Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Organocatalytic Atroposelective Construction of Axial Chiral Nonsymmetric Biaryltriols and their Applications on Asymmetric Synthesis and Heavy Metal Ion Detection

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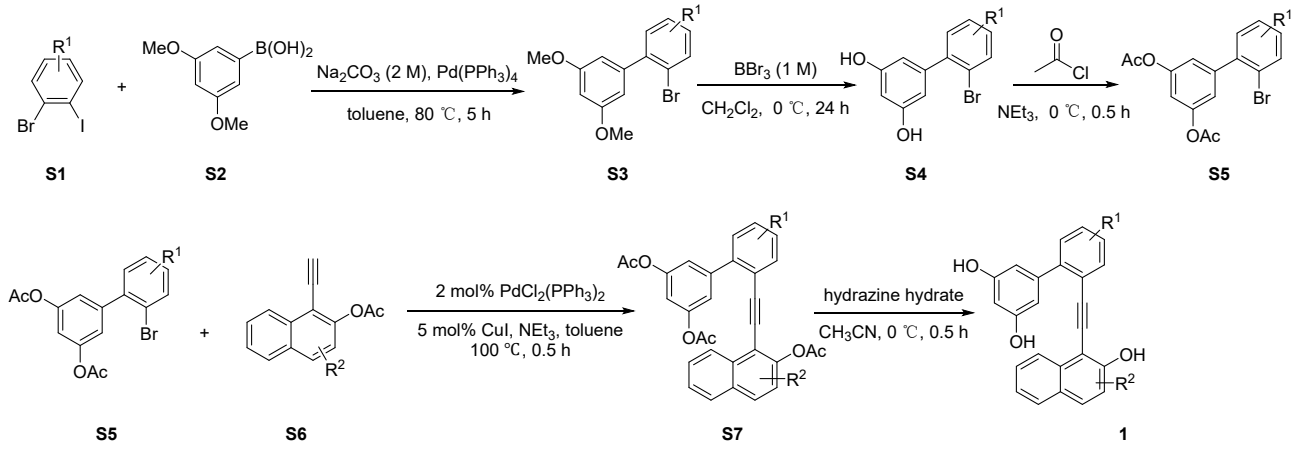
Supporting Information

I. General procedure for the synthesis of substrate 1a-1u.



General procedure for the synthesis of derivatives S3: **S1** (10 mmol, 1.0 equiv) were dissolved in toluene (20 mL). Then, 3,5-dimethoxyphenylboronic acid **S2** (1.1 equiv) in EtOH (3 mL) and aqueous Na_2CO_3 (2 M, 3.0 equiv) were added to each reactor, and the resulting mixtures were deoxygenated with a stream of N_2. After 10 min, $Pd(PPh_3)_4$ (0.02 equiv) was added, and stirred under N_2 at 80 ℃ for 5 h, cooled to room temperature, and treated as follows. Each solution was poured into a mixture of H_2O and EA, and the two phases were separated. The aqueous layer was washed with EA, and the organic phases were combined and washed with 1 M NaOH followed by brine. The ethereal solution was dried over Na_2SO_4 and evaporated. Purification of each crude product by flash chromathography using PE/EA = 95:5 yielded the corresponding **S3** as colorless oil.

General procedure for the synthesis of derivatives S4: S3 (1 equiv) were dissolved in anhydrous CH_2Cl_2 (30 mL) at -78 °C. Then, BBr_3 (1 M in CH_2Cl_2, 3 equiv) was added to solution, and the resulting reaction mixture was allowed to warm to room temperature for 24 h, cooled to 0 °C, and treated as follows. The CH_3OH and H_2O was injected into solution slowly, and the two phases were separated. The aqueous layer was washed twice with CH_2Cl_2, and the organic phases were combined and washed with a 1 M solution of sodium thiosulfate followed by H_2O. The organic layer was dried over Na_2SO_4 and evaporated to dryness, which was directly used without purification.

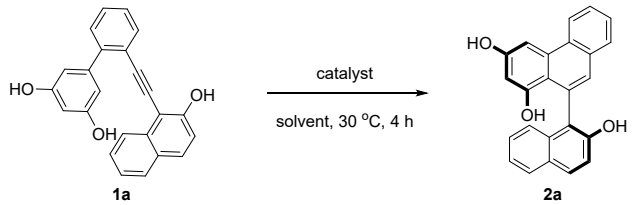
General procedure for the synthesis of derivatives S5: In a 100 mL Schlenk flask, **S4** was dissolved in CH_2Cl_2 (25 mL) and NEt_3 (3 equiv). Acetyl chloride (3 equiv) was added slowly to the solution at 0 °C, which was then stirred for 30 min at room temperature. The reaction was quenched by addition of $NaHSO_3$ solution and extracted with CH_2Cl_2 several times. The combined organic phases were dried over Na_2SO_4, which was directly used without purification.

General procedure for the synthesis of derivatives S6: see reference 1.

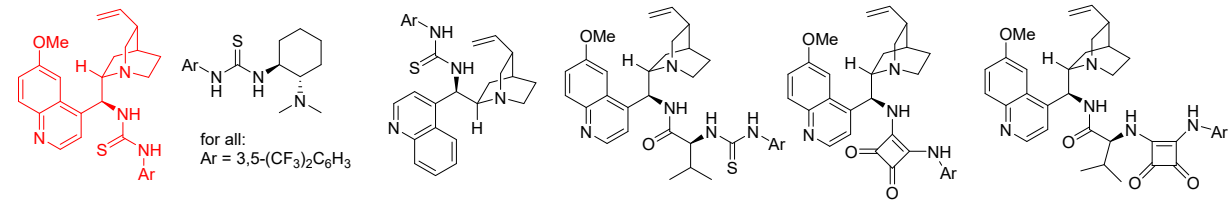
General procedure for the synthesis of derivatives S7: To a dry flask under N_2 containing **S5** was sequentially added Et_3N (20 mL) and toluene (20 mL), $PdCl_2(PPh_3)_2$ (0.02 equiv), CuI (0.05 equiv). then appropriate alkynes (1.1 equiv) was injected into solution at 100 °C, The mixture was stirred for 30 minutes. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel (PE/EA= 5:1) to afford **S7**.

General procedure for the synthesis of derivatives 1: Hydrazine monohydrate (4 equiv) was dropwise added to a solution of **S7** in CH_3CN (20 mL). After the resulted mixture was stirred at room temperature for 30 minutes, the mixture was treated with sat. aq. NH_4Cl and extracted with EA and dried over Na_2SO_4. Removal of solvent under reduced pressure afforded a residue which is purified by column chromatography on silica gel (PE/Acetone = 2:1) to afford the compound **1**.

II. Optimization of the reaction conditions[a]



1a 2a



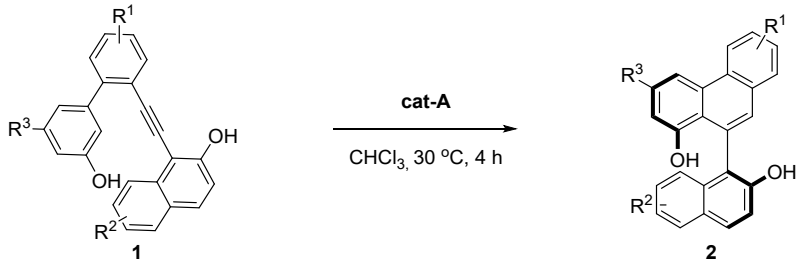
A B C D E F

entry	catalyst	solvent	yield (%)[b]	ee (%)[c]
1	A	$CHCl_3$	98	98
2	B	$CHCl_3$	80	92
3	C	$CHCl_3$	75	-95
4	D	$CHCl_3$	10	87
5	E	$CHCl_3$	96	98
6	F	$CHCl_3$	10	73

7	**A**	**CH_2Cl_2**	**78**	**96**
8	**A**	**$ClCH_2CH_2Cl$**	**88**	**96**
9	**A**	**toluene**	**67**	**98**
10	**A**	**CH_3OH**	**33**	**97**
11	**A (5 mol%)**	**$CHCl_3$**	**50**	**97**
12	**A (20 mol%)**	**$CHCl_3$**	**98**	**98**
13[d]	**A**	**$CHCl_3$**	**98**	**97**
14[e]	**A**	**$CHCl_3$**	**98**	**98**

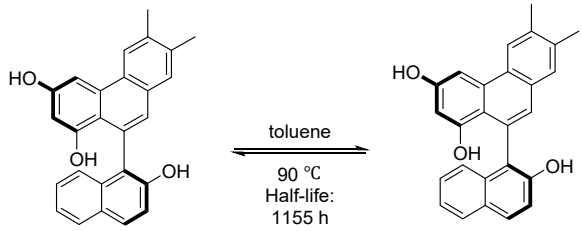
[a] Reaction conditions: **1a** (0.1 mmol), catalyst (10 mol%) in solvent (2.0 mL) at 30 °C for 4 h, unless otherwise specified. [b]: Isolated yields. [c]: The ee value was determined by HPLC analysis. [d]: 4.0 mL $CHCl_3$. [e] 1.0 mL $CHCl_3$, 12 h.

III. General procedure for the asymmetric reaction.



The substrate **1** (0.1 mmol), **cat-A** (10 mol%) were added to a 10 mL flame-dried schlenk tube with a magnetic stirring bar. Chloroform (2 mL) was injected into the tube. After stirring for specific time, The mixture was evaporated and purified by flash column chromatography (SiO_2, DCM: Acetone = 20:1 or PE: Acetone = 2:1) to afford the product **2**. Racemic samples were prepared with NEt_3 as additive base.

IV. Racemization studies of 2n



(*R*)-**2n** (*S*)-**2n**

Thermal Racemization of **2n:** A solution of **2n** (5 mg, 98% ee) in toluene (15 mL) was heated at 90 ℃. At intervals, small samples were taken and the solvent was removed by evaporation. The enantiomeric excess was determined by using HPLC (HPLC conditions: Chiralcel OD-H, Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm).

Time (h)	(%t)	ln ((%t-50)/(%0-50))
0	98.442	-1.1E-16
3	98.226	-0.00447
12	97.832	-0.01267
24	97.566	-0.01825
37	97.268	-0.02453

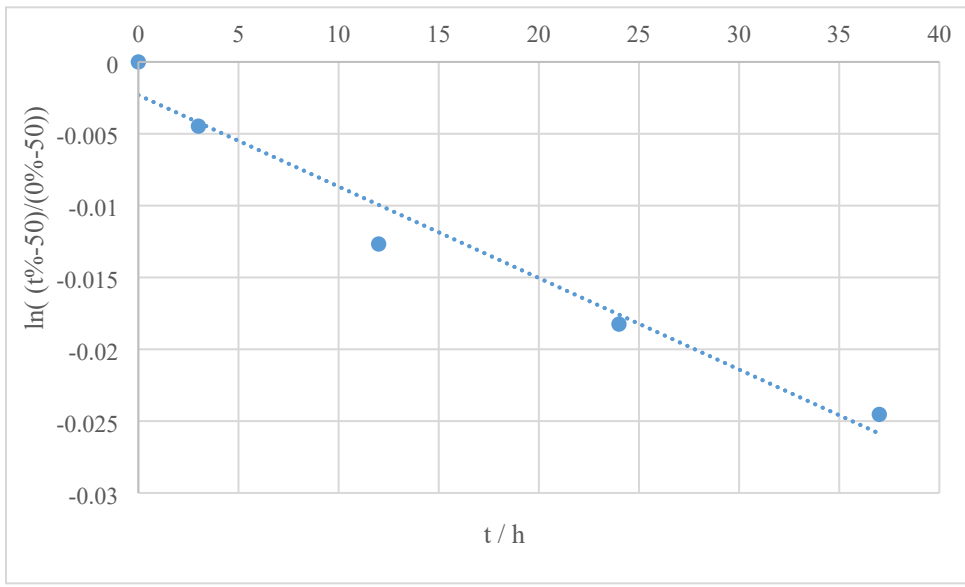


Fig S1. Kinetic line

V. Application as selective fluorescence sensors toward heavy metal detectives.

General fluorescence spectra measurements: The stock solutions of **2p** were prepared by directly dissolving in CH_3CN For the spectroscopic determination, A variety of stock solutions of metal salts (1×10^{-1} M) including Fe^{2+}, Na^{+}, Ce^{3+}, Mg^{2+}, Fe^{3+}, Zn^{2+}, In^{3+}, Ca^{2+}, Ni^{3+}, Ir^{3+}, K^{+}, Ag^{+}, Ba^{2+}, Rb^{+}, Ru^{3+} were also dissolved in H_2O and diluted to the desired concentrations. For titration of metallic ions, aliquots of 2 μL aqueous metallic ion solutions were added to 200 μL diluted **2p** solution. The measurements were performed after 1 min of response time. All experiments were carried out at 298 K. To make sure the reproducibility and stability of experimental data, all experiments were tested at least three times.

The fluorescence response behaviors of the prepared axial chiral biaryltriols **2p** on various main group and transition metal ions have been investigated. Ru^{3+} ion exhibited the most pronounced fluorescence response of **2p**, Beyond Ru^{3+} ion (Fig. S2). The fluorescence intensities of **2p** are almost not significantly affected by the addition of other ions respectively. It is indicated that **2p** may be potentially applied as heavey metal detective reagent in pharmaceutical and everomental analysis.

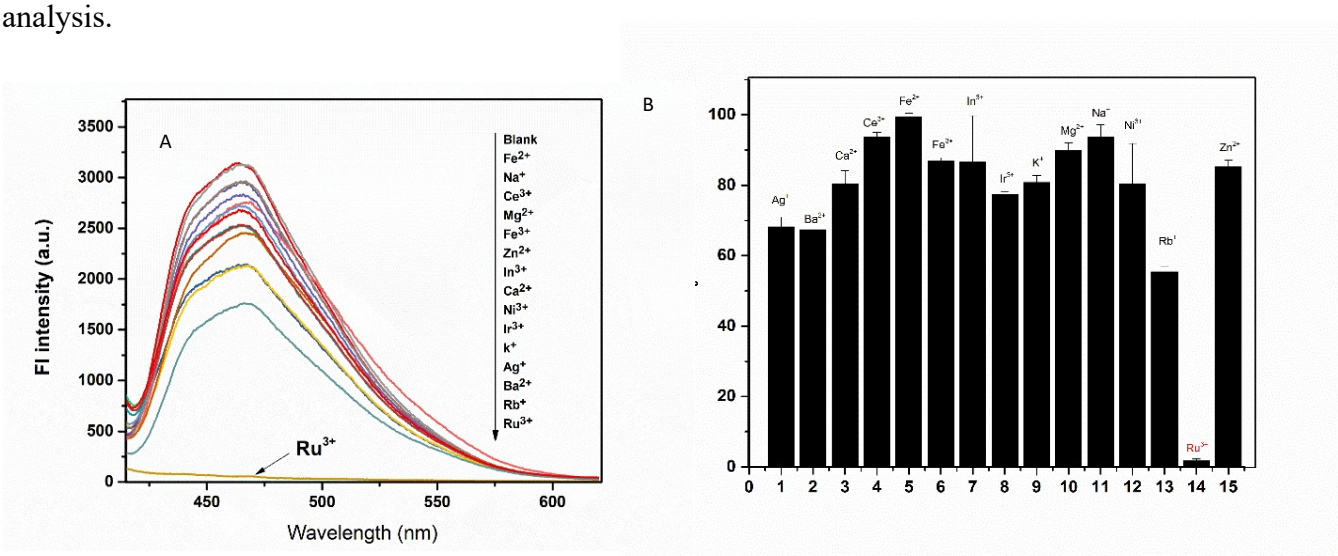
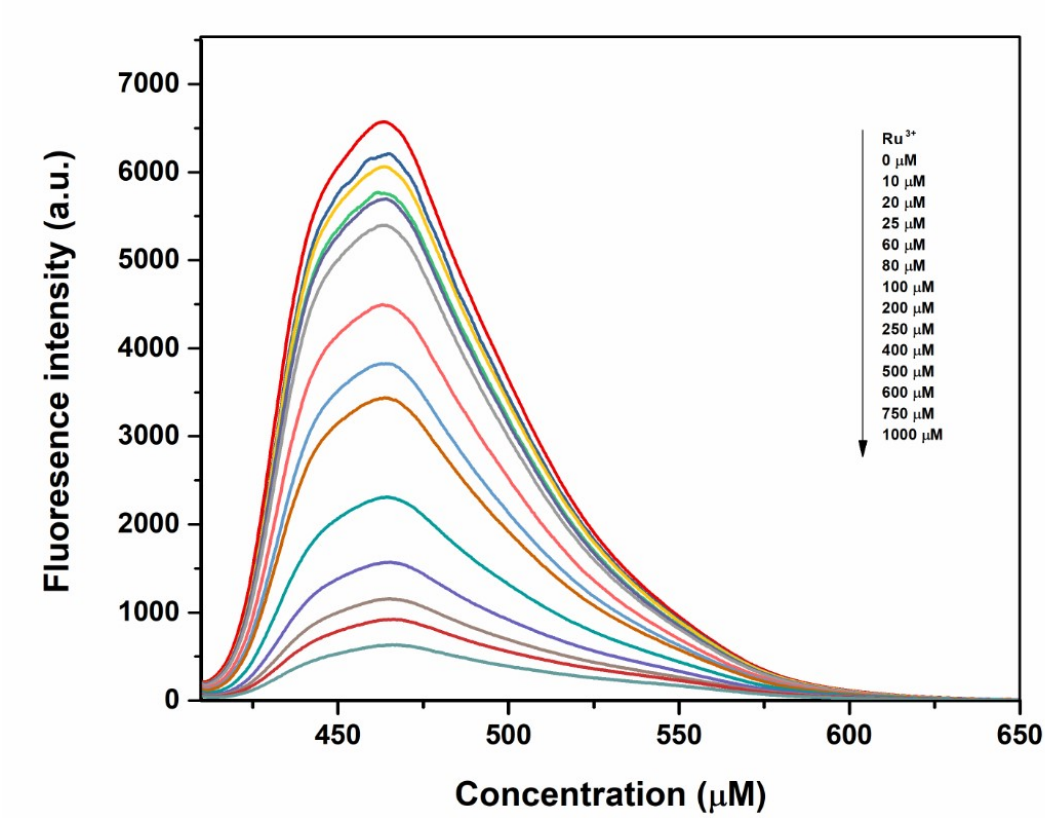


Fig S2. The influence of different main group and transition metal ions.

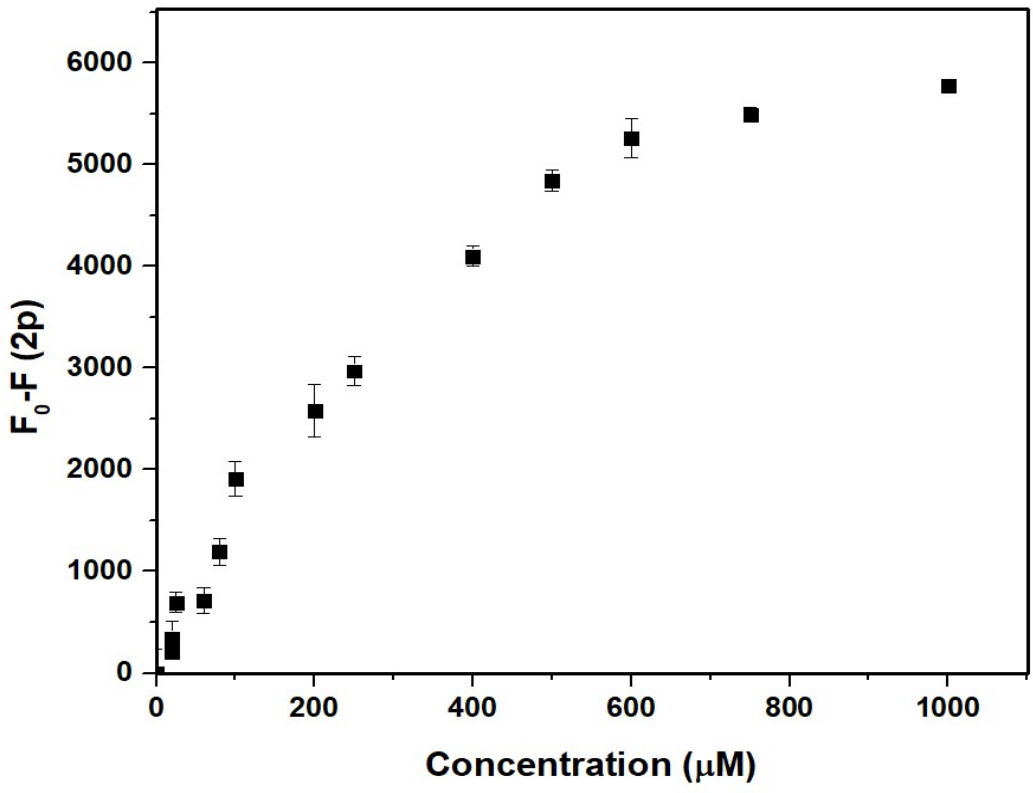
Fig S2. A: Emission spectra of **2p** (1.0×10^{-3} M) in CH_3CN solution in the absence and the presence of 1.0×10^{-3} M of different various main group and transition metal ions at 25 ºC. excitation wavelength: 400 nm; excitation and emission slits (nm): 5.0 nm and 5.0 nm, respectively. Voltage: 800 V. B: Representative bar chart of **2p** (F/F_0 %), where F_0 and F were emission intensities of

sensor **2p** at 463 nm (λ_{ex} = 400 nm) in the absence and the presence of different various main group and transition metal ions.

A



B



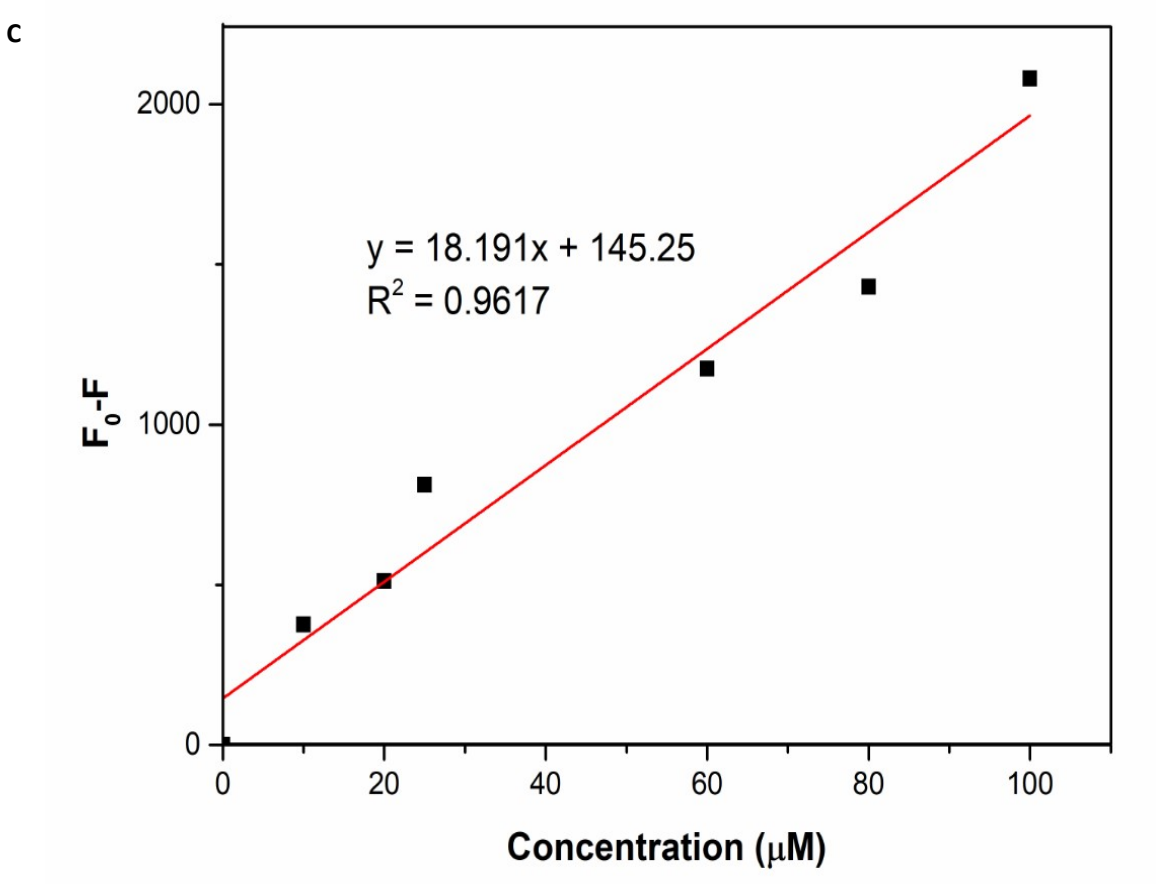


Fig S3. A: Fluorescence intensity response in the presence of 1×10^{-2} M. **2p** and with increasing concentration of Ru^{3+}: 0, 10, 20, 25, 60, 80, 100, 200, 250, 400, 500, 600, 750, 1000 μM. (excitation wavelength: 400 nm; excitation 3and emission slits (nm): 5.0 nm and 5.0 nm, respectively. Voltage: 700 V). **B**: Plot of F_0-F where F_0 and F were emission intensities of sensor **2p** at 463 nm (λ_{ex} = 400 nm) in the absence and the presence of different concentration of Ru^{3+}. **C**: Linear relationship of F_0 – F versus the concentration of Ru^{3+} over the range of 0-100 μM. the detective concentration limitation of **2p** toward Ru^{3+} was then calculated to be 25 μM according to **3σ** method.[4]

$$Limit\ of\ Detection = \frac{3X\ Standard\ deviation\ of\ the\ intercept}{Slope\ of\ the\ intercept}$$

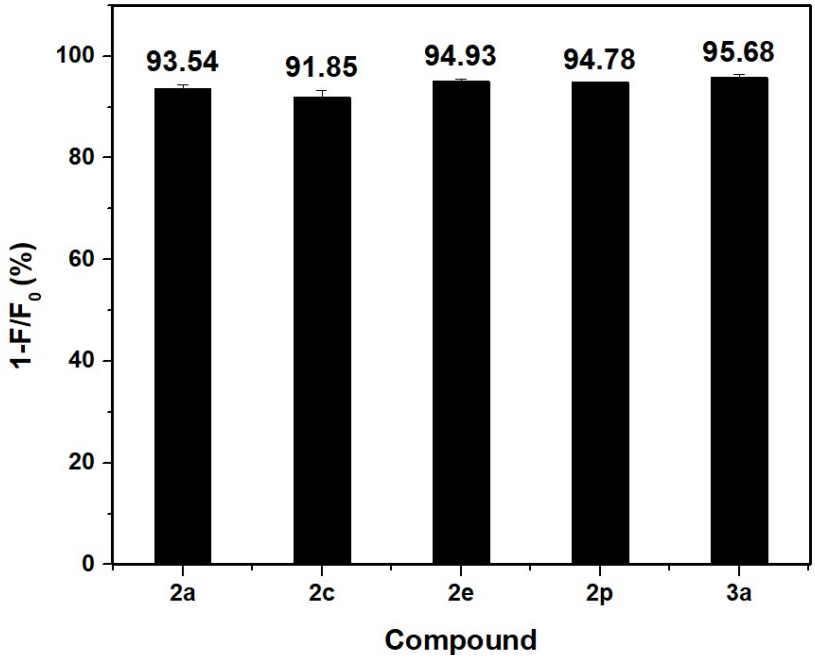


Fig S4: Bar chart of fluorescence intensity of **2a**, **2c**, **2e**, **2p**, **3a** (1.0×10^{-2} M)

Fig S4: Fluorescence quenching degrees ($1\text{-}F/F_0$) in the presence of Ru^{3+} (1.0×10^{-3} M). F and F_0 are taken as the fluorescence intensity in the absence and the presence of Ru^{3+} at 463 nm.

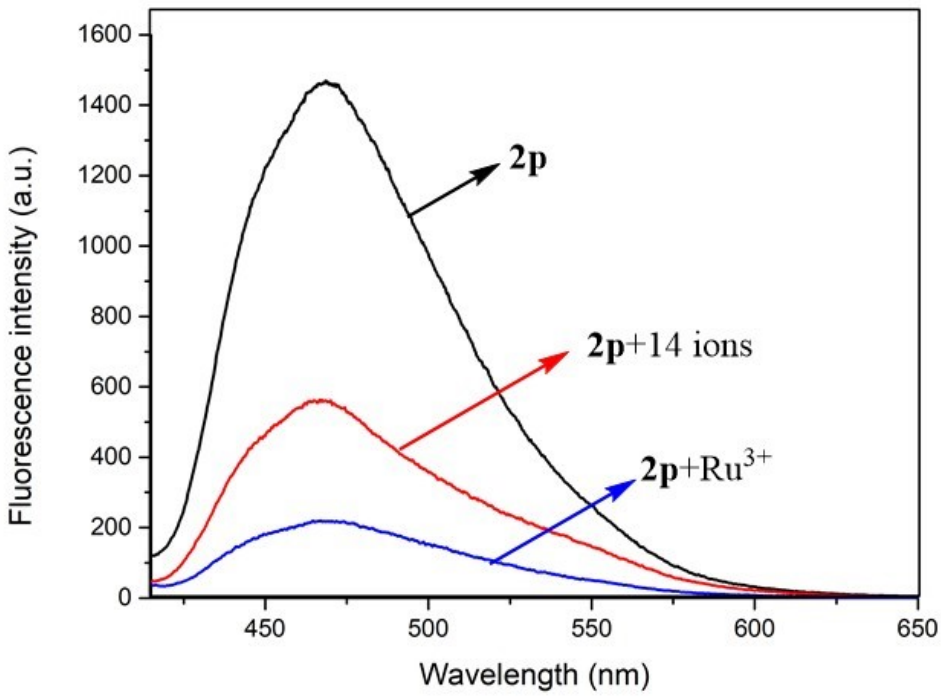


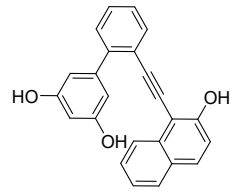
Fig S5: Metal ion specificity.

Fig S5: Emission spectra of a CH_3CN solution of **2p** (1.0×10^{-2} M). the concentration of each metal

ion added is 1.0 ×10^{-3} M; emission spectra of **2p** with 14 interference ions (black); emission spectra of **2p** with only Ru^{3+} ion (red); emission spectra of **2p** with 14 interference ions and Ru^{3+} ion (blue).

VI. ^{1}H, ^{13}C NMR and HRMS data of compounds (1a-1u)

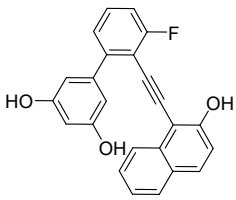
2'-((2-hydroxynaphthalen-1-yl)ethynyl)-[1,1'-biphenyl]-3,5-diol (1a)



1a

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.44 (s, 3H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.78 (dd, *J* = 8.1, 4.2 Hz, 2H), 7.49 – 7.38 (m, 4H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.19 (d, *J* = 8.9 Hz, 1H), 6.71 (s, 2H), 6.55 (s, 1H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 159.25, 157.60, 144.69, 143.87, 135.02, 133.35, 131.04, 129.89, 129.02, 128.90, 128.60, 128.08, 127.85, 125.85, 124.38, 122.71, 118.04, 108.60, 103.97, 102.60, 99.92, 86.96. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{16}NaO_3, M+Na]^+$: 375.0992, Found: 375.0912.

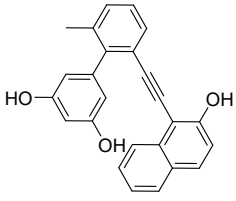
3'-fluoro-2'-((2-hydroxynaphthalen-1-yl)ethynyl)-[1,1'-biphenyl]-3,5-diol (1b)



1b

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.41 (s, 3H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.81 (t, *J* = 8.1 Hz, 2H), 7.54 – 7.44 (m, 2H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.27 (dd, *J* = 14.6, 8.2 Hz, 2H), 7.22 (d, *J* = 8.9 Hz, 1H), 6.74 (d, *J* = 2.1 Hz, 2H), 6.53 (t, *J* = 2.0 Hz, 1H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 163.38 (d, *J* = 248.0 Hz), 159.33, 157.91, 146.67, 142.45, 134.90, 131.50, 130.30 (d, *J* = 9.0 Hz), 128.91, 128.77, 128.24, 125.75 (d, *J* = 3.0 Hz), 125.62, 124.51, 117.91, 114.75, 114.54, 111.58 (d, *J* = 16.0 Hz), 108.52, 103.71, 103.06, 92.65. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{15}FNaO_3, M + Na]^+$: 393.0897, Found: 393.0845

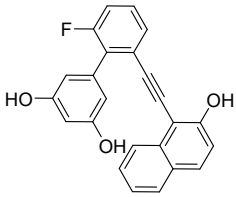
2'-((2-hydroxynaphthalen-1-yl)ethynyl)-6'-methyl-[1,1'-biphenyl]-3,5-diol (1c)



1c

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.17 (s, 1H), 9.34 (s, 2H), 7.77 – 7.70 (m, 2H), 7.51 (d, *J* = 6.2 Hz, 1H), 7.30 (q, *J* = 7.4, 5.8 Hz, 4H), 7.17 (t, *J* = 7.9 Hz, 2H), 6.36 (s, 1H), 6.16 (s, 2H), 2.11 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 158.79, 157.25, 143.90, 142.10, 135.87, 134.29, 130.13, 129.72, 129.32, 127.91, 127.45, 127.34, 127.26, 124.97, 123.43, 123.08, 117.88, 107.19, 102.82, 101.59, 98.14, 87.36, 20.28. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{18}NaO_3, M + Na]^+$: 389.1148, Found: 389.1093.

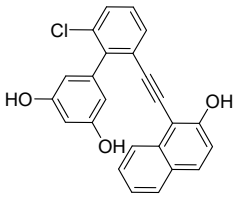
2'-fluoro-6'-((2-hydroxynaphthalen-1-yl)ethynyl)-[1,1'-biphenyl]-3,5-diol (1d)



1d

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.32 (s, 1H), 9.41 (s, 2H), 7.80 – 7.74 (m, 2H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.45 (q, *J* = 7.8 Hz, 1H), 7.35 – 7.27 (m, 4H), 7.18 (d, *J* = 8.9 Hz, 1H), 6.39 (s, 1H), 6.32 (s, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 159.21 (d, *J* = 242.0 Hz), 158.69, 157.85, 135.67, 134.32, 131.26 (d, *J* = 18.0 Hz), 130.73, 129.30 (d, *J* = 10.0 Hz), 128.16 (d, *J* = 2.0 Hz), 128.08, 127.51 (d, *J* = 4.0 Hz), 125.23, 127.49, 124.74, 123.56, 117.94, 115.67 (d, *J* = 23.0 Hz), 108.13, 102.39, 102.23, 96.50 (d, *J* = 4.0 Hz), 88.75. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{15}FNaO_3, M + Na]^+$: 393.0897, Found: 393.0852.

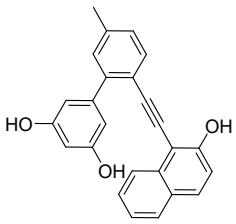
2'-chloro-6'-((2-hydroxynaphthalen-1-yl)ethynyl)-[1,1'-biphenyl]-3,5-diol (1e)



1e

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.35 (s, 1H), 9.48 (s, 2H), 7.78 (dd, *J* = 8.3, 5.6 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.28 – 7.20 (m, 2H), 6.49 (t, *J* = 2.0 Hz, 1H), 6.31 (d, *J* = 2.1 Hz, 2H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 158.84, 157.82, 142.33, 140.03, 134.33, 132.85, 130.77, 130.68, 129.12, 129.03, 128.09, 127.57, 127.51, 125.48, 124.83, 123.61, 117.99, 107.56, 102.36, 102.29, 96.92, 88.99. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{15}ClNaO_3, M + Na]^+$: 409.0602, Found: 409.0583.

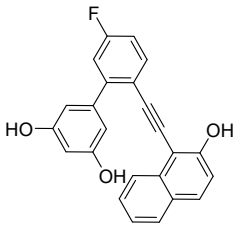
2'-((2-hydroxynaphthalen-1-yl)ethynyl)-5'-methyl-[1,1'-biphenyl]-3,5-diol (1f)



1f

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.38 (s, 3H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.25 (s, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.9 Hz, 1H), 6.69 (d, *J* = 2.2 Hz, 2H), 6.53 (t, *J* = 2.2 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 159.25, 157.41, 144.67, 143.99, 139.15, 135.01, 133.31, 130.81, 130.60, 128.95, 128.62, 128.59, 128.03, 125.92, 124.35, 119.78, 118.01, 108.59, 104.22, 102.56, 100.21, 86.16, 21.28. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{18}NaO_3, M + Na]^+$: 389.1148, Found: 389.1105.

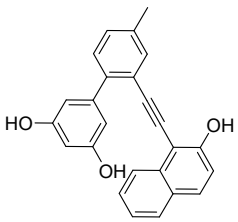
5'-fluoro-2'-((2-hydroxynaphthalen-1-yl)ethynyl)-[1,1'-biphenyl]-3,5-diol (1g)



1g

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.28 (s, 1H), 9.48 (s, 2H), 7.80 (t, *J* = 9.3 Hz, 3H), 7.68 (d, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.37 – 7.19 (m, 4H), 6.53 (s, 2H), 6.43 (s, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 161.57 (d, *J* = 246.0 Hz), 158.63, 157.68, 146.18 (d, *J* = 8.0 Hz), 141.42, 134.85 (d, *J* = 8.0 Hz), 134.33, 130.35, 128.09, 127.56, 127.43, 124.87, 123.53, 118.58 (d, *J* = 3.0 Hz), 118.00, 116.18 (d, *J* = 22.0 Hz), 114.72 (d, *J* = 22.0 Hz), 107.43, 102.66, 102.29, 96.80, 87.44. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{15}FNaO_3, M + Na]^+$:393.0897, Found: 393.0847.

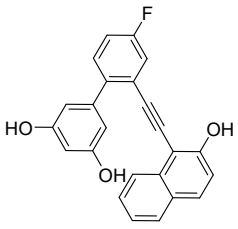
2'-((2-hydroxynaphthalen-1-yl)ethynyl)-4'-methyl-[1,1'-biphenyl]-3,5-diol (1h)



1h

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.42 (s, 3H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.77 (dd, *J* = 8.4, 2.9 Hz, 2H), 7.64 (s, 1H), 7.49 – 7.43 (m, 1H), 7.32 (dd, *J* = 7.3, 5.7 Hz, 2H), 7.27 – 7.22 (m, 1H), 7.19 (d, *J* = 8.9 Hz, 1H), 6.69 (d, *J* = 2.1 Hz, 2H), 6.53 (t, *J* = 2.1 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 159.24, 157.58, 143.83, 141.98, 137.49, 135.04, 133.71, 130.96, 129.88, 129.83, 128.93, 128.60, 128.07, 125.90, 124.37, 122.48, 118.03, 108.63, 104.07, 102.46, 100.20, 86.53, 20.73. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{18}NaO_3, M + Na]^+$: 389.1148, Found: 389.1112.

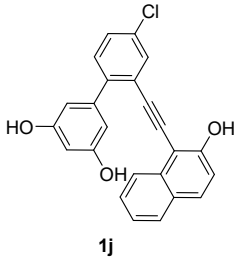
4'-fluoro-2'-((2-hydroxynaphthalen-1-yl)ethynyl)-[1,1'-biphenyl]-3,5-diol (1i)



1i

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.47 (s, 3H), 7.83 – 7.76 (m, 3H), 7.61 (dd, *J* = 9.7, 2.8 Hz, 1H), 7.47 – 7.42 (m, 2H), 7.33 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 7.23 (td, *J* = 8.5, 2.8 Hz, 1H), 7.19 (d, *J* = 9.0 Hz, 1H), 6.65 (d, *J* = 2.2 Hz, 2H), 6.53 (t, *J* = 2.2 Hz, 1H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 162.19 (d, *J* = 244.0 Hz), 159.34, 158.02, 142.88, 141.21, 135.06, 131.83 (d, *J* = 8.0 Hz), 131.53, 128.91, 128.65, 128.24, 125.81, 124.64 (d, *J* = 9.0 Hz), 124.47, 119.27 (d, *J* = 23.0 Hz), 118.14, 116.02, (d, *J* = 21.0 Hz), 108.73, 103.46, 102.74, 98.71, 88.06. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{15}FNaO_3, M + Na]^+$: 393.0897, Found: 393.0847.

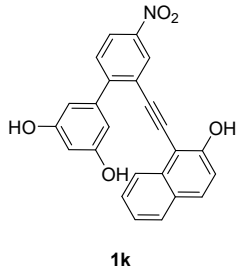
4'-chloro-2'-((2-hydroxynaphthalen-1-yl)ethynyl)-[1,1'-biphenyl]-3,5-diol (1j)



1j

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.59 (s, 3H), 7.91 (s, 1H), 7.84 (d, *J* = 8.3 Hz, 1H), 7.81 – 7.74 (m, 2H), 7.45 (d, *J* = 12.8 Hz, 3H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 8.9 Hz, 1H), 6.74 (s, 2H), 6.62 (s, 1H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 159.26, 157.95, 143.23, 142.57, 134.94, 133.03, 132.45, 131.51, 131.42, 128.83, 128.79, 128.60, 128.18, 125.69, 124.51, 124.41, 118.11, 108.55, 103.34, 102.87, 98.47, 88.32. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{15}ClNaO_3$, M + Na$]^+$: 409.0602, Found: 409.0583.

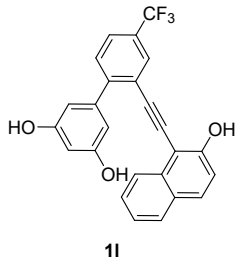
2'-((2-hydroxynaphthalen-1-yl)ethynyl)-4'-nitro-[1,1'-biphenyl]-3,5-diol (1k)



1k

^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ 8.85 (s, 1H), 8.68 (s, 1H), 8.54 (s, 2H), 8.27 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 6.73 (s, 2H), 6.61 (s, 1H). **^{13}C NMR** (150 MHz, $(CD_3)_2CO$): δ 159.63, 158.52, 150.62, 147.81, 141.94, 135.15, 131.99, 131.34, 128.96, 128.74, 128.38, 127.88, 127.84, 125.72, 124.57, 124.49, 123.37, 123.34, 118.35, 108.45, 103.66, 103.11, 97.77, 89.52. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{15}NNaO_5$, M + Na$]^+$: 420.0842, Found: 420.0782

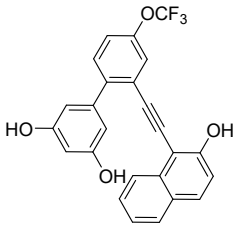
2'-((2-hydroxynaphthalen-1-yl)ethynyl)-4'-(trifluoromethyl)-[1,1'-biphenyl]-3,5-diol (1l)



1l

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.34 (s, 1H), 9.53 (s, 2H), 8.11 (s, 1H), 7.81 (q, *J* = 8.1Hz, 3H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.38 (dt, *J* = 18.4, 6.7 Hz, 2H), 7.23 (d, *J* = 8.9 Hz, 1H), 6.60 – 6.51 (m, 2H), 6.45 (s, 1H). **^{13}C NMR** (100 MHz, DMSO-*d*6): δ 158.76, 158.15, 147.44, 141.21, 134.29, 131.03, 130.37, 129.02, 129.01, 128.26 (q, *J* = 31.0 Hz), 128.15, 127.61, 127.56, 124.77, 124.10 (q, *J* = 271.0 Hz), 123.66, 123.09, 120.56, 118.12, 107.33, 102.46, 102.01, 96.51, 89.28. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{15}F_3NaO_3$, M + Na$]^+$: 443.0866, Found: 443.0811.

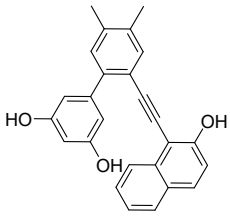
2'-((2-hydroxynaphthalen-1-yl)ethynyl)-4'-(trifluoromethoxy)-[1,1'-biphenyl]-3,5-diol (1m)



1m

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.33 (s, 1H), 9.47 (s, 2H), 7.81 (t, J = 7.8 Hz, 2H), 7.74 (d, J = 7.1 Hz, 1H), 7.61 (t, J = 9.4 Hz, 1H), 7.52 (dd, J = 8.2, 5.8 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.37 (dq, J = 14.6, 7.1 Hz, 2H), 7.22 (dd, J = 8.8, 5.7 Hz, 1H), 6.54 – 6.46 (m, 2H), 6.45 – 6.38 (m, 1H). **^{13}C NMR** (100 MHz, DMSO-*d*6): δ 158.63, 158.62, 158.07, 147.29, 143.02, 141.18, 134.26, 131.21, 130.96, 128.10, 127.55, 127.51, 124.74, 124.33, 123.86, 123.84, 123.61, 120.99, 120.26, 118.04 (q, J = 255.0 Hz), 107.43, 102.14, 102.00, 96.44, 89.13. **HRMS (ESI)** m/z Calcd for [$C_{25}H_{15}F_3NaO_4$, M + Na]$^+$: 459.0815, Found: 459.0769.

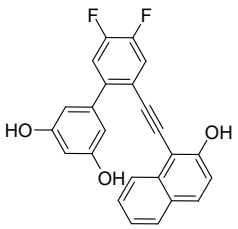
2'-((2-hydroxynaphthalen-1-yl)ethynyl)-4',5'-dimethyl-[1,1'-biphenyl]-3,5-diol (1n)



1n

^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ 8.30 (s, 3H), 7.89 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.58 (s, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.31 (t, J = 7.3 Hz, 1H), 7.23 – 7.15 (m, 2H), 6.67 (s, 2H), 6.50 (s, 1H), 2.32 (d, J = 9.6 Hz, 6H). **^{13}C NMR** (150 MHz, $(CD_3)_2CO$): δ 159.24, 157.39, 143.95, 142.43, 137.97, 136.27, 135.04, 134.23, 131.15, 130.75, 129.01, 128.60, 128.03, 125.99, 124.37, 119.92, 118.02, 108.65, 104.33, 102.43, 100.49, 85.79, 19.61, 19.10. **HRMS (ESI)** m/z Calcd for [$C_{26}H_{20}NaO_3$, M + Na]$^+$: 403.1305, Found: 403.1258.

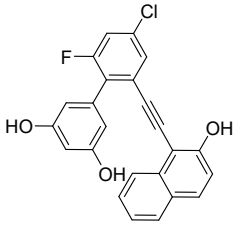
4',5'-difluoro-2'-((2-hydroxynaphthalen-1-yl)ethynyl)-[1,1'-biphenyl]-3,5-diol (1o)



1o

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.29 (s, 1H), 9.47 (s, 2H), 7.89 – 7.72 (m, 3H), 7.60 (s, 1H), 7.53 – 7.46 (m, 1H), 7.35 (dt, J = 14.4, 7.5 Hz, 2H), 7.21 (d, J = 8.8 Hz, 1H), 6.48 (s, 2H), 6.41 (s, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ 158.61, 157.95, 149.00 (dd, J = 254.5, 13.0 Hz), 148.42 (dd, J = 245.5, 13.0 Hz), 141.55 (dd, J = 5.0, 3.0 Hz), 140.57, 134.25, 130.78, 128.11, 127.51, 124.74, 123.59, 121.40 (dd, J = 18.0, 3.0 Hz), 119.08, (dd, J = 9.0, 4.0 Hz) , 118.39 (dd, J = 19.0, 3.0 Hz), 118.01, 107.50 (d, J = 5.0 Hz), 102.28 (d, J = 5.0 Hz), 102.07, 95.87, 88.22. **HRMS (ESI)** m/z Calcd for [$C_{24}H_{14}F_2NaO_3$, M+Na]$^+$: 411.0803, Found: 411.0795.

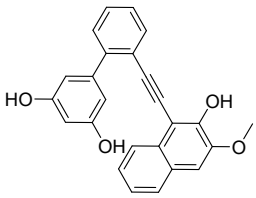
4'-chloro-2'-fluoro-6'-((2-hydroxynaphthalen-1-yl)ethynyl)-[1,1'-biphenyl]-3,5-diol (1p)



1p

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.35 (s, 1H), 9.48 (s, 2H), 7.87 – 7.74 (m, 2H), 7.66 (s, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.33 (s, 3H), 7.18 (d, J = 8.4 Hz, 1H), 6.41 (s, 1H), 6.33 (s, 2H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 160.25 (d, J = 246.0 Hz), 159.47, 158.23, 135.90, 134.99, 133.77 (d, J = 12.0 Hz), 131.92, 131.02 (d, J = 18.0 Hz), 128.81, 128.64, 128.33, 127.28 (d, J = 2.0 Hz), 125.62, 124.50, 118.17, 116.79, 116.51, 109.29, 103.50, 102.93, 97.30 (d, J = 3.0 Hz), 89.53. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{14}ClFNaO_3, M+Na]^+$: 427.0508, Found: 427.0486.

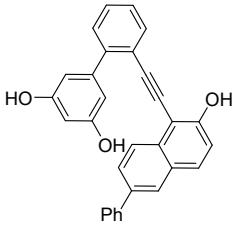
2'-((2-hydroxy-3-methoxynaphthalen-1-yl)ethynyl)-[1,1'-biphenyl]-3,5-diol (1q)



1q

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.72 (s, 1H), 9.37 (s, 2H), 7.70 (d, J = 7.3 Hz, 2H), 7.56 (d, J = 8.1 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.40 – 7.36 (m, 1H), 7.34 (s, 1H), 7.30 (t, J = 7.3 Hz, 1H), 7.25 (d, J = 7.8 Hz, 1H), 6.50 – 6.42 (m, 2H), 6.36 (s, 1H), 3.94 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-*d*6): δ 158.46, 149.46, 148.09, 143.90, 142.52, 132.61, 129.22, 129.10, 128.44, 127.92, 127.41, 126.66, 124.92, 124.67, 123.99, 121.79, 107.61, 107.59, 107.46, 107.39, 103.57, 101.82, 97.64, 87.38, 55.96. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{18}NaO_4, M + Na]^+$: 405.1097, Found: 405.1023.

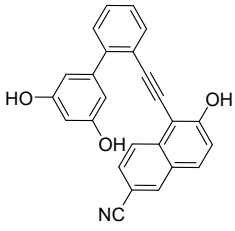
2'-((2-hydroxy-6-phenylnaphthalen-1-yl)ethynyl)-[1,1'-biphenyl]-3,5-diol (1r)



1r

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.51 (d, J = 26.8 Hz, 3H), 8.06 (s, 1H), 7.93 (d, J = 8.6 Hz, 1H), 7.86 (dd, J = 15.0, 8.0 Hz, 2H), 7.80 – 7.71 (m, 3H), 7.43 (ddt, J = 24.9, 14.7, 7.3 Hz, 6H), 7.23 (d, J = 8.9 Hz, 1H), 6.72 (s, 2H), 6.58 (s, 1H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 159.32, 157.77, 144.84, 143.96, 141.45, 136.91, 134.37, 133.36, 131.42, 129.90, 129.61, 129.26, 129.05, 127.88, 127.62, 127.32, 126.66, 126.34, 122.79, 118.60, 108.69, 104.00, 102.63, 99.91, 87.02. **HRMS (ESI)** m/z Calcd for $[C_{30}H_{20}NaO_3, M + Na]^+$: 451.1305, Found: 451.1289.

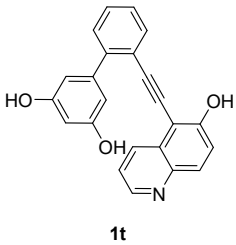
5-((3',5'-dihydroxy-[1,1'-biphenyl]-2-yl)ethynyl)-6-hydroxy-2-naphthonitrile (1s)



1s

^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ 9.18 (s, 1H), 8.41 (s, 2H), 8.32 (s, 1H), 7.95 (d, *J* = 8.9 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.81 (d, *J* = 7.4 Hz, 1H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 8.9 Hz, 1H), 6.64 (d, *J* = 1.9 Hz, 2H), 6.57 (s, 1H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 159.99, 159.33, 145.11, 143.99, 137.00, 134.65, 133.33, 131.57, 129.91, 129.33, 128.46, 127.98, 127.96, 127.29, 122.51, 120.19, 119.76, 108.71, 107.53, 104.75, 102.67, 100.50, 85.98. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{15}NaO_3, M + Na]^+$: 400.0944, Found: 400.0876.

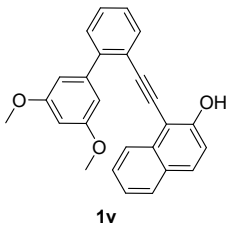
2'-((6-hydroxyquinolin-5-yl)ethynyl)-[1,1'-biphenyl]-3,5-diol (1t)



1t

^{1}H NMR (400 MHz, DMSO-d_6): δ 10.70 (s, 1H), 9.49 (s, 2H), 8.75 (s, 1H), 7.94 (t, *J* = 8.6 Hz, 2H), 7.76 (d, *J* = 6.5 Hz, 1H), 7.47 (dd, *J* = 17.6, 9.5 Hz, 4H), 7.37 (dd, *J* = 8.0, 3.6 Hz, 1H), 6.51 (s, 2H), 6.43 (s, 1H). **^{13}C NMR** (100 MHz, DMSO-*d*6): δ 158.57, 157.65, 147.75, 143.99, 142.82, 142.59, 132.94, 132.59, 131.36, 129.61, 129.24, 128.68, 127.51, 122.29, 121.62, 121.52, 107.58, 107.51, 102.68, 101.86, 101.85, 97.99, 86.72. **HRMS (ESI)** m/z Calcd for $[C_{23}H_{15}NNaO_3, M + Na]^+$: 376.0944, Found: 376.0895.

1-((3',5'-dimethoxy-[1,1'-biphenyl]-2-yl)ethynyl)naphthalen-2-ol (1u)

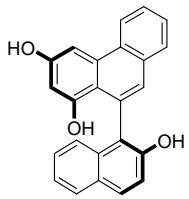


1v

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 7.1 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.38 (dq, *J* = 21.1, 7.0 Hz, 3H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 8.9 Hz, 1H), 6.77 (d, *J* = 1.8 Hz, 2H), 6.58 (s, 1H), 5.89 (s, 1H), 3.77 (s, 6H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 160.83, 156.20, 143.55, 142.98, 133.37, 132.27, 130.55, 129.32, 128.55, 128.28, 128.11, 127.42, 127.21, 124.79, 123.93, 121.42, 116.41, 107.06, 102.81, 100.93, 100.04, 85.20, 55.35. **HRMS (ESI)** m/z Calcd for $[C_{26}H_{20}NaO_3, M + Na]^+$: 403.1305, Found: 403.1285.

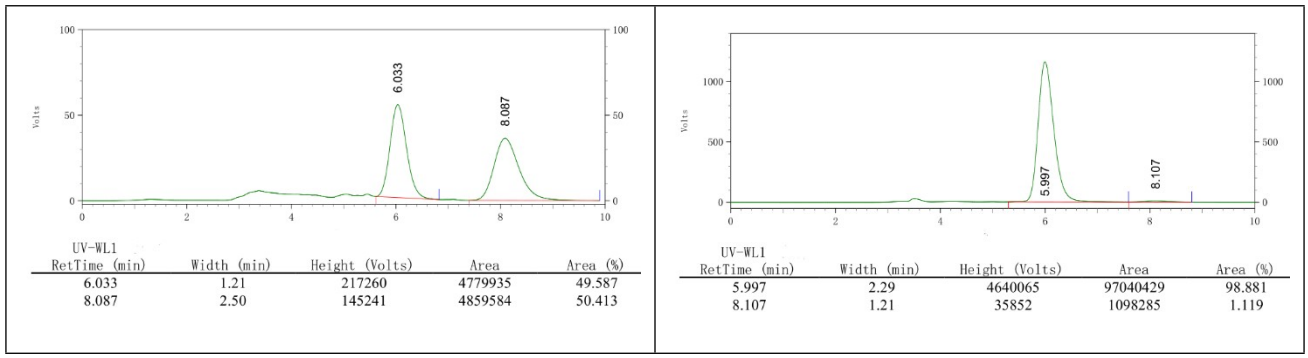
VII. ^{1}H, ^{13}C NMR, HRMS data and HPLC traces of compounds (2a-2u)

10-(2-hydroxynaphthalen-1-yl)phenanthrene-1,3-diol (2a)

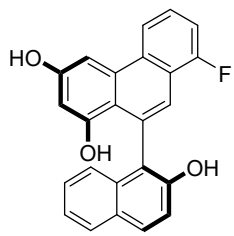


2a

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 6.0 Hz, 1H), 7.80 (d, *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 7.4 Hz, 1H), 7.66 – 7.58 (m, 1H), 7.55 (s, 1H), 7.46 (s, 2H), 7.30 (s, 1H), 7.18 (dd, *J* = 22.9, 9.7 Hz, 4H), 6.31 (s, 1H), 6.03 (s, 1H), 5.83 (s, 1H), 5.58 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.38, 151.27, 134.52, 133.33, 131.52, 131.37, 129.93, 128.87, 128.79, 128.39, 128.16, 127.59, 127.40, 127.28, 125.53, 124.60, 124.28, 123.39, 118.60, 117.58, 114.66, 103.39, 100.78. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{16}NaO_3, M + Na]^+$: 375.0992, Found: 375.0949. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 5.997 min (major), t_R = 8.107 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -54.5 (*c* = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 98%, 35 mg.



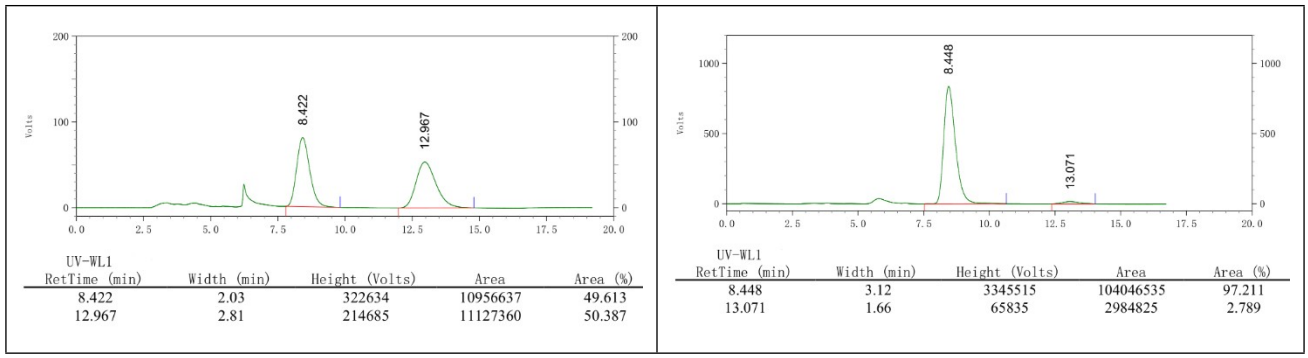
8-fluoro-10-(2-hydroxynaphthalen-1-yl)phenanthrene-1,3-diol (2b)



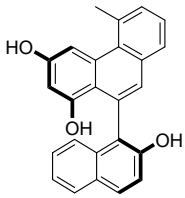
2b

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.80 (s, 1H), 9.32 (s, 1H), 9.14 (s, 1H), 8.44 (d, *J* = 8.5 Hz, 1H), 7.77 (dd, *J* = 16.3, 8.1 Hz, 2H), 7.66 (d, *J* = 1.7 Hz, 1H), 7.61 (q, *J* = 8.0 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.29 (s, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.18 (dt, *J* = 14.3, 6.3 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 1H), 6.44 (d, *J* = 2.2 Hz, 1H). **^{13}C NMR** (100 MHz, DMSO-*d*6): δ 158.43 (d, *J* = 215.0 Hz), 157.30, 157.05, 150.96, 134.46, 133.37, 133.35, 132.93, 130.97 (d, *J* = 5.0 Hz), 127.60 (d, *J* = 5.0 Hz), 127.28, 126.04 (d, *J* = 9.0 Hz), 125.57, 125.20, 124.70, 121.99, 121.25 (d, *J* = 15.0 Hz), 119.50 (d, *J* = 1.0 Hz), 118.30, 116.27 (d, *J* = 6.0 Hz), 116.19, 111.13 (d, *J* = 20.0 Hz), 102.79, 98.81. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{15}FNaO_3, M + Na]^+$: 393.0897, Found: 393.0812. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R =

8.448 min (major), t_R = 13.071 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -36.5 (c = 1.0, $(CH_3)_2CO$); **Physical properties**: white solid; **Yield:** 97%, 36 mg.

