Supporting Information for

Rh(III)-Catalyzed [3+2] Spiroannulation of 2,3-Dihydro-1,4-benzoxazines with 4-Hydroxy-2-alkynoates through *ortho*-C-H Bond Functionalization

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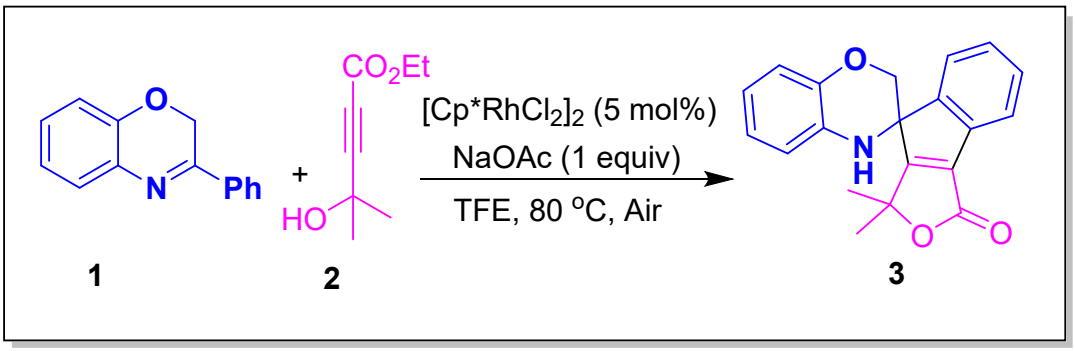
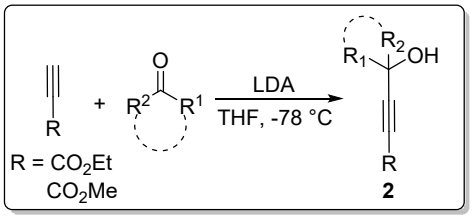


1. General methods

All reagents and solvents were purchased from commercial sources and used without purification. NMR spectra were recorded on300, 400 or 500 MHz spectrometer for ^{1}H NMR, 100 or 125 MHz for ^{13}C NMR spectroscopy. Chemical shifts are reported relative to the residual signals of tetramethylsilane in $CDCl_3$ for ^{1}H and ^{13}C NMR spectroscopy. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of triplets (dt), triplet (t), quartet (q), multiplet (m). HRMS arerecorded using ORBITRAP and ESI mass spectrometer. Column chromatography was performed usingsilica gel (100–200 mesh) as astationary phase. All reactions were monitored by TLC.

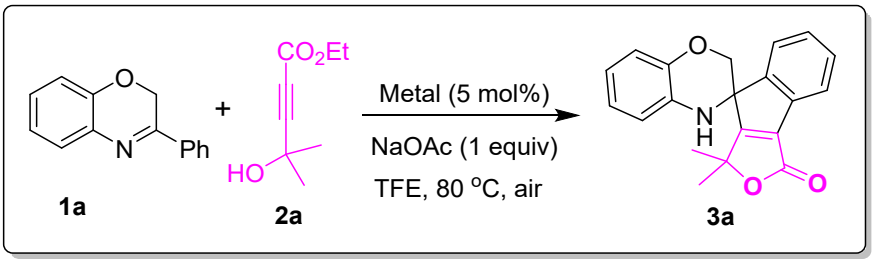
2. Experimental procedures & optimization studies



Preparation of 4-hydroxy-2-alkynoates:

To astirredsolution of alkyl propiolate (4.5 mmol) in tetrahydrofuran (20 mL), lithiumdiisopropylamide(1.6 M in hexane, 4.5 mmol) was added drop wise by syringe at -78 °C. After stirring for 1 h, a solution of ketone (3 mmol) in THF (5 mL) was addedand the mixture was stirred at the same temperature for 2 h. The solution was then allowed to room temperature, and quenched with sat.NH_4Cl and thenextracted with ethyl acetate. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure.The crude product was purified by flash chromatography on silica gel (EtOAc:*n*-Hexanes) to give the desired4-hydroxy-2-alkynoates **2**.

Table S1. Optimization of metal catalyst

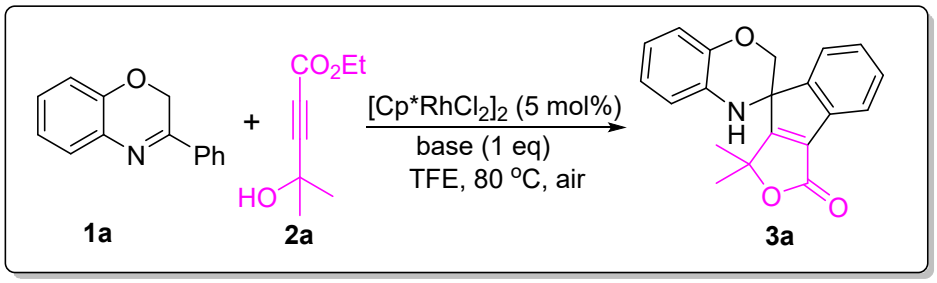


Entry	Metal Catalyst	Yield of **3a**
1	$Pd(OAc)_2$(5mole%)	--
2	--	--
3	$[RuCl_2(p\text{-cymene})]_2$(5 mole%)	trace
4	$[Cp^*RhCl_2]_2$(3 mole%)	60%
5	**$[Cp^*RhCl_2]_2$** (5 mole%)	**85%**
6	$[Cp^*Co(CO)I_2]$ (5 mole%)	--
7	$MnBr(CO)_5$(5 mole%)	--
8	$Co(acac)_2$(5 mole%)	--

9	[Cp*Rh(MeCN)$_3$](SbF$_6$)$_2$(5mole%)	75%

[a]Reaction conditions:**1a** (0.5 mmol), **2a** (0.6 mmol), metal (5 mol %), NaOAc (1 equiv),TFE, 80 °C for 8h, air balloon.

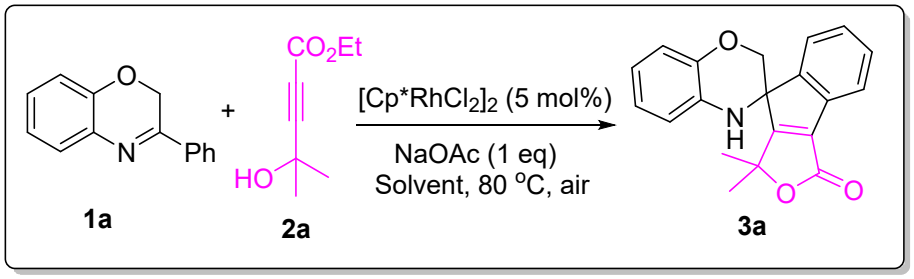
Table S2. Optimization of base



Entry	base	Yield of **3a**
1	KOAc	72%
2	CsOAc	50%
3	**NaOAc**	**85%**
4	K_2CO_3	5%
5	NaOPiv	62%
6	NH_4OAc	---
7	---	---
[b]8	NaOAc	20%
[c]9	NaOAc	73%

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), [RhCp*Cl$_2$]$_2$ (5 mol %), NaOAc (1 equiv), TFE, 80 °C for 8 h, air balloon.[b]0.5 equiv of base, [c]2 equiv of base.

Table S3. Optimization of solvent

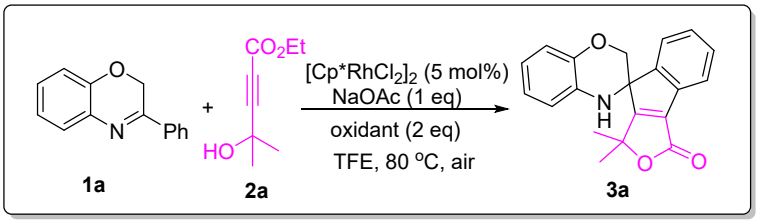


Entry	Solvent	Yield of **3a**
1	THF	22%
2	MeCN	17%
3	Toluene	13%
4	EtOH	10%
5	**TFE**	**85%**

6	DCE	50%
7	1,4-Dioxan	5%

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), $[RhCp^*Cl_2]_2$ (5 mol %), NaOAc (1 equiv), solvent, 80 °C for 8 h, air balloon.

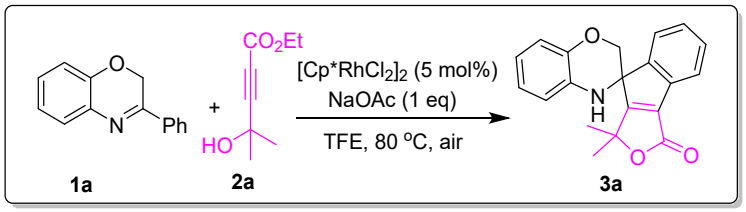
Table S4. Optimization of oxidant



Entry	Oxidant	Yield of **3a**
1	$Cu(OAc)_2.H_2O$	65%
2	AgOAc	68%
3	$Zn(OAc)_2.2H_2O$	54%.
4	$PhI(OAc)_2$	n.r.

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), $[RhCp^*Cl_2]_2$ (5 mol %), NaOAc (1 equiv), oxidant (2 equiv), TFE, 80 °C for 8h, air balloon.

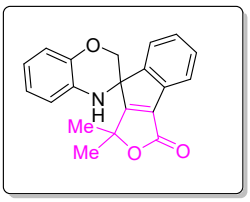
General procedure for title compounds 3a and Characteristic data



To a stirred solutionof 3-aryl-2H-1,4-benzoxazine**1a**(100 mg, 0.5 mmol) and ethyl propiolate**2a** (90 mg, 0.6 mmol) in TFE were added$[RhCp^*Cl_2]_2$ (5 mol %), sodium acetate (40 mg, 0.5mmol) and then the reaction mixture was stirred at 80 °C (oil bath) for overnight under air balloon. After completion of the reaction (as monitored by TLC), TFE was evaporated, water was added, and the contents were extracted with ethyl acetate (2×10 mL). The organic layer was evaporated and the residue was purified by column chromatography (R_f= 0.50) (SiO_2, EtOAc:Hexane, 1:99) to give the product**3a** as a yellow solid in 81% (0.189 g) yield, mp 186-190 °C.

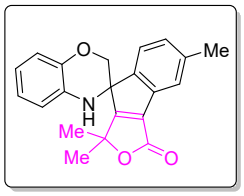
3. Characterization data of the products:

1',1'-Dimethyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan]-3'(*1'H*)-one (3a)



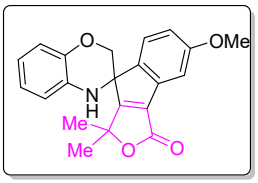
Yellow solid (0.189 g ,81%), mp 186-190 °C.**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.45-7.48 (m, 2H),7.38-7.40 (m, 2H), 6.97 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.85 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.79 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.65 (dd, *J* = 7.7, 1.5 Hz, 1H), 4.55 (d, *J* = 9.2 Hz, 1H), 4.07 (d, *J* = 9.6 Hz, 1H), 3.97 (s, 1H), 1.76 (s, 3H), 1.73 (s, 3H) ; **^{13}C NMR (125 MHz, $CDCl_3$)** δ 178.3, 165.6, 155.0, 143.2, 135.7, 132.1, 131.5, 130.6, 129.1, 125.3, 122.2, 122.1, 119.6, 116.8, 116.3, 82.8, 68.9, 60.8, 25.8, 25.7. **HRMS (ESI)** calcd for $C_{20}H_{18}NO_3$ $[M+H]^+$ 320.1281, found:320.1289.

1',1',5'-Trimethyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan]-3'(*1'H*)-one (3b)



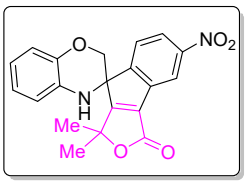
Yellow solid (0.199g,75%),mp 235-240 °C .**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 (d, *J* = 8.3 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 2H), 7.00 – 6.92 (m, 1H), 6.84 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.78 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.64 (dd, *J* = 7.7, 1.4 Hz, 1H), 4.53 (d, *J* = 9.1 Hz, 1H), 4.04 (d, *J* = 9.5 Hz, 1H), 3.93 (s, 1H), 2.42 (s, 3H), 1.75 (s, 3H), 1.72 (s, 3H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.3, 165.7, 152.1, 143.2, 139.2, 136.0, 132.2, 131.7, 131.1, 125.0, 122.8, 122.1, 119.6, 116.8, 116.2,82.7,69.1,60.5,25.8,25.8,21.4;**HRMS(ESI)**calcdfor$C_{21}H_{20}NO_3$$[M+H]^+$334.1437,found: 334.1439.

5'-Methoxy-1',1'-Dimethyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan]-3'(*1'H*)-one (3c)



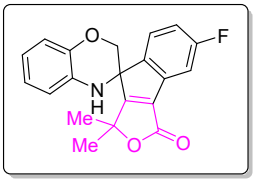
Yellow solid (0.178g,82%),mp 238-240°C .**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.36 (d, *J* = 8.3 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.91 – 6.82 (m, 3H), 6.78 (d, *J* = 7.4 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 4.51 (d, *J* = 9.1 Hz, 1H), 4.06 (d, *J* = 9.2 Hz, 1H), 3.92 (s, 1H), 3.84 (s, 3H), 1.75 (s, 3H), 1.72 (s, 3H);**^{13}C NMR (125 MHz, $CDCl_3$)** δ 177.7, 165.5, 160.5, 146.7, 143.2, 137.1, 133.4, 131.7, 125.9, 122.1, 119.6, 116.8, 116.3, 114.5, 108.9, 82.7, 69.3, 60.3, 55.8, 25.8, 25.7;**HRMS (ESI)**calcd for $C_{21}H_{20}NO_4$$[M+H]^+$350.1386,found:350.1394.

1',1'-Dimethyl-5'-nitro-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan]-3'(*1'H*)-one (3d)



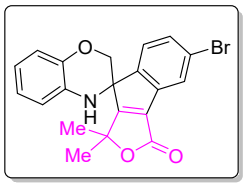
Yellow solid (0.188g,76%),mp 220-224°C;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.42 (d, *J* = 2.0 Hz, 1H), 8.21 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.03 – 6.88 (m, 2H), 6.87 – 6.82 (m, 1H), 6.69 (dd, *J* = 7.7, 1.3 Hz, 1H), 4.48 (d, *J* =8.5 Hz, 1H), 4.25 (dd, *J* = 8.7, 1.6 Hz, 1H), 4.07 (s, 1H), 1.69 (s, 3H), 1.38 (s, 3H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ 183.6, 165.0,154.7,149.2,142.1,134.4,134.3,130.8,125.0,123.4,123.0,120.6,117.2,116.5, 115.8,87.2,69.2,63.8,25.3,24.8;**HRMS(ESI)**calcd for $C_{20}H_{17}N_2O_5[M+H]^+$365.1132,found:365.1142.

5'-Fluoro-1',1'-dimethyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan]-3'(*1'H*)-one (3e)



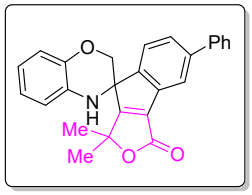
Yellow solid (0.203g,73%),mp 180-185°C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 7.39 (m, 1H), 7.05 (dd, *J* = 8.7, 5.5 Hz, 2H), 6.97 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.86 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.80 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.66 (dd, *J* = 7.7, 1.6 Hz, 1H), 4.54 (d, *J* = 9.1 Hz, 1H), 4.03 (dd, *J* = 7.8, 1.1 Hz, 1H), 3.94 (s, 1H), 1.75 (s, 3H), 1.72 (s, 3H);**^{19}F NMR (376 MHz, $CDCl_3$)** δ -111.61 (d, *J* = 32.6 Hz),**^{13}C NMR (100 MHz, $CDCl_3$) δ** 176.8, 165.1(d, ^{1}JC-F= 251.7 Hz, A-F), 164.2, 143.1, 137.7, 133.7, 131.3, 126.6, 126.5(d, J = 9.3 Hz), 122.3, 119.9, 116.9, 116.8, 116.3, 109.7, 109.5(d, ^{2}JC-F = 24.2 Hz, A-F), 82.7, 68.9, 60.5, 25.8,25.7;**HRMS (ESI)** calcd for $C_{20}H_{17}FNO_3[M+H]^+$338.1187,found: 338.1196

5'-Bromo-1',1'-Dimethyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan]-3'(*1'H*)-one (3f)



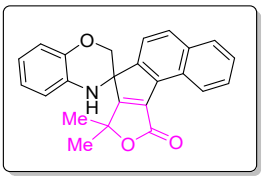
Yellow solid (0.153g,79%),mp 229-232 °C;**^{1}H NMR (500 MHz, $CDCl_3$)**δ 7.80 (s, 1H), 7.46 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.88 (td, *J* = 7.6, 1.2 Hz, 1H), 6.81 (td, *J* = 7.8, 1.3 Hz, 1H), 6.65 (dd, *J* = 7.8, 1.1 Hz, 1H), 4.44 (d, *J* = 6.8 Hz, 1H), 4.17 (dd, *J* = 8.0, 1.8 Hz, 1H), 3.98 (s, 1H), 1.66 (s, 3H), 1.31 (s, 3H) ;**^{13}C NMR (125 MHz, $CDCl_3$)** δ 183.1, 165.6, 142.0, 134.7, 134.6, 131.4, 130.7, 125.6, 124.9, 123.9, 122.8, 120.1, 117.0,115.5, 87.2, 69.5, 63.5, 25.3,24.8;**HRMS(ESI)**calcd for $C_{20}H_{17}BrNO_3[M+H]^+$398.0386 , found:398.0392

1',1'-Dimethyl-5'-phenyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan]-3'(*1'H*)-one (3g)



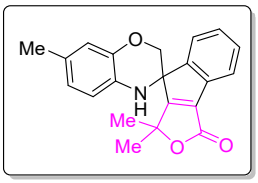
White solid (0.173g,80%),mp 330-335°C .**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.51 – 7.44 (m, 5H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 6.91 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.78 (tt, *J* = 9.2, 4.6 Hz, 1H), 6.73 (td, *J* = 7.8, 1.2 Hz, 1H), 6.59 (dd, *J* = 7.7, 1.1 Hz, 1H), 4.52 (d, *J* = 9.5 Hz, 1H), 4.02 (d, *J* = 10.0 Hz, 1H), 1.72 (s, 3H), 1.69 (s, 3H);**^{13}C NMR (125 MHz, $CDCl_3$)** δ 178.1, 165.6, 153.8, 143.2, 142.8, 140.1, 136.3, 132.8, 131.5, 129.5, 129.0, 128.0, 127.3, 125.5, 122.3, 120.8, 119.7, 116.9, 116.3, 82.8, 68.9, 60.7, 25.9, 25.8; **HRMS(ESI)**calcd for $C_{26}H_{22}NO_3[M+H]^+$396.1594 ,found:396.1589.

8',8'-Dimethyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,7'-benzo[6,7]indeno[1,2-c]furan]-10'(*8'H*)-one (3h)



Brown solid (0.170g,0.84%),mp 222-227°C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.84 (d, *J* = 9.0 Hz, 2H), 7.56 (dd, *J* = 7.0, 1.5 Hz, 2H), 7.04 – 6.96 (m, 1H), 6.90 (d, *J* = 6.5 Hz, 1H), 6.88 – 6.79 (m, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 4.57 (d, *J* =8.8 Hz, 1H), 4.27 (d, *J* = 8.6 Hz, 1H), 1.73 (d, *J* = 7.7 Hz, 3H), 1.36 (d, *J* = 7.6 Hz, 3H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ 182.1, 166.2, 145.5, 142.2, 135.2, 134.1, 132.5, 131.8, 130.2, 128.6, 128.5, 127.1, 126.8, 124.1, 122.7, 120.6, 119.8, 117.0, 115.3, 87.1, 70.4, 63.1, 25.3, 25.0;**HRMS (ESI)**calcd for $C_{24}H_{20}NO_3[M+H]^+$ 370.1437 ,found:370.1442.

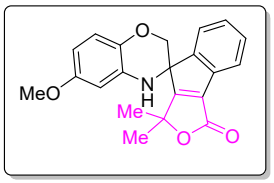
1',1',7-Trimethyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan]-3'(*1'H*)-one (3i)



Brown solid (0.188g,76%),mp 225-230 °C.**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.65 (d, *J* = 7.4 Hz, 1H), 7.41 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.37 (d, *J* = 7.2 Hz, 1H), 7.32 (dd, *J* = 7.5, 0.9 Hz, 1H), 6.75 (s, 1H), 6.68 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.53 (d, *J* = 7.9 Hz, 1H), 4.46 (d, *J* = 7.2 Hz, 1H), 4.15 (dd, *J* = 7.2, 1.7 Hz, 1H), 3.86 (s, 1H), 2.28 (s, 3H), 1.66 (s, 3H), 1.31 (s, 3H);**^{13}C NMR (125 MHz, $CDCl_3$)** δ 182.1, 166.2, 148.3, 142.0, 135.4, 133.0, 129.8, 129.7, 129.1,

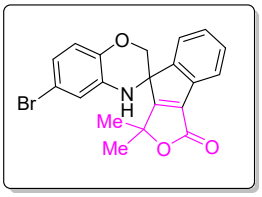
127.8, 124.3, 123.1, 121.6, 117.4, 115.3, 87.0, 70.0, 63.7, 25.4, 25.0, 20.7:**HRMS(ESI)**calcd for $C_{21}H_{20}NO_3$[M+H]348.1468,found:348

6-Methoxy-1',1'-dimethyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan]-3'(*1'H*)-one(3j)



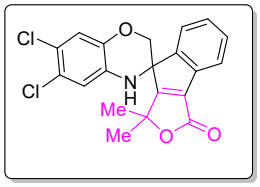
Yellow solid (0.183g,80%),mp 224-230°C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (d, *J* = 7.3 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 3H), 6.86 (d, *J* = 8.8 Hz, 1H), 6.35 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.20 (d, *J* = 2.6 Hz, 1H), 4.42 (d, *J* = 8.2 Hz, 1H), 4.13 (d, *J* = 8.1 Hz, 1H), 3.95 (d, *J* = 9.7 Hz, 1H), 3.74 (d, *J* = 6.1 Hz, 3H), 1.68 (s, 3H), 1.36 (s, 3H), **^{13}C NMR (100 MHz, $CDCl_3$)** δ182.0,166.2,155.2,148.0,136.2,135.3,133.0,132.3,129.8,127.8,124.2,121.6,117.3,104.6,101.0,87.0,69.8,63.7,55.6,25.4,25.1;**HRMS(ESI)**calcdfor$C_{21}H_{20}NO_4$[M+H]$^+$350.1386 ,found:350.1400.

6-Bromo-1',1'-dimethyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan]-3'(*1'H*)-one (3k)



Yellow solid (0.191g,72%),mp 240-245°C.**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.45 (dd, *J* = 8.3, 4.1 Hz, 2H), 7.42 – 7.38 (m, 2H), 6.87 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 1H), 6.77 (d, *J* = 2.1 Hz, 1H), 4.49 (d, *J* = 8.6 Hz, 1H), 4.07 (dd, *J* = 9.0, 1.3 Hz, 1H), 4.03 (s, 1H), 1.76 (s, 3H), 1.73 (s, 3H);**^{13}C NMR (125 MHz, $CDCl_3$)** δ 178.5, 165.6, 154.5, 142.1, 135.5, 133.2, 132.1, 130.7, 129.3, 125.2, 122.2, 121.9, 118.3, 118.2, 114.1, 83.0, 69.0, 60.4, 25.8, 25.7; **HRMS(ESI)** calcd for $C_{20}H_{17}BrNO_3$[M+H]$^+$398.0386,found:398.0380.

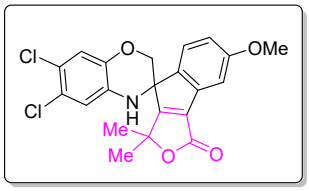
6,7-Dichloro-1',1'-dimethyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]fura]-3'(*1'H*)-one (3l)



Yellow solid (0.178g,78%), mp 280-285°C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 – 7.38 (m, 4H), 7.06 (s, 1H), 6.71 (s, 1H), 4.46 (d, *J* = 8.6 Hz, 1H), 4.11 (d, *J* = 6.3 Hz, 1H), 4.07 (s, 1H), 1.76 (s, 3H), 1.73 (s, 3H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.5, 165.4, 153.9, 142.1,

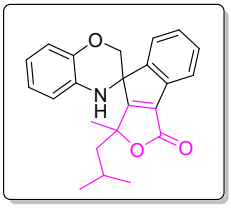
135.6, 132.1, 131.5, 130.7, 129.5, 125.2, 124.9, 122.3, 121.7, 118.3, 116.5, 82.9, 69.2, 60.3, 25.7, 25.7;**HRMS(ESI)**calcd for $C_{20}H_{16}Cl_2NO_3[M+H]^+$388.0501,found: 388.0488

6,7-Dichloro-5'-methoxy-1',1'-dimethyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan]-3'(*1'H*)-one(3m)



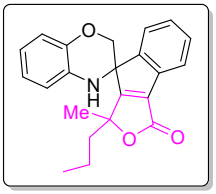
White solid (0.171g,79%),mp 226-230°C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 (d, *J* = 9.0 Hz, 1H), 7.05 (s, 1H), 6.91 (s, 2H), 6.70 (s, 1H), 4.41 (d, *J* = 8.5 Hz, 1H), 4.08 (d, *J* = 8.6 Hz, 1H), 4.01 (s, 1H), 3.86 (s, 3H), 1.74 (s, 3H), 1.71 (s, 3H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.9, 165.4, 160.8, 145.4, 142.2, 137.0, 133.5, 131.7, 125.8, 124.8, 121.6, 118.3, 116.4, 114.5,109.1,82.8,69.6,59.8,55.8,25.7,25.7;**HRMS(ESI)**calcdfor $C_{21}H_{18}Cl_2NO_4[M+H]^+$418.0607 found: 418.0590.

1'-Isobutyl-1'-methyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan]-3'(*1'H)*-one (3n)



Yellow solid (0.222g,78%),mp 170-175°C. **^{1}H NMR (400 MHz, $CDCl_3$)**) δ 7.46 (m, 2H), 7.38 (m, 2H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.86 (t, *J* = 7.0 Hz, 1H), 6.79 (t, *J* = 7.0 Hz, 1H), 6.67 (d, *J* = 6.7 Hz, 1H), 4.58 (d, *J* = 9.5 Hz, 1H), 4.03 (d, *J* = 9.0 Hz, 1H), 3.92 (s, 1H), 2.10 (dd, *J* = 10.0, 5.1 Hz, 1H), 1.81 (ddd, *J* = 10.5, 12.5, 5.5 Hz, 2H), 1.69 (s, 3H), 0.98 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 6.4 Hz, 3H);**^{13}CNMR (100 MHz, $CDCl_3$)** δ 177.9, 165.9, 155.0, 143.1, 136.1, 132.4, 131.5, 130.5, 129.1, 125.3, 122.2, 122.2, 119.6, 116.9, 116.3, 85.5, 68.8,60.8,46.8,25.4,24.4,24.3,24.0;**HRMS(ESI)**calcdfor$C_{23}H_{24}NO_3[M+H]^+$362.1750,found:362.1762.

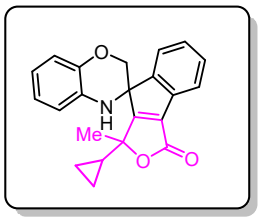
1'-Methyl-1'-propyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan]-3'(*1'H*)-one (3o)



Yellow solid (0.240g,69%),mp 186-190 °C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 (dd, *J* = 8.6, 7.1 Hz, 4H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 6.9 Hz, 1H), 6.79 (d, *J* = 7.0 Hz, 1H), 6.66

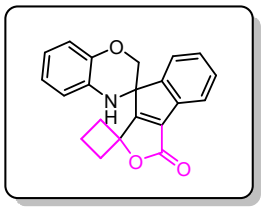
(d, *J* = 7.6 Hz, 1H), 4.57 (d, *J* = 9.1 Hz, 1H), 4.04 (d, *J* = 9.2 Hz, 1H), 3.92 (s, 1H), 2.15 – 2.04 (m, 1H), 2.00 – 1.86 (m, 1H), 1.70 (s, 3H), 1.26 (dd, *J* = 9.8, 5.9 Hz, 2H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.5, 165.9, 155.1, 143.1, 136.3, 132.3, 131.5, 130.6, 129.0, 125.3, 122.2, 119.6, 116.9, 116.3, 85.4, 68.8, 60.8, 50.6, 40.5, 24.6, 17.2, 14.0;**HRMS(ESI)**calcd for $C_{21}H_{20}NO_3[M+H]^+$ 348.1468,found:348.1476.

1'-Cyclopropyl-1'-methyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan]-3'(*1'H*)-one(3q)



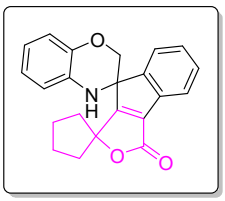
White solid (0.180 g,79%), mp 180-183 °C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 – 7.41 (m, 3H), 7.40 -7.34 (m, 1H), 6.97 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.86 (td, *J* = 7.5, 1.5 Hz, 1H), 6.79 (td, *J* = 7.6, 1.6 Hz, 1H), 6.69 -6.63 (m, 1H), 4.56 (dd, *J* = 9.9, 5.0 Hz, 1H), 4.05 - 4.00 (m, 1H), 3.96 (s, 1H), 1.72 (s, 3H), 1.37 (ddd, *J* = 10.0, 7.6, 5.9 Hz, 1H), 0.75 - 0.62 (m, 2H), 0.58 - 0.47 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.7, 163.5, 152.9, 140.9, 133.3, 130.0, 129.3, 128.3, 126.8, 123.1, 120.3, 120.0, 117.3, 114.6, 114.1, 81.7, 66.6, 58.5, 21.2, 16.3, 0.0, -0.7.**HRMS (ESI)** calcd for $C_{22}H_{19}NO_3$ $[M+H]^+$ 346.1461, found:346.1469.

1'-Cyclobutyl-1'-methyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan]-3'(*1'H*)-one(3r)



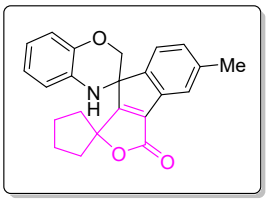
White solid (0.186 g,80 %), mp 189-192 °C.**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.56 (d, *J* = 7.4 Hz, 1H), 7.32 (ddd, *J* = 7.6, 5.9, 2.2 Hz, 2H), 7.24 (td, *J* = 7.6, 1.1 Hz, 1H), 6.93 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.84 (td, *J* = 7.6, 1.4 Hz, 1H), 6.76 - 6.72 (m, 1H), 6.61 (dd, *J* = 7.8, 1.5 Hz, 1H), 4.38 (d, *J* = 10.9 Hz, 1H), 4.21 (d, *J* = 9.0 Hz, 1H), 2.98 - 2.82 (m, 1H), 2.53 (dddd, *J* = 9.3, 6.6, 4.2, 1.8 Hz, 1H), 2.46 -2.35 (m, 1H), 2.35 -2.21 (m, 1H), 1.88 (dtt, *J* = 10.0, 10.1, 6.5 Hz, 1H), 1.48 – 1.34 (m, 1H) ;**^{13}C NMR (126 MHz, $CDCl_3$)** δ 177.1, 166.0, 148.7, 142.7, 135.9, 132.6, 131.7, 129.8, 127.9, 124.2, 122.8, 121.7, 119.9, 117.2, 115.4, 88.5, 69.9, 63.85, 31.8,31.6,13.5.**HRMS (ESI)** calcd for $C_{21}H_{17}NO_3[M+H]^+$ 332.1286, found:332.1291.

***2H,3'H,4H*-Dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cyclopentan]-3'-one (5a)**



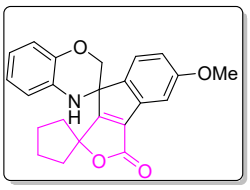
Yellow solid (0.203g, 83%), mp 235-239 °C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 -7.44 (m, 1H), 7.43 -7.33 (m, 3H), 6.97 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.85 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.78 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.65 (dd, *J* = 7.7, 1.6 Hz, 1H), 4.58 (d, *J* = 8.5 Hz, 1H), 4.06 (dd, *J* = 8.6, 1.1 Hz, 1H), 3.98 (s, 1H), 2.31 -2.20 (m, 2H), 2.19 -2.08 (m, 4H), 2.03 -1.93 (m, 2H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.8, 165.9, 155.2, 136.2, 132.2, 131.6, 130.5, 129.0, 125.3, 122.2, 121.9, 119.6, 116.8, 116.3, 92.7, 68.8, 60.8, 37.7, 37.7, 29.7, 25.2, 25.2; **HRMS (ESI)**calcd for $C_{22}H_{20}NO_3$ $[M+H]^+$346.1437 ,found :346.1445.

5'-Methyl-*2H,3'H,4H*-dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cyclopentan]-3'-one (5b)



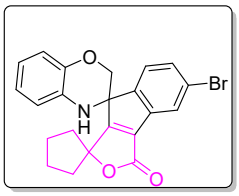
Yellow solid (0.221g,73%),mp 134-140 °C.**^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.27 (d, *J* = 7.8 Hz, 1H), 7.12 – 7.06 (m, 2H), 6.89 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.77 (td, *J* = 7.6, 1.5 Hz, 1H), 6.71 (td, *J* = 7.7, 1.5 Hz, 1H), 6.57 (dd, *J* = 7.7, 1.5 Hz, 1H), 4.48 (d, *J* = 9.5 Hz, 1H), 3.97 (d, *J* = 9.0 Hz, 1H), 2.34 (s, 3H), 2.17 (td, *J* = 9.8, 6.5 Hz, 2H), 2.09 – 2.01 (m, 4H), 1.93 (t, *J* = 10.0 Hz, 2H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.8, 165.9, 152.3, 143.2, 139.1, 136.5, 132.5, 131.7, 131.1, 125.0, 122.6, 122.1, 119.5, 116.8, 116.3, 92.7, 69.0, 60.5, 37.7, 37.7, 25.2, 25.2, 21.4;**HRMS(ESI)**calcd for $C_{23}H_{22}NO_3$ $[M+H]^+$360.1594,found:360.1601.

5'-Methoxy-*2H,3'H,4H*-Dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cyclopentan]-3'-one (5c)



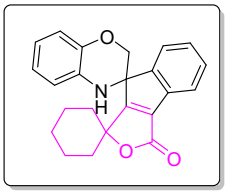
Yellow solid (0.191g,82%),mp 219-225°C .**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.33 (m, 1H), 6.96 (dd, *J* = 5.8, 4.3 Hz, 1H), 6.89 – 6.80 (m, 3H), 6.77 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.63 (dd, *J* = 7.7, 1.6 Hz, 1H), 4.53 (d, *J* = 8.4 Hz, 1H), 4.03 (d, *J* = 8.6 Hz, 1H), 3.92 (d, *J* = 9.1 Hz, 1H), 3.83 (s, 3H), 2.26 – 2.18 (m, 2H), 2.18 – 2.07 (m, 4H), 2.02 -1.94 (m, 2H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.3, 160.4, 146.9, 143.2, 133.6, 131.8, 125.9, 122.1, 119.5, 116.8, 116.3, 114.4, 108.8, 92.6, 69.2, 60.3, 55.8, 37.7, 37.6, 25.2, 25.2; **HRMS(ESI)**calcd for $C_{23}H_{22}NO_4$$[M+H]^+$376.1543 $[M+H]^+$,found:376.1557.

5'-Bromo-*2H,3'H,4H*-Dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cyclopentan]-3'-one(5d)



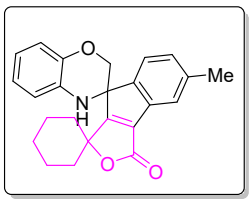
Yellow solid (0.193g,76%),mp 190-196°C .**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79 (s, 1H), 7.45 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.25 (d, *J* = 5.7 Hz, 1H), 6.94 – 6.85 (m, 2H), 6.78 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.63 (dd, *J* = 7.8, 1.2 Hz, 1H), 4.43 (d, *J* = 8.0 Hz, 1H), 4.19 (dd, *J* = 8.5, 1.6 Hz, 1H), 4.00 (s, 1H), 2.57 – 2.43 (m, 1H), 1.91 (dd, *J* = 9.1, 6.3 Hz, 2H), 1.77 (dd, *J* = 9.3, 10.0 Hz, 3H), 1.69 – 1.62 (m, 2H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ 180.3, 147.2, 142.1, 135.5, 134.7, 131.2, 130.6, 125.6, 124.7, 123.9, 122.8, 120.1, 117.1, 115.4, 96.9, 69.6, 63.5, 36.5, 25.0, 24.8;**HRMS(ESI)** calcd for $C_{22}H_{19}Br\ NO_3[M+H]^+$424.0542,found:424.0541.

***2H,3'H,4H*-Dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cyclohexan]-3'-one (5e)**



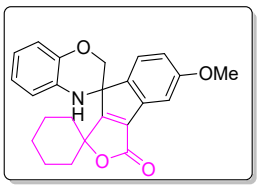
Yellow solid (0.202 g, 85%), mp 224-226 °C .**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.47 -7.39 (m, 1H), 7.36 (dd, *J* = 8.9, 6.8, Hz, 1H), 7.63 – 6.17 (m, 3H), 6.97 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.82 (dd, *J* = 8.5, 7.5, Hz, 1H), 6.65 (dd, *J* = 7.7, 1.6 Hz, 1H), 4.60 (d, *J* = 8.5 Hz, 1H), 4.01 (dd, *J* = 8.6, 1.3 Hz, 1H), 3.96 (s, 1H), 2.04 – 1.75 (m, 10H);**^{13}CNMR (100 MHz, $CDCl_3$)** δ 178.5, 166.0, 155.3, 143.1, 135.4, 132.2, 131.5, 130.5, 1289, 125.3, 122.3, 122.2, 119.6, 116.8, 116.3, 84.7, 68.8, 60.7, 34.8, 34.8, 24.6, 21.7, 21.7;**HRMS (ESI)**calcd for $C_{23}H_{22}NO_3$ $[M+H]^+$ 360.1594 ,found:360.1604.

5'-Methyl-*2H,3'H,4H*-dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cyclohexan]-3'-one (5f)



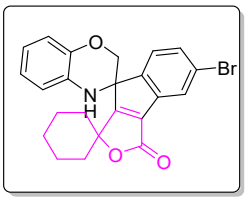
Yellow solid (0.220g,76%),mp 236-240 °C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 (d, *J* = 7.8 Hz, 1H), 7.22 (s, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.95 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.83 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.77 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.63 (dd, *J* = 7.7, 1.5 Hz, 1H), 4.56 (d, *J* = 8.5 Hz, 1H), 3.99 (dd, *J* = 8.6, 0.9 Hz, 1H), 3.93 (s, 1H), 2.41 (s, 3H), 2.04 – 1.77 (m, 10H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.5, 166.1, 152.4, 143.2, 139.1, 135.6, 132.4, 131.7, 131.1, 125.0, 123.0, 122.1, 119.5, 116.8, 116.3, 69.0, 60.4, 34.8, 34.8, 24.6, 21.7, 21.7, 21.4;**HRMS(ESI)**calcd for $C_{24}H_{24}NO_3$ $[M+H]^+$374.1750 , found:374.1755.

