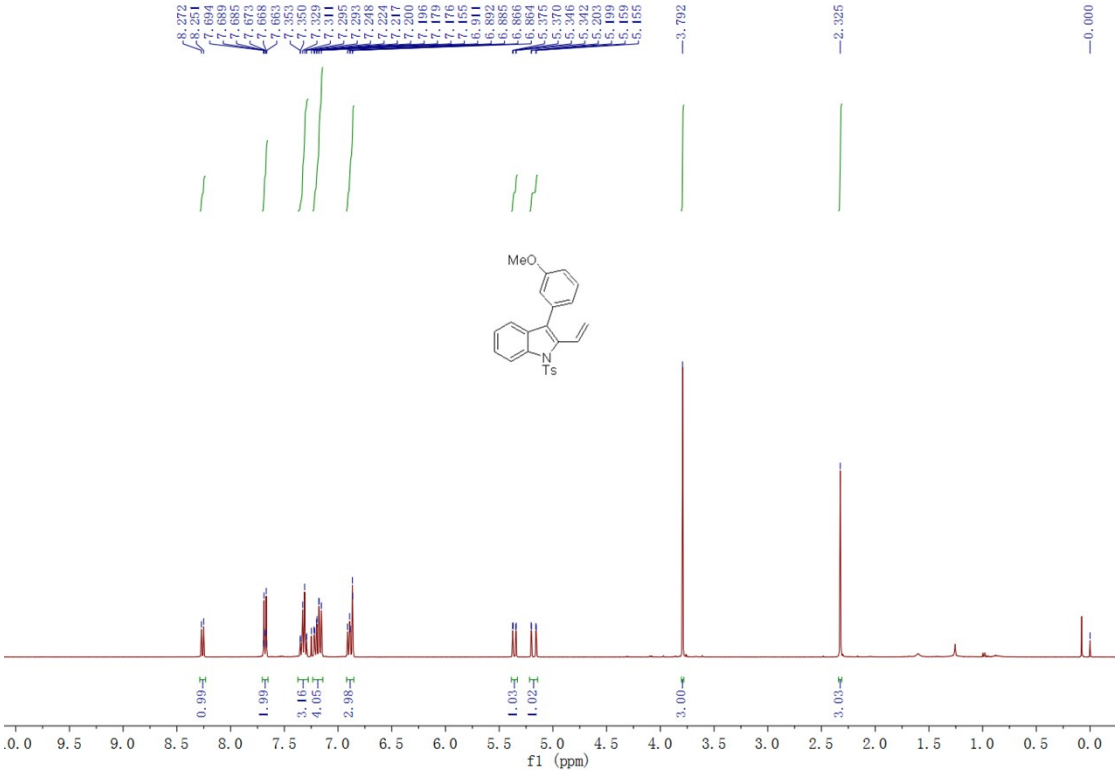




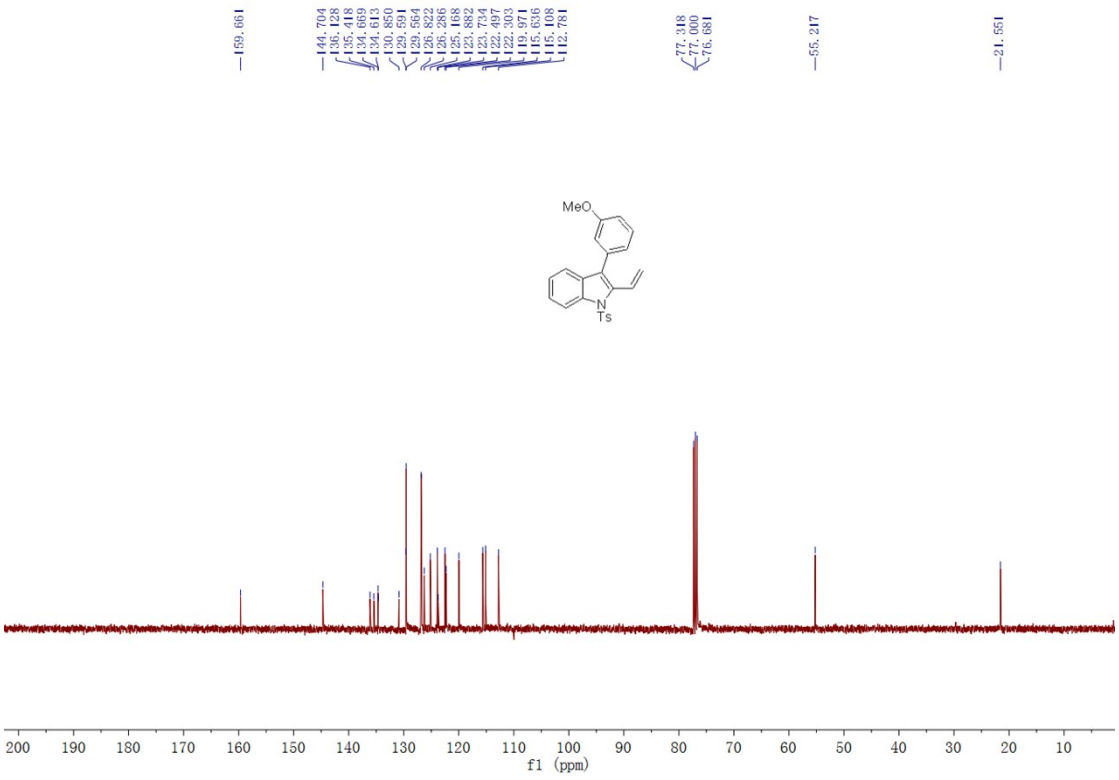
3-(3-methoxyphenyl)-1-tosyl-2-vinyl-1*H*-indole 2d

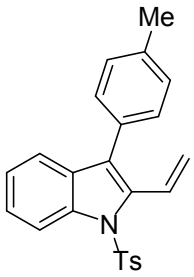
A faint yellow solid, 65% yield (53 mg). M.p.: 49-51 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.33 (s, 3H), 3.79 (s, 3H), 5.18 (dd, *J* = 1.6 Hz, 17.6 Hz, 1H), 5.36 (dd, *J* = 1.6 Hz, 11.2 Hz, 1H), 6.86-6.92 (m, 3H), 7.16-7.23 (m, 4H), 7.29-7.36 (m, 3H), 7.66-7.70 (m, 2H), 8.26 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 55.2, 112.8, 115.1, 115.6, 120.0, 122.3, 122.5, 123.7, 123.9, 125.2, 126.3, 126.8, 129.56, 129.59, 130.9, 134.6, 134.7, 135.4, 136.1, 144.7, 159.7. IR (neat) $\bar{\nu}$ 3067, 3042, 3029, 2998, 2959, 2923, 2870, 2859, 2831, 1727, 1598, 1574, 1488, 1449, 1374, 1285, 1253, 1228, 1186, 1173, 1149, 1090, 1026, 983, 808, 748, 702, 669 cm^{-1}. HRMS (APCI) Calcd. for $C_{24}H_{22}NO_3S^{+1}(M+H)^+$ requires: 404.1315, Found: 404.1314.

^{1}H NMR spectrum of 2d:



^{13}C NMR spectrum of 2d:

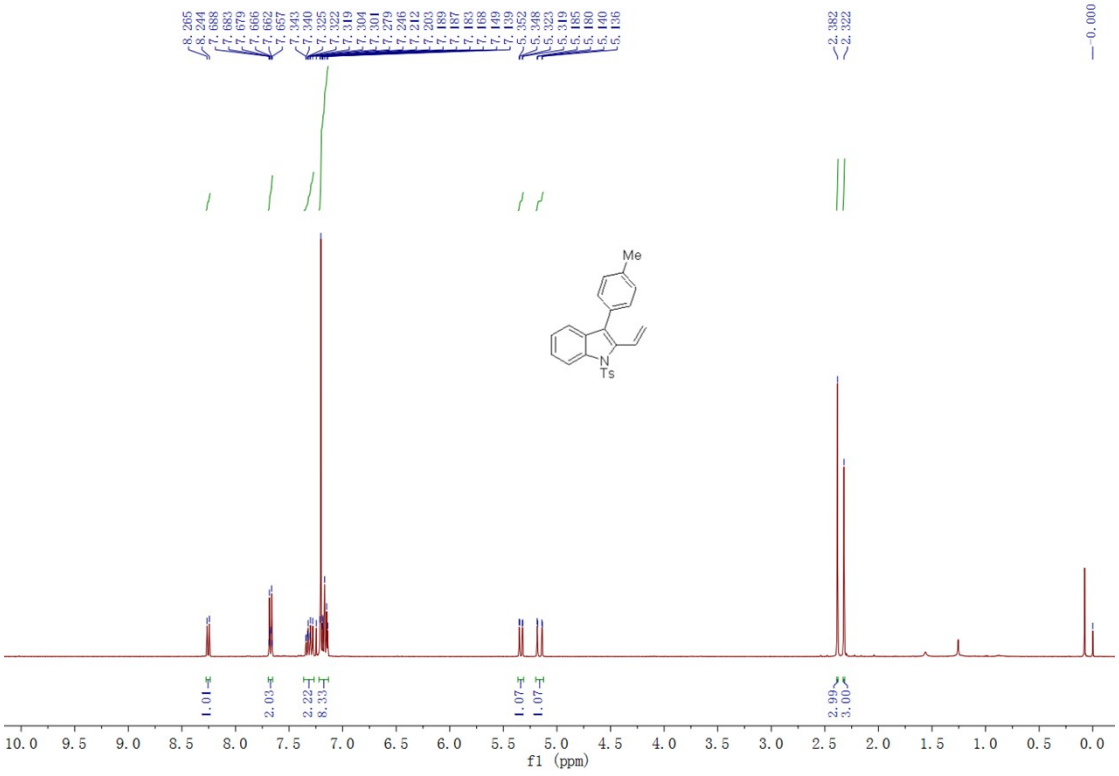




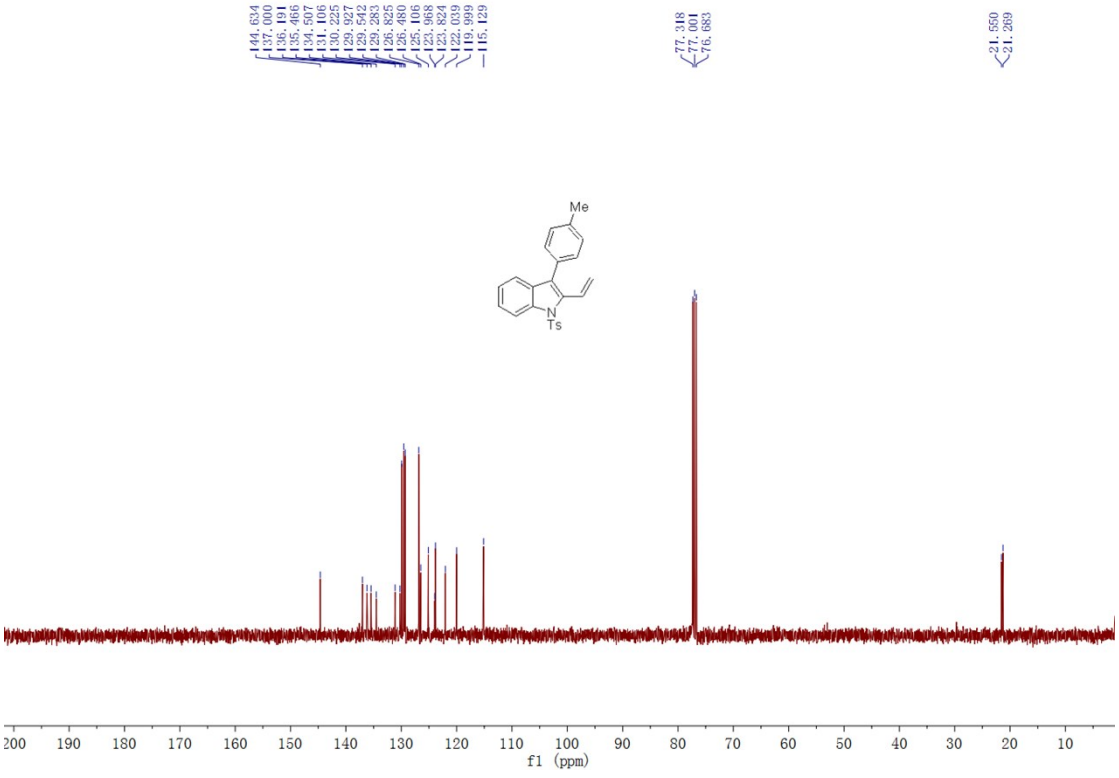
3-(*p*-tolyl)-1-tosyl-2-vinyl-1*H*-indole 2e

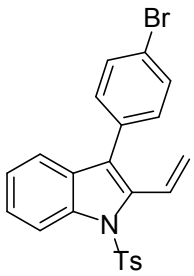
A faint yellow solid, 56% yield (44 mg). M.p.: 136-138 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.32 (s, 3H), 2.38 (s, 3H), 5.16 (dd, J = 1.6 Hz, 17.6 Hz, 1H), 5.34 (dd, J = 1.6 Hz, 11.6 Hz, 1H), 7.13-7.22 (m, 8H), 7.27-7.35 (m, 2H), 7.65-7.69 (m, 2H), 8.25 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.3, 21.6, 115.1, 120.0, 122.0, 123.8, 124.0, 125.1, 126.5, 126.8, 129.3, 129.5, 129.9, 130.2, 131.1, 134.5, 135.5, 136.2, 137.0, 144.6. IR (neat) $\bar{\nu}$ 3072, 3042, 2962, 2923, 2868, 2854, 1594, 1510, 1449, 1374, 1324, 1260, 1230, 1174, 1148, 1091, 1029, 1014, 933, 894, 818, 802, 747, 667 cm^{-1}. HRMS (APCI) Calcd. for $C_{24}H_{22}NO_2S^{+1}(M+H)^+$ requires: 388.1366, Found: 388.1359.

^{1}H NMR spectrum of 2e:



^{13}C NMR spectrum of 2e:

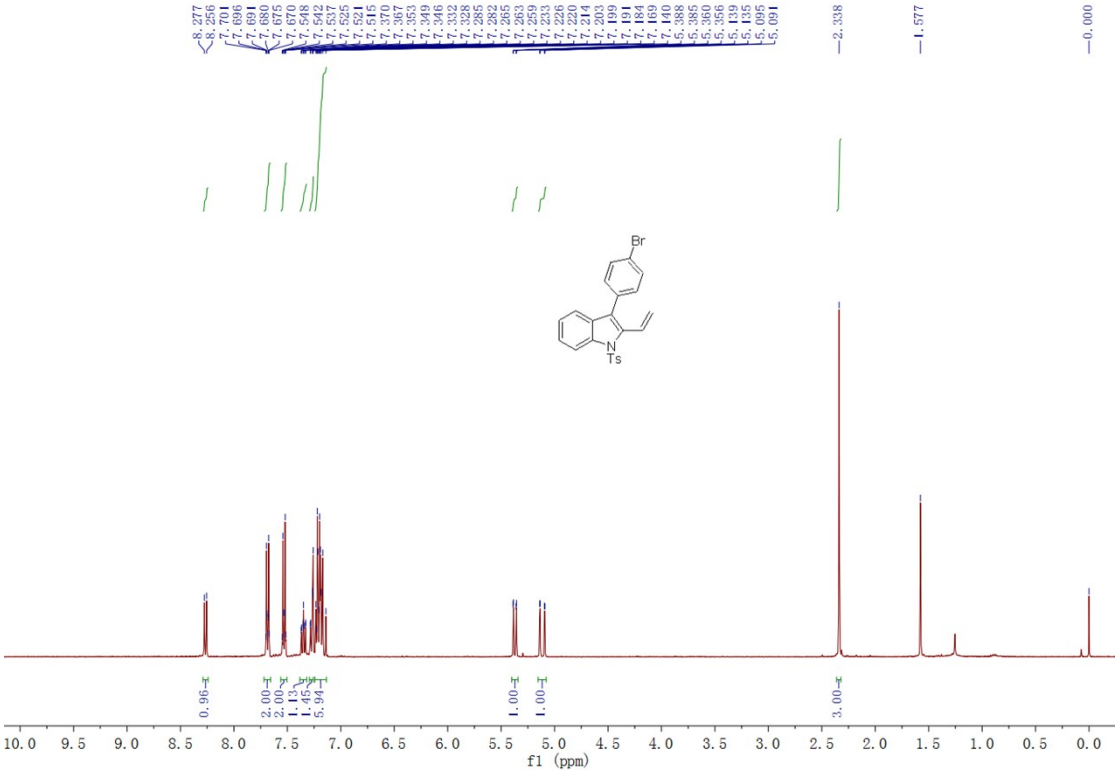




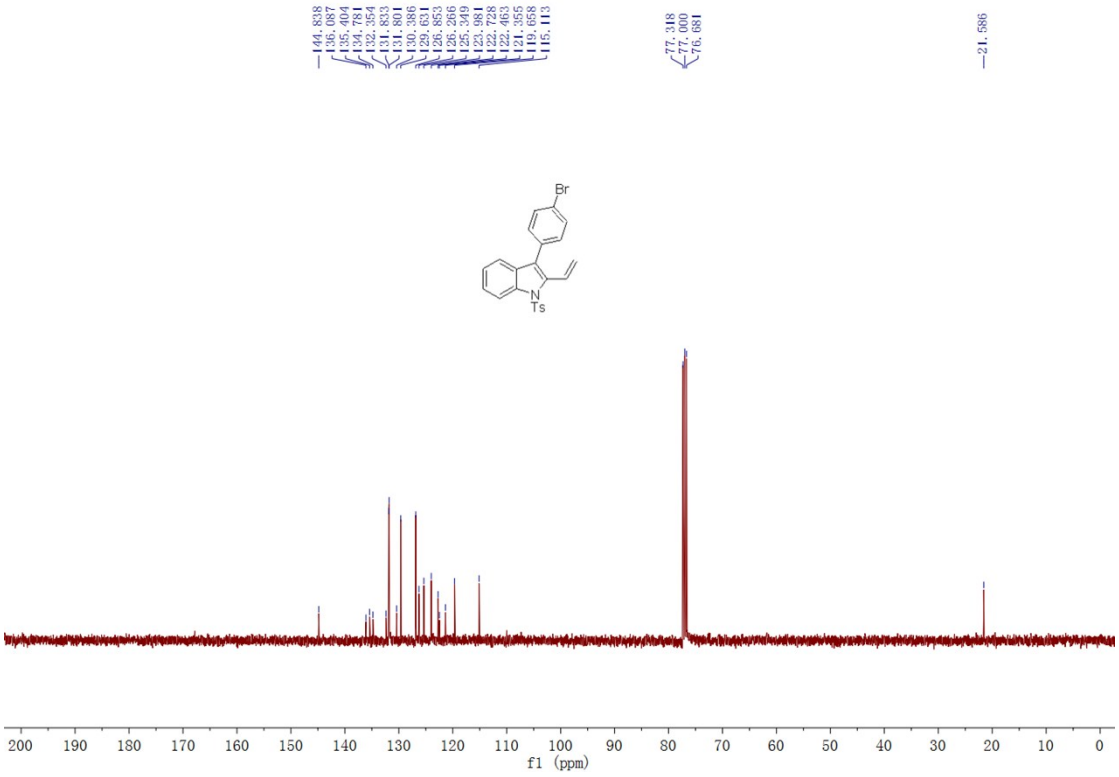
3-(4-bromophenyl)-1-tosyl-2-vinyl-1*H*-indole 2f

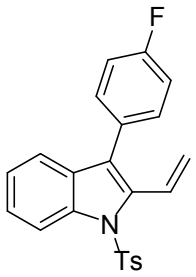
A white solid, 33% yield (30 mg). M.p.: 133-135 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.34 (s, 3H), 5.12 (dd, *J* = 1.6 Hz, 17.6 Hz, 1H), 5.37 (dd, *J* = 1.6 Hz, 11.6 Hz, 1H), 7.14-7.24 (m, 6H), 7.27 (dd, *J* = 0.8 Hz, 8.0 Hz, 1H), 7.32-7.37 (m, 1H), 7.51-7.55 (m, 2H), 7.67-7.71 (m, 2H), 8.27 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 115.1, 119.7, 121.4, 122.5, 122.7, 124.0, 125.3, 126.3, 126.9, 129.6, 130.4, 131.80, 131.83, 132.4, 134.8, 135.4, 136.1, 144.8. IR (neat) $\bar{\nu}$ 3067, 3045, 2956, 2924, 2854, 1596, 1487, 1449, 1375, 1229, 1174, 1150, 1090, 1075, 1026, 1008, 927, 894, 826, 812, 765, 748, 704, 667 cm^{-1}. HRMS (EI) Calcd. for $C_{23}H_{18}BrNO_2S$ requires: 451.0242, Found: 451.0246.