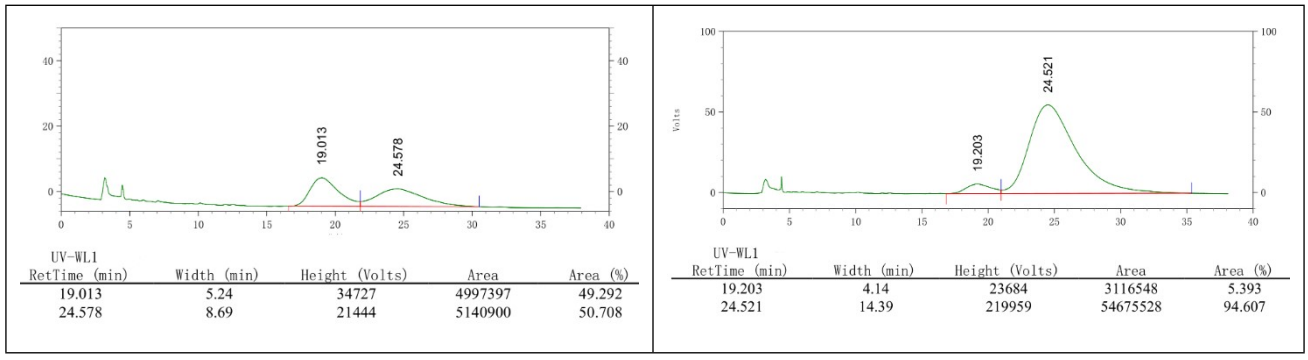


10-(2-hydroxynaphthalen-1-yl)-5-methylphenanthrene-1,3-diol (2c)

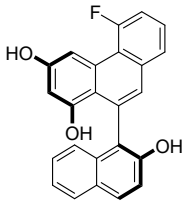


2c

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (dt, J = 17.6, 8.3 Hz, 3H), 7.49 (s, 1H), 7.37 (s, 2H), 7.31 – 7.12 (m, 5H), 6.33 (s, 1H), 5.85 (s, 3H), 2.93 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 154.92, 154.11, 151.23, 135.72, 135.58, 133.30, 133.15, 131.99, 131.28, 130.38, 129.90, 128.88, 128.16, 127.56, 127.07, 126.70, 124.98, 124.60, 124.25, 118.64, 117.59, 115.50, 106.55, 102.73, 27.18. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{18}NaO_3, M + Na]^+$: 389.1148, Found: 389.1112. **HPLC analysis**: Chiralcel OJ-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 19.203 min (minor), t_R = 24.521 min (major). **Optical Rotation:** $[\alpha]_D^{20}$ = -14.6 (c = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 98%, 35.8 mg.

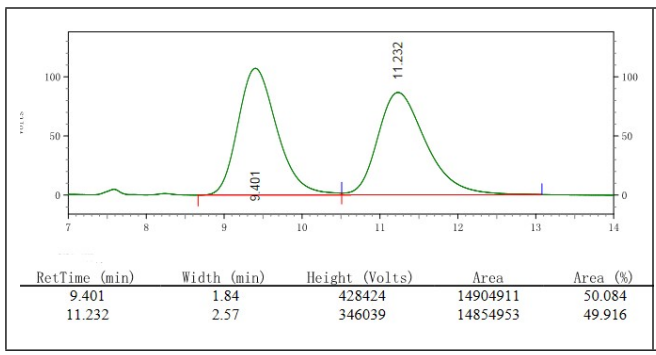


5-fluoro-10-(2-hydroxynaphthalen-1-yl)phenanthrene-1,3-diol (2d)

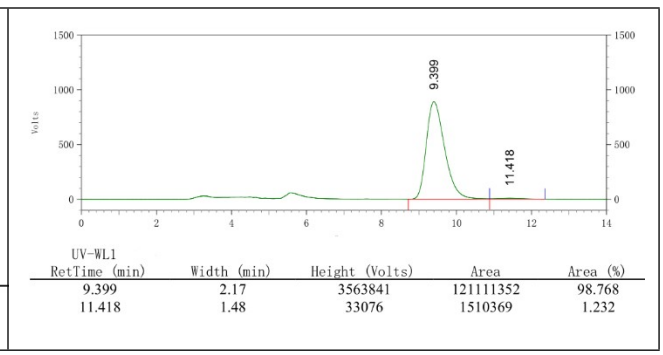


2d

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.73 (s, 1H), 8.32 (dd, *J* = 11.7, 2.2 Hz, 1H), 7.96 (s, 1H), 7.91 (dd, *J* = 8.7, 6.1 Hz, 1H), 7.82 (dd, *J* = 8.2, 6.2 Hz, 2H), 7.78 – 7.73 (m, 2H), 7.42 (td, *J* = 8.6, 2.4 Hz, 1H), 7.36 (s, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 7.24 (dt, *J* = 8.0, 4.1 Hz, 1H), 7.19 (d, *J* = 3.4 Hz, 2H), 6.59 (d, *J* = 2.2 Hz, 1H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 161.94 (d, *J* = 251.0 Hz), 157.81, 156.93, 152.02, 136.06 (d, *J* = 4.0 Hz), 135.22, 132.87 (d, *J* = 5.0 Hz), 131.97, 129.26, 129.12, 128.40, 127.85 (d, *J* = 11.0 Hz), 127.67, 126.66, 125.50, 125.20, 123.93, 123.30, 119.49 (d, *J* = 8.0 Hz), 118.96, 117.10, 113.52 (d, *J* = 26.0 Hz), 105.06 (d, *J* = 27.0 Hz), 103.48. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{15}FNaO_3$, M + Na$]^+$: 393.0897, Found: 393.0814. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 9.399 min (major), t_R = 11.418 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -51.3 (*c* = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 94%, 34.7 mg.



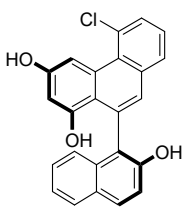
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
9.401	1.84	428424	14904911	50.084
11.232	2.57	346039	14854953	49.916



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
9.399	2.17	3563841	121111352	98.768
11.418	1.48	33076	1510369	1.232

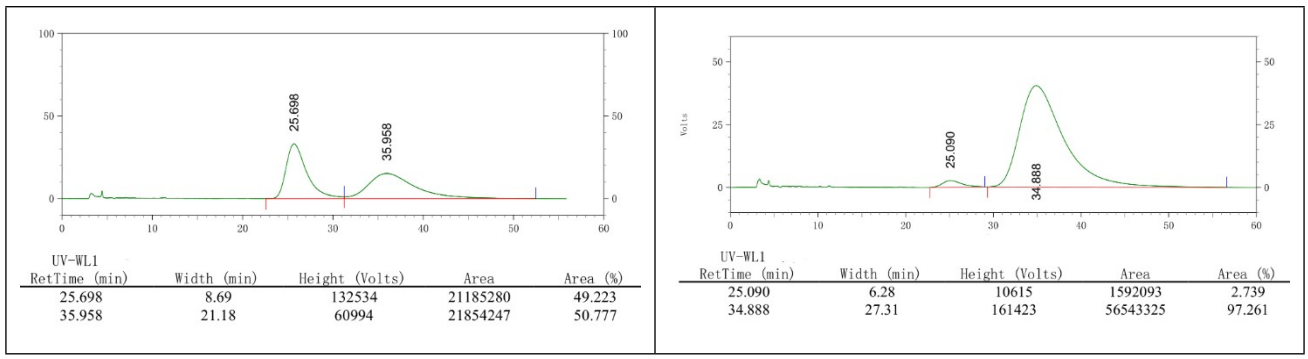
5-chloro-10-(2-hydroxynaphthalen-1-yl)phenanthrene-1,3-diol (2e)



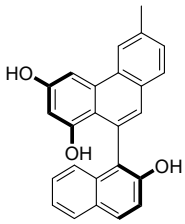
2e

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.99 (d, *J* = 2.3 Hz, 1H), 8.81 (s, 1H), 7.98 (s, 1H), 7.89 (s, 1H), 7.86 – 7.79 (m, 3H), 7.73 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.33 (s, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.21 – 7.17 (m, 2H), 6.62 (d, *J* = 2.4 Hz, 1H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 156.85, 156.64, 151.99, 136.39, 135.23, 134.07, 131.87, 131.66, 130.97, 129.14, 128.86, 128.39, 128.17, 127.48, 127.39, 126.62, 125.53, 124.06, 123.26, 118.99, 117.83, 105.34, 103.56. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{15}ClNaO_3$, M + Na$]^+$: 409.0602, Found: 409.0582. **HPLC**

analysis: Chiralcel OJ-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 25.090 min (minor), t_R = 34.888 min (major). **Optical Rotation:** $[\alpha]_D^{20}$ = -26.6 (*c* = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 96%, 37.0 mg.

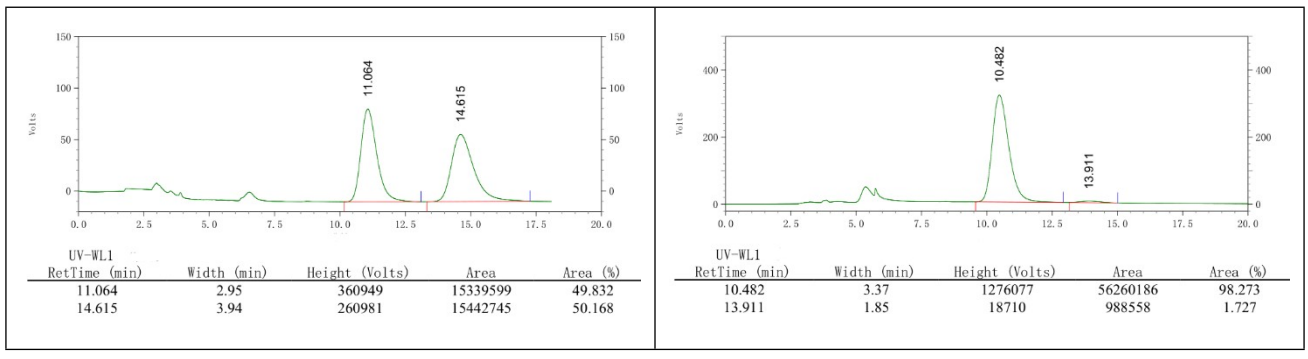


10-(2-hydroxynaphthalen-1-yl)-6-methylphenanthrene-1,3-diol (2f)

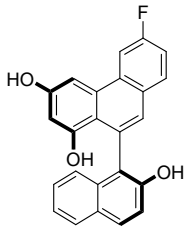


2f

^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ 8.56 (s, 1H), 8.45 (s, 1H), 7.90 (s, 1H), 7.83 (t, *J* = 9.4 Hz, 3H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.54 (s, 1H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 2H), 7.24 (dt, *J* = 8.0, 3.9 Hz, 1H), 7.19 (d, *J* = 3.6 Hz, 2H), 6.53 (d, *J* = 2.0 Hz, 1H), 2.61 (s, 3H). **^{13}C NMR** (150 MHz, $(CD_3)_2CO$): δ 157.51, 157.20, 152.39, 136.63, 135.51, 135.00, 131.12, 130.51, 129.41, 129.20, 129.13, 128.96, 128.42, 127.87, 126.68, 125.65, 123.76, 123.57, 123.35, 119.01, 116.79, 103.12, 100.03, 21.98. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{18}NaO_3, M + Na]^+$: 389.1148, Found: 389.1011. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 10.482 min (major), t_R = 13.911 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -36.2 (*c* = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 97%, 35.5 mg.

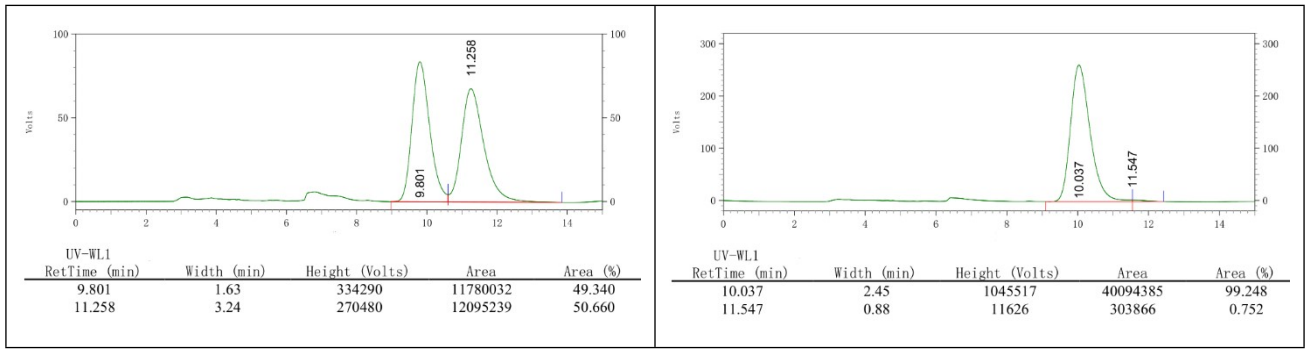


6-fluoro-10-(2-hydroxynaphthalen-1-yl)phenanthrene-1,3-diol (2g)

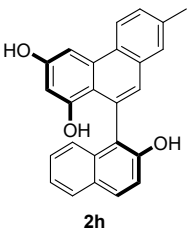


2g

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.77 (s, 1H), 8.36 – 8.28 (m, 1H), 7.99 (s, 1H), 7.90 – 7.78 (m, 3H), 7.67 (d, *J* = 7.8 Hz, 1H), 7.54 (td, *J* = 7.8, 4.9 Hz, 1H), 7.41 – 7.32 (m, 2H), 7.29 (d, *J* = 8.9 Hz, 1H), 7.26 – 7.14 (m, 3H), 6.64 (s, 1H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 162.07 (d, *J* = 242.0 Hz), 157.71, 157.34, 152.29, 135.43, 134.61, (d, *J* = 4.0 Hz), 131.79 (d, *J* = 8.0 Hz), 131.43 (d, *J* = 9.0 Hz), 130.02, 129.88 (d, *J* = 2.0 Hz), 129.35, 129.15, 128.41, 127.31, 126.67, 125.56, 123.72, 123.31, 118.98, 116.96, 116.37 (d, *J* = 24.0 Hz), 108.69 (d, *J* = 23.0 Hz), 103.78, 100.27. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{15}FNaO_3, M + Na]^+$: 393.0897, Found: 393.0841. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 10.037 min (major), t_R = 11.547 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -47.5 (*c* = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 98%, 36.2 mg.



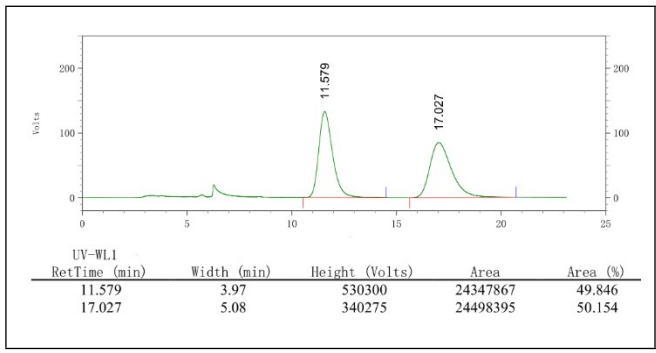
10-(2-hydroxynaphthalen-1-yl)-7-methylphenanthrene-1,3-diol (2h)



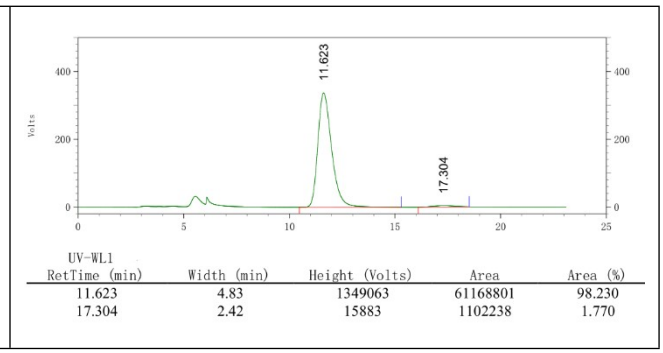
2h

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.57 (s, 1H), 9.04 (d, *J* = 12.4 Hz, 2H), 8.45 (d, *J* = 8.6 Hz, 1H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 7.20 – 7.11 (m, 2H), 7.11 – 7.05 (m, 2H), 6.32 (d, *J* = 1.8 Hz, 1H), 2.48 (s, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 157.68, 157.26, 152.32, 137.14, 135.44, 135.28, 133.27, 130.30, 129.33, 129.14, 128.67, 128.42, 128.39, 128.32, 127.69, 126.62, 125.63, 123.88, 123.85, 123.29, 119.01, 116.32, 102.82, 99.74, 21.23. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{18}NaO_3, M + Na]^+$: 389.1148, Found: 389.1112. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate =

1.0 mL/min, wave length = 254 nm, t_R = 11.623 min (major), t_R = 17.304 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -72.7 (c = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 95%, 34.7 mg.

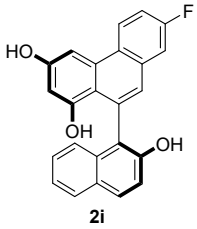


UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
11.579	3.97	530300	24347867	49.846
17.027	5.08	340275	24498395	50.154



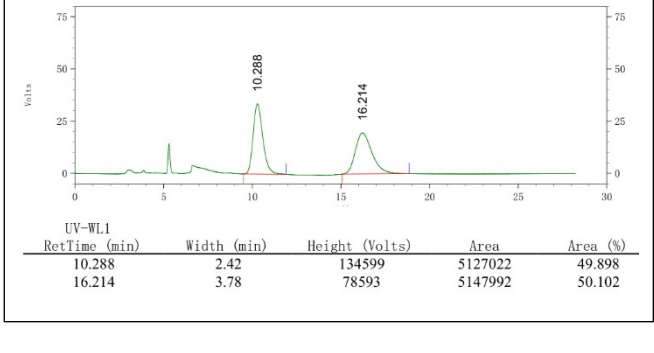
UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
11.623	4.83	1349063	61168801	98.230
17.304	2.42	15883	1102238	1.770

7-fluoro-10-(2-hydroxynaphthalen-1-yl)phenanthrene-1,3-diol (2i)

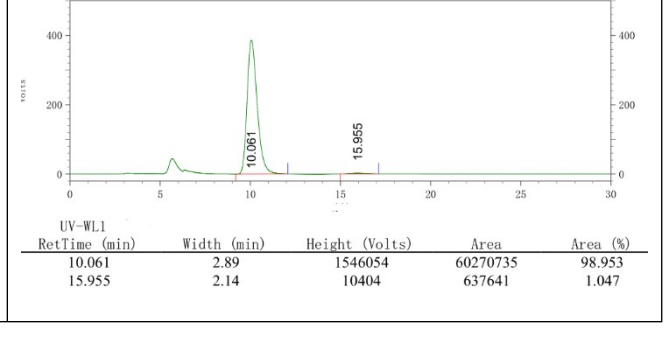


2i

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.70 (dd, J = 9.2, 5.4 Hz, 2H), 7.99 (s, 1H), 7.83 (dd, J = 8.2, 4.7 Hz, 2H), 7.81 – 7.74 (m, 2H), 7.58 (dd, J = 9.7, 2.6 Hz, 1H), 7.43 (td, J = 8.9, 2.7 Hz, 1H), 7.33 (s, 1H), 7.30 – 7.22 (m, 2H), 7.19 (dt, J = 5.7, 3.5 Hz, 2H), 6.55 (d, J = 2.1 Hz, 1H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 162.20 (d, J = 243.0 Hz), 158.01, 157.46, 152.16, 135.32, 135.10, 134.68 (d, J = 9.0 Hz), 132.29, 129.33, 129.14, 128.41, 127.14, 127.06 (d, J = 4.0 Hz), 126.80 (d, J = 9.0 Hz), 126.67, 125.54, 123.81, 123.30, 118.99, 116.41, 115.53 (d, J = 23.0 Hz), 112.50 (d, J = 21.0 Hz), 103.00, 99.88. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{15}FNaO_3, M + Na]^+$: 393.0897, Found: 393.0831. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 10.061 min (major), t_R = 15.955 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -53.6 (c = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 96%, 35.5 mg.

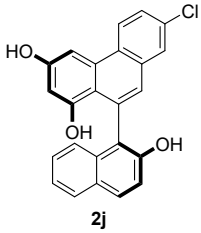


UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
10.288	2.42	134599	5127022	49.898
16.214	3.78	78593	5147992	50.102



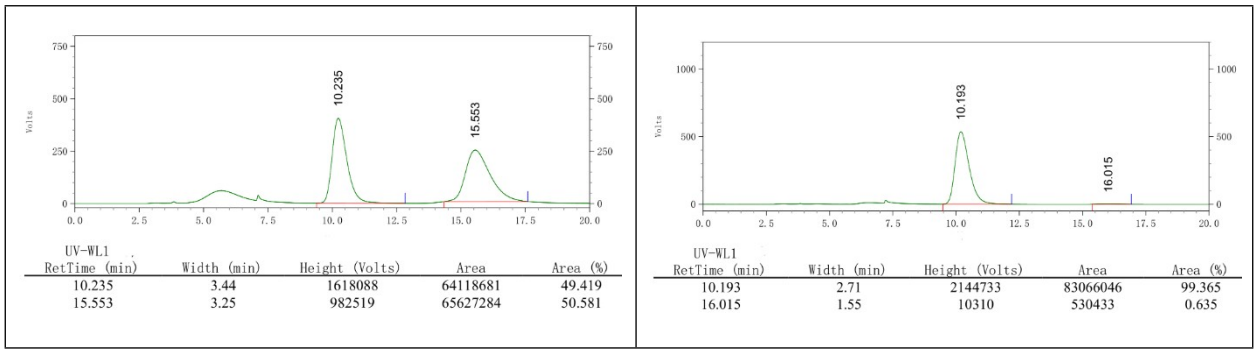
UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
10.061	2.89	1546054	60270735	98.953
15.955	2.14	10404	637641	1.047

7-chloro-10-(2-hydroxynaphthalen-1-yl)phenanthrene-1,3-diol (2j)

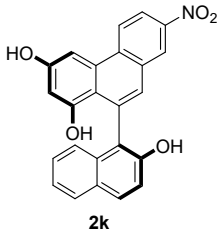


2j

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.66 (s, 1H), 9.16 (s, 1H), 9.02 (s, 1H), 8.56 (d, J = 8.9 Hz, 1H), 7.92 (s, 1H), 7.73 (dd, J = 20.0, 8.2 Hz, 2H), 7.57 (s, 2H), 7.15 (dq, J = 14.8, 7.8, 6.4 Hz, 4H), 7.04 (d, J = 8.0 Hz, 1H), 6.36 (s, 1H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 158.03, 157.44, 152.12, 135.28, 134.84, 134.36, 132.76, 132.44, 129.29, 129.10, 128.80, 128.39, 127.59, 126.98, 126.65, 126.13, 125.51, 123.80, 123.28, 118.96, 116.77, 103.43, 99.94. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{15}ClNaO_3, M + Na]^+$: 409.0602 Found: 409.0583. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 10.193 min (major), t_R = 16.015 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -117.7 (c = 1.0, CH_3OH); **Physical properties:** white solid; **Yield:** 98%, 37.8 mg.

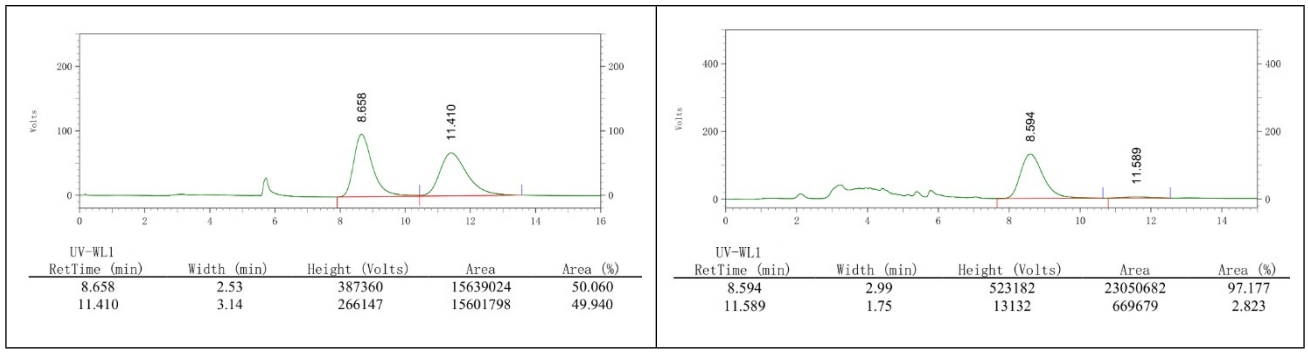


10-(2-hydroxynaphthalen-1-yl)-7-nitrophenanthrene-1,3-diol (2k)

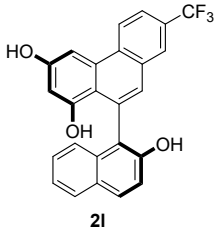


2k

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.95 – 8.87 (m, 2H), 8.81 (d, J = 2.0 Hz, 1H), 8.39 (dd, J = 9.2, 2.1 Hz, 1H), 8.09 (d, J = 16.4 Hz, 2H), 7.93 – 7.89 (m, 1H), 7.84 (dd, J = 8.1, 3.2 Hz, 2H), 7.59 (s, 1H), 7.29 (d, J = 9.0 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.21 (d, J = 3.4 Hz, 2H), 6.68 (d, J = 1.8 Hz, 1H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 158.35, 157.64, 152.10, 146.94, 135.24, 134.33, 134.13, 133.86, 132.79, 129.32, 129.13, 128.44, 127.67, 126.68, 125.93, 125.45, 124.42, 123.74, 123.28, 120.09, 118.96, 118.18, 104.82, 100.94. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{15}NNaO_5, M + Na]^+$: 420.0842, Found: 420.0811. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 8.594 min (major), t_R = 11.589 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -44.8 (c = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 94%, 37.3 mg.

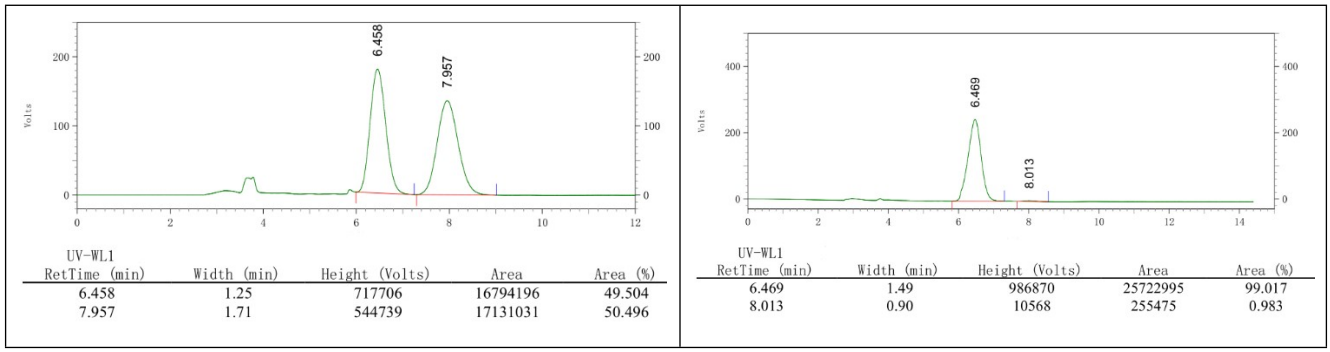


10-(2-hydroxynaphthalen-1-yl)-7-(trifluoromethyl)phenanthrene-1,3-diol (2l)

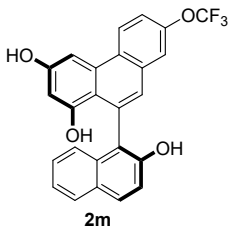


2l

^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ 8.86 (d, *J* = 8.8 Hz, 1H), 8.80 (s, 1H), 8.27 (s, 1H), 7.98 (s, 1H), 7.92 – 7.87 (m, 3H), 7.84 (t, *J* = 8.0 Hz, 2H), 7.51 (s, 1H), 7.29 (d, *J* = 8.9 Hz, 1H), 7.25 (ddd, *J* = 8.1, 4.7, 3.2 Hz, 1H), 7.21 (d, *J* = 3.7 Hz, 2H), 6.64 (d, *J* = 2.2 Hz, 1H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.67, 155.41, 151.09, 133.74, 133.21, 131.78, 131.57, 130.90, 129.06 (q, *J* = 16.0 Hz), 128.93, 128.25, 127.74, 127.65, 125.71, 125.67, 125.64, 125.63, 124.43, 124.30, 124.06 (q, *J* = 272.0 Hz), 122.80, 118.33, 117.60, 115.36, 104.31 (d, *J* = 8.0 Hz), 101.26. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{15}F_3NaO_3$, M + Na$]^+$: 443.0866, Found: 443.0814. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 6.469 min (major), t_R = 8.013 (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -58.2 (*c* = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 94%, 39.4 mg.



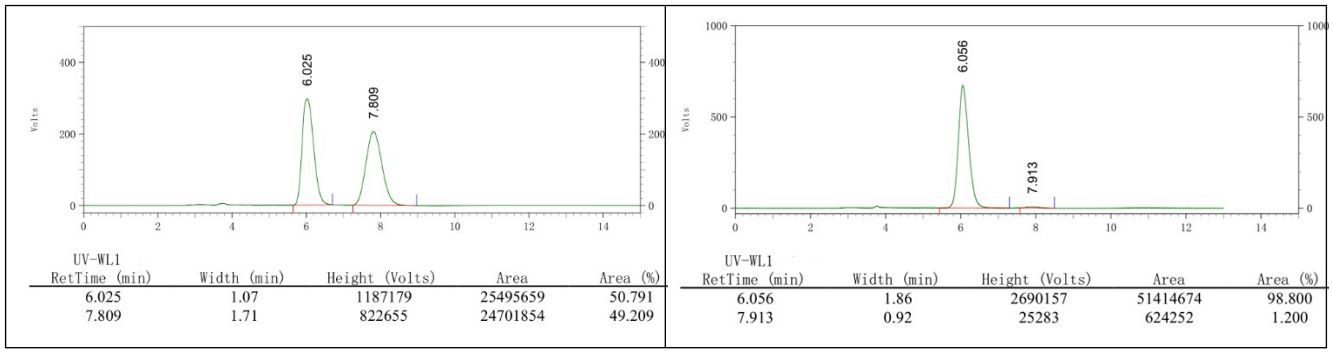
10-(2-hydroxynaphthalen-1-yl)-7-(trifluoromethoxy)phenanthrene-1,3-diol (2m)



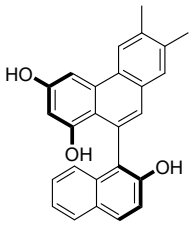
2m

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 9.1 Hz, 1H), 7.83 (d, *J* = 8.9 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 16.7 Hz, 2H), 7.29 (q, *J* = 9.9, 9.2 Hz, 3H), 7.21 (t, *J* = 7.4 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 1H), 6.31 (s, 1H), 6.06 (s, 1H), 5.80 (s, 1H), 5.52 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.75, 155.57, 151.24, 148.08, 134.05, 133.17, 132.45, 131.66, 128.92, 128.27, 127.91, 127.78,

127.51, 125.63, 124.44, 120.5 (q, J = 256.0 Hz), 120.40, 118.64, 118.06, 117.63, 114.66, 103.67, 100.83. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{15}F_3NaO_4, M + Na]^+$: 459.0815, Found: 459.0796. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 6.056 min (major), t_R = 7.913 (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -61.7 (c = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 96%, 41.8 mg.

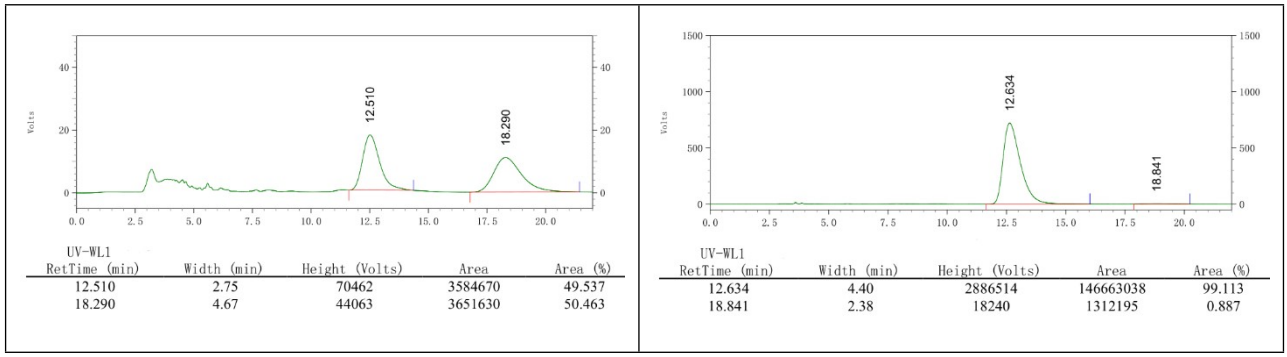


10-(2-hydroxynaphthalen-1-yl)-6,7-dimethylphenanthrene-1,3-diol (2n)

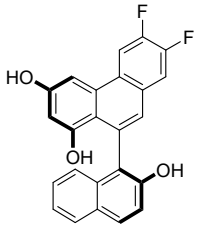


2n

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.57 (s, 1H), 8.41 (s, 1H), 7.90 (s, 1H), 7.82 (dd, J = 14.6, 8.3 Hz, 3H), 7.59 (s, 1H), 7.52 (s, 1H), 7.31 – 7.22 (m, 3H), 7.19 (d, J = 3.4 Hz, 2H), 6.50 (s, 1H), 2.54 (s, 3H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 157.46, 157.17, 152.36, 136.82, 136.22, 135.52, 135.01, 131.72, 129.36, 129.18, 129.05, 129.00, 128.87, 128.40, 127.55, 126.64, 125.67, 124.14, 123.85, 123.32, 119.00, 116.37, 102.71, 99.78, 20.46, 19.72. **HRMS (ESI)** m/z Calcd for $[C_{26}H_{20}NaO_3, M + Na]^+$: 403.1305, Found: 403.1283. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 12.634 min (major), t_R = 18.841 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -52.1 (c = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 97%, 36.8 mg.

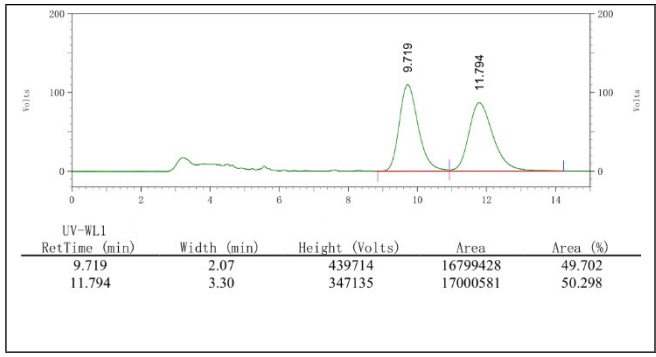


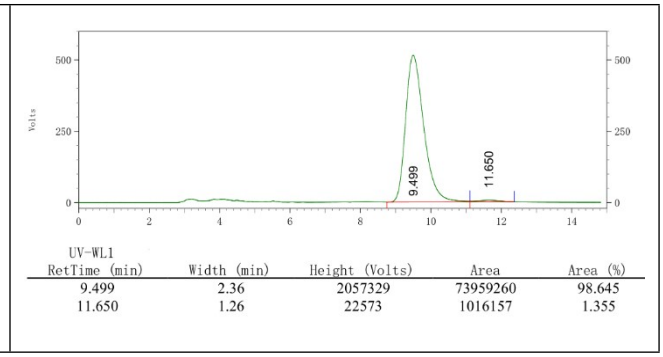
6,7-difluoro-10-(2-hydroxynaphthalen-1-yl)phenanthrene-1,3-diol (2o)



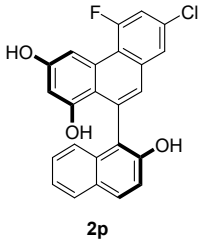
2o

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.74 (dd, *J* = 26.9, 6.8 Hz, 2H), 7.20 (q, *J* = 24.0, 23.6 Hz, 7H), 6.24 (s, 2H), 6.06 (s, 1H), 5.75 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.37, 155.25, 151.27, 150.135 (dd, *J* = 247.0, 20.0 Hz), 150.05 (dd, *J* = 246.0, 16.0 Hz), 133.45 (d, *J* = 2.0 Hz), 133.24, 131.43, 128.88, 128.59 (d, *J* = 6.0 Hz), 128.19, 127.65, 127.09, 126.81, 126.75, 126.67, 124.39 (d, *J* = 4.0 Hz), 118.49, 117.54, 114.67, 114.49, 111.08 (d, *J* = 8.0 Hz), 103.57, 100.81. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{14}F_2NaO_3, M + Na]^+$: 411.0803, Found: 411.0789. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 9.499 min (major), t_R = 11.650 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -50.1 (*c* = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 95%, 36.8 mg.





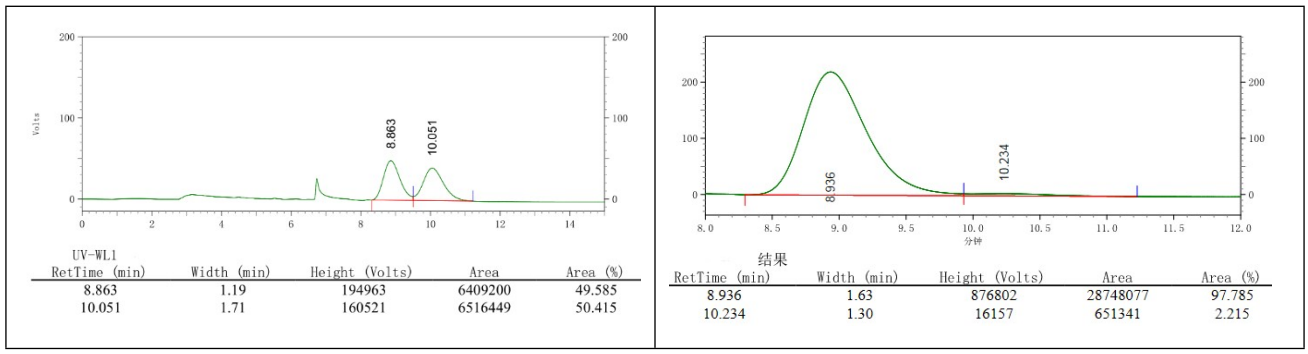
7-chloro-5-fluoro-10-(2-hydroxynaphthalen-1-yl)phenanthrene-1,3-diol (2p)



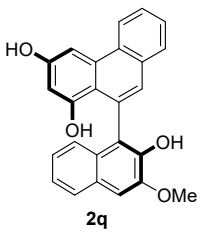
2p

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.81 (s, 1H), 8.21 – 8.16 (m, 1H), 8.01 (d, *J* = 14.0 Hz, 2H), 7.86 – 7.77 (m, 3H), 7.46 (dd, *J* = 14.4, 1.9 Hz, 1H), 7.34 (d, *J* = 1.7 Hz, 1H), 7.22 (dt, *J* = 24.5, 8.7 Hz, 4H), 6.64 – 6.60 (m, 1H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 161.95 (d, *J* = 255.0 Hz), 158.26, 157.20, 151.92, 136.77 (d, *J* = 5.0 Hz), 135.15, 134.03, 132.50 (d, *J* = 5.0 Hz), 131.92 (d, *J* = 12.0 Hz), 129.20, 129.12, 128.41, 126.65, 126.56 (d, *J* = 3.0 Hz), 125.46, 124.15 (d, *J* = 3.0 Hz), 123.97, 123.27, 118.95, 118.13 (d, *J* = 7.0 Hz), 117.23, 114.11 (d, *J* = 30.0 Hz), 104.72 (d, *J* = 26.0 Hz), 103.72. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{14}ClFNaO_3, M + Na]^+$: 427.0508, Found: 427.0496. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm,

t_R = 8.936 min (major), t_R = 10.234 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -81.0 (c = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 98%, 39.6 mg.

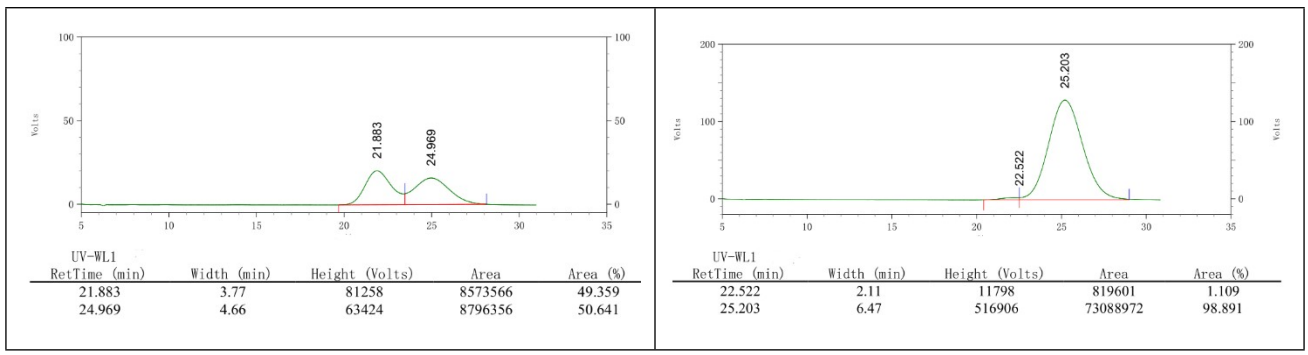


10-(2-hydroxy-3-methoxynaphthalen-1-yl)phenanthrene-1,3-diol (2q)

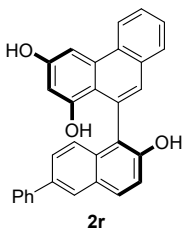


2q

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.73 – 8.62 (m, 2H), 7.84 (t, J = 6.5 Hz, 2H), 7.74 (t, J = 10.3 Hz, 2H), 7.61 (ddt, J = 17.9, 7.1, 2.7 Hz, 3H), 7.36 (s, 1H), 7.32 (d, J = 3.8 Hz, 1H), 7.21 (dt, J = 13.7, 6.0 Hz, 2H), 7.09 (ddt, J = 8.1, 6.7, 1.3 Hz, 1H), 6.57 (d, J = 4.3 Hz, 1H), 4.02 (s, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 157.53, 157.24, 148.89, 144.27, 135.08, 133.10, 130.93, 130.70, 130.22, 129.42, 128.88, 127.49, 127.27, 126.80, 125.52, 124.43, 124.39, 123.89, 116.68, 106.00, 103.18, 103.14, 99.93, 56.00. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{18}NaO_4, M + Na]^+$: 405.1097, Found: 405.1010. **HPLC analysis**: Chiralcel AS-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 22.522 min (minor), t_R = 25.203 min (major). **Optical Rotation:** $[\alpha]_D^{20}$ = -79.9 (c = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 98%, 37.4 mg.



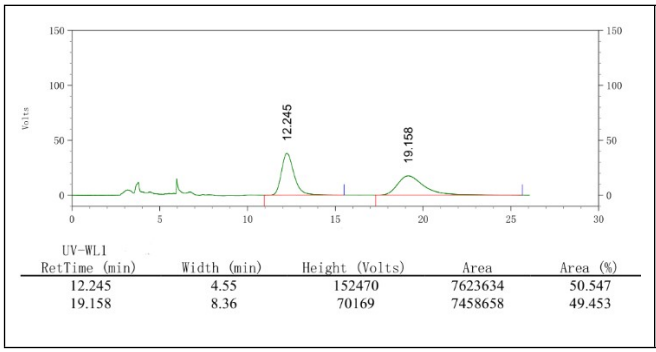
10-(2-hydroxy-6-phenylnaphthalen-1-yl)phenanthrene-1,3-diol (2r)



2r

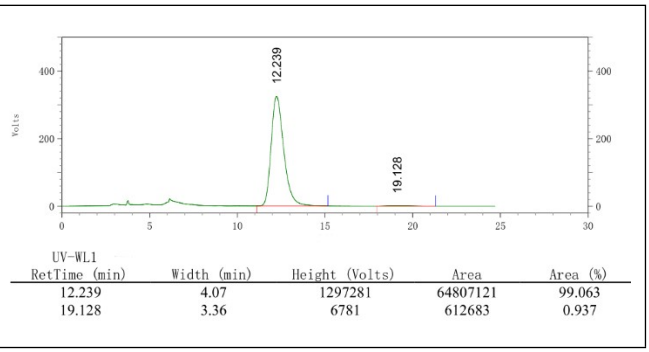
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, J = 8.0 Hz, 1H), 7.94 (s, 1H), 7.88 (d, J = 8.9 Hz, 1H), 7.66 (d, J = 7.4 Hz, 1H), 7.62 (s, 1H), 7.55 – 7.41 (m, 5H), 7.34 (t, J =

7.2 Hz, 3H), 7.24 (t, J = 8.8 Hz, 3H), 6.37 (s, 1H), 6.05 (s, 1H), 5.57 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 155.51, 151.41, 140.60, 137.07, 134.59, 132.48, 131.66, 131.55, 129.99, 129.16, 128.84, 128.81, 128.46, 127.48, 127.37, 127.27, 127.19, 126.08, 125.42, 125.15, 123.41, 118.48, 118.04, 114.66, 103.46, 100.78. **HRMS (ESI)** m/z Calcd for $[C_{30}H_{20}NaO_3, M + Na]^+$: 451.1305, Found: 451.1278. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 12.239 min (major), t_R = 19.128 (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -37.4 (c = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 97%, 41.5 mg.



UV-WL1

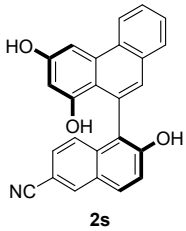
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
12.245	4.55	152470	7623634	50.547
19.158	8.36	70169	7458658	49.453



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
12.239	4.07	1297281	64807121	99.063
19.128	3.36	6781	612683	0.937

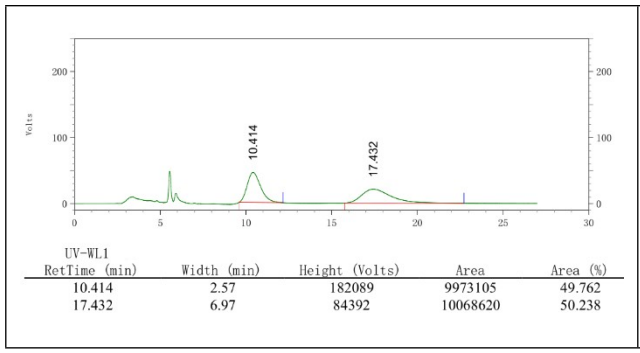
5-(6,8-dihydroxyphenanthren-9-yl)-6-hydroxy-2-naphthonitrile (2s)



2s

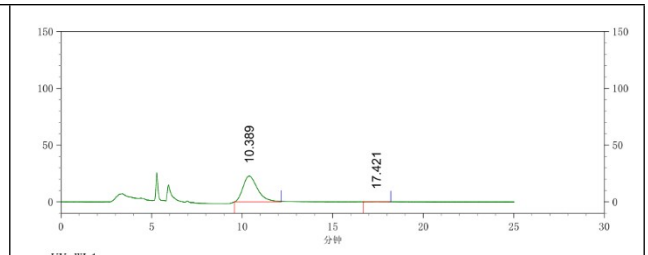
^{1}H NMR (600 MHz, $(CD_3)_2CO$): δ 8.67 (s, 1H), 8.64 (d, J = 8.3 Hz, 1H), 8.33 (d, J = 6.2 Hz, 2H), 8.22 (s, 1H), 7.95 (d, J = 8.9 Hz, 1H), 7.86 (d, J = 7.7 Hz, 1H), 7.82 (d, J = 2.2 Hz, 1H), 7.68 – 7.64 (m, 1H), 7.63 – 7.59 (m, 1H), 7.41 – 7.37 (m, 2H), 7.35 (s, 2H), 6.57 (d, J = 2.2 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 155.77, 155.28, 153.76, 135.30, 134.85, 134.14, 131.50, 131.32, 130.12, 129.14, 128.59, 127.95, 127.77, 127.75, 127.69, 125.98, 124.46, 123.45, 120.25, 119.55, 119.19, 114.55, 107.40, 103.61, 100.98. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{15}NaO_3, M + Na]^+$: 400.0944 Found: 400.0853.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH) = 75:15, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 10.389 min (major), t_R = 17.421 (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -3.0 (c = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 98%, 36.9 mg.



UV-WL1

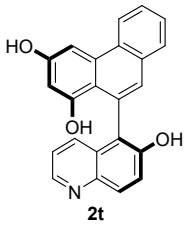
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
10.414	2.57	182089	9973105	49.762
17.432	6.97	84392	10068620	50.238



UV-WL1

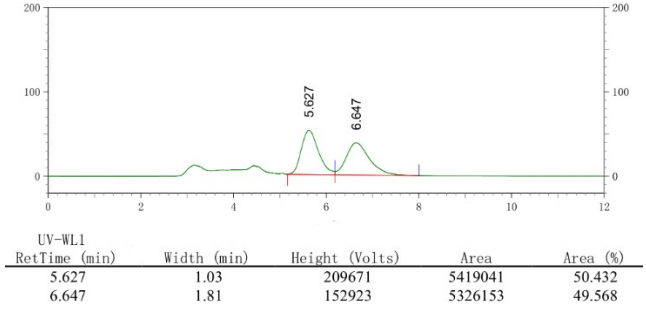
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
10.389	2.60	91327	5140614	99.745
17.421	1.54	239	13140	0.255

10-(6-hydroxyquinolin-5-yl)phenanthrene-1,3-diol (2t)



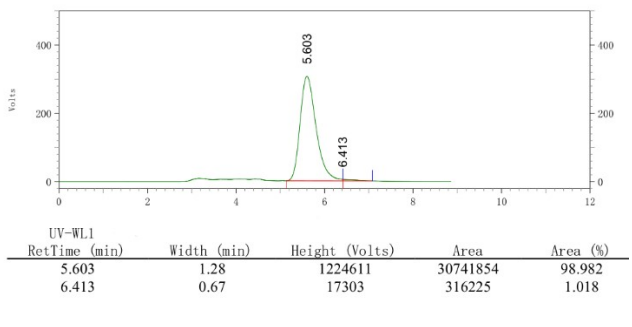
2t

^{1}H NMR (600 MHz, DMSO-d_6) δ 9.64 (s, 1H), 9.32 (s, 1H), 9.19 (s, 1H), 8.58 – 8.52 (m, 2H), 7.84 (d, J = 9.1 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.61 (d, J = 1.9 Hz, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.54 (t, J = 7.3 Hz, 1H), 7.46 (d, J = 8.5 Hz, 1H), 7.43 (d, J = 9.1 Hz, 1H), 7.20 (s, 1H), 7.15 (dd, J = 8.6, 4.0 Hz, 1H), 6.36 (d, J = 1.9 Hz, 1H). **^{13}C NMR** (150 MHz, DMSO-d_6): δ 156.83, 156.56, 151.12, 146.25, 142.80, 133.85, 132.83, 131.91, 130.38, 129.40, 128.99, 128.11, 127.95, 126.77, 126.14, 125.69, 125.31, 123.15, 121.43, 120.73, 115.79, 102.24, 98.41. **HRMS (ESI)** m/z Calcd for [$C_{23}H_{15}NNaO_3$, M + Na]$^+$: 376.0944, Found: 376.0912. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 5.603 min (major), t_R = 6.413 (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -23.2 (c = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 95%, 33.5 mg.



UV-WL1

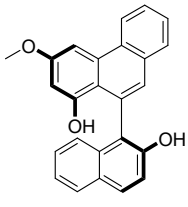
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
5.627	1.03	209671	5419041	50.432
6.647	1.81	152923	5326153	49.568



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
5.603	1.28	1224611	30741854	98.982
6.413	0.67	17303	316225	1.018

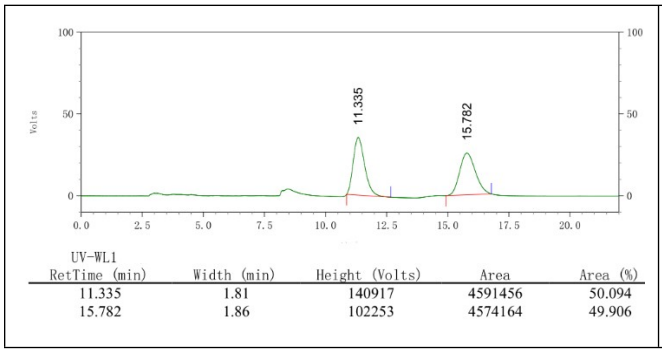
10-(2-hydroxynaphthalen-1-yl)-3-methoxyphenanthren-1-ol (2u)

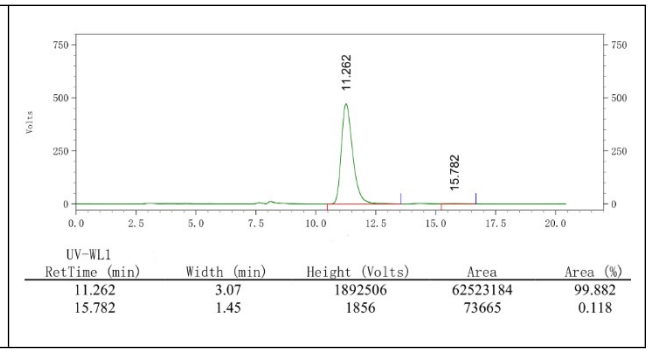


2u

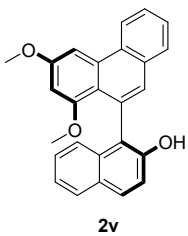
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.66 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 9.0 Hz, 1H), 7.87 – 7.84 (m, 2H), 7.79 (d, J = 7.7 Hz, 1H), 7.70 (t, J = 7.2 Hz, 1H), 7.62 (t, J = 7.4 Hz, 1H), 7.45 (s, 1H), 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 6.63 (d, J = 2.4

Hz, 1H), 6.03 (s, 1H), 5.41 (s, 1H), 3.96 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 159.58, 155.69, 151.62, 134.34, 133.36, 131.63, 131.51, 130.31, 128.94, 128.88, 128.54, 128.22, 127.69, 127.41, 127.38, 125.44, 124.59, 124.33, 123.39, 118.22, 117.66, 114.78, 102.59, 98.70, 55.45. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{18}NaO_3, M + Na]^+$: 389.1148, Found: 389.1135. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 11.262 min (major), t_R = 15.782 (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -38.2 (*c* = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 70 %, 25.6 mg.



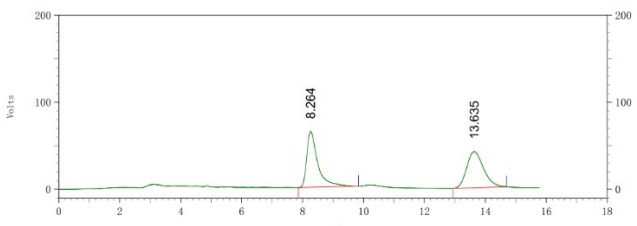


1-(6,8-dimethoxyphenanthren-9-yl)naphthalen-2-ol (2v)



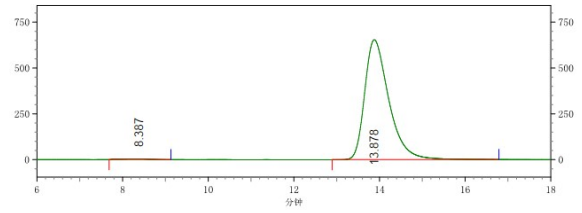
2v

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.65 (d, *J* = 8.4 Hz, 1H), 7.83 – 7.75 (m, 4H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.55 (s, 1H), 7.29 (d, *J* = 8.9 Hz, 1H), 7.25 (t, *J* = 7.0 Hz, 1H), 7.15 (q, *J* = 8.5 Hz, 2H), 6.51 (s, 1H), 5.08 (s, 1H), 3.97 (s, 3H), 3.09 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 159.24, 158.77, 149.02, 134.18, 133.99, 132.08, 129.84, 129.04, 128.59, 128.40, 127.96, 127.89, 127.65, 127.23, 126.90, 125.76, 124.89, 124.72, 123.17, 122.72, 117.89, 117.01, 99.40, 96.61, 55.79, 55.38. **HRMS (ESI)** m/z Calcd for $[C_{26}H_{20}NaO_3, M + Na]^+$: 403.1305, Found: 403.1295. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 8.387 min (minor), t_R = 13.878 (major). **Optical Rotation:** $[\alpha]_D^{20}$ = -52.0 (*c* = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 85 %, 32.3 mg.