5'-Methoxy-*2H,3'H,4H*-Dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cyclohexan]-3'-one (5g)



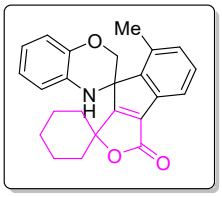
Yellow solid (0.193g,84%), mp 228-231 °C .**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35 (d, *J* = 8.4 Hz, 1H), 6.98 – 6.91 (m, 2H), 6.87 – 6.81 (m, 2H), 6.77 (td, *J* = 7.6, 1.6 Hz, 1H), 6.63 (dd, *J* = 7.7, 1.6 Hz, 1H), 4.55 (d, *J* = 9.4 Hz, 1H), 4.00 (d, *J* = 9.0 Hz, 1H), 3.84 (s, 3H), 2.01 – 1.74 (m, 10H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.9, 165.9, 160.4, 147.1, 143.2, 136.7, 133.6, 131.7, 125.9, 122.1, 119.5, 116.8, 116.3, 114.4, 109.1, 84.6, 69.2, 60.2, 55.8, 34.8, 34.7, 24.6, 21.7, 21.7;**HRMS(ESI)**calcd for $C_{24}H_{24}NO_4$[M+H]$^+$390.1699 found:390.1707.

5'-Bromo-*2H,3'H,4H*-Dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cyclohexan]-3'-one (5h)



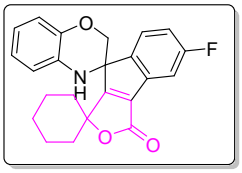
Yellow solid (0.187g,81%),mp 266-270°C .**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 1.7 Hz, 1H), 7.46 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 6.96 (dd, *J* = 7.9, 1.2 Hz, 1H), 6.85 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.79 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.65 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.58 (d, *J* = 8.5 Hz, 1H), 3.97 (d, *J* = 8.6 Hz, 1H), 3.95 (s, 1H), 2.05-1.89(m, 10H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 177.0, 165.5, 154.0, 142.9, 136.7, 134.0, 133.0, 131.2, 126.7, 125.3, 122.8, 122.4, 119.8, 116.9, 116.4, 84.7, 68.5, 60.6, 34.8, 34.7, 24.5, 21.7;**HRMS(ESI)**calcd for $C_{23}H_{21}Br\ NO_3$[M+H]$^+$438.0699 ,found:438.0692.

7'-Methyl-*2H,3'H,4H*-dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cyclohexan]-3'-one (5i)



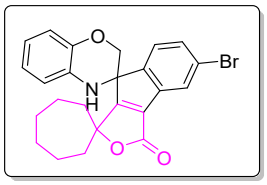
Yellow solid (0.215g,78%),mp 190-196 °C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33 (d, *J* = 7.5 Hz, 1H), 7.23 (dd, *J* = 8.2, 8.1 Hz, 2H), 6.97 (d, *J* = 7.7 Hz, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 7.2 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 1H), 4.65 (d, *J* = 8.7 Hz, 1H), 4.07 (d, *J* = 8.6 Hz, 1H), 3.87 (s, 1H), 2.52 (s, 3H), 2.03 – 1.72 (m, 10H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ 175.7, 165.8, 148.3, 143.6, 139.4 137.4, 133.8, 132.9, 131.8, 129.4, 122.0, 120.1, 119.4, 117.0, 115.4, 83.9, 68.4, 63.4,34.7,24.6,21.7,17.8;**HRMS (ESI)** calcd for $C_{24}H_{24}NO_3$[M+H]$^+$374.1750,found: 374.1738.

5'-Fluoro-*2H,3'H,4H*-dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cyclohexan]-3'-one (5j)



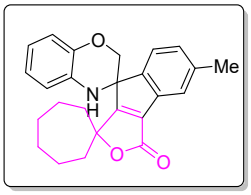
White solid (0.224g,74%),mp 269-273°C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 (dd, *J* = 8.4, 4.9 Hz, 1H), 7.11 (dd, *J* = 7.9, 2.3 Hz, 1H), 7.03 (dd, *J* = 8.9, 2.4 Hz, 1H), 6.96 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.86 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.79 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.65 (dd, *J* = 7.7, 1.6 Hz, 1H), 4.57 (d, *J* = 8.5 Hz, 1H), 3.99 (d, *J* = 8.6 Hz, 1H), 3.94 (s, 1H), 1.97 – 1.78 (m, 10H);**^{19}F NMR (471 MHz, $CDCl_3$)** δ -111.87 (s);**^{13}C NMR (100 MHz, $CDCl_3$)** δ 177.0, 165.5, 164.1(d, ^{1}JC-F= 251.9 Hz, A-F), 164.0, 162.1, 150.8, 143.0, 137.3, 133.9, 133.9, 131.3, 126.5, 126.5, 122.3, 119.7(d, J = 6.5 Hz), 116.9, 116.9, 116.7, 116.4(d, ^{2}JC-F = 25.6 Hz, A-F), 84.7,68.8,60.4,34.8,34.7,24.5,21.7,21.69;**HRMS(ESI)**calcd for $C_{23}H_{20}FNO_3$[M+H]$^+$378.1477 ,found:378.1479.

5'-Bromo-*2H,3'H,4H*-dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cycloheptan]-3'-one(5k)



Brown solid (0.189g,83%),mp 256-260°C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 1.6 Hz, 1H), 7.47 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 6.96 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.85 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.79 (dd, *J* = 7.7, 1.6 Hz, 1H), 6.65 – 6.62 (m, 1H), 4.56 (d, *J* = 8.5 Hz, 1H), 3.98 (s, 1H), 3.93 (s, 1H), 2.14 – 1.92 (m, 6H), 1.88 – 1.65 (m, 6H);**^{13}C NMR (100 MHz, $CDCl_3$)** δ 178.1, 165.5, 154.2, 142.9, 135.6, 134.0, 133.1, 131.2, 126.7, 125.5, 122.8, 122.4, 119.7, 116.9, 116.4, 88.7, 68.5, 60.4, 38.0, 38.0, 28.7, 23.0, 23.0;**HRMS(ESI)**calcd for $C_{24}H_{22}BrNO_3$[M+H]$^+$ 452.0639, found:452.0642.

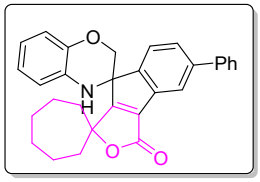
5'-Methyl-*2H,3'H,4H*-dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cycloheptan]-3'-one (5l)



Brown solid (0.197g,84%),mp 243-250°C;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (s, 1H), 7.29 – 7.20 (m, 2H), 7.10 (d, *J* = 7.5 Hz, 1H), 6.86 (dd, *J* = 8.7, 7.5 Hz, 3H), 6.62 (d, *J* = 7.3 Hz, 1H), 4.39 (d, *J* = 8.9 Hz, 1H), 4.19 (d, *J* = 9.0 Hz, 1H), 3.88 (s, 1H), 2.39 (s, 3H), 1.94 – 1.50 (m, 12H).**^{13}C NMR (100 MHz, $CDCl_3$)** δ 182.8, 166.8, 145.6, 142.2, 140.0, 134.6, 132.9,

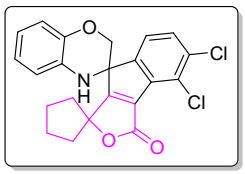
131.8, 123.9, 122.6, 122.3, 119.8, 117.0, 115.4, 92.2, 69.8, 63.6, 37.4, 37.0, 27.6, 27.5, 22.6,22.3,21.4;**HRMS (ESI)**calcd for $C_{25}H_{26}NO_3[M+H]^+$388.1907,found:388.1891.

5'-Phenyl-*2H,3'H,4H*-dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cycloheptan]-3'-one (5m)



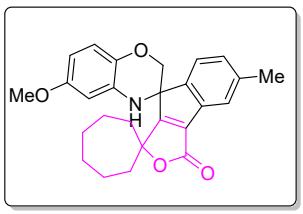
Yellow solid (0.182g,80%),mp 256-260°C;**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.52 (dd, *J* = 8.9, 8.1, Hz, 7H), 7.41 (d, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 6.9 Hz, 1H), 6.86 (dd, *J* = 7.4, 6.4 Hz, 1H), 6.80 (dd, *J* = 7.5, 6.4 Hz, 1H), 6.69 – 6.64 (m, 1H), 4.62 (d, *J* = 8.5 Hz, 1H), 4.05 (d, *J* = 8.6 Hz, 1H), 3.98 (s, 1H), 2.22 – 1.94 (m, 6H), 1.90 – 1.66 (m, 6H);**^{13}C NMR (100 MHz, $CDCl_3$)**δ 182.9, 166.6, 147.4, 143.1, 142.3, 140.1, 134.6, 133.5, 131.6, 128.9, 127.8, 127.2, 126.6, 124.5, 122.7, 120.3, 119.9, 117.0, 115.5, 92.3, 69.7, 63.6, 37.5, 37.0, 27.7, 27.5, 22.6, 22.4;**HRMS (ESI**) calcd for $C_{30}H_{28}NO_3[M+H]^+$450.2063,found:450.2044.

4',5'-Dichloro-*2H,3'H,4H*-dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cyclopentan]-3'-one (5n)



White solid (0.159g,78%),mp 252-256°C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.71 (s, 1H), 7.46 (s, 1H), 6.90 (dd, *J* = 8.0, 7.9 Hz, 2H), 6.80 (d, *J* = 7.1 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 4.41 (d, *J* = 8.0 Hz, 1H), 4.21 (dd, *J* = 8.1, 1.5 Hz, 1H), 4.02 (s, 1H), 2.55 – 2.43 (m, 1H), 1.97 – 1.87 (m, 2H), 1.85 – 1.74 (m, 3H), 1.65 (dd, *J* = 11.4, 7.5 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 180.2, 165.4, 148.1, 142.1, 135.1, 134.1, 132.5, 131.9, 130.9, 126.4, 123.1, 122.9, 120.3, 117.1, 115.5, 97.0, 69.5, 63.5, 36.6, 25.0, 24.8; **HRMS(ESI)** calcd for $C_{22}H_{17}Cl_2NO_3[M+H]^+$ 414.0634 , found: 414.0618.

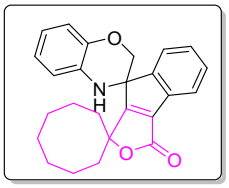
6-Methoxy-5'-methyl-*2H,3'H,4H*-dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cycloheptan]-3'-one (5o)



Yellow solid (0.198g,83%),mp 186-190°C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.34 (d, *J* = 7.8 Hz, 1H), 7.22 (s, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 1H), 6.33 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.20 (d, *J* = 2.8 Hz, 1H), 4.50 (d, *J* = 8.6 Hz, 1H), 3.93 (d, *J* = 8.3 Hz, 1H), 3.92 (s,

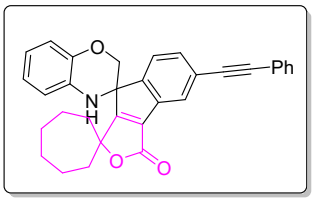
1H), 3.72 (s, 3H), 2.42 (s, 3H), 2.17 – 1.94 (m, 6H), 1.86 -1.68 (m, 6H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 179.7, 166.1, 154.9, 152.6, 139.0, 137.3, 134.4, 132.3, 132.2, 131.1, 125.0, 123.2, 117.1, 104.5, 101.8, 88.6, 69.0, 60.4, 55.5, 38.0, 29.7, 28.8, 23.1, 23.0, 21.5; **HRMS(ESI)** calcd for $C_{26}H_{28}NO_4[M+H]^+$418.2012,found:418.1996.

***2H,3'H,4H*-Dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cyclooctan]-3'-one (5p)**



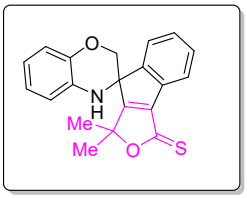
Yellow solid (0.232 g,80%),mp 190-196 °C.**^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.65 (d, *J* = 7.4 Hz, 1H), 7.39 (dd, *J* = 8.4, 8.2, Hz, 2H), 7.32 – 7.25 (m, 1H), 6.97 (dd, *J* = 8.0, 1.1 Hz, 1H), 6.88 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.79 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.63 (dd, *J* = 7.8, 1.5 Hz, 1H), 4.43 (d, *J* = 8.0 Hz, 1H), 4.21 (d, *J* = 8.6, 6.3 Hz, 1H), 3.93 (s, 1H), 2.40 (dd, *J* = 8.2, 8.3 Hz, 1H), 2.06 – 1.29 (m, 13H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 183.4, 166.6, 148.5, 142.2, 134.9, 132.9, 131.8, 129.7, 127.8, 124.2, 122.6, 121.5, 119.8, 117.1, 115.5, 91.6, 69.8, 63.8, 33.7, 29.7, 27.6, 27.5, 21.8, 21.4, 21.1; **HRMS(ESI)**calcd for $C_{25}H_{26}NO_3[M+H]^+$388.1907 found:388.1913.

5'-(Phenylethynyl)-*2H,3'H,4H*-dispiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan-1',1''-cycloheptan]-3'-one(5k′)



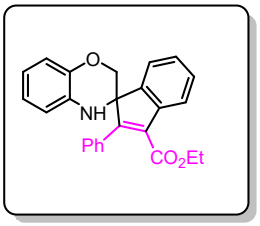
Yellow solid (0.190g,0.86%),mp 212-218°C.**^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.58 – 7.53 (m, 3H), 7.50 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.42 (d, *J* = 5.8 Hz, 1H), 7.40 – 7.35 (m, 3H), 6.98 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.86 (d, *J* = 7.6, 1.5 Hz, 1H), 6.80 (d, *J* = 7.7, 1.6 Hz, 1H), 6.66 (dd, *J* = 7.8, 1.5 Hz, 1H), 4.60 (d, *J* = 8.5 Hz, 1H), 4.01 (d, *J* = 8.6 Hz, 1H), 3.96 (s, 1H), 2.22 – 1.94 (m, 6H), 1.89 – 1.67 (m, 6H). **^{13}C NMR (125 MHz, $CDCl_3$)** δ 178.9, 165.7, 135.0, 133.7, 132.4, 131.7, 128.8, 128.5, 125.3, 125.2, 124.3, 124.1, 122.5, 122.3, 117.0, 116.5, 88.7, 88.2, 68.6, 60.6, 38.0, 29.7, 28.7, 23.0, 20.9. **HRMS (ESI)**calcd for $C_{32}H_{27}NO_3[M+H]^+$473.1991, found:473.1998.

1',1'-Dimethyl-*2H,4H*-spiro[benzo[b][1,4]oxazine-3,8'-indeno[1,2-c]furan]-3'(1'H)-thione(3a′)



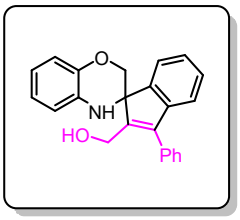
Yellow solid (0.170g,0.71%), mp 193-196°C.**^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.48 – 7.35 (m, 4H), 6.99 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.88 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.82 (dd, *J* = 7.6, 1.7 Hz, 1H), 6.73 (dd, *J* = 7.7, 1.6 Hz, 1H), 4.83 (d, *J* = 9.2 Hz, 1H), 4.13 (s, 1H), 3.90 (d, *J* = 9.8 Hz, 1H), 1.85 (s, 3H), 1.82 (s, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 202.2, 175.3, 156.4, 144.6, 143.3, 131.5, 131.4, 131.1, 129.1, 125.5, 122.7, 122.3, 119.7, 117.1, 117.0, 91.9, 68.3, 60.7. **HRMS (ESI)** calcd for $C_{20}H_{17}NO_2S[M+H]^+$335.0980, found: 335.0987.

Ethyl 2'-phenyl-2H,4H-spiro[benzo[b][1,4]oxazine-3,1'-indene]-3'-carboxylate (5q)



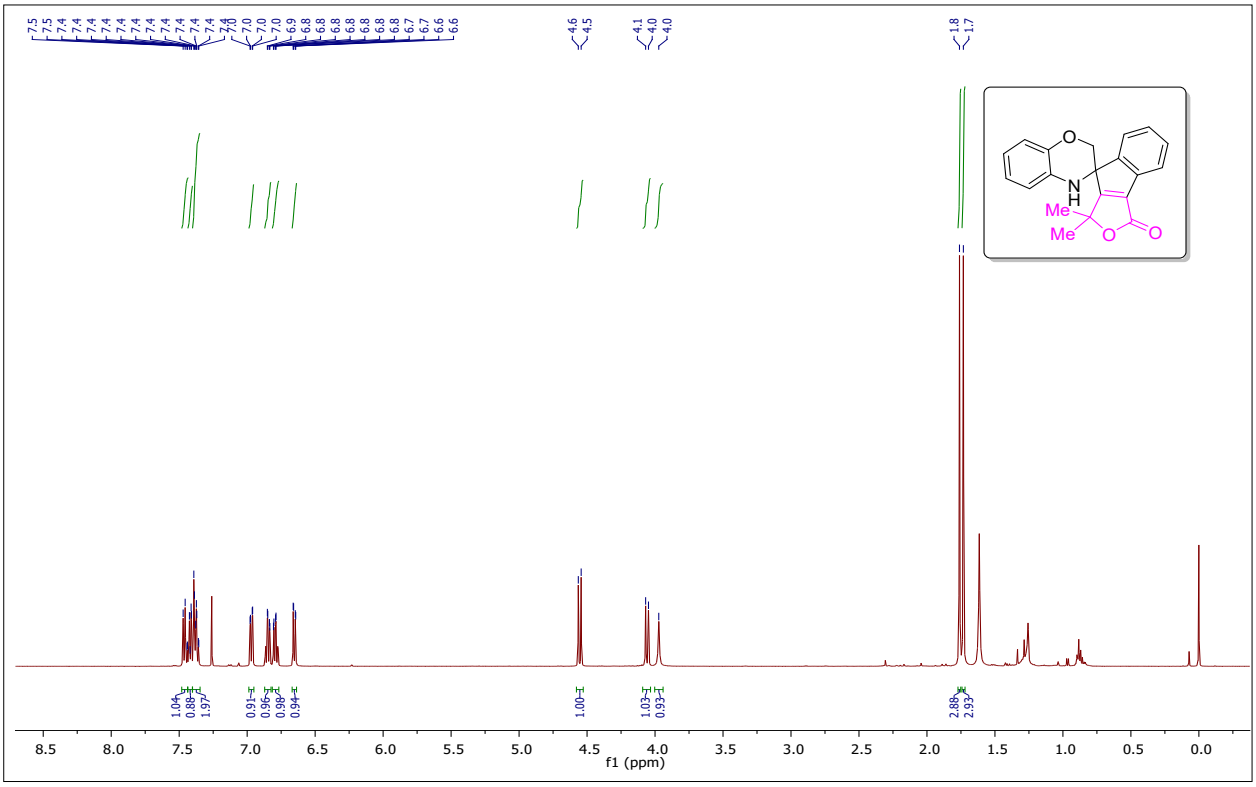
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 3H), 7.41 (ddd, *J* = 5.6, 4.0, 1.8 Hz, 3H), 7.32 – 7.27 (m, 2H), 7.22 (dt, *J* = 6.3, 3.6 Hz, 1H), 6.99 (dd, *J* = 7.9, 1.5 Hz, 1H), 6.87 (td, *J* = 7.5, 1.5 Hz, 1H), 6.79 (td, *J* = 7.7, 1.5 Hz, 1H), 6.73 (dd, *J* = 7.7, 1.5 Hz, 1H), 4.86 (d, *J* = 10.4 Hz, 1H), 4.06 (ddd, *J* = 13.2, 6.6, 3.1 Hz, 2H), 4.02 – 3.99 (m, 1H), 0.95 (t, *J* = 7.1 Hz, 3H).

(3'-Phenyl-2H,4H-spiro[benzo[b][1,4]oxazine-3,1'-inden]-2'-yl)methanol (5r)

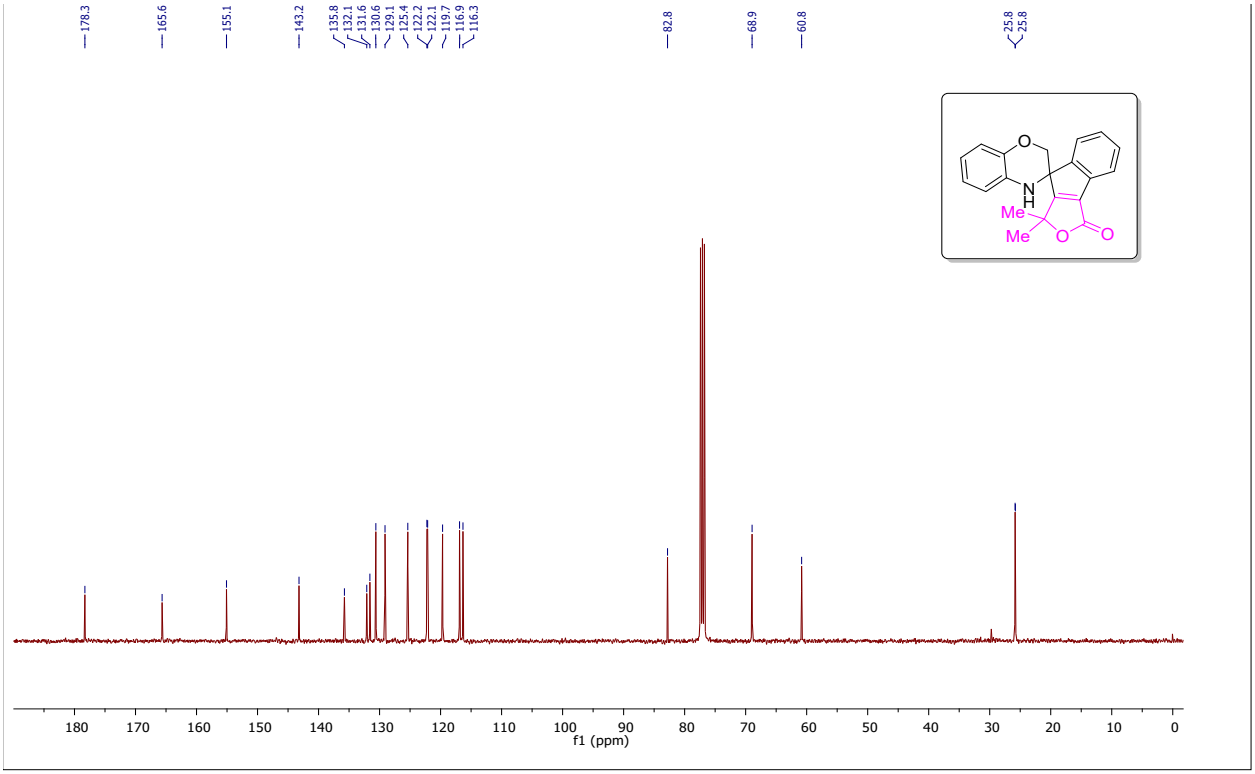


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.3 Hz, 1H), 7.47 (d, *J* = 4.7 Hz, 2H), 7.33 (s, 4H), 7.13 (dd, *J* = 25.0, 17.5 Hz, 2H), 6.83 (dd, *J* = 12.9, 7.5 Hz, 2H), 6.76 – 6.61 (m, 2H), 4.66 (t, *J* = 15.1 Hz, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 4.14 (t, *J* = 12.8 Hz, 1H), 3.96 (d, *J* = 10.6 Hz, 1H).

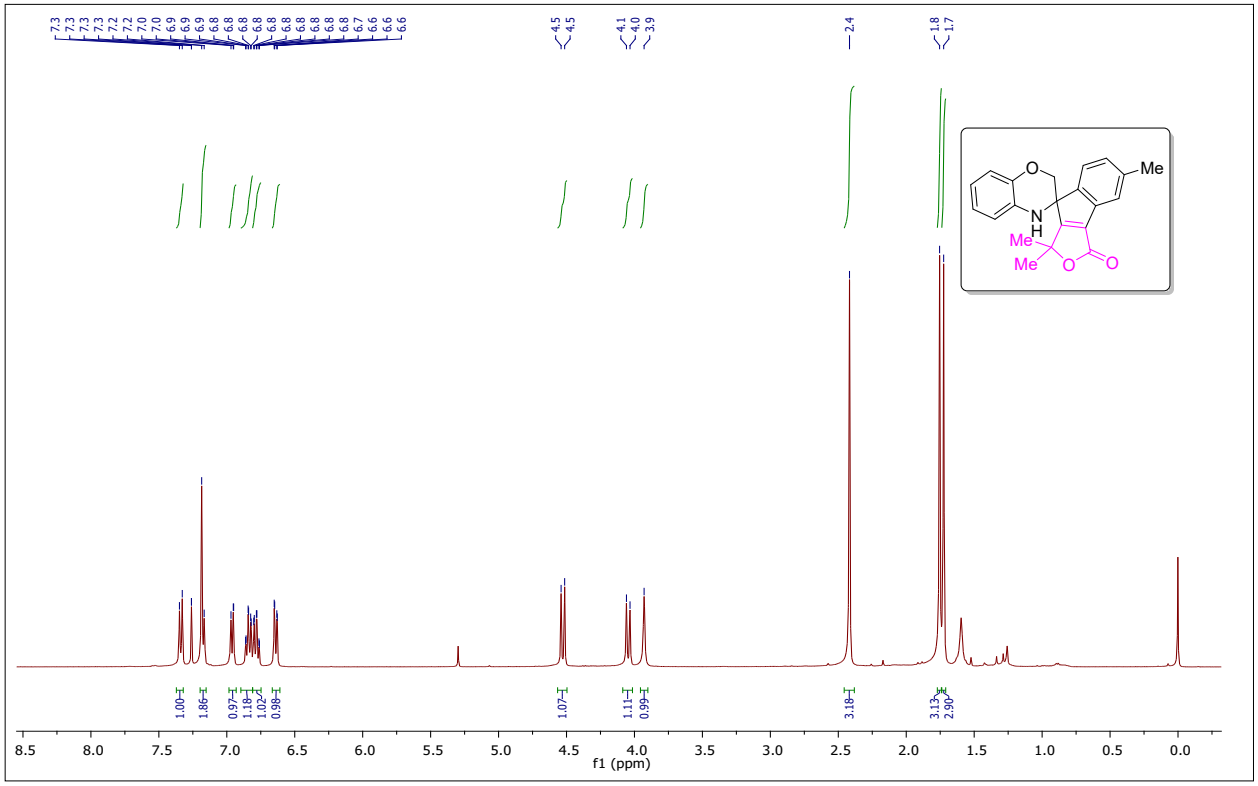
4. NMR spectra of the products:^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3a**



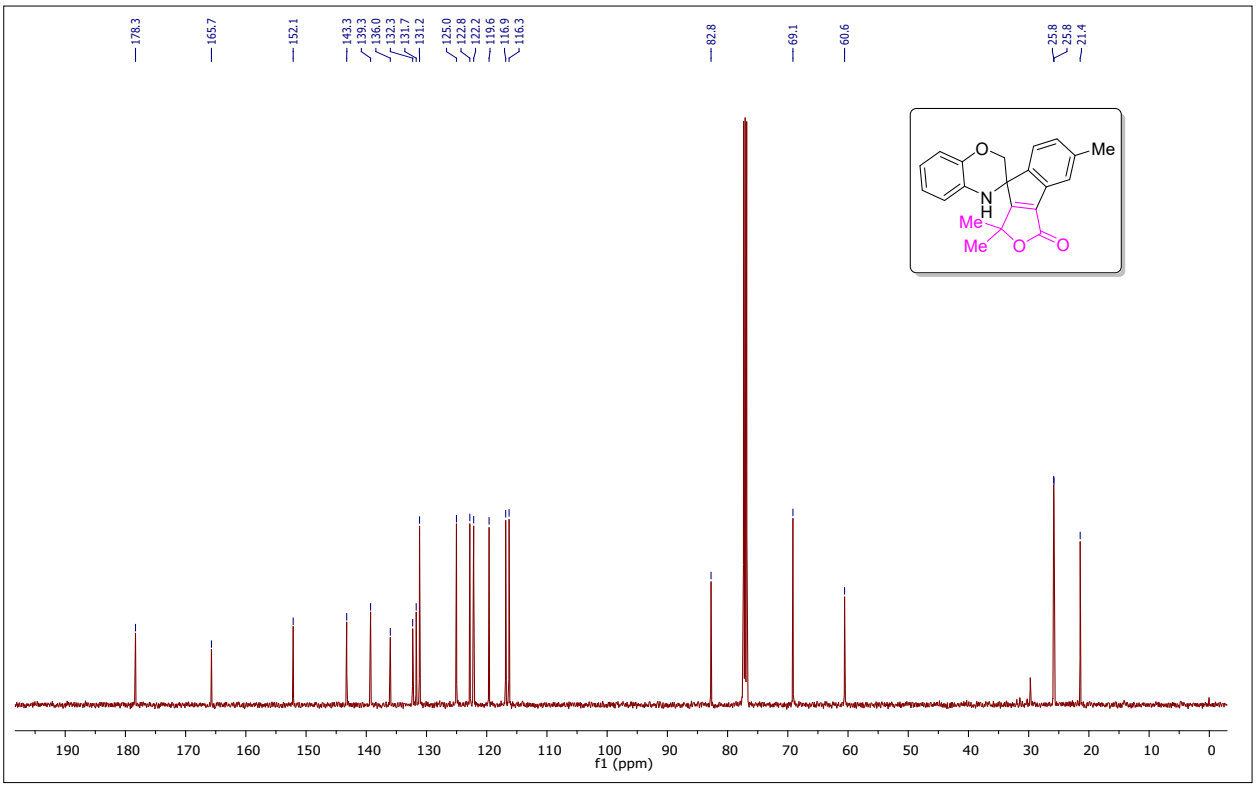
^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) spectrum of compound **3a**



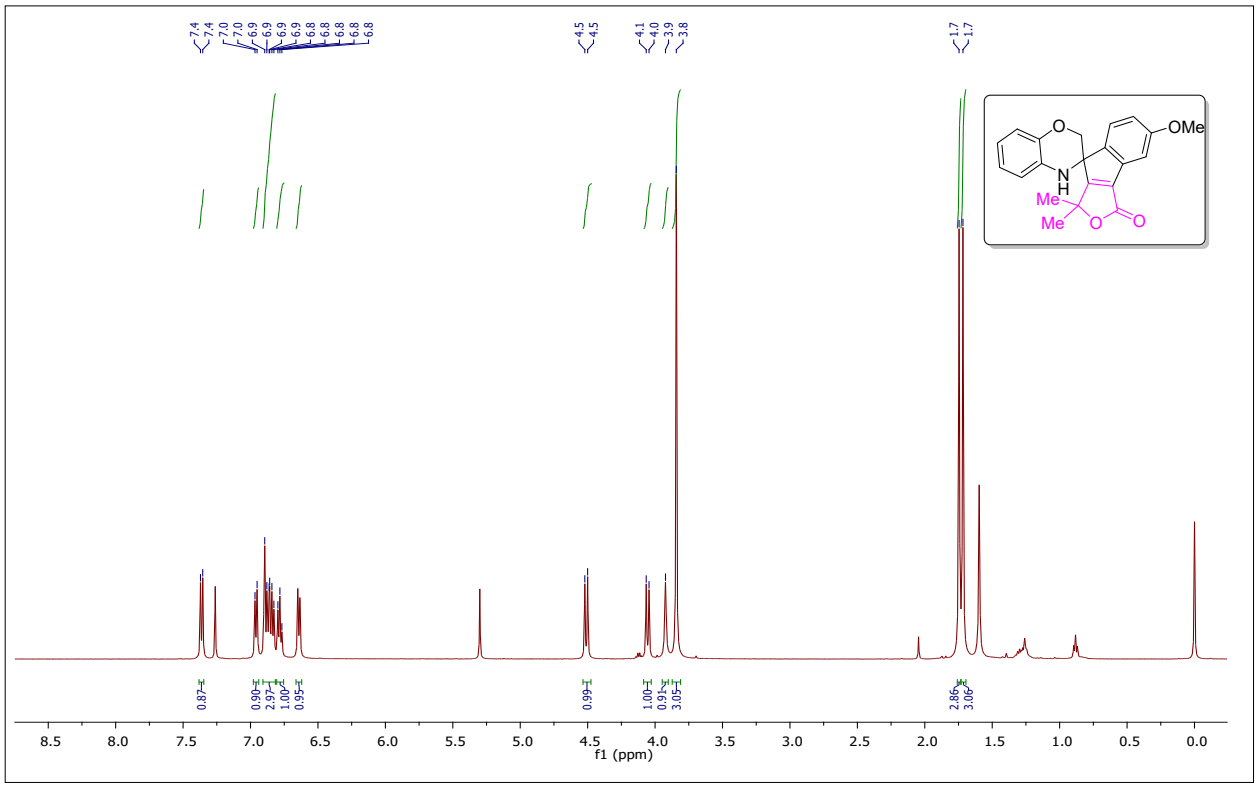
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3b**



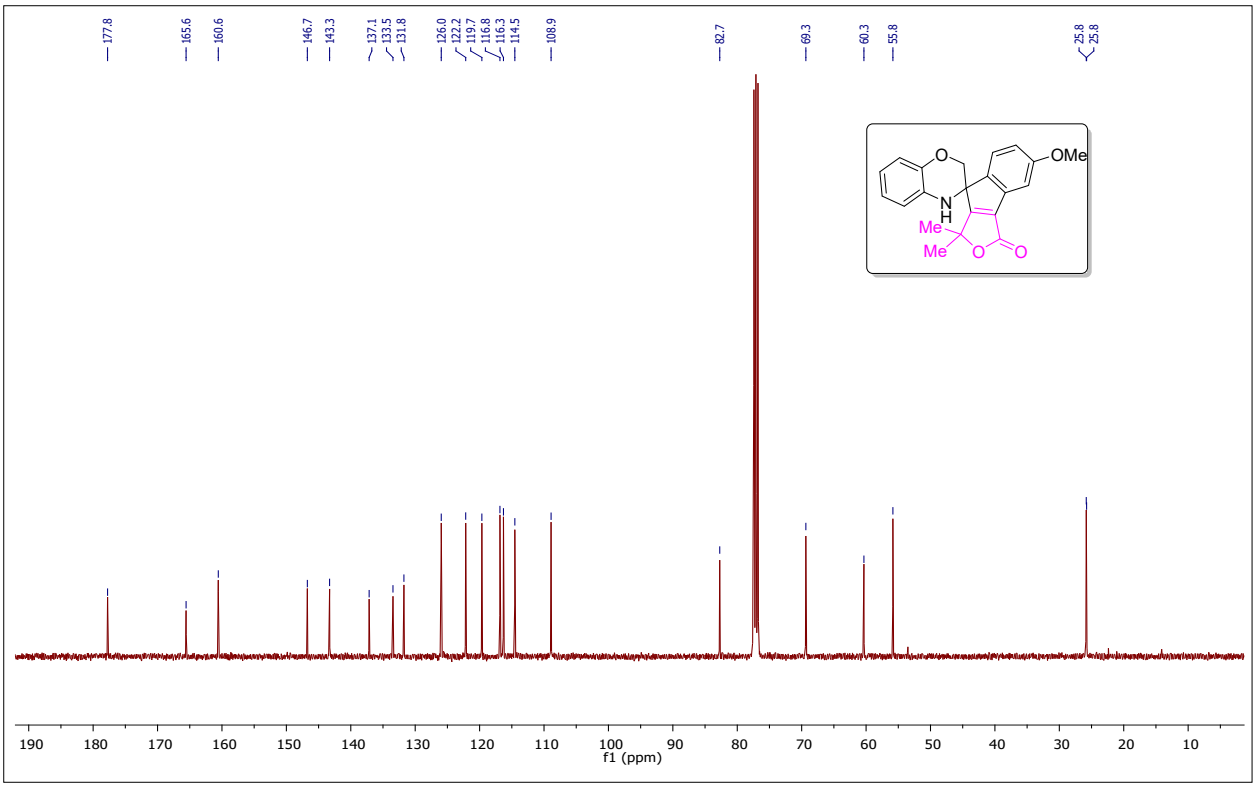
^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) spectrum of compound **3b**



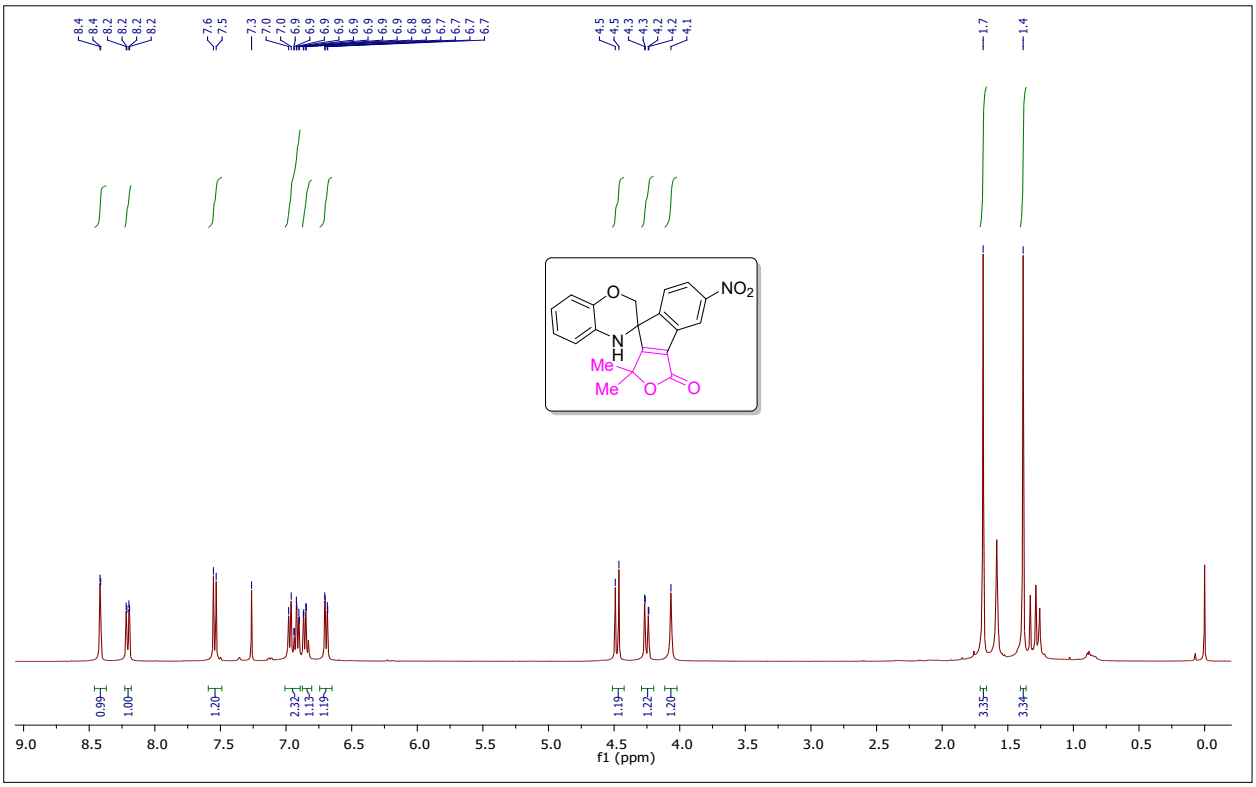
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3c**



