Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Cooperative Palladium-Catalyzed and $P(NEt_2)_3$-Mediated (4+1) Annulation of Isatins with 2-Hydroxymethylallylcarbonates

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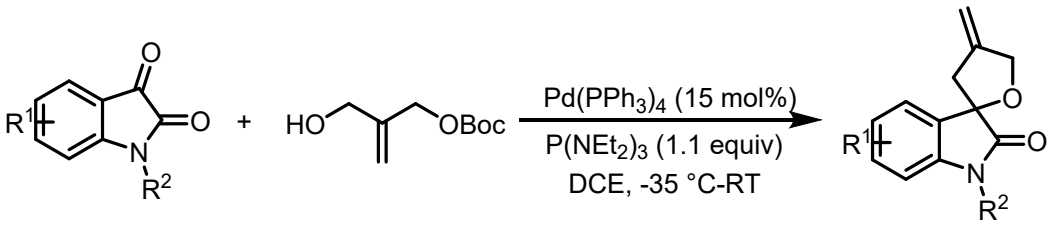
1. General experimental details.

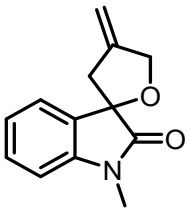
All reactions were performed under nitrogen using solvents dried by standard methods. NMR spectra were obtained using Bruker AV300 spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from internal TMS. HRMS spectra were obtained on an Agilent 1290-6540 UHPLC Q-Tof HR-MS spectrometer. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini Ediffractometer. Melting Point: heating rate: 4°C/min, the thermometer was not corrected. Enantiomer excesses were determined by chiral HPLC analysis on AD-H in comparison with the authentic racemates. Chiral HPLC analysisrecorded on Shanghaiyice instruments and Equipment Co. Ltd. and ShimadzuLC-20A. Silica gel (200-300 mesh) was used for the chromatographic separations. All commercially available reagents were used without further purification. N-substituted isatins[1] **1** and allyl carbonates[2] **2** were synthesized according to previous procedures.

2. General procedure for reactions



1 **2** **3**

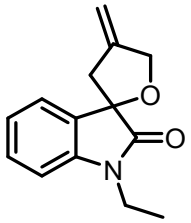
To a dry flask filled with nitrogen were added **1** (0.10 mmol) and **2** (0.20 mmol) in 2 mL DCE, $Pd(PPh_3)_4$ (0.015 mmol) was next added. The mixture was cooled to -35 ℃, and then a solution of $P(NEt_2)_3$ (0.11 mmol, 30.0 uL) was added dropwise by a syringe. Upon the complete addition of $P(NEt_2)_3$, the resulting solution was allowed to warm to room temperature. This solution was stirred at r.t. until the complete consumption of the starting material as monitored by TLC. After the removal of the solvent, the residue was subjected to chromatography on a silica gel (60 - 120 mesh) column (eluant: petroleum ether / EtOAc = 6:1) to afford **3**.



1'-Methyl-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3a

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 2.5 h) and afforded **3a** (20.2 mg, 94% yield).

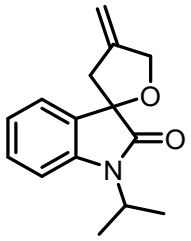
Colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35 - 7.30 (m, 2H), 7.07 (t, J = 7.4 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 5.18 - 5.13 (m, 2H), 4.90 (d, J = 12.6 Hz, 1H), 4.69 (dd, J = 12.5, 1.2 Hz, 1H), 3.18 (s, 3H), 3.04 (d, J = 15.8 Hz, 1H), 2.80 (dd, J = 15.8, 1.5 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.4, 146.0, 143.6, 130.0, 129.5, 123.6, 123.1, 108.4, 105.9, 82.7, 72.1, 41.2, 26.1 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{14}NO_2$: 216.1019; Found: 216.1057.



1'-Ethyl-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3b

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3 h) and afforded **3b** (18.2 mg, 85% yield).

Light-pink oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33 - 7.27 (m, 2H), 7.04 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 7.7 Hz, 1H), 5.18 - 5.10 (m, 2H), 4.89 (d, J = 12.6 Hz, 1H), 4.67 (dd, J = 12.6, 1.6 Hz, 1H), 3.71 (q, J = 7.2 Hz, 2H), 3.03 (d, J = 15.8 Hz, 1H), 2.78 (dd, J = 15.8, 1.7 Hz, 1H), 1.24 (t, J = 7.2 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.0, 146.0, 142.7, 129.9, 129.8, 123.8, 122.9, 108.5, 105.9, 82.7, 72.1, 41.2, 34.6, 12.6 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{16}NO_2$: 230.1176; Found: 230.1193.

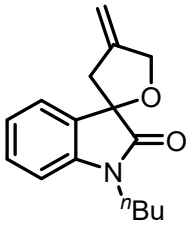


1'-Isopropyl-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3c

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3 h) and afforded **3c** (19.4 mg, 80% yield).

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35 - 7.31 (m, 1H), 7.29 - 7.26 (m, 1H), 7.07 - 7.01 (m, 1H), 6.97 (d, J = 7.9 Hz, 1H), 5.18 - 5.11 (m, 2H), 4.90 (d, J = 12.6 Hz, 1H), 4.68 (dd, J = 12.6, 1.6 Hz, 1H), 4.60 - 4.51 (m, 1H), 3.03 (d, J = 15.7 Hz, 1H), 2.78 (dd, J = 15.8, 1.9 Hz, 1H), 1.49 (s, 3H), 1.47 (s, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.2, 146.2, 142.3, 130.0, 129.6, 124.0, 122.5, 110.0, 105.8, 82.5,

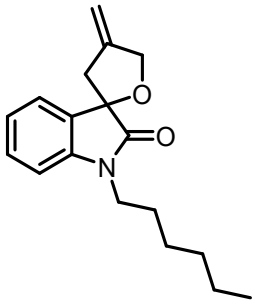
72.1, 43.8, 41.3, 19.4, 19.2 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{18}NO_2$: 244.1332; Found: 244.1381.



1'-Butyl-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3d

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3 h) and afforded **3d** (25.5mg, > 99% yield).

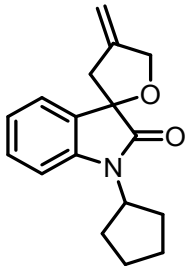
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34 - 7.28 (m, 2H), 7.05 (t, J = 7.5 Hz, 1H), 6.83 (d, J = 7.7 Hz, 1H), 5.18 - 5.12 (m, 2H), 4.90 (d, J = 12.6 Hz, 1H), 4.69 (dd, J = 12.6, 1.4 Hz, 1H), 3.67 (t, J = 7.2 Hz, 2H), 3.04 (d, J = 15.7 Hz, 1H), 2.79 (dd, J = 15.8, 1.6 Hz, 1H), 1.71 - 1.61 (m, 2H), 1.45 - 1.33 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.3, 146.1, 143.1, 129.8, 129.7, 123.8, 122.8, 108.6, 105.8, 82.6, 72.1, 41.2, 39.6, 29.4, 20.1, 13.7 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}NO_2$: 258.1489; Found: 258.1530.



1'-Hexyl-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3e

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 5 h) and afforded **3e** (24.4 mg, 85% yield).

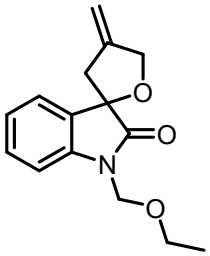
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34 - 7.28 (m, 2H), 7.05 (t, J = 7.4 Hz, 1H), 6.82 (d, J = 7.7 Hz, 1H), 5.19 - 5.12 (m, 2H), 4.90 (d, J = 12.6 Hz, 1H), 4.69 (dd, J = 12.7, 1.6 Hz, 1H), 3.66 (t, J = 7.3 Hz, 2H), 3.04 (d, J = 15.8 Hz, 1H), 2.79 (dd, J = 15.8, 1.8 Hz, 1H), 1.72 - 1.62 (m, 2H), 1.44 - 1.27 (m, 6H), 0.89 (t, J = 6.7 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.3, 146.1, 143.1, 129.8, 129.7, 123.8, 122.8, 108.6, 105.8, 82.6, 72.1, 41.2, 39.9, 31.4, 27.2, 26.5, 22.5, 14.0 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{24}NO_2$: 286.1802; Found: 286.1771.



1'-Cyclopentyl-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3f

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 1.5 h) and afforded **3f** (23.3 mg, 87% yield).

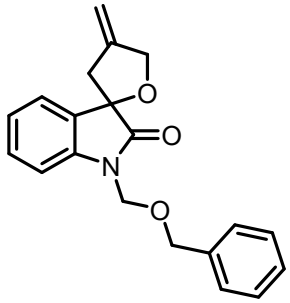
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34 (d, J = 7.4 Hz, 1H), 7.29 (td, J = 7.9, 1.3 Hz, 1H), 7.05 (t, J = 7.4 Hz, 1H), 6.91 (d, J = 7.9 Hz, 1H), 5.19 - 5.11 (m, 2H), 4.90 (d, J = 12.6 Hz, 1H), 4.77 - 4.66 (m, 2H), 3.04 (d, J = 15.8 Hz, 1H), 2.78 (dd, J = 15.8, 1.8 Hz, 1H), 2.13 - 2.02 (m, 2H), 2.00 - 1.88 (m, 4H), 1.74 - 1.69 (m, 2H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.4, 146.2, 142.2, 130.0, 129.6, 123.9, 122.6, 109.9, 105.8, 82.5, 72.1, 52.3, 41.3, 27.8, 27.4, 25.2, 25.1 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{20}NO_2$: 270.1489; Found: 270.1466.



1'-(Ethoxymethyl)-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3g

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3 h) and afforded **3g** (18.4 mg, 71% yield).

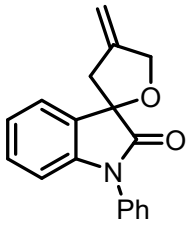
Light-yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37 - 7.31 (m, 2H), 7.11 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 5.20 - 5.17 (m, 1H), 5.14 (d, J = 3.5 Hz, 3H), 4.90 (d, J = 12.6 Hz, 1H), 4.70 (dd, J = 12.6, 1.6 Hz, 1H), 3.60 - 3.51 (m, 2H), 3.05 (d, J = 15.8 Hz, 1H), 2.84 (dd, J = 15.8, 1.8 Hz, 1H), 1.18 (t, J = 7.0 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.0, 145.8, 142.0, 130.1, 128.9, 123.8, 123.6, 110.0, 106.0, 82.9, 72.2, 69.9, 64.3, 41.4, 14.9 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{18}NO_3$: 260.1281; Found: 260.1284.



1'-((Benzyloxy)methyl)-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3h

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3 h) and afforded **3h** (21.4 mg, 67% yield).

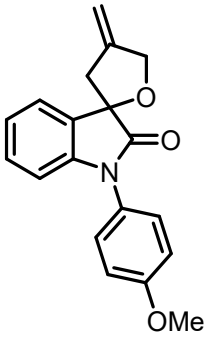
Light-pink oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37 - 7.30 (m, 7H), 7.15 - 7.07 (m, 2H), 5.26 (d, J = 11.1 Hz, 1H), 5.22 - 5.15 (m, 3H), 4.92 (d, J = 12.5 Hz, 1H), 4.72 (dd, J = 12.7, 1.4 Hz, 1H), 4.57 (q, J = 11.8 Hz, 2H), 3.01 (d, J = 15.8 Hz, 1H), 2.81 (dd, J = 15.9, 1.7 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.0, 145.8, 141.9, 137.3, 130.1, 128.9, 128.4, 127.91, 127.87, 123.8, 123.6, 110.0, 106.0, 82.9, 72.2, 70.8, 69.8, 41.4 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}NO_3$: 322.1438; Found: 322.1453.



4-Methylene-1'-phenyl-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3i

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3 h) and afforded **3i** (23.2 mg, 84% yield).

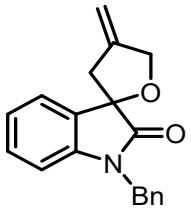
Yellow solid. **MP**: 130.5 - 132.6 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53 - 7.50 (m, 2H), 7.45 - 7.38 (m, 4H), 7.27 (td, J = 7.6, 1.1 Hz, 1H), 7.12 (t, J = 7.4 Hz, 1H), 6.84 (d, J = 7.9 Hz, 1H), 5.22 - 5.16 (m, 2H), 4.95 (d, J = 12.6 Hz, 1H), 4.75 (dd, J = 12.6, 1.4 Hz, 1H), 3.18 (d, J = 15.8 Hz, 1H), 2.92 (dd, J = 15.8, 1.7 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 175.7, 145.9, 143.6, 134.1, 129.9, 129.6, 129.2, 128.1, 126.3, 124.1, 123.6, 109.7, 106.1, 82.8, 72.2, 41.6 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{16}NO_2$: 278.1176; Found: 278.1218.



1'-(4-Methoxyphenyl)-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3j

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 1.5 h) and afforded **3j** (23.8 mg, 77% yield).

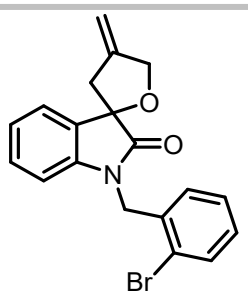
Yellow solid. **MP**: 129.1 - 130.8 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 (d, J = 7.4 Hz, 1H), 7.35 - 7.30 (m, 2H), 7.24 (dd, J = 7.7, 1.1 Hz, 1H), 7.10 (t, J = 7.4 Hz, 1H), 7.06 - 7.00 (m, 2H), 6.76 (d, J = 7.8 Hz, 1H), 5.22 - 5.15 (m, 2H), 4.94 (d, J = 12.6 Hz, 1H), 4.73 (dd, J = 12.6, 1.6 Hz, 1H), 3.86 (s, 3H), 3.17 (d, J = 15.8 Hz, 1H), 2.91 (dd, J = 15.8, 1.8 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 175.9, 159.2, 146.0, 144.1, 129.9, 129.2, 127.8, 126.7, 124.0, 123.4, 114.9, 109.6, 106.0, 82.8, 72.2, 55.5, 41.5 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{18}NO_3$: 308.1281; Found: 308.1327.



1'-Benzyl-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3k

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 2.5 h) and afforded **3k** (25.1 mg, 86% yield).

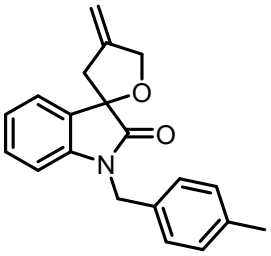
White solid. **MP**: 88.6 - 90.3 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 - 7.27 (m, 6H), 7.21 (td, J = 7.8, 1.1 Hz, 1H), 7.04 (t, J = 7.3 Hz, 1H), 6.70 (d, J = 7.8 Hz, 1H), 5.22 - 5.16 (m, 2H), 4.96 (d, J = 12.2 Hz, 1H), 4.88 (d, J = 2.2 Hz, 2H), 4.73 (dd, J = 12.6, 1.5 Hz, 1H), 3.12 (d, J = 15.8 Hz, 1H), 2.86 (dd, J = 15.8, 1.8 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.6, 145.9, 142.7, 135.5, 129.9, 129.5, 128.8, 127.7, 127.3, 123.8, 123.1, 109.4, 106.0, 82.8, 72.2, 43.6, 41.4 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{18}NO_2$: 292.1332; Found: 292.1372.



1'-(2-Bromobenzyl)-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3l

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3.5 h) and afforded **3l** (21.5 mg, 58% yield).

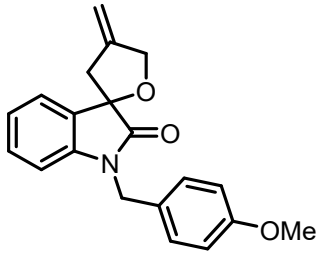
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.60 (dd, J = 7.7, 0.9 Hz, 1H), 7.38 (d, J = 7.3 Hz, 1H), 7.25 - 7.19 (m, 2H), 7.14 (td, J = 7.6, 1.7 Hz, 1H), 7.07 (t, J = 7.4 Hz, 2H), 6.65 (d, J = 7.8 Hz, 1H), 5.22 - 5.16 (m, 2H), 4.96 (d, J = 14.1 Hz, 3H), 4.74 (dd, J = 12.6, 1.6 Hz, 1H), 3.14 (d, J = 15.8 Hz, 1H), 2.89 (dd, J = 15.8, 1.8 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.7, 145.8, 142.4, 134.2, 133.0, 130.0, 129.4, 129.1, 127.9, 127.8, 123.9, 123.4, 122.8, 109.5, 106.1, 82.8, 72.2, 43.6, 41.4 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}BrNO_2$: 370.0437; Found: 370.0404.



1'-(4-Methylbenzyl)-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3m

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 2 h) and afforded **3m** (24.5 mg, 80% yield).

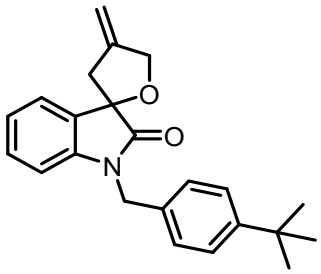
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34 (dd, J = 7.3, 0.6 Hz, 1H), 7.23 - 7.18 (m, 3H), 7.13 (d, J = 8.0 Hz, 2H), 7.06 - 7.01 (m, 1H), 6.71 (d, J = 7.8 Hz, 1H), 5.21 - 5.16 (m, 2H), 4.96 (d, J = 12.6 Hz, 1H), 4.84 (d, J = 3.8 Hz, 2H), 4.73 (dd, J = 12.6, 1.5 Hz, 1H), 3.11 (d, J = 15.8 Hz, 1H), 2.85 (dd, J = 15.8, 1.7 Hz, 1H), 2.32 (s, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.6, 146.0, 142.8, 137.4, 132.5, 129.8, 129.51, 129.48, 127.3, 123.7, 123.1, 109.4, 106.0, 82.8, 72.2, 43.4, 41.4, 21.1 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}NO_2$: 306.1489; Found: 306.1528.



1'-(4-Methoxybenzyl)-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3n

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 2 h) and afforded **3n** (22.9 mg, 71% yield).

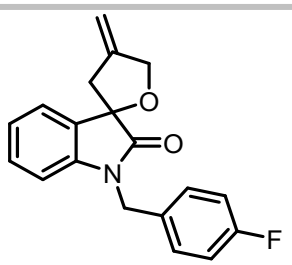
Pink oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.33 (d, J = 7.3 Hz, 1H), 7.27 - 7.18 (m, 3H), 7.03 (t, J = 7.4 Hz, 1H), 6.85 (d, J = 8.6 Hz, 2H), 6.72 (d, J = 7.8 Hz, 1H), 5.21 - 5.15 (m, 2H), 4.95 (d, J = 12.6 Hz, 1H), 4.81 (s, 2H), 4.72 (dd, J = 12.6, 1.3 Hz, 1H), 3.78 (s, 3H), 3.10 (d, J = 15.8 Hz, 1H), 2.84 (dd, J = 15.8, 1.6 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.5, 159.1, 146.0, 142.8, 129.8, 129.5, 128.7, 127.6, 123.7, 123.0, 114.2, 109.4, 106.0, 82.8, 72.2, 55.2, 43.1, 41.3 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}NO_3$: 322.1438; Found: 322.1476.



1'-(4-(Tert-butyl)benzyl)-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3o

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 2.5 h) and afforded **3o** (30.9 mg, 89% yield).

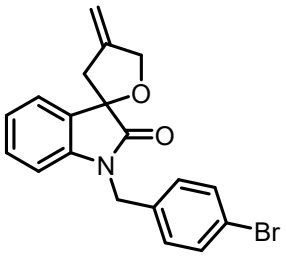
White solid. **MP**: 113.2 - 115.1 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 3H), 7.58 - 7.50 (m, 3H), 7.35 (t, J = 7.4 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 5.52 - 5.46 (m, 2H), 5.26 (d, J = 12.7 Hz, 1H), 5.15 (d, J = 7.0 Hz, 2H), 5.03 (dd, J = 12.7, 1.5 Hz, 1H), 3.42 (d, J = 15.8 Hz, 1H), 3.16 (dd, J = 15.8, 1.7 Hz, 1H), 1.61 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.8, 150.9, 146.3, 143.2, 132.8, 130.2, 129.8, 127.4, 126.0, 124.0, 123.4, 109.7, 106.3, 83.1, 72.5, 43.6, 41.6, 34.8, 31.6 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{26}NO_2$: 348.1958; Found: 348.1980.



1'-(4-Fluorobenzyl)-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3p

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 2.5 h) and afforded **3p** (25.0 mg, 81% yield).

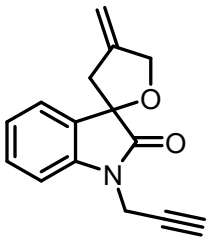
Light-yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35 (dd, J = 7.3, 0.6 Hz, 1H), 7.31 - 7.25 (m, 2H), 7.22 (dd, J = 7.8, 1.2 Hz, 1H), 7.07 - 6.98 (m, 3H), 6.69 (d, J = 7.8 Hz, 1H), 5.21 - 5.15 (m, 2H), 4.94 (d, J = 12.6 Hz, 1H), 4.84 (s, 2H), 4.72 (dd, J = 12.6, 1.5 Hz, 1H), 3.10 (d, J = 15.8 Hz, 1H), 2.86 (dd, J = 15.8, 1.7 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.6, 162.3 (d, J = 244.5 Hz), 145.8, 142.5, 131.3 (d, J = 3.8 Hz), 129.9, 129.5, 129.1, 129.0, 123.9, 123.3, 115.9, 115.6, 109.2, 106.1, 82.7, 72.2, 43.0, 41.3 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}FNO_2$: 310.1238; Found: 310.1270.



1'-(4-Bromobenzyl)-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3q

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3.5 h) and afforded **3q** (22.6 mg, 61% yield).

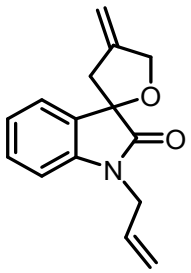
Reddish brown oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.47 - 7.43 (m, 2H), 7.35 (dd, J = 7.3, 0.7 Hz, 1H), 7.25 - 7.16 (m, 3H), 7.08 - 7.03 (m, 1H), 6.66 (d, J = 7.8 Hz, 1H), 5.22 - 5.15 (m, 2H), 4.94 (d, J = 12.6 Hz, 1H), 4.82 (s, 2H), 4.72 (dd, J = 12.6, 1.6 Hz, 1H), 3.10 (d, J = 15.8 Hz, 1H), 2.86 (dd, J = 15.8, 1.8 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.6, 145.8, 142.4, 134.6, 132.0, 129.9, 129.4, 129.0, 123.9, 123.3, 121.6, 109.2, 106.1, 82.7, 72.2, 43.1, 41.3 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{17}BrNO_2$: 370.0437; Found: 370.0485.



4-Methylene-1'-(prop-2-yn-1-yl)-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3r

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 5 h) and afforded **3r** (14.3 mg, 60% yield).

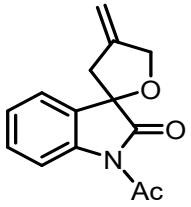
Orange oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.38 - 7.33 (m, 2H), 7.11 (t, J = 7.2 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 5.20 - 5.13 (m, 2H), 4.90 (d, J = 12.6 Hz, 1H), 4.70 (dd, J = 12.6, 1.5 Hz, 1H), 4.55 (dd, J = 17.7, 2.5 Hz, 1H), 4.39 (dd, J = 17.7, 2.5 Hz, 1H), 3.06 (d, J = 15.9 Hz, 1H), 2.83 (dd, J = 15.9, 1.8 Hz, 1H), 2.25 (t, J = 2.5 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 175.5, 145.7, 141.7, 129.9, 129.3, 123.8, 123.5, 109.4, 106.0, 82.7, 76.6, 72.5, 72.2, 41.2, 29.2 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{14}NO_2$: 240.1019; Found 240.1069.



1'-Allyl-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3s

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3.5 h) and afforded **3s** (20.8 mg, 86% yield).

Light-yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.35 - 7.32 (m, 1H), 7.29 - 7.26 (m, 1H), 7.06 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 7.8 Hz, 1H), 5.90 - 5.78 (m, 1H), 5.27 - 5.14 (m, 4H), 4.91 (d, J = 12.6 Hz, 1H), 4.70 (d, J = 12.6 Hz, 1H), 4.38 - 4.24 (m, 2H), 3.06 (d, J = 15.8 Hz, 1H), 2.82 (dd, J = 15.8, 1.2 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.1, 145.9, 142.8, 131.2, 129.8, 129.4, 123.8, 123.0, 117.7, 109.3, 106.0, 82.6, 72.1, 42.2, 41.3 ppm. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{16}NO_2$: 242.1176; Found: 242.1216.

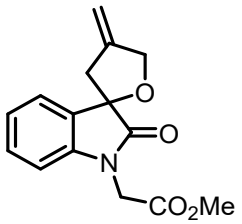


1'-Acetyl-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3t

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3 h) and afforded **3t** (8.5 mg, 35% yield).

Colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.26 - 8.23 (m, 1H), 7.43 - 7.37 (m, 2H), 7.27 - 7.22 (m, 1H), 5.22 - 5.16 (m, 2H), 4.88 (d, J = 12.7 Hz, 1H), 4.74 (dd, J = 12.6, 1.2 Hz, 1H), 3.06 (d, J = 16.0 Hz,

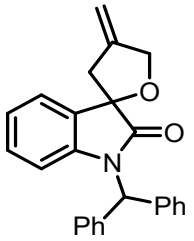
1H), 2.88 (dd, J = 16.0, 1.9 Hz, 1H), 2.68 (s, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.4, 170.6, 145.2, 140.1, 130.5, 128.2, 125.8, 123.6, 116.8, 106.3, 82.6, 72.4, 42.1, 26.5 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{14}NO_3$: 244.0968; Found: 244.0997.



Methyl 2-(4-methylene-2'-oxo-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-1'-yl)acetate 3u

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 2 h) and afforded **3u** (21.9 mg, 80% yield).

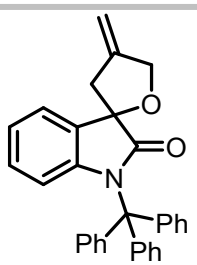
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 (d, J = 7.4 Hz, 1H), 7.32 (dd, J = 7.8, 1.0 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.71 (d, J = 7.8 Hz, 1H), 5.20 - 5.12 (m, 2H), 4.90 (d, J = 12.6 Hz, 1H), 4.71 (dd, J = 12.7, 1.4 Hz, 1H), 4.57 (d, J = 17.6 Hz, 1H), 4.30 (d, J = 17.6 Hz, 1H), 3.76 (s, 3H), 3.08 (d, J = 15.9 Hz, 1H), 2.85 (dd, J = 15.9, 1.7 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.4, 167.9, 145.7, 142.2, 130.0, 129.2, 124.0, 123.5, 108.4, 106.1, 82.6, 72.2, 52.6, 41.5, 41.1 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{15}H_{16}NO_4$: 274.1074; Found: 274.1096.



1'-Benzhydryl-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3v

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3 h) and afforded **3v** (29.8 mg, 81% yield).

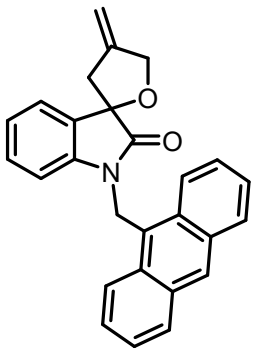
Yellow solid. **MP**: 83.4 – 85.1 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.39 - 7.32 (m, 11H), 7.07 - 7.00 (m, 2H), 6.97 (s, 1H), 6.50 - 6.43 (m, 1H), 5.21 - 5.15 (m, 2H), 4.96 (d, J = 12.5 Hz, 1H), 4.74 (d, J = 12.6 Hz, 1H), 3.10 (d, J = 15.8 Hz, 1H), 2.88 (dd, J = 15.8, 1.5 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.8, 146.0, 142.4, 137.6, 137.3, 129.5, 129.4, 128.63, 128.60, 128.5, 128.4, 127.8, 123.7, 122.8, 112.2, 106.0, 82.4, 72.2, 58.1, 41.6 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{22}NO_2$: 368.1645; Found: 368.1695.



4-Methylene-1'-trityl-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3w

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3 h) and afforded **3w** (38.2 mg, 86% yield).

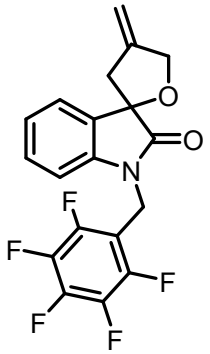
Light-yellow solid. **MP**: 114.6 - 116.3 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50 (d, J = 7.3 Hz, 6H), 7.33 (d, J = 7.0 Hz, 7H), 7.30 (s, 3H), 7.23 (s, 1H), 7.00 - 6.92 (m, 2H), 5.17 - 5.09 (m, 2H), 4.90 (d, J = 12.5 Hz, 1H), 4.70 (d, J = 12.5 Hz, 1H), 3.10 (d, J = 15.9 Hz, 1H), 2.85 (dd, J = 15.9, 1.2 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.6, 146.1, 143.4, 141.9, 129.7, 129.3, 128.4, 127.9, 127.7, 126.9, 123.2, 122.5, 116.0, 105.7, 82.6, 74.2, 72.3, 41.2 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{31}H_{26}NO_2$: 444.1958; Found: 444.1982.



1'-(Anthracen-9-ylmethyl)-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3x

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 7 h) and afforded **3x** (21.7 mg, 55% yield).

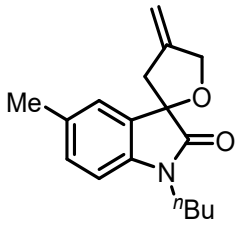
Yellow solid. **MP**: 203.8 - 204.7 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.46 (d, J = 7.5 Hz, 2H), 8.42 (s, 1H), 8.04 (d, J = 8.4 Hz, 2H), 7.64 - 7.58 (m, 2H), 7.50 (t, J = 7.8 Hz, 2H), 7.21 (dd, J = 7.3, 1.4 Hz, 1H), 6.84 - 6.74 (m, 2H), 6.26 - 6.23 (m, 1H), 6.04 (d, J = 15.5 Hz, 1H), 5.74 (d, J = 15.5 Hz, 1H), 5.24 - 5.19 (m, 2H), 5.06 (d, J = 12.6 Hz, 1H), 4.76 (dd, J = 12.6, 1.3 Hz, 1H), 3.12 (d, J = 15.8 Hz, 1H), 2.78 (dd, J = 15.8, 1.6 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.8, 145.9, 142.7, 131.4, 130.9, 129.66, 129.61, 129.55, 128.9, 126.9, 125.8, 125.1, 123.6, 123.4, 122.7, 110.4, 106.0, 82.8, 72.4, 41.9, 37.5 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{22}NO_2$: 392.1645; Found: 392.1686.



4-Methylene-1'-((perfluorophenyl)methyl)-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3y

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 2.5 h) and afforded **3y** (30.2 mg, 79% yield).

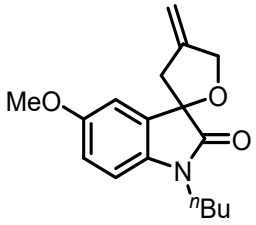
Light-pink oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.34 (dd, J = 7.4, 0.7 Hz, 1H), 7.30 - 7.25 (m, 1H), 7.09 - 7.04 (m, 1H), 6.78 (d, J = 7.8 Hz, 1H), 5.20 - 5.13 (m, 2H), 5.05 (d, J = 15.5 Hz, 1H), 4.92 - 4.84 (m, 2H), 4.69 (dd, J = 12.6, 1.4 Hz, 1H), 3.03 (d, J = 15.8 Hz, 1H), 2.82 (dd, J = 15.8, 1.7 Hz, 1H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.0, 147.4 - 146.9 (m), 145.6, 144.1 - 143.6 (m), 143.1 - 142.7 (m), 141.7, 139.7 - 139.0 (m), 136.2 - 135.7 (m), 130.0, 129.3, 124.1, 123.5, 109.2 - 108.7 (m), 108.2 (t, J = 2.3 Hz), 106.1, 82.4, 72.2, 41.4, 31.8 ppm. **HRMS (ESI)** m/z: $[M+H]^+$ calcd for $C_{19}H_{13}F_5NO_2$: 382.0861; Found: 382.0853.



1'-Butyl-7'-methyl-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3aa.

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 1 h) and afforded **3aa** (24.1 mg, 89% yield).

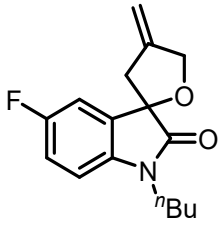
Light-yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.17 (d, J = 7.0 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H), 6.95 (t, J = 7.4 Hz, 1H), 5.16 - 5.10 (m, 2H), 4.89 (d, J = 12.6 Hz, 1H), 4.67 (dd, J = 12.6, 1.4 Hz, 1H), 3.94 - 3.78 (m, 2H), 3.00 (d, J = 15.8 Hz, 1H), 2.75 (dd, J = 15.8, 1.7 Hz, 1H), 2.49 (s, 3H), 1.69 - 1.59 (m, 2H), 1.46 - 1.34 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.4, 146.3, 140.8, 133.8, 130.5, 122.9, 121.7, 119.6, 105.7, 82.0, 72.1, 41.5, 41.4, 31.7, 19.9, 18.9, 13.8 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{22}NO_2$: 272.1645; Found: 272.1673.



1'-Butyl-5'-methoxy-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3ba.

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 1 h) and afforded **3ba** (27.6mg, 96% yield).

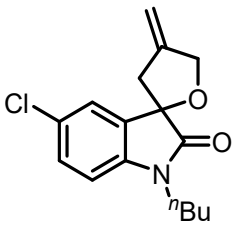
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.93 (d, J = 2.4 Hz, 1H), 6.81 (dd, J = 8.5, 2.4 Hz, 1H), 6.71 (d, J = 8.5 Hz, 1H), 5.16 - 5.10 (m, 2H), 4.88 (d, J = 12.6 Hz, 1H), 4.66 (d, J = 12.6 Hz, 1H), 3.77 (s, 3H), 3.66 - 3.60 (m, 2H), 3.02 (d, J = 15.7 Hz, 1H), 2.75 (dd, J = 15.7, 1.3 Hz, 1H), 1.67 - 1.58 (m, 2H), 1.42 - 1.30 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.0, 156.2, 146.0, 136.3, 130.9, 114.13, 111.1, 109.1, 105.9, 82.9, 72.1, 55.8, 41.4, 39.7, 29.3, 20.1, 13.7 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{22}NO_3$: 288.1594; Found: 288.1625.



1'-Butyl-5'-fluoro-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3ca

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 1 h) and afforded **3ca** (27.5 mg, > 99% yield).

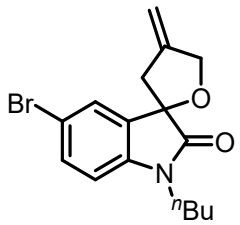
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.07 (dd, J = 7.6, 2.6 Hz, 1H), 7.00 (td, J = 8.8, 2.6 Hz, 1H), 6.74 (dd, J = 8.5, 4.0 Hz, 1H), 5.19 - 5.14 (m, 2H), 4.89 (d, J = 12.6 Hz, 1H), 4.67 (dd, J = 12.6, 1.6 Hz, 1H), 3.65 (t, J = 7.2 Hz, 2H), 3.05 (d, J = 15.7 Hz, 1H), 2.75 (dd, J = 15.7, 1.7 Hz, 1H), 1.69 - 1.59 (m, 2H), 1.44 - 1.31 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.0, 159.3 (d, J = 240.0 Hz), 145.5, 138.8 (d, J = 2.3 Hz), 131.4 (d, J = 7.5 Hz), 115.9 (d, J = 23.2 Hz), 112.0 (d, J = 24.8 Hz), 109.2 (d, J = 8.2 Hz), 106.3, 82.6, 72.2, 41.3, 39.8, 29.2, 20.1, 13.7 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{19}FNO_2$: 276.1394; Found: 276.1429.



1'-Butyl-5'-chloro-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3da

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 0.5 h) and afforded **3da** (26.6 mg, 91% yield).

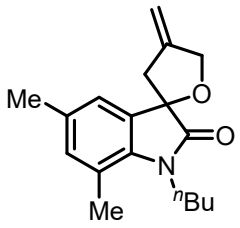
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.29 - 7.25 (m, 2H), 6.75 (d, J = 8.0 Hz, 1H), 5.19 - 5.14 (m, 2H), 4.88 (d, J = 12.6 Hz, 1H), 4.67 (dd, J = 12.6, 1.6 Hz, 1H), 3.64 (t, J = 7.2 Hz, 2H), 3.04 (d, J = 15.7 Hz, 1H), 2.76 (dd, J = 15.7, 1.7 Hz, 1H), 1.68 - 1.58 (m, 2H), 1.43 - 1.31 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 175.9, 145.4, 141.5, 131.5, 129.6, 128.2, 124.4, 109.6, 106.4, 82.4, 72.2, 41.3, 39.8, 29.2, 20.1, 13.7 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{19}ClNO_2$: 292.1099; Found: 292.1138.



5'-Bromo-1'-butyl-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3ea

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 0.5 h) and afforded **3ea** (32.5 mg, 97% yield).

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.44 - 7.40 (m, 2H), 6.70 (d, J = 8.8 Hz, 1H), 5.20 - 5.13 (m, 2H), 4.87 (d, J = 12.6 Hz, 1H), 4.67 (dd, J = 12.6, 1.7 Hz, 1H), 3.64 (t, J = 7.2 Hz, 2H), 3.04 (d, J = 15.6 Hz, 1H), 2.76 (dd, J = 15.8, 1.8 Hz, 1H), 1.68 - 1.58 (m, 2H), 1.43 - 1.30 (m, 2H), 0.94 (t, J = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 175.8, 145.3, 142.1, 132.6, 131.8, 127.1, 115.4, 110.1, 106.4, 82.4, 72.2, 41.3, 39.8, 29.2, 20.1, 13.7 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{19}BrNO_2$: 336.0594; Found: 336.0639.

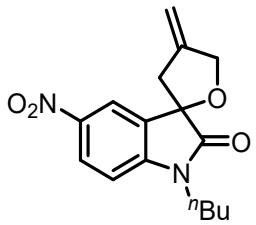


1'-Butyl-5',7'-dimethyl-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3fa

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3.5 h) and afforded **3fa** (23.0 mg, 81% yield).

Colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.00 (s, 1H), 6.86 (s, 1H), 5.16 - 5.10 (m, 2H), 4.89 (d, J = 12.5 Hz, 1H), 4.67 (dd, J = 12.6, 1.4 Hz, 1H), 3.92 - 3.76 (m, 2H), 2.99 (d, J = 15.8 Hz, 1H), 2.75 (dd, J

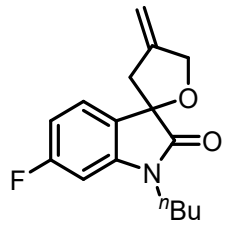
= 15.8, 1.7 Hz, 1H), 2.45 (s, 3H), 2.28 (s, 3H), 1.68 - 1.58 (m, 2H), 1.46 - 1.33 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.4, 146.4, 138.3, 134.2, 132.4, 130.6, 122.4, 119.3, 105.6, 82.2, 72.1, 41.5, 41.3, 31.6, 20.6, 19.9, 18.7, 13.8 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{24}NO_2$: 286.1802; Found: 286.1845.



1'-Butyl-4-methylene-5'-nitro-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3ga

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 12 h) and afforded **3ga** (28.9 mg, 96% yield).

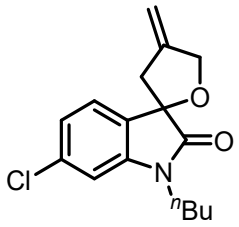
Reddish brown oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 8.7, 2.3 Hz, 1H), 8.06 (d, *J* = 2.2 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 1H), 5.14 - 5.09 (m, 2H), 4.78 (d, *J* = 12.6 Hz, 1H), 4.63 (dd, *J* = 12.6, 0.9 Hz, 1H), 3.64 (t, *J* = 7.2 Hz, 2H), 2.97 (d, *J* = 15.8 Hz, 1H), 2.77 (dd, *J* = 15.8, 1.3 Hz, 1H), 1.63 - 1.53 (m, 2H), 1.36 - 1.23 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.4, 148.8, 144.7, 143.3, 130.5, 126.9, 119.6, 108.4, 106.8, 81.8, 72.3, 41.1, 40.0, 29.2, 20.0, 13.6 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{19}N_2O_4$: 303.1339; Found: 330.1387.



1'-Butyl-6'-fluoro-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3ha

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3 h) and afforded **3ha** (21.1 mg, 77% yield).

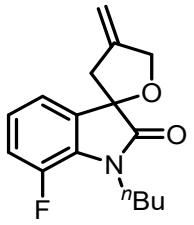
Pink oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.29 - 7.24 (m, 1H), 6.75 - 6.69 (m, 1H), 6.56 (dd, *J* = 9.0, 2.0 Hz, 1H), 5.15 (d, *J* = 13.9 Hz, 2H), 4.88 (d, *J* = 12.6 Hz, 1H), 4.66 (dd, *J* = 12.6, 0.7 Hz, 1H), 3.63 (t, *J* = 7.2 Hz, 2H), 3.02 (d, *J* = 15.8 Hz, 1H), 2.76 (dd, *J* = 15.8, 1.2 Hz, 1H), 1.69 - 1.60 (m, 2H), 1.44 - 1.32 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.6, 164.1 (d, *J* = 245.2 Hz), 145.7, 144.8 (d, *J* = 11.2 Hz), 125.1 (d, *J* = 9.8 Hz), 124.9, 108.8 (d, *J* = 22.5 Hz), 106.1, 97.5 (d, *J* = 27.8 Hz), 82.2, 72.0, 41.2, 39.8, 29.3, 20.1, 13.7 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{19}FNO_2$: 276.1394; Found: 276.1417.



1'-Butyl-6'-chloro-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3ia

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 1.5 h) and afforded **3ia** (22.9 mg, 78% yield).

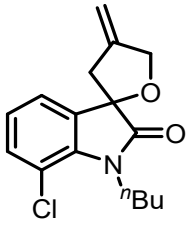
Grey oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.23 (d, J = 15.8 Hz, 1H), 7.02 (dd, J = 7.9, 1.7 Hz, 1H), 6.81 (d, J = 1.6 Hz, 1H), 5.18 - 5.12 (m, 2H), 4.88 (d, J = 12.7 Hz, 1H), 4.66 (dd, J = 12.6, 1.5 Hz, 1H), 3.64 (t, J = 7.2 Hz, 2H), 3.02 (d, J = 15.8 Hz, 1H), 2.75 (dd, J = 15.8, 1.7 Hz, 1H), 1.70 - 1.60 (m, 2H), 1.44 - 1.32 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.3, 145.6, 144.3, 135.7, 128.1, 124.8, 122.6, 109.3, 106.2, 82.2, 72.1, 41.2, 39.8, 29.2, 20.1, 13.7 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{19}ClNO_2$: 292.1099; Found: 292.1128.