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
8.264	1.97	257139	6476589	50.319
13.635	1.76	166244	6394522	49.681

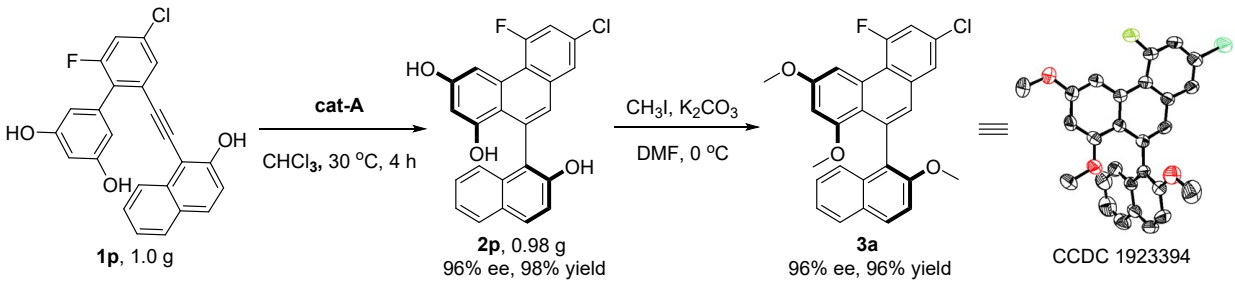


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
8.387	1.44	14964	722916	0.701
13.878	3.89	2615283	102464757	99.299

VIII. General information

^{1}H and ^{13}C NMR spectra were recorded on Agilent 400MR DD2 (400 MHz) spectrometer and Agilent 600MR DD2 (600 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and tetramethylsilane or the residual solvent peak was used as an internal reference: ^{1}H (tetramethylsilane δ 0.00), ^{13}C (chloroform δ 77.00, acetone δ 29.70, DMSO δ 39.60). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. Enantiomeric excesses (*ee*) were determined by HPLC analysis on Hitachi Chromaster using DAICEL CHIRALCEL AD-H, 4.6mm *Φ* × 250mmL, DAICEL CHIRALCEL OD-H, 4.6mm *Φ* × 250mmL and DAICEL CHIRALCEL OJ-H, 4.6mm *Φ* × 250mmL. High resolution mass spectra (HRMS) were performed on Bruker Solarix 7.0 T. X-ray crystallography analysis of single crystal was performed on an Agilent SuperNova-CCD X-Ray diffractometer. Optical rotations were measured on a Rudolph Autopol I polarimeter and are reported as follows: $[\alpha]_D^{20}$ (c in g per 100 mL solvent). All fluorescence spectra were measured using a Hitachi F-7000 FL spectrophotometer. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification.

IX. Scale-up experiment and transformation.

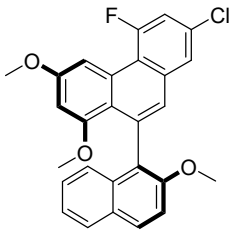


General procedure for scale-up experiment: To a solution of **1p** (1.0 g, 2.47 mmol) and **cat-A** (10 mol %) in $CHCl_3$ (50.0 mL). The mixture was stirred at 30 °C for 4 h. Then the reaction mixture was concentrated under the reduced pressure and purified by silica gel chromatography (PE: Acetone = 2:1) to afford the product **2p** (0.98 g, 98% yield, 96% ee) as white solid.

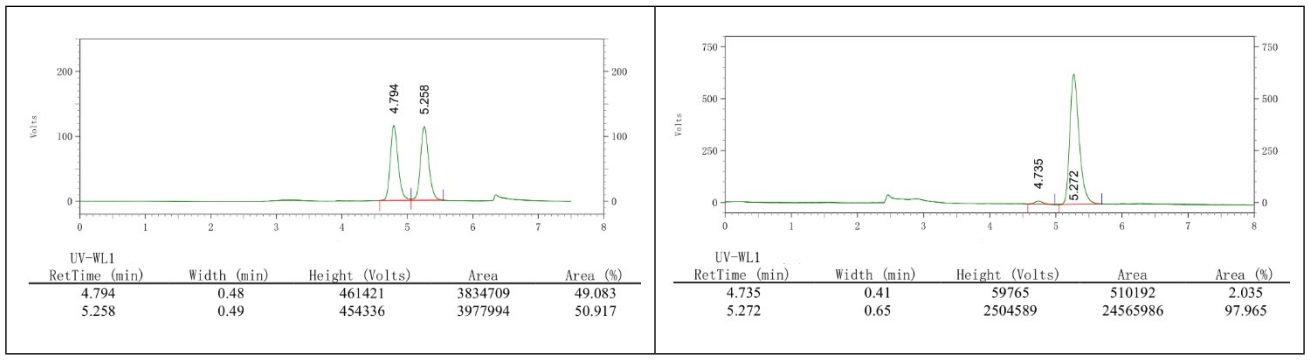
General procedure for synthesis 3a: To an oven-dried round-bottom flask equipped with a stirring bar was added K_2CO_3 (0.4 mmol, 55.2 mg) under nitrogen atmosphere. The flask was cooled to 0 °C, and anhydrous DMF (2.5 mL) was added. **2p** (0.1 mmol, 40.4 mg) was added slowly during stirring

at 0 °C. The resulting clear solution was stirred during the rapid addition of iodomethane (0.4 mmol, 24.9 μL). The reaction mixture was allowed to stir at room temperature for 3 h. The reaction was quenched with water and extracted with EtOAc. The combined organic phase was washed with 10% NaOH, water, and brine, then dried over $MgSO_4$ and concentrated. The crude product was purified by column chromatography (PE:EA = 25:1) to give product **3a** as white solid.

7-chloro-5-fluoro-1,3-dimethoxy-10-(2-methoxynaphthalen-1-yl)phenanthrene (3a)

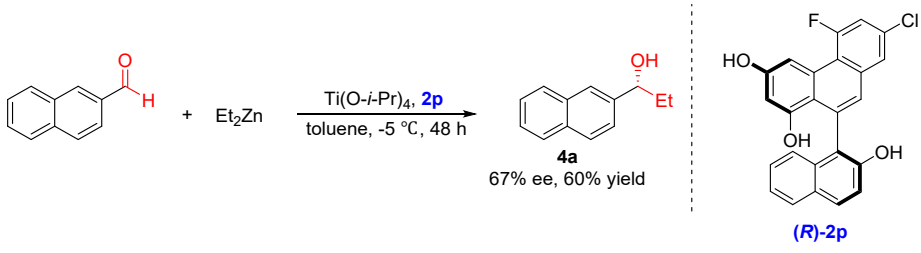


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 – 8.26 (m, 1H), 7.88 (dd, *J* = 13.8, 8.7 Hz, 2H), 7.60 (s, 1H), 7.43 – 7.28 (m, 4H), 7.23 (d, *J* = 5.8 Hz, 2H), 6.60 (s, 1H), 4.02 (s, 3H), 3.79 (s, 3H), 3.13 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 161.2 (d, *J* = 256.0 Hz), 159.10, 158.30, 152.78, 135.39 (d, *J* = 4.0 Hz), 133.49 (d, *J* = 4.0 Hz), 131.56 (d, *J* = 13.0 Hz), 131.40 (d, *J* = 6.0 Hz), 128.58 (d, *J* = 9.0 Hz), 127.77, 127.60, 126.37, 125.81, 125.23, 123.50 (d, *J* = 4.0 Hz), 123.14, 119.00, 117.44, (d, *J* = 7.0 Hz), 113.76, 113.72, 113.46, 101.34, 101.06, 99.98, 56.84, 55.74, 55.31. **HRMS (ESI)** m/z Calcd for $[C_{27}H_{20}ClFNaO_3$, M+ Na$]^+$: 469.0977, Found: 469.0975. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 4.735 min (minor), t_R = 5.272 min (major). **Optical Rotation:** $[\alpha]_D^{20}$ = -101.3 (*c* = 1.0, $(CH_3)_2CO$); **Physical properties:** white solid; **Yield:** 96%, 42.8 mg.



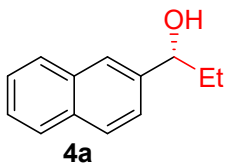
X. Nonsymmetric axial chiral biaryltriols were used in asymmetric synthesis.

a) 2p applied as chiral ligand for enantioselective preparation of chiral *sec*-alcohols.



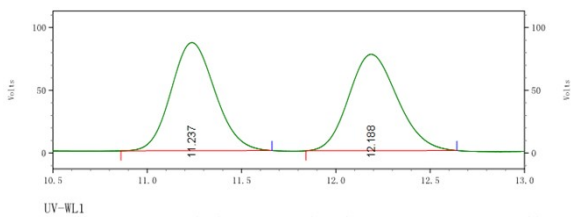
Titanium tetraisopropoxide (0.6 mmol) was added to a solution of **2p** (0.2 mmol) in toluene (1 mL) at -5 °C under argon and the mixture was stirred for 1 h followed by addition of diethylzinc (0.6 mL, 1.0 mol/L solution in hexane). After 2 h, 2-naphthylaldehyde (0.2 mmol) in toluene (1 mL) was added and the mixture was stirred at -5 °C. When TLC analysis indicated the completion of reaction (about 48 h), the reaction was quenched with 2 mL of saturated NH_4Cl solution, the organic layer was separated and the water layer was extracted with EA. The organic layer and extraction were combined. The combined solution was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure and the residue was purified by column chromatography on silica gel to obtain the addition product. The absolute configuration was determined by comparison with the references.[2]

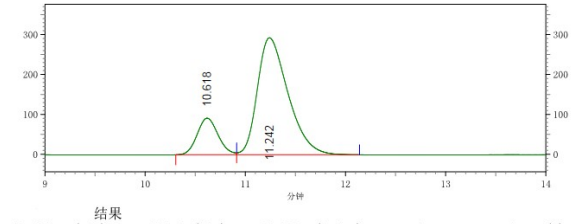
1-(naphthalen-2-yl)propan-1-ol (4a)



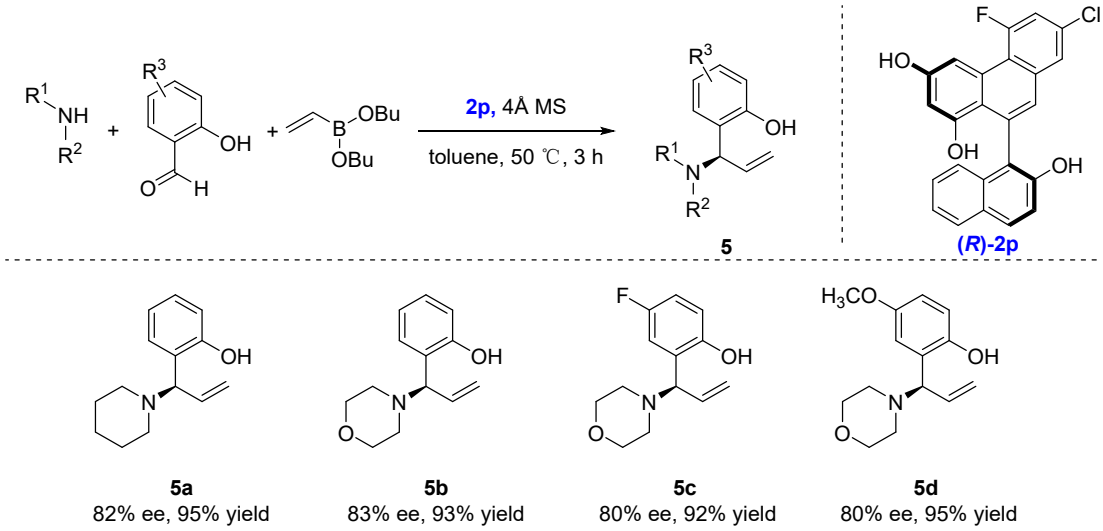
4a

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (dt, *J* = 12.3, 6.7 Hz, 3H), 7.65 (s, 1H), 7.45 – 7.35 (m, 3H), 4.60 (t, *J* = 6.5 Hz, 1H), 2.66 (s, 1H), 1.77 (ddh, *J* = 20.9, 13.9, 7.2 Hz, 2H), 0.85 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 141.83, 133.10, 132.80, 128.01, 127.80, 127.54, 125.92, 125.58, 124.60, 124.06, 75.84, 31.57, 10.03. **HRMS (ESI)** m/z Calcd for $[C_{13}H_{14}NaO, M + Na]^+$: 209.0937, Found: 209.0934. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 10.618 min (minor), t_R = 11.242 min (major). **Optical Rotation:** $[\alpha]_D^{20}$ = 14.5° (c = 1.0, CH_3OH); **Physical properties:** white solid; **Yield:** 60 %, 22.3 mg.





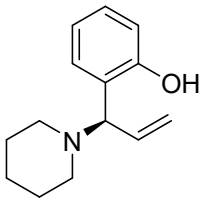
b) 2p as a new catalyst for asymmetric Petasis reaction.



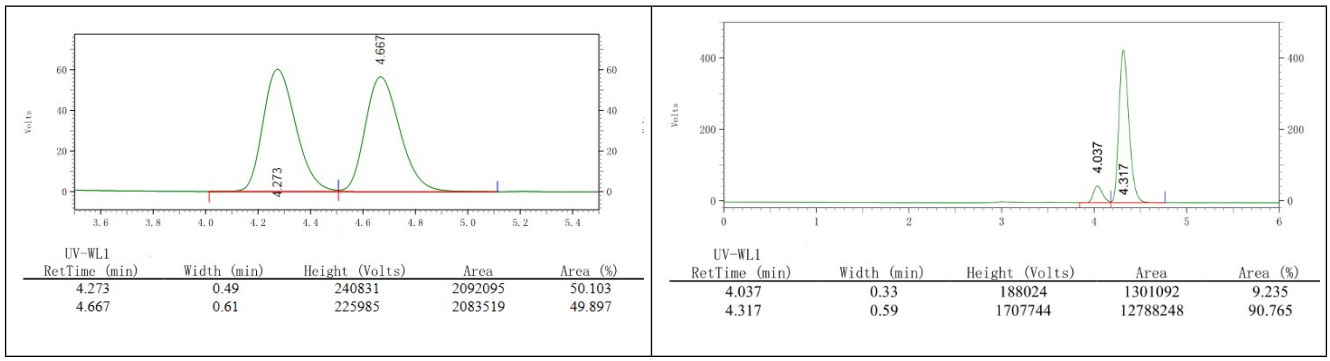
Representative Procedure for Catalytic Asymmetric Petasis Reactions:[3]

Preparation of 2-(1-(Piperidin-1-yl)allyl)phenol (5): To a magnetically stirred mixture of 2-hydroxybenzaldehyde (1.2 equiv, 0.1 mmol), **2p** (8.0 mg, 0.02 mmol, 0.02 equiv), 4Å molecular sieves (80 mg), and dibutyl vinylboronate (0.12 mmol, 1.2 equiv) in toluene (1 mL) was added piperidine (0.12 mmol, 1.2 equiv). The mixture was stirred at 50 °C for 3 h and then filtered through a celite bed. The combined filtrates were washed with dilute brine (three times), dried over anhydrous Na_2SO_4, filtered, and concentrated on a rotary evaporator. The residue was isolated by flash chromatography, and the fractions containing product **5** were combined and concentrated on a rotary evaporator to give **5** as colorless oil.

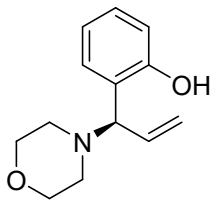
2-(1-(piperidin-1-yl)allyl)phenol (5a)



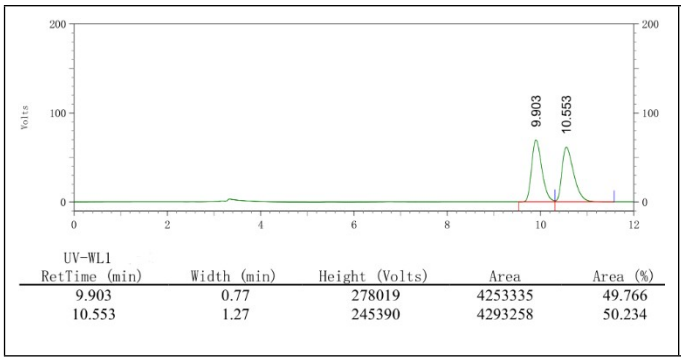
^{1}H NMR (600 MHz, $CDCl_3$): δ 11.87 (br, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.4 Hz, 1H), 6.83 – 6.72 (m, 2H), 6.00 (dt, *J* = 16.9, 9.9 Hz, 1H), 5.28 – 5.19 (m, 2H), 3.95 (d, *J* = 9.6 Hz, 1H), 2.53 (s, 4H), 1.68 – 1.58 (m, 4H), 1.47 (s, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 157.29, 134.84, 128.49, 128.11, 124.65, 118.98, 118.62, 116.34, 74.04, 26.00, 24.16. **HRMS (ESI)** m/z Calcd for [$C_{14}H_{19}NNaO$, M + Na] $^+$: 240.1359, Found: 240.1356. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 98:2, flow rate = 1.0 mL/min, wave length = 280 nm, t_R = 4.037 min (minor), t_R = 4.317 min (major). **Optical Rotation:** $[\alpha]_D^{20}$ = -32.9 (*c* = 1.0, CH_3OH); **Physical properties:** colorless oil; **Yield:** 95 %, 21 mg.



2-(1-morpholinoallyl)phenol (5b)

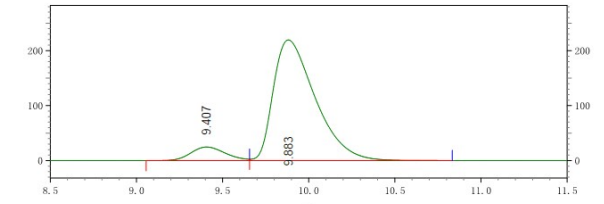


^{1}H NMR (600 MHz, $CDCl_3$): δ 10.99 (br, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 6.96 (d, *J* = 7.4 Hz, 1H), 6.84 – 6.76 (m, 2H), 5.98 (dt, *J* = 17.0, 9.8 Hz, 1H), 5.29 (d, *J* = 16.9 Hz, 1H), 5.24 (d, *J* = 10.0 Hz, 1H), 3.88 (d, *J* = 9.5 Hz, 1H), 3.73 (s, 4H), 2.57 (d, *J* = 66.2 Hz, 4H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 156.28, 134.68, 128.85, 128.45, 123.76, 119.50, 119.04, 116.45, 74.54, 66.78, 50.89. **HRMS (ESI)** m/z Calcd for [$C_{13}H_{17}NNaO_2$, M + Na] $^+$: 242.1151, Found: 242.1152. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 98:2, flow rate = 1.0 mL/min, wave length = 280 nm, t_R = 9.407min (minor), t_R = 9.883 min (major). **Optical Rotation:** $[\alpha]_D^{20}$ = -148.6 (*c* = 1.0, CH_3OH); **Physical properties:** colorless oil; **Yield:** 93 %, 20.3 mg.



UV-WL1

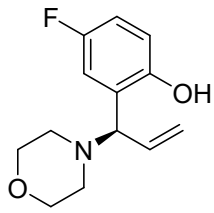
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
9.903	0.77	278019	4253335	49.766
10.553	1.27	245390	4293258	50.234



UV-WL1

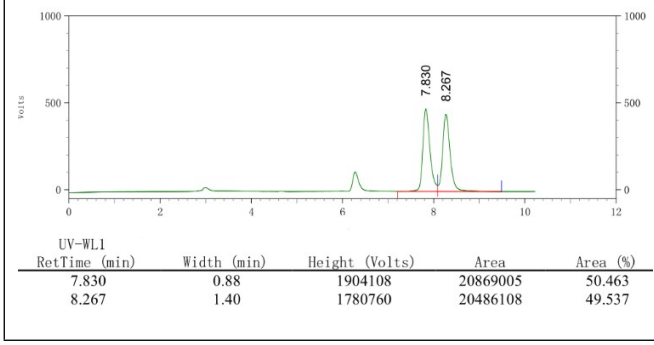
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
9.407	0.60	98791	1369651	8.451
9.883	1.18	877572	14836421	91.549

4-fluoro-2-(1-morpholinoallyl)phenol (5c)



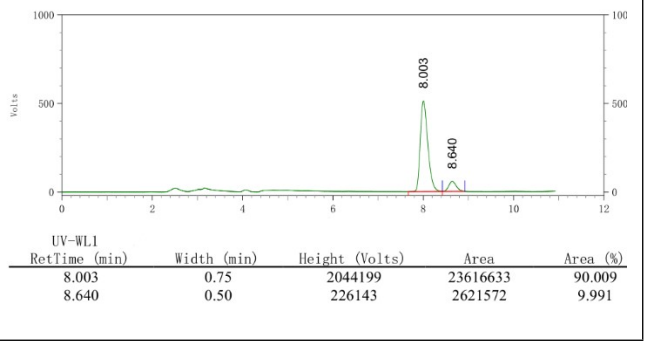
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.83 (br, 1H), 6.85 (td, *J* = 8.6, 2.6 Hz, 1H), 6.72 (ddd, *J* = 15.7, 8.7, 3.5 Hz, 2H), 5.96 (dt, *J* = 19.1, 9.8 Hz, 1H), 5.35 – 5.26 (m, 2H), 3.86 (d, *J* = 9.5 Hz, 1H), 3.81 – 3.67 (m, 4H), 2.58 (d, *J* = 38.5 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.18 (d, *J* = 236.0 Hz), 152.32, 133.84, 124.63 (d, *J* = 7.0 Hz), 119.87, 117.18 (d, *J* = 8.0 Hz), 115.13 (d, *J* = 22.0 Hz), 114.81 (d, *J* = 23.0 Hz), 74.05, 74.04, 66.74, 50.74. **HRMS (ESI)** m/z Calcd for $[C_{13}H_{16}FNNaO_2, M + Na]^+$: 260.1057, Found: 260.1055. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 220 nm, t_R = 8.003 min (major), t_R = 8.640 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -97.3 (*c* = 1.0, CH_3OH); **Physical properties:** colorless oil; **Yield:** 92 %, 22.0 mg.



UV-WL1

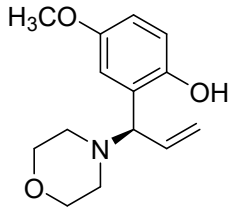
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
7.830	0.88	1904108	20869005	50.463
8.267	1.40	1780760	20486108	49.537



UV-WL1

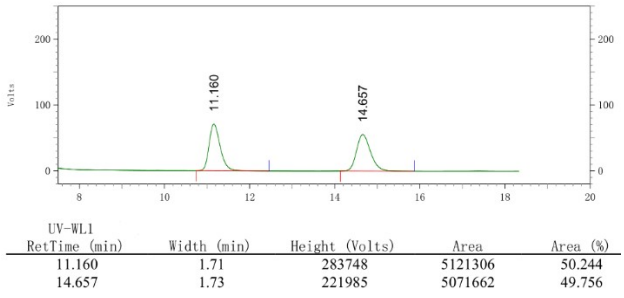
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
8.003	0.75	2044199	23616633	90.009
8.640	0.50	226143	2621572	9.991

4-methoxy-2-(1-morpholinoallyl)phenol (5d)



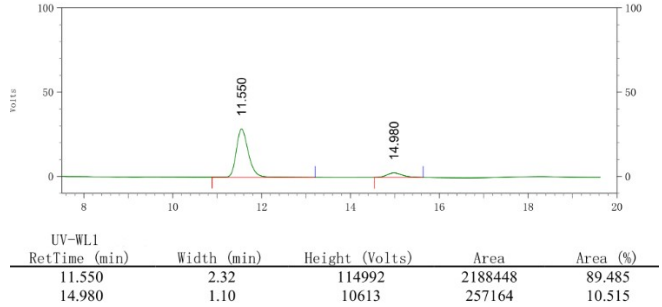
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.46 (s, 1H), 6.77 – 6.69 (m, 2H), 6.55 (d, *J* = 2.1 Hz, 1H), 5.98 (dt, *J* = 17.2, 9.7 Hz, 1H), 5.34 – 5.21 (m, 2H), 3.82 (d, *J* = 9.5 Hz, 1H), 3.72 (s, 7H), 2.57 (d, *J* = 38.6 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.72, 149.99, 134.57, 124.40, 119.17, 116.83, 114.25, 114.17, 113.68, 74.67, 74.58, 66.76, 55.50, 50.90. **HRMS (ESI)** m/z Calcd for $[C_{14}H_{19}NNaO_3, M + Na]^+$: 272.1257,

Found: 272.1255. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 220 nm, t_R = 11.550 min (major), t_R = 14.980 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = -109.0 (*c* = 1.0, CH_3OH); **Physical properties:** colorless oil; **Yield:** 95 %, 24.0 mg.



UV-WL1

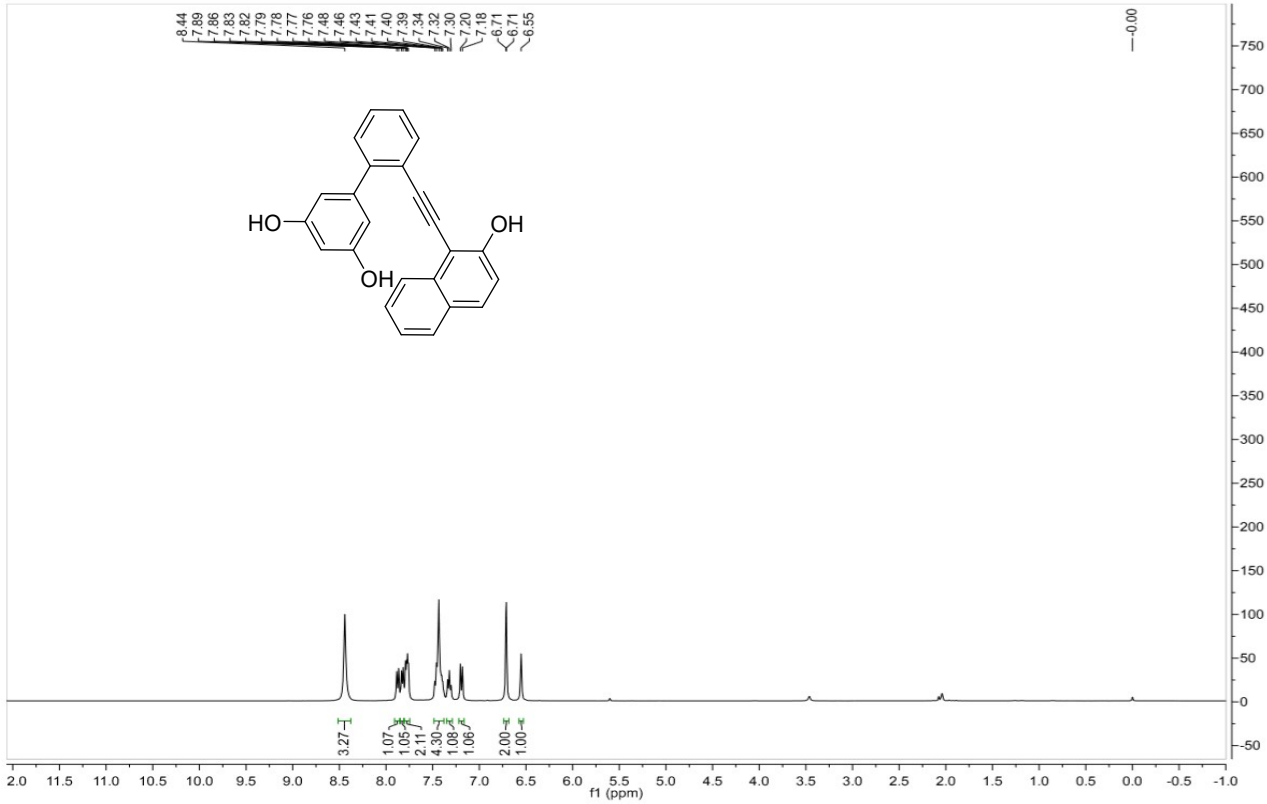
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
11.160	1.71	283748	5121306	50.244
14.657	1.73	221985	5071662	49.756

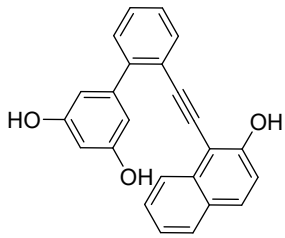


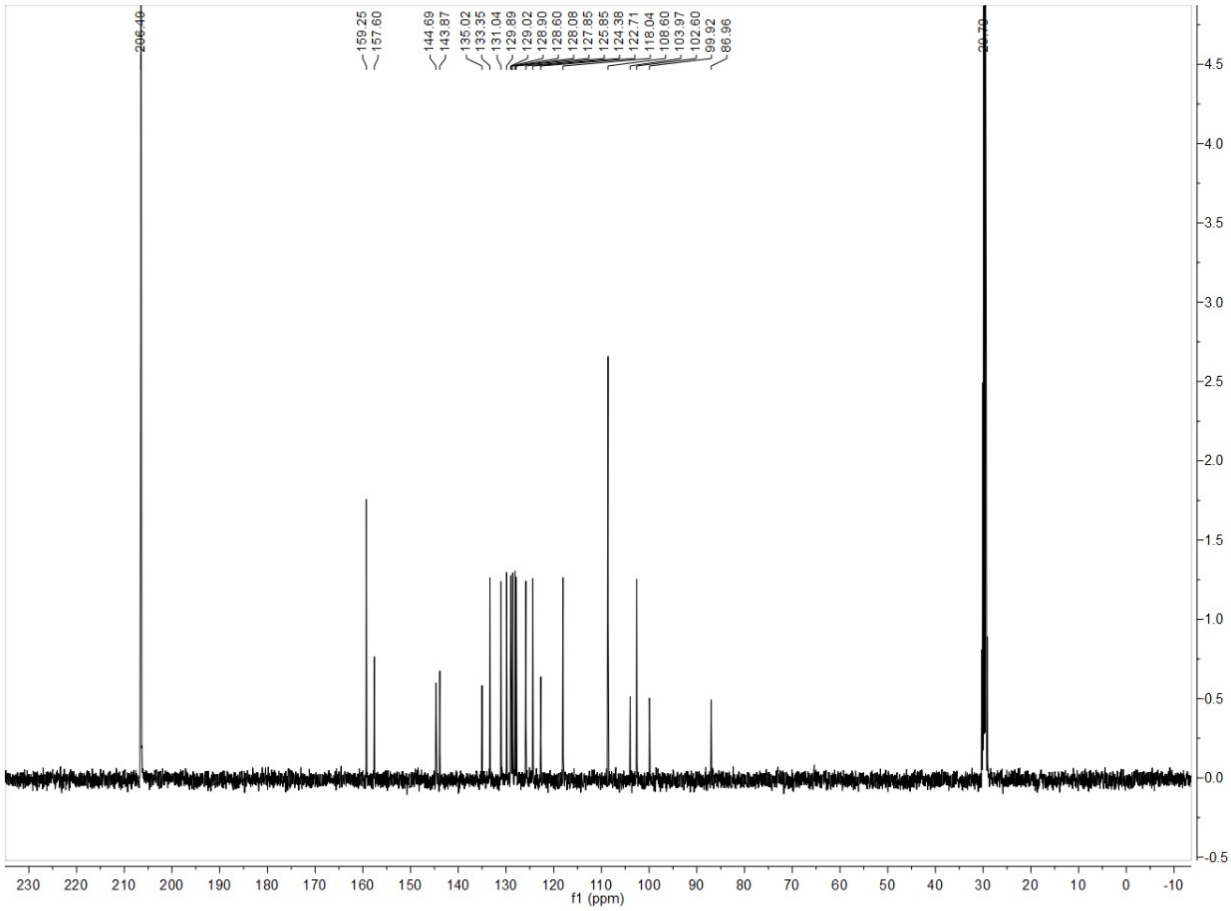
UV-WL1

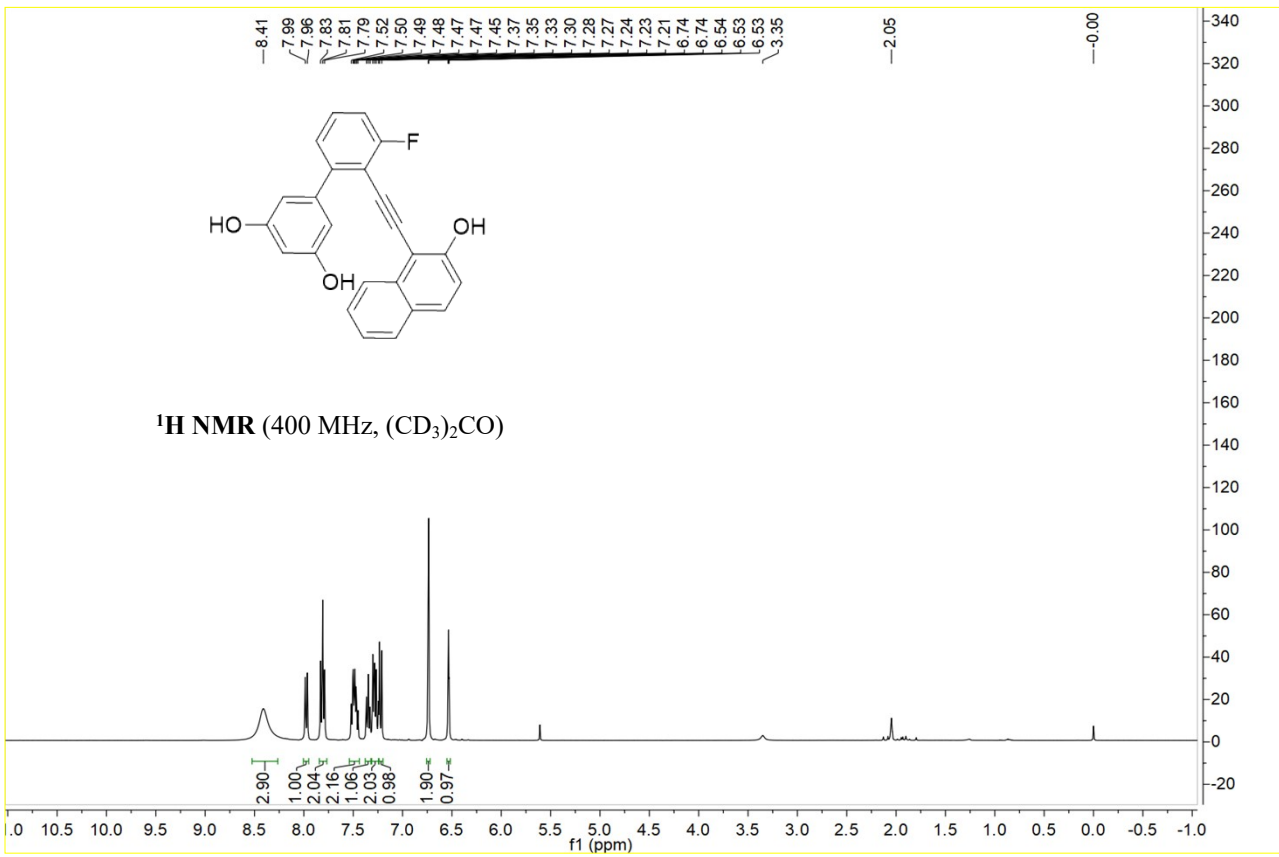
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
11.550	2.32	114992	2188448	89.485
14.980	1.10	10613	257164	10.515

XI. ^{1}H and ^{13}C NMR spectra of substrates

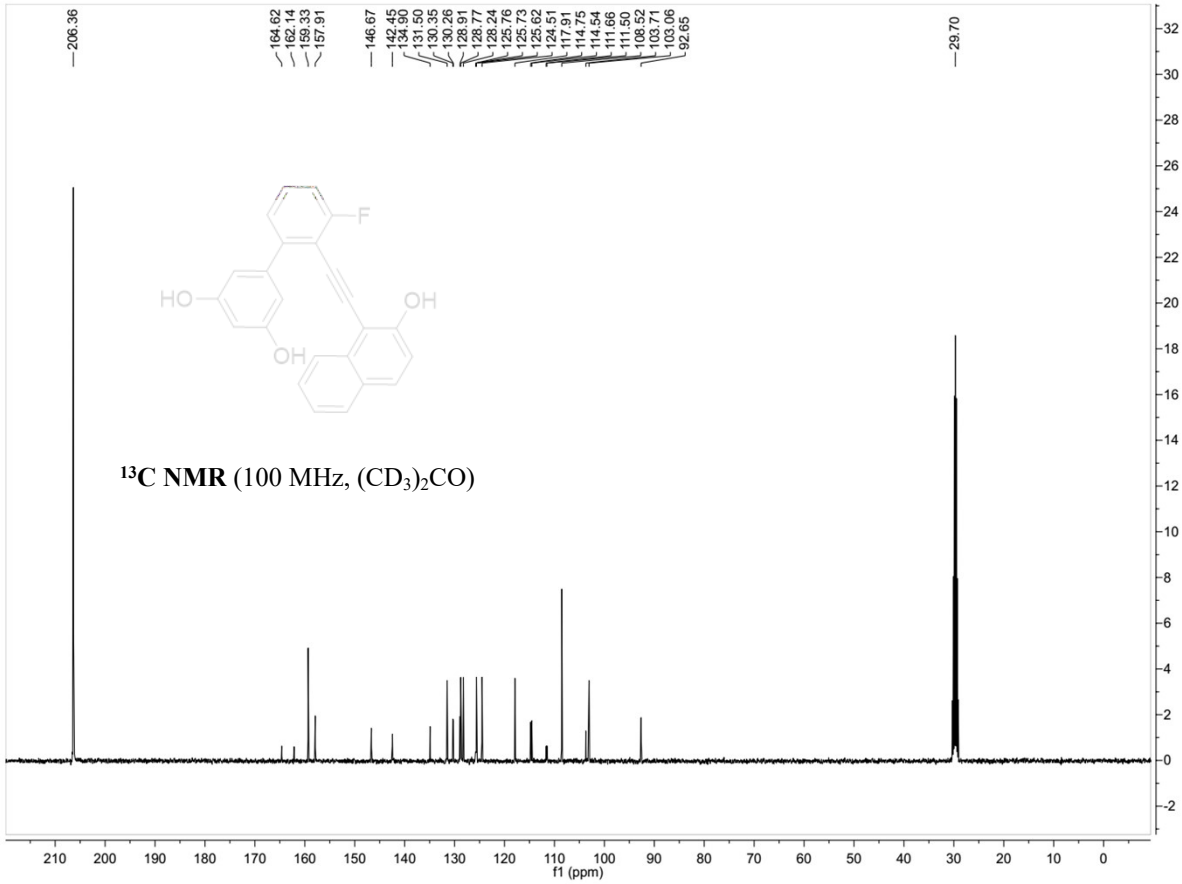




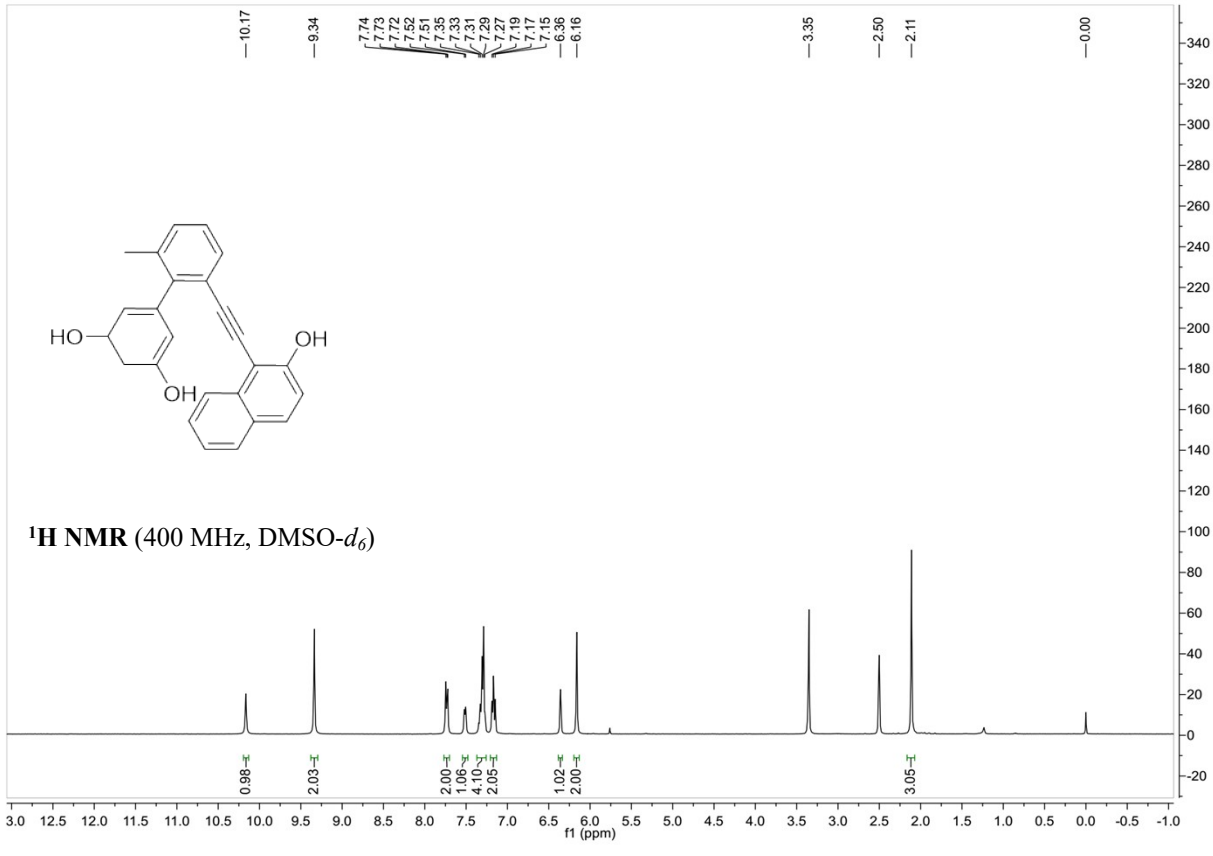




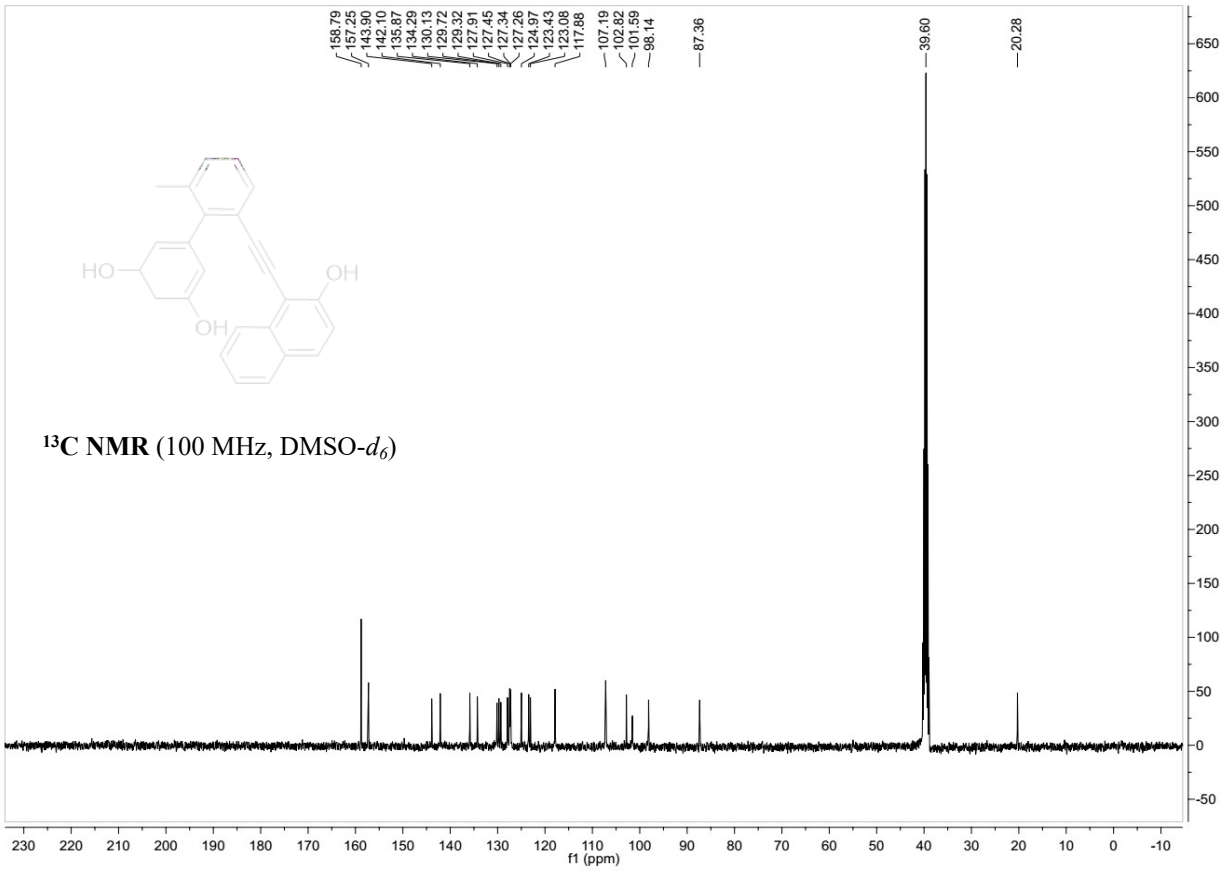
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



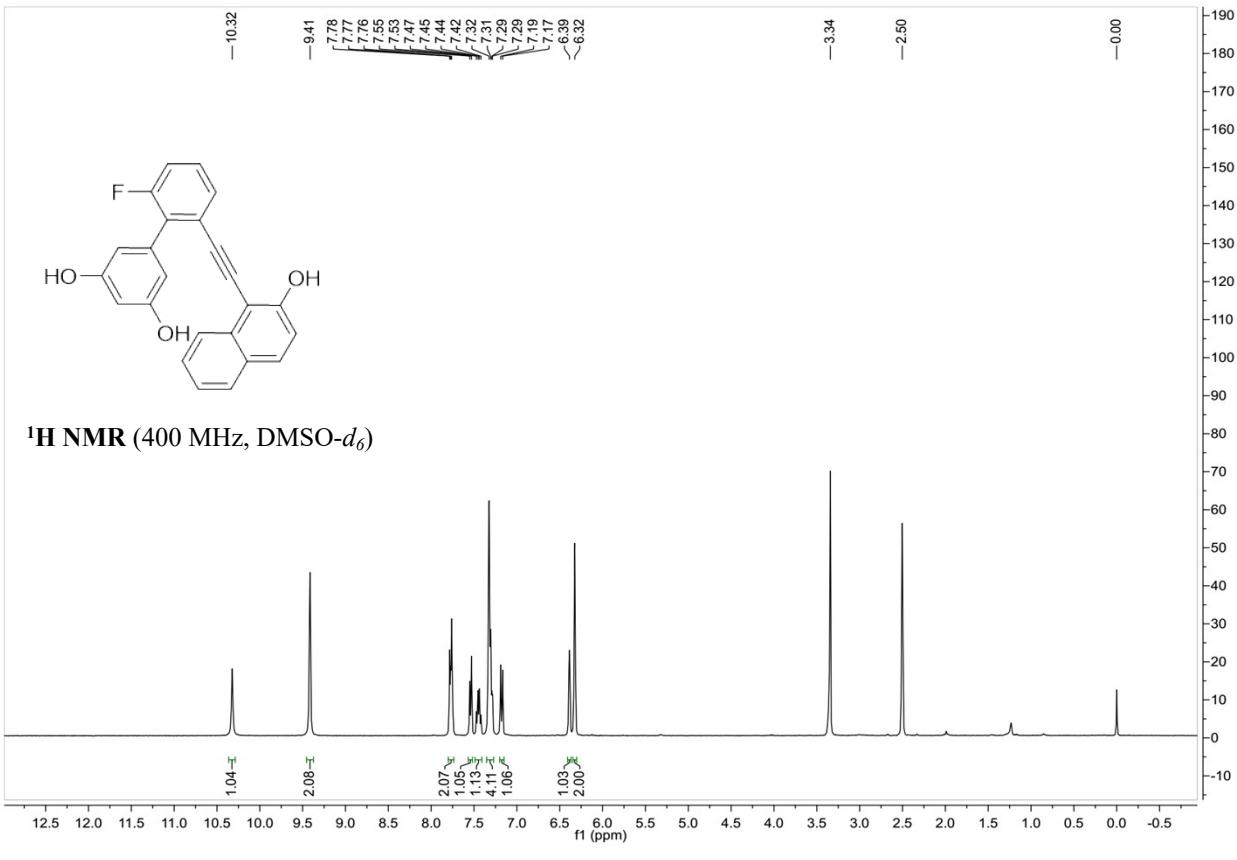
^{13}C NMR (100 MHz, $(CD_3)_2CO$)



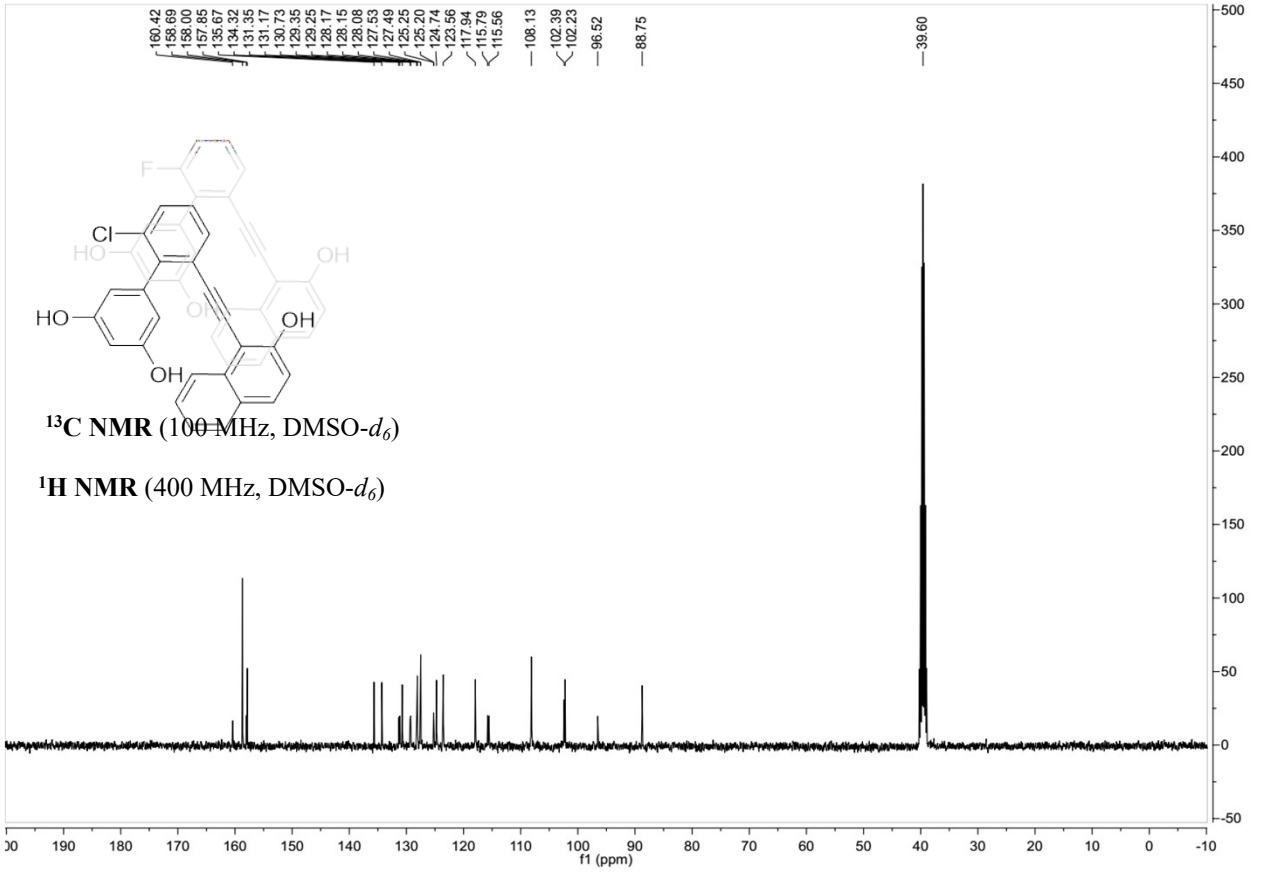
^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (100 MHz, DMSO-d_6)

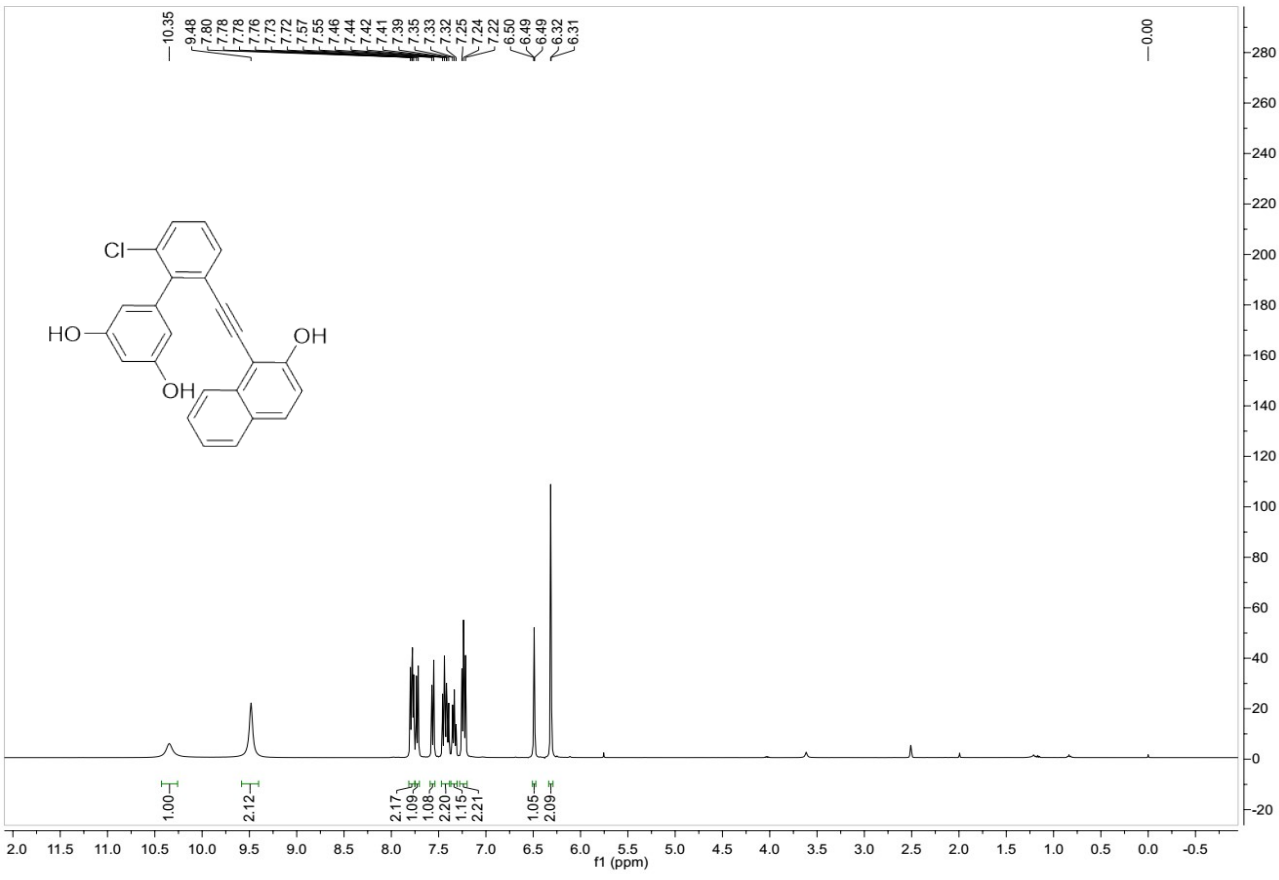


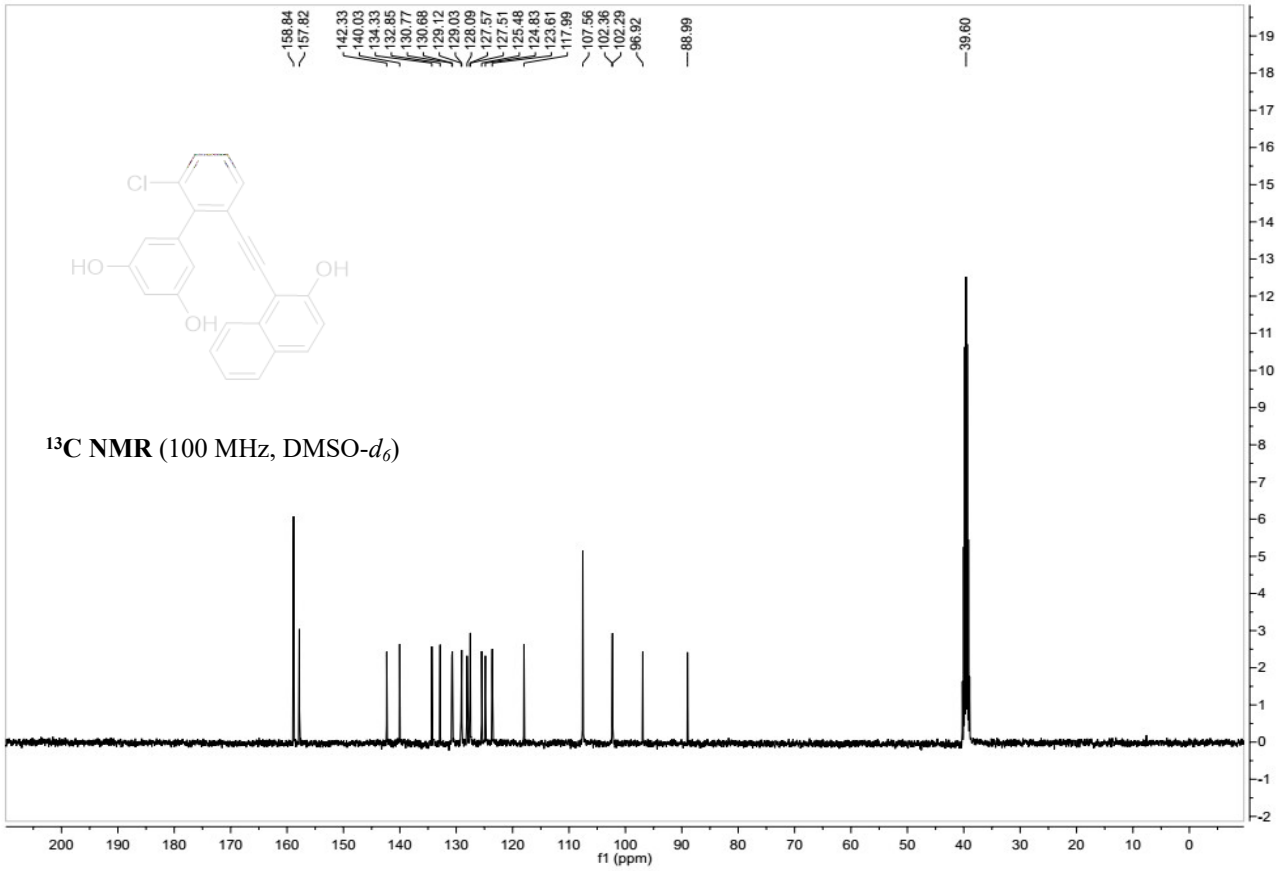
^{1}H NMR (400 MHz, DMSO-d_6)