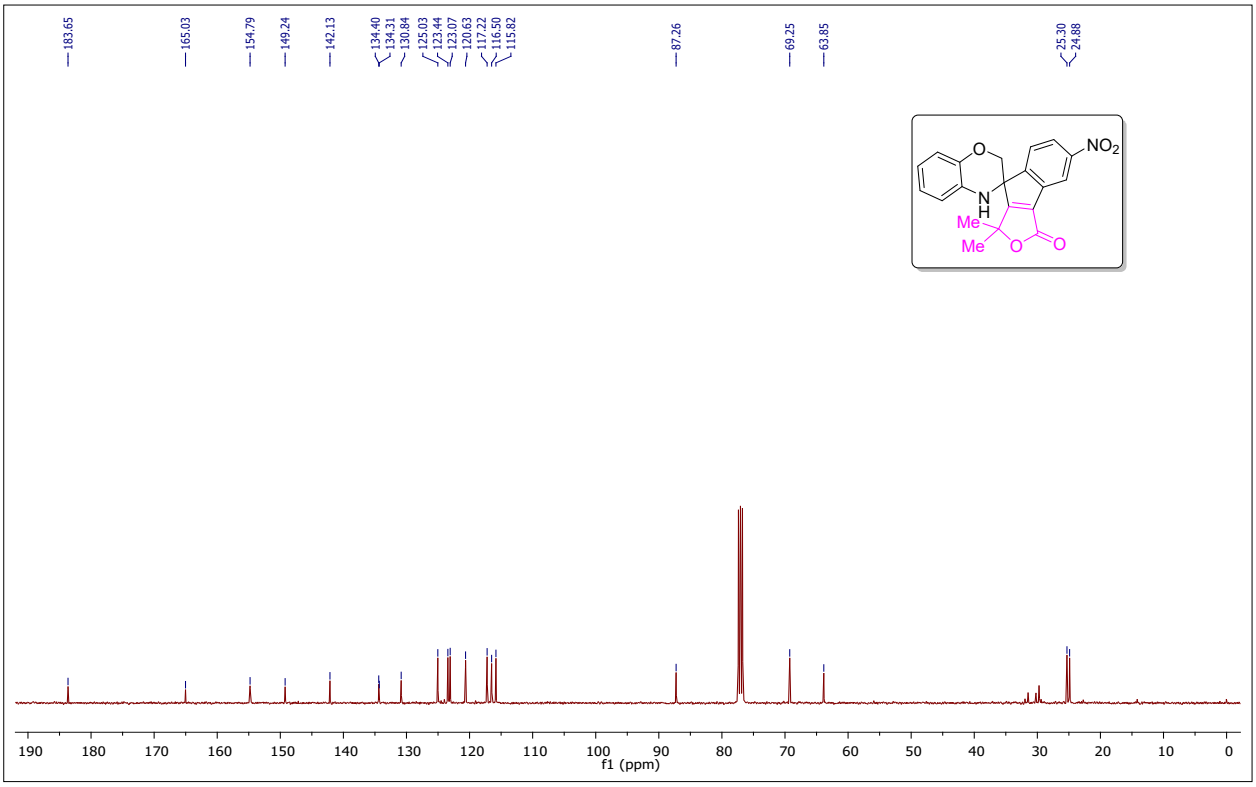
^{13}C{^{1}H}NMR (125MHz, $CDCl_3$) spectrum of compound **3c**



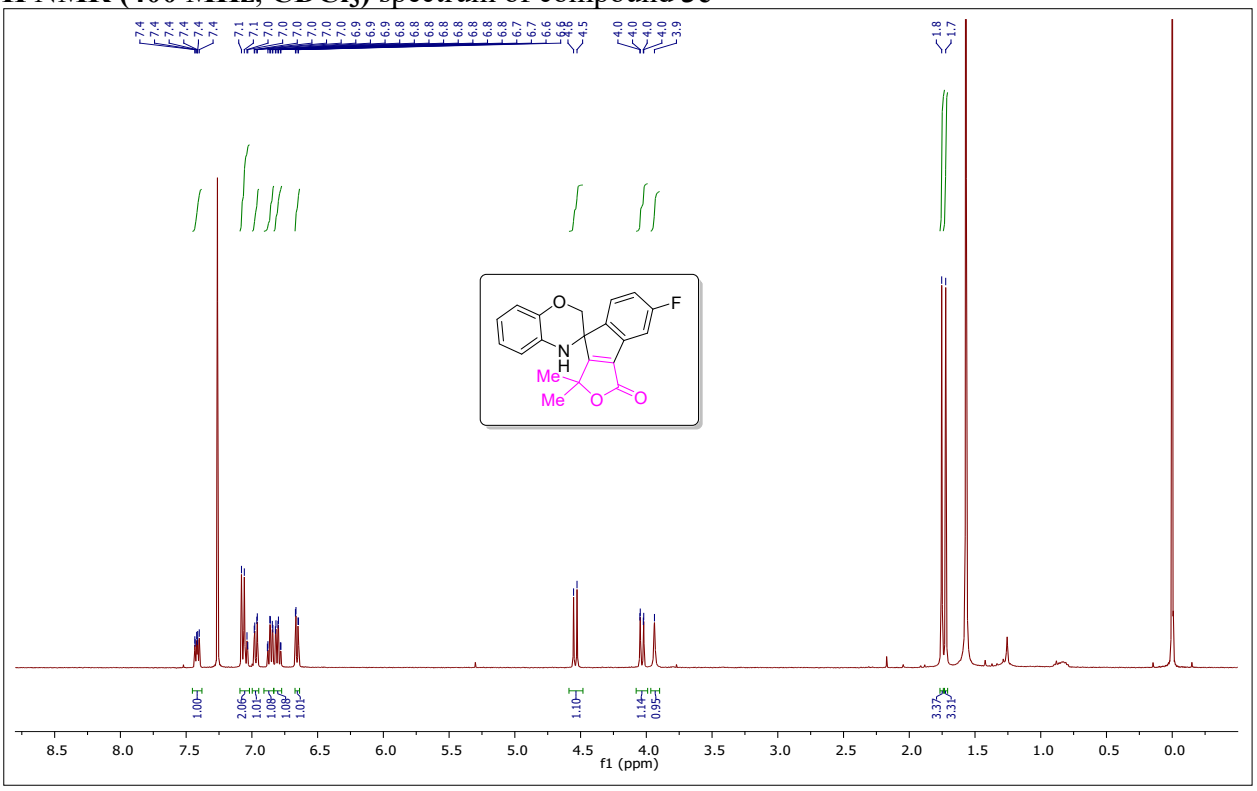
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3d**



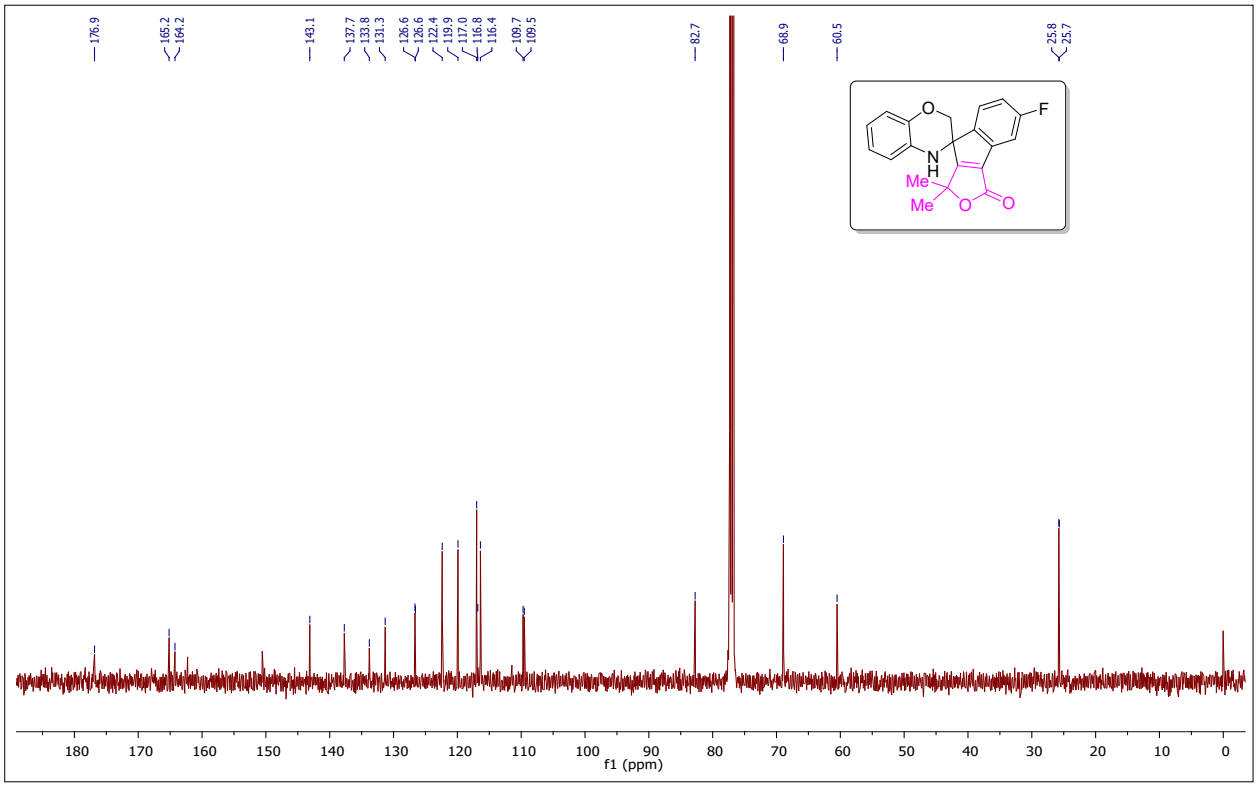
^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) spectrum of compound **3d**



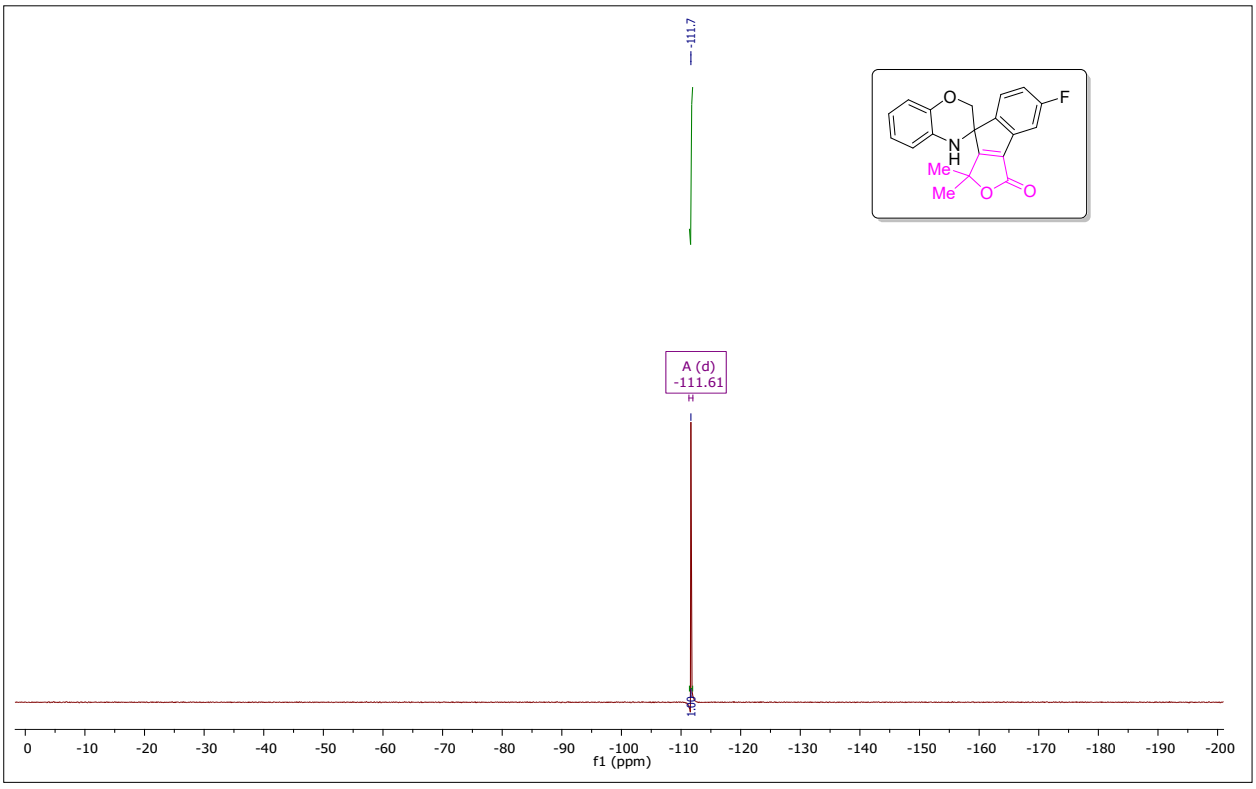
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3e**



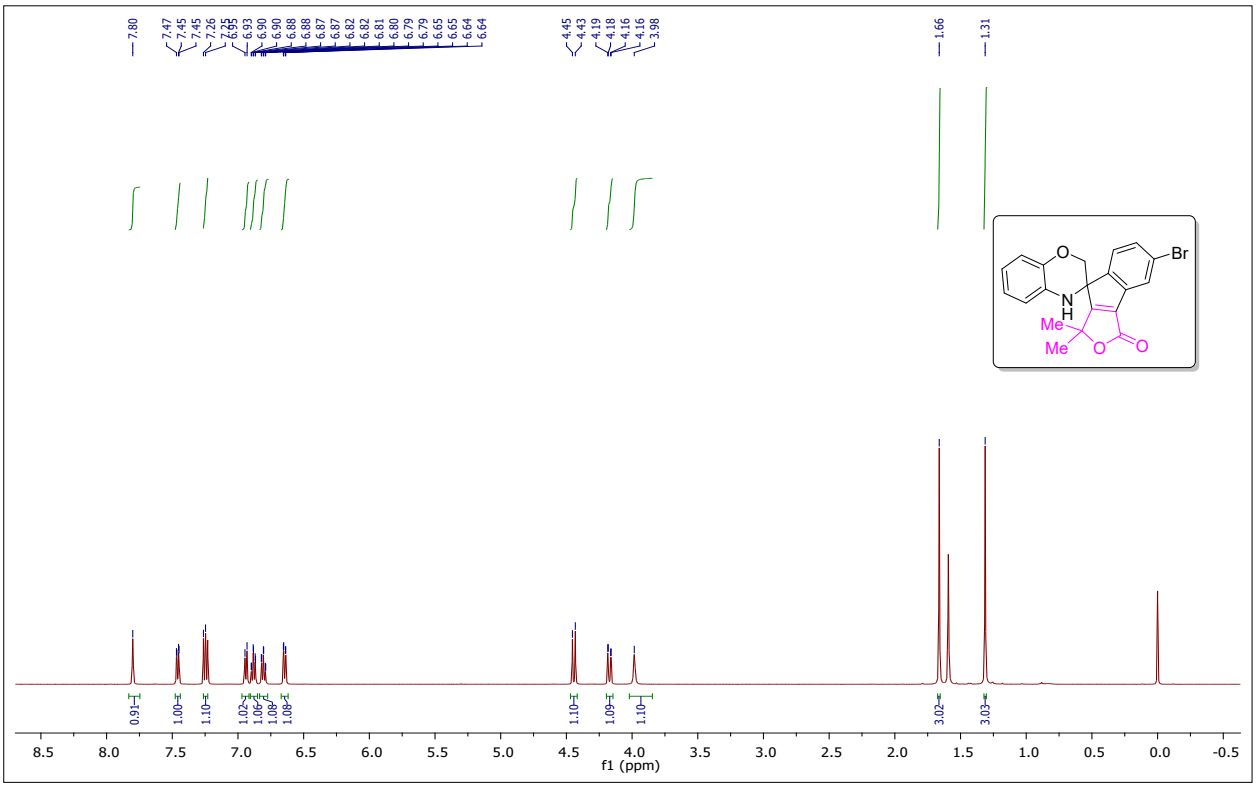
^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) spectrum of compound **3e**



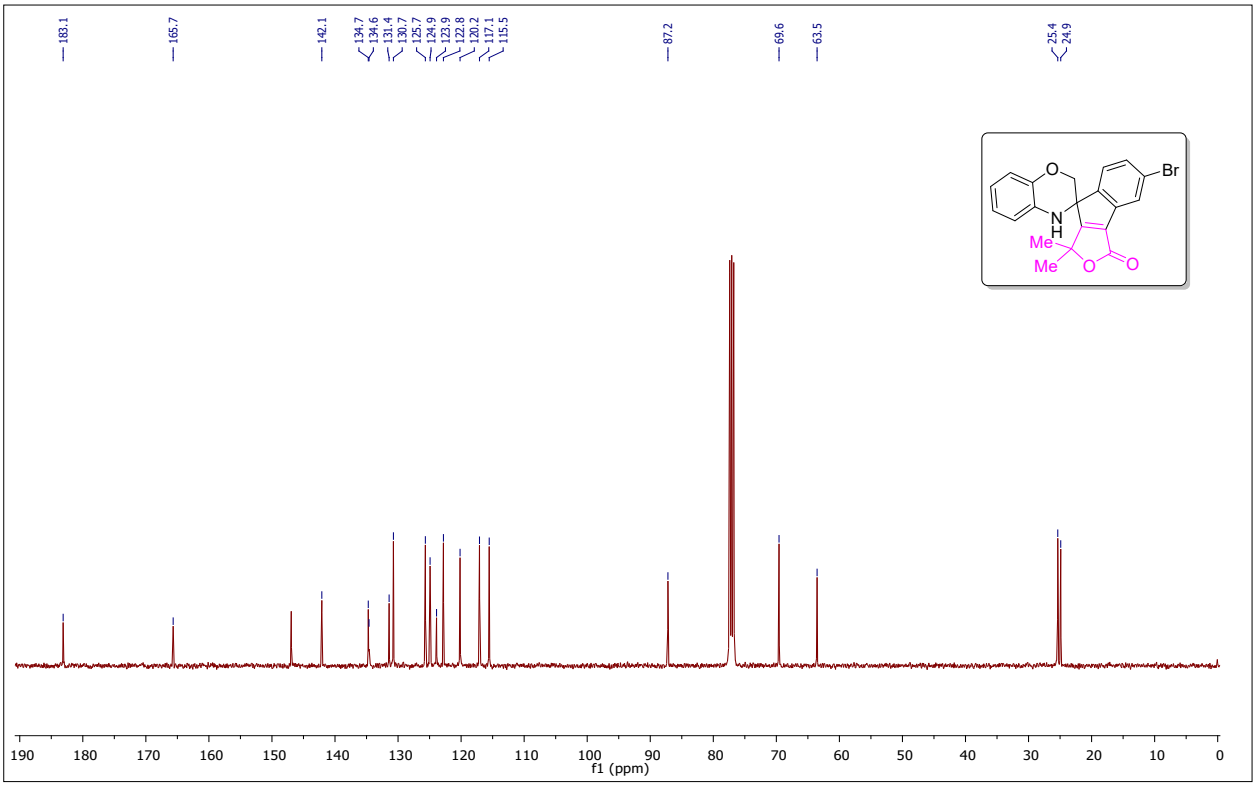
^{F}19NMR (400 MHz, $CDCl_3$) spectrum of compound **3e**



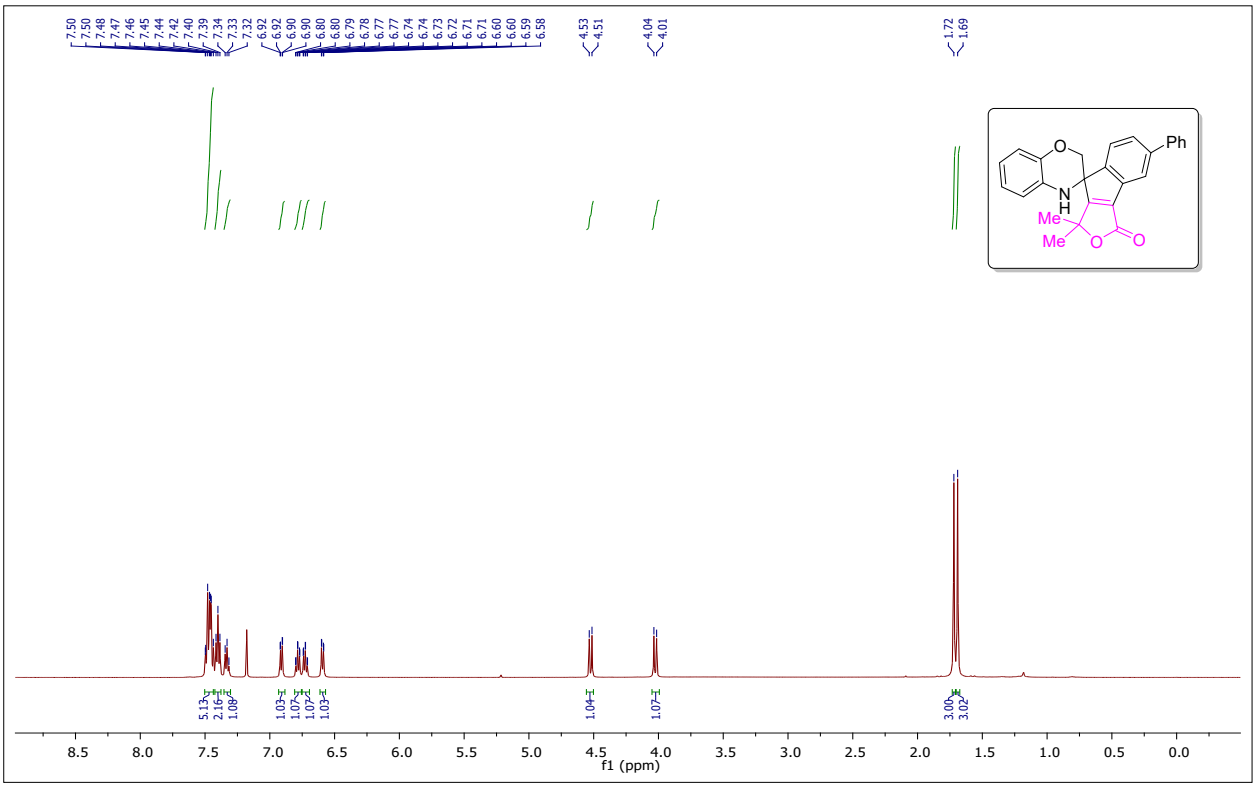
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3f**



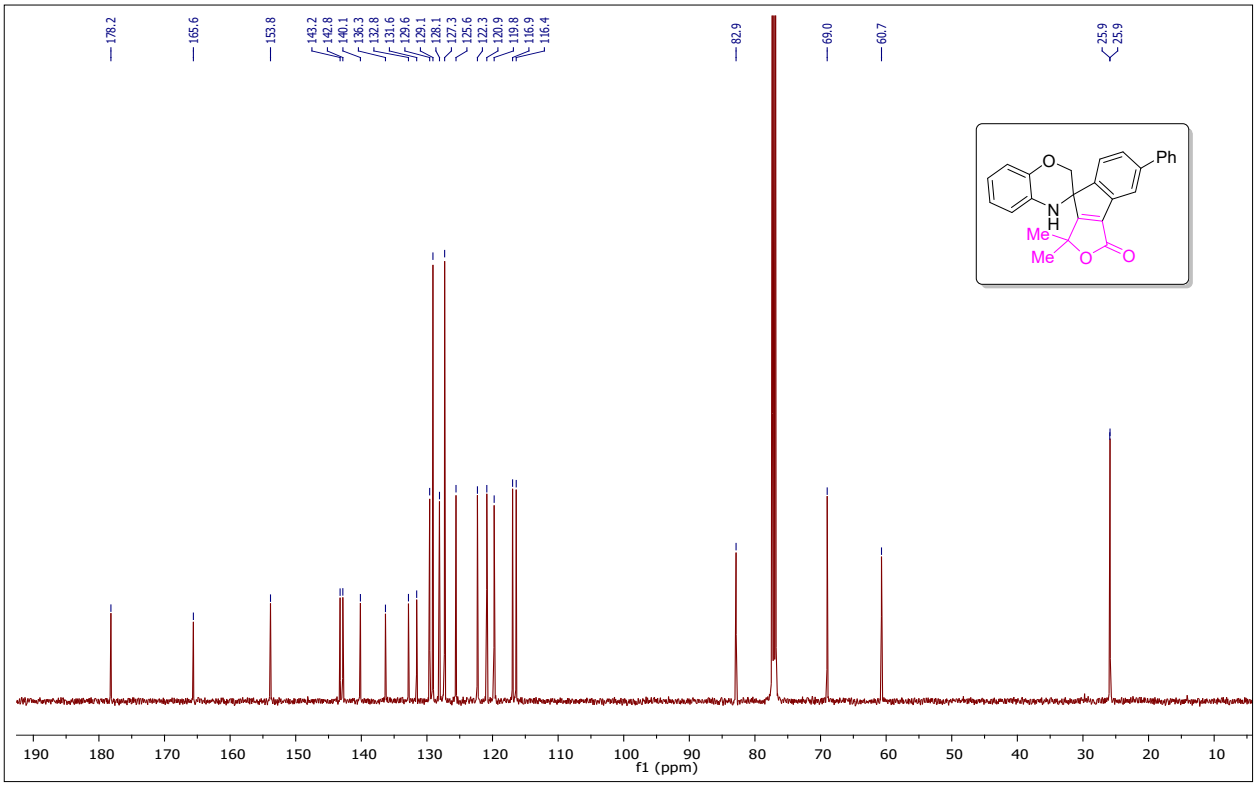
^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) spectrum of compound **3f**



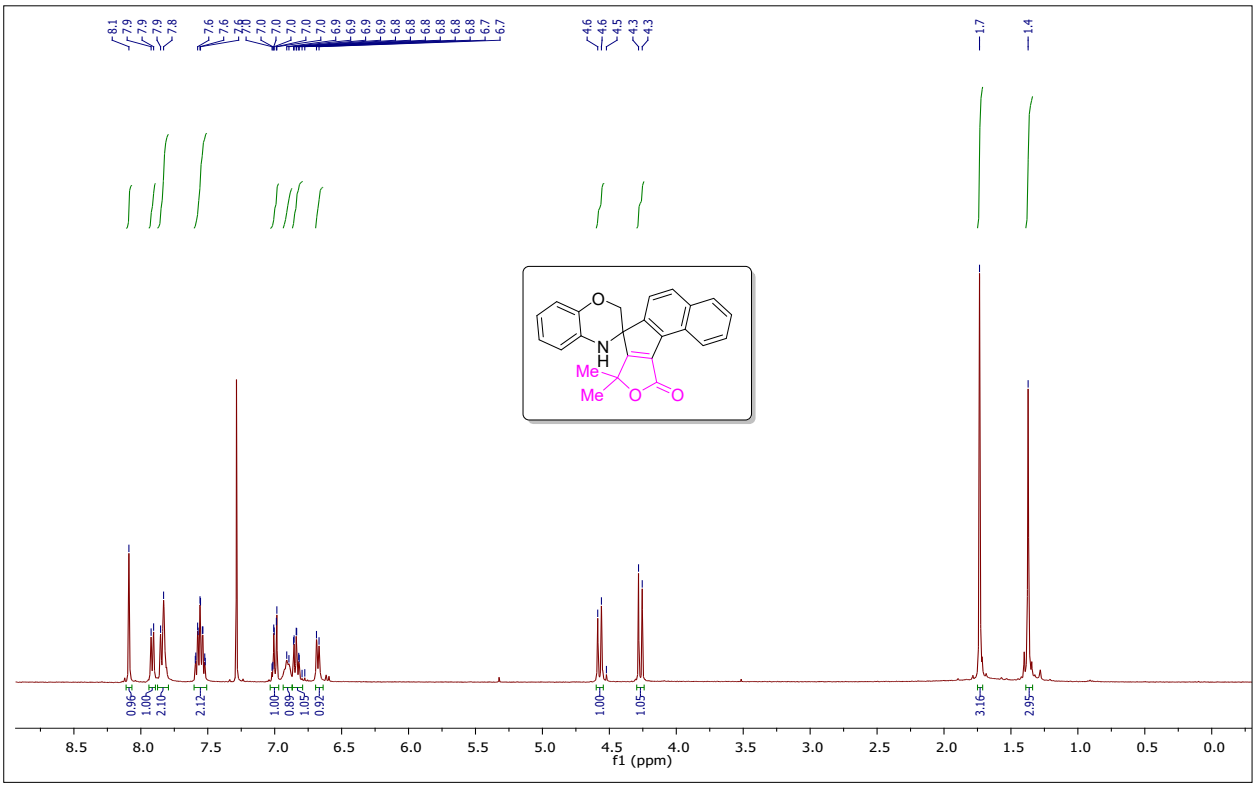
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3g**



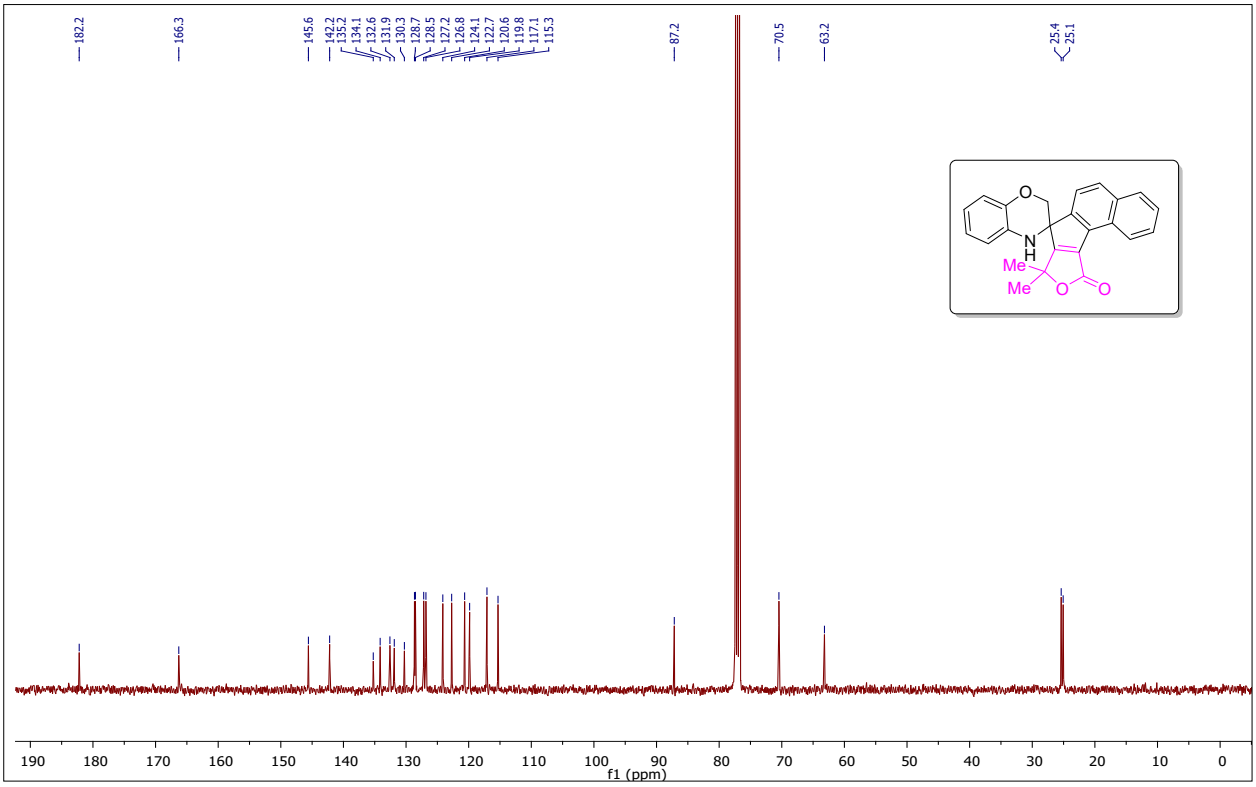
^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$) spectrum of compound **3g**



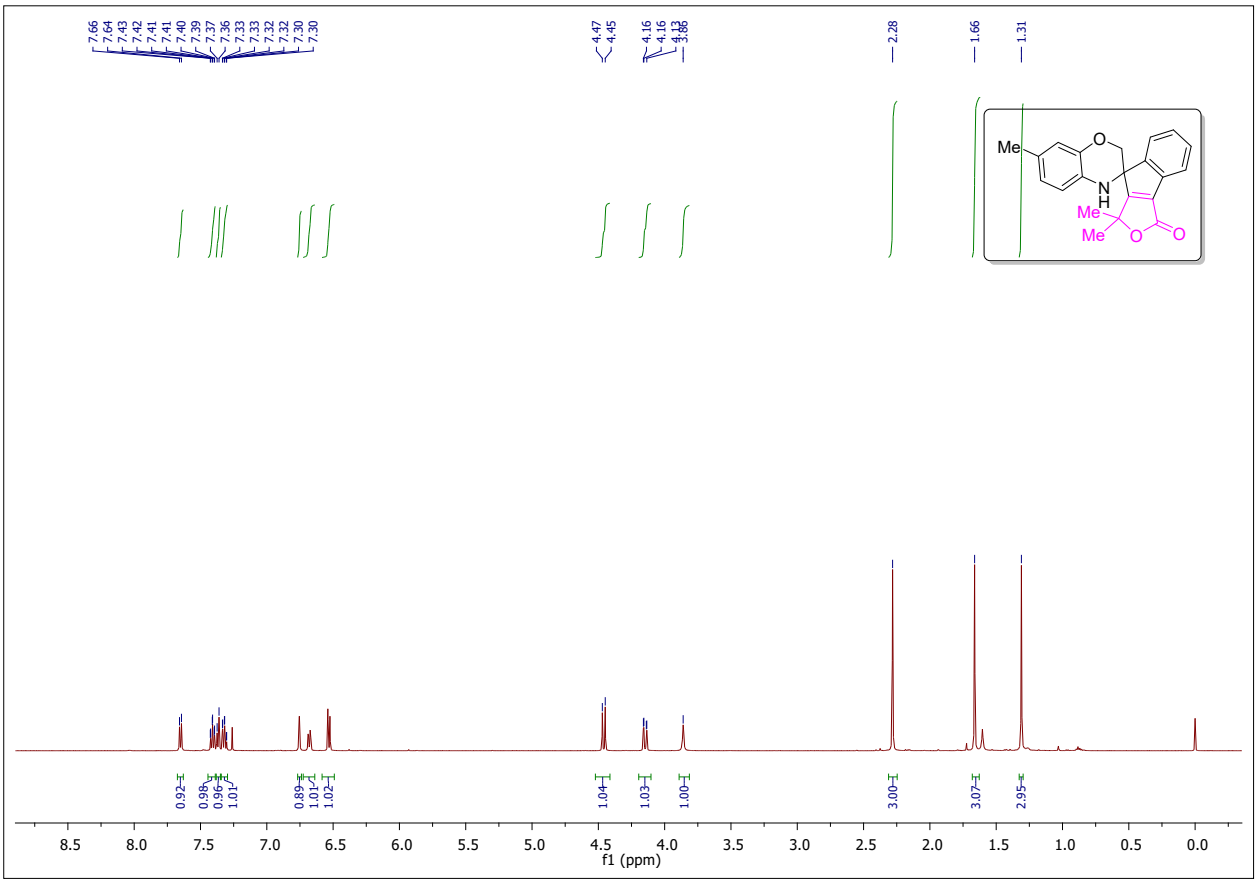
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3h**



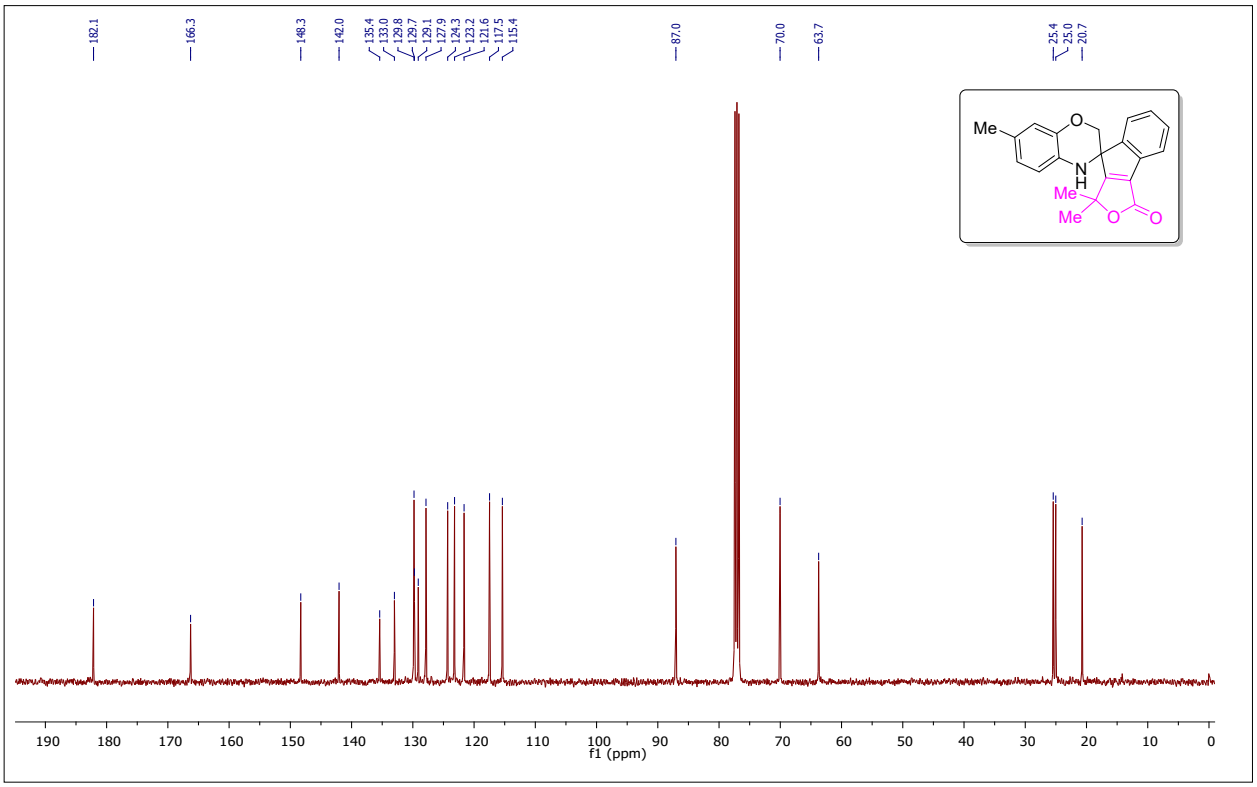
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3h**



