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Supporting Information

Zinc Triflate-Mediated Cyclopropanation of Oxindoles with Vinyl Diphenyl Sulfonium Triflate: a Mild Reaction with Broad Functional Group Compatibility

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1. General information

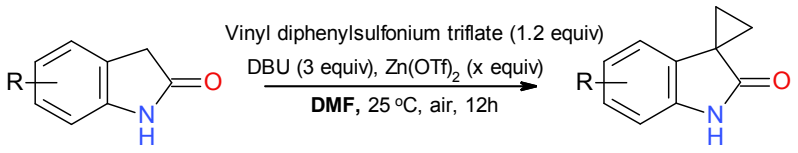
NMR spectra were obtained on a Bruker AV II-400 MHz spectrometer (^{1}H NMR at 400 MHz, ^{13}C NMR at 100 MHz). The ^{1}H NMR chemical shifts were measured relative to CDCl3, MeOD or DMSO-d_6 as the internal reference ($CDCl_3$: δ= 7.26 ppm; MeOD: δ= 3.31 ppm; DMSO-d_6: δ= 2.50 ppm). The ^{13}C NMR chemical shifts were given using MeOD or DMSO-d_6 as the internal standard ($CDCl_3$: δ= 77.16 ppm; MeOD: δ= 49.00 ppm; DMSO-d_6: δ= 39.52 ppm). Mass spectroscopy data were collected on an HRMS-ESI instrument. Reagents, solvents and starting materials were obtained from commercial sources and used without further purification unless otherwise noted. Anhydrous Zn (OTf) $_2$ and starting materials 1a-1o was purchased from Aldrich, Acros, Sinopharma.

2. Praparation of vinyl diphenylsulfonium triflate

Vinyl diphenylsulfonium were synthesized from the 2-bromoethanol and phenylsulfanylbenzene according to the reported procedure. (Reference: Muhammad Yar; Matthew G. Unthank; Eoghan M. McGarrigle;Varinder K. Aggarwal *Chem. Asian J.* **2011**, 6, 372 – 375)

3.General Procedure for oxindole's cyclopropanation

General Procedure A: for the N-Nonsubsituted oxindole substrate's Cyclopropanation

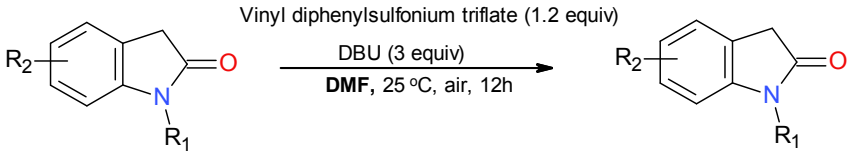


7 **9**

To a 25 mL Schlenk tube were added amide **7** (0.2 mmol, 1.0 equiv), vinyl diphenylsulfonium triflate (0.24 mmol, 1.2 equiv), $Zn(OTf)_2$ (0.2 mmol, 1.0 equiv) DMF (1 mL). The mixture was stirred at room temperature for 2 min and DBU (91.2 mg, 0.6 mmol, 3.0 equiv) was added into it. The mixture was stirred for 4 hours at

room temperature till the reaction completed, and quenched with saturated ammonium chloride solution (5 mL), then was extracted with EtOAc (3 x 50 mL). The combined organic layer washed with H_2O (2 x 10 mL), dried with anhydrous sodiumsulfate. After concentration, product 9 was purified using column chromatography on silica gel using appropriate eluent.

General Procedure B: for the N-subsituted oxindole substrate's Cyclopropanation

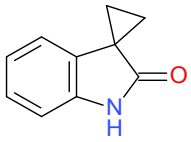


11 **12**

To a 25 mL Schlenk tube were added amide **11** (0.2 mmol, 1.0 equiv), vinyl diphenylsulfonium triflate (86.9 mg, 0.24 mmol, 1.2 equiv), DMF (1 mL). The mixture was stirred at room temperature for 2 min and DBU (91.2 mg, 0.6 mmol, 3.0 equiv) was added into it. The mixture was stirred for 4 hours at room temperature till the reaction completed, quenched with saturated ammonium chloride solution (5 mL), and was extracted with EtOAc (3 x 50 mL). The combined organic layer washed with H_2O (2 x 10 mL), dried with anhydrous sodium sulfate. After concentration, product was purified using column chromatography on silica gel using appropriate eluent.

4. Charaterization of product

spiro[cyclopropane-1,3'-indoline]-2'-one (9a)



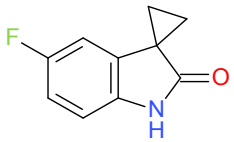
The title compound **9a** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 20: 1 to 3:1) gave **9a** as a white solid in 91% yield, mp 181-183 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (br s, 1H), 7.06-7.19 (m, 1H), 6.88-6.95(m, 2H), 6.75 (d, *J*=7.34 Hz, 1H), 1.63-1.74 (m, 2H), 1.40-1.54 (m, 2H)

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.6, 140.6, 131.2, 126.8, 122.1, 118.6, 110.0, 27.6, 19.6

HRMS (ESI-TOF) calcd for $C_{10}H_9NO$ $[M + H]^+$: 160.07569 found: 160.07610.

5'-fluorospiro[cyclopropane-1,3'-indoline]-2'-one (9b)



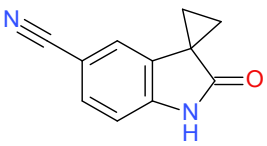
The title compound **9b** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 20: 1 to 3:1) gave **9b** as a white solid in 89% yield, mp 207-210 °C.

^{1}H NMR (400 MHz, METHANOL-d4) δ 6.92-6.94 (m, 2H), 6.77 (d, *J*=8.46 Hz, 1H), 1.59-1.70 (m, 4H)

^{13}C NMR (400 MHz, METHANOL-d4) δ 179.8, 160.3-158.0 (d, $J_{C\text{-}F}$ = 238Hz) , 137.2, 133.3-133.2 (d, $J_{C\text{-}F}$ = 9.6Hz), 112.6-112.4 (d, $J_{C\text{-}F}$ = 24Hz), 110.1-110.0 (d, $J_{C\text{-}F}$ = 8.2Hz), 106.6-106.3 (d, $J_{C\text{-}F}$ = 26Hz), 27.6, 19.0

HRMS (ESI-TOF) calcd for $C_{10}H_8NFO$ $[M + H]^+$: 178.06627 found: 178.06639

2'-oxospiro[cyclopropane-1,3'-indoline]-5'-carbonitrile (9c)



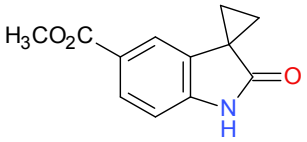
The title compound **9c** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 20: 1 to 3:1) gave **9c** as a white solid in 93% yield, mp 303-306 °C.

^{1}H NMR (400 MHz, DMSO-d6) δ 11.04 (br s, 1H), 7.62 (dd, *J*=1.59, 8.07 Hz, 1H), 7.49(s, 1H), 7.04 (d, *J*=8.07 Hz, 1H), 1.62-1.81 (m, 2H), 1.45-1.62 (m, 2H)

^{13}C NMR (101 MHz, DMSO-d6) δ 178.1, 146.4, 132.7, 132.3, 123.5, 120.1, 110.4, 103.5, 27.4, 19.7

HRMS (ESI-TOF) calcd for $C_{11}H_8N_2O$ $[M + H]^+$: 185.07094 found: 185.07126

methyl 2'-oxospiro[cyclopropane-1,3'-indoline]-5'-carboxylate (9d)



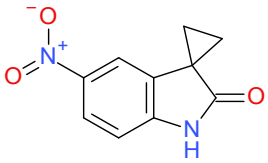
The title compound **9d** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 20: 1 to 3:1) gave **9d** as a white solid in 78% yield, mp 227-230 °C.

^{1}H NMR (400 MHz, DMSO-d6) δ10.95 (br s, 1H), 7.84 (dd, *J*=1.71, 8.19 Hz, 1H), 7.56(d, *J*=1.47 Hz, 1H), 7.00 (d, *J*=8.19 Hz, 1H), 3.81 (s, 3H), 1.60-1.79 (m, 2H), 1.45-1.57(m, 2H)

^{13}C NMR (400 MHz, DMSO-d6) δ178.5, 166.7, 146.7, 131.7, 129.5, 123.0, 120.6, 109.6, 52.3, 27.5, 19.3

HRMS (ESI-TOF) calcd for $C_{12}H_{11}NO_3$ $[M + H]^+$: 218.08117 found: 218.08168

5'-nitrospiro[cyclopropane-1,3'-indoline]-2'-one (9e)



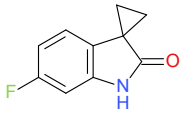
The title compound **9e** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 20: 1 to 3:1) gave **9e** as a white solid in 91% yield, Decom. 235 °C.

^{1}H NMR (400 MHz, DMSO-d6) δ 8.14 (dd, *J*=2.38, 8.62 Hz, 1H), 7.96 (d, *J*=2.32 Hz,1H), 7.08 (d, *J*=8.68 Hz, 1H), 1.82-1.85 (m, 2H),1.55-1.58 (m, 2H)

^{13}C NMR (101 MHz, DMSO-d6) δ 178.5, 148.6, 142.4, 132.6, 124.4, 115.8, 109.7, 27.9, 20.0

HRMS (ESI-TOF) calcd for $C_{10}H_8N_2O_3$ $[M + H]^+$: 205.06077 found: 205.06097

6'-fluorospiro[cyclopropane-1,3'-indoline]-2'-one (9f)



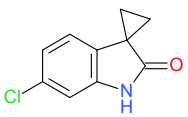
The title compound **9f** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 20: 1 to 3:1) gave **9f** as a white solid in 83% yield, mp 180-182 °C.

^{1}H NMR (400 MHz, METHANOL-d4) δ 6.89 (dd, *J*=5.14, 8.19 Hz, 1H), 6.68-6.77 (m, 2H), 1.55-1.65 (m, 4H)

^{13}C NMR (101 MHz, METHANOL-d4) δ 180.2, 163.5-161.1 (d, $J_{C\text{-}F}$ = 241Hz), 142.5-142.4 (d, $J_{C\text{-}F}$ = 12.0Hz), 126.7-126.6 (d, $J_{C\text{-}F}$ = 2.5Hz), 119.6-119.5 (d, $J_{C\text{-}F}$ = 10.2Hz), 107.8-107.5 (d, $J_{C\text{-}F}$ = 24.3Hz), 97.9-97.6 (d, $J_{C\text{-}F}$ = 28.7Hz), 26.7, 18.1

HRMS (ESI-TOF) calcd for $C_{10}H_8NFO$ $[M + H]^+$: 178.06627 found: 178.06639

6'-chlorospiro[cyclopropane-1,3'-indoline]-2'-one **(9g)**



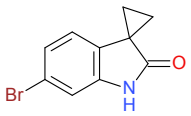
The title compound **9g** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 20: 1 to 3:1) gave **9g** as a white solid in 95% yield, mp 230-236 °C.

^{1}H NMR (400 MHz, DMSO-d6) δ 10.68 (br s, 1H), 6.94-7.03 (m, 2H), 6.90 (dd, *J*=0.67,1.65 Hz, 1H), 1.53-1.64 (m, 2H), 1.42-1.53 (m, 2H)

^{13}C NMR (400 MHz, DMSO-d6) δ 178.1, 143.5, 131.2, 130.4, 121.2, 121.1, 109.8, 27.3, 19.1

HRMS (ESI-TOF) calcd for $C_{10}H_8ClNO$ [M + H] $^{+}$: 194.03672 found: 194.03727

6'-bromospiro[cyclopropane-1,3'-indoline]-2'-one (9h)



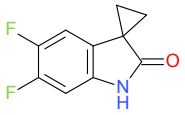
The title compound **9h** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 20: 1 to 3:1) gave **9h** as a white solid in 87% yield, mp 190-194 °C.

^{1}H NMR (400 MHz, DMSO-d6) δ 10.67 (br s, 1H), 7.11 (dd, *J*=1.83, 7.95 Hz, 1H), 7.03 (d, *J*=1.71 Hz, 1H), 6.93 (d, *J*=7.95 Hz, 1H), 1.53-1.63 (m, 2H), 1.45-1.53 (m, 2H)

^{13}C NMR (400 MHz, DMSO-d6) δ 178.0, 143.8, 130.8, 124.0, 121.5, 119.3, 112.5, 27.3,19.1

HRMS (ESI-TOF) calcd for $C_{10}H_8BrNO$ [M + H] $^{+}$: 237.98620 found: 237.98672

5',6'-difluorospiro[cyclopropane-1,3'-indoline]-2'-one (9i)



The title compound **9i** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 20: 1 to 3:1) gave **9i** as a white solid in 95% yield, mp 213-215 °C.

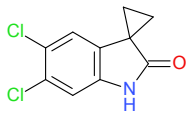
^{1}H NMR (400 MHz, METHANOL-d4) δ 6.86-6.98 (m, 2H), 1.57-1.71 (m, 5H)

^{13}C NMR (100 MHz, METHANOL-d4) δ 179.8, 150.7-148.1 (dd, $^{1}J_{C\text{-}F}$ = 14.3Hz, $^{2}J_{C\text{-}F}$ = 242.9Hz), 147.7-145.2 (dd, $^{1}J_{C\text{-}F}$ = 13.4 Hz, $^{2}J_{C\text{-}F}$ = 239.7Hz), 137.3-137.2 (d, $J_{C\text{-}F}$

= 12.7Hz), 127.2-127.1 (dd, $^{1}J_{C\text{-}F}$ = 3.5Hz, $^{2}J_{C\text{-}F}$ = 7.3Hz), 108.4-108.2 (d, $J_{C\text{-}F}$ = 20.8Hz), 99.4-99.1(d, $J_{C\text{-}F}$ = 23.1Hz), 27.2, 18.5

HRMS (ESI-TOF) calcd for $C_{10}H_7NF_2O$ $[M + H]^+$: 196.05685 found: 196.05695

5',6'-dichlorospiro[cyclopropane-1,3'-indoline]-2'-one (9j)



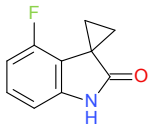
The title compound **9j** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 20: 1 to 3:1) gave 9**j** as a white solid in 91% yield, mp 242-246 °C.

^{1}H NMR (400 MHz, DMSO-d6) δ 10.78 (s, 1H), 7.32 (s, 1H), 7.06 (s, 1H), 1.59-1.77 (m, 2H), 1.50 (q, *J*=3.83 Hz, 2H)

^{13}C NMR (400 MHz, DMSO-d6) δ 177.8, 142.2, 132.6, 129.0, 123.6, 121.9, 111.2, 27.6,19.6

HRMS (ESI-TOF) calcd for $C_{10}H_7Cl_2NO$ $[M + H]^+$: 227.99775 found: 227.99830

4'-fluorospiro[cyclopropane-1,3'-indoline]-2'-one (9k)



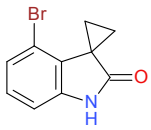
The title compound **9k** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 20: 1 to 3:1) gave **9k** as a white solid in 82% yield, mp 168-170 °C.

^{1}H NMR (400 MHz, DMSO-d6) δ 10.80 (br s, 1H), 7.19 (dt, *J*=5.75, 8.13 Hz, 1H),6.67-6.86 (m, 2H), 1.71-1.78 (m, 2H), 1.39-1.62 (m, 2H)

^{13}C NMR (100 MHz, DMSO-d6) δ 177.4, 158.2-155.8 (d, $J_{C\text{-}F}$ = 243Hz),, 144.6-144.5 (d, $J_{C\text{-}F}$ = 9.6Hz), 128.8-128.7 (d, $J_{C\text{-}F}$ = 9.6Hz), 116.3-116.2 (d, $J_{C\text{-}F}$ = 18.1Hz), 108.8-108.6 (d, $J_{C\text{-}F}$ = 19.6Hz), 106.7(d, $J_{C\text{-}F}$ = 3.1Hz), 26.4, 16.5

HRMS (ESI-TOF) calcd for $C_{10}H_8NFO$ $[M + H]^+$: 178.06627 found: 178.06621

4'-bromospiro[cyclopropane-1,3'-indoline]-2'-one (9l)



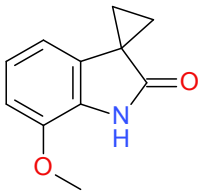
The title compound **9l** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 20: 1 to 3:1) gave **9l** as a white solid in 85% yield, mp 211-214 °C.

^{1}H NMR (400 MHz, METHANOL-d4) δ 7.08-7.14 (m, 2H), 6.98 (dd, *J*=2.32, 6.48 Hz, 1H), 2.31 (q, *J*=3.79 Hz, 2H), 1.49 (q, *J*=3.87 Hz, 2H)

^{13}C NMR (400 MHz, METHANOL-d4) δ 178.8, 143.5, 128.0, 127.4, 125.6, 114.5, 108.9, 28.7, 14.5

HRMS (ESI-TOF) calcd for $C_{10}H_8BrNO$ $[M + H]^+$: 237.98620 found: 237.98630

7'-methoxyspiro[cyclopropane-1,3'-indoline]-2'-one (9m)



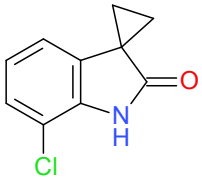
The title compound **9m** was prepared according to general procedure A with 1.5 equiv $Zn(OTf)_2$. A purification by flash chromatography (petroleum ether: ethyl acetate = 20: 1 to 3:1) gave **9m** as a white solid in 82% yield, mp 166-169 °C.

^{1}H NMR (400 MHz, METHANOL-d4) δ 6.99 (dd, *J*=7.58, 8.31 Hz, 1H), 6.89 (d, *J*=8.41Hz, 1H), 6.56 (dd, *J*=0.92, 7.52 Hz, 1H), 3.91 (s, 3H), 1.54-1.65 (m, 4H)

^{13}C NMR (101 MHz, METHANOL-d4) δ 179.8, 144.3, 132.1, 129.6, 122.5, 111.0, 109.3, 54.8, 27.6, 18.2

HRMS (ESI-TOF) calcd for $C_{11}H_{11}NO_2$ $[M + H]^+$: 190.08626 found: 190.08630

7'-chlorospiro[cyclopropane-1,3'-indoline]-2'-one (9n)



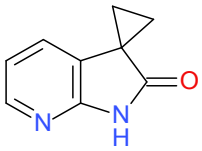
The title compound **9n** was prepared according to general procedure A with 1.5 equiv $Zn(OTf)_2$. A purification by flash chromatography (petroleum ether: ethyl acetate = 20: 1 to 3:1) gave **9n** as a white solid in 85% yield, mp 158-163 °C.

^{1}H NMR (400 MHz, DMSO-d6) δ 10.97 (br s, 1H), 7.17-7.30 (m, 1H), 6.94-6.95 (m, 2H), 1.57-1.66 (m, 2H), 1.46-1.57 (m, 2H)

^{13}C NMR (400 MHz, DMSO-d6) δ178.1, 139.6, 133.4, 127.0, 122.9, 118.3, 114.1, 28.2,19.5

HRMS (ESI-TOF) calcd for $C_{10}H_8ClNO$ $[M + H]^+$: 194.03672 found: 194.03709

spiro[1H-pyrrolo[2,3-b]pyridine-3,1'-cyclopropane]-2-one (9o)



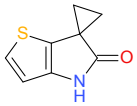
The title compound **9o** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 10: 1 to 1:1) gave **9o** as a white solid in 95% yield, mp 164-167 °C.

^{1}H NMR (400 MHz, METHANOL-d4) δ 8.02-8.16 (m, 1H), 7.34 (dd, *J*=1.47, 7.46 Hz,1H), 7.00 (dd, *J*=5.32, 7.40 Hz, 1H), 1.59-1.80 (m, 4H)

^{13}C NMR (101 MHz, METHANOL-d4) δ 179.1, 155.9, 144.7, 126.7, 126.1, 117.5, 26.6, 18.2

HRMS (ESI-TOF) calcd for $C_9H_8N_2O$ $[M + H]^+$: 161.07094 found: 161.07114

spiro[4H-thieno[3,2-b]pyrrole-6,1'-cyclopropane]-5-one (9p)



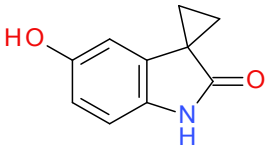
The title compound **9p** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 10: 1 to 10:3) gave **9p** as a white solid in 90% yield, mp 186-188 °C.

