[4+1] Annulation reaction of cyclic pyridinium ylides with *in situ* generated azoalkenes for the construction of spirocyclic skeletons

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Supporting Information

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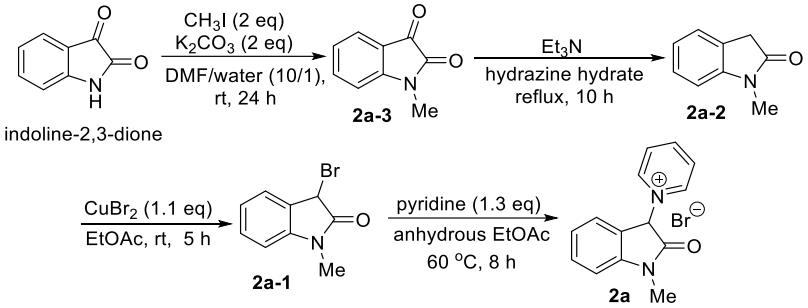
1. General Information

Chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. Solvents were dried and purified according to the standard procedures before use. Reactions were monitored by TLC. Flash column chromatography was performed on silica gels (200-300 mesh). ^{1}H NMR and ^{13}C NMR (300 and 75 MHz, respectively) spectra were recorded on a Bruker 300 MHz NMR spectrometer in $CDCl_3$. ^{1}H NMR chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$, δ 7.26 ppm, DMSO-d_6 δ 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, td = triplet of doublets, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$, δ 77.00 ppm, DMSO-d_6 at 39.51 ppm). HRMS data were obtained on a Bruker Daltonics. Inc mass instrument (ESI). Melting points were recorded on a Buchi Melting Point B-545.

2 Representative procedure for preparation of 2a and 4a

(a) Representative procedure for preparation of **2a**



A mixture of indoline-2,3-dione (4.50 g, 30.6 mmol, 1.0 equiv) and K_2CO_3 (8.45 g, 61.2 mmol, 2.0 equiv) in DMF/water (*v*:*v* = 10:1) (25 mL) was stirred at room temperature for 24 h, then it was poured into icy water (75 mL) and filtered to collect the red solid product. The filtrate was extract with EtOAc (30 mL × 3), and the organic phase was combined, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography to give 1-methylindoline-2,3-dione (**2a-3**) (4.7 g, yield 95%) as red solid.

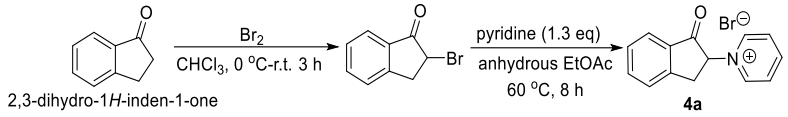
To a suspension of 1-methylindoline-2,3-dione (1.1 g, 6.8 mmol, 1.0 eq) in hydrazine hydrate (10 mL) was added Et_3N (1 mL), and the mixture was stirred at reflux for 10 h. When reaction completed, it was cooled down to room temperature and then poured into water (100 mL), extracted EtOAc (50 mL × 3), dried over Na_2SO_4 and evaporated to give residue which was purified by column chromatography (silica gel) to afford 1-methylindolin-2-one (**2a-2**) (800 mg, yield 80%) as light yellow solid.

A solution of 1-methylindolin-2-one (1.0 g, 6.80 mmol, 1 equiv) in EtOAc (34 mL, 0.2 M) was added $CuBr_2$ (1.67 g, 7.48 mmol, 1.1 equiv). The mixture was stirred at room temperature in open air for 5 h. Then the reaction mixture was concentrated in vacuo and the residue was purified by column chromatography (silica gel, petrol ether/EtOAc = 50/1~10/1) to give 3-bromo-1-methylindolin-2-one (**2a-1**) (826 mg, yield 54%) as brown solid.

A solution of 3-bromo-1-methylindolin-2-one (260 mg, 1.16 mmol, 1.0 equiv) and pyridine (119 mg, 1.51 mmol, 1.3 equiv) in anhydrous EtOAc (4 mL) under Ar was stirred at 60 °C for 8 h. The reaction mixture was cooled down to room temperature and filtered to collect the solid (**2a**) (265 mg, yield 75%) as off-white solid.

Characterizations data of **2a**: ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.07 (d, *J* = 5.8 Hz, 2H), 8.77 (t, *J* = 7.6 Hz, 1H), 8.29-8.25 (m, 2H), 7.59-7.53 (m, 2H), 7.28 (d, *J* = 7.8 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.97 (s, 1H), 3.22 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 169.2, 147.4, 144.9, 144.6, 131.6, 128.7, 125.9, 123.4, 121.2, 110.2, 68.8, 27.0. HRMS (ESI) Calcd for $C_{14}H_{13}N_2O$ $[M+H]^+$ 225.1022; Found: 225.1023.

(b) Representative procedure for preparation of **4a**



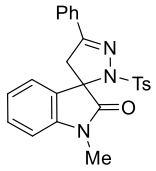
To a solution of 2,3-dihydro-1*H*-inden-1-one (2.64 g, 20.0 mmol, 1 equiv) in $CHCl_3$ (40 mL) was added Br_2 (3.20 g, 20.0 mmol, 1 equiv) at 0 °C dropwise. Reaction mixture was stirred at room temperature for 3 h, quenched with aqueous $Na_2S_2O_3$ and extracted with EtOAc (30 mL × 3). The organic phase was combined, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography to give 2-bromo-2,3-dihydro-1*H*-inden-1-one (1.54 g, yield 37%) as brown oil.

A solution of 2-bromo-2,3-dihydro-1*H*-inden-1-one (210 mg, 1.0 mmol, 1.0 equiv) and pyridine (103 mg, 1.3 mmol, 1.3 equiv) in anhydrous EtOAc (4 mL) under argon was stirred at 60 °C for 48 h. The reaction mixture was cooled down to room temperature and filtered to collect the solid (**4a**) (170 mg, yield 59%) as slight yellow solid.

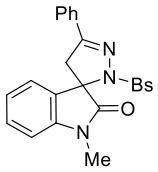
Characterizations data of **4a**: ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.21 (d, J = 5.7 Hz, 2H), 8.73 (t, J = 7.8 Hz, 1H), 8.28-2.23 (m, 2H), 7.90-7.81 (m, 2H), 7.75 (d, J = 7.7 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 6.33-6.28 (m, 1H), 4.03 (dd, J = 17.1, 8.3 Hz, 1H), 3.75 (dd, J = 17.0, 5.8 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 197.5, 151.0, 146.8, 145.1, 136.8, 132.9, 128.9, 128.4, 127.1, 124.4, 73.3, 34.2. HRMS (ESI) Calcd for $C_{14}H_{12}NO$ $[M+H]^+$ 210.0913; Found: 210.0904.

3 Representative procedure of preparing products 3

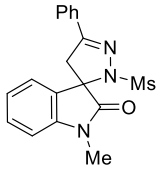
A mixture of **1** (0.2 mmol, 1 equiv), **2** (0.22 mmol, 1.1 equiv) and K_2CO_3 (0.6 mmol, 3 equiv) in $CHCl_3$ (6 mL) was stirred at room temperature under nitrogen. When the reaction was completed, water (6 mL) was added, and the mixture was extracted with CH_2Cl_2 (4 mL × 4). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (silica gel, petrol ether/EtOAc = 20/1~4/1) to give **3a** (83.6 mg, yield 97%) as white solid.



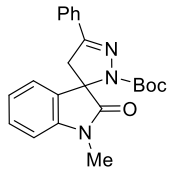
1-methyl-5'-phenyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3a). White solid, m.p.: 217.0-218.7 °C. Yield 97%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.68 (m, 2H), 7.57 (d, J = 8.3 Hz, 2H), 7.41-7.29 (m, 4H), 7.17 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 7.9 Hz, 1H), 6.80-6.76 (m, 2H), 3.82 (d, J = 16.8 Hz, 1H), 3.38 (d, J = 16.8 Hz, 1H), 3.33 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 153.1, 143.7, 143.1, 135.8, 130.5 (2C), 130.2, 129.1, 128.7, 128.1, 127.7, 126.7, 123.4, 122.8, 108.7, 70.5, 45.9, 26.9, 21.6. HRMS (ESI) Calcd for $C_{24}H_{22}N_3O_3S$ $[M+H]^+$ 432.1376; Found: 432.1372.



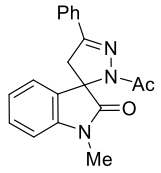
1-methyl-5'-phenyl-2'-(phenylsulfonyl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3b). White solid, m.p.: 219.7-220.6 °C. Yield 98%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.64 (m, 4H), 7.50 (t, J = 7.2 Hz, 1H), 7.42-7.26 (m, 6H), 6.90 (d, J = 7.8 Hz, 1H), 6.75-6.64 (m, 2H), 3.83 (d, J = 16.8 Hz, 1H), 3.38 (d, J = 16.9 Hz, 1H), 3.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 153.3, 143.1, 138.6, 132.8, 130.5, 130.3, 130.2, 128.6, 128.4, 127.9, 127.3, 126.7, 123.3, 122.8, 108.7, 70.5, 45.8, 26.9. HRMS (ESI) Calcd for $C_{23}H_{20}N_3O_3S$ $[M+H]^+$ 418.1220; Found: 418.1211.



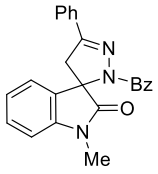
1-methyl-2'-(methylsulfonyl)-5'-phenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3c). White solid, m.p.: 225.4-226.0 °C. Yield 81%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76-7.73 (m, 2H), 7.46-7.34 (m, 5H), 7.11 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 7.7 Hz, 1H), 3.89 (d, J = 17.3 Hz, 1H), 3.52 (d, J = 17.3 Hz, 1H), 3.27 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1, 153.5, 142.9, 130.7, 130.2, 130.1, 129.8, 128.8, 126.8, 123.7, 123.3, 108.9, 70.5, 46.5, 40.5, 26.7. HRMS (ESI) Calcd for $C_{18}H_{18}N_3O_3S$ $[M+H]^+$ 356.1063; Found: 356.1051.



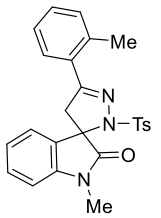
***tert*-butyl 1-methyl-2-oxo-5'-phenylspiro[indoline-3,3'-pyrazole]-2'(4'*H*)-carboxylate (3d)**. White solid, m.p.: 169.0-170.0 °C. Yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.68 (m, 2H), 7.40-7.32 (m, 4H), 7.23 (d, *J* = 7.1 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 3.86-3.74 (m, 1H), 3.51-3.37 (m, 1H), 3.29-3.25 (m, 3H), 1.11 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.1, 150.9, 150.0, 142.9, 130.9, 130.8, 130.1, 129.7, 128.5, 126.7, 123.4, 122.4, 108.1, 81.7, 67.9, 46.1, 45.3, 28.2, 27.6, 26.5. HRMS (ESI) Calcd for $C_{22}H_{23}NaN_3O_3$ $[M+Na]^+$ 400.1632; Found: 400.1621.



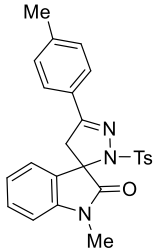
2'-acetyl-1-methyl-5'-phenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3e). White solid, m.p.: 254.5-255.5 °C. Yield 72%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75-7.72 (m, 2H), 7.46-7.44 (m, 3H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.3 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 3.82 (d, *J* = 17.6 Hz, 1H), 3.45 (d, *J* = 17.6 Hz, 1H), 3.30 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.5, 167.9, 152.5, 143.5, 130.7, 130.5, 129.7, 129.6, 128.8, 126.6, 123.2, 122.1, 108.5, 67.1, 44.9, 26.7, 21.8. HRMS (ESI) Calcd for $C_{19}H_{18}N_3O_2$ $[M+H]^+$ 320.1394; Found: 320.1379.



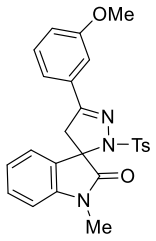
2'-benzoyl-1-methyl-5'-phenyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3f). White solid, m.p.: 205.0-206.0 °C. Yield 63%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.0 Hz, 2H), 7.73-7.71 (m, 2H), 7.51-7.33 (m, 7H), 7.25-7.23 (m, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 3.86 (d, *J* = 17.6 Hz, 1H), 3.49 (d, *J* = 17.5 Hz, 1H), 3.36 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.5, 165.1, 153.3, 143.6, 133.2, 131.3, 130.7, 130.6, 130.3, 129.8, 129.6, 128.8, 127.6, 126.8, 123.2, 122.0, 108.5, 68.4, 44.1, 26.8. HRMS (ESI) Calcd for $C_{24}H_{20}N_3O_2$ $[M+H]^+$ 382.1550; Found: 382.1550.



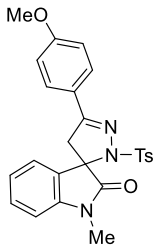
1-methyl-5'-(o-tolyl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3g). White solid, m.p.: 204.7-205.1 °C. Yield 98%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.36-7.15 (m, 7H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.82-6.75 (m, 2H), 3.90 (d, *J* = 16.5 Hz, 1H), 3.42-3.34 (m, 4H), 2.62 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2, 153.8, 143.8, 143.1, 138.2, 135.5, 131.8, 130.2, 129.7, 129.3, 129.0, 128.7, 128.3, 127.6, 125.9, 123.4, 122.8, 108.7, 69.9, 48.0, 26.9, 23.3, 21.6. HRMS (ESI) Calcd for $C_{25}H_{24}N_3O_3S$ $[M+H]^+$ 446.1533; Found: 446.1527.



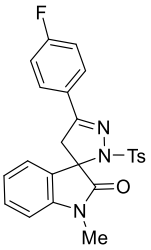
1-methyl-5'-(p-tolyl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3h). White solid, m.p.: 199.5-200.5 °C, yield 96%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.54 (m, 4H), 7.33-7.28 (m, 1H), 7.21-7.14 (m, 4H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.78-6.71 (m, 2H), 3.80 (d, *J* = 16.7 Hz, 1H), 3.39-3.32 (m, 4H), 2.38 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 153.2, 143.6, 143.1, 140.9, 135.8, 130.1, 129.3, 129.0, 128.1, 127.7, 126.7, 123.4, 122.8, 108.7, 70.4, 45.9, 26.8, 21.54, 21.46. HRMS (ESI) Calcd for $C_{25}H_{24}N_3O_3S$ $[M+H]^+$ 446.1533; Found: 446.1523.



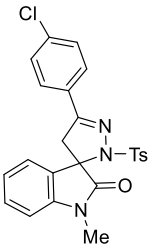
5'-(3-methoxyphenyl)-1-methyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3i). White solid, m.p.: 199.8-200.4 °C. yield 86%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.35-7.26 (m, 3H), 7.21-7.15 (m, 3H), 6.96 (dd, *J* = 8., 1.6 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.80-6.73 (m, 2H), 3.84-3,78 (m, 4H), 3.39-3.33 (m, 4H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 159.6, 153.0, 143.7, 143.1, 135.8, 131.7, 130.2, 129.7, 129.1, 128.1, 127.7, 123.4, 122.8, 119.4, 116.4, 111.7, 108.7, 70.5, 55.4, 45.9, 26.9, 21.6. HRMS (ESI) Calcd for $C_{25}H_{24}N_3O_4S$ $[M+H]^+$ 462.1482; Found: 462.1462.



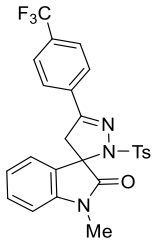
5'-(4-methoxyphenyl)-1-methyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3j). White solid, m.p.: 201.3-202.0 °C. Yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.33-7.28 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.92-6.88 (m, 3H), 6.78-6.74 (m, 2H), 3.83-3.75 (m, 4H), 3.37-3.32 (m, 4H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1, 161.4, 152. 9, 143.6, 143.1, 135.8, 130.1, 129.0, 128.4, 128.1, 127.7, 123.4, 123.1, 122.8, 114.0, 108.7, 70.4, 55.4, 45.9, 26.9, 21.6. HRMS (ESI) Calcd for $C_{25}H_{24}N_3O_4S$ $[M+H]^+$ 462.1482; Found: 462.1468.



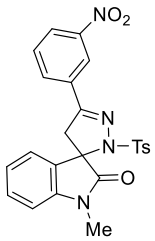
5'-(4-fluorophenyl)-1-methyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3k). White solid, m.p.: 209.5-210.3 °C. Yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69-7.64 (m, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.35-7.31 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.11-7.05 (m, 2H), 6.90 (d, *J* = 7.9 Hz, 1H), 6.82-6.78 (m, 2H), 3.79 (d, *J* = 16.8 Hz, 1H), 3.38-3.32 (m, 4H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 164.0 (d, *J* = 149.8 Hz, 1C), 152.0, 143.8, 143.1, 135.7, 130.2, 129.1, 128.7 (d, *J* = 9.0 Hz, 2C), 128.1, 127.7, 126.7 (d, *J* = 3.0 Hz, 1C), 123.4, 122.9, 115.9 (d, *J* = 21.8 Hz, 2C), 108.8, 70.6, 45.9, 26.9, 21.6. HRMS (ESI) Calcd for $C_{24}H_{21}FN_3O_3S$ $[M+H]^+$ 450.1282; Found: 450.1276.



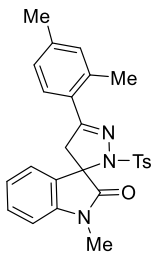
5'-(4-chlorophenyl)-1-methyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3l). White solid, m.p.: 174.2-175.0 °C. Yield 90%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.55 (m, 4H), 7.38-7.31 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.84-6.79 (m, 2H), 3.79 (d, *J* = 16.7 Hz, 1H), 3.38-3.33 (m, 4H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 151.9, 143.9, 143.2, 136.5, 135.8, 130.3, 129.2, 129.0, 128.1, 127.9, 127.8, 123.4, 122.9, 108.8, 70.7, 45.8, 26.9, 21.6.HRMS (ESI) Calcd for $C_{24}H_{21}ClN_3O_3S$ $[M+H]^+$ 466.0987; Found: 466.0964.



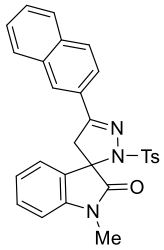
1-methyl-2'-tosyl-5'-(4-(trifluoromethyl)phenyl)-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3m). White solid, m.p.:213.0-214.5 °C. Yield 96%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.31 (m, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.84 – 6.77 (m, 2H), 3.82 (d, *J* = 16.9 Hz, 1H), 3.40 (d, *J* = 16.9 Hz, 1H), 3.32 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8, 151.5, 144.0, 143.2, 135.7, 133.8, 131.9 (q, *J* = 32.3 Hz, 1C), 130.4, 129.2, 128.1 127.6, 126.9, 125.6 (q, *J* = 3.0 Hz, 2C), 123.7 (q, *J* = 270.8 Hz, 1C), 123.3, 122.9, 108.8, 70.8, 45.6, 26.8, 21.5. HRMS (ESI) Calcd for $C_{25}H_{21}F_3N_3O_3S$ $[M+H]^+$ 500.1250; Found: 500.1257.



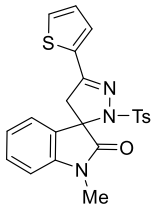
1-methyl-5'-(3-nitrophenyl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3n). White solid, m.p.:211.0-212.2 °C. Yield 92%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.62-7.58 (m, 3H), 7.38-7.33 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.86-6.84 (m, 2H), 3.85 (d, *J* = 16.9 Hz, 1H), 3.45 (d, *J* = 17.0 Hz, 1H), 3.33 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 150.6, 148.4, 144.2, 143.2, 135.6, 132.3, 132.2, 130.5, 129.8, 129.3, 128.1, 127.7, 124.7, 123.4, 123.1, 121.4, 108.9, 70.9, 45.7, 26.9, 21.6. HRMS (ESI) Calcd for $C_{24}H_{21}N_4O_5S$ $[M+H]^+$ 477.1227; Found: 477.1223.



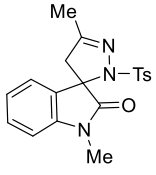
5'-(2,4-dimethylphenyl)-1-methyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3o). White solid, m.p.:159.1-160.0 °C. Yield 89%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.34-7.30 (m, 1H), 7.17-7.10 (m, 4H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.81-6.74 (m, 2H), 3.88 (d, *J* = 16.5 Hz, 1H), 3.40-3.33 (m 4H), 2.60 (s, 3H), 2.38 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.2, 153.8, 143.7, 143.1, 139.9, 138.1, 135.6, 132.6, 130.1, 128.9, 128.7, 128.3, 127.7, 126.5, 123.4, 122.7, 108.7, 69.8, 48.0, 26.8, 23.2, 21.5, 21.2. HRMS (ESI) Calcd for $C_{26}H_{26}N_3O_3S$ $[M+H]^+$ 460.1689; Found: 460.1692.



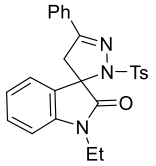
1-methyl-5'-(naphthalen-2-yl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3p). White solid, m.p.: 225.7-226.7 °C. Yield 89%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 8.6, 1.5 Hz, 1H), 7.87-7.80 (m, 4H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.56-7.46 (m, 2H), 7.36-7.30 (m, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 7.9 Hz, 1H), 6.79-7.77 (m, 2H), 3.93 (d, *J* = 16.7 Hz, 1H), 3.53 (d, *J* = 16.7 Hz, 1H), 3.35 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 153.2, 143.8, 143.1, 135.8, 134.1, 132.7, 130.2, 129.1, 128.5, 128.4, 128.1, 127.8, 127.7, 127.3, 127.1, 126.7, 123.5, 123.4, 122.8, 108.7, 70.6, 45.8, 26. 9, 21.6. HRMS (ESI) Calcd for $C_{28}H_{24}N_3O_3S$ $[M+H]^+$ 482.1533; Found: 482.1520.



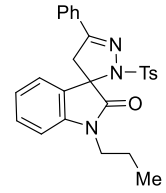
1-methyl-5'-(thiophen-2-yl)-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3q). White solid, m.p.:218.0-219.0 °C. Yield 93%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 5.0 Hz, 1H), 7.34-7.29 (m, 1H), 7.17-7.14 (m, 3H), 7.04-7.02 (m, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.79-6.75 (m, 2H), 3.81 (d, *J* = 16.5 Hz, 1H), 3.37-3.31 (m, 4H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 148.7, 143.7, 143.1, 135.7, 133.8, 130.2, 129.1, 129.0, 128.8, 128.1, 127.5, 127.4, 123.4, 122.8, 108.7, 70.5, 46.5, 26.8, 21.5. HRMS (ESI) Calcd for $C_{22}H_{20}N_3O_3S_2$ $[M+H]^+$ 438.0941; Found: 438.0941.



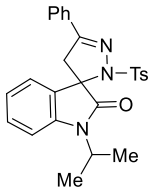
1,5'-dimethyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3r). White solid, m.p.:193.0-194.5 °C. Yield 85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.33-7.26 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.87-6.80 (m, 3H), 3.42 (d, *J* = 18.2 Hz, 1H), 3.27 (s, 3H), 2.90 (d, *J* = 17.2 Hz, 1H), 2.38 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1, 154.3, 143.5, 142.9, 135.9, 130.0, 129.0, 127.9, 127.8, 123.2, 122.7, 108.6, 69.9, 49.6, 26.7, 21.5, 15.8. HRMS (ESI) Calcd for $C_{19}H_{20}N_3O_3S$ $[M+H]^+$ 370.1220; Found: 370.1223.



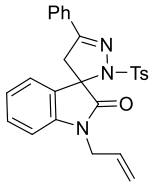
1-ethyl-5'-phenyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3s). White solid, m.p.: 216.5-217.5 °C. Yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 7.67 (m, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.41-7.36 (m, 3H), 7.34-7.28 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.75-6.74 (m, 2H), 4.03-3.91 (m, 1H), 3.85-3.70 (m, 2H), 3.38 (d, *J* = 16.8 Hz, 1H), 2.38 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 153.0, 143.6, 142.2, 135.8, 130.4, 130.1, 129.0, 128.6, 128.0, 127.9, 126.7, 123.6, 122.6, 108.8, 70.5, 45.8, 35.3, 21.5, 12.2. HRMS (ESI) Calcd for $C_{25}H_{24}N_3O_3S$ $[M+H]^+$ 446.1533; Found: 446.1525.



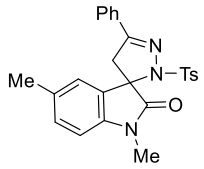
5'-phenyl-1-propyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3t). White solid, m.p.:175.0-176.0 °C. Yield 82%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.67 (m, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.41-7.36 (m, 3H), 7.33-7.27 (m, 1H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.77-6.73 (m, 2H), 3.90-3.79 (m, 2H), 3.72-3.63 (m, 1H), 3.38 (d, *J* = 16.7 Hz, 1H), 2.38 (s, 3H), 1.89 – 1.77 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 153.0, 143.7, 142.6, 135.8, 130.4, 130.0, 129.1, 128.6, 128.1, 128.0, 126.7, 123.5, 122.5, 108.9, 70.5, 46.1, 42.3, 21.6, 20.5, 11.4. HRMS (ESI) Calcd for $C_{26}H_{26}N_3O_3S$ $[M+H]^+$ 460.1689; Found: 460.1697.



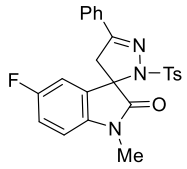
1-isopropyl-5'-phenyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3u). White solid, m.p.:215.4-216.2 °C. Yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.67 (m, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.41-7.40 (m, 3H), 7.31-7.25 (m, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.73-6.71 (m, 2H), 4.76-4.66(m, 1H), 3.82 (d, *J* = 16.7 Hz, 1H), 3.38 (d, *J* = 16.7 Hz, 1H), 2.38 (s, 3H), 1.60-1.56 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 153.0, 143.6, 141.9, 135.9, 130.5, 130.4, 129.8, 129.0, 128.6, 128.1, 128.0, 126.7, 123.7, 122.2, 110.3, 70.4, 45.9, 44.6, 21.5, 19.3, 18.9. HRMS (ESI) Calcd for $C_{26}H_{26}N_3O_3S$ $[M+H]^+$ 460.1689; Found: 460.1700.



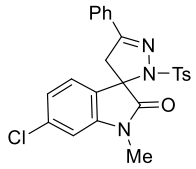
1-allyl-5'-phenyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3v). White solid, m.p.: 173.0-174.0 °C. Yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.67 (m, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.41-7.40 (m, 3H), 7.31-7.25 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 7.9 Hz, 1H), 6.79-6.78 (m, 2H), 6.00-5.87 (m, 1H), 5.43 (d, *J* = 17.2 Hz, 1H), 5.30 (d, *J* = 10.1 Hz, 1H), 4.56 (dd, *J* = 16.4, 4.7 Hz, 1H), 4.34 (dd, *J* = 16.5, 5.7 Hz, 1H), 3.83 (d, *J* = 16.7 Hz, 1H), 3.41 (d, *J* = 16.7 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.8, 153.0, 143.7, 142.2, 135. 8, 131.0, 130.5, 130.4, 130.0, 129.1, 128.6, 128.1, 127.8, 126.7, 123.4, 122.8, 118.0, 109.7, 70.5, 46.2, 43.0, 21.6. HRMS (ESI) Calcd for $C_{26}H_{24}N_3O_3S$ $[M+H]^+$ 458.1533; Found: 458.1537.



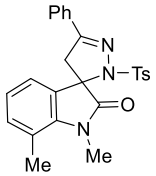
1,5-dimethyl-5'-phenyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3w). White solid, m.p.: 130.1-131.0 °C. Yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.73-7.70 (m, 2H), 7.49-7.41 (m, 5H), 7.14-7.08 (m, 3H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.32 (s, 1H), 3.82 (d, *J* = 16.7 Hz, 1H), 3.37-3.30 (m, 4H), 2.37 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.9, 153.2, 143.5, 140.8, 137.4, 135.8, 132.1, 130.5, 130.4, 128.9, 128.7, 128.0, 126.9, 126.7, 124.4, 108.4, 70.6, 45.7, 26.9, 21.4, 20.5. HRMS (ESI) Calcd for $C_{25}H_{24}N_3O_3S$ $[M+H]^+$ 446.1533; Found: 446.1527.