1'-Butyl-7'-chloro-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3ja

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 1 h) and afforded **3ja** (26.2 mg, 95% yield).

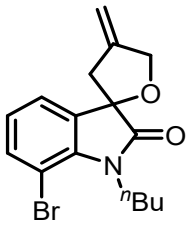
Light-yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.12 (d, J = 6.9 Hz, 1H), 7.08 - 6.96 (m, 2H), 5.18 - 5.13 (m, 2H), 4.89 (d, J = 12.6 Hz, 1H), 4.68 (d, J = 12.7 Hz, 1H), 3.81 (t, J = 7.3 Hz, 2H), 3.04 (d, J = 15.8 Hz, 1H), 2.77 (d, J = 15.8 Hz, 1H), 1.72 - 1.62 (m, 2H), 1.45 - 1.32 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.0, 150.5 (d, J = 231.0 Hz), 145.6, 132.7 (d, J = 3.0 Hz), 129.6 (d, J = 9.0 Hz), 123.6 (d, J = 6 Hz), 119.6 (d, J = 3.0 Hz), 118.0 (d, J = 20.2 Hz), 106.1, 82.6 (d, J = 2.3 Hz), 72.2, 41.7 (d, J = 5.3 Hz), 41.5, 30.9 (d, J = 3.0 Hz), 19.9, 13.7 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{19}FNO_2$: 276.1394; Found: 276.1360.



1'-Butyl-7'-chloro-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3ka

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 1 h) and afforded **3ka** (29.1 mg, >99% yield).

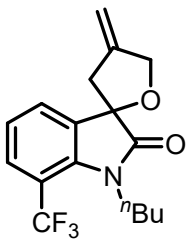
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.24 - 7.20 (m, 2H), 6.96 (t, J = 7.9 Hz, 1H), 5.17 - 5.12 (m, 2H), 4.88 (d, J = 12.6 Hz, 1H), 4.67 (dd, J = 12.6, 1.5 Hz, 1H), 4.02 (t, J = 7.5 Hz, 2H), 3.01 (d, J = 15.8 Hz, 1H), 2.74 (dd, J = 15.8, 1.8 Hz, 1H), 1.74 - 1.64 (m, 2H), 1.44 - 1.32 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.8, 145.6, 139.0, 132.8, 132.3, 123.8, 122.3, 115.3, 106.2, 81.9, 72.2, 41.6, 41.3, 31.7, 19.8, 13.8 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{19}ClNO_2$: 292.1099; Found: 292.1104.



7'-Bromo-1'-butyl-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3la

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3 h) and afforded **3la** (28.7 mg, 85% yield).

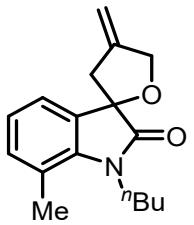
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.41 (dd, J = 8.2, 1.1 Hz, 1H), 7.25 (dd, J = 7.3, 1.0 Hz, 1H), 6.92 - 6.87 (m, 1H), 5.17 - 5.11 (m, 2H), 4.88 (d, J = 12.6 Hz, 1H), 4.66 (dd, J = 12.6, 1.5 Hz, 1H), 4.05 (t, J = 7.6 Hz, 2H), 3.01 (d, J = 15.8 Hz, 1H), 2.74 (dd, J = 15.8, 1.8 Hz, 1H), 1.74 - 1.64 (m, 2H), 1.45 - 1.33 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.0, 145.6, 140.5, 135.6, 133.2, 124.1, 122.9, 106.2, 102.4, 81.8, 72.2, 41.6, 40.9, 31.6, 19.8, 13.8 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{19}BrNO_2$: 336.0594; Found: 336.0563.



1'-Butyl-4-methylene-7'-(trifluoromethyl)-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3ma

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 1 h) and afforded **3ma** (30.8 mg, 95% yield).

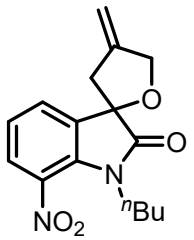
Light-yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.59 (d, J = 8.1 Hz, 1H), 7.49 (d, J = 7.1 Hz, 1H), 7.11 (t, J = 7.7 Hz, 1H), 5.18 - 5.13 (m, 2H), 4.90 (d, J = 12.5 Hz, 1H), 4.69 (dd, J = 12.6, 1.5 Hz, 1H), 3.91 - 3.75 (m, 2H), 3.02 (d, J = 15.8 Hz, 1H), 2.76 (dd, J = 15.8, 1.8 Hz, 1H), 1.65 - 1.54 (m, 2H), 1.42 - 1.30 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.7, 145.4, 141.1 (q, J = 2.3 Hz), 132.5, 127.8 (q, J = 6.0 Hz), 127.4, 123.4 (q, J = 269.9 Hz), 122.3, 112.7 (q, J = 33.0 Hz), 106.3, 80.6, 72.2, 42.1 (q, J = 4.5 Hz), 41.5, 29.8 (q, J = 2.3 Hz), 20.0, 13.6 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{19}F_3NO_2$: 326.1362; Found: 326.1340.



1'-Butyl-7'-methyl-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3na

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3.5 h) and afforded **3na** (23.5 mg, 87% yield).

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.17 (d, J = 7.0 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H), 6.95 (t, J = 7.4 Hz, 1H), 5.16 - 5.10 (m, 2H), 4.89 (d, J = 12.6 Hz, 1H), 4.67 (dd, J = 12.6, 1.4 Hz, 1H), 3.94 - 3.78 (m, 2H), 3.00 (d, J = 15.8 Hz, 1H), 2.75 (dd, J = 15.8, 1.7 Hz, 1H), 2.49 (s, 3H), 1.69 - 1.59 (m, 2H), 1.46 - 1.34 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.4, 146.3, 140.8, 133.8, 130.5, 122.9, 121.7, 119.6, 105.7, 82.0, 72.1, 41.5, 41.4, 31.7, 19.9, 18.9, 13.8 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{22}NO_2$: 272.1645; Found: 272.1689.

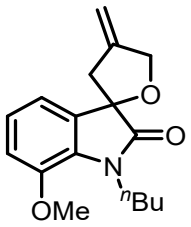


1'-Butyl-4-methylene-7'-nitro-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3oa

The reaction was conducted on a 0.11 mmol scale according to the general procedures (reaction time: 3 h) and afforded **3oa** (29.7 mg, 89% yield).

Reddish brown oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.69 (d, J = 8.3 Hz, 1H), 7.53 (d, J = 6.6 Hz, 1H), 7.14 (t, J = 8.0 Hz, 1H), 5.21 - 5.16 -(m, 2H), 4.91 (d, J = 12.6 Hz, 1H), 4.71 (dd, J = 12.6, 1.2 Hz, 1H),

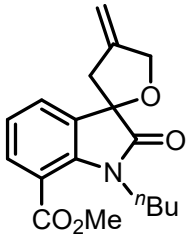
3.97 - 3.87 (m, 1H), 3.76 - 3.67 (m, 1H), 3.07 (d, *J* = 15.8 Hz, 1H), 2.80 (dd, *J* = 15.8, 1.6 Hz, 1H), 1.45 - 1.35 (m, 2H), 1.32 - 1.20 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.3, 148.8, 144.8, 135.9, 133.7, 127.6, 125.8, 122.7, 106.8, 80.8, 72.4, 41.9, 41.7, 29.7, 19.7, 13.6 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{19}N_2O_4$: 303.1339; Found: 303.1385.



1'-Butyl-7'-methoxy-4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one 3pa

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3 h) and afforded **3pa** (29.7 mg, 72% yield).

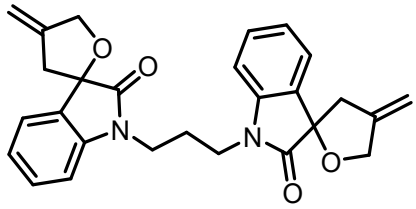
Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.04 - 6.94 (m, 2H), 6.90 (d, *J* = 8.0 Hz, 1H), 5.16 - 5.10 (m, 2H), 4.89 (d, *J* = 12.6 Hz, 1H), 4.67 (dd, *J* = 12.6, 1.4 Hz, 1H), 3.90 (t, *J* = 7.3 Hz, 2H), 3.86 (s, 3H), 3.01 (d, *J* = 15.8 Hz, 1H), 2.75 (dd, *J* = 15.8, 1.6 Hz, 1H), 1.69 - 1.59 (m, 2H), 1.43 - 1.30 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.6, 146.2, 145.0, 131.4, 130.9, 123.6, 116.3, 113.7, 105.8, 82.7, 72.1, 55.9, 42.0, 41.5, 31.4, 20.0, 13.8 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{22}NO_3$: 288.1594; Found: 288.1569.



Methyl 1'-butyl-4-methylene-2'-oxo-4,5-dihydro-3H-spiro[furan-2,3'-indoline]-7'-carboxylate 3qa

The reaction was conducted on a 0.35 mmol scale according to the general procedures (reaction time: 3 h) and afforded **3qa** (74.7 mg, 69% yield).

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 6.8 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 5.16 - 5.11 (m, 2H), 4.89 (d, *J* = 12.6 Hz, 1H), 4.67 (dd, *J* = 12.6, 0.7 Hz, 1H), 4.01 - 3.78 (m, 5H), 3.01 (d, *J* = 15.8 Hz, 1H), 2.75 (dd, *J* = 15.8, 1.4 Hz, 1H), 1.47 - 1.37 (m, 2H), 1.32 - 1.19 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 177.6, 167.2, 145.6, 141.1, 131.8, 130.9, 126.4, 122.2, 116.4, 106.2, 81.3, 72.3, 52.6, 41.5, 41.3, 29.1, 19.8, 13.7 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{22}NO_4$: 316.1543; Found: 316.1552.



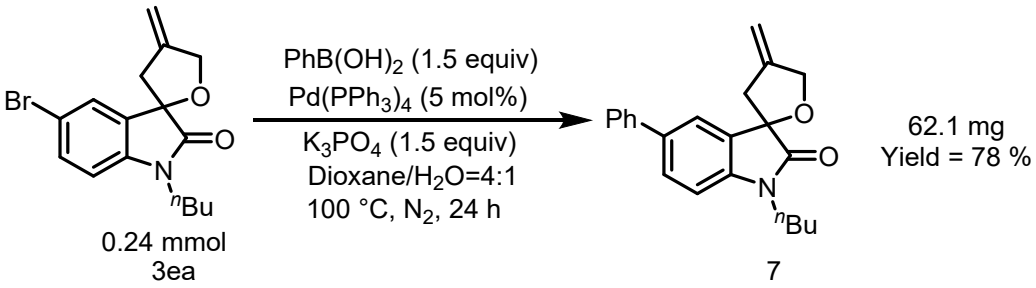
1',1'''-(Propane-1,3-diyl)bis(4-methylene-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one) 3ra

The reaction was conducted on a 0.10 mmol scale according to the general procedures (reaction time: 3 h) and afforded **3ra** (43.2 mg, 98% yield).

Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 - 7.30 (m, 4H), 7.05 (t, J = 7.5 Hz, 2H), 6.76 (dd, J = 7.8, 3.1 Hz, 2H), 5.17 - 5.12 (m, 4H), 4.88 (d, J = 12.6 Hz, 2H), 4.68 (dd, J = 12.6, 1.0 Hz, 2H), 3.83 – 3.67 (m, 4H), 3.01 (d, J = 15.8 Hz, 2H), 2.79 (d, J = 15.8 Hz, 2H), 2.13 - 2.04 (m, 2H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.50, 176.45, 145.9, 142.5, 142.4, 130.0, 129.6, 129.5, 124.0, 123.2, 108.5, 108.4, 106.0, 82.6, 82.5, 72.1, 41.2, 37.6, 37.5, 25.3 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{27}H_{27}N_2O_4$: 443.1965; Found: 443.1996.

3. Transformations of products 3ea, 3ga and 3la.

(1) The Suzuki Coupling Reaction of **3ea**

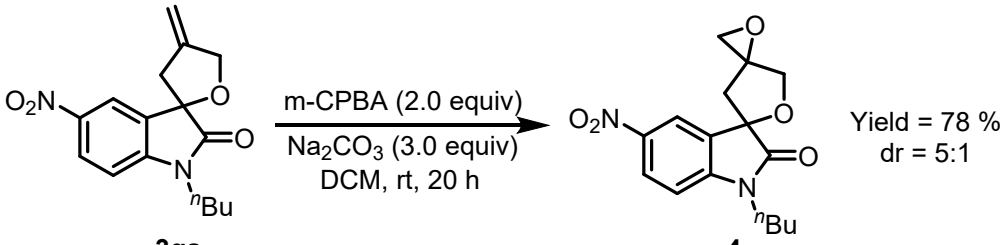


3ea (82.2 mg, 0.24mmol, 1.0 equiv), $PhB(OH)_2$ (44 mg, 0.36 mmol, 1.5 equiv), $Pd(PPh_3)_4$ (14 mg, 0.012 mmol, 5 mol%), K_3PO_4 (77 mg, 0.36 mmol, 1.5 equiv), 1,4-dioxane (2 mL) and H_2O (0.5 mL) were added into a 10 mL glass vial. The vial was purged with N_2. The reaction mixture was heated at 100 °C for 24 h. After being cooled to room temperature, the mixture was poured into water (3 mL), then extracted with EtOAc (5 mL×3). The combined organic layer was washed with brine (20 mL), dried with anhydrous Na_2SO_4 and filtered. The filtrate was concentrated in vacuo and the residue was purified by silica gel column chromatography to give the desired product 7 as a yellow oil in 78 % yield (62.1 mg).

1'-Butyl-4-methylene-5'-phenyl-4,5-dihydro-3H-spiro[furan-2,3'-indolin]-2'-one (7), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 - 7.54 (m, 4H), 7.45 (t, J = 7.4 Hz, 2H), 7.35 (t, J = 7.2 Hz, 1H), 6.92 (d, J = 8.2

Hz, 1H), 5.22 - 5.16 (m, 2H), 4.96 (d, *J* = 12.6 Hz, 1H), 4.75 (d, *J* = 12.7 Hz, 1H), 3.72 (t, *J* = 7.2 Hz, 2H), 3.11 (d, *J* = 15.8 Hz, 1H), 2.88 (dd, *J* = 15.8, 1.3 Hz, 1H), 1.76 - 1.66 (m, 2H), 1.49 - 1.37 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.4, 145.9, 142.4, 140.7, 136.4, 130.3, 128.8, 128.7, 127.1, 126.8, 122.8, 108.9, 106.1, 82.8, 72.2, 41.4, 39.8, 29.4, 20.2, 13.8 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{24}NO_2$: 334.1802; Found: 334.1819.

(2) Oxidation of 3ga with m-chloroperoxybenzoic acid (m-CPBA)

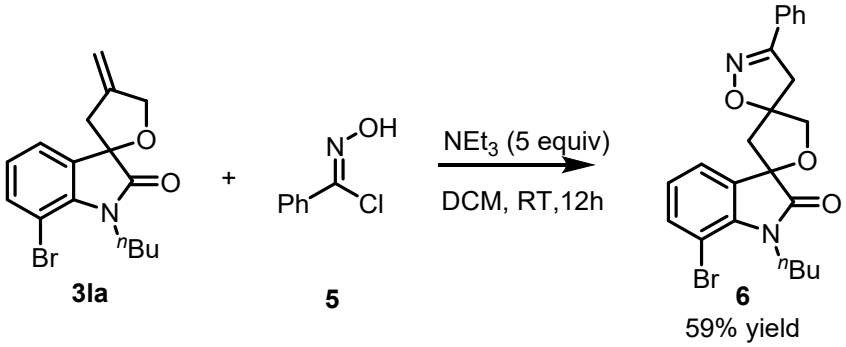


3ga **4**

To a solution of 3ga (106.7 mg, 0.35 mmol) in DCM (4 mL) was sequentially added an aqueous solution of Na_2CO_3 (111.3 mg, 3.0 equiv.) and 3-chloroperoxybenzoic acid (m-CPBA, 120.8 mg, 2.0 equiv.) at r.t. The reaction mixture was stirred for 20 h and poured into a saturated solution of aqueous sodium bicarbonate. The two layers were separated and the organic layer was washed with a saturated solution of aqueous sodium bicarbonate. This procedure was repeated twice more. The organic layer was dried over MgSO4, filtered, and concentrated on a rotary evaporator. The crude product was purified by column chromatography to give 4 as a brown oil in 78 % yield, dr = 5:1 (86.7 mg).

1-Butyl-5-nitro-3'H,5'H-dispiro[indoline-3,2'-furan-4',2''-oxiran]-2-one (4), ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (d, *J* = 2.3 Hz, 1H), 8.26 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.93 (d, *J* = 8.7 Hz, 1H), 4.59 (d, *J* = 10.0 Hz, 1H), 4.06 (d, *J* = 10.0 Hz, 1H), 3.72 (td, *J* = 7.1, 2.5 Hz, 2H), 3.18 (d, *J* = 4.1 Hz, 1H), 3.11 (d, *J* = 4.1 Hz, 1H), 2.87 (d, *J* = 14.0 Hz, 1H), 2.17 (d, *J* = 14.0 Hz, 1H), 1.71 - 1.61 (m, 2H), 1.43 - 1.31 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 4H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 176.3, 148.6, 143.7, 130.5, 127.0, 120.7, 108.4, 82.2, 73.0, 64.1, 48.4, 40.3, 40.0, 29.2, 20.0, 13.6. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{16}H_{19}N_2O_5$: 319.1288; Found: 319.1308.

(3) The Transformation of 3la.



3la **5** **6**

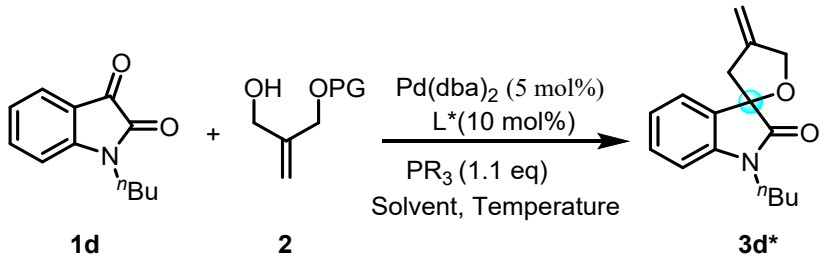
59% yield

A flame-dried Schlenk tube was charged compound **3la** (52.8 mg, 0.16 mmol) and purged with nitrogen. CH_2Cl_2 (1.0 mL) was added via syringe to the reaction tube. A second flame-dried tube was charged with benzaldoxime chloride **5** (123.7 mg, 0.8 mmol, 5.0 equiv.) and CH_2Cl_2 (1.0 mL) and purged with nitrogen. Triethylamine (112.0 μL, 0.8 mmol, 5.0 equiv.) was added to the second tube, which was stirred 15 minutes at room temperature. The oxime chloride solution was then transferred to the tube containing 3m via syringe. The mixture was stirred 12 hours at room temperature. After completion, the reaction mixture was quenched with water and extracted with CH_2Cl_2 for three times. The resulted filtrate was separated. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The crude mixture was purified by silica gel column chromatography (petroleum ether/ethyl acetate= 10:1) to give product 6 as a yellow solid in 59% yield (43.1 mg).

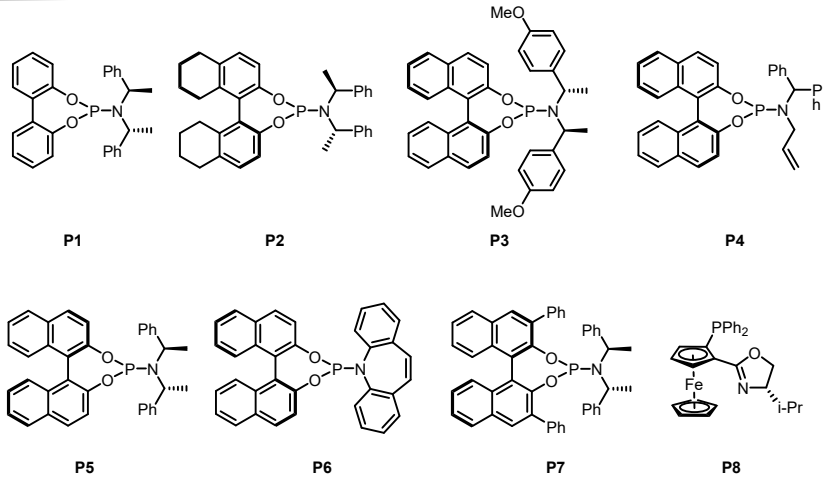
7-Bromo-1-butyl-3''-phenyl-3'H,4''H,5'H-dispiro[indoline-3,2'-furan-4',5''-isoxazol]-2-one (6), Yellow solid. **MP**: 126.9 - 128.6 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.74 - 7.67 (m, 3H), 7.44 - 7.42 (m, 4H), 6.97 (t, J = 7.9 Hz, 1H), 4.44 (q, J = 9.6 Hz, 2H), 4.09 - 4.04 (m, 2H), 3.64 - 3.49 (m, 2H), 2.70 (q, J = 14.0 Hz, 2H), 1.76 – 1.66 (m, 2H), 1.47 - 1.34 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 178.0, 156.7, 140.4, 135.8, 133.0, 130.4, 129.2, 128.8, 126.6, 124.8, 124.7, 102.2, 93.1, 82.3, 78.8, 47.2, 41.1, 40.9, 31.6, 19.8, 13.8 ppm. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{24}BrN_2O_3$ 455.0965; Found 455.0998.

4. Screening Asymmetric Reaction Conditions

Table S1. Selected Screening Asymmetric Reaction Conditions of **1d** and **2** [a]



1d **2** **3d***



P1 **P2** **P3** **P4** **P5** **P6** **P7** **P8**

entry	PG	L*	PR_3	Solvent	T(℃)	yield[b]	ee[c]
1	Boc	**P1**	$P(NMe_2)_3$	DCM	-78-rt	34%	25%
2	Boc	**P2**	$P(NMe_2)_3$	DCM	-78-rt	50%	40%
3	Boc	**P3**	$P(NMe_2)_3$	DCM	-78-rt	82%	38%
4	Boc	**P4**	$P(NMe_2)_3$	DCM	-78-rt	59%	38%
5	Boc	**P5**	$P(NMe_2)_3$	DCM	-78-rt	87%	31%
6	Boc	**P6**	$P(NMe_2)_3$	DCM	-78-rt	83%	5%
7	Boc	**P7**	$P(NMe_2)_3$	DCM	-78-rt	ND[d]	-
8	Boc	**P8**	$P(NMe_2)_3$	DCM	-78-rt	ND	-
9	Boc	**P5**	$P(NMe_2)_3$	DCE	-35-rt	trace	-

10	Boc	**P5**	$P(NMe_2)_3$	CH_3CN	-40-rt	59%	18%
11	Boc	**P5**	$P(NMe_2)_3$	$HCCl_3$	-60-rt	ND	-
12	Boc	**P5**	$P(NMe_2)_3$	THF	-78-rt	ND	-
13	Boc	**P5**	$P(NMe_2)_3$	Et_2O	-78-rt	trace	-
14	Boc	**P5**	$P(NMe_2)_3$	CH_3OH	-78-rt	17%	27%
15	Boc	**P5**	$P(NMe_2)_3$	EA	-78-rt	17%	rac
16	Boc	**P5**	$P(NMe_2)_3$	toluene	-78-rt	trace	-
17	Boc	**P5**	$P(NMe_2)_3$	*n*-hexane	-78-rt	trace	-
18	Boc	**P5**	$P(NEt_2)_3$	DCM	-78-rt	42%	22%
19[d]	Boc	**P5**	$P(pyrrolidinyl)_3$	DCM	-78-rt	67%	12%
20	Boc	**P5**	$P(OMe)_3$	DCM	-78-rt	ND	-
21	$CO_2{}^iPr$	**P5**	$P(NMe_2)_3$	DCM	-78-rt	10%	41%
22	CO_2Bn	**P5**	$P(NMe_2)_3$	DCM	-78-rt	14%	31%
23	CO_2Me	**P5**	$P(NMe_2)_3$	DCM	-78-rt	69%	18%
24	COMe	**P5**	$P(NMe_2)_3$	DCM	-78-rt	18%	40%

[a] Conducted with **1d** (0.1 mmol), **2** (0.2 mmol), [Pd] (5 mol %), ligand (10 mol %) in solvent (1.0 mL) at corresponding temperature under N_2 atmosphere.

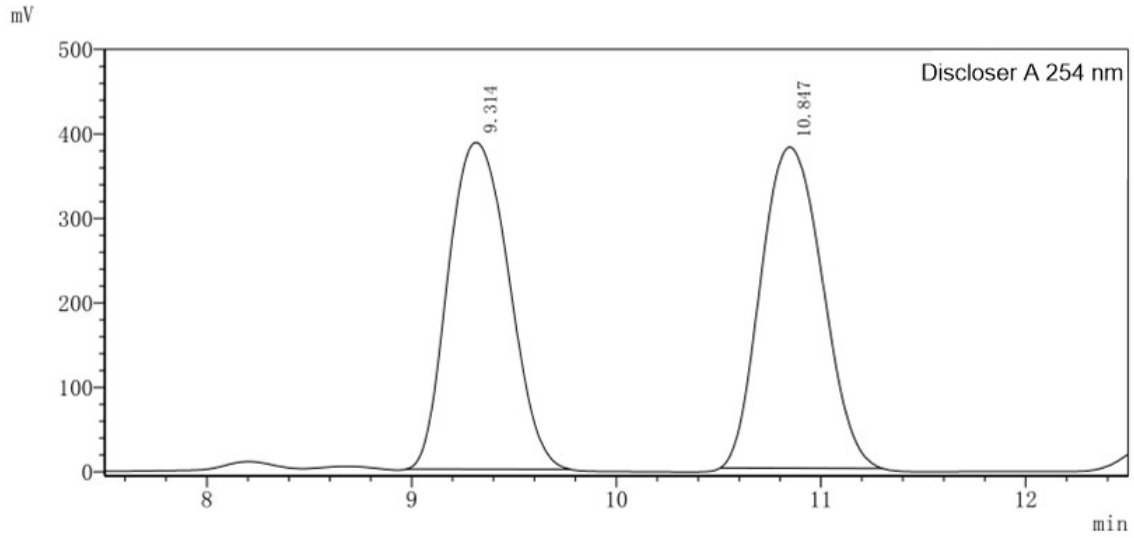
[b] Isolated yield.

[c] Determined by HPLC analysis using a chiral stationary phase.

[d] ND = no detected.

HPLC acquisition parameters: Chiral column: CHIRALCEL ® AD-H, Wave length: 254 nm, Mobile phase: iPrOH:Hex=3:97, Flow rate: 1mL/min

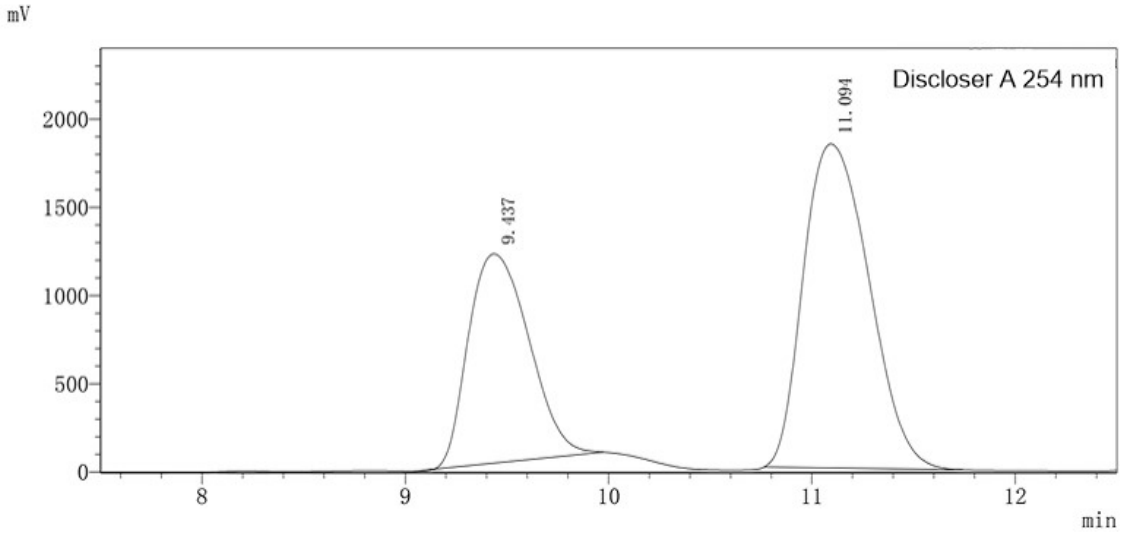
HPLC Spectra of racemic **3d***



Discloser A 254 nm

Peak	Reten time (min)	Area(%)
1	9.314	50.033
2	10.847	49.967
total		100

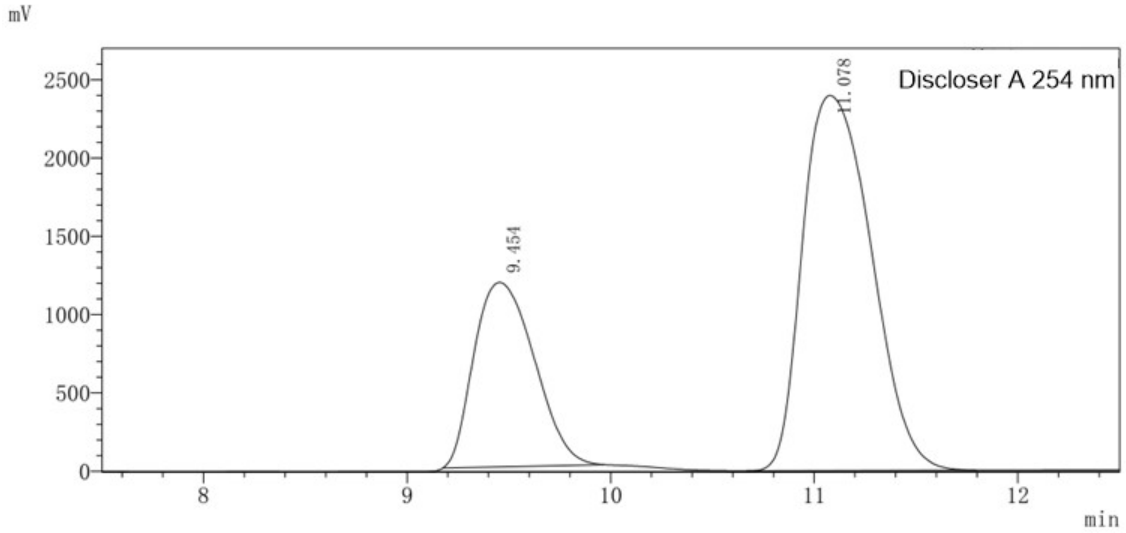
HPLC Spectra of enantiomeric **3d*** using **P1**



Discloser A 254 nm

Peak	Reten time (min)	Area(%)
1	9.437	37.341
2	11.094	62.659
total		100

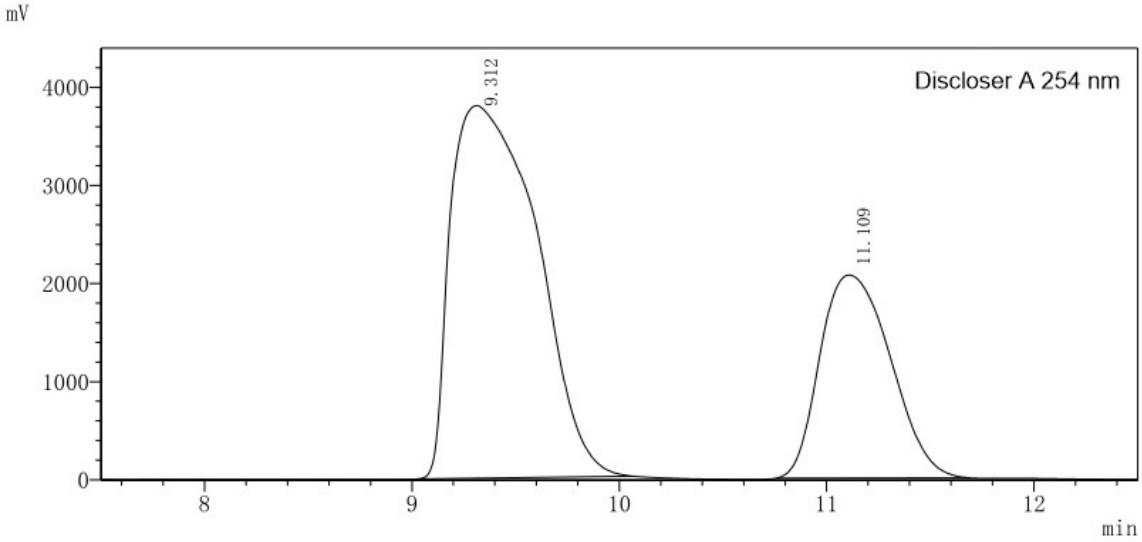
HPLC Spectra of enantiomeric **3d*** using **P2**



Discloser A 254 nm

Peak	Reten time (min)	Area(%)
1	9.454	30.127
2	11.078	69.873
total		100

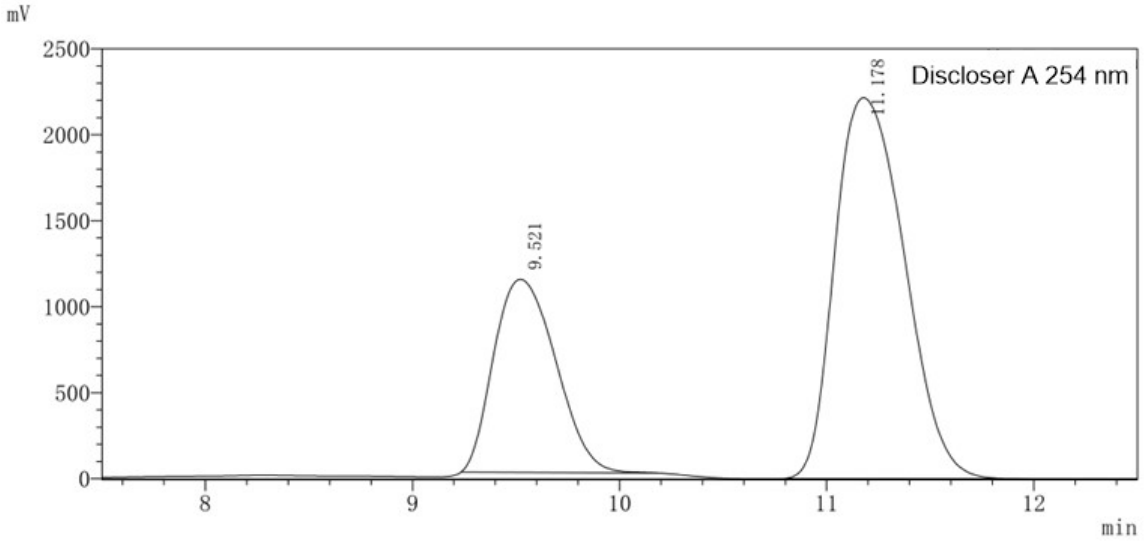
HPLC Spectra of enantiomeric **3d*** using **P3**



Discloser A 254 nm

Peak	Reten time (min)	Area(%)
1	9.312	69.167
2	11.109	30.833
total		100

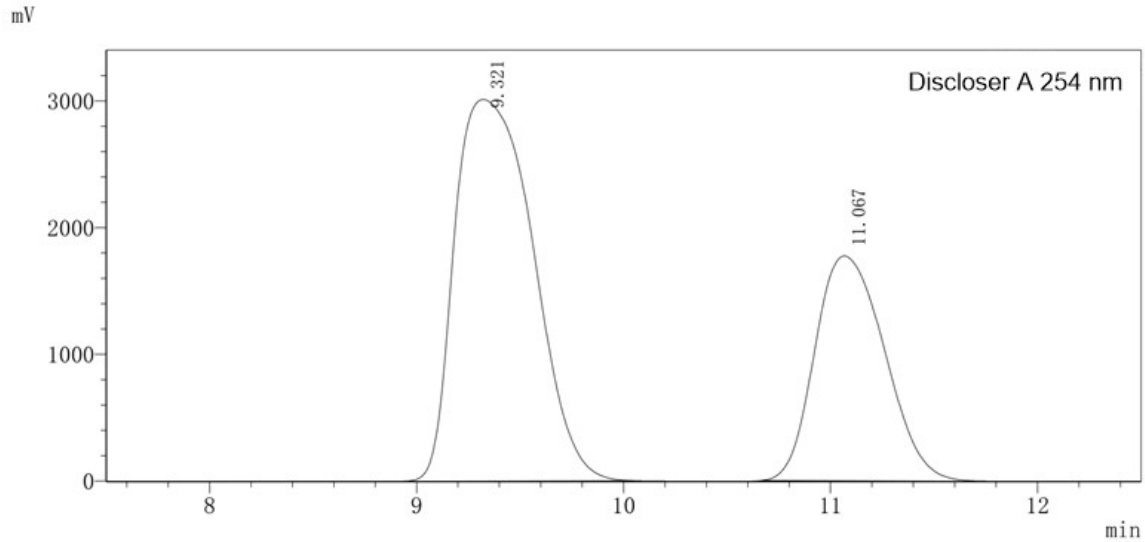
HPLC Spectra of enantiomeric **3d*** using **P4**



Discloser A 254 nm

Peak	Reten time (min)	Area(%)
1	9.521	31.196
2	11.178	68.804
total		100

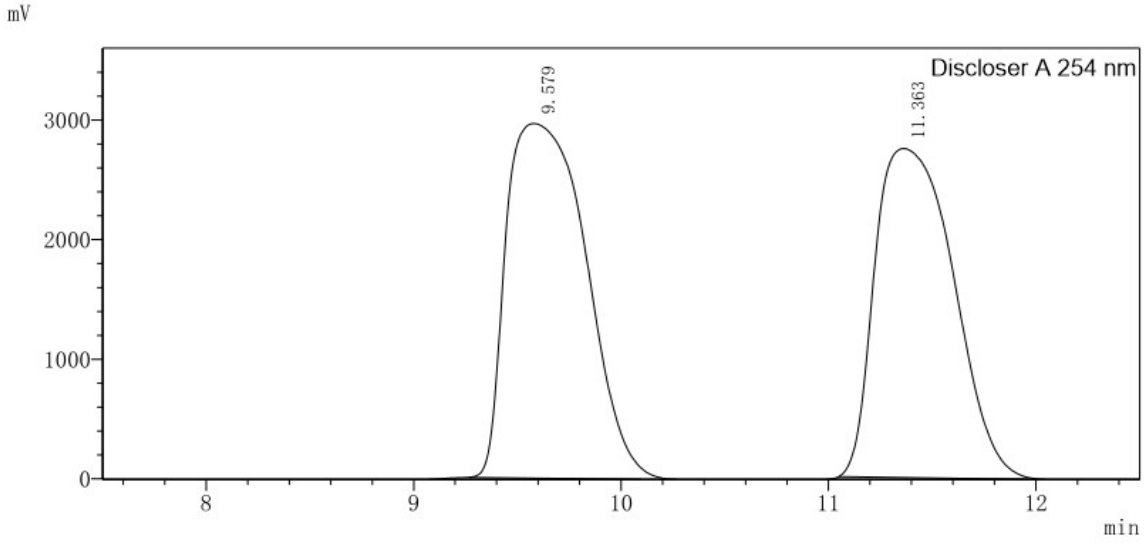
HPLC Spectra of enantiomeric **3d*** using **P5**



Discloser A 254 nm

Peak	Reten time (min)	Area(%)
1	9.321	65.651
2	11.067	34.349
total		100

HPLC Spectra of enantiomeric **3d*** using **P6**



Discloser A 254 nm

Peak	Reten time (min)	Area(%)
1	9.579	52.272
2	11.363	47.728
total		100

5. Reference

[1] a) Feng Shi, Zhonglin Tao, *Chem. Eur. J.* **2012**, *18*, 6885-6894; b) Ping Zhao, Yanzhong Li, *Eur. J. Med. Chem.* **2014**, *86*, 165-174; c) Jie Zheng, Yujin Li, *Tetrahedron.* **2015**, *71,* 3802-3809.

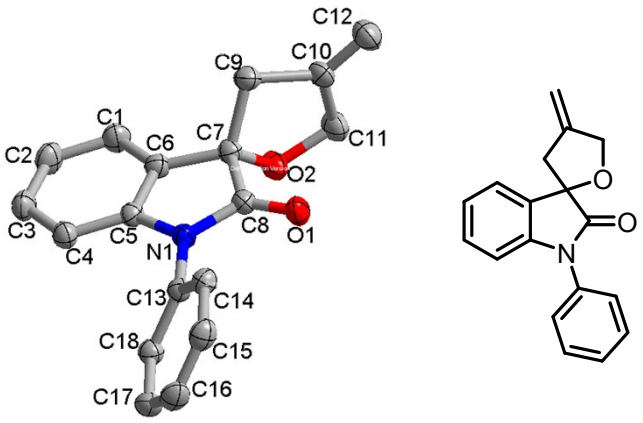
[2] a) Zhengbo Yuan, Rui Pan, *Adv. Synth. Catal.* **2017**, *359*, 4244-4249; b) Barry M. Trost, Guillaume Mata, *Angew. Chem. Int. Ed.* **2018**, *57*, 12333-12337.

6. X-Ray single crystal data of product 3i

The X-ray crystallographic structures for **3i**. ORTEP view of the molecules of complex **3i**, showing ellipsoids at 30% probability level. Crystal data have been deposited to CCDC, number **3i (2127377)**.

A summary of the fundamental crystal and refinement data are given in the Table S**2** of the Supporting Information. Atomic coordinates, anisotropic displacement parameters and bond lengths and angles can be found in the cif files.

Yellow crystals suitable for X-ray diffraction (Gemini E) were grown by n-hexane/dichloromethane solution of **3i** inside a penicillin bottle.



