Supporting Information

NHC Catalyzed Oxidative γ-Addition of α,β-unsaturated Aldehyde to Isatins: A High-efficiency Synthesis of Spirocyclic Oxindole-dihydropyranones

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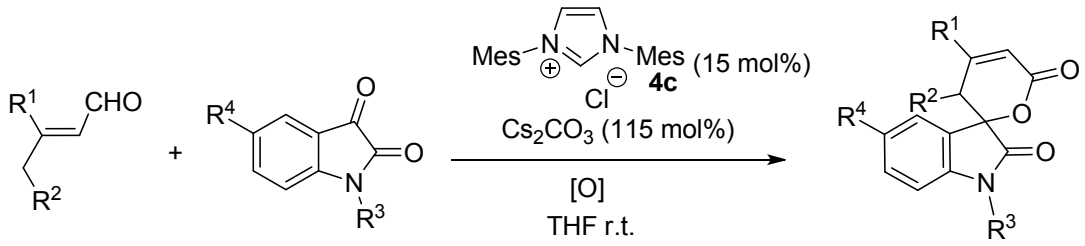
1 General methods

Common reagents and materials were purchased from commercial sources and purified by recrystallization or distillation. Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a FT-IR-Tensor 27 spectrometer in KBr pellets and reported in cm^{-1}. ^1H NMR spectra were measured on a Bruker DPX 400 MHz spectrometer in DMSO-d_6 (100 MHz, ^{13}C NMR) or $CDCl_3$ with chemical shift (δ) given in ppm relative to TMS as internal standard. High-resolution mass spectra (HRMS) were obtained on a micrOTOF-QⅡ HRMS/MS instrument (Bruker) with the technique of electrospray ionization.

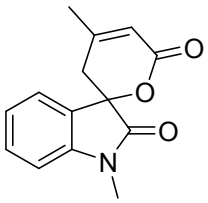
2. Experimental section



Into an oven-dried 25 mL vial were weighed precatalyst **4c** (25.5 mg, 15 mol %) and Cs_2CO_3 (186.9 mg, 115 mol %). THF (5 mL) was added to the mixture. The resulting mixture was stirred at room temperature for 5 min followed by the addition of a solution of 3-methylbut-2-enal (0.5 mmol), isatins **2** (0.5 mmol) and 3,3′,5,5′-tetra-tert-butyldiphenoquinone (203 mg), in THF (3 mL). The mixture was stirred at room temperature until completion (monitored by TLC). After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (silica gel, mixtures of ethyl acetate / petroleum ether, 1:3, v/v).

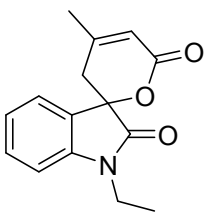
3. Spectral data for all compounds

Compound 3a: 1,4'-dimethylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione



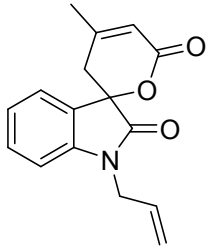
White solid; M.P: 178-179 ^oC (reported 178-180 ^oC[1]); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J_1 = 7.6 Hz, J_2= 0.6 Hz, 1H, ArH), 7.39 (td, J_1 = 8.0 Hz, J_2= 1.2 Hz, 1H, ArH), 7.07 (td, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H, ArH), 6.88 (d, J = 8.0 Hz, 1H, ArH), 6.06 (q, J = 1.6 Hz, 1H, CH=), 3.20 (s, 3H, NCH_3), 2.87 (ddd, J_1 = 18.0 Hz, J_2 = 1.6 Hz, J_3 = 0.8 Hz, 1H, *H*CH), 2.63 (d, J = 18.4 Hz, 1H, HC*H*), 2.08 (d, J = 1.2 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 162.7, 154.2, 143.2, 131.0, 127.9, 123.9, 123.4, 116.5, 108.9, 79.6, 35.1, 26.4, 23.2; IR (potassium bromide) (v, cm^{-1}): 1725, 1616, 1472, 1420, 1374, 1349, 1255, 1133, 1092, 1005, 752; HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{14}H_{13}NNaO_3$: 266.0793, found: 266.0750.

Compound 3b: ethyl-4'-methylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione



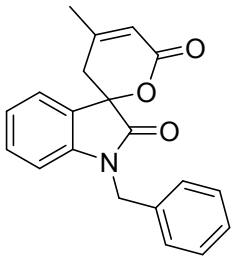
White solid; M.P: 84-86 ^{o}C (reported 84-86 ^{o}C[1]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.2 Hz, 1H, ArH), 7.35 (td, J_1 = 7.6 Hz, J_2= 0.8 Hz, 1H, ArH), 7.05 (t, J = 7.6 Hz, 1H, ArH), 6.87 (d, J = 7.6 Hz, 1H, ArH), 6.05 (d, J =1.2 Hz, 1H, CH=), 3.77-3.70 (m, 2H, NCH_2), 2.88 (d, J = 18.4 Hz, 1H, *H*CH), 2.59 (d, J = 18.0 Hz, 1H, HC*H*), 2.05 (s, 3H, CH_3), 1.28 (t, J = 7.2 Hz, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 162.8, 154.3, 142.2, 131.0, 128.2, 124.1, 123.2, 116.5, 109.0, 79.6, 35.2, 35.0, 23.2, 12.4; IR (potassium bromide) (v, cm^{-1}): 1721, 1611, 1490, 1469, 1377, 1353, 1227, 1138, 1081, 1017, 844, 757, 595; HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{15}H_{15}NNaO_3$: 280.0950, found: 280.0930.

Compound 3c: allyl-4'-methylspiro[indoline-3,2'-pyran]-2,6'(3'*H*)-dione



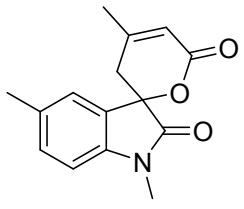
White solid; M.P: 93-95 ^{o}C (reported 98-99 ^{o}C[1]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.2 Hz, 1H, ArH), 7.34 (t, J = 7.6 Hz, 1H, ArH), 7.06 (t, J = 7.2 Hz, 1H, ArH), 6.85 (d, J = 7.6 Hz, 1H, ArH), 6.06 (s, 1H, CH=), 5.83-5.80 (m, 1H, CH=), 5.26 (d, J = 13.6 Hz, 2H, CH_2=), 4.31 (d, J = 1.2 Hz, 2H, CH_2), 2.88 (d, J = 18.0 Hz, 1H, *H*CH), 2.62 (d, J = 18.4 Hz, 1H, HC*H*), 2.06 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 162.7, 154.2, 142.3, 130.9, 130.6, 127.9, 123.9, 123.4, 118.2, 116.6, 109.8, 79.6, 42.6, 35.3, 23.2; IR (potassium bromide) (v, cm^{-1}): 2985, 2919, 1727, 1646, 1612, 1467, 1378, 1243, 1086, 760; HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{16}H_{15}NNaO_3$: 292.0950, found: 292.0927.

Compound 3d: benzyl-4'-methylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione



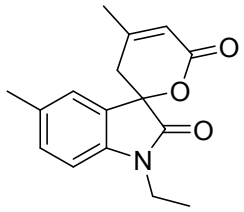
White solid; M.P: 136-138 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J_1 = 7.2 Hz, J_2 = 0.4 Hz, 1H, ArH), 7.36-7.25 (m, 6H, ArH), 7.05 (td, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H, ArH), 6.75 (d, J = 7.6 Hz, 1H, ArH), 6.11 (dd, J_1 = 2.8 Hz, J_2 = 1.2 Hz, 1H, CH=), 4.90 (s, 2H, Ar-CH_2), 2.97 (dd, J_1 = 18.0 Hz, J_2 = 0.4 Hz, *H*CH), 2.67 (d, J = 18.0 Hz, 1H, HC*H*), 2.10 (s, 3H, CH_3); ^{13} C NMR (100 MHz, $CDCl_3$) δ 172.9, 162.8, 154.5, 142.2, 135.0, 130.9, 129.0, 128.0, 127.9, 127.3, 124.0, 123.5, 116.5, 110.0, 79.7, 43.9, 35.3, 23.2; IR (potassium bromide) (v, cm^{-1}) IR (potassium bromide) (v, cm^{-1}): 3677, 3650, 2888, 1734, 1610, 1489, 1348, 1249, 1073, 820, 859; HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{20}H_{17}NNaO_3$: 342.1106, found: 342.1092.

Compound 3e: 1,4',5-trimethylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione



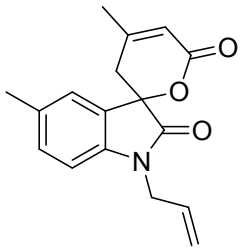
White solid; M.P: 170-172 °C (reported 173-176 °C[1]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H, ArH), 7.17 (d, *J* = 8.0 Hz, 1H, ArH), 6.74 (d, *J* = 8.0 Hz, 1H, ArH), 6.05 (d, *J* = 1.2 Hz, 1H, CH=), 3.17 (s, 3H, CH_3), 2.86 (d, *J* = 18.0 Hz, 1H, *H*CH), 2.60 (d, *J* = 18.4 Hz, 1H, HC*H*), 2.31 (s, 3H, CH_3), 2.05 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 162.8, 154.3, 140.7, 133.1, 131.2, 128.0, 124.6, 116.5, 108.7, 79.8, 35.2, 26.4, 23.2, 21.0; IR (potassium bromide) (*v*, cm^{-1}): 2914, 1718, 1627, 1607, 1505, 1470, 1352, 1256, 1101, 811; HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{15}H_{15}NNaO_3$: 280.0950, found: 280.0944.

Compound 3f: ethyl-4',5-dimethylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione



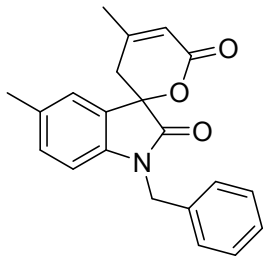
White solid; M.P: 101-102 °C (reported 101-104 °C[1]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H, ArH), 7.17 (d, *J* = 8.0 Hz, 1H, ArH), 6.74 (d, *J* = 8.0 Hz, 1H, ArH), 6.05 (d, *J* = 1.2 Hz, 1H, CH=), 3.17 (s, 3H, CH_3), 2.86 (d, *J* = 18.0 Hz, 1H, *H*CH), 2.60 (d, *J* = 18.4 Hz, 1H, HC*H*), 2.31 (s, 3H, CH_3), 2.05 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 162.9, 154.4, 139.8, 132.9, 131.1, 128.2, 124.8, 116.5, 108.8, 79.8, 35.2, 35.0, 23.2, 21.0, 12.4; IR (potassium bromide) (*v*, cm^{-1}): 2983, 2946, 1713, 1623, 1605, 1496, 1375, 1252, 847, 689; HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{16}H_{17}NNaO_3$: 294.1106, found: 294.1092.

Compound 3g: allyl-4',5-dimethylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione



White solid; M.P: 108-110 °C (reported 108-110 °C[1]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (s, 1H, ArH), 7.13 (d, *J* = 8.0 Hz, 1H, ArH), 6.74 (d, *J* = 8.0 Hz, 1H, ArH), 6.07 (s, 1H, CH=), 5.26 (d, *J* = 1.2 Hz, CH=), 5.23 (dd, J_1 = 2.8 Hz, J_2= 0.8 Hz, 1H, CH=), 4.29 (d, *J* = 4.0 Hz, 2H, NCH_2), 2.89 (d, *J* = 18.4 Hz, 1H, *H*CH), 2.61 (d, *J* = 18.4 Hz, 1H, HC*H*), 2.30 (s, 3H, CH_3), 2.06 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 162.8, 154.3, 139.9, 133.1, 131.1, 130.7, 128.0, 124.7, 118.1, 116.5, 109.6, 79.7, 42.5, 35.3, 23.2, 21.0; IR (potassium bromide) (*v*, cm^{-1}): 2982, 2917, 1731, 1645, 1618, 1493, 1373, 1249, 1170, 996, 926, 825; HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{17}H_{17}NNaO_3$: 306.1106, found: 306.1088.

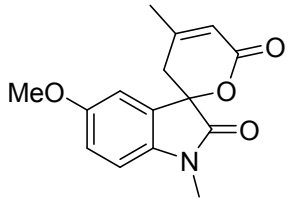
Compound 3h: benzyl-4',5-dimethylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione



White solid; M.P: 179-180 °C (reported 179-181 °C[1]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.22 (m, 6H, ArH), 7.03 (d, *J* = 8.0 Hz, 1H, ArH), 6.61 (d, *J* = 8.0 Hz, 1H, ArH), 6.08 (d, *J* = 1.6 Hz,

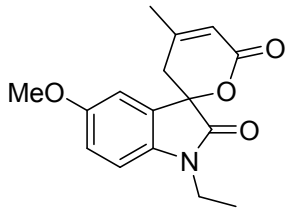
1H, CH=), 4.86 (s, 2H, CH_2), 2.93 (d, *J* = 18.4 Hz, 1H, *H*CH), 2.63 (d, *J* = 18.0 Hz, 1H, HC*H*), 2.27 (s, 3H, CH_3), 2.07 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 162.8, 154.3, 139.8, 135.0, 133.2, 131.1, 128.9, 128.0, 127.9, 127.2, 124.7, 116.6, 109.8, 79.8, 44.0, 35.4, 23.3, 21.0; IR (potassium bromide) (*v*, cm^{-1}): 1716, 1619, 1494, 1377, 1252, 1083, 999, 819, 721; HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{21}H_{19}NNaO_3$: 356.1263, found: 356.1245.