5-fluoro-1-methyl-5'-phenyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3x). White solid, m.p.: 180.7-182.0 °C. Yield 98%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.67 (m, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.42-7.40 (m, 3H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.02 (td, *J* = 8.8, 2.4 Hz, 1H), 6.82 (dd, *J* = 8.6, 4.0 Hz, 1H), 6.40 (dd, *J* = 7.5, 2.5 Hz, 1H), 3.82 (d, *J* = 16.8 Hz, 1H), 3.39-3.31 (m, 4H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 158.9 (d, *J* = 241.5 Hz, 1C), 153.1, 144.1, 139.1, 135.6, 130.6, 130.2, 129.2, 128.7, 128.6, 126.7, 116.4 (d, *J* = 23.3 Hz, 1C), 111.7 (d, *J* = 24.8 Hz, 1C), 109.3 (d, *J* = 7.5 Hz, 1C), 70.5, 45.8, 27.0, 21.5. HRMS (ESI) Calcd for $C_{24}H_{21}FN_3O_3S$ $[M+H]^+$ 450.1282; Found: 450.1282.



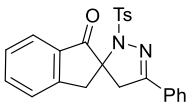
6-chloro-1-methyl-5'-phenyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3y). White solid, m.p.: 212.3-213.0 °C. Yield 75%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.61 (m, 4H), 7.42-7.39 (m, 3H), 7.21 (d, *J* = 8.2 Hz, 2H), 6.90 (s, 1H), 6.80-6.73 (m, 2H), 3.80 (d, *J* = 16.7 Hz, 1H), 3.39-3.31 (m, 4H), 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.1, 152.9, 144.4, 144.0, 136.1, 135.8, 130.6, 130.4, 129.2, 128.7, 128.1, 126.8, 126.5, 124.4, 122.7, 109.5, 70.1, 45.9, 27.0, 21.6. HRMS (ESI) Calcd for $C_{24}H_{21}ClN_3O_3S$ $[M+H]^+$ 466.0987; Found: 466.0993.



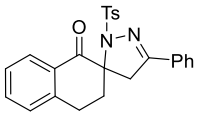
1,7-dimethyl-5'-phenyl-2'-tosyl-2',4'-dihydrospiro[indoline-3,3'-pyrazol]-2-one (3z). White solid, m.p.: 263.3-264.0 °C. Yield 65%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.65 (m, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.40-7.38 (m, 3H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.04 (d, *J* = 6.8 Hz, 1H), 6.70-7.62 (m, 2H), 3.80 (d, *J* = 16.7 Hz, 1H), 3.60 (s, 3H), 3.34 (d, *J* = 16.8 Hz, 1H), 2.61 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.9, 152.8, 143.7, 140.8, 136.0, 133.8, 130.5, 130.4, 129.1, 128.7, 128.6, 128.1, 126.7, 122.9, 121.3, 120.4, 70.2, 46.4, 30.3, 21.5, 19.0. HRMS (ESI) Calcd for $C_{25}H_{24}N_3O_3S$ $[M+H]^+$ 446.1533; Found: 446.1542.

4 Representative procedure of preparing products 5

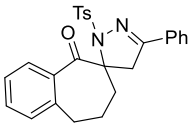
To a mixture of **1** (0.2 mmol, 1 equiv) and **4** (0.22 mmol, 1.1 equiv) in $CHCl_3$ (6 mL), DIPEA (0.6 mmol, 3 equiv) was added. Then the mixture was stirred at room temperature under nitrogen. When reaction completed, water (6 mL) was added, and the mixture was extracted with CH_2Cl_2 (4 mL × 4). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (silica gel, petrol ether/EtOAc = 20/1~4/1) to give **5** as white solid.



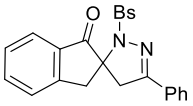
5'-phenyl-2'-tosyl-2',4'-dihydrospiro[indene-2,3'-pyrazol]-1(3*H*)-one (5a). White solid, m.p.: 170.0-171.0 °C, yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90-7.86 (m, 3H), 7.71-7.60 (m, 3H), 7.49-7.44 (m, 2H), 7.37-7.30 (m, 5H), 4.06 (d, *J* = 17.5 Hz, 1H), 3.55 (d, *J* = 16.8 Hz, 1H), 3.41 (d, *J* = 17.4 Hz, 1H), 3.24 (d, *J* = 16.8 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.4, 152.5, 150.4, 144.0, 136.2, 136.1, 134.3, 130.6, 130.2, 129.2, 128.5, 128.2, 128.1, 126.5, 124.8, 74.1, 47.5, 42.9, 21.6. HRMS (ESI) Calcd for $C_{24}H_{21}N_2O_3S$ $[M+H]^+$ 417.1267; Found: 417.1257.



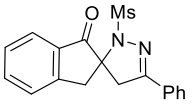
5'-phenyl-2'-tosyl-2',3,4,4'-tetrahydro-1*H*-spiro[naphthalene-2,3'-pyrazol]-1-one (5b). White solid, m.p.: 178.7-179.6 °C. Yield 99%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.7 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 2H), 7.61-7.52 (m, 3H), 7.40-7.28 (m, 7H), 3.47 (d, *J* = 16.8 Hz, 1H), 3.32-3.12 (m, 4H), 2.42-2.37 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 150.6, 143.5, 142.5, 137.0, 134.2, 130.7, 130.1, 129.0, 128.7, 128.6, 128.4, 128.2, 127.2, 126.4, 75.3, 43.3, 33.7, 26.4, 21.6.HRMS (ESI) Calcd for $C_{25}H_{23}N_2O_3S$ $[M+H]^+$ 431.1424; Found: 431.1417.



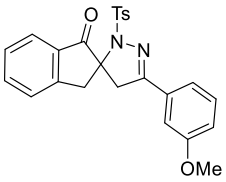
5'-phenyl-2'-tosyl-2',4',8,9-tetrahydrospiro[benzo[7]annulene-6,3'-pyrazol]-5(7*H*)-one (5c). White solid, m.p.: 119.8-120.3 °C. Yield 52%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.72-7.65 (m, 3H), 7.49-7.29 (m, 7H), 7.15 (d, *J* = 7.1 Hz, 1H), 3.56-3.42 (m, 2H), 2.80-2.68 (m, 3H), 2.41 (s, 3H), 2.12-1.99 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.0, 151.1, 143.7, 138.4, 137.1, 136.8, 132.3, 130.9, 130.1, 129.8, 129.2, 128.5, 128.3, 127.9, 127.2, 126.5, 76.3, 41.6, 31.0, 29.8, 21.9, 21.6. HRMS (ESI) Calcd for $C_{26}H_{25}N_2O_3S$ $[M+H]^+$ 445.1580; Found: 445.1587.



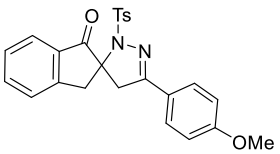
5'-phenyl-2'-(phenylsulfonyl)-2',4'-dihydrospiro[indene-2,3'-pyrazol]-1(3*H*)-one (5d). White solid, m.p.: 189.0-189.4 °C. Yield 80%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03-8.00 (m, 2H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.72-7.45 (m, 8H), 7.41-7.33 (m, 3H), 4.08 (d, *J* = 17.5 Hz, 1H), 3.57 (d, *J* = 16.8 Hz, 1H), 3.43 (d, *J* = 17.5 Hz, 1H), 3.25 (d, *J* = 16.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.3, 152.7, 150.4, 139.2, 136.1, 134.3, 133.1, 130.5, 130.3, 128.6, 128.5, 128.2, 126.6, 124.8, 74.1, 47.6, 43.0. HRMS (ESI) Calcd for $C_{23}H_{19}N_2O_3S$ $[M+H]^+$ 403.1111; Found: 403.1121.



2'-(methylsulfonyl)-5'-phenyl-2',4'-dihydrospiro[indene-2,3'-pyrazol]-1(3*H*)-one (5e). White solid, m.p.: 187.5-188.4 °C. Yield 85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.71-7.66 (m, 3H), 7.48-7.41 (m, 5H), 4.03 (d, *J* = 17.3 Hz, 1H), 3.70 (d, *J* = 17.2 Hz, 1H), 3.45 (d, *J* = 17.4 Hz, 1H), 3.36-3.30 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.2, 153.1, 150.8, 136.3, 133.6, 130.6, 130.4, 128.7, 128.2, 126.7, 126.5, 124.9, 74.0, 47.7, 44.2, 40.9. HRMS (ESI) Calcd for $C_{18}H_{17}N_2O_3S$ $[M+H]^+$ 341.0954; Found: 341.0947.

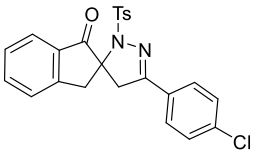


5'-(3-methoxyphenyl)-2'-tosyl-2',4'-dihydrospiro[indene-2,3'-pyrazol]-1(3*H*)-one (5f). White solid, m.p.: 178.2-179.0 °C. Yield 90%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93-7.82 (m, 3H), 7.69 (t, *J* = 7.1 Hz, 1H), 7.49-7.43 (m, 2H), 7.32-7.20 (m, 4H), 7.13 (d, *J* = 7.7 Hz, 1H), 6.92 (dd, *J* = 8.1, 1.7 Hz, 1H), 4.07 (d, *J* = 17.4 Hz, 1H), 3.81 (s, 3H), 3.55 (d, *J* = 16.7 Hz, 1H), 3.41 (d, *J* = 17.5 Hz, 1H), 3.22 (d, *J* = 16.8 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.3, 159.6, 152.4, 150.4, 144.0, 136.2 136.1, 134.3, 131.9, 129.6, 129.3, 128.3, 128.1, 126.6, 124.8, 119.2, 116.2, 111.6, 74.1, 55.4, 47.7, 43.0, 21.6. HRMS (ESI) Calcd for $C_{25}H_{23}N_2O_4S$ $[M+H]^+$ 447.1373; Found: 447.1373.

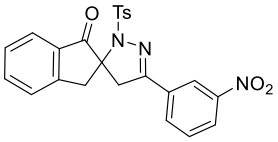


5'-(4-methoxyphenyl)-2'-tosyl-2',4'-dihydrospiro[indene-2,3'-pyrazol]-1(3*H*)-one (5g). White solid, m.p.: 202.1-203.5 °C. Yield 81%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89-7.85 (m, 3H), 7.66 (t, *J* = 6.7 Hz, 1H), 7.55 (d, *J* = 8.9 Hz, 2H), 7.48-7.43 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 4.07 (d, *J* = 17.4 Hz, 1H), 3.81 (s, 3H), 3.53 (d, *J* = 16.7 Hz, 1H), 3.41 (d, *J* = 17.5 Hz, 1H), 3.21 (d, *J* =

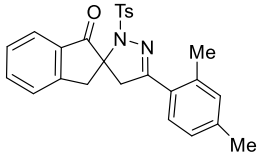
16.7 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.4, 161.2, 152.3, 150.5, 143.9, 136.3, 136.0, 134.4, 129.2, 128.2 (4C), 128.1, 126.6, 124.8, 123.3, 114.0, 74.0, 55.3, 47.7, 42.9, 21.6. HRMS (ESI) Calcd for $C_{25}H_{23}N_2O_4S$ $[M+H]^+$ 447.1373; Found: 447.1371.



5'-(4-chlorophenyl)-2'-tosyl-2',4'-dihydrospiro[indene-2,3'-pyrazol]-1(3*H*)-one (5h). White solid, m.p.: 220.7-221.6 °C. Yield 91%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 3H), 7.72-7.67 (m, 1H), 7.55-7.44 (m, 4H), 7.33-7.31 (m, 4H), 4.08 (d, *J* = 17.5 Hz, 1H), 3.53 (d, *J* = 16.8 Hz, 1H), 3.42 (d, *J* = 17.5 Hz, 1H), 3.21 (d, *J* = 16.8 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.2, 151.4, 150.4, 144.1, 136.2, 136.1 (2C), 134.2, 129.3, 129.1, 128.8, 128.2, 128.1, 127.8, 126.6, 124.8,74.2, 47.4, 42.9, 21.6. HRMS (ESI) Calcd for $C_{24}H_{20}ClN_2O_3S$ $[M+H]^+$ 451.0878; Found: 451.0877.



5'-(3-nitrophenyl)-2'-tosyl-2',4'-dihydrospiro[indene-2,3'-pyrazol]-1(3*H*)-one (5i). White solid, m.p.: 211.5-212.4 °C. Yield 82%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.35 (s, 1H), 8.24-8.22 (m, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.90-7.87 (m, 3H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.59-7.46 (m, 3H), 7.34 (d, *J* = 8.1 Hz, 2H), 4.13 (d, *J* = 17.4 Hz, 1H), 3.62 (d, *J* = 17.0 Hz, 1H), 3.47 (d, *J* = 17.2 Hz, 1H), 3.31 (d, *J* = 16.9 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.9, 150.4, 150.1, 148.5, 144.4, 136.3, 136.0, 134.2, 132.5, 132.1, 129.7, 129.4, 128.4, 128.3, 126.6, 125.0, 124.6, 121.3, 74.6, 47.3, 43.0, 21.7. HRMS (ESI) Calcd for $C_{24}H_{20}N_3O_5S$ $[M+H]^+$ 462.1118; Found: 462.1108.

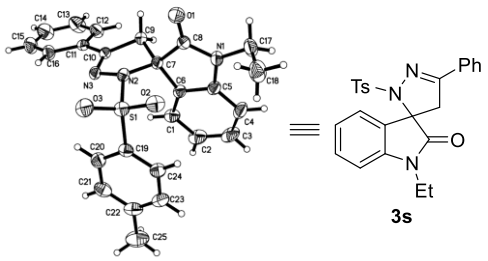


5'-(2,4-dimethylphenyl)-2'-tosyl-2',4'-dihydrospiro[indene-2,3'-pyrazol]-1(3*H*)-one (5j). White solid, m.p.: 88.9-90.5 °C. Yield 52%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.3 Hz, 3H), 7.70 (t, *J* = 7.1 Hz, 1H), 7.50-7.45 (m, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.11-7.06 (m, 2H), 6.98 (d, *J* = 7.7 Hz, 1H), 4.10 (d, *J* = 17.4 Hz, 1H), 3.61 (d, *J* = 16.5 Hz, 1H), 3.42 (d, *J* = 17.5 Hz, 1H), 3.27 (d, *J* = 16.6 Hz, 1H), 2.53 (s, 3H), 2.43 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.7, 153.1, 150.5, 144.0, 139.7, 138.2, 136.1, 136.0, 134.5, 132.6, 129.2, 128.6, 128.4, 128.1, 126.6, 126.4, 124.8, 73.2, 49.8, 42.6, 23.2, 21.6, 21.2. HRMS (ESI) Calcd for $C_{26}H_{25}N_2O_3S$ $[M+H]^+$ 445.1580; Found: 445.1588.

5 Procedure for the scale-up experiment

A mixture of **1a** (1.0 g, 2.72 mmol, 1 equiv), **2a** (0.92 g, 3.0 mmol, 1.1 equiv) and K_2CO_3 (1.13 g, 8.16 mmol, 3 equiv) in $CHCl_3$ (50 mL) was stirred at room temperature under nitrogen for 48 h. When reaction completed, water (50 mL) was added, and the mixture was extracted with CH_2Cl_2 (25 mL × 4). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (silica gel, petrol ether/EtOAc = 20/1~4/1) to give **3a** (1.12 g, yield 95%) as white solid.

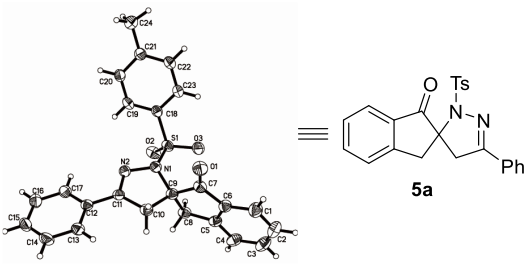
6. X-ray crystal structure of compound 3s and 5a



Crystal data and structure refinement for 3s

Identification code	**3s**
Empirical formula	$C_{25}H_{23}N_3O_3S$

Formula weight	445.52
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.3770(5)
b/Å	23.6227(13)
c/Å	12.1418(7)
α/°	90
β/°	109.819(7)
γ/°	90
Volume/Å^3	2260.4(2)
Z	4
ρ_{calc}g/cm^3	1.309
μ/mm^{-1}	1.533
F(000)	936.0
Crystal size/mm^3	0.15 × 0.13 × 0
Radiation	CuK$^{\alpha}$ (λ = 1.54184)
2Θ range for data collection/°	7.484 to 134.16
Index ranges	$-10 \le h \le 6$, $-26 \le k \le 28$, $-14 \le l \le 14$
Reflections collected	8914
Independent reflections	4023 [R_{int} = 0.0309, R_{sigma} = 0.0410]
Data/restraints/parameters	4023/0/291
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0453, wR_2 = 0.1112
Final R indexes [all data]	R_1 = 0.0599, wR_2 = 0.1235
Largest diff. peak/hole / e Å^{-3}	0.21/-0.32

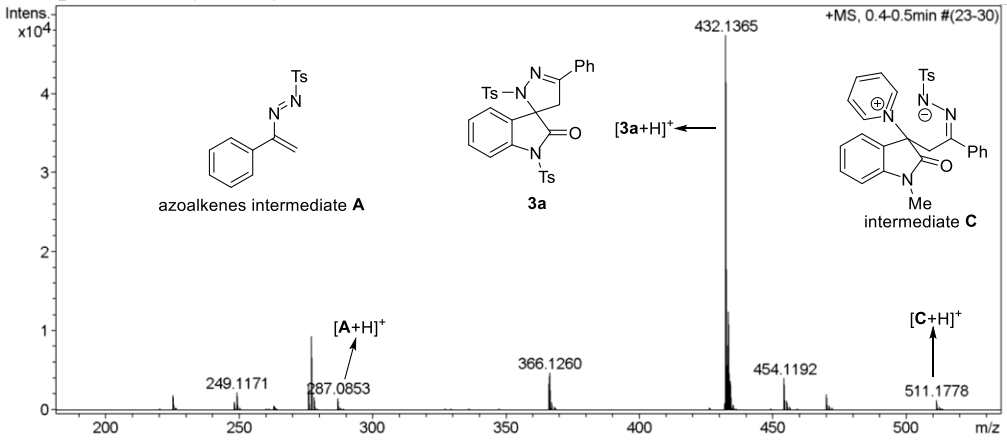


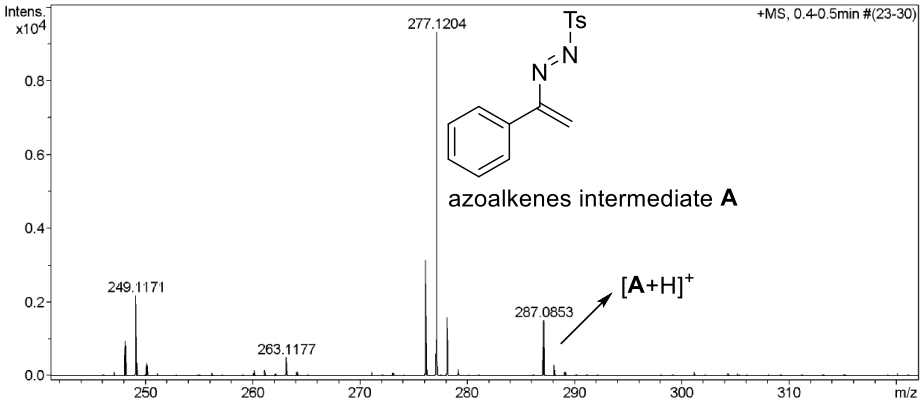
Crystal data and structure refinement for 5a

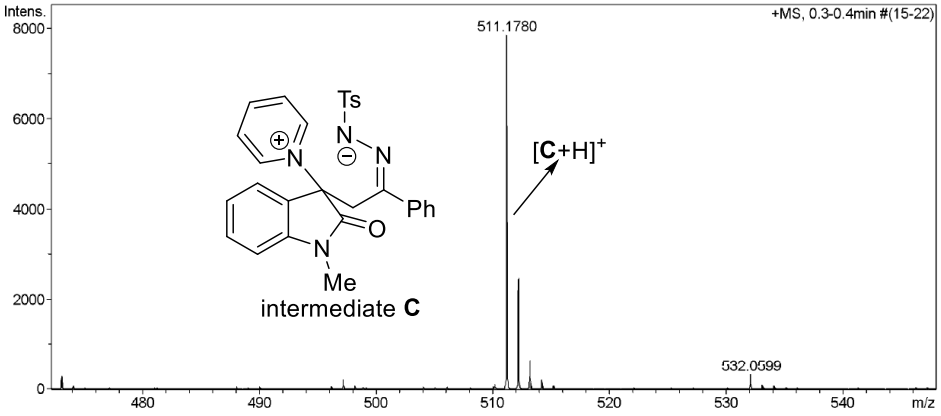
Identification code	**5a**
Empirical formula	$C_{24}H_{20}N_2O_3S$
Formula weight	416.48
Temperature/K	293(2)
Crystal system	monoclinic

Space group	$P2_1/n$
a/Å	11.3284(5)
b/Å	8.7436(6)
c/Å	20.6742(9)
α/°	90
β/°	96.103(4)
γ/°	90
Volume/Å^3	2036.18(18)
Z	4
ρ_{calc}g/cm^3	1.359
μ/mm^{-1}	1.650
F(000)	872.0
Crystal size/mm^3	0.19 × 0.14 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.54 to 134.106
Index ranges	$-13 \leq h \leq 13$, $-10 \leq k \leq 8$, $-18 \leq l \leq 24$
Reflections collected	7291
Independent reflections	3620 [R_{int} = 0.0335, R_{sigma} = 0.0467]
Data/restraints/parameters	3620/0/273
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0476, wR_2 = 0.1197
Final R indexes [all data]	R_1 = 0.0669, wR_2 = 0.1362
Largest diff. peak/hole / e Å^{-3}	0.26/-0.29

7. Mass spectrometry of key intermediates A and C

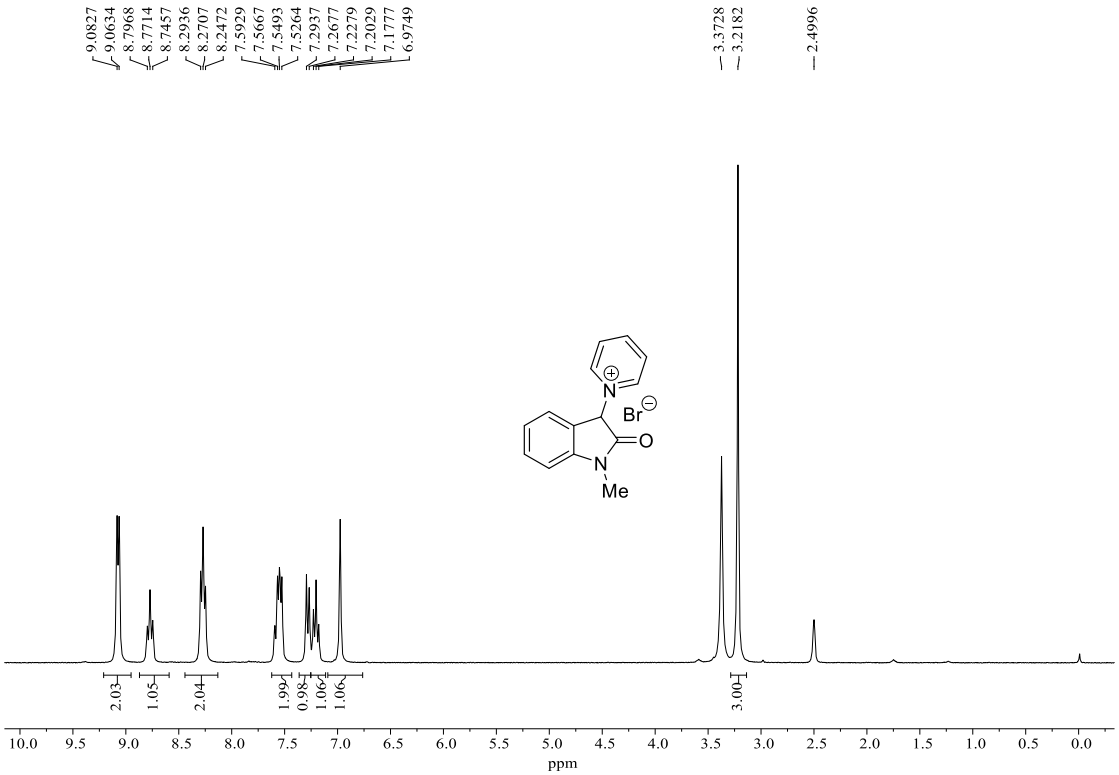


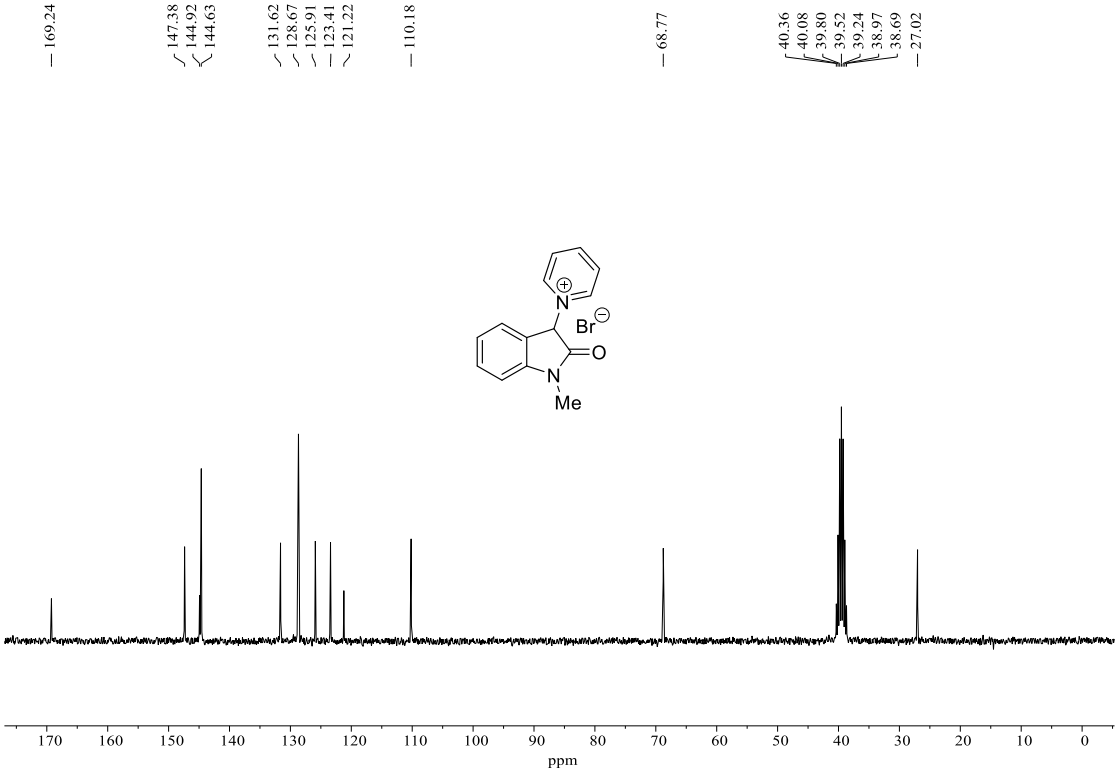




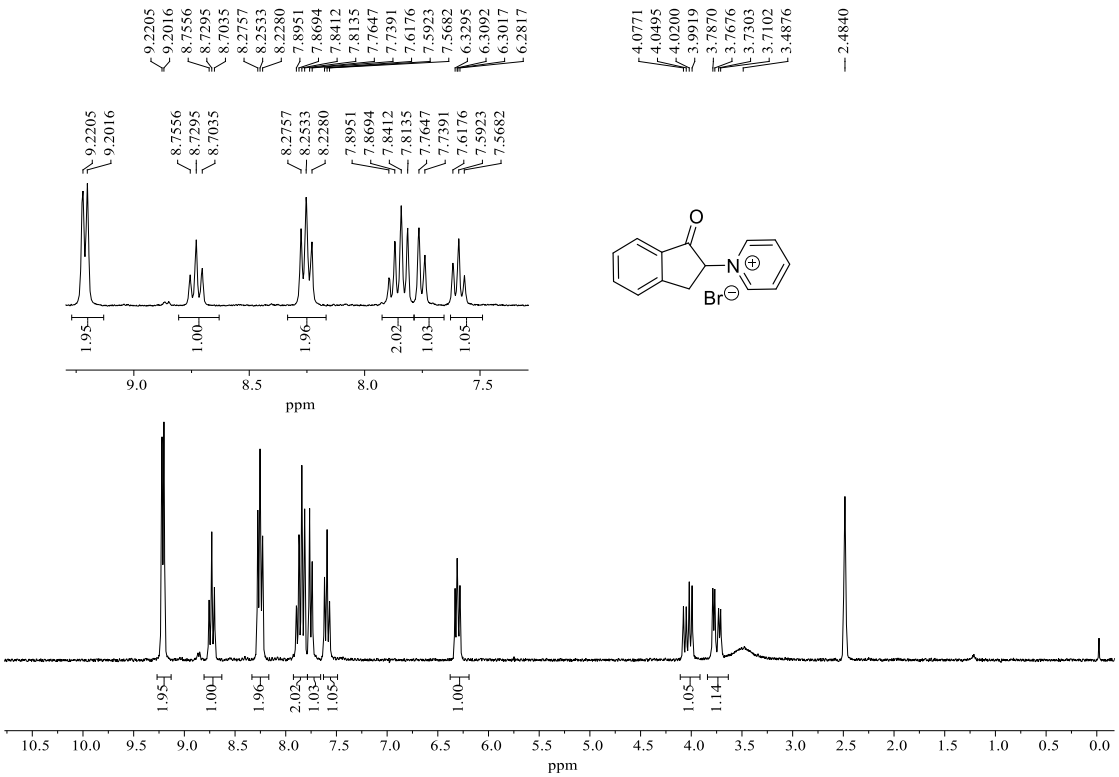
8 ^{1}H NMR and ^{13}C NMR spectra

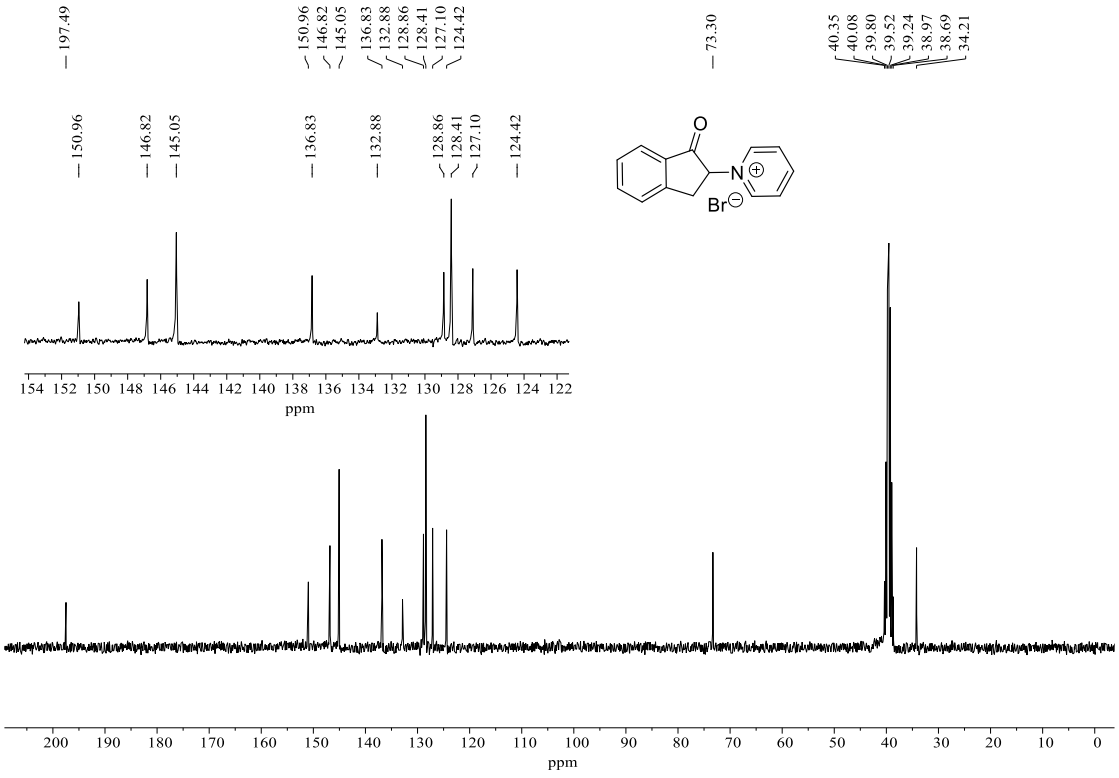
^{1}H NMR and ^{13}C NMR spectra of **2a**