^{1}H NMR spectrum of 2f:



^{13}C NMR spectrum of 2f:

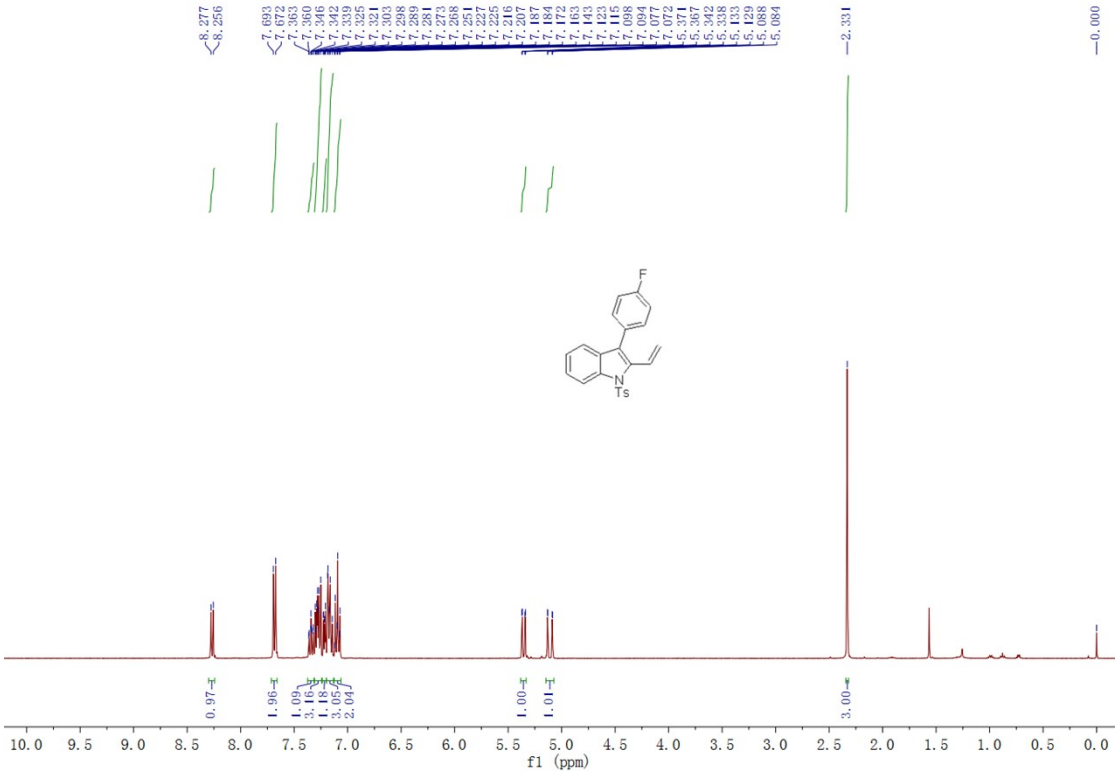




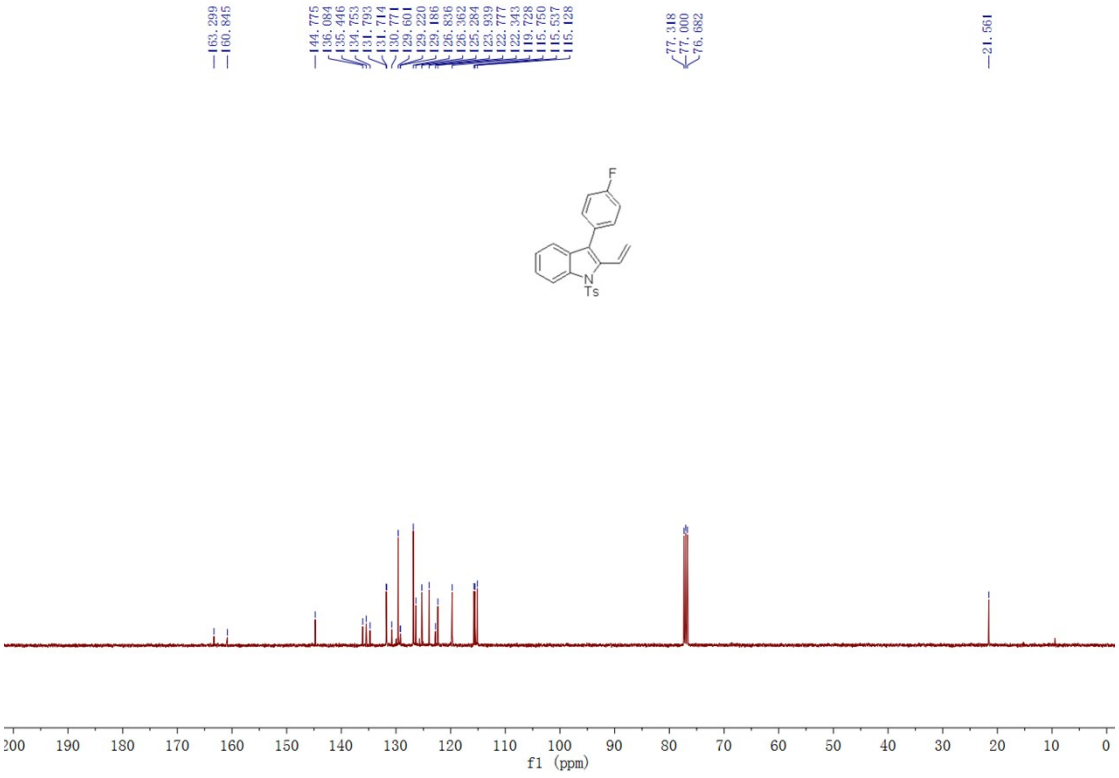
3-(4-fluorophenyl)-1-tosyl-2-vinyl-1*H*-indole 2g

A faint yellow solid, 70% yield (55 mg). M.p.: 70-72 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.33 (s, 3H), 5.11 (dd, *J* = 1.6 Hz, 18.0 Hz, 1H), 5.35 (dd, *J* = 1.6 Hz, 11.6 Hz, 1H), 7.07-7.13 (m, 2H), 7.14-7.19 (m, 3H), 7.20-7.23 (m, 1H), 7.25-7.31 (m, 3H), 7.32-7.37 (m, 1H), 7.68 (d, *J* = 8.4 Hz, 2H), 8.27 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 115.1, 115.6 (d, *J* = 21.3 Hz), 119.7, 122.3, 122.8, 123.9, 125.3, 126.4, 126.8, 129.2 (d, *J* = 3.4 Hz), 129.6, 130.8, 131.8 (d, *J* = 7.9 Hz), 134.8, 135.4, 136.1, 144.8, 162.1 (d, *J* = 245.4 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -114.68- -114.60 (m). IR (neat) $\bar{\nu}$ 3070, 3048, 3026, 2970, 2923, 2859, 1621, 1597, 1557, 1506, 1449, 1373, 1355, 1223, 1173, 1148, 1090, 1045, 1025, 1012, 928, 894, 837, 812, 760, 747, 714, 665 cm^{-1}. HRMS (APCI) Calcd. for $C_{23}H_{19}FNO_2S^{+1}(M+H)^+$ requires: 392.1115, Found: 392.1110.

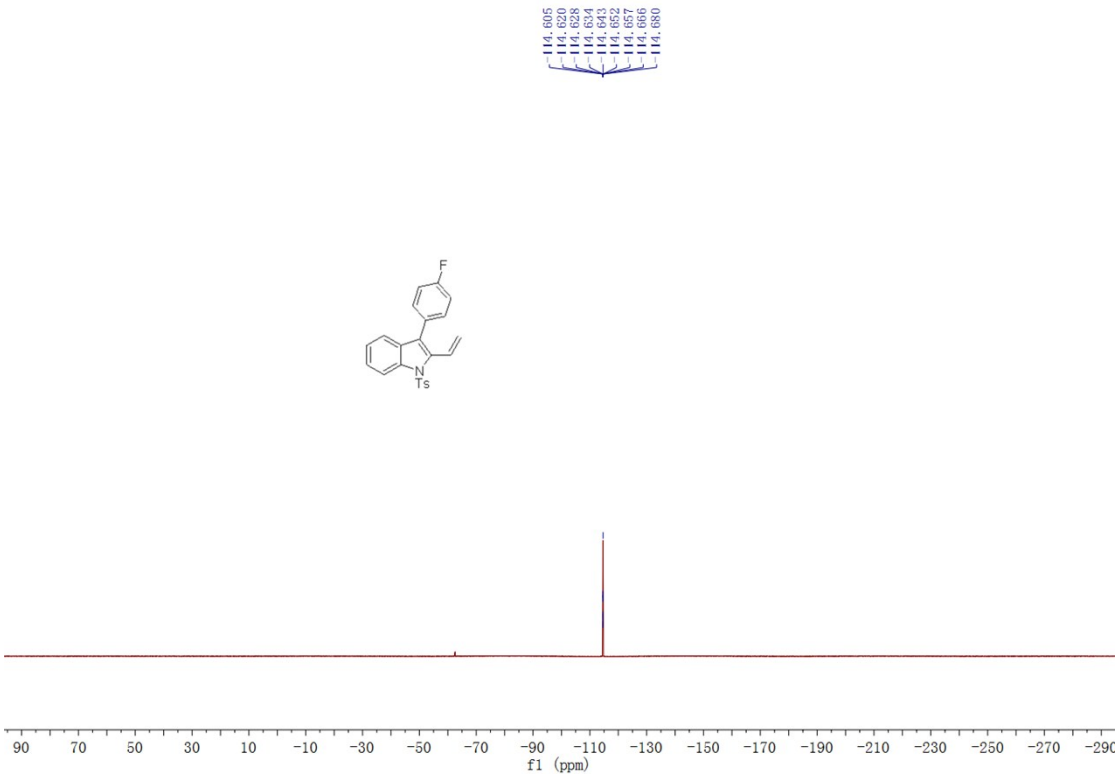
^{1}H NMR spectrum of 2g:

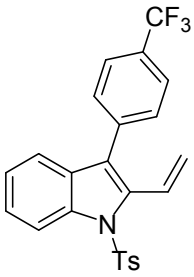


^{13}C NMR spectrum of 2g:



^{19}F NMR spectrum of 2g:

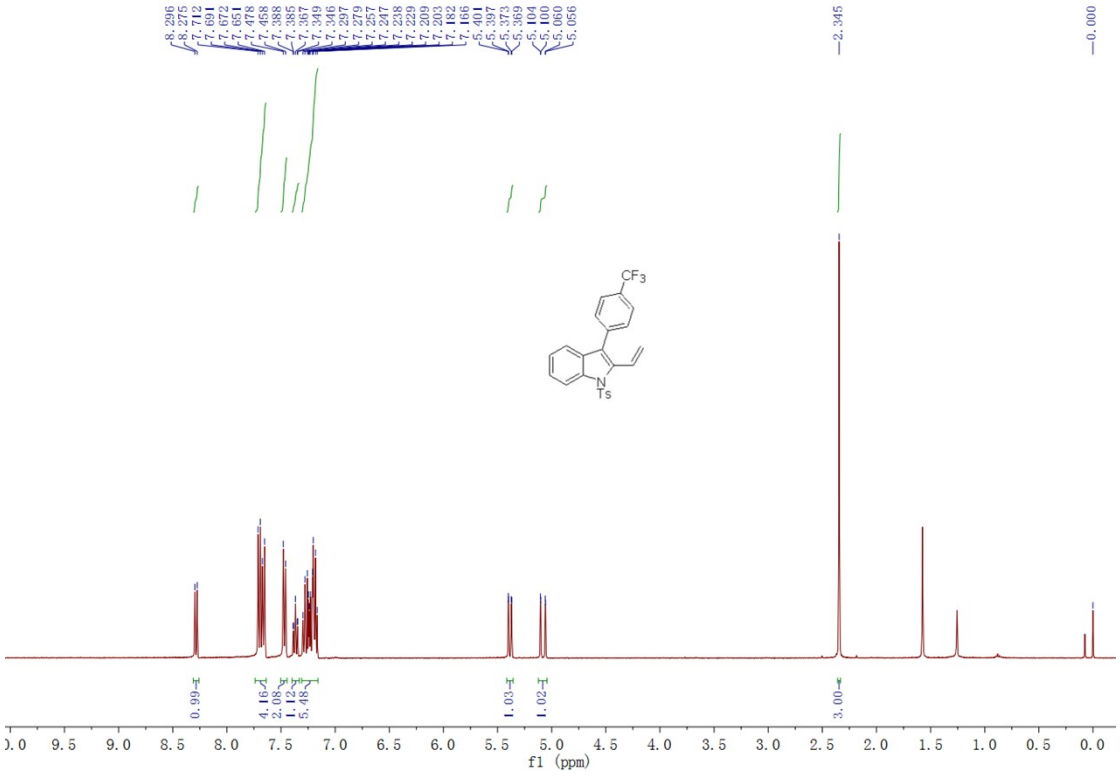




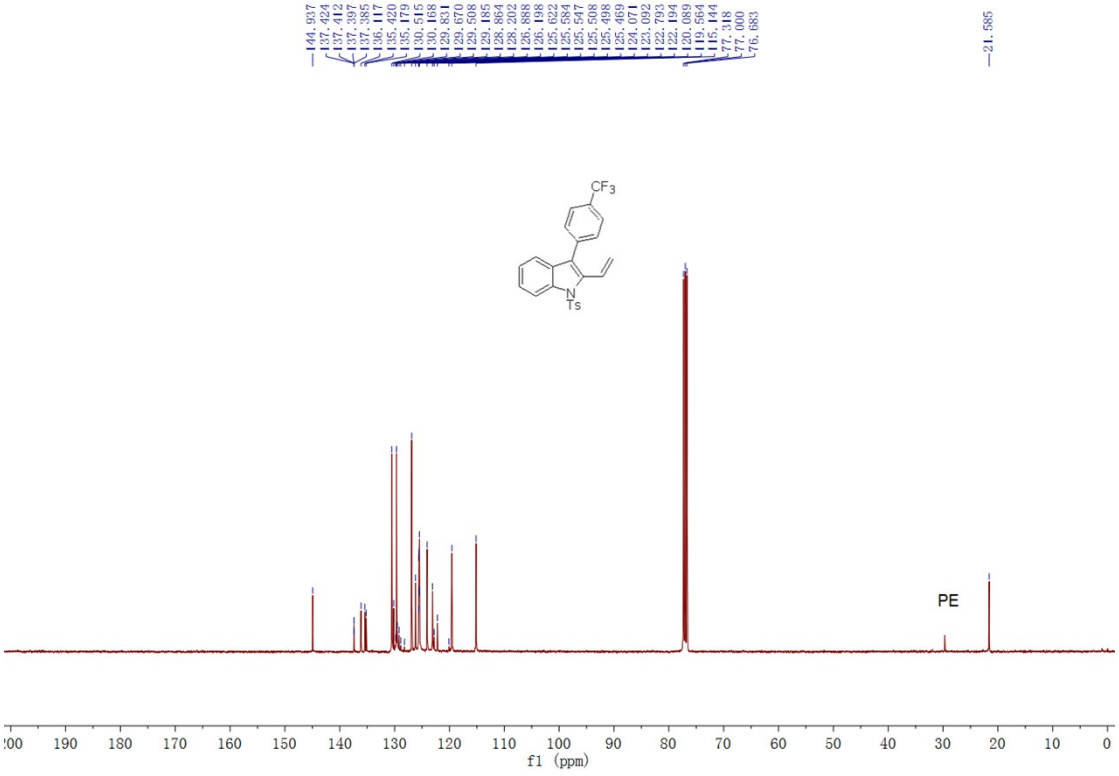
1-tosyl-3-(4-(trifluoromethyl)phenyl)-2-vinyl-1*H*-indole 2h

A faint yellow solid, 59% yield (53 mg). M.p.: 138-140 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.35 (s, 3H), 5.08 (dd, *J* = 1.6 Hz, 17.6 Hz, 1H), 5.39 (dd, *J* = 1.6 Hz, 11.2 Hz, 1H), 7.16-7.30 (m, 5H), 7.34-7.39 (m, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 8.29 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 115.1, 119.6, 122.2, 123.1, 124.07, 124.15 (q, *J* = 270.4 Hz), 125.5, 125.6 (q, *J* = 3.9 Hz), 126.2, 126.9, 129.3 (q, *J* = 21.3 Hz), 129.7, 130.2, 130.5, 135.2, 135.4, 136.1, 137.4 (q, *J* = 1.2 Hz), 144.9. ^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$) δ -62.5. IR (neat) $\bar{\nu}$ 3067, 3048, 2956, 2918, 1845, 1616, 1594, 1446, 1405, 1371, 1322, 1227, 1771, 1118, 1106, 1088, 1068, 1010, 932, 838, 812, 763, 749, 703, 665, 653 cm^{-1}. HRMS (APCI) Calcd. for $C_{24}H_{19}F_3NO_2S^{+1}(M+H)^+$ requires: 442.1083, Found: 442.1078.

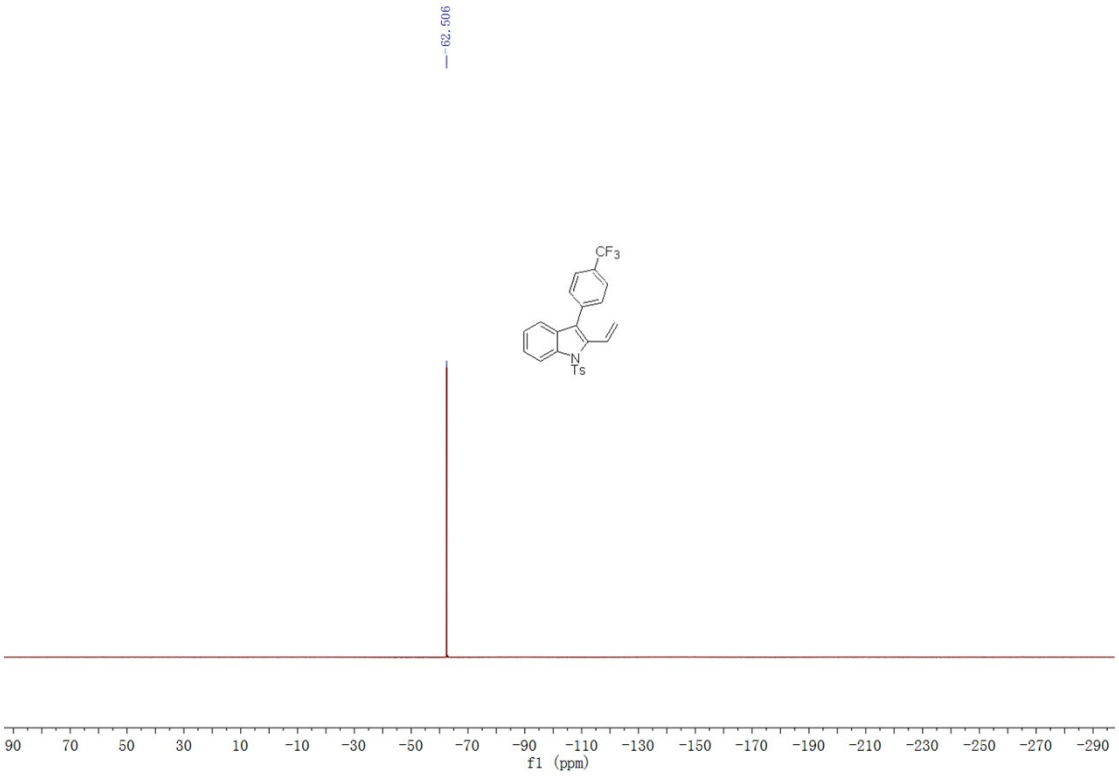
^{1}H NMR spectrum of 2h:

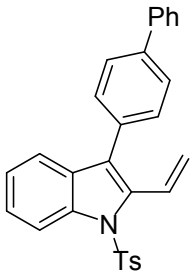


^{13}C NMR spectrum of 2h:



^{19}F NMR spectrum of 2h:

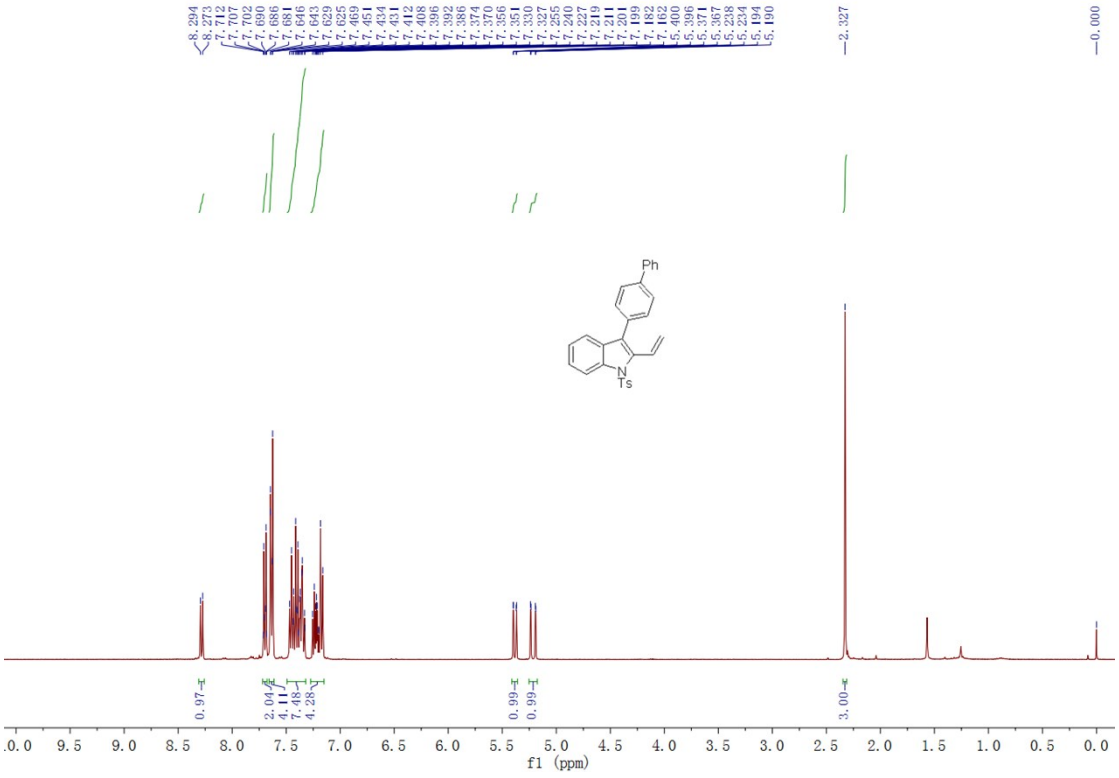




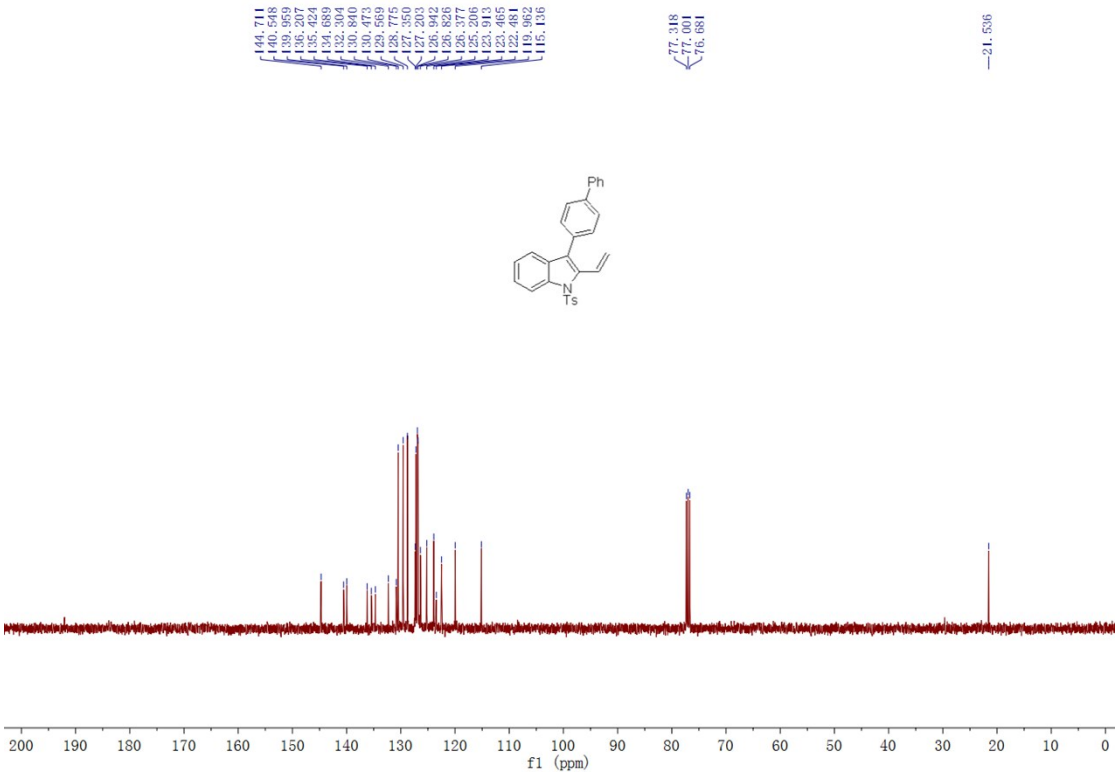
3-([1,1'-biphenyl]-4-yl)-1-tosyl-2-vinyl-1*H*-indole 2i

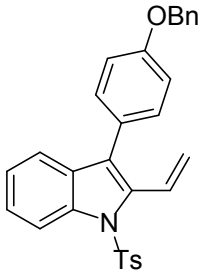
A white solid, 56% yield (51 mg). M.p.: 186-188 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.33 (s, 3H), 5.11 (dd, *J* = 1.6 Hz, 17.6 Hz, 1H), 5.38 (dd, *J* = 1.6 Hz, 11.6 Hz, 1H), 7.16-7.24 (m, 4H), 7.32-7.47 (m, 7H), 7.62-7.65 (m, 4H), 7.68-7.72 (m, 2H), 8.28 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 115.1, 120.0, 122.5, 123.5, 123.9, 125.2, 126.4, 126.8, 126.9, 127.2, 127.4, 128.8, 129.6, 130.5, 130.8, 132.3, 134.7, 135.4, 136.2, 140.0, 140.5, 144.7. IR (neat) $\bar{\nu}$ 3059, 3031, 2956, 2925, 2854, 1725, 1598, 1487, 1449, 1372, 1324, 1227, 1173, 1147, 1123, 1090, 1029, 1008, 916, 809, 771, 762, 728, 699, 666 cm^{-1}. HRMS (APCI) Calcd. for $C_{29}H_{24}NO_2S^{+1}$(M+H)$^+$ requires: 450.1522, Found: 450.1537.