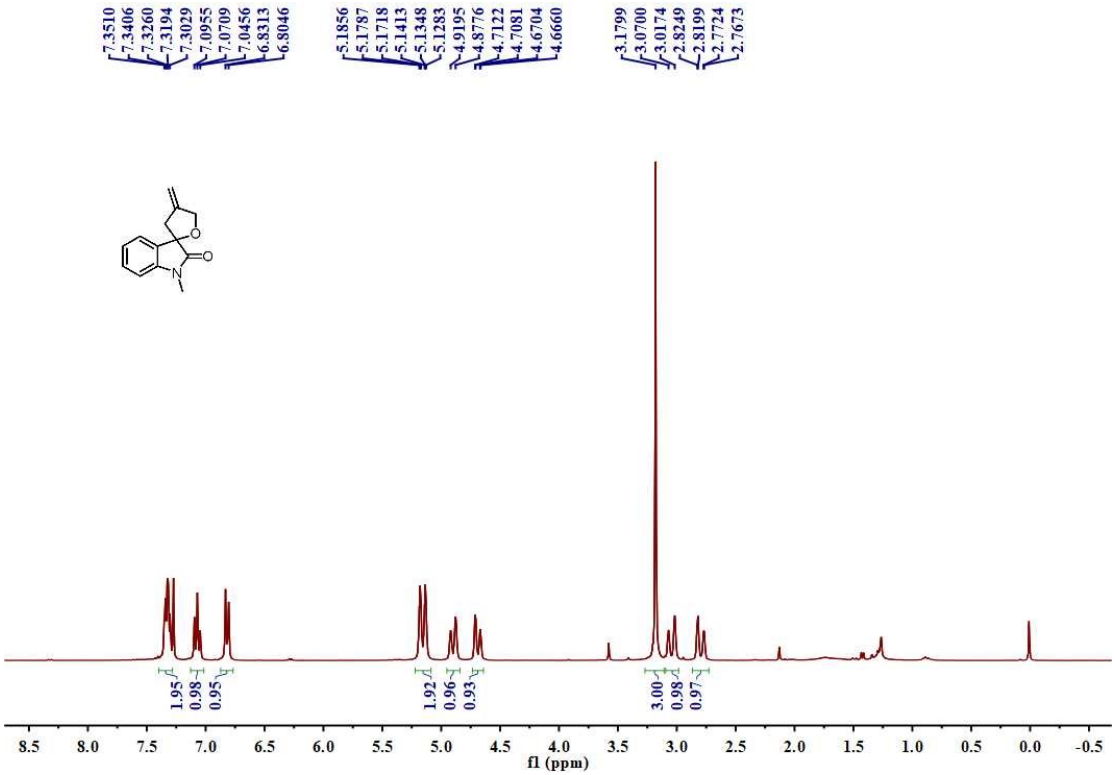
Crystal structure of **3i (CCDC 2127377)**

Table S2 Crystal data and structure refinement for 3i.

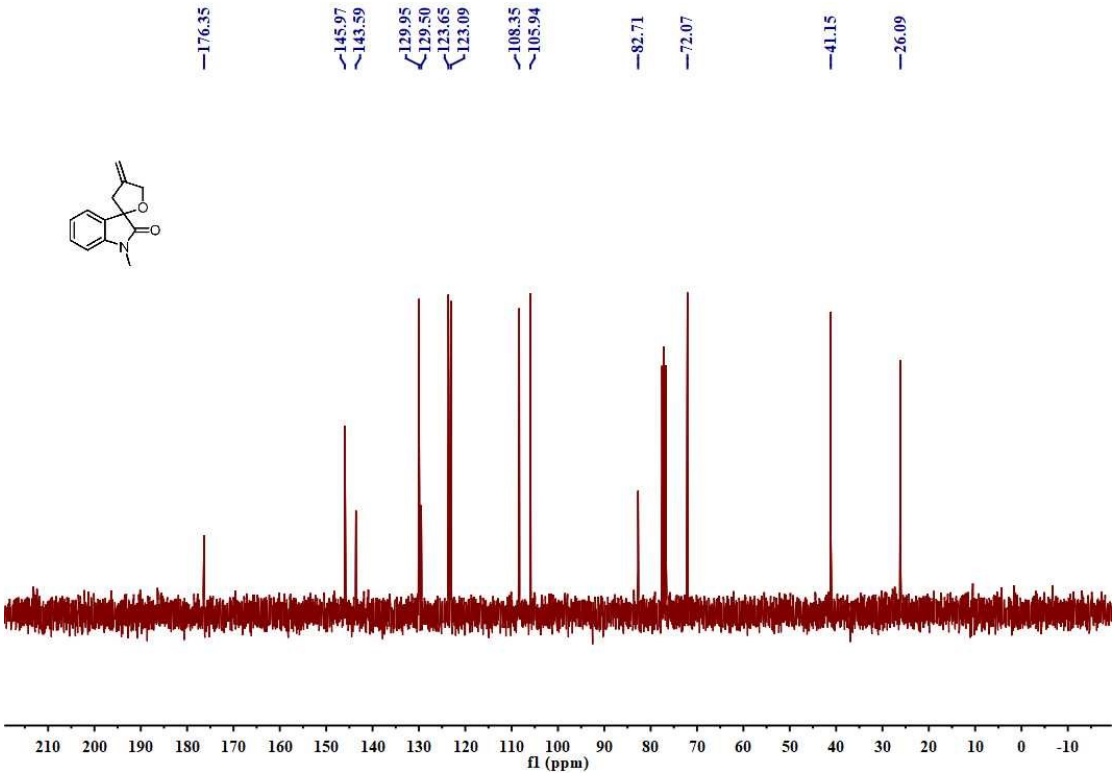
Identification code	**3i**
Empirical formula	$C_{18}H_{15}NO_2$
Formula weight	277.31
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	27.2600(5)
b/Å	5.69779(8)
c/Å	18.9861(4)
α/°	90
β/°	107.276(2)
γ/°	90
Volume/Å^3	2815.92(9)
Z	8
ρ_{calc}g/cm^3	1.308
μ/mm^{-1}	0.684
F(000)	1168.0
Crystal size/mm^3	0.17 × 0.1 × 0.04
Radiation	CuKα (λ = 1.54184)

2Θ range for data collection/°	6.792 to 141.622
Index ranges	$-32 \leq h \leq 32$, $-6 \leq k \leq 6$, $-23 \leq l \leq 20$
Reflections collected	9601
Independent reflections	2674 [R_{int} = 0.0261, R_{sigma} = 0.0215]
Data/restraints/parameters	2674/0/190
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0419, wR_2 = 0.1078
Final R indexes [all data]	R_1 = 0.0505, wR_2 = 0.1160
Largest diff. peak/hole / e $Å^{-3}$	0.18/-0.21

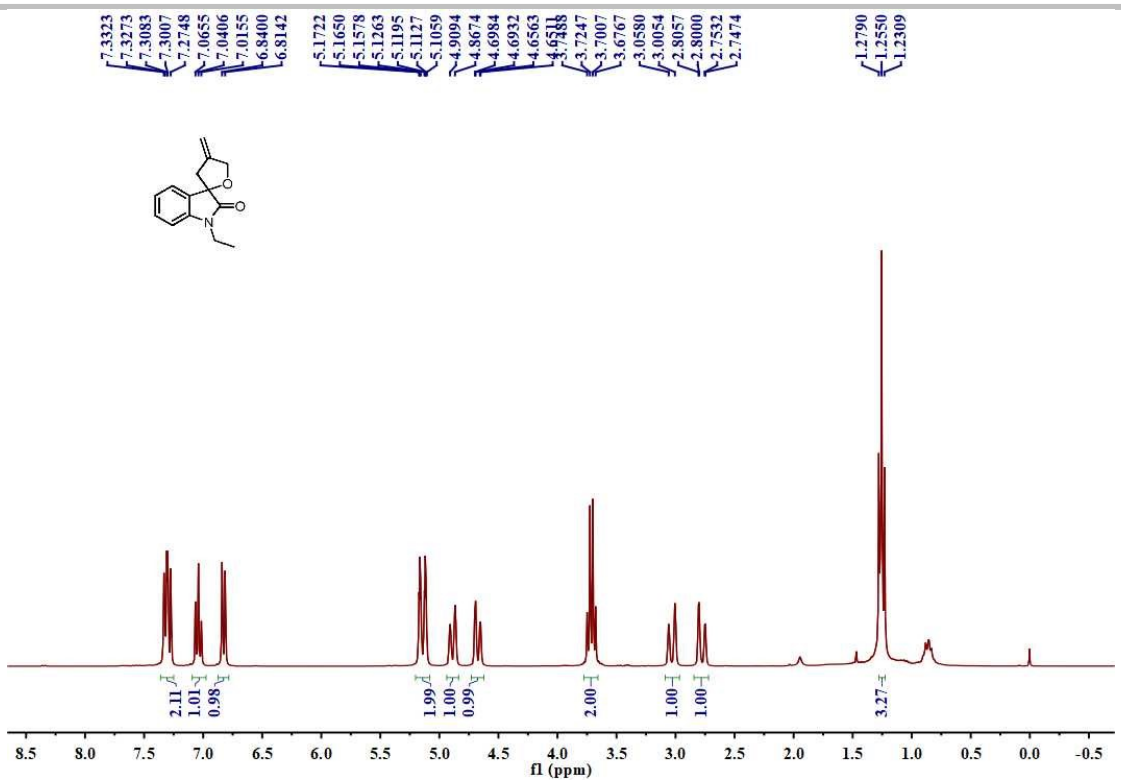
7. Copies of ^{1}H NMR, ^{13}C NMR spectra



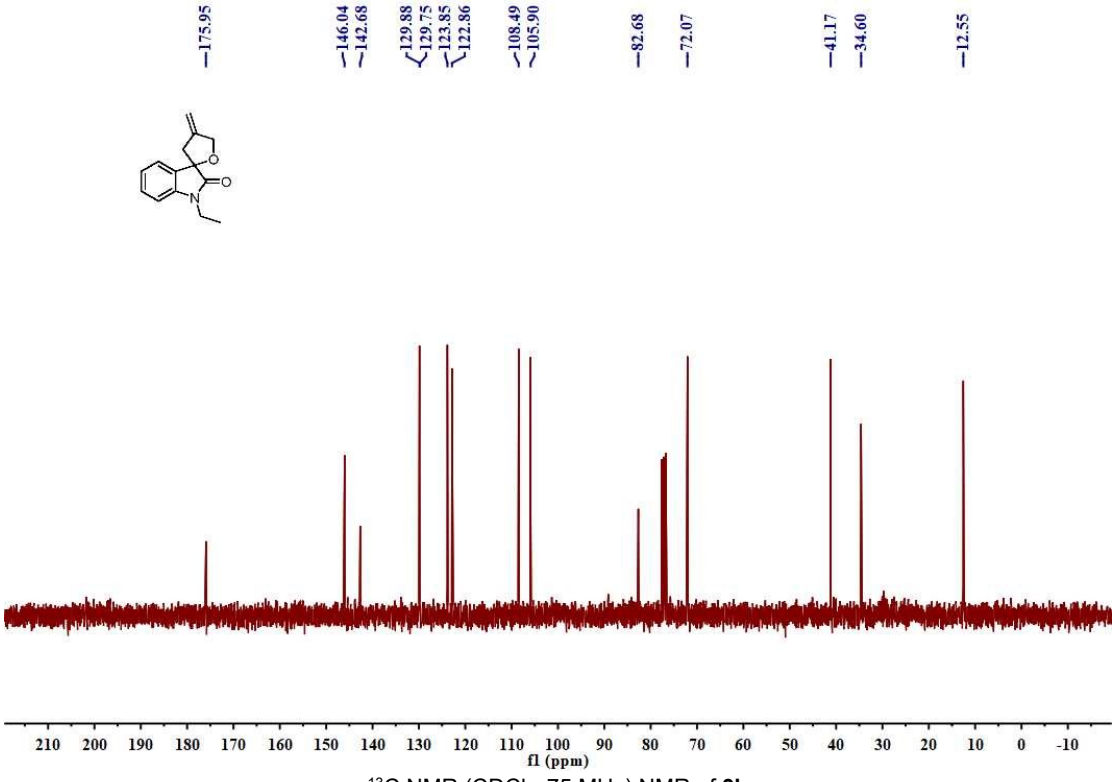
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3a**



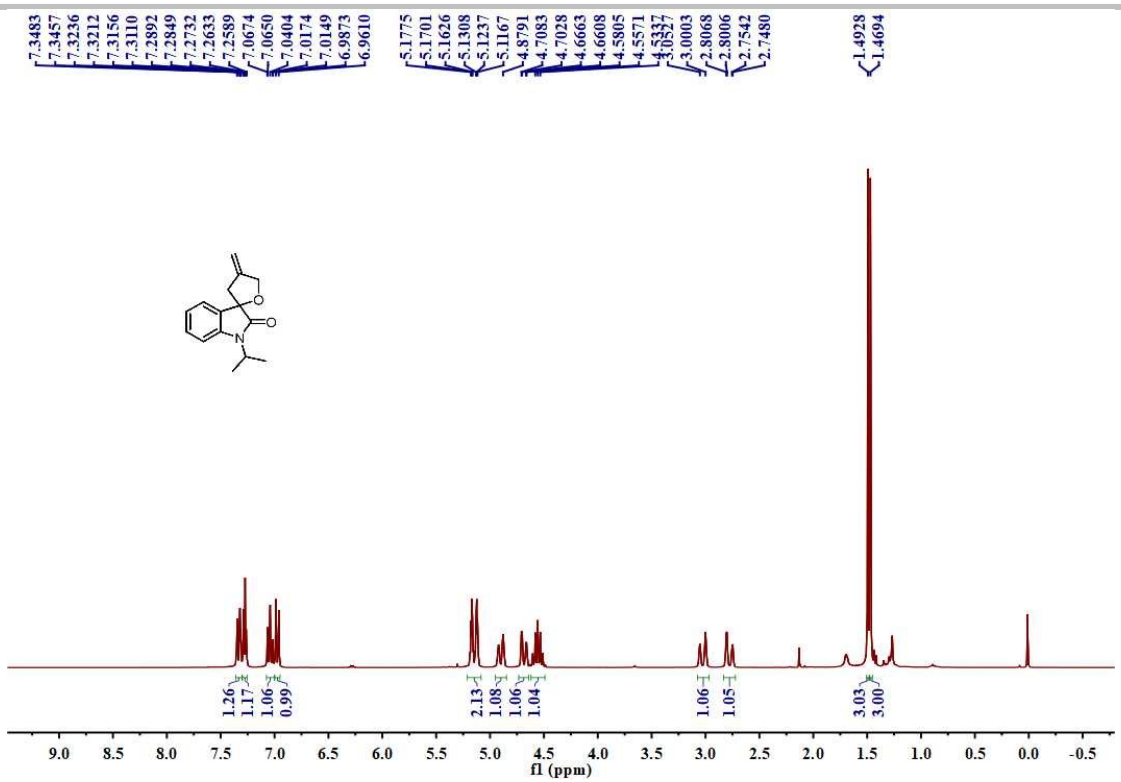
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3a**



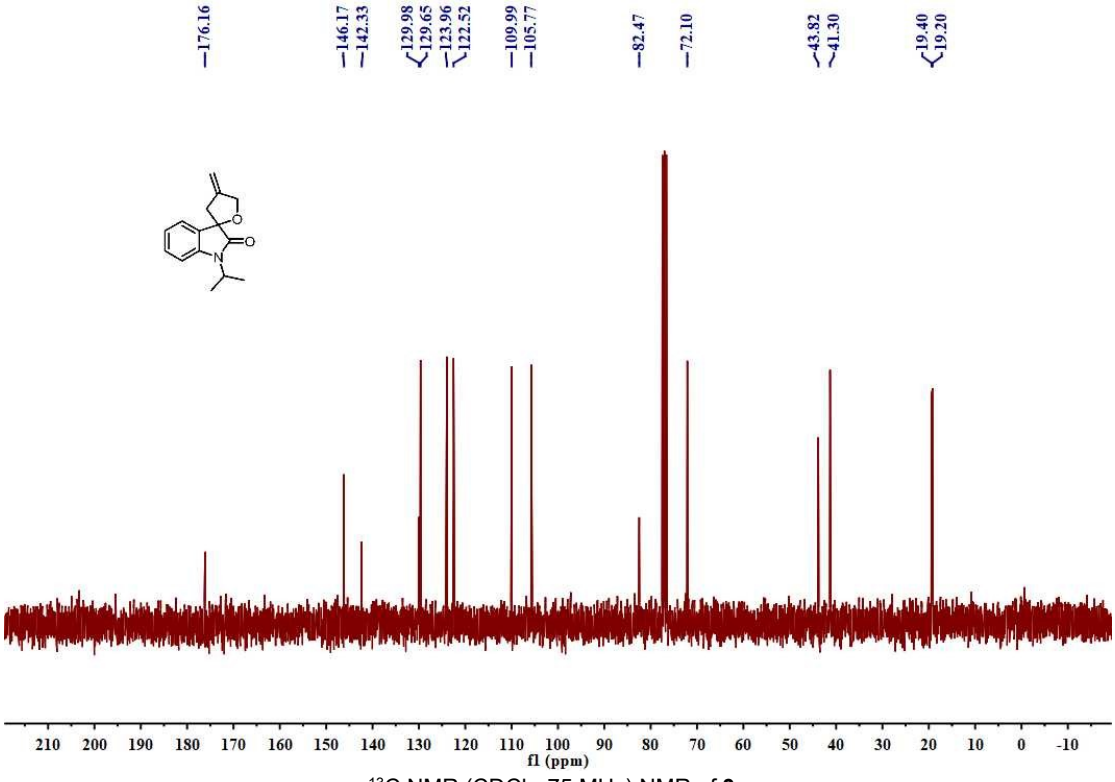
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3b**



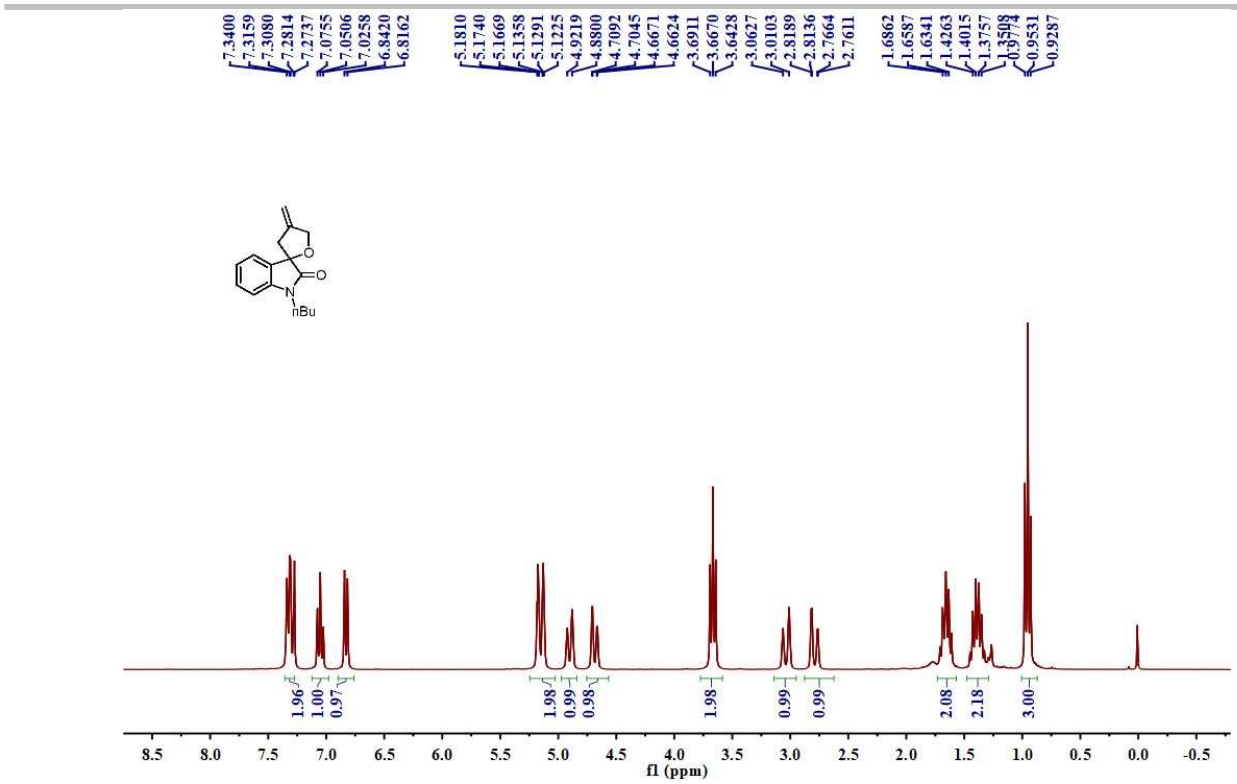
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3b**



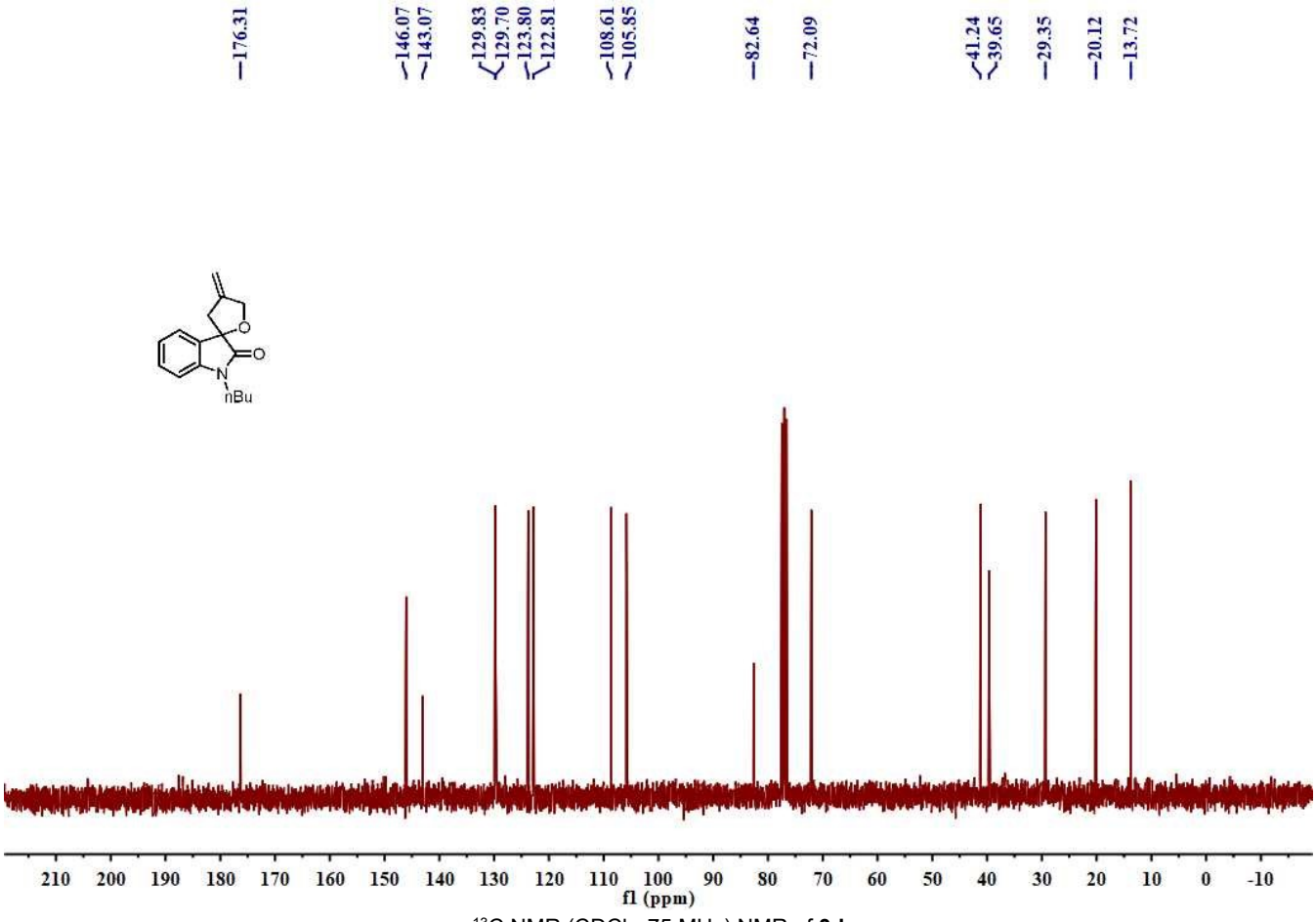
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3c**



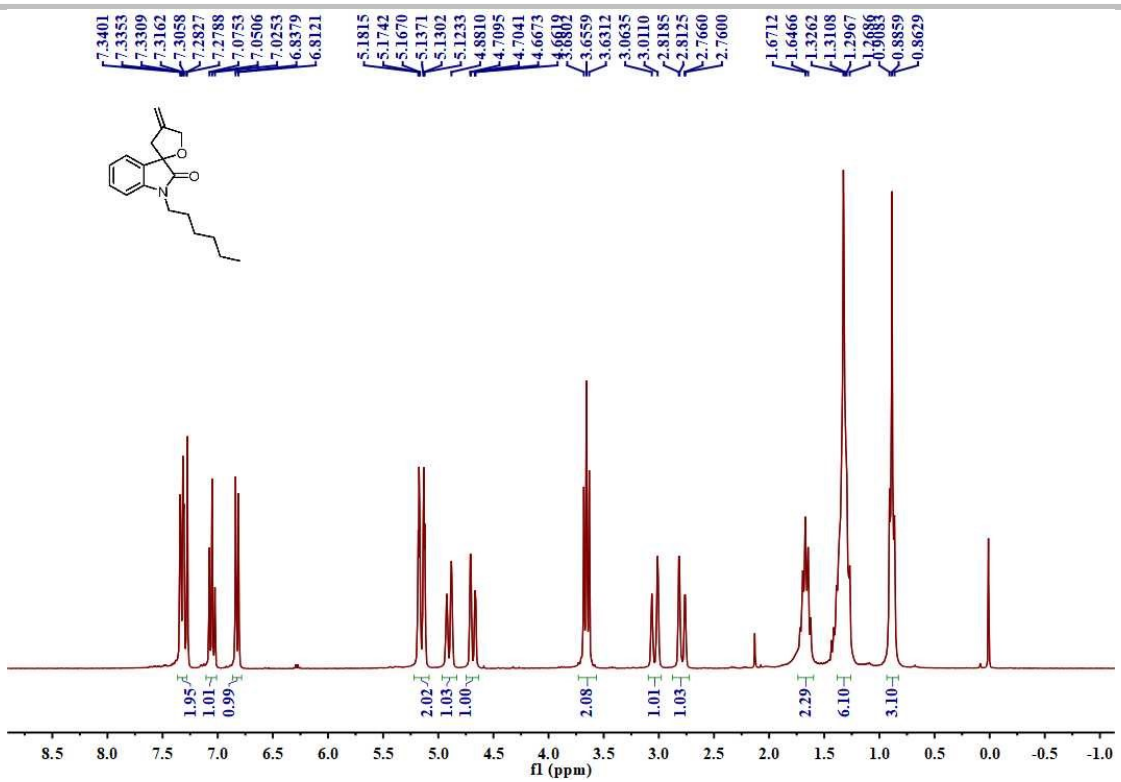
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3c**



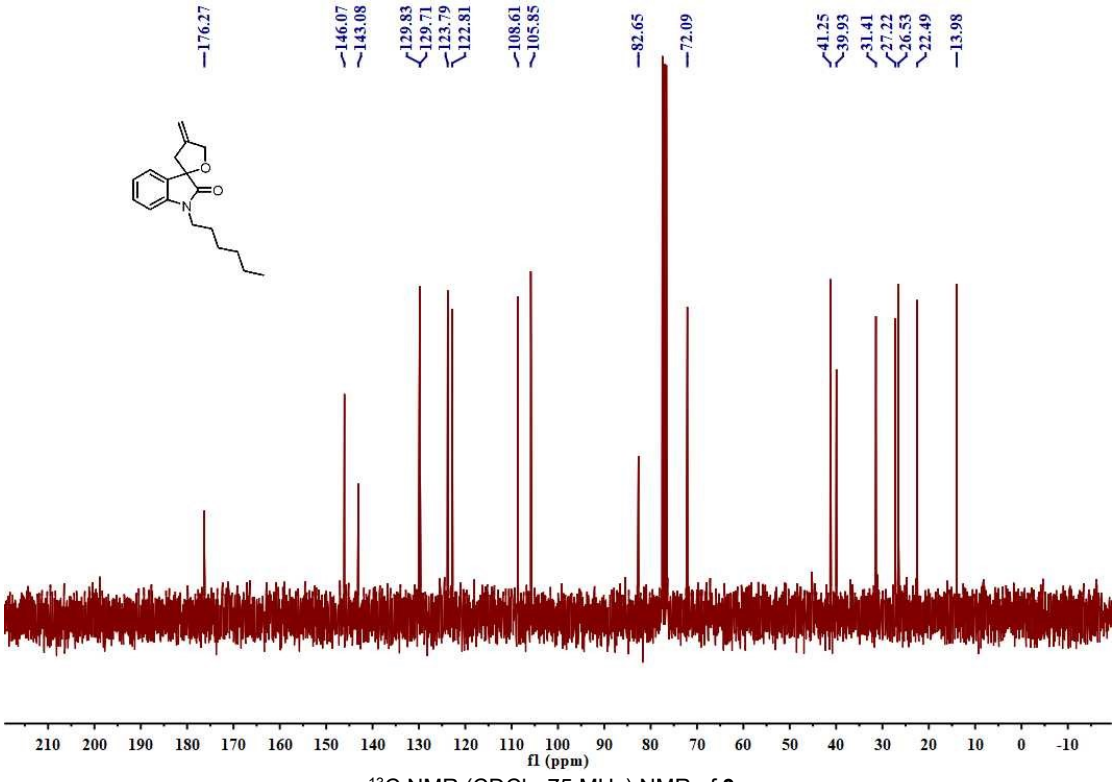
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3d**



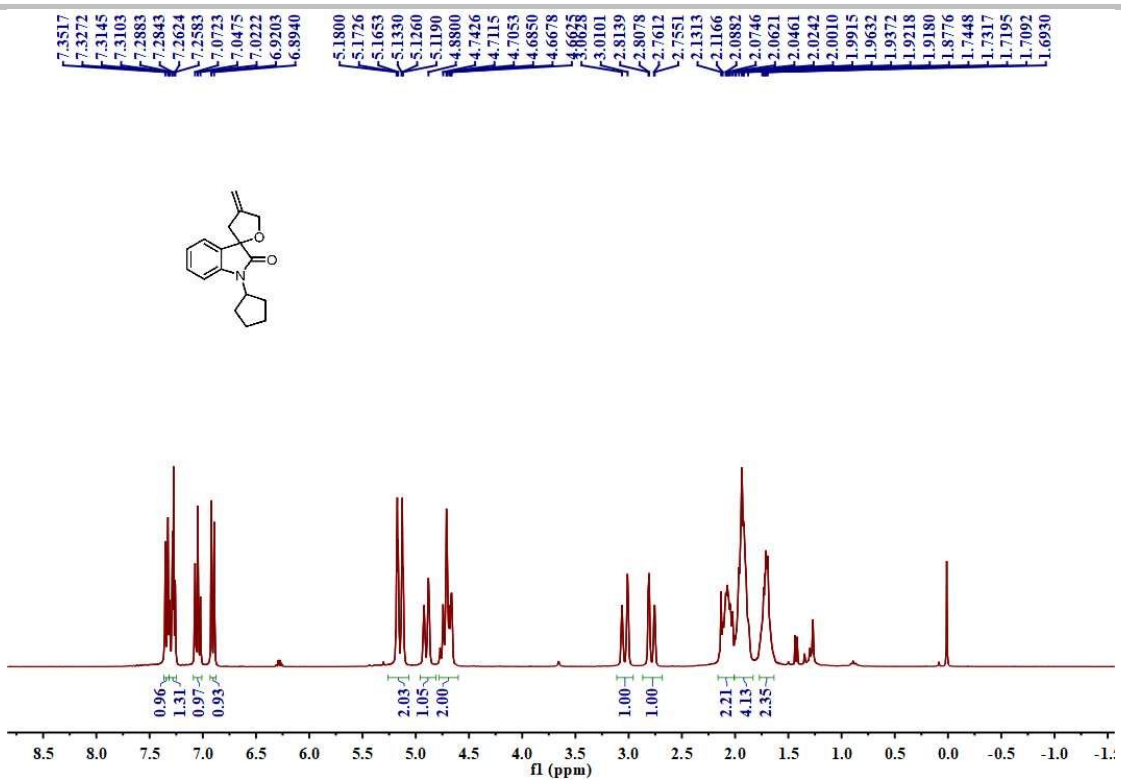
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3d**



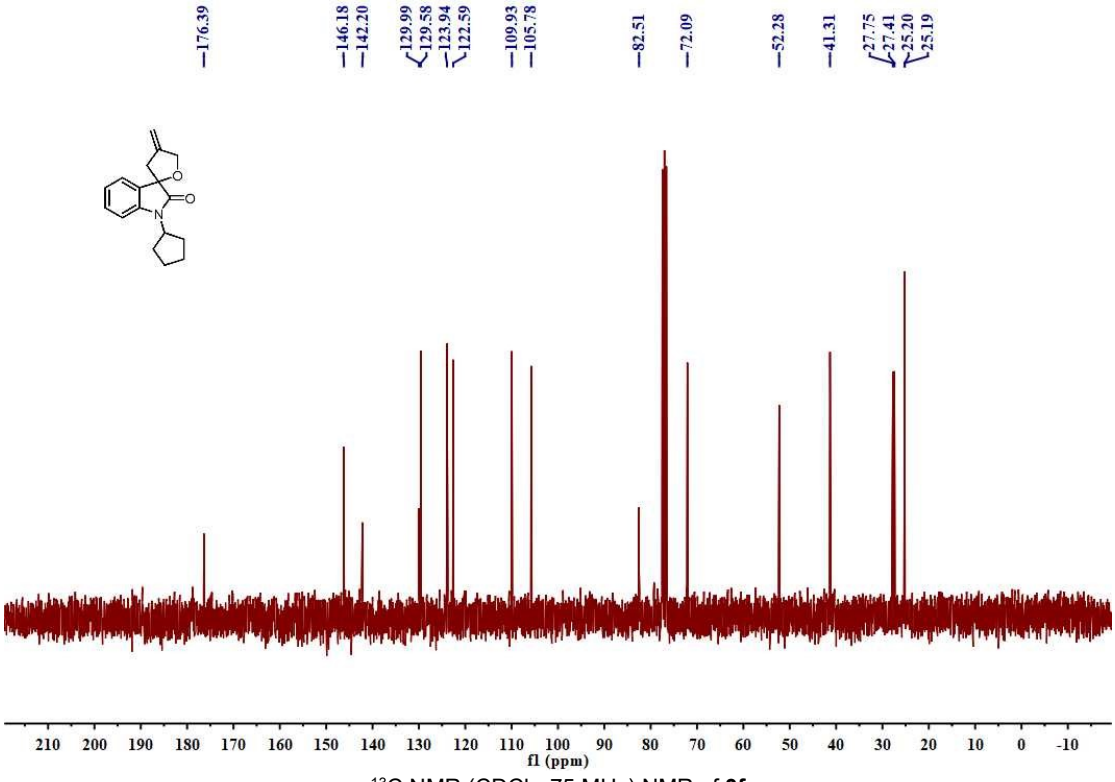
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3e**



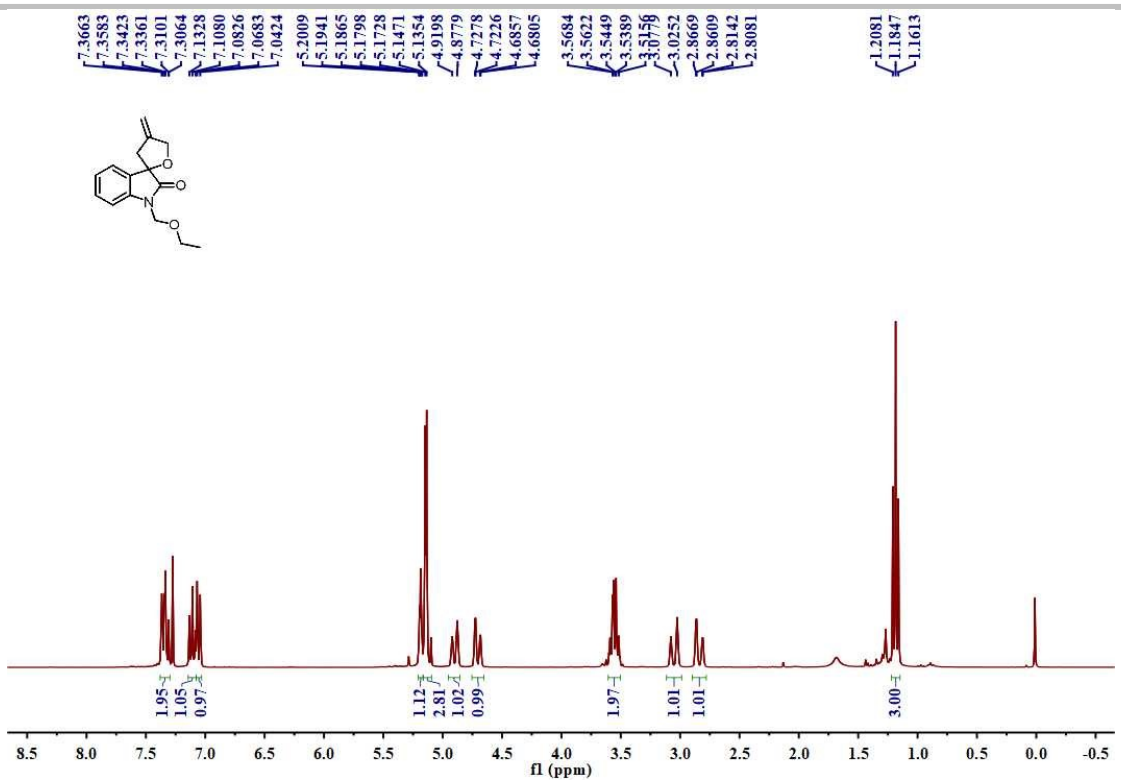
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3e**



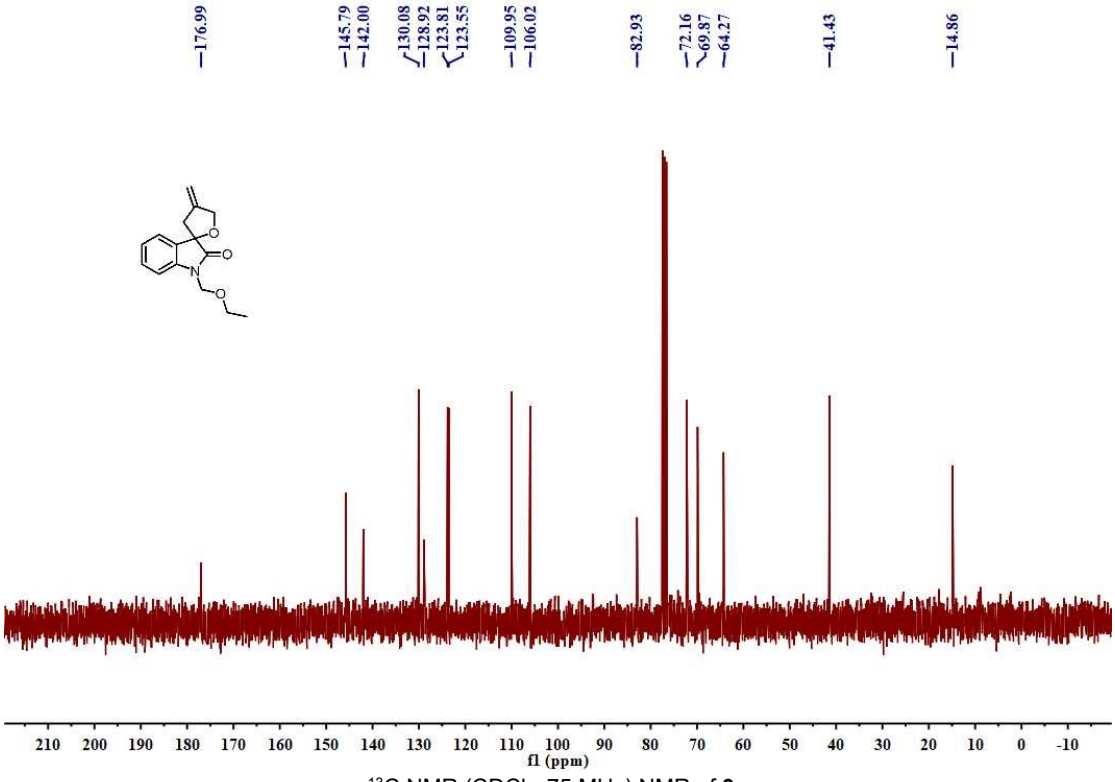
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3f**



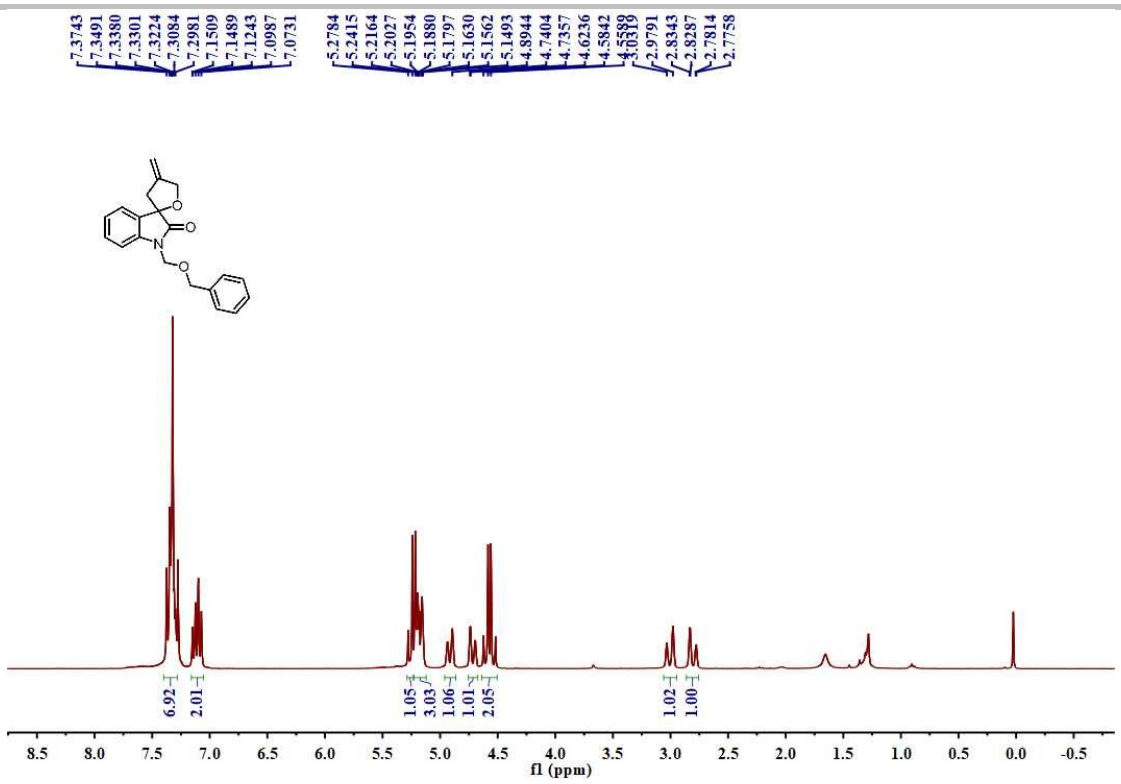
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3f**