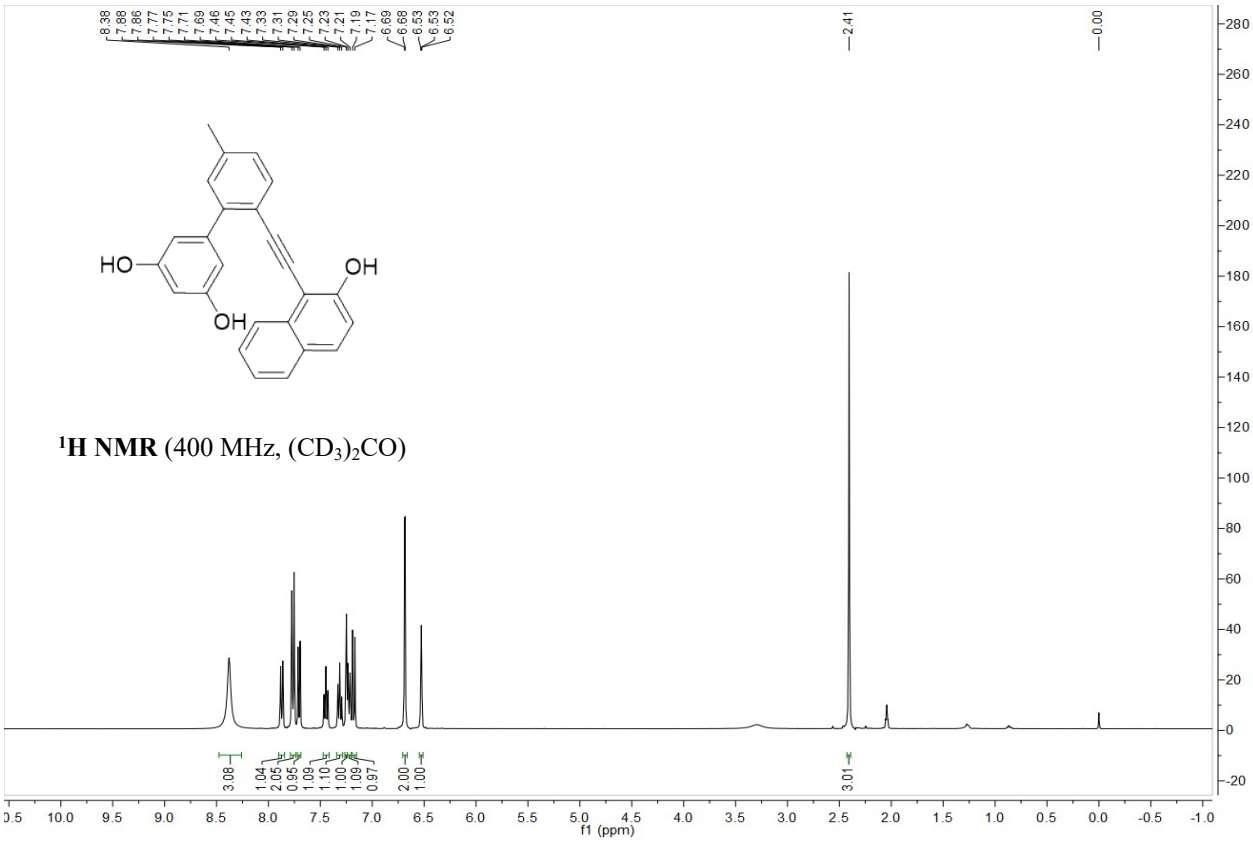
^{13}C NMR (100 MHz, DMSO-d_6)

^{1}H NMR (400 MHz, DMSO-d_6)

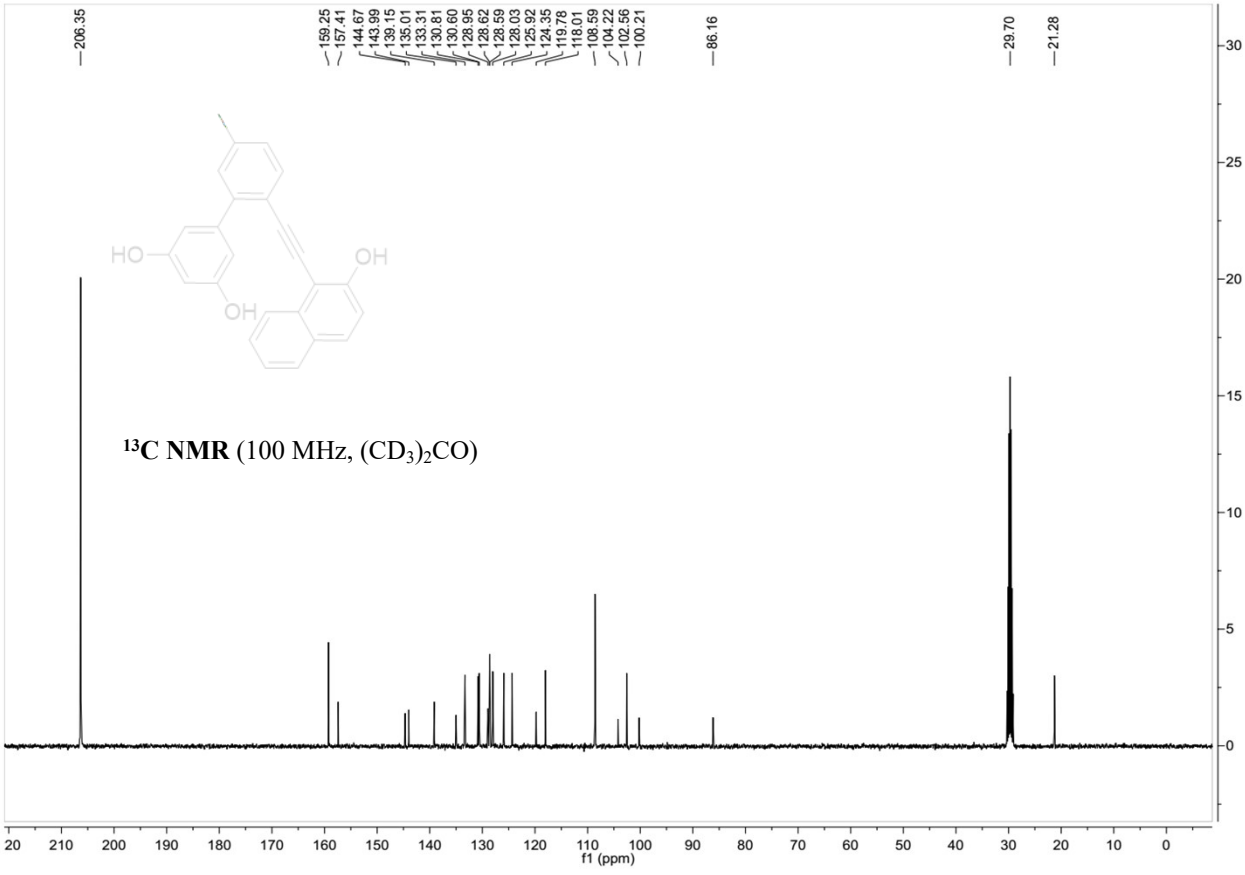




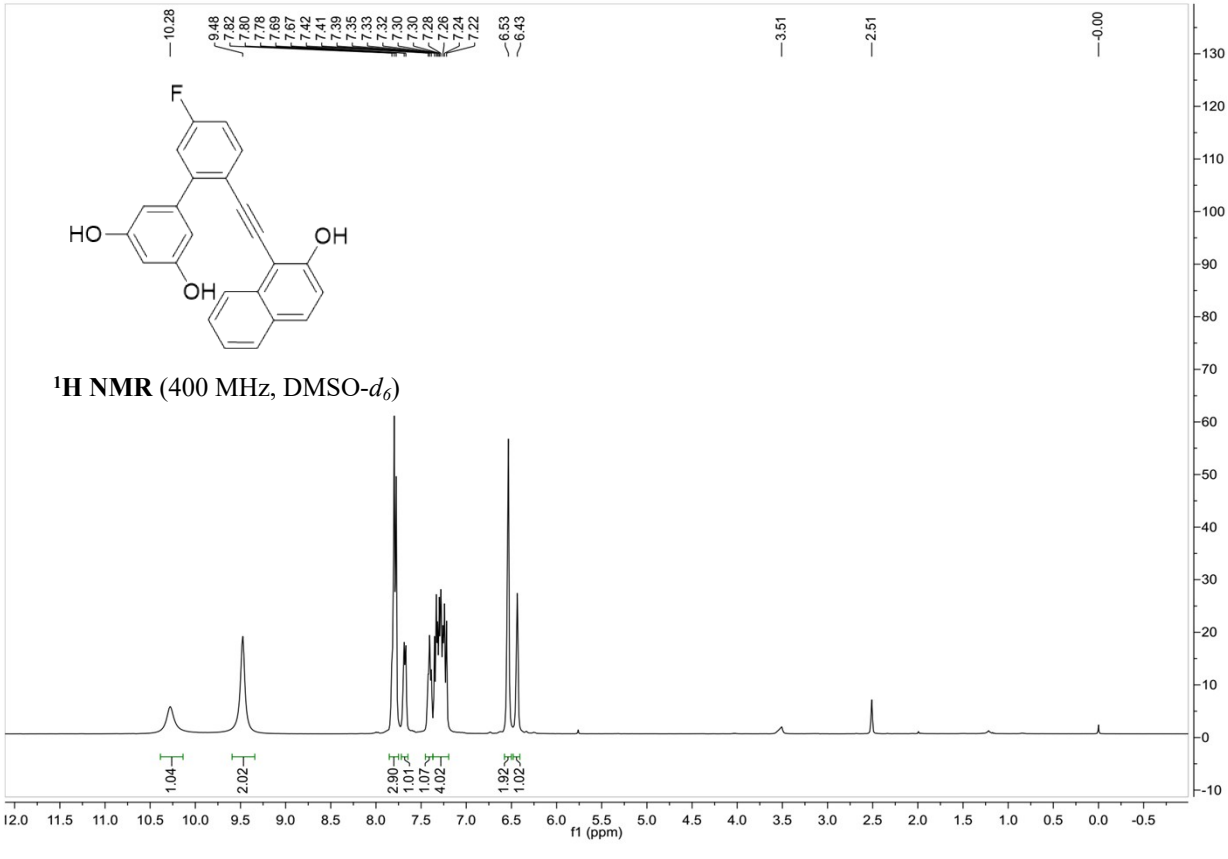
^{13}C NMR (100 MHz, DMSO-d_6)



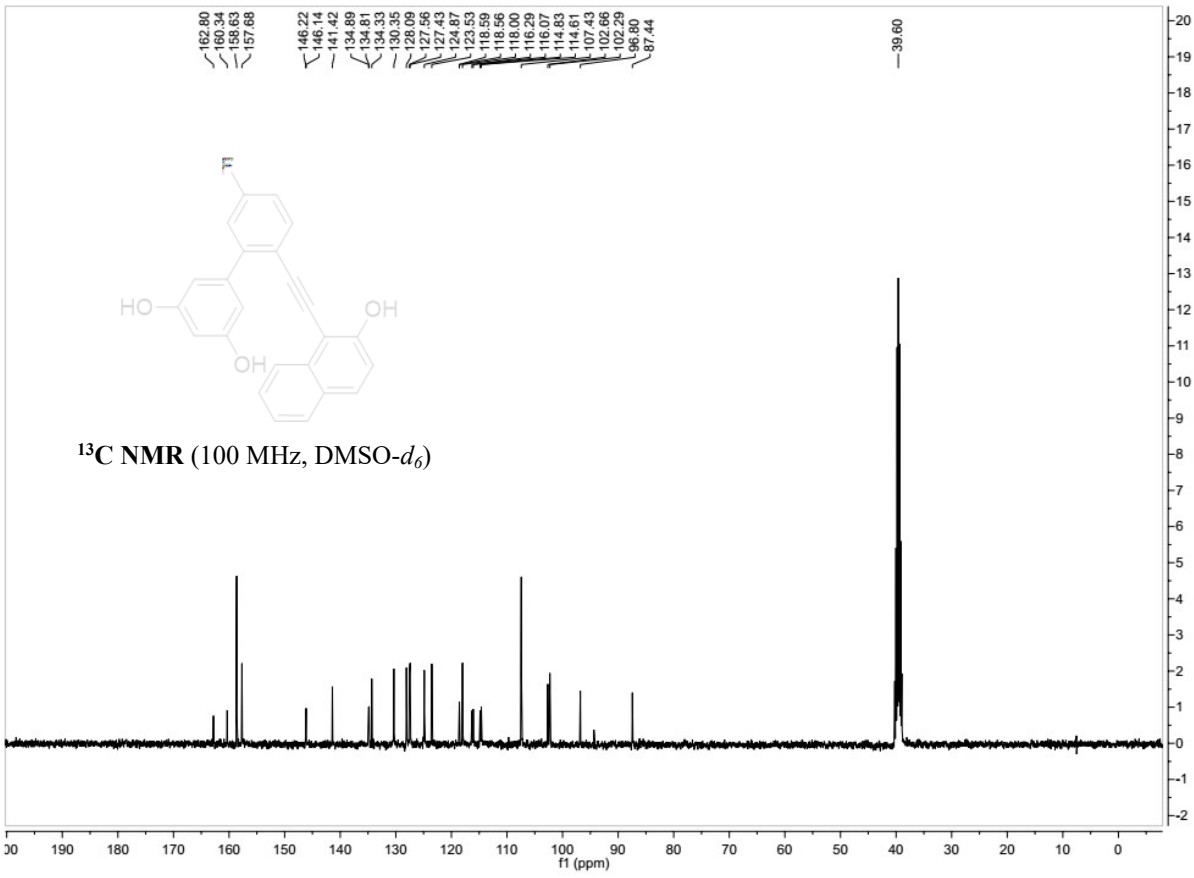
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



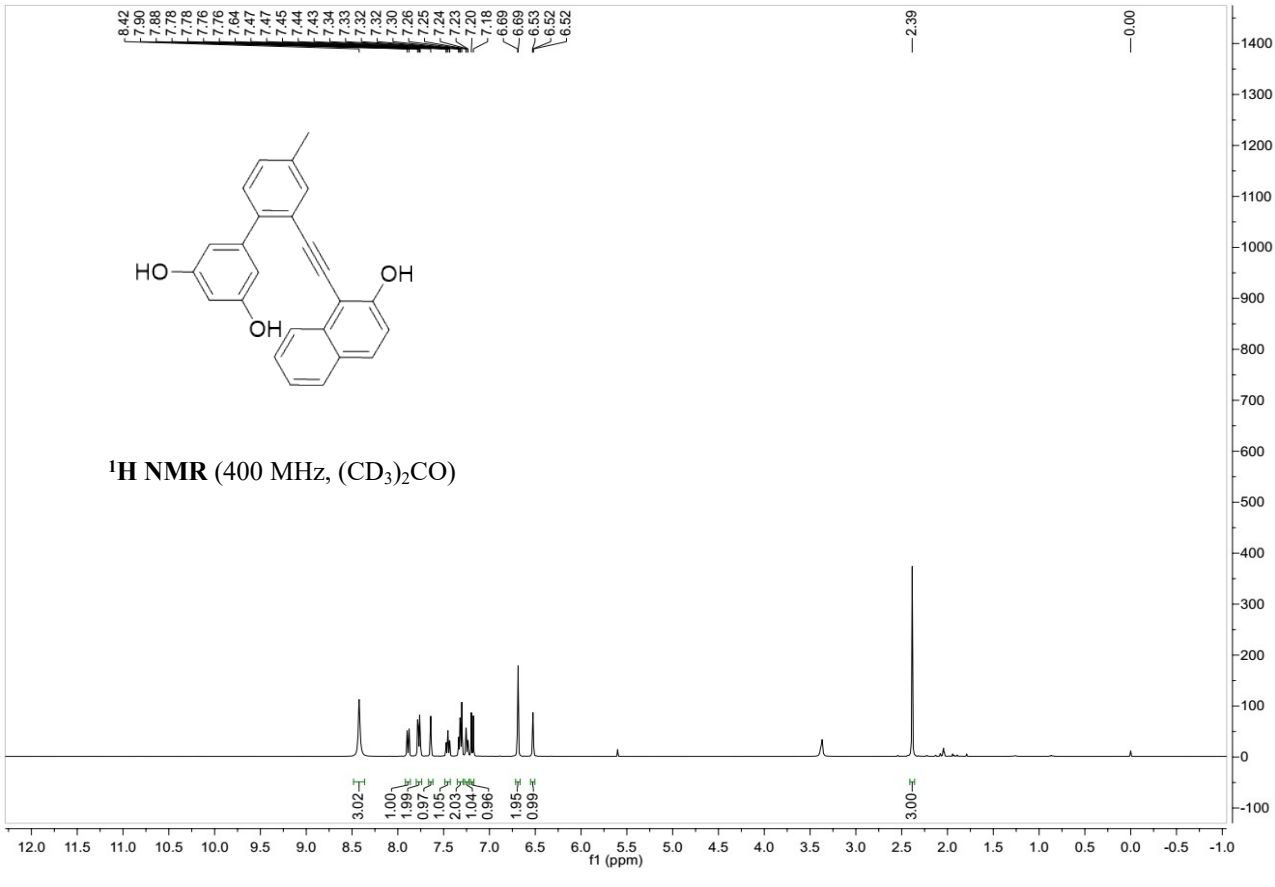
^{13}C NMR (100 MHz, $(CD_3)_2CO$)



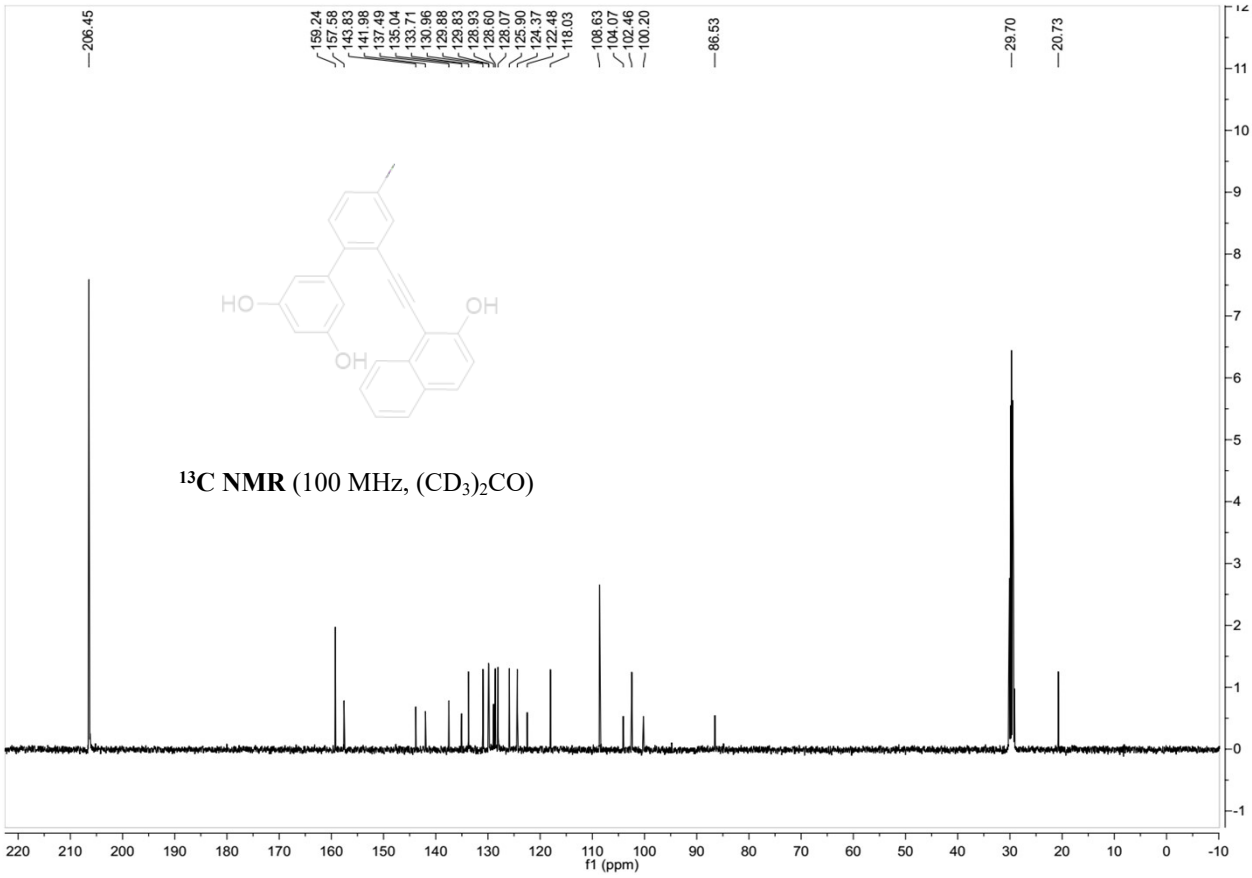
^{1}H NMR (400 MHz, DMSO-d_6)



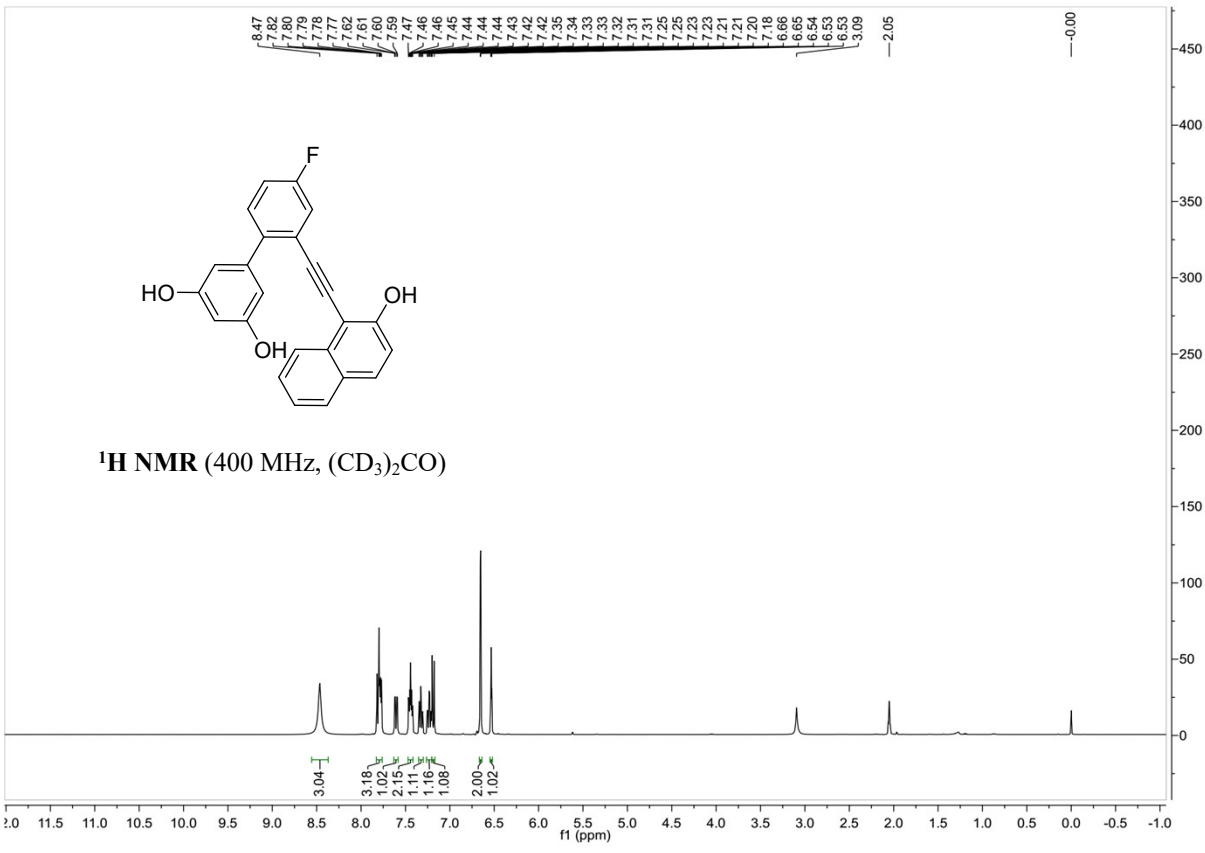
^{13}C NMR (100 MHz, DMSO-d_6)



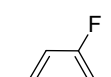
^{1}H NMR (400 MHz, $(CD_3)_2CO$)

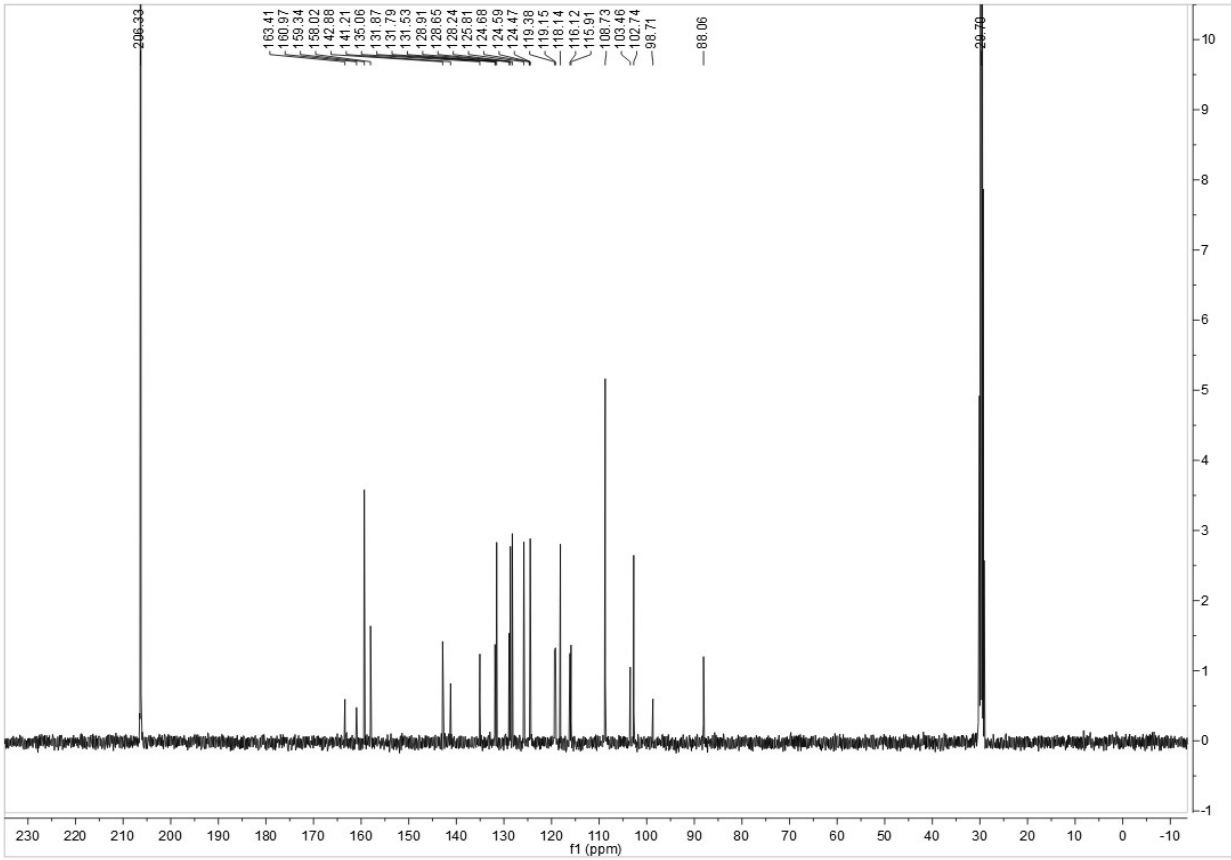


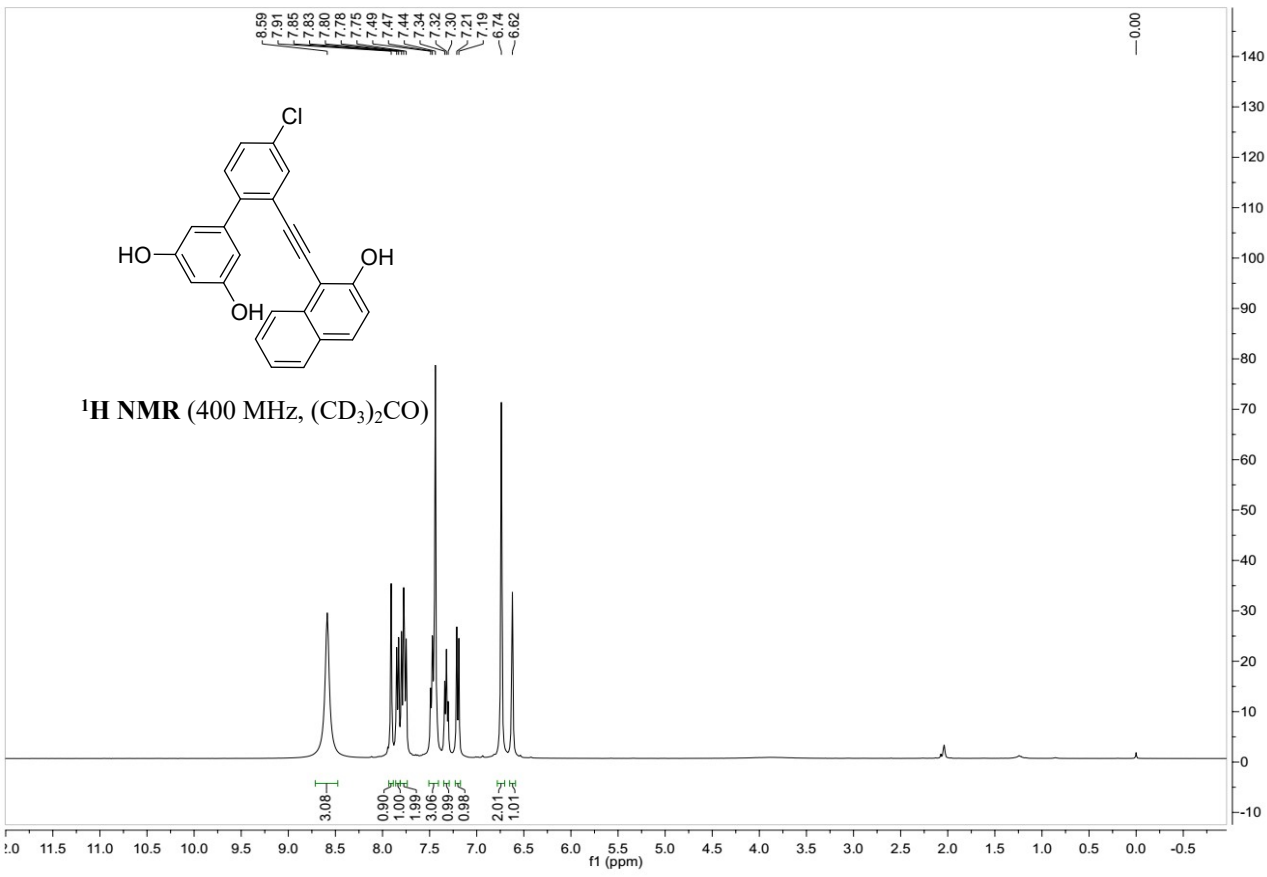
^{13}C NMR (100 MHz, $(CD_3)_2CO$)



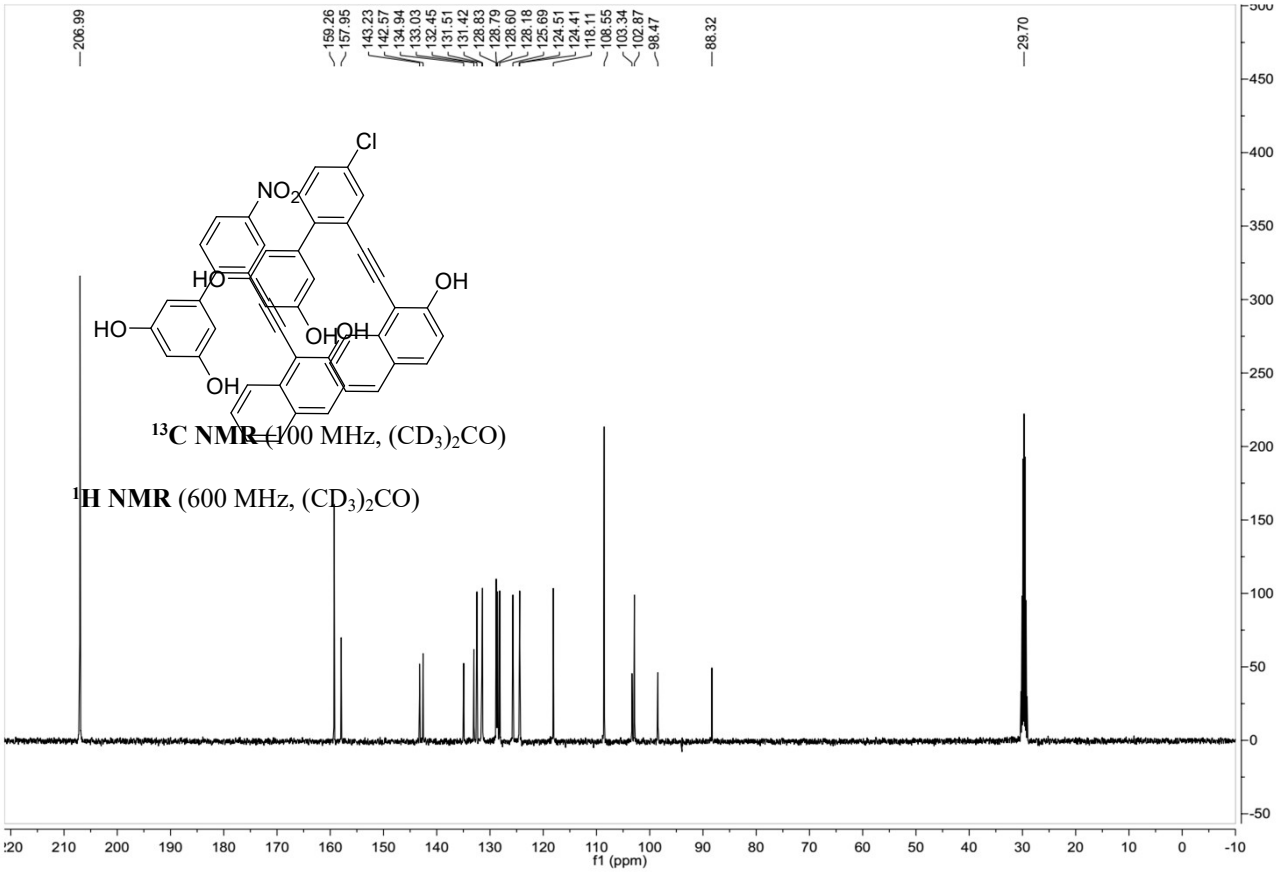
^{1}H NMR (400 MHz, $(CD_3)_2CO$)





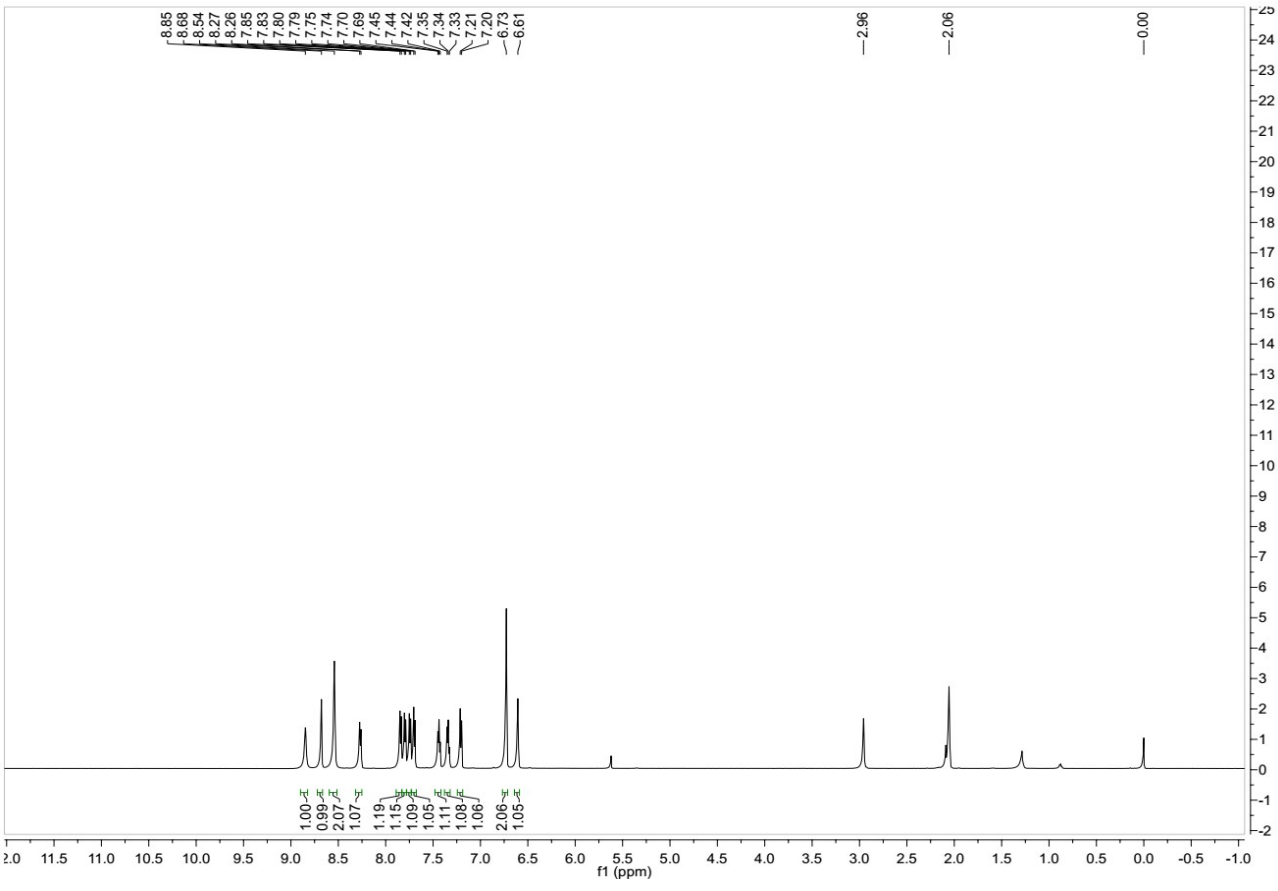


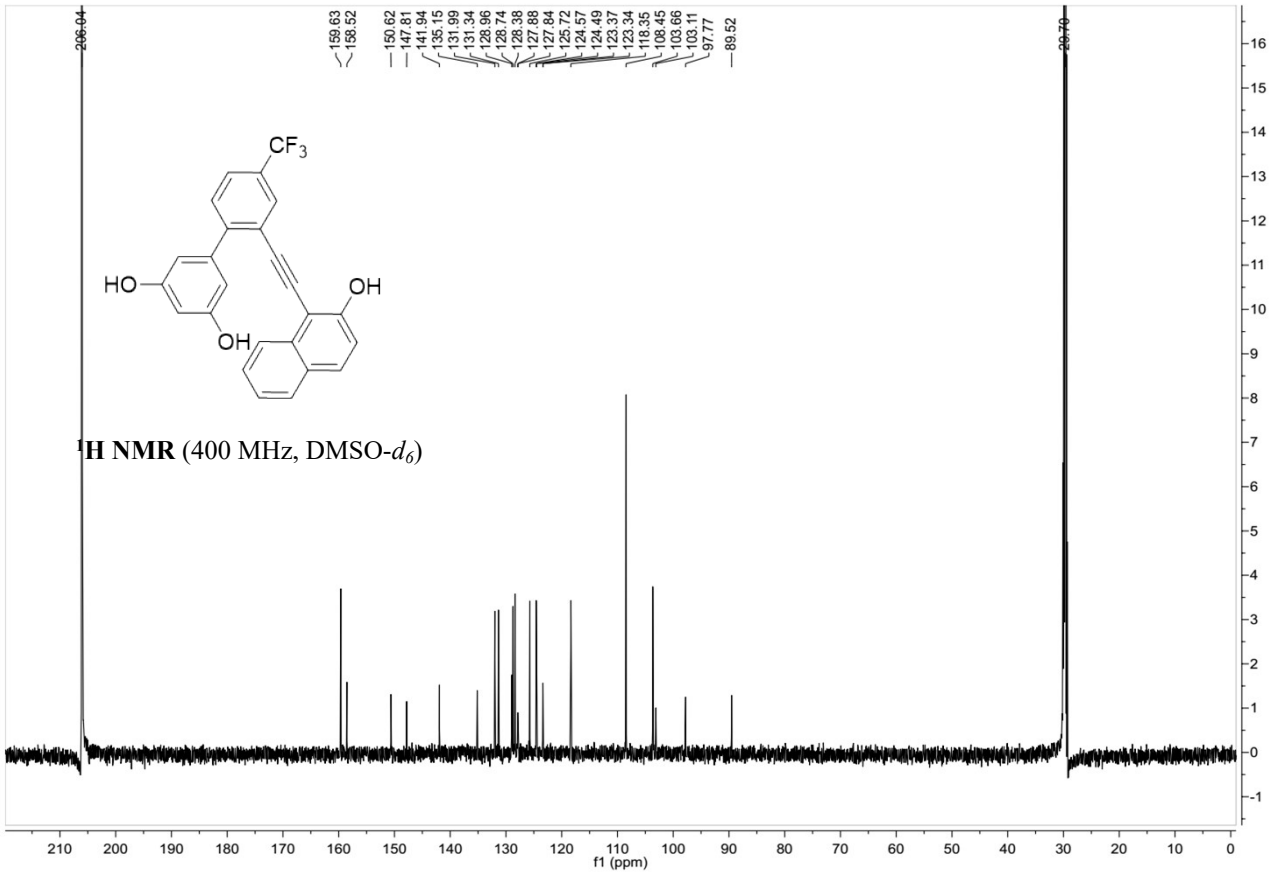
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



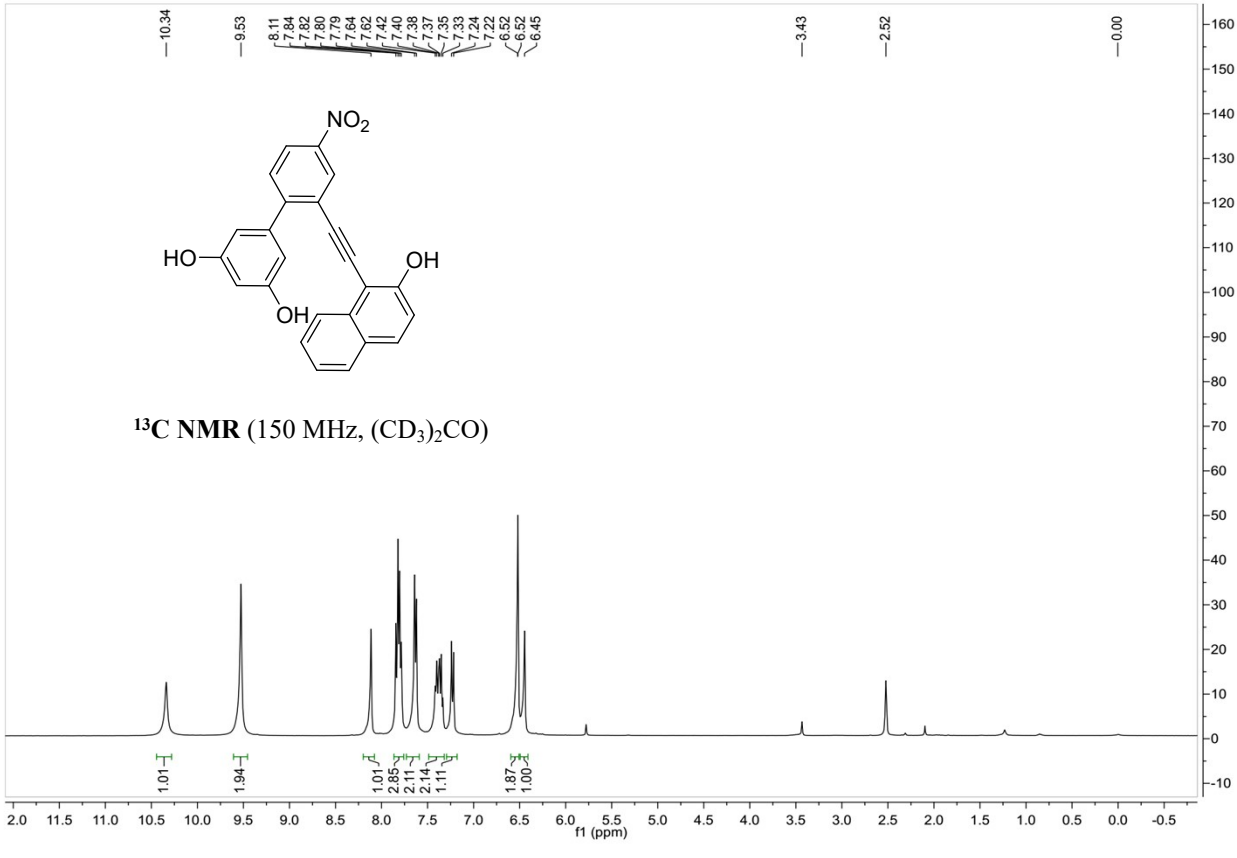
^{13}C NMR (100 MHz, $(CD_3)_2CO$)

^{1}H NMR (600 MHz, $(CD_3)_2CO$)

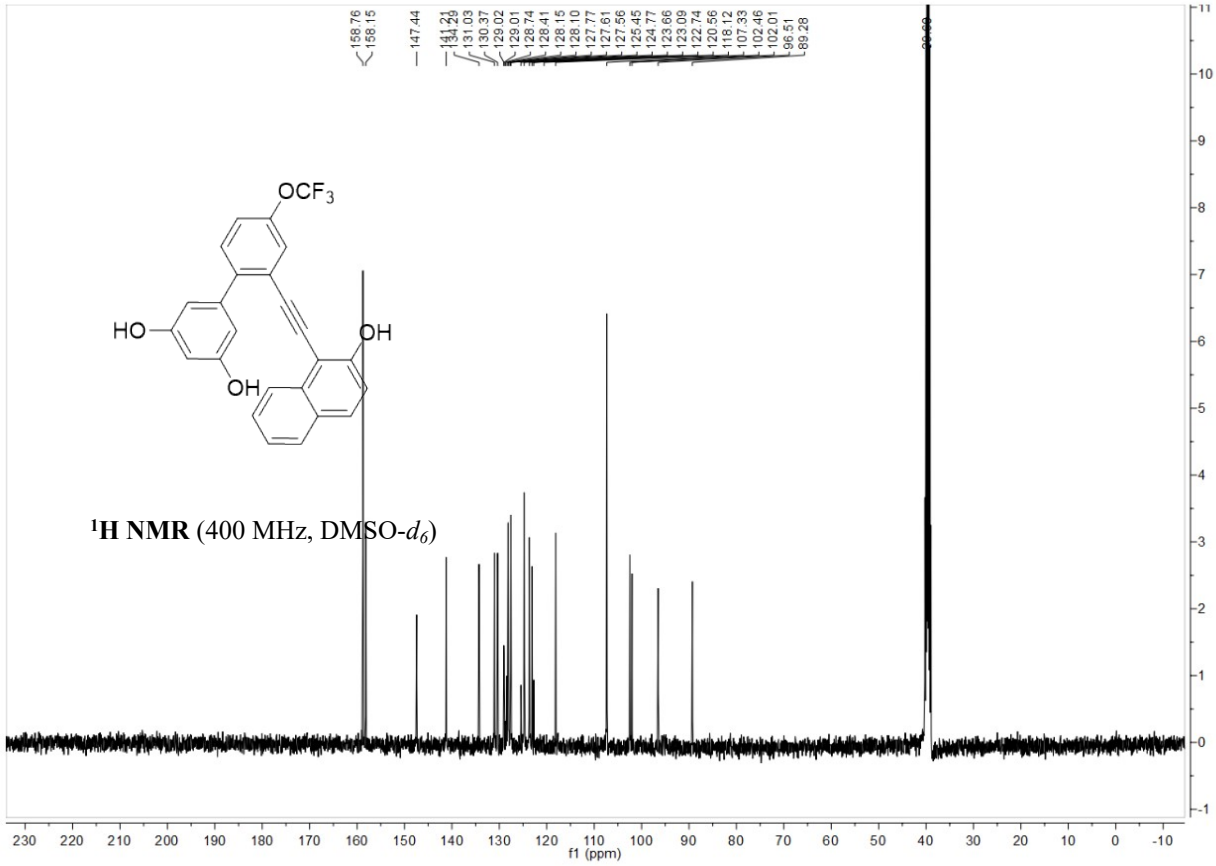




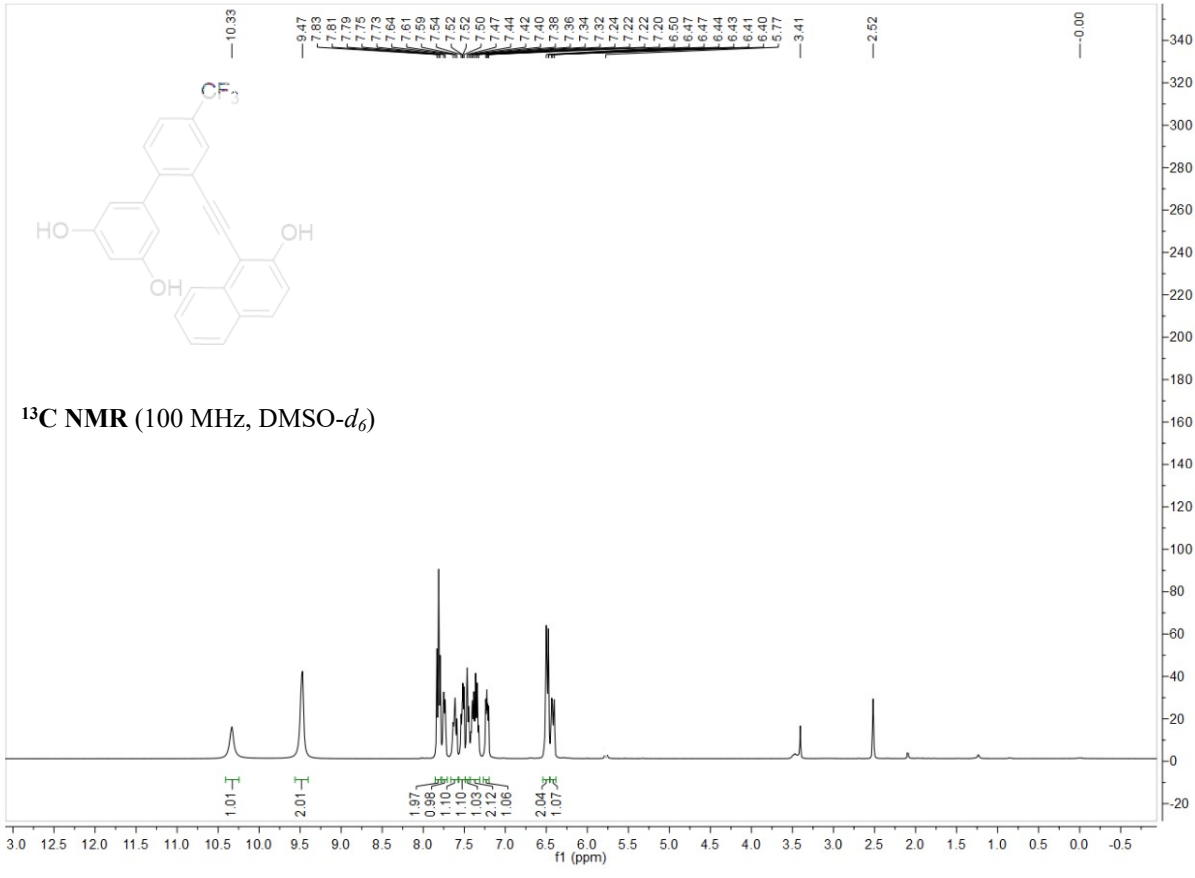
^{1}H NMR (400 MHz, DMSO-d_6)



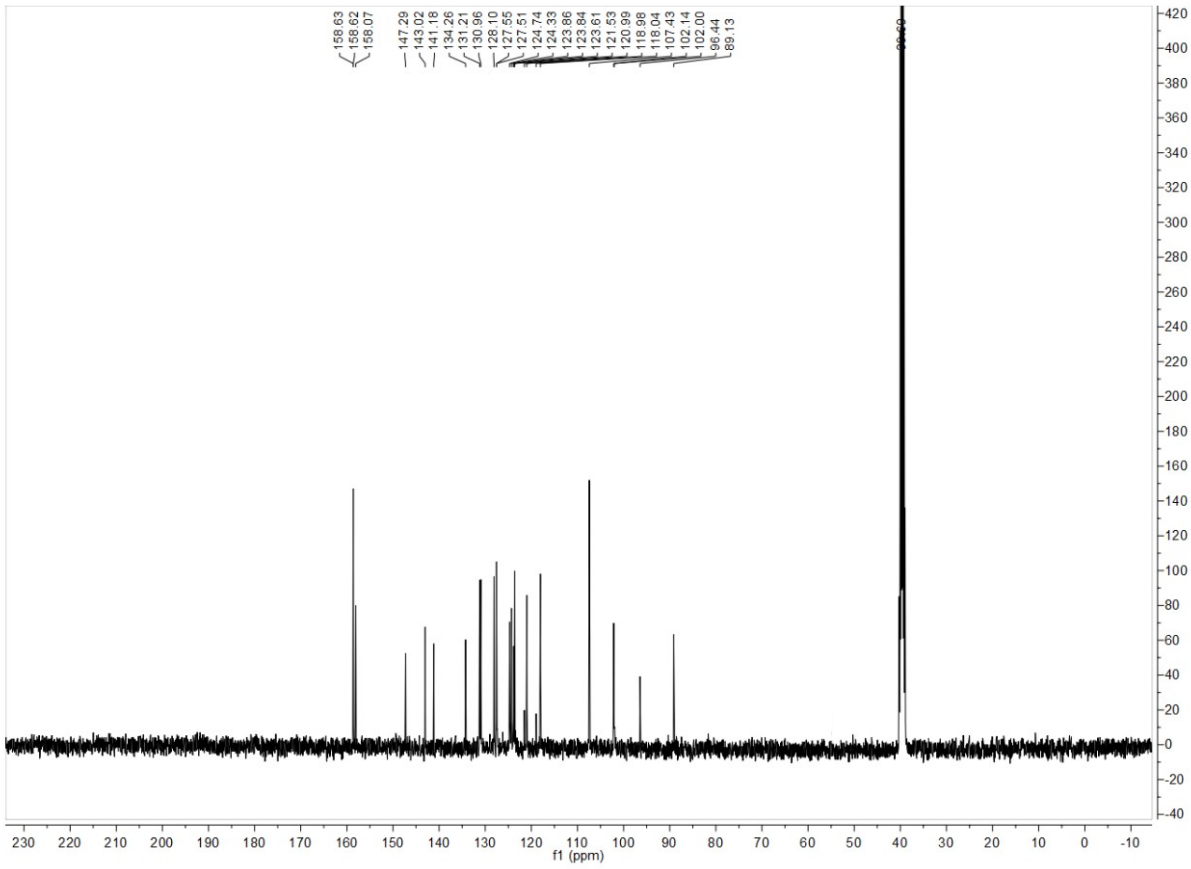
^{13}C NMR (150 MHz, $(CD_3)_2CO$)

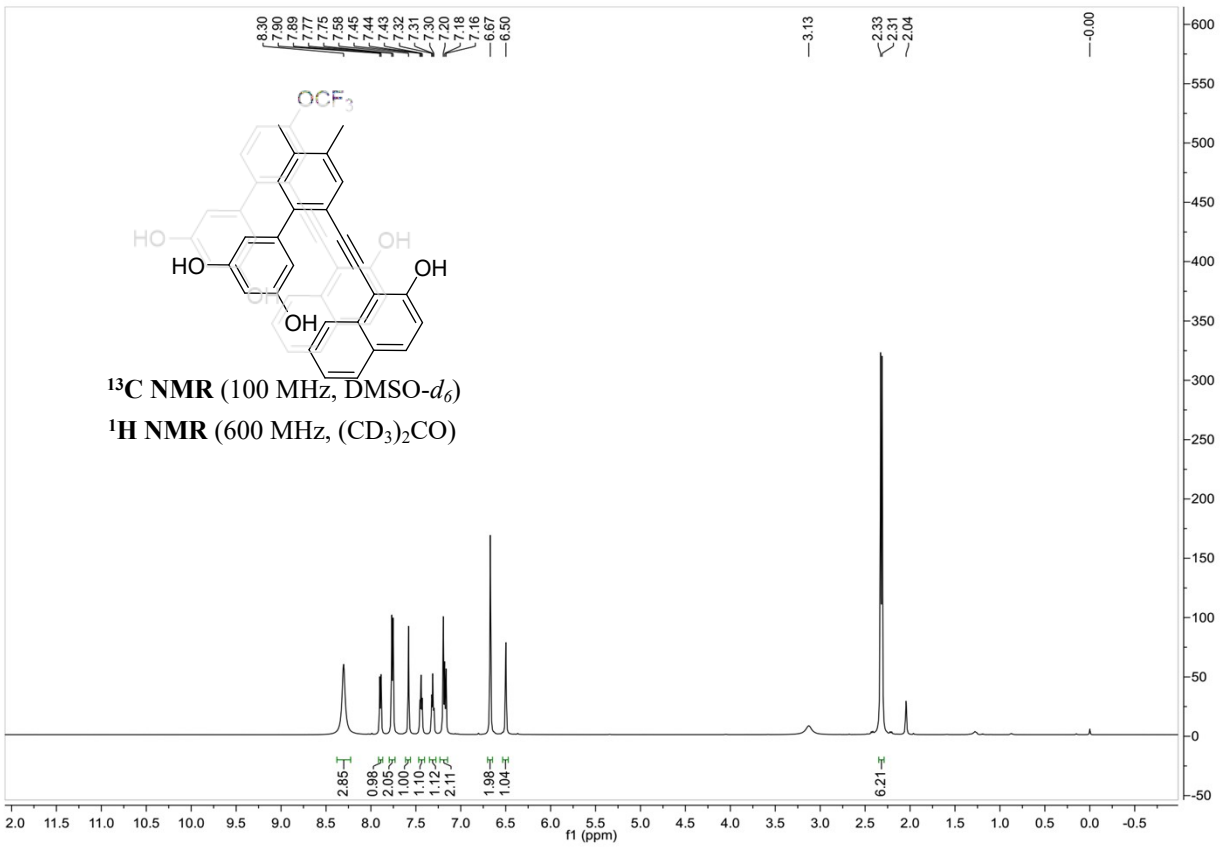


^{1}H NMR (400 MHz, DMSO-d_6)