^{1}H NMR spectrum of 2i:



^{13}C NMR spectrum of 2i:

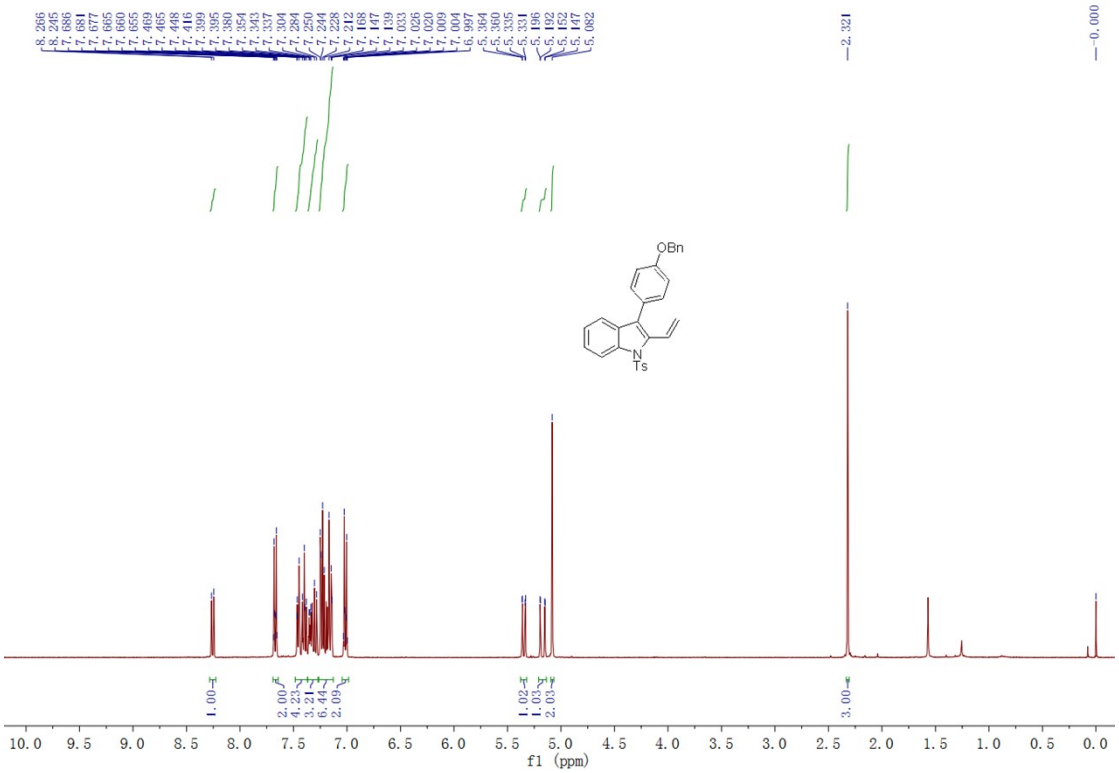




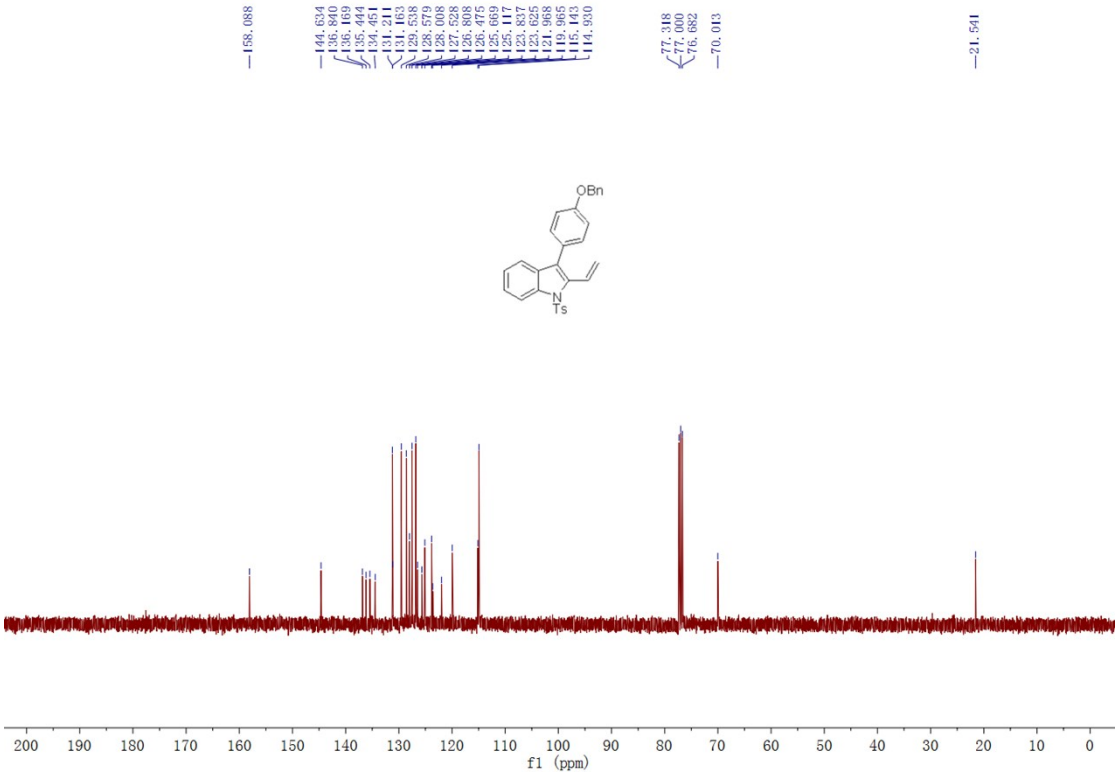
3-(4-(benzyloxy)phenyl)-1-tosyl-2-vinyl-1*H*-indole 2j

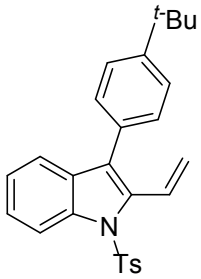
A faint yellow solid, 52% yield (50 mg). M.p.: 118-120 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.32 (s, 3H), 5.08 (s, 2H), 5.17 (dd, *J* = 1.6 Hz, 17.6 Hz, 1H), 5.35 (dd, *J* = 1.6 Hz, 11.6 Hz, 1H), 6.99-7.04 (m, 2H), 7.13-7.25 (m, 6H), 7.28-7.36 (m, 3H), 7.38-7.47 (m, 4H), 7.65-7.69 (m, 2H), 8.26 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.5, 70.0, 114.9, 115.1, 120.0, 122.0, 123.6, 123.8, 125.1, 125.7, 126.5, 126.8, 127.5, 128.0, 128.6, 129.5, 131.16, 131.21, 134.5, 135.4, 136.2, 136.8, 144.6, 158.1. IR (neat) $\bar{\nu}$ 3065, 3029, 2923, 2851, 1610, 1598, 1560, 1507, 1449, 1374, 1358, 1283, 1240, 1173, 1148, 1090, 1023, 1007, 925, 891, 832, 812, 764, 747, 699, 667 cm^{-1}. HRMS (APCI) Calcd. for $C_{30}H_{26}NO_3S^{+1}(M+H)^+$ requires: 480.1628, Found: 480.1636.

^{1}H NMR spectrum of 2j:



^{13}C NMR spectrum of 2j:

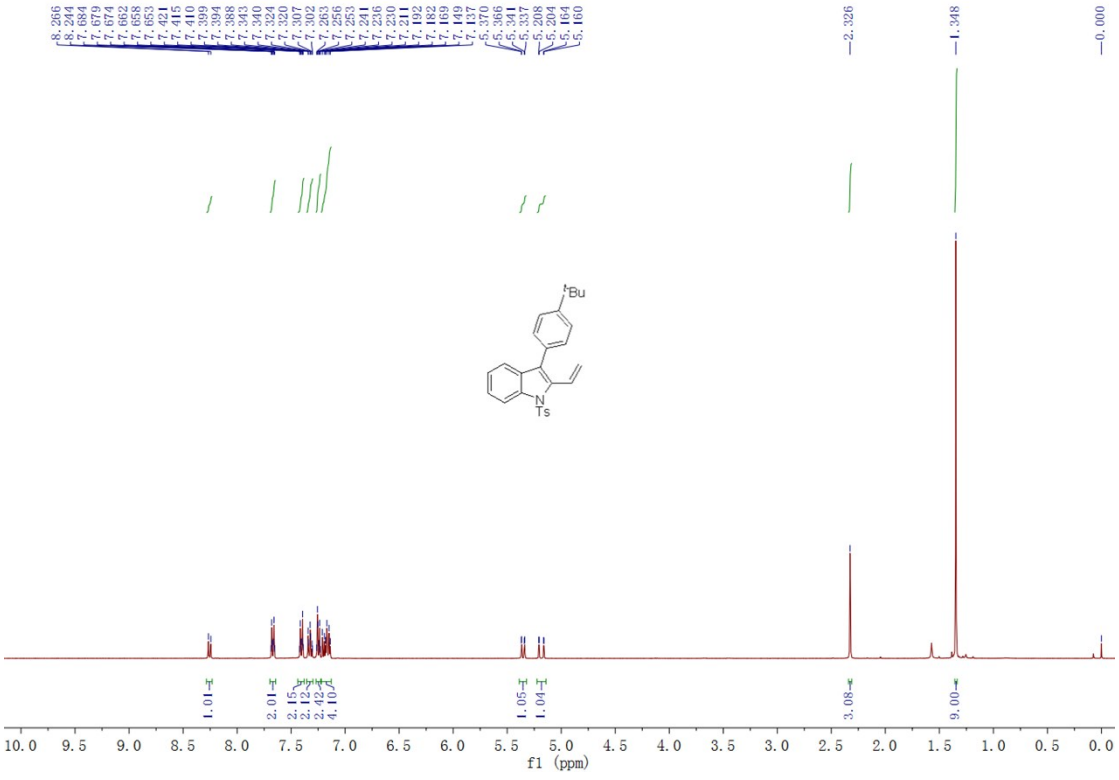




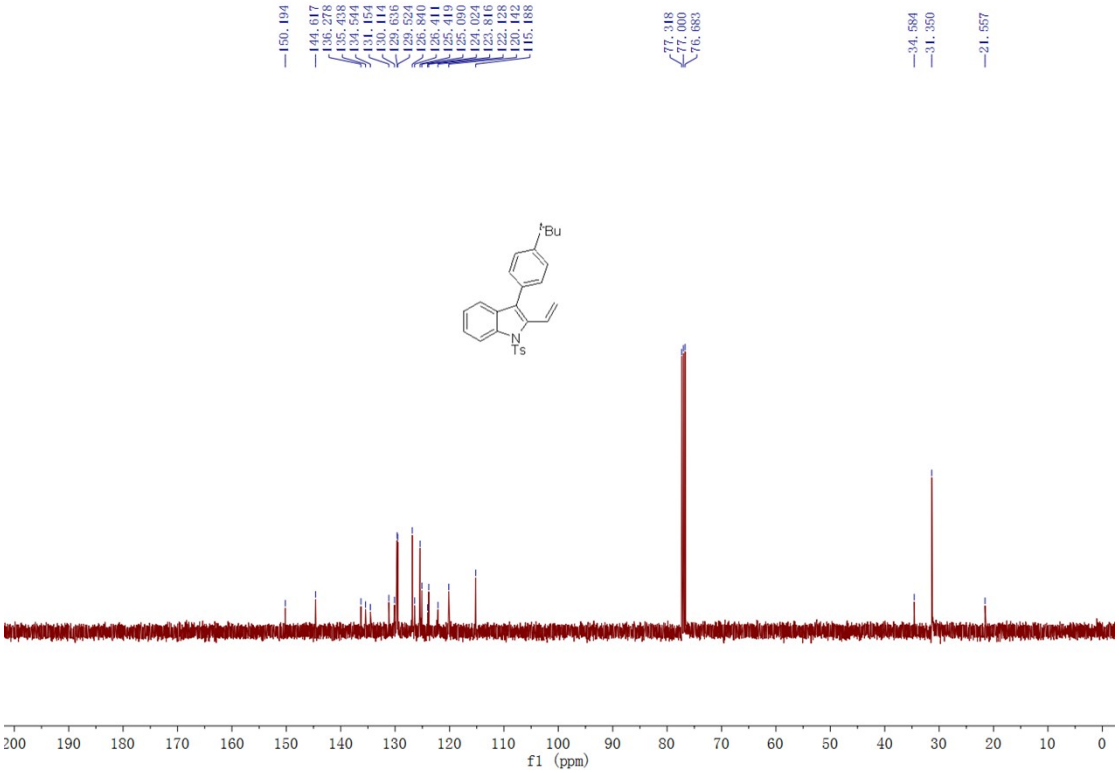
3-(4-(tert-butyl)phenyl)-1-tosyl-2-vinyl-1*H*-indole 2k

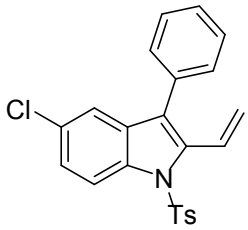
A faint yellow solid, 45% yield (39 mg). M.p.: 159-161 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.34 (s, 9H), 2.33 (s, 3H), 5.18 (dd, J = 1.6 Hz, 17.6 Hz, 1H), 5.35 (dd, J = 1.6 Hz, 11.6 Hz, 1H), 7.13-7.27 (m, 6H), 7.30-7.35 (m, 2H), 7.38-7.42 (m, 2H), 7.65-7.69 (m, 2H), 8.26 (d, J = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 31.4, 34.6, 115.2, 120.1, 122.1, 123.8, 124.0, 125.1, 125.4, 126.4, 126.8, 129.5, 129.6, 130.1, 131.2, 134.5, 135.4, 136.3, 144.6, 150.2. IR (neat) $\bar{\nu}$ 3061, 3048, 2958, 2925, 2854, 1738, 1716, 1596, 1507, 1450, 1376, 1261, 1229, 1174, 1149, 1109, 1091, 1012, 833, 811, 767, 747, 668 cm^{-1}. HRMS (APCI) Calcd. for $C_{27}H_{28}NO_2S^{+1}(M+H)^+$ requires: 430.1835, Found: 430.1835.

^{1}H NMR spectrum of 2k:



^{13}C NMR spectrum of 2k:

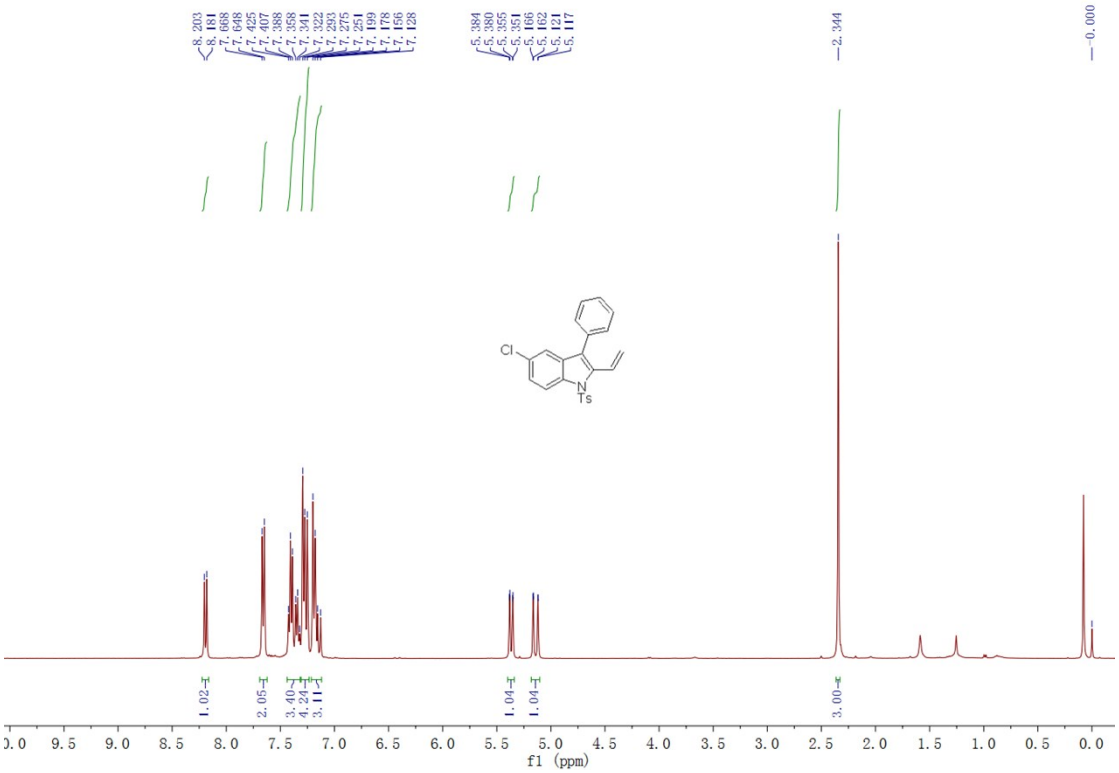




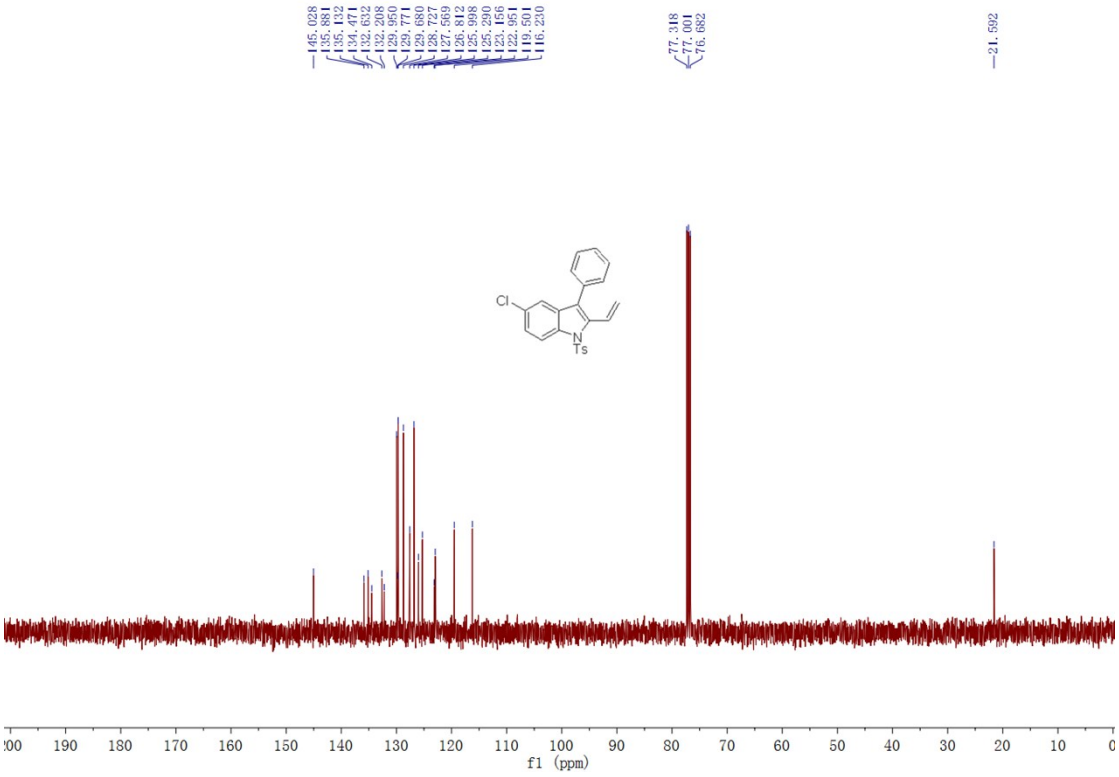
5-chloro-3-phenyl-1-tosyl-2-vinyl-1*H*-indole 2l

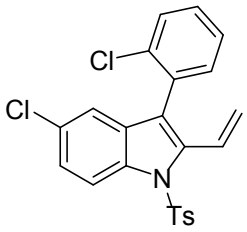
A white solid, 59% yield (48 mg). M.p.: 142-145 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.34 (s, 3H), 5.14 (dd, *J* = 1.6 Hz, 18.0 Hz, 1H), 5.37 (dd, *J* = 1.6 Hz, 11.6 Hz, 1H), 7.12-7.20 (m, 3H), 7.25-7.30 (m, 4H), 7.32-7.43 (m, 3H), 7.66 (d, *J* = 8.0 Hz, 2H), 8.19 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 116.2, 119.5, 123.0, 123.2, 125.3, 126.0, 126.8, 127.6, 128.7, 129.7, 129.8, 130.0, 132.2, 132.6, 134.5, 135.1, 135.9, 145.0. IR (neat) $\bar{\nu}$ 3059, 3031, 2956, 2925, 2854, 1724, 1597, 1494, 1446, 1377, 1324, 1264, 1230, 1166, 1133, 1090, 1036, 1014, 958, 927, 898, 810, 787, 771, 728, 703, 688, 665 cm^{-1}. HRMS (EI) Calcd. for $C_{23}H_{18}ClNO_2S$ requires: 407.0747, Found: 407.0750.

