Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Rh(III)-catalyzed [3+3] spirocyclization of 3-aryl-3-hydroxyisoindolinones with vinylene carbonate as a three-atom unit

Hai-Shan Jin* and Cai-Cai Liang

School of Chemistry and Materials Science, Jiangsu Normal University, Xuzhou 221116, Jiangsu, China

*E-mail: hsjin@jsnu.edu.cn

Table of Contents

General Methods. Solvents and reagents were used as purchased without further purification. The reaction progress was monitored by thin-layer chromatography (TLC) on silica gel GF_{254} precoated plates. Visualization of the developed plates was performed under a UV lamp. Chromatographic purification was performed with silica gel (100-200 mesh size). Melting points were uncorrected. Nuclear magnetic resonance spectra (^{1}H and ^{13}C NMR) were recorded on Bruker DPX 400 MHz and 100 MHz spectrometers in $CDCl_3$ or DMSO-d_6 with the chemical shift (δ) given in parts per million (ppm). Multiplicities were indicated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), and so forth; the coupling constant (*J*) was given in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on an Agilent Q-TOF mass spectrometer. 3-Aryl-3-hydroxyisoindolinones **1** were prepared according to literature procedure.[1]

General Procedure for the Synthesis of Compound 3. To a solution of 3-aryl-3-hydroxyisoindolinones **1** (0.1 mmol) in dichloroethane (1.5 mL) was added $[Cp^*RhCl_2]_2$ (0.0025 mmol), $AgSbF_6$ (0.01 mmol), AgOAc (0.025 mmol), and vinylene carbonate **2** (0.2 mmol). The reaction mixture was stirred at 60 ℃ on a heating block for 2 h. After completion of the reaction, the solvent was removed in vacuo and the residue was purified by silica gel column chromatography to afford the compound **3**.

*Spiro[isochromene-1,1'-isoindolin]-3'-one (**3a**).* White solid (21.2 mg, 85%), petroleum ether/ethyl acetate = 5:1, mp 199-200 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.90 (s, 1H), 7.74 (d, *J* = 6.8 Hz, 1H), 7.67-7.60 (m, 2H), 7.51 (d, *J* = 6.8 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 5.6 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.14 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.5, 147.9, 144.5, 133.7, 131.0,

130.8, 130.4, 129.8, 128.6, 127.9, 124.6, 124.5, 123.9, 123.5, 104.9, 90.5. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{11}NO_2Na$ 272.0682; found 272.0680.

*6-Methylspiro[isochromene-1,1'-isoindolin]-3'-one (**3b**).* White solid (22.9 mg, 87%), petroleum ether/ethyl acetate = 5:1, mp 174-175 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.2 Hz, 1H), 7.64-7.57 (m, 2H), 7.53 (d, *J* = 7.2 Hz, 1H), 6.98 (s, 1H), 6.94-6.91 (m, 2H), 6.72 (d, *J* = 5.6 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 6.01 (d, *J* = 5.6 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 147.1, 144.0, 139.7, 133.3, 130.6, 130.4, 129.6, 128.5, 125.2, 124.9, 124.4, 123.9, 123.8, 105.0, 90.1, 21.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}NO_2$ 264.1019; found 264.1022.

*6-Methoxyspiro[isochromene-1,1'-isoindolin]-3'-one (**3c**).* White solid (23.2 mg, 83%), petroleum ether/ethyl acetate = 5:1, mp 142-143 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.2 Hz, 1H), 7.64-7.55 (m, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 6.91 (s, 1H), 6.74 (d, *J* = 5.6 Hz, 1H), 6.71-6.64 (m, 3H), 6.00 (d, *J* = 6.0 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 160.6, 147.1, 144.4, 133.3, 131.2, 130.6, 130.4, 126.0, 123.9, 123.8, 120.3, 113.4, 109.1, 104.9, 90.2, 55.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}NO_3$ 280.0968; found 280.0969.

*6-Chlorospiro[isochromene-1,1'-isoindolin]-3'-one (**3d**).* White solid (21.3 mg, 75%), petroleum ether/ethyl acetate = 5:1, mp 201-202 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.96 (s, 1H), 7.75 (d, *J* = 6.8 Hz, 1H), 7.68-7.61 (m, 2H), 7.52 (d, *J* = 6.8 Hz, 1H), 7.38 (s, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 5.6 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.16 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.5, 147.5, 145.9, 134.4, 133.8, 132.6, 131.2, 130.8, 127.6, 127.2, 126.7, 124.0, 123.9, 123.6, 103.9, 90.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{11}ClNO_2$ 284.0473; found 284.0472.

*6-Fluorospiro[isochromene-1,1'-isoindolin]-3'-one (**3e**).* White solid (20.3 mg, 76%), petroleum ether/ethyl acetate = 5:1, mp 186-187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) 7.87 (d, *J* = 7.2 Hz, 1H), 7.66-7.58 (m, 2H), 7.53 (d, *J* = 6.8 Hz, 1H), 6.97 (s, 1H), 6.86 (d, *J* = 9.2 Hz, 1H), 6.83-6.74 (m, 3H), 6.02 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 163.5 (*J* = 247 Hz), 146.7, 145.1, 133.5, 132.0 (*J* = 9.1 Hz), 130.7, 130.5, 126.6 (*J* = 8.9 Hz), 124.0, 123.8, 114.5 (*J* = 22.2 Hz), 110.8 (*J* = 22.6 Hz), 104.3, 89.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{11}FNO_2$ 268.0768; found 268.0770.

*7-Methylspiro[isochromene-1,1'-isoindolin]-3'-one (**3h**).* White solid (20.5 mg, 78%), petroleum ether/ethyl acetate = 5:1, mp 185-186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2 Hz, 1H), 7.64-7.57 (m, 2H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.09 (s, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 5.6 Hz, 1H), 6.57 (s, 1H), 6.03 (d, *J* = 6.0 Hz, 1H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 147.0, 143.2, 137.8, 133.3, 130.6, 130.5, 130.4, 127.9, 127.0, 124.8, 124.3, 123.9, 123.8, 104.9, 90.2, 21.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}NO_2$ 264.1019; found 264.1020.

*7-Methoxyspiro[isochromene-1,1'-isoindolin]-3'-one (**3i**).* White solid (20.6 mg, 74%), petroleum ether/ethyl acetate = 5:1, mp 150-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.2 Hz, 1H), 7.64-7.56 (m, 2H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.12-7.06 (m, 1H), 6.88 (s, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 6.0 Hz, 1H), 6.41 (d, *J* = 6.0 Hz, 1H), 6.36 (d, *J* = 8.0 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 153.3, 146.9, 143.2, 133.3, 130.7, 130.5, 128.8, 128.3, 125.7, 123.9, 119.3, 116.4, 111.0, 99.5, 90.0, 56.0. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{13}NO_3Na$ 302.0788; found 302.0786.

*7-Chlorospiro[isochromene-1,1'-isoindolin]-3'-one (**3j**).* White solid (18.7 mg, 66%),

petroleum ether/ethyl acetate = 5:1, mp 203-204 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.2 Hz, 1H), 7.67-7.60 (m, 2H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 7.01 (s, 1H), 6.75 (s, 2H), 6.04 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 146.3, 144.3, 133.6, 132.9, 130.8, 130.5, 129.9, 129.5, 128.3, 125.6, 124.5, 124.1, 123.8, 104.2, 89.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{11}ClNO_2$ 284.0473; found 284.0474.

*7-Fluorospiro[isochromene-1,1'-isoindolin]-3'-one (**3k**).* White solid (13.6 mg, 51%), petroleum ether/ethyl acetate = 5:1, mp 177-178 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.2 Hz, 1H), 7.67-7.60 (m, 2H), 7.54 (d, *J* = 7.2 Hz, 1H), 7.17-7.14 (m, 1H), 7.04 (t, *J* = 8.4 Hz, 1H), 6.83 (s, 1H), 6.72 (d, *J* = 5.6 Hz, 1H), 6.49 (d, *J* = 8.8 Hz, 1H), 6.05 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 162.0 (*J* = 246.3 Hz), 146.3, 143.3, 133.5, 130.8, 130.6, 129.9 (*J* = 6.8 Hz), 126.1 (*J* = 8.0 Hz), 124.1, 123.8, 116.8 (*J* = 21.9 Hz), 111.6 (*J* = 23.8 Hz), 104.3, 90.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{11}FNO_2$ 268.0768; found 268.0769.

*8-Methoxyspiro[isochromene-1,1'-isoindolin]-3'-one (**3l**).* White solid (20.4 mg, 73%), petroleum ether/ethyl acetate = 5:1, mp 203-204 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.2 Hz, 1H), 7.57-7.49 (m, 2H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 6.0 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.62 (s, 1H), 5.93 (d, *J* = 6.0 Hz, 1H), 3.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 155.8, 150.0, 143.7, 132.6, 131.7, 130.6, 130.1, 129.3, 123.4, 122.5, 117.3, 114.7, 110.7, 103.4, 88.1, 55.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}NO_3$ 280.0968; found 280.0968.

*5,7-Dimethylspiro[isochromene-1,1'-isoindolin]-3'-one (**3m**).* White solid (5.8 mg, 21%),

petroleum ether/ethyl acetate = 5:1, mp 142-143 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.2 Hz, 1H), 7.65-7.56 (m, 2H), 7.55 (d, *J* = 5.6 Hz, 1H), 7.00 (s, 1H), 6.74 (s, 1H), 6.73 (d, *J* = 6.0 Hz, 2H), 6.40 (s, 1H), 6.16 (d, *J* = 5.6 Hz, 1H), 2.36 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 147.0, 143.0, 137.3, 134.4, 133.3, 131.9, 130.7, 130.4, 128.0, 125.4, 123.9, 123.7, 122.5, 102.2, 90.3, 21.3, 18.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{16}NO_2$ 278.1176; found 278.1175.

*5'-Methoxyspiro[isochromene-1,1'-isoindolin]-3'-one (**3n**).* White solid (22.3 mg, 80%), petroleum ether/ethyl acetate = 5:1, mp 186-187 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.17-7.12 (m, 2H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.01 (s, 1H), 6.83 (s, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 5.6 Hz, 1H), 6.05 (d, *J* = 5.6 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 164.1, 149.2, 143.9, 129.6, 128.0, 127.7, 125.3, 124.5, 124.2, 123.0, 117.0, 108.5, 104.9, 89.6, 55.9. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{17}H_{13}NO_3Na$ 302.0788; found 302.0788.

*5'-Chlorospiro[isochromene-1,1'-isoindolin]-3'-one (**3o**).* White solid (21.8 mg, 77%), petroleum ether/ethyl acetate = 5:1, mp 205-206 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.18-7.12 (m, 2H), 7.02 (s, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 5.6 Hz, 1H), 6.06 (d, *J* = 5.6 Hz, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 145.0, 143.8, 136.9, 133.4, 132.4, 129.9, 129.6, 127.9, 127.4, 125.2, 124.4, 124.3, 124.2, 105.1, 89.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{11}ClNO_2$ 284.0473; found 284.0479.

*5'-Bromospiro[isochromene-1,1'-isoindolin]-3'-one (**3p**).* White solid (24.9 mg, 76%), petroleum ether/ethyl acetate = 5:1, mp 200-201 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H),

7.74 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 7.18-7.12 (m, 2H), 6.88 (s, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 5.6 Hz, 1H), 6.06 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 145.5, 143.8, 136.3, 132.6, 129.9, 129.6, 127.9, 127.3, 127.2, 125.5, 124.8, 124.5, 124.3, 105.1, 89.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{11}BrNO_2$ 327.9968; found 327.9970.

*5',6'-Dichlorospiro[isochromene-1,1'-isoindolin]-3'-one (**3q**).* White solid (20.9 mg, 66%), petroleum ether/ethyl acetate = 5:1, mp 210-211 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.64 (s, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.19-7.12 (m, 2H), 7.08 (s, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 5.6 Hz, 1H), 6.07 (d, *J* = 5.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 146.1, 143.6, 137.8, 135.5, 130.2, 130.1, 129.6, 128.1, 126.9, 126.1, 125.9, 124.6, 124.2, 105.2, 89.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{11}Cl_2NO_2$ 318.0083; found 318.0091.

*4',5',6',7'-Tetrahydrospiro[isochromene-1,1'-isoindol]-3'(2'H)-one (**3r**).* White solid (15.7 mg, 62%), petroleum ether/ethyl acetate = 5:1, mp 127-128 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 5.6 Hz, 1H), 6.46 (s, 1H), 5.90 (d, *J* = 6.0 Hz, 1H), 2.36-2.26 (m, 3H), 2.11-2.06 (m, 1H), 1.81-1.70 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 156.0, 144.1, 132.9, 129.9, 129.5, 127.8, 126.7, 124.3, 123.8, 104.1, 90.6, 21.9, 21.8, 21.7, 19.9. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{16}H_{15}NO_2Na$ 276.0995; found 276.0994.

*5'-Chloro-6-methylspiro[isochromene-1,1'-isoindolin]-3'-one (**3t**).* White solid (20.2 mg, 68%), petroleum ether/ethyl acetate = 5:1, mp 189-190 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 6.98 (s, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 6.0 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.01 (d, *J* = 6.0 Hz, 1H), 2.33

(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 145.2, 143.8, 139.9, 136.8, 133.4, 132.4, 129.5, 128.6, 125.1, 125.0, 124.6, 124.2, 124.1, 105.1, 89.9, 21.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{13}ClNO_2$ 298.0629; found 298.0632.

*5'-Bromo-6-methoxyspiro[isochromene-1,1'-isoindolin]-3'-one (**3u**).* White solid (24 mg, 67%), petroleum ether/ethyl acetate = 5:1, mp 188-189 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.25 (s, 1H), 6.72-6.63 (m, 4H), 5.99 (d, *J* = 5.6 Hz, 1H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 160.7, 145.8, 144.3, 136.2, 132.6, 131.1, 127.1, 125.8, 125.4, 124.6, 119.6, 113.5, 109.2, 105.0, 90.1, 55.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{13}BrNO_3$ 358.0073; found 358.0073.

*5'-Bromo-7-methylspiro[isochromene-1,1'-isoindolin]-3'-one (**3v**).* White solid (20.8 mg, 61%), petroleum ether/ethyl acetate = 5:1, mp 152-153 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.10 (s, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 5.6 Hz, 1H), 6.56 (s, 1H), 6.03 (d, *J* = 5.6 Hz, 1H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 145.7, 143.0, 138.0, 136.3, 132.6, 130.6, 127.3, 127.1, 126.9, 125.5, 124.7, 124.6, 124.4, 105.0, 90.0, 21.4. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{13}BrNO_2$ 342.0124; found 342.0122.

*5',6'-Dichloro-6-methylspiro[isochromene-1,1'-isoindolin]-3'-one (**3w**).* White solid (13.2 mg, 40%), petroleum ether/ethyl acetate = 5:1, mp 203-204 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.62 (s, 1H), 7.21 (s, 1H), 6.98 (s, 1H), 6.97 (d, *J* = 9.2 Hz, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.69 (d, *J* = 6.0 Hz, 1H), 6.01 (d, *J* = 6.0 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 146.3, 143.6, 140.2, 137.8, 135.3, 130.2, 129.5, 128.8, 126.0, 125.8, 125.2, 124.2, 124.1, 105.1, 89.7, 21.3. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{12}Cl_2NO_2$ 332.0240;

found 332.0239.

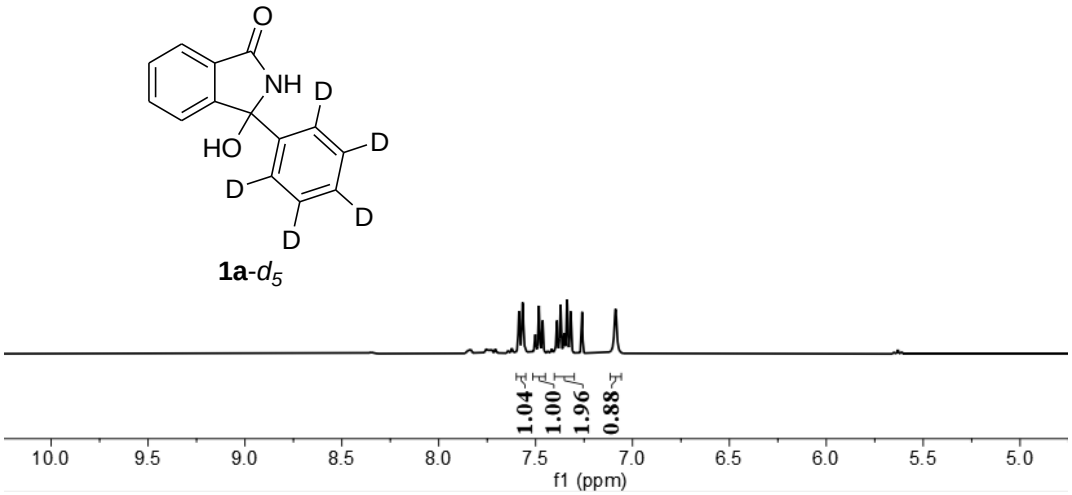
1.0 mmol Scale Synthesis of 3a. To a solution of 3-hydroxy-3-phenylisoindolinone **1a** (225 mg, 1.0 mmol) in dichloroethane (10 mL) was added $[Cp^*RhCl_2]_2$ (15.5 mg, 0.025 mmol), $AgSbF_6$ (34 mg, 0.1 mmol), AgOAc (42 mg, 0.25 mmol), and vinylene carbonate **2** (130 μL, 2.0 mmol). The reaction mixture was stirred at 60 ℃ on a heating block for 2 h. After completion of the reaction, the solvent was removed in vacuo and the residue was purified by silica gel column chromatography to afford the compound **3a** as a white solid (213 mg, 86%).

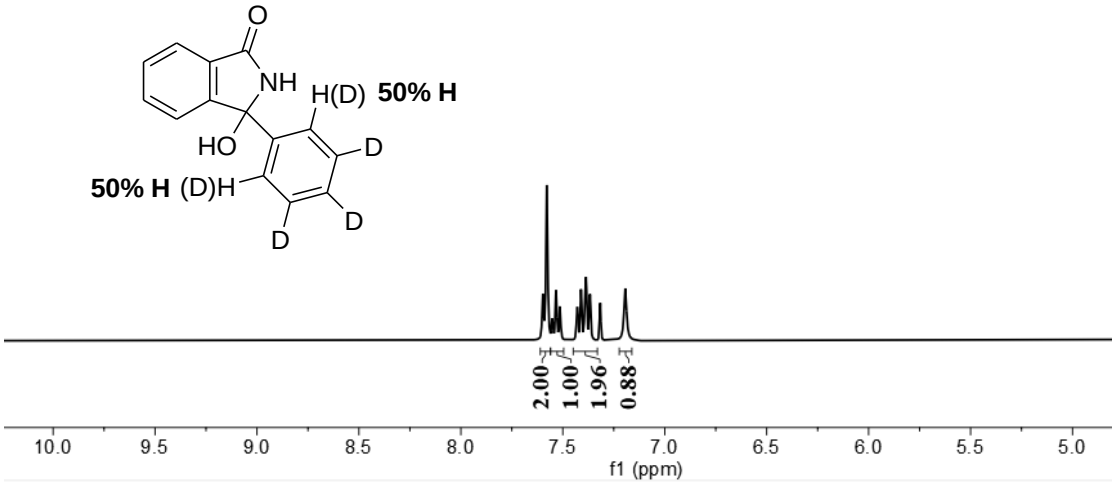
Procedure for the Synthesis of Compound 5. To a solution of compound **3a** (25 mg, 0.1 mmol) in THF (2 mL) was added NaH (60% oil dispersion) (6 mg, 0.15 mmol). After stirring at 0 °C for 40 min, prenyl bromide (20 μL, 0.15 mmol) was added at 0 °C and the reaction mixture was warmed slowly to room temperature and stirred for additional 1 h. Then, the resulting mixture was quenched by water and extracted with DCM. The combined organic layers were dried and concentrated under reduced pressure followed by silica gel column chromatography to afford the compound **5**.