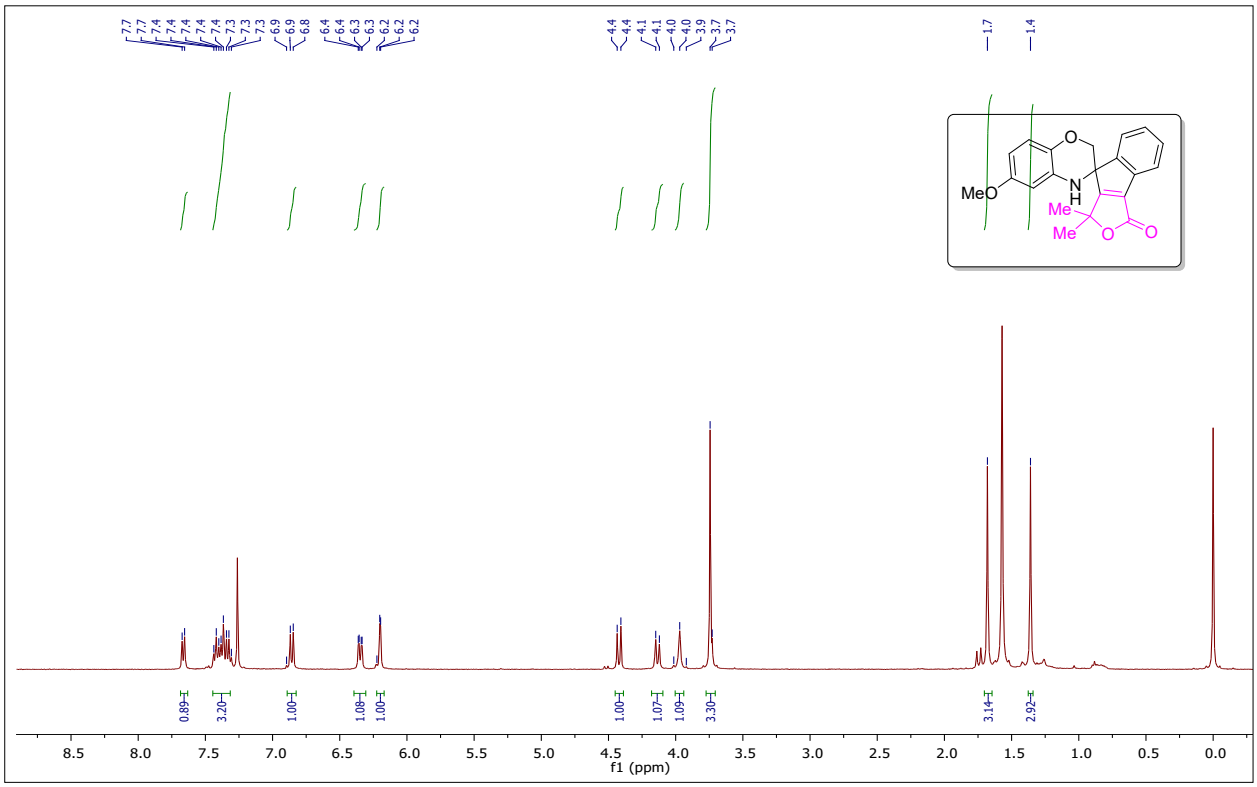
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3i**



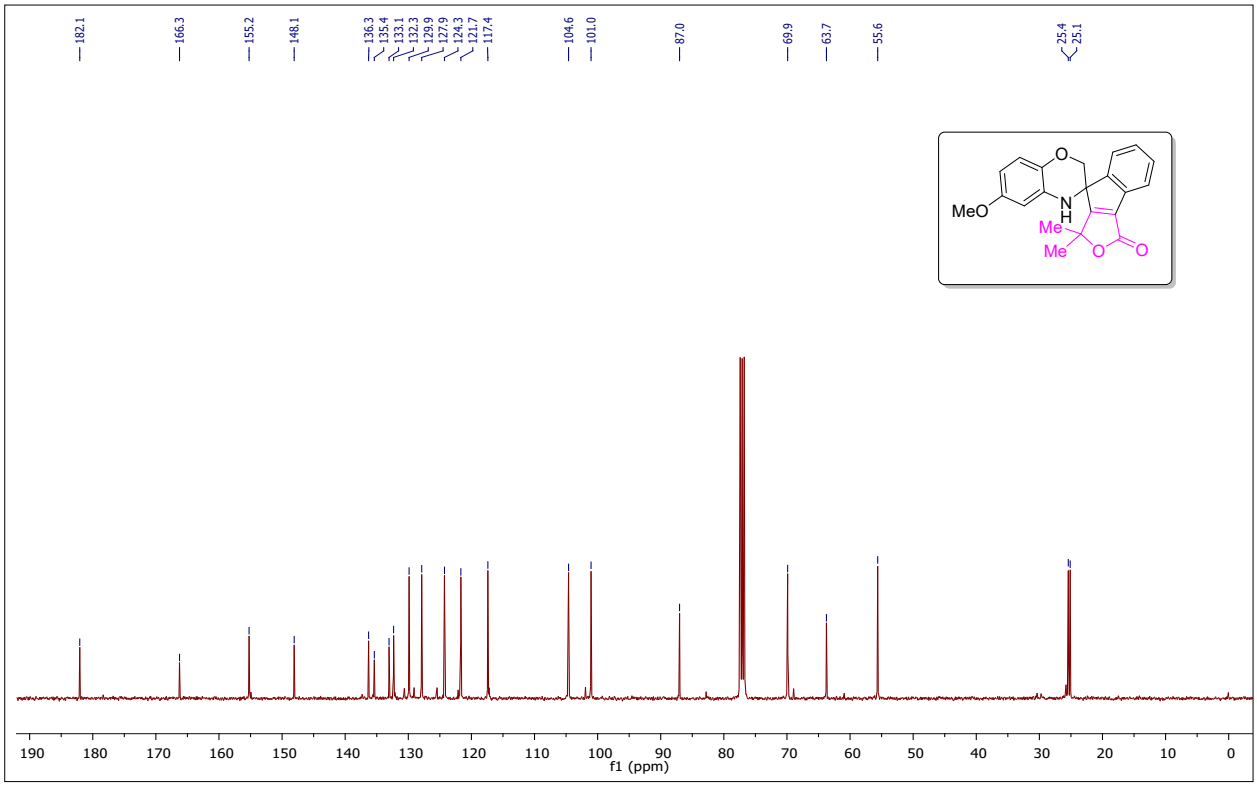
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of compound **3i**



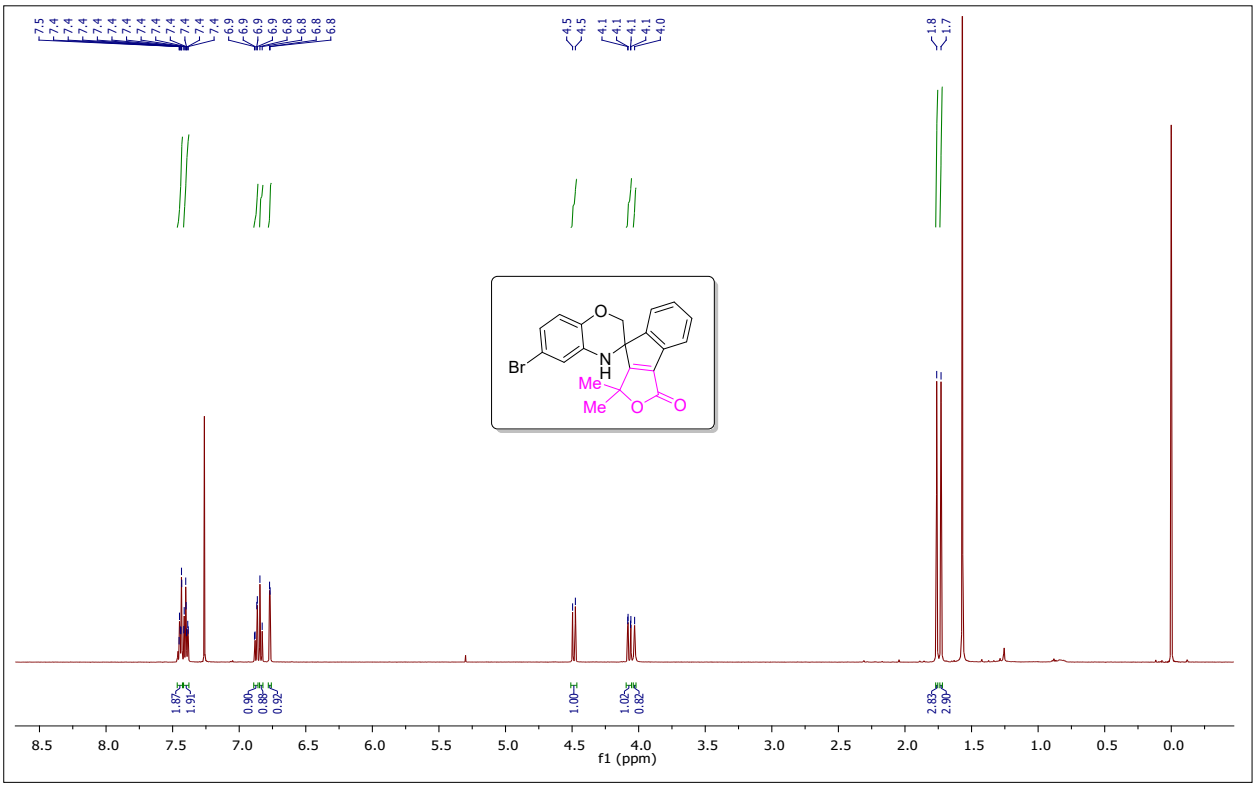
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3j**



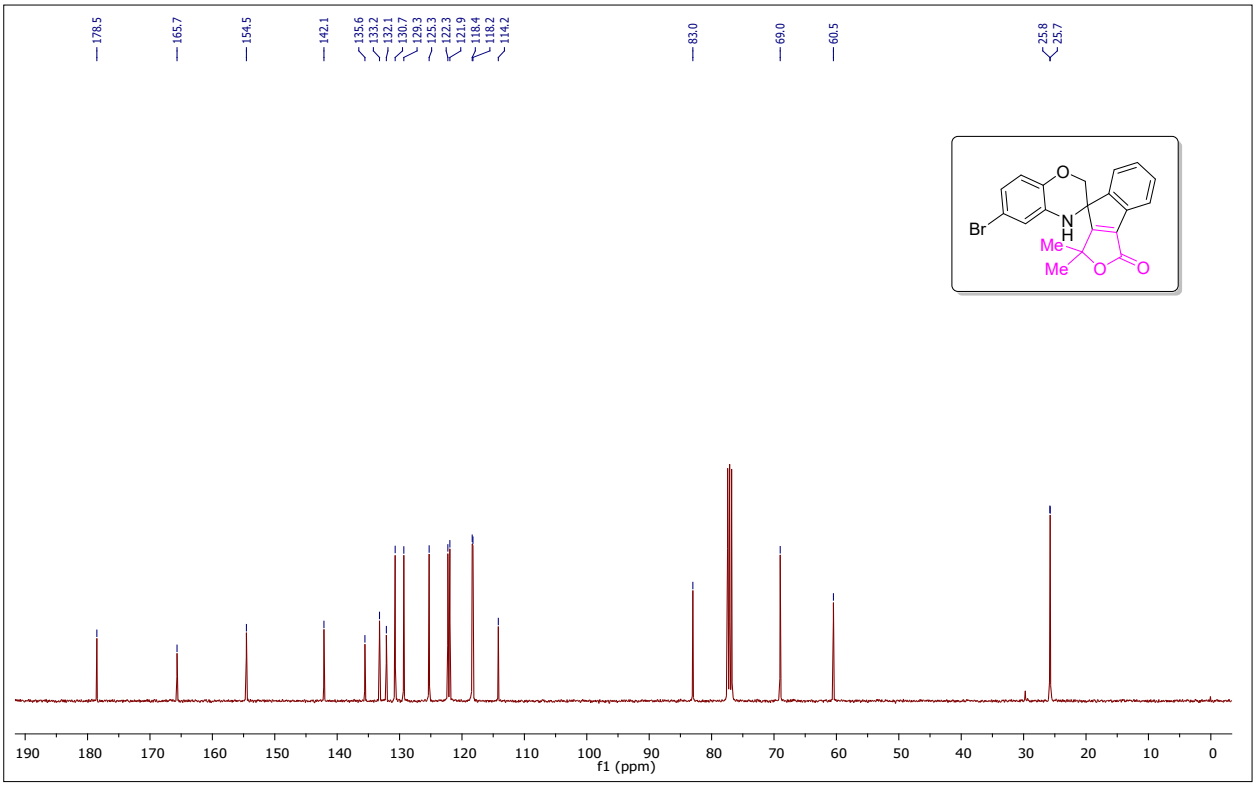
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) spectrum of compound **3j**



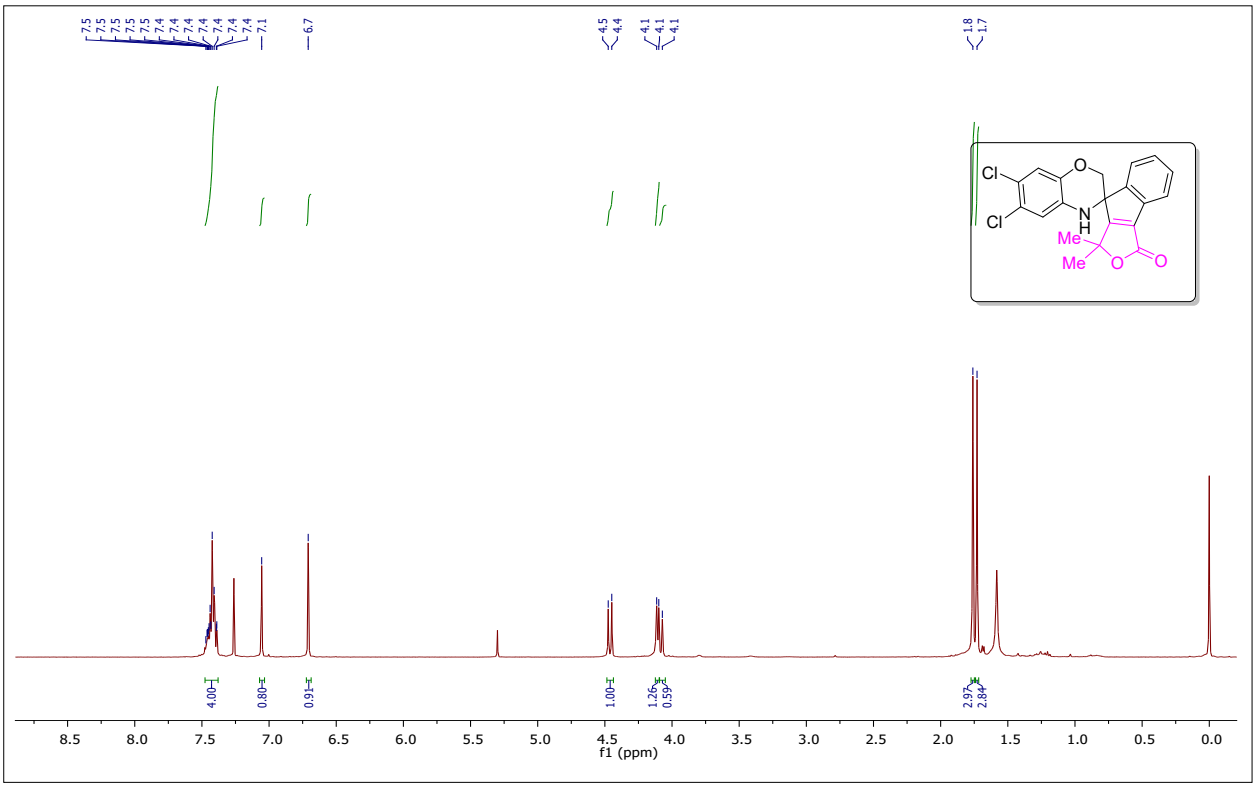
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **3k**



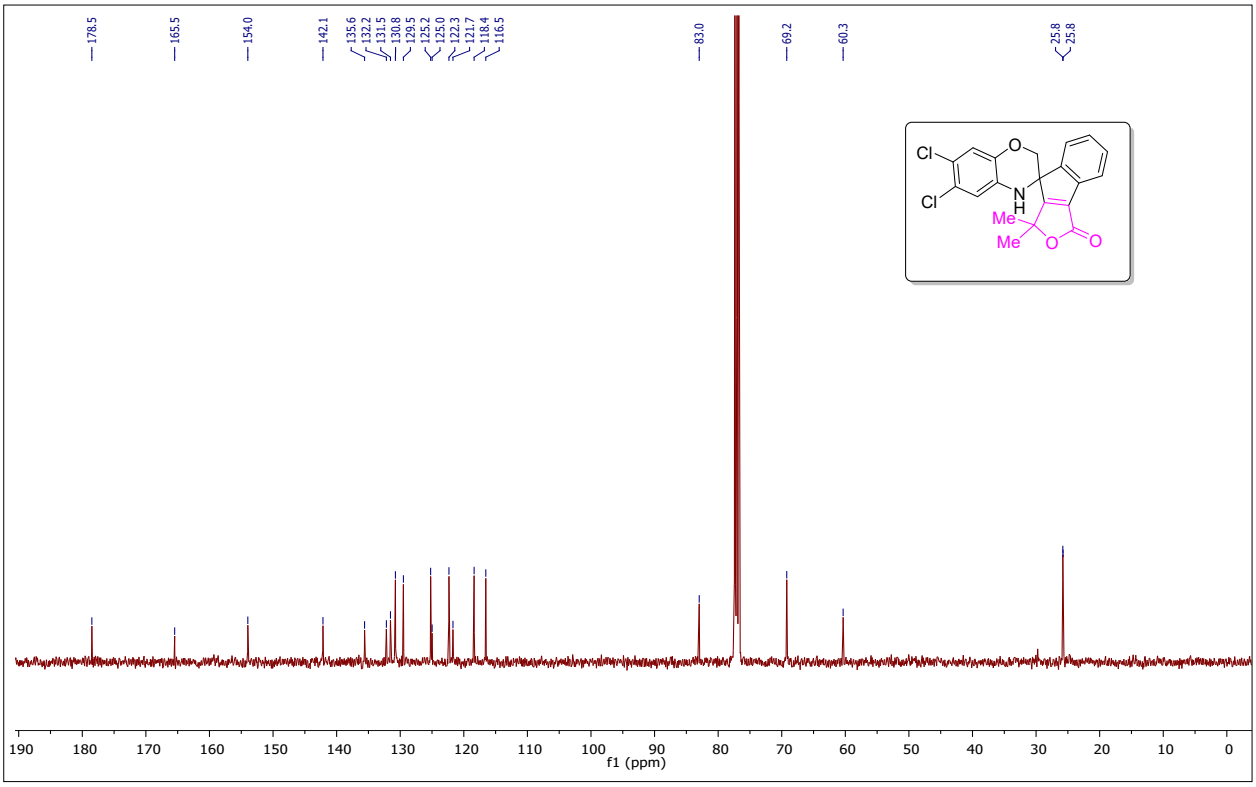
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) spectrum of compound **3k**



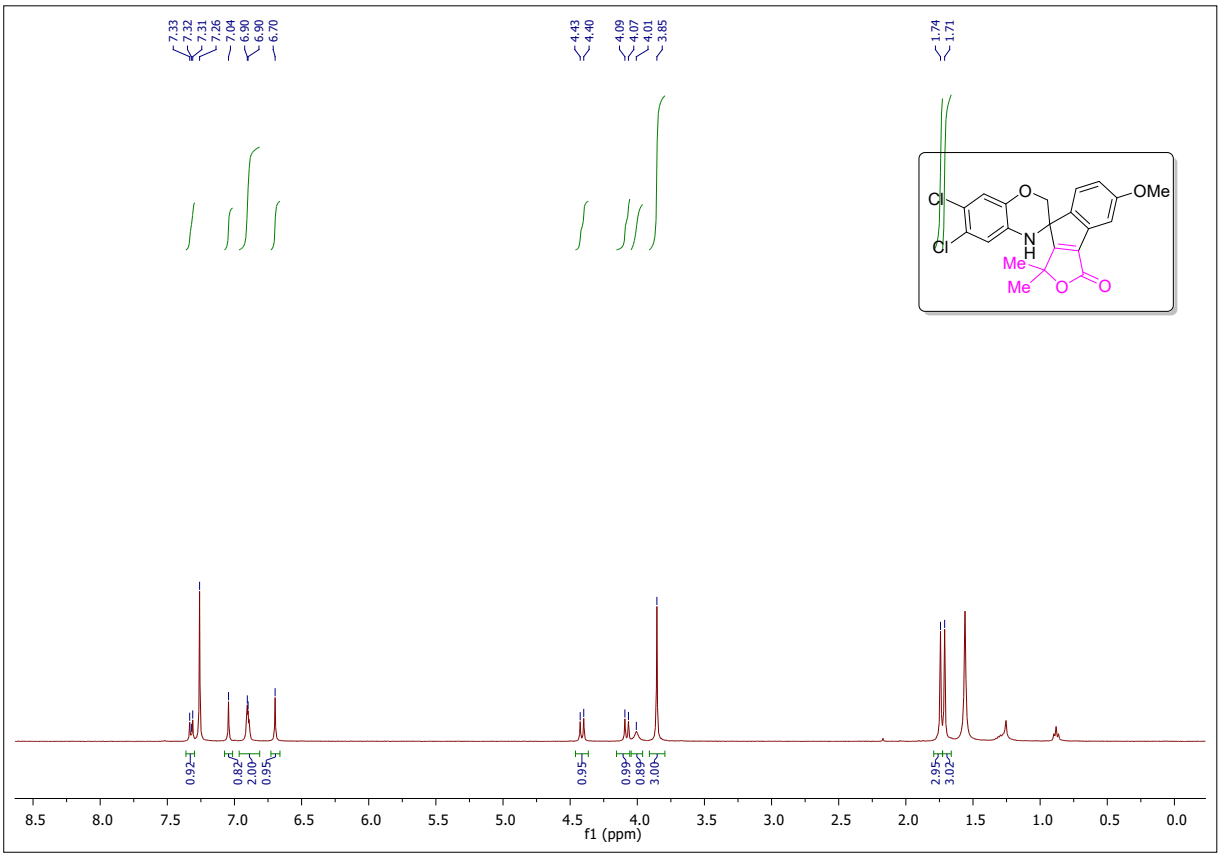
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3l**



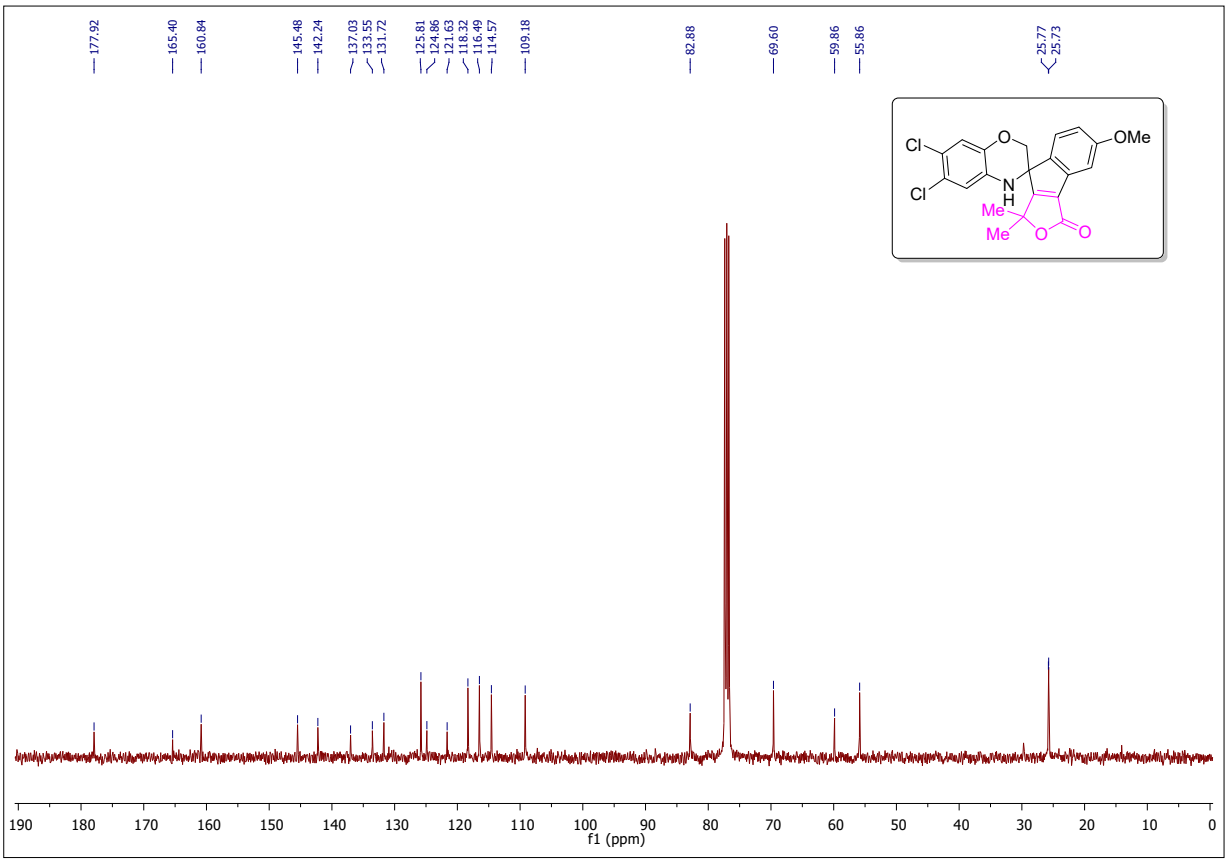
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **3l**



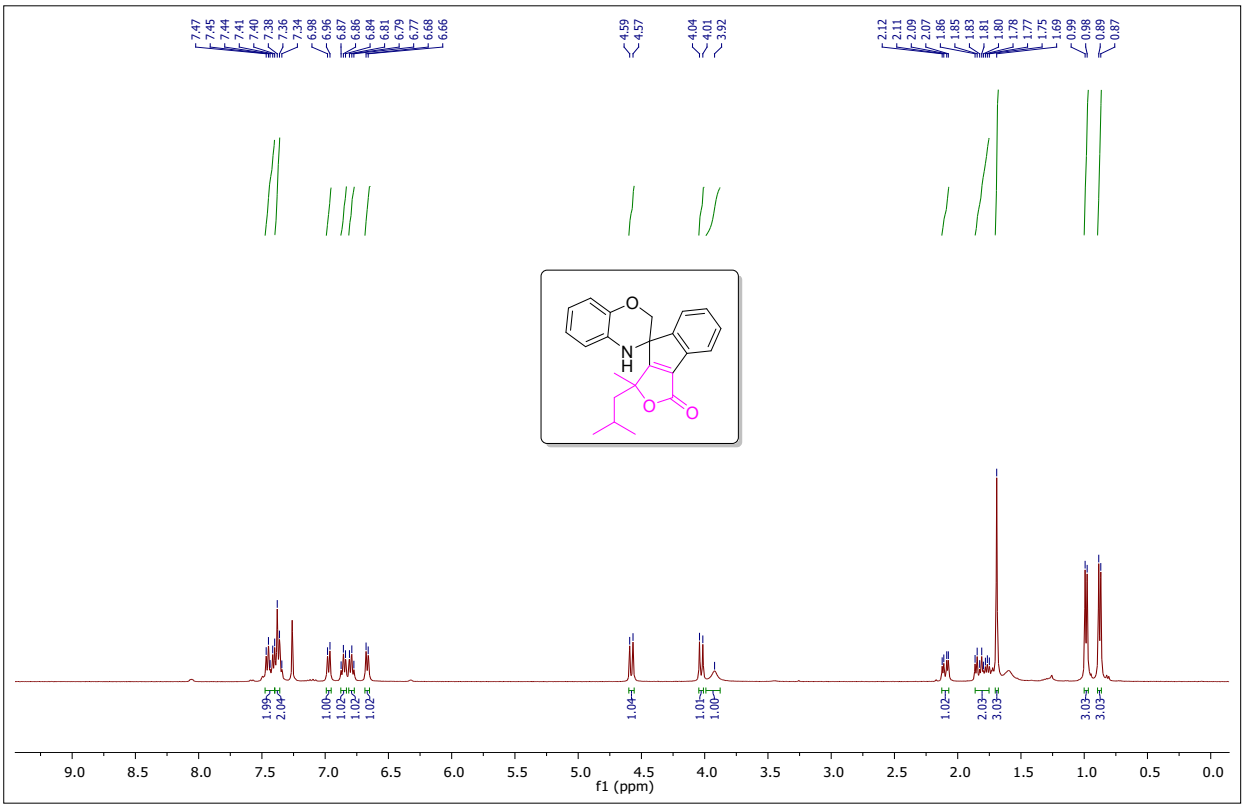
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3m**



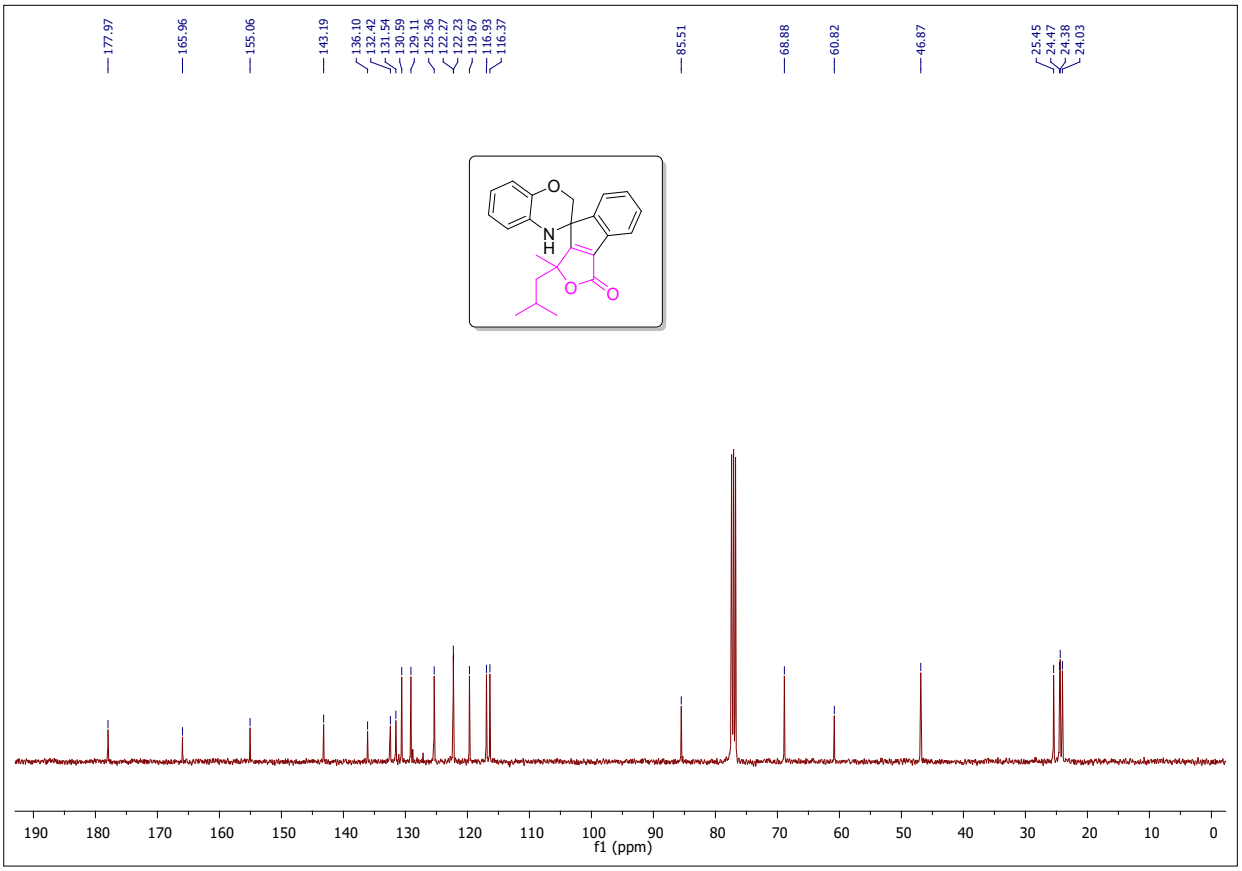
^{13}C{^{1}H}NMR (100MHz, $CDCl_3$) spectrum of compound **3m**



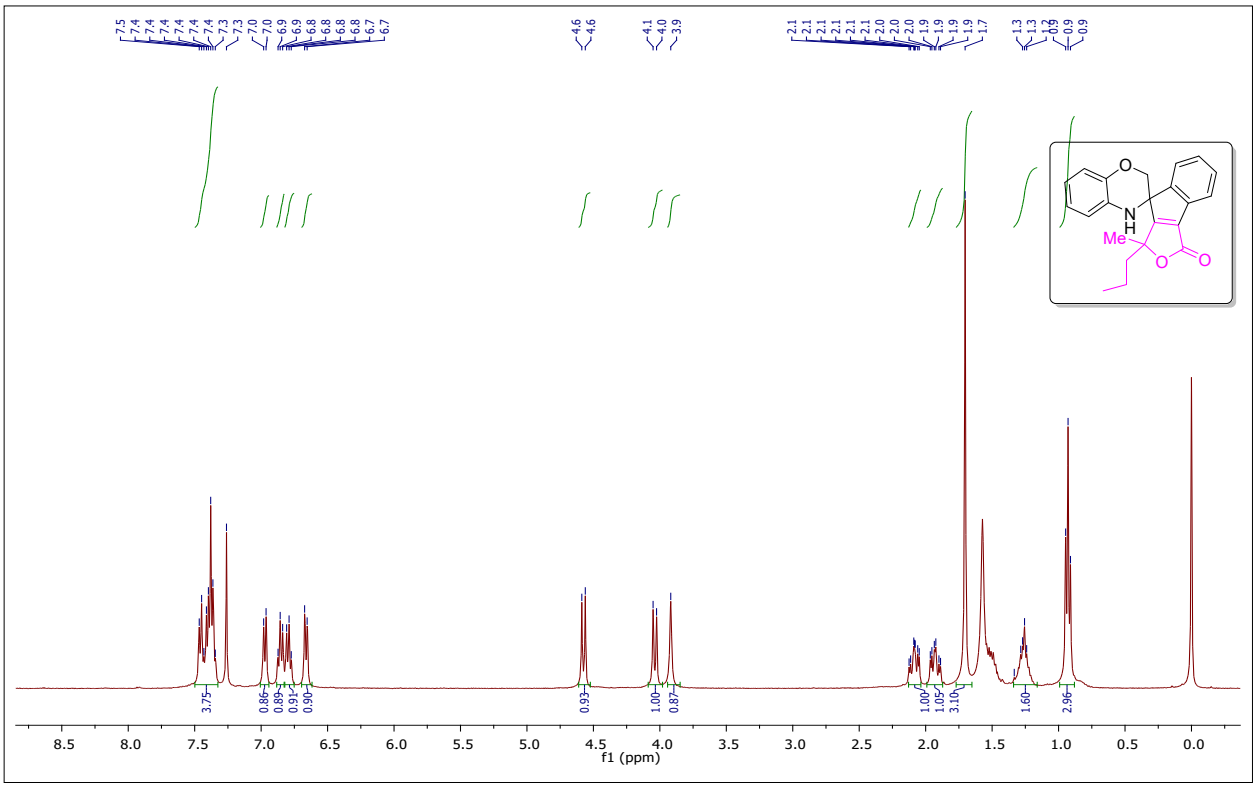
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3n**



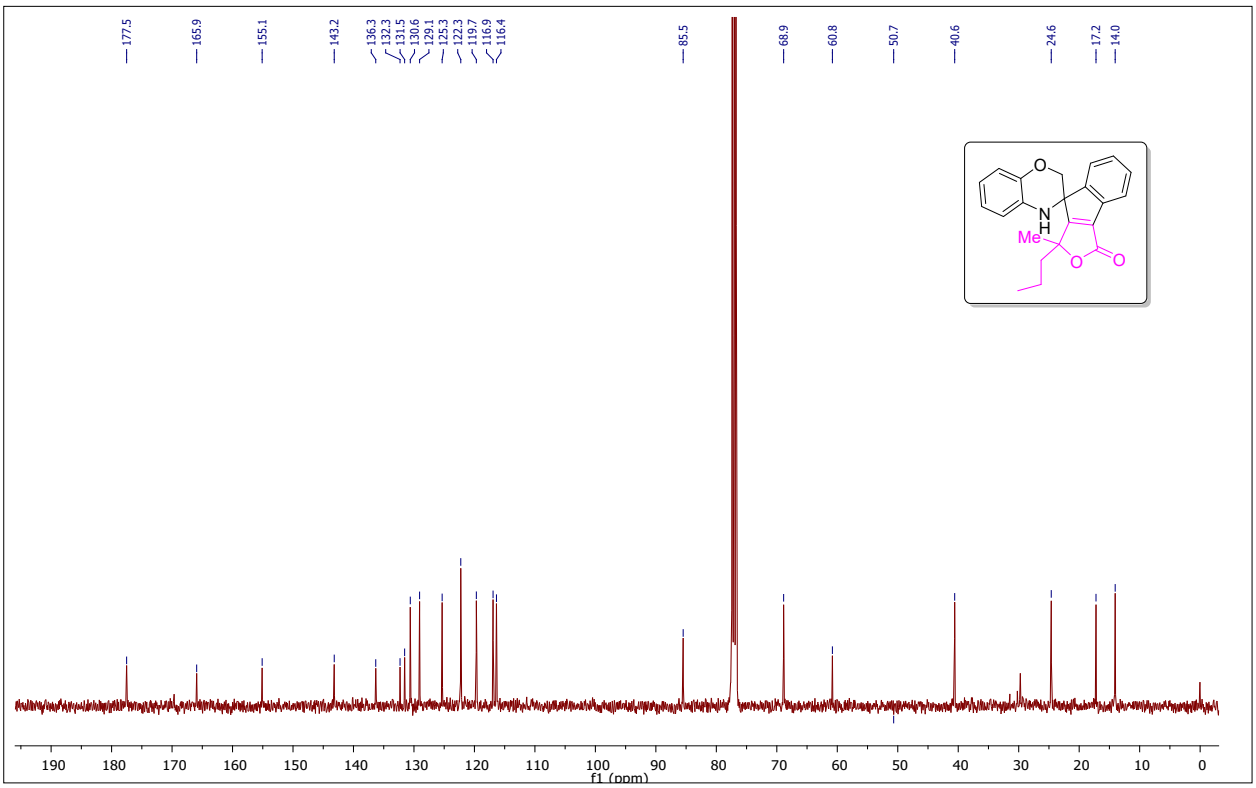
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **3n**