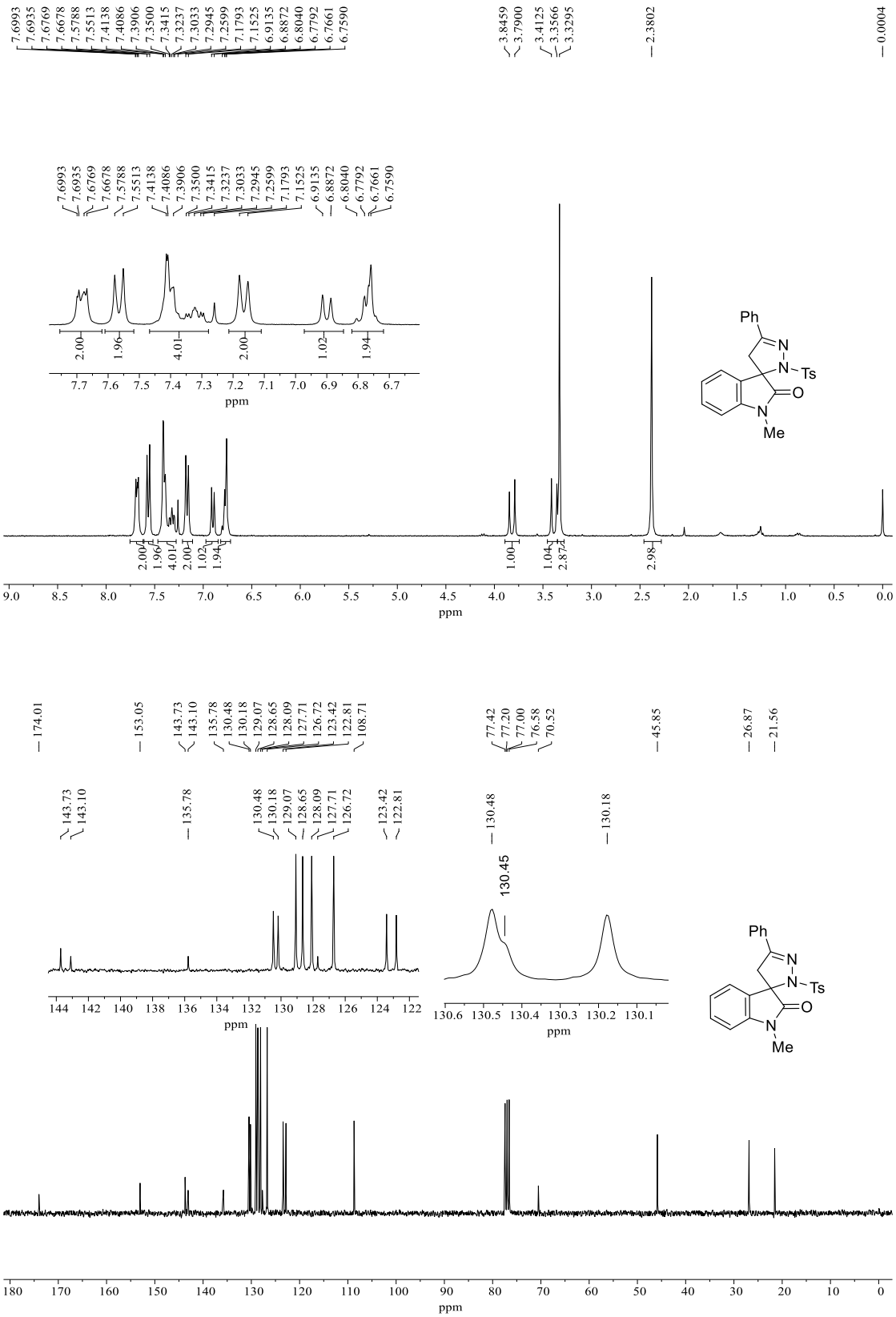


^{1}H NMR and ^{13}C NMR spectra of **4a**

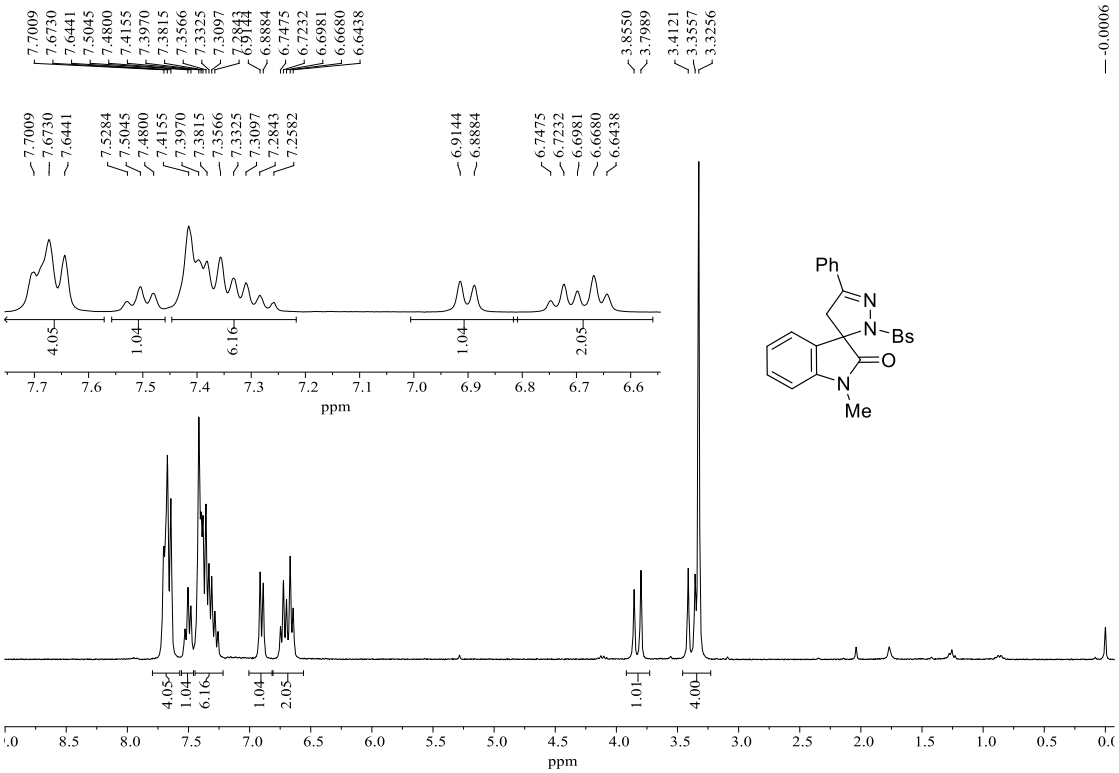


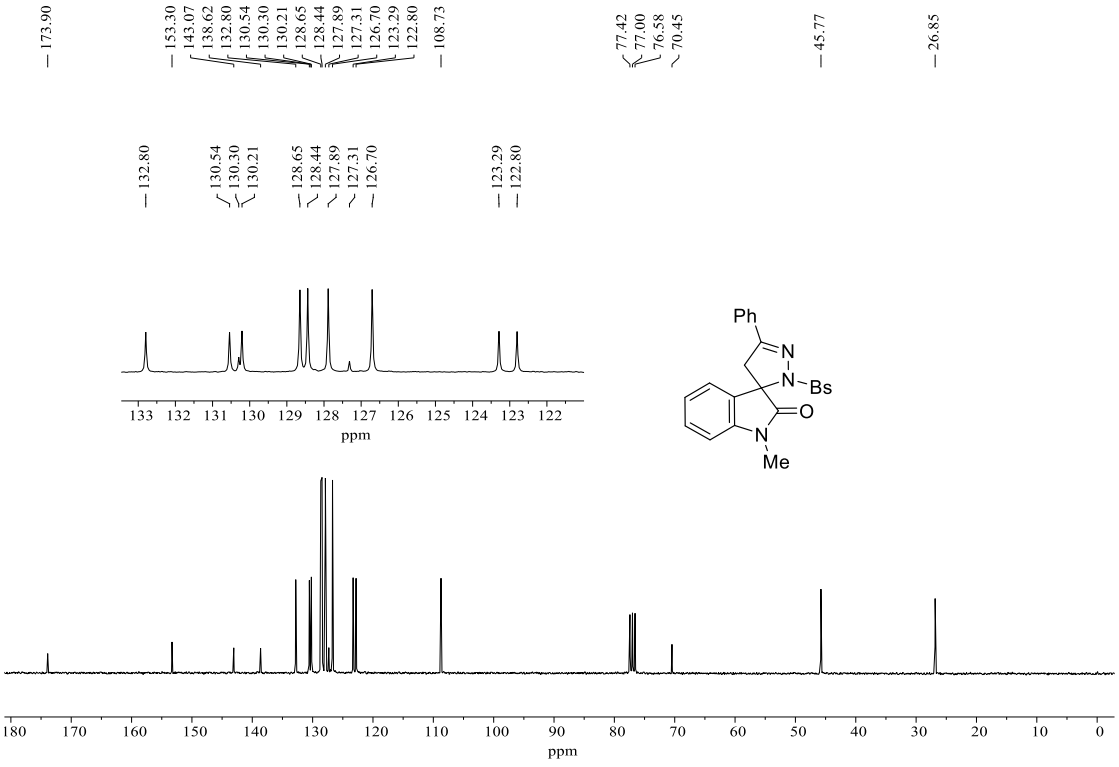


^{1}H NMR and ^{13}C NMR spectra of **3a**

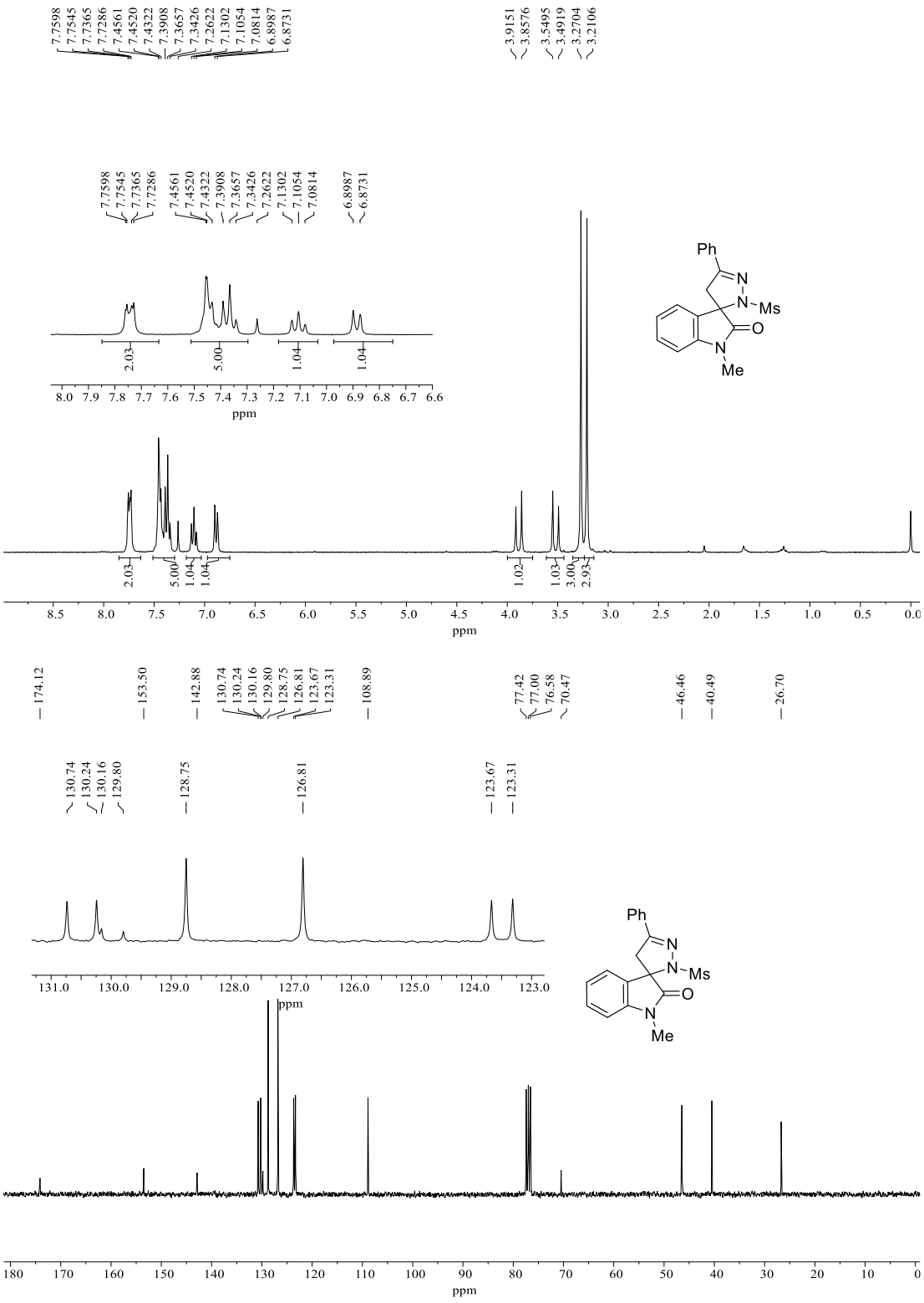


^{1}H NMR and ^{13}C NMR spectra of **3b**

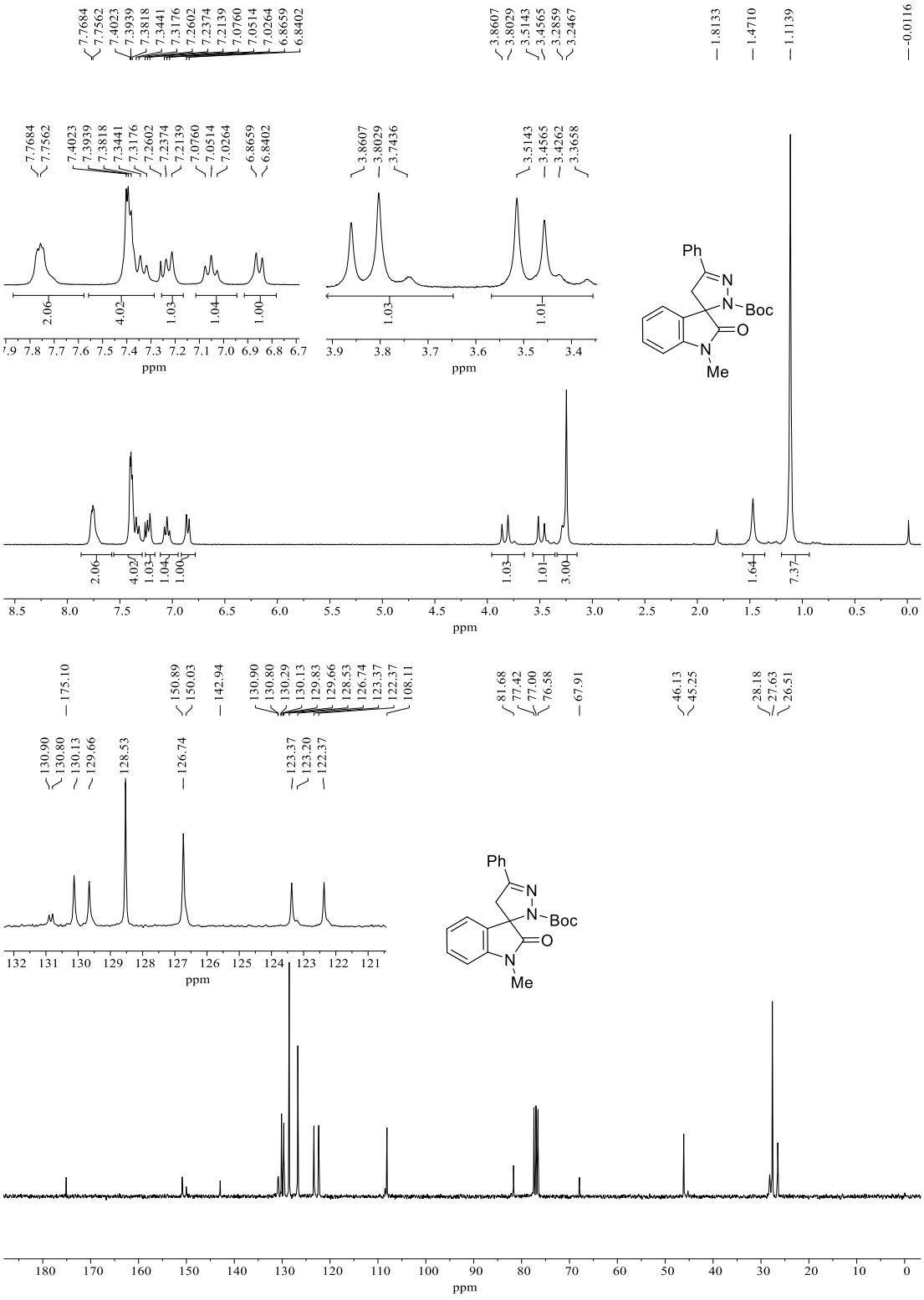




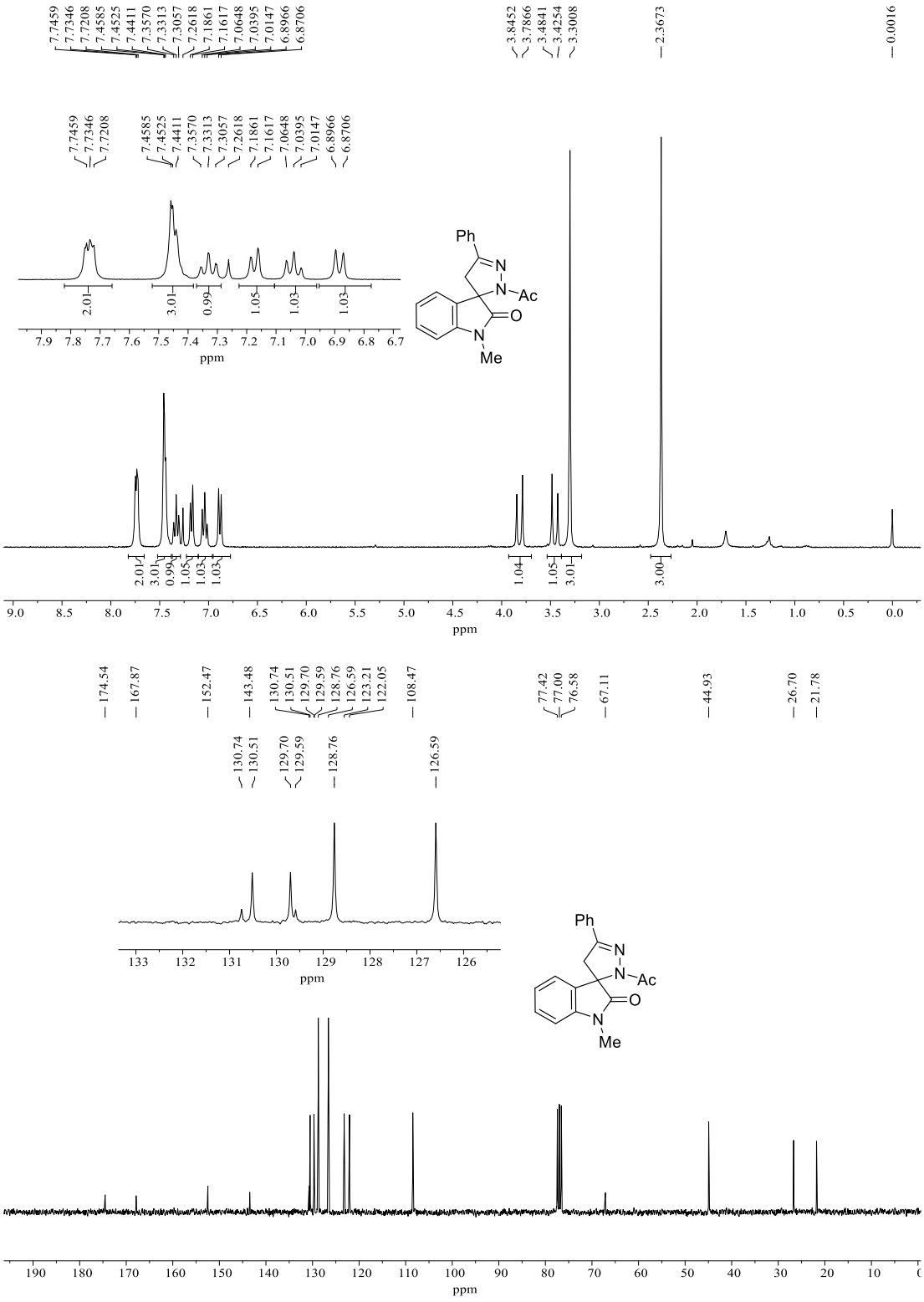
^{1}H NMR and ^{13}C NMR spectra of **3c**



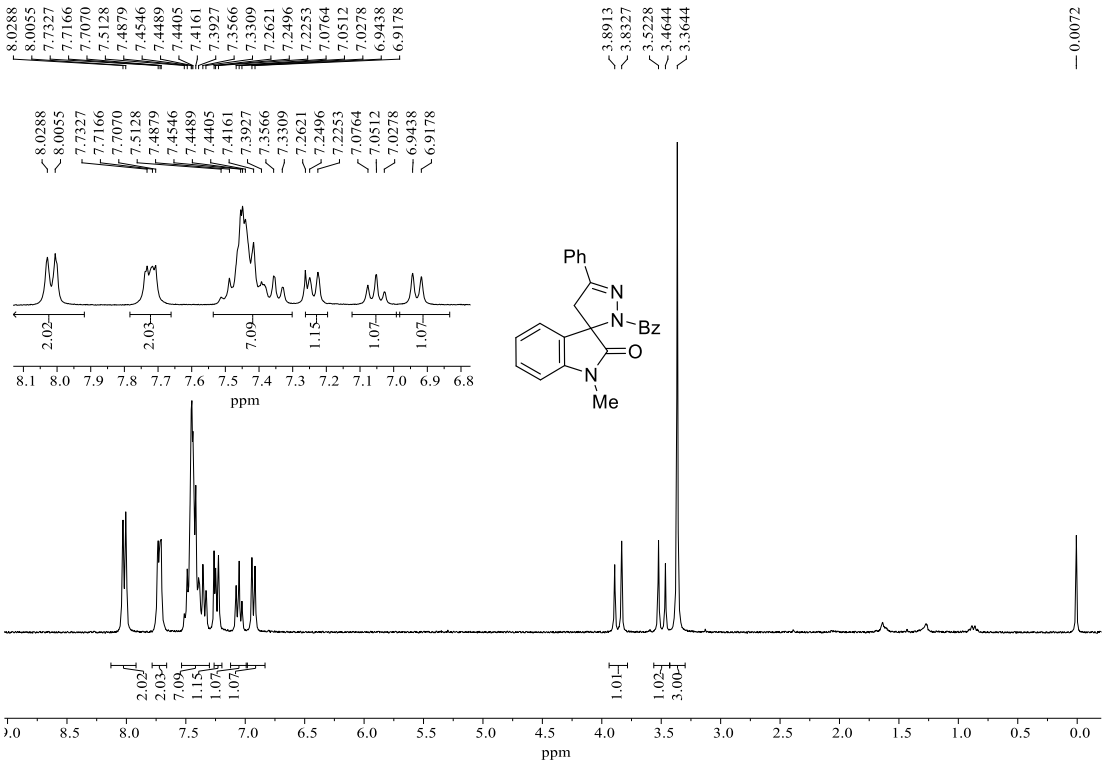
^{1}H NMR and ^{13}C NMR spectra of **3d**