*2'-(3-Methylbut-2-en-1-yl) spiro[isochromene-1,1'-isoindolin]-3'-one (**5**).* White solid (15.9 mg, 50%), petroleum ether/ethyl acetate = 5:1, mp 83-84 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.83 (m, 1H), 7.54-7.49 (m, 2H), 7.42-7.38 (m, 1H), 7.29-7.26 (m, 1H), 7.11-7.04 (m, 2H), 6.72 (d, *J* = 5.6 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 1H), 5.87 (d, *J* = 6.0 Hz, 1H), 5.04 (t, *J* = 6.4 Hz, 1H), 4.15 (dd, *J* = 15.6, 7.2 Hz, 1H), 3.82 (dd, *J* = 15.6, 6.4 Hz, 1H), 1.55 (s, 3H), 1.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 148.2, 144.1, 134.8, 132.8, 130.7, 130.3, 130.1, 129.5, 127.4, 126.6, 126.0, 124.2, 123.3, 123.3, 120.1, 102.4, 93.7, 38.2, 25.7, 17.7. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{19}NO_2Na$ 340.1308; found 340.1308.

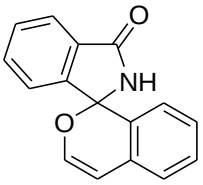
Mechanistic Studies.

(a) H/D exchange experiment. To a solution of **1a-*d*$_5$** (23 mg, 0.1 mmol) in DCE (1.5 mL) was added $[Cp^*RhCl_2]_2$ (1.6 mg, 0.0025 mmol), $AgSbF_6$ (3.4 mg, 0.01 mmol), AgOAc (4.2 mg, 0.025 mmol), and H_2O (9 μL, 0.5 mmol). The reaction mixture was stirred at 60 ℃ on a heating block for 10 min. Then, the solvent was removed and the residue was purified to recover the compound **1a** in 85% yield (19.6 mg). And H/D exchanges at the ortho-position (50% H) of the phenyl ring were observed by ^{1}H NMR analysis.

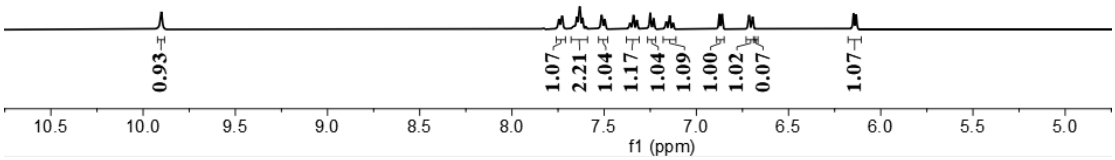


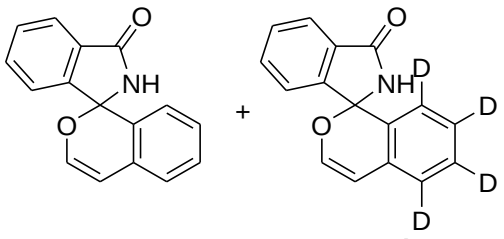


(b) KIE study (competition experiment). To a mixture of **1a** (22.5 mg, 0.1 mmol) and **1a-*d*$_5$** (23 mg, 0.1 mmol) in DCE (1.5 mL) was added $[Cp^*RhCl_2]_2$ (1.6 mg, 0.0025 mmol), $AgSbF_6$ (3.4 mg, 0.01 mmol), AgOAc (4.2 mg, 0.025 mmol), and vinylene carbonate **2** (13 μL, 0.2 mmol). The reaction mixture was stirred at 60 ℃ on a heating block for 20 min. Then, the solvent was removed and the residue was purified to afford a mixture of **3a** and **3a-*d*$_4$**. ^{1}H NMR analysis of the product mixture gave a **3a:3a-*d*$_4$** ratio of 2.33.

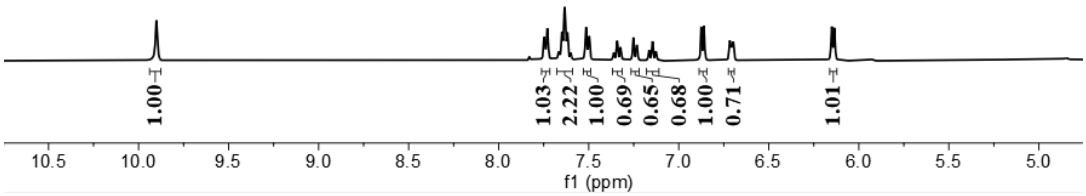


3a



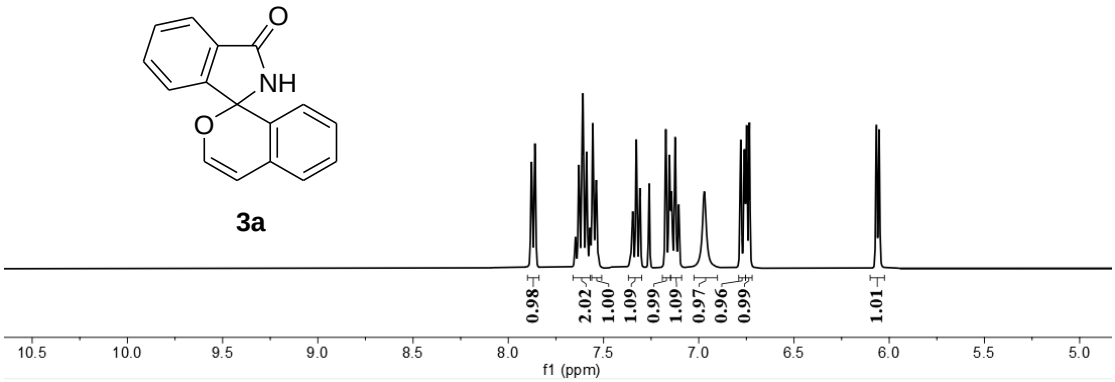


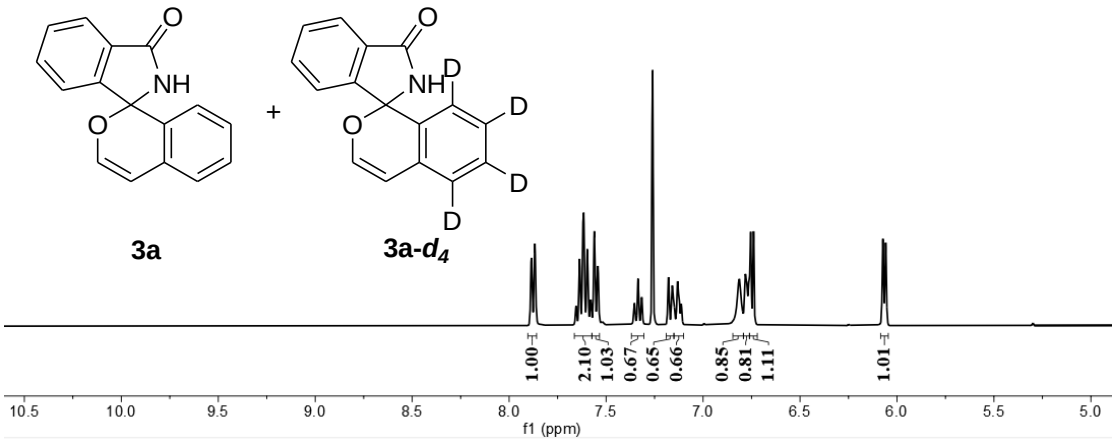
3a **3a-*d*$_4$**



KIE study (parallel experiment). To a mixture of **1a** (22.5 mg, 0.1 mmol) or **1a-*d*$_5$** (23 mg, 0.1 mmol) in DCE (1.5 mL) was added $[Cp^*RhCl_2]_2$ (1.6 mg, 0.0025 mmol), $AgSbF_6$ (3.4 mg, 0.01 mmol), AgOAc (4.2 mg, 0.025 mmol), and vinylene carbonate **2** (13 μL, 0.2 mmol). The resulting mixtures were stirred separately at 60 ℃ on a heating block for 20 min. Then,

these two reaction mixtures were combined, and the solvent was removed and the residue was purified to afford a mixture of **3a** and **3a-*d*$_4$**. ^{1}H NMR analysis of the product mixture gave a **3a:3a-*d*$_4$** ratio of 1.94.

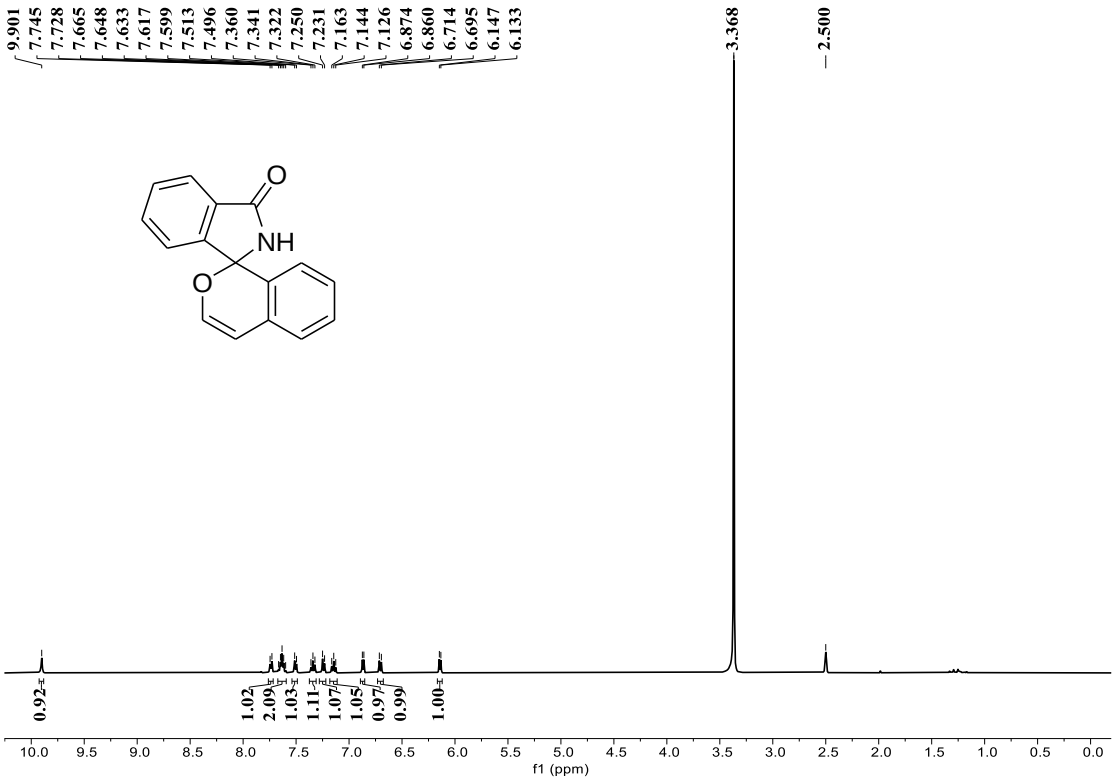




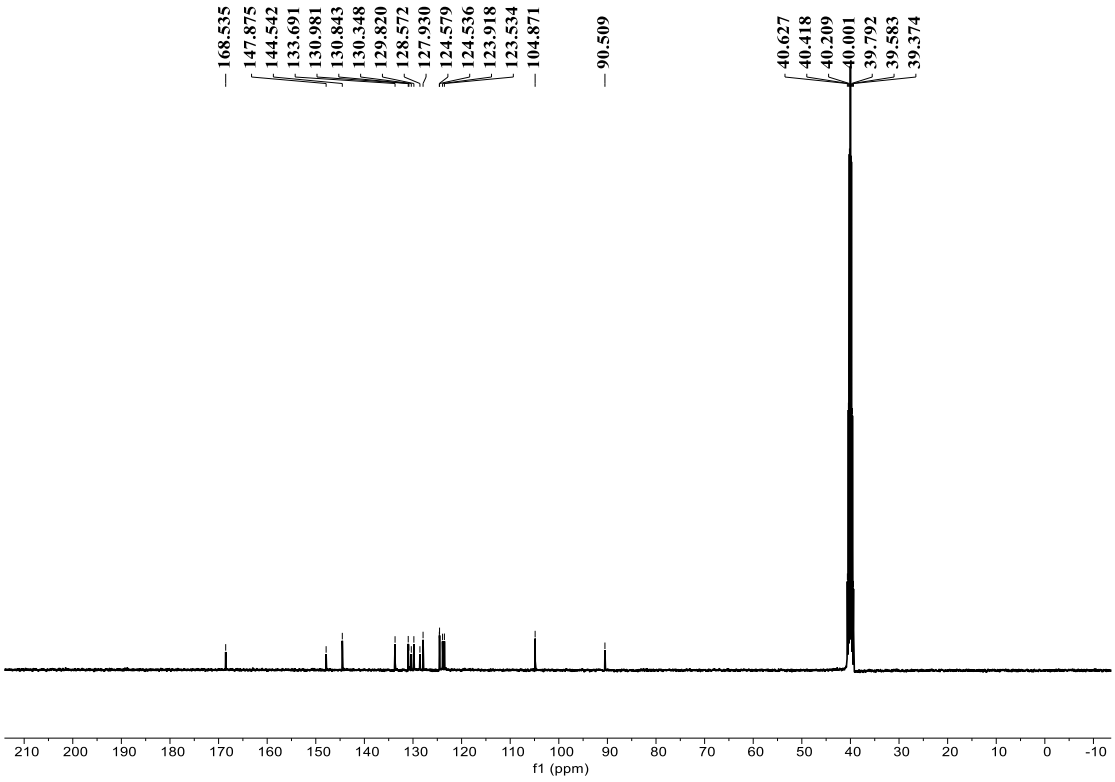
(c) Intermolecular Competition Experiment between 1c and 1e. To a solution of **1c** (25.5 mg, 0.1 mmol) and compound **1e** (24.3 mg, 0.1 mmol) in dichloroethane (1.5 mL) was added $[Cp^*RhCl_2]_2$ (1.6 mg, 0.0025 mmol), $AgSbF_6$ (3.4 mg, 0.01 mmol), AgOAc (4.2 mg, 0.025 mmol), and vinylene carbonate **2** (13 μL, 0.2 mmol). The reaction mixture was stirred at 60 ℃ on a heating block for 2 h. After completion of the reaction, the solvent was removed and the residue was purified to afford **3c** (12.7 mg, 0.046 mmol) and **3e** (8.1 mg, 0.03 mmol). The molar ratio of **3c** and **3e** was thus calculated as 1.5:1.

References

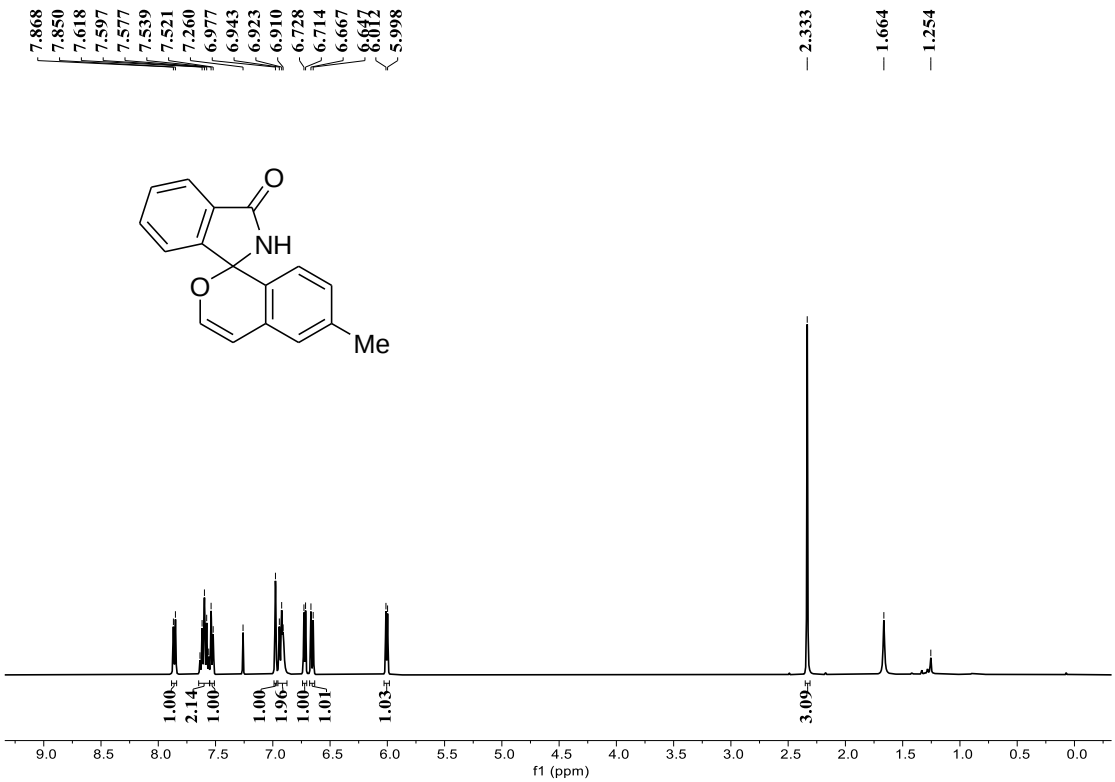
(1) (a) Nishimura, T.; Noishiki, A.; Ebe, Y.; Hayashi, T. Hydroxorhodium/Chiral Diene Complexes as Effective Catalysts for the Asymmetric Arylation of 3-Aryl-3-hydroxyisoindolin-1-ones. *Angew. Chem., Int. Ed.* **2013**, *52*, 1777-1780. (b) Sharma, S.; Oh, Y.; Mishra, N. K.; De, U.; Jo, H.; Sachan, R.; Kim, H. S.; Jung, Y. H.; Kim, I. S. Rhodium-Catalyzed [3 + 2] Annulation of Cyclic N-Acyl Ketimines with Activated Olefins: Anticancer Activity of Spiroisoindolinones. *J. Org. Chem.* **2017**, *82*, 3359-3367. (c) Hu, H.; Li, B.-S.; Xu, J.-L.; Sun, W.; Wang, Y.; Sun, M. Rh-Catalyzed spiroannulation of ketimines with cyclopropenones via sequential C-H/C-C bond activation. *Chem. Commun.* **2022**, *58*, 4743-4746.



