Supporting Information

Catalytic Asymmetric Construction of Bridged Bicyclo[m.3.1] Rings by Intramolecular Diels-Alder Reaction

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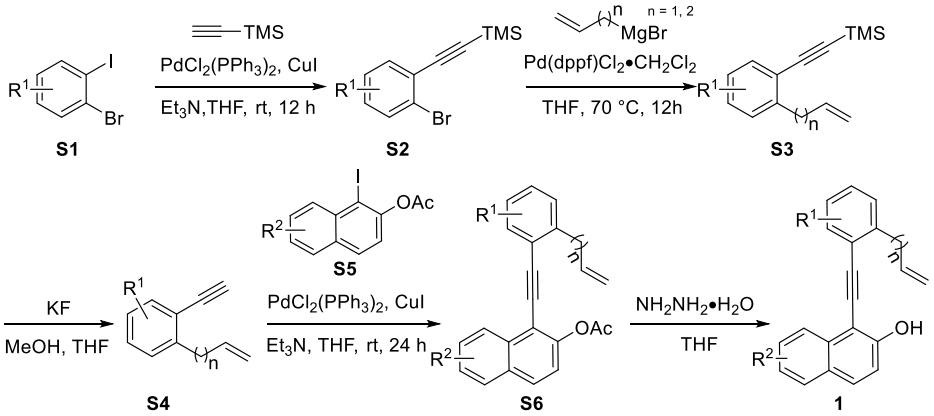
I. General information

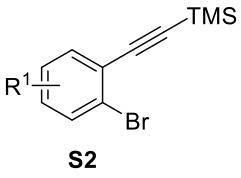
^{1}H and ^{13}C NMR spectra were recorded on Agilent 400MR DD2 (400 MHz) spectrometer and Agilent 600MR DD2 (600 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and tetramethylsilane or the residual solvent peak was used as an internal reference: $CDCl_3$ (^{1}H NMR tetramethylsilane δ 0.00, ^{13}C NMR δ 77.00), data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad or as a combination of them), coupling constants (Hz) and integration. Enantiomeric excesses (ee) were determined by HPLC analysis on Hitachi Chromaster using DAICEL CHIRALCEL AD-H, 4.6mm*Φ*×250mm, DAICEL CHIRALCEL AS-H, 4.6mm*Φ*×250mm, DAICEL CHIRALCEL OD-H, 4.6mm*Φ*×250mm, DAICEL CHIRALCEL IA-H, 4.6mm*Φ*×250mm, DAICEL CHIRALCEL IB-H, 4.6mm*Φ*×250mm. High resolution mass spectra (HRMS) were performed on Bruker Solarix 7.0 T and ThermoFisher Q Exactive Plus. 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: $[\alpha]_D^{25}$ (*c* in g per 100 mL solvent). Unless otherwise stated, all reagents were purchased from commercial suppliers (Adamas, J&K, Sigma-Aldrich, TCI) and used without further purification.

II. General procedure for the synthesis of the substrates

Method A: (1a-1n, 1s-1v)

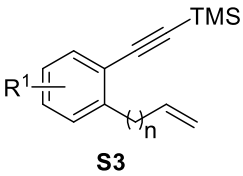


General procedure for the synthesis of S2:



This step was carried out according to a literature method[1] with some modifications. To a solution of **S1** (8.0 mmol, 1.0 equiv.) in THF (20 mL) were added $PdCl_2(PPh_3)_2$ (112 mg, 0.16 mmol, 0.02 equiv.), CuI (76 mg, 0.40 mmol, 0.05 equiv.), trimethylsilylacetylene (1.4 mL, 8.8 mmol, 1.1 equiv.) and Et_3N (20 mL) under a nitrogen atmosphere at room temperature. After being stirred for 12 h, the mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with hexane. The extract was washed with water and brine, dried and concentrated to dryness. Purification by flash chromatography eluting with hexane to give **S2** (70-90% yield).

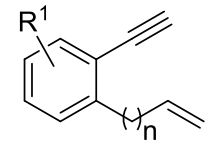
General procedure for the synthesis of S3:



This step was carried out according to a literature method[2] with some modifications. **S2** (8 mmol, 1.0 equiv.) was dissolved in dry THF (20 ml) and placed in a pressure vessel. Alkenyl magnesium bromide (16 mL, 1.0 M in THF, 2.0 equiv) was added dropwise under a nitrogen atmosphere. After completion of the addition, Pd-catalyst (2 mol%) was added. The flask was sealed and heated at 70 °C for 12 h. The reaction was carefully quenched with water. The mixture is extracted

with EA and the combined organic layers were passed through $MgSO_4$ plug to remove residual water. After evaporation of solvents the crude product was purified by flash chromatography eluting with hexane to give **S3** (65-87% yield).

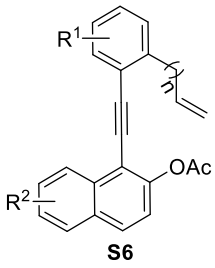
General procedure for the synthesis of S4:



S4

This step was carried out according to a literature method[3] with some modifications. To a stirred solution of **S3** (6.0 mmol, 1.0 equiv) in MeOH (15 mL) and THF (15 mL) was added KF (1.04 g, 18.0 mmol, 3.0 equiv). The reaction mixture was stirred for 4 hours at room temperature. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl and extracted with EA. The organic phase was dried (Na_2SO_4) and concentrated. Purification by flash chromatography eluting with hexane to give **S4** (68-83% yield).

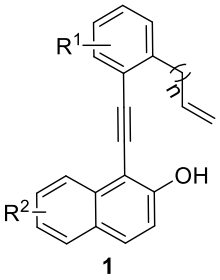
General procedure for the synthesis of S6:



S6

This step was carried out according to a literature method[4] with some modifications. **S5** (2 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (28 mg, 0.04 mmol, 0.02 equiv) and CuI (19.1 mg, 0.1 mmol, 0.05 equiv) were weighed and added into an oven dried flask, evacuated and backfilled with nitrogen (3 times). Et_3N (4 mL) and THF (4 mL) was injected into the flask. Then **S4** (310 mg, 2.2 mmol, 1.1 equiv) was added. The resulting mixture kept stirring for 24 h. Then the mixture was filtered through a pad of celite and washed with EA. Removal of solvent under reduced pressure, purified by column chromatography on silica gel (PE/EA = 20:1) to afford **S6** (60-78% yield).

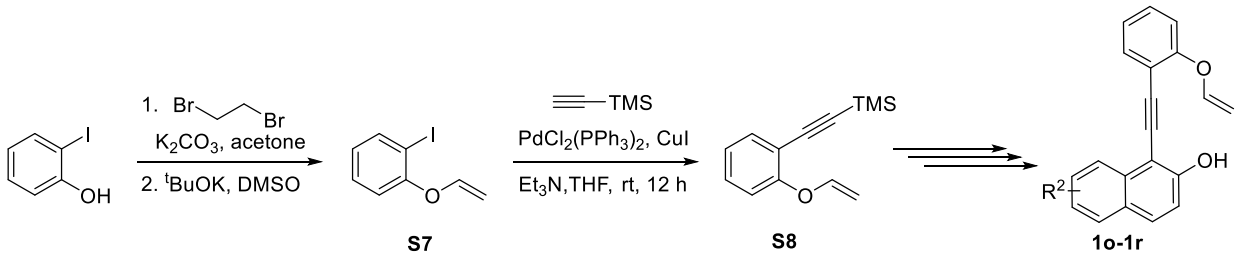
General procedure for the synthesis of 1:



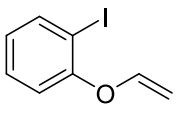
1

This step was carried out according to a literature method[3] with some modifications. To a stirred solution of **S6** (1.5 mmol, 1.0 equiv) in THF (10 mL) was added hydrazine monohydrate (0.73 mL, 7.5 mmol, 5.0 equiv, 50%) dropwise at rt. Then, the resulting solution was kept stirring until **S6** was consumed. Quenched with sat. aq. NH_4Cl, extracted with EA, washed with brine, dried over Na_2SO_4 and filtered, concentrated under reduced pressure and purified by column chromatography on silica gel (PE/EA = 20:1) to afford the desired product **1** (70-88% yield).

Method B: (1a-3(1o), 1p-1r)



General procedure for the synthesis of S7:



S7

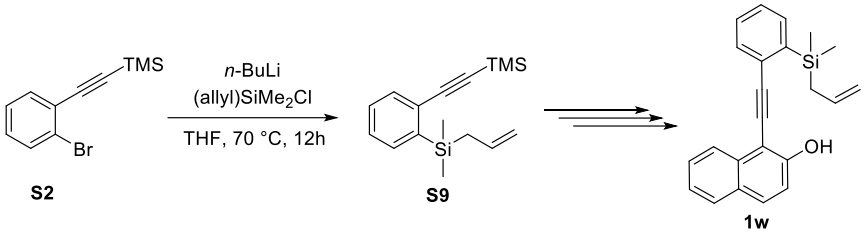
This step was carried out according to a literature method[5] with some modifications. O-iodophenol (2.2 g, 10 mmol, 1.0 equiv.) was weighed and added into a round bottom flask. Acetone (50ml) was sequentially added. Slowly add 1, 2-dibromoethane (4.3 ml, 50 mmol, 5.0 equiv.). Finally, add potassium carbonate (2.76 g, 20 mmol, 2.0 equiv.), stir at room temperature for 14 hours, then the reaction was stirred at reflux for 6 hours. Quenched with sat. aq. NH_4Cl, the organic phase is extracted with EA, concentrated and passed through the column to obtain the product. Dissolve the obtained product in dimethyl

sulfoxide, add potassium tert-butoxide (15 mL, 1.0 M in THF, 1.5 equiv.). React at room temperature for 24 hours, add water to quench the reaction at the end of the reaction. The organic phase is extracted with hexane, concentrated and passed through a column for separation to obtain **S7**(1.89 g, 7.7 mmol, 77% yield) as a orange oil.

Compound **S8** was prepared according to the general procedure as described for **S3**.

Compound **1a-3(1o), 1p-1r** was prepared according to the general procedure as described for **1**.

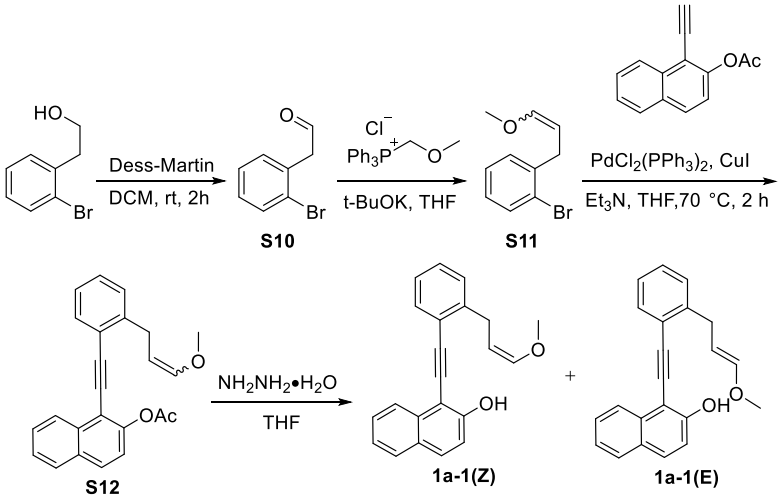
Method C: (1w)



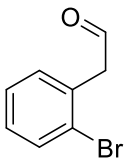
This step was carried out according to a literature method[6] with some modifications. To a solution of **S2** (2.53 g, 10 mmol) in THF (20 mL) was added dropwise *n*-BuLi (2.5 M in hexane, 12 mmol, 1.2 equiv.) at –78 °C. After stirring at –78 °C for 1 h, allylchlorodimethylsilane (2.03 g, 15 mmol, 1.5 equiv.) was added dropwise to the mixture. The reaction mixture was stirred at –78 °C for 1 h, and then allowed to warm to room temperature. The volatile materials were removed in vacuo, and the residue was subjected to column chromatography on silica gel (PE/EA = 100:1) to give **S9**(1.77 g, 6.5 mmol, 65% yield) as a pale yellow oil.

Compound **1w** was prepared according to the general procedure as described for **1**.

Method D: (1a-1 (Z))



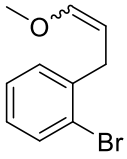
2-(2-bromophenyl)acetaldehyde(S10)



S10

This step was carried out according to a literature method[7] with some modifications. A mixture of 2-(2-bromophenyl)ethanol(6.0 g, 29.8 mmol, 1.0 equiv.) and Dess-Martin periodinane (l3.9 g, 32.8mmol, 1.1 equiv.) in DCM (60 mL) was stirred at room temperature for 2 hours. Solvent was removed in vacuo, and the residue was purified by silica gel column (PE/EA = 10:1) to give **S10** (4.5g, 22.6 mmol, 76% yield) as a colorless oil.

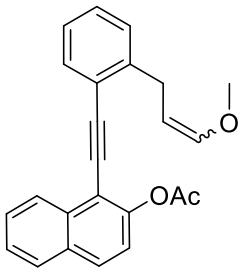
1-bromo-2-(3-methoxyallyl)benzene(S11)



S11

This step was carried out according to a literature method[8] with some modifications. (Methoxymethyl)triphenylphosphonium chloride (5.70 g, 16.6 mmol, 1.1 equiv.) was weighed and added into a round bottom flask, evacuated and backfilled with nitrogen (3 times). THF (20 mL) was injected into the flask. Potassium tert-butoxide (2.02 g, 18.1 mmol, 1.2 equiv.) was added in portions at 0 ºC. The color of the mixture turned from dark orange to red. After stiring for 40 min at 0 ºC the reaction was allowed to warm up to room temperature. Then a solution of **S8**(3.0 g, 15.1 mmol, 1.0 equiv.) in THF (10 mL) was added dropwise and the mixture was stirred overnight. The reaction was quenched by addition of sat. aq. NH_4Cl solution and the aqueous phase was extracted with EA. The combined organic layers were dried over $MgSO_4$ and the solvents were evaporated. Chromatographic purification (PE/EA = 10:1) of the crude material to give **S11** (2.50 g, 11 mmol, 73% yield) as a yellow oil.

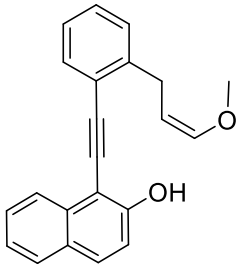
1-((2-(3-methoxyallyl)phenyl)ethynyl)naphthalen-2-yl acetate (S12)



S12

This step was carried out according to a literature method[4] with some modifications. $PdCl_2(PPh_3)_2$ (140 mg, 0.2 mmol, 0.02 equiv) and CuI (95 mg, 0.5 mmol, 0.05 equiv) were weighed and added into an oven dried flask, evacuated and backfilled with nitrogen (3 times). Triethylamine (15 mL) was injected into the flask. **S11** (2.26 g, 10 mmol, 1.0 equiv) dissolved in THF (15 mL) was added. The mixture was stirred for 30 min at 70 °C. After that, the alkyne (2.31 g, 11 mmol, 1.1 equiv) dissolved in THF (10 mL) was added slowly. The resulting mixture kept stirring for 2 h at 70 °C. Then the mixture was filtered through a pad of celite and washed with EA. Removal of solvent under reduced pressure, purified by flash chromatography on silica gel (PE/EA = 15:1) to afford **S12** (2.56 g, 7.2 mmol, 72% yield) as a yellow oil.

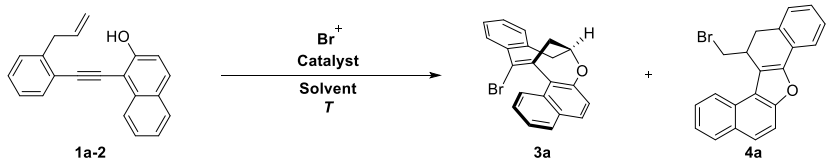
(Z)-1-((2-(3-methoxyallyl)phenyl)ethynyl)naphthalen-2-ol (1a-1(Z))



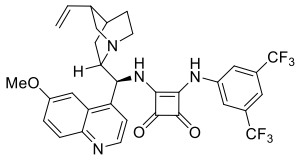
1a-1(Z)

This step was carried out according to a literature method[3] with some modifications. To a stirred solution of **S12** (2.56 g, 7.2 mmol, 1.0 equiv) in THF (20 mL) was added hydrazine monohydrate (3.5 mL, 36 mmol, 5.0 equiv, 50%) dropwise at rt. Then, the resulting solution was kept stirring until **S12** was consumed. Quenched with sat. aq. NH_4Cl, extracted with EA, washed with brine, dried over Na_2SO_4 and filtered, concentrated under reduced pressure and purified by column chromatography on silica gel (PE/EA = 30:1 to 15:1) to afford the desired product **1a-Z** (815 mg, 2.59 mmol, 36% yield) as an orange oil.

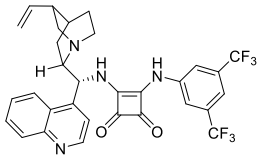
III. Optimization of the reaction conditions (Table S1[a])



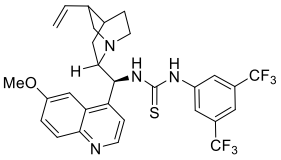
Catalyst



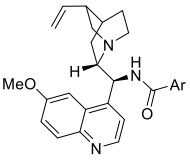
C1



C2



C3



C4: Ar = C_6H_5

C5: Ar = 2-$CF_3C_6H_5$

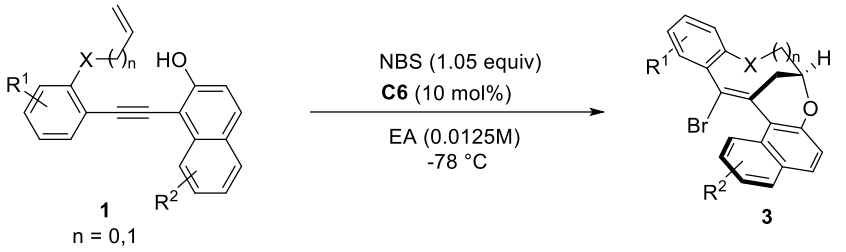
C6: Ar = 4-$CF_3C_6H_5$

C7: Ar = 3,5-$(CF_3)_2C_6H_5$

Entry	Catalyst	Solvent	T (°C)	Br^+	Yield[b] of **3a** (%)	ee[c] (%) of **3a**	ee[d] (%) of **4a**	**3a**/**4a**[e]
1	**C1**	DCM	-40	NBS	30	92	90	57/43
2	**C2**	DCM	-40	NBS	28	-73	-65	60/40
3	**C3**	DCM	-40	NBS	30	-10	-7	58/42
4	**C4**	DCM	-40	NBS	29	72	58	60/40
5	**C5**	DCM	-40	NBS	33	85	2	58/42
6	**C6**	DCM	-40	NBS	34	92	93	64/36
7	**C7**	DCM	-40	NBS	30	89	80	62/38
8	**C6**	toluene	-40	NBS	31	95	90	62/38
9	**C6**	acetone	-40	NBS	40	52	45	80/20
10	**C6**	THF	-40	NBS	45	41	25	80/20
11	**C6**	$CHCl_3$	-40	NBS	35	60	88	67/33
12	**C6**	EA	-40	NBS	55	90	69	87/13
13	**C6**	EA	-60	NBS	60	93	91	88/12
14	**C6**	EA	-78	NBS	62	95	93	90/10
15	**C6**	EA	-78	NBP	63	85	83	88/12
16	**C6**	EA	-78	DBDMH	57	65	75	88/12
17[f]	**C6**	EA	-78	NBS	60	93	96	90/10
18[g]	**C6**	EA	-78	NBS	65	97	92	91/9
19[h]	**C6**	EA	-78	NBS	65	92	91	91/9

[a]Reaction conditions: **1a-2** (0.025 mmol, 1.0 equiv), catalyst (0.0025 mmol, 10 mol%) in solvent (1 mL) at corresponding temperature for 30 min, then brominating reagents (1.05 equiv) at corresponding temperature, 0.5-6 h. [b]Isolated yield of **3a**. [c]Enantiomeric excess (ee) of **3a** determined by HPLC. [d] Enantiomeric excess (ee) of **4a** determined by HPLC. [e]The ratio of (**3a**:**4a**) were determined by the ^{1}H NMR analysis. [f]Reaction in EA (0.5 mL). [g]Reaction in EA (2 mL). [h]Reaction in EA (3.0 mL).

IV. General procedure for asymmetric reaction



Condition[A]:

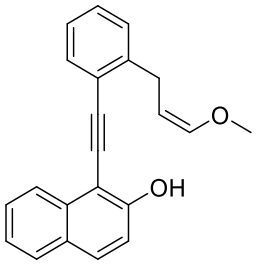
A solution of **1** (1.0 equiv) and **catalyst-6** (10 mol%) in EA (0.0125M) was stirred at -78 °C for 30 min, then NBS (1.05 equiv) was added. After stirring at -78 °C for 6-24 h, the reaction mixture was concentrated under reduced pressure. The resulting residue was purified by silica gel flash column chromatography using PE/EA eluent (60:1 to 50:1) to afford the annulation product **3**.

V. General procedure for initial experimental

Condition[B]:

A solution of **1** (1.0 equiv.) and **catalyst-6** (10 mol%) in DCM (0.025M) was stirred at -40 °C for 30 min, then NBS (1.05 equiv) was added. After stirring at -40 °C for 6 h, the reaction mixture was concentrated under reduced pressure. The resulting residue was purified by silica gel flash column chromatography using PE/EA eluent (60:1 to 50:1) to afford the annulation product **2**, **3**, **4**.

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



1a-1 (Z)

(Z)-1-((2-(3-methoxyallyl)phenyl)ethynyl)naphthalen-2-ol (1a-1 (Z))

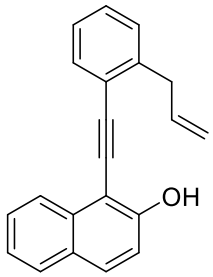
Compound **1a-1 (Z)** is an unknown compound. The compound was synthesized in 36% yield (815 mg, 2.59 mmol) following the general procedure (**Method D**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

Yellow oil. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.3 Hz, 1H), 7.77 (t, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.40 – 7.30 (m, 3H), 7.27 – 7.21 (m, 2H), 6.58 (s, 1H), 6.02 (d, *J* = 6.1 Hz, 1H), 4.61 (q, *J* = 7.0 Hz, 1H), 3.73 (d, *J* = 6.6 Hz, 2H), 3.61 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.97, 146.80, 142.96, 133.63, 132.39, 130.51, 128.92, 128.88, 128.43, 128.22, 127.31, 126.05, 124.94, 123.97, 122.19, 116.65, 104.65, 103.22, 99.85, 85.52, 59.80, 29.60.

HRMS (ESI) *m/z* Calcd for $C_{22}H_{17}O_2^-$[M - H]$^-$: 313.1234, Found: 313.1219.



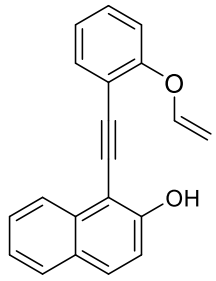
1a-2

1-((2-allylphenyl)ethynyl)naphthalen-2-ol (1a-2)

Compound **1a-2** is an unknown compound. The compound was synthesized in 85% yield (363 mg, 1.28 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

White solid. (R_f = 0.5, PE/EA = 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 9.0 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 7.22 – 7.14 (m, 3H), 6.31 (s, 1H), 6.07 (ddt, *J* = 16.4, 10.1, 6.0 Hz, 1H), 5.20 – 5.10 (m, 1H), 5.10 – 4.98 (m, 1H), 3.64 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.99, 141.06, 136.26, 133.40, 132.24, 130.58, 129.25, 128.92, 128.32, 128.19, 127.28, 126.30, 124.75, 123.92, 122.33, 116.36, 116.31, 102.89, 99.66, 85.38, 38.72.
HRMS (ESI) *m/z* Calcd for $C_{21}H_{15}O^-$[M - H]$^-$: 283.1128, Found: 283.1115.



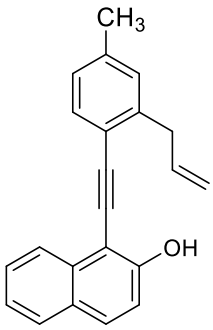
1a-3 (1o)

1-((2-(vinyloxy)phenyl)ethynyl)naphthalen-2-ol (1a-3 (1o))

Compound **1a-3 (1o)** is an unknown compound. The compound was synthesized in 88% yield (378 mg, 1.32 mmol) following the general procedure (**Method B**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

White solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.3 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.24 (d, *J* = 8.7 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.84 (s, 1H), 6.76 (dd, *J* = 13.7, 6.0 Hz, 1H), 4.97 (dd, *J* = 13.7, 2.0 Hz, 1H), 4.61 (dd, *J* = 6.0, 2.0 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 156.80, 156.58, 147.65, 133.05, 132.03, 130.71, 129.82, 128.33, 128.22, 127.31, 124.98, 123.98, 123.38, 116.46, 116.04, 113.93, 102.96, 96.95, 96.40, 87.81.
HRMS (ESI) *m/z* Calcd for $C_{20}H_{13}O_2^-$[M - H]$^-$: 285.0921, Found: 285.0909.



1b

1-((2-allyl-4-methylphenyl)ethynyl)naphthalen-2-ol (1b)

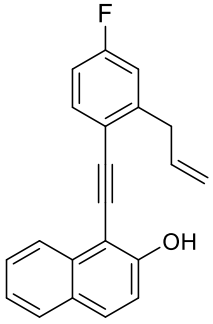
Compound **1b** is an unknown compound. The compound was synthesized in 78% yield (349 mg, 1.17 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

Yellow solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.77 (t, *J* = 8.7 Hz, 2H), 7.58 – 7.51 (m, 2H), 7.42 – 7.34 (m, 1H), 7.22 (d, *J* = 8.9 Hz, 1H), 7.12 – 7.07 (m, 2H), 6.26 (s, 1H), 6.12 (ddt, *J* = 16.5, 9.8, 6.0 Hz, 1H), 5.17 (dd, *J* = 10.1, 1.9 Hz, 1H), 5.08 (dd, *J* = 17.1, 2.0 Hz, 1H), 3.67 (d, *J* = 5.8 Hz, 2H), 2.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.95, 141.13, 139.37, 136.47, 133.47, 132.28, 130.48, 130.19, 128.43, 128.26, 127.33, 127.26, 124.91, 124.00, 119.40, 116.36, 103.15, 99.99, 84.59, 38.83, 21.54.

HRMS (ESI) *m/z* Calcd for $C_{22}H_{17}O^-$[M - H]$^-$: 297.1285, Found: 297.1276.



1c

1-((2-allyl-4-fluorophenyl)ethynyl)naphthalen-2-ol (1c)

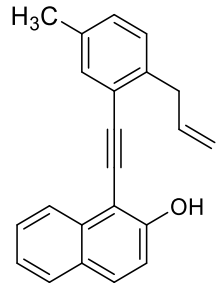
Compound **1c** is an unknown compound. The compound was synthesized in 79% yield (358 mg, 1.19 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

White solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.78 (t, *J* = 7.1 Hz, 2H), 7.68 – 7.47 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.26 – 7.19 (m, 1H), 7.12 – 6.86 (m, 2H), 6.20 (s, 1H), 6.08 (ddt, *J* = 16.6, 11.3, 6.2 Hz, 1H), 5.21 (d, *J* = 10.2 Hz, 1H), 5.10 (d, *J* = 17.1 Hz, 1H), 3.69 (d, *J* = 6.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.83 (d, *J* = 250.7 Hz), 156.07, 144.14 (d, *J* = 7.7 Hz), 135.43, 134.12 (d, *J* = 8.4 Hz), 133.45, 130.78, 128.43, 128.32, 127.43, 124.78, 124.09, 118.51 (d, *J* = 3.0 Hz), 117.13, 116.45(d, *J* = 22.2 Hz), 116.41, 113.76 (d, *J* = 21.9 Hz), 102.76, 98.64, 85.07, 38.76.

HRMS (ESI) *m/z* Calcd for $C_{21}H_{14}FO^-$[M - H]$^-$: 301.1034, Found: 301.1027.



1d

1-((2-allyl-5-methylphenyl)ethynyl)naphthalen-2-ol (1d)

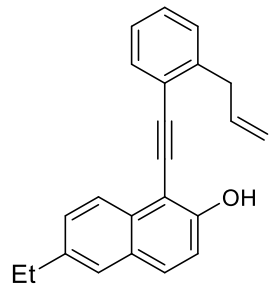
Compound **1d** is an unknown compound. The compound was synthesized in 82% yield (367 mg, 1.23 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

White solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.76 (t, *J* = 8.5 Hz, 2H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.46 (s, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.24 – 7.12 (m, 3H), 6.18 – 6.01 (m, 1H), 5.22 – 5.11 (m, 1H), 5.11 – 4.99 (m, 1H), 3.66 (d, *J* = 5.8 Hz, 2H), 2.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.00, 138.10, 136.57, 135.94, 133.42, 132.71, 130.52, 129.91, 129.24, 128.35, 128.21, 127.28, 124.82, 123.94, 122.14, 116.32, 116.17, 102.99, 99.96, 84.93, 38.36, 20.75.

HRMS (ESI) *m/z* Calcd for $C_{22}H_{17}O^-$[M - H]$^-$: 297.1285, Found: 297.1274.



1e

1-((2-allylphenyl)ethynyl)-6-ethylnaphthalen-2-ol (1e)

Compound **1e** is an unknown compound. The compound was synthesized in 80% yield (375 mg, 1.2 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

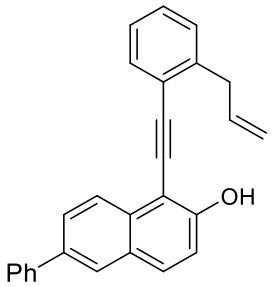
Pale yellow solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.63 (d, *J* = 7.2 Hz, 1H), 7.55 (s, 1H), 7.41 (d, *J* = 8.5 Hz, 1H), 7.36 – 7.30 (m, 1H), 7.30 – 7.23 (m, 2H), 7.18 (d, *J* = 8.9 Hz, 1H), 6.18 (s, 1H), 6.16 – 6.04 (m,

1H), 5.17 (d, *J* = 10.2 Hz, 1H), 5.07 (d, *J* = 17.1 Hz, 1H), 3.70 (d, *J* = 5.9 Hz, 2H), 2.78 (q, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 155.52, 141.23, 139.91, 136.33, 132.34, 131.81, 130.22, 129.37, 129.01, 128.63, 128.54, 126.41, 126.07, 124.82, 122.51, 116.44, 116.27, 102.76, 99.50, 85.57, 38.85, 28.69, 15.57.

HRMS (ESI) *m/z* Calcd for $C_{23}H_{19}O^-$[M - H]$^-$: 311.1441, Found: 311.1432.



1f

1-((2-allylphenyl)ethynyl)-6-phenylnaphthalen-2-ol (1f)

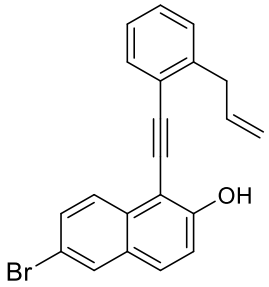
Compound **1f** is an unknown compound. The compound was synthesized in 88% yield (476 mg, 1.32mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

White solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.1 Hz, 1H), 7.98 (s, 1H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 6.7 Hz, 1H), 7.51 – 7.43 (m, 2H), 7.41 – 7.33 (m, 2H), 7.33 – 7.26 (m, 2H), 7.24 (d, *J* = 8.7 Hz, 1H), 6.20 – 6.07 (m, 1H), 5.18 (d, *J* = 10.3 Hz, 1H), 5.09 (d, *J* = 17.1 Hz, 1H), 3.73 (d, *J* = 9.1 Hz, 2H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.17, 141.33, 140.82, 136.88, 136.35, 132.70, 132.42, 130.94, 129.43, 129.14, 128.85, 128.72, 127.24, 127.22, 127.01, 126.46, 126.19, 125.45, 122.44, 116.86, 116.49, 102.93, 99.78, 85.34, 38.89.

HRMS (ESI) *m/z* Calcd for $C_{27}H_{19}O^-$[M - H]$^-$: 359.1441, Found: 359.1434.



1g

1-((2-allylphenyl)ethynyl)-6-bromonaphthalen-2-ol (1g)

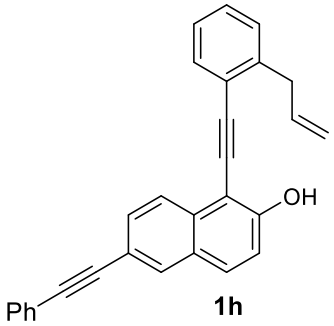
Compound **1g** is an unknown compound. The compound was synthesized in 81% yield (441 mg, 1.22 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

White solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 1H), 7.92 (s, 1H), 7.71 – 7.55 (m, 3H), 7.40 – 7.33 (m, 1H), 7.33 – 7.26 (m, 2H), 7.25 – 7.20 (m, 1H), 6.28 (s, 1H), 6.11 (ddt, *J* = 16.4, 10.1, 5.9 Hz, 1H), 5.23 – 5.12 (m, 1H), 5.12 – 5.00 (m, 1H), 3.69 (d, *J* = 5.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.24, 141.28, 136.28, 132.41, 132.02, 130.54, 130.18, 129.58, 129.49, 129.30, 126.69, 126.49, 122.16, 117.73, 117.54, 116.52, 103.25, 100.09, 84.69, 38.83.

HRMS (ESI) *m/z* Calcd for $C_{21}H_{14}BrO^-$[M - H]$^-$: 361.0234, Found: 361.0225.



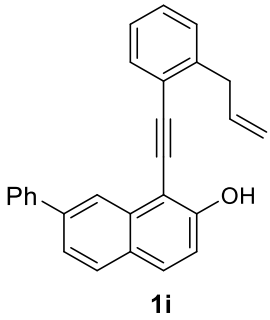
1h

1-((2-allylphenyl)ethynyl)-6-(phenylethynyl)naphthalen-2-ol (1h)

Compound **1h** is an unknown compound. The compound was synthesized in 83% yield (479 mg, 1.25 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

Pale yellow solid. (R_f = 0.4, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.6 Hz, 1H), 7.98 (s, 1H), 7.72 (d, *J* = 8.9 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.61 – 7.53 (m, 2H), 7.41 – 7.31 (m, 4H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.21 (s, 1H), 6.30 (s, 1H), 6.12 (ddt, *J* = 16.2, 10.1, 6.0 Hz, 1H), 5.22 – 5.13 (m, 1H), 5.12 – 5.01 (m, 1H), 3.70 (d, *J* = 5.7 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.66, 141.27, 136.30, 132.97, 132.42, 131.73, 131.58, 130.49, 129.98, 129.45, 129.22, 128.34, 128.22, 128.05, 126.47, 125.01, 123.26, 122.26, 118.76, 117.11, 116.50, 103.24, 99.98, 89.59, 89.47, 84.91, 38.84.
HRMS (ESI) *m/z* Calcd for $C_{29}H_{19}O^-$[M - H]$^-$: 383.1441, Found: 3831.1436.



1i

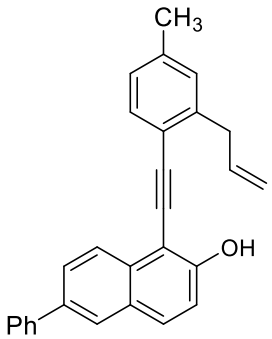
1-((2-allylphenyl)ethynyl)-7-phenylnaphthalen-2-ol (1i)

Compound **1i** is an unknown compound. The compound was synthesized in 80% yield (433 mg, 1.20 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

White solid. (R_f = 0.4, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.88 – 7.69 (m, 4H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.41 – 7.23 (m, 4H), 7.20 (d, *J* = 8.0 Hz, 1H), 6.28 (s, 1H), 6.20 – 6.02 (m, 1H), 5.23 – 4.95 (m, 2H), 3.73 (d, *J* = 6.0 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.44, 141.35, 141.03, 140.12, 136.27, 133.79, 132.32, 130.38, 129.32, 129.08, 128.84, 128.81, 127.63, 127.49, 126.43, 123.74, 122.91, 122.43, 116.54, 116.39, 103.25, 100.11, 85.40, 38.88.

HRMS (ESI) *m/z* Calcd for $C_{27}H_{19}O^-$[M - H]$^-$: 359.1441, Found: 359.1437.



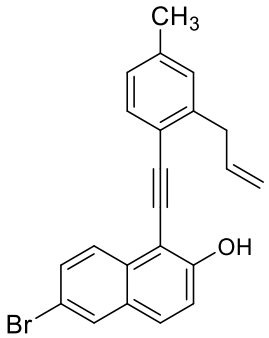
1j

1-((2-allyl-4-methylphenyl)ethynyl)-6-phenylnaphthalen-2-ol (1j)

Compound **1j** is an unknown compound. The compound was synthesized in 82% yield (461 mg, 1.23 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

White solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.6 Hz, 1H), 7.98 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.11 (d, *J* = 9.9 Hz, 2H), 6.29 (s, 1H), 6.13 (ddt, *J* = 16.5, 10.7, 6.0 Hz, 1H), 5.23 – 5.14 (m, 1H), 5.13 – 5.03 (m, 1H), 3.69 (d, *J* = 5.8 Hz, 2H), 2.39 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.01, 141.16, 140.83, 139.42, 136.79, 136.49, 132.67, 132.30, 130.73, 130.20, 128.84, 128.69, 127.27, 127.21, 126.94, 126.16, 125.49, 119.37, 116.81, 116.38, 100.01, 84.57, 38.86, 21.55.
HRMS (ESI) *m/z* Calcd for $C_{28}H_{21}O^-$[M - H]$^{-+}$: 373.1598, Found: 373.1589.



1k

1-((2-allyl-4-methylphenyl)ethynyl)-6-bromonaphthalen-2-ol (1k)

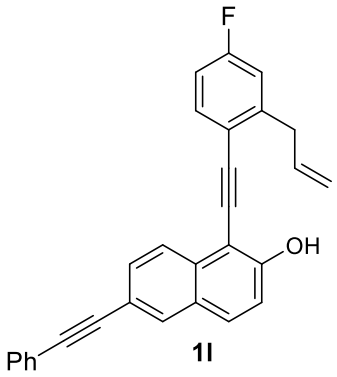
Compound **1k** is an unknown compound. The compound was synthesized in 75% yield (424 mg, 1.13 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

White solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.7 Hz, 1H), 7.90 (s, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 8.7 Hz, 1H), 7.14 – 7.02 (m, 2H), 6.27 (s, 1H), 6.18 – 6.01 (m, 1H), 5.17 (d, *J* = 10.0 Hz, 1H), 5.06 (d, *J* = 17.1 Hz, 1H), 3.64 (d, *J* = 4.5 Hz, 2H), 2.38 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.09, 141.13, 139.59, 136.41, 132.29, 132.00, 130.45, 130.24, 130.14, 129.50, 129.35, 127.29, 126.72, 119.11, 117.68, 117.48, 116.40, 103.46, 100.36, 83.98, 38.80, 21.55.

HRMS (ESI) *m/z* Calcd for $C_{22}H_{16}BrO^-$[M - H]$^-$: 375.0390, Found: 375.0382.



1l

1-((2-allyl-4-fluorophenyl)ethynyl)-6-(phenylethynyl)naphthalen-2-ol (1l)

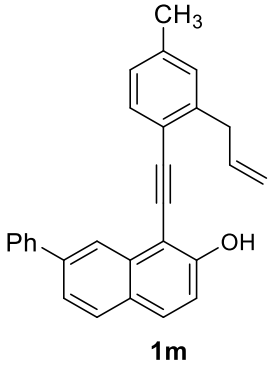
Compound **1l** is an unknown compound. The compound was synthesized in 77% yield (465 mg, 1.16 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

Pale yellow solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.6 Hz, 1H), 8.00 (s, 1H), 7.75 (d, *J* = 8.9 Hz, 1H), 7.69 – 7.60 (m, 2H), 7.60 – 7.52 (m, 2H), 7.42 – 7.29 (m, 3H), 7.24 – 7.17 (m, 1H), 7.08 – 6.93 (m, 2H), 6.25 (s, 1H), 6.08 (ddt, *J* = 16.4, 11.8, 6.0 Hz, 1H), 5.22 (dd, *J* = 10.2, 1.9 Hz, 1H), 5.15 – 5.04 (m, 1H), 3.69 (d, *J* = 5.8 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.90 (d, *J* = 250.9 Hz), 156.65, 144.19 (d, *J* = 8.0 Hz), 135.41, 134.19 (d, *J* = 8.6 Hz), 132.95, 131.76, 131.58, 130.58, 130.03, 128.36, 128.26, 128.06, 124.94, 123.22, 118.82, 118.34, 117.15 (d, *J* = 4.0 Hz), 116.52 (d, *J* = 22.1 Hz), 113.81 (d, *J* = 22.1 Hz), 103.07, 98.87, 89.52, 84.63, 38.74.

HRMS (ESI) *m/z* Calcd for $C_{29}H_{18}FO^-$[M - H]$^-$: 401.1347, Found: 401.1329.



1m

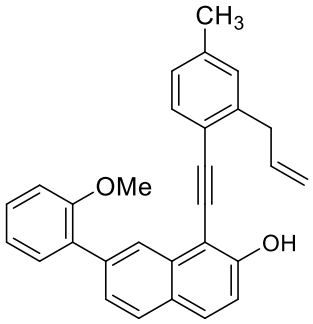
1-((2-allyl-4-methylphenyl)ethynyl)-7-phenylnaphthalen-2-ol (1m)

Compound **1m** is an unknown compound. The compound was synthesized in 79% yield (444 mg, 1.19 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

White solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (s, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.81 – 7.71 (m, 3H), 7.67 – 7.61 (m, 1H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.21 (d, *J* = 8.9 Hz, 1H), 7.15 – 7.04 (m, 2H), 6.29 (s, 1H), 6.12 (m, 1H), 5.20 – 5.11 (m, 1H), 5.12 – 5.03 (m, 1H), 3.70 (d, *J* = 6.0 Hz, 2H), 2.38 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.28, 141.22, 141.04, 140.03, 139.39, 136.41, 133.76, 132.22, 130.18, 130.11, 128.83, 128.79, 127.62, 127.49, 127.25, 123.70, 122.96, 119.36, 116.43, 116.36, 103.44, 100.32, 84.62, 38.87, 21.55.

HRMS (ESI) *m/z* Calcd for $C_{28}H_{21}O^-$[M - H]$^-$: 373.1598, Found: 373.1588.



1n

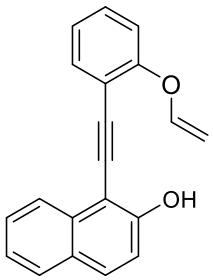
1-((2-allyl-4-methylphenyl)ethynyl)-7-(2-methoxyphenyl)naphthalen-2-ol (1n)

Compound **1n** is an unknown compound. The compound was synthesized in 70% yield (425 mg, 1.05 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

colorless oil. (R_f = 0.4, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.81 – 7.70 (m, 2H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 5.7 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 8.9 Hz, 1H), 7.10 – 7.01 (m, 3H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.27 (s, 1H), 6.06 (ddt, *J* = 16.5, 9.9, 6.0 Hz, 1H), 5.12 – 4.97 (m, 2H), 3.80 (s, 3H), 3.64 (d, *J* = 6.0 Hz, 2H), 2.34 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.60, 156.02, 141.13, 139.22, 137.83, 136.40, 133.51, 132.18, 131.15, 130.61, 130.14, 130.06, 128.83, 127.52, 127.40, 127.17, 126.26, 125.24, 120.90, 119.43, 116.30, 116.17, 111.19, 103.33, 100.04, 84.80, 55.53, 38.79, 21.50.

HRMS (ESI) *m/z* Calcd for $C_{29}H_{23}O_2^-$[M - H]$^-$: 403.1704, Found: 403.1700.



1o(1a-3)

1-((2-(vinyloxy)phenyl)ethynyl)naphthalen-2-ol (1o (1a-3))

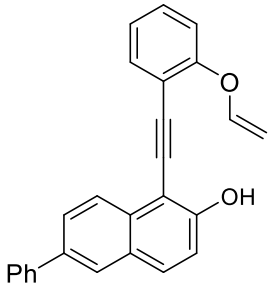
Compound **1a-3 (1o)** is an unknown compound. The compound was synthesized in 88% yield (378 mg, 1.32 mmol) following the general procedure (**Method B**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

White solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.3 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.24 (d, *J* = 8.7 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.84 (s, 1H), 6.76 (dd, *J* = 13.7, 6.0 Hz, 1H), 4.97 (dd, *J* = 13.7, 2.0 Hz, 1H), 4.61 (dd, *J* = 6.0, 2.0 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 156.80, 156.58, 147.65, 133.05, 132.03, 130.71, 129.82, 128.33, 128.22, 127.31, 124.98, 123.98, 123.38, 116.46, 116.04, 113.93, 102.96, 96.95, 96.40, 87.81.

HRMS (ESI) *m/z* Calcd for $C_{20}H_{13}O_2^-$[M - H]$^-$: 285.0921, Found: 285.0909.



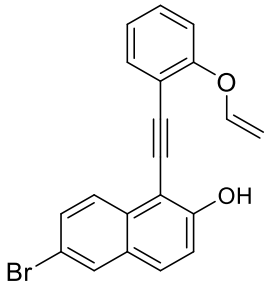
1p

6-phenyl-1-((2-(vinyloxy)phenyl)ethynyl)naphthalen-2-ol (1p)

Compound **1p** is an unknown compound. The compound was synthesized in 85% yield (462 mg, 1.28 mmol) following the general procedure (**Method B**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

White solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.6 Hz, 1H), 7.97 (s, 1H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.63 (d, *J* = 7.1 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.30 (m, 2H), 7.26 (d, *J* = 8.9 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.2 Hz, 1H), 6.86 (s, 1H), 6.77 (dd, *J* = 13.7, 6.0 Hz, 1H), 4.99 (dd, *J* = 13.7, 2.0 Hz, 1H), 4.62 (dd, *J* = 6.0, 2.1 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.87, 156.62, 147.64, 140.90, 136.81, 132.23, 132.05, 130.96, 129.87, 128.84, 128.59, 127.22, 126.93, 126.14, 125.55, 123.39, 116.89, 116.03, 113.88, 102.92, 96.99, 96.45, 87.77.
HRMS (ESI) *m/z* Calcd for $C_{26}H_{17}O_2^-$[M - H]$^-$: 361.1234, Found: 361.1231.



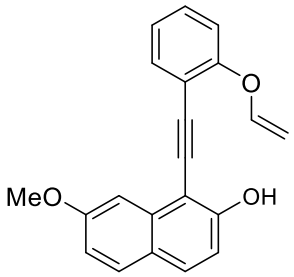
1q

6-bromo-1-((2-(vinyloxy)phenyl)ethynyl)naphthalen-2-ol (1q)

Compound **1q** is an unknown compound. The compound was synthesized in 86% yield (471 mg, 1.29 mmol) following the general procedure (**Method B**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

Gray solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.8 Hz, 1H), 7.91 (d, *J* = 2.0 Hz, 1H), 7.65 (d, *J* = 8.9 Hz, 1H), 7.63 – 7.56 (m, 2H), 7.36 (td, *J* = 7.9, 1.7 Hz, 1H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.14 (td, *J* = 7.6, 1.1 Hz, 1H), 7.11 – 7.04 (m, 1H), 6.84 (s, 1H), 6.76 (dd, *J* = 13.7, 6.0 Hz, 1H), 4.97 (dd, *J* = 13.6, 2.0 Hz, 1H), 4.62 (dd, *J* = 6.0, 2.0 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.93, 156.67, 147.54, 132.02, 131.57, 130.47, 130.15, 130.06, 129.59, 129.44, 126.81, 123.40, 117.67, 117.58, 115.97, 113.59, 103.29, 97.37, 96.58, 87.17.
HRMS (ESI) *m/z* Calcd for $C_{20}H_{12}BrO_2^-$[M - H]$^-$: 363.0026, Found: 363.0012.



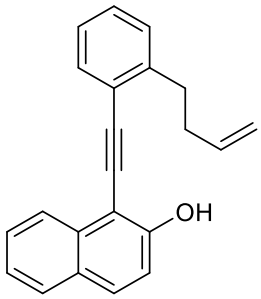
1r

7-methoxy-1-((2-(vinyloxy)phenyl)ethynyl)naphthalen-2-ol (1r)

Compound **1r** is an unknown compound. The compound was synthesized in 83% yield (394 mg, 1.25 mmol) following the general procedure (**Method B**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

Gray solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 2.6 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 2.6 Hz, 1H), 7.07 (d, *J* = 2.1 Hz, 1H), 7.03 (dd, *J* = 8.9, 2.5 Hz, 1H), 6.80 (s, 1H), 6.76 (dd, *J* = 13.7, 6.0 Hz, 1H), 4.96 (dd, *J* = 13.7, 2.0 Hz, 1H), 4.62 (dd, *J* = 6.0, 2.0 Hz, 1H), 3.98 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.14, 157.29, 156.50, 147.60, 134.61, 132.01, 130.53, 129.81, 129.77, 123.58, 123.33, 116.21, 116.01, 113.86, 113.80, 103.89, 102.14, 97.03, 96.65, 87.84, 55.35.
HRMS (ESI) *m/z* Calcd for $C_{20}H_{15}O_3^-$[M - H]$^-$: 315.1027, Found: 315.1014.



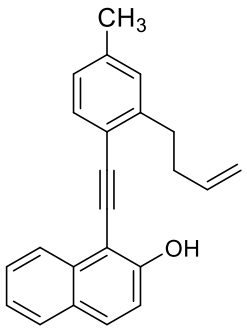
1s

1-((2-(but-3-en-1-yl)phenyl)ethynyl)naphthalen-2-ol (1s)

Compound **1s** is an unknown compound. The compound was synthesized in 80% yield (358 mg, 1.2 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

Pale yellow solid. (R_f = 0.6, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.3 Hz, 1H), 7.78 (t, *J* = 7.4 Hz, 2H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.26 – 7.21 (m, 2H), 6.18 (s, 1H), 5.94 (ddt, *J* = 13.2, 10.2, 6.5 Hz, 1H), 5.07 (dd, *J* = 29.5, 13.7 Hz, 2H), 3.06 (t, *J* = 8.0 Hz, 2H), 2.52 (q, *J* = 7.2, 6.6 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.83, 143.43, 137.70, 133.50, 132.37, 130.65, 129.07, 128.94, 128.47, 128.31, 127.43, 126.13, 124.87, 124.08, 122.09, 116.38, 115.31, 103.07, 100.02, 85.04, 34.83, 34.45.
HRMS (ESI) *m/z* Calcd for $C_{22}H_{17}O^-$[M - H]$^-$: 297.1285, Found: 297.1276.



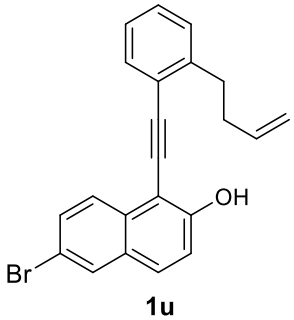
1t

1-((2-(but-3-en-1-yl)-4-methylphenyl)ethynyl)naphthalen-2-ol (1t)

Compound **1t** is an unknown compound. The compound was synthesized in 79% yield (370 mg, 1.19 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

Pale yellow solid. (R_f = 0.6, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.3 Hz, 1H), 7.87 – 7.78 (m, 2H), 7.65 – 7.56 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.9 Hz, 1H), 7.16 (s, 1H), 7.11 (d, *J* = 7.9 Hz, 1H), 6.34 (s, 1H), 6.12 – 5.97 (m, 1H), 5.19 (dd, *J* = 30.7, 13.7 Hz, 2H), 3.09 (t, *J* = 8.0 Hz, 2H), 2.60 (q, *J* = 7.5 Hz, 2H), 2.44 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.63, 143.22, 139.03, 137.76, 133.45, 132.17, 130.35, 129.76, 128.41, 128.22, 127.28, 126.89, 124.86, 123.94, 119.00, 116.29, 115.13, 103.26, 100.23, 84.35, 34.86, 34.34, 21.48.
HRMS (ESI) *m/z* Calcd for $C_{23}H_{19}O^-$[M - H]$^-$: 311.1441, Found: 311.1432.



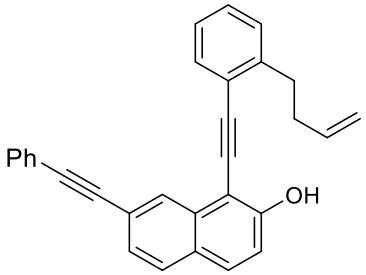
1u

6-bromo-1-((2-(but-3-en-1-yl)phenyl)ethynyl)naphthalen-2-ol (1u)

Compound **1u** is an unknown compound. The compound was synthesized in 71% yield (402 mg, 1.07 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

Pale yellow solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.8 Hz, 1H), 7.94 (d, *J* = 2.0 Hz, 1H), 7.68 (d, *J* = 9.0 Hz, 1H), 7.66 – 7.54 (m, 2H), 7.39 – 7.26 (m, 3H), 7.26 – 7.22 (m, 1H), 6.19 (s, 1H), 5.93 (ddt, *J* = 16.8, 10.0, 6.5 Hz, 1H), 5.16 – 5.00 (m, 2H), 3.09 – 3.00 (m, 2H), 2.51 (q, *J* = 7.6, 7.2 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.92, 143.43, 137.60, 132.35, 131.98, 130.53, 130.18, 129.50, 129.11, 129.05, 126.63, 126.14, 121.75, 117.74, 117.46, 115.33, 103.34, 100.36, 84.39, 34.78, 34.35.
HRMS (ESI) *m/z* Calcd for $C_{22}H_{16}BrO^-$[M - H]$^-$: 375.0390, Found: 375.0372.



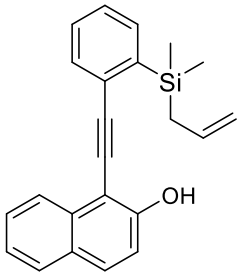
1v

1-((2-(but-3-en-1-yl)phenyl)ethynyl)-7-(phenylethynyl)naphthalen-2-ol (1v)

Compound **1v** is an unknown compound. The compound was synthesized in 76% yield (454 mg, 1.14 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

Pale yellow solid. (R_f = 0.6, PE/EA= 5:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.76 (dd, *J* = 8.7, 3.4 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 7.1 Hz, 2H), 7.50 (d, *J* = 8.3 Hz, 1H), 7.38 – 7.33 (m, 4H), 7.31 (d, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 6.21 (s, 1H), 6.01 – 5.92 (m, 1H), 5.10 (d, *J* = 17.0 Hz, 1H), 4.99 (d, *J* = 10.2 Hz, 1H), 3.08 (t, *J* = 7.9 Hz, 2H), 2.56 (q, *J* = 7.4 Hz, 2H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 156.31, 143.52, 137.55, 133.24, 132.47, 131.67, 130.32, 129.09, 129.04, 128.33, 127.85, 126.79, 126.12, 123.21, 122.22, 121.95, 117.02, 115.53, 103.02, 100.50, 90.46, 89.92, 84.67, 34.85, 34.50.
HRMS (ESI) *m/z* Calcd for $C_{30}H_{21}O^-$[M - H]$^-$: 397.1598, Found: 397.1584.



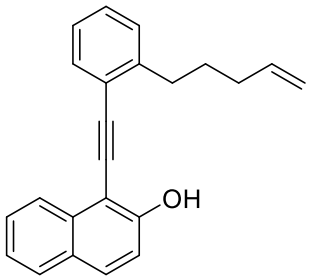
1w

1-((2-(allyldimethylsilyl)phenyl)ethynyl)naphthalen-2-ol (1w)

Compound **1w** is an unknown compound. The compound was synthesized in 74% yield (380 mg, 1.11 mmol) following the general procedure (**Method C**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent.

Orange oil. (R_f = 0.4, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.4 Hz, 1H), 7.78 (dd, *J* = 8.6, 5.2 Hz, 2H), 7.69 (d, *J* = 7.1 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.44 – 7.34 (m, 3H), 7.26 – 7.20 (m, 1H), 6.19 (s, 1H), 5.79 (td, *J* = 17.7, 8.1 Hz, 1H), 4.91 – 4.79 (m, 2H), 2.00 (d, *J* = 8.1 Hz, 2H), 0.44 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 156.12, 140.66, 134.54, 134.36, 133.64, 133.47, 130.77, 129.09, 128.50, 128.33, 128.07, 127.69, 127.40, 124.83, 124.06, 116.45, 113.76, 102.80, 102.27, 84.49, 23.14, -2.92.
HRMS (ESI) *m/z* Calcd for $C_{23}H_{21}OSi^-$[M - H]$^-$: 341.1367, Found: 341.1354.



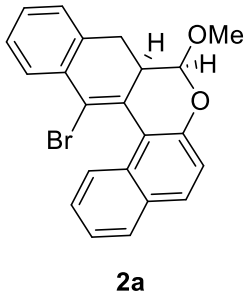
1x

1-((2-(pent-4-en-1-yl)phenyl)ethynyl)naphthalen-2-ol (1x)

Compound **1x** is an unknown compound. The compound was synthesized in 70% yield (718 mg, 2.3 mmol) following the general procedure (**Method A**) and was purified by silica gel column chromatography using PE:EA (30:1 to 15:1) as eluent. Pale yellow oil. (Rf = 0.6, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.3 Hz, 1H), 7.74 (d, *J* = 9.0 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.31 – 7.10 (m, 4H), 6.20 (s, 1H), 5.83 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.04 (d, *J* = 17.1 Hz, 1H), 4.96 (d, *J* = 10.1 Hz, 1H), 3.00 – 2.83 (m, 2H), 2.17 (q, *J* = 7.1 Hz, 2H), 1.85 (p, *J* = 7.6 Hz, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 155.82, 144.07, 138.25, 133.53, 132.41, 130.60, 128.98, 128.90, 128.49, 128.31, 127.36, 125.97, 124.81, 124.04, 122.03, 116.36, 115.03, 103.13, 100.11, 84.94, 34.45, 33.50, 29.88.
HRMS (ESI) *m/z* Calcd for $C_{23}H_{19}O^-$[M - H]$^-$: 311.1441, Found: 311.1434.

VII. ^{1} H, ^{13} C NMR and HRMS data of compounds (2a-4a)



2a

14-bromo-8-methoxy-8a,9-dihydro-8H-benzo[f]naphtho[2,3-c] chromene (2a)

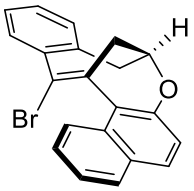
Compound **2a** was synthesized in 49% yield (116 mg, 0.6 mmol scale) under condition [B]. **2a** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

White solid. (R_f = 0.5, PE/EA= 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.5 Hz, 1H), 7.85 – 7.74 (m, 3H), 7.49 (t, *J* = 7.0 Hz, 1H), 7.37 (t, *J* = 6.9 Hz, 1H), 7.30 – 7.17 (m, 2H), 7.18 – 7.11 (m, 2H), 4.97 (d, *J* = 3.8 Hz, 1H), 3.54 (s, 3H), 3.37 (dd, *J* = 16.3, 8.8 Hz, 1H), 3.27 – 3.20 (m, 1H), 3.14 (dd, *J* = 16.3, 6.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.26, 133.99, 133.53, 130.25, 129.34, 129.11, 128.16, 128.10, 127.78, 127.66, 127.08, 126.53, 125.48, 123.73, 120.57, 120.08, 117.83, 104.09, 57.12, 42.15, 26.94.

HRMS (ESI) *m/z* Calcd for $C_{22}H_{17}BrNaO_2^+$[M + Na]$^+$: 415.0304, Found: 415.0305



3a

(*S*)-14-bromo-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine (3a)

Compound **3a** was synthesized in 65% yield (142 mg, 0.6 mmol scale) under condition [A]. **3a** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

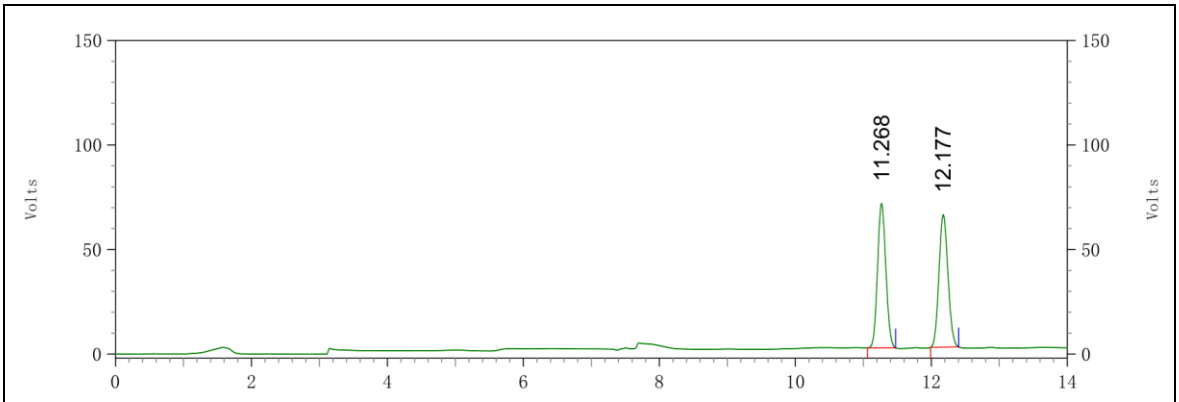
Yellow solid. (R_f = 0.5, PE/EA= 30:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.41 – 7.32 (m, 2H), 7.27 – 7.20 (m, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.9 Hz, 1H), 5.34 – 5.25 (m, 1H), 3.26 – 3.11 (m, 2H), 2.81 (d, *J* = 12.1 Hz, 1H), 2.54 (dd, *J* = 12.2, 3.7 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.65, 141.39, 136.09, 135.20, 130.13, 129.40, 129.24, 128.95, 128.64, 128.42, 127.92, 127.79, 126.70, 125.74, 123.46, 121.41, 118.12, 115.01, 84.01, 40.58, 35.24.

HRMS (APCI) *m/z* Calcd for $C_{21}H_{16}BrO^+$[M + H]$^+$: 363.0379, Found: 363.0366.

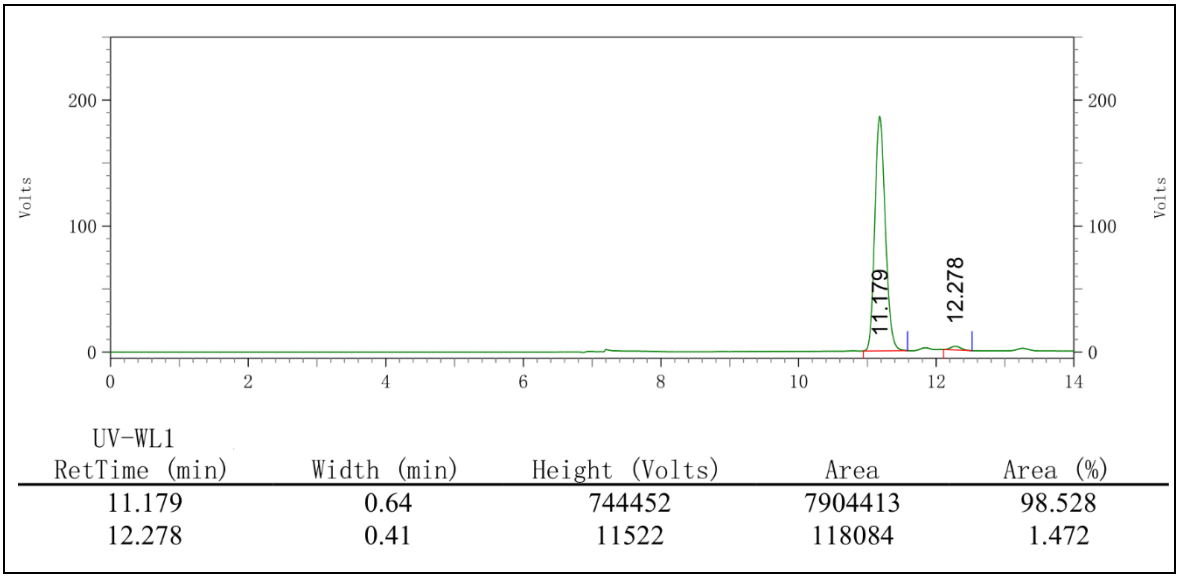
Optical Rotation: $[\alpha]_D^{25}$ = -360.4° (*c* = 0.9, DCM).

HPLC analysis: Chiralcel ADAD-H (Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 11.179 min (major), t_R = 12.278 min (minor), 97% **ee**.



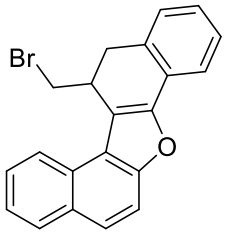
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
11.268	0.42	276550	2349144	50.088
12.177	0.41	253713	2340885	49.912



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
11.179	0.64	744452	7904413	98.528
12.278	0.41	11522	118084	1.472



4a

13-(bromomethyl)-12,13-dihydrodinaphtho[1,2-b:1',2'-d] furan (4a)

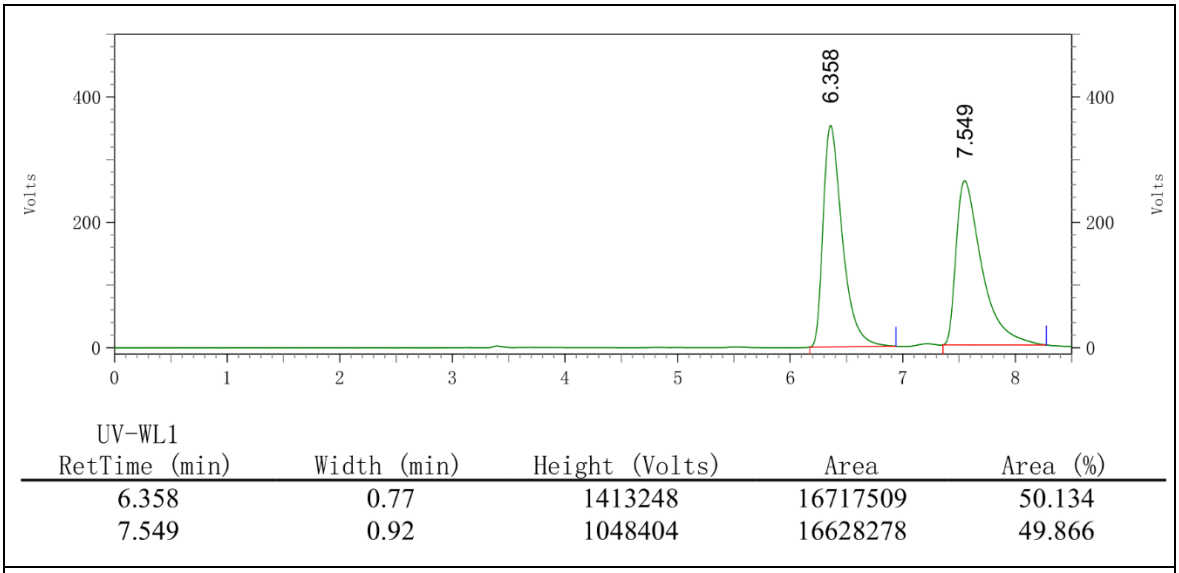
Compound **4a** was synthesized in 19% yield (41 mg, 0.6 mmol scale) under condition [B]. **4a** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

Yellow solid. (R_f = 0.6, PE/EA= 30:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.79 – 7.68 (m, 3H), 7.68 – 7.61 (m, 1H), 7.52 (td, *J* = 7.4, 6.9, 1.2 Hz, 1H), 7.41 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 4.07 – 3.97 (m, 1H), 3.76 – 3.68 (m, 1H), 3.55 (dd, *J* = 16.3, 1.5 Hz, 1H), 3.39 (dd, *J* = 16.2, 6.9 Hz, 1H), 3.24 (t, *J* = 10.9 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.83, 151.33, 132.40, 130.80, 129.32, 129.18, 128.14, 127.79, 127.27, 126.76, 126.65, 125.62, 124.62, 122.79, 120.97, 120.48, 115.96, 112.54, 35.48, 33.63, 31.67.

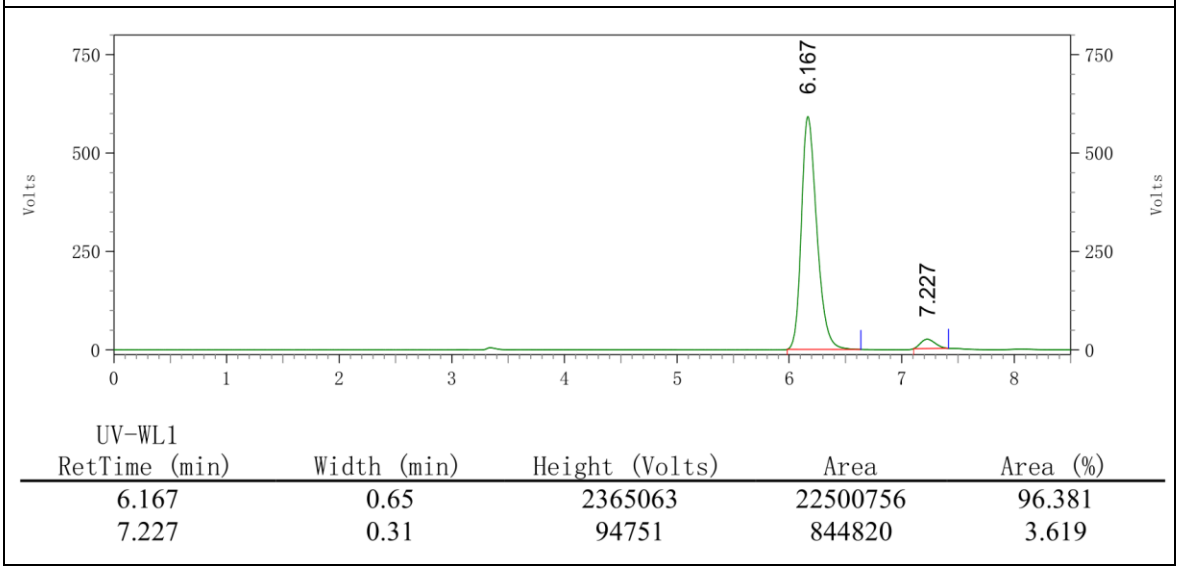
HRMS (APCI) *m/z* Calcd for $C_{21}H_{16}BrO^+[M + H]^+$: 363.0379, Found: 363.0366.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 99:1, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 6.167min (major), t_R = 7.227 min (minor), 93% **ee**.



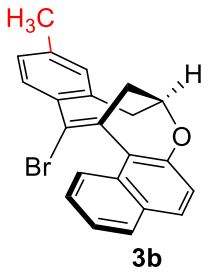
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.358	0.77	1413248	16717509	50.134
7.549	0.92	1048404	16628278	49.866



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.167	0.65	2365063	22500756	96.381
7.227	0.31	94751	844820	3.619



3b

(*S*)-14-bromo-11-methyl-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine (3b)

Compound **3b** was synthesized in 65% yield (147 mg, 0.6 mmol scale) under condition [A]. **3b** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

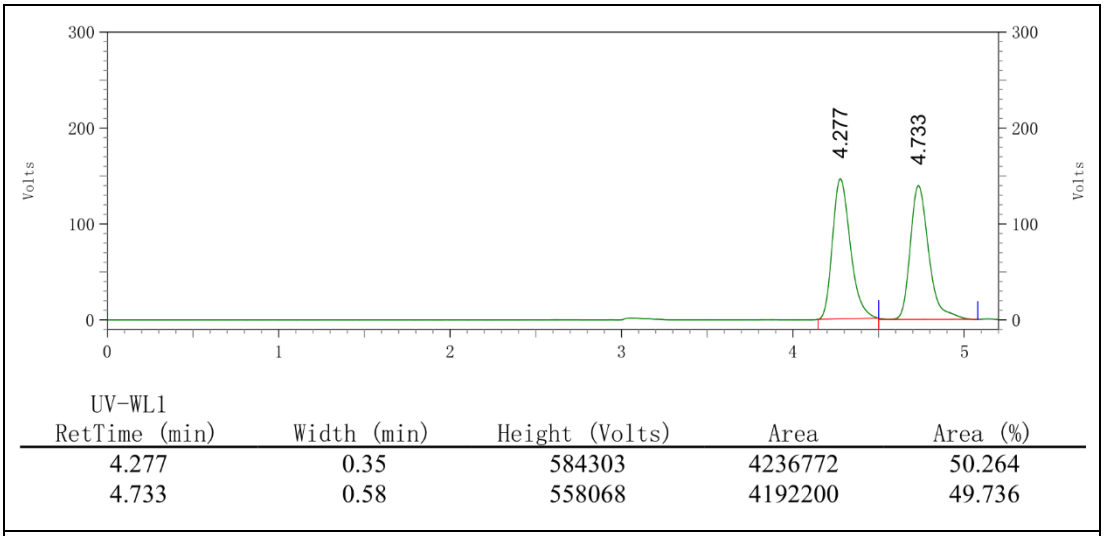
Yellow solid. (R_f = 0.5, PE/EA= 30:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.08 (d, *J* = 8.9 Hz, 1H), 6.97 (s, 1H), 5.35 – 5.24 (m, 1H), 3.19 – 3.12 (m, 2H), 2.82 (d, *J* = 12.1 Hz, 1H), 2.53 (dd, *J* = 12.2, 3.6 Hz, 1H), 2.36 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 151.62, 139.03, 138.56, 135.95, 134.76, 130.07, 129.99, 129.31, 128.74, 128.47, 128.36, 127.90, 126.78, 125.69, 123.44, 121.54, 118.11, 115.34, 84.03, 40.62, 35.33, 21.39.

