Supporting Information for *New J. Chem*.

Synthesis of 3'*H*-Spiro[cyclohexane-1,1'-isobenzofuran]-2,5-dien-4- one and Skeleton Construction of Type D Spirobisnaphthalene Structure via Dearomatization by Highvalance Iodine Reagent and Diels-Alder Reaction

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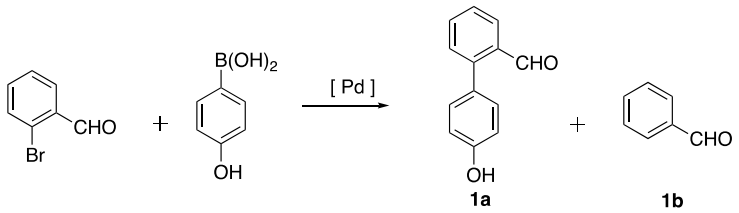
Content

1. Optimization of Suzuki-Miyaura coupling reaction conditions and synthesis of 1,1'-biphenyl-4-ol derivatives **2**

To optimize the Suzuki–Miyaura coupling reaction, 2-bromobenzaldehyde was chosen as the model substrate to be coupled with (4-hydroxyphenyl) boronic acid in the presence of acatalyst $Pd(PPh_3)_4$. Initially, there was no target product **1a** obtained when CH_3OH and H_2O were used as solvents[1] (Entry 1-2). When the solvent was changed to dioxane and H_2O, a small amount of product **1a** was generated, and the yield of **1a** at 90℃ was higher than that at 80℃ or 100℃. (Entry 3-5). Replacing different palladiums as catalysts, it was found that the raw material only could complete reaction under the $Pd(PPh_3)_2Cl_2$ or $Pd(dppf)_2Cl_2$ as catalysts, and no debromination products were formed (Entry 6-12). While it was found that the catalytic efficiency of $Pd(dppf)_2Cl_2$ was lower than that of $Pd(PPh_3)_2Cl_2$ as the amount of reaction was increased to the gram level, and the simultaneous generation of debromination by-products was observed (Entry 13-14). Reducing the temperature to 80℃, it was found that $Pd(PPh_3)_2Cl_2$ as catalyst was more favourable for the gram-scale reaction and the product **1a** could be obtained in 92% yield (Entry 15-17).

Table S1 Condition optimization for Suzuki–Miyaura coupling reaction

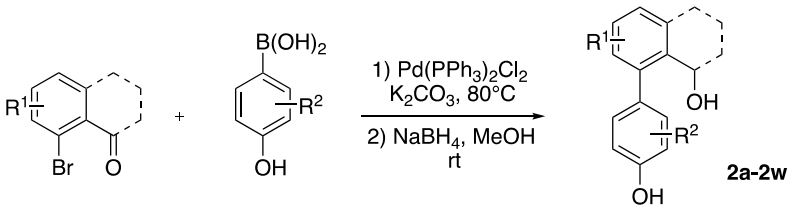


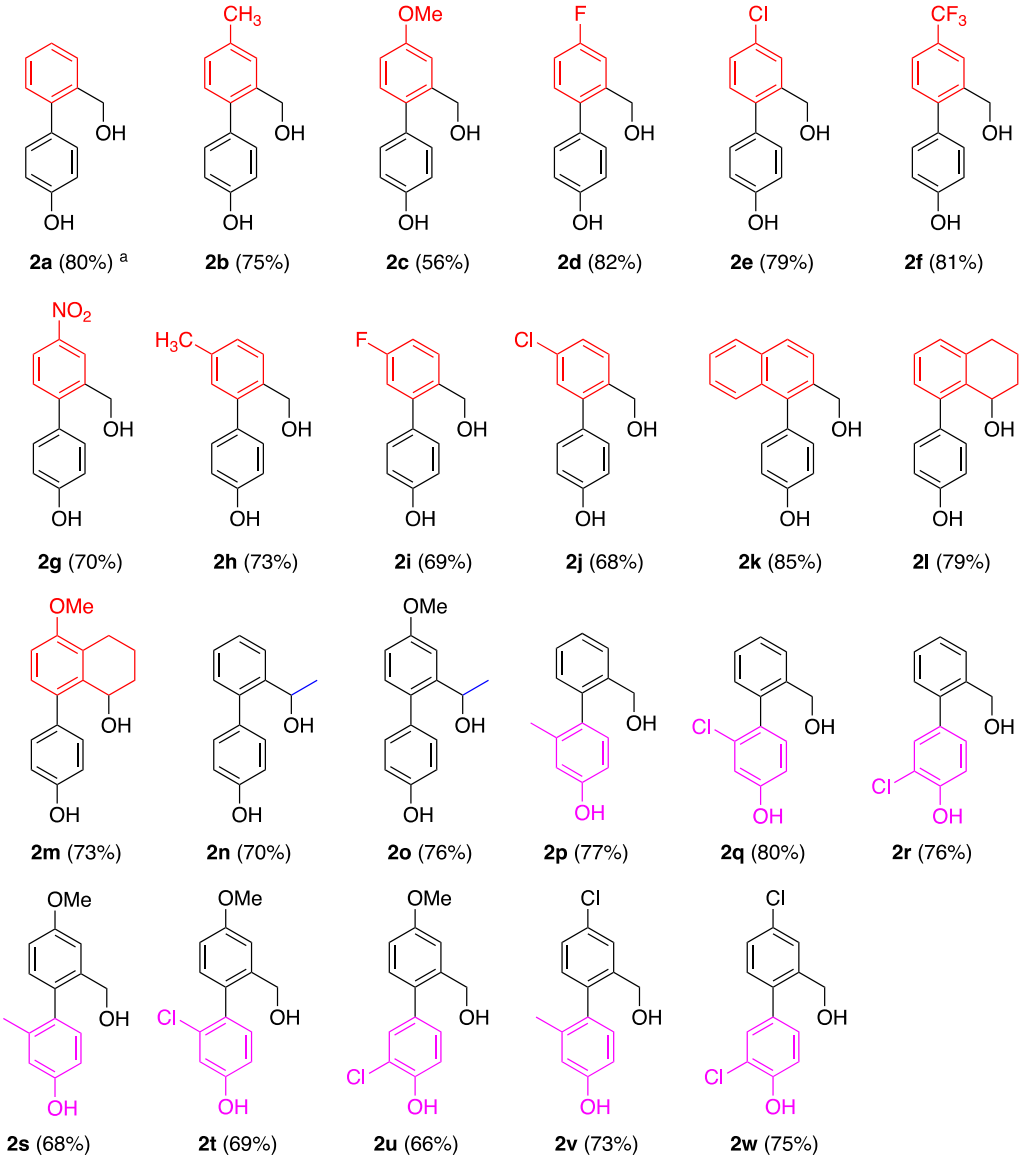
Entry	T/°C	Cat[c]	n/mmol[a]	Yield of **1a** (%)[b]	**1b**
1[d]	60	$Pd(PPh_3)_4$	0.1	-	-
2[d]	80	$Pd(PPh_3)_4$	0.1	-	-
3	80	$Pd(PPh_3)_4$	0.1	32%	with
4	90	$Pd(PPh_3)_4$	0.1	35%	with
5	100	$Pd(PPh_3)_4$	0.1	28%	with
6	90	$Pd(PPh_3)_2Cl_2$	0.1	85%	-
7	90	$Pd(dppf)_2Cl_2$	0.1	83%	-
8	90	$Pd(dba)_2$	0.1	#	with
9	90	$Pd_2(dba)_3$	0.1	#	with
10	90	$Pd(pppp)_2Cl_2$	0.1	#	with
11	90	$Pd(dppp)_2Cl_2$	0.1	#	with
12	90	$Pd(OAc)_2$	0.1	#	with
13	90	$Pd(PPh_3)_2Cl_2$	2	80%	-
14	90	$Pd(dppf)_2Cl_2$	2	74%	with
15	90	$Pd(PPh_3)_2Cl_2$	4	79%	with
16	80	$Pd(PPh_3)_2Cl_2$	4	92%	-
17	70	$Pd(PPh_3)_2Cl_2$	4	78%	-

[a] Amount of raw material (mmol). [b] Isolated yield. [c] Catalysts (0.1 eq). [d] The solvent is CH_3OH/H_2O = 1 : 1. [–] No product detected. [#] Incomplete reaction, the raw material was recovered.

Under optimal reaction conditions (**Table S1**, Entry 16), the substrate scopes of various substituted 2-bromobenzaldehydes and (4-hydroxyphenyl)boronic acids were explored. The results showed that these reaction conditions were tolerant to different substituents (electron-donating groups or electron-withdrawing groups) of the R^1 and R^2 at the aromatic rings, and the coupling products (**1b-1w**) were obtained in moderate to good yields. Subsequently, the one-pot method was directly used to reduce the coupling product by $NaBH_4$ to obtain the alcohols **2a-2w** (**Table S2**).

Table S2 Scope of the bisphenol alcohols (**2a-2w**)





[a] Isolated yields.

2'-(Hydroxymethyl)-[1,1'-biphenyl]-4-ol **(2a)**

White solid, yield 80%, mp 121-123 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.50 (s, 1H), 7.54 (dd, J = 7.1, 1.9 Hz, 1H), 7.29 (pd, J = 7.3, 1.7 Hz, 2H), 7.23-7.13 (m, 3H), 6.88-6.77 (m, 2H), 5.11 (t, J = 5.3 Hz, 1H), 4.40 (d, J = 5.2 Hz, 2H). NMR data were consistent with that of literature report[2].

2'-(Hydroxymethyl)-4'-methyl-[1,1'-biphenyl]-4-ol **(2b)**

White solid, yield 75%, mp 144-146 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.47 (s, 1H), 7.34 (s, 1H), 7.19-7.11 (m, 2H), 7.11-7.01 (m, 2H), 6.85-6.71 (m, 2H), 5.07 (t, J = 5.3 Hz, 1H), 4.36 (d, J = 5.3 Hz, 2H), 2.33 (s, 3H).

2'-(Hydroxymethyl)-4'-methoxy-[1,1'-biphenyl]-4-ol **(2c)**

White solid, yield 56%, mp 175-177 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.44 (s, 1H), 7.20-7.01 (m, 4H), 6.92-6.75 (m, 3H), 5.12 (t, J = 5.4 Hz, 1H), 4.38 (d, J = 5.4 Hz, 2H), 3.78 (s, 3H), 3.36 (s, 1H).

2'-(Hydroxymethyl)- 4'-fluoro-[1,1'-biphenyl]-4-ol **(2d)**

White solid, yield 82%, mp 131-134 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.52 (s, 1H), 7.31 (dd, J = 10.5, 2.8 Hz, 1H), 7.23-7.04 (m, 4H), 6.88-6.74 (m, 2H), 5.27 (t, J = 5.4 Hz, 1H), 4.39 (d, J = 5.4 Hz, 2H).

2'-(Hydroxymethyl)- 4'-chloro-[1,1'-biphenyl]-4-ol **(2e)**

White solid, yield 79%, mp 141-144 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.54 (s, 1H), 7.53 (d, J = 2.4 Hz, 1H), 7.30 (dd, J = 8.2, 2.4 Hz, 1H), 7.22-7.05 (m, 3H), 6.92-6.73 (m, 2H), 5.27 (t, J = 5.5 Hz, 1H), 4.37 (d, J = 5.5 Hz, 2H).

2'-(Hydroxymethyl)-4'-(trifluoromethyl)-[1,1'-biphenyl]-4-ol **(2f)**

Light yellow solid, yield 81%, mp 178-180 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.65 (s, 1H), 7.87 (d, J = 2.1 Hz, 1H), 7.62 (dd, J = 8.2, 2.1 Hz, 1H), 7.39 (d, J = 7.9 Hz, 1H), 7.28-7.16 (m, 2H), 6.91-6.77 (m, 2H), 5.39 (t, J = 5.4 Hz, 1H), 4.48 (d, J = 5.3 Hz, 2H).

2'-(Hydroxymethyl)-4'-nitro-[1,1'-biphenyl]-4-ol **(2g)**

Brown solid, yield 70%, mp 130-132 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.93 (s, 1H), 8.37 (d, J = 2.6 Hz, 1H), 8.12 (dd, J = 8.5, 2.6 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.22 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.70 (t, J = 5.4 Hz, 1H), 4.49 (d, J = 5.4 Hz, 2H).

2'-(Hydroxymethyl)-5'-methyl-[1,1'-biphenyl]-4-ol **(2h)**

White solid, yield 73%, mp 149-151 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.47 (s, 1H), 7.40 (d, J = 7.8 Hz, 1H), 7.24-7.07 (m, 3H), 6.99 (d, J = 1.9 Hz, 1H), 6.88-6.74 (m, 2H), 5.02 (t, J = 5.3 Hz, 1H), 4.35 (d, J = 5.3 Hz, 2H), 2.30 (s, 3H).

2'-(Hydroxymethyl)- 5'-fluoro-[1,1'-biphenyl]-4-ol **(2i)**

Light yellow solid, yield 69%, mp 149-150 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.58 (s, 1H), 7.54 (dd, $^4J_{HF}$ = 6.2 Hz, $^3J_{HH}$ = 8.6 Hz, 1H), 7.22 (d, J = 8.5 Hz, 2H), 7.13 (ddd, $^3J_{HF}$ = 8.6 Hz, J_{HH} = 8.6, 2.8 Hz, 1H), 6.99 (dd, $^3J_{HF}$ = 10.1 Hz, $^4J_{HH}$ = 2.7

Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 2H), 5.16 (t, *J* = 5.3 Hz, 1H), 4.36 (d, *J* = 5.3 Hz, 2H).

2'-(Hydroxymethyl)- 5'-chloro-[1,1'-biphenyl]-4-ol **(2j)**

Light yellow solid, yield 68%, mp 177-179 °C; H NMR (300 MHz, DMSO-d_6) δ 7.52 (d, *J* = 8.4 Hz, 1H), 7.35 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.17 (dd, *J* = 5.5, 3.1 Hz, 3H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.38 (t, *J* = 5.3 Hz, 1H), 4.35 (d, *J* = 4.1 Hz, 2H).

4-(2-(Hydroxymethyl) naphthalen-1-yl) phenol **(2k)**

Light yellow solid, yield 85%, mp 184-186 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 9.60 (s, 1H), 7.92 (d, *J* = 8.7 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 1H), 7.50-7.41 (m, 1H), 7.38 (d, *J* = 3.5 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.5 Hz, 2H), 5.14 (t, *J* = 5.4 Hz, 1H), 4.35 (d, *J* = 5.4 Hz, 2H).

8-(4-Hydroxyphenyl)-1,2,3,4-tetrahydronaphthalen-1-ol **(2l)**

White solid, yield 79%, mp 144-146 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.40 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 2H), 4.61 (d, *J* = 5.1 Hz, 1H), 4.56-4.46 (m, 1H), 2.88 (dd, *J* = 17.1, 5.9 Hz, 1H), 2.69 (ddd, *J* = 17.1, 11.1, 6.3 Hz, 1H), 2.17-1.97 (m, 1H), 1.85 (dd, *J* = 12.9, 3.4 Hz, 1H), 1.69-1.41 (m, 2H).

8-(4-Hydroxyphenyl)-5-methoxy-1,2,3,4-tetrahydronaphthalen-1-ol **(2m)**

Yellow solid, yield 73%, mp 152-153 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.32 (s, 1H), 7.28 (d, *J* = 8.5 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.75 (d, *J* = 8.6 Hz, 2H), 4.58 (d, *J* = 5.2 Hz, 1H), 4.51-4.39 (m, 1H), 3.78 (s, 3H), 2.79 (dd, *J* = 16.9, 5.9 Hz, 1H), 2.40 (ddd, *J* = 18.1, 11.6, 6.8 Hz, 1H), 2.08-1.95 (m, 1H), 1.87-1.73 (m, 1H), 1.65 (s, 1H), 1.44 (t, *J* = 13.5 Hz, 1H).

2'-(1-Hydroxyethyl)-[1,1'-biphenyl]-4-ol **(2n)**

White solid, yield 70%, mp 197-198 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.50 (s, 1H), 7.59 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.33 (td, *J* = 7.5, 1.5 Hz, 1H), 7.23 (td, *J* = 7.4, 1.5 Hz, 1H), 7.15-7.01 (m, 3H), 6.87-6.77 (m, 2H), 4.99 (d, *J* = 4.0 Hz, 1H), 4.78 (dd, *J* = 6.4, 4.0 Hz, 1H), 1.19 (d, *J* = 6.3 Hz, 3H). Known compound (CAS: 1541061-57-7).

2'-(1-Hydroxyethyl)-4'-methoxy-[1,1'-biphenyl]-4-ol **(2o)**

White solid, yield 76%, mp 127-129 °C; ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.44 (s, 1H), 7.16 (d, *J* = 2.8 Hz, 1H), 7.08 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.88-6.72 (m, 3H), 5.03 (d, *J* = 4.1 Hz, 1H), 4.79 (qd, *J* = 6.3, 4.0 Hz, 1H), 3.78 (s, 3H), 1.20 (d, *J* = 6.4 Hz, 3H).

2'-(Hydroxymethyl)-2-methyl-[1,1'-biphenyl]-4-ol **(2p)**

Light yellow solid, yield 77%, mp 145-147 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.36 (s, 1H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.33 (td, *J* = 7.6, 1.5 Hz, 1H), 7.24 (td, *J* = 7.4, 1.5 Hz, 1H), 6.99 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.67 (d, *J* = 2.5 Hz, 1H), 6.60 (dd, *J* = 8.2, 2.6 Hz, 1H), 5.03 (td, *J* = 5.4, 1.6 Hz, 1H), 4.15 (qd, *J* = 13.8, 5.3 Hz, 2H), 1.89 (s, 3H).

2'-(Hydroxymethyl)-2-chloro-[1,1'-biphenyl]-4-ol **(2q)**

Brown solid, yield 80%, mp 147-149 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.95 (s, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.37 (td, *J* = 7.5, 1.4 Hz, 1H), 7.27 (td, *J* = 7.4, 1.5 Hz, 1H), 7.11-7.03 (m, 2H), 6.91 (d, *J* = 2.4 Hz, 1H), 6.79 (dd, *J* = 8.3, 2.5 Hz, 1H), 5.06 (t, *J* = 5.4 Hz, 1H), 4.23 (qd, *J* = 13.9, 5.4 Hz, 2H).

2'-(Hydroxymethyl)-3-chloro-[1,1'-biphenyl]-4-ol **(2r)**

Light yellow solid, yield 76%, mp 105-108 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.26 (s, 1H), 7.53 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.43-7.25 (m, 3H), 7.23-7.11 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 5.15 (t, *J* = 5.3 Hz, 1H), 4.38 (d, *J* = 5.3 Hz, 2H). Known compound (CAS: 1261904-56-6).

2'-(Hydroxymethyl)-4'-methoxy-2-methyl-[1,1'-biphenyl]-4-ol **(2s)**

Light yellow solid, yield 68%, mp 80-81°C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.27 (s, 1H), 7.10 (d, *J* = 2.7 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.80 (dd, *J* = 8.3, 2.8 Hz, 2H), 6.66 (d, *J* = 2.6 Hz, 1H), 6.59 (dd, *J* = 8.2, 2.6 Hz, 1H), 5.02 (t, *J* = 5.4 Hz, 1H), 4.11 (qd, *J* = 14.0, 5.4 Hz, 2H), 3.78 (s, 3H), 1.89 (s, 3H).

2'-(Hydroxymethyl)-2-chloro-4'-methoxy-[1,1'-biphenyl]-4-ol **(2t)**

Light yellow liquid, yield 69%; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.91 (s, 1H), 7.11 (d, *J* = 2.7 Hz, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 2.4 Hz, 1H), 6.82 (dd, *J* = 8.3, 2.8 Hz, 1H), 6.77 (dd, *J* = 8.3, 2.4 Hz, 1H), 5.09 (t, *J* = 5.4 Hz, 1H), 4.30-4.09 (m, 2H), 3.79 (s, 3H).

2'-(Hydroxymethyl)-3-chloro-4'-methoxy-[1,1'-biphenyl]-4-ol **(2u)**

Light yellow solid, yield 66%, mp 93-95°C; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 10.19 (s, 1H), 7.29 (d, *J* = 2.1 Hz, 1H), 7.16-7.05 (m, 3H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.86 (dd, *J* = 8.4, 2.8 Hz, 1H), 5.17 (t, *J* = 5.4 Hz, 1H), 4.36 (d, *J* = 5.4 Hz, 2H), 3.78 (s, 3H).

2'-(Hydroxymethyl)-2-methyl-4'-chloro-[1,1'-biphenyl]-4-ol **(2v)**

Light yellow solid, yield 73%, mp 132-134°C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.38 (s, 1H), 7.54 (d, *J* = 2.3 Hz, 1H), 7.30 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 2.5 Hz, 1H), 6.62 (dd, *J* = 8.2, 2.6 Hz, 1H), 5.20 (t, *J* = 5.5 Hz, 1H), 4.31-3.98 (m, 2H), 1.89 (s, 3H).

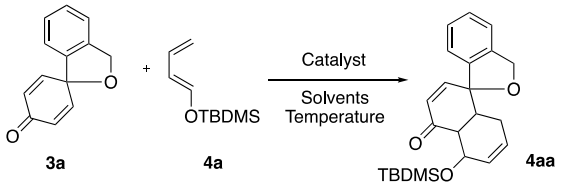
2'-(Hydroxymethyl)-3,4'-dichloro-[1,1'-biphenyl]-4-ol **(2w)**

White solid, yield 75%, mp 125-126 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.34 (s, 1H), 7.55 (d, *J* = 2.3 Hz, 1H), 7.39-7.27 (m, 2H), 7.21 (d, *J* = 8.2 Hz, 1H), 7.13 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.02 (d, *J* = 8.3 Hz, 1H), 5.33 (t, *J* = 5.4 Hz, 1H), 4.38 (d, *J* = 5.4 Hz, 2H).

2. Optimization of Diels-Alder reaction conditions and synthesis of 5'-hydroxy-4a',5',8',8a'-tetrahydro-3*H*,4'*H*-spiro[isobenzofuran-1,1'-naphthalen]-4'-one derivatives **4**

We chose **3a** as the substrate and optimized its Diels-Alder reaction conditions with (*E*)-(buta-1,3-dien-1-yloxy) (*tert*-butyl) dimethylsilane (**4a**). Initially, an excess of **4a** was used as reagent and a solvent, it was found that the reaction did not take place at room temperature (Table S2, Entry 1). Considering that **4a** could be recovered, the amount of **4a** was increased so that the reaction was set up as a 0.1 M solution, but only a small amount of the product **4aa** was obtained after 24 h (Entry 2). Subsequently, we added $AlCl_3$ as a catalyst and found that the addition of 0.35 eq of $AlCl_3$ increased the yield to 64% (Entry 3), but the reaction system was relatively viscous.[3] While, continuing to increase the amount of $AlCl_3$ (1.2 eq), the reaction system was so viscous that magnetic stirring was not possible (Entry 4). We tried to increase the amount of **4a** to dilute the reaction system and found that the yield could be significantly increased to 77% (Entry 5). However, adding DCM to dilute the reaction system causes the reaction to fail without the product **4aa** being produced (Entry 6). We also tried an attempt to raise the reaction temperature without catalyst and found that raising the temperature was effective in increasing the yield (Entry 7-9), which reached 82% when the reaction temperature was raised to 120°C. Considering the convenience of post-reaction treatment, **3a** and **4a** (10 eq) were selected to react at 120°C for 8 h to obtain product **4aa** (Entry 9). In order to verify the feasibility of the screened Diels-Alder reaction conditions, several substrates were selected for general studies, and it was found that they all gave the corresponding target products in good yields. (**Table S4**).

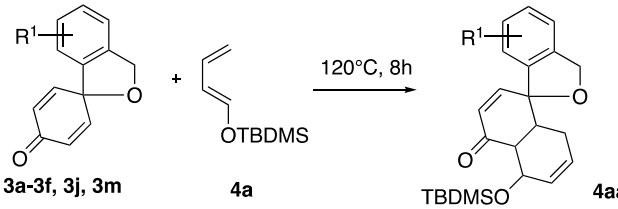
Table S3 Condition optimization for Diels-Alder reaction

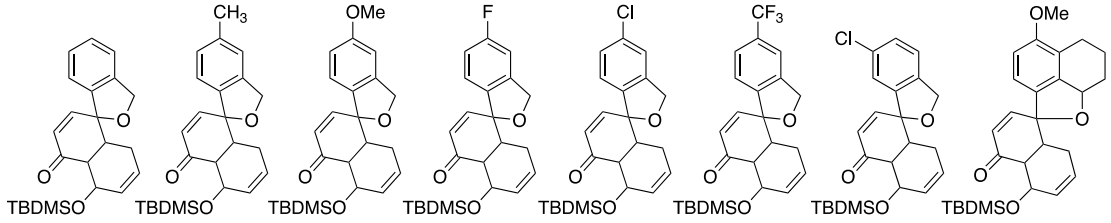


Entry	**4a** (eq)	$AlCl_3$ (eq)	T/°C	Solvent	Yield of **4aa**[a]
1	10 eq	-	rt	-	none
2	>20 eq	-	rt	**4a** (0.1 M)	<5%
3	10 eq	0.35 eq	rt	-	64%
4[b]	10 eq	1.2 eq	rt	-	53%
5	20 eq	1.2 eq	rt	-	77%
6[c]	10 eq	1.2 eq	rt	DCM (0.1 M)	none
7	10 eq	-	40 °C	-	40%
8	10 eq	-	80 °C	-	53%
9	10 eq	-	120 °C	-	82%

[a] Isolated yield. [b] The reaction system is too viscous for magnetic stirring, the raw material was recovered. [c] Only unknown by-products, **4aa** was not produced.

Table S4 Scope of the Diels-Alder reaction products (**4aa**-**4ah**)





5'-((*tert*-Butyldimethylsilyl)oxy)-4a',5',8',8a'-tetrahydro-3*H*,4'*H*-spiro[isobenzofuran-1,1'-naphthalen]-4'-one **(4aa)**

Light yellow liquid, yield 82%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.27 (m, 3H), 7.25-7.19 (m, 1H), 6.48 (dd, *J* = 10.2, 1.4 Hz, 1H), 6.01 (d, *J* = 10.2 Hz, 1H), 5.75 (dd, *J* = 10.2, 2.3 Hz, 1H), 5.70-5.57 (m, 1H), 5.11 (s, 2H), 4.37 (dt, *J* = 4.8, 2.5 Hz, 1H), 3.17 (t, *J* = 4.8 Hz, 1H), 2.73-2.54 (m, 1H), 2.34-2.17 (m, 1H), 2.18-2.00 (m, 1H), 0.89 (s, 9H), 0.07 (s, 6H). HR-MS (ESI), m/z $[M + H]^+$ calcd for $C_{23}H_{31}O_3Si$ 383.2037, found 383.2038.

5'-((*tert*-Butyldimethylsilyl)oxy)-5-methyl-4a',5',8',8a'-tetrahydro-3*H*,4'*H*-spiro[isobenzofuran-1,1'-naphthalen]-4'-one **(4ab)**

Light yellow liquid, yield 48%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17-7.07 (m, 3H), 6.45 (dd, *J* = 10.1, 1.4 Hz, 1H), 5.97 (d, *J* = 10.2 Hz, 1H), 5.78-5.70 (m, 1H), 5.62 (dtd, *J* = 10.2, 3.5, 1.9 Hz, 1H), 5.07 (s, 2H), 4.36 (dt, *J* = 4.9, 2.5 Hz, 1H), 3.18 (t, *J* = 4.7 Hz, 1H), 2.66-2.55 (m, 1H), 2.40 (s, 3H), 2.31-2.16 (m, 1H), 2.09 (ddt, *J* = 16.2, 8.0, 2.9 Hz, 1H), 0.88 (s, 9H), 0.05 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.18, 147.22, 140.25, 139.40, 138.68, 130.48, 129.05, 128.56, 126.02, 122.31, 121.71, 87.21, 71.81, 68.02, 48.96, 42.80, 25.98, 25.04, 21.38, 18.31, -4.36, -4.64. HR-MS (ESI), m/z $[M + H]^+$ calcd for $C_{24}H_{32}O_3Si$ 397.2193, found 397.2194.

5'-((*tert*-Butyldimethylsilyl)oxy)-5-methoxy-4a',5',8',8a'-tetrahydro-3*H*,4'*H*-spiro[isobenzofuran-1,1'-naphthalen]-4'-one **(4ac)**

Light yellow liquid, yield 77%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.3 Hz, 1H), 6.90-6.78 (m, 2H), 6.45 (dd, *J* = 10.2, 1.4 Hz, 1H), 5.96 (d, *J* = 10.2 Hz, 1H), 5.76-5.72 (m, 1H), 5.66-5.60 (m, 1H), 5.06 (s, 2H), 4.36 (m, 1H), 3.83 (s, 3H), 3.15 (t, *J* = 4.8 Hz, 1H), 2.63-2.57 (m, 1H), 2.28-2.18 (m, 1H), 2.13-2.03 (m, 1H), 0.88 (s, 9H), 0.05 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.25, 160.53, 147.34, 141.75, 134.24, 130.48, 129.00, 126.09, 122.76, 113.75, 107.07, 87.04, 71.82, 68.02, 55.70, 49.01, 42.87, 26.00, 25.03, 18.34, -4.33, -4.63. HR-MS (ESI), m/z $[M + H]^+$ calcd for $C_{24}H_{33}O_4Si$ 413.2143 found 413.2144.

5'-((*tert*-Butyldimethylsilyl)oxy)-5-fluoro-4a',5',8',8a'-tetrahydro-3*H*,4'*H*-spiro

[isobenzofuran-1,1'-naphthalen]-4'-one **(4ad)**

Light yellow solid yield 87%, mp 150-151°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (dd, $^4J_{HF}$ = 4.7 Hz, $^3J_{HH}$ = 8.3 Hz, 1H), 7.05-6.94 (m, 2H), 6.45 (dd, *J* = 10.2, 1.3 Hz, 1H), 6.00 (d, *J* = 10.2 Hz, 1H), 5.77-5.72 (m, 1H), 5.67-5.62 (m, 1H), 5.07 (s, 2H), 4.37 (m, 1H), 3.09 (t, *J* = 4.8 Hz, 1H), 2.63-2.59 (m, 1H), 2.27-2.16 (m, 1H), 2.09-1.99 (m, 1H), 0.87 (s, 9H), 0.05 (s, 3H) , 0.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.29, 163.37 (d, $^1J_{CF}$ = 246.9 Hz), 146.79, 142.42 (d, $^3J_{CF}$ = 8.4 Hz), 138.04 (d, $^4J_{CF}$ = 2.4 Hz), 129.87, 126.09, 123.26 (d, $^3J_{CF}$ = 9.5 Hz), 115.01 (d, $^2J_{CF}$ = 23.0 Hz), 109.13 (d, $^2J_{CF}$ = 23.6 Hz), 86.86, 71.61 (d, $^4J_{CF}$ = 2.7 Hz), 67.57, 48.95, 42.14, 25.98, 24.90, 18.33, -4.28, -4.67. HR-MS (ESI), m/z [M + H]$^+$ calcd for $C_{23}H_{30}FO_3Si$ 401.1943, found 401.1945.

5'-((*tert*-Butyldimethylsilyl)oxy)-5-chloro-4a',5',8',8a'-tetrahydro-3*H*,4'*H*-spiro [isobenzofuran-1,1'-naphthalen]-4'-one **(4ae)**

Light yellow liquid, yield 99%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.26 (m, 2H), 7.13 (dd, *J* = 7.9, 0.8 Hz, 1H), 6.44 (dd, *J* = 10.1, 1.2 Hz, 1H), 6.01 (d, *J* = 10.2 Hz, 1H), 5.84-5.69 (m, 1H), 5.69-5.58 (m, 1H), 5.06 (s, 2H), 4.37 (m, 1H), 3.07 (t, *J* = 4.8 Hz, 1H), 2.63-2.59 (m, 1H), 2.26-2.16 (m, 1H), 2.07-1.97 (m, 1H), 0.87 (s, 9H), 0.05 (s, 3H) , 0.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.24, 146.51, 142.14, 141.16, 134.71, 130.17, 129.69, 128.11, 126.05, 123.08, 122.18, 86.94, 71.53, 67.46, 48.92, 41.89, 25.96, 24.87, 18.30, -4.28, -4.68. HR-MS (ESI), m/z [M + H]$^+$ calcd for $C_{23}H_{30}ClO_3Si$ 417.1647, found 417.1649.

5'-((*tert*-Butyldimethylsilyl)oxy)-5-(trifluoromethyl)-4a',5',8',8a'-tetrahydro-3*H*,4'*H*-spiro[isobenzofuran-1,1'-naphthalen]-4'-one **(4af)**

Light yellow solid, yield 87%, mp 150-152°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.56 (s, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 6.46 (dd, *J* = 10.2, 1.1 Hz, 1H), 6.05 (d, *J* = 10.2 Hz, 1H), 5.76 (dq, *J* = 10.3, 2.3 Hz, 1H), 5.65 (dtd, *J* = 10.2, 3.5, 1.6 Hz, 1H), 5.21-5.07 (m, 2H), 4.39 (ddd, *J* = 4.8, 2.7, 1.8 Hz, 1H), 3.07 (t, *J* = 4.9 Hz, 1H), 2.79-2.56 (m, 1H), 2.32-2.11 (m, 1H), 2.09-1.95 (m, 1H), 0.87 (s, 9H), 0.05 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.24, 146.64, 146.05, 141.13, 131.40 (q, $^2J_{CF}$ = 32.5 Hz), 130.06, 126.03, 125.29 (q, $^3J_{CF}$ = 3.8 Hz), 124.10 (q, $^1J_{CF}$ = 272.6 Hz), 122.47, 122.30, 119.05 (q, $^3J_{CF}$ = 4.0 Hz), 87.07, 71.77, 67.23, 48.91, 41.52, 25.95, 24.83, 18.31, -4.24, -4.68. HR-MS (ESI), m/z [M + H]$^+$ calcd for $C_{24}H_{30}F_3O_3Si$ 451.1911, found 451.1913.

5'-((*tert*-Butyldimethylsilyl)oxy)-6-chloro-4a',5',8',8a'-tetrahydro-3*H*,4'*H*-spiro [isobenzofuran-1,1'-naphthalen]-4'-one **(4ag)**

Light yellow liquid, yield 61%; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.24-7.15 (m, 2H), 6.46 (dd, *J* = 10.2, 1.1 Hz, 1H), 6.03 (d, *J* = 10.2 Hz, 1H), 5.79-5.71 (m, 1H), 5.69-5.58 (m, 1H), 5.14-5.00 (m, 2H), 4.44 -4.32 (m, 1H), 3.08 (t, *J* = 4.9 Hz, 1H), 2.68-2.52 (m, 1H), 2.25-2.13 (m, 1H), 2.07-1.94 (m, 1H), 0.87 (s, 9H), 0.06 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.36, 146.38, 144.79, 138.53, 133.81, 130.03, 129.85, 128.90, 126.10, 122.89, 122.44, 86.94, 71.79, 67.28, 48.93, 41.62, 25.97, 25.78, 24.81, 18.34, -4.27, -4.72. HR-MS (ESI), m/z [M + H]$^+$ calcd for $C_{23}H_{30}ClO_3Si$ 417.1647, found 417.1649.

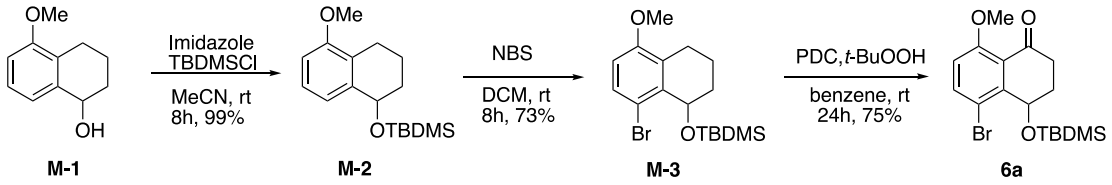
5-((tert-butyldimethylsilyl)oxy)-5'-methoxy-6',7',8',8a'-tetrahydro-4H-

spiro[naphthalene-1,2'-naphtho[1,8-bc]furan]-4-one (**4ah**)

Light yellow liquid, yield 63%, ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.32 (dd, *J* = 10.2, 2.2 Hz, 1H), 5.95 (d, *J* = 10.2 Hz, 1H), 5.76 (m, 1H), 5.63-5.56 (m, 1H), 4.93 (dd, *J* = 10.9, 5.2 Hz, 1H), 4.34 (m, 1H), 3.85 (s, 3H), 3.27 (t, *J* = 4.4 Hz, 1H), 2.80-2.71 (m, 2H), 2.59-2.47 (m, 1H), 2.37-2.27 (m, 2H), 2.21-2.11 (m, 2H), 1.82-1.67 (m, 1H), 1.45-1.31 (m, 1H), 0.90 (s, 9H), 0.06 (s, 3H) , 0.04 (s, 3H); HR-MS (ESI), m/z $[M + H]^+$ calcd for $C_{27}H_{37}O_4Si$ 453.2456, found 453.2458.

3. Synthesis of coupled substrate **6a**

The synthetic route for the coupling substrate **6a** is as follows in Scheme S1.



Scheme S1. The synthetic route for the coupling substrate **6a**

((8-Bromo-5-methoxy-1,2,3,4-tetrahydronaphthalen-1-yl)oxy)(*tert*-butyl)dimethylsilane (**M-3**)

M-1 (5.340 g, 0.03 mol, 1 eq), imidazole (8.160 g, 0.12 mol, 4 eq) and 250 mL MeCN were respectively added to a 500 mL round-bottom flask. Then TBDMSCl (13.590 g, 0.09 mol, 3 eq) was added slowly in an ice-water bath and stirred at room temperature for 8 h, removed the solvent. Then 200 mL of deionized H_2O was added, extracted by ethyl acetate (200 mL x 3), the organic phase was washed with saturated NaCl solution, dried with anhydrous $NaSO_4$. Then the solvent was evaporated under reduced pressure, and a colourless liquid (**M-2**, yield 99%) was obtained by rapid column chromatography. Then, the **M-2** was placed in a 300 mL round-bottomed flask, 150 mL of anhydrous CH_2Cl_2 was added. NBS (5.445 g, 39 mmol, 1.03 eq) was added slowly under an ice-water bath, and stirred at room temperature for 8 h, removed the solvent. The reaction solution was transferred to a 500 mL separatory funnel, and 150 mL of ethyl acetate and 150 mL of deionized H_2O were added to dilute the solution, the organic phase was combined and washed with saturated NaCl solution, dried with anhydrous $NaSO_4$. The solvent was evaporated under reduced pressure, and the crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1 : 50) to produce 8.072 g **M-3**. Light yellow solid, yield 73%, mp 133-135^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.7 Hz, 1H), 6.64 (d, *J* = 8.7 Hz, 1H), 5.05 (s, 1H), 3.80 (s, 3H), 2.91 (dd, *J* = 18.6, 5.7 Hz, 1H), 2.43 (ddd, *J* = 18.4, 12.0, 6.8 Hz, 1H), 2.15-2.03 (m, 2H), 1.81-1.72 (m, 1H), 1.66-1.53 (m, 1H), 0.91 (s, 9H), 0.25 (s, 3H), 0.23 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.70, 138.21, 130.19, 129.10, 116.55, 110.26, 67.56, 55.54, 31.52, 26.24, 23.41, 18.53, 15.65, -3.73, -4.25. HR-MS (ESI), m/z $[M + H]^+$ calcd for $C_{17}H_{28}BrO_2Si$ 371.1036, found 371.1038.

5-Bromo-4-((*tert*-butyldimethylsilyl)oxy)-8-methoxy-3,4-dihydronaphthalen-1(2*H*)-one **(6a)**

M-3 (3.710 g, 10 mmol, 1 eq), PDC (11.190 g, 30 mmol, 3 eq), celite (10 g) and benzene (150 mL) were sequentially put a 500 mL round-bottomed flask, then *t*-BuOOH (27.8 mL, 20 eq) was added at ice-water bath, the reaction was carried out for 24 h in dark at room temperature. The insoluble material was removed by filtration, the solvent was evaporated under reduced pressure, ethyl acetate (150 mL) was added and washed with 100 mL of dilute HCl solution, then washed twice with deionized H_2O, once with saturated NaCl solution. The organic phase was dried with anhydrous $NaSO_4$, the solvent was evaporated under reduced pressure, and the crude product was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1: 10) to obtain 2.887 g **6a**. Light yellow solid, yield 75%, mp 91-94^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 9.0 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 5.32 (dd, *J* = 3.8, 1.8 Hz, 1H), 3.88 (s, 3H), 2.98 (ddd, *J* = 18.3, 12.2, 6.4 Hz, 1H), 2.57-2.45 (m, 1H), 2.26-2.17 (m, 1H), 2.05 (tdd, *J* = 12.1, 6.5, 3.3 Hz, 1H), 0.81 (s, 9H), 0.18 (s, 3H), 0.02 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.08, 158.90, 145.37, 137.72, 123.72, 113.79, 113.02, 67.87, 56.41, 33.23, 29.84, 25.81, 18.20, -4.29, -4.54. HR-MS (ESI), m/z $[M + H]^+$ calcd for $C_{17}H_{26}BrO_3Si$ 385.0829, found 385.0830.

References

1. M. Farhang, A. R. Akbarzadeh, M. Rabbani and A. M. Ghadiri, *Polyhedron*, 2022, **227**, 116124.
2. J. D. Winkler, *Chem Rev*, 1996, **96**, 167-176.
3. Y. J Shi, P Wan. Solvolysis and ring closure of quinone methides photogenerated from biaryl systems. *Can. J. Chem.* 2005, **83**, 1306-1323.