^{1}HNMR (400 MHz, METHANOL-d4) δ 7.26 (d, *J*=5.01 Hz, 1H), 6.84 (d, *J*=5.01 Hz, 1H), 1.52-1.62 (m, 4H)

^{13}CNMR (101 MHz, METHANOL-d4) δ 182.6, 142.2, 124.2, 121.7, 112.5, 29.2, 18.1

HRMS (ESI-TOF) calcd for $C_9H_9BN_2O_3$ $[M + H]^+$: 166.03211 found: 166.03235

5'-hydroxyspiro[cyclopropane-1,3'-indoline]-2'-one (9q)



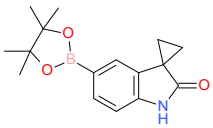
The title compound **9q** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 4: 1 to 1:1) gave **9q** as a white solid in 78% yield, mp 243-246 °C.

^{1}H NMR (400 MHz, METHANOL-d4) δ 6.80 (d, *J*=8.31 Hz, 1H), 6.64 (dd, *J*=2.45, 8.31Hz, 1H), 6.40 (d, *J*=2.45 Hz, 1H), 1.60-1.63 (m, 2H), 1.51-1.54 (m, 2H)

^{13}C NMR (101 MHz, METHANOL-d4) δ 180.0, 152.9, 133.5, 132.5, 112.7, 110.0, 106.3, 27.4, 18.1

HRMS (ESI-TOF) calcd for $C_{10}H_9NO_2$ $[M + H]^+$: 176.07060 found: 176.07035

5'-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)spiro[cyclopropane-1,3'-indoline]-2'-one **(9r)**



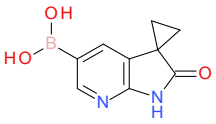
The title compound **9r** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 10: 1 to 1:1) gave **9r** as a white solid in 85% yield, mp 212-215 °C.

^{1}H NMR (400 MHz, METHANOL-d4) δ 7.63 (dd, *J*=1.10, 7.82 Hz, 1H), 7.29 (s, 1H), 6.99 (d, *J*=7.82 Hz, 1H), 1.58-1.69 (m, 4H), 1.34 (s, 12H)

^{13}C NMR (101 MHz, METHANOL-d4) δ 180.1, 144.2, 133.7, 130.5, 124.4, 108.9, 83.5, 26.8, 23.8, 18.2

HRMS (ESI-TOF) calcd for $C_{16}H_{20}BNO_3$ [M + H] $^{+}$: 285.16453 found: 285.16483

(2-oxospiro[1H-pyrrolo[2,3-b]pyridine-3,1'-cyclopropane]-5-yl)boronic acid **(9s)**



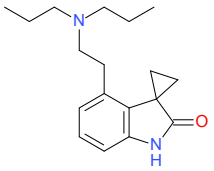
The title compound **9s** was prepared according to general procedure A. A purification by flash chromatography (DCM: MeOH = 10:0.1 to 10:1) gave **9s** as a white solid in 75% yield, Decom. 320 °C.

^{1}H NMR (400 MHz, DMSO-d6) δ 11.19 (s, 1H), 8.44 (d, *J*=1.59 Hz, 1H), 8.06 (s, 2H), 7.59 (d, *J*=1.47 Hz, 1H), 1.56-1.67 (m, 2H), 1.46-1.56 (m, 2H)

^{13}C NMR (101 MHz, DMSO-d6) δ 178.2, 158.3, 152.2, 132.0, 124.6, 26.8, 18.6

HRMS (ESI-TOF) calcd for $C_9H_9BN_2O_3$ [M + H] $^{+}$: 204.08153 found: 204.08150

4'-[2-(dipropylamino)ethyl]spiro[cyclopropane-1,3'-indoline]-2'-one (1b)



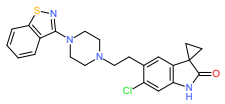
The title compound **1b** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 10: 1 to 1:2) gave **1b** as a white solid in 85% yield, mp 99-101 °C.

^{1}H NMR (400 MHz, METHANOL-d4) δ 7.14 (t, *J*=7.50 Hz, 1H), 6.81-6.87 (m, 2H), 2.60-2.71 (m, 2H), 2.44-2.60 (m, 6H), 1.83-1.98 (m, 2H), 1.49-1.61 (m, 6H), 0.94 (t, *J*=7.34 Hz, 6H)

^{13}C NMR (101 MHz, METHANOL-d4) δ 179.6, 141.9, 134.3, 126.8, 126.5, 123.3, 107.7, 56.1, 55.7, 27.6, 27.4, 19.4, 16.3, 10.8

HRMS (ESI-TOF) calcd for $C_{18}H_{26}N_2O$ $[M + H]^+$: 287.21179 found: 287.21204

5'-[2-[4-(1,2-benzothiazol-3-yl)piperazin-1-yl]ethyl]-6'-chloro-spiro[cyclopropane-1,3'-indoline]-2'-one (2b)



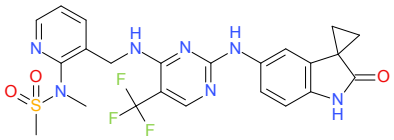
The title compound **2b** was prepared according to general procedure A. A purification by flash chromatography (petroleum ether: ethyl acetate = 10: 1 to 1:5) gave **2b** as a white solid in 95% yield, mp 262-264 °C.

^{1}H NMR (400 MHz, DMSO-d6) δ 10.60 (s, 1H), 8.06 (d, *J*=8.93 Hz, 2H), 7.56 (t, *J*=7.89 Hz, 1H), 7.22-7.48 (m, 1H), 7.01 (s, 1H), 6.90 (s, 1H), 3.37-3.56 (m, 4H), 2.76-2.99 (m, 2H), 2.63-2.74 (m, 4H), 2.52-2.61 (m, 2H), 1.52-1.68 (m, 2H), 1.41-1.52 (m, 2H)

^{13}C NMR (101 MHz, DMSO-d6) δ 178.1, 164.0, 152.5, 141.6, 130.8, 130.3, 128.3, 127.8, 124.9, 124.6, 122.2, 121.5, 110.2, 58.6, 52.9, 50.2, 30.7, 27.2, 19.0

HRMS (ESI-TOF) calcd for $C_{23}H_{23}ClN_4OS$ $[M + H]^+$: 439.13539 found: 439.13549

N-methyl-N-[3-[[[2-[(2'-oxospiro[cyclopropane-1,3'-indoline]-5'-yl)amino]-5-(trifluoromethyl)pyrimidin-4-yl]amino]methyl]-2-pyridyl]methanesulfonamide (3b)



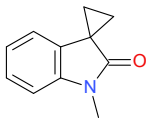
The title compound **3b** was prepared according to general procedure A. A purification by flash chromatography (DCM: MeOH = 100: 1 to 10:2) gave **3b** as a white solid in 92% yield, mp 267-269 °C.

^{1}H NMR (400 MHz, DMSO-d6) δ 10.40 (br s, 1H), 9.21-9.46 (m, 1H), 8.44 (dd, *J*=1.77,4.71 Hz, 1H), 8.20 (s, 1H), 7.69 (br d, *J*=7.21 Hz, 1H), 7.39-7.50 (m, 2H), 7.11-7.26 (m, 1H), 7.09 (s, 1H), 6.66 (br d, *J*=7.58 Hz, 1H), 4.75 (br d, *J*=5.50 Hz, 2H), 3.04-3.18 (m, 6H), 1.22-1.44 (m, 4H)

^{13}C NMR (101 MHz, DMSO-d6) δ 178.2, 161.6, 158.8, 155.4(d, $J_{C\text{-}F}$ = 6.5Hz), 155.3, 152.6, 147.9, 137.8, 137.4, 134.7, 134.1, 131.4, 126.9, 124.6, 124.2, 119.5, 113.0, 109.4, 37.5, 36.4, 27.5, 23.9,18.7

HRMS (ESI-TOF) calcd for $C_{23}H_{22}F_3N_7O_3S$ $[M + H]^+$: 534.15297 found: 534.15284

1'-methylspiro[cyclopropane-1,3'-indoline]-2'-one (12a)



a. The title compound **12a** was prepared according to general procedure B. A purification by flash chromatography (petroleum ether: ethyl acetate = 100: 1 to 10:3) gave **12a** as a white solid in 97% yield, mp 81-83 °C.

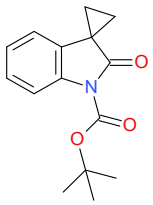
b. The title compound **12a** was prepared according to general procedure **A** with 98% yield.

^{1}HNMR (400 MHz, DMSO-d6) δ 7.25 (ddd, *J*=3.06, 5.75, 7.82 Hz, 1H), 6.98-7.08 (m,3H), 3.21 (s, 3H), 1.46-1.64 (m, 4H)

^{13}CNMR (101 MHz, DMSO-d6) δ 176.3, 143.7, 130.6, 127.2, 122.2, 119.3, 108.7, 27.0, 26.8, 18.8

HRMS (ESI-TOF) calcd for $C_{11}H_{11}NO$ $[M + H]^+$: 174.09134 found: 174.09128

tert-butyl 2'-oxospiro[cyclopropane-1,3'-indoline]-1'-carboxylate (12b)



a. The title compound **12b** was prepared according to general procedure **B**. A purification by flash chromatography (petroleum ether: ethyl acetate = 100: 1 to 10:3) gave **12b** as a white solid in 85% yield, mp 111-112 °C.

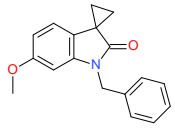
b. The title compound **12b** was prepared according to general procedure **A** with 50% yield.

^{1}H NMR (400 MHz, METHANOL-d4) δ 7.84 (d, *J*=7.91 Hz, 1H), 7.29 (dt, *J*=1.34, 7.89 Hz, 1H), 7.17 (dt, *J*=1.04, 7.55 Hz, 1H), 6.98 (dd, *J*=0.86, 7.46 Hz, 1H), 1.64-1.76 (m,13H)

^{13}C NMR (101 MHz, METHANOL-d4) δ 176.2, 149.2, 139.0, 129.5, 126.7, 124.2, 118.2, 114.5, 84.1, 27.2, 26.9, 20.5

HRMS (ESI-TOF) calcd for $C_{15}H_{17}NO_3$ $[M + H]^+$: 260.12812 found: 204.06580

1'-benzyl-6'-methoxy-spiro[cyclopropane-1,3'-indoline]-2'-one (12c)



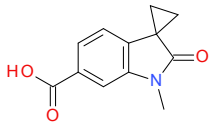
The title compound **12c** was prepared according to general procedure **B**. A purification by flash chromatography (petroleum ether: ethyl acetate = 100: 1 to 10:3) gave **12c** as a white solid in 87% yield, mp 116-117 °C.

^{1}HNMR (400 MHz, DMSO-d6) δ 7.23-7.38 (m, 5H), 6.85 (d, *J*=7.80 Hz, 1H), 6.72 (s,1H), 6.72 (d, *J*=7.50 Hz, 2H), 4.93 (s, 2H), 3.33 (s, 2H), 1.52-1.70 (m, 4H)

^{13}CNMR (101 MHz, DMSO-d6) δ 176.4, 155.9, 137.4, 136.1, 132.1, 129.1, 127.8, 127.7, 111.8, 109.7, 107.0, 56.0, 43.5, 27.5, 19.3

HRMS (ESI-TOF) calcd for $C_{18}H_{17}NO_2$ $[M+H]^+$: 280.13321 found: 280.13339

1'-methyl-2'-oxo-spiro[cyclopropane-1,3'-indoline]-6'-carboxylic acid (12d)



a. The title compound **12d** was prepared according to general procedure **B**. A purification by flash chromatography (DCM: MeOH = 100: 1 to 10:2) gave **12d** as a white solid in 95% yield, mp 272-275 °C.

b. The title compound **12d** was prepared according to general procedure **A** with 97% yield.

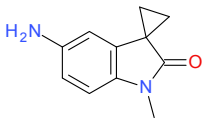
c. To a 25 mL Schlenk tube were added amide 11d (0.2 mmol, 1.0 equiv), vinyl diphenylsulfonium triflate (86.9 mg, 0.24 mmol, 1.2 equiv), water (1 mL). The mixture was stirred at room temperature for 2 min and DBU (91.2 mg, 0.6 mmol, 3.0 equiv) was added into it. The mixture was stirred for 4 hours at room temperature till the reaction completed, quenched with saturated ammonium chloride solution (5 mL), and was extracted with EtOAc (3 x 50 mL). The combined organic layer washed with H_2O (2 x 10 mL), dried with anhydrous sodium sulfate. After concentration, product was purified using column chromatography on silica gel using eluent (DCM: MeOH = 100: 1 to 10:2).

^{1}H NMR (400 MHz, DMSO-d6) δ 12.94 (s, 1H), 7.65 (dd, *J*=1.34, 7.70 Hz, 1H), 7.54 (d, *J*=1.10 Hz, 1H), 7.14 (d, *J*=7.70 Hz, 1H), 3.25-3.27 (m, 3H), 1.65-1.77 (m, 2H), 1.58-1.65 (m, 2H)

^{13}C NMR (400 MHz, DMSO-d6) δ176.1, 167.7, 143.9, 136.1, 129.9, 123.9, 119.3, 108.9, 27.5, 26.8, 19.8

HRMS (ESI-TOF) calcd for $C_{12}H_{11}NO_3$ $[M + H]^+$: 218.08117 found: 218.08148

5'-amino-1'-methyl-spiro[cyclopropane-1,3'-indoline]-2'-one (12e)



a. The title compound **12e** was prepared according to general procedure A. A purification by flash chromatography (DCM: MeOH = 100: 1 to 10:2) gave **12e** as a white solid in 82% yield, mp 146-149 °C.

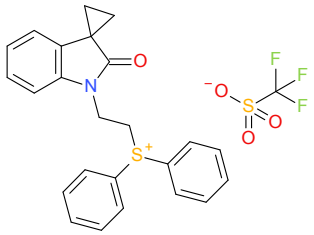
b. To a 25 mL Schlenk tube were added amine 11d (0.2 mmol, 1.0 equiv), vinyl diphenylsulfonium triflate (76 mg, 0.21 mmol, 1.05 equiv), DMSO (1 mL). The mixture was stirred at room temperature for 2 min and DBU (91.2 mg, 0.6 mmol, 3.0 equiv) was added into it. The mixture was heating for 1 hour at 130 degree with microwave till the reaction completed, quenched with saturated ammonium chloride solution (5 mL), and was extracted with EtOAc (3 x 50 mL). The combined organic layer washed with H_2O (2 x 10 mL), dried with anhydrous sodium sulfate. After concentration, product was purified using column chromatography on silica gel using eluent (DCM: MeOH = 100: 1 to 10:2).

^{1}H NMR (400 MHz, DMSO-d6) δ 6.73 (d, *J*=8.19 Hz, 1H), 6.47 (dd, *J*=2.08, 8.19 Hz, 1H), 6.24 (d, *J*=2.08 Hz, 1H), 4.71 (br s, 2H), 3.12 (s, 3H), 1.37-1.47 (m, 4H)

^{13}C NMR (100 MHz, DMSO-d6) δ/ppm = 175.7, 144.6, 133.9, 131.3, 112.1, 109.0, 106.3, 27.2, 26.7, 18.4

HRMS (ESI-TOF) calcd for $C_{11}H_{12}N_2O$ $[M + H]^+$: 189.10224 found: 189.10212

2-(2'-oxospiro[cyclopropane-1,3'-indoline]-1'-yl)ethyl-diphenyl-sulfonium;trifluoromethanesulfonate (13a)



To a 25 mL Schlenk tube were added oxaindole 7a (0.2 mmol, 1.0 equiv), vinyl diphenylsulfonium triflate (86.9 mg, 0.24 mmol, 1.2 equiv) and DCM (1 mL). The mixture was stirred for 2 minutes at room temperature and TEA (91.2 mg, 0.6 mmol,

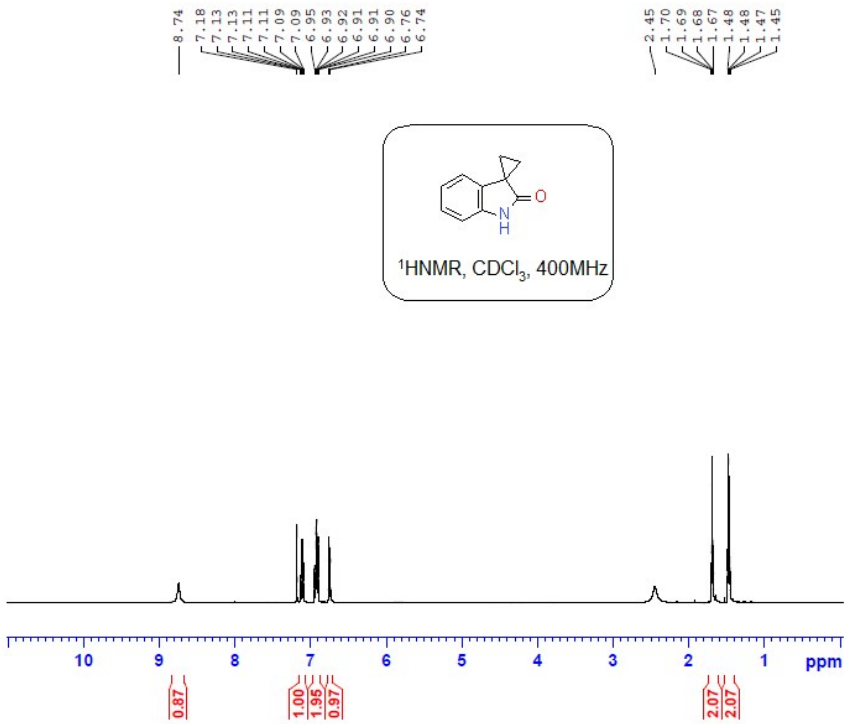
3.0 equiv) was added into it. After stirring for 4 hour at room temperature, the mixture was diluted with DCM (20mL) and washed with water (3 x 5mL). The organic layer was dried over sodium sulfate and concentrated under reduced pressure. The residue solid was washed with ethyl acetate (3 x 1mL) to afford the pure product which was dried over vacum in 32% yield as white solid.