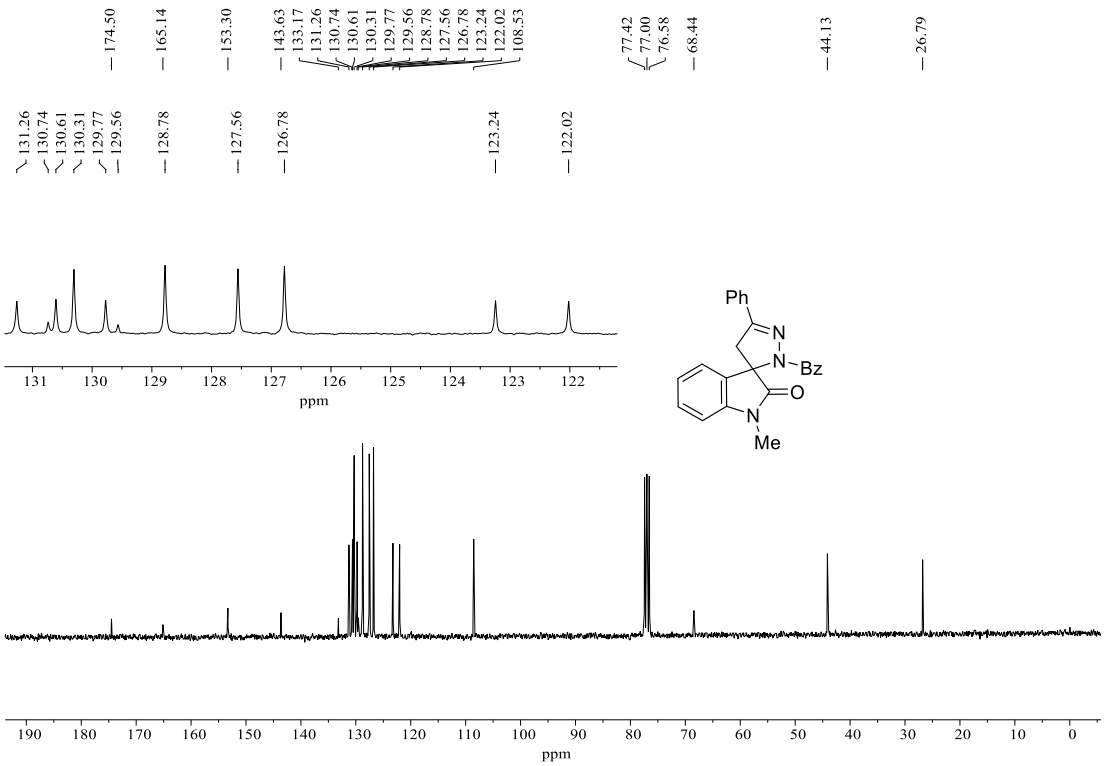


^{1}H NMR and ^{13}C NMR spectra of **3e**

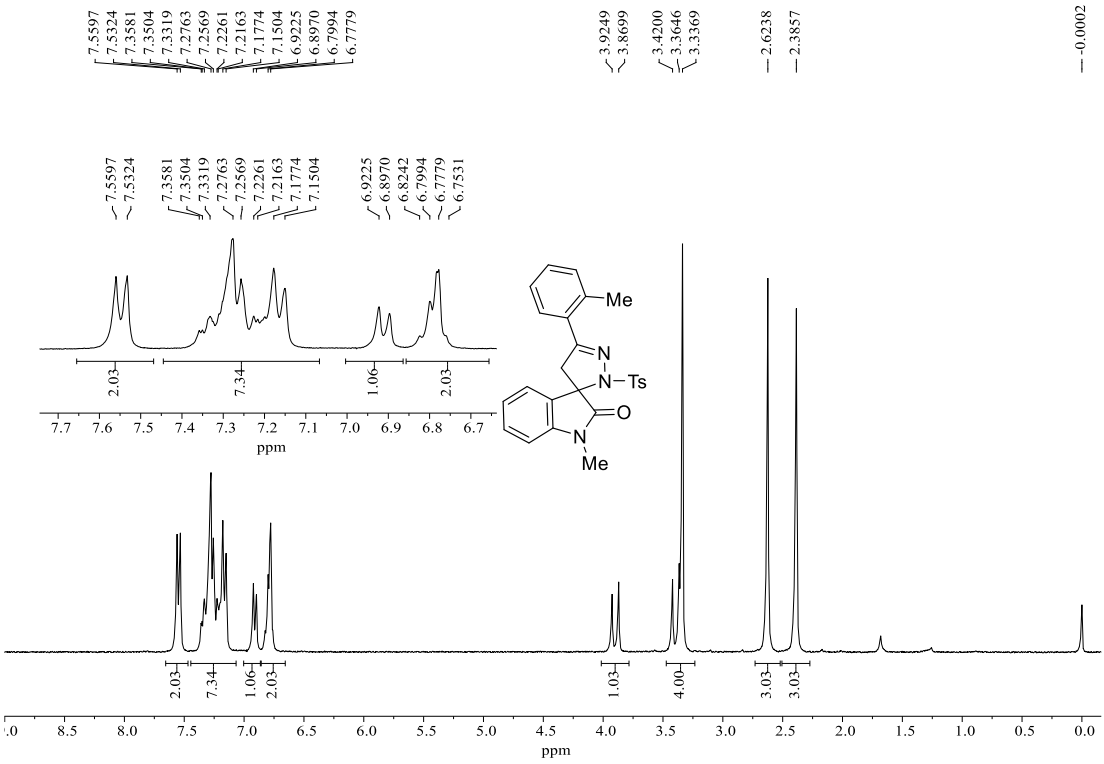


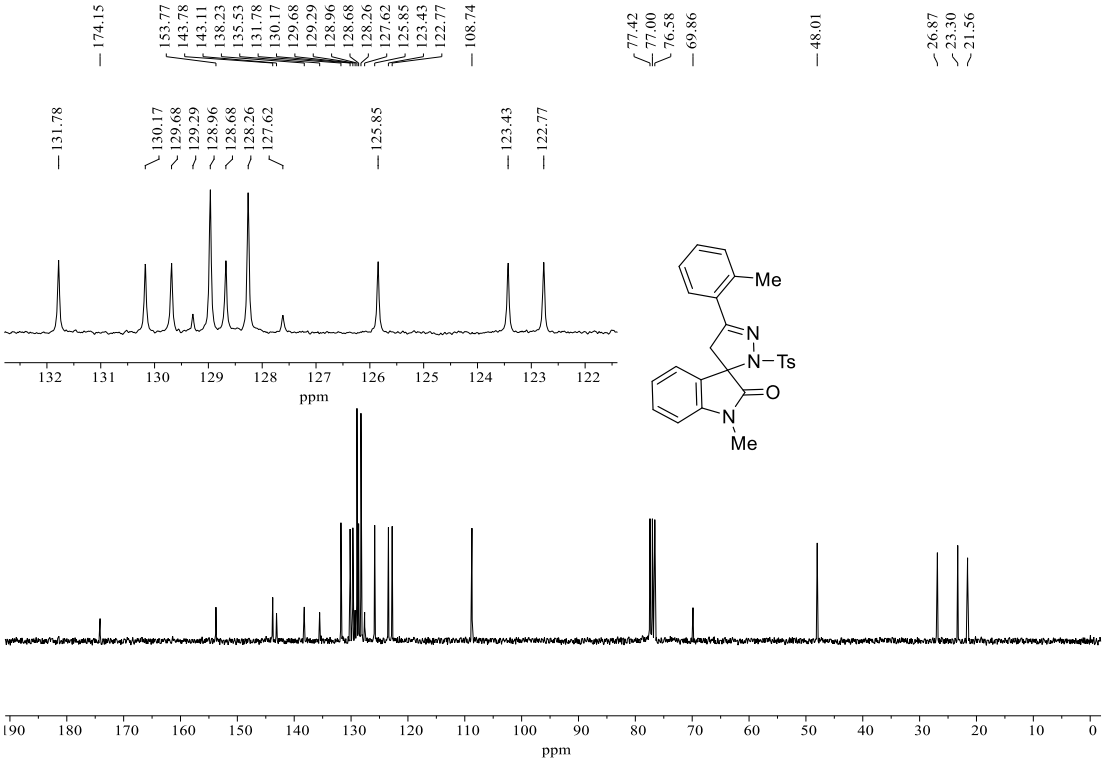
^{1}H NMR and ^{13}C NMR spectra of **3f**



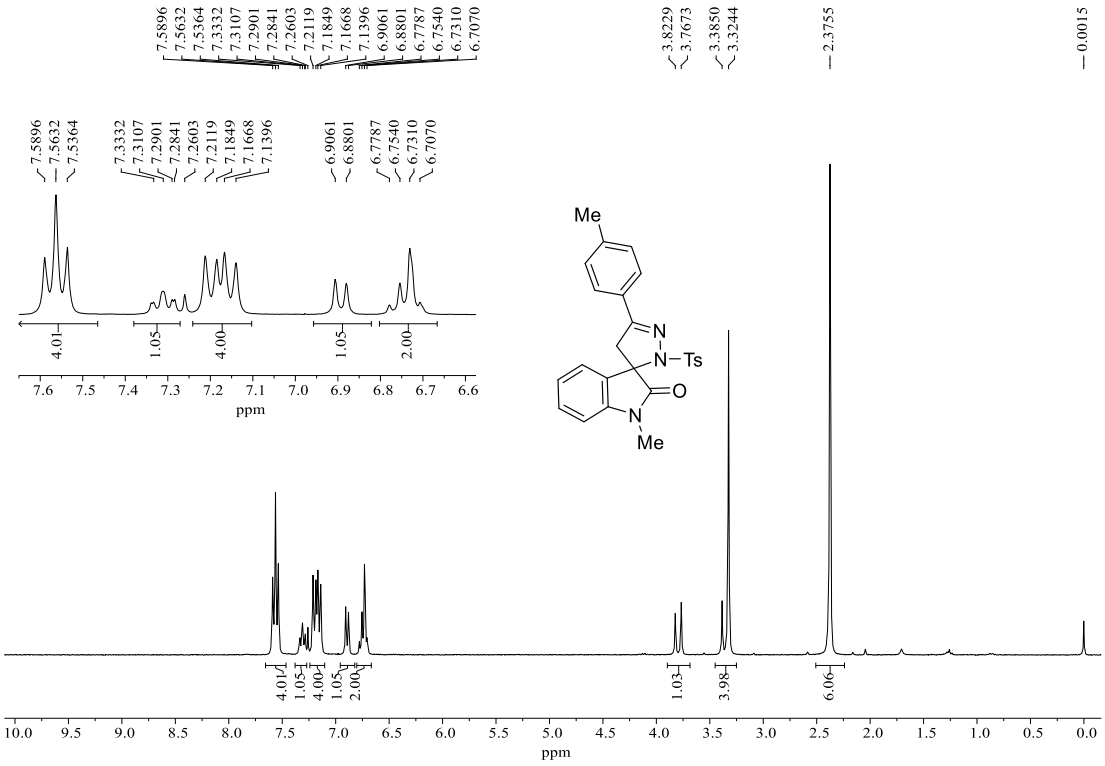


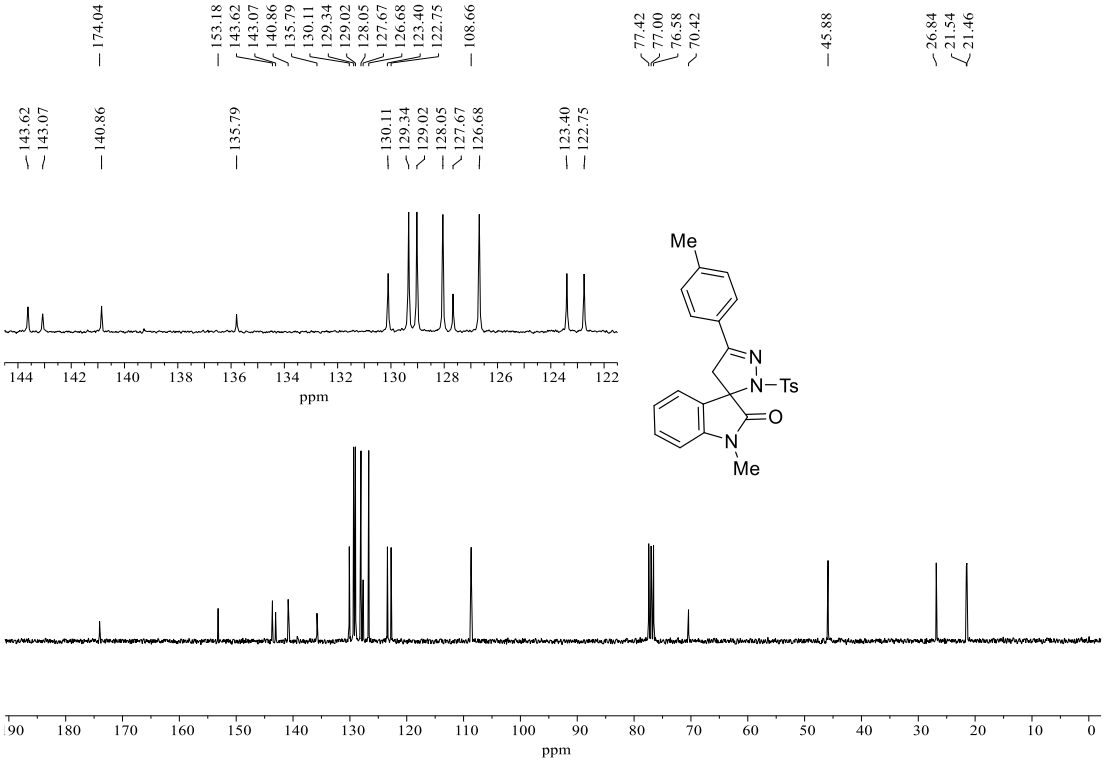
^{1}H NMR and ^{13}C NMR spectra of **3g**



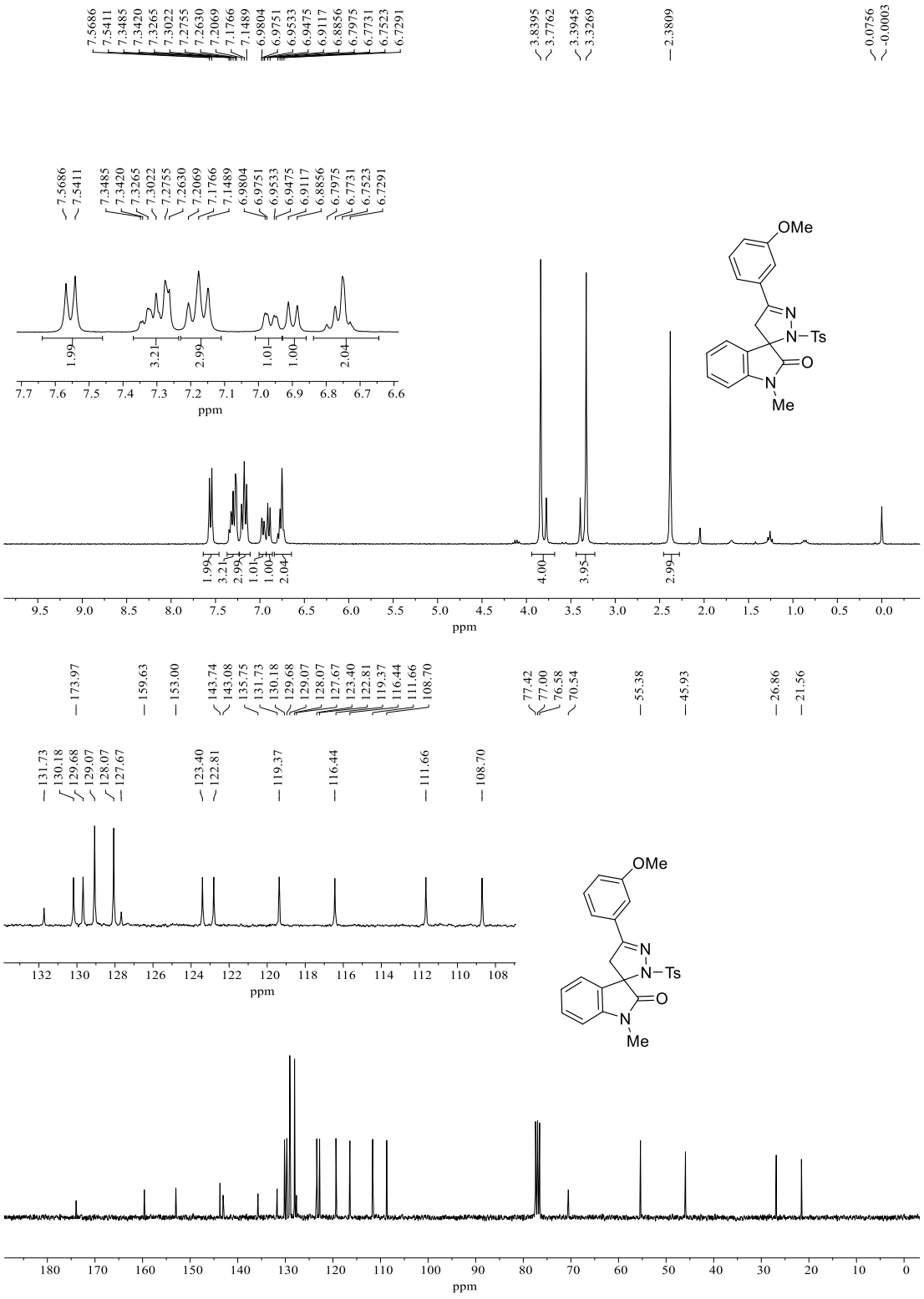


^{1}H NMR and ^{13}C NMR spectra of **3h**

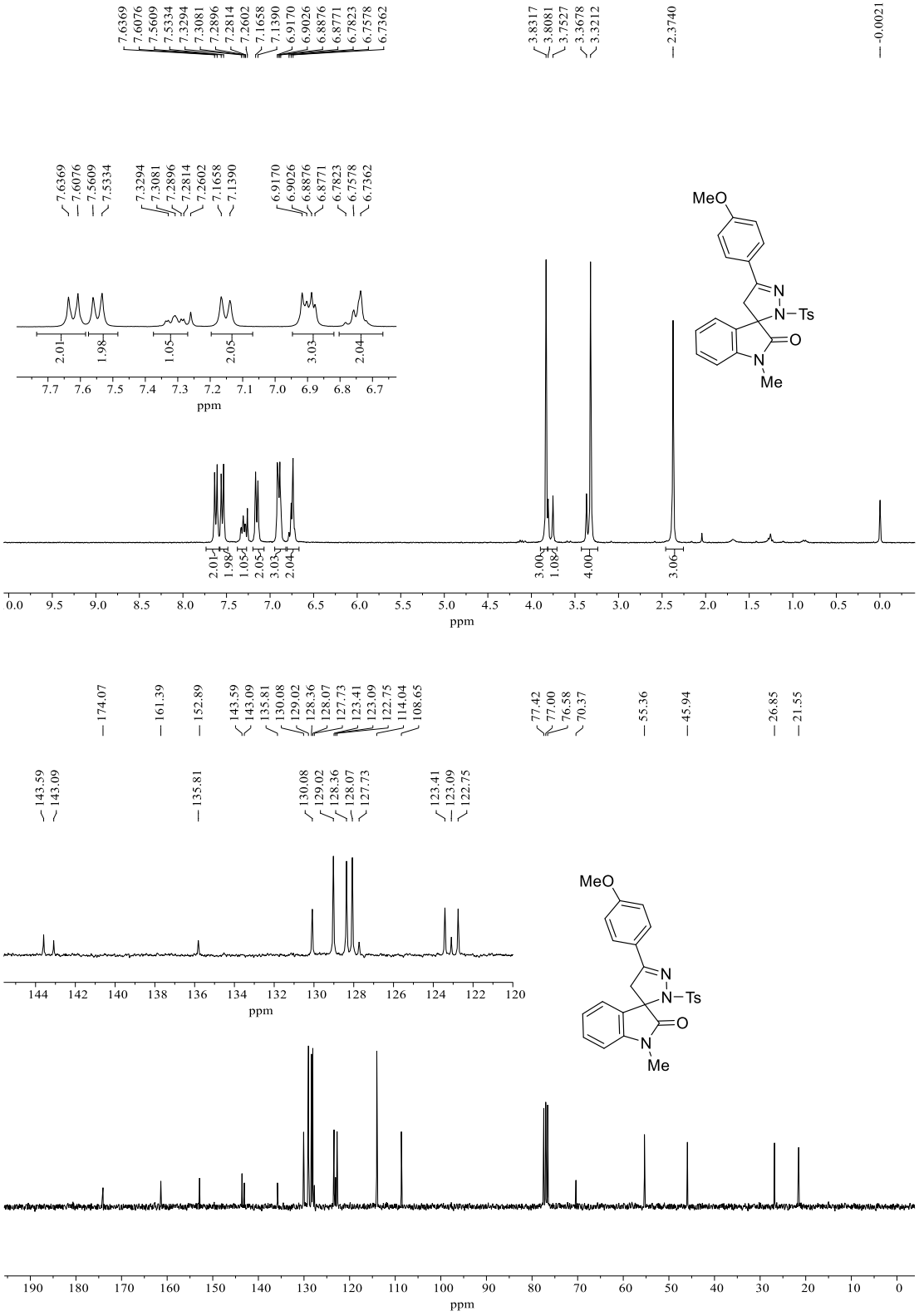




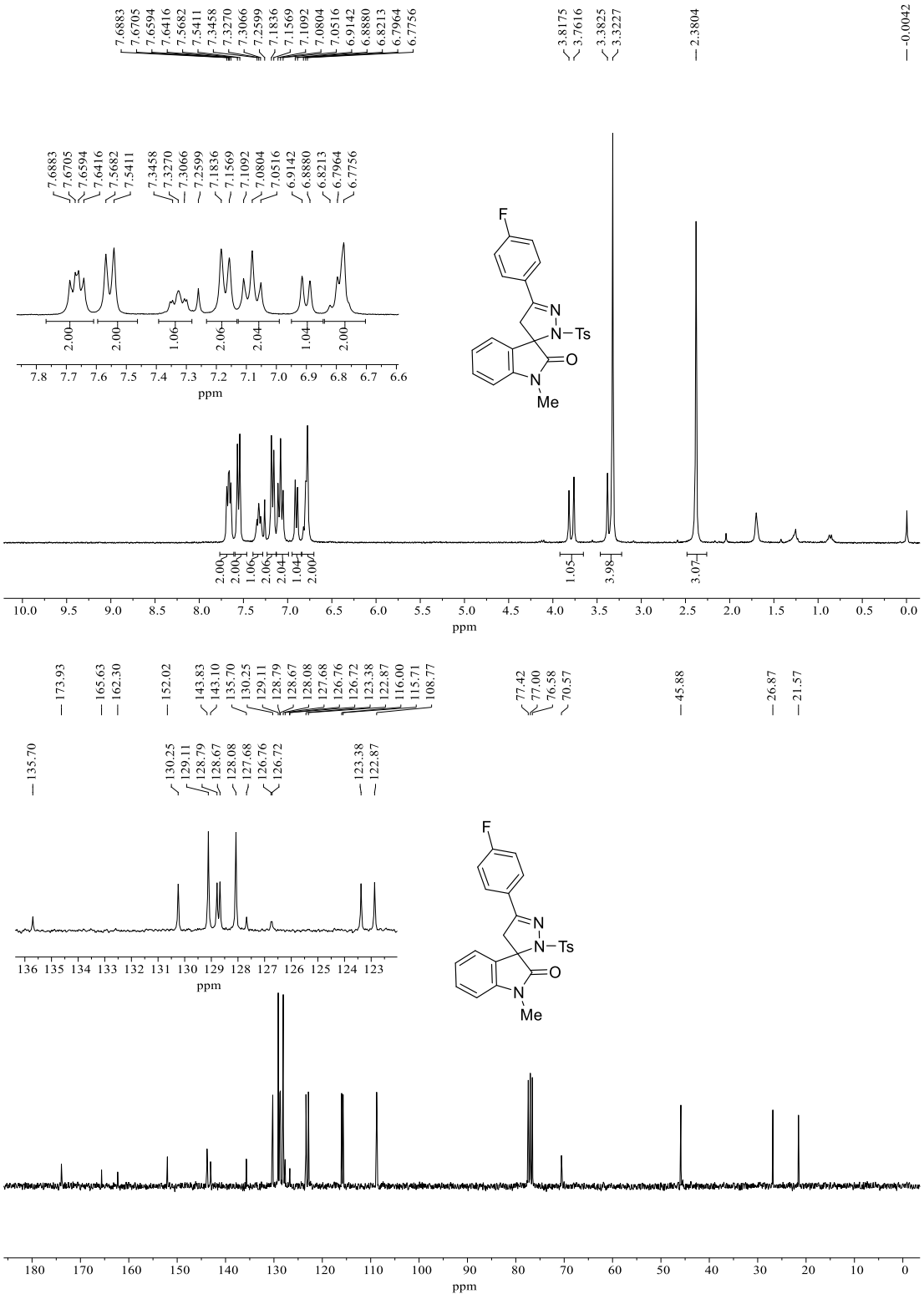
^{1}H NMR and ^{13}C NMR spectra of **3i**



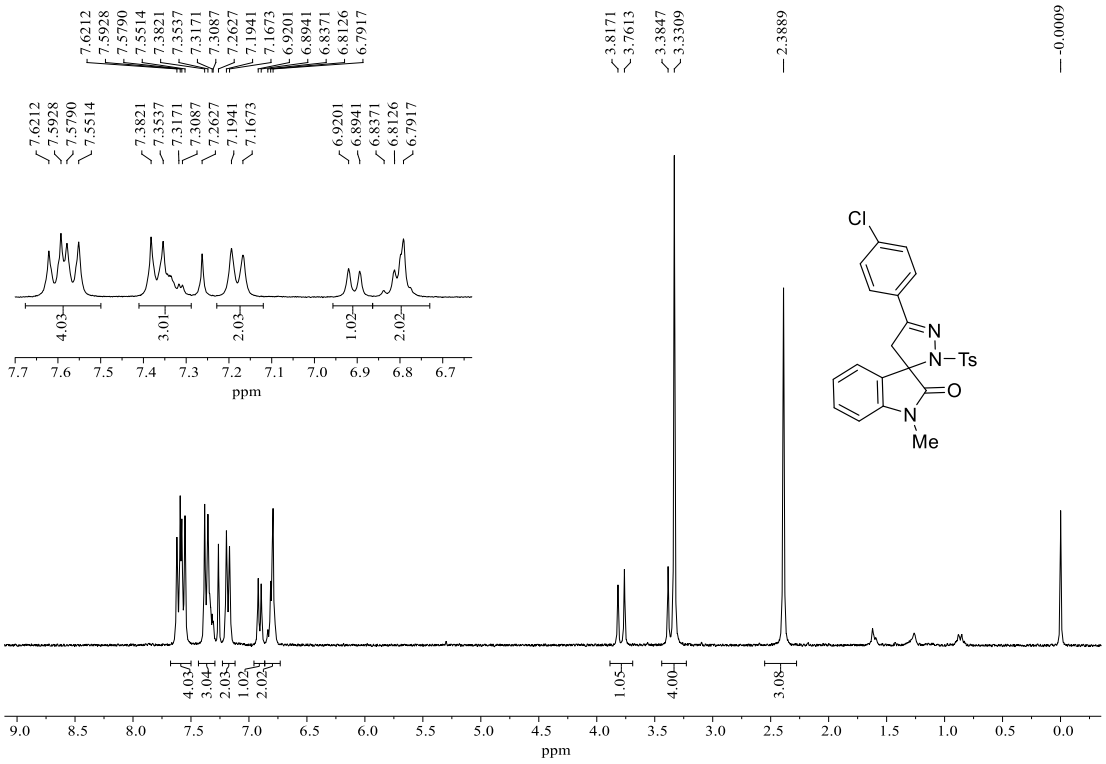
^{1}H NMR and ^{13}C NMR spectra of **3j**

