Supporting Information

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1. Experimental procedures and spectroscopic data

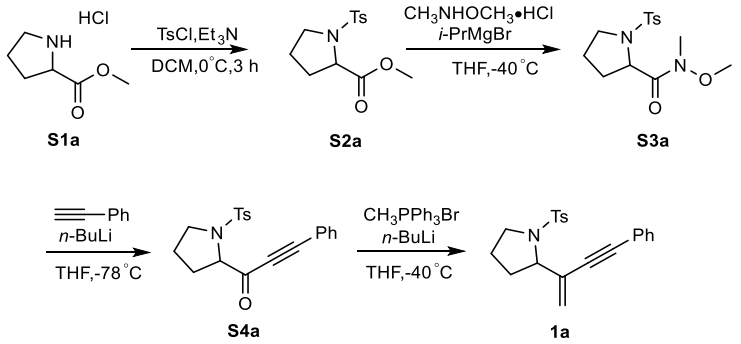
1. 1 General information

All reactions were carried out under an inert atmosphere of dry N_2 in Schlenk tube, Solvents were purified by standard method. Unless otherwise specified, the anhydrous DCE distilled form the refluxing mixture with CaH_2 was used. MeOH and AcOH were A. R. pure and used as received from commercial sources without further purification. ^1H, ^{13}C, ^{19}F NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for ^1H; 100 MHz for ^{13}C; 376 MHz for ^{19}F), ^1H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and ^{19}F NMR chemical shifts were determined relative to $CFCl_3$ as external standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra (MS) were obtained using LTQ FTICR DART and ESI mass spectrometer. Melting points were determined using a hot stage apparatus. All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

1. 2 Preparation of substrates 1a-1v

1.2.1 Preparation of substrates 1a-1o

For the synthesis of substrates **1a** – **1o**, the general procedure was described using substrate **1a** as example.



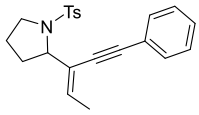
S2a: Et_3N (9.15 g, 90.6 mmol) was added dropwise into a solution of methyl prolinate hydrochloride **S1a** (5.0 g, 30.2 mmol) and TsCl (5.18 g, 27.2 mmol) in dichloromethane (DCM, 150 mL) cooling with ice bath. The reaction was stirred at 0 °C and monitored by TLC. After the TsCl was completely consumed in about 3 h, the reaction mixture was poured into ice water and extracted with DCM (2× 100 mL). The organic phase was washed with 1M HCl (2×50 mL), brine and dried with anhydrous Na_2SO_4. The solvent was distilled using rotary evaporator to obtain **S2a** (6.78 g, 88%) without further purification.

S3a: Under N_2 atmosphere, the solution of *i*-PrMgBr (17.6 mL, 52.8 mmol) in 2-methyltetrahydrofuran (3 mol/L) was added dropwise into the suspension of Ts-protected methyl prolinate **S2a** (5.0 g, 17.6 mmol) and N, O-dimethylhydroxylamine hydrochloride (2.58 g, 26.4 mmol) in anhydrous THF (150 mL) at -40 °C with vigorous stir. After the complete consumption of **S2a** (determined by TLC, about 2 h), the reaction was quenched by 100 mL saturated NH_4Cl (aq), and extracted with ethyl acetate (EtOAc, 3×100 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator to obtain **S3a** (5.2g, 95%) without further purification.

S4a: Under N_2 atmosphere, *n*-BuLi (0.9 mL, 2.2 mmol, 2.5 M) in hexane was added dropwise into the solution of phenylacetylene (245 mg, 2.4 mmol) in anhydrous THF (10 mL) at -78 °C. After stir for 1 h, the Weinreb amide **S3a** (625 mg, 2.0 mmol) dissolved in THF (2 mL) was added dropwise into the reaction mixture. After the reaction temperature raised to room temperature, the reaction was quenched using saturated 20 mL NH_4Cl (aq), and extracted with EtOAc (3×20 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. **S4a** (565 mg, 80%) was obtained after purified by chromatography (SiO_2, PE: EA = 5: 1, R_f = 0.3).

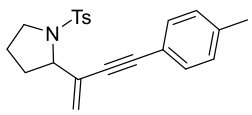
1a: Under N_2 atmosphere, *n*-BuLi (0.6 mL, 1.56 mmol, 2.5 M) in hexane was added dropwise into the suspension of CH_3PPh_3Br (667 mg, 1.87 mmol) in anhydrous THF (6 mL) at -40 °C. The reaction mixture was stirred for 1 h until it turned to clear orange solution. After **S4a** (500 mg, 1.42 mmol) dissolved in anhydrous THF (1 mL) was added into the reaction dropwise, the reaction temperature was raised to 0 °C and maintained until the entire consumption of **S4a**. And then the reaction was quenched using 5 mL saturated NH_4Cl (aq), and extracted with EtOAc (2×20 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. The resulting residue was purified by chromatography (SiO_2, PE: EA = 5: 1) to yield **1a** (328 mg, 60%).

2-(4-phenylbut-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1a)



Pale wihte solid, m.p. = 76 - 77 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.28 (m, 4H), 7.26 (d, J = 2.4 Hz, 1H), 5.68 (s, 1H), 5.57 (s, 1H), 4.39 (dd, J = 8.1, 2.9 Hz, 1H), 3.50 (ddd, J = 9.8, 7.3, 4.1 Hz, 1H), 3.34 (dt, J = 9.6, 7.4 Hz, 1H), 2.40 (s, 3H), 2.00 – 2.08 (m, 1H), 1.98 – 1.88 (m, 1H), 1.84 – 1.75 (m, 1H), 1.75 – 1.65 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.3, 135.5, 132.2, 131.5, 129.6, 128.4, 128.3, 127.5, 122.9, 122.3, 90.9, 87.5, 63.7, 49.1, 31.9, 24.0, 21.5. **IR** (KBr, cm^{-1}) 305, 2976, 2874, 1822, 1597, 1490, 1444, 1347, 1159, 1065, 1008, 912, 845, 691, 588; **HRMS** (DART) Calcd for $C_{21}H_{22}NO_2S$ $(M+H)^+$ 352.1366, found 352.1366.

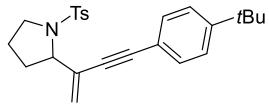
2-(4-(p-tolyl)but-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1b)



Pale white solid, m.p. = 68 - 69 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.2 Hz, 2H), 7.34 – 7.11 (m, 4H), 7.03 (d, J = 7.9 Hz, 2H), 5.59 (s, 1H), 5.47 (s, 1H), 4.32 (dd, J = 7.9, 2.5 Hz, 1H), 3.42 (ddd, J = 11.2, 7.4, 4.1 Hz, 1H), 3.30 – 3.13 (m, 1H), 2.32 (s, 3H), 2.27 (s, 3H), 2.00 – 1.91 (m, 1H), 1.91 – 1.81 (m, 1H), 1.76 – 1.67 (m, 1H), 1.67 – 1.58 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.3, 138.6, 135.6, 132.2, 131.4, 129.6, 129.1, 127.5, 121.9, 119.8, 91.1, 86.8, 63.8, 49.0,

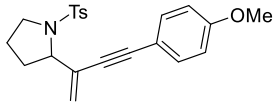
31.9, 24.0, 21.5; **IR** (KBr, cm^{-1}) 3029, 2975, 2873, 2199, 1663, 1599, 1347, 1159, 1093, 816, 671, 548; **HRMS** (DART) Calcd for $C_{22}H_{24}NO_2S$ $(M+H)^+$ 366.1522, found 366.1522 .

2-(4-(4-(tert-butyl)phenyl)but-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1c)



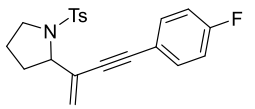
White solid, m.p. = 83 - 84 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.39 – 7.34 (m, 6H), 5.68 (s, 1H), 5.57 (s, 1H), 4.53 – 3.45 (m, 1H), 3.50 (ddd, J = 9.8, 7.3, 4.1 Hz, 1H), 3.34 (dt, J = 9.6, 7.4 Hz, 1H), 2.40 (s, 3H), 2.08 – 1.99 (m, 1H), 1.98 – 1.88 (m, 1H), 1.84 – 1.75 (m, 1H), 1.75 – 1.65 (m, 1H), 1.30 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.7, 143.3, 135.5, 132.3, 131.3, 129.6, 127.5, 125.3, 121.9, 119.9, 91.1, 86.9, 63.8, 49.1, 34.8, 31.9, 31.2, 24.0, 21.5; **IR** (KBr, cm^{-1}) 3034, 2962, 2870, 2201, 1916, 1812, 1598, 1503, 1461, 1399, 1193, 1159, 1063, 1008, 907, 836, 815, 671, 588, 548; **HRMS** (DART) Calcd for $C_{25}H_{30}NO_2S$ $(M+H)^+$ 408.1992, found 408.1994.

2-(4-(4-methoxyphenyl)but-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1d)



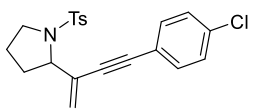
Yellow solid, m.p. = 85 - 86 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.1 Hz, 2H), 7.32 – 7.25 (m, 4H), 7.07 – 6.73 (m, 2H), 5.64 (s, 1H), 5.52 (s, 1H), 4.38 (d, J = 7.7 Hz, 1H), 3.79 (s, 3H), 3.53 – 3.44 (m, 1H), 3.32 (dd, J = 16.2, 8.4 Hz, 1H), 2.38 (s, 3H), 2.02 (ddd, J = 16.5, 8.7, 5.8 Hz, 1H), 1.92 (dt, J = 23.0, 8.1 Hz, 1H), 1.82 – 1.73 (m, 1H), 1.73 – 1.63 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 143.3, 135.5, 133.0, 132.4, 129.6, 127.4, 121.5, 115.0, 114.0, 91.0, 86.2, 63.8, 55.3, 49.1, 31.9, 23.9, 21.5; **IR** (KBr, cm^{-1}) 3060, 2956, 2840, 2194, 1720, 1601, 1510, 1344, 1250, 1092, 1030, 911, 736, 589, 548; **HRMS** (DART) Calcd for $C_{22}H_{24}NO_3S$ $(M+H)^+$ 382.1471, found 382.1471 .

2-(4-(4-fluorophenyl)but-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1e)



Yellow solid, m.p. = 82 - 83 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** δ 7.75 (d, J = 8.2 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.04 – 6.95 (m, 2H), 5.68 (s, 1H), 5.57 (s, 1H), 4.37 (dd, J = 8.1, 2.9 Hz, 1H), 3.50 (ddd, J = 10.0, 7.3, 4.1 Hz, 1H), 3.33 (dt, J = 9.7, 7.4 Hz, 1H), 2.40 (s, 3H), 2.06 – 1.97 (m, 1H), 1.97- 1.87 (m, 1H), 1.84 – 1.75 (m, 1H), 1.75 – 1.65 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5 (d, $J_{C\text{-}F}$ = 249.8 Hz), 143.3, 135.4, 133.4 (d, $J_{C\text{-}F}$ = 8.3 Hz), 132.1, 129.6, 127.5, 122.4, 119.0 (d, $J_{C\text{-}F}$ = 3.5 Hz), 115.6 (d, $J_{C\text{-}F}$ = 22.1 Hz), 89.8, 87.2, 63.7, 49.1, 32.0, 23.9, 21.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.65. **IR** (KBr, cm^{-1}) 3062, 2976, 2926, 2874, 2204, 1918, 1596, 1490, 1346, 1158, 1091, 1101, 817, 737, 707, 589, 547; **HRMS** (DART) Calcd for $C_{21}H_{21}FNO_2S$ $(M+H)^+$ 370.1272, found 370.1272.

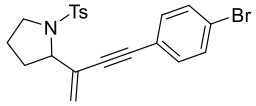
2-(4-(4-chlorophenyl)but-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1f)



Yellow solid, m.p. = 79 - 80 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.34 – 7.25 (m, 6H), 5.72 (s, 1H), 5.60 (s, 1H), 4.38 (dd, J = 8.0, 2.8 Hz, 1H), 3.54 – 3.46 (m, 1H), 3.39 – 3.28 (m, 1H), 2.40 (s, 3H), 2.02 (ddd, J = 14.6, 6.8, 3.6 Hz, 1H), 1.93 (ddd, J = 18.7, 11.4, 5.5 Hz, 1H), 1.79 (ddd, J = 16.4, 11.6, 8.0 Hz, 1H), 1.70 (ddd, J = 11.3, 6.9, 3.0 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 135.4, 134.4, 132.7, 132.0, 129.6, 128.6, 127.4, 122.7, 121.4,

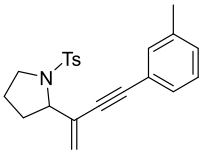
89.8, 88.5, 63.6, 49.1, 32.0, 23.9, 21.5. **IR** (KBr, cm^{-1}) 3063, 2976, 2926, 2874, 2204, 1918, 1724, 1670, 1490, 1345, 1158, 1091, 1011, 817, 736, 589, 547; **HRMS** (DART) Calcd for $C_{21}H_{21}ClNO_2S$ $(M+H)^+$ 386.0976, found 386.0975.

2-(4-(4-bromophenyl)but-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1g)



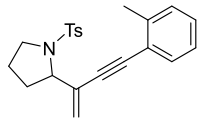
Yellow solid, m.p. = 85 - 86 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** δ 7.79 – 7.72 (m, 2H), 7.46 – 7.41 (m, 1H), 7.38 – 7.34 (m, 1H), 7.30 (m, 3H), 7.25 – 7.19 (m, 1H), 5.72 –5.66 (m, 1H), 5.60 – 5.55 (m, 1H), 4.42 – 4.34 (m, 1H), 3.53 – 3.45 (m, 1H), 3.42 – 3.27 (m, 1H), 2.40 – 2.38 (m, 3H), 2.08 – 1.88 (m, 2H), 1.83– 1.76 (m, 1H), 1.75 – 1.65 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 143.3, 135.6, 135.4, 132.9, 132.1, 132.0, 131.6, 131.5, 129.62, 129.59, 128.4, 128.3, 127.5, 122.9, 122.8, 122.6, 122.3, 121.9, 90.9, 89.8, 88.6, 87.5, 63.7, 63.6, 49.1, 32.0, 24.0, 23.9, 21.5.; **IR** (KBr, cm^{-1}) 3062, 2975, 2874, 2202, 1597, 1486, 1346, 1157, 1068, 1008, 817, 707, 577, 547; **HRMS** (DART) Calcd for $C_{21}H_{21}BrNO_2S$ $(M+H)^+$ 430.0471, found 430.0470.

2-(4-(m-tolyl)but-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1h)



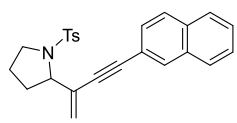
Colorless viscous liquid, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.15 – 7.09 (m, 1H), 5.68 (s, 1H), 5.57 (s, 1H), 4.39 (dd, J = 8.1, 3.2 Hz, 1H), 3.54 – 3.46 (m, 1H), 3.42 – 3.27 (m, 1H), 2.39 (s, 6H), 2.06 – 1.99 (m, 1H), 1.99 – 1.88 (m, 1H), 1.82 – 1.76 (m, 1H), 1.73 – 1.60 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.3, 138.0, 135.5, 132.1, 132.0, 129.6, 129.3, 128.6, 128.2, 127.5, 122.7, 122.2, 91.1, 87.1, 63.8, 49.1, 31.9, 24.0, 21.5, 21.2. **IR** (KBr, cm^{-1}) 3062, 3024, 2975, 2736, 1921, 1811, 1665, 1597, 1485, 1454, 1400, 1380, 1093, 1063, 846, 758, 711, 667, 620,588, 548; **HRMS** (DART) Calcd for $C_{22}H_{24}NO_2S$ $(M+H)^+$ 366.1522, found 366.1523.

2-(4-(o-tolyl)but-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1i)



Colourless viscous liquid, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 7.6 Hz, 1H), 7.28 (d, J = 8.1 Hz, 2H), 7.23 – 7.16 (m, 2H), 7.15 – 7.09 (m, 1H), 5.68 (s, 1H), 5.57 (s, 1H), 4.39 (dd, J = 8.1, 3.2 Hz, 1H), 3.53 – 3.46 (m, 1H), 3.42 – 3.27 (m, 1H), 2.39 (s, 6H), 2.10 – 2.02 (m, 1H), 2.00 – 1.88 (m, 1H), 1.86 – 1.76 (m, 1H), 1.73 – 1.60 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.3, 140.0, 135.5, 132.3, 131.9, 129.6, 129.4, 128.4, 127.5, 125.5, 122.7, 122.0, 91.3, 89.9, 63.8, 49.1, 32.0, 24.0, 21.5, 20.7. **IR** (KBr, cm^{-1}) 3029, 2953, 2924, 2872, 2735, 2415, 2307, 2198, 1915, 1724, 1668, 1599, 1494,1449, 1379, 1159, 1092, 1063, 1007, 910, 816, 736, 707, 669, 587, 525, 492; **HRMS** (DART) Calcd for $C_{22}H_{24}NO_2S$ $(M+H)^+$ 366.1522, found 366.1522.

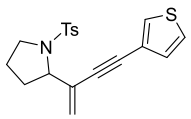
2-(4-(naphthalen-2-yl)but-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1j)



White solid, m.p. = 117 - 118 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.83 – 7.71 (m, 5H), 7.52 – 7.45 (m, 2H), 7.40 (dd, J = 8.5, 1.3 Hz, 1H), 7.27 (d, J = 8.1 Hz, 2H), 5.72 (s, 1H), 5.62 (s, 1H), 4.44 (dd, J = 8.1, 2.8 Hz, 1H), 3.57– 3.49 (m, 1H), 3.42 – 3.31 (m, 1H), 2.36 (s, 3H), 2.12– 2.03 (m, 1H), 2.02 – 1.92 (m, 1H), 1.87 – 1.75 (m, 1H), 1.76 – 1.67 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.3, 135.6, 132.9, 132.8, 132.2, 131.4, 129.6, 128.2, 128.0, 127.8, 127.7, 127.5,

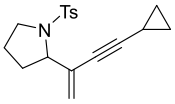
126.8, 126.6, 122.5, 120.2, 91.4, 87.8, 63.8, 49.1, 32.0, 24.0, 21.5. **IR** (KBr, cm^{-1}) 3056, 2974, 2925, 2873, 1920, 1813, 1597, 1449, 1400, 1346, 1268, 1191, 1159, 1094, 1064, 1008, 908, 860, 816, 749, 708, 673, 588, 548, 475; **HRMS** (DART) Calcd for $C_{25}H_{24}NO_2S$ $(M+H)^+$ 402.1522, found 402.1521.

2-(4-(thiophen-3-yl)but-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1k)



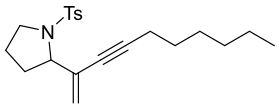
White solid, m.p. = 67 - 68 ºC, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 1.9 Hz, 1H), 7.34 – 7.19 (m, 3H), 7.05 (d, J = 4.9 Hz, 1H), 5.68 (s, 1H), 5.56 (s, 1H), 4.36 (d, J = 7.8 Hz, 1H), 3.56 – 3.41 (m, 1H), 3.35 – 3.27 (m, 1H), 2.40 (s, 3H), 2.05 – 1.97 (m, 1H), 1.96 – 1.84 (m, 1H), 1.82 – 1.63 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.4, 135.3, 132.1, 129.7, 129.6, 128.8, 127.5, 125.4, 122.2, 121.9, 87.0, 86.1, 63.7, 49.1, 31.9, 23.9, 21.5. **IR** (KBr, cm^{-1}) 3107, 2952, 2926, 2873, 1921, 1721, 1669, 1597, 1493, 1448, 1379, 1255, 1191, 1159, 1094, 1063, 1008, 909, 845, 815, 783, 742, 707, 670, 626, 588, 548; **HRMS** (DART) Calcd for $C_{19}H_{20}NO_2S_2$ $(M+H)^+$ 358.0930, found 358.0930.

2-(4-cyclopropylbut-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1l)



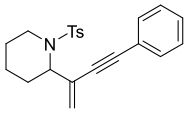
Yellow viscous liquid, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.51 (t, J = 1.3 Hz, 1H), 5.36 (s, 1H), 4.27 – 4.21 (m, 1H), 3.47– 4.39 (m, 1H), 3.33 – 3.24 (m, 1H), 2.43 (s, 3H), 1.98 – 1.79 (m, 2H), 1.73 – 1.60 (m, 2H), 1.33 – 1.25 (m, 1H), 0.83 – 0.75 (m, 2H), 0.68 – 0.62 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.2, 135.5, 132.3, 129.5, 127.4, 120.8, 95.0, 73.8, 63.8, 48.9, 31.7, 23.8, 21.5, 8.5, 0.0. **IR** (KBr, cm^{-1}**)** 3093, 2977, 2874, 1922, 1814, 1673, 1589, 1493, 1450, 1400, 1346, 1194, 1159, 1093, 1006, 872, 847, 815, 760, 736, 588, 547; **HRMS** (DART) Calcd for $C_{18}H_{22}NO_2S$ $(M+H)^+$ 316.1366, found 316.1366.

2-(dec-1-en-3-yn-2-yl)-1-tosylpyrrolidine (1m)



Yellow viscous liquid, purified by chromatography (PE/EA = 5/1, R_f= 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 7.9 Hz, 2H), 5.54 (s, 1H), 5.40 (s, 1H), 4.27 (d, J = 7.6 Hz, 1H), 3.52 – 3.40 (m, 1H), 3.30 (dd, J = 17.1, 7.5 Hz, 1H), 2.44 (s, 3H), 2.26 (t, J = 7.0 Hz, 2H), 2.02 – 1.83 (m, 2H), 1.76 – 1.61 (m, 2H), 1.54 – 1.45 (m, 2H), 1.35 (m, 6H), 0.91 (t, J = 6.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.2, 135.5, 132.4, 129.5, 127.5, 120.7, 92.1, 78.6, 63.9, 49.0, 31.7, 31.3, 28.6, 23.8, 22.6, 21.5, 19.3, 14.1. **IR** (KBr, cm^{-1}**)** 3028, 2929, 2858, 1614, 1598, 1493, 1458, 1379, 1244, 1191, 1094, 1008, 903, 815, 758, 708, 588, 548; **HRMS** (DART) Calcd for $C_{21}H_{30}NO_2S$ $(M+H)^+$ 360.1992, found 360.1992.

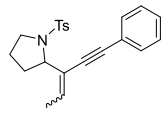
2-(4-phenylbut-1-en-3-yn-2-yl)-1-tosylpiperidine (1n)



Yellow viscous liquid, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.0 Hz, 2H), 7.38 (m, 2H), 7.32 – 7.28 (m, 3H), 7.26 (d, J = 8.1 Hz, 2H), 5.69 (s, 1H), 5.55 (s, 1H), 4.85 – 4.76 (m, 1H), 3.78 (dt, J = 14.2, 2.9 Hz, 1H), 3.18 (td, J = 13.5, 2.9 Hz, 1H), 2.40 (s, 3H), 2.28 – 2.20 (m, 1H), 1.67 – 1.45 (m, 5H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.0, 138.4, 131.4, 129.6, 129.5, 128.4, 128.3, 127.0, 123.7, 122.9, 91.0, 88.2, 55.9, 41.6, 27.8, 24.4, 21.5, 19.1. **IR** (KBr, cm^{-1}) 3060, 2942, 2861, 2361, 1666, 1598, 1491, 1446, 1378, 1337, 1217, 1188, 1156, 1109, 1053, 961, 938, 917, 855, 815, 758, 735, 709, 692, 661, 617, 575, 547; **HRMS** (DART) Calcd for $C_{22}H_{24}NO_2S$ $(M+H)^+$ 366.1522, found 366.1521.

For the synthesis of **1o**, $CH_3CH_2PPh_3Br$ was used instead of CH_3PPh_3Br in the last step.

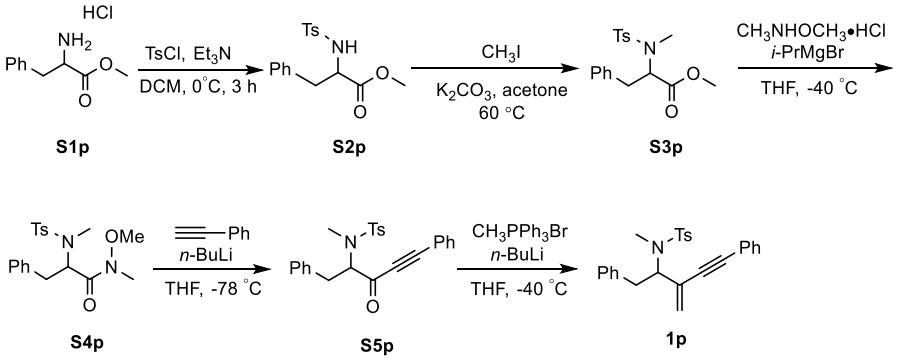
2-(1-phenylpent-3-en-1-yn-3-yl)-1-tosylpyrrolidine (1o)



Yellow viscous liquid, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 2H), 7.35 – 7.19 (m, 7H), 6.14 (q, J = 6.8 Hz, 0.2H), 6.03 (q, J = 7.2 Hz, 0.8H), 4.80 (dd, J = 7.5, 5.4 Hz, 0.8H), 4.37 (dd, J = 8.1, 3.0Hz, 0.2H), 3.65 – 3.53 (m, 0.8H), 3.50 – 3.37 (m, 1.2H), 2.36 (s, 0.6H), 2.33 (s, 2.4H), 2.20 – 1.92 (m, 3H), 1.91 (s, 1.5H), 1.89 (s, 1.5H), 1.80 – 1.68 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.9, 136.7, 134.2, 131.3, 131.2, 129.4, 129.3, 128.3, 128.2, 128.1, 127.8, 127.4, 127.3, 125.7, 123.5, 89.1, 88.2, 85.8, 57.3, 49.1, 49.0, 32.5, 32.1, 25.3, 24.2, 21.4, 16.0, 14.0. **IR** (KBr, cm^{-1}) 3031, 2925, 2871, 2362, 2340, 1596, 1490, 1442, 1440, 1344, 1244, 1200, 1158, 1094, 1068, 986, 814, 757, 691, 666, 589, 547; **HRMS** (DART) Calcd for $C_{22}H_{24}NO_2S$ $(M+H)^+$ 366.1522, found 366.1521.

1.2.2 Preparation of substrates 1p-1v

For the synthesis of substrates **1p** – **1v**, the general procedure was described using substrate **1p** as example.



S2p: Et_3N (4.21 g, 41.7 mmol) was added dropwise into a solution of phenylalanine methyl ester hydrochloride **S1p** (3.0 g, 13.9 mmol) and TsCl (2.38 g, 12.5 mmol) in DCM (100 mL) cooling with ice bath. The reaction was stirred at 0 °C and monitored by TLC. After the TsCl was completely consumed, the reaction mixture was poured into ice water and extracted with DCM (2×100 mL). The organic phase was washed with 1M HCl (2×50 mL), brine and dried with anhydrous Na_2SO_4. The solvent was removed using rotary evaporator to obtain **S2p** (4.03 g, 87%) without further purification.

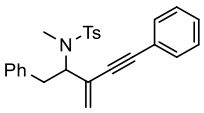
S3p: A solution of Ts-protected phenylalanine methyl ester **S2p** (3.0 g, 9.0 mmol) and iodomethane (1.53 g, 10.8 mmol) in acetone (50 mL) was added K_2CO_3 (2.49 g, 18.0 mmol), the reaction mixture was stirred at 60 °C overnight. The reaction was then filtrated and the solvent was distillled using rotary evaporator to obtain **S3p** (2.91 g, 93%) without further purification.

S4p: Under N_2 atmosphere, the solution of *i*-PrMgBr (5.8 mL, 17.3 mmol) in 2-methyltetrahydrofuran (3 M) was added dropwise into the suspension of **S3p** (2 g, 5.7 mmol) and N,O-dimethylhydroxylamine hydrochloride (843 mg, 8.64 mmol) in anhydrous THF at -40 °C with vigorous stir. After the complete consumption of **S3p** (determined by TLC, about 2 h), the reaction was quenched by 20 mL saturated NH_4Cl (aq), and extracted with EtOAc (2×50 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator to obtain **S4p** (1.36 g, 63%) without further purification.

S5p: Under N_2 atmosphere, *n*-BuLi (0.9 mL, 2.2 mmol, 2.5 M) in hexane was added dropwise into the solution of phenylacetylene (245 mg, 2.4 mmol) in anhydrous THF (10 mL) at -78 °C. After stir for 1 h, the Weinreb amide **S4p** (753 mg, 2 mmol) dissolved in THF (2 mL) was added dropwise into the reaction mixture. After the reaction temperature raised to room temperature, the reaction was quenched using saturated NH_4Cl (aq), and extracted with EtOAc. The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. The desired **S5p** (417 mg, 50%) was obtained after purified by chromatography (SiO_2, PE: EA = 6: 1).

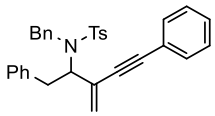
1p: Under N_2 atmosphere, *n*-BuLi (0.5 mL, 1.1 mmol, 2.5 M) in hexane was added dropwise into the suspension of CH_3PPh_3Br (428 mg, 1.2 mmol) in anhydrous THF at -40 °C. The reaction mixture was stirred for 1 h until it turned to clear orange solution. After **S5p** (417 mg, 1.0 mmol) dissolved in anhydrous THF was added into the reaction dropwise, the reaction temperature was raised to 0 °C and maintained until the entire consumption of **S5p**. And then the reaction was quenched using 5 mL saturated NH_4Cl (aq), and extracted with EtOAc (2×20 mL). The organic phase was washed with brine and dried with anhydrous Na_2SO_4, the solvent was removed by rotary evaporator. The resulting residue was purified by chromatography (SiO_2, PE: EA = 6: 1) to yield **1p** (174 mg, 42%).

N,4-dimethyl-N-(3-methylene-1,5-diphenylpent-4-yn-2-yl)benzenesulfonamide (1p)



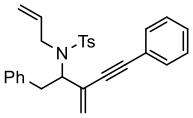
Pale white solid, m. p. = 93 - 94 °C, purified by chromatography (PE/EA = 6/1, R_f = 0.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 4H), 7.39 – 7.35 (m, 3H), 7.33 – 7.25 (m, 5H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.63 (s, 1H), 5.51 (s, *J* = 9.5, 1H), 5.11 (t, *J* = 7.7 Hz, 6.5 Hz, 1H), 3.30 (dd, *J* = 14.0, 7.8 Hz, 1H), 2.99 (s, 3H), 2.96 (dd, *J* = 13.9, 7.7 Hz, 1H), 2.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.0, 137.7, 136.8, 131.6, 129.54, 129.50, 129.3, 128.7, 128.6, 128.5, 127.4, 126.7, 125.4, 122.8, 92.1, 88.1, 62.3, 37.3, 29.6, 21.5. **IR** (KBr, cm^{-1}) 3061, 3029, 2926, 1951, 1808, 1667, 1599, 1492, 1453, 1400, 1336, 1219, 1158, 1088, 1042, 976, 926, 885, 847, 814, 779, 757, 694, 663, 617, 589, 548; **HRMS** (DART) Calcd for $C_{26}H_{26}NO_2S$ $(M+H)^+$ 416.1679, found 416.1676.

N-benzyl-4-methyl-N-(3-methylene-1,5-diphenylpent-4-yn-2-yl)benzenesulfonamide (1q)



Pale white solid, m.p. = 102 - 103 °C, purified by chromatography (PE/EA = 6/1, R_f = 0.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.39 (dd, *J* = 7.3, 2.2 Hz, 2H), 7.29 (s, 5H), 7.25 – 7.13 (m, 6H), 7.13 – 7.08 (m, 4H), 5.46 (d, *J* = 1.2 Hz, 1H), 5.19 (s, 1H), 4.85 (dd, *J* = 10.1, 4.9 Hz, 1H), 4.79 (d, *J* = 16.1 Hz, 1H), 4.63 (d, *J* = 16.1 Hz, 1H), 2.98 (qd, *J* = 13.7, 7.5 Hz, 2H), 2.28 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 138.2, 138.1, 137.9, 131.6, 129.4, 129.3, 128.7, 128.45, 128.43, 128.41, 128.3, 127.5, 127.4, 127.2, 126.5, 122.7, 92.1, 88.4, 63.6, 48.8, 39.5, 21.5. **IR** (KBr, cm^{-1}) 3062, 3029, 2955, 2926, 2857, 1949, 1808, 1737, 1600, 1493, 1454, 1399, 1338, 1289, 1204, 1158, 1092, 1028, 979, 920, 888, 850, 813, 778, 756, 696, 665, 635, 594, 546; **HRMS** (DART) Calcd for $C_{32}H_{30}NO_2S$ $(M+H)^+$ 492.1992, found 492.1990.

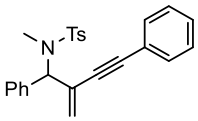
N-allyl-4-methyl-N-(3-methylene-1,5-diphenylpent-4-yn-2-yl)benzenesulfonamide (1r)



Yellow liquid, purified by chromatography (PE/EA = 6/1, R_f = 0.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.19 – 7.16 (m, 3H), 7.13 (d, *J* = Hz, 4H), 7.09 – 7.06 (m, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 5.80 – 5.63 (m, 1H), 5.40 (s, 1H), 5.28 – 5.20 (m, 1H), 5.10 (dt, *J* = 17.1, 1.7 Hz, 1H), 4.96 (dd, *J* = 10.1, 1.6

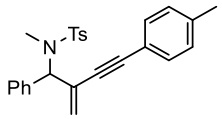
Hz, 1H), 4.77 (ddd, *J* = 9.0, 5.9, 2.3 Hz, 1H), 3.97 (d, *J* = 5.6 Hz, 2H), 3.15 (ddd, *J* = 13.8, 9.3, 1.5 Hz, 1H), 2.99 – 2.91 (m, 1H), 2.17 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.0, 138.1, 137.8, 136.1, 131.5, 129.4, 129.2, 128.7, 128.5, 128.5, 127.6, 126.6, 126.4, 122.8, 117.3, 91.9, 88.3, 63.1, 47.5, 38.8, 21.5. **IR** (KBr, cm^{-1}) 3062, 3029, 2925, 2859, 1950, 1720, 1667, 1599, 1542, 1493, 1452, 1418, 1400, 1338, 1289, 1158, 1122, 1090, 1052, 1027, 920, 867, 845, 814, 781, 757, 694, 664, 588; **HRMS** (DART) Calcd for $C_{28}H_{28}NO_2S$ $(M+H)^+$ 442.1835, found 442.1834.

N,4-dimethyl-N-(2-methylene-1,4-diphenylbut-3-yn-1-yl)benzenesulfonamide (1s)



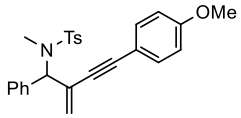
Yellow liquid, purified by chromatography (PE/EA = 6/1, R_f = 0.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.15 (m, 12H), 5.95 (s, 1H), 5.73 (d, *J* = 1.2 Hz, 1H), 5.46 (d, *J* = 1.4 Hz, 1H), 2.78 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 136.8, 136.8, 131.4, 129.5, 129.2, 128.6, 128.4, 128.4, 128.2, 127.9, 127.4, 125.6, 122.7, 92.0, 88.2, 64.6, 31.2, 21.5. **IR** (KBr, cm^{-1}) 3061, 3029, 2856, 1910, 1811, 1736, 1653, 1599, 1508, 1494, 1451, 1401, 1338, 1261, 1211, 1162, 1087, 1019, 970, 949, 918, 843, 814, 741, 701, 674, 657, 608, 588, 573, 547; **HRMS** (DART) Calcd for $C_{25}H_{24}NO_2S$ $(M+H)^+$ 402.1522, found 402.1523.

N,4-dimethyl-N-(2-methylene-1-phenyl-4-(p-tolyl)but-3-yn-1-yl)benzenesulfonamide (1t)



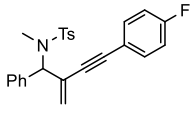
Yellow liquid, purified by chromatography (PE/EA = 6/1, R_f = 0.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.32 – 7.26 (m, 5H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.05 (q, *J* = 8.0 Hz, 4H), 5.94 (s, 1H), 5.70 (s, 1H), 5.43 (s, 1H), 2.78 (s, 3H), 2.35 (s, 3H), 2.30 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.1, 136.8, 136.8, 131.4, 129.5, 129.2, 128.6, 128.4, 128.4, 128.2, 127.9, 127.4, 125.6, 122.7, 92.0, 88.2, 64.6, 31.2, 21.5. **IR** (KBr, cm^{-1}) 3061, 3029, 2856, 1910, 1811, 1736, 1653, 1599, 1508, 1494, 1451, 1401, 1338, 1261, 1211, 1162, 1087, 1019, 970, 949, 918, 843, 814, 741, 701, 674, 657, 608, 588, 573, 547; **HRMS** (DART) Calcd for $C_{26}H_{26}NO_2S$ $(M+H)^+$ 416.1679, found 416.1677.

N-(4-(4-methoxyphenyl)-2-methylene-1-phenylbut-3-yn-1-yl)-N,4-dimethylbenzenesulfonamide (1u)



Yellow liquid, purified by chromatography (PE/EA = 6/1, R_f= 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.3 Hz, 2H), 7.36 – 7.29 (m, 5H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.11 (m, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 5.97 (s, 1H), 5.72 (t, *J* = 1.2 Hz, 1H), 5.44 (t, *J* = 1.4 Hz, 1H), 3.80 (s, 3H), 2.81 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.8, 143.1, 136.9, 136.5, 132.9, 129.4, 129.3, 128.6, 128.4, 127.8, 127.4, 124.8, 114.8, 113.9, 92.1, 87.0, 64.7, 55.3, 31.2, 21.5. **IR** (KBr, cm^{-1}) 3031, 2956, 2925, 2851, 1917, 1665, 1599, 1571, 1509, 1454, 1400, 1336, 1305, 1288, 1249, 1162, 1108, 1087, 1029, 970, 949, 919, 832, 812, 738, 701, 674, 658, 608, 575; **HRMS** (DART) Calcd for $C_{26}H_{26}NO_3S$ $(M+H)^+$ 432.1628, found 432.1626.

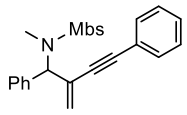
N-(4-(4-fluorophenyl)-2-methylene-1-phenylbut-3-yn-1-yl)-N,4-dimethylbenzenesulfonamide (1v)



Yellow liquid, purified by chromatography (PE/EA = 6/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.25 – 7.12 (m, 7H), 7.12 – 7.06 (m, 2H), 6.85 (t, *J* = 8.7 Hz, 2H), 5.87 (s, 1H), 5.65 (d, *J* = 1.2 Hz, 1H), 5.38 (t, *J* = 1.3 Hz, 1H), 2.68 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.6 (d, J_{C-F} = 250.1 Hz), 143.2, 136.8

(d, $J_{C\text{-}F}$ = 15.3 Hz), 133.3 (d, $J_{C\text{-}F}$ = 8.4 Hz), 129.5, 129.1, 128.6, 128.4, 127.9, 127.4, 125.5, 118.8 (d, $J_{C\text{-}F}$ = 3.5 Hz), 115.5 (d, J = 22.2 Hz), 90.88, 87.86, 64.59, 31.10, 21.48. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.45. **IR** (KBr, cm^{-1}) 3063, 3031, 2955, 2925, 2854, 1736, 1671, 1597, 1505, 1452, 1400, 1338, 1228, 1161, 1088, 1017, 969, 950, 919, 837, 812, 739, 701, 676, 658, 607, 588, 573; **HRMS** (DART) Calcd for $C_{25}H_{23}NFO_2S$ $(M+H)^+$ 420.1428, found 420.1426.

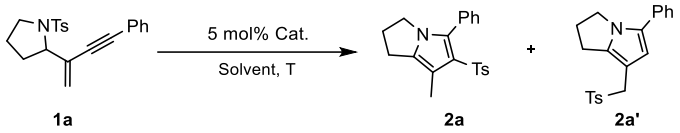
4-methoxy-N-methyl-N-(2-methylene-1,4-diphenylbut-3-yn-1-yl)benzenesulfonamide (1w)



Yellow liquid, purified by chromatography (PE/EA = 6/1, R_f = 0.3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, J = 8.8 Hz, 2H), 7.37 – 7.20 (m, 12H), 6.92 (d, J = 8.8 Hz, 2H), 5.98 (s, 1H), 5.77 (s, 1H), 5.50 (s, 1H), 3.83 (s, 3H), 2.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.7, 136.9, 131.5, 131.4, 129.5, 129.2, 128.5, 128.4, 128.4, 128.2, 127.8, 125.6, 122.7, 114.0, 92.0, 88.2, 64.6, 55.5, 31.1. **IR** (KBr, cm^{-1}) 3062, 3030, 2930, 2842, 2566, 2054, 1957, 1899, 1723, 1672, 1596, 1579, 1495, 1413, 1338, 1304, 1259, 1159, 1112, 1090, 1026, 951, 919, 835, 819, 757, 693, 669, 629, 614, 589, 558; **HRMS** (DART) Calcd for $C_{25}H_{24}NO_3S$ $(M+H)^+$ 418.1471, found 418.1471.

1.3 Optimization of the reaction conditions

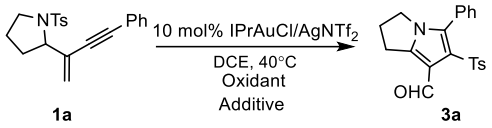
Table S1. Optimization of the reaction conditions of 2[a]



Entry	Cat.	Solvent	T (°C)	**2a**[b]	**2a'**[c]	Note
1	$PPh_3AuCl/AgBF_4$	DCE	25	17	4	76% SM
2	$PtCl_2$	DCE	60	30	12	-
3	$PdCl_2(CH_3CN)_2$	DCE	80	-	-	degradation
4[d]	$In(OTf)_3$	DCE	100	-	-	n.r.
5	*t*BuPhosAuCl/$AgBF_4$	DCE	25	trace	-	85% SM
6	IPrAuCl/$AgBF_4$	DCE	25	56	13	-
7	IPrAuCl/$AgBF_4$	DCE	40	72	14	-
8	IPrAuCl/AgOTf	DCE	40	60	12	-
9	IPrAuCl/$AgSbF_6$	DCE	40	44	15	-
10	IPrAuCl/$AgNTf_2$	DCE	40	74	17	-
11	IPrAuCl/$AgNTf_2$	Toluene	40	53	12	-
12	IPrAuCl/$AgNTf_2$	CH_3CN	40	24	8	17% SM
13	IPrAuCl/$AgNTf_2$	THF	40	36	8	-
14	IPrAuNTf_2	DCE	40	73	14	-
15	IPrAuCl/$AgNTf_2$	DCE	40	73	0	AcOH 2 eq
16	IPrAuCl/$AgNTf_2$	DCE	40	57	0	TsOH 2eq
17	IPrAuCl/$AgNTf_2$	DCE	40	63	11	MeOH 2eq
18	IPrAuCl/$AgNTf_2$	DCE	40	26	0	TfOH 2eq
19	IPrAuCl/$AgNTf_2$	DCE	40	45	0	CF_3COOH 2eq
20	IPrAuCl/$AgNTf_2$	DCE	40	10	trace	Anisole 2 eq
21	IPrAuCl/$AgNTf_2$	DCE	40	-	-	n.r.
22	$AgNTf_2$	DCE	40	-	-	n.r.

[a] Reaction conditions: 1a (0.1 mmol), 1 mL Solvent, N_2 atmosphere, 12 h, full conversion unless the yield of recovered staring material was noted. [b] Isolated yield. [c] The yield of **2a'** was determined by ^1H NMR spectrum of the crude product. [d] 10 mol%.

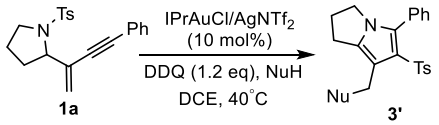
Table S2. Optimization of the reaction conditions of 3[a]

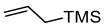


Entry	Oxidation (eq)	Additive	T (°C)	**3a**[b]	note
1[c]	DDQ (2.0)	MeOH 20 μL	25	20	75% SM
2[c]	SeO_2 (2.0)	MeOH 20 μL	25	-	degradation
3[c]	TCQ (2.0)	MeOH 20 μL	25	-	90% SM
4	DDQ (2.2)	HOAc 40 μL	40	28	20% **3a'**
5	DDQ (2.2)	MeOH 20 μL/AcOH 40 μL	40	66	-
6	DDQ (3.0)	MeOH 20 μL/AcOH 40 μL	40	46	-

[a] Reaction conditions: 1a (0.1 mmol), 1 mL Solvent, N_2 atmosphere, 4 h, full conversion unless the yield of recovered staring material was noted. [b] Isolated yield. [c] 5 mol% catalyst.

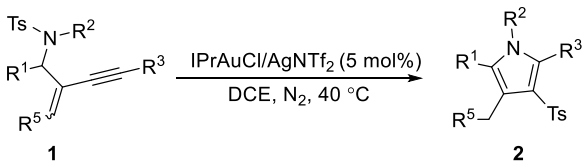
Table S3. Attempts to trap the azafulvenium intermediate[a]



Entry	NuH (2.0 eq)	**3'**[b]
1	1,3,5-trimethoxybenzene	n.d.
2	Anisole	n.d.
3	Dimethyaniline	n.d.
4	Dimethyl malonate	n.d.
5	Saccharin	n.d.
6	AcOH	34%
7		n.d.

[a] Reaction conditions: 1a (0.1 mmol), 1 mL Solvent, N_2 atmosphere, 12 h [b] Isolated yield.

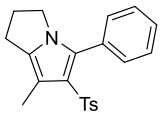
1.4 General procedure for the synthesis of 2a – 2w



In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added IPrAuCl (5 mol%) and $AgNTf_2$ (5 mol %) in dry dichloroethane (DCE, 1 mL). After stirred for 5 min, the substrate **1** was added. The mixture was stirred at 40 °C until the starting material was completely consumed (monitored by TLC). Then the solvent was evaporated by rotary evaporator, and the residue was

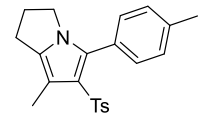
purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product **2**.

7-methyl-5-phenyl-6-tosyl-2,3-dihydro-1H-pyrrolizine (2a)



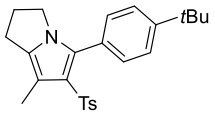
74%, 52 mg, pale white solid, m.p. = 184 - 185 °C, purified by chromatography (PE/EA = 5/1, 1 = 0.3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.1 Hz, 2H), 7.46 – 7.29 (m, 5H), 7.15 (d, J = 8.0 Hz, 2H), 3.71 (t, J = 7.1 Hz, 2H), 2.79 (t, J = 7.2 Hz,2H), 2.42 (q, J = 7.2 Hz, 2H), 2.36 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.4, 141.9, 134.6, 131.4, 131.0, 130.6, 129.1, 128.4, 127.7, 126.5, 121.5, 110.1, 45.9, 26.8, 23.2, 21.4, 11.0. **IR** (KBr, cm^{-1}) 3058, 2957, 2923, 2859, 1541, 1447, 1401, 1339, 1310, 1229, 1159, 1136, 1088, 1060, 1019, 921, 854, 736, 700, 655, 617, 574, 540; **HRMS** (DART) Calcd for $C_{21}H_{22}NO_2S$ $(M+H)^+$ 352.1366, found 352.1365.

7-methyl-5-(p-tolyl)-6-tosyl-2,3-dihydro-1H-pyrrolizine (2b)



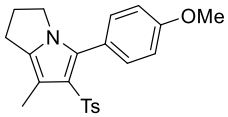
66%, 48 mg, pale white solid, m.p. = 161- 162 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 2H), 7.30 – 7.18 (m, 4H), 7.16 (d, J = 8.1 Hz, 2H), 3.71 (t, J = 7.1 Hz, 2H), 2.79 (t, J = 7.3 Hz, 2H), 2.42 (m, 5H), 2.37 (s, 3H), 2.23 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ142.3, 142.0, 138.3, 134.4, 131.6, 130.4, 129.1, 128.5, 128.0, 126.5, 121.3, 110.0, 45.9, 26.7, 23.1, 21.4, 11.0.; **IR** (KBr, cm^{-1}) 3024, 2958, 2923, 2864, 2745, 2584, 1912, 1798, 1735, 1701, 1652, 1596, 1531, 1492, 1460, 1417, 1394, 1337, 1311, 1233, 1211, 1182, 1159, 1137, 1114, 1088, 1058, 1018, 946, 914, 862, 815, 723; **HRMS** (DART) Calcd for $C_{22}H_{24}NO_2S$ $(M+H)^+$ 366.1522, found 366.1523.

5-(4-(tert-butyl)phenyl)-7-methyl-6-tosyl-2,3-dihydro-1H-pyrrolizine (2c)



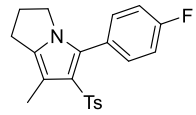
69%, 42 mg, white solid, m.p. = 193 - 194 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.1 Hz, 2H), 3.70 (t, J = 7.1 Hz, 2H), 2.77 (t, J = 7.2 Hz, 2H), 2.39 (q, J = 7.2 Hz, 2H), 2.33 (s, 3H), 2.21 (s, 3H), 1.35 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.3, 142.2, 141.8, 134.3, 131.6, 130.2, 129.0, 127.8, 126.6, 124.6, 121.3, 110.2, 46.0, 34.7, 31.4, 26.8, 23.1, 21.4, 11.0; **IR** (KBr, cm^{-1}) 3061, 2959, 2925, 2865, 2746, 1913, 1731, 1648, 1597, 1558, 1530, 1460, 1417, 1396, 1363, 1338, 1311, 1268, 1234, 1200, 1181, 1160, 1137, 1114, 1087, 1058, 1017, 968, 915, 863, 731, 664; **HRMS** (DART) Calcd for $C_{25}H_{30}NO_2S$ $(M+H)^+$ 408.1992, found 408.1991.

5-(4-methoxyphenyl)-7-methyl-6-tosyl-2,3-dihydro-1H-pyrrolizine (2d)



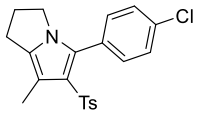
75%, 43 mg, yellow solid, m.p. = 131-132 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.1 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 3.88 (s, 3H), 3.71 (t, J = 7.1 Hz, 2H), 2.78 (t, J = 7.3 Hz, 2H), 2.41 (q, J = 7.4 Hz, 2H), 2.36 (s, 3H), 2.23 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 142.3, 142.0, 134.2, 131.8, 131.4, 129.1, 126.5, 123.2, 121.3, 113.2, 110.0, 55.3, 45.8, 26.7, 23.1, 21.4, 11.0; **IR** (KBr, cm^{-1}) 2958, 2924, 2854, 2746, 2538, 1718, 1653, 1611, 1574, 1530, 1462, 1441, 1422, 1398, 1338, 1289, 1249, 1177, 1059, 1027, 966, 914, 861, 733, 704, 665, 592; **HRMS** (DART) Calcd for $C_{22}H_{24}NO_3S$ $(M+H)^+$ 382.1471, found 382.1470 .

5-(4-fluorophenyl)-7-methyl-6-tosyl-2,3-dihydro-*1H*-pyrrolizine (2e)



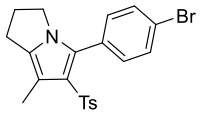
70%, 38mg, white solid, m.p. = 169 - 170 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** δ 7.52 (d, J = 8.3 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.16 (d, J = 8.1 Hz, 2H), 7.14 – 7.07 (m, 2H), 3.70 (t, J = 7.1 Hz, 2H), 2.80 (t, J = 7.3 Hz, 2H), 2.43 (q, J = 7.3 Hz, 2H), 2.37 (s, 3H), 2.23 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.8 (d, $J_{C\text{-}F}$ = 248.1 Hz), 142.5, 141.7, 134.7, 132.4 (d, $J_{C\text{-}F}$ = 8.3 Hz), 130.2, 129.2, 126.9, 126.5, 121.7, 114.9 (d, $J_{C\text{-}F}$ = 21.6 Hz), 110.2, 45.9, 26.7, 23.1, 21.5, 10.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.94. **IR** (KBr, cm^{-1}) 3063, 2956, 2923, 2861, 1912, 1735, 1650, 1598, 1527, 1462, 1421, 1393, 1338, 1300, 1225, 1158, 1136, 1088, 1057, 1016, 966, 914, 862, 841, 812, 725, 704, 666, 619, 573; **HRMS** (DART) Calcd for $C_{21}H_{21}FNO_2S$ $(M+H)^+$ 370.1272, found 370.1272.

5-(4-chlorophenyl)-7-methyl-6-tosyl-2,3-dihydro-1H-pyrrolizine (2f)



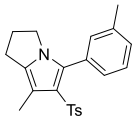
68%, 39mg, yellow solid, m.p. = 190 - 191 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 3.71 (t, J = 7.1 Hz, 2H), 2.79 (t, J = 7.3 Hz, 2H), 2.42 (p, J = 7.3 Hz, 2H), 2.37 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.6, 141.6, 135.0, 134.6, 131.9, 123.0, 129.4, 129.2, 128.1, 126.5, 121.9, 110.4, 46.0, 26.7, 23.1, 21.5, 10.9. **IR** (KBr, cm^{-1}) 2955, 2855, 1920, 1773, 1736, 1718, 1685, 1651, 1597, 1561, 1542, 1510, 1458, 1416, 1385, 1339, 1309, 1233, 1159, 1136, 1088, 1055, 1014, 947, 915, 862, 834, 812, 721, 703, 666, 619, 574; **HRMS** (DART) Calcd for $C_{21}H_{21}ClNO_2S$ $(M+H)^+$ 386.0976, found 386.0974 .

5-(4-bromophenyl)-7-methyl-6-tosyl-2,3-dihydro-*1H*-pyrrolizine (2g)



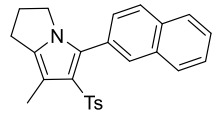
67%, 43 mg, yellow solid, m.p. = 189 - 190 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** δ 7.57 – 7.51 (m, 3H), 7.43 – 7.35 (m, 1H), 7.29 – 7.22 (m, 2H), 7.20 – 7.12 (m, 2H), 3.71 (t, J = 7.1 Hz, 2H), 2.79 (t, J = 7.2 Hz, 2H), 2.48 – 2.34 (m, 5H), 2.23 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ142.6, 142.4, 141.6, 141.3, 135.1, 134.6, 132.2, 131.0, 130.6, 123.0 129.8, 129.2, 129.1, 128.4, 127.8, 126.54, 126.50, 122.9, 121.9, 110.4, 110.1, 46.0, 26.7, 23.2, 21.5, 10.9; **IR** (KBr, cm^{-1}) 3060, 2957, 2923, 2856, 2747, 1511, 1493, 1458, 1416, 1340, 1311, 1233, 1159, 1137, 1088, 1071, 1011, 968, 916, 862, 833, 812, 736, 701, 668, 616, 574; **HRMS** (DART) Calcd for $C_{21}H_{21}BrNO_2S$ $(M+H)^+$ 430.0471, found 430.0471.

7-methyl-5-(m-tolyl)-6-tosyl-2,3-dihydro-1H-pyrrolizine (2h)



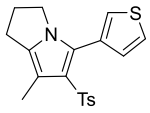
60%, 33 mg, white solid, m.p. = 158 - 159 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.2 Hz, 2H), 7.30 – 7.23 (m, 1H), 7.19 (m, 1H), 7.16 – 7.09 (m, 4H), 3.69 (t, J = 7.1 Hz, 2H), 2.77 (t, J = 7.3 Hz, 2H), 2.37 (m, 8H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.3, 141.9, 137.2, 134.5, 131.6, 131.2, 130.8, 129.2, 129.0, 127.6, 127.5, 126.6, 121.4, 110.1, 45.9, 26.8, 23.1, 21.4, 11.0. **IR** (KBr, cm^{-1}) 3062, 2960, 2925, 2865, 1734, 1597, 1529, 1460, 1417, 1363, 1338, 1311, 1234, 1160, 1137, 1087, 1058, 1017, 915, 863, 840, 813, 735, 703, 663, 617, 573; **HRMS** (DART) Calcd for $C_{22}H_{24}NO_2S$ $(M+H)^+$ 366.1522, found 366.1522.

7-methyl-5-(naphthalen-2-yl)-6-tosyl-2,3-dihydro-1H-pyrrolizine (2j)



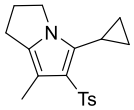
72%, 43 mg, white solid, m.p. = 164 - 165 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (m, 3H), 7.78 (s, 1H), 7.49 (m, 5H), 7.08 (d, J = 8.1 Hz, 2H), 3.72 (t, J = 7.1 Hz, 2H), 2.80 (t, J = 7.3 Hz, 2H), 2.40 (p, J = 7.2 Hz, 2H), 2.31 (s, 3H), 2.25 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.4, 141.8, 134.8, 133.0, 132.7, 131.3, 129.8, 129.1, 128.5, 128.3, 128.2, 127.7, 127.2, 126.6, 126.5, 126.2, 121.9, 110.3, 46.0, 26.8, 23.2, 21.4, 11.0. **IR** (KBr, cm^{-1}) 3054, 2956, 2923, 2858, 2746, 1917, 1729, 1630, 1494, 1442, 1407, 1334, 1309, 1214, 1188, 1159, 1136, 1086, 1057, 1018, 950, 899, 865, 816, 747, 701, 664, 614, 573; **HRMS** (DART) Calcd for $C_{25}H_{24}NO_2S$ $(M+H)^+$ 402.1522, found 402.1523.