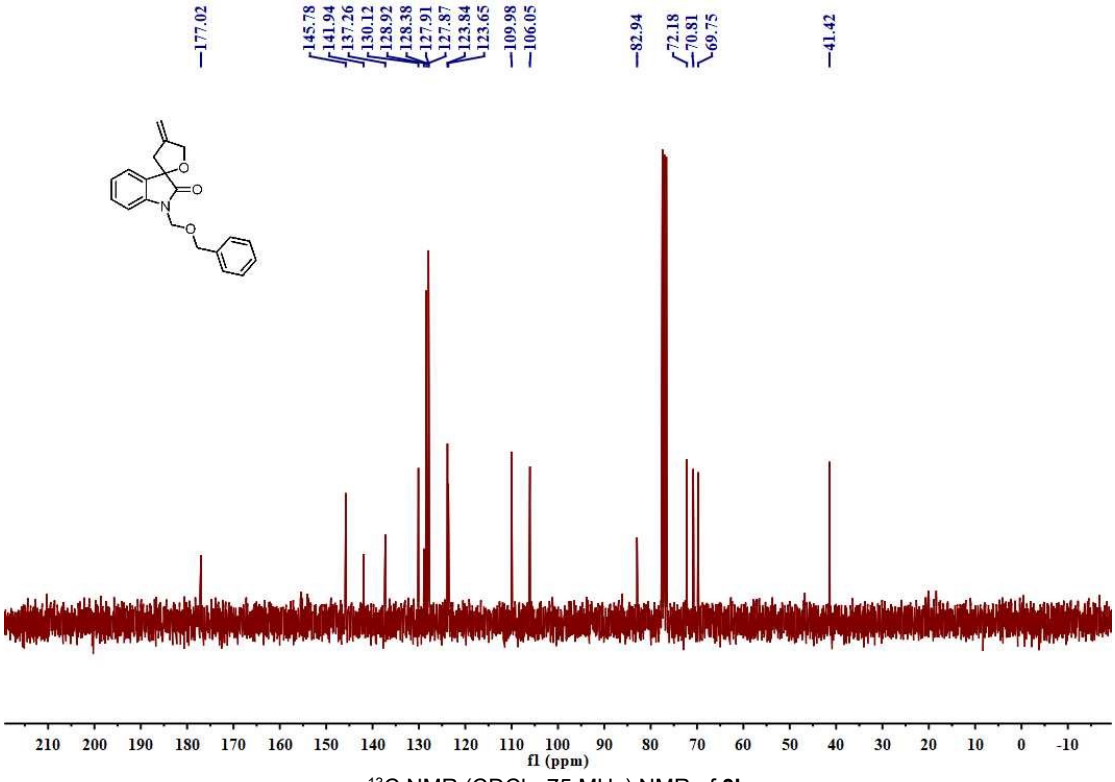
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3g**



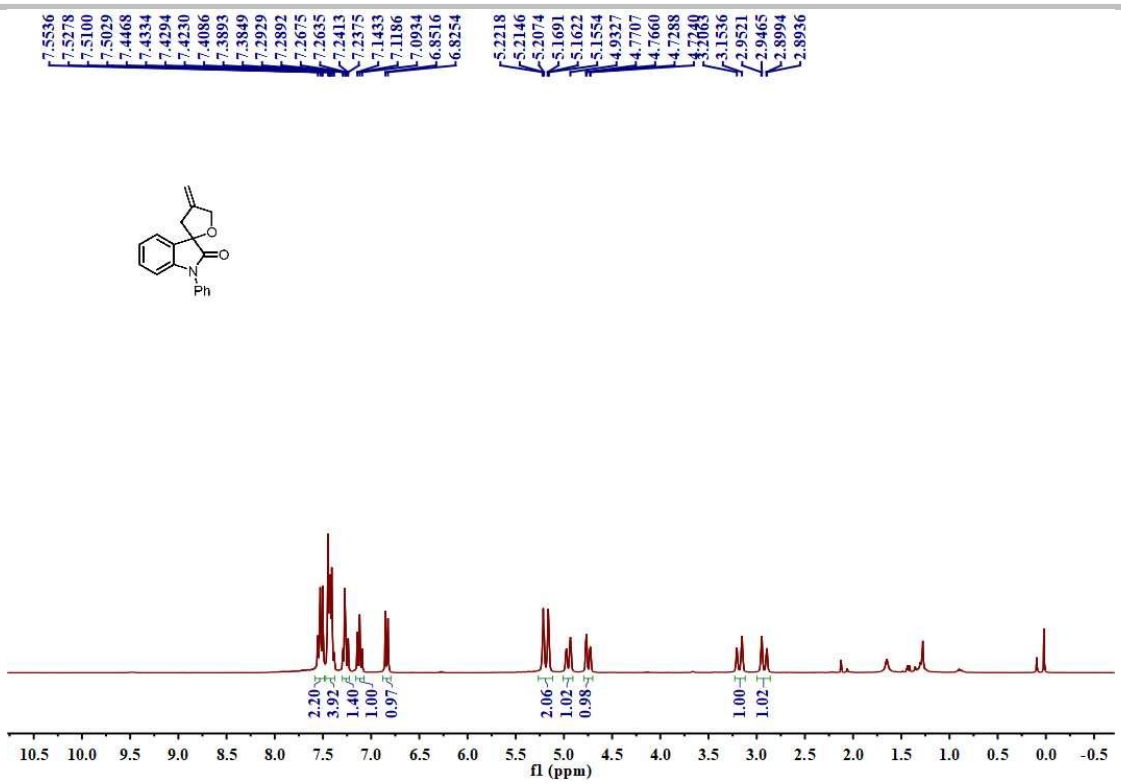
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3g**



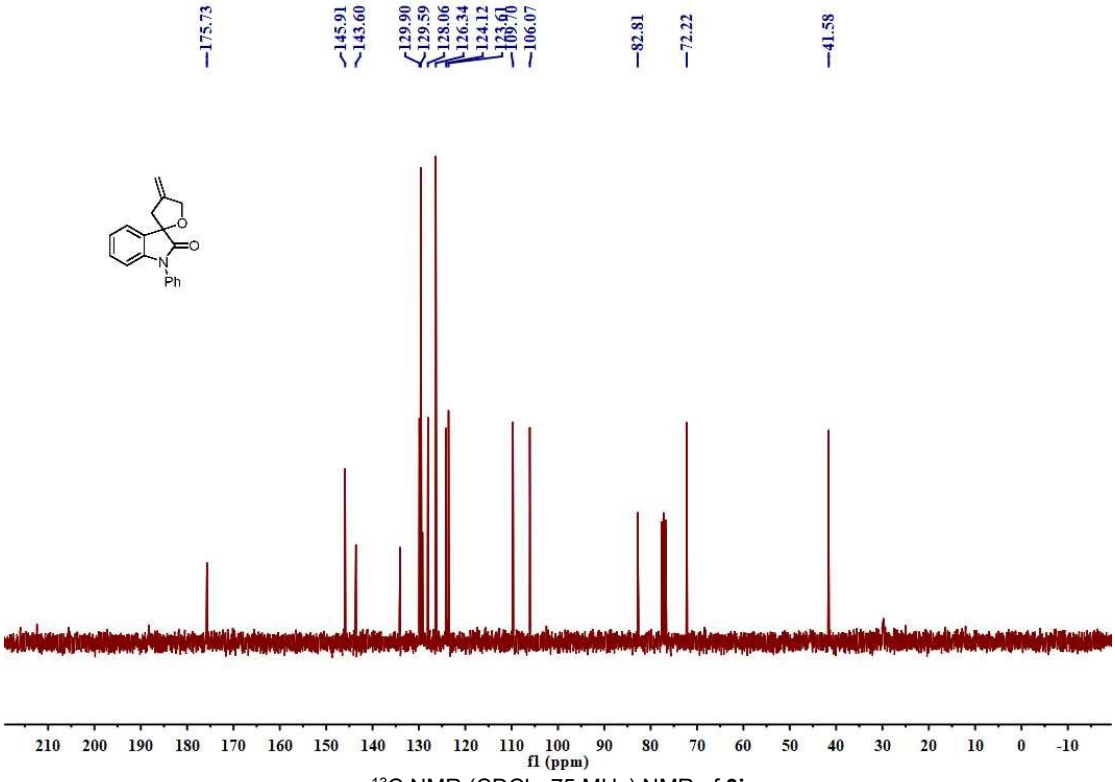
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3h**



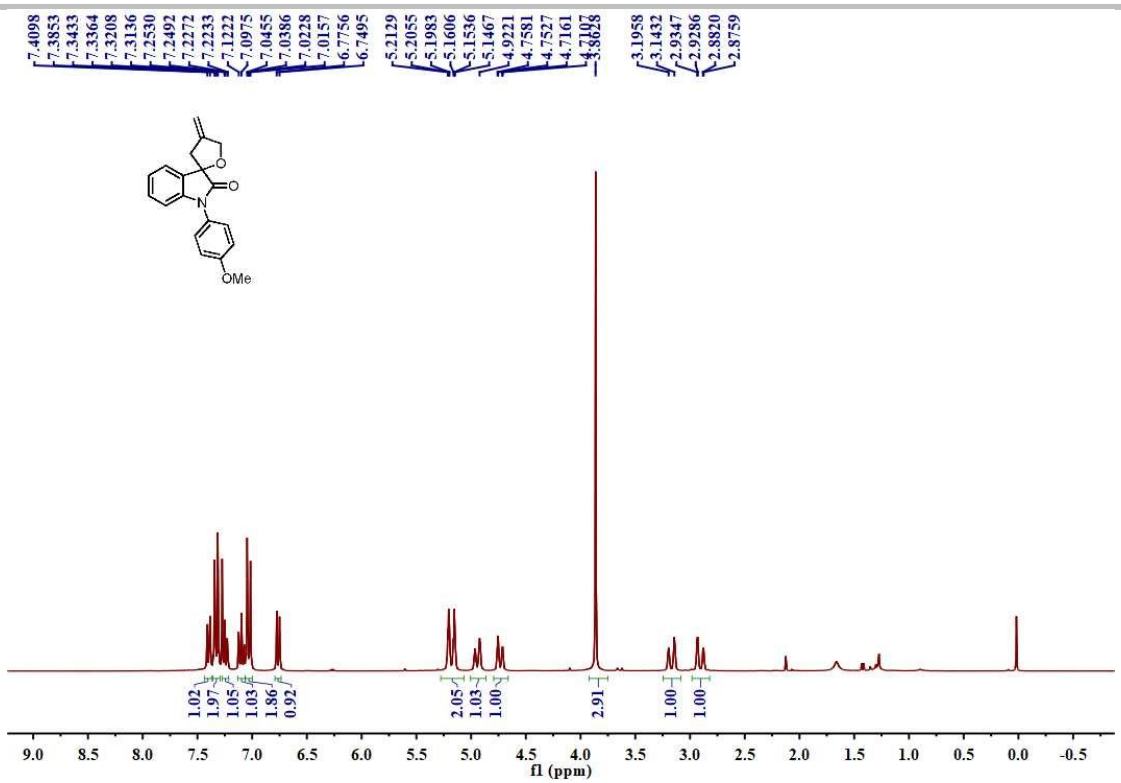
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3h**



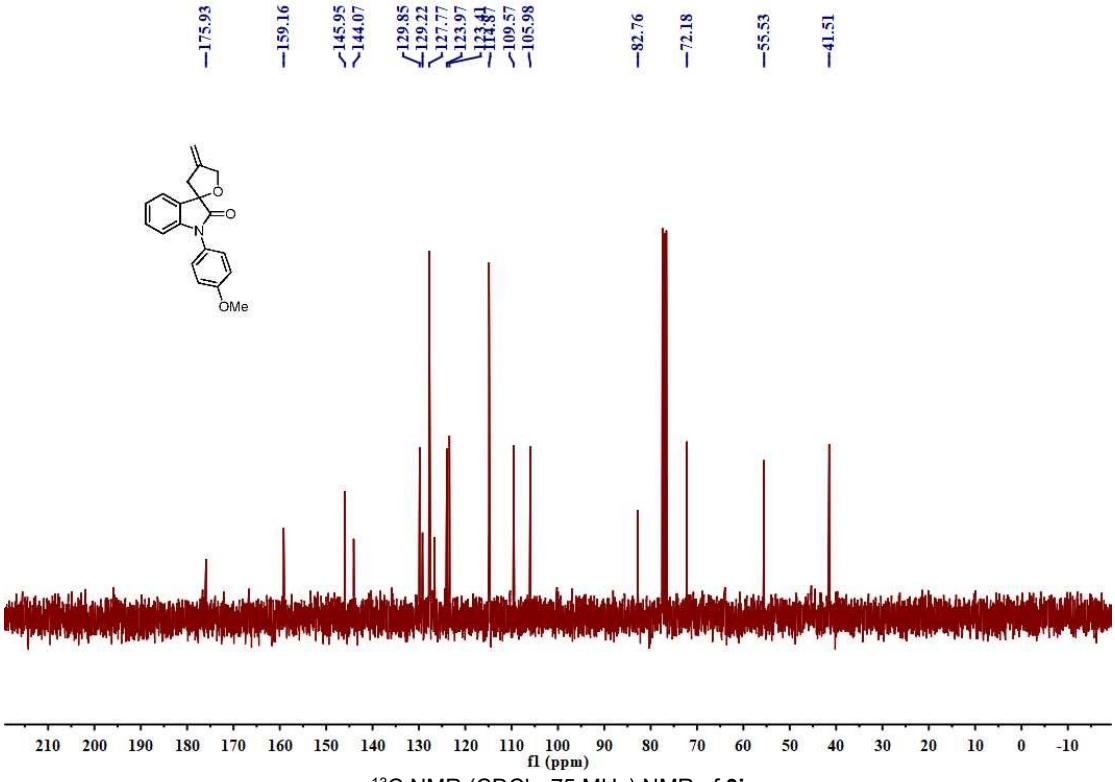
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3i**



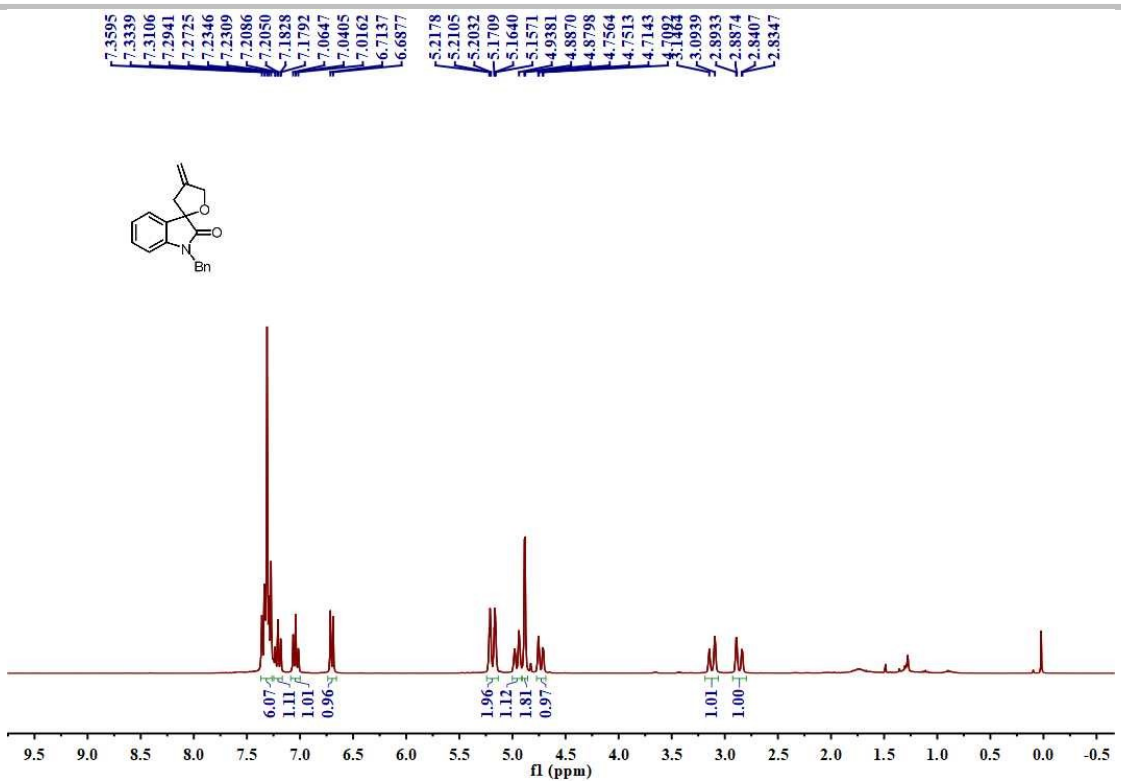
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3i**



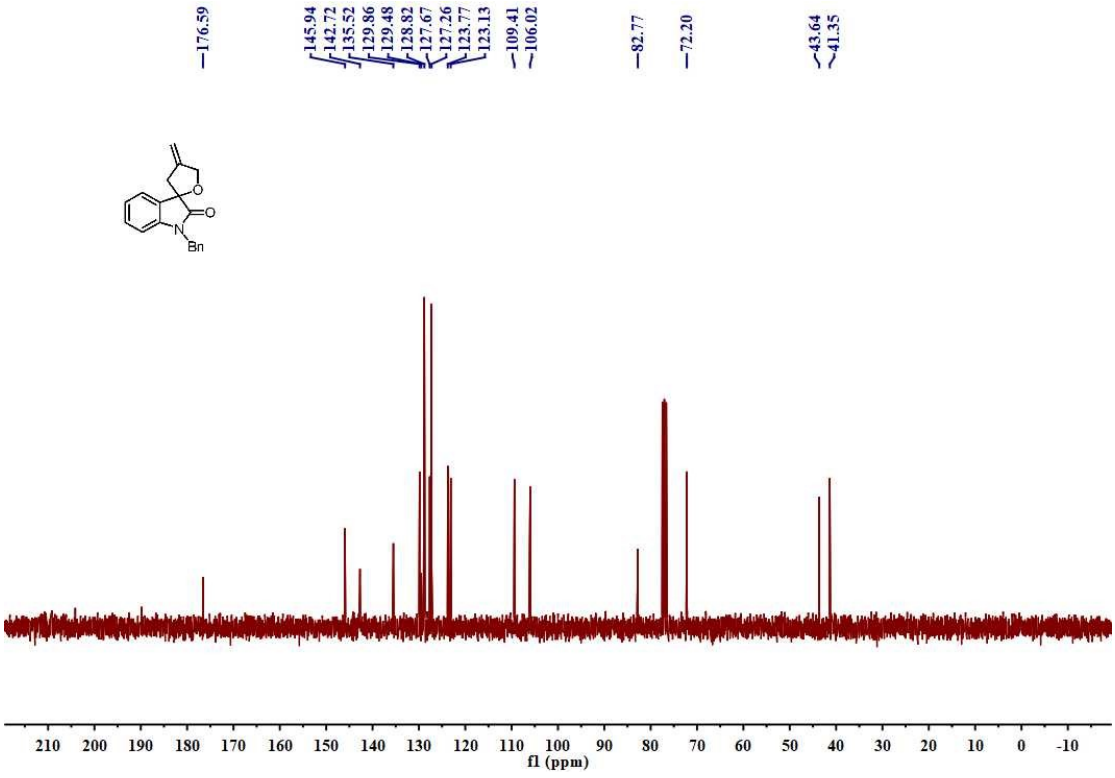
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3j**



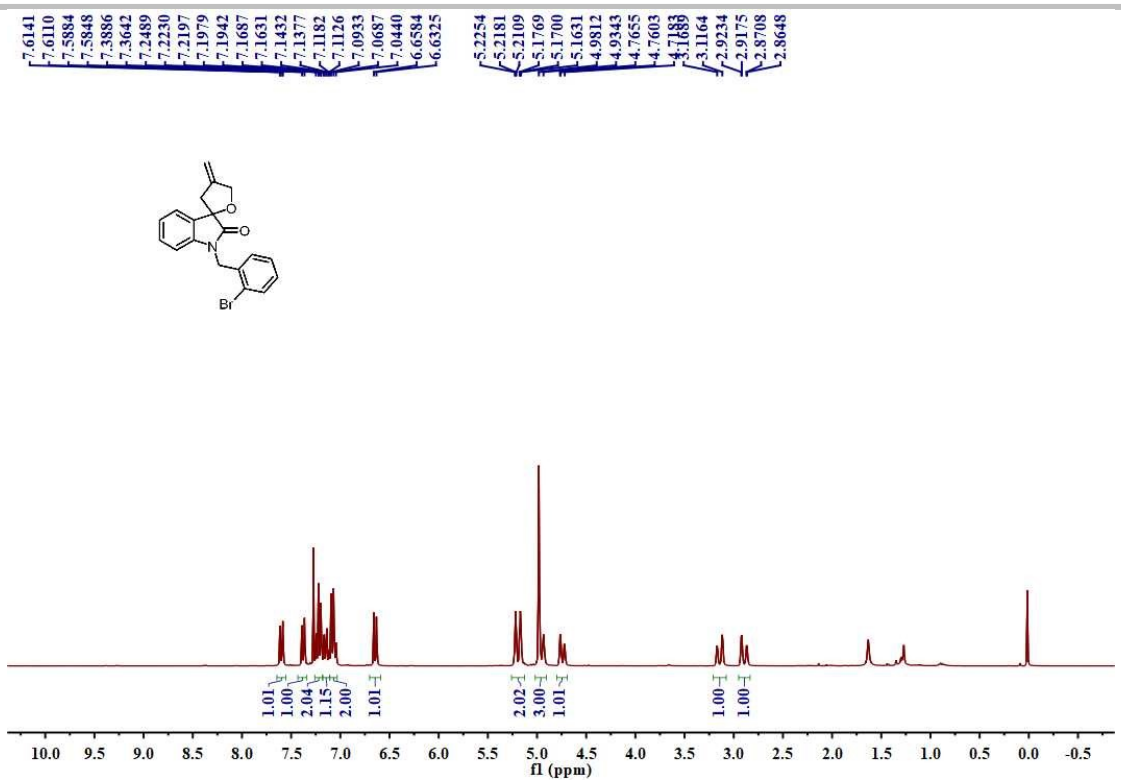
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3j**



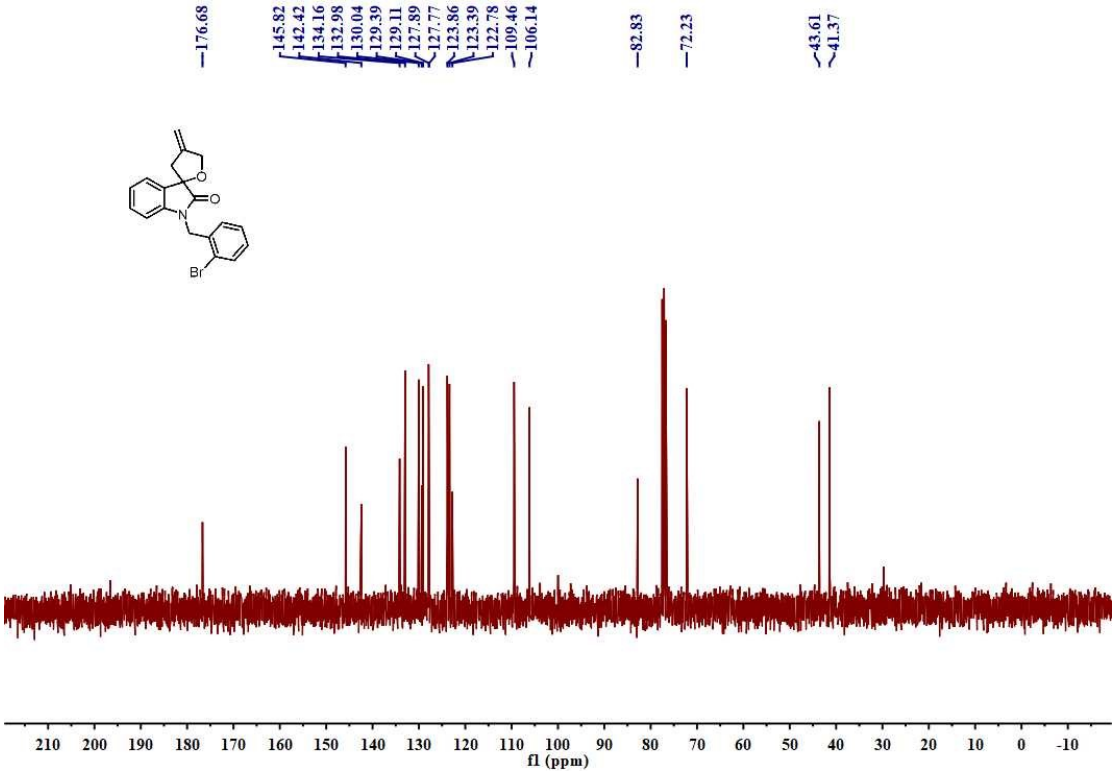
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3k**



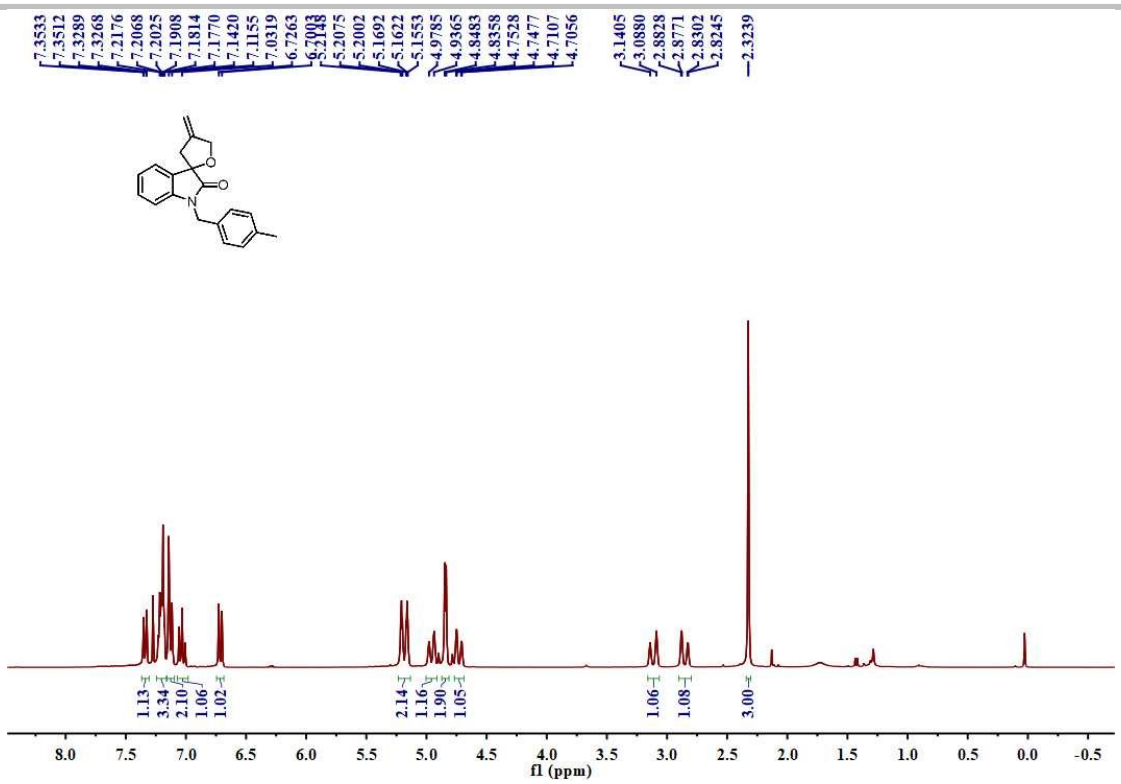
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3k**



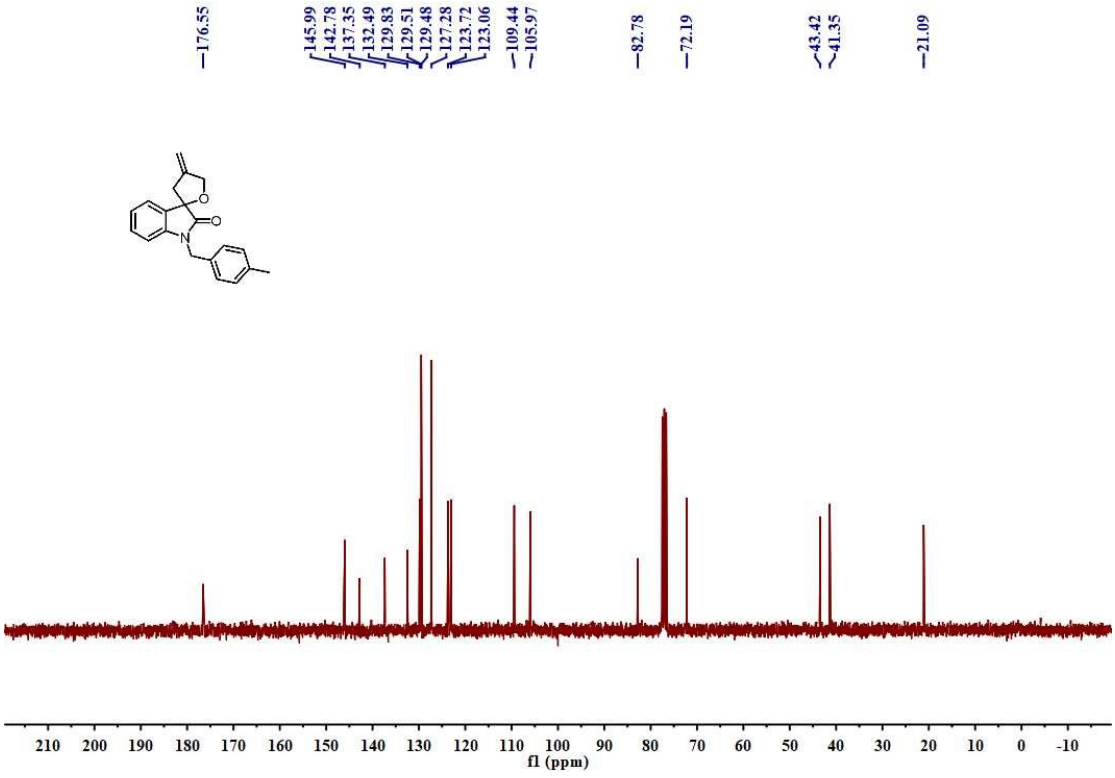
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3l**



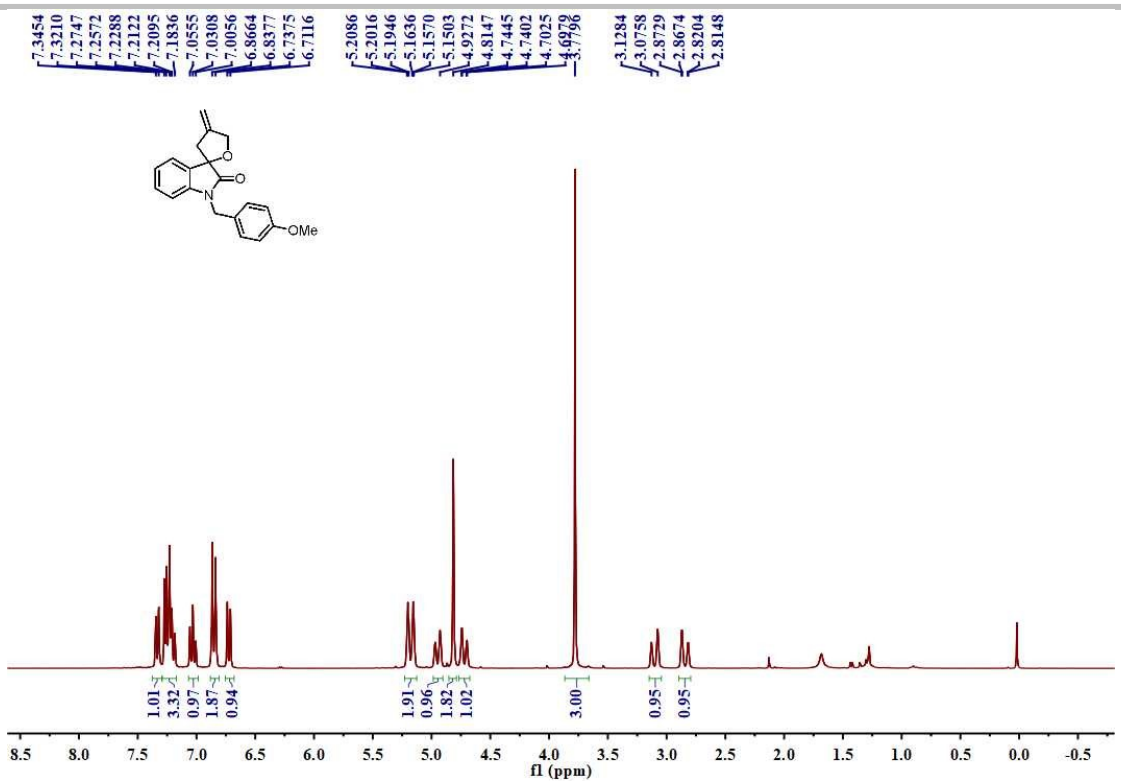
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3l**



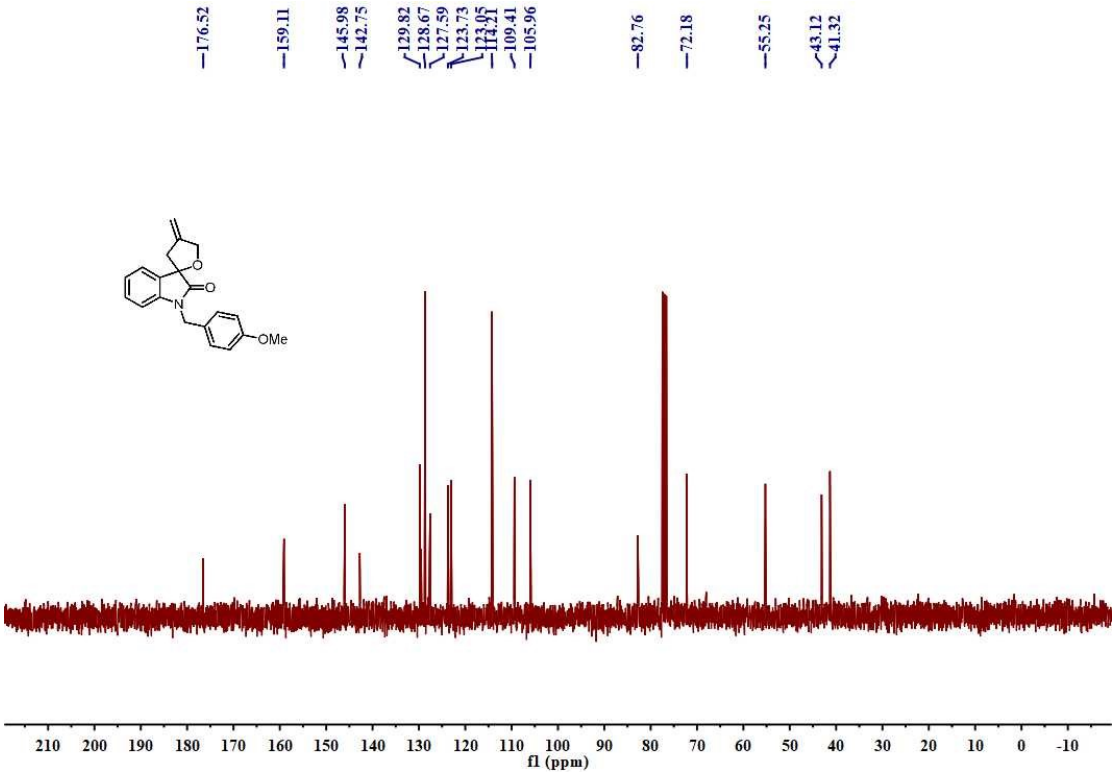
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3m**



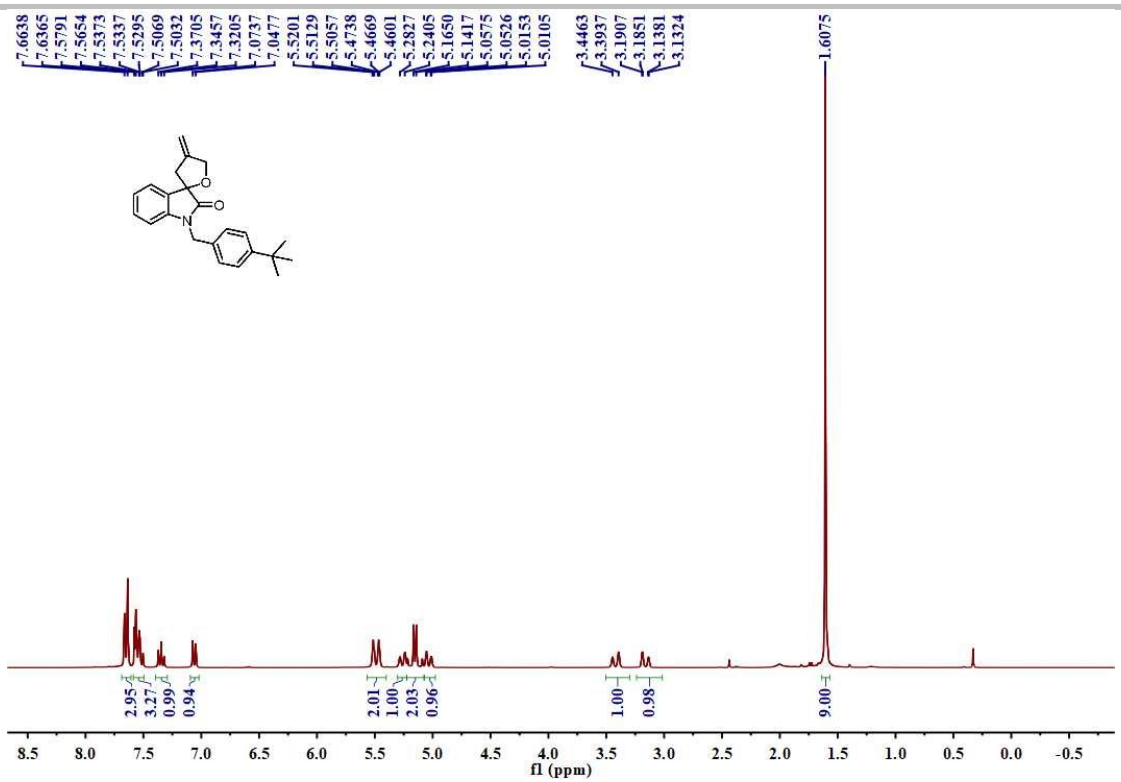
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3m**



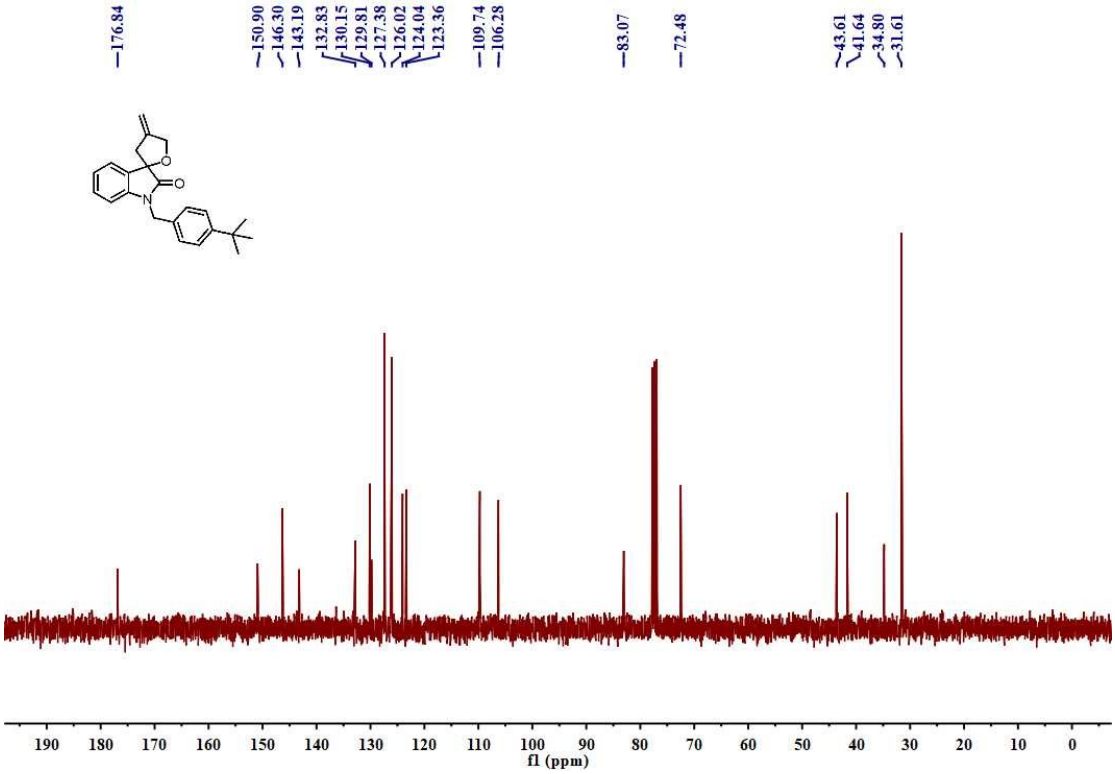
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3n**