Compound 3i: 5-methoxy-1,4'-dimethylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione



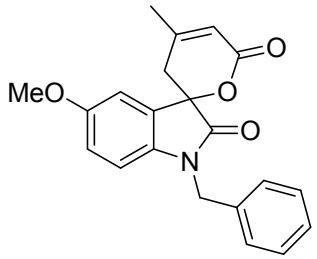
White solid; M.P: 174-176 °C (reported 175-178 °C[1]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 2.4 Hz, 1H, ArH), 6.88 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H, ArH), 6.76 (d, *J* = 8.4 Hz, 1H, ArH), 6.05 (s, 1H, CH=), 3.78 (s, 3H, OCH_3), 3.17 (s, 3H, NCH_3), 2.85 (d, *J* = 18.4 Hz, 1H, *H*CH), 2.60 (d, *J* = 18.0 Hz, 1H, HC*H*), 2.05 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 162.7, 156.4, 154.3, 136.4, 129.0, 116.5, 114.9, 111.6, 109.4, 79.9, 55.9, 35.2, 26.5, 23.2; IR (potassium bromide) (*v*, cm^{-1}): 3410, 3015, 2944, 2842, 1715, 1613, 1151, 1472, 1433, 1362, 1255, 1131, 1027, 810, 690; HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{15}H_{15}NNaO_4$: 296.0899, found: 296.0865.

Compound 3j: ethyl-5-methoxy-4'-methylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione



White solid; M.P: 119-121 °C (reported 115-118 °C[1]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (s, 1H, ArH), 6.88 (d, *J* = 8.0 Hz, 1H, ArH), 6.78 (d, *J* = 8.4 Hz, 1H, ArH), 6.04 (s, 1H, CH=), 3.77 (s, 3H, OCH_3), 3.74-3.67 (m, 2H, C*H*$_2$CH$_3$), 2.87 (d, *J* = 18.4 Hz, 1H, *H*CH), 2.58 (d, *J* = 18.4 Hz, 1H, HC*H*), 2.05 (s, 3H, CH_3), 1.26 (t, *J* = 6.4 Hz, 3H, CH_2CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 162.7, 156.2, 154.3, 135.4, 129.3, 116.5, 114.9, 111.7, 109.5, 79.9, 55.9, 35.2, 35.1, 23.2, 12.4; IR (potassium bromide) (*v*, cm^{-1}): 3067, 2984, 2935, 2838, 1718, 1604, 1499, 1461, 1212, 1026, 860, 809; HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{16}H_{17}NNaO_4$: 310.1055, found: 310.1030.

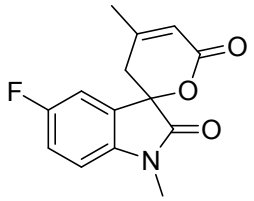
Compound 3k: benzyl-5-methoxy-4'-methylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione



White solid; M.P: 144-145 °C (reported 147-149 °C[1]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 5H, ArH), 7.02 (d, *J* = 2.4 Hz, 1H, ArH), 6.75 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H, ArH), 6.62 (d, *J* = 8.8 Hz, 1H, ArH), 6.07 (d , *J* = 1.2 Hz, 1H, CH=), 4.85 (s, 2H, CH_2), 3.73 (s, 3H, OCH_3), 2.93 (d, *J* = 18.0 Hz, 1H, *H*CH), 2.64 (d, *J* = 18.0 Hz, 1H, HC*H*), 2.07 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 162.7, 156.4, 154.2, 135.4, 135.0, 129.1, 128.9, 127.9, 127.3, 116.6, 114.9, 111.5, 110.5, 79.9, 55.9, 44.1, 35.4, 23.3; IR (potassium bromide) (*v*, cm^{-1}): 3056, 2943, 1721,

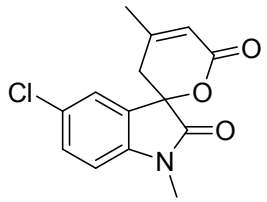
1608, 1499, 1435, 1345, 1244, 1172, 1029, 848, 699; HRMS (ESI) m/z: Calcd. for $[M+H]^+$ $C_{21}H_{20}NO_4$: 350.1392, found: 350.1381.

Compound 3l: fluoro-1,4'-dimethylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione



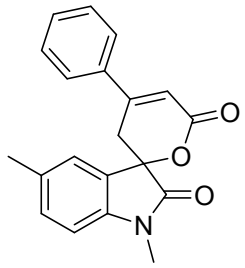
White solid; M.P: 195-196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, J_1 = 7.6 Hz, J_2 = 2.8 Hz, 1H, ArH), 7.11 (td, J_1 = 8.8 Hz, J_2 = 2.8 Hz, 1H, ArH), 6.82 (dd, J_1 = 8.8 Hz, J_2 = 4.0 Hz, 1H, ArH), 6.08 (dd, J_1 = 8.8 Hz, J_2 = 4.0 Hz, 1H, CH=), 3.21 (s, 3H, NCH_3), 2.90 (d, J = 18.0 Hz, 1H, *H*CH), 2.60 (d, J = 18.4 Hz, 1H, HC*H*), 2.08 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 159.2 ($J_{C\text{-}F}$ = 241.5 Hz), 162.2, 154.1, 139.1 ($J_{C\text{-}F}$ = 2.2 Hz), 129.1 ($J_{C\text{-}F}$ = 7.8 Hz), 117.2 ($J_{C\text{-}F}$ = 23.4 Hz), 116.5, 112.2 ($J_{C\text{-}F}$ = 25.3 Hz), 109.6 ($J_{C\text{-}F}$ = 7.9 Hz), 79.5, 35.0, 26.6, 23.2; IR (potassium bromide) (v, cm^{-1}): 2948, 1652, 1557, 1494, 1470, 1421, 1411, 1382, 806, 757, 690; HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{14}H_{12}FNNaO_3$: 284.0699, found: 284.0699.

Compound 3m: 5-chloro-1,4'-dimethylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione



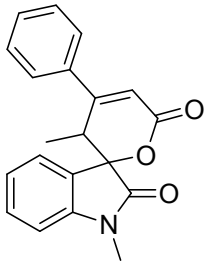
White solid; M.P: 190-192 °C (reported 190-193 °C[1]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, J = 2.0 Hz, 1H, ArH), 7.36 (dd, J_1= 8.4 Hz, J_2= 2.4 Hz, 1H, ArH), 6.80 (d, J =8.4 Hz, 1H, ArH), 6.08 (dd, J_1= 2.8 Hz, J_2= 1.2 Hz, 1H, CH=), 3.19 (s, 3H, CH_3), 2.87 (d, J =18.0 Hz, 1H, *H*CH), 2.59 (d, J = 18.4 Hz, 1H, HC*H*), 2.06 (d, J= 0.8 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 162.2, 154.1, 141.7, 130.9, 129.4, 128.8, 124.5, 116.5, 110.0, 79.4, 34.9, 26.6, 23.3; IR (potassium bromide) (v, cm^{-1}): 3630, 2888, 1734, 1610, 1489, 1472, 1348, 1249, 1089, 1073, 859, 820, 547; HRMS (ESI) m/z: Calcd. for $[M+Na]^+$ $C_{14}H_{12}ClNNaO_3$: 300.0403, found: 300.0397.

Compound 3n: 1,5-dimethyl-4'-phenylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione



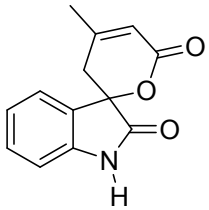
White solid; M.P: 191-194 °C (reported 198-199 °C[1]); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2H, ArH), 7.46-7.42 (m, 3H, ArH), 7.27 (s, 1H, ArH), 7.18 (d, J =7.6 Hz, 1H, ArH), 6.76 (d, J = 7.6 Hz, 1H, ArH), 6.59 (s, 1H, CH=), 3.34 (dd, J_1 = 17.6 Hz, J_2 = 1.6 Hz, 1H, *H*CH), 3.20 (s, 3H, CH_3), 3.09 (dd, J_1 = 17.6 Hz, J_2 = 0.8 Hz, 1H, HC*H*), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 158.1, 146.7, 135.5, 130.8, 128.0, 126.1, 125.7, 123.9, 122.6, 120.9, 119.6, 109.5, 103.5, 74.7, 27.3, 21.3, 15.8; IR (potassium bromide) (v, cm^{-1}): 1731, 1715, 1619, 1496, 1363, 1269, 1077, 760, 682; HRMS (ESI) m/z: Calcd. for $[M-H]^-$ $C_{20}H_{16}NO_3$: 318.1130, found: 318.1139.

Compound 3o: 1,3'-dimethyl-4'-phenylspiro[indoline-3,2'-pyran]-2,6'(3'H)-dione



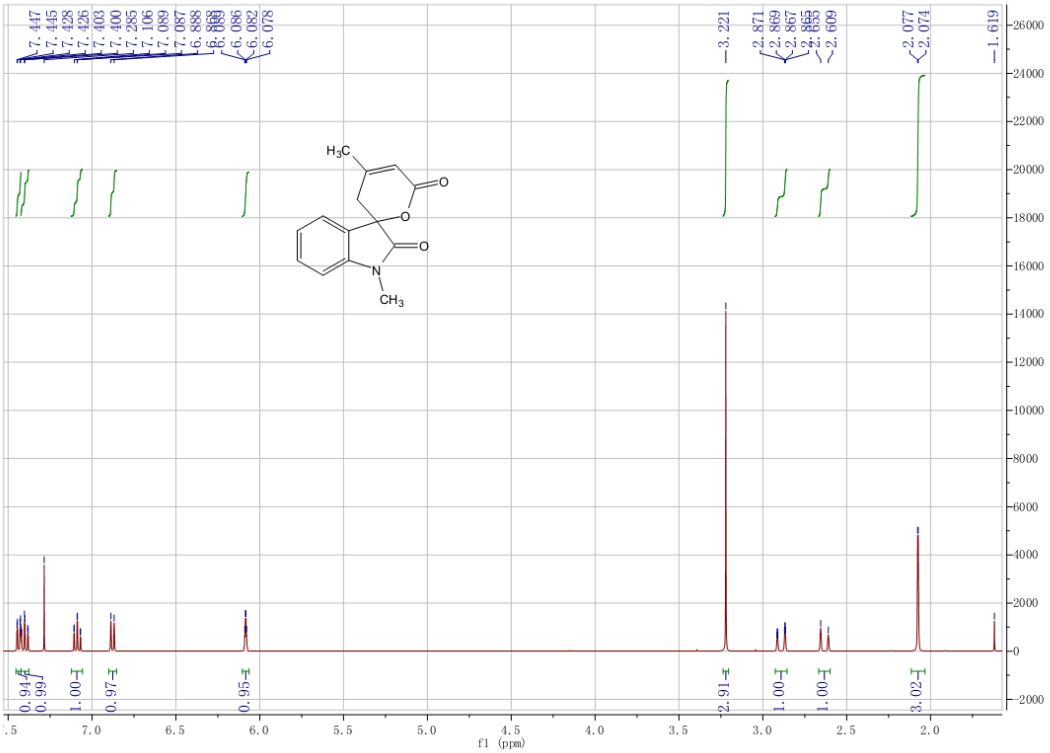
White solid; M.P: 167-170 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.37 (m, 7H, ArH), 7.03 (t, *J* =8.0 Hz, 1H, ArH), 6.88 (d, *J* = 8.0 Hz, 1H, ArH), 6.39 (s, 1H, CH=), 3.40 (q, *J* = 8.0 Hz, 1H, CH_3CH), 3.23 (s, 3H, NCH_3), 1.25 (d, *J* = 4.0 Hz, 3H, CH_3CH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 163.1, 159.0, 143.5, 136.1, 131.0, 130.3, 129.0, 128.0, 126.6, 124.0, 123.3, 115.5, 108.8, 82.6, 37.4, 26.4, 14.6; IR (potassium bromide) (*v*, cm^{-1}): 1732, 1447, 1491, 1372, 1254, 1164,1098, 691; HRMS (ESI) m/z: Calcd. for $[M+H]^+$ $C_{20}H_{18}NO_3$: 320.1287, found: 320.1277.