7-methyl-5-(thiophen-3-yl)-6-tosyl-2,3-dihydro-1H-pyrrolizine (2k)



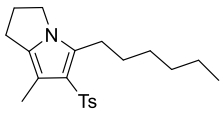
75%, 40 mg, white solid, m.p. = 189- 190 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, J = 8.1 Hz, 2H), 7.36 (d, J = 2.6 Hz, 1H), 7.33 – 7.30 (m, 1H), 7.16 – 7.07 (m, 3H), 3.75 (t, J = 7.1 Hz, 2H), 2.77 (d, J = 7.2 Hz, 2H), 2.40 (p, J = 7.0 Hz, 2H), 2.33 (s, 3H), 2.23 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.4, 141.7, 134.7, 130.4, 129.5, 129.1, 126.4, 126.3, 126.1, 124.5, 121.4, 110.6, 46.2, 26.7, 23.1, 21.4, 11.1. **IR** (KBr, cm^{-1}) 3104, 2955, 2923, 1719, 1595, 1555, 1492, 1416, 1335, 1300, 1232, 1181, 1156, 1136, 1087, 1061, 1019, 922, 870, 837, 809, 735, 698, 622, 622, 575; **HRMS** (DART) Calcd for $C_{19}H_{20}NO_2S_2$ $(M+H)^+$ 358.0930, found 358.0930.

5-cyclopropyl-7-methyl-6-tosyl-2,3-dihydro-1H-pyrrolizine (2l)



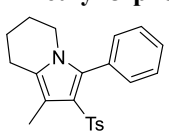
78%, 37 mg, white solid, m.p. = 135 - 136 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 3.86 (t, J = 7.0 Hz, 2H), 2.64 (t, J = 7.3 Hz, 2H), 2.39 (d, J = 6.6 Hz, 5H), 2.12 (m, 4H), 0.94 (q, J = 5.5, 4.9 Hz, 2H), 0.70 (q, J = 5.5 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ142.4, 142.2, 133.3, 132.2, 129.2, 126.4, 121.4, 109.6, 46.3, 27.2, 22.5, 21.5, 10.8, 7.2, 6.6. **IR** (KBr, cm^{-1}**)** 2929, 2854, 2662, 1613, 1598, 1448, 1349, 1192, 1159, 1094, 1063, 1008, 903,846, 815, 707, 588, 547; **HRMS** (DART) Calcd for $C_{18}H_{22}NO_2S$ $(M+H)^+$ 316.1366, found 316.1364.

5-hexyl-7-methyl-6-tosyl-2,3-dihydro-1H-pyrrolizine (2m)



48%, 34 mg, white solid, m.p. =121 - 122 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 7.9 Hz, 2H), 3.83 (t, J = 7.0 Hz, 2H), 2.93 – 2.85 (m, 2H), 2.70 (t, J = 7.2 Hz, 2H), 2.42 (d, J = 15.2 Hz, 5H), 2.08 (s, 3H), 1.55 (q, J = 7.7 Hz, 2H), 1.41 – 1.21 (m, 6H), 0.90 (t, J = 5.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.4, 142.2, 133.3, 133.2, 129.3, 126.4, 118.8, 109.0, 45.0, 31.6, 30.2, 29.4, 26.9, 26.0, 22.8, 22.6, 21.5, 14.1, 10.7. **IR** (KBr, cm^{-1}**)** 2955, 2927, 2853, 2216, 1915, 1705, 1598, 1493, 1439, 1381, 1345, 1299, 1184, 1159, 1133, 1084, 1015, 916, 813, 767, 670, 576; **HRMS** (DART) Calcd for $C_{21}H_{30}NO_2S$ $(M+H)^+$ 360.1992, found 360.1992.

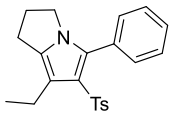
1-methyl-3-phenyl-2-tosyl-5,6,7,8-tetrahydroindolizine (2n)



42%, 23 mg, white solid, m.p. = 180 - 181 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 6.6 Hz, 3H), 7.27 – 7.23 (m, 2H), 7.15 (d, J = 8.1 Hz, 2H), 3.48 (s, 2H), 2.67 (s, 2H), 2.37 (s, 3H), 2.22 (s, 3H), 1.85 – 1.76 (m, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.4, 141.8, 134.6,

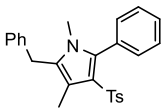
131.2, 130.7, 129.1, 128.6, 127.8, 126.7, 126.4, 119.4, 113.4, 44.4, 23.4, 21.6, 21.4, 20.6, 9.6. **IR** (KBr, cm^{-1}) 3060, 2926, 2861, 1732, 1716, 1699, 1649, 1572, 1539, 1492, 1460, 1445, 1388, 1365, 1310, 1299, 1269, 1216, 1186, 1151, 1095, 1071, 1032, 969, 919, 876, 814, 778, 735, 701,670, 641, 594, 571; **HRMS** (DART) Calcd for $C_{22}H_{24}NO_2S$ $(M+H)^+$ 366.1522, found 366.1521.

7-ethyl-5-phenyl-6-tosyl-2,3-dihydro-1H-pyrrolizine (2o)



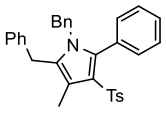
45%, 25 mg, white solid, m.p. = 160 - 161 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.2 Hz, 2H), 7.39 – 7.30 (m, 5H), 7.10 (d, J = 8.1 Hz, 2H), 3.67 (t, J = 7.1 Hz, 2H), 2.84 (t, J = 7.3 Hz, 2H), 2.75 (q, J = 7.5 Hz, 2H), 2.39 (p, J = 7.1 Hz, 2H), 2.33 (s, 3H), 1.18 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.2, 142.0, 133.9, 131.3, 131.1, 130.7, 129.0, 128.4, 127.7, 126.6, 121.0, 116.9, 45.6, 26.8, 23.9, 21.4, 18.8, 15.1. **IR** (KBr, cm^{-1}) 3061, 2963, 2926, 2870, 2071, 1913, 1674, 1597, 1515, 1492, 1448, 1404, 1351, 1300, 1259, 1230, 1160, 1138, 1091, 1023, 967, 920, 863, 811, 759, 736, 707, 665, 615, 575; **HRMS** (DART) Calcd for $C_{22}H_{24}NO_2S$ $(M+H)^+$ 366.1522, found 366.1522.

2-benzyl-1,3-dimethyl-5-phenyl-4-tosyl-1H-pyrrole (2p)



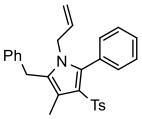
53%, 33 mg, pale white solid, m.p. = 147 - 148 °C, purified by chromatography (PE/EA = 6/1, R_f = 0.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.2 Hz, 2H), 7.42 – 7.34 (m, 3H), 7.31 – 7.24 (m, 2H), 7.23 – 7.17 (m, 2H), 7.14 (d, J = 8.1 Hz, 1H), 3.95 (s, 2H), 3.03 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.4, 141.7, 138.3, 136.7, 131.3, 130.7, 129.1, 128.8, 128.6, 127.9, 127.8, 126.6, 126.5, 119.2, 116.4, 31.8, 30.2, 21.5, 10.5. **IR** (KBr, cm^{-1}) 3060, 3028, 2925, 1915, 1805, 1736, 1653, 1599, 1520, 1493, 1461, 1386, 1311, 1233, 1181, 1144, 1096, 1074, 1018, 970, 923, 838, 813, 762, 733, 703, 661, 614, 589, 563; **HRMS** (DART) Calcd for $C_{26}H_{26}NO_2S$ $(M+H)^+$ 416.1679, found 419.1679.

1,2-dibenzyl-3-methyl-5-phenyl-4-tosyl-1H-pyrrole (2q)



49%, 36 mg, pale white solid, m.p. = 167 - 168 °C, purified by chromatography (PE/EA = 6/1, R_f = 0.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.2 Hz, 2H), 7.33 (t, J = 7.4 Hz, 1H), 7.28 – 7.10 (m, 12H), 6.96 (d, J = 7.2 Hz, 2H), 6.71 – 6.66 (m, 2H), 4.60 (s, 2H), 3.74 (s, 2H), 2.38 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 141.6, 138.5, 137.4, 137.3, 131.3, 130.3, 129.1, 128.8, 128.7, 128.6, 127.8, 127.7, 127.3, 126.7, 126.5, 125.5, 119.9, 117.2, 47.9, 30.0, 21.5, 10.6. **IR** (KBr, cm^{-1}) 3061, 3028, 2926, 1953, 1807, 1736, 1600, 1521, 1494, 1454, 1396, 1356, 1312, 1181, 1157, 1135, 1090, 1060, 1028, 973, 919, 849, 812, 763, 735, 699, 667, 606, 588, 566, 540; **HRMS** (DART) Calcd for $C_{32}H_{30}NO_2S$ $(M+H)^+$ 492.1992, found 492.1990.

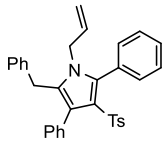
1-allyl-2-benzyl-3-methyl-5-phenyl-4-tosyl-1H-pyrrole (2r)



49%, 36 mg, pale white solid, m. p. = 167 - 168 °C, purified by chromatography (PE/EA = 6/1, Rf = 0.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.2 Hz, 2H), 7.42 (m, 1H), 7.36 (t, J = 7.4 Hz, 2H), 7.31 (m, 2H), 7.27 – 7.15 (m, 5H), 7.06 (d, J = 7.3 Hz, 2H), 5.67 – 5.47 (m, 1H), 5.70 – 5.49 (m, 1H), 5.04 (d, J = 10.4 Hz, 1H), 4.66 (d, J = 17.1 Hz, 1H), 4.05 – 3.97 (m, 2H of of CH_2-CH=), 3.94 (s, 2H), 2.39 (s, 3H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 141.7, 138.6, 136.8, 133.6, 131.3, 130.5, 129.1, 128.9, 128.7, 128.3, 127.8, 127.6, 126.7, 126.5, 119.6, 116.8, 116.4, 46.7, 29.9, 21.5, 10.5. **IR** (KBr, cm^{-1}) 3061, 3027, 2925, 2854, 1719,

1642, 1598, 1520, 1493, 1453, 1394, 1312, 1141, 1089, 1024, 923, 813, 762, 734, 701, 664, 589; **HRMS** (ESI) Calcd for $C_{28}H_{28}NO_2S$ $(M+H)^+$ 442.1835, found 442.1844.

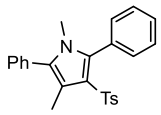
1-allyl-2-benzyl-3,5-diphenyl-4-tosyl-1H-pyrrole (2b from ref 2)



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 – 7.33 (m, 5H), 7.30 – 7.22 (m, 7H), 7.18 – 7.14 (m, 3H), 7.00 – 6.98 (m, 4H), 5.59 – 5.51 (m, 1H), 5.04 (dd, J = 10.4, 0.92 Hz, 2H), 4.66 (dd, J = 17.1, 0.9 Hz, 1H), 4.01 – 4.00 (m, 2H of CH_2-CH=), 3.78 (s, 2H), 2.32 (s, 3H).

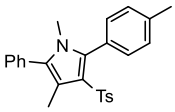
The structure of the product **2r** about the migration group was determined with the reference of ref S2 (J. Org. Chem., **2013**, 78, 7508–7517). The chemical shift of the methylene in the allyl of product **2r** was consistent with the product **2b** from ref S2 which was very similar to **2r**.

1,3-dimethyl-2,5-diphenyl-4-tosyl-*1H*-pyrrole (2s)



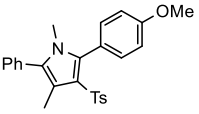
59%, 36 mg, pale white solid, m. p. = 162 - 163 ºC, purified by chromatography (PE/EA = 6/1, R_f = 0.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.1 Hz, 2H), 7.48 – 7.36 (m, 6H), 7.35 – 7.27 (m, 4H), 7.15 (d, J = 8.1 Hz, 2H), 3.10 (s, 3H), 2.36 (s, 3H), 2.22 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 141.6, 136.9, 132.3, 131.3, 131.2, 130.9, 130.9, 129.1, 128.9, 128.5, 128.1, 127.9, 126.8, 112.0, 116.7, 33.1, 21.5, 10.9. **IR** (KBr, cm^{-1}) 3056, 2955, 2925, 2855, 1912, 1682, 1599, 1522, 1491, 1462, 1382, 1312, 1265, 1181, 1147, 1100, 1078, 1014, 920, 854, 813, 758, 737, 702, 669, 655, 591; **HRMS** (DART) Calcd for $C_{25}H_{24}NO_2S$ $(M+H)^+$ 402.1522, found 402.1521.

1,3-dimethyl-2-phenyl-5-(p-tolyl)-4-tosyl-*1H*-pyrrole (2t)



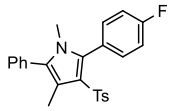
73%, 44 mg, pale white solid, m. p. = 173 - 174 ºC, purified by chromatography (PE/EA = 6/1, R_f = 0.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, J = 8.2 Hz, 2H), 7.47 – 7.34 (m, 3H), 7.32 – 7.19 (m, 6H), 7.16 (d, J = 8.1 Hz, 2H), 3.10 (s, 3H), 2.43 (s, 3H), 2.37 (s, 3H), 2.20 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 141.7, 138.8, 137.1, 132.2, 131.3, 131.1, 130.9, 129.1, 128.7, 128.4, 128.0, 127.8, 126.8, 119.8, 116.6, 33.1, 21.5, 10.9. **IR** (KBr, cm^{-1}) 3028, 2954, 2924, 2857, 1910, 1735, 1700, 1652, 1599, 1558, 1538, 1492, 1461, 1379, 1312, 1211, 1182, 1147, 1100, 1079, 1014, 969, 919, 860, 816, 767, 731, 705, 664, 620, 590; **HRMS** (DART) Calcd for $C_{26}H_{26}NO_2S$ $(M+H)^+$ 416.1679, found 416.1680.

2-(4-methoxyphenyl)-1,4-dimethyl-5-phenyl-3-tosyl-*1H*-pyrrole (2u)



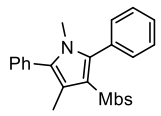
48%, 31 mg, pale white solid, m. p. = 184 - 185 ºC, white solid, purified by chromatography (PE/EA = 6/1, R_f = 0.3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.1 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.31 (d, J = 7.1 Hz, 1H), 7.24 – 7.13 (m, 4H), 7.09 (d, J = 8.0 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H), 3.03 (s, 3H), 2.29 (s, 3H), 2.14 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.0, 142.5, 141.7, 136.8, 132.5, 132.1, 131.3, 130.9, 129.1, 128.4, 128.0, 126.8, 122.8, 119.9, 116.6, 113.4, 55.3, 33.0, 21.5, 11.0. **IR** (KBr, cm^{-1}) 3059, 2956, 2924, 2851, 2042, 1892, 1732, 1649, 1612, 1574, 1533, 1492, 1464, 1379, 1290, 1249, 1177, 1147, 1101, 1079, 1066, 1030, 968, 921, 861, 831, 768, 729, 704, 664, 622, 586; **HRMS** (DART) Calcd for $C_{26}H_{26}NO_3S$ $(M+H)^+$ 432.1628, found 432.1628.

2-(4-fluorophenyl)-1,4-dimethyl-5-phenyl-3-tosyl-*1H*-pyrrole (2v)



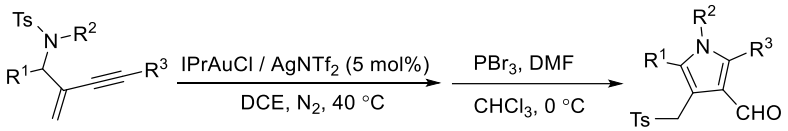
64%, 40 mg, pale white solid, m. p. = 147 – 148 °C, purified by chromatography (PE/EA = 6/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.1 Hz, 2H), 7.46 – 7.36 (m, 3H), 7.32 – 7.24 (m, 4H), 7.17 (d, J = 8.1 Hz, 2H), 7.12 (t, J = 8.6 Hz, 2H), 3.10 (s, 3H), 2.37 (s, 3H), 2.21 (s, 3H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 163.1 (d, $J_{C\text{-}F}$= 249.0 Hz), 142.7, 141.4, 135.6, 133.2 (d, $J_{C\text{-}F}$ = 8.3 Hz), 132.5, 131.1, 130.9, 129.2, 128.5, 128.2, 126.8, 120.3, 116.8, 115.1 (d, $J_{C\text{-}F}$ = 21.7 Hz), 33.1, 21.5, 10.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.45. **IR** (KBr, cm^{-1}) 3060, 2955, 2925, 2855, 1895, 1733, 1653, 1599, 1530, 1493, 1464, 1381, 1312, 1228, 1181, 1147, 1099, 1079, 1015, 968, 921, 864, 838, 812, 768, 732, 705, 664, 641, 622, 590, 574; **HRMS** (DART) Calcd for $C_{25}H_{23}NFO_2S$ $(M+H)^+$ 420.1428, found 420.1426.

3-((4-methoxyphenyl)sulfonyl)-1,4-dimethyl-2,5-diphenyl-*1H*-pyrrole (2w)



60%, 38 mg, pale white solid, m. p. = 155 – 156 °C, purified by chromatography (PE/EA = 6/1, R_f = 0.3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.7 Hz, 2H), 7.49 – 7.37 (m, 6H), 7.33 (m, 4H), 6.84 (d, J = 8.7 Hz, 2H), 3.84 (s, 3H), 3.12 (s, 3H), 2.25 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4, 136.6, 136.4, 132.2, 131.3, 131.3, 130.9, 128.9, 128.4, 128.1, 128.0, 120.4, 116.6, 113.7, 55.5, 33.1, 10.9. **IR** (KBr, cm^{-1}) 3060, 2957, 2926, 2844, 1899, 1729, 1695, 1595, 1495, 1463, 1411, 1381, 1311, 1297, 1258, 1179, 1144, 1102, 1074, 1022, 922, 853, 833, 802, 759, 736, 702, 671, 593, 562; **HRMS** (ESI) Calcd for $C_{25}H_{24}NO_3S$ $(M+H)^+$ 418.1471, found 418.1482.

1.4 General procedure for the synthesis of 2a'', 2p'' and 2s''.

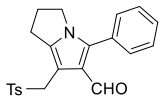


1a, 1p, 1s **2a'', 2p'', 2s''**

Taking **2a''** as an example: in a Schlenk tube with a magnetic bar under nitrogen atmosphere was added IPrAuCl (5 mol%), $AgNTf_2$ (5 mol%) in dry dichloroethane (DCE, 2 mL). After stirred for 5 min, the substrate **1a** (or **1p**, **1s**) (0.2 mmol) was added. The mixture was stirred at 40 °C until the starting materia was completely consumed (monitored by TLC). Then the solvent was evaporated by rotary evaporator to get the crude products.

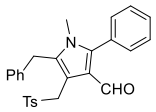
Under N_2 atmosphere, PBr_3 (0.2 mmol, 1 eq) in hexane was added dropwise into the solution of DMF (2 mmol, 1 eq) in anhydrous $CHCl_3$ (2 mL) at 0 °C. The reaction mixture was stirred for 1 h before the addition of the solution of crude product in $CHCl_3$ obtained in the previous step. The reaction temperature was raised to room temperature and maintained for 2 h. After the reaction completed, the reaction mixture was poured into ice saturated $NaHCO_3$ (aq.) with violent stirring. The mixture was extracted with DCM, and the organic phase was washed with brine and dried with anhydrous Na_2SO_4. Then the solvent was removed by rotary evaporator. The resulting residue was purified by chromatography (SiO_2, PE: EA = 5: 1) to obtain **2a''** as a white solid (8 mg, 11%).

5-phenyl-7-(tosylmethyl)-2,3-dihydro-*1H*-pyrrolizine-6-carbaldehyde (2a'')



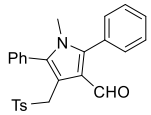
11%, 8 mg, white solid, m.p. = 145 - 146 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.51 – 7.38 (m, 3H), 7.33 – 7.28 (m, 2H), 7.24 (d, J = 8.2 Hz, 2H), 4.77 (s, 2H), 3.96 (t, J = 7.1 Hz, 2H), 3.03 (t, J = 7.4 Hz, 2H), 2.61 – 2.48 (m, 2H), 2.40 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.6 144.2, 140.9, 138.8, 136.2, 129.7, 129.4, 129.2, 128.8, 128.8, 128.7, 123.9, 101.4, 53.19, 46.1, 27.2, 23.5, 21.6. **IR** (KBr, cm^{-1}) 3062, 3028, 2955, 2923, 2851, 2736, 1796, 1735, 1652, 1601, 1541, 1525, 1488, 1459, 1388, 1361, 1314, 1171, 1136, 1085, 1025, 973, 912, 834, 814, 741, 700, 647, 621, 547; **HRMS** (DART) Calcd for $C_{22}H_{22}NO_3S$ $(M+H)^+$ 380.1315, found 380.1316.

5-benzyl-1-methyl-2-phenyl-4-(tosylmethyl)-*1H*-pyrrole-3-carbaldehyde (2p'')



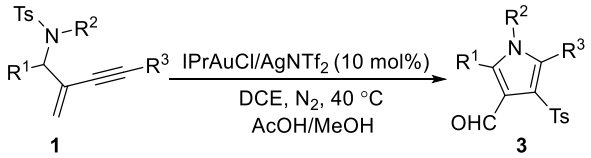
15%, 13 mg, white solid, m.p. = 117 - 118 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 7.78 (d, J =8.1, 2H), 7.5 – 7.45 (m, 3H), 7.36 – 7.27 (m, 6H), 7.25 (t, J = 7.3 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 4.87 (s, 2H), 4.32 (s, 2H), 3.27 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.6, 144.6, 144.3, 137.6, 136.4, 134.8, 131.0, 129.2, 128.9, 128.8, 128.5, 127.9, 126.7, 120.8, 107.8, 52.6, 32.1, 30.2, 21.6. **IR** (KBr, cm^{-1}) 3071, 3021, 2966, 2923, 2766, 1793, 1765, 1632, 1600, 1541, 1489, 1461, 1366, 1361, 1315, 1211, 1037, 1025, 973, 834, 814, 742, 701, 647, 624, 544; **HRMS** (DART) Calcd for $C_{27}H_{26}NO_3S$ $(M+H)^+$ 444.1628, found 444.1626.

1-methyl-2,5-diphenyl-4-(tosylmethyl)-*1H*-pyrrole-3-carbaldehyde (2s'')



10%, 8 mg, white solid, m.p. = 107 – 108 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.38 (s, 1H), 7.70 (d, J = 8.1 Hz, 2H), 7.54 – 7.44 (m, 8H), 7.43 – 7.40 (m, 2H), 7.25 – 7.22 (m, 2H), 4.68 (s, 2H), 3.30 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.5, 144.4, 144.0, 137. 9, 136.9, 131.0, 130.98, 129.6, 129.3, 129.2, 129.0, 128.9, 128.8, 128.6, 128.6, 121.2, 107.7, 53.3, 33.3, 21.6. **IR** (KBr, cm^{-1}) 3061, 2955, 2924, 2852, 1659, 1526, 1484, 1456, 1382, 1315, 1178, 1145, 1084, 969, 934, 800, 763, 702, 658, 593, 555, 511; **HRMS** (DART) Calcd for $C_{26}H_{24}NO_3S$ $(M+H)^+$ 430.1471, found 430.1472.

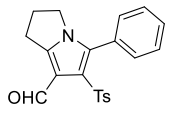
1.5 General procedure for the Synthesis of 3



1 **3**

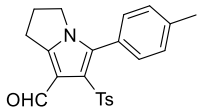
In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added IPrAuCl (10 mol%), $AgNTf_2$ (10 mol%), MeOH (30 μL) and AcOH (60 μL) in dry dichloroethane (DCE, 1.5 mL). After stirred for 5 min, the substrate **1** (0.15 mmol), 2, 3-dicyano-5, 6-dichlorobenzoquinone (DDQ, 0.33 mmol) were added respectively. The mixture was stirred at 40 °C until the starting materials was completely consumed monitored by TLC. After that, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product.

5-phenyl-6-tosyl-2, 3-dihydro-1H-pyrrolizine-7-carbaldehyde (3a)



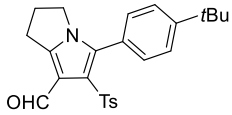
66%, 36 mg, yellow solid, m. p. = 173 – 174 °C, purified by chromatography (PE/EA = 3/1, R_f = 0.3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.43 (m, 5H), 7.31 (d, J = 7.6 Hz, 2H), 7.12 (d, J = 7.9 Hz, 2H), 3.73 (t, J = 7.3 Hz, 2H), 3.17 (t, J = 7.4 Hz, 2H), 2.54 – 2.43 (m, 2H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.5, 144.6, 143.3, 140.7, 132.9, 130.5, 129.4, 129.4, 128.9, 128.1, 126.8, 124.2, 115.5, 46.3, 26.3, 26.1, 21.5. **IR** (KBr, cm^{-1}) 3061, 2922, 2852, 1893, 1719, 1657, 1599, 1543, 1491, 1465, 1428, 1398, 1363, 1302, 1181, 1141, 1085, 1057, 1024, 968, 923, 887, 848, 812, 783, 763, 735, 700, 666, 575; **HRMS** (DART) Calcd for $C_{21}H_{20}NO_3S$ $(M+H)^+$ 366.1158, found 366.1157.

5-(p-tolyl)-6-tosyl-2, 3-dihydro-*1H*-pyrrolizine-7-carbaldehyde (3b)



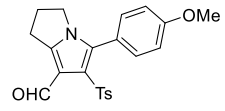
73%, 41 mg, pale white solid, m. p. = 180 - 181 °C, purified by chromatography (PE/EA = 3/1, R_f = 0.3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.49 (d, J = 8.1 Hz, 2H), 7.24 (m, 4H), 7.16 (d, J = 8.1 Hz, 2H), 3.74 (t, J = 7.3 Hz, 2H), 3.18 (t, J = 7.5 Hz, 2H), 2.50 (m, 2H), 2.45 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.4, 144.6, 143.3, 140.8, 139.5, 133.2, 130.4, 129.4, 128.8, 126.8, 125.9, 124.0, 115.4, 46.2, 26.3, 26.1, 21.5; **IR** (KBr, cm^{-1}) 3028, 2957, 2923, 1918, 1662, 1597, 1490, 1429, 1404, 1363, 1307, 1235, 1210, 1182, 1142, 1085, 1052, 1018, 968, 922, 887, 817, 737, 703, 666, 604, 577, 541; **HRMS** (DART) Calcd for $C_{22}H_{22}NO_3S$ $(M+H)^+$ 380.1315, found 380.1313.

5-(4-(tert-butyl)phenyl)-6-tosyl-2,3-dihydro-*1H*-pyrrolizine-7-carbaldehyde (3c)



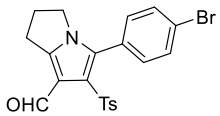
57%, 36 mg, white solid, m.p. = 195 - 196 °C, purified by chromatography (PE/EA = 3/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.43 (dd, J = 8.0, 5.2 Hz, 4H), 7.23 (d, J = 8.2 Hz, 2H), 7.11 (d, J = 8.1 Hz, 2H), 3.76 (t, J = 7.3 Hz, 2H), 3.18 (t, J = 7.5 Hz, 2H), 2.58 – 2.42 (m, 2H), 2.35 (s, 3H), 1.39 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.6, 152.6, 144.5, 143.2, 140.5, 133.1, 130.2, 129.3, 126.9, 125.8, 125.0, 124.0, 115.5, 46.3, 34.8, 31.3, 26.3, 26.2, 21.5; **IR** (KBr, cm^{-1}) 3061, 2961, 2871, 1662, 1597, 1543, 1488, 1429, 1399, 1364, 1305, 1236, 1204, 1180, 1143, 1115, 1084, 1053, 1017, 922, 887, 841, 812, 735, 702, 666, 601, 577; **HRMS** (ESI) Calcd for $C_{25}H_{28}NO_3S$ $(M+H)^+$ 422.1784, found 422.1796.

5-(4-methoxyphenyl)-6-tosyl-2, 3-dihydro-*1H*-pyrrolizine-7-carbaldehyde (3d)



75%, 43 mg, white solid, m. p. = 129 -130 °C, purified by chromatography (PE/EA = 3/1, R_f = 0.2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.45 (s, 1H), 7.45 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 8.3 Hz, 2H), 3.87 (s, 3H), 3.72 (t, J = 7.3 Hz, 2H), 3.16 (t, J = 7.5 Hz, 2H), 2.48 (m, 2H), 2.34 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.5, 160.5, 144.5, 143.3, 140.8, 133.0, 131.9, 129.4, 126.8, 123.9, 120.9, 115.4, 113.6, 55.3, 46.2, 26.3, 26.1, 21.4; **IR** (KBr, cm^{-1}) 3033, 2960, 2931, 1900, 1667, 1596, 1493, 1422, 1400 1361, 1307, 1232, 1211, 1180, 1142, 1085, 1042, 1010, 968, 922, 888, 813, 737, 700, 666, 604, 577, 541; **HRMS** (ESI) Calcd for $C_{22}H_{22}NO_4S$ $(M+H)^+$ 396.1264, found 396.1277 .

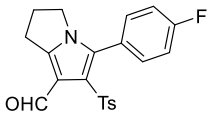
5-(4-bromophenyl)-6-tosyl-2,3-dihydro-*1H*-pyrrolizine-7-carbaldehyde (3e)



61%, 41 mg, yellow solid, m. p. = 190 - 191 °C, purified by chromatography (PE/EA = 3/1, R_f = 0.3); **^{1}H NMR** δ 10.43 (s, 1H), 7.57 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 7.19 (m, 4H), 3.74 (t, J = 7.3 Hz, 2H), 3.16 (t, J = 7.5 Hz,

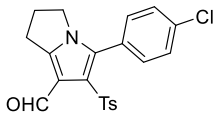
2H), 2.57 – 2.43 (m, 2H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.1, 145.1, 143.6, 140.5, 132.1, 131.5, 131.4, 129.6, 127.8, 126.8, 124.5, 124.1, 115.5, 46.4, 26.2, 26.1, 21.5; **IR** (KBr, cm^{-1}) 3060, 2958, 2923, 1913, 1662, 1596, 1543, 1485, 1465, 1429, 1395, 1365, 1307, 1232, 1181, 1142, 1083, 1048, 1010, 967, 922, 886, 834, 813, 735, 703, 666, 574, 540; **HRMS** (ESI) Calcd for $C_{21}H_{19}BrNO_3S$ $(M+H)^+$ 444.0264, found 444.0275.

5-(4-fluorophenyl)-6-tosyl-2, 3-dihydro-*1H*-pyrrolizine-7-carbaldehyde (3f)



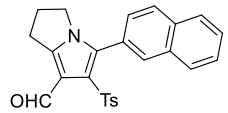
70%, 40 mg, white solid, m. p. = 182 - 183 °C, purified by chromatography (PE/EA = 3/1, R_f = 0.3); **^{1}H NMR** δ 10.47 (s, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.32 (dd, J = 8.2, 5.5 Hz, 2H), 7.15 (m, 4H), 3.74 (t, J = 7.3 Hz, 2H), 3.19 (t, J = 7.5 Hz, 2H), 2.57 – 2.45 (m, 2H), 2.37 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.3, 163.4 (d, $J_{C\text{-}F}$ = 250.0 Hz), 144.7, 143.5, 140.6, 132.5 (d, $J_{C\text{-}F}$ = 8.5 Hz), 131.7, 129.5, 126.8, 124.8, 124.7 (d, $J_{C\text{-}F}$ = 35.0 Hz), 115.5, 115.4 (d, $J_{C\text{-}F}$ = 21.9 Hz), 46.2, 26.2, 26.1, 21.4; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -110.91. **IR** (KBr, cm^{-1}) 3063, 2959, 2922, 1910, 1662, 1599, 1542, 1488, 1430, 1403, 1365, 1304, 1229, 1181, 1142, 1084, 1051, 1015, 921, 887, 842, 814, 735, 702, 667, 605, 576, 540; **HRMS** (ESI) Calcd for $C_{21}H_{19}FNO_3S$ $(M+H)^+$ 384.1064, found 384.1072.

5-(4-chlorophenyl)-6-tosyl-2, 3-dihydro-*1H*-pyrrolizine-7-carbaldehyde (3g)



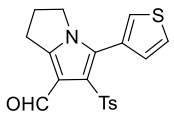
64%, 38 mg, yellow solid, m. p. = 186 - 187 °C, purified by chromatography (PE/EA = 3/1, R_f = 0.3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 7.46 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 8.3 Hz, 2H), 7.26 (d, J = 6.4 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 3.73 (t, J = 7.3 Hz, 2H), 3.16 (t, J = 7.5 Hz, 2H), 2.57 – 2.44 (m, 2H), 2.36 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.2, 145.0, 143.6, 140.5, 135.8, 131.9, 131.5, 129.5, 128.5, 127.3, 126.8, 124.6, 115.5, 46.3, 26.2, 26.1, 21.5. **IR** (KBr, cm^{-1}) 3060, 2959, 2922, 1914, 1663, 1597, 1544, 1485, 1465, 1430, 1399, 1365, 1307, 1232, 1181, 1142, 1088, 1050, 1014, 968, 921, 886, 837, 814, 735, 706, 667, 600, 675, 575, 540; **HRMS** (ESI) Calcd for $C_{21}H_{19}ClNO_3S$ $(M+H)^+$ 400.0769, found 400.0779 .

5-(naphthalen-2-yl)-6-tosyl-2,3-dihydro-*1H*-pyrrolizine-7-carbaldehyde (3h)



55%, 34 mg, white solid, m. p. = 145 - 146 °C, purified by chromatography (PE/EA = 3/1, R_f = 0.3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.50 (s, 1H), 7.89 (t, J = 8.4 Hz, 2H), 7.84 (d, J = 7.1 Hz, 1H), 7.77 (d, J = 1.6 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.44 (d, J = 8.2 Hz, 2H), 7.40 – 7.35 (m, 1H), 7.06 (d, J = 8.1 Hz, 2H), 3.75 (t, J = 7.3 Hz, 2H), 3.19 (t, J = 7.5 Hz, 2H), 2.55 – 2.41 (m, 2H), 2.30 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.4, 144.8, 143.4, 140.6, 133.4, 132.8, 132.6, 130.4, 129.4, 128.3, 127.8, 127.4, 127.2, 126.92, 126.7, 126.3, 124.5, 115.6, 46.4, 26.3, 26.2, 21.4; **IR** (KBr, cm^{-1}) 3055, 2959, 2924, 1926, 1661, 1698, 1543, 1497, 1454, 1428, 1402, 1369, 1305, 1222, 1142, 1084, 1053, 1017, 951, 922, 899, 867, 817, 754, 734, 663, 603, 574; **HRMS** (ESI) Calcd for $C_{25}H_{22}NO_3S$ $(M+H)^+$ 416.1315, found 416.1326.

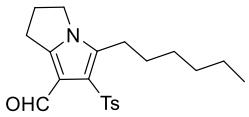
5-(thiophen-3-yl)-6-tosyl-2,3-dihydro-*1H*-pyrrolizine-7-carbaldehyde (3i)



61%, 34 mg, white solid, m. p. = 168 - 169 °C, purified by chromatography (PE/EA = 3/1, R_f = 0.3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.44 (m, J = 8.3 Hz, 3H), 7.38 (dd, J = 4.8, 3.0 Hz, 1H), 7.13 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 4.9 Hz, 1H), 3.80 (t, J = 7.3 Hz, 2H), 3.16 (t, J = 7.5 Hz, 2H), 2.60 – 2.42 (m, 2H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 187.6, 144.7, 143.4, 140.4, 129.4, 129.0, 128.2, 129.0, 127.8, 126.7, 125.4, 124.5,

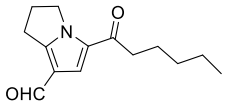
115.7, 46.6, 26.3, 26.2, 21.5. **IR** (KBr, cm^{-1}) 3105, 2958, 2923, 1661, 1596, 1540, 1492, 1431, 1381, 1350, 1304, 1232, 1193, 1142, 1084, 1059, 1017, 930, 878, 808, 734, 702, 661, 606, 573; **HRMS** (ESI) Calcd for $C_{19}H_{18}NO_3S_2$ $(M+H)^+$ 372.0723, found 372.0732.

5-hexyl-6-tosyl-2,3-dihydro-*1H*-pyrrolizine-7-carbaldehyde (3j)



24%, 13 mg, white solid, m.p. = 109 – 110 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 7.77 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 5.0 Hz, 2H), 3.89 (t, J = 7.3 Hz, 2H), 3.08 (t, J = 7.5 Hz, 2H), 2.96 – 2.82 (m, 2H), 2.58 – 2.47 (m, 2H), 2.39 (s, 3H), 1.58 – 1.46 (m, 2H), 1.33 (m, 6H), 0.89 (t, J = 6.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 186.7, 144.5, 143.4, 141.3, 135.2, 129.7, 126.6, 121.7, 114.8, 45.5, 31.5, 29.7, 29.3, 26.3, 25.9, 25.5, 22.5, 21.5, 14.0. **IR** (KBr, cm^{-1}**)** 3108, 2955, 2927, 2857, 2719, 1652, 1540, 1474, 1414, 1388, 1287, 1192, 1143, 975, 862, 824, 726, 636, 578, 543; **HRMS** (ESI) Calcd for $C_{21}H_{28}NO_3S$ $(M+H)^+$ 374.1784, found 374.1796.

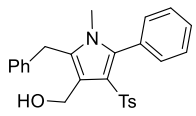
5-hexanoyl-2,3-dihydro-*1H*-pyrrolizine-7-carbaldehyde (3j')



33%, 11 mg, viscous liquid, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 7.32 (s, 1H), 4.37 (t, J = 7.3 Hz, 2H), 3.11 (d, J = 7.6 Hz, 2H), 2.74 (t, J = 7.5 Hz, 2H), 2.67 – 2.50 (m, 2H), 1.83 – 1.65 (m, 2H), 1.48 – 1.30 (m, 4H), 0.92 (t, J = 6.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ **IR** (KBr, cm^{-1}) 3108, 2955, 2927, 2857, 2719, 1652, 1540, 1474, 1414, 1388, 1287, 1192, 1143, 975, 862, 824, 726, 636, 578, 543; **HRMS** (ESI) Calcd for $C_{14}H_{20}NO_2$ $(M+H)^+$ 234.1489, found 234.1494.

(2-benzyl-1-methyl-5-phenyl-4-tosyl-1H-pyrrol-3-yl)methanol (3k')

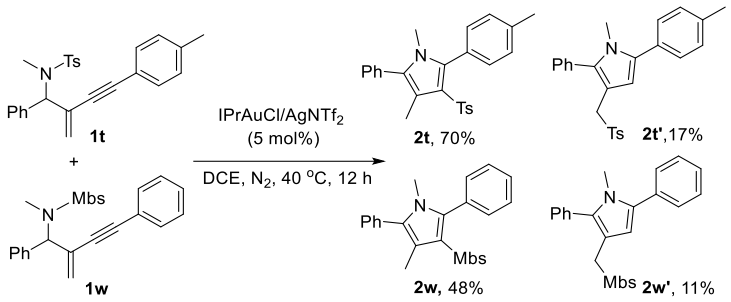
The crude mixture obtained from the general preparation procedure of **3k** was concerntrated by rotary evaporator. The residue was dissolved in 2 mL methanol at 0 °C before $NaBH_4$ (0.3 mmol, 2 eq) was added. The reaction mixture was stirred for another 30 min before quenched with saturated NH_4Cl solution and etracted with DCM.Then the organic phase was washed with brine and dried with anhydrous Na_2SO_4, and the solvent was removed by rotary evaporator. The resulting residue was purified by chromatography.



48%, 31 mg, white solid, m. p. = 161 – 162 °C, purified by chromatography (PE/EA = 3/1, R_f = 0.3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 3H), 7.30 – 7.19 (m, 4H), 7.14 (t, J = 7.3 Hz, 1H), 7.04 (t, J = 8.5 Hz, 6H), 4.71 (d, J = 6.9 Hz, 2H), 3.98 (s, 2H), 3.59 (t, J = 7.1 Hz, 1H), 2.97 (s, 3H), 2.28 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.0, 140.8, 137.7, 137.6, 131.2, 129.9, 129.7, 129.2, 129.1, 128.8, 128.1, 128.0, 126.70, 126.67, 121.2, 119.3, 55.6, 31.9, 30.2, 21.5. **IR** (KBr, cm^{-1}) 3061, 3028, 2954, 2924, 1731, 1598, 1524, 1493, 1465, 1386, 1294, 1234, 1164, 1138, 1071, 981, 914, 841, 814, 761, 732, 701, 668, 590, 541; **HRMS** (ESI) Calcd for $C_{26}H_{25}NO_3NaS$ $(M+Na)^+$ 454.1447, found 454.1456.

1.6 Control experiment

1.6.1 Crossover experiment



In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added IPrAuCl (5 mol%) and $AgNTf_2$ (5 mol %) in dry dichloroethane (DCE, 1 mL). After stirred for 5 min, the substrates **1t** (0.12 mmol) and **2w** (0.1 mmol) were added. The mixture was stirred at 40 °C until the starting material was completely consumed (monitored by TLC). Then the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute. The yield of products were calculated based on the isolated yield of **2t.**

Comparison of the ^{1}H NMR spectras of crude reaction mixtures (Figure **S1**) illustrated that there was no crossover product.

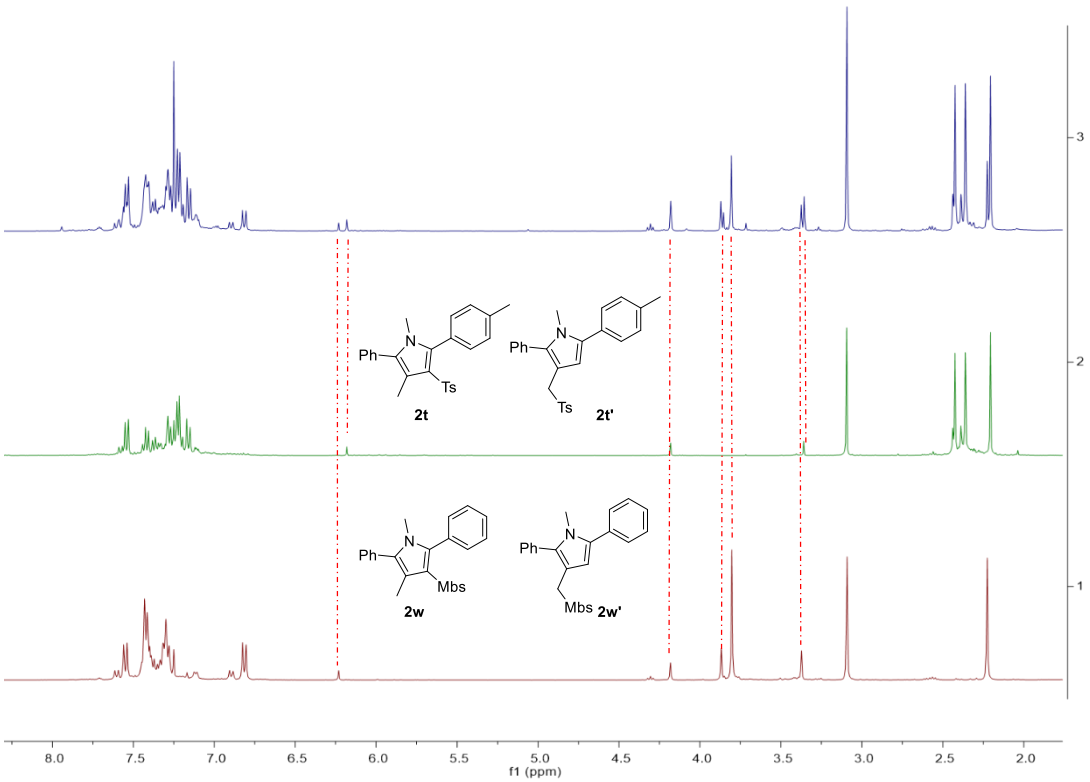
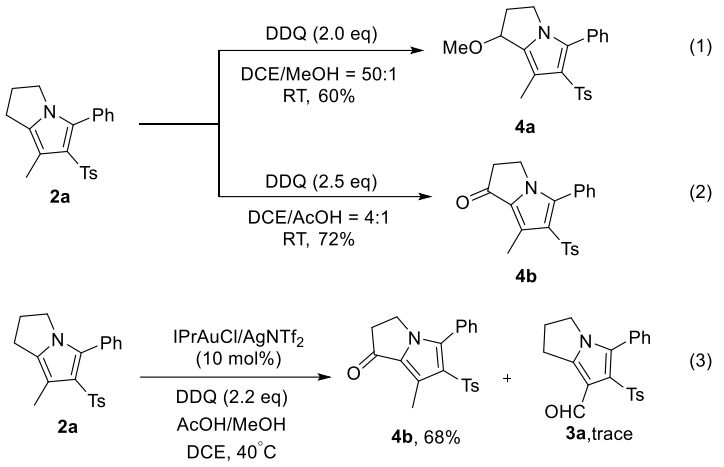


Figure **S1**. The ^{1}H NMR spectras of crude reaction mixtures (top: the mixure of crossover experiment; middle: the reaction mixure with **1t** as starting material; down: the reaction mixure with **1t** as starting material.

1.6.2 Oxidation experiment of 2a

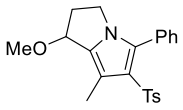


(1): In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added **2a** (0.1 mmol), methanol (20 μL) and DDQ (0.2 mmol) in dichloroethane (1 mL). The mixture was stirred at room temperature until the starting material was completely consumed (monitored by TLC, about 6 h). After that, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product.

(2): In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added **2a** (0.1 mmol), AcOH (250 μL) and DDQ (0.25 mmol) in dichloroethane (1 mL). The mixture was stirred at room temperature until the starting materials was completely consumed (monitored by TLC, about 4 h). After that, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product.

(**3**): In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added IPrAuCl (10 mol%) and $AgNTf_2$ (10 mol %) in dry dichloroethane (DCE, 1 mL). After stirred for 5 min, the substrates **2a** (0.1 mmol), DDQ (0.22 mmol), AcOH (40 μL) and MeOH (20 μL) were added respectively. The mixture was stirred at at 40 °C until the starting materials was completely consumed. After that, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product.

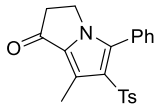
1-methoxy-7-methyl-5-phenyl-6-tosyl-2,3-dihydro-*1H*-pyrrolizine (4a)



60%, 22 mg, white solid, m.p. = 99 - 100 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.2 Hz, 2H), 7.43 – 7.30 (m, 5H), 7.12 (d, J = 8.1 Hz, 2H), 4.68 (d, J = 5.0 Hz, 1H), 3.92 (ddd, J = 11.2, 9.0, 6.9 Hz, 1H), 3.59 (ddd, J = 11.0, 8.7, 1.9 Hz, 1H), 3.34 (s, 3H), 2.54 (ddd, J = 14.6, 9.7, 5.7 Hz, 1H), 2.43 (dd, J = 13.6, 6.6 Hz, 1H), 2.36 (s, 3H), 2.34 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 141.5, 133.6, 132.5, 130.5, 130.4, 129.1, 128.7, 127.8, 126.6, 122.1, 114.2, 75.0, 56.3, 44.2, 35.0, 21.4, 11.3. **IR** (KBr, cm^{-1}) 3061, 2957, 2925, 2855, 2360, 1700, 1620, 1598, 1519, 1492, 1449, 1408, 1341,

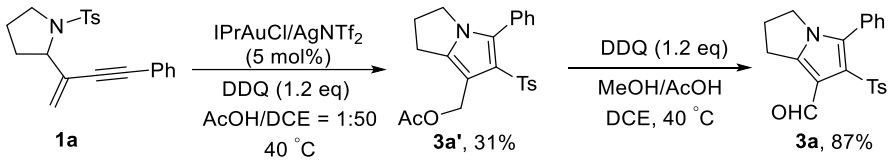
1300, 1226, 1139, 1089, 1019, 967, 923, 846, 811, 734, 702, 655, 583, 543; **HRMS** (DART) Calcd for $C_{22}H_{24}O_3NS$ $(M+H)^+$ 382.1471, found 382.1470.

7-methyl-5-phenyl-6-tosyl-2,3-dihydro-*1H*-pyrrolizin-1-one (4b)



72%, 26 mg, white solid, m.p. = 206 - 207 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.3); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.41 (m, 5H), 7.32 (d, J = 6.8 Hz, 2H), 7.13 (d, J = 8.1 Hz, 2H), 3.96 (t, J = 6.5 Hz, 2H), 2.98 (t, J = 6.5 Hz, 2H), 2.60 (s, 3H), 2.35 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 189.0, 143.4, 140.4, 137.4, 130.2, 129.7, 129.3, 128.6, 128.6, 128.3, 127.2, 126.8, 122.9, 41.1, 38.7, 21.5, 10.3. **IR** (KBr, cm^{-1}) 3061, 2977, 2946, 2890, 2370, 1720, 1670, 1577, 1494, 1421, 1330, 1226, 1130, 1083, 1014, 900, 846, 811, 734, 702, 655, 523, 533; **HRMS** (DART) Calcd for $C_{21}H_{20}O_3NS$ $(M+H)^+$ 366.1158, found 366.1158.

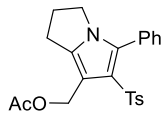
1.6.3 Transformation of 1a to 3a' and 3a



3a': In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added IPrAuCl (5 mol%) and $AgNTf_2$ (5 mol%) in dry dichloroethane (DCE, 1 mL). After stirred for 5 min, the **1a** and AcOH (20 μL), DDQ (1.2 eq) was added respectively. The mixture was stirred at 40 °C until the starting materials was completely consumed monitored by TLC. After that, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product.

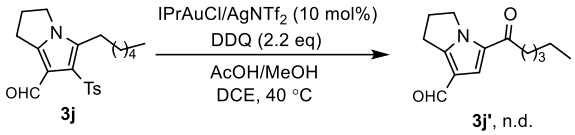
3a: In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added **3a'** and DDQ (1.2 eq) in dry dichloroethane (DCE, 1 mL). MeOH (20 μL) and AcOH (20 μL) was added and mixture was stirred at 40 °C until the starting materials was completely consumed monitored by TLC. After that, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate as elute to afford the pure product.

(5-phenyl-6-tosyl-2,3-dihydro-*1H*-pyrrolizin-7-yl)methyl acetate (3a')



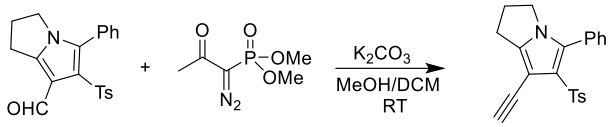
31%, 13 mg, white solid, m.p. = 150 - 151 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.2); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.0 Hz, 2H), 7.43 – 7.36 (m, 3H), 7.31 (d, J = 6.8 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 5.32 (s, 2H), 3.70 (t, J = 7.1 Hz, 2H), 2.93 (t, J = 7.3 Hz, 2H), 2.41 (dd, J = 14.5, 7.2 Hz, 2H), 2.33 (s, 3H), 2.02 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.0, 142.6, 141.5, 137.8, 132.4, 130.6, 130.2, 129.0, 128.8, 127.9, 126.8, 122.1, 109.3, 58.1, 46.1, 26.5, 23.9, 21.4, 21.1. **IR** (KBr, cm^{-1}) 3062, 2956, 2853, 1734, 1646, 1598, 1520, 1488, 1460, 1401, 1382, 1364, 1307, 1232, 1161, 1061, 1020, 952, 921, 853, 808, 701, 658, 573, 541, 491; **HRMS** (ESI) Calcd for $C_{23}H_{23}O_4NaNS$ $(M+Na)^+$ 432.1248, found 432.1249.

1.6.4 Control reaction for the conversion of 3j to 3j'



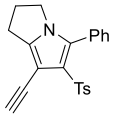
In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added IPrAuCl (10 mol%), $AgNTf_2$ (10 mol%), MeOH (10 μL) and AcOH 20 μL) in dry dichloroethane (DCE, 0.5 mL). After stirred for 5 min, the **3j** (0.05mmol), 2, 3-dicyano-5, 6-dichlorobenzoquinone (DDQ, 0.33 mmol) were added respectively. The reaction was stirred at 40 °C for 12h.

1.7 Derivatization reactions of 3a

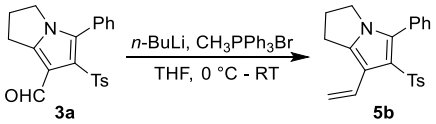


In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added DCM and MeOH (0.6 mL and 0.4 mL) and K_2CO_3 (0.15 mmol), and then the **3a** (0.1 mmol) and Bestmann Reagent[1] (0.12 mmol) were added respectively. The mixture was stirred at room temperature until the starting materials was completely consumed monitored by TLC. After that, the solvent was filtrated and evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (PE/EA = 5/1) to afford the pure product.

7-ethynyl-5-phenyl-6-tosyl-2,3-dihydro-*1H*-pyrrolizine (5a)

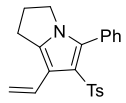


85%, 31 mg, white solid, m.p. = 214 - 215 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.4); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.48 – 7.42 (m, 3H), 7.37 (m, 2H), 7.21 (d, J = 8.1 Hz, 2H), 3.75 (t, J = 7.1 Hz, 2H), 3.28 (s, 1H), 2.96 (t, J = 7.4 Hz, 2H), 2.52 – 2.41 (m, 2H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.3, 142.9, 141.0, 131.6, 130.4, 129.9, 129.2, 129.0, 128.0, 127.2, 124.8, 95.7, 80.8, 76.2, 46.6, 26.4, 24.3, 21.5. **IR** (KBr, cm^{-1}) 3225, 3060, 2957, 2922, 2853, 2108, 1666, 1596, 1554, 1521, 1487, 1463, 1387, 1315, 1233, 1158, 1137, 1084, 1020, 918, 809, 735, 702, 666, 575, 540; **HRMS** (ESI) Calcd for $C_{22}H_{20}O_2NS$ $(M+H)^+$ 362.1209, found 362.1216.



Under N_2 atmosphere, *n*-BuLi (1.1 eq, 2.5 M) in hexane was added dropwise into the suspension of CH_3PPh_3Br (1.2 eq) in anhydrous THF (1 mL) at 0 °C. After stir for 1h, **3a** (0.1 mmol) dissolved in THF (0.5 mL) was added dropwise into the reaction mixture. After the reaction temperature raised to room temperature, the reaction was quenched using saturated NH_4Cl (aq), and extracted with EtOAc. The organic phase was washed with brine and dried with anhydrous Na_2SO_4, then the solvent was removed by rotary evaporator. **5c** was obtained after purified by chromatography (SiO_2, EA: PE = 1: 5, R_f = 0.5).

5-phenyl-6-tosyl-7-vinyl-2,3-dihydro-*1H*-pyrrolizine (5b)



72%, 26 mg, white solid, m.p. = 163 - 164 °C, purified by chromatography (PE/EA = 5/1, R_f = 0.5); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, J = 7.8 Hz, 2H), 7.44 – 7.27 (m, 6H), 7.12 (d, J = 7.7 Hz, 2H), 5.22 (m, 2H), 3.69 (t, J = 7.0 Hz, 2H), 2.97 (t, J = 7.1 Hz, 2H), 2.54 – 2.39 (m, 2H), 2.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.5, 141.8, 134.9, 131.8, 130.6, 130.5, 129.2, 128.9, 128.7, 127.8, 126.6, 120.8, 113., 113.0, 45.7, 26.7, 25.6, 21.4. **IR** (KBr, cm^{-1}) 3301, 3061, 2956, 2923, 2855, 1731, 1619, 1599, 1518, 1488, 1461, 1391, 1317, 1294, 1231, 1180, 1141, 1086, 1037, 1019, 999, 920, 893, 861, 839, 810, 700, 663, 581, 539; **HRMS** (ESI) Calcd for $C_{22}H_{22}O_2NS$ $(M+H)^+$ 364.1366, found 364.1378.

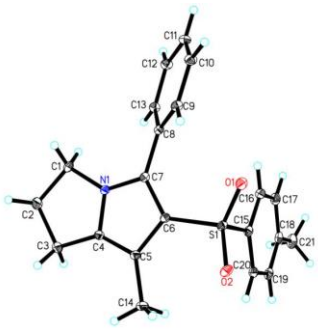
2. References:

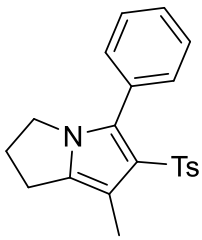
[1] a) S. Müller, B. Liepold, G. J. Roth, H. J. Bestmann, *Synlett* **1996**, 521–522; (b) G. Roth, B. Liepold, S. Müller, H. Bestmann, *Synthesis* **2003**, *2004*, 59–62.

[2] W. T. Teo, W. Rao, M. J. Koh and P. W. H. Chan, *J. Org. Chem.*, 2013, **78**, 7508–7517.

3. X-Ray diffraction analysis

3.1 Crystal data and structure refinement for 2a



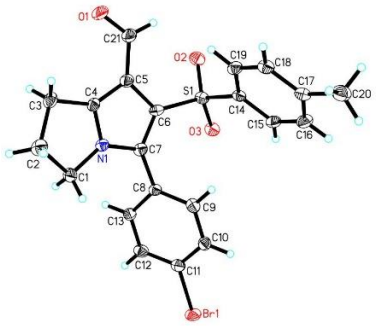


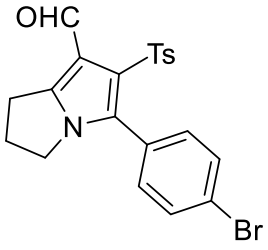
2a (CCDC 1578144)

Identification code	**2a**	
Empirical formula	C21 H21 N O2 S	
Formula weight	351.45	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 31.1655(5) Å	α = 90 °.
	b = 8.49460(10) Å	β = 98.752(2) °.
	c = 13.3472(2) Å	γ = 90(4) °.
Volume	3492.37(9) Å^3	

Z	8
Density (calculated)	1.337 Mg/m^3
Absorption coefficient	1.753 mm^{-1}
F(000)	1488
Crystal size	0.250 x 0.200 x 0.160 mm^3
Theta range for data collection	5.402 to 73.559 °.
Index ranges	-26<=h<=37, -9<=k<=10, -16<=l<=16
Reflections collected	6848
Independent reflections	3443 [R(int) = 0.0194]
Completeness to theta = 66.97 °	99.88 %
Absorption correction	spherical harmonics
Max. and min. transmission	1.000 and 0.552
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3443 / 0 / 228
Goodness-of-fit on F^2	1.082
Final R indices [I>2sigma(I)]	R_1 = 0.0423, wR_2 = 0.1101
R indices (all data)	R_1 = 0.0434, wR_2 = 0.1111
Extinction coefficient	n/a
Largest diff. peak and hole	0.32 and -0.75 e.$Å^{-3}$

3.2 Crystal data and structure refinement for 3e





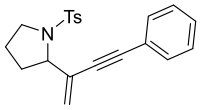
3e (CCDC 1836652)

Identification code	**3e**	
Empirical formula	C21 H18 Br N O3 S	
Formula weight	444.33	
Temperature	172.95(10) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 8.6549(5) Å	α = 90 °.
	b = 18.2100(11) Å	β = 94.769(5) °.