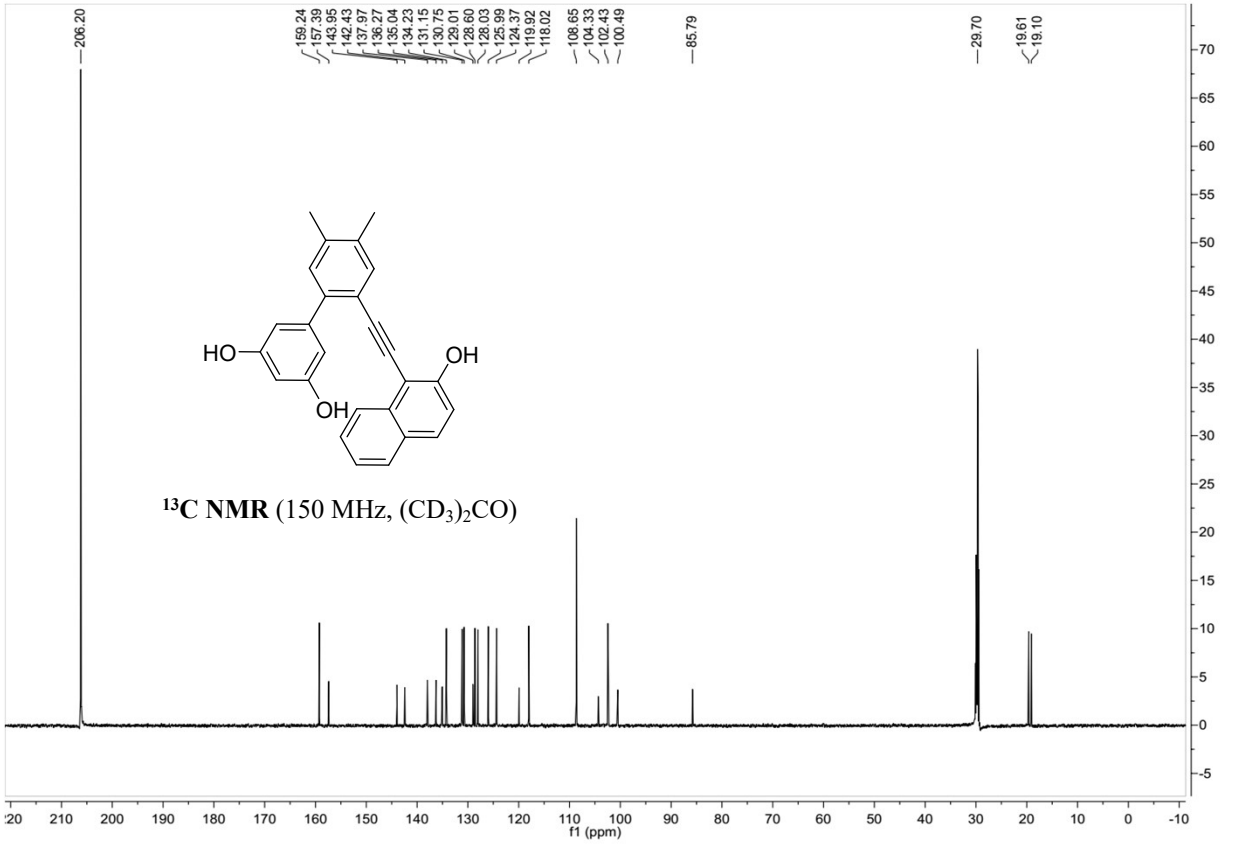
^{13}C NMR (100 MHz, DMSO-d_6)



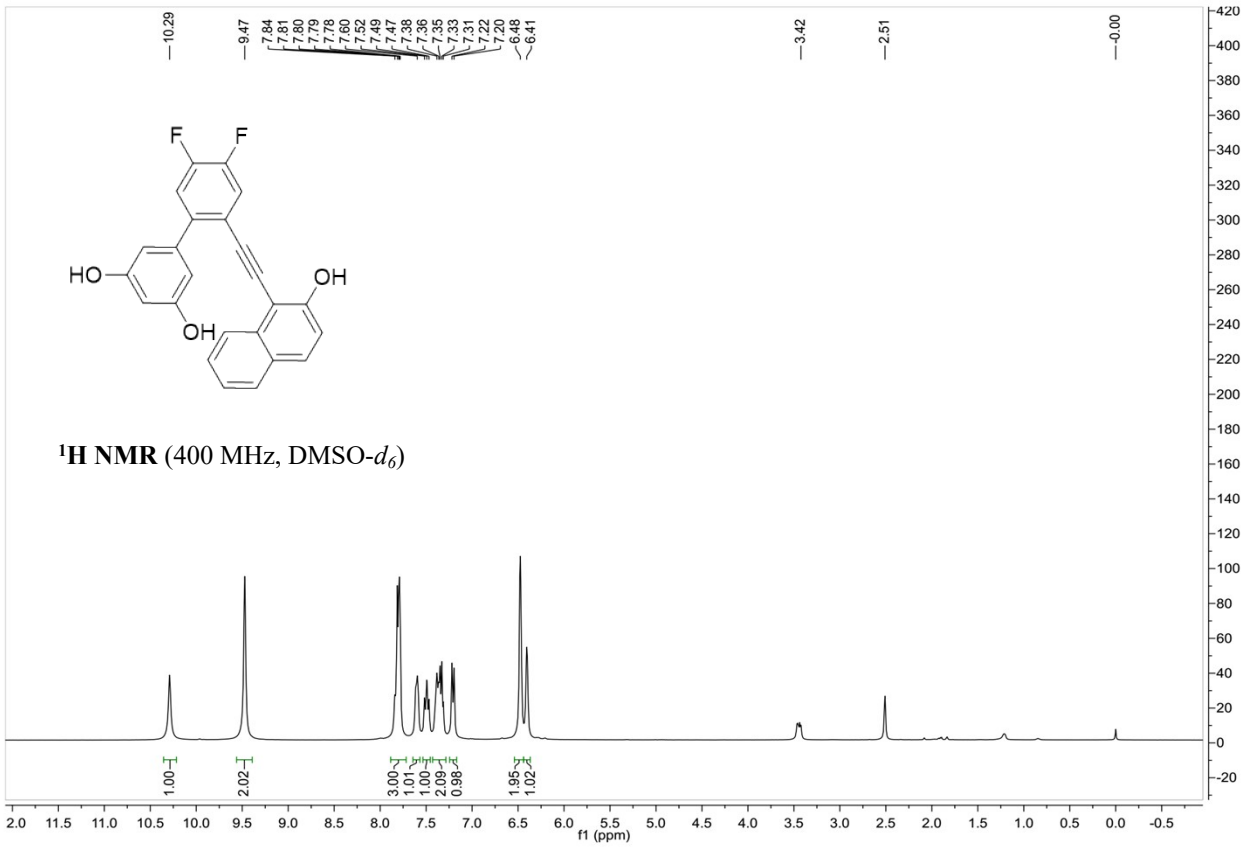


^{13}C NMR (100 MHz, DMSO-d_6)

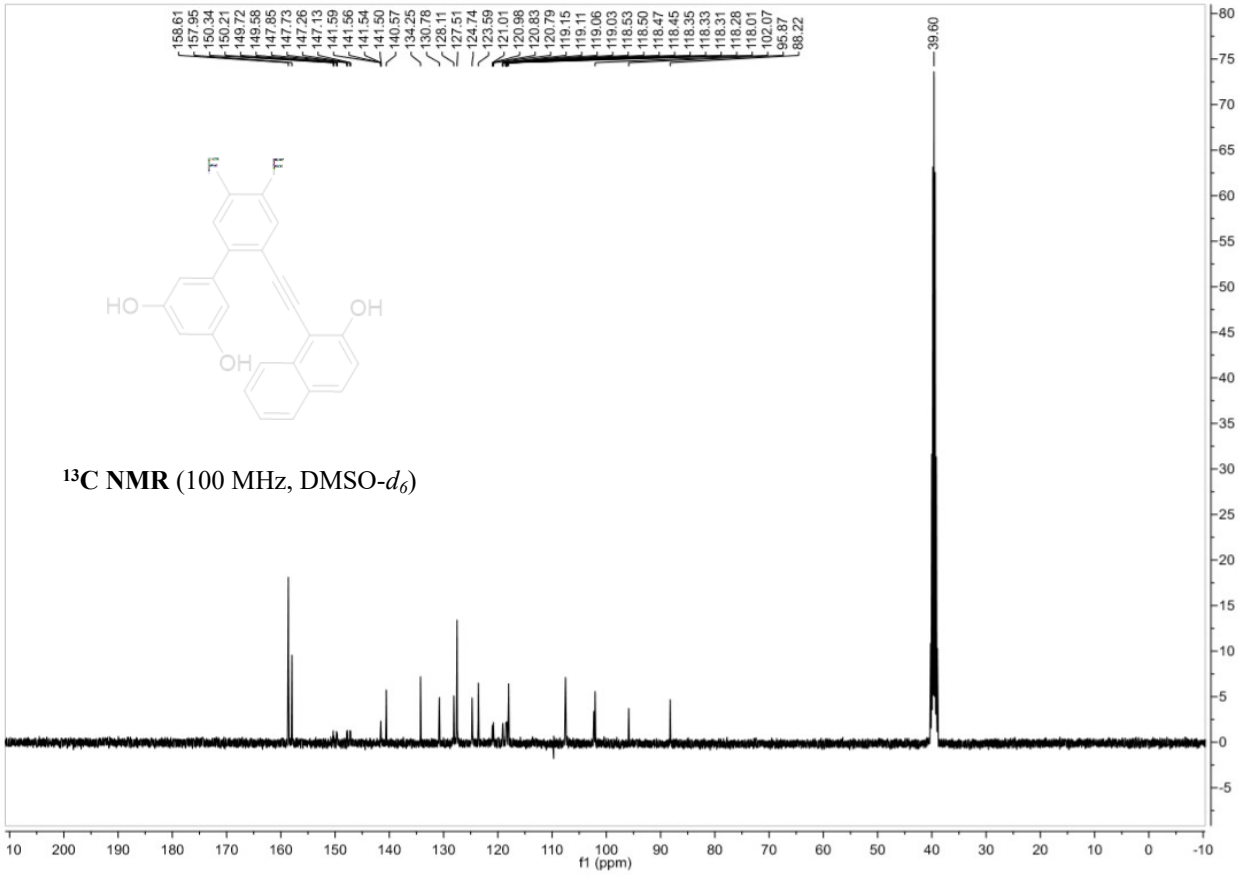
^{1}H NMR (600 MHz, $(CD_3)_2CO$)



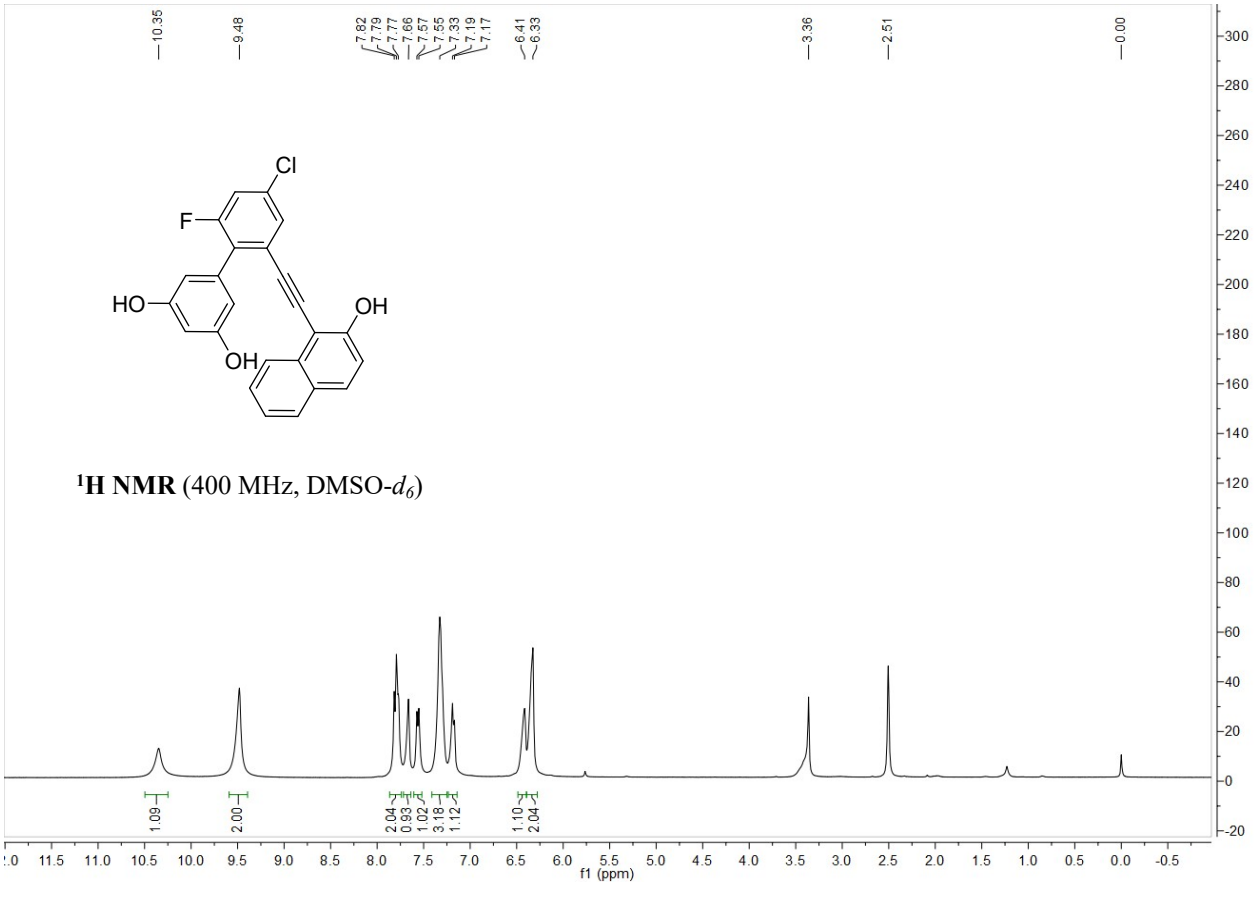
^{13}C NMR (150 MHz, $(CD_3)_2CO$)



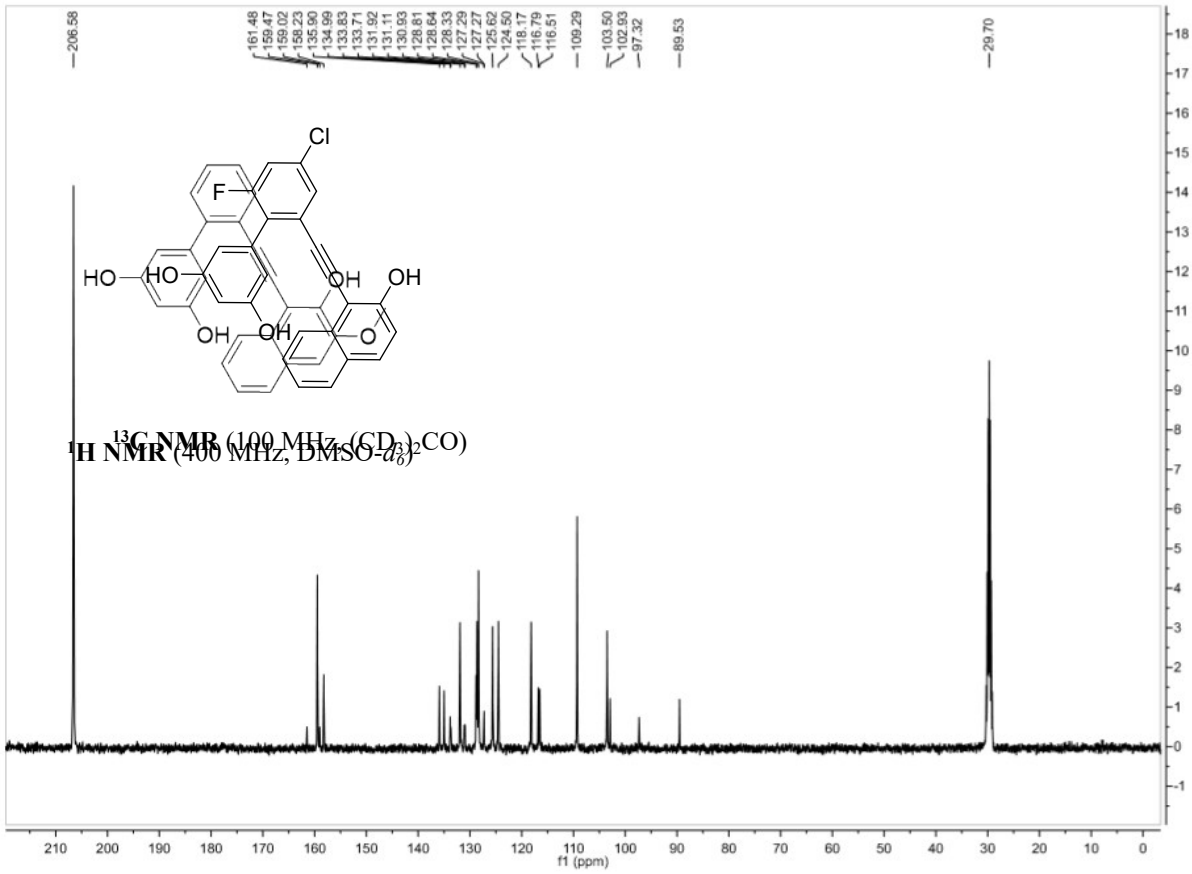
^{1}H NMR (400 MHz, DMSO-d_6)



^{13}C NMR (100 MHz, DMSO-d_6)

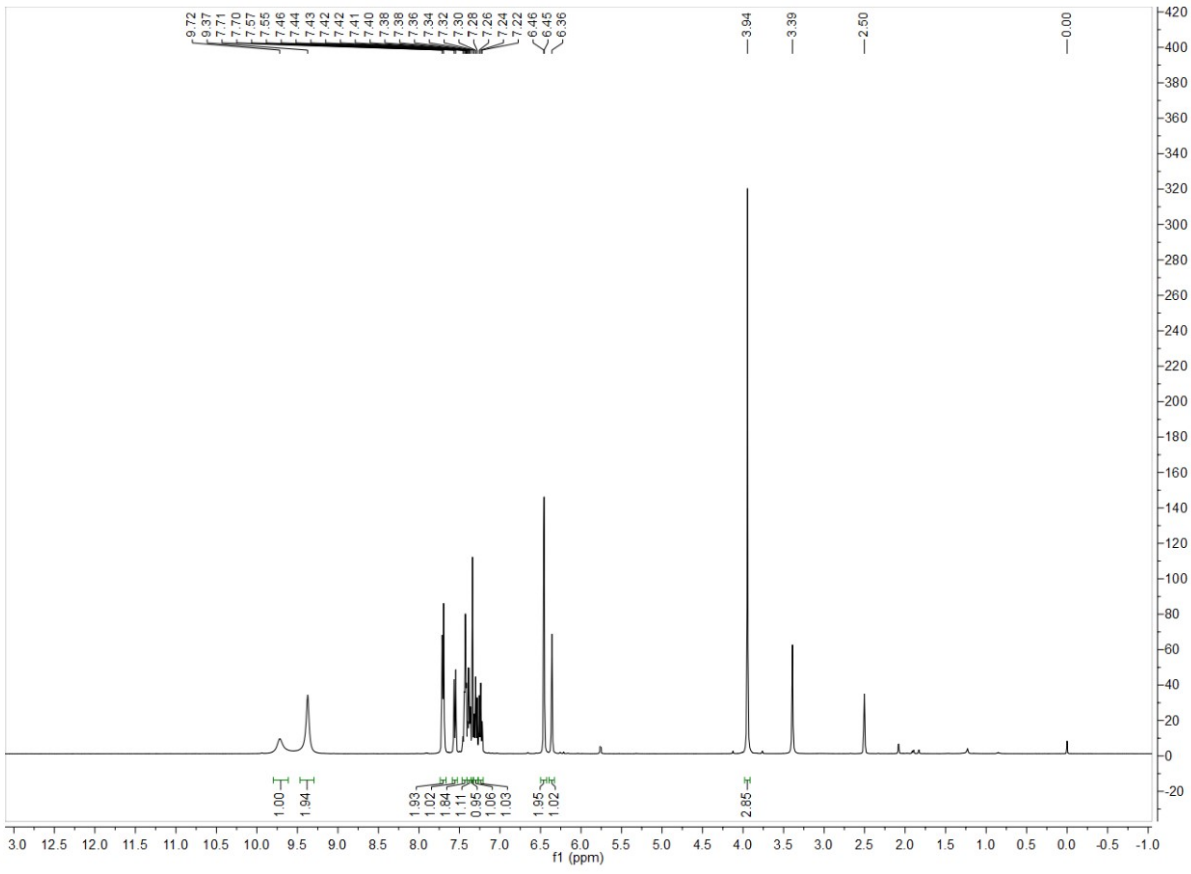


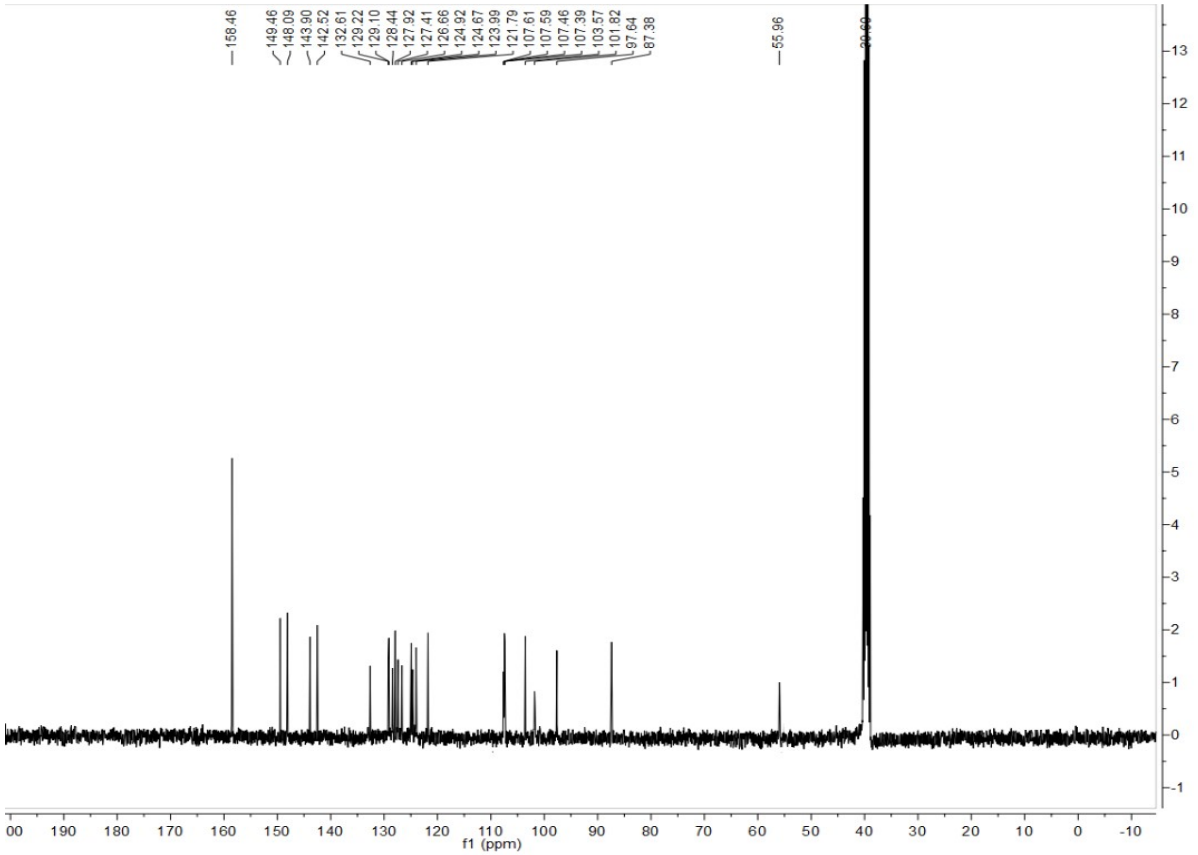
^{1}H NMR (400 MHz, DMSO-d_6)

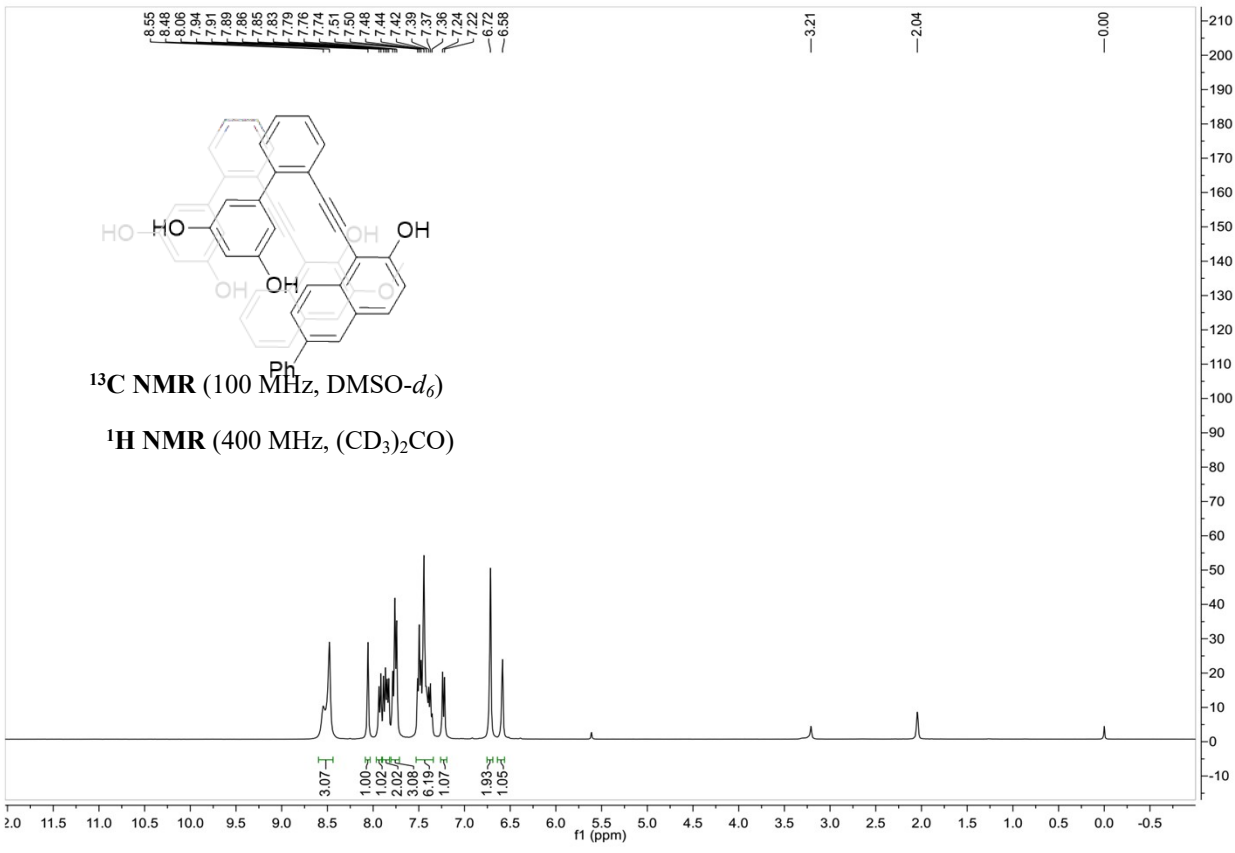


^{13}C NMR (100 MHz, $(CD_3)_2CO$)

^{1}H NMR (400 MHz, DMSO-d_6)

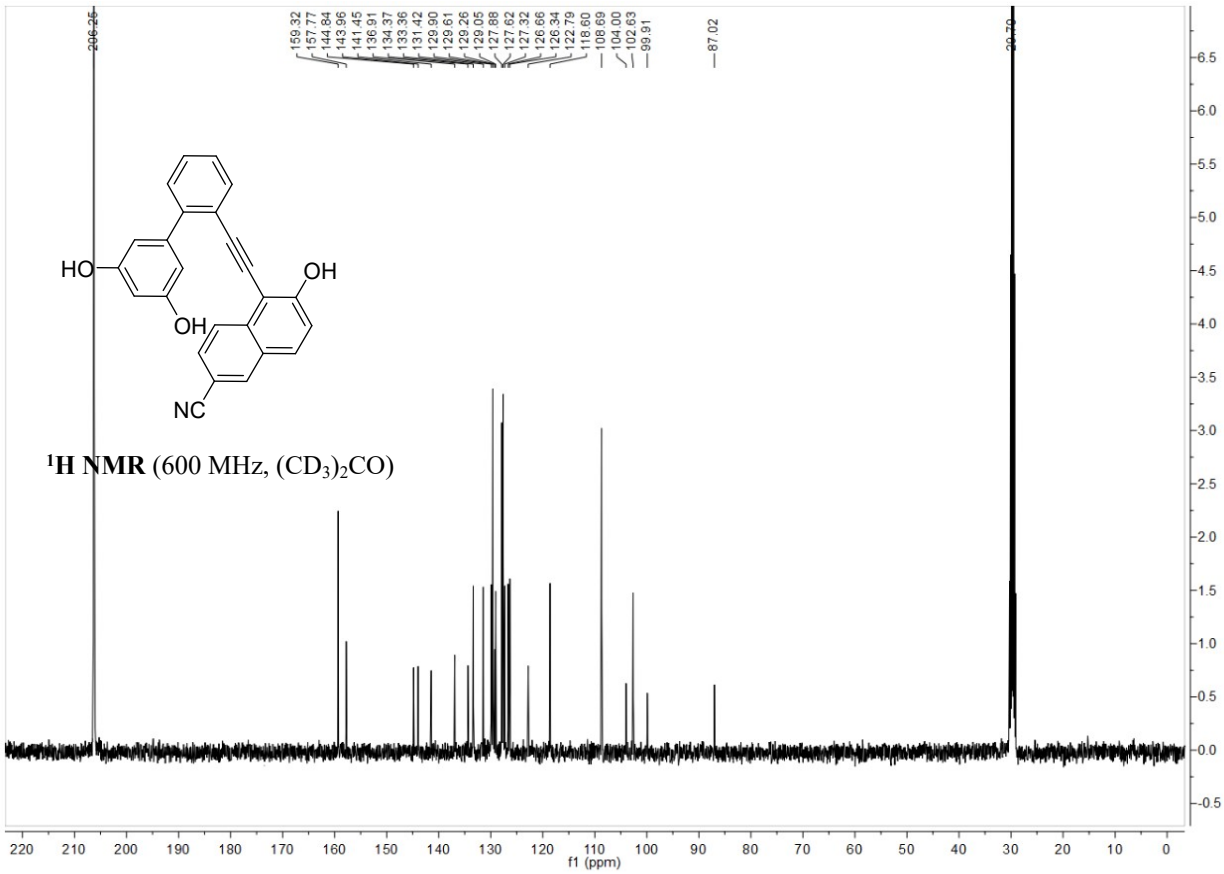




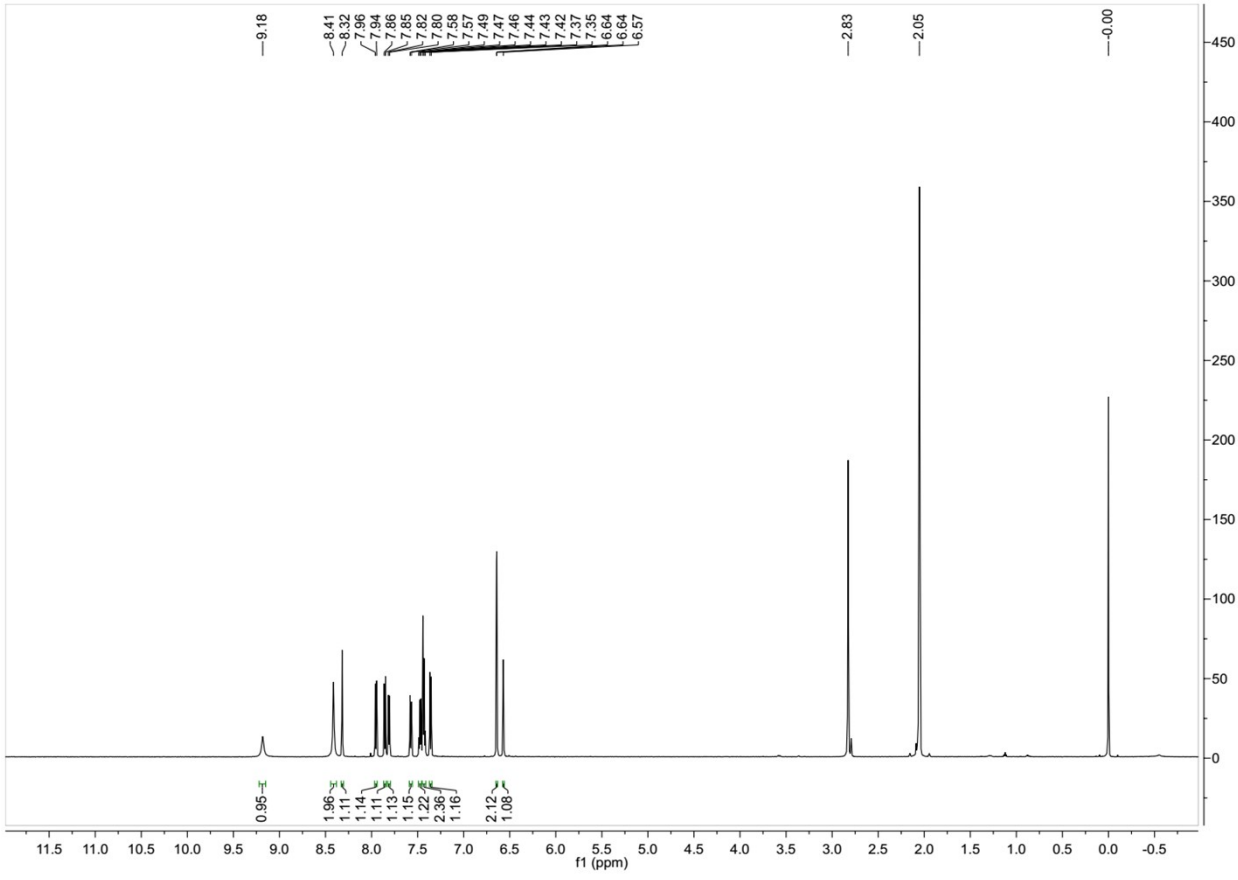


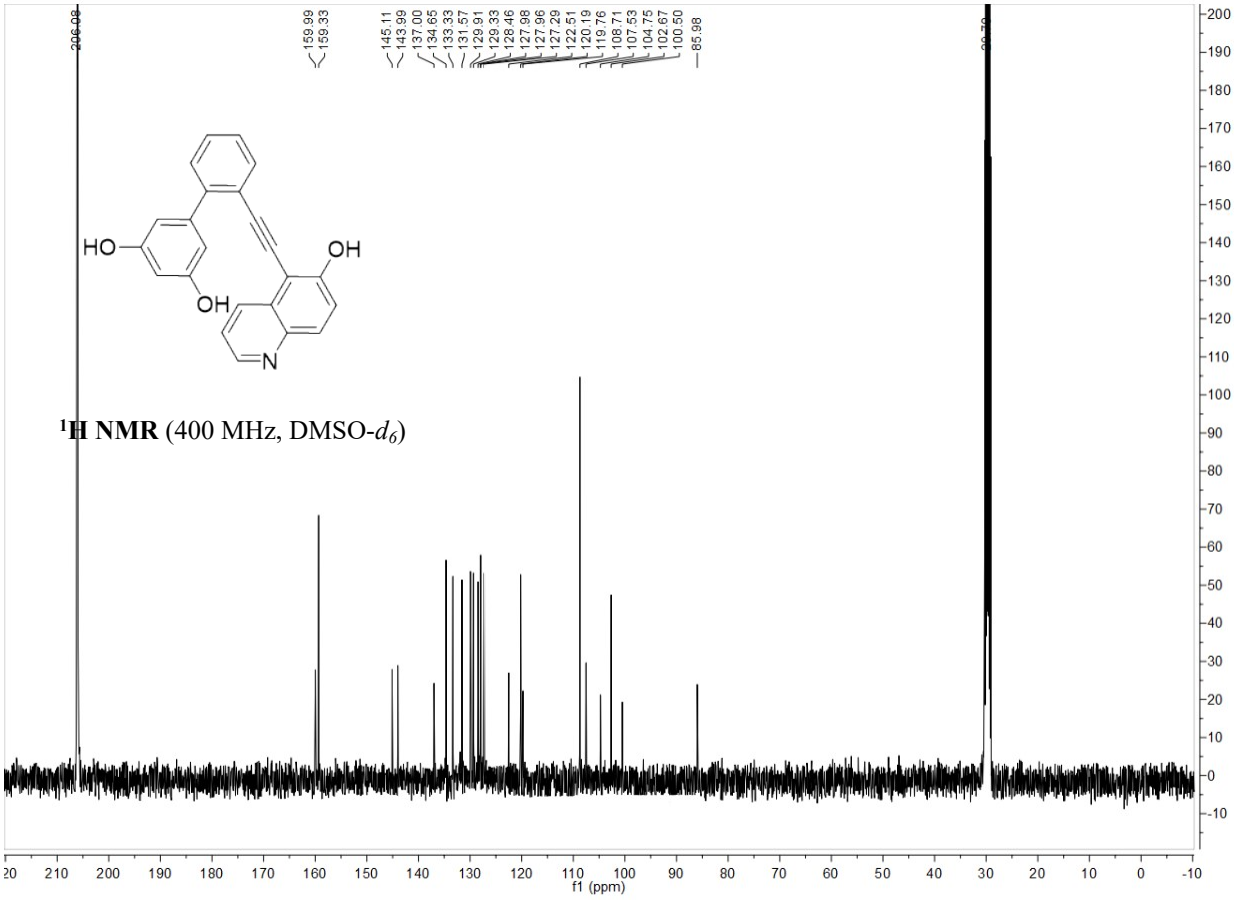
^{13}C NMR (100 MHz, DMSO-d_6)

^{1}H NMR (400 MHz, $(CD_3)_2CO$)

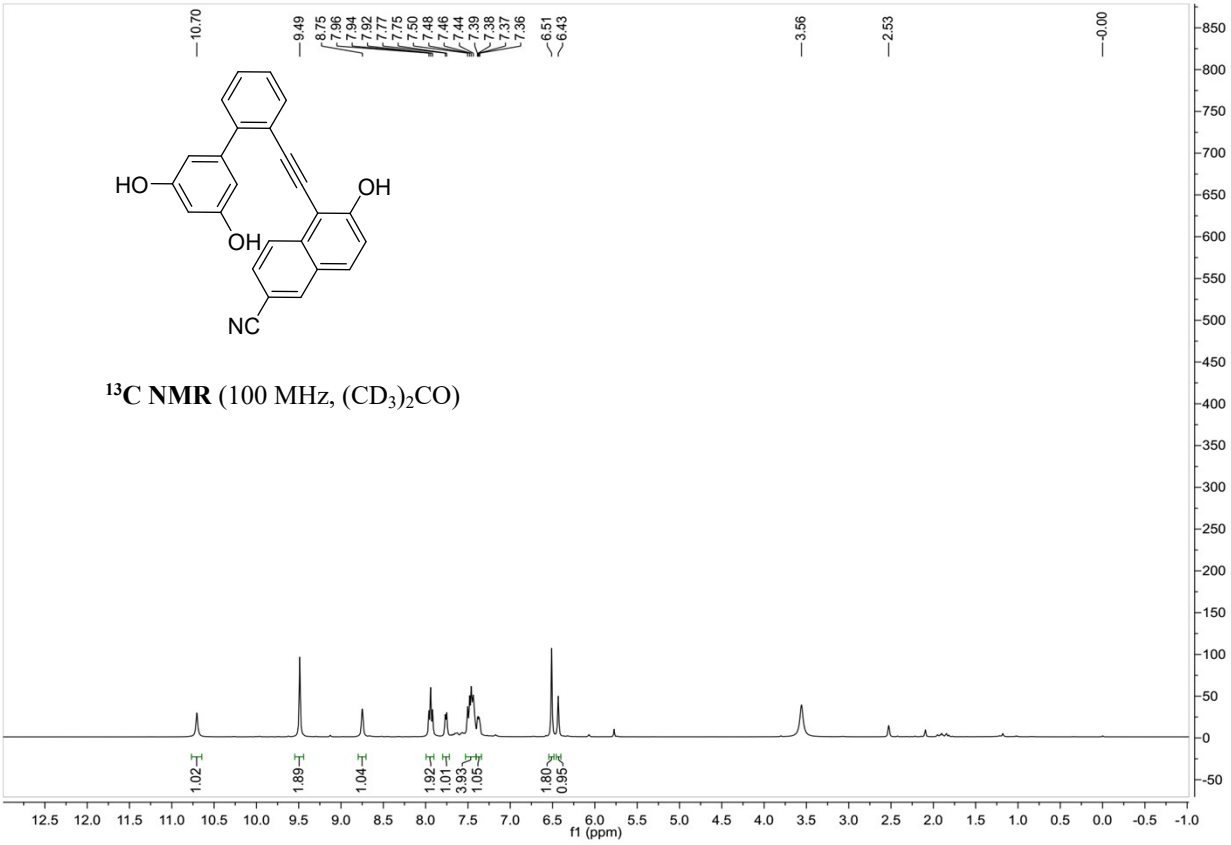


^{1}H NMR (600 MHz, $(CD_3)_2CO$)

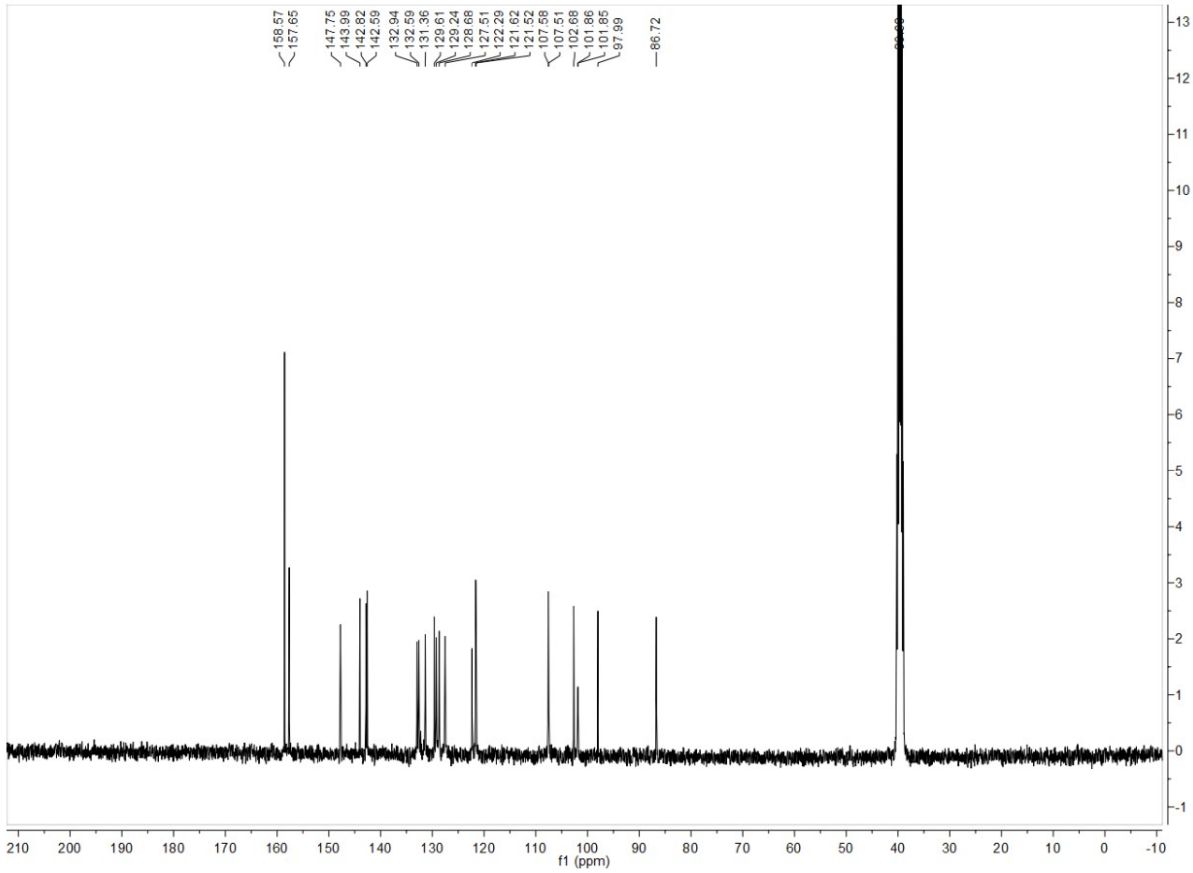


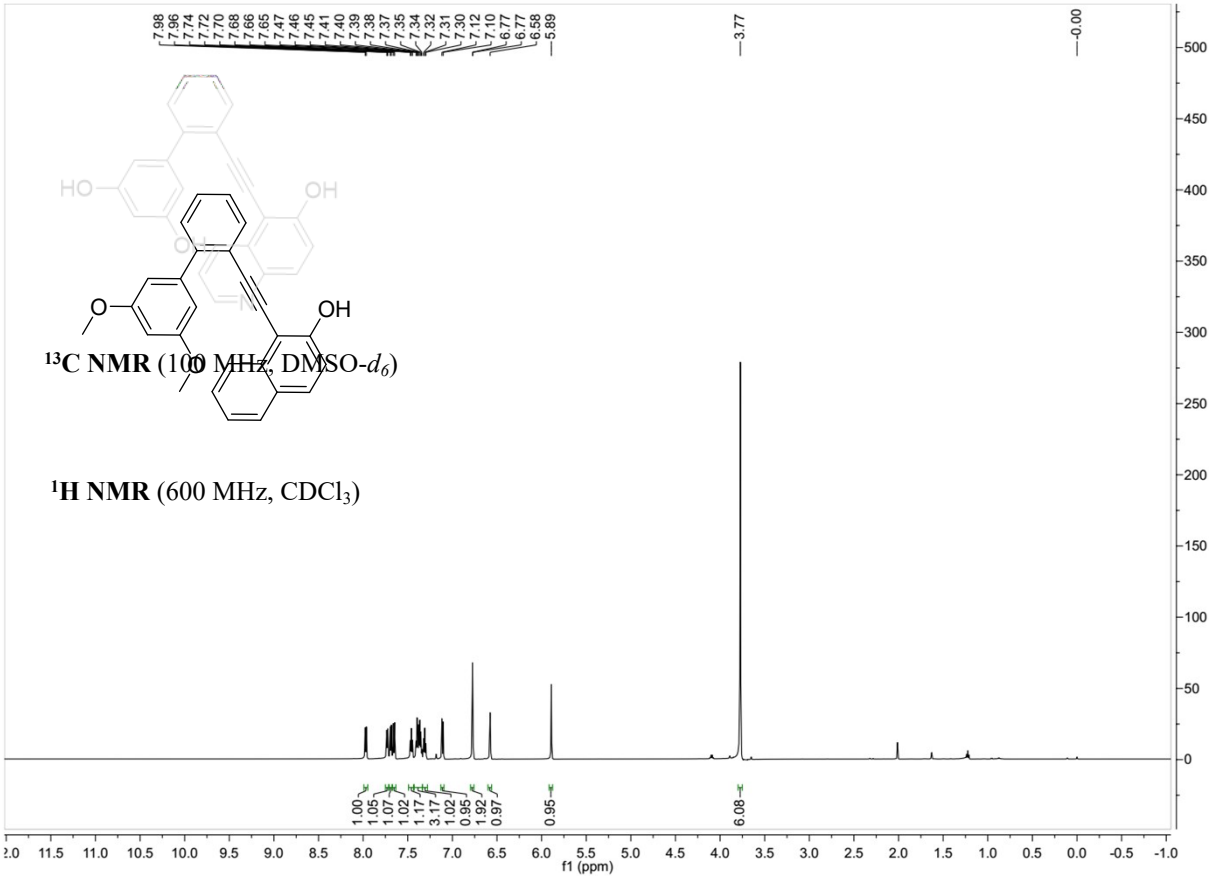


^{1}H NMR (400 MHz, DMSO-d_6)



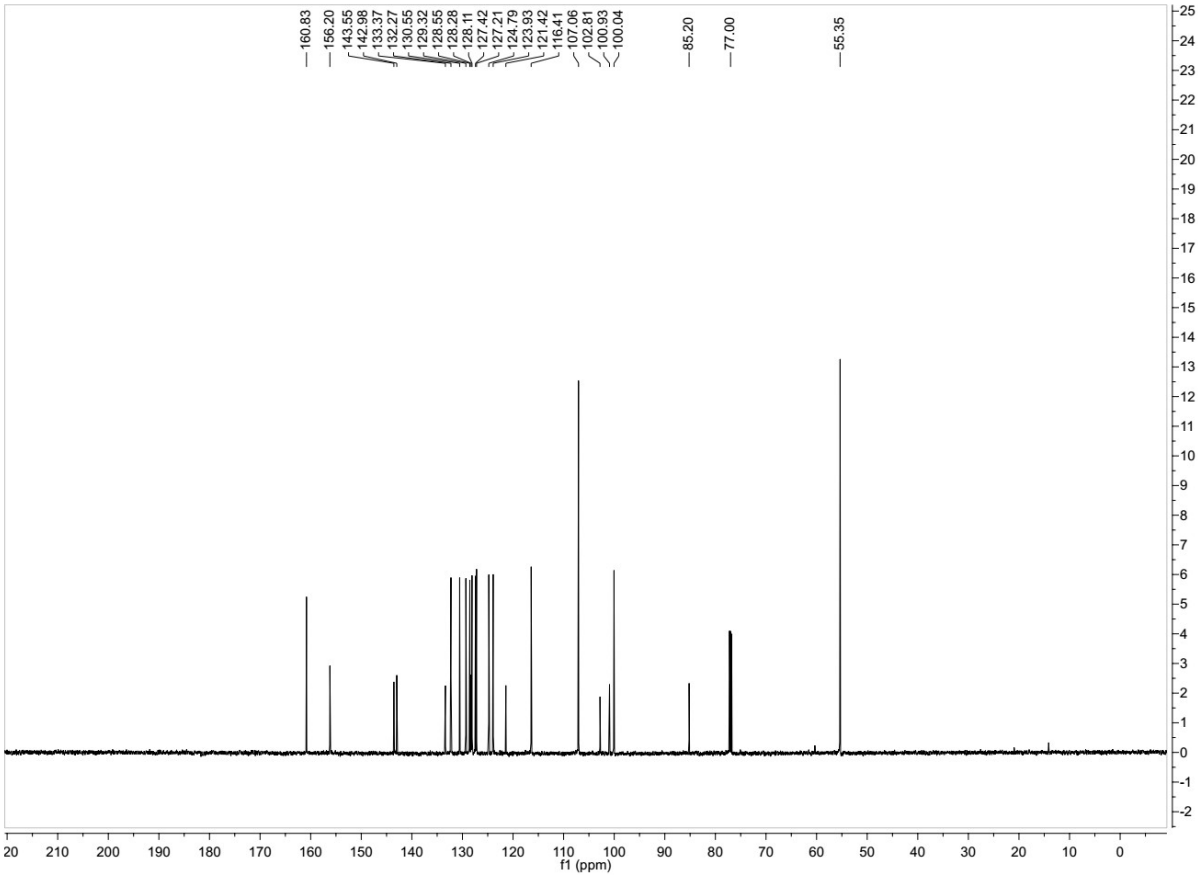
^{13}C NMR (100 MHz, $(CD_3)_2CO$)

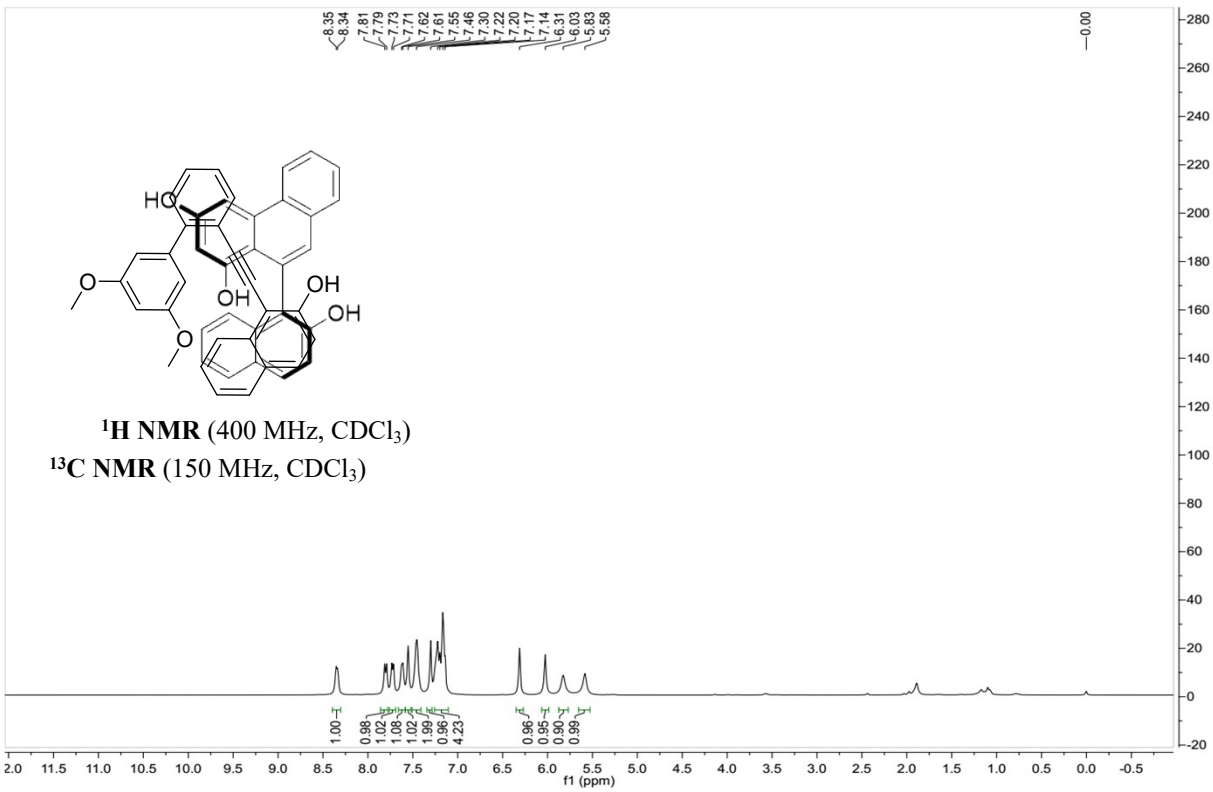




^{13}C NMR (100 MHz, DMSO-d_6)

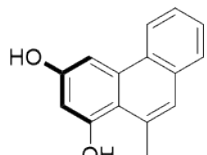
^{1}H NMR (600 MHz, $CDCl_3$)

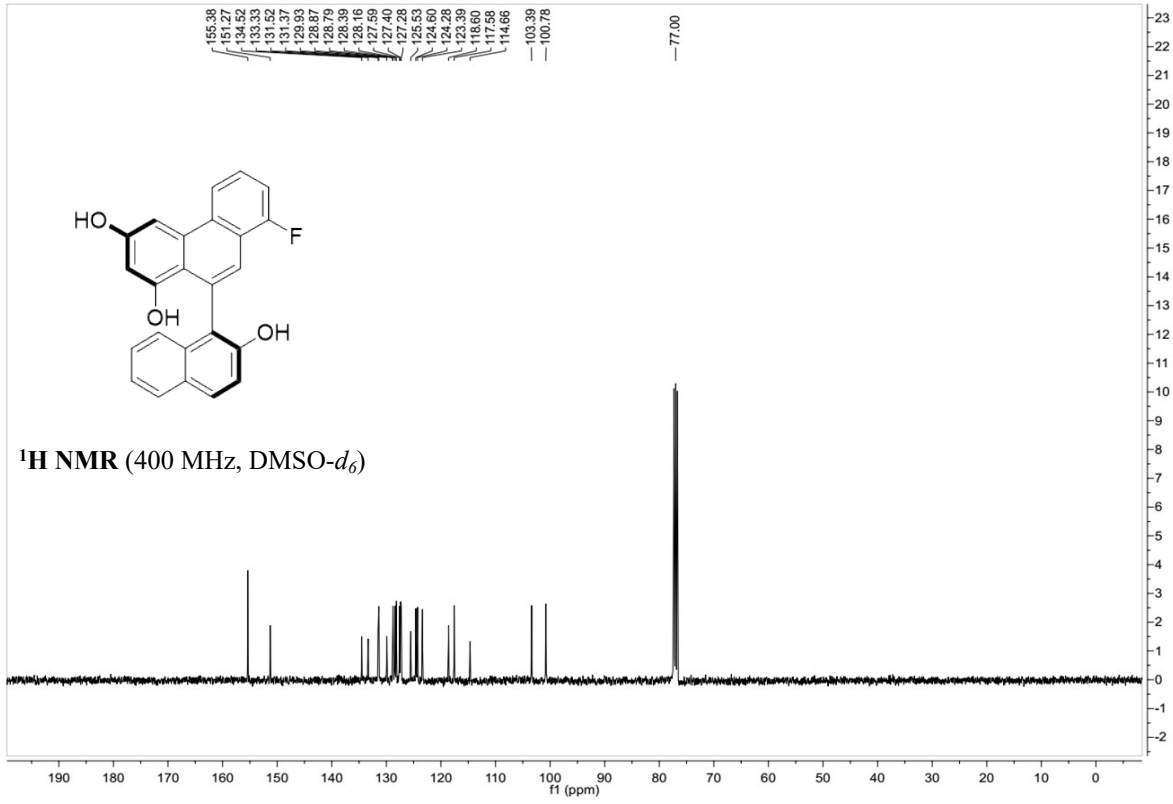




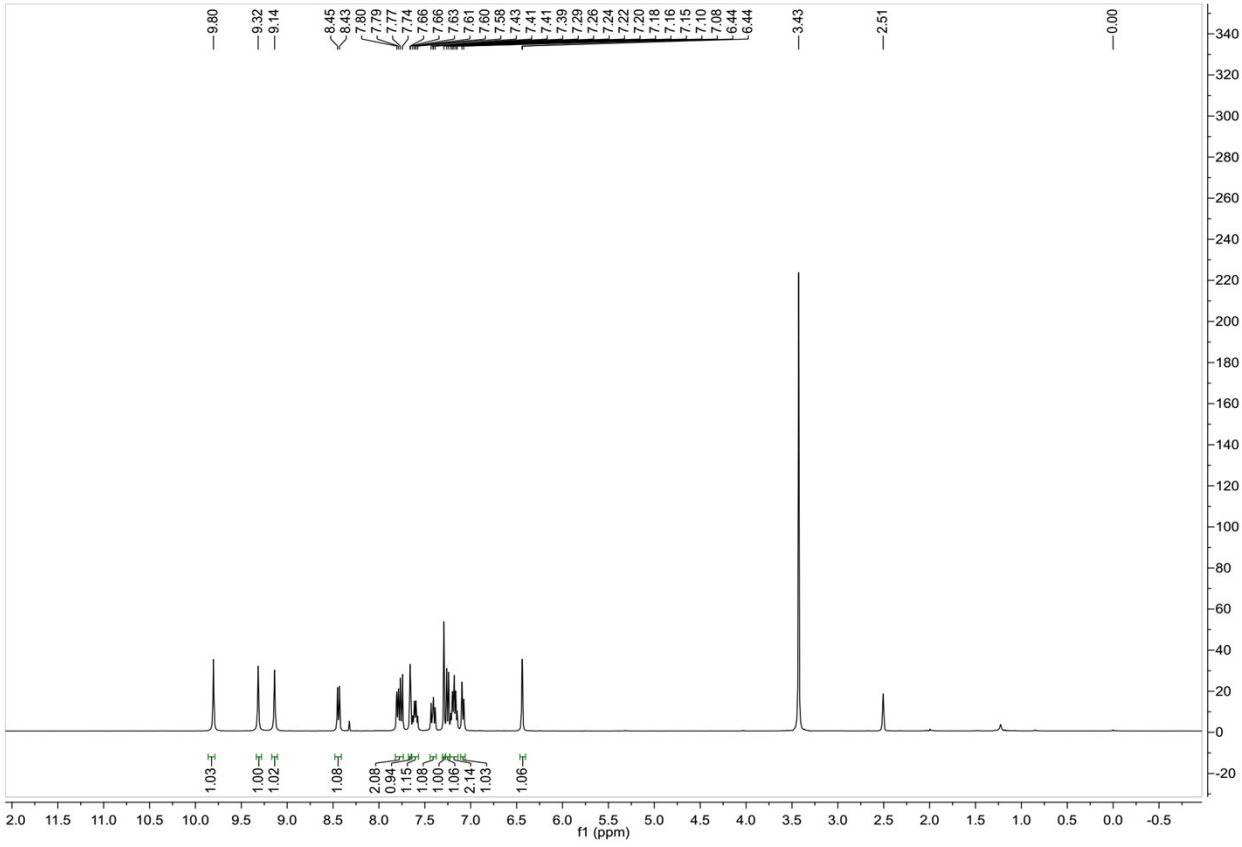
^{1}H NMR (400 MHz, $CDCl_3$)