Compound 3p: 4'-methylspiro[indoline-3,2'-pyran]-6'(3'H)-one

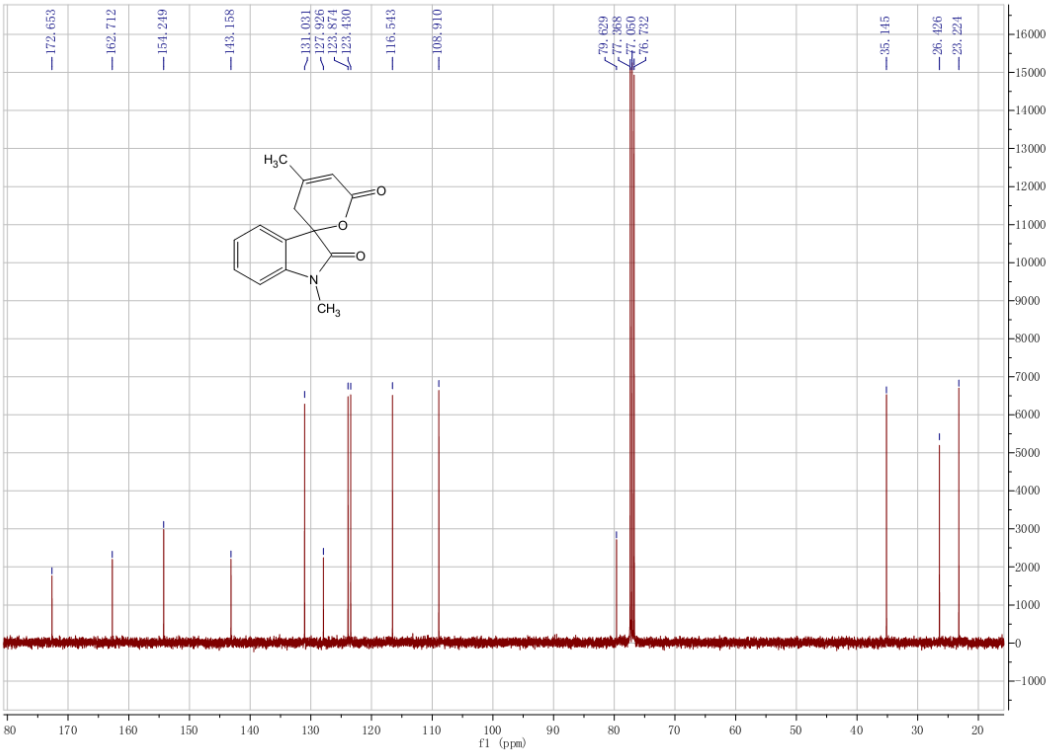


White solid; M.P: 217-219 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.72 (s, 1H, NH), 7.45 (d, *J* = 8.0 Hz, 1H, ArH), 7.34 (td, J_1 = 8.0 Hz, J_2= 1.2 Hz, 1H, ArH), 7.03 (td, J_1= 7.8 Hz, J_2= 0.8 Hz, 1H, ArH), 6.90 (d, *J* = 8.0 Hz, 1H, ArH), 5.99 (d, *J* = 1.2 Hz, 1H, CH=), 2.87 (d, *J* = 20.0 Hz, 1H, *H*CH), 2.78 (d, *J* = 20.0 Hz, 1H, HC*H*), 1.99 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ 174.6, 163.1, 156.7, 142.0, 131.3, 128.7, 124.7, 122.9, 115.5, 110.9, 80.3, 34.5, 23.1; IR (potassium bromide) (*v*, cm^{-1}): 3190, 3093, 2978, 1717, 1621, 1205, 1239, 1100, 840, 769; HRMS (ESI) m/z: Calcd. for $[M+H]^+$ $C_{13}H_{11}NO_3$: 230.0817, found: 230.0811.

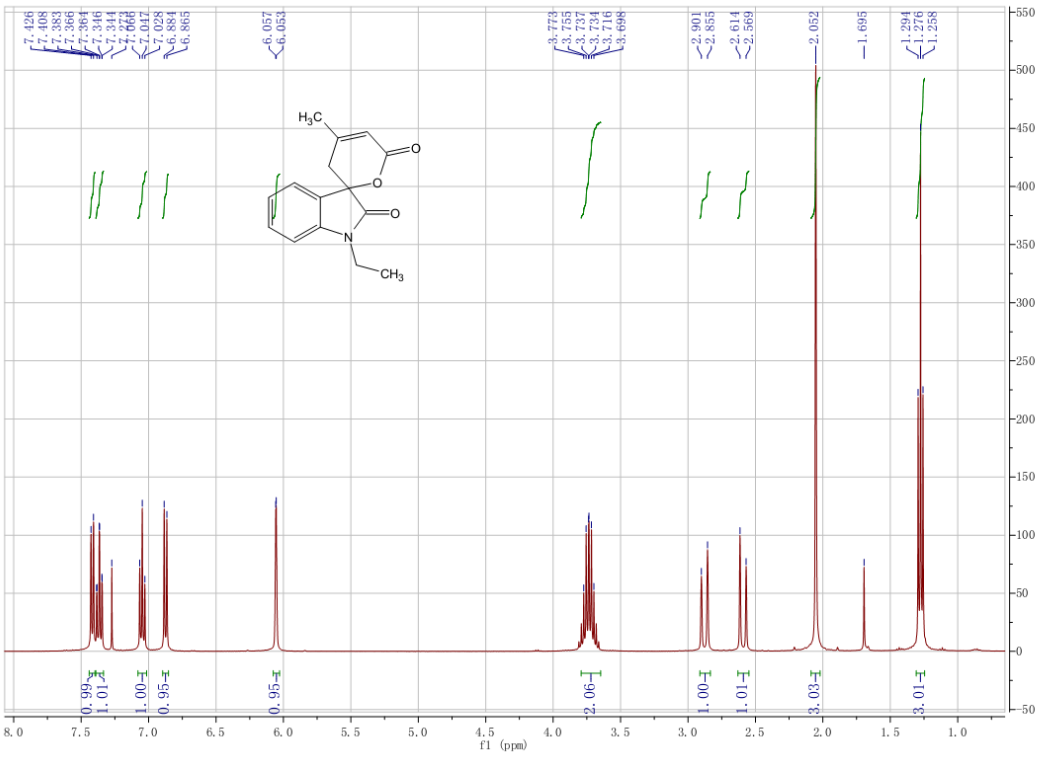
1. C. Yao, Z. Xiao; R. Liu, T. Li, W. Jiao and C. Yu, *Chem. Eur. J.*, 2013, **19**, 456.



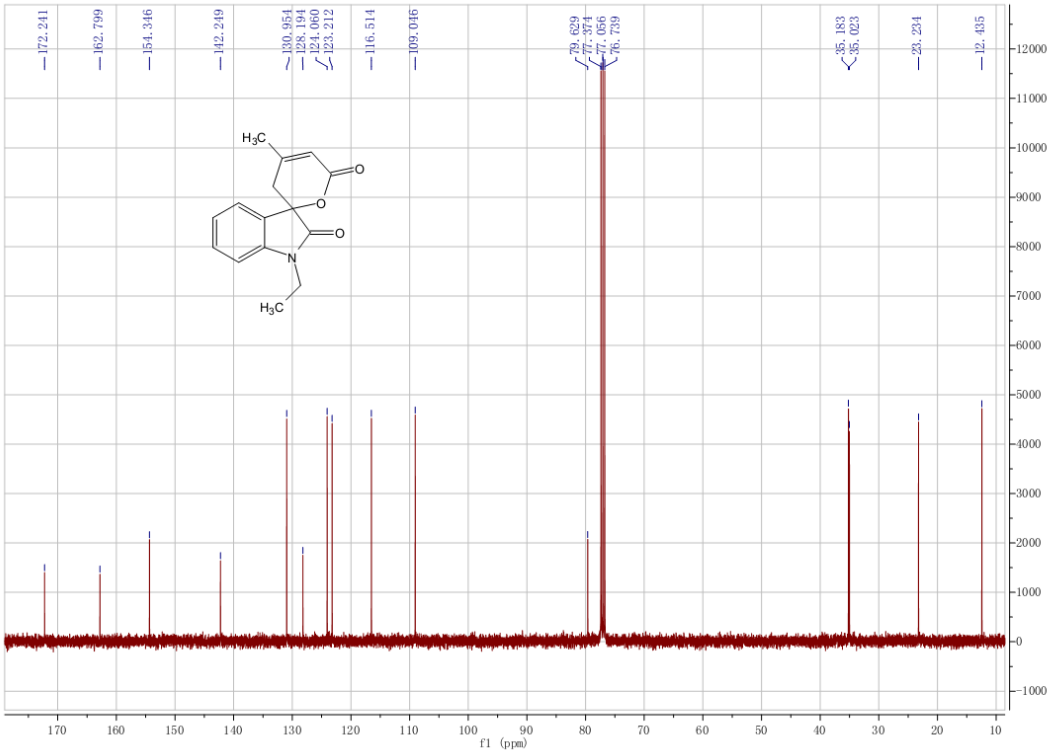
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3a**



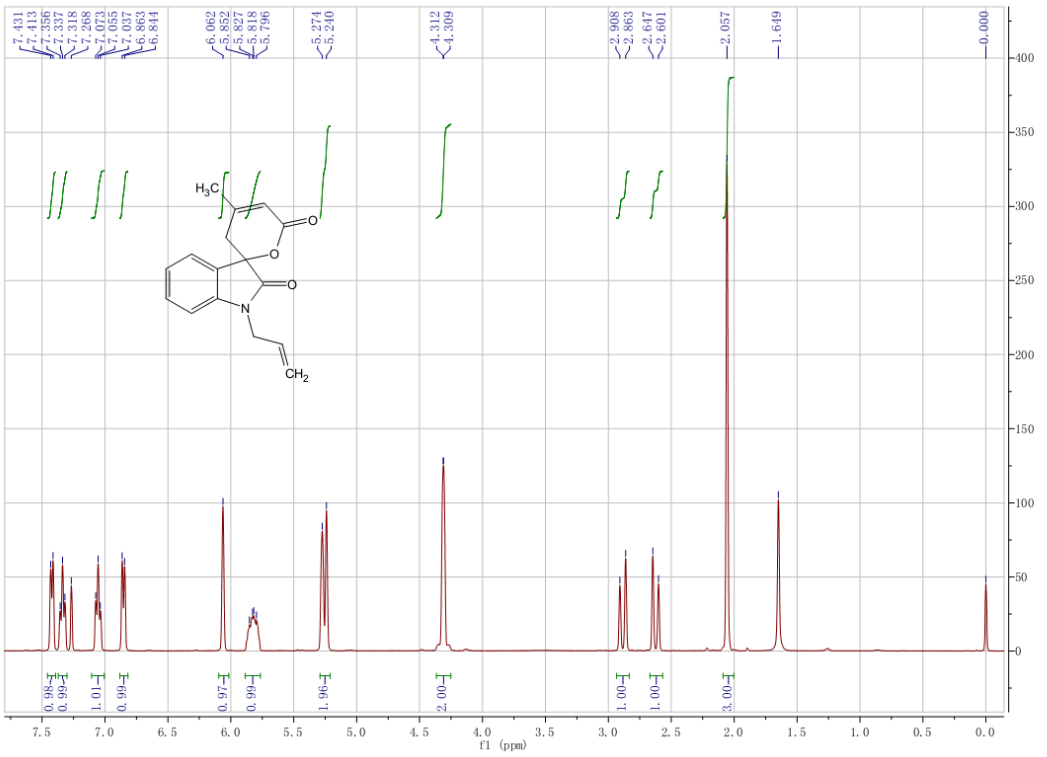
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3a**



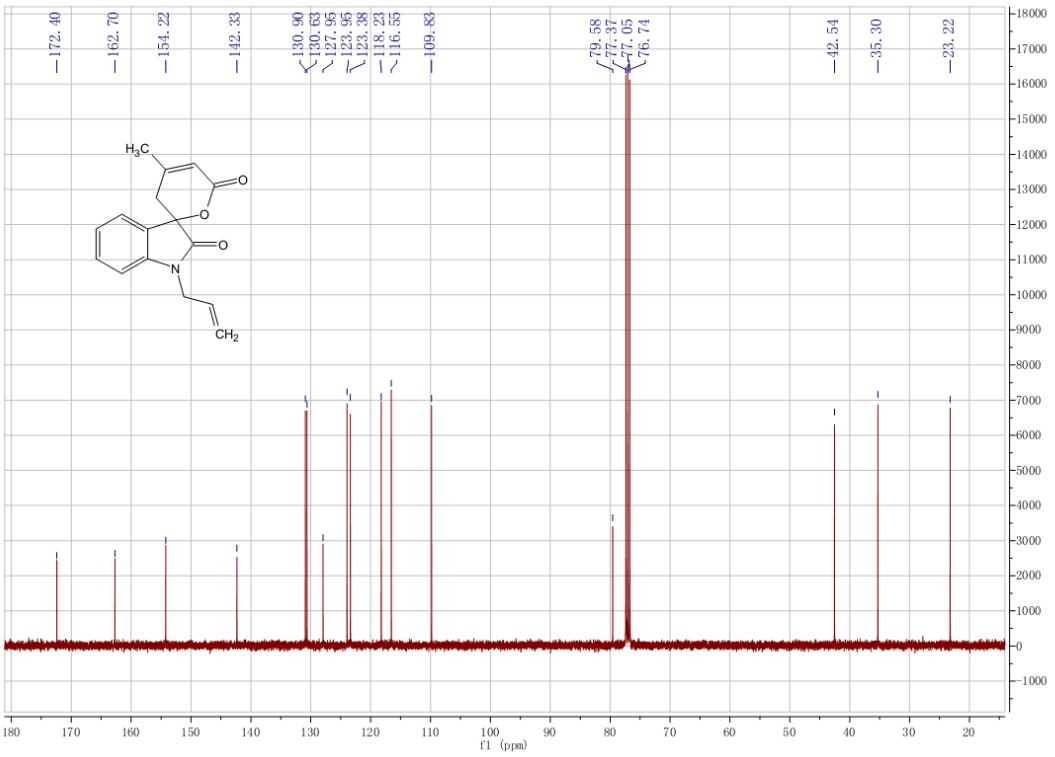
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3b**