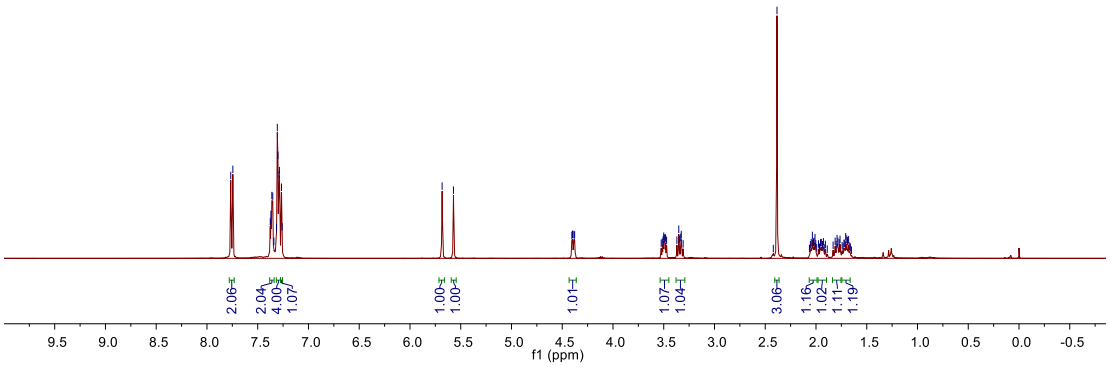
	c = 11.9124(6) Å γ = 90(4) °.
Volume	1870.96(18) $Å^3$
Z	4
Density (calculated)	1.577 Mg/m^3
Absorption coefficient	1.7.223 mm^{-1}
F(000)	904
Crystal size	0.160 x 0.140 x 0.120 mm^3
Theta range for data collection	4.446 to 74.477 °.
Index ranges	-10<=h<=7, -22<=k<=20, -12<=l<=14
Reflections collected	9309
Independent reflections	3679 [R(int) = 0.0766]
Completeness to theta = 66.97 °	99.74 %
Absorption correction	spherical harmonics
Max. and min. transmission	1.000 and 0.552
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3679 / 0 / 245
Goodness-of-fit on F^2	1.017
Final R indices [I>2sigma(I)]	R_1 = 0.0759, wR_2 = 0.2101
R indices (all data)	R_1 = 0.0832, wR_2 = 0.2302
Extinction coefficient	n/a
Largest diff. peak and hole	1.31 and -1.54 e.$Å^{-3}$

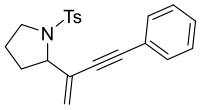
4. Copies of NMR spectra

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1a**

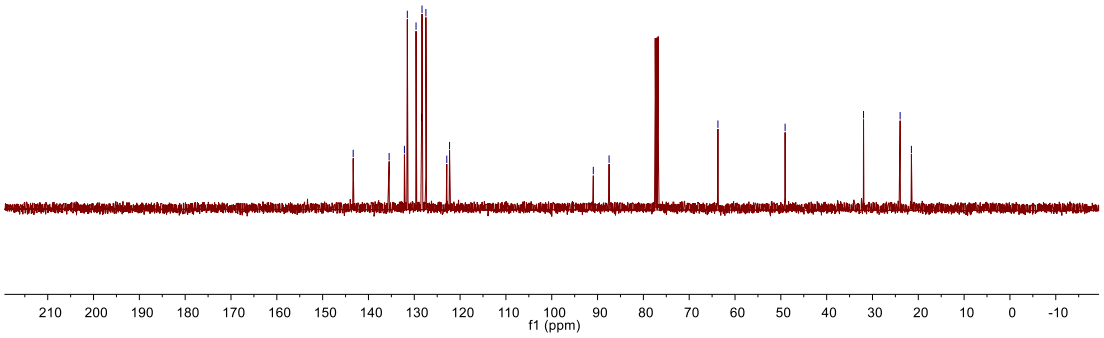


1a

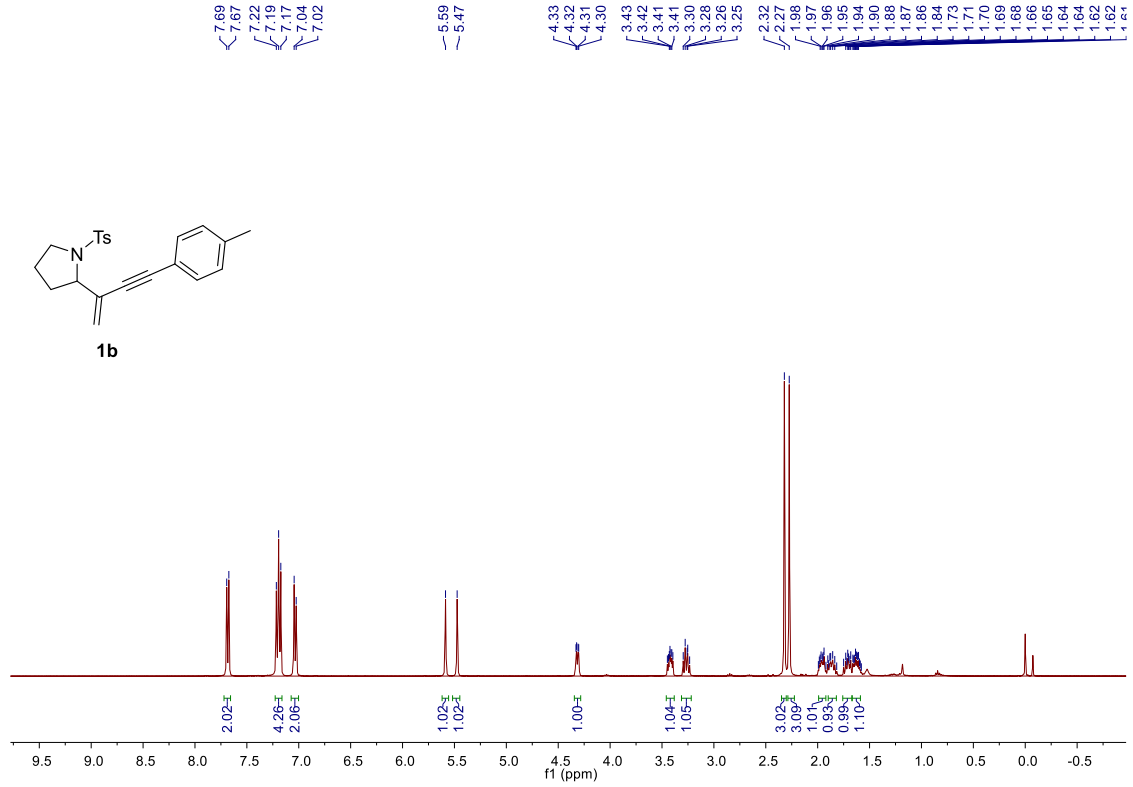


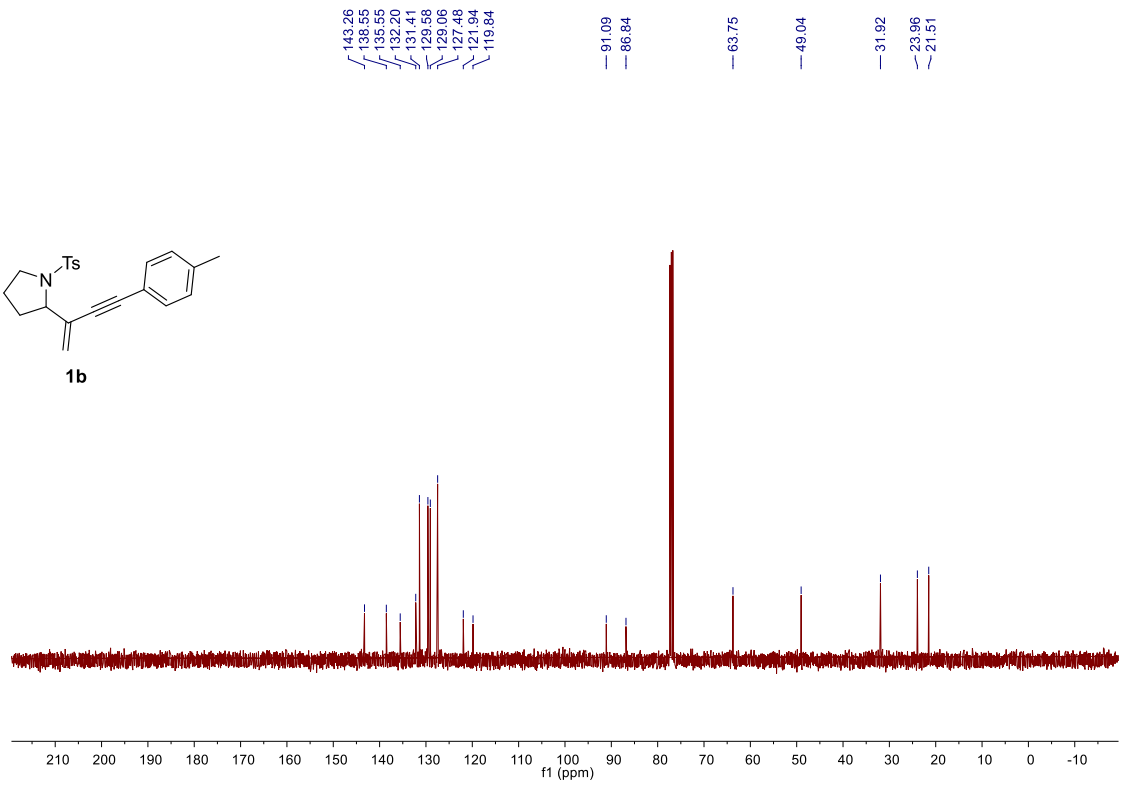


1a

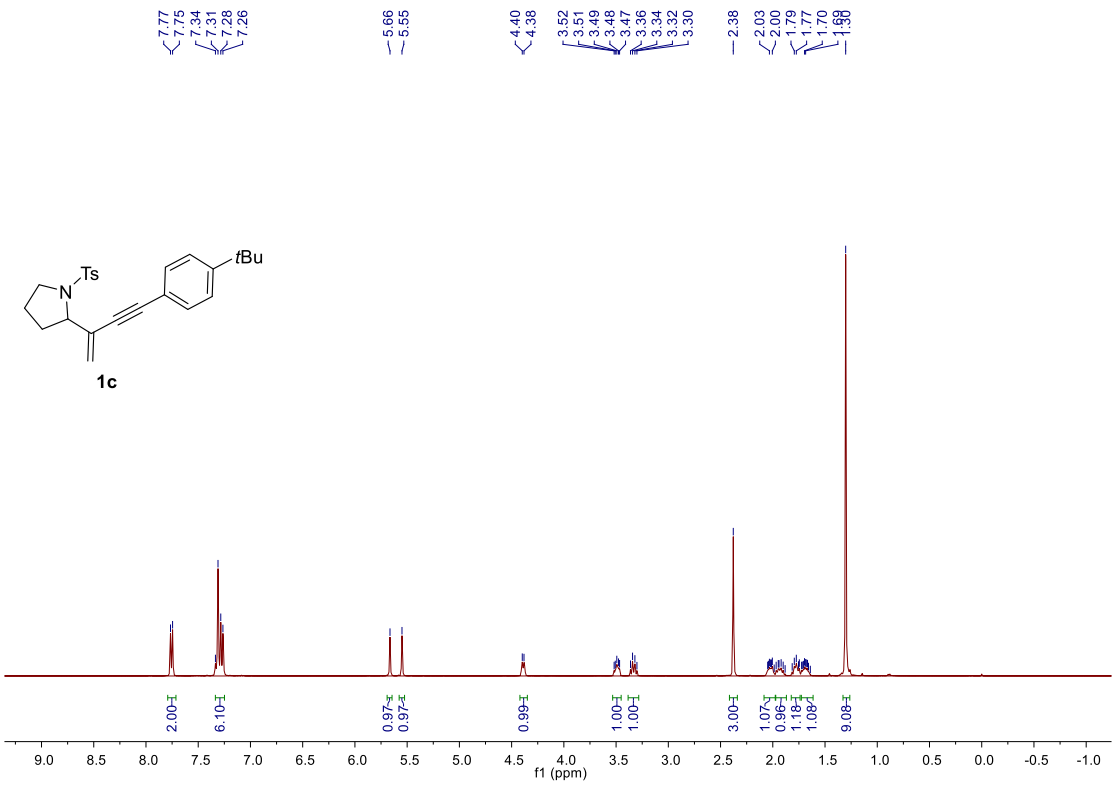


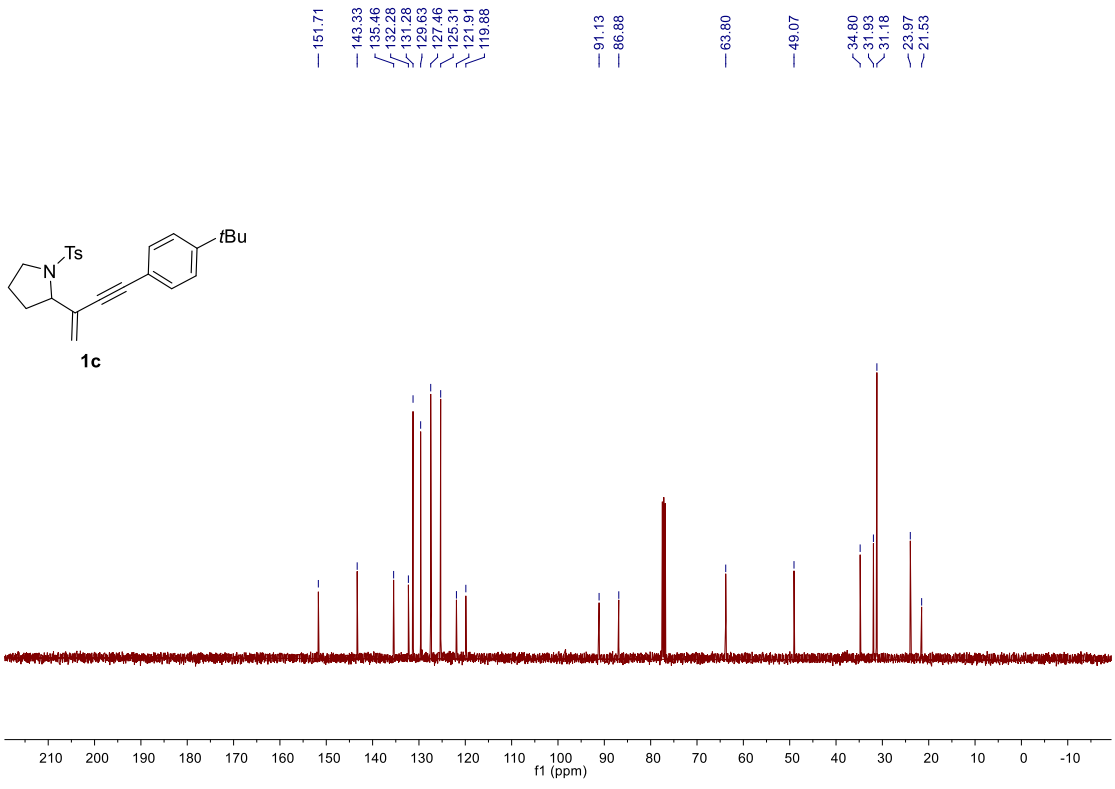
^{1}H NMR (400 MHz, CDCl3) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1b**



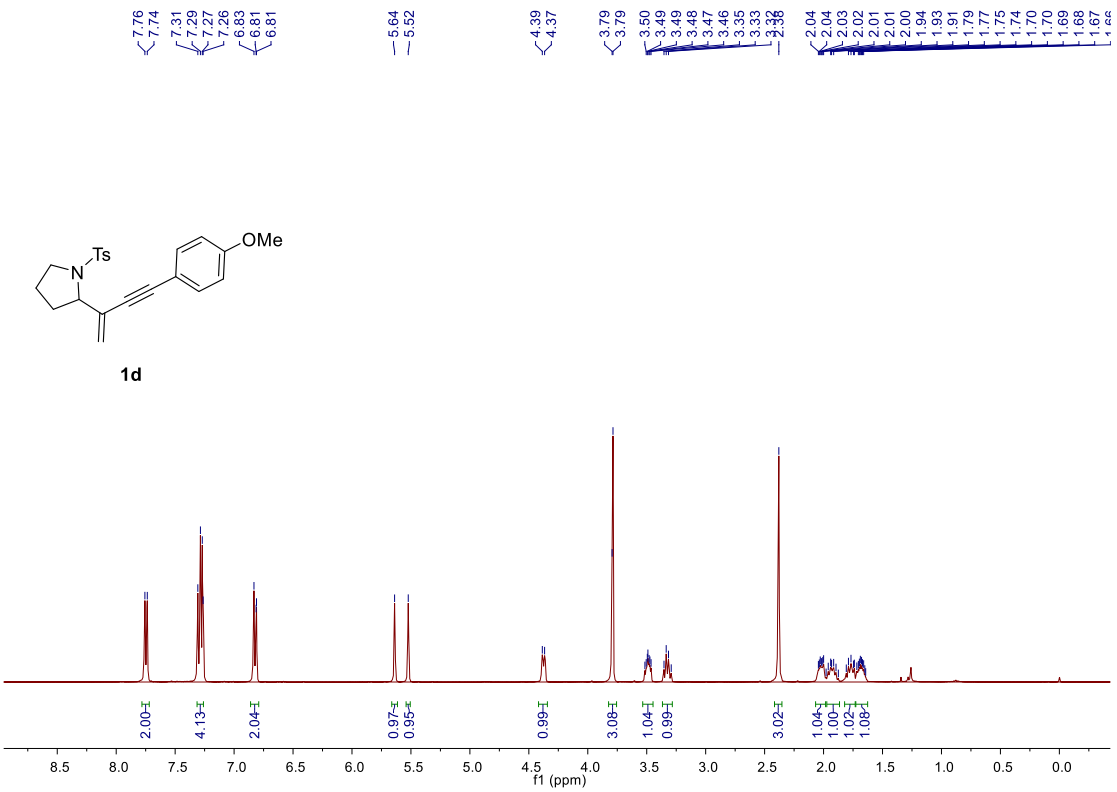


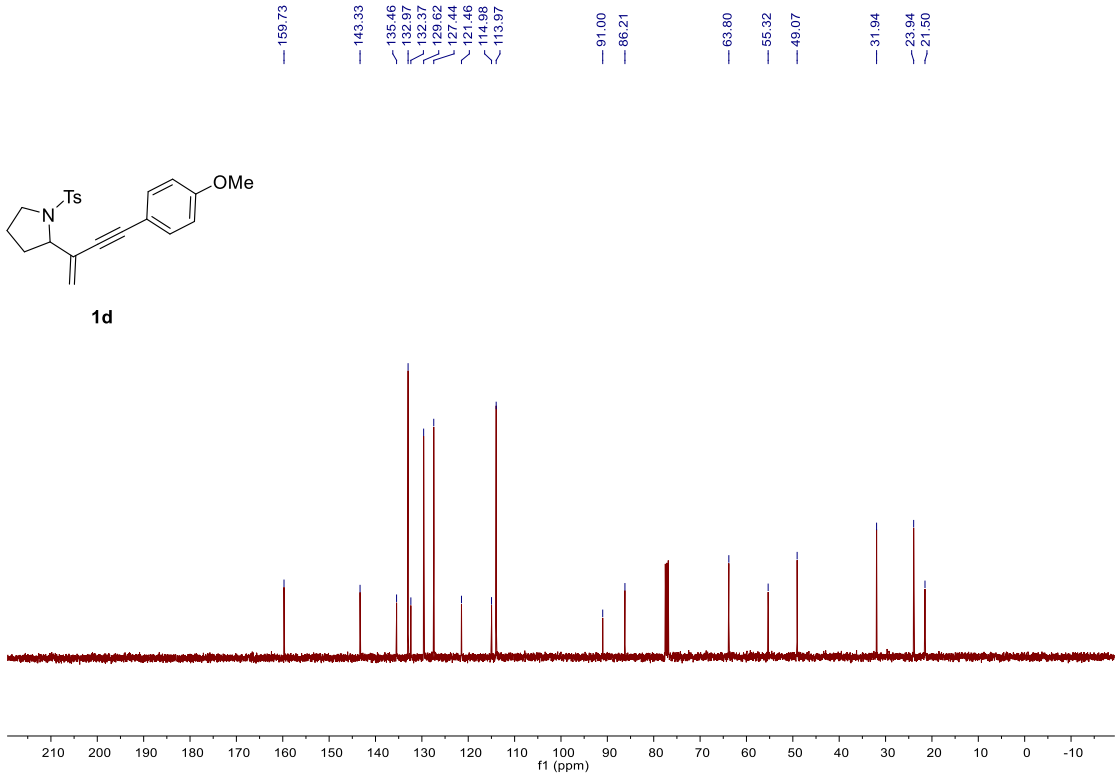
^{1}H NMR (400 MHz, CDCl3) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1c**



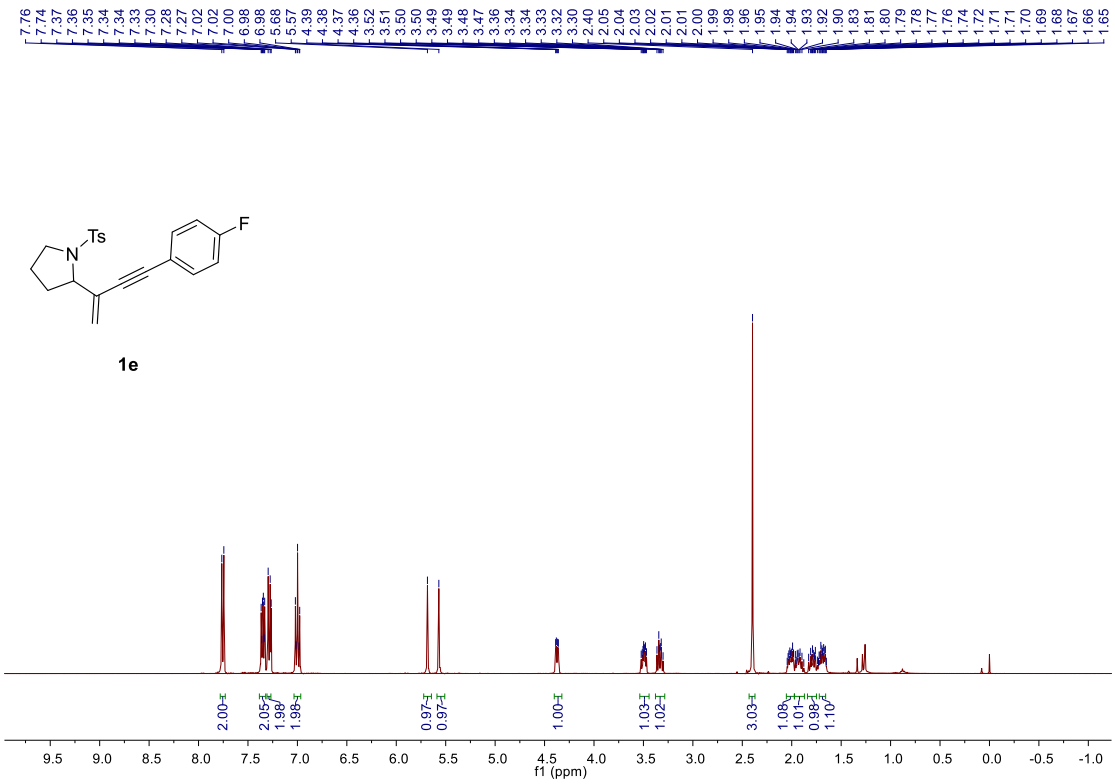


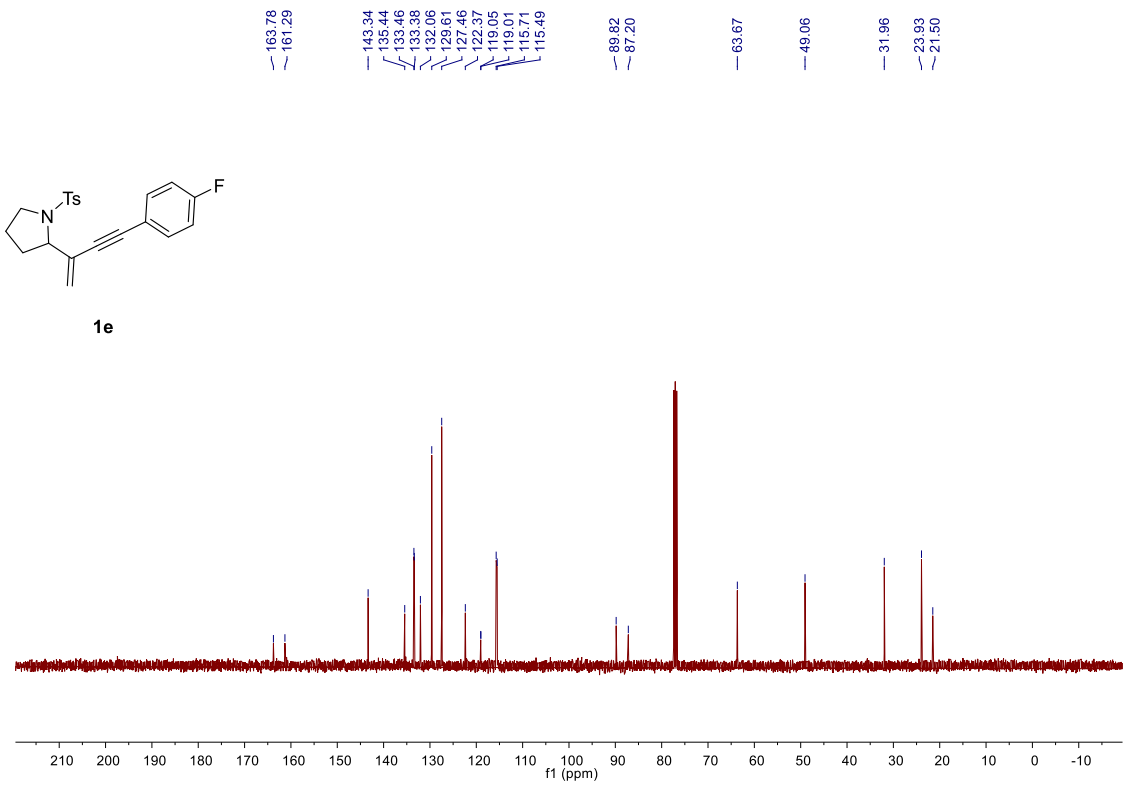
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1d**

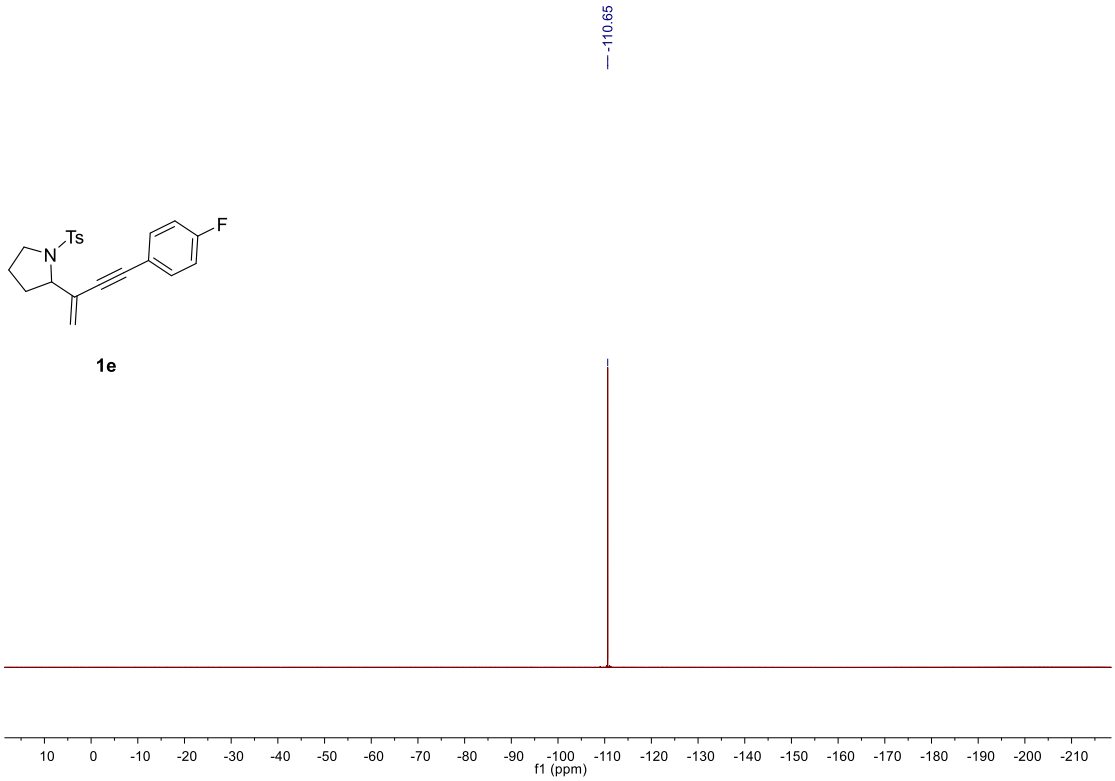




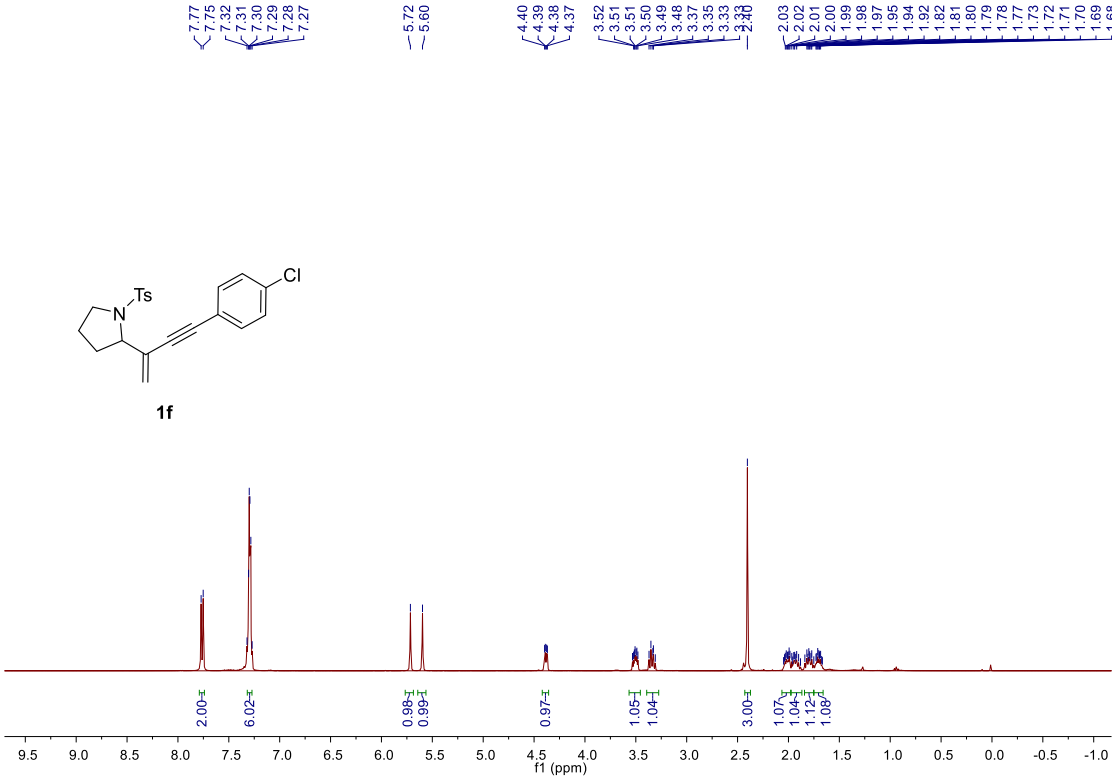
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of substrate **1e**

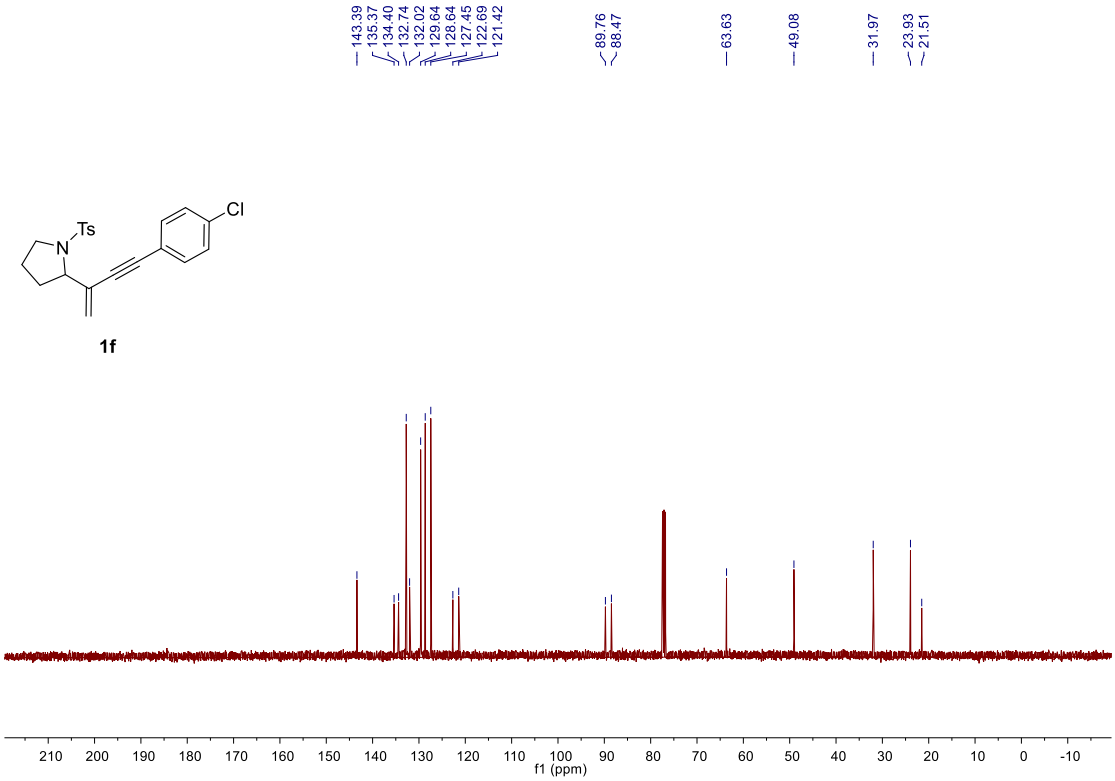




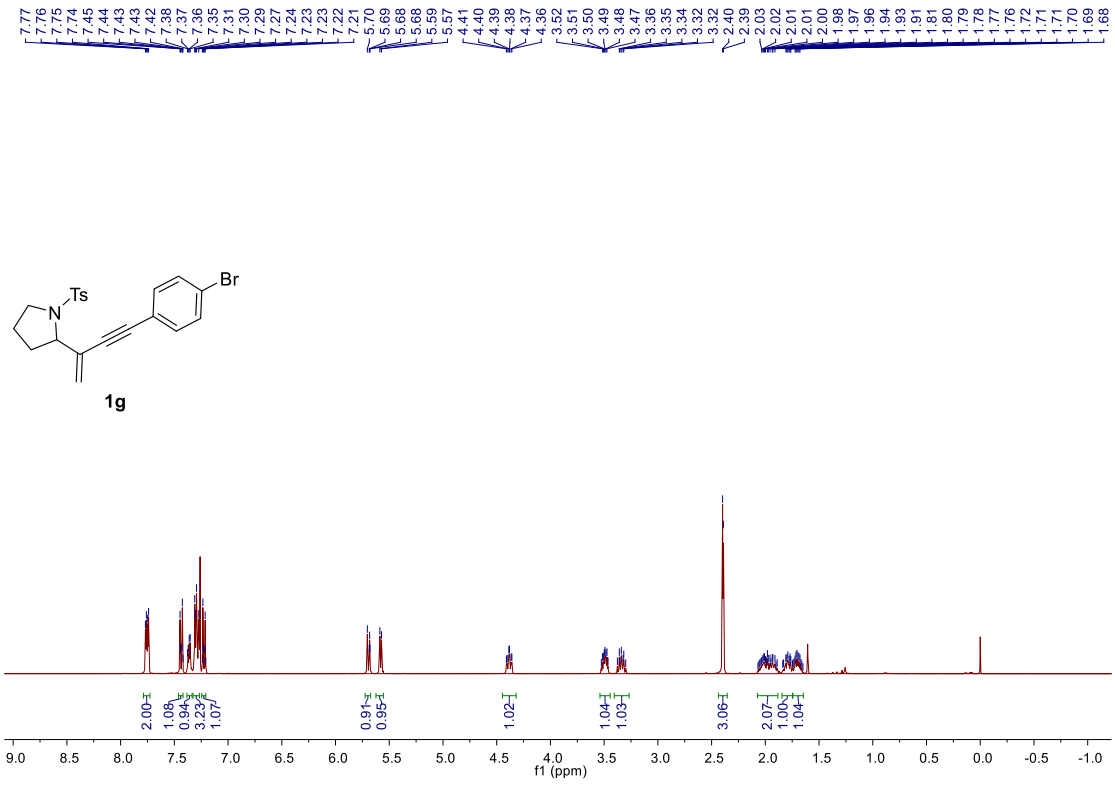


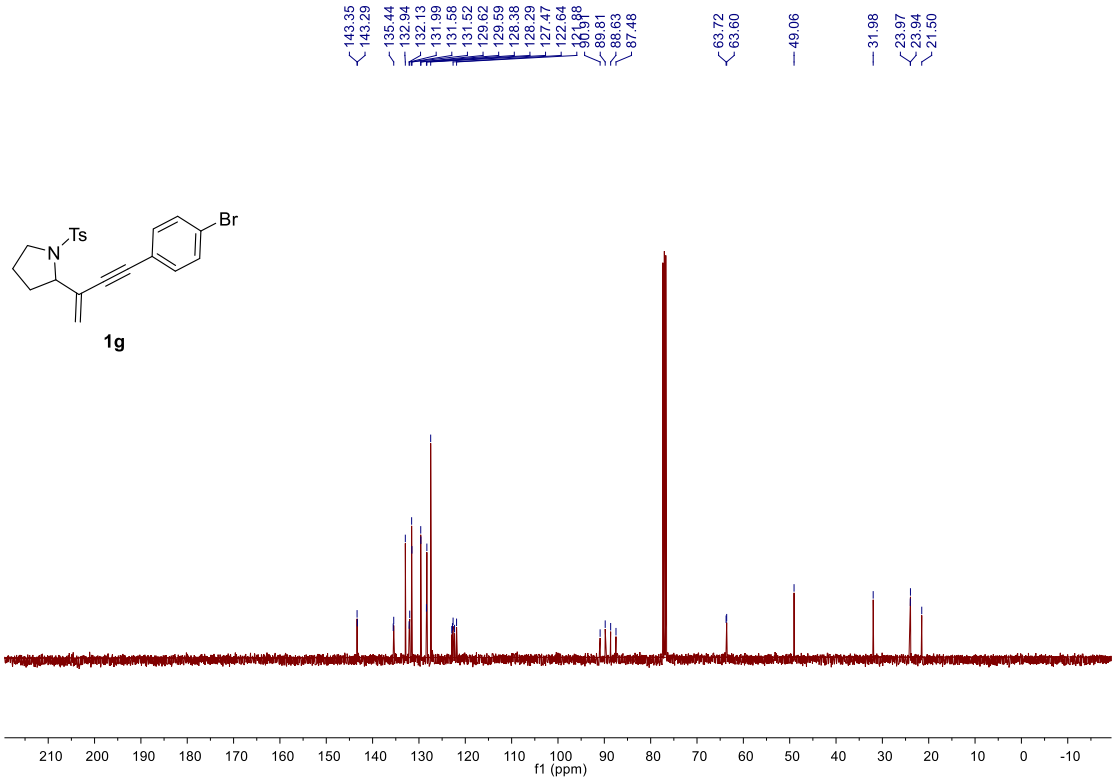
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1f**



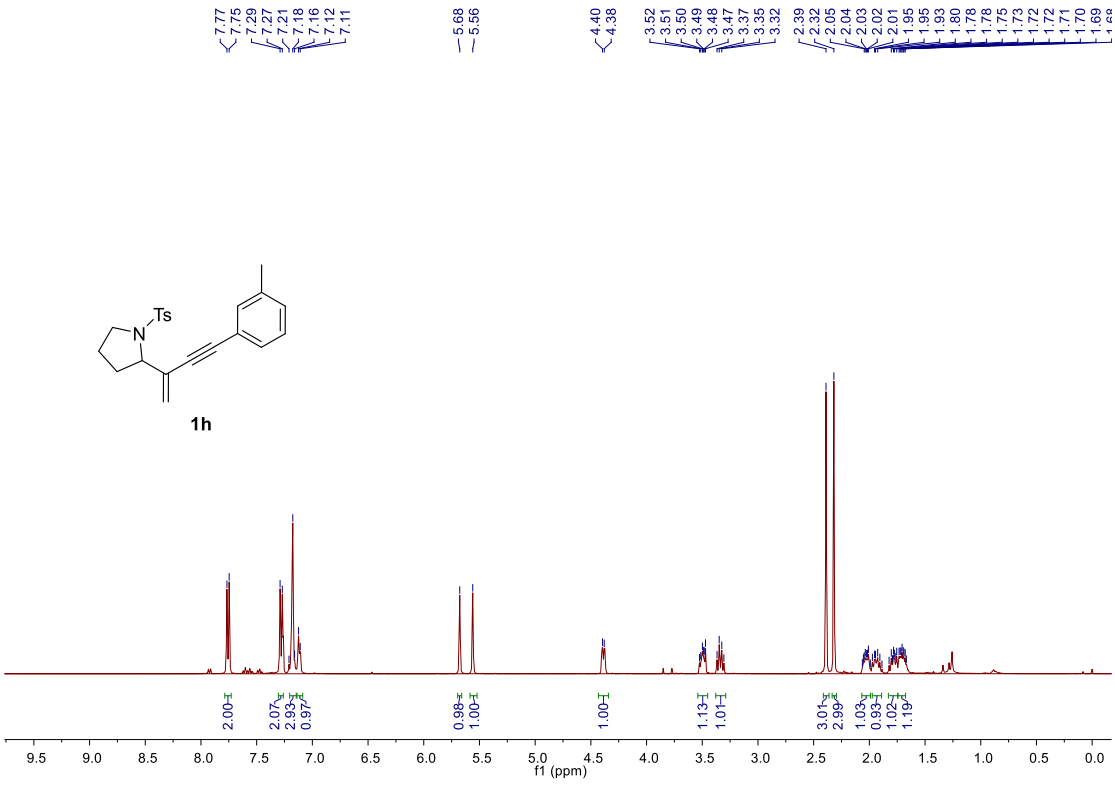


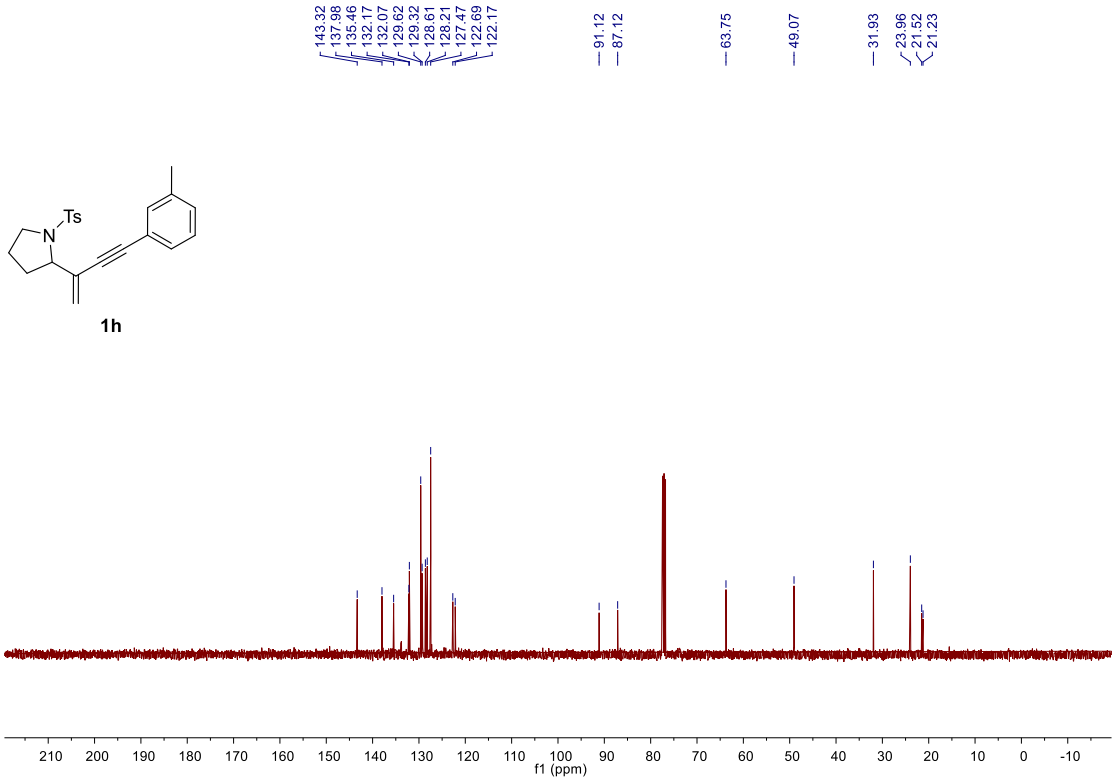
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$) and spectrum of substrate **1g**



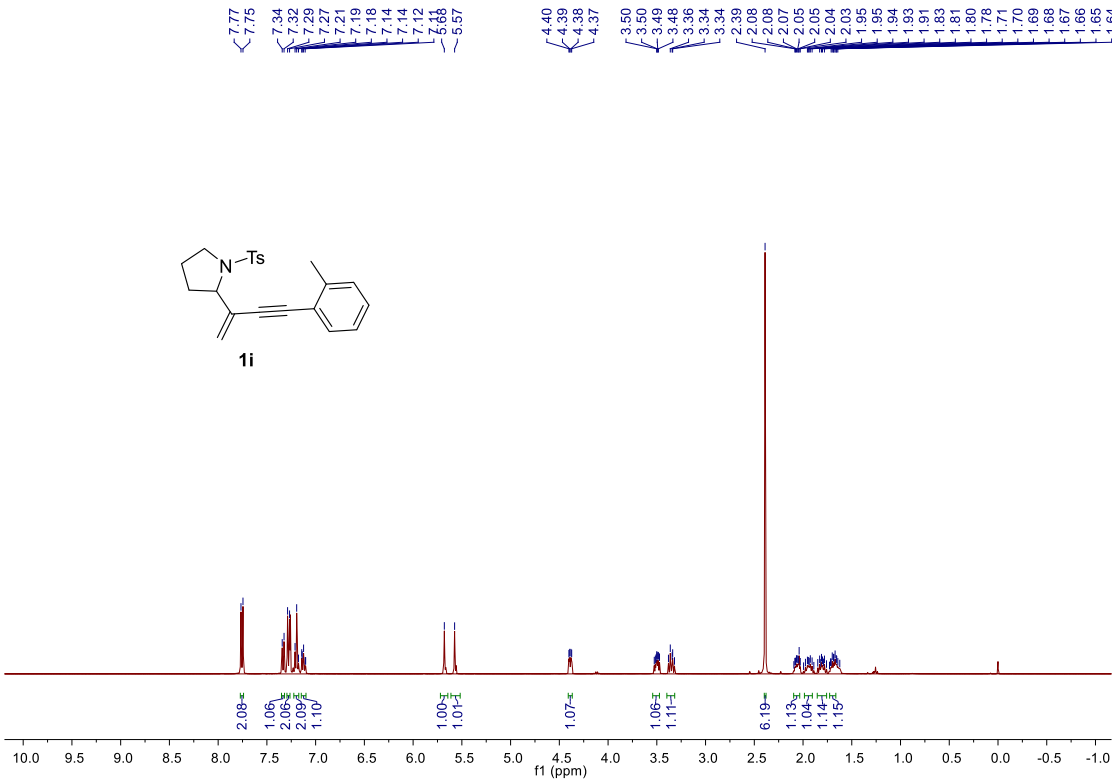


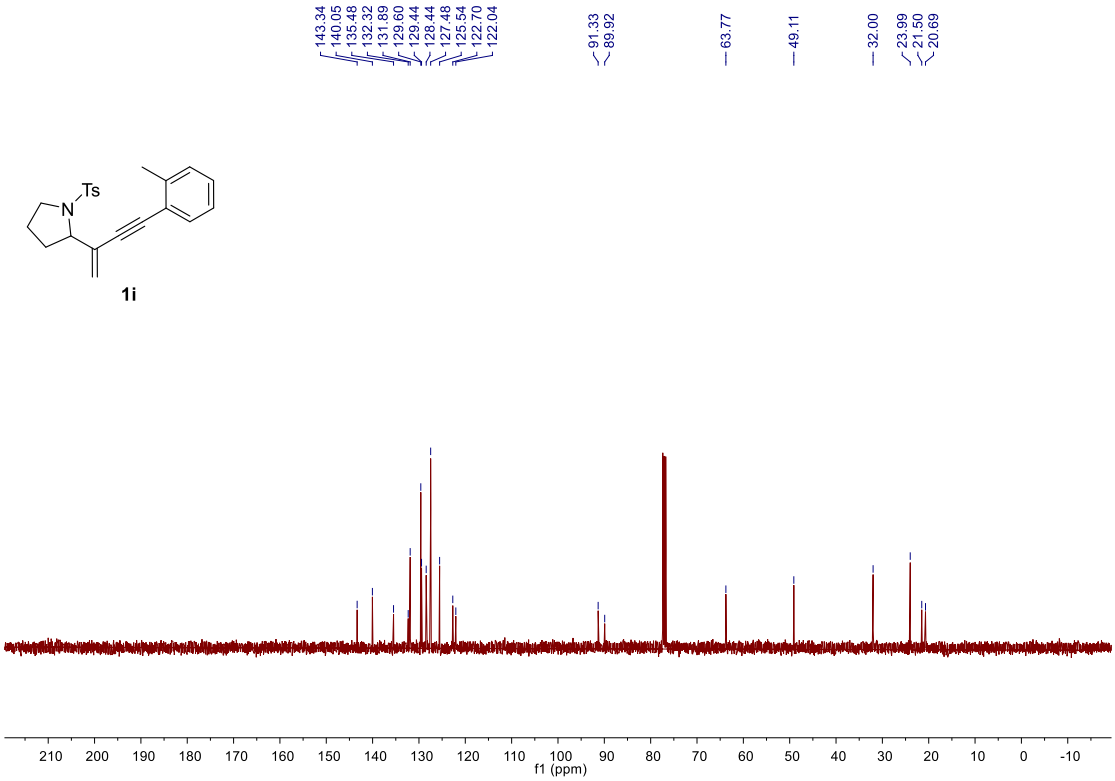
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1h**



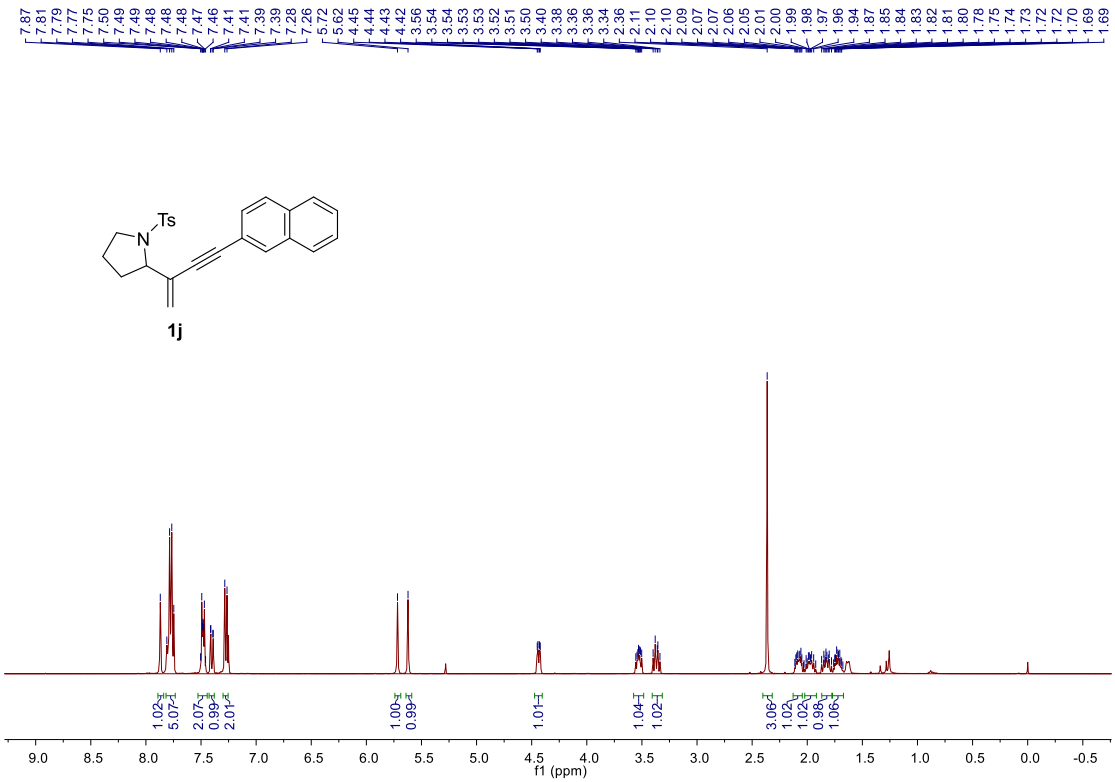


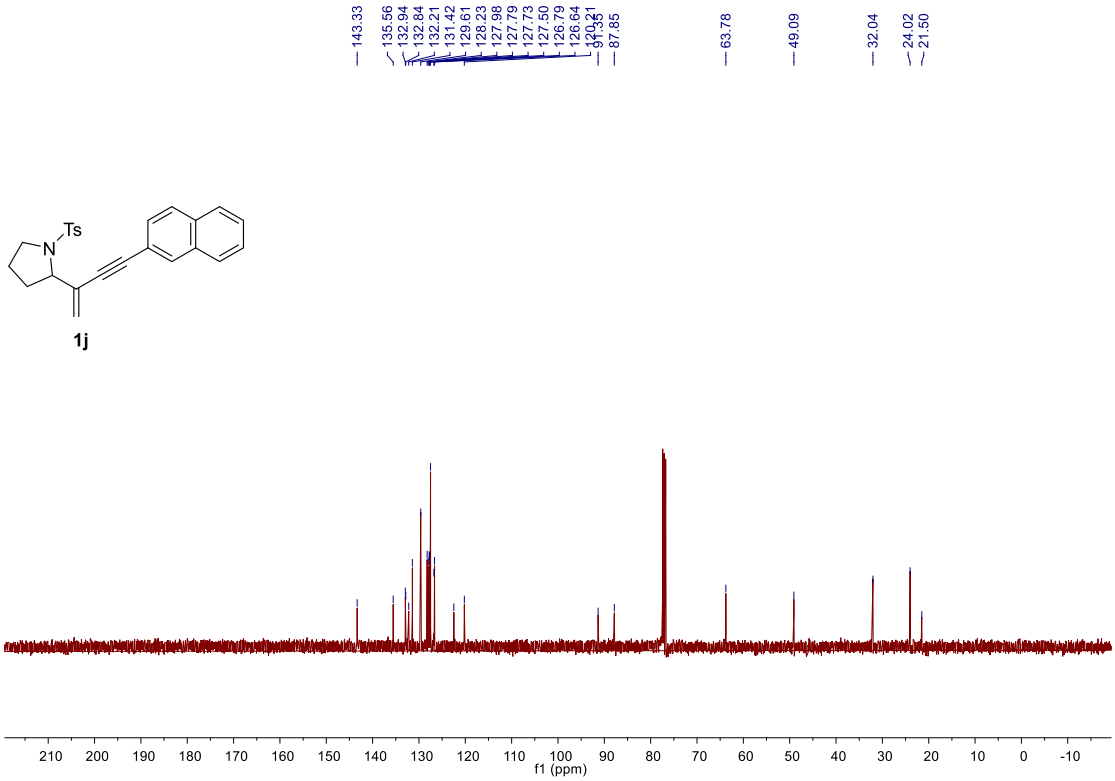
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1i**