^{1}HNMR (400 MHz, METHANOL-d4) δ 7.83-8.05 (m, 4H), 7.68-7.83 (m, 2H), 7.55-7.67(m, 4H), 7.26-7.46 (m, 21), 7.20 (d, J=7.83 Hz, 1H), 6.98-7.15 (m, 1H), 6.85 (dd, J=0.61, 7.46 Hz, 1H), 4.64-4.87 (m, 2H), 4.55 (dd, J=4.71, 6.30 Hz, 2H), 1.35-1.59 (m, 4H)

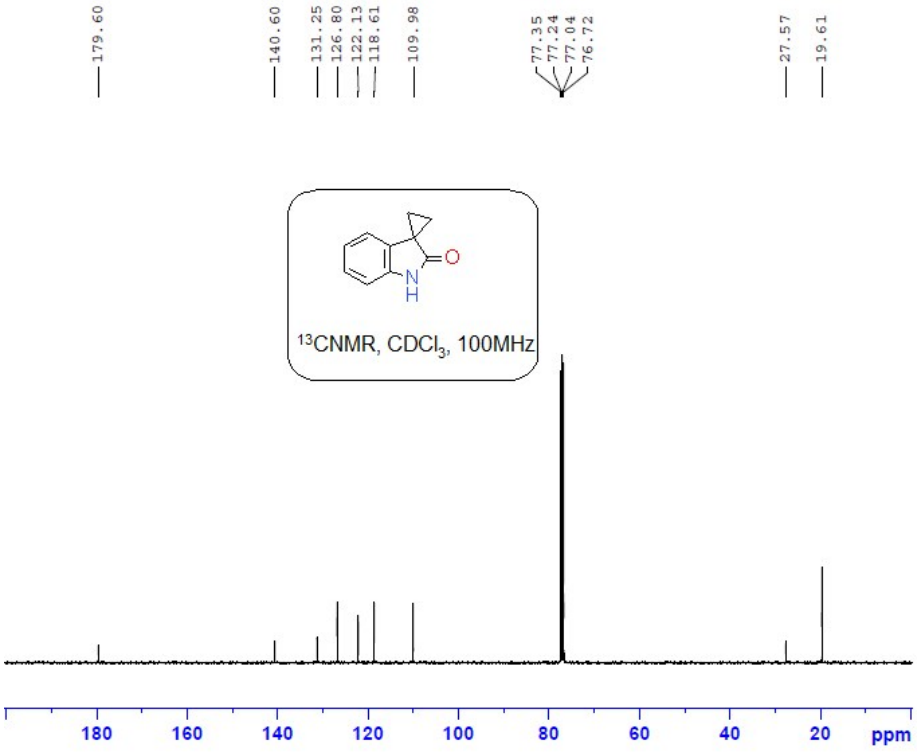
^{13}CNMR (101 MHz, METHANOL-d4) δ177.9, 140.7, 134.2, 130.2, 129.8, 130.9, 126.7,125.5, 122.8, 118.6, 108.4, 43.5, 35.9, 26.3, 19.2