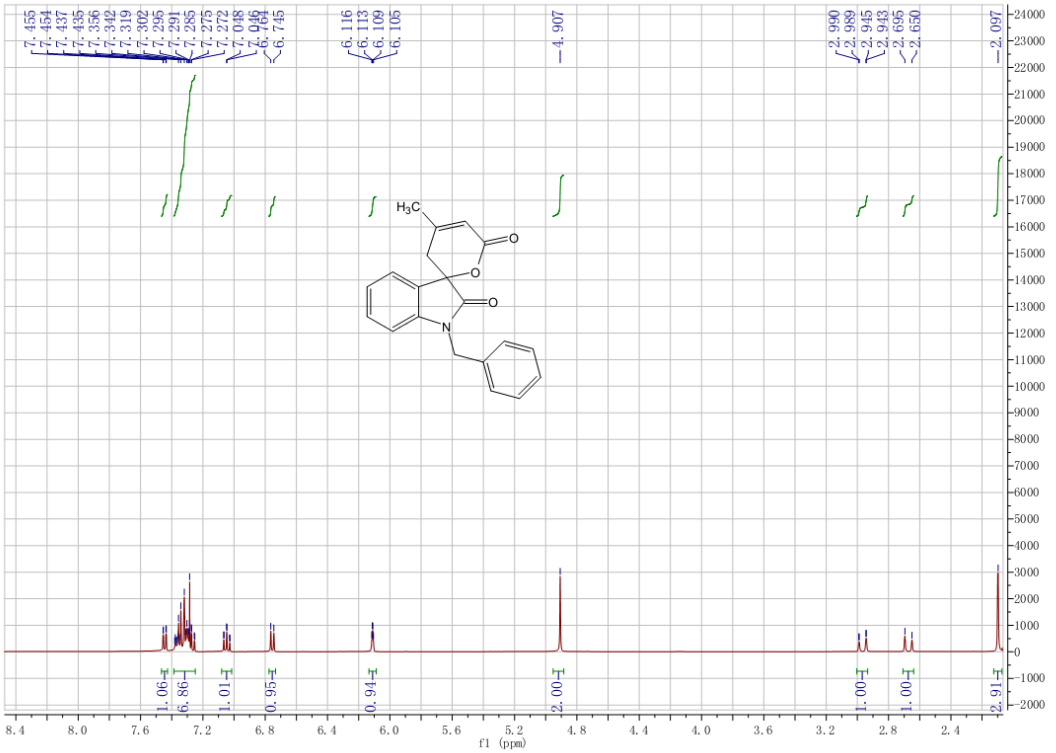
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3b**



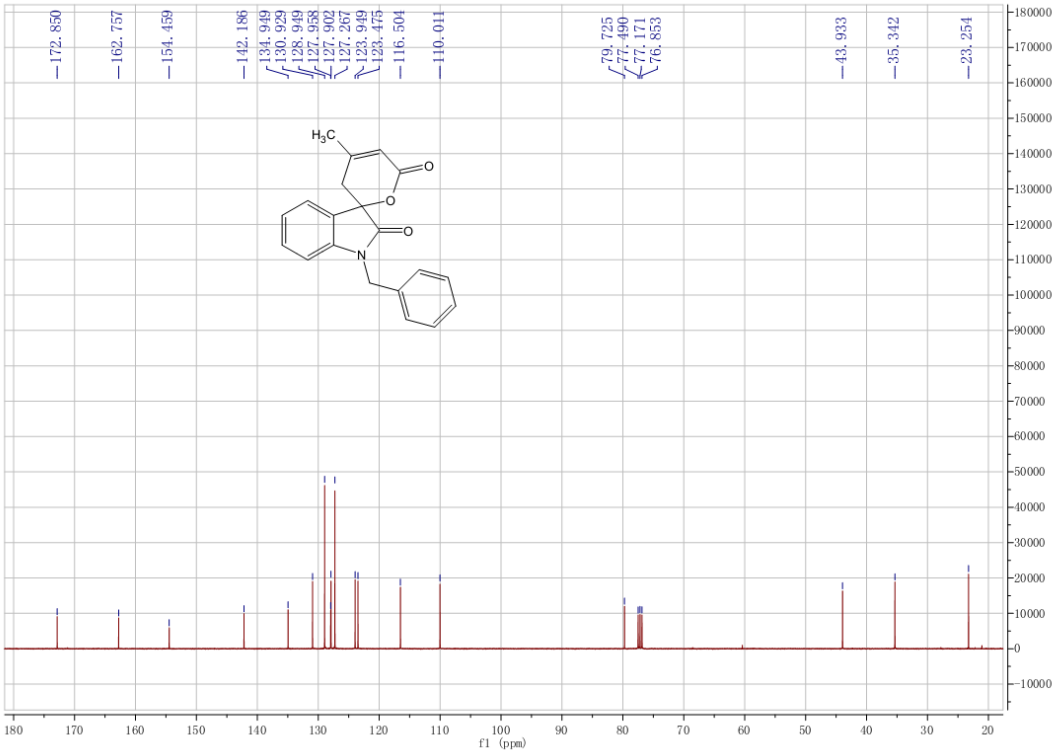
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3c**



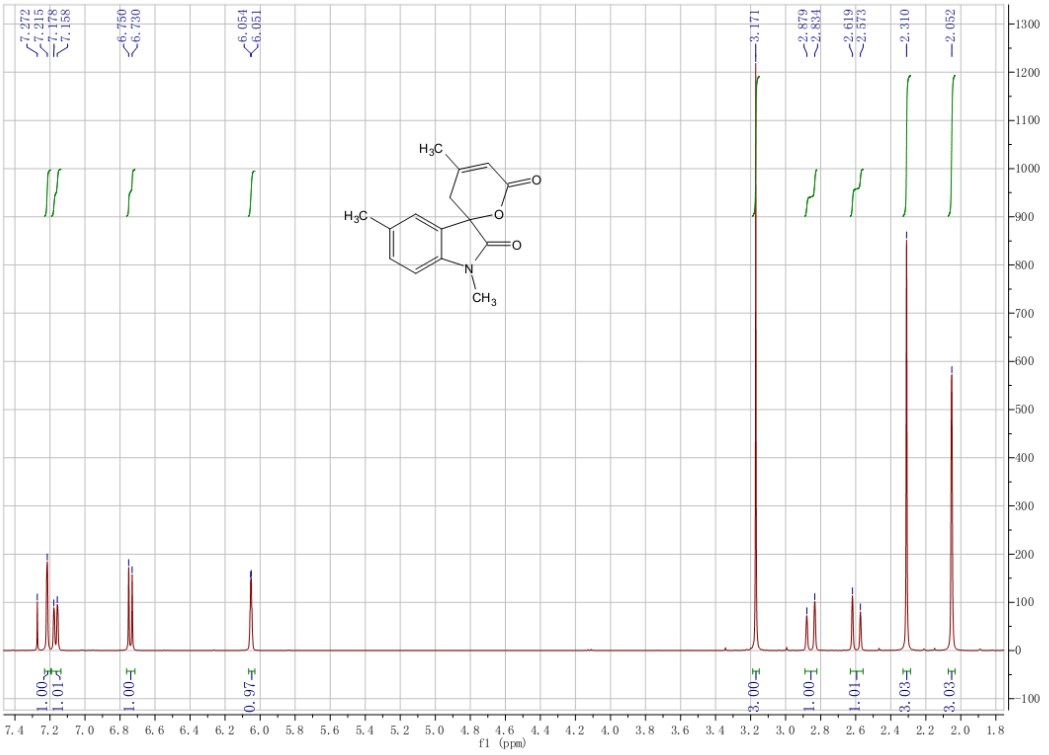
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3c**



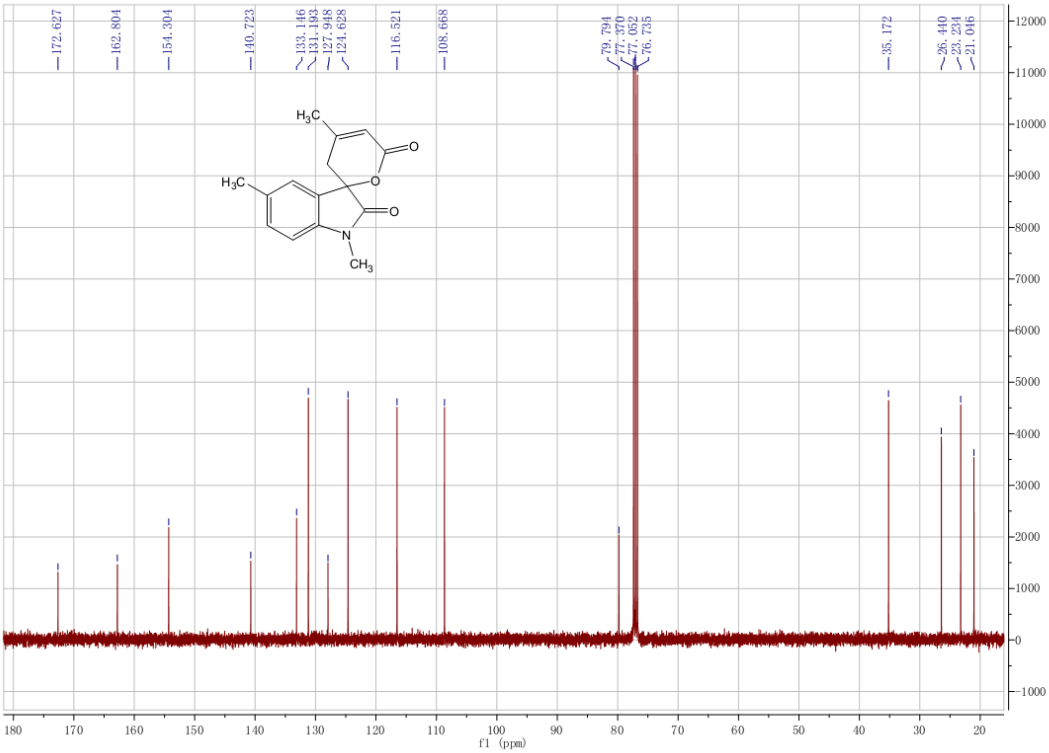
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3d**



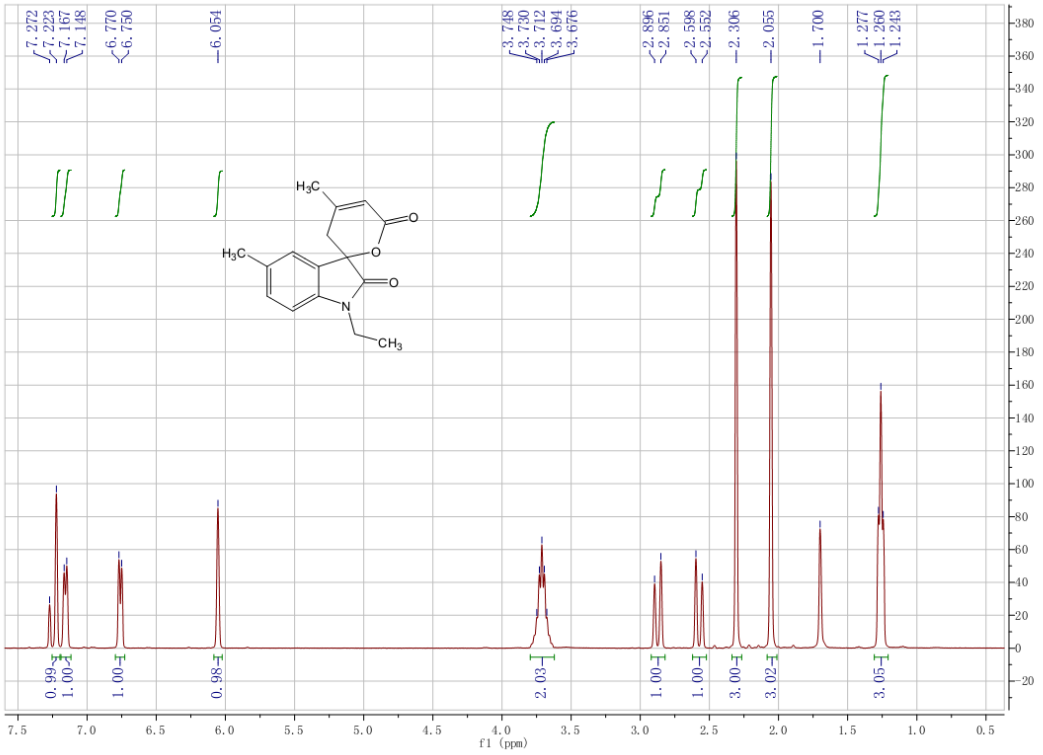
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3d**