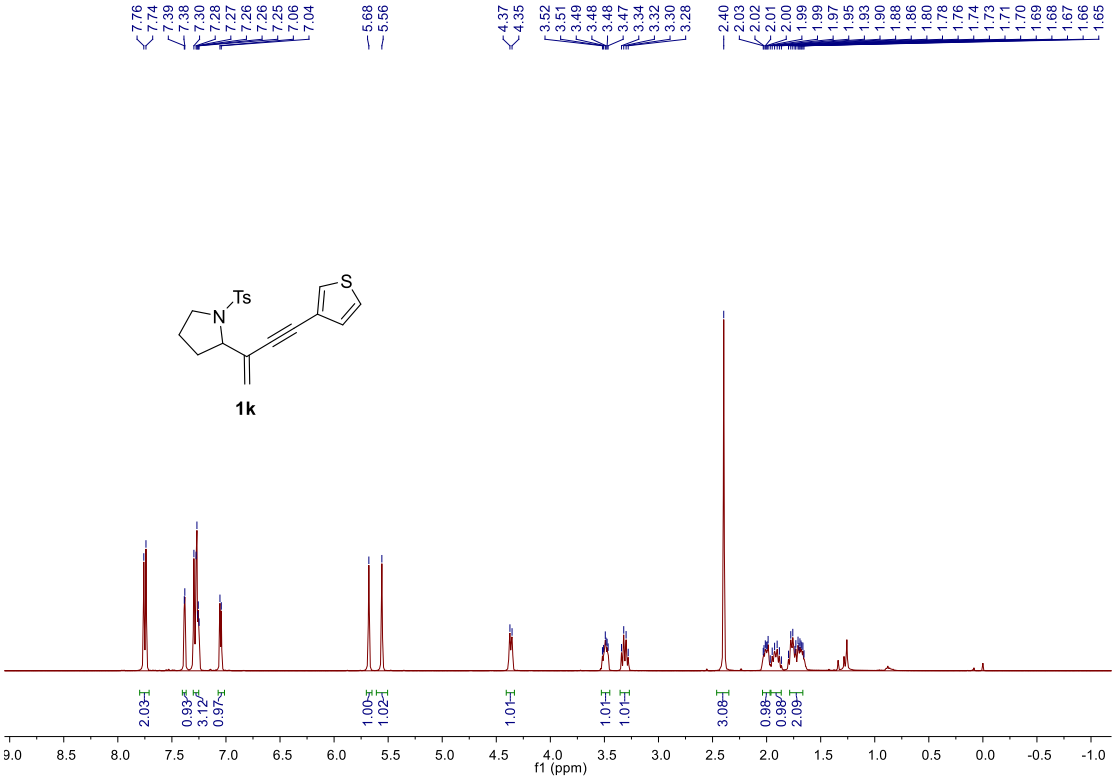


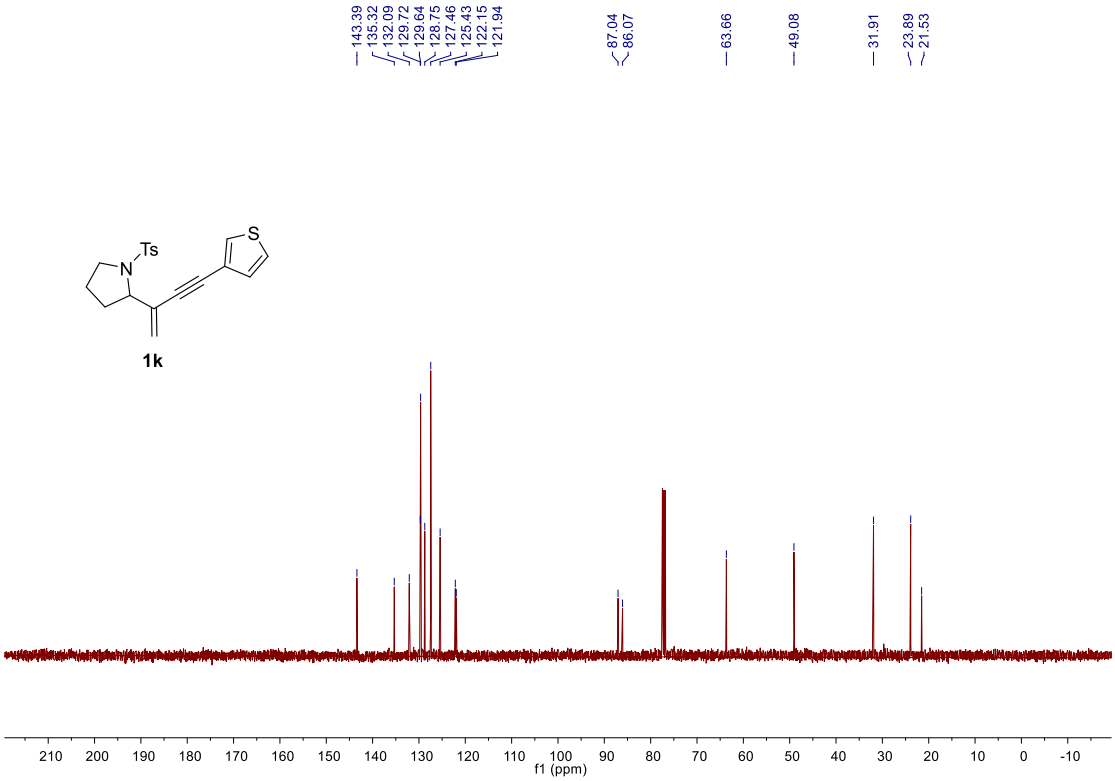
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1*J***



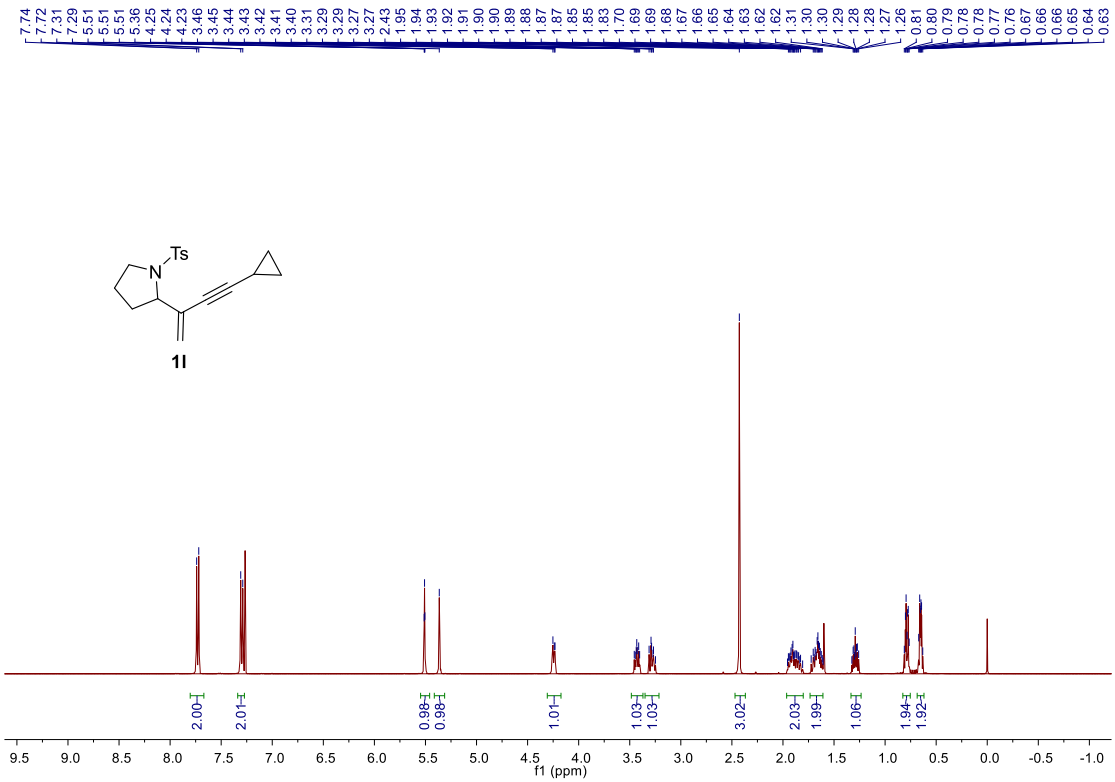


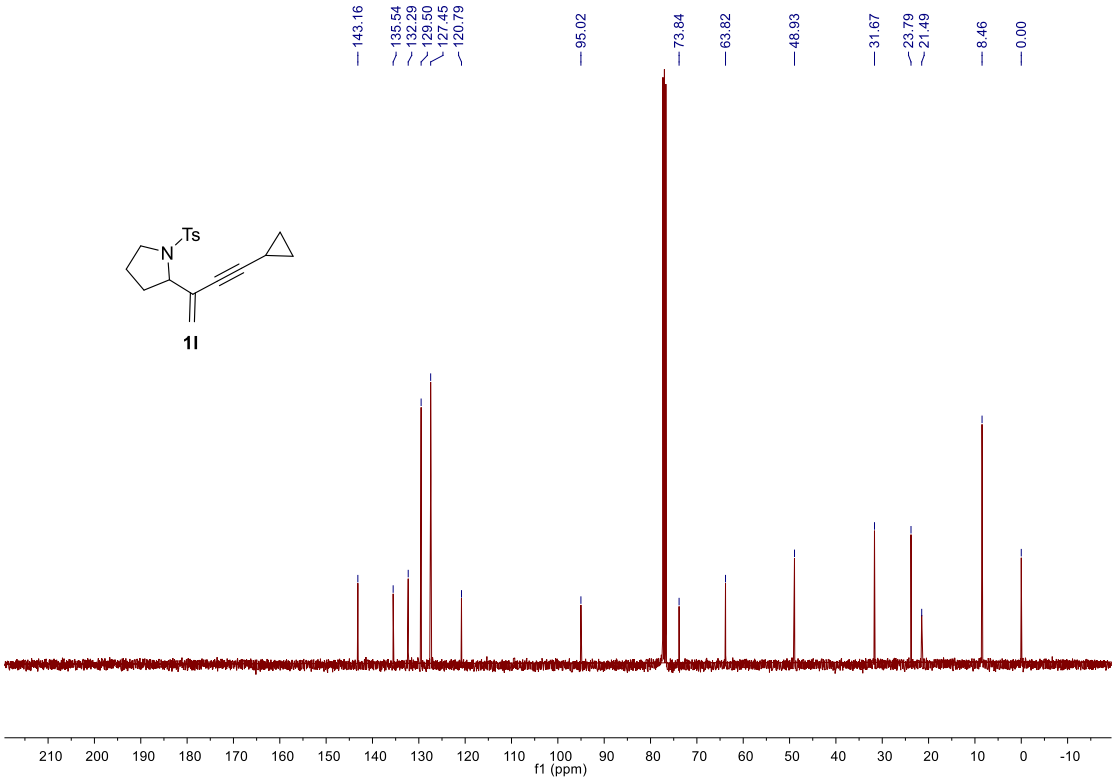
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1k**



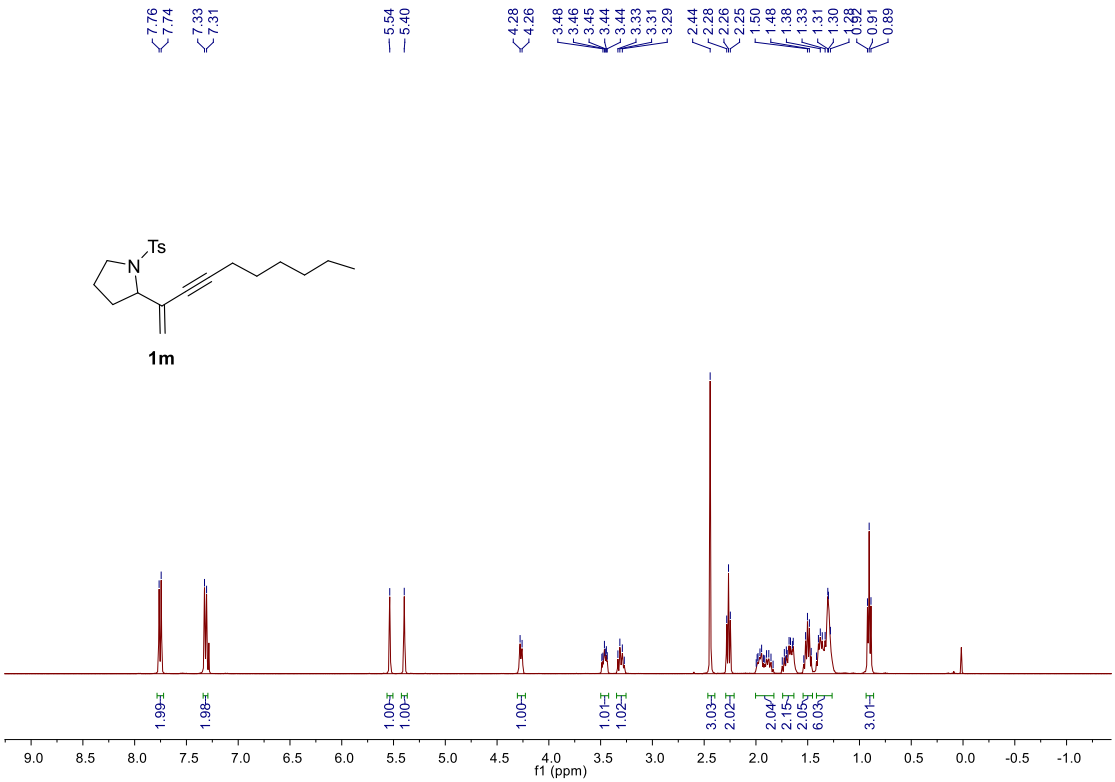


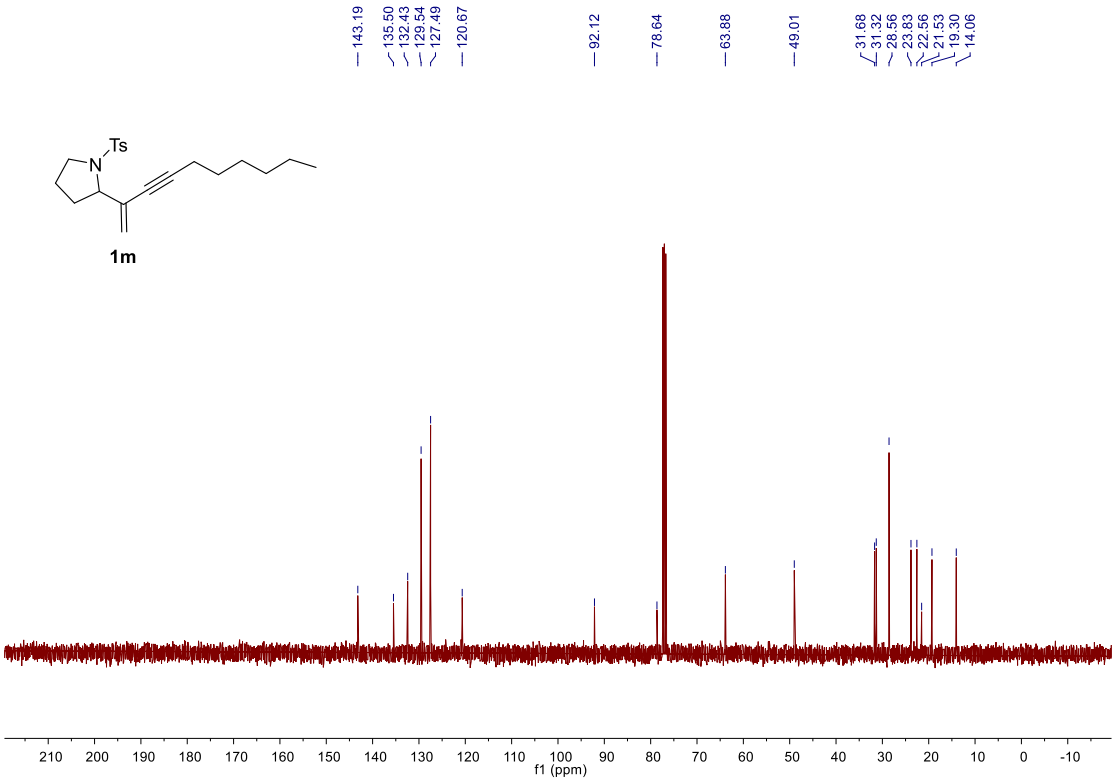
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1l**



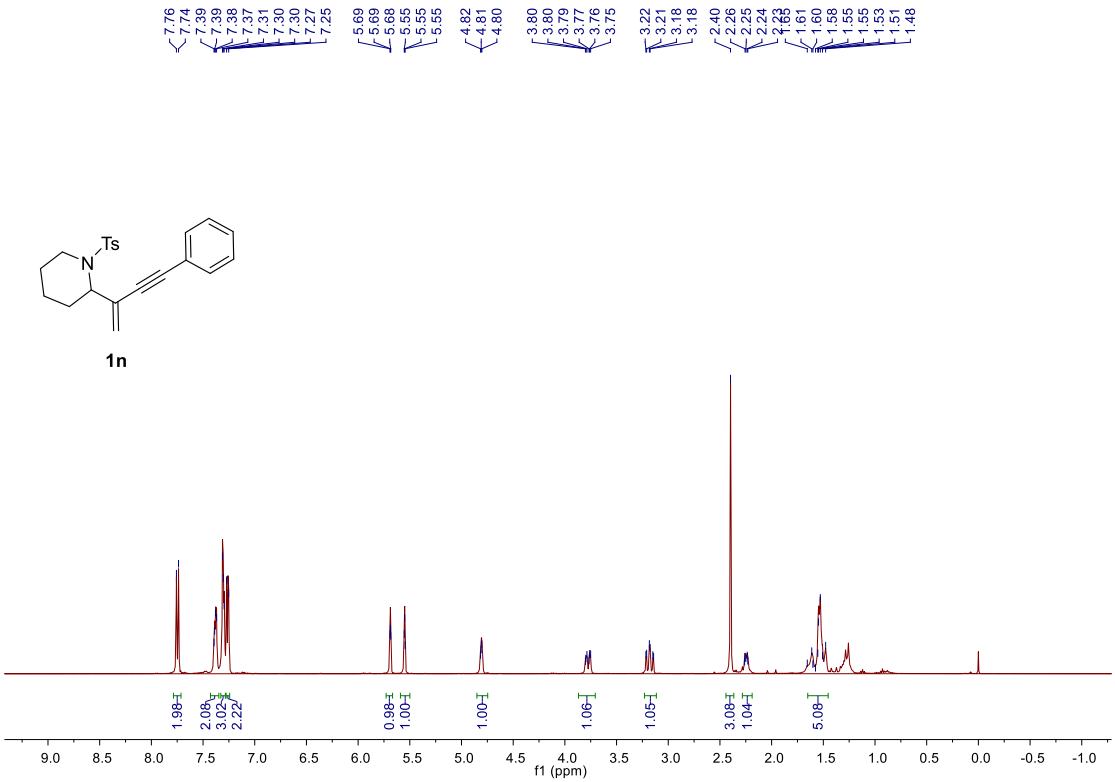


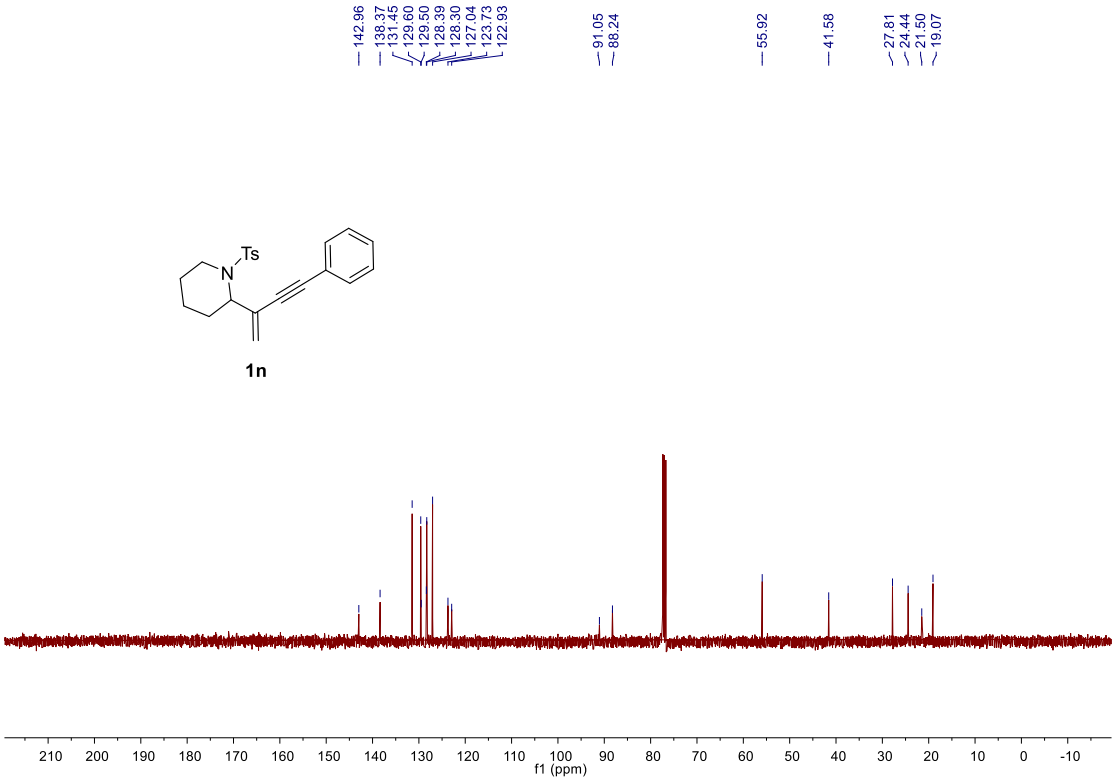
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1m**



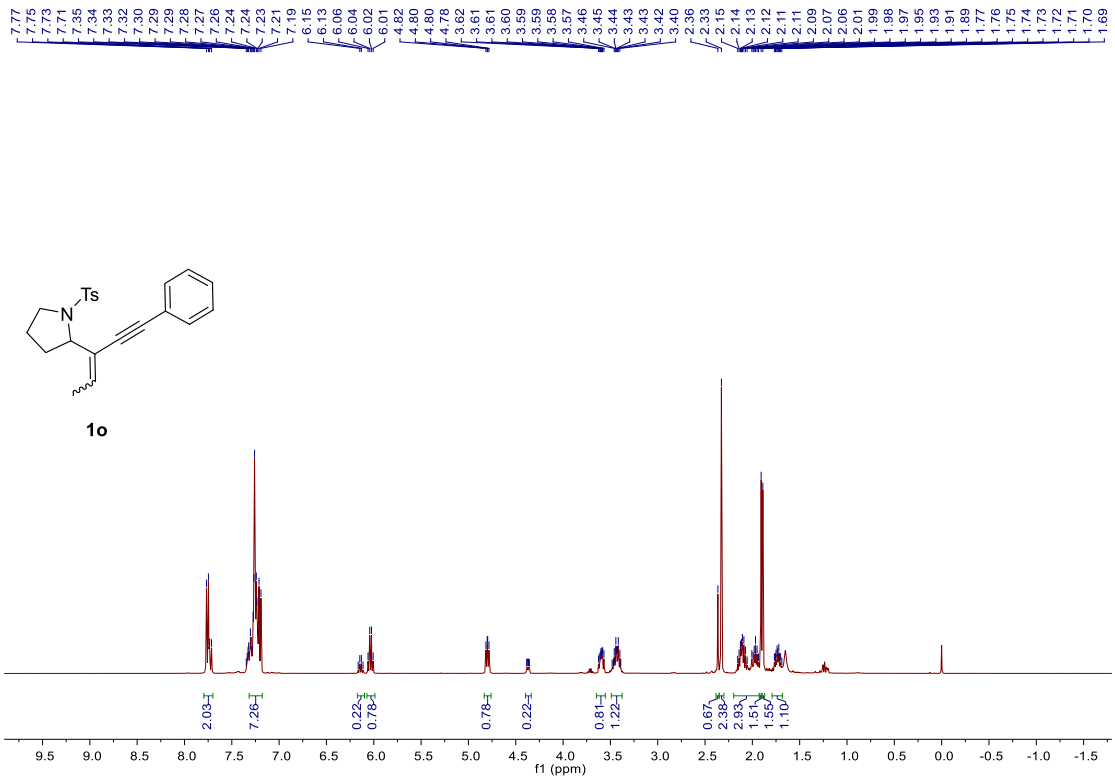


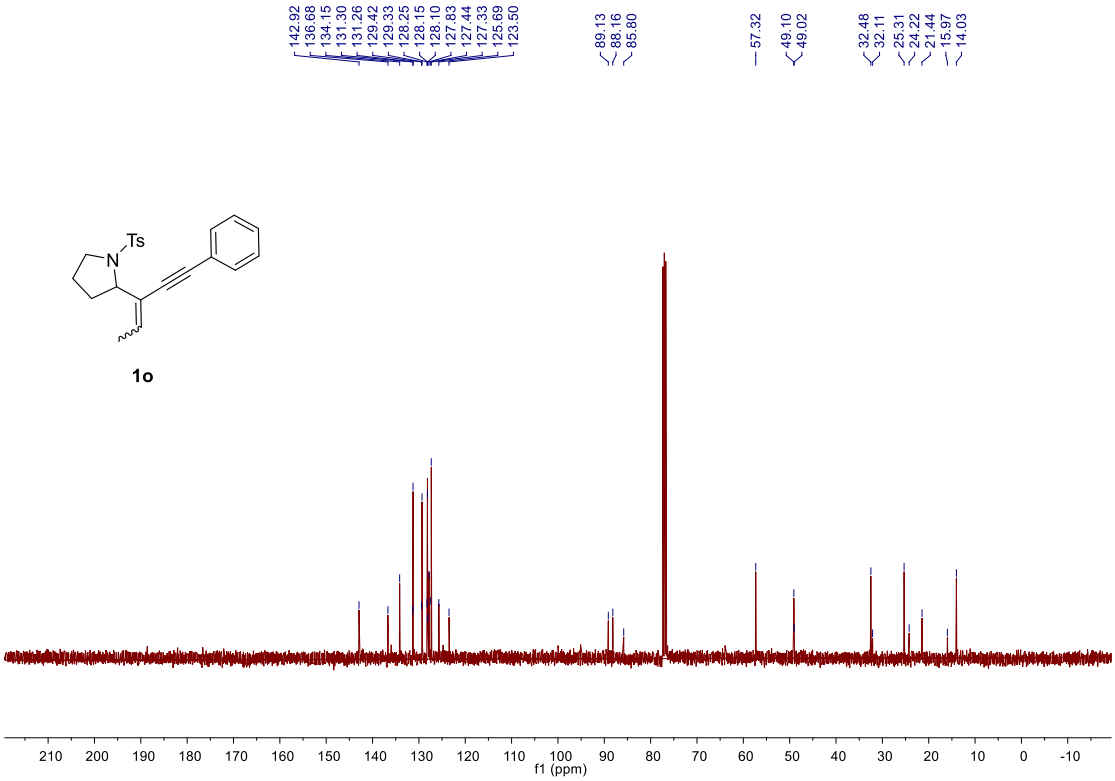
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1n**



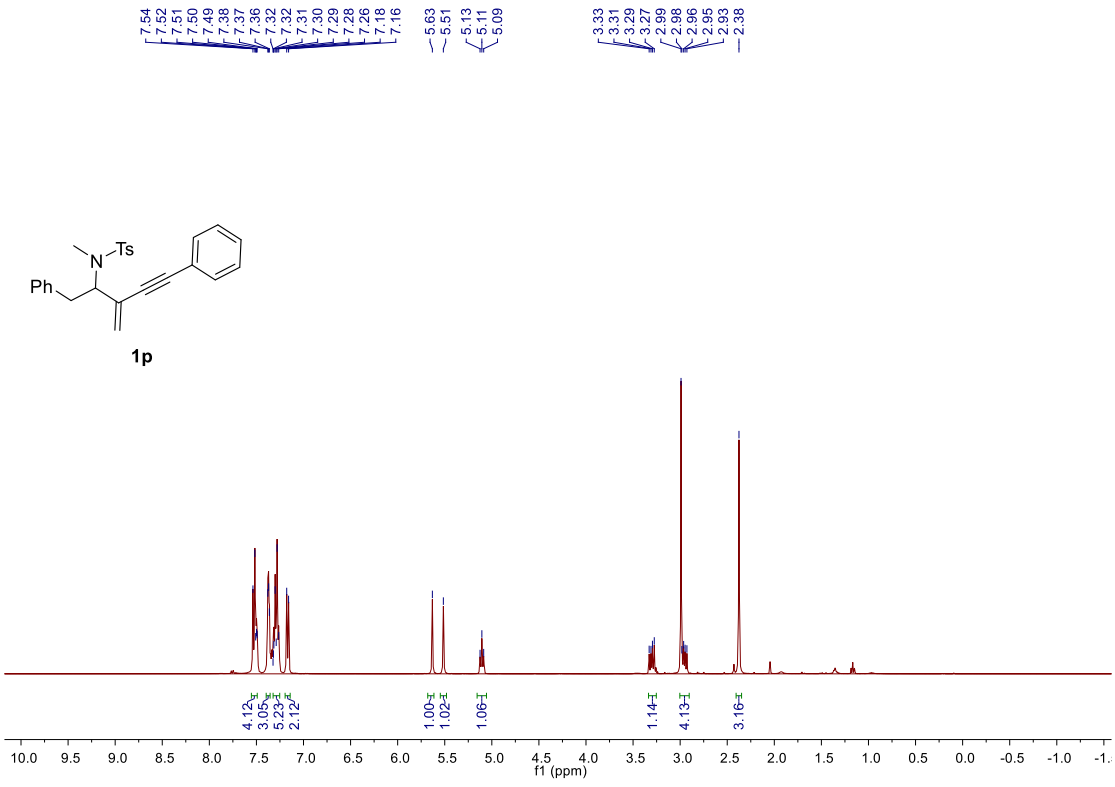


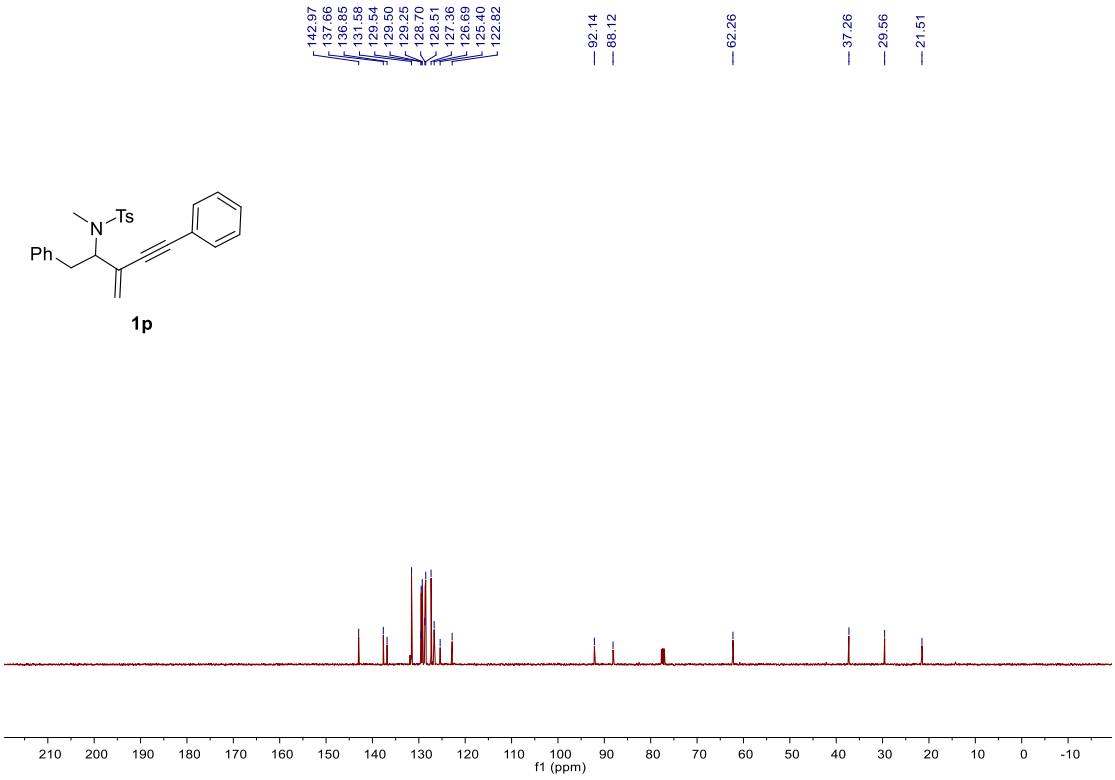
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1o**



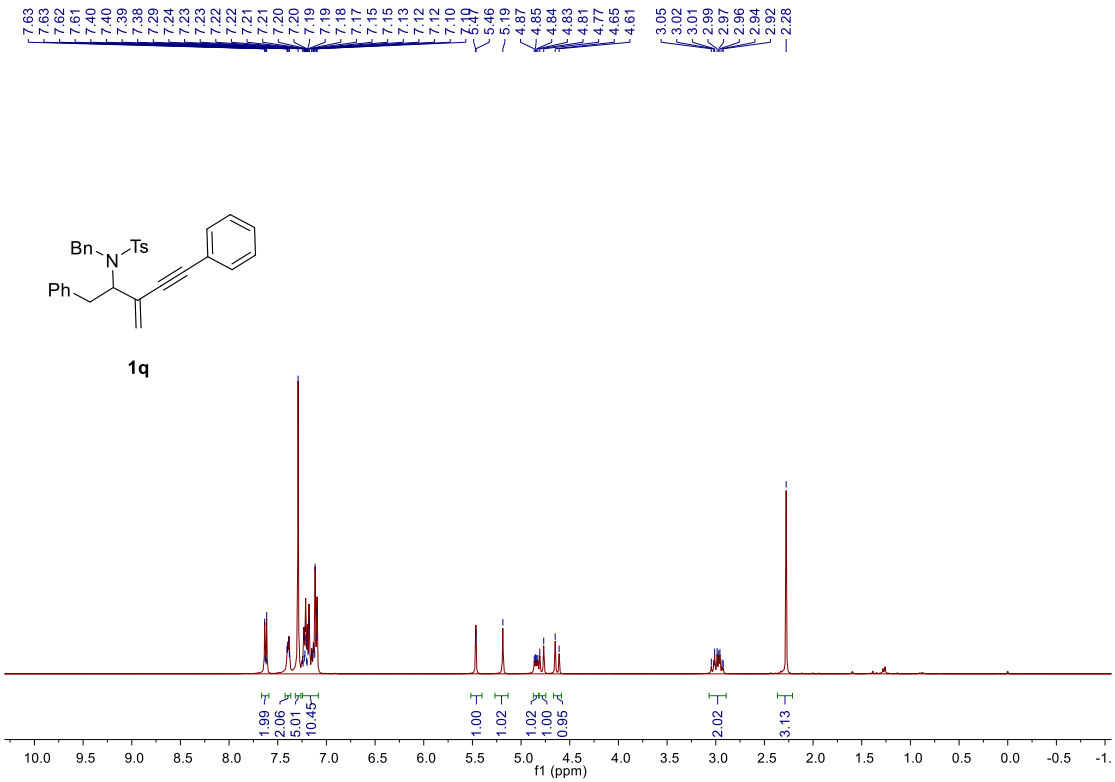


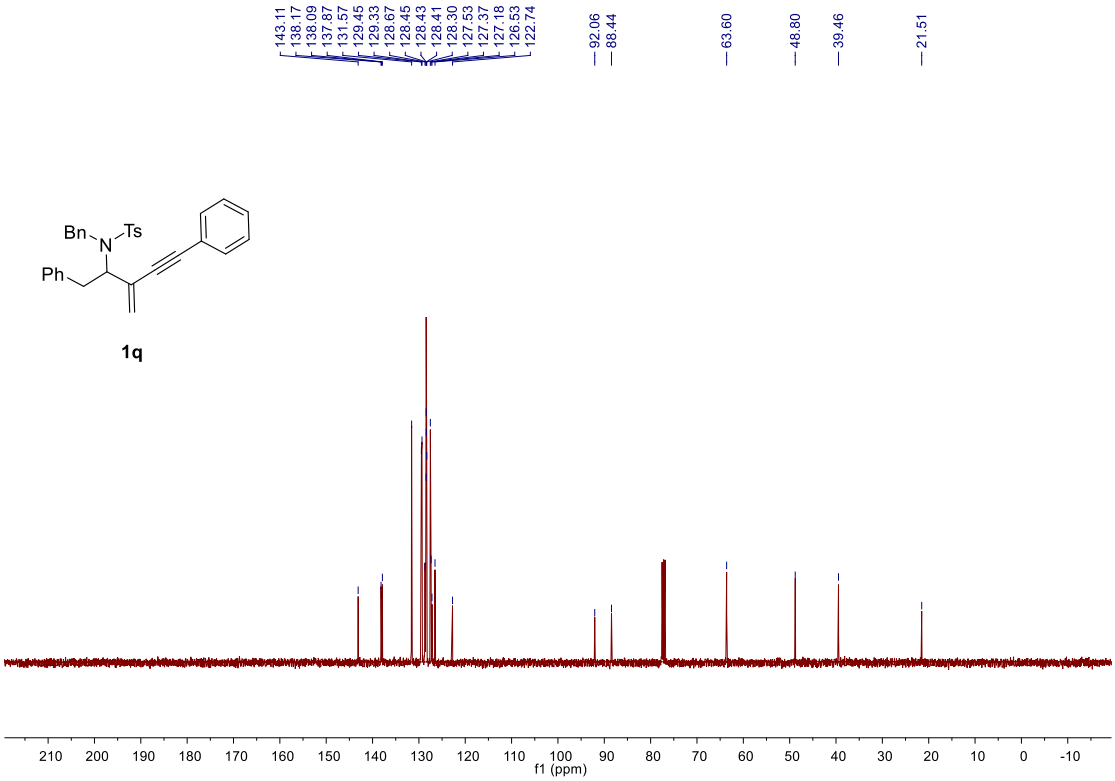
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1p**



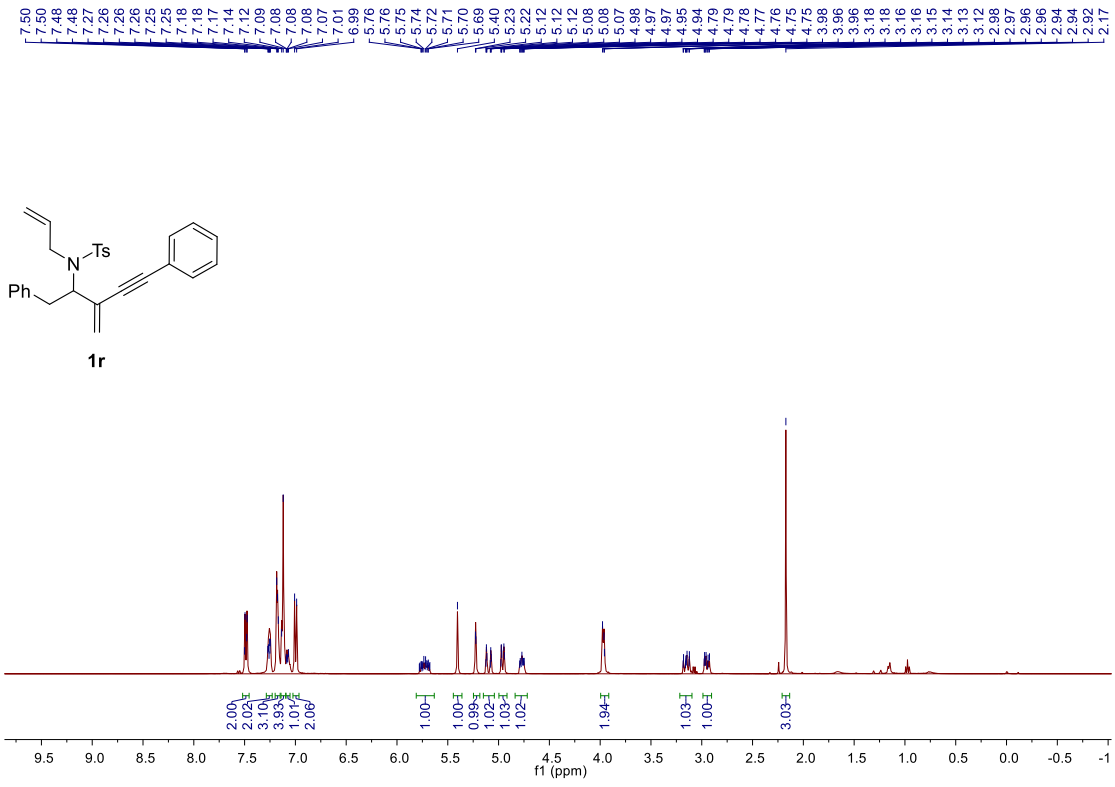


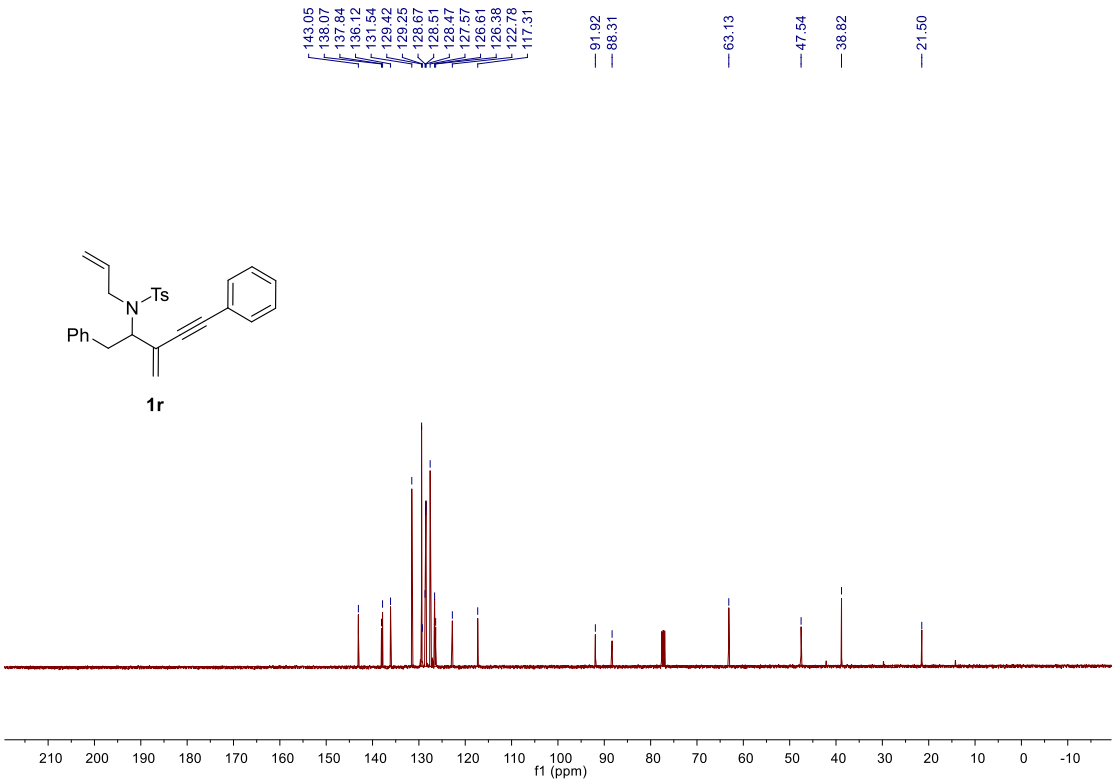
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1q**



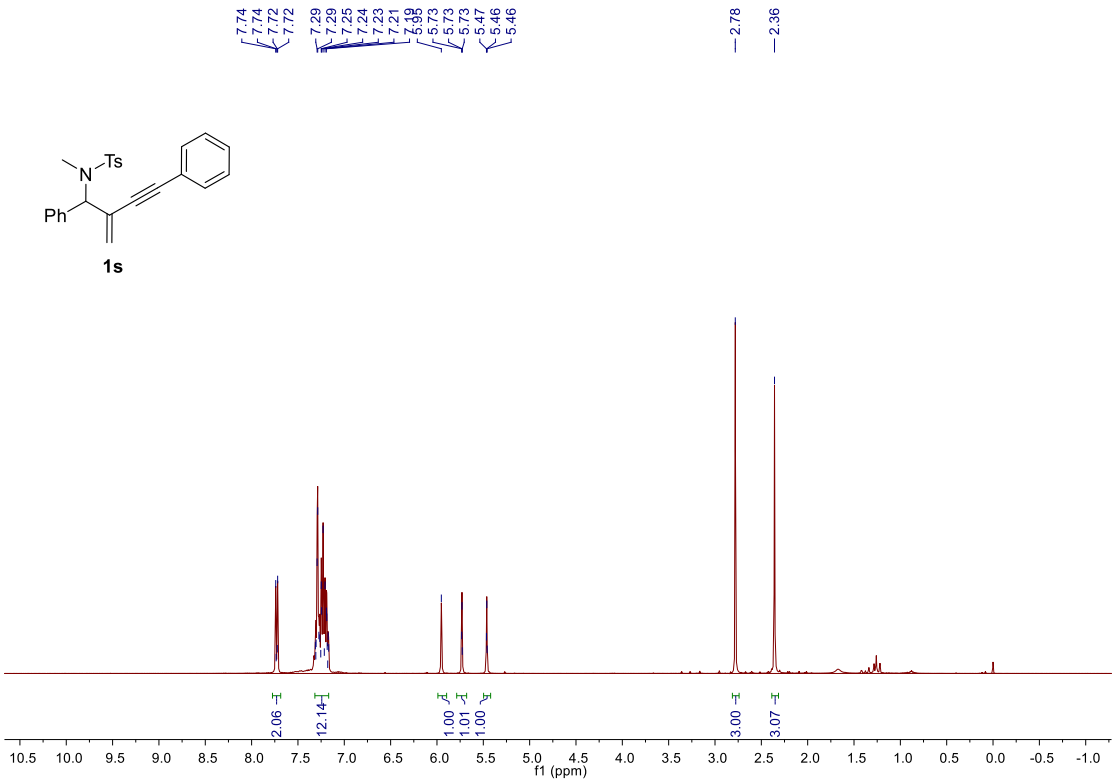


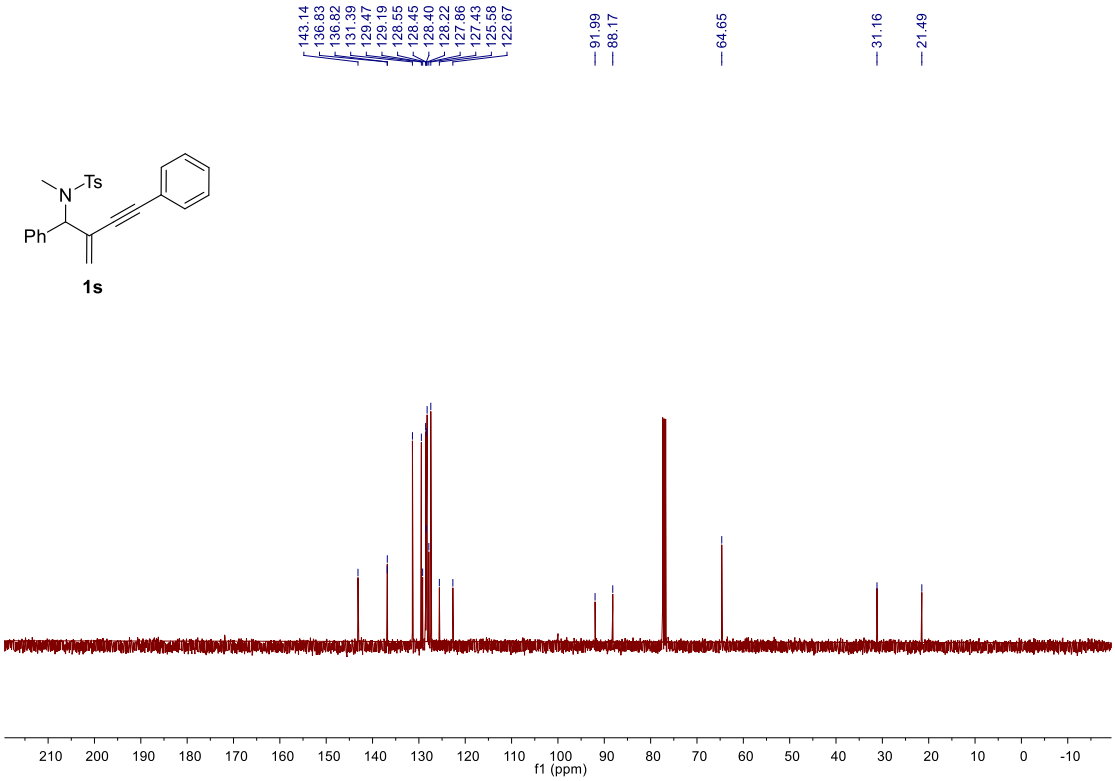
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1r**



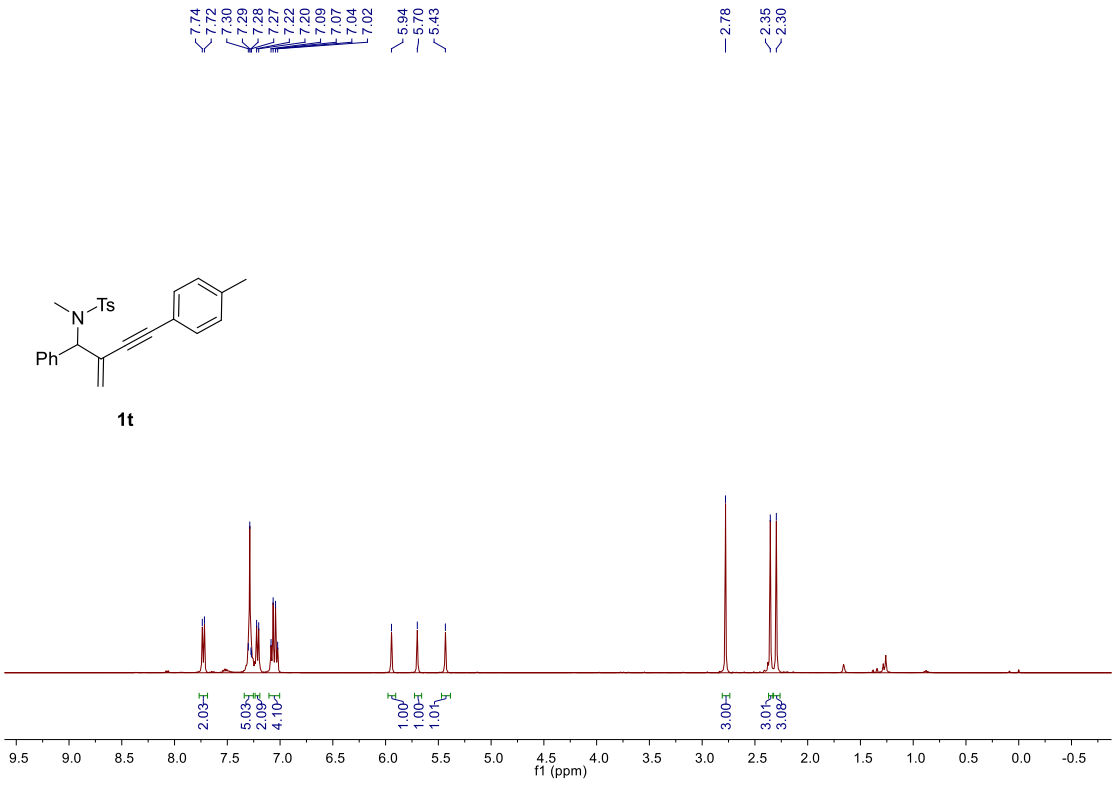


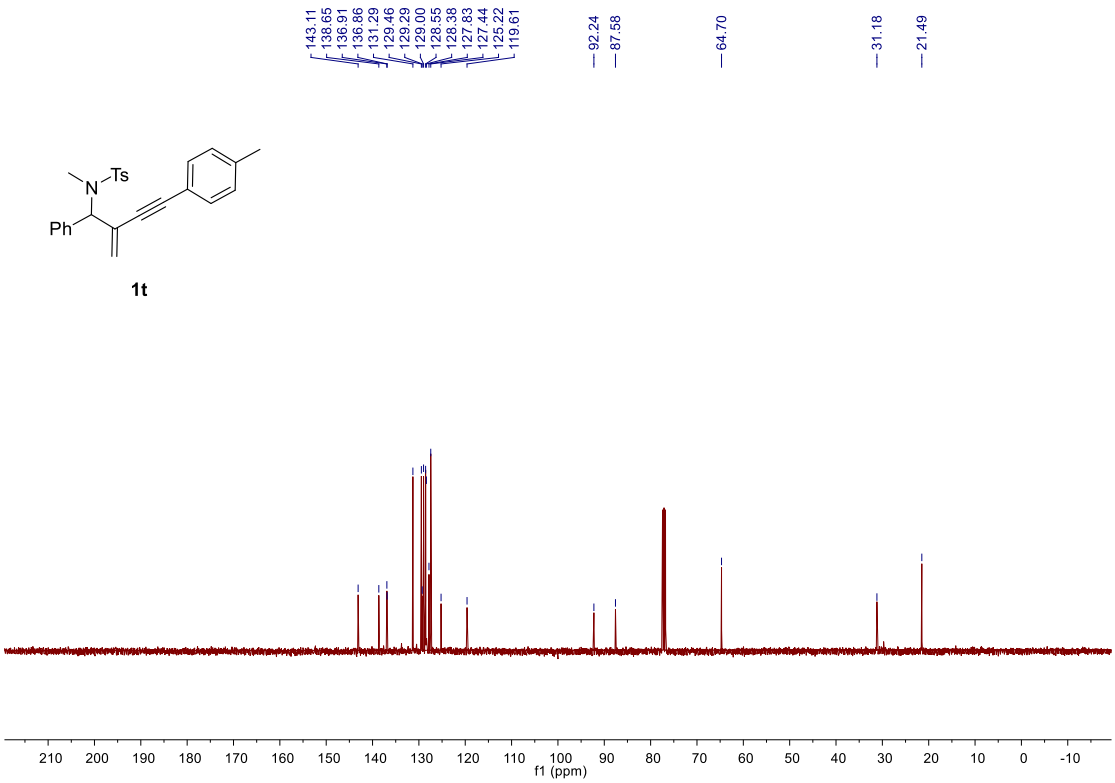
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1s**



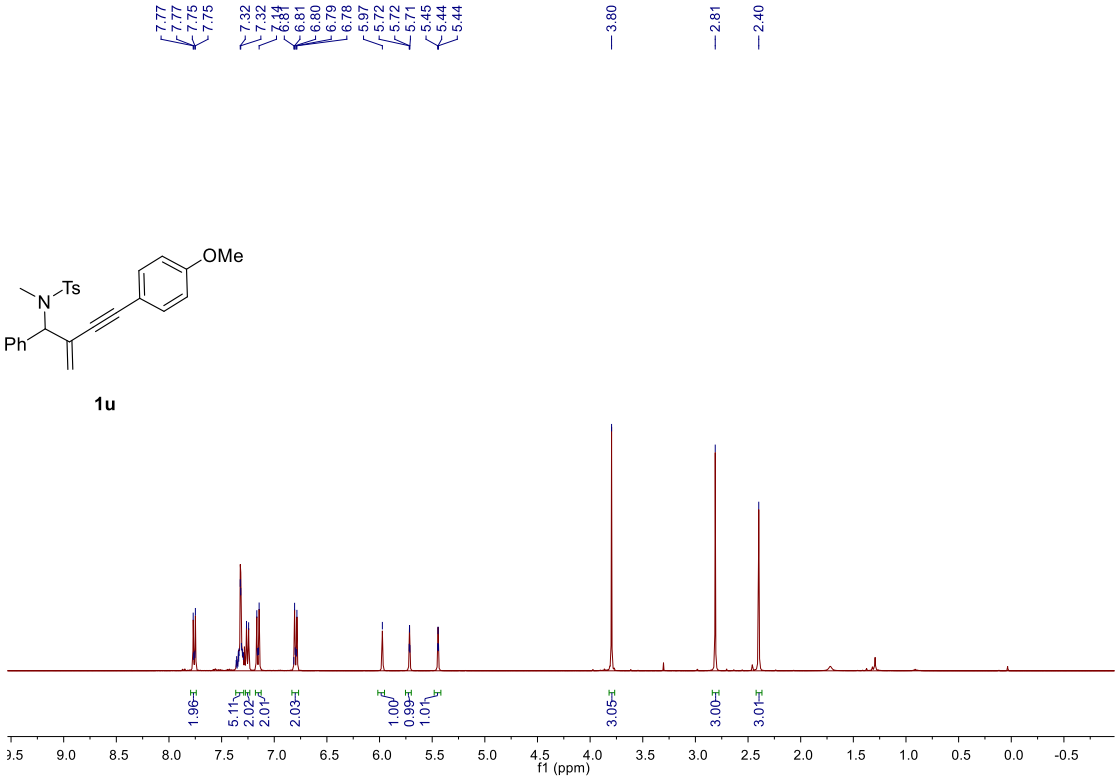


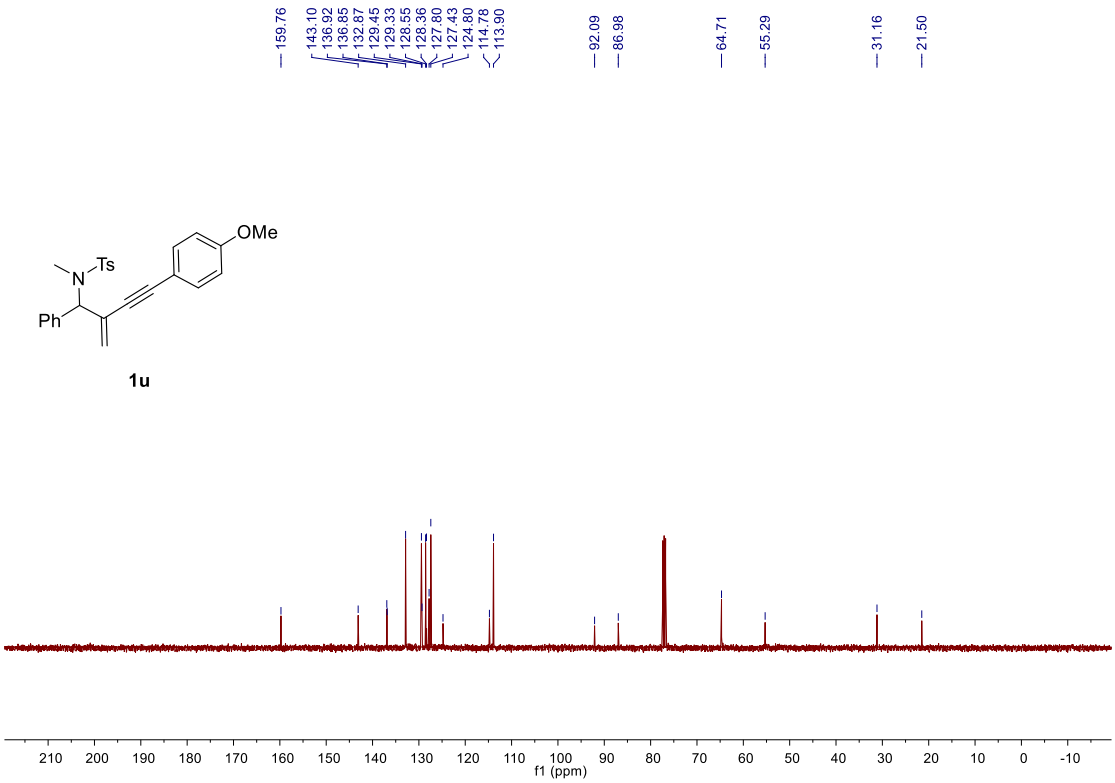
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1t**