5. NMR spectra of product

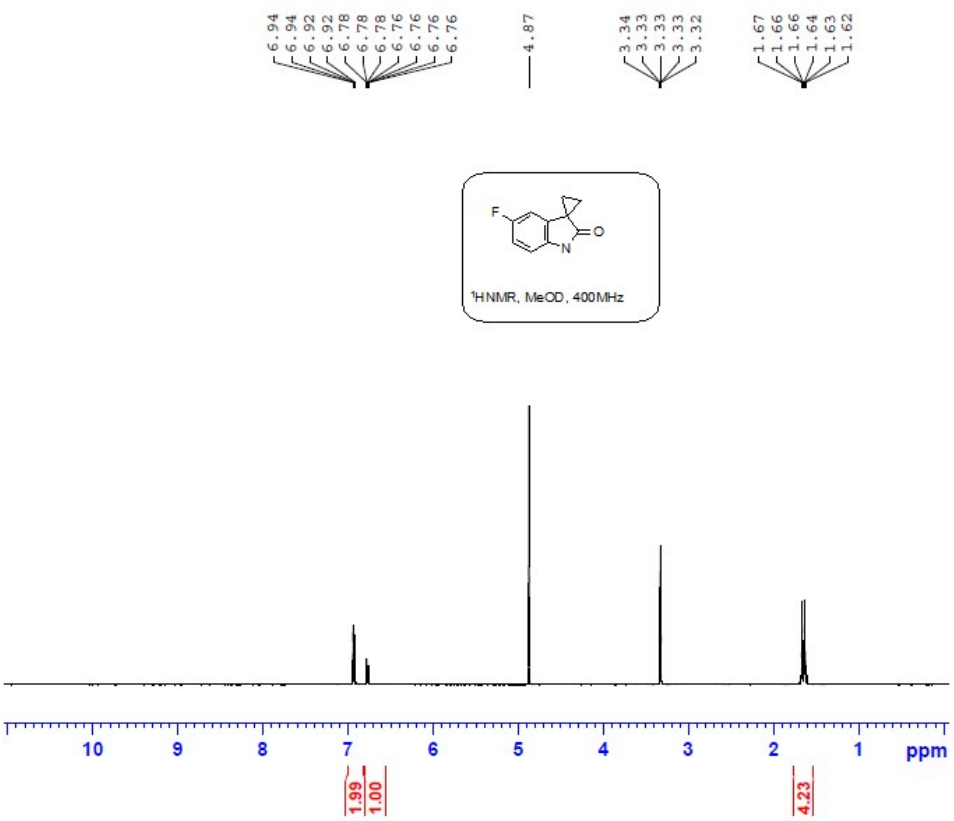
^{1}H NMR of Compond 9a



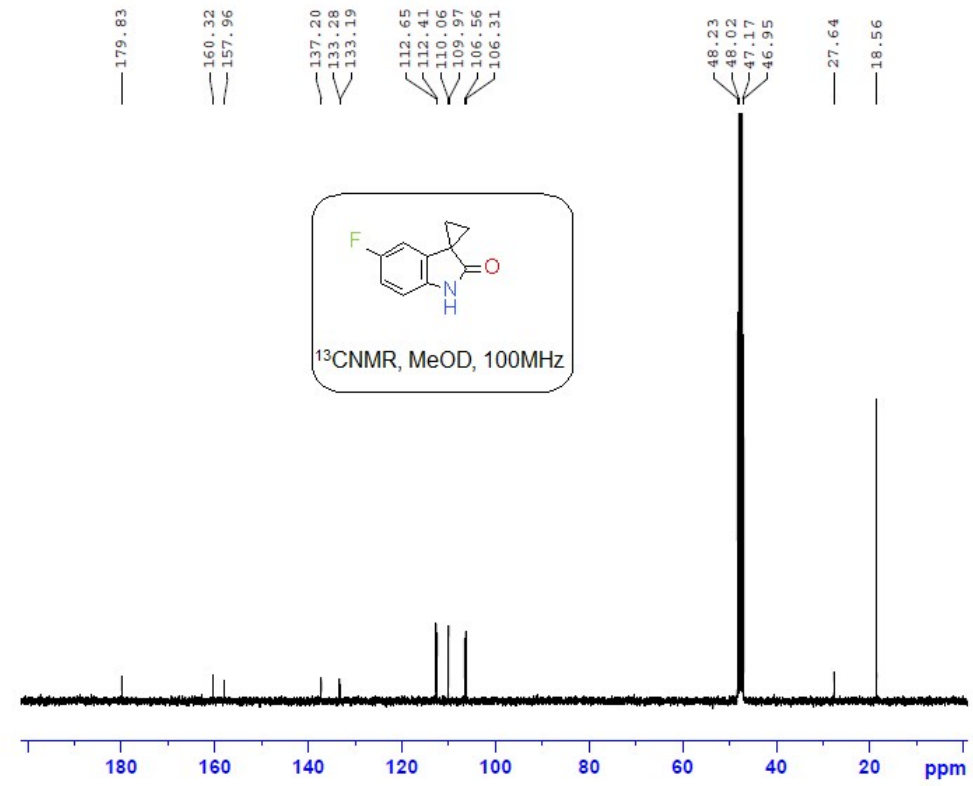
^{13}C NMR of Compond 9a



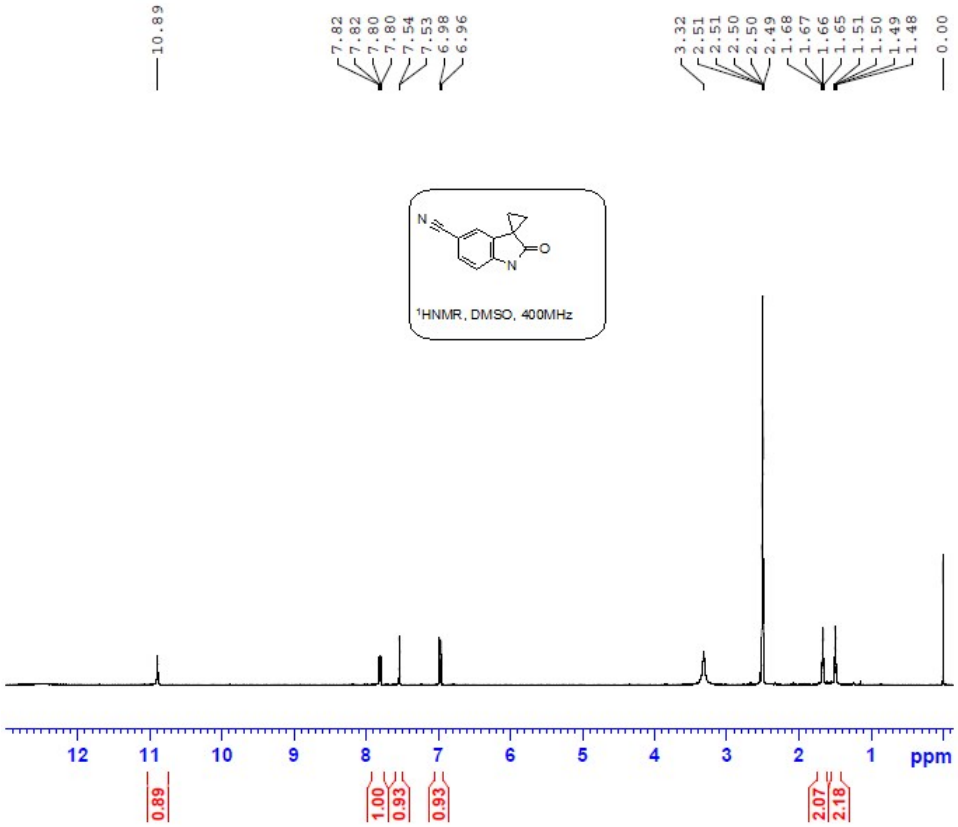
^{1}H NMR of Compond 9b



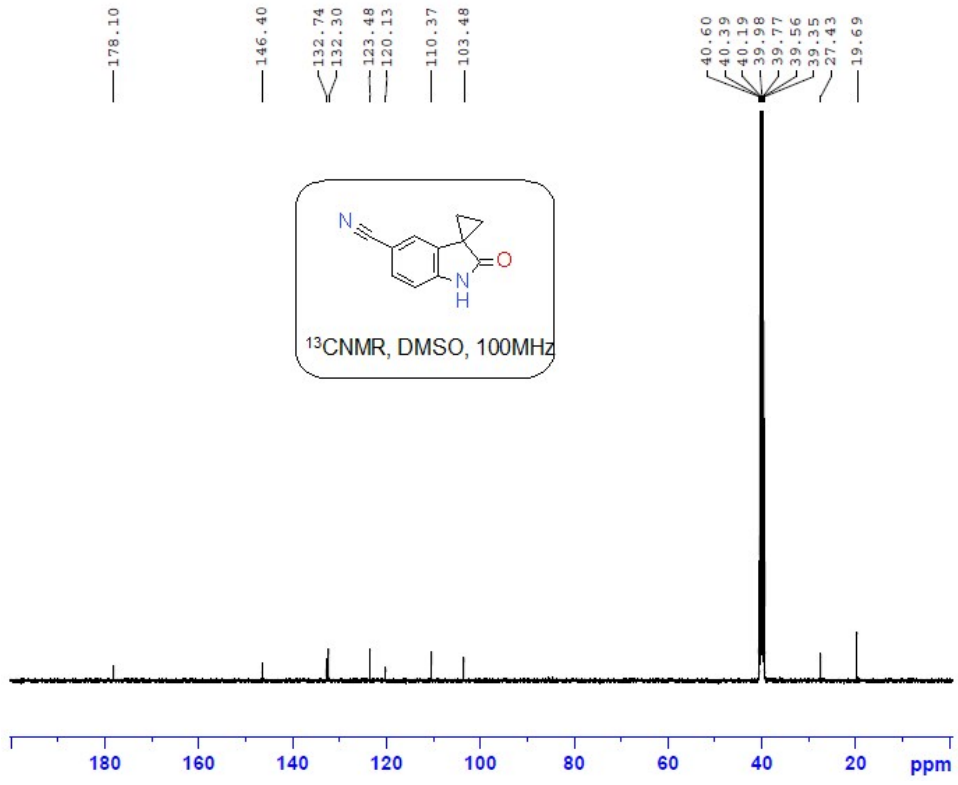
^{13}C NMR of Compond 9b



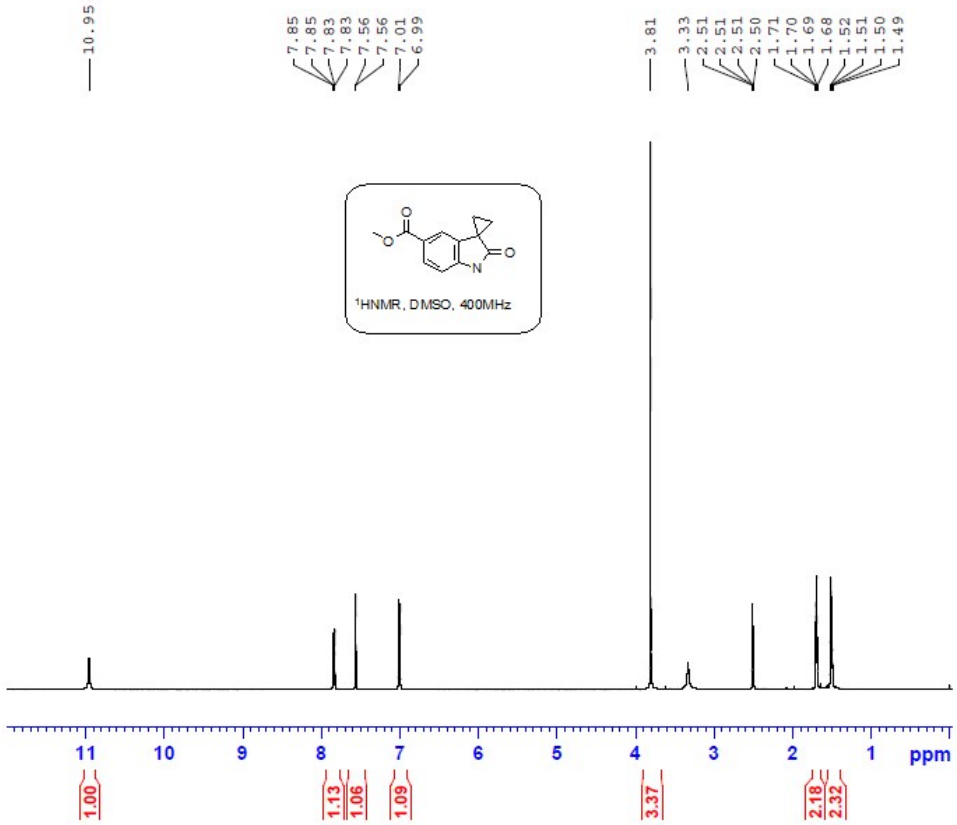
[1]H NMR of Compond 9c



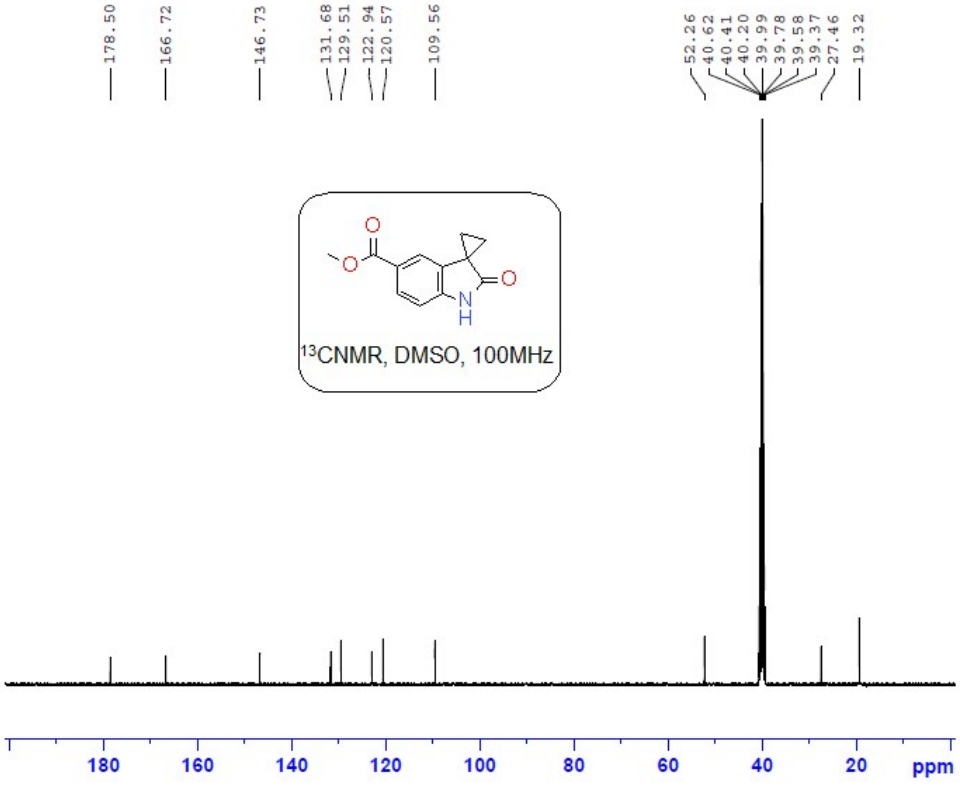
[13]C NMR of Compond 9c



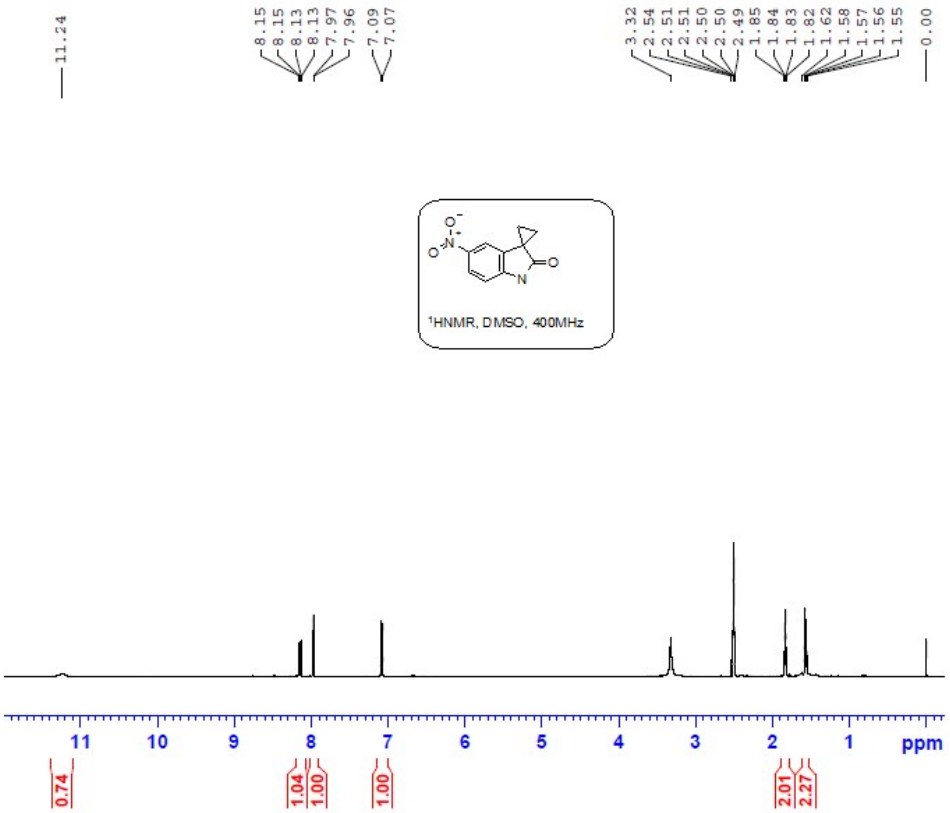
[1]H NMR of Compond 9d



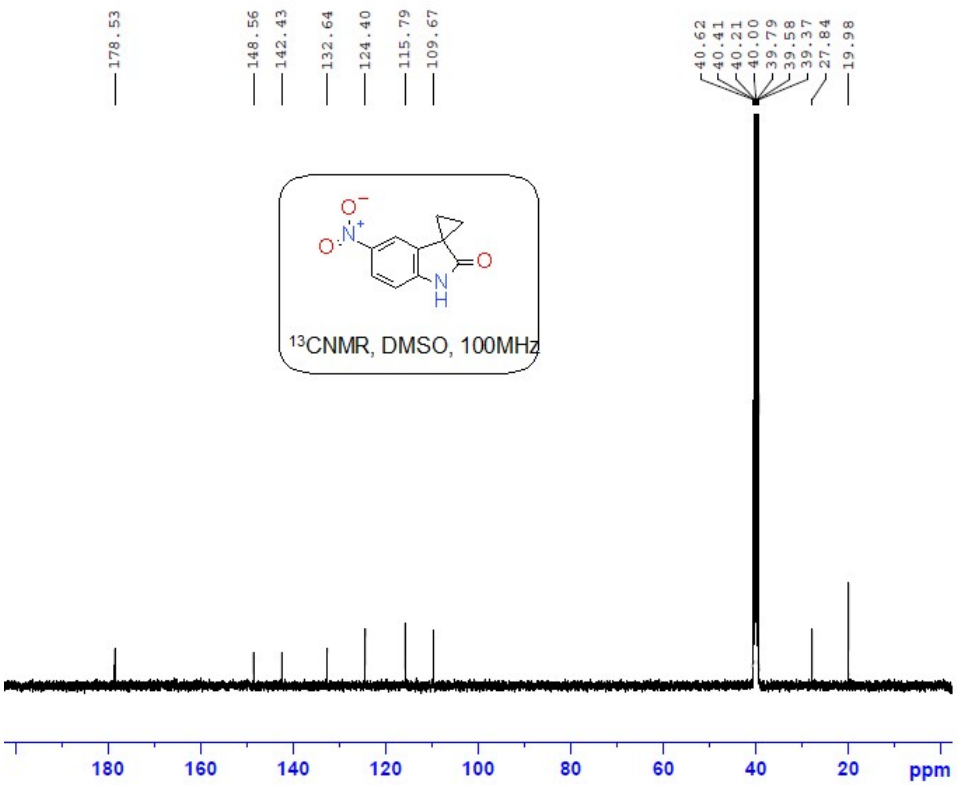
[13]C NMR of Compond 9d



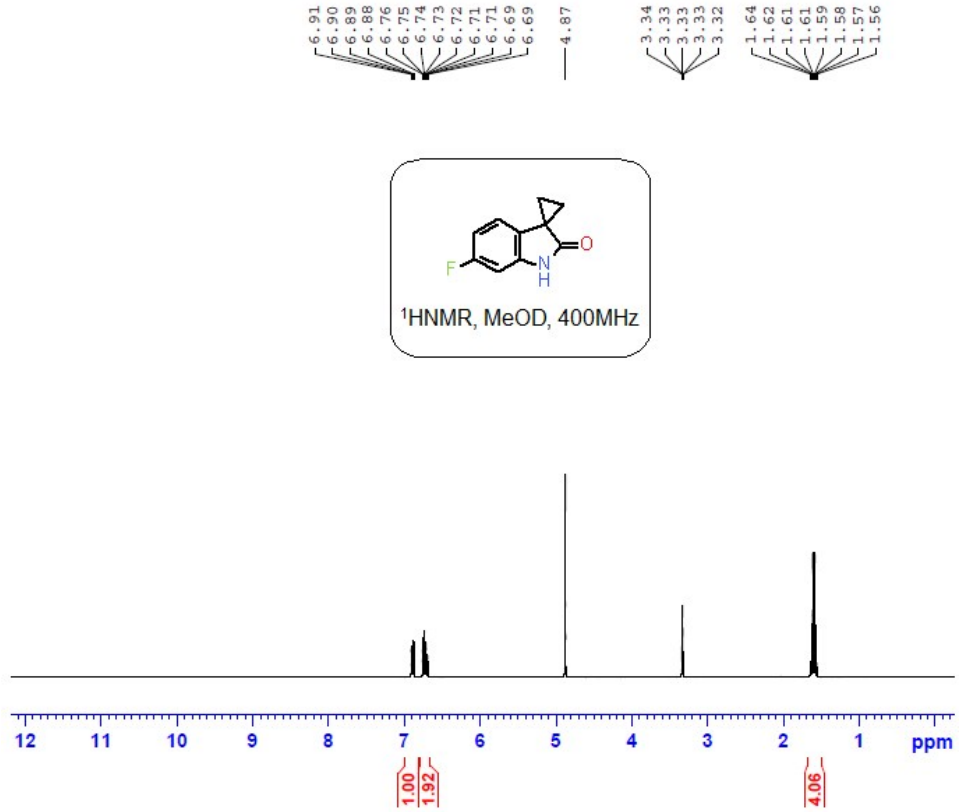
[1]H NMR of Compond 9e



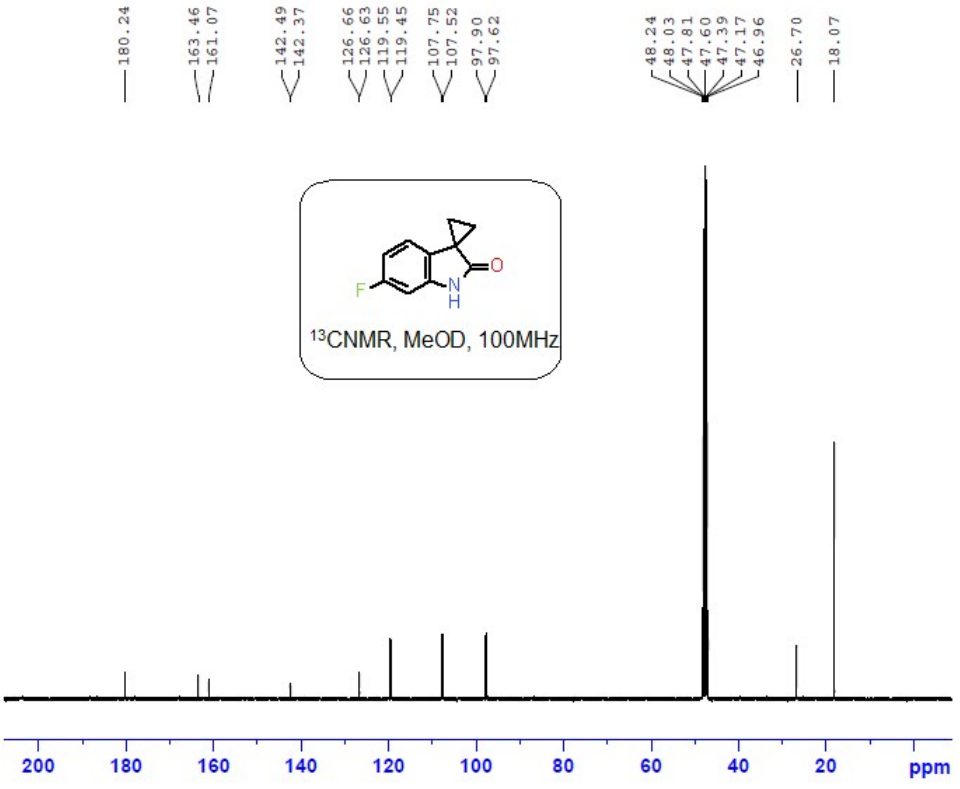
[13]C NMR of Compond 9e



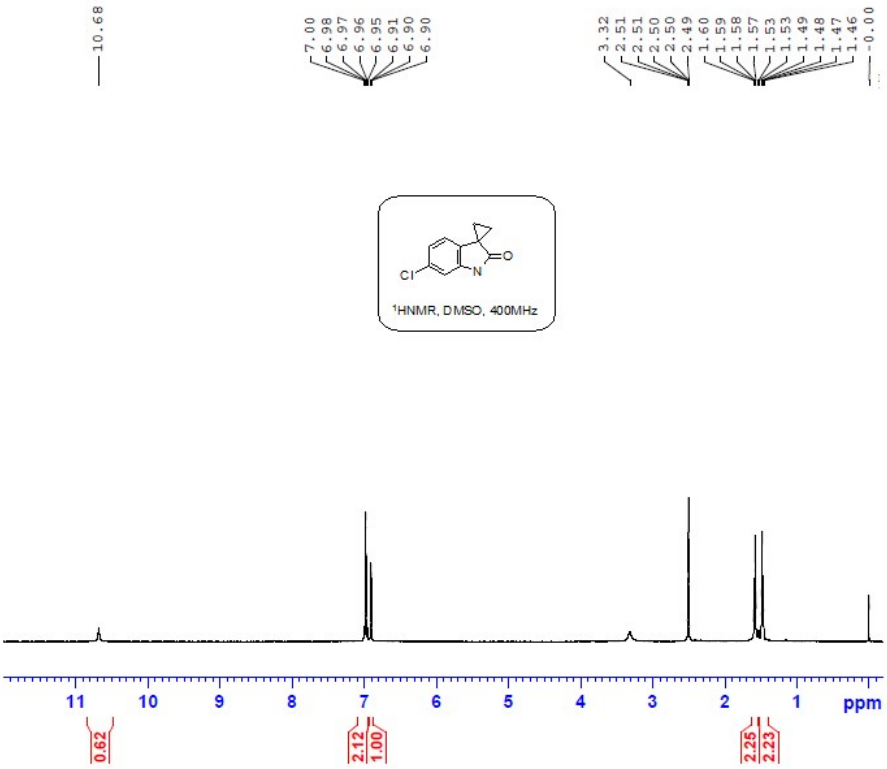
^{1}H NMR of Compond 9f