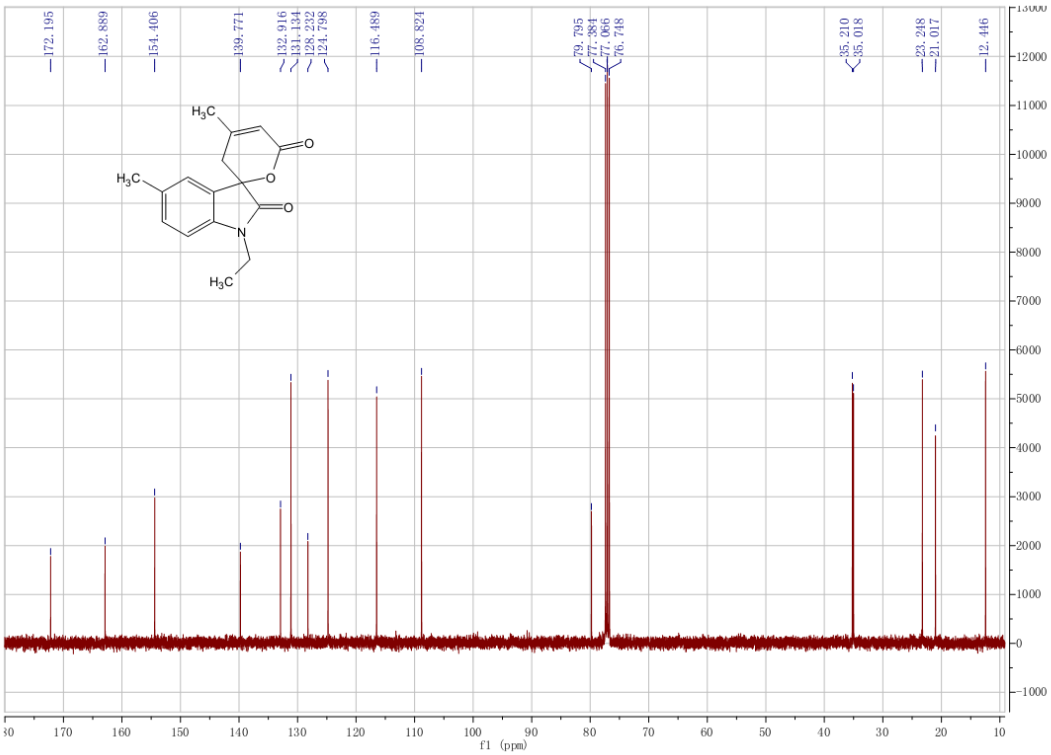
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3e**



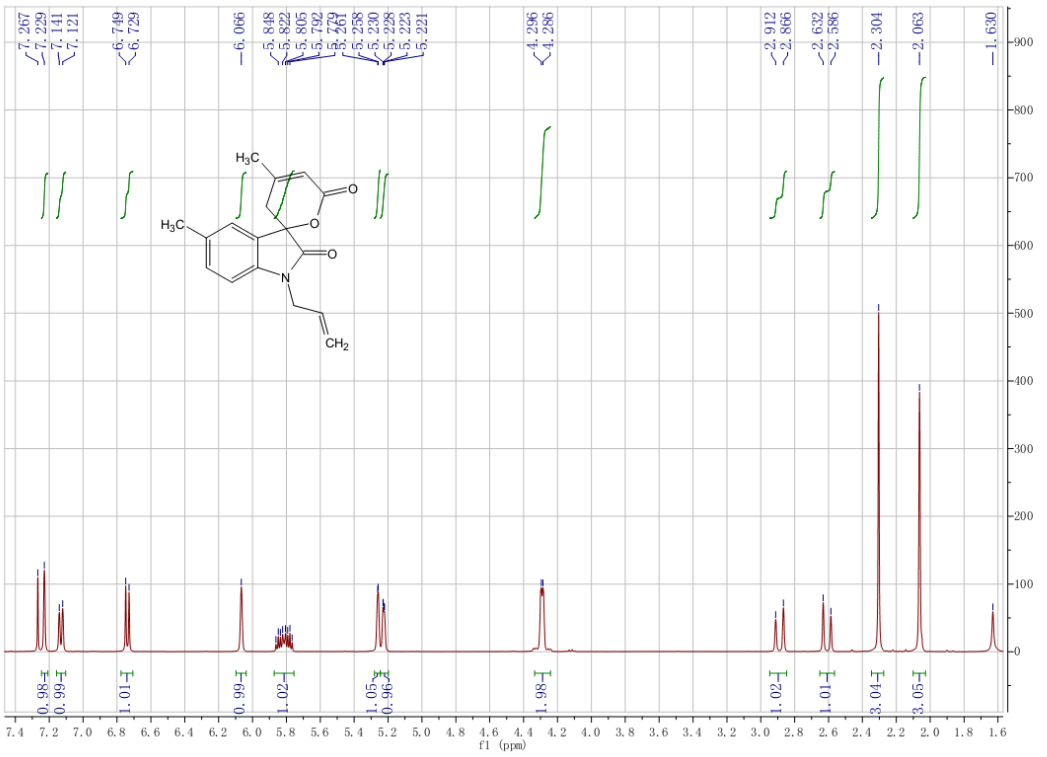
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3e**



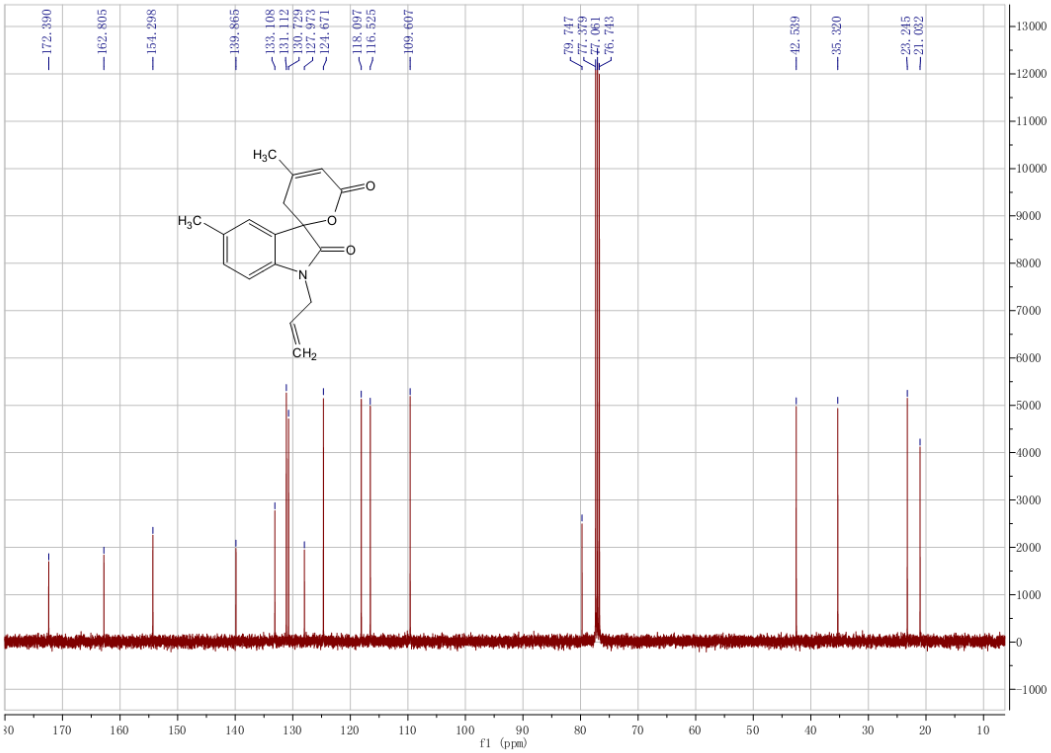
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3f**



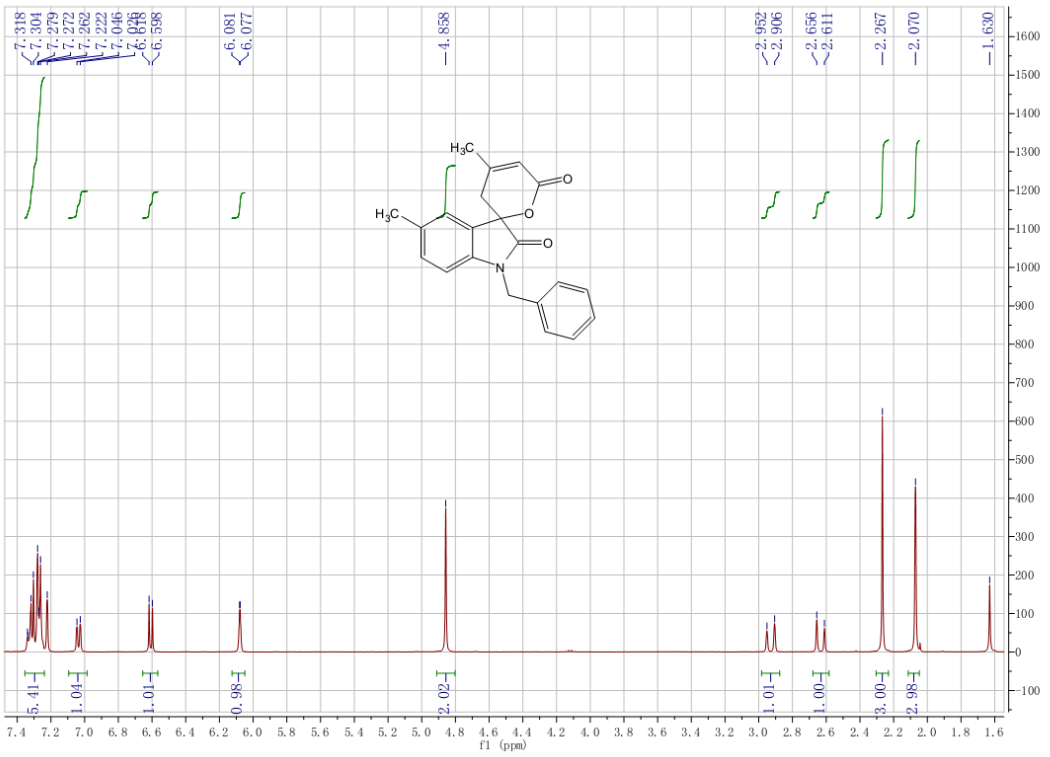
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3f**



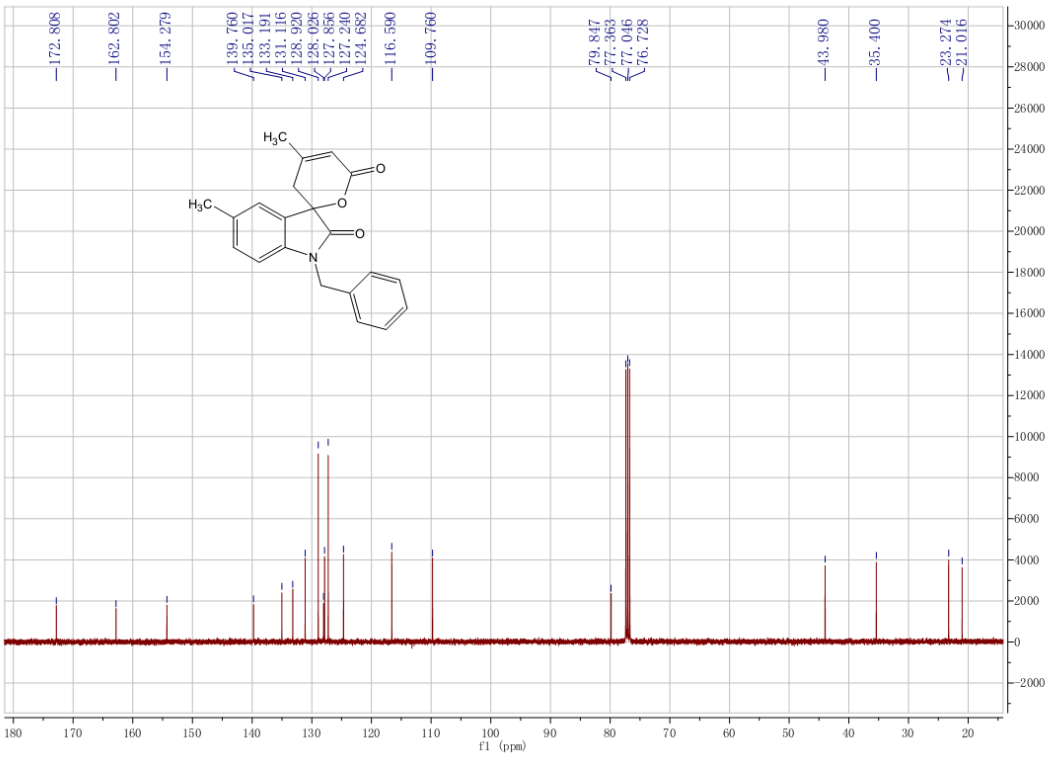
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3g**