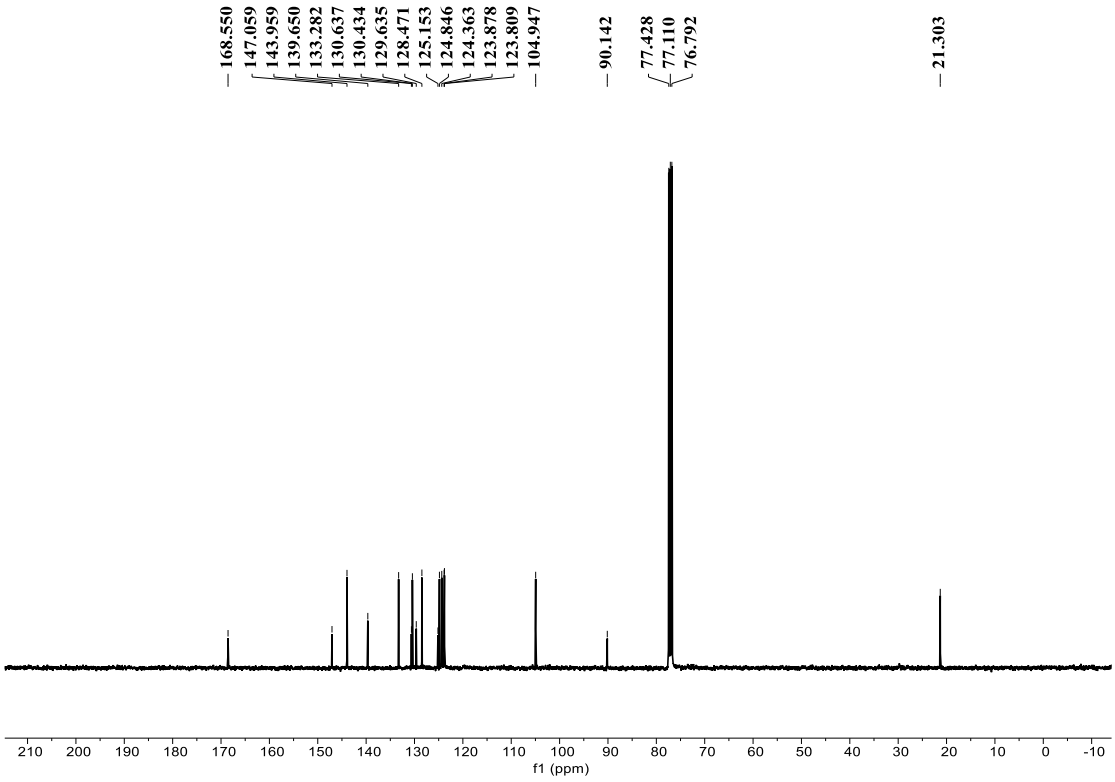
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **3a**



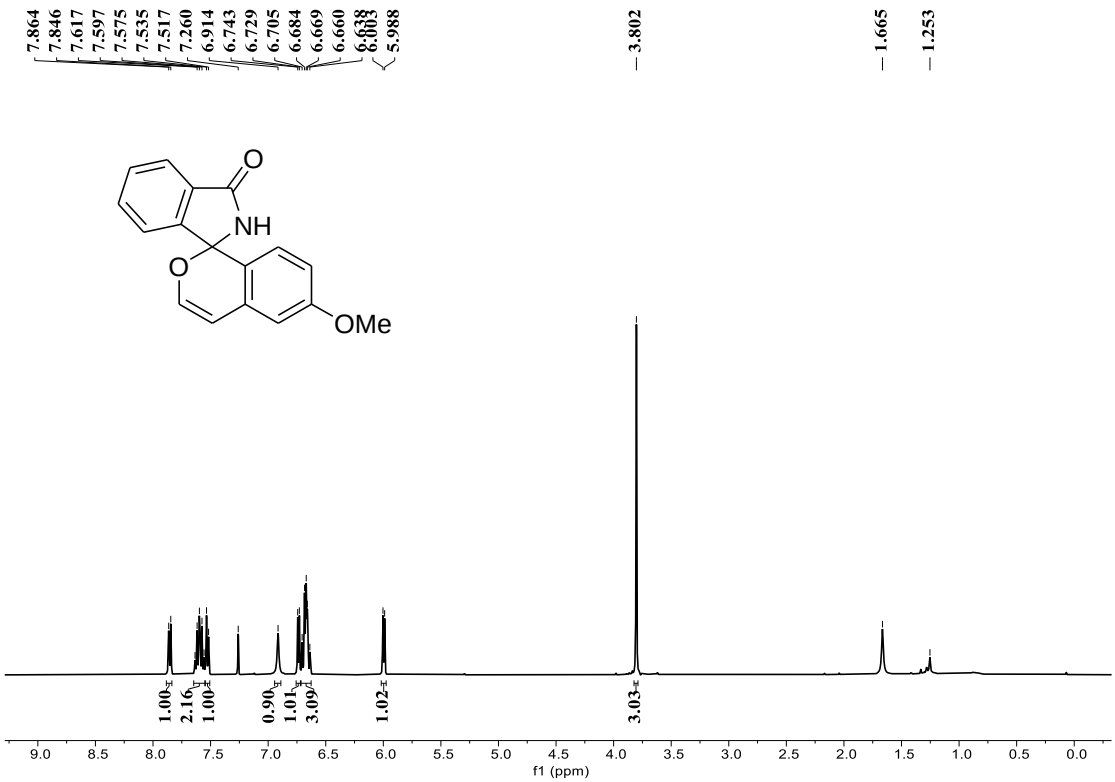
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **3a**



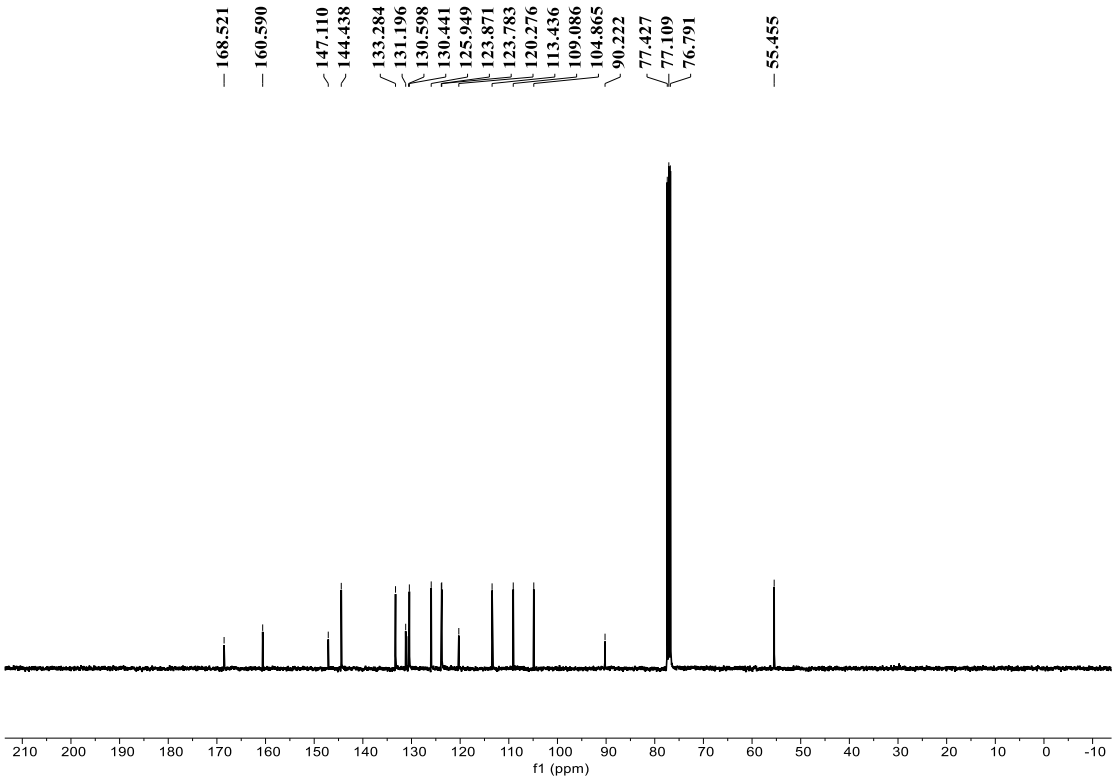
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3b**



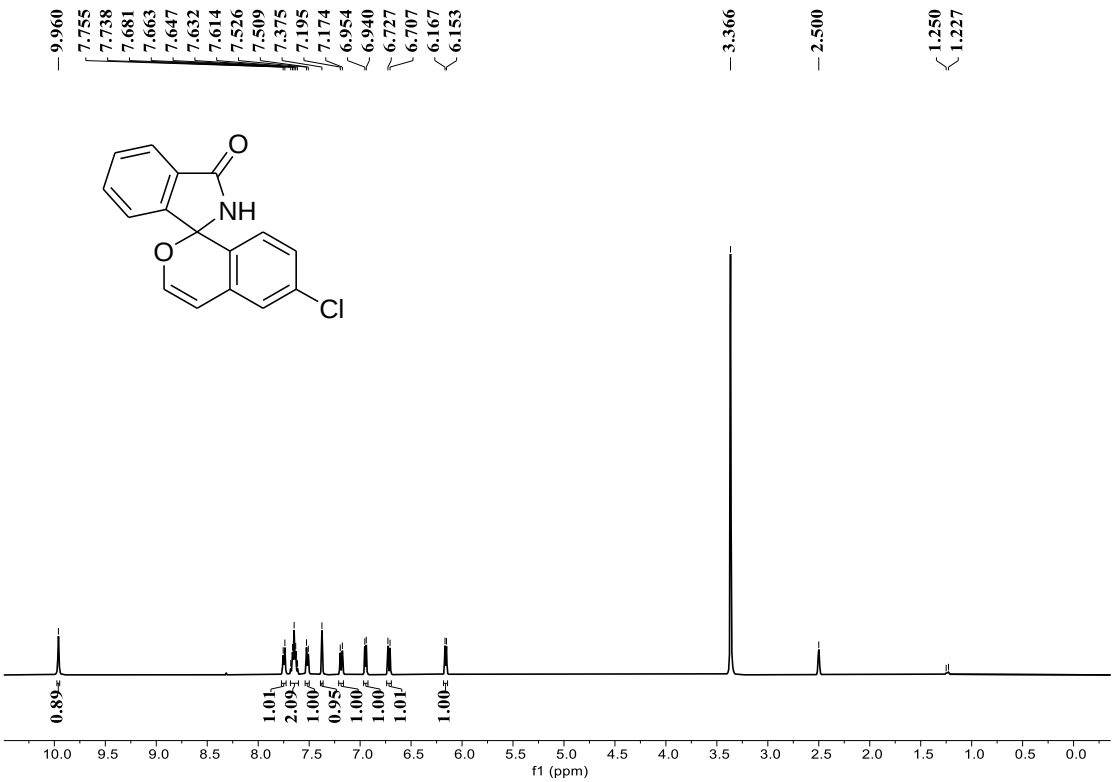
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3b**



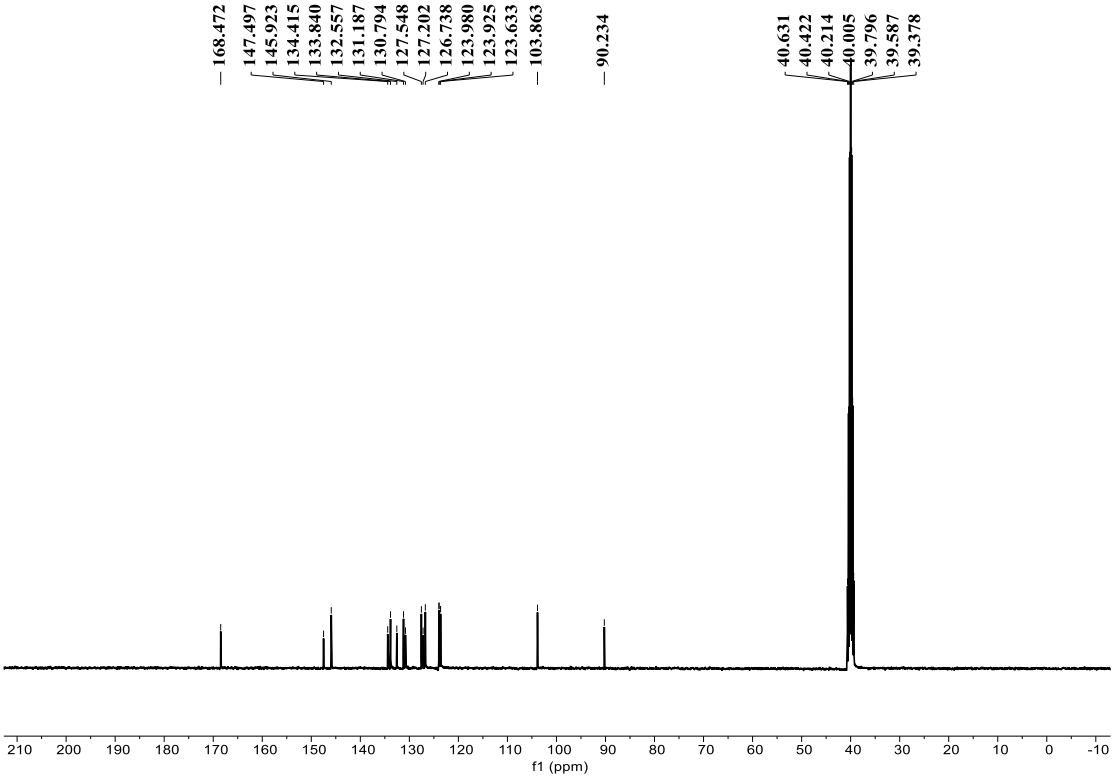
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3c**



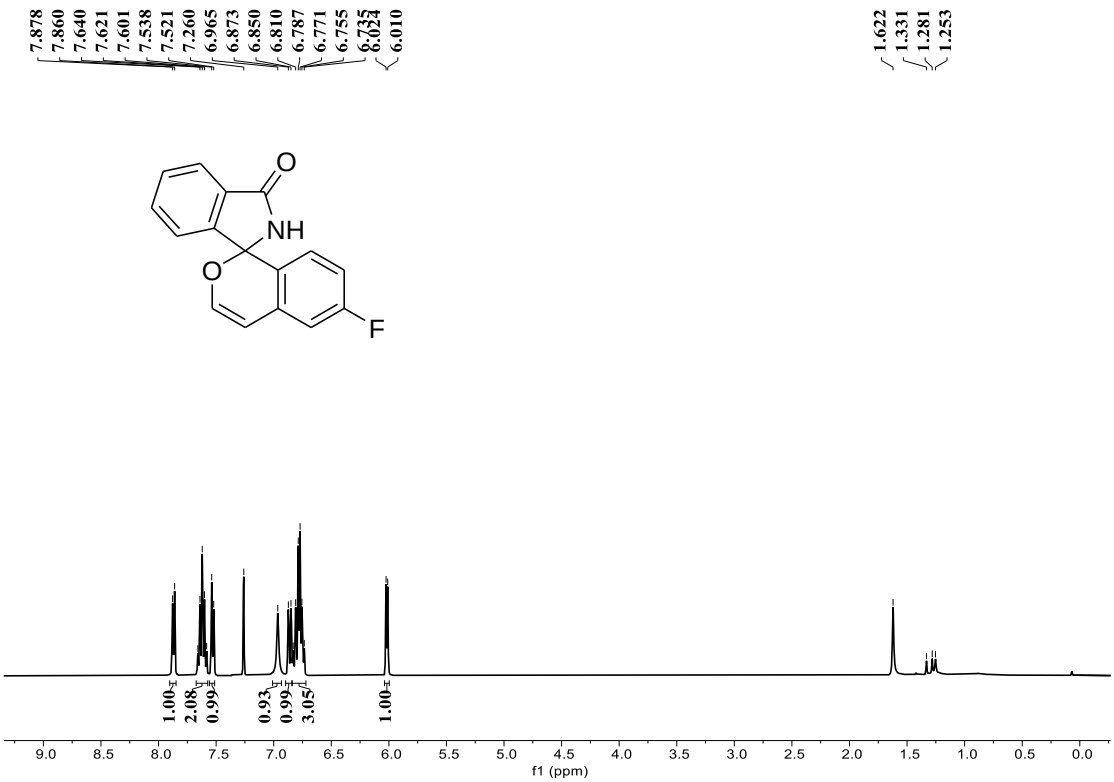
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3c**



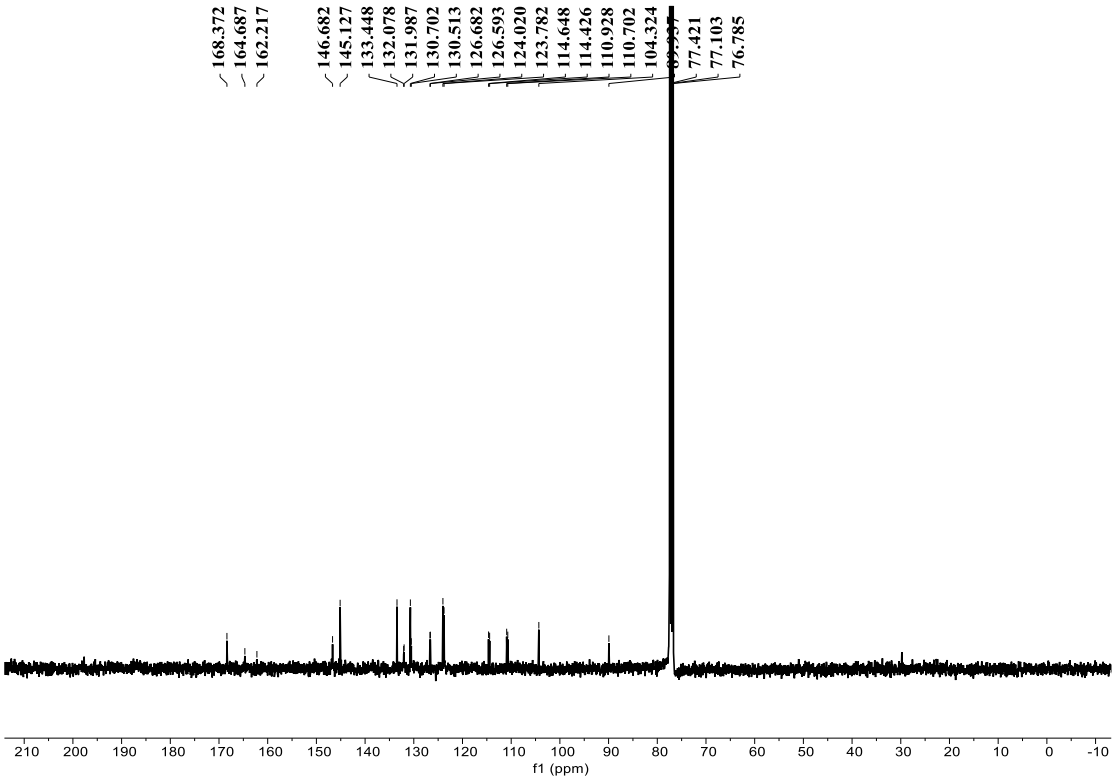
^{1}H NMR Spectrum (400 MHz, DMSO-d_6) of Compound **3d**