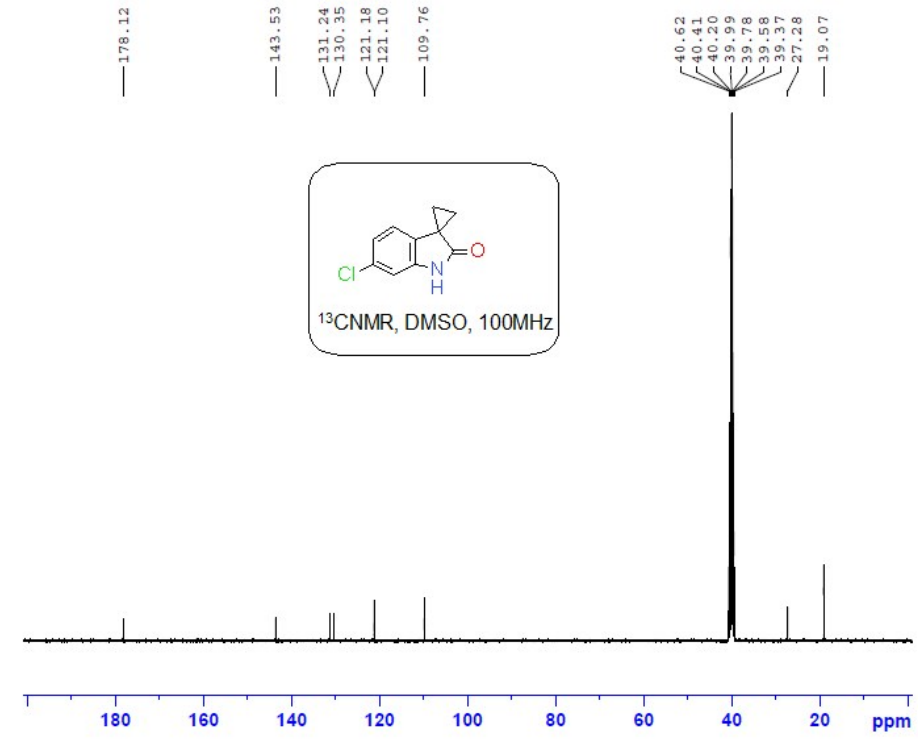
^{13}C NMR of Compond 9f



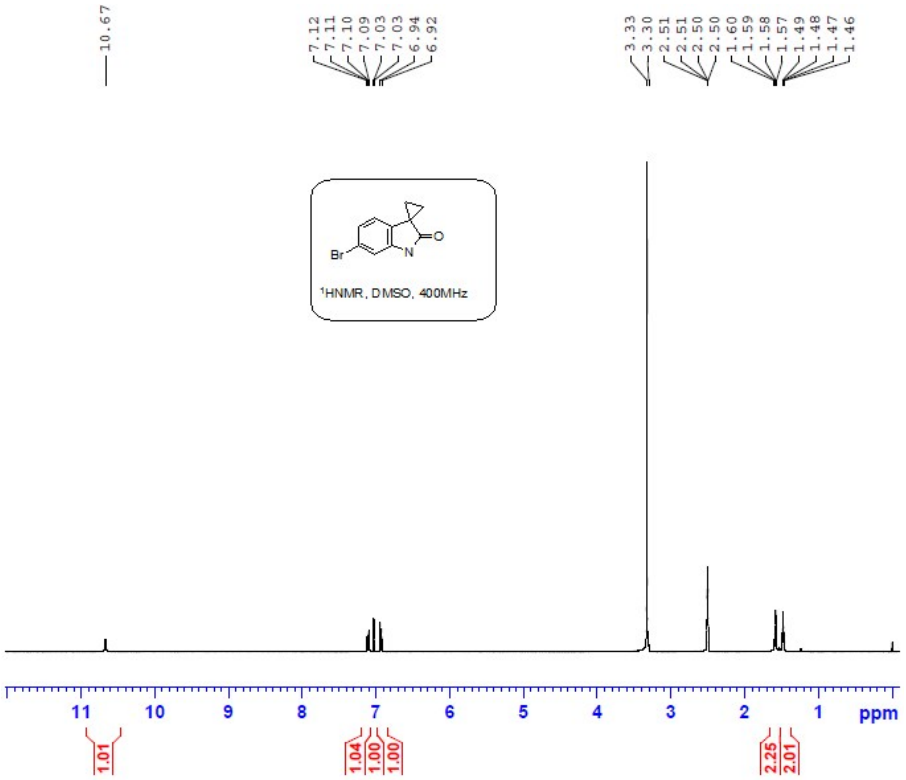
^{1}H NMR of Compond 9g



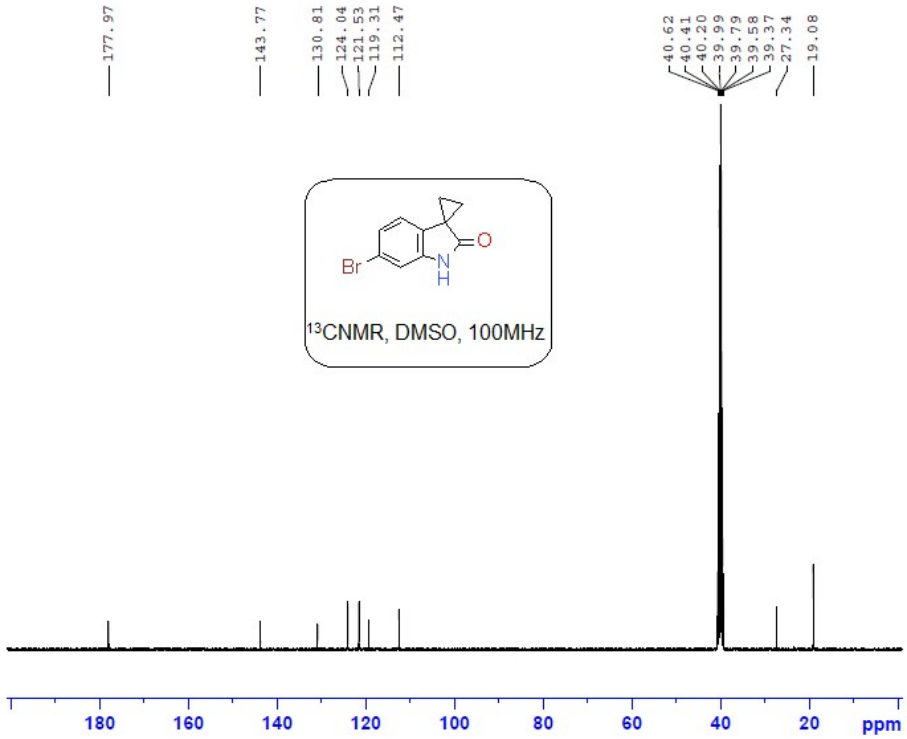
^{13}C NMR of Compond 9g



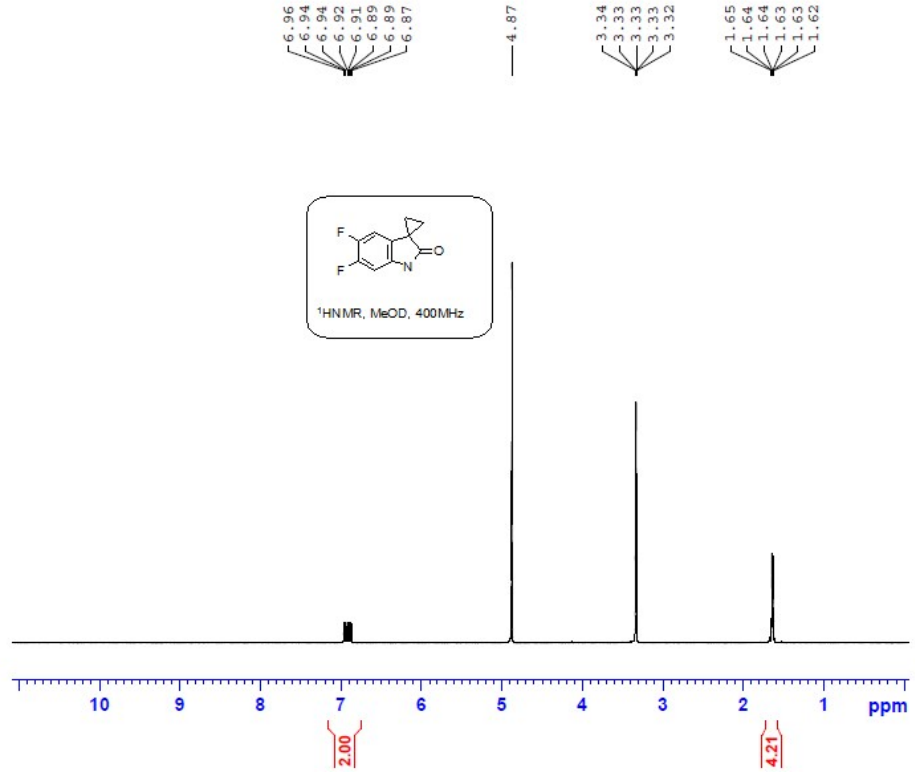
^{1}H NMR of Compond 9h



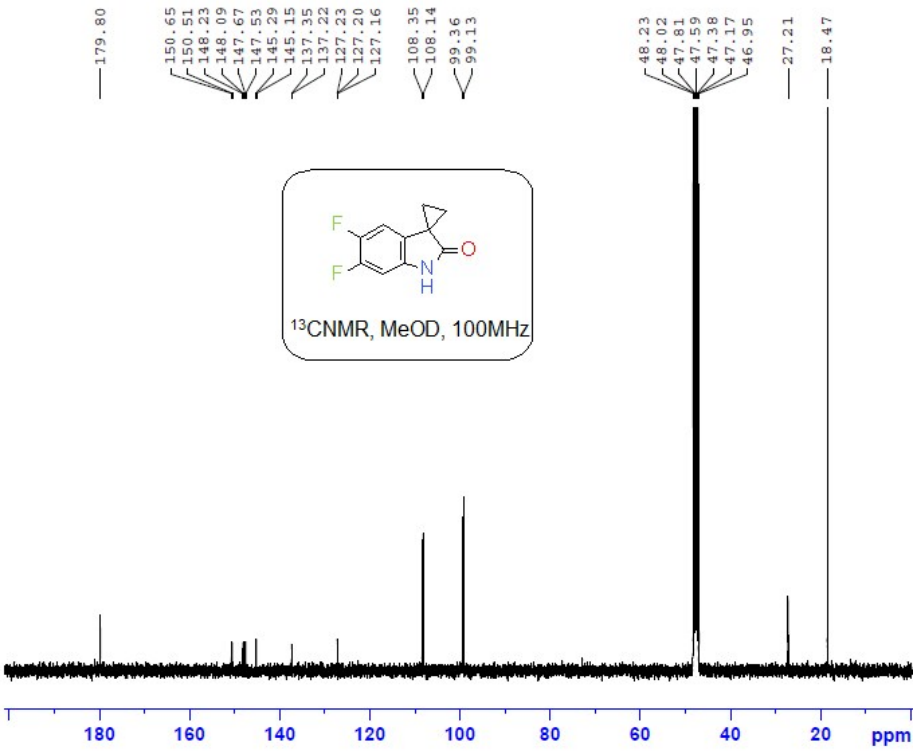
^{13}C NMR of Compond 9h



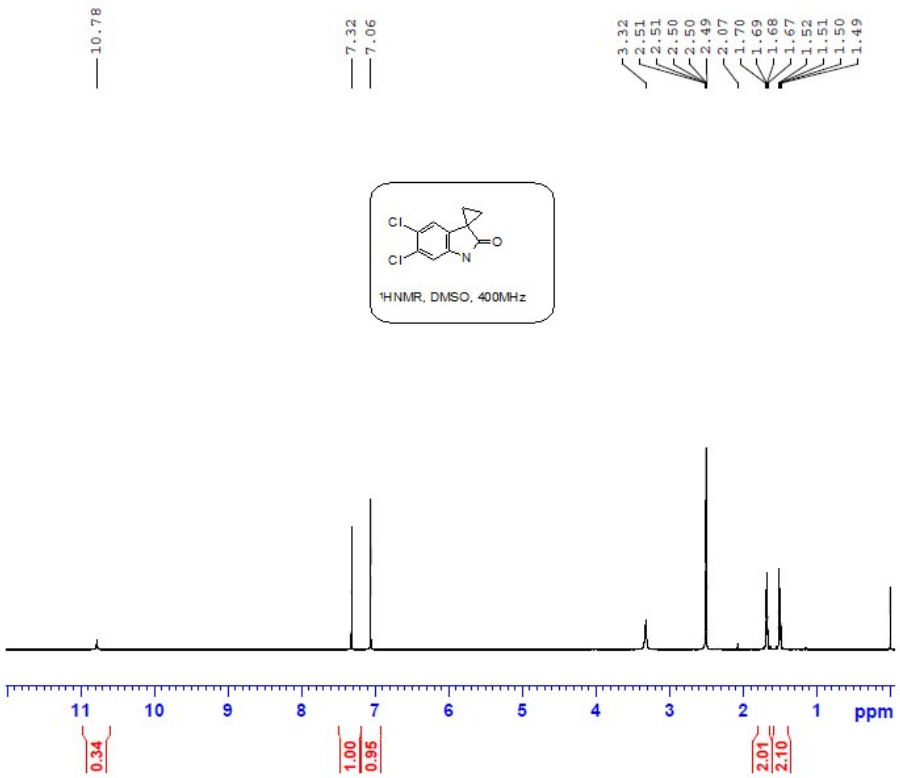
^{1}H NMR of Compond 9i



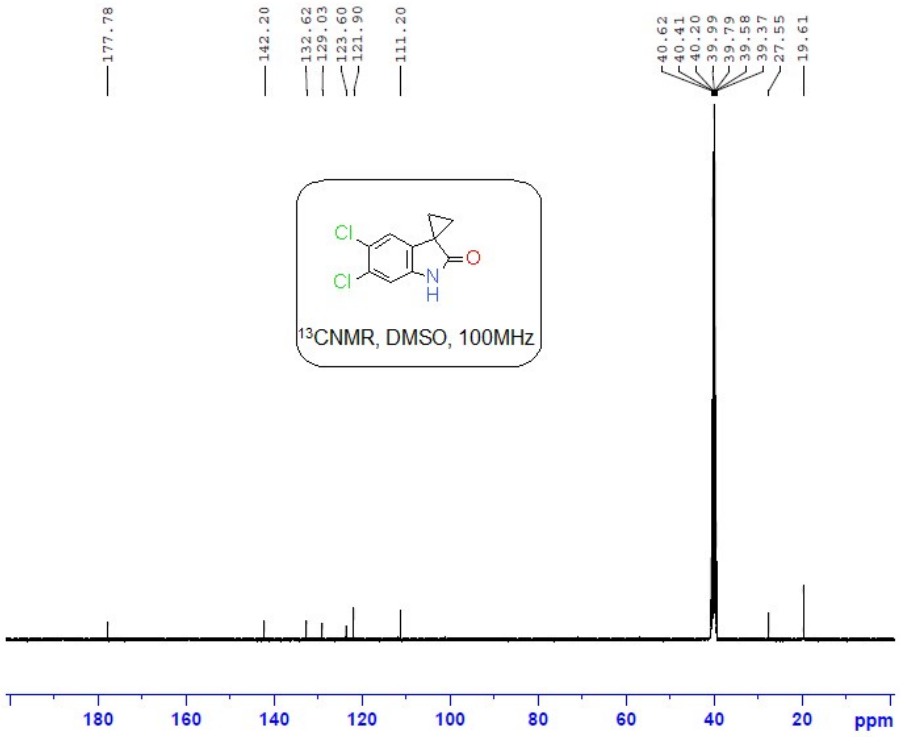
^{13}C NMR of Compond 9i



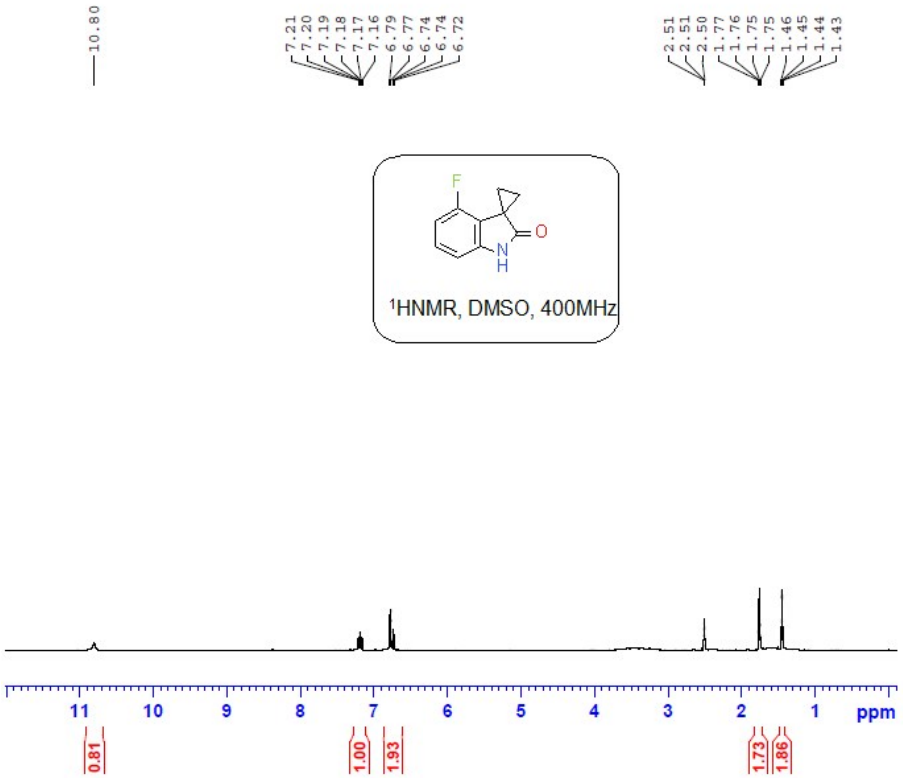
[1]H NMR of Compond 9j



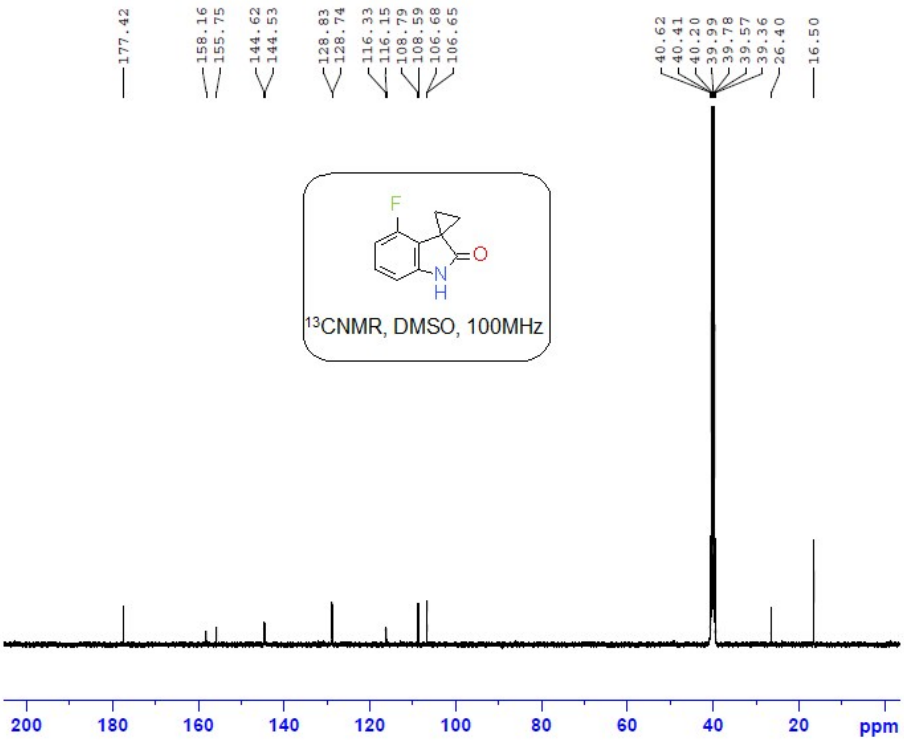
[13]C NMR of Compond 9j



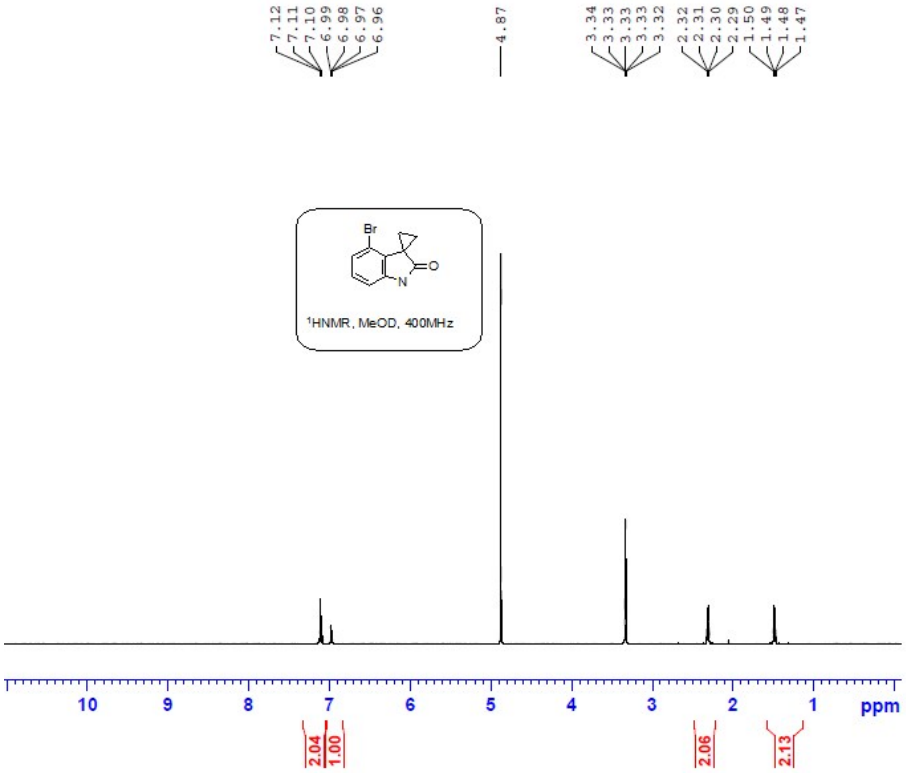
[1]H NMR of Compond 9k



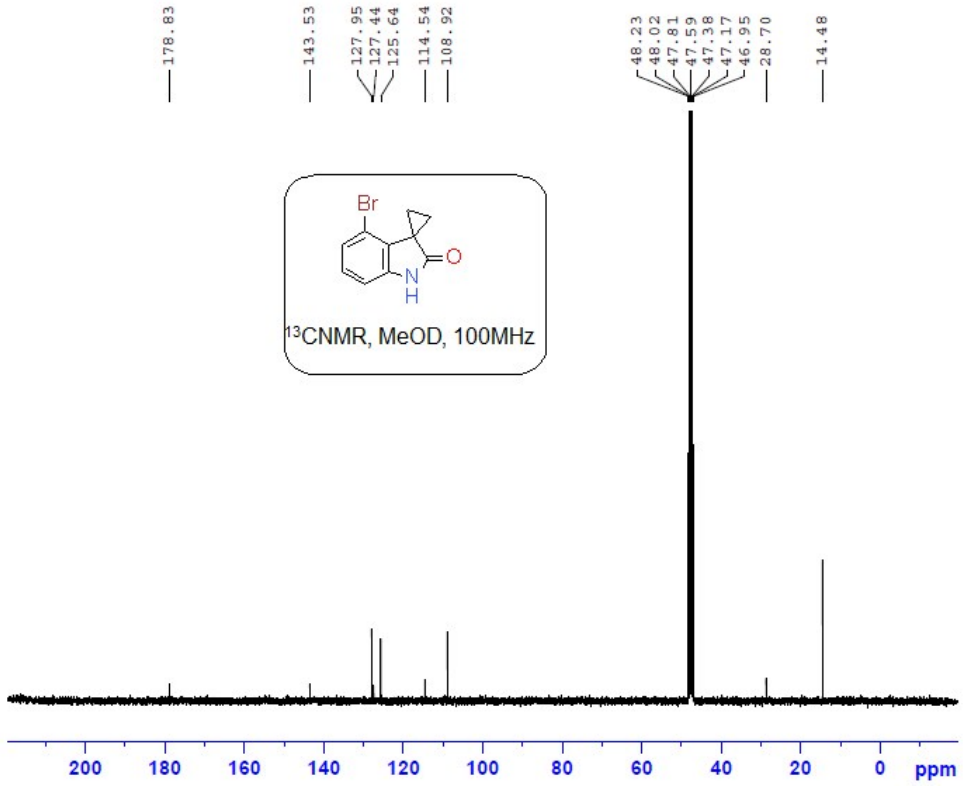
[13]C NMR of Compond 9k