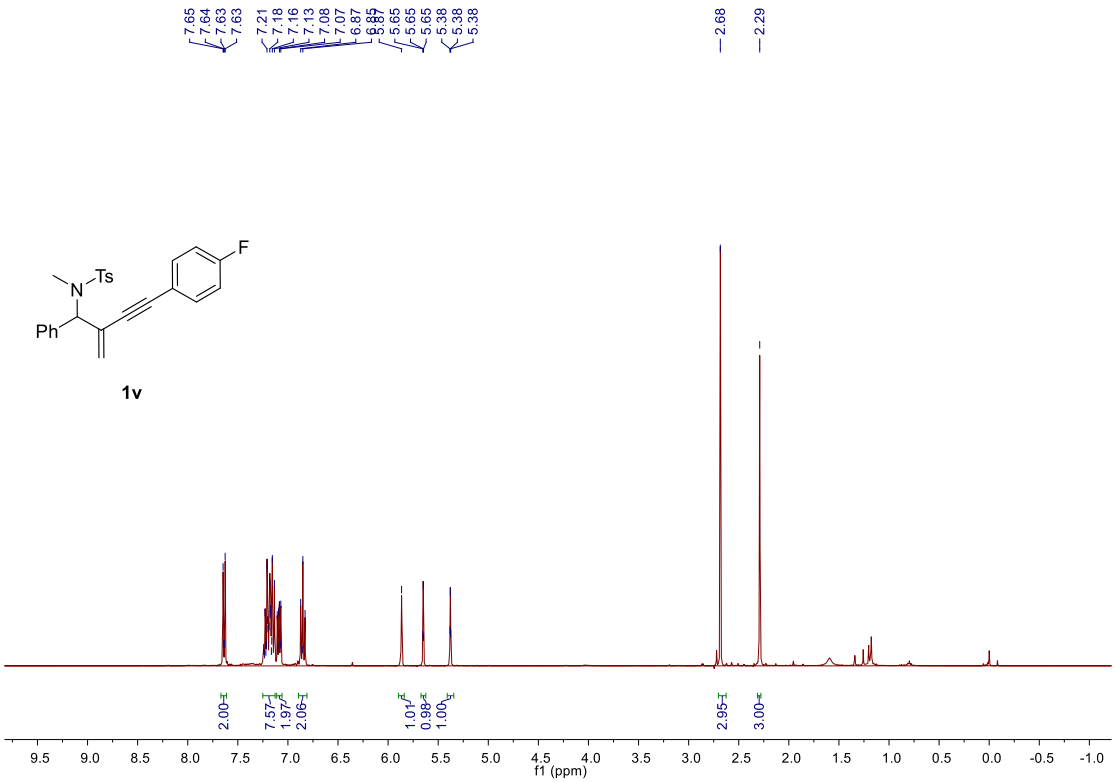


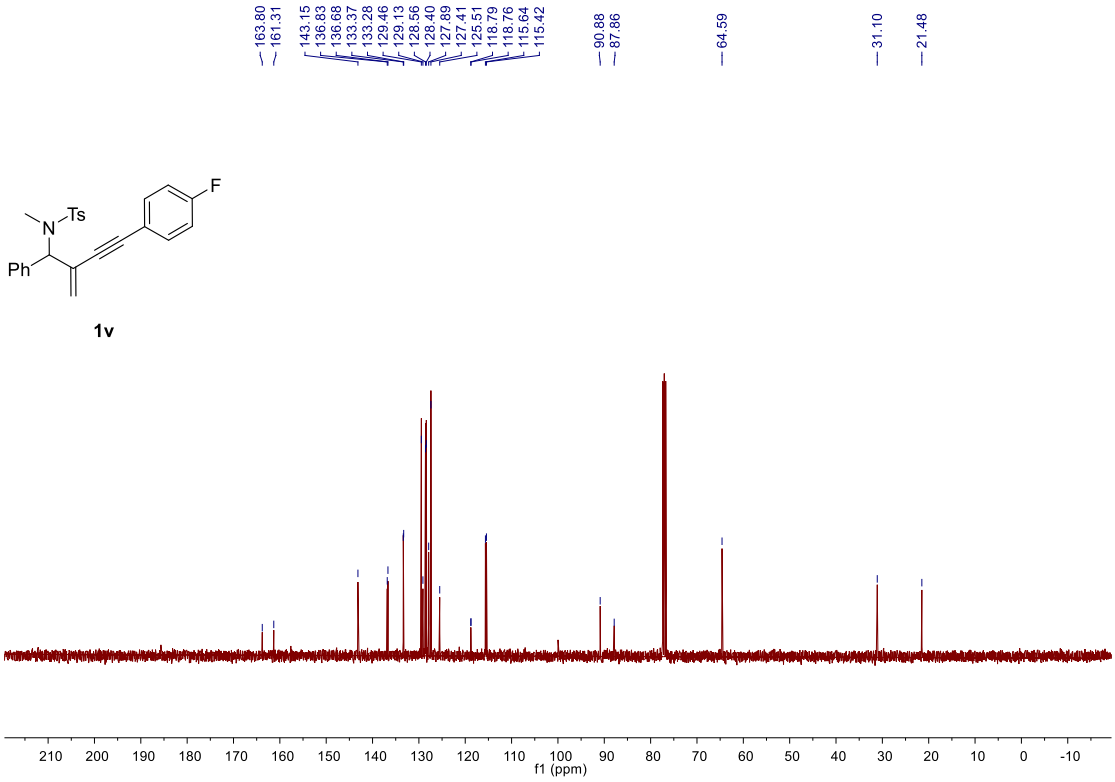
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1u**

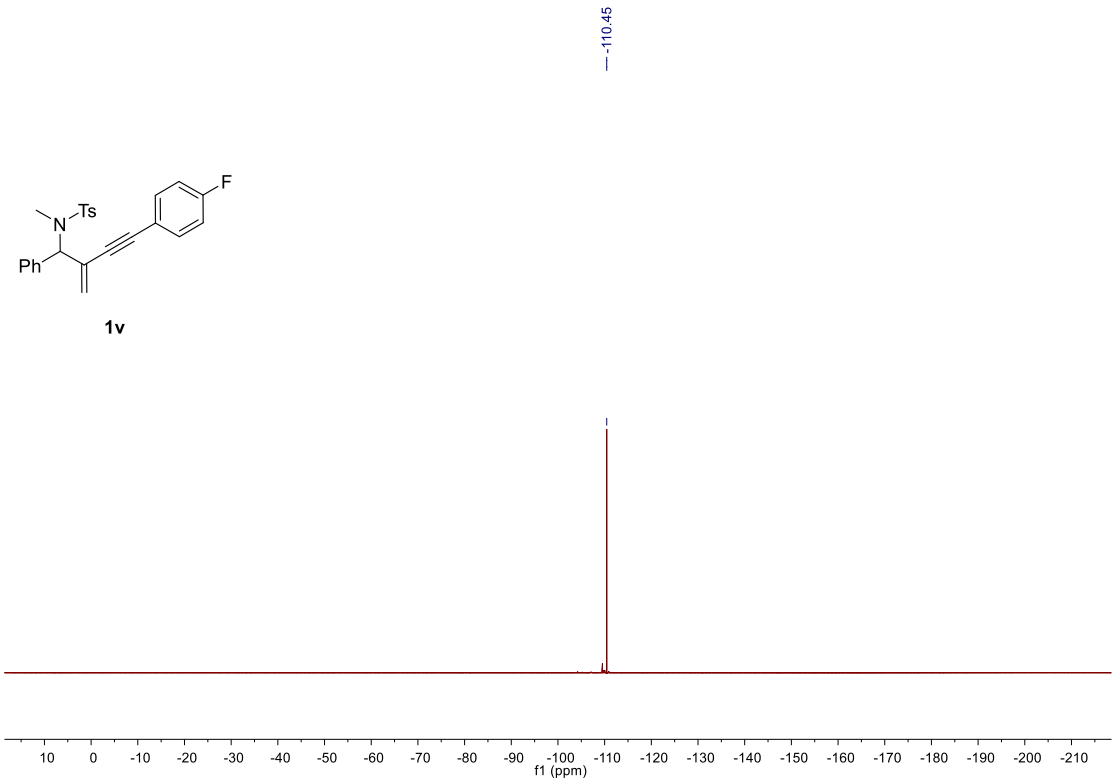




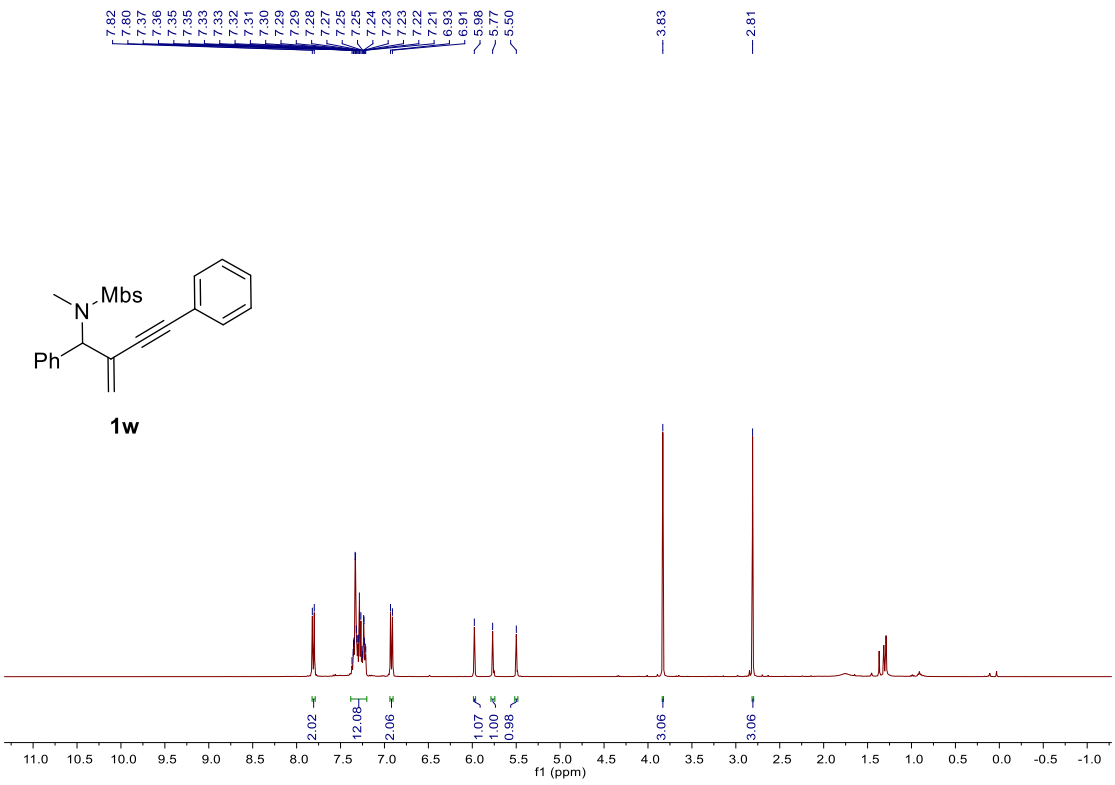
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$) and 19F NMR (376 MHz, $CDCl_3$) spectrum of substrate **1v**

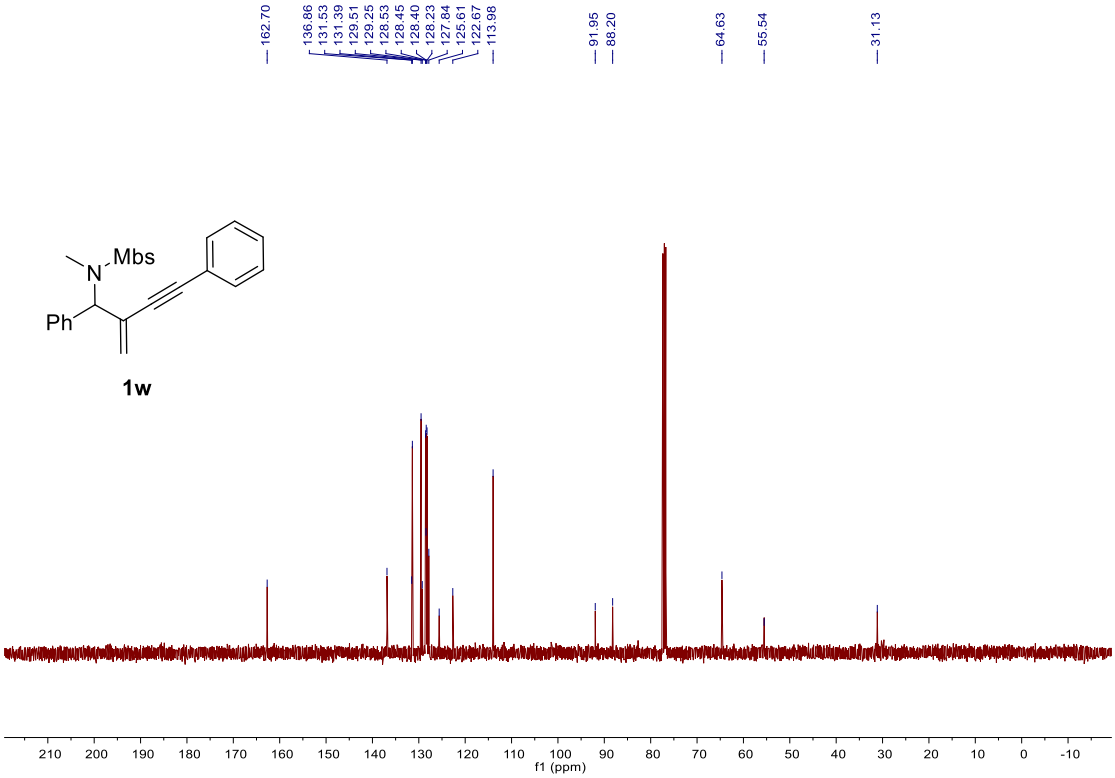



163.80
161.31
143.15
136.83
136.68
133.37
133.28
129.46
129.13
128.56
128.40
127.89
127.41
125.51
118.79
118.76
115.64
115.42
90.88
87.86
64.59
31.10
21.48
F
Ts
N
Ph
1v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-110.45
F
Ts
N
Ph
1v
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

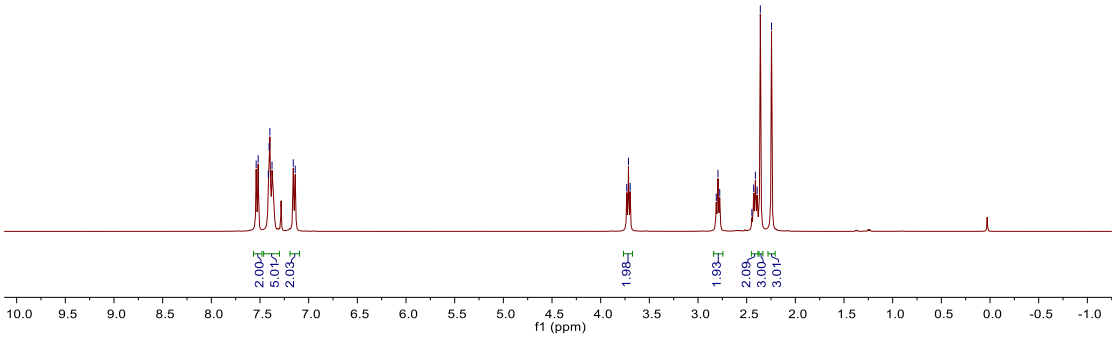
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **1w**

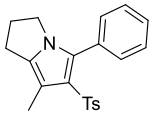




^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2a**

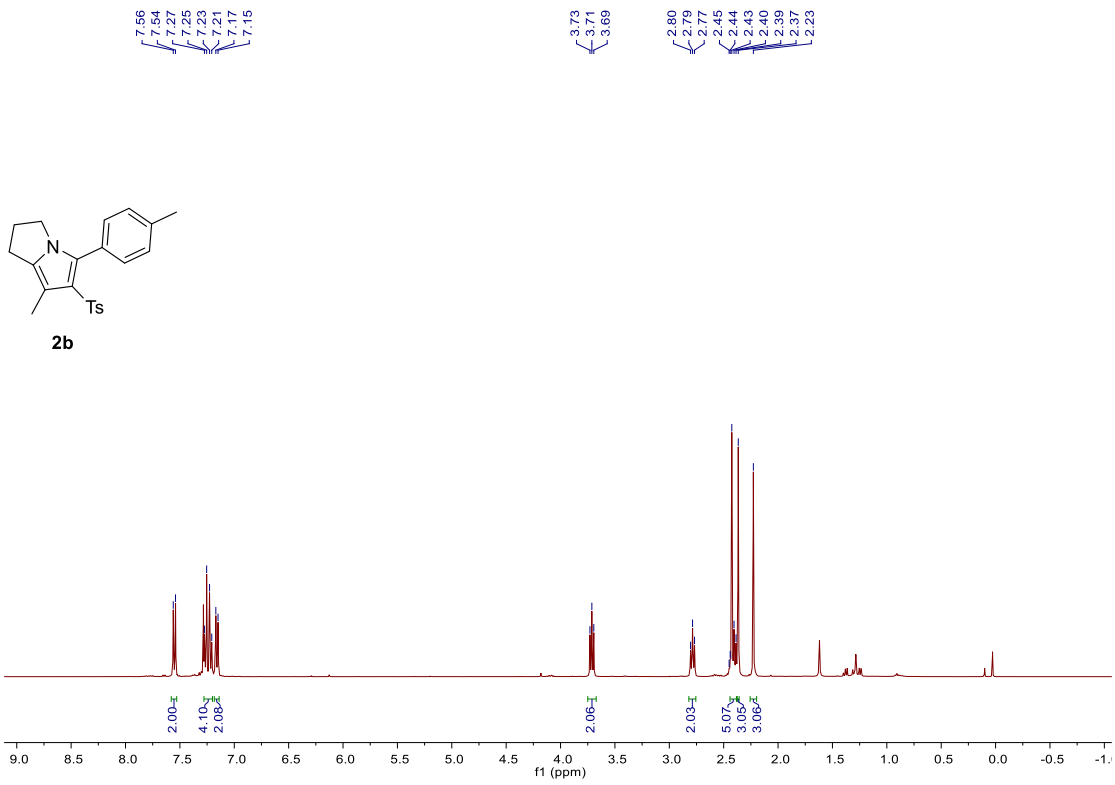
2a

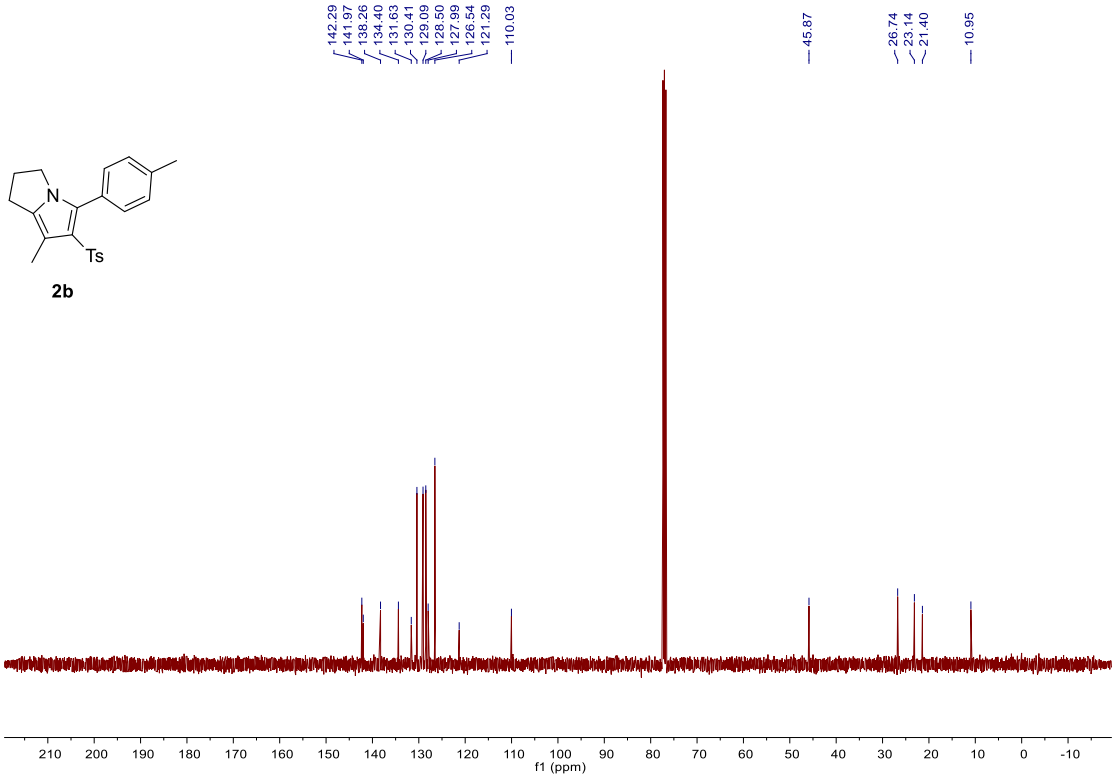




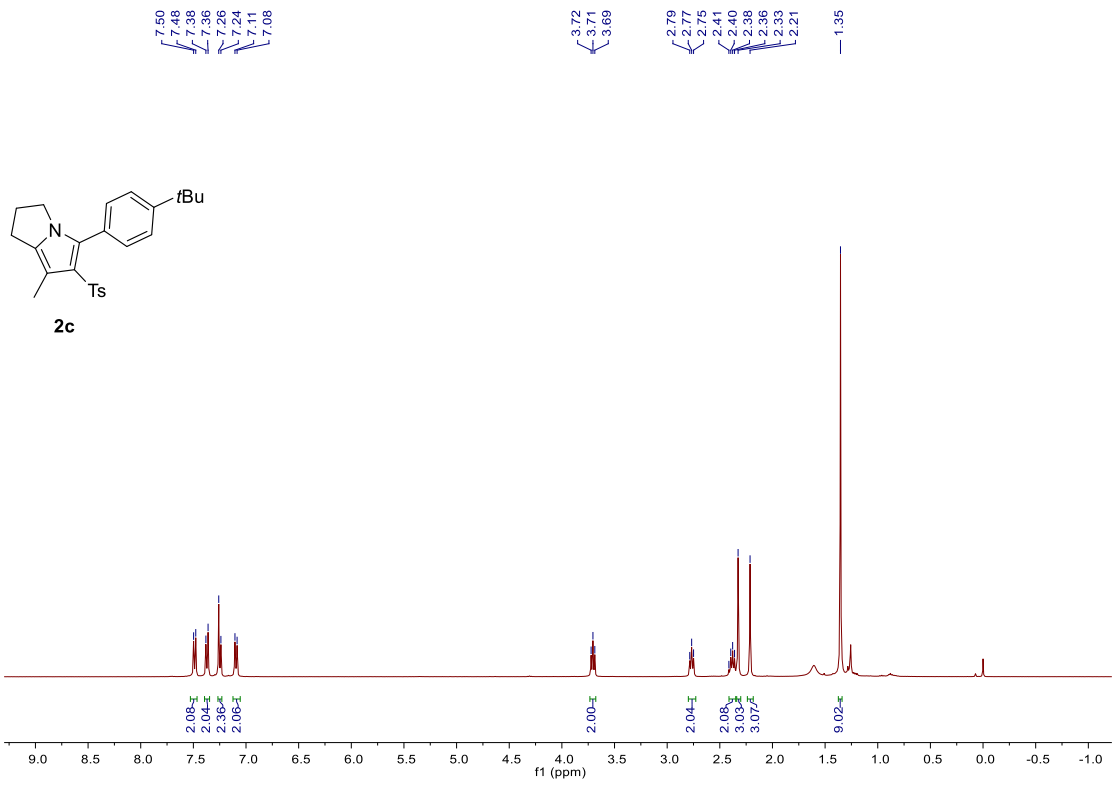
2a

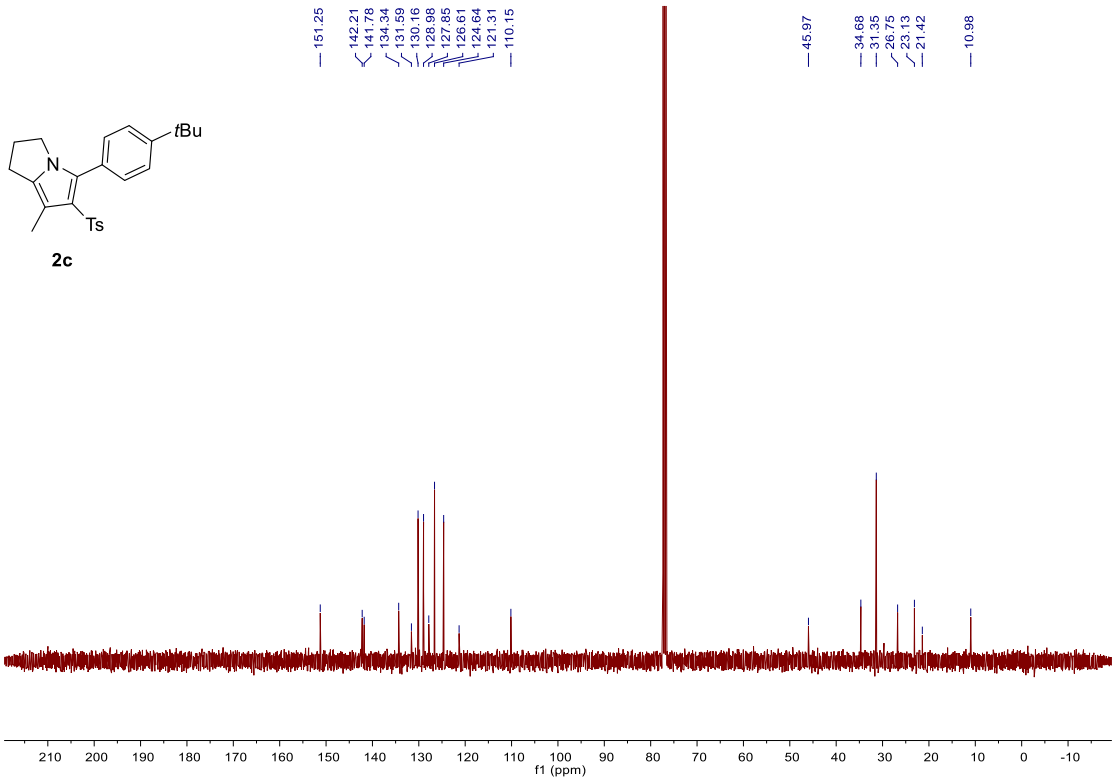
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2b**



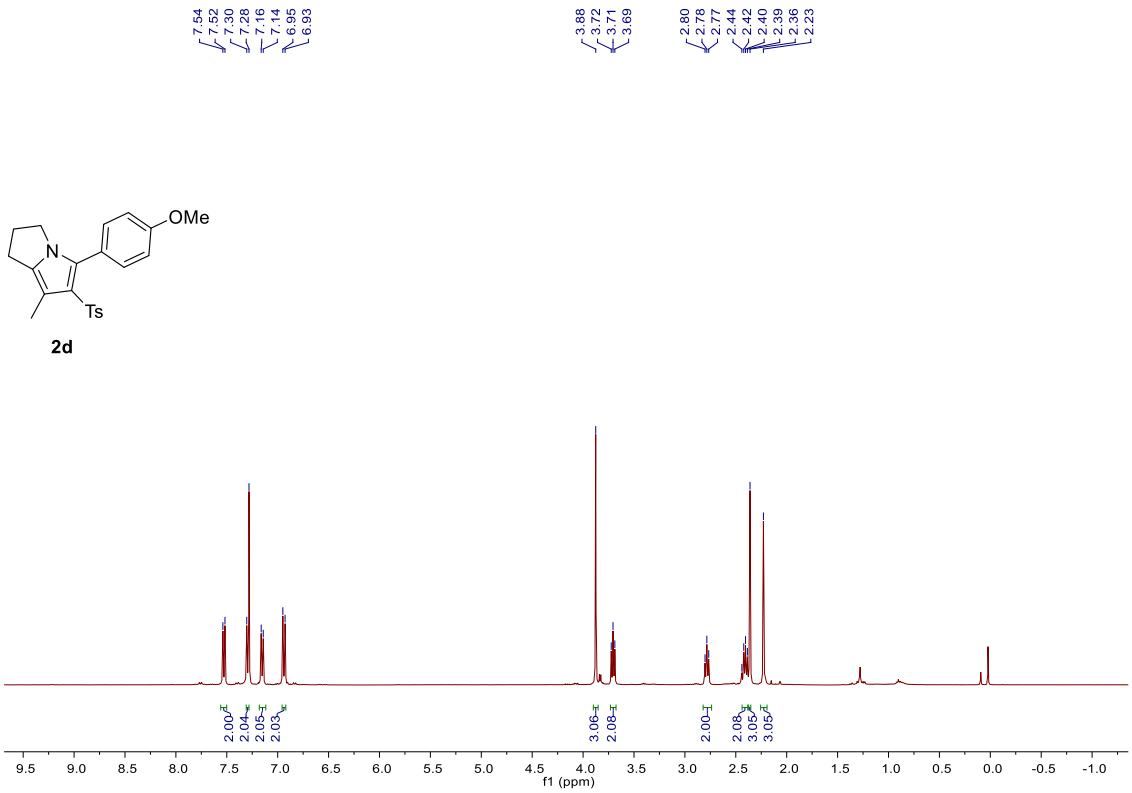


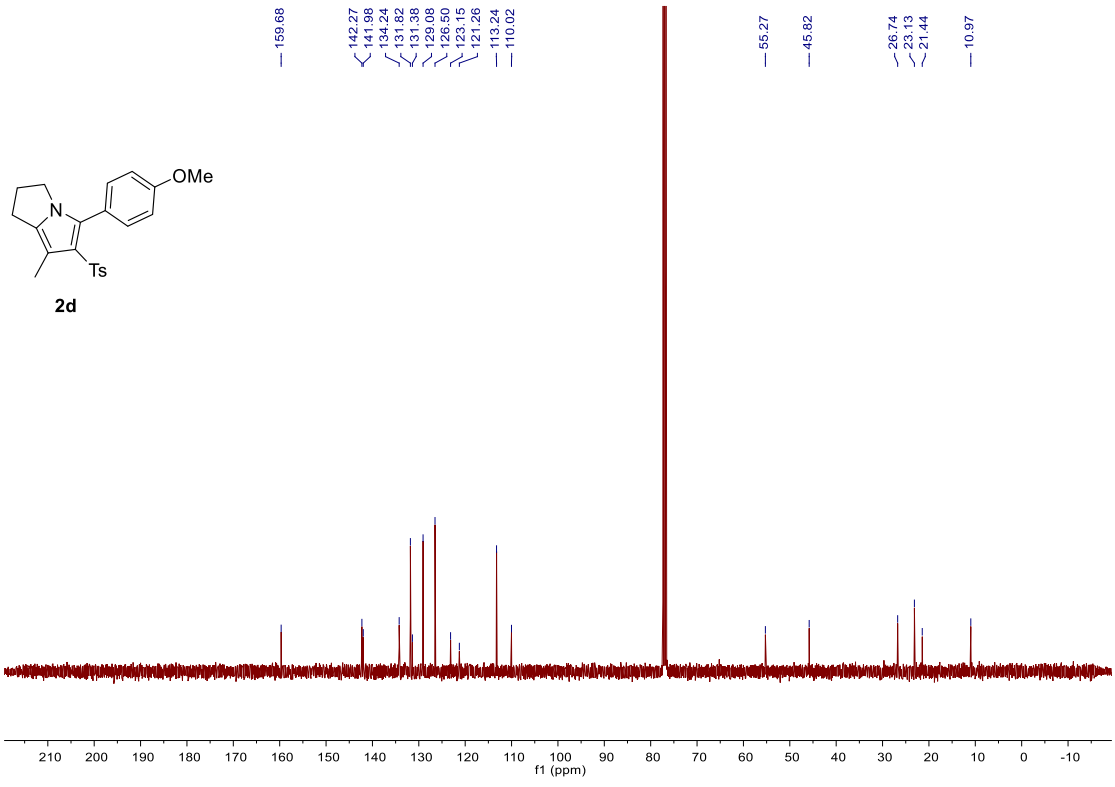
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2c**



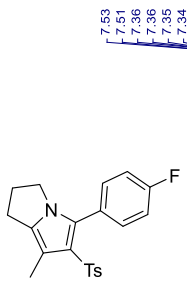


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2d**

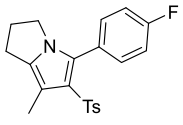




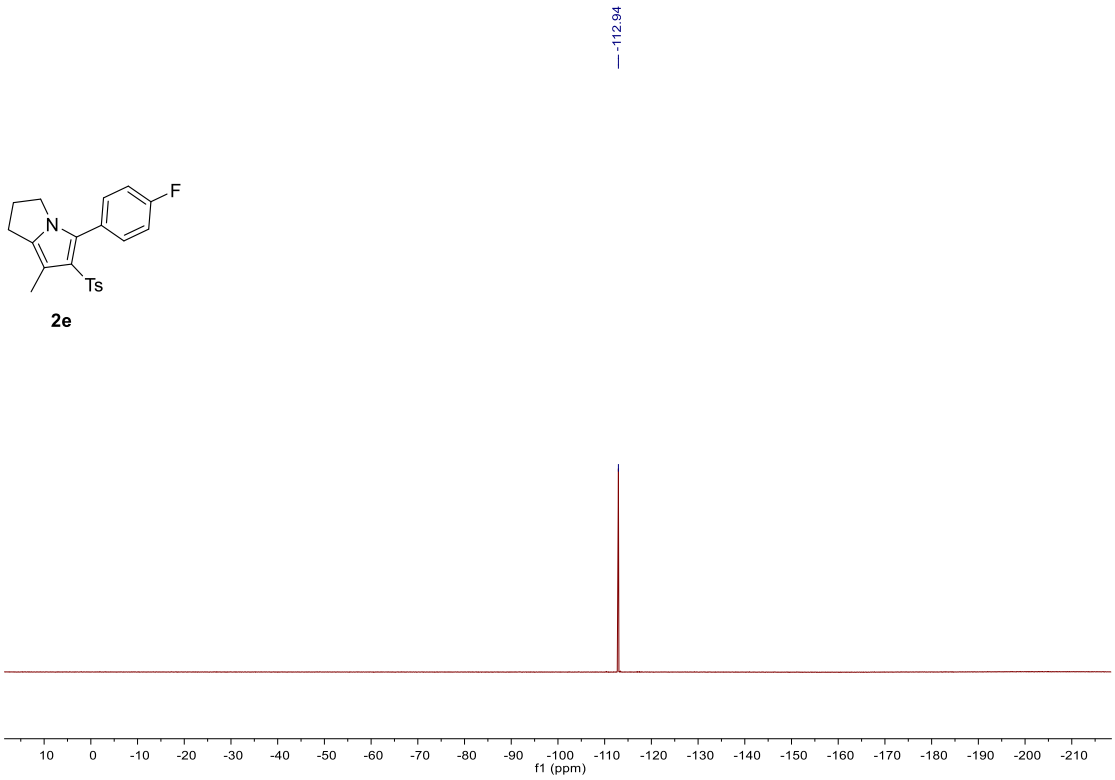
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of substrate **2e**



2e

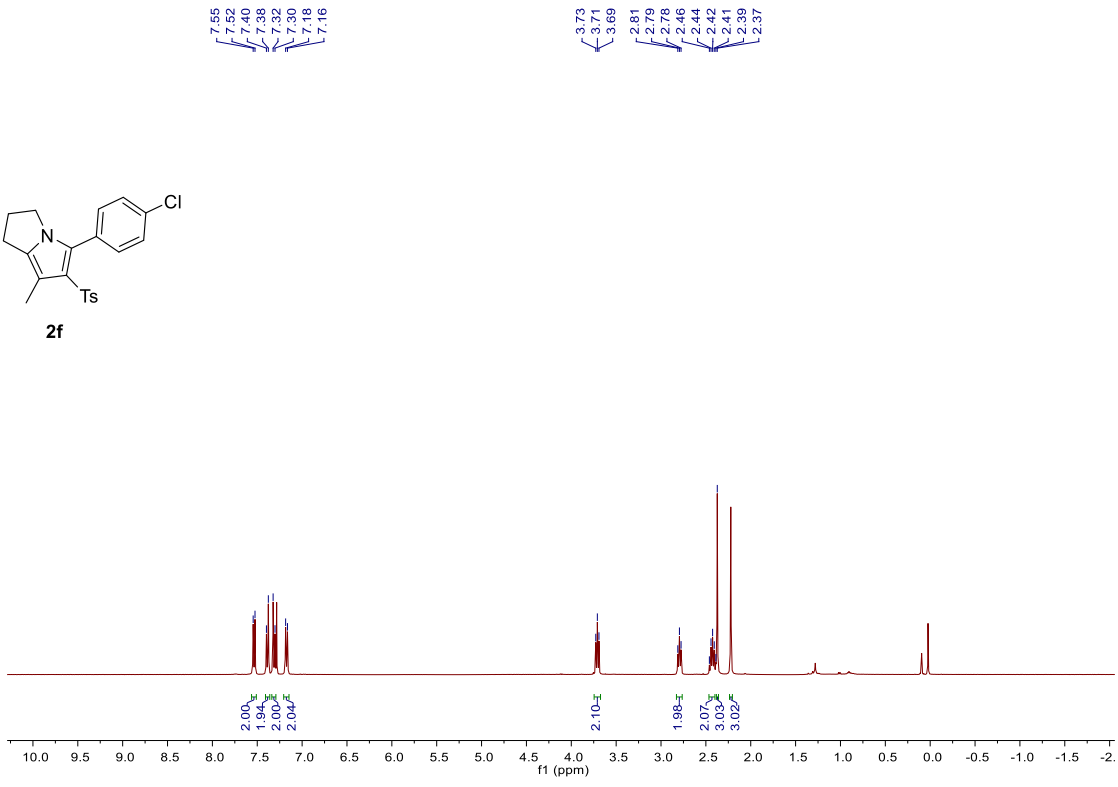


2e

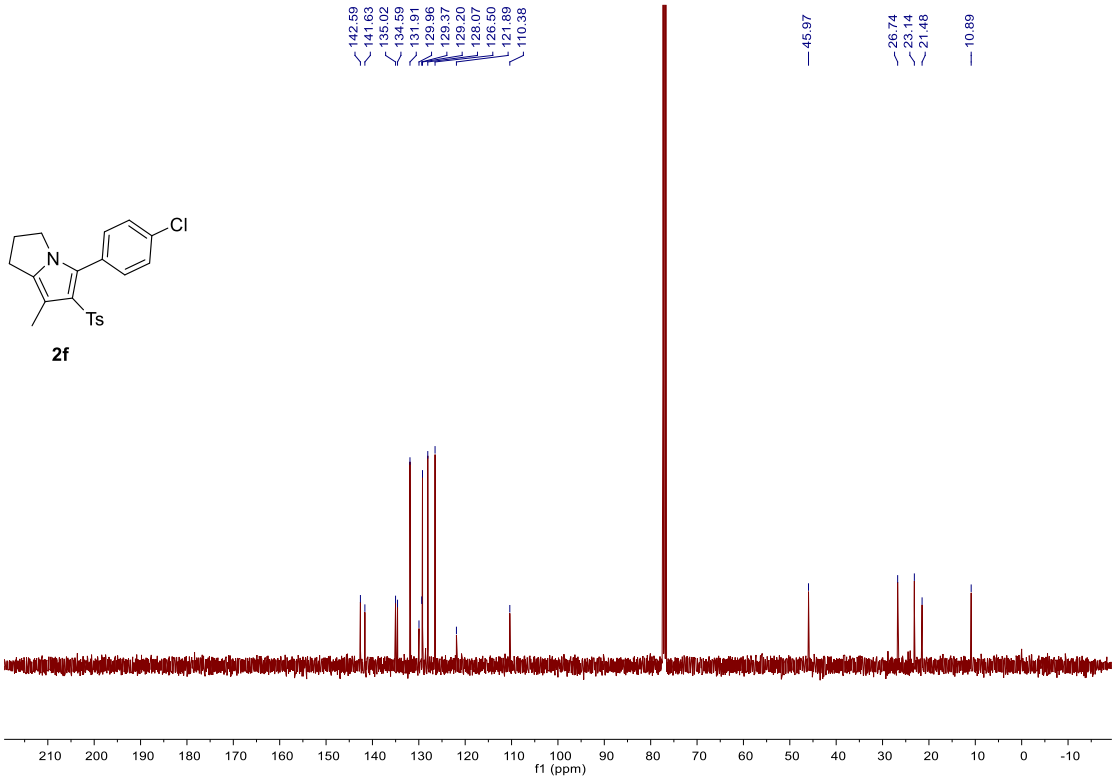


2e

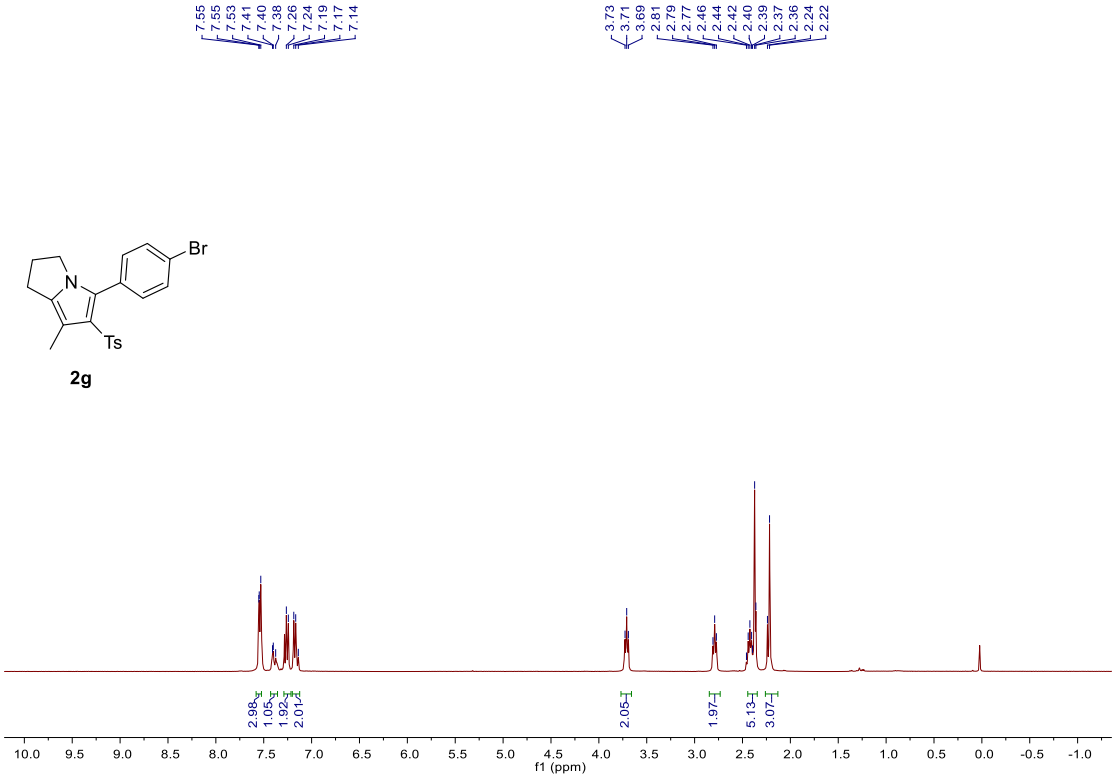
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2f**

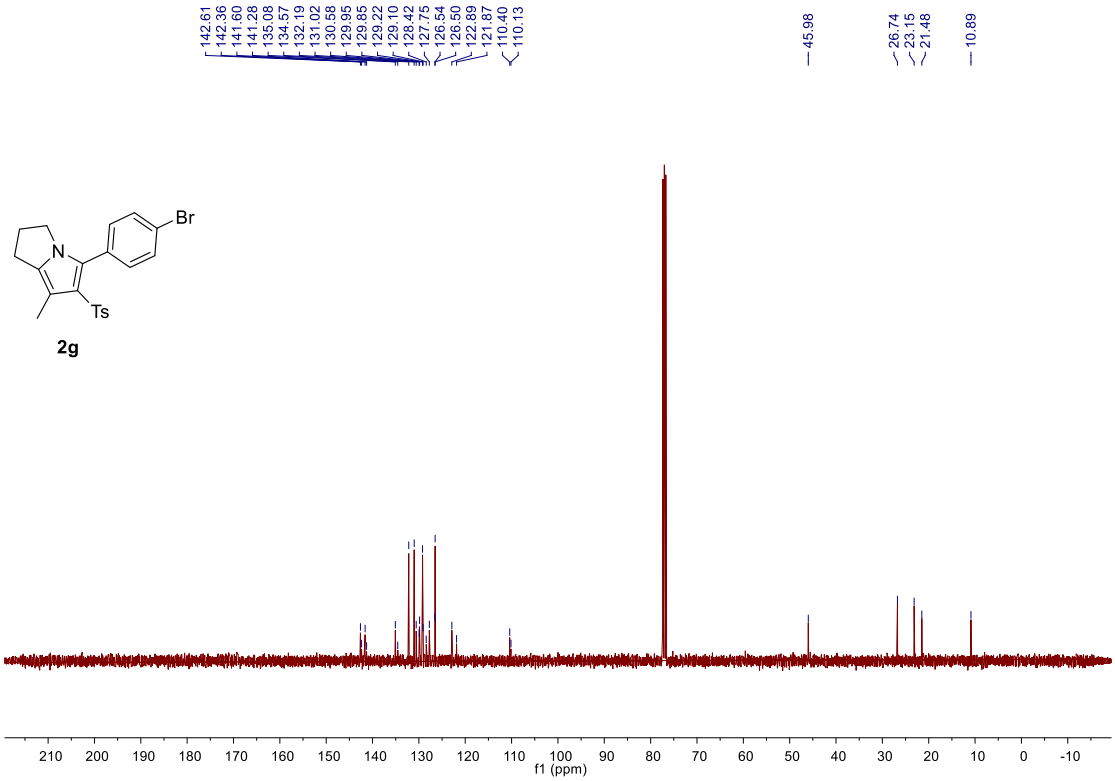


2f

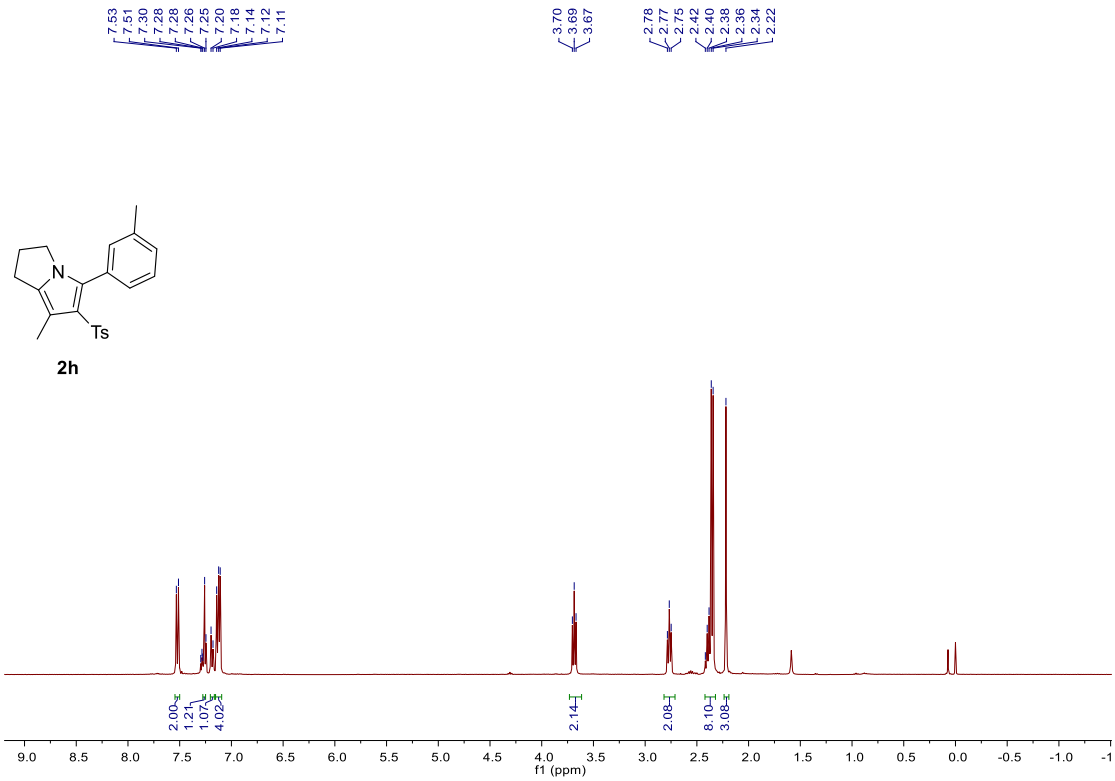


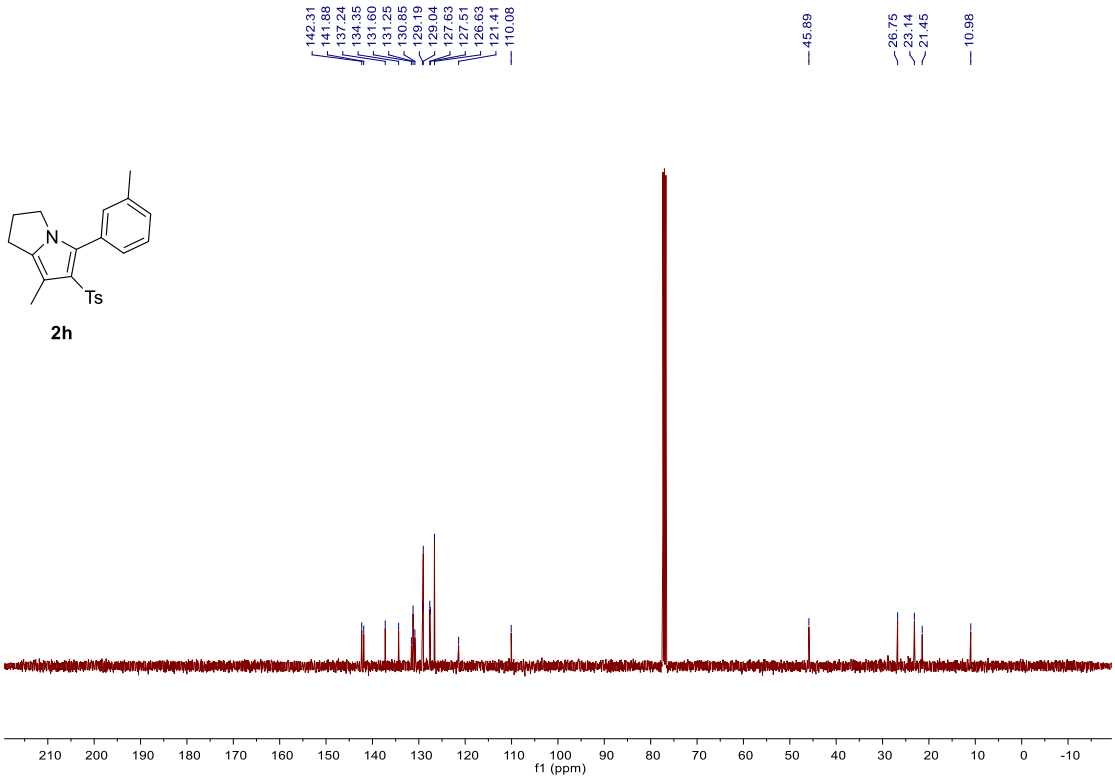
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2g**



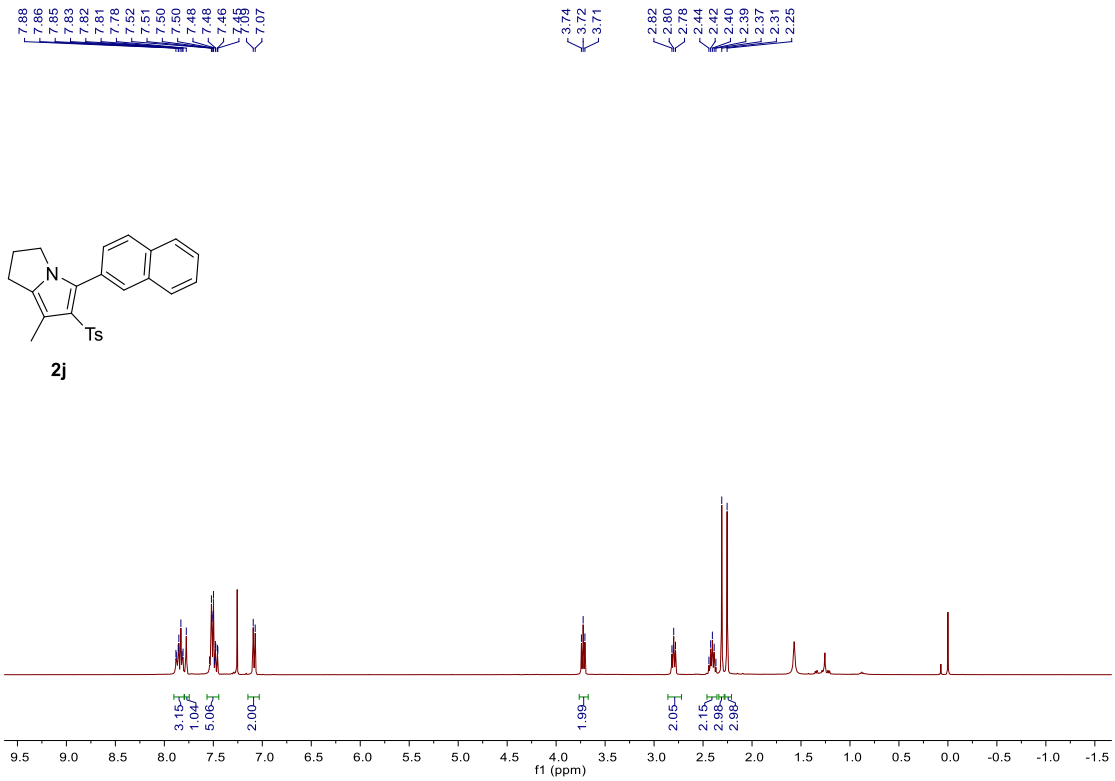


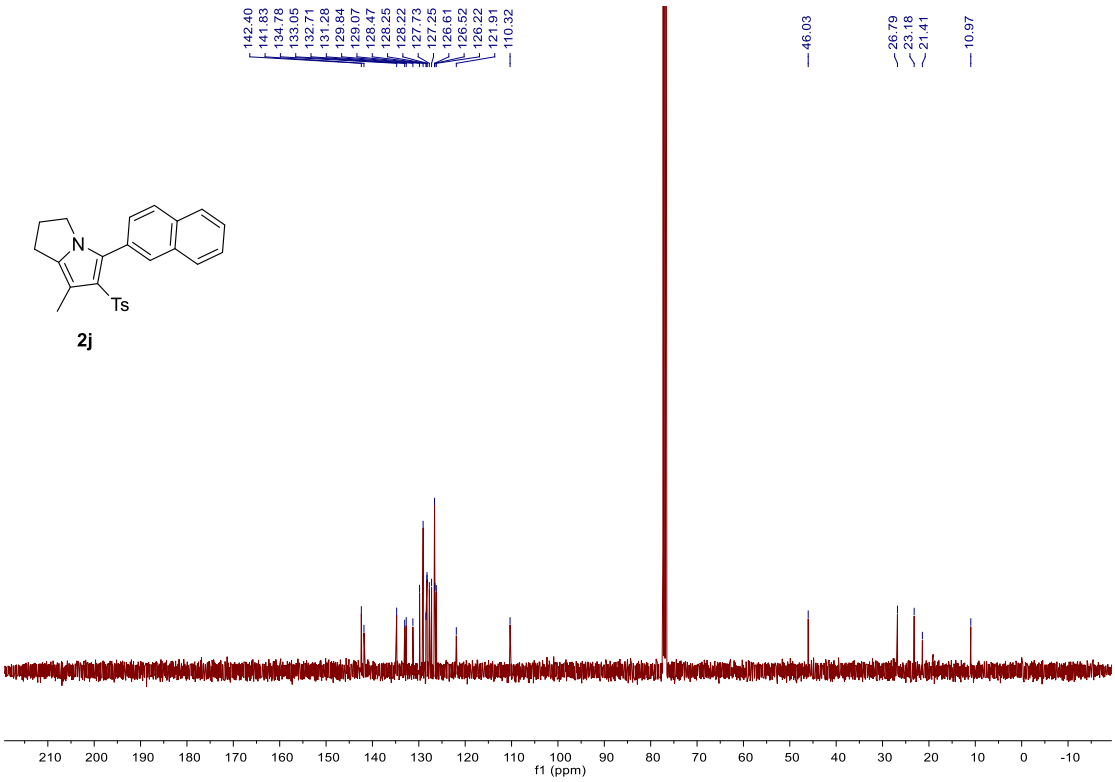
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2h**