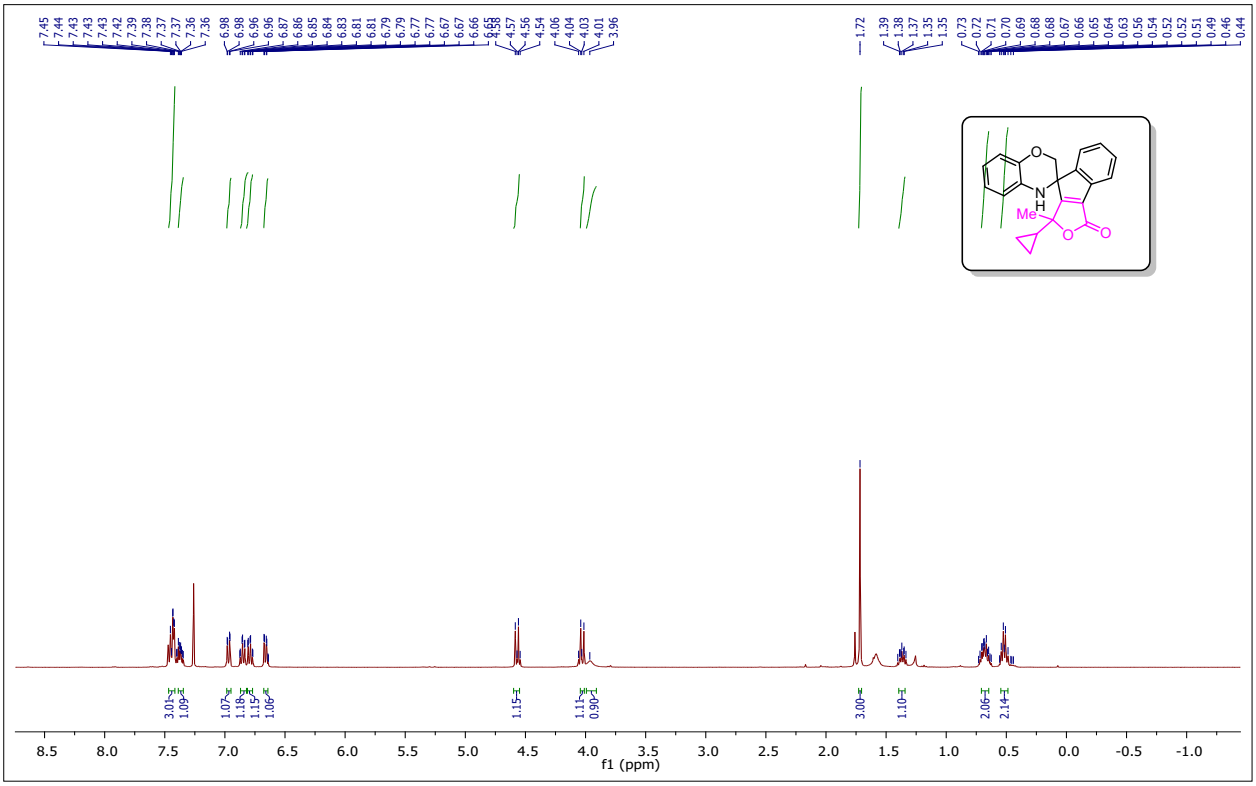
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3o**



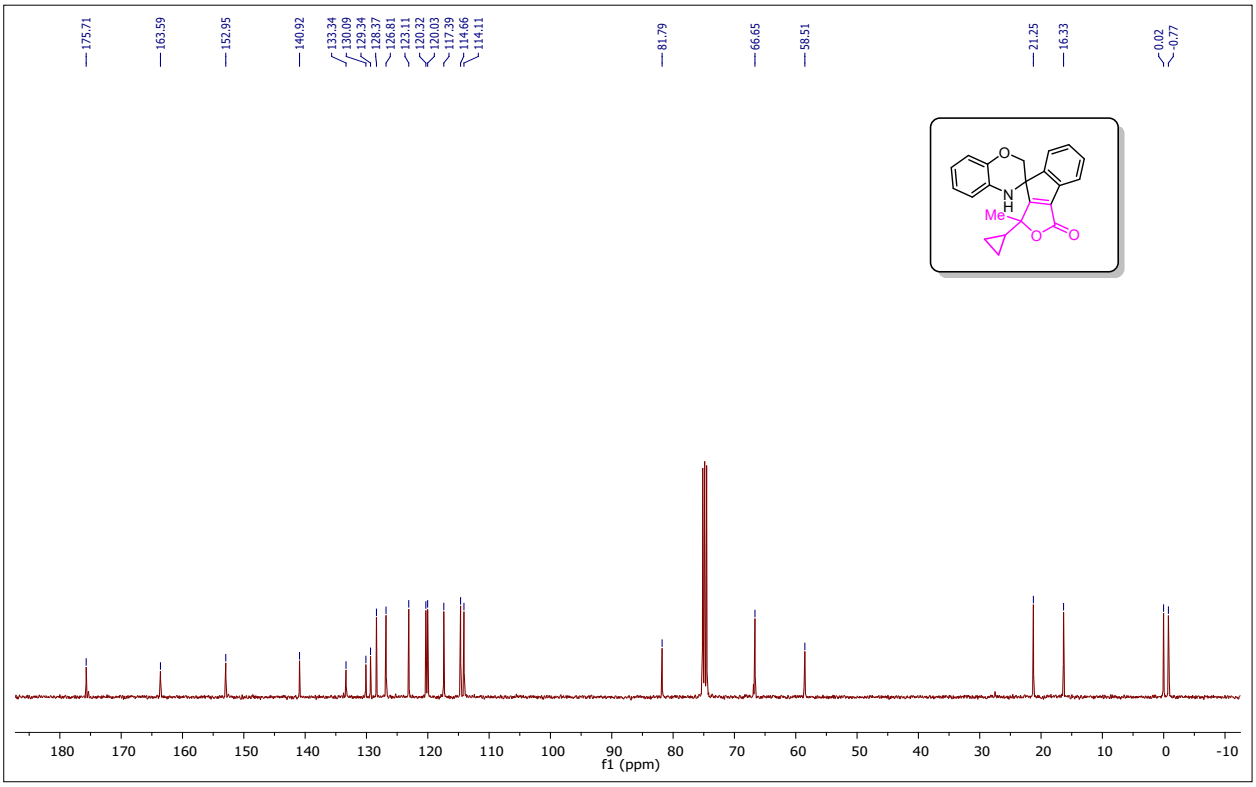
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **3o**



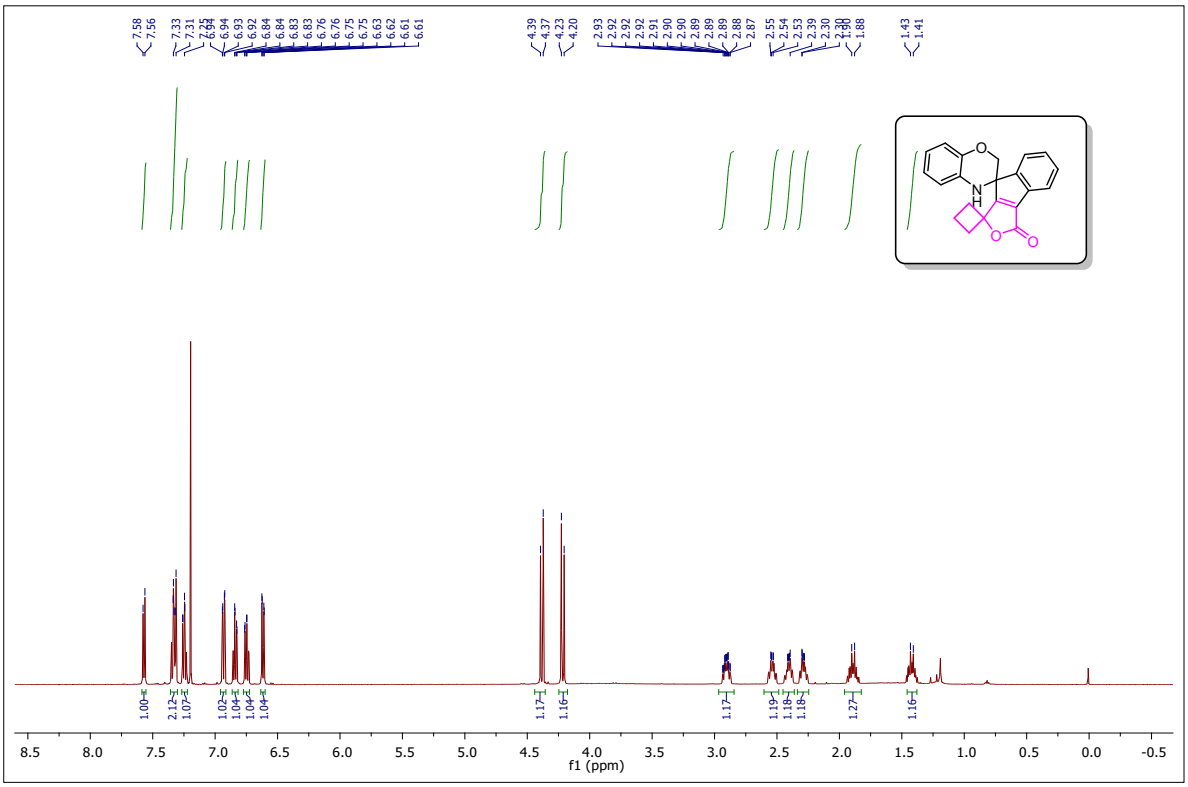
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3q**



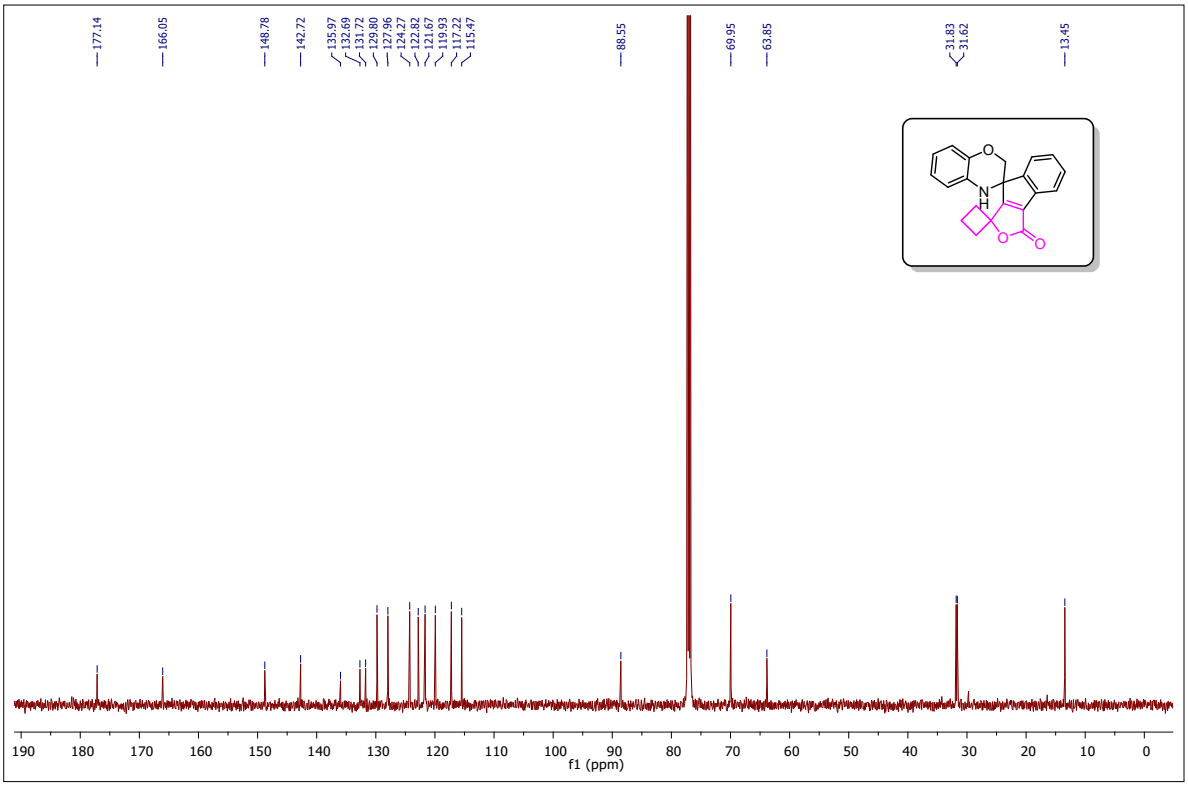
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **3q**



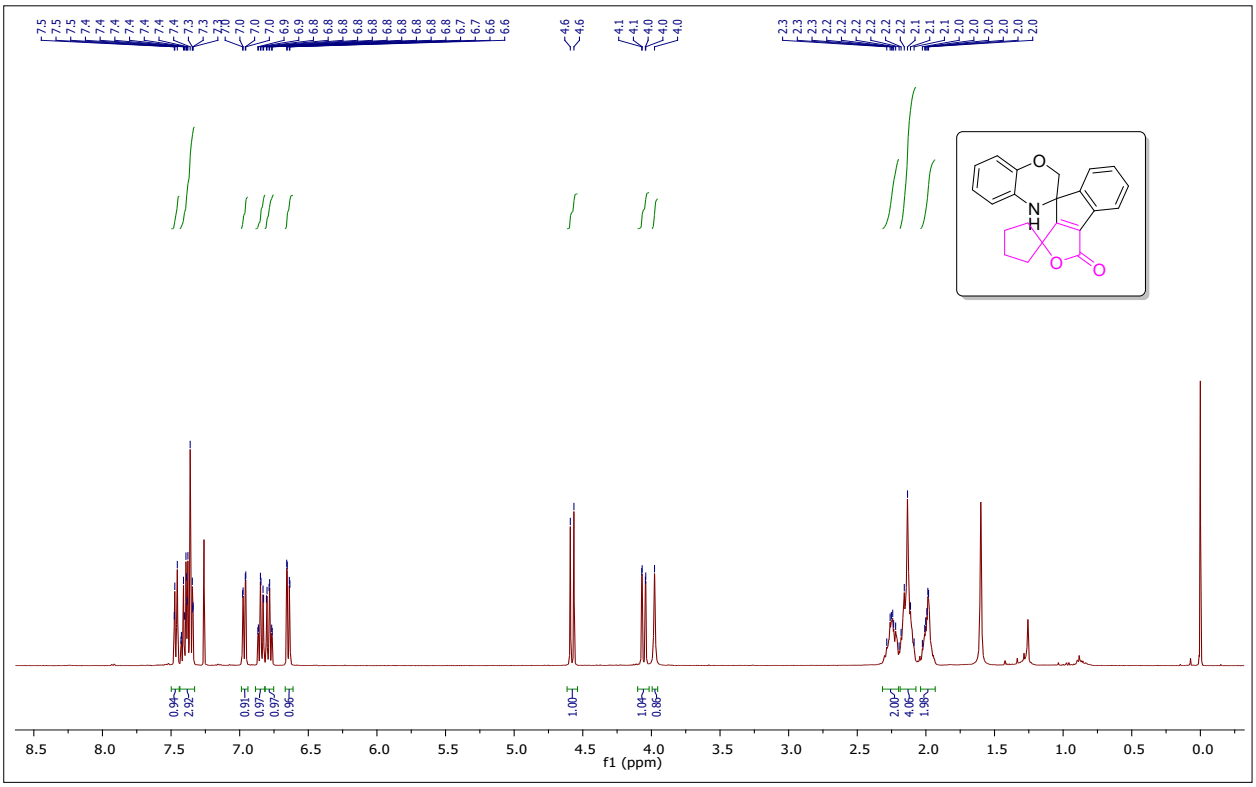
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3r**



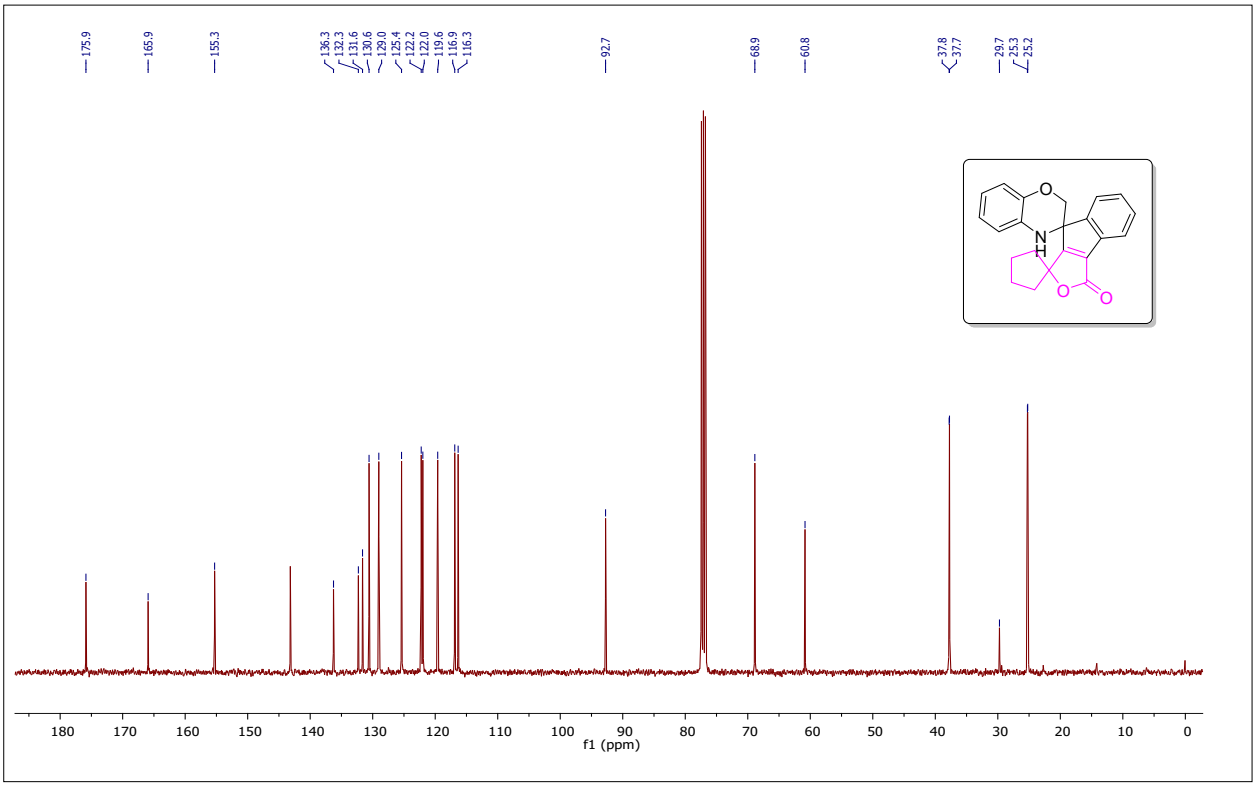
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **3r**



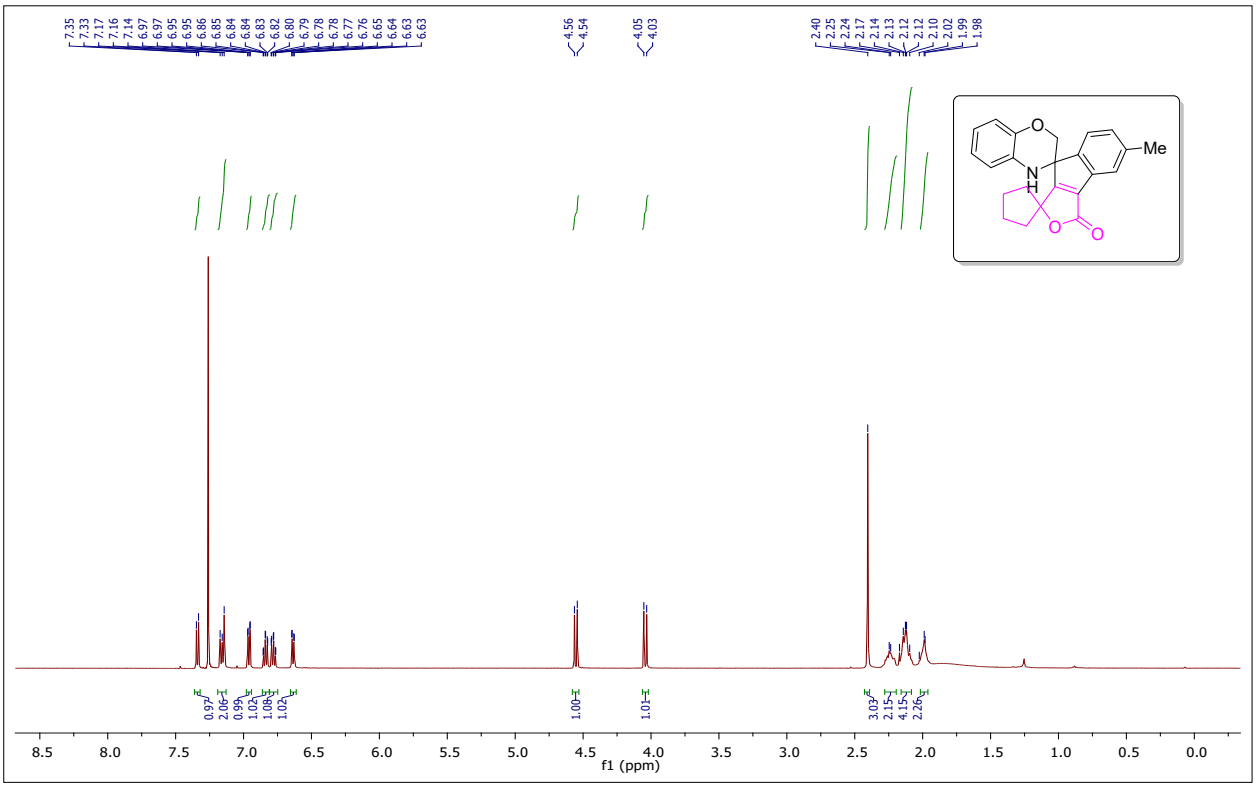
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **5a**



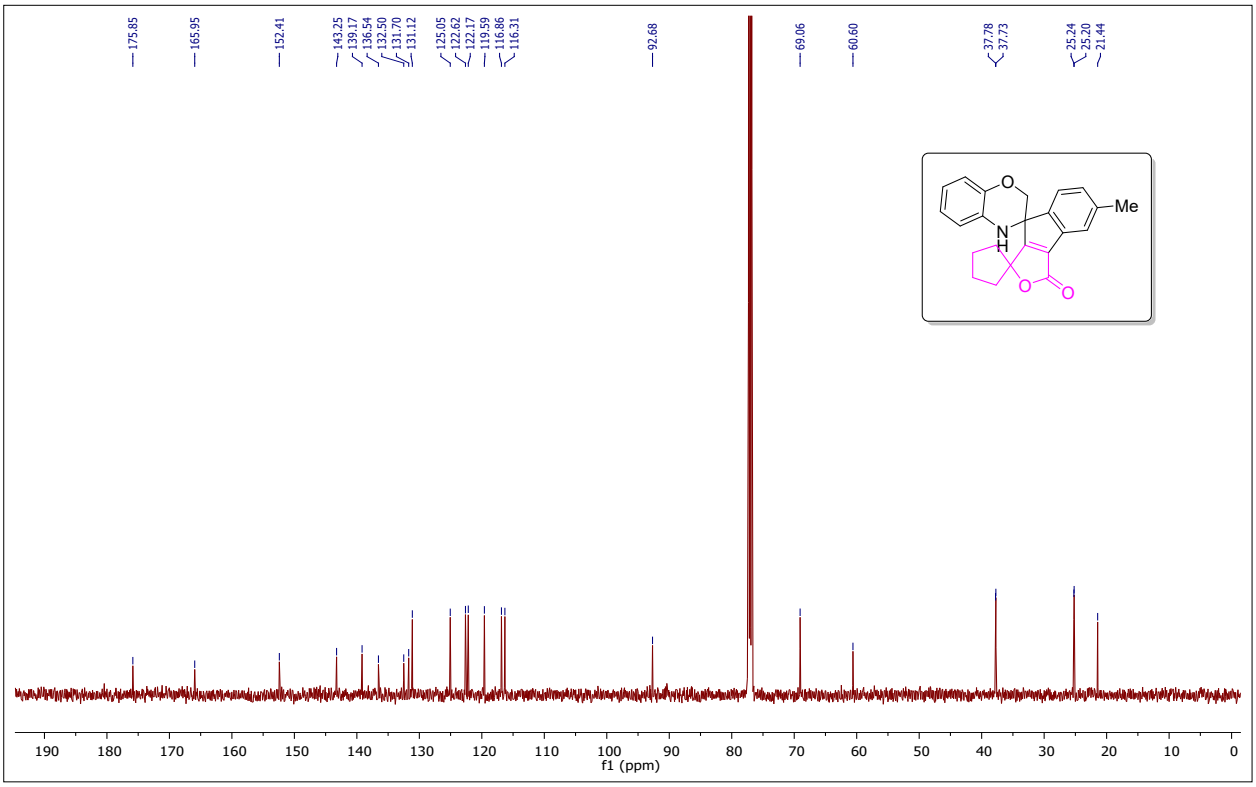
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **5a**



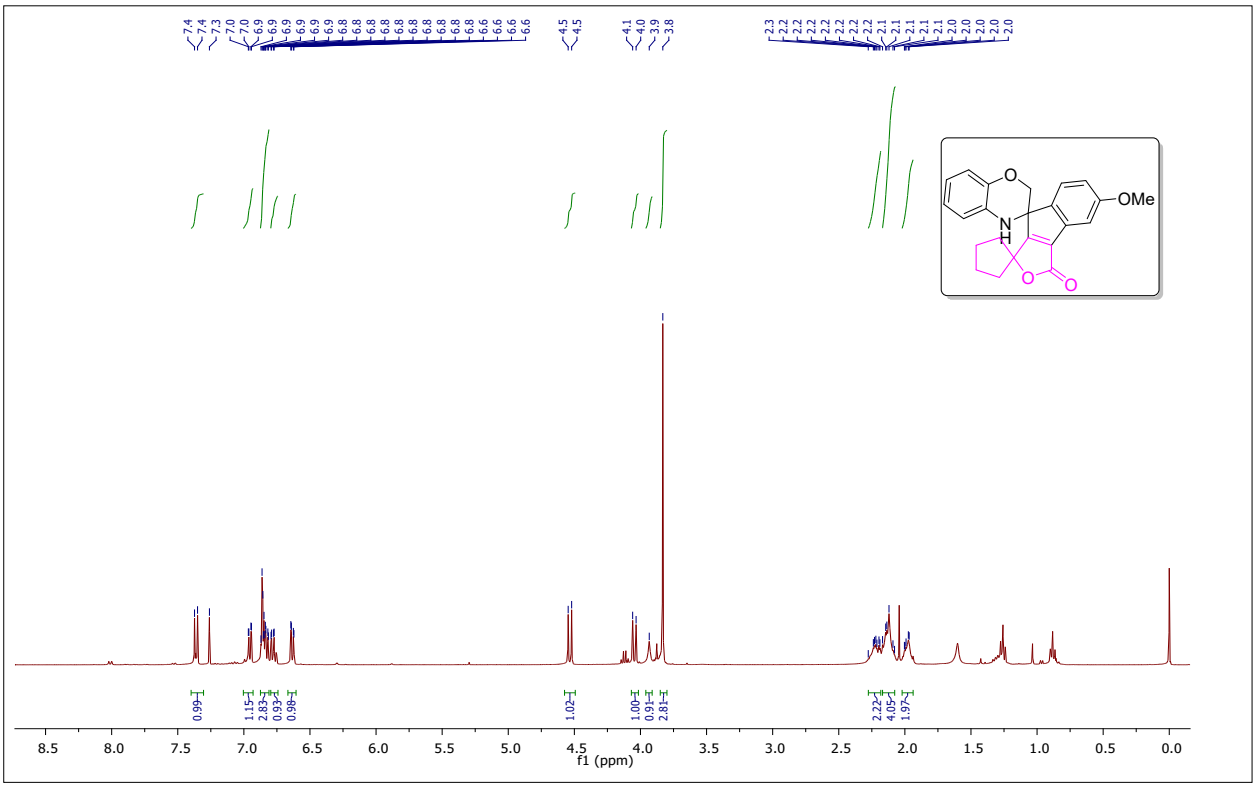
^{1}H NMR (400 MHz,$CDCl_3$) spectrum of compound **5b**



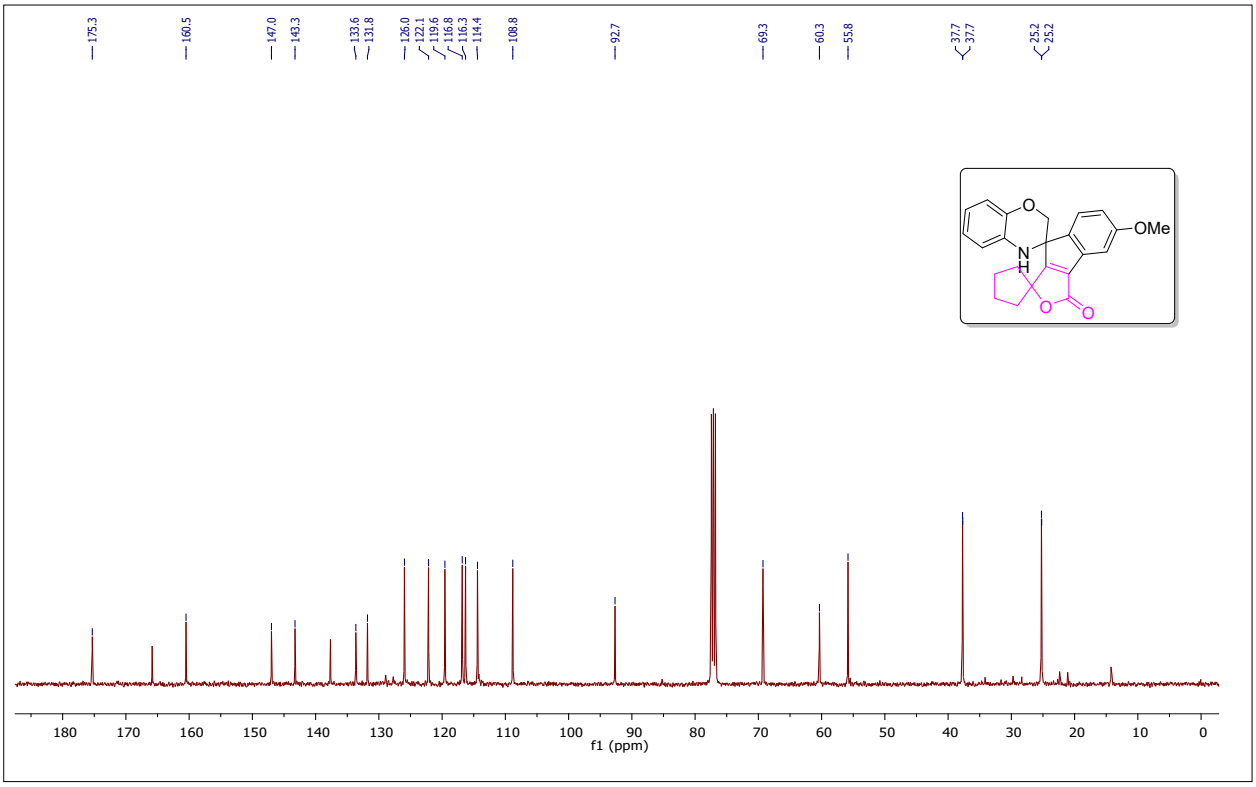
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound 5**b**



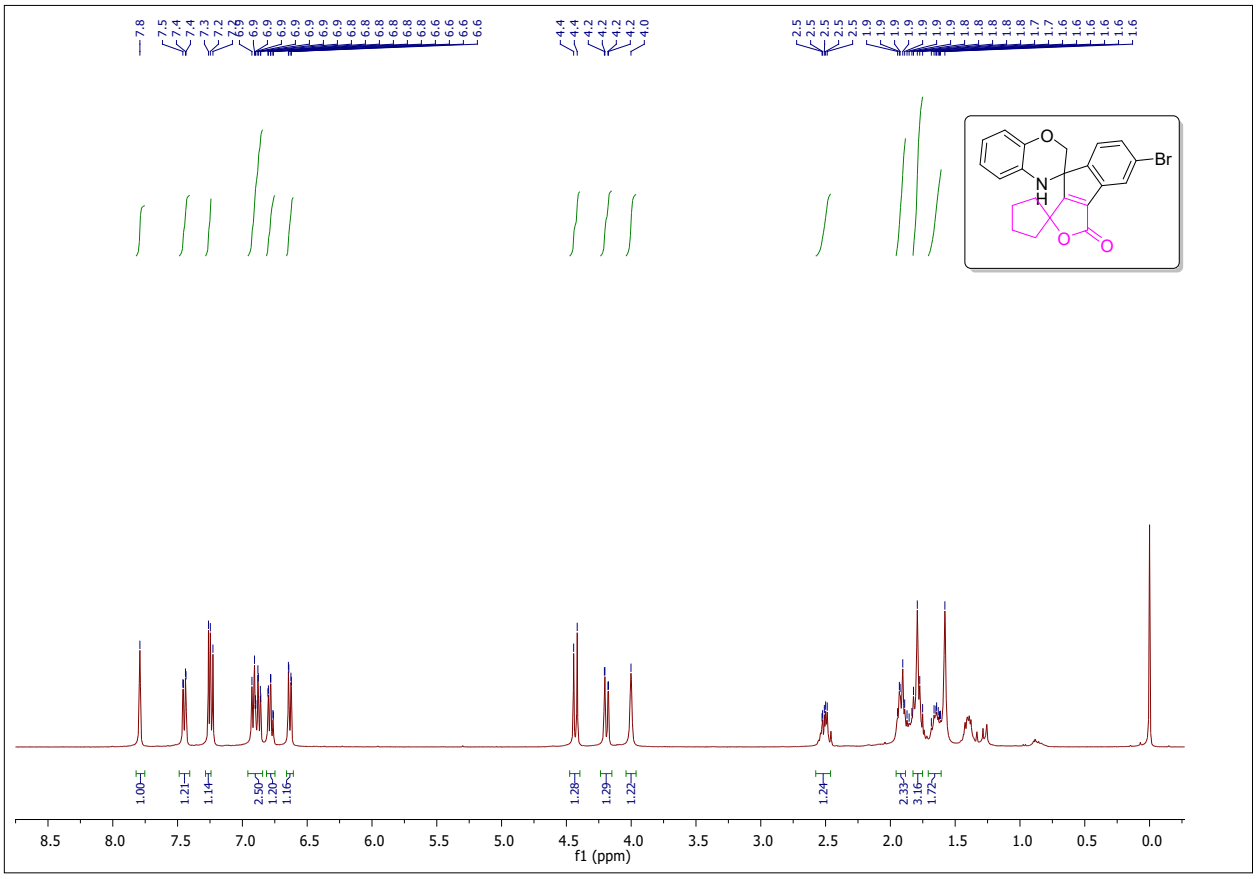
^{1}H NMR (400 MHz,$CDCl_3$) spectrum of compound **5c**



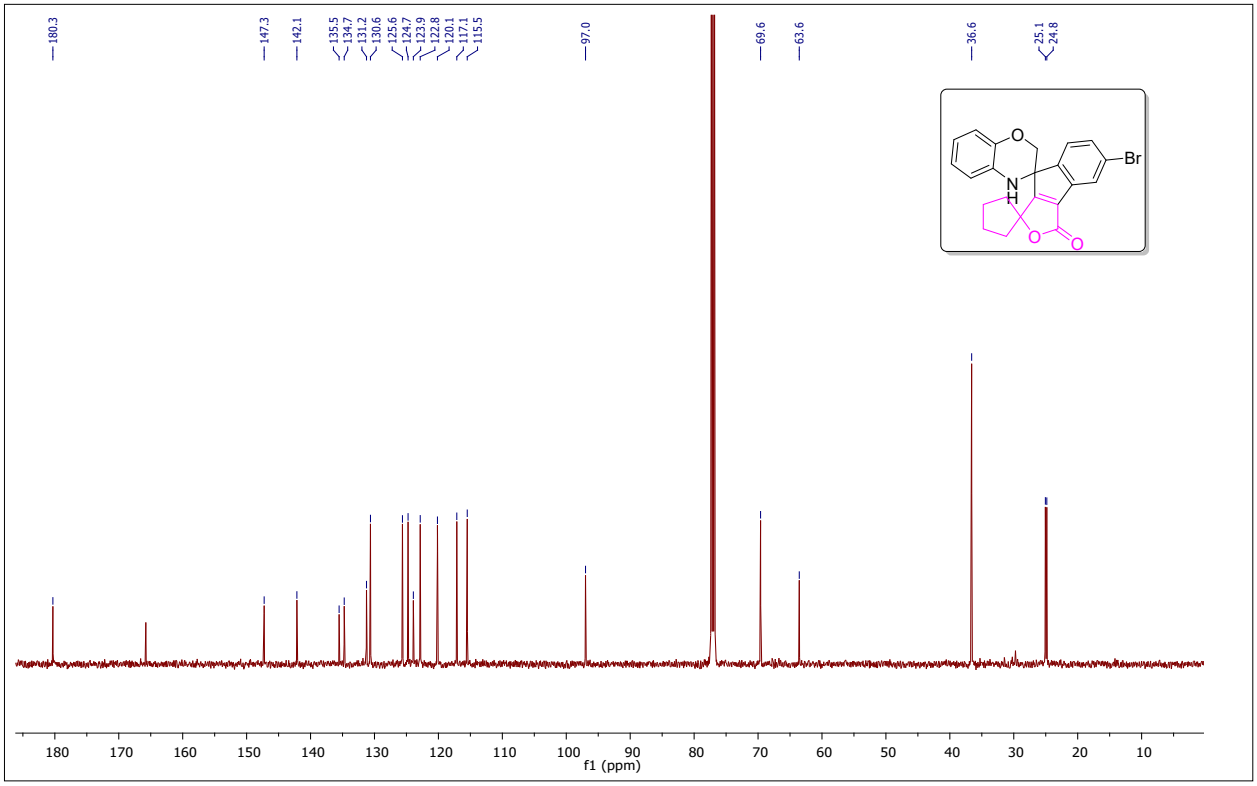
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **5c**



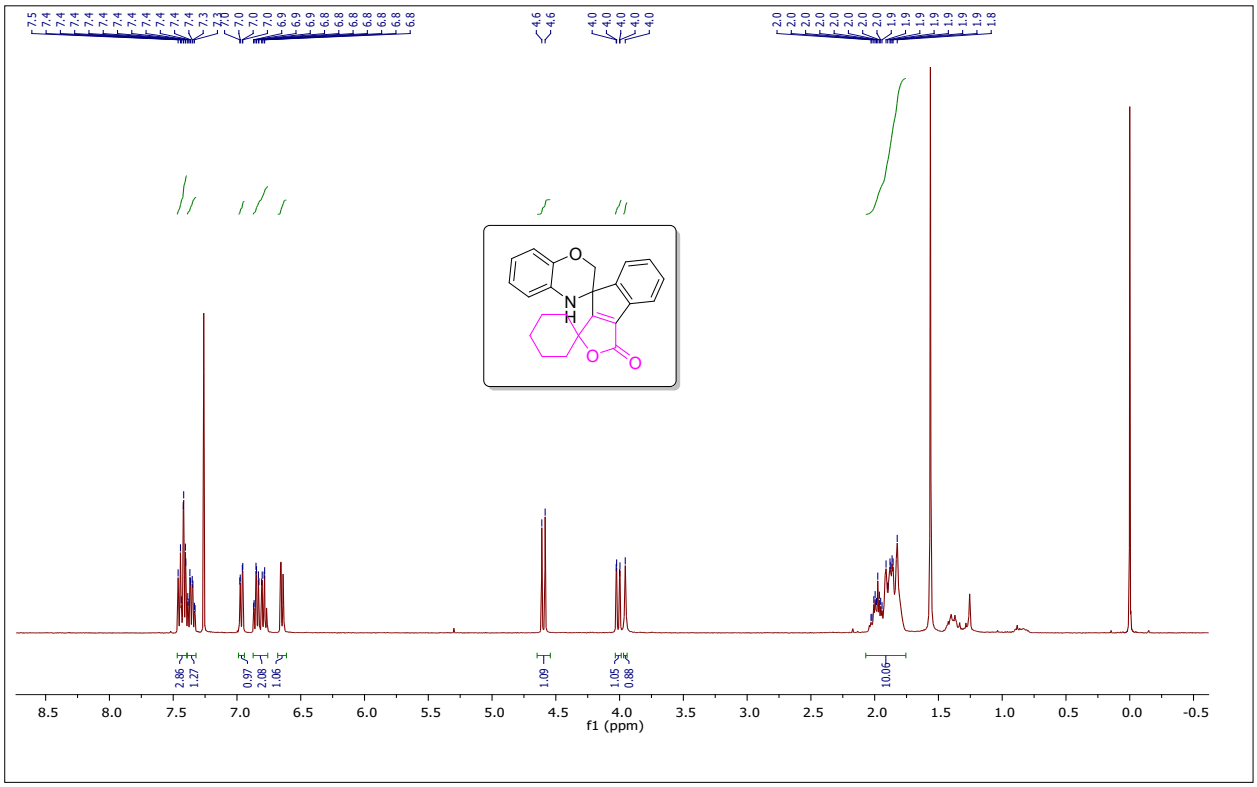
^{1}H NMR (400 MHz,$CDCl_3$) spectrum of compound **5d**