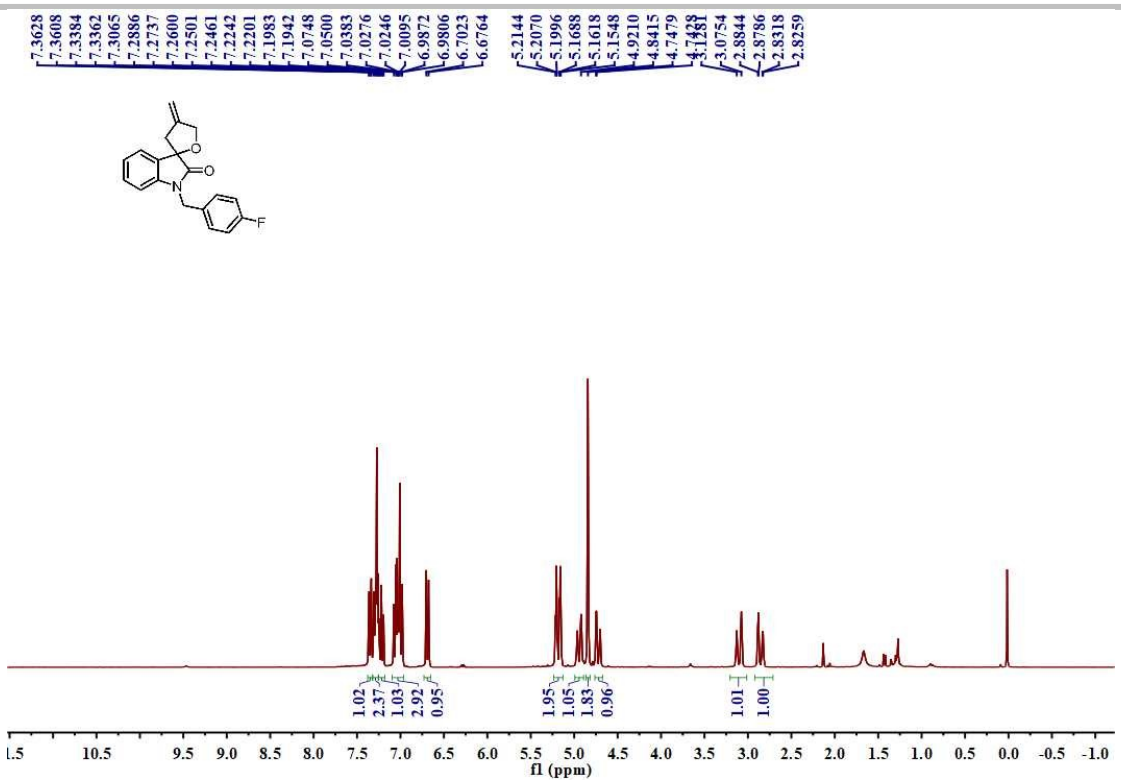
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3n**



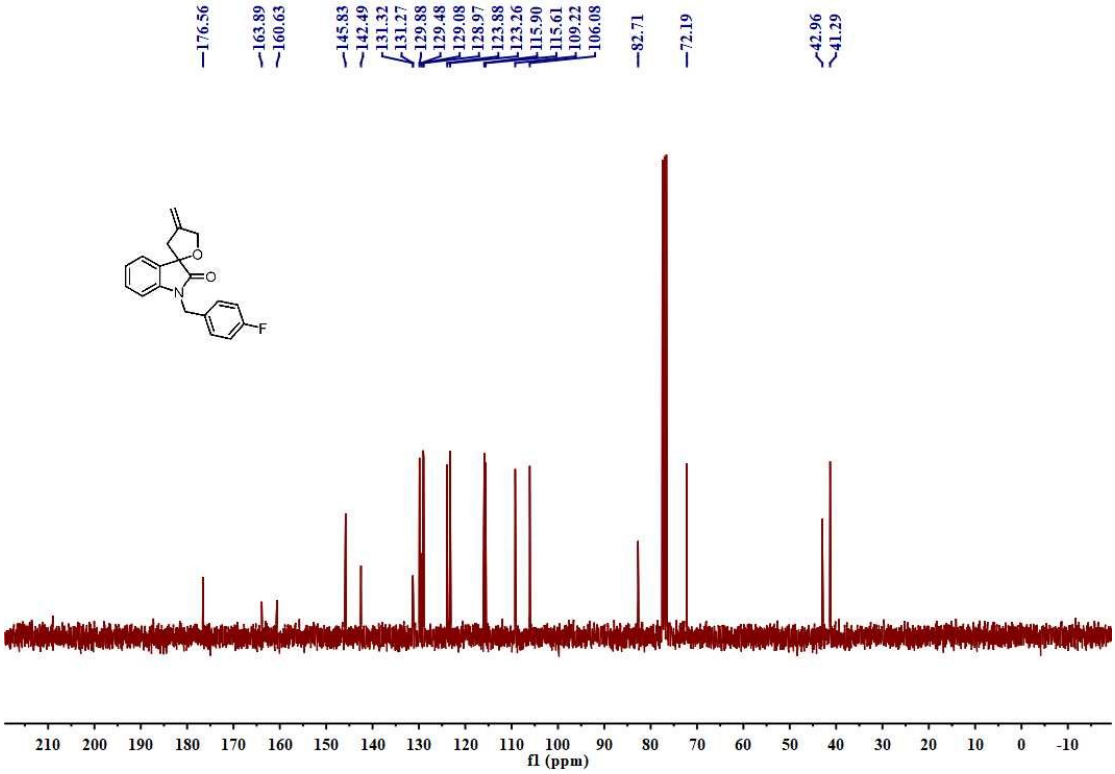
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3o**



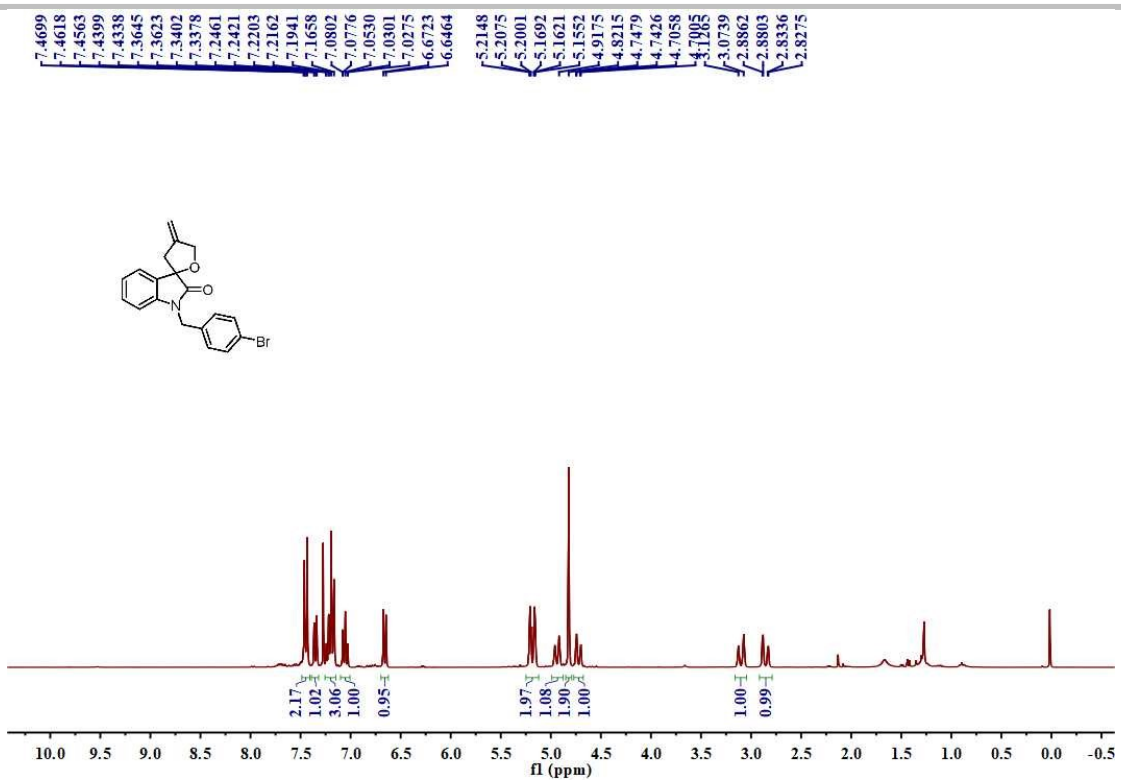
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3o**



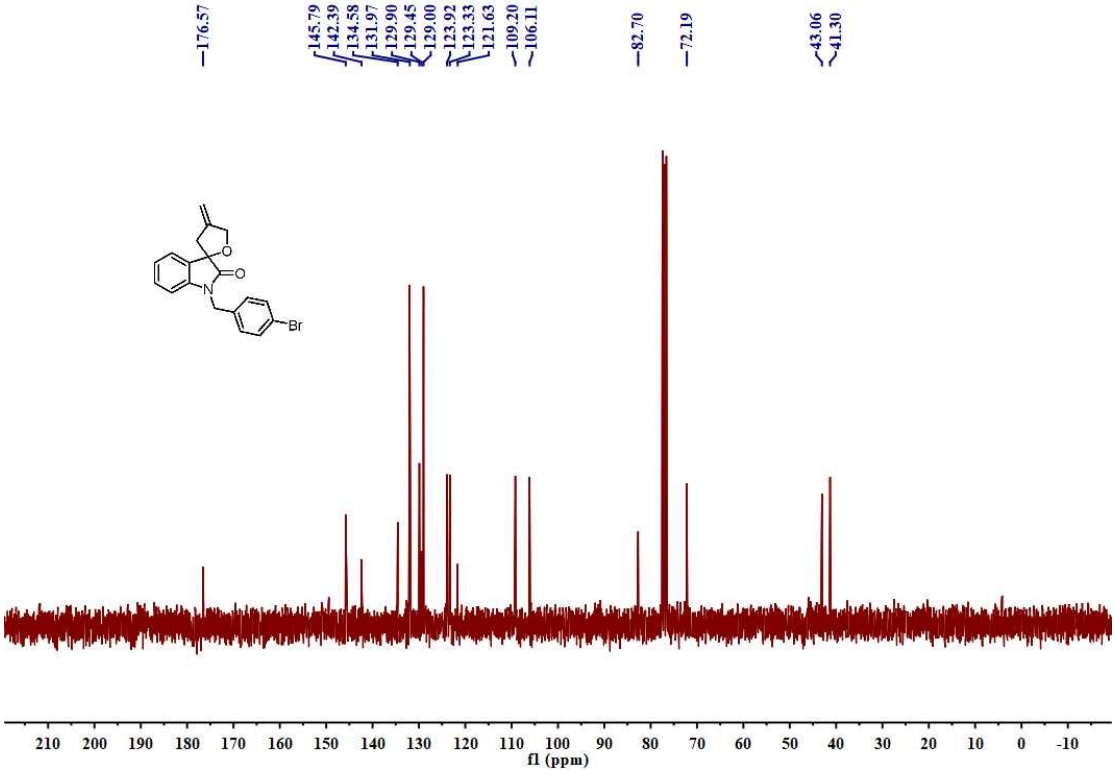
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3p**



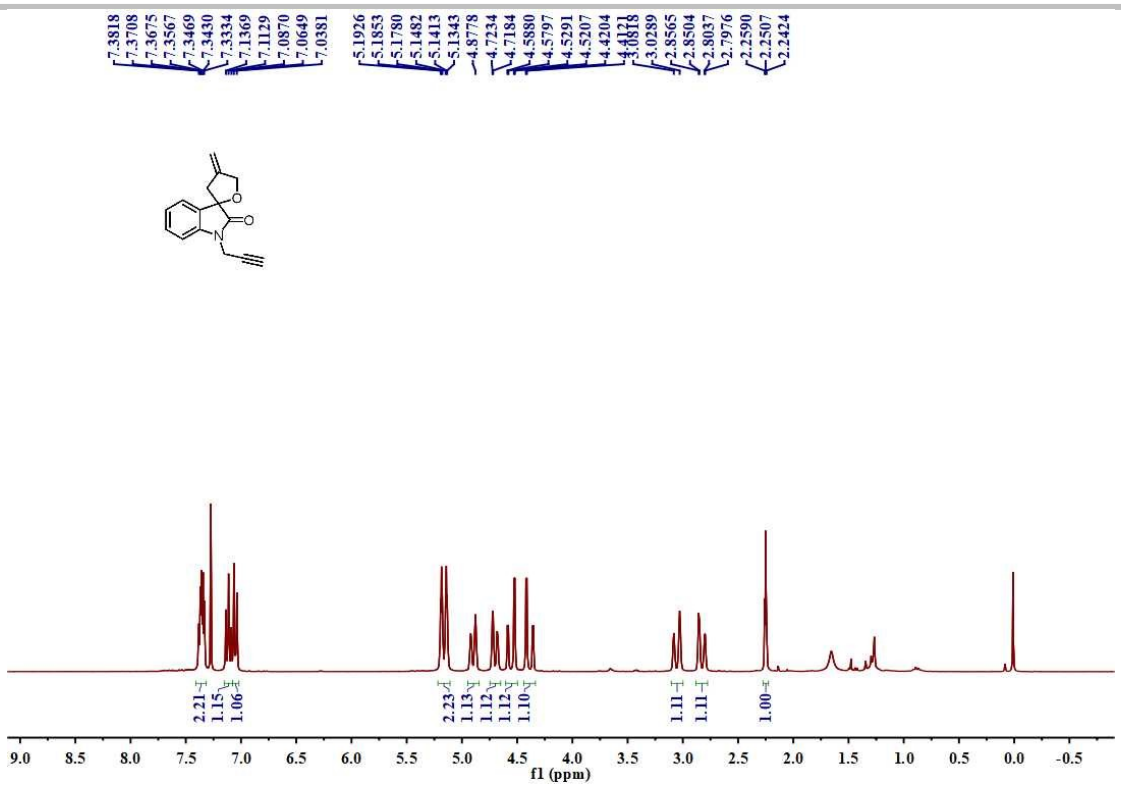
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3p**



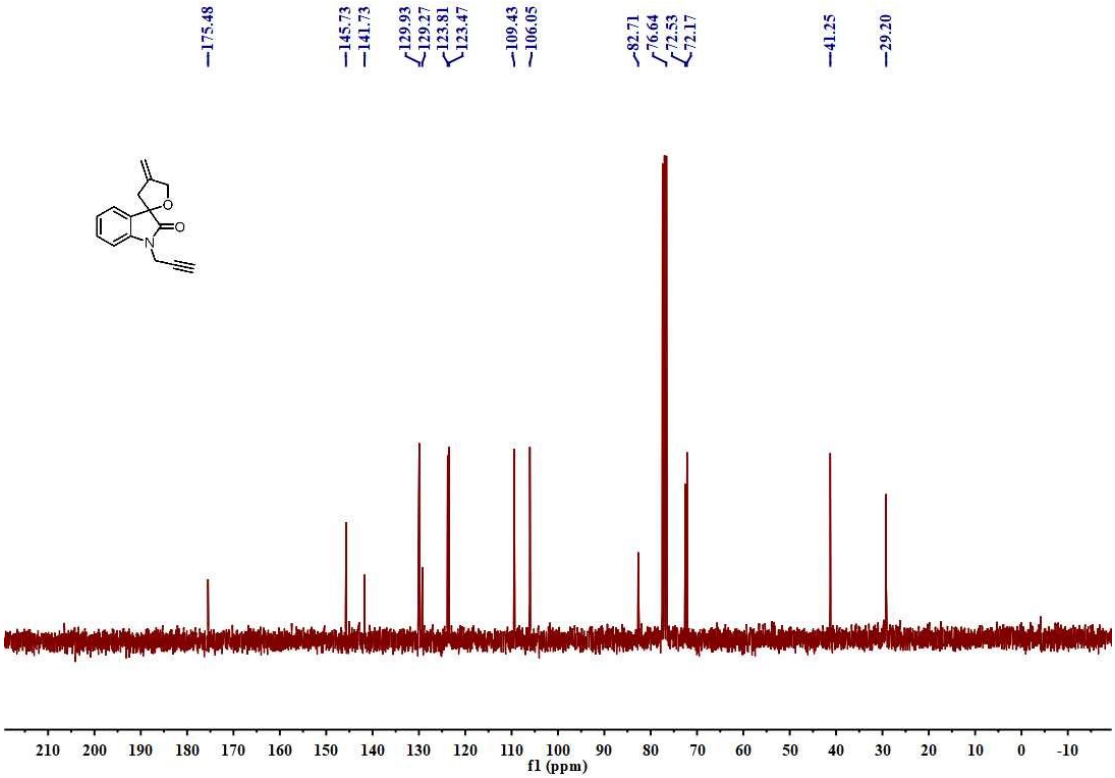
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3q**



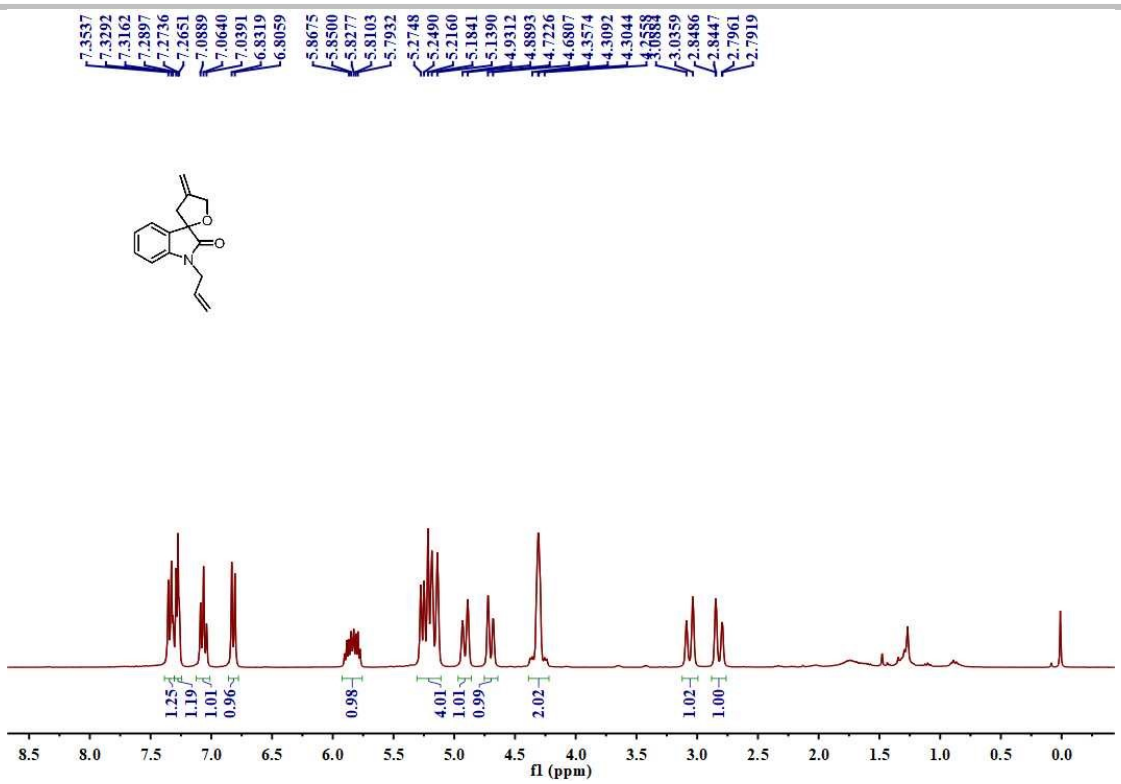
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3q**



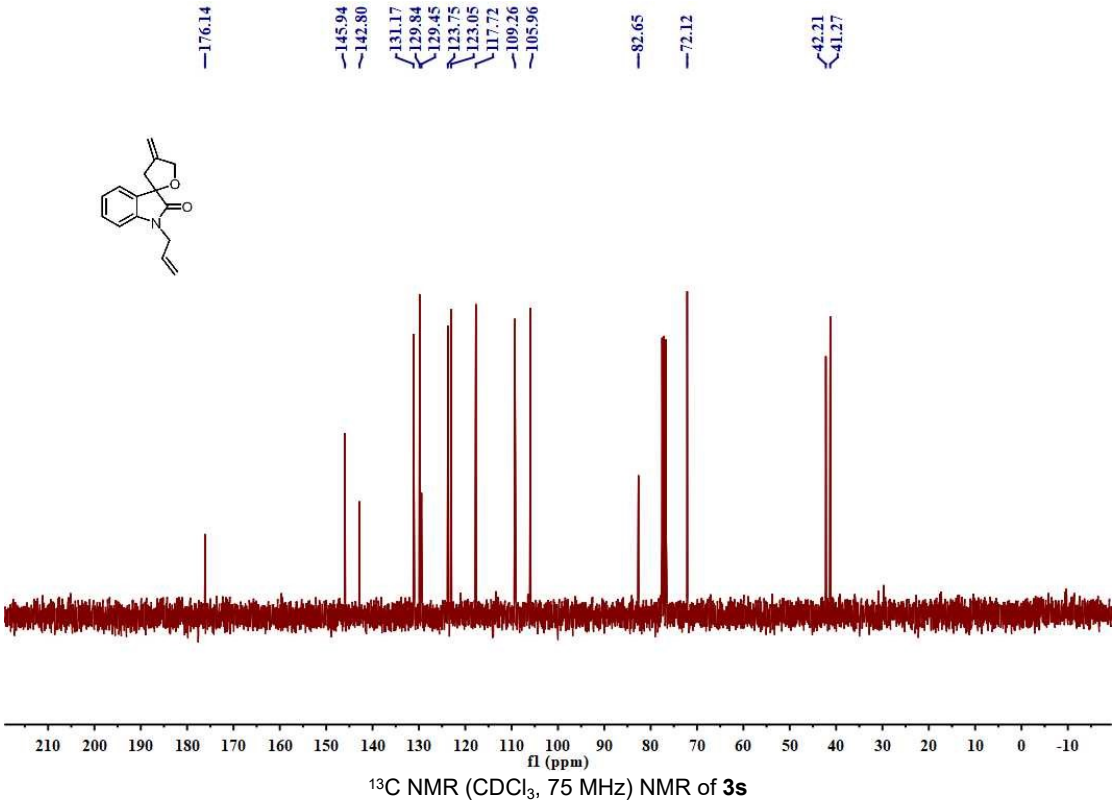
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3r**



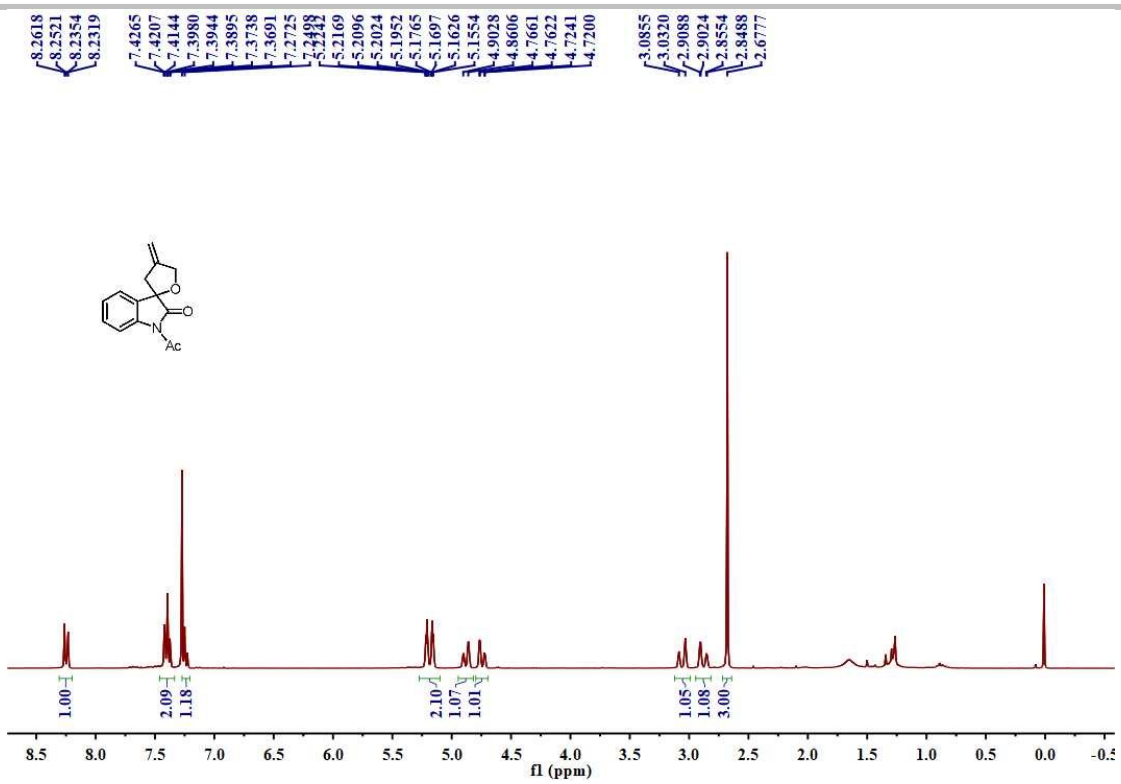
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3r**



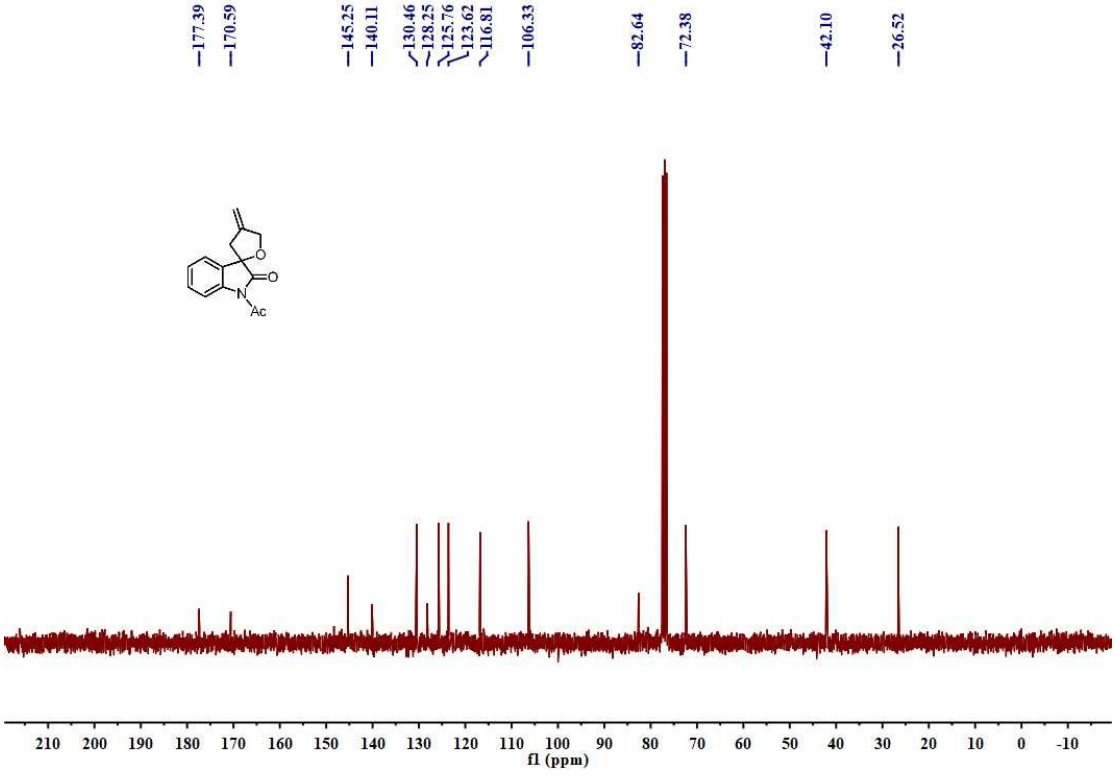
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3s**



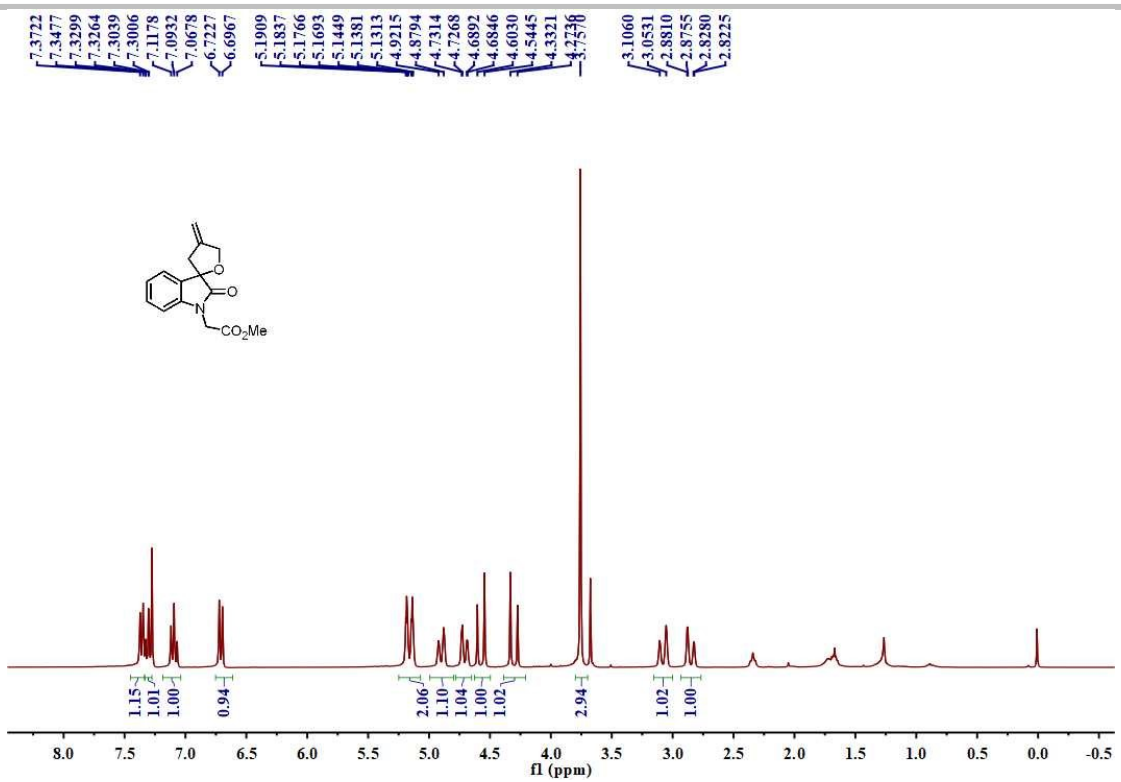
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3s**



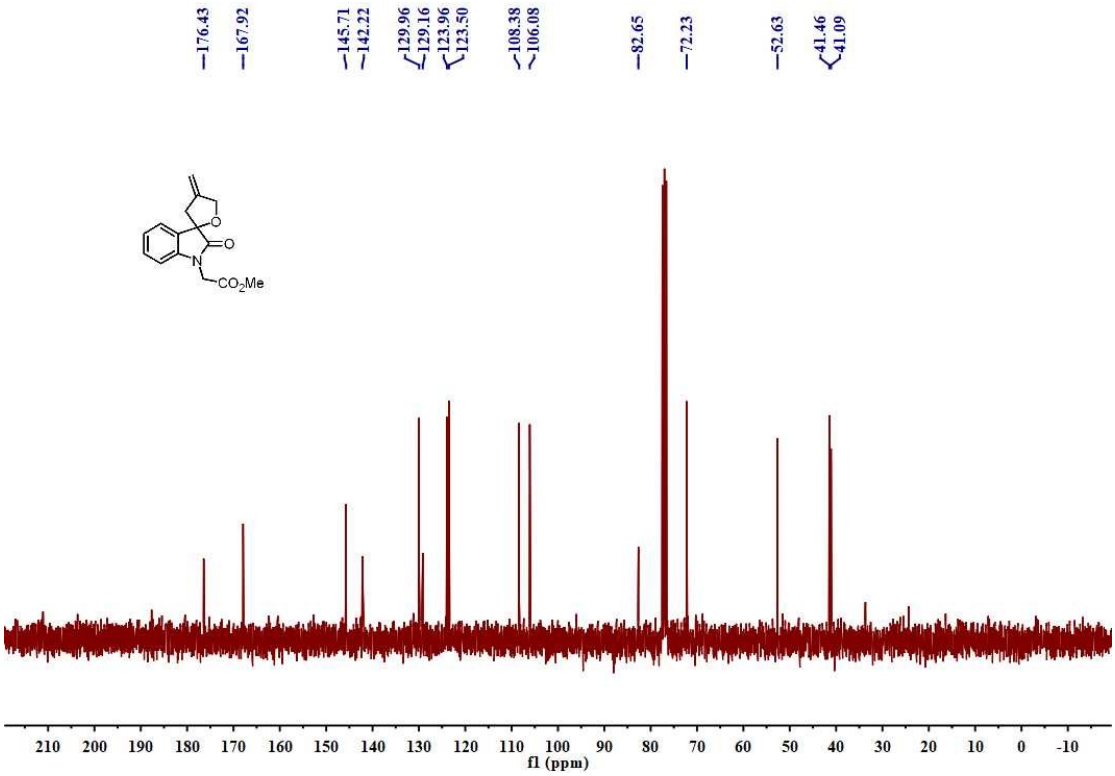
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3t**



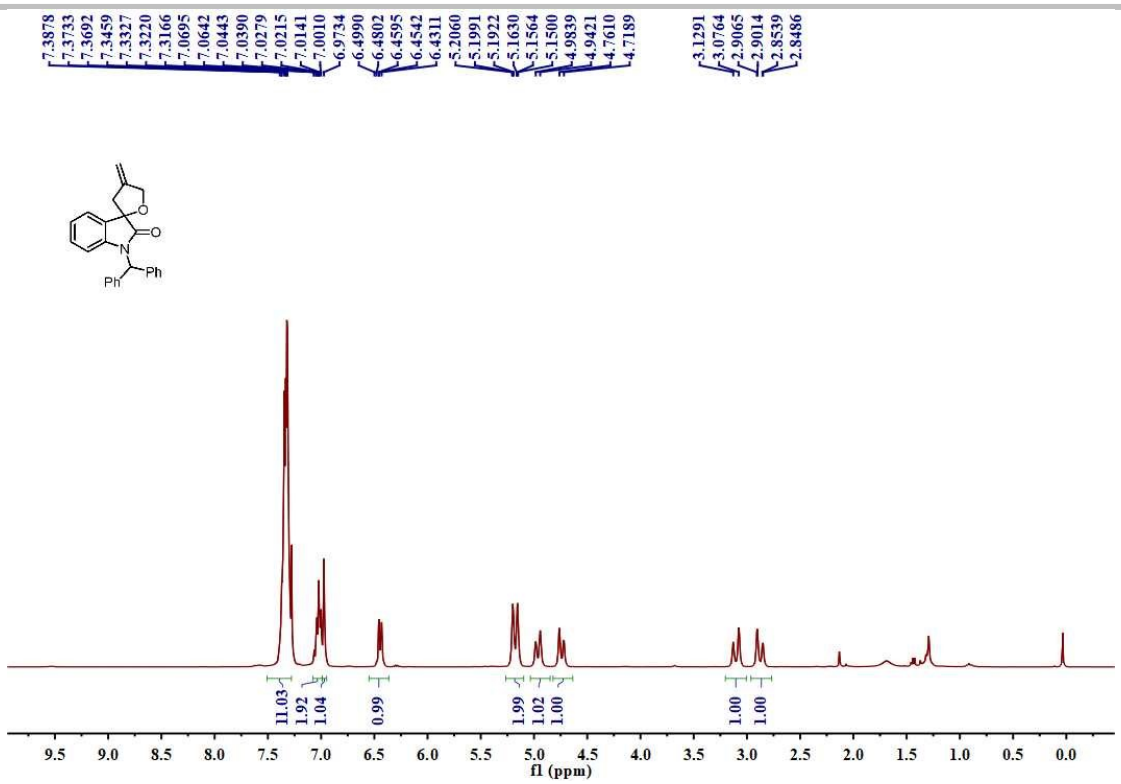
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3t**



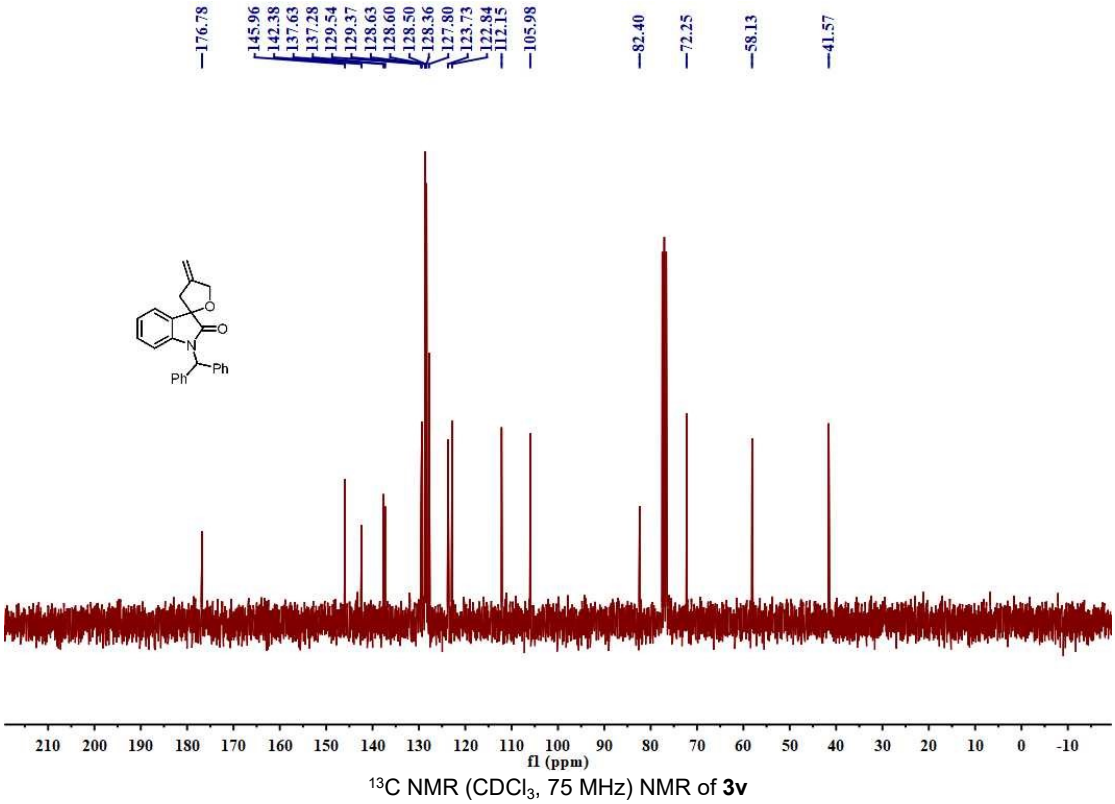
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3u**



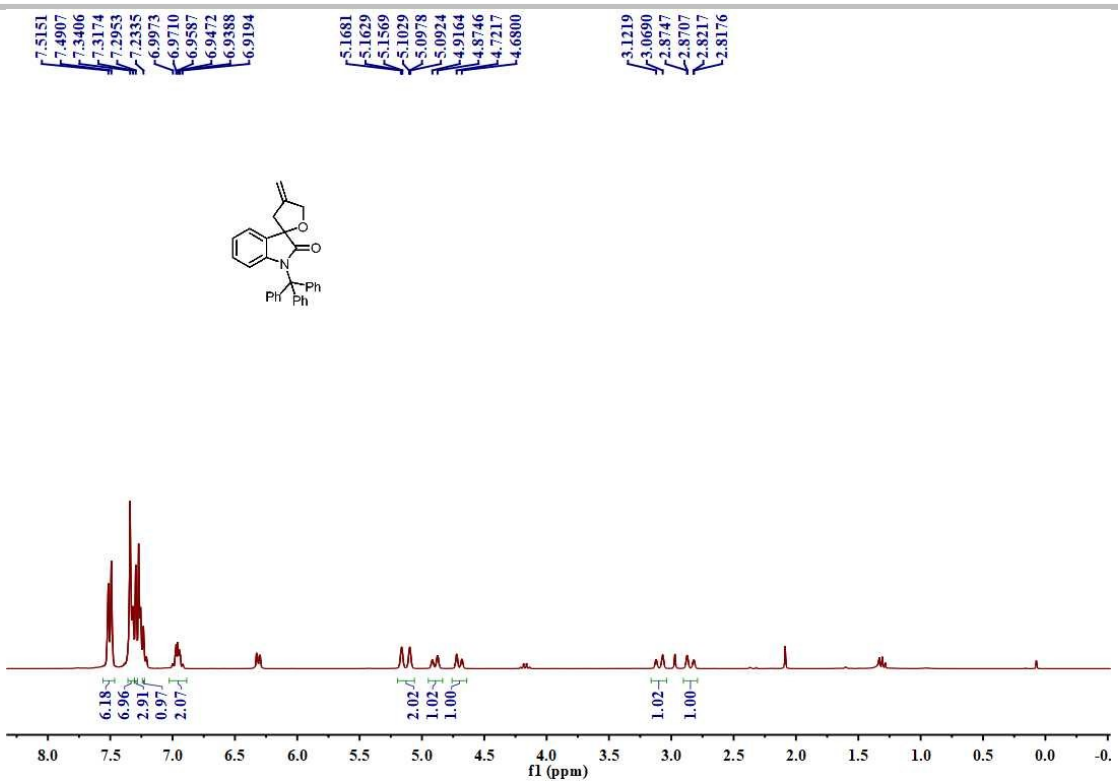
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3u**



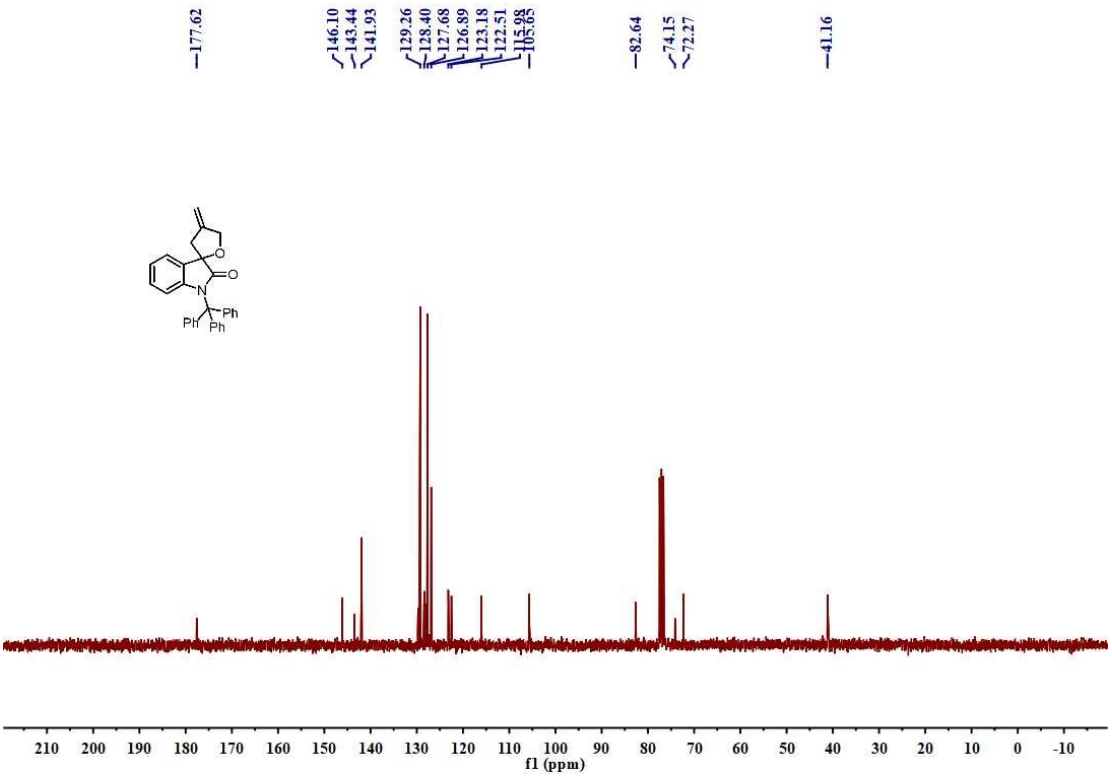
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3v**