5. ^{1}H and ^{13}C NMR spectra of compounds

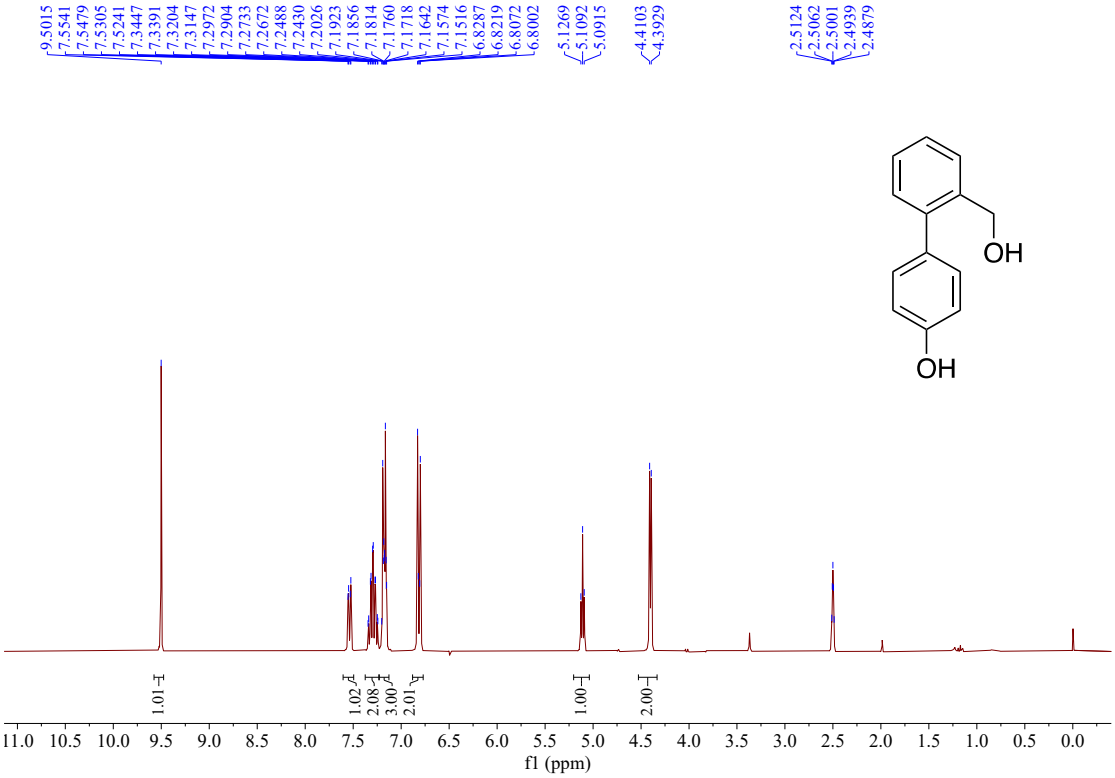


Figure S1. ^{1}H NMR of compound **2a** in DMSO-d_6

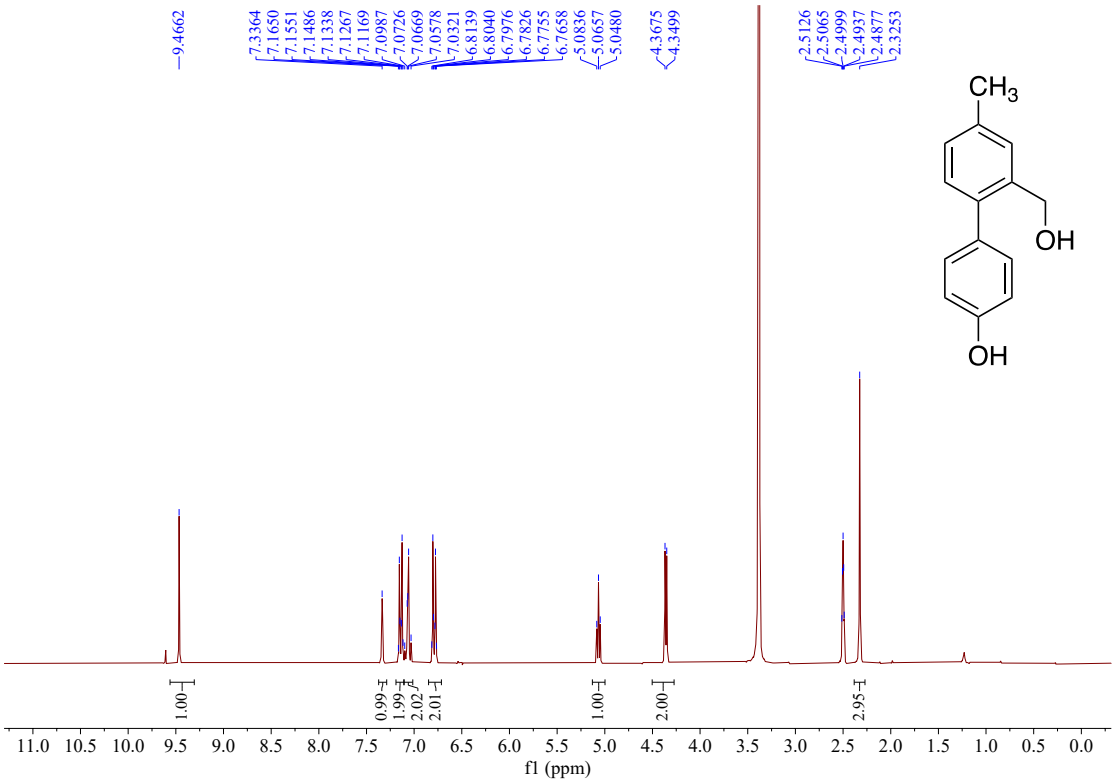


Figure S2. ^{1}H NMR of compound **2b** in DMSO-d_6

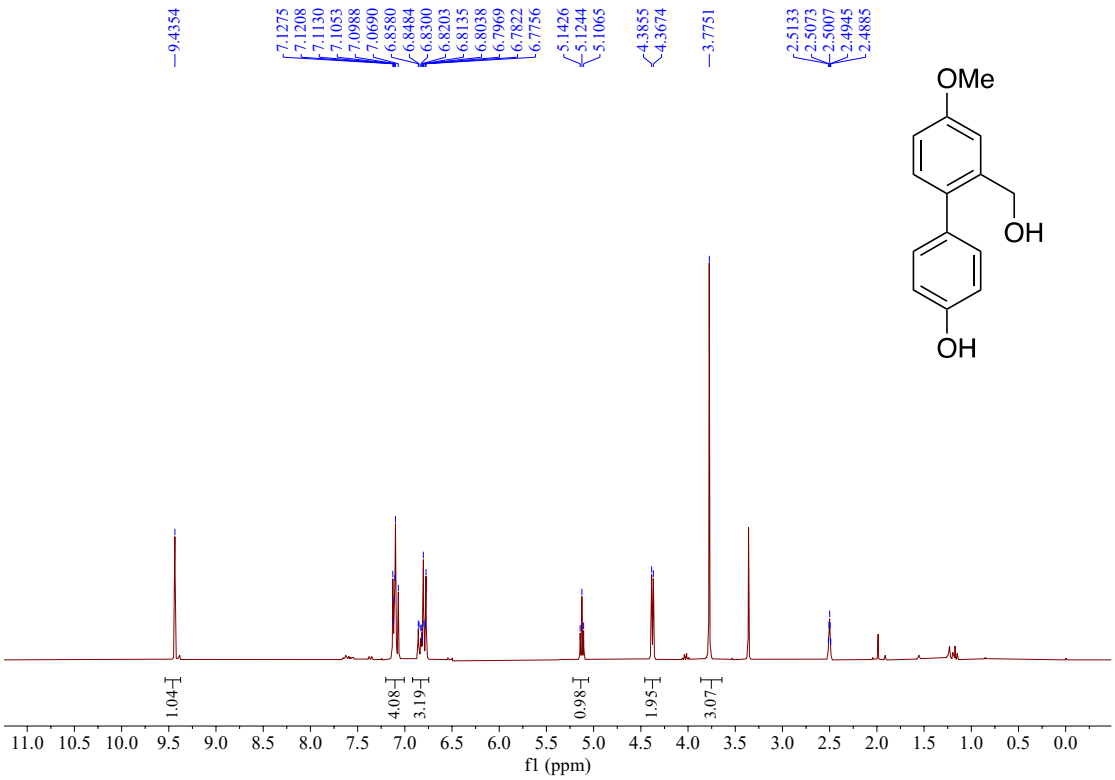


Figure S3. ^{1}H NMR of compound **2c** in DMSO-d_6

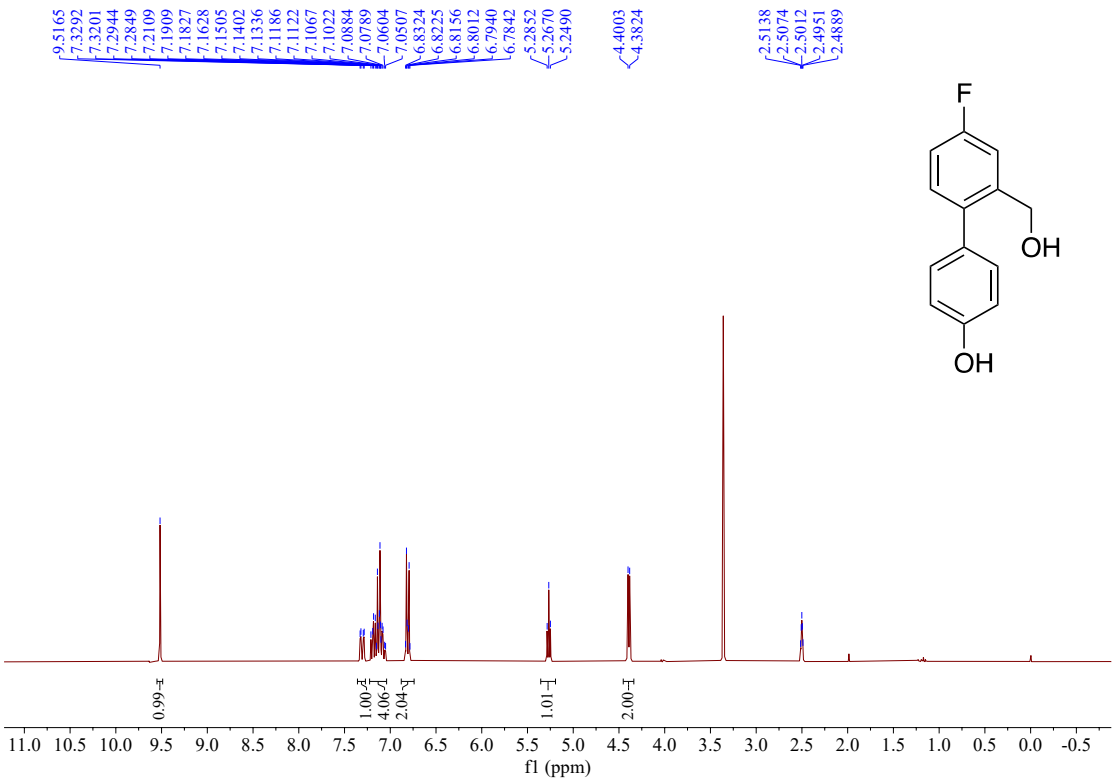


Figure S4. ^{1}H NMR of compound **2d** in DMSO-d_6

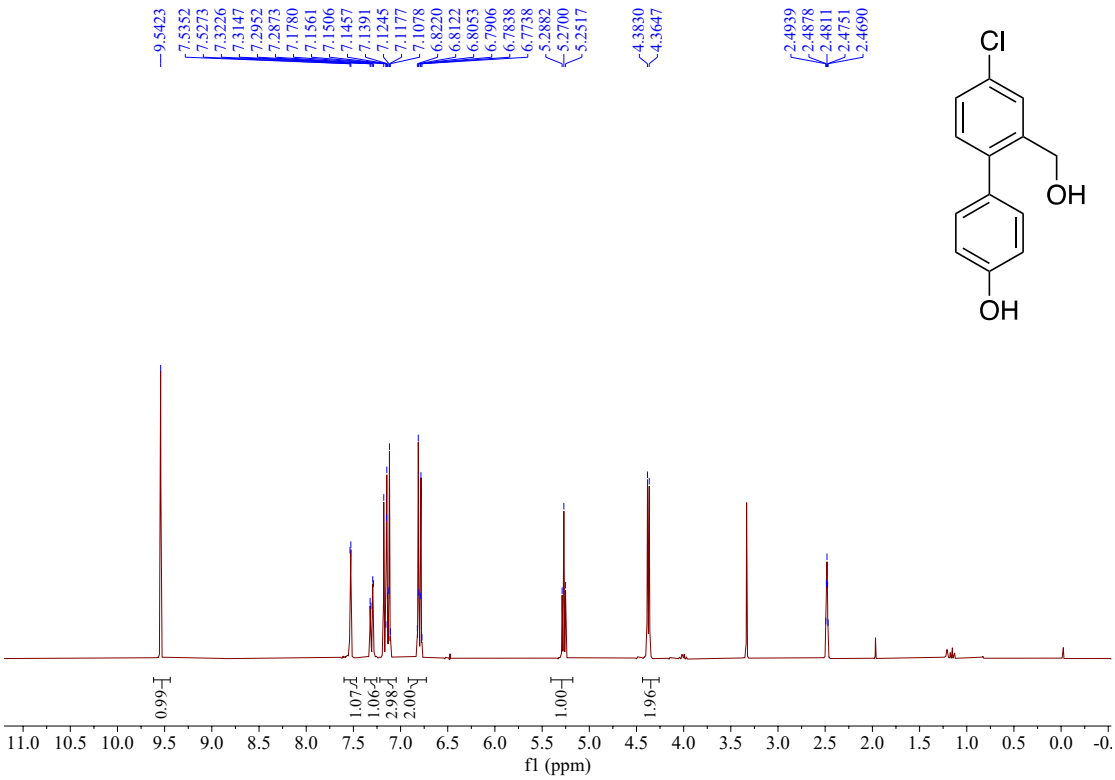


Figure S5. ^{1}H NMR of compound **2e** in DMSO-d_6

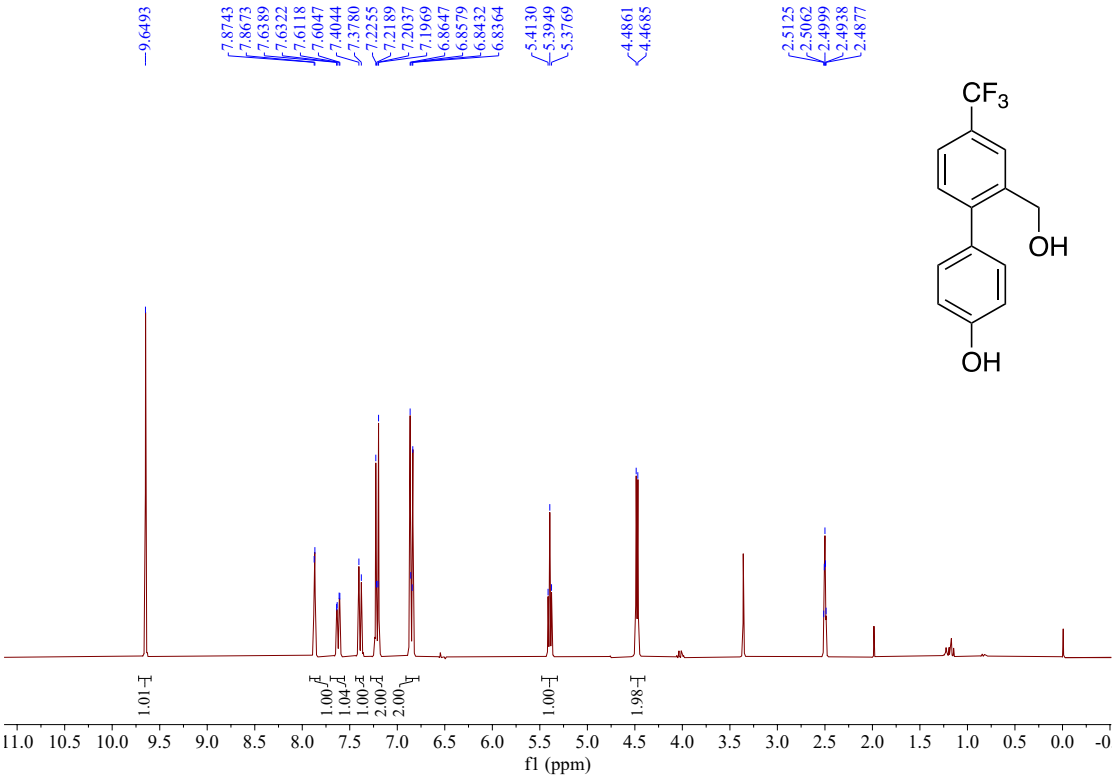


Figure S6. ^{1}H NMR of compound **2f** in DMSO-d_6

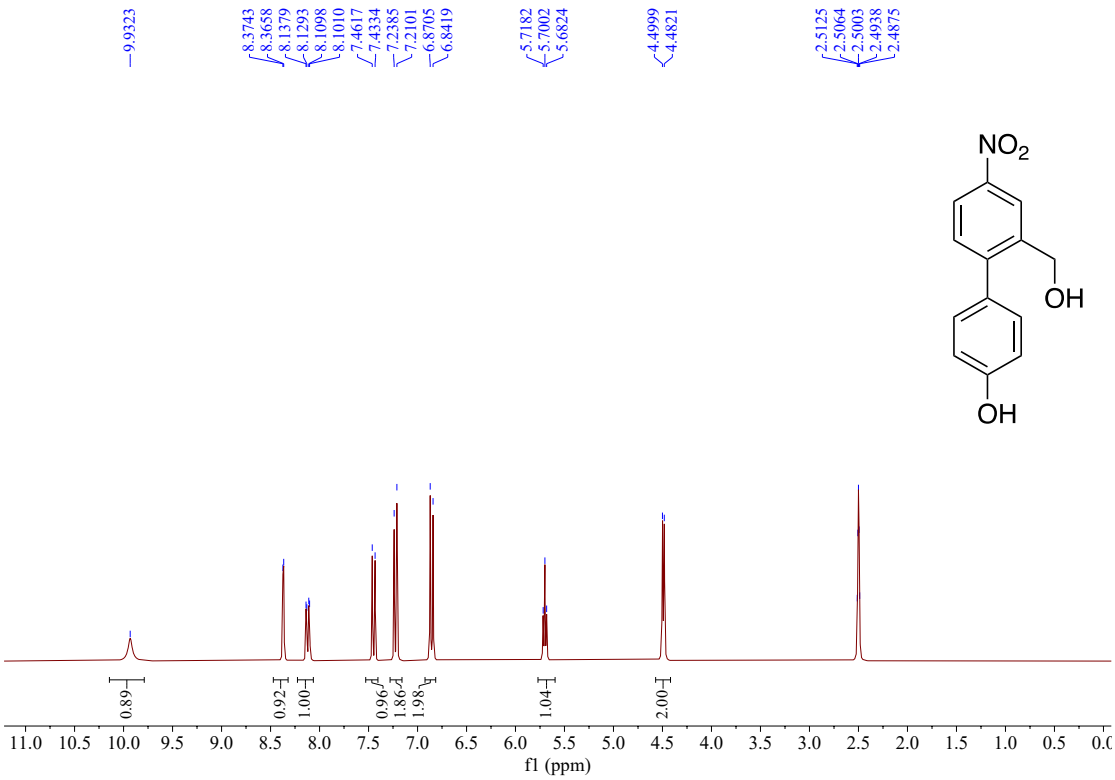


Figure S7. ^{1}H NMR of compound **2g** in DMSO-d_6

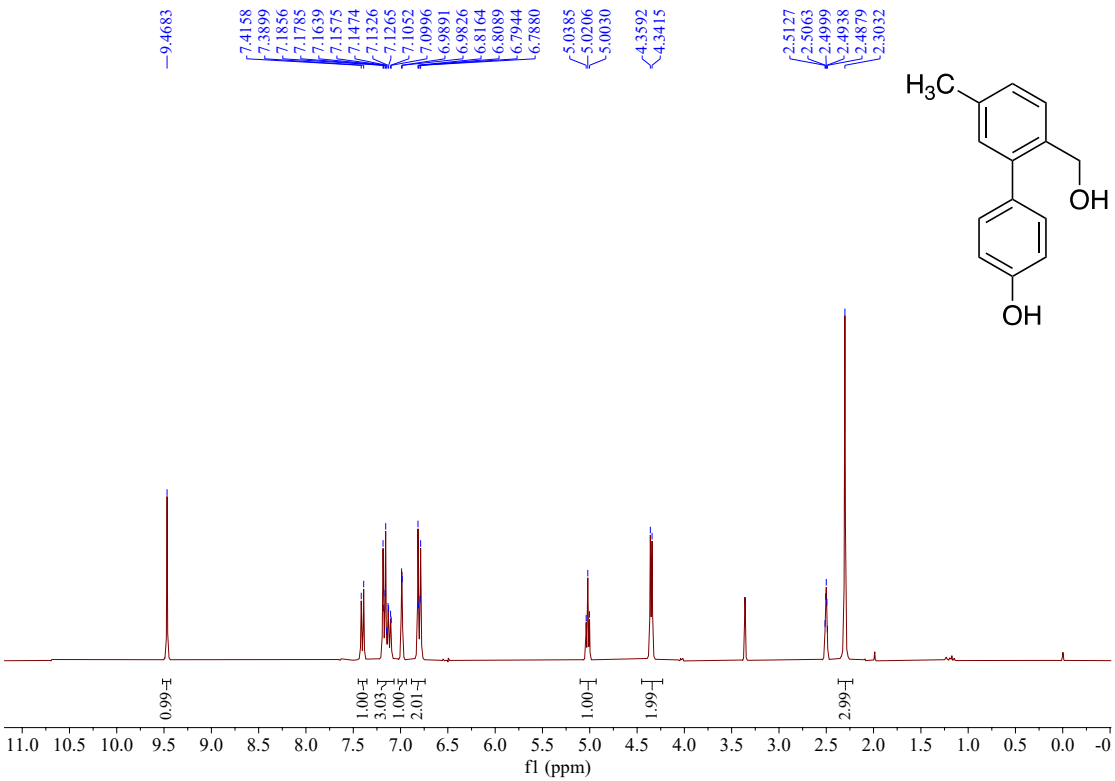


Figure S8. ^{1}H NMR of compound **2h** in DMSO-d_6

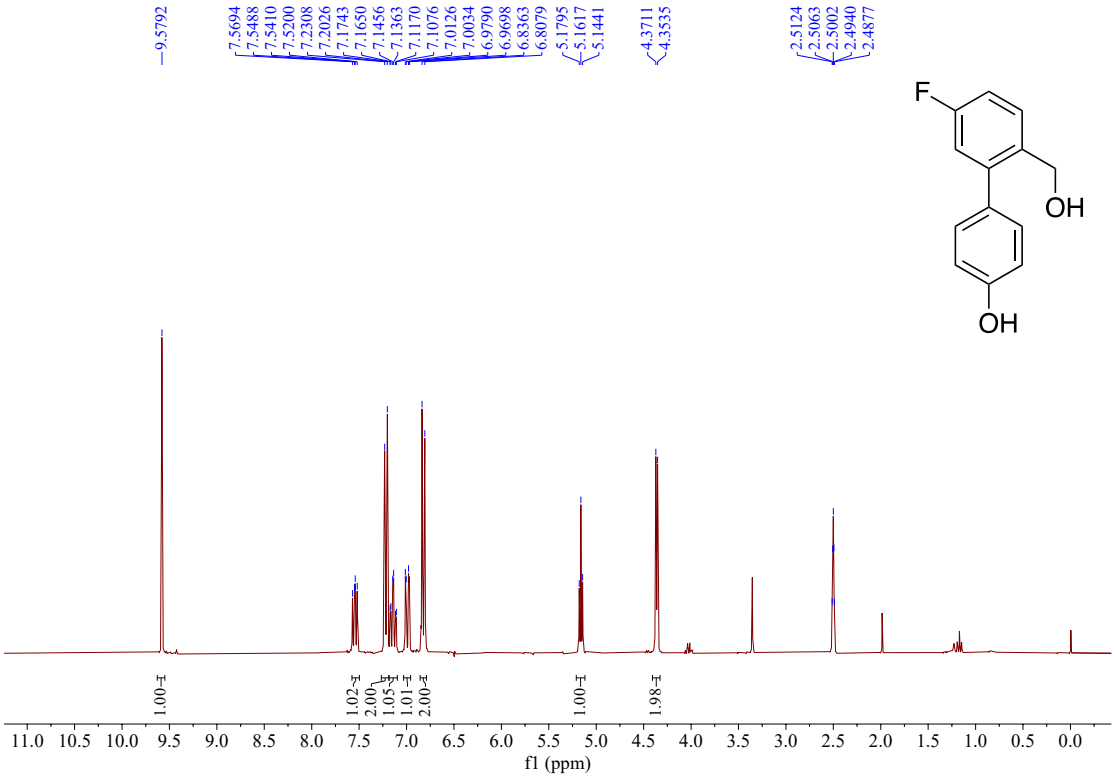


Figure S9. ^{1}H NMR of compound **2i** in DMSO-d_6

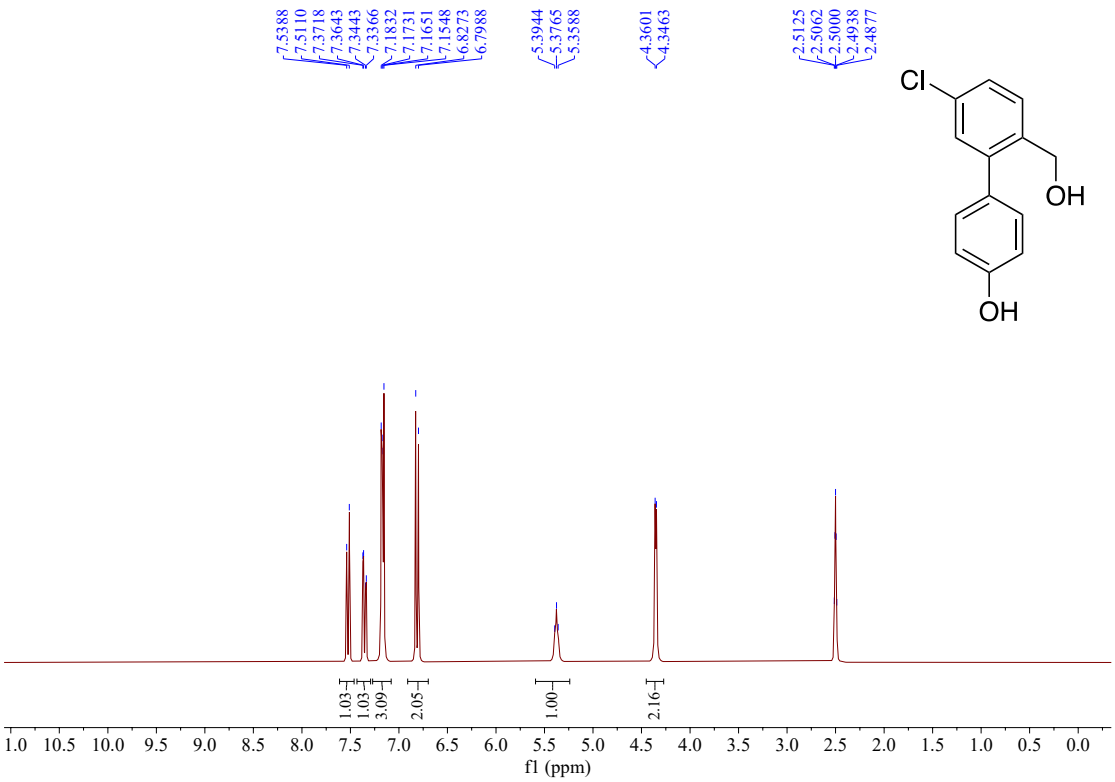


Figure S10. ^{1}H NMR of compound **2j** in DMSO-d_6

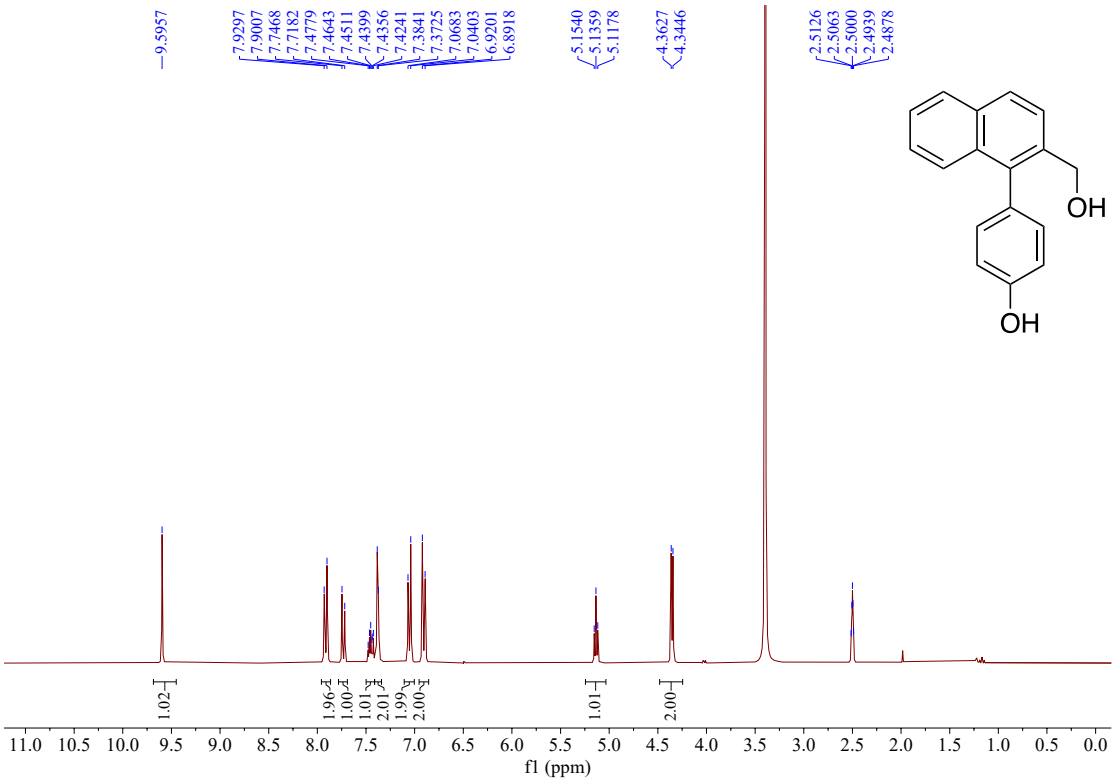


Figure S11. ^{1}H NMR of compound **2k** in DMSO-d_6

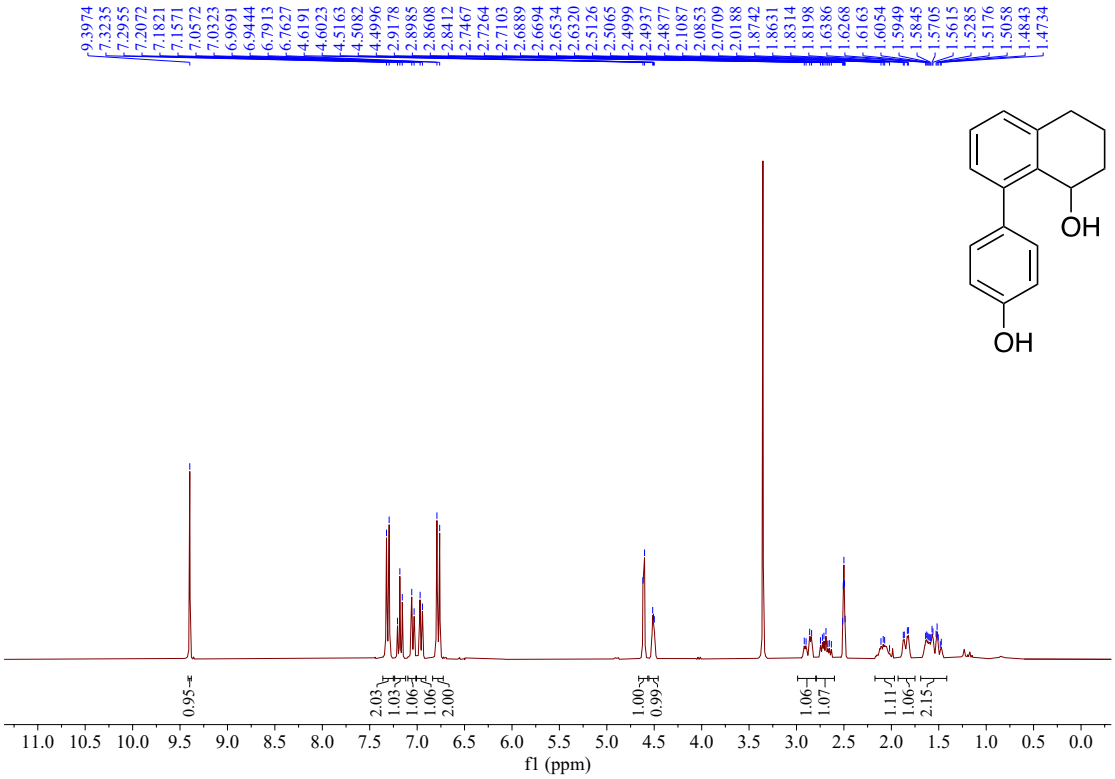


Figure S12. ^{1}H NMR of compound **2l** in DMSO-d_6

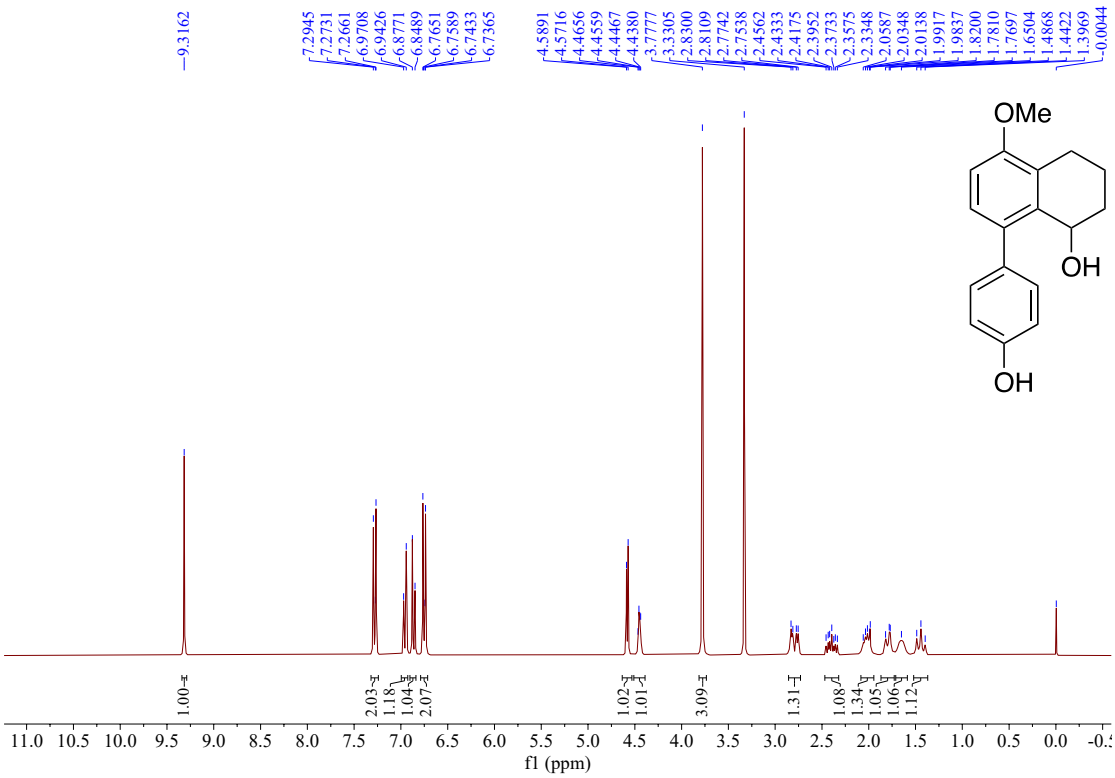


Figure S13. ^{1}H NMR of compound **2m** in DMSO-d_6

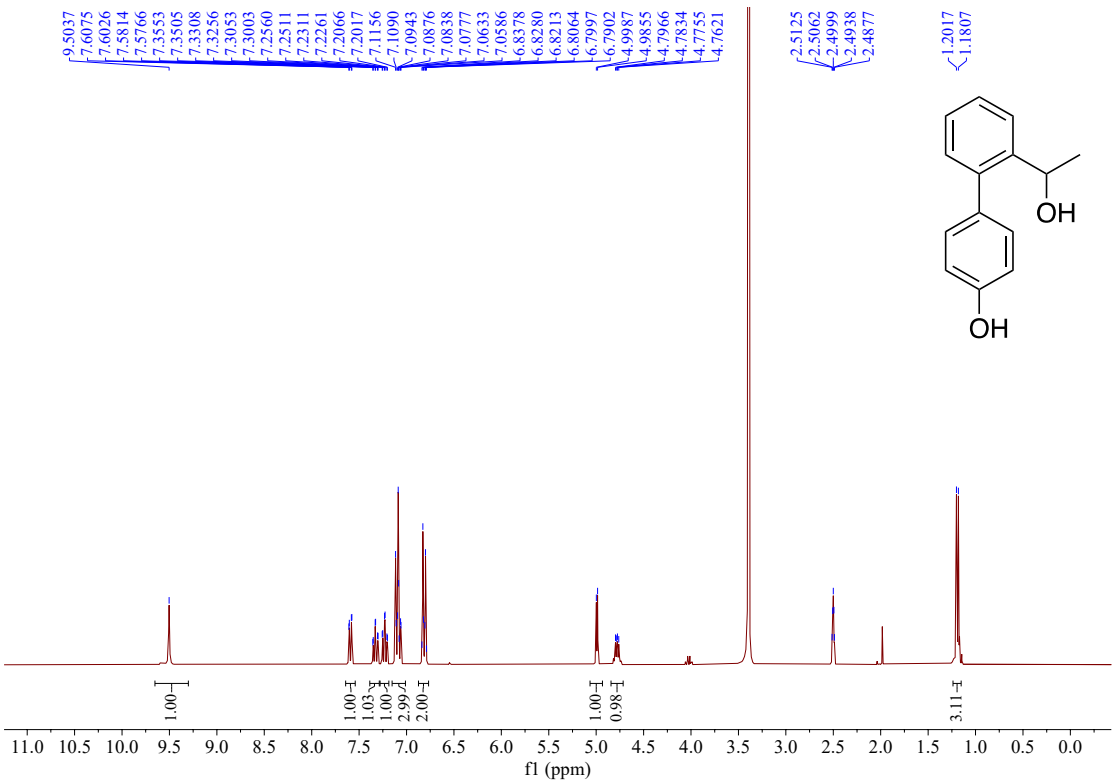


Figure S14. ^{1}H NMR of compound **2n** in DMSO-d_6

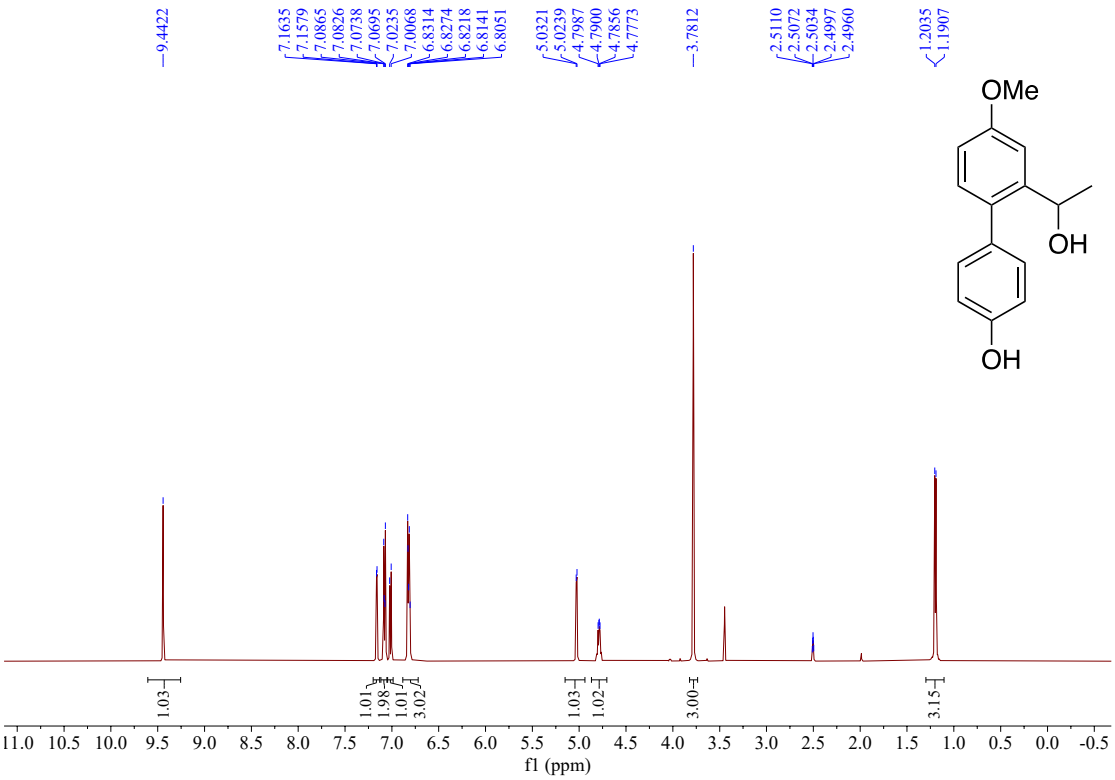


Figure S15. ^{1}H NMR of compound **2o** in DMSO-d_6

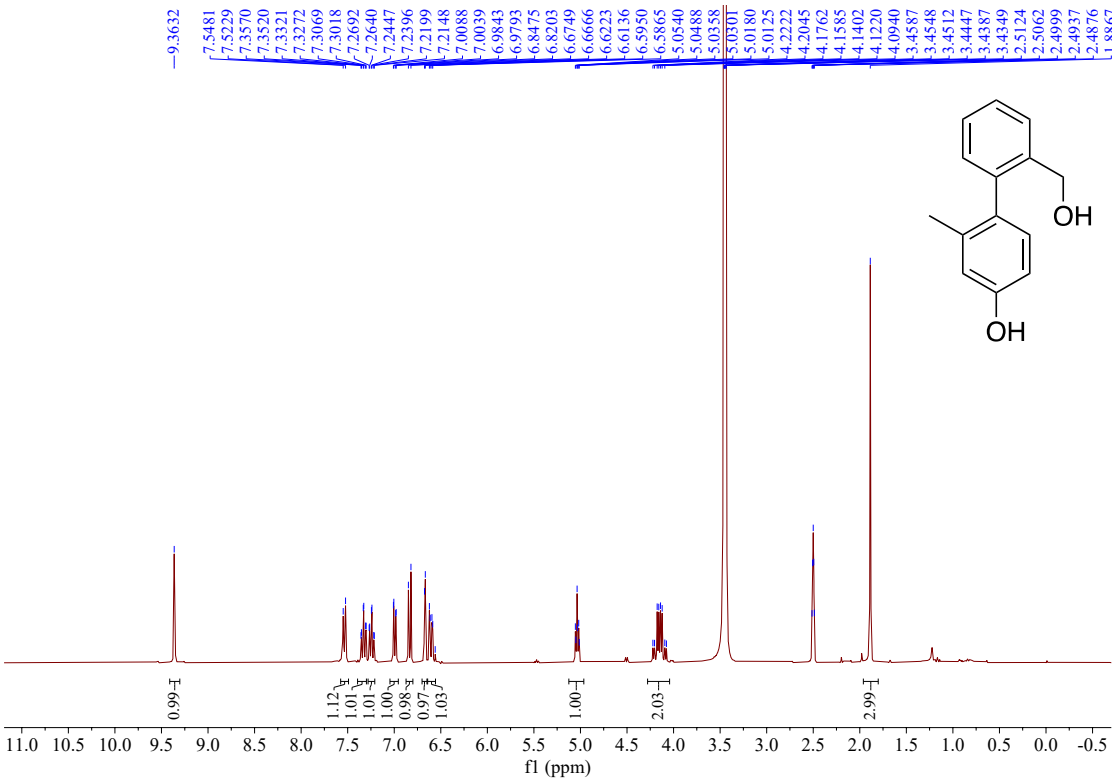


Figure S16. ^{1}H NMR of compound **2p** in DMSO-d_6

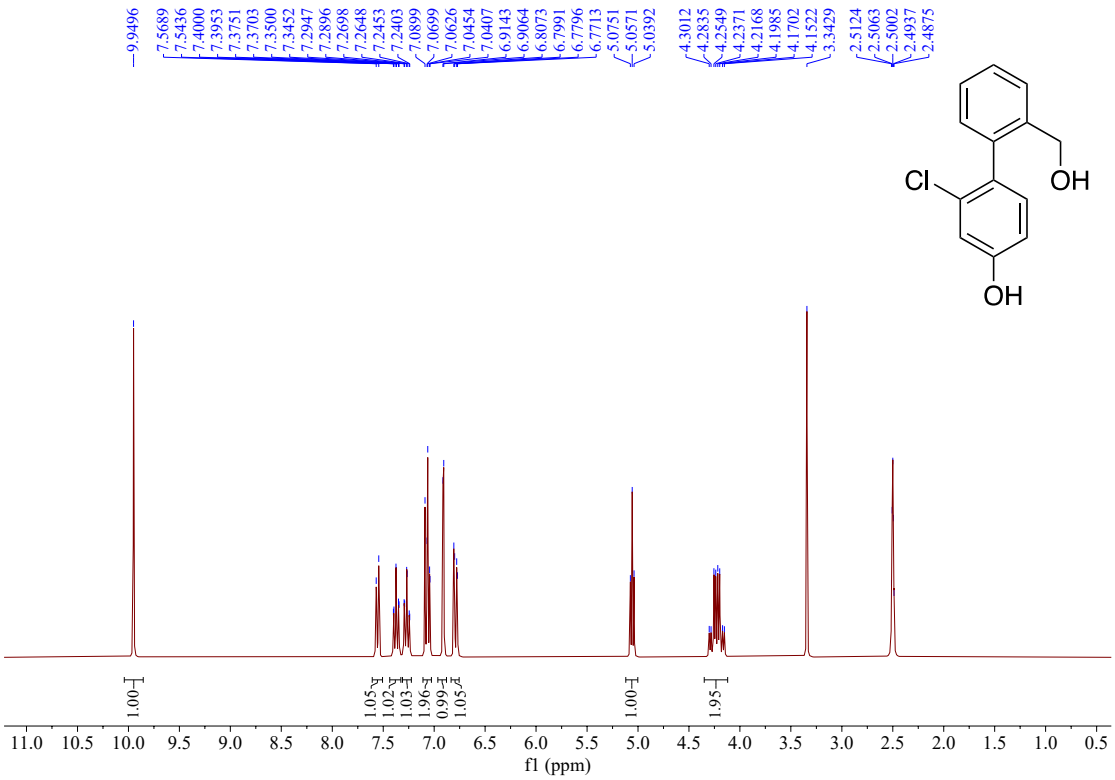


Figure S17. ^{1}H NMR of compound **2q** in DMSO-d_6