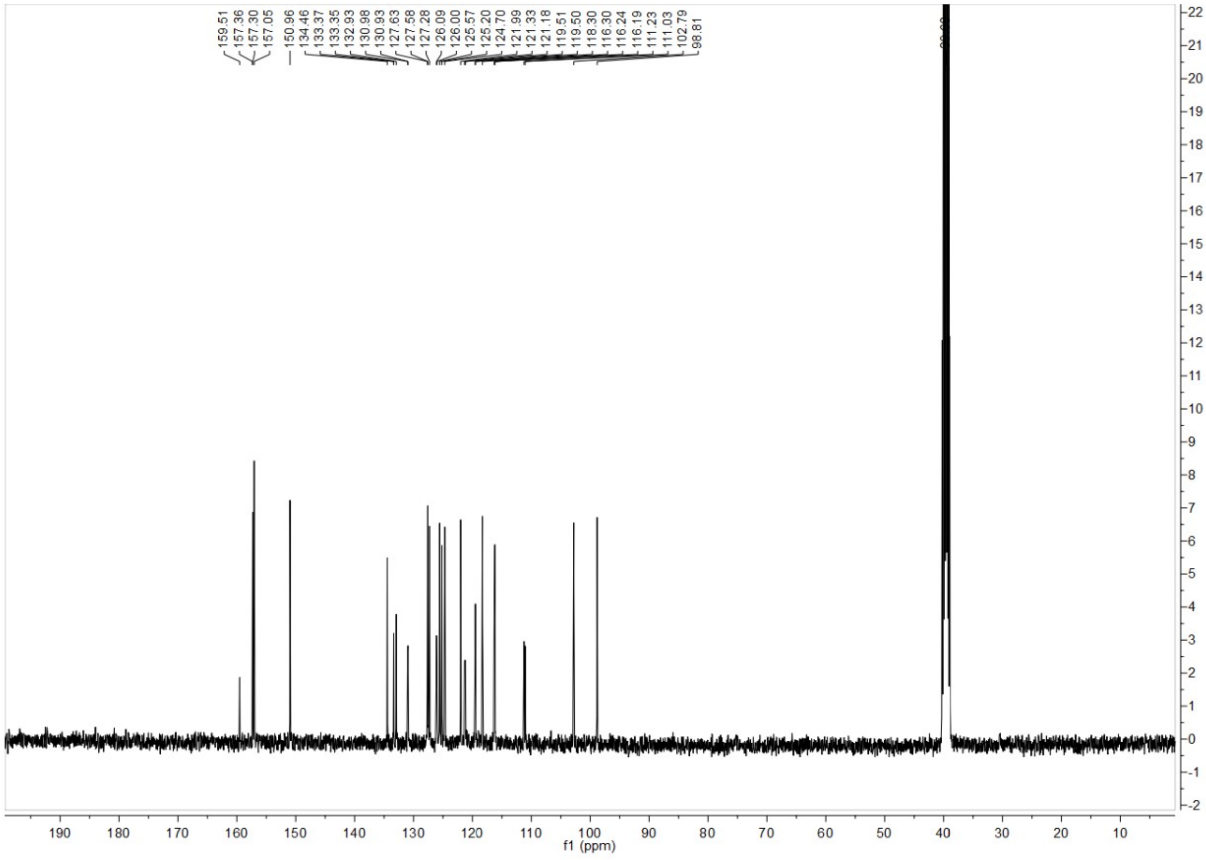
^{13}C NMR (150 MHz, $CDCl_3$)

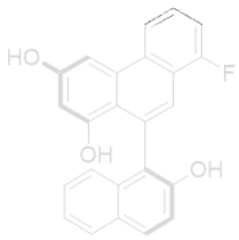




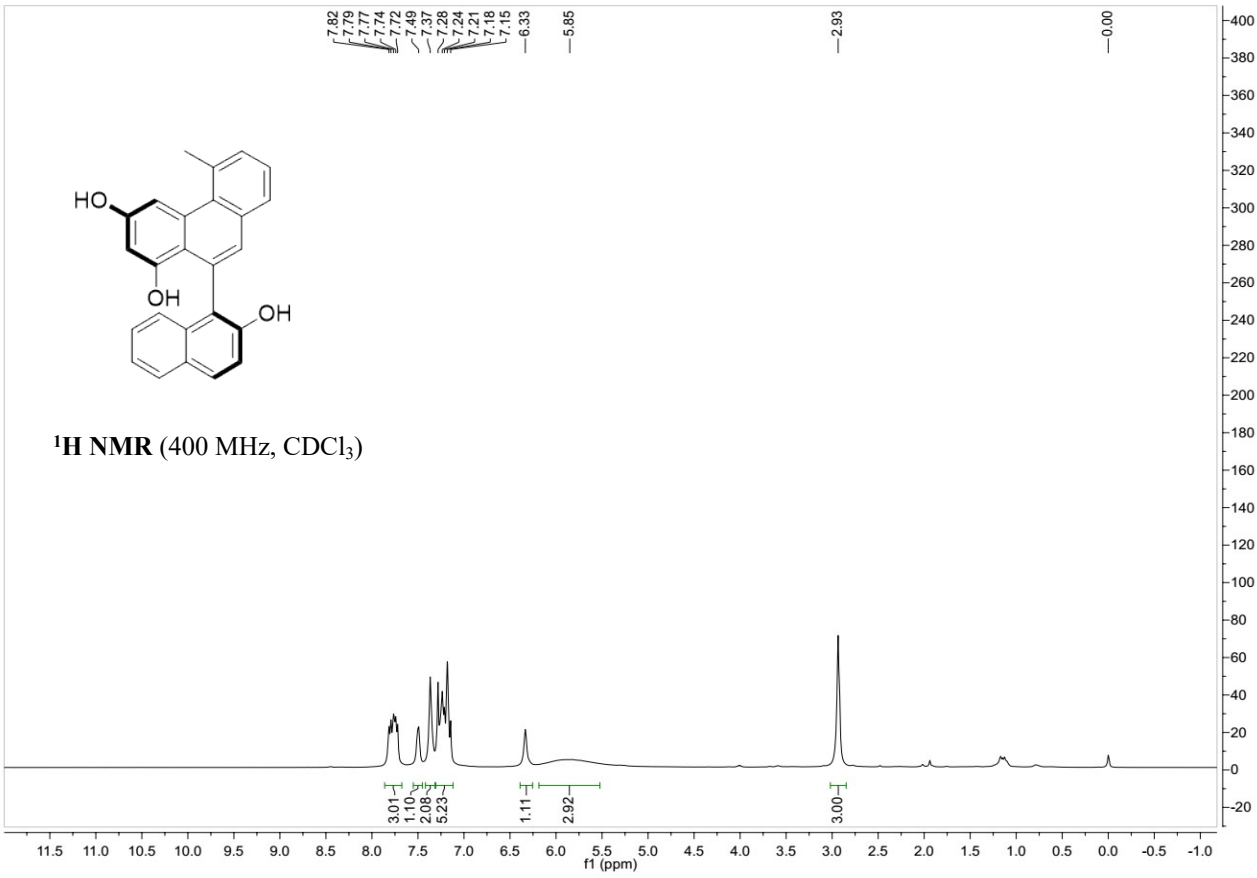
^{1}H NMR (400 MHz, DMSO-d_6)



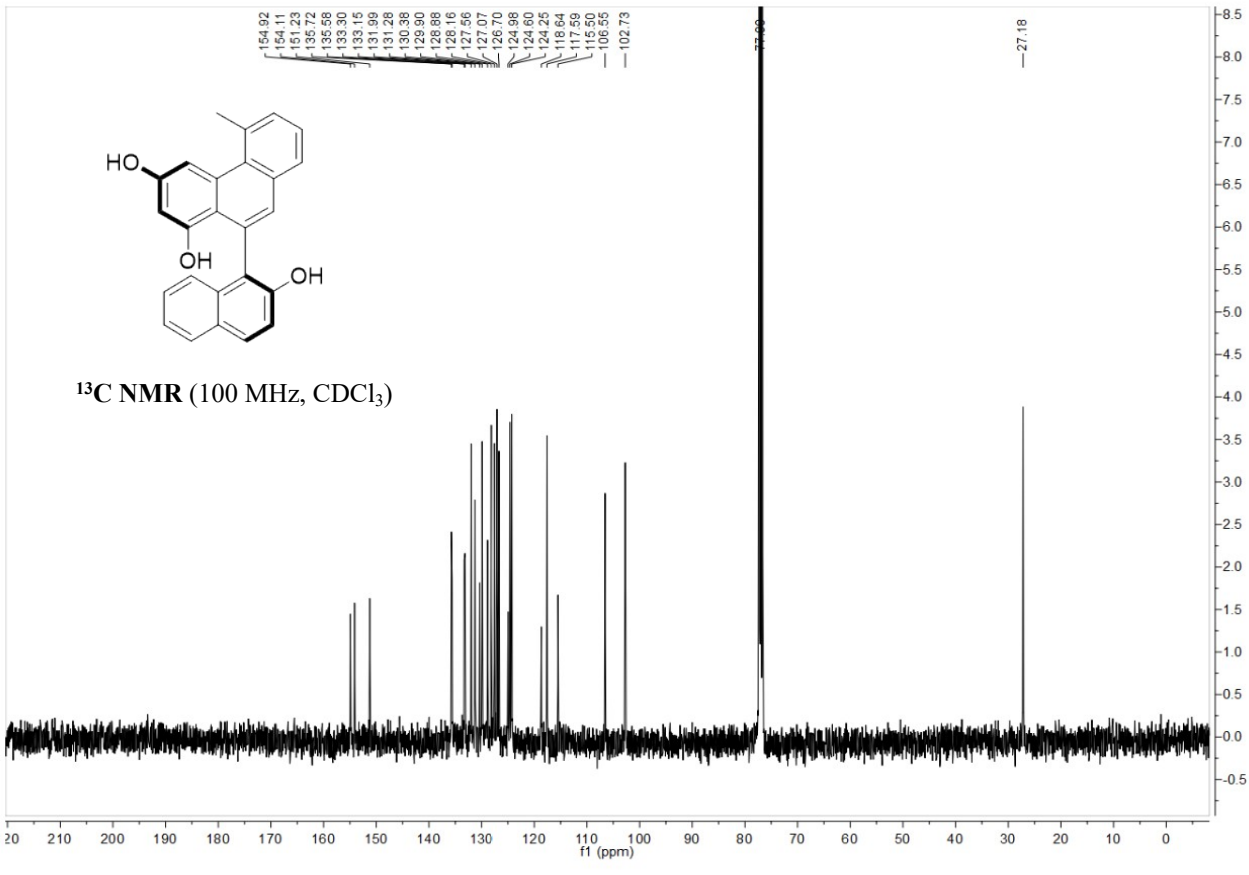




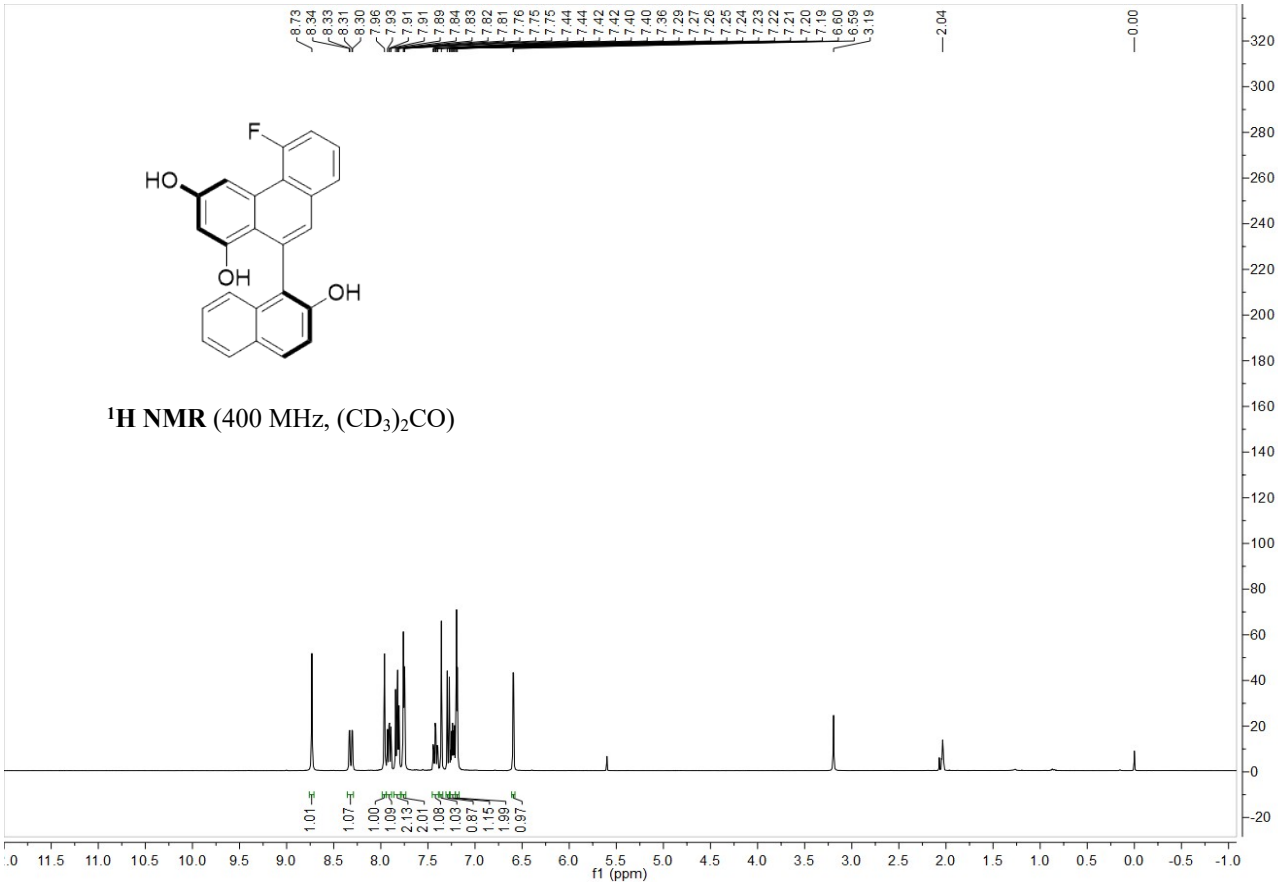
^{13}C NMR (100 MHz, DMSO-d_6)



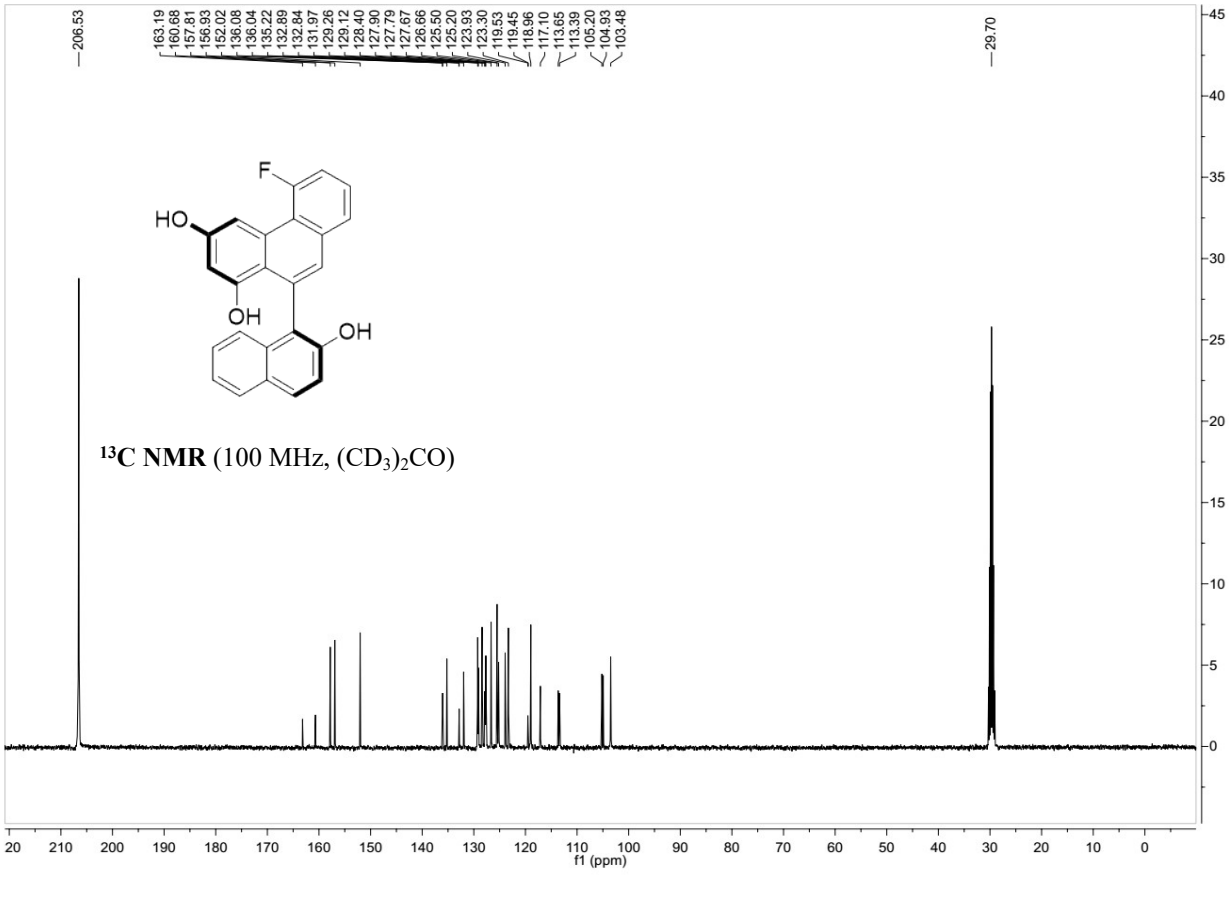
^{1}H NMR (400 MHz, $CDCl_3$)



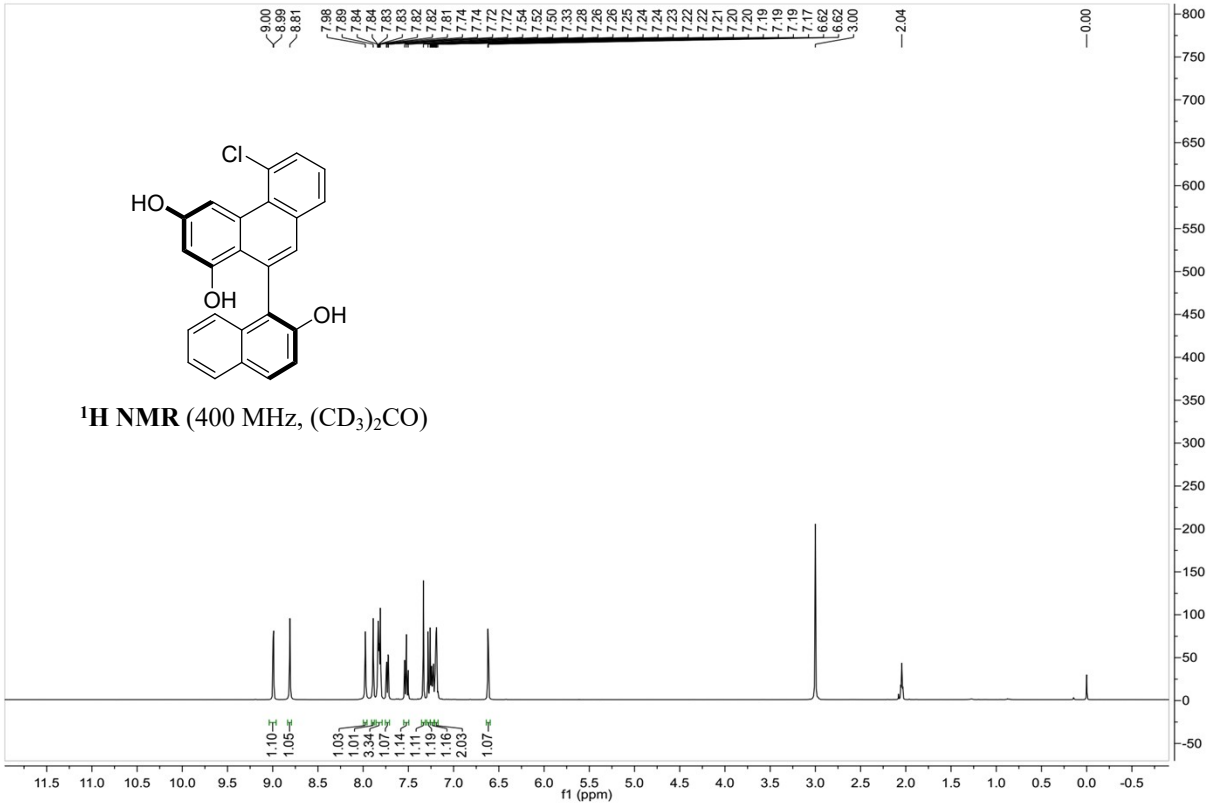
^{13}C NMR (100 MHz, $CDCl_3$)



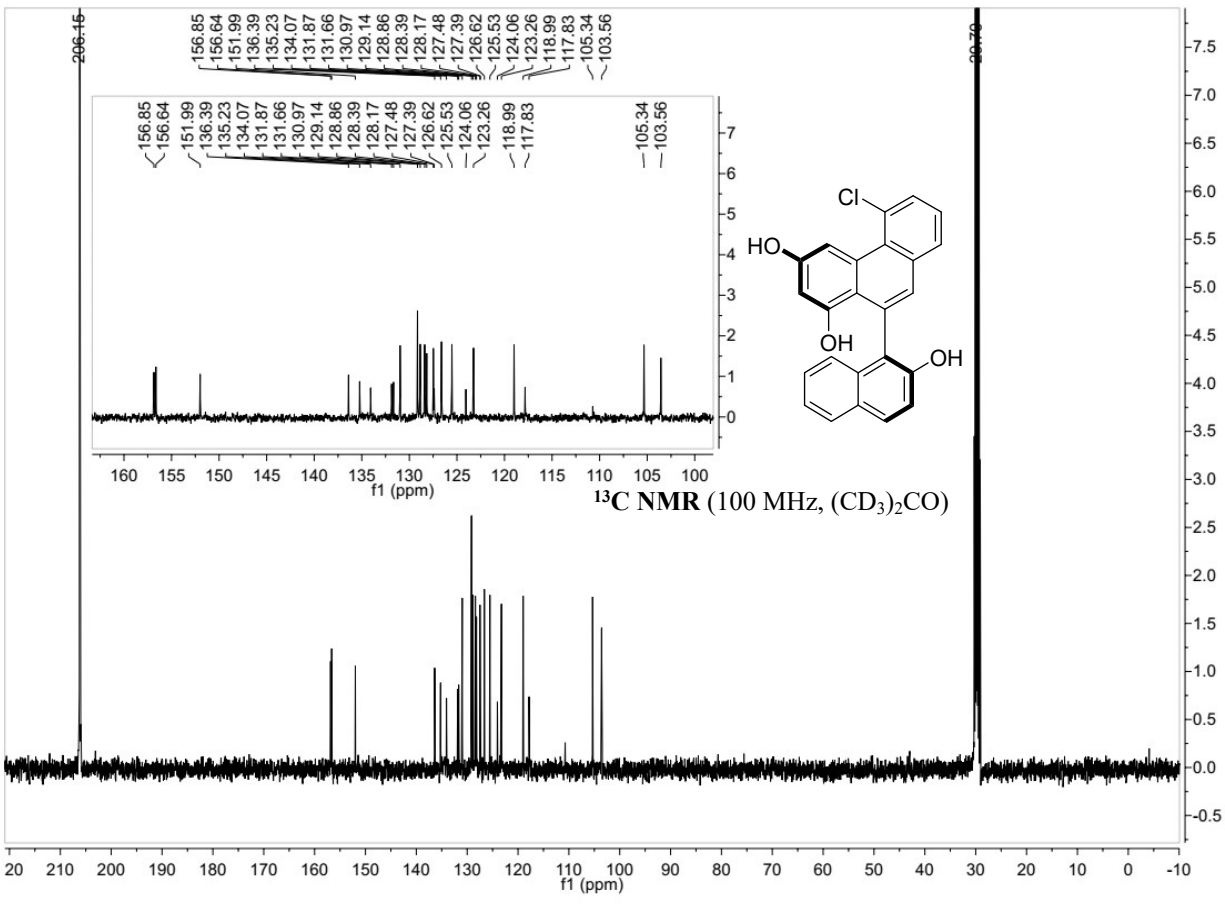
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



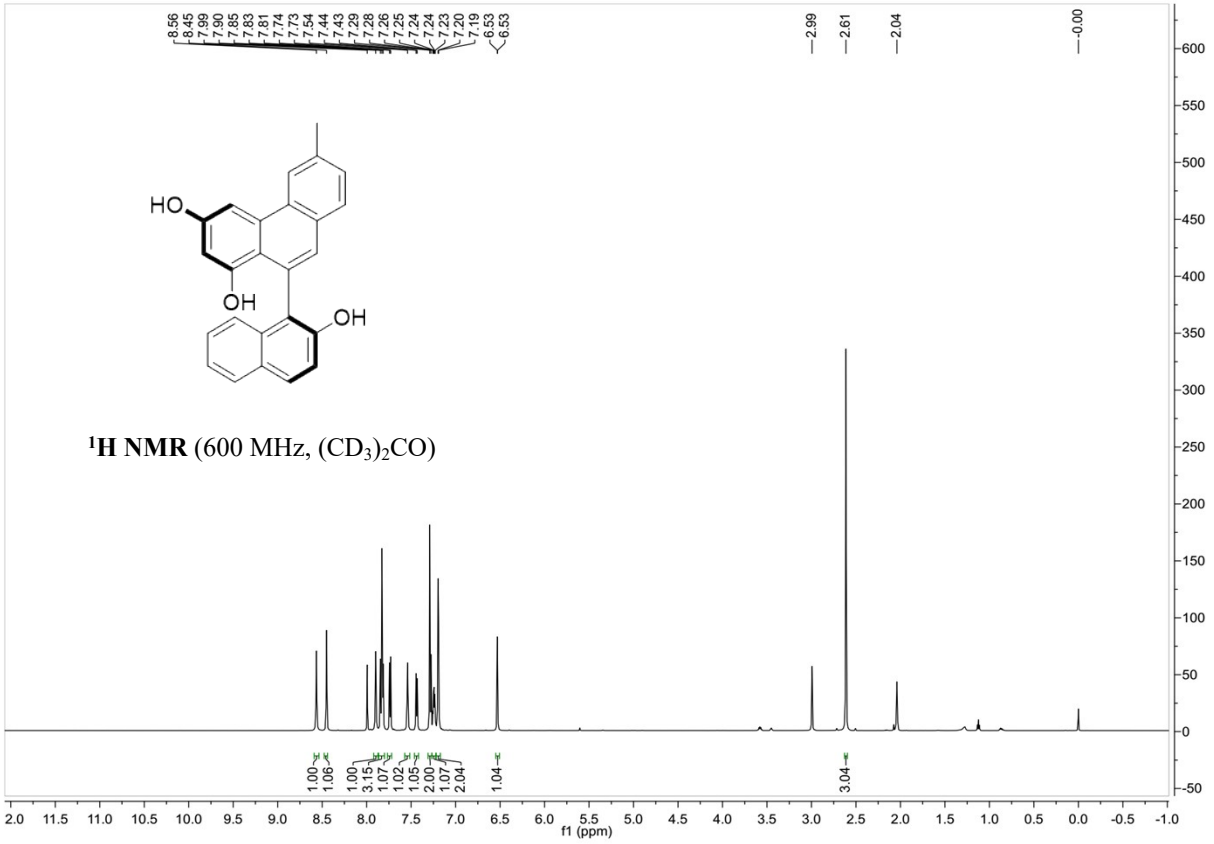
^{13}C NMR (100 MHz, $(CD_3)_2CO$)



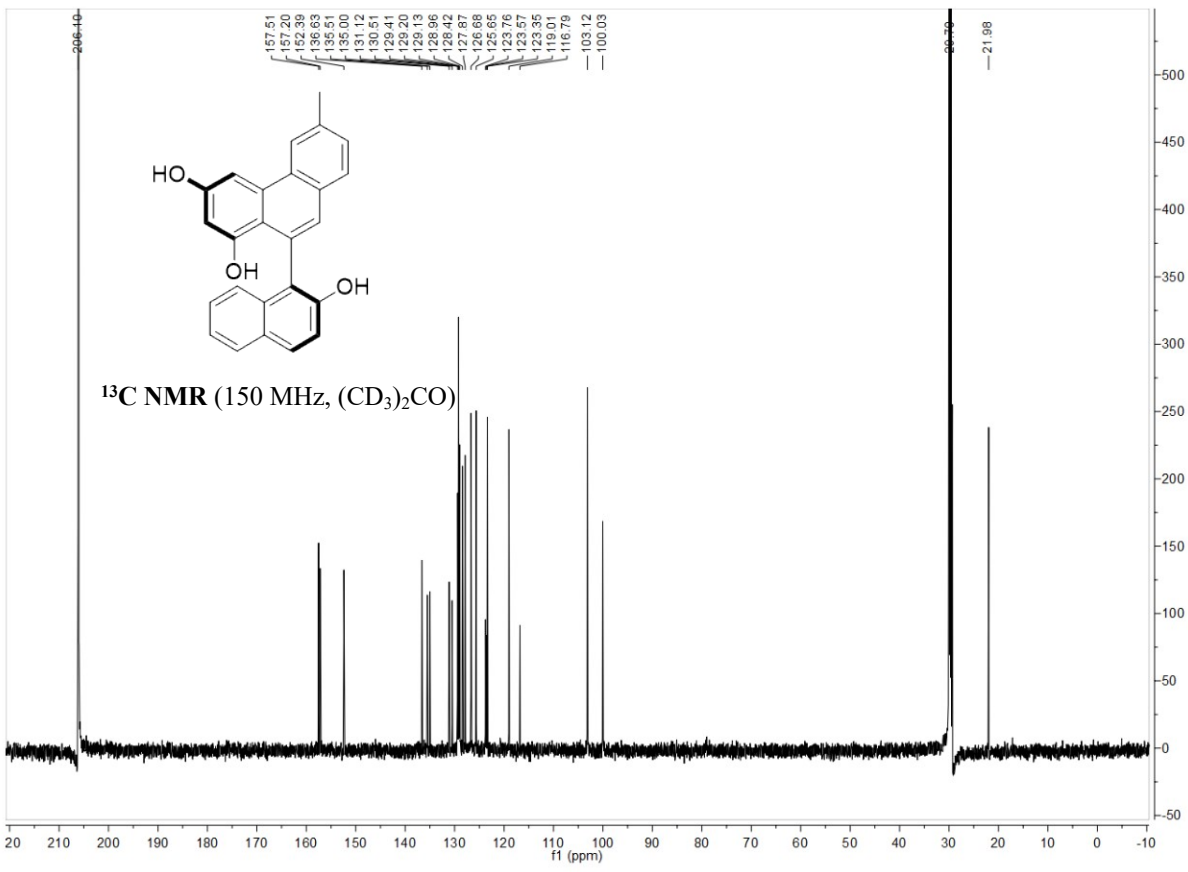
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



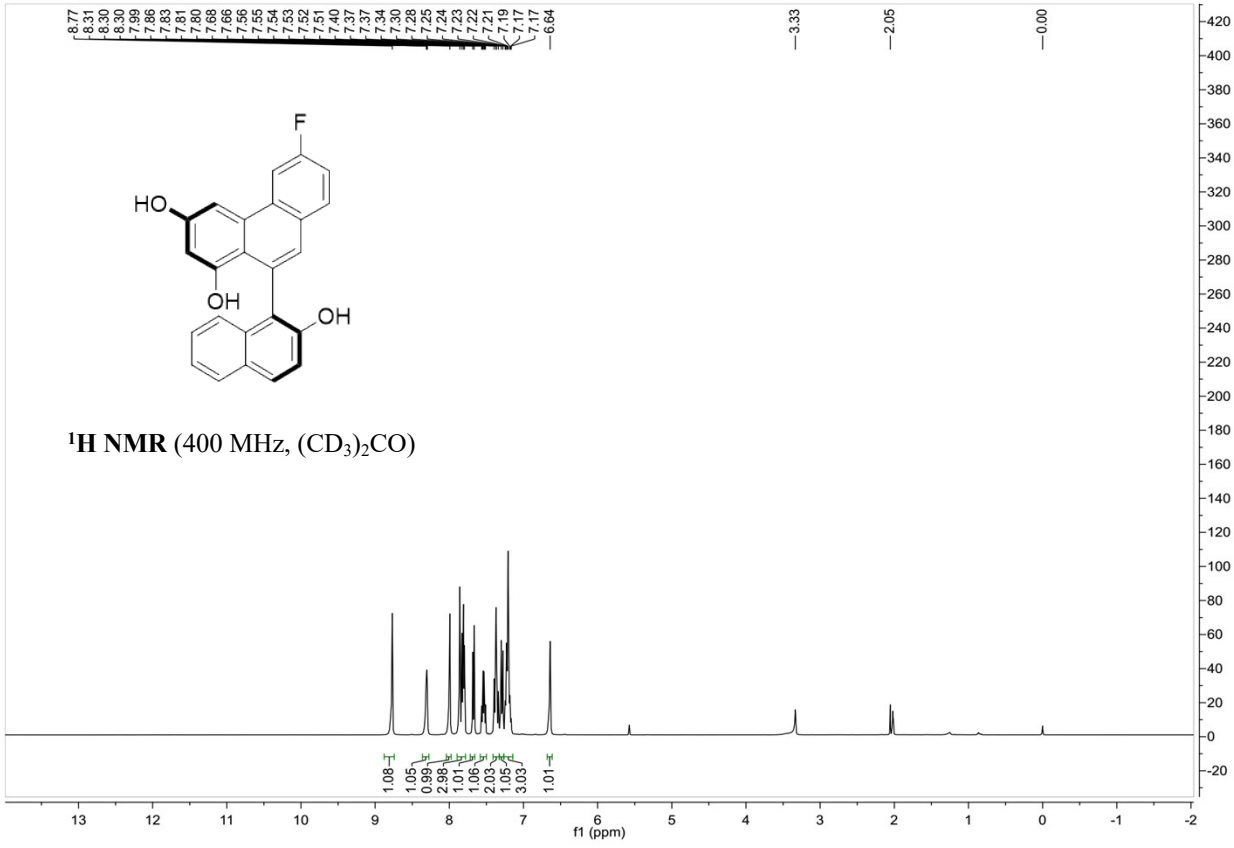
^{13}C NMR (100 MHz, $(CD_3)_2CO$)



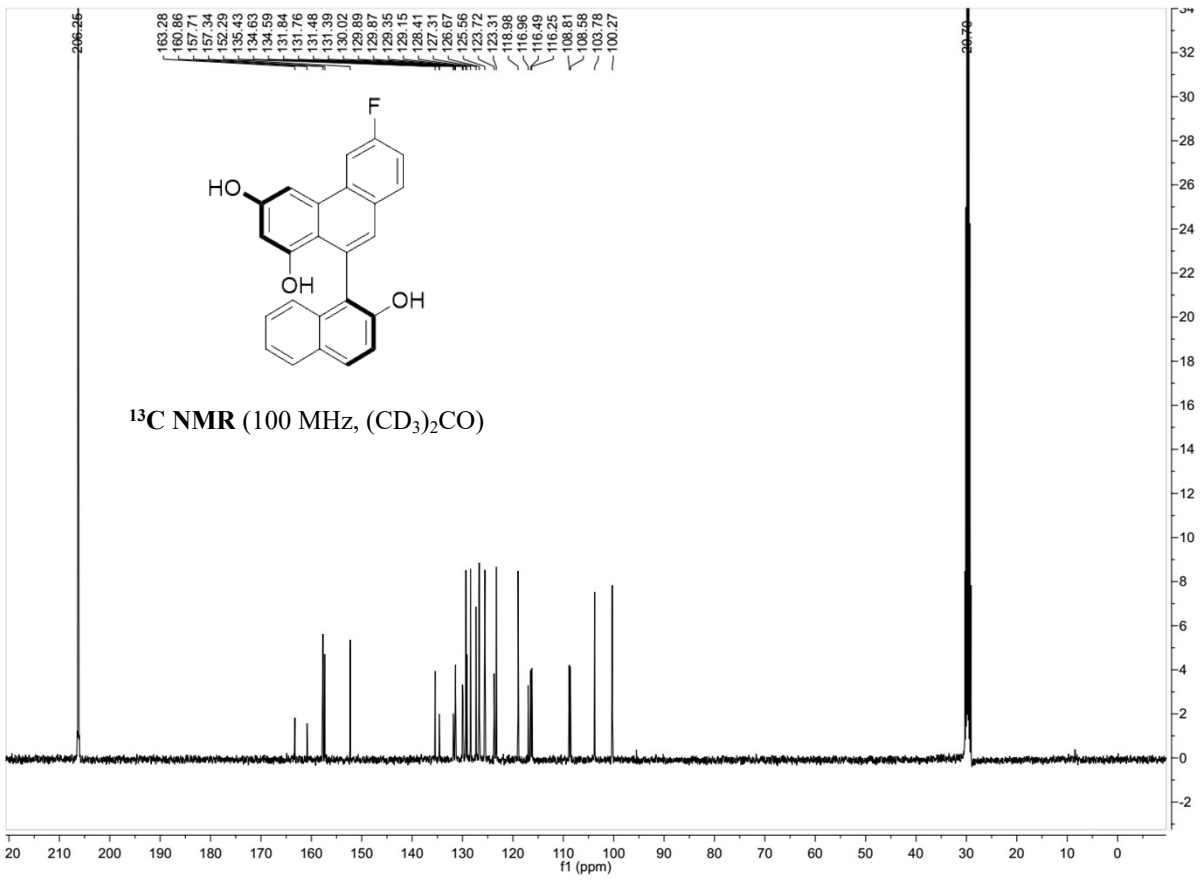
^{1}H NMR (600 MHz, $(CD_3)_2CO$)



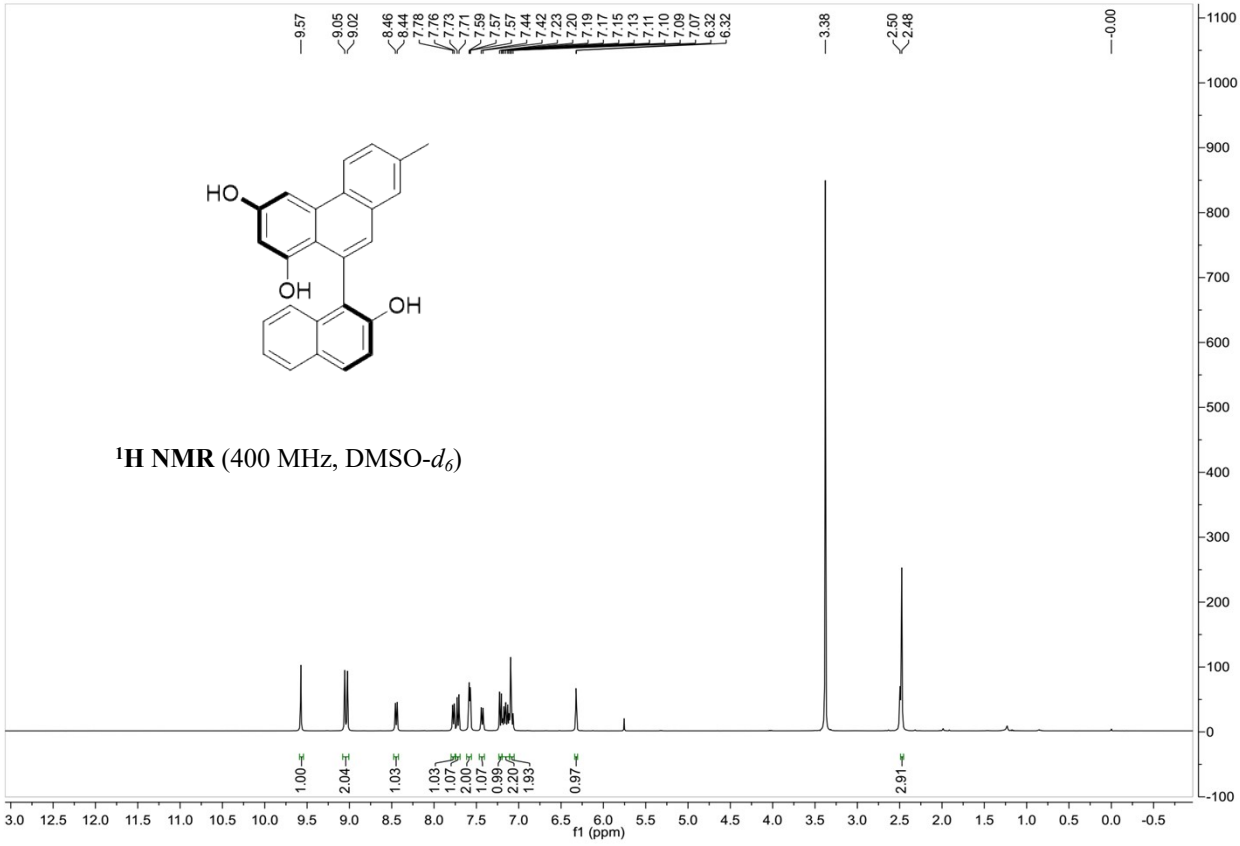
^{13}C NMR (150 MHz, $(CD_3)_2CO$)



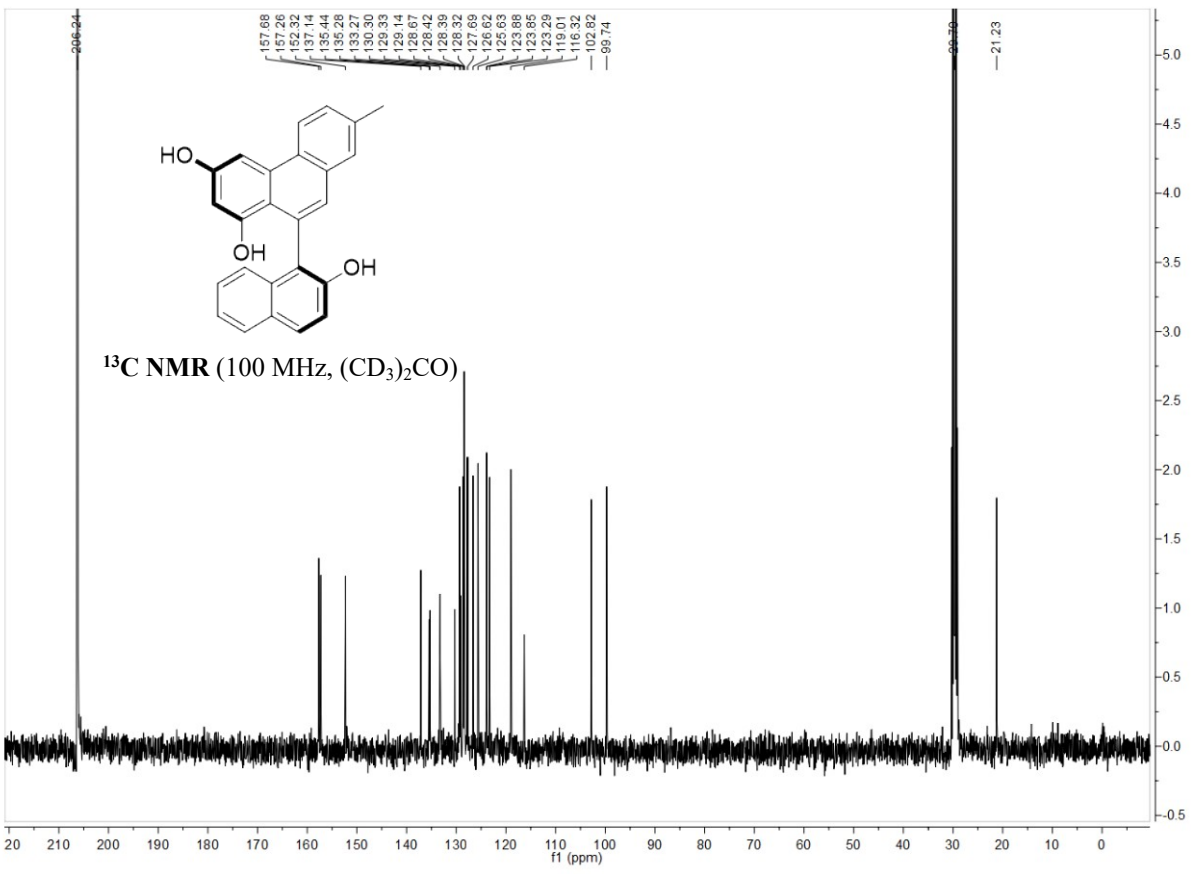
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



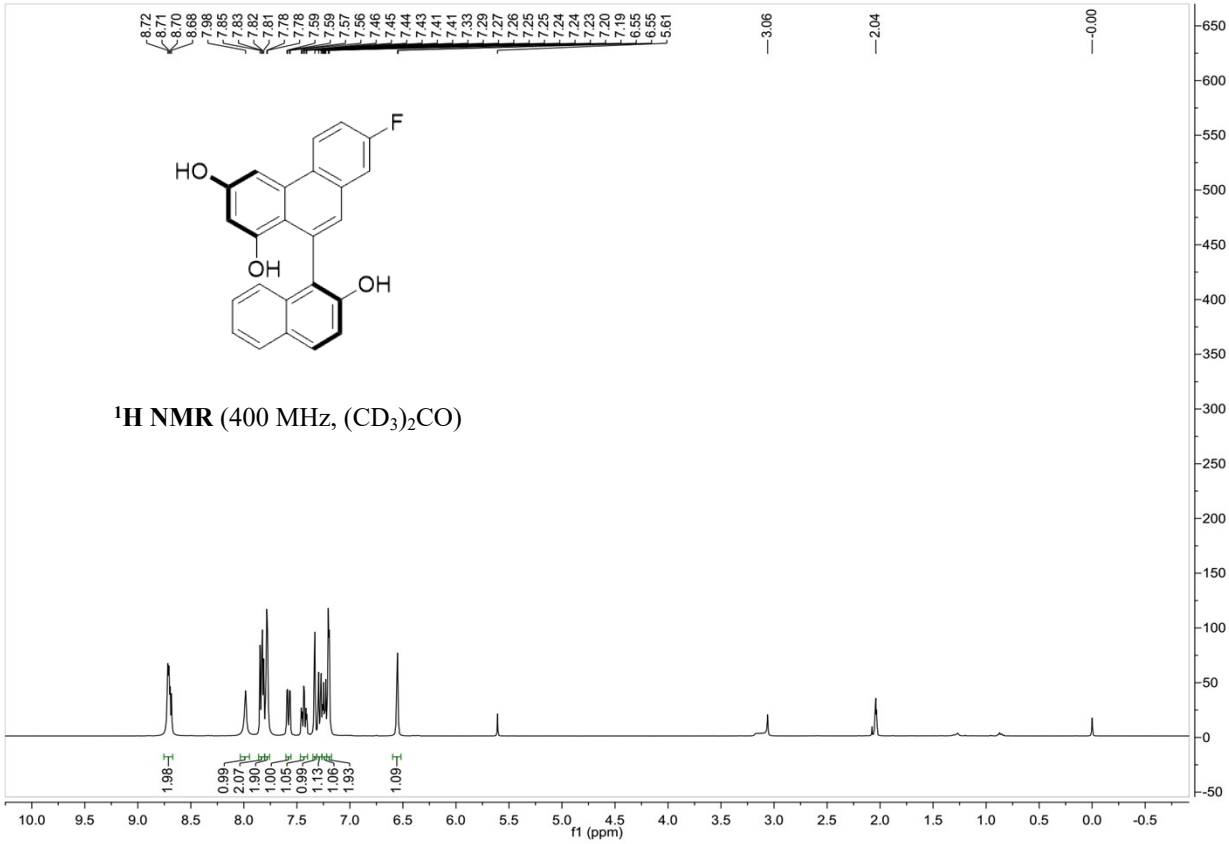
^{13}C NMR (100 MHz, $(CD_3)_2CO$)



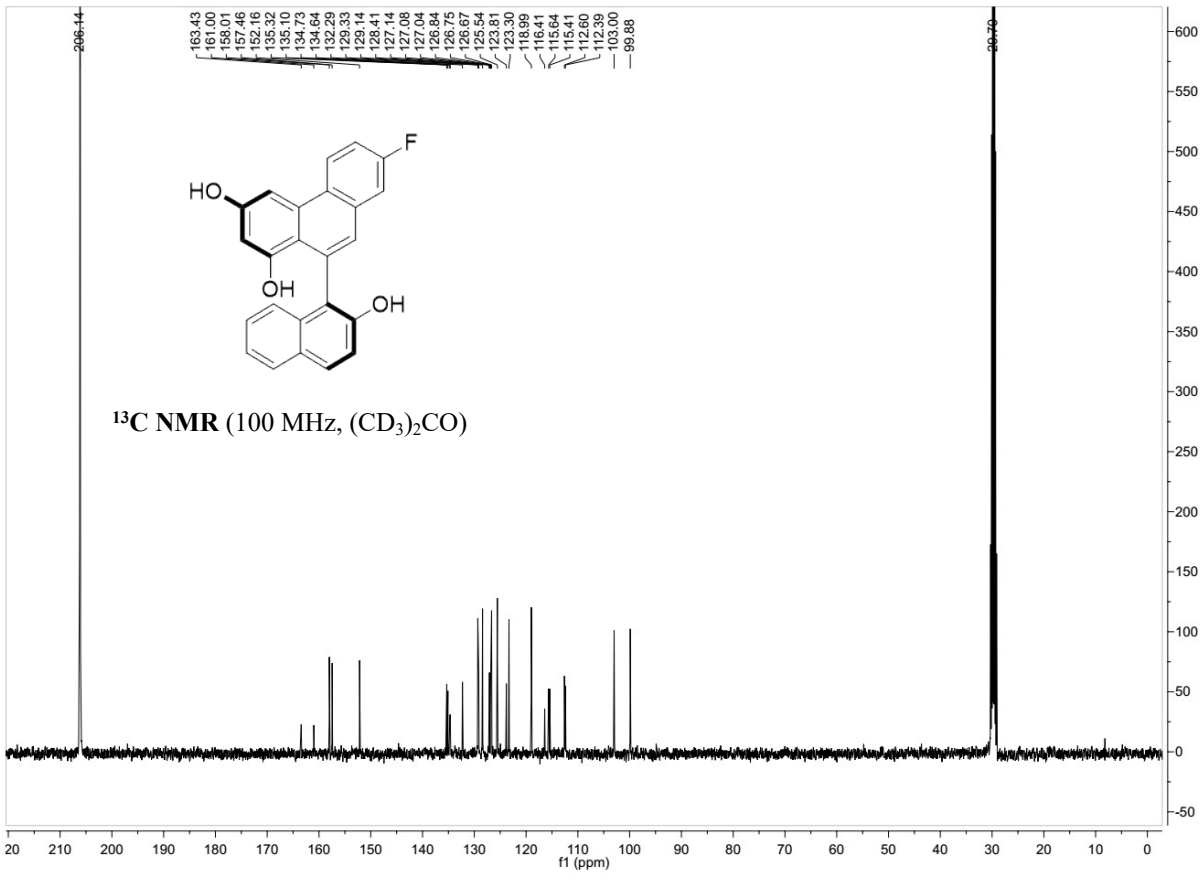
^{1}H NMR (400 MHz, DMSO-d_6)



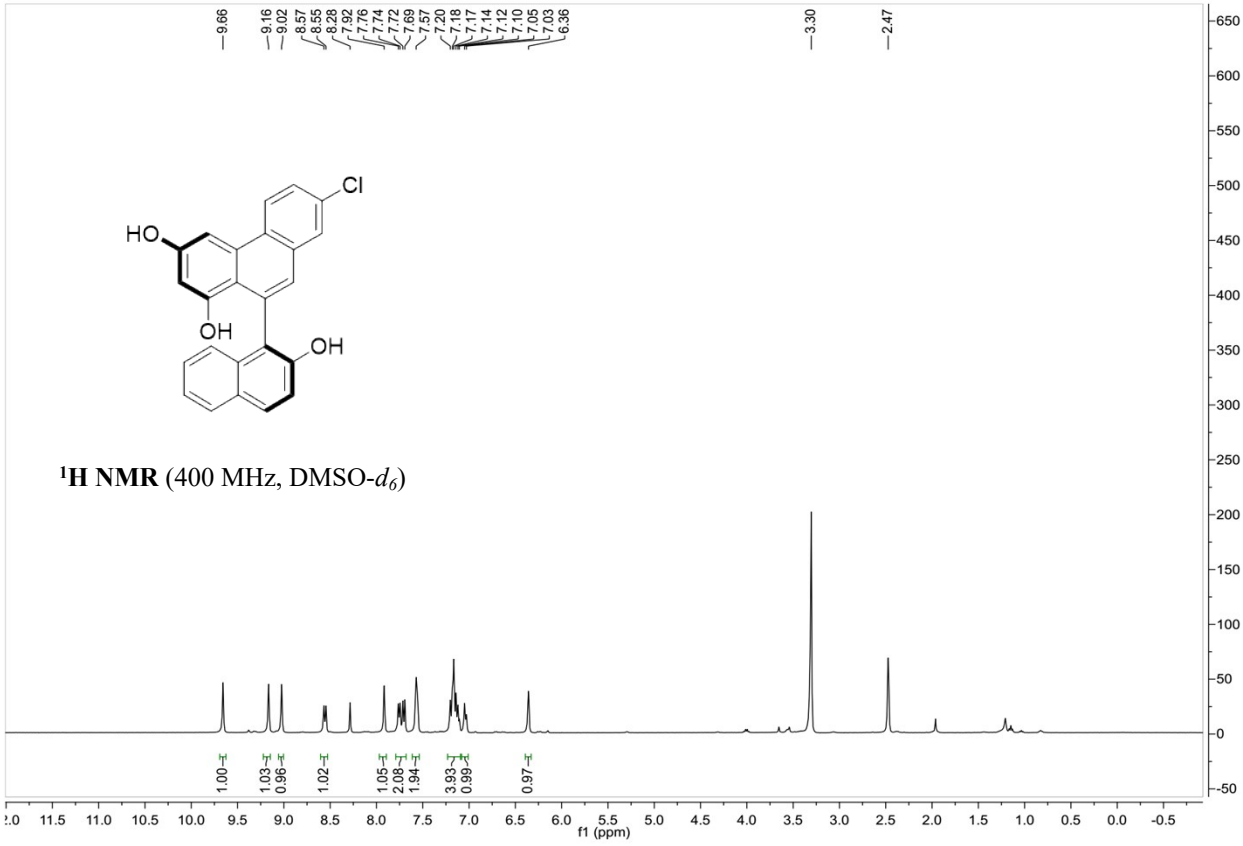
^{13}C NMR (100 MHz, $(CD_3)_2CO$)



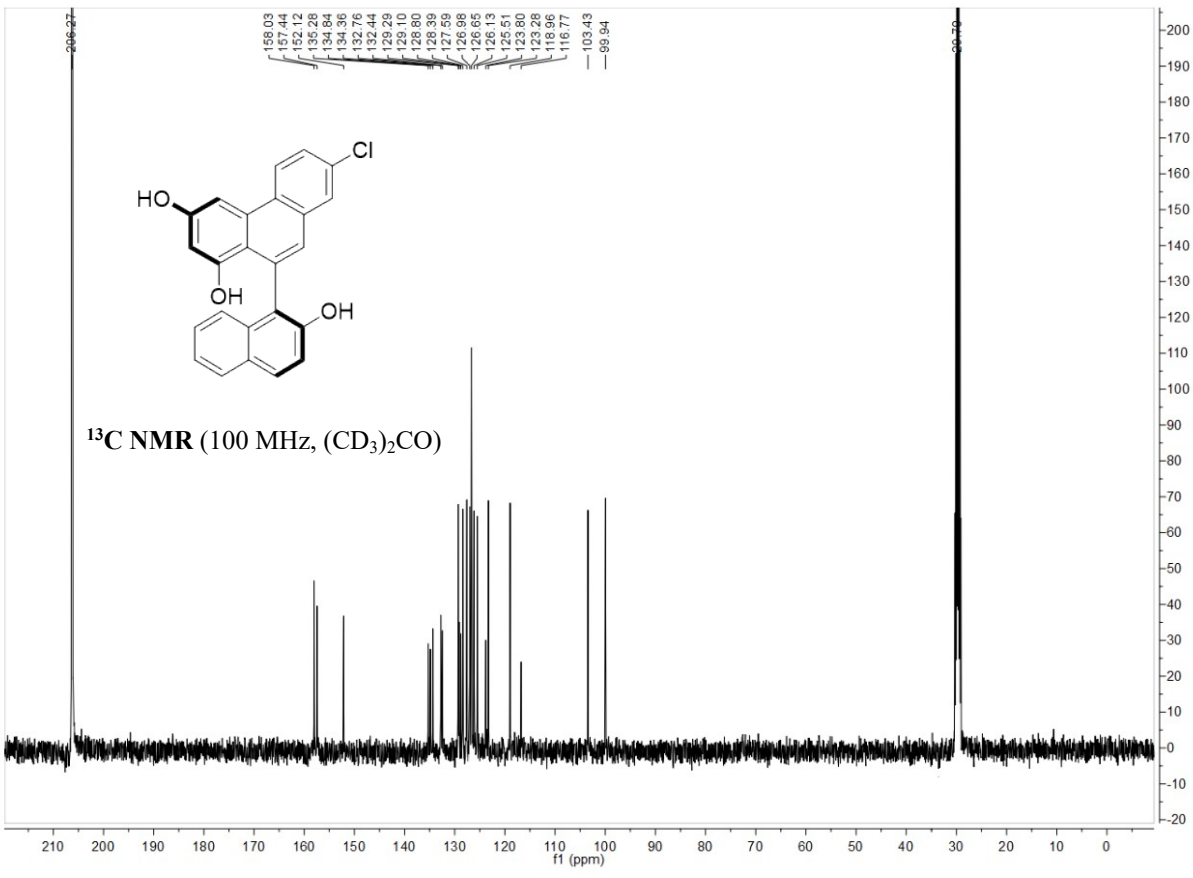
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