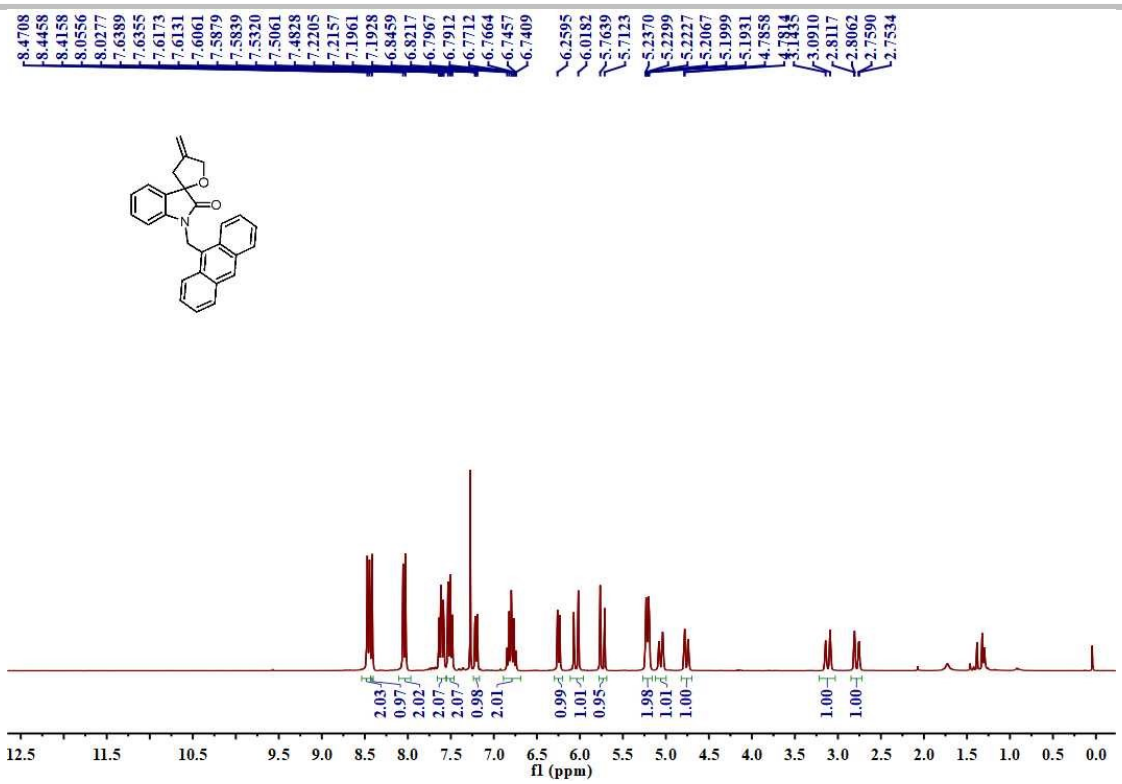
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3v**



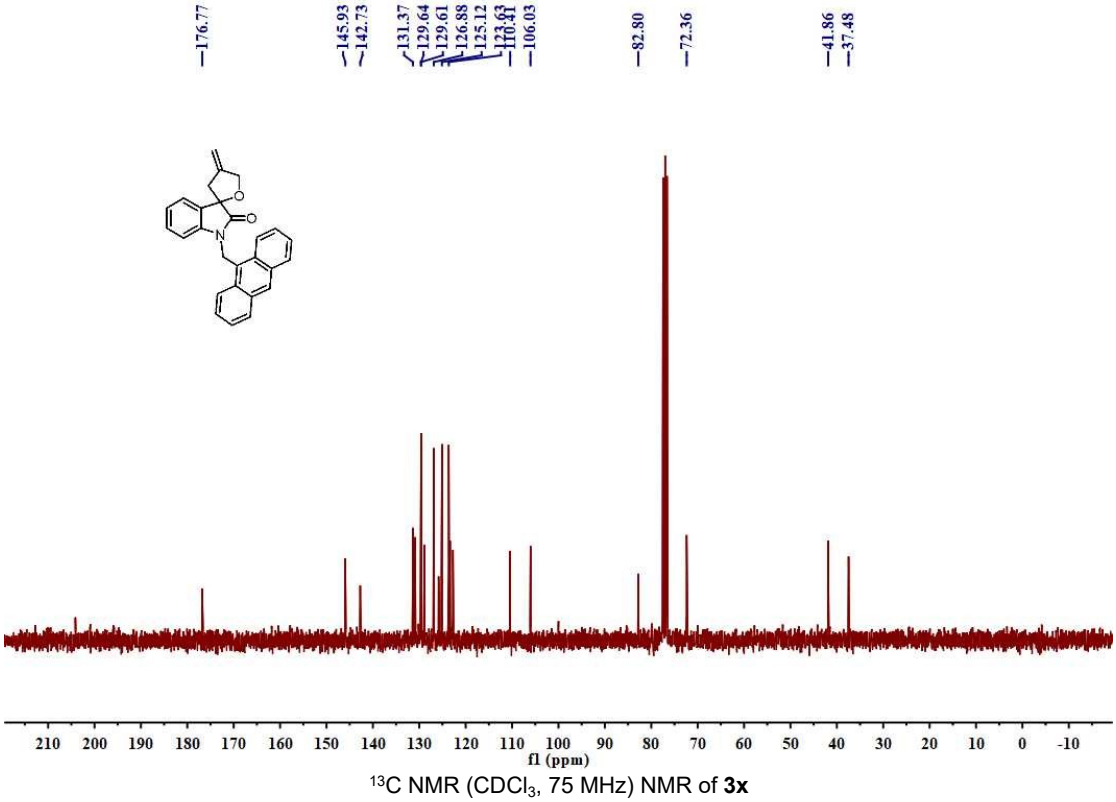
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3w**



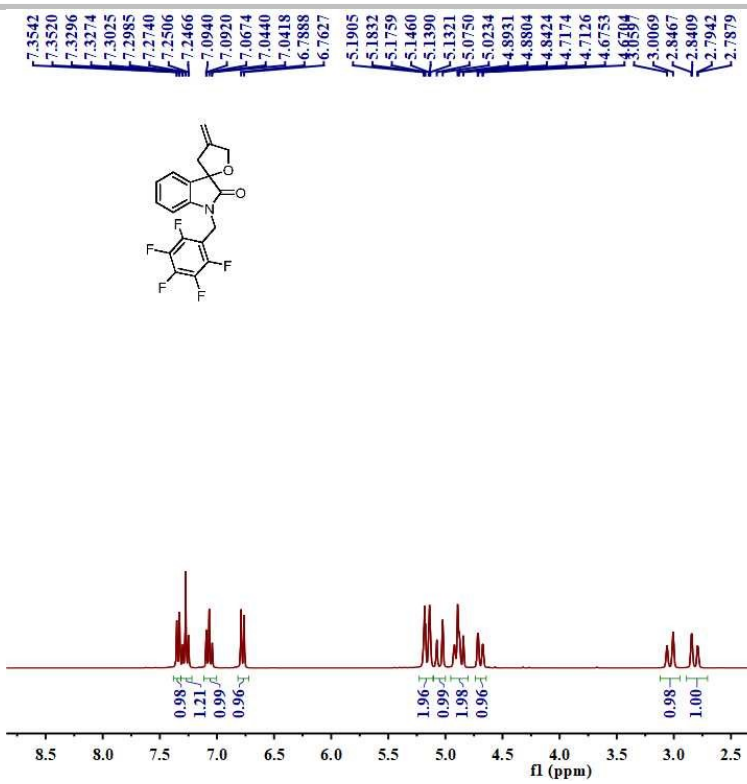
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3w**



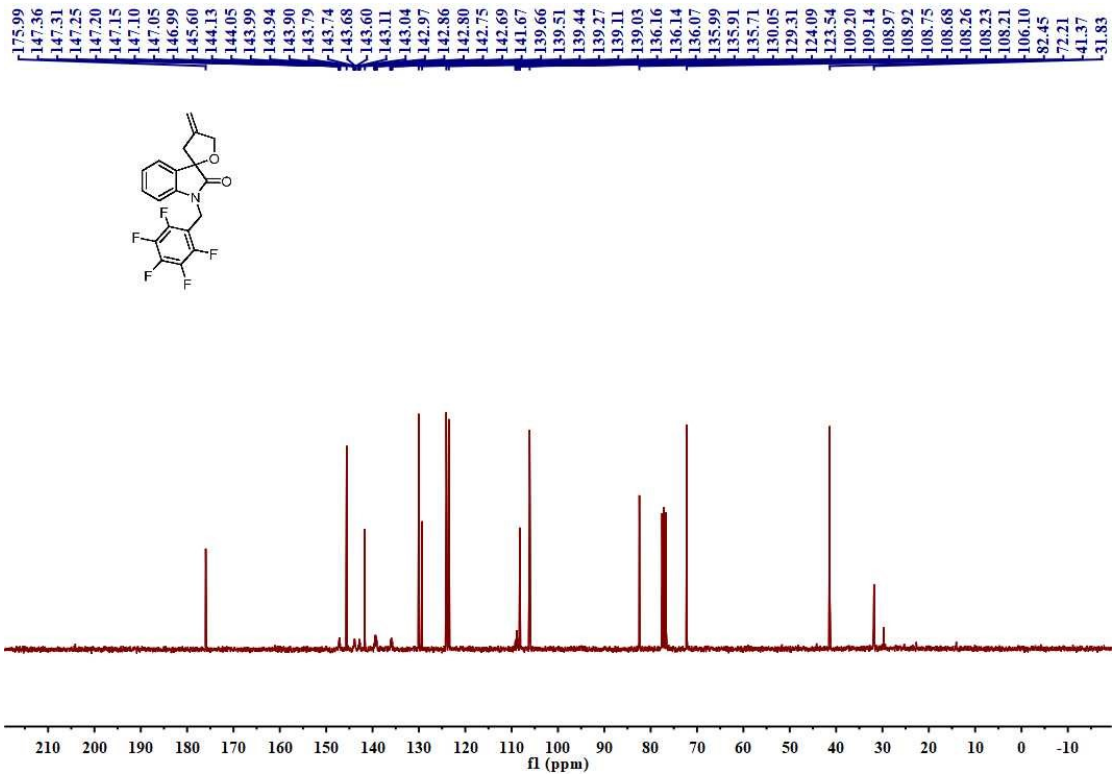
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3x**



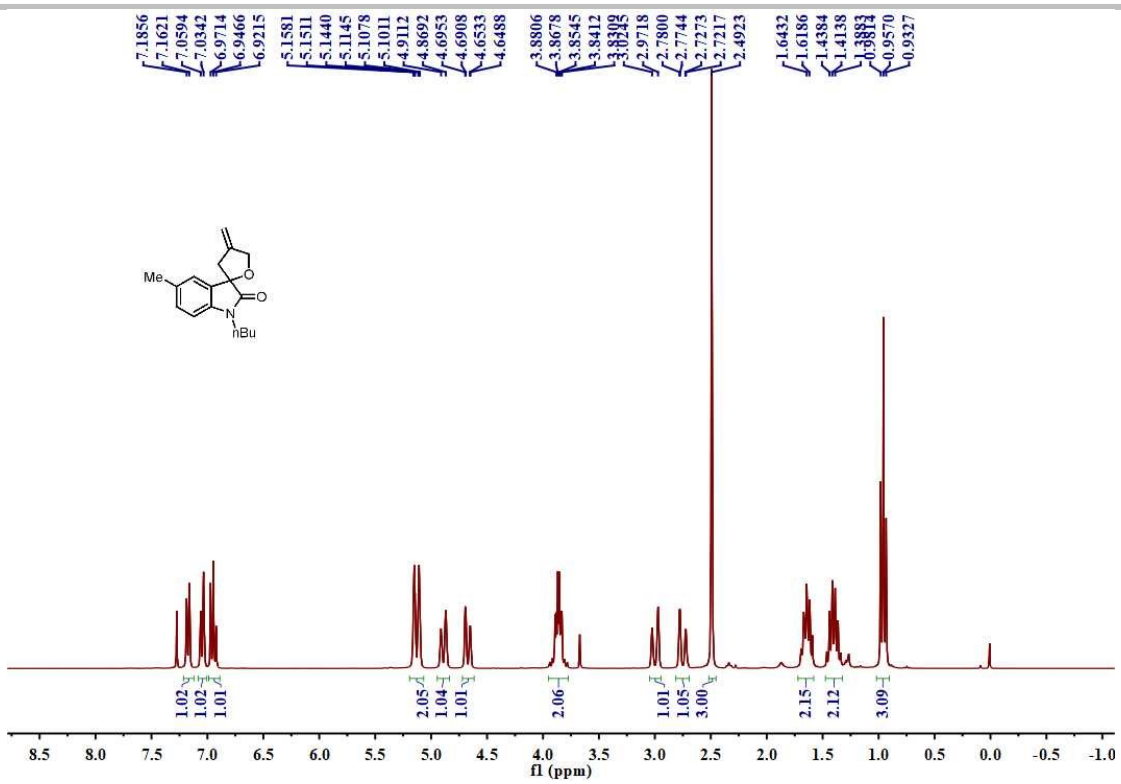
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3x**



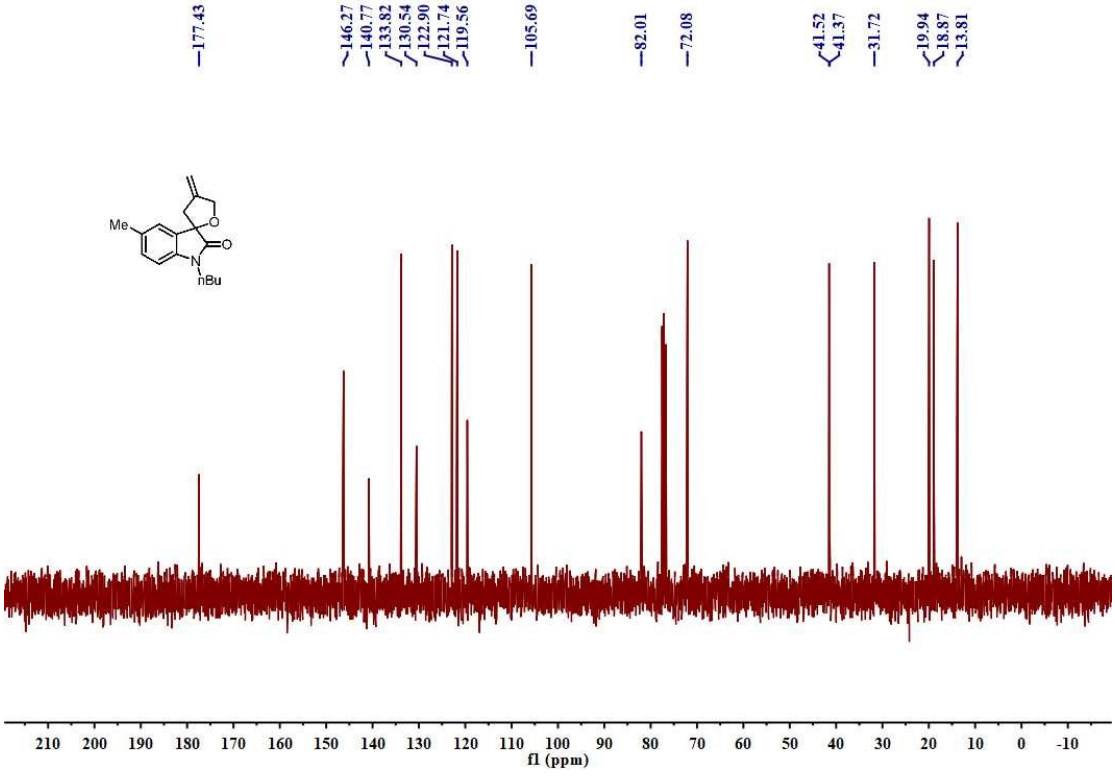
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3y**



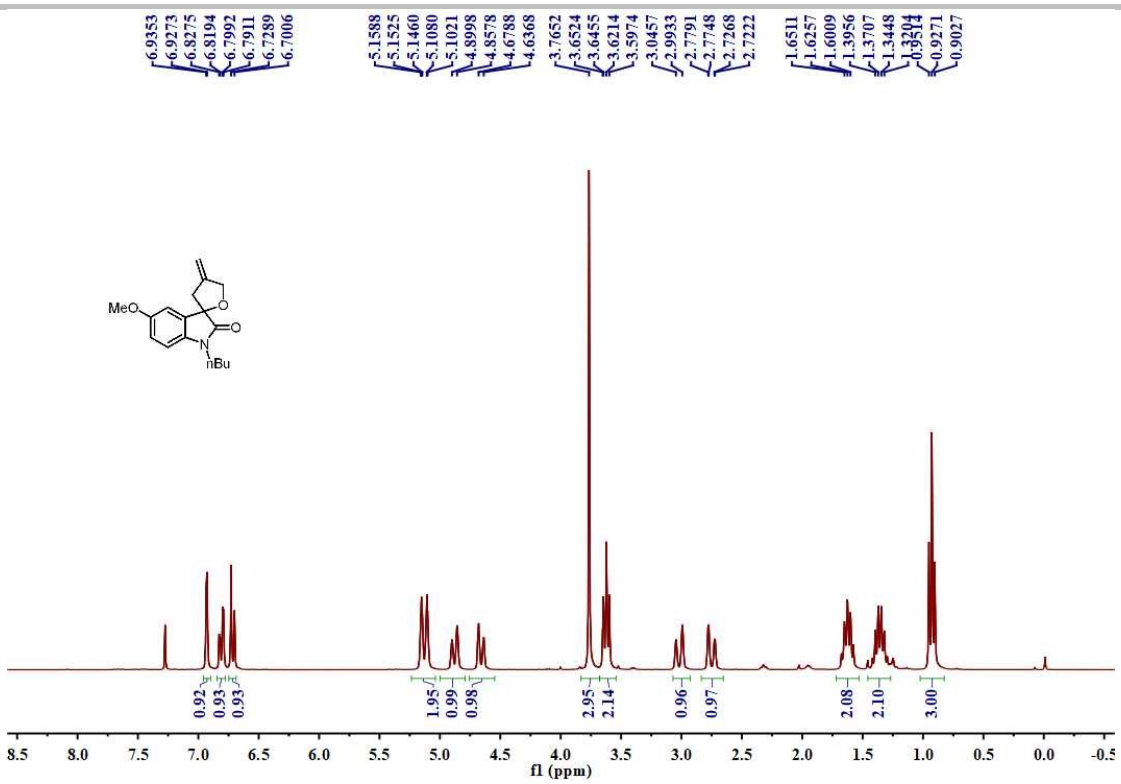
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3y**



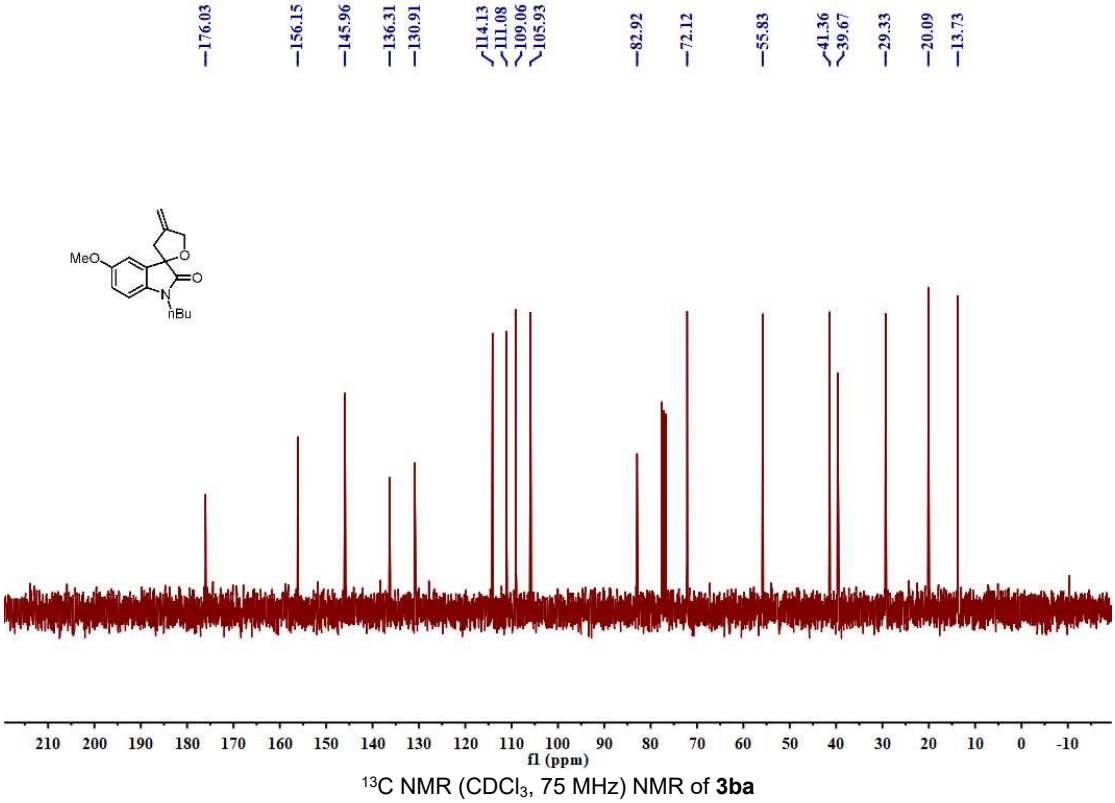
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3aa**



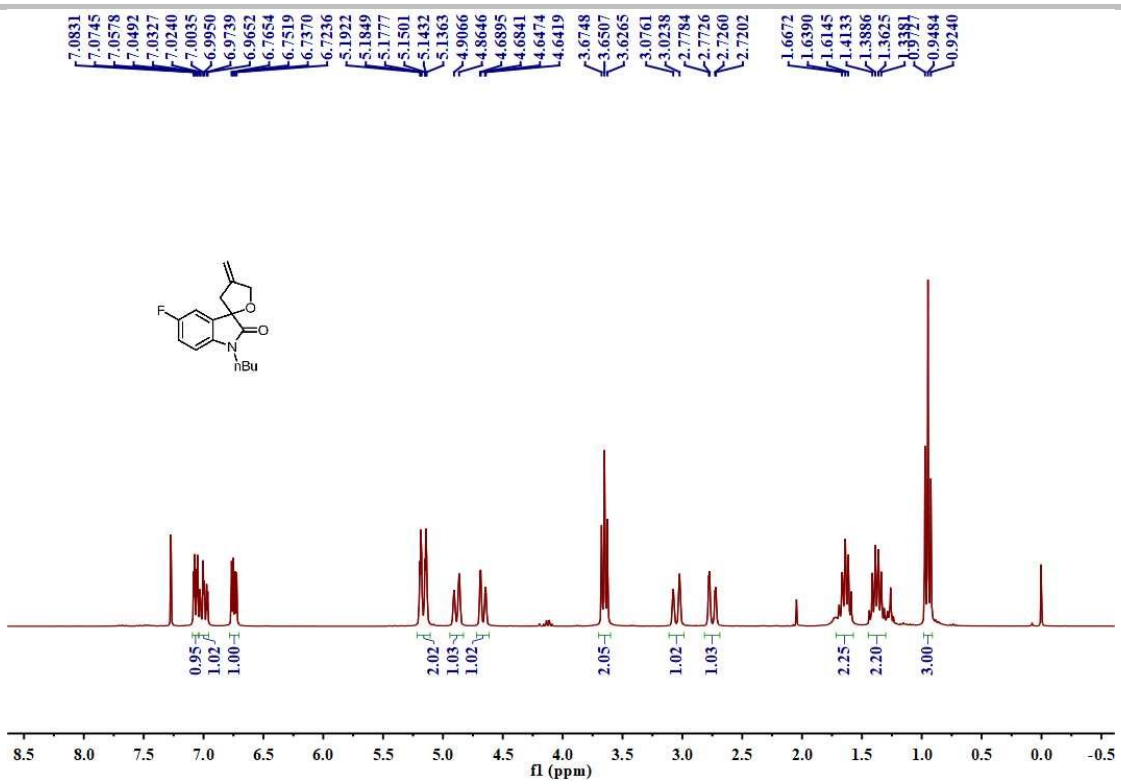
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3aa**



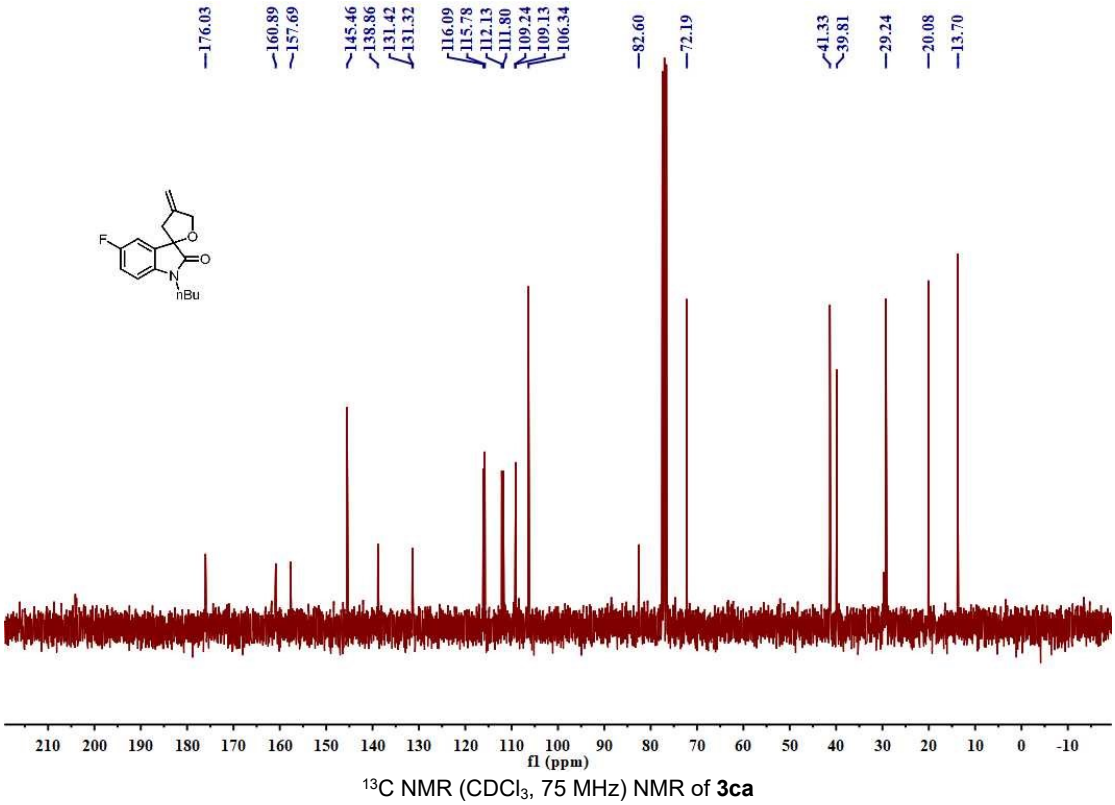
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3ba**



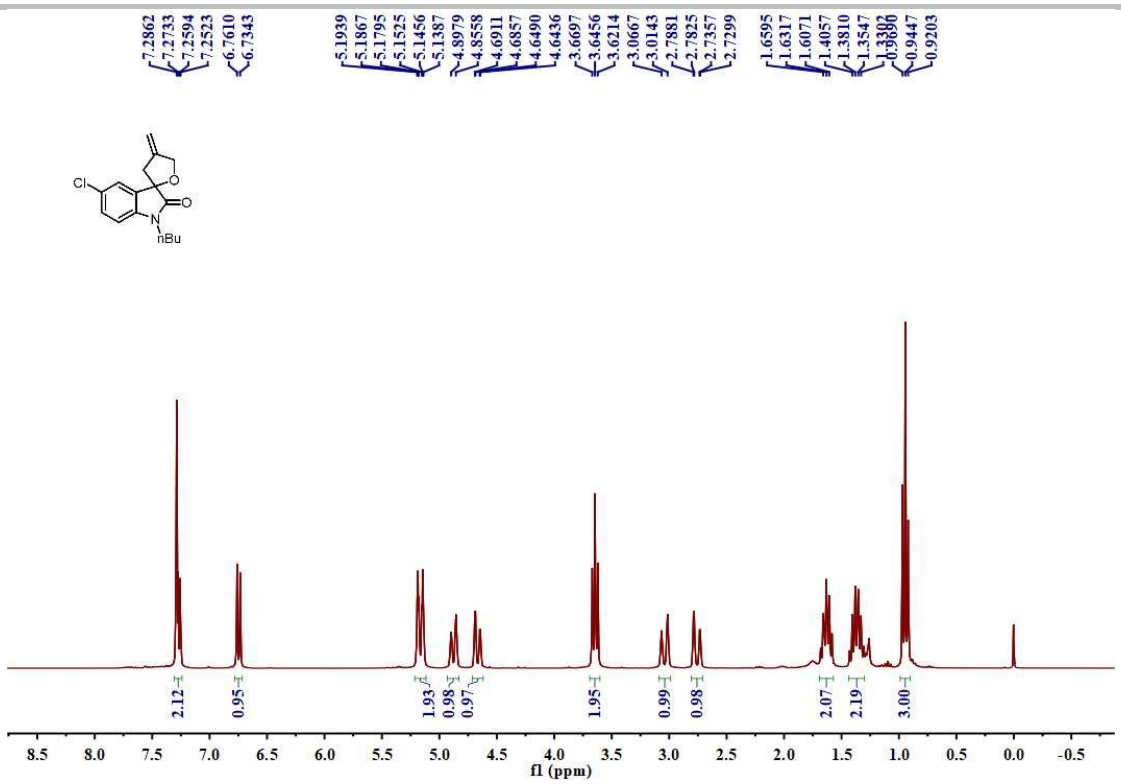
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3ba**



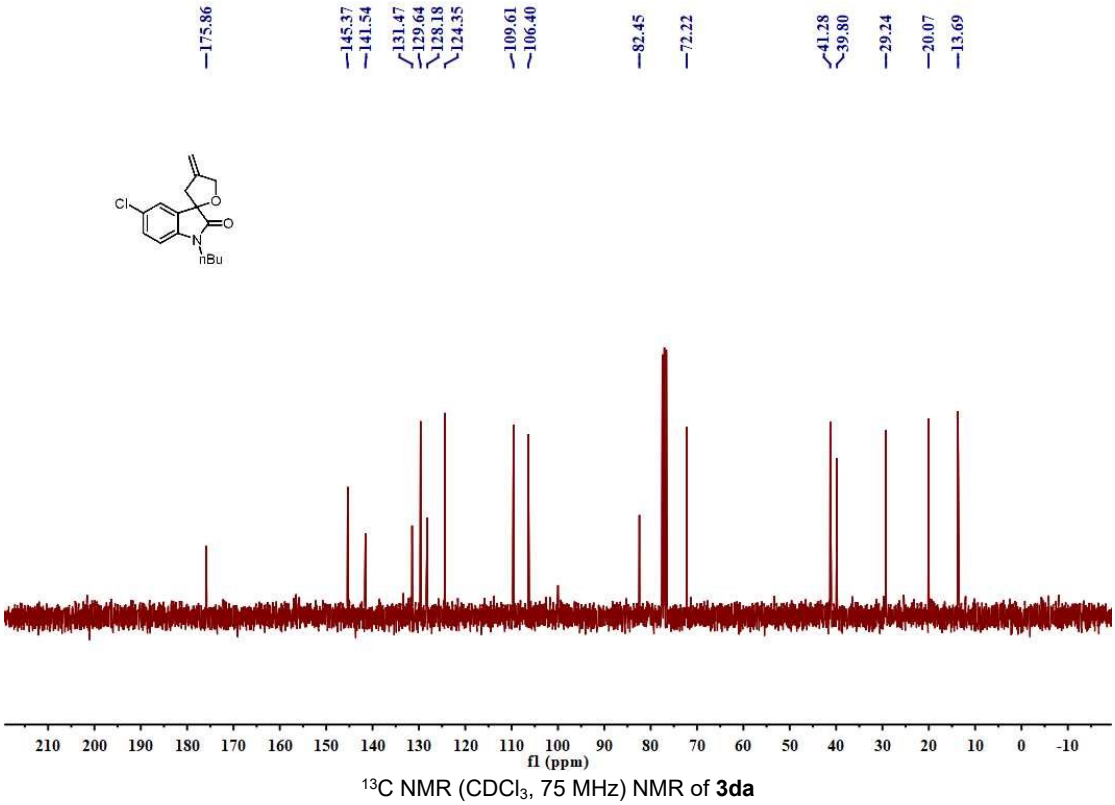
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3ca**



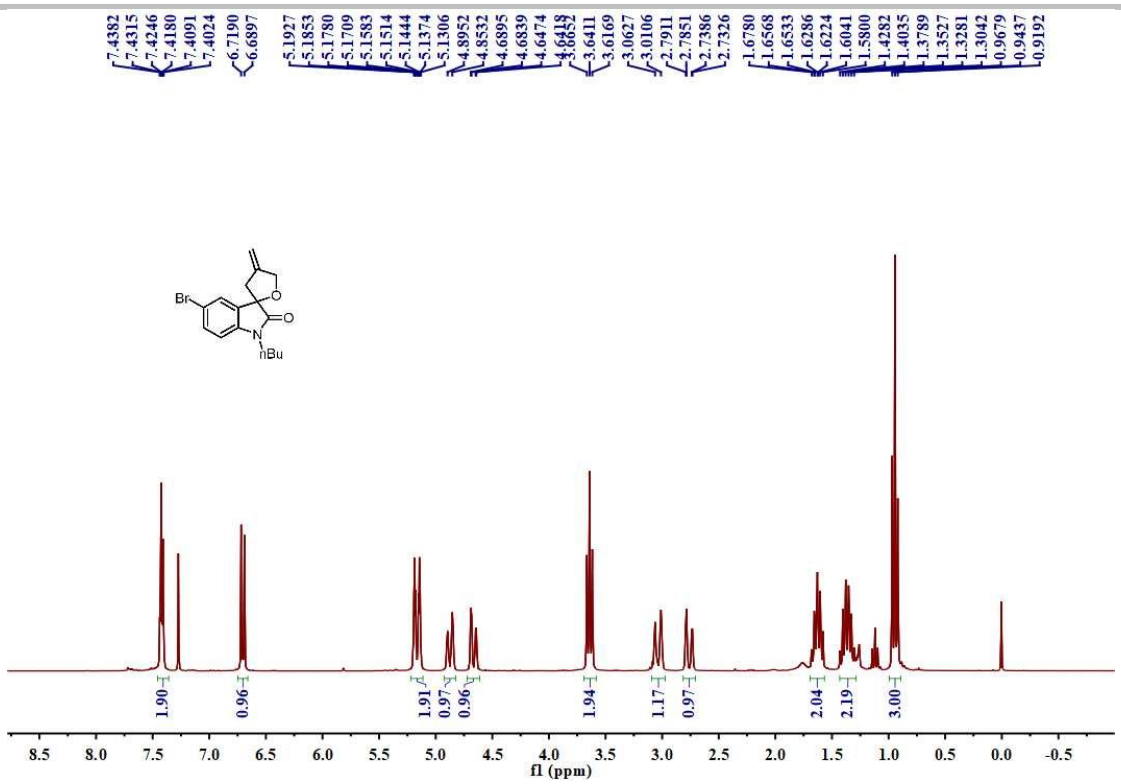
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3ca**



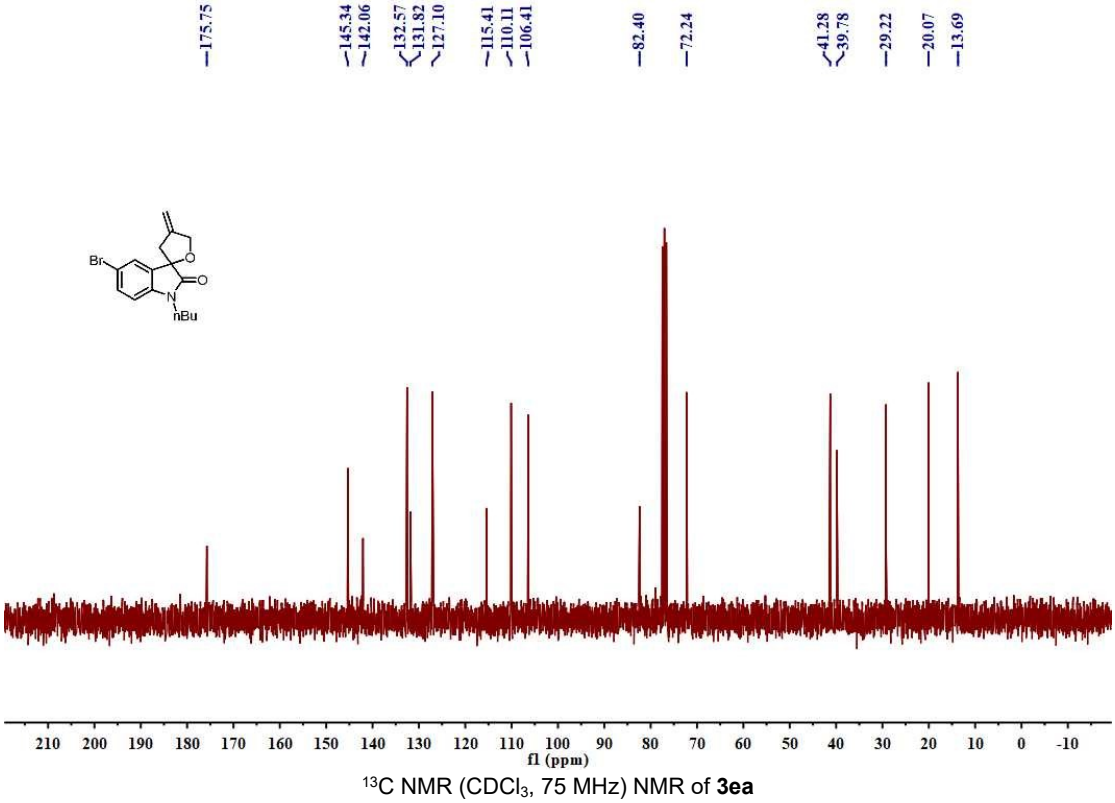
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3da**



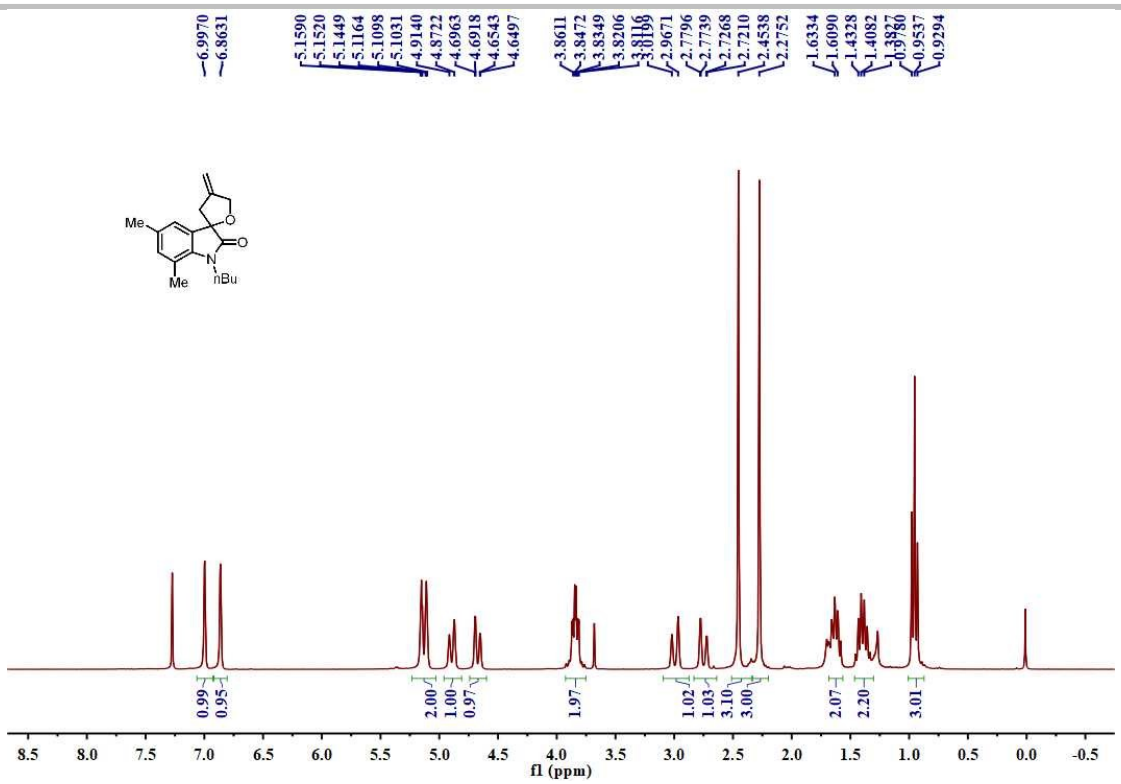
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3da**