^{1}H NMR spectrum of 2l:



^{13}C NMR spectrum of 2l:

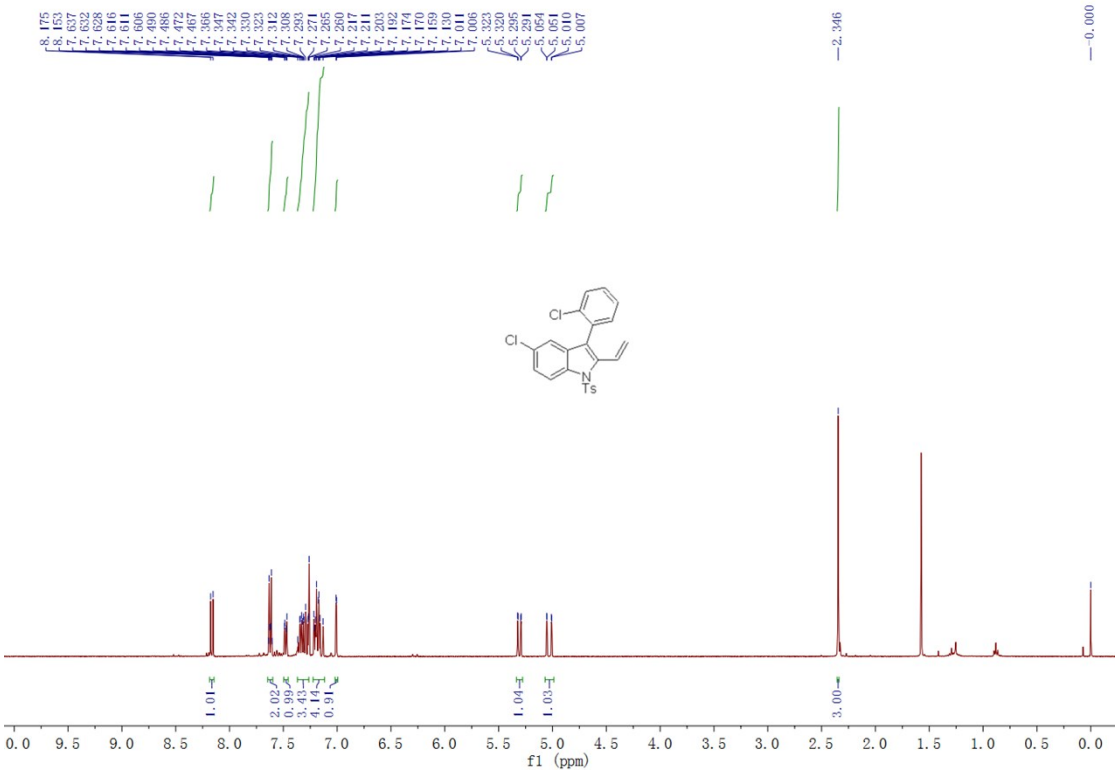




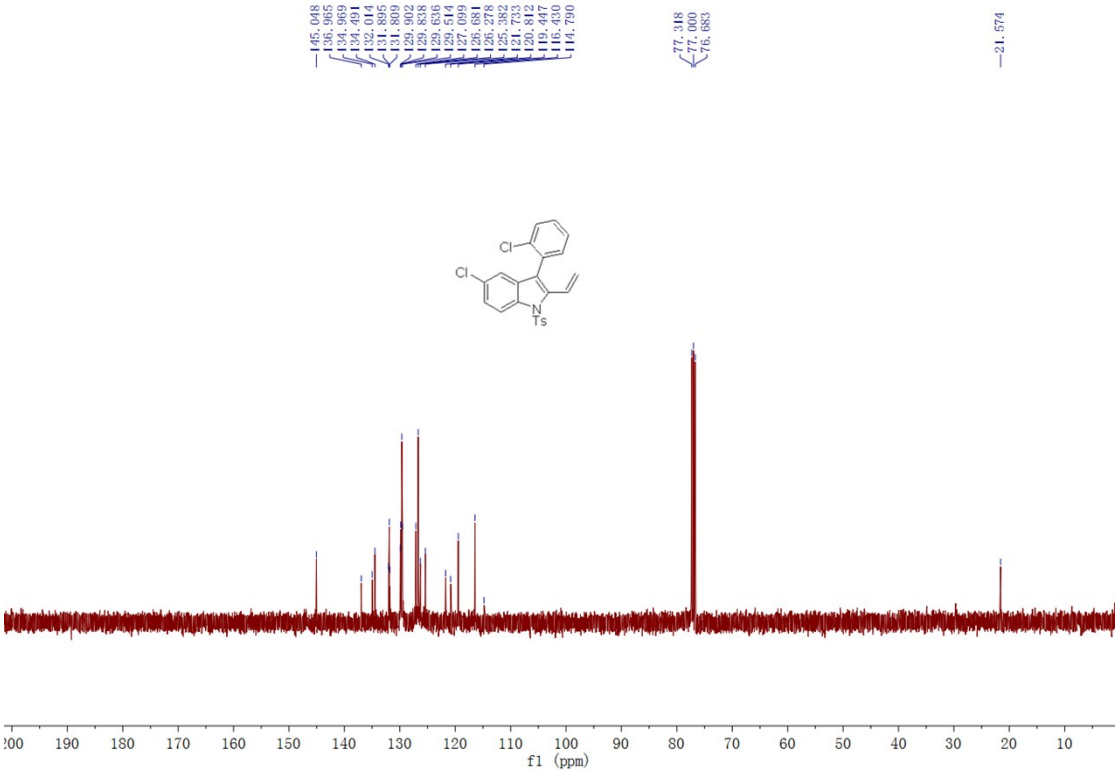
5-chloro-3-(2-chlorophenyl)-1-tosyl-2-vinyl-1*H*-indole 2m

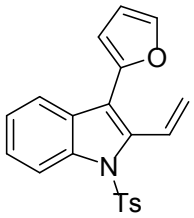
A faint yellow solid, 60% yield (53 mg). M.p.: 69-70 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.35 (s, 3H), 5.03 (dd, *J* = 1.2 Hz, 17.6 Hz, 1H), 5.31 (dd, *J* = 1.2 Hz, 11.6 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 7.13-7.22 (m, 4H), 7.26-7.37 (m, 3H), 7.46-7.49 (m, 1H), 7.60-7.64 (m, 2H), 8.16 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 114.8, 116.4, 119.4, 120.8, 121.7, 125.4, 126.3, 126.7, 127.1, 129.5, 129.6, 129.8, 129.9, 131.8, 131.9, 132.0, 134.5, 135.0, 137.0, 145.0. IR (neat) $\bar{\nu}$ 3067, 3026, 2967, 2920, 2848, 1597, 1474, 1447, 1375, 1348, 1324, 1228, 1166, 1089, 1075, 1014, 927, 810, 760, 740, 709, 664 cm^{-1}. HRMS (APCI) Calcd. for $C_{23}H_{18}Cl_2NO_2S^{+1}$(M+H)$^+$ requires: 442.0430, Found: 442.0418.

^{1}H NMR spectrum of 2m:



^{13}C NMR spectrum of 2m:

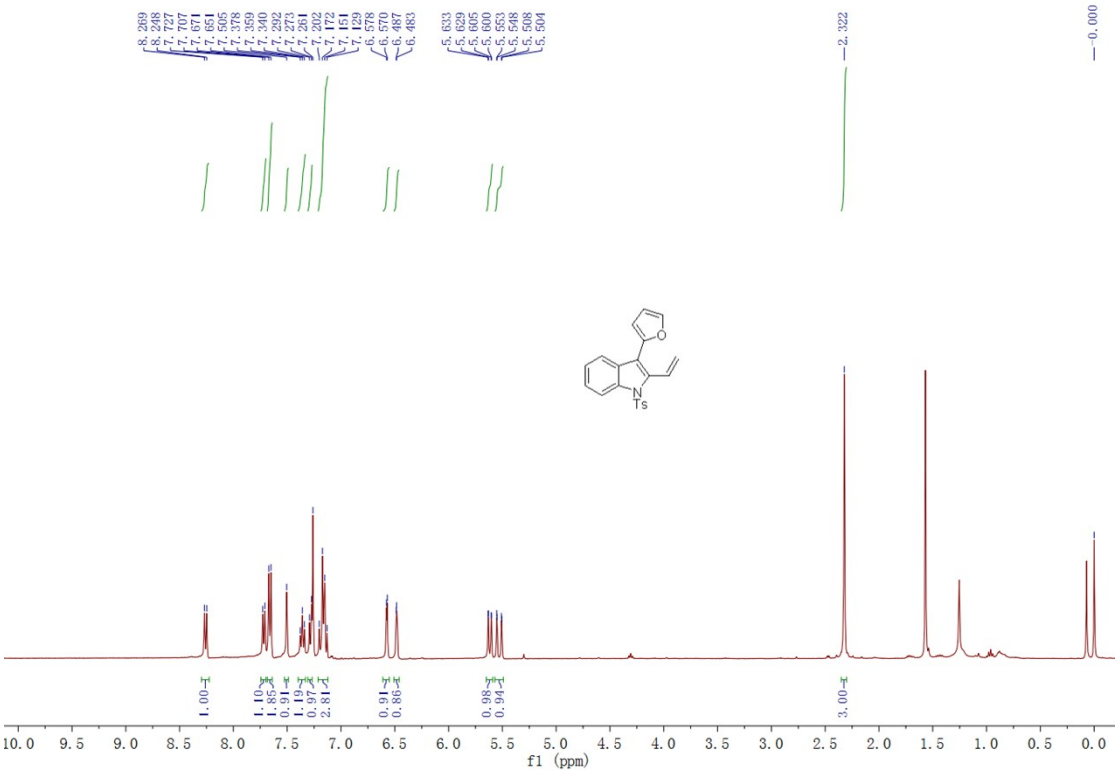




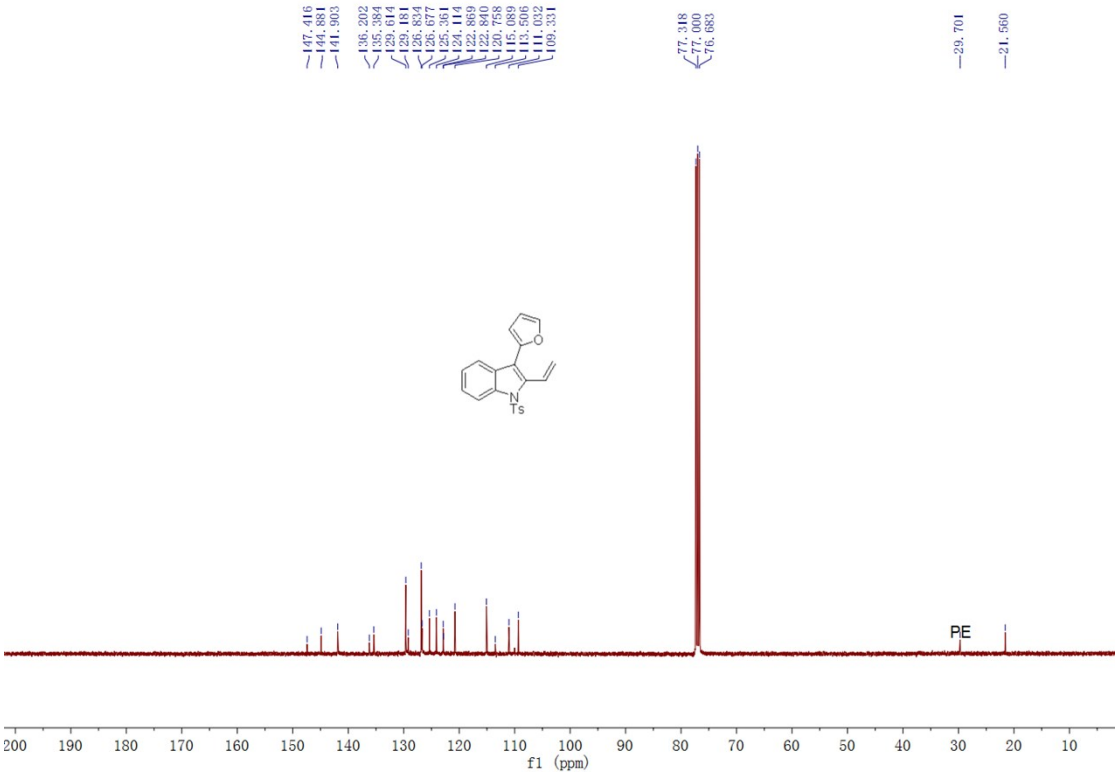
3-(furan-2-yl)-1-tosyl-2-vinyl-1*H*-indole 2n

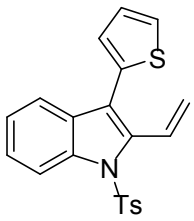
An orange solid, 18% yield (14 mg). M.p.: 101-103 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.32 (s, 3H), 5.53 (dd, *J* = 1.6 Hz, 17.6 Hz, 1H), 5.62 (dd, *J* = 1.6 Hz, 11.6 Hz, 1H), 6.47-6.49 (m, 1H), 6.57 (d, *J* = 3.2 Hz, 1H), 7.12-7.21 (m, 3H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.34-7.38 (m, 1H), 7.51 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 109.3, 111.0, 113.5, 115.1, 120.8, 122.8, 122.9, 124.1, 125.4, 126.7, 126.8, 129.2, 129.6, 135.4, 136.2, 141.9, 144.9, 147.4. IR (neat) $\bar{\nu}$ 3109, 3078, 2940, 2926, 2868, 1619, 1602, 1529, 1488, 1452, 1379, 1350, 1313, 1223, 1186, 1171, 1147, 1087, 1018, 1010, 994, 934, 851, 785, 774, 754, 739, 723, 703, 683 cm^{-1}. HRMS (APCI) Calcd. for $C_{21}H_{18}NO_3S^{+1}(M+H)^+$ requires: 364.1002, Found: 364.1018.

^{1}H NMR spectrum of 2n:



^{13}C NMR spectrum of 2n:

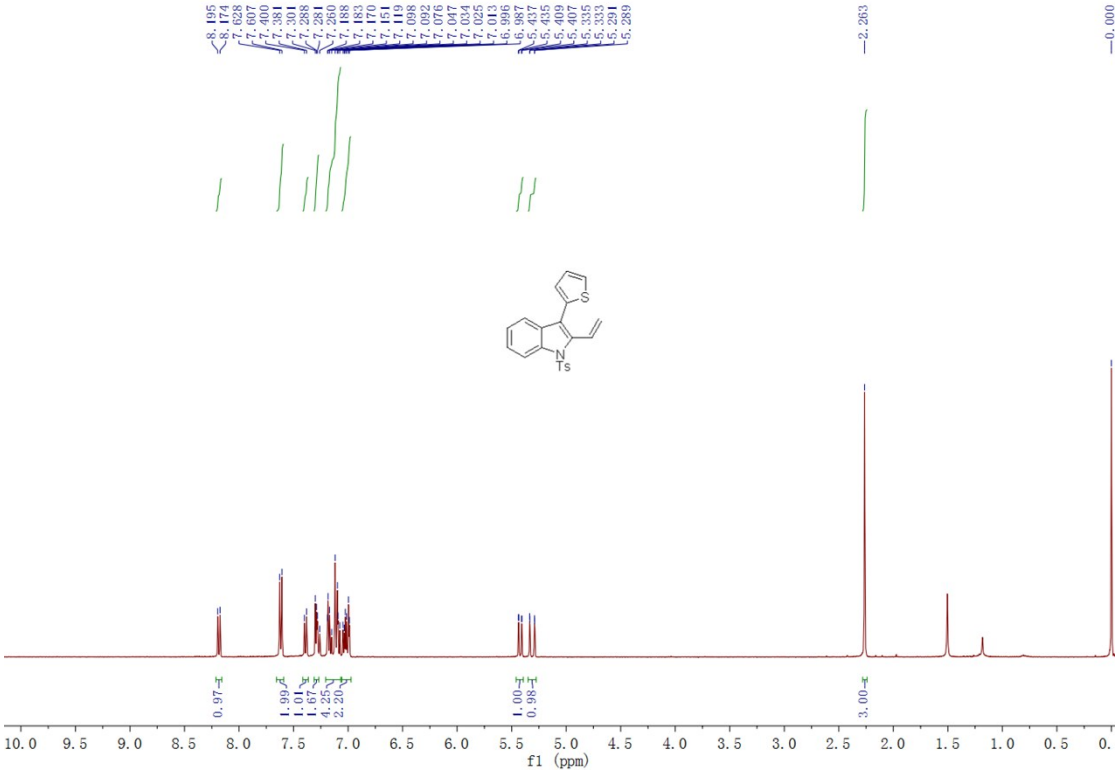




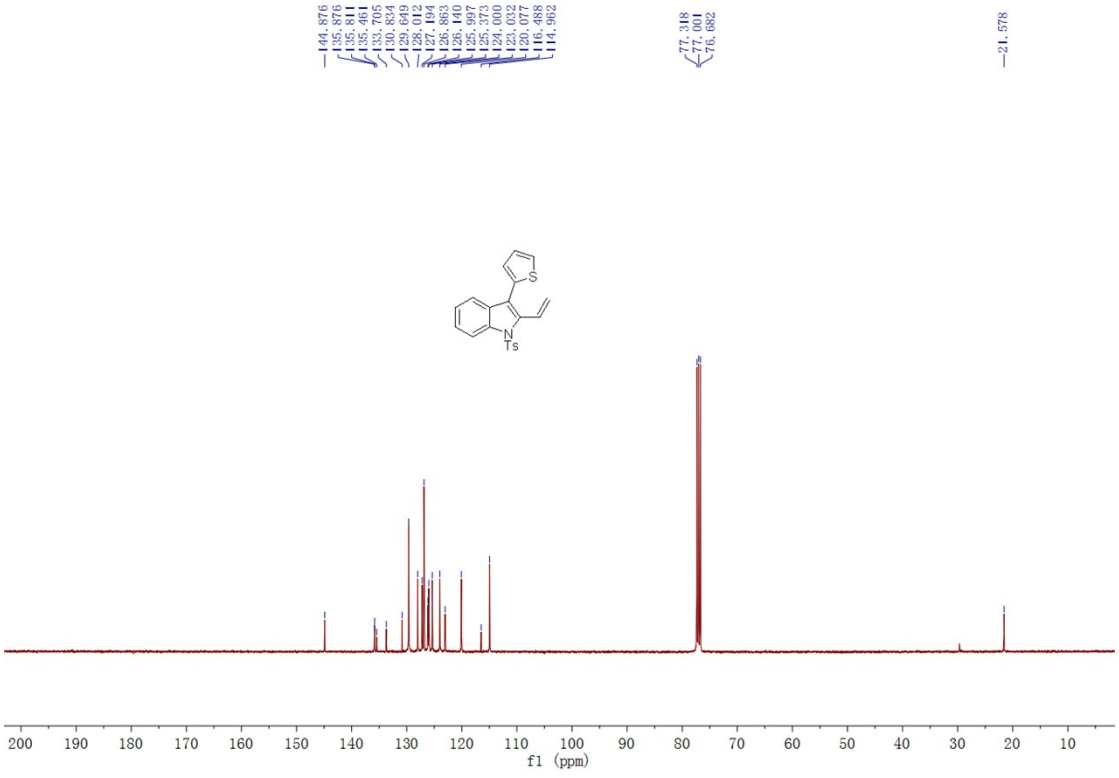
3-(thiophen-2-yl)-1-tosyl-2-vinyl-1*H*-indole 2o

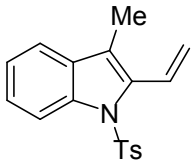
A yellow solid, 40% yield (30 mg). M.p.: 69-71 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.26 (s, 3H), 5.21 (dd, *J* = 0.8 Hz, 17.6 Hz, 1H), 5.42 (dd, *J* = 0.8 Hz, 11.2 Hz, 1H), 6.89-7.05 (m, 2H), 7.07-7.19 (m, 4H), 7.28-7.31 (m, 2H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 115.0, 116.5, 120.1, 123.0, 124.0, 125.4, 126.0, 126.1, 126.9, 127.2, 128.0, 129.6, 130.8, 133.7, 135.5, 135.8, 135.9, 144.9. IR (neat) $\bar{\nu}$ 3106, 3070, 3045, 3031, 2959, 2926, 2851, 1682, 1596, 1449, 1373, 1226, 1173, 1149, 1089, 998, 927, 844, 812, 747, 702, 668 cm^{-1}. HRMS (APCI) Calcd. for $C_{21}H_{18}NO_2S_2^{+1}$(M+H)$^+$ requires: 380.0773, Found: 380.0781.

^{1}H NMR spectrum of 2o:



^{13}C NMR spectrum of 2o:

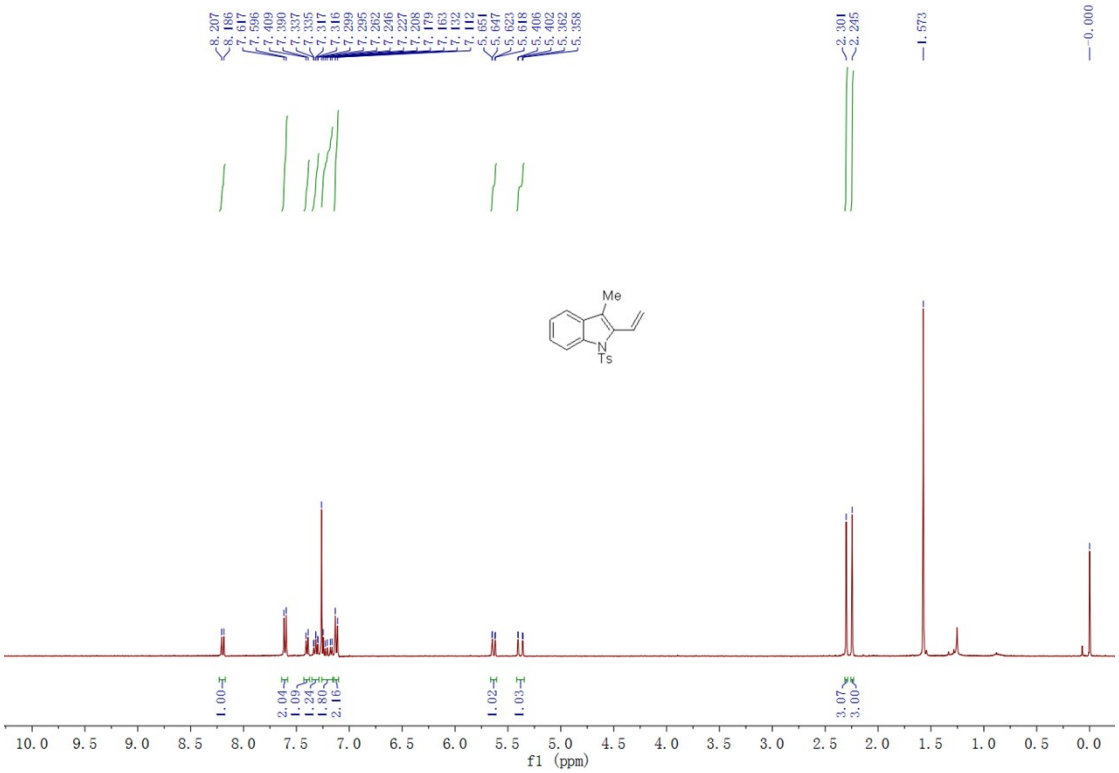




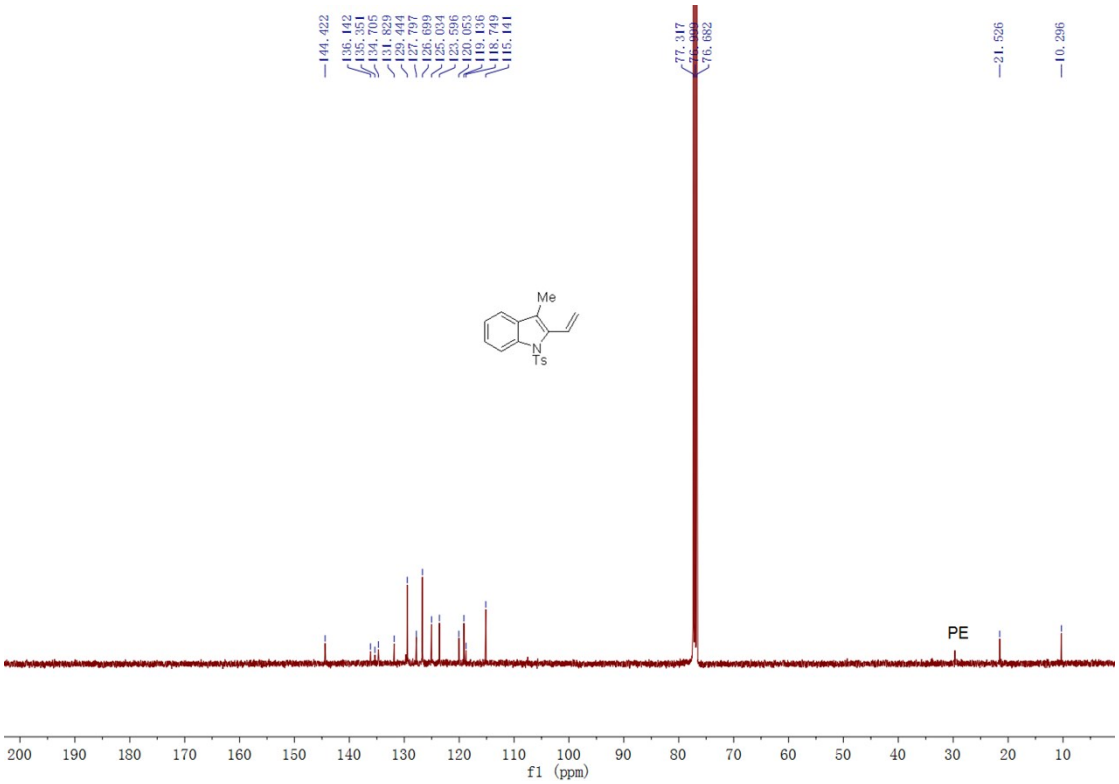
3-methyl-1-tosyl-2-vinyl-1*H*-indole 2p

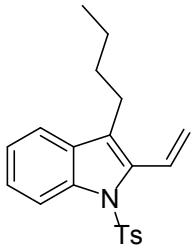
A white solid, 5% yield (3 mg). M.p.: 146-148 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.25 (s, 3H), 2.30 (s, 3H), 5.38 (dd, J = 1.6 Hz, 17.6 Hz, 1H), 5.64 (dd, J = 1.6 Hz, 11.6 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 7.16-7.25 (m, 2H), 7.29-7.34 (m, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H), 8.20 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 10.3, 21.5, 115.1, 118.7, 119.1, 120.1, 123.6, 125.0, 126.7, 127.8, 129.4, 131.8, 134.7, 135.4, 136.1, 144.4. IR (neat) $\bar{\nu}$ 3067, 3042, 2961, 2926, 2856, 1619, 1599, 1491, 1453, 1370, 1305, 1294, 1228, 1204, 1187, 1174, 1142, 1092, 1019, 956, 913, 812, 801, 791, 757, 747, 683, 666 cm^{-1}. HRMS (APCI) Calcd. for $C_{18}H_{18}NO_2S^{+1}(M+H)^+$ requires 312.1053, Found: 312.1048.