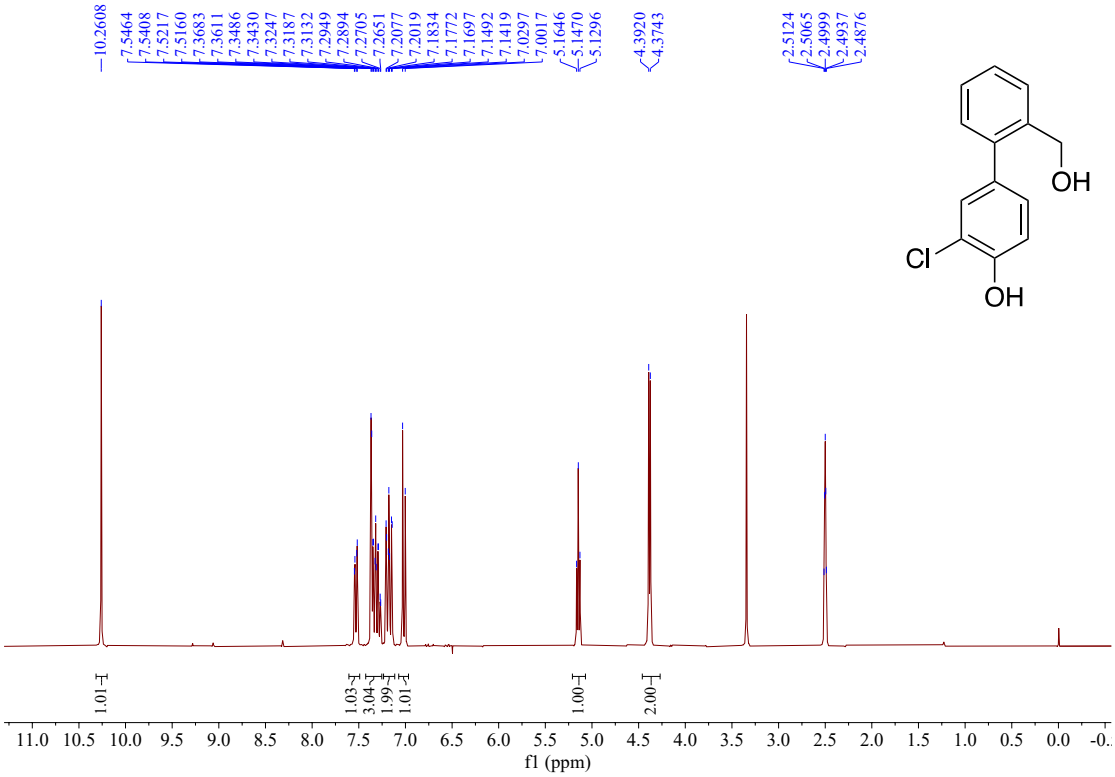


Figure S18. ^{1}H NMR of compound **2r** in DMSO-d_6

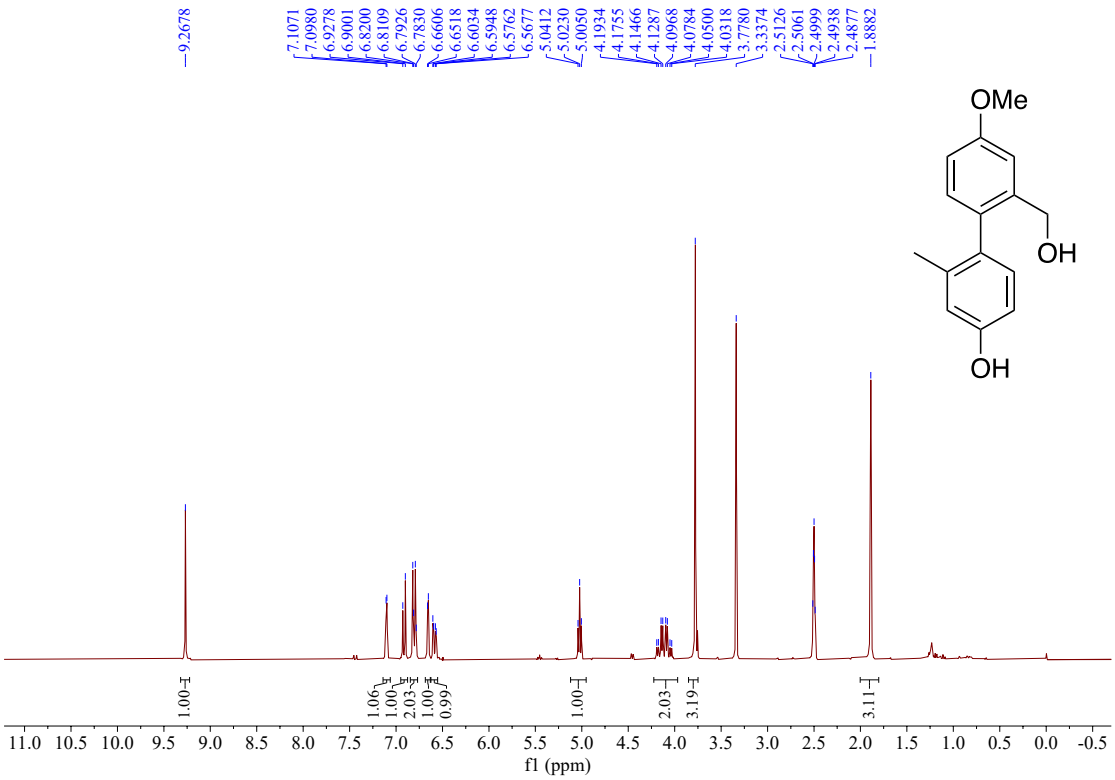


Figure S19. ^{1}H NMR of compound **2s** in DMSO-d_6

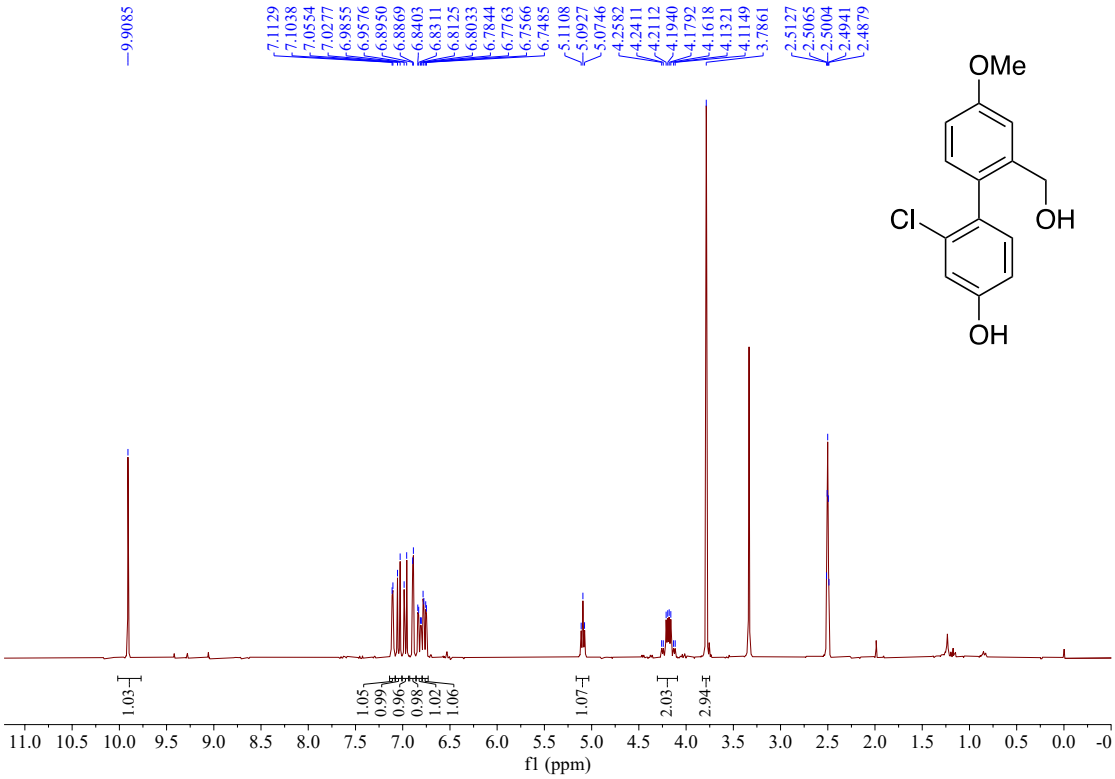


Figure S20. ^{1}H NMR of compound **2t** in DMSO-d_6

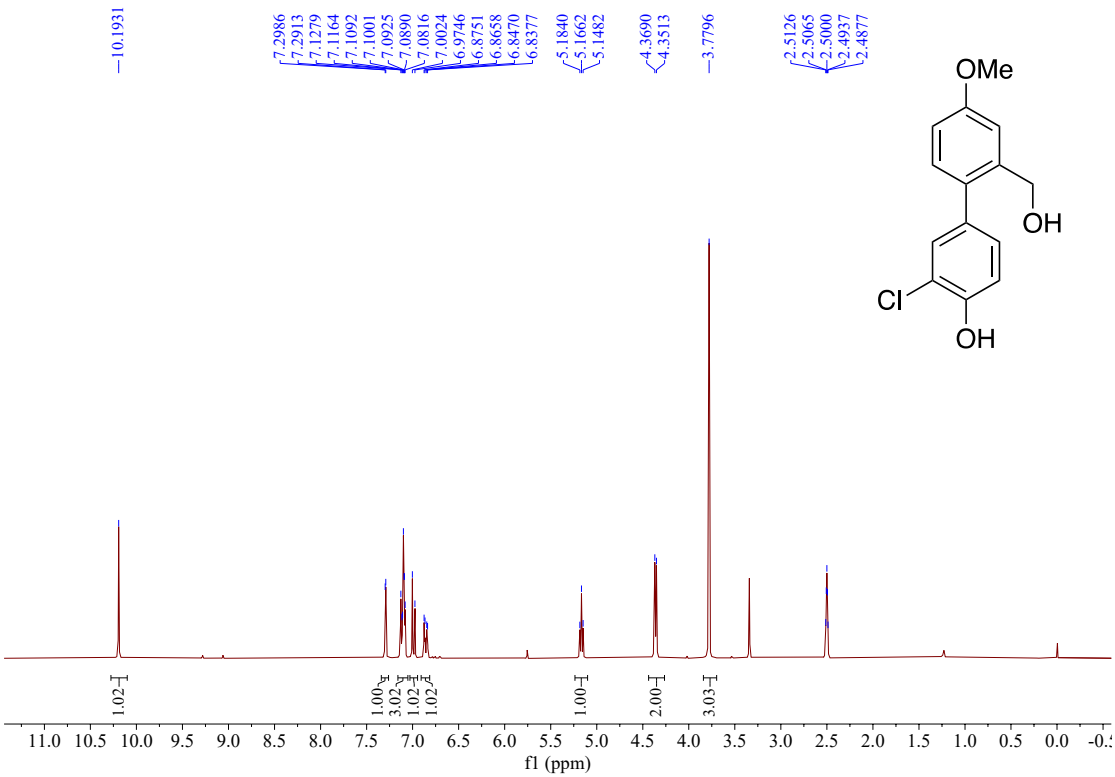


Figure S21. ^{1}H NMR of compound **2u** in DMSO-d_6

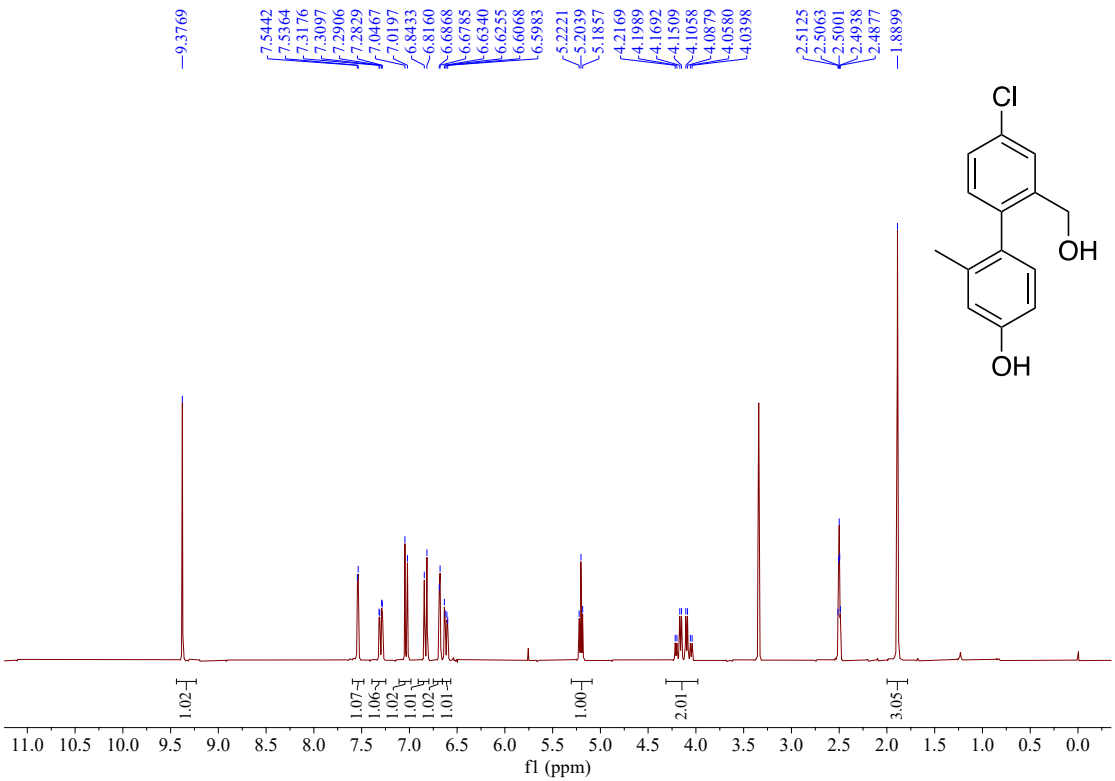


Figure S22. ^{1}H NMR of compound **2v** in DMSO-d_6

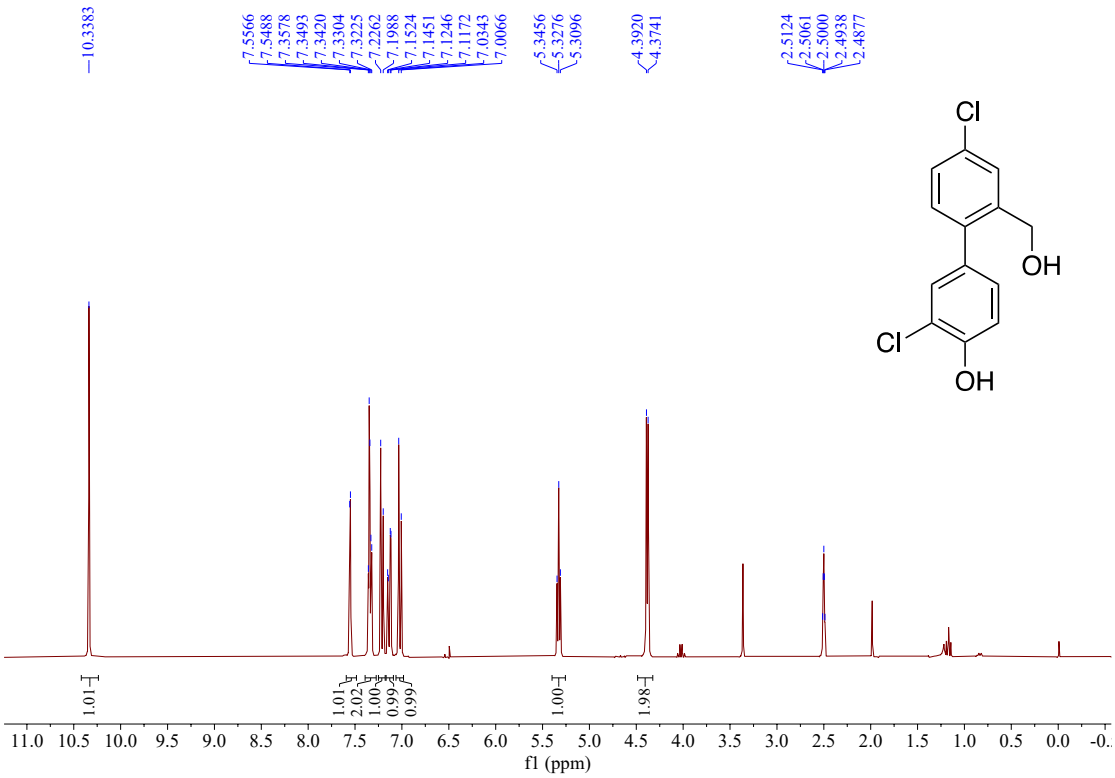


Figure S23. ^{1}H NMR of compound **2w** in DMSO-d_6

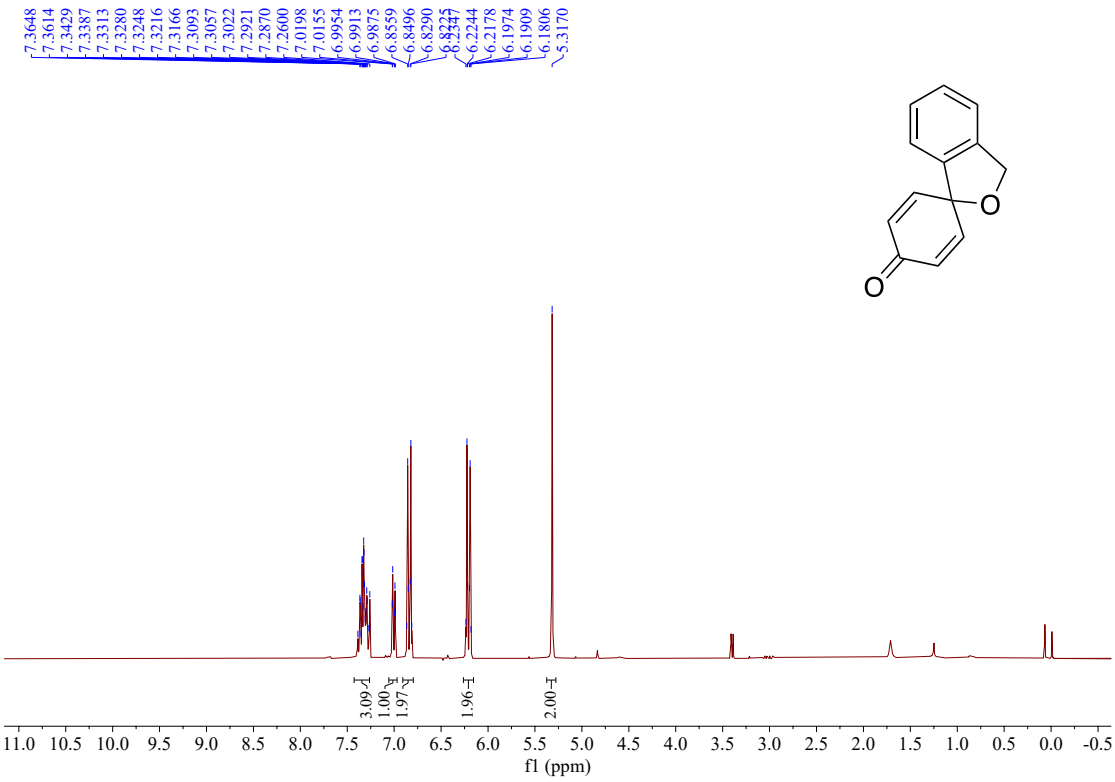


Figure S24. ^{1}H NMR of compound **3a** in $CDCl_3$

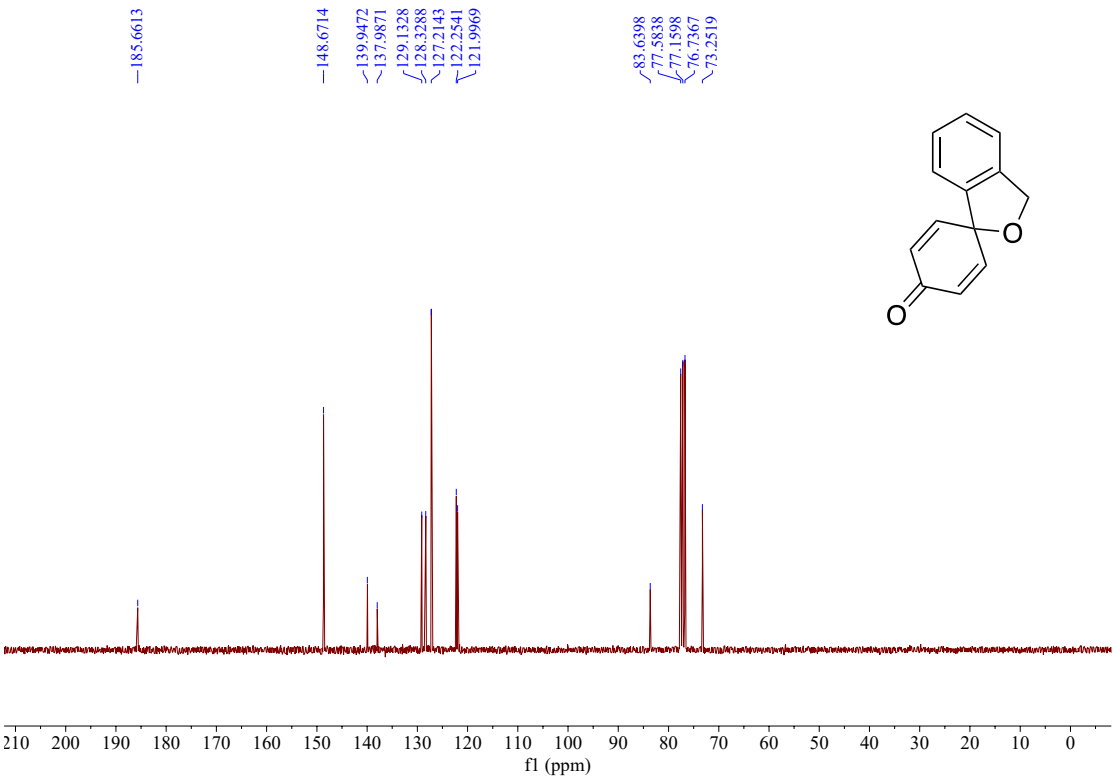


Figure S25. ^{13}C NMR of compound **3a** in $CDCl_3$

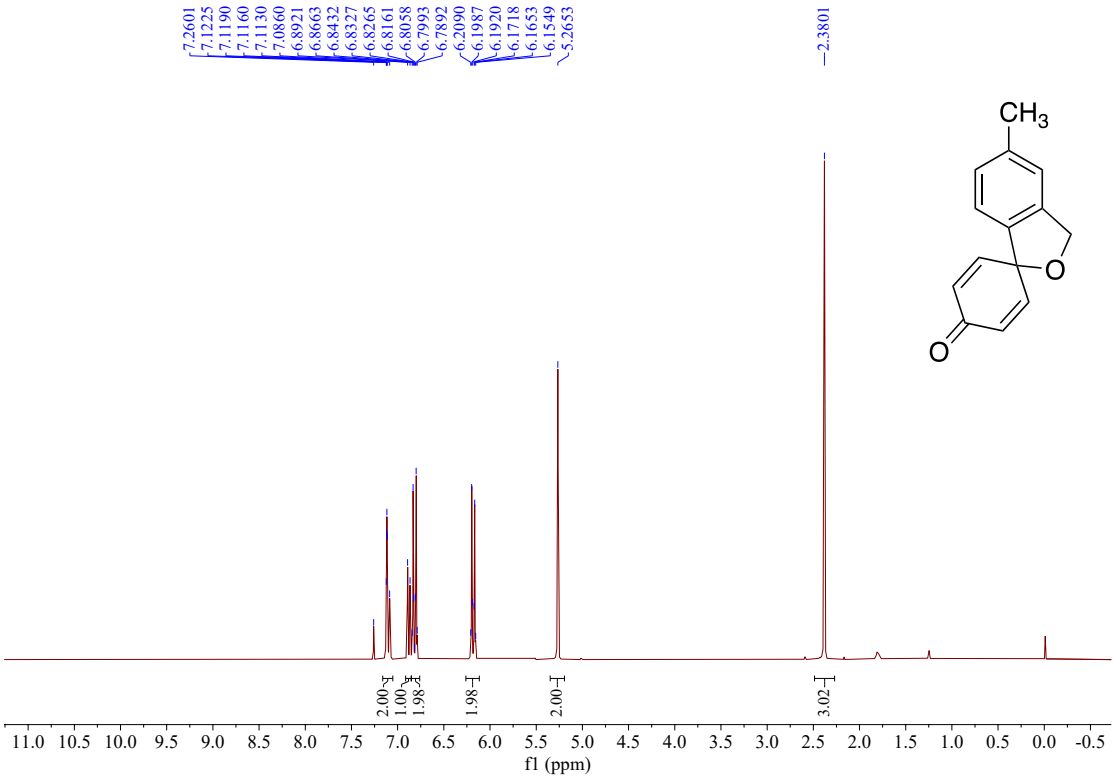


Figure S26. ^{1}H NMR of compound **3b** in $CDCl_3$

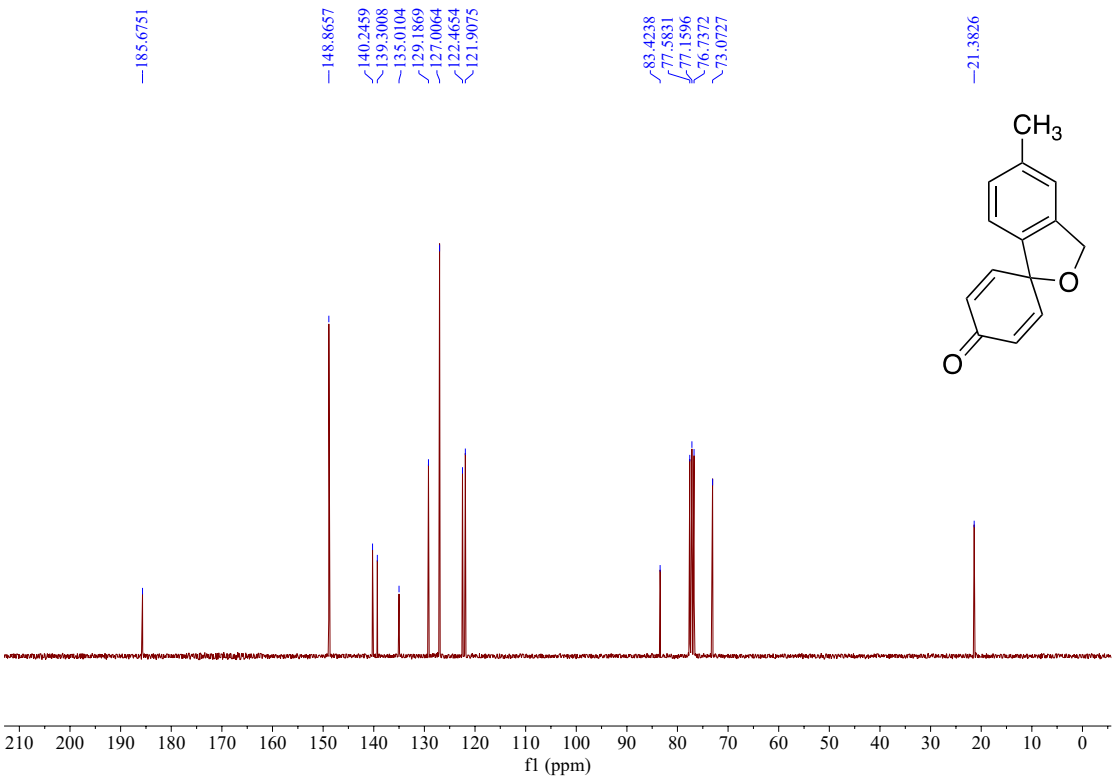


Figure S27. ^{13}C NMR of compound **3b** in $CDCl_3$

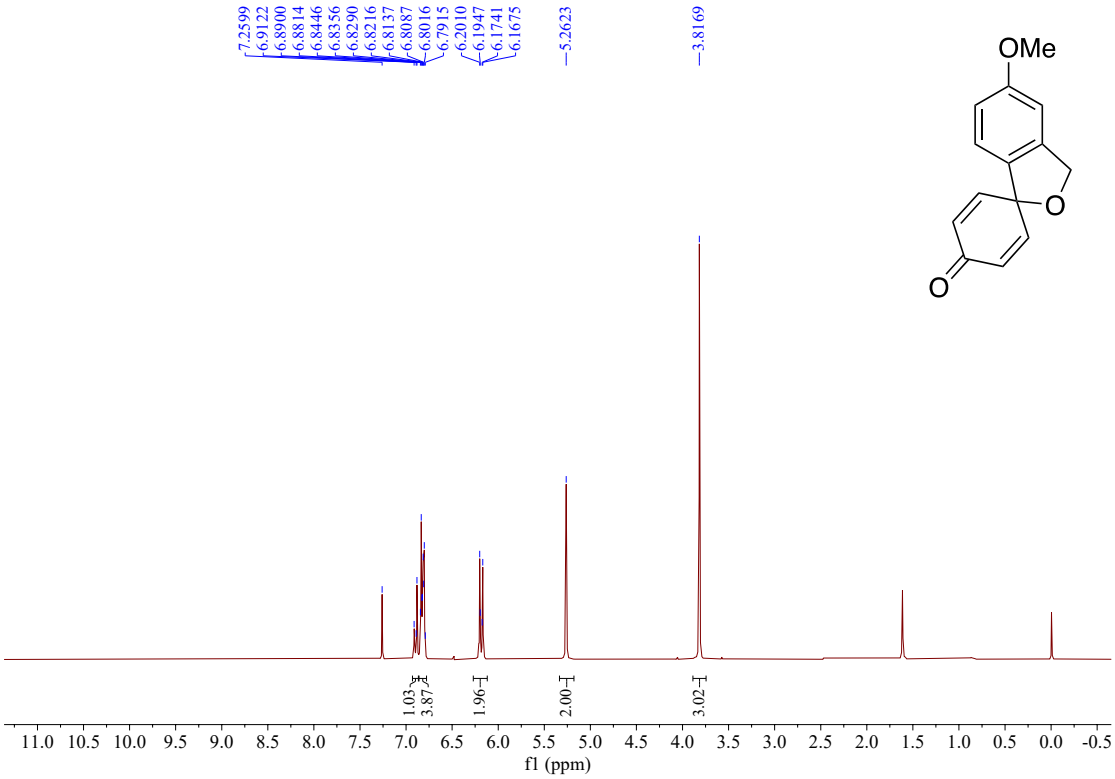


Figure S28. ^{1}H NMR of compound **3c** in $CDCl_3$

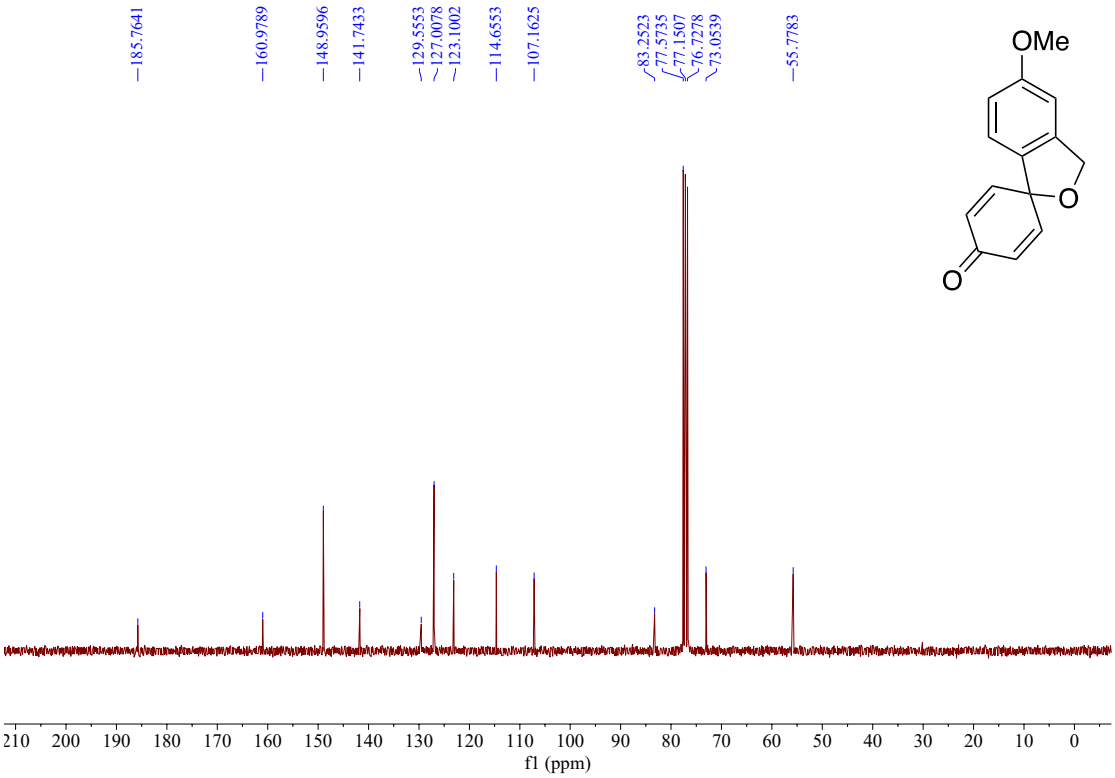


Figure S29. ^{13}C NMR of compound **3c** in $CDCl_3$

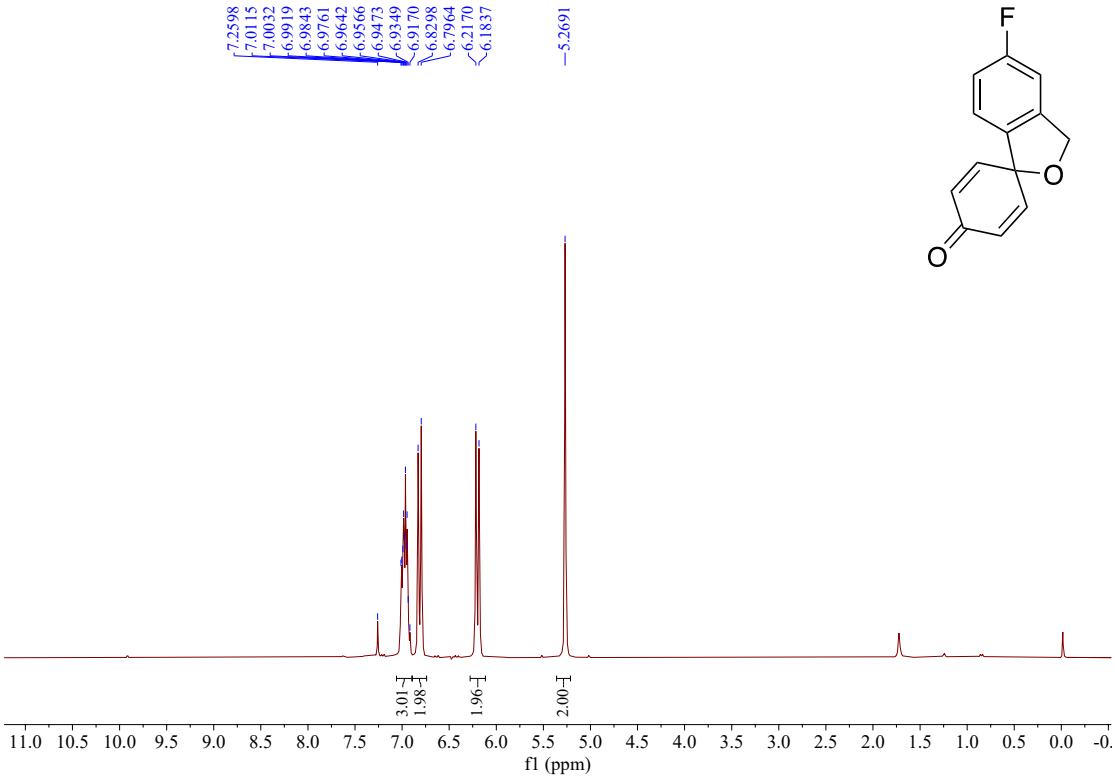


Figure S30. ^{1}H NMR of compound **3d** in $CDCl_3$

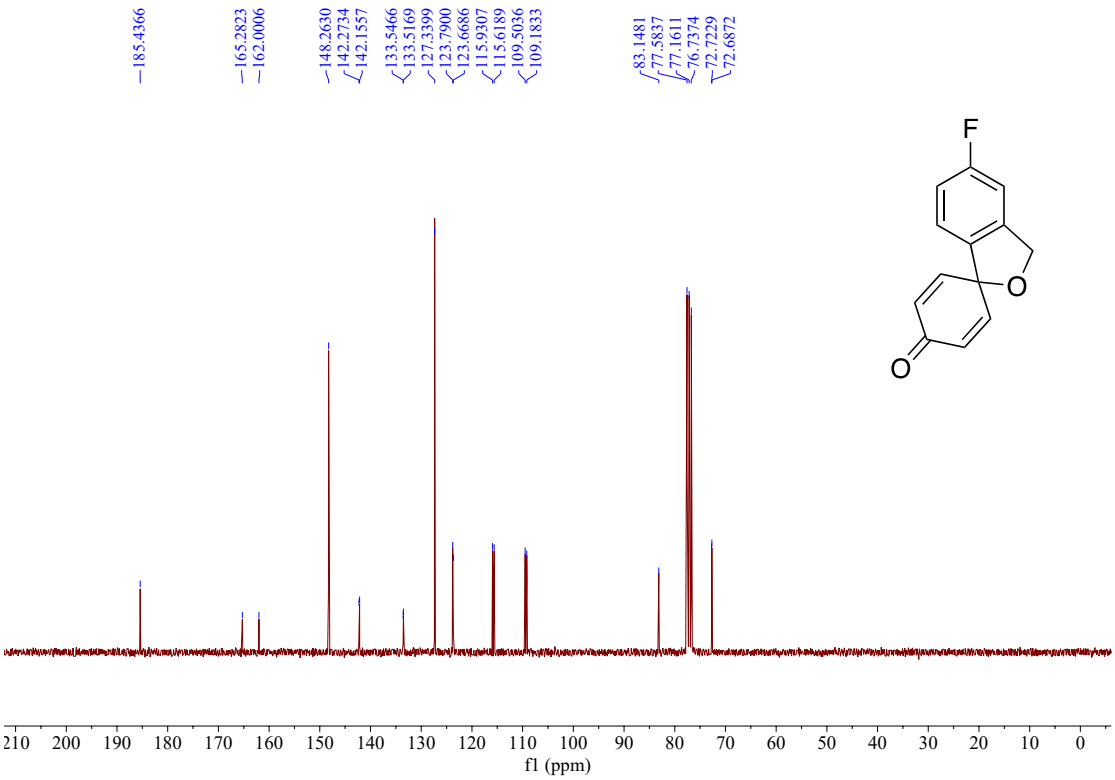


Figure S31. ^{13}C NMR of compound **3d** in $CDCl_3$

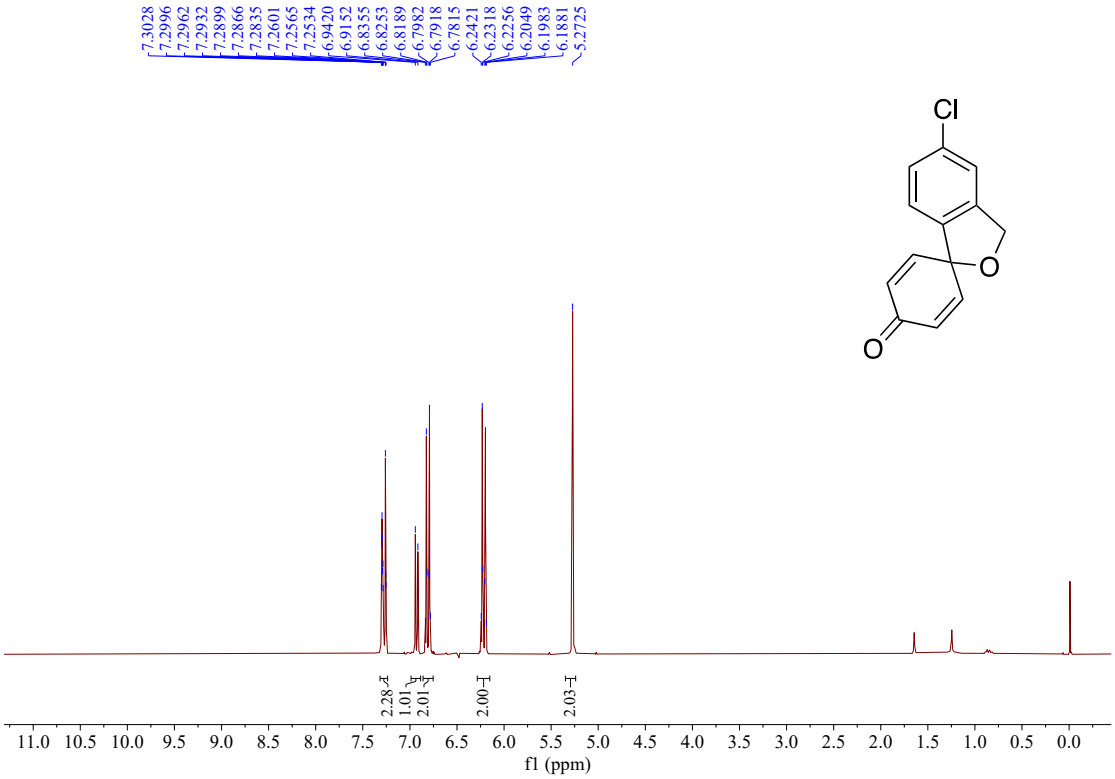


Figure S32. ^{1}H NMR of compound **3e**

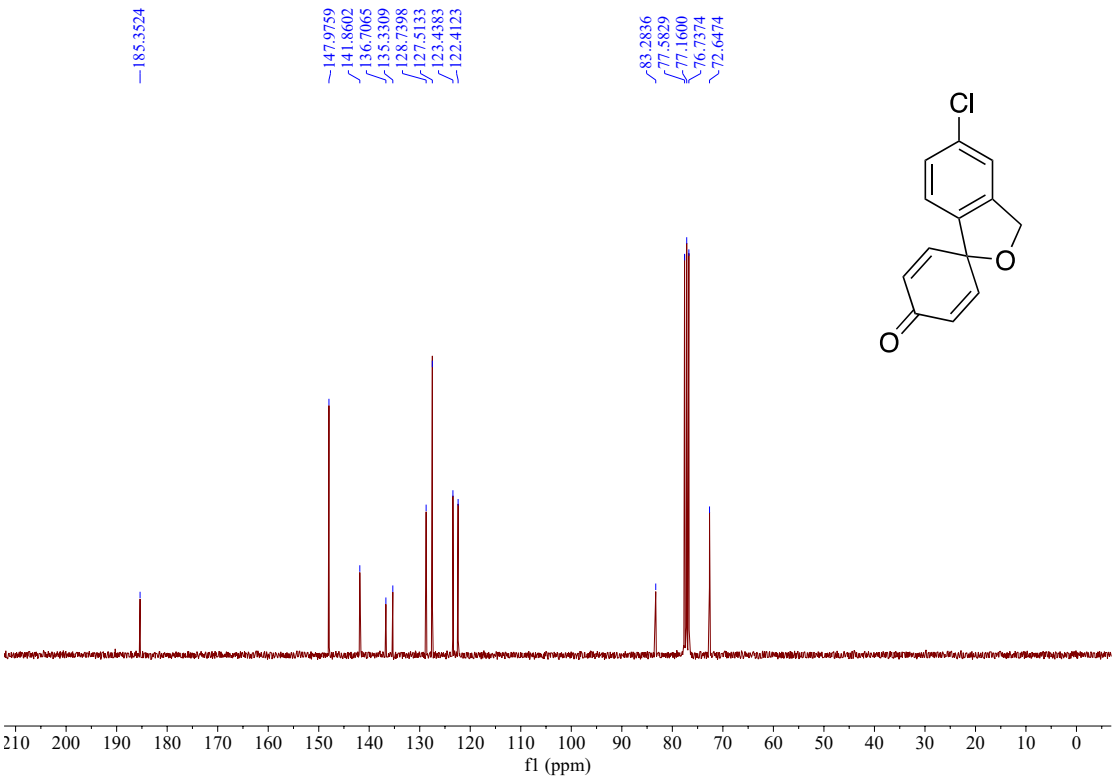


Figure S33. ^{13}C NMR of compound **3e** in $CDCl_3$

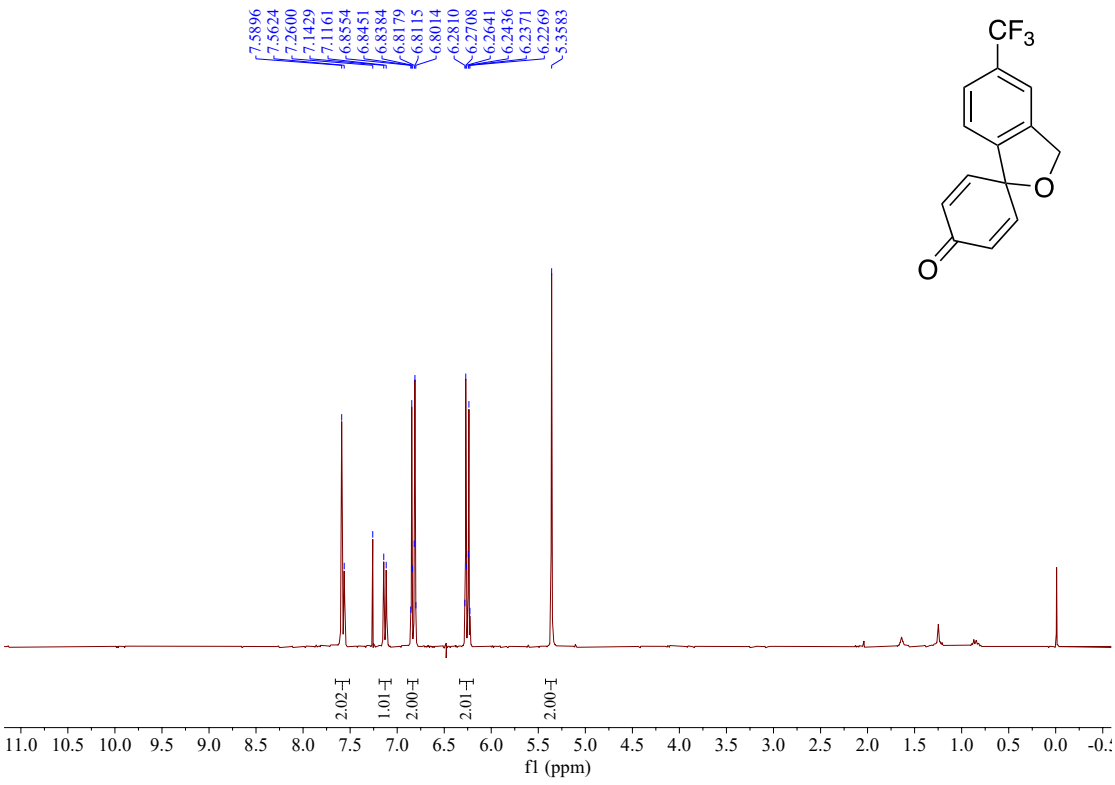


Figure S34. ^{1}H NMR of compound **3f** in $CDCl_3$