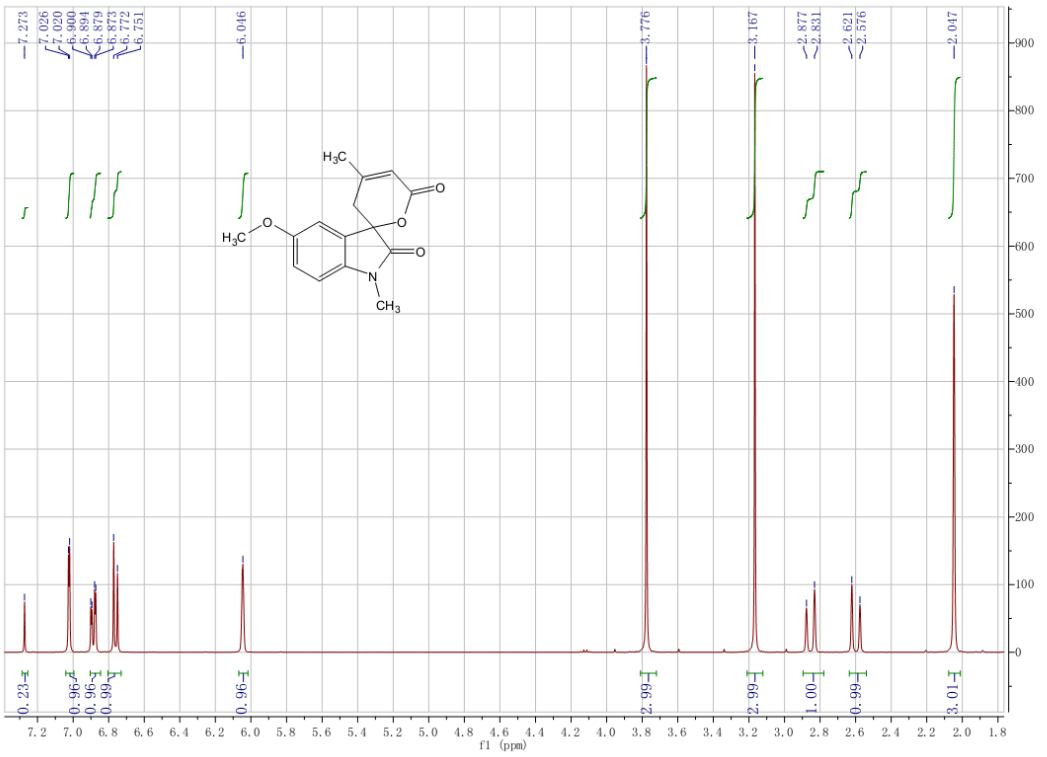
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3g**



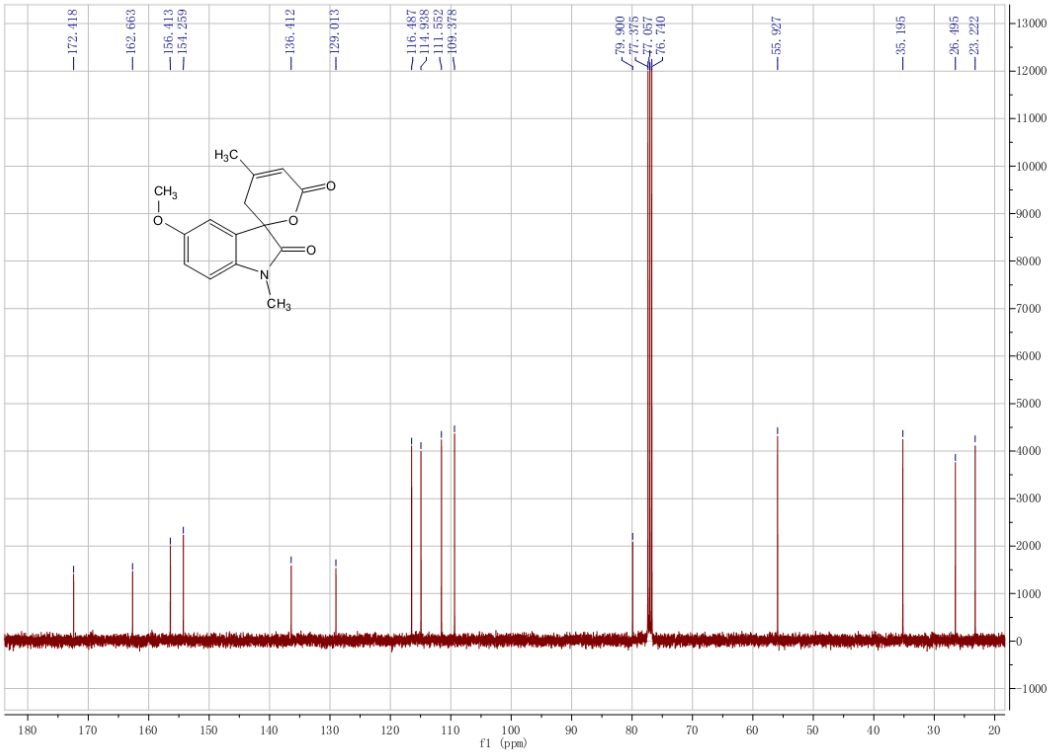
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3h**



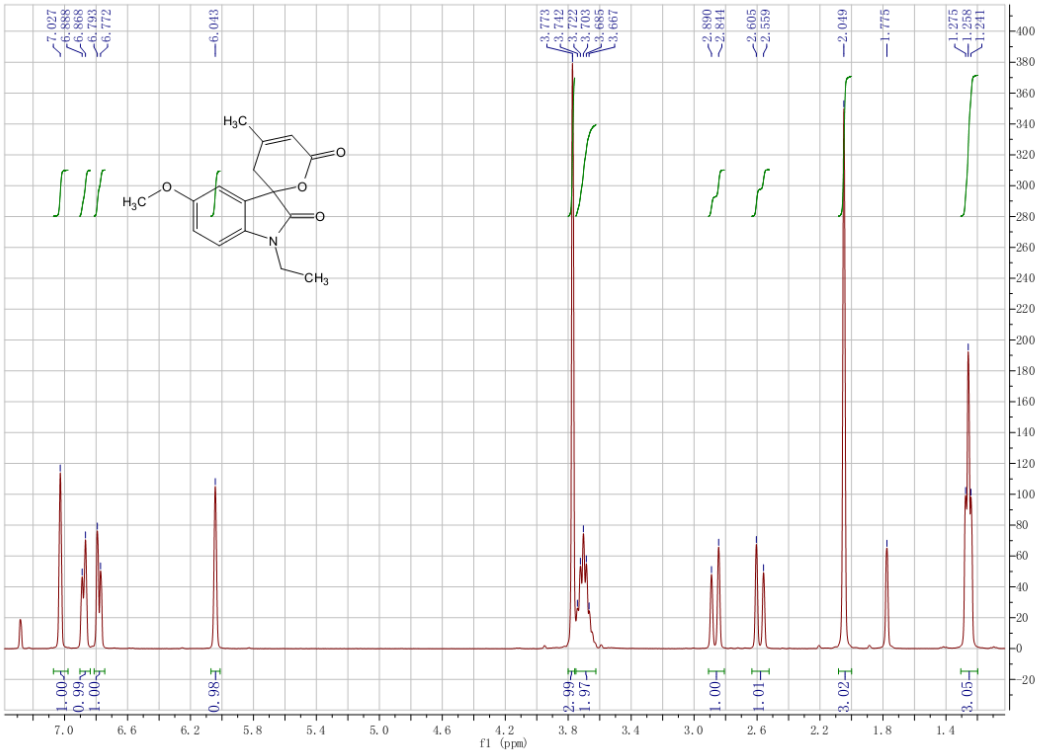
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3h**



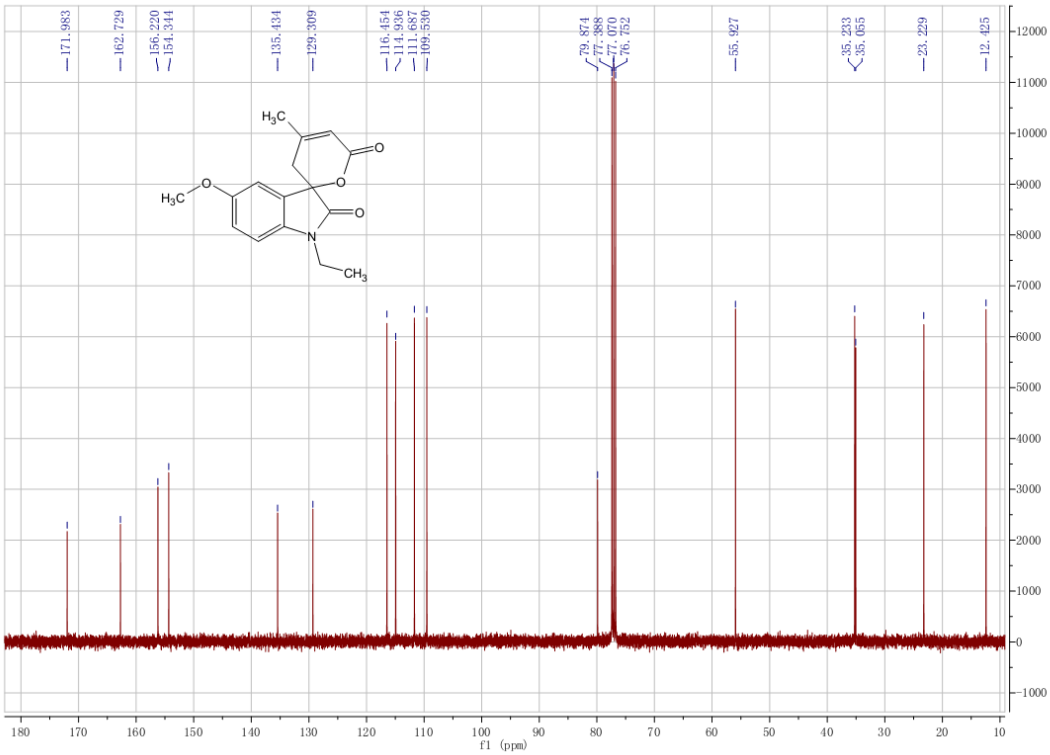
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3i**



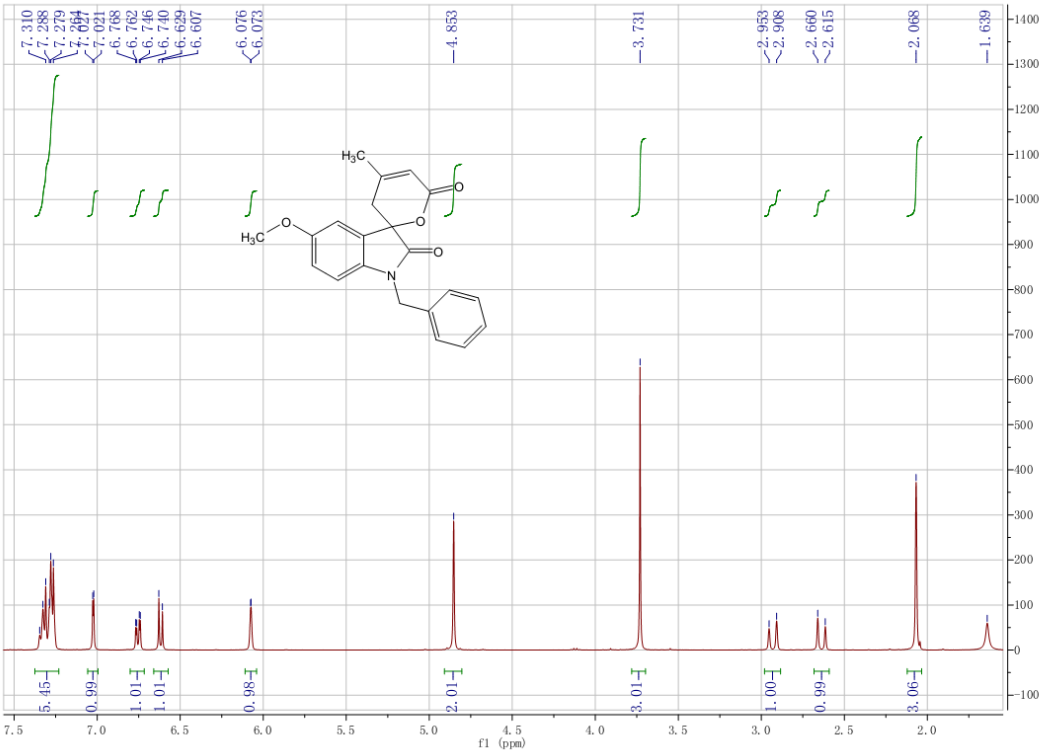
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3i**



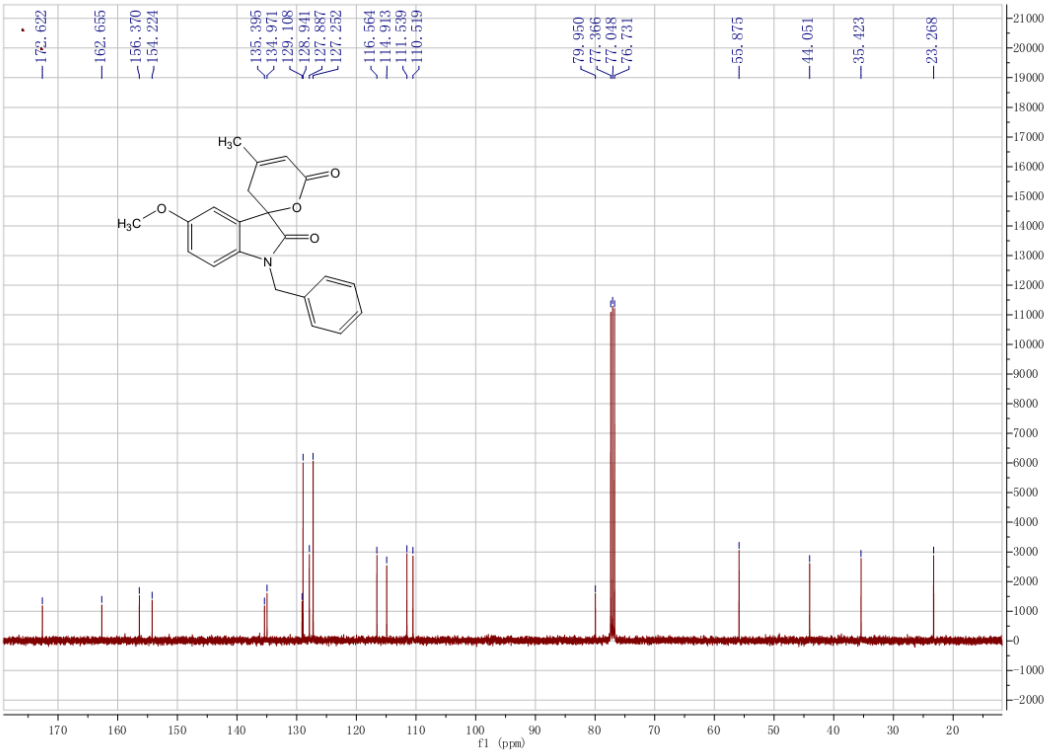
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3j**