HRMS (APCI) *m/z* Calcd for $C_{22}H_{18}BrO^{+}[M + H]^{+}$: 377.0536, Found: 377.0525.

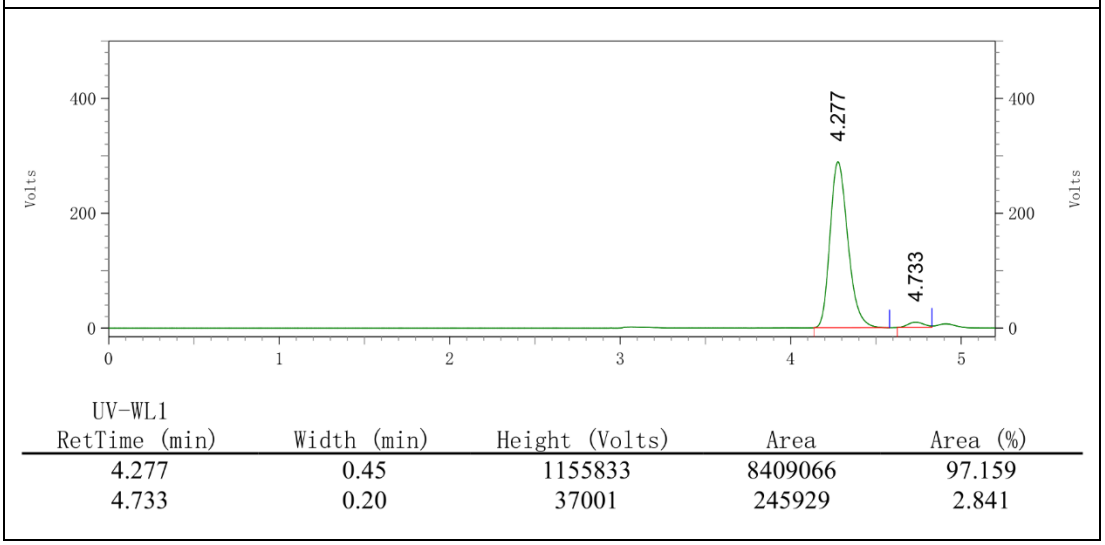
Optical Rotation: $[\alpha]_D^{25}$ = -290.4° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 4.277 min (major), t_R = 4.733 min (minor), 94% **ee**.



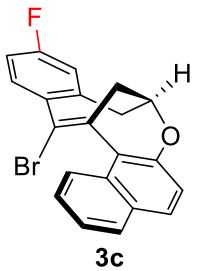
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
4.277	0.35	584303	4236772	50.264
4.733	0.58	558068	4192200	49.736



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
4.277	0.45	1155833	8409066	97.159
4.733	0.20	37001	245929	2.841



3c

(*S*)-14-bromo-11-fluoro-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine (3c)

Compound **3c** was synthesized in 66% yield (151 mg, 0.6 mmol scale) under condition [A]. **3c** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

Pale yellow solid. (R_f = 0.4, PE/EA = 30:1)

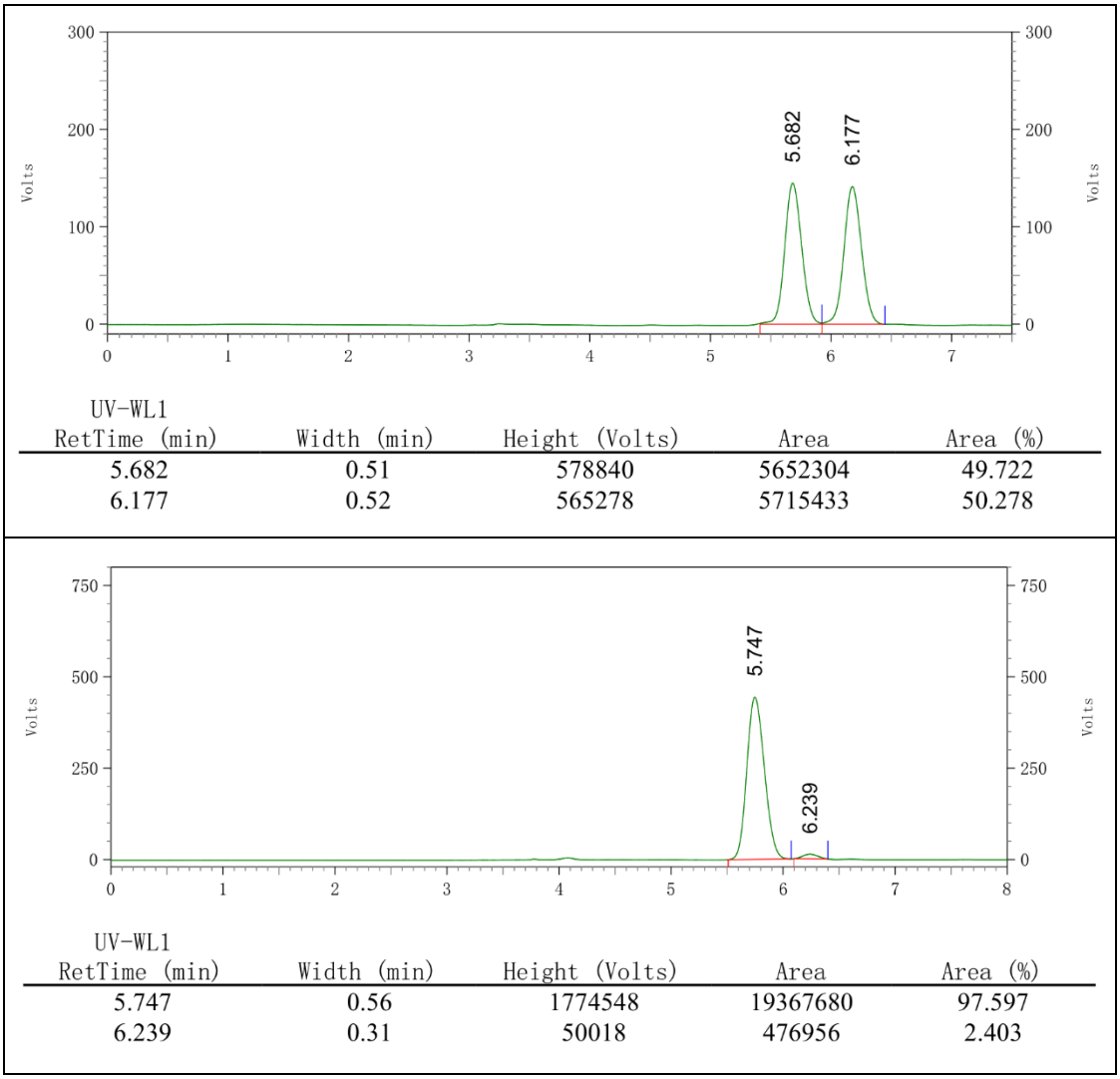
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.3 Hz, 1H), 7.85 – 7.63 (m, 2H), 7.64 – 7.43 (m, 2H), 7.36 (t, *J* = 7.3 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.9 Hz, 1H), 5.36 – 5.23 (m, 1H), 3.26 – 3.06 (m, 2H), 2.78 (d, *J* = 12.1 Hz, 1H), 2.56 (d, *J* = 12.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.17 (d, *J* = 249.6 Hz), 151.50, 138.71 (d, *J* = 7.9 Hz), 137.37 (d, *J* = 3.1 Hz), 135.50, 131.96 (d, *J* = 8.8 Hz), 129.52, 128.59, 128.47, 127.95, 126.64, 125.80, 123.54, 121.26, 118.07, 116.40 (d, *J* = 21.9 Hz), 114.55 (d, *J* = 21.7 Hz), 114.10, 83.54, 40.64, 35.26.

HRMS (APCI) *m/z* Calcd for $C_{21}H_{15}BrFO^+[M + H]^+$: 381.0285, Found: 381.0276.

Optical Rotation: $[\alpha]_D^{25}$ = -335.8° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel IA-H (Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 5.747 min (major), t_R = 6.239 min (minor), 95% **ee**.

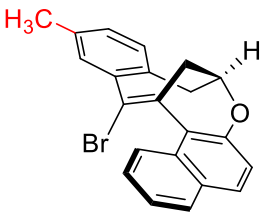


UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
5.682	0.51	578840	5652304	49.722
6.177	0.52	565278	5715433	50.278

UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
5.747	0.56	1774548	19367680	97.597
6.239	0.31	50018	476956	2.403



3d

(*S*)-14-bromo-12-methyl-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine (3d)

Compound **3d** was synthesized in 62% yield (140 mg, 0.6 mmol scale) under condition [A]. **3d** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

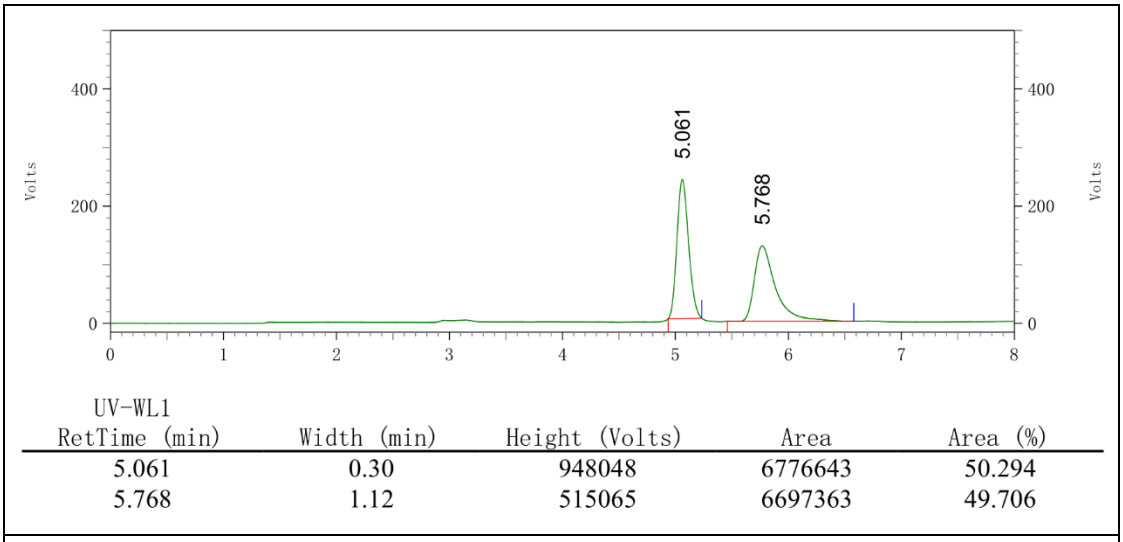
Yellow solid. (R_f = 0.6, PE/EA = 20:1)

^{1}H NMR (400 MHz, $CDCl_3$)δ 7.99 (d, *J* = 8.4 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.9 Hz, 1H), 7.52 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 7.40 (s, 1H), 7.38 – 7.33 (m, 1H), 7.15 – 6.97 (m, 3H), 5.34 – 5.23 (m, 1H), 3.16 (qd, *J* = 14.5, 7.2 Hz, 2H), 2.82 (dd, *J* = 12.1, 1.8 Hz, 1H), 2.54 (dd, *J* = 12.1, 3.7 Hz, 1H), 2.40 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.69, 141.21, 137.55, 135.04, 133.06, 130.77, 129.67, 129.35, 129.08, 128.71, 128.47, 127.92, 126.73, 125.71, 123.44, 121.53, 118.14, 115.29, 84.05, 40.18, 35.31, 21.12.

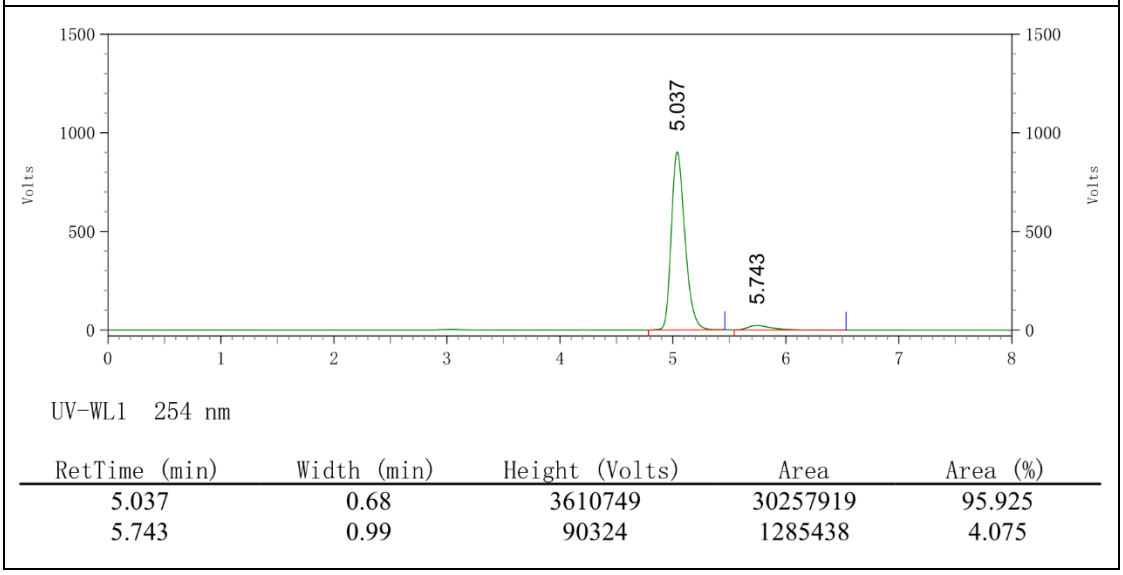
HRMS (APCI) *m/z* Calcd for $C_{22}H_{18}BrO^+[M + H]^+$: 377.0536, Found: 377.0523.

Optical Rotation: $[\alpha]_D^{25}$ = -271.4° (*c* = 0.5, acetone).

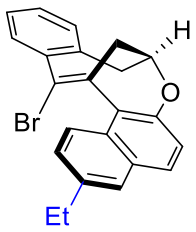
HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 5.037 min (major), t_R = 5.743 min (minor), 92% **ee**.



RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
5.061	0.30	948048	6776643	50.294
5.768	1.12	515065	6697363	49.706



RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
5.037	0.68	3610749	30257919	95.925
5.743	0.99	90324	1285438	4.075



3e

(*S*)-14-bromo-3-ethyl-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine(3e)

Compound **3e** was synthesized in 63% yield (148 mg, 0.6 mmol scale) under condition [A]. **3e** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

White solid. (R_f = 0.4, PE/EA = 20:1)

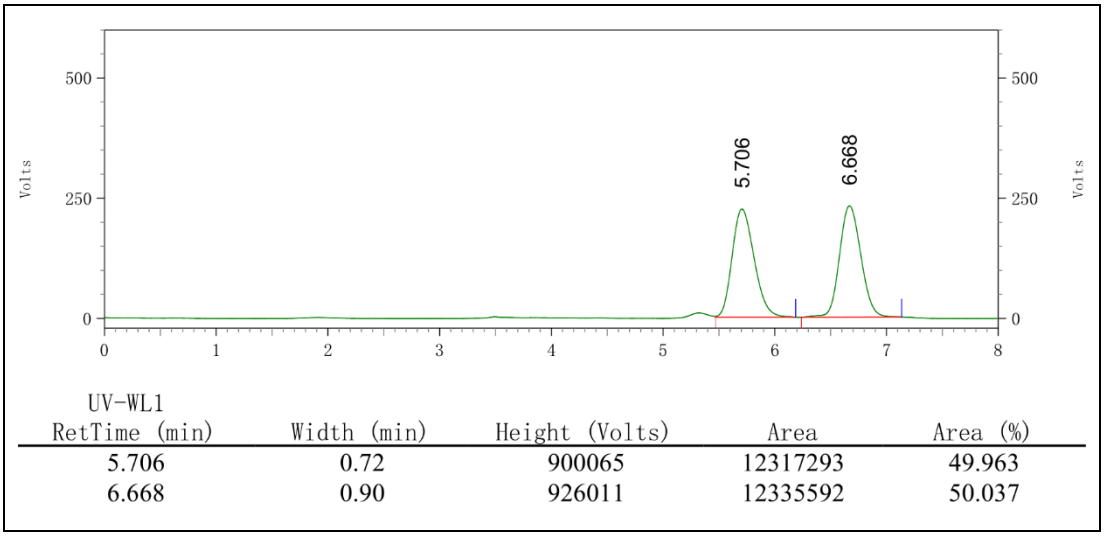
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.5 Hz, 1H), 7.66 (d, *J* = 8.9 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.43 – 7.35 (m, 2H), 7.27 – 7.23 (m, 1H), 7.15 (d, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 8.8 Hz, 1H), 5.33 – 5.27 (m, 1H), 3.24 – 3.15 (m, 2H), 2.84 – 2.78 (m, 3H), 2.54 (dd, *J* = 12.6, 2.9 Hz, 1H), 1.34 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.11, 141.50, 139.27, 136.23, 135.46, 130.16, 129.24, 128.93, 128.72, 127.78, 127.06, 127.01, 126.67, 125.64, 121.39, 118.03, 114.84, 83.94, 40.65, 35.34, 28.76, 15.45.

HRMS (APCI) *m/z* Calcd for $C_{23}H_{20}BrO^+[M + H]^+$: 391.0692, Found: 391.0678.

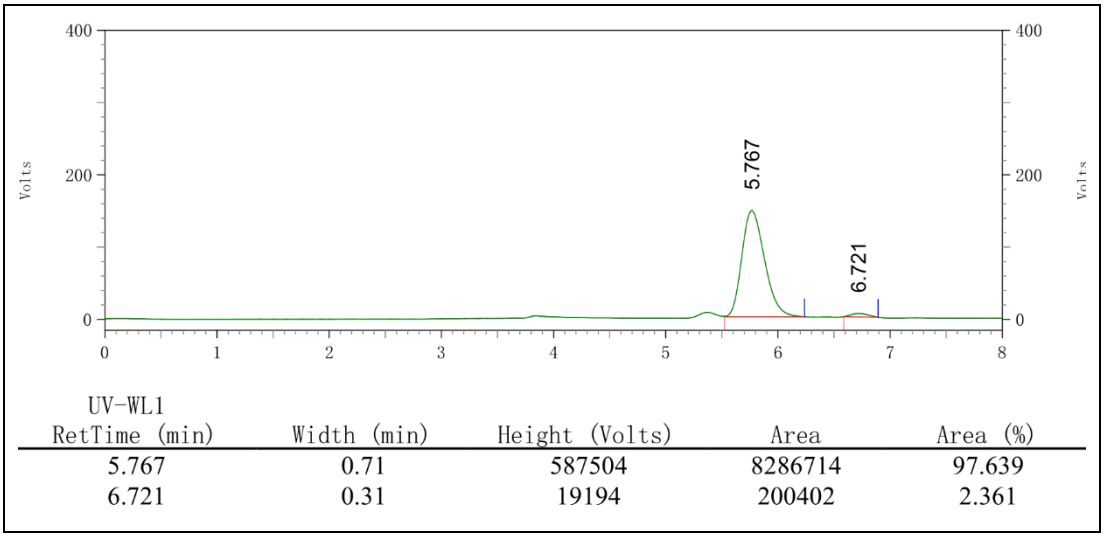
Optical Rotation: $[\alpha]_D^{25}$ = -299.8° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel IA-H (Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 5.767 min (major), t_R = 6.721 min (minor), 95% **ee**.



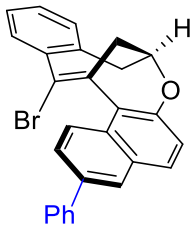
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
5.706	0.72	900065	12317293	49.963
6.668	0.90	926011	12335592	50.037



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
5.767	0.71	587504	8286714	97.639
6.721	0.31	19194	200402	2.361



3f

(*S*)-14-bromo-3-phenyl-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine (3f)

Compound **3f** was synthesized in 55% yield (145 mg, 0.6 mmol scale) under condition [A]. **3f** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

White solid. (R_f = 0.6, PE/EA = 20:1)

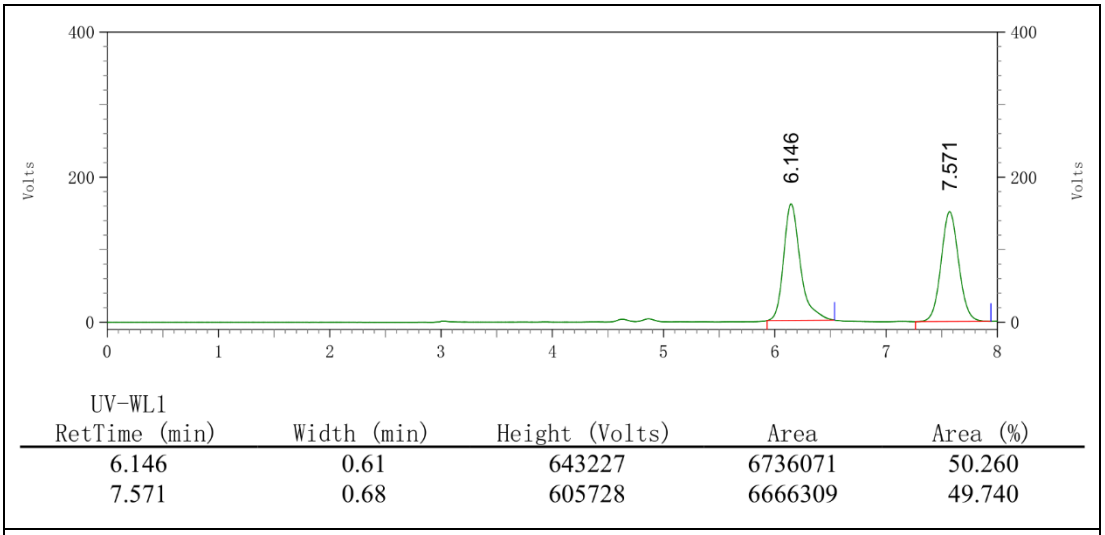
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 1H), 7.98 (s, 1H), 7.83 – 7.77 (m, 2H), 7.74 (d, *J* = 7.2 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.43 – 7.33 (m, 2H), 7.29 – 7.25 (m, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 8.8 Hz, 1H), 5.39 – 5.29 (m, 1H), 3.27 – 3.17 (m, 2H), 2.84 (d, *J* = 12.2 Hz, 1H), 2.58 (dd, *J* = 12.2, 3.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.84, 141.43, 141.15, 136.21, 136.16, 135.19, 130.20, 129.74, 129.28, 129.02, 128.80, 128.75, 127.91, 127.85, 127.27, 127.24, 127.23, 127.06, 125.84, 125.47, 121.40, 118.59, 115.19, 84.14, 40.63, 35.32.

HRMS (APCI) *m/z* Calcd for $C_{27}H_{20}BrO^+[M + H]^+$: 439.0692, Found: 439.0690.

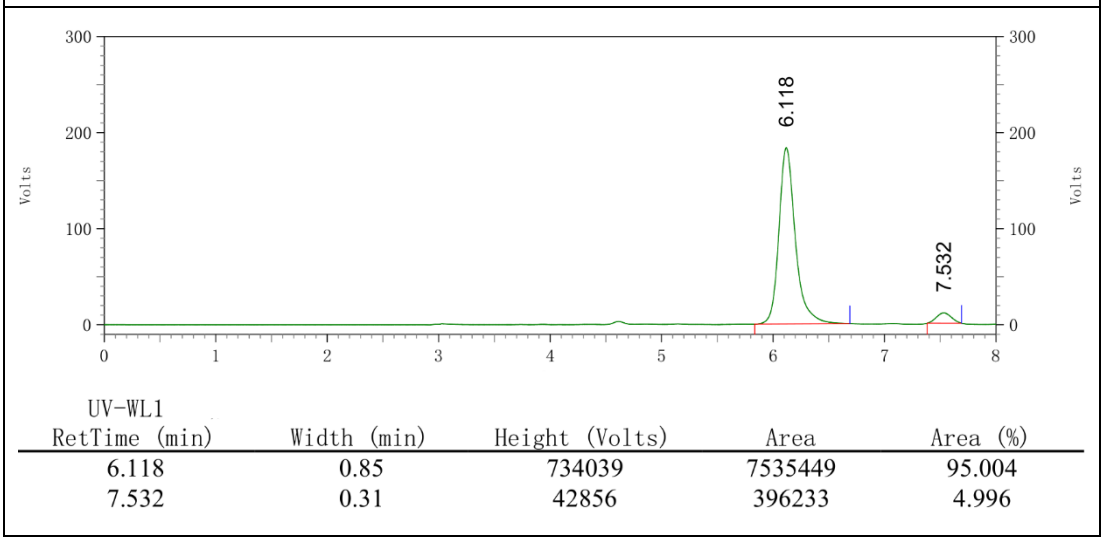
Optical Rotation: $[\alpha]_D^{25}$ = -131.4° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel IA-H (Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 6.118 min (major), t_R = 7.532 min (minor), 90% **ee**.



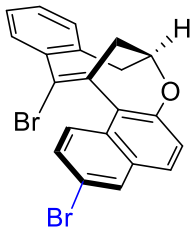
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.146	0.61	643227	6736071	50.260
7.571	0.68	605728	6666309	49.740



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.118	0.85	734039	7535449	95.004
7.532	0.31	42856	396233	4.996



3g

(*S*)-3,14-dibromo-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine (3g)

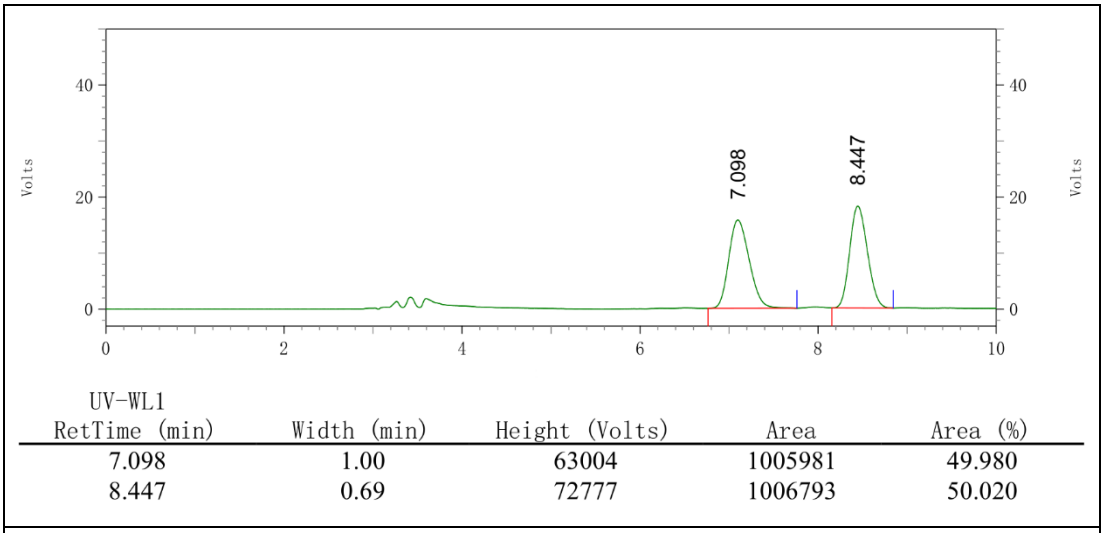
Compound **3g** was synthesized in 59% yield (157 mg, 0.6 mmol scale) under condition [A]. **3g** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

Yellow solid. (R_f = 0.4, PE/EA = 20:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.87 (d, *J* = 8.9 Hz, 1H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 8.9 Hz, 1H), 5.37 – 5.27 (m, 1H), 3.23 (dd, *J* = 14.6, 8.3 Hz, 1H), 3.16 (dd, *J* = 14.7, 6.3 Hz, 1H), 2.83 (d, *J* = 12.2 Hz, 1H), 2.55 (dd, *J* = 12.2, 3.2 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 151.98, 141.22, 135.99, 134.66, 130.18, 129.83, 129.58, 129.29, 129.12, 129.04, 128.48, 128.43, 127.89, 127.24, 121.60, 119.26, 117.12, 115.59, 84.23, 40.55, 35.17.
HRMS (APCI) *m/z* Calcd for Chemical Formula: $C_{21}H_{15}Br_2O^+$ $[M + H]^+$: 442.9464, Found: 442.9456.

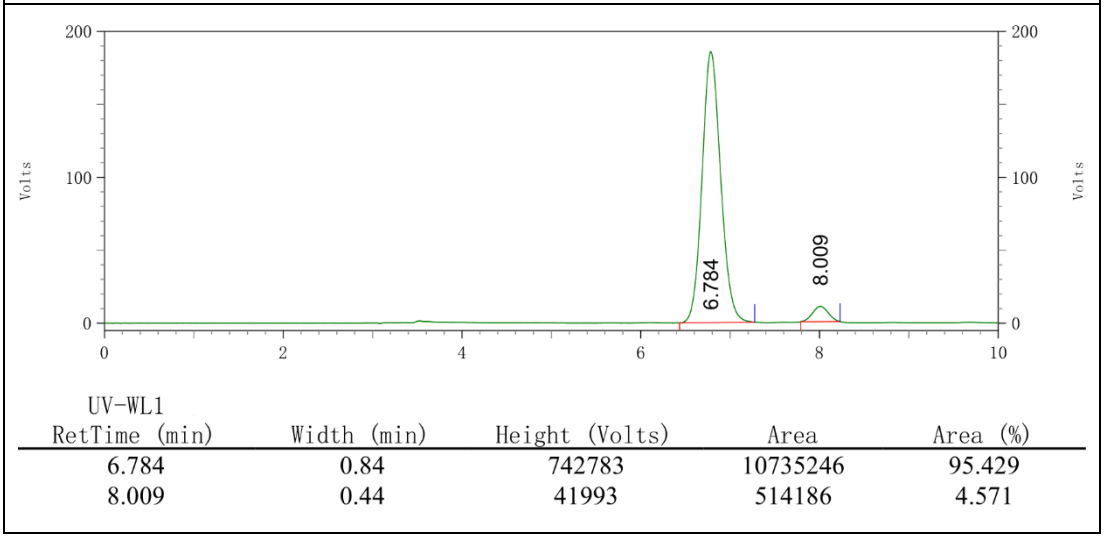
Optical Rotation: $[\alpha]_D^{25}$ = -320.4° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 6.784 min (major), t_R = 8.009 min (minor), 91% **ee**.



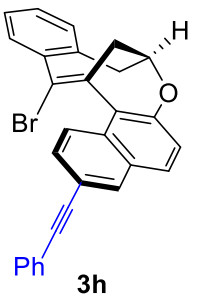
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
7.098	1.00	63004	1005981	49.980
8.447	0.69	72777	1006793	50.020



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.784	0.84	742783	10735246	95.429
8.009	0.44	41993	514186	4.571



3h

(*S*)-14-bromo-3-(phenylethynyl)-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine (3h)

Compound **3h** was synthesized in 61% yield (170 mg, 0.6 mmol scale) under condition [A]. **3h** was purified by silica gel column chromatography using PE : EA (60:1 to 50:1) as eluent.

White solid. (R_f = 0.4, PE/EA = 20:1)

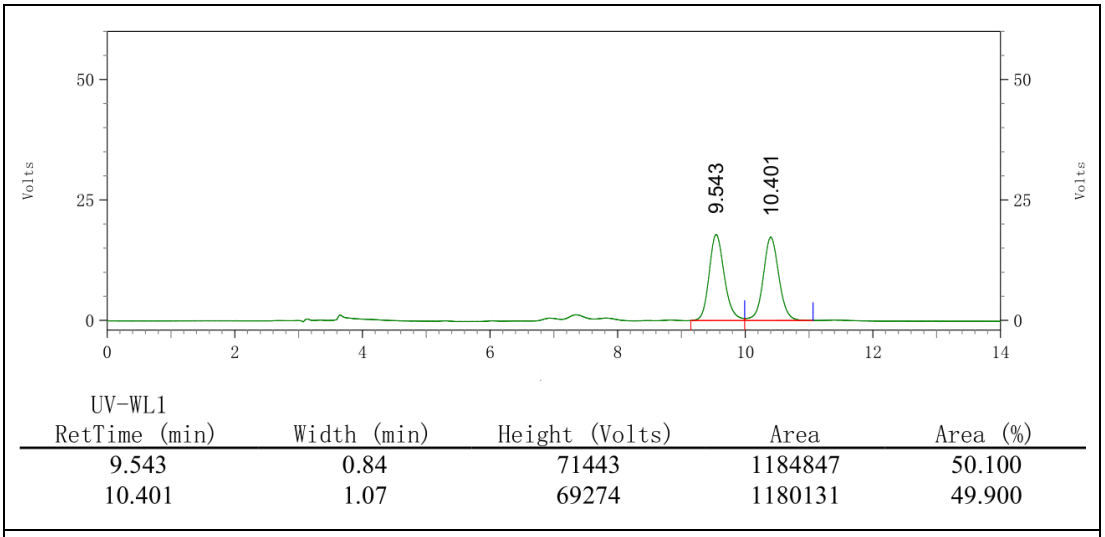
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.92 (m, 2H), 7.68 (d, *J* = 8.9 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.61 – 7.52 (m, 3H), 7.42 – 7.30 (m, 4H), 7.25 (t, *J* = 7.9 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 1H), 5.36 – 5.27 (m, 1H), 3.24 – 3.13 (m, 2H), 2.81 (d, *J* = 12.3 Hz, 1H), 2.55 (dd, *J* = 12.3, 3.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.45, 141.25, 135.98, 134.78, 131.57, 131.50, 130.16, 129.30, 129.26, 129.04, 128.36, 128.33, 128.16, 128.09, 128.03, 127.85, 126.83, 123.45, 121.57, 118.85, 118.00, 115.44, 90.04, 89.16, 84.24, 40.53, 35.16.

HRMS (APCI) *m/z* Calcd for $C_{29}H_{20}BrO^+$ $[M + H]^+$: 463.0692, Found: 463.0683.

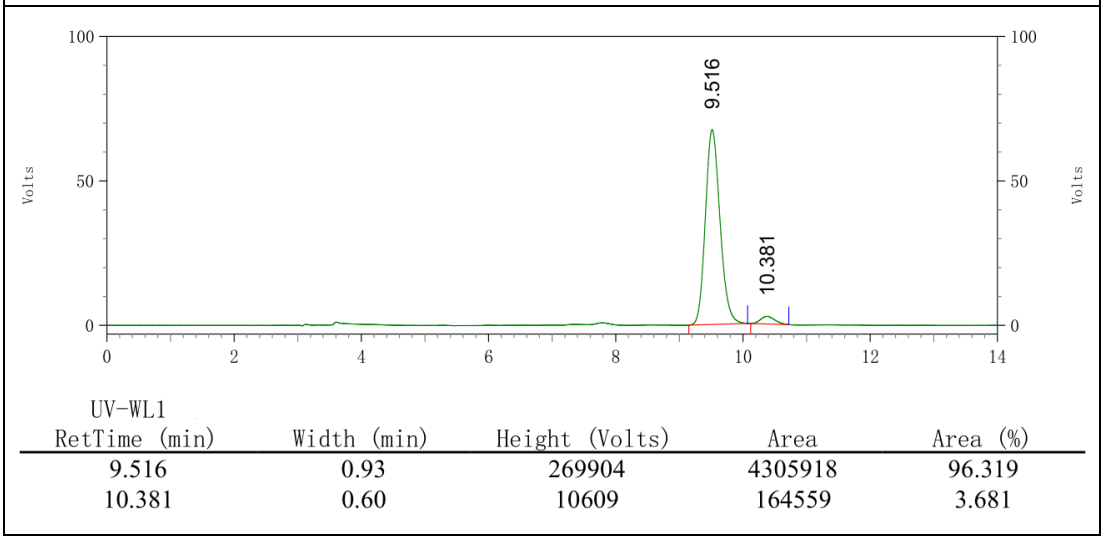
Optical Rotation: $[\alpha]_D^{25}$ = -431.0° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 9.516 min (major), t_R = 10.381 min (minor), 93% **ee**.



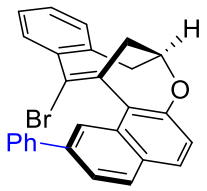
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
9.543	0.84	71443	1184847	50.100
10.401	1.07	69274	1180131	49.900



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
9.516	0.93	269904	4305918	96.319
10.381	0.60	10609	164559	3.681



3i

(*S*)-14-bromo-2-phenyl-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine (3i)

Compound **3i** was synthesized in 57% yield (150 mg, 0.6 mmol scale) under condition [A]. **3i** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

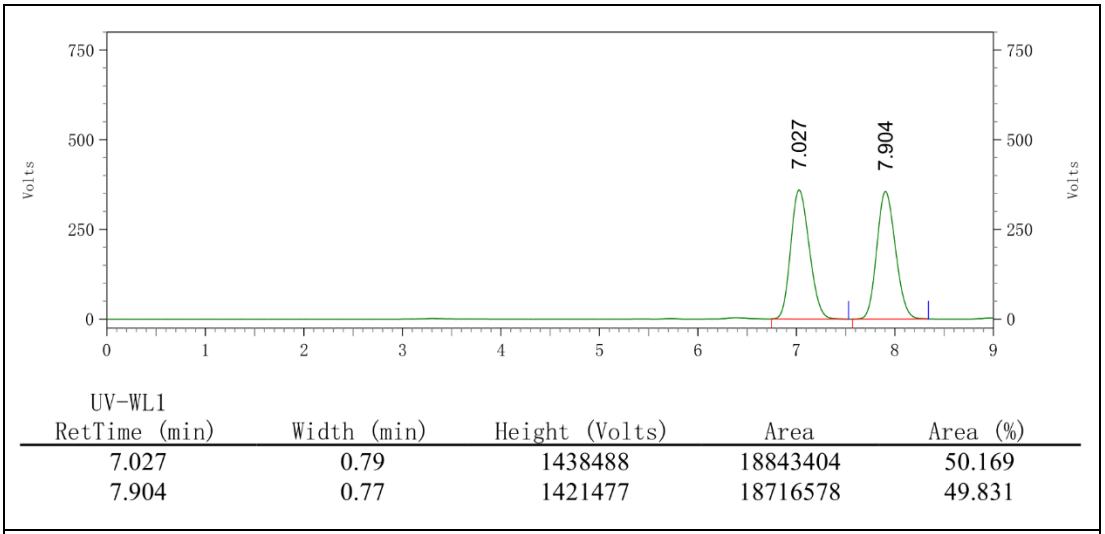
White solid. (R_f = 0.5, PE/DCM = 1:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.88 – 7.80 (m, 3H), 7.74 (d, *J* = 8.9 Hz, 1H), 7.63 (t, *J* = 8.4 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 6.4 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 1H), 5.35 – 5.30 (m, 1H), 3.24 – 3.20 (m, 2H), 2.84 (d, *J* = 12.2 Hz, 1H), 2.58 (dd, *J* = 12.2, 3.6 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 152.07, 141.46, 141.44, 138.54, 136.17, 135.24, 130.29, 129.26, 129.15, 129.01, 128.90, 128.78, 128.43, 127.83, 127.67, 127.58, 127.29, 124.90, 123.25, 121.69, 118.19, 115.23, 84.12, 40.63, 35.35.

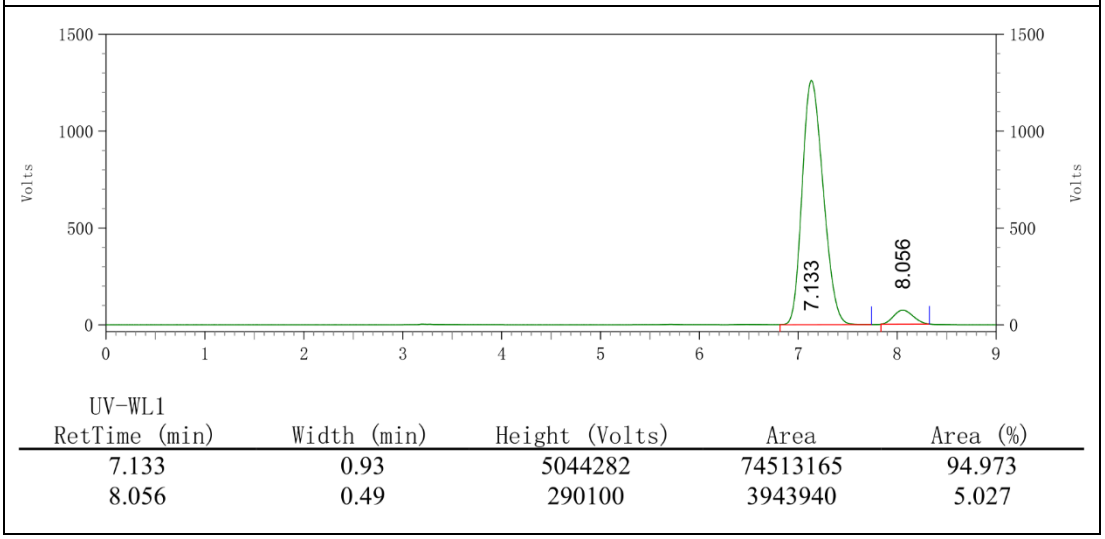
HRMS (APCI) *m/z* Calcd for $C_{27}H_{20}BrO^+[M + H]^+$: 439.0692, Found: 439.0683.

Optical Rotation: $[\alpha]_D^{25}$ = -276.2° (*c* = 0.5, acetone).

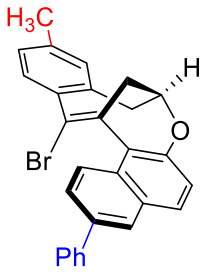
HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 7.133 min (major), t_R = 8.056 min (minor), 90% **ee**.



RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
7.027	0.79	1438488	18843404	50.169
7.904	0.77	1421477	18716578	49.831



RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
7.133	0.93	5044282	74513165	94.973
8.056	0.49	290100	3943940	5.027



3j

(*S*)-14-bromo-11-methyl-3-phenyl-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine (3j)

Compound **3j** was synthesized in 64% yield (174 mg, 0.6 mmol scale) under condition [A]. **3j** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

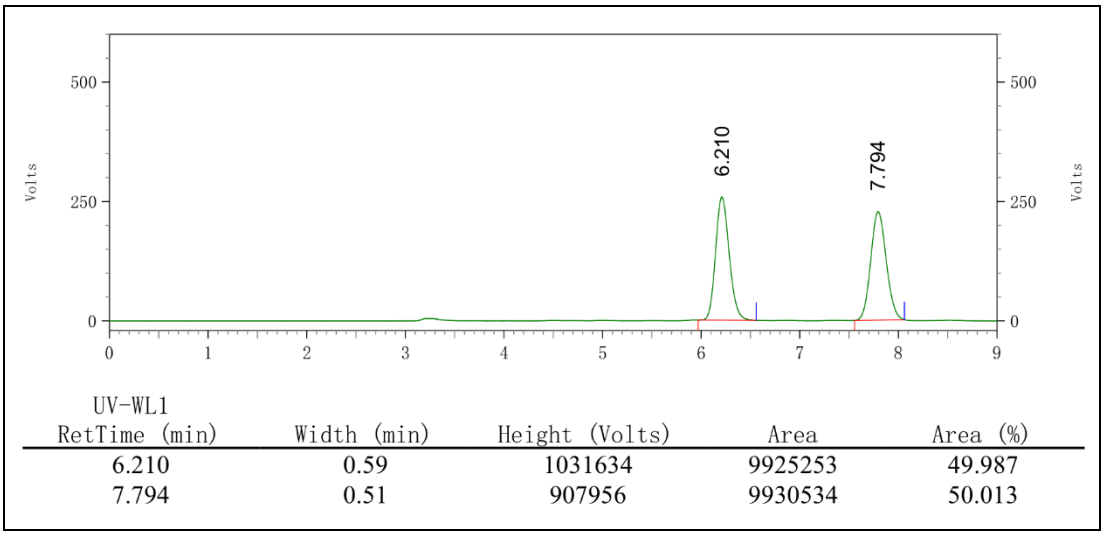
Yellow solid. (R_f = 0.6, PE/EA = 15:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.6 Hz, 1H), 7.97 (s, 1H), 7.80 – 7.76 (m, 2H), 7.73 (d, *J* = 7.6 Hz, 2H), 7.50 – 7.44 (m, 3H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 7.11 (d, *J* = 8.8 Hz, 1H), 6.98 (s, 1H), 5.33 – 5.29 (m, 1H), 3.18 – 3.16 (m, 2H), 2.83 (d, *J* = 12.1 Hz, 1H), 2.55 (dd, *J* = 12.1, 3.2 Hz, 1H), 2.36 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 151.76, 141.15, 139.07, 138.52, 136.14, 135.95, 134.69, 130.09, 130.02, 129.64, 128.77, 128.72, 128.38, 127.95, 127.32, 127.29, 127.21, 127.03, 125.80, 125.39, 121.46, 118.56, 115.46, 84.11, 40.61, 35.34, 21.39.

HRMS (APCI) *m/z* Calcd for $C_{28}H_{22}BrO^+$[M + H]$^+$: 453.0849, Found: 453.0837.

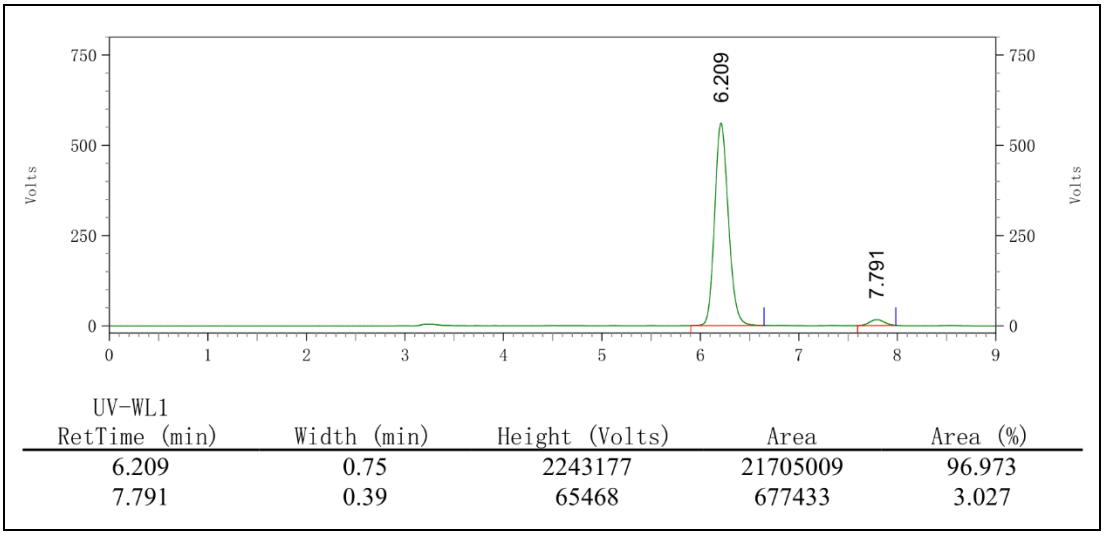
Optical Rotation: $[\alpha]_D^{25}$ = -298.8° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 6.209 min (major), t_R = 7.791 min (minor), 94% **ee**.



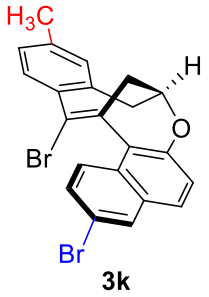
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.210	0.59	1031634	9925253	49.987
7.794	0.51	907956	9930534	50.013



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.209	0.75	2243177	21705009	96.973
7.791	0.39	65468	677433	3.027



3k

(*S*)-3,14-dibromo-11-methyl-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine (3k)

Compound **3k** was synthesized in 52% yield (142 mg, 0.6 mmol scale) under condition [A]. **3k** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

White solid. (R_f = 0.5, PE/EA = 20:1)

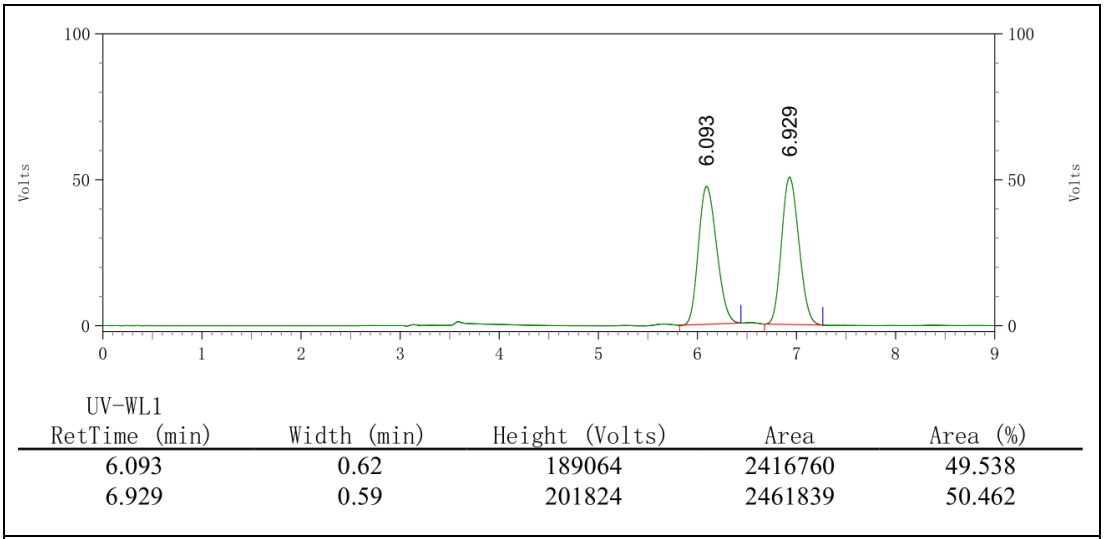
^{1}H NMR (600 MHz, CDCl) δ 7.91 (s, 1H), 7.87 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 8.9 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 8.9 Hz, 1H), 6.98 (s, 1H), 5.34 – 5.27 (m, 1H), 3.20 – 3.08 (m, 2H), 2.82 (d, *J* = 12.3 Hz, 1H), 2.52 (d, *J* = 12.1 Hz, 1H), 2.36 (s, 3H).

^{13}C NMR (150 MHz, CDCl) δ 151.92, 139.23, 138.33, 135.81, 134.18, 130.12, 130.11, 130.02, 129.80, 129.57, 128.97, 128.55, 128.45, 128.34, 127.29, 121.69, 119.24, 117.09, 115.88, 84.21, 40.53, 35.20, 21.39.

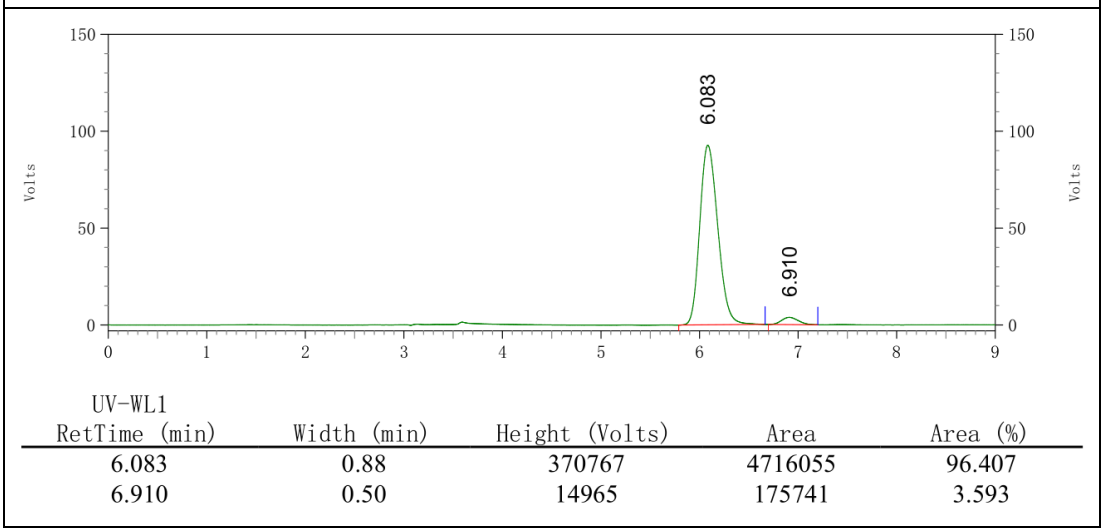
HRMS (APCI) *m/z* Calcd for $C_{22}H_{17}Br_2O^+[M + H]^+$: 456.9620, Found: 456.9612.

Optical Rotation: $[\alpha]_D^{25}$ = -221° (*c* = 0.5, acetone).

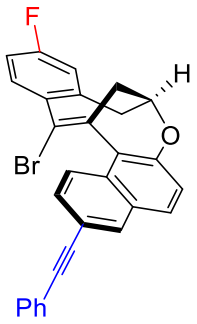
HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 6.083 min (major), t_R = 6.910 min (minor), 93% **ee**.



UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.093	0.62	189064	2416760	49.538
6.929	0.59	201824	2461839	50.462



UV-WL1 RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.083	0.88	370767	4716055	96.407
6.910	0.50	14965	175741	3.593



3l

(*S*)-14-bromo-11-fluoro-3-(phenylethynyl)-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine (3l)

Compound **3l** was synthesized in 66% yield (191 mg, 0.6 mmol scale) under condition [A]. **3l** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

Yellow solid. (R_f = 0.6, PE/EA = 20:1)

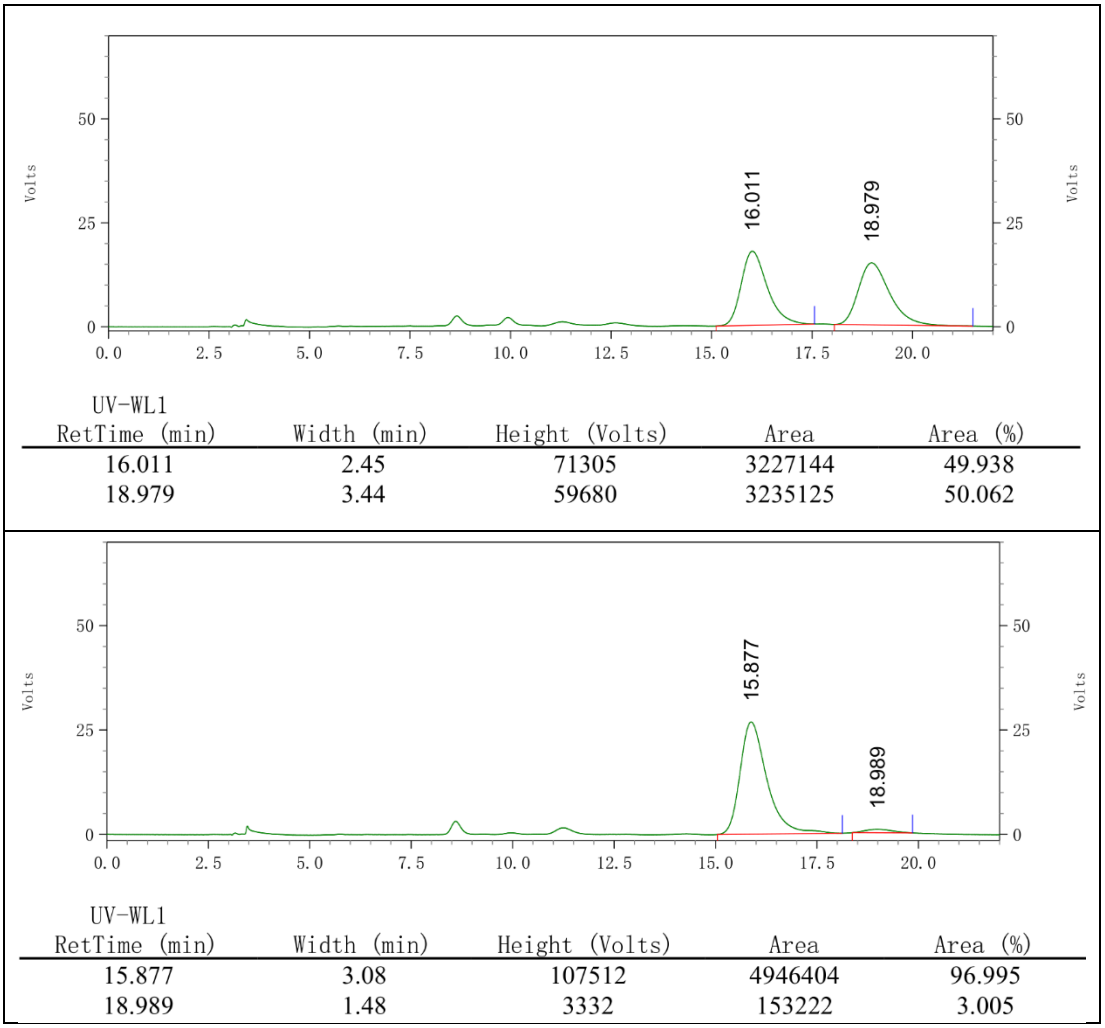
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.94 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 9.0 Hz, 1H), 7.63 (d, *J* = 8.7 Hz, 1H), 7.61 – 7.52 (m, 3H), 7.44 – 7.28 (m, 3H), 7.15 – 7.04 (m, 2H), 6.90 (dd, *J* = 9.1, 2.6 Hz, 1H), 5.36 – 5.29 (m, 1H), 3.23 – 3.12 (m, 2H), 2.80 (d, *J* = 12.3 Hz, 1H), 2.58 (dd, *J* = 12.3, 3.6 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 162.26 (d, *J* = 250.2 Hz), 152.30, 138.64 (d, *J* = 7.9 Hz), 137.28 (d, *J* = 3.2 Hz), 135.10, 132.02 (d, *J* = 8.7 Hz), 131.59, 131.52, 129.44, 128.45, 128.35, 128.13, 126.78, 123.47, 121.46, 118.82, 118.15, 116.45 (d, *J* = 21.9 Hz), 114.65 (d, *J* = 21.8 Hz), 114.55, 89.97, 89.23, 83.79, 40.62, 35.20.

HRMS (APCI) *m/z* Calcd for $C_{29}H_{19}BrFO^+[M + H]^+$: 481.0598, Found: 481.0587.

Optical Rotation: $[\alpha]_D^{25}$ = - 223.8° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 15.877 min (major), t_R = 18.989 min (minor), 94% **ee**.

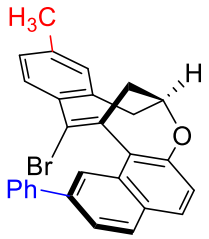


UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
16.011	2.45	71305	3227144	49.938
18.979	3.44	59680	3235125	50.062

UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
15.877	3.08	107512	4946404	96.995
18.989	1.48	3332	153222	3.005



3m

(*S*)-14-bromo-11-methyl-2-phenyl-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine (3m)

Compound **3m** was synthesized in 65% yield (177 mg, 0.6 mmol scale) under condition [A]. **3m** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

Yellow solid. (R_f = 0.5, PE/EA = 20:1)

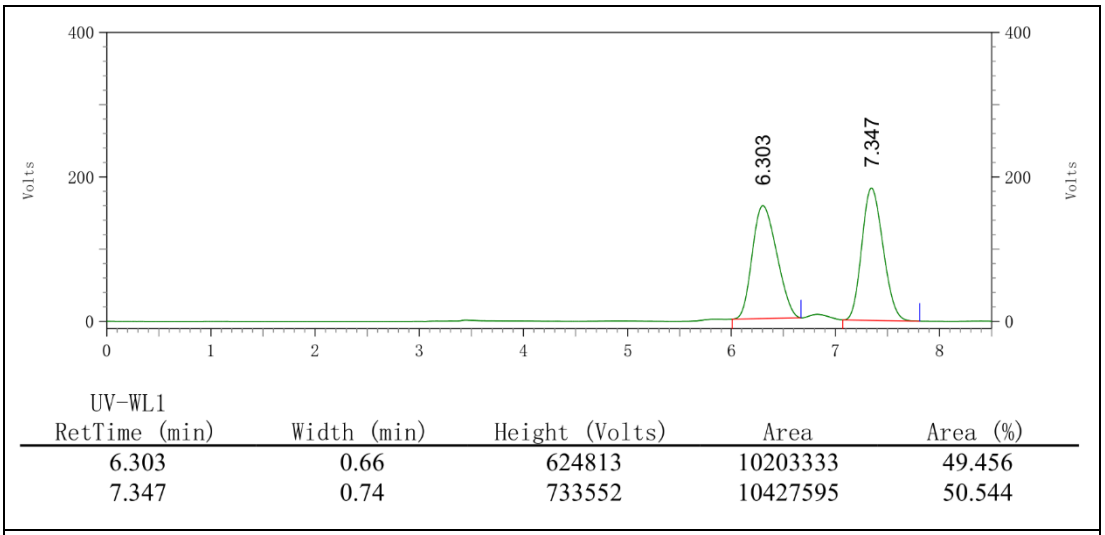
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 1.7 Hz, 1H), 7.85 – 7.82 (m, 3H), 7.73 (d, *J* = 8.8 Hz, 1H), 7.62 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.53 – 7.49 (m, 3H), 7.41 – 7.37 (m, 1H), 7.21 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 1.7 Hz, 1H), 5.33 – 5.30 (m, 1H), 3.18 (d, *J* = 7.3 Hz, 2H), 2.84 (dd, *J* = 12.2, 1.7 Hz, 1H), 2.57 – 2.55 (m, 1H), 2.37 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 152.00, 141.46, 139.09, 138.55, 138.45, 135.98, 134.74, 130.11, 130.09, 129.06, 128.94, 128.77, 128.39, 127.66, 127.57, 127.27, 124.97, 123.20, 121.76, 118.16, 115.51, 84.10, 40.61, 35.38, 21.39.

HRMS (APCI) *m/z* Calcd for $C_{28}H_{22}BrO^+$ [M + H] $^+$: 453.0849, Found: 453.0839.

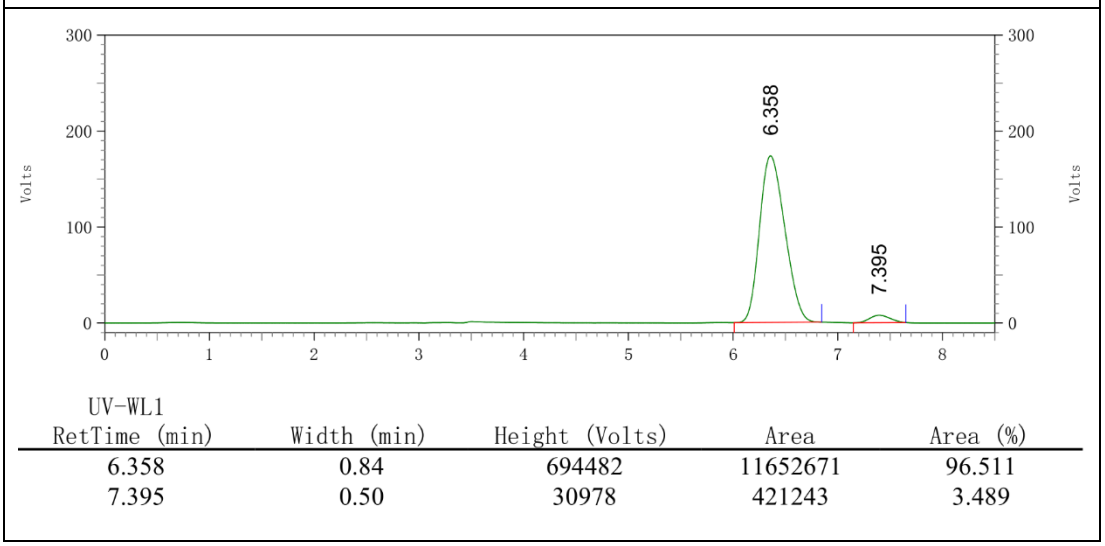
Optical Rotation: $[\alpha]_D^{25}$ = -457.4° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 6.358 min (major), t_R = 7.395 min (minor), 93% **ee**.



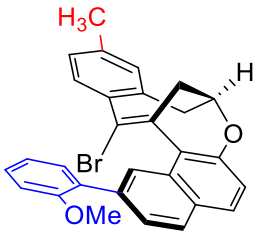
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.303	0.66	624813	10203333	49.456
7.347	0.74	733552	10427595	50.544



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.358	0.84	694482	11652671	96.511
7.395	0.50	30978	421243	3.489



3n

(*S*)-14-bromo-2-(2-methoxyphenyl)-11-methyl-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine (3n)

Compound **3n** synthesized in 62% yield (180 mg, 0.6 mmol scale) under condition [A]. **3n** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

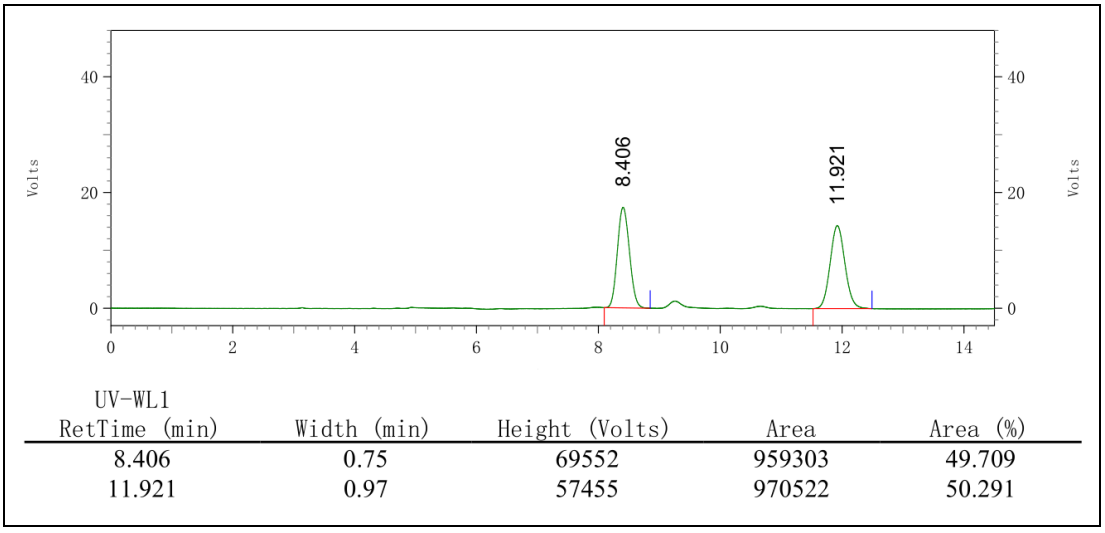
Yellow solid. (R_f = 0.5, PE/EA = 20:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.98 (s, 1H), 5.33 – 5.27 (m, 1H), 3.85 (s, 3H), 3.17 (d, *J* = 7.2 Hz, 2H), 2.80 (d, *J* = 12.1 Hz, 1H), 2.52 (dd, *J* = 12.2, 3.5 Hz, 1H), 2.36 (s, 3H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 156.76, 151.68, 138.99, 138.59, 136.41, 136.00, 134.88, 131.47, 131.11, 130.06, 130.02, 129.02, 128.84, 128.67, 128.33, 127.48, 127.08, 126.93, 125.81, 121.77, 120.89, 117.96, 115.31, 111.24, 84.03, 55.59, 40.66, 35.32, 21.38.

HRMS (APCI) *m/z* Calcd for $C_{29}H_{24}BrO_2^+$[M + H]$^+$: 483.0954, Found: 483.0941.

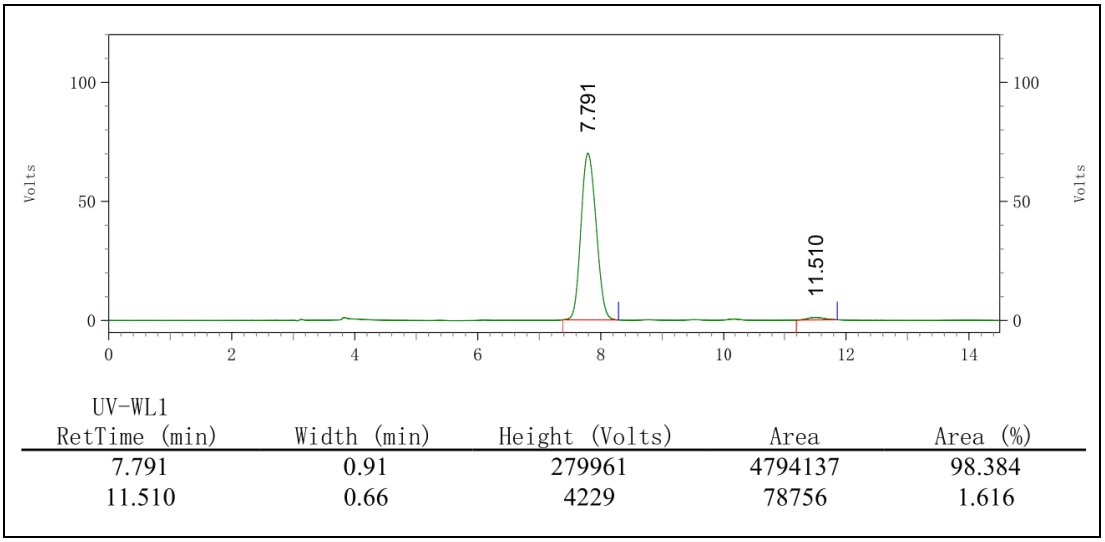
Optical Rotation: $[\alpha]_D^{25}$ = -343.8° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 7.791 min (major), t_R = 11.510 min (minor), 97% **ee**.



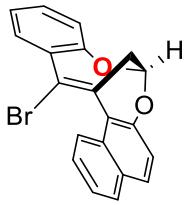
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
8.406	0.75	69552	959303	49.709
11.921	0.97	57455	970522	50.291



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
7.791	0.91	279961	4794137	98.384
11.510	0.66	4229	78756	1.616



3o (3a-3)

(*S*)-14-bromo-8,15-methanobenzo[d]naphtho[1,2-h][1,3]dioxonine (3o (3a-3))

Compound **3o (3a-3)** was synthesized in 85% yield (186 mg, 0.6 mmol scale) under condition [A]. **3o (3a-3)** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

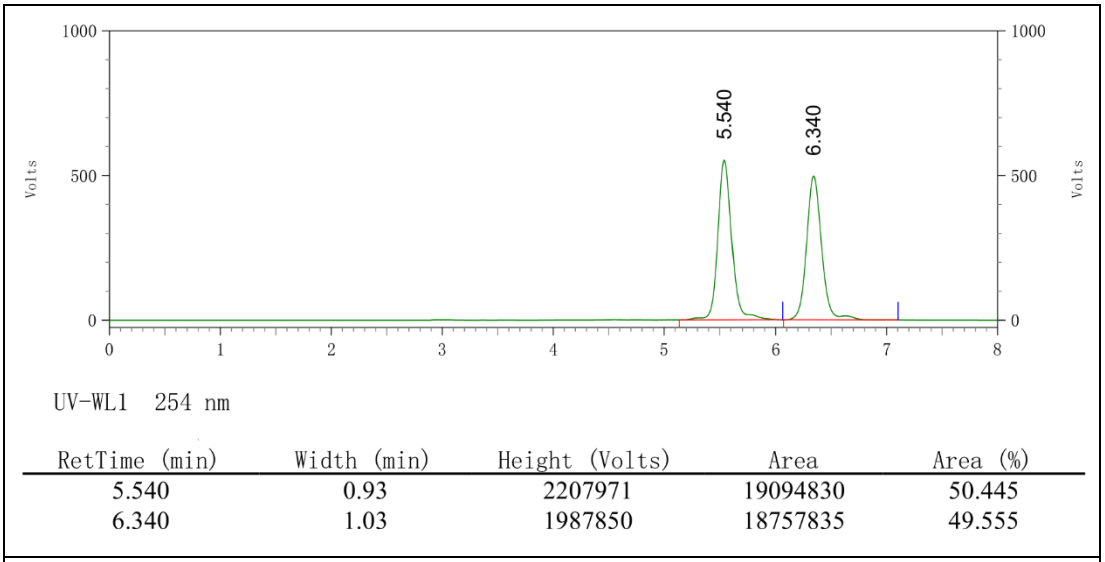
White solid. (R_f = 0.5, PE/EA = 20:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.22 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.62 (s, 1H), 3.08 (d, *J* = 13.3 Hz, 1H), 2.53 (d, *J* = 13.3 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 151.42, 148.35, 133.63, 131.82, 131.35, 130.75, 129.36, 129.17, 128.42, 128.04, 126.65, 126.05, 124.58, 124.14, 123.77, 122.00, 117.40, 115.75, 110.81, 34.94.

HRMS (APCI) *m/z* Calcd for $C_{20}H_{14}BrO_2^+$[M + H]$^+$: 365.0172, Found: 365.0160.

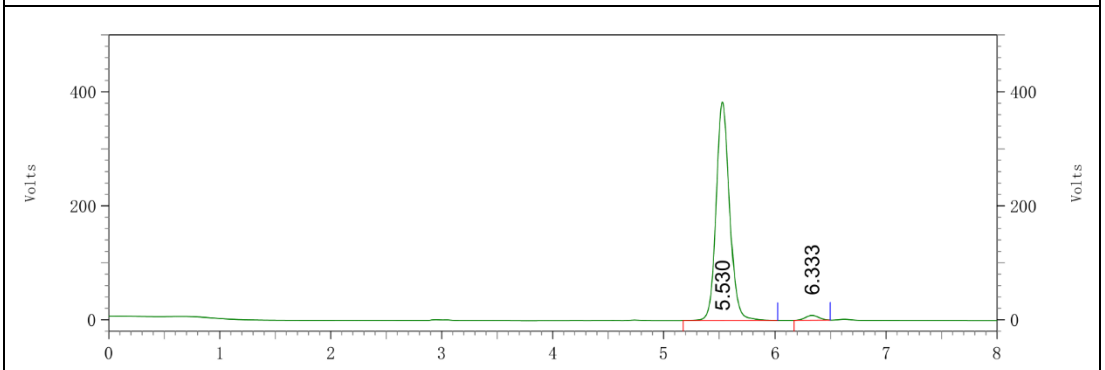
Optical Rotation: $[\alpha]_D^{25}$ = -388° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel IA-H (Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 5.530 min (major), t_R = 6.333 min (minor), 96% **ee**.