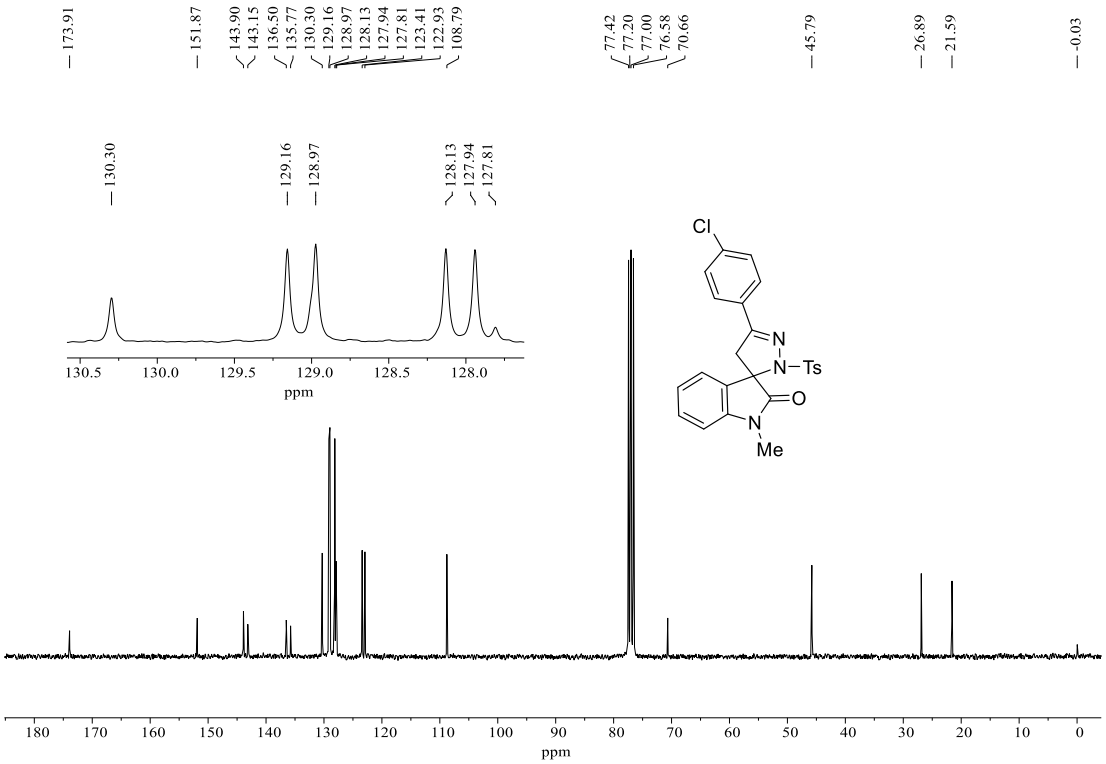


^{1}H NMR and ^{13}C NMR spectra of **3k**

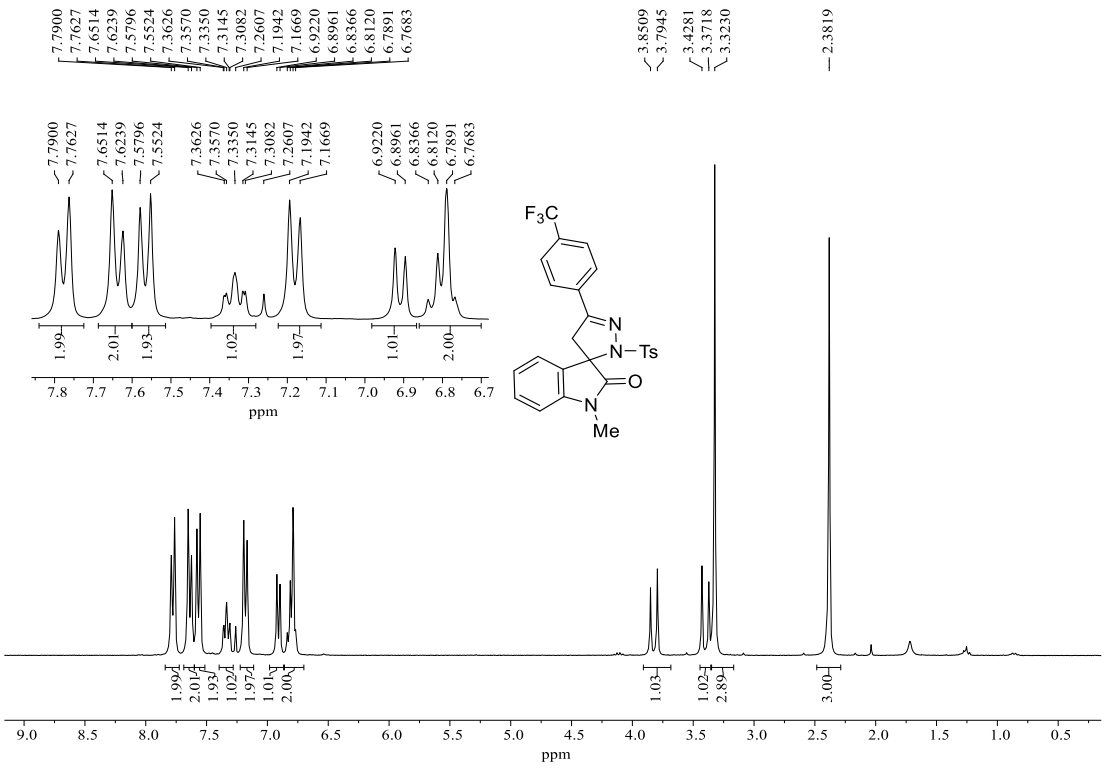


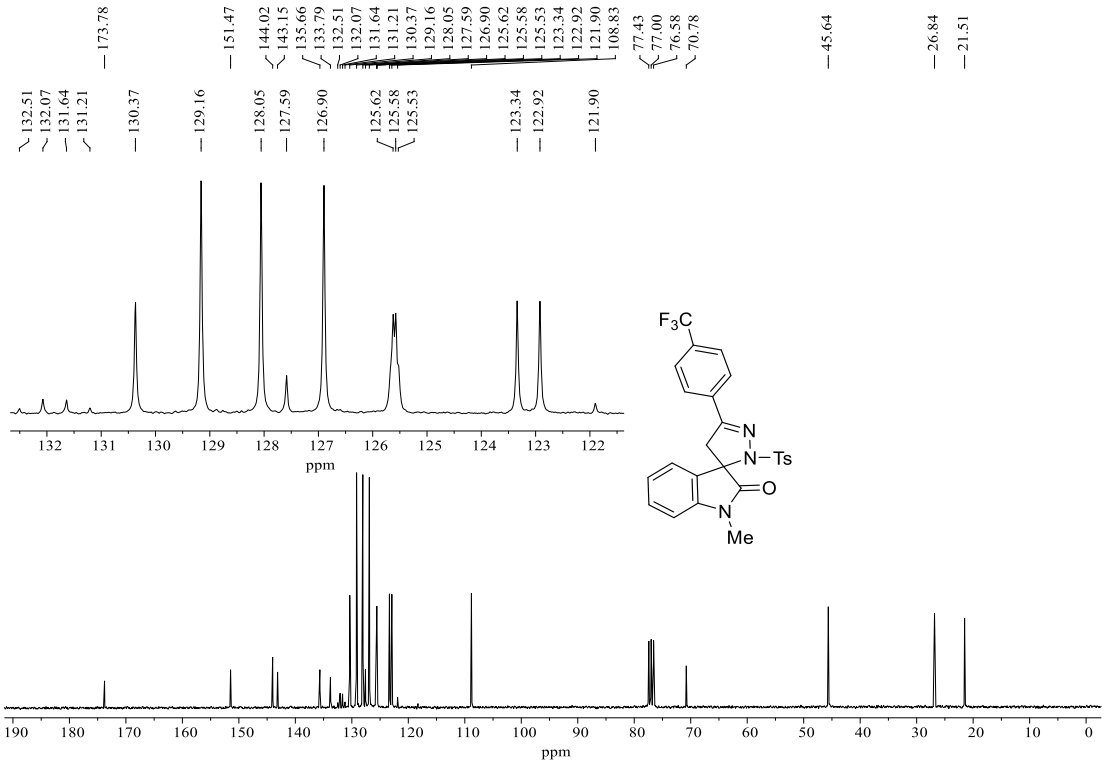
^{1}H NMR and ^{13}C NMR spectra of **3l**



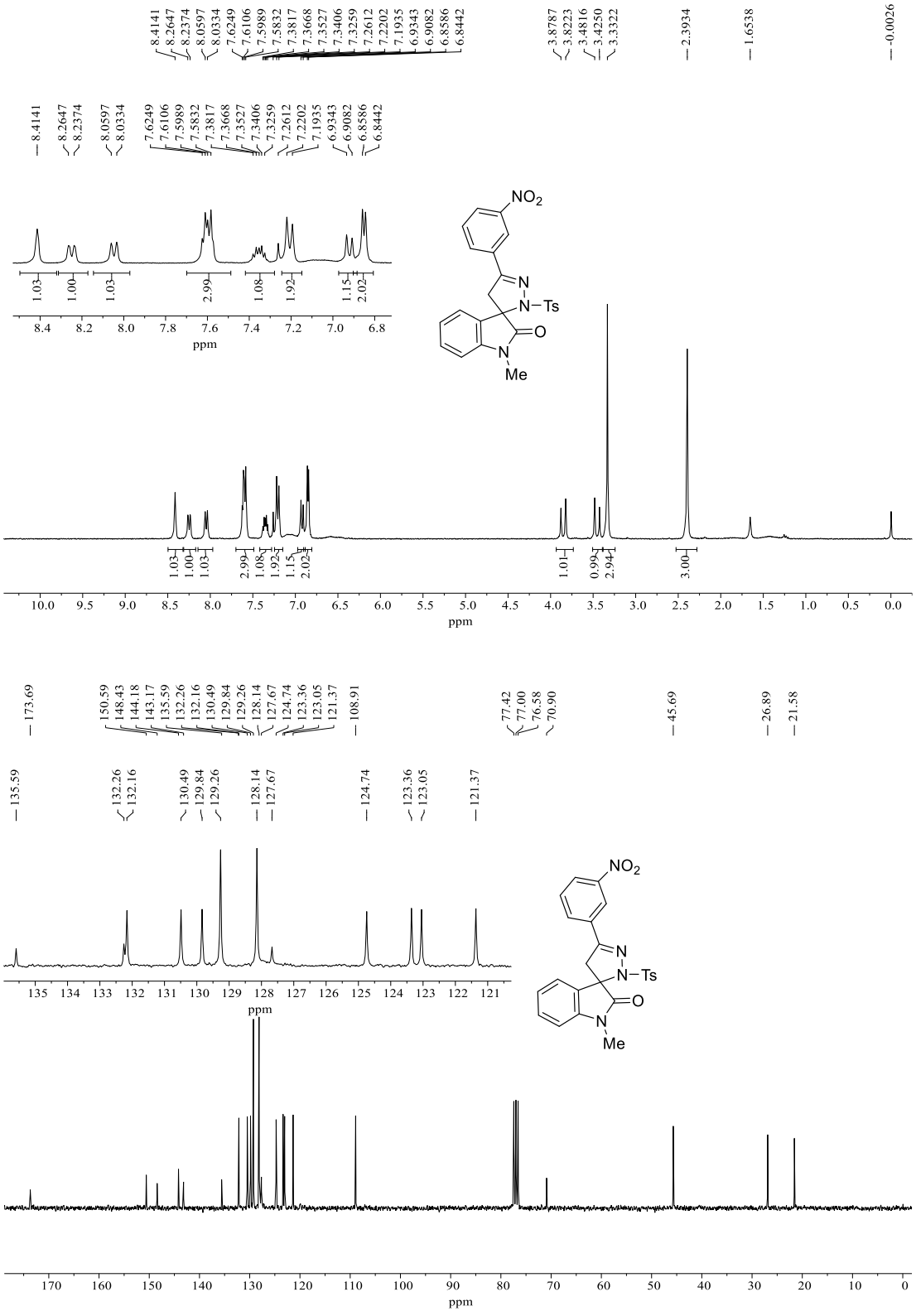


^{1}H NMR and ^{13}C NMR spectra of **3m**

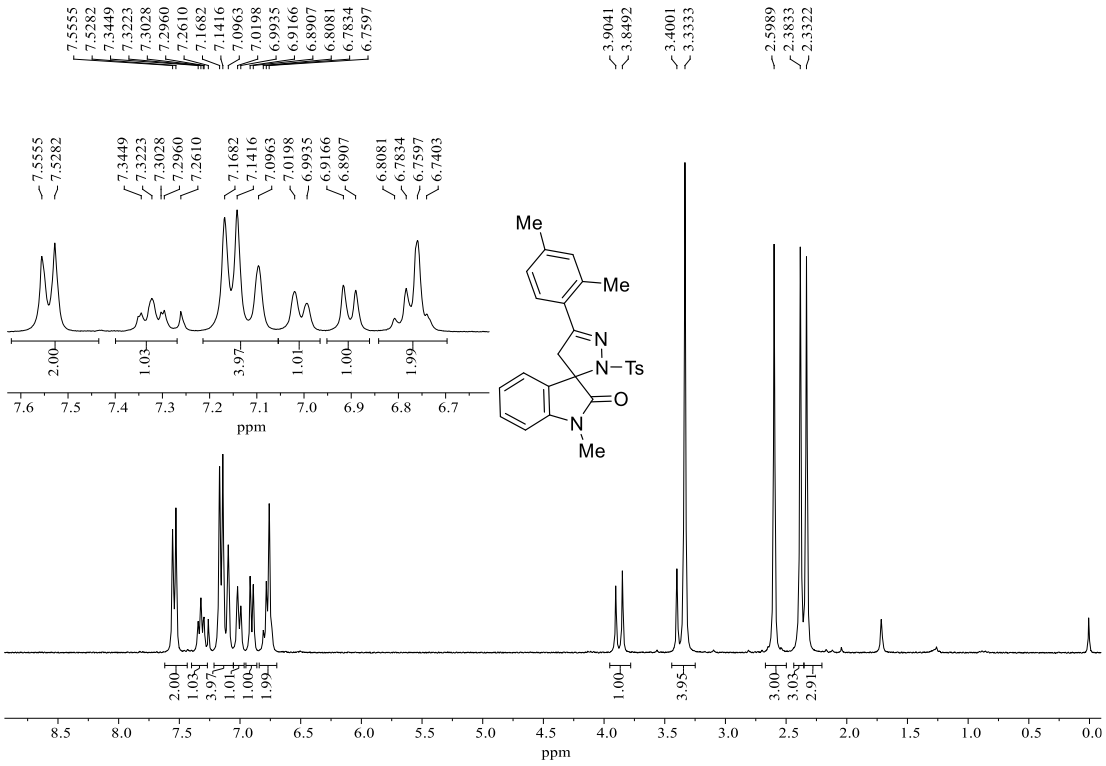


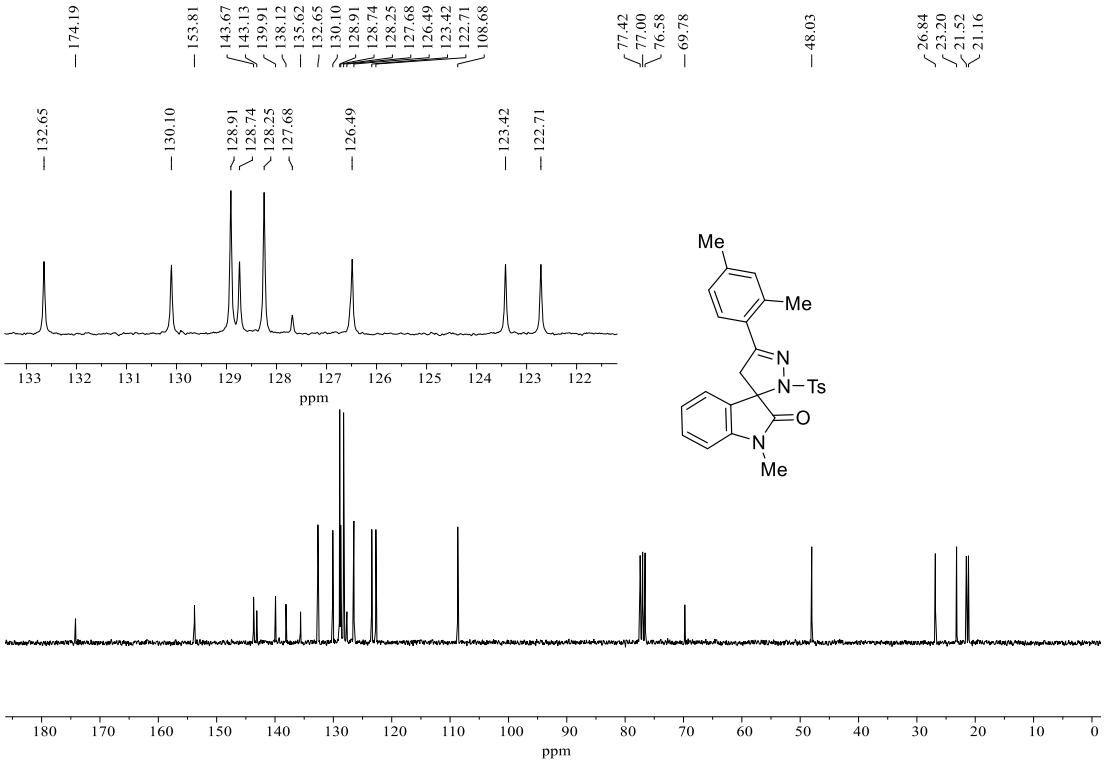


^{1}H NMR and ^{13}C NMR spectra of **3n**

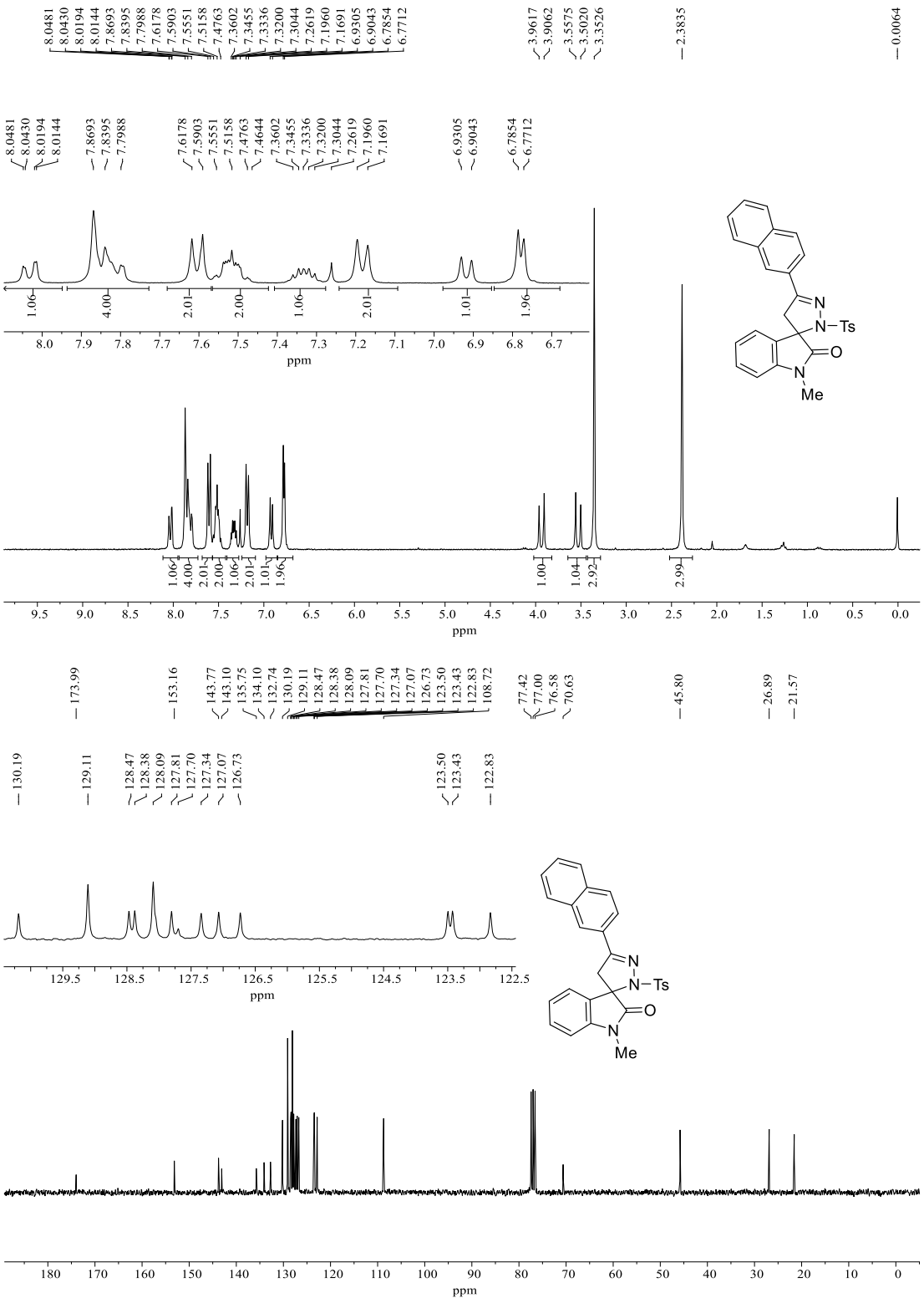


^{1}H NMR and ^{13}C NMR spectra of **3o**

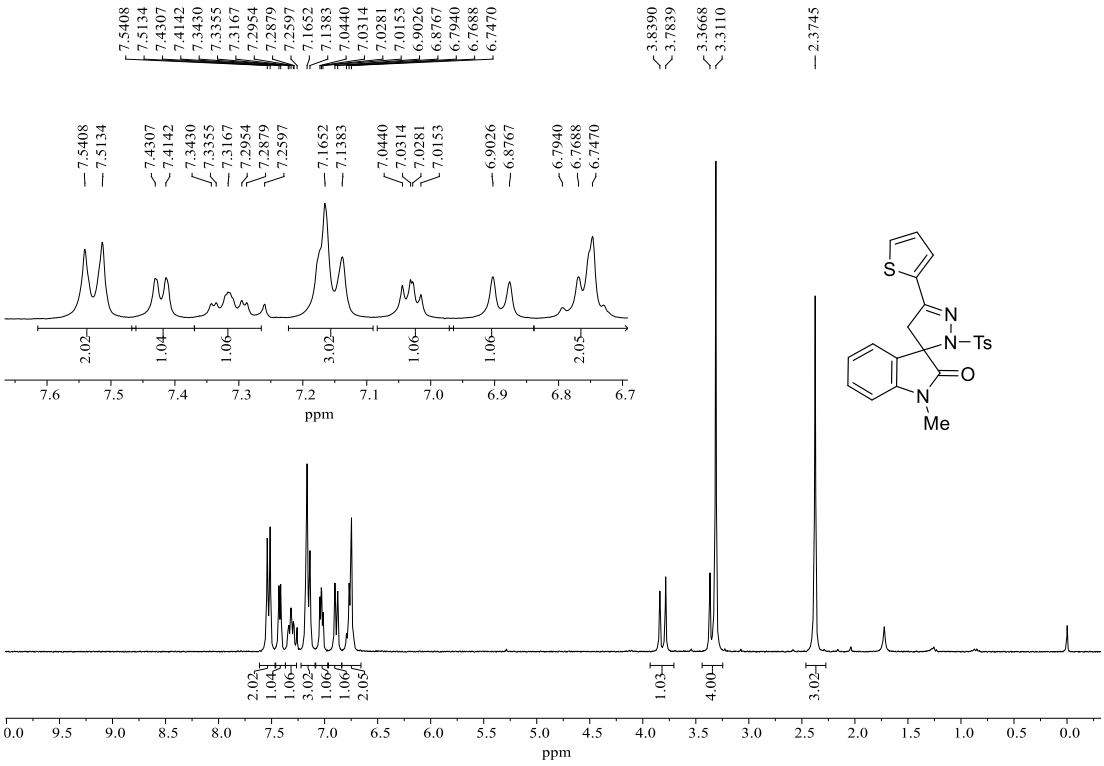


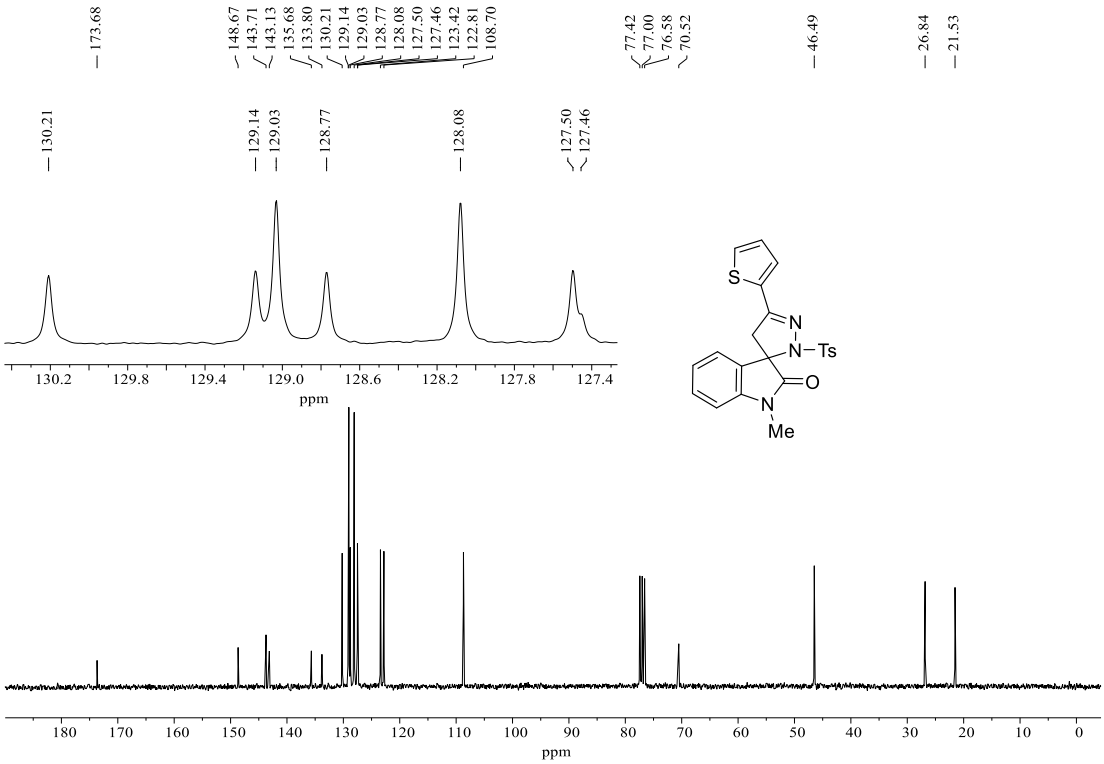


^{1}H NMR and ^{13}C NMR spectra of **3p**

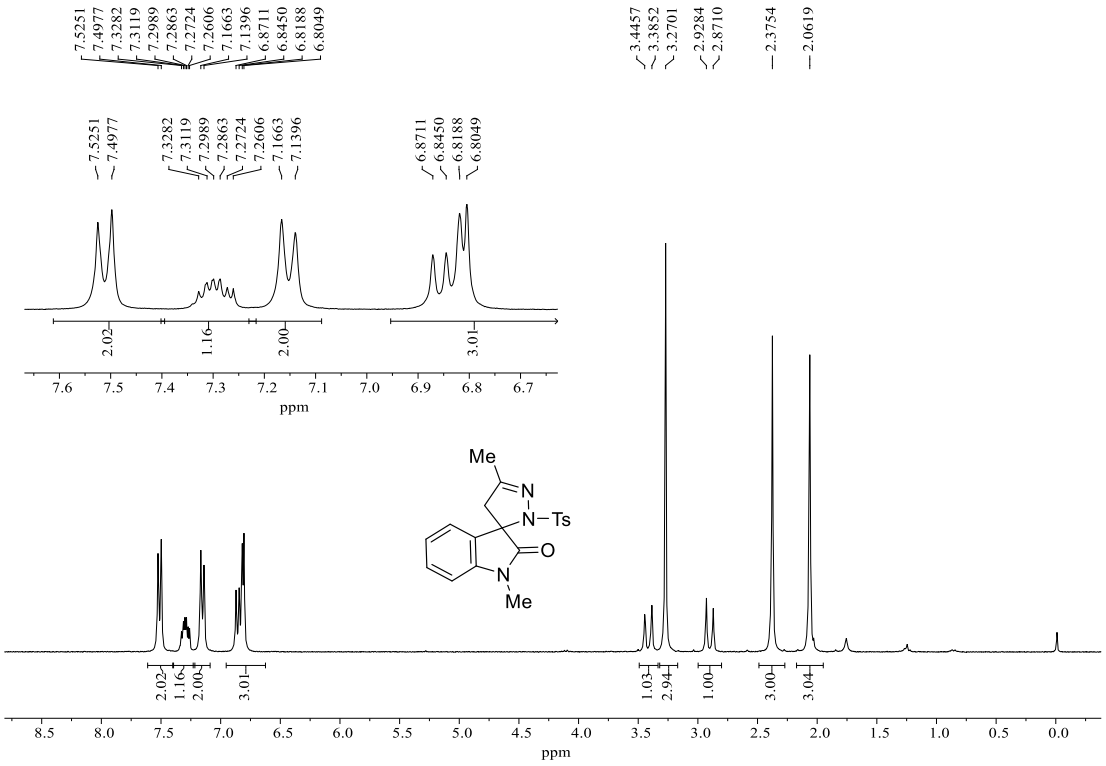


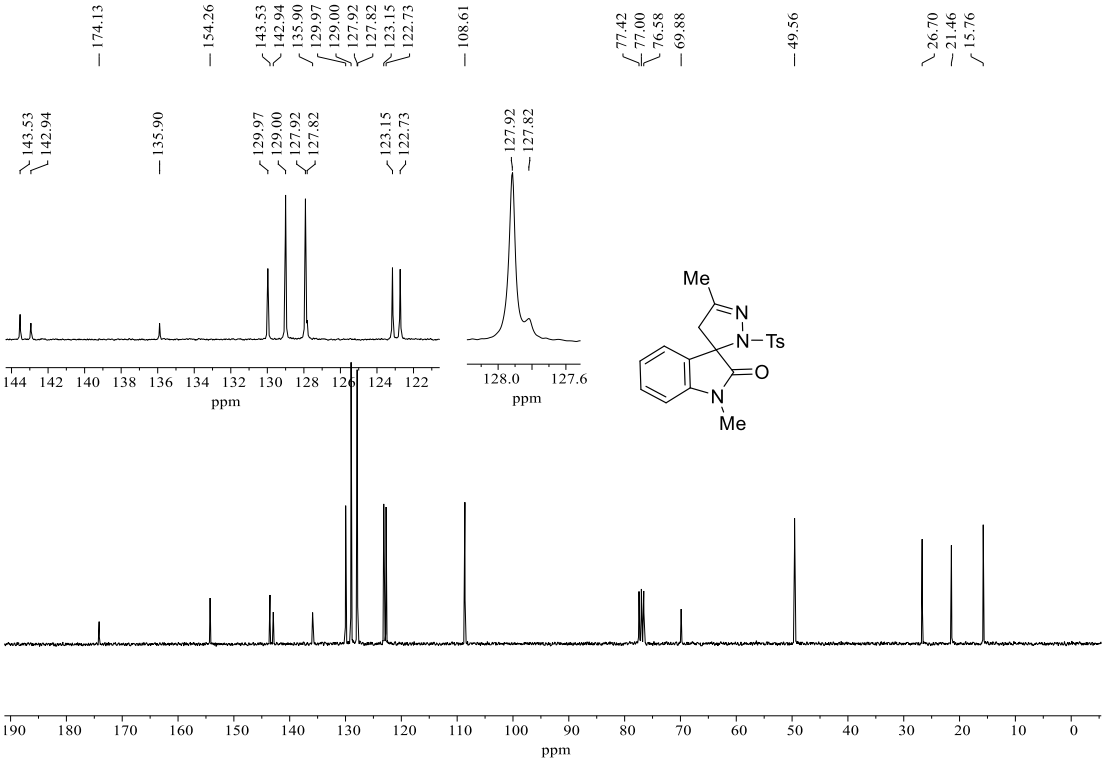
^{1}H NMR and ^{13}C NMR spectra of **3q**