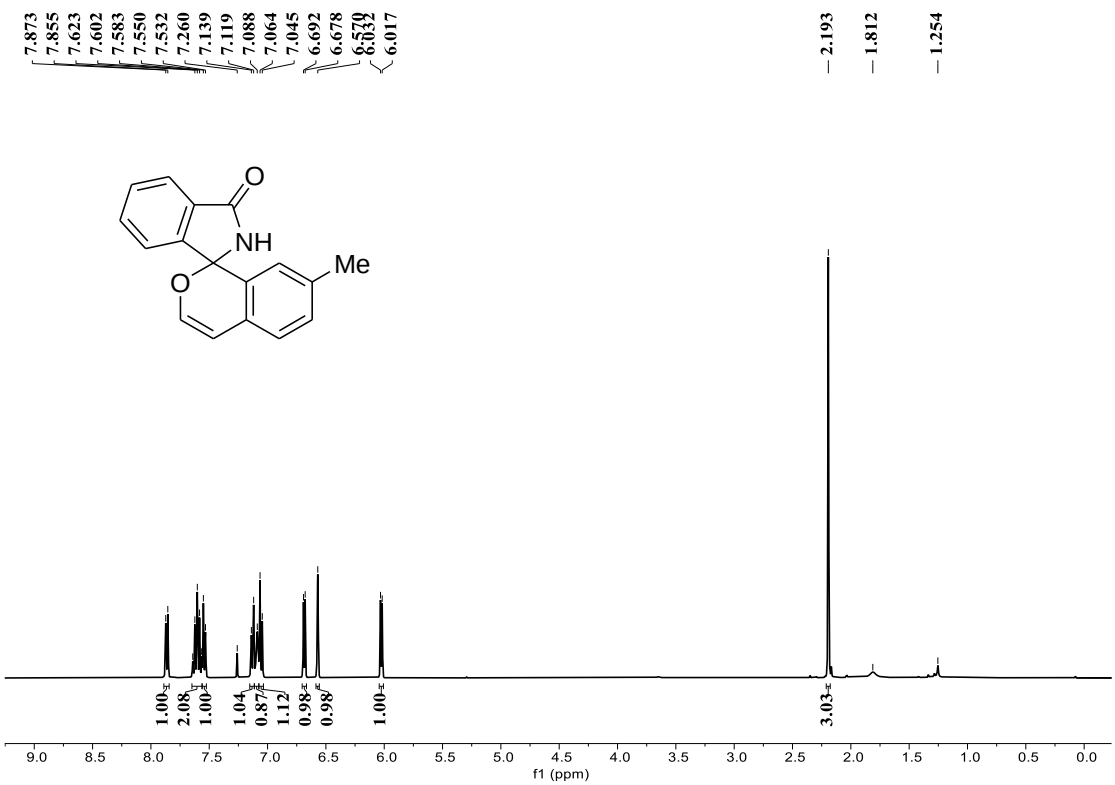
^{13}C NMR Spectrum (100 MHz, DMSO-d_6) of Compound **3d**



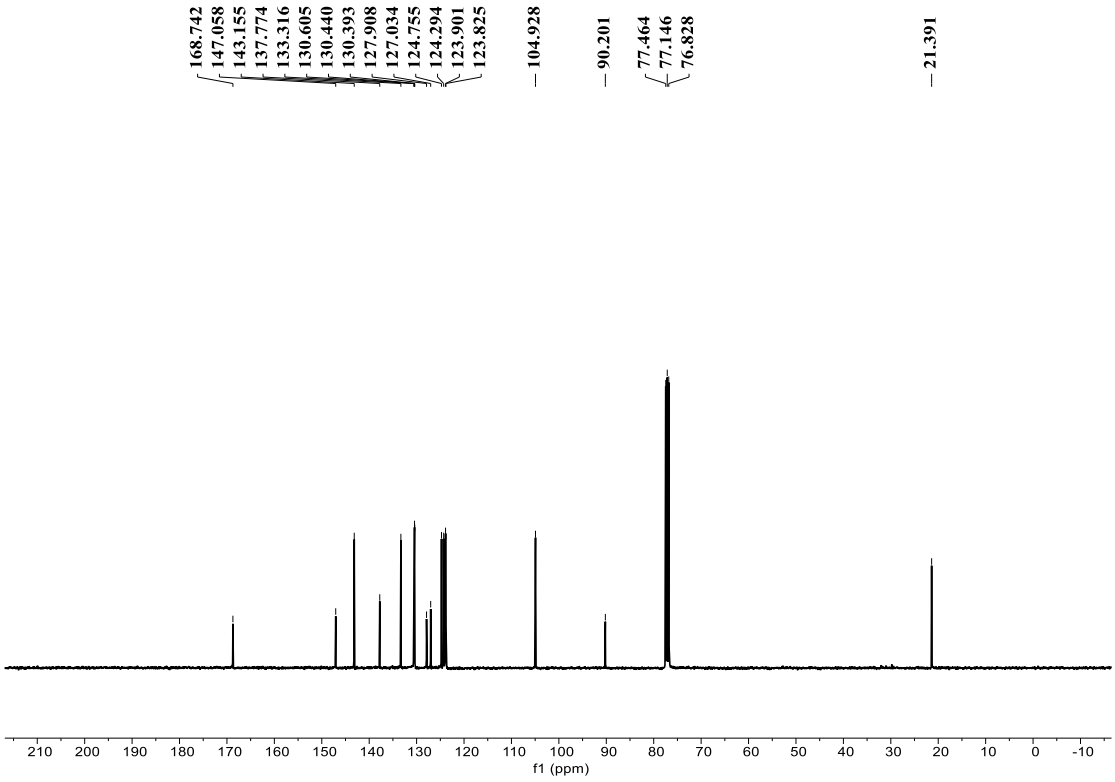
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3e**



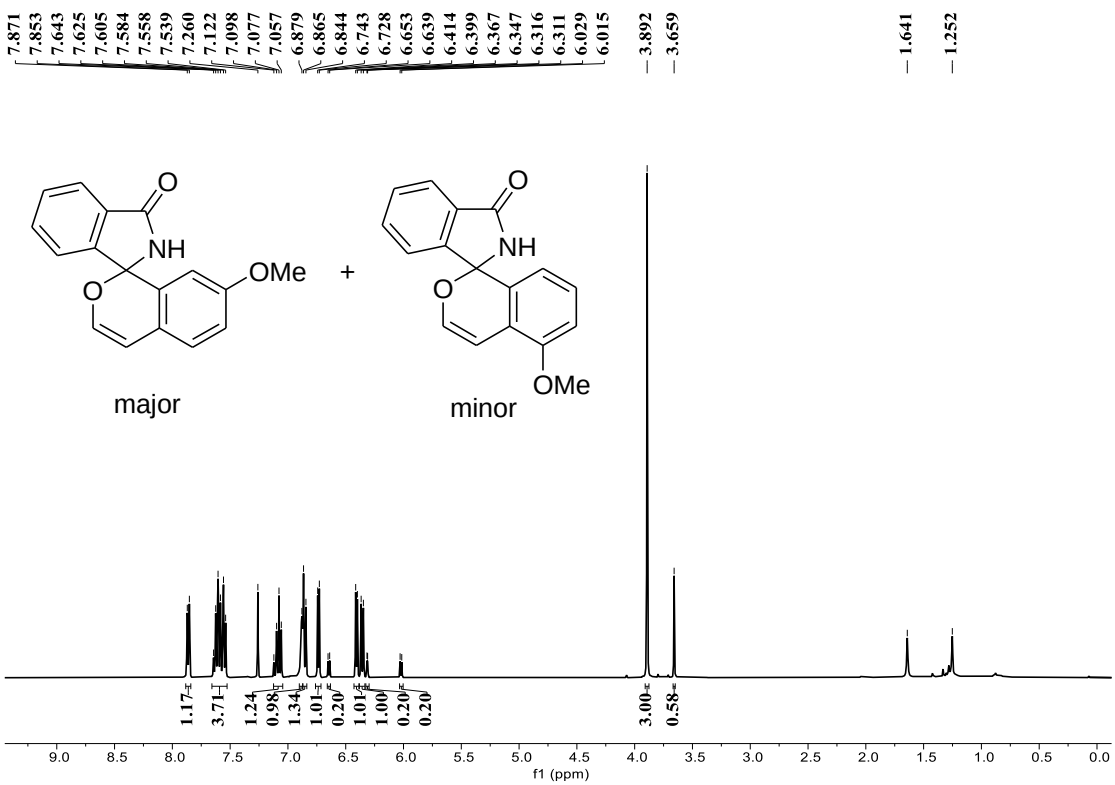
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3e**



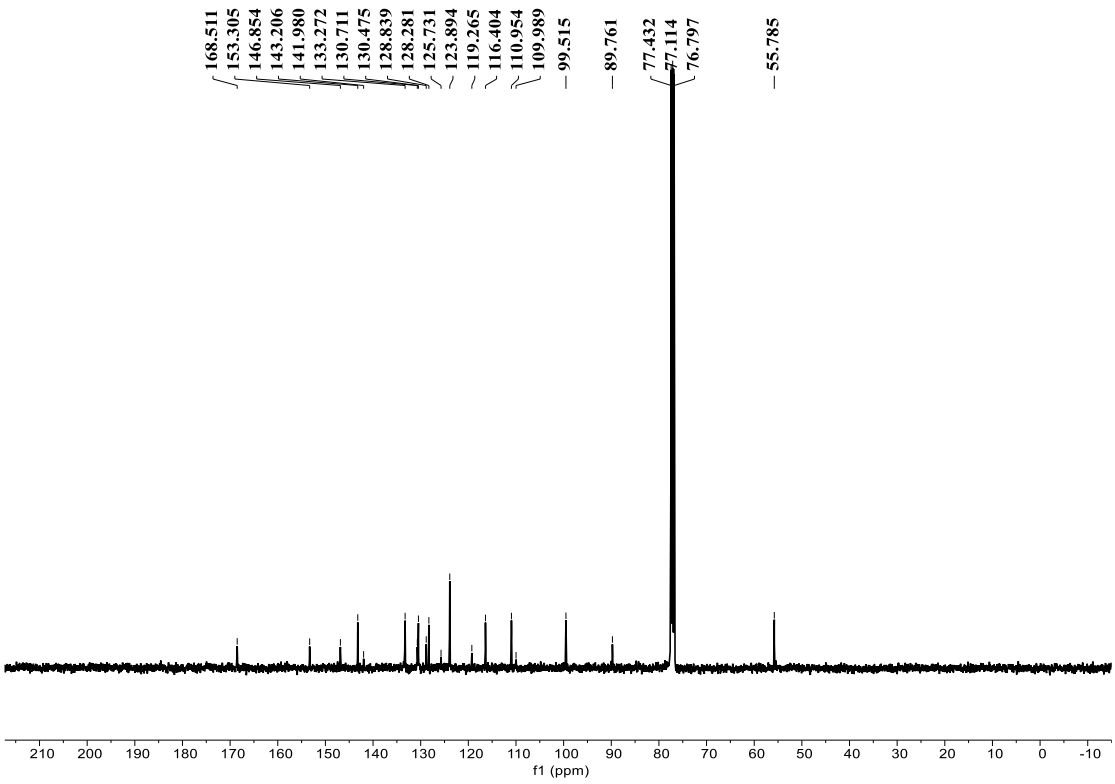
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3h**



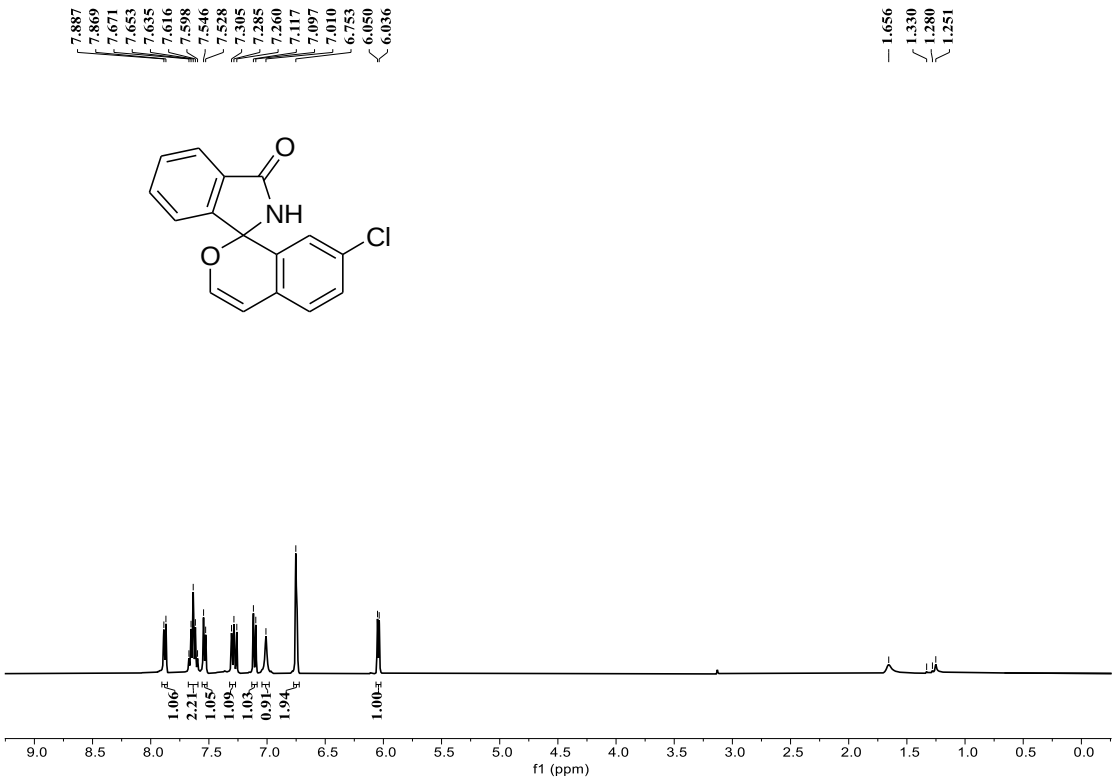
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3h**



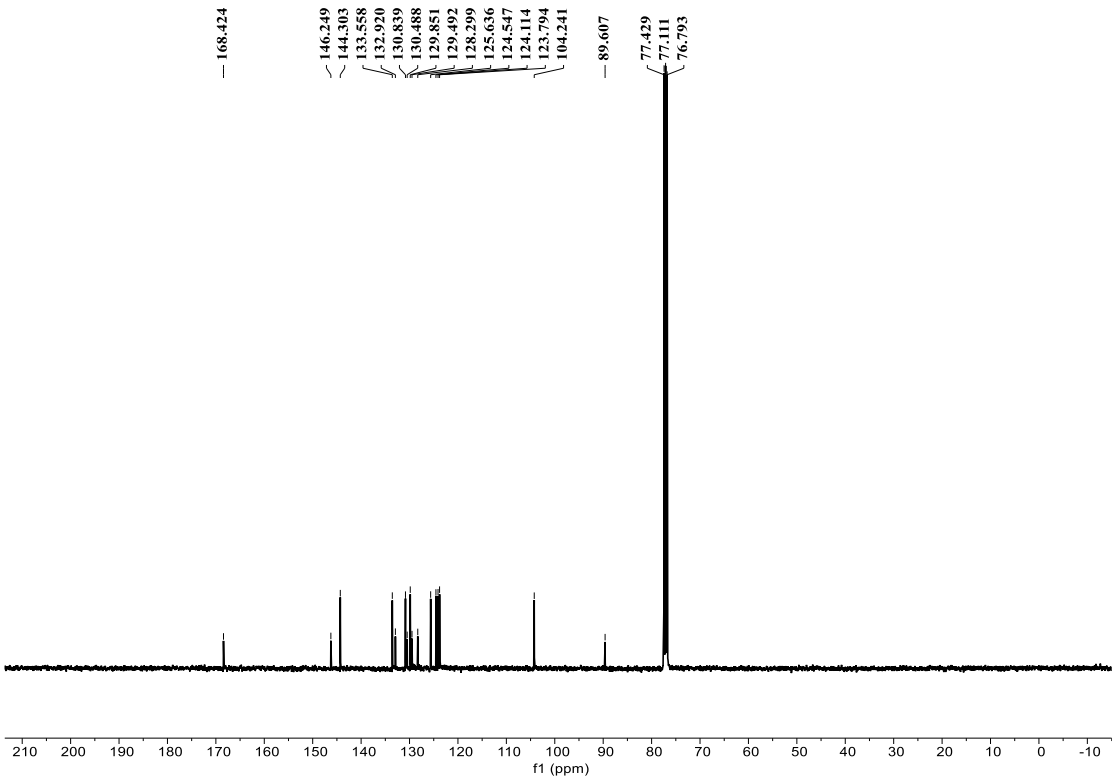
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3i**