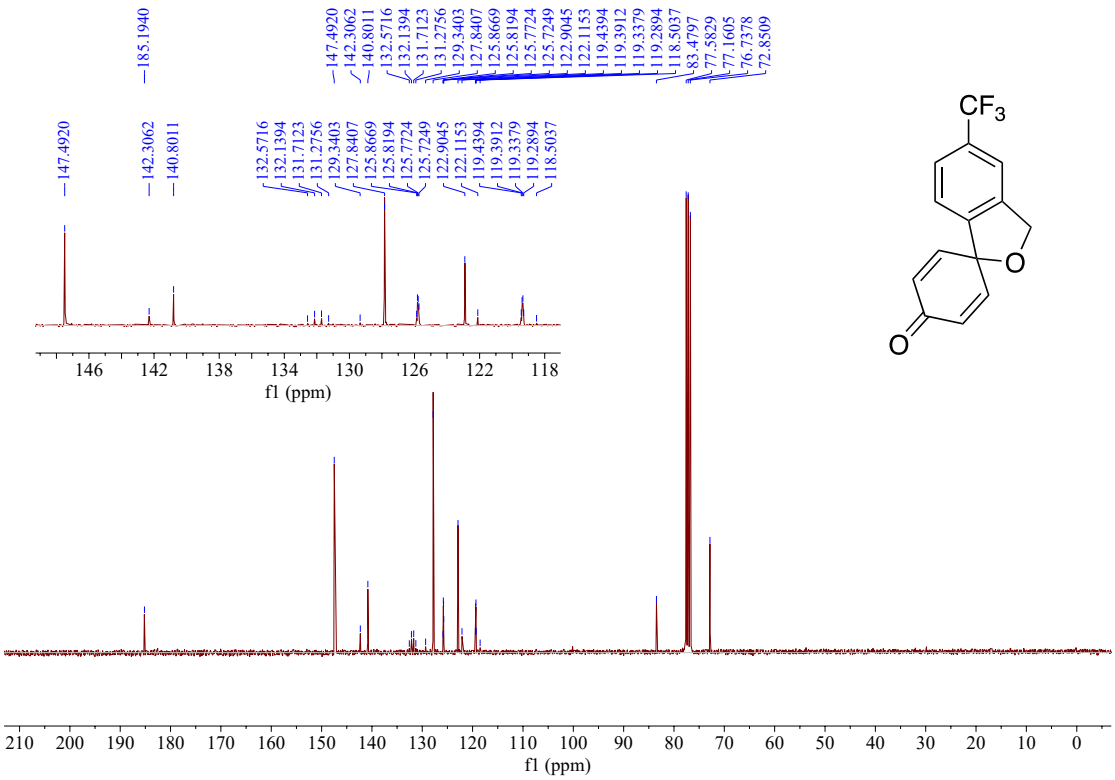


Figure S35. ^{13}C NMR of compound **3f** in $CDCl_3$

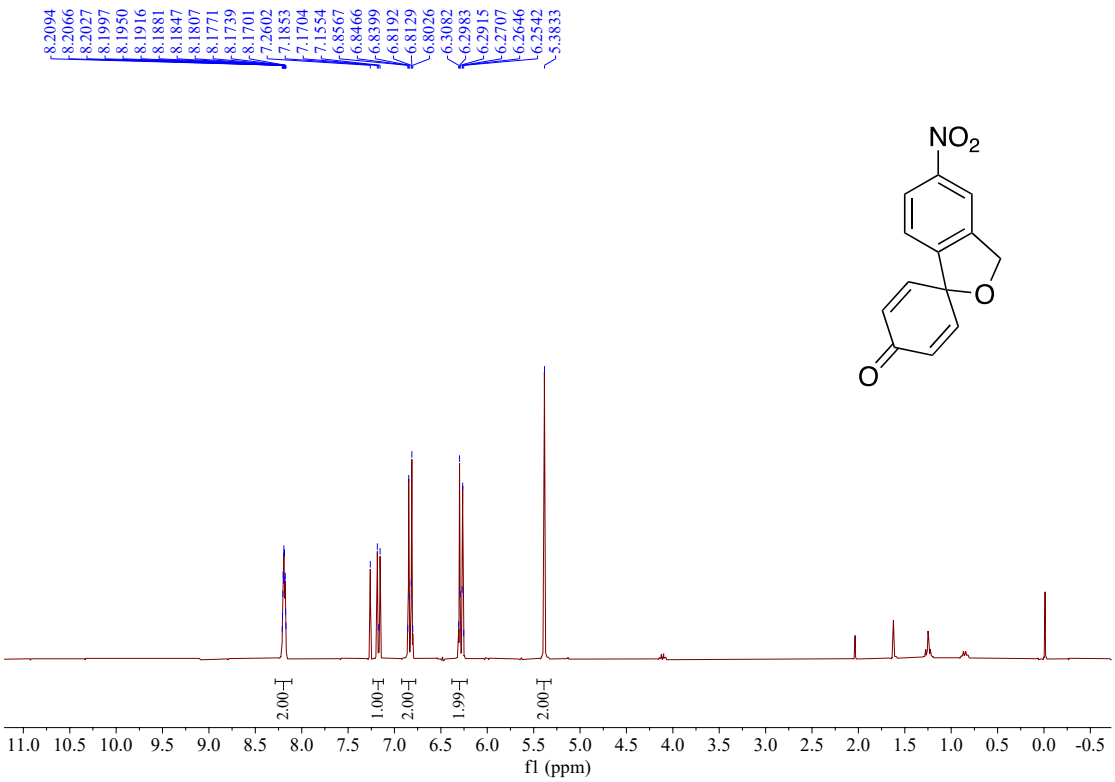


Figure S36. ^{1}H NMR of compound **3g** in $CDCl_3$

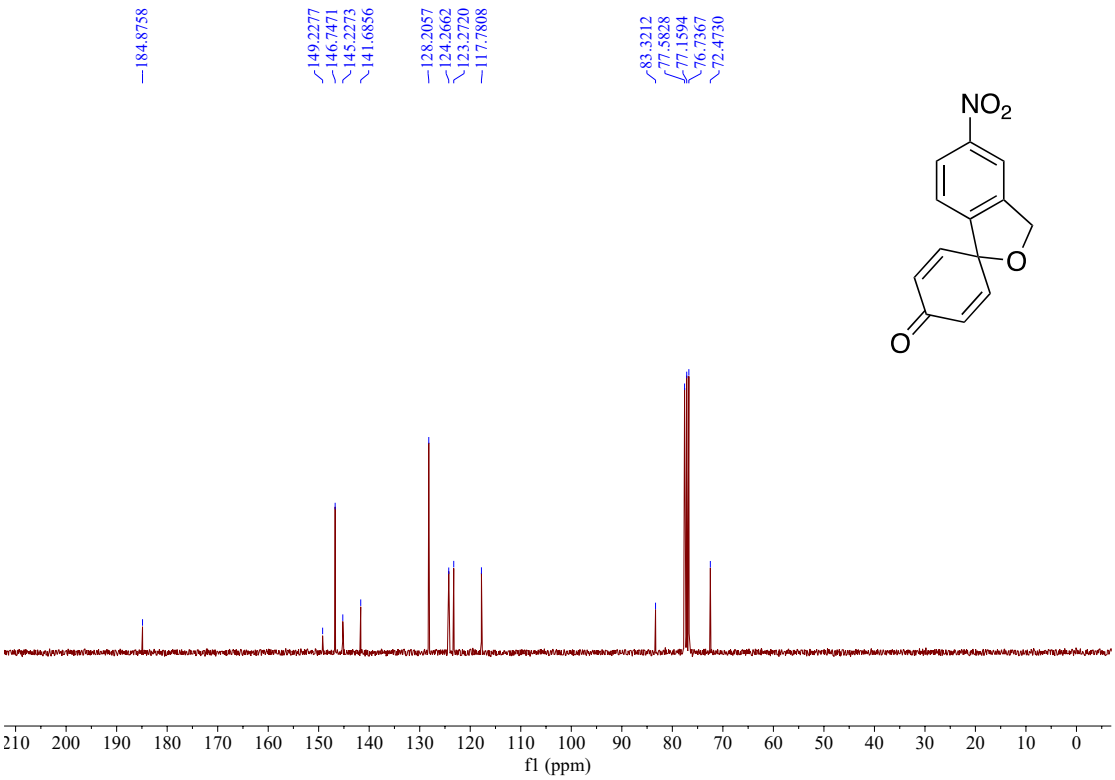


Figure S37. ^{13}C NMR of compound **3g** in $CDCl_3$

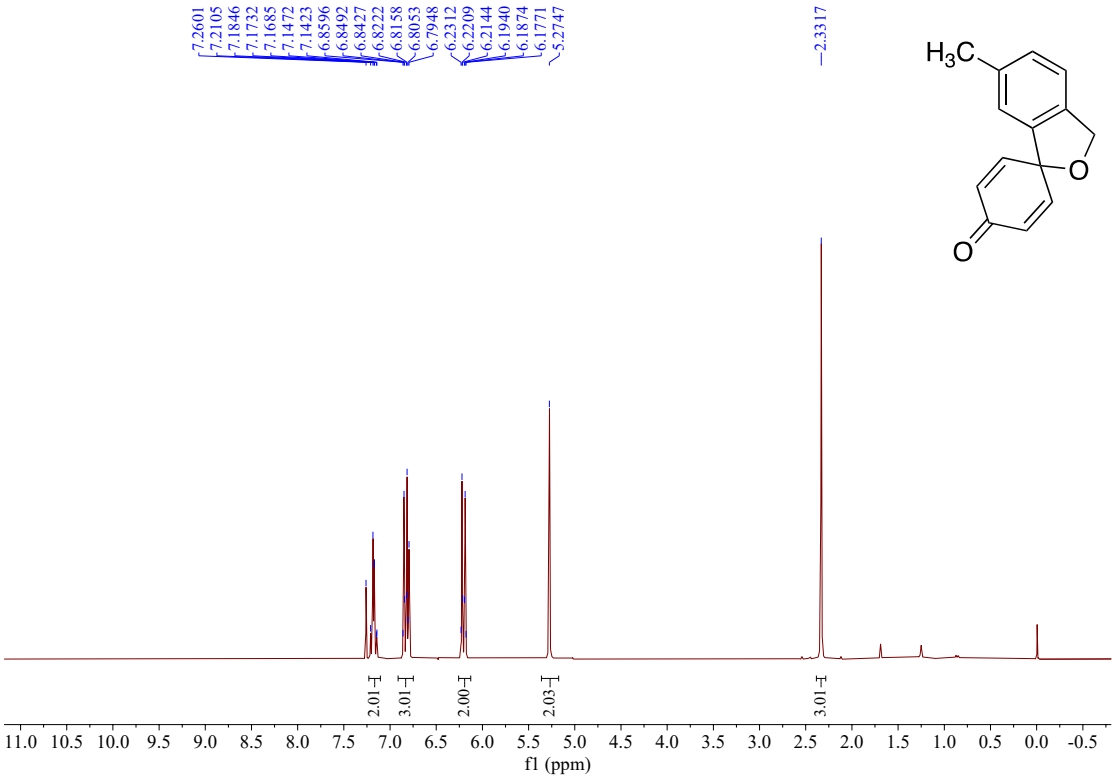


Figure S38. ^{1}H NMR of compound **3h** in $CDCl_3$

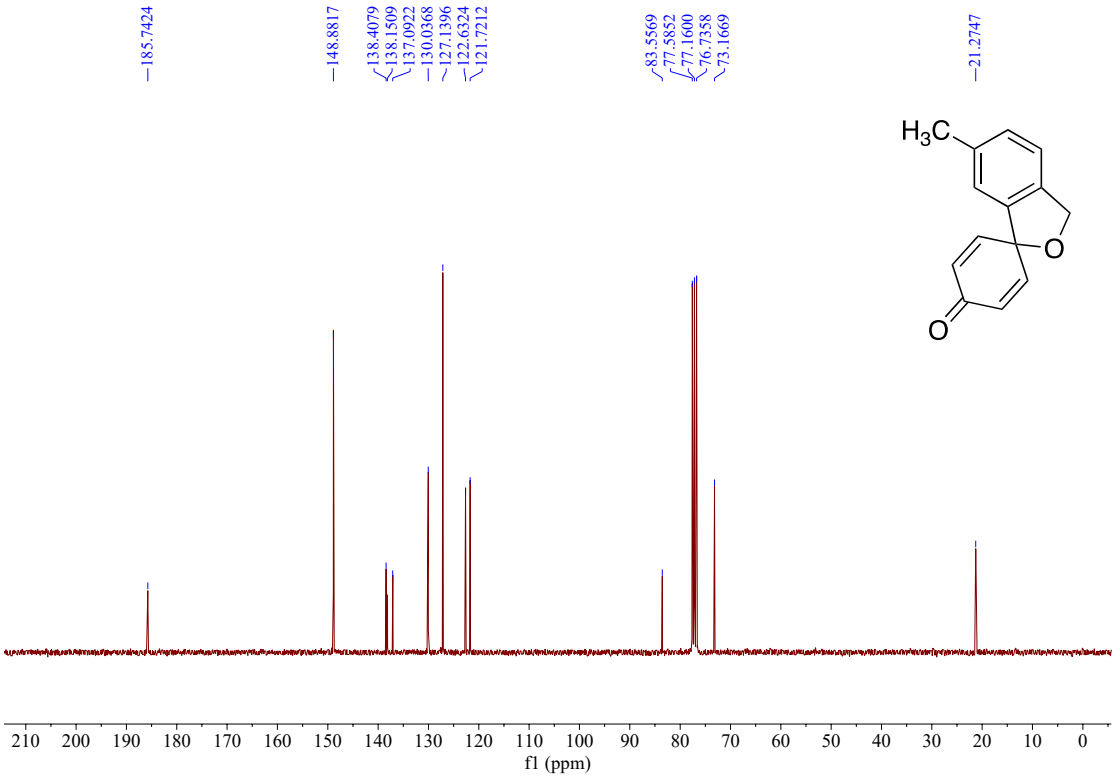


Figure S39. ^{13}C NMR of compound **3h** in $CDCl_3$

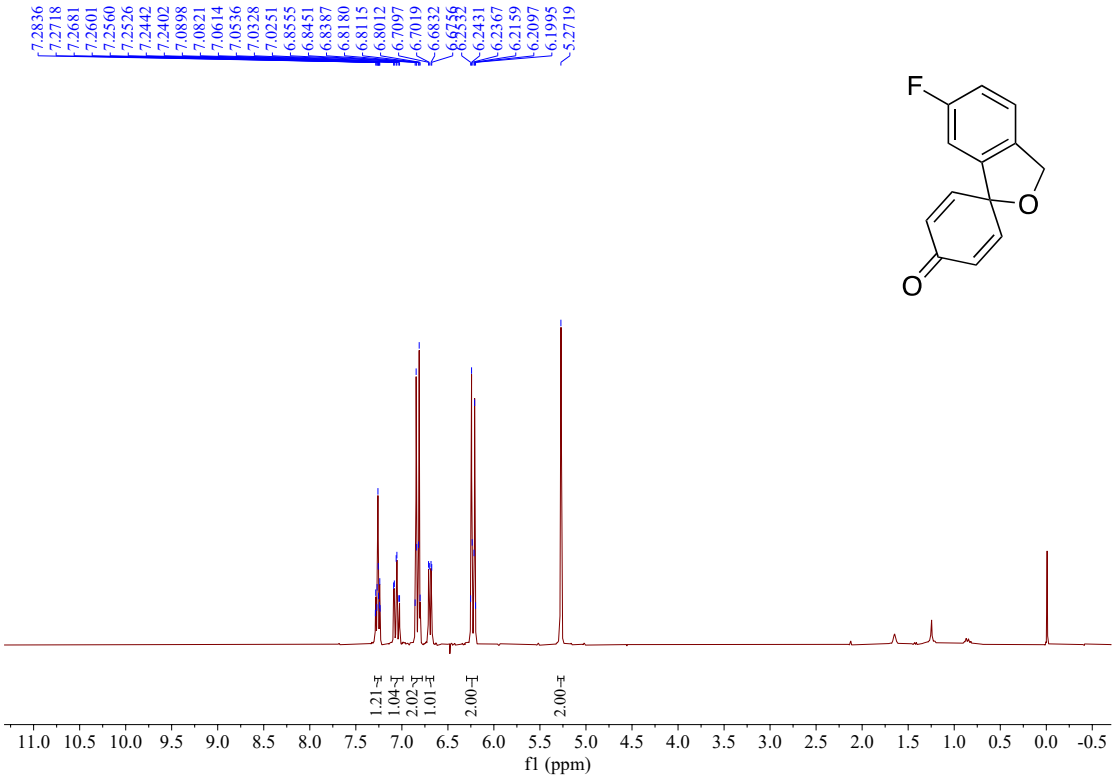


Figure S40. ^{1}H NMR of compound **3i** in $CDCl_3$

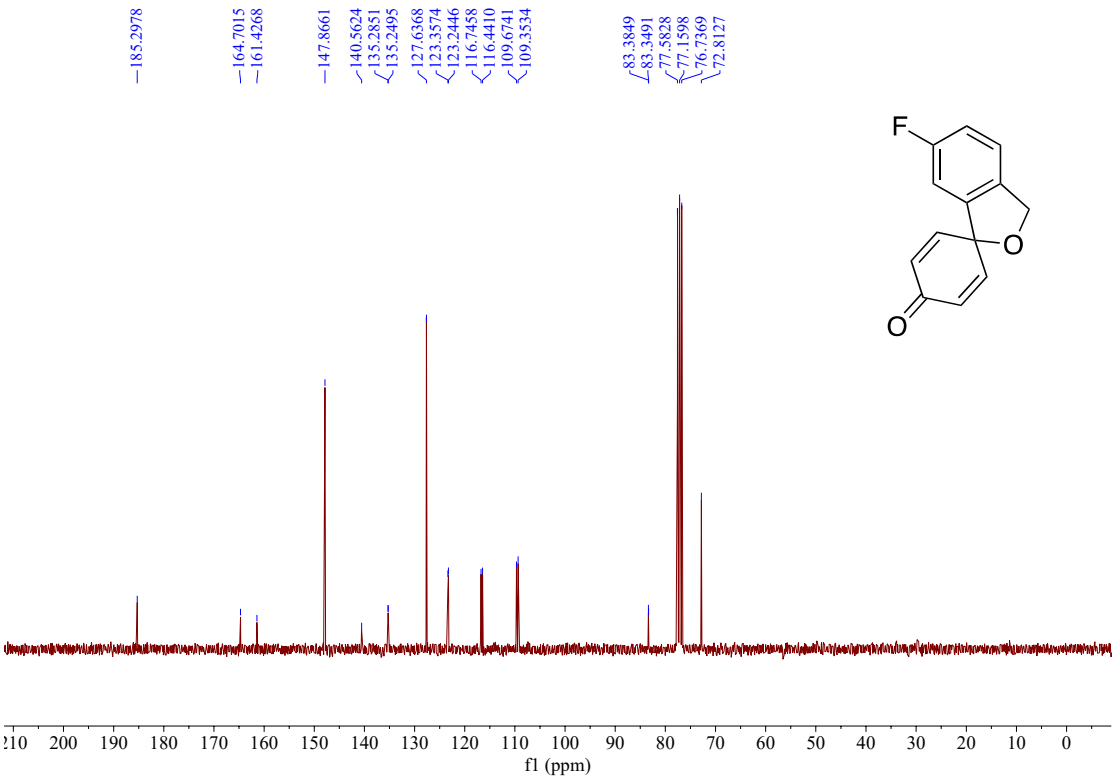


Figure S41. ^{13}C NMR of compound **3i** in $CDCl_3$

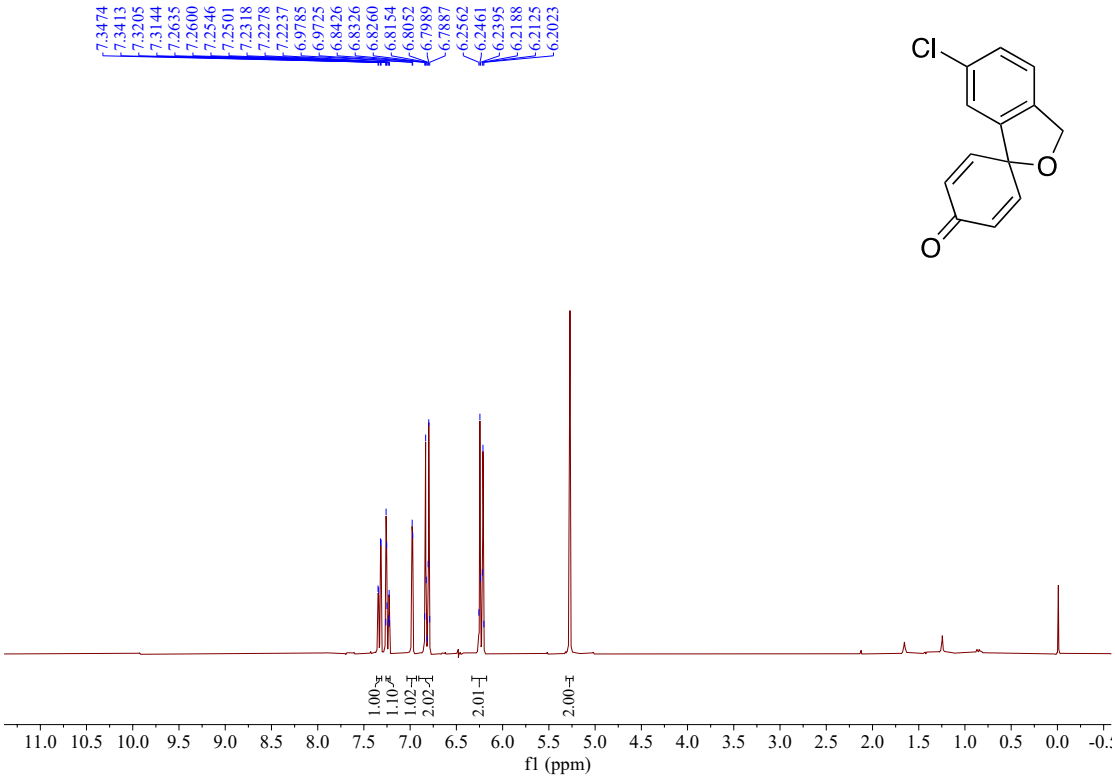


Figure S42. ^{1}H NMR of compound **3j** in $CDCl_3$

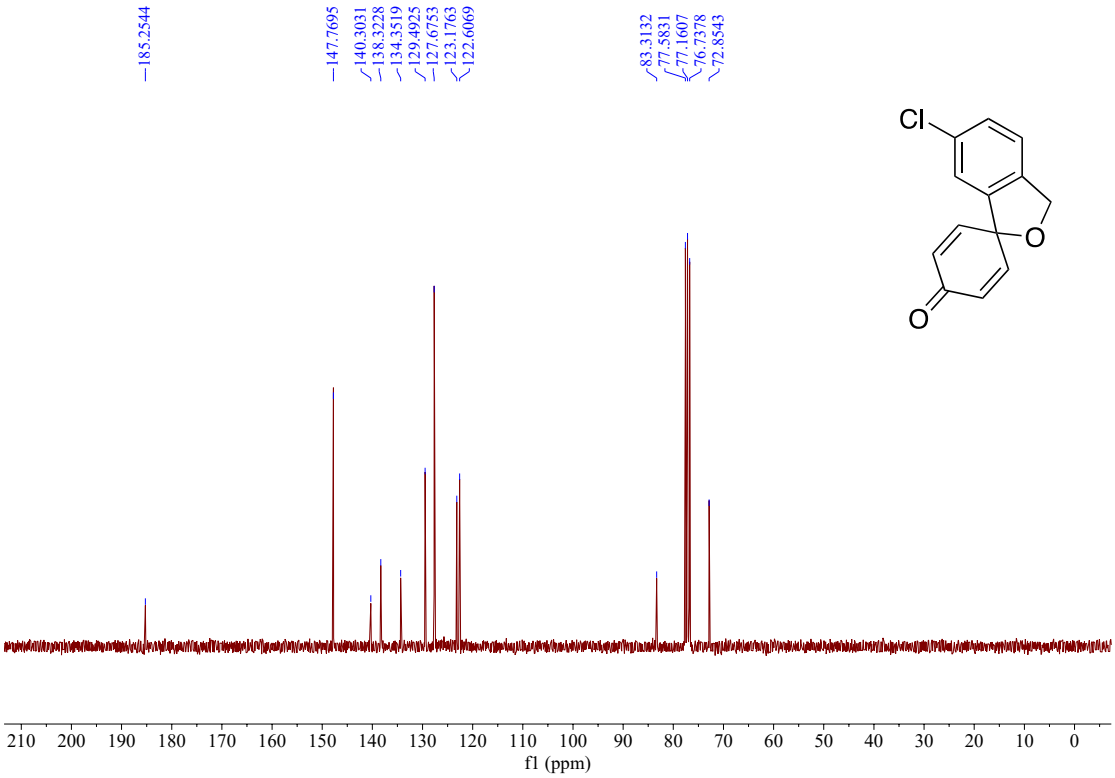


Figure S43. ^{13}C NMR of compound **3j** in $CDCl_3$

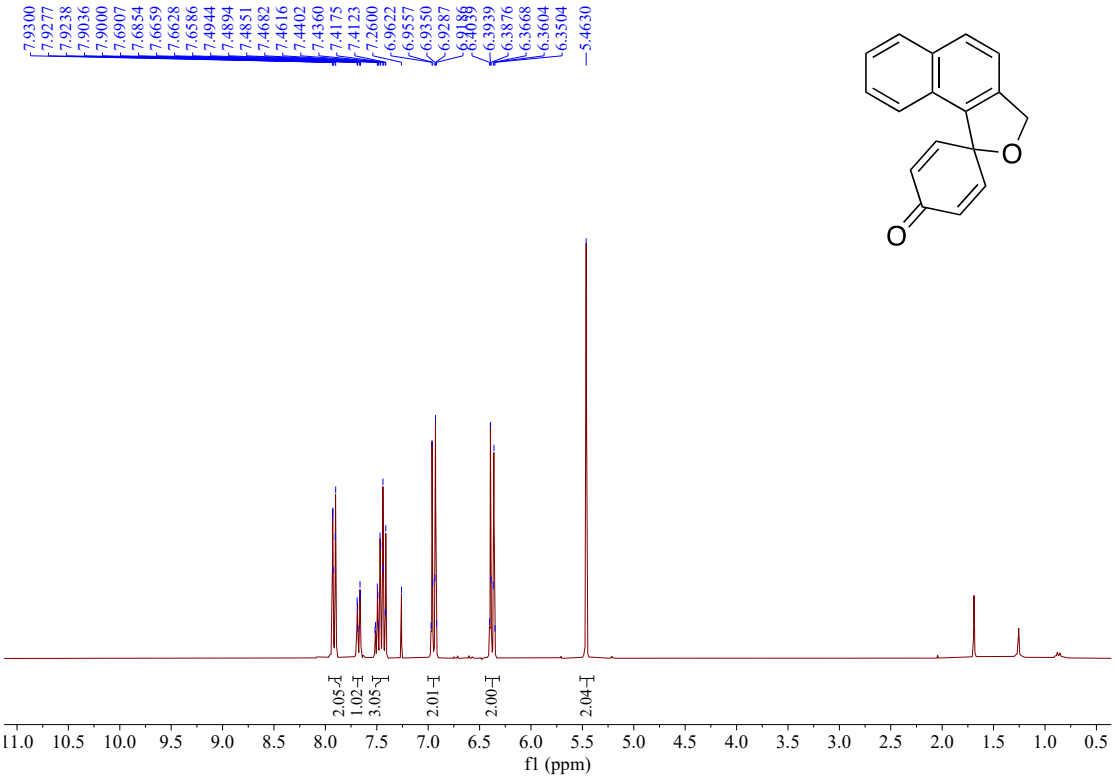


Figure S44. ^{1}H NMR of compound **3k** in $CDCl_3$

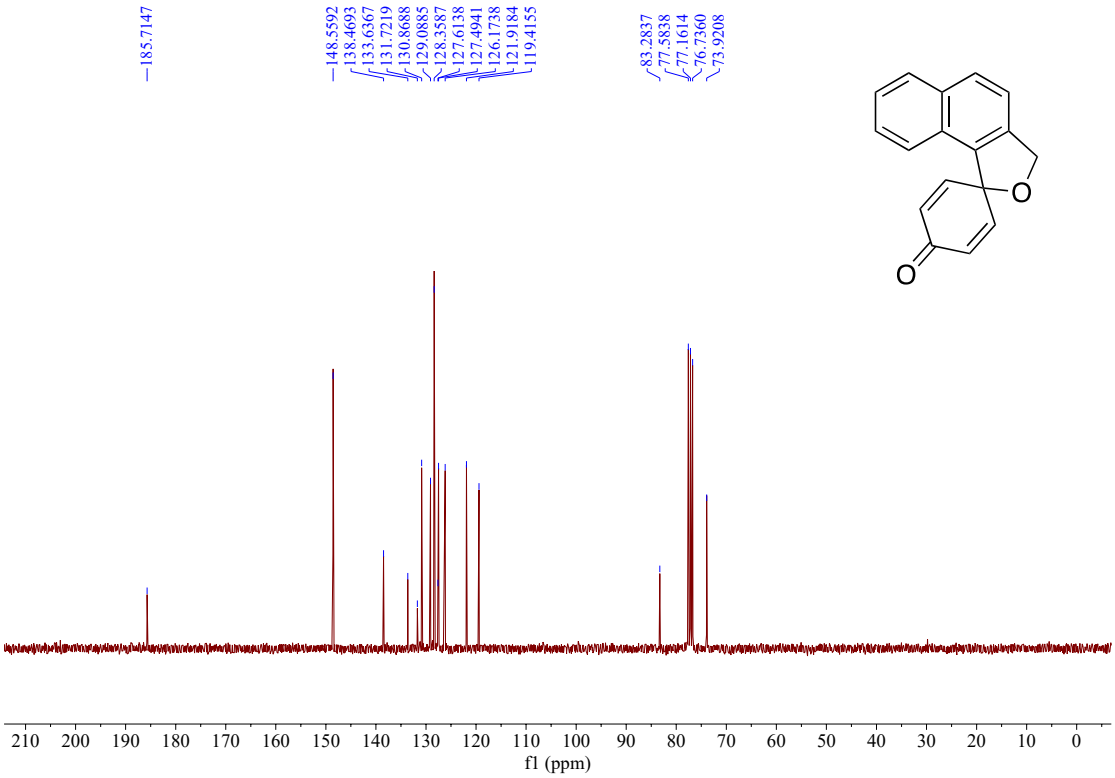


Figure S45. ^{13}C NMR of compound **3k** in $CDCl_3$

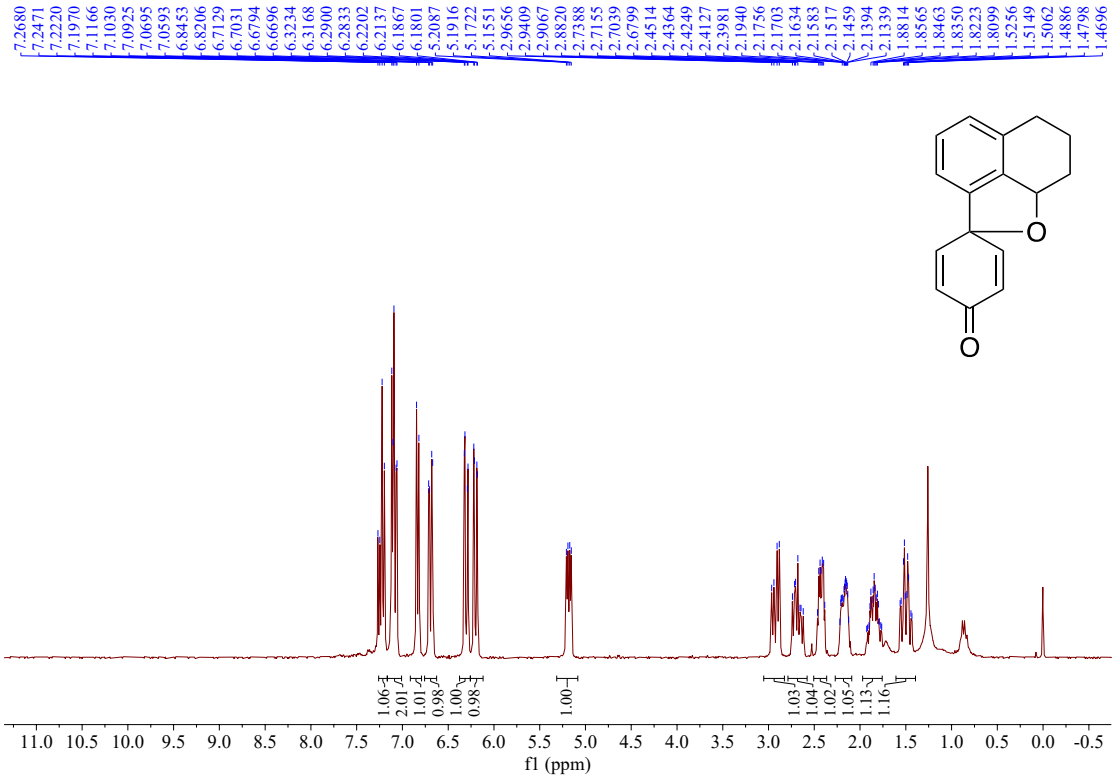


Figure S46. ^{1}H NMR of compound **3l** in $CDCl_3$

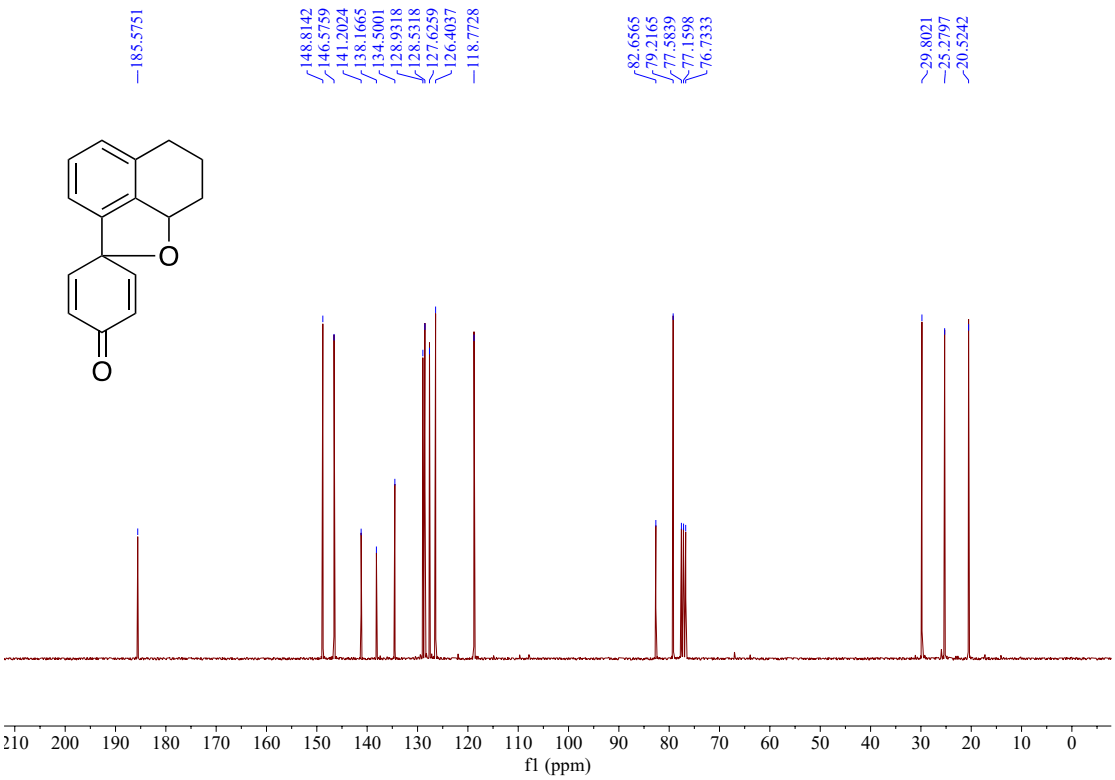


Figure S47. ^{13}C NMR of compound **3l** in $CDCl_3$

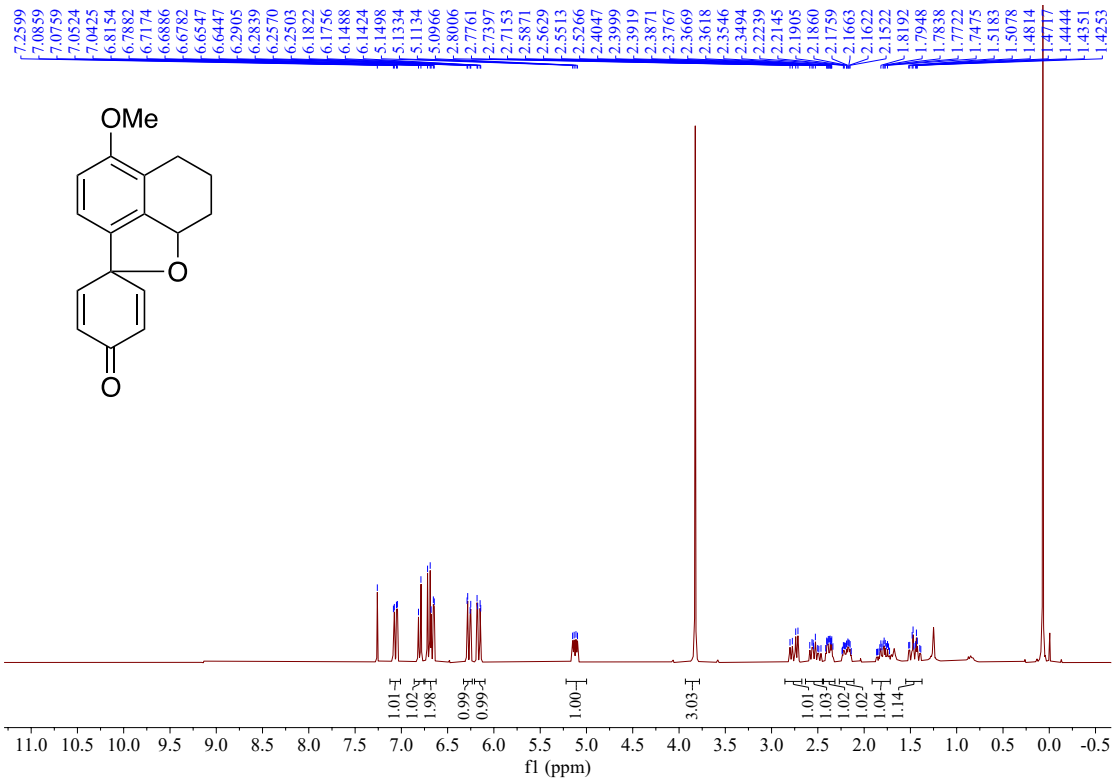


Figure S48. ^{1}H NMR of compound **3m** in $CDCl_3$

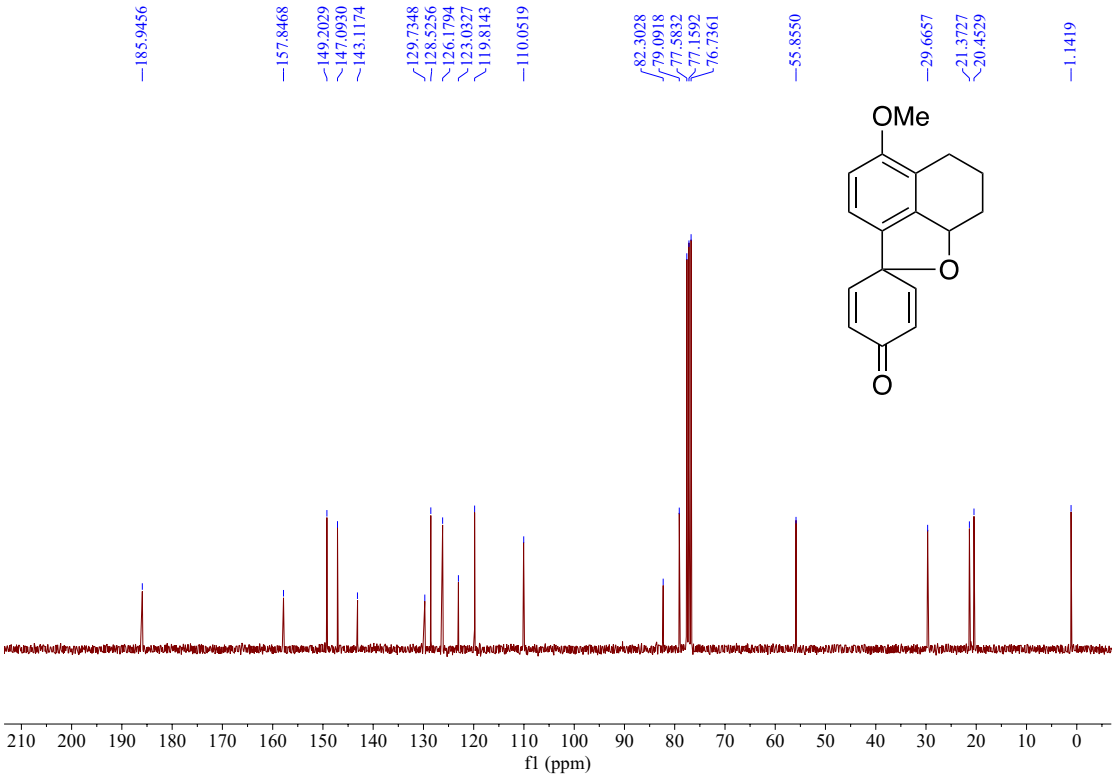


Figure S49. ^{13}C NMR of compound **3m** in $CDCl_3$

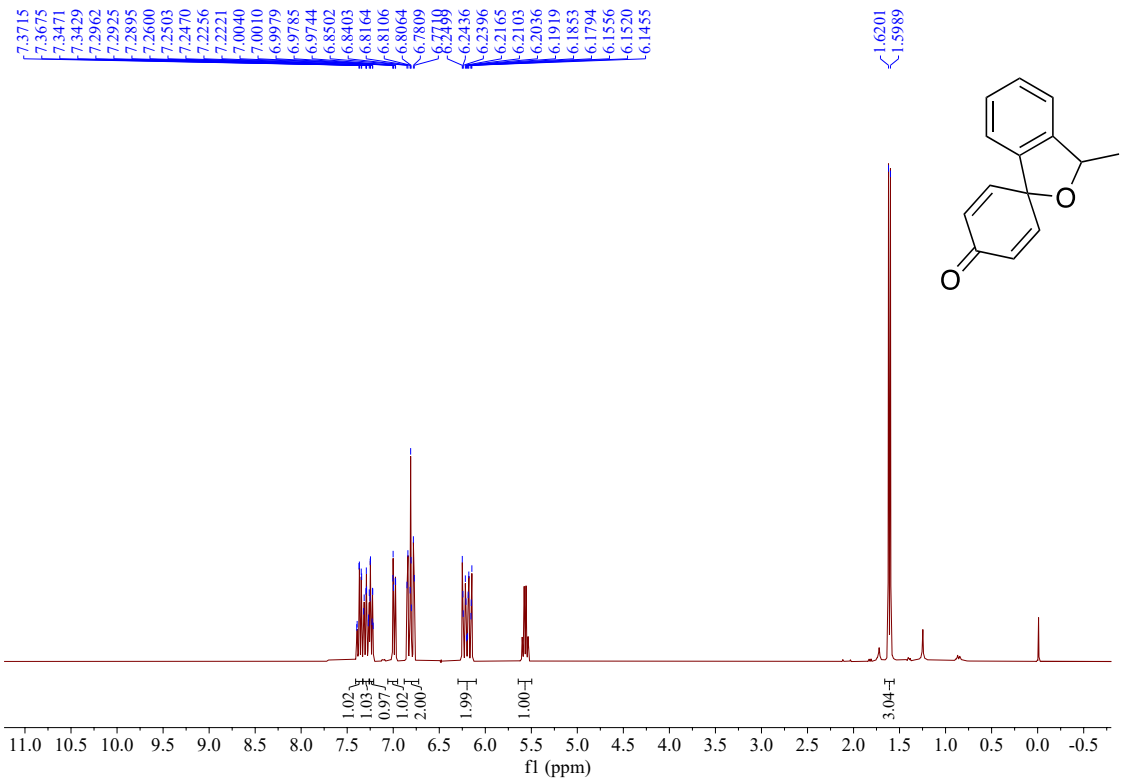


Figure S50. ^{1}H NMR of compound **3n** in $CDCl_3$

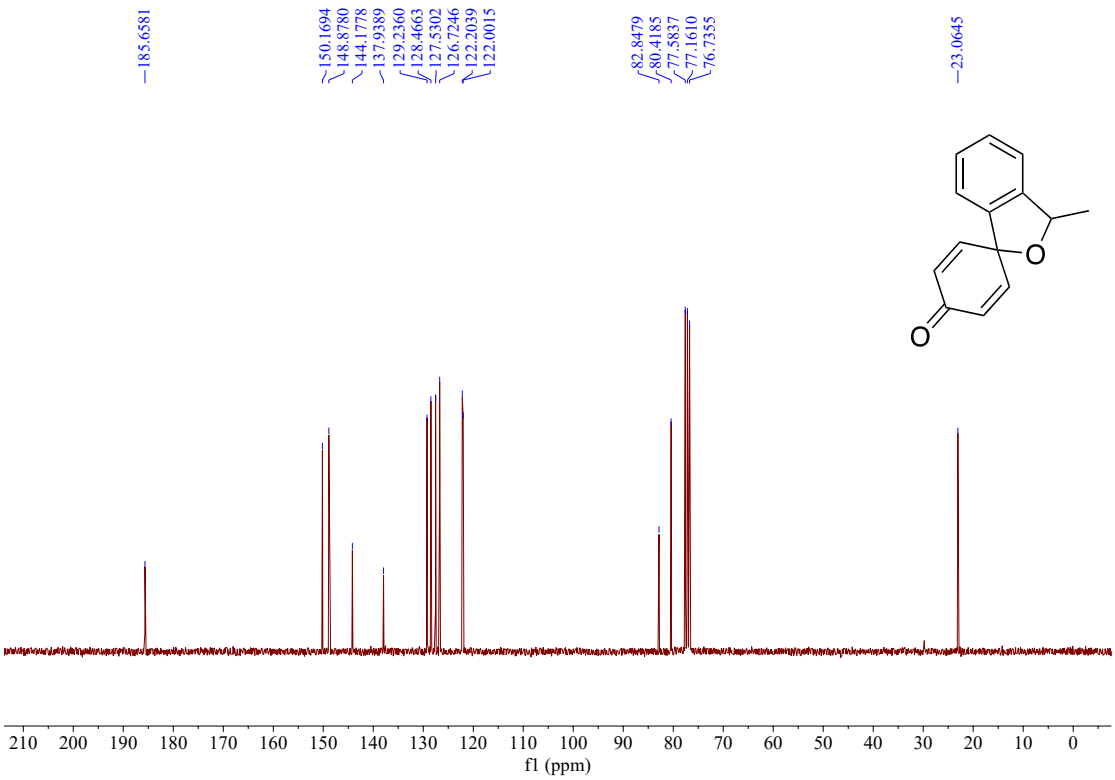


Figure S51. ^{13}C NMR of compound **3n** in $CDCl_3$