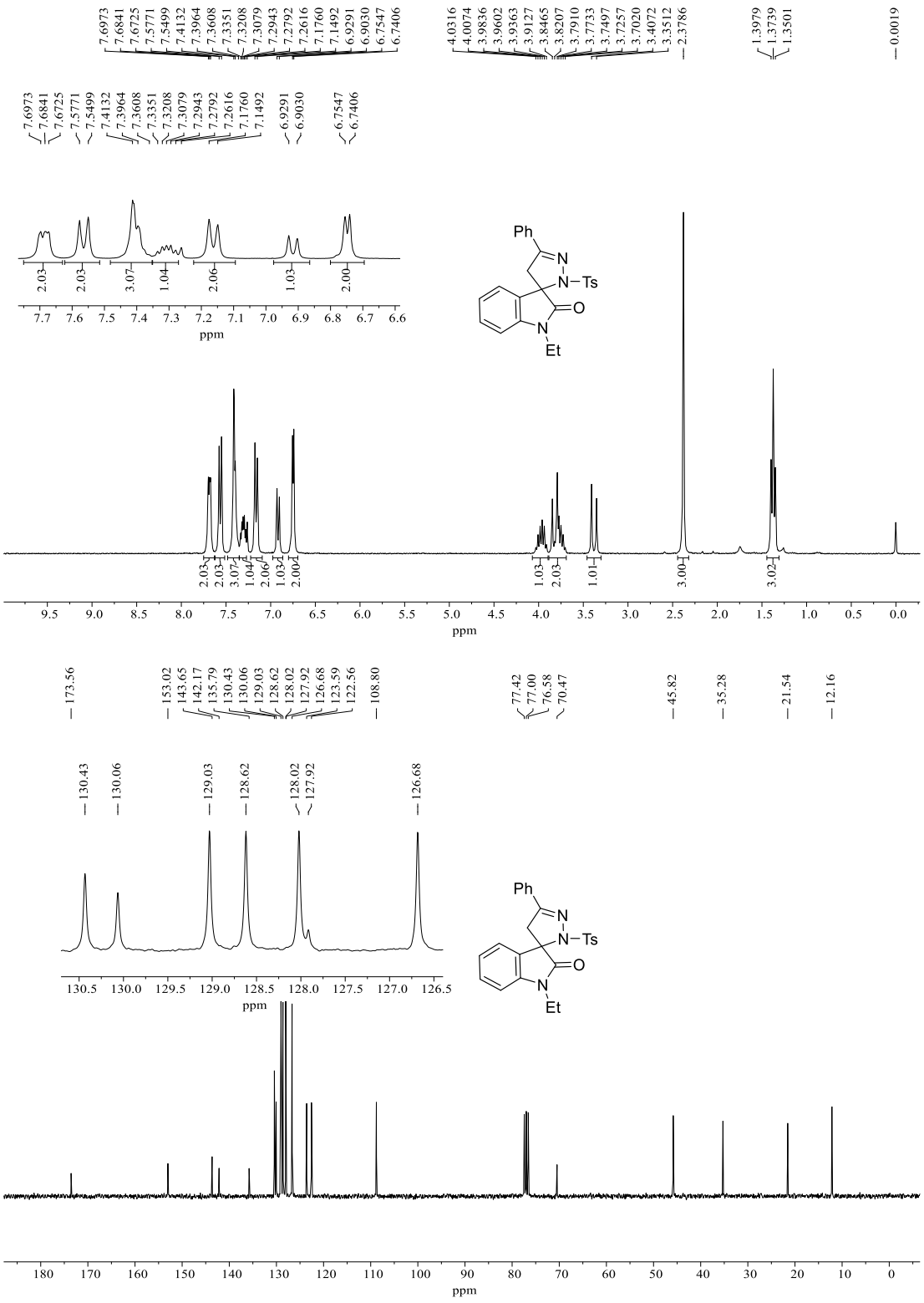


^{1}H NMR and ^{13}C NMR spectra of **3r**

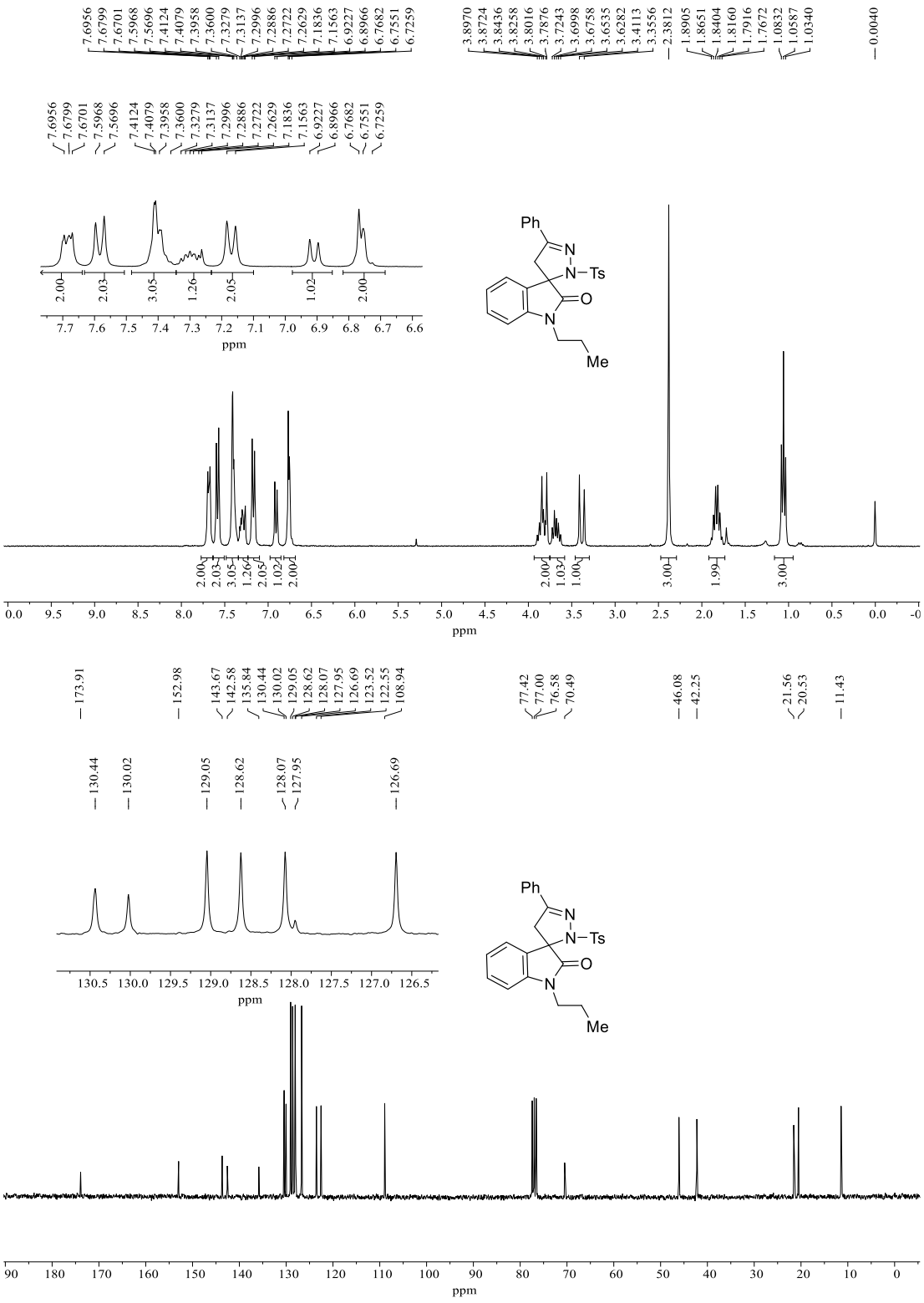




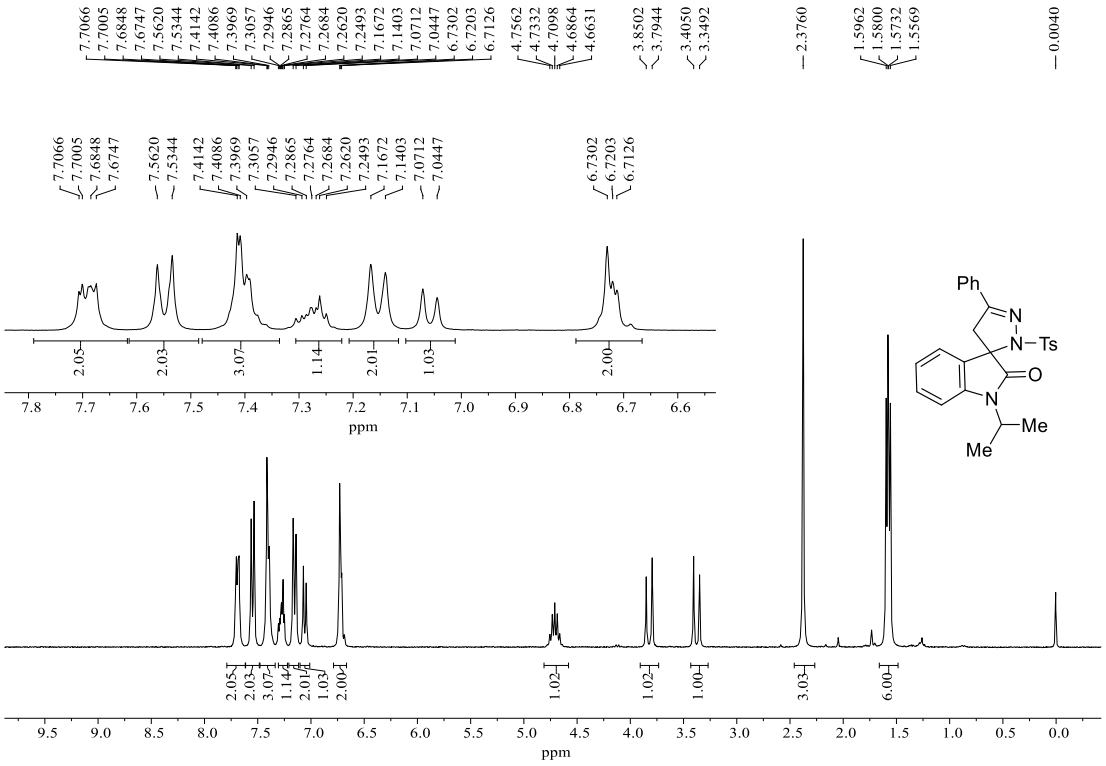
^{1}H NMR and ^{13}C NMR spectra of **3s**

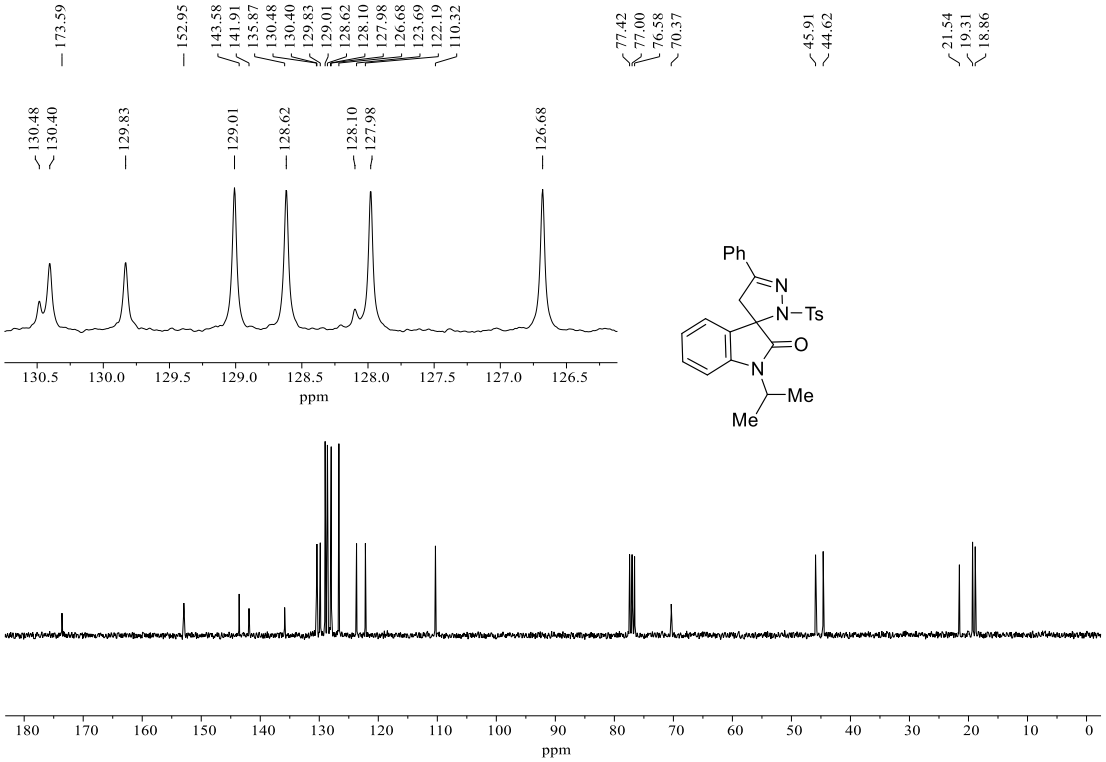


^{1}H NMR and ^{13}C NMR spectra of **3t**

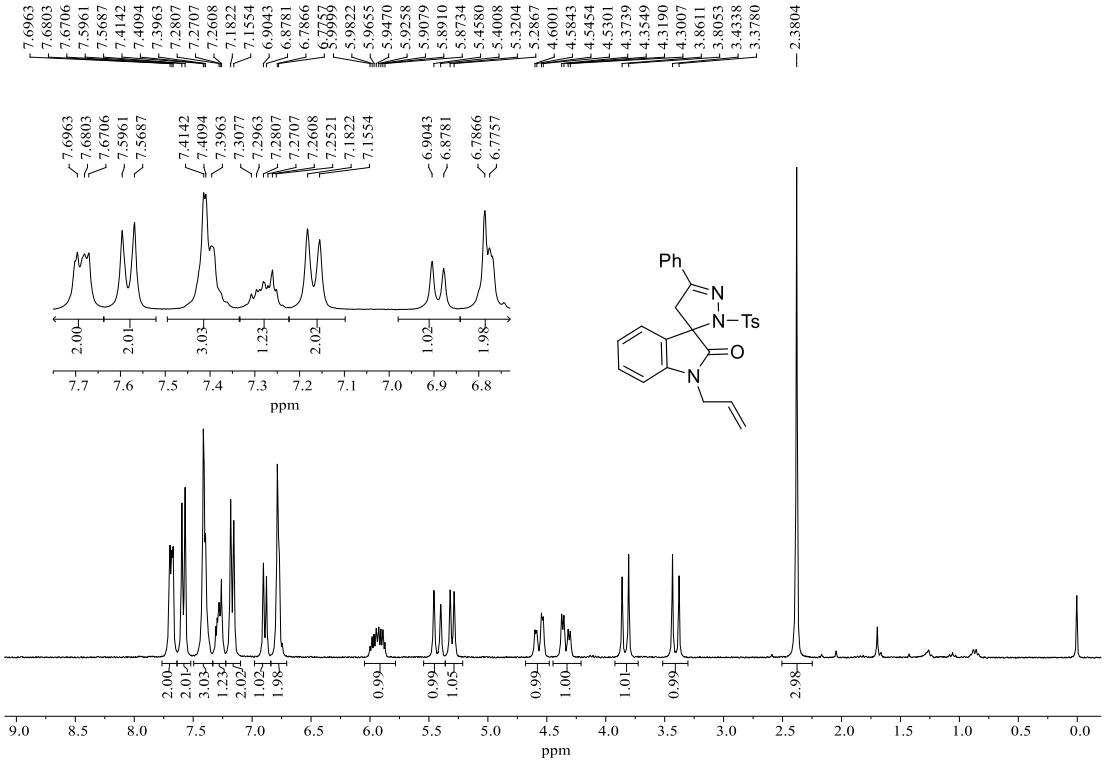


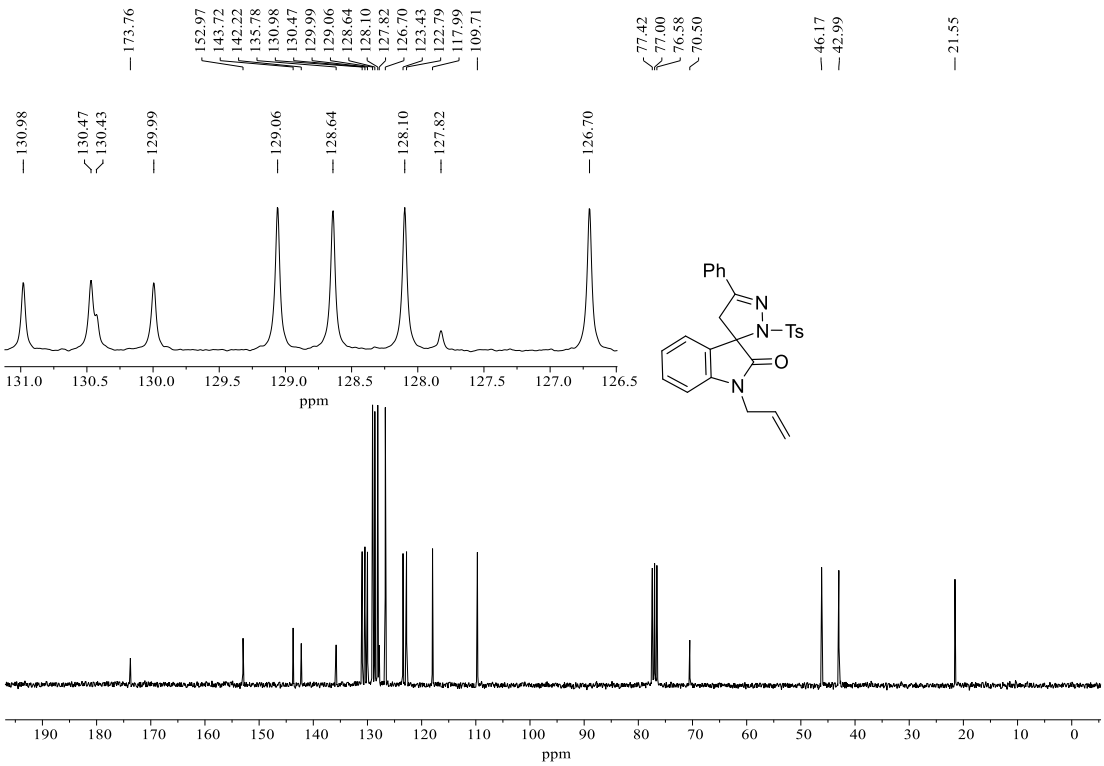
^{1}H NMR and ^{13}C NMR spectra of **3u**



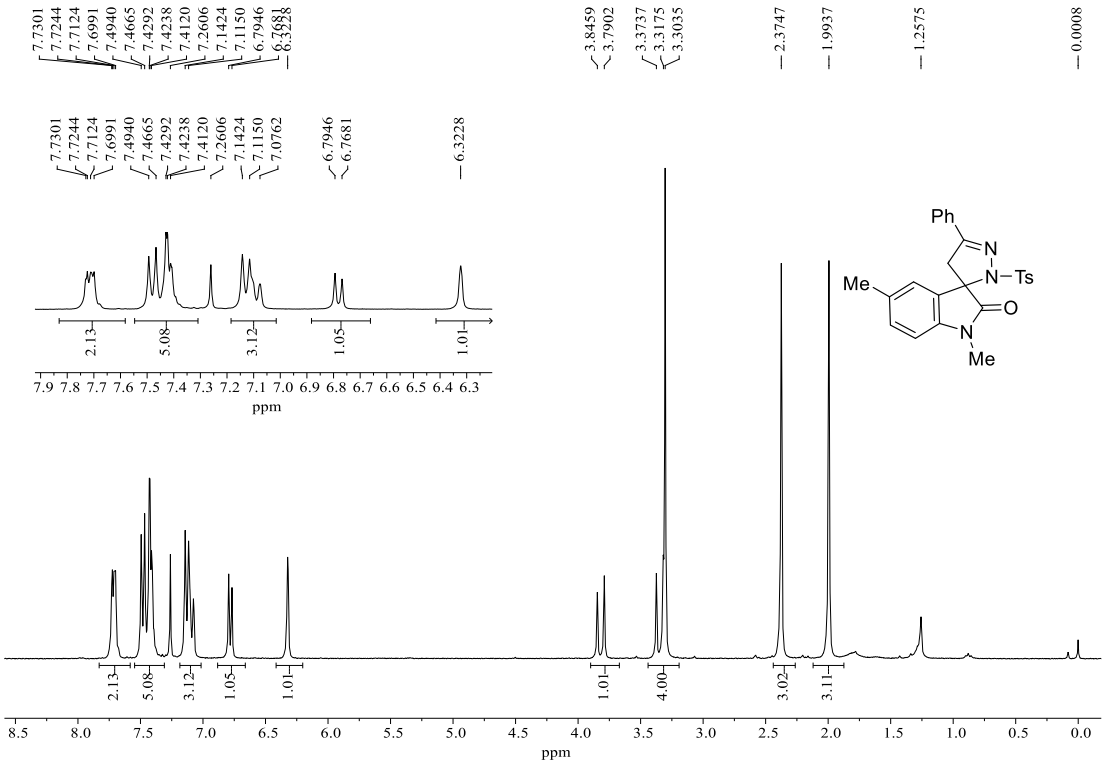


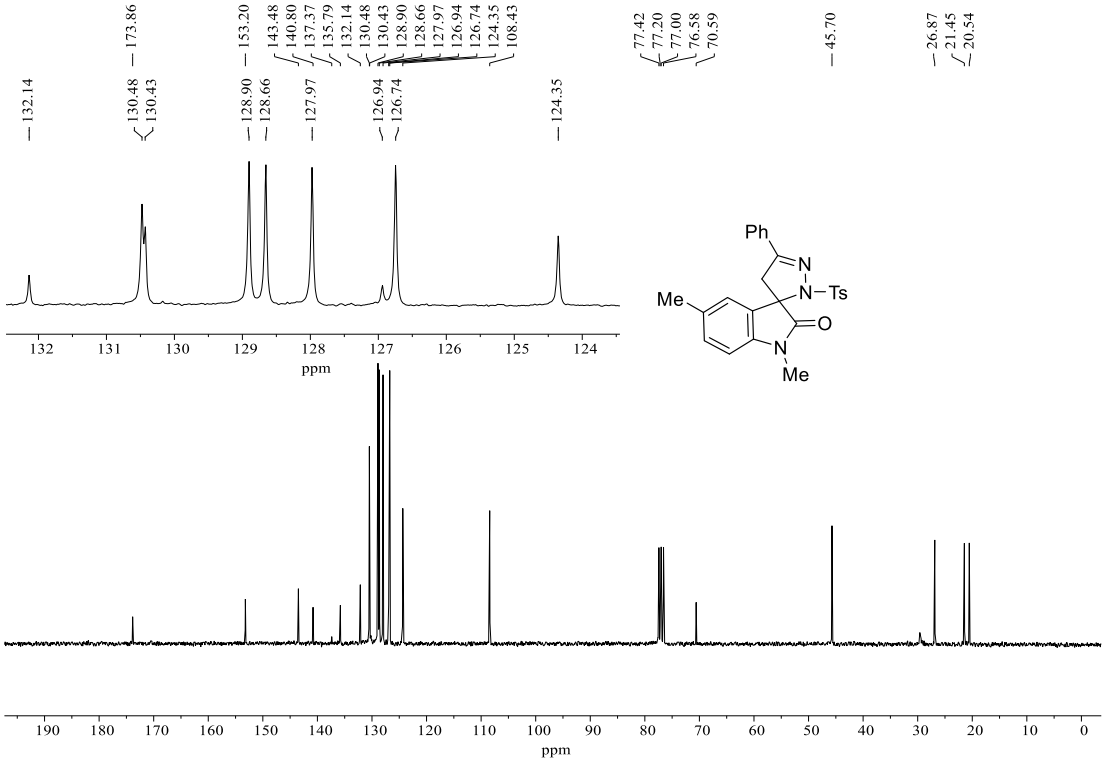
^{1}H NMR and ^{13}C NMR spectra of **3v**