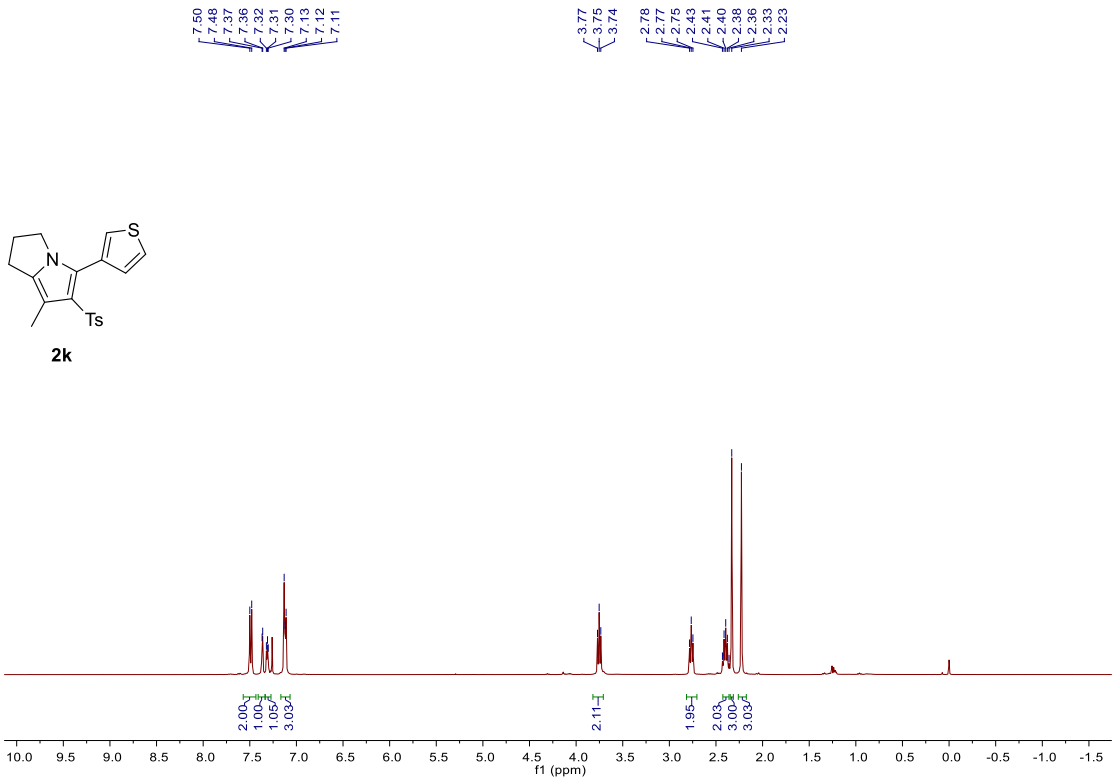


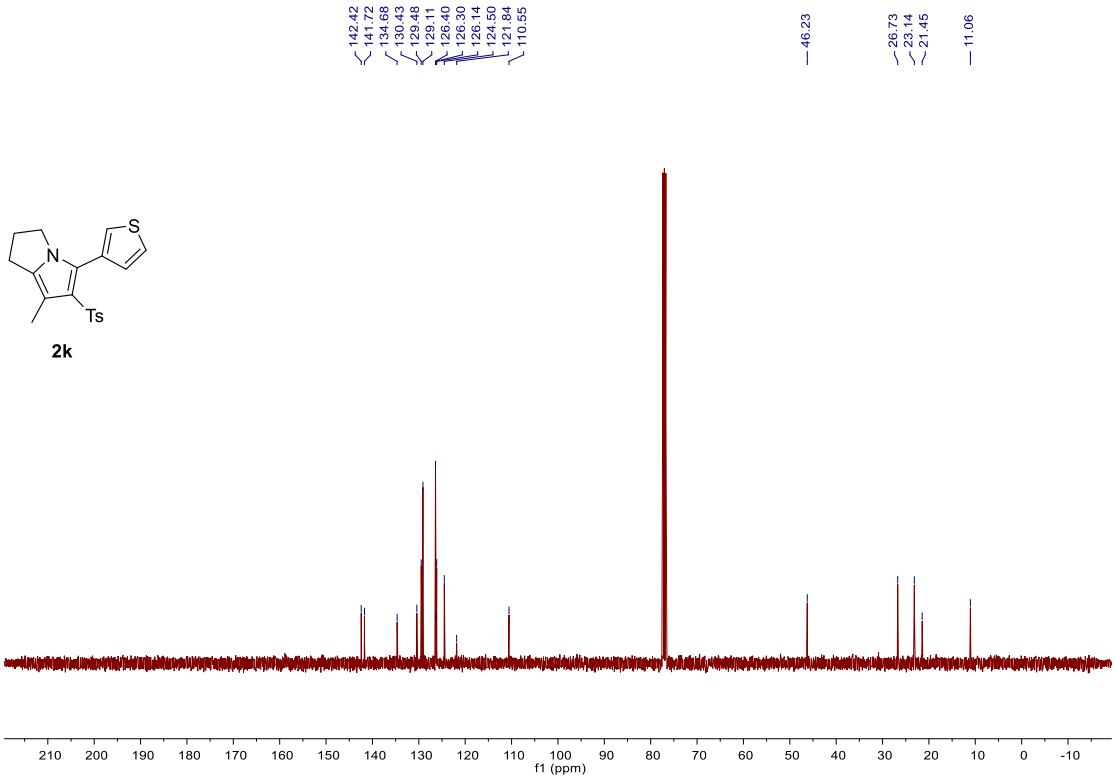
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2j**



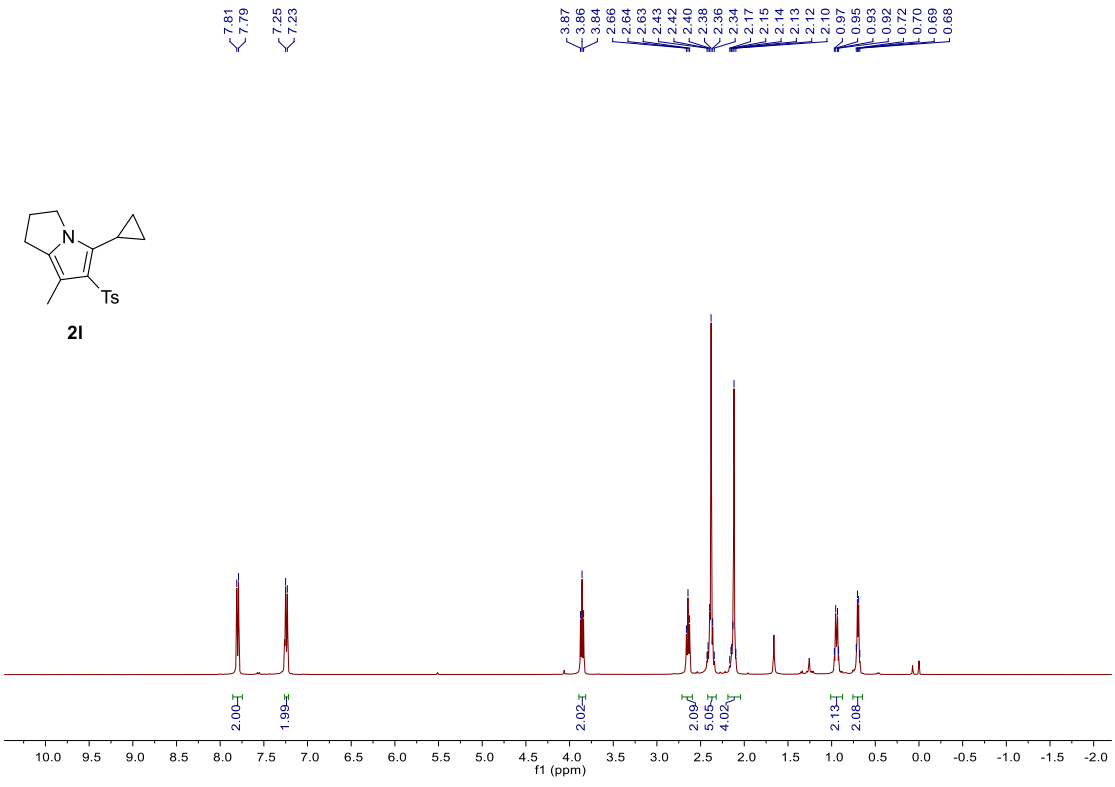


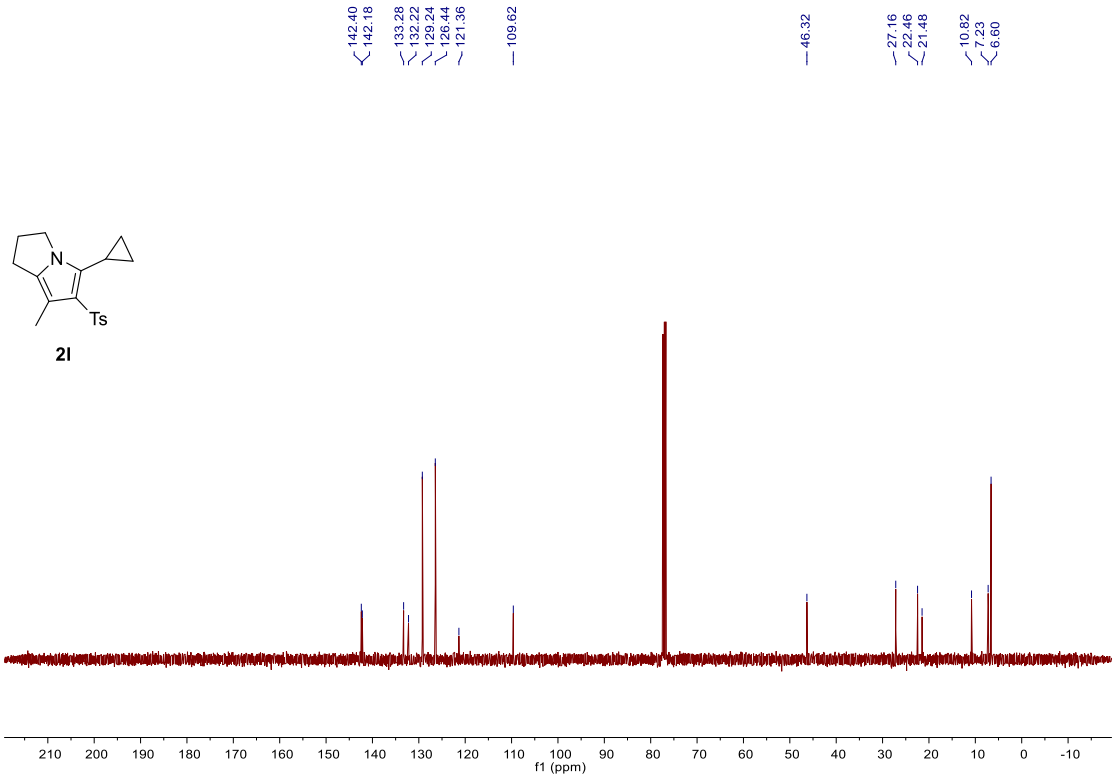
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2k**





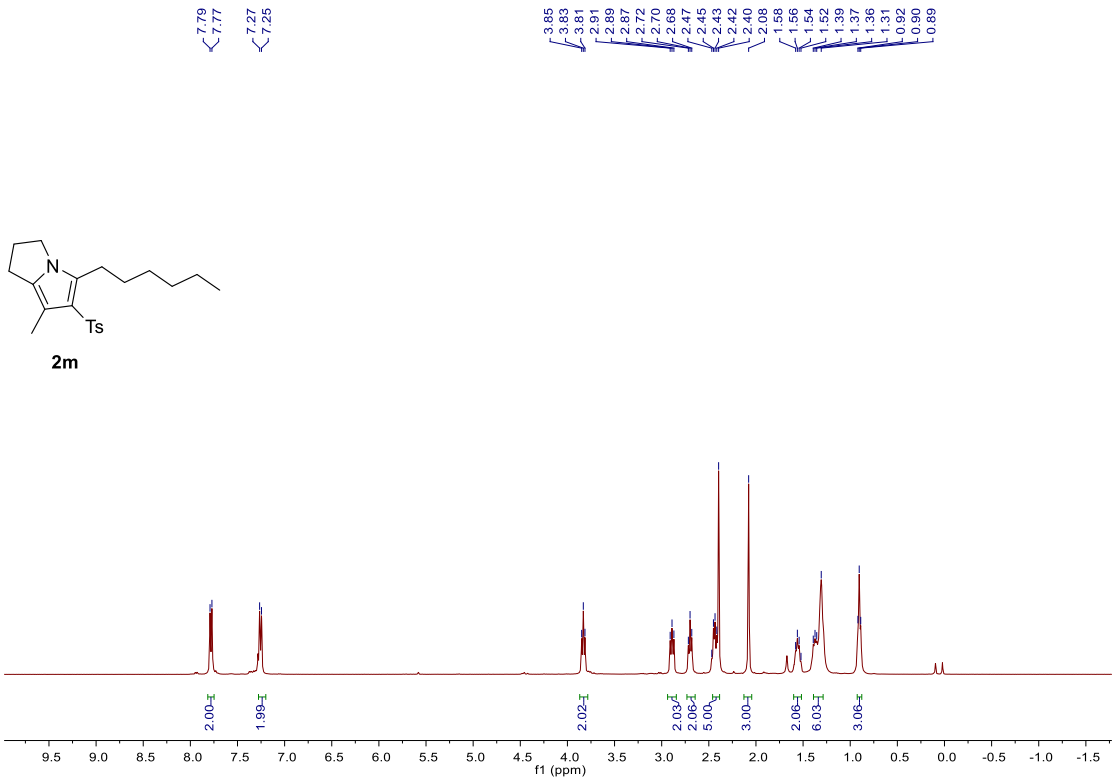
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2l**



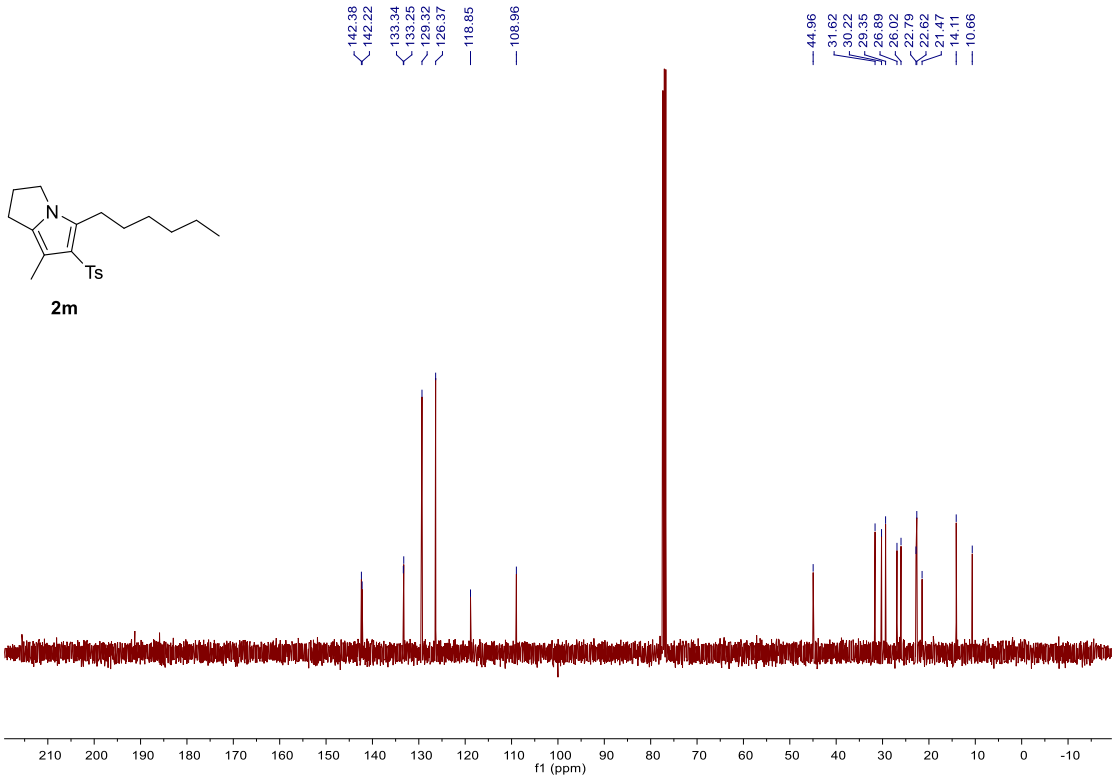


2l

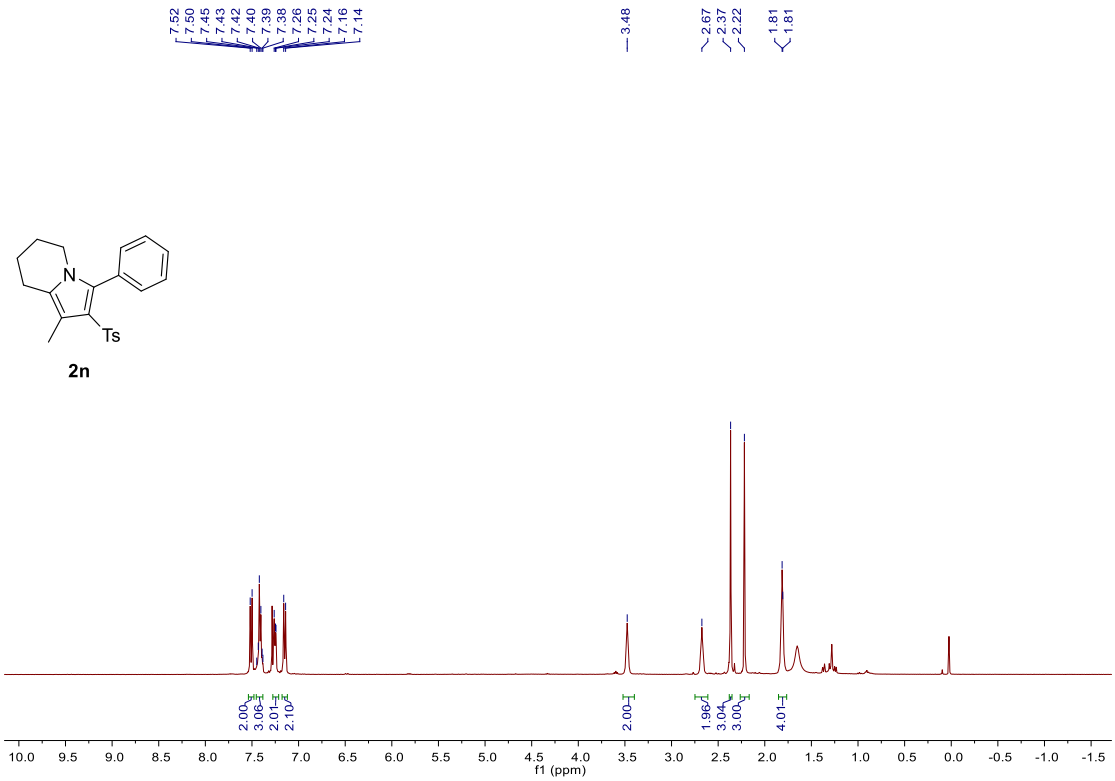
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2m**

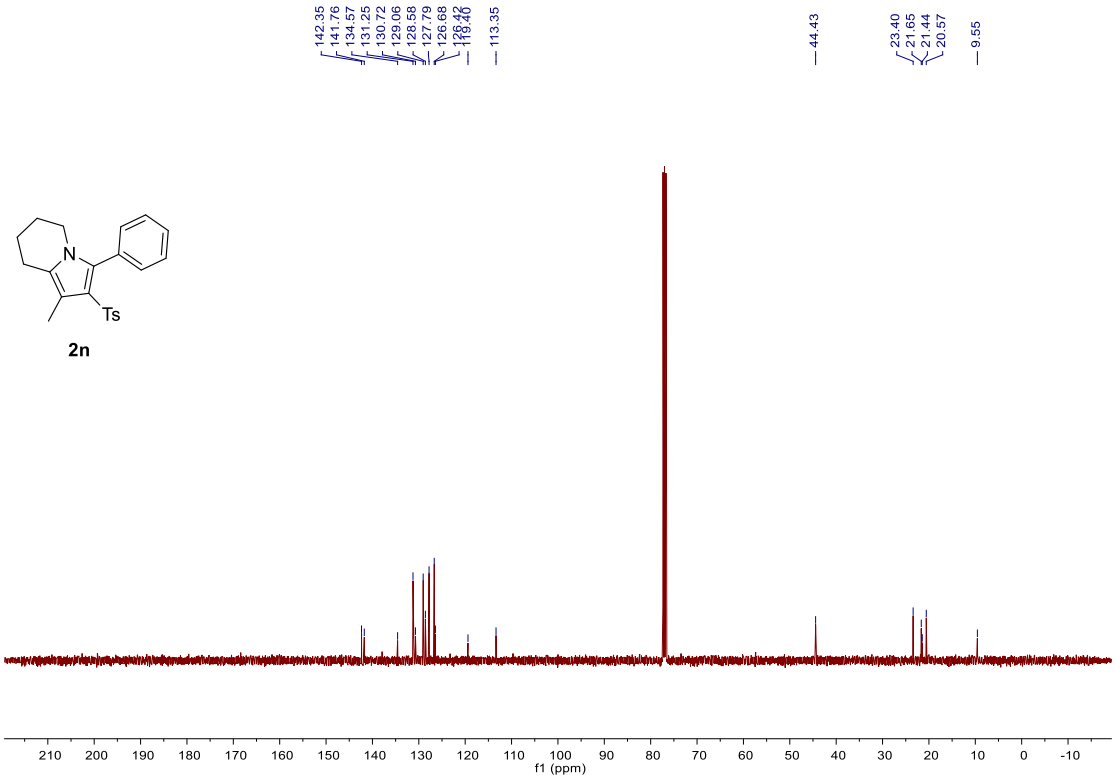


2m

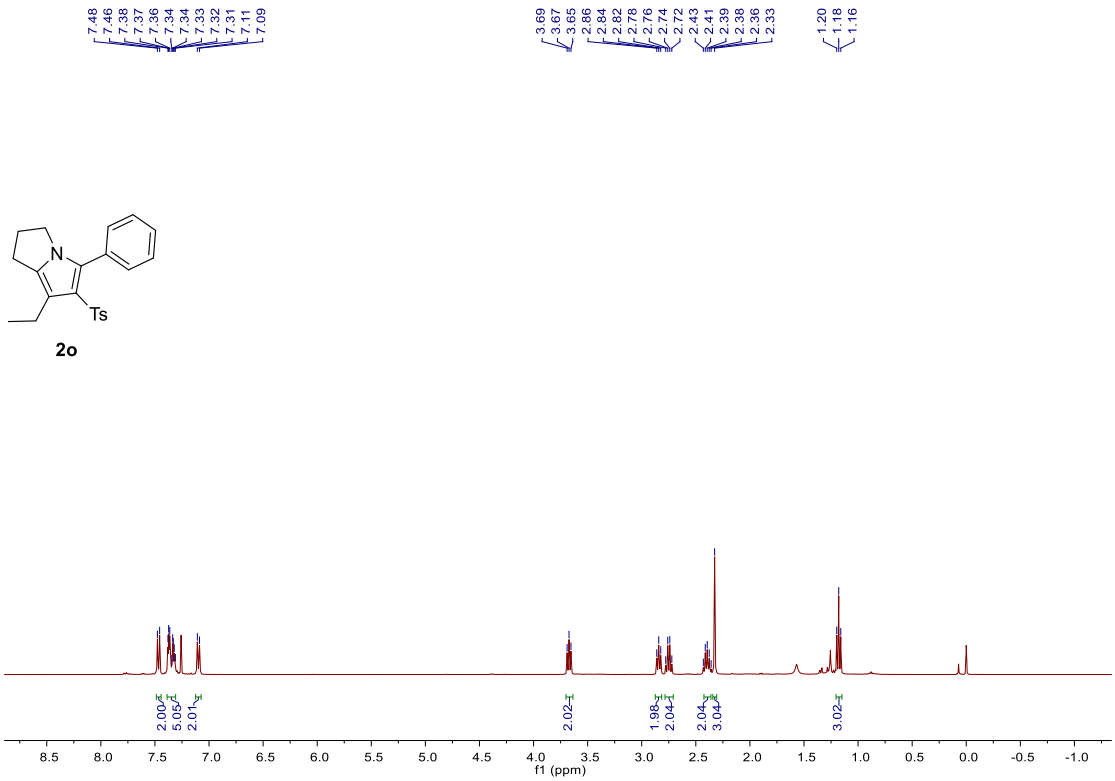


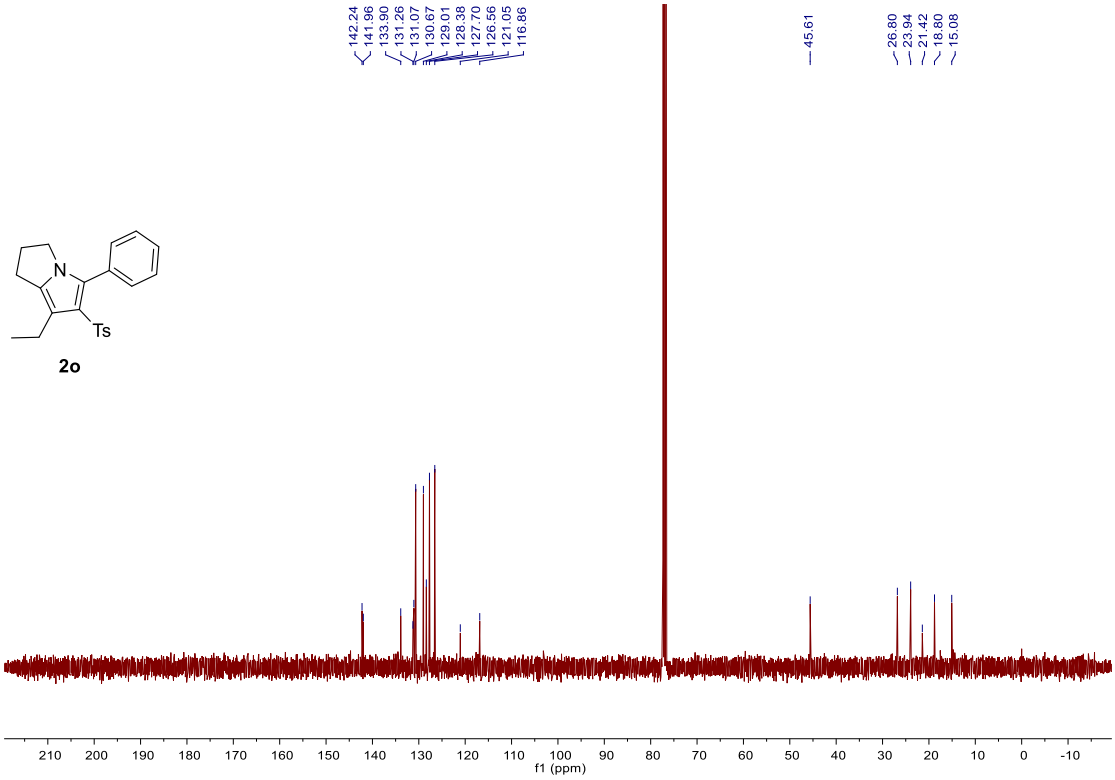
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2n**



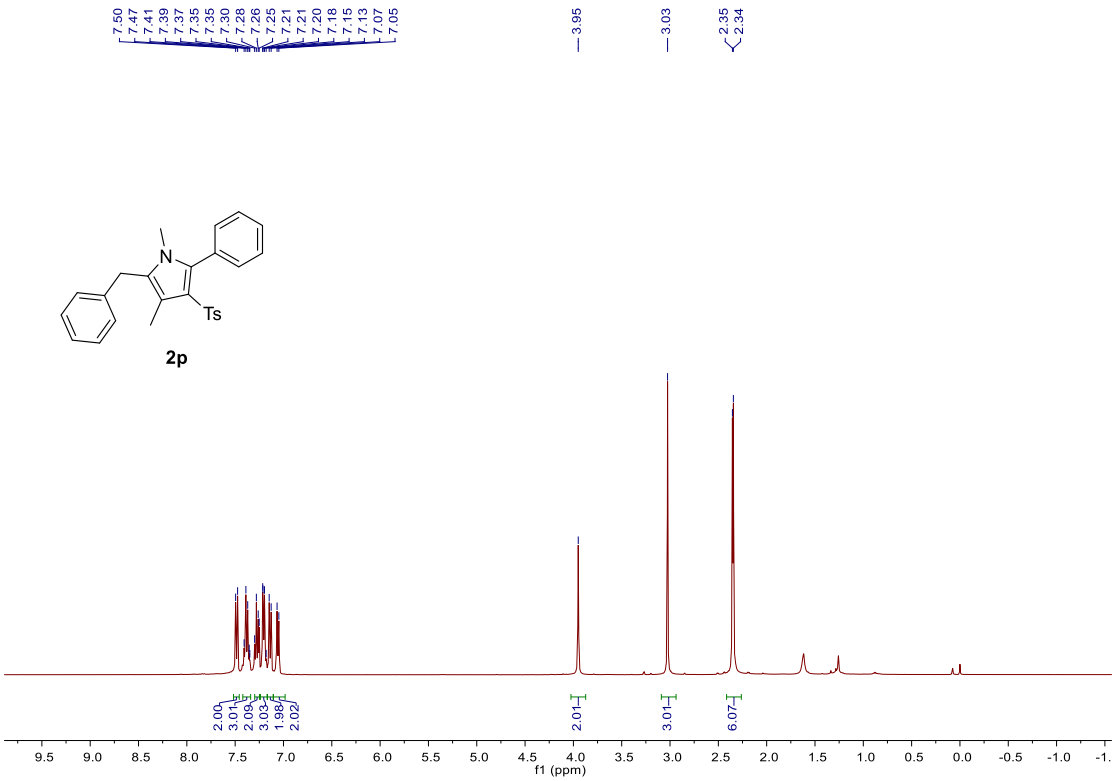


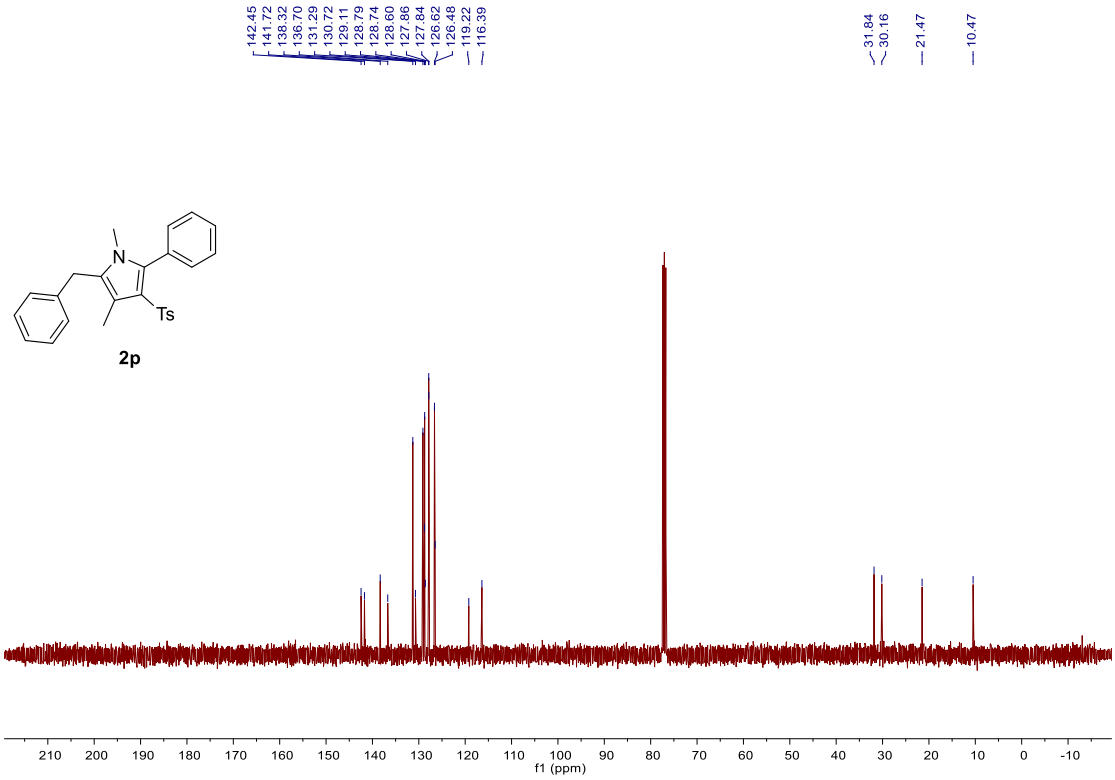
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2o**



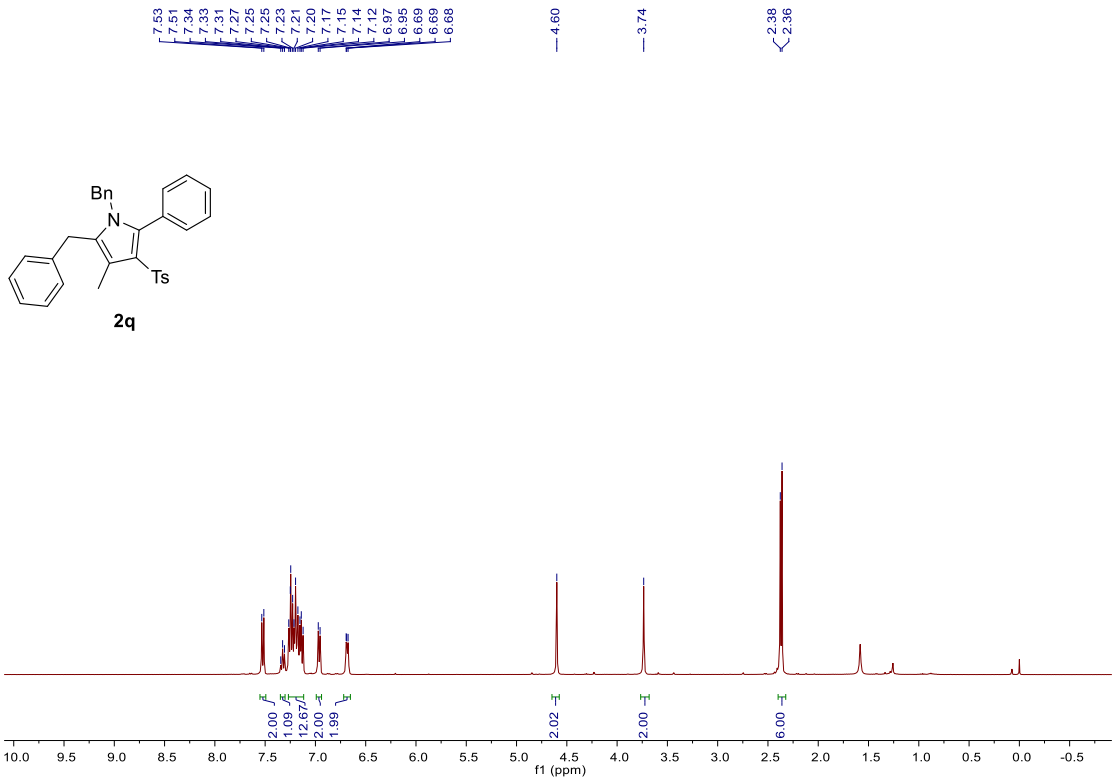


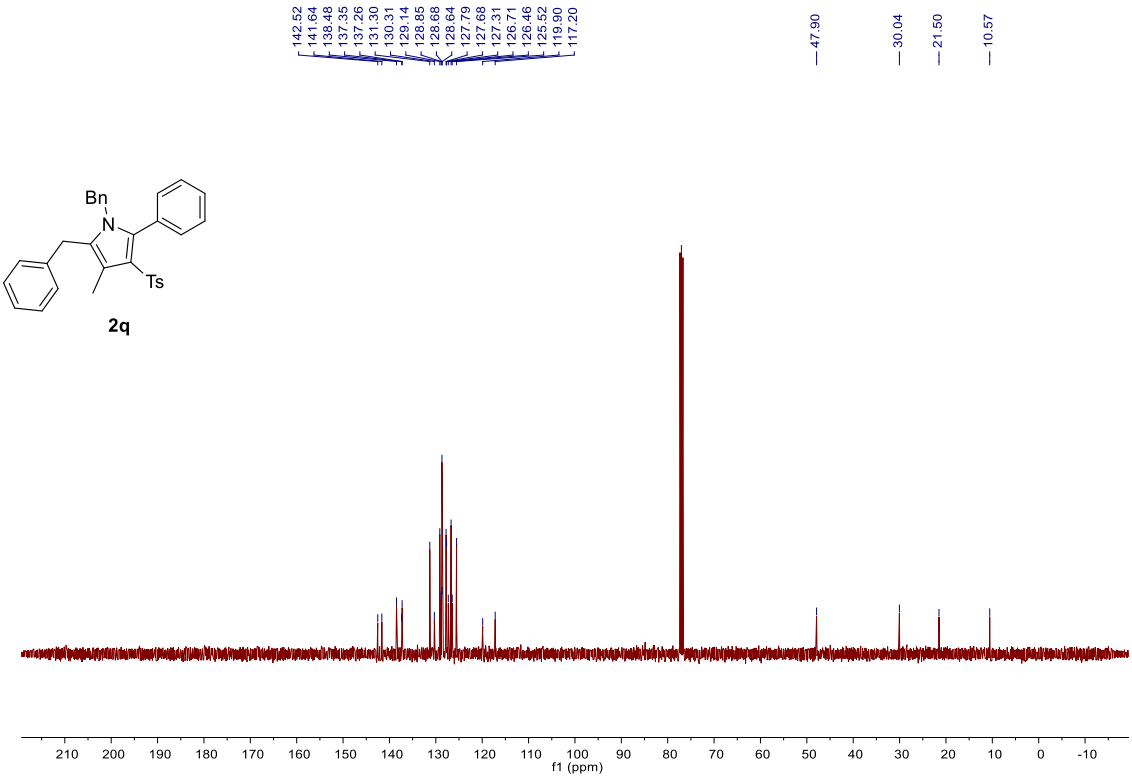
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2p**



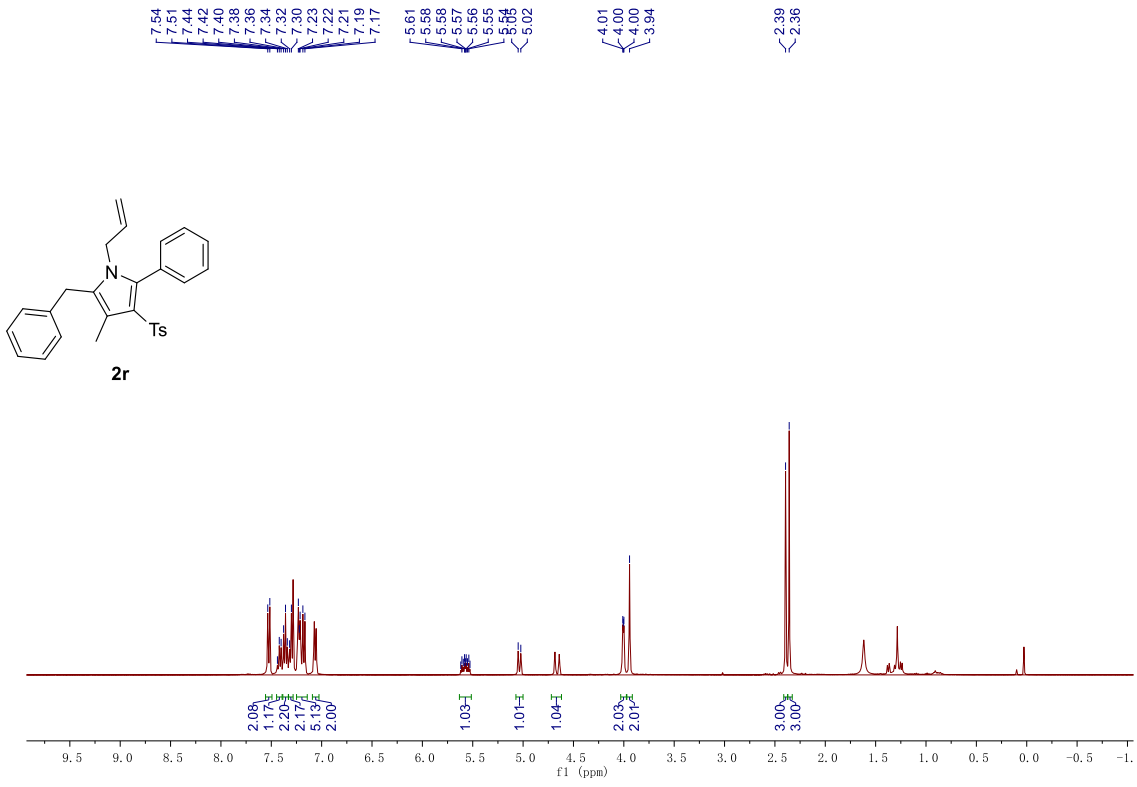


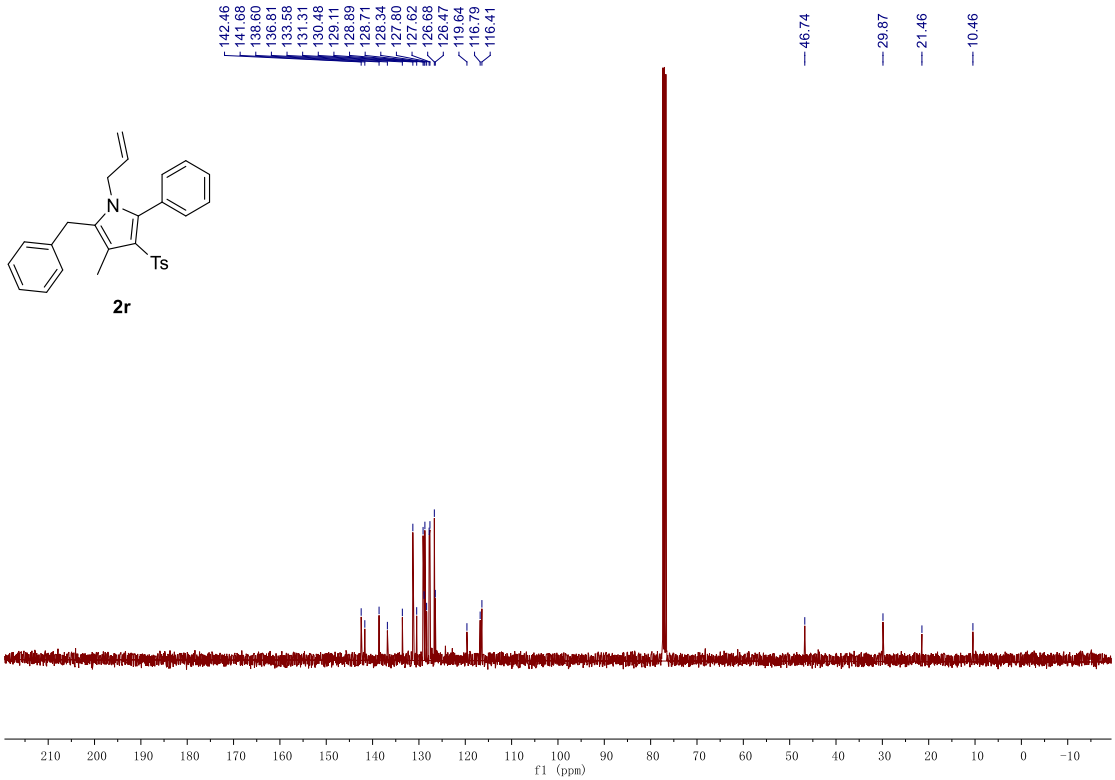
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2q**



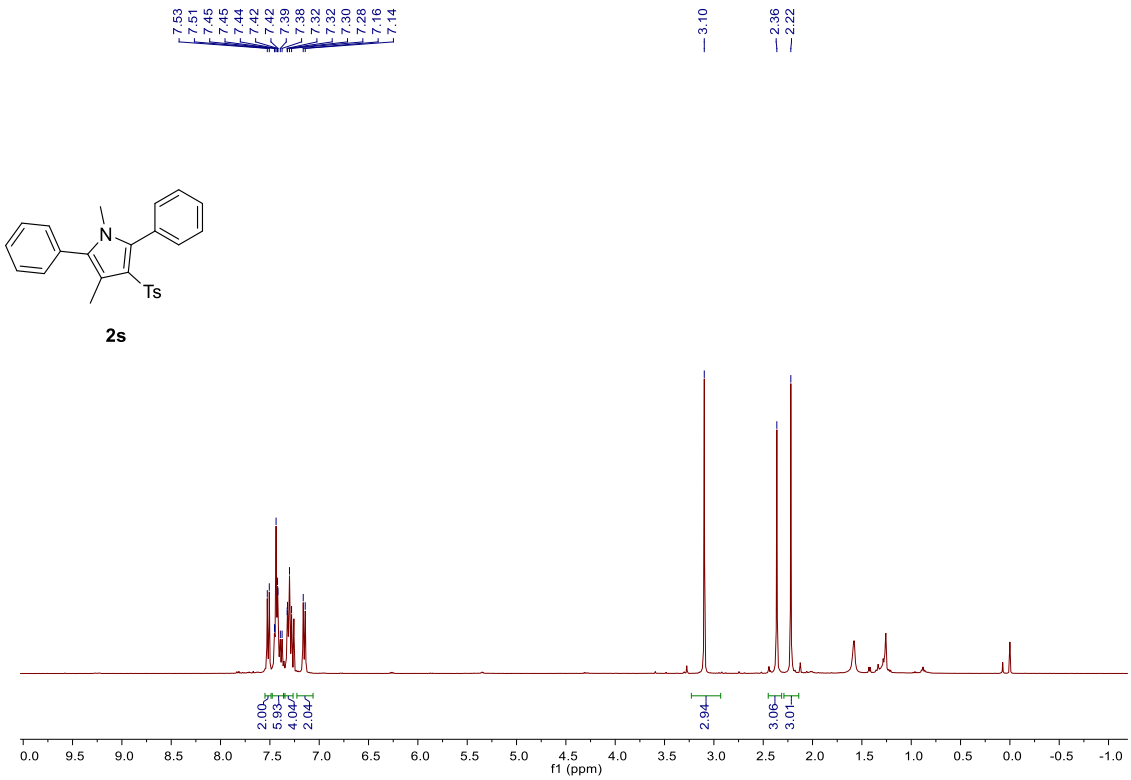


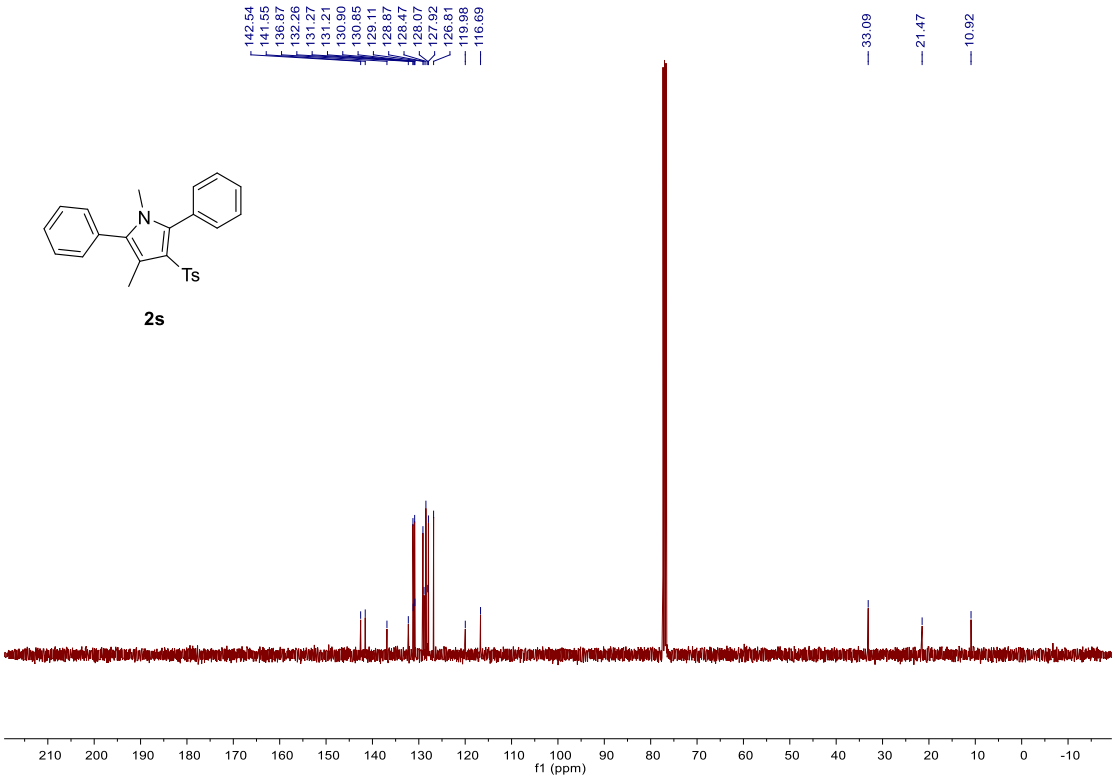
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2r**



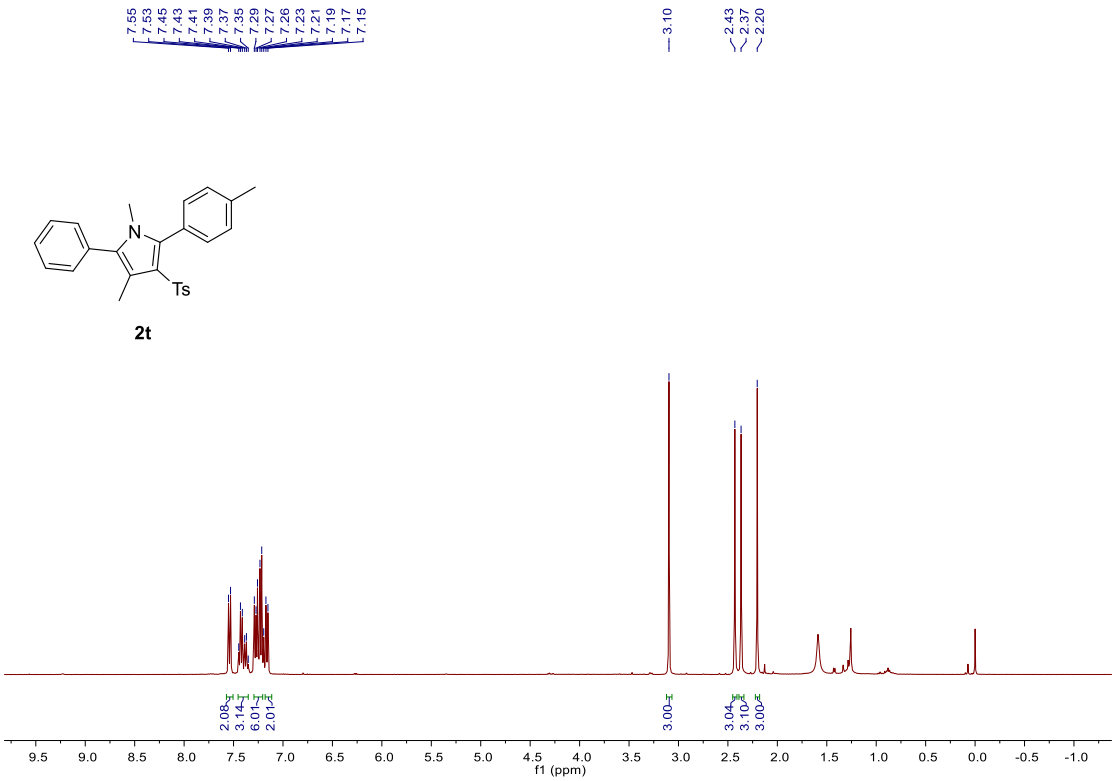


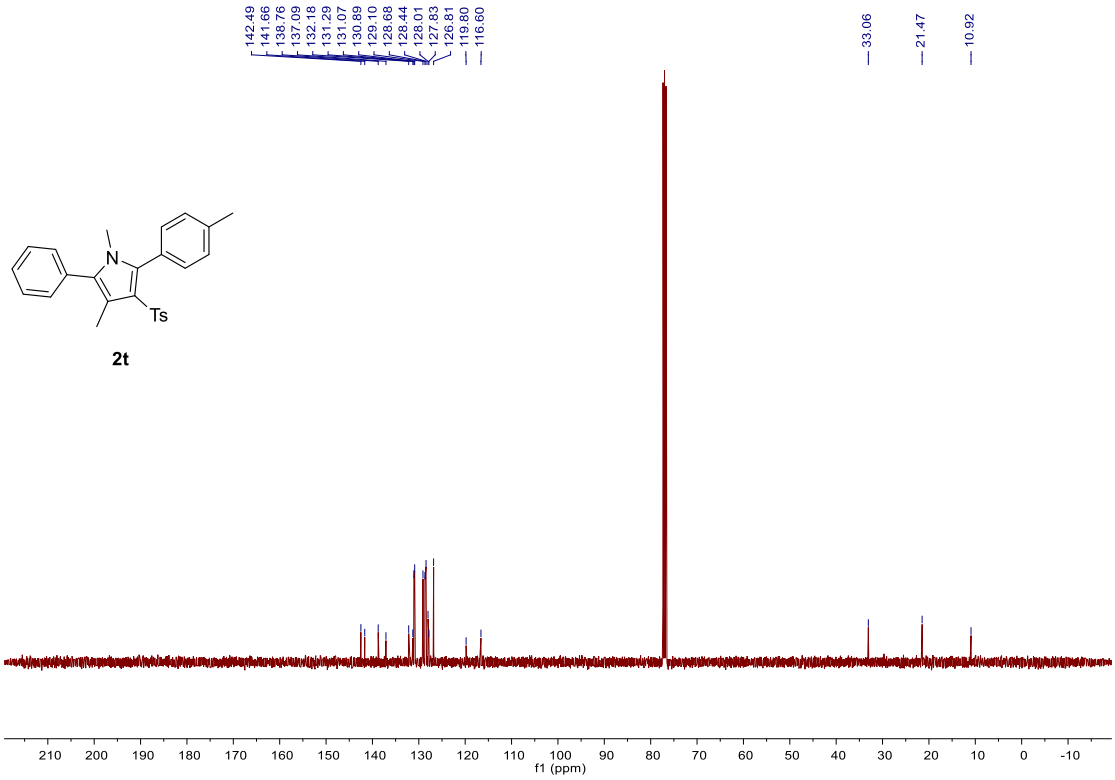
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2s**



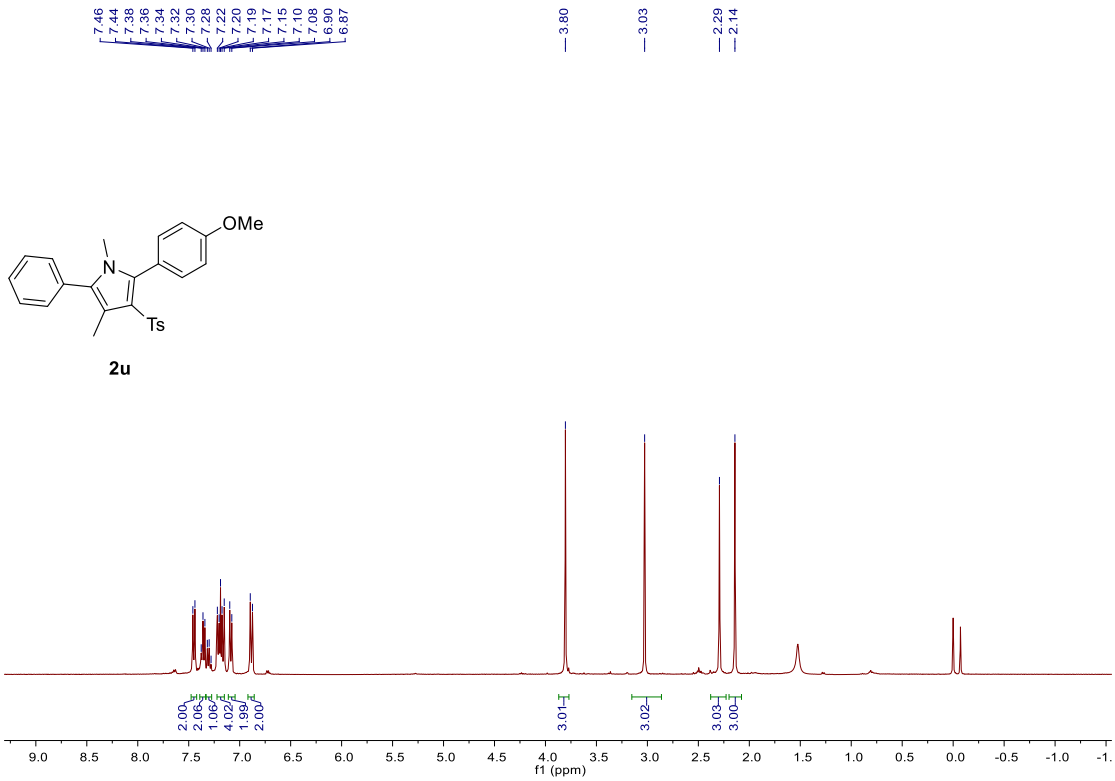


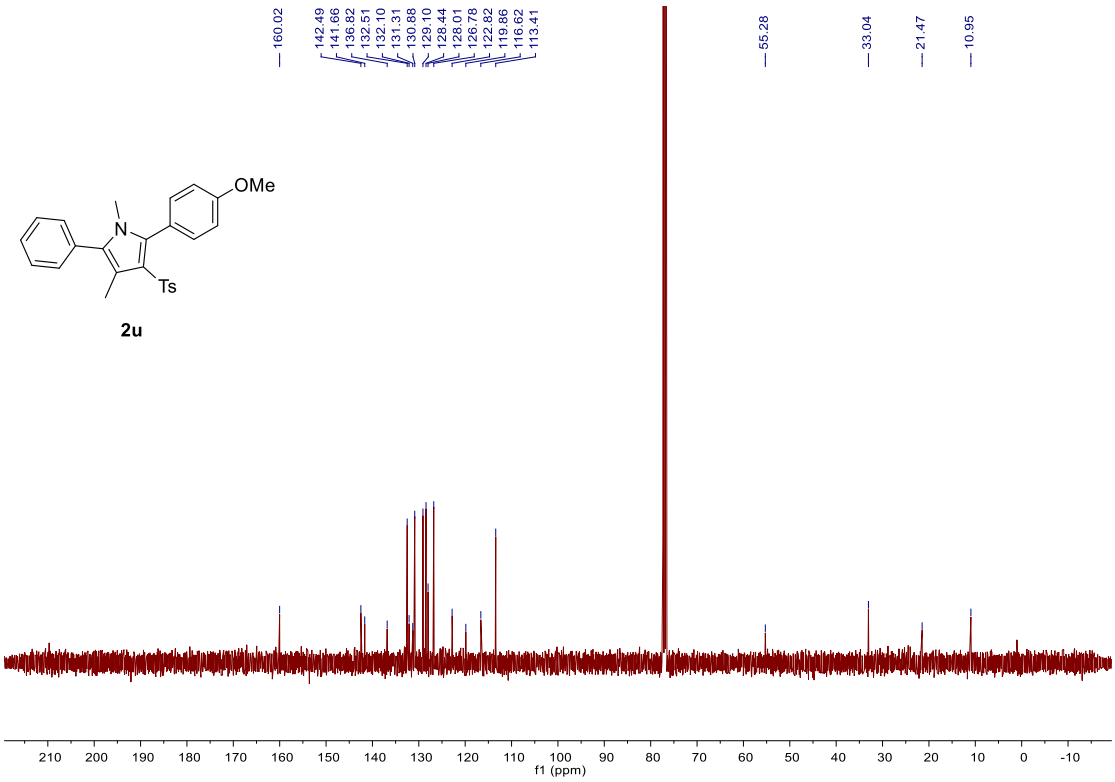
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2t**