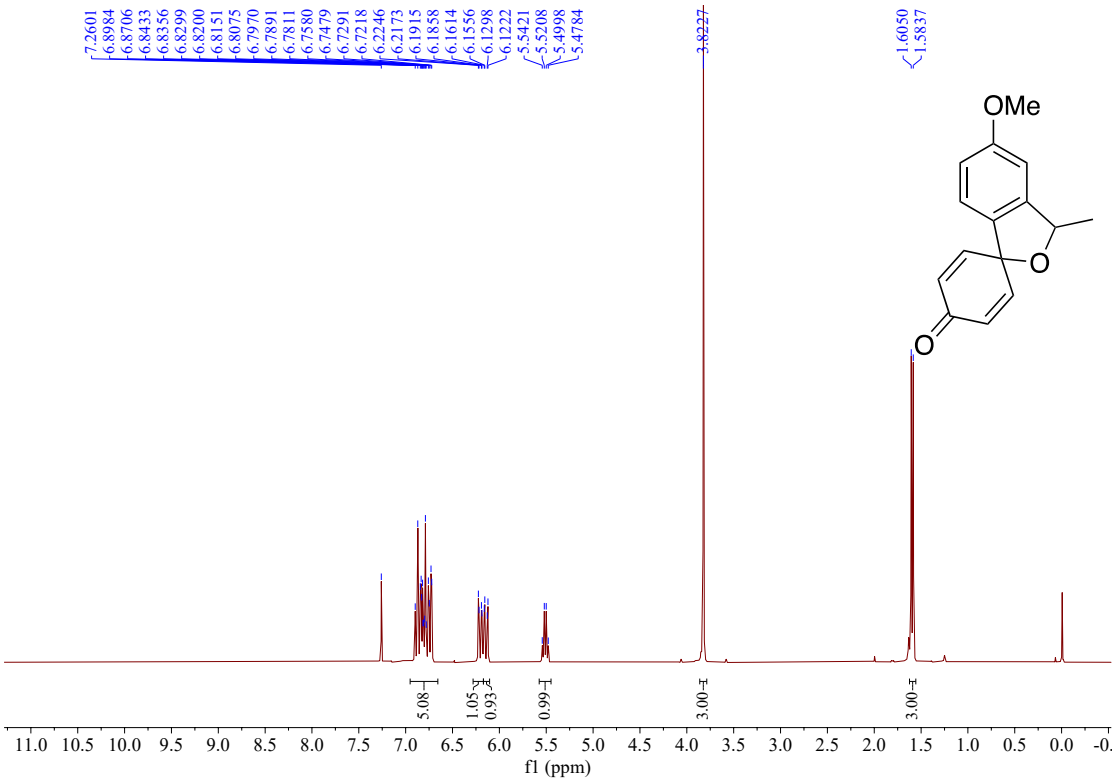


Figure S52. ^{1}H NMR of compound **3o** in $CDCl_3$

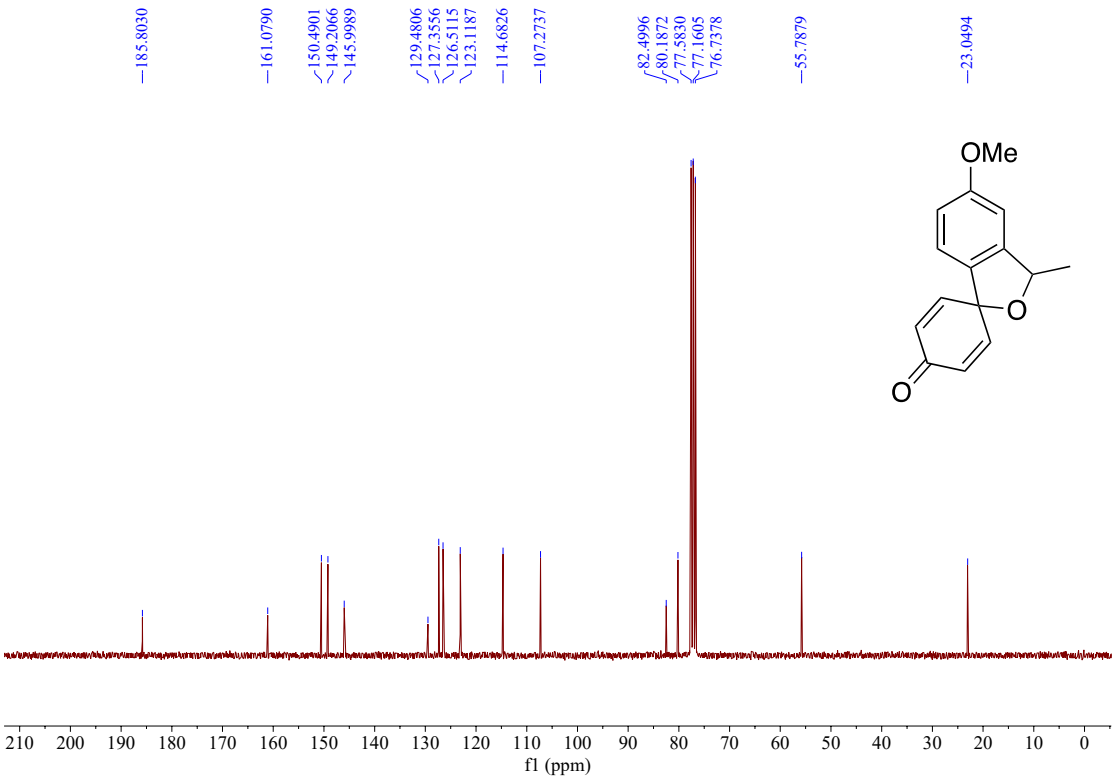


Figure S53. ^{13}C NMR of compound **3o** in $CDCl_3$

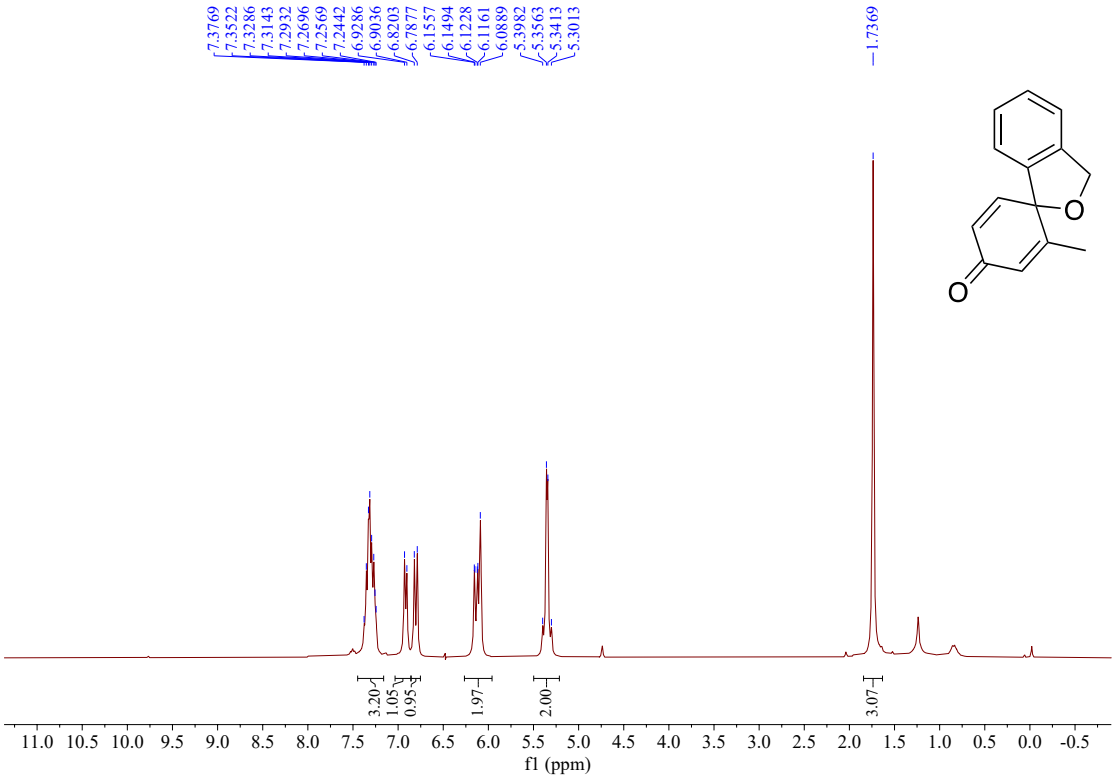


Figure S54. ^{1}H NMR of compound **3p** in $CDCl_3$

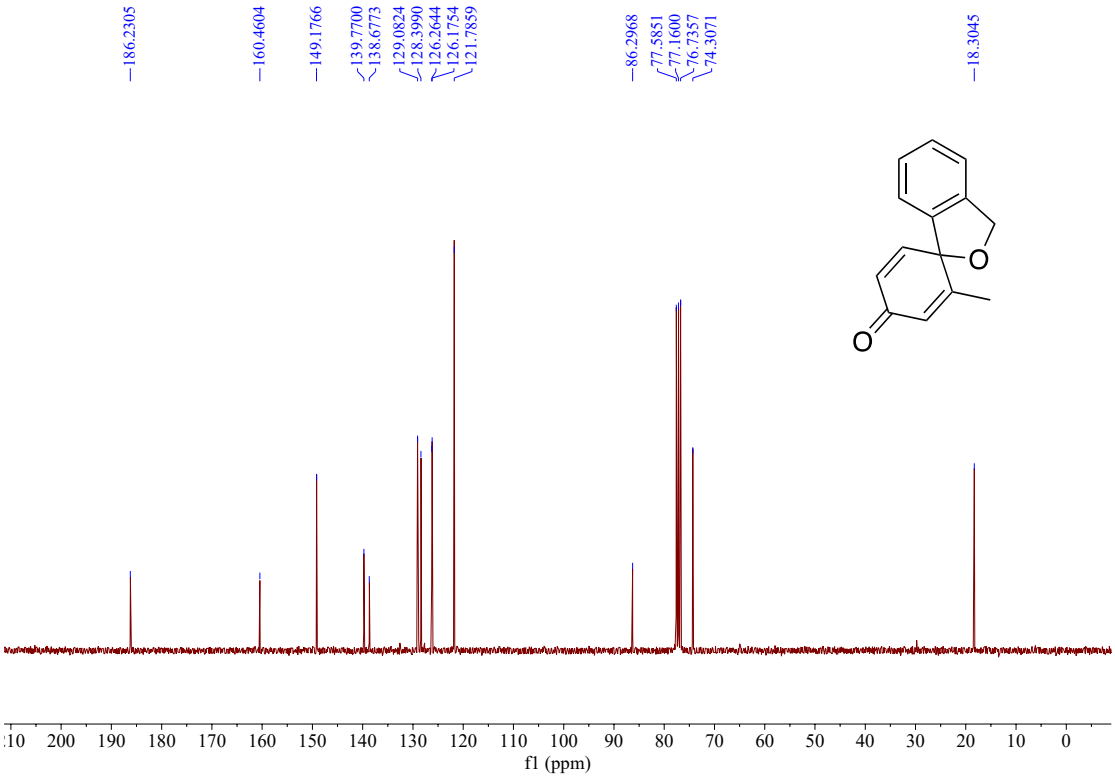


Figure S55. ^{13}C NMR of compound **3p** in $CDCl_3$

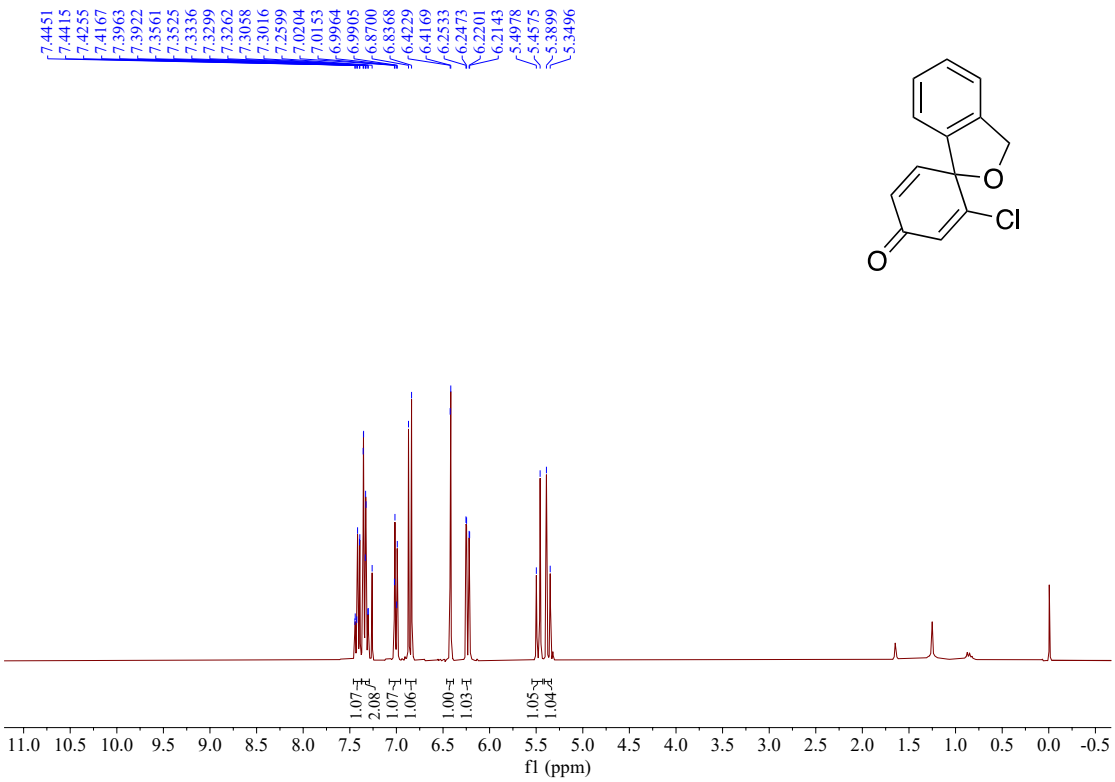


Figure S56. ^{1}H NMR of compound **3q** in $CDCl_3$

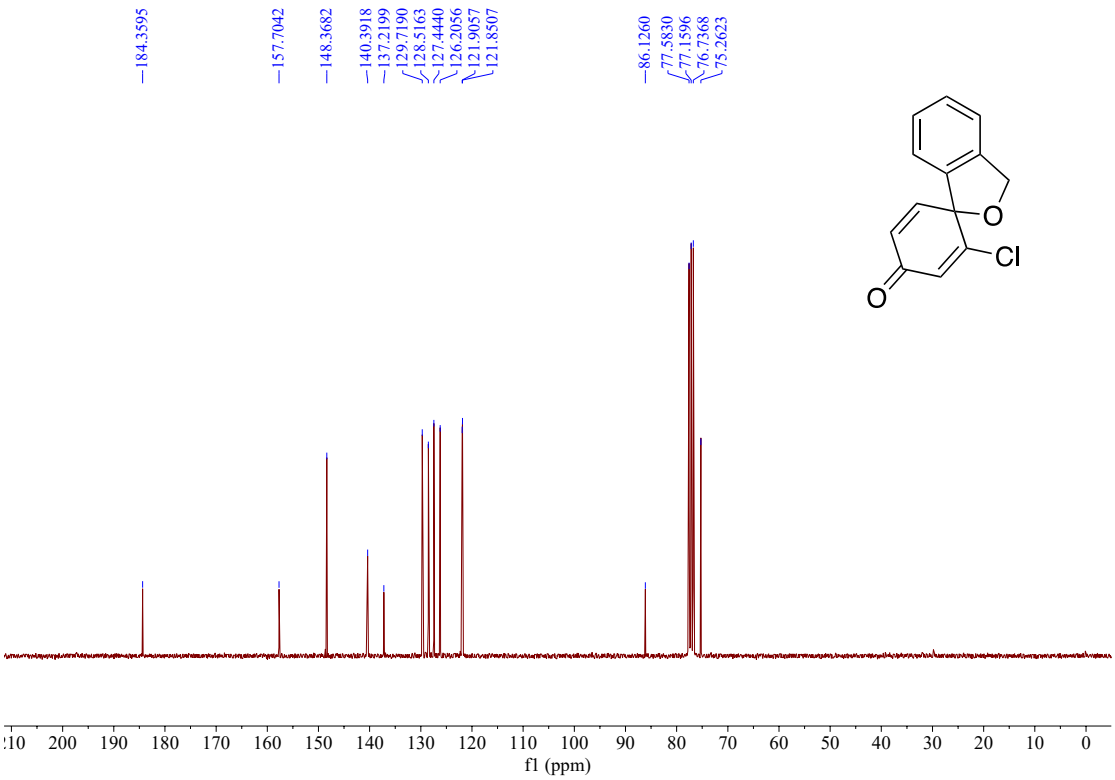


Figure S57. ^{13}C NMR of compound **3q** in $CDCl_3$

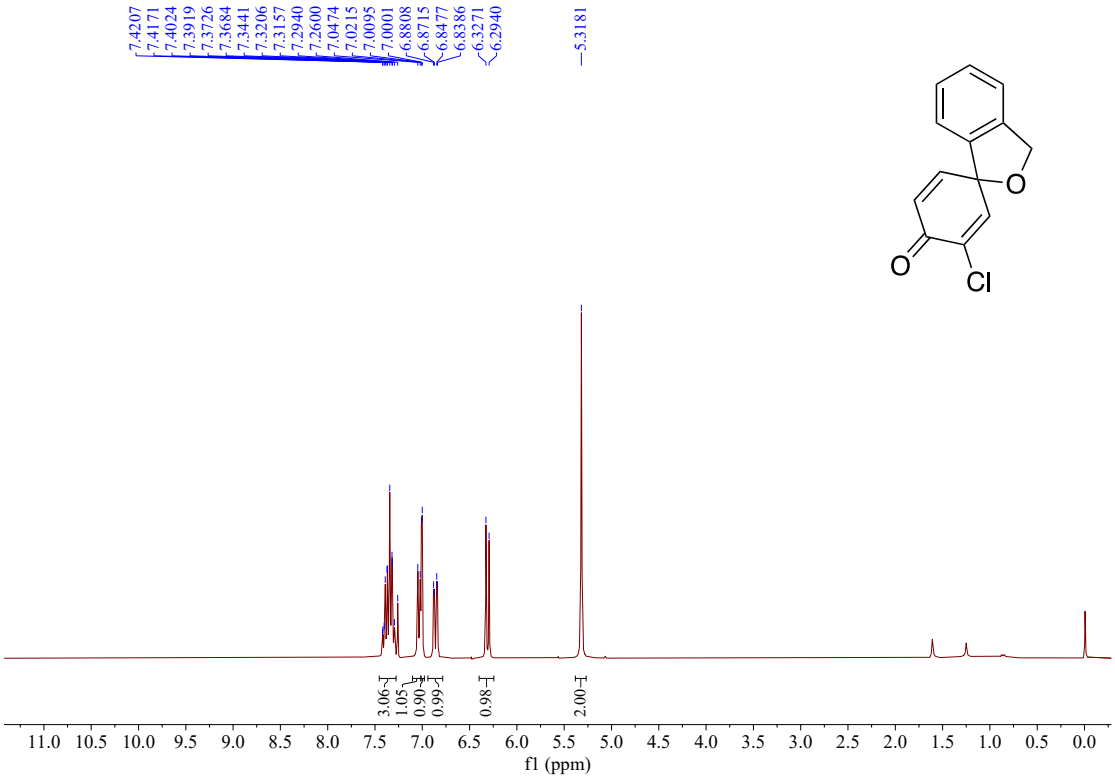


Figure S58. ^{1}H NMR of compound **3r** in $CDCl_3$

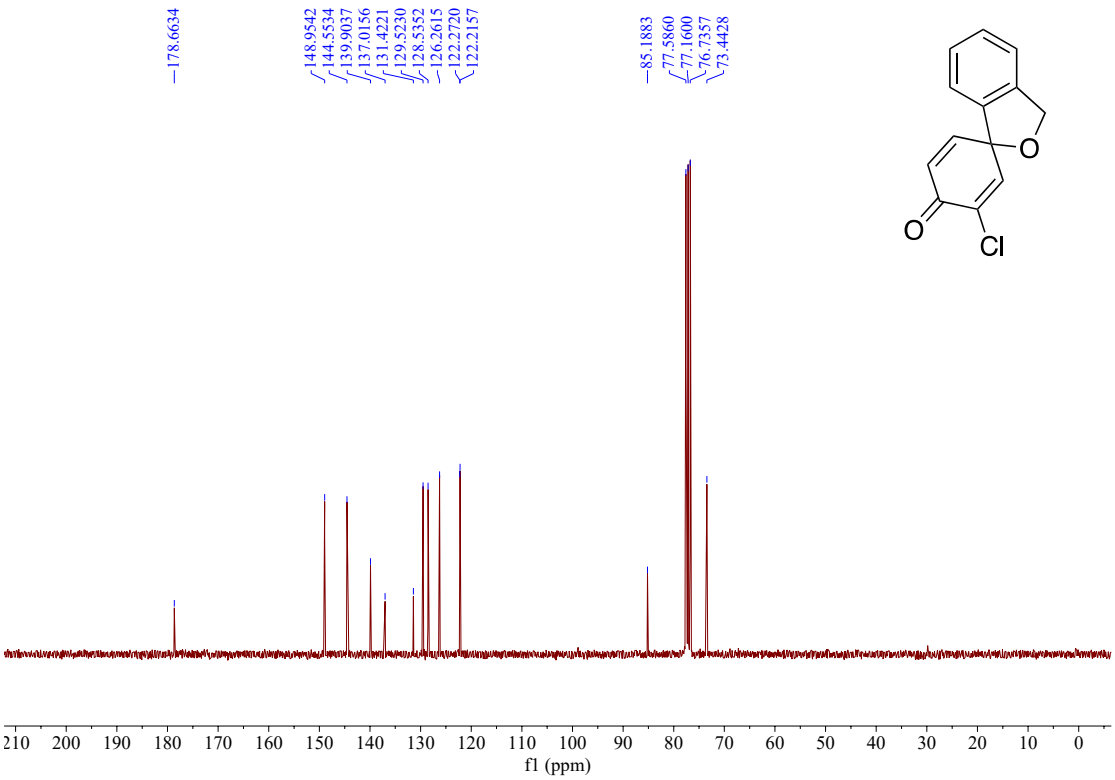


Figure S59. ^{13}C NMR of compound **3r** in $CDCl_3$

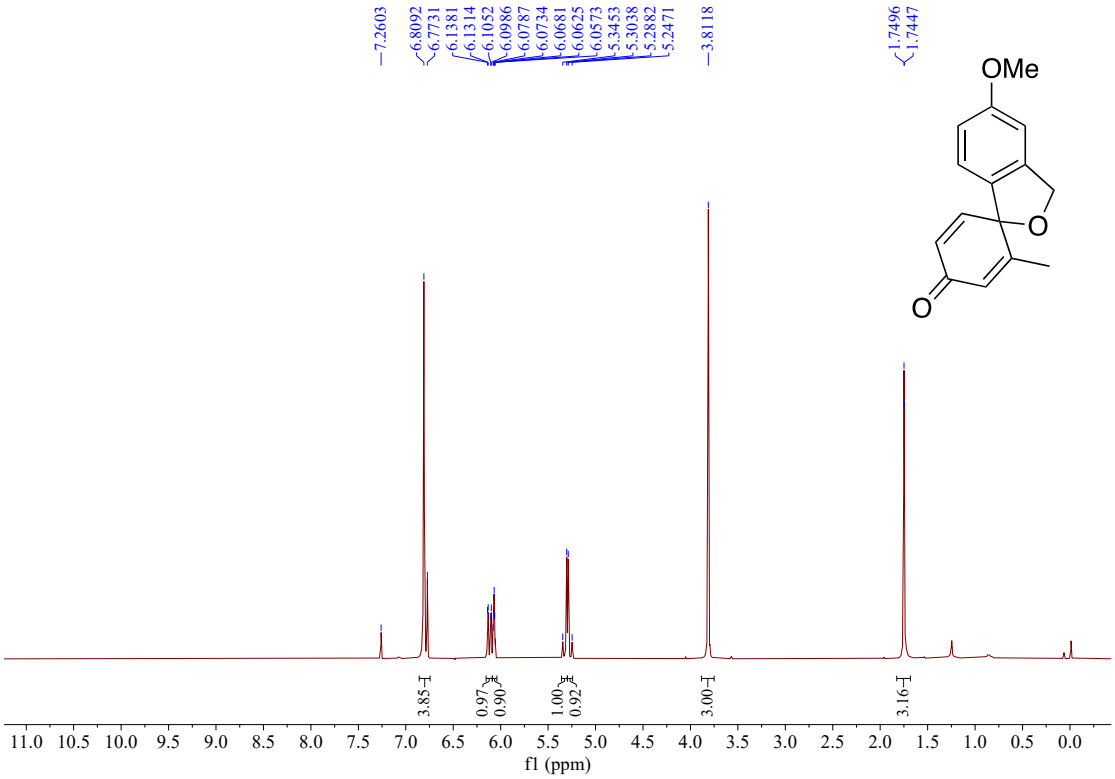


Figure S60. ^{1}H NMR of compound **3s** in $CDCl_3$

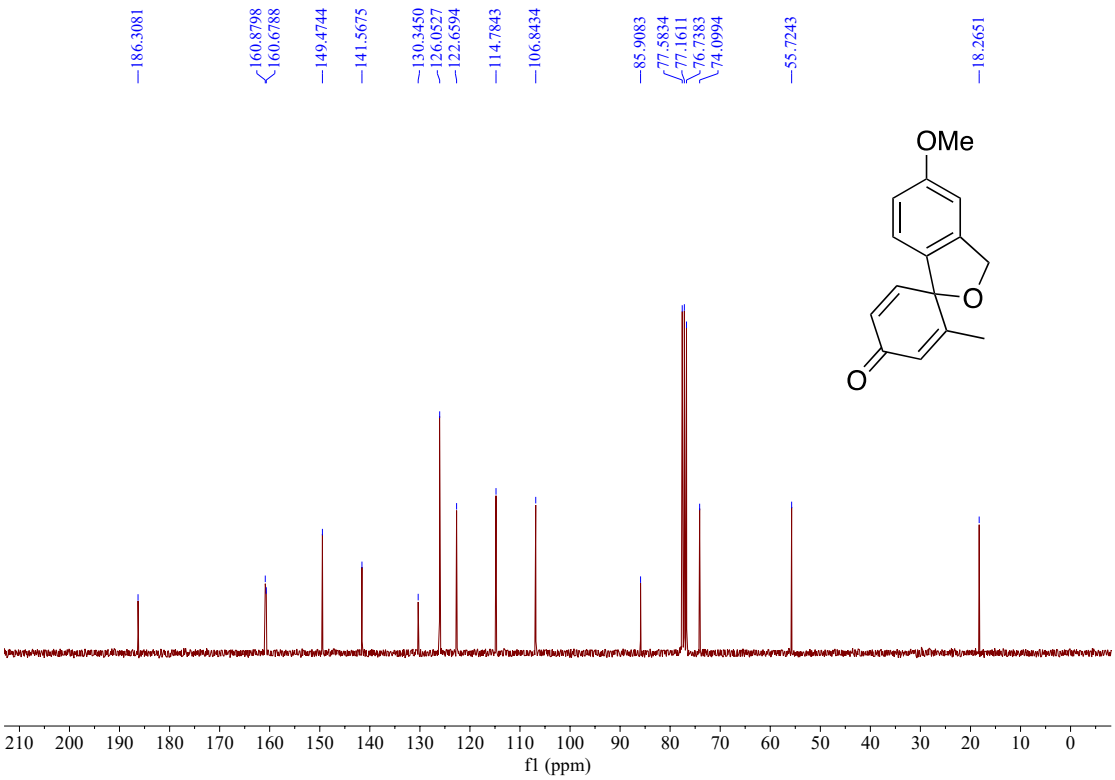


Figure S61. ^{13}C NMR of compound **3s** in $CDCl_3$

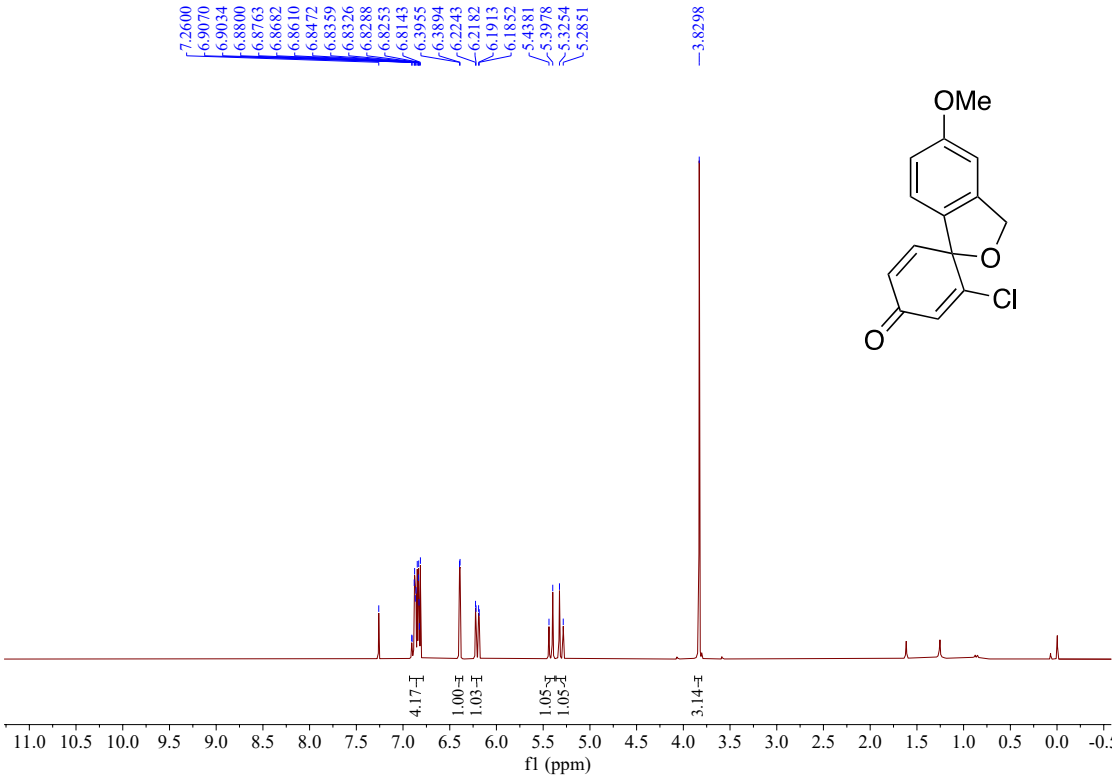


Figure S62. ^{1}H NMR of compound **3t** in $CDCl_3$

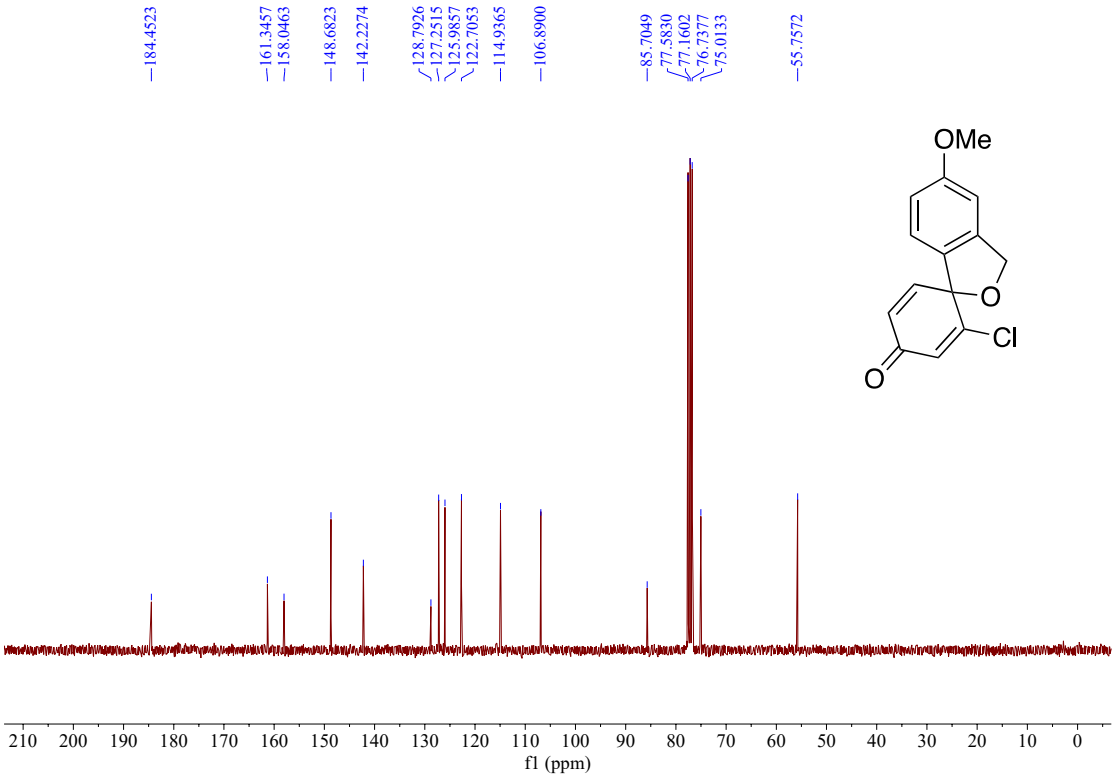


Figure S63. ^{13}C NMR of compound **3t** in $CDCl_3$

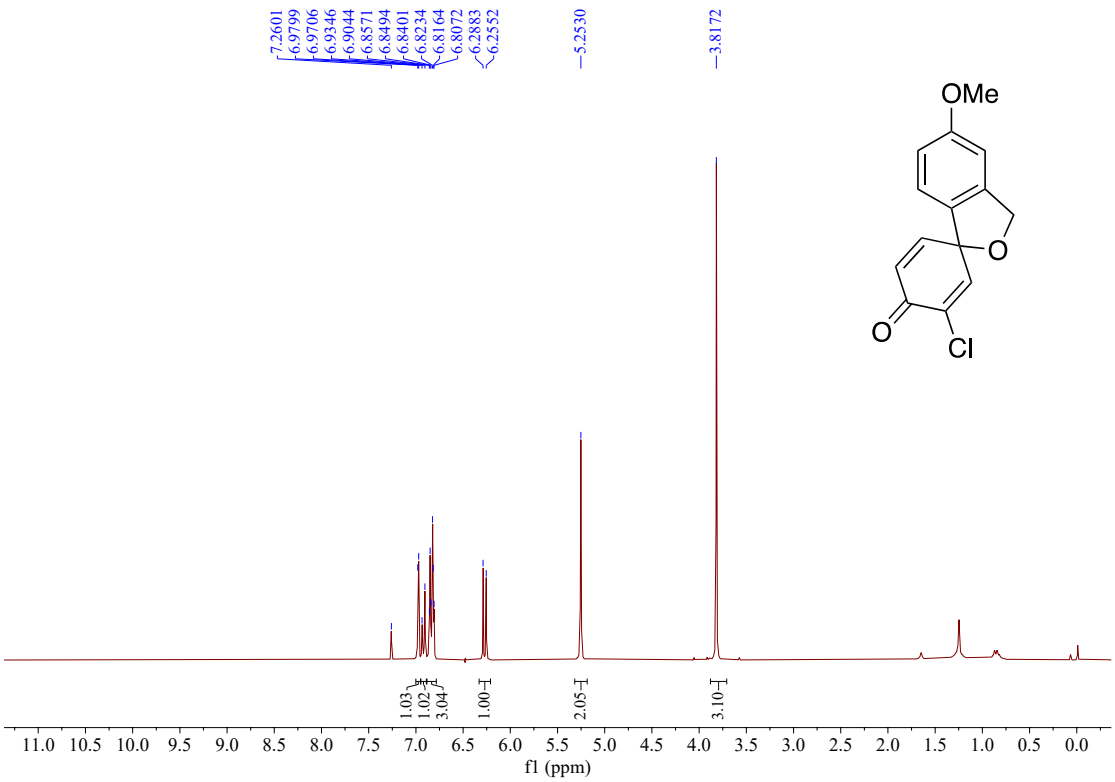


Figure S64. ^{1}H NMR of compound **3u** in $CDCl_3$

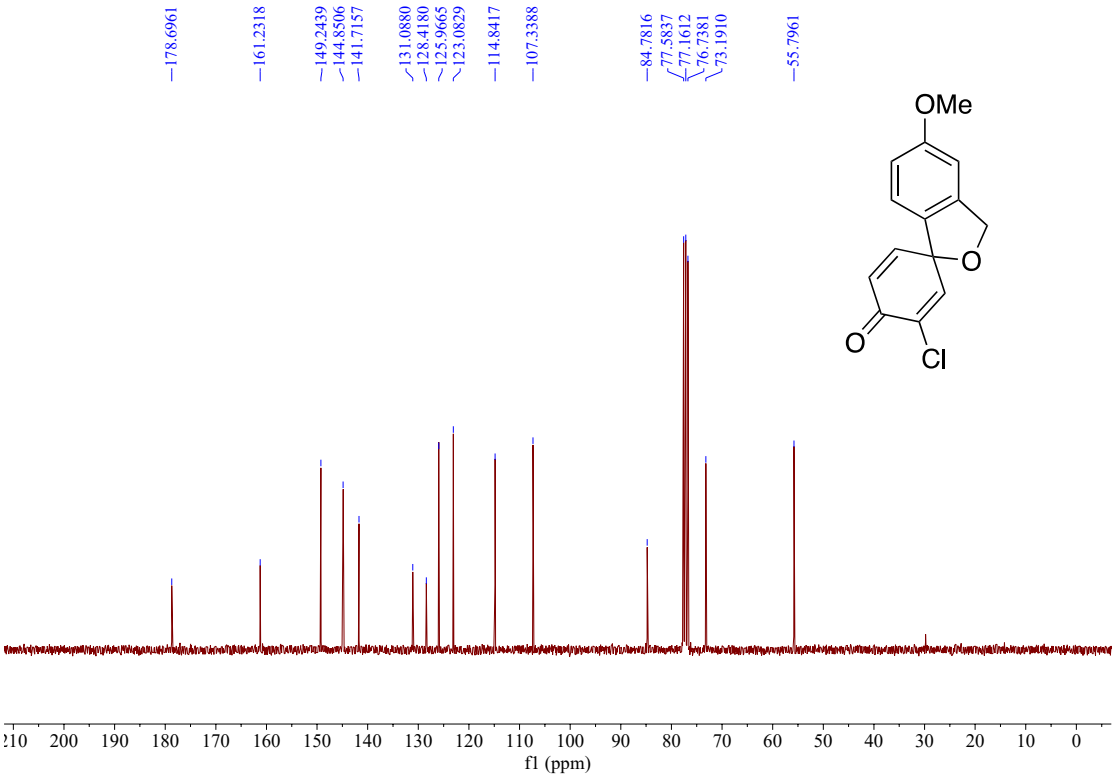


Figure S65. ^{13}C NMR of compound **3u** in $CDCl_3$

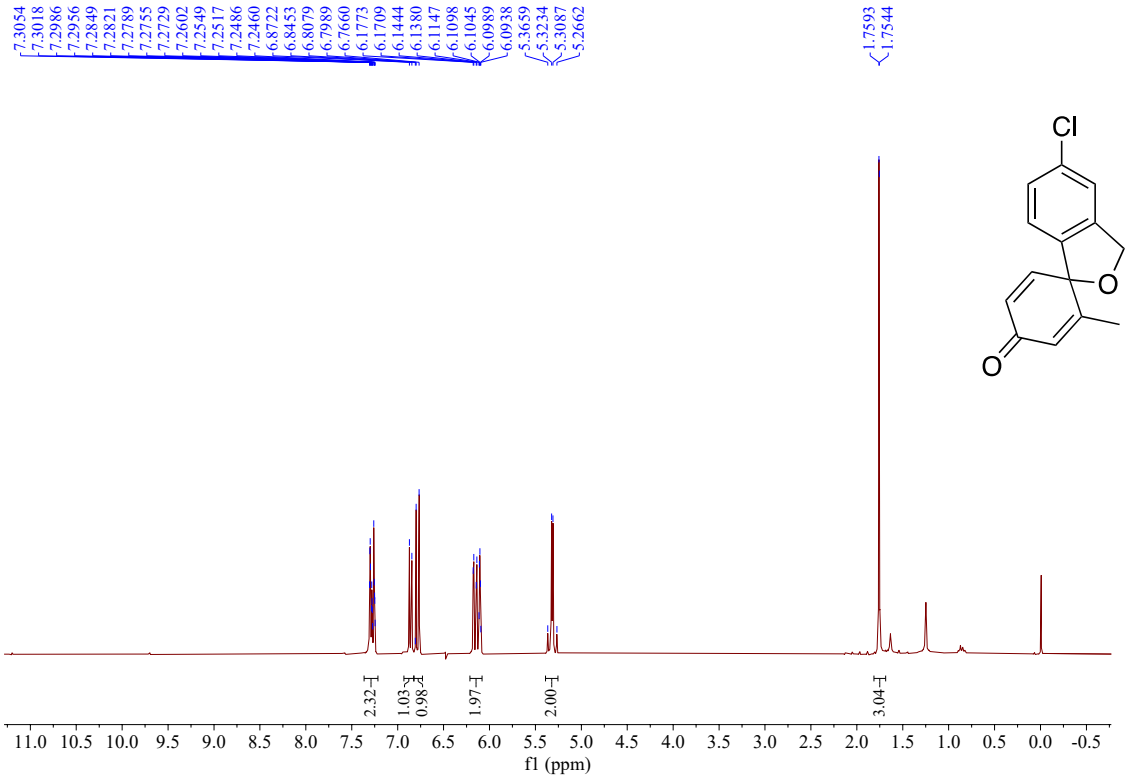


Figure S66. ^{1}H NMR of compound **3v** in $CDCl_3$

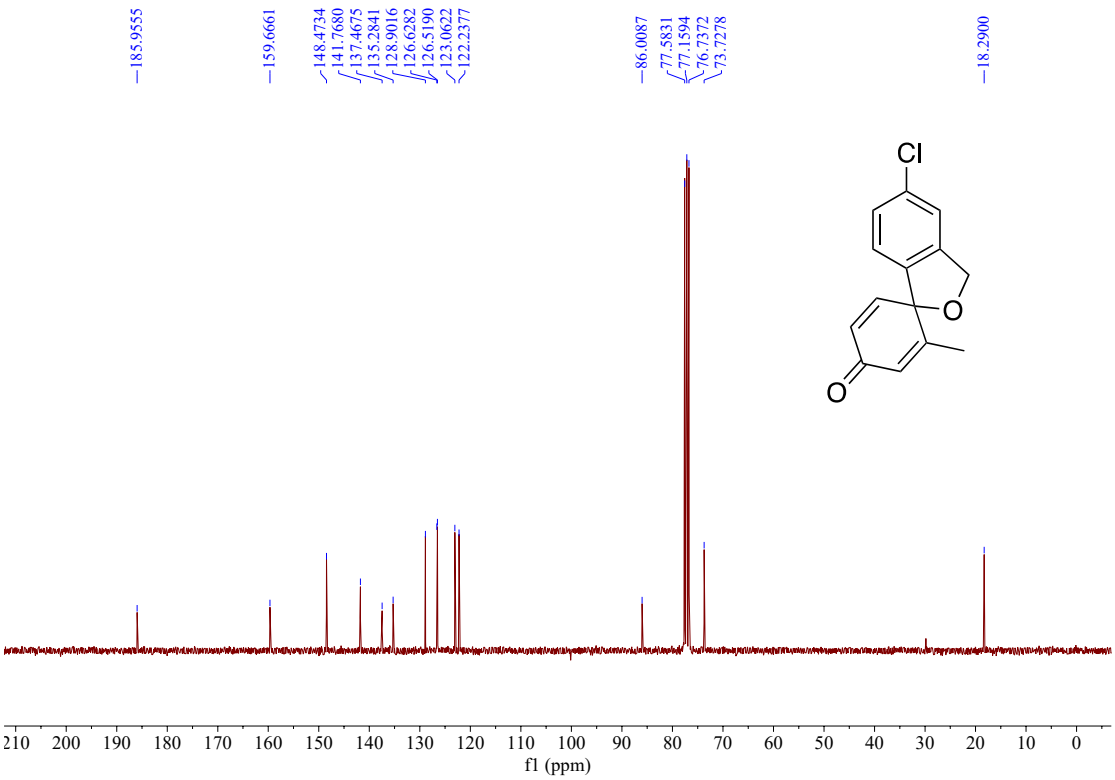


Figure S67. ^{13}C NMR of compound **3v** in $CDCl_3$

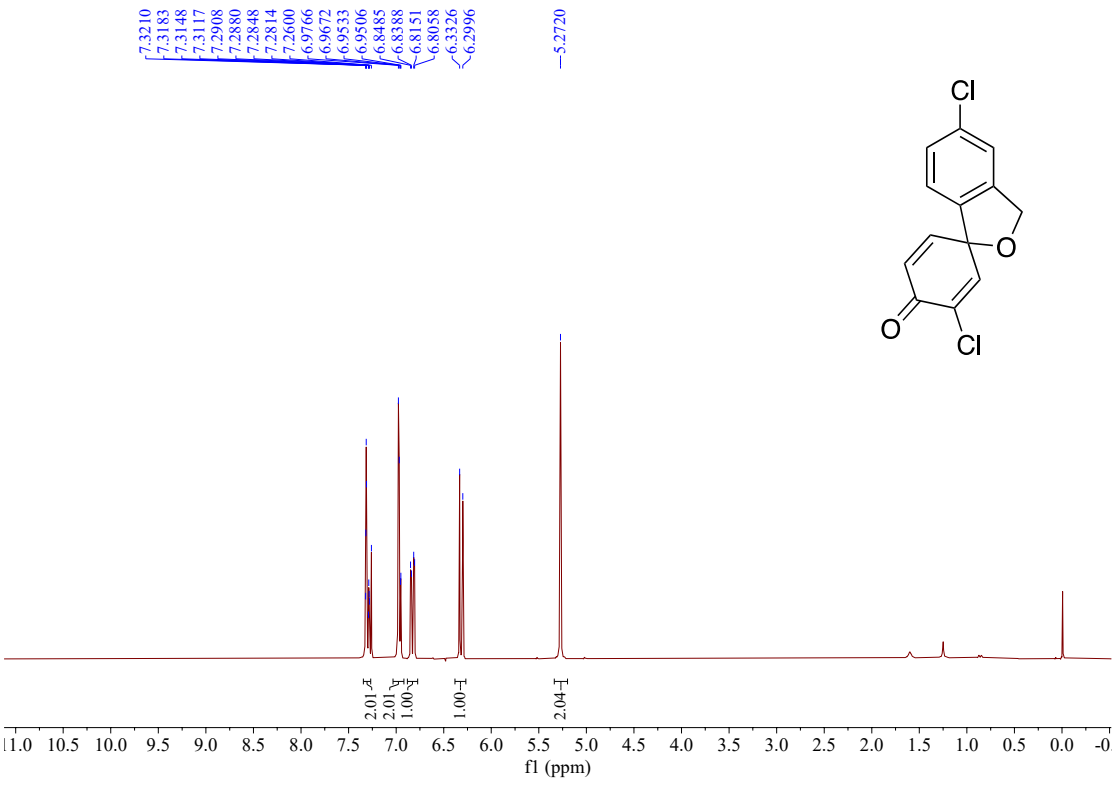


Figure S68. ^{1}H NMR of compound **3w** in $CDCl_3$