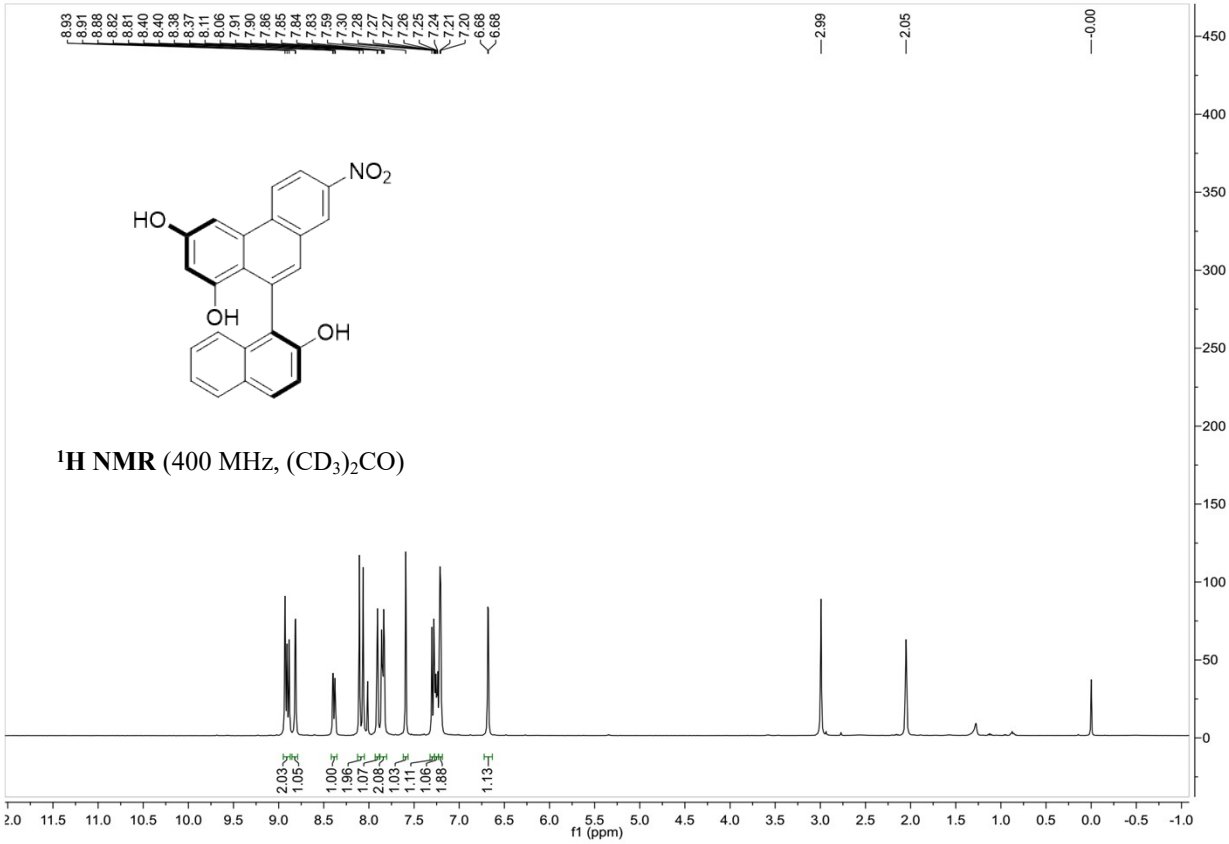
^{13}C NMR (100 MHz, $(CD_3)_2CO$)



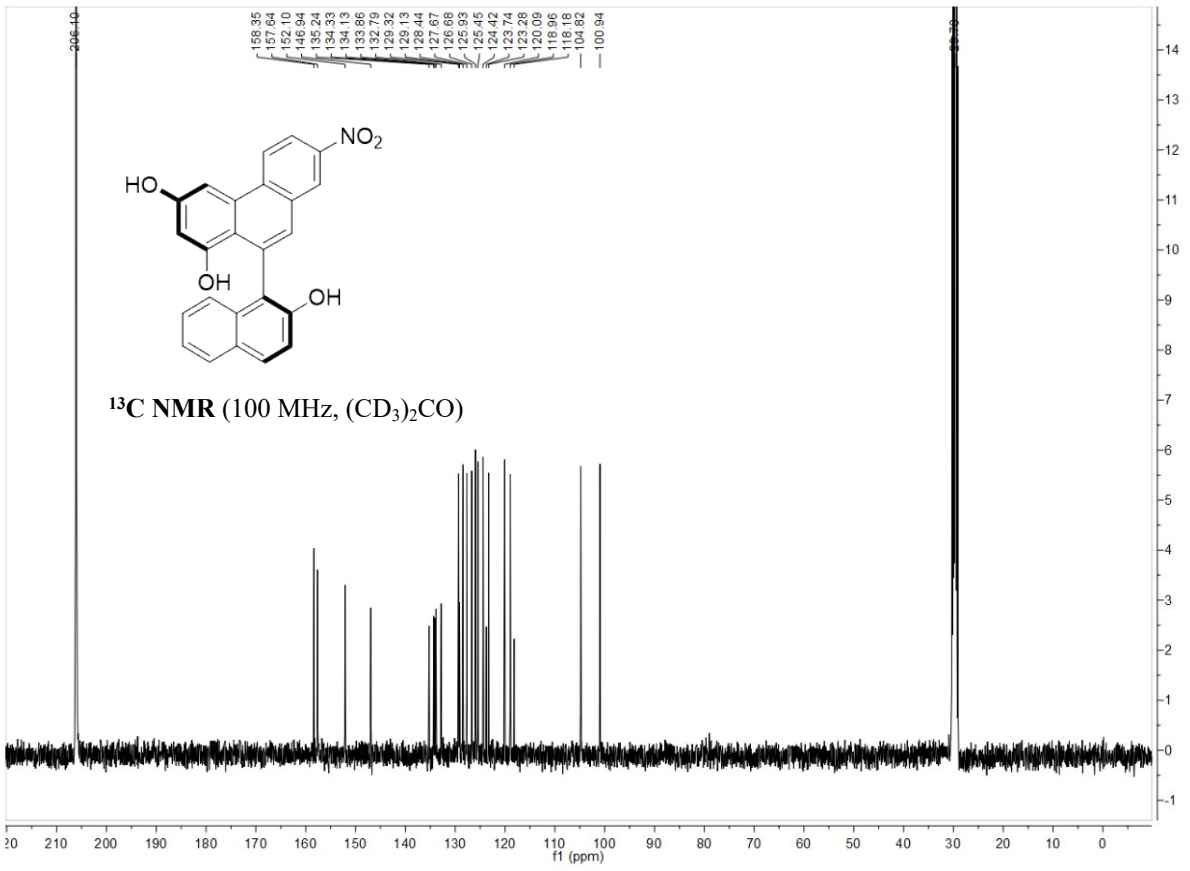
^{1}H NMR (400 MHz, DMSO-d_6)



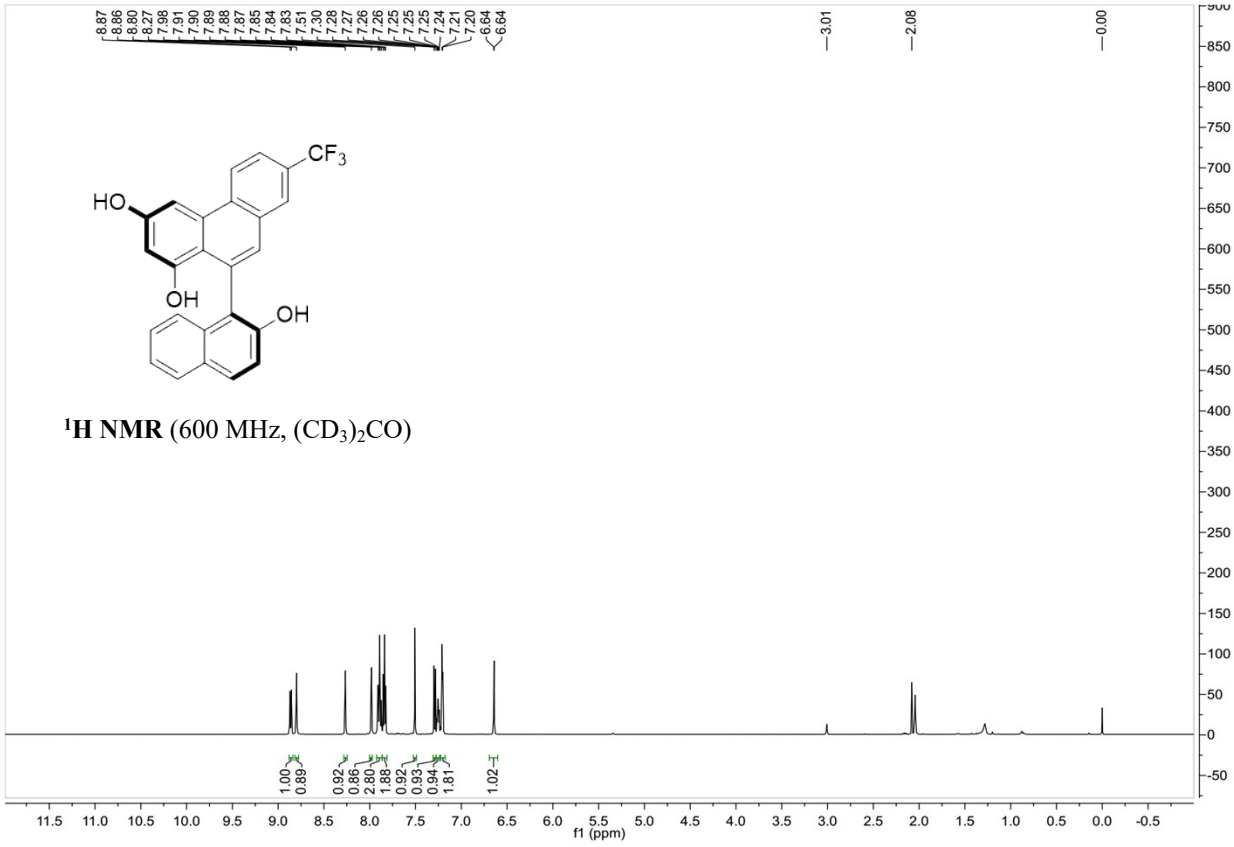
^{13}C NMR (100 MHz, $(CD_3)_2CO$)



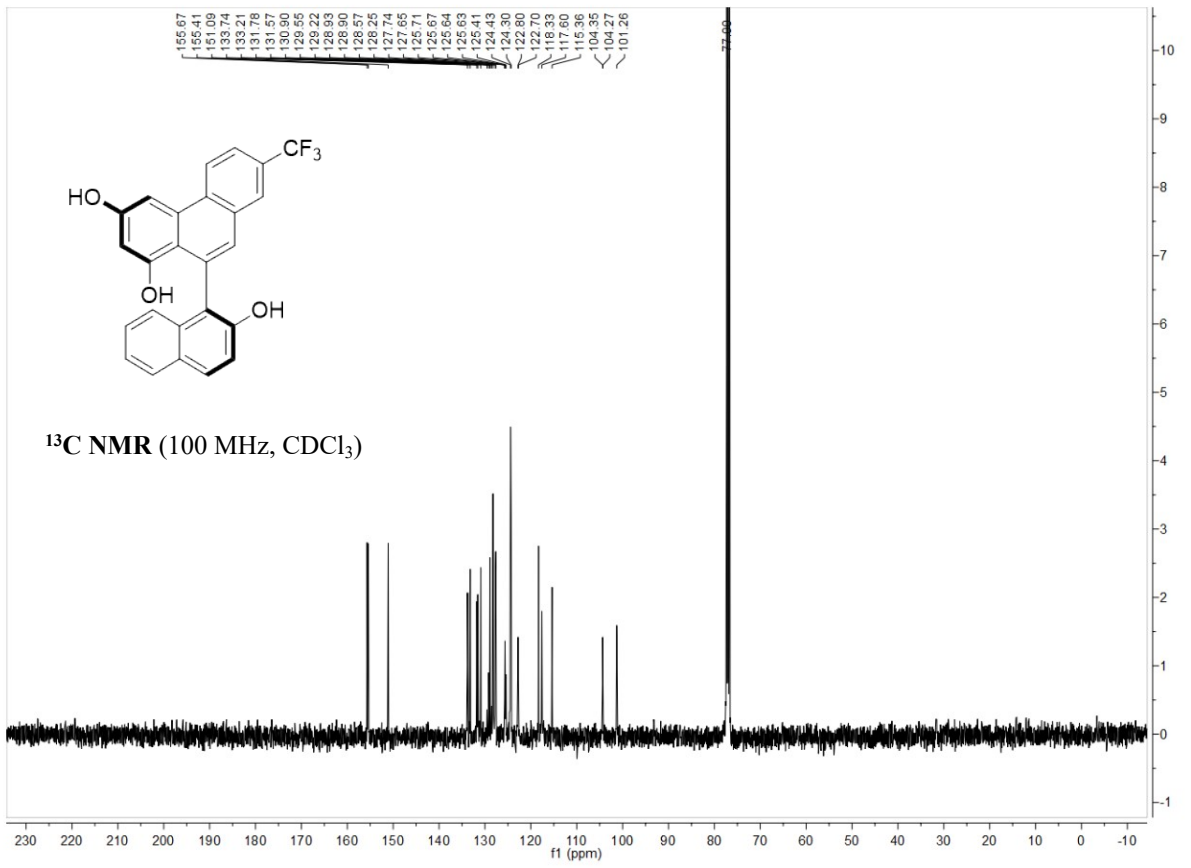
[1]H NMR (400 MHz, $(CD_3)_2CO$)



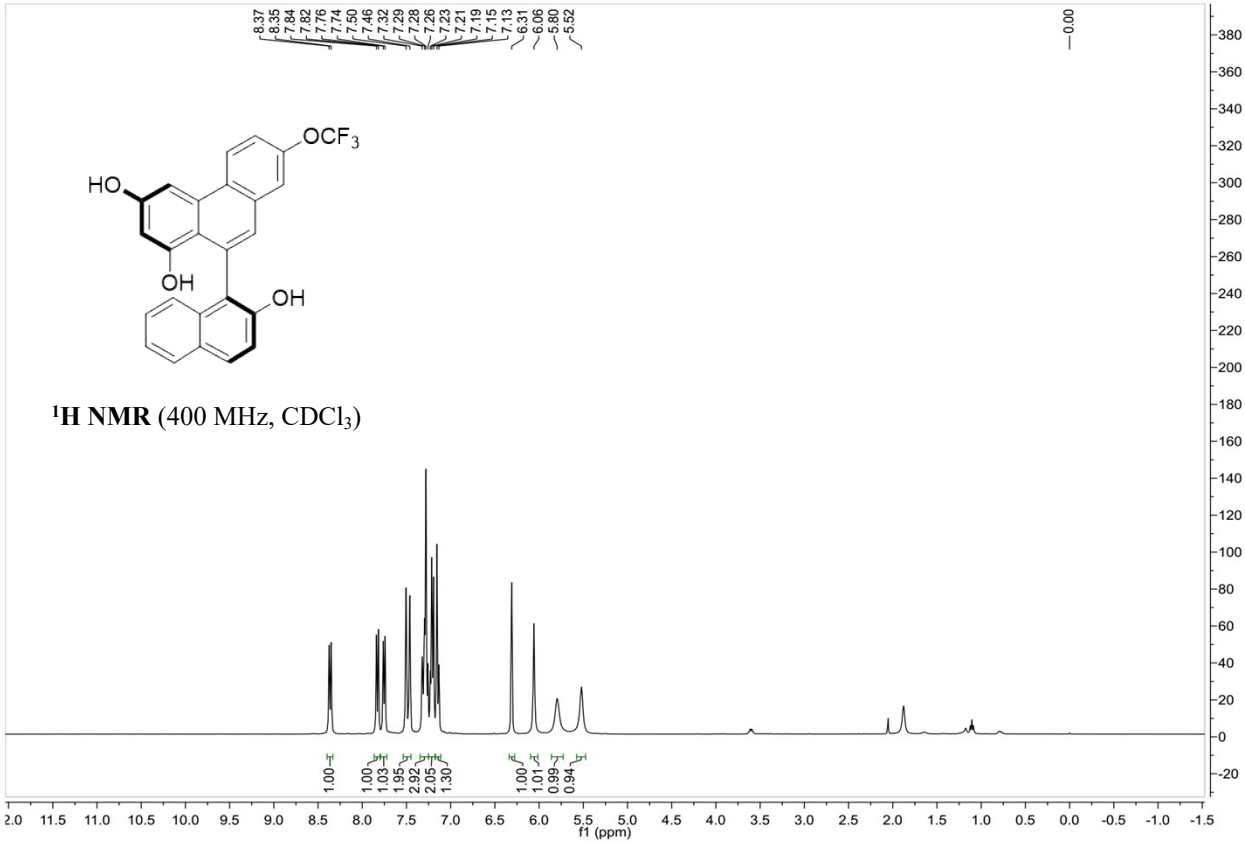
[13]C NMR (100 MHz, $(CD_3)_2CO$)



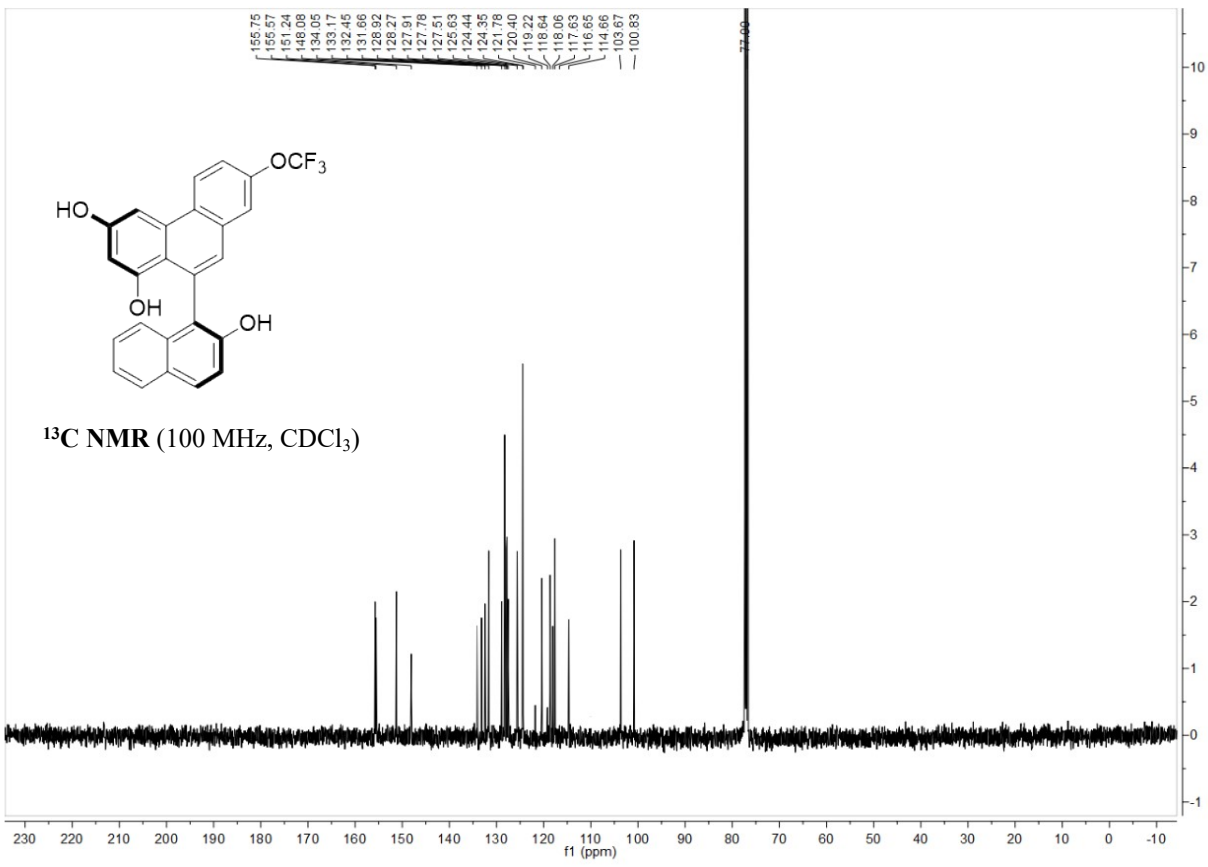
^{1}H NMR (600 MHz, $(CD_3)_2CO$)



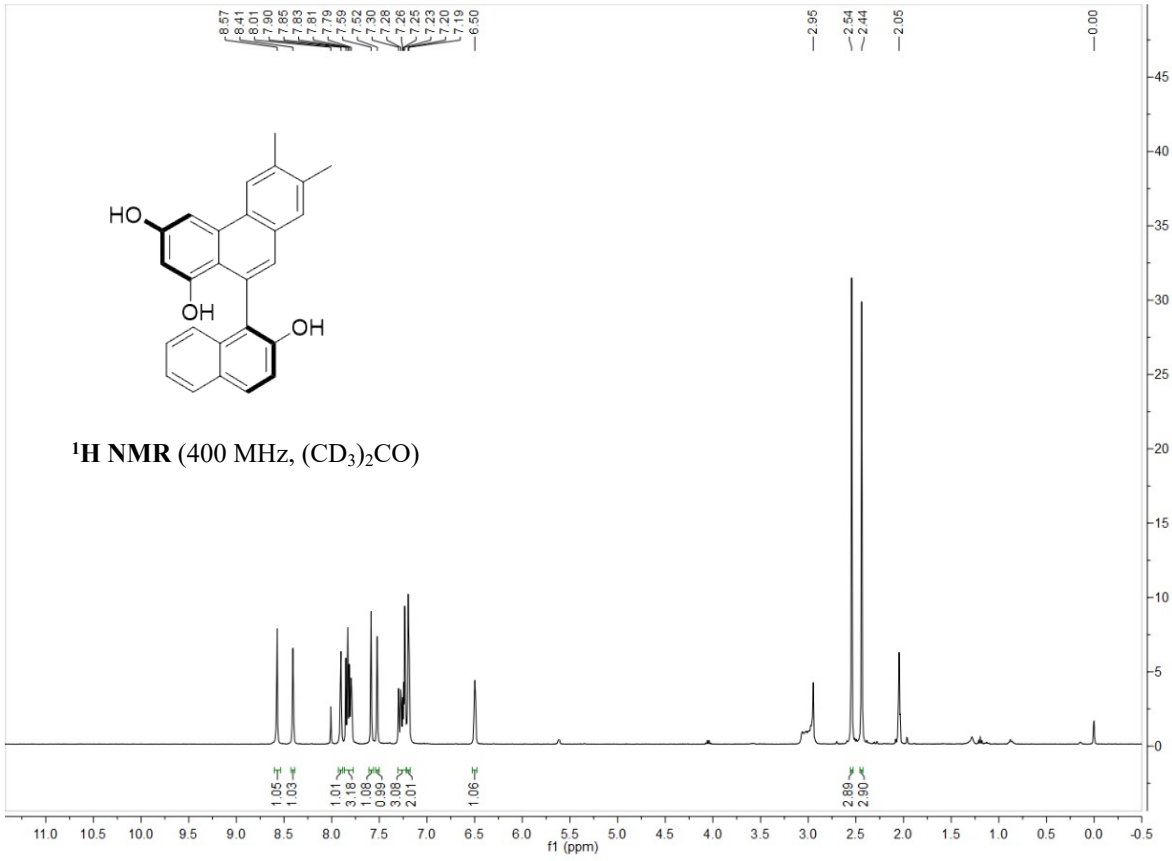
^{13}C NMR (100 MHz, $CDCl_3$)



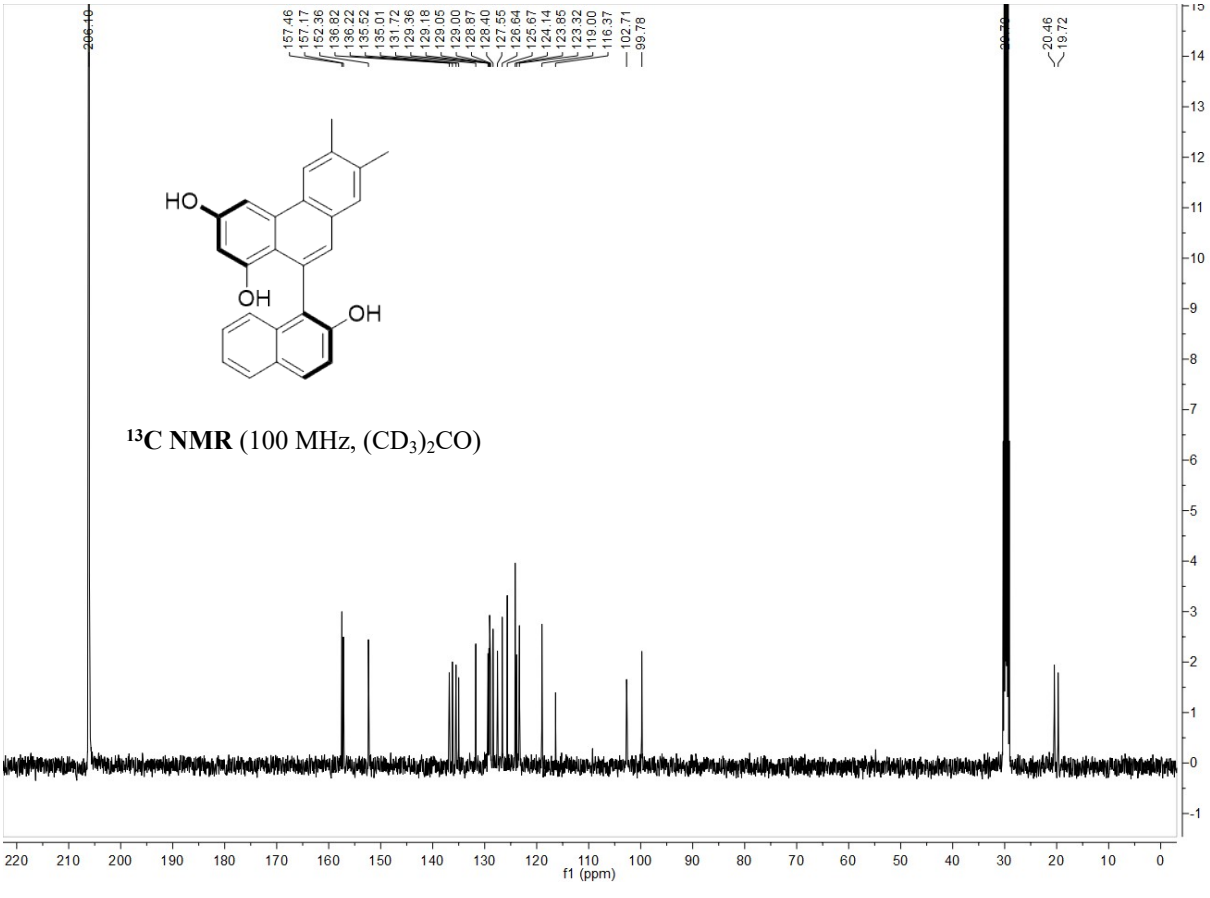
^{1}H NMR (400 MHz, $CDCl_3$)



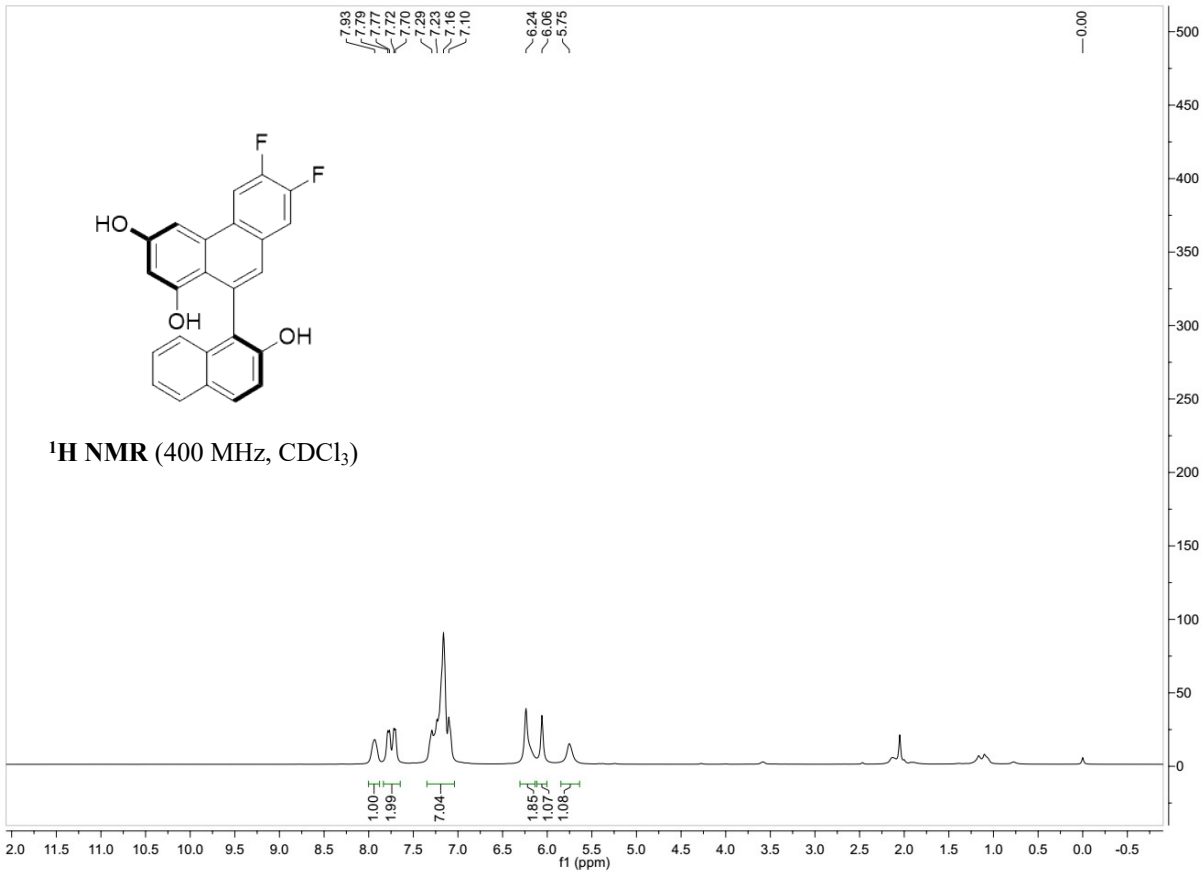
^{13}C NMR (100 MHz, $CDCl_3$)



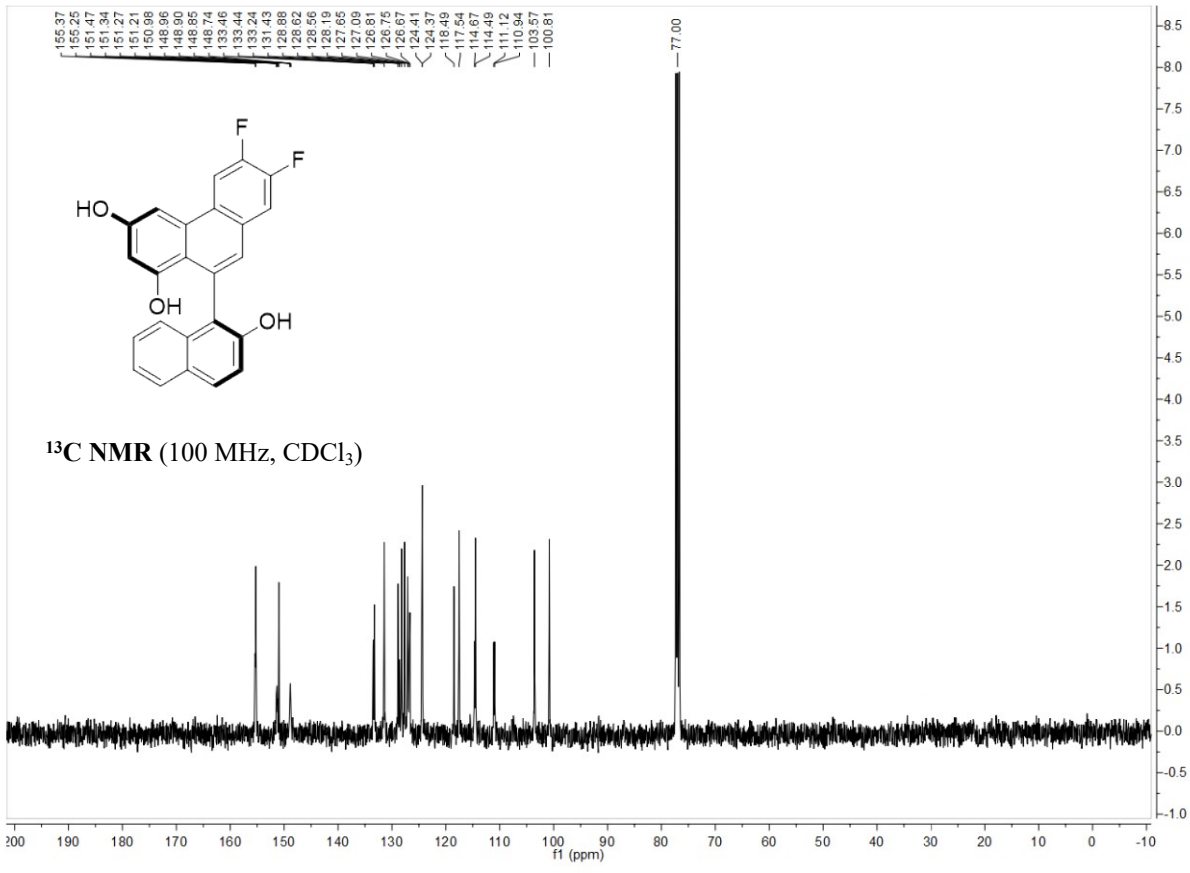
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



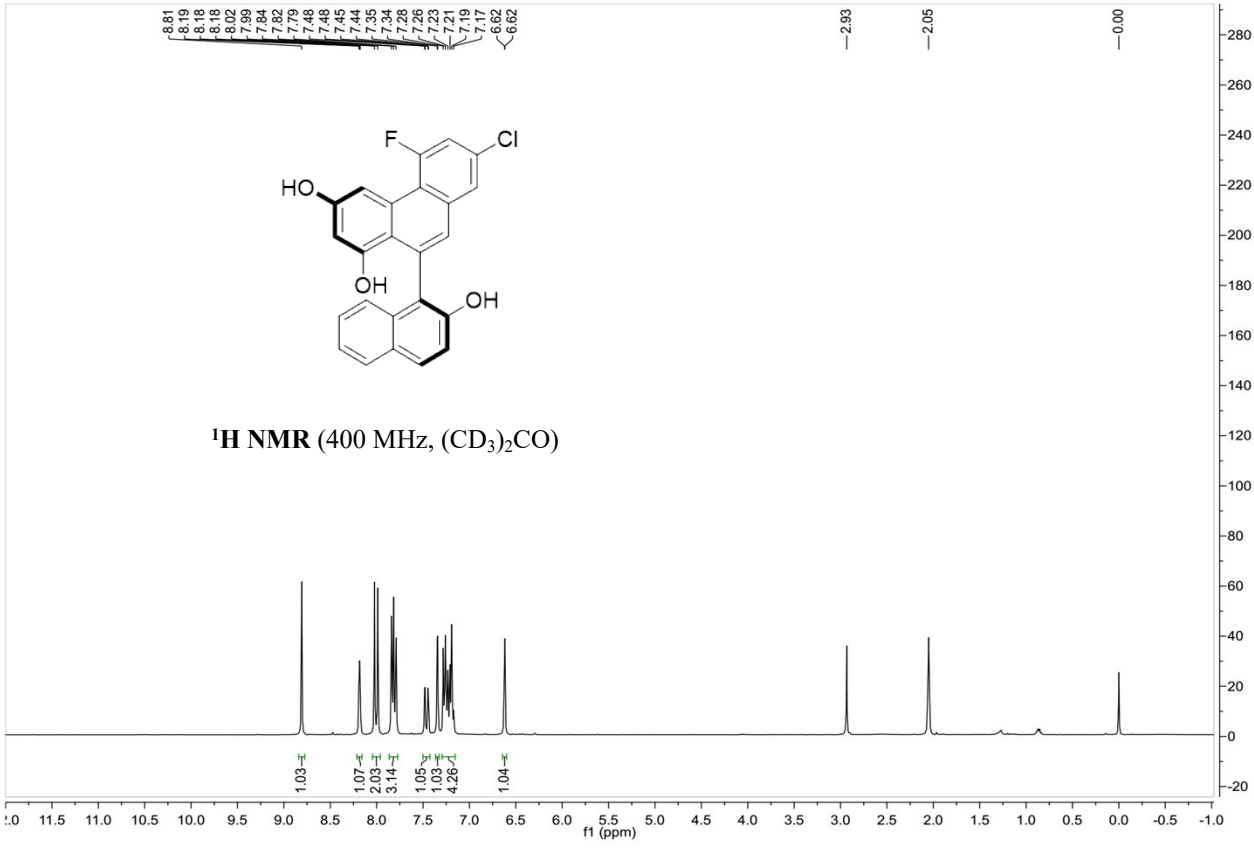
^{13}C NMR (100 MHz, $(CD_3)_2CO$)



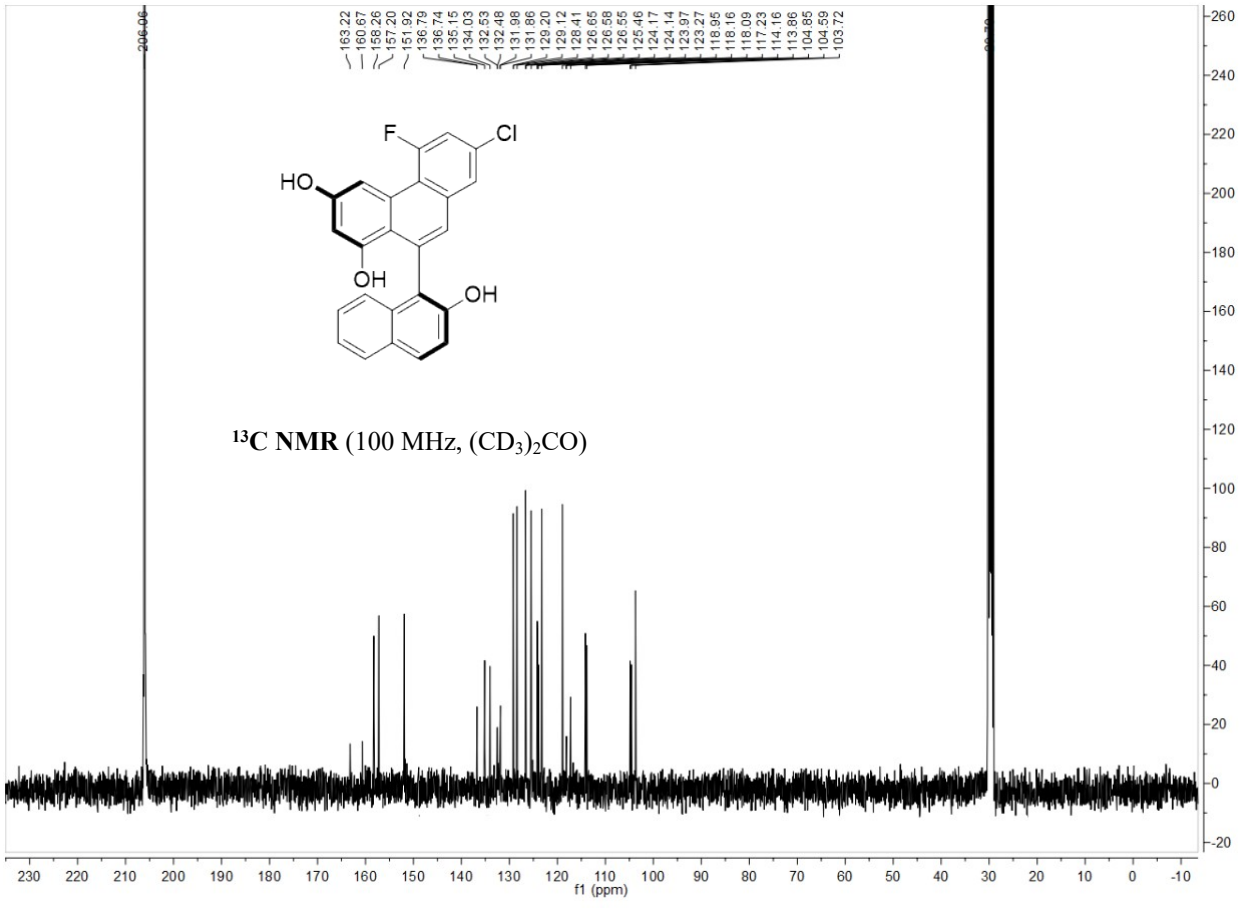
^{1}H NMR (400 MHz, $CDCl_3$)



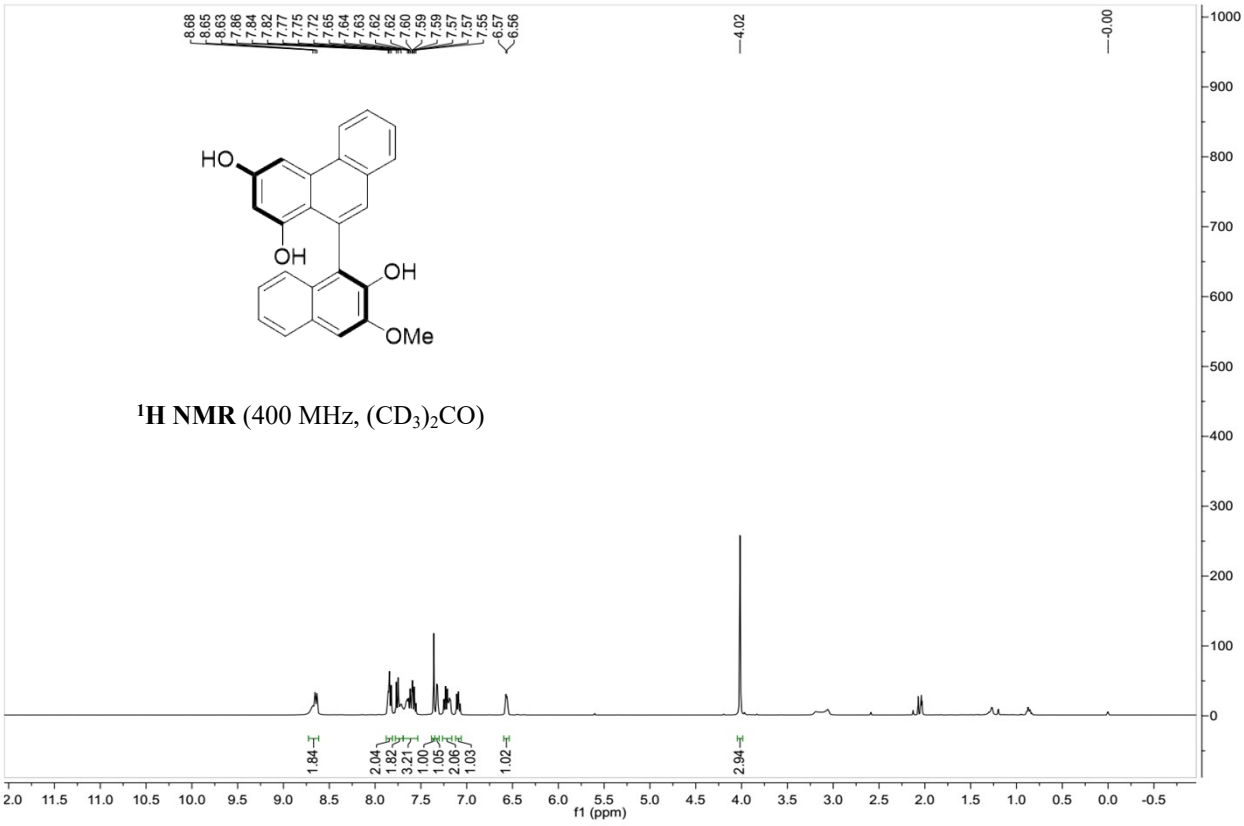
^{13}C NMR (100 MHz, $CDCl_3$)

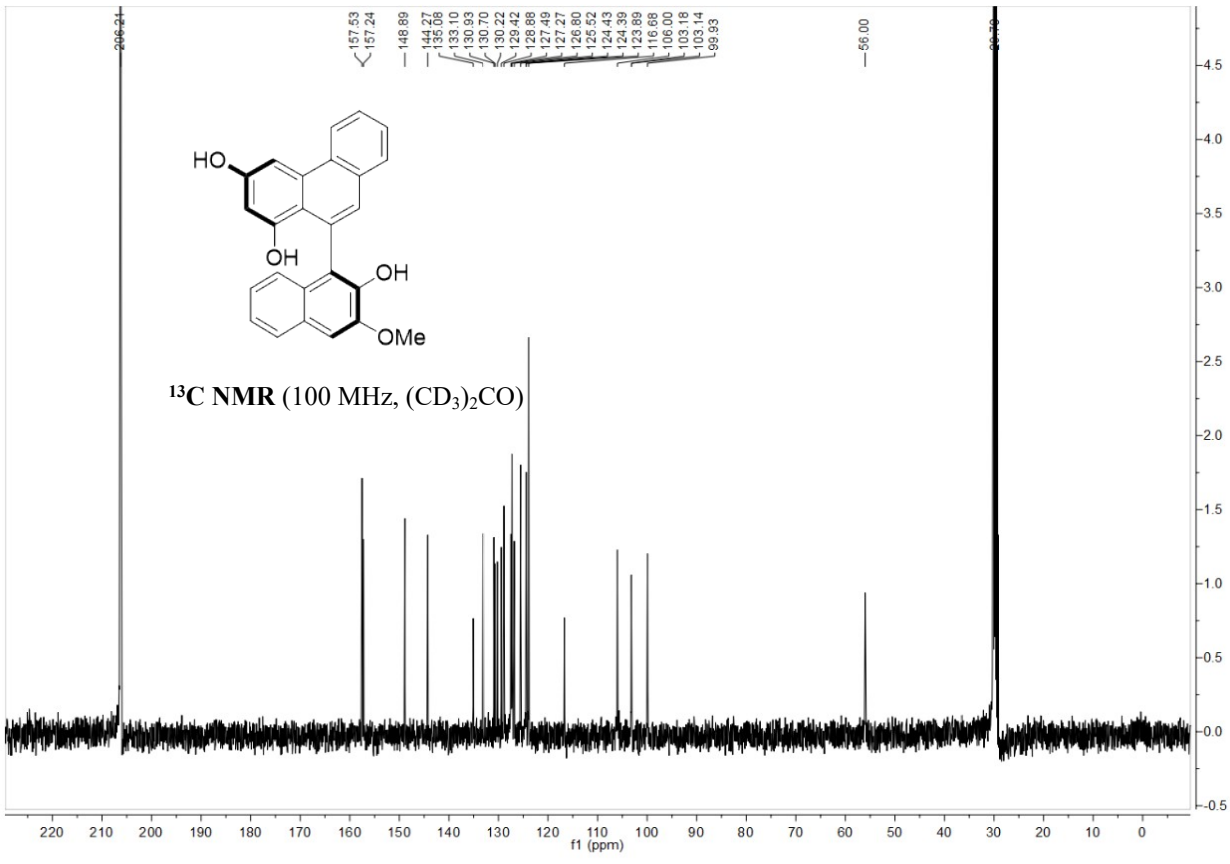


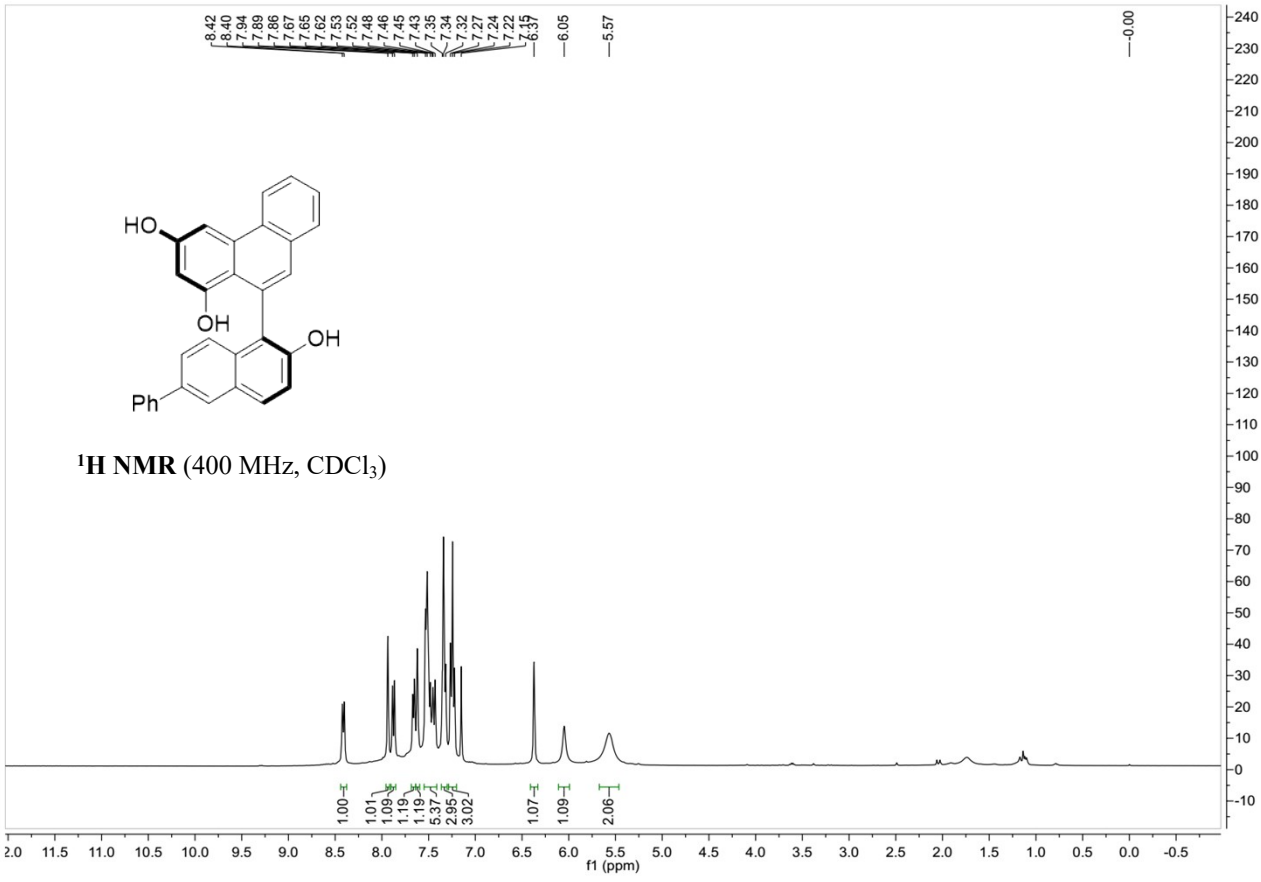
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



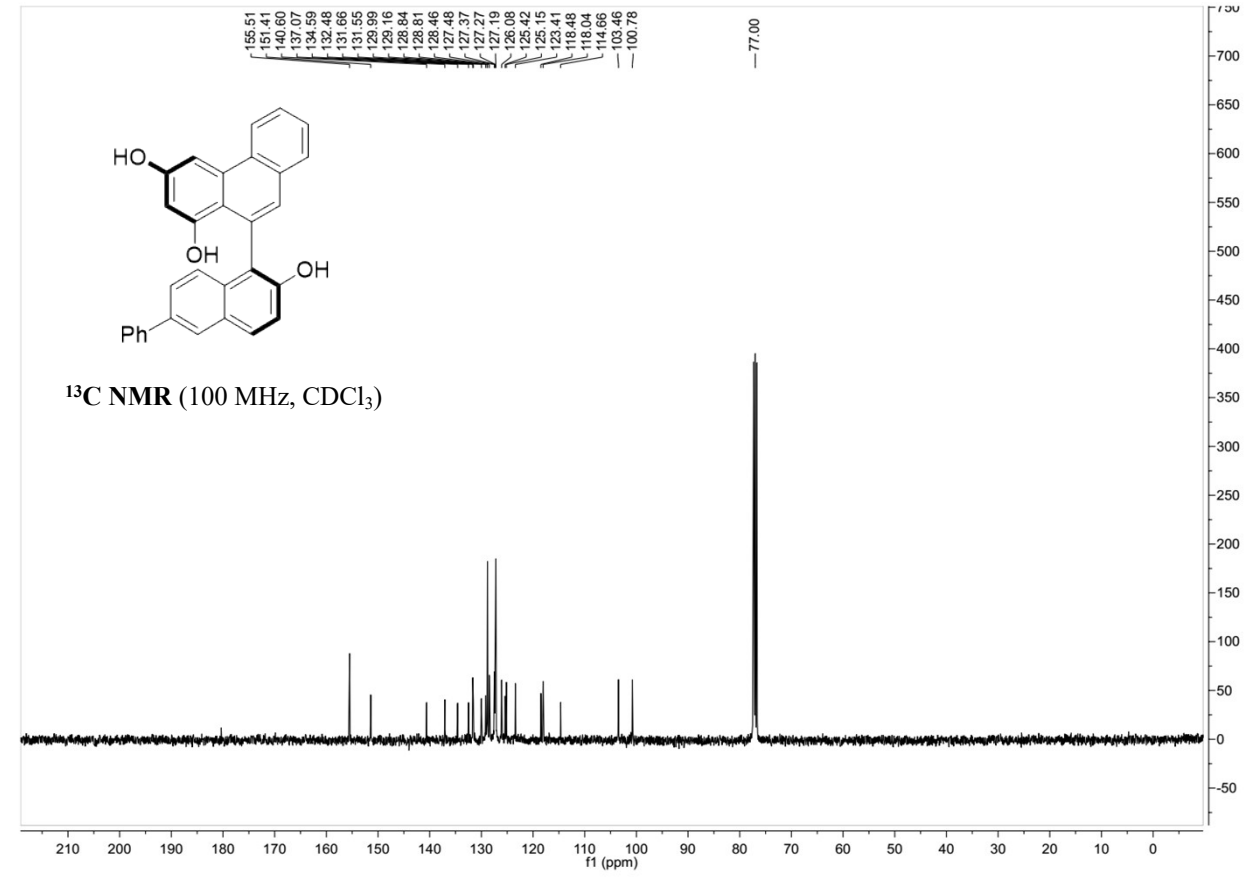
^{13}C NMR (100 MHz, $(CD_3)_2CO$)


HO
OH
OH
OMe
1H NMR (400 MHz, (CD3)2CO)
f1 (ppm)

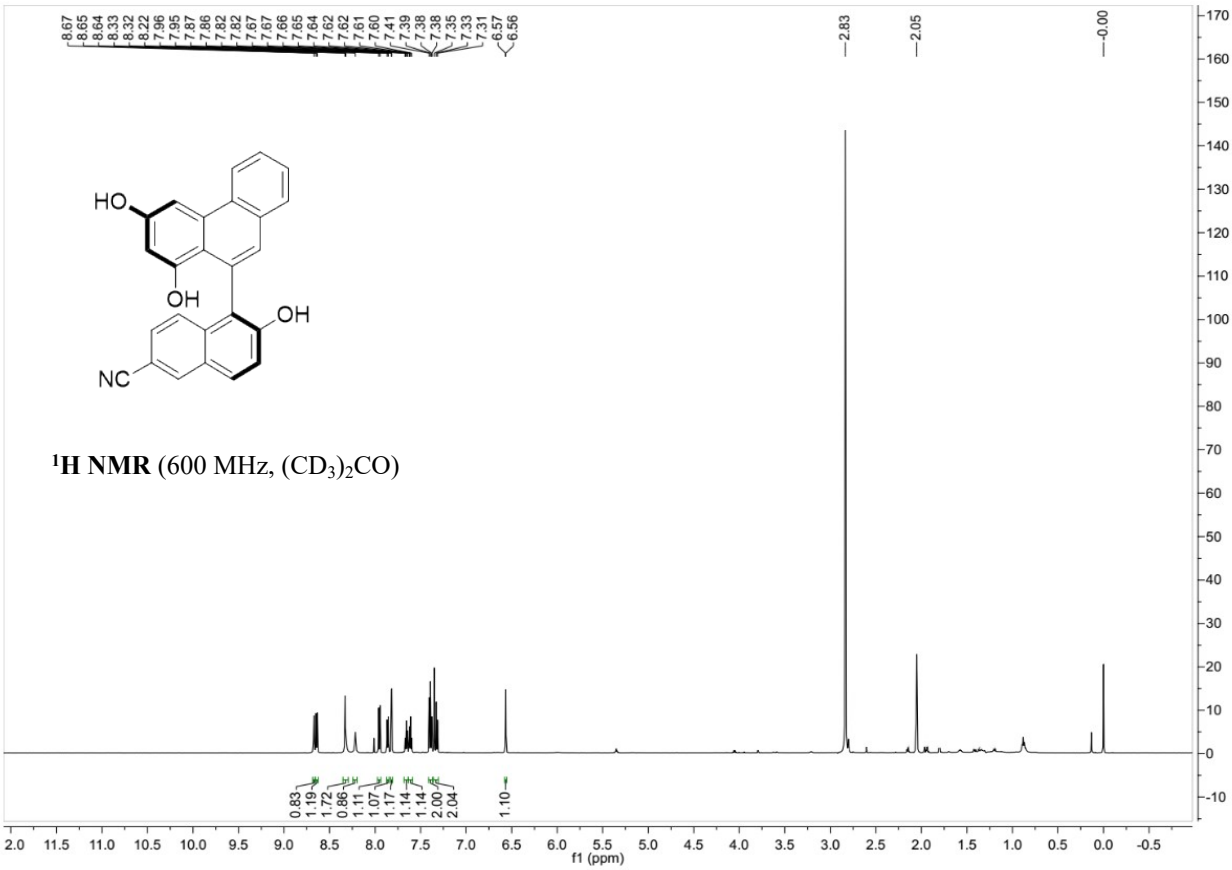

HO
OH
OH
OMe
13C NMR (100 MHz, (CD3)2CO)
f1 (ppm)