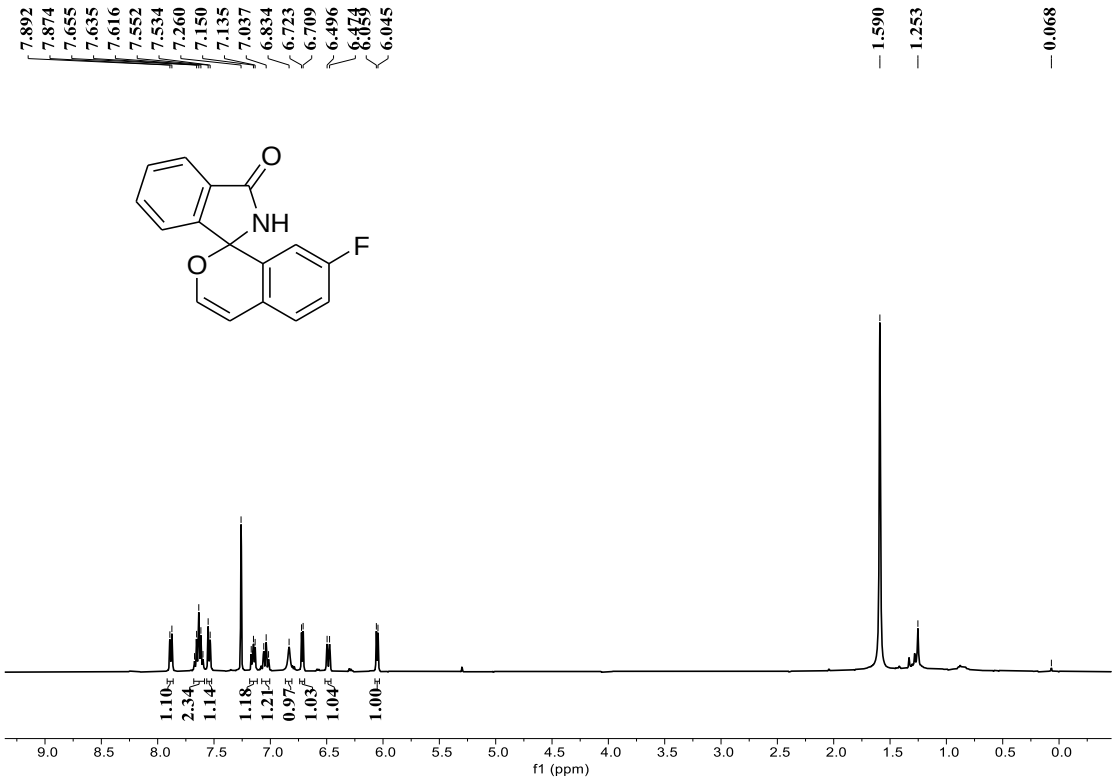
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3i**



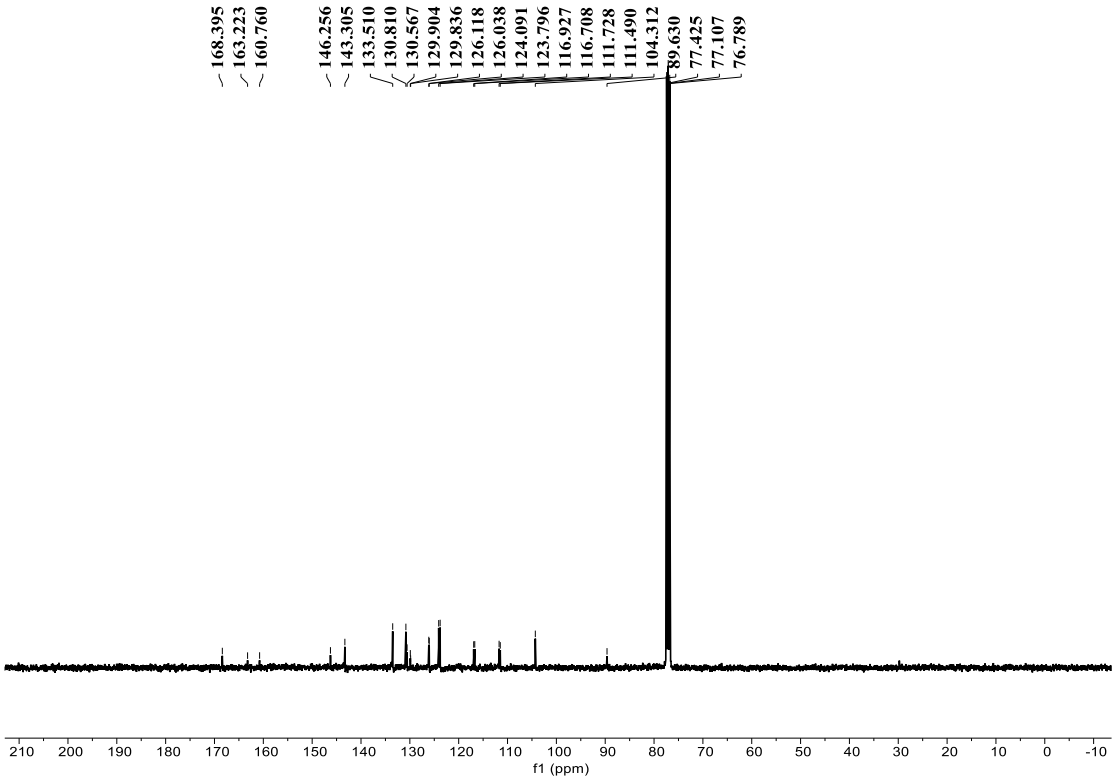
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3j**



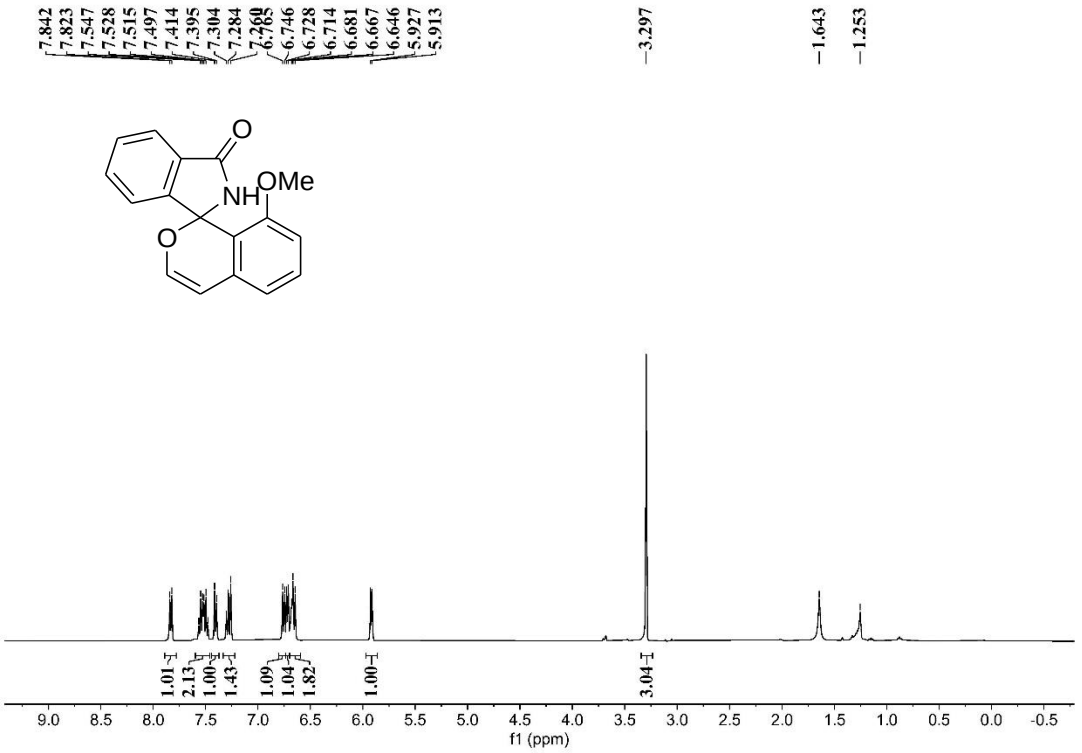
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3j**



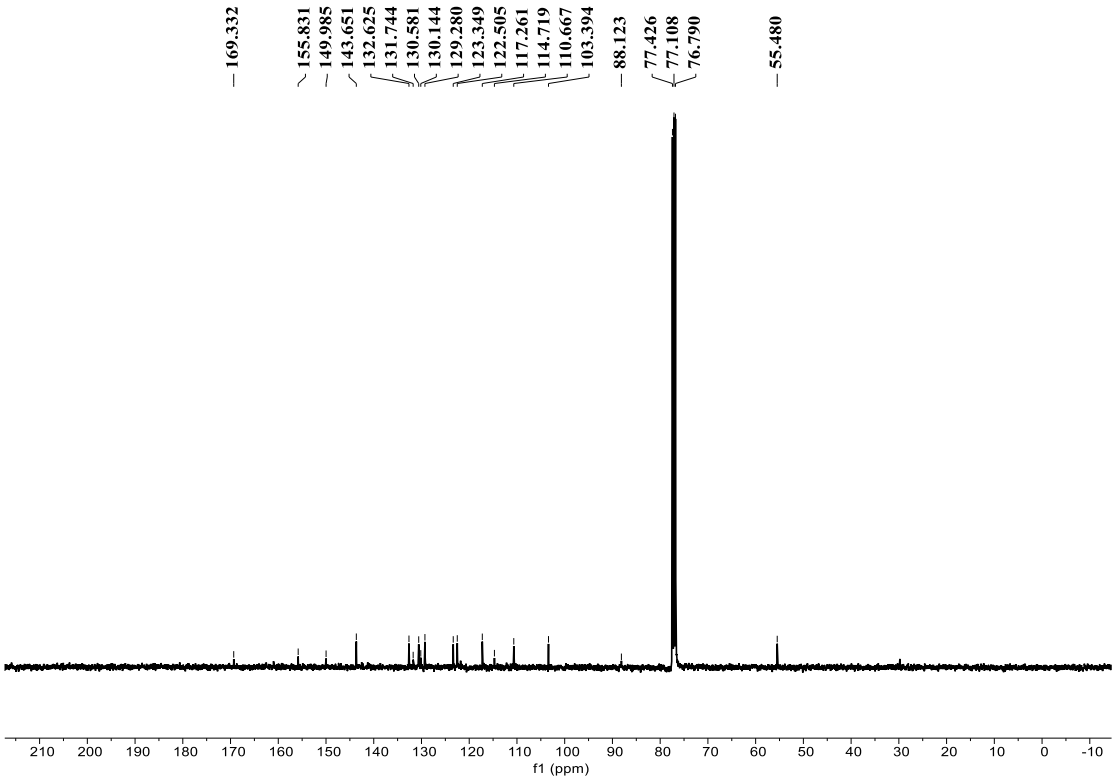
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3k**



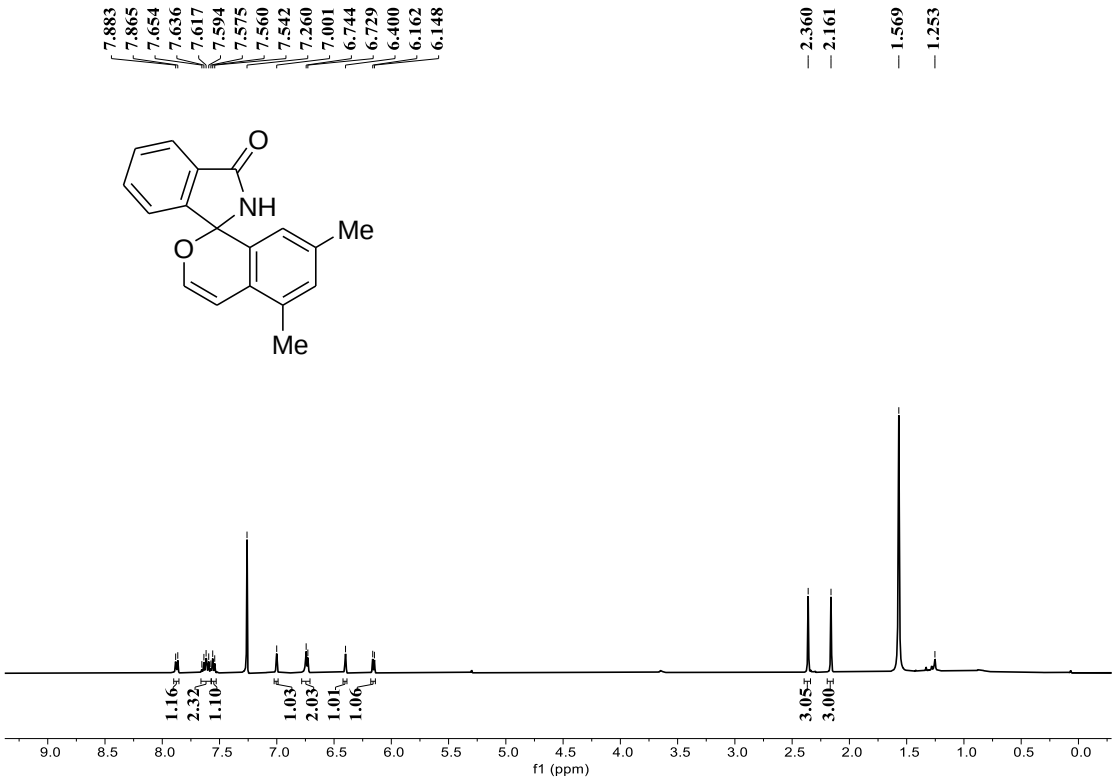
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3k**



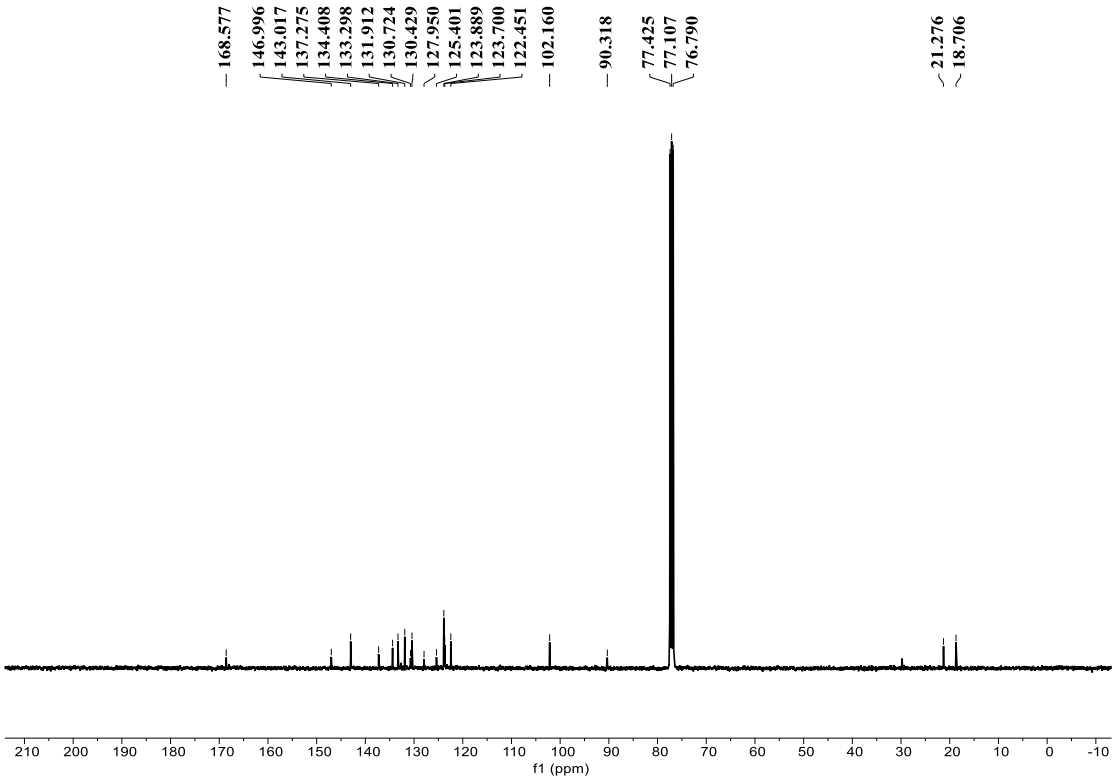
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3l**



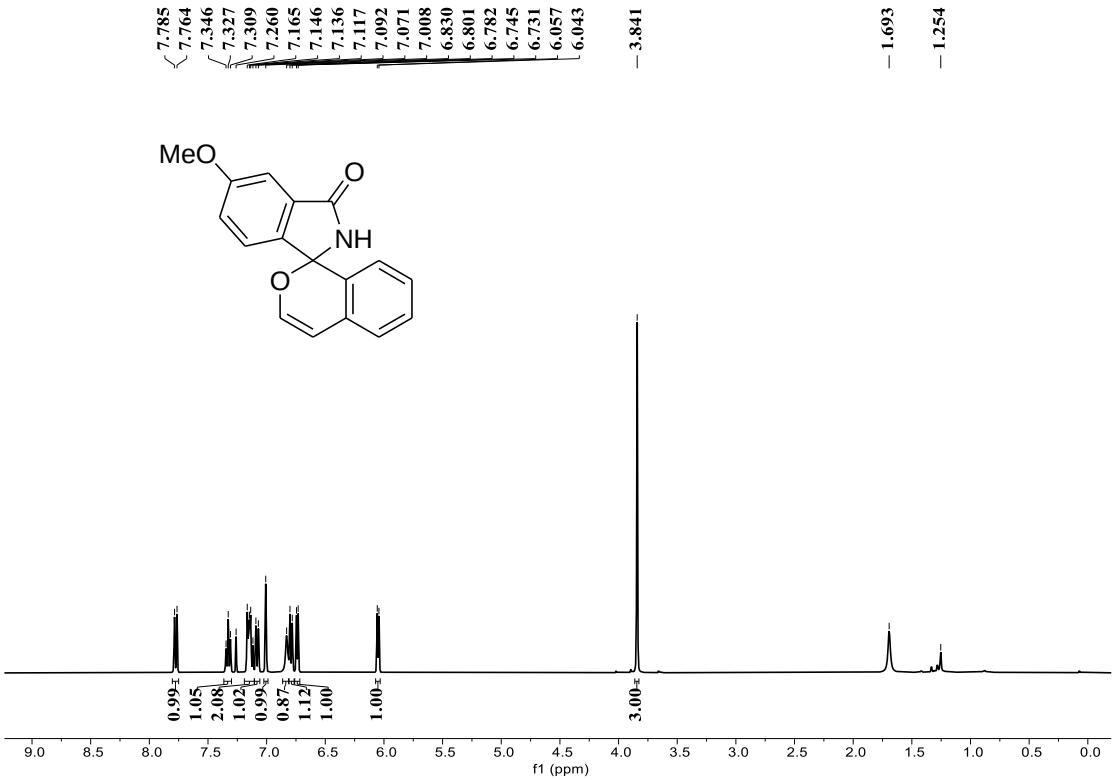
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3l**