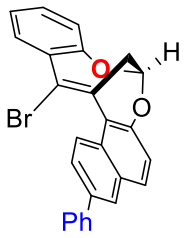
UV-WL1 254 nm

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
5.540	0.93	2207971	19094830	50.445
6.340	1.03	1987850	18757835	49.555



UV-WL1 254 nm

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
5.530	0.85	1534260	12773378	97.789
6.333	0.33	34375	288741	2.211



3p

(*S*)-14-bromo-3-phenyl-8,15-methanobenzo[d]naphtho[1,2-h][1,3]dioxonine (3p)

Compound **3p** was synthesized in 85% yield (225 mg, 0.6 mmol scale) under condition [A]. **3p** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

Pale yellow solid. (R_f = 0.4, PE/DCM = 1:1)

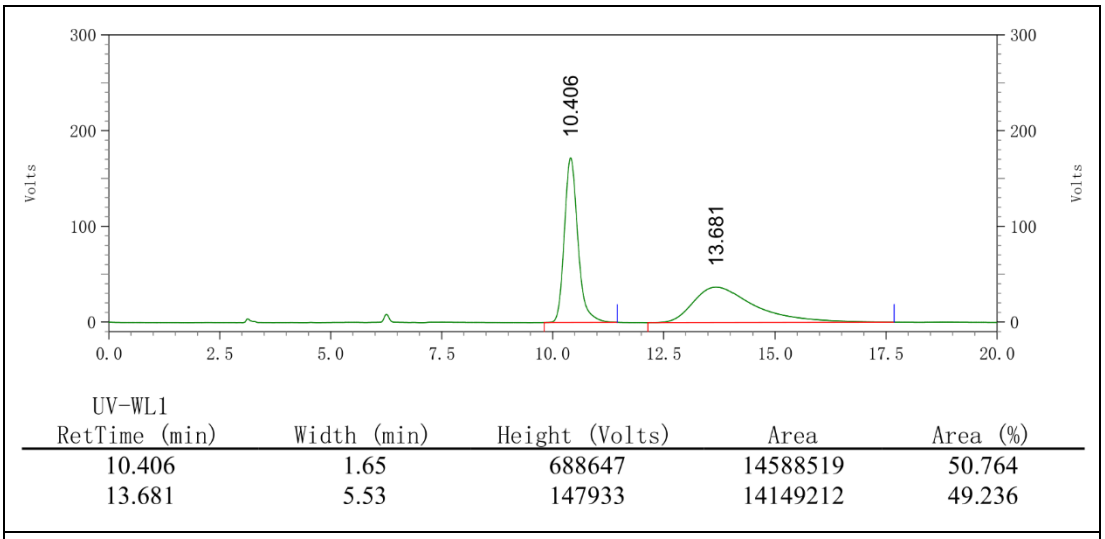
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.6 Hz, 1H), 8.01 (s, 1H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41 – 7.30 (m, 2H), 7.29 – 7.24 (m, 2H), 7.12 (d, *J* = 8.1 Hz, 1H), 6.62 (s, 1H), 3.08 (d, *J* = 13.2 Hz, 1H), 2.53 (d, *J* = 13.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.41, 148.45, 140.99, 136.89, 133.59, 131.75, 131.35, 130.78, 129.65, 129.42, 128.82, 127.59, 127.27, 127.21, 127.17, 125.91, 125.80, 124.60, 123.68, 122.01, 117.83, 115.86, 110.85, 34.93.

HRMS (APCI) *m/z* Calcd for $C_{26}H_{18}BrO_2^+[M + H]^+$: 441.0485, Found: 441.0478.

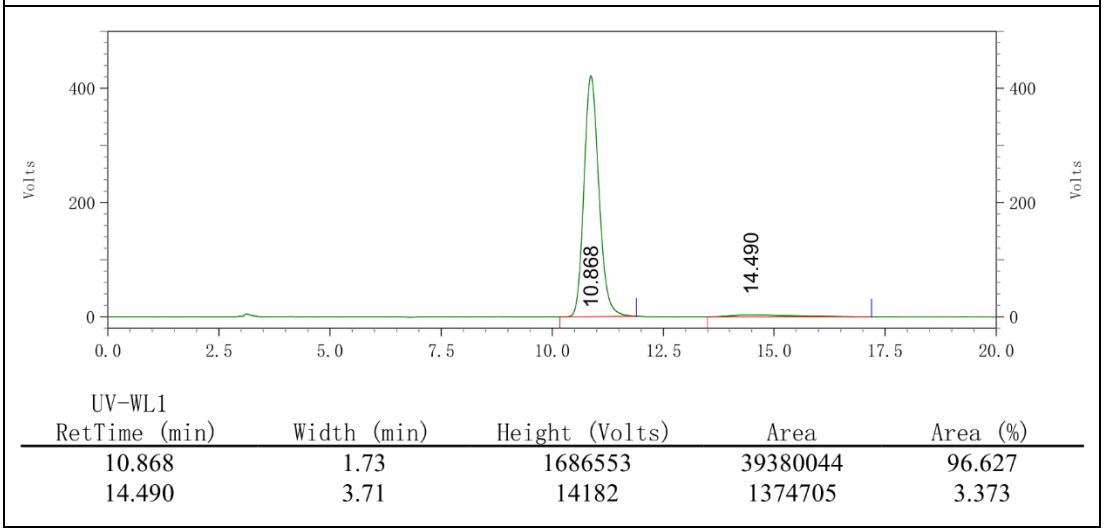
Optical Rotation: $[\alpha]_D^{25}$ = -265.4° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel AS-H (Hexane/*i*-PrOH = 94:6, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 10.868 min (major), t_R = 14.490 min (minor), 93% **ee**.



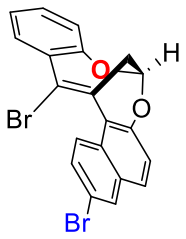
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
10.406	1.65	688647	14588519	50.764
13.681	5.53	147933	14149212	49.236



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
10.868	1.73	1686553	39380044	96.627
14.490	3.71	14182	1374705	3.373



3q

(*S*)-3,14-dibromo-8,15-methanobenzo[d]naphtho[1,2-h][1,3]dioxonine (3q)

Compound **3q** was synthesized in 79% yield (211 mg, 0.6 mmol scale) under condition [A]. **3q** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

Gray solid. (R_f = 0.6, PE/EA = 20:1)

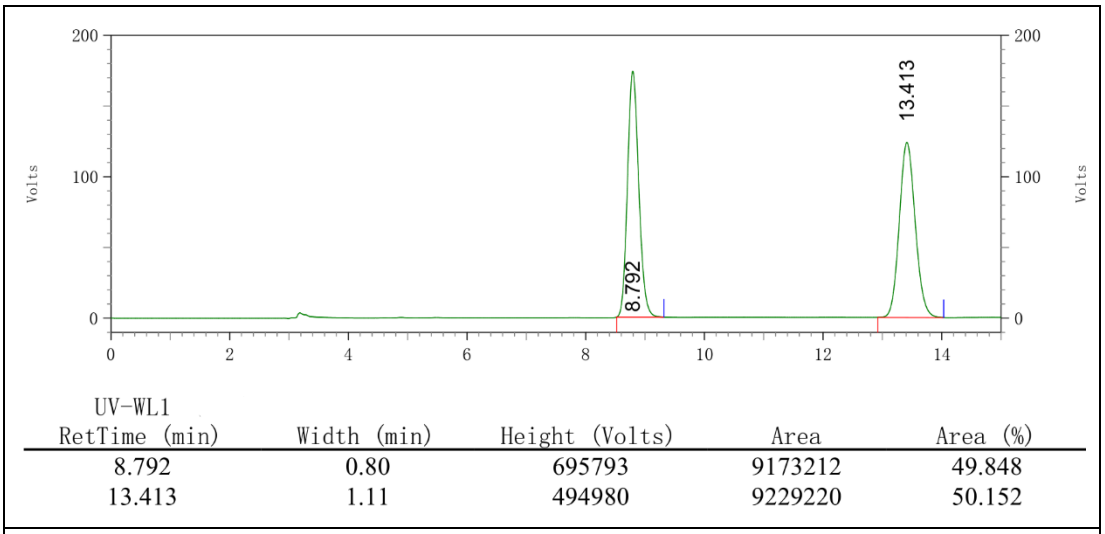
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.89 (d, *J* = 8.9 Hz, 1H), 7.68 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.61 (s, 1H), 3.07 (d, *J* = 13.2 Hz, 1H), 2.51 (d, *J* = 13.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.31, 148.61, 133.42, 131.35, 131.19, 130.91, 130.21, 129.96, 129.38, 128.38, 126.95, 124.69, 123.89, 122.02, 118.51, 117.90, 116.28, 110.83, 34.79.

HRMS (APCI) *m/z* Calcd for $C_{20}H_{13}Br_2O_2^+[M + H]^+$: 444.9256, Found: 444.9247

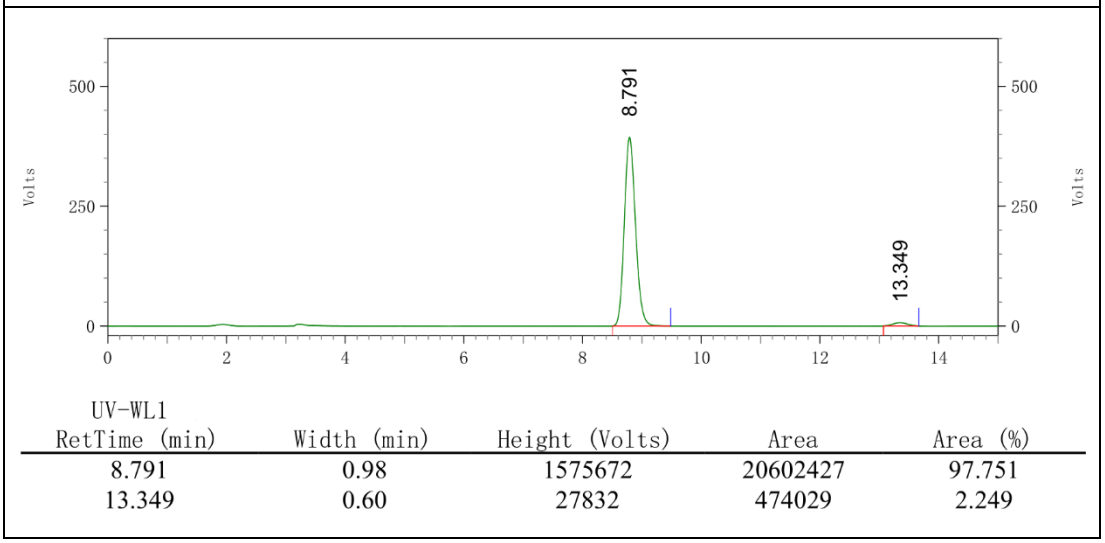
Optical Rotation: $[\alpha]_D^{25}$ = -345.4° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 8.791 min (major), t_R = 13.349 min (minor), 96% **ee**.



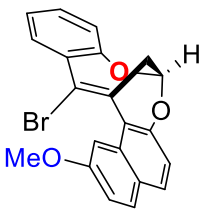
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
8.792	0.80	695793	9173212	49.848
13.413	1.11	494980	9229220	50.152



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
8.791	0.98	1575672	20602427	97.751
13.349	0.60	27832	474029	2.249



3r

(*S*)-14-bromo-2-methoxy-8,15-methanobenzo[d]naphtho[1,2-h][1,3]dioxonine (3r)

Compound **3r** was synthesized in 84% yield (199 mg, 0.6 mmol scale) under condition [A]. **3r** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

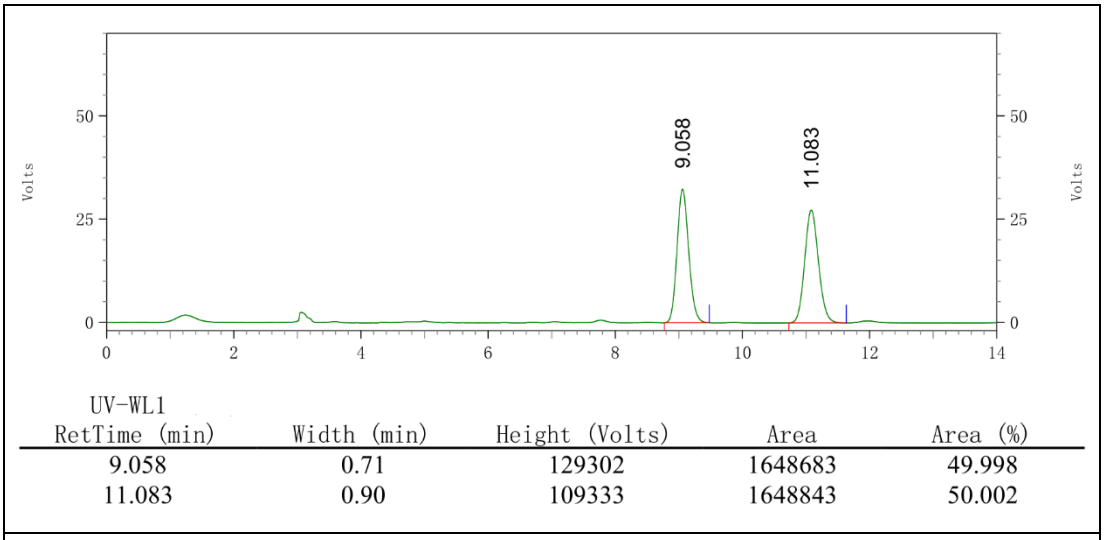
White solid. (R_f = 0.5, PE/EA= 20:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.9 Hz, 2H), 7.64 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.30 – 7.26 (m, 1H), 7.25 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.10 – 7.02 (m, 2H), 6.61 (d, *J* = 1.9 Hz, 1H), 4.00 (s, 3H), 3.07 (d, *J* = 13.2 Hz, 1H), 2.53 (dd, *J* = 13.2, 2.1 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.97, 151.51, 148.98, 133.67, 132.04, 131.29, 130.74, 129.66, 129.47, 129.07, 124.61, 124.53, 122.91, 122.02, 116.99, 115.57, 114.83, 110.75, 105.20, 55.47, 35.14.

HRMS (APCI) *m/z* Calcd for $C_{21}H_{16}BrO_3^+[M + H]^+$: 395.0277, Found: 395.0265.

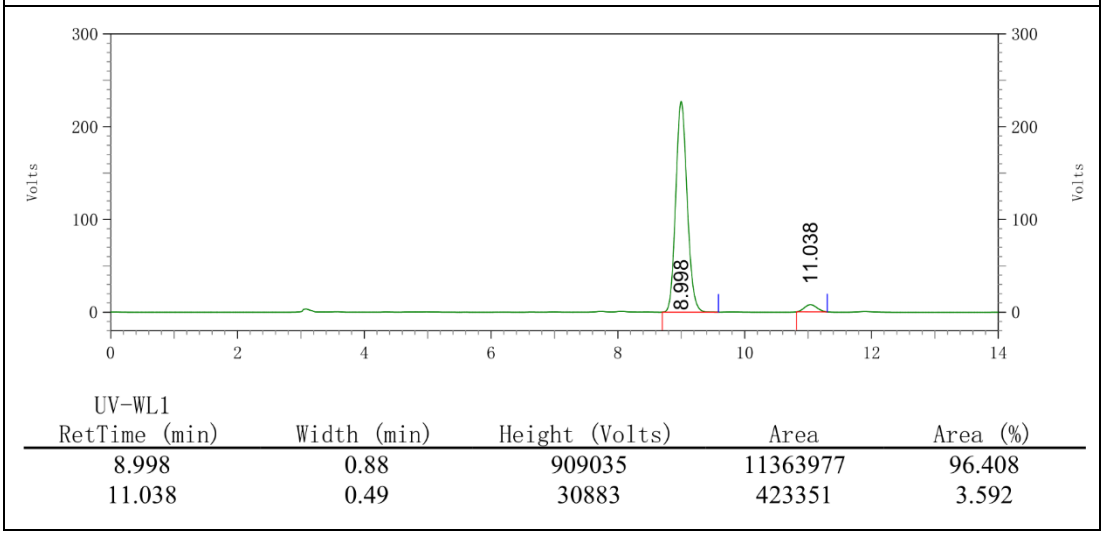
Optical Rotation: $[\alpha]_D^{25}$ = -199.6° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 8.998 min (major), t_R = 11.038 min (minor), 93% **ee**.



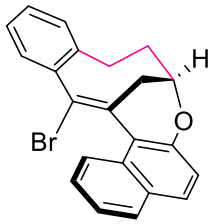
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
9.058	0.71	129302	1648683	49.998
11.083	0.90	109333	1648843	50.002



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
8.998	0.88	909035	11363977	96.408
11.038	0.49	30883	423351	3.592



3s

(*S*, *Z*)-15-bromo-9,10-dihydro-8H-8,16-methanobenzo[f]naphtho[2,1-b]oxecine (3s)

Compound **3s** was synthesized in 33% yield (75 mg, 0.6 mmol scale) under condition [A]. **3s** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

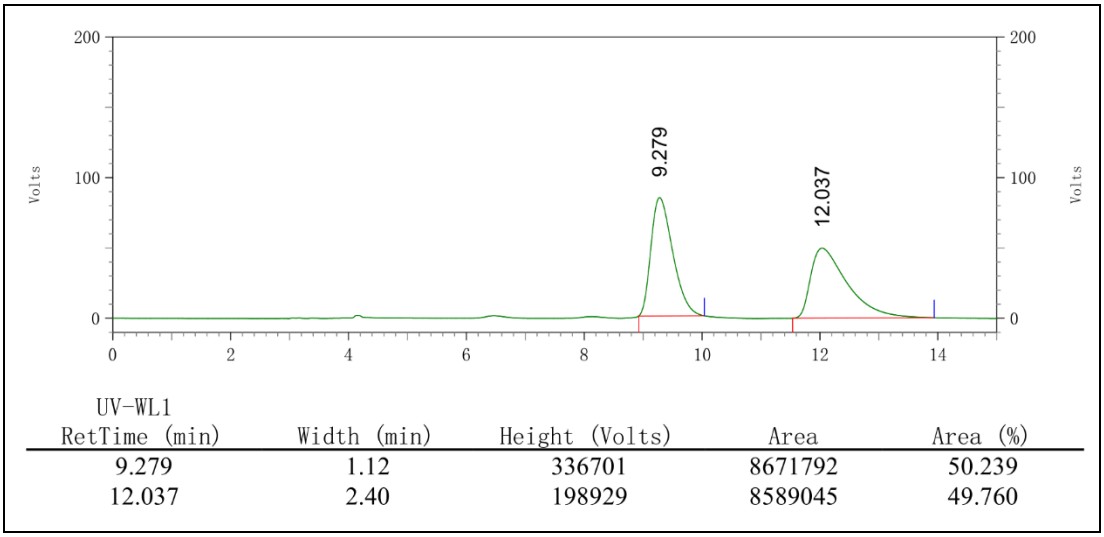
Yellow solid. (R_f = 0.5, PE/EA = 20:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.61 – 7.52 (m, 2H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.35 – 7.29 (m, 3H), 7.18 (d, *J* = 8.8 Hz, 1H), 4.73 – 4.70 (m, 1H), 3.07 (t, *J* = 13.5 Hz, 1H), 2.72 – 2.67 (m, 1H), 2.63 (d, *J* = 12.6 Hz, 1H), 2.52 – 2.43 (m, 2H), 1.81 – 1.74 (m, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 152.97, 141.81, 140.15, 130.40, 129.49, 129.45, 129.18, 128.92, 128.59, 128.38, 128.15, 126.50, 126.48, 125.73, 123.54, 122.59, 118.64, 118.43, 73.90, 36.14, 35.34, 27.53.

HRMS (APCI) *m/z* Calcd for $C_{22}H_{18}BrO^+[M + H]^+$: 377.0536, Found: 377.0521.

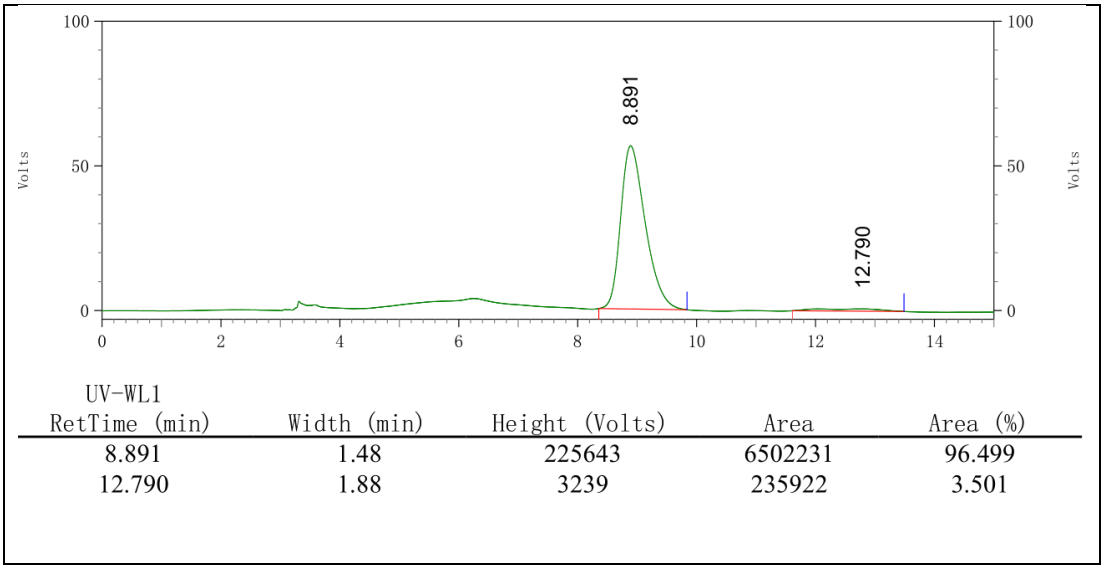
Optical Rotation: $[\alpha]_D^{25}$ = -442.4° (*c* = 0.55, DCM).

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH = 99:1, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 8.891 min (major), t_R = 12.790 min (minor), 93% **ee**.



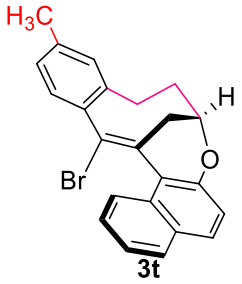
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
9.279	1.12	336701	8671792	50.239
12.037	2.40	198929	8589045	49.760



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
8.891	1.48	225643	6502231	96.499
12.790	1.88	3239	235922	3.501



(*S*, *Z*)-15-bromo-12-methyl-9,10-dihydro-8H-8,16-methanobenzo[f]naphtho[2,1-b]oxecine (3t)

Compound **3t** was synthesized in 35% yield (82 mg, 0.6 mmol scale) under condition [A]. **3t** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

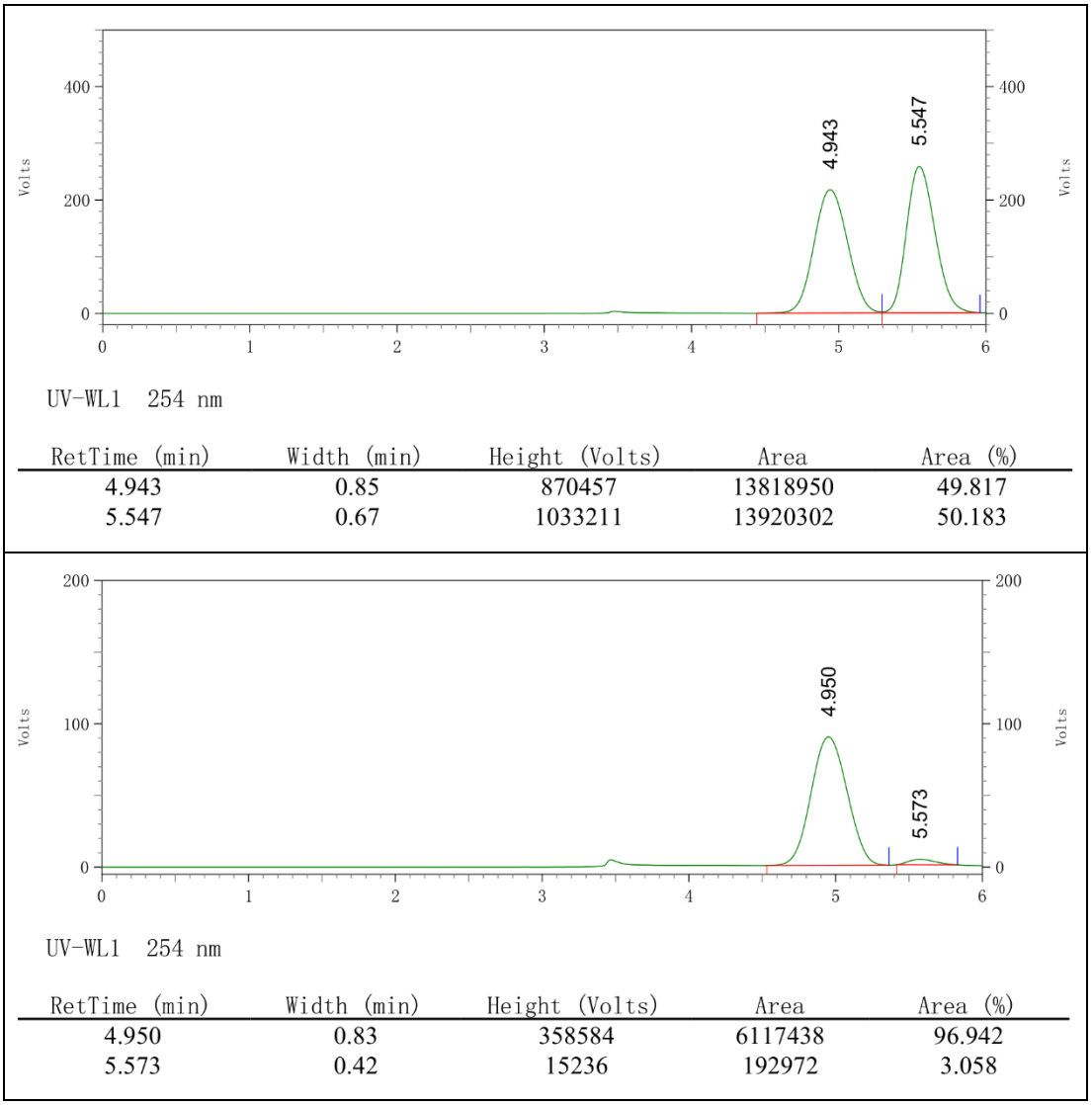
Yellow solid. (R_f = 0.5, PE/EA = 20:1)

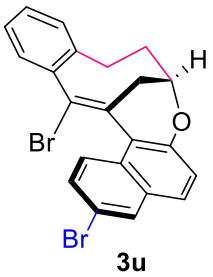
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.8 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.38 (t, 1H), 7.18 (d, *J* = 8.8 Hz, 1H), 7.16 – 7.09 (m, 2H), 4.73 – 4.69 (m, 1H), 3.03 (t, *J* = 13.5 Hz, 1H), 2.67 – 2.62 (m, 2H), 2.50 – 2.42 (m, 2H), 2.38 (s, 3H), 1.76 (t, *J* = 14.0 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 152.99, 141.67, 139.08, 137.42, 130.17, 130.13, 129.41, 128.91, 128.44, 128.41, 128.12, 127.29, 126.54, 125.67, 123.50, 122.70, 118.91, 118.43, 74.02, 36.12, 35.39, 27.50, 21.34.

HRMS (APCI) *m/z* Calcd for $C_{23}H_{20}BrO^+[M + H]^+$: 391.0692, Found: 391.0683.

Optical Rotation: $[\alpha]_D^{25}$ = -266.6° (*c* = 0.5, DCM).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 4.950 min (major), t_R = 5.573 min (minor), 94% **ee**.





3u

(*S*, *Z*)-3,15-dibromo-9,10-dihydro-8H-8,16-methanobenzo[f]naphtho[2,1-b]oxecine (3u)

Compound **3u** was synthesized in 32% yield (88 mg, 0.6 mmol scale) under condition [A]. **3u** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

White solid. (R_f = 0.5, PE/EA = 20:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.86 (m, 2H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.61 (dd, *J* = 8.8, 1.9 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.37 – 7.28 (m, 3H), 7.19 (d, *J* = 8.8 Hz, 1H), 4.75 – 4.70 (m, 1H), 3.03 (t, *J* = 13.5 Hz, 1H), 2.69 (dd, *J* = 14.1,

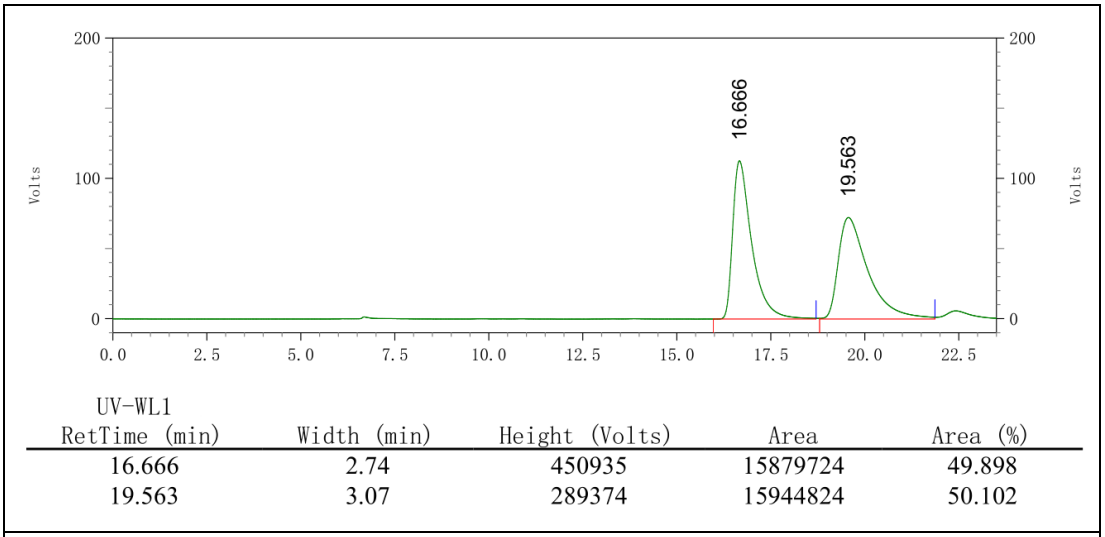
7.0 Hz, 1H), 2.63 (d, *J* = 12.7 Hz, 1H), 2.49 (dd, *J* = 15.2, 6.9 Hz, 1H), 2.44 (dd, *J* = 12.7, 8.7 Hz, 1H), 1.78 (t, *J* = 14.1 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 153.29, 141.71, 139.93, 130.04, 130.01, 129.92, 129.48, 129.31, 129.01, 128.55, 128.53, 128.27, 126.93, 126.56, 122.66, 119.56, 119.13, 117.23, 74.09, 36.08, 35.18, 27.49.

HRMS (APCI) *m/z* Calcd for $C_{22}H_{17}Br_2O^+[M + H]^+$: 456.9620, Found: 456.9609.

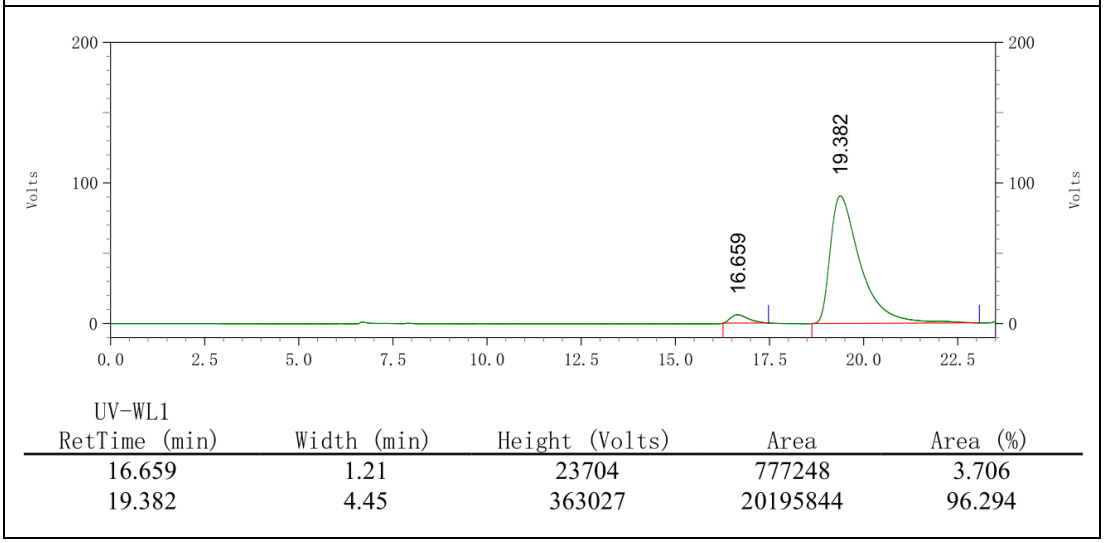
Optical Rotation: $[\alpha]_D^{25}$ = -388° (*c* = 0.3, DCM).

HPLC analysis: Chiralcel ADAD-H (Hexane/*i*-PrOH = 99:1, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 16.659 min (minor), t_R = 19.382 min (major), 93% **ee**.



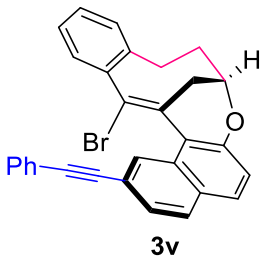
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
16.666	2.74	450935	15879724	49.898
19.563	3.07	289374	15944824	50.102



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
16.659	1.21	23704	777248	3.706
19.382	4.45	363027	20195844	96.294



3v

(*S*, *Z*)-15-bromo-2-(phenylethynyl)-9,10-dihydro-8H-8,16-methanobenzo[f]naphtho[2,1-b]oxecine (3v)

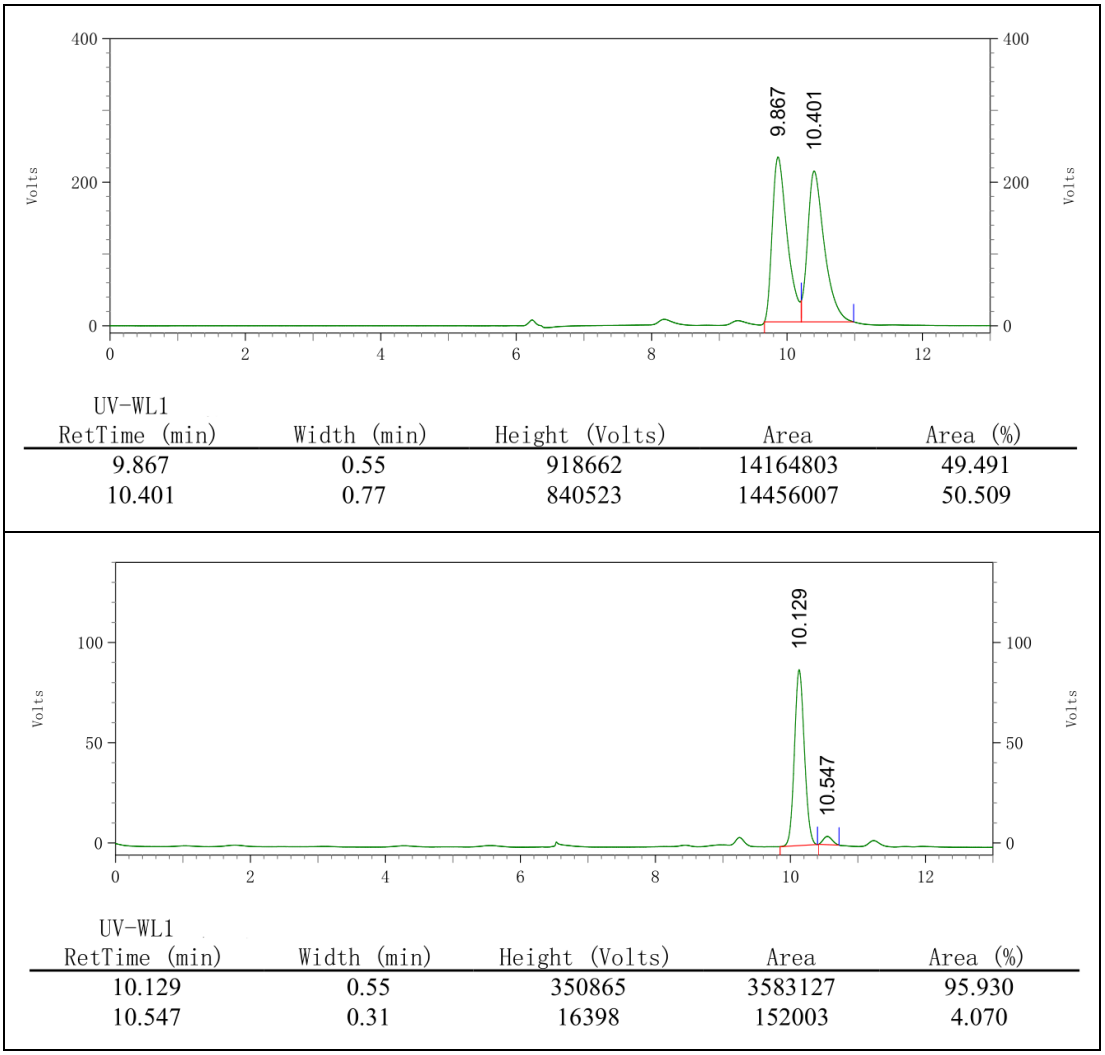
Compound **3v** was synthesized in 33% yield (95 mg, 0.6 mmol scale) under condition [A]. **3v** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

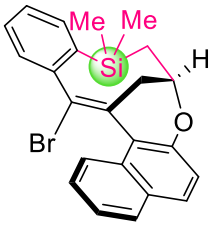
White solid. (R_f = 0.5, PE/EA = 20:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.76 (dd, *J* = 16.8, 8.6 Hz, 2H), 7.63 (d, *J* = 7.2 Hz, 3H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.33 (d, *J* = 5.7 Hz, 3H), 7.19 (d, *J* = 8.7 Hz, 1H), 4.74 – 4.72 (m, 1H), 3.05 (s, 1H), 2.70 (d, *J* = 7.1 Hz, 1H), 2.64 (s, 1H), 2.51 – 2.45 (m, 2H), 1.79 (d, *J* = 14.2 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 153.56, 141.71, 140.05, 131.75, 129.98, 129.93, 129.44, 129.29, 129.24, 128.73, 128.35, 128.29, 128.24, 128.13, 126.54, 126.24, 123.47, 122.45, 120.55, 119.18, 119.08, 90.39, 89.63, 74.07, 36.14, 35.21, 27.50.
HRMS (APCI) *m/z* Calcd for $C_{30}H_{22}BrO^+[M + H]^+$: 477.0849, Found: 477.0841.

Optical Rotation: $[\alpha]_D^{25}$ = -411.4° (*c* = 0.5, DCM).

HPLC analysis: Chiralcel ADAD-H (Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 10.129 min (major), t_R = 10.547 min (minor), 92% **ee**.





3w

(*R, Z*)-16-bromo-5,5-dimethyl-6,7-dihydro-5H-7,15-methanobenzo[e]naphtho[1,2-i][1,4]oxasilecine (3w)

Compound **3w** was synthesized in 52% yield (131 mg, 0.6 mmol scale) under condition [A]. **3w** was purified by silica gel column chromatography using PE:EA (60:1 to 50:1) as eluent.

White solid. (R_f = 0.5, PE/EA = 20:1)

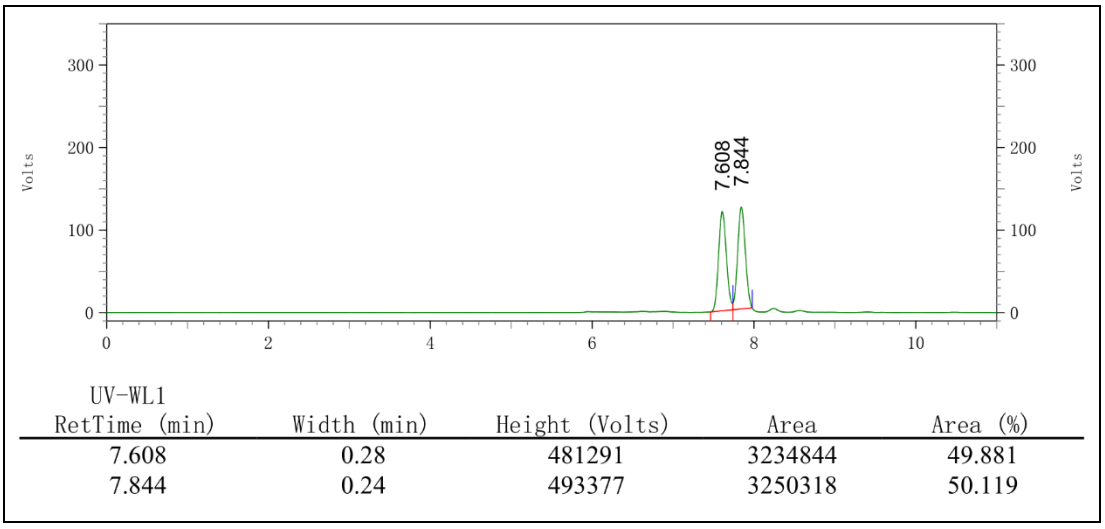
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.88 – 7.70 (m, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.41 – 7.28 (m, 2H), 7.10 (d, *J* = 8.8 Hz, 1H), 4.99 – 4.90 (m, 1H), 2.88 (d, *J* = 12.6 Hz, 1H), 2.54 (dd, *J* = 12.6, 5.9 Hz, 1H), 1.51 (dd, *J* = 14.7, 7.4 Hz, 1H), 1.29 (dd, *J* = 14.7, 4.9 Hz, 1H), 0.39 (s, 3H), 0.24 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 152.28, 145.87, 138.59, 133.85, 130.36, 130.33, 129.36, 129.03, 128.82, 128.71, 128.18, 127.77, 126.60, 125.66, 123.32, 121.63, 119.10, 118.58, 75.09, 35.96, 23.81, -0.93, -1.74.

HRMS (APCI) *m/z* Calcd for $C_{23}H_{22}BrOSi^+[M + H]^+$: 421.0618, Found: 421.0607.

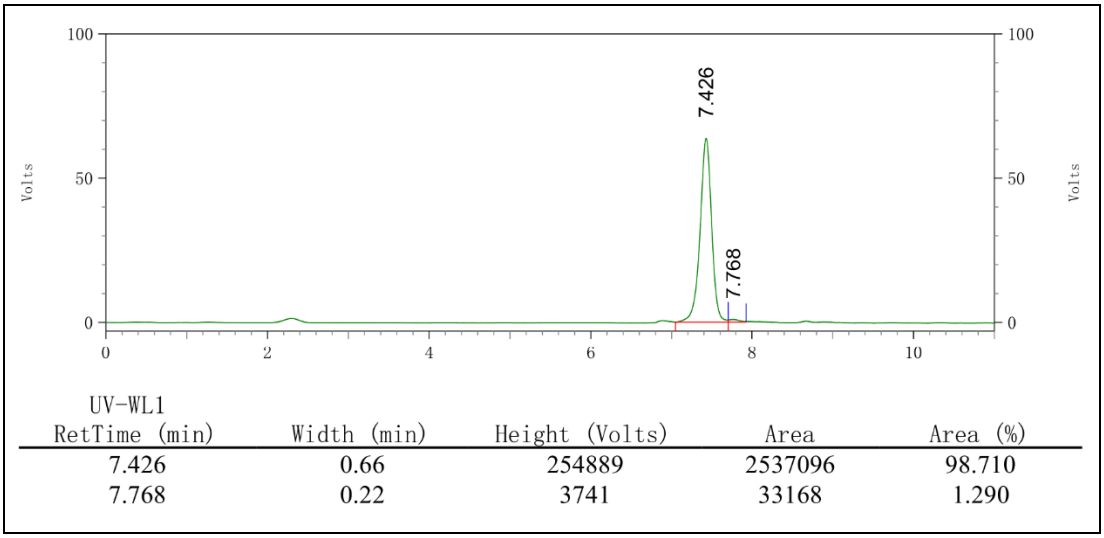
Optical Rotation: $[\alpha]_D^{25}$ = -323.3° (*c* = 0.75, DCM).

HPLC analysis: Chiralcel ADAD-H (Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 7.426 min (major), t_R = 7.768 min (minor), 97% **ee**.



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
7.608	0.28	481291	3234844	49.881
7.844	0.24	493377	3250318	50.119



UV-WL1

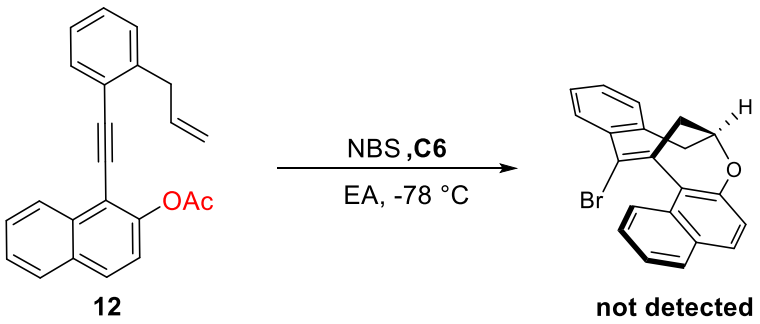
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
7.426	0.66	254889	2537096	98.710
7.768	0.22	3741	33168	1.290

Unsuccessful attempt for the construction of the [6.3.1] ring system

We synthesized substrate **1x** and evaluated the construction of the [6.3.1] ring system under the standard reaction conditions. Unfortunately, we did not observe the trace of the generation of the [6.3.1] ring system.

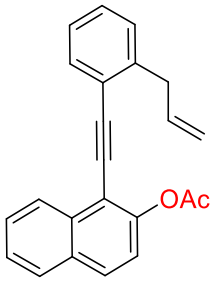
VIII. Mechanistic studies

1) Control experiments



12 **not detected**

Compound **12** was prepared according to the general procedure. The control experiment was carried out following the general procedure (Condition [A]).



12

1-((2-allylphenyl)ethynyl)naphthalen-2-yl acetate (12)

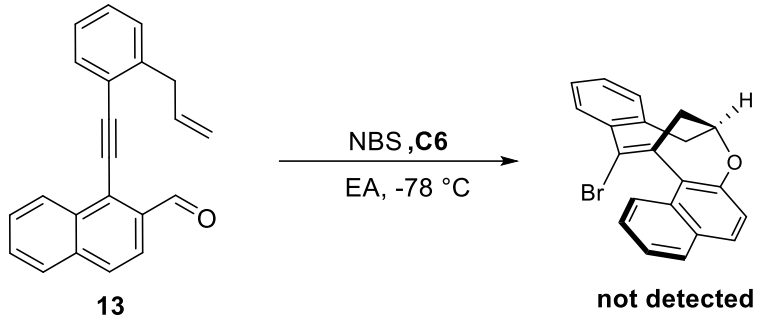
Compound **12** is an unknown compound, and was synthesized in 43% yield (280 mg, 2 mmol scale) following the general procedure (**Method A**).

yellow solid. (R_f = 0.5, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.4 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.27 – 7.12 (m, 4H), 6.06 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.19 – 5.03 (m, 2H), 3.70 (d, *J* = 6.7 Hz, 2H), 2.33 (s, 3H).

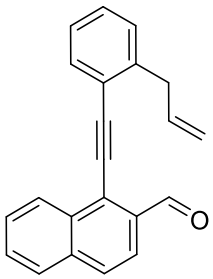
^{13}C NMR (100 MHz, $CDCl_3$) δ 168.66, 149.94, 141.54, 136.14, 133.53, 132.18, 131.00, 129.45, 128.74, 128.69, 128.01, 127.14, 126.04, 125.93, 125.83, 122.39, 121.00, 116.20, 113.07, 97.85, 86.26, 38.57, 20.75.

HRMS (ESI) *m/z* Calcd for $C_{23}H_{16}NaO_2^+$[M + Na]$^+$: 349.1199, Found: 349.1186.



13 **not detected**

Compound **13** was prepared according to the general procedure as described for **S6**. The control experiment was carried out following the general procedure (Condition [A]).



13

1-((2-allylphenyl)ethynyl)-2-naphthaldehyde (13)

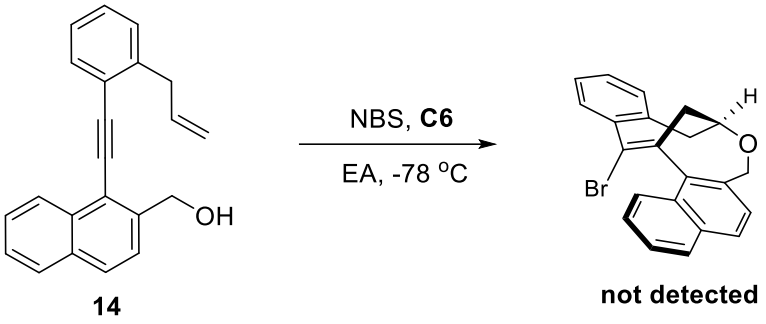
Compound **13** was synthesized following the general procedure (**Method A**).

Pale yellow solid. (R_f = 0.6, PE/EA= 10:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.88 (s, 1H), 8.61 (dd, *J* = 6.3, 3.4 Hz, 1H), 7.99 (d, *J* = 8.6 Hz, 1H), 7.93 – 7.82 (m, 2H), 7.74 – 7.62 (m, 3H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.31 (dd, *J* = 13.9, 7.1 Hz, 2H), 6.16 – 6.03 (m, 1H), 5.20 – 5.01 (m, 2H), 3.75 (d, *J* = 6.0 Hz, 2H).

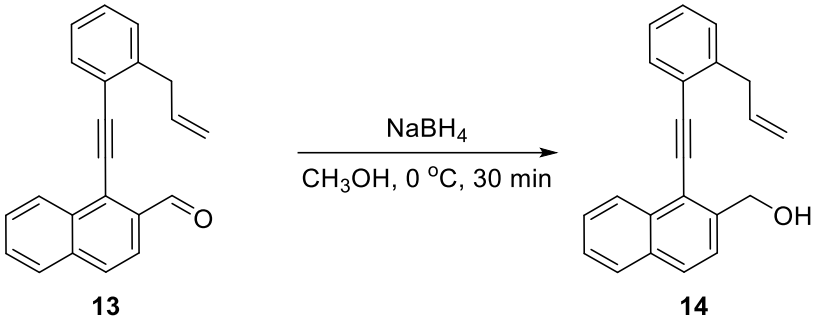
^{13}C NMR (100 MHz, $CDCl_3$) δ 192.09, 142.12, 136.16, 135.79, 134.19, 133.14, 132.71, 129.59, 129.34, 129.31, 128.86, 128.47, 127.67, 127.56, 127.27, 126.43, 122.08, 121.99, 116.56, 101.05, 86.57, 38.89.

HRMS (ESI) *m/z* Calcd for $C_{22}H_{16}NaO^+$[M + Na]$^+$: 319.1093, Found: 319.1105.



14 **not detected**

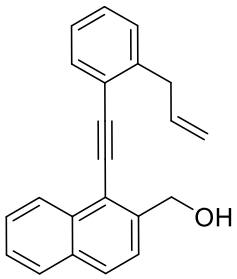
Compound **14** was prepared according to the general procedure as following. The control experiment was carried out following the general procedure (Condition [A]).



13 **14**

General procedure for the synthesis of **14**:

To a solution of the **13** (1.48 g, 5.0 mmol, 1.0 equiv.) in methanol (0.5 M) was added $NaBH_4$ (190 mg, 5 mmol, 1.0 equiv.) under a nitrogen atmosphere at 0°C. After 30 min, the mixture was quenched with saturated aqueous $NHCl_4$ solution, extracted with EA, and then washed 3 times with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (PE/EA = 10:1) to afford compound **14** (90% yield).



14

(1-((2-allylphenyl)ethynyl)naphthalen-2-yl)methanol (14)

Pale yellow solid. (R_f = 0.4, PE/EA= 5:1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.5 Hz, 2H), 7.71 – 7.44 (m, 4H), 7.36 – 7.19 (m, 3H), 6.18 – 6.02 (m, 1H), 5.26 – 4.96 (m, 4H), 3.73 (d, *J* = 6.3 Hz, 2H), 2.28 (s, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 141.59, 141.19, 136.44, 133.27, 132.54, 132.48, 129.12, 128.90, 128.80, 128.18, 126.97, 126.27, 126.14, 125.11, 122.69, 118.40, 116.28, 98.30, 88.55, 64.32, 38.82.

HRMS (ESI) *m/z* Calcd for $C_{22}H_{17}O^-$[M - H]$^-$: 297.1285, Found: 297.1279.

2) Density Functional Theory (DFT) Experiments

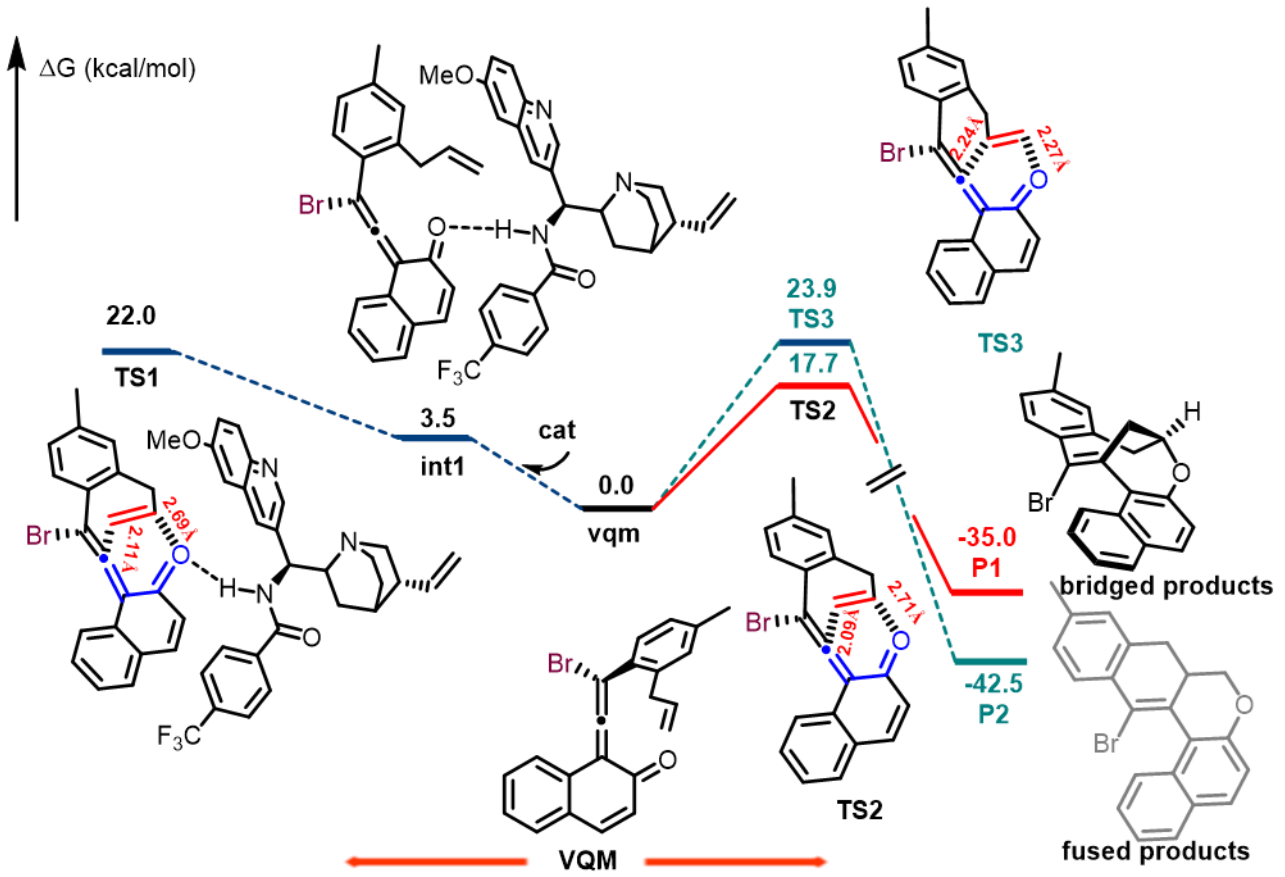
Computational Methods.

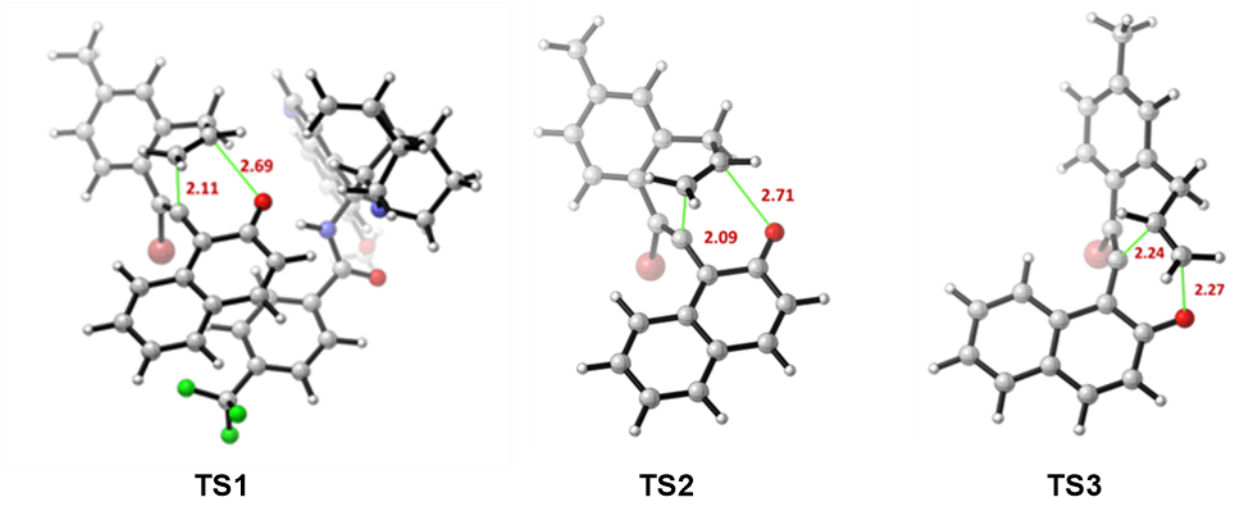
All density functional theory (DFT) calculations were performed with the Gaussian 09[1] software package. Geometries were optimized in toluene with the SMD solvation model[2] using the B3-LYP-D3[3] functional and a basis set of 6-31G(d)[4]. Vibrational frequencies were computed at the same level to evaluate its zero-point vibrational energy and thermal corrections at 298 K, and to check whether each optimized structure is a transition state or not. The single-point energies and solvent effects in ethylethanoate were computed at the M06-2X level of theory with the 6-311+G(d,p)[5] basis set, using the solvent-phase optimized structures. Intrinsic reaction coordinate (IRC) calculations have demonstrated that the transition state connects two corresponding intermediates along the reaction coordinate.

B3-LYP-D3 and M06-2X calculated absolute energies, and free energies of all structures

Geometry	$E_{(elec\text{-}B3\text{-}LYP\text{-}D3)}$[1]	$G_{(corr\text{-}B3\text{-}LYP\text{-}D3)}$[2]	$H_{(corr\text{-}B3\text{-}LYP\text{-}D3)}$[3]	$E_{(solv\text{-}M06\text{-}2X)}$[4]	IF[5]
VQM	-3495.19	0.2686	0.3444	-3497.78	
TS1	-5193.34	0.7559	0.8985	-5195.68	-326.12 *i*
TS2	-3495.17	0.2717	0.3429	-3497.75	-382.09*i*
TS3	-3495.17	0.2733	0.3431	-3497.74	-388.57 *i*
P1	-3495.25	0.2818	0.3482	-3497.85	
P2	-3495.27	0.2813	0.3482	-3497.86	
cat	-1698.13	0.4576	0.5532	-1697.90	
int1	-5193.35	0.7493	0.9001	-5195.70	
OMe-TS2	-3609.70	0.3035	0.3786	-3612.27	-368.24 *i*
OMe-TS3	-3609.71	0.3026	0.3792	-3612.28	-184.53 *i*
O-TS2	-3531.07	0.2470	0.3185	-3533.66	-314.23 *i*
O-TS3	-3531.06	0.2486	0.3182	-3533.65	-406.59 *i*

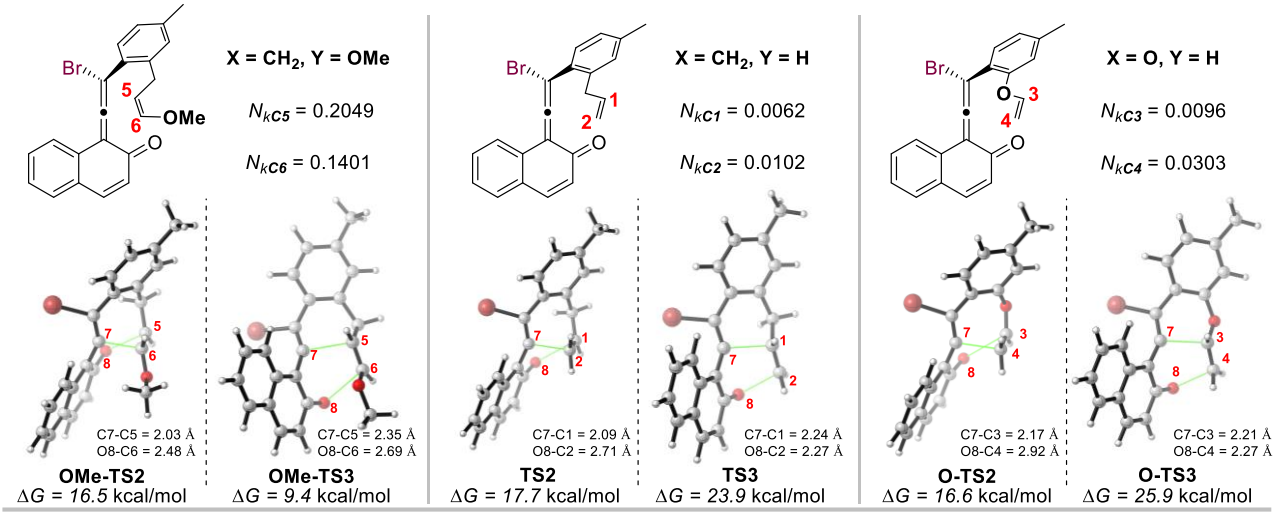
[1]The electronic energy calculated by B3-LYP-D3 in ethylethanoate solvent. [2]The thermal correction to Gibbs free energy calculated by B3-LYP-D3 in ethylethanoate solvent. [3]The thermal correction to enthalpy calculated by B3-LYP-D3 in ethylethanoate solvent. [4]The electronic energy calculated by M06-2X in ethylethanoate solvent. [5]The B3-LYP-D3 calculated imaginary frequencies for the transition states.


ΔG (kcal/mol)
22.0
TS1
3.5
int1
cat
0.0
vqm
23.9
TS3
17.7
TS2
-35.0
P1
-42.5
P2
TS3
bridged products
fused products
TS2
VQM
Bifunctional-catalyed IEDHDAR process
Chirality transfer process


2.69
2.11
2.71
2.09
2.24
2.27

TS1 TS2 TS3

b. Optimized transition state structures associated with pathway A-1 and pathway A-2 for three different substituted VQM intermediates



References:

1. 9 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E.Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov,J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J.Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R.Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H.Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F.Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov,T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C.Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C.Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas,J. B. Foresman, D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.
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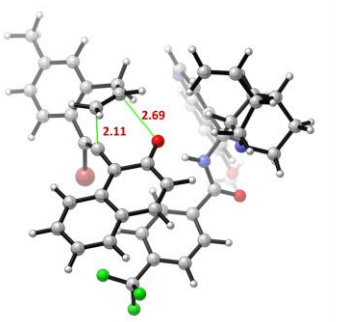
5. Krishnan, R., Binkley, J. S., Seeger, R. & Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650-654.