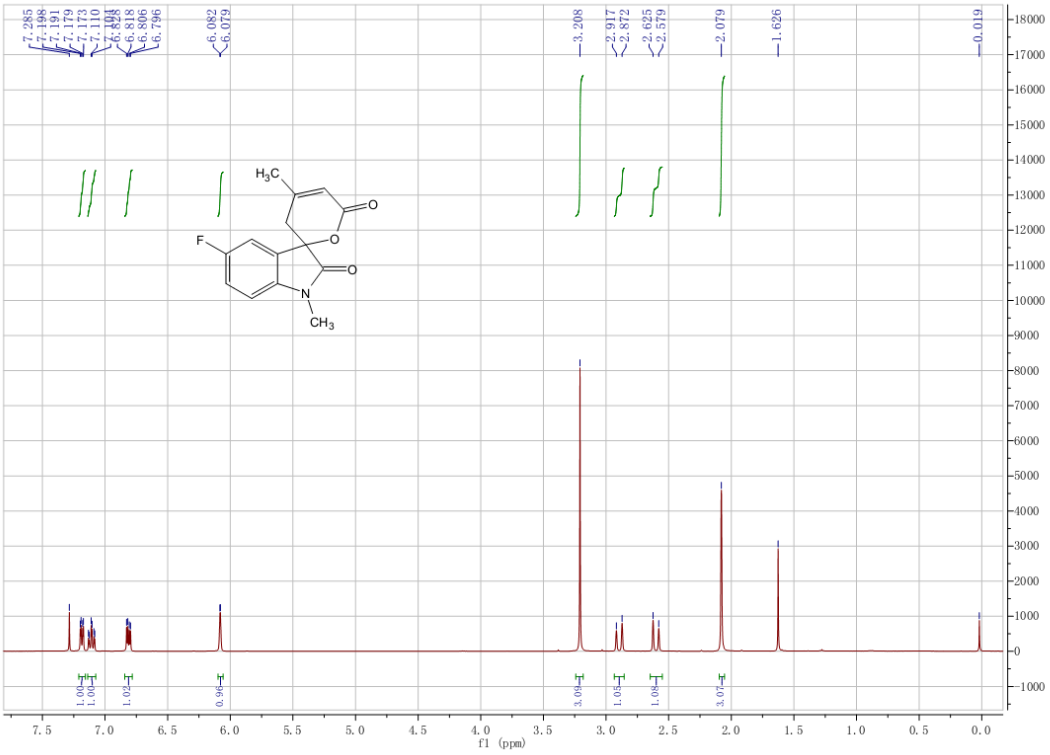
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3j**



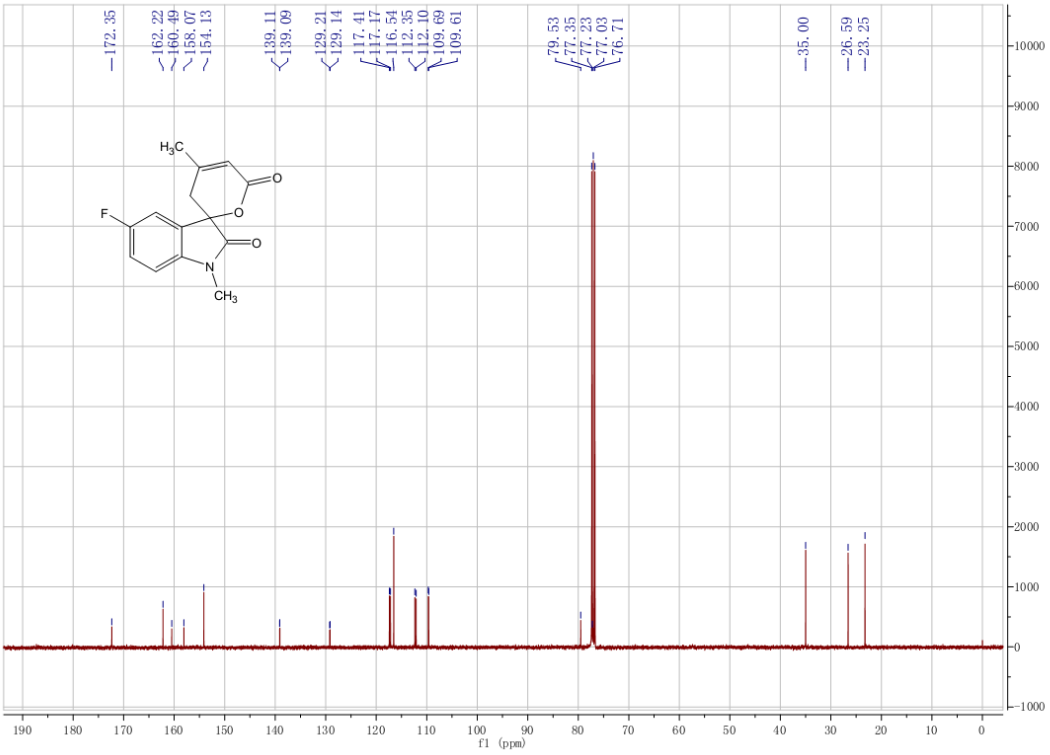
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3k**



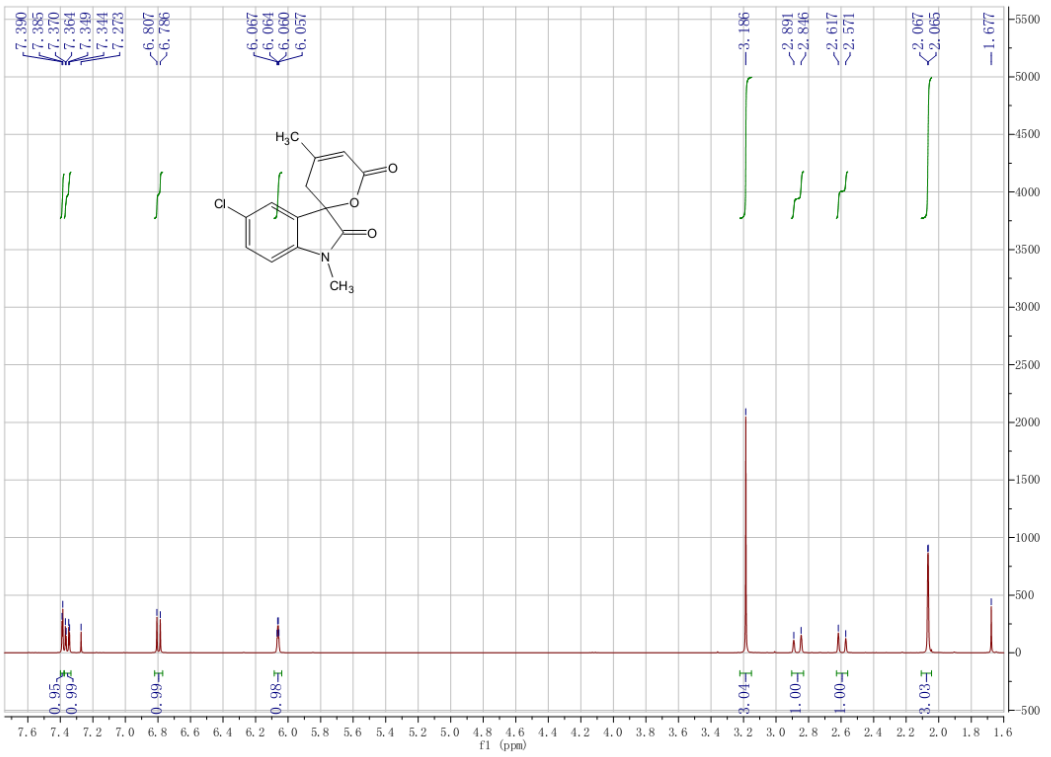
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3k**



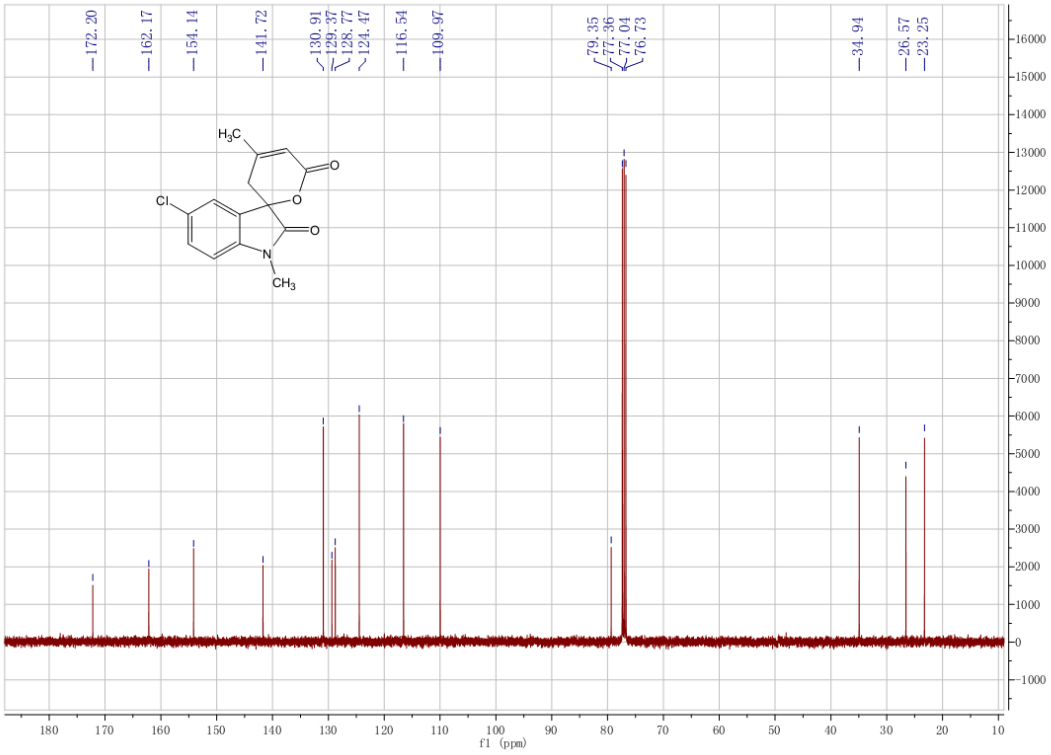
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3l**



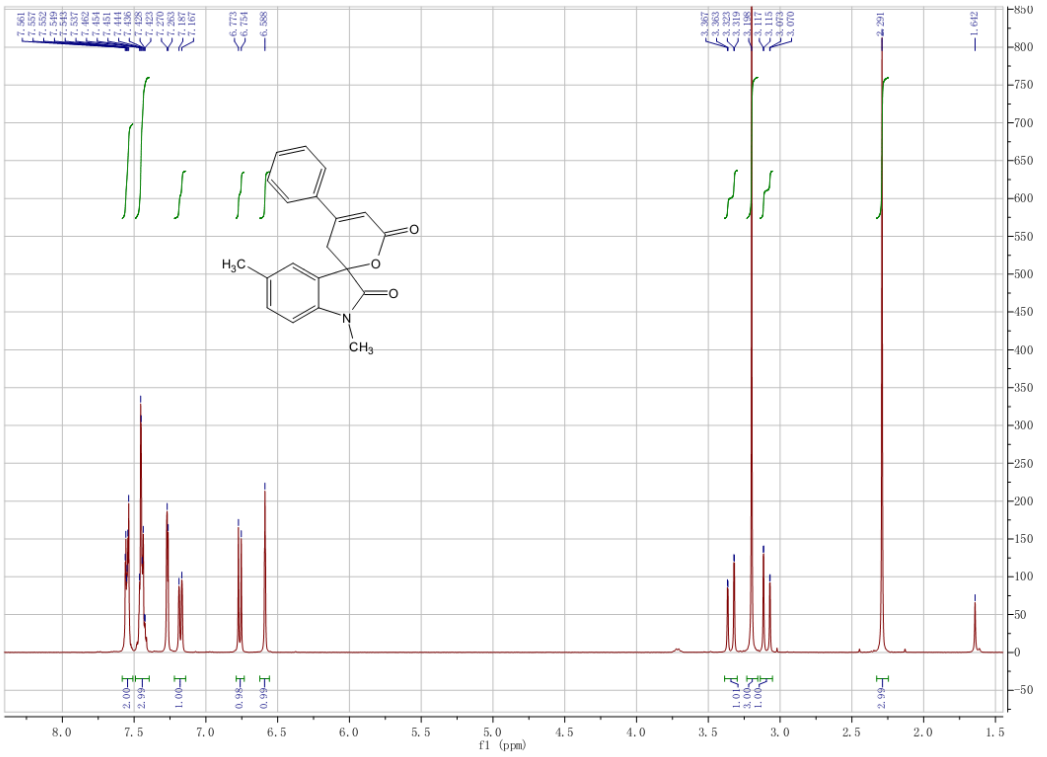
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3l**