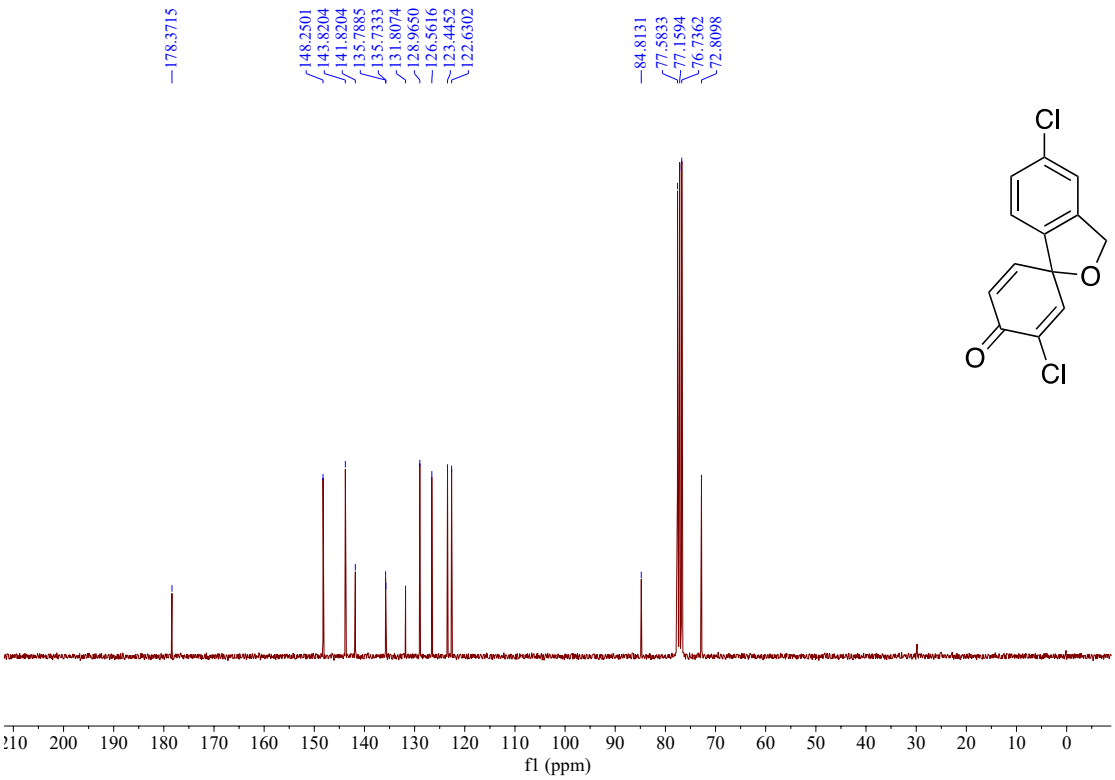


Figure S69. ^{13}C NMR of compound **3w** in $CDCl_3$

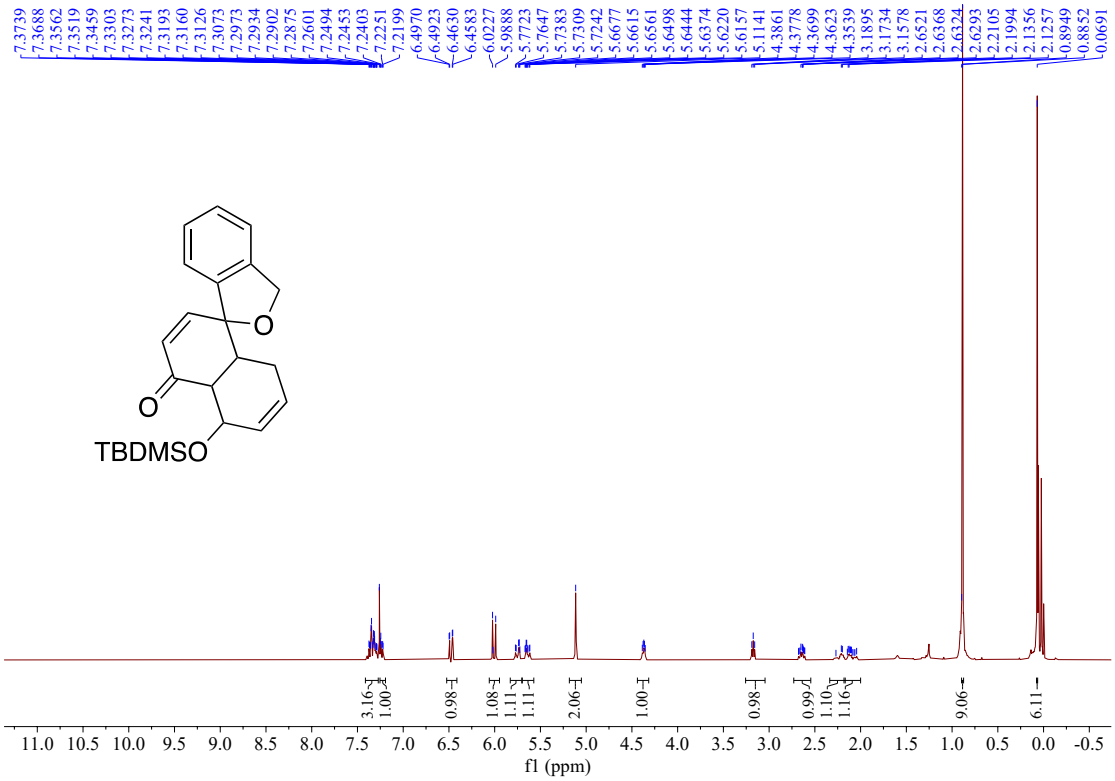


Figure S70. ^{1}H NMR of compound **4aa** in $CDCl_3$

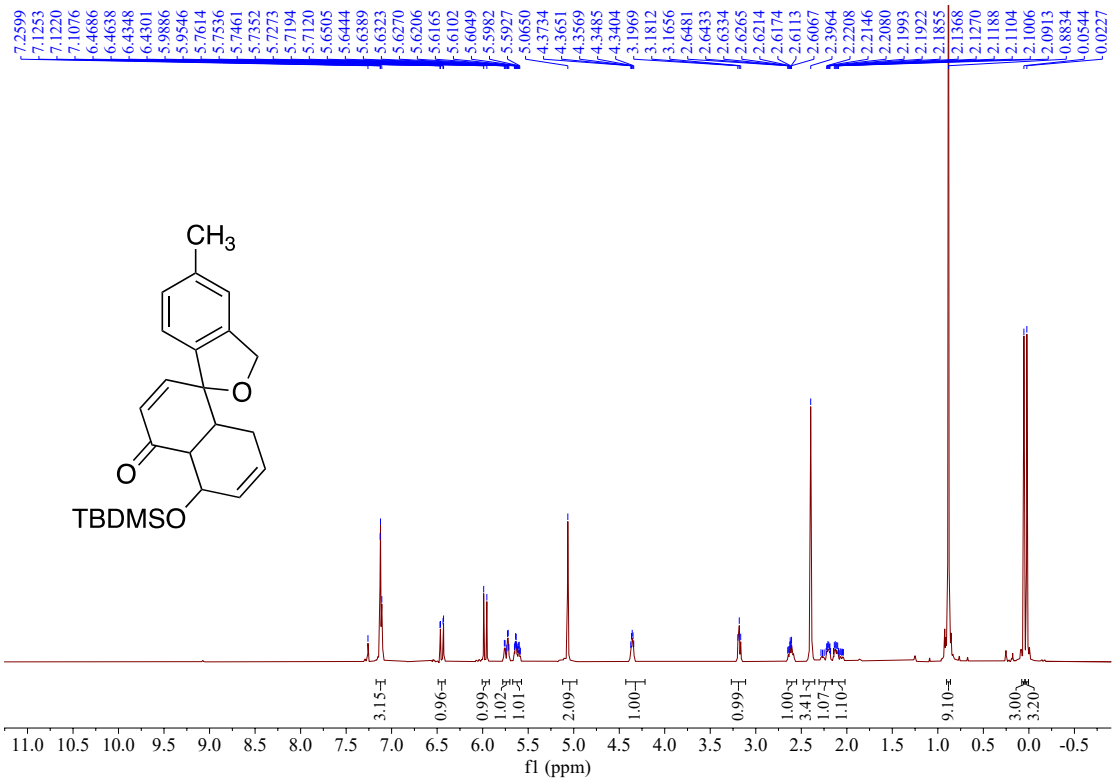


Figure S71. ^{1}H NMR of compound **4ab** in $CDCl_3$

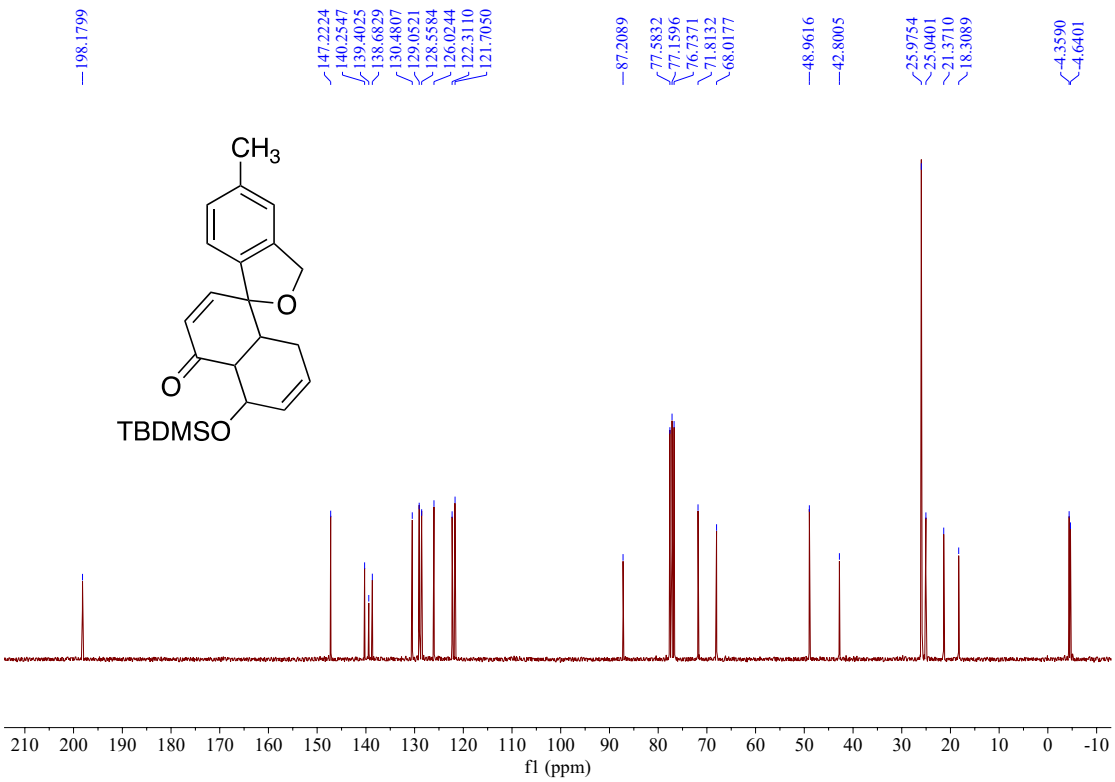


Figure S72. ^{13}C NMR of compound **4ab** in $CDCl_3$

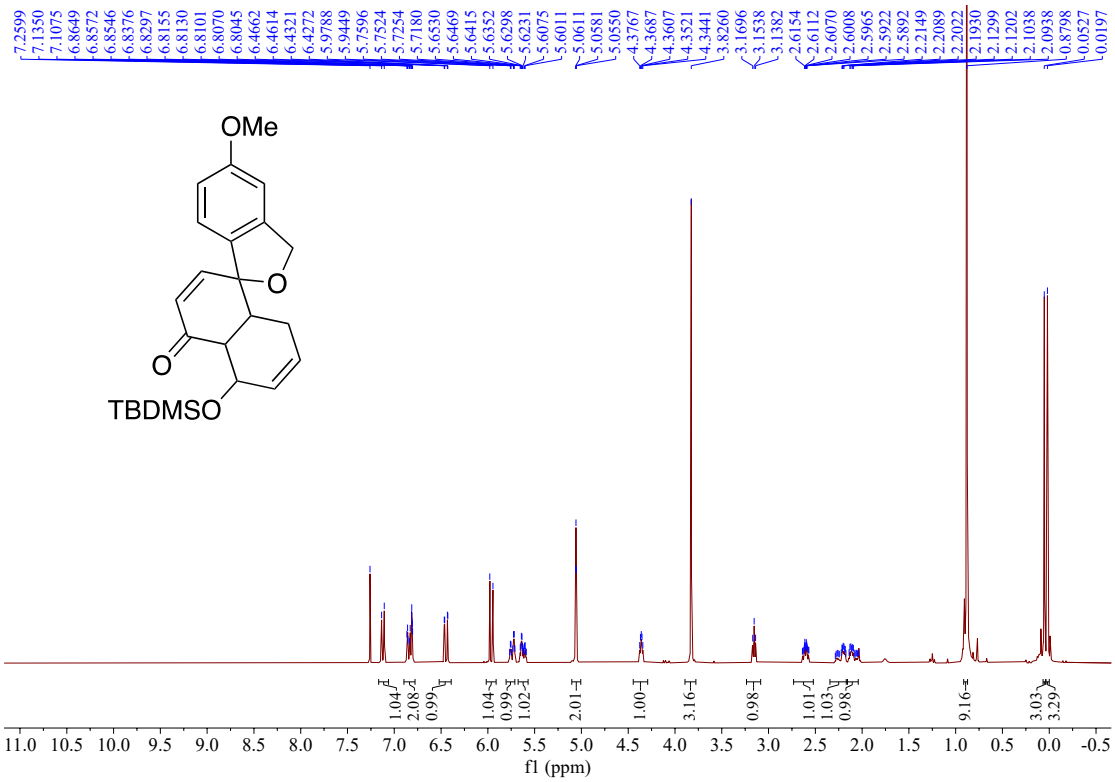


Figure S73. ^{1}H NMR of compound **4ac** in $CDCl_3$

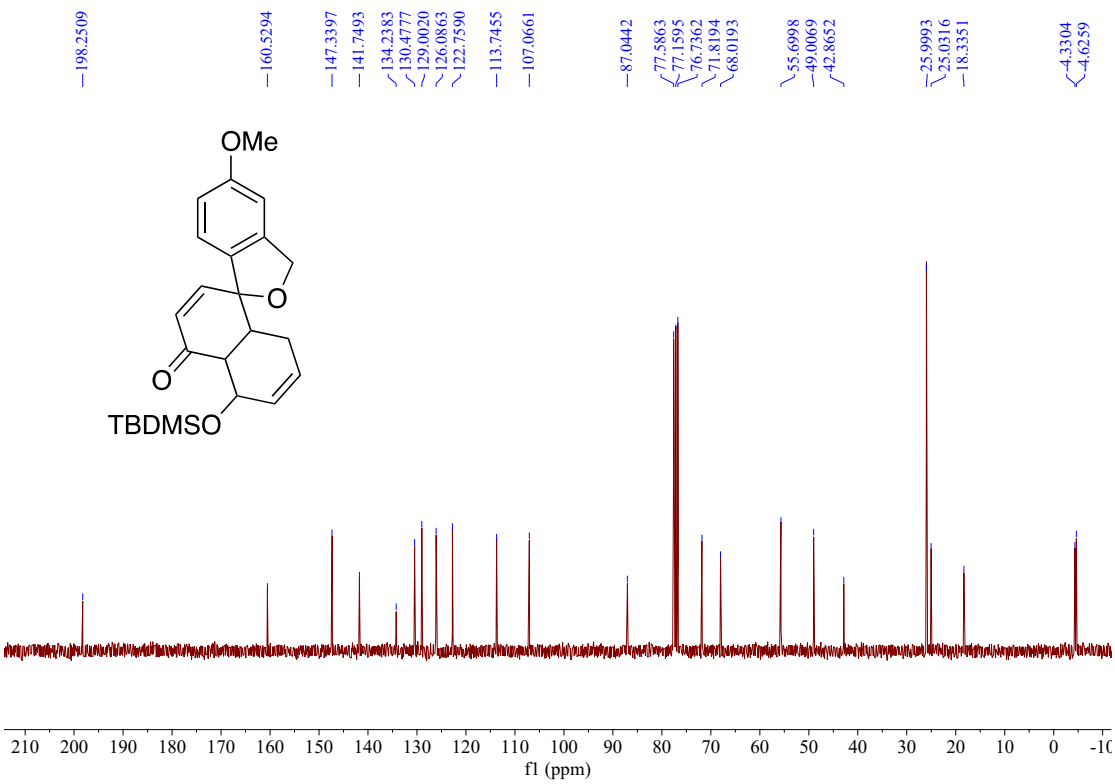


Figure S74. ^{13}C NMR of compound **4ac** in $CDCl_3$

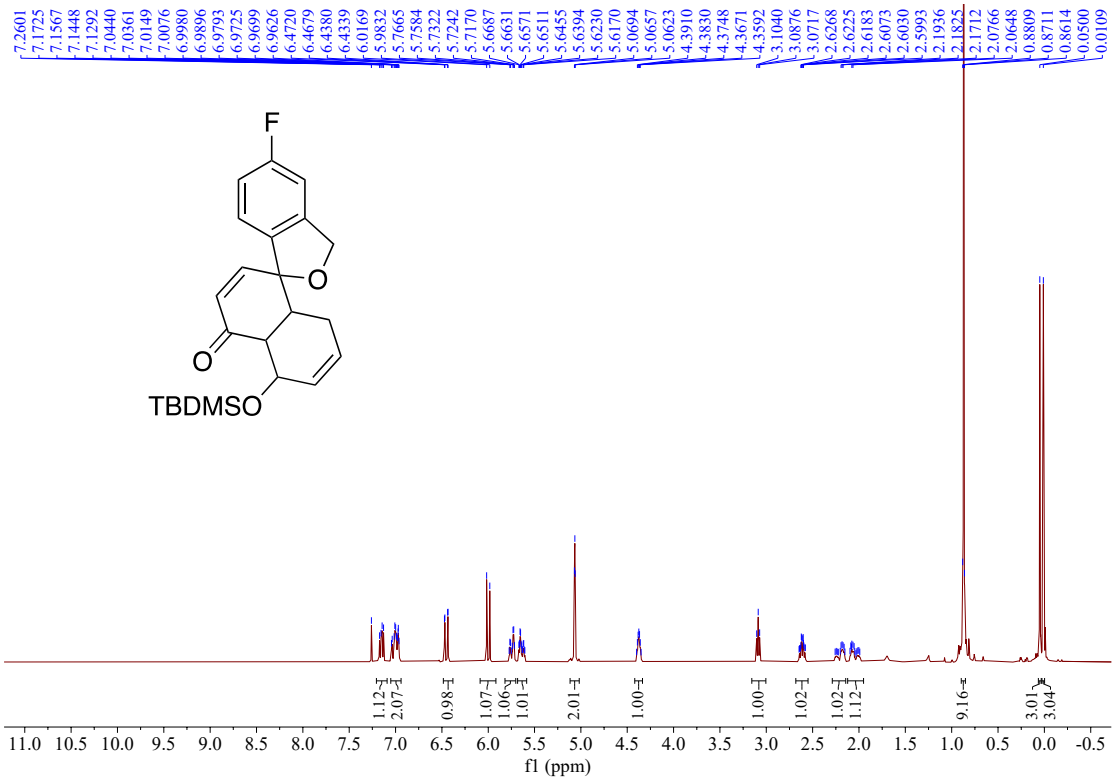


Figure S75. ^{1}H NMR of compound **4ad** in $CDCl_3$

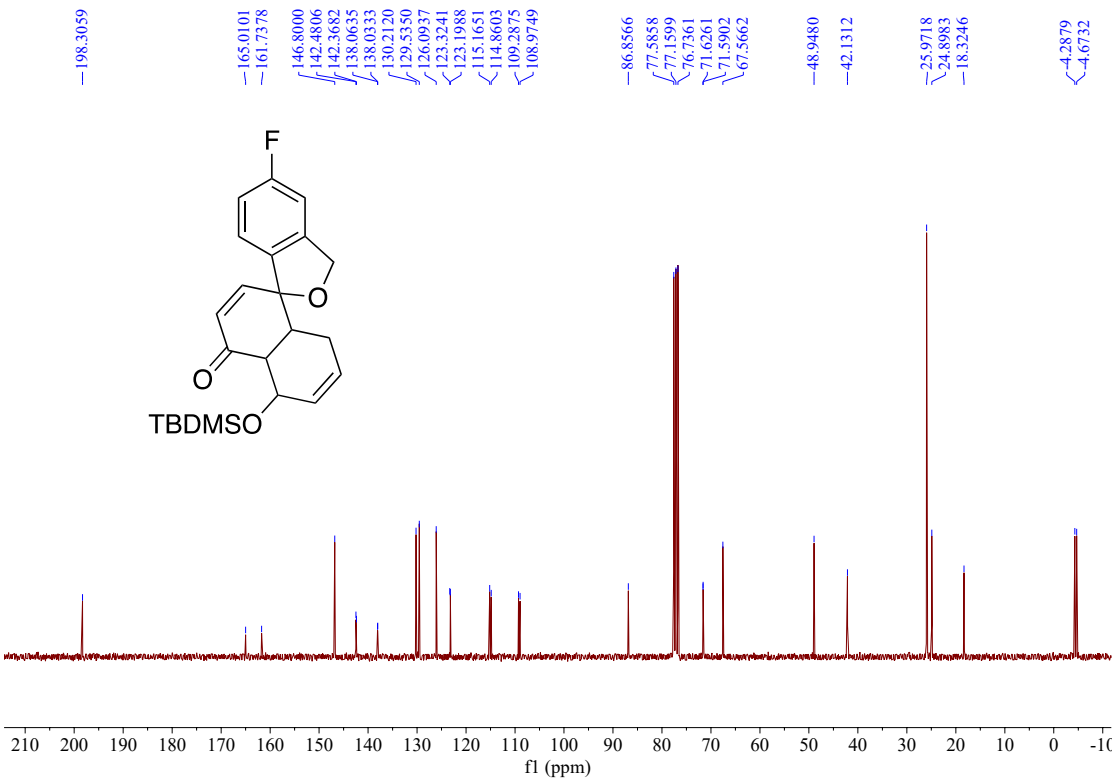


Figure S76. ^{13}C NMR of compound **4ad** in $CDCl_3$

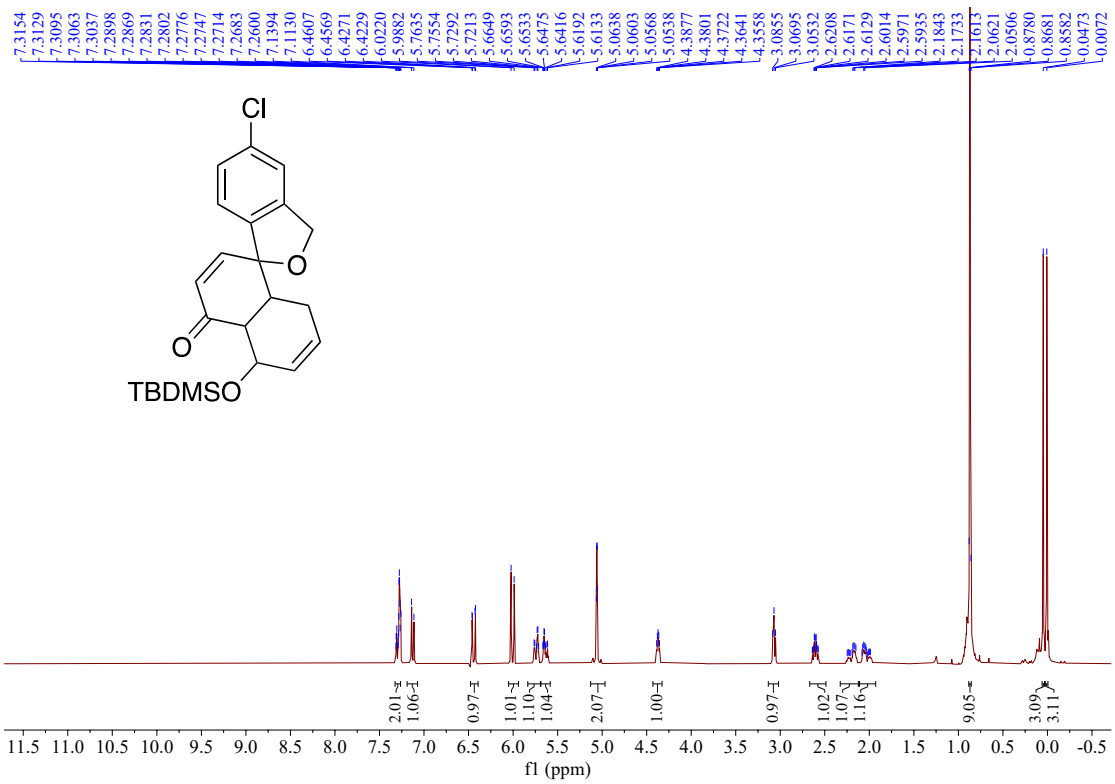


Figure S77. ^{1}H NMR of compound **4ae** in $CDCl_3$

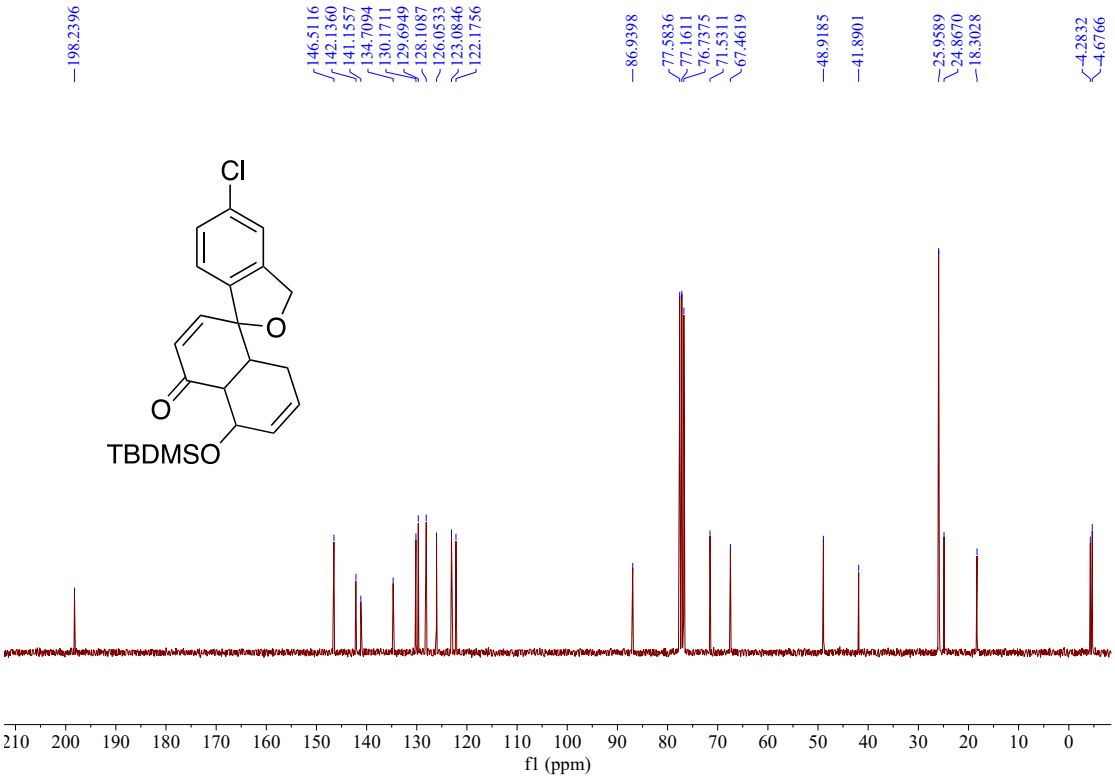


Figure S78. ^{13}C NMR of compound **4ae** in $CDCl_3$

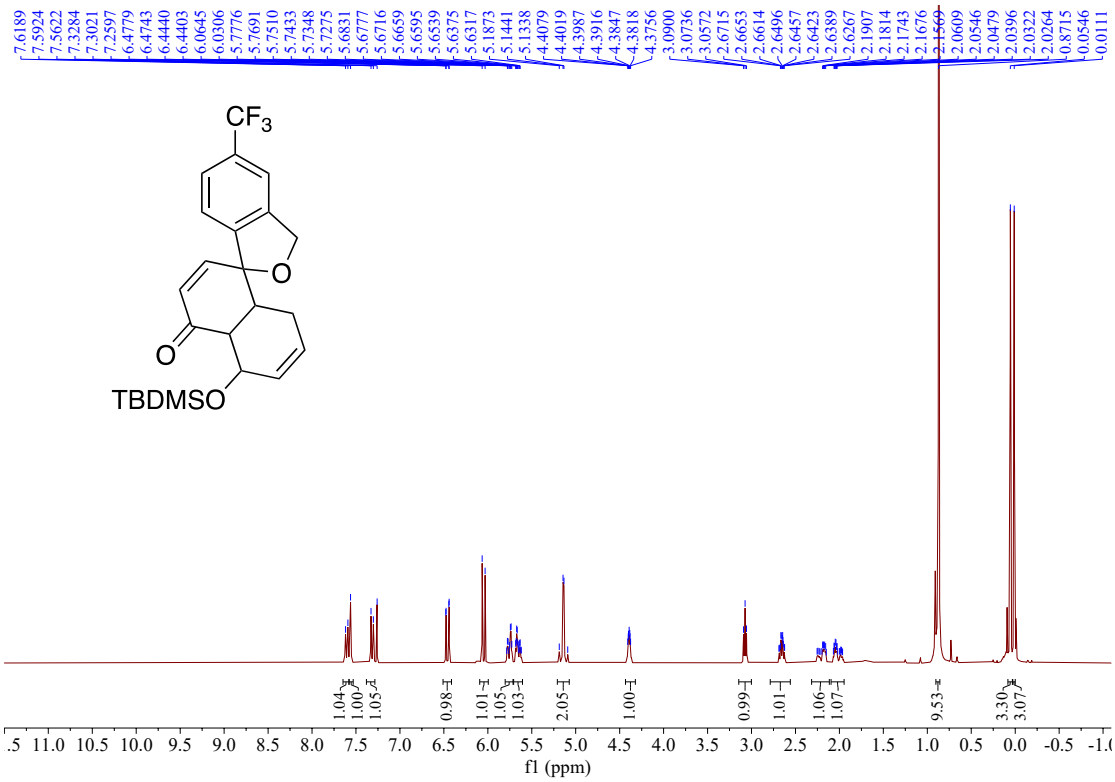


Figure S79. ^{1}H NMR of compound **4af** in $CDCl_3$

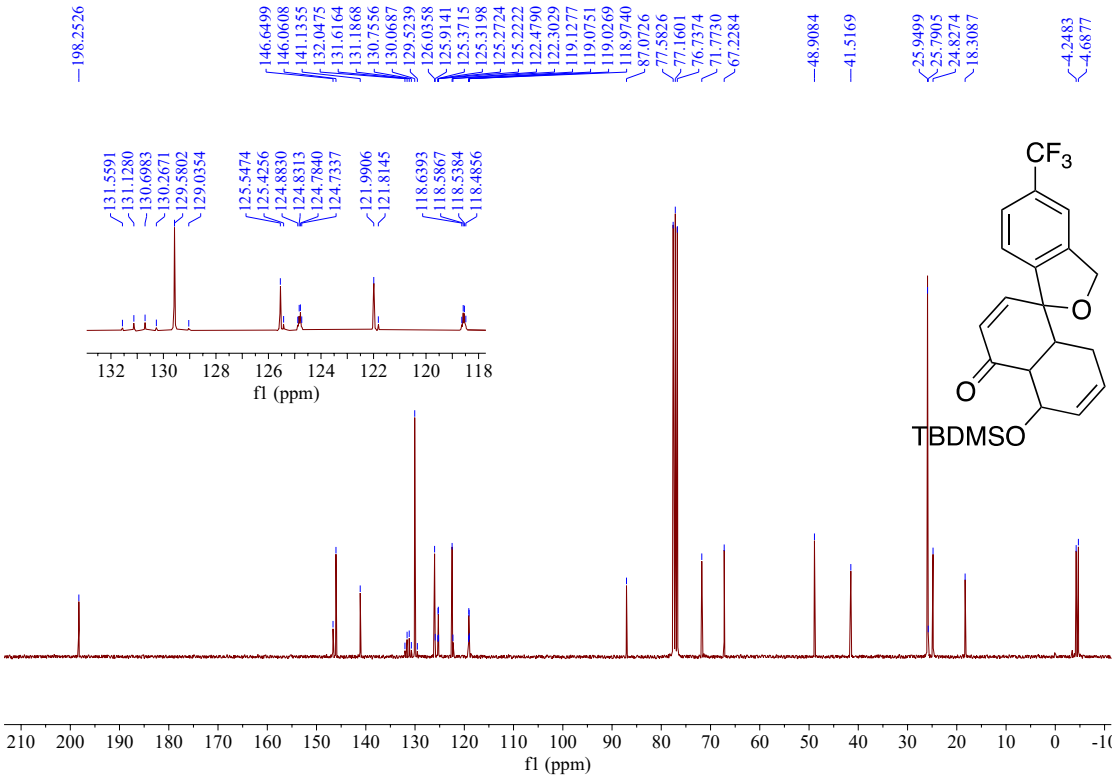


Figure S80. ^{13}C NMR of compound **4af** in $CDCl_3$

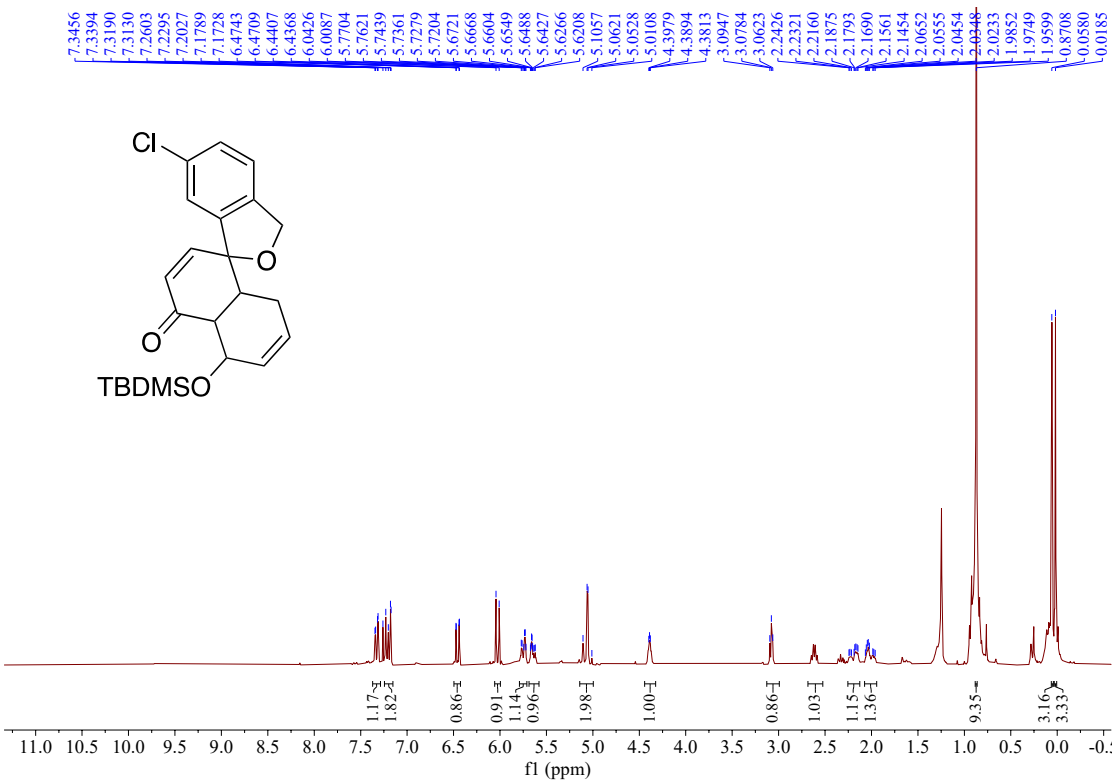


Figure S81. ^{1}H NMR of compound **4ag** in $CDCl_3$

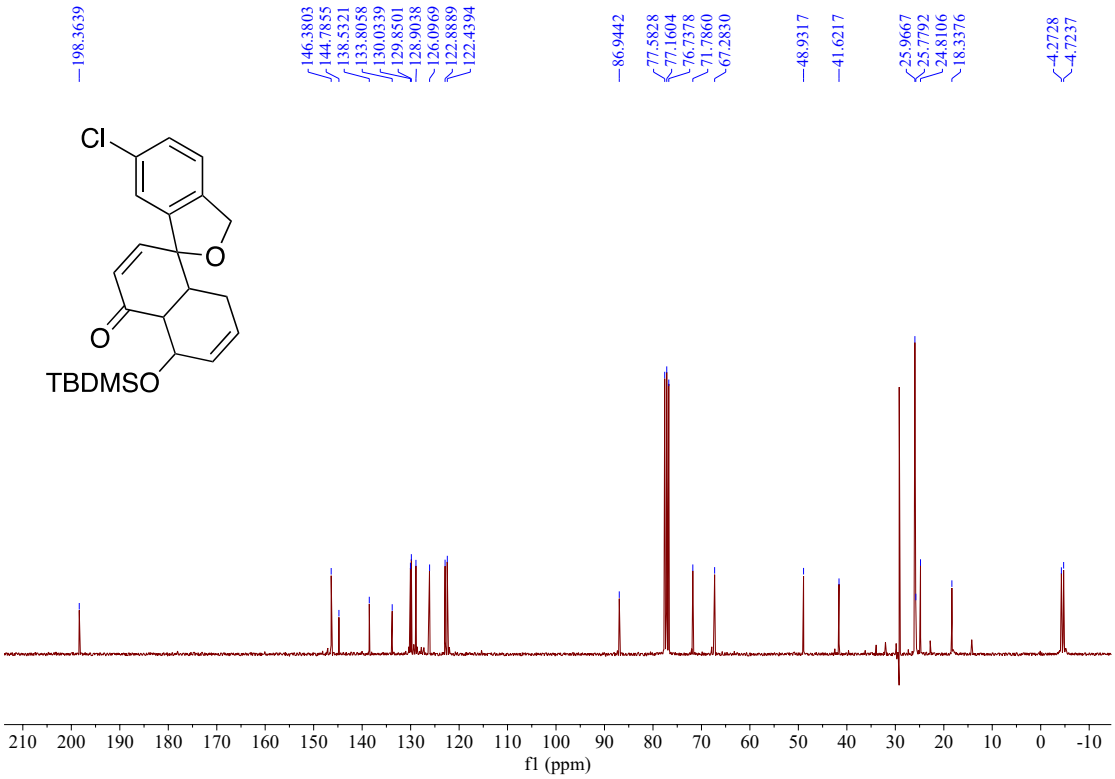


Figure S82. ^{13}C NMR of compound **4ag** in $CDCl_3$

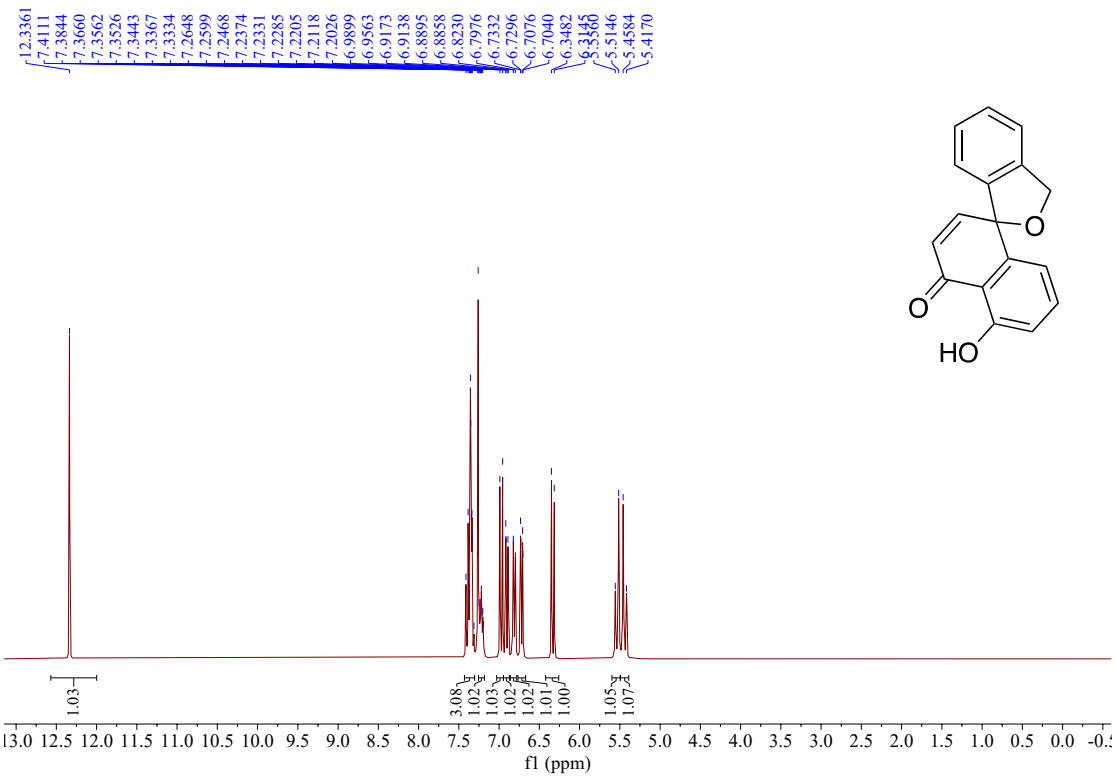


Figure S83. ^{1}H NMR of compound **5aa** in $CDCl_3$

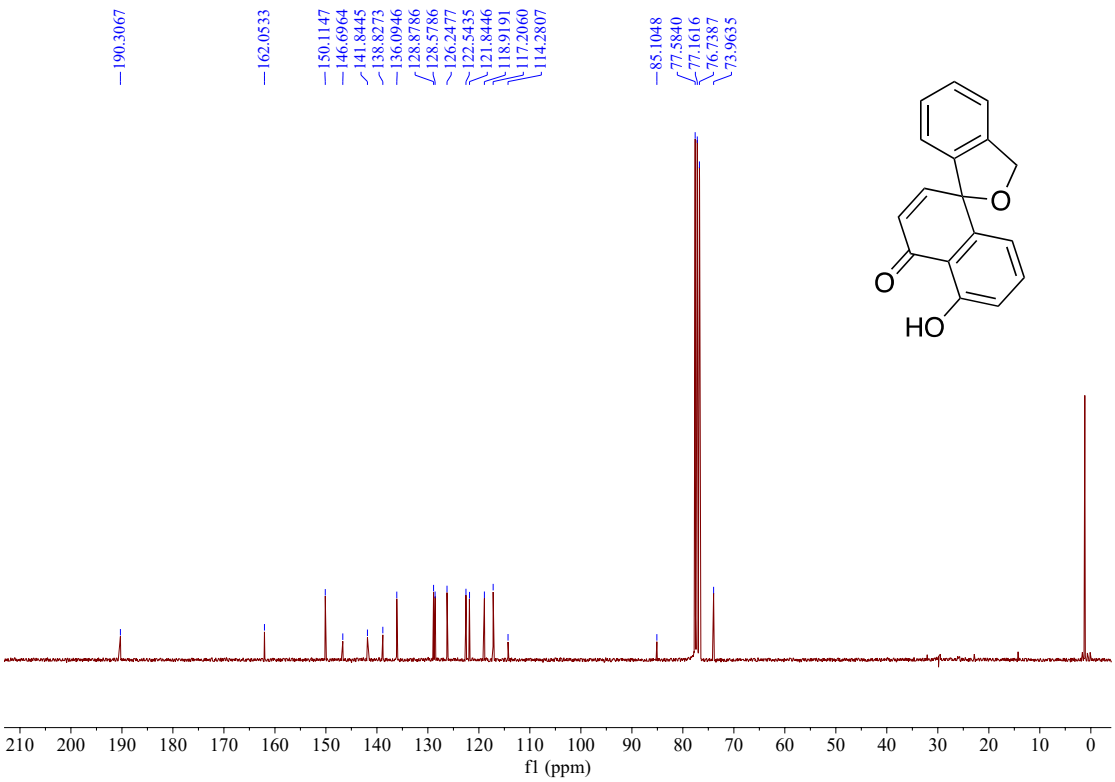


Figure S84. ^{13}C NMR of compound **5aa** in $CDCl_3$

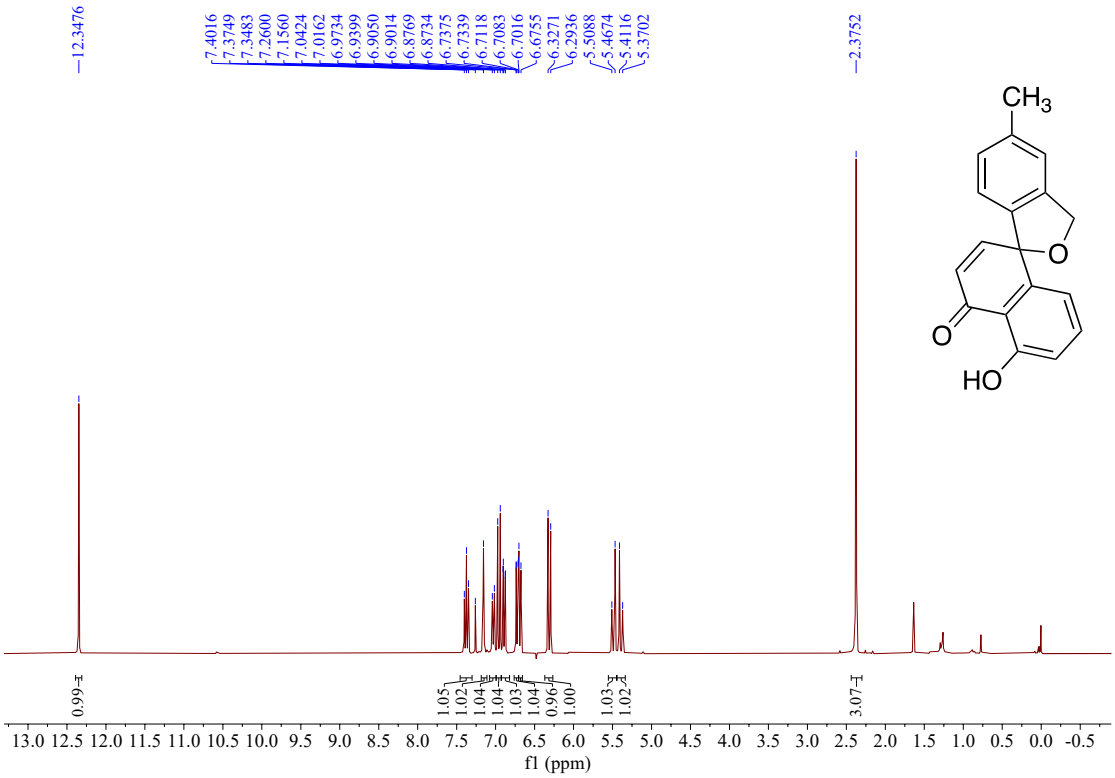


Figure S85. ^{1}H NMR of compound **5ab** in $CDCl_3$