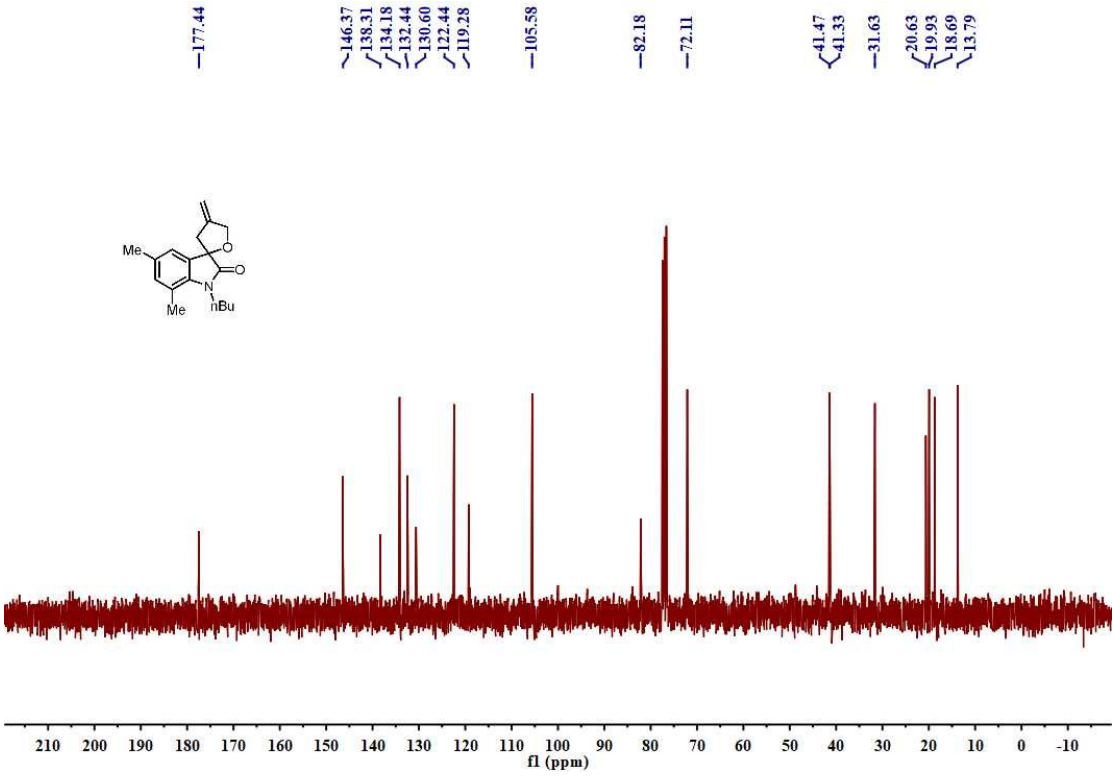
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3ea**



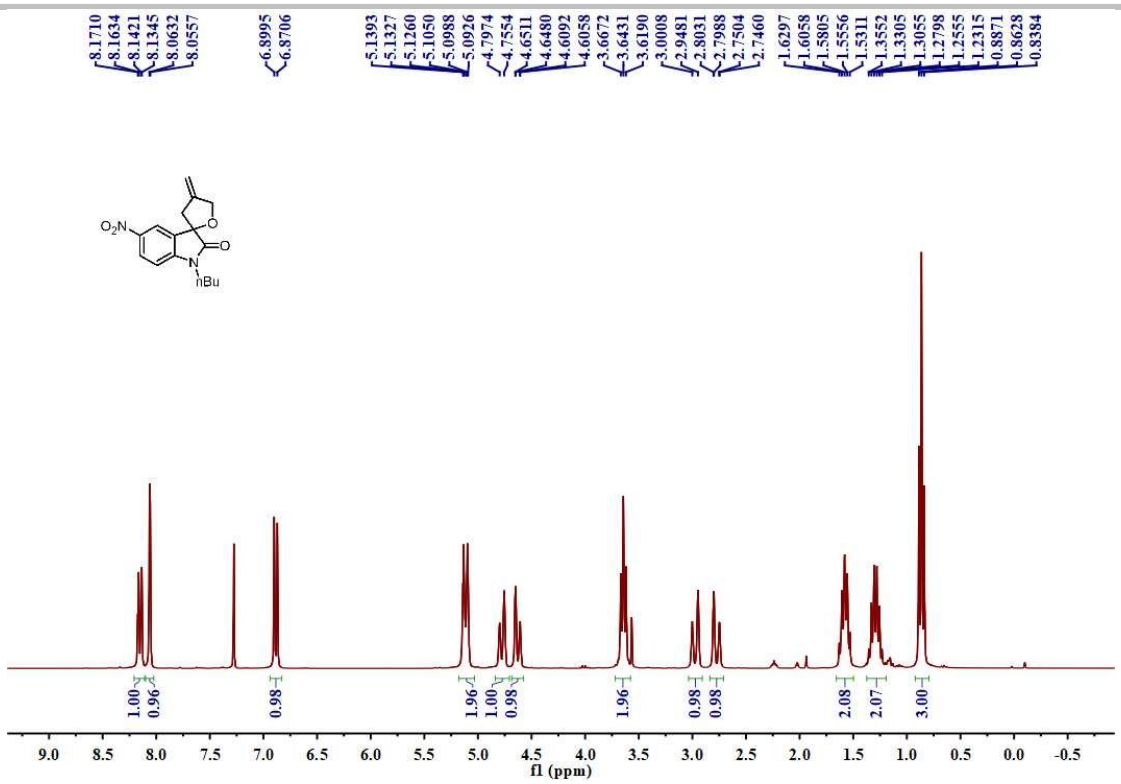
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3ea**



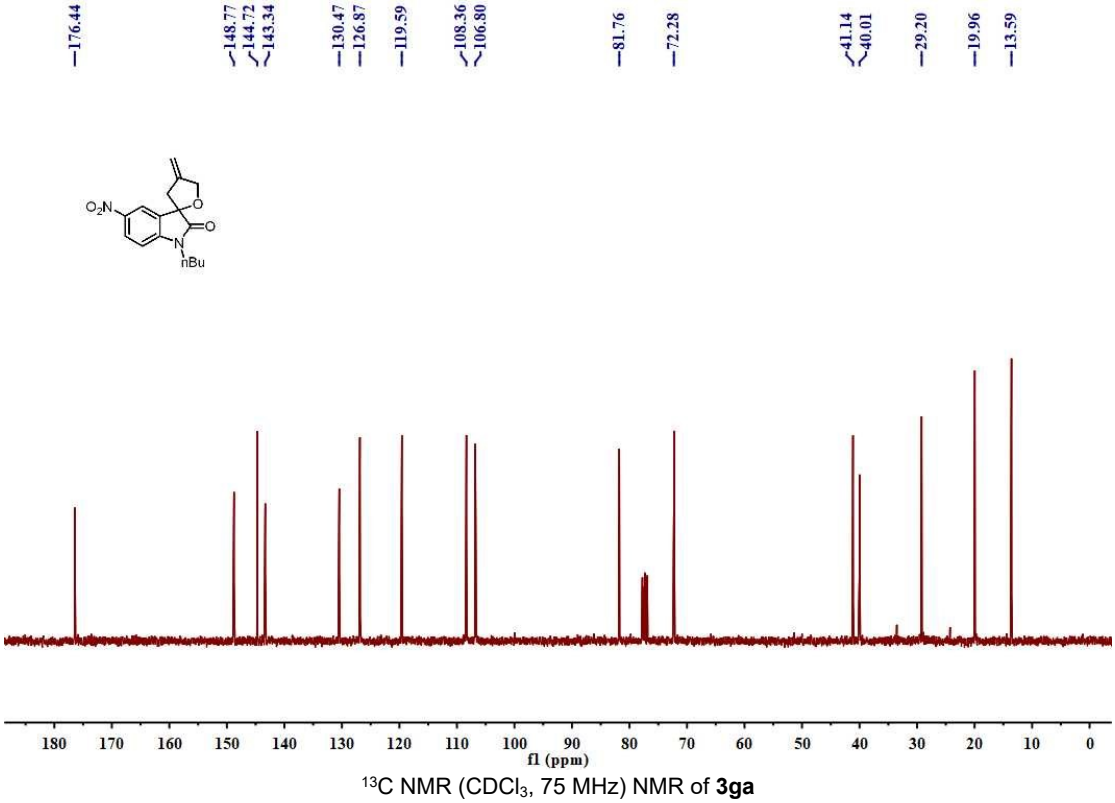
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3fa**



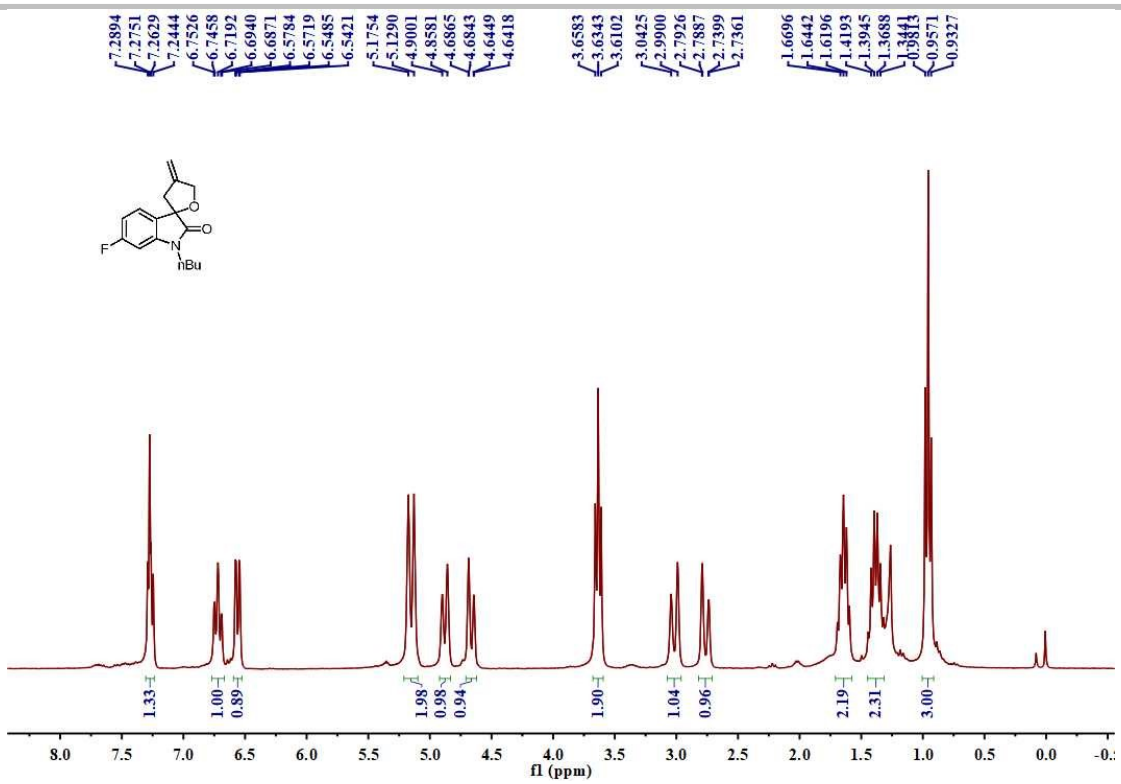
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3fa**



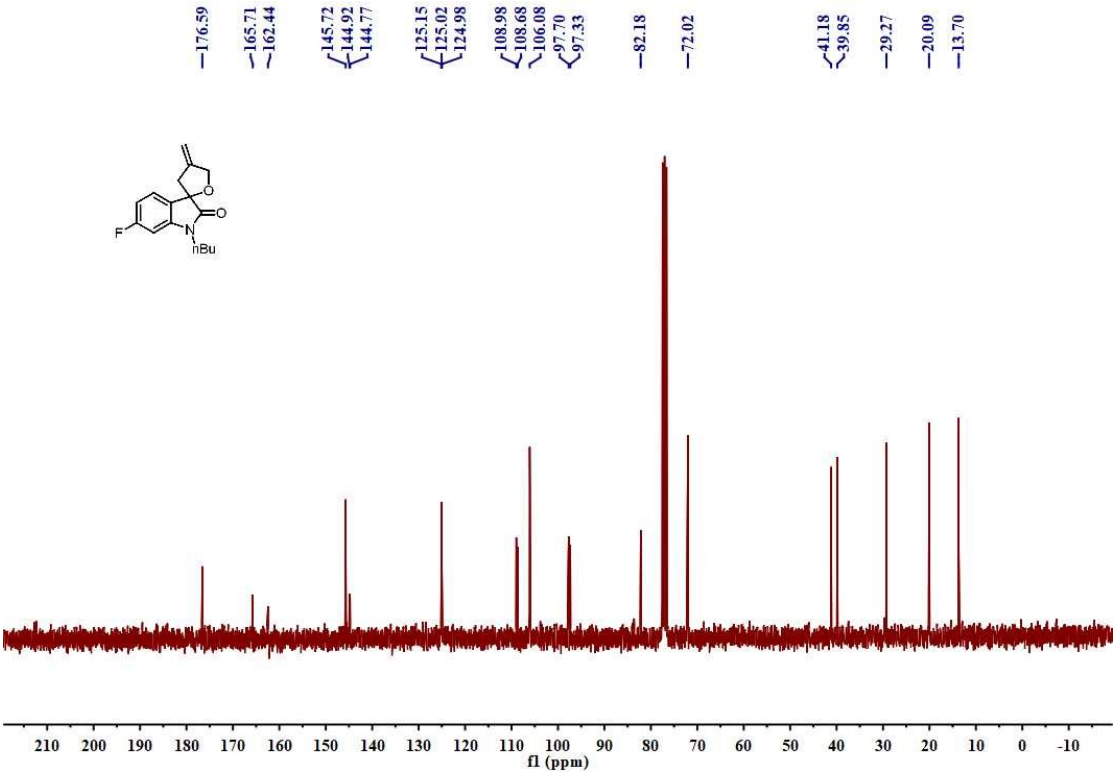
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3ga**



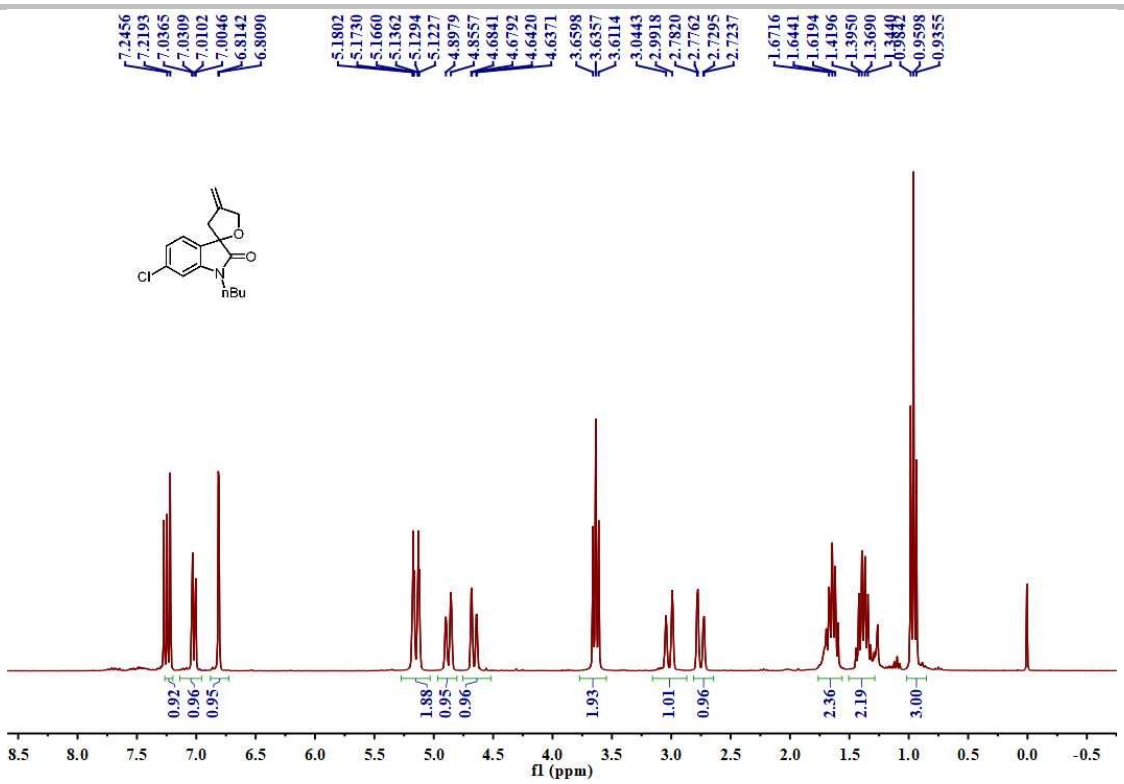
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3ga**



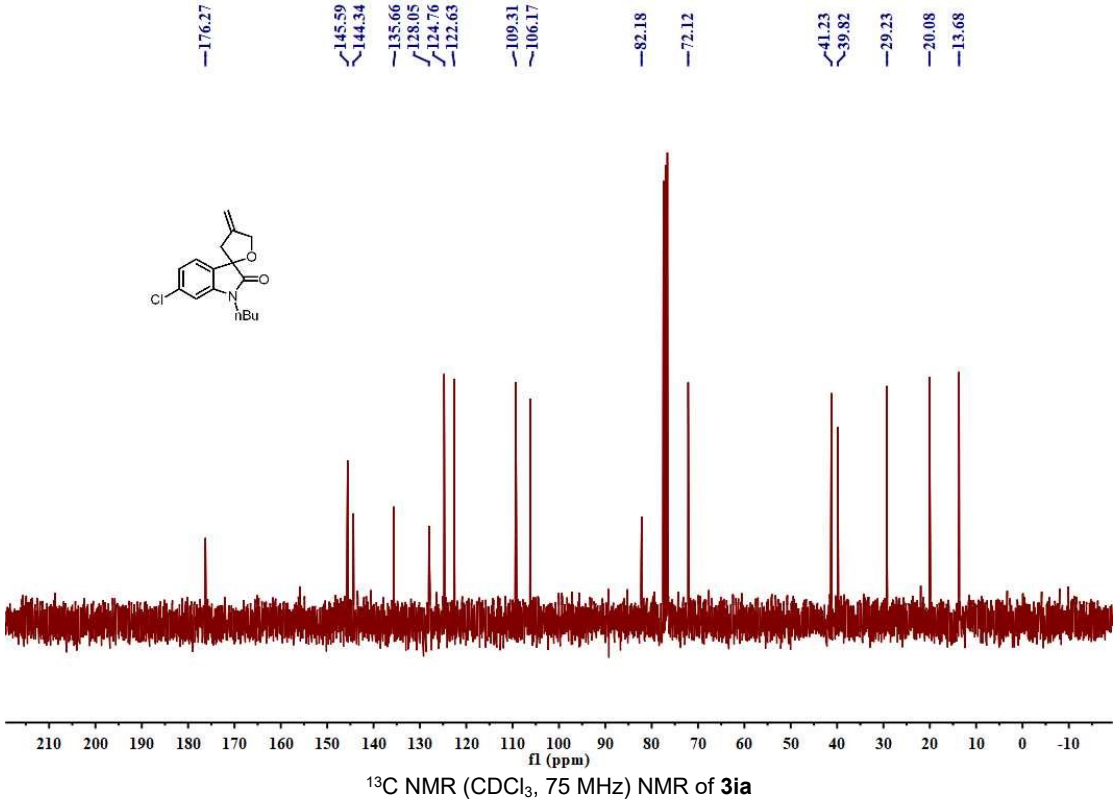
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3ha**



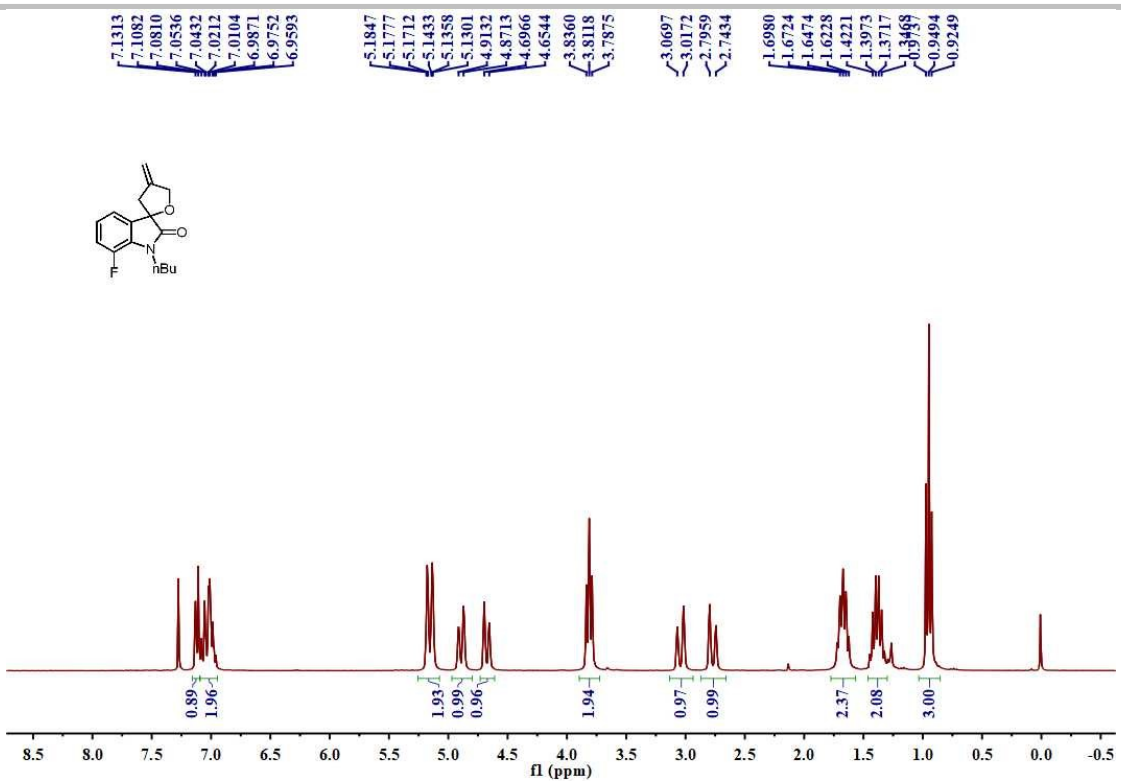
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3ha**



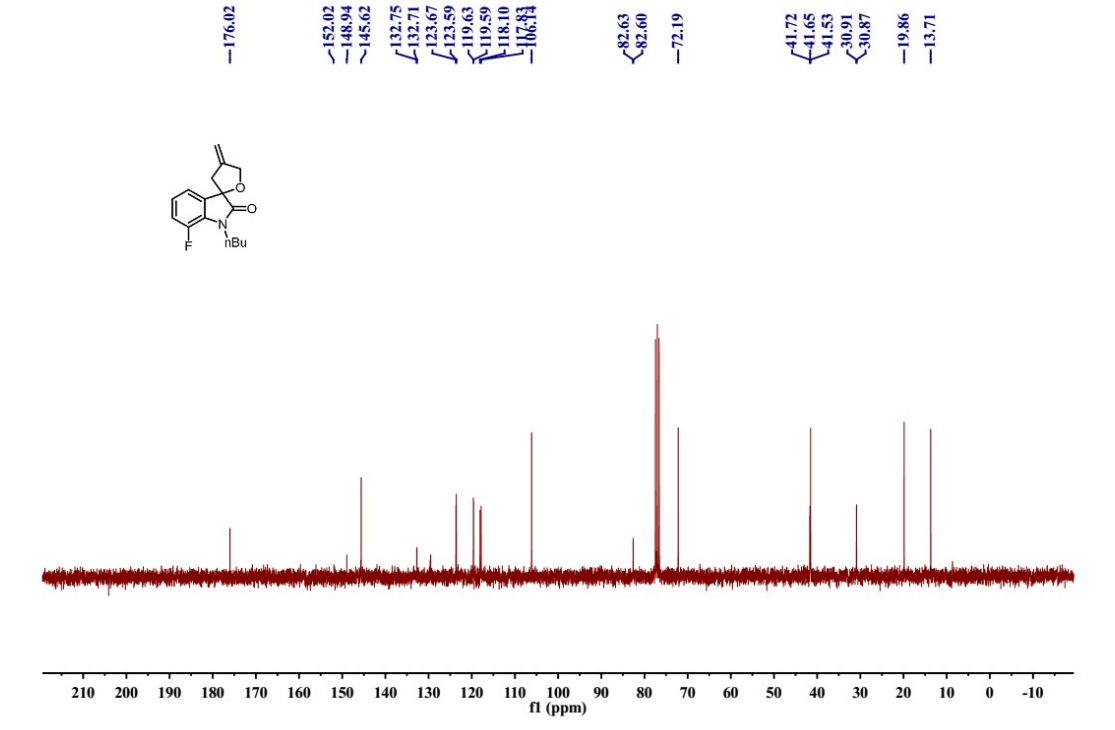
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3ia**



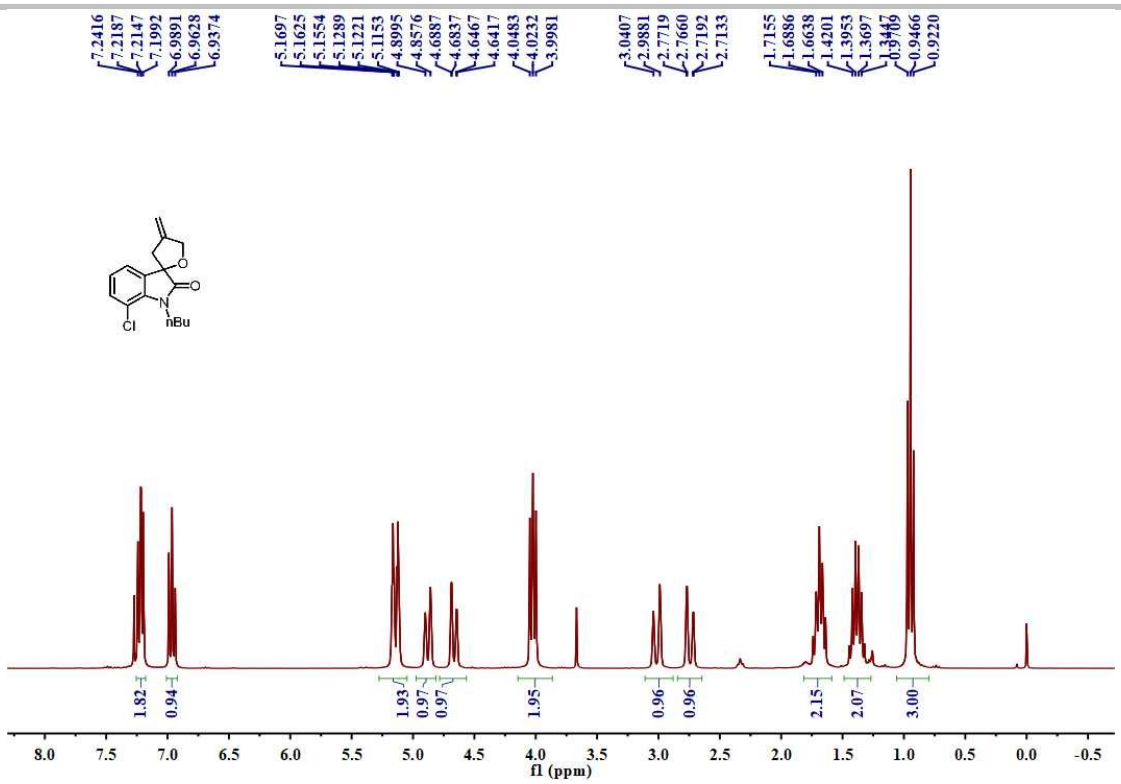
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3ia**



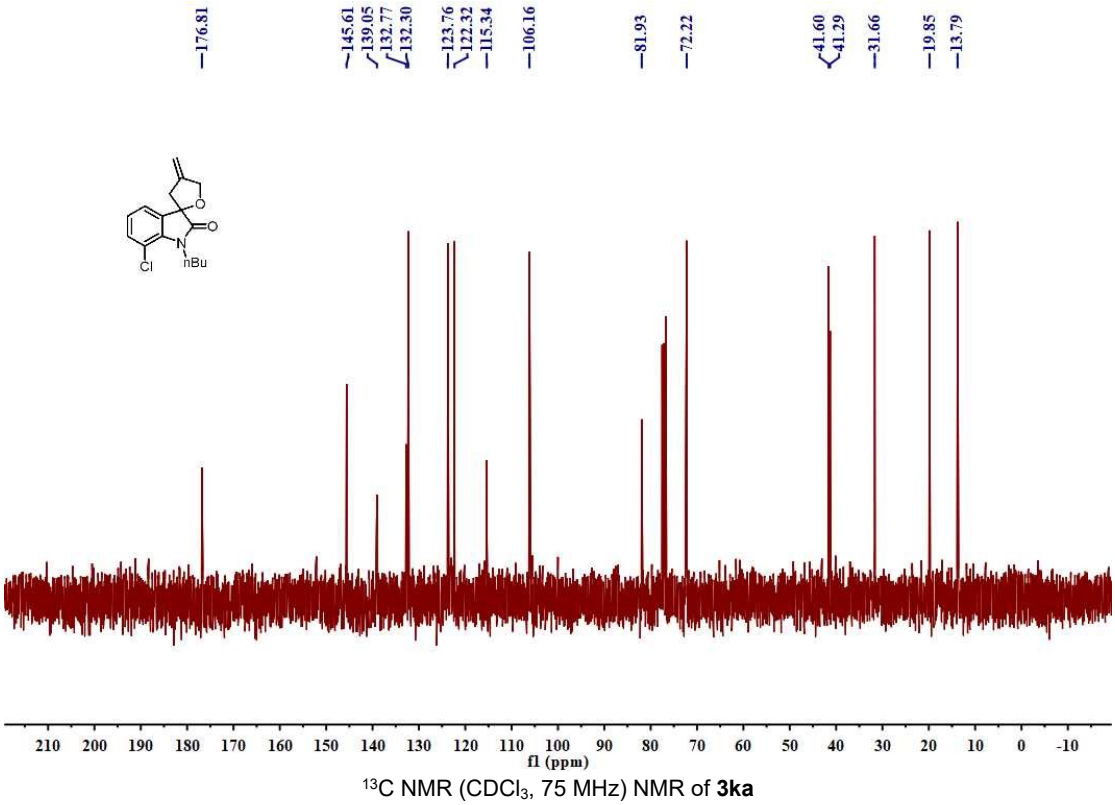
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3ja**



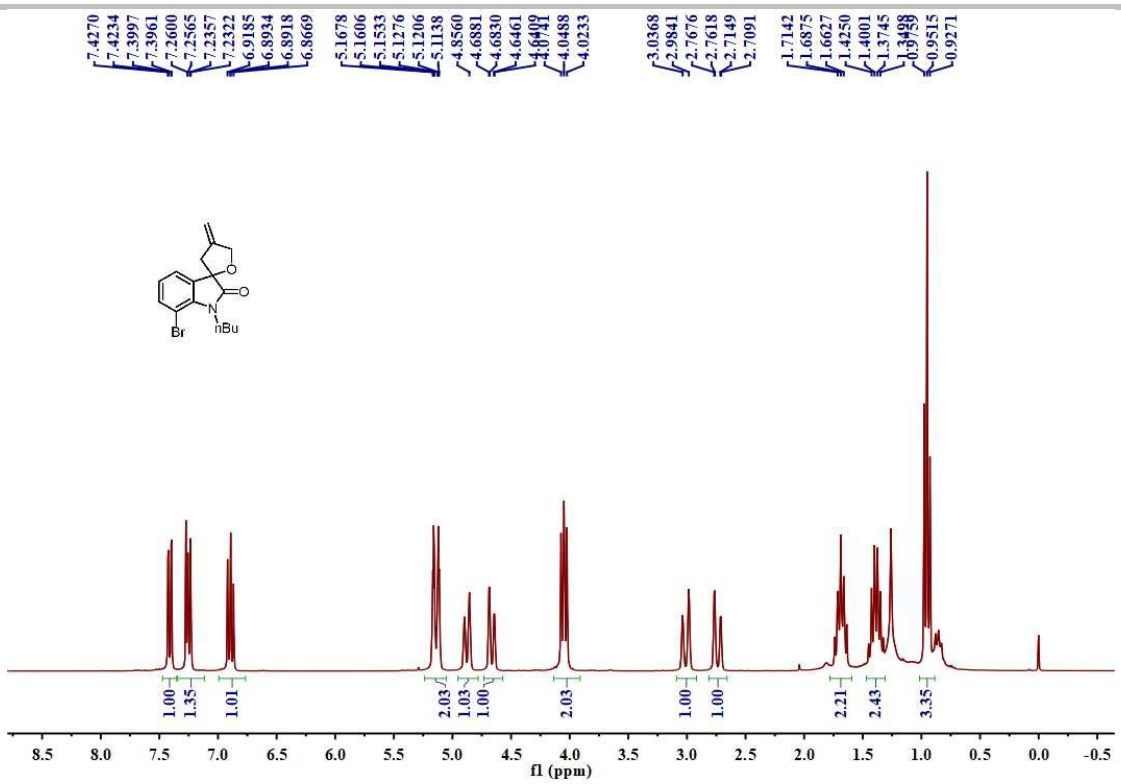
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3ja**



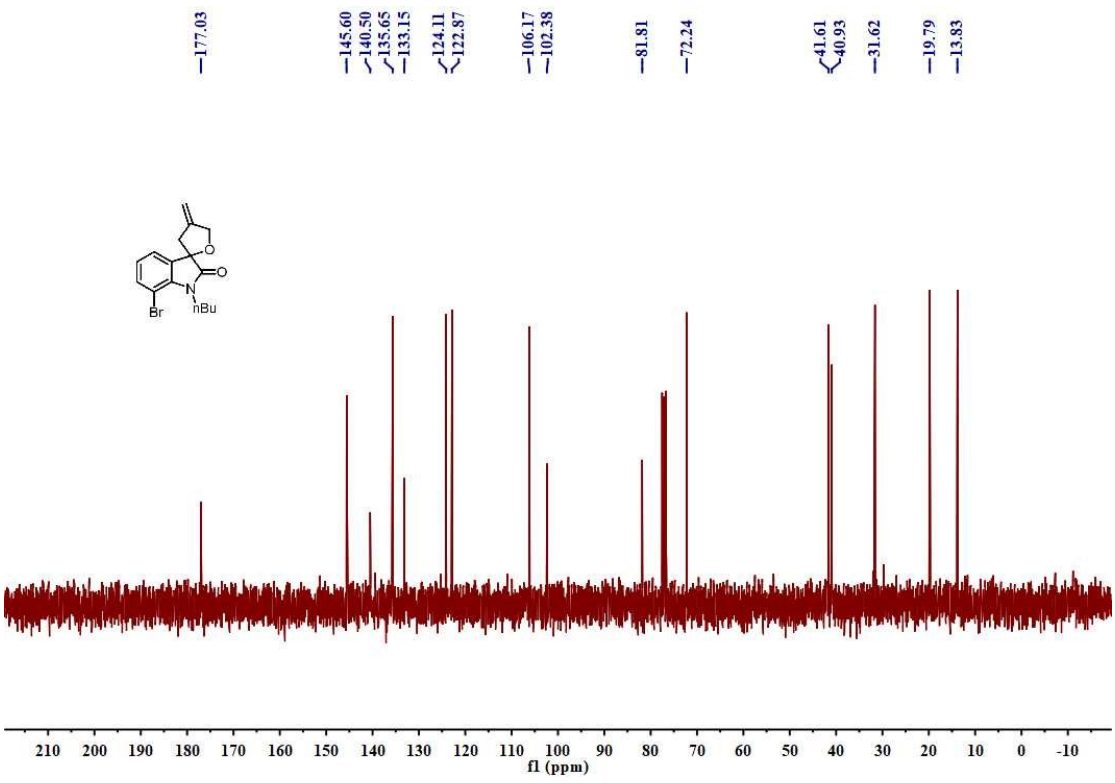
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3ka**



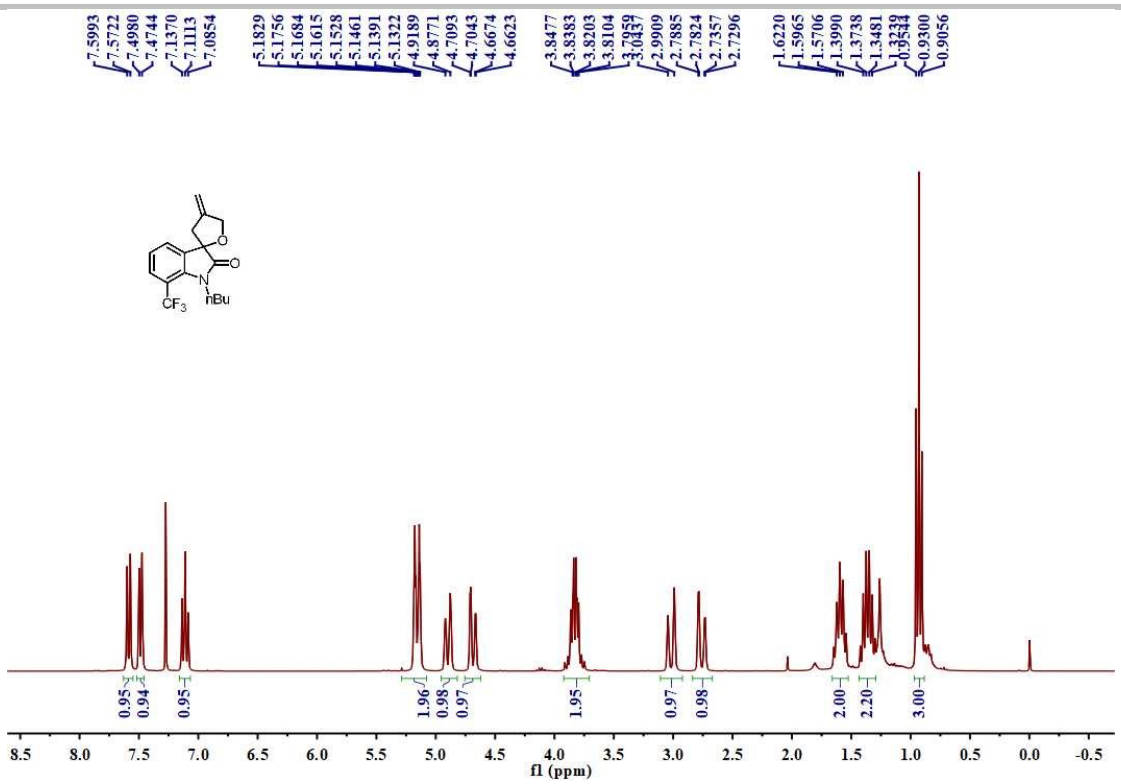
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3ka**



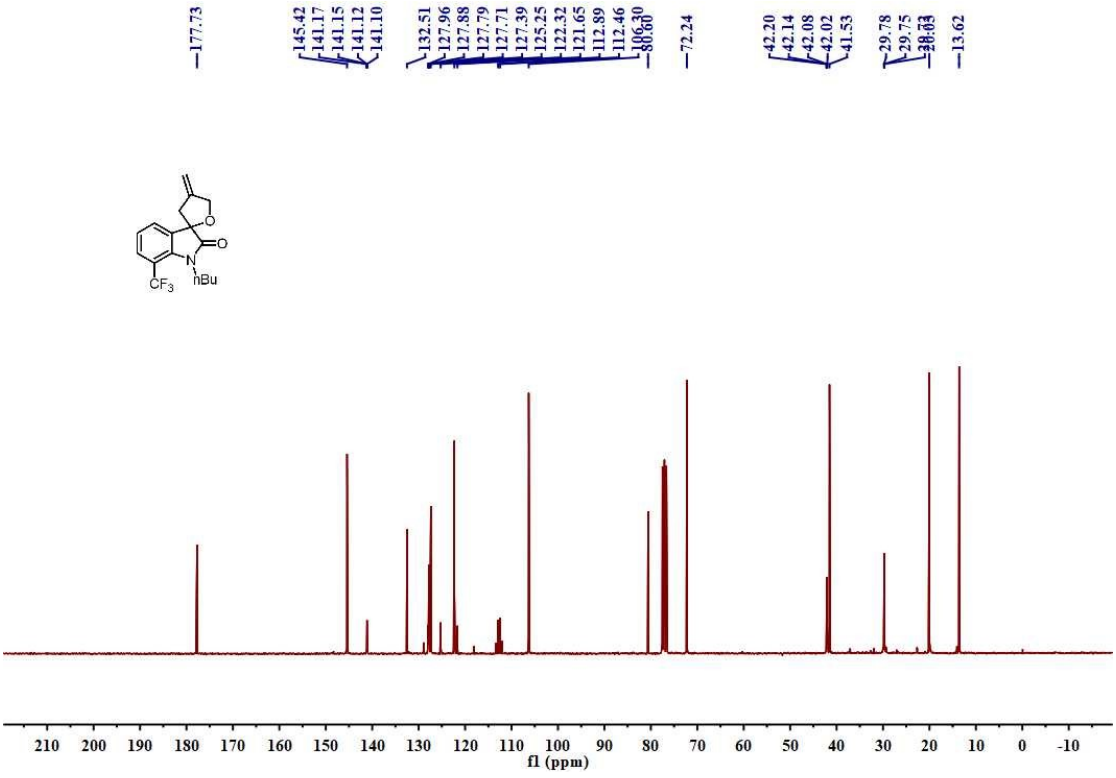
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3la**



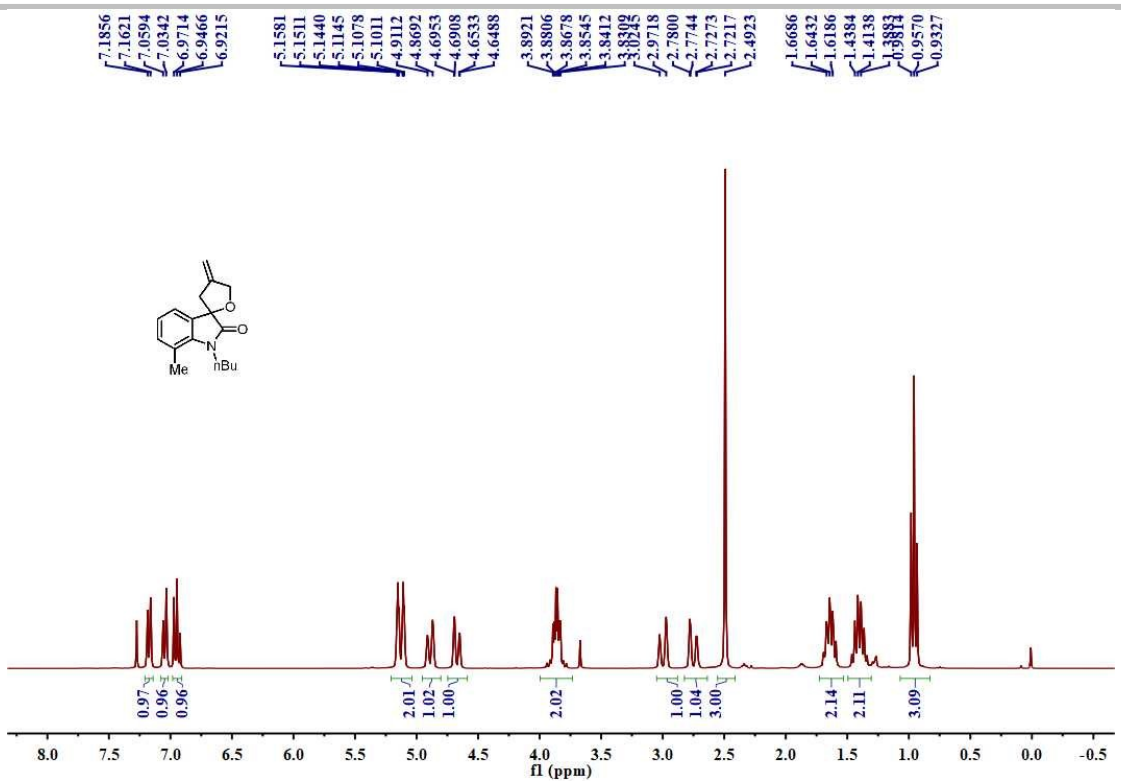
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3la**