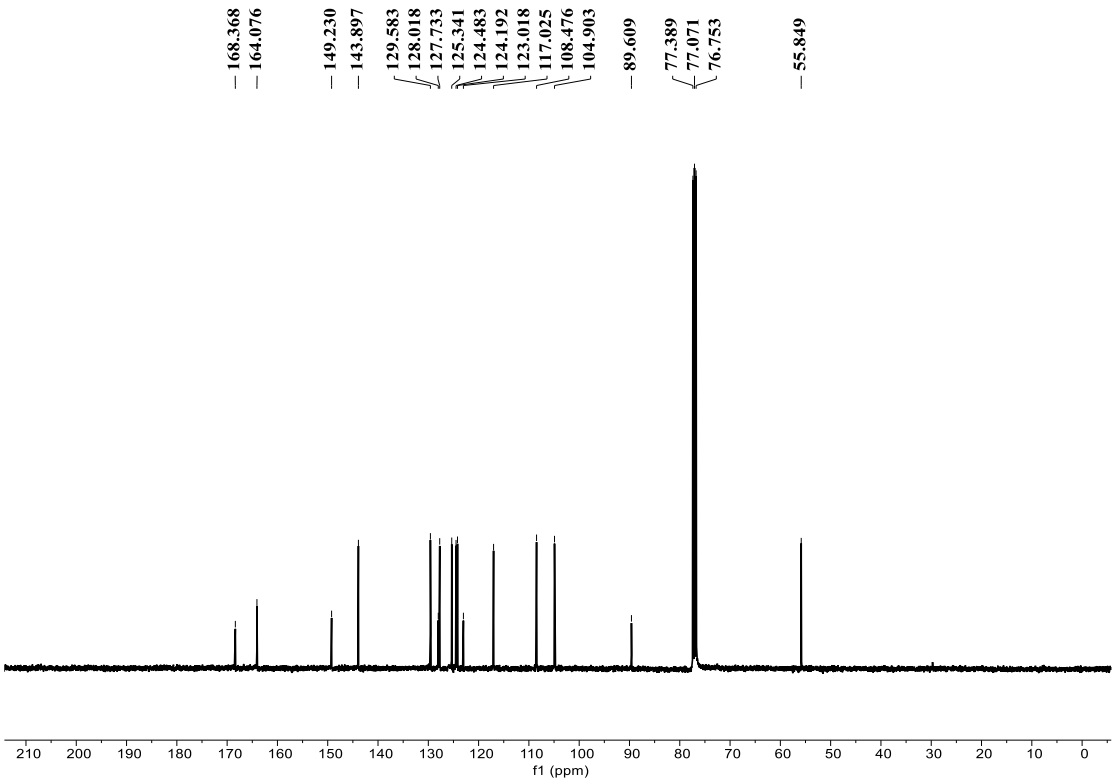
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3m**



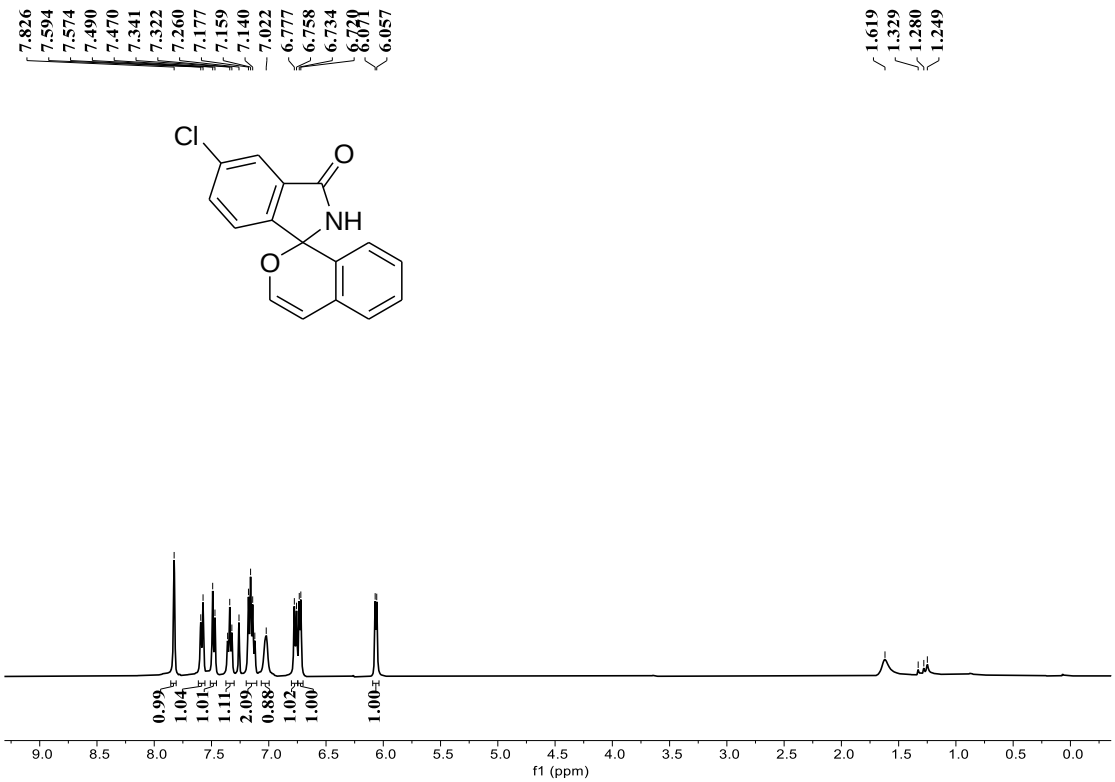
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3m**



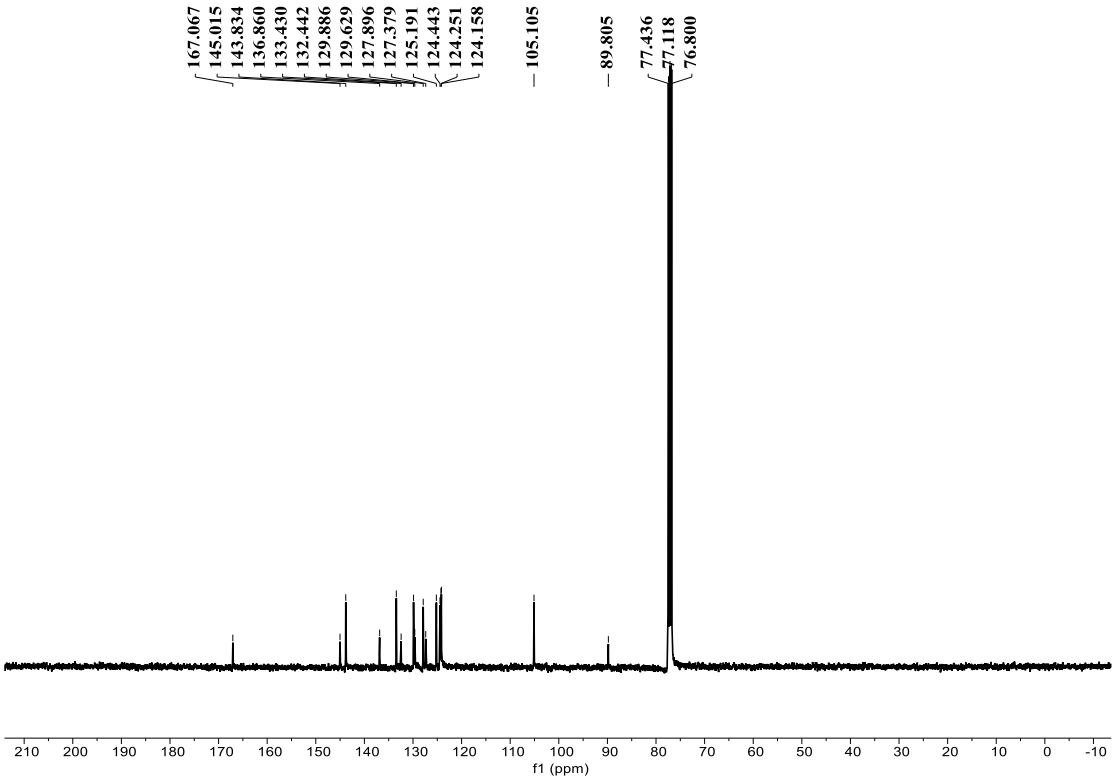
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3n**



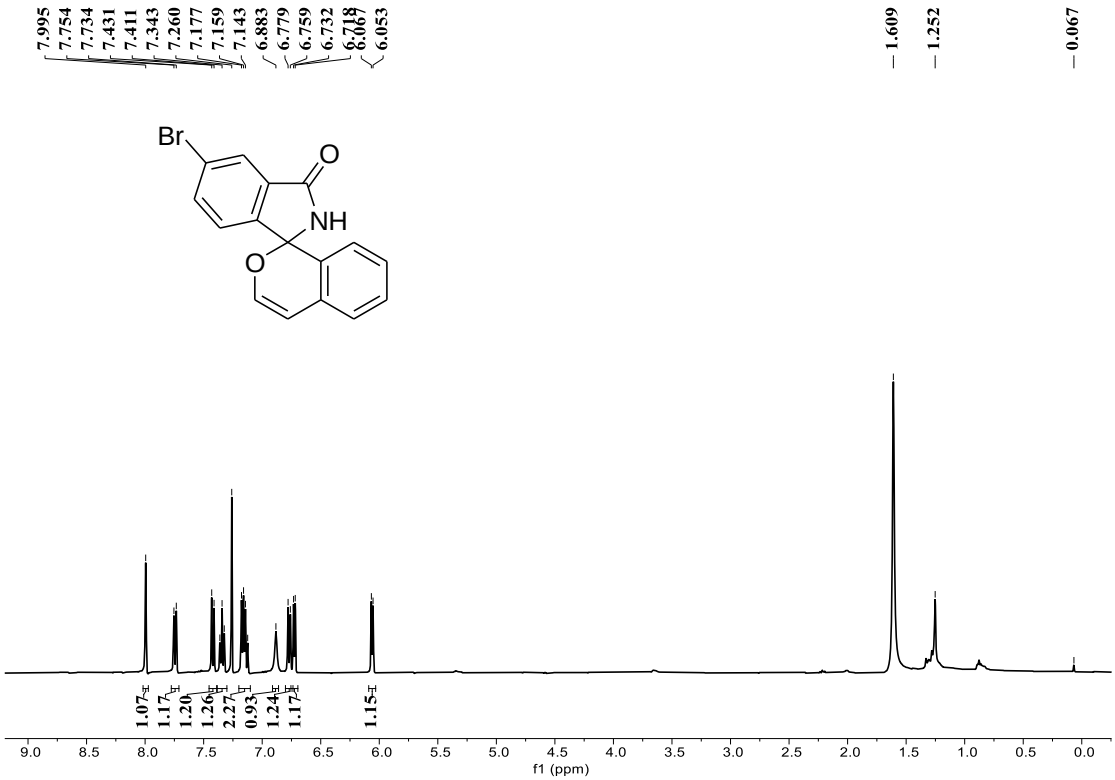
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3n**



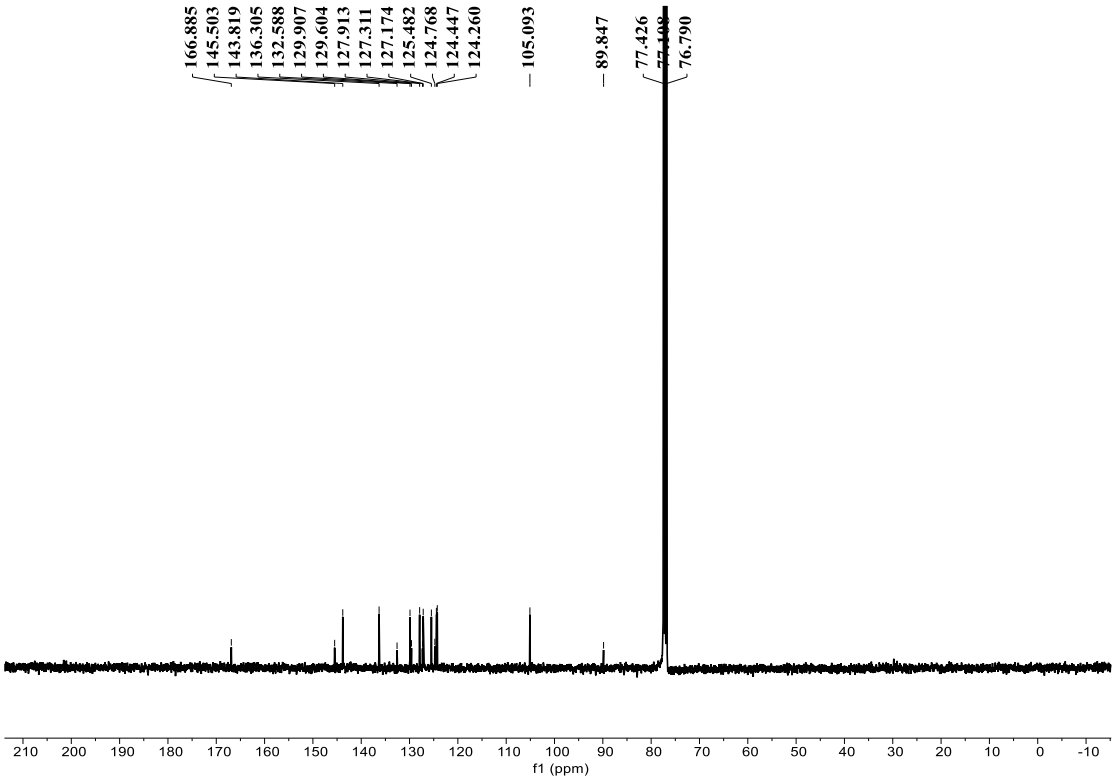
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3o**



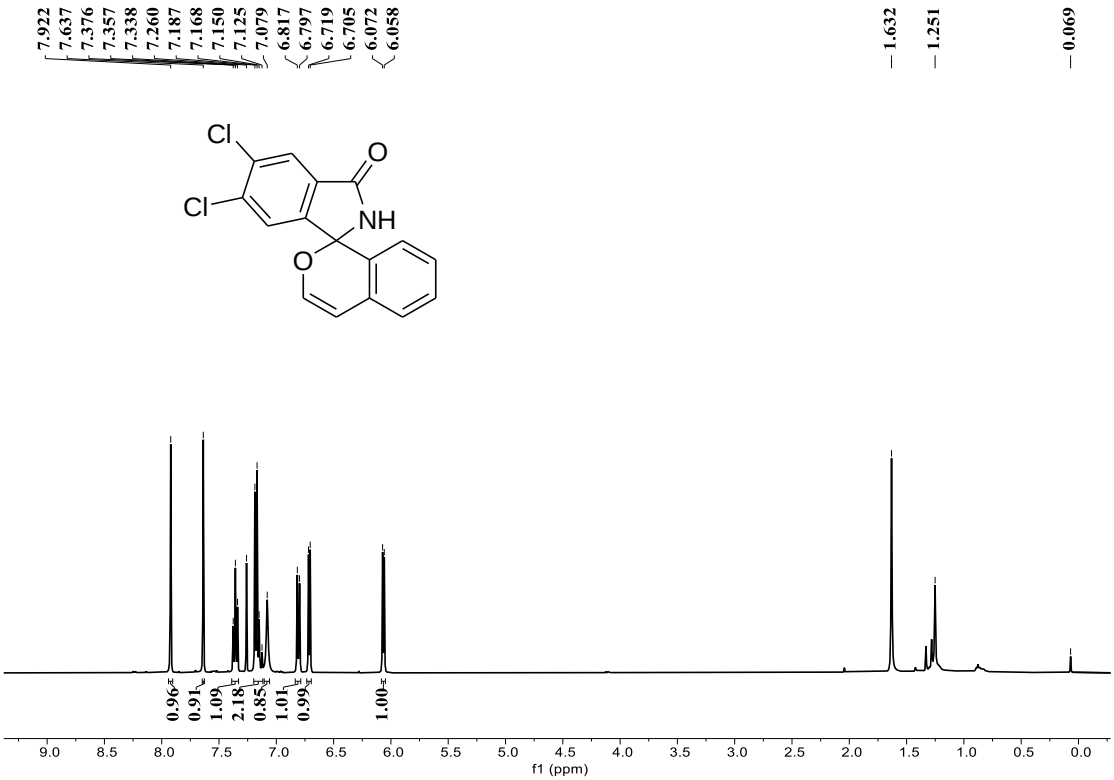
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3o**



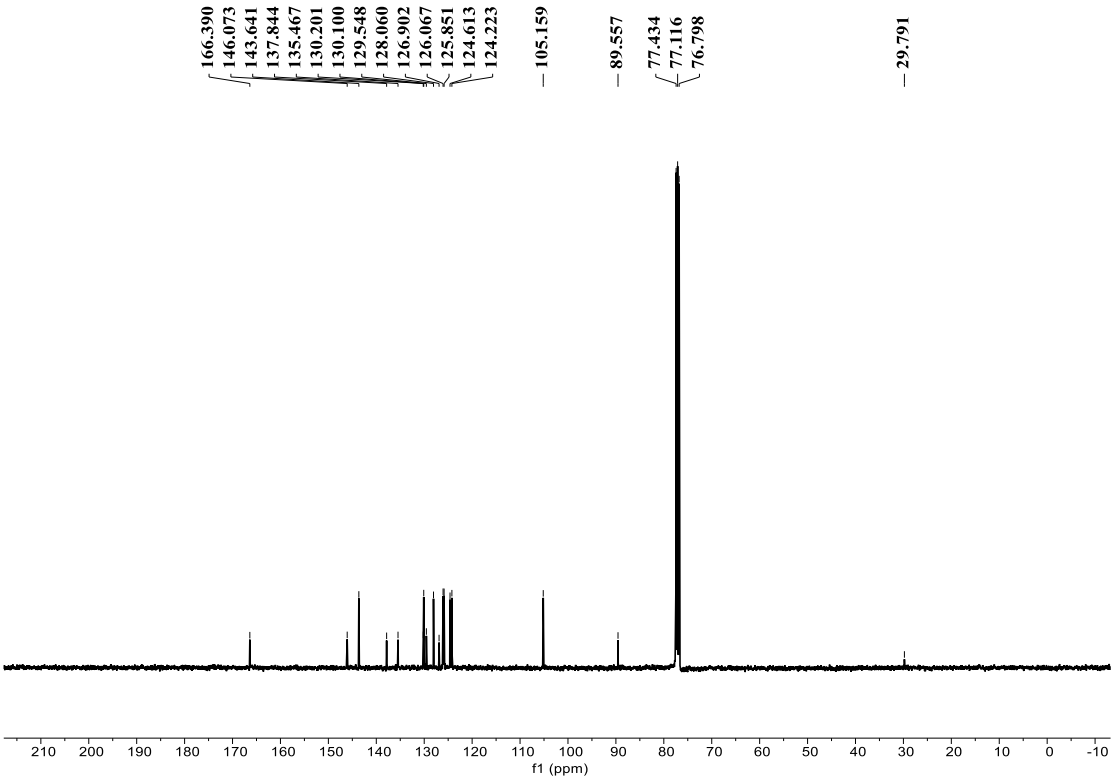
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3p**