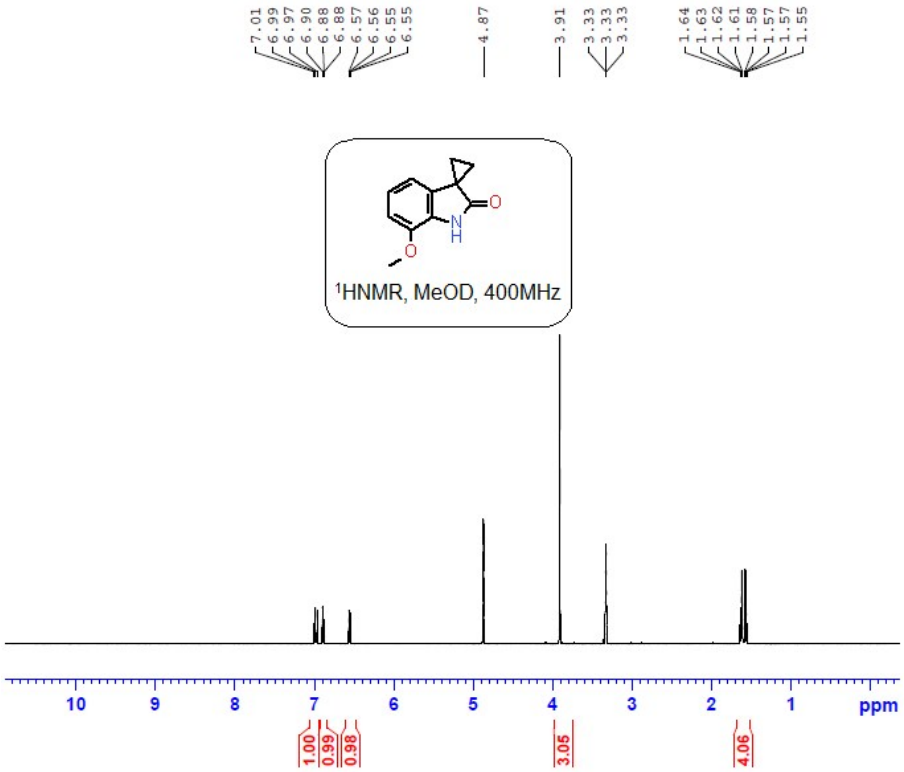
^{1}H NMR of Compond 9l



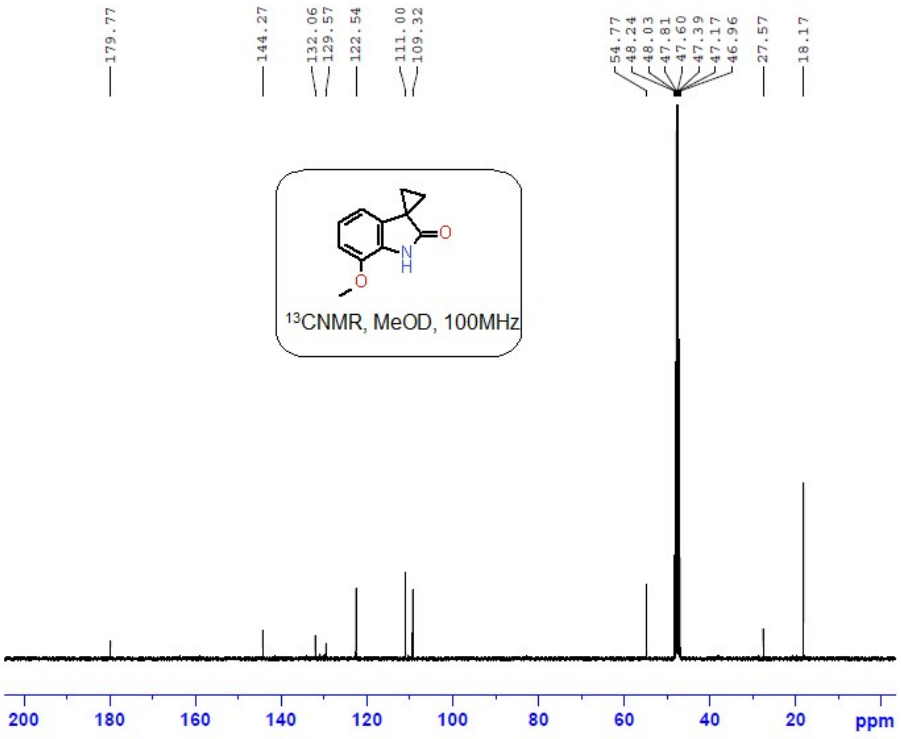
^{13}C NMR of Compond 9l



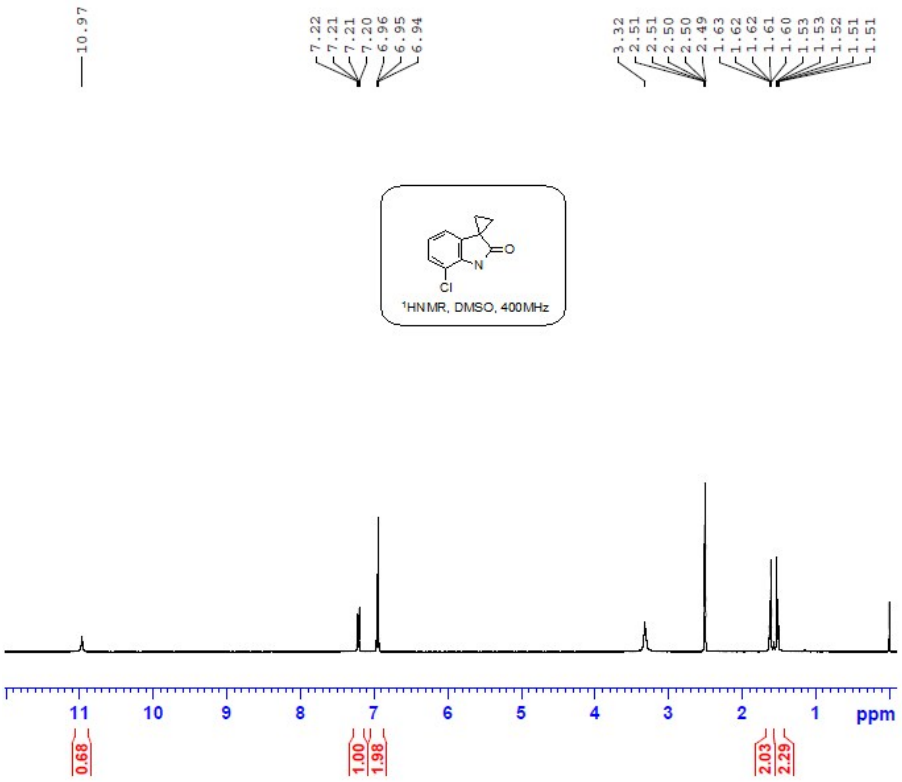
[1]H NMR of Compond 9m



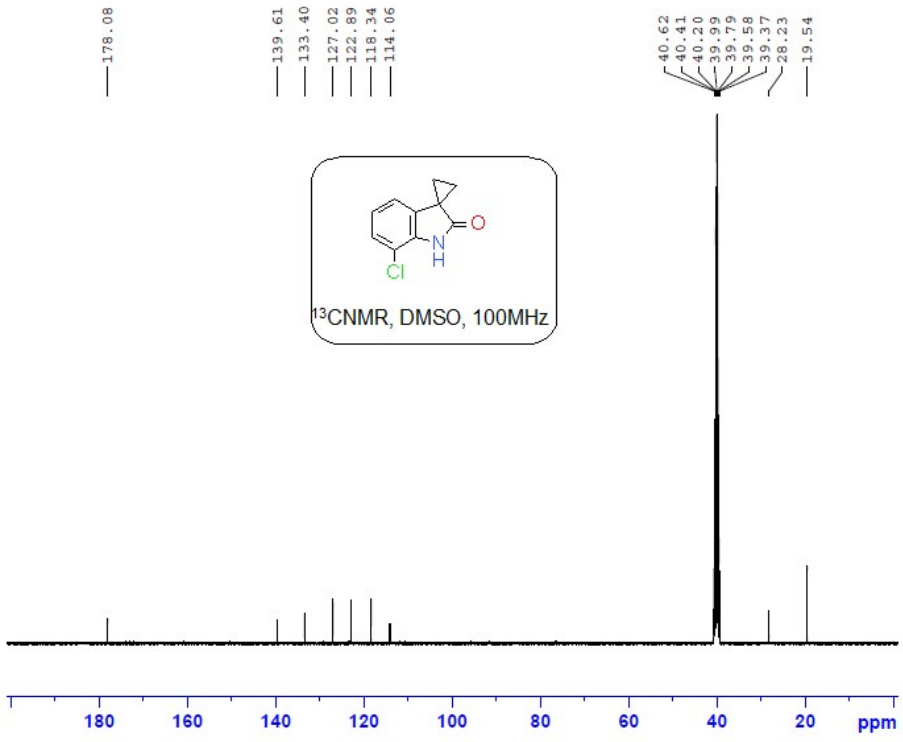
[13]C NMR of Compond 9m



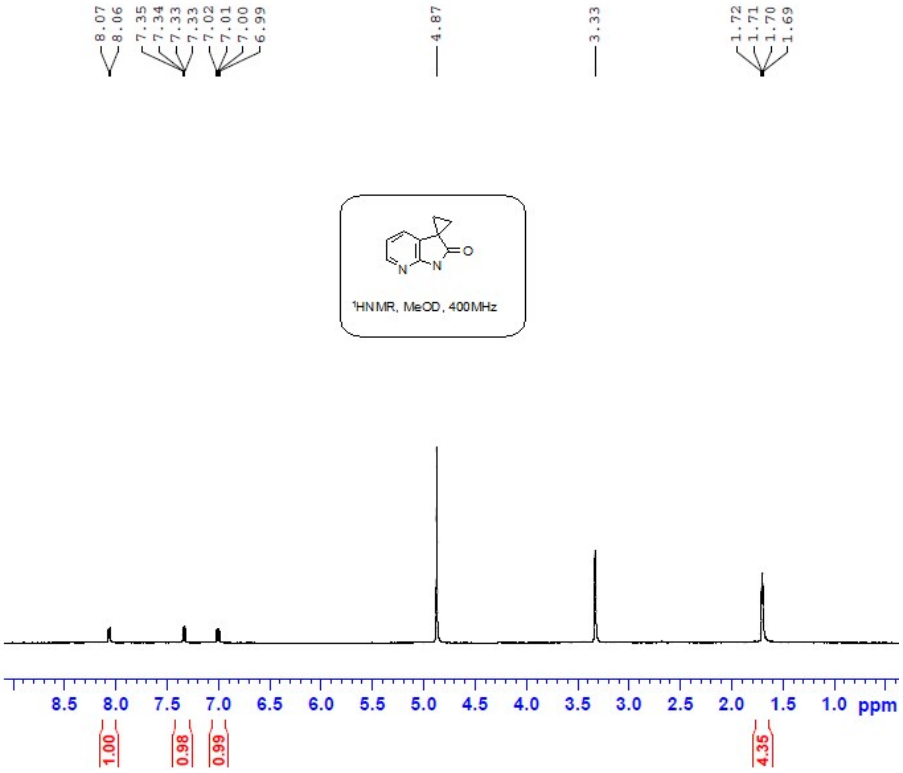
^{1}H NMR of Compond 9n



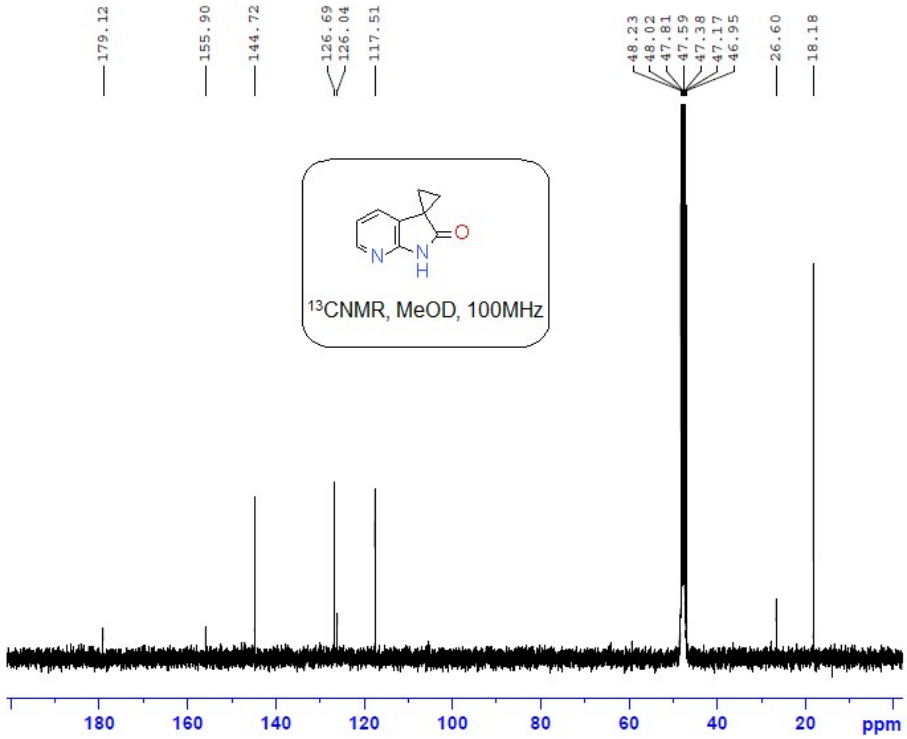
^{13}C NMR of Compond 9n



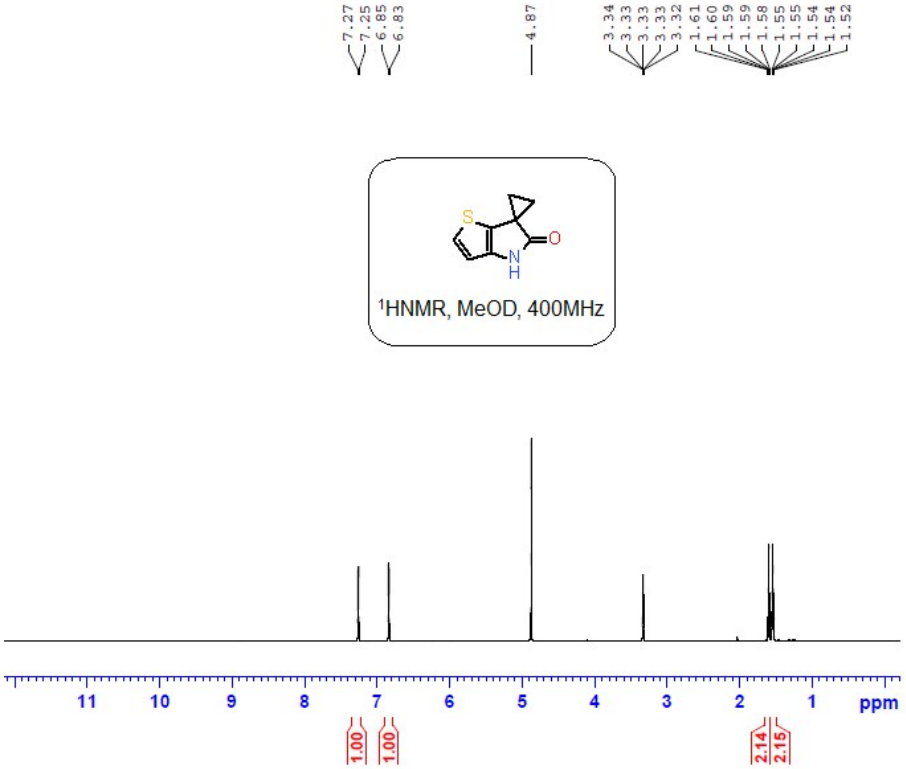
[1]H NMR of Compond 9o



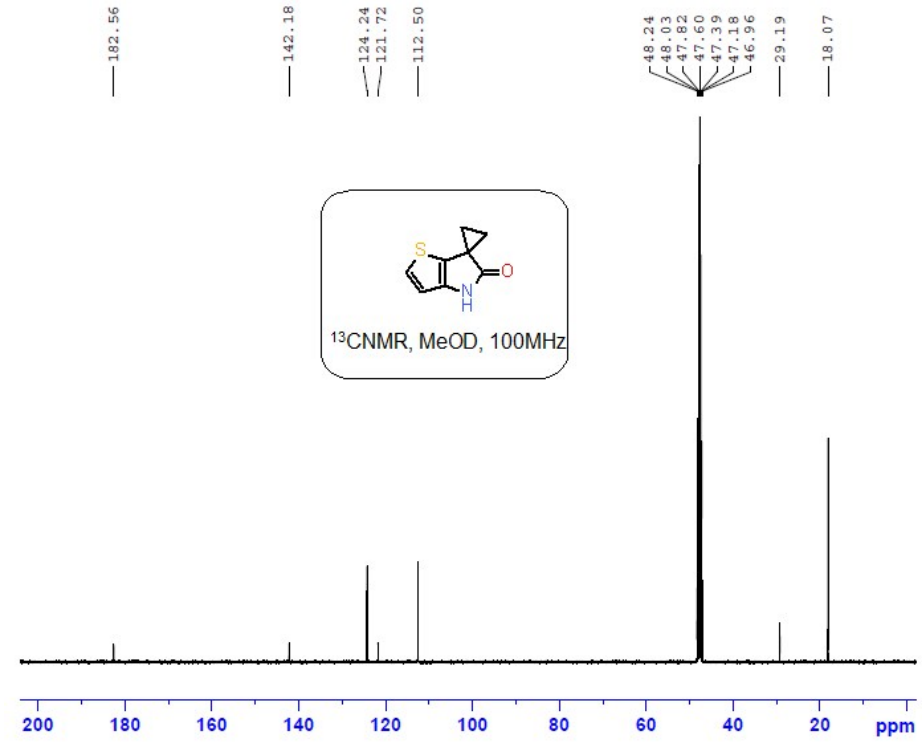
[13]C NMR of Compond 9o



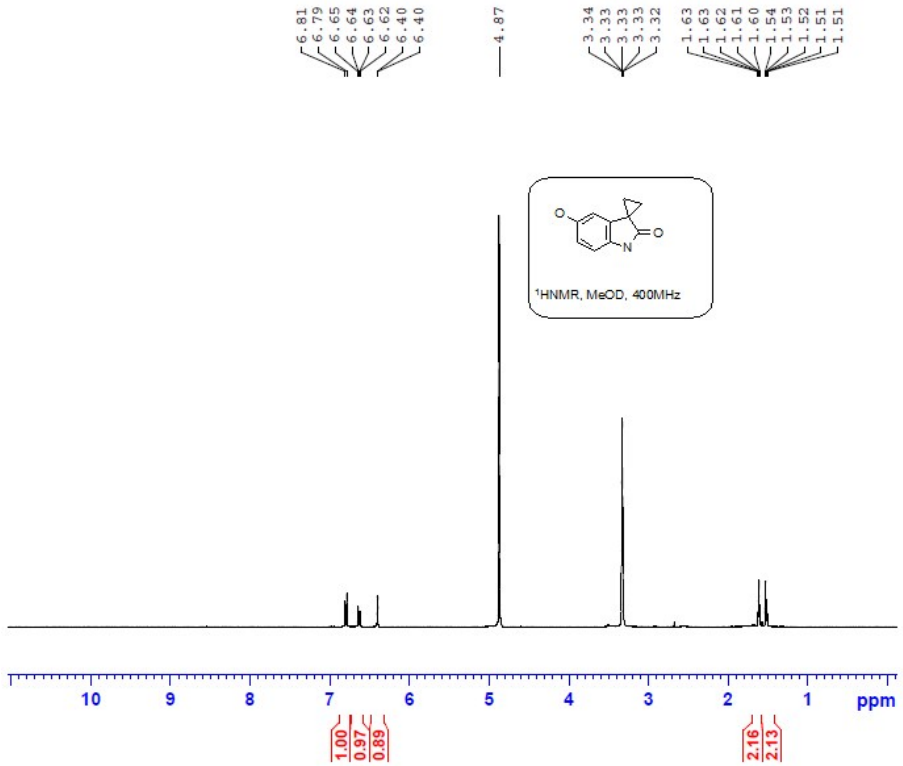
[1]H NMR of Compond 9p



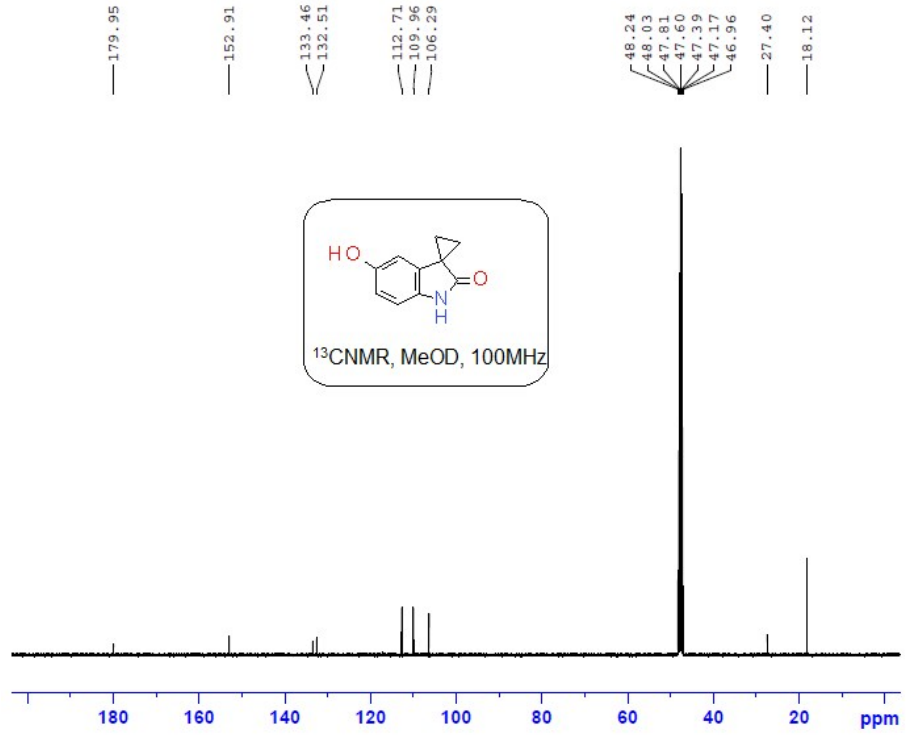
[13]C NMR of Compond 9p



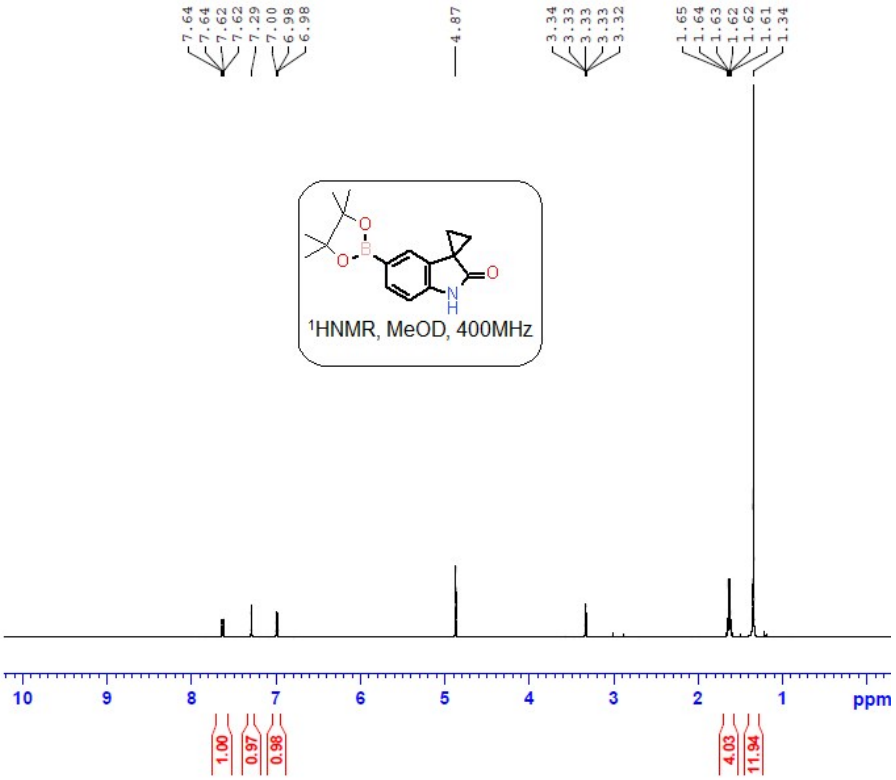
[1]H NMR of Compond 9q



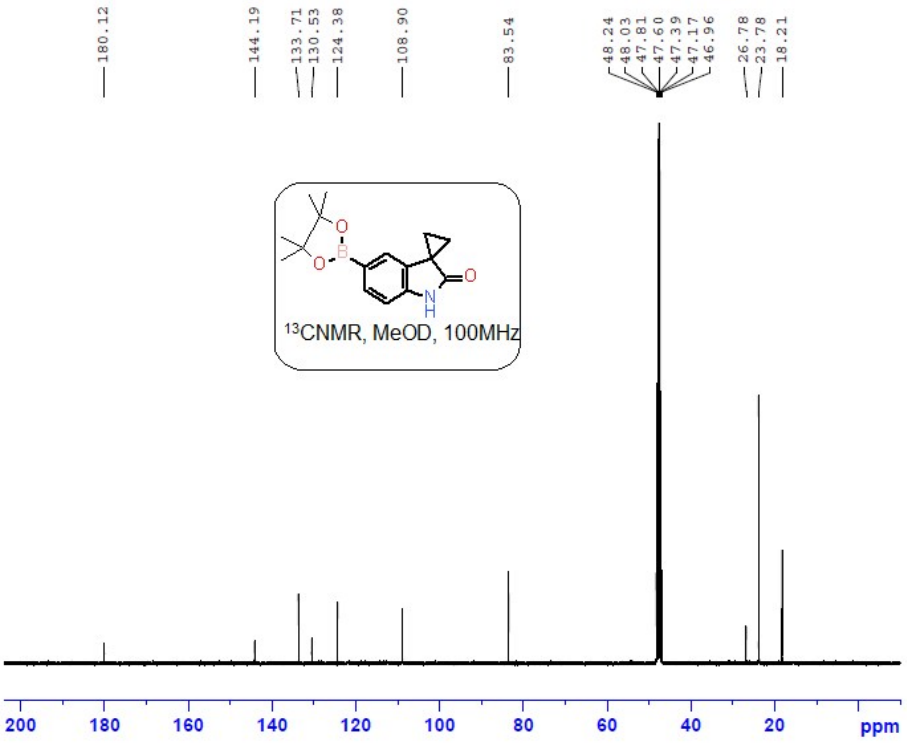