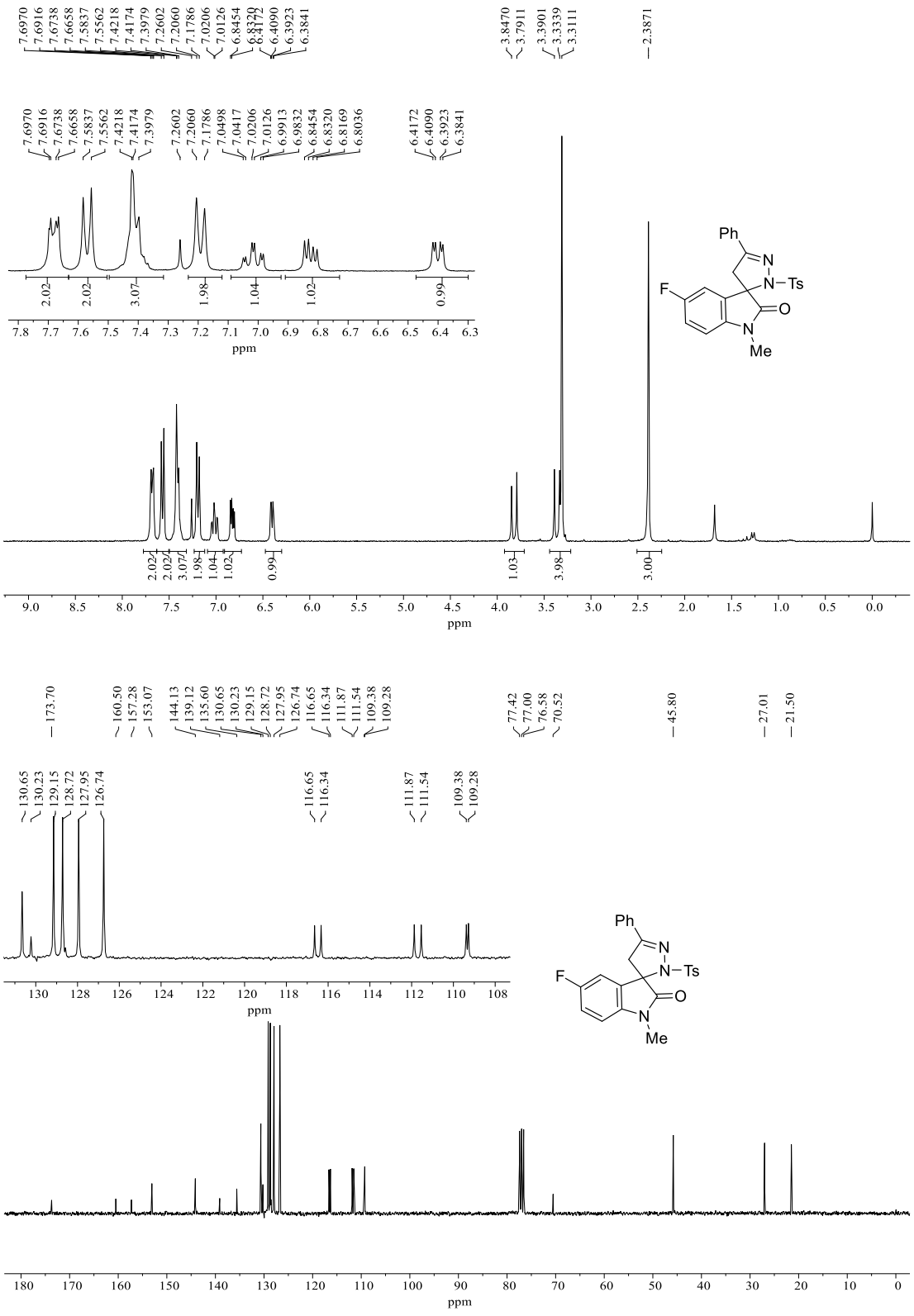


^{1}H NMR and ^{13}C NMR spectra of **3w**

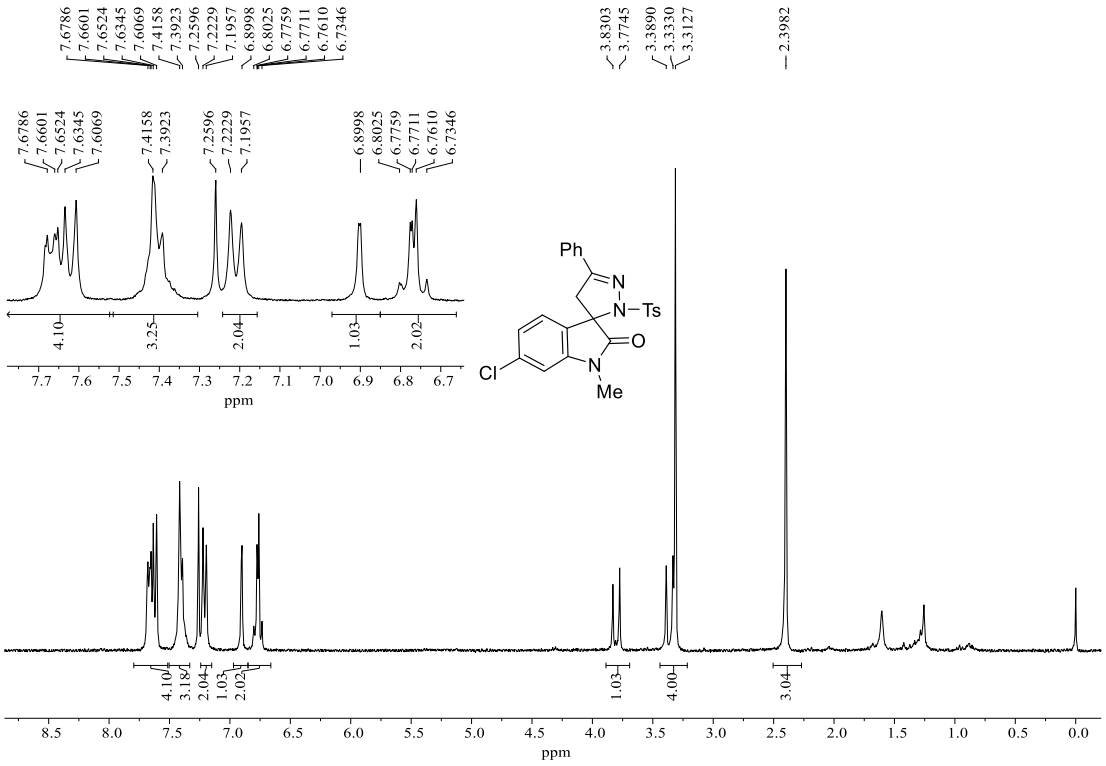


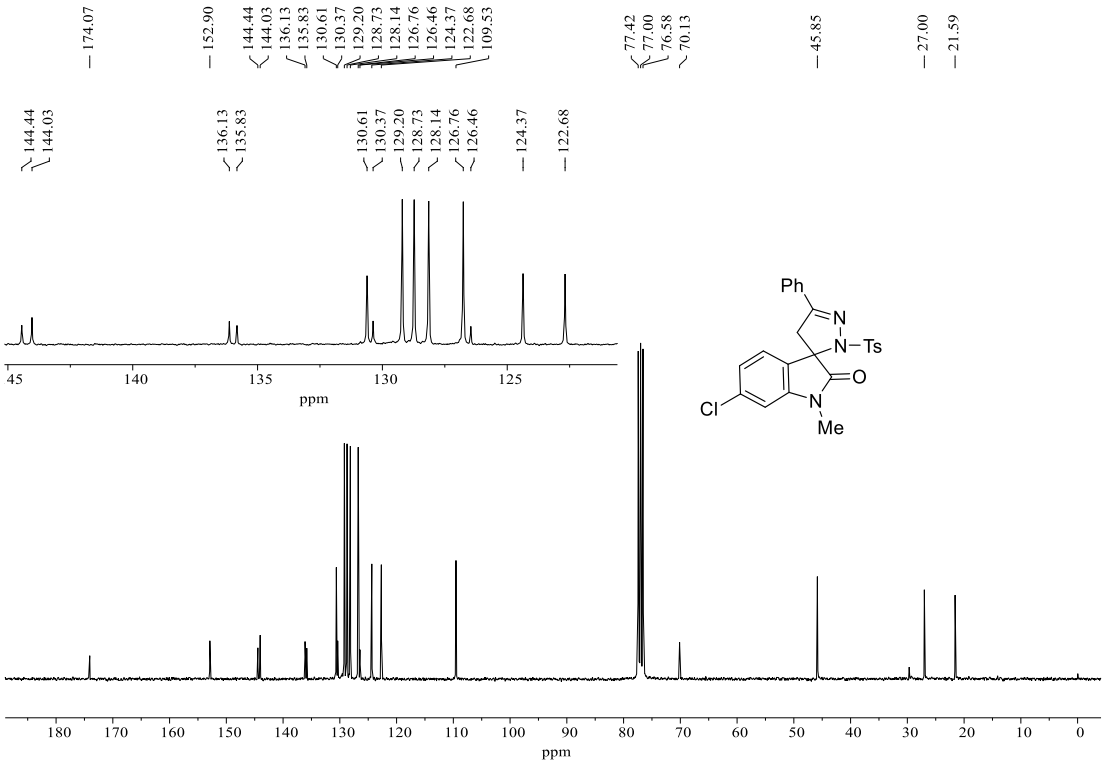


^{1}H NMR and ^{13}C NMR spectra of **3x**

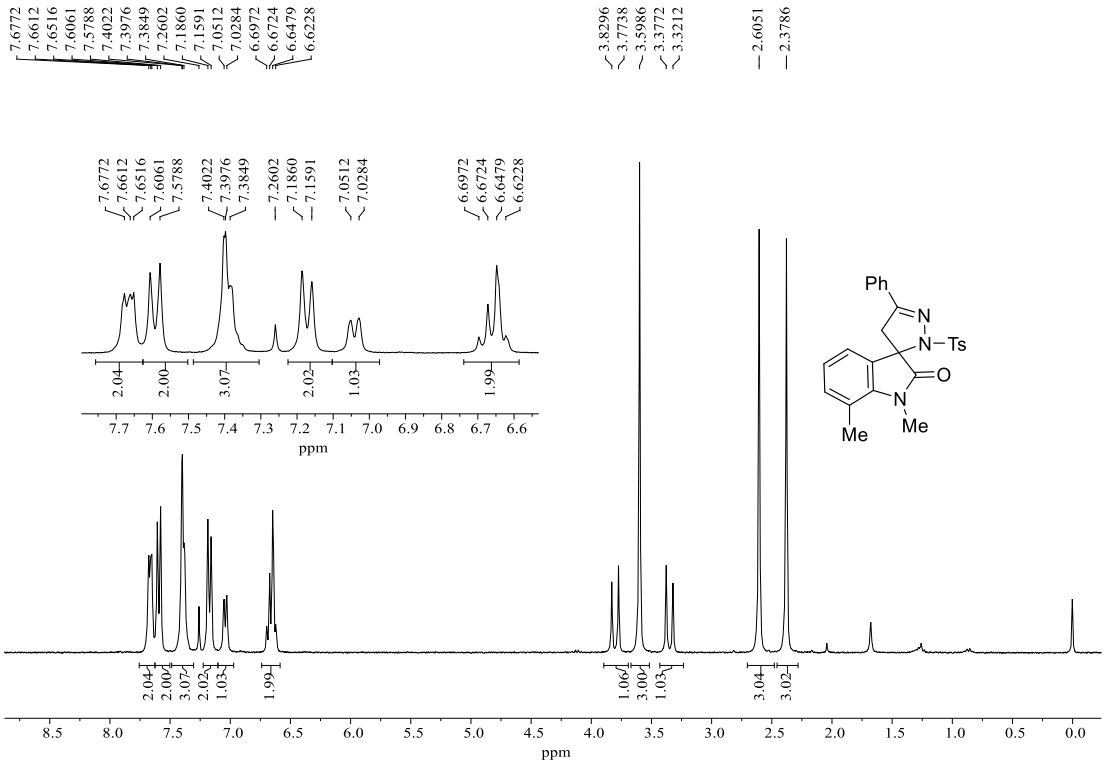


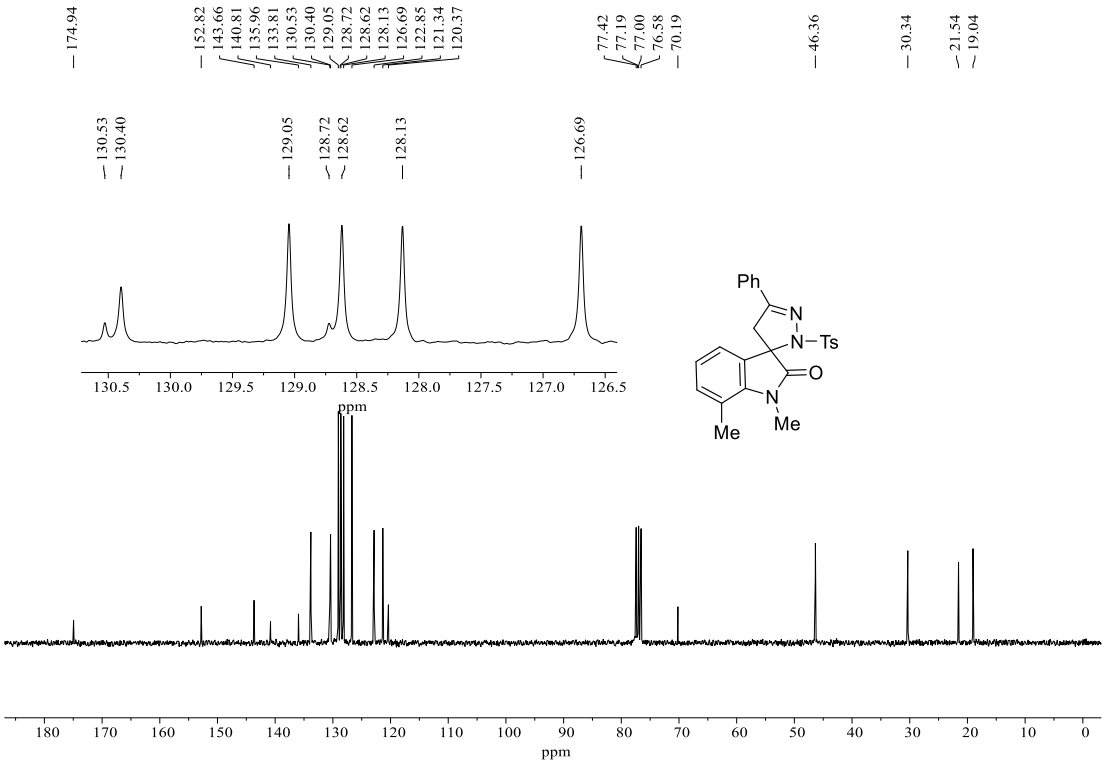
^{1}H NMR and ^{13}C NMR spectra of **3y**



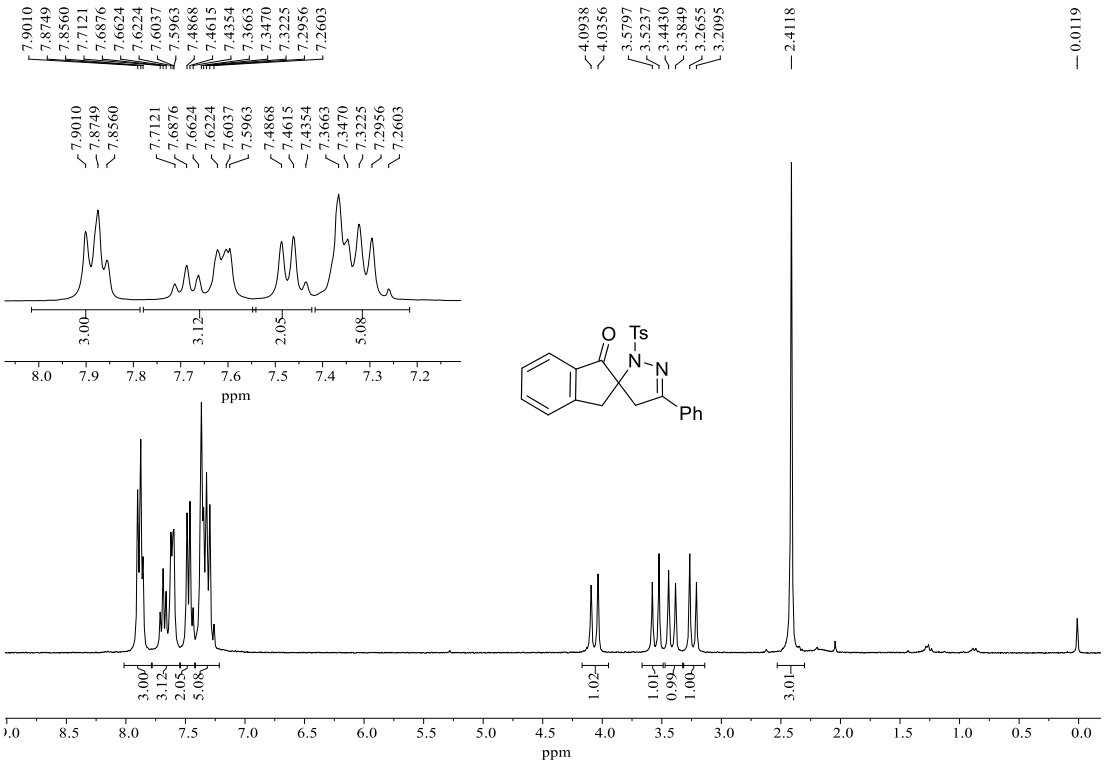


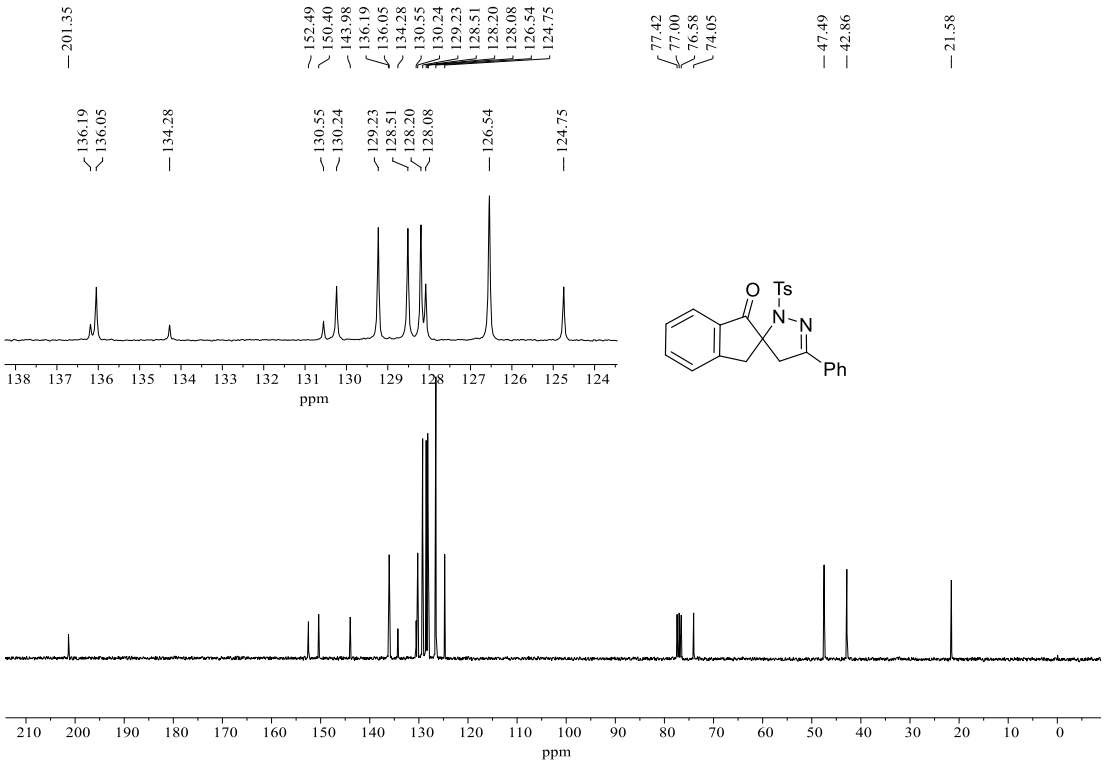
^{1}H NMR and ^{13}C NMR spectra of **3z**



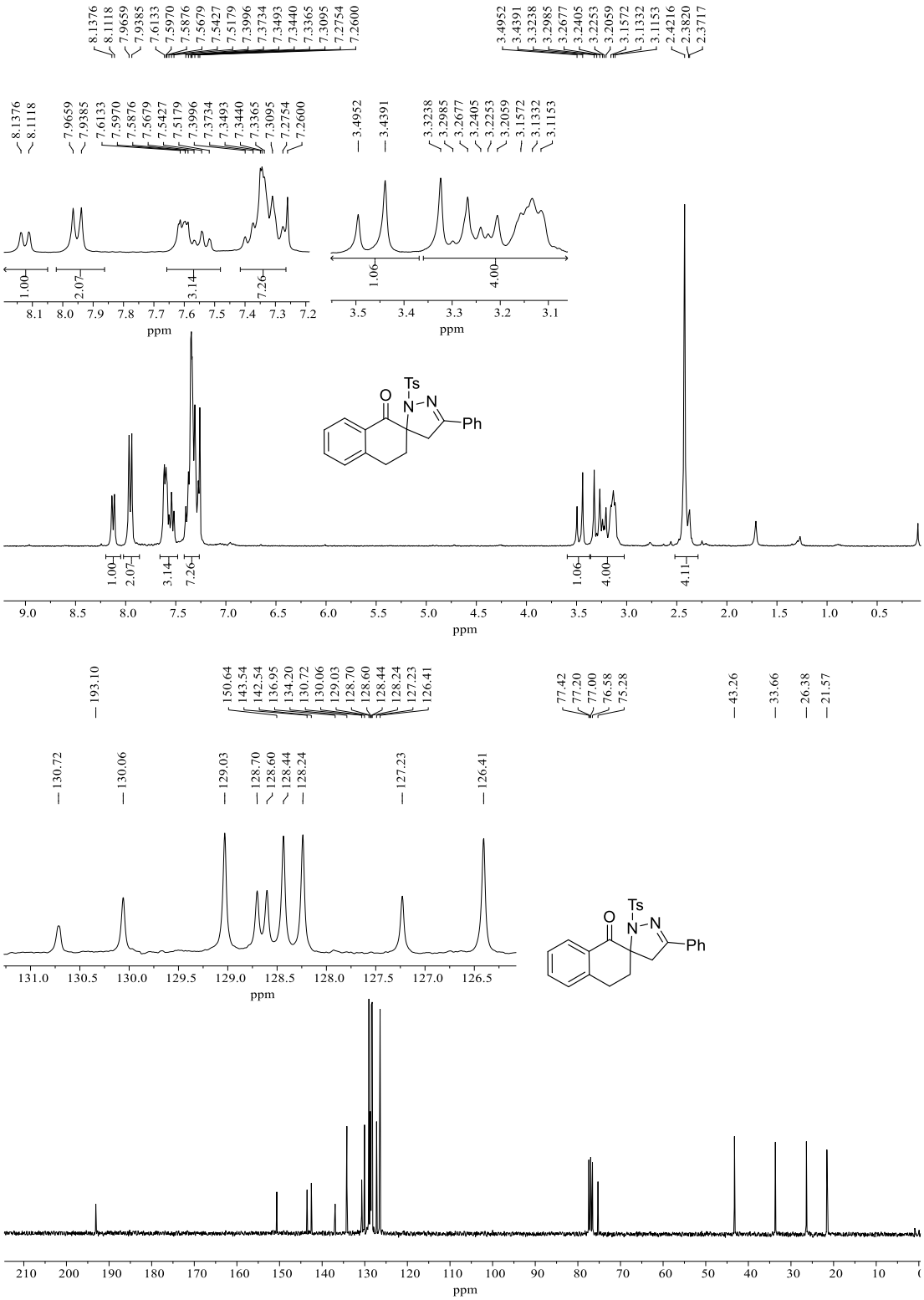


^{1}H NMR and ^{13}C NMR spectra of **5a**

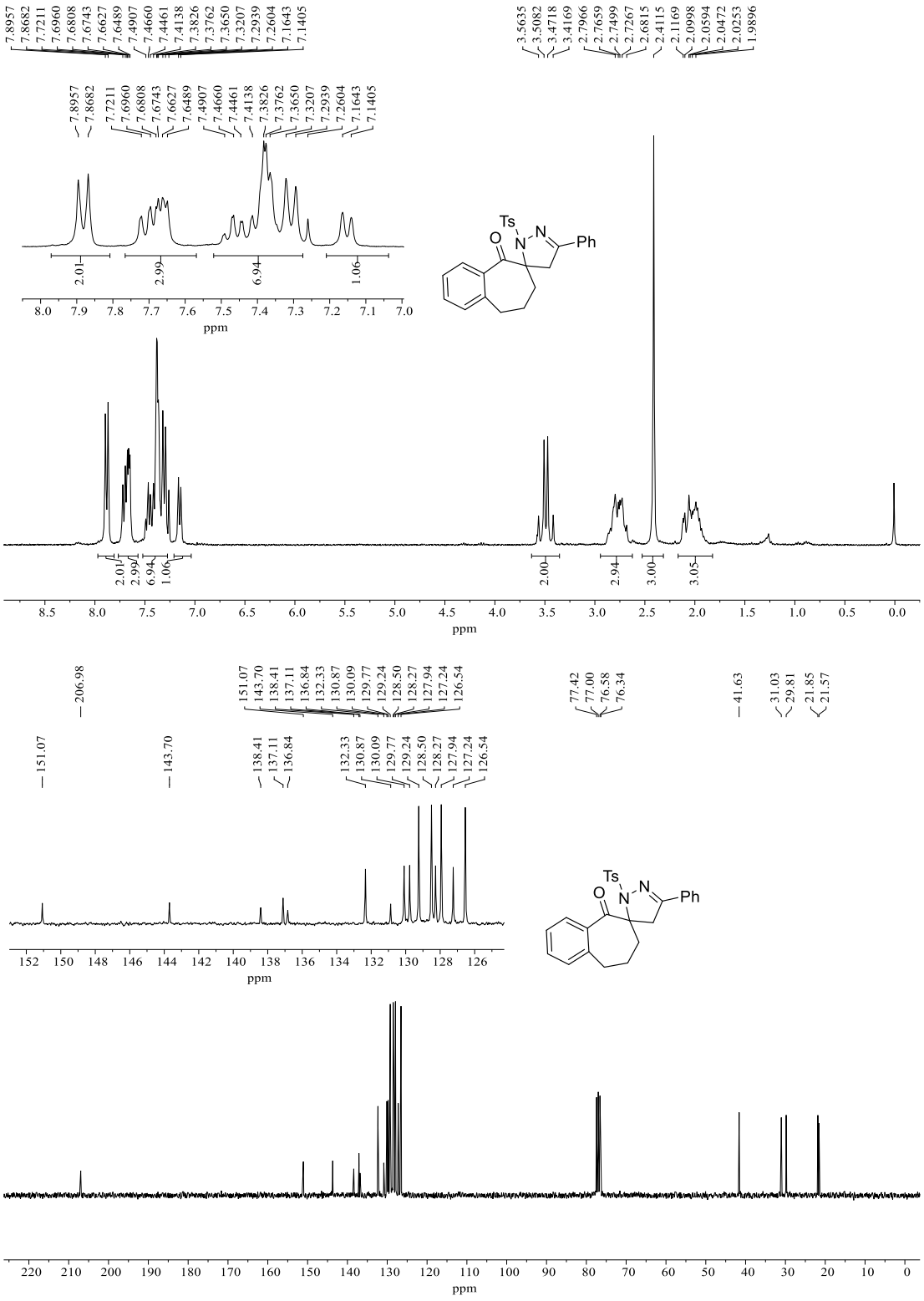




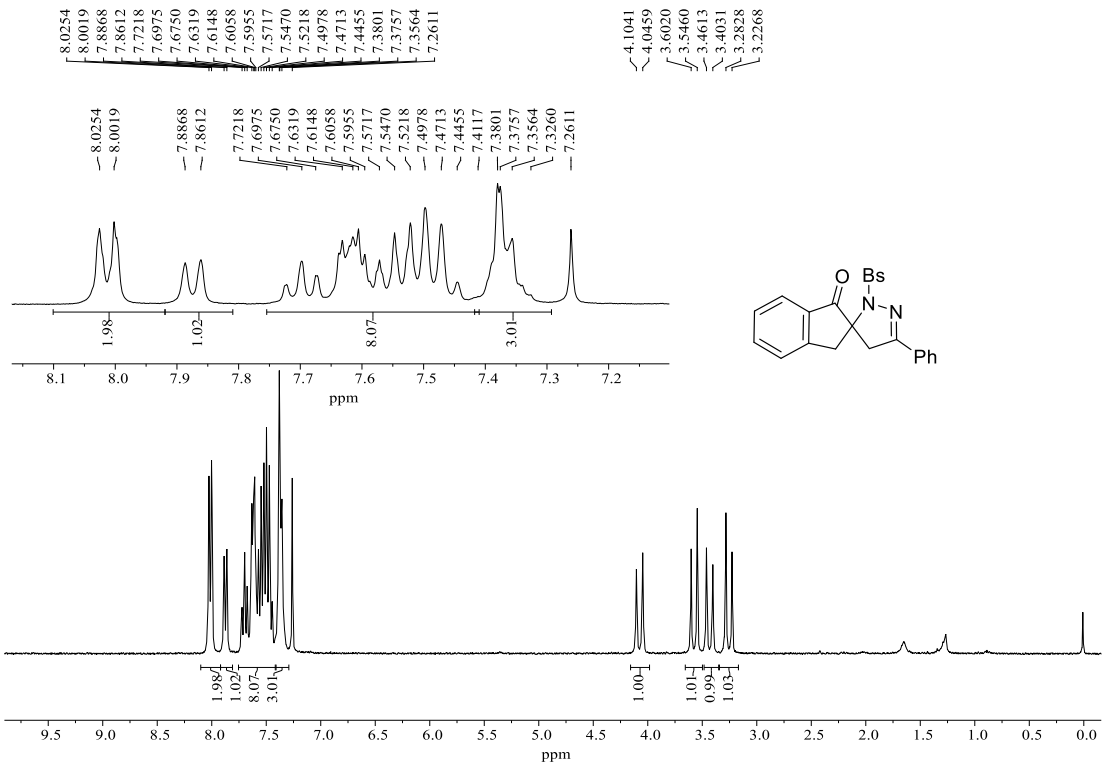
^{1}H NMR and ^{13}C NMR spectra of **5b**