Cartesian coordinates of the structures

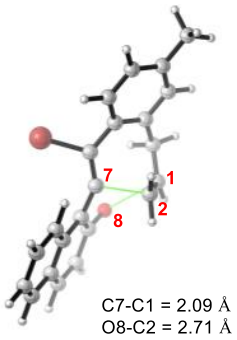


TS1

C	-3.91548500	2.42402200	-0.33569900
C	-4.33148900	1.68027000	1.79159100
C	-3.88788000	0.35060000	1.48183400
C	-3.43897100	0.09423400	0.14069200
C	-3.45294800	1.14849900	-0.74692000
H	-5.10344000	2.97636700	3.32356600
H	-3.92324900	3.24256100	-1.05508700
C	-4.77237700	1.96460300	3.10779800
C	-3.89984000	-0.62801400	2.50307700
H	-3.11172600	1.03191100	-1.76876700
C	-4.33690100	-0.31699000	3.78212100
C	-4.77854100	0.99746200	4.08879200
H	-3.55391400	-1.63954500	2.32039900
H	-5.11817400	1.24972100	5.08650900
N	-4.34385900	2.69894100	0.87801500
O	-4.30884800	-1.33418500	4.68596000
C	-4.70411400	-1.07190600	6.03042500
H	-5.75394900	-0.75668800	6.09189200
H	-4.58462400	-2.01743000	6.56392700
H	-4.06618800	-0.31160800	6.49935900
C	-2.89089800	-1.28422800	-0.21692500
H	-3.53042800	-2.04362600	0.23683800
N	-1.57586500	-1.41550500	0.40109300
H	-0.85416200	-0.87034000	-0.07127300
C	-1.21237700	-2.51422700	1.10860700
C	-2.79908600	-1.55622100	-1.73387700
C	-4.18896100	-1.53567800	-2.43298000
H	-2.15553900	-0.78450900	-2.16072300
C	-2.96590600	-3.99258700	-1.78650400
C	-1.69909400	-2.81092000	-3.44299500
C	-4.19540000	-2.64543000	-3.50173500
H	-4.99479200	-1.71869500	-1.70966500
H	-4.38105700	-0.55835400	-2.88469300
H	-2.35329400	-4.89462500	-1.89408400
H	-3.29809700	-3.96435700	-0.74590100
C	-4.16646700	-4.00650600	-2.78082400
C	-2.91402900	-2.52273000	-4.38252800
H	-1.26898600	-3.79058800	-3.67776500
H	-0.90022700	-2.07638600	-3.57235300

H	-5.08832800	-2.56276300	-4.13198300
H	-4.06466100	-4.81752600	-3.51324700
H	-5.11203800	-4.16765200	-2.24884300
H	-2.97505400	-3.31366600	-5.14408700
N	-2.09061800	-2.82639700	-2.02092500
C	-2.89739700	-1.20476900	-5.12294800
C	-2.04567000	-0.18372800	-4.98800400
H	-3.71627500	-1.09553500	-5.83794700
H	-2.15943300	0.72167200	-5.58014900
H	-1.20556300	-0.20371500	-4.29868100
O	-2.00169900	-3.39200700	1.47728100
C	0.25688800	-2.59977700	1.42201400
C	1.04546400	-1.46488400	1.65082800
C	0.85030700	-3.86938100	1.43803200
C	2.41788600	-1.59234200	1.85569600
H	0.59878600	-0.47620400	1.66037600
C	2.22238800	-3.99995200	1.62382600
H	0.22726500	-4.74298700	1.27696300
C	3.00579700	-2.85655500	1.82232500
H	3.02686400	-0.70964500	2.00744600
H	2.68779900	-4.98068300	1.60159500
C	4.48741400	-3.01737600	2.00423800
F	5.01441200	-3.85450900	1.07401300
F	4.79523000	-3.55614900	3.21187300
F	5.15474100	-1.84737500	1.91438500
Br	2.21562200	2.18078200	1.80542400
O	0.10410300	0.06628800	-1.40140700
C	1.36165700	4.08953600	-0.21277300
C	1.27215600	-0.41958000	-1.40649100
C	3.76870900	-0.08545200	-1.17658600
C	1.86849600	2.71190800	-0.05405300
C	2.01466300	5.16223700	0.41490100
H	2.89795300	4.96794400	1.01567700
C	2.10367700	1.76458600	-0.94318100
C	1.58573200	2.56148500	-2.83390400
H	2.09974500	1.91140400	-3.53583400
H	2.10425400	3.48340800	-2.58399700
C	4.90071700	0.71326600	-0.91149900
H	4.76489300	1.77120300	-0.70489600

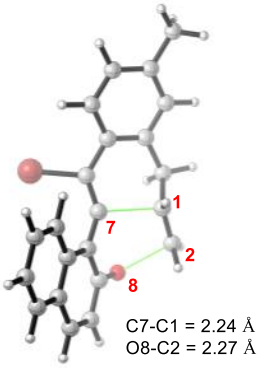
C	1.52805700	-1.82291800	-1.67111000
H	0.66172100	-2.46233800	-1.81188800
C	0.23173500	2.43827200	-2.66245200
H	-0.31134700	1.66187100	-3.19008500
C	2.41826800	0.43585700	-1.13960200
C	1.54873700	6.46474600	0.27560600
H	2.07759400	7.27877900	0.76500600
C	3.95067000	-1.47479800	-1.43591800
C	5.25269400	-2.01476800	-1.42381400
H	5.38096000	-3.07808300	-1.60733600
C	-0.55357000	3.22661700	-1.66378700
H	-1.46645500	3.61331900	-2.13437300
H	-0.89419900	2.48922000	-0.91868600
C	6.17263300	0.15883000	-0.90720400
H	7.03335000	0.78832900	-0.69765700
C	0.40230500	6.73703400	-0.48425200
C	-0.13632100	8.14117900	-0.60212000
H	-0.80249200	8.37485800	0.23954300
H	-0.71442800	8.27485700	-1.52277000
H	0.67075000	8.88215300	-0.59176100
C	0.20281100	4.34417000	-0.98290900
C	2.79729600	-2.31026500	-1.67305100
H	2.97069000	-3.37081400	-1.84236400
C	6.35343200	-1.21188400	-1.16412500
H	7.35111700	-1.64135500	-1.15134300
C	-0.24612300	5.66276900	-1.10470700
H	-1.13834900	5.85514100	-1.69665800



TS2

Br	0.28872400	-1.66783500	1.72118600
O	-1.02579100	2.60678300	1.20027400
C	2.15794200	-0.28984800	-0.03773800

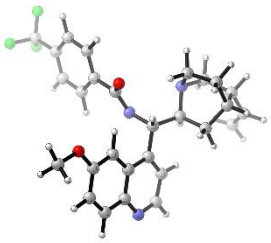
C	-1.94173900	1.88058900	0.74676900
C	-2.69250400	-0.19122500	-0.51956400
C	0.72977600	-0.35260800	0.33304800
C	2.87213700	-1.46600300	-0.32193800
H	2.36267900	-2.42287300	-0.26151400
C	-0.30210100	0.35023400	-0.10045500
C	0.40895500	1.67792600	-1.54598300
H	-0.47970500	1.95101900	-2.10738700
H	1.01184400	0.88839900	-1.98706100
C	-2.42881400	-1.40032200	-1.19917000
H	-1.39940500	-1.72775800	-1.31337500
C	-3.34883100	2.25619400	0.83315300
H	-3.57590000	3.18936200	1.34116300
C	0.95080800	2.57274500	-0.65910000
H	0.45733600	3.52090700	-0.47599300
C	-1.64413600	0.62080400	0.06349700
C	4.21484800	-1.42085800	-0.67575000
H	4.74381600	-2.34486900	-0.89691500
C	-4.04568900	0.22908300	-0.36837200
C	-5.08173900	-0.57069900	-0.89194800
H	-6.11125000	-0.24263600	-0.76696000
C	2.11921500	2.25123400	0.21888200
H	2.82875400	3.08818500	0.21446200
H	1.70519800	2.21463100	1.24032100
C	-3.46481700	-2.16734400	-1.71228300
H	-3.24099400	-3.09442300	-2.23366700
C	4.89620400	-0.19636800	-0.74572700
C	6.35948600	-0.15243400	-1.11039000
H	6.97147800	-0.64225800	-0.34180200
H	6.71849300	0.87614300	-1.21835600
H	6.54924000	-0.67987800	-2.05336100
C	2.82862300	0.95355500	-0.09919200
C	-4.32819700	1.46819600	0.31891300
H	-5.37117400	1.76538000	0.41229000
C	-4.80076100	-1.75503000	-1.55855800
H	-5.60821400	-2.36187400	-1.95878800
C	4.18196500	0.97105800	-0.45696300
H	4.69502300	1.92923100	-0.50355700



TS3

Br	0.26080300	-1.57895800	1.88228900
O	-1.53935800	2.79123000	1.14372500
C	2.13581100	-0.23925700	0.07896200
C	-2.25243400	1.88518700	0.63075000
C	-2.45029500	-0.34268800	-0.54866100
C	0.73475500	-0.21370200	0.53633600
C	2.82838300	-1.44687700	-0.09141500
H	2.33835800	-2.38494100	0.14734100
C	-0.26884400	0.56947900	0.18651000
C	-0.11814500	3.39713900	-0.52203100
H	-0.97347500	3.58213500	-1.16230100
H	0.13989000	4.18105600	0.18096900
C	-1.90771100	-1.52611700	-1.09280600
H	-0.83678100	-1.69004900	-1.05094700
C	-3.68562100	2.04624300	0.46538400
H	-4.12492800	2.96348500	0.84637600
C	0.73144100	2.34153700	-0.75438000
C	-1.63786000	0.66928600	0.12216900
C	4.13760700	-1.45951700	-0.56730500
H	4.64868600	-2.41014500	-0.69816800
C	-3.85865600	-0.13890100	-0.63286200
C	-4.66913400	-1.12339900	-1.23591400
H	-5.74234900	-0.95607200	-1.28884800
C	2.06758200	2.28349300	-0.04133000
H	2.70685900	3.10047000	-0.39870900
H	1.89511600	2.46292400	1.02943100
C	-2.72398700	-2.47805200	-1.68683400
H	-2.28189700	-3.38076300	-2.09991700
C	4.80126700	-0.26617200	-0.87449700

C	6.23132100	-0.26161600	-1.35537100
H	6.91714100	0.01941700	-0.54455600
H	6.37956200	0.46117000	-2.16628000
H	6.53710100	-1.24897000	-1.71728300
C	2.78916600	0.97315300	-0.22994700
C	-4.43965500	1.07383700	-0.10866500
H	-5.51737300	1.19619500	-0.19573900
C	-4.11399700	-2.28207500	-1.75720000
H	-4.74865600	-3.03258700	-2.22016200
C	4.10267200	0.93698600	-0.69794600
H	4.59992000	1.87682900	-0.93050900
H	0.64760400	1.80571900	-1.69830300

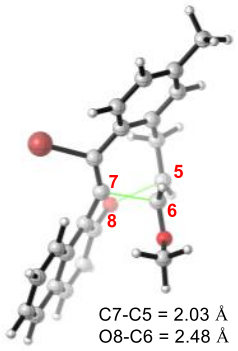


Cat 6

C	3.43183000	1.53371400	2.78828200
C	2.63589800	3.19858400	1.42754300
C	2.01109900	2.26134400	0.53722400
C	2.15325400	0.86316800	0.83997400
C	2.86007300	0.52399200	1.97347000
H	3.00697200	5.27756100	1.83232000
H	3.99048700	1.24512300	3.67806700
C	2.52440300	4.58388100	1.14999000
C	1.29525800	2.75372500	-0.57892900
H	3.00148500	-0.51058700	2.26551600
C	1.20324600	4.11643700	-0.82122000
C	1.82745700	5.04399500	0.05469000
H	0.79278600	2.08545400	-1.26944600
H	1.76097700	6.10989500	-0.12908300
N	3.33779300	2.82296900	2.53991100
O	0.49372300	4.47890400	-1.92361200
C	0.37277100	5.86415900	-2.24073400
H	1.35220400	6.32611800	-2.42009900
H	-0.21581600	5.90766800	-3.15956900

H	-0.15290400	6.41623400	-1.45094500
C	1.48573500	-0.17334700	-0.05838200
H	1.59828000	0.14991000	-1.09413800
N	0.04856200	-0.16853800	0.20617100
H	-0.23926500	-0.53611500	1.10413900
C	-0.87961400	-0.06811800	-0.78222000
C	2.07603400	-1.59389100	0.06136200
C	3.57849600	-1.64035400	-0.35036700
H	1.97554000	-1.91370600	1.10494500
C	1.53913600	-2.44890600	-2.16485600
C	1.69834300	-3.92655200	-0.28309600
C	3.80056500	-2.91052400	-1.19329900
H	3.84721900	-0.75723300	-0.94473200
H	4.22230400	-1.63792200	0.53352500
H	0.86134400	-3.14278400	-2.67442100
H	1.24697600	-1.44371600	-2.47708900
C	3.02578500	-2.75877100	-2.51473900
C	3.23994000	-4.14888900	-0.42912000
H	1.15636900	-4.64988700	-0.90137400
H	1.36067700	-4.07571600	0.74693600
H	4.86984700	-3.05015900	-1.38990800
H	3.10934100	-3.68004500	-3.10479300
H	3.46427100	-1.95034100	-3.11258600
H	3.41384400	-5.02245400	-1.07382100
N	1.28765400	-2.57712700	-0.71363300
C	4.02167000	-4.38565800	0.84177400
C	3.61101600	-4.28881500	2.10908600
H	5.06882100	-4.64180800	0.66454900
H	4.29635800	-4.47155900	2.93373800
H	2.59045000	-4.03648500	2.38527000
O	-0.59022100	0.17270100	-1.95893000
C	-2.31404500	-0.23944900	-0.36142100
C	-2.76786600	0.03672800	0.93668200
C	-3.22735300	-0.66716200	-1.33388500
C	-4.11230800	-0.12912100	1.26091800
H	-2.08405900	0.40887700	1.69356500
C	-4.57015300	-0.84318000	-1.01251800
H	-2.87028100	-0.86083100	-2.33970600
C	-5.00984200	-0.57622400	0.28726500

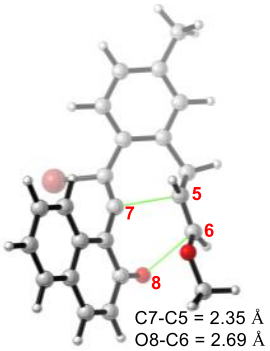
H	-4.46214600	0.08901300	2.26486600
H	-5.27190300	-1.18812000	-1.76452400
C	-6.46713100	-0.70179000	0.63237200
F	-7.11292700	-1.57379700	-0.17429400
F	-7.11397900	0.48561900	0.52020800
F	-6.65069900	-1.12006800	1.90707600



OMe-TS2

Br	0.42836000	2.35337200	-1.23070500
O	-0.88520400	-1.99667900	-2.02577300
C	2.23774500	0.42317500	0.00262100
C	-1.82651000	-1.42389200	-1.40893100
C	-2.61357200	0.29224600	0.26729500
C	0.82204000	0.64090200	-0.34958500
C	2.98252200	1.40851500	0.67112200
H	2.50836700	2.35383700	0.91704100
C	-0.20151200	-0.18012500	-0.19023400
C	0.39252400	-1.88677800	0.73748100
H	1.03133700	-1.32494700	1.41903300
C	-2.37420000	1.33552300	1.19151900
H	-1.35221100	1.65623700	1.36980300
C	-3.21710300	-1.81923700	-1.57339600
H	-3.42132700	-2.62663400	-2.27109700
C	0.93496600	-2.46427900	-0.40090900
H	0.48737100	-3.36384800	-0.80249800
C	-1.55144600	-0.35756400	-0.46310900
C	4.30983300	1.18880100	1.01917200
H	4.86370400	1.96462400	1.54250600
C	-3.95935600	-0.11485700	0.02743900
C	-5.01033600	0.53206500	0.71173600
H	-6.03315000	0.21607400	0.51858400
C	2.12275600	-1.88378800	-1.09512200
H	2.81149300	-2.69410400	-1.36340800
H	1.74207300	-1.48306800	-2.04899500

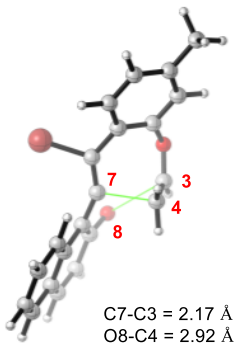
C	-3.42371800	1.94977900	1.85718300
H	-3.21854900	2.74989400	2.56375600
C	4.94359100	-0.02216600	0.70150200
C	6.39183700	-0.24799300	1.05950600
H	7.05005500	0.38340300	0.44800400
H	6.68995000	-1.28962400	0.90162600
H	6.58696500	0.00770400	2.10799900
C	2.86249000	-0.79961700	-0.33473900
C	-4.21680800	-1.18219300	-0.90721200
H	-5.25295400	-1.47537300	-1.06600500
C	-4.75232200	1.54954100	1.61779400
H	-5.57087600	2.03845600	2.13879700
C	4.19971300	-0.99728800	0.02825400
H	4.67653000	-1.93946500	-0.23326300
O	-0.69158100	-2.49665900	1.28291800
C	-1.10418900	-1.95721900	2.54330100
H	-1.27990800	-0.87791500	2.47774300
H	-2.03882600	-2.45733300	2.80441800
H	-0.35202600	-2.16055100	3.31735300



OMe-TS3

Br	-0.74218600	-2.14861300	-1.65862900
O	1.59308600	1.83733000	-1.96851600
C	-2.35449200	-0.26608400	-0.08413000
C	2.21948900	1.03937200	-1.23913600
C	2.26330700	-0.76613700	0.55926400
C	-0.97602700	-0.52080200	-0.55121800
C	-3.22067800	-1.32853400	0.21591100
H	-2.88419900	-2.35004500	0.07683600
C	0.15480200	0.11989500	-0.34991600
C	0.42615700	2.97411900	0.17051500
H	0.38665700	3.63934400	-0.68782200
C	1.63123700	-1.65469500	1.45239800
H	0.54718900	-1.68081700	1.49779900
C	3.67871200	1.00625200	-1.20859600
H	4.19466500	1.68458500	-1.88213900

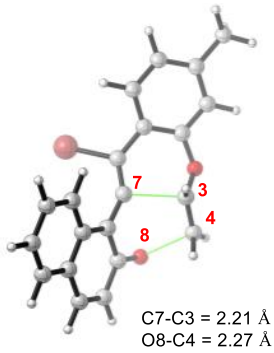
C	-0.61048800	2.16040500	0.51814900
C	1.51773700	0.10765600	-0.34460000
C	-4.51019200	-1.09869300	0.69108200
H	-5.15246200	-1.94553300	0.91994600
C	3.68570400	-0.73921800	0.51858300
C	4.42235700	-1.59723800	1.35918300
H	5.50868600	-1.56813400	1.31498400
C	-1.93204200	2.24087800	-0.20719600
H	-2.46736000	3.16035400	0.06237700
H	-1.74015800	2.29102900	-1.28816300
C	2.37636300	-2.48995400	2.27478200
H	1.86647600	-3.16605100	2.95601700
C	-4.98434700	0.20359200	0.87490600
C	-6.37669100	0.47772900	1.38728500
H	-6.94622400	1.09378700	0.67988700
H	-6.34830100	1.02684000	2.33728700
H	-6.93472500	-0.44972700	1.55178500
C	-2.81982800	1.05745500	0.09914900
C	4.35617000	0.16581600	-0.38794100
H	5.44460500	0.15817800	-0.39159200
C	3.77992900	-2.46607300	2.23045900
H	4.35860300	-3.12280900	2.87407400
C	-4.11695800	1.26213400	0.56999600
H	-4.46483500	2.28475600	0.70386800
H	-0.57777600	1.67805700	1.49193100
O	1.57274300	2.91959300	0.85325400
C	2.60118600	3.82602900	0.41728800
H	2.34606300	4.85166200	0.70799800
H	3.51780000	3.51527800	0.91986300
H	2.72676800	3.76192200	-0.66811800



O-TS2

Br	0.33193300	-1.59755000	1.84853100
O	-1.18336700	2.60709400	1.31243900
C	2.12891400	-0.25721400	0.00214100

C	-2.04707000	1.84690100	0.82757500
C	-2.68077800	-0.20436700	-0.54856600
C	0.71724900	-0.30507300	0.42608100
C	2.86996200	-1.43439400	-0.20921100
H	2.38407000	-2.39195300	-0.05294900
C	-0.33729000	0.36353700	-0.00305300
C	0.44031300	1.71173600	-1.51840400
H	-0.47122300	2.08713100	-1.96716500
H	0.96909500	0.93173500	-2.05572900
C	-2.35179100	-1.36116300	-1.28673100
H	-1.30882500	-1.64976300	-1.38220600
C	-3.47552900	2.14701800	0.89957400
H	-3.75642600	3.04385400	1.44474000
C	1.05045700	2.49178300	-0.57894300
H	0.61562900	3.40202200	-0.18761300
C	-1.68071200	0.61136900	0.11962300
C	4.19951900	-1.39509500	-0.60864600
H	4.73612100	-2.32655500	-0.76930900
C	-4.05221100	0.16096200	-0.42892900
C	-5.03939100	-0.63698500	-1.04039400
H	-6.08320000	-0.34872300	-0.93808700
C	-3.34062300	-2.12828700	-1.88759100
H	-3.06378800	-3.01337900	-2.45449200
C	4.86192500	-0.17225800	-0.80396300
C	6.30757600	-0.13970600	-1.23032200
H	6.94548300	-0.64041300	-0.49127900
H	6.67044100	0.88562200	-1.35113600
H	6.44755000	-0.66505600	-2.18324900
C	2.80522700	0.95938900	-0.20029100
C	-4.40492700	1.34895200	0.31572700
H	-5.46179900	1.59889000	0.39147500
C	-4.69410400	-1.76970200	-1.76499100
H	-5.46452400	-2.37536900	-2.23394800
C	4.14103400	1.00524900	-0.59102500
H	4.60680400	1.97718500	-0.72231600
O	2.19717200	2.18579200	0.05214800

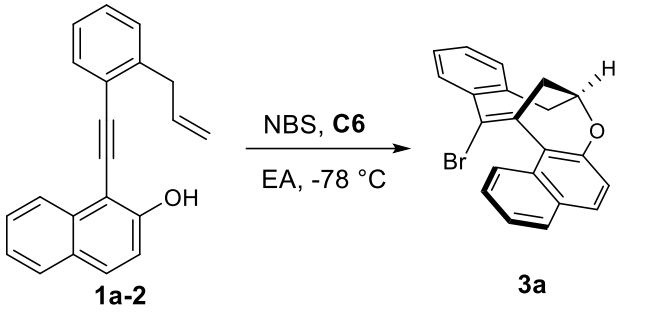


O-TS3

Br	0.26446900	-1.78877300	1.67717500
O	-1.35148100	2.70206700	1.31214600
C	2.12968500	-0.28824900	0.00201900
C	-2.14739900	1.87398100	0.78674100
C	-2.53273100	-0.25441500	-0.52229400
C	0.72735800	-0.32532700	0.44182300
C	2.92221600	-1.44010600	-0.12853000
H	2.48462100	-2.40895600	0.08565000
C	-0.27003300	0.49195700	0.16287600
C	0.04361200	3.30094000	-0.38083800
H	-0.83471400	3.53622100	-0.96646600
H	0.41354300	4.04243600	0.31542500
C	-2.08493900	-1.42764800	-1.16600600
H	-1.02467900	-1.65510000	-1.18119400
C	-3.57321900	2.12965400	0.70007600
H	-3.93922000	3.04364800	1.15835600
C	0.80501300	2.20773500	-0.71064300
C	-1.63391000	0.65915500	0.17403100
C	4.25550500	-1.36308900	-0.51974400
H	4.83500000	-2.27739600	-0.61588300
C	-3.92839300	0.03570700	-0.52544200
C	-4.82137000	-0.85817300	-1.15264300
H	-5.88406300	-0.62764000	-1.14457600
C	-2.98145400	-2.28866700	-1.78213000
H	-2.61332500	-3.18570600	-2.27271000
C	4.86214800	-0.12598300	-0.78003900
C	6.31968800	-0.03253800	-1.15580400
H	6.94249200	0.11921000	-0.26377300
H	6.50831600	0.81033200	-1.82961200
H	6.66658100	-0.94901100	-1.64501600
C	2.74263100	0.94699400	-0.28252000
C	-4.41040600	1.24224300	0.10277900
H	-5.48139500	1.43245200	0.07652600

C	-4.35900800	-2.00815000	-1.77420400
H	-5.05701900	-2.68782400	-2.25496700
C	4.07913600	1.02806200	-0.66120300
H	4.49849100	2.01066200	-0.85740100
H	0.69919500	1.70803200	-1.67188400
O	2.05960300	2.13183500	-0.13757800

IX. Gram-scale preparation and transformations



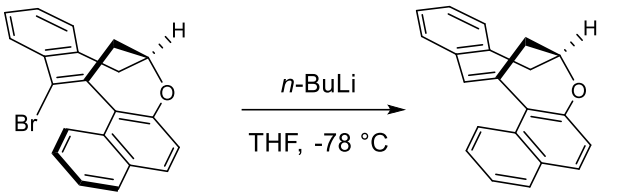
1a-2

1.0 g

3a

831 mg
65% yield, 97% ee

A solution of **1a-2** (1.0 g, 3.52 mmol, 1.0 equiv.) and **C6** (10 mol%) in EA (0.0125M) was stirred at -78 °C for 30 min, then NBS (660 mg, 3.70 mmol, 1.05 equiv.) was added in 10 portions. After stirring at -78 °C for 12 h, the reaction mixture was concentrated under reduced pressure. The resulting residue was purified by silica gel flash column chromatography using PE/EA eluent (30:1 to 15:1) to afford the product **3a** (831 mg, 65% yield) as a pale yellow solid.



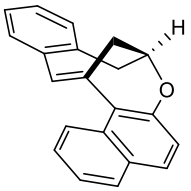
3a

99% ee

5

65% yield, 96% ee

3a (73 mg, 0.2 mmol, 1.0 equiv.) was dissolved in freshly distilled THF (2mL) at room temperature under nitrogen atmosphere. The solution was cooled to -78 °C. Titrated *n*-BuLi (0.25 mmol, 1.25 equiv.) was added dropwise. After stirred for 30 min at -78°C, the reaction was allowed to warm to room temperature. Solvent was removed under reduced pressure. The product was then dried under vacuum and flash chromatography on a silica column (PE: EA = 20:1) to afforded compound **5** as a yellow oil in 65% yield.



5

8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine(5)

Yellow oil. (R_f = 0.6, PE/EA= 20:1)

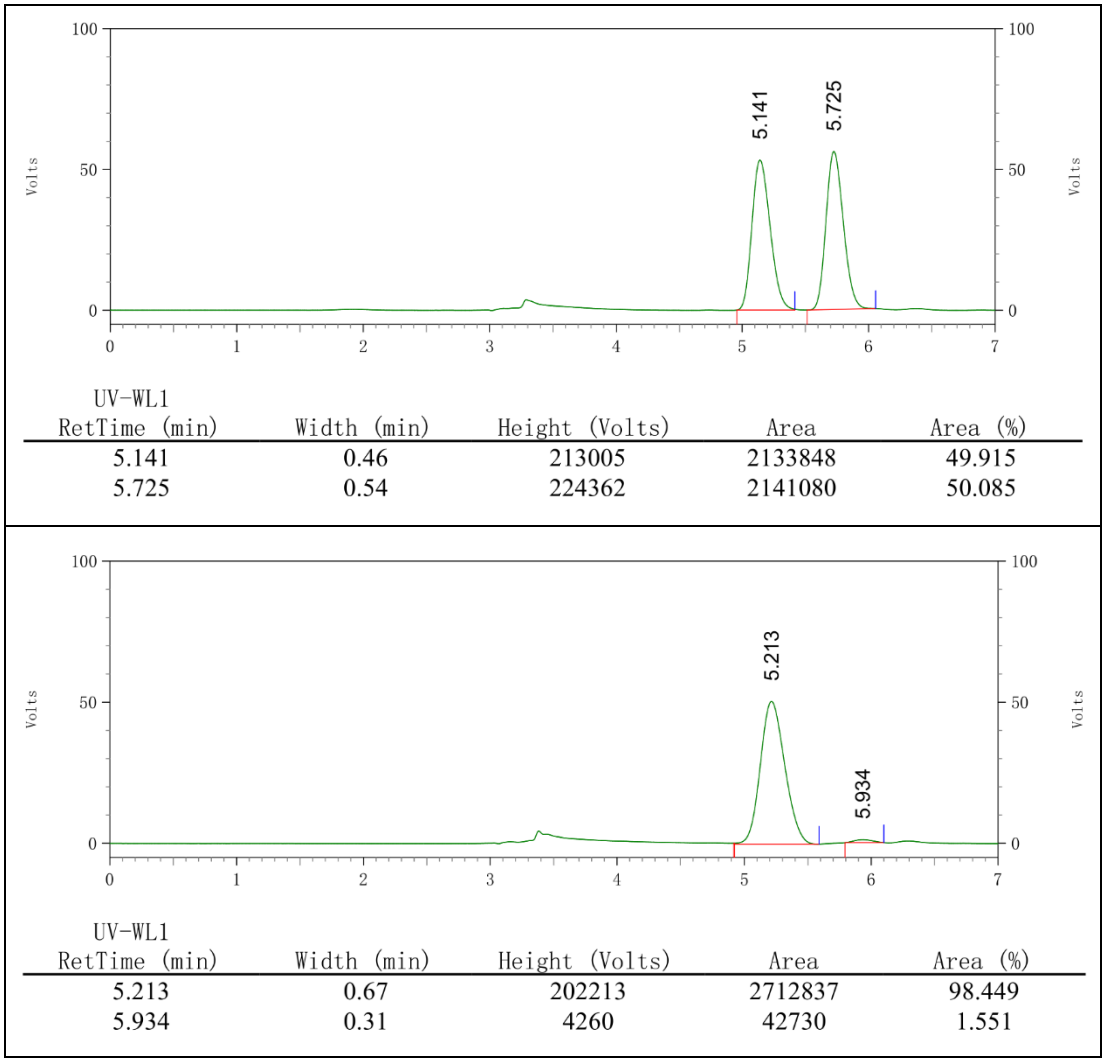
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.52 (t, *J* = 7.0 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.31 (t, *J* = 6.4 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.09 (d, *J* = 8.8 Hz, 1H), 6.76 (s, 1H), 5.54 – 5.40 (m, 1H), 3.18 (dd, *J* = 14.2, 6.3 Hz, 1H), 3.10 (dd, *J* = 14.1, 8.3 Hz, 1H), 2.97 (d, *J* = 11.5 Hz, 1H), 2.47 (d, *J* = 11.6 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.28, 139.53, 137.72, 137.49, 129.81, 129.63, 128.63, 128.28, 128.20, 127.82, 127.33, 127.26, 126.44, 125.69, 123.68, 123.43, 121.86, 118.41, 85.99, 40.97, 32.66.

HRMS (APCI) *m/z* Calcd for $C_{21}H_{17}O^+[M + H]^+$: 285.1274, Found: 285.1265.

Optical Rotation: $[\alpha]_D^{25}$ = -126.4° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 5.213min (major), t_R = 5.934 min (minor), 96% **ee**.

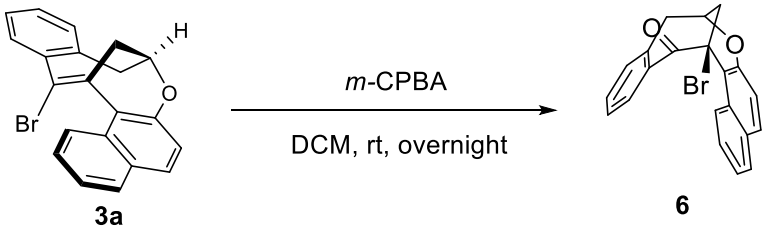


UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
5.141	0.46	213005	2133848	49.915
5.725	0.54	224362	2141080	50.085

UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
5.213	0.67	202213	2712837	98.449
5.934	0.31	4260	42730	1.551



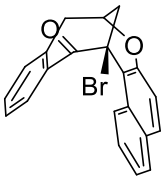
3a

99% ee

6

60% yield, 99% ee

3a (73 mg, 0.2 mmol, 1.0 equiv.) and *m*-CPBA (138 mg, 0.8 mmol, 4 equiv.) was dissolved in DCM (4 mL). The mixture was stirred overnight at room temperature. Removal of solvent under reduced pressure, purified by flash chromatography on silica gel (PE/EA = 5:1) to afford the product **6** (45.5 mg, 0.12 mmol, 60% yield) as a white solid.



6

White solid. (R_f = 0.4, PE/EA= 5:1)

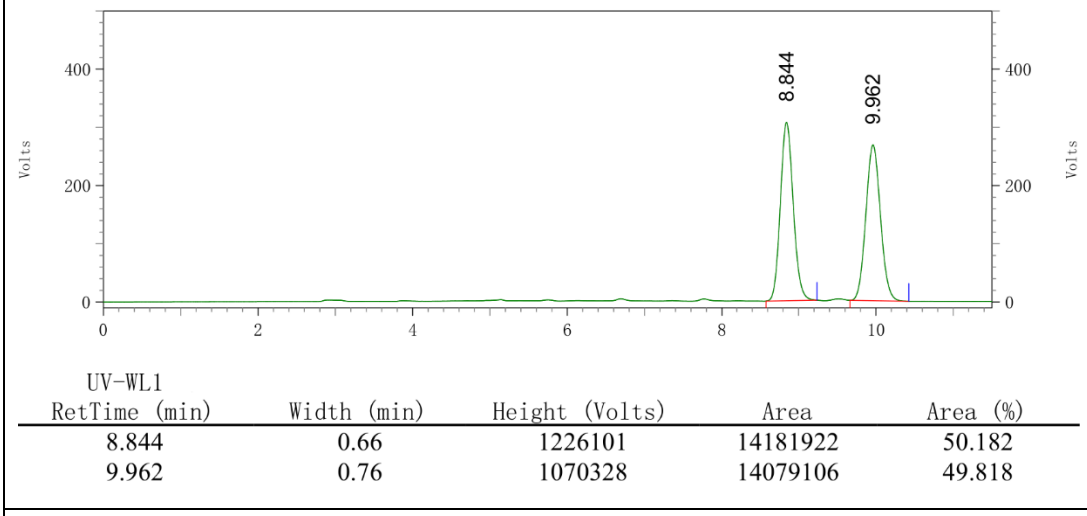
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.6 Hz, 1H), 7.60 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.55 (d, *J* = 9.0 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.32 – 7.27 (m, 1H), 7.21 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.07 (td, *J* = 7.5, 1.4 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.95 – 6.84 (m, 2H), 4.87 – 4.81 (m, 1H), 3.65 – 3.57 (m, 1H), 3.36 – 3.29 (m, 1H), 3.27 – 3.18 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.59, 151.79, 136.97, 132.59, 131.99, 131.58, 131.10, 130.05, 129.37, 128.81, 128.41, 126.90, 126.03, 125.29, 123.72, 118.84, 114.02, 71.42, 65.39, 43.45, 40.98.

HRMS (ESI) *m/z* Calcd for $C_{21}H_{15}BrNaO_2^+$[M + Na]$^+$: 401.0148, Found: 401.0148.

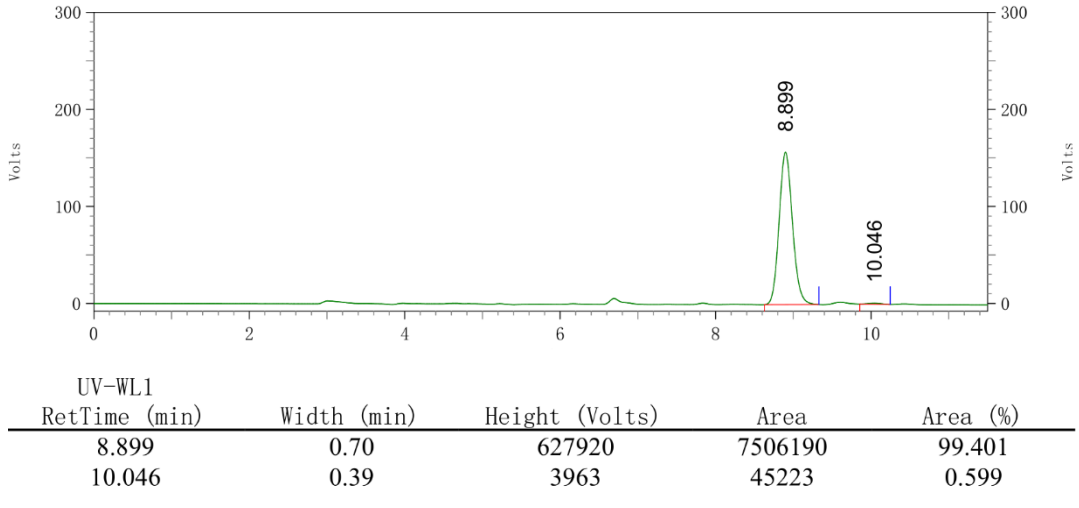
Optical Rotation: $[\alpha]_D^{25}$ = + 34.6° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 8.899 min (major), t_R = 10.046 min (minor), 99% **ee**.



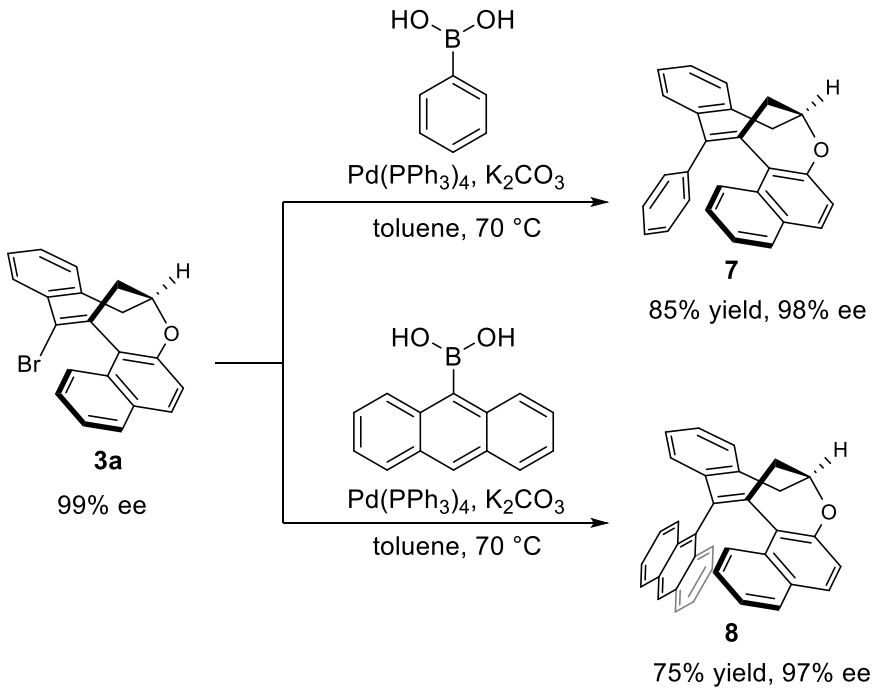
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
8.844	0.66	1226101	14181922	50.182
9.962	0.76	1070328	14079106	49.818

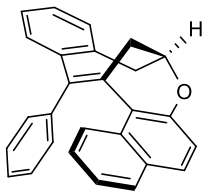


UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
8.899	0.70	627920	7506190	99.401
10.046	0.39	3963	45223	0.599



$Pd(PPh_3)_4$ (12 mg, 0.01 mmol, 0.05 equiv.), K_2CO_3 (138 mg, 1 mmol, 5.0 equiv.), **3a** (73 mg, 0.2 mmol, 1.0 equiv.) and the boronic acid (0.24 mmol, 1.2 equiv.) was dissolved in THF (2 mL) and H_2O (0.5 mL) under nitrogen atmosphere. The mixture was stirred for 4 hours at 70 °C. Then the mixture was filtered through a pad of celite and washed with EA. Removal of solvent under reduced pressure, purified by flash chromatography on silica gel (PE/EA = 20:1) to afford the product.



7

(*S*)-14-phenyl-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine(7)

White solid. (R_f = 0.5, PE/EA = 15:1)

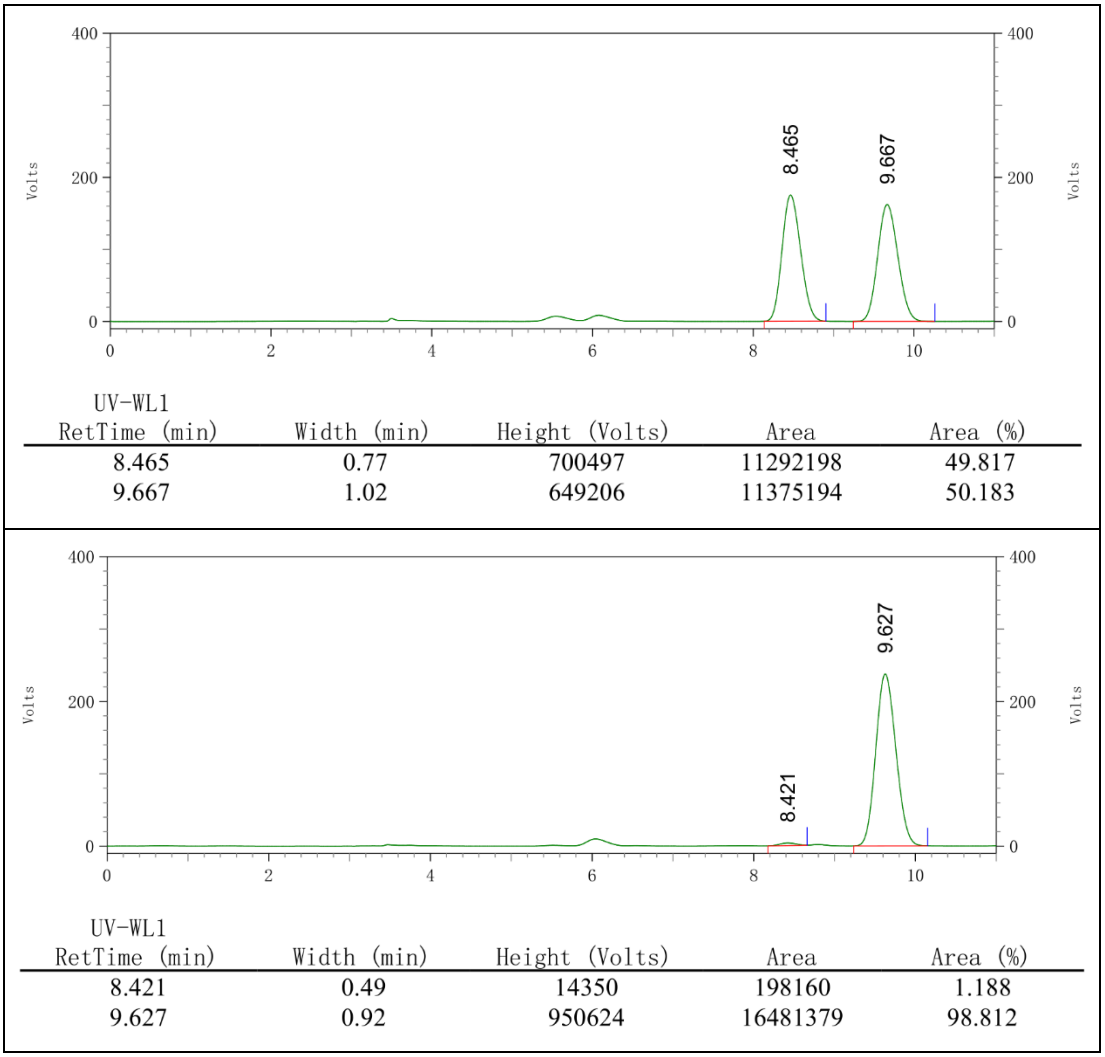
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.54 (m, 3H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.22 – 7.13 (m, 4H), 7.09 (t, *J* = 10.2 Hz, 2H), 7.05 – 6.90 (m, 4H), 5.51 – 5.42 (m, 1H), 3.38 (dd, *J* = 14.4, 6.3 Hz, 1H), 3.25 (dd, *J* = 14.4, 8.1 Hz, 1H), 2.94 (d, *J* = 11.9 Hz, 1H), 2.49 (d, *J* = 11.5 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.19, 142.50, 141.10, 136.68, 134.75, 132.04, 129.55, 128.85, 128.76, 128.41, 128.13, 127.99, 127.79, 127.48, 127.29, 126.49, 125.41, 125.08, 122.86, 121.23, 118.11, 84.83, 41.53, 34.27.

HRMS (ESI) *m/z* Calcd for $C_{27}H_{21}O^+[M + H]^+$: 361.1587, Found: 361.1595.

Optical Rotation: $[\alpha]_D^{25}$ = -176.6° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 8.421 min (minor), t_R = 9.627 min (major), 98% **ee**.

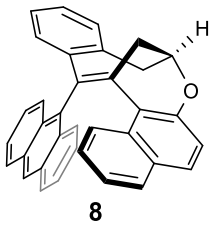


UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
8.465	0.77	700497	11292198	49.817
9.667	1.02	649206	11375194	50.183

UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
8.421	0.49	14350	198160	1.188
9.627	0.92	950624	16481379	98.812



8

(*S*)-14-(anthracen-9-yl)-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonine(8)

White solid. (R_f = 0.5, PE/EA = 15:1)

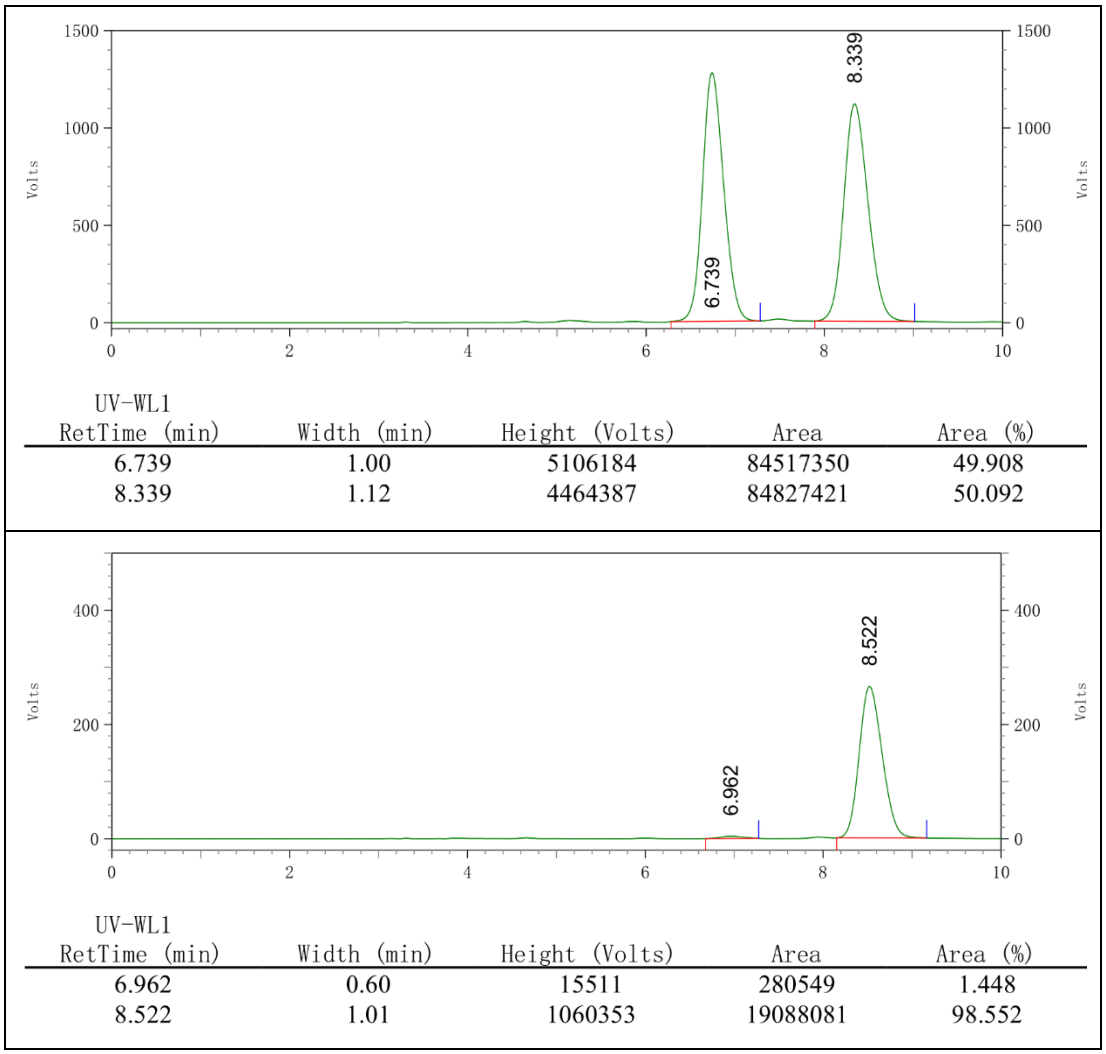
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 8.7 Hz, 1H), 8.19 (s, 1H), 8.01 (d, *J* = 8.5 Hz, 1H), 7.79 – 7.71 (m, 1H), 7.70 – 7.49 (m, 3H), 7.42 – 7.29 (m, 2H), 7.23 (t, 2H), 7.19 – 6.88 (m, 6H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.20 (t, *J* = 7.6 Hz, 1H), 5.80 – 5.70 (m, 1H), 3.96 (dd, *J* = 15.8, 4.8 Hz, 1H), 3.61 (dd, *J* = 15.9, 8.9 Hz, 1H), 3.45 (d, *J* = 11.3 Hz, 1H), 2.81 (dd, *J* = 11.5, 4.6 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.40, 141.76, 138.16, 136.31, 135.94, 134.02, 131.72, 131.62, 131.27, 130.64, 129.85, 128.89, 128.80, 128.67, 128.24, 128.13, 127.82, 127.52, 127.10, 126.88, 126.68, 126.00, 125.70, 125.35, 125.01, 124.79, 124.65, 124.00, 123.66, 122.50, 117.82, 86.68, 44.06, 35.39.

HRMS (ESI) *m/z* Calcd for $C_{35}H_{24}NaO^+$ $[M + Na]^+$: 483.1719, Found: 483.1743.

Optical Rotation: $[\alpha]_D^{25}$ = - 307.3° (*c* = 0.3, DCM).

HPLC analysis: Chiralcel IA-H (Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 6.962 min (minor), t_R = 8.522 min (major), 97% **ee**.

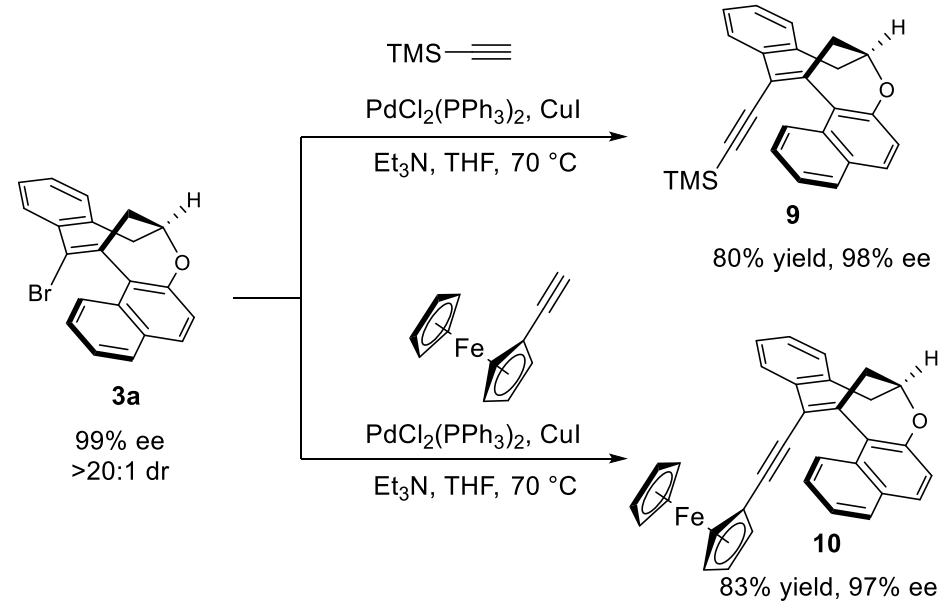


UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.739	1.00	5106184	84517350	49.908
8.339	1.12	4464387	84827421	50.092

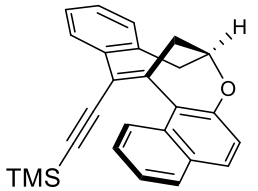
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.962	0.60	15511	280549	1.448
8.522	1.01	1060353	19088081	98.552



$PdCl_2(PPh_3)_2$ (7 mg, 0.01 mmol, 0.05 equiv.), CuI (4 mg, 0.02 mmol, 0.1 equiv.), and **3a** (73 mg, 0.2 mmol, 1.0 equiv.) were weighed and added into a schlenk tube, evacuated and backfilled with nitrogen (3 times). THF (1.0 mL) and Et_3N

(1.0 mL) were injected into the flask. Then, the mixture was stirred for 2h at 70 °C. After that, the alkyne (0.22 mmol, 1.1 equiv.) dissolved in THF (1.0 mL) was added. The resulting mixture kept stirring for 4 h at 70 °C. Then the mixture was filtered through a pad of celite. Removal of the solvent under reduced pressure afforded a residue which is purified by chromatography on silica gel (PE/EA = 20:1) to afford the product.



9

(*S*)-((8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonin-14-yl)ethynyl)trimethylsilane (9)

Yellow solid. (R_f = 0.6, PE/EA = 15:1)

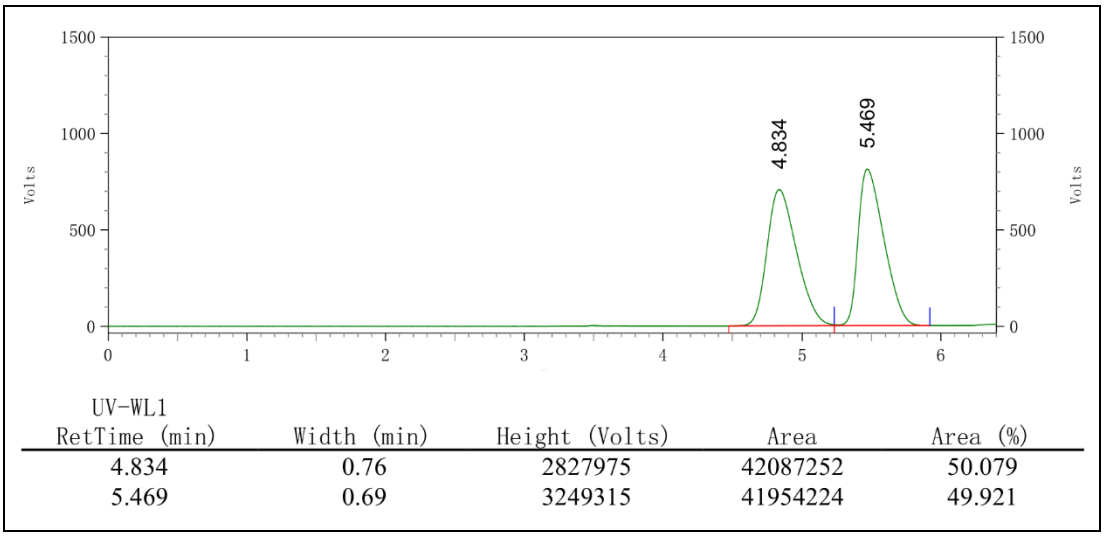
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.42 – 7.31 (m, 2H), 7.27 – 7.22 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 8.9 Hz, 1H), 5.45 – 5.37 (m, 1H), 3.23 (dd, *J* = 14.6, 6.5 Hz, 1H), 3.15 (dd, *J* = 14.5, 8.3 Hz, 1H), 2.87 (d, *J* = 11.8 Hz, 1H), 2.57 (dd, *J* = 11.9, 3.7 Hz, 1H), -0.13 (s, 9H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 151.80, 142.24, 140.16, 137.00, 129.40, 129.36, 129.00, 128.93, 128.41, 128.03, 127.66, 127.60, 127.28, 125.26, 123.27, 122.10, 118.37, 117.97, 103.93, 100.57, 84.67, 40.46, 34.10, -0.37.

HRMS (ESI) *m/z* Calcd for $C_{26}H_{25}OSi^+[M + H]^+$: 381.1669, Found: 381.1676.

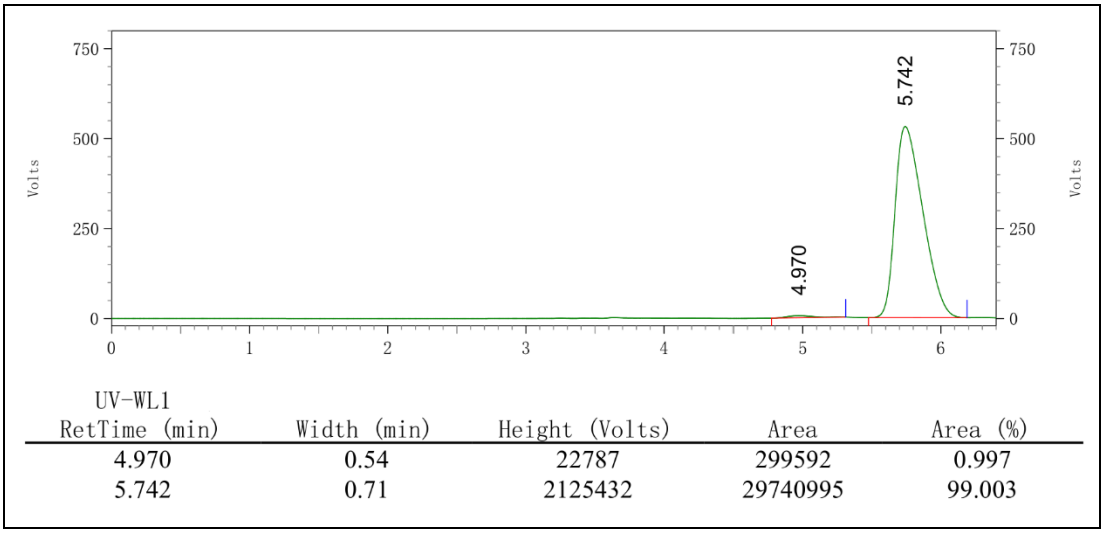
Optical Rotation: $[\alpha]_D^{25}$ = -146.0° (*c* = 1.0, acetone).

HPLC analysis: Chiralcel IB-H (Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 4.970 min (minor), t_R = 5.742 min (major), 98% **ee**.



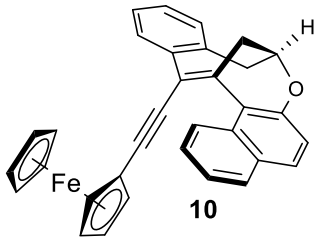
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
4.834	0.76	2827975	42087252	50.079
5.469	0.69	3249315	41954224	49.921



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
4.970	0.54	22787	299592	0.997
5.742	0.71	2125432	29740995	99.003



10

(*S*)-((8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonin-14-yl)ethynyl)ferrocene (10)

Red solid. (R_f = 0.6, PE/EA = 15:1)

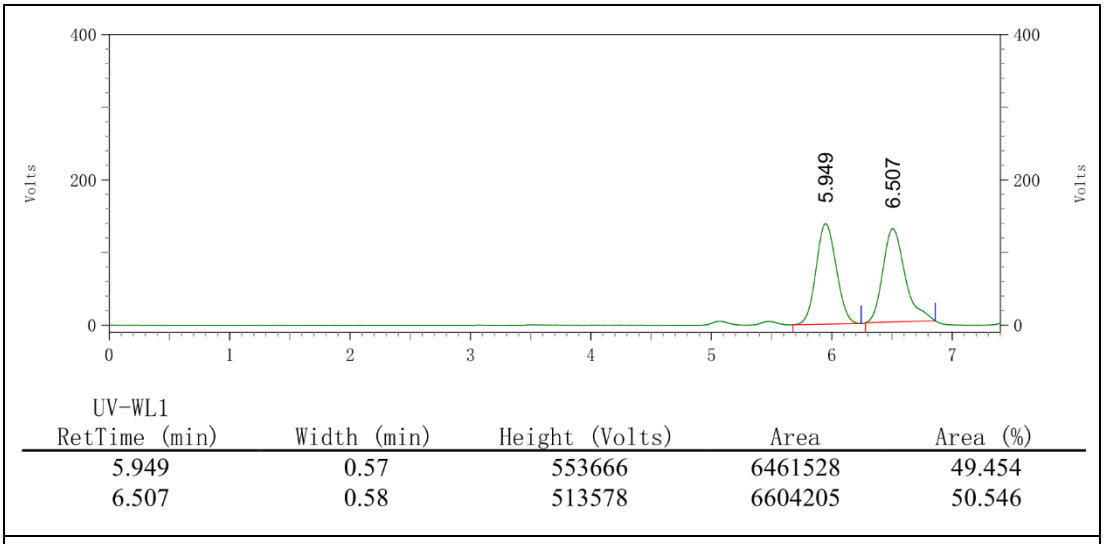
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.20 (d, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 8.9 Hz, 1H), 5.46 – 5.39 (m, 1H), 4.06 – 3.99 (m, 4H), 3.70 (s, 5H), 3.30 – 3.15 (m, 2H), 2.90 (d, *J* = 13.1 Hz, 1H), 2.57 (dd, *J* = 11.8, 3.7 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.55, 140.41, 139.10, 136.97, 129.48, 129.40, 129.23, 128.81, 128.56, 128.01, 127.87, 127.66, 127.27, 125.29, 123.38, 122.37, 118.95, 118.31, 94.17, 85.50, 84.77, 71.61, 70.71, 69.91, 68.70, 40.53, 33.81.

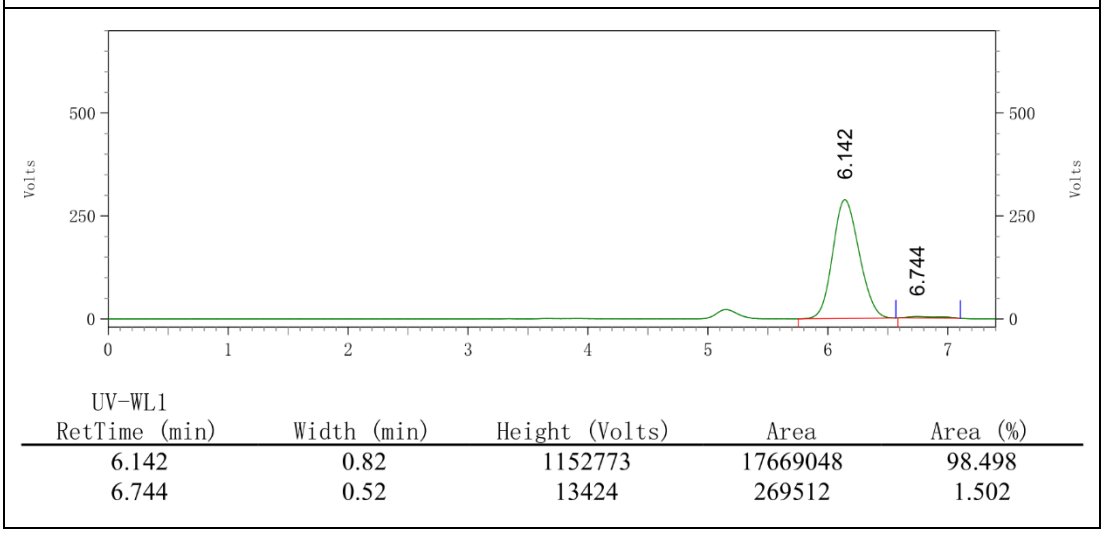
HRMS (ESI) *m/z* Calcd for $C_{33}H_{24}FeNaO^+$ $[M + Na]^+$: 515.1069, Found: 515.1085.

Optical Rotation: $[\alpha]_D^{25}$ = - 171.0° (*c* = 0.2, acetone).

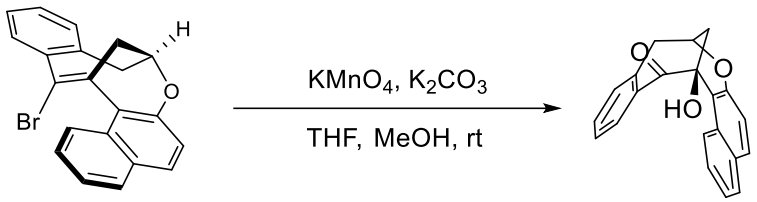
HPLC analysis: Chiralcel IA-H (Hexane/*i*-PrOH = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 6.142 min (major), t_R = 6.744 min (minor), 97% **ee**.



RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
5.949	0.57	553666	6461528	49.454
6.507	0.58	513578	6604205	50.546



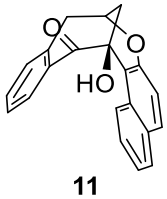
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.142	0.82	1152773	17669048	98.498
6.744	0.52	13424	269512	1.502



3a
99% ee

11
55% yield, 98% ee

3a (73 mg, 0.2 mmol, 1.0 equiv.) $KMnO_4$ (126 mg, 0.8 mmol, 4 equiv.) and K_2CO_3 (110 mg, 0.8 mmol, 4 equiv.) was dissolved in THF (2 mL) and MeOH (2 mL). The mixture was stirred overnight at room temperature. Removal of solvent under reduced pressure, purified by flash chromatography on silica gel (PE/EA = 5:1) to afford the product **11** (34.8 mg, 0.11 mmol, 55% yield) as a white solid.



11

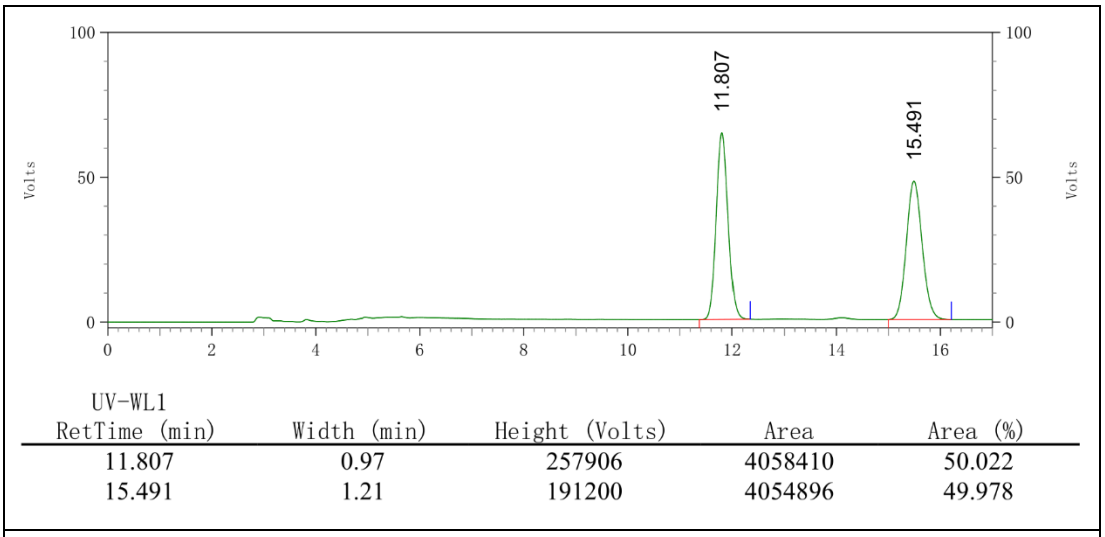
(15*S*)-15-hydroxy-8,9-dihydro-8,15-methanobenzo[f]naphtho[2,1-b]oxonin-14(15H)-one (11)

Yellow solid. (R_f = 0.5, PE/EA = 3:1)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.7 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.9 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 8.5 Hz, 2H), 7.10 – 6.99 (m, 2H), 6.92 – 6.81 (m, 2H), 4.96 (s, 1H), 4.91 – 4.85 (m, 1H), 3.39 (dd, *J* = 16.2, 5.6 Hz, 1H), 3.15 (d, *J* = 16.2 Hz, 1H), 3.04 (dd, *J* = 14.0, 5.7 Hz, 1H), 2.58 (d, *J* = 14.0 Hz, 1H).
^{13}C NMR (150 MHz, $CDCl_3$) δ 206.62, 153.22, 136.41, 133.73, 131.52, 131.14, 130.90, 130.84, 129.14, 128.64, 128.37, 127.00, 126.47, 123.92, 123.01, 118.34, 114.36, 74.51, 71.82, 42.34, 39.75.
HRMS (ESI) *m/z* Calcd for $C_{21}H_{16}NaO_3^+$ $[M + Na]^+$: 339.0992, Found: 339.0990.

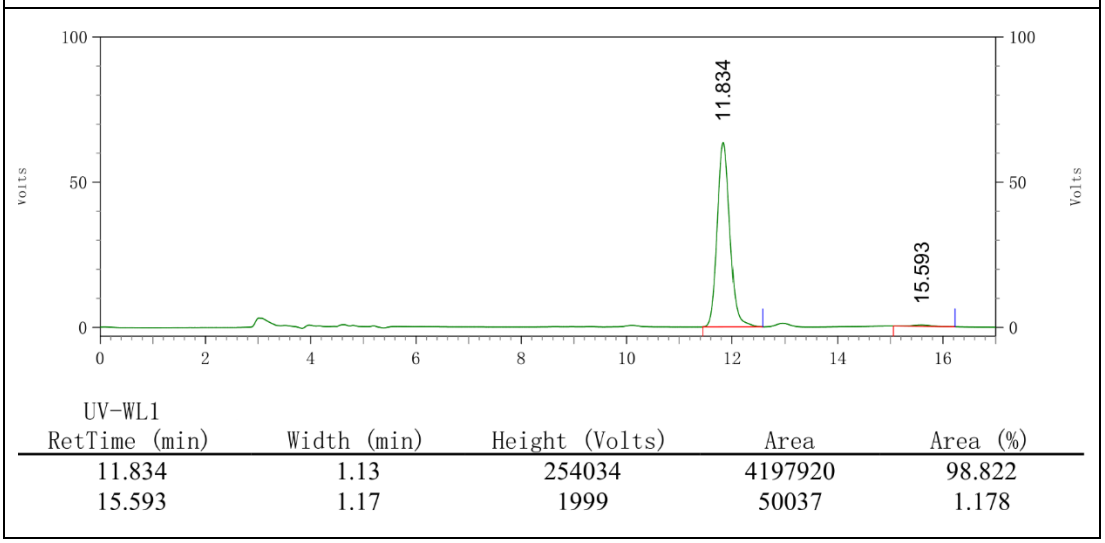
Optical Rotation: $[\alpha]_D^{25}$ = +44.8° (*c* = 0.5, acetone).

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm), t_R = 11.834 min (major), t_R = 15.593 min (minor), 98% **ee**.



UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
11.807	0.97	257906	4058410	50.022
15.491	1.21	191200	4054896	49.978



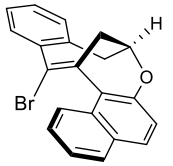
UV-WL1

RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
11.834	1.13	254034	4197920	98.822
15.593	1.17	1999	50037	1.178

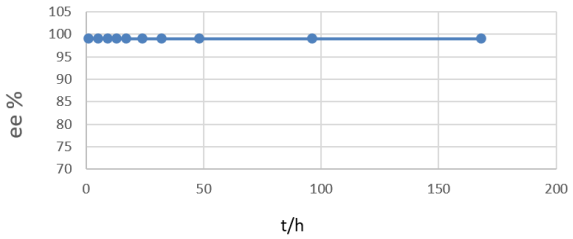
X. Thermal stability experiments

Thermal stability of 3a:

A solution of **3a** (5 mg, 99% ee after recrystallization) in DMF (1 mL) was heated at 120 °C. At intervals, the enantiomeric excess was determined by HPLC.

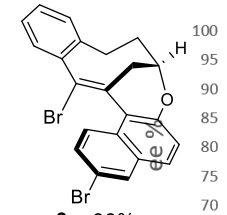


3a, 99% ee
120 °C after one week
99% ee

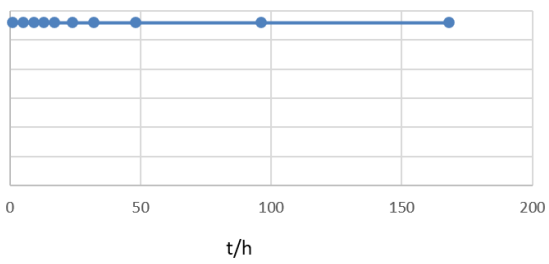


Thermal stability of 3s:

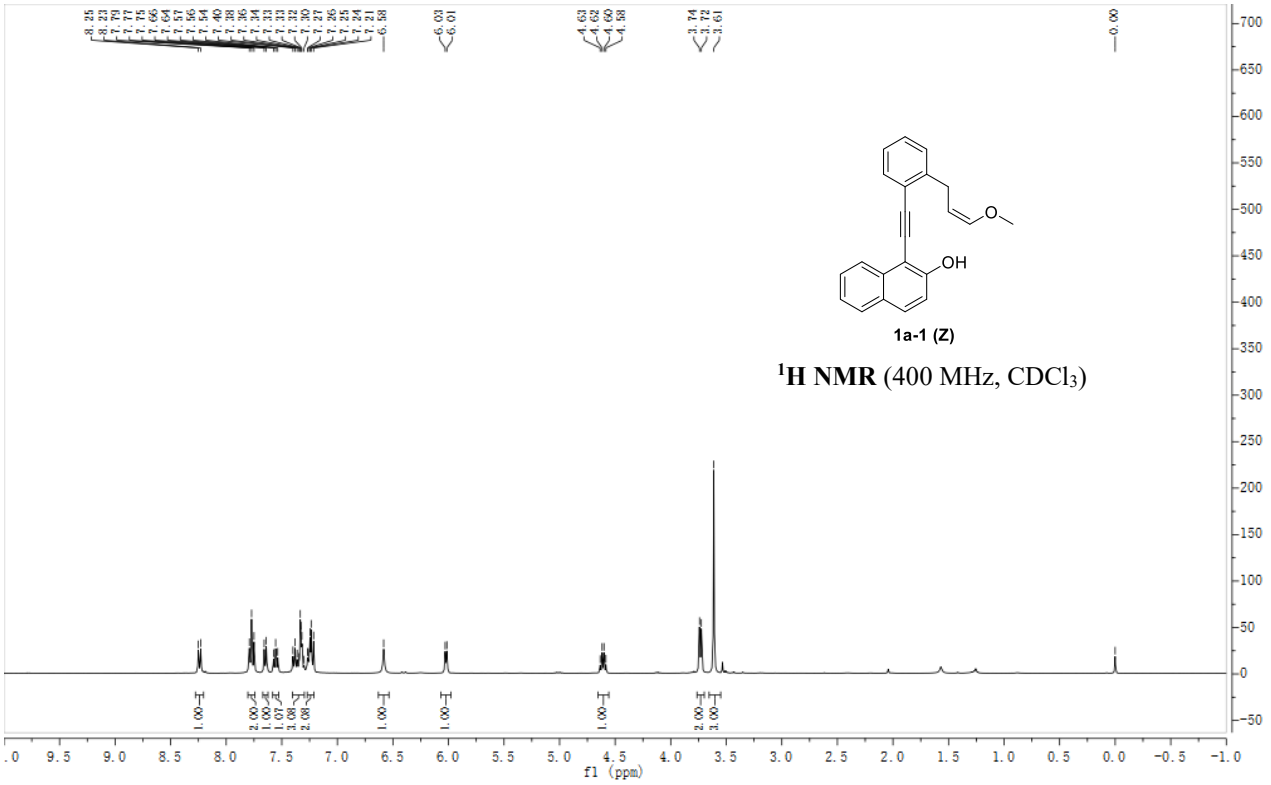
A solution of **3s** (5 mg, 98% ee, after recrystallization) in DMF (1 mL) was heated at 120 °C. At intervals, the enantiomeric excess was determined by HPLC.