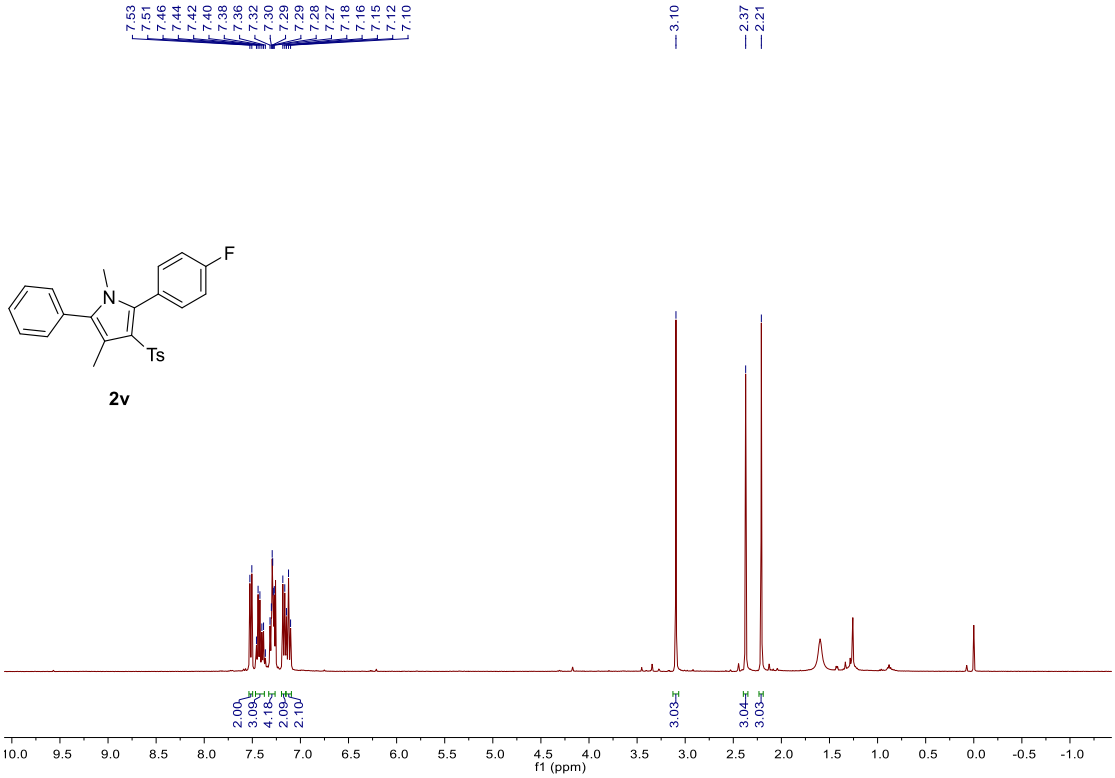


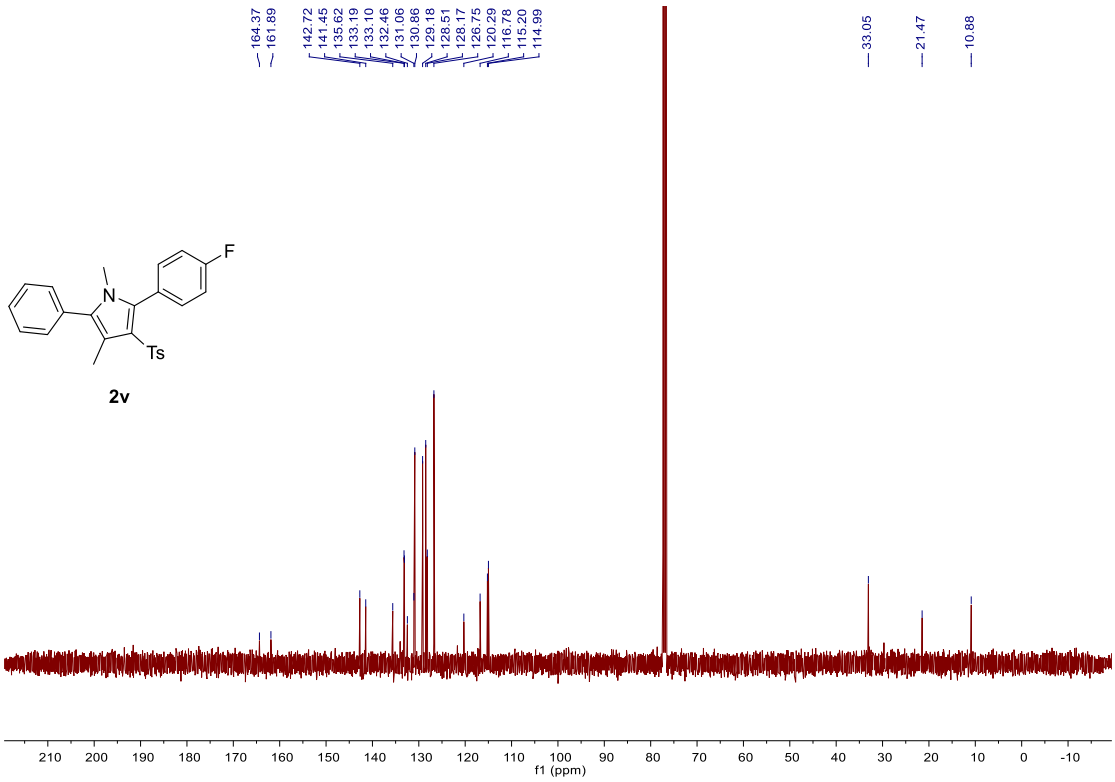
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2u**





^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of substrate **2v**




164.37
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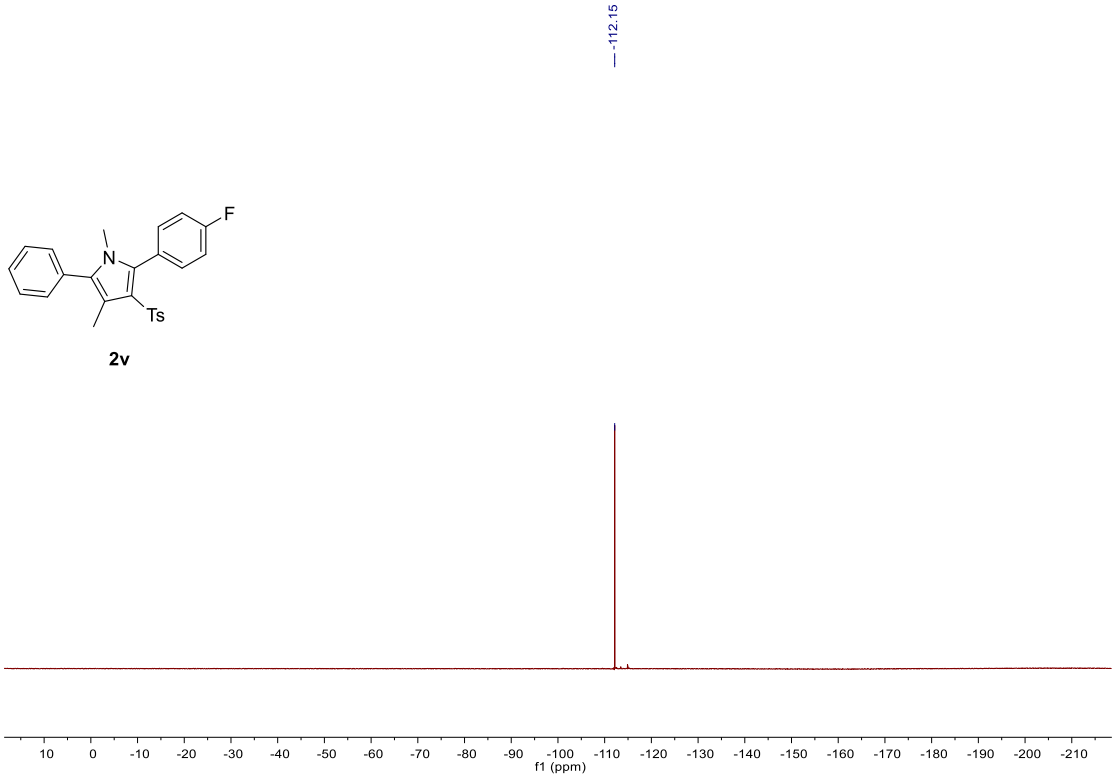
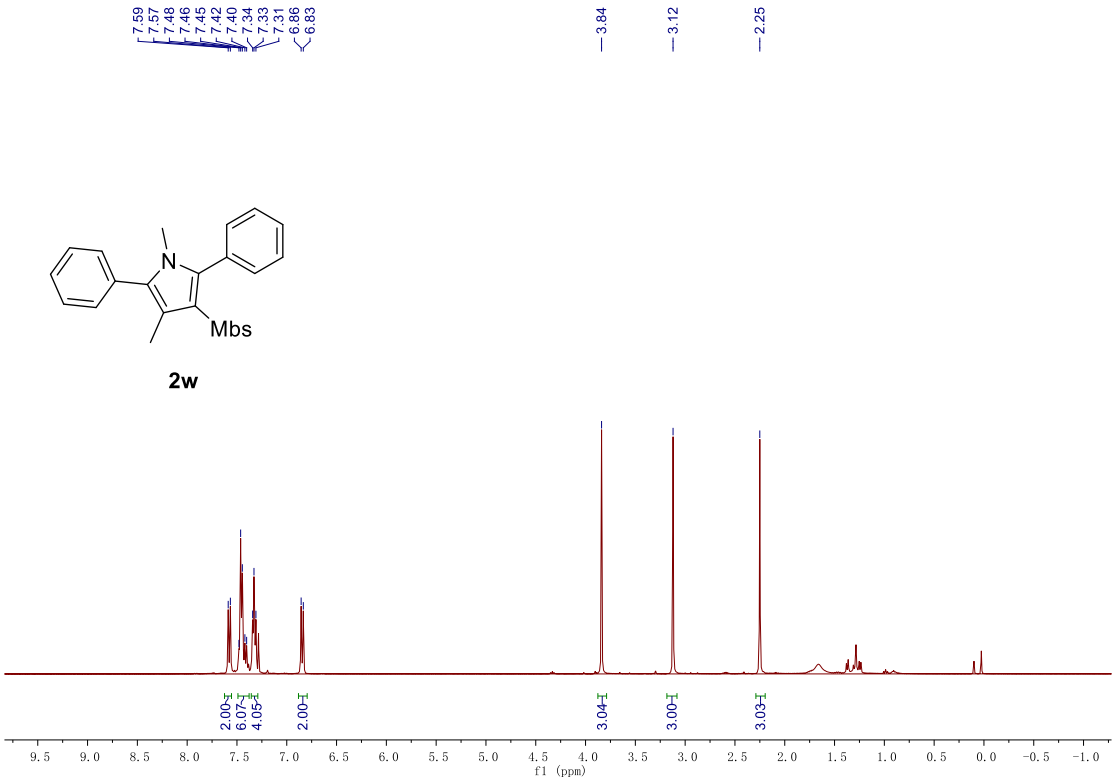
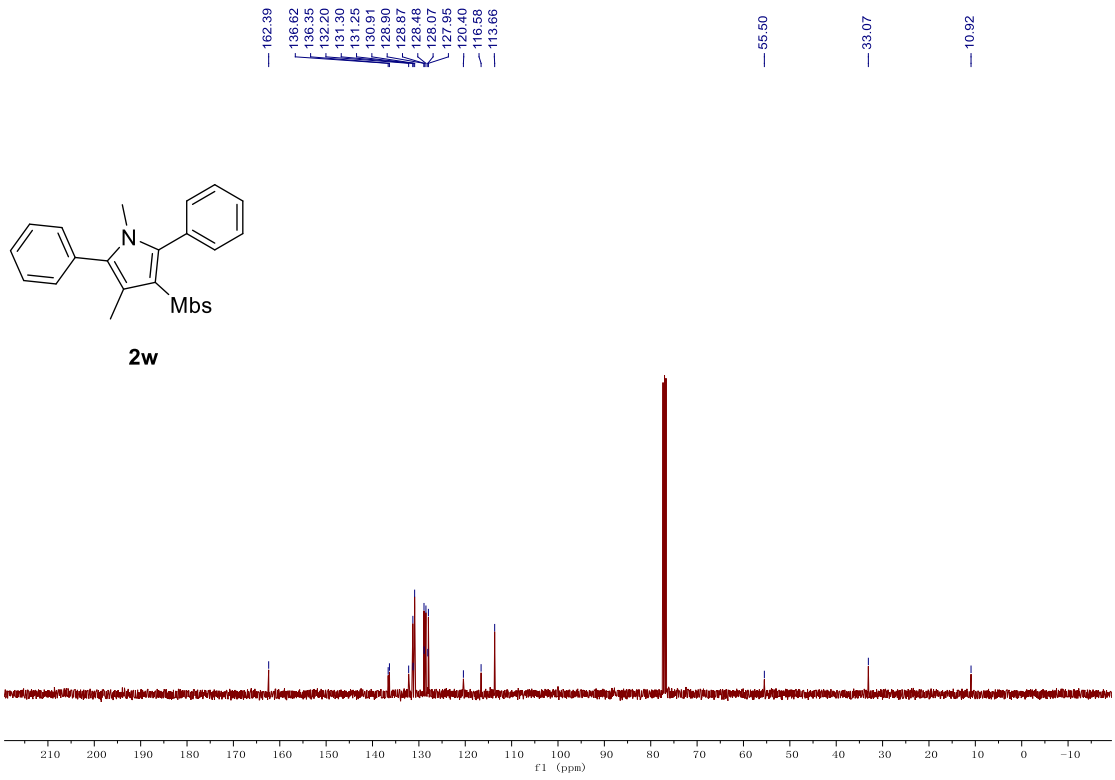
141.45
135.62
133.19
133.10
132.46
131.06
130.86
129.18
128.51
128.17
126.75
120.29
116.78
115.20
114.99
33.05
21.47
10.88
F
N
Ts
2v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

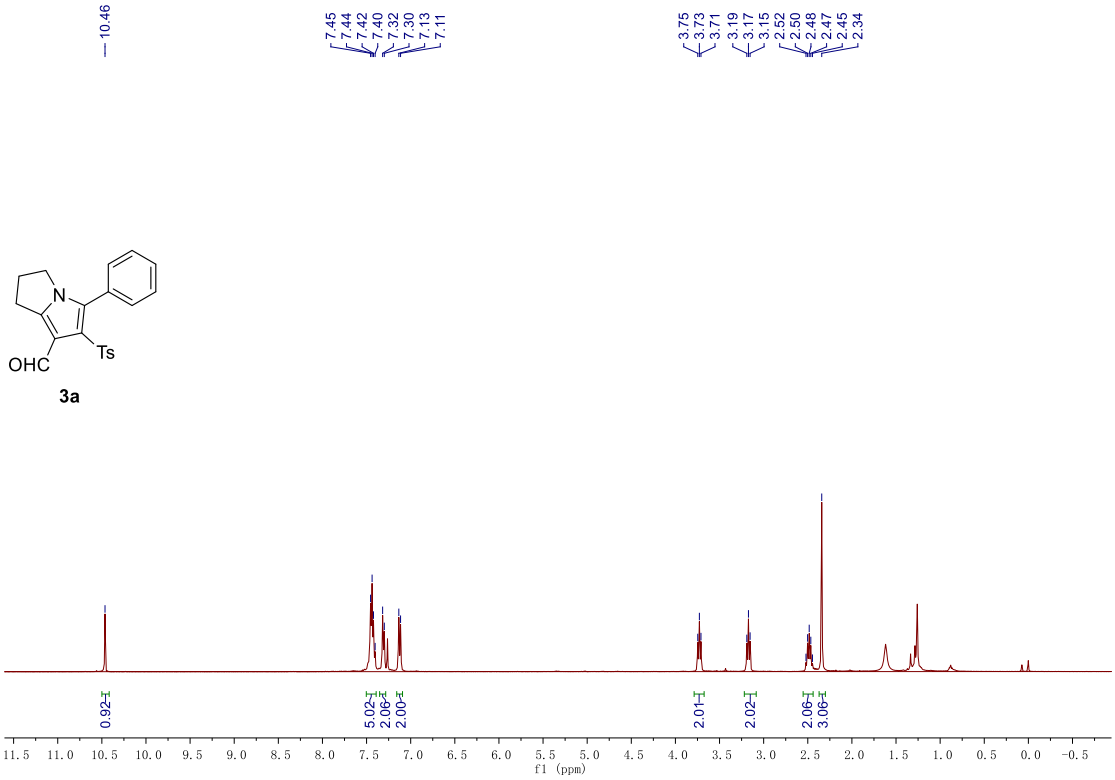

-112.15
F
N
Ts
2v
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

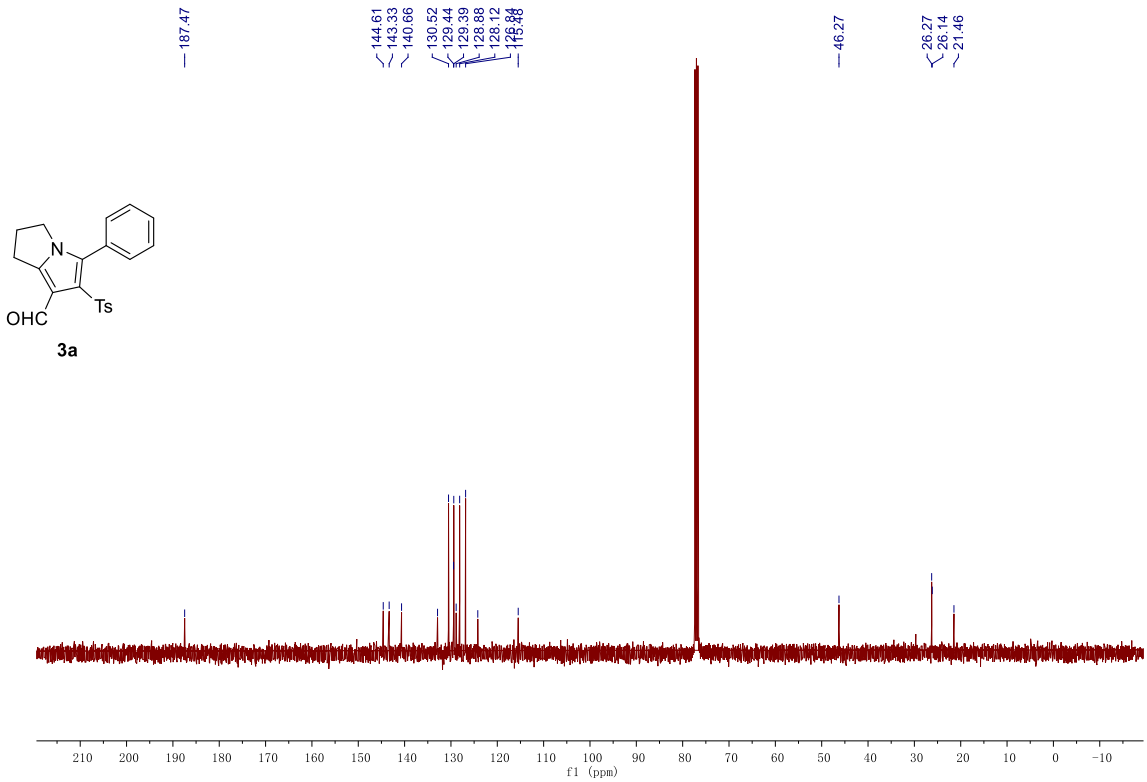
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **2w**



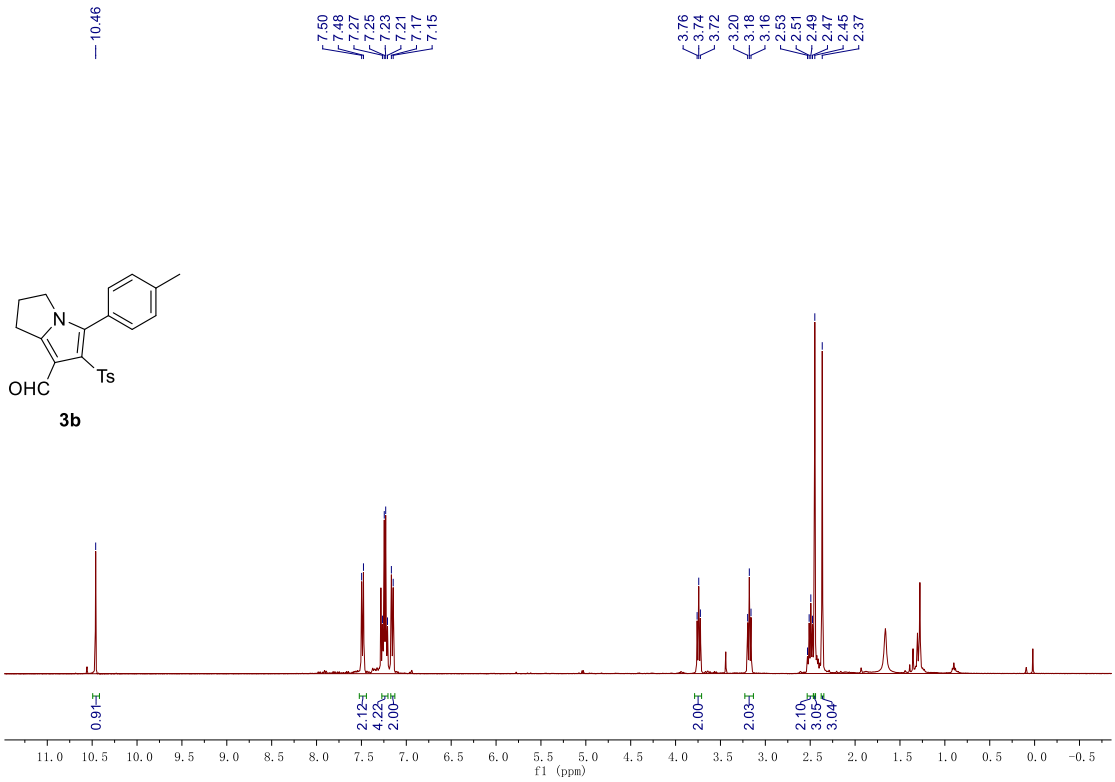


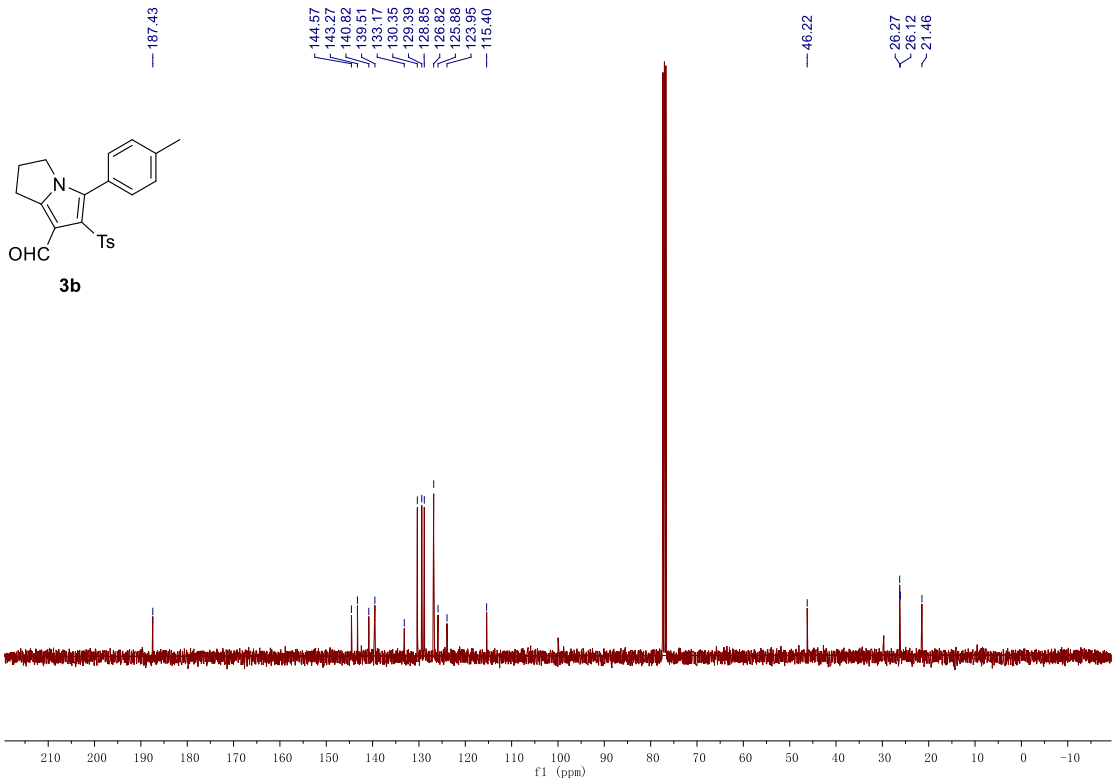
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **3a**



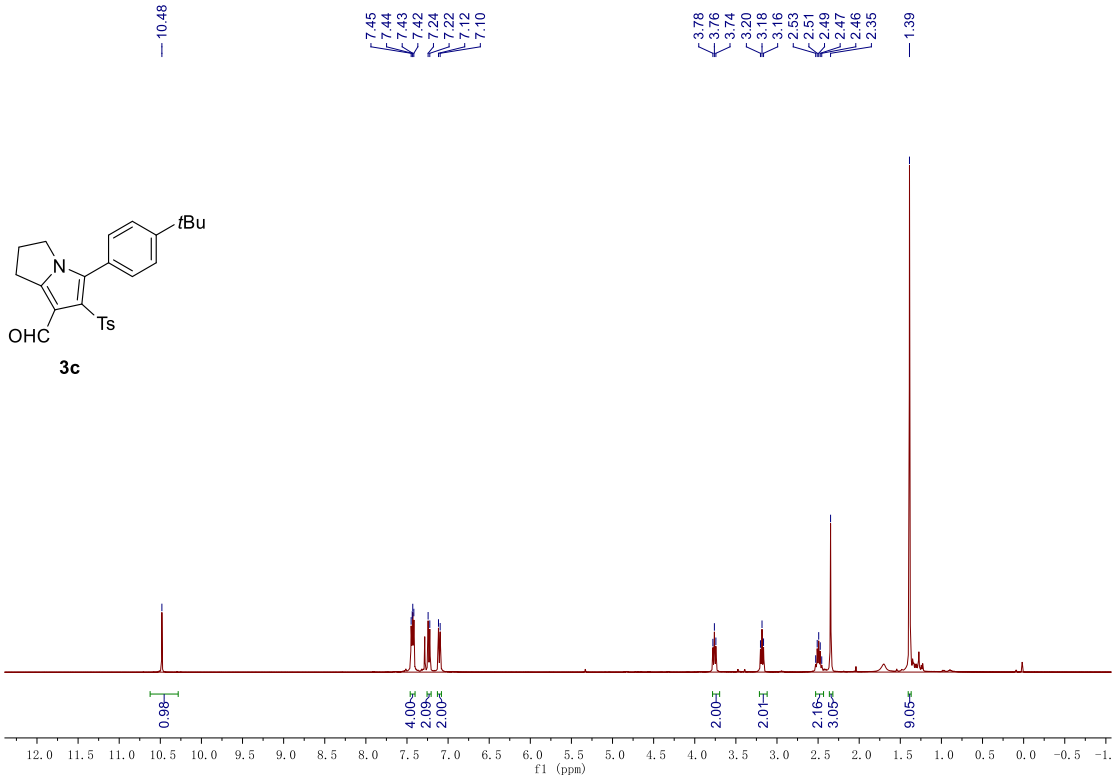


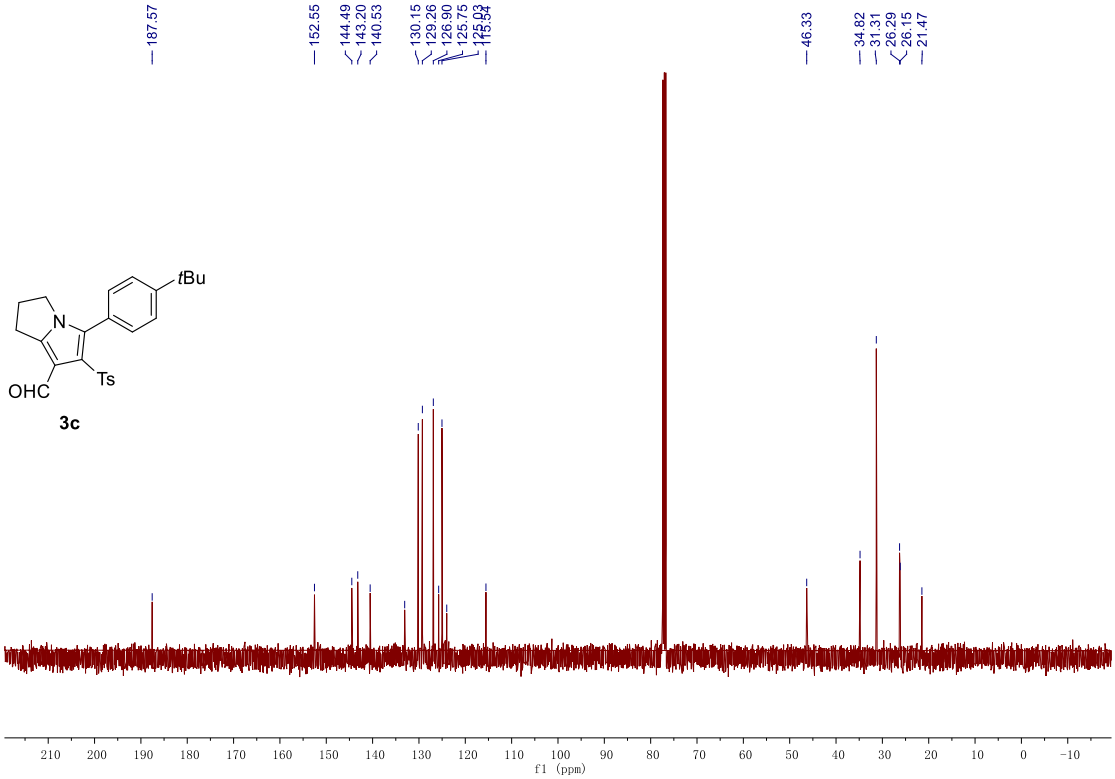
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **3b**



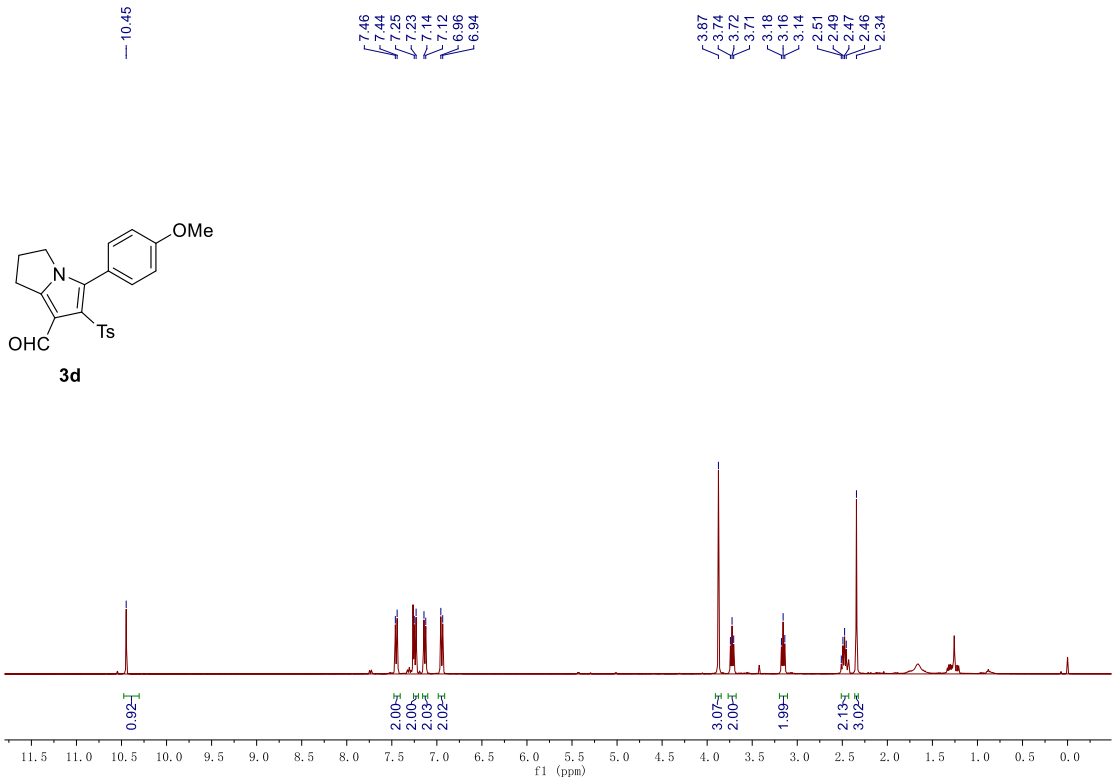


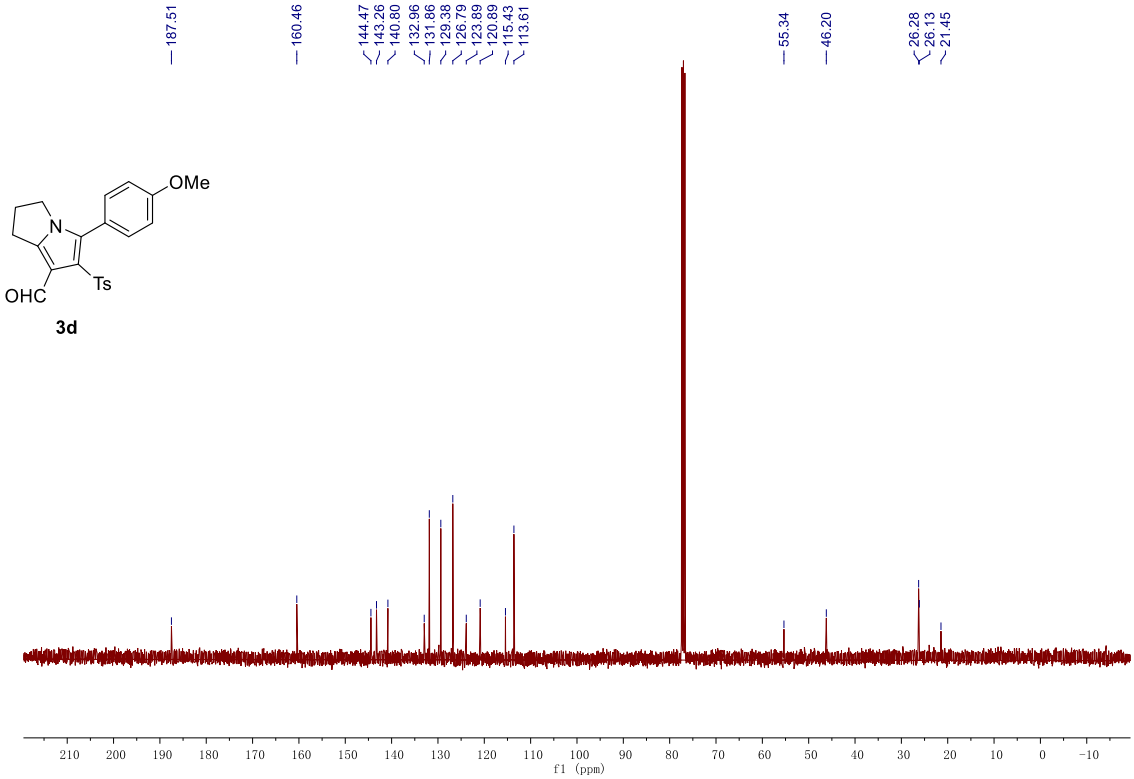
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **3c**



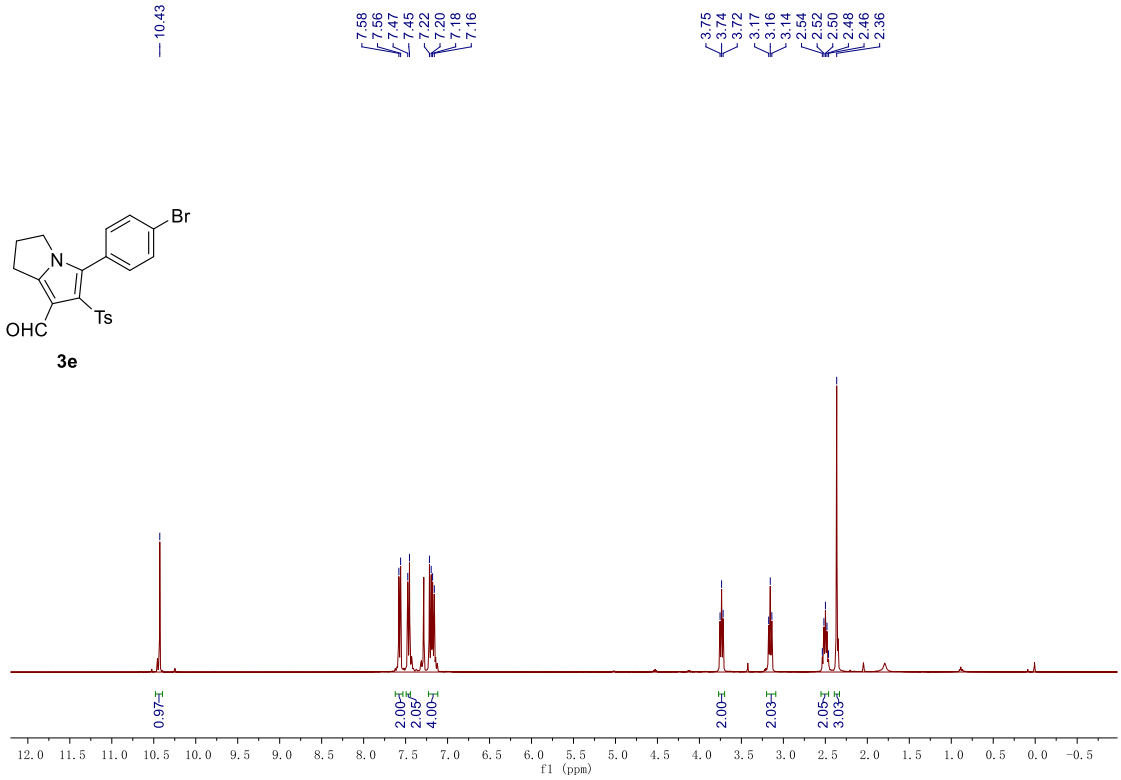


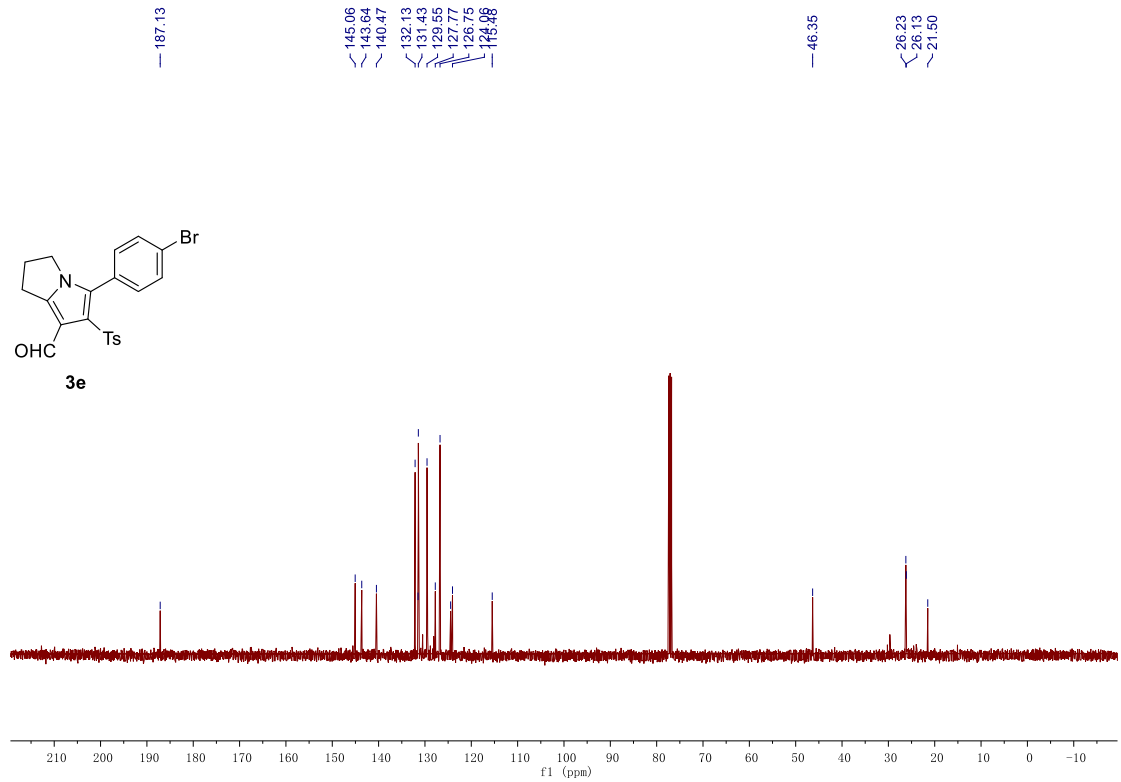
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **3d**



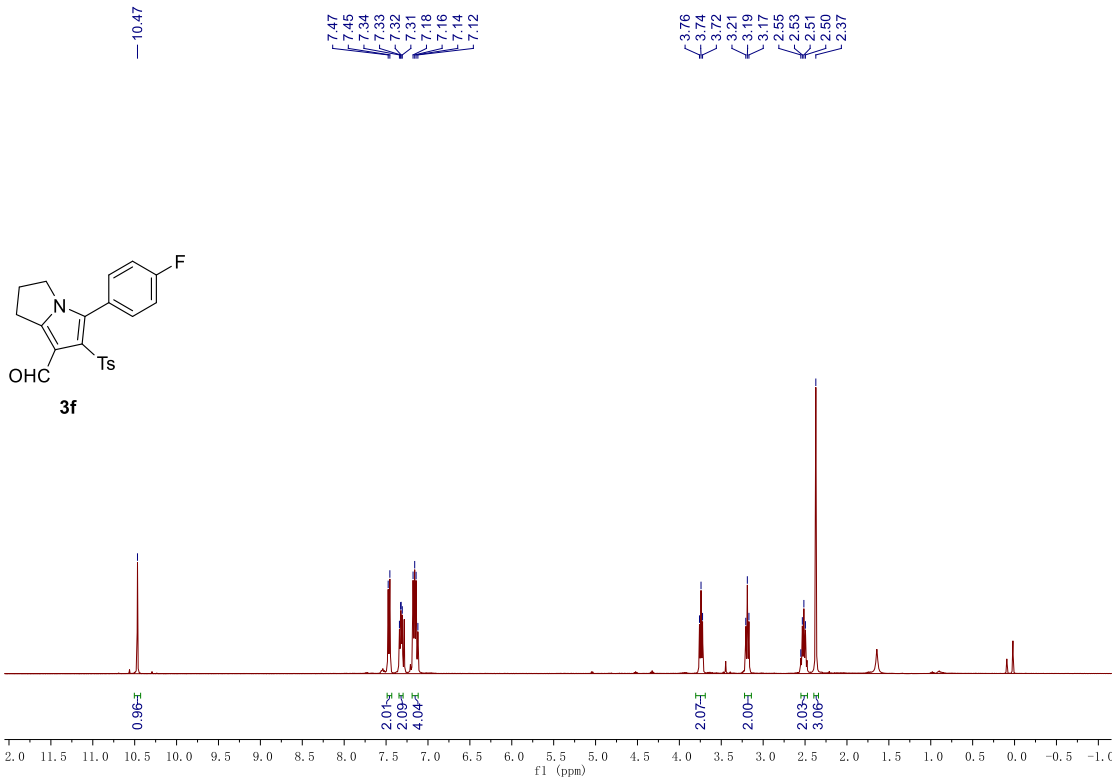


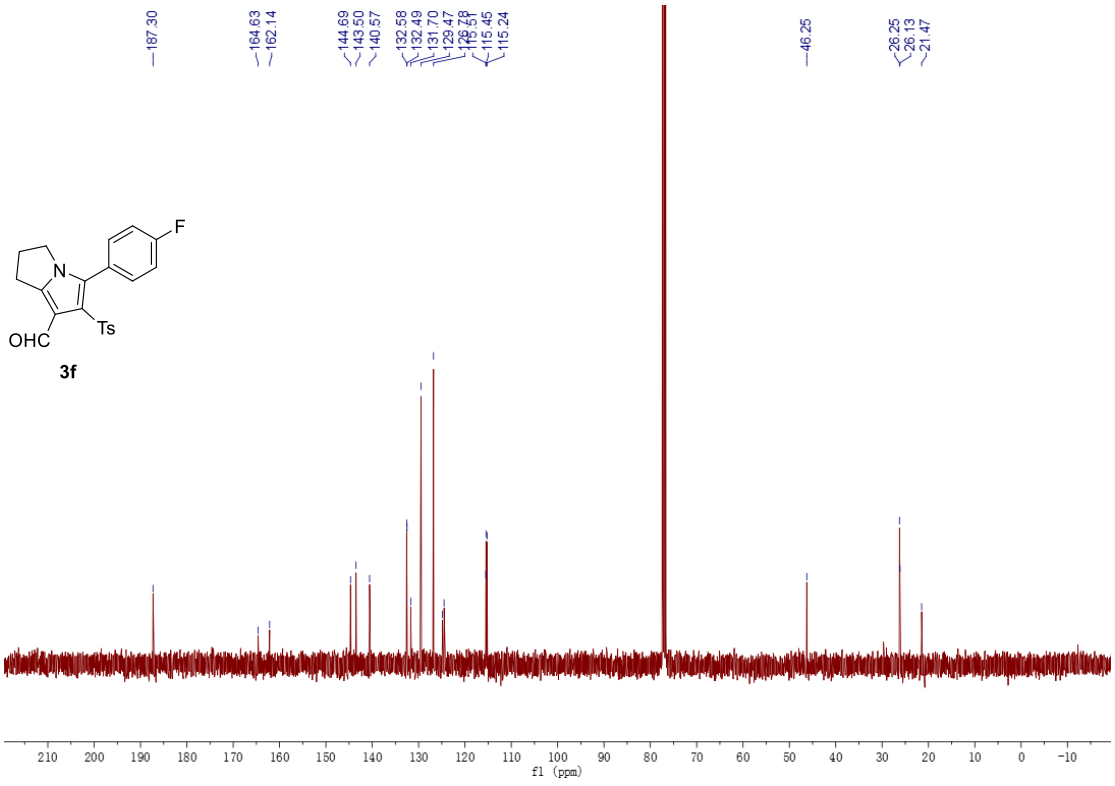
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **3e**

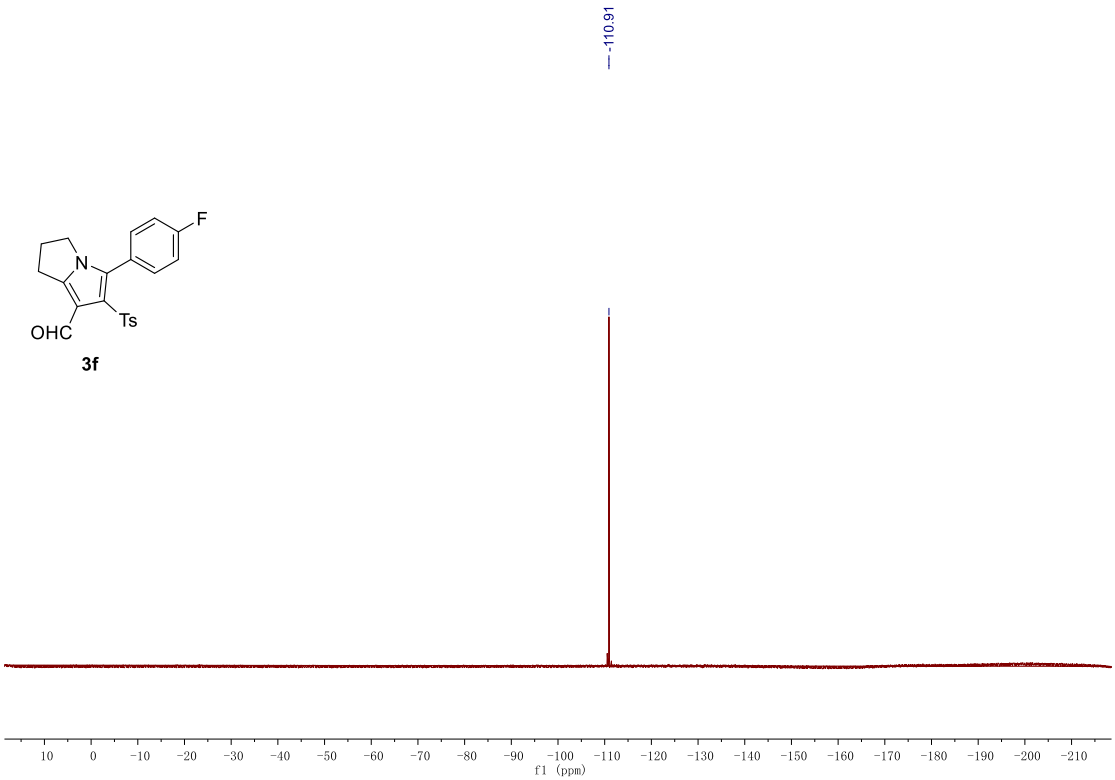




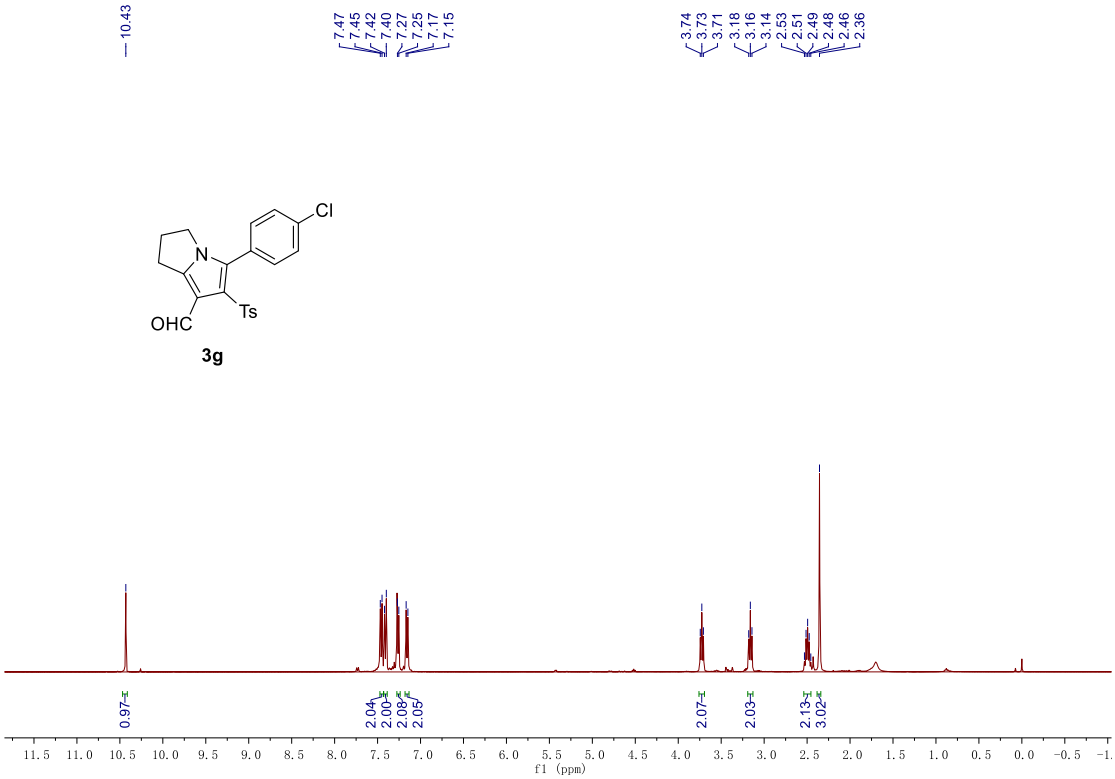
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (101 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectrum of substrate **3f**