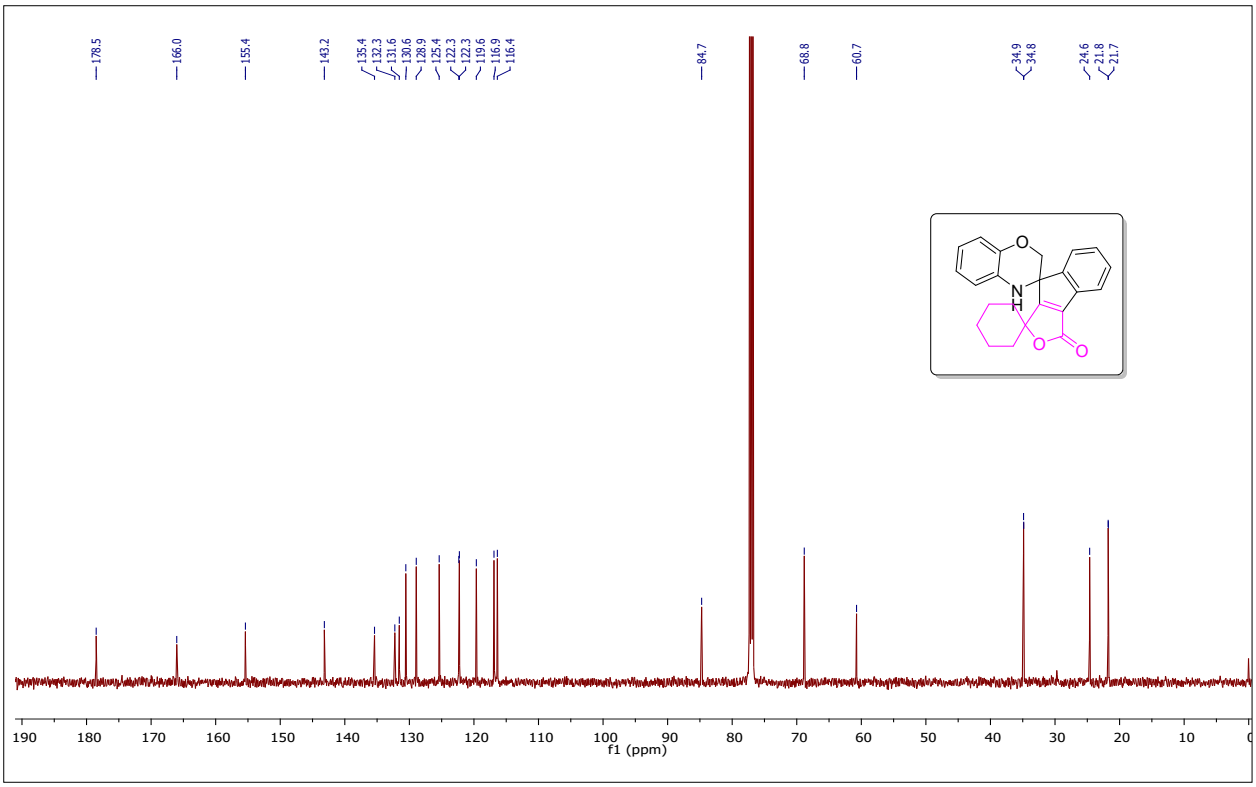
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **5d**



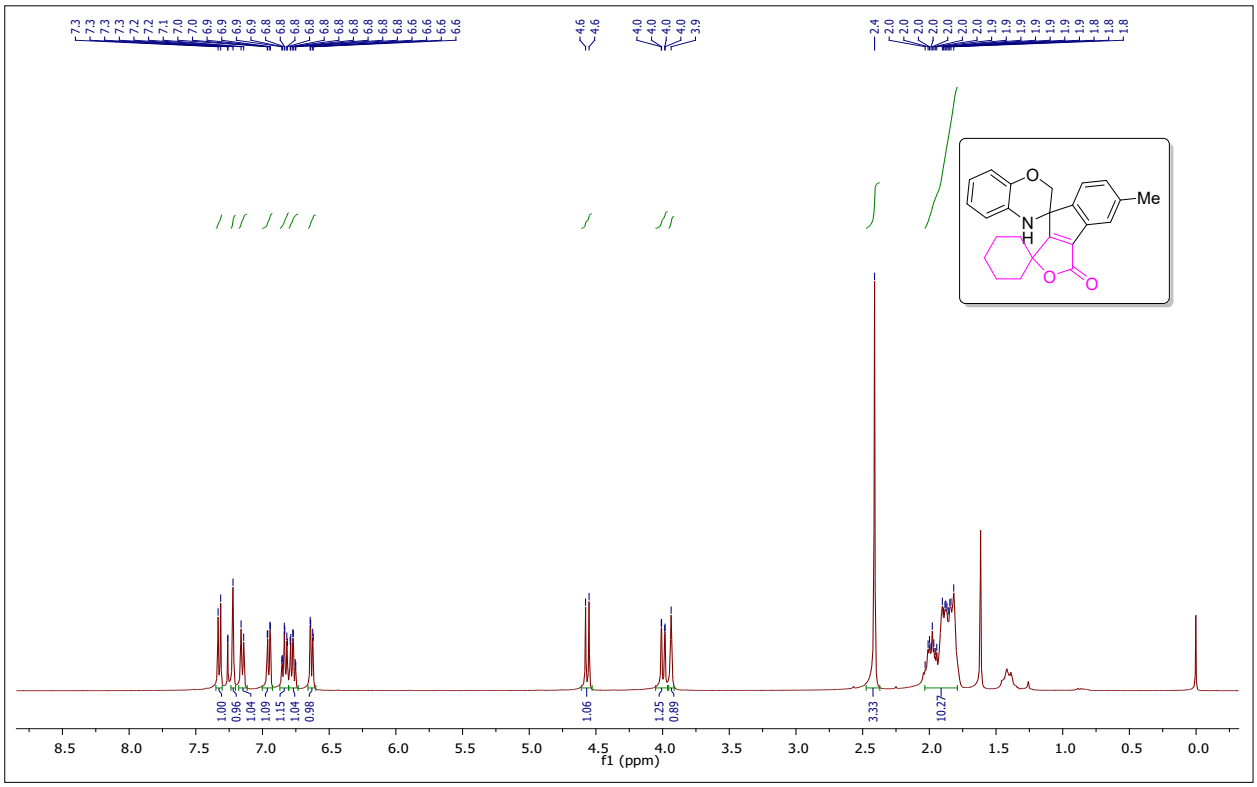
^{1}H NMR (400 MHz,$CDCl_3$) spectrum of compound **5e**



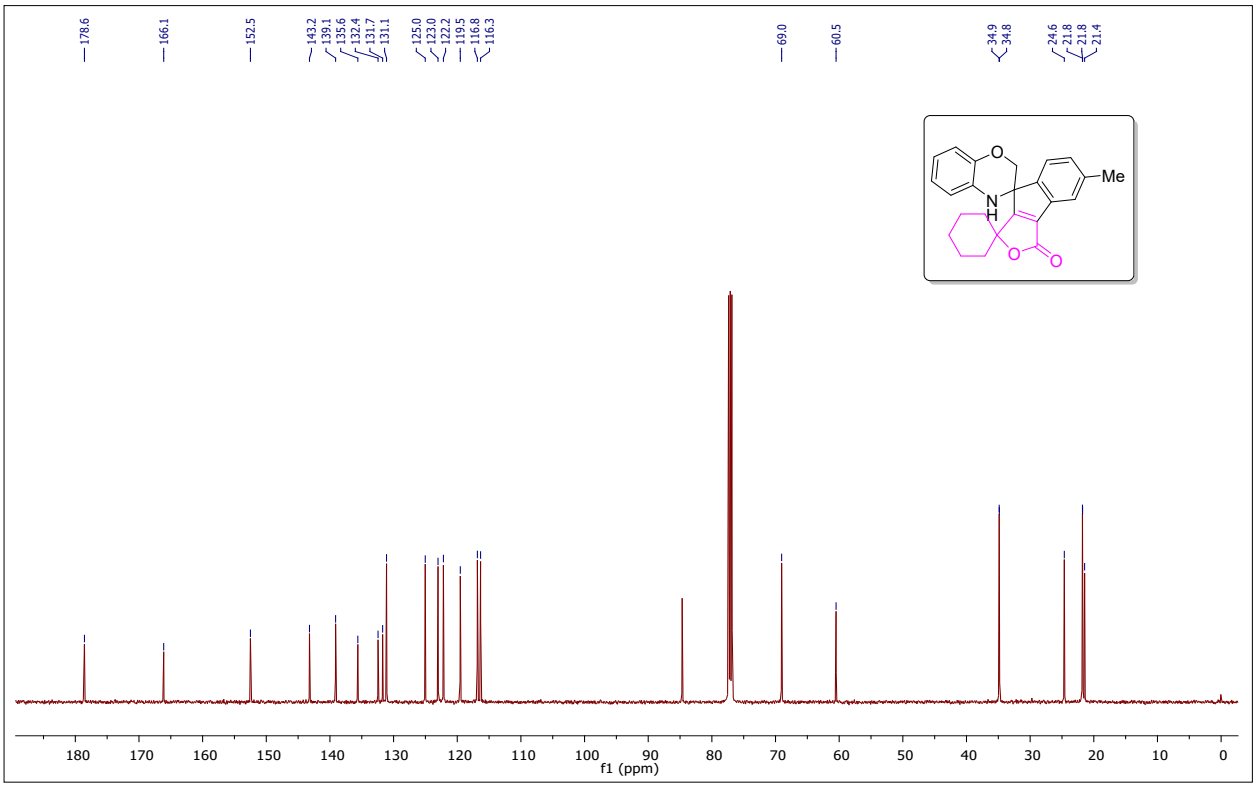
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **5e**



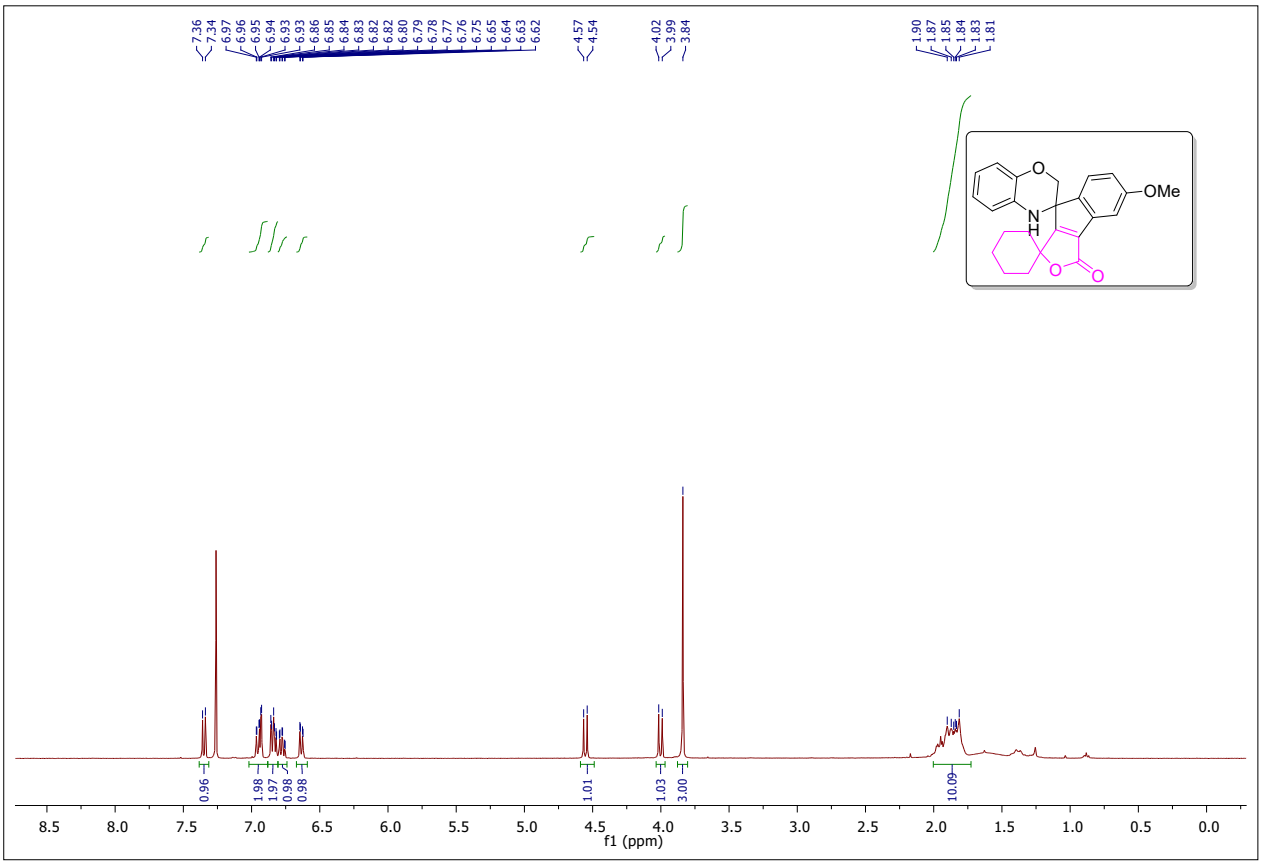
^{1}H NMR (400MHz,$CDCl_3$) spectrum of compound **5f**



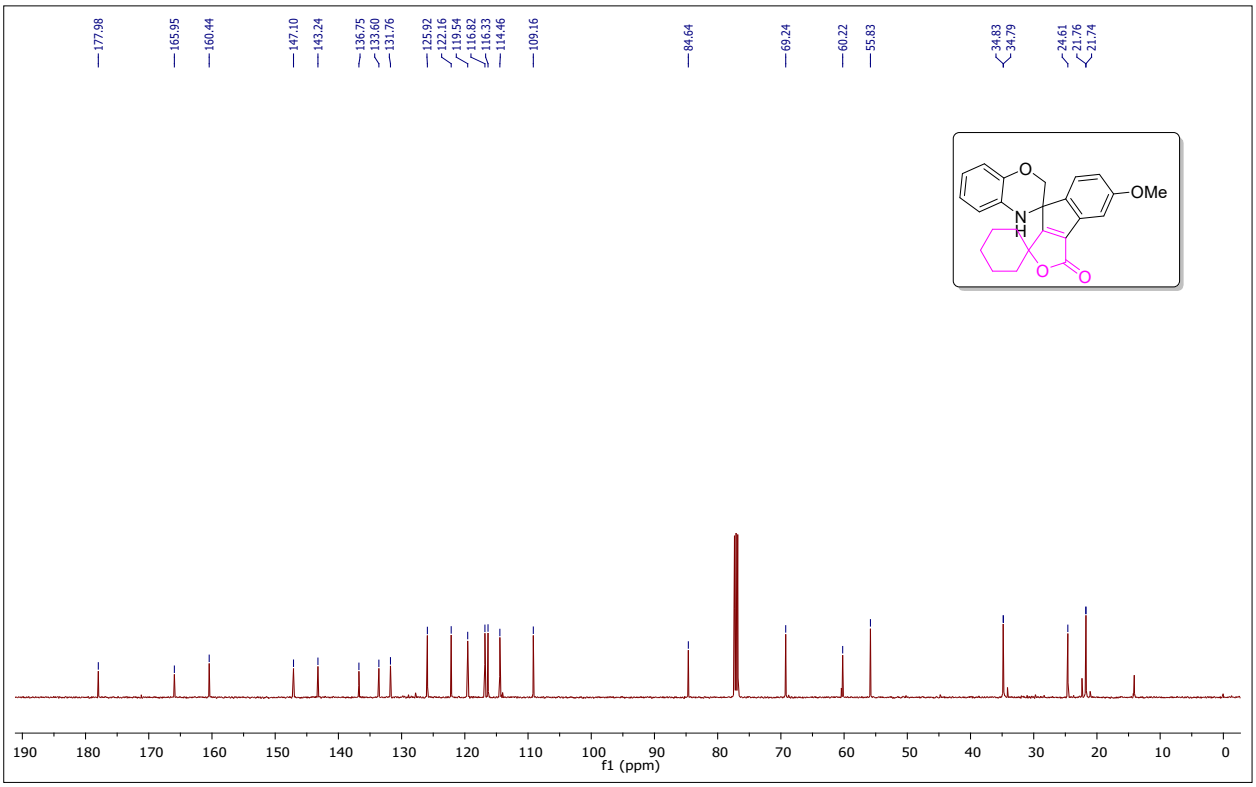
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **5f**



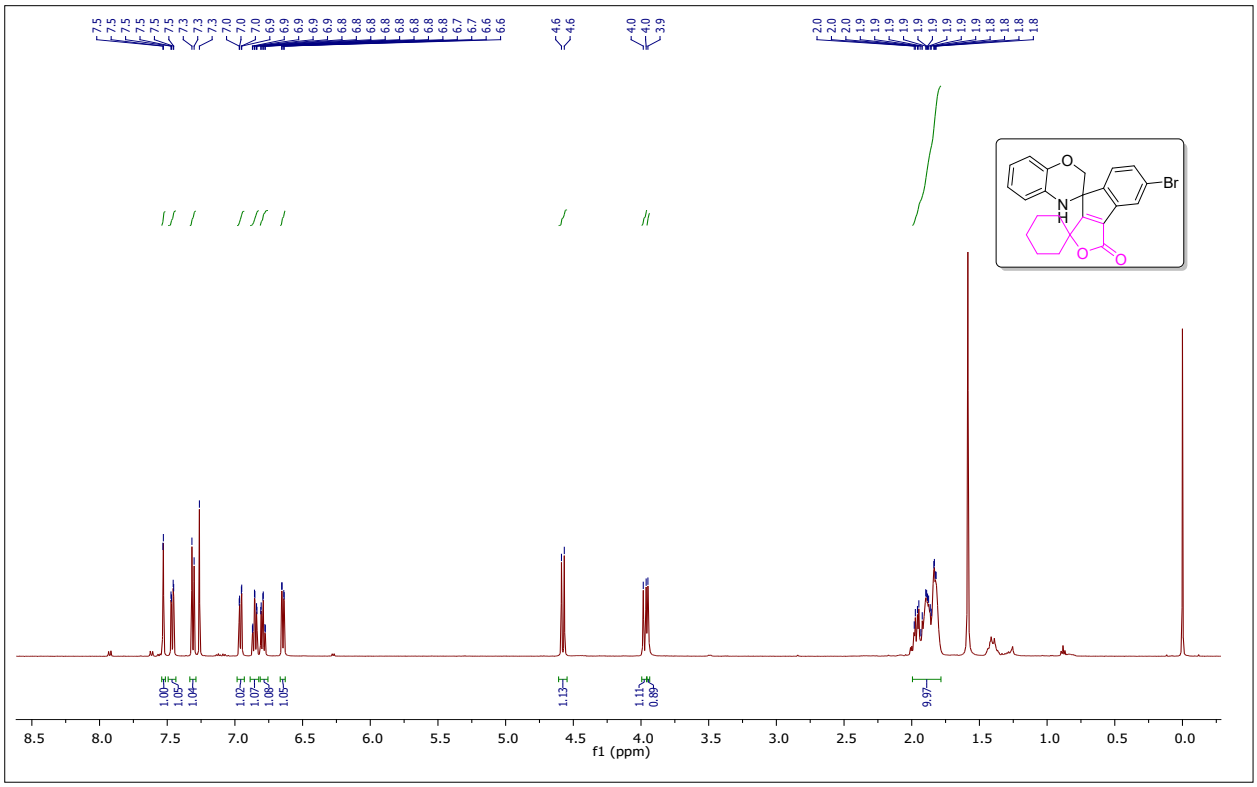
^{1}H NMR (400MHz,$CDCl_3$) spectrum of compound **5g**



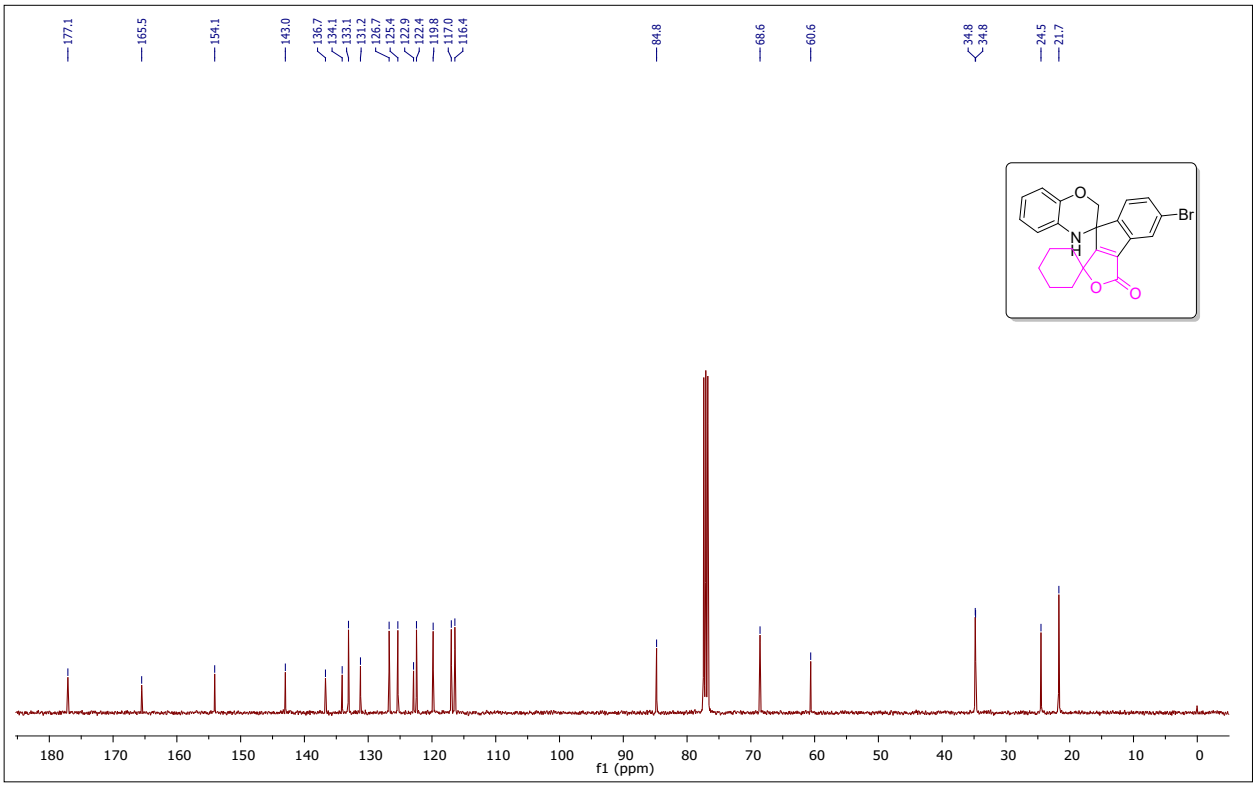
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **5g**



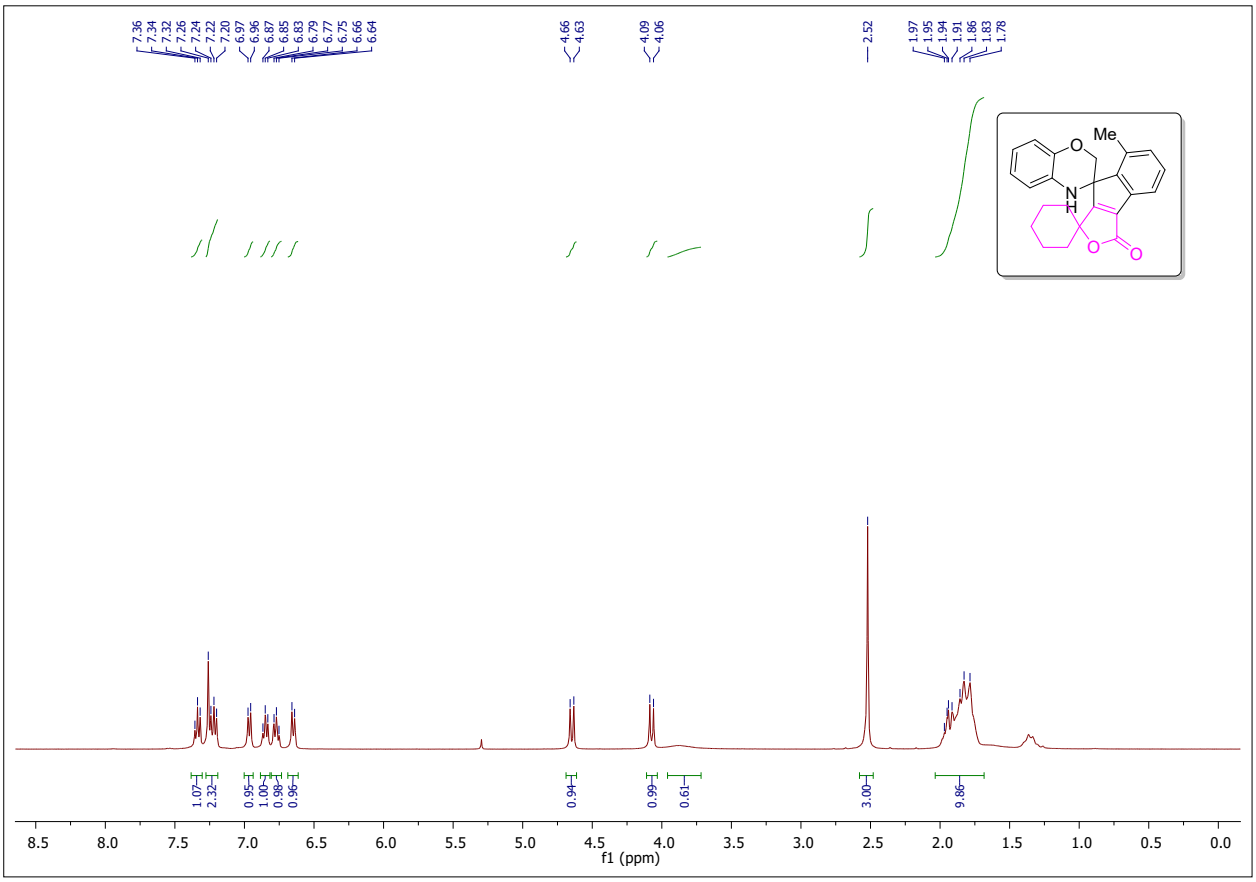
^{1}H NMR (400 MHz,$CDCl_3$) spectrum of compound **5h**



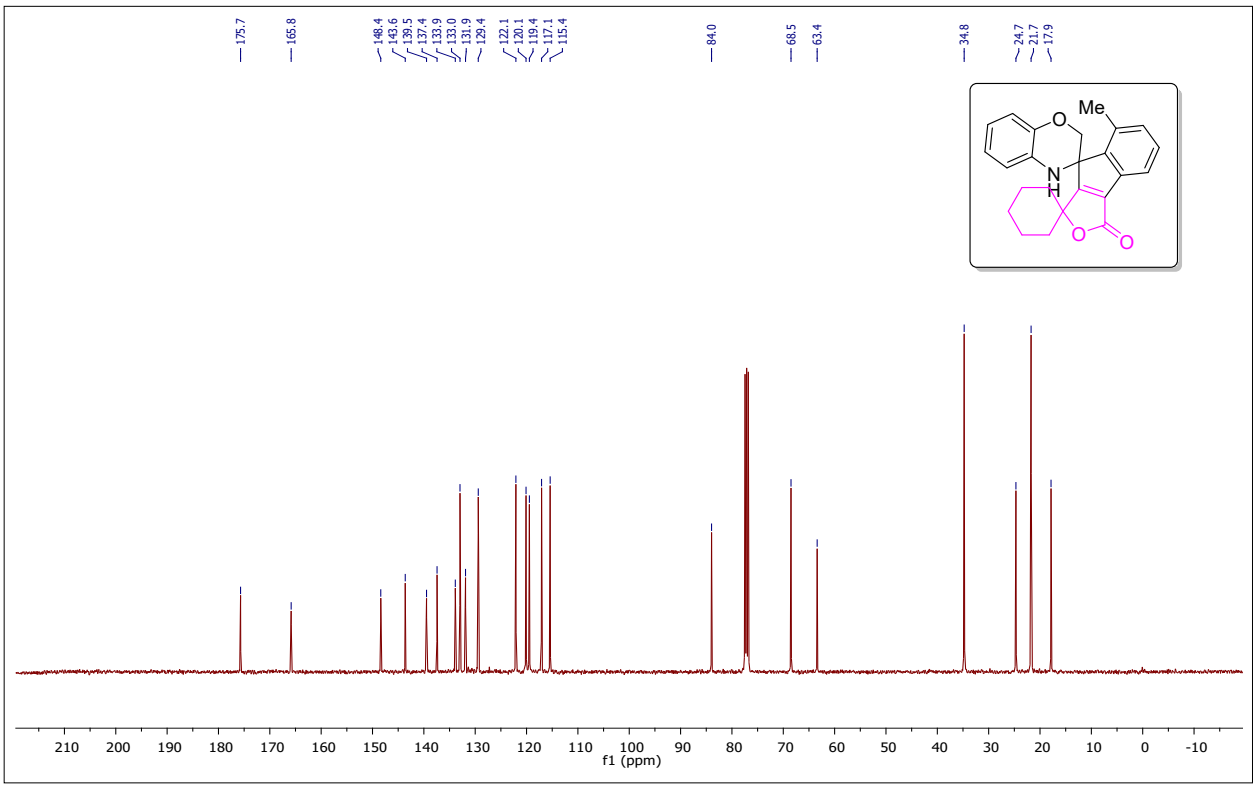
^{3}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **5h**



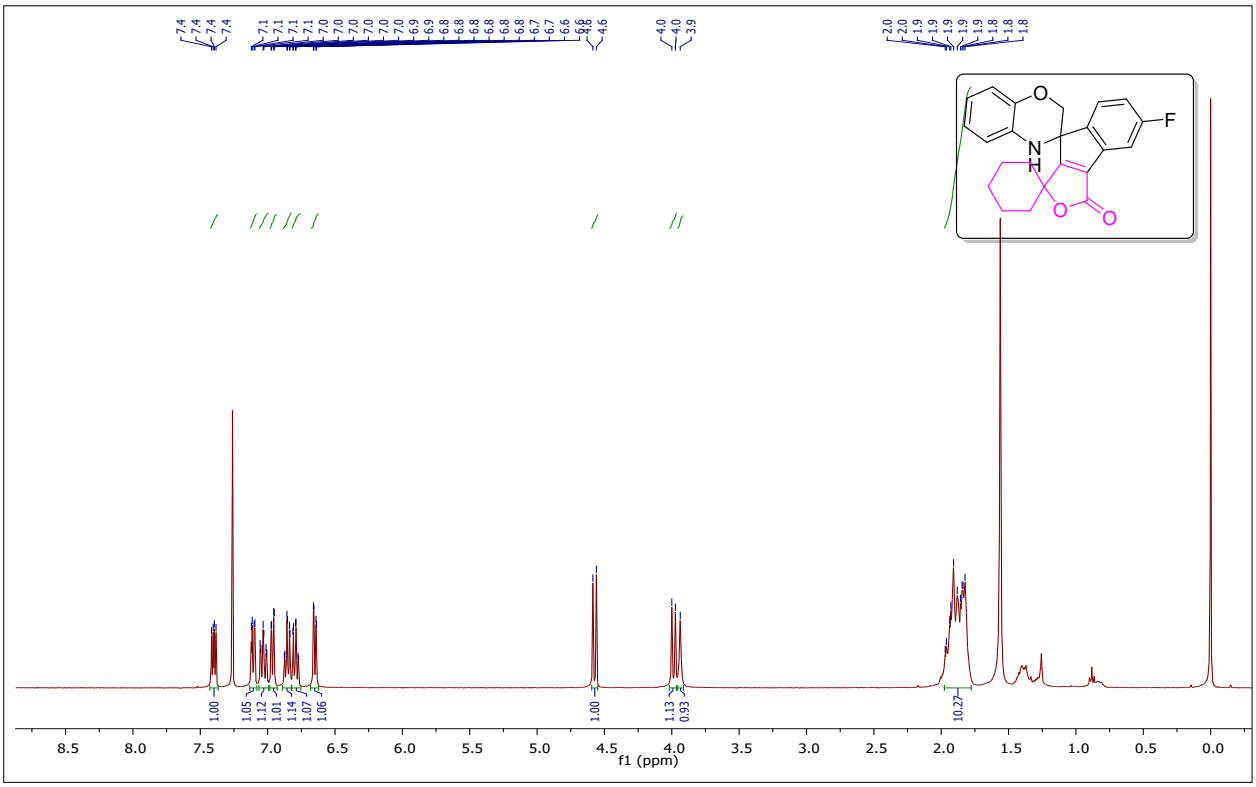
^{1}H NMR (500MHz,$CDCl_3$) spectrum of compound **5i**



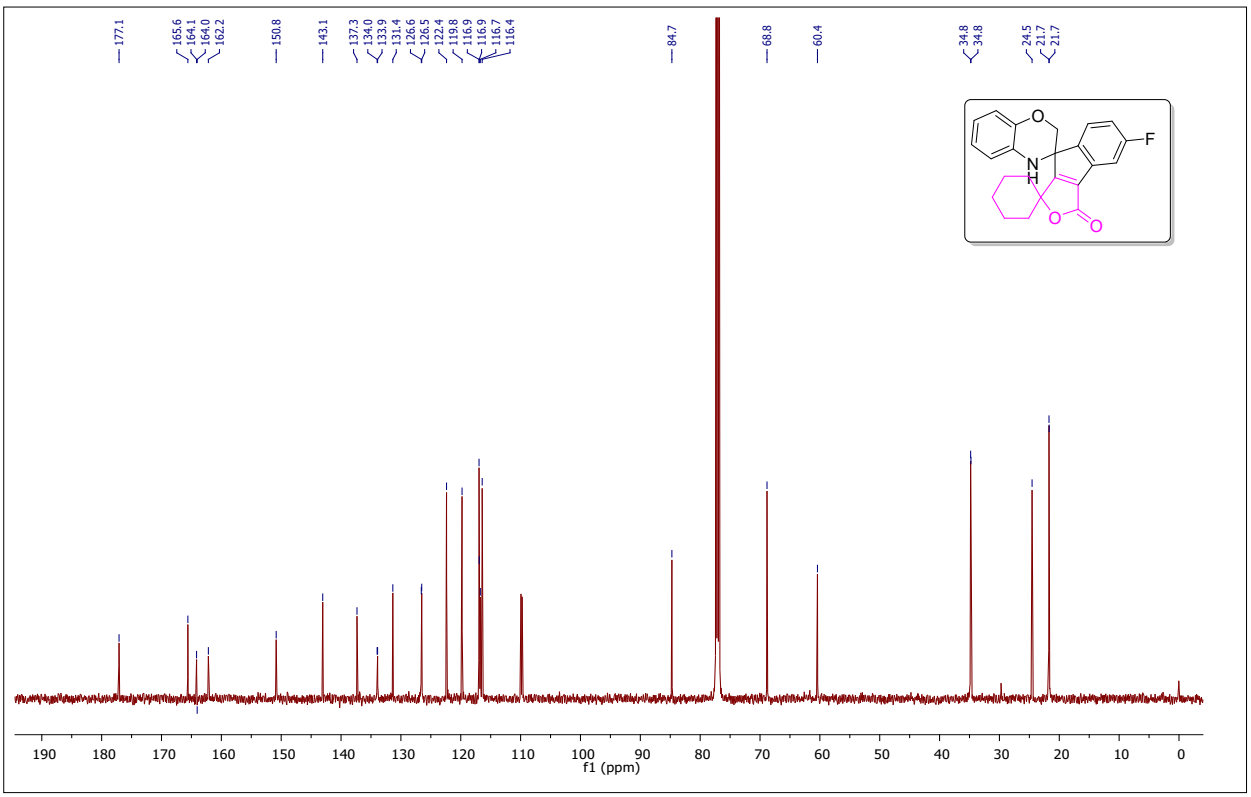
^{13}C{^{1}H}NMR (125MHz, $CDCl_3$) spectrum of compound 5**i**