[13]C NMR of Compond 9q



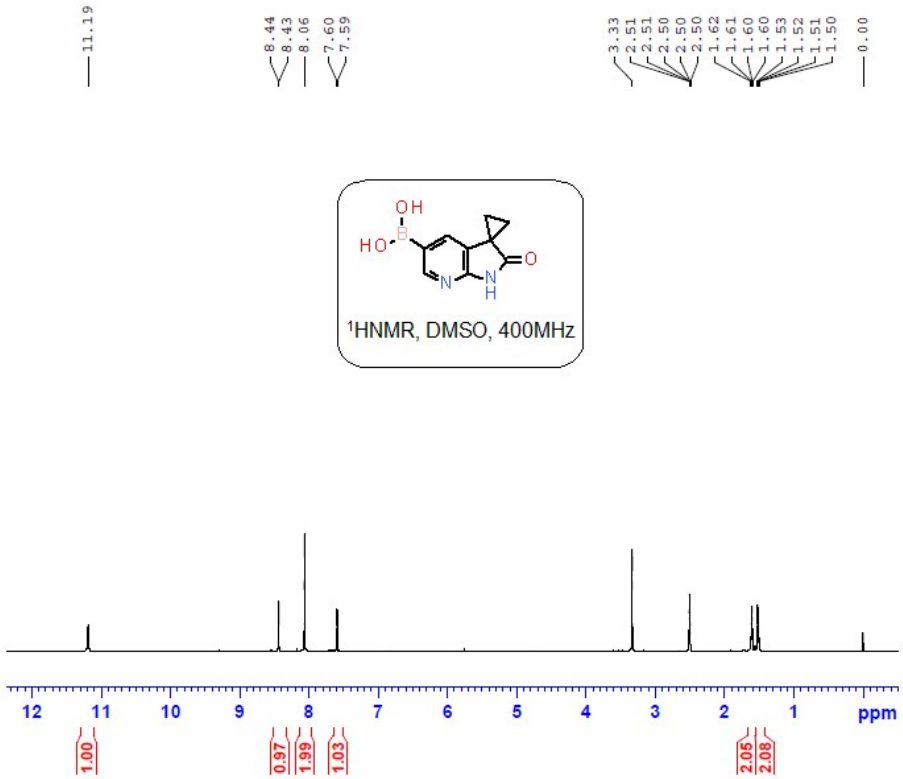
^{1}H NMR of Compond 9r



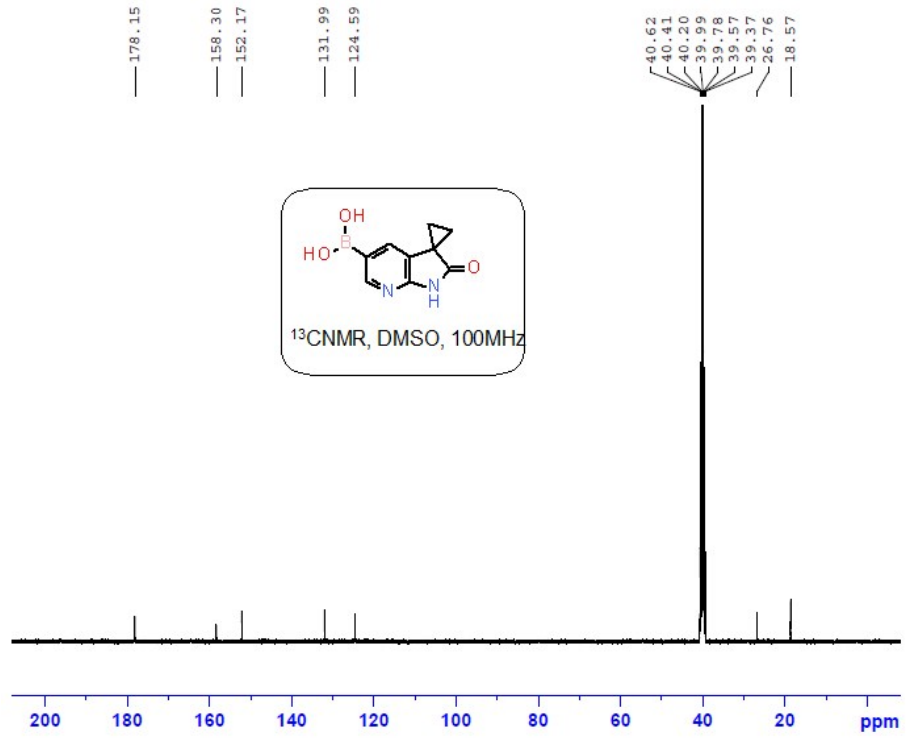
^{13}C NMR of Compond 9r



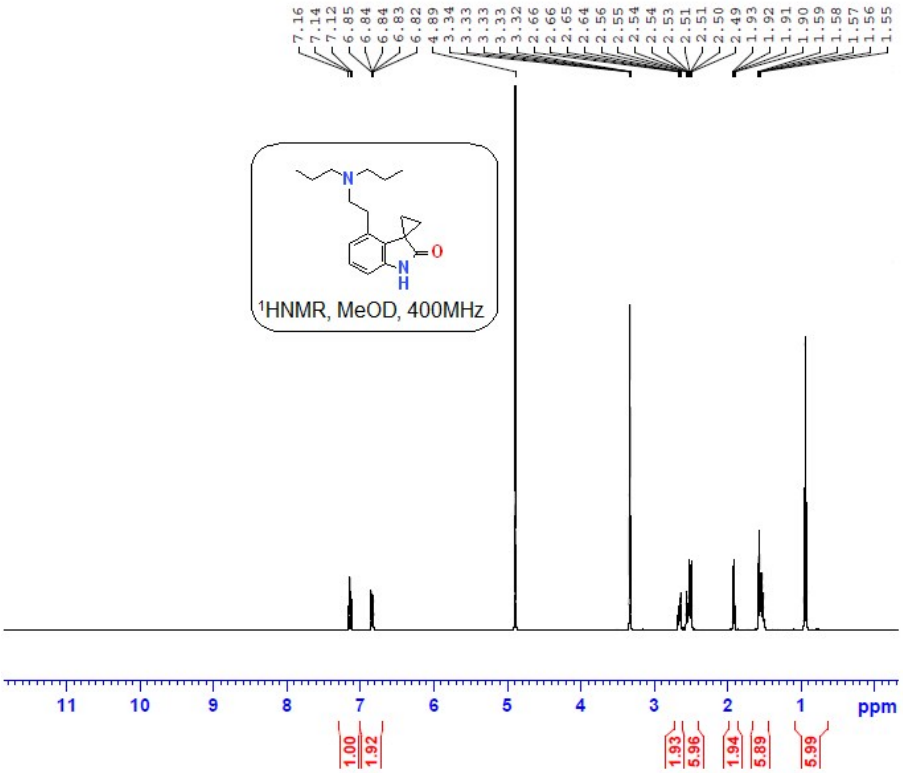
^{1}H NMR of Compond 9s



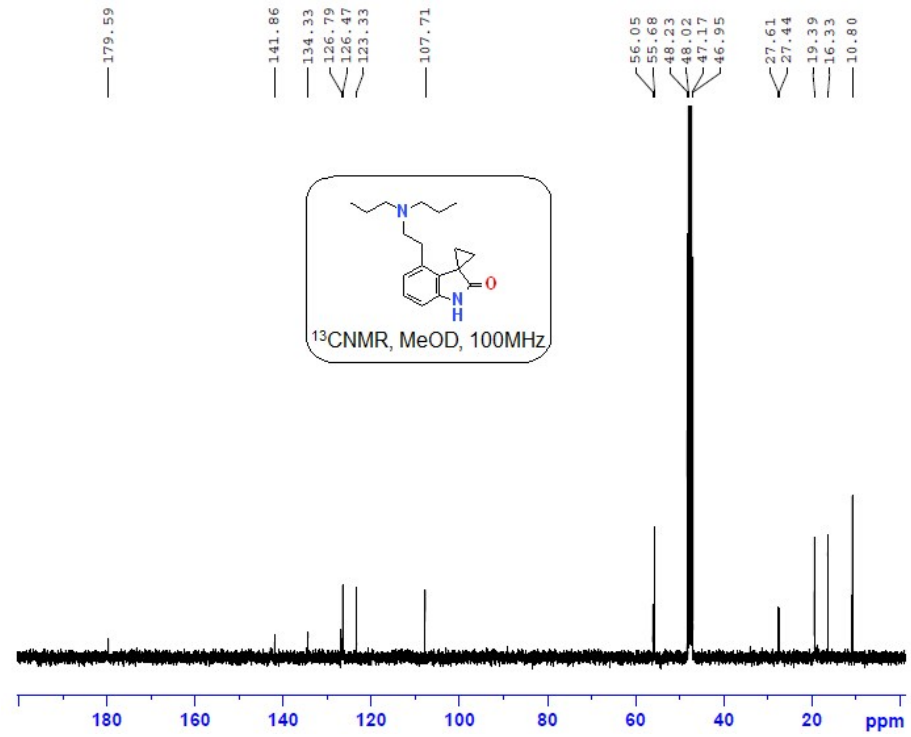
^{13}C NMR of Compond 9s



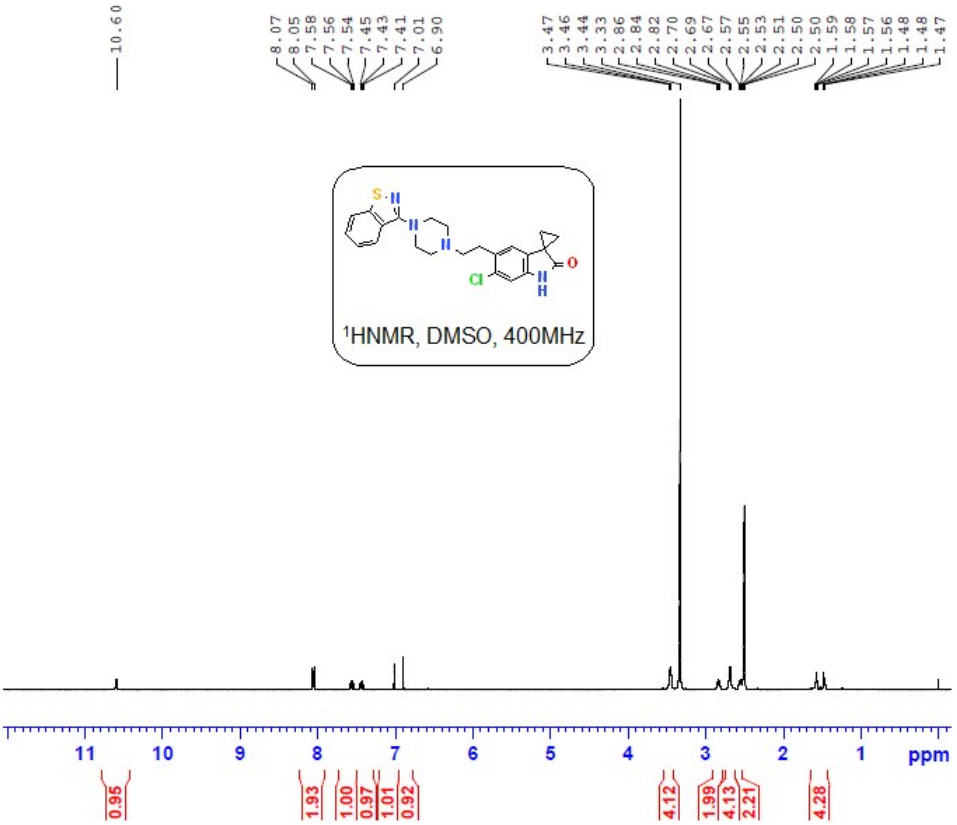
^{1}H NMR of Compond 1b



^{13}C NMR of Compond 1b



[1]H NMR of Compond 2b



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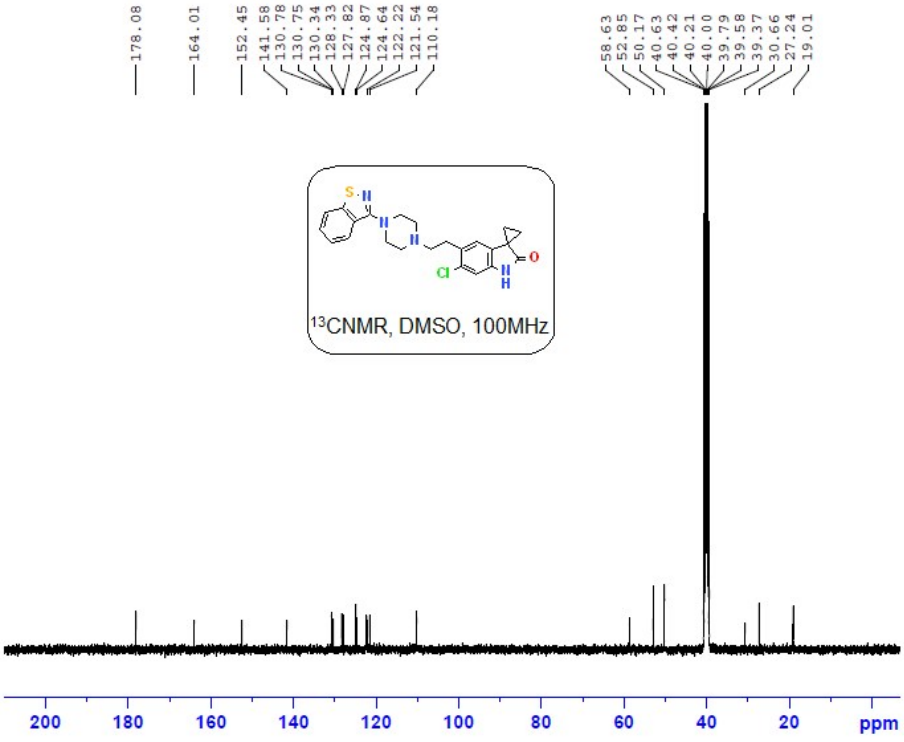
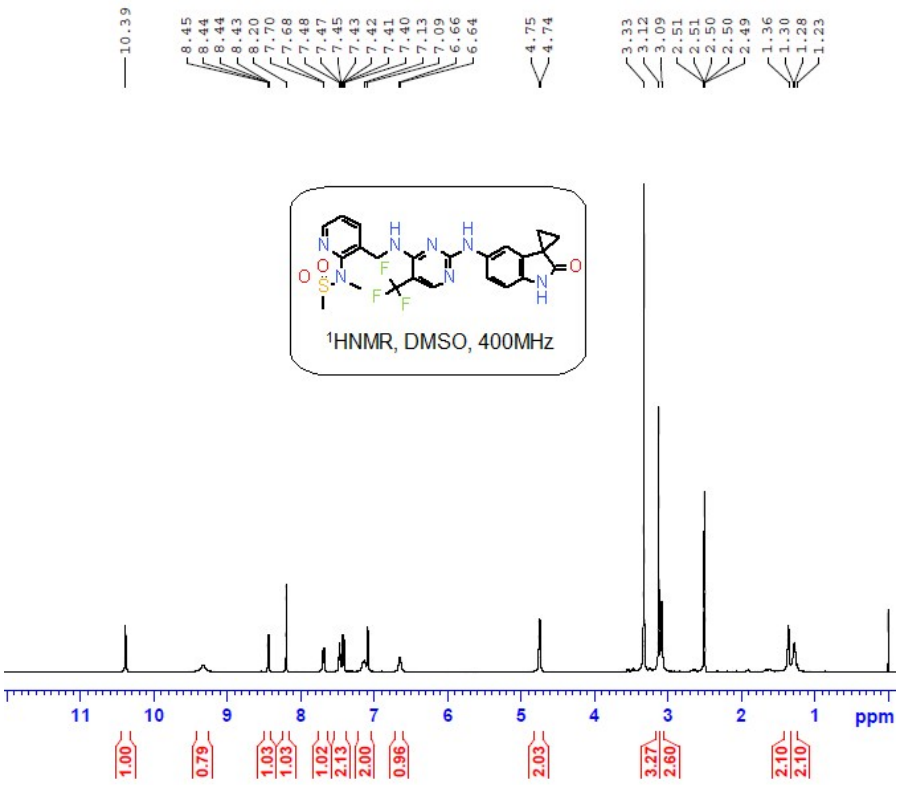


[1]H NMR of Compond 3b



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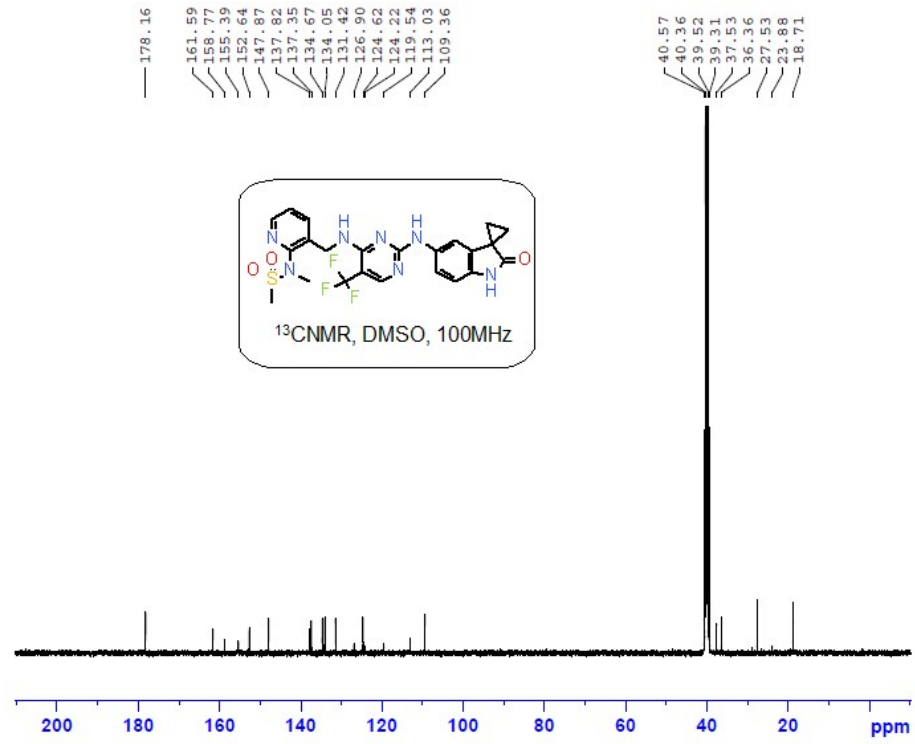
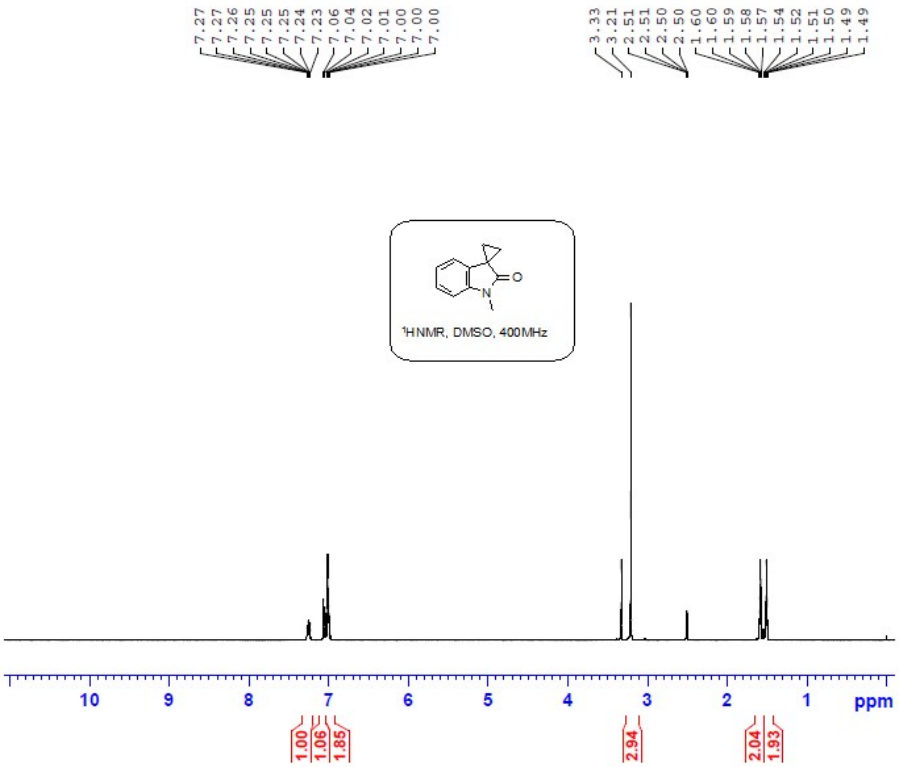
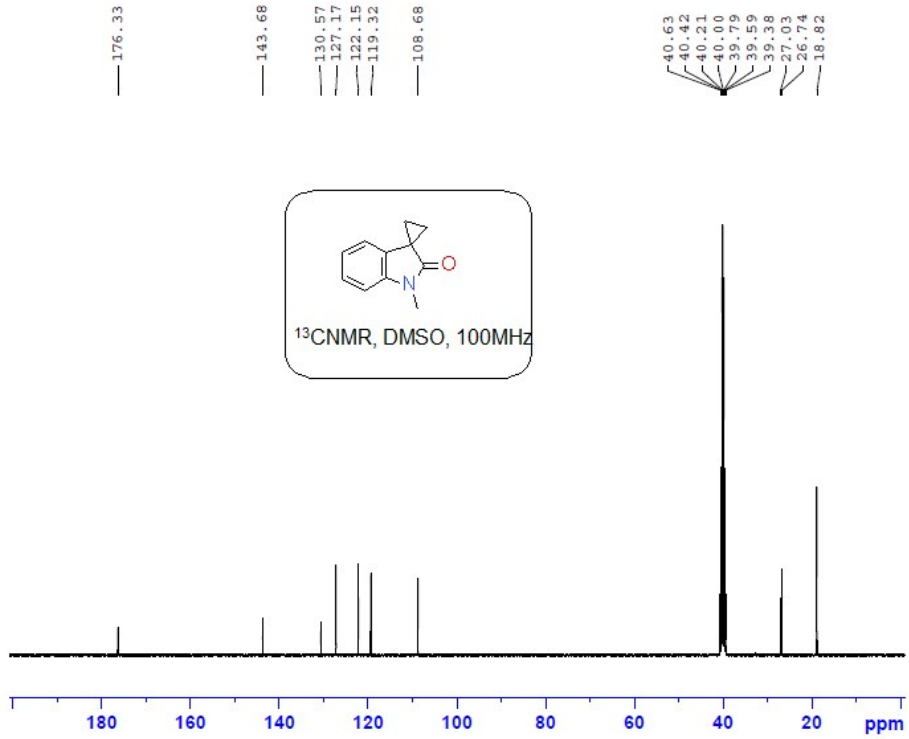