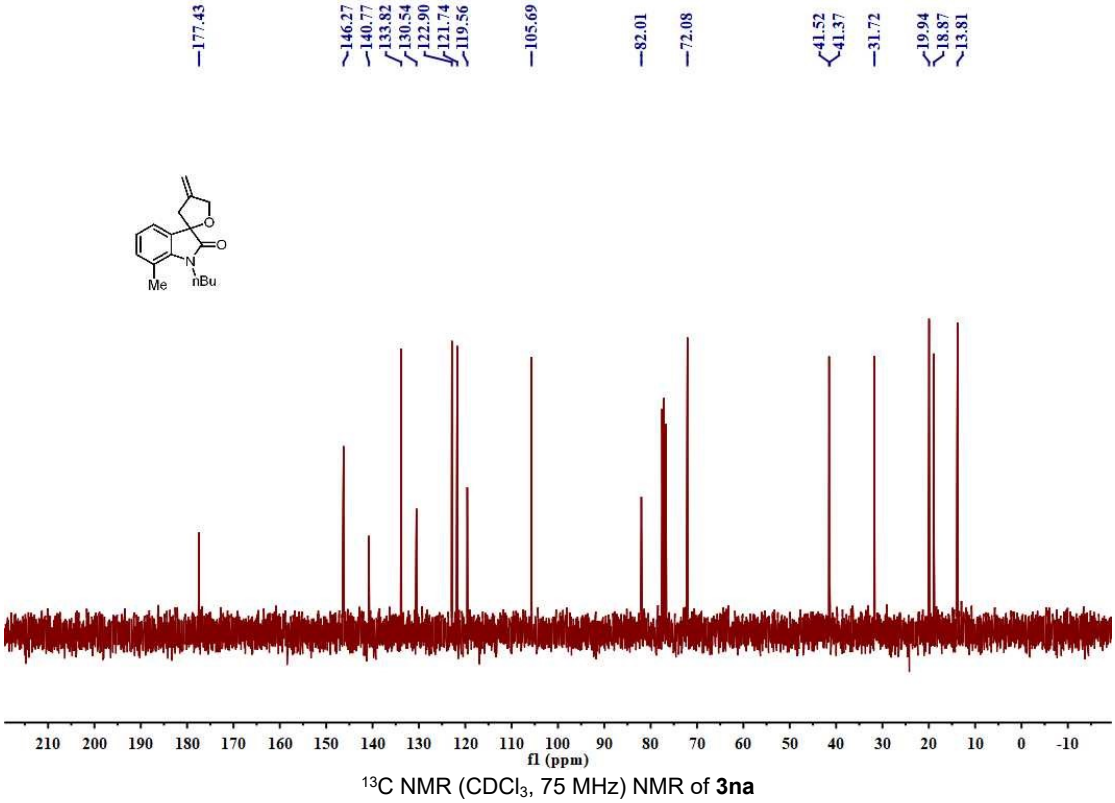
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3ma**



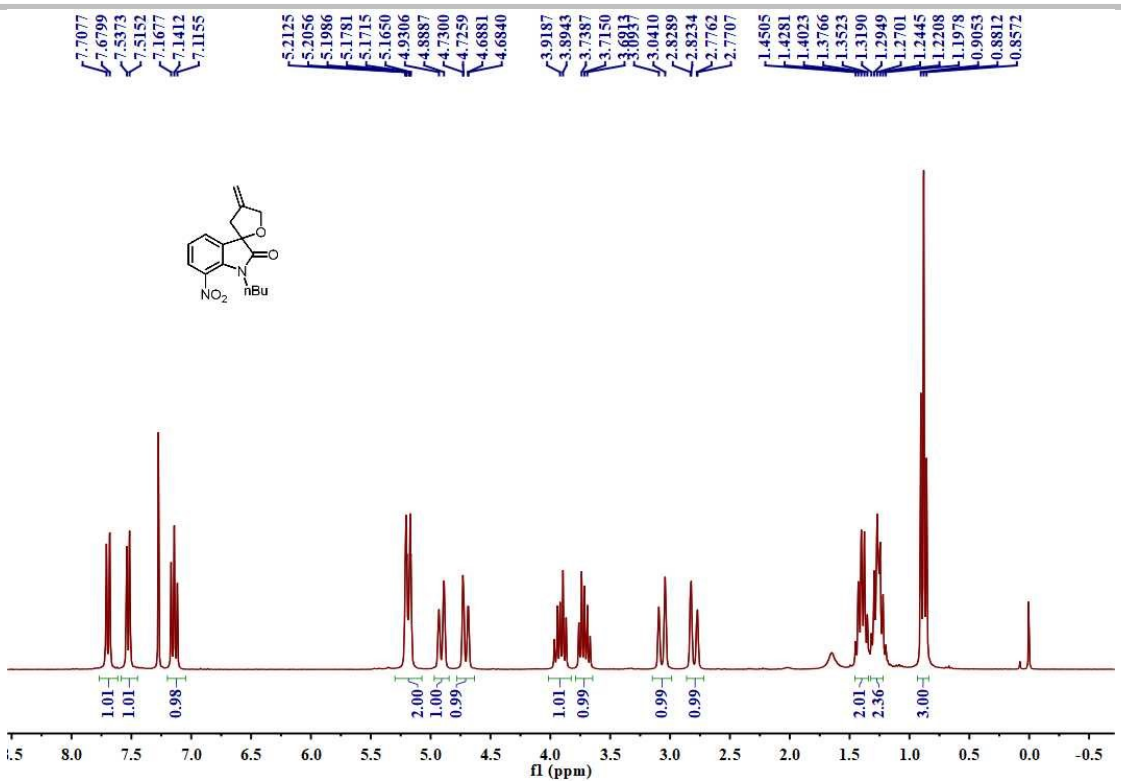
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3ma**



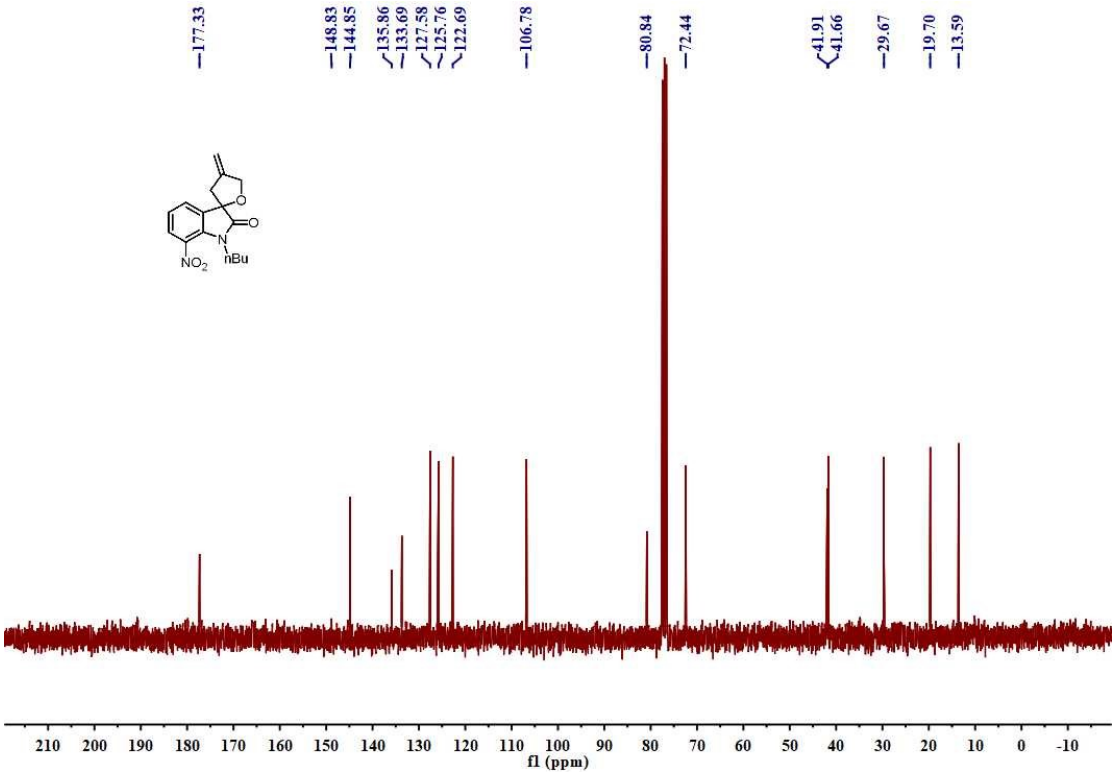
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3na**



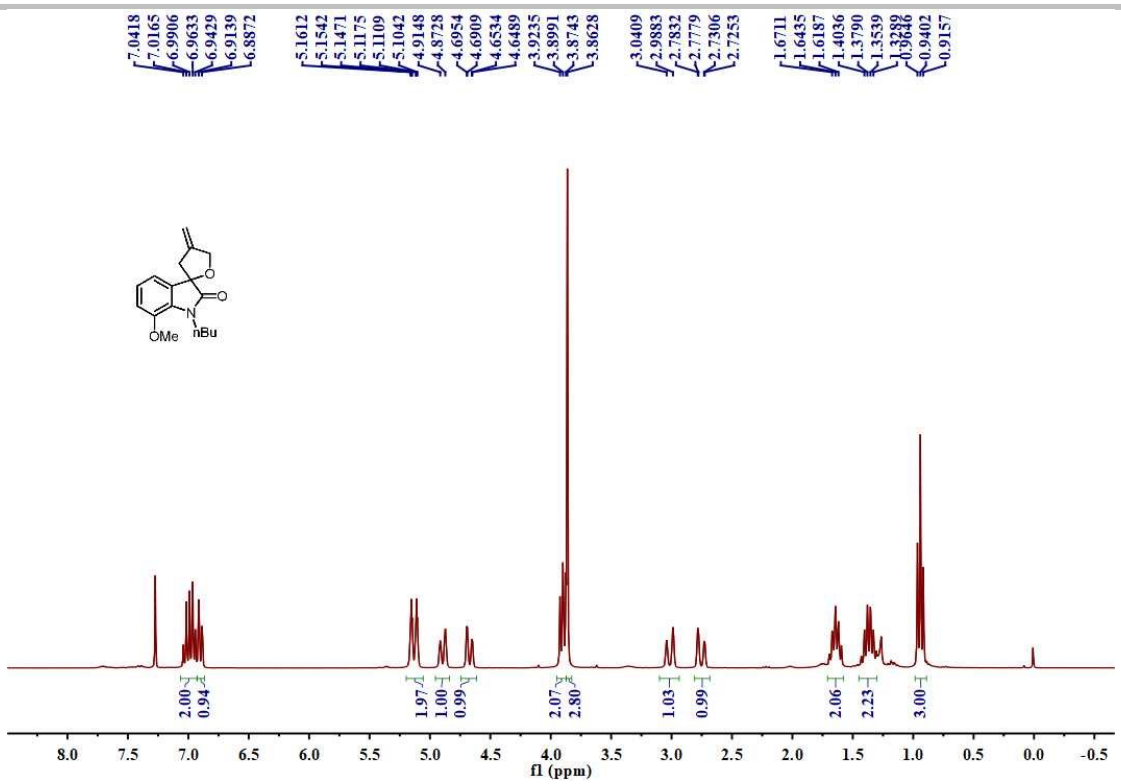
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3na**



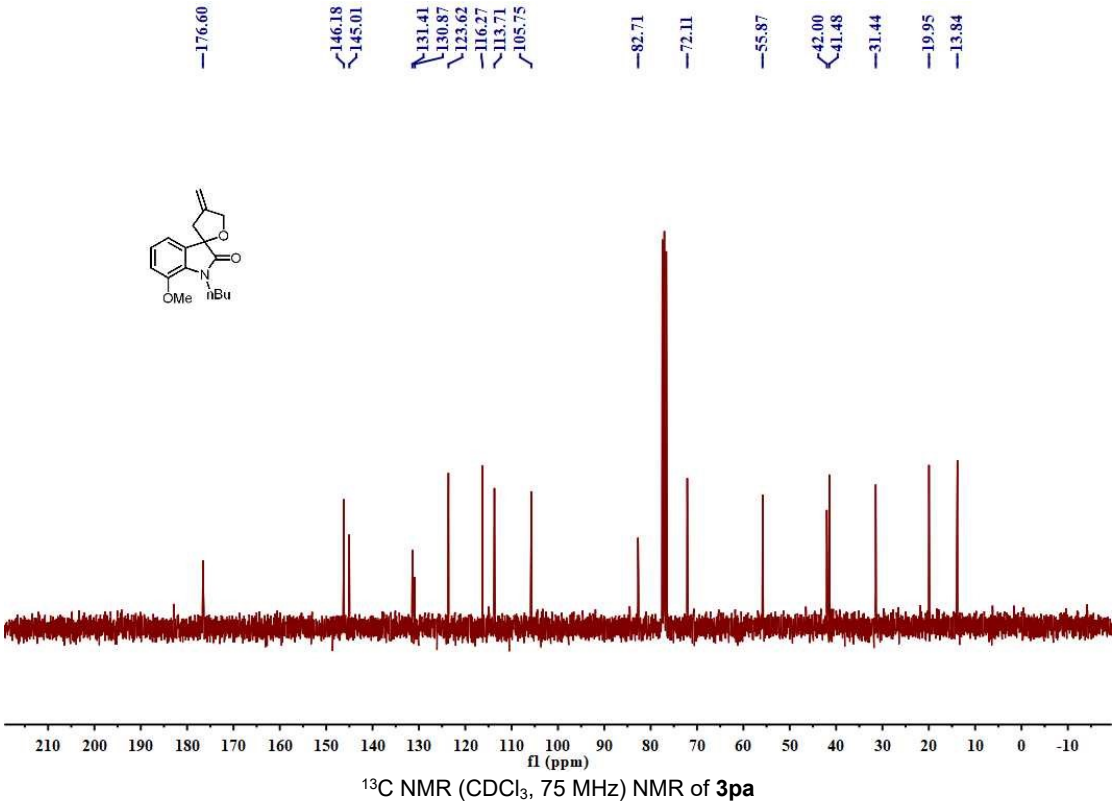
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3oa**



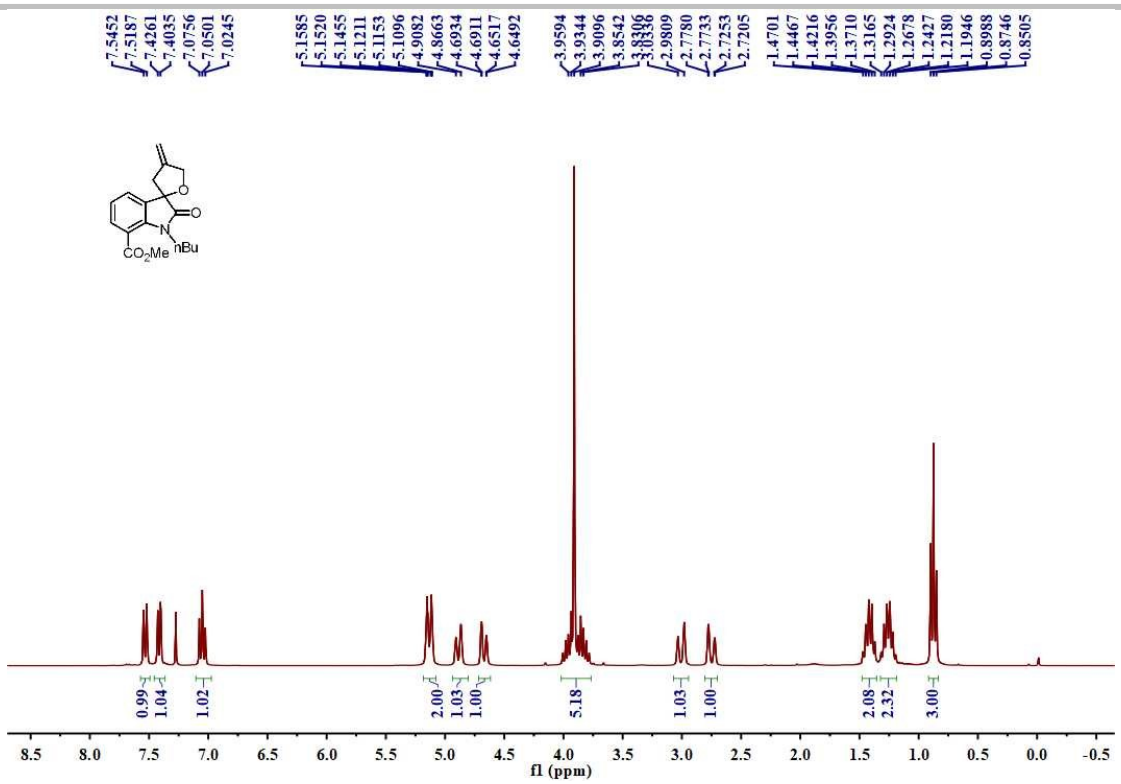
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3oa**



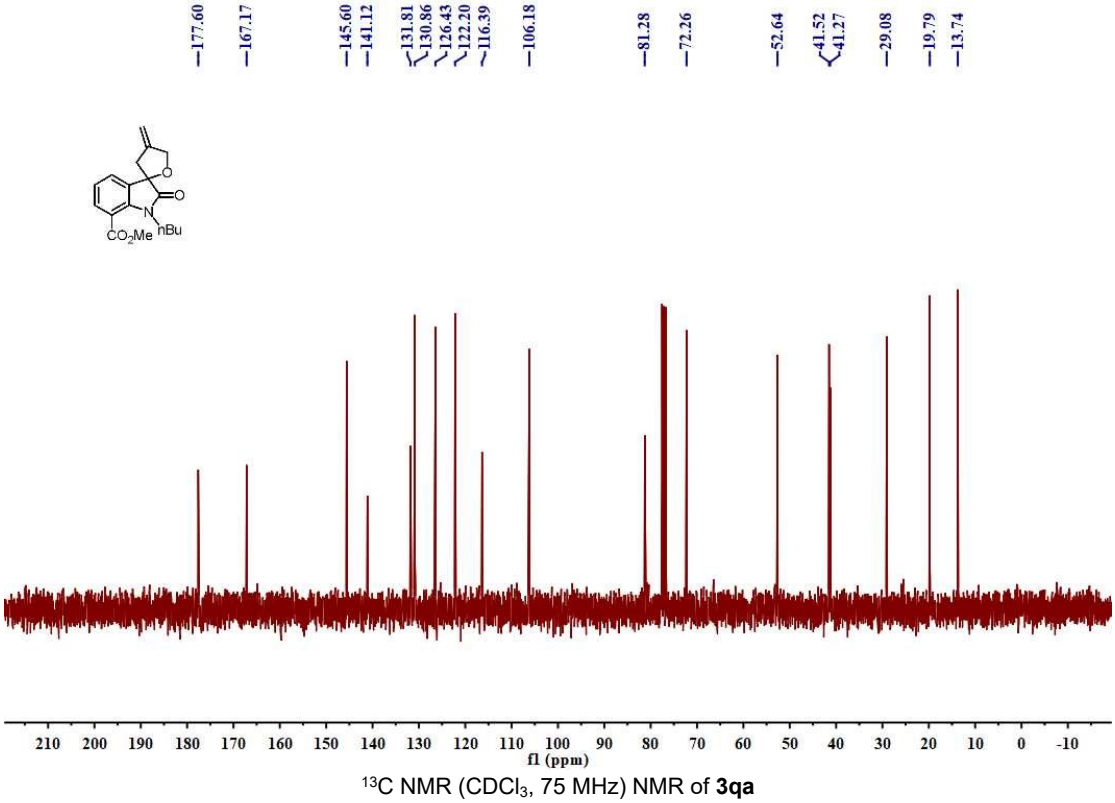
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3pa**



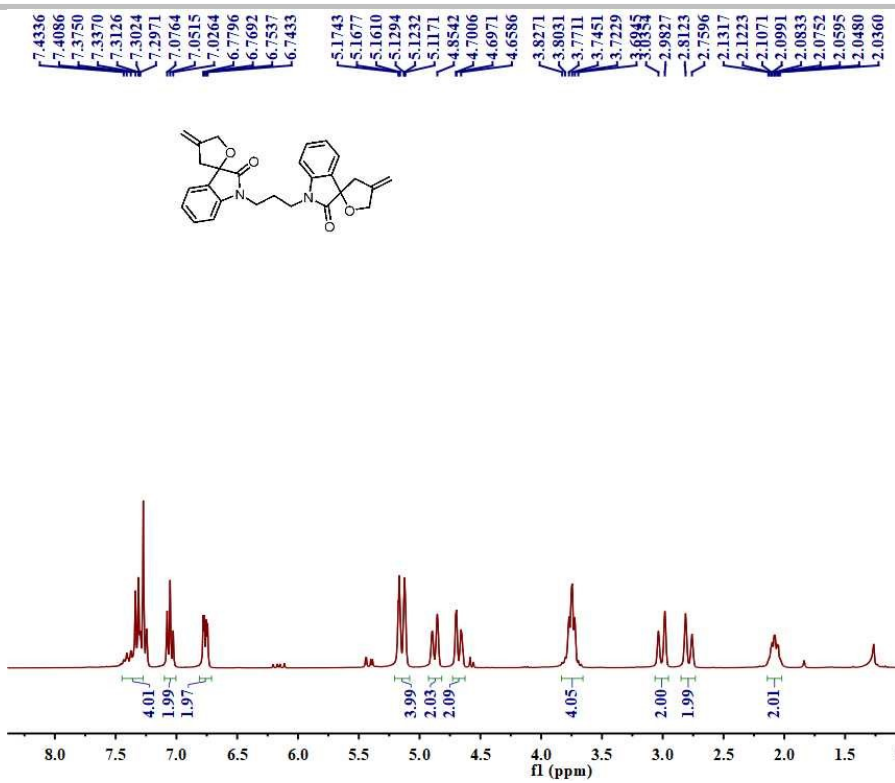
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3pa**



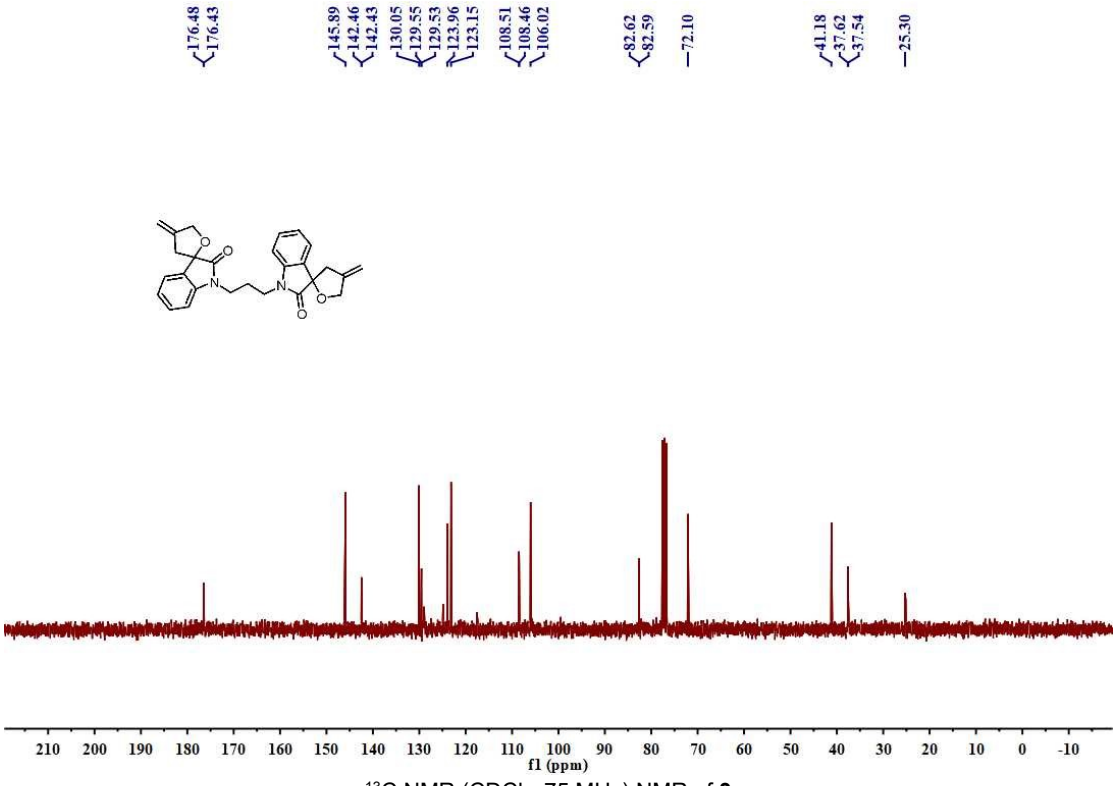
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3qa**



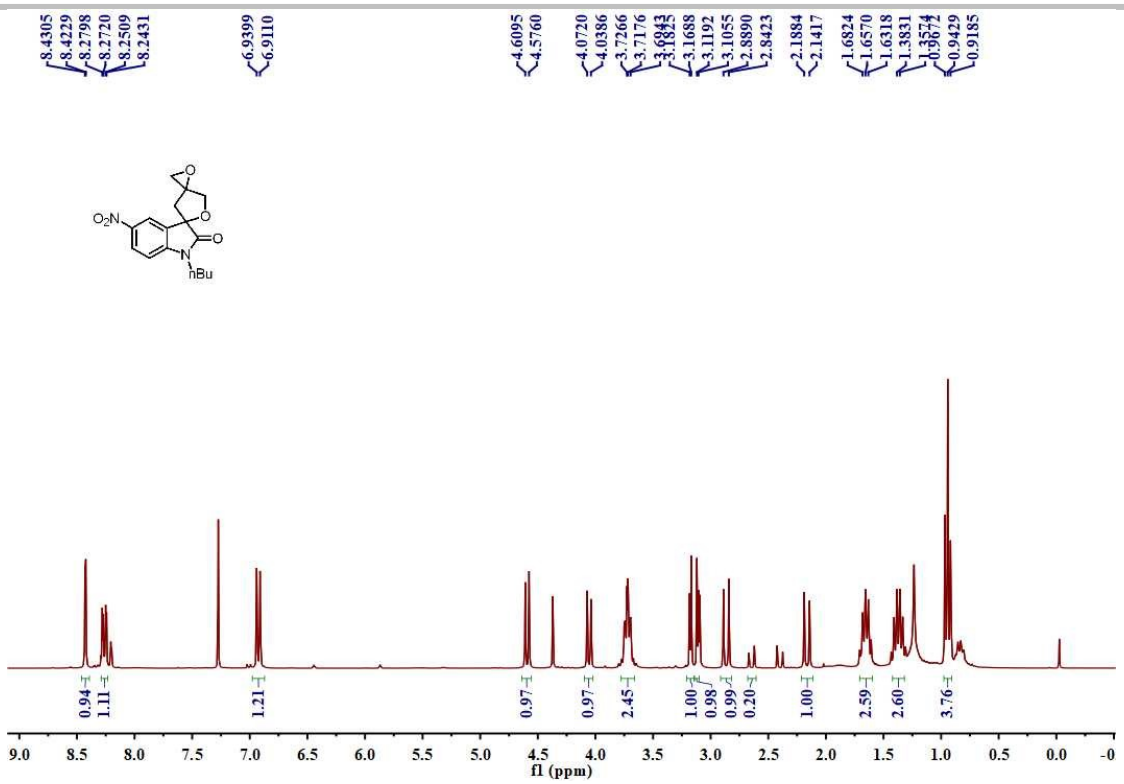
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3qa**



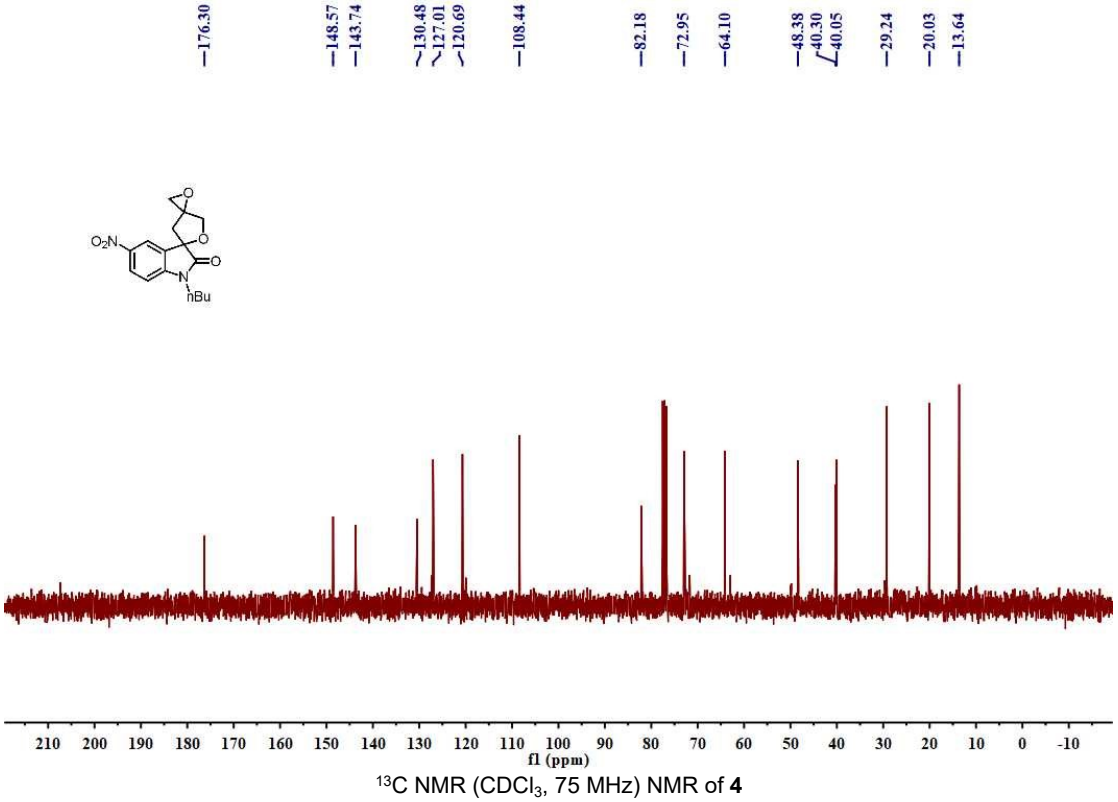
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **3ra**



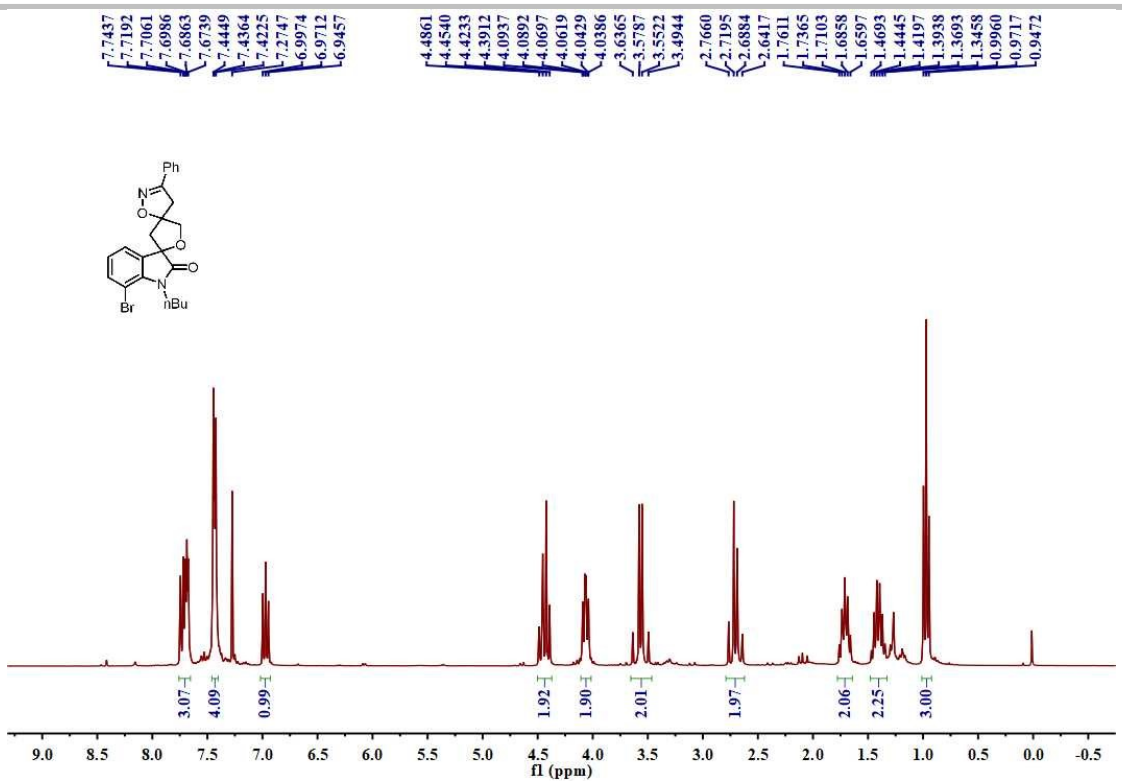
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **3ra**



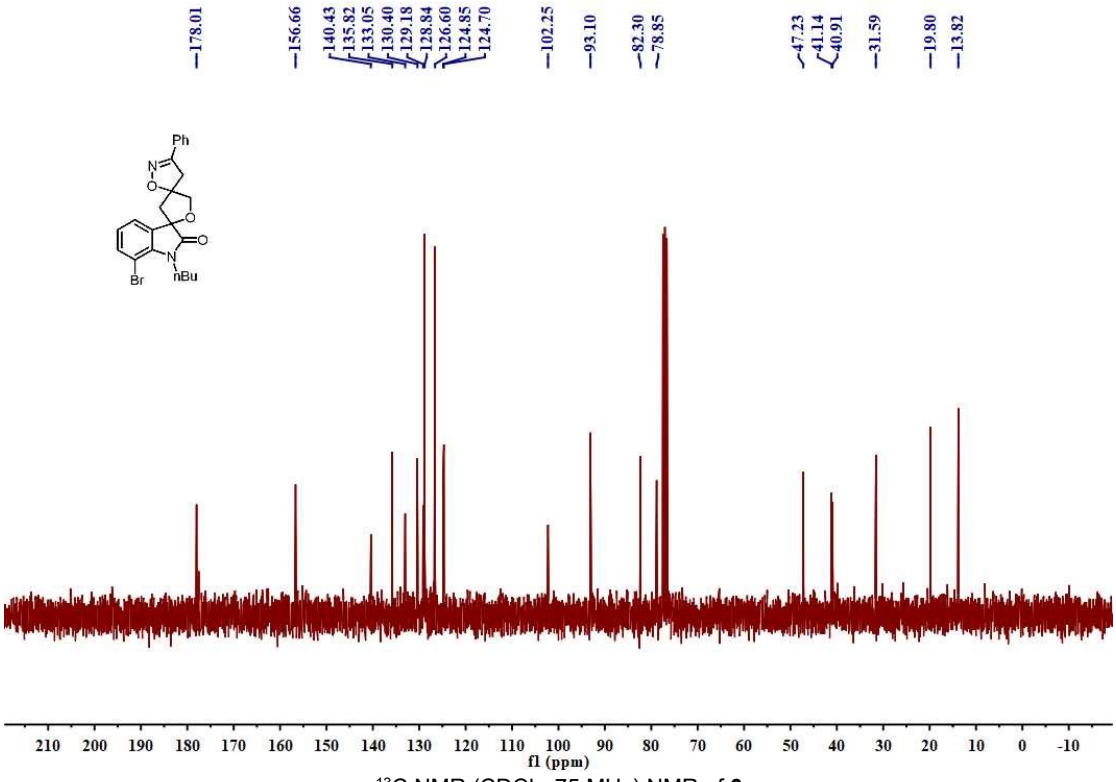
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **4**



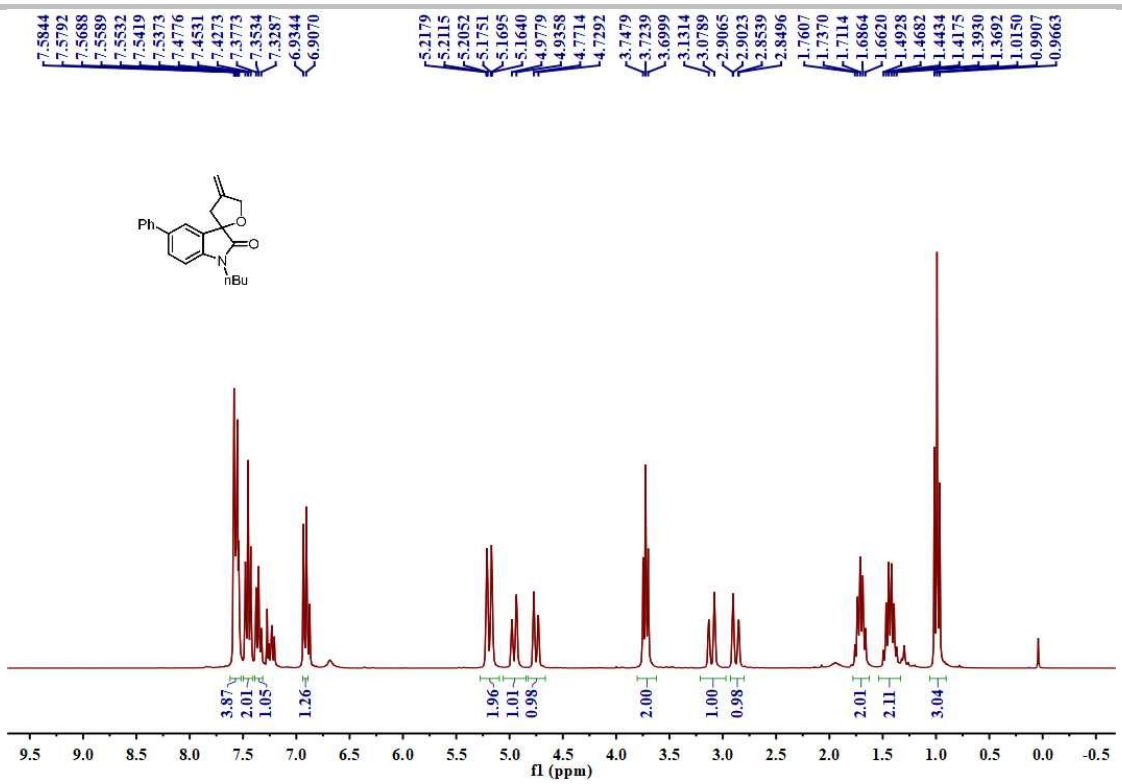
^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **4**



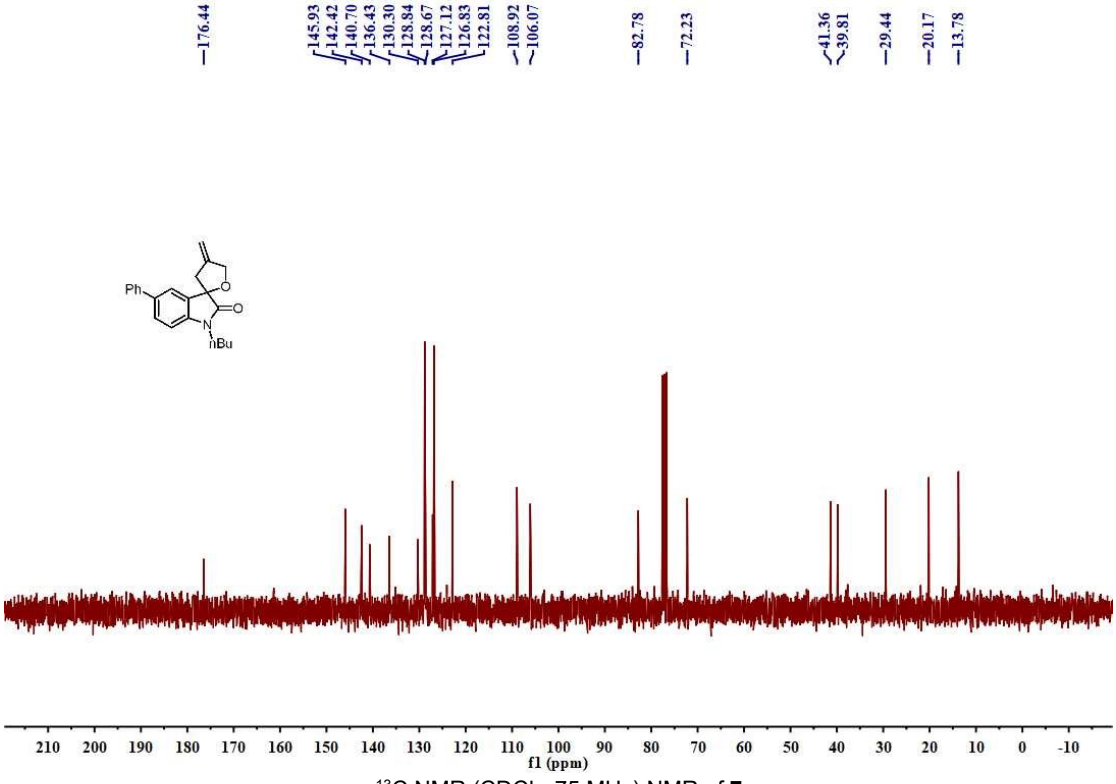
^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **6**



^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **6**



^{1}H NMR ($CDCl_3$, 300 MHz) NMR of **7**



^{13}C NMR ($CDCl_3$, 75 MHz) NMR of **7**