^{1}H NMR spectrum of 2p:



^{13}C NMR spectrum of 2p:

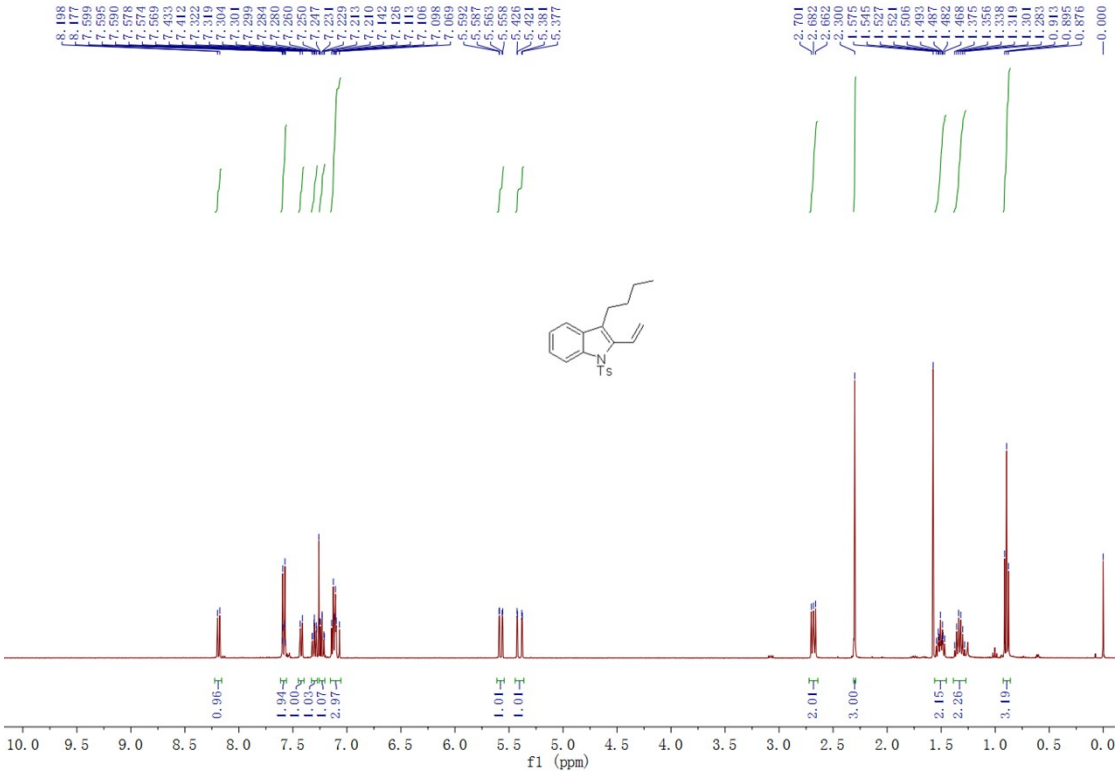




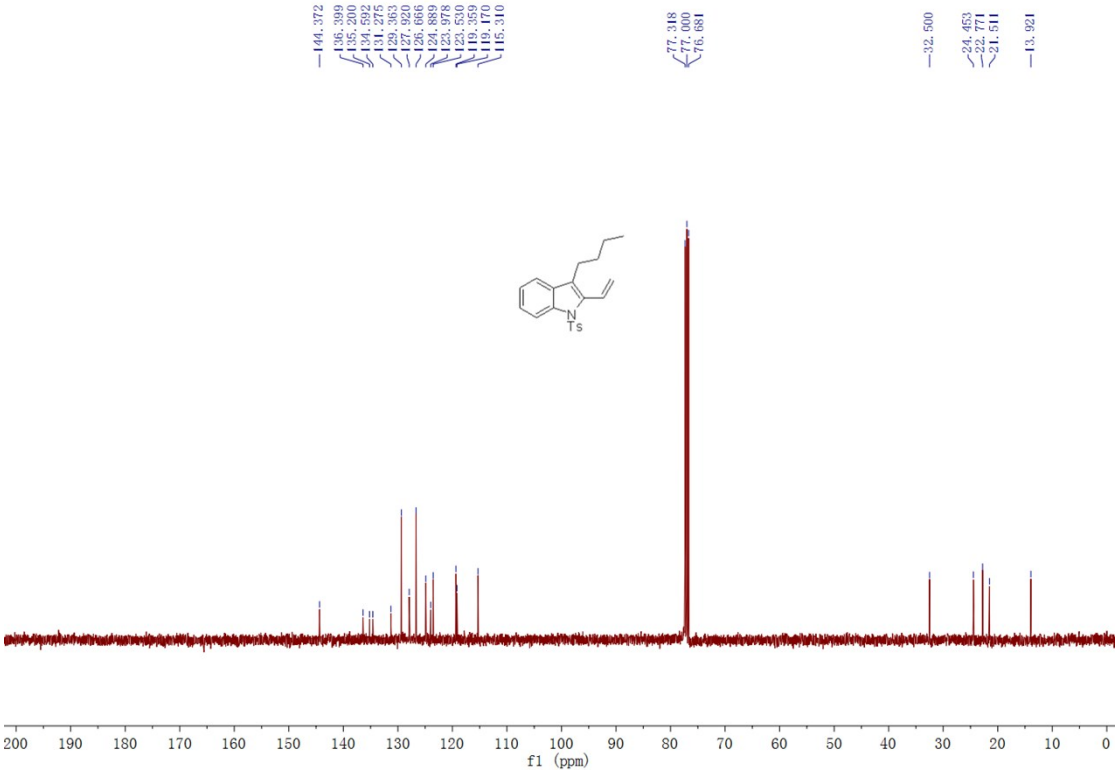
3-butyl-1-tosyl-2-vinyl-1*H*-indole 2q

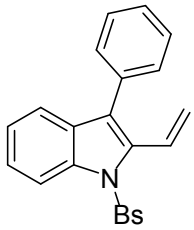
A faint yellow solid, 45% yield (52 mg). M.p.: 85-88 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.90 (t, *J* = 7.6 Hz, 3H), 1.28-1.38 (m, 2H), 1.47-1.55 (m, 2H), 2.30 (s, 3H), 2.68 (t, *J* = 8.0 Hz, 2H), 5.40 (dd, *J* = 1.6 Hz, 17.6 Hz, 1H), 5.58 (dd, *J* = 1.6 Hz, 11.6 Hz, 1H), 7.11 (dd, *J* = 11.6 Hz, 17.6 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.21-7.25 (m, 1H), 7.28-7.33 (m, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.56-7.60 (m, 2H), 8.19 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 21.5, 22.8, 24.5, 32.5, 115.3, 119.2, 119.4, 123.5, 124.0, 124.9, 126.7, 127.9, 129.4, 131.3, 134.6, 135.2, 136.4, 144.4. IR (neat) $\bar{\nu}$ 3067, 3048, 2957, 2928, 2873, 2859, 1621, 1598, 1491, 1452, 1371, 1305, 1231, 1186, 1172, 1150, 1090, 1041, 1019, 986, 972, 934, 812, 748, 704, 666 cm^{-1}. HRMS (APCI) Calcd. for $C_{21}H_{24}NO_2S^{+1}(M+H)^+$ requires: 354.1522, Found: 354.1531.

^{1}H NMR spectrum of 2q:



^{13}C NMR spectrum of 2q:

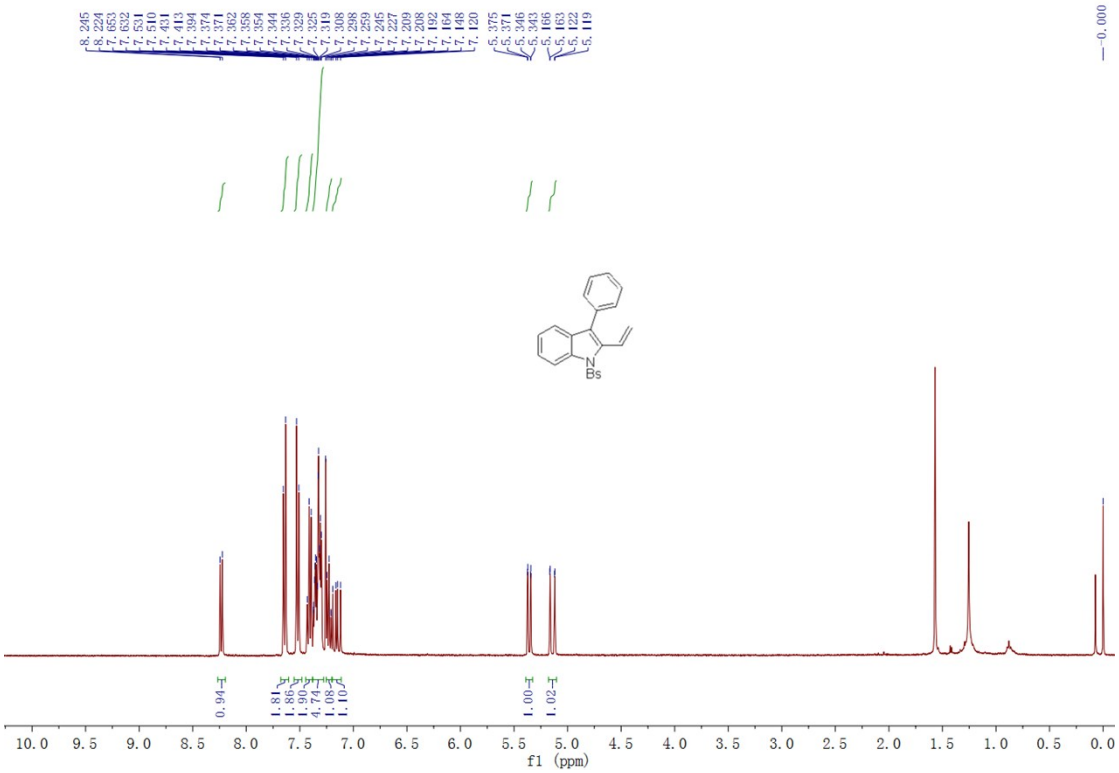




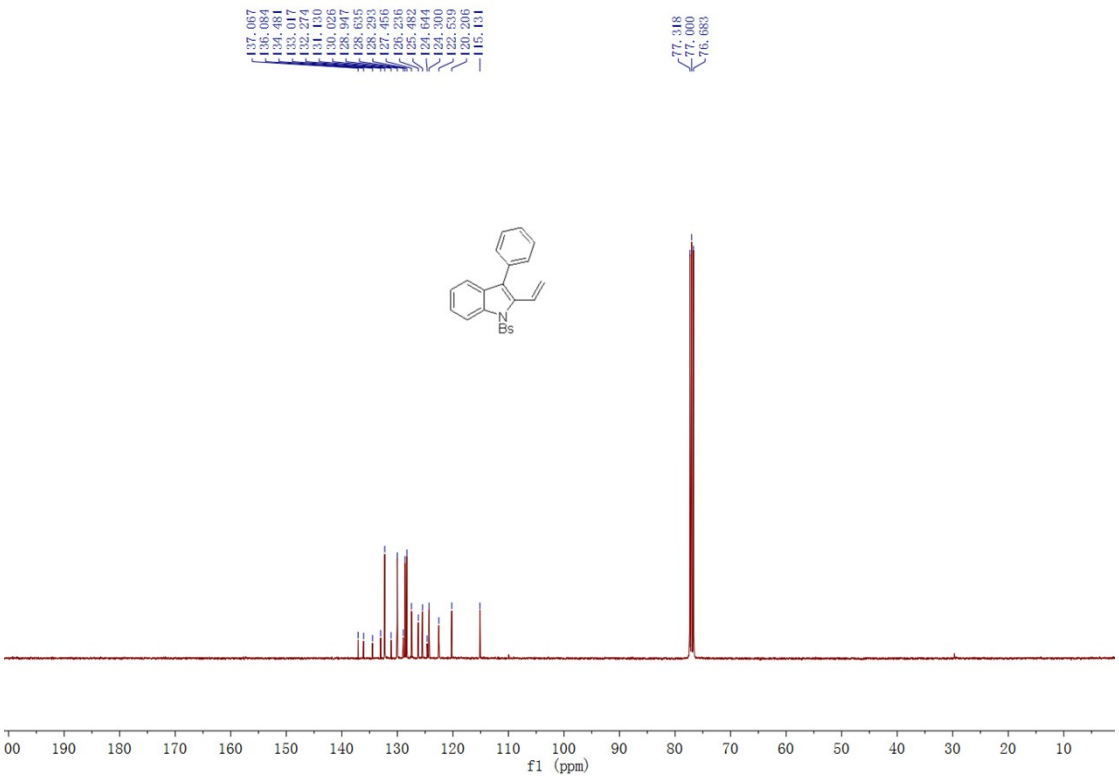
1-((4-bromophenyl)sulfonyl)-3-phenyl-2-vinyl-1H-indole 2r

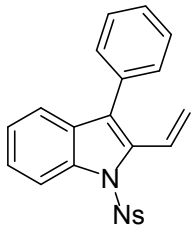
A white solid, 27% yield (36 mg). M.p.: 136-138 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 5.14 (dd, J = 1.2 Hz, 17.6 Hz, 1H), 5.36 (dd, J = 1.2 Hz, 11.2 Hz, 1H), 7.15 (dd, J = 11.2 Hz, 17.6 Hz, 1H), 7.20-7.25 (m, 1H), 7.29-7.38 (m, 5H), 7.39-7.44 (m, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 8.23 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 115.1, 120.2, 122.5, 124.3, 124.6, 125.5, 126.2, 127.5, 128.3, 128.6, 128.9, 130.0, 131.1, 132.3, 133.0, 134.5, 136.1, 137.1. IR (neat) $\bar{\nu}$ 3067, 3054, 3032, 2951, 2925, 2873, 2853, 1574, 1536, 1493, 1472, 1449, 1390, 1377, 1227, 1174, 1148, 1120, 1088, 1070, 1018, 1008, 917, 889, 842, 820, 809, 782, 750, 741, 720, 701, 686, 668, 656 cm^{-1}. HRMS (APCI) Calcd. for $C_{22}H_{17}BrNO_2S^{+1}(M+H)^+$ requires 438.0158, Found: 438.0167.

^{1}H NMR spectrum of 2r:



^{13}C NMR spectrum of 2r:

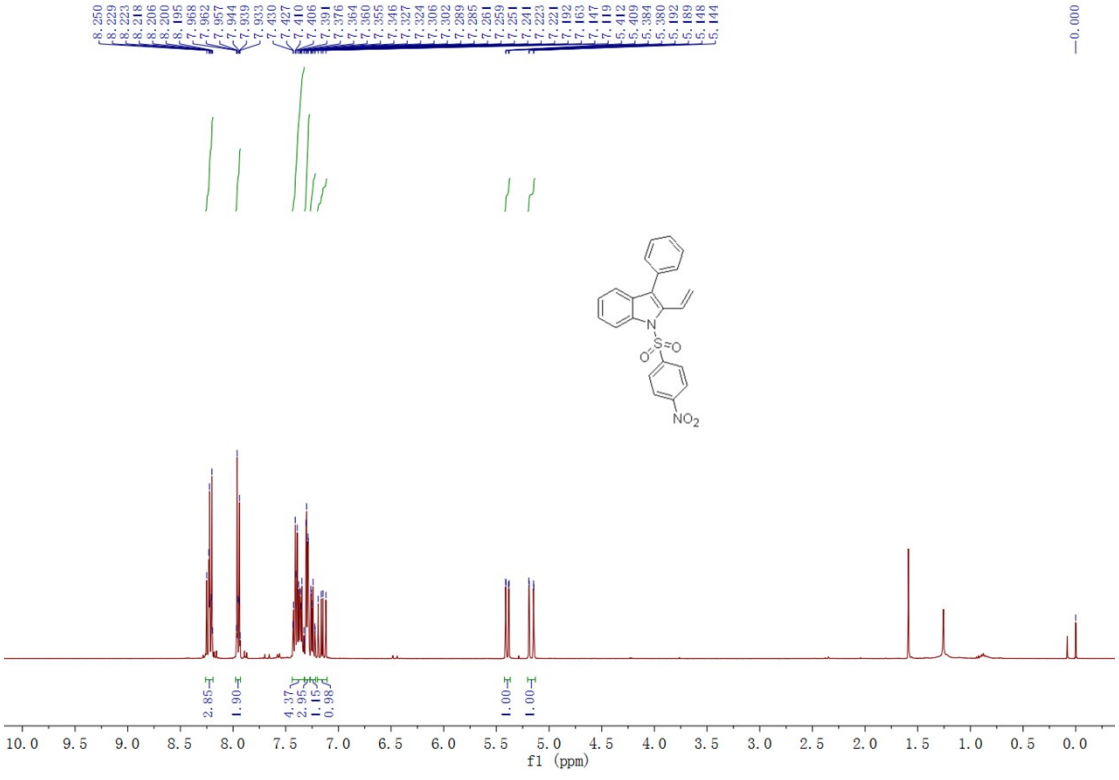




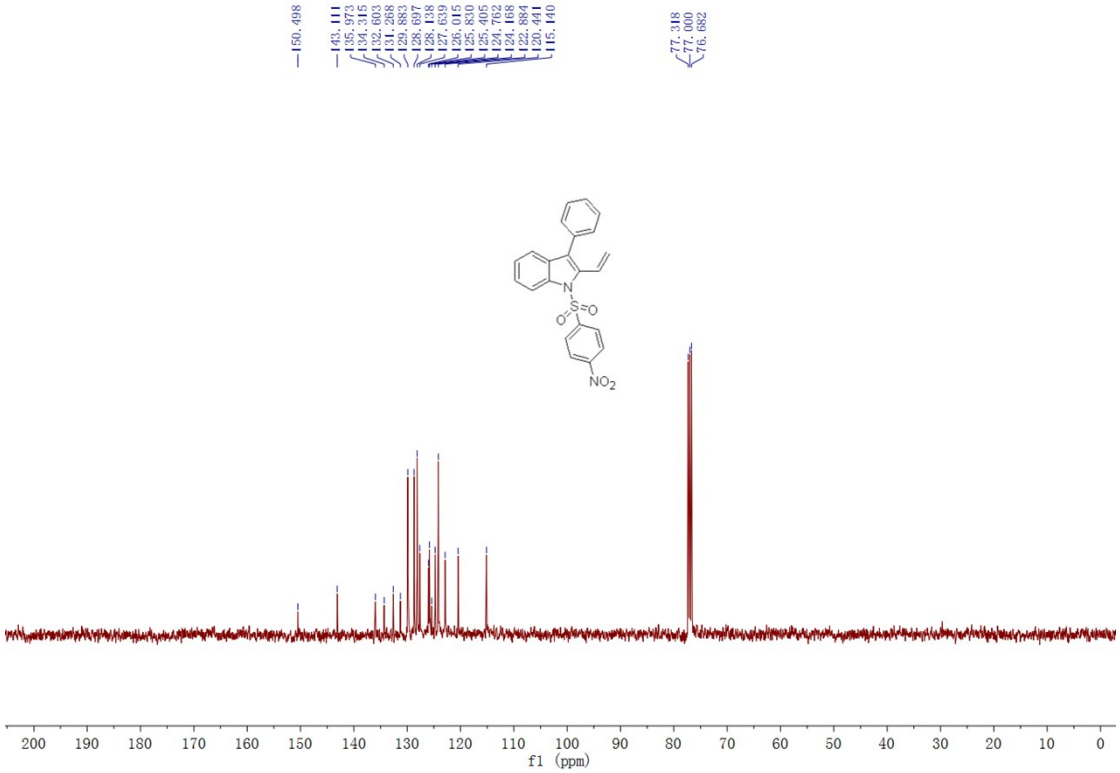
1-((4-nitrophenyl)sulfonyl)-3-phenyl-2-vinyl-1*H*-indole 2s

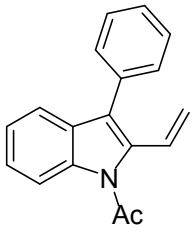
A yellow solid, 61% yield (49 mg). M.p.: 1148-1150 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 5.17 (dd, *J* = 1.6 Hz, 17.6 Hz, 1H), 5.40 (dd, *J* = 1.6 Hz, 11.6 Hz, 1H), 7.16 (dd, *J* = 11.6 Hz, 17.6 Hz, 1H), 7.22-7.27 (m, 1H), 7.28-7.31 (m, 3H), 7.32-7.43 (m, 4H), 7.93-7.97 (m, 2H), 8.19-8.25 (m, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 115.1, 120.4, 122.9, 124.2, 124.8, 125.4, 125.8, 126.0, 127.6, 128.1, 128.7, 129.9, 131.3, 132.6, 134.3, 136.0, 143.1, 150.5. IR (neat) $\bar{\nu}$ 3109, 3070, 3029, 2959, 2920, 2870, 2845, 1624, 1605, 1529, 1449, 1379, 1350, 1310, 1299, 1224, 1185, 1170, 1146, 1086, 1018, 1010, 994, 934, 851, 784, 775, 754, 739, 703, 683 cm^{-1}. HRMS (APCI) Calcd. for $C_{22}H_{17}N_2O_4S^{+1}$(M+H)$^+$ requires 405.0904, Found: 405.0912.