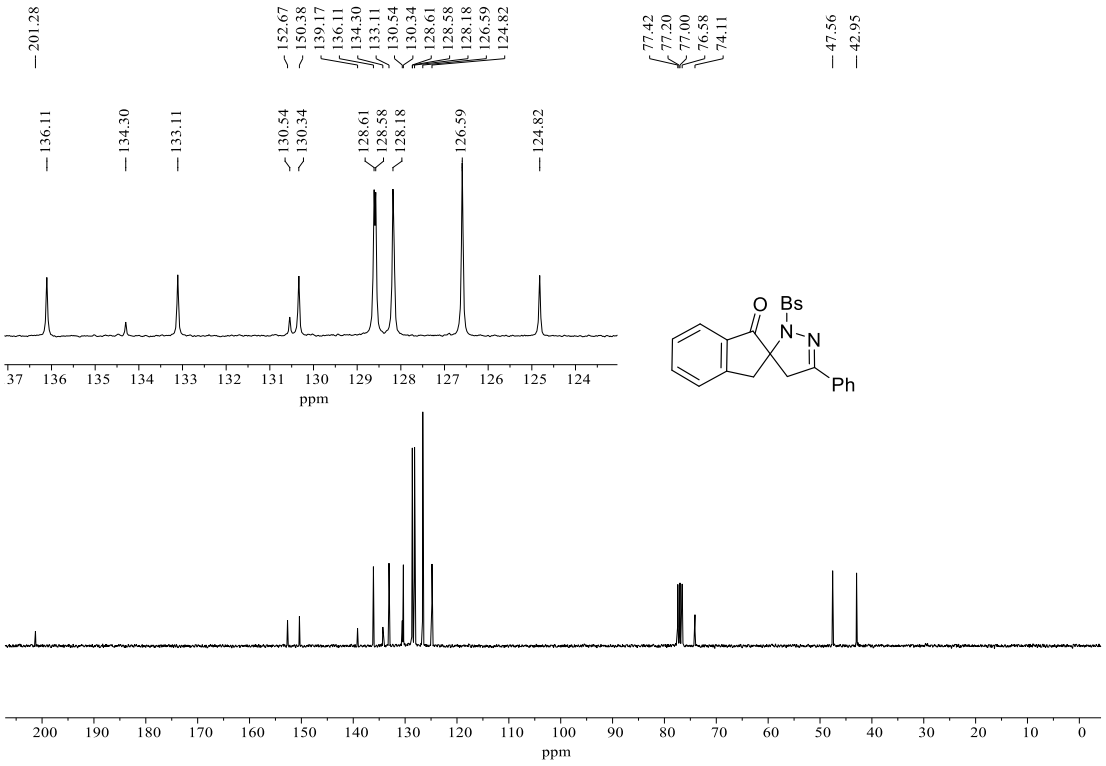


^{1}H NMR and ^{13}C NMR spectra of **5c**

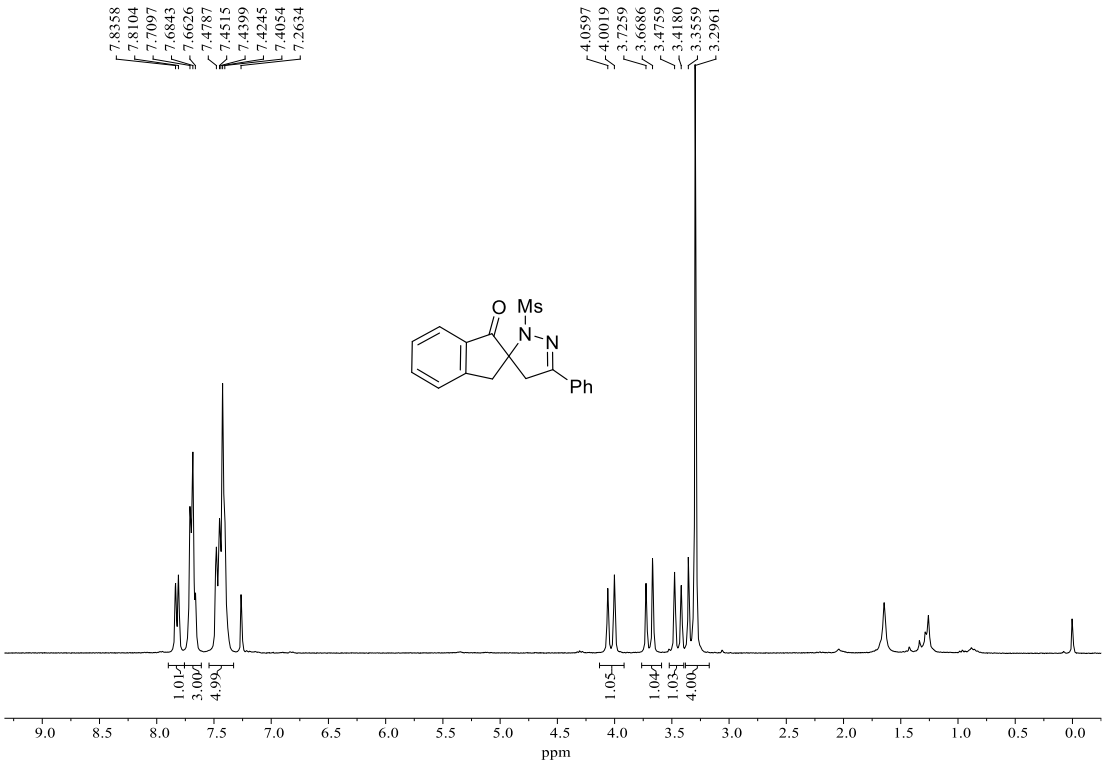


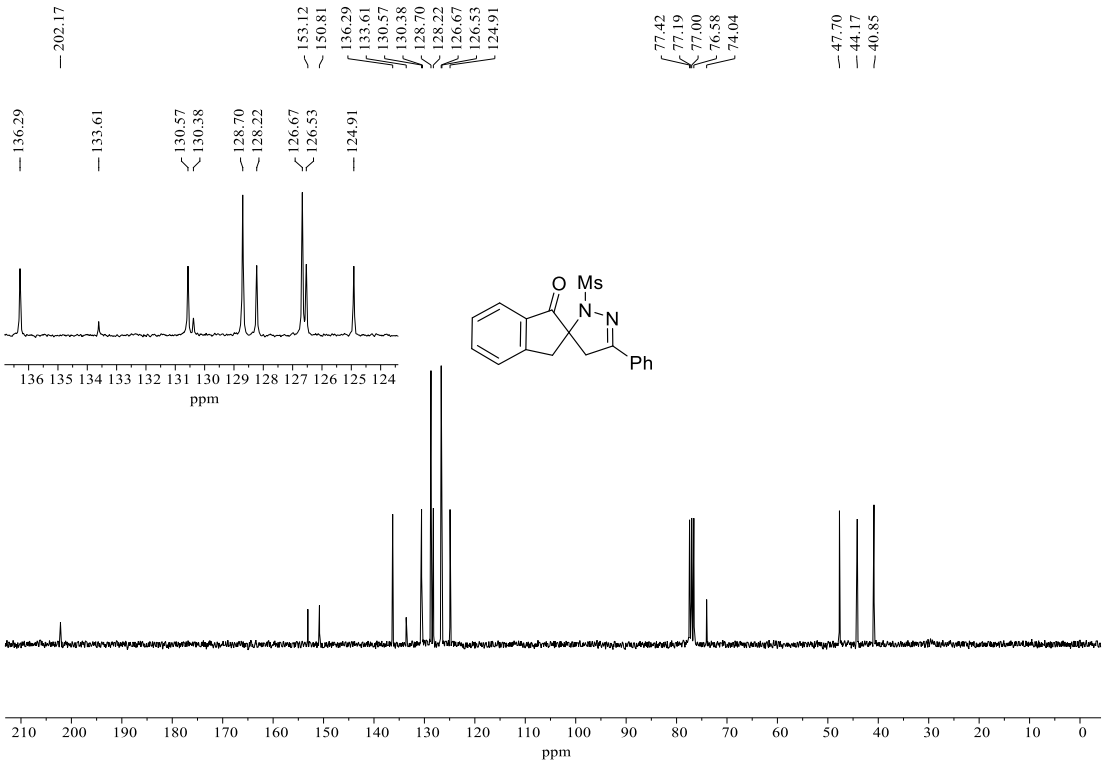
^{1}H NMR and ^{13}C NMR spectra of **5d**



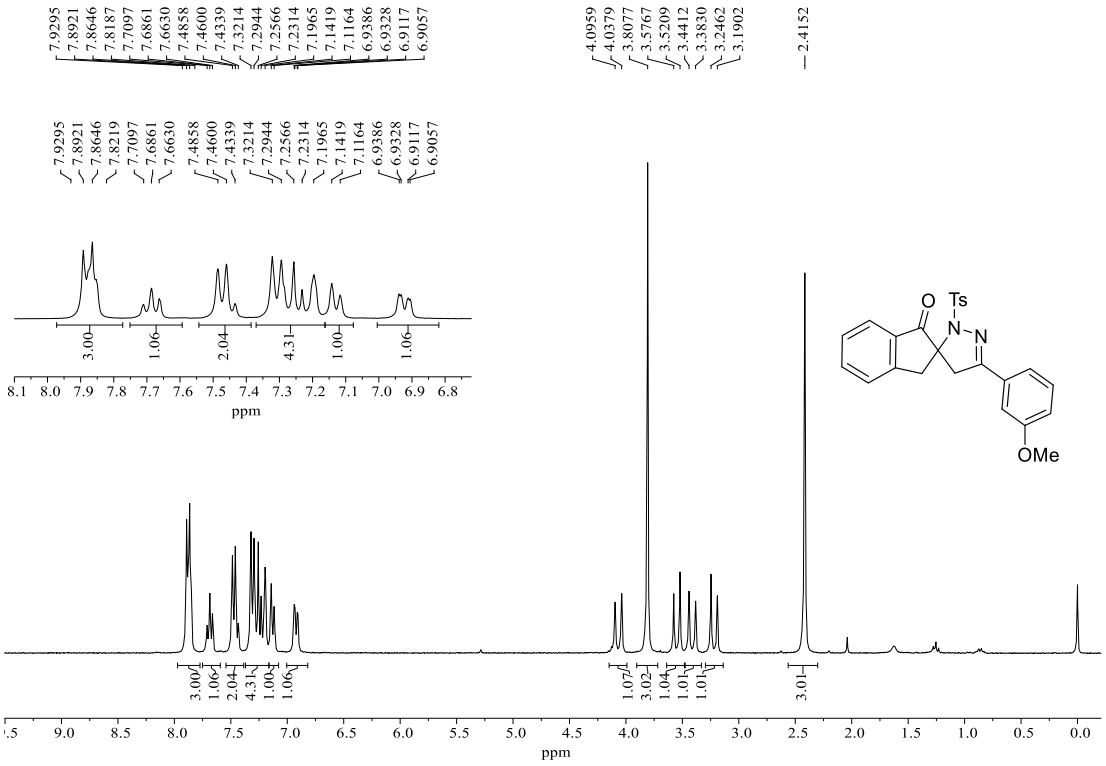


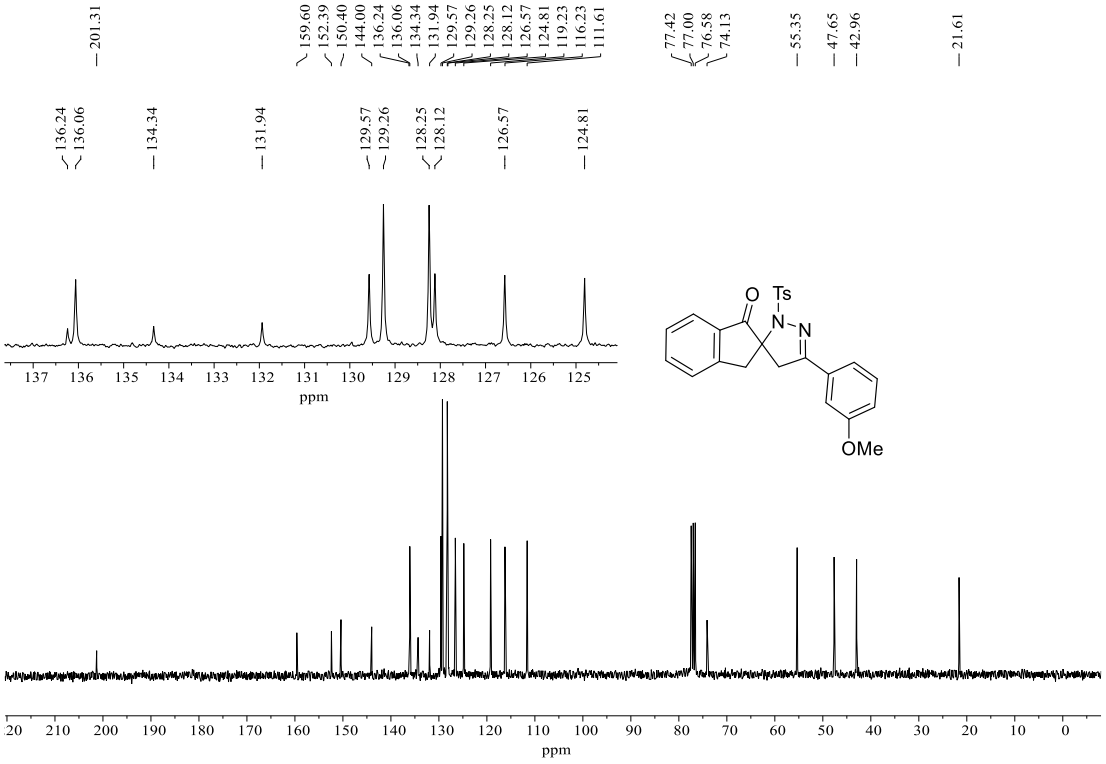
^{1}H NMR and ^{13}C NMR spectra of **5e**



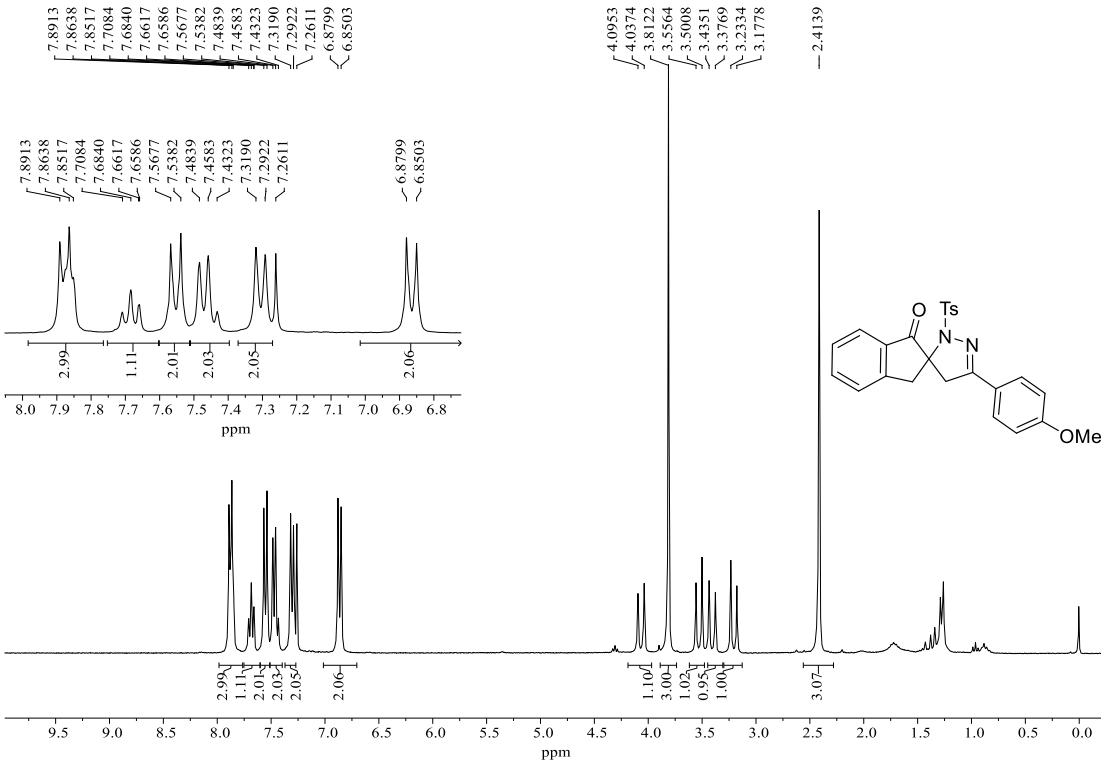


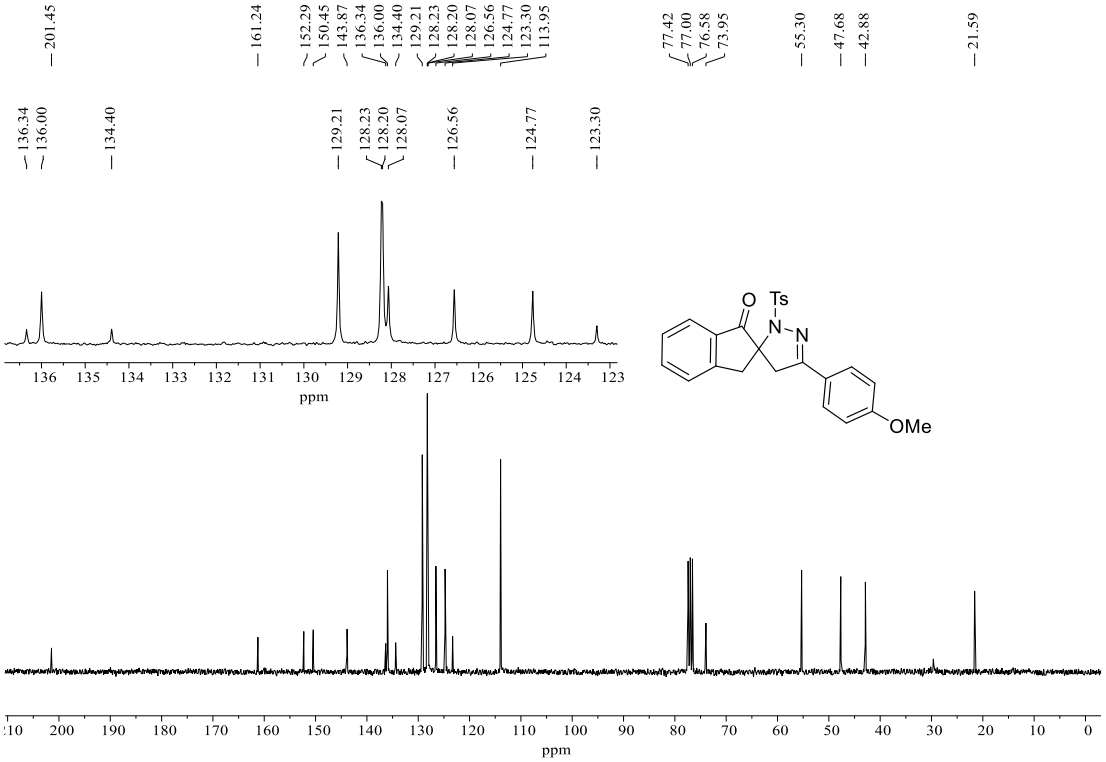
^{1}H NMR and ^{13}C NMR spectra of **5f**



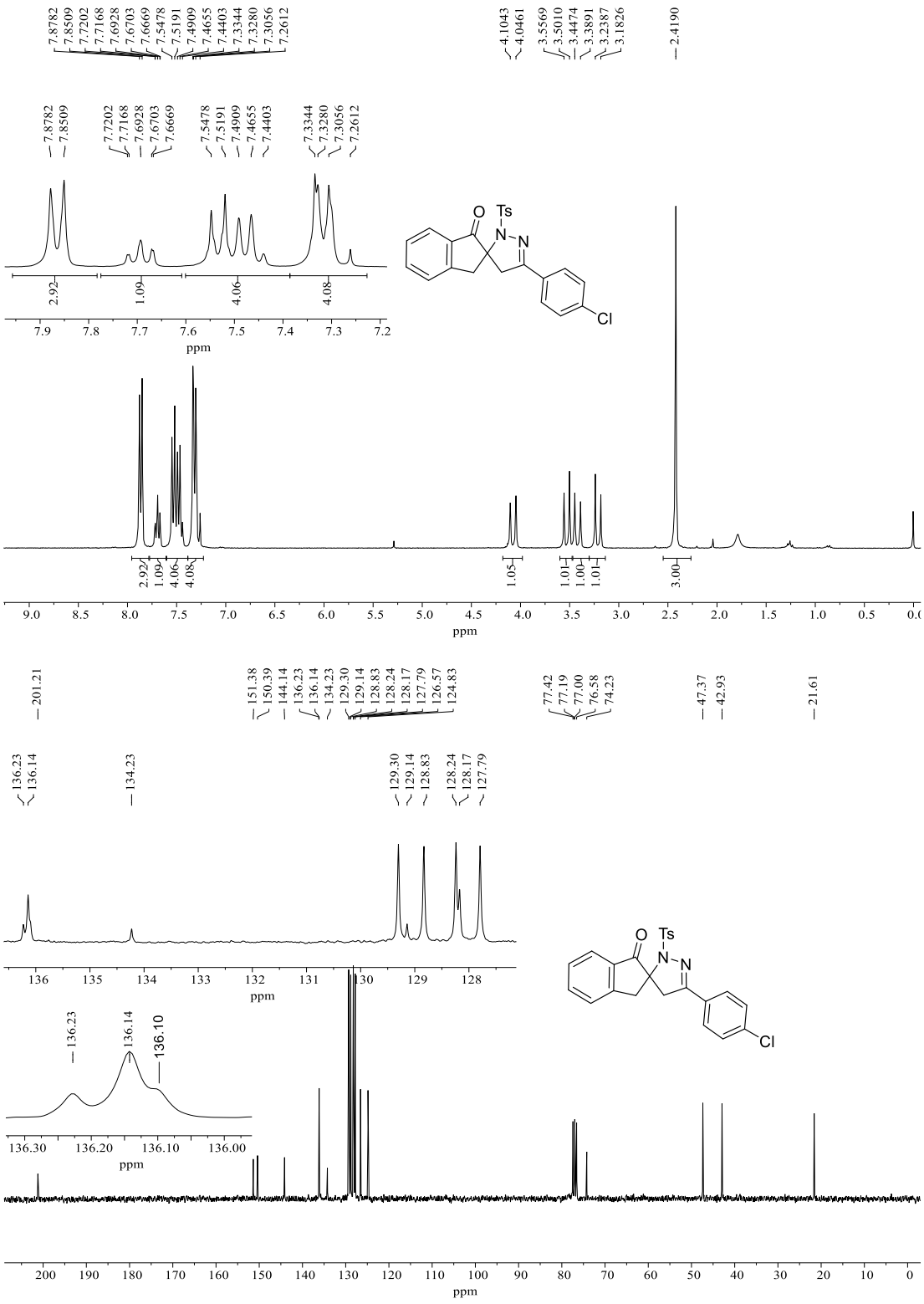


^{1}H NMR and ^{13}C NMR spectra of **5g**

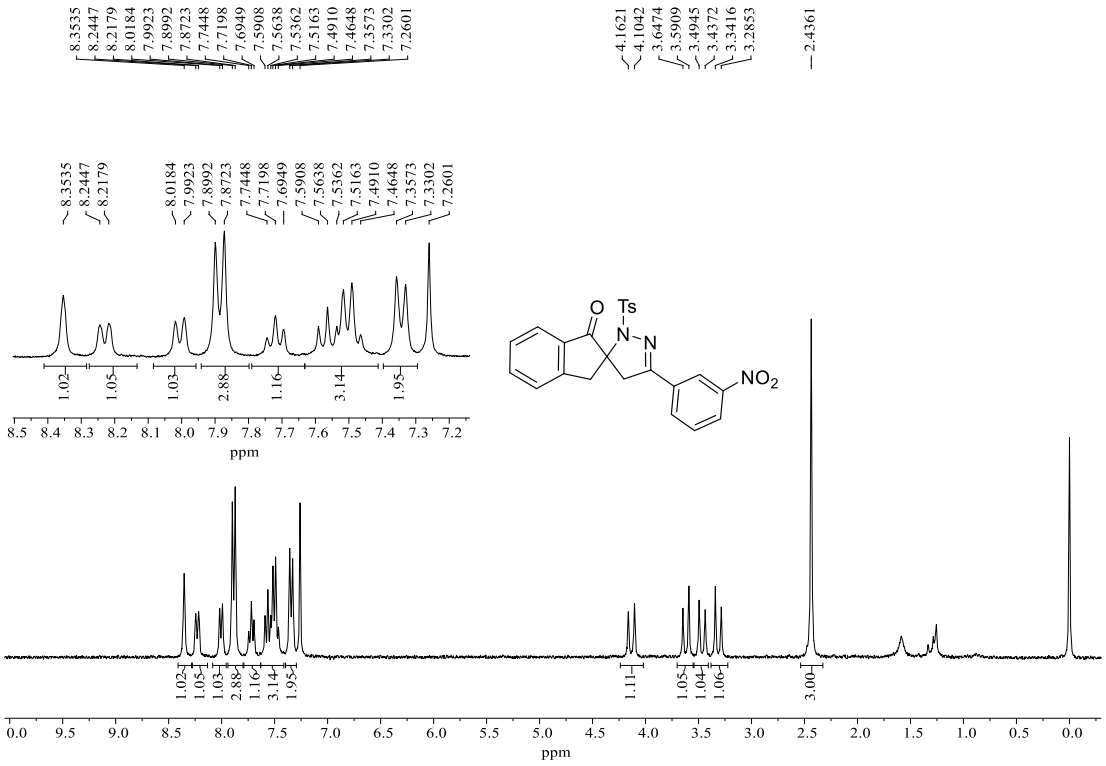


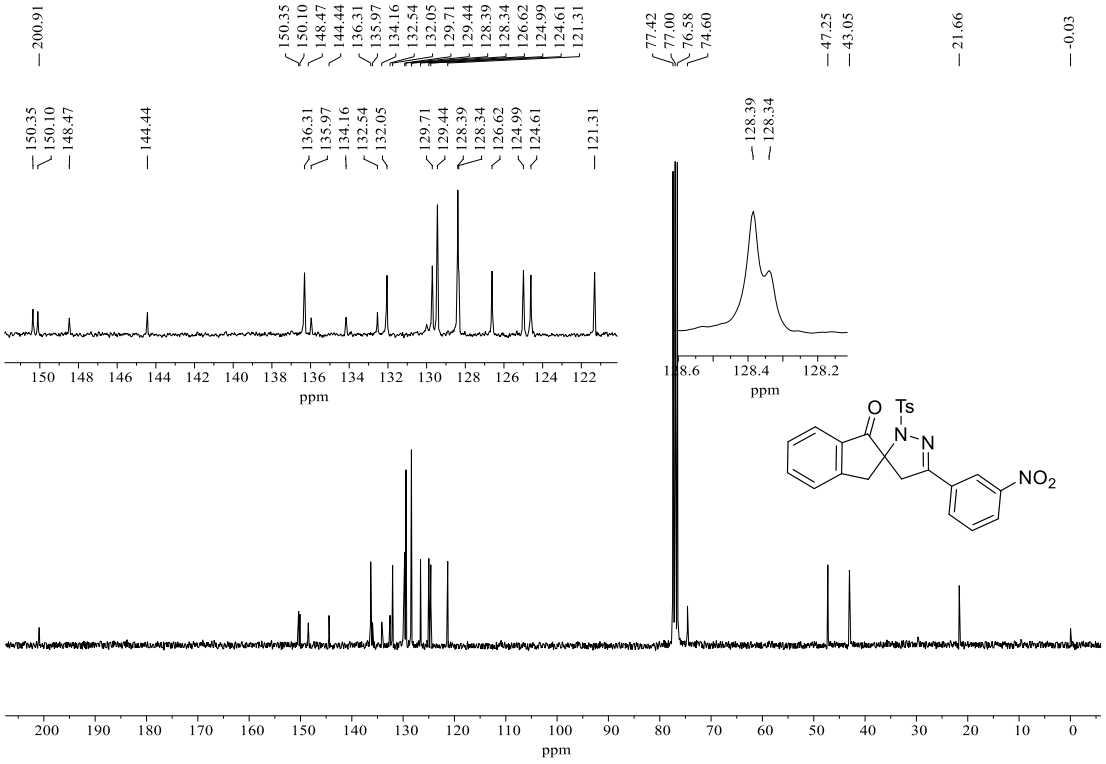


^{1}H NMR and ^{13}C NMR spectra of **5h**



^{1}H NMR and ^{13}C NMR spectra of **5i**





^{1}H NMR and ^{13}C NMR spectra of **5j**