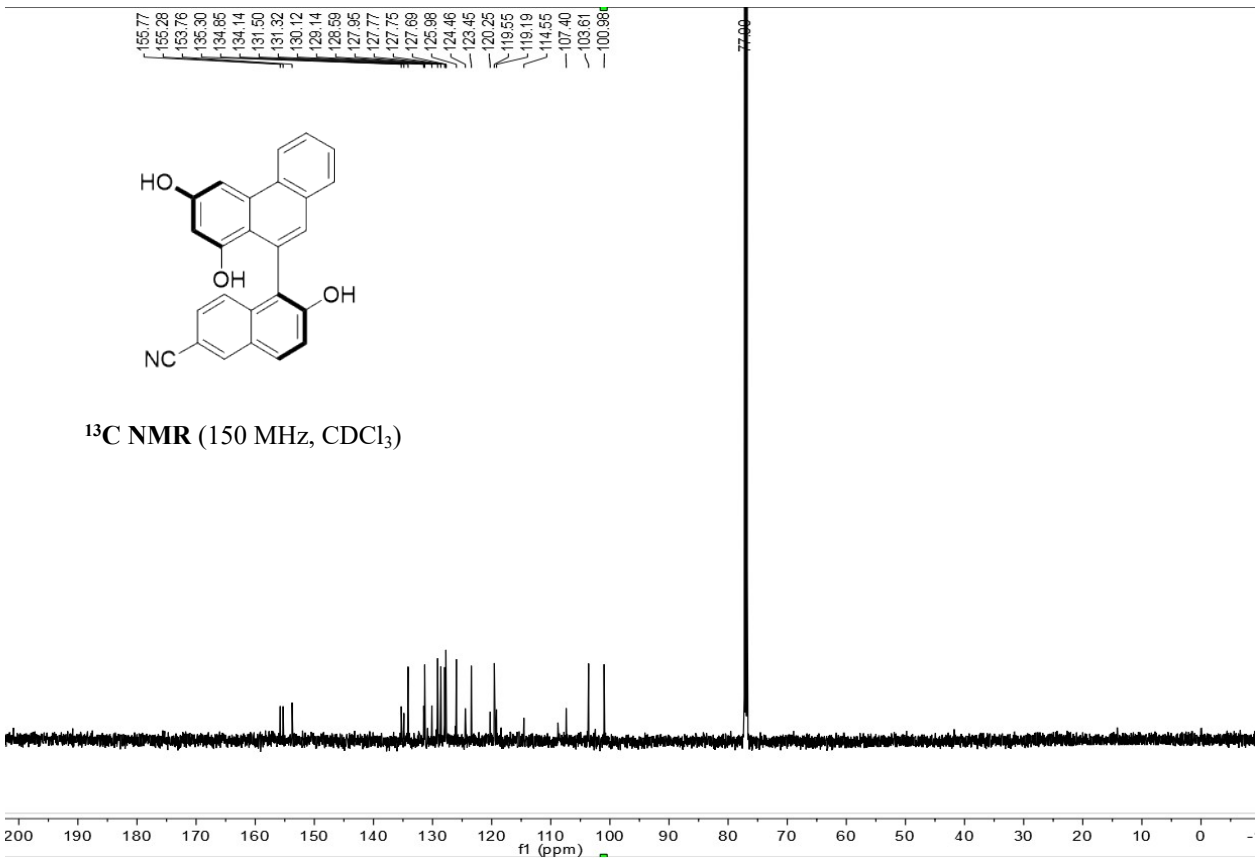
^{1}H NMR (400 MHz, $CDCl_3$)



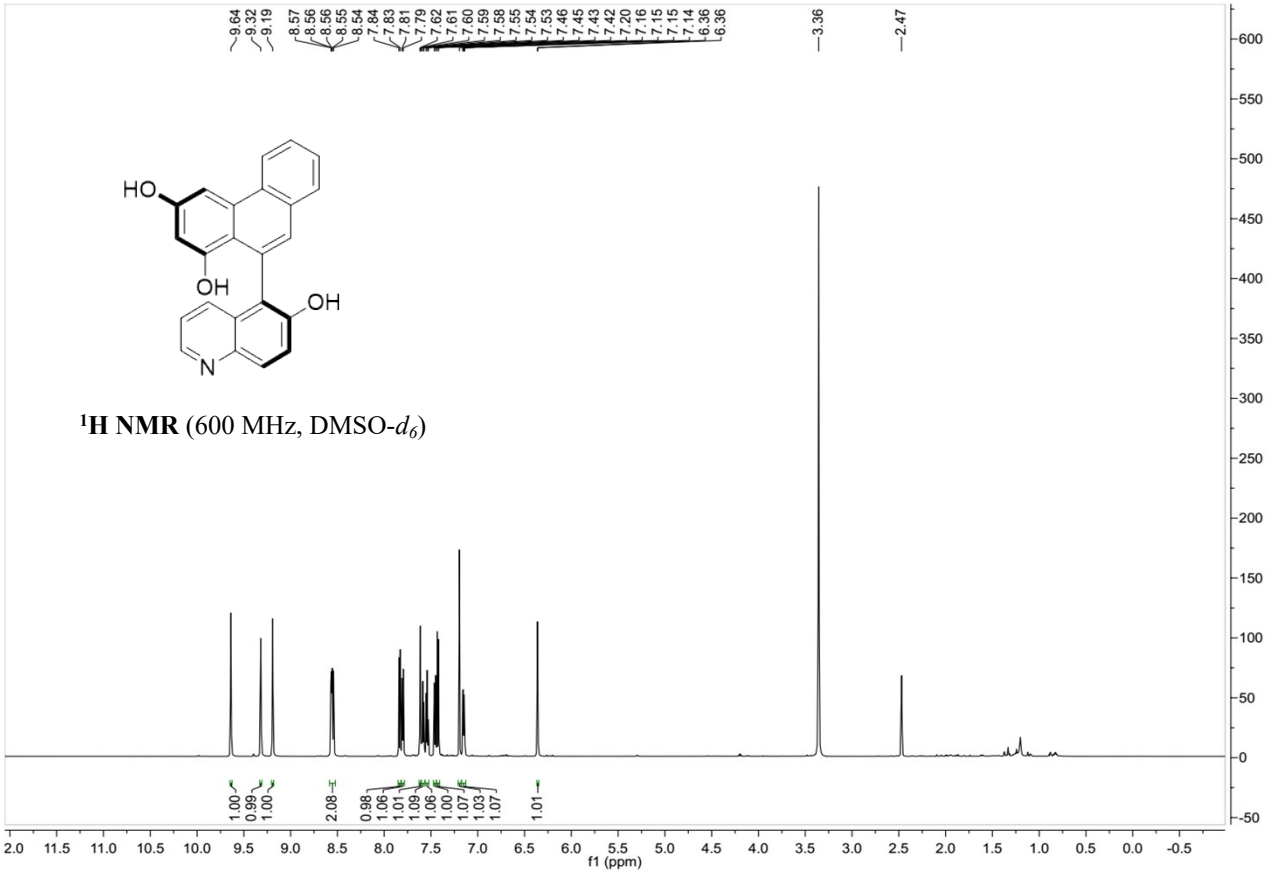
^{13}C NMR (100 MHz, $CDCl_3$)



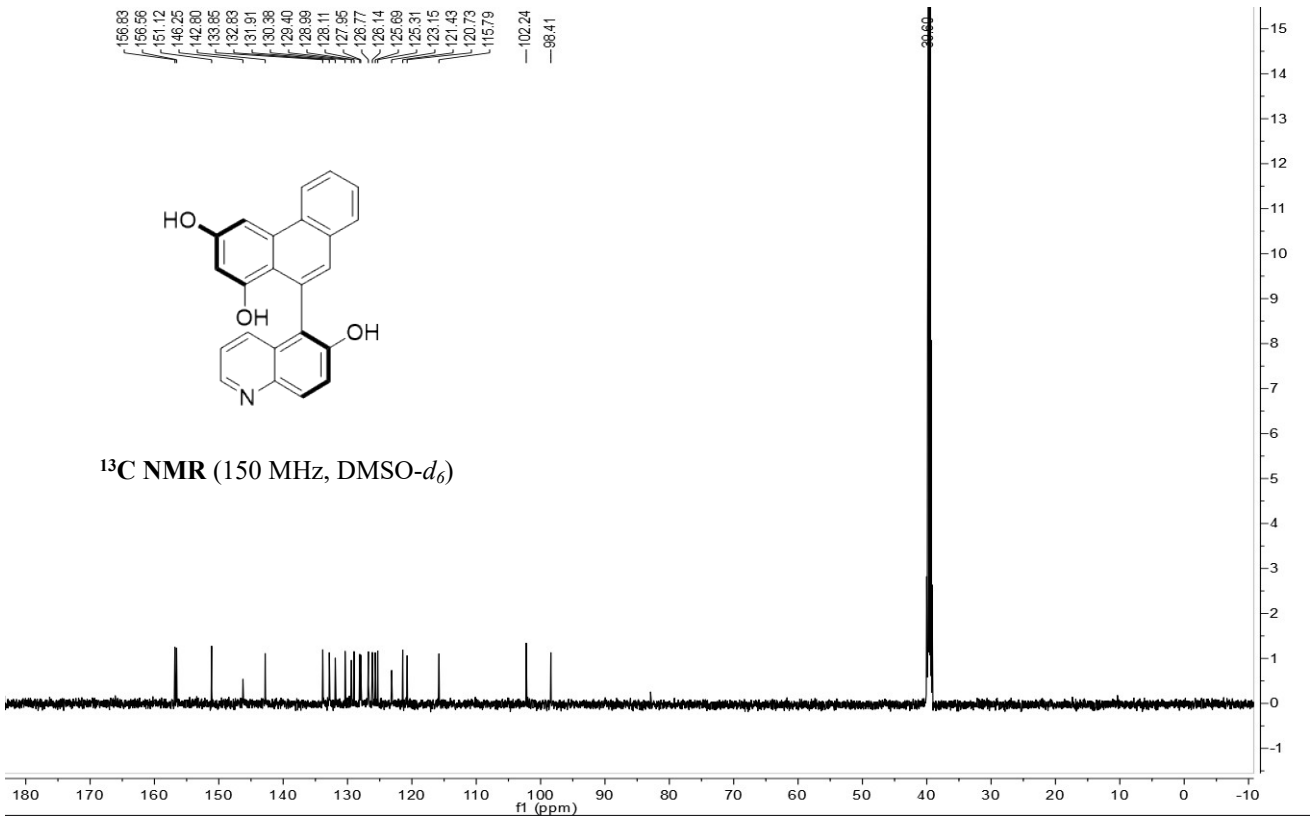
^{1}H NMR (600 MHz, $(CD_3)_2CO$)



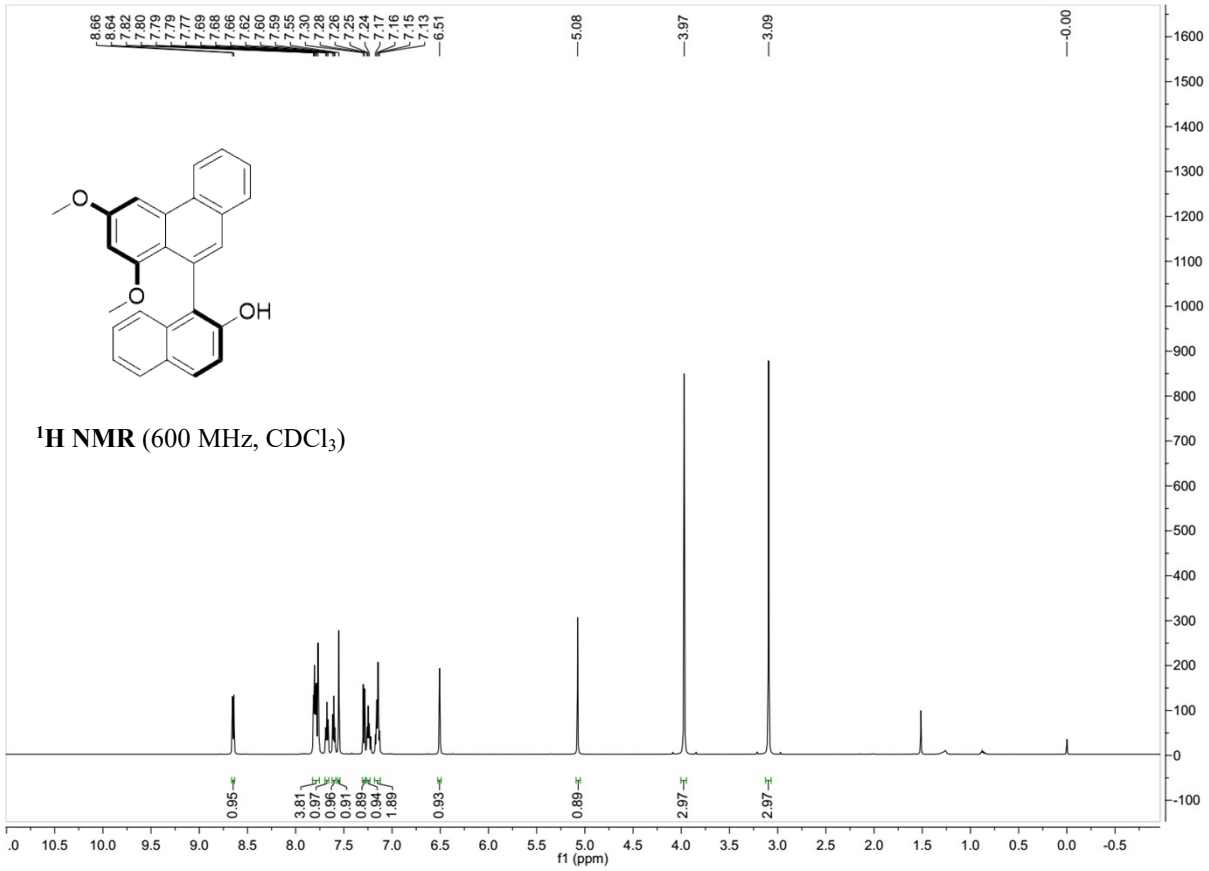
^{13}C NMR (150 MHz, $CDCl_3$)



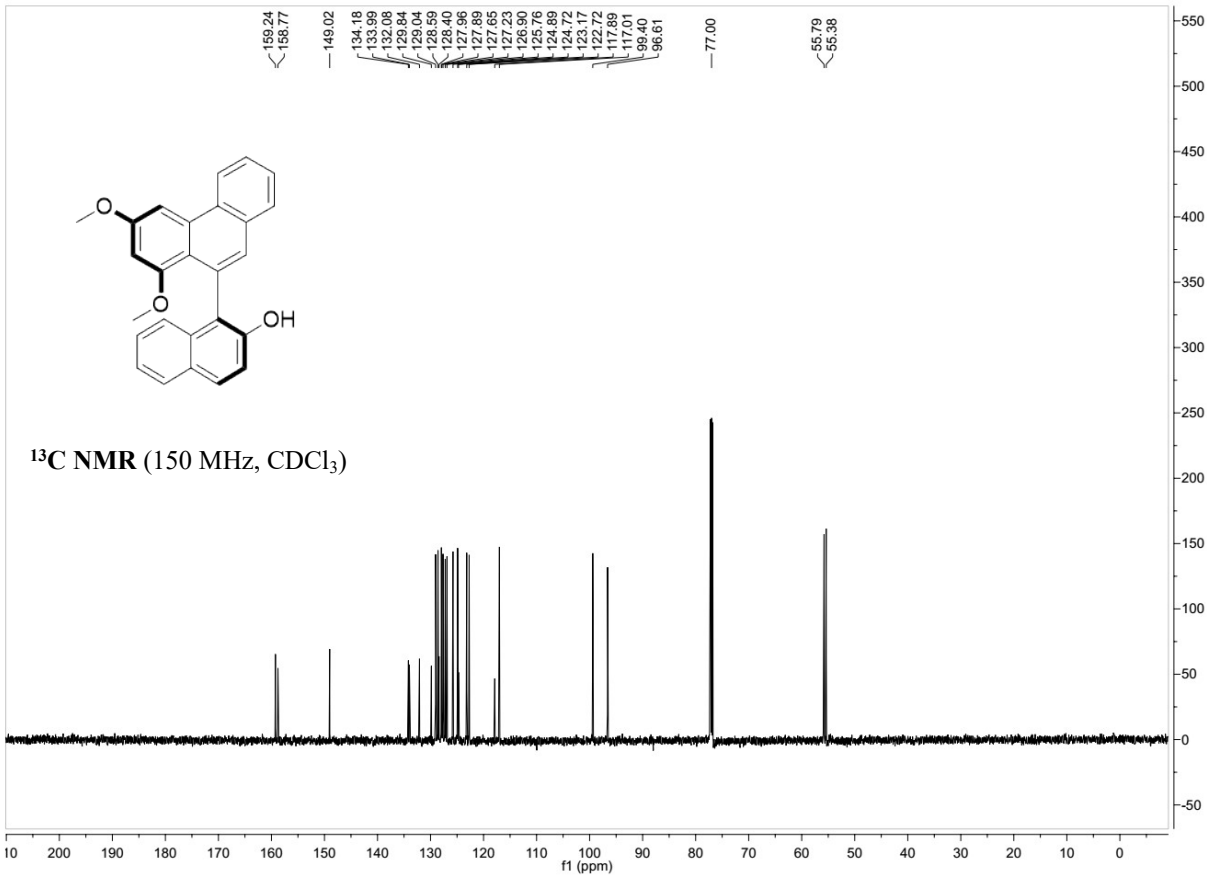
[1]H NMR (600 MHz, DMSO-d_6)



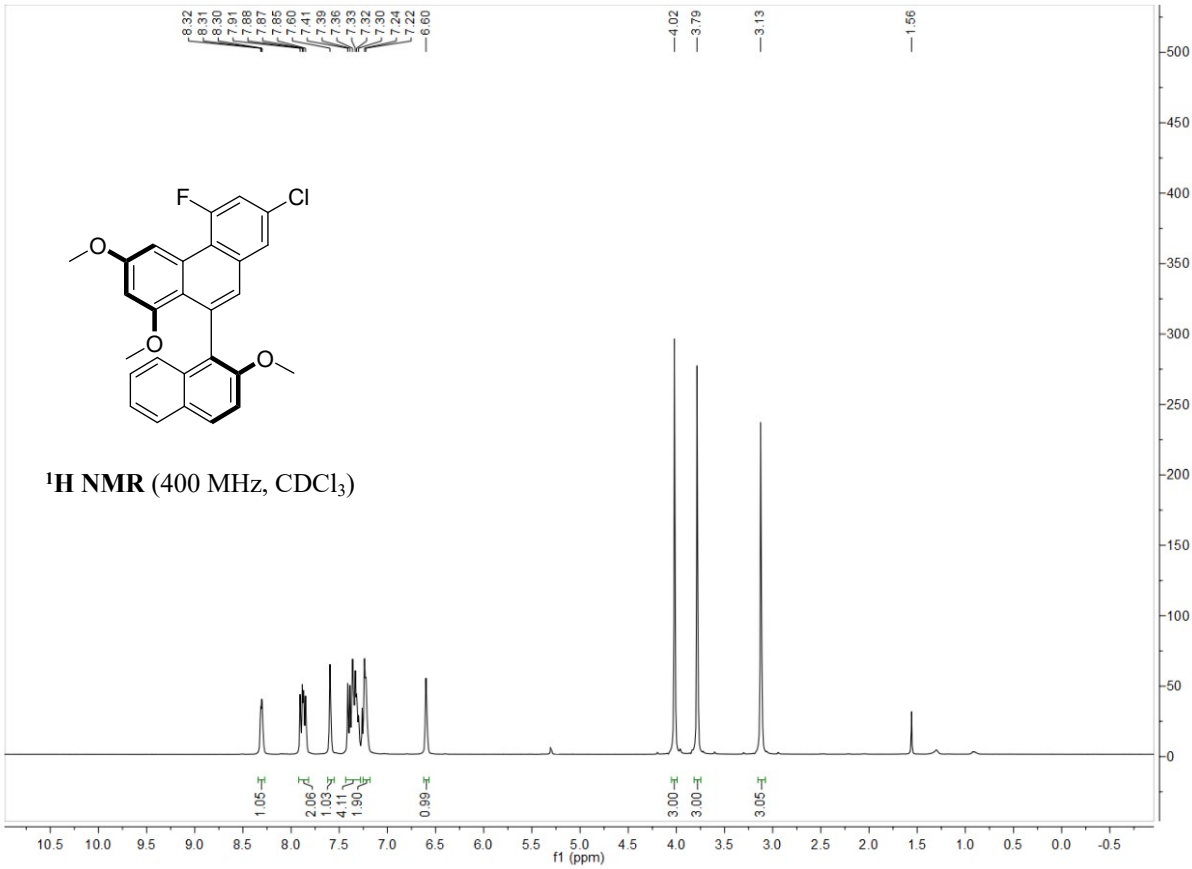
[13]C NMR (150 MHz, DMSO-d_6)



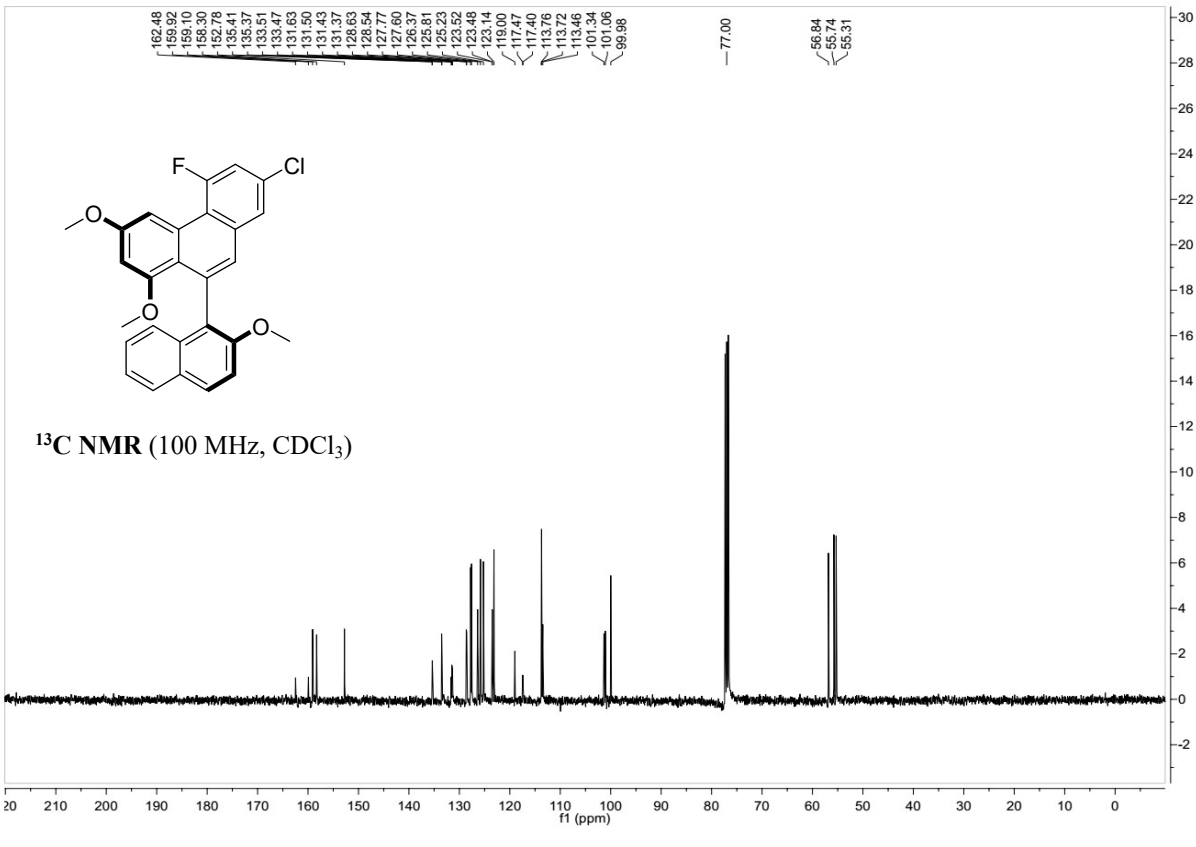
^{1}H NMR (600 MHz, $CDCl_3$)



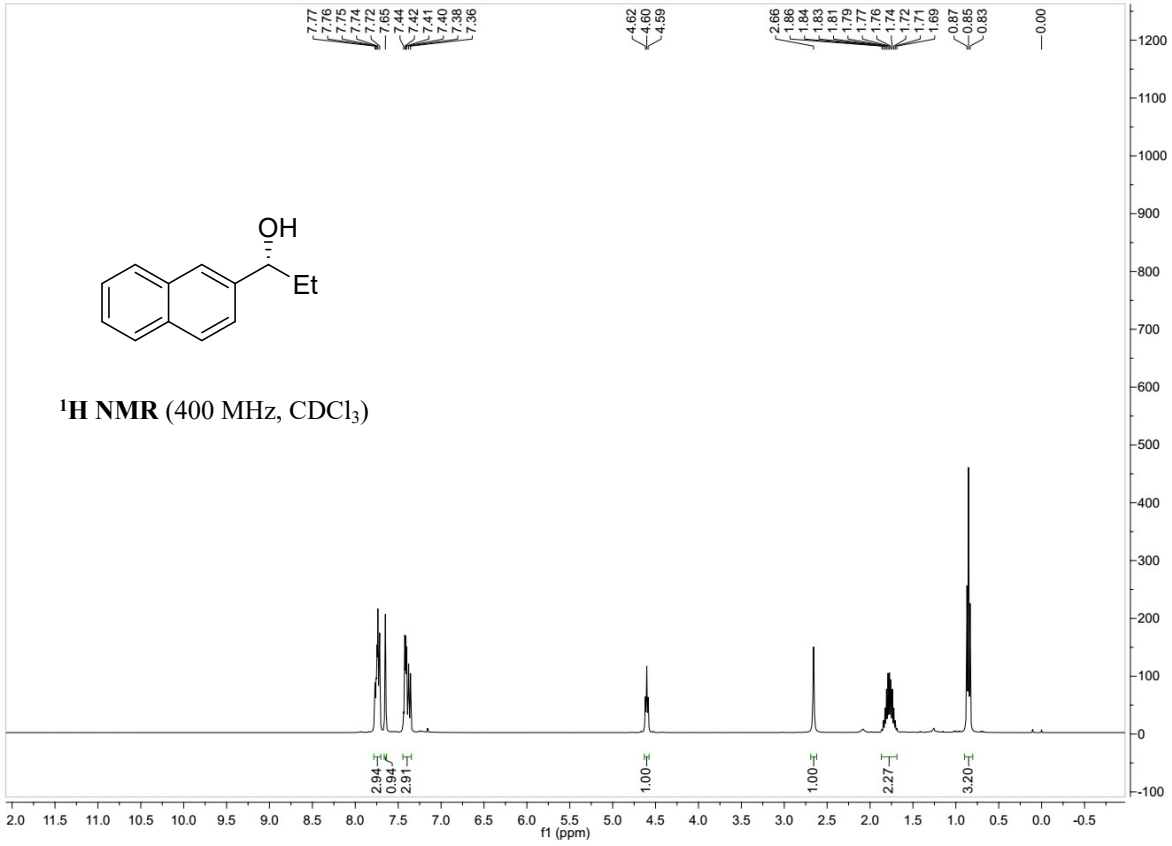
^{13}C NMR (150 MHz, $CDCl_3$)



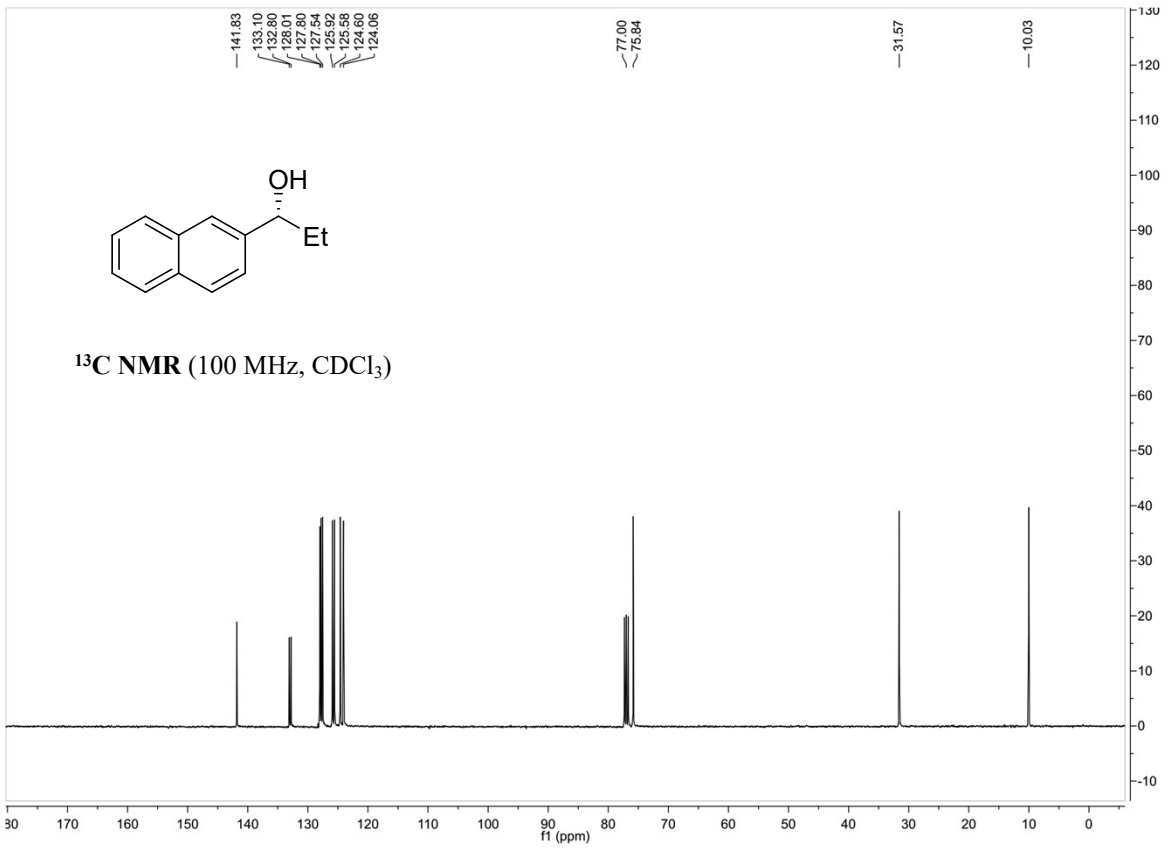
^{1}H NMR (400 MHz, $CDCl_3$)



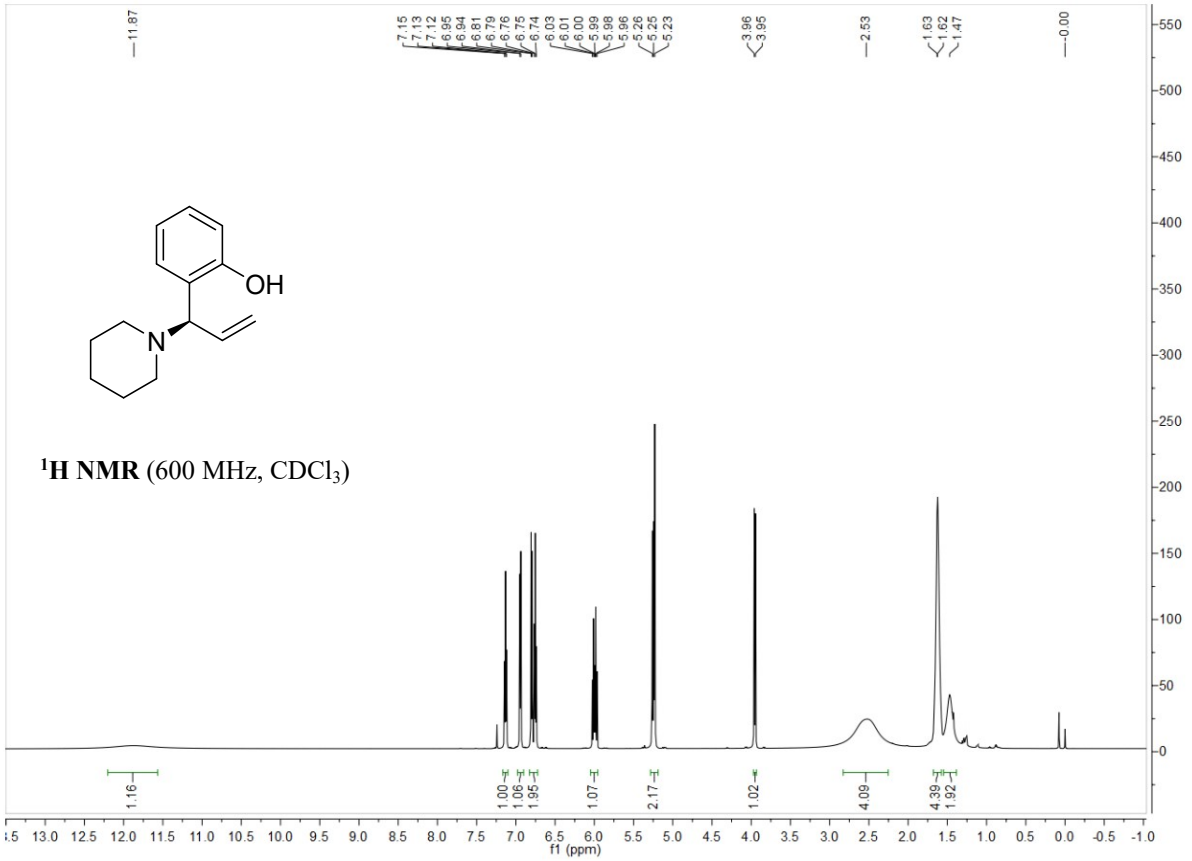
^{13}C NMR (100 MHz, $CDCl_3$)



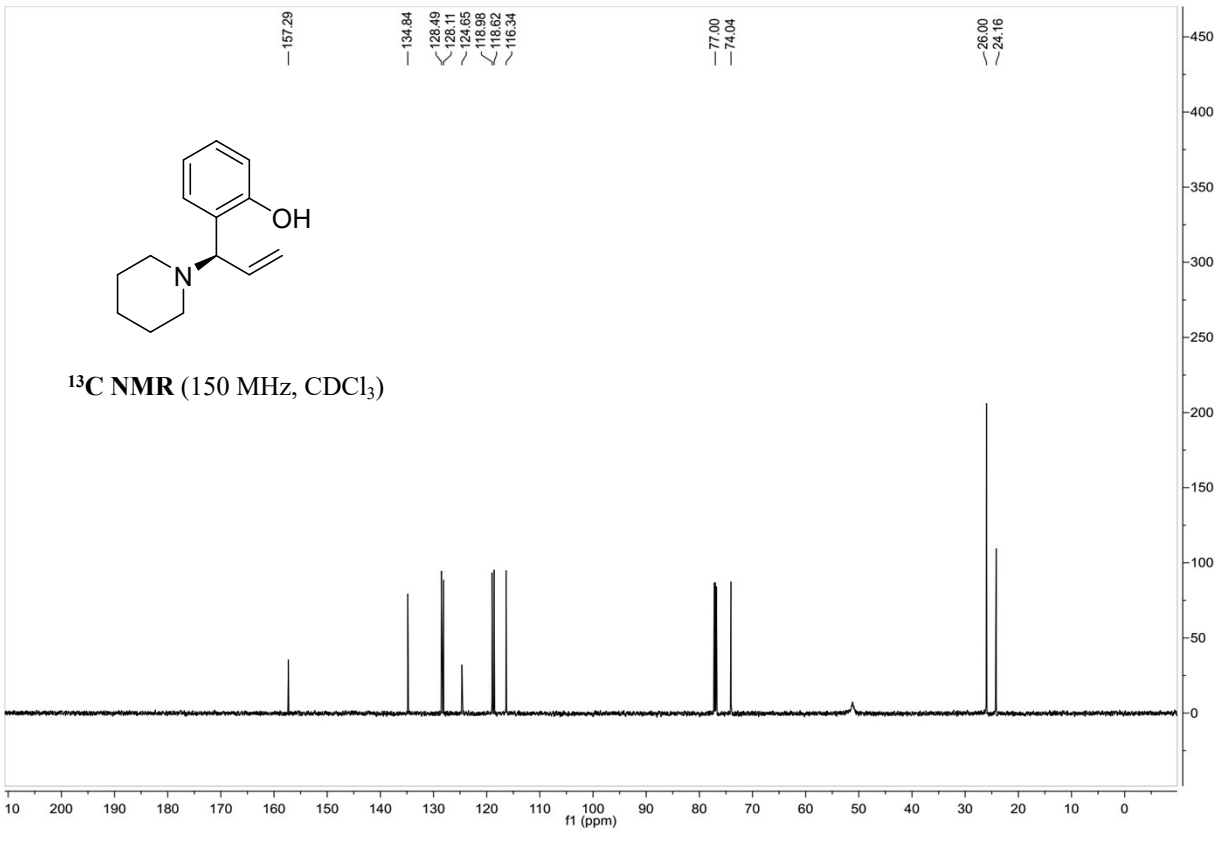
^{1}H NMR (400 MHz, $CDCl_3$)



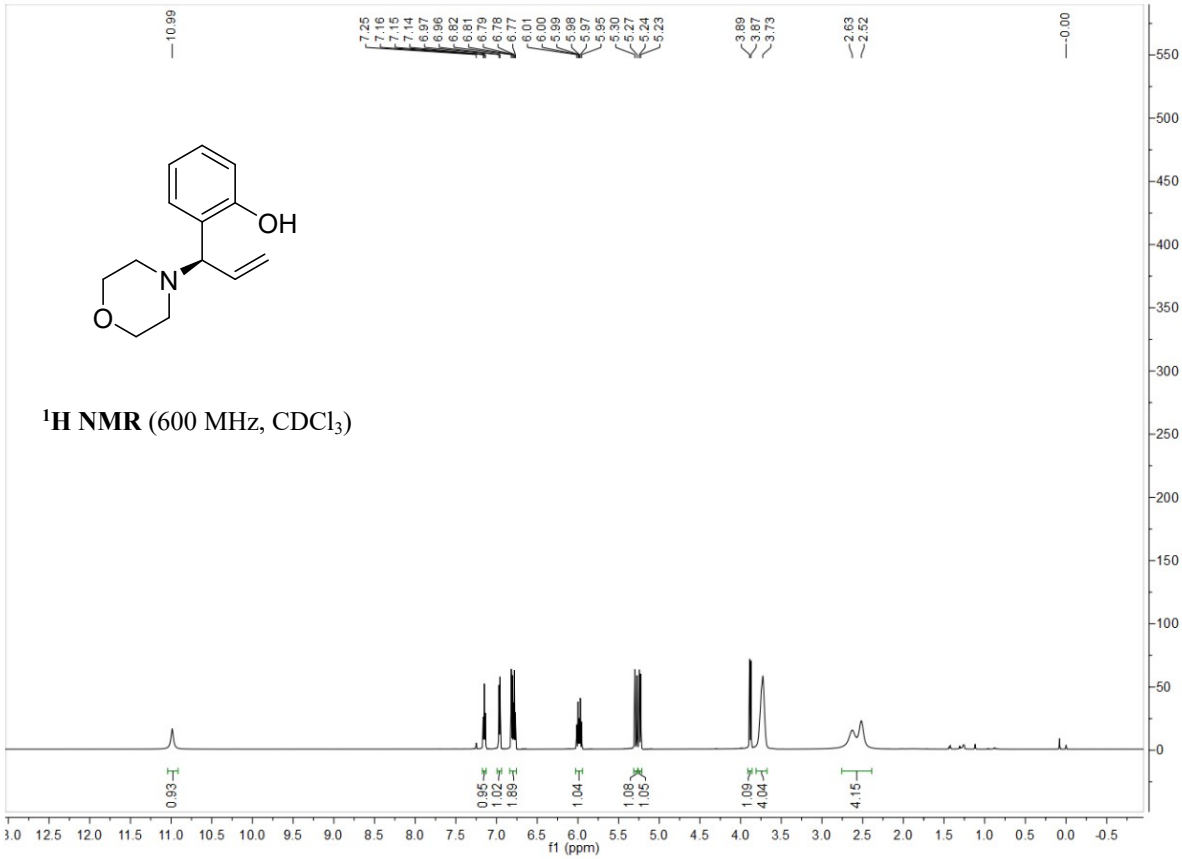
^{13}C NMR (100 MHz, $CDCl_3$)



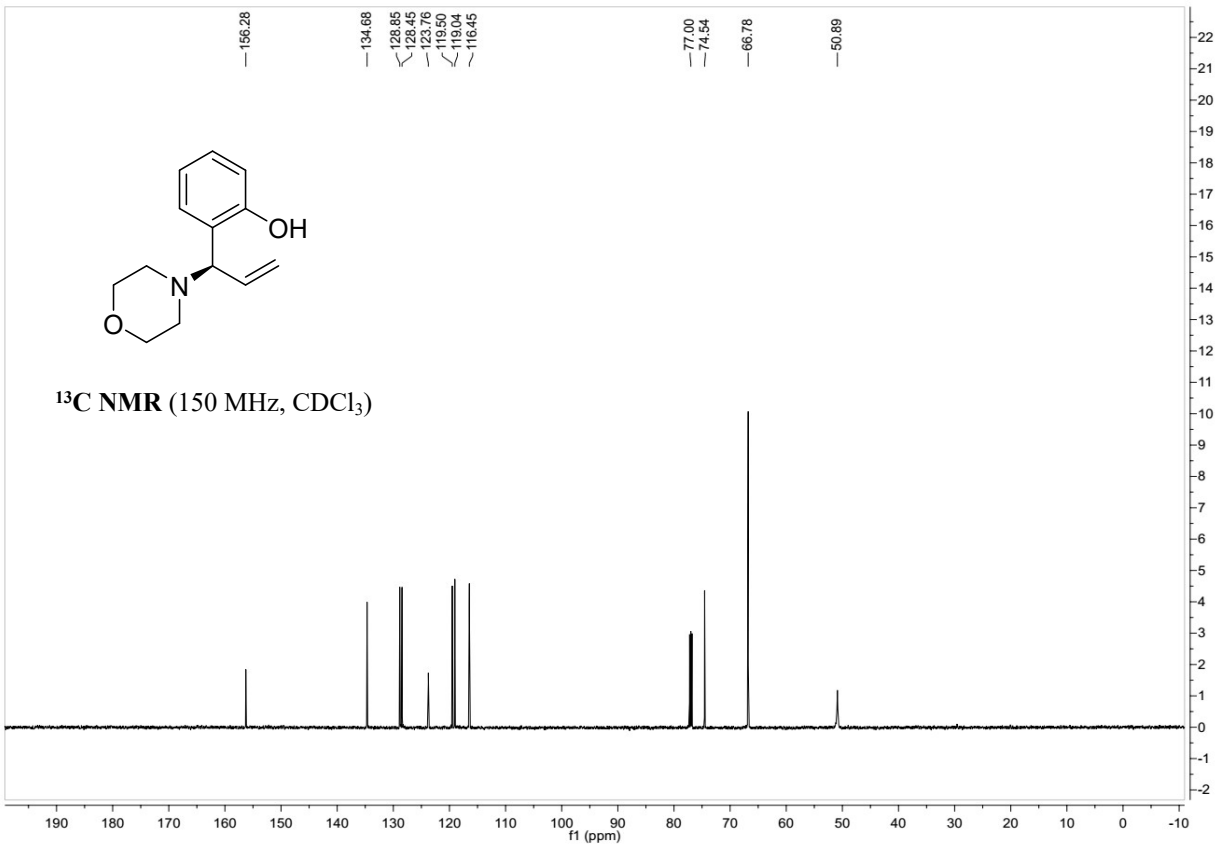
^{1}H NMR (600 MHz, $CDCl_3$)



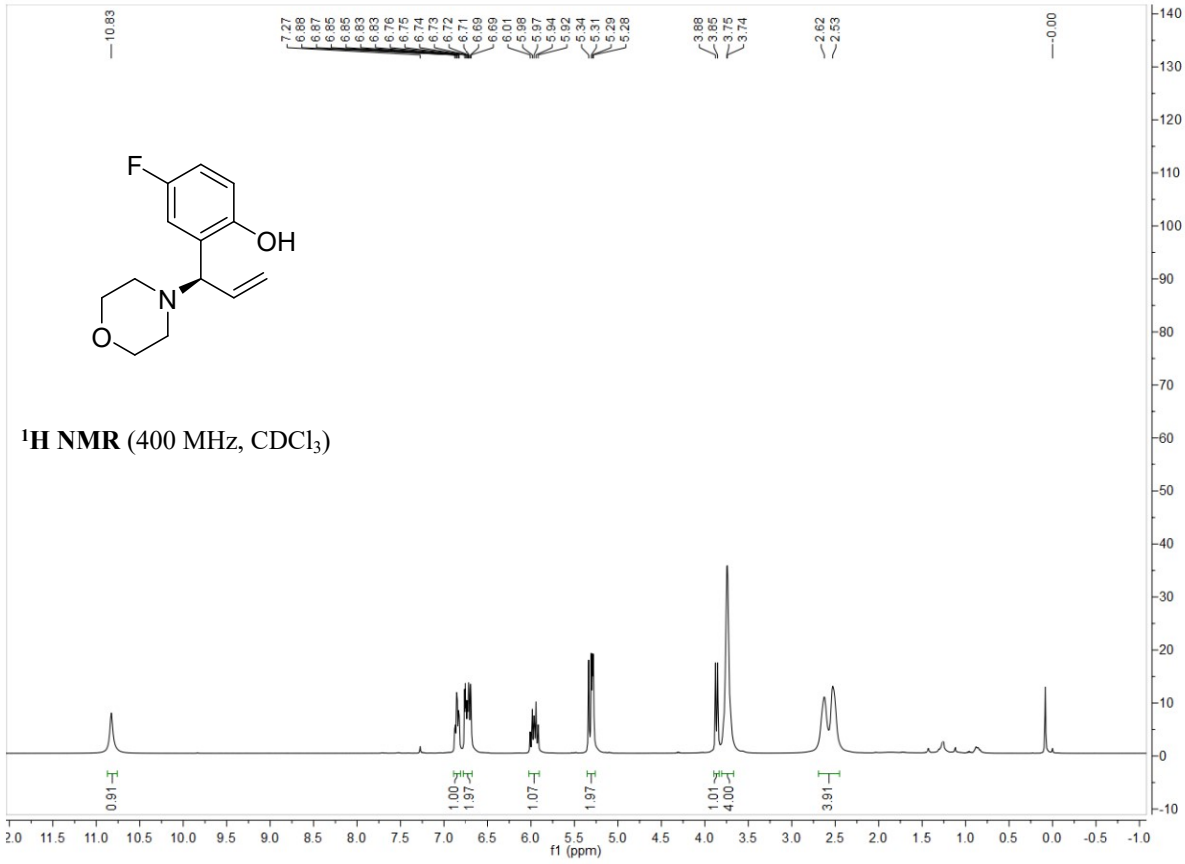
^{13}C NMR (150 MHz, $CDCl_3$)



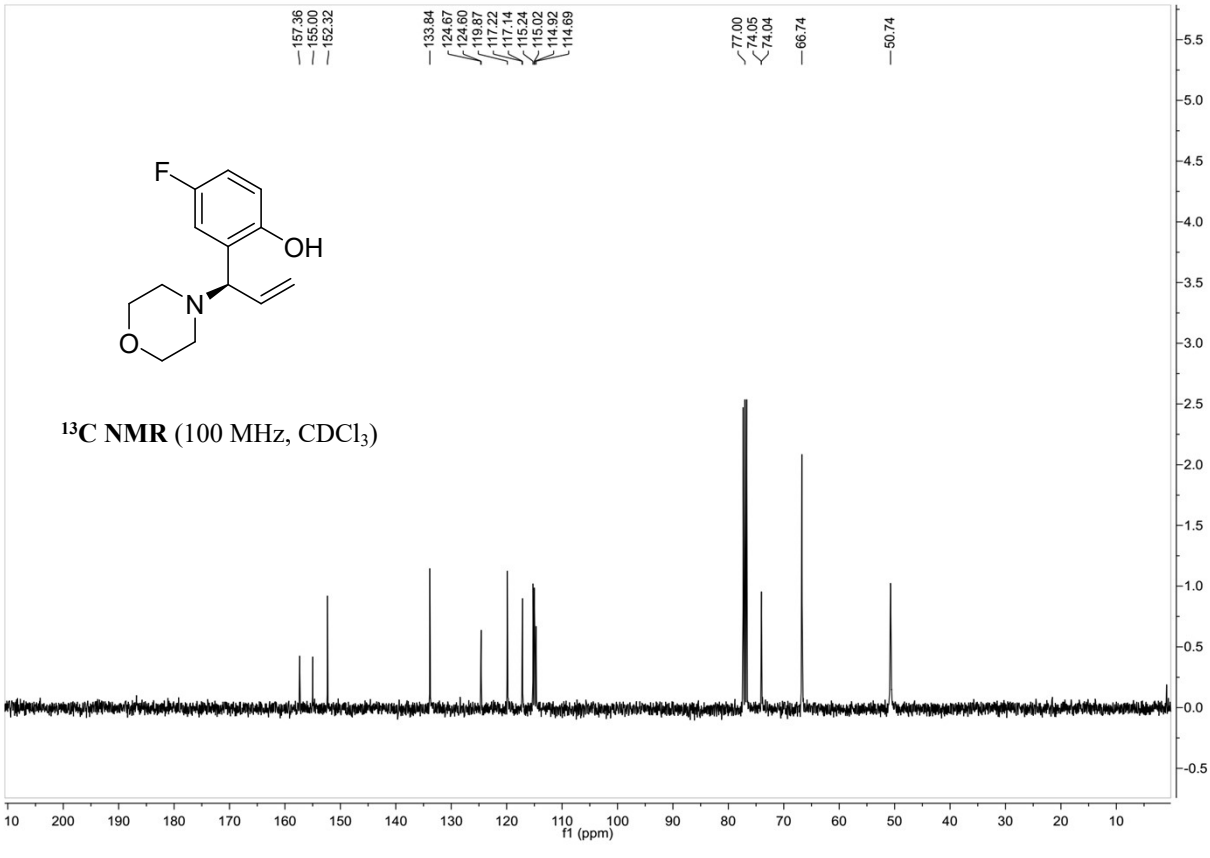
^{1}H NMR (600 MHz, $CDCl_3$)



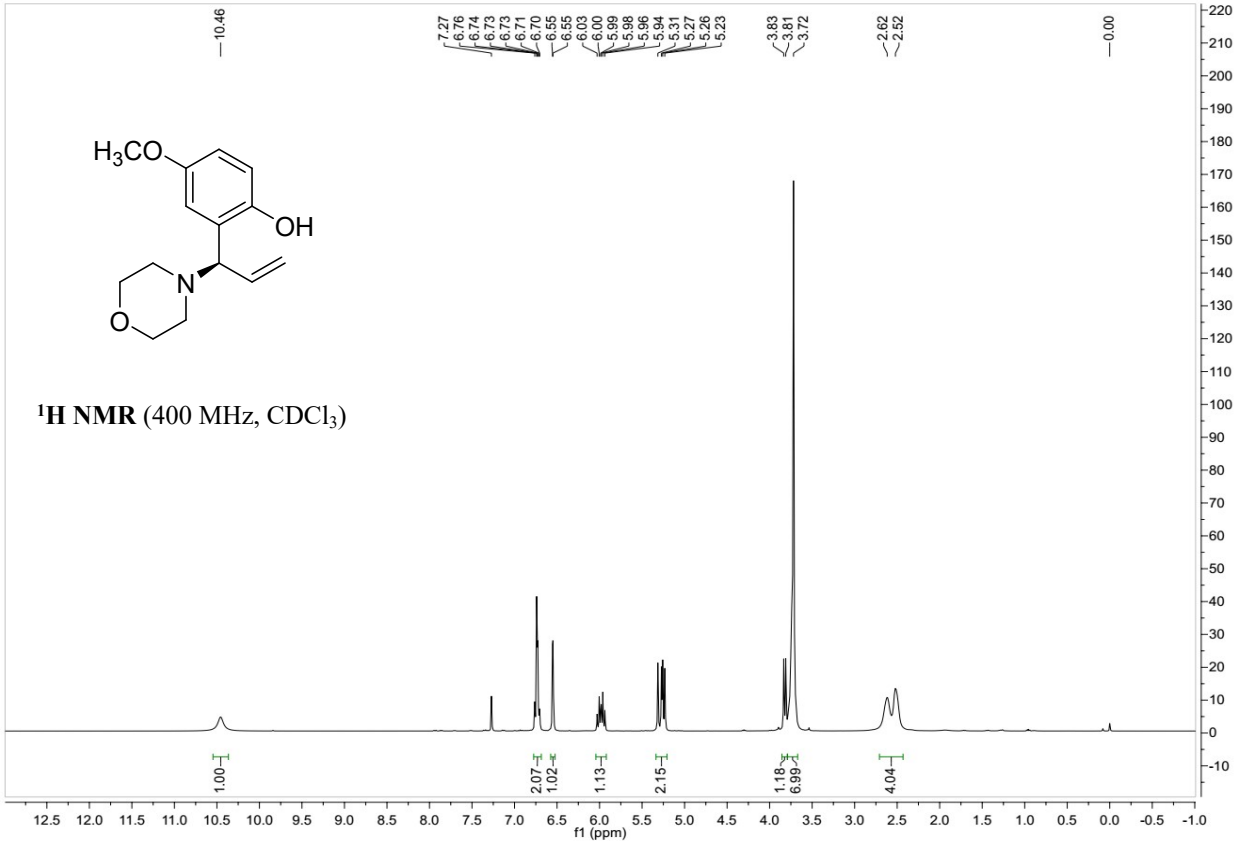
^{13}C NMR (150 MHz, $CDCl_3$)



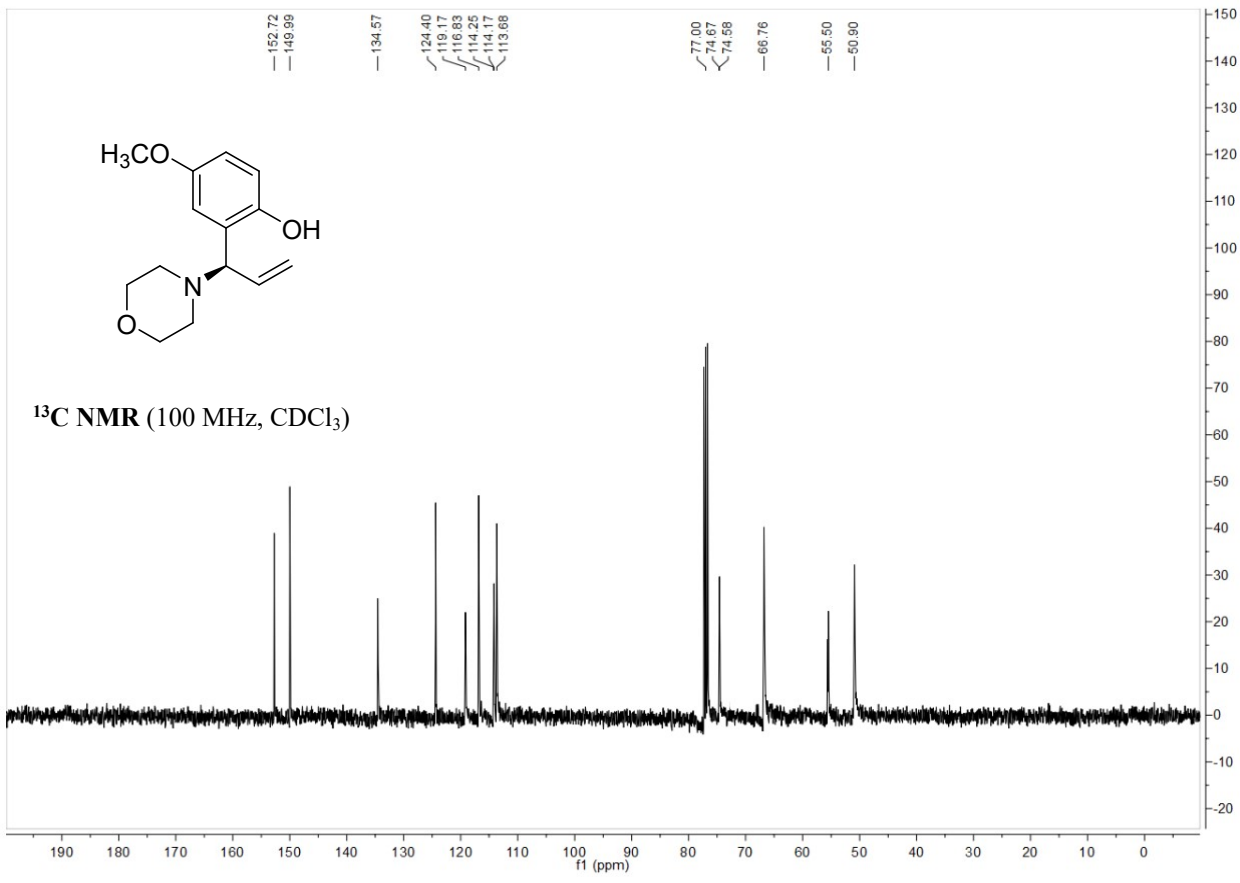
[1]H NMR (400 MHz, $CDCl_3$)



[13]C NMR (100 MHz, $CDCl_3$)

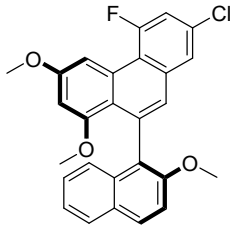


[1]H NMR (400 MHz, $CDCl_3$)



[13]C NMR (100 MHz, $CDCl_3$)

XII. X-Ray crystallographic information of 3a



(*R*)-**3a**

CCDC 1923394

Identification code 3a-cif
Empirical formula C27H20ClFO3
Formula weight 446.88
Temperature/K 295(2)
Crystal system triclinic
Space group P1
a/Å 12.4631(3)
b/Å 12.5987(3)
c/Å 15.6878(4)
α/° 97.484(2)
β/° 106.179(2)
γ/° 105.721(2)
Volume/Å3 2220.12(11)
Z 4
ρcalcg/cm3 1.337
μ/mm 1 0.207
F(000) 928.0
Crystal size/mm3 0.3 × 0.26 × 0.25
Radiation MoKα (λ = 0.71073)
2Θ range for data collection/° 6.666 to 52.742
Index ranges -15 ≤ h ≤ 15, -15 ≤ k ≤ 15, -19 ≤ l ≤ 19
Reflections collected 35999
Independent reflections 17912 [Rint = 0.0206, Rsigma = 0.0349]
Data/restraints/parameters 17912/13/1165
Goodness-of-fit on F2 1.028
Final R indexes [I>=2σ (I)] R1 = 0.0631, wR2 = 0.1559
Final R indexes [all data] R1 = 0.0984, wR2 = 0.1835
Largest diff. peak/hole / e Å-3 0.46/-0.34
Flack parameter 0.019(17)

XIII. Reference

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(3) Shi, X.; Kiesman, W. F.; Levina, A.; Xin, Z. Catalytic Asymmetric Petasis Reactions of Vinylboronates. *J. Org. Chem.* **2013**, *78*, 9415.

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