^{1}H NMR spectrum of 2s:



^{13}C NMR spectrum of 2s:

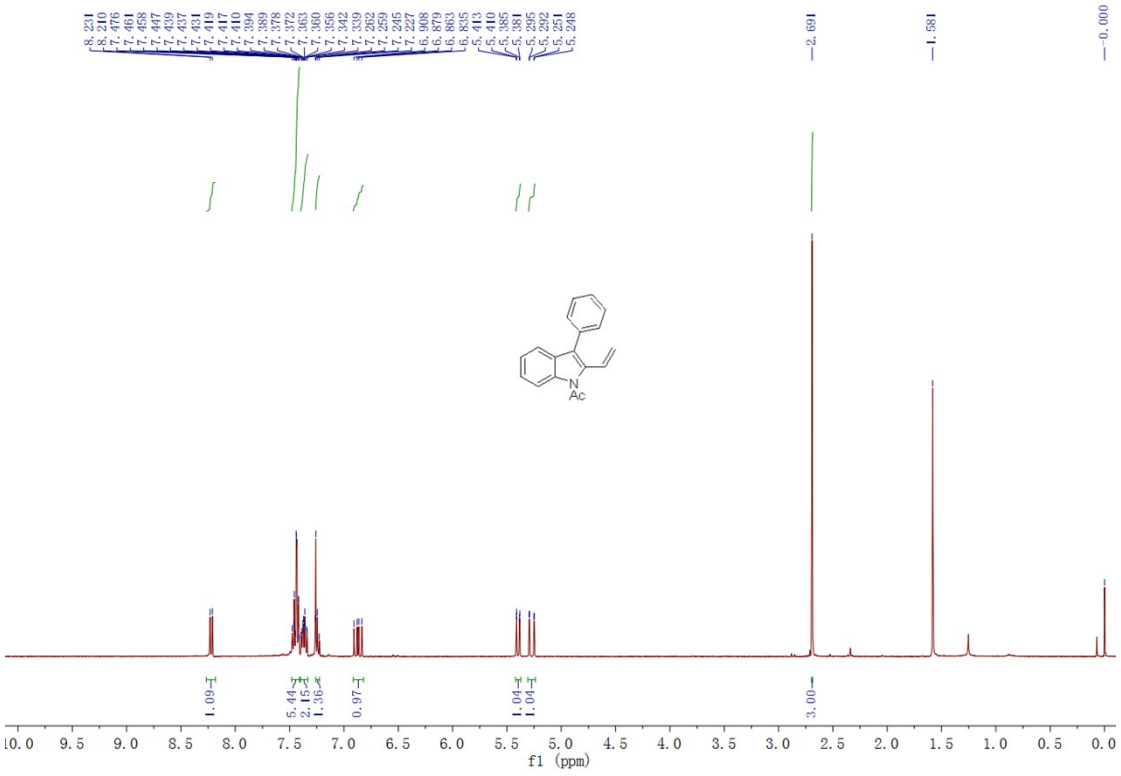




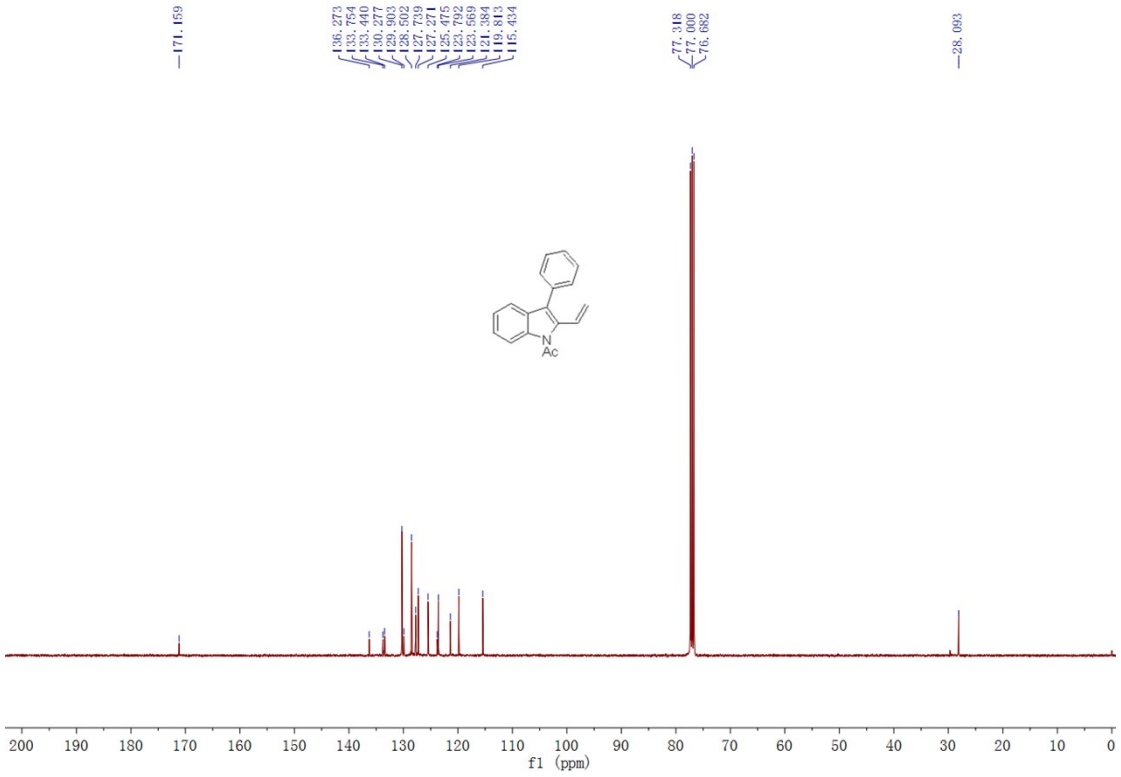
1-(3-phenyl-2-vinyl-1H-indol-1-yl)ethan-1-one 2t

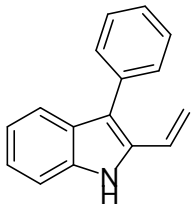
A faint yellow solid, 46% yield (25 mg). M.p.: 159-161 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.69 (s, 3H), 5.27 (dd, J = 1.2 Hz, 17.6 Hz, 1H), 5.40 (dd, J = 1.2 Hz, 11.6 Hz, 1H), 6.87 (dd, J = 11.6 Hz, 17.6 Hz, 1H), 7.22-7.26 (m, 1H), 7.33-7.40 (m, 2H), 7.41-7.48 (m, 5H), 8.22 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 28.1, 115.4, 119.8, 121.4, 123.6, 123.8, 125.5, 127.3, 127.7, 128.5, 129.9, 130.3, 133.4, 133.8, 136.3, 171.2. IR (neat) $\bar{\nu}$ 3053, 3026, 2959, 2926, 2854, 1749, 1702, 1621, 1604, 1450, 1416, 1369, 1345, 1305, 1222, 1206, 1180, 1149, 1078, 1025, 1003, 937, 919, 773, 749, 702, 673 cm^{-1}. HRMS (APCI) Calcd. for $C_{18}H_{16}NO^{+1}(M+H)^{+}$ requires 262.1226, Found: 262.1236.

^{1}H NMR spectrum of 2t:



^{13}C NMR spectrum of 2t:

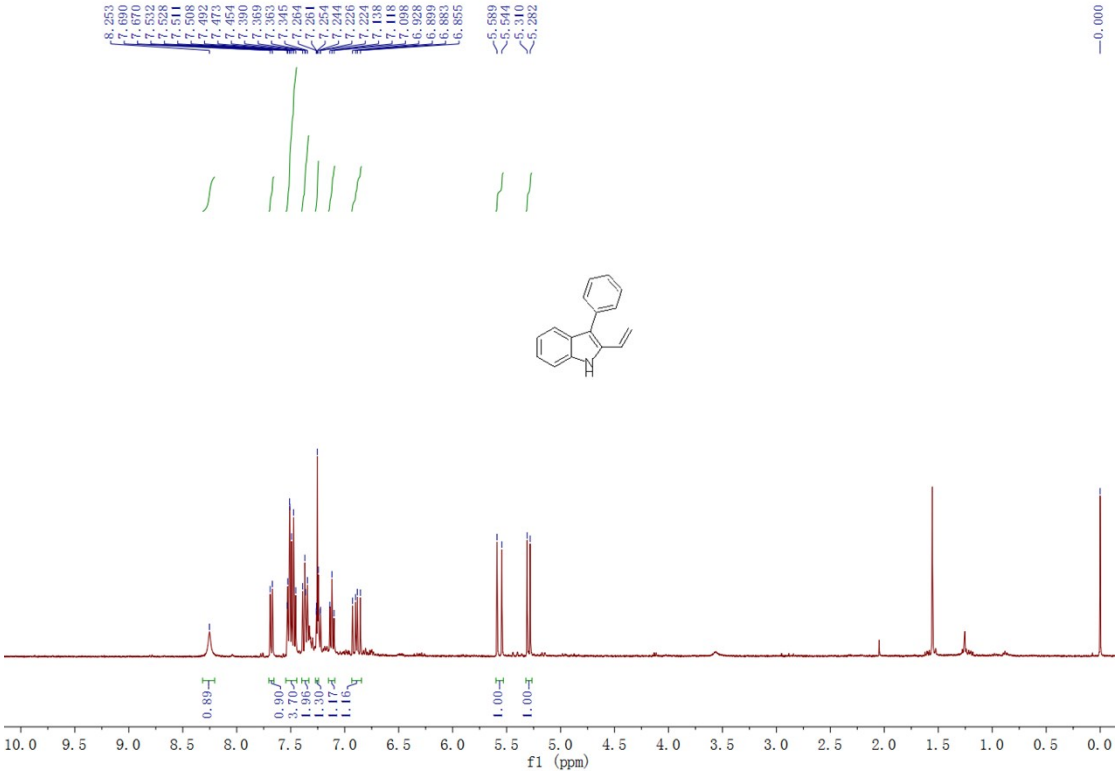




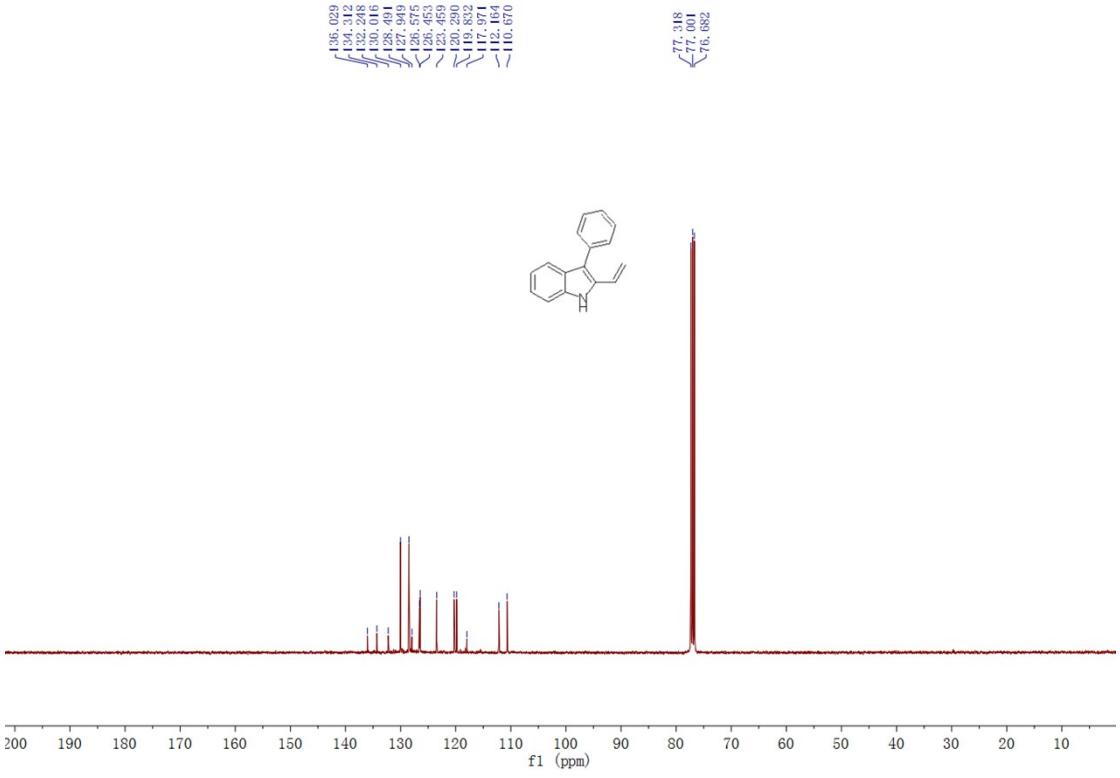
3-phenyl-2-vinyl-1*H*-indole 2u

A yellow solid, 31% yield (20 mg). M.p.: 125-127 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 5.30 (d, J = 11.2 Hz, 1H), 5.57 (d, J = 18.0 Hz, 1H), 6.89 (dd, J = 11.2 Hz, 18.0 Hz, 1H), 7.09-7.14 (m, 1H), 7.22-7.27 (m, 1H), 7.34-7.39 (m, 2H), 7.45-7.54 (m, 4H), 7.68 (d, J = 8.0 Hz, 1H), 8.25 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 110.7, 112.2, 118.0, 119.8, 120.3, 123.5, 126.5, 126.6, 127.9, 128.5, 130.0, 132.2, 134.3, 136.0. IR (neat) $\bar{\nu}$ 3409, 3281, 3081, 3054, 3026, 2967, 2920, 1640, 1602, 1492, 1456, 1445, 1320, 1247, 1186, 1075, 1045, 1016, 902, 878, 773, 745, 700 cm^{-1}. HRMS (APCI) Calcd. for $C_{16}H_{14}N^{+1}(M+H)^+$ requires 220.1121, Found: 220.1118.

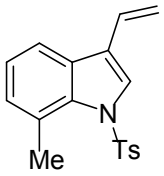
^{1}H NMR spectrum of 2u:



^{13}C NMR spectrum of 2u:



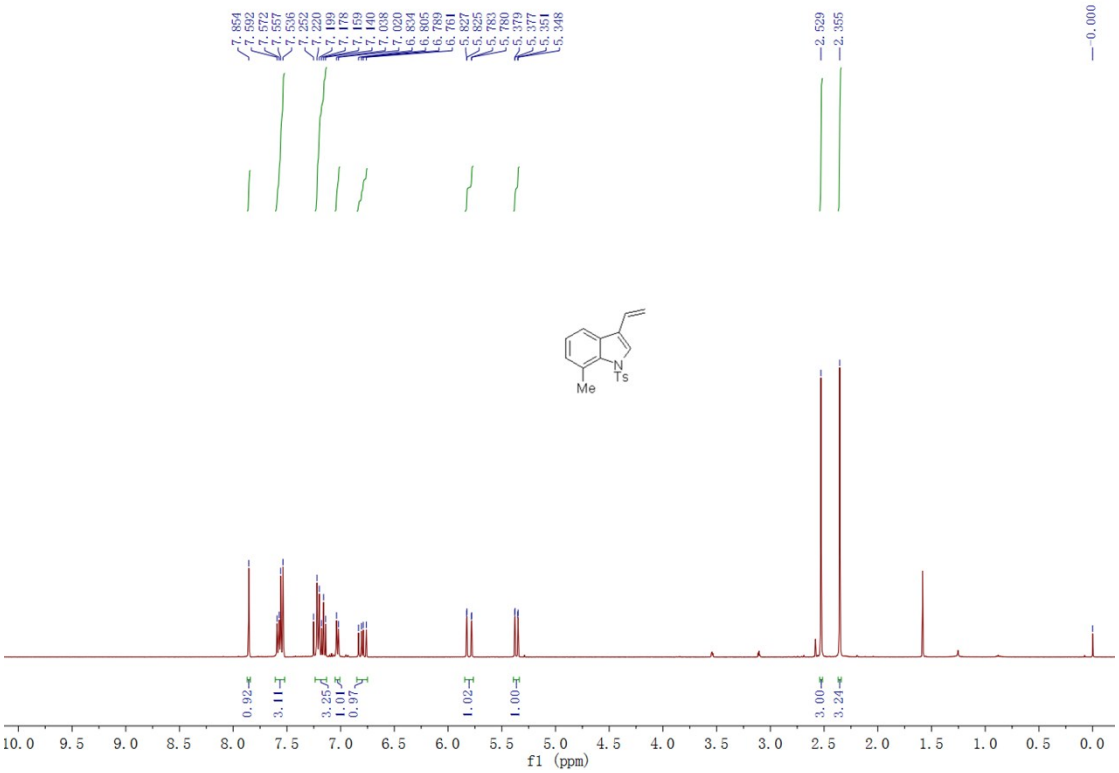
Characterization and spectra charts for 4



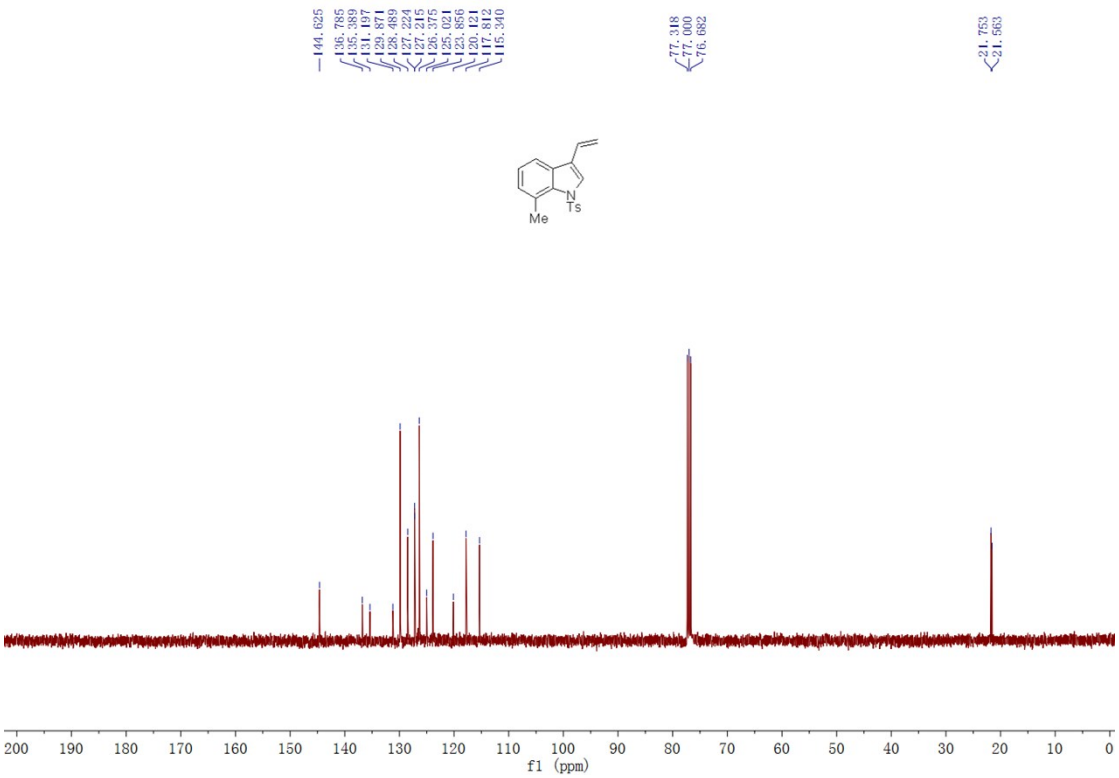
7-methyl-1-tosyl-3-vinyl-1*H*-indole 4b

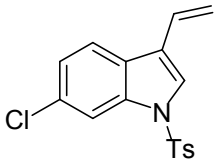
A faint yellow solid, 51% yield (48 mg). M.p.: 88-90 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.36 (s, 3H), 2.53 (s, 3H), 5.36 (dd, J = 1.2 Hz, 11.6 Hz, 1H), 5.80 (dd, J = 1.2 Hz, 17.6 Hz, 1H), 6.80 (dd, J = 11.6 Hz, 17.6 Hz, 1H), 7.03 (d, J = 7.2 Hz, 1H), 7.14-7.22 (m, 3H), 7.53-7.60 (m, 3H), 7.85 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 21.8, 115.3, 117.8, 120.1, 123.9, 125.0, 126.4, 127.21, 127.23, 128.5, 129.9, 131.2, 135.4, 136.8, 144.6. IR (neat) $\bar{\nu}$ 3134, 3090, 3065, 3048, 2970, 2926, 2870, 2854, 1763, 1721, 1682, 1641, 1596, 1491, 1457, 1359, 1272, 1213, 1188, 1171, 1123, 1087, 1038, 1019, 979, 888, 812, 786, 746, 703, 669 cm^{-1}. HRMS (APCI) Calcd. for $C_{18}H_{18}NO_2S^{+1}(M+H)^+$ requires 312.1053, Found: 312.1052.