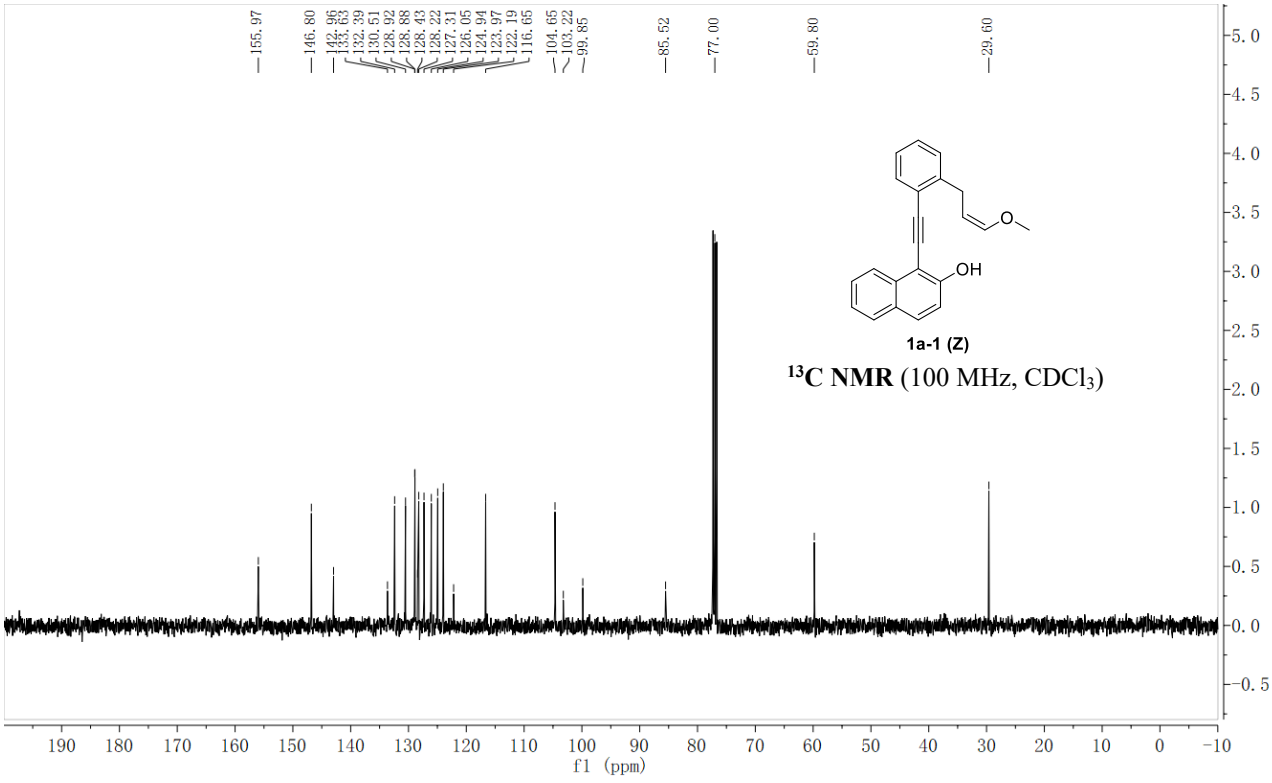
3s, 98% ee
120 °C after one week
98% ee



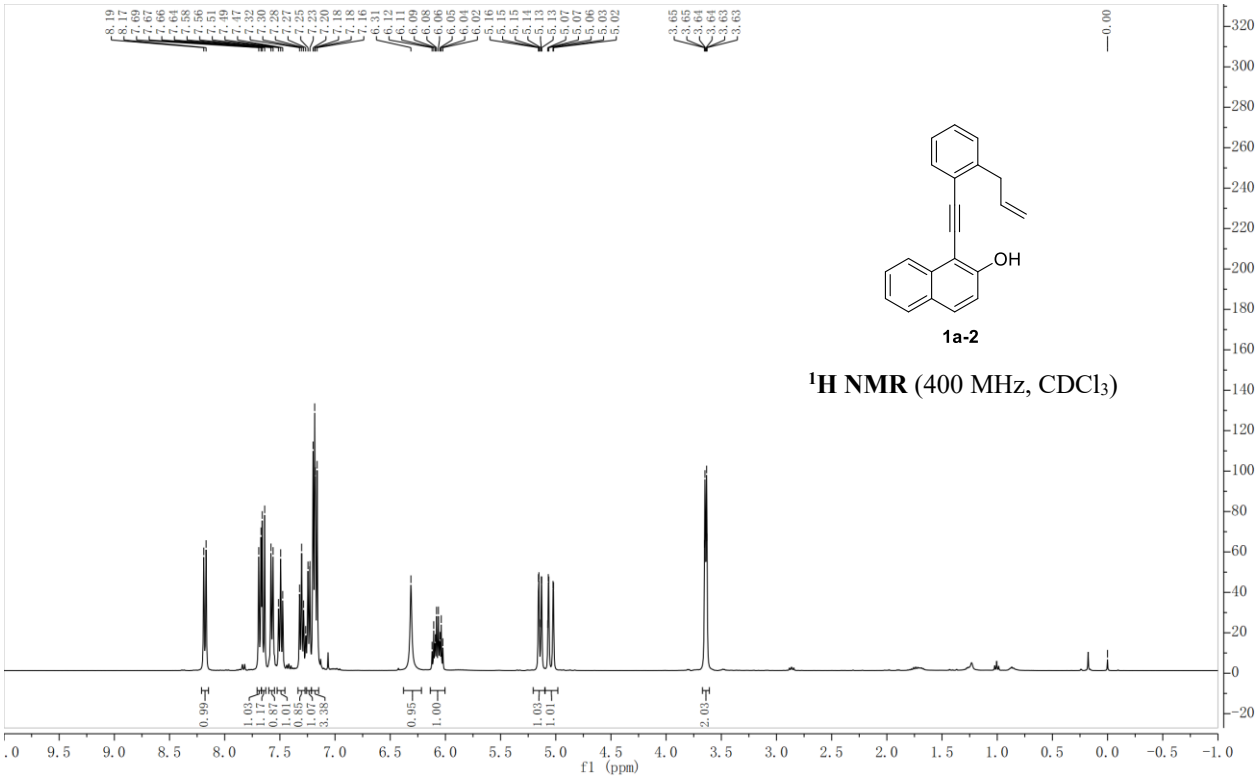
XI. ^{1}H and ^{13}C NMR spectra



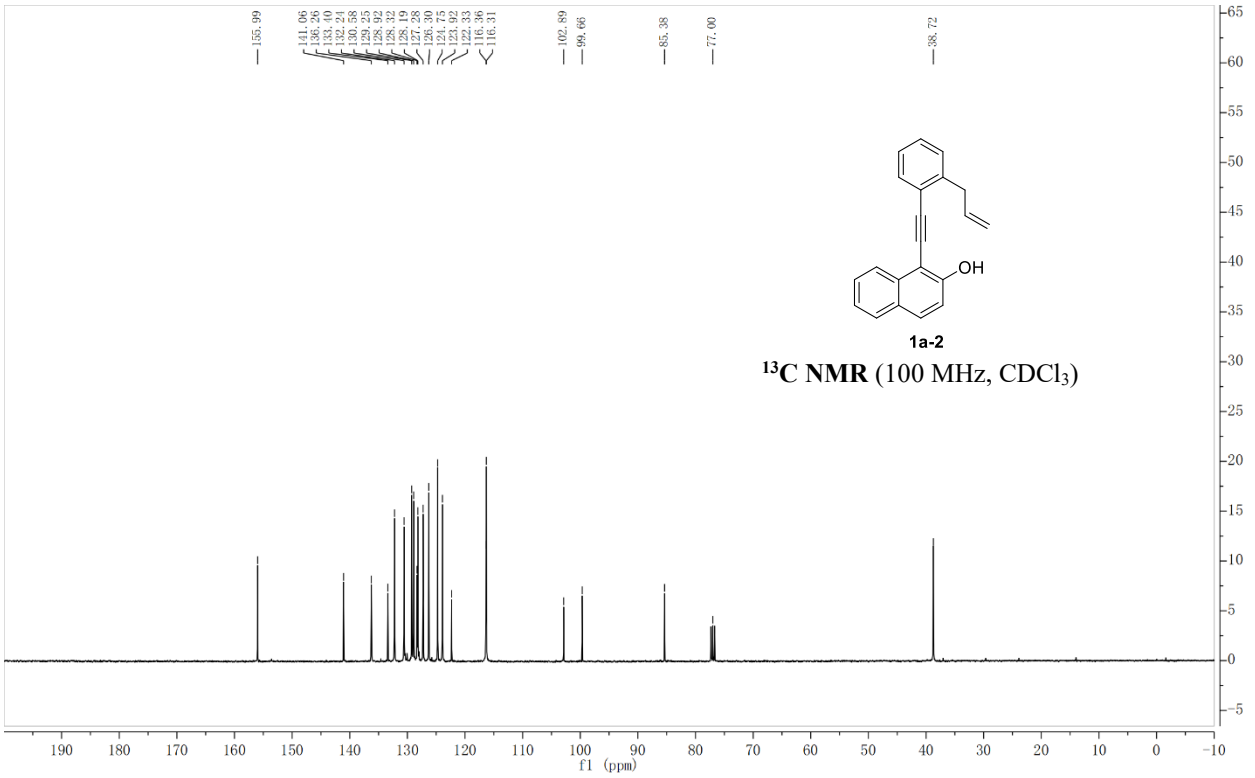
^{1}H NMR (400 MHz, $CDCl_3$)



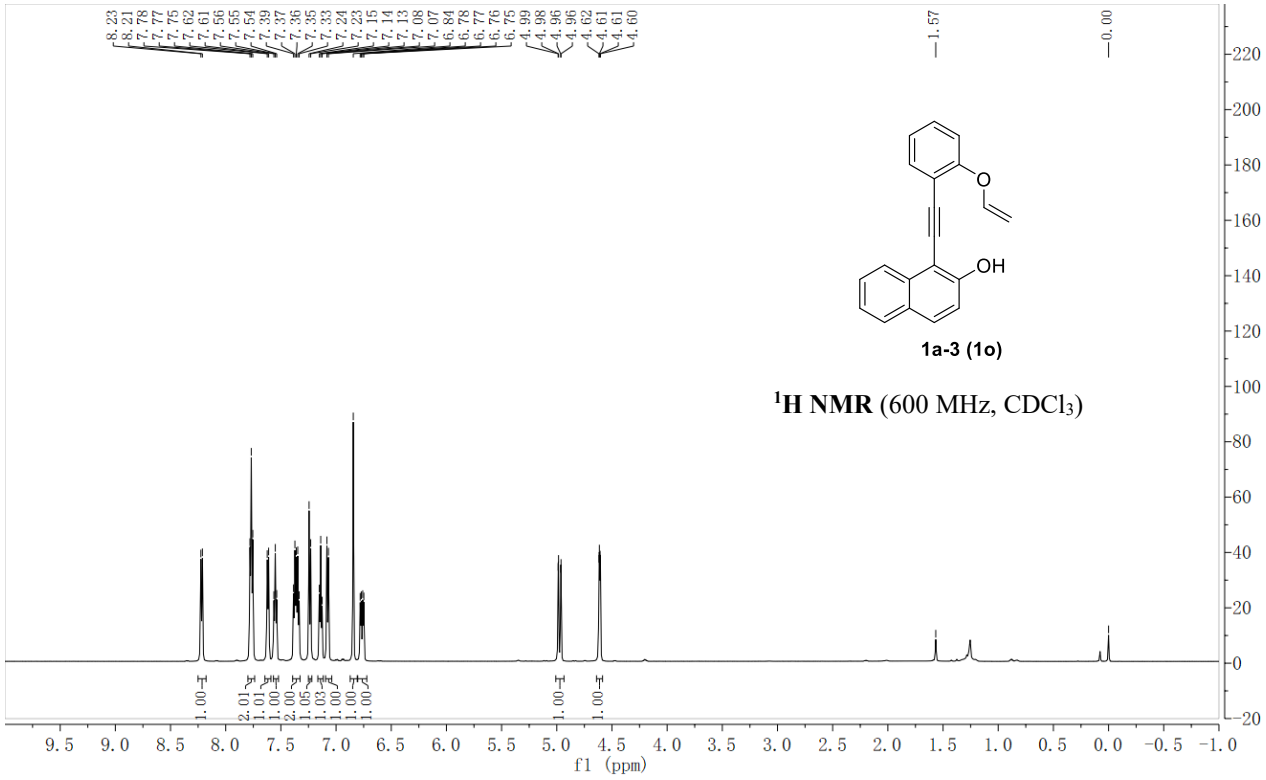
^{13}C NMR (100 MHz, $CDCl_3$)



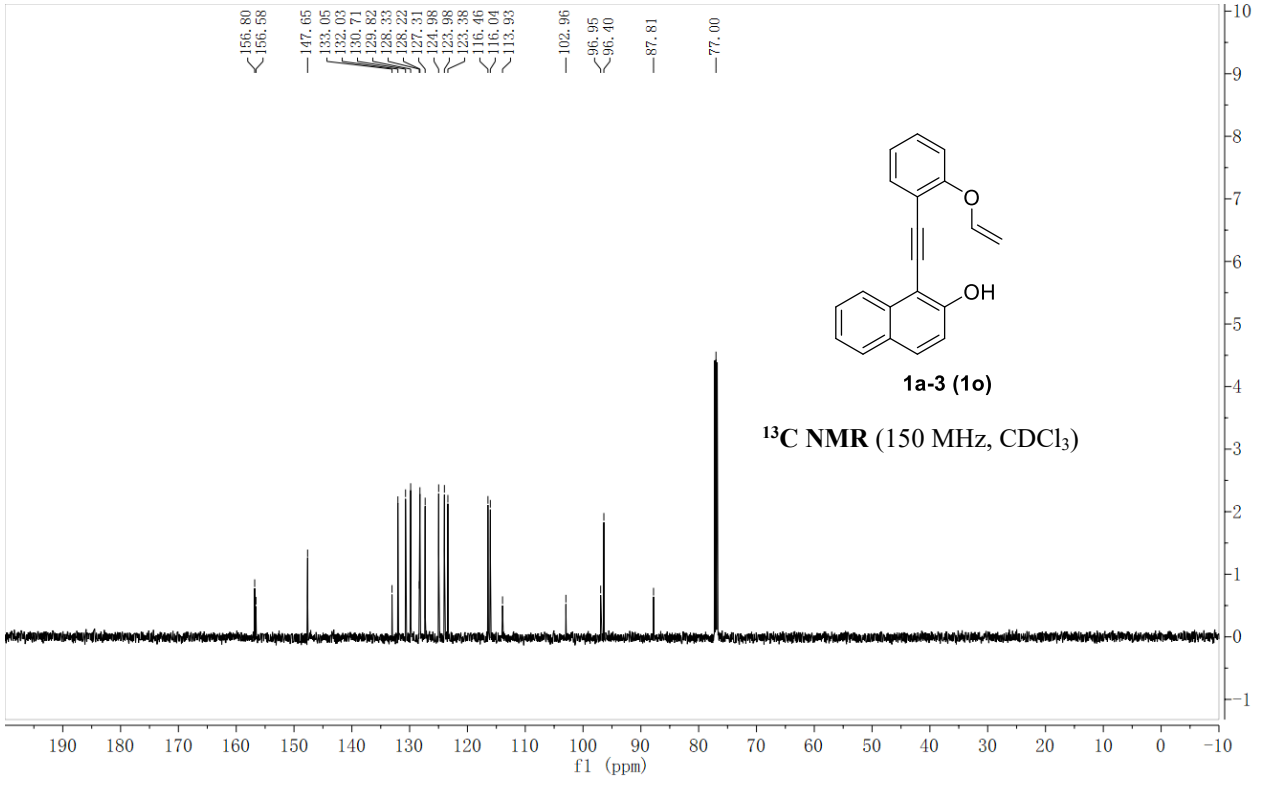
^{1}H NMR (400 MHz, $CDCl_3$)



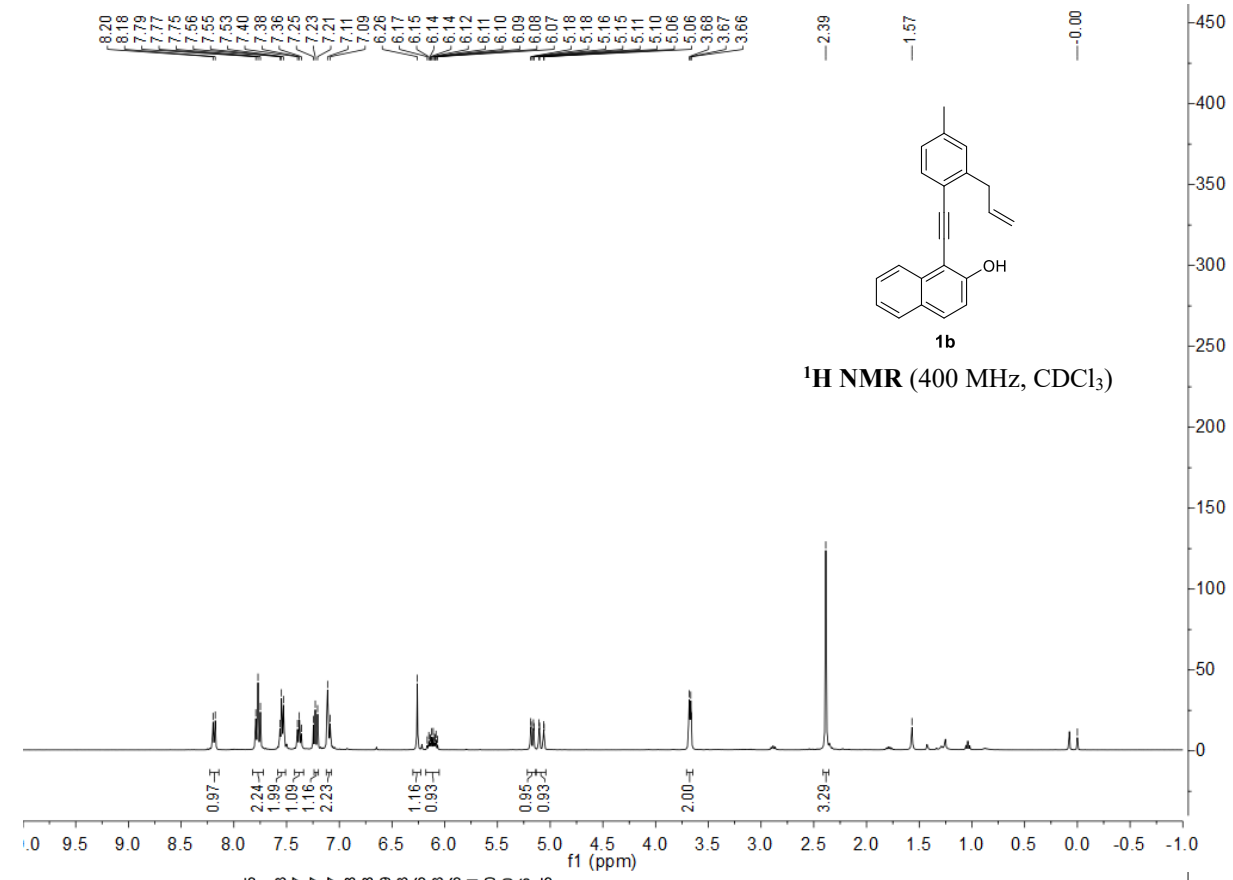
^{13}C NMR (100 MHz, $CDCl_3$)



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

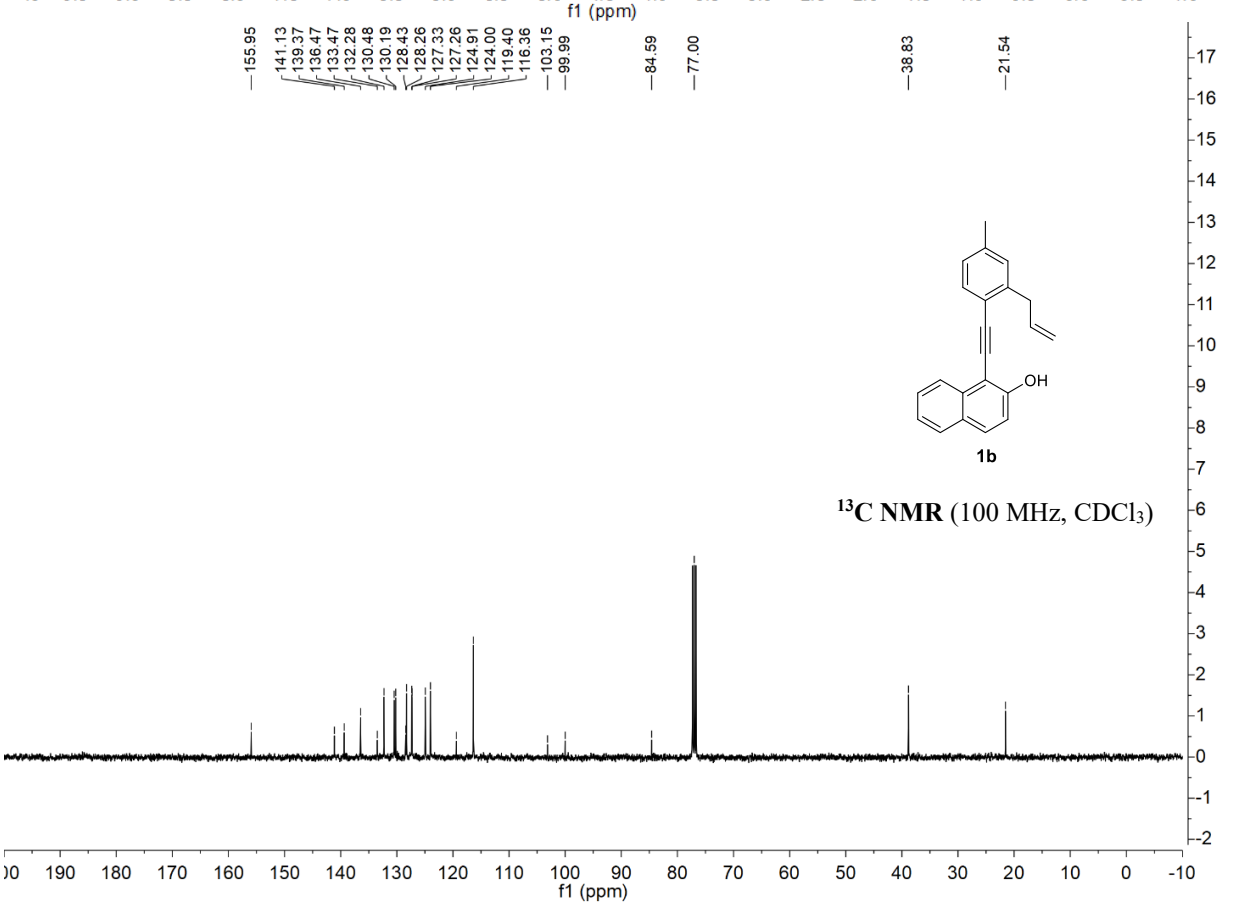


^{13}C NMR (150 MHz, $CDCl_3$)



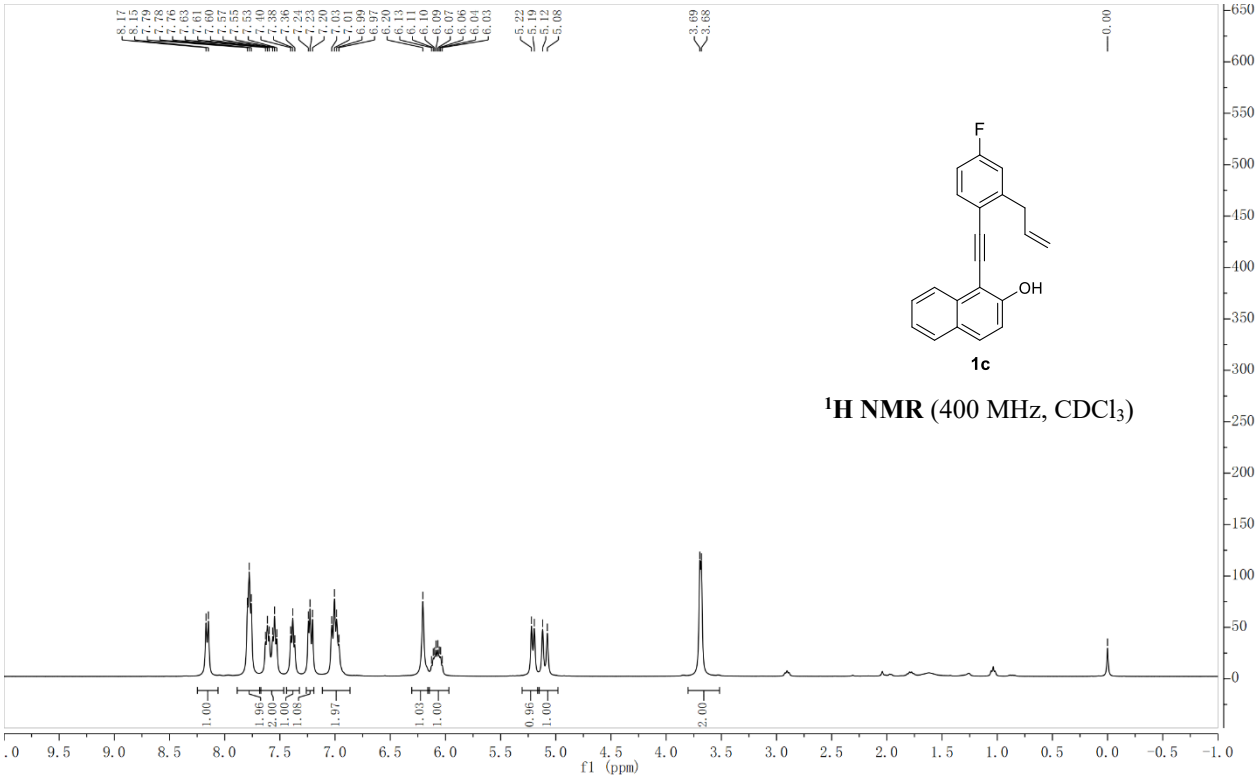
1b

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

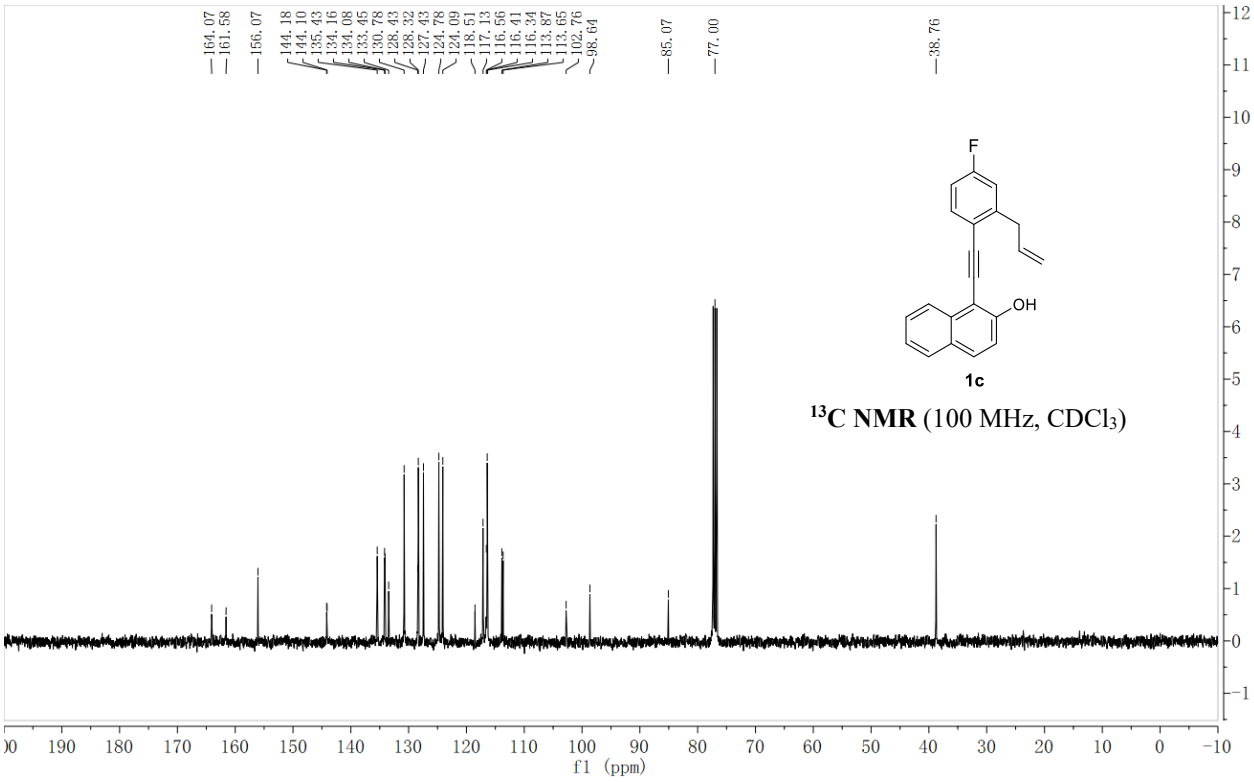


1b

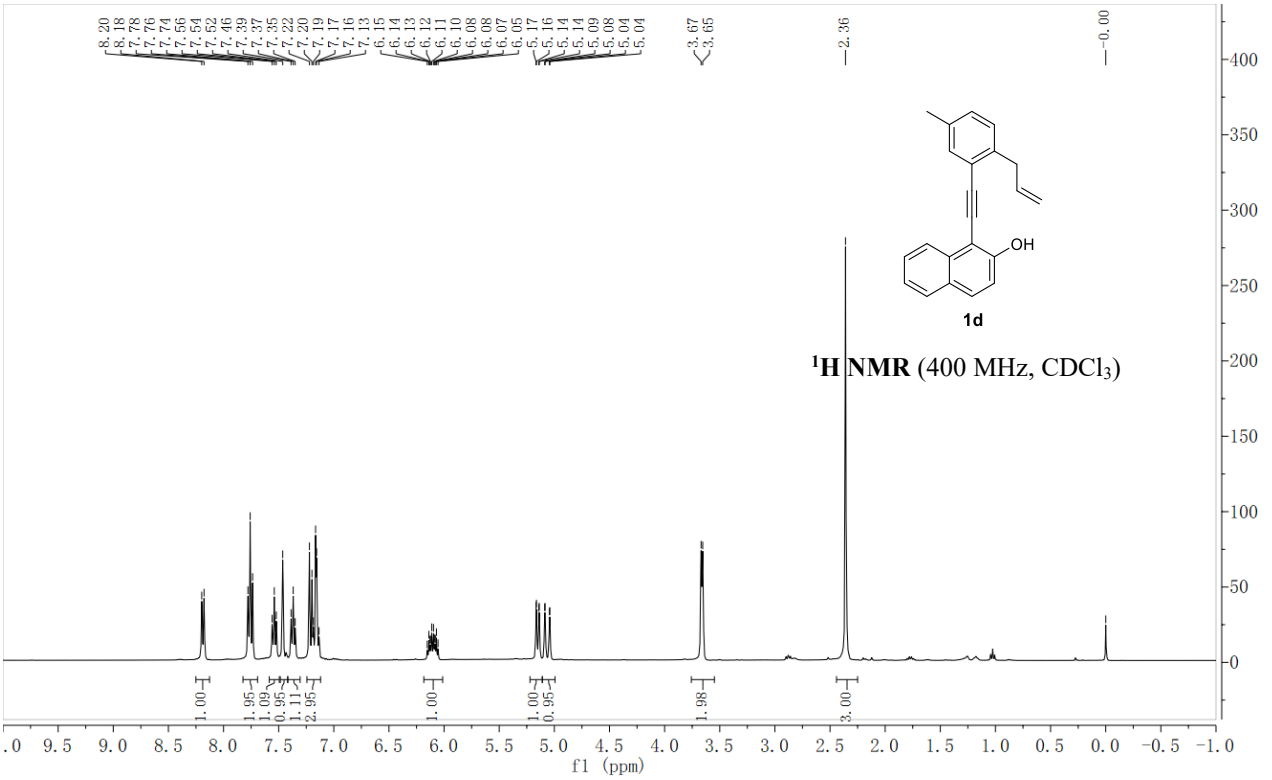
^{13}C NMR (100 MHz, $CDCl_3$)

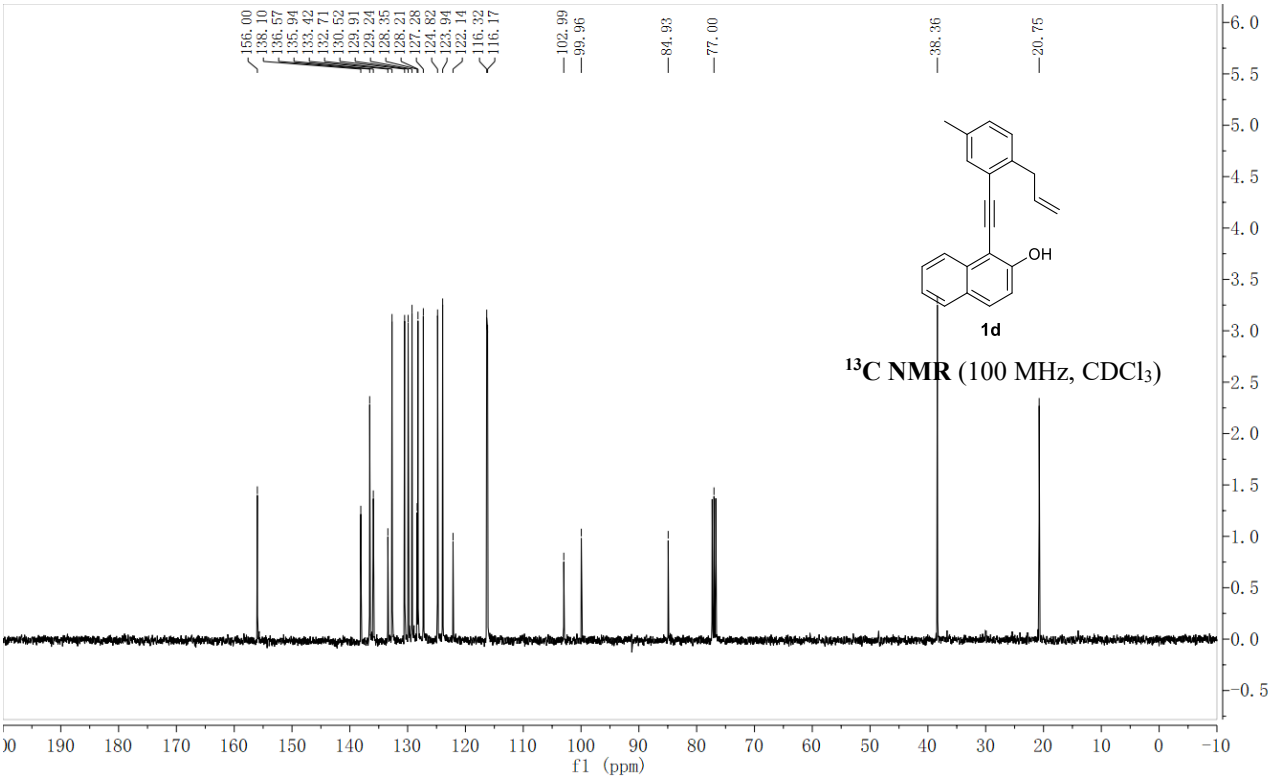


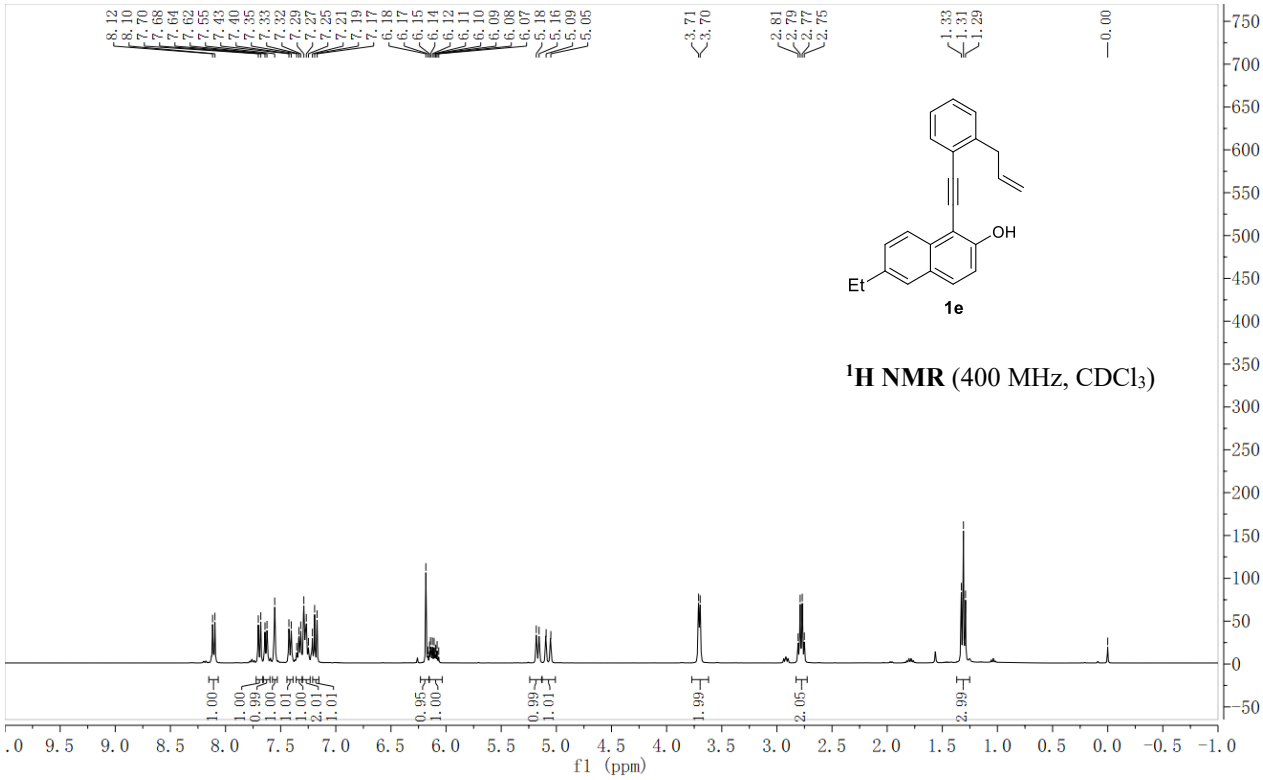
^{1}H NMR (400 MHz, $CDCl_3$)



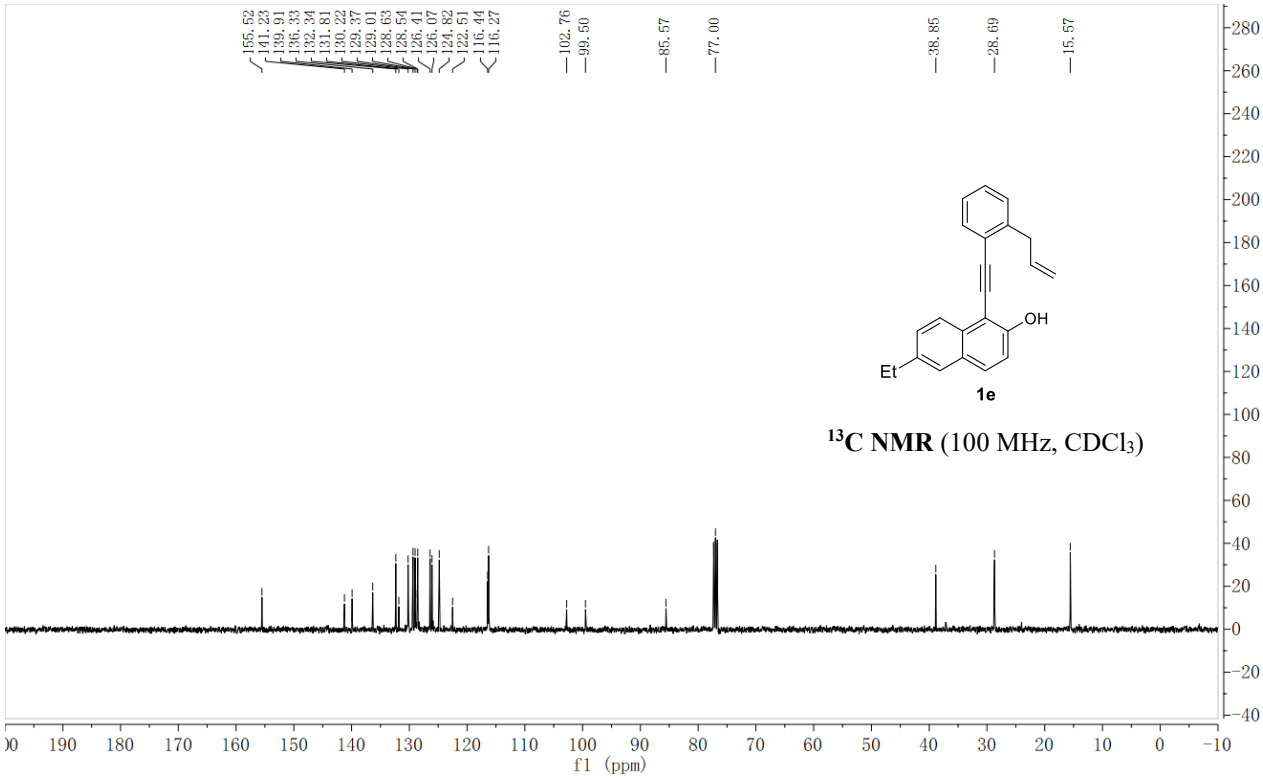
^{13}C NMR (100 MHz, $CDCl_3$)


OH
1d
1H NMR (400 MHz, CDCl3)
f1 (ppm)

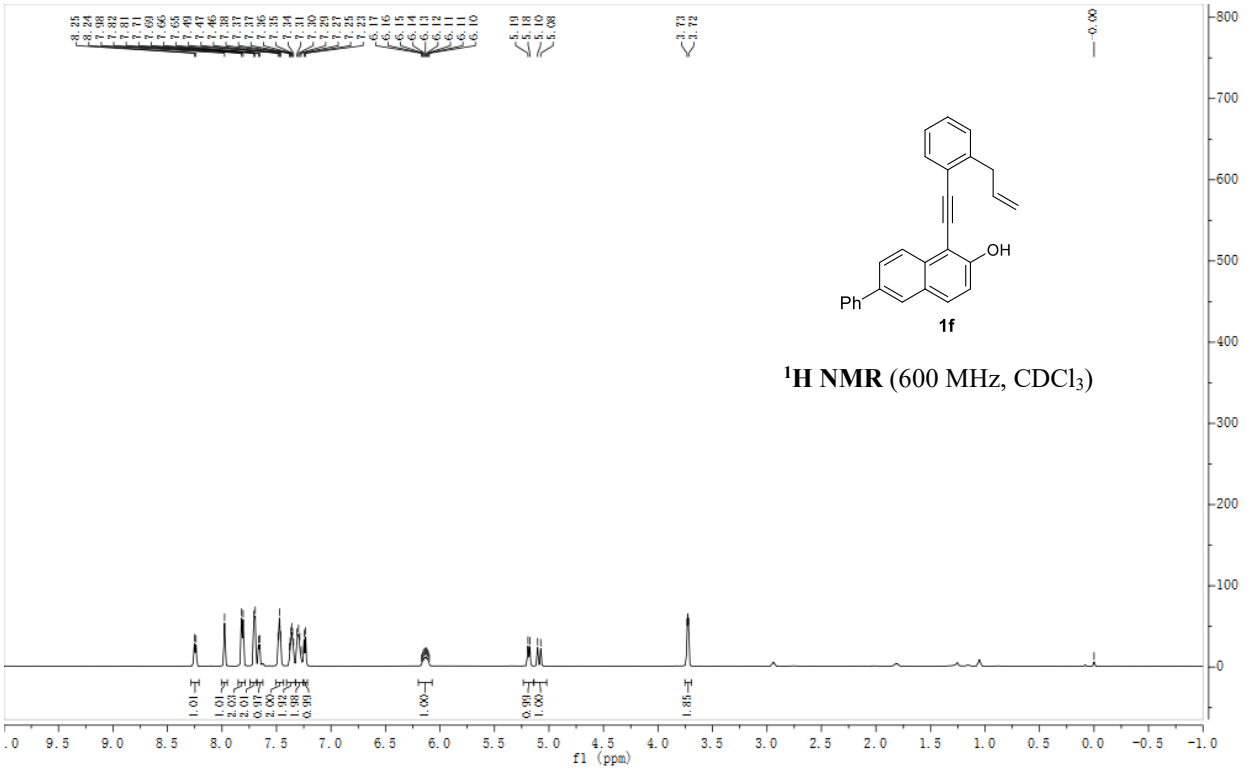

OH
1d
13C NMR (100 MHz, CDCl3)
f1 (ppm)



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

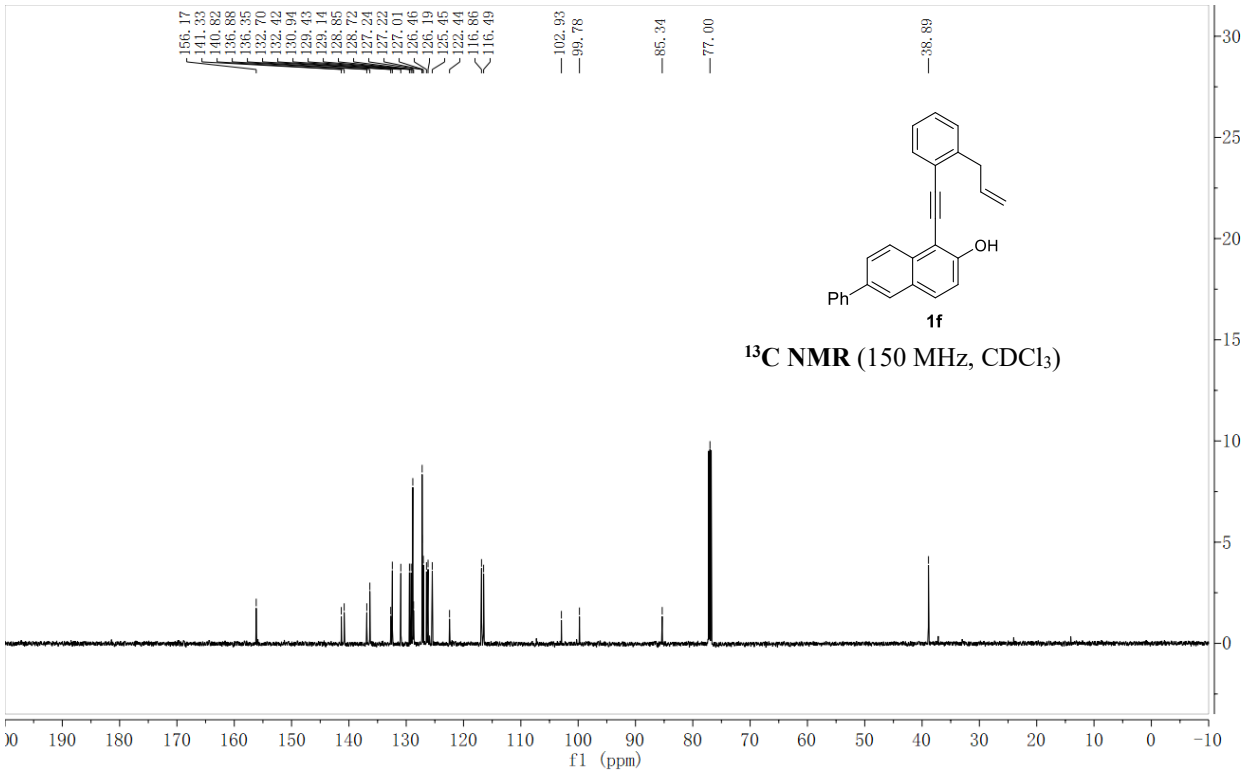


^{13}C NMR (100 MHz, $CDCl_3$)



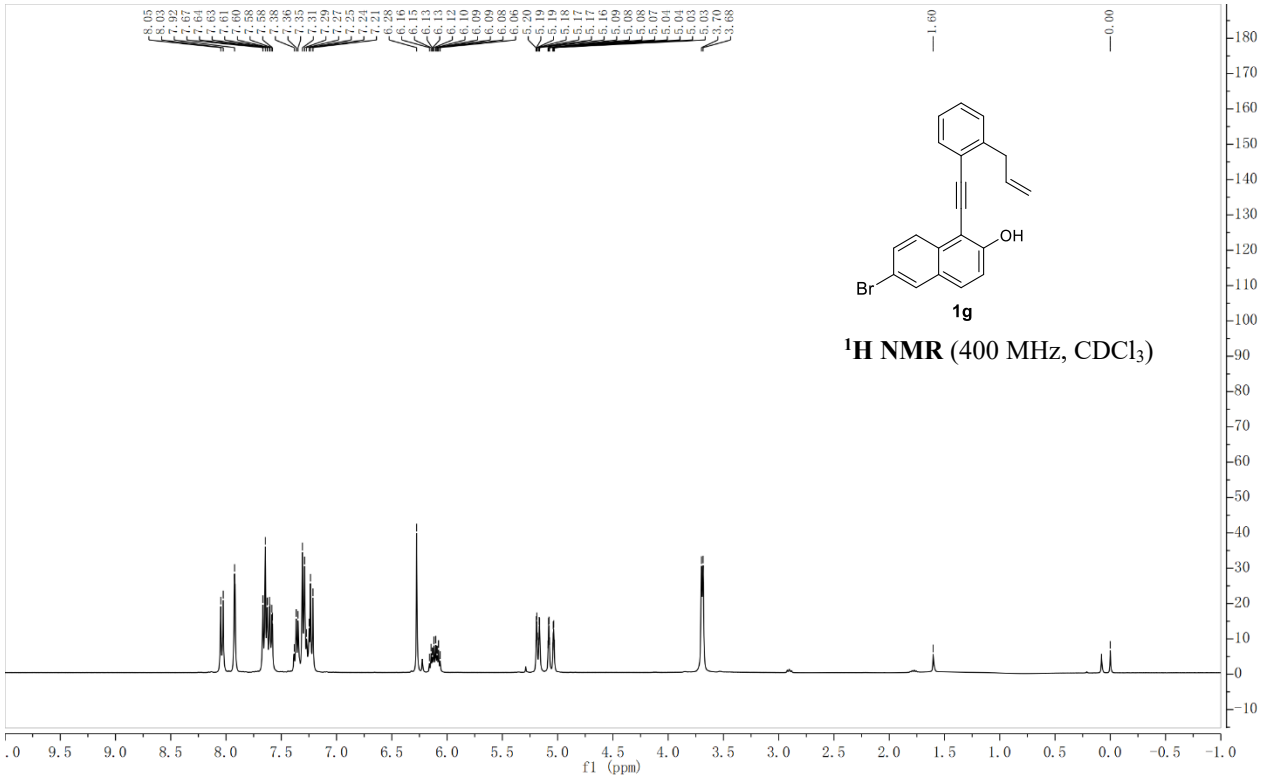
1f

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

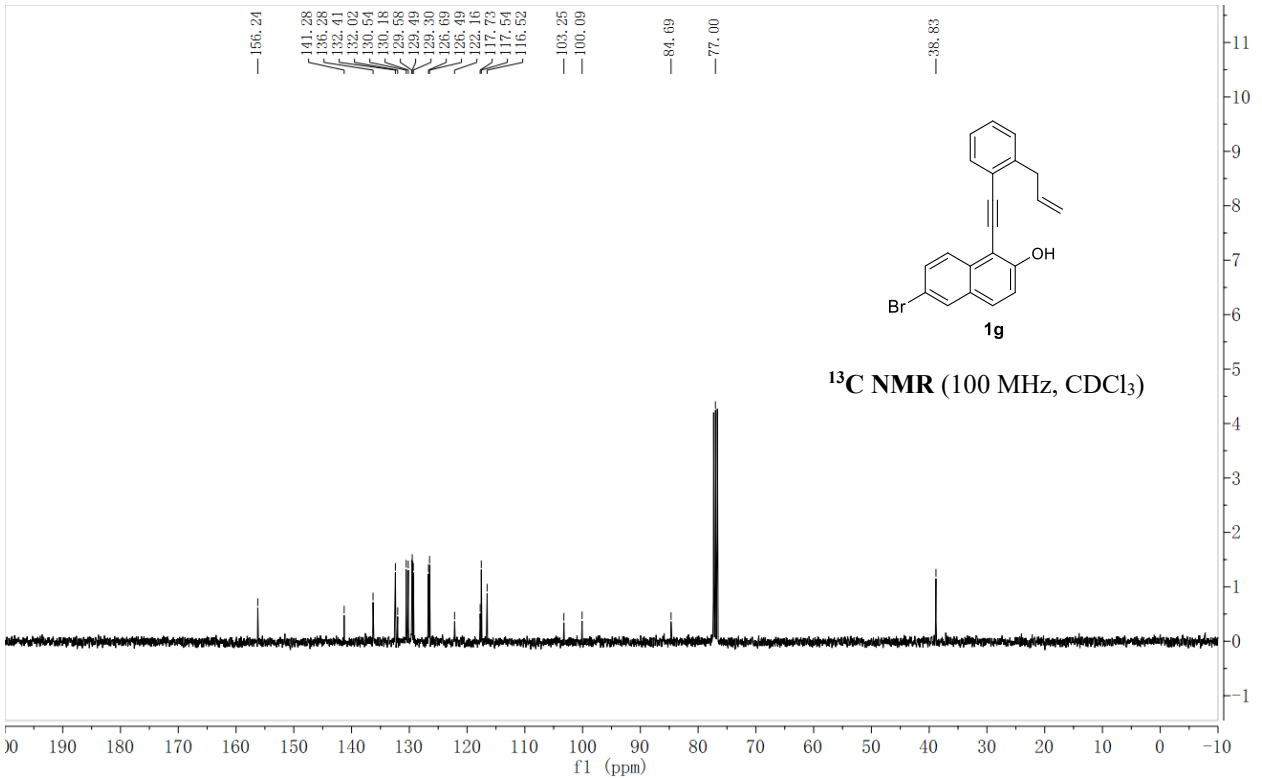


1f

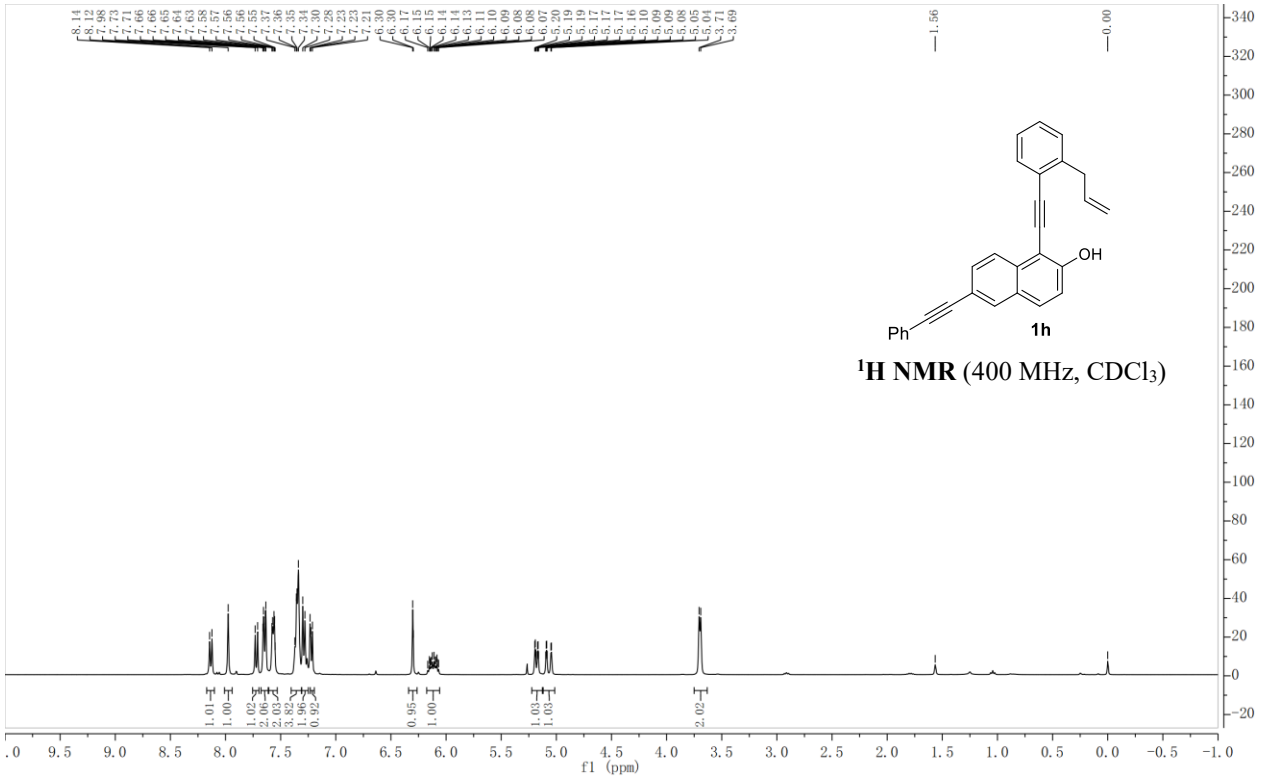
^{13}C NMR (150 MHz, $CDCl_3$)



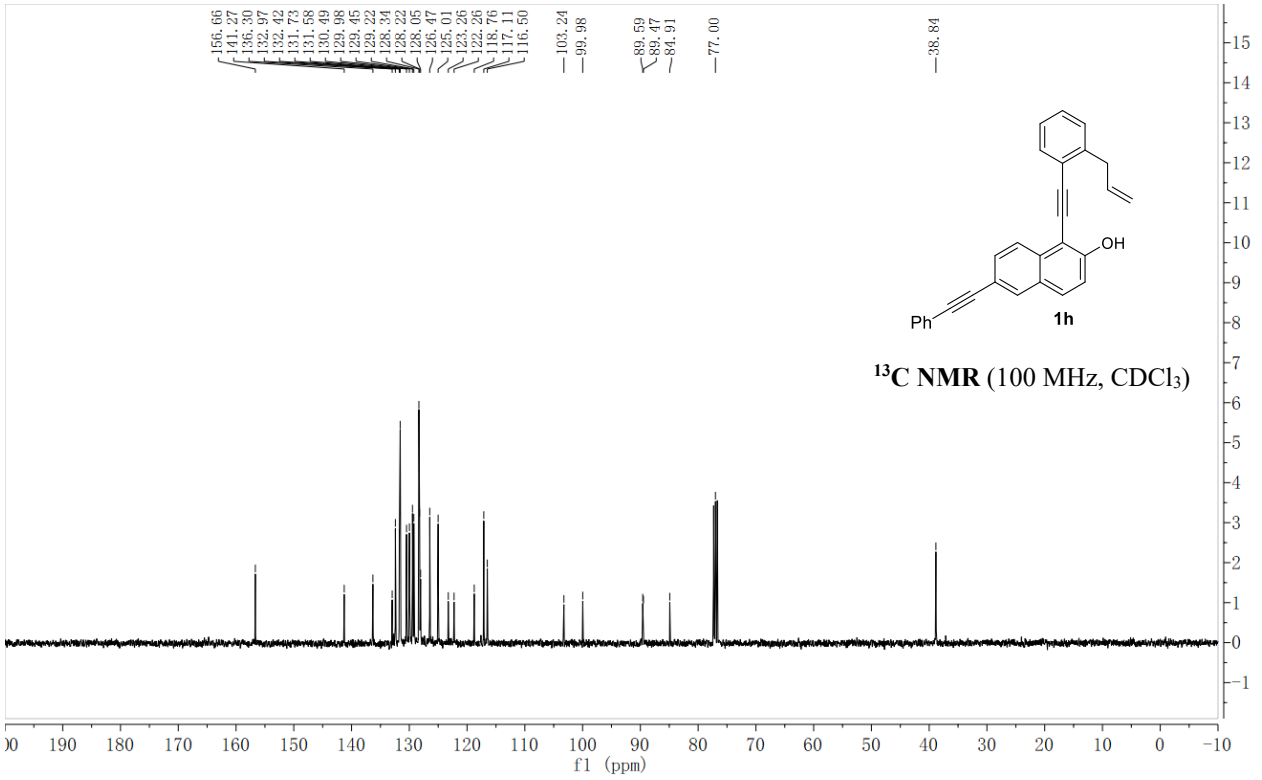
^{1}H NMR (400 MHz, $CDCl_3$)



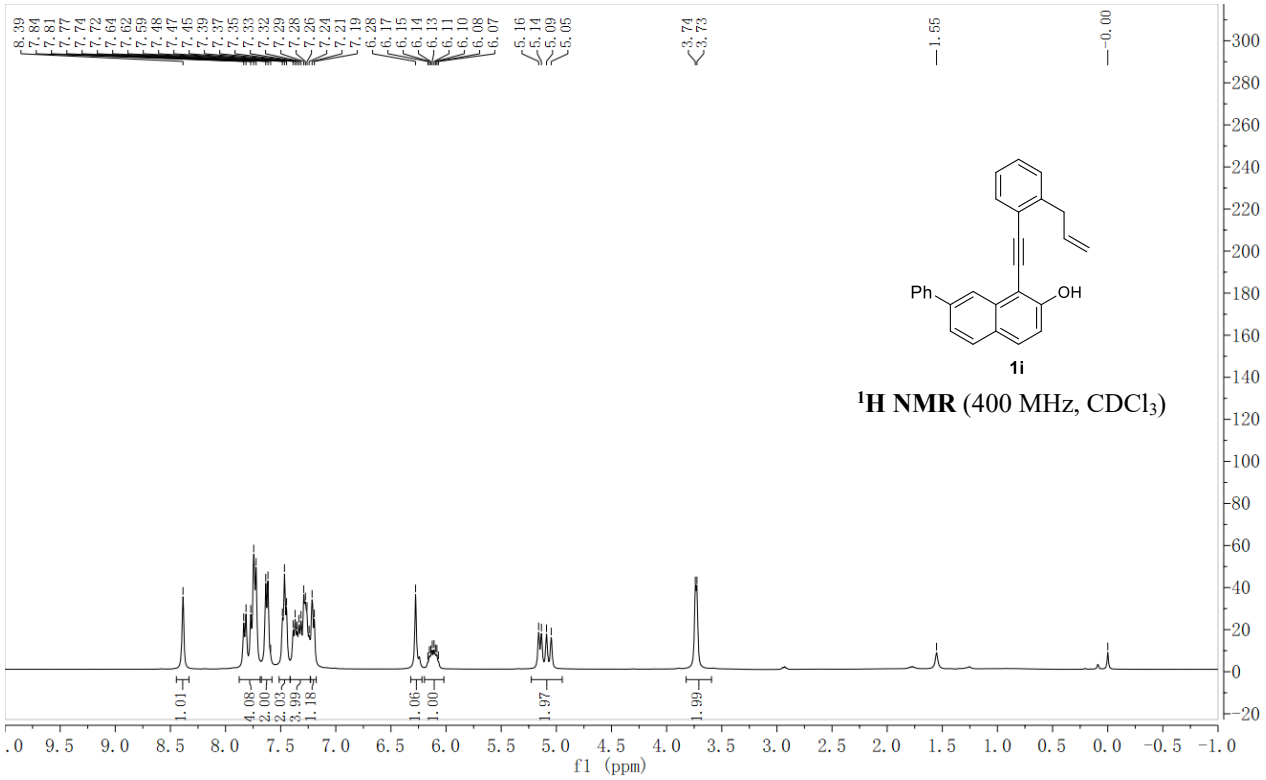
^{13}C NMR (100 MHz, $CDCl_3$)



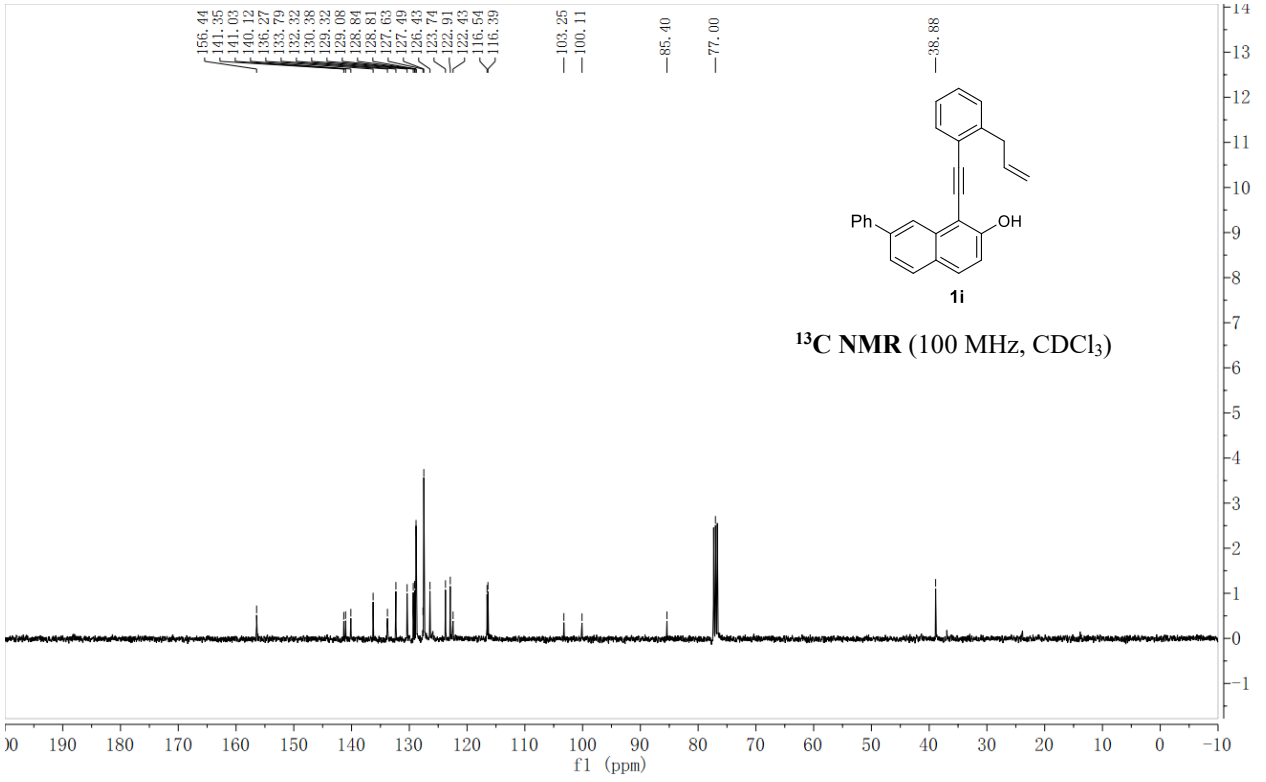
^{1}H NMR (400 MHz, $CDCl_3$)



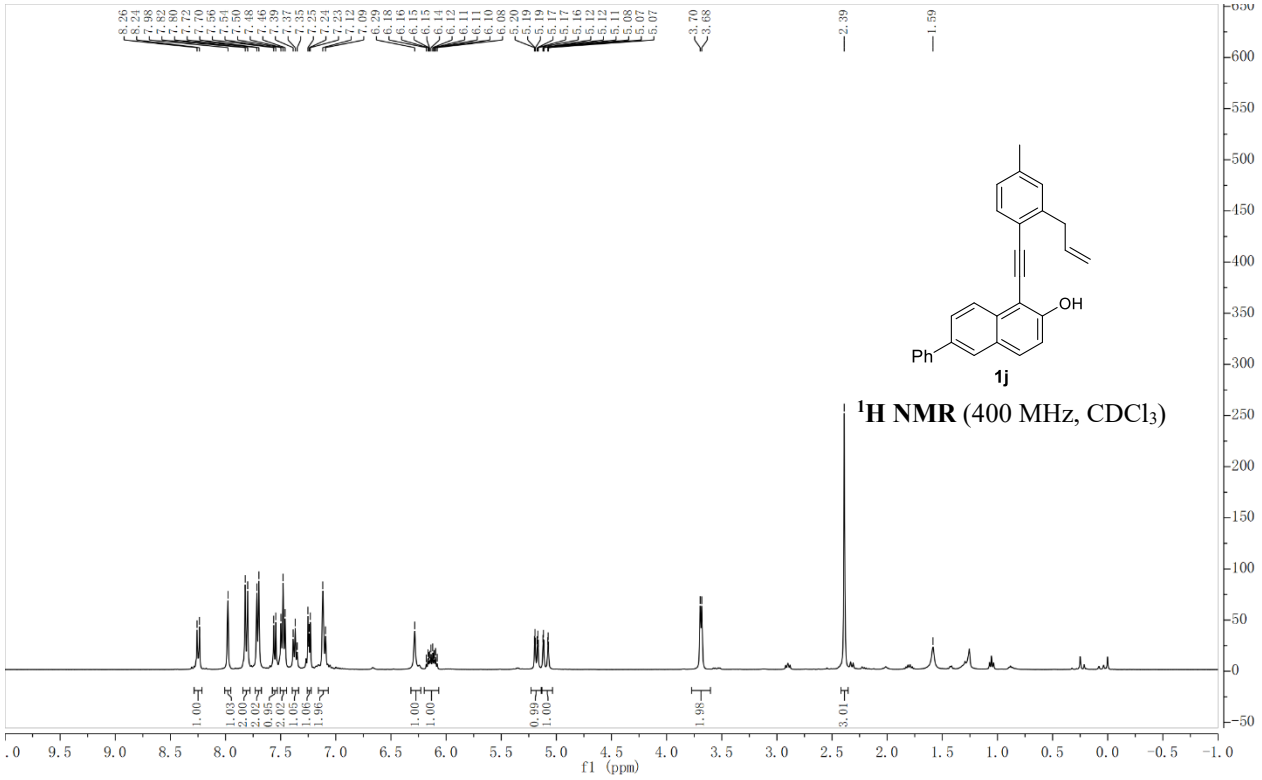
^{13}C NMR (100 MHz, $CDCl_3$)

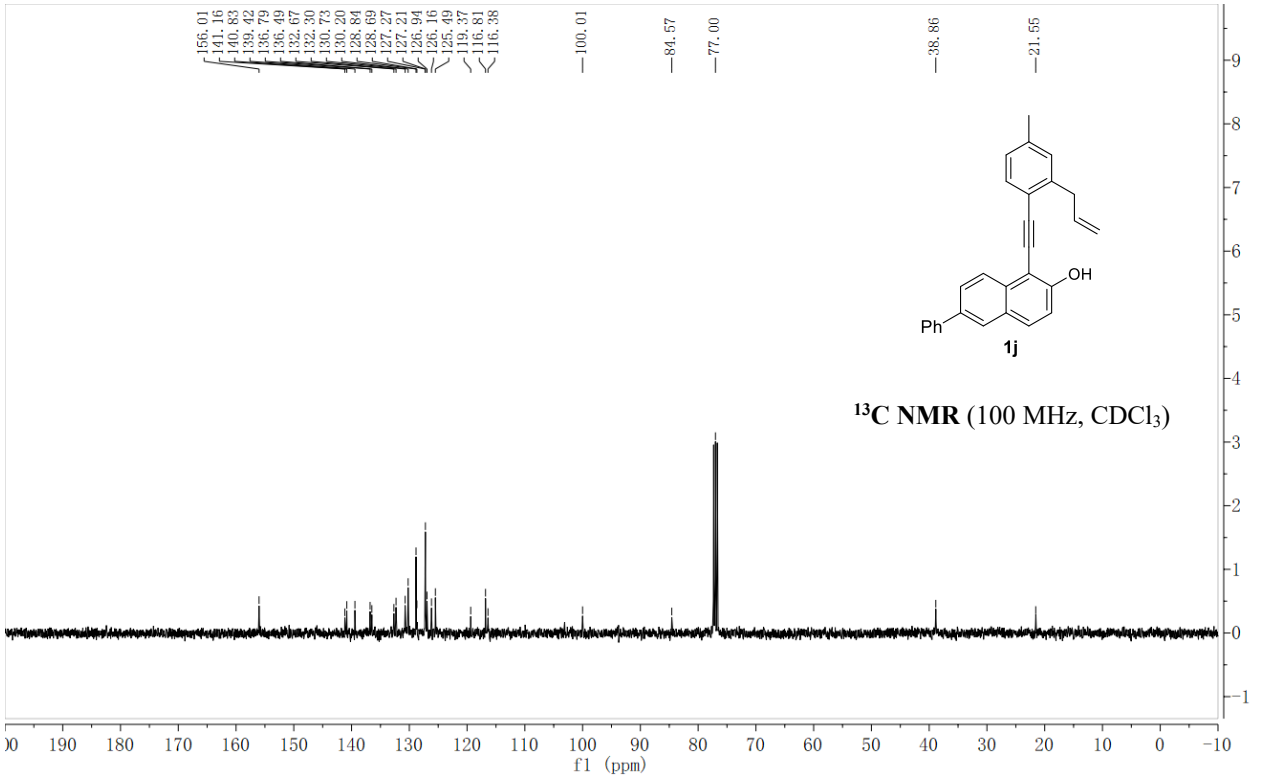


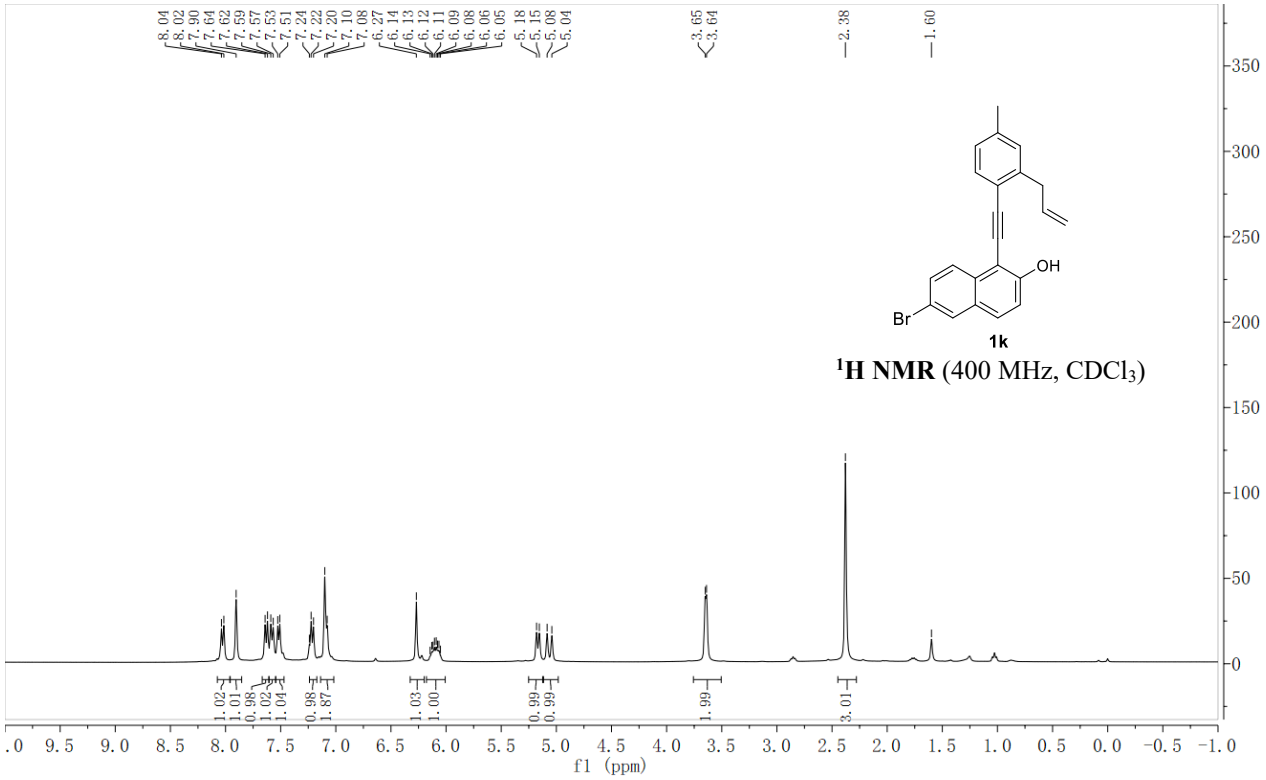
^{1}H NMR (400 MHz, $CDCl_3$)



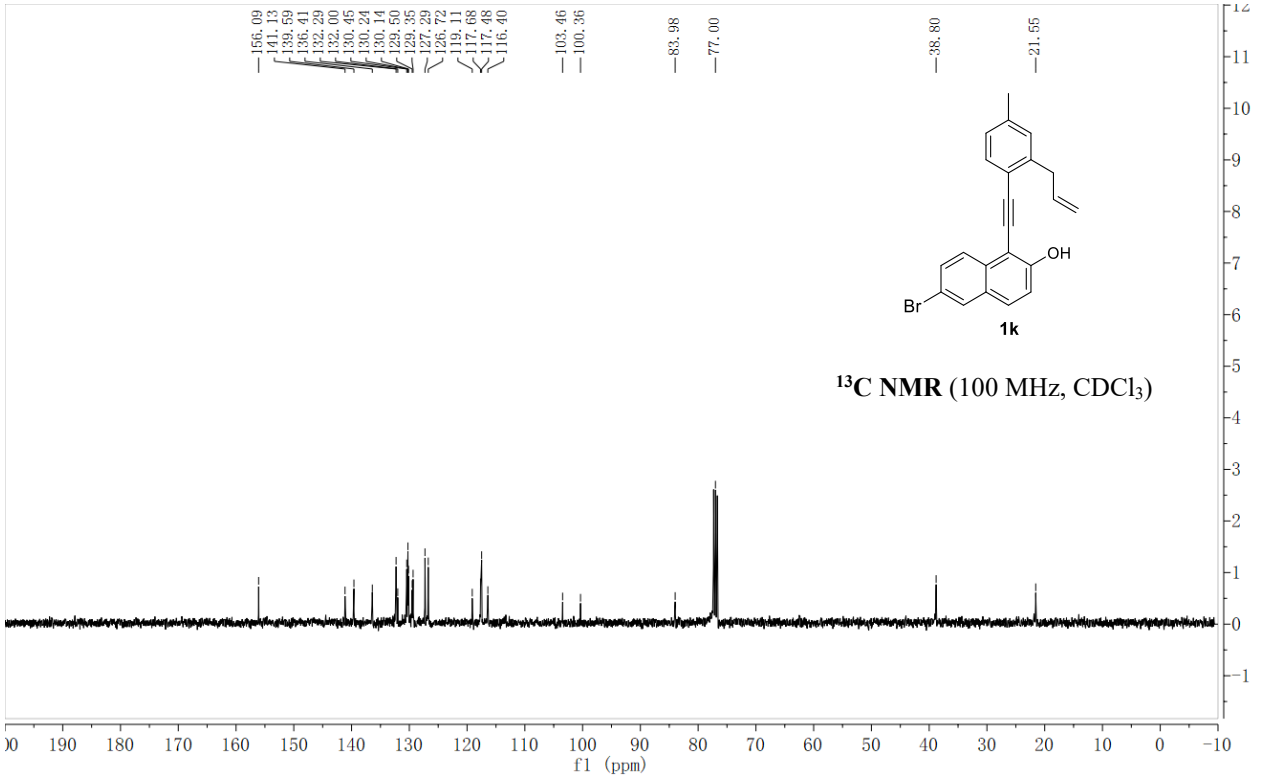
^{13}C NMR (100 MHz, $CDCl_3$)


OH
Ph
1j
1H NMR (400 MHz, CDCl3)
f1 (ppm)