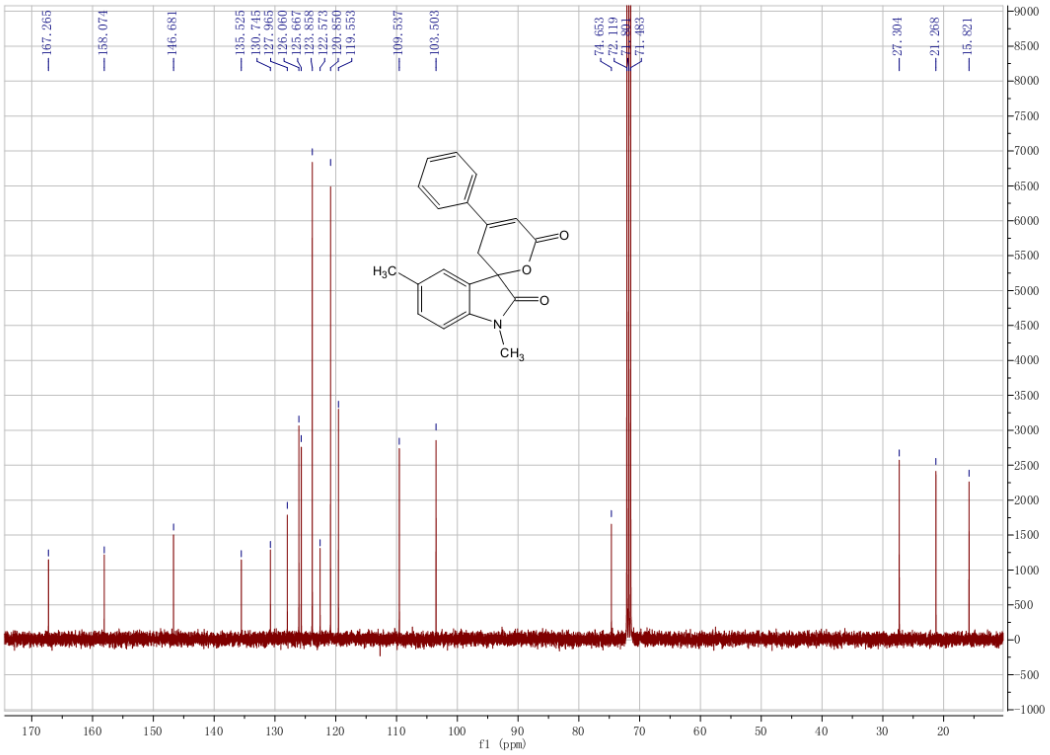
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3m**



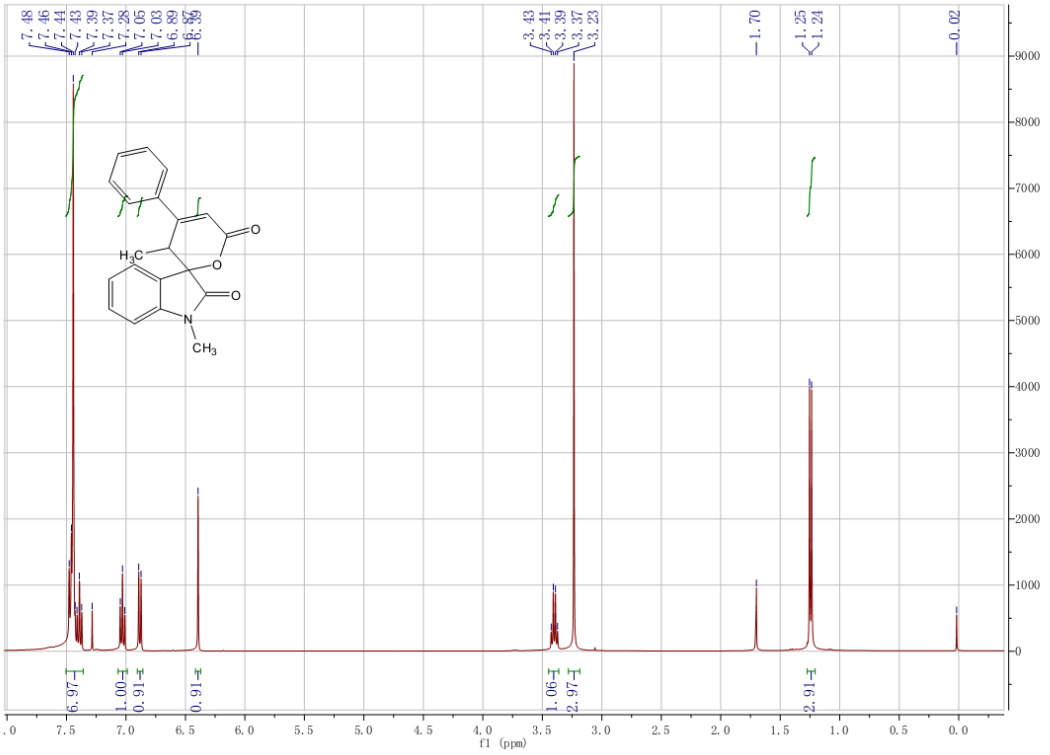
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3m**



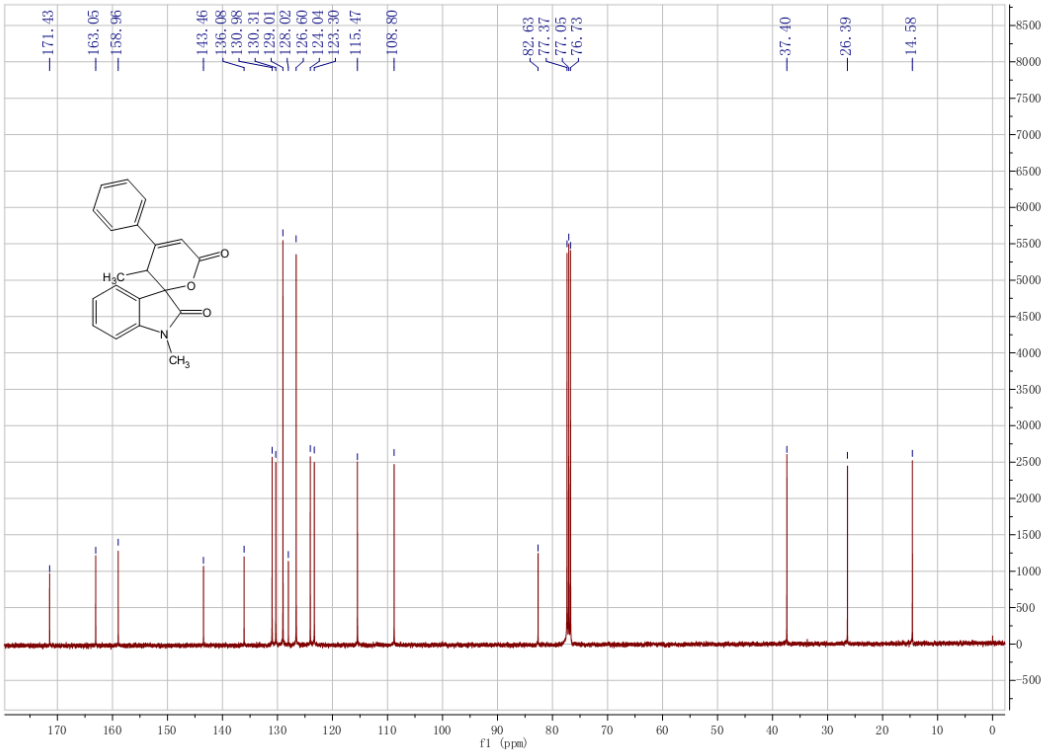
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3n**



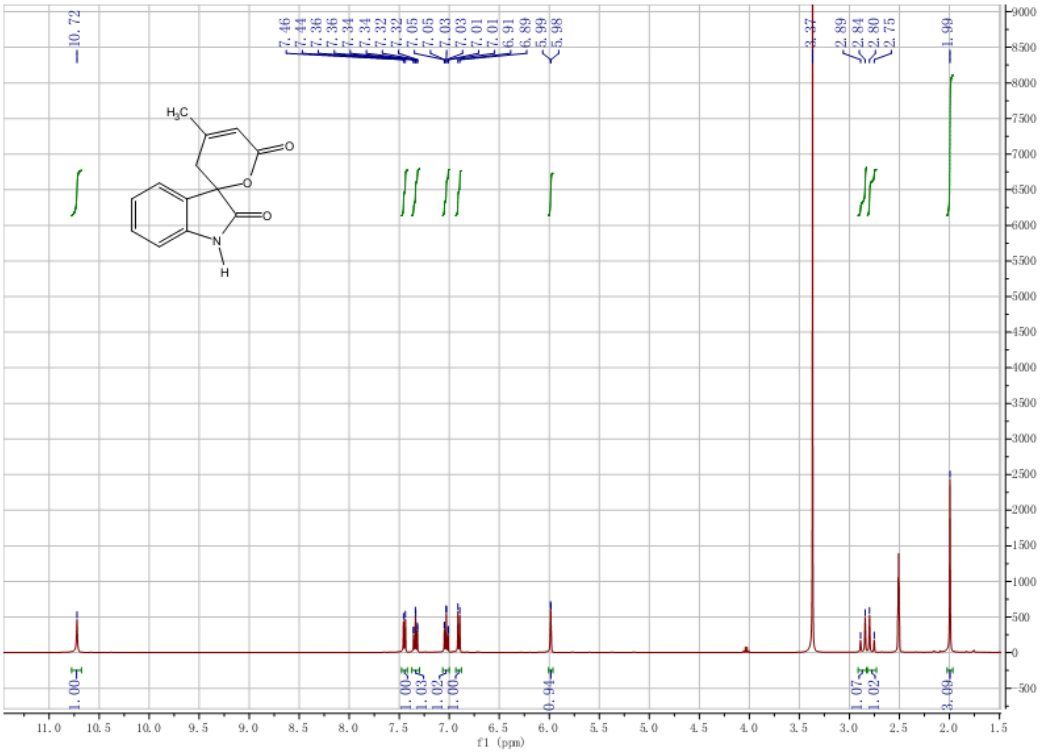
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3n**



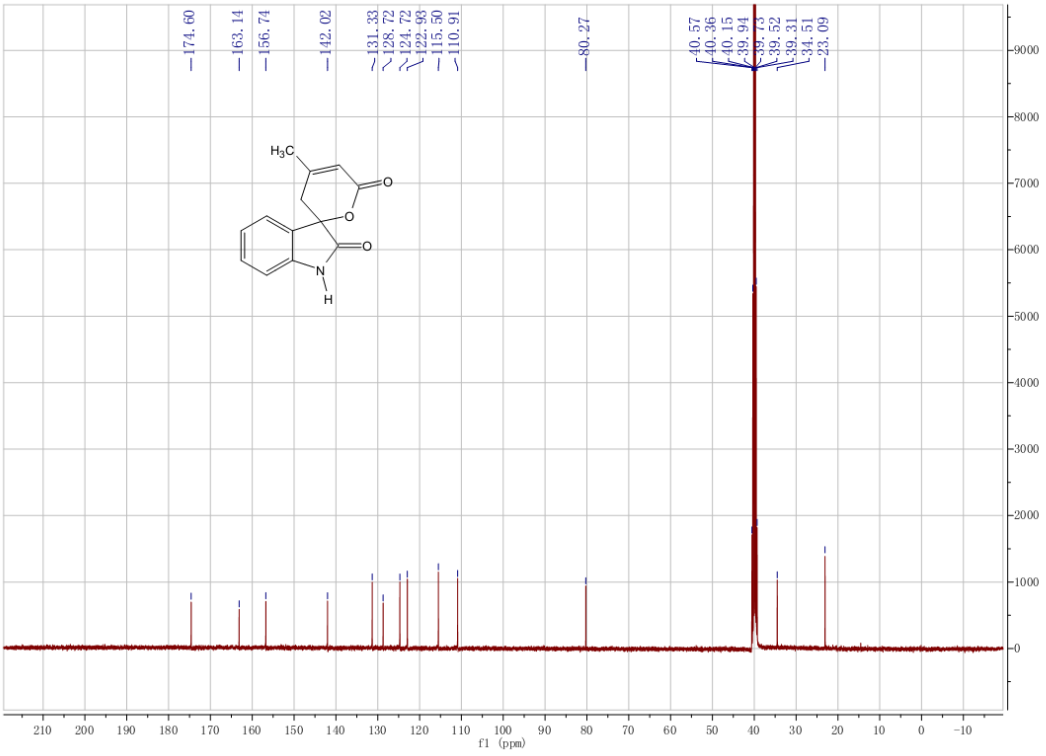
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3o**



^{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**