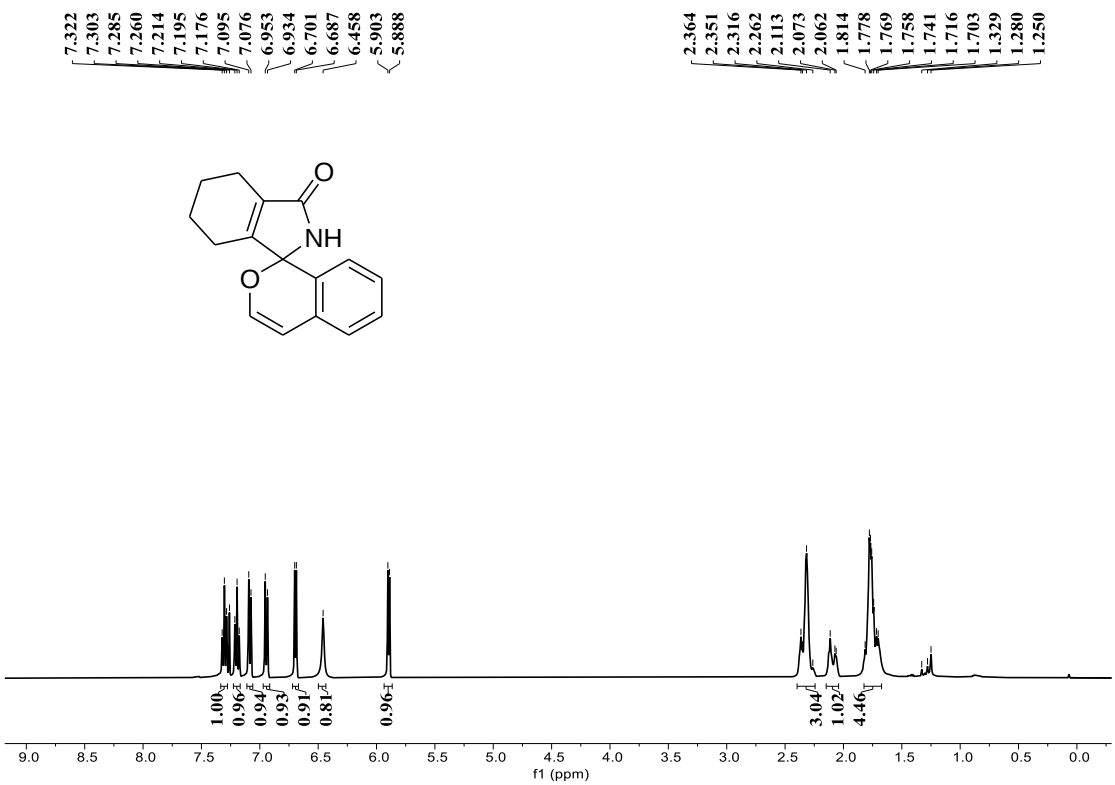
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3p**



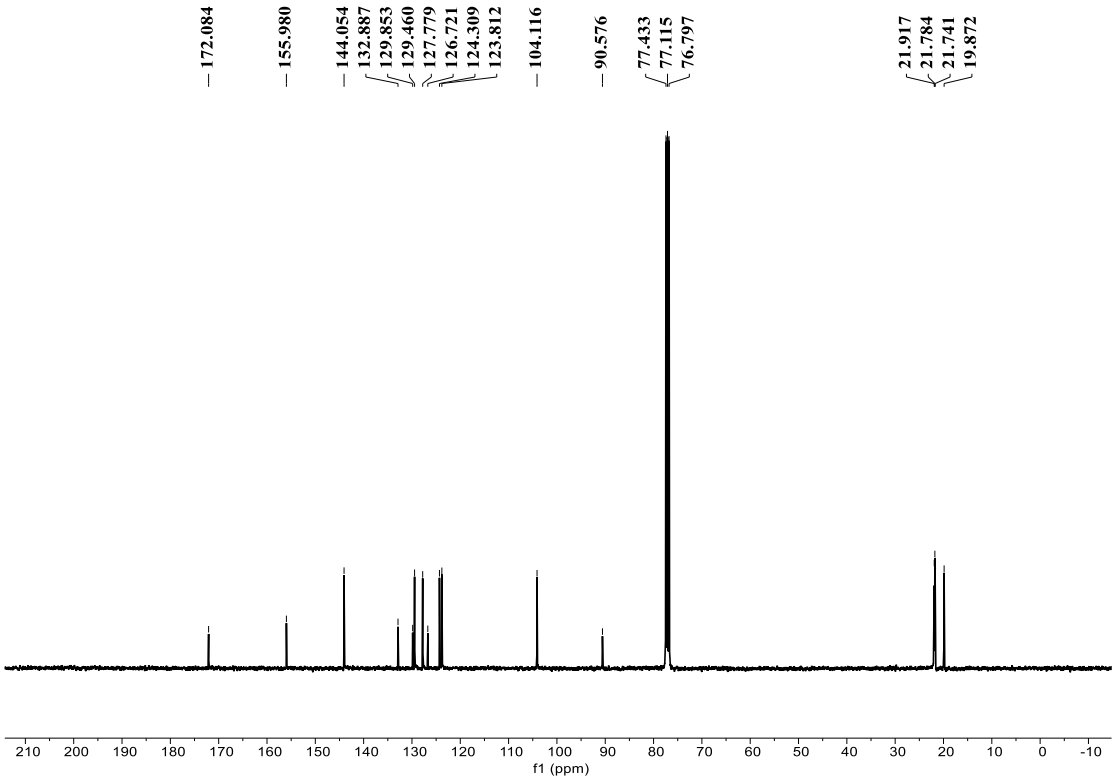
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3q**



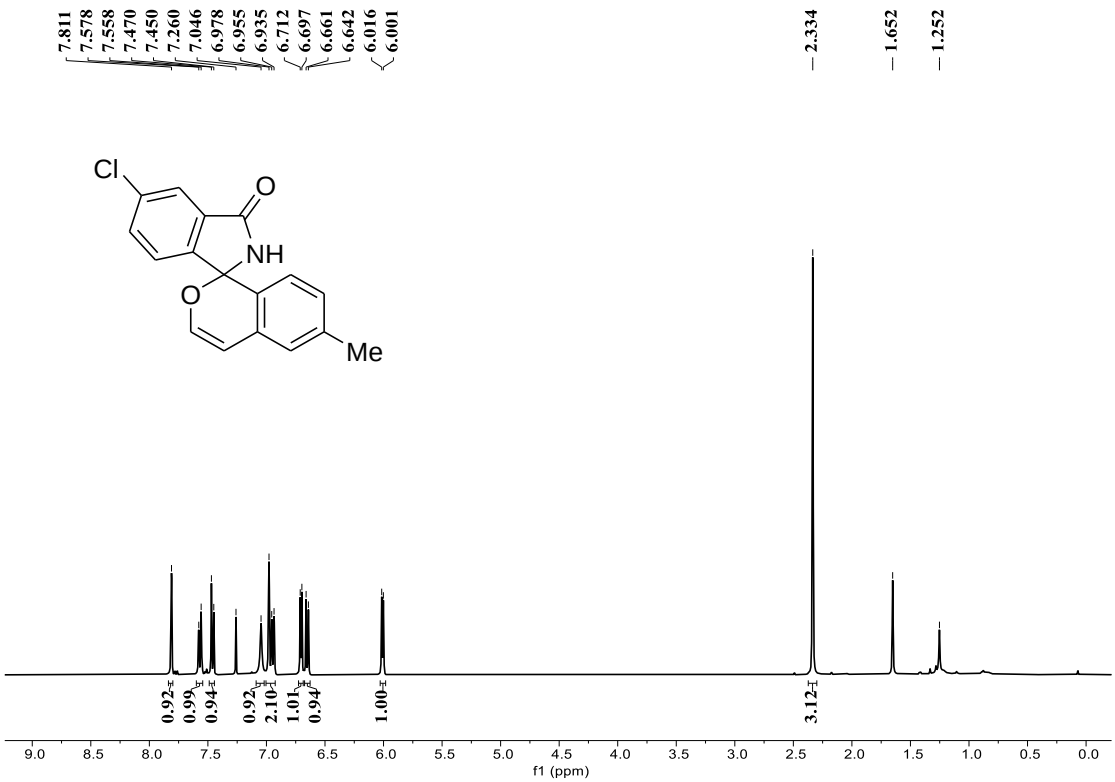
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3q**



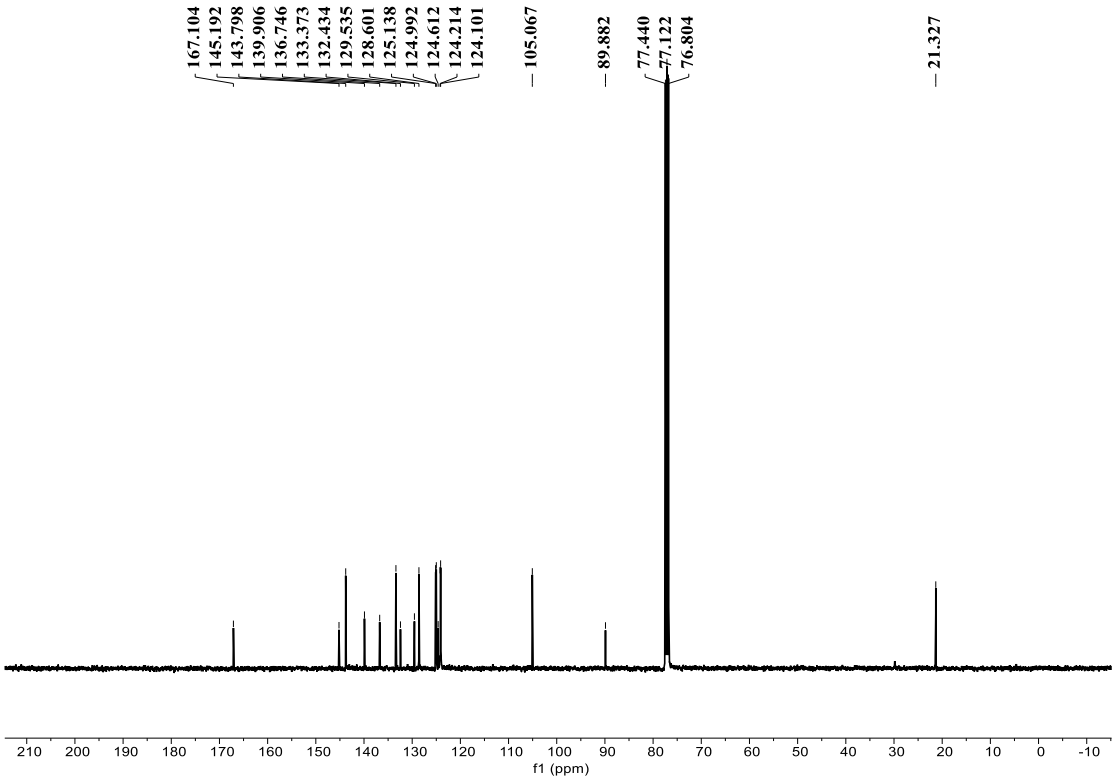
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3r**



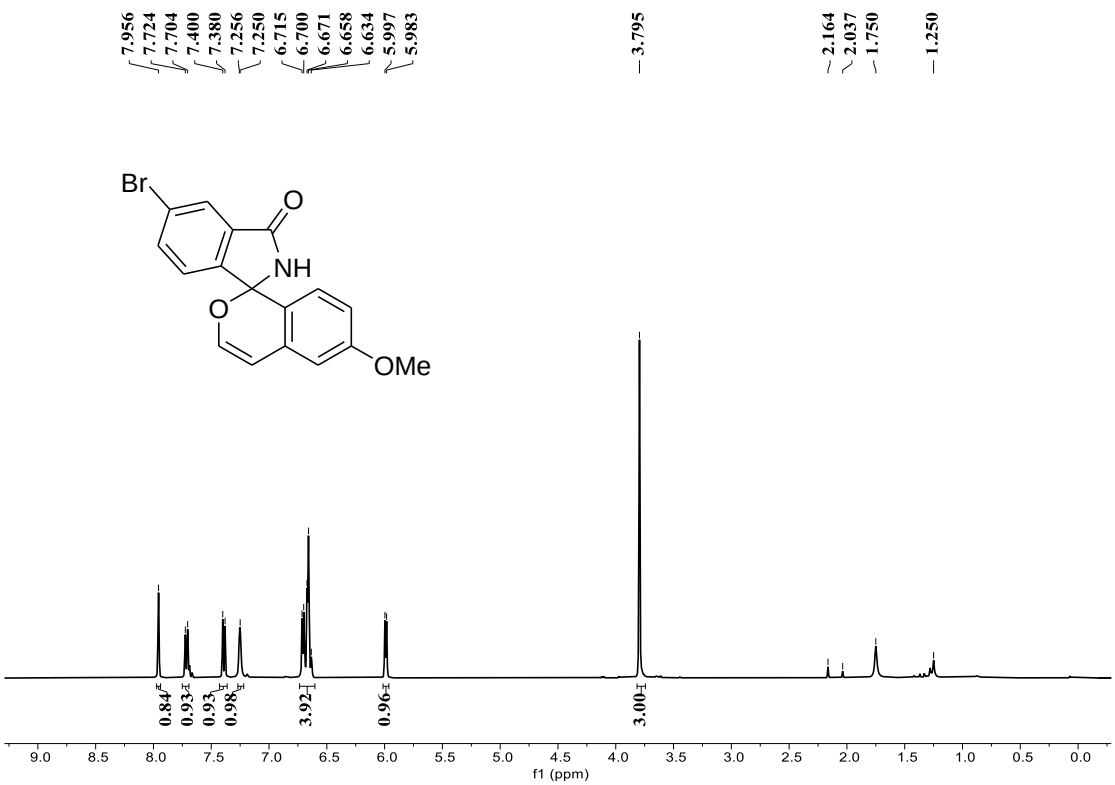
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3r**



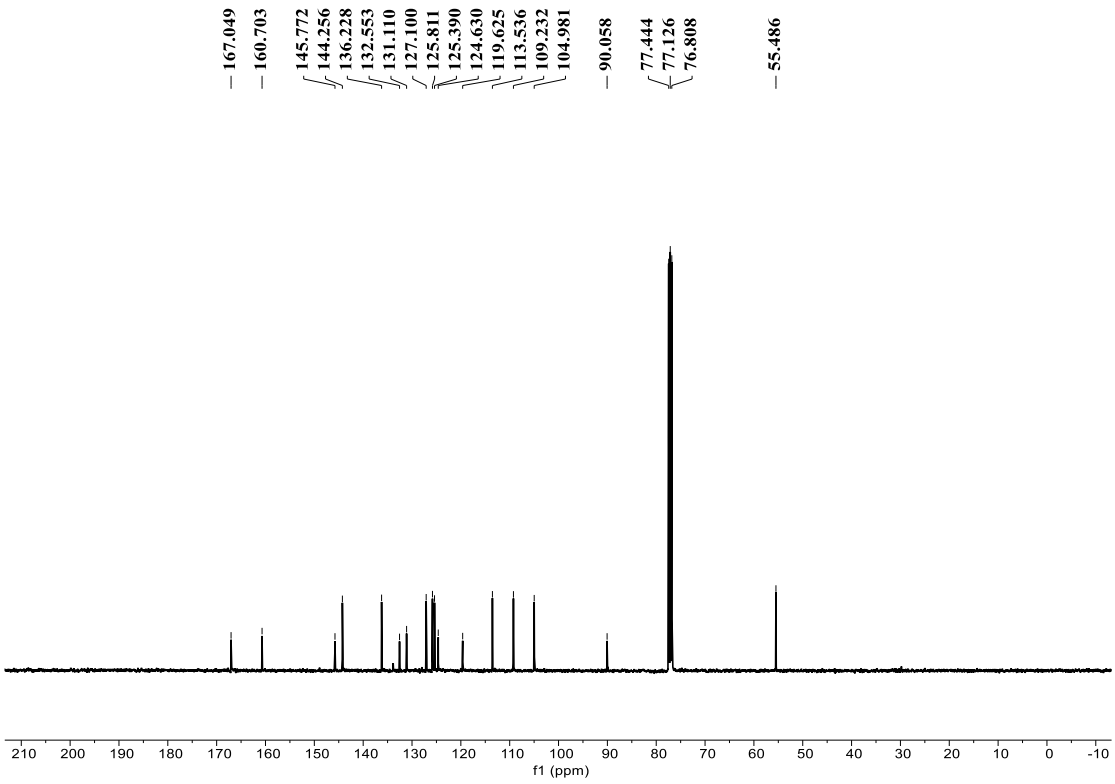
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3t**



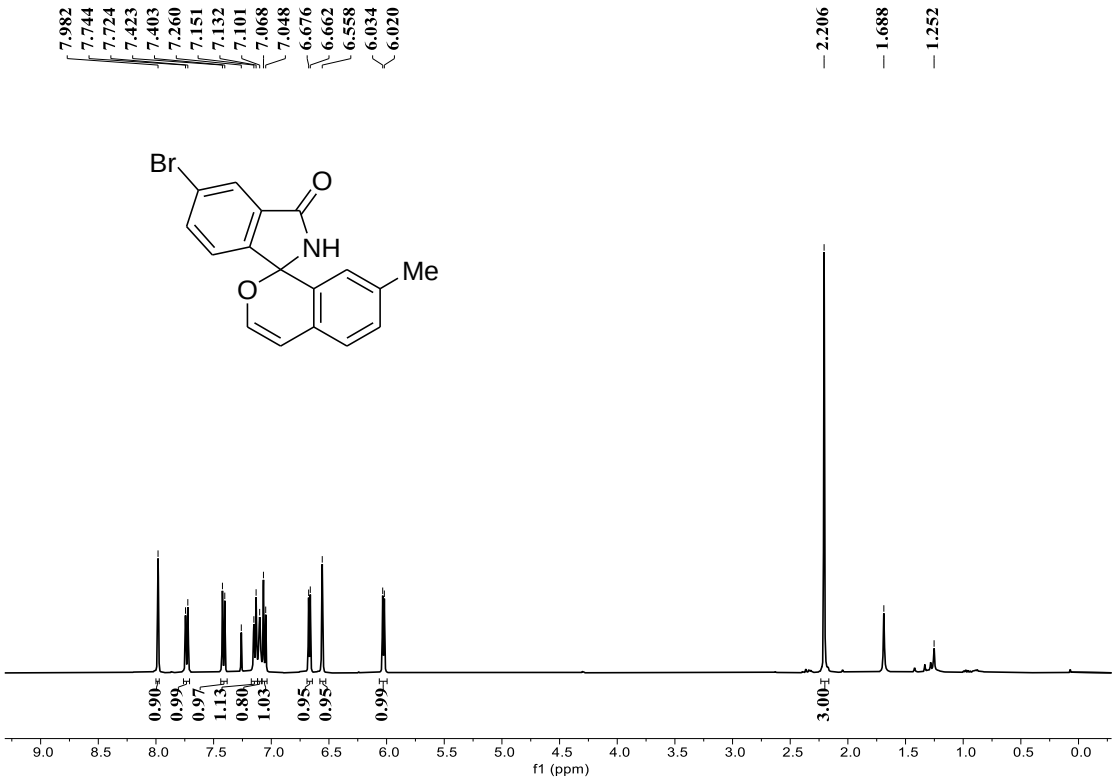
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3t**