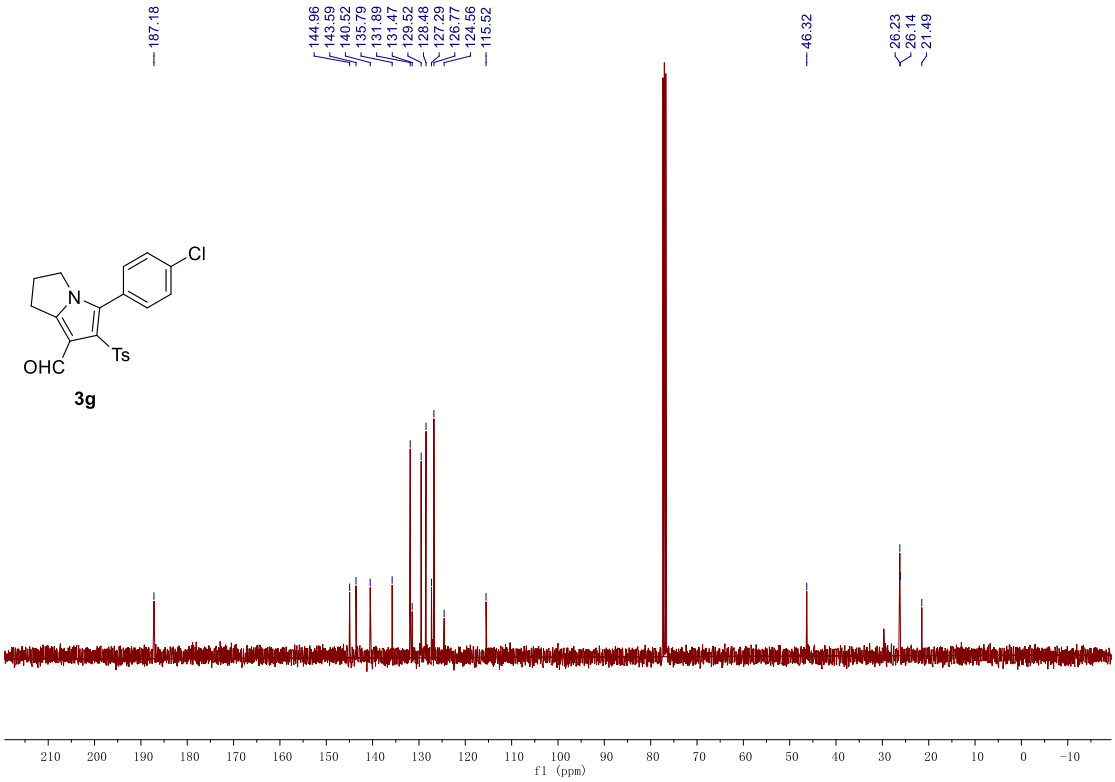




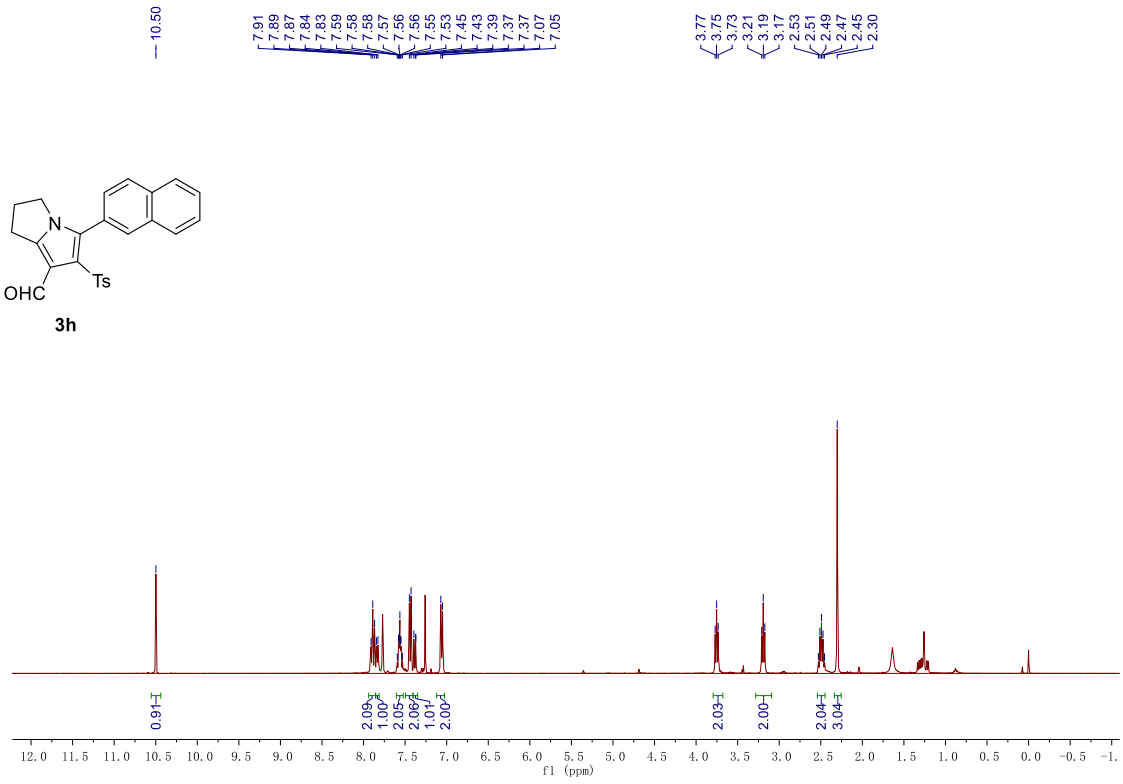


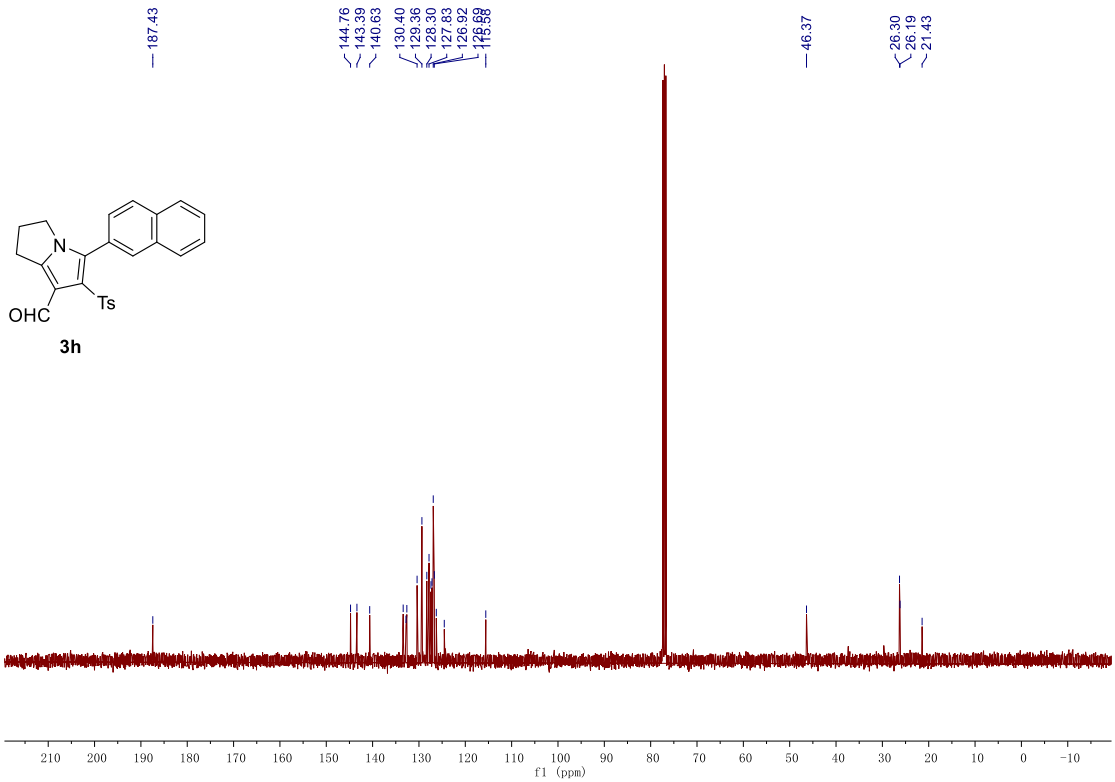
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **3g**



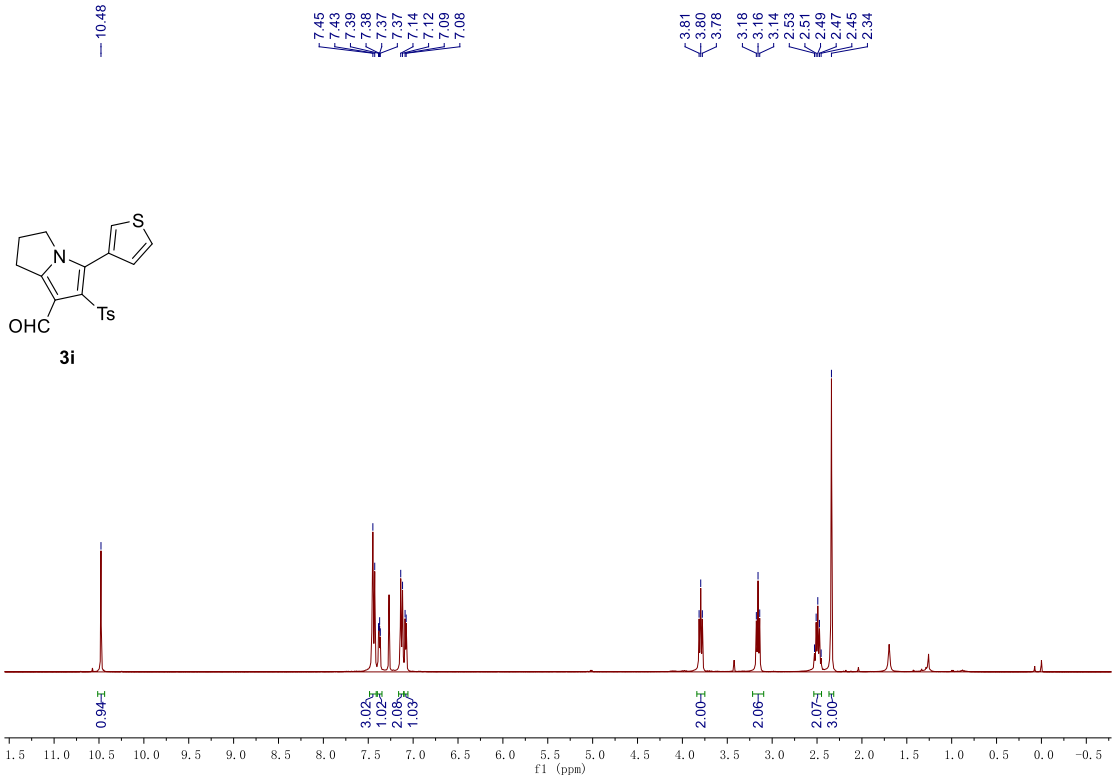


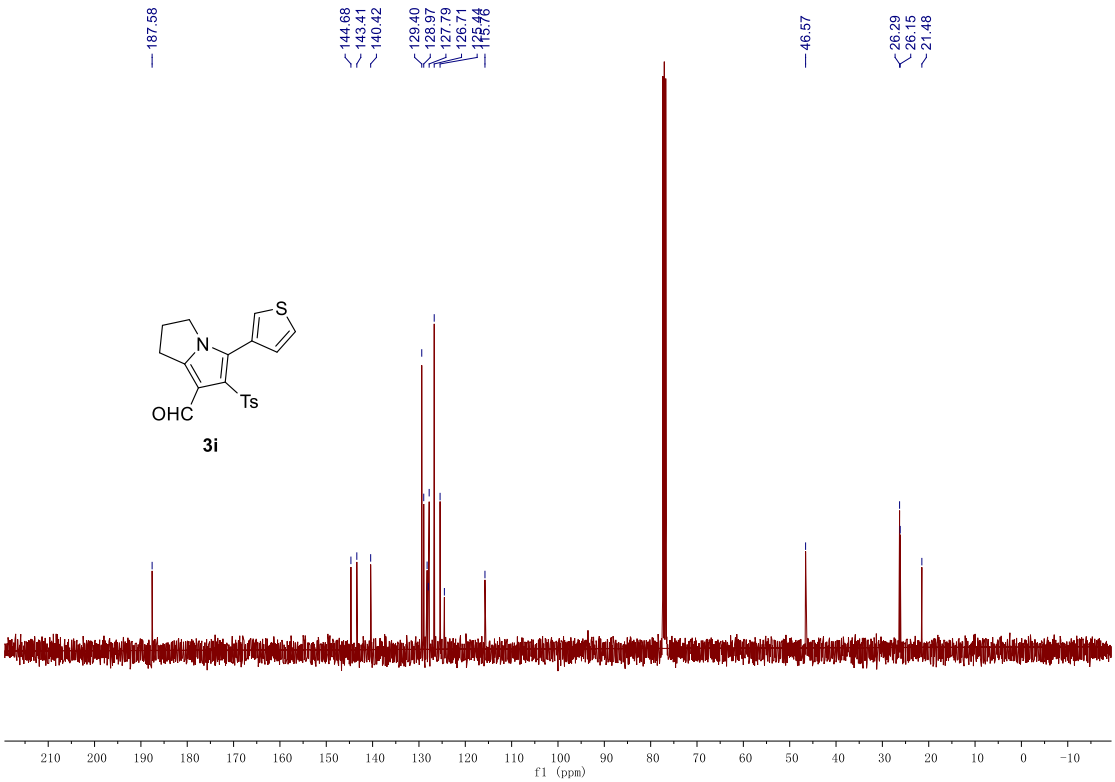
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **3h**



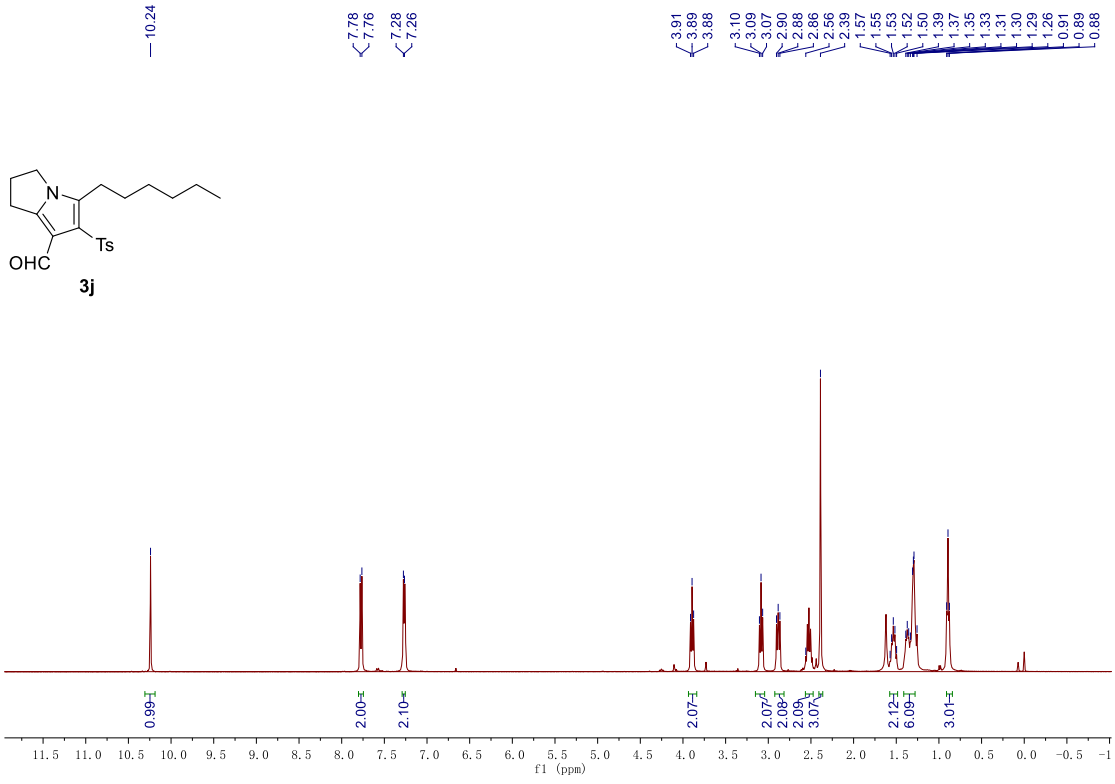


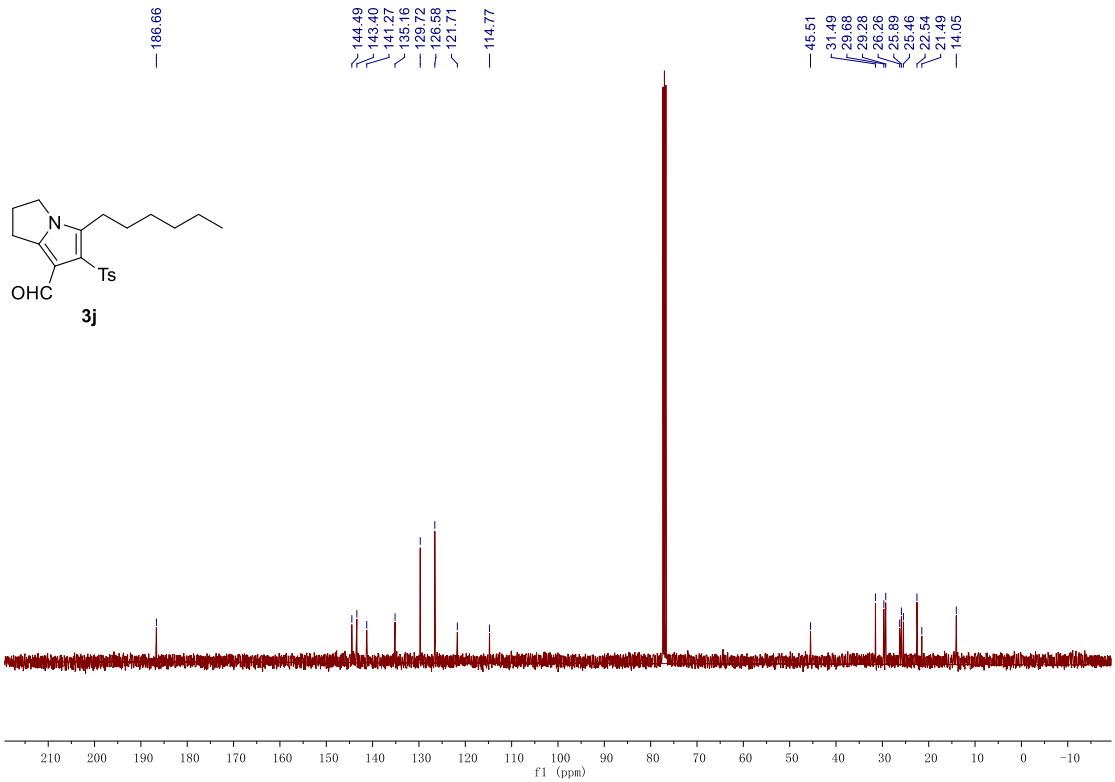
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **3i**



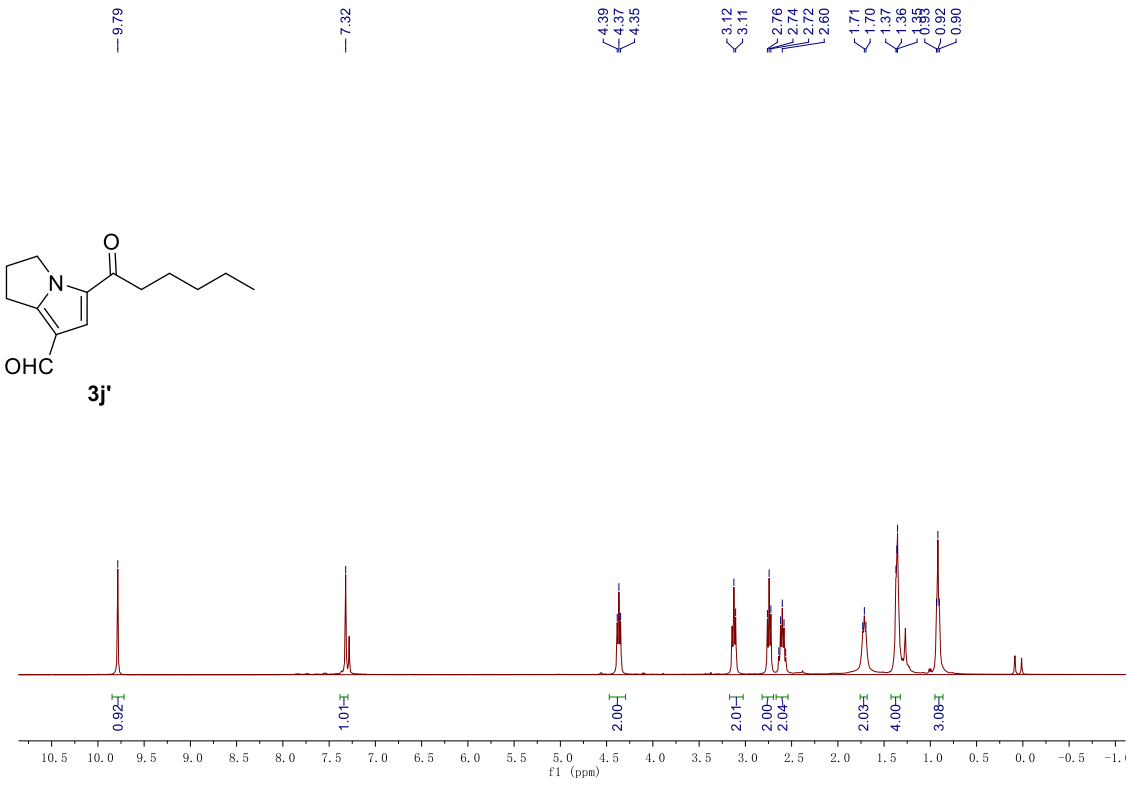


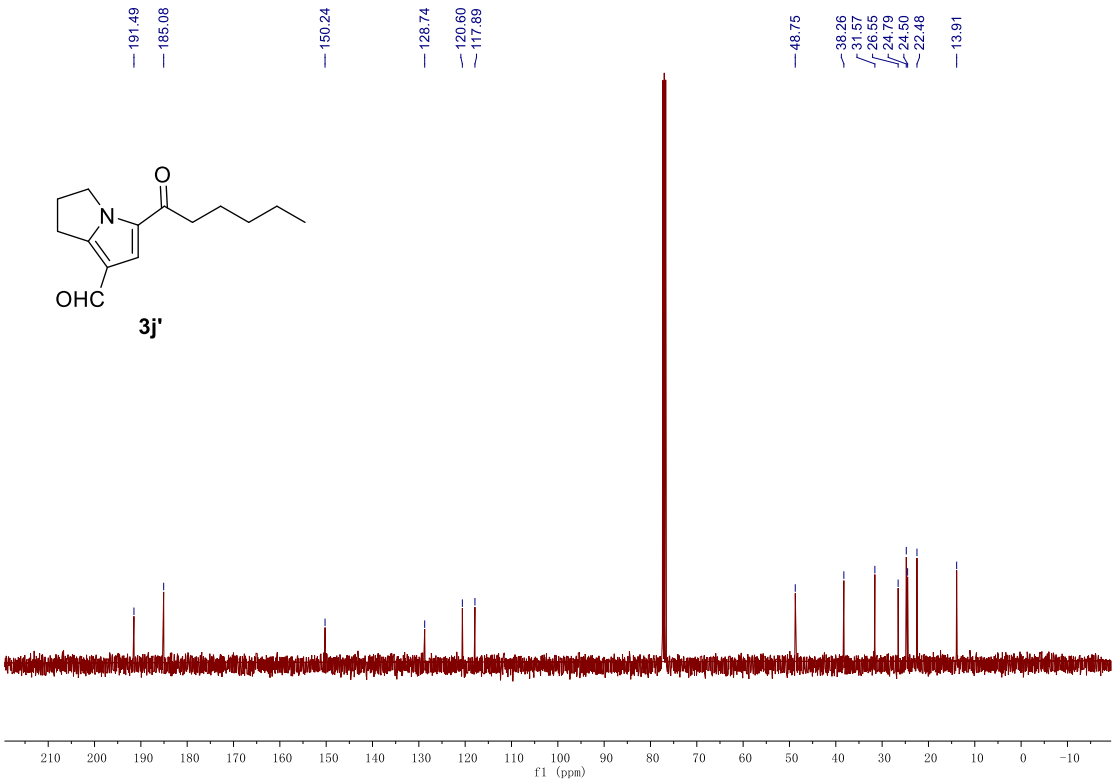
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of substrate **3j**



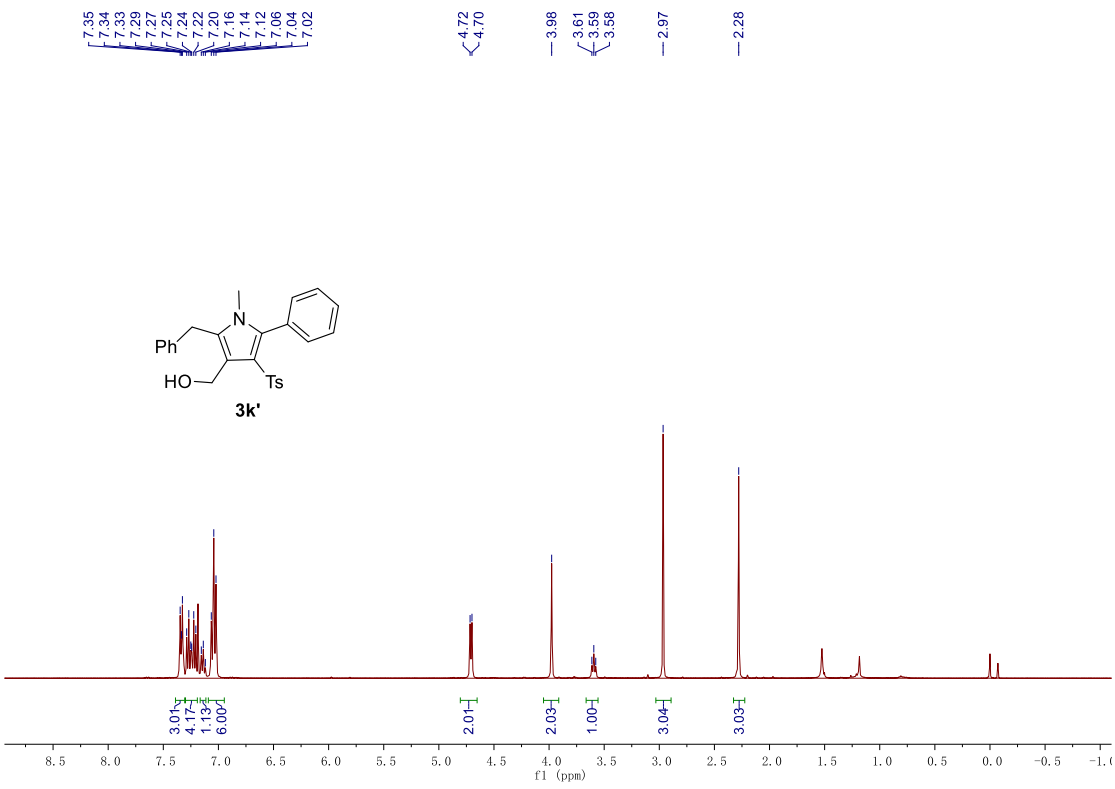


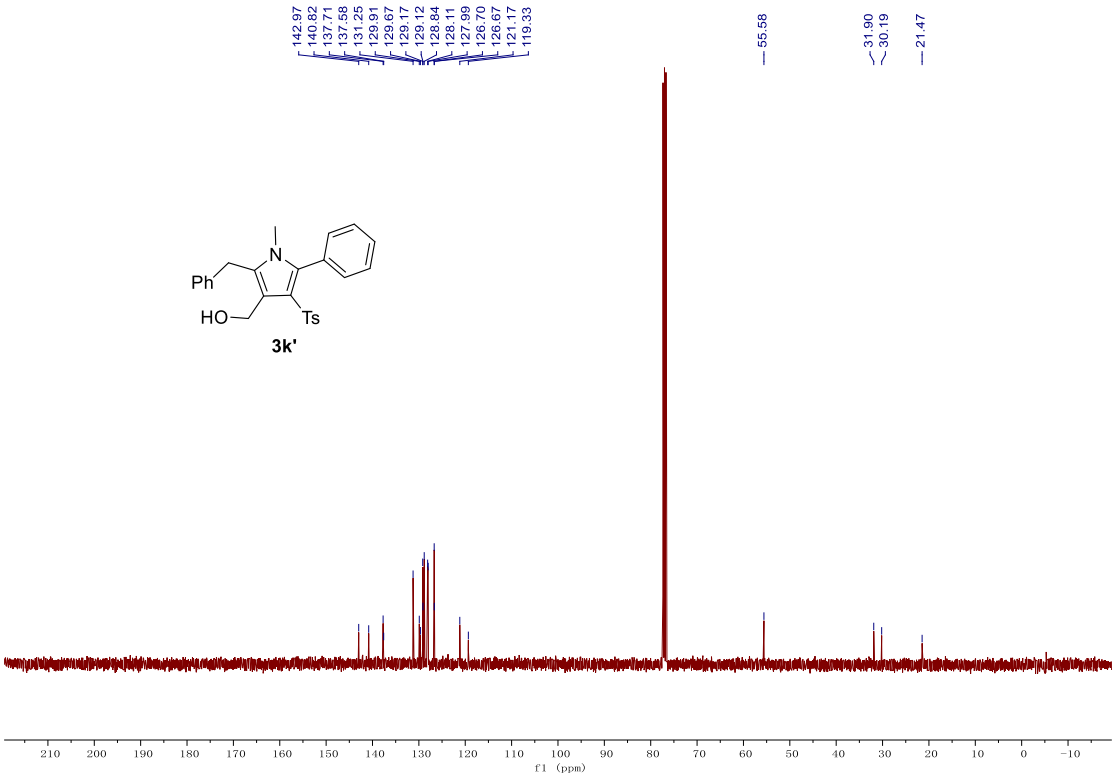
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of product **3j'**



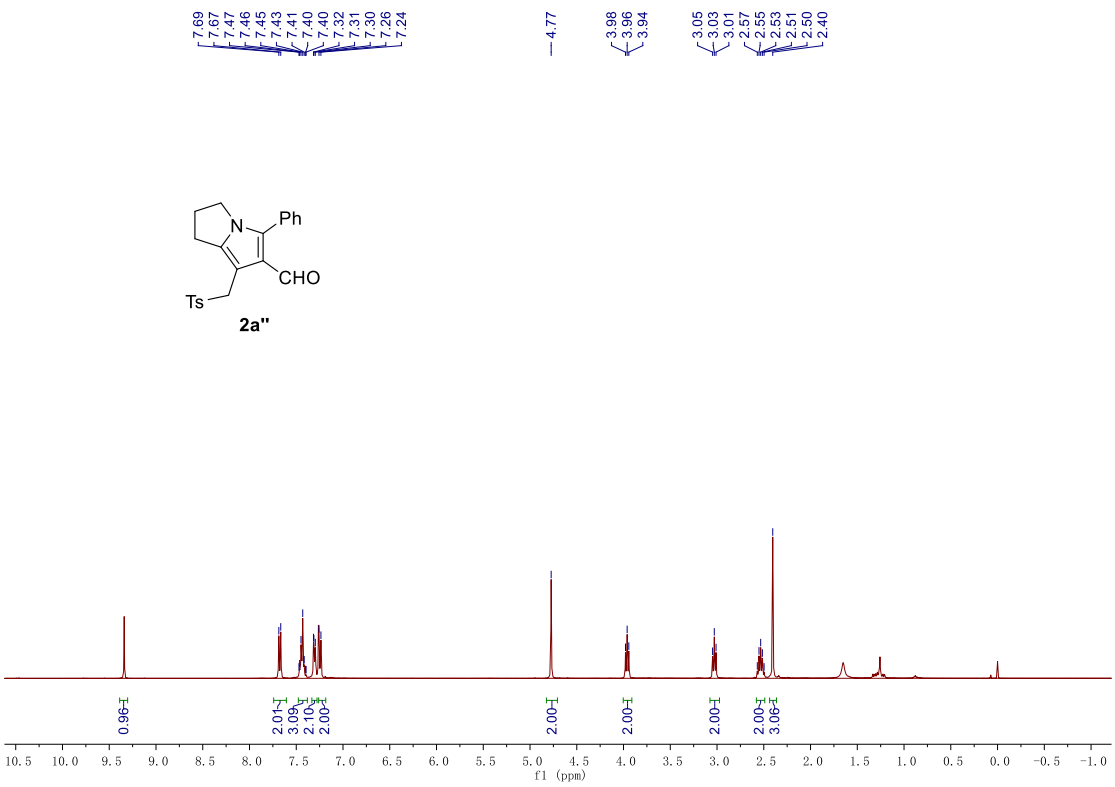


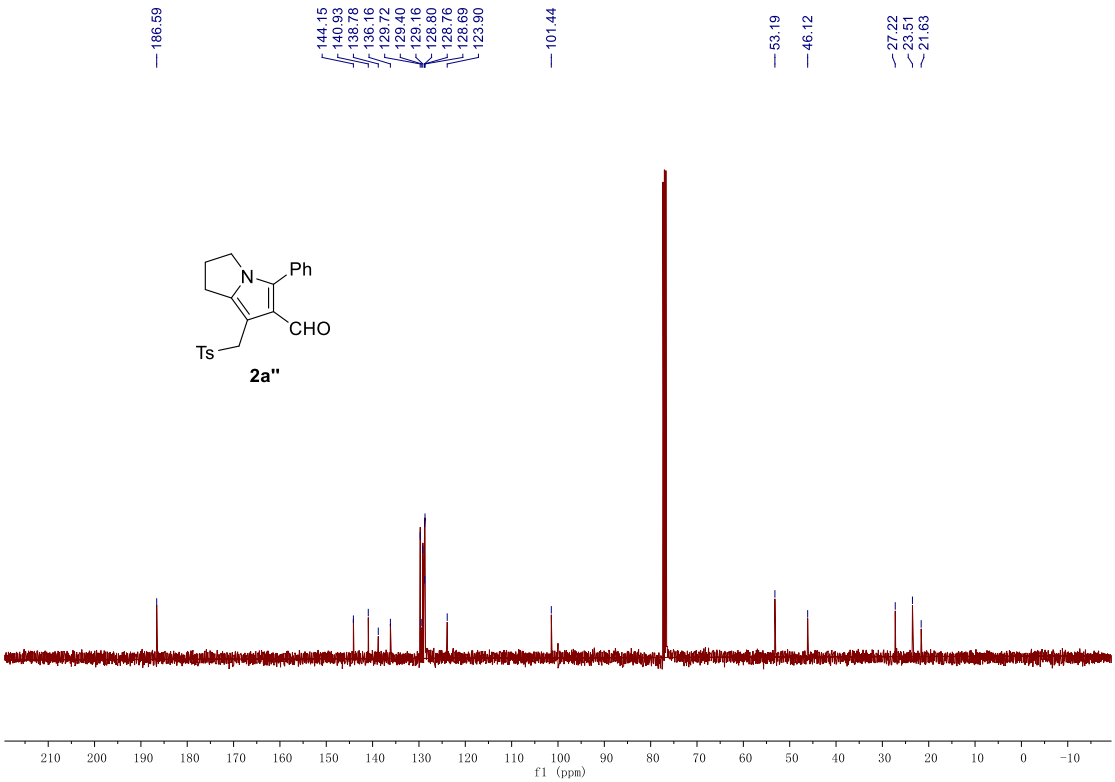
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of product **3k'**



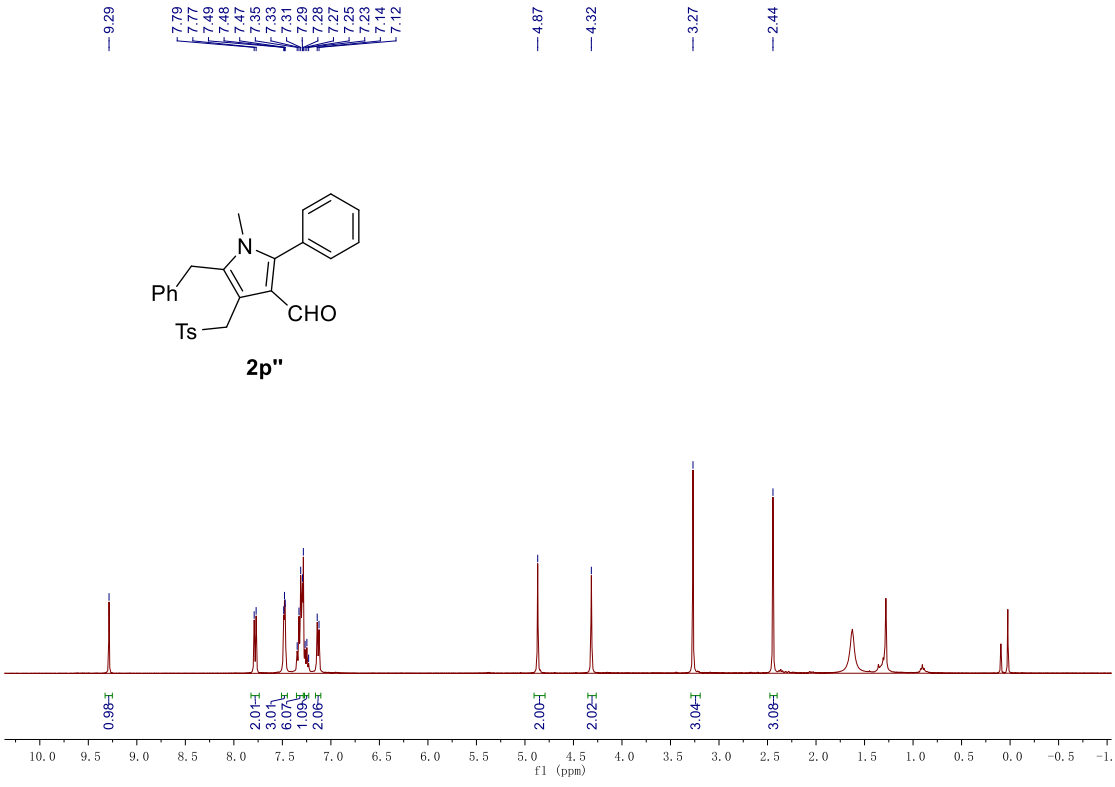


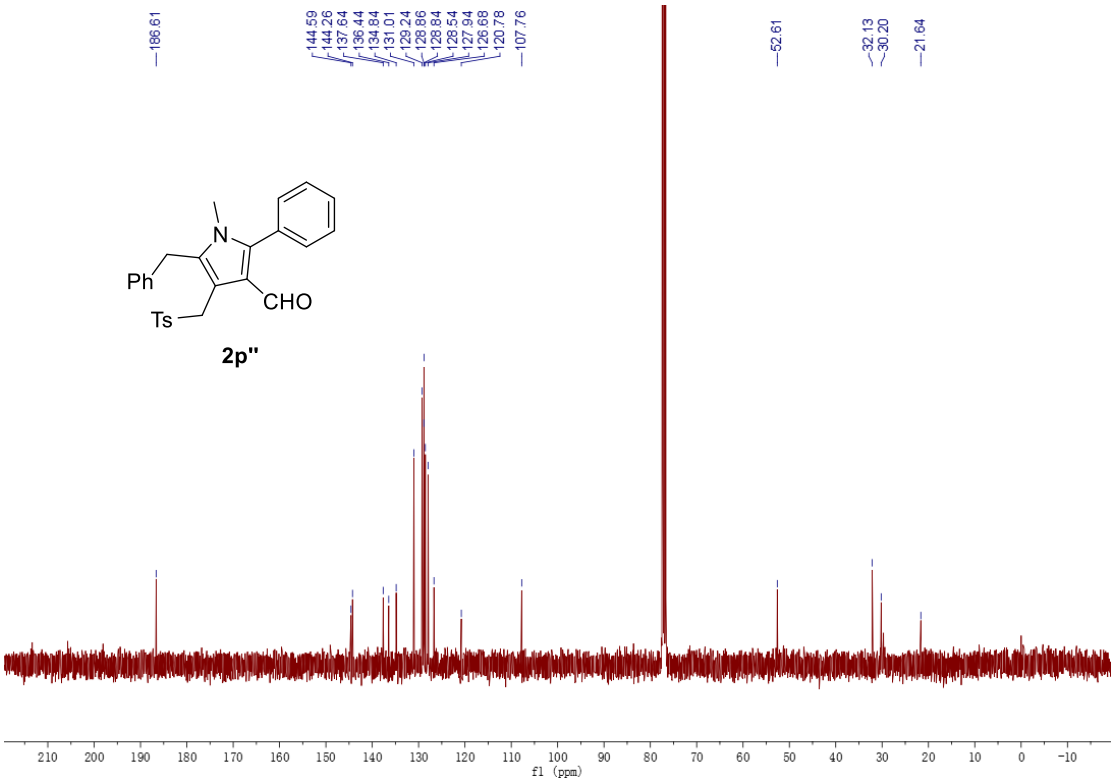
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of product **2a''**



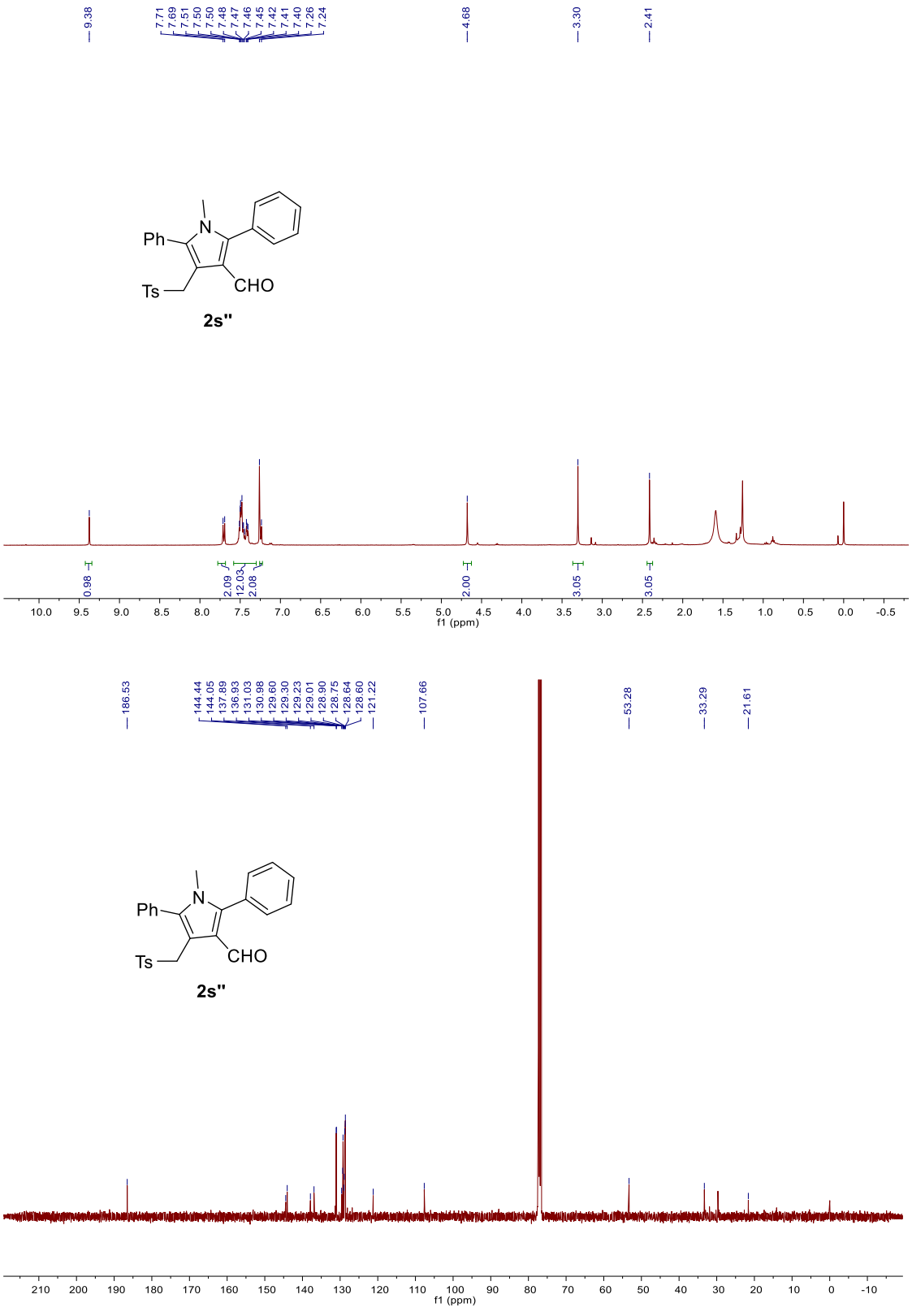


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of product **2p''**

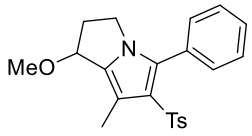




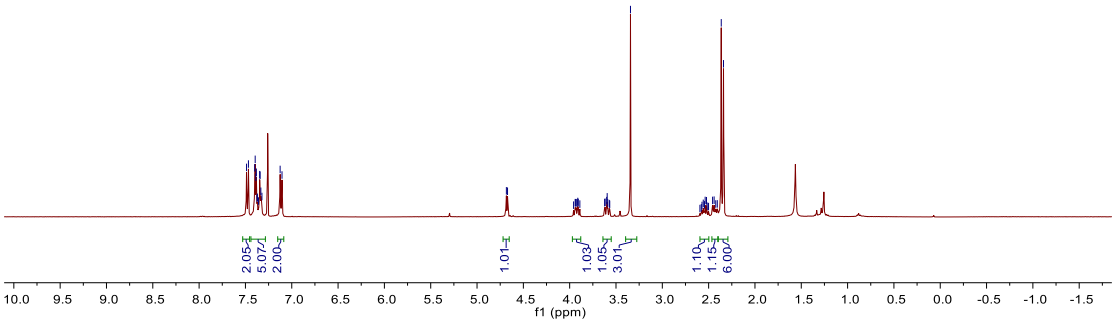
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of product **2s''**

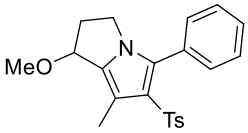


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of product **4a**



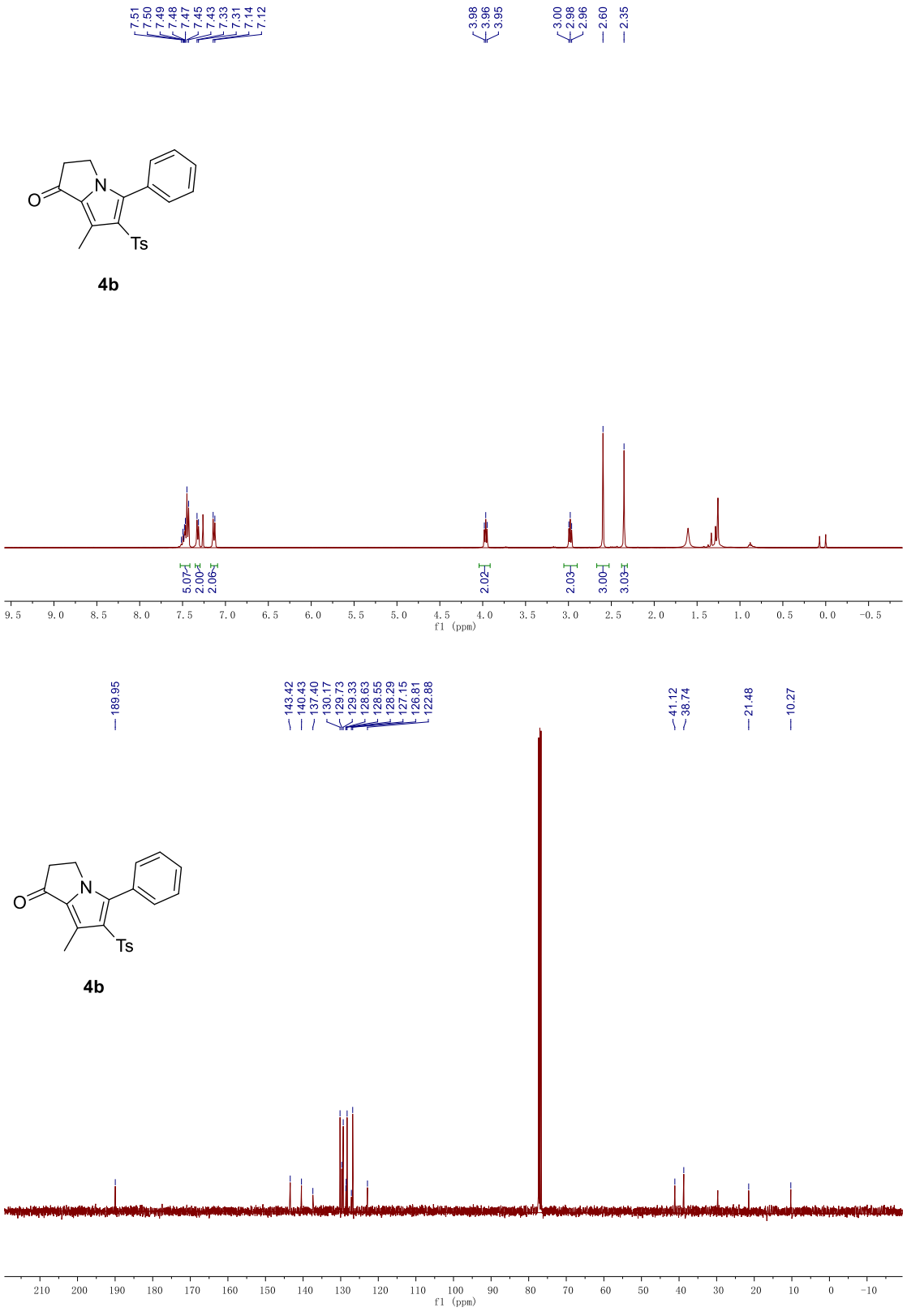
4a



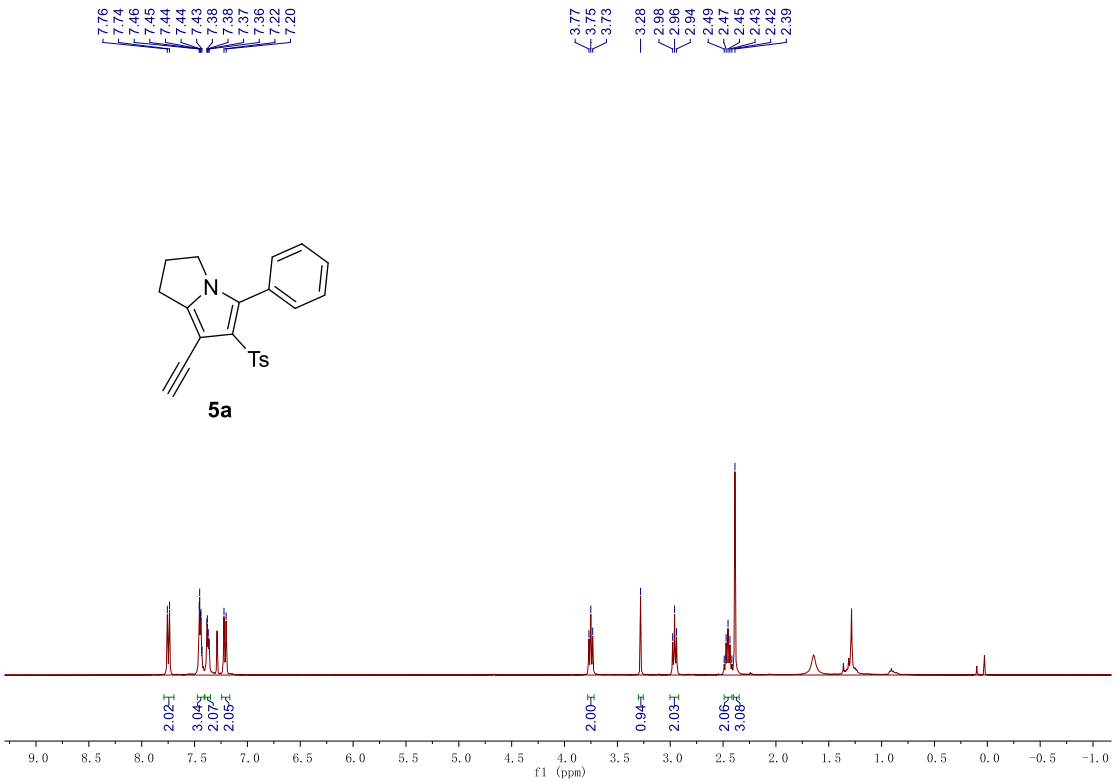


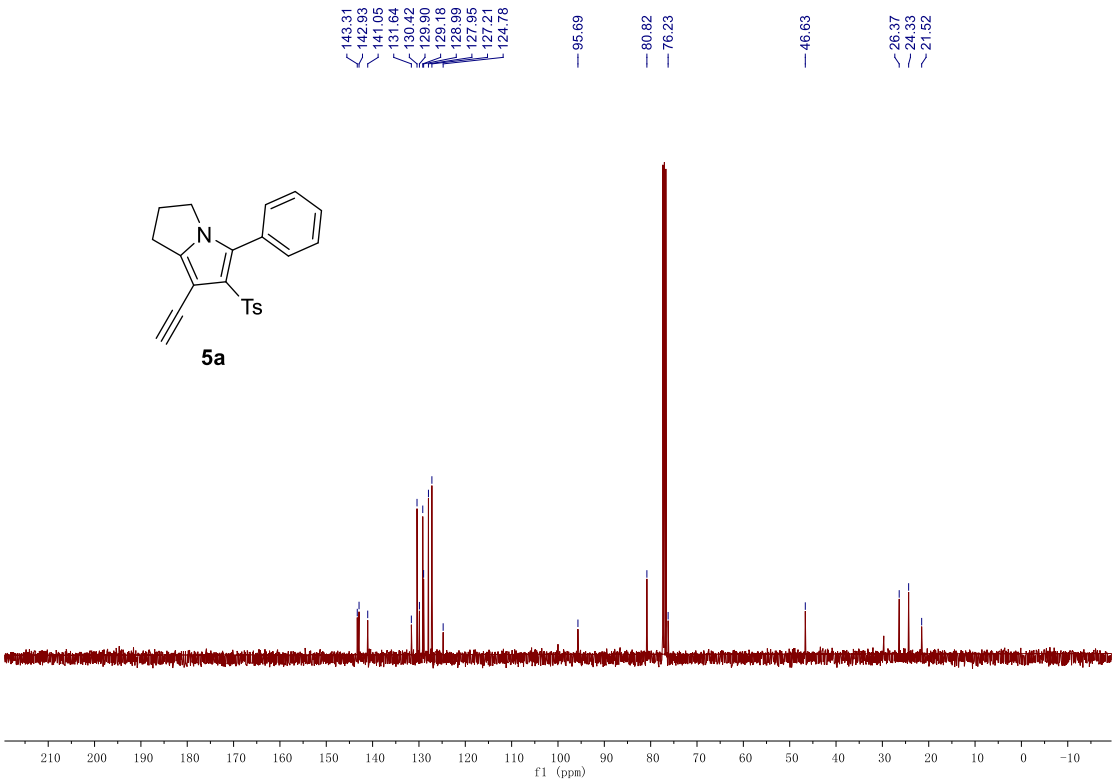
4a

^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of product **4b**

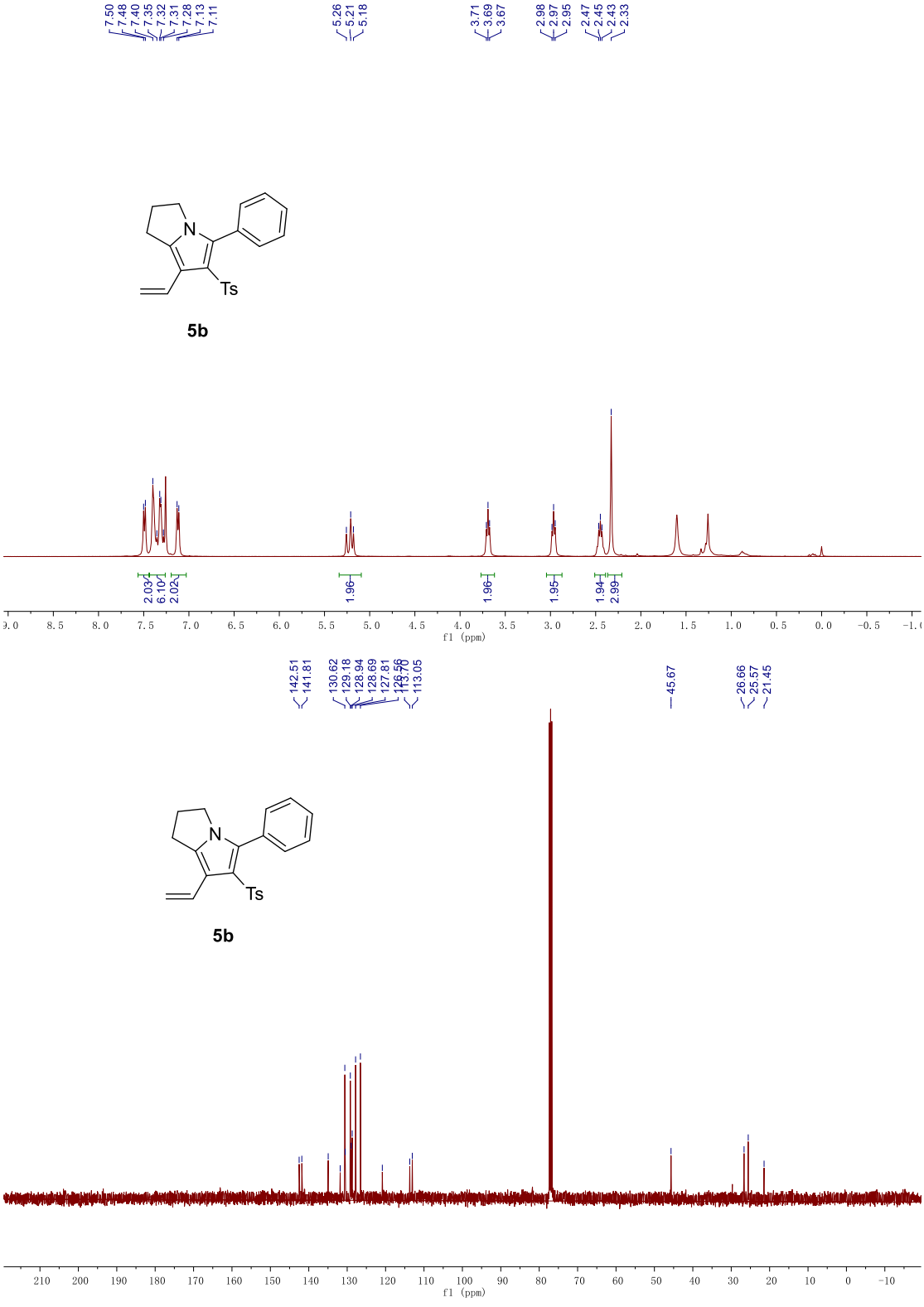


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of product **5a**





^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of product **5b**



^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of product **3a'**


7.49
7.47
7.43
7.40
7.39
7.37
7.32
7.30
7.11
7.09
5.32
3.72
3.70
3.68
2.95
2.93
2.92
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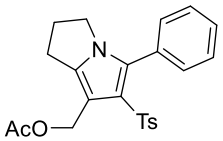
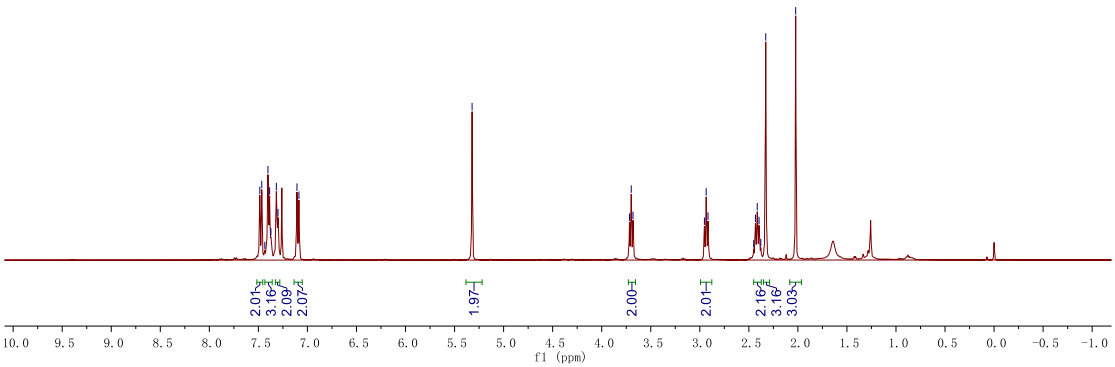
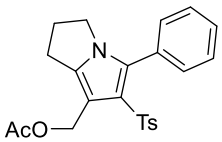
2.43
2.41
2.40
2.38
2.33
2.02


N
AcO
Ts

3a'


2.01
3.16
2.09
2.07
1.97
2.00
2.01
2.16
3.16
3.03
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 -0.5 -1.0
f1 (ppm)


170.97
142.62
141.53
137.75
132.39
130.60
130.22
129.00
128.83
127.88
126.85
122.06
109.28
58.11
46.13
26.54
23.88
21.41
21.11


N
AcO
Ts

3a'

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)