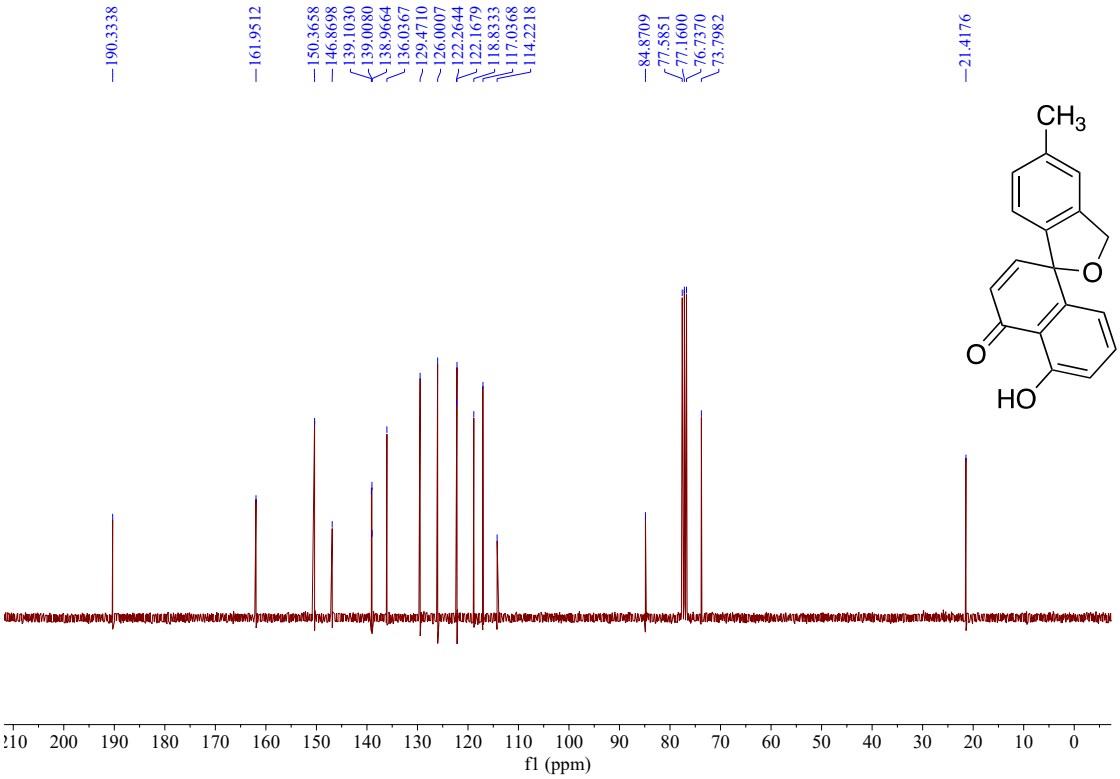


Figure S86. ^{13}C NMR of compound **5ab** in $CDCl_3$

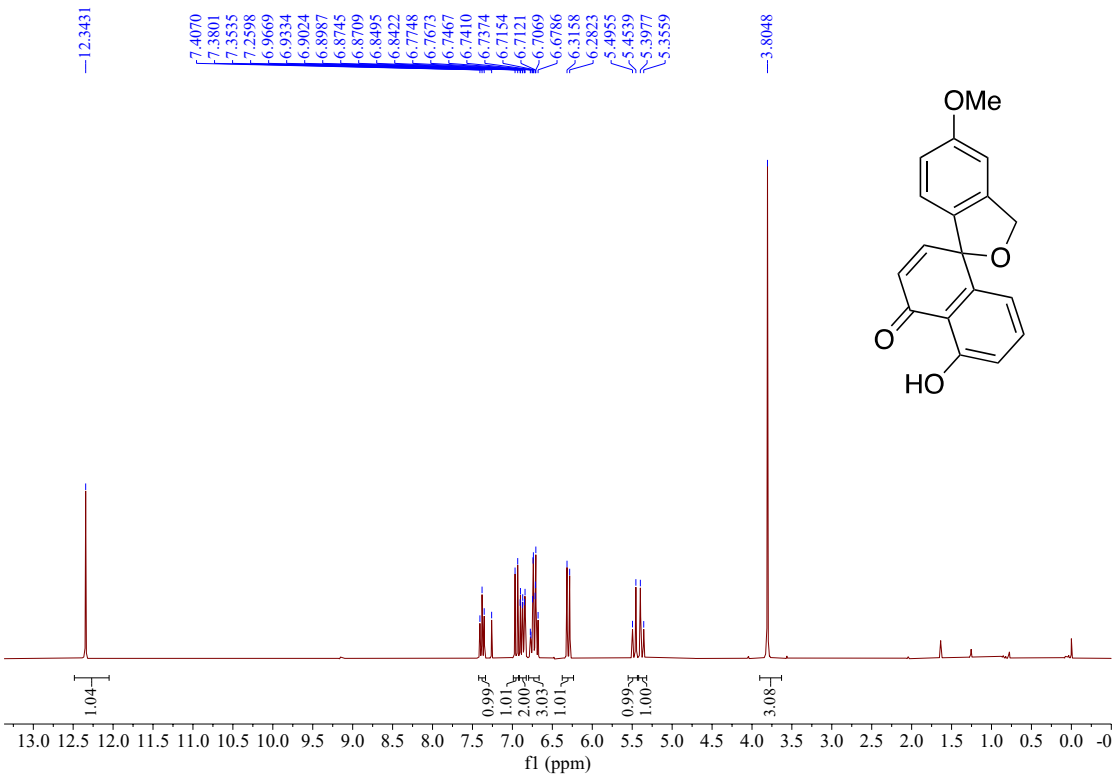


Figure S87. ^{1}H NMR of compound **5ac** in $CDCl_3$

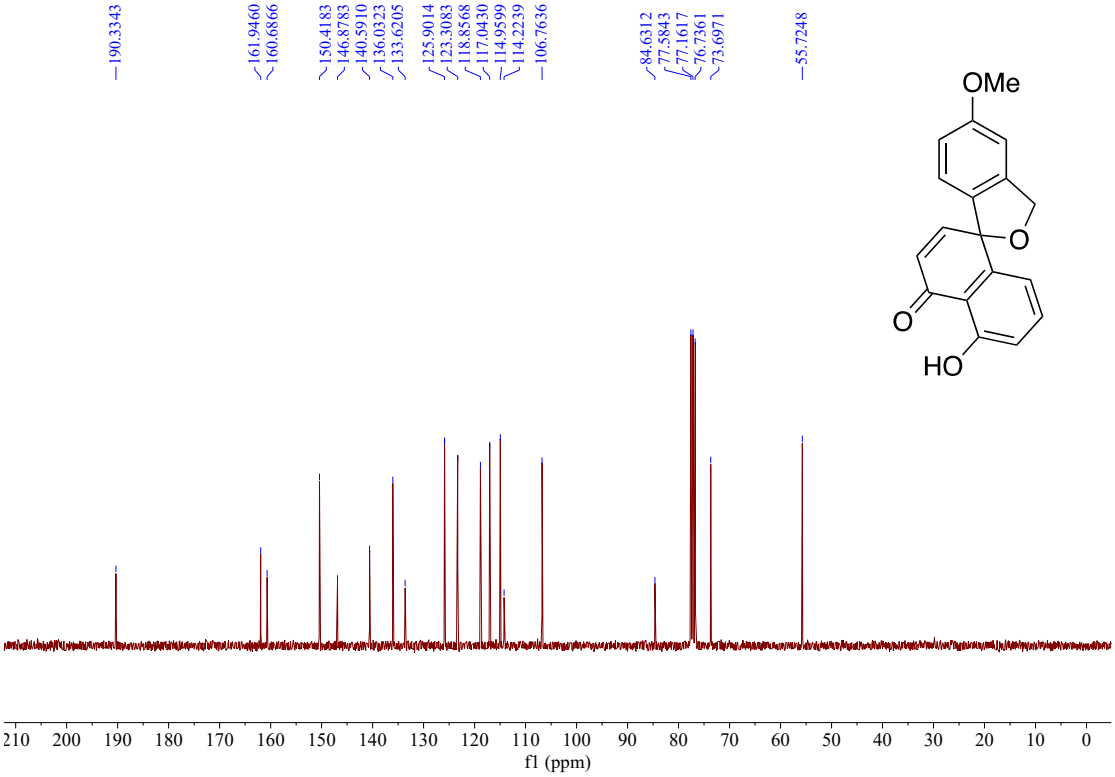


Figure S88. ^{13}C NMR of compound **5ac** in $CDCl_3$

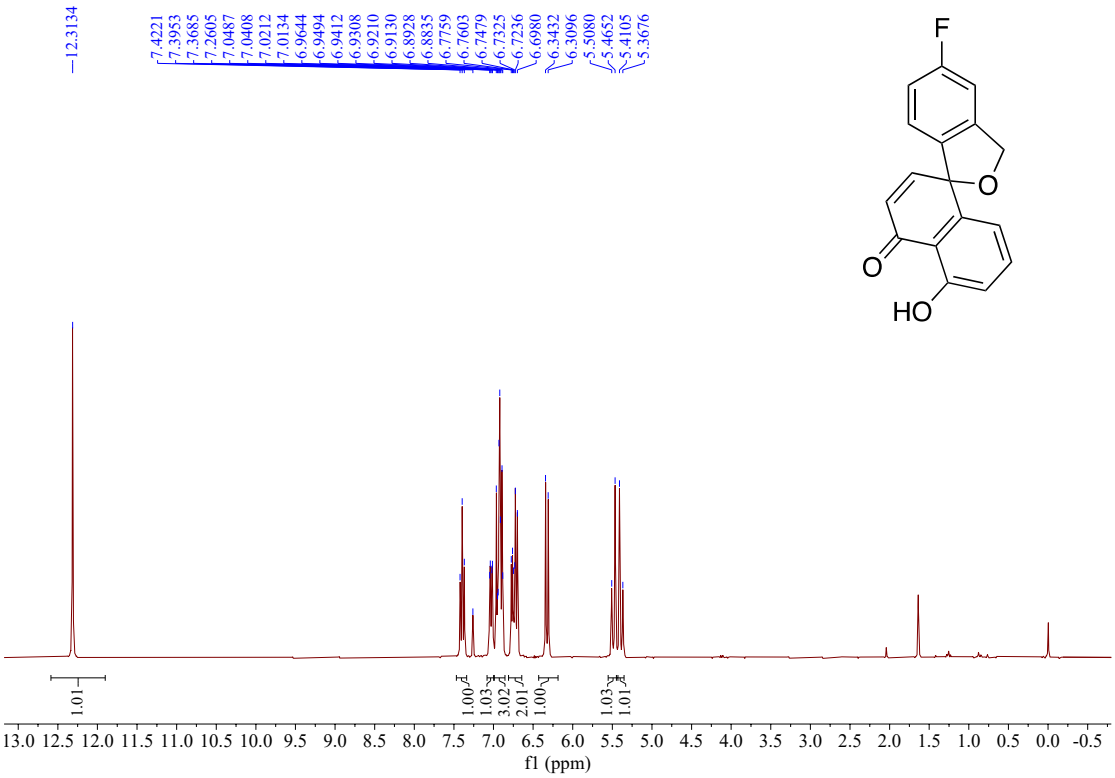


Figure S89. ^{1}H NMR of compound **5ad** in $CDCl_3$

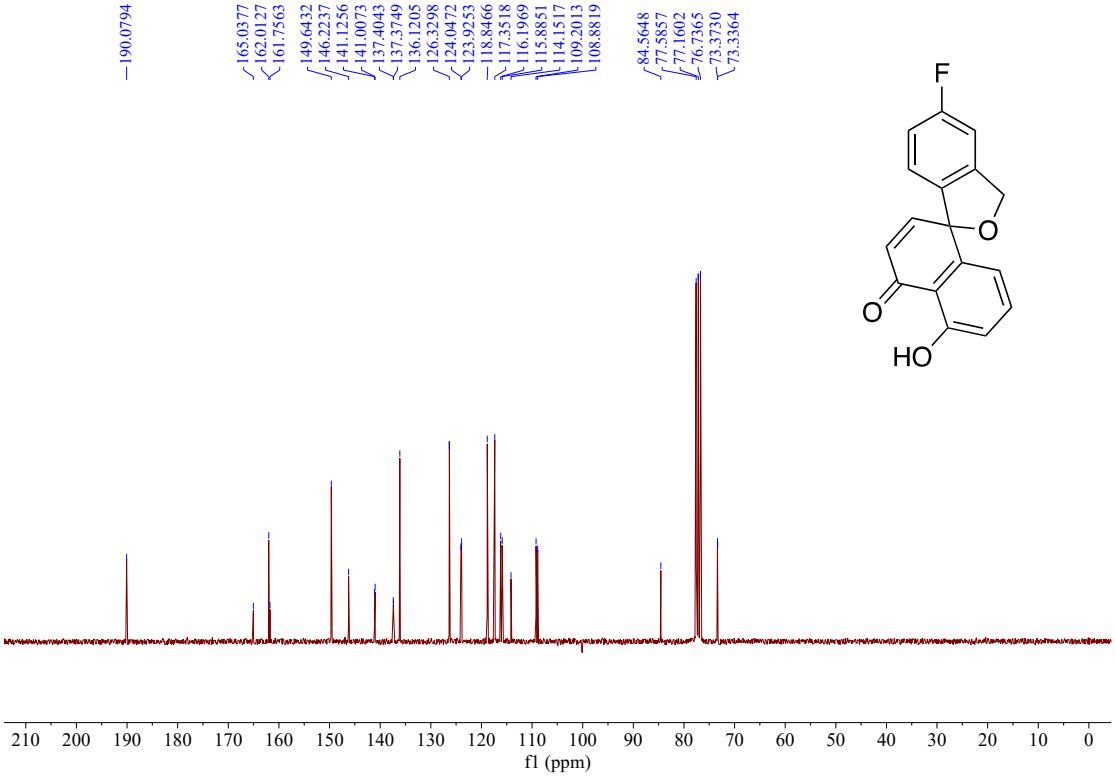


Figure S90. ^{13}C NMR of compound **5ad** in $CDCl_3$

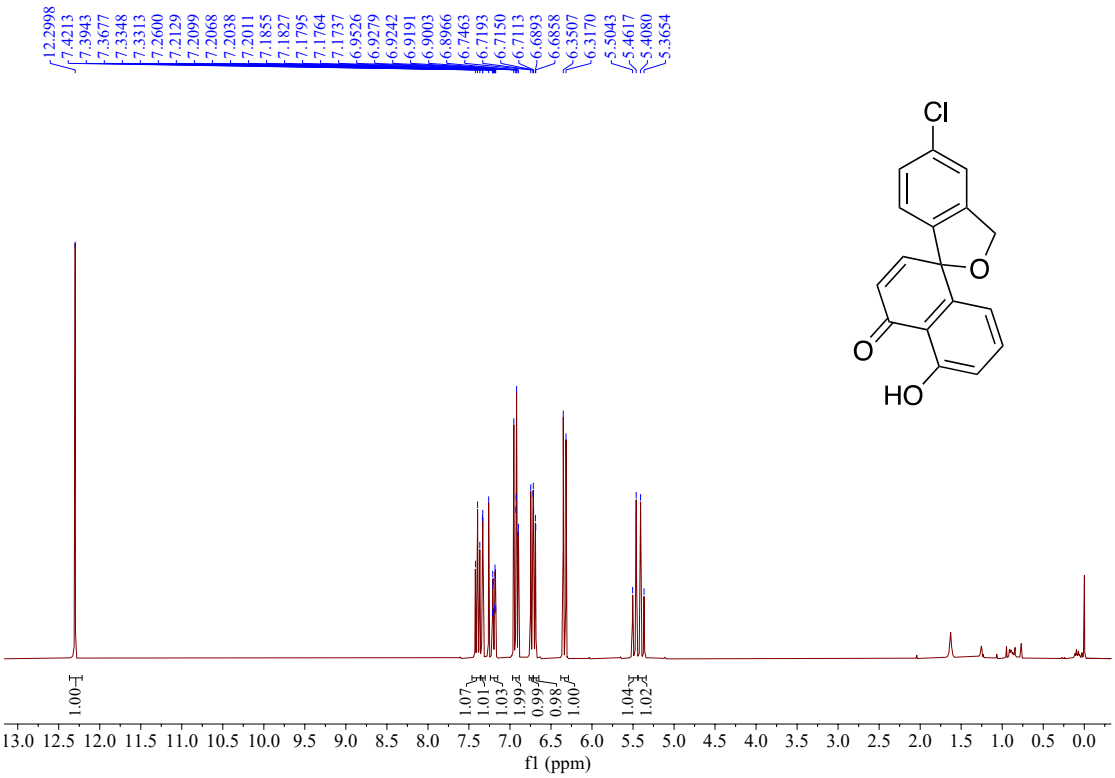


Figure S91. ^{1}H NMR of compound **5ae** in $CDCl_3$

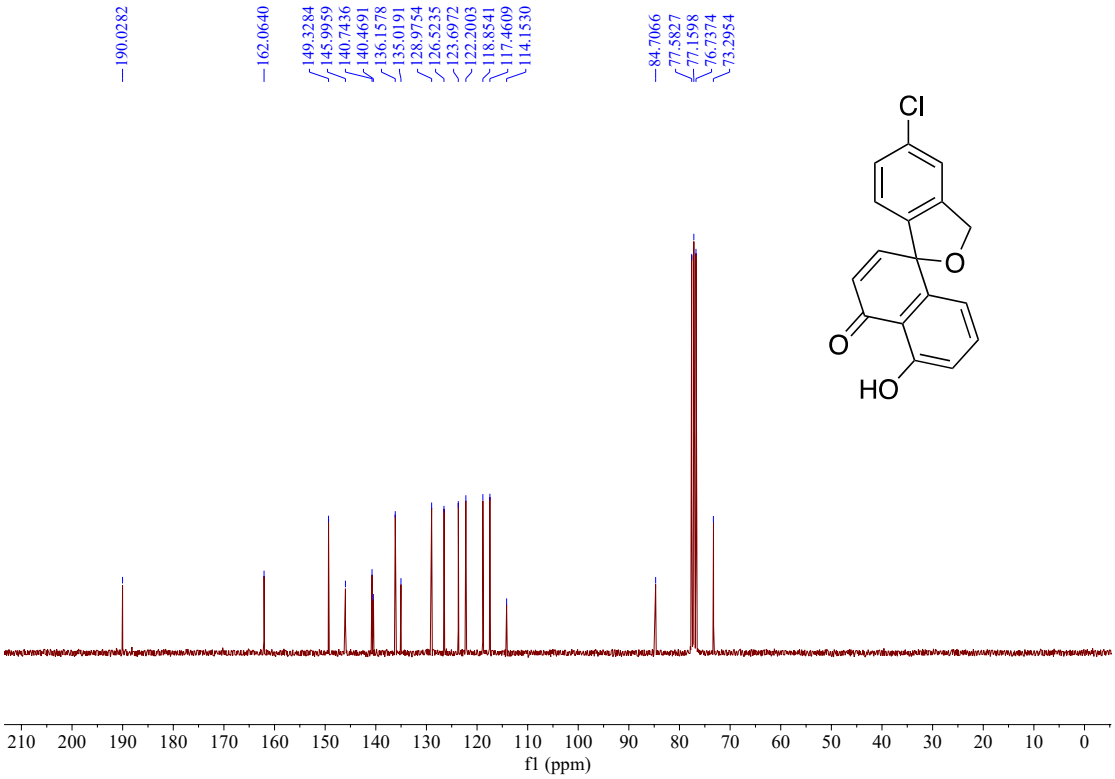


Figure S92. ^{13}C NMR of compound **5ae** in $CDCl_3$

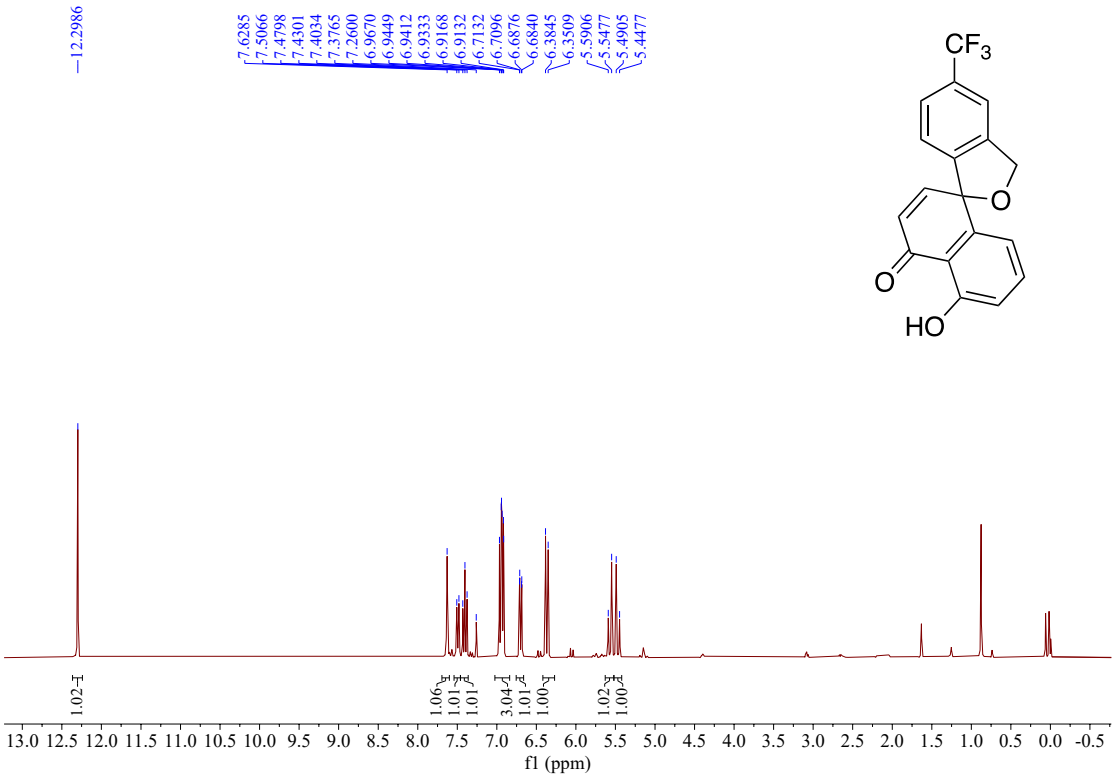


Figure S93. ^{1}H NMR of compound **5af** in $CDCl_3$

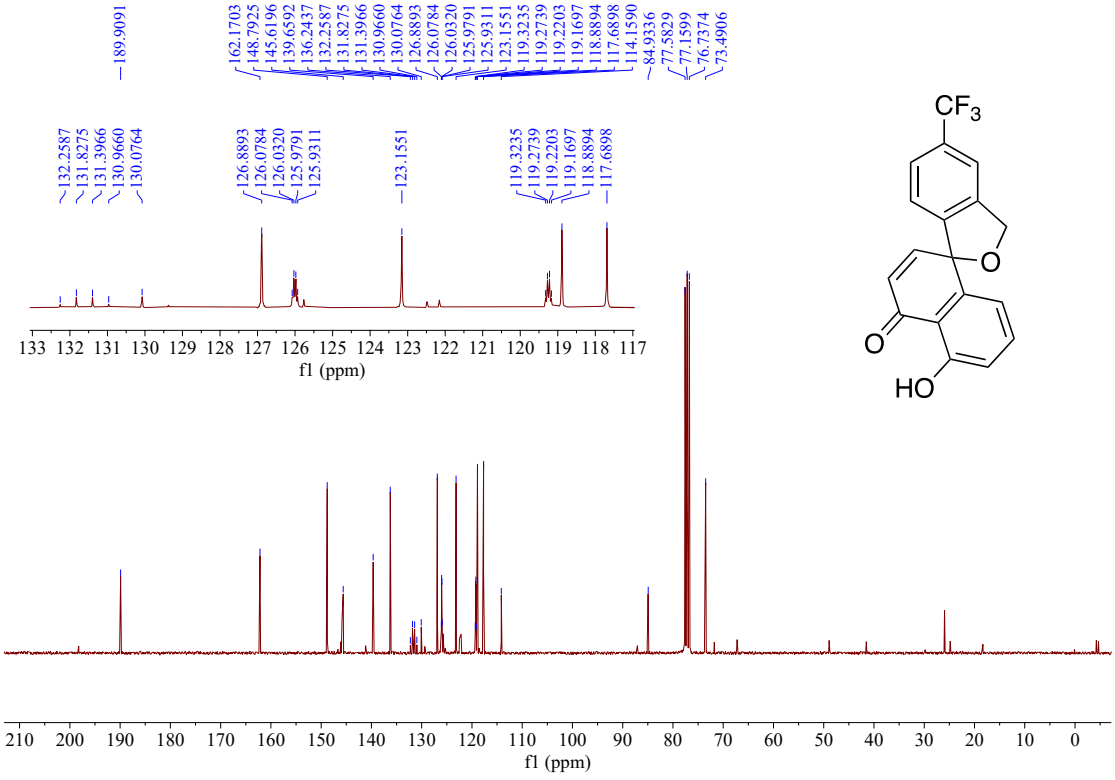


Figure S94. ^{13}C NMR of compound **5af** in $CDCl_3$

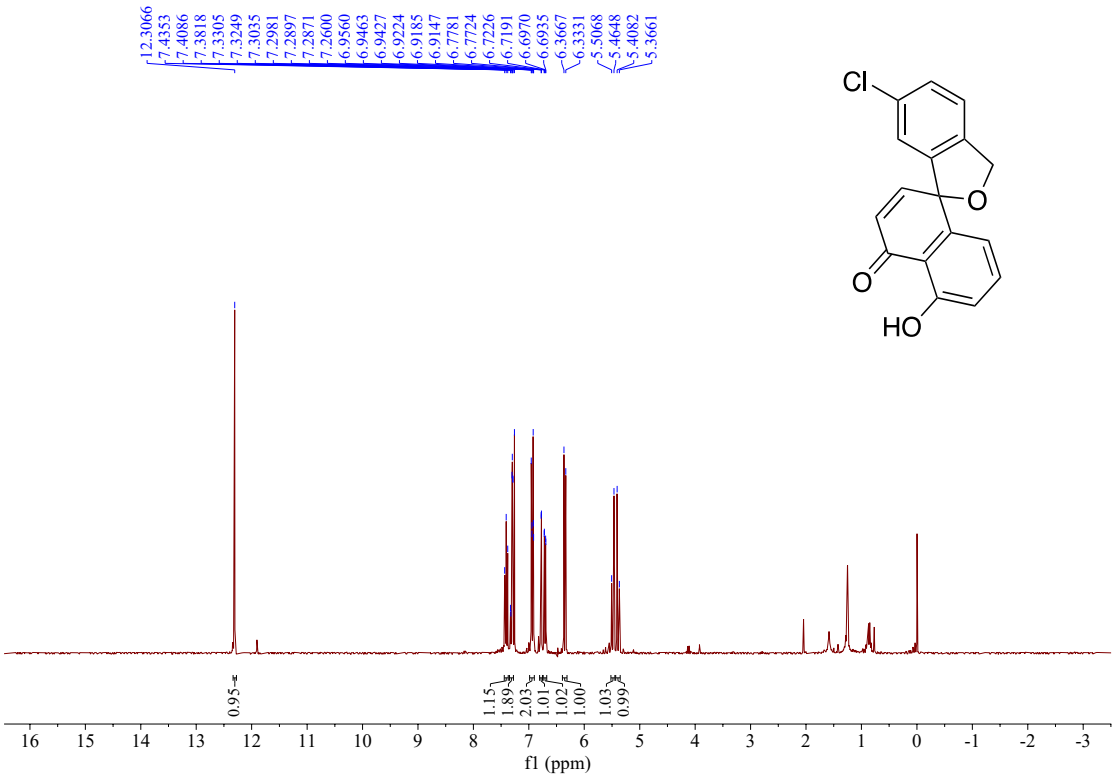


Figure S95. ^{1}H NMR of compound **5ag** in $CDCl_3$

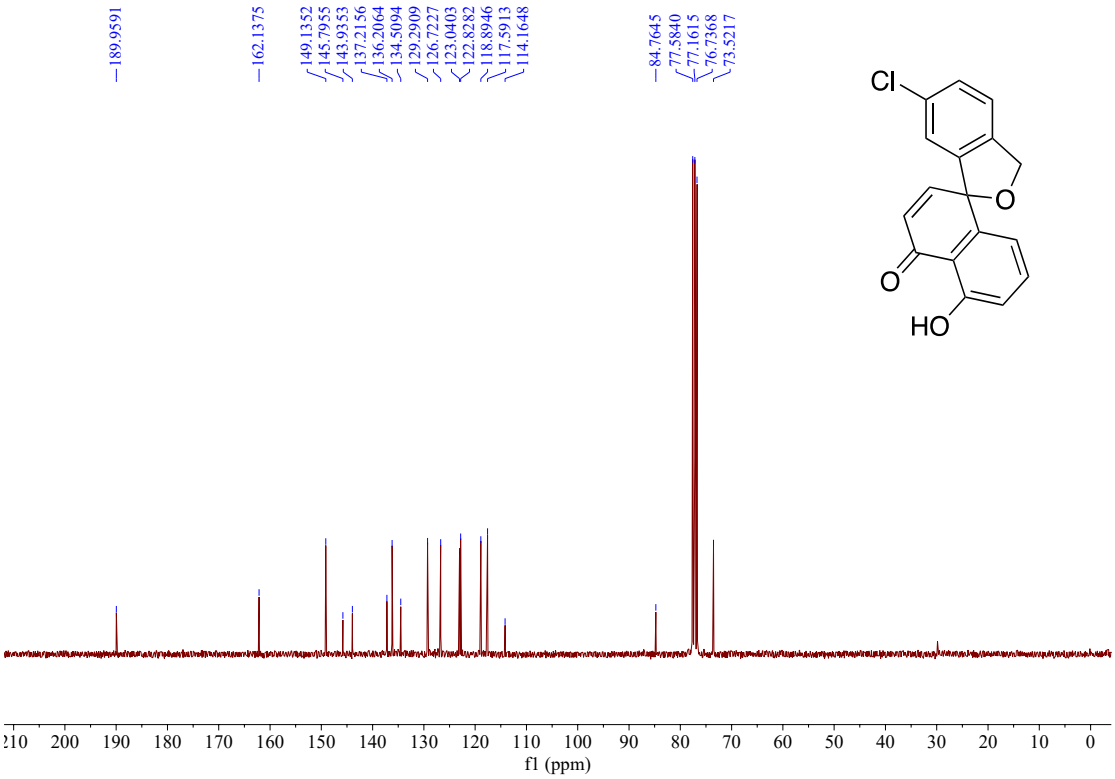


Figure S96. ^{13}C NMR of compound **5ag** in $CDCl_3$

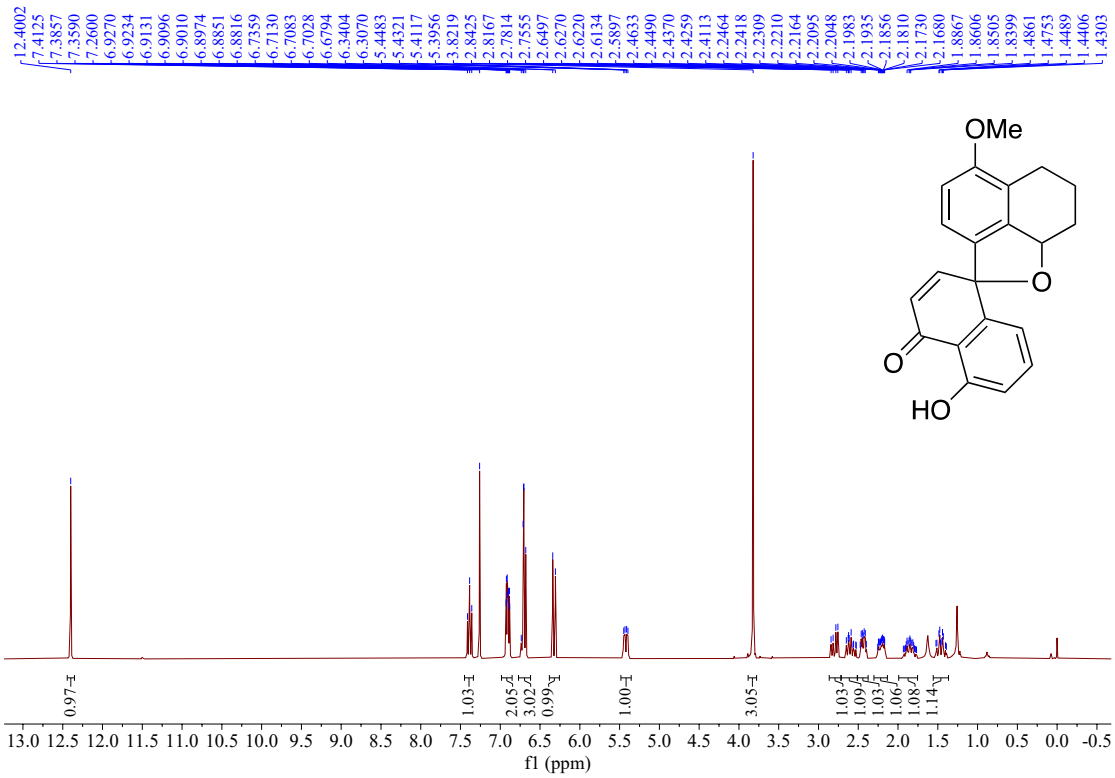


Figure S97. ^{1}H NMR of compound **5ah** in $CDCl_3$

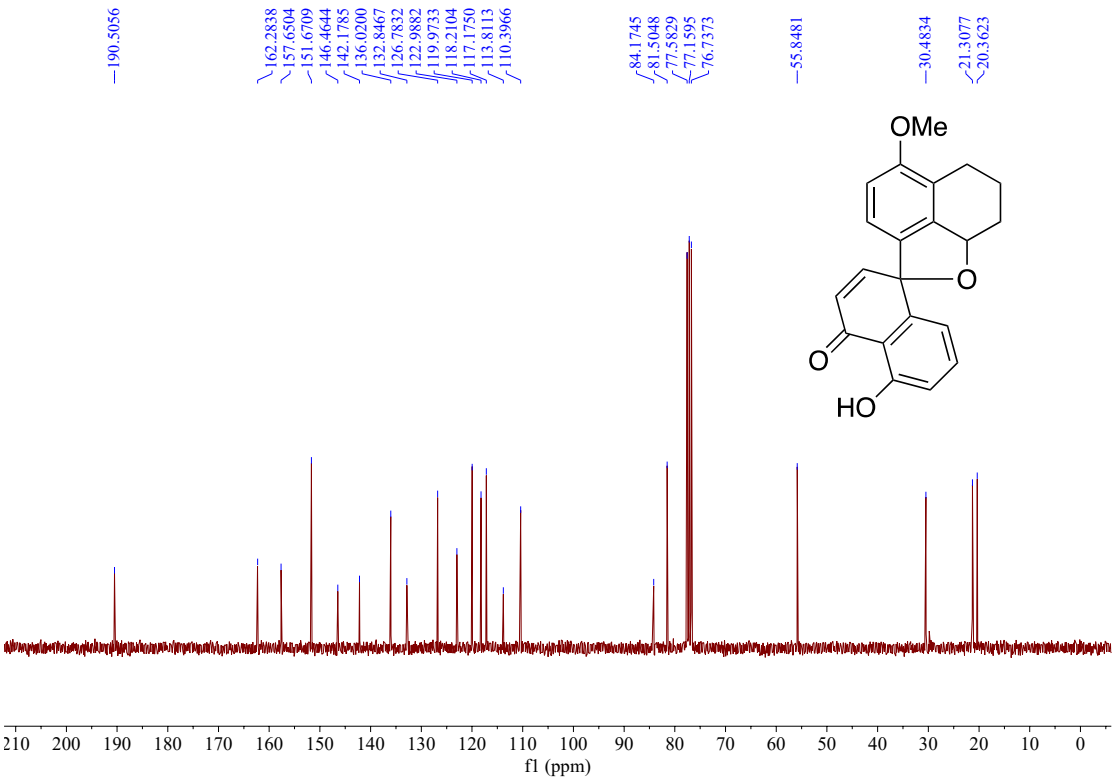


Figure S98. ^{13}C NMR of compound **5ah** in $CDCl_3$

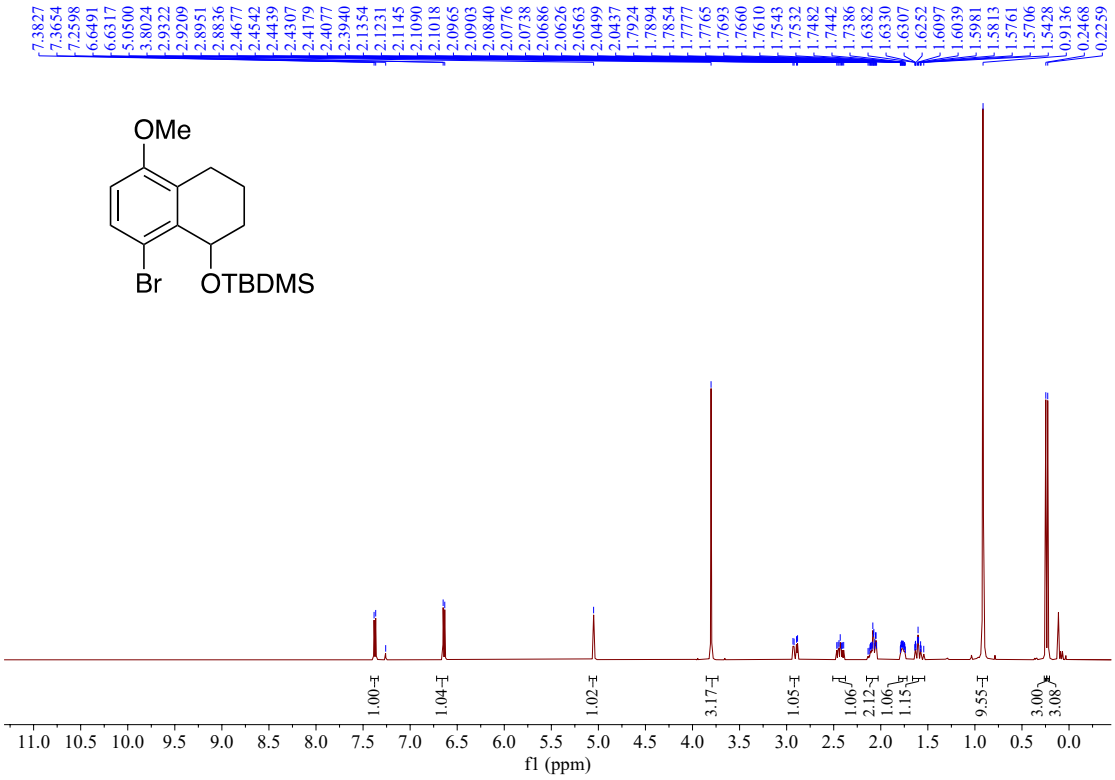


Figure S99. ^{1}H NMR of compound **M-3** in $CDCl_3$

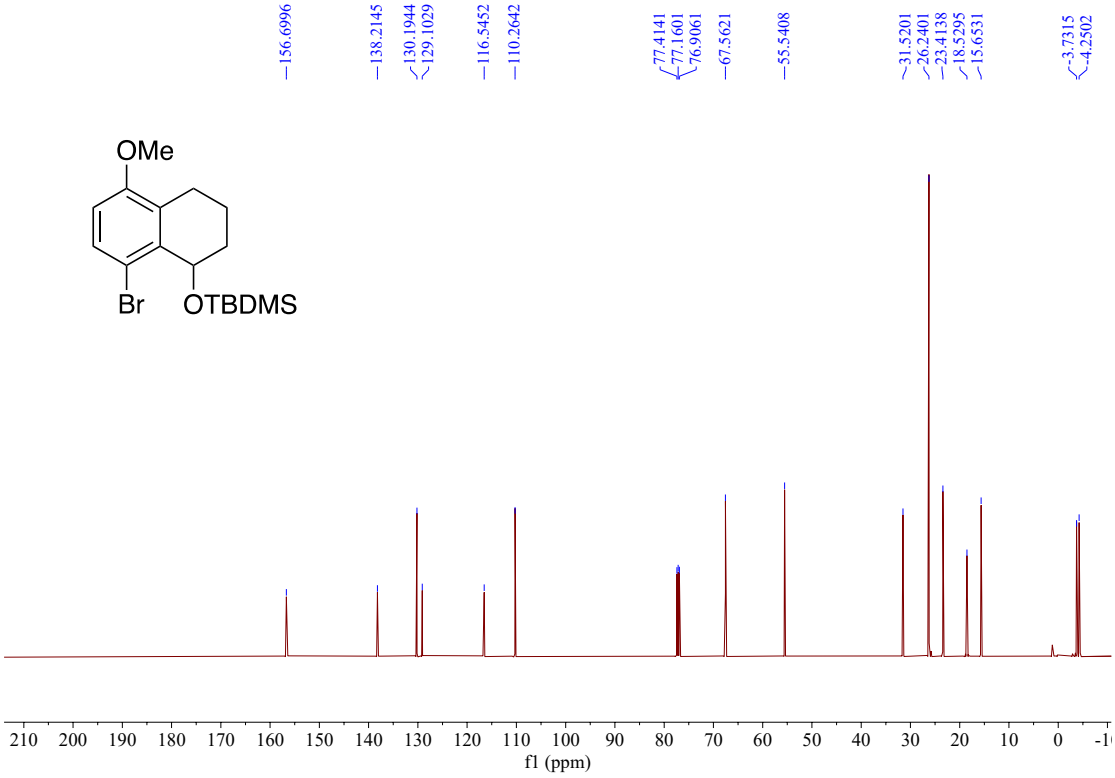


Figure S100. ^{13}C NMR of compound **M-3** in $CDCl_3$

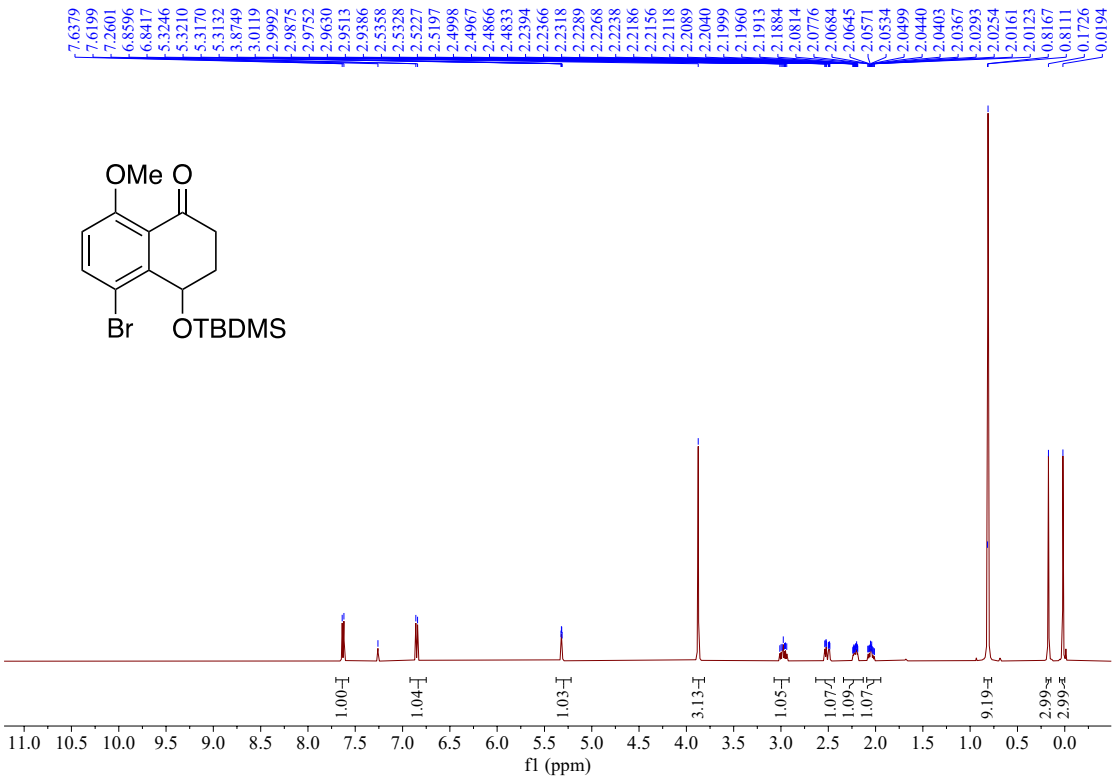


Figure S101. ^{1}H NMR of compound **6a** in $CDCl_3$

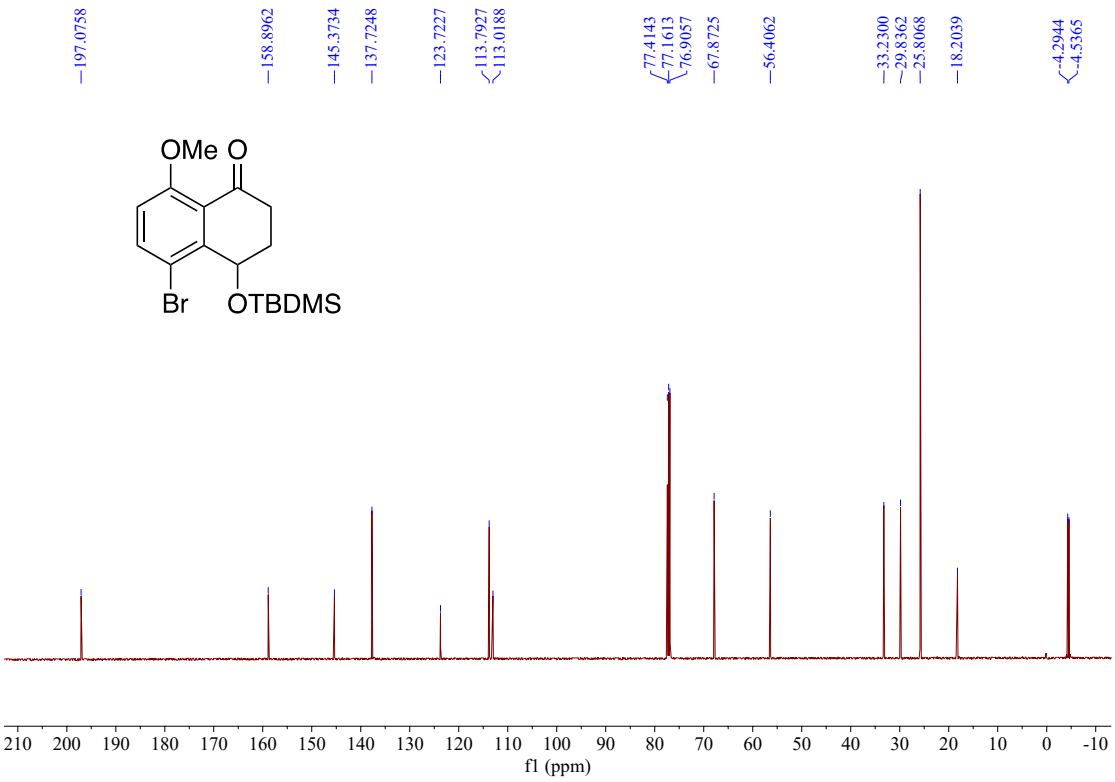