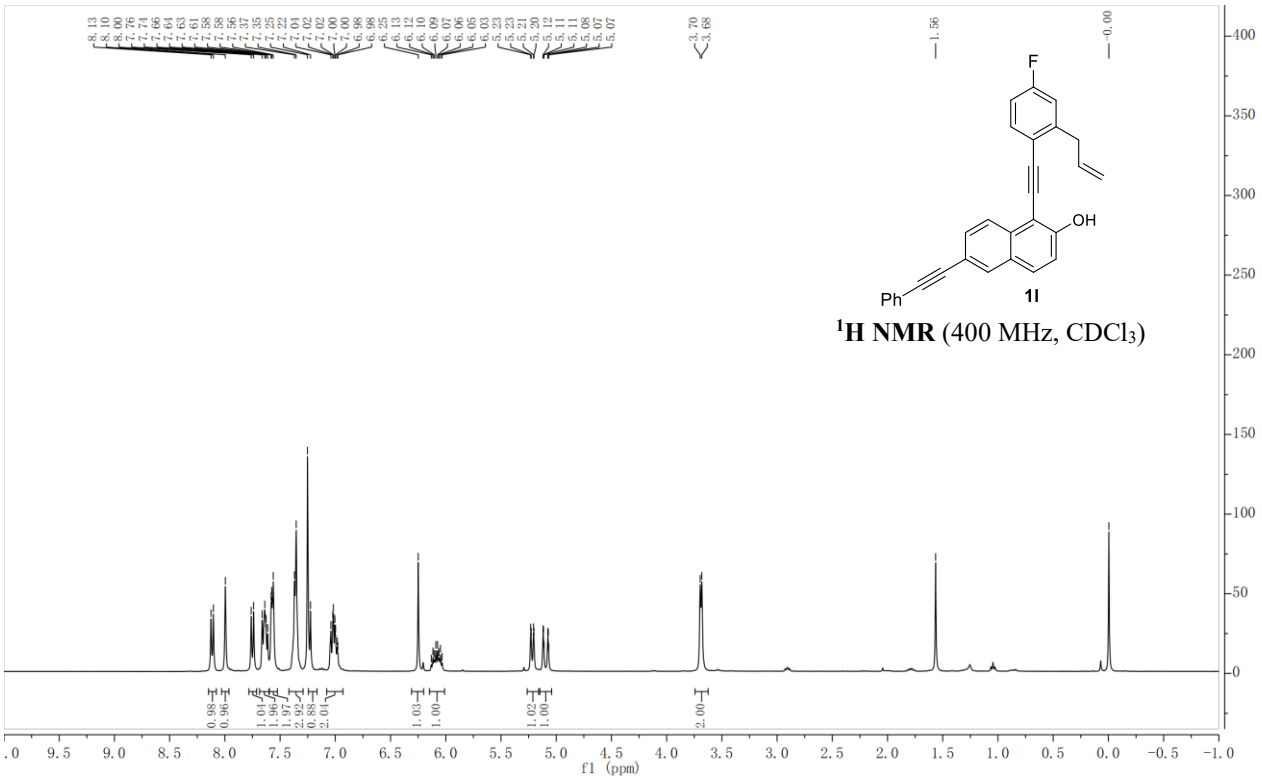

OH
Ph
1j
13C NMR (100 MHz, CDCl3)
f1 (ppm)



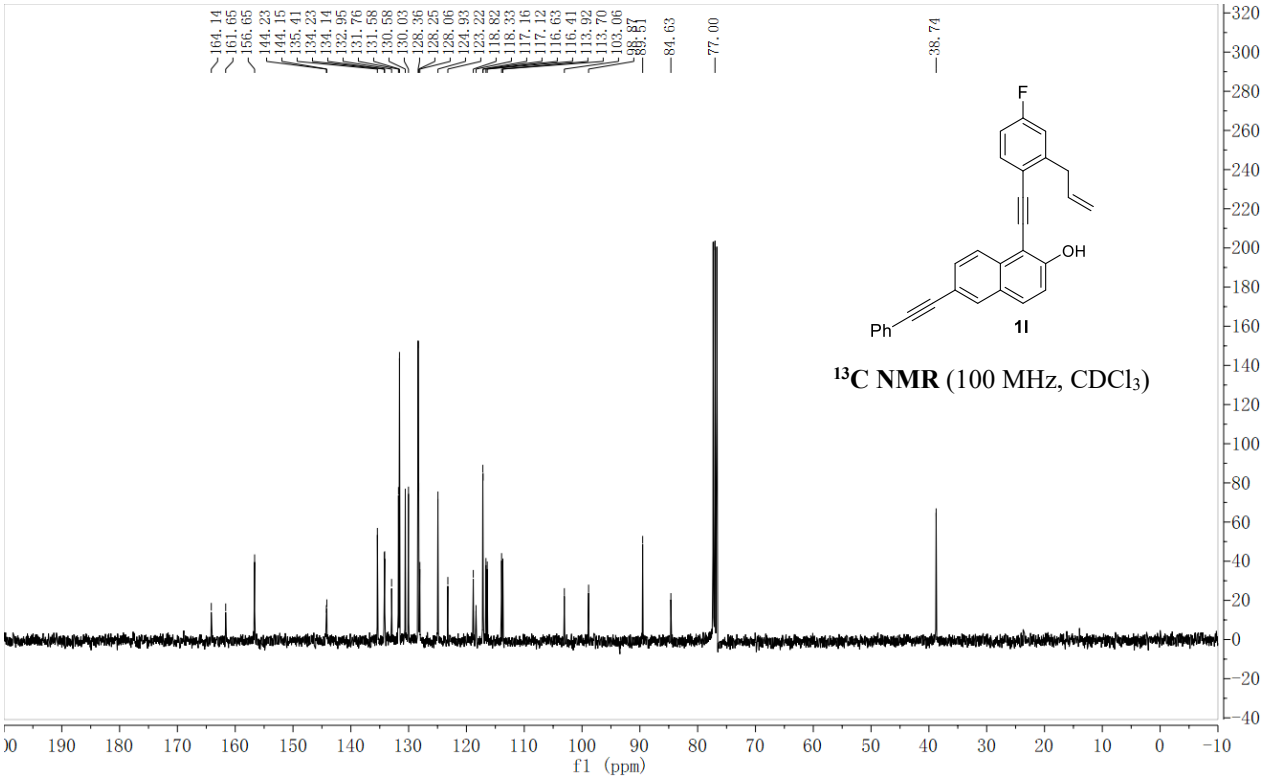
^{1}H NMR (400 MHz, $CDCl_3$)



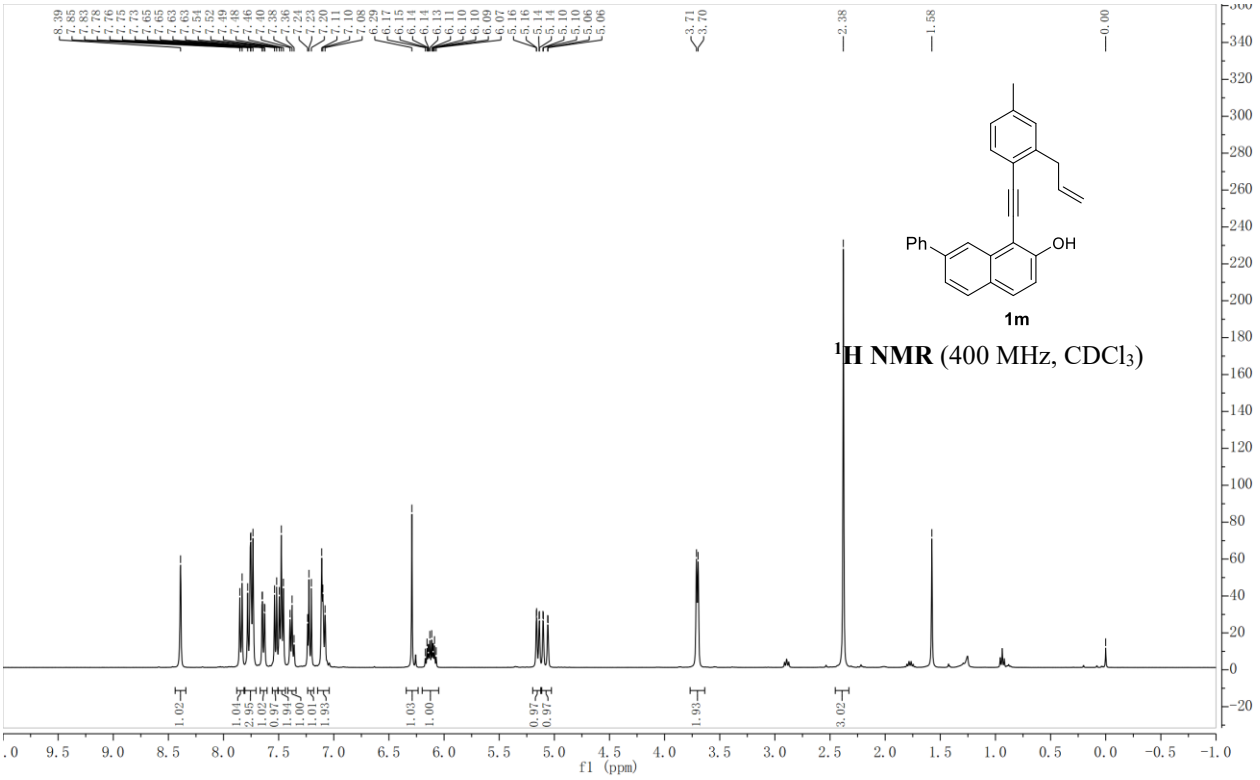
^{13}C NMR (100 MHz, $CDCl_3$)



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

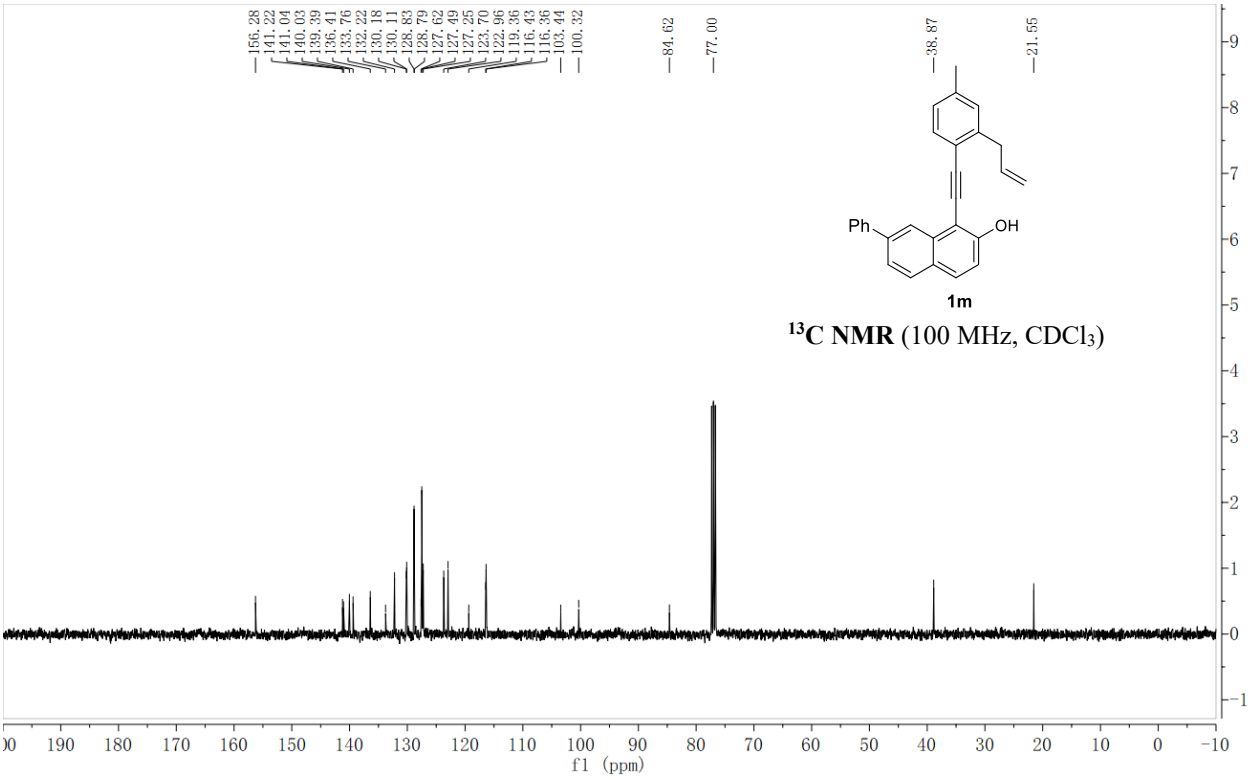


^{13}C NMR (100 MHz, $CDCl_3$)



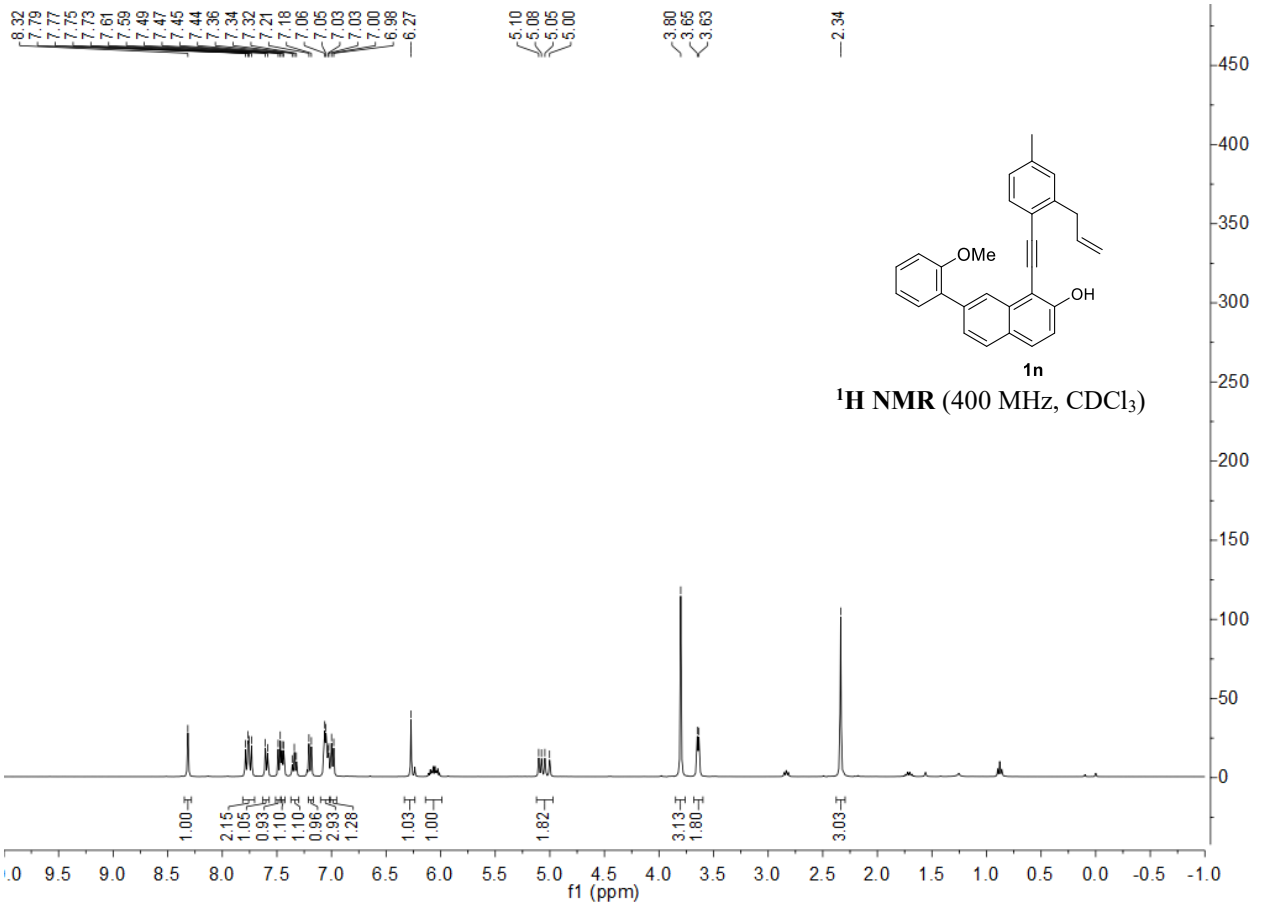
1m

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

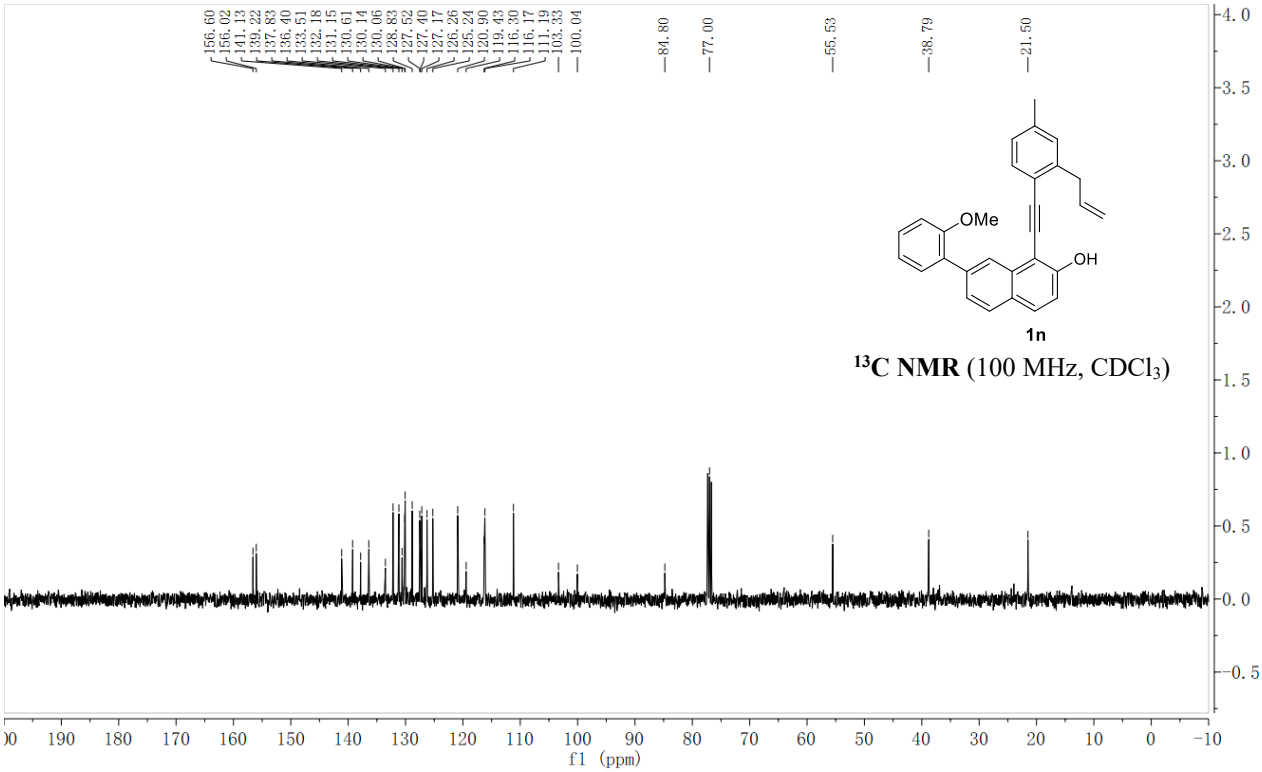


1m

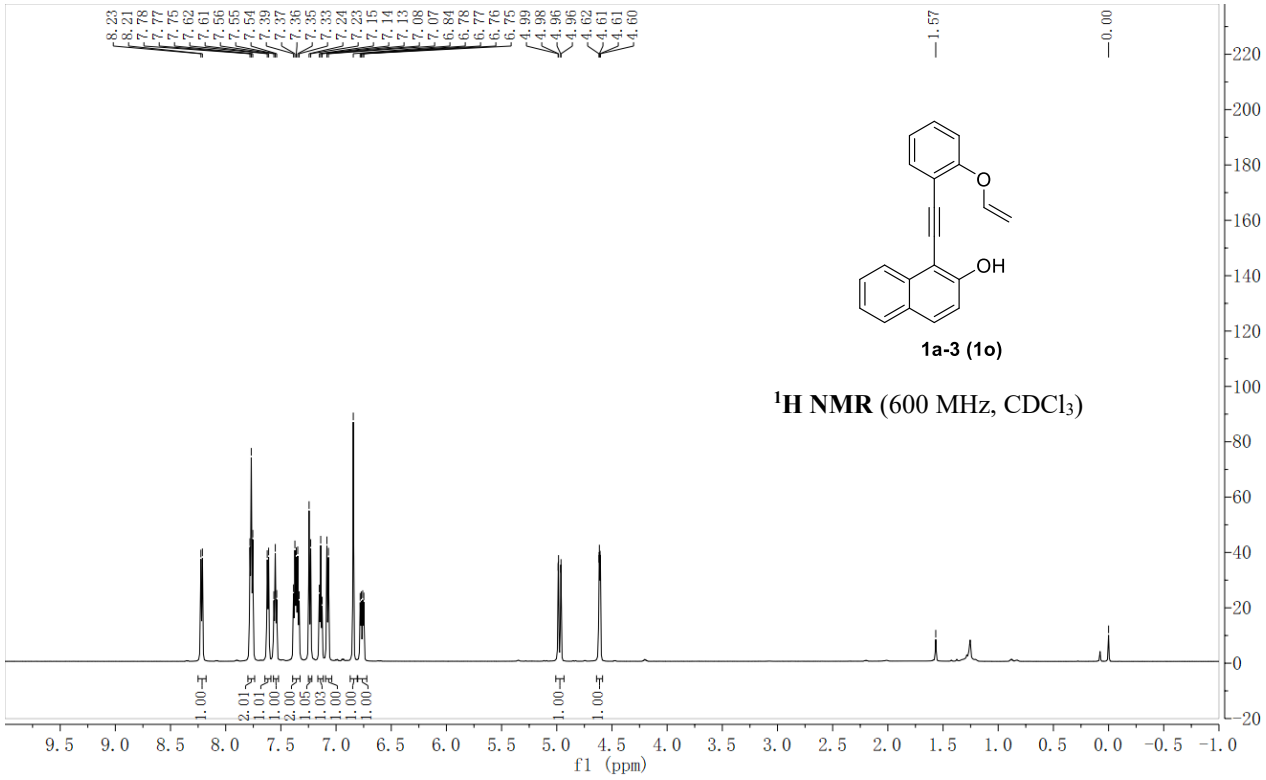
^{13}C NMR (100 MHz, $CDCl_3$)



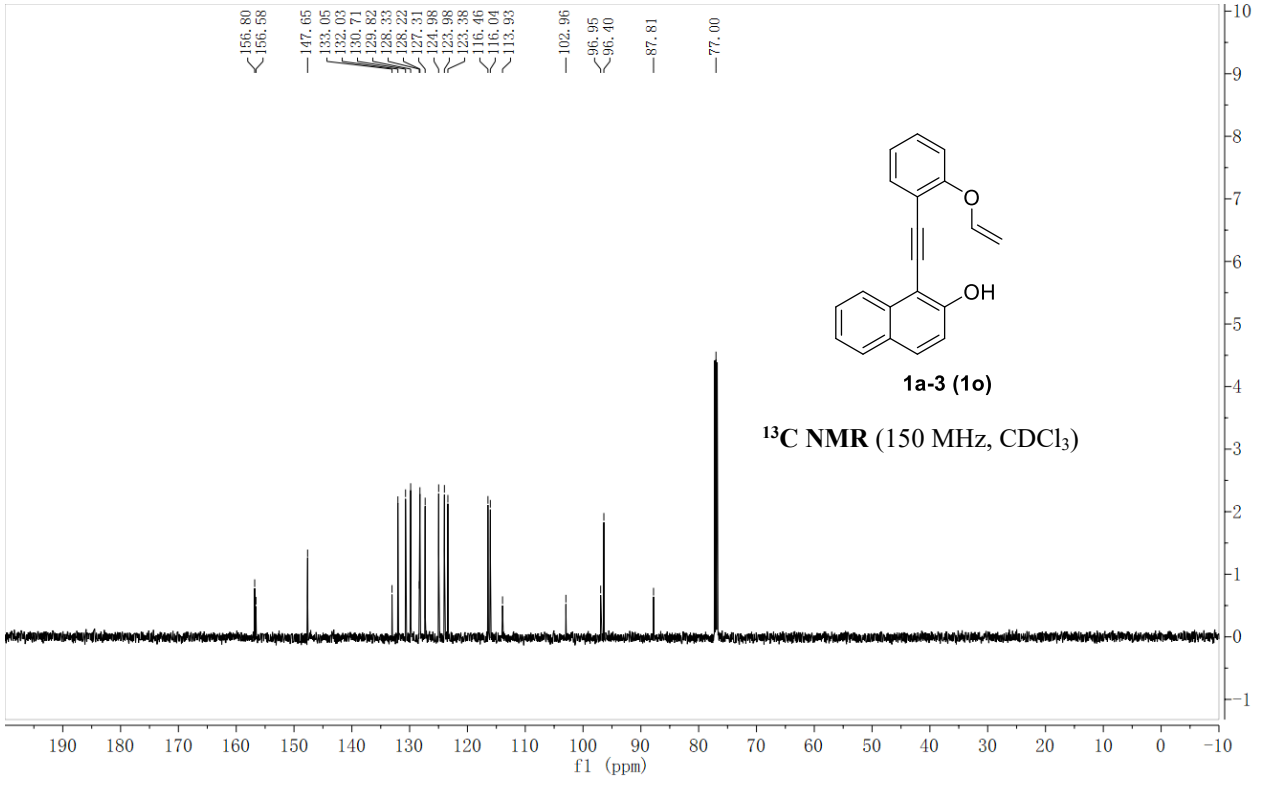
^{1}H NMR (400 MHz, $CDCl_3$)



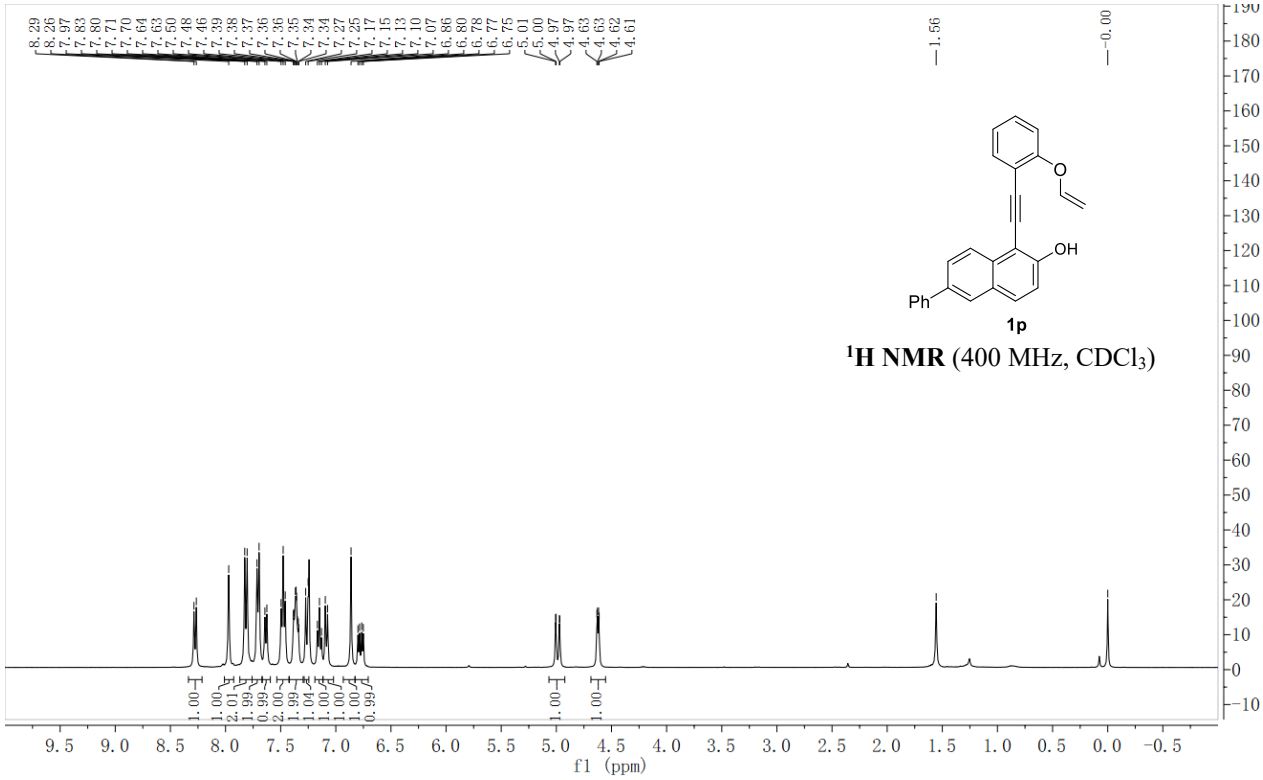
^{13}C NMR (100 MHz, $CDCl_3$)



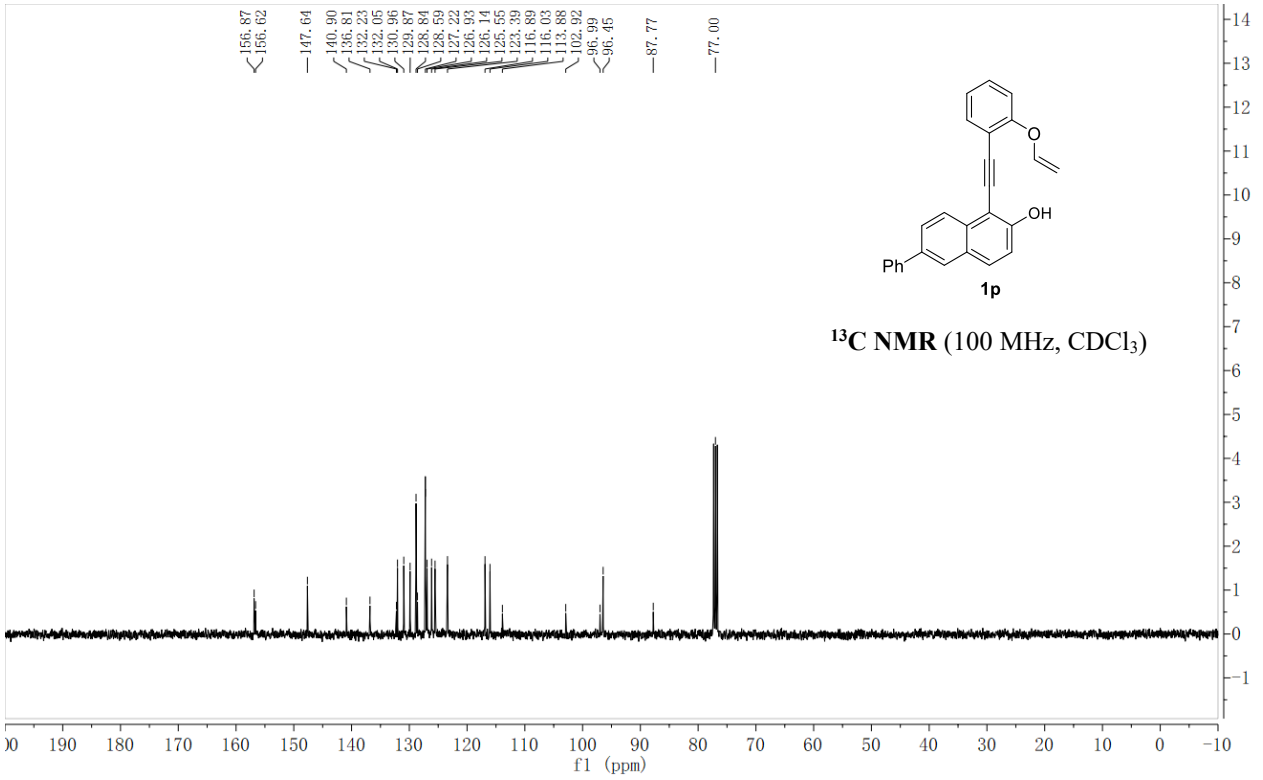
^{1}H NMR (600 MHz, $CDCl_3$)



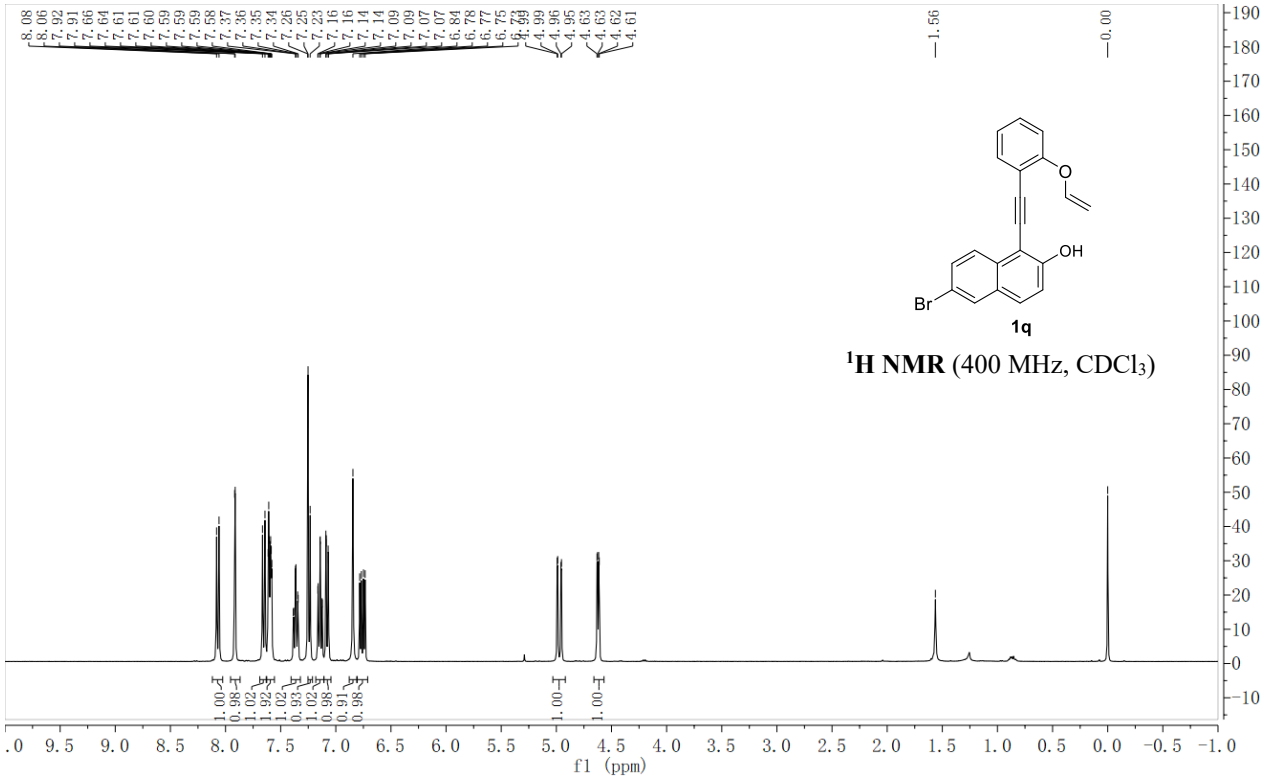
^{13}C NMR (150 MHz, $CDCl_3$)



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

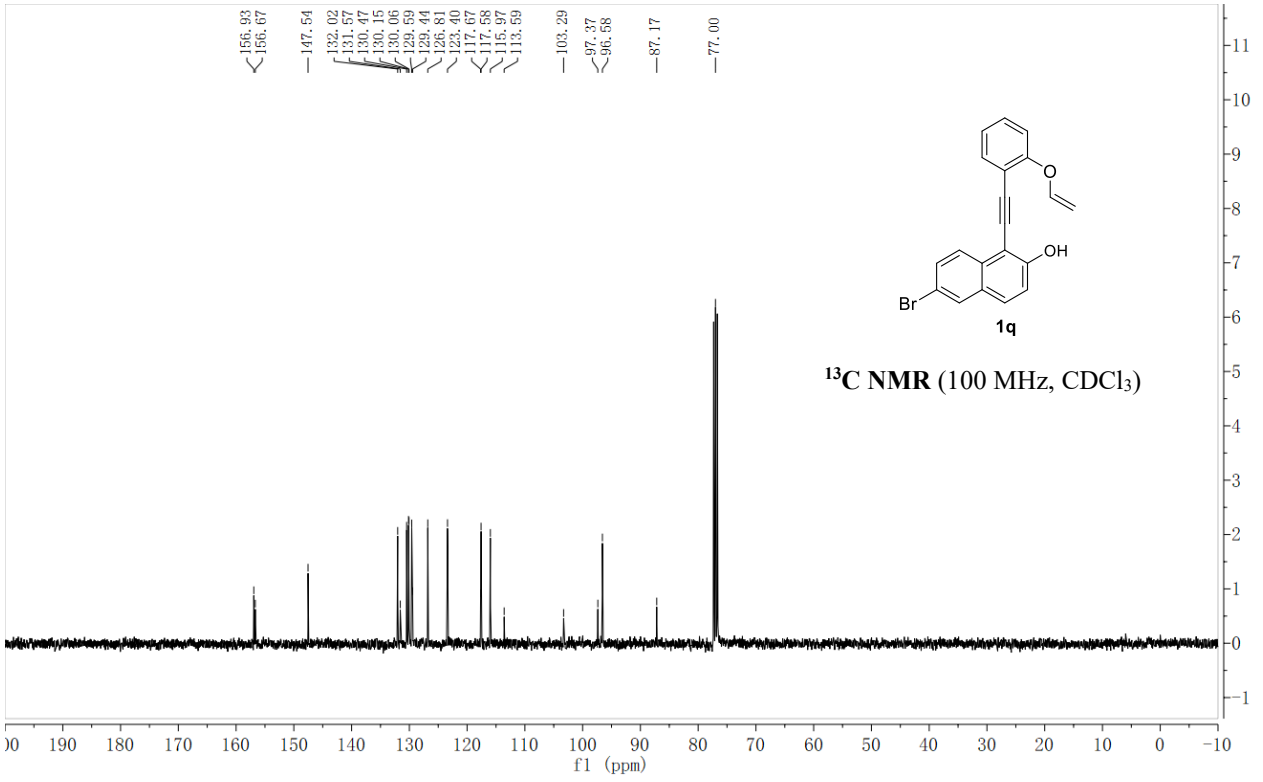


^{13}C NMR (100 MHz, $CDCl_3$)



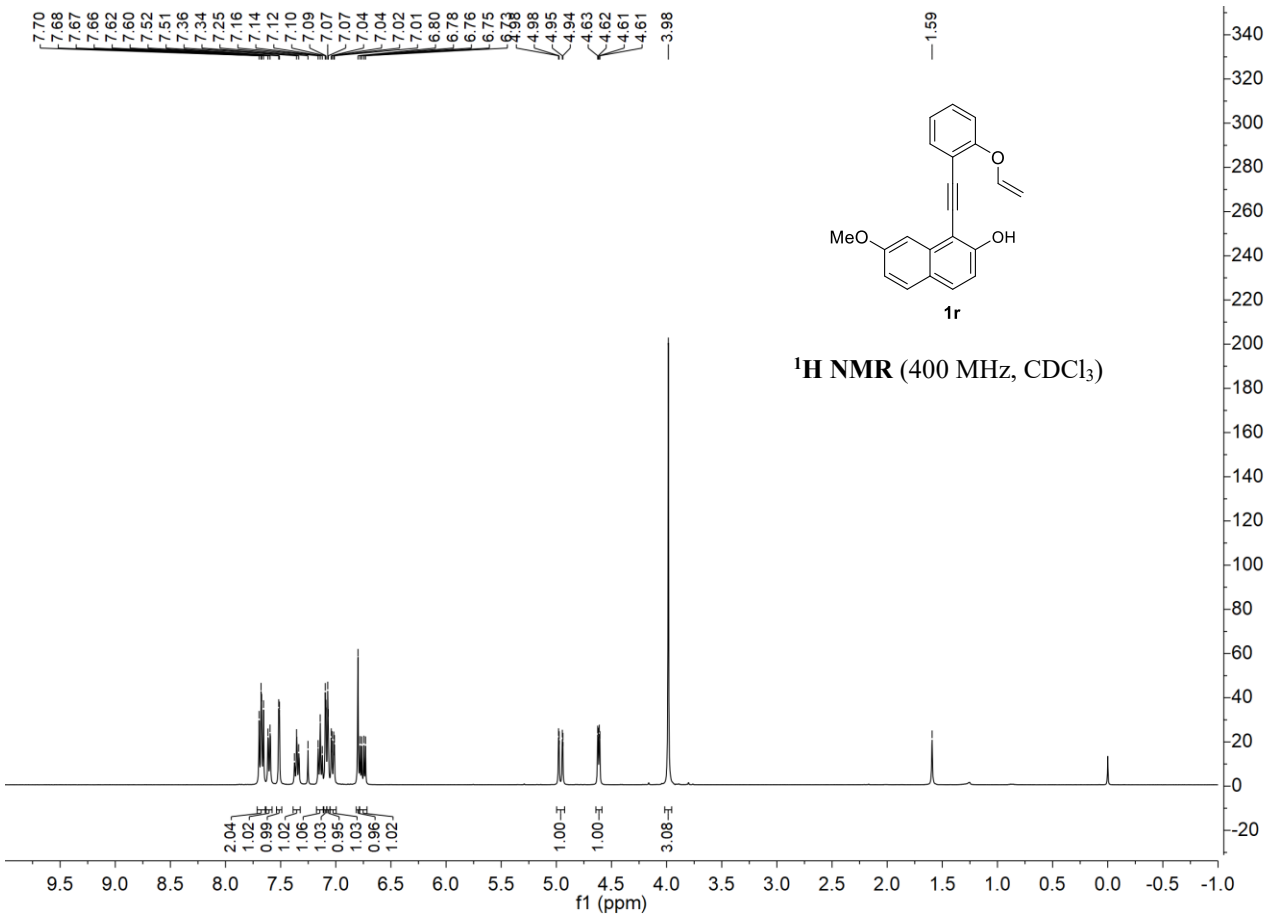
1q

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



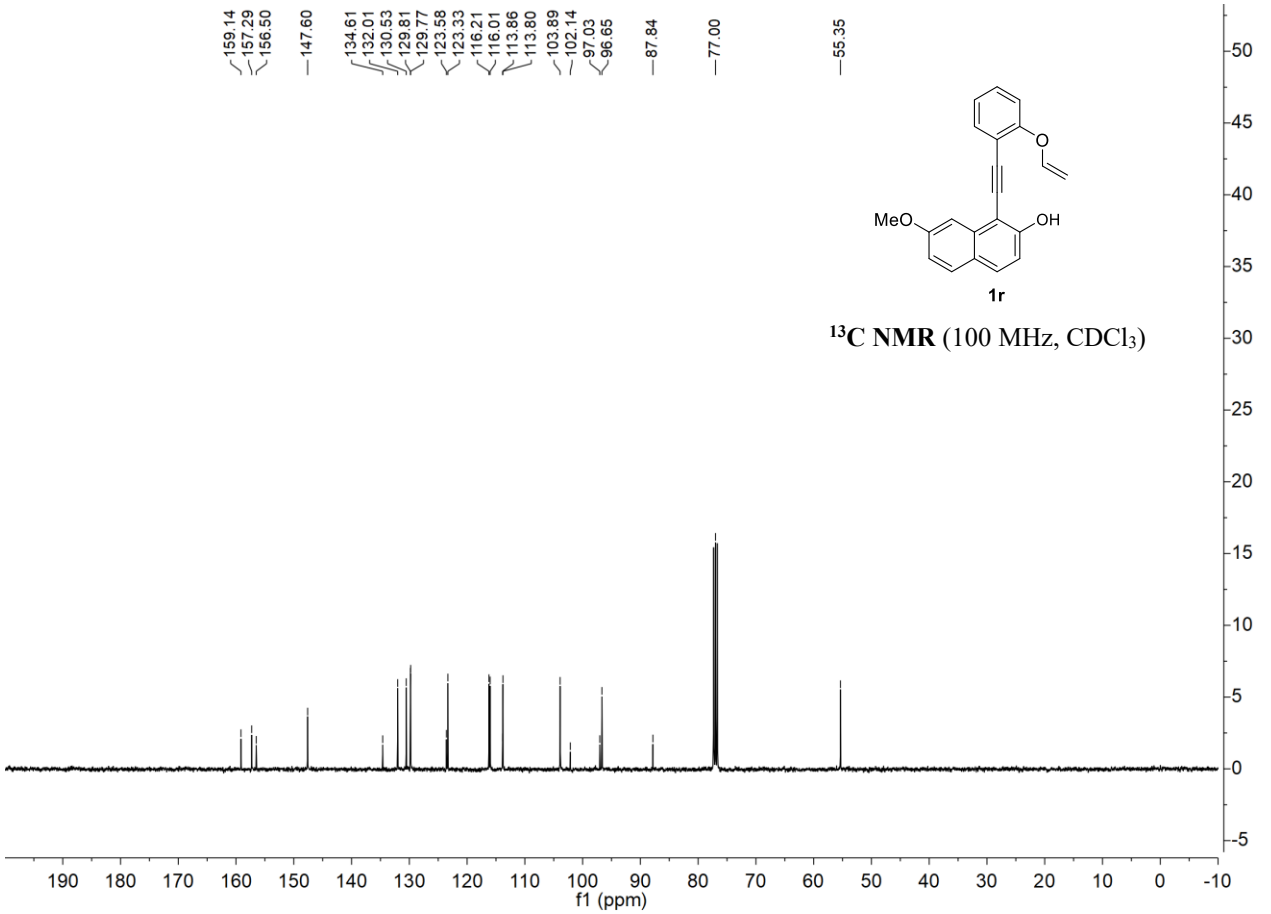
1q

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



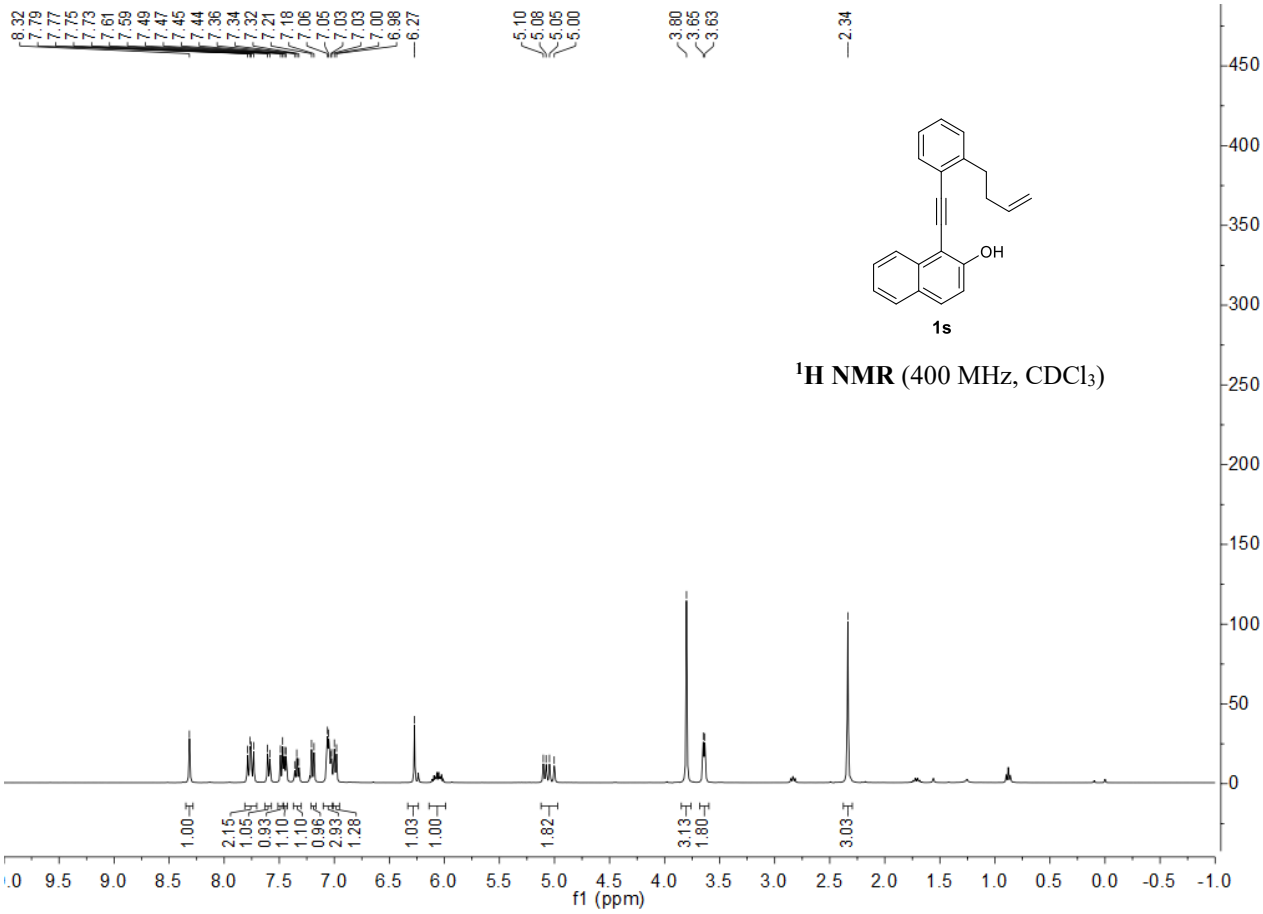
1r

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

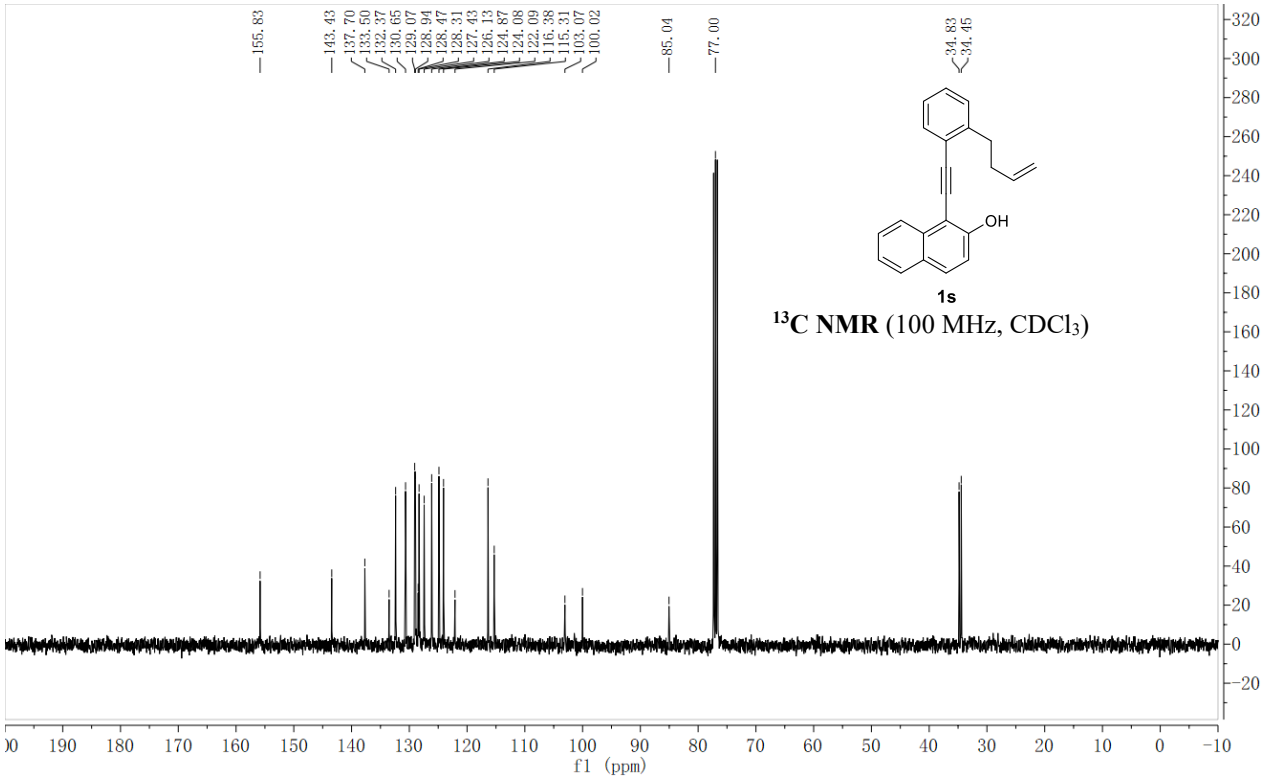


1r

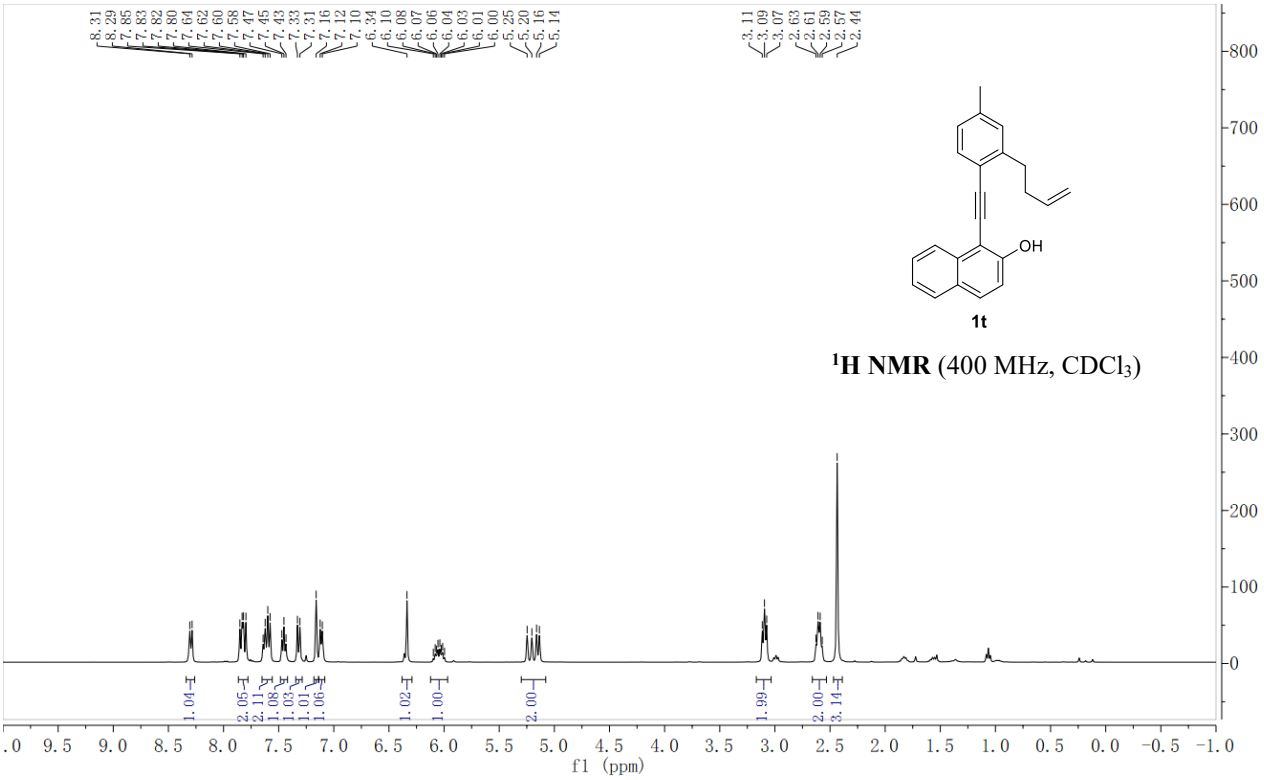
^{13}C NMR (100 MHz, $CDCl_3$)



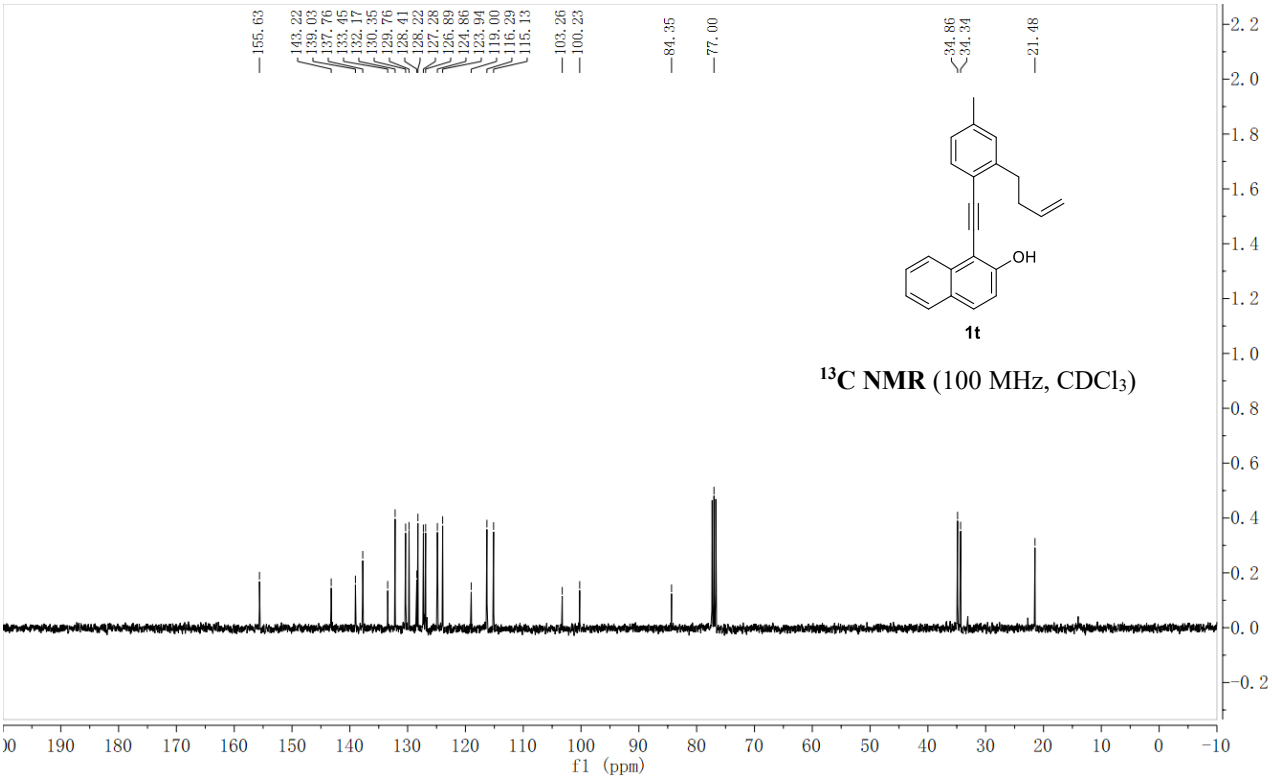
^{1}H NMR (400 MHz, $CDCl_3$)



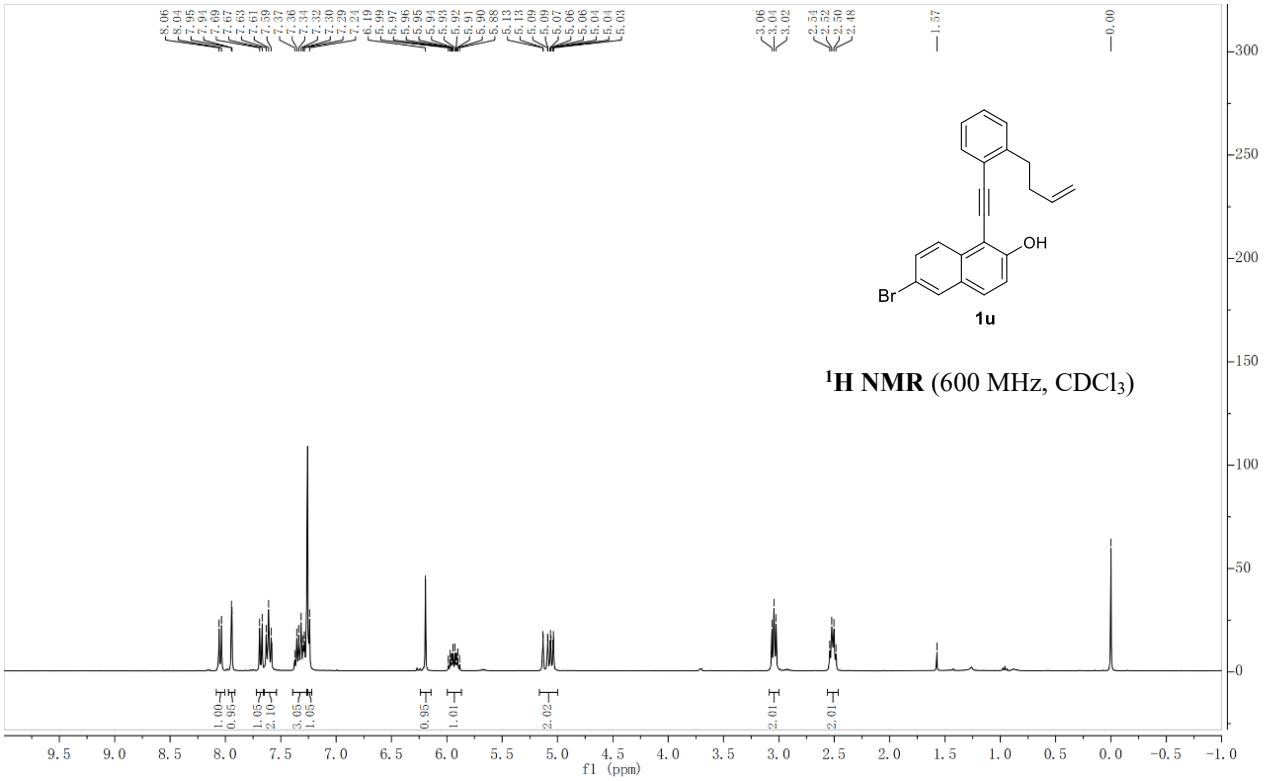
^{13}C NMR (100 MHz, $CDCl_3$)



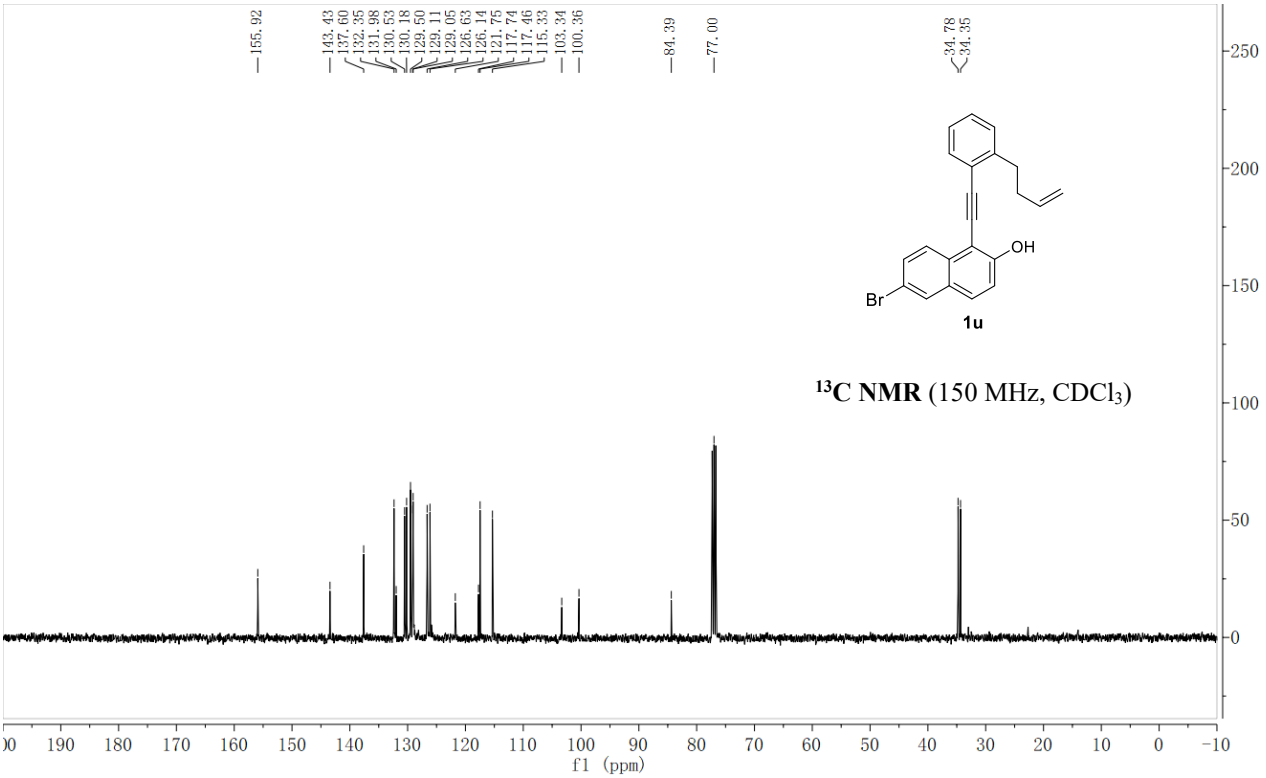
^{1}H NMR (400 MHz, $CDCl_3$)



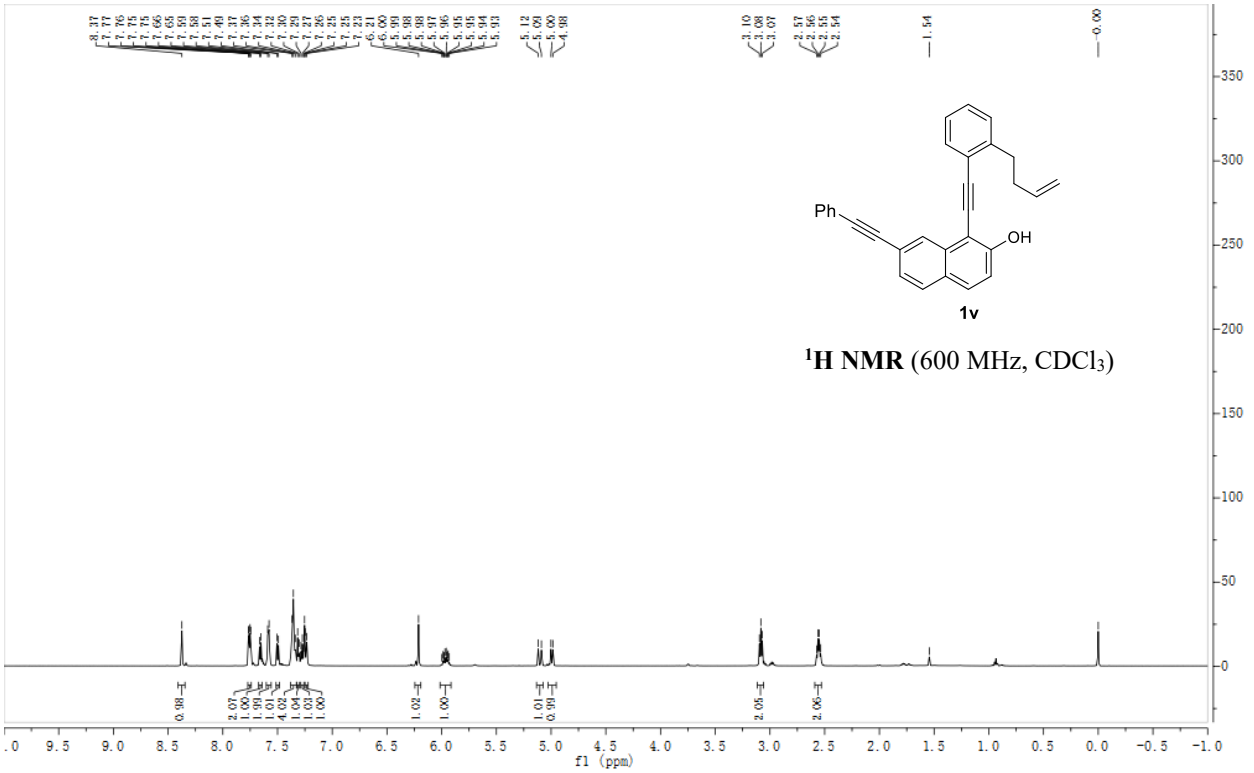
^{13}C NMR (100 MHz, $CDCl_3$)



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

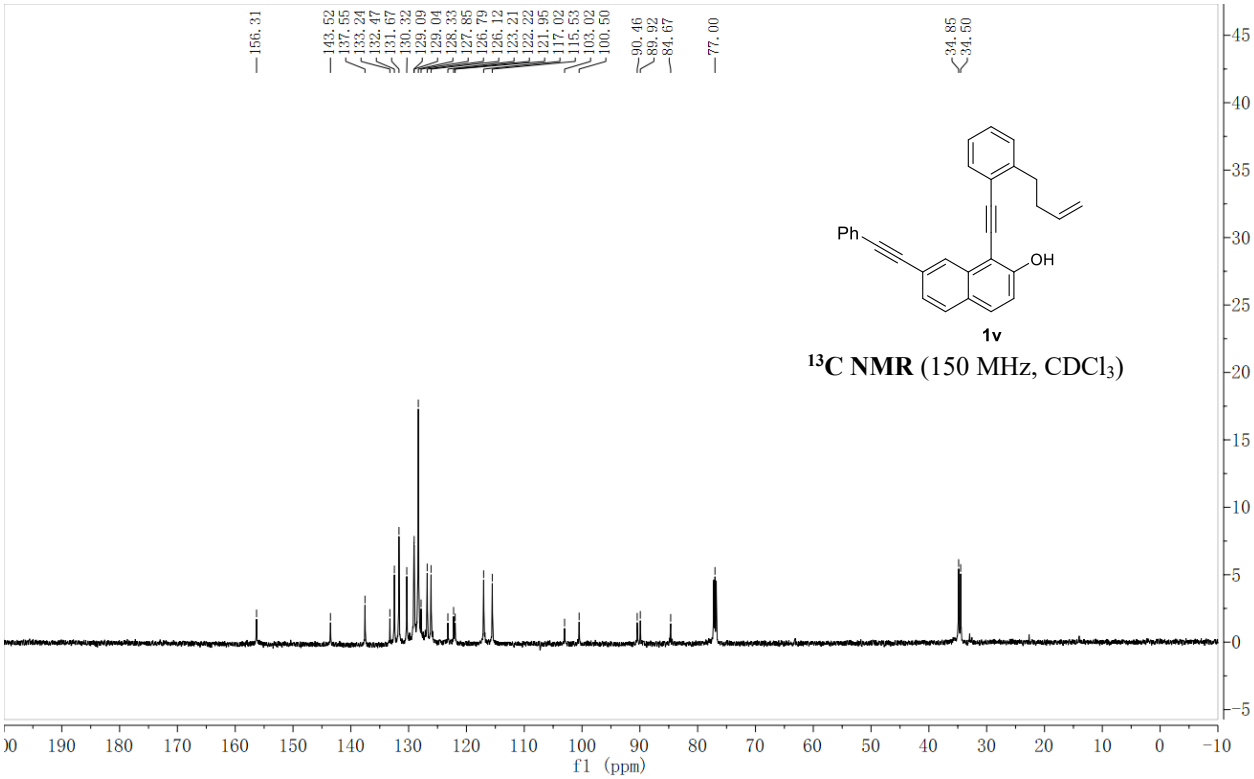


^{13}C NMR (150 MHz, $CDCl_3$)