^{1}H NMR spectrum of 4b:



^{13}C NMR spectrum of 4b:

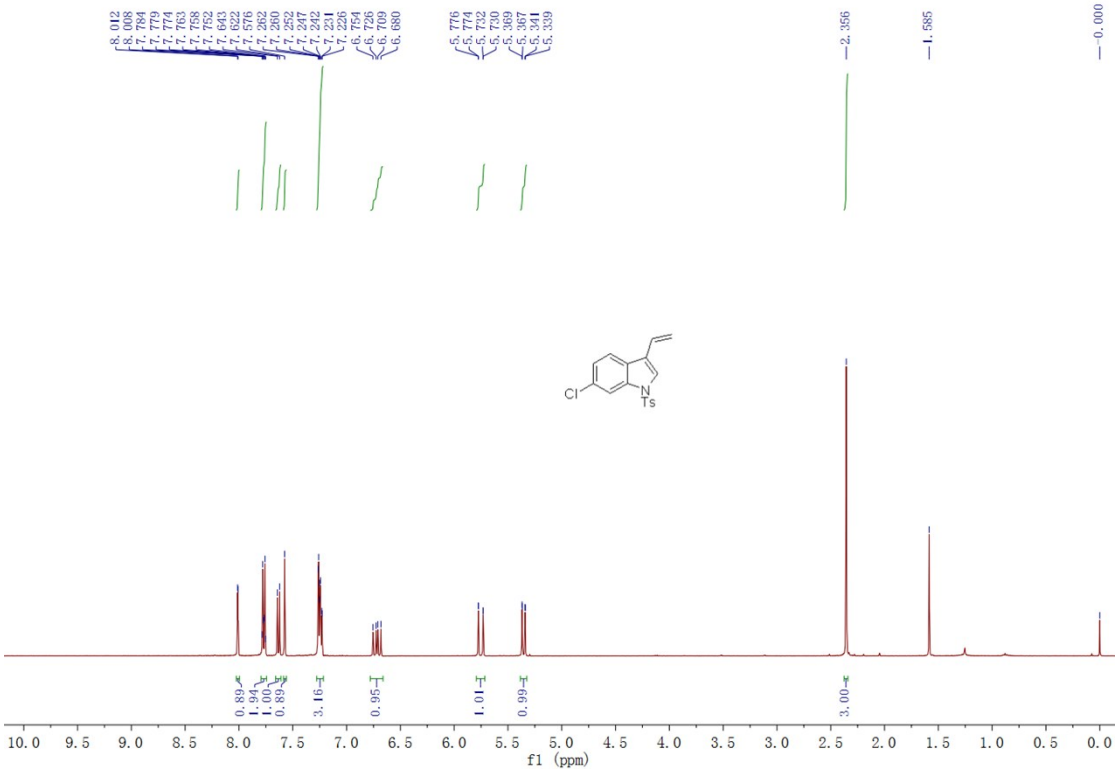




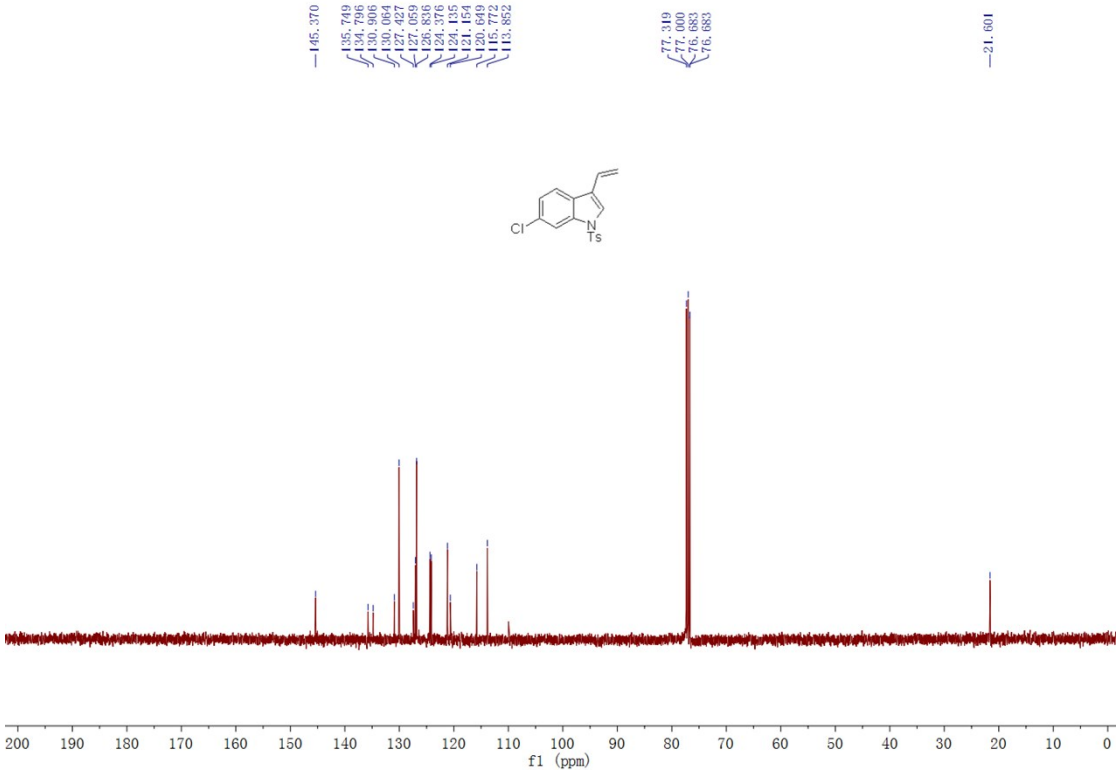
6-chloro-1-tosyl-3-vinyl-1*H*-indole 4c

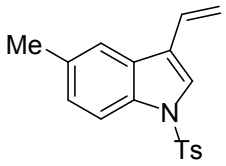
A white solid, 46% yield (46 mg). M.p.: 137-140 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.36 (s, 3H), 5.35 (dd, *J* = 1.2 Hz, 11.2 Hz, 1H), 5.75 (dd, *J* = 1.2 Hz, 17.6 Hz, 1H), 6.72 (dd, *J* = 11.2 Hz, 17.6 Hz, 1H), 7.22-7.27 (m, 3H), 7.58 (s, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.75-7.79 (m, 2H), 8.01 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 113.9, 115.8, 120.6, 121.2, 124.1, 124.4, 126.8, 127.1, 127.4, 130.1, 130.9, 134.8, 135.7, 145.4. IR (neat) $\bar{\nu}$ 3054, 3026, 2940, 2856, 1598, 1460, 1424, 1375, 1272, 1213, 1189, 1173, 1141, 1089, 1024, 970, 811, 669 cm^{-1}. HRMS (APCI) Calcd. for $C_{17}H_{15}ClNO_2S^{+1}(M+H)^+$ requires 332.0507, Found: 332.0503.

^{1}H NMR spectrum of 4c:



^{13}C NMR spectrum of 4c:

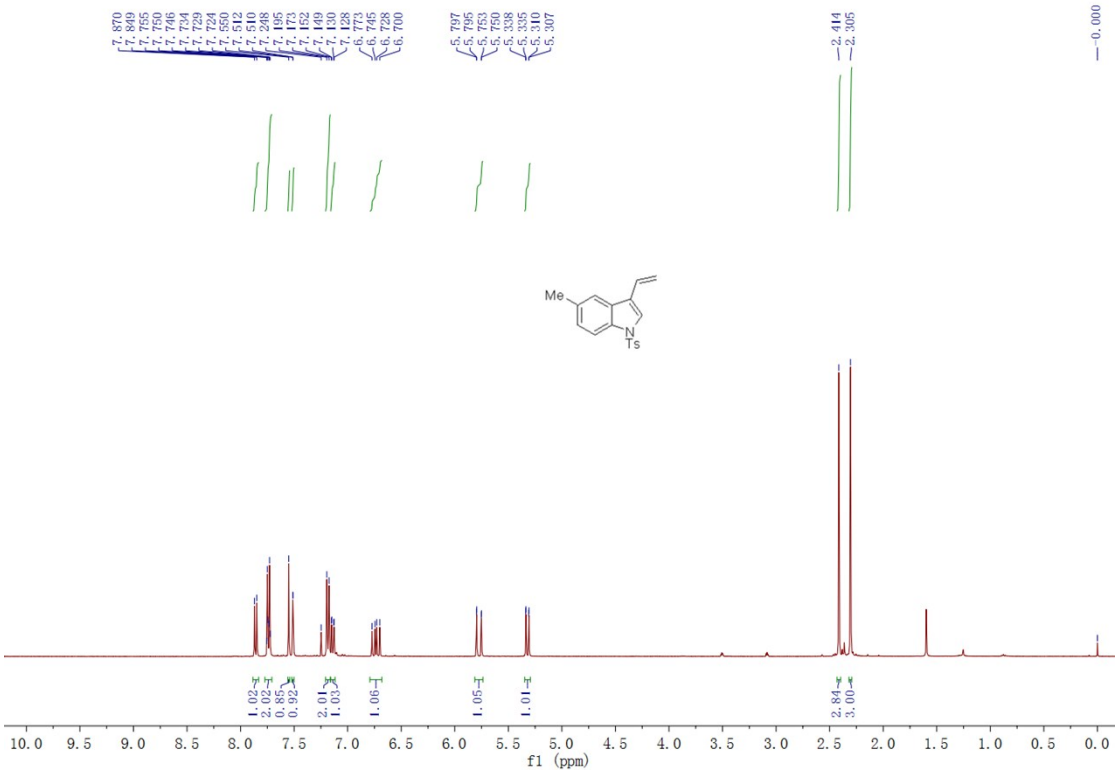




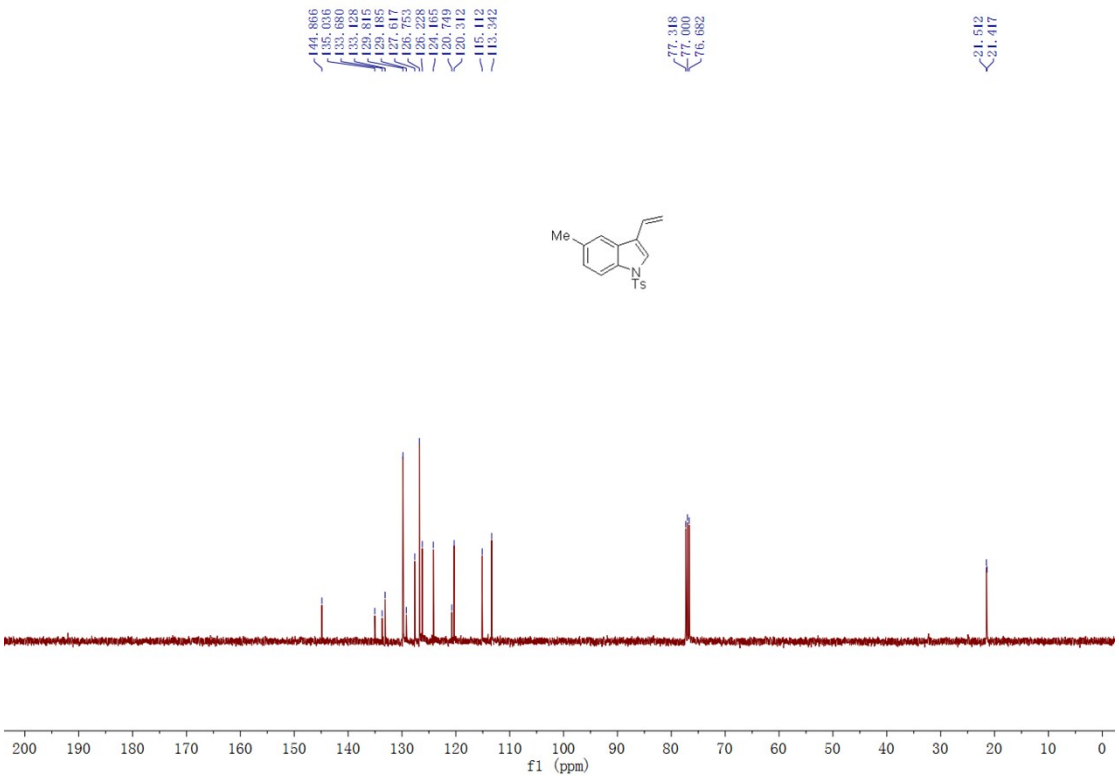
5-methyl-1-tosyl-3-vinyl-1*H*-indole 4e

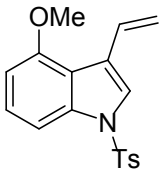
A yellow solid, 58% yield (54 mg). M.p.: 83-85 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.31 (s, 3H), 2.41 (s, 3H), 5.32 (dd, J = 1.2 Hz, 11.2 Hz, 1H), 5.77 (dd, J = 1.2 Hz, 17.6 Hz, 1H), 6.74 (dd, J = 11.2 Hz, 17.6 Hz, 1H), 7.14 (dd, J = 0.8 Hz, 8.4 Hz, 1H), 7.18 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 0.8 Hz, 1H), 7.55 (s, 1H), 7.72-7.76 (m, 2H), 7.86 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.4, 21.5, 113.3, 115.1, 120.3, 120.7, 124.2, 126.2, 126.8, 127.6, 129.2, 129.8, 133.1, 133.7, 135.0, 144.9. IR (neat) $\bar{\nu}$ 3123, 3070, 3034, 2923, 2859, 1752, 1718, 1680, 1635, 1596, 1544, 1469, 1453, 1369, 1292, 1268, 1188, 1171, 1152, 1124, 1092, 1022, 975, 866, 801, 703, 667 cm^{-1}. HRMS (APCI) Calcd. for $C_{18}H_{18}NO_2S^{+1}(M+H)^+$ requires 312.1053, Found: 312.1057.

^{1}H NMR spectrum of 4e:



^{13}C NMR spectrum of 4e:

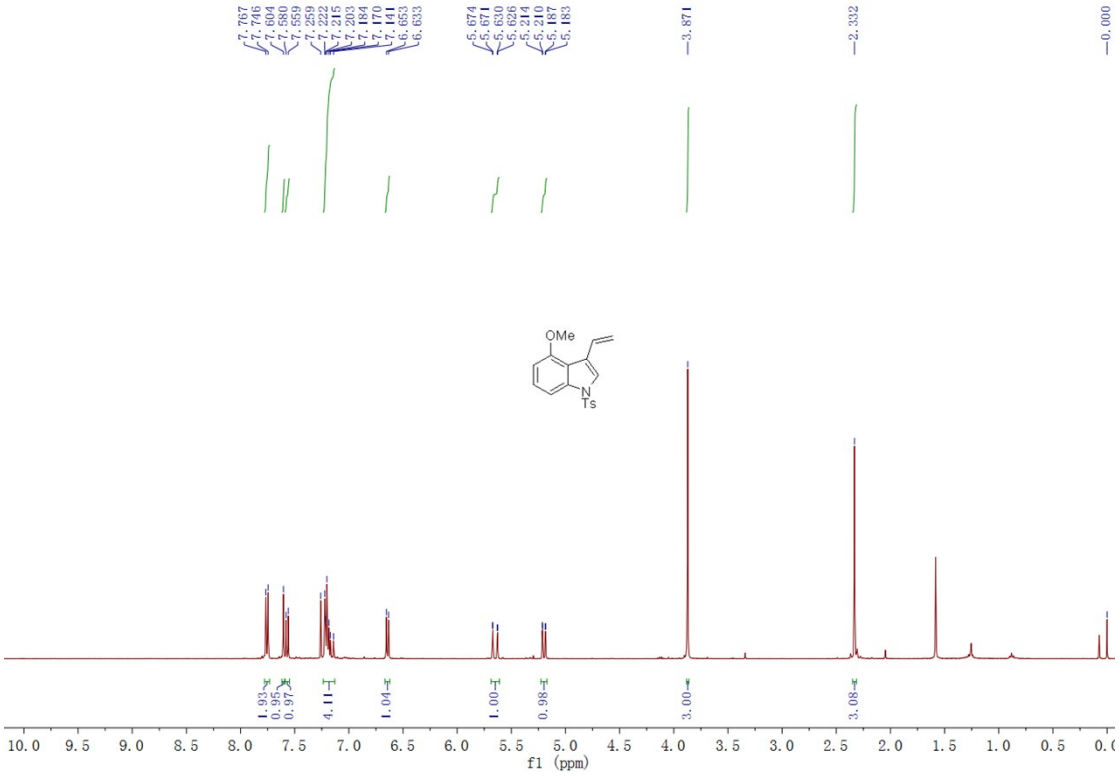




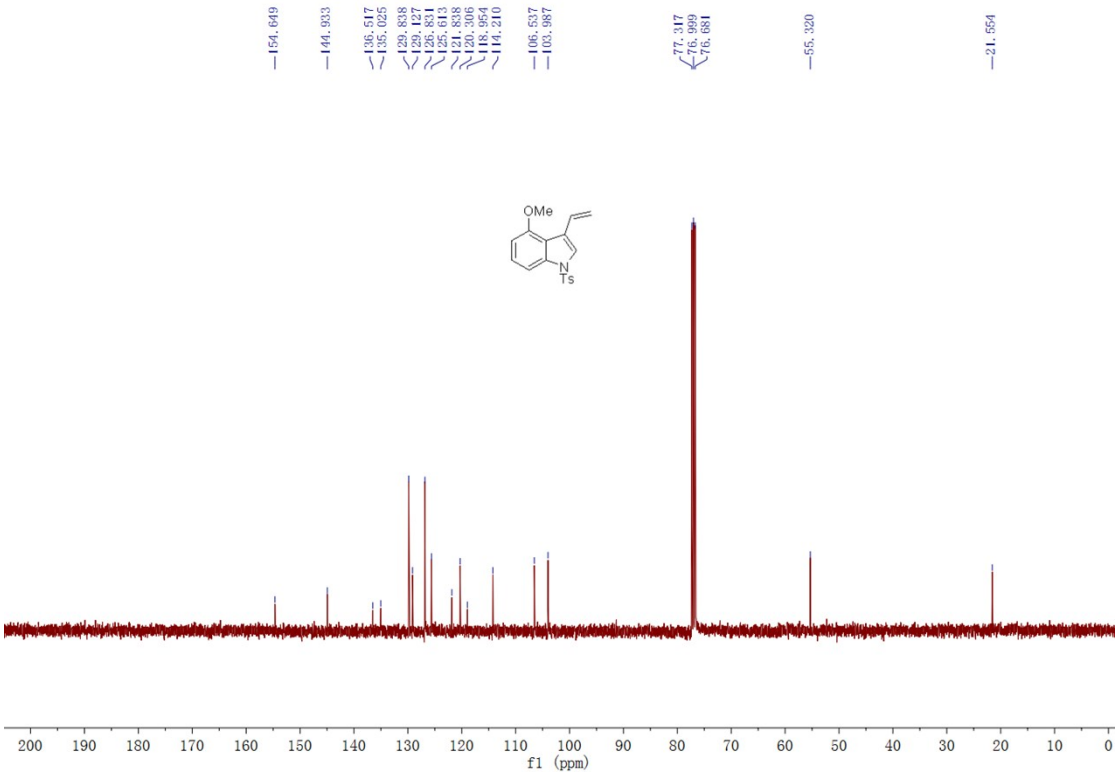
4-methoxy-1-tosyl-3-vinyl-1*H*-indole 4f

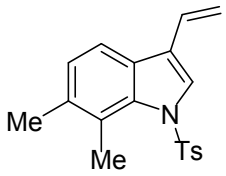
A faint yellow solid, 40% yield (39 mg). M.p.: 84-87 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.33 (s, 3H), 3.87 (s, 3H), 5.20 (dd, J = 1.6 Hz, 10.8 Hz, 1H), 5.65 (dd, J = 1.6 Hz, 17.6 Hz, 1H), 6.64 (d, J = 8.0 Hz, 1H), 7.14-7.23 (m, 4H), 7.57 (d, J = 8.4 Hz, 1H), 7.60 (s, 1H), 7.74-7.78 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 21.6, 55.3, 104.0, 106.5, 114.2, 119.0, 120.3, 121.8, 125.6, 126.8, 129.1, 129.8, 135.0, 136.5, 144.9, 154.6. IR (neat) $\bar{\nu}$ 2962, 2942, 2923, 2837, 1596, 1557, 1492, 1460, 1427, 1366, 1266, 1251, 1189, 1177, 1106, 1038, 991, 911, 889, 877, 813, 784, 745, 703, 667 cm^{-1}. HRMS (APCI) Calcd. for $C_{18}H_{18}NO_3S^{+1}(M+H)^+$ requires 328.1002, Found: 328.1005.

^{1}H NMR spectrum of 4f:



^{13}C NMR spectrum of 4f:

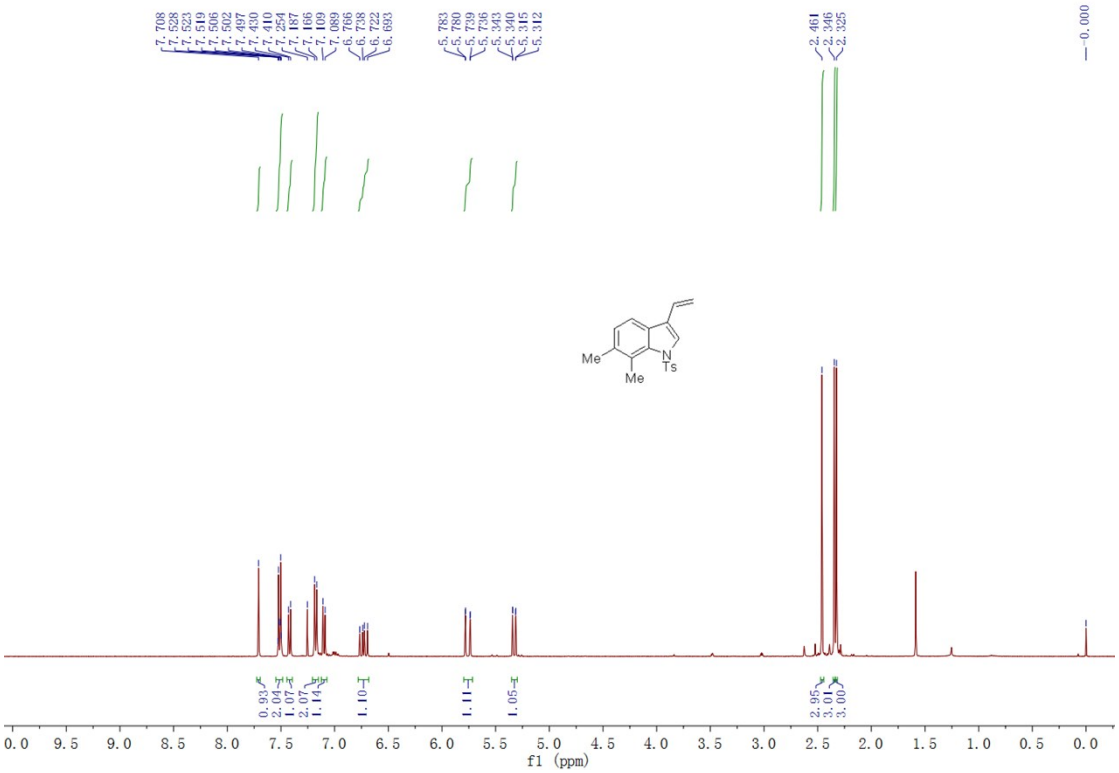




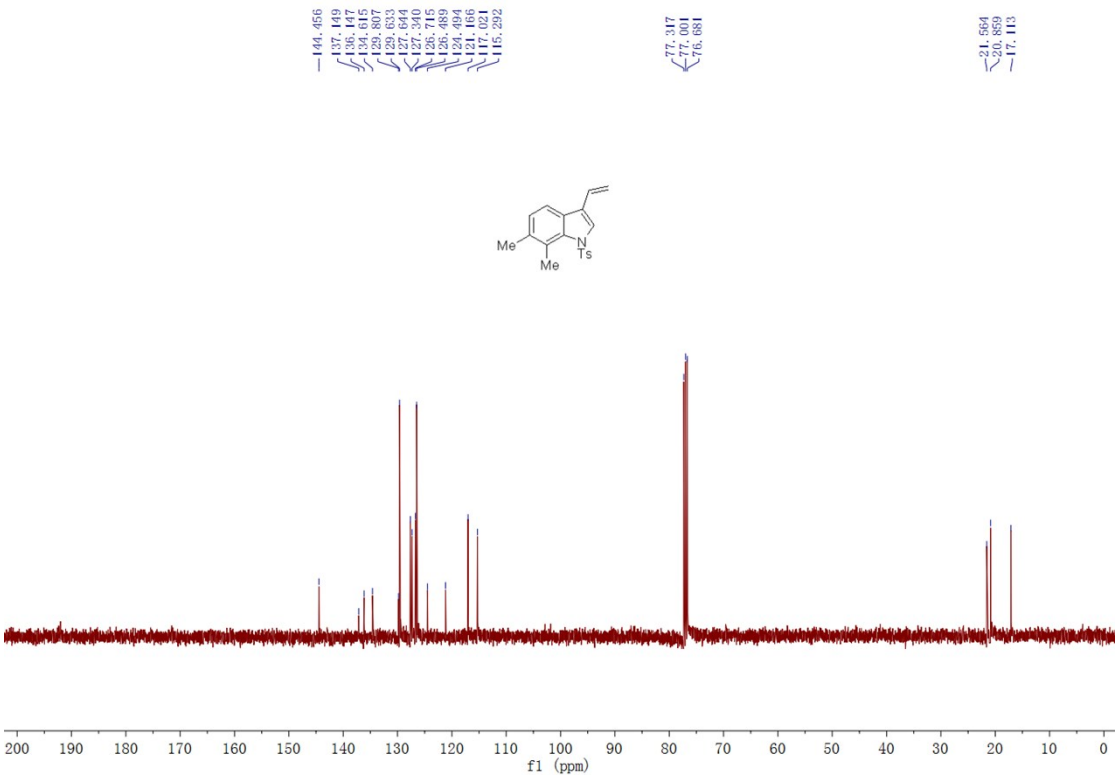
6,7-dimethyl-1-tosyl-3-vinyl-1*H*-indole 4g

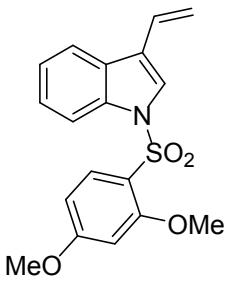
An orange solid, 42% yield (39 mg). M.p.: 159-161 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.33 (s, 3H), 2.35 (s, 3H), 2.46 (s, 3H), 5.33 (dd, *J* = 1.2 Hz, 11.2 Hz, 1H), 5.76 (dd, *J* = 1.2 Hz, 17.6 Hz, 1H), 6.73 (dd, *J* = 11.2 Hz, 17.6 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.49-7.53 (m, 2H), 7.71 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 17.1, 20.9, 21.6, 115.3, 117.0, 121.2, 124.5, 126.5, 126.7, 127.3, 127.6, 129.6, 129.8, 134.6, 136.1, 137.1, 144.5. IR (neat) $\bar{\nu}$ 2954, 2924, 2856, 1760, 1724, 1680, 1638, 1596, 1450, 1358, 1188, 1168, 1090, 1070, 1017, 987, 888, 811, 703, 673 cm^{-1}. HRMS (APCI) Calcd. for $C_{19}H_{20}NO_2S^{+1}(M+H)^+$ requires 326.1209, Found: 326.1216.