Figure S102. ^{13}C NMR of compound **6a** in $CDCl_3$

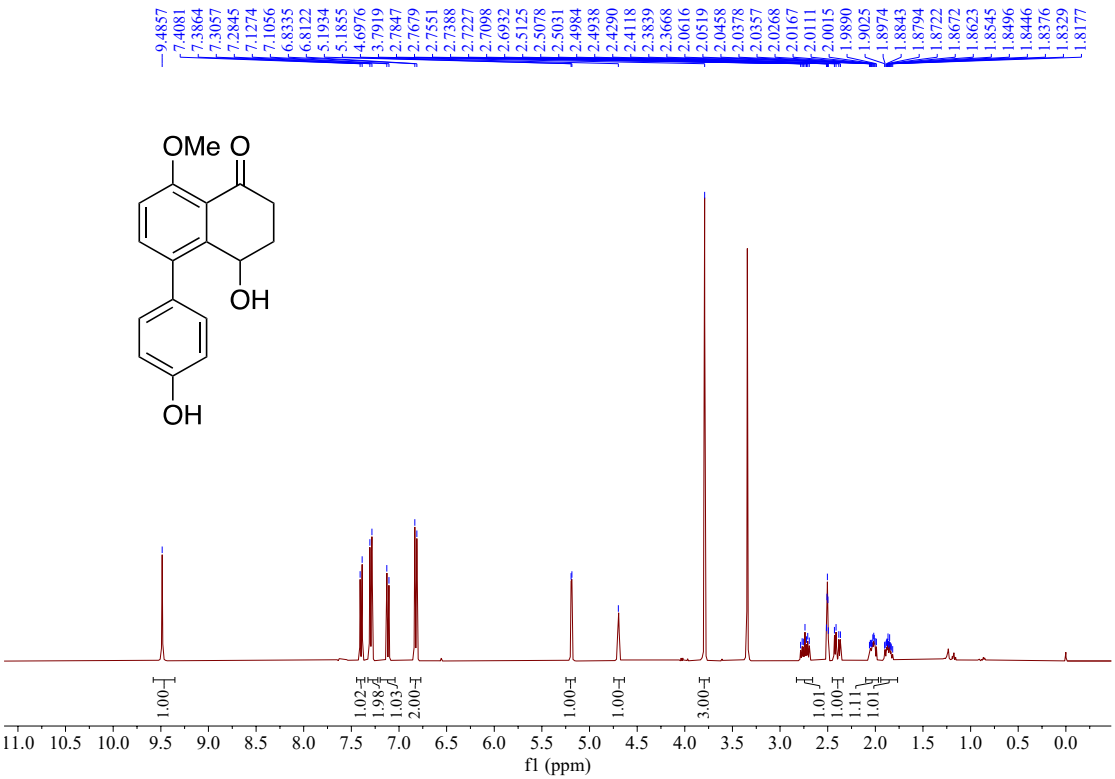


Figure S103. ^{1}H NMR of compound **6b** in DMSO-d_6

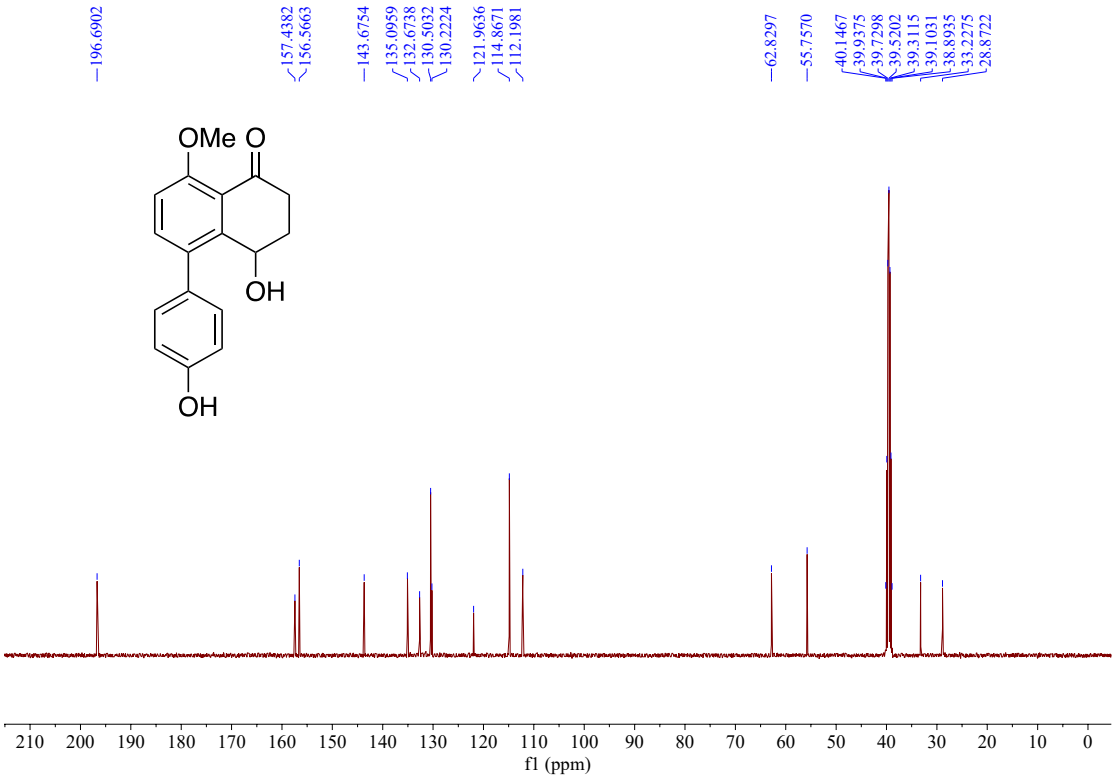


Figure S104. ^{13}C NMR of compound **6b** in DMSO-d_6

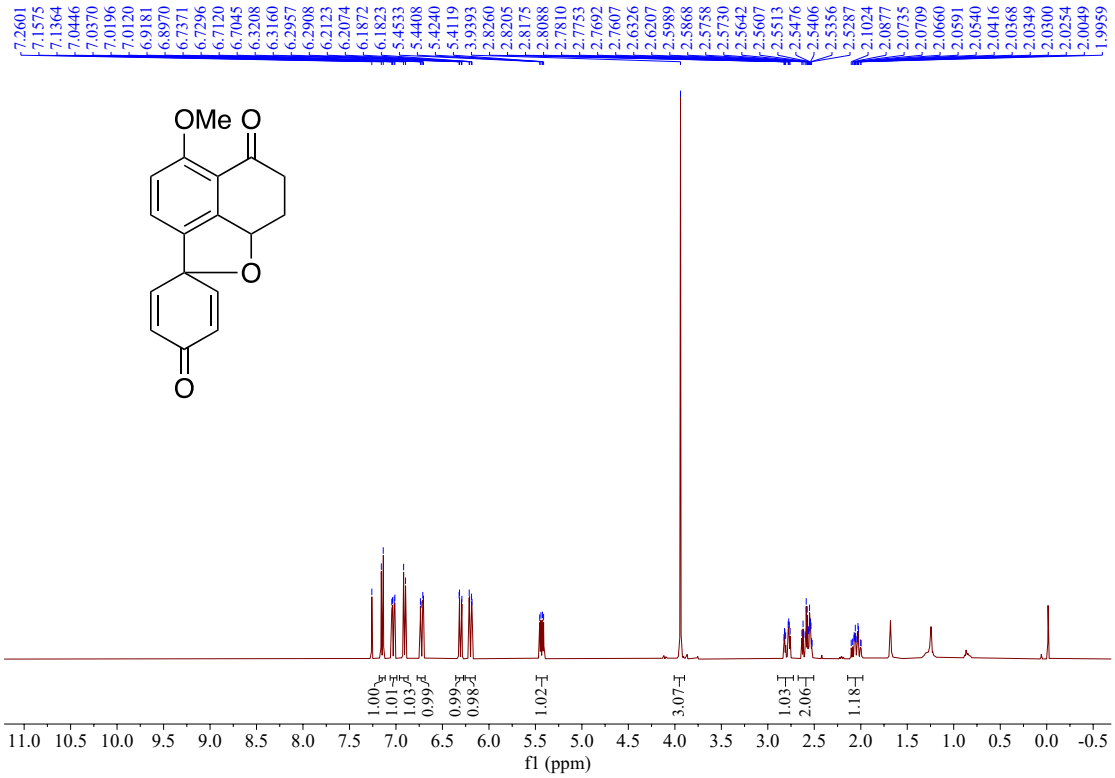


Figure S105. ^{1}H NMR of compound **6c** in $CDCl_3$

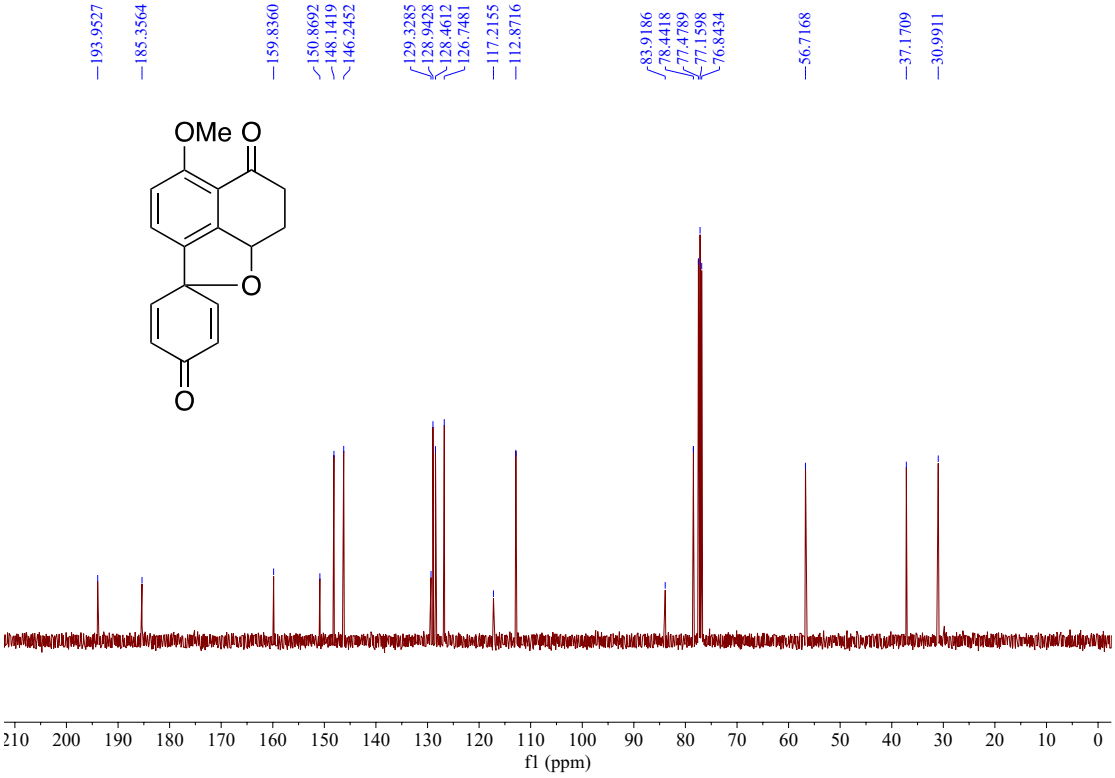


Figure S106. ^{13}C NMR of compound **6c** in $CDCl_3$

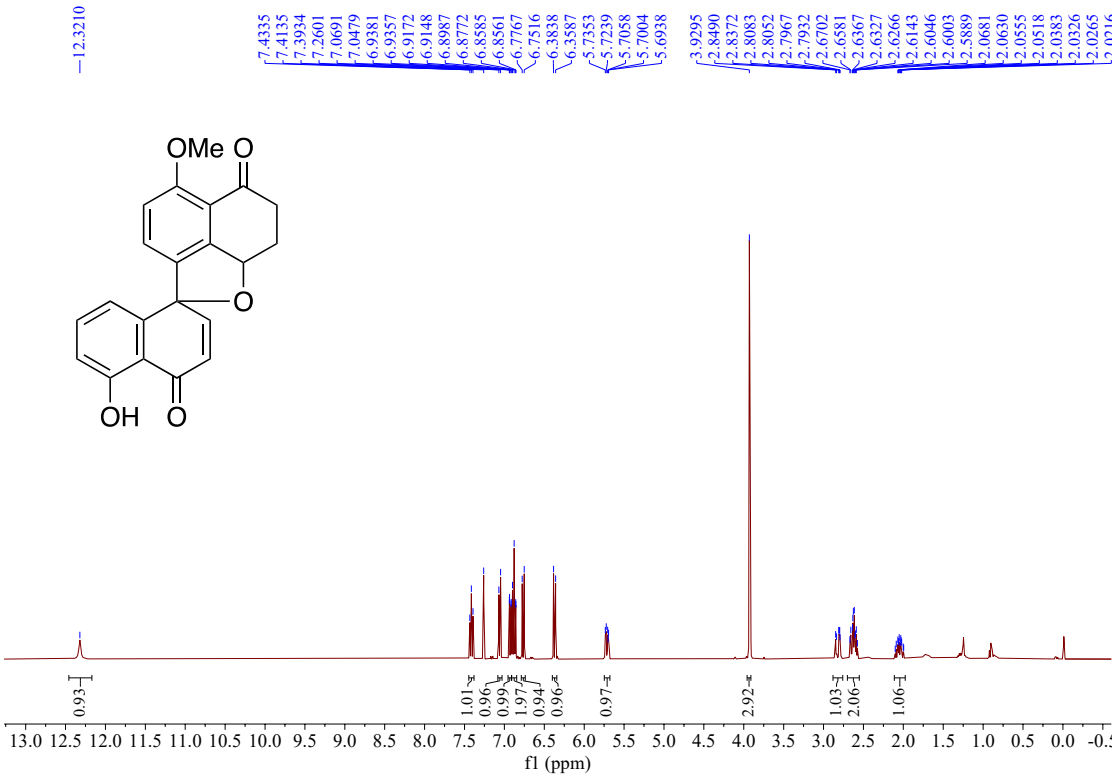


Figure S107. ^{1}H NMR of compound **6d** in $CDCl_3$

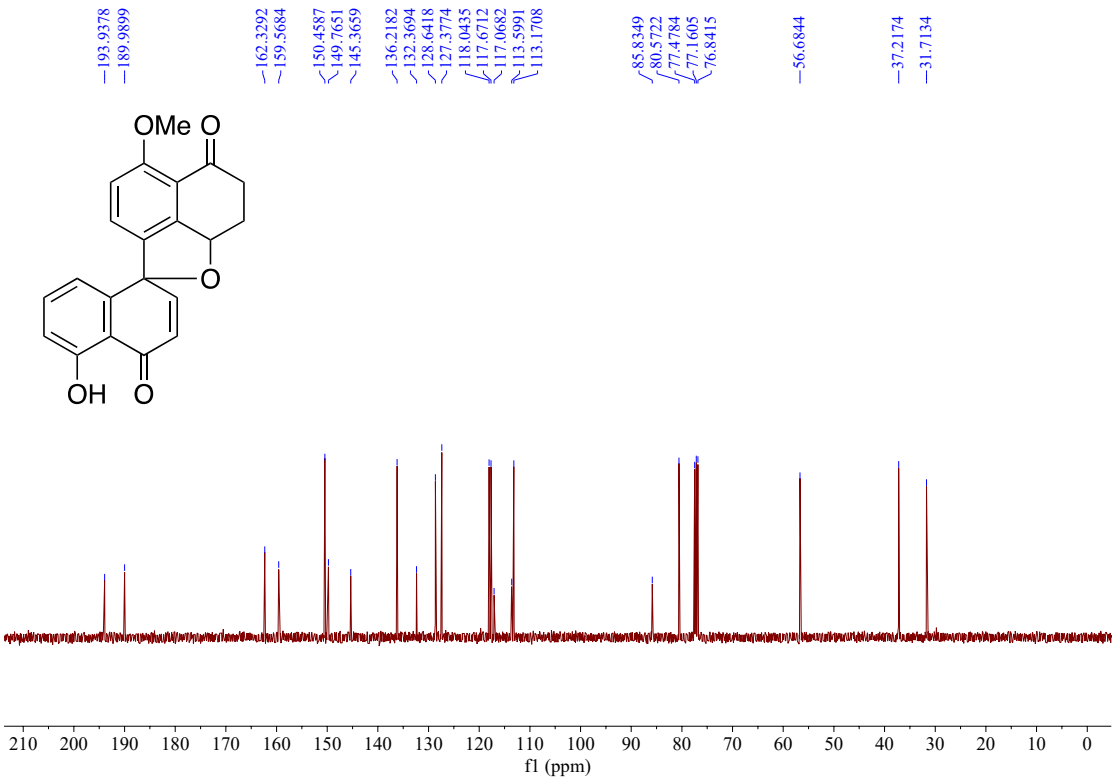


Figure S108. ^{13}C NMR of compound **6d** in $CDCl_3$

6. X-ray data for compound 6c

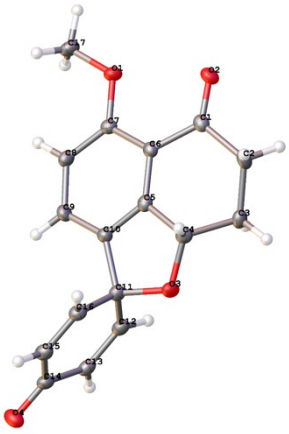


Table 1: Crystal data and structure refinement for exp_6702 (**6c**, **CCDC 2362105**)

Identification code	exp_6702
Empirical formula	$C_{17}H_{14}O_4$
Formula weight	282.28
Temperature / K	111.10(14)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a / Å, b / Å, c / Å	7.8979(2), 11.9743(4), 14.4105(4)
α/°, β/°, γ/°	90.00, 90.00, 90.00
Volume / Å^3	1362.81(7)
Z	4
ρ_{calc} / mg mm^{-3}	1.376
μ / mm^{-1}	0.808
F(000)	592
Crystal size / mm^3	0.24 × 0.23 × 0.17
2Θ range for data collection	9.6 to 142.08°
Index ranges	$-9 \le h \le 6$, $-14 \le k \le 12$, $-17 \le l \le 11$
Reflections collected	6221
Independent reflections	2583[R(int) = 0.0252 (inf-0.9Å)]
Data/restraints/parameters	2583/0/191
Goodness-of-fit on F^2	1.057
Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	R_1 = 0.0365, wR_2 = 0.0975
Final R indexes [all data]	R_1 = 0.0384, wR_2 = 0.0997
Largest diff. peak/hole / e Å^{-3}	0.260/-0.240
Flack Parameters	0.1(2)
Completeness	0.9979