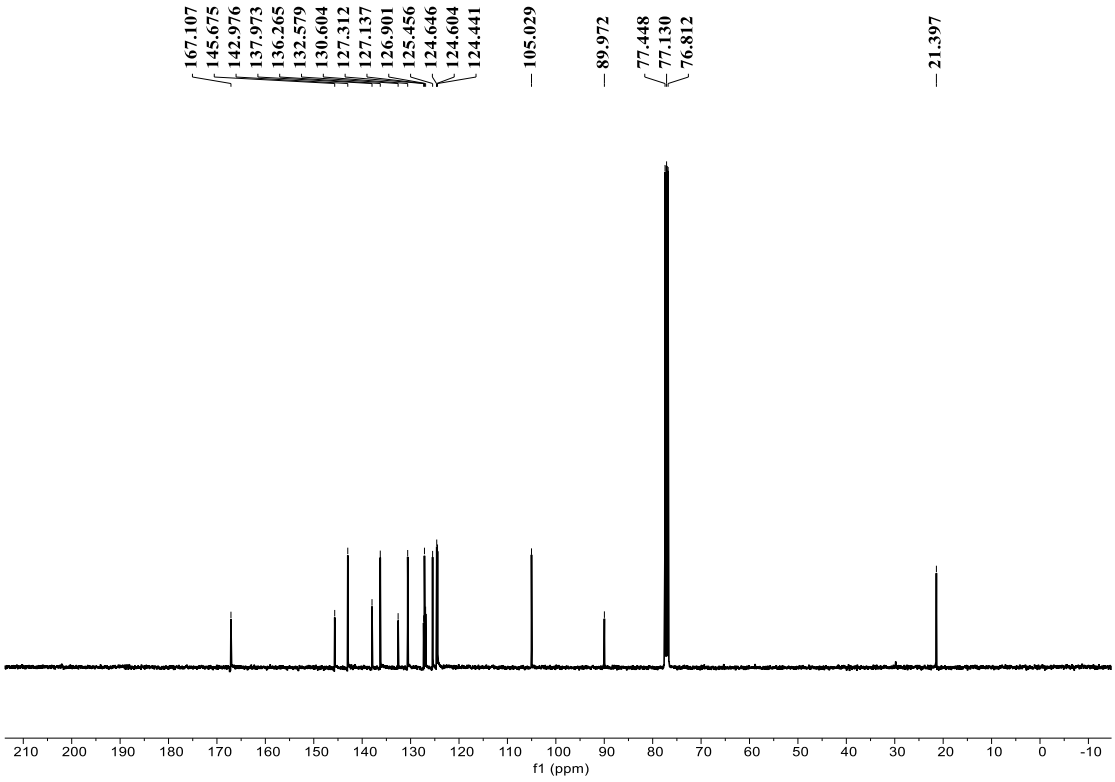
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3u**



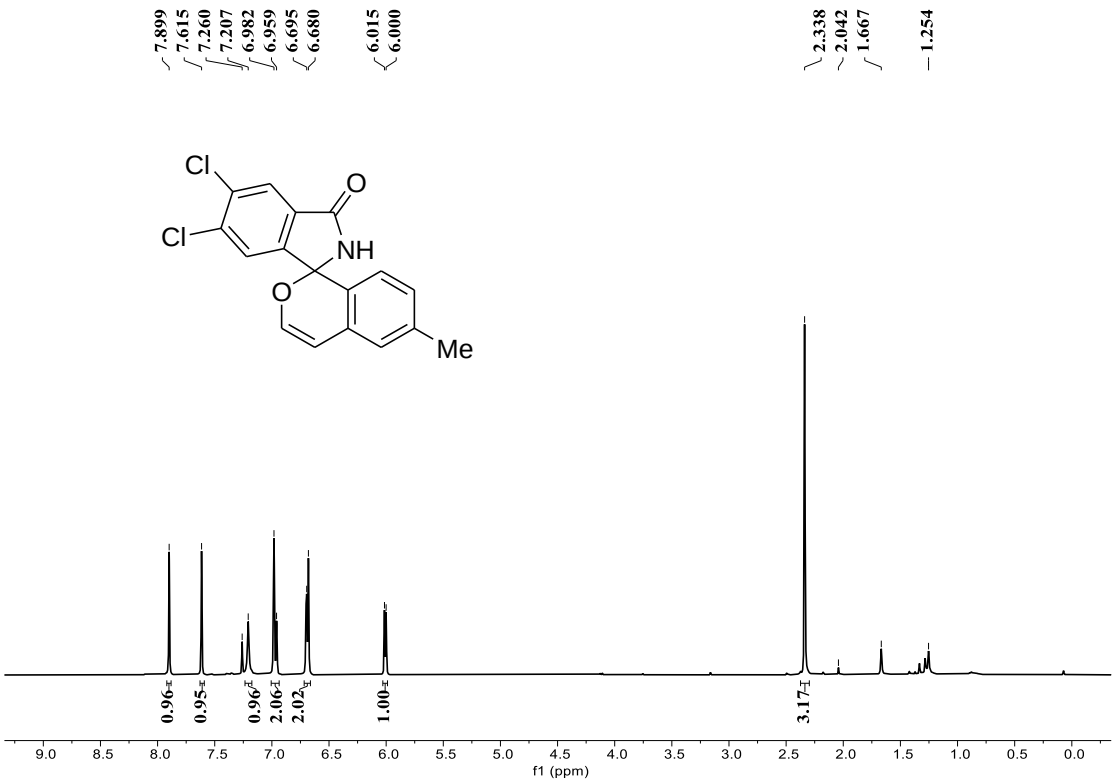
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3u**



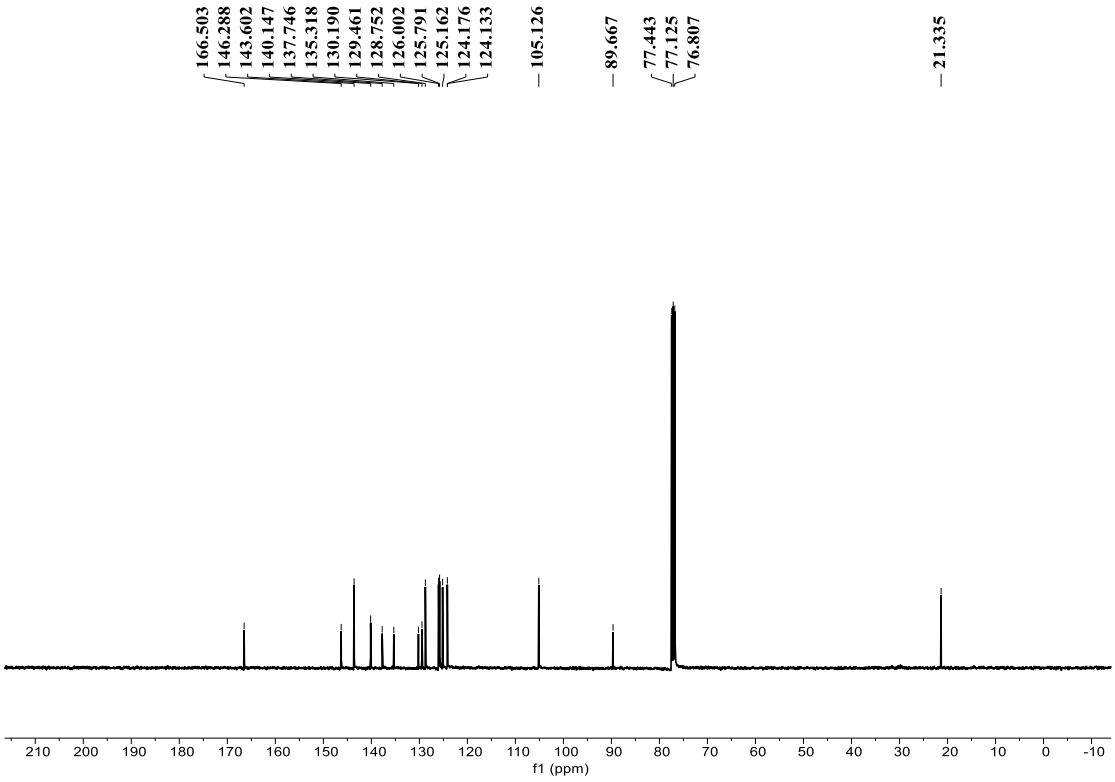
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3v**



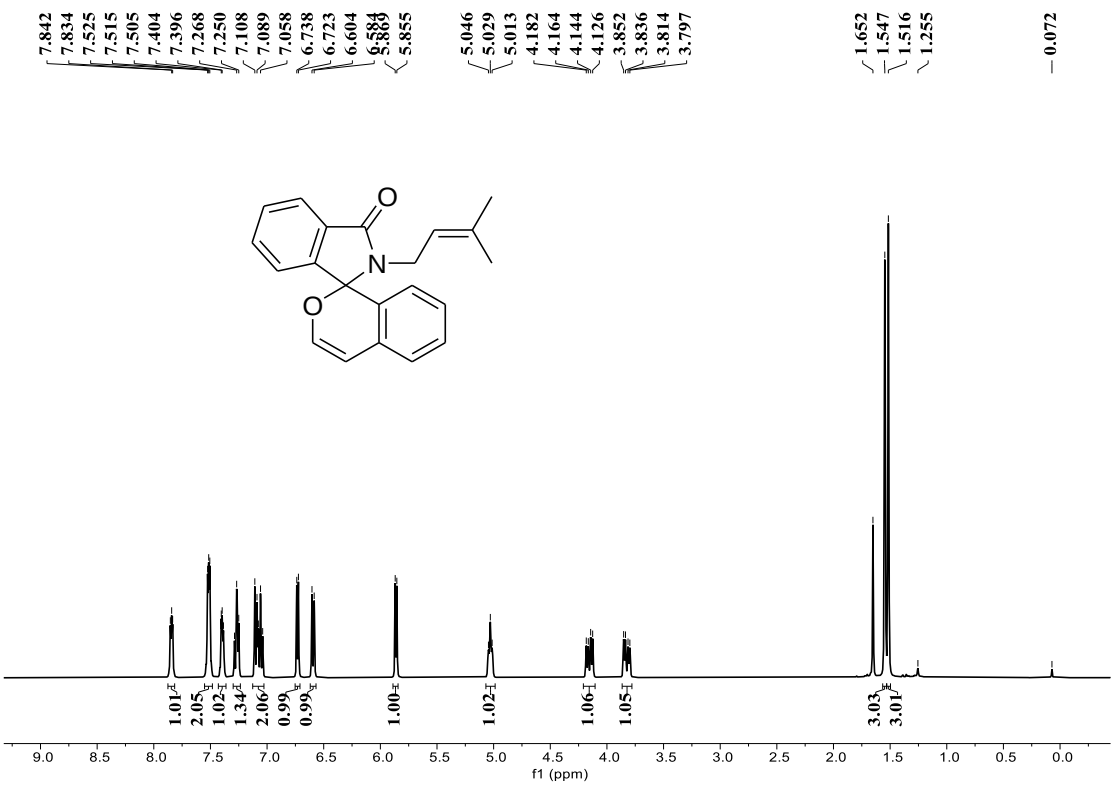
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3v**



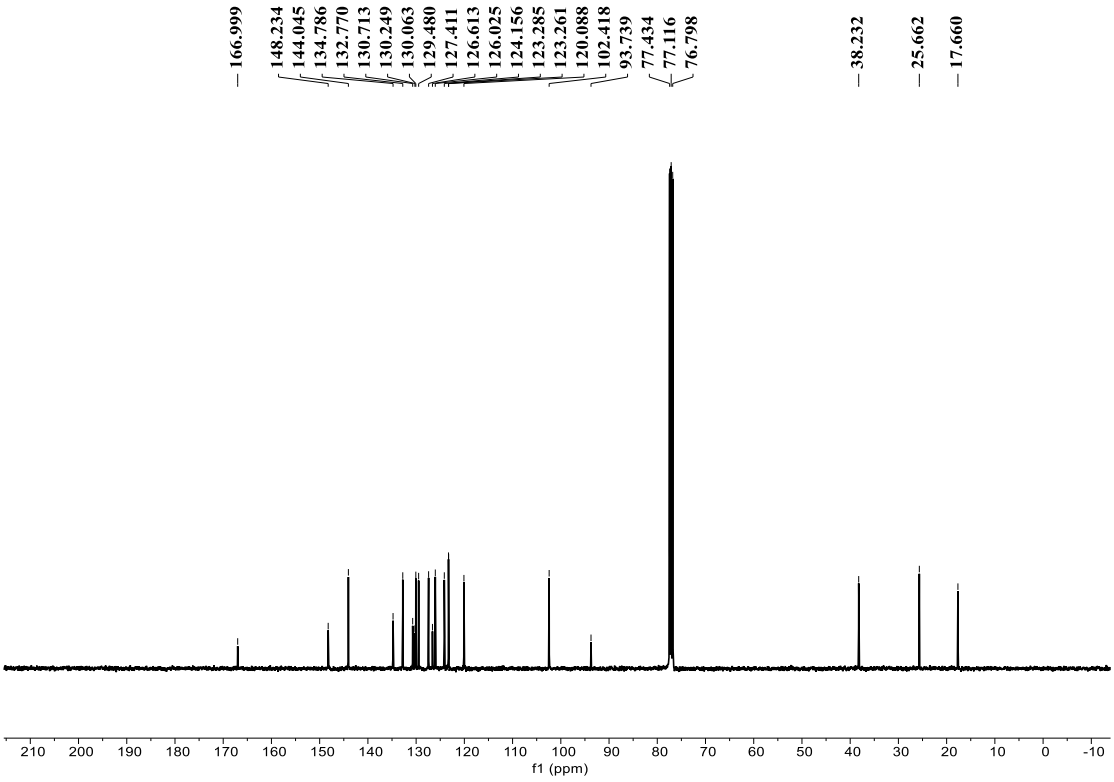
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3w**



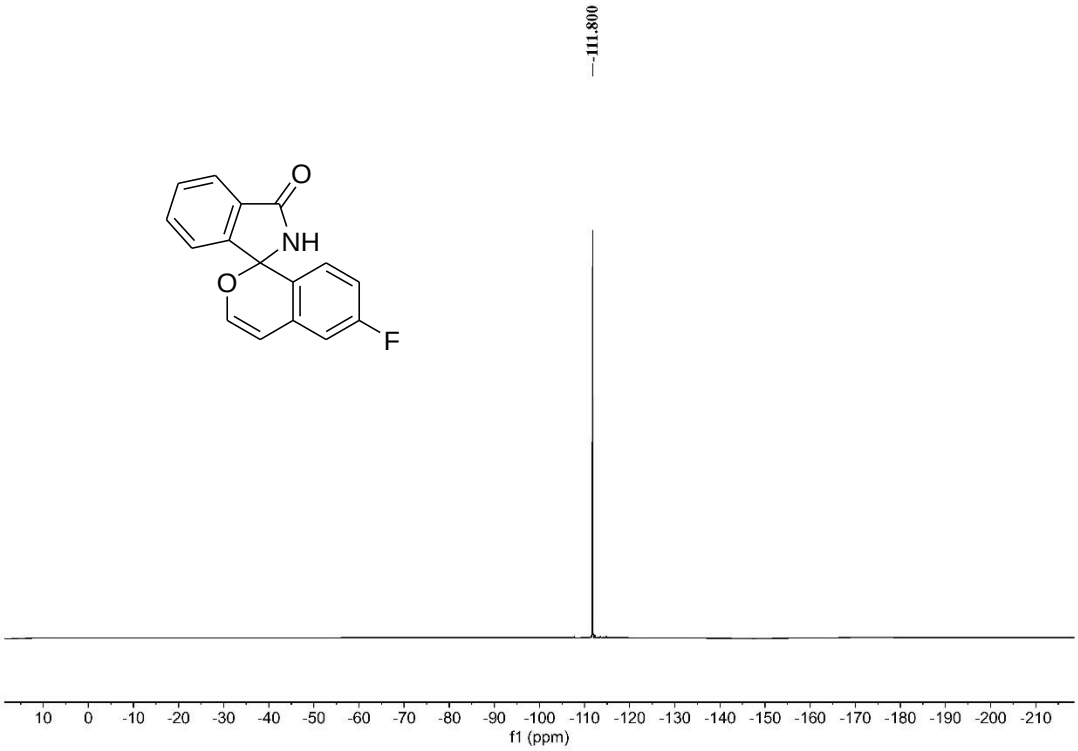
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3w**



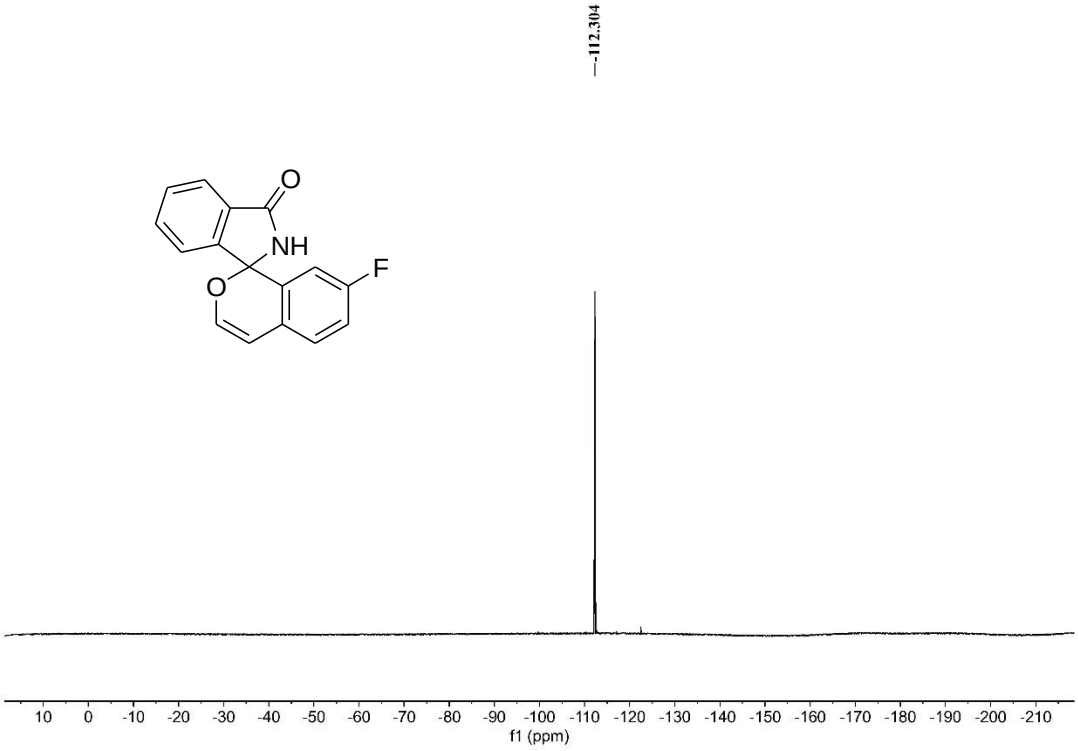
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **5**



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



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



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