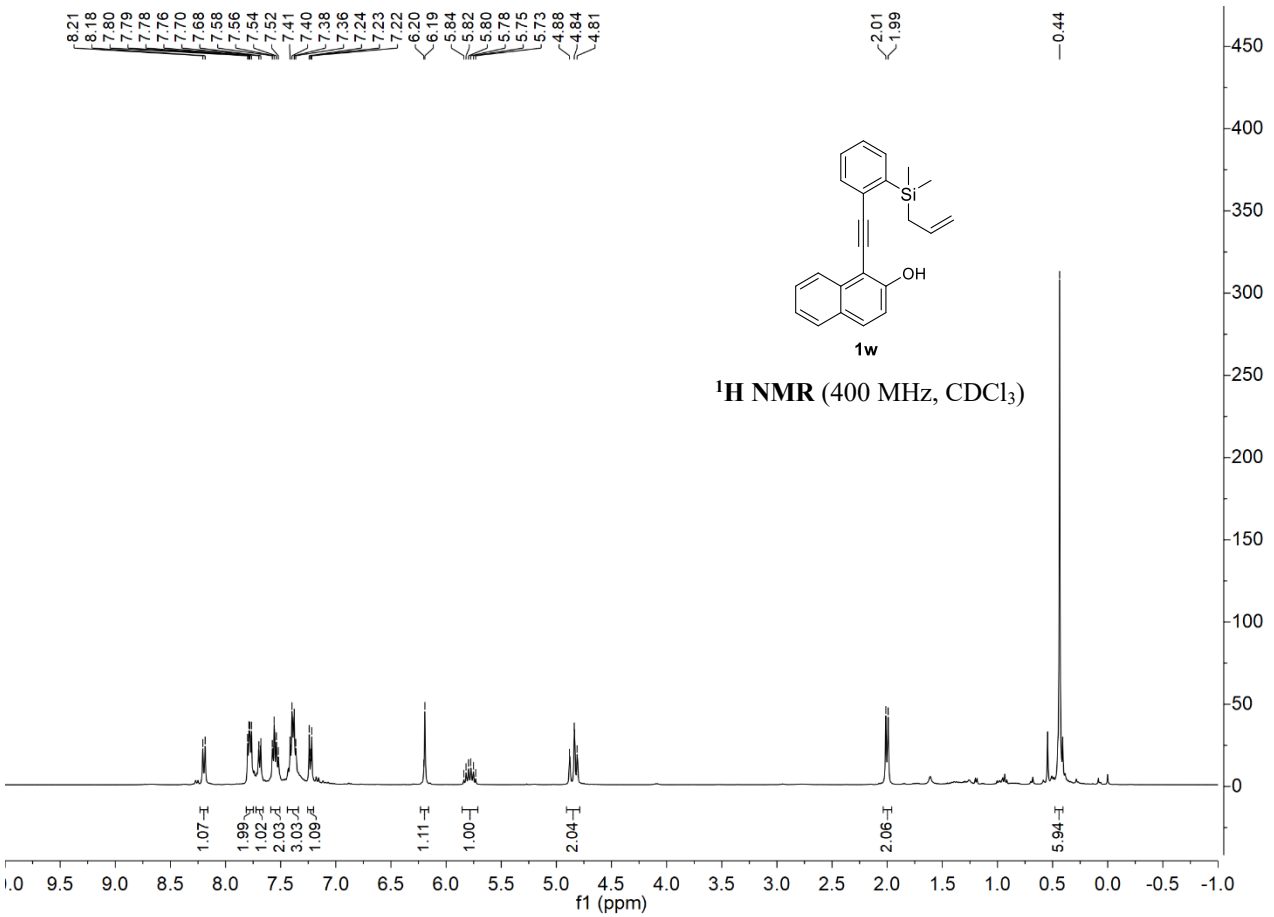
1v

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

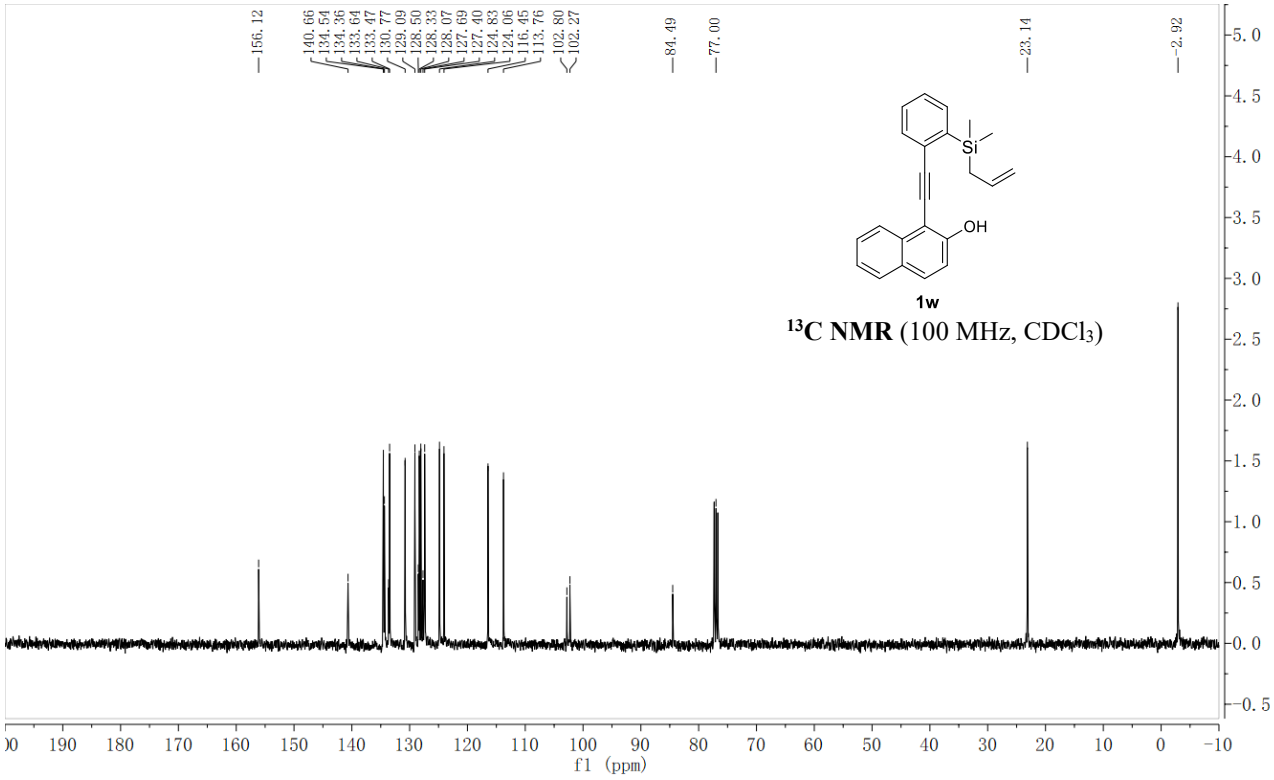


1v

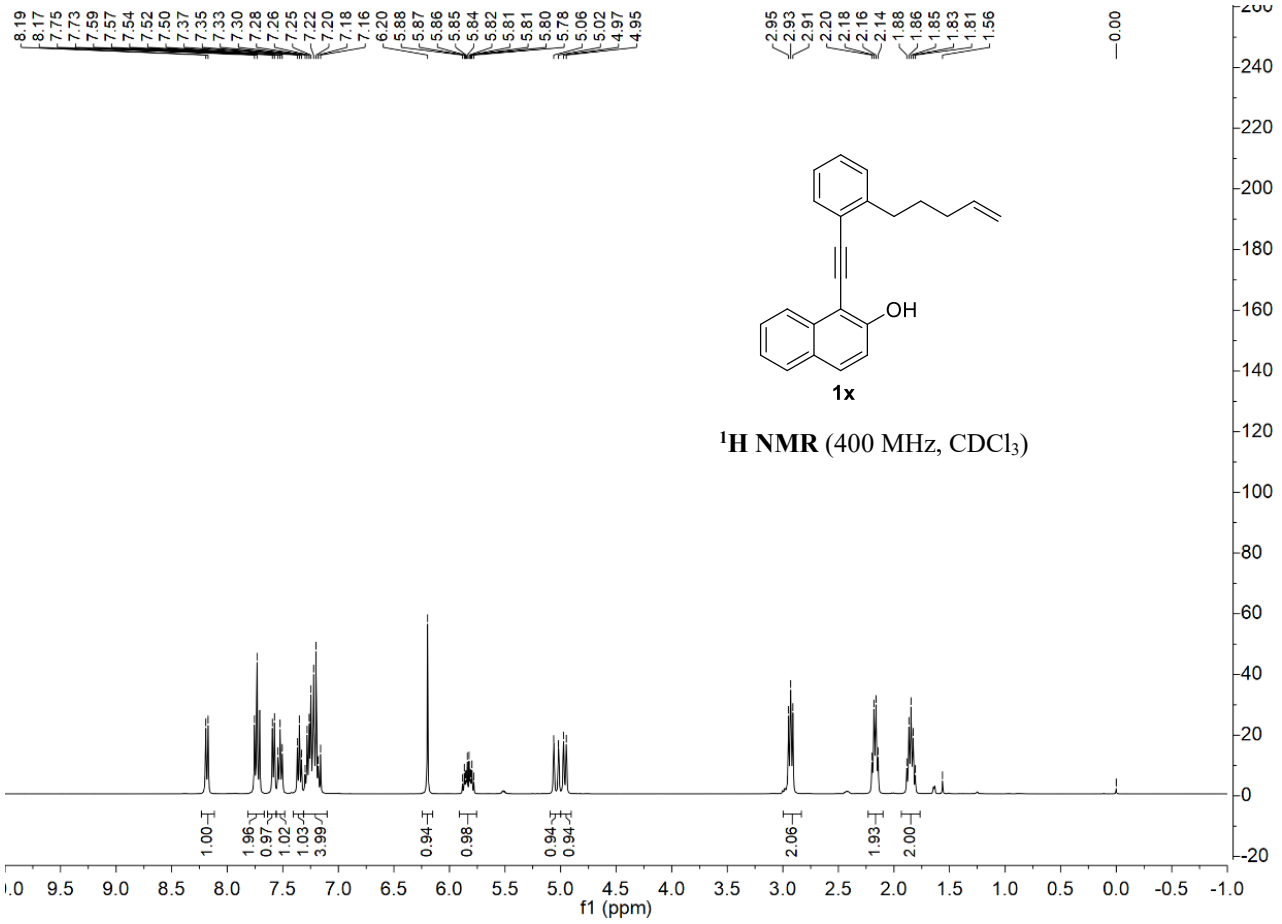
^{13}C NMR (150 MHz, $CDCl_3$)



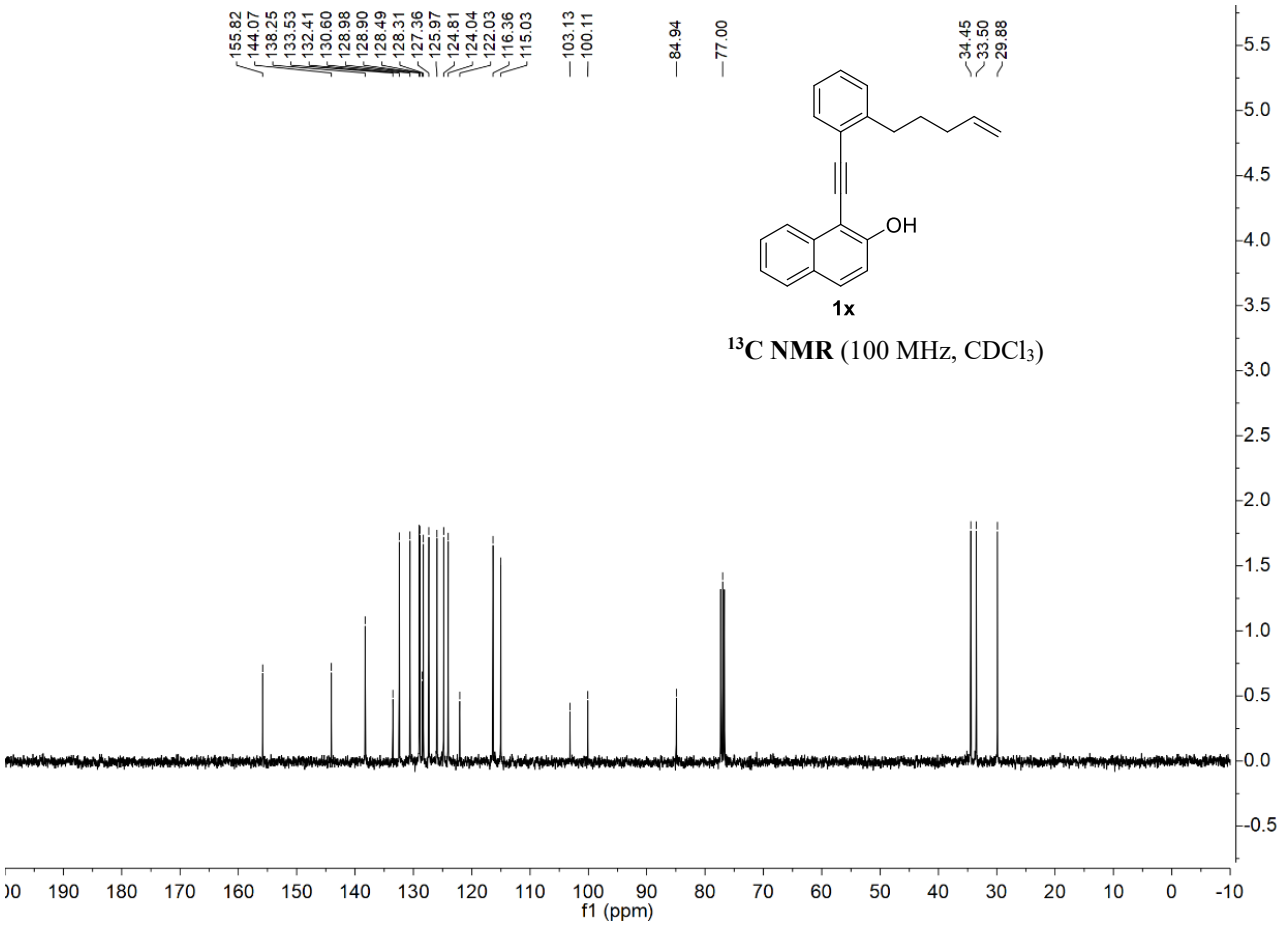
^{1}H NMR (400 MHz, $CDCl_3$)



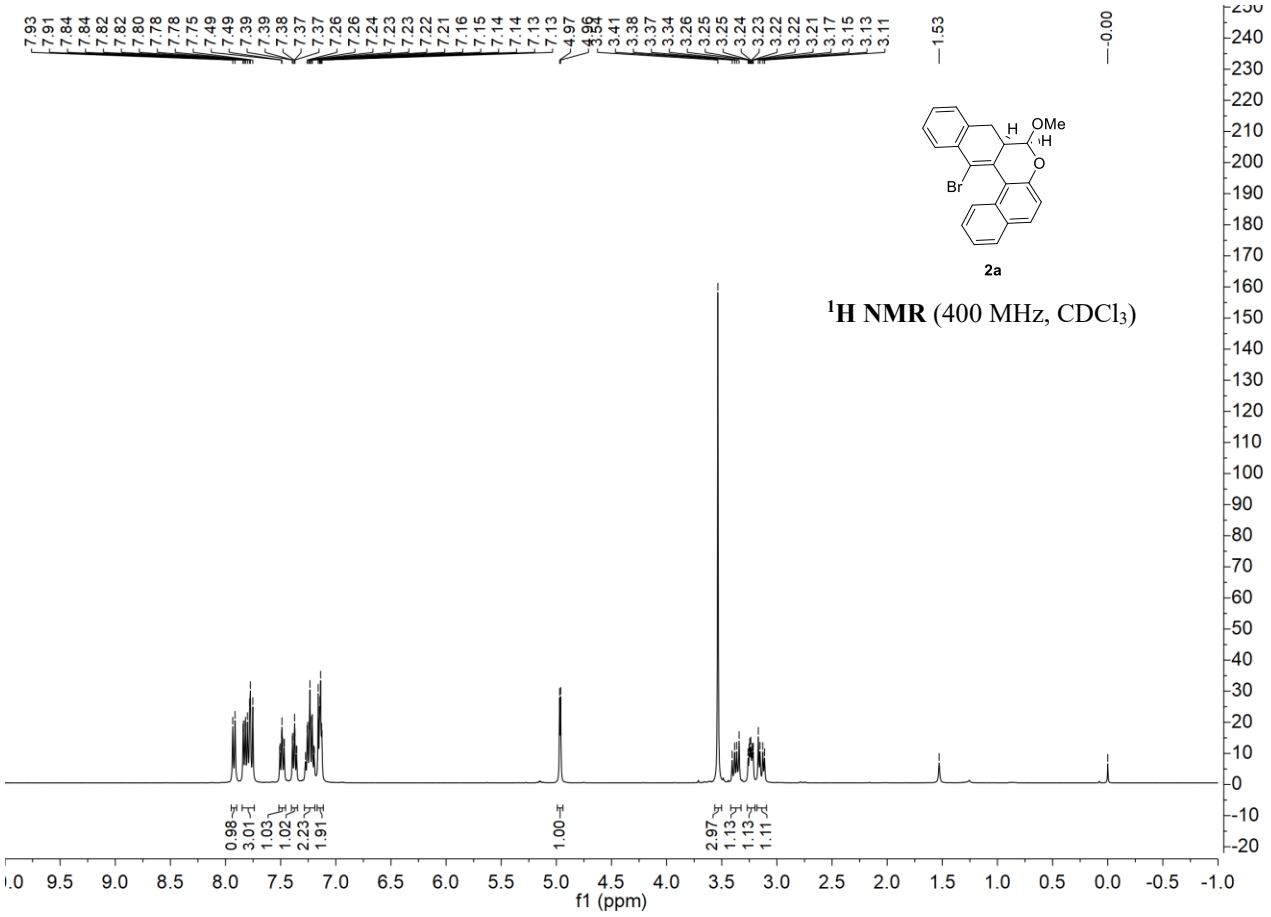
^{13}C NMR (100 MHz, $CDCl_3$)



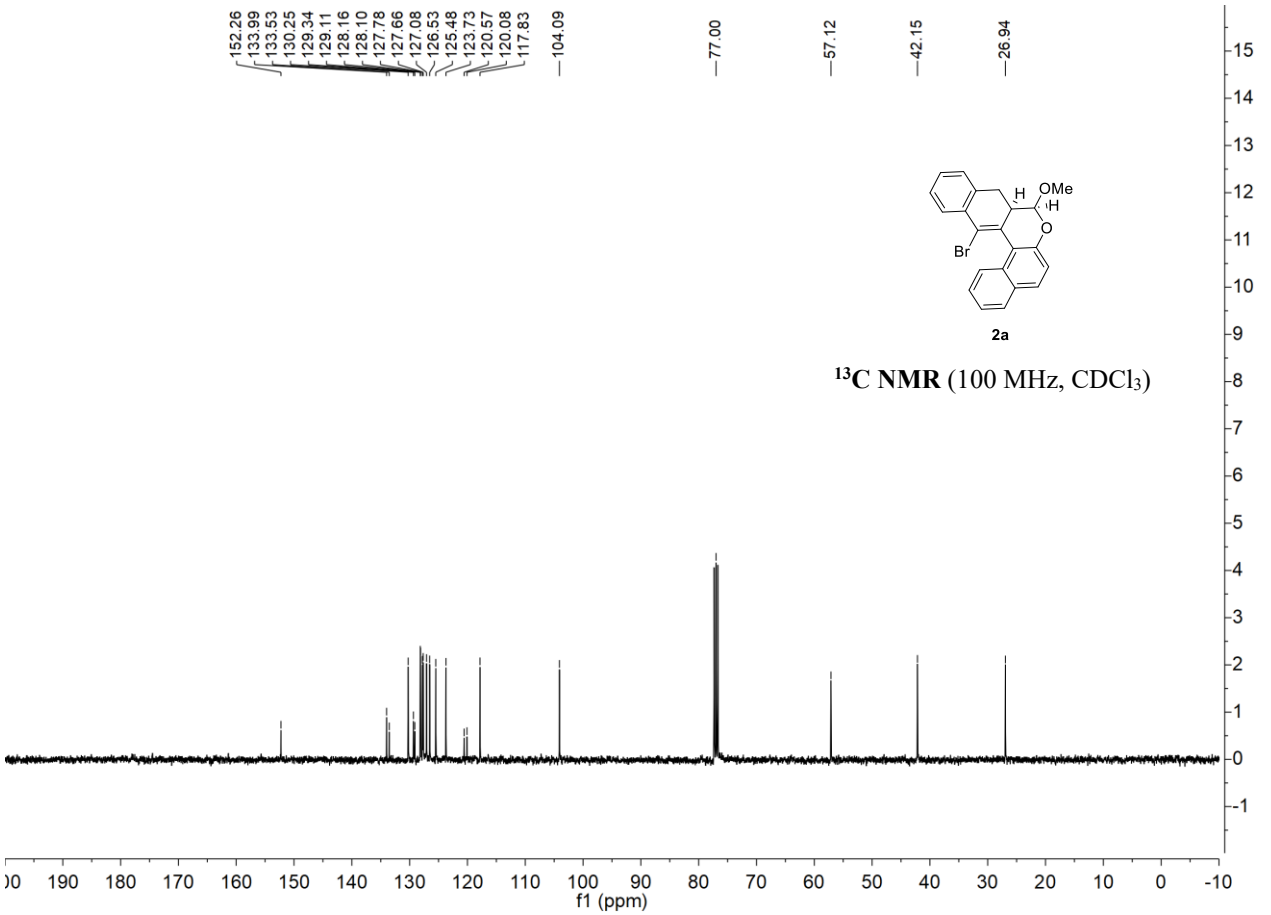
^{1}H NMR (400 MHz, $CDCl_3$)



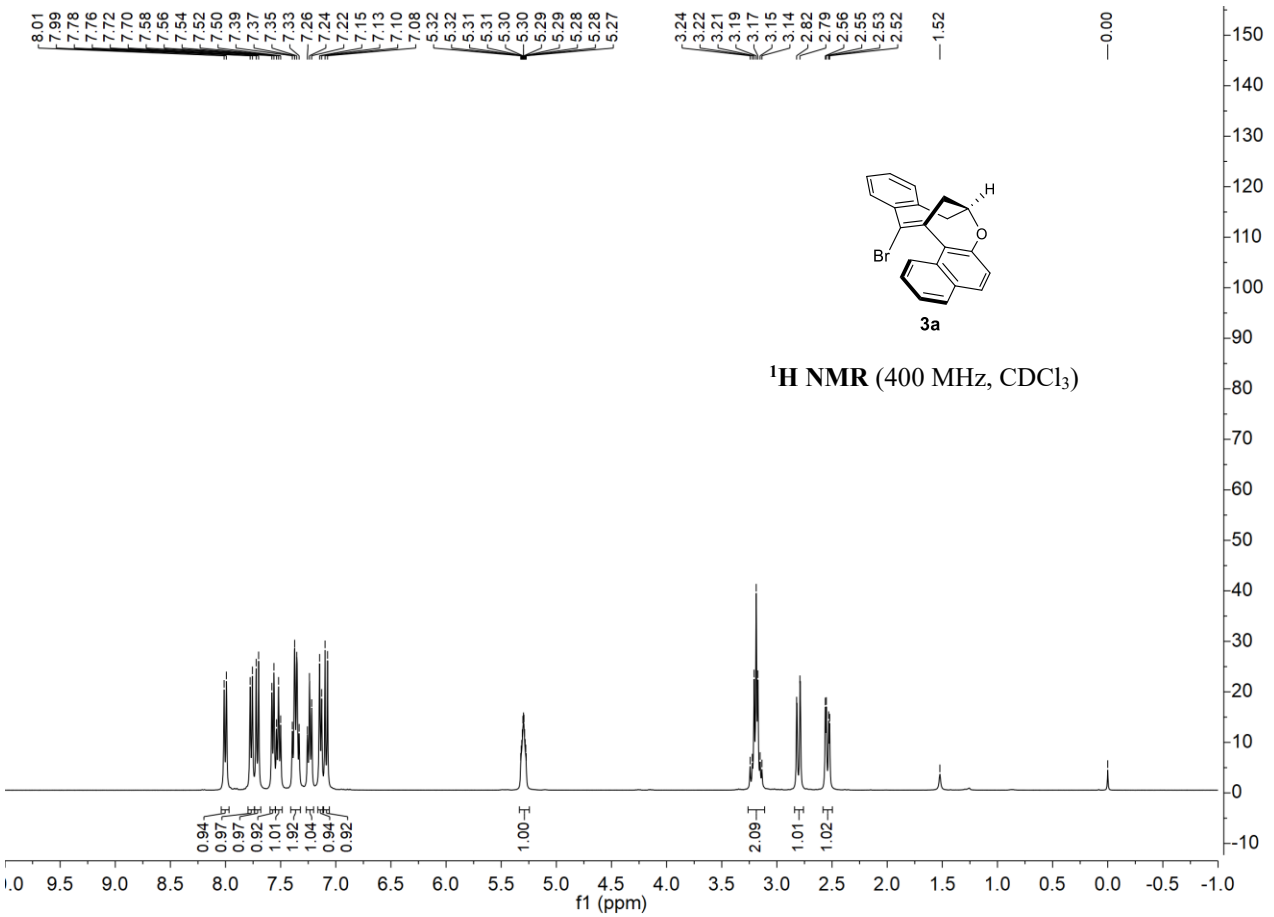
^{13}C NMR (100 MHz, $CDCl_3$)



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

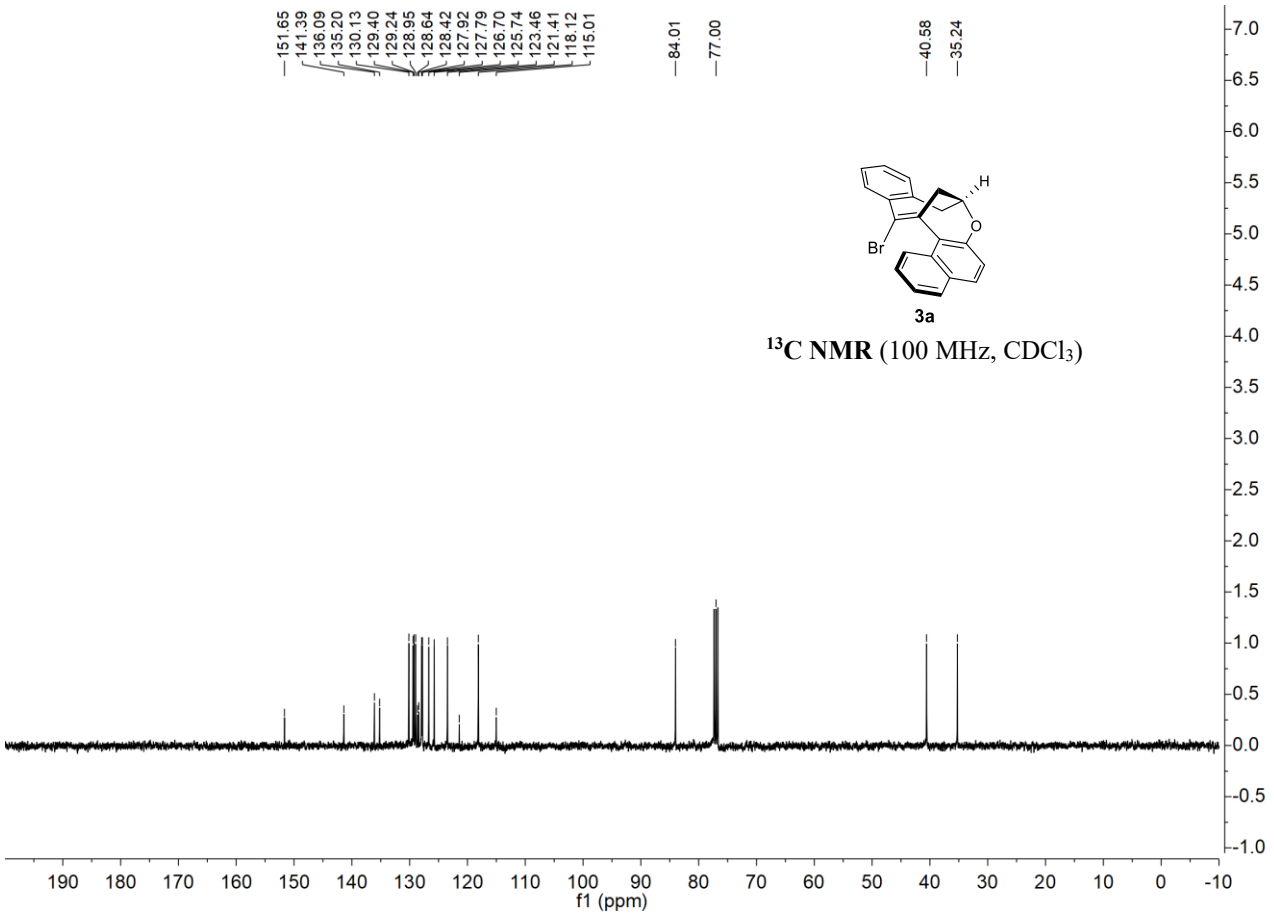


^{13}C NMR (100 MHz, $CDCl_3$)



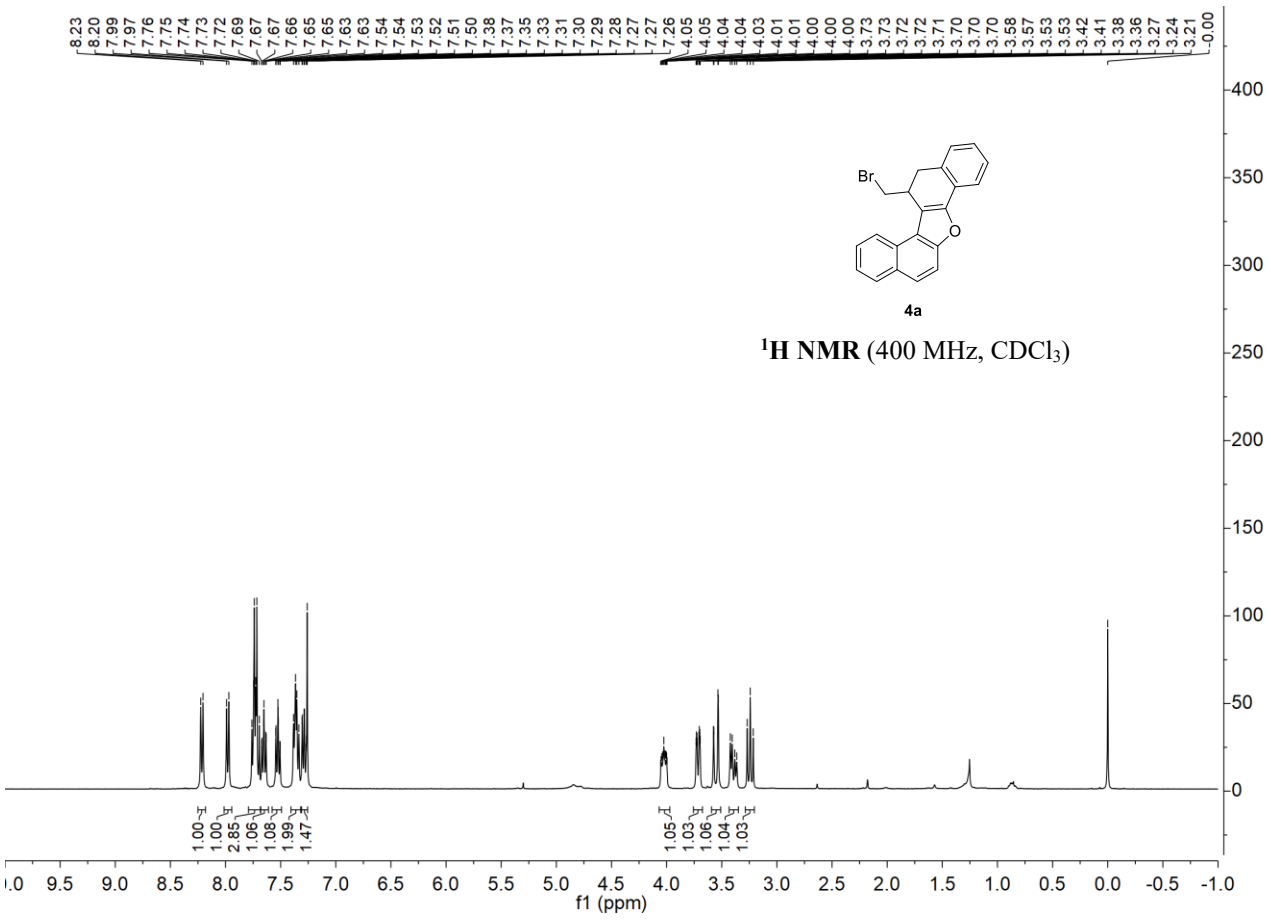
3a

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

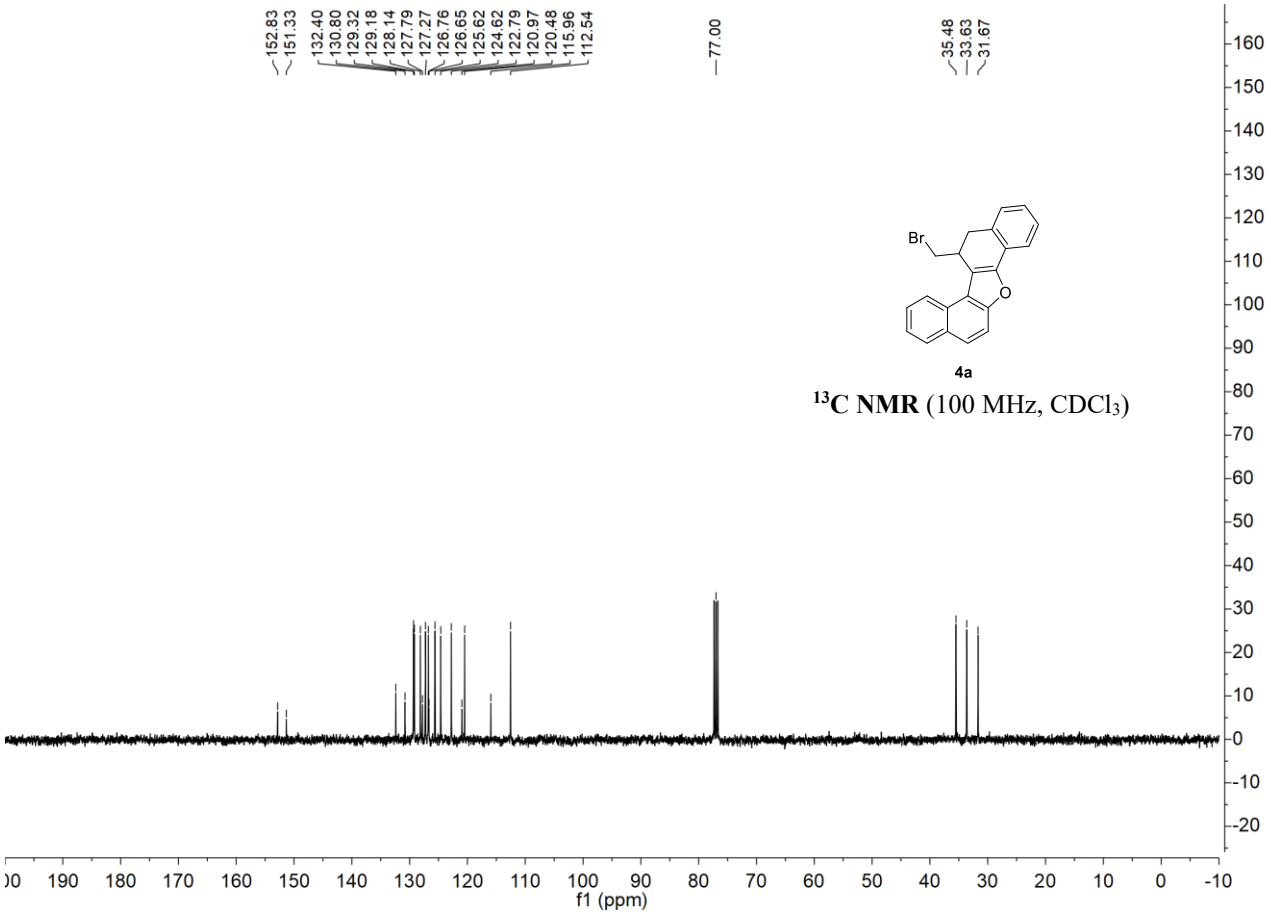


3a

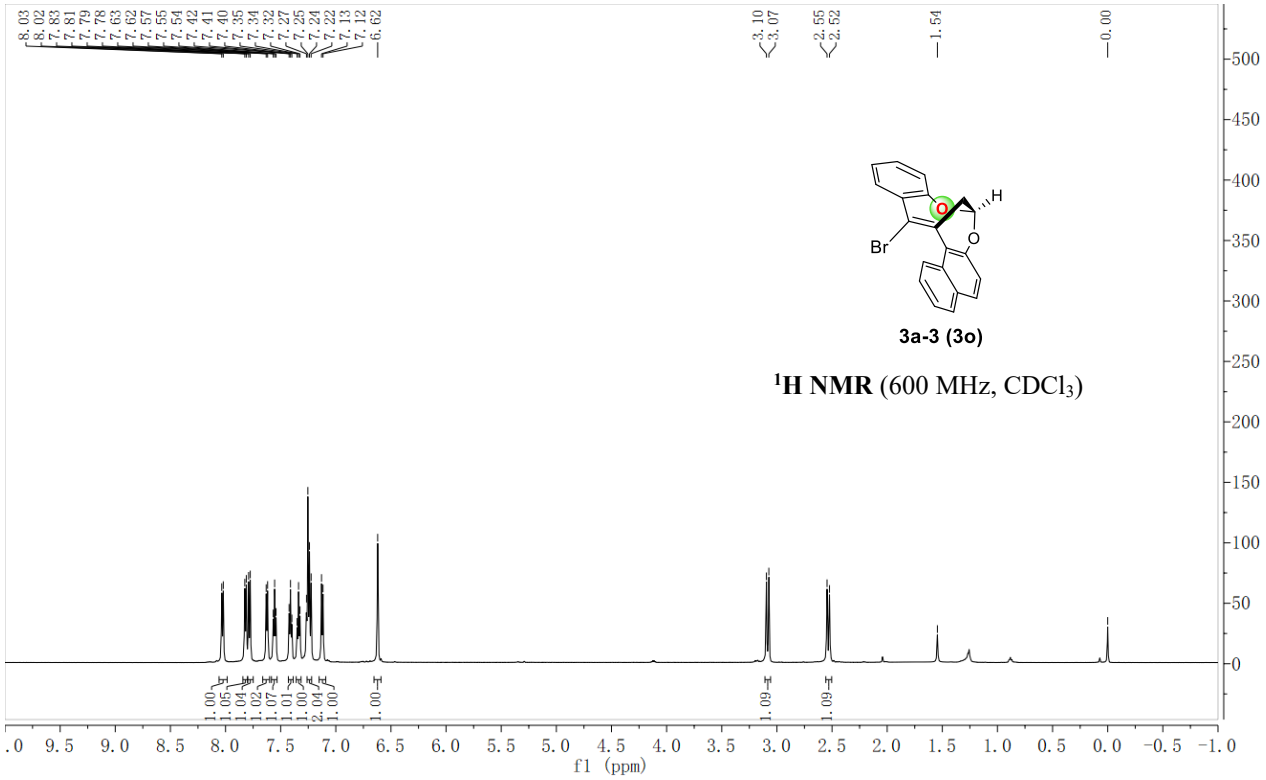
^{13}C NMR (100 MHz, $CDCl_3$)



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

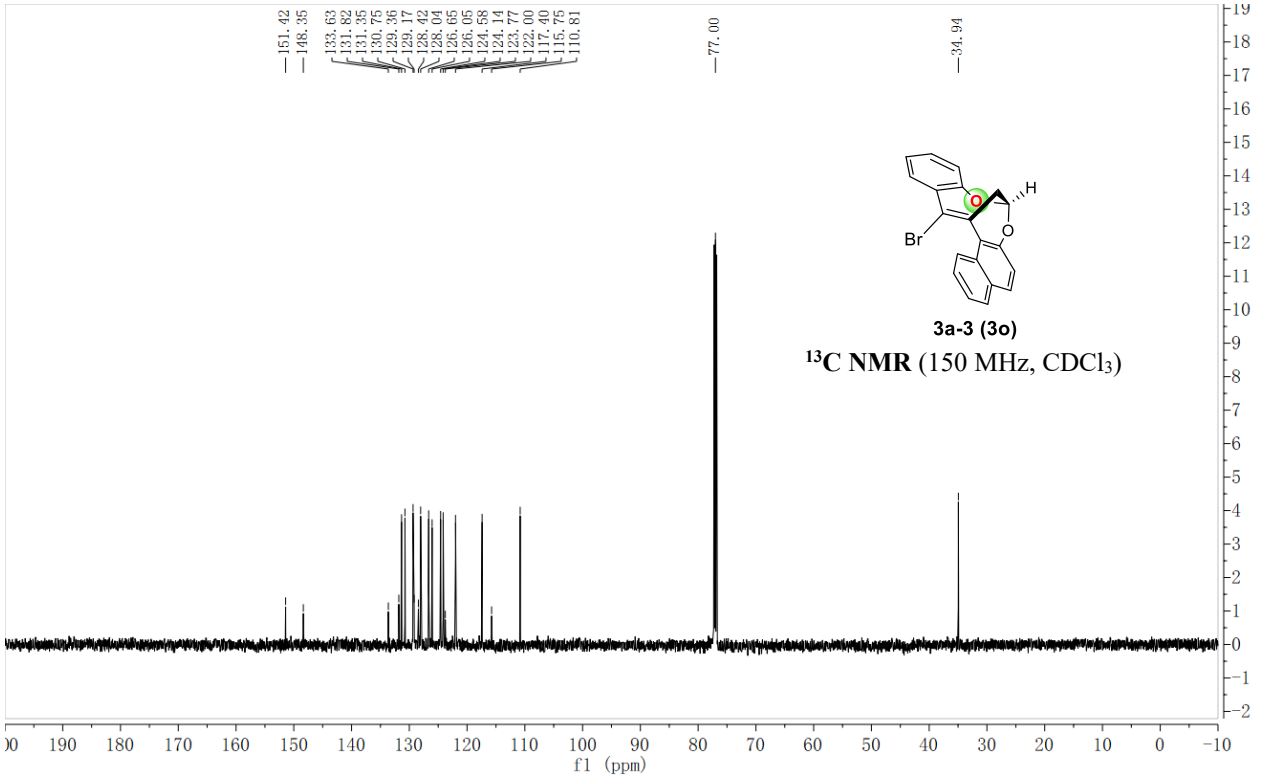


^{13}C NMR (100 MHz, $CDCl_3$)



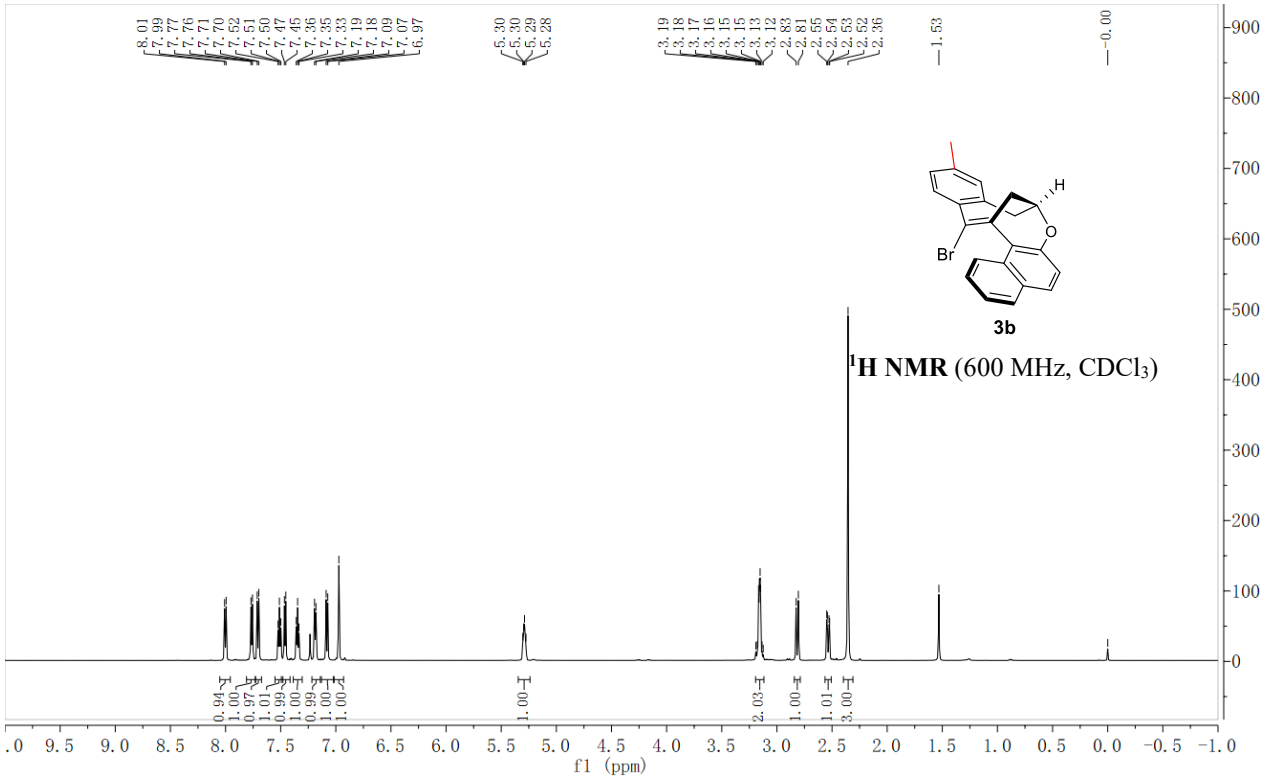
3a-3 (3o)

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

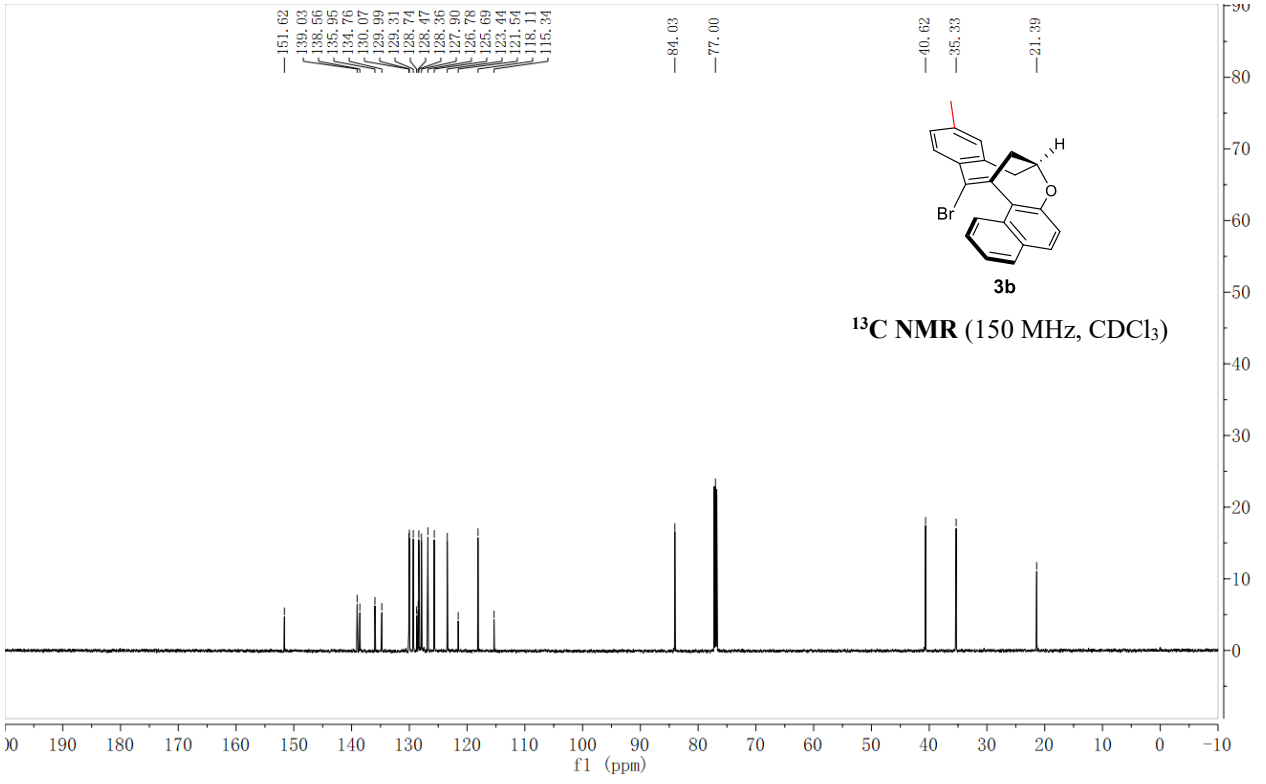


3a-3 (3o)

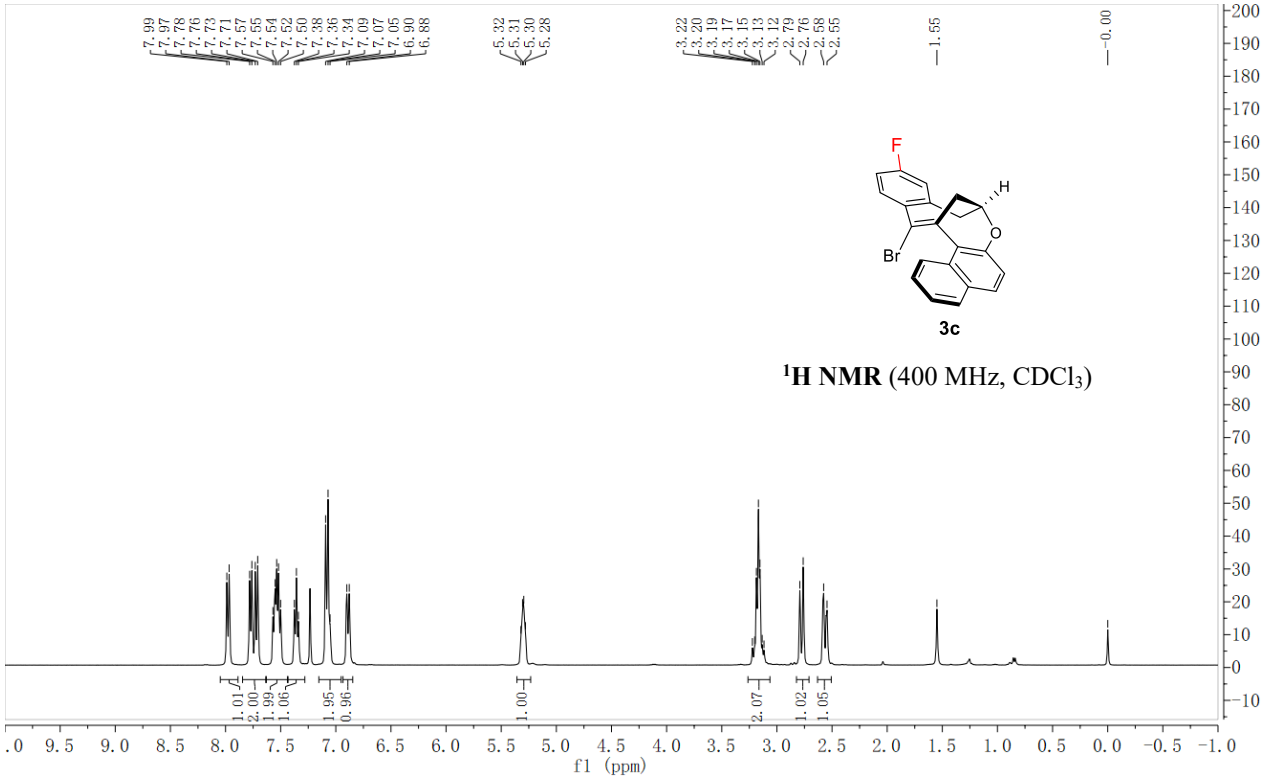
^{13}C NMR (150 MHz, $CDCl_3$)

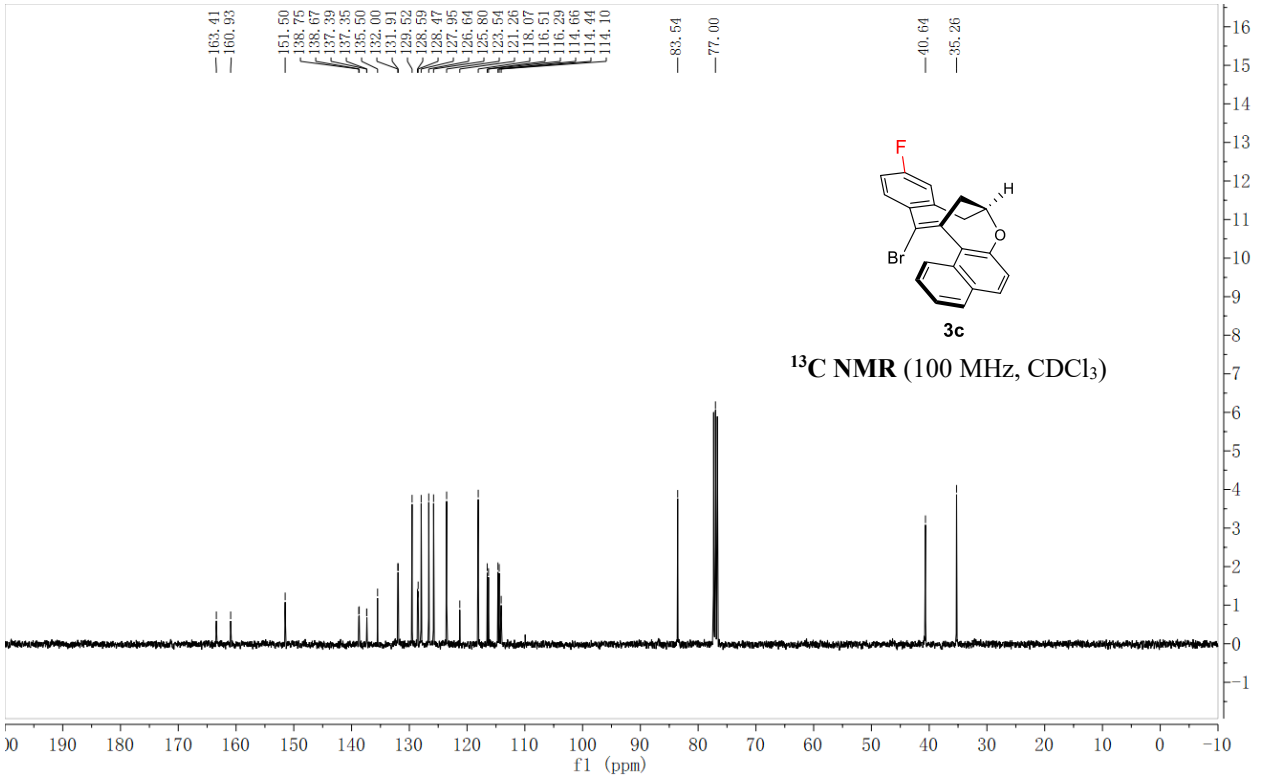


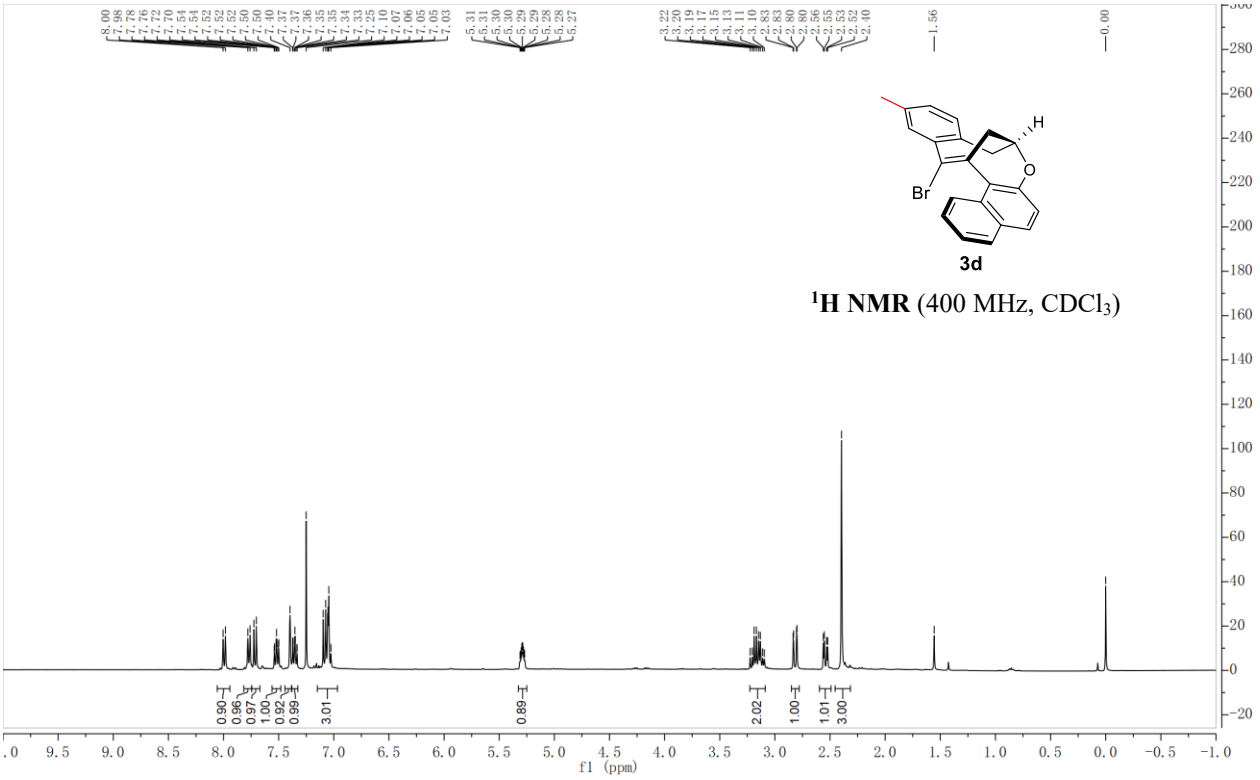
^{1}H NMR (600 MHz, $CDCl_3$)



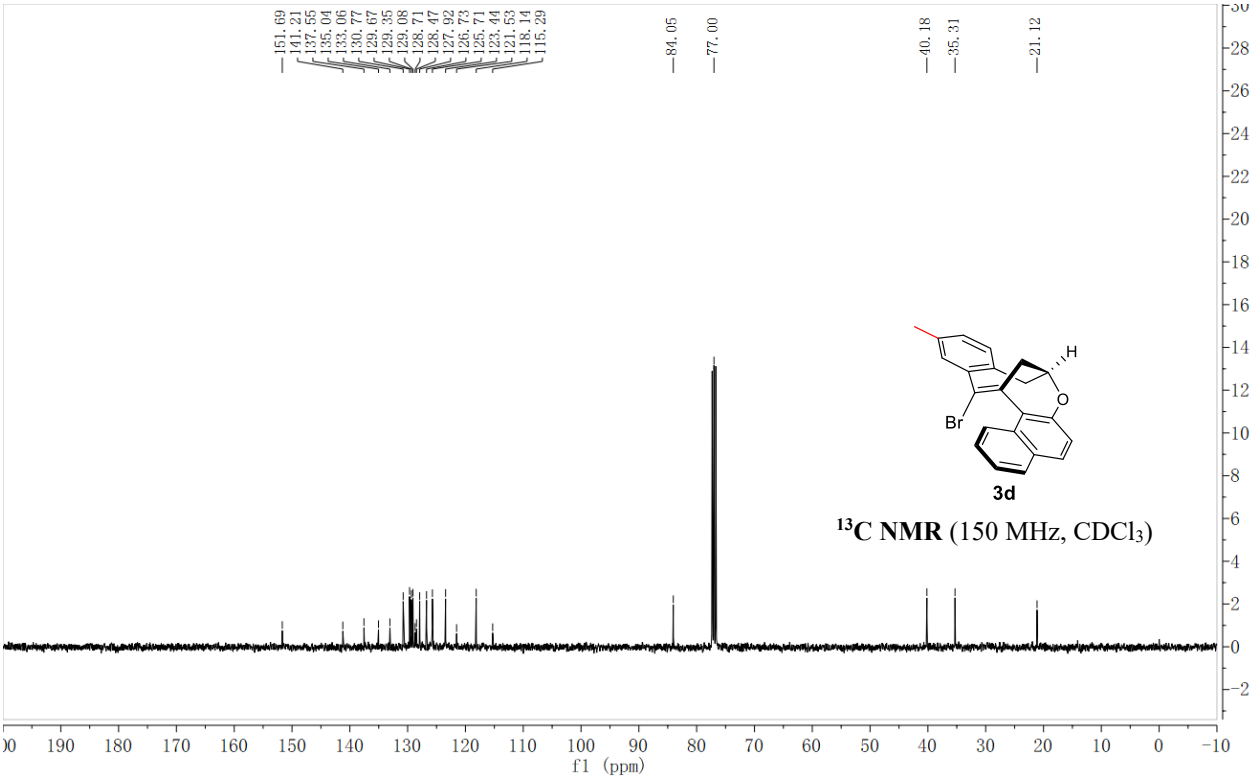
^{13}C NMR (150 MHz, $CDCl_3$)


F
H
O
Br
3c
1H NMR (400 MHz, CDCl3)
f1 (ppm)

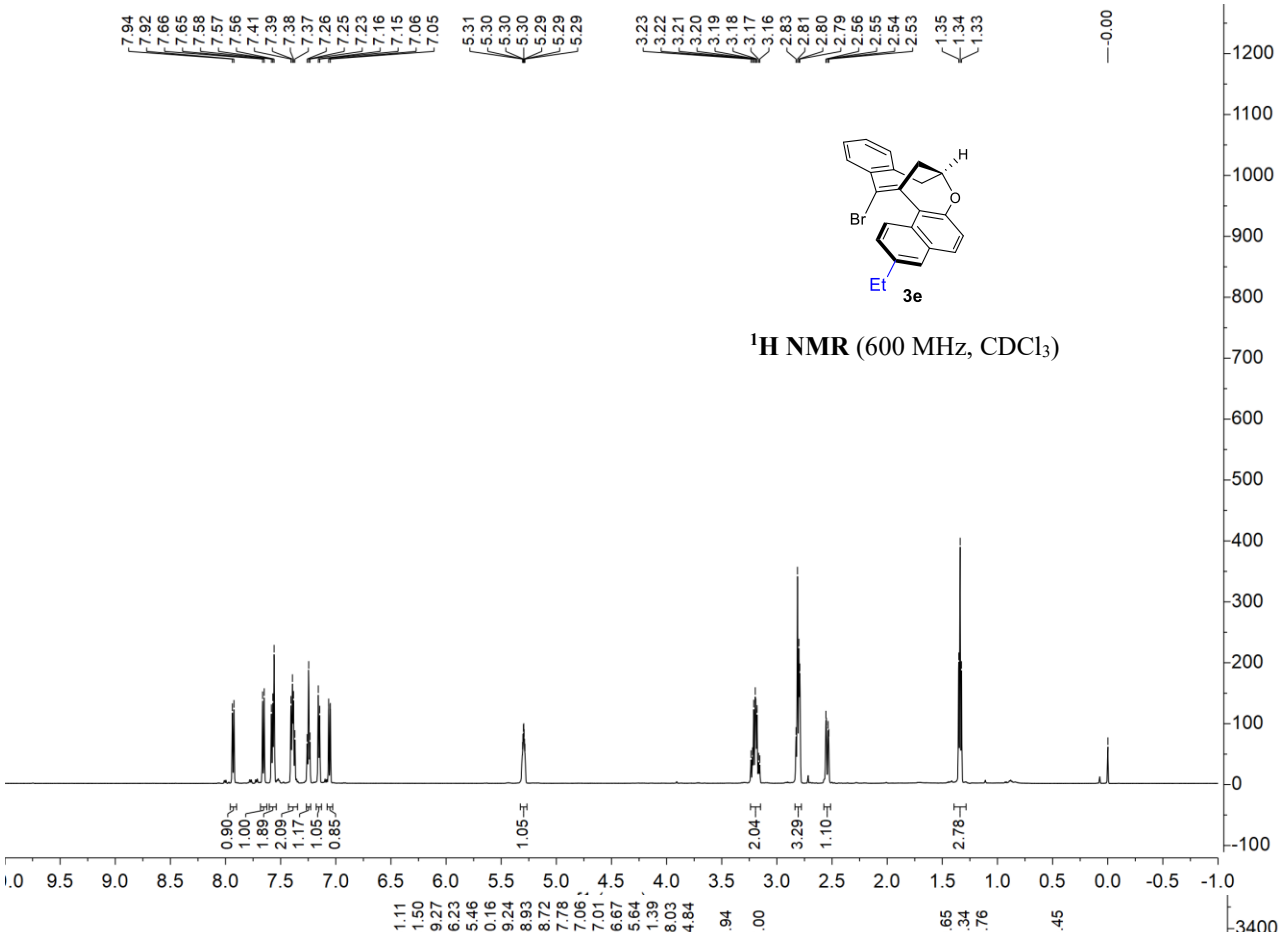

F
H
O
Br
3c
13C NMR (100 MHz, CDCl3)
f1 (ppm)



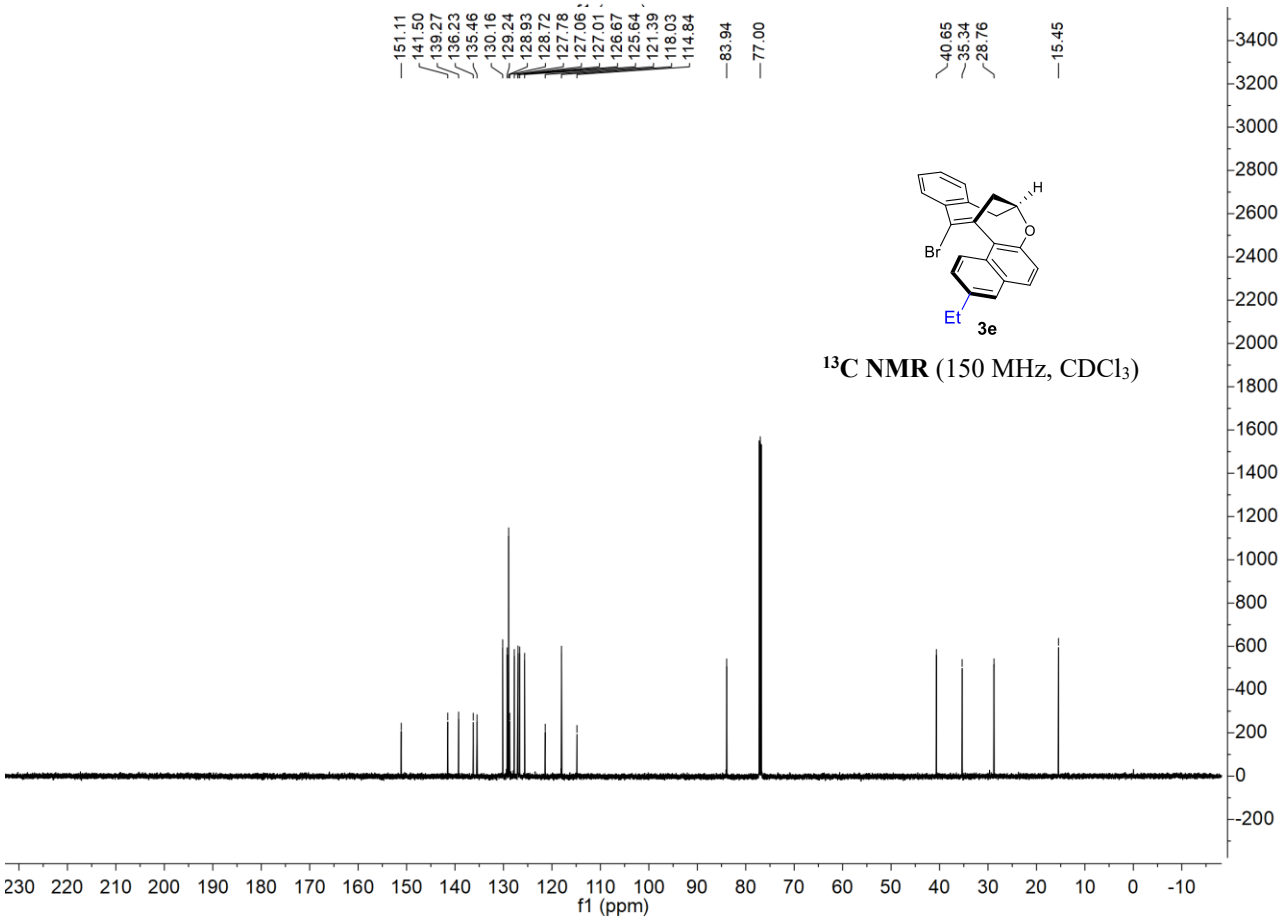
^{1}H NMR (400 MHz, $CDCl_3$)



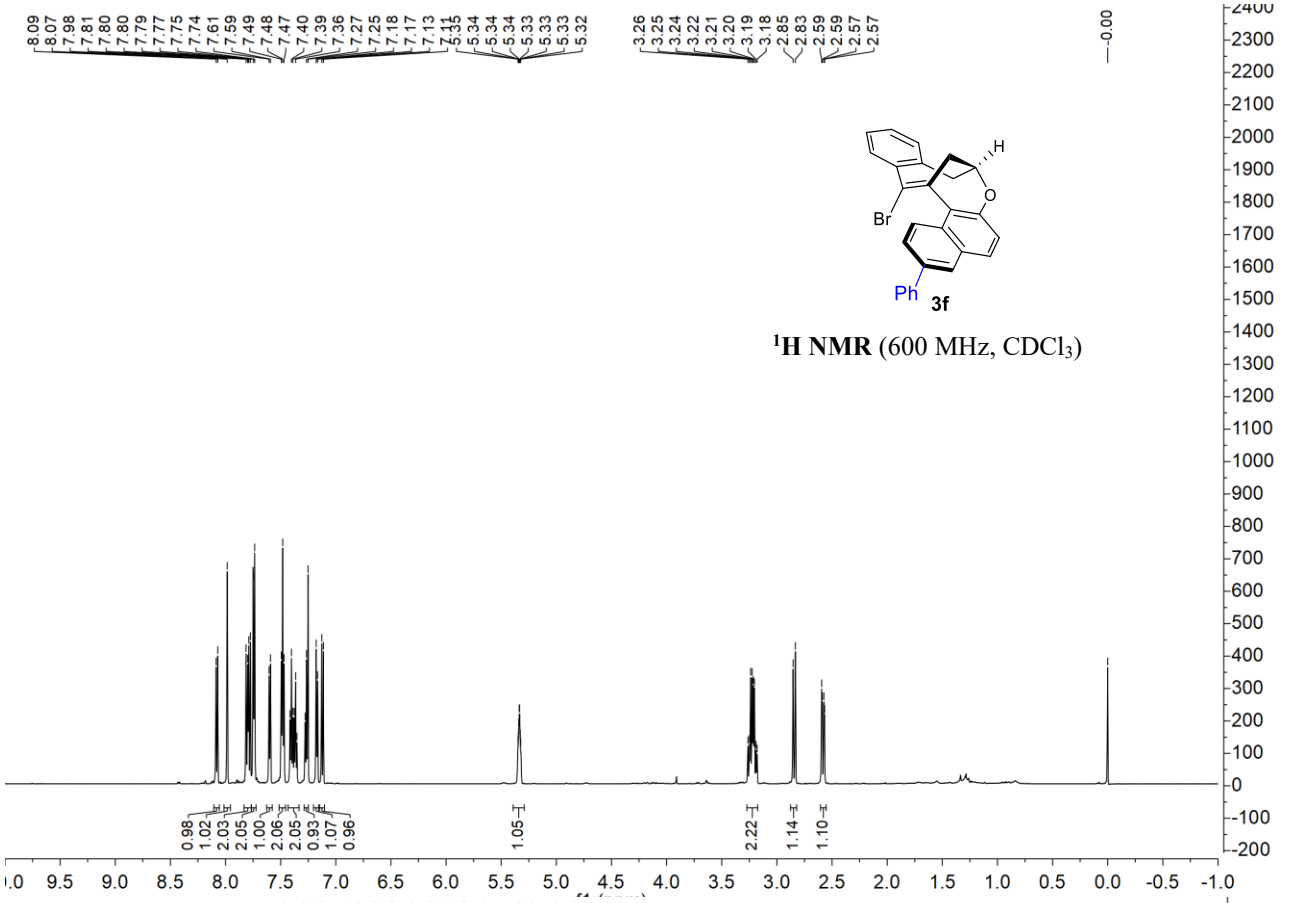
^{13}C NMR (150 MHz, $CDCl_3$)



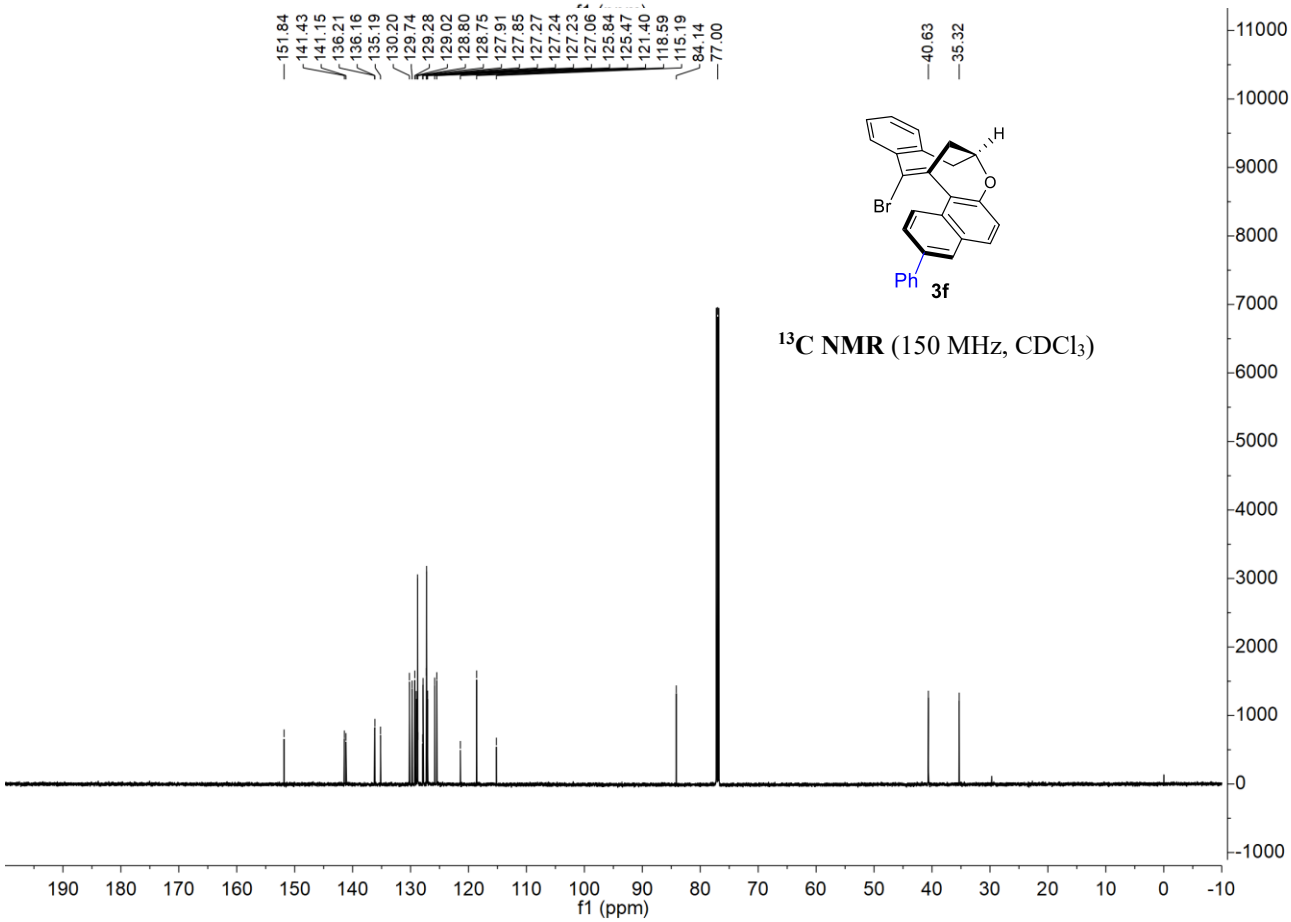
^{1}H NMR (600 MHz, $CDCl_3$)