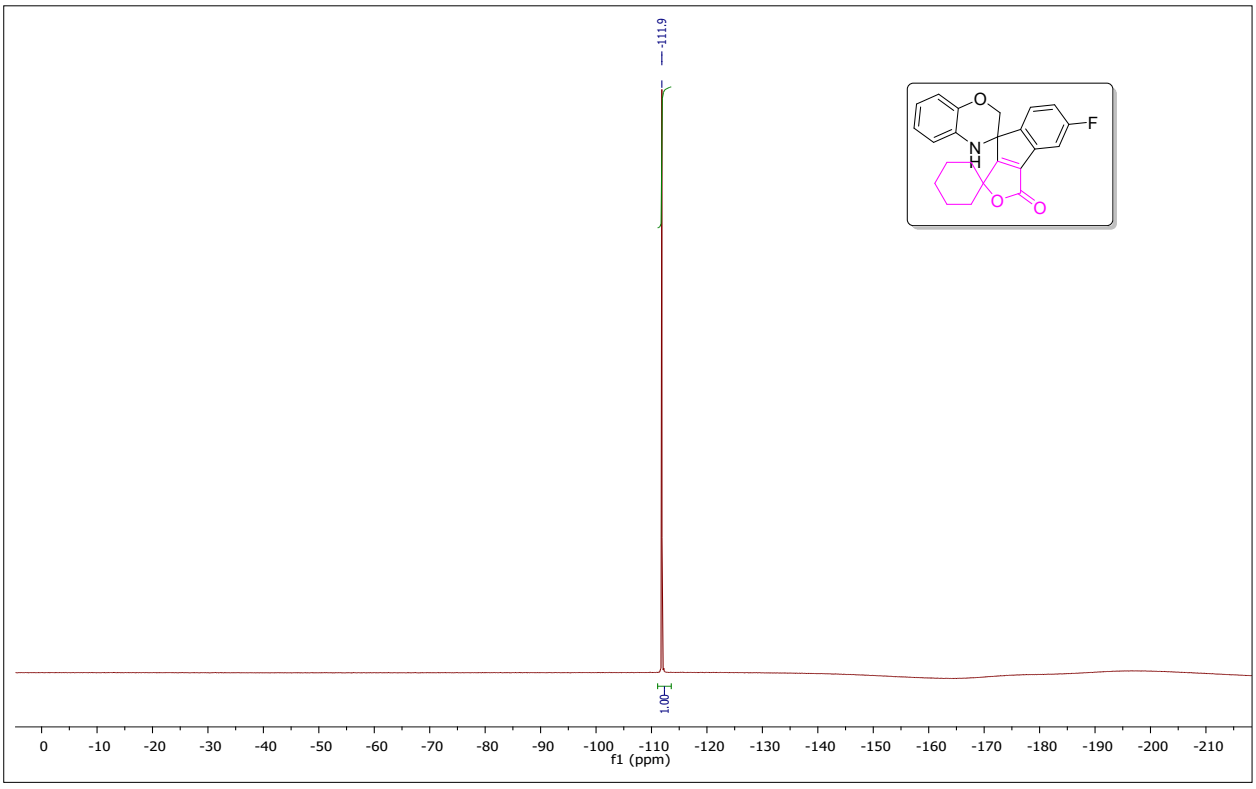
^{1}H NMR (400 MHz,$CDCl_3$) spectrum of compound **5j**



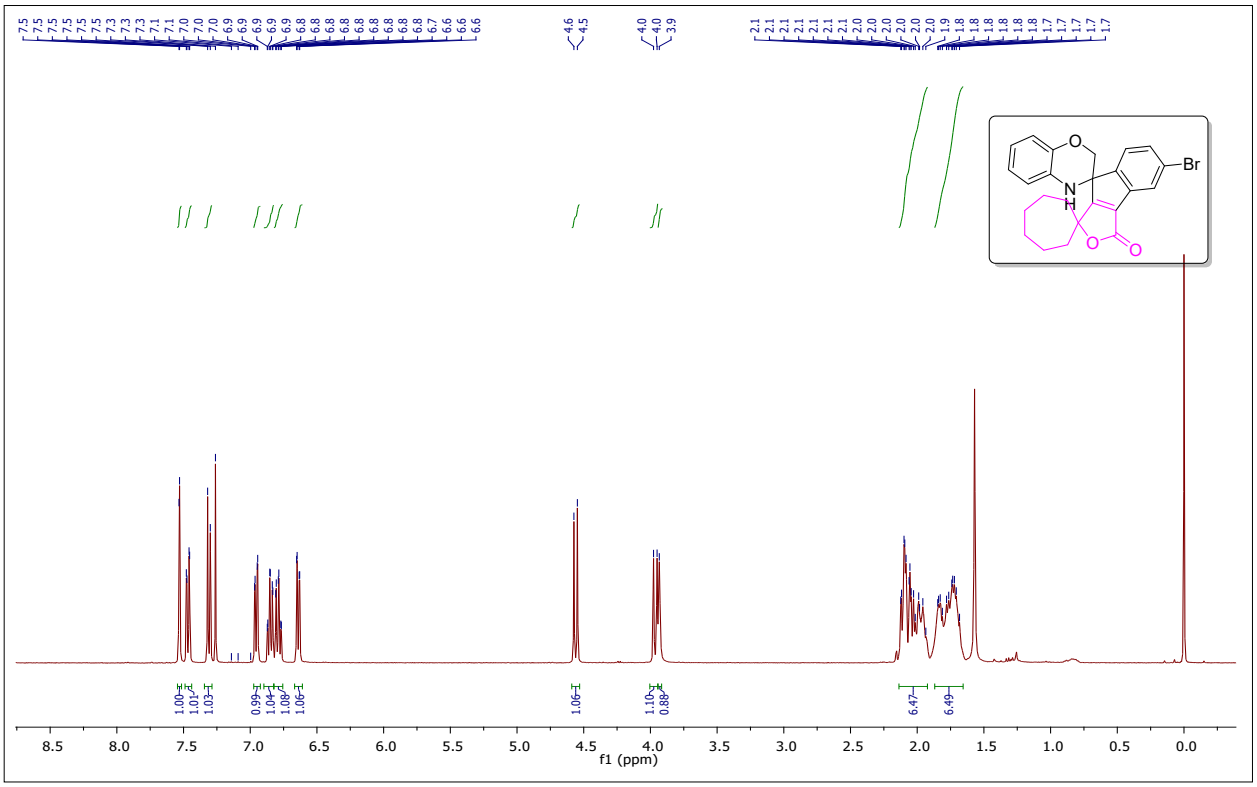
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound 5**j**



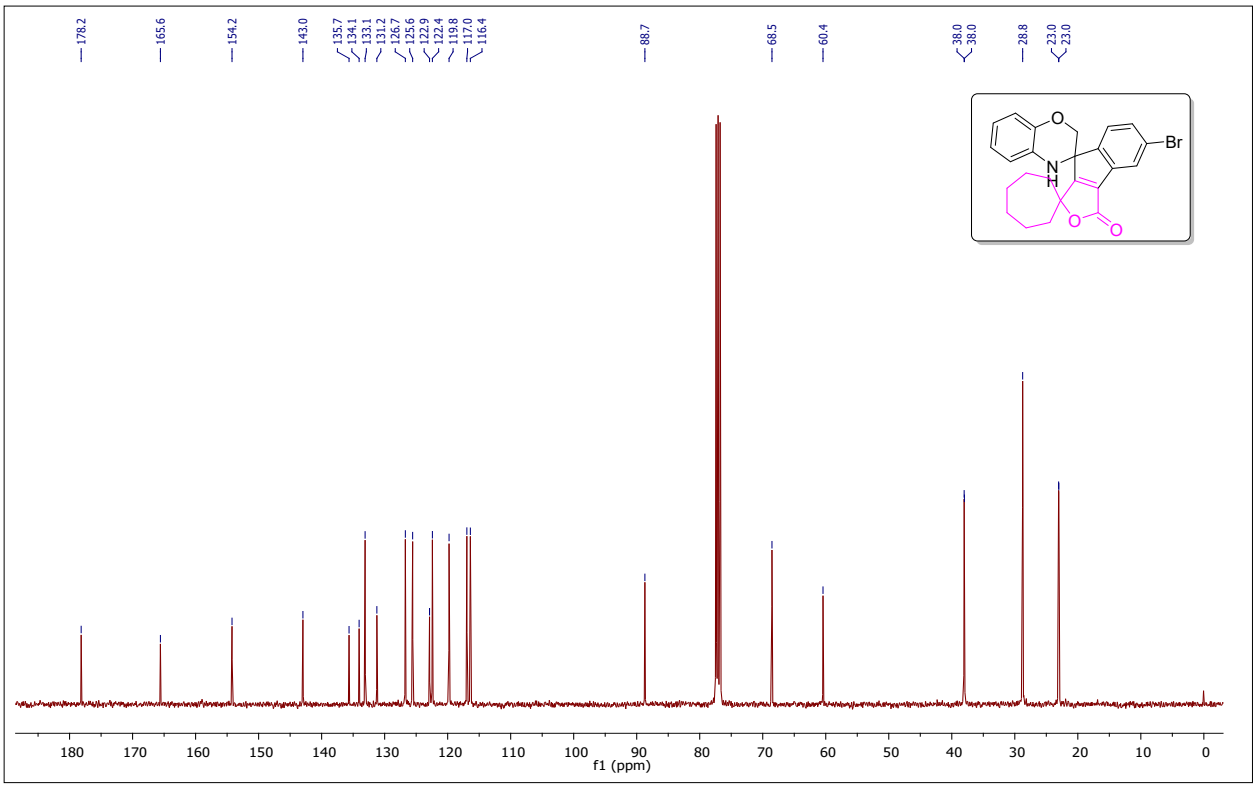
F^{19}NMR (400MHz,$CDCl_3$) spectrum of compound **5j**



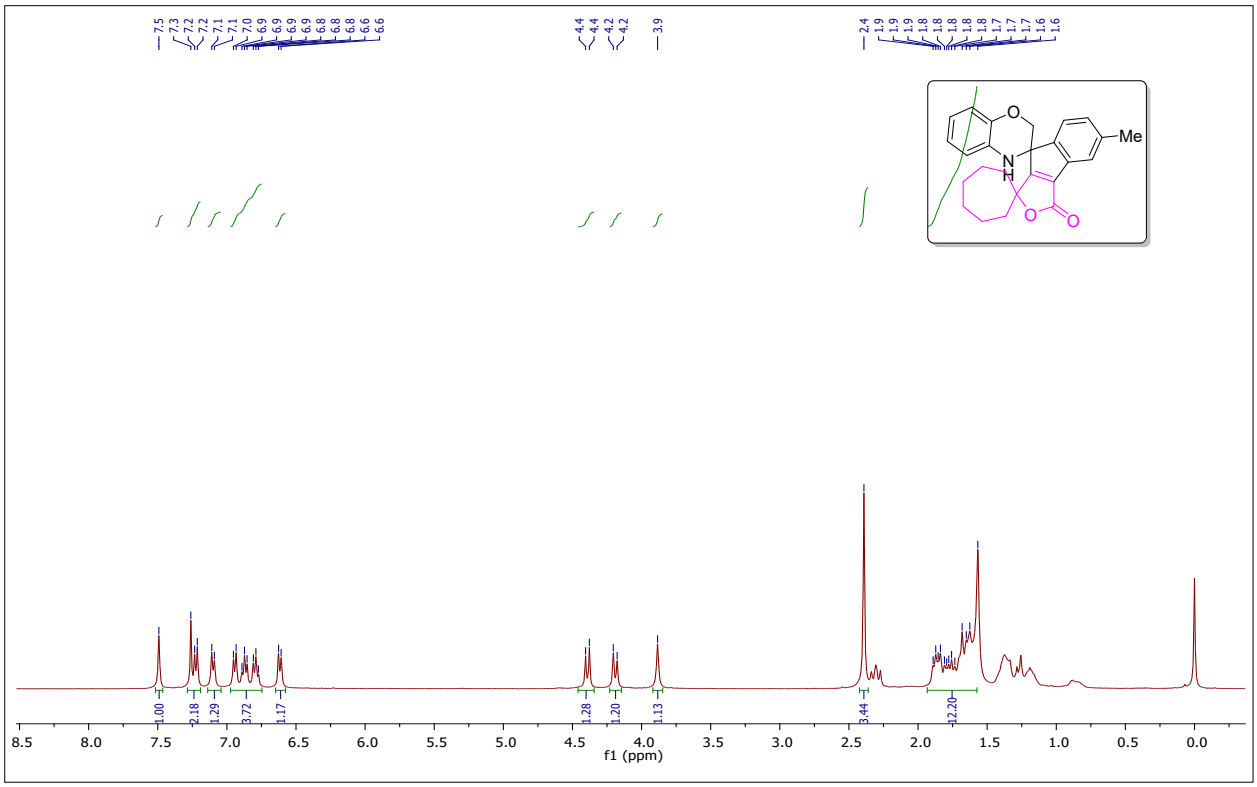
^{1}H NMR (400 MHz,$CDCl_3$) spectrum of compound **5k**



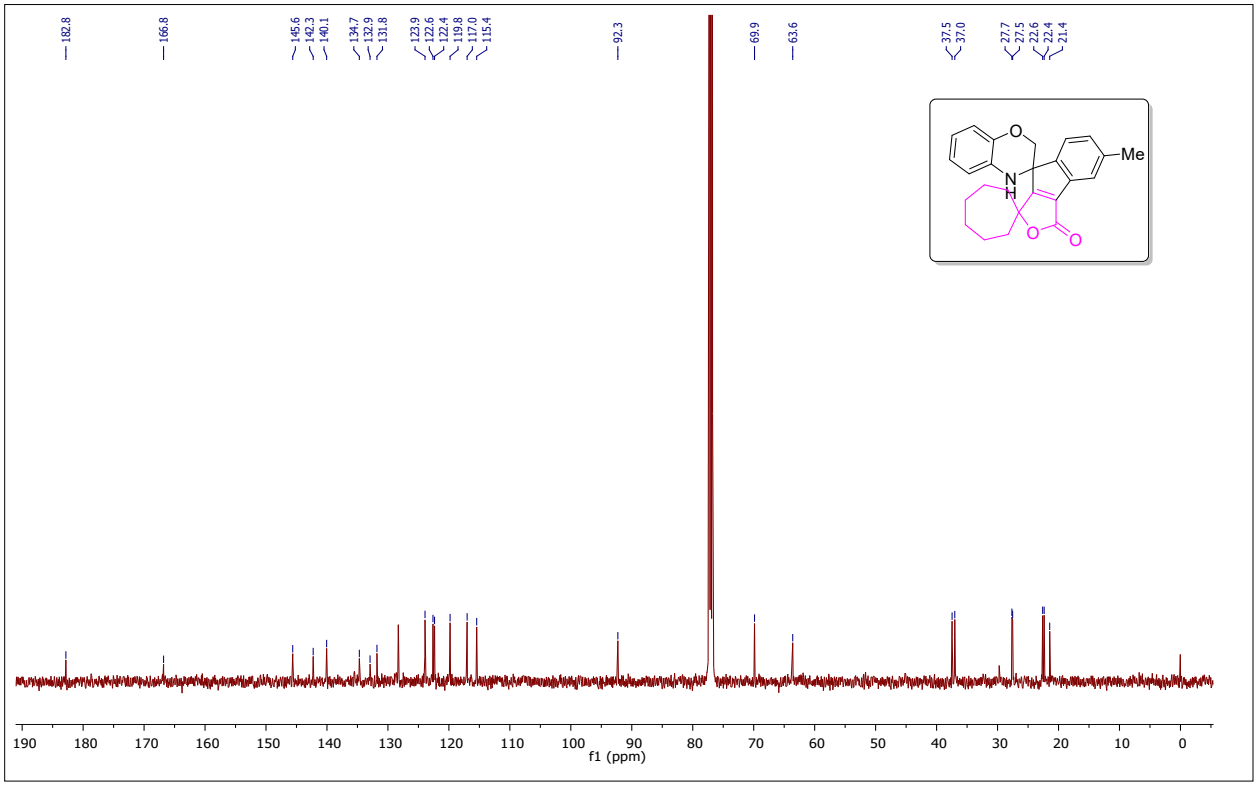
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **5k**



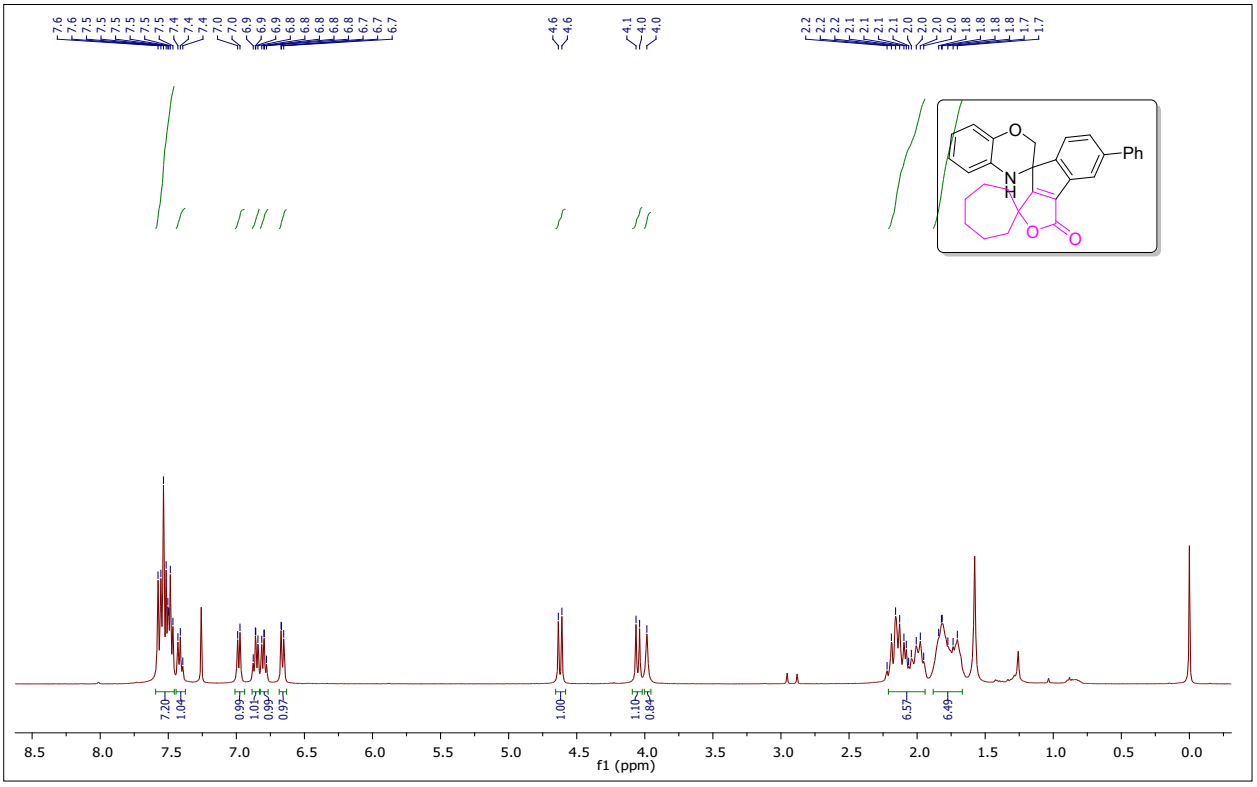
^{1}H NMR (400 MHz,$CDCl_3$) spectrum of compound **5l**



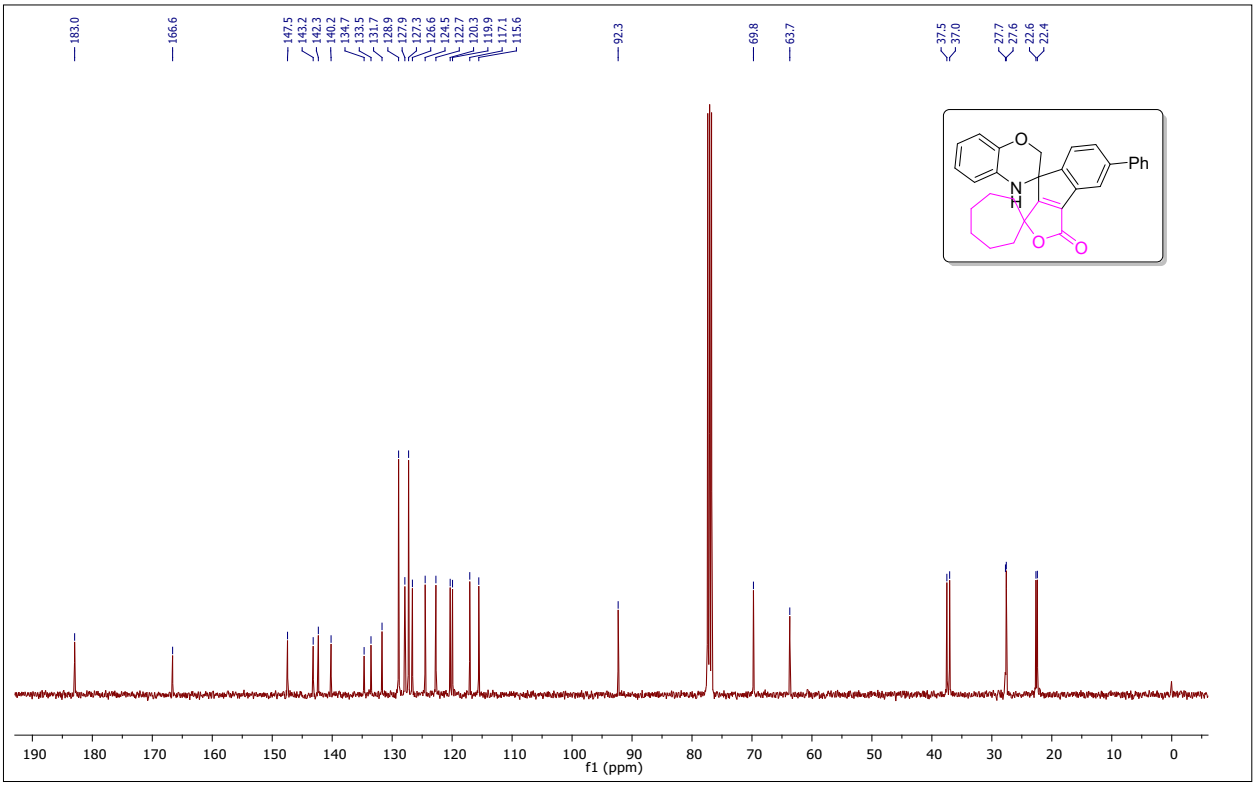
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **5l**



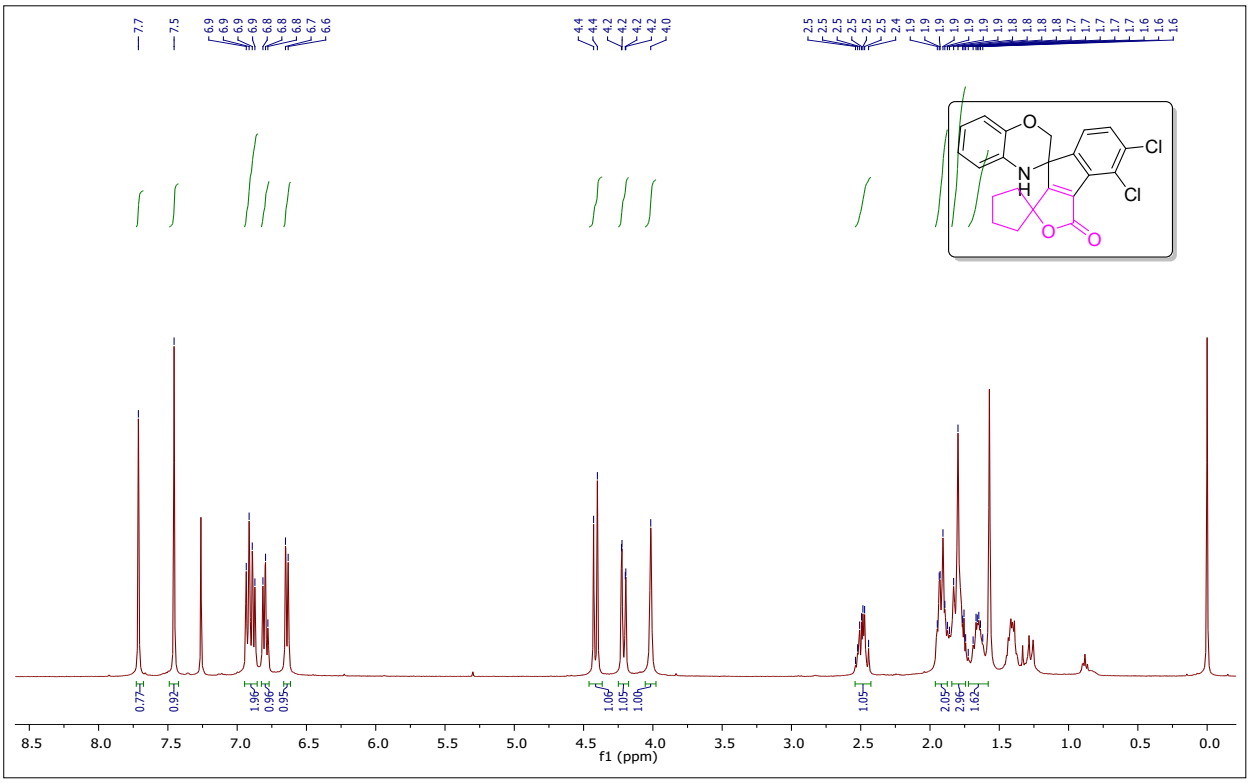
^{1}H NMR (400 MHz,$CDCl_3$) spectrum of compound **5m**



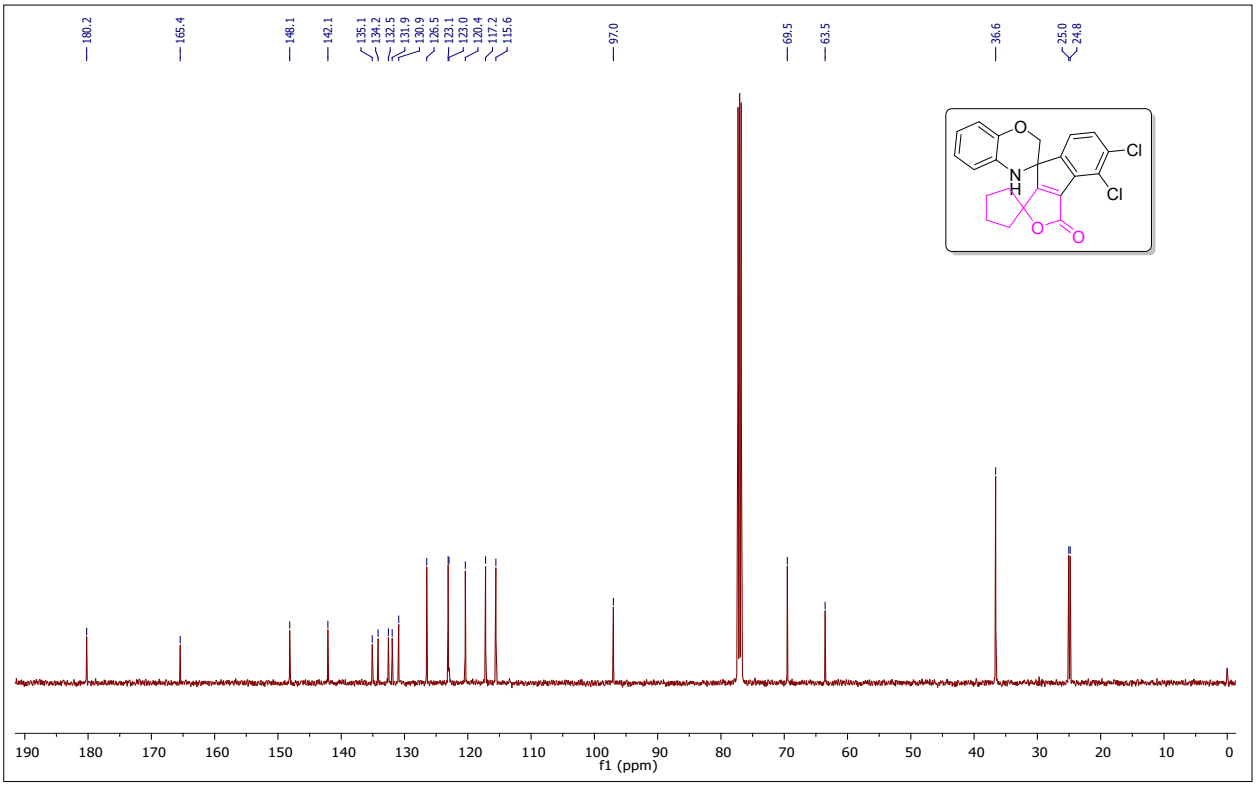
^{13}C{^{1}H}NMR (100MHz, $CDCl_3$) spectrum of compound **5m**



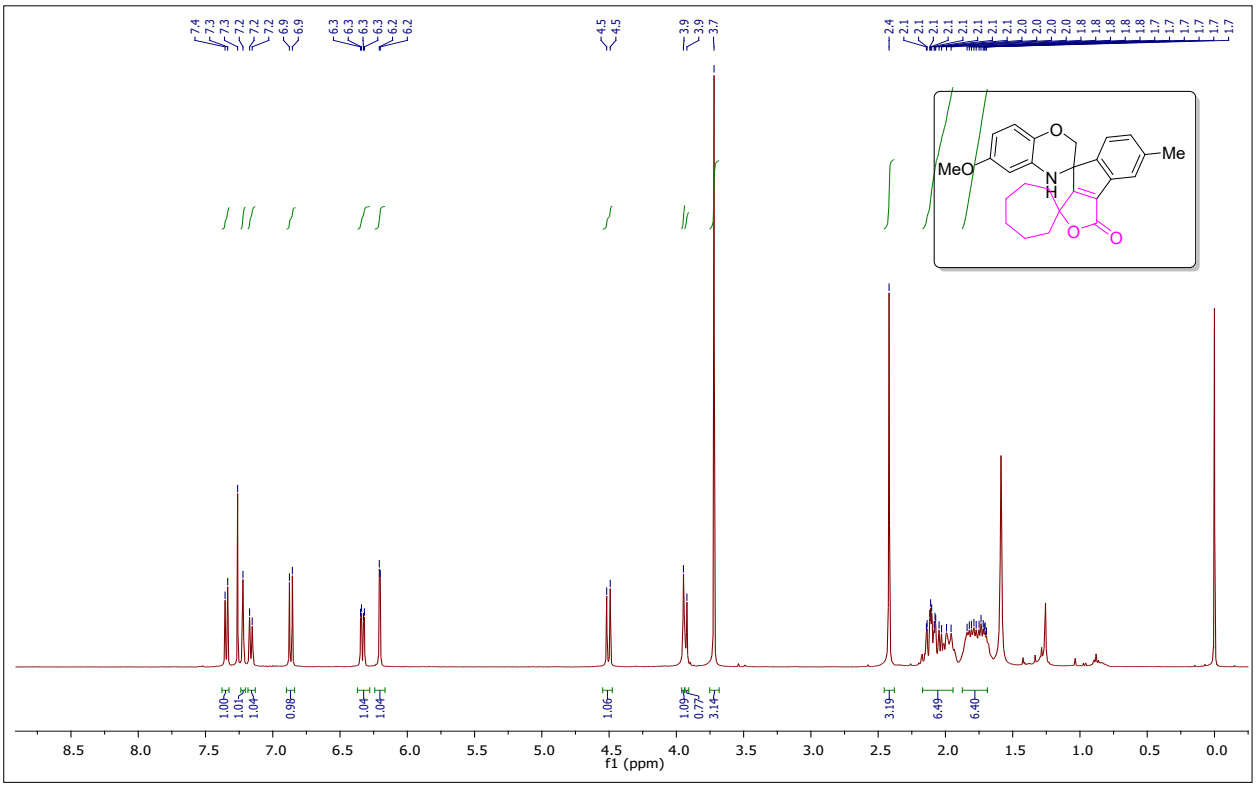
^{1}H NMR (400 MHz,$CDCl_3$) spectrum of compound **5n**



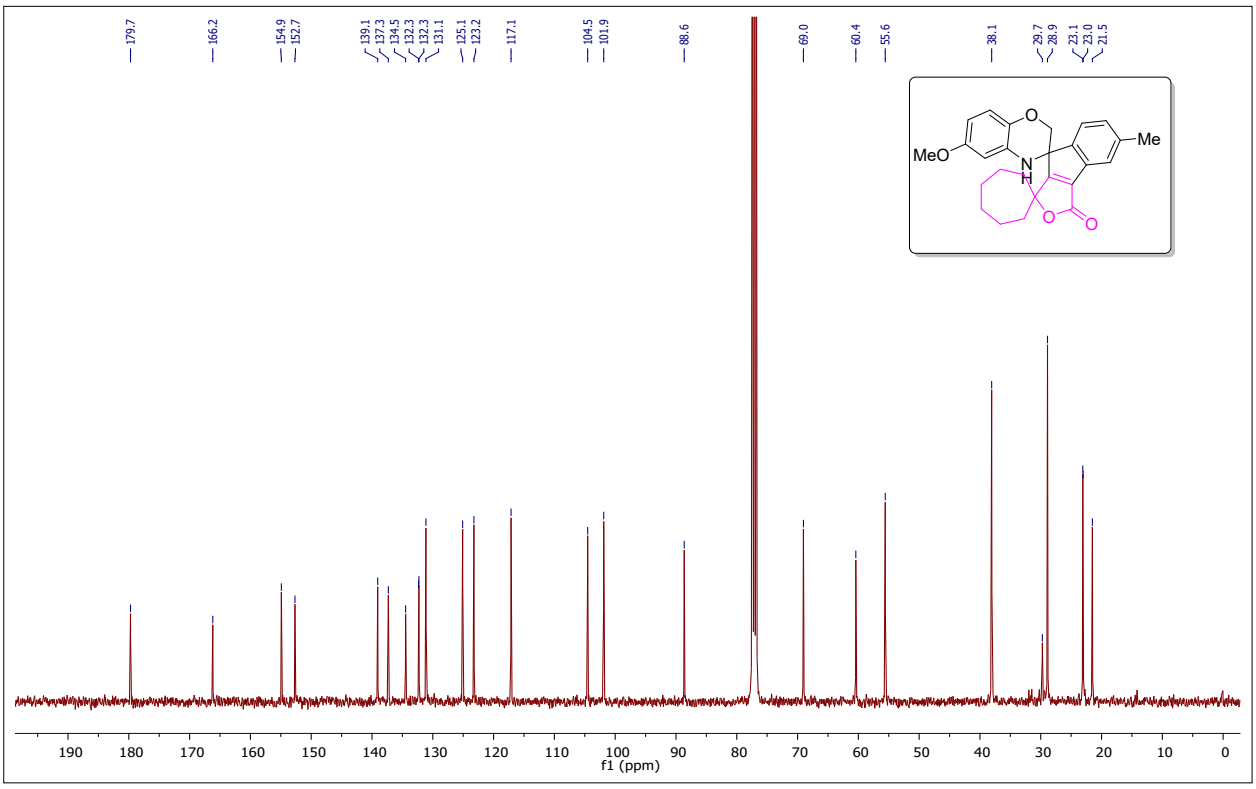
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **5n**



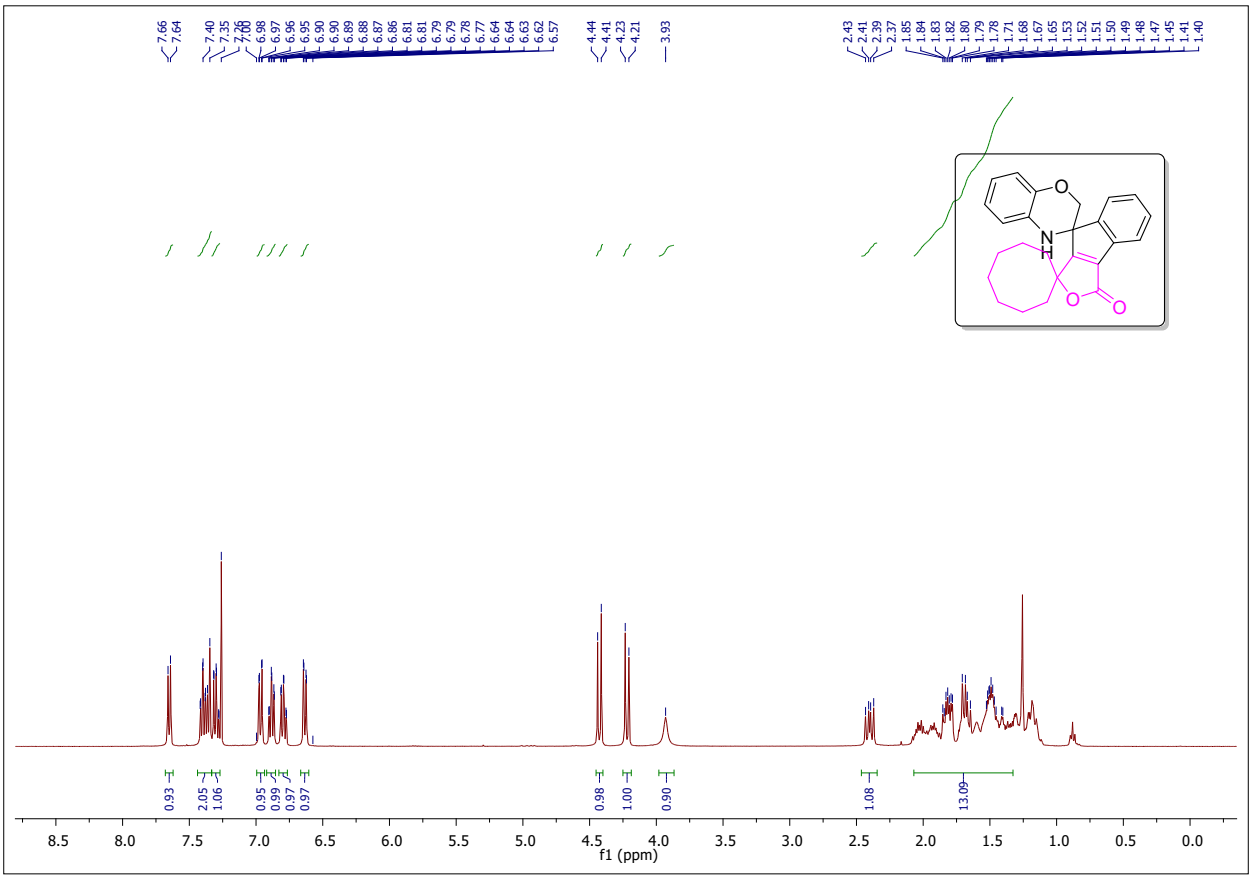
^{1}H NMR (400MHz,$CDCl_3$) spectrum of compound **5o**



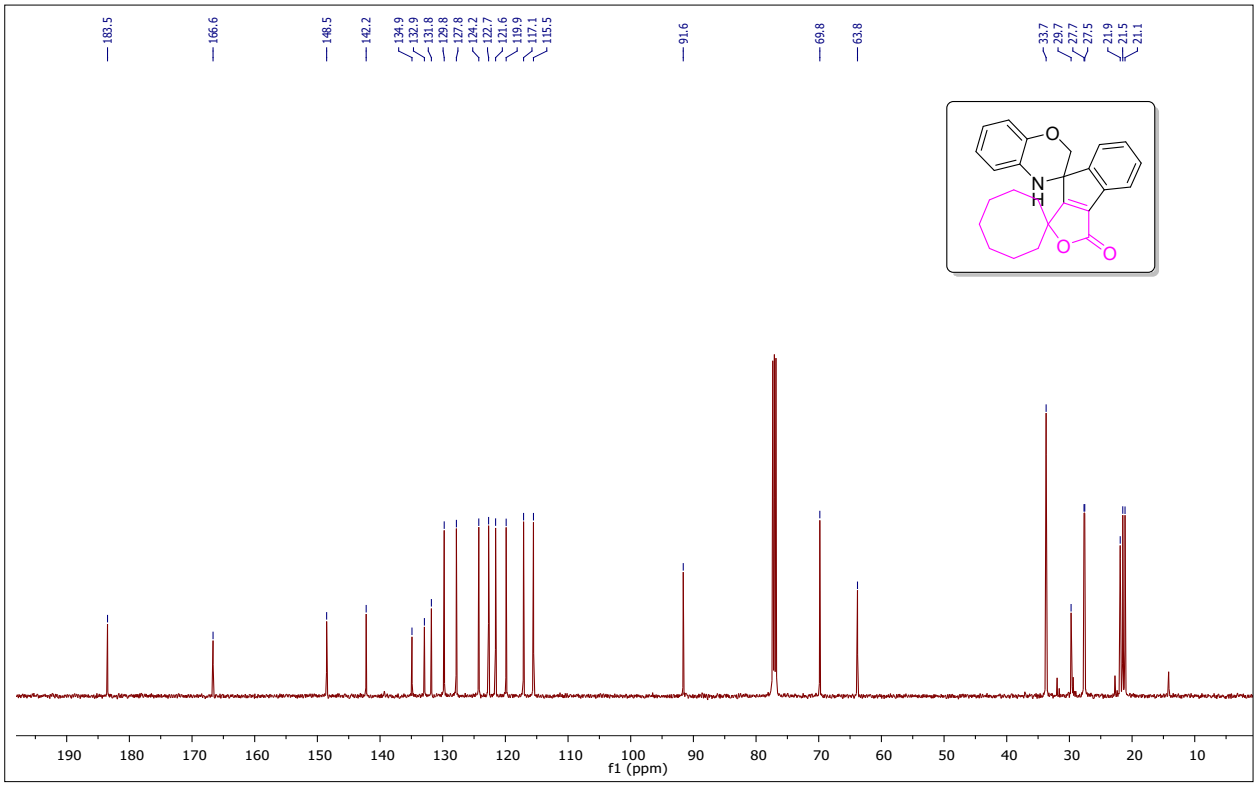
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **5o**