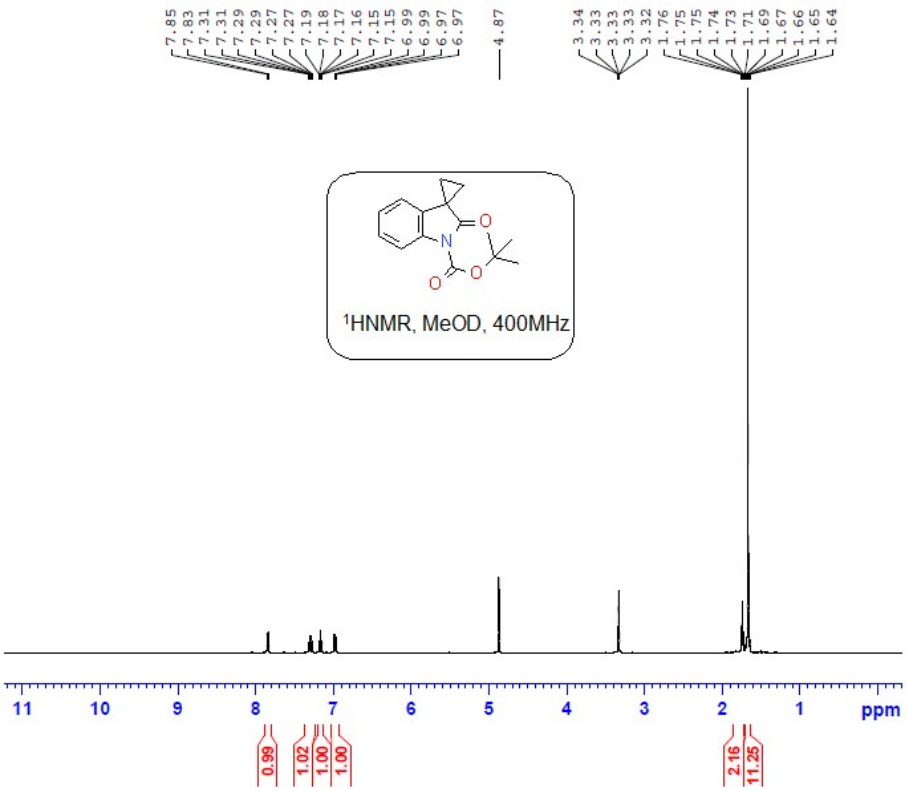
^{1}H NMR of Compond 12a



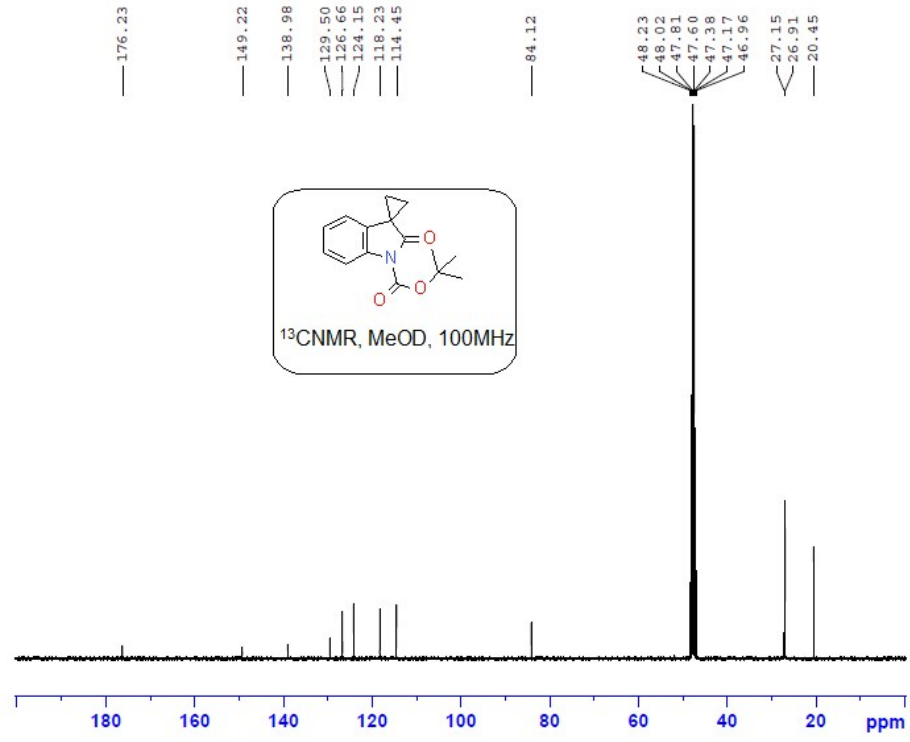
^{13}C NMR of Compond 12a



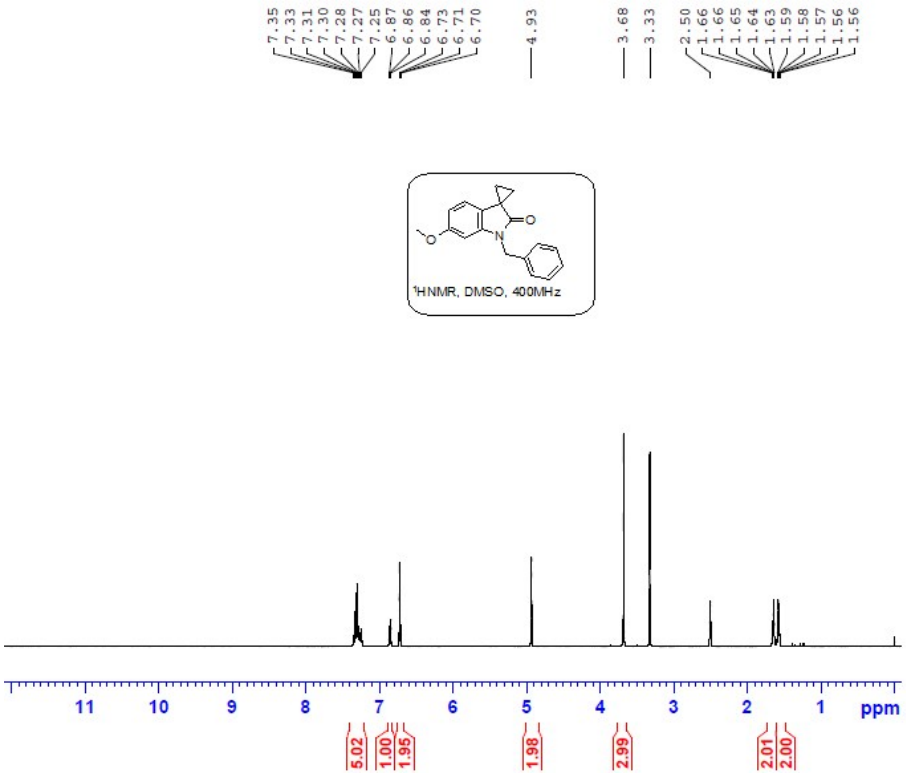
[1]H NMR of Compond 12b



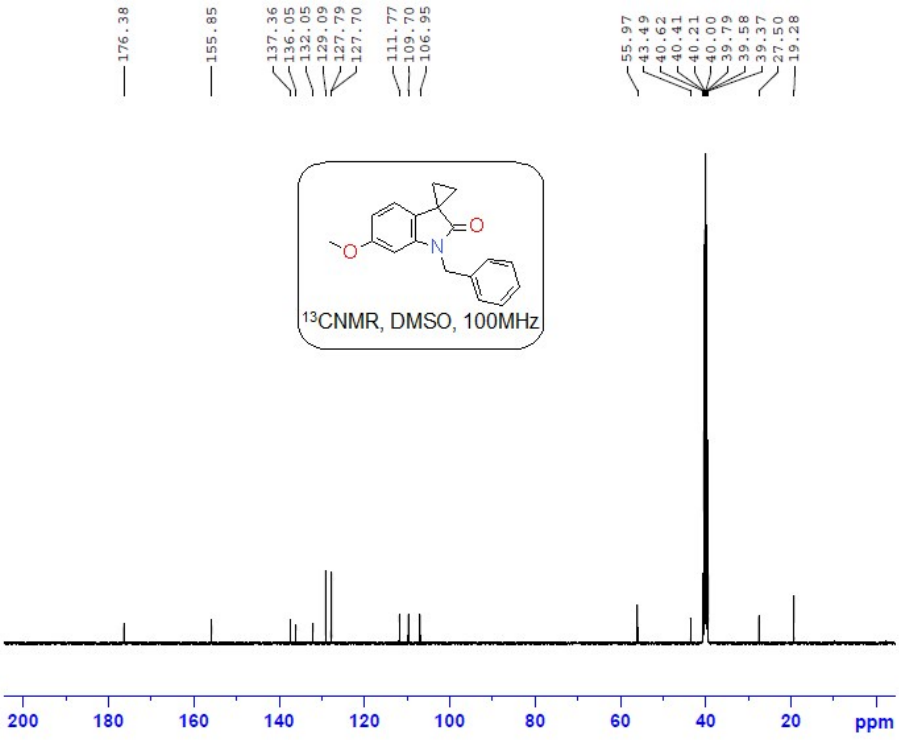
[13]C NMR of Compond 12b



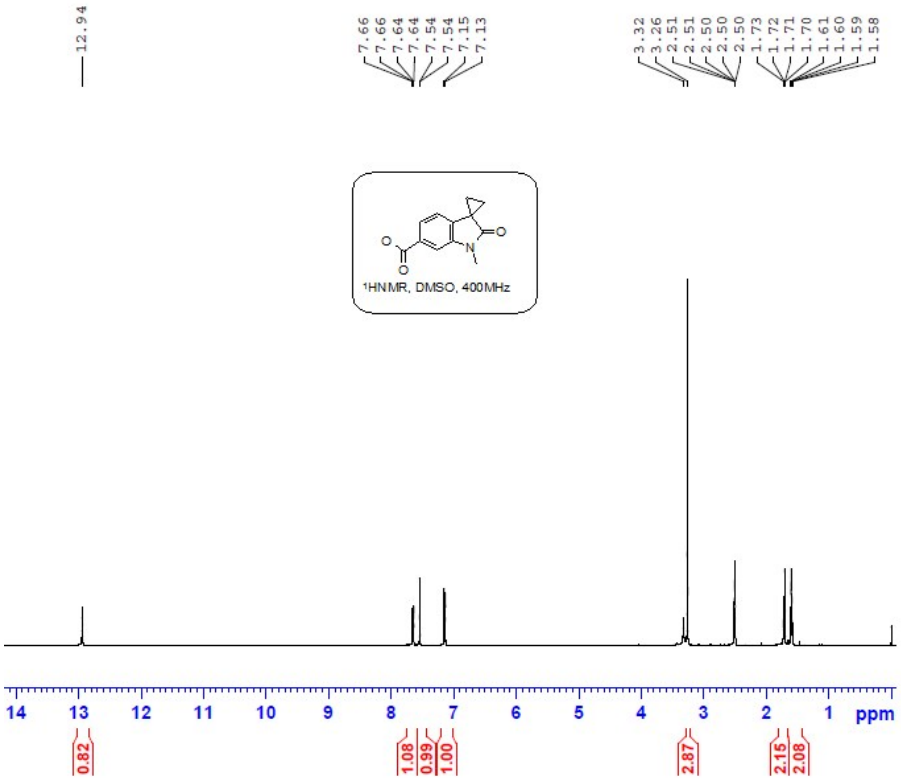
^{1}H NMR of Compond 12c



^{13}C NMR of Compond 12c



[1]H NMR of Compond 12d



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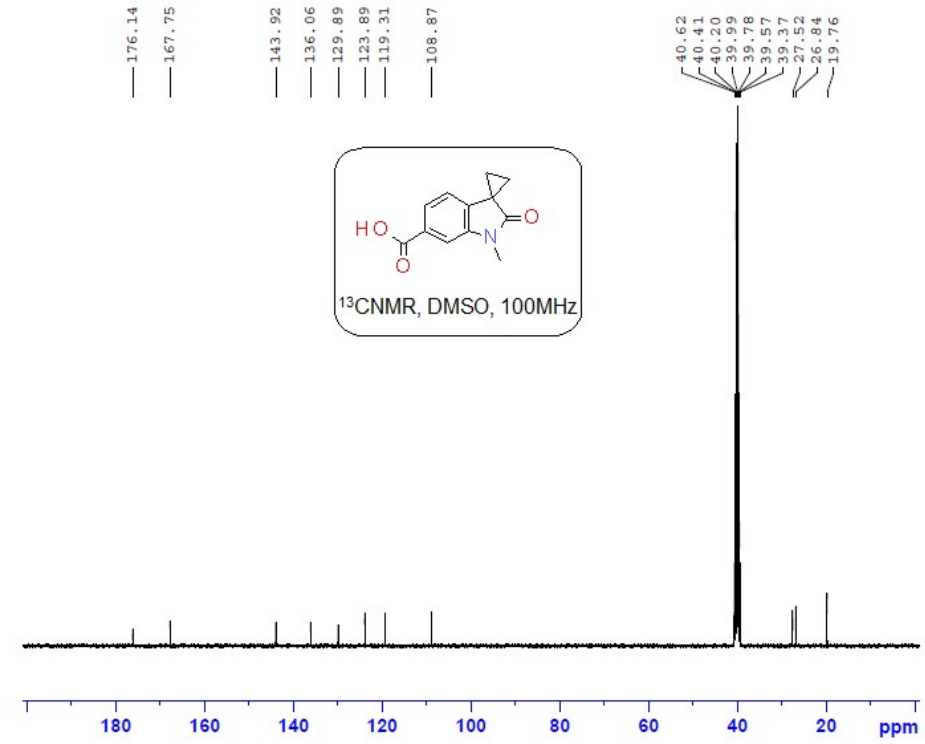

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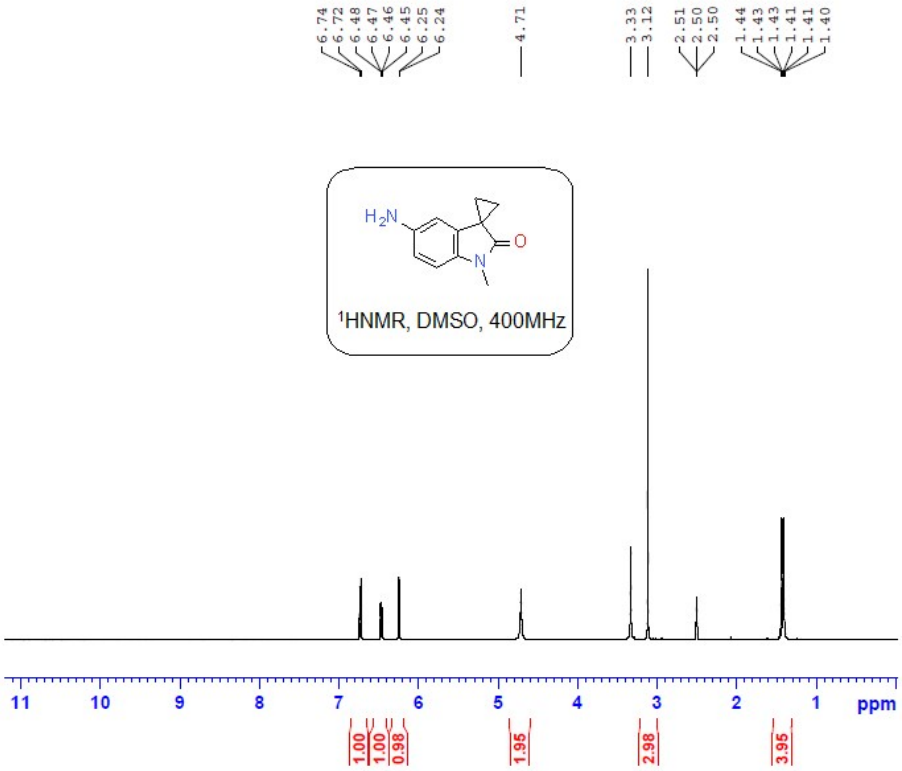

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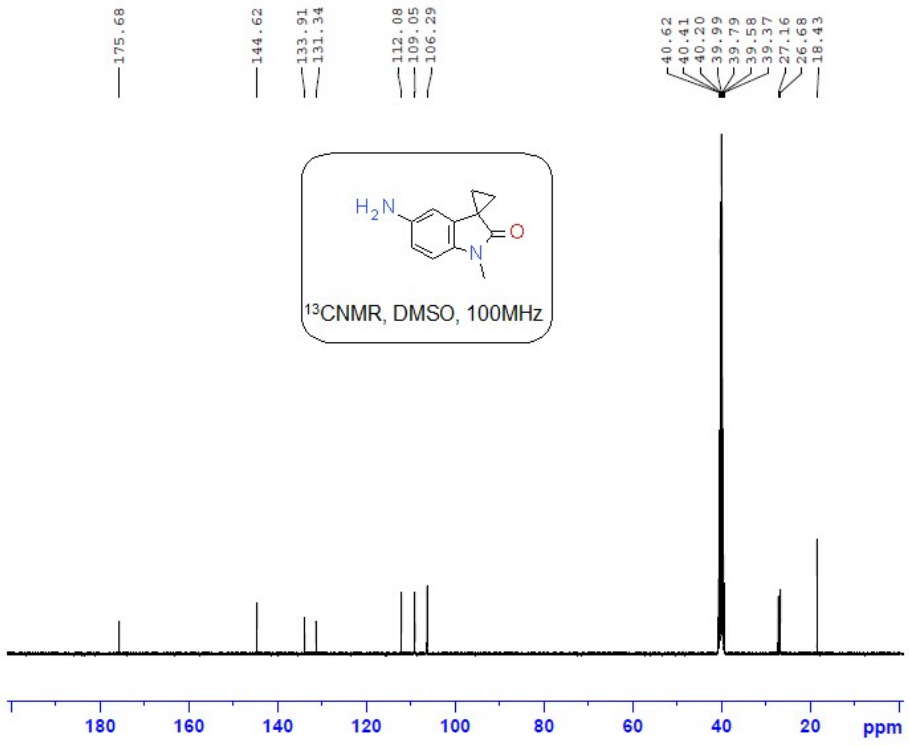
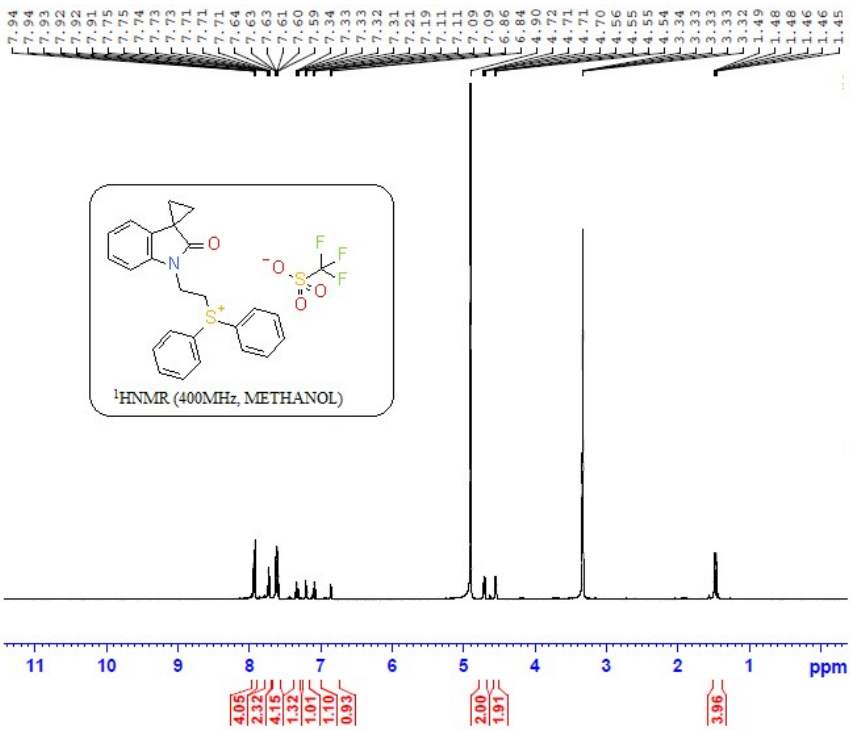


^{1}H NMR of Compond 13a



^{13}C NMR of Compond 13a