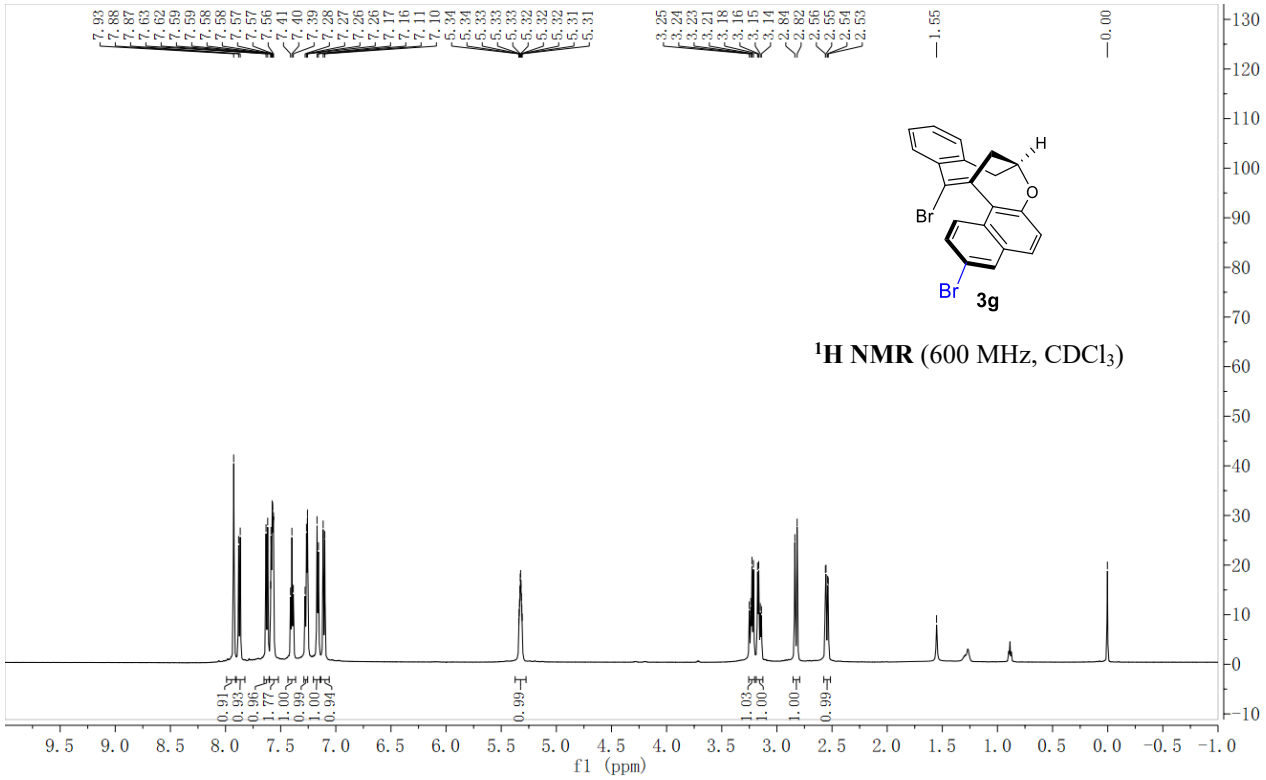
^{13}C NMR (150 MHz, $CDCl_3$)



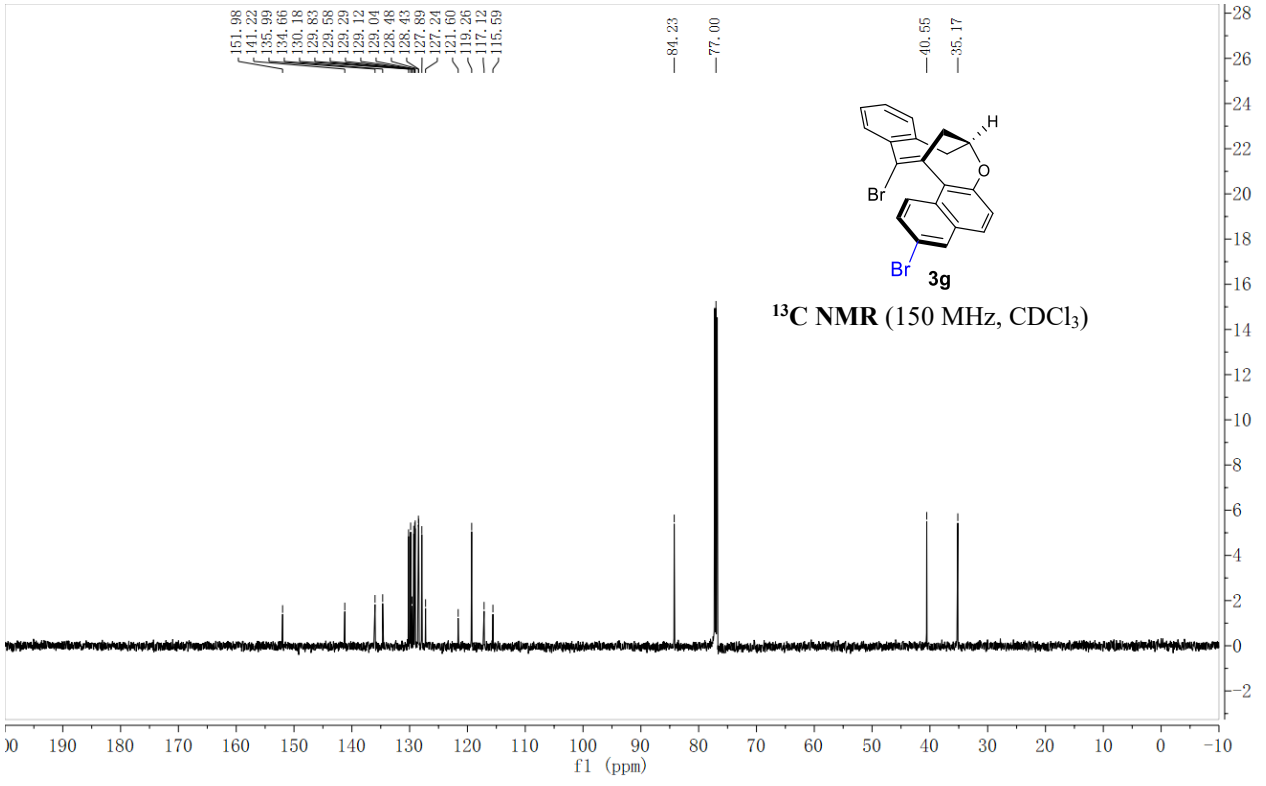
^{1}H NMR (600 MHz, $CDCl_3$)



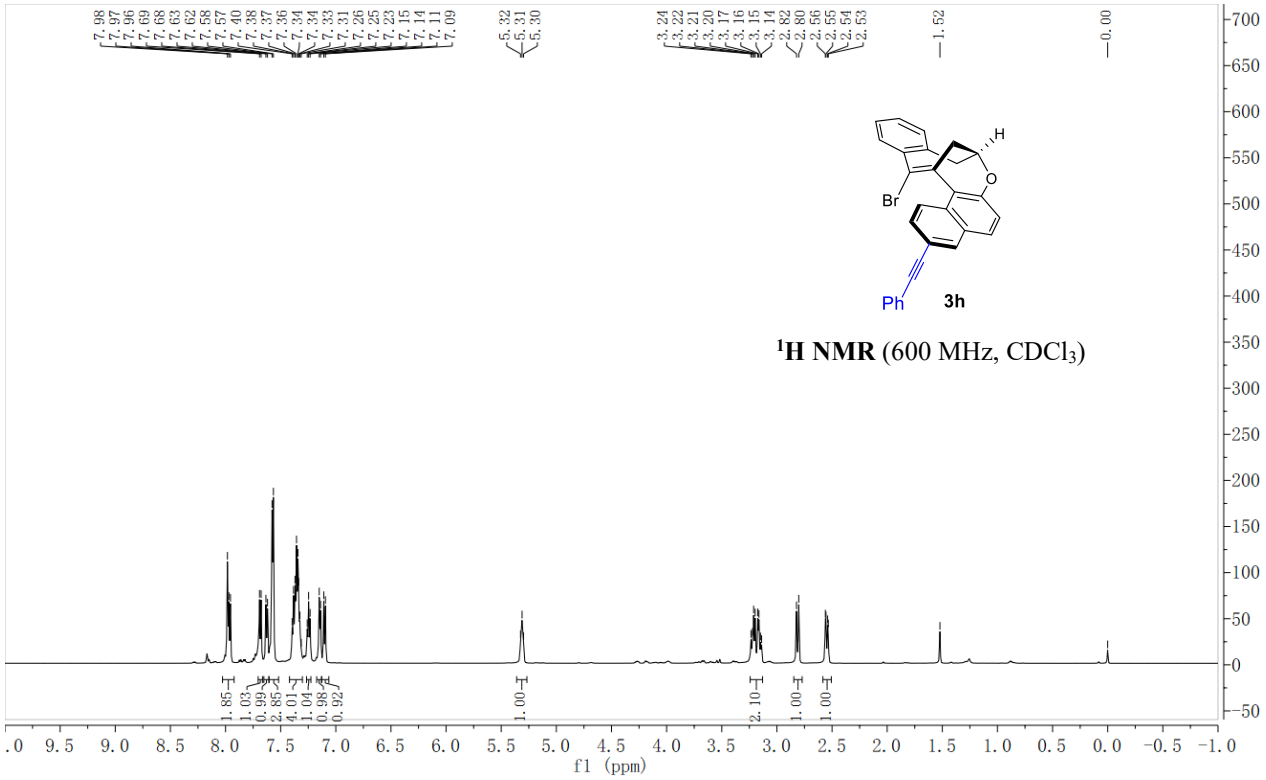
^{13}C NMR (150 MHz, $CDCl_3$)



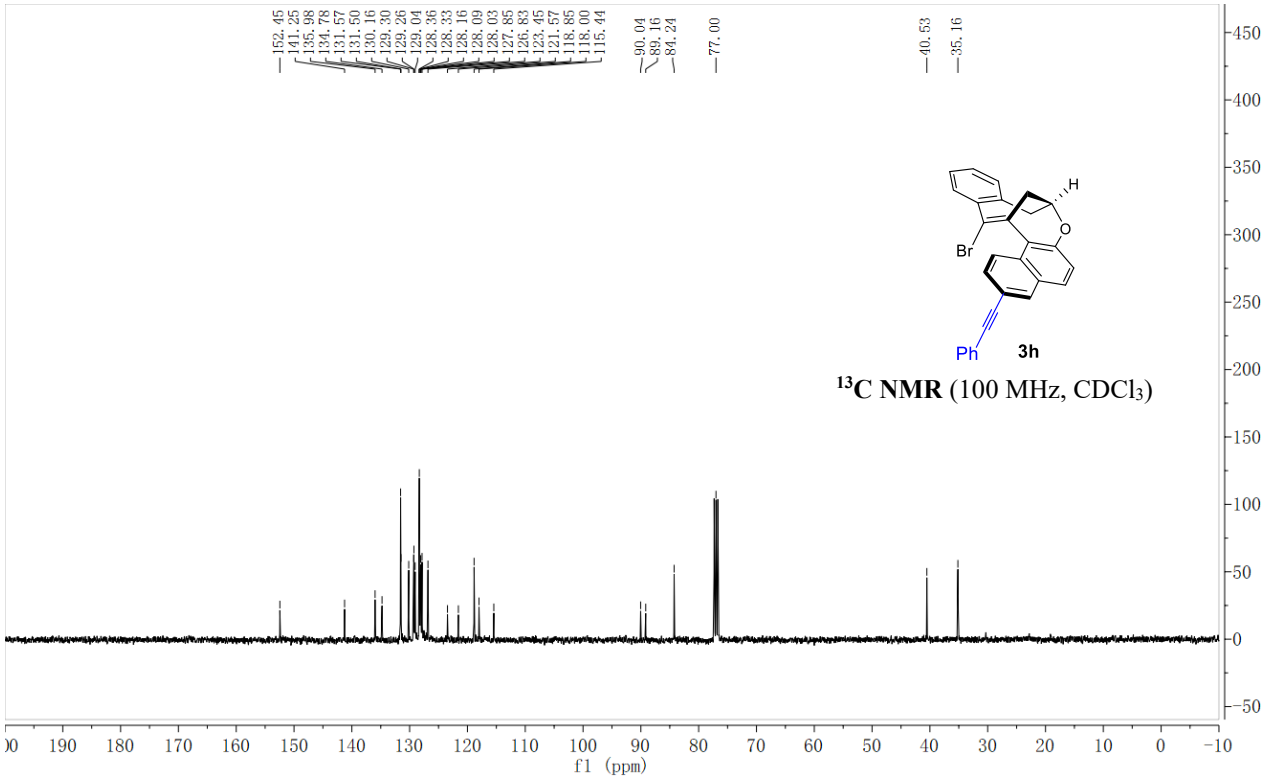
^{1}H NMR (600 MHz, $CDCl_3$)



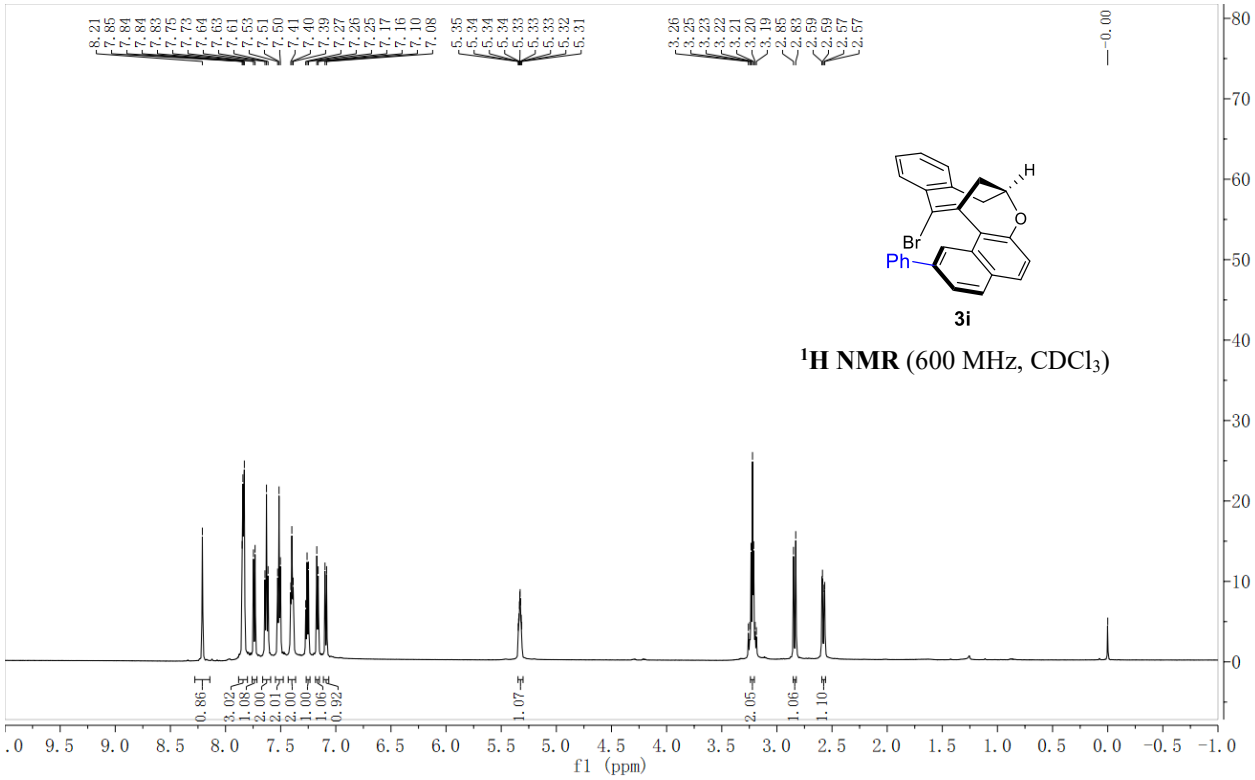
^{13}C NMR (150 MHz, $CDCl_3$)



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

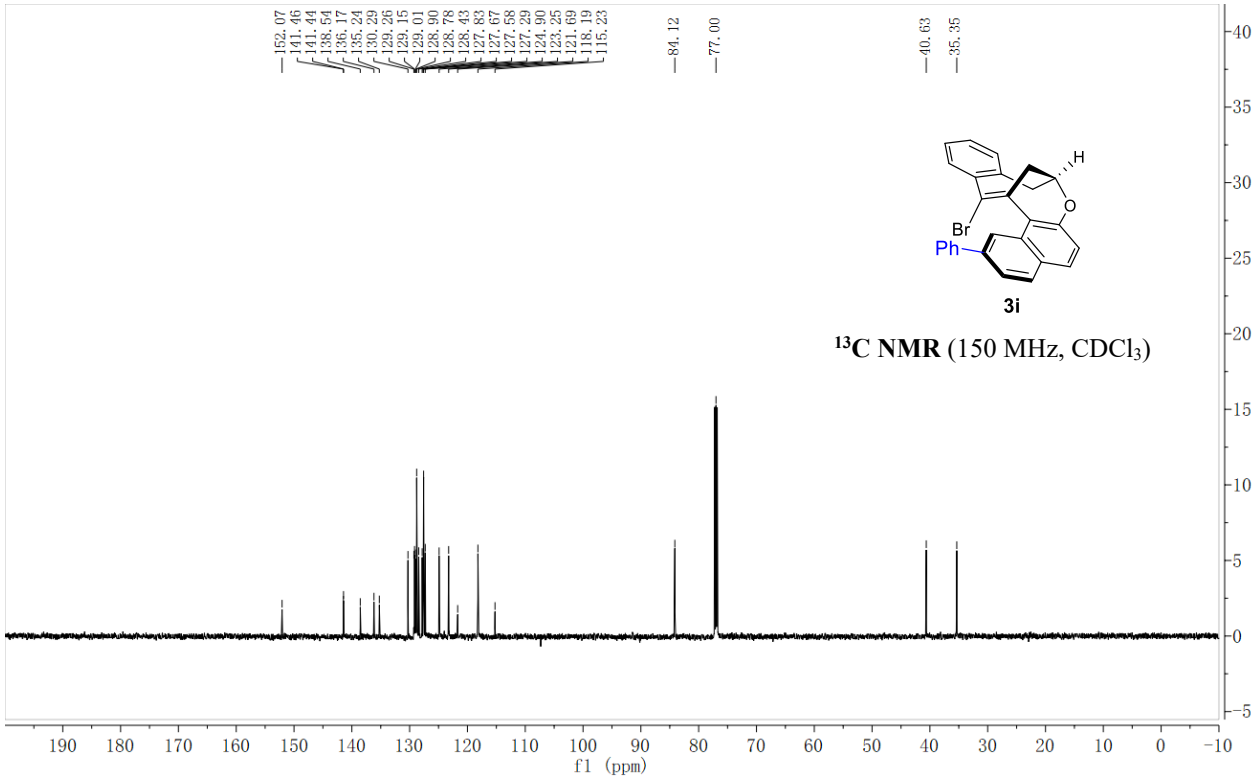


^{13}C NMR (100 MHz, $CDCl_3$)



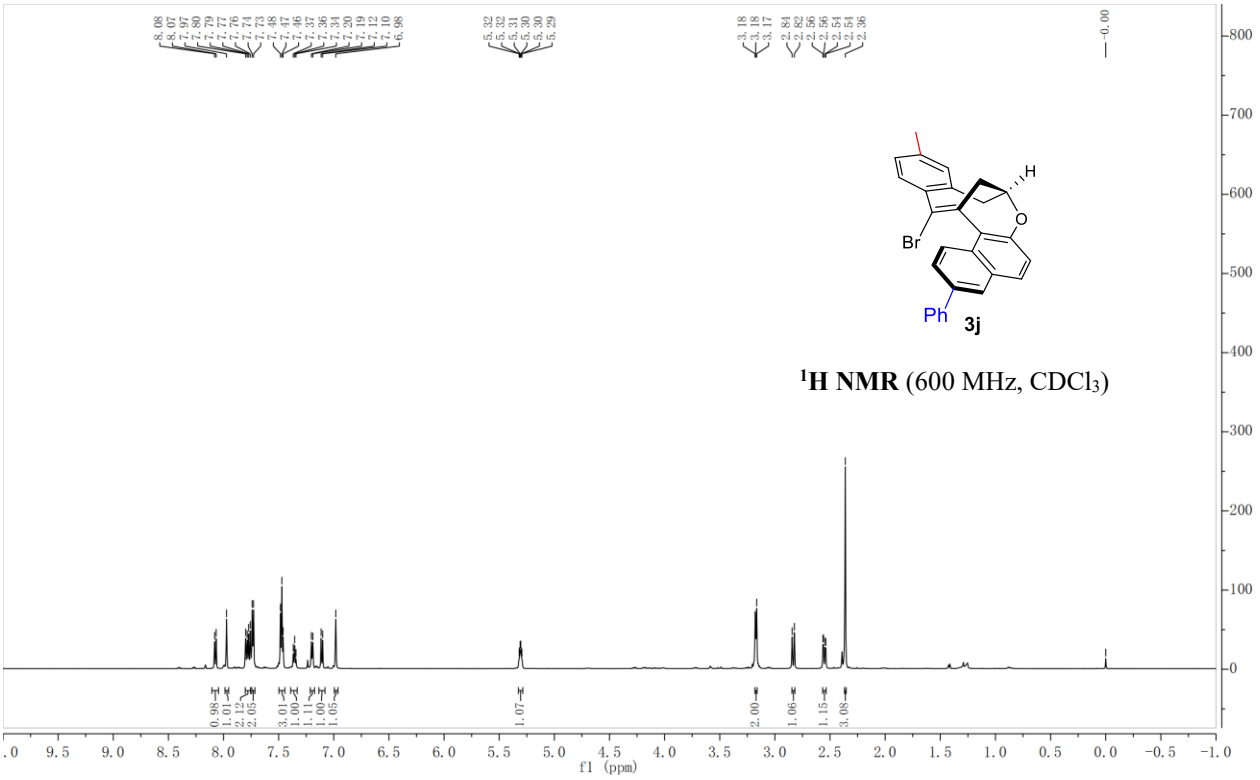
3i

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

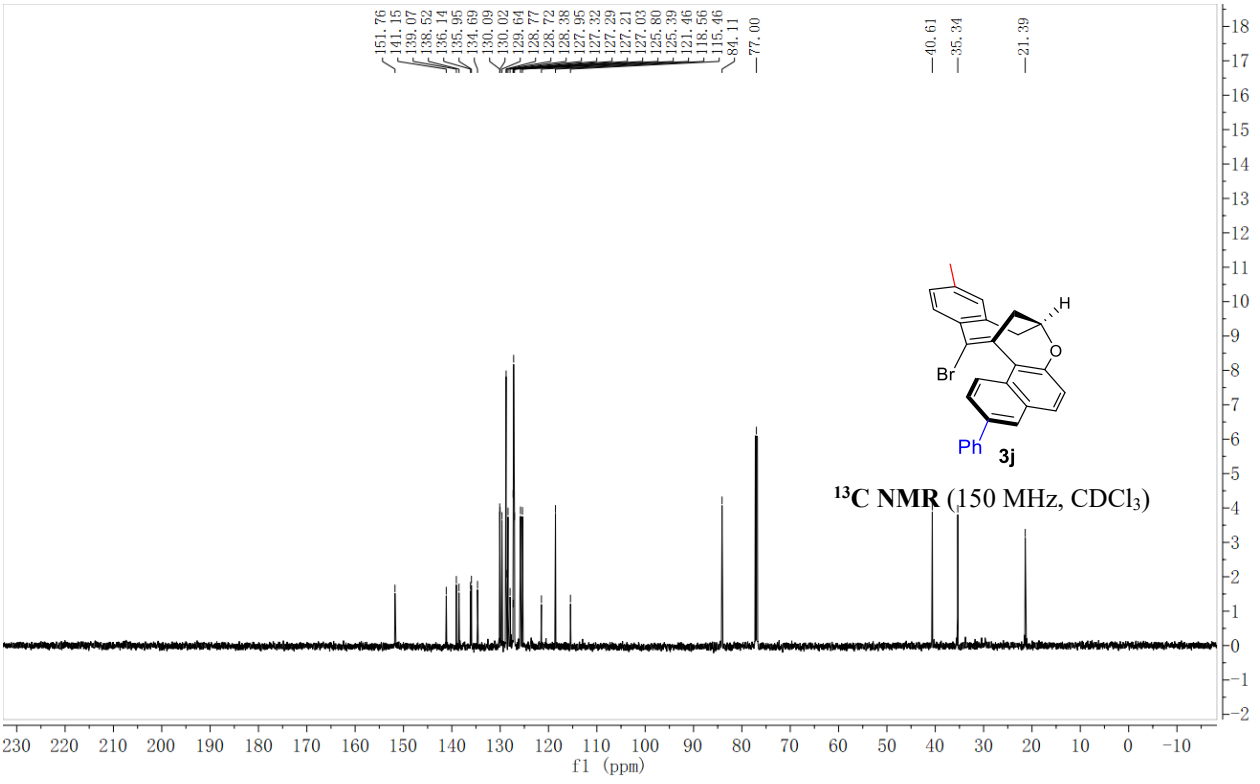


3i

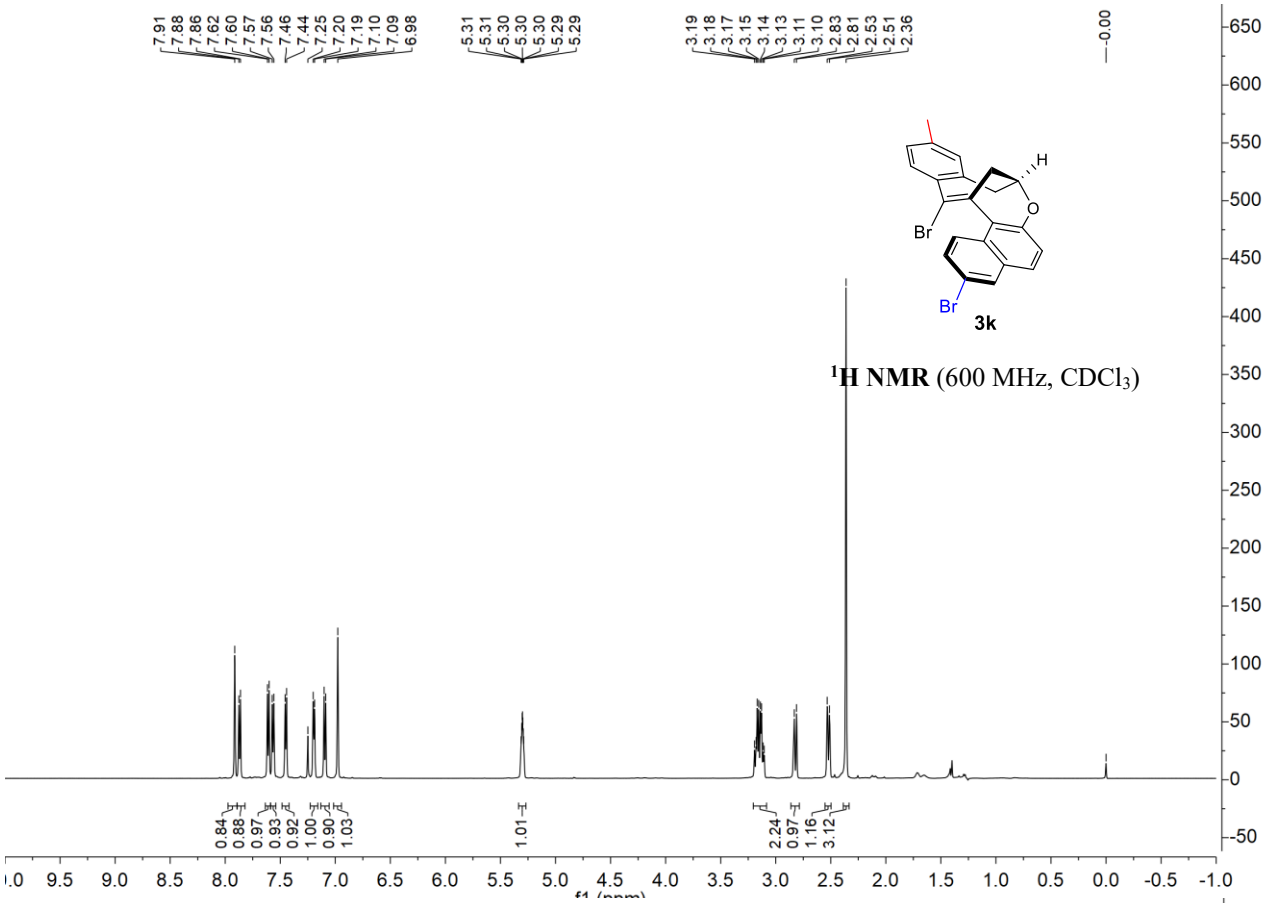
^{13}C NMR (150 MHz, $CDCl_3$)



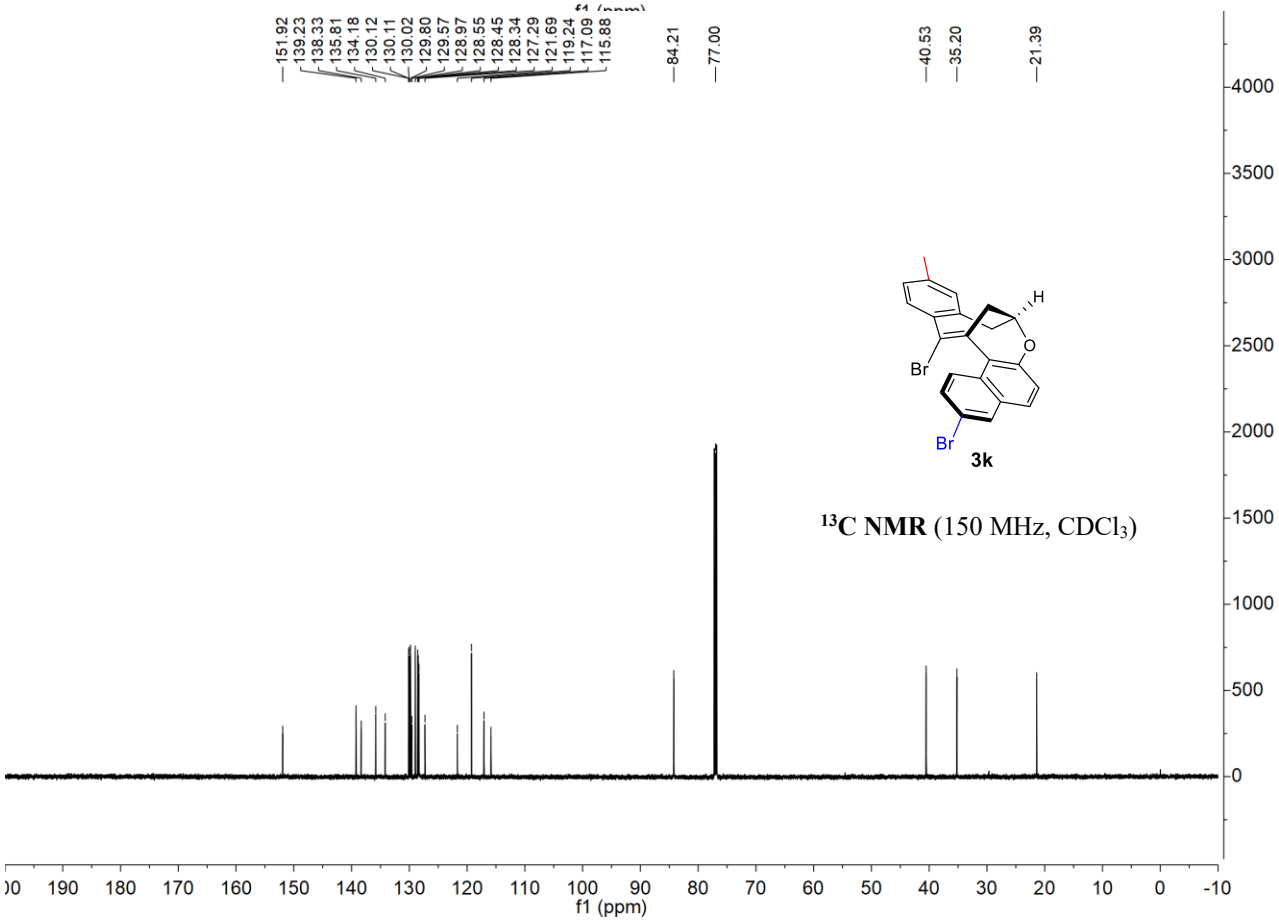
^{1}H NMR (600 MHz, $CDCl_3$)



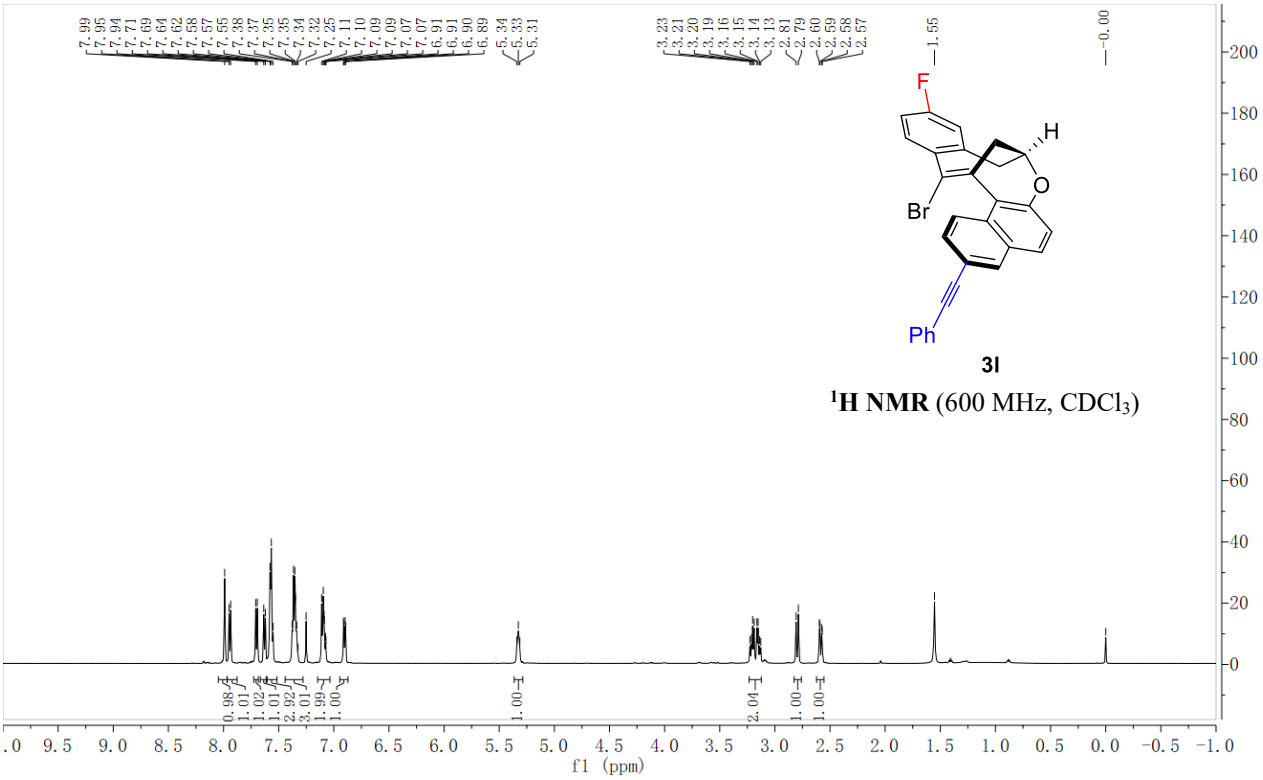
^{13}C NMR (150 MHz, $CDCl_3$)



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

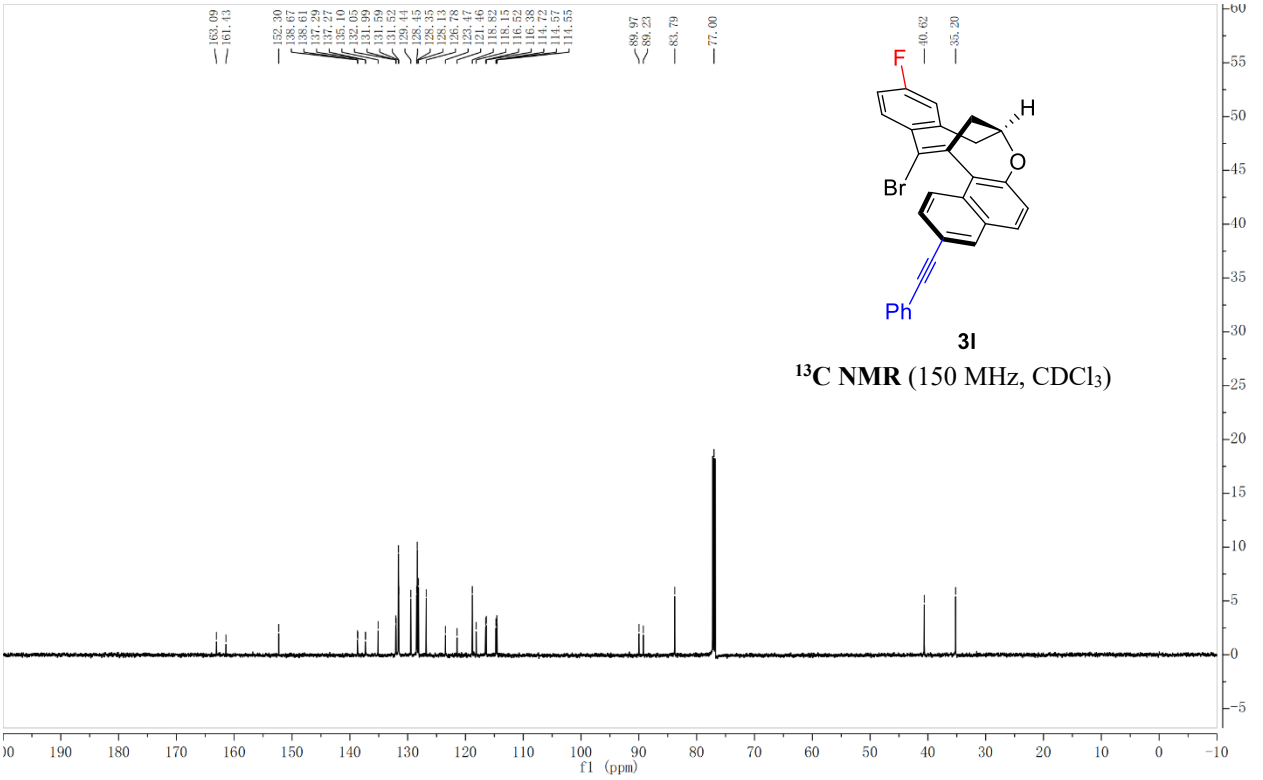


^{13}C NMR (150 MHz, $CDCl_3$)



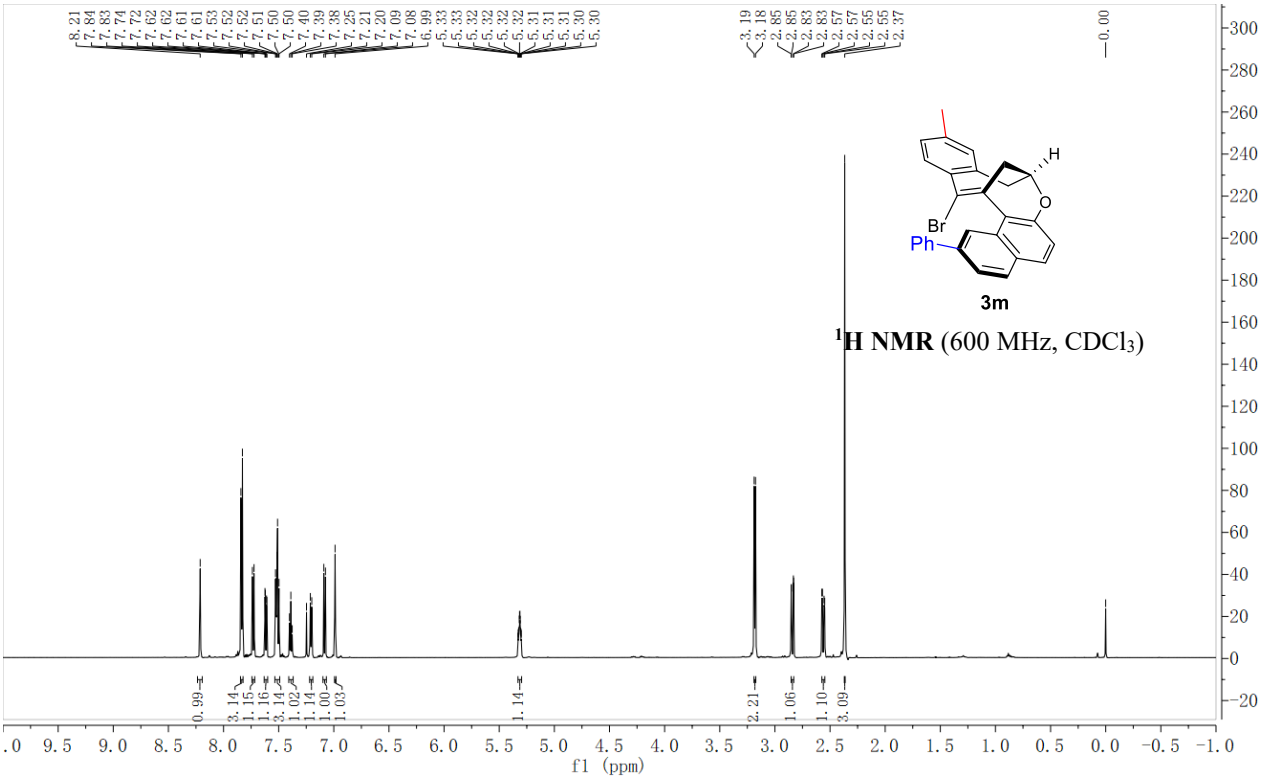
3l

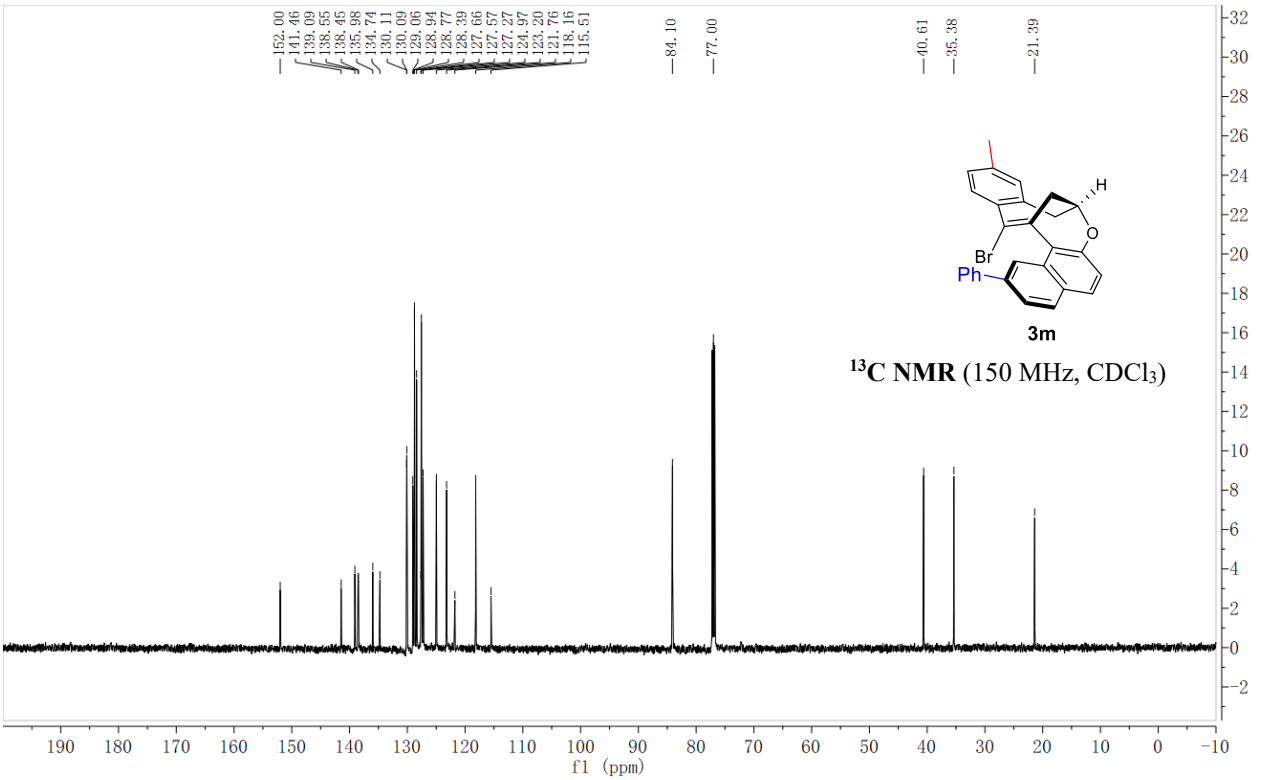
^{1}H NMR (600 MHz, $CDCl_3$)

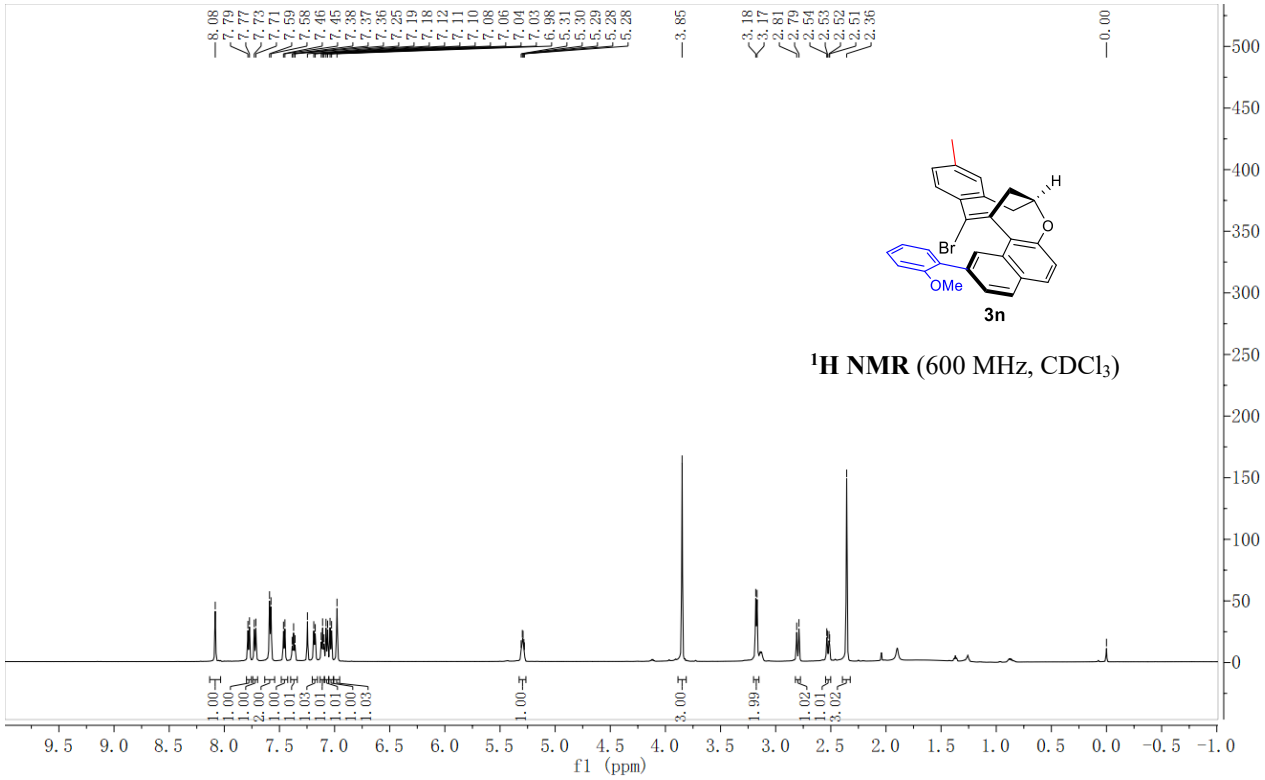


3l

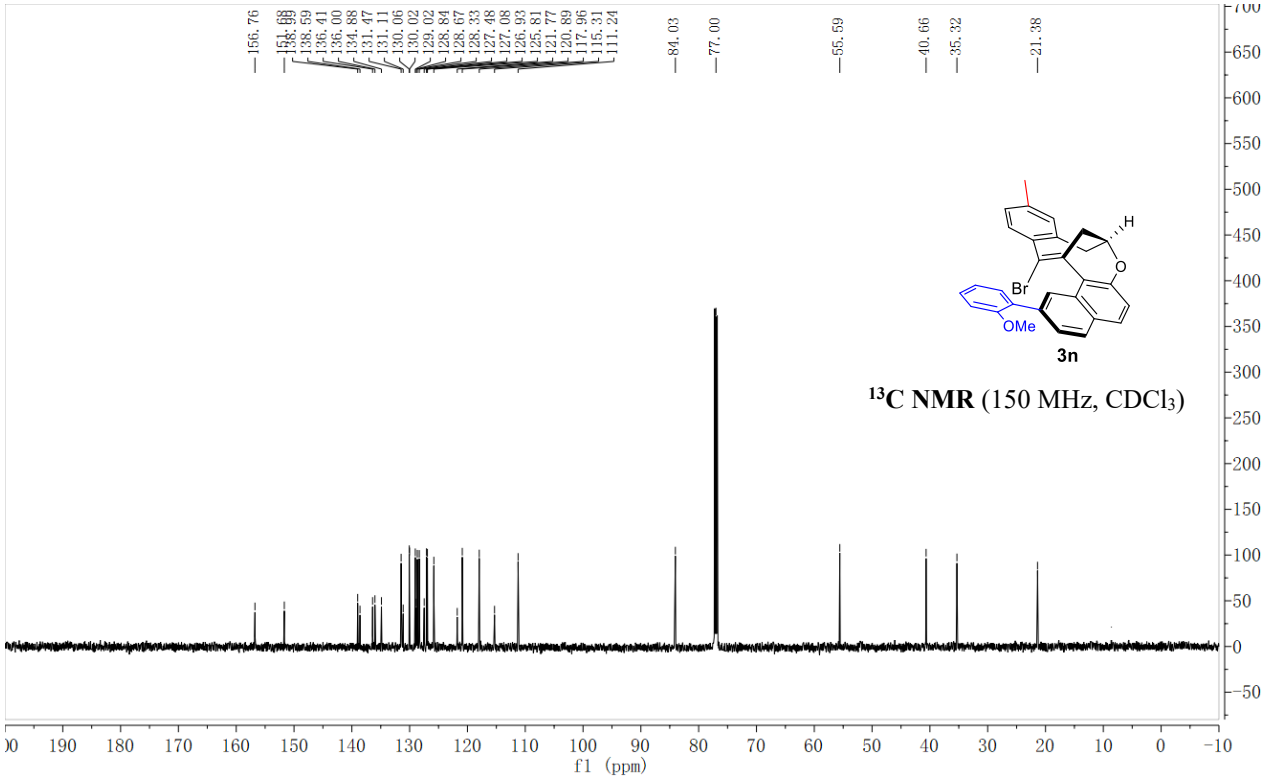
^{13}C NMR (150 MHz, $CDCl_3$)


Br
Ph
H
O
3m
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)

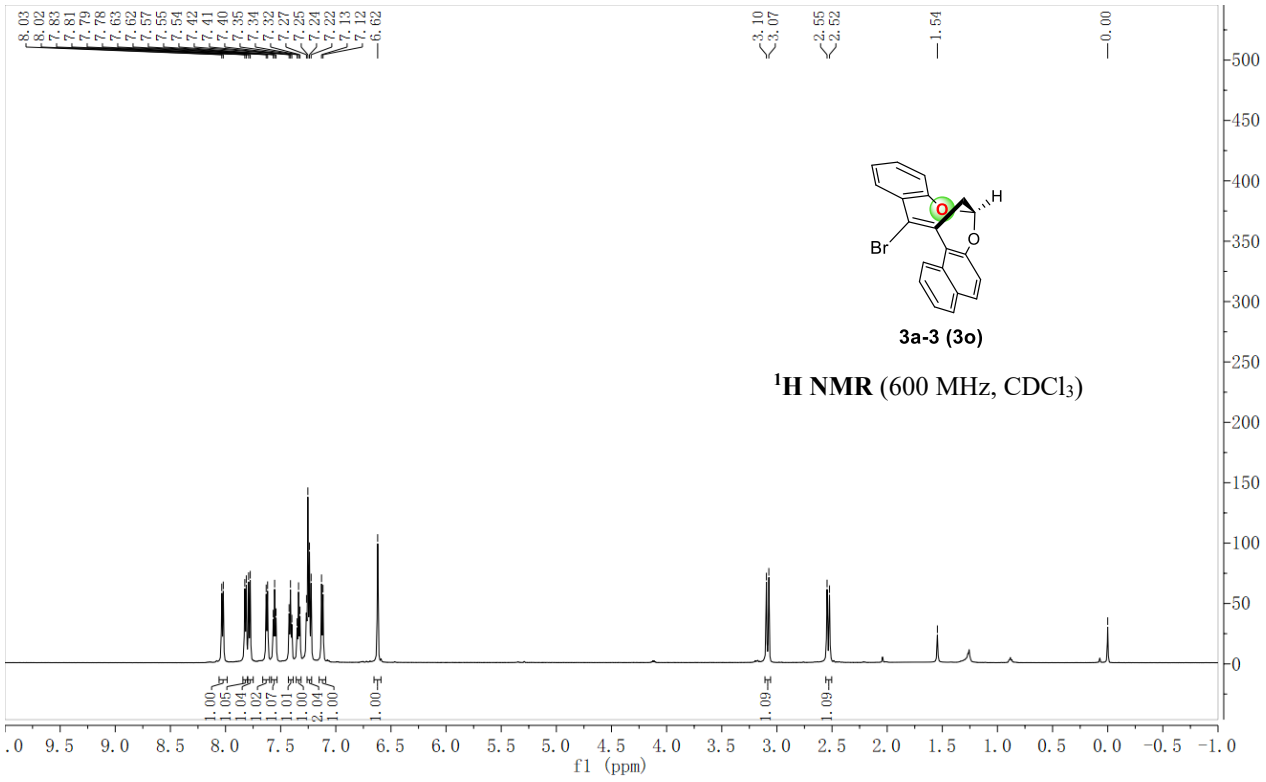

Br
Ph
H
O
3m
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)



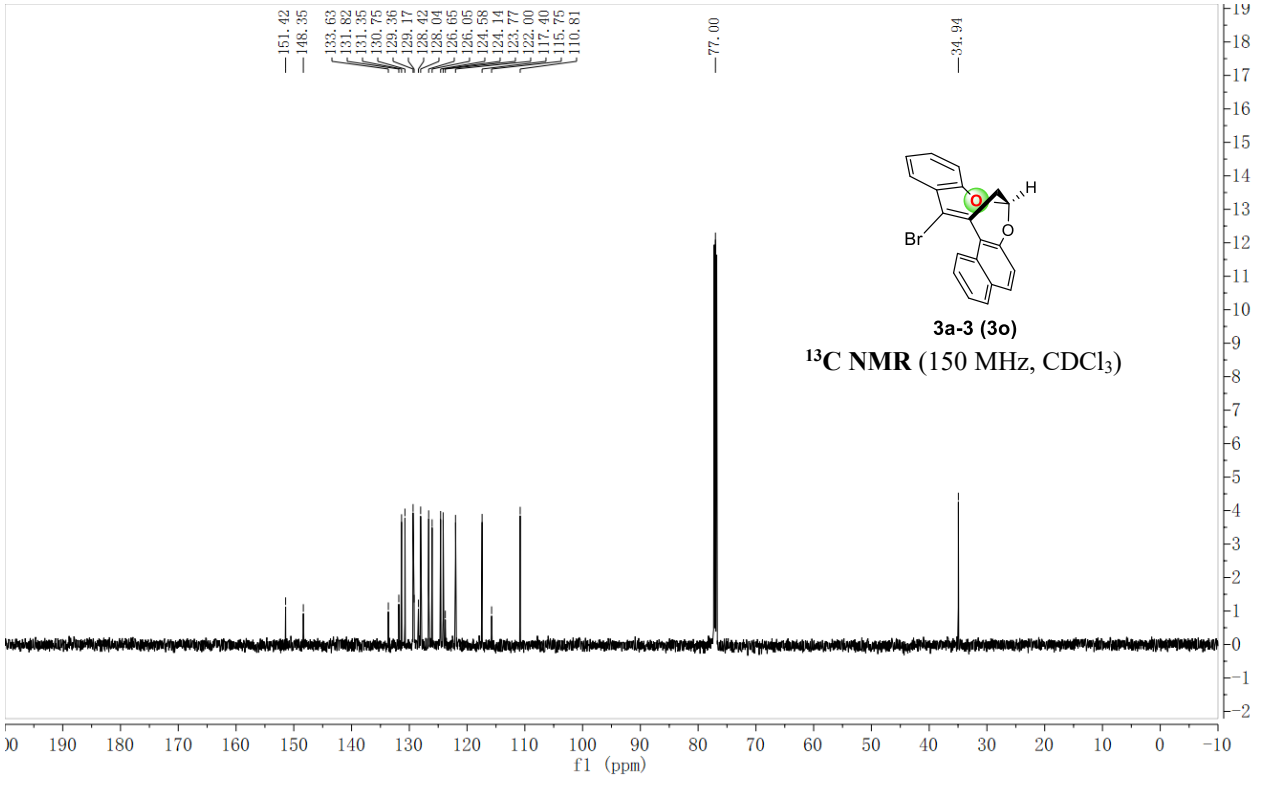
^{1}H NMR (600 MHz, $CDCl_3$)



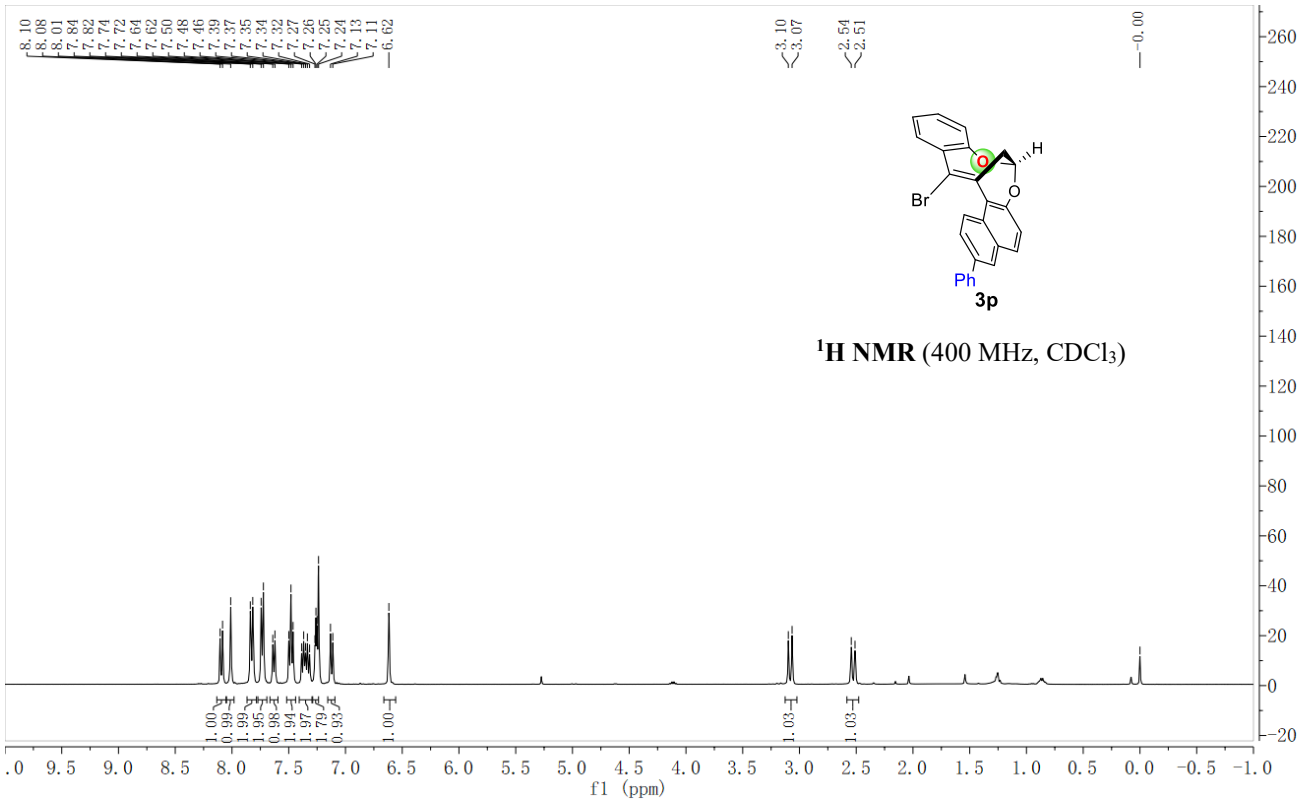
^{13}C NMR (150 MHz, $CDCl_3$)



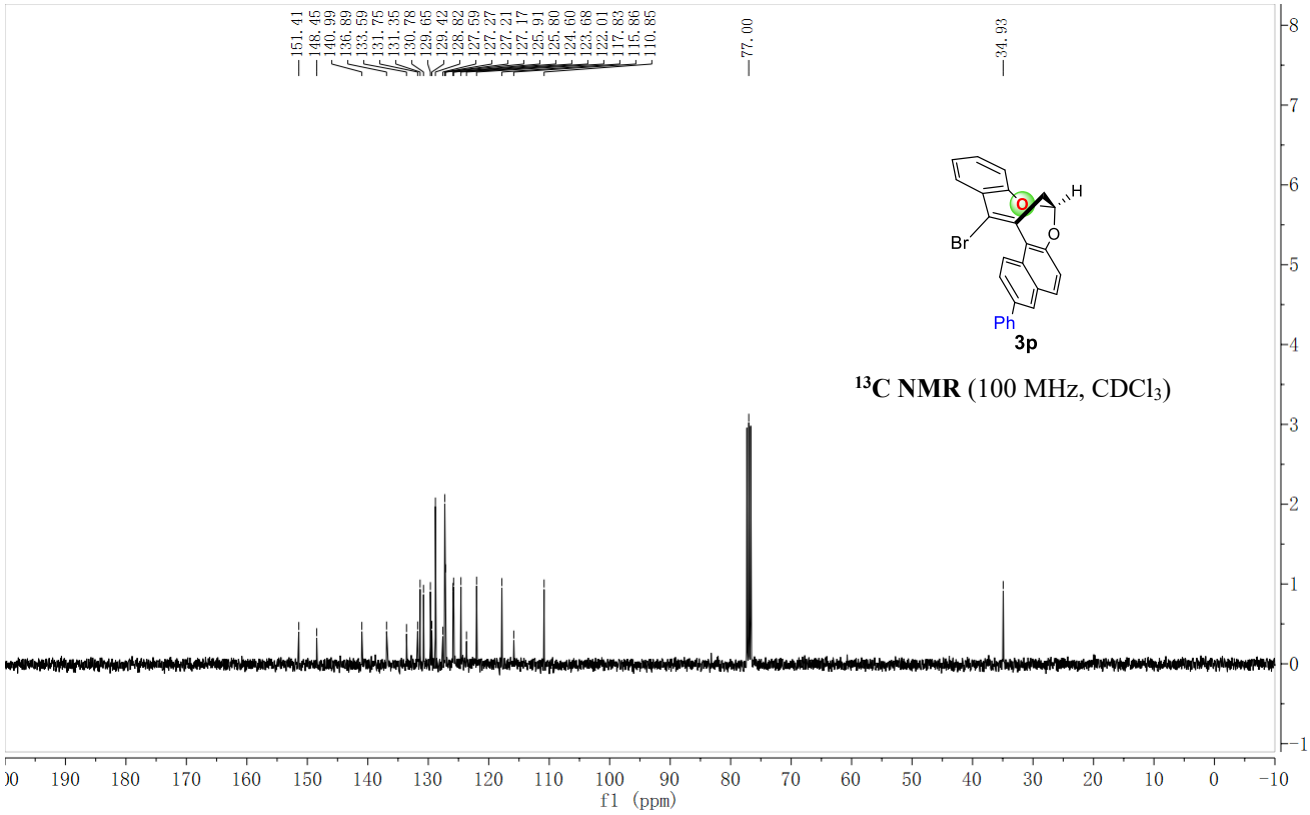
^{1}H NMR (600 MHz, $CDCl_3$)



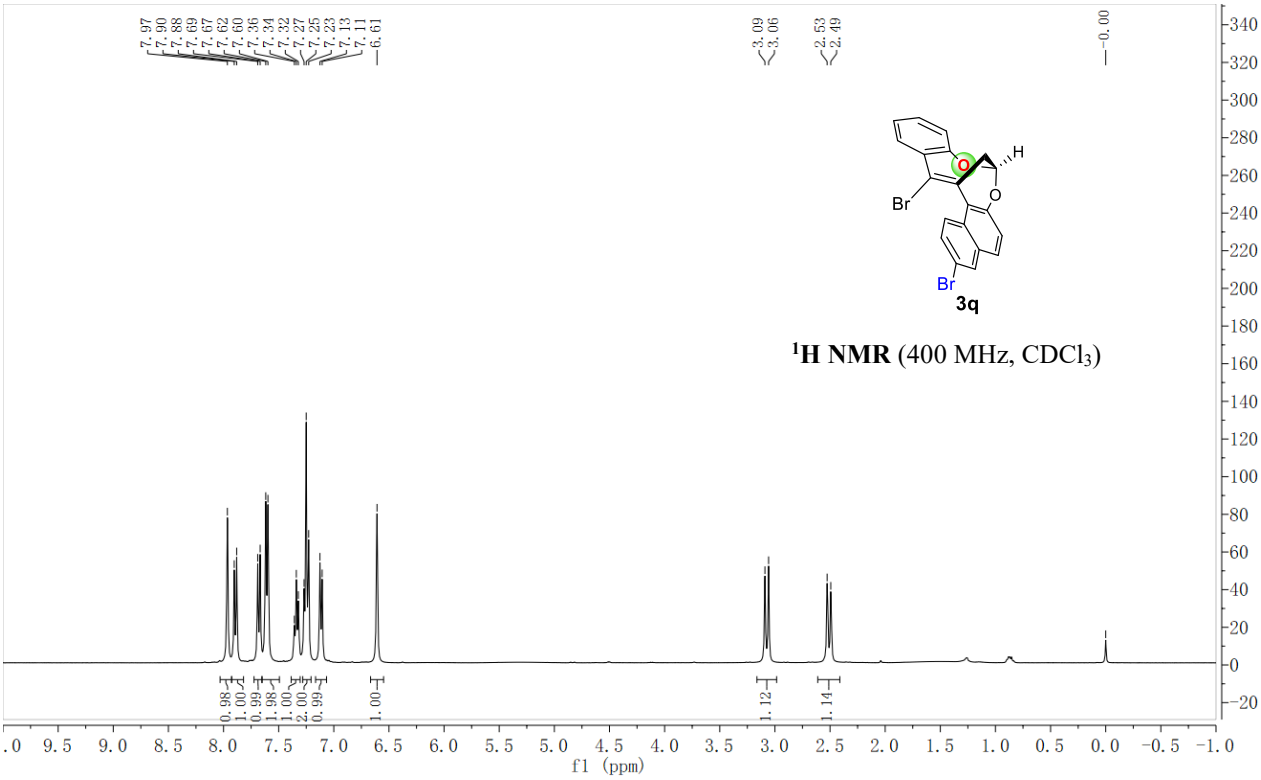
^{13}C NMR (150 MHz, $CDCl_3$)



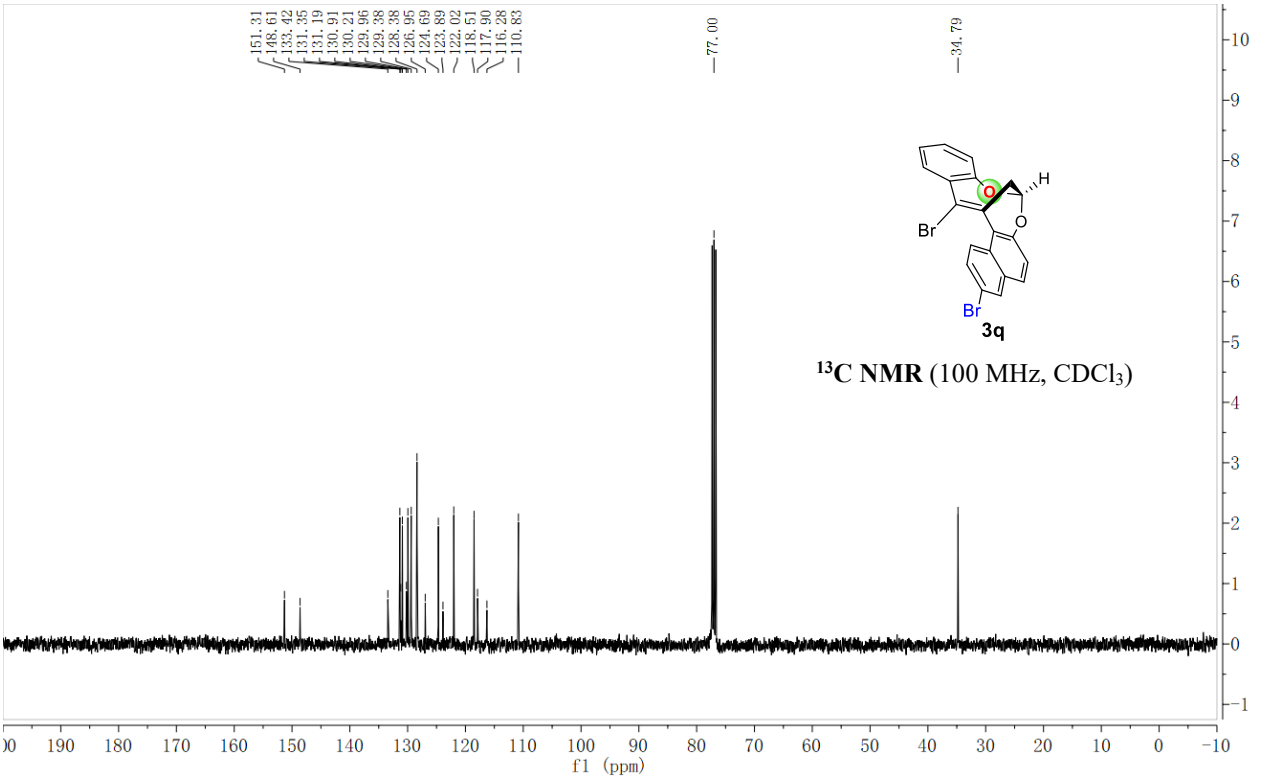
^{1}H NMR (400 MHz, $CDCl_3$)



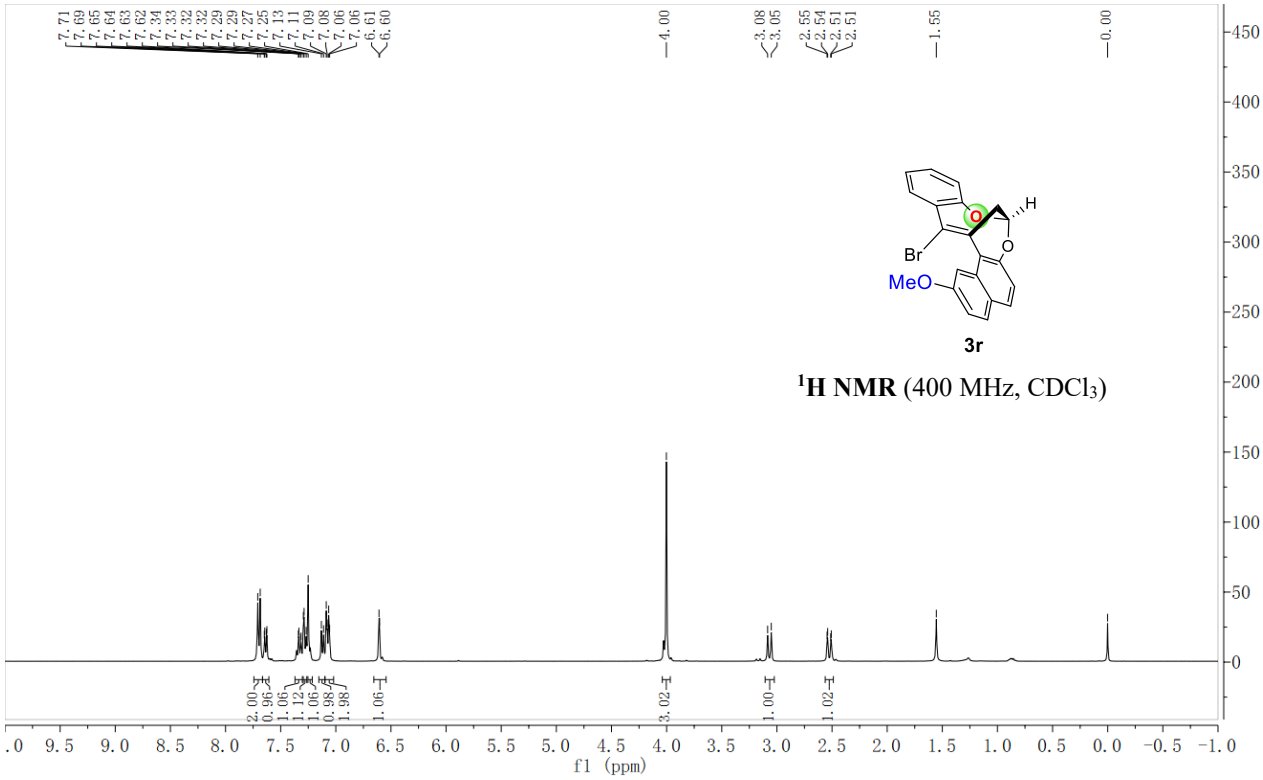
^{13}C NMR (100 MHz, $CDCl_3$)