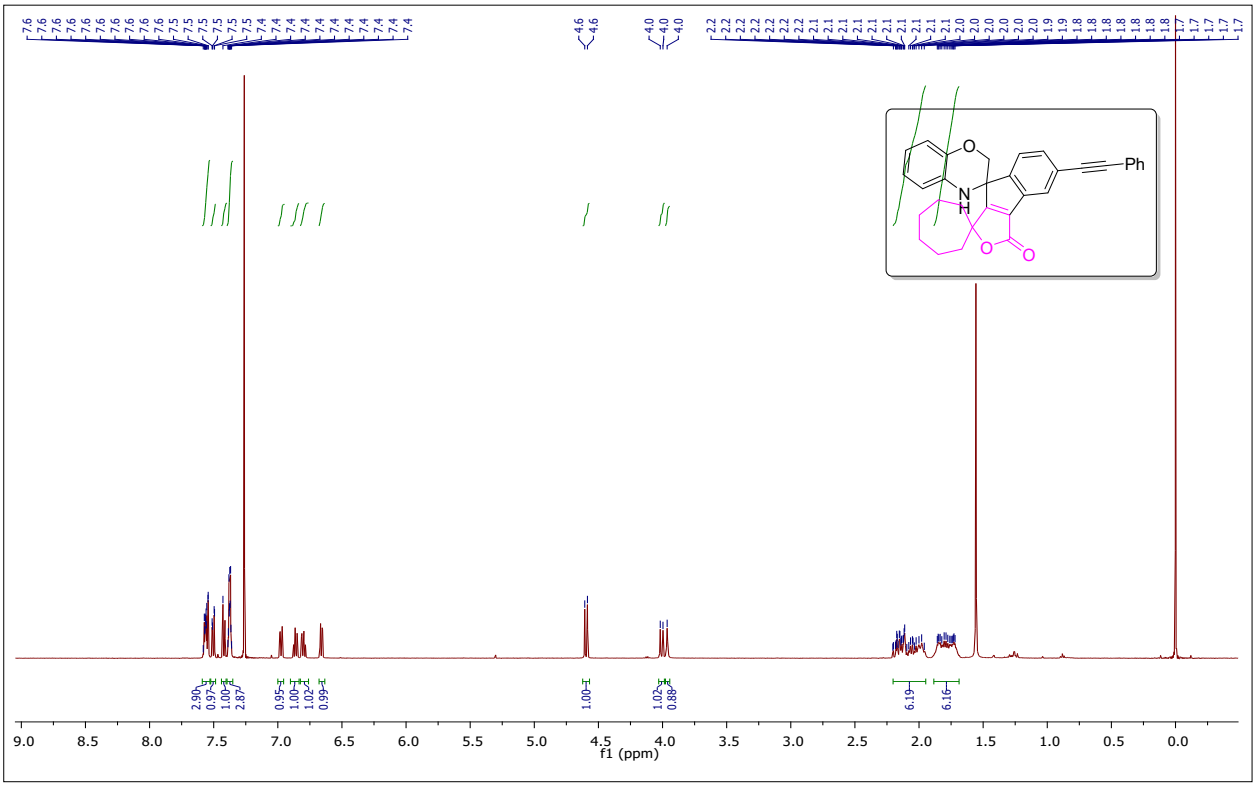
^{1}H NMR (400MHz,$CDCl_3$) spectrum of compound **5p**



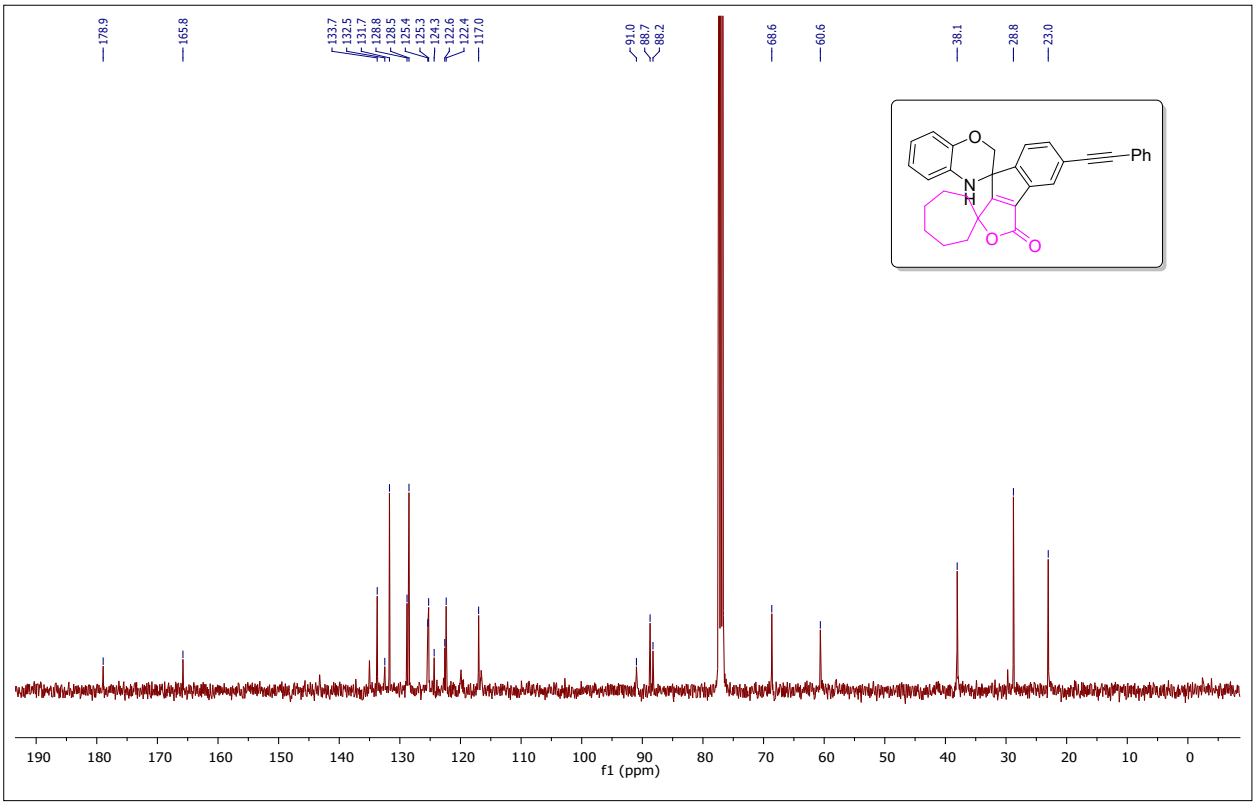
^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) spectrum of compound **5p**



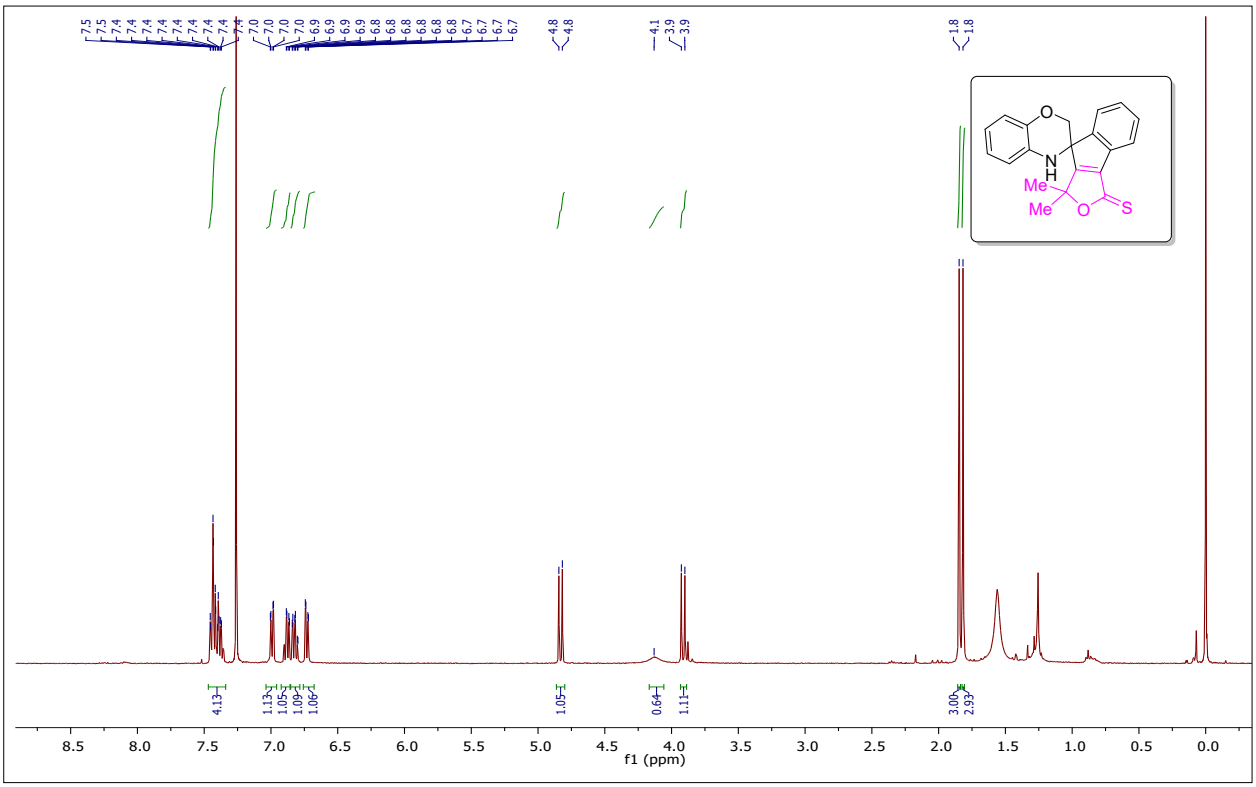
^{1}H NMR (500MHz,$CDCl_3$) spectrum of compound **5k′**



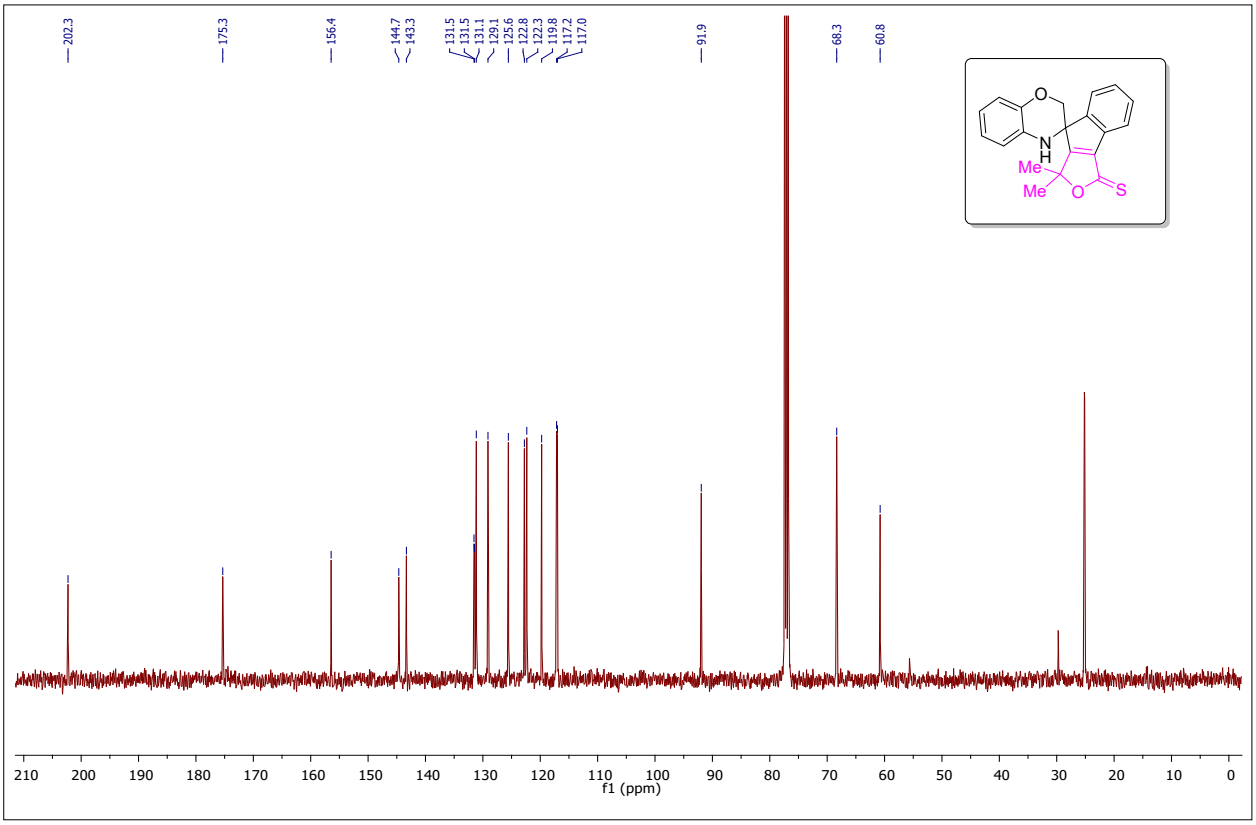
^{13}C{^{1}H} NMR 125MHz, $CDCl_3$) spectrum of compound**5k′**



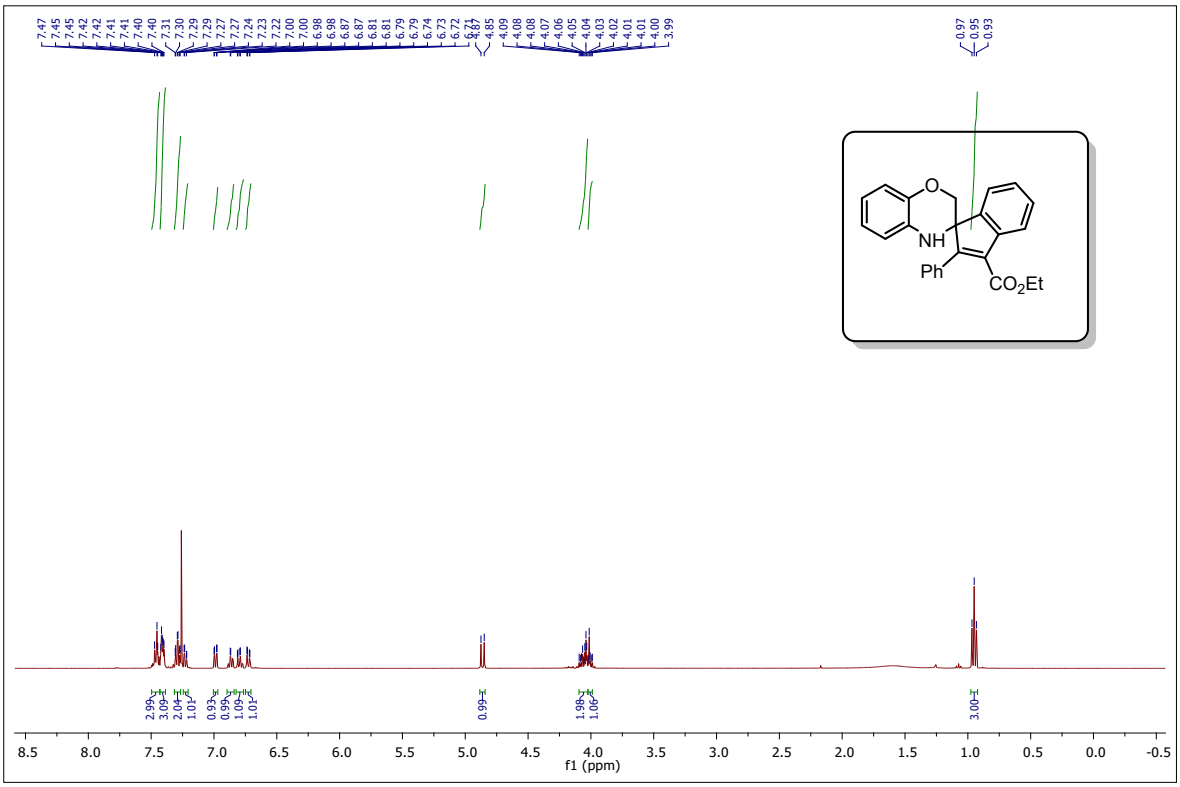
^{1}H NMR (400MHz,$CDCl_3$) spectrum of compound**3a′**



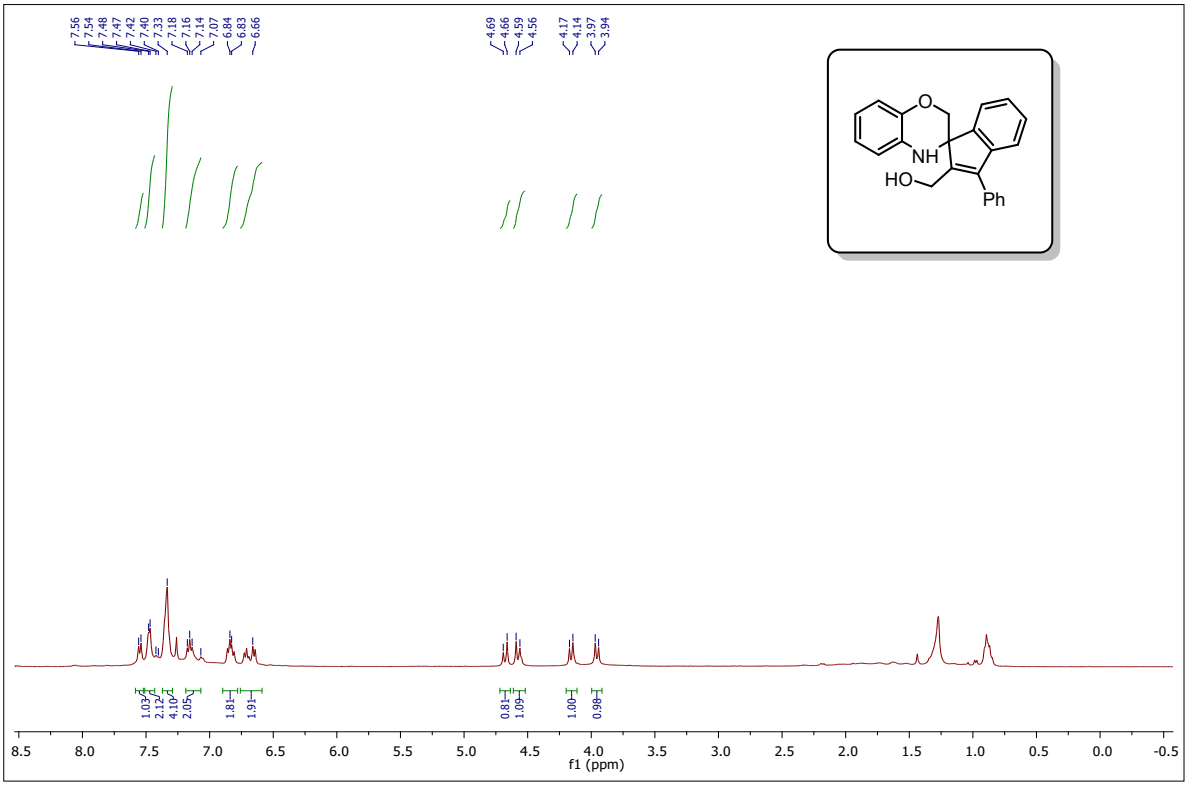
^{13}C{^{1}H} NMR 100MHz, $CDCl_3$) spectrum of compound **3a′**



^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **5q**

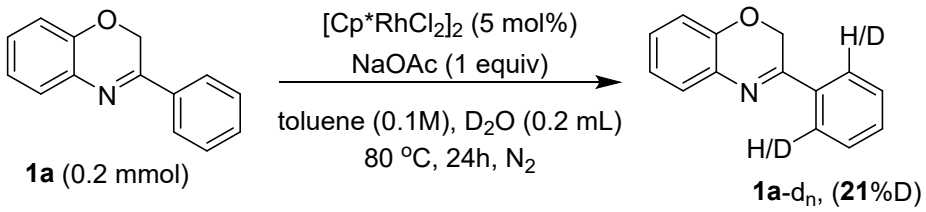


^{1}H NMR (400MHz, $CDCl_3$) spectrum of compound **5r**



Control experiments using D_2O:

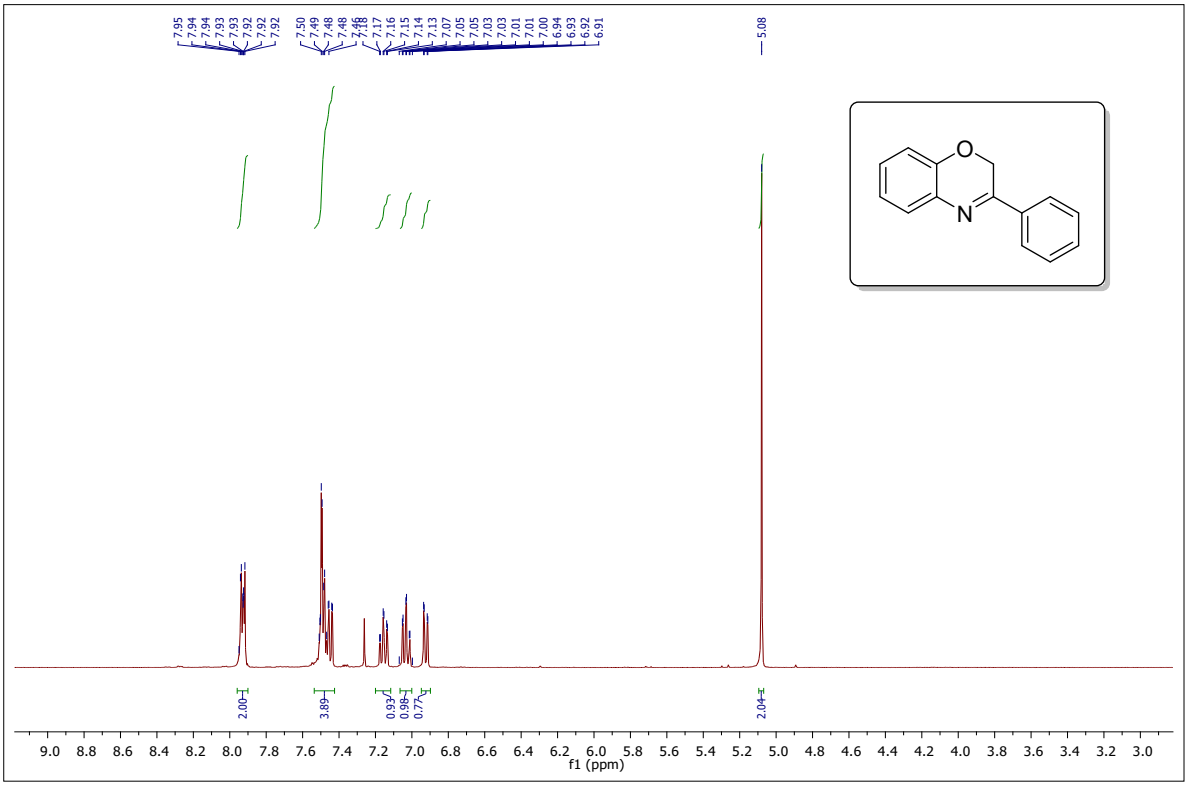
(a) H/D exchange experiment:

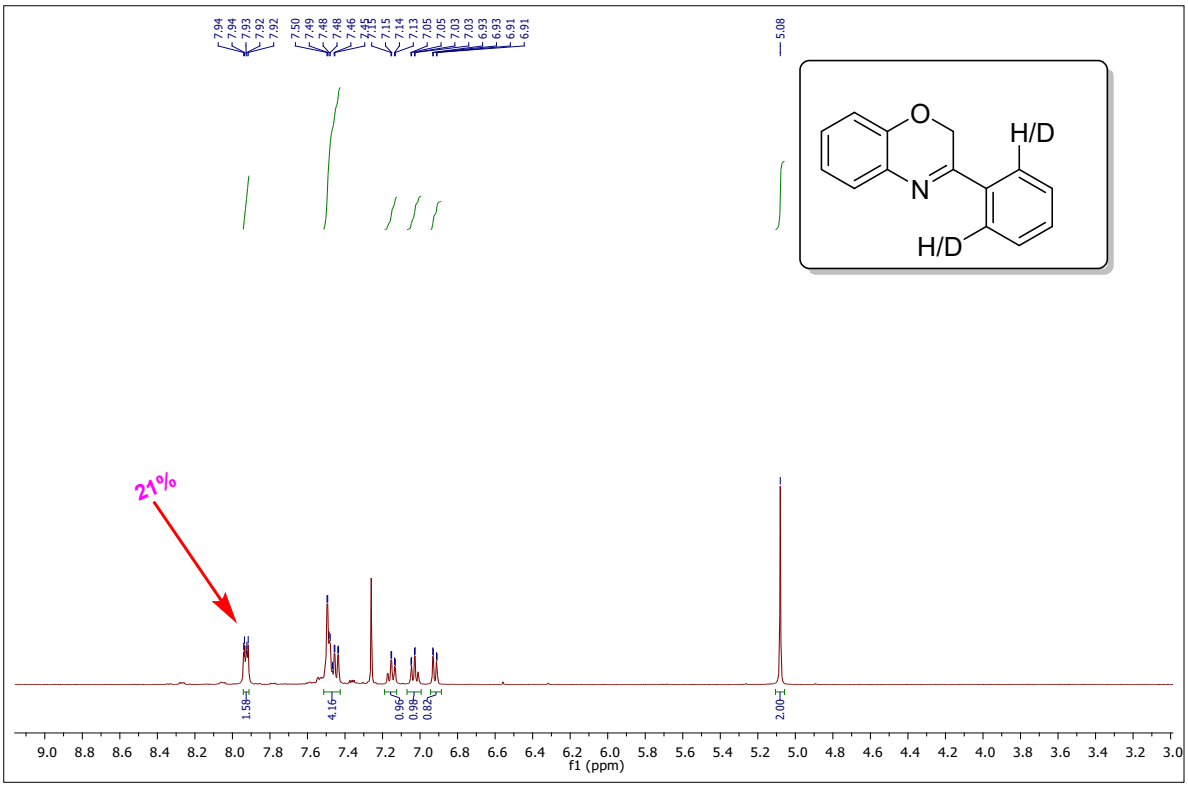


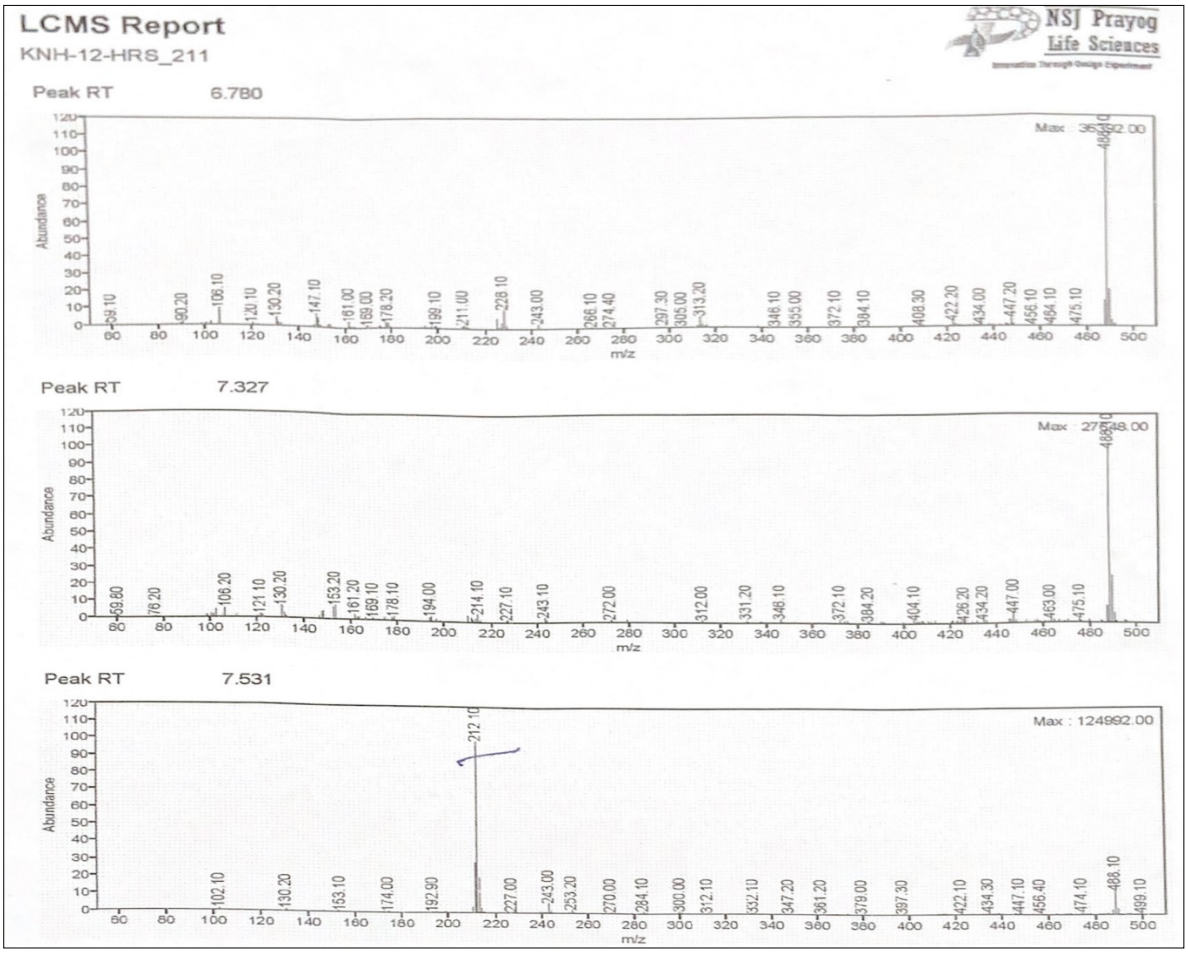
1a (0.2 mmol)

1a-d_n, (**21**%D)

An oven dried 10 mL schlenk tube was charged with 3-phenyl-2H-benzo[b][1,4]oxazine (**1a**) (41.8 mg, 0.2 mmol), sodium acetate (16.4 mg, 1.0 equiv) and catalyst [Cp*RhCl2]2 (6.2 mg, 5 mol %). The tube was evacuated and backfilled with nitrogen and to it was added toluene (2.0 mL, 0.1 M) and D_2O (0.2 mL) under nitrogen atmosphere. The reaction mixture was degassed and backfilled with nitrogen 3 times. It was then closed with teflon-lined cap and heated at 80 °C (oil bath temperature) while stirring for 24 h. The reaction mixture was filtered through a short pad of celite, the solvent was removed under reduced pressure and the crude reaction mixture was directly purified through column chromatography on silica gel using petroleum ether/ ethyl acetate (9:1). The deuterium incorporation (21%) was determined by ^{1}H NMR spectroscopy

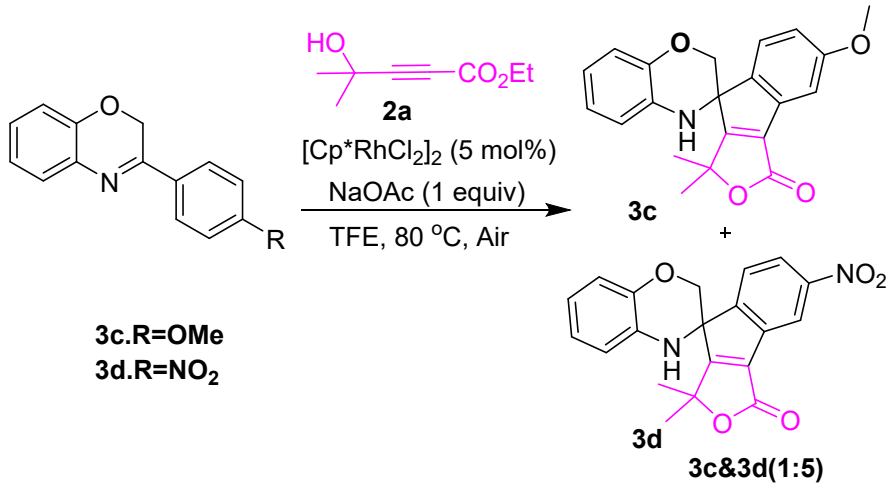


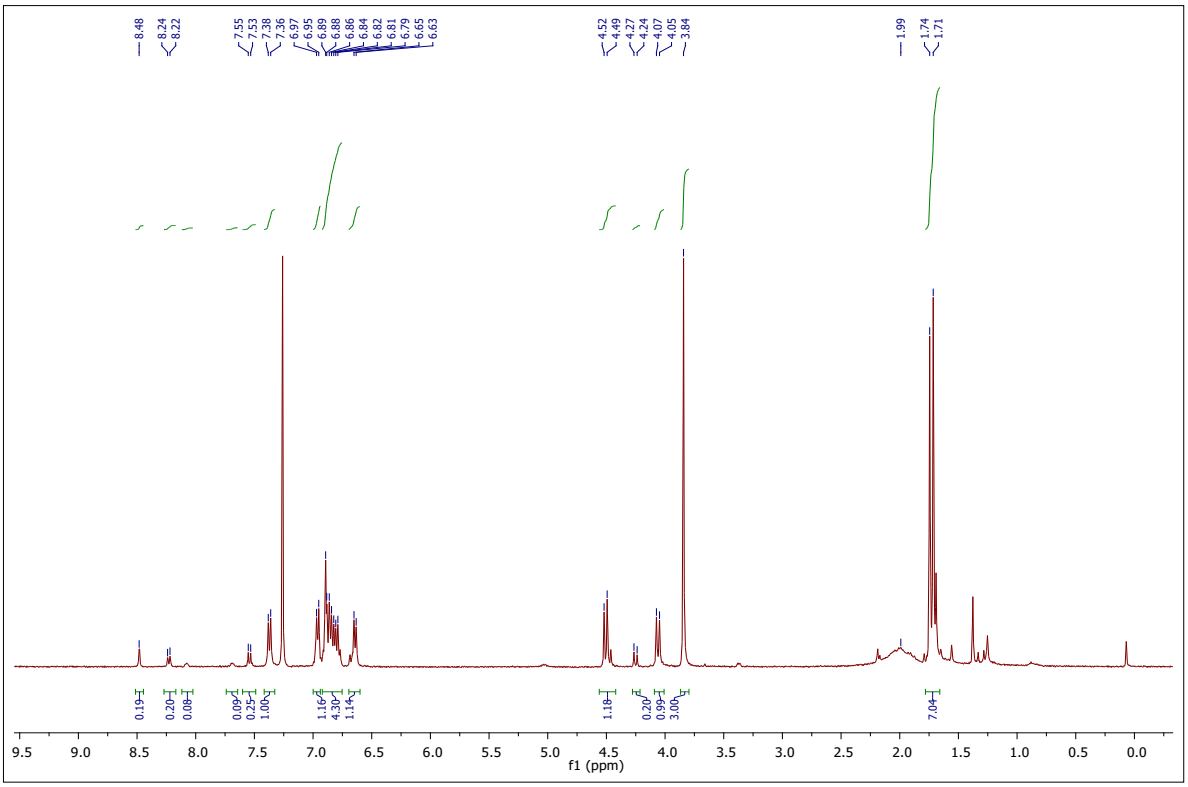

21%
O
N
H/D
H/D
f1 (ppm)


LCMS Report
KNH-12-HRS_211
NSJ Prayog Life Sciences
Peak RT 6.780
Peak RT 7.327
Peak RT 7.531
Abundance
m/z

(b) Competitive experiment between substituted benzoxazines:

An oven dried 10 mL schlenk tube was charged with 3-phenyl-2H-benzo[b][1,4]oxazine(100 mg, 0.5 mmol) (**3c&3d**)and ethyl propiolate**2a** (90 mg, 0.6 mmol) in TFE were added[$RhCp^*Cl_2]_2$ (5 mol %), sodium acetate (40 mg, 0.5mmol) and then the reaction mixture was stirred at 80 °C (oil bath) for overnight under air balloon. After completion of the reaction (as monitored by TLC), TFE was evaporated, water was added, and the contents were extracted with ethyl acetate (2×10 mL). The organic layer was evaporated and the residue was purified by column chromatography (R_f = 0.50) (SiO_2, EtOAc:Hexane, 1:99) to give the mixture of products **3c** and **3d** in **1:5** ratio, which wasdetermined by ^{1}H NMR spectroscopy.

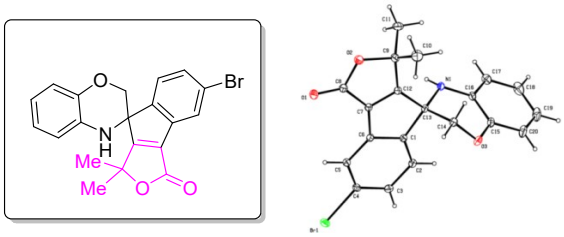




5.X-ray crystallography

X-ray data for the compound was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-III detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. The absolute configuration was confirmed by unambiguous refinement of the absolute structure parameter [3].All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

Crystal structure determination of 3f



Crystal Data for $C_{20}H_{16}NO_3Br$ (M =398.25 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 9.5218(11) Å, b = 10.0470(12) Å, c = 18.931(3) Å, V = 1811.1(4) Å^3, Z = 4, T = 294.15 K, μ(MoKα) = 2.287 mm^{-1}, *Dcalc* = 1.461 g/cm^3, 14903 reflections measured (4.59° ≤ 2Θ ≤ 54.998°), 4082 unique (R_{int} = 0.0368, R_{sigma} = 0.0488) which were used in all calculations. The final R_1 was 0.0280 (I > 2σ(I)) and wR_2 was 0.0726 (all data). **CCDC 2247998** deposition numbers contain the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015).ActaCrystallogr C71: 3-8.
3. Flack, H. D. &Bernardinelli, G. (2000). J. Appl. Cryst. 33, 1143–1148.