^{1}H NMR spectrum of 4g:



^{13}C NMR spectrum of 4g:

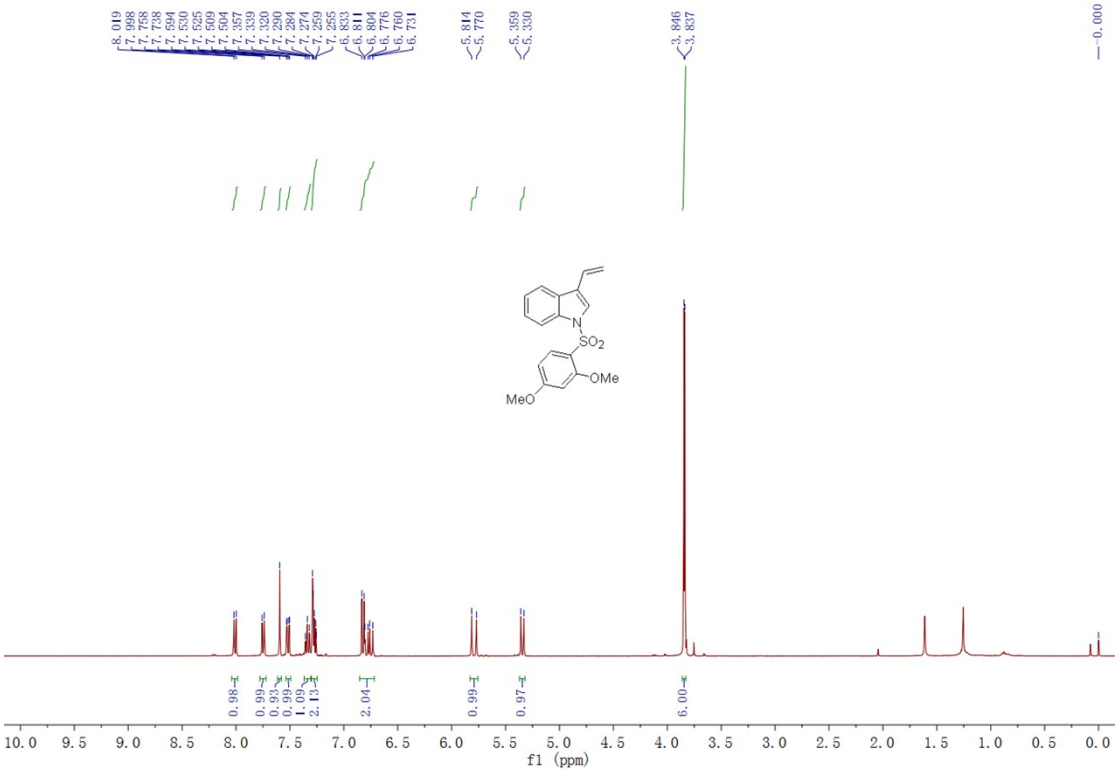




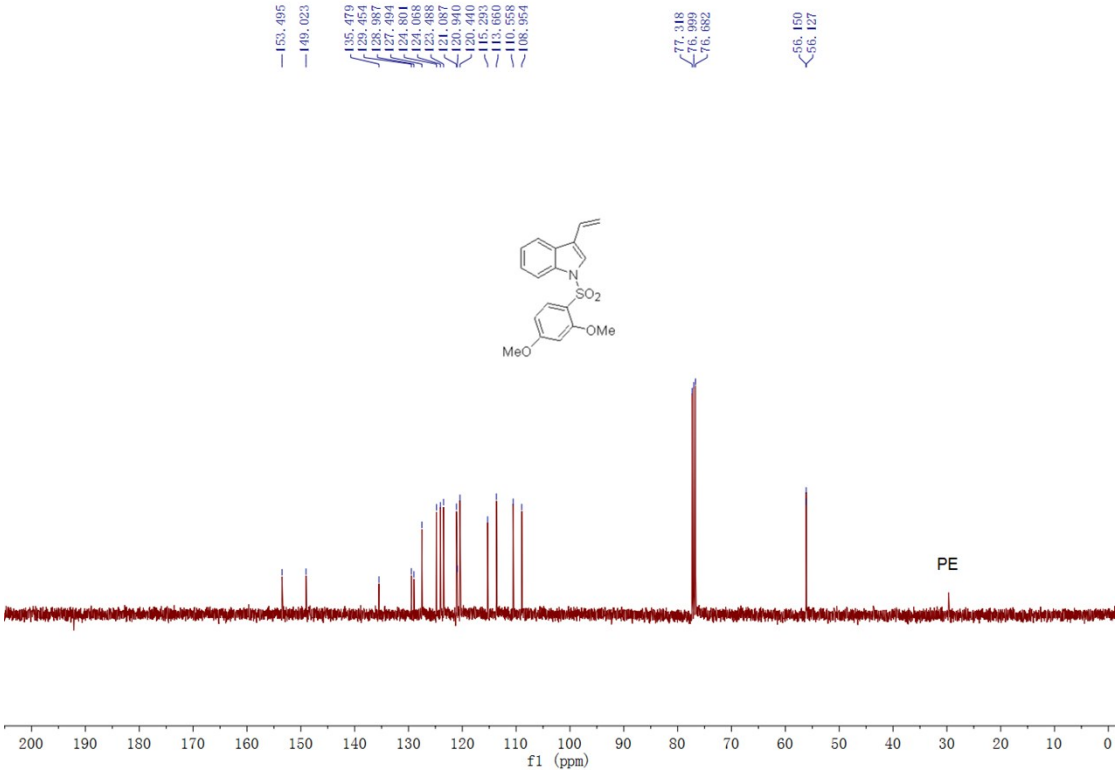
1-((2,4-dimethoxyphenyl)sulfonyl)-3-vinyl-1*H*-indole 4i

A white solid, 48% yield (34 mg). M.p.: 150-152 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 3.84 (s, 3H), 3.85 (s, 3H), 5.34 (d, J = 11.6 Hz, 1H), 5.79 (d, J = 17.6 Hz, 1H), 6.77 (dd, J = 11.6 Hz, 17.6 Hz, 1H), 6.82 (d, J = 8.8 Hz, 1H), 7.25-7.29 (m, 2H), 7.32-7.36 (m, 1H), 7.52 (dd, J = 2.0 Hz, 8.4 Hz, 1H), 7.59 (s, 1H), 7.75 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.4 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 56.1, 56.2, 109.0, 110.6, 113.7, 115.3, 120.4, 120.9, 121.1, 123.5, 124.1, 124.8, 127.5, 129.0, 129.5, 135.5, 149.0, 153.5. IR (neat) $\bar{\nu}$ 3123, 3084, 3009, 2956, 2924, 2854, 1730, 1716, 1632, 1586, 1509, 1463, 1446, 1407, 1371, 1264, 1240, 1216, 1185, 1168, 1141, 1123, 1092, 1019, 962, 891, 850, 808, 765, 747, 670 cm^{-1}. HRMS (APCI) Calcd. for $C_{18}H_{18}NO_4S^{+1}(M+H)^+$ requires 344.0951, Found: 344.0945.

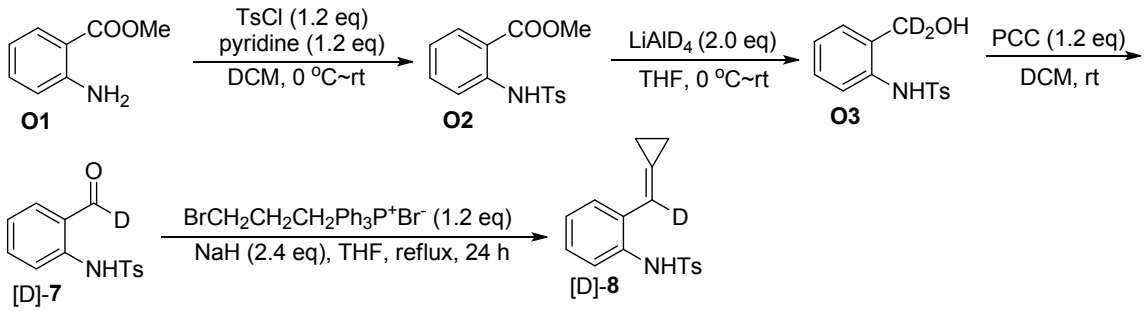
^{1}H NMR spectrum of 4i:



^{13}C NMR spectrum of 4i:



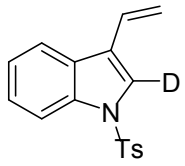
8. General procedure for synthesis of 5 and its and spectra chart



To a solution of **O1** (10.0mmol) and pyridine (1.0 mL, 12.0 mmol) in DCM (30 mL) was added a solution of *p*-TsCl (2.3 g, 12.0 mmol) in DCM (10 mL), and the mixture was stirred at rt for 3 hours. Upon completion monitored by TLC, 10 mL of saturated sodium bicarbonate was added to the reaction mixture. The aqueous phase was extracted with CH_2Cl_2 (3×15 mL), and the combined organic phases were washed with H_2O (1 × 20 mL), and brine (1 × 20 mL) respectively. The organic phase was separated and dried over anhydrous Na_2SO_4. The residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the product **O2** in 96% yield as a white solid.

To a solution of **O2** (2 mmol, 1.0 eq) in dry THF was added dropwise into a solution of $LiAlD_4$ (4 mmol, 2.0 eq) in THF while the temperature was maintained at 0 °C. The resulting mixture was allowed to warm to room temperature and was stirred for 2 hours. Then the mixture was hydrolyzed by addition of H_2O (2.5 mL) and 5% NaOH (7.5 mL). The resulting suspension was filtered, and the precipitate was washed with ethyl acetate. Next, the combined organic collection was evaporated. After concentration, the resulting solid was added to a suspension of PCC (2.4 mmol, 1.2 eq) in DCM (20 mL). After being stirred at rt for 2 h, the mixture was filtered and concentrated. The residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 8 / 1) to afford the product **O3** in 57% yield as a white solid.

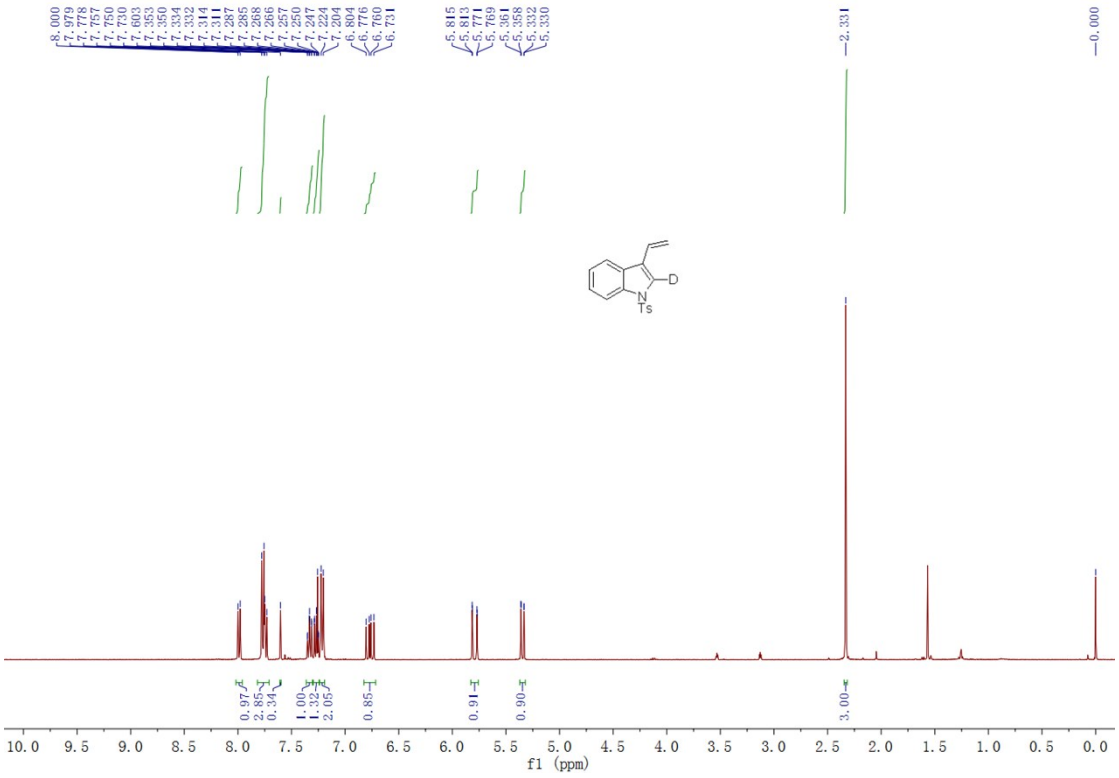
A solution of 3-bromopropyltriphenylphosphonium bromide (2.63 mmol, 3.0 eq), NaH (2.63 mmol, 3.0 eq) and [D]-**7** (0.88 mmol, 1.0 eq) in THF (8 mL) was stirred at 70 °C for 12 h. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 20 / 1) to afford the product [D]-**8** in 65% yield as a white solid.



Compound 8

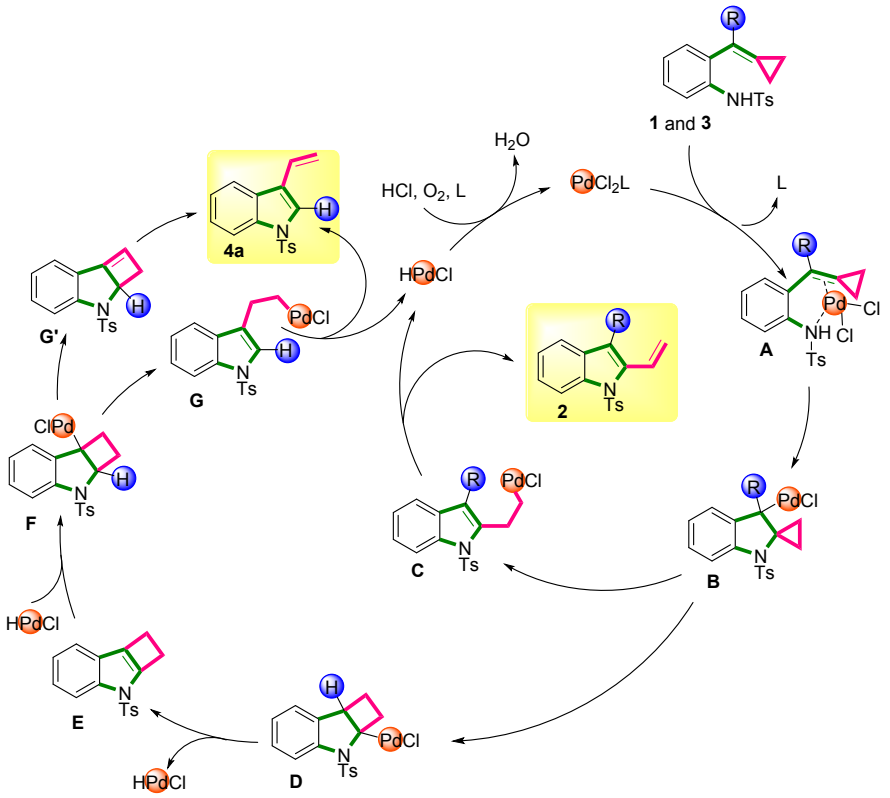
^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.33 (s, 3H), 5.35 (dd, *J* = 0.8 Hz, 11.2 Hz, 1H), 5.79 (dd, *J* = 0.8 Hz, 17.6 Hz, 1H), 6.77 (dd, *J* = 11.2 Hz, 17.6 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.24-7.29 (m, 1H), 7.31-7.36 (m, 1H), 7.60 (s, 0.34H), 7.73-7.78 (m, 3H), 7.99 (d, *J* = 8.4 Hz, 1H).

^{1}H NMR spectrum of 8:


8.000
7.979
7.778
7.757
7.750
7.730
7.603
7.353
7.350
7.334
7.332
7.314
7.311
7.287
7.285
7.268
7.266
7.257
7.250
7.247
7.224
7.204
6.804
6.776
6.760
6.731
5.815
5.813
5.771
5.769
5.361
5.358
5.332
5.330
2.331
0.000
D
N
Ts
0.97
2.85
0.34
1.00
1.32
2.05
0.85
0.91
0.90
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

9. Proposed mechanism

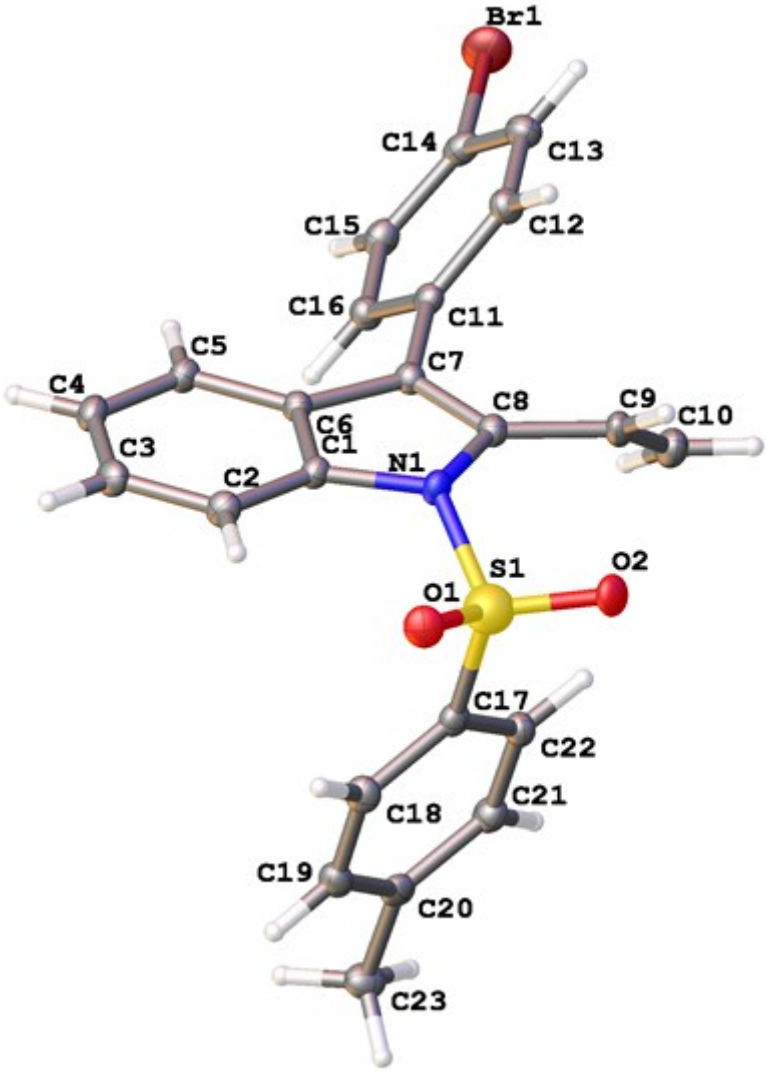
Scheme SI-3. Alternative Proposed Mechanism for the Synthesis of 2 and 3-Vinylindoles



For the clarity, the ligand and noncoordinating counterion are not depicted.
L = P(4-$CF_3C_6H_4$)$_3$ or P(4-$MeOC_6H_4$)$_3$

On the basis of previous reports and on our control experiments, a plausible mechanism for this reaction is outlined in Scheme SI-3. First, electrophilic Pd(II) species coordinated with the nitrogen atom of the substrate activates the double bond of the ACPs to form **A**, that undergoes an intramolecular aminopalladation reaction to generate intermediate **B**. Then following a β-carbon elimination, the Pd-alkyl intermediate **C** is obtained. If R ≠ H, **C** could undergo a β-hydride elimination to form the product **2**. The reduced Pd catalyst was then oxidized directly by molecular oxygen to regenerate the Pd(II) catalyst. However, if R = H, intermediate **B** would directly undergo a ring-expansion to yield **D**. Following again a β-hydride elimination, the intermediate **E** would be formed and could re-insert into the in-situ generated HPdX to provide the Pd-alkyl intermediate **F**. The latter could either undergo a β-carbon elimination to give **G** to finally generate **4** after a last β-hydride elimination reaction. On the other hand, **F** could initiate a β-hydride elimination to form intermediate **G'**, which would undergo a [2+2] retro-electrocyclization to furnish product **4**.

10. X-ray crystallographic information of product 2f



The crystal data of **2f** have been deposited in CCDC with number 1491285. Empirical Formula: $C_{23}H_{18}BrNO_2S$; Formula Weight: 452.35; Crystal Color, Habit: colorless, Crystal Dimensions: 0.35 x 0.3 x 0.25 mm^3; Crystal System: Triclinic; Lattice Parameters: a = 9.1381(12)Å, b = 10.1764(13)Å, c = 10.7753(14)Å, α = 99.900(2)^o, β = 92.142(2)^o, γ = 100.863(2)^o, V = 966.9(2)$Å^3$; Space group: P -1; Z = 2; D_{calc}= 1.554 g/cm^3; F_{000} = 460; Final R indices [I>2sigma(I)] R1 = 0.0403, wR2 = 0.1024.

11. **References**

[1] S. V. Frye, M. C. Johnson, N. L. Valvano, *J. Org. Chem.* **1991**, *56*, 3750.

[2] (a) K. Chen, Z. Zhang, Y. Wei, M. Shi, *Chem. Commun.* **2012**, *48*, 7696. (b) K. Chen, R. Sun, Q. Xu, Y. Wei, M. Shi, *Org. Biomol. Chem.* **2013**, *11*, 3949. (c) Y.-C. Yuan, H.-B. Yang, X.-Y. Tang, Y. Wei, M. Shi, *Chem.-Eur. J.* **2016**, *22*, 5146. (d) Y.-C. Yuan, H.-L. Liu, X.-B. Hu, Y. Wei, M. Shi, *Chem.-Eur. J.* **2016**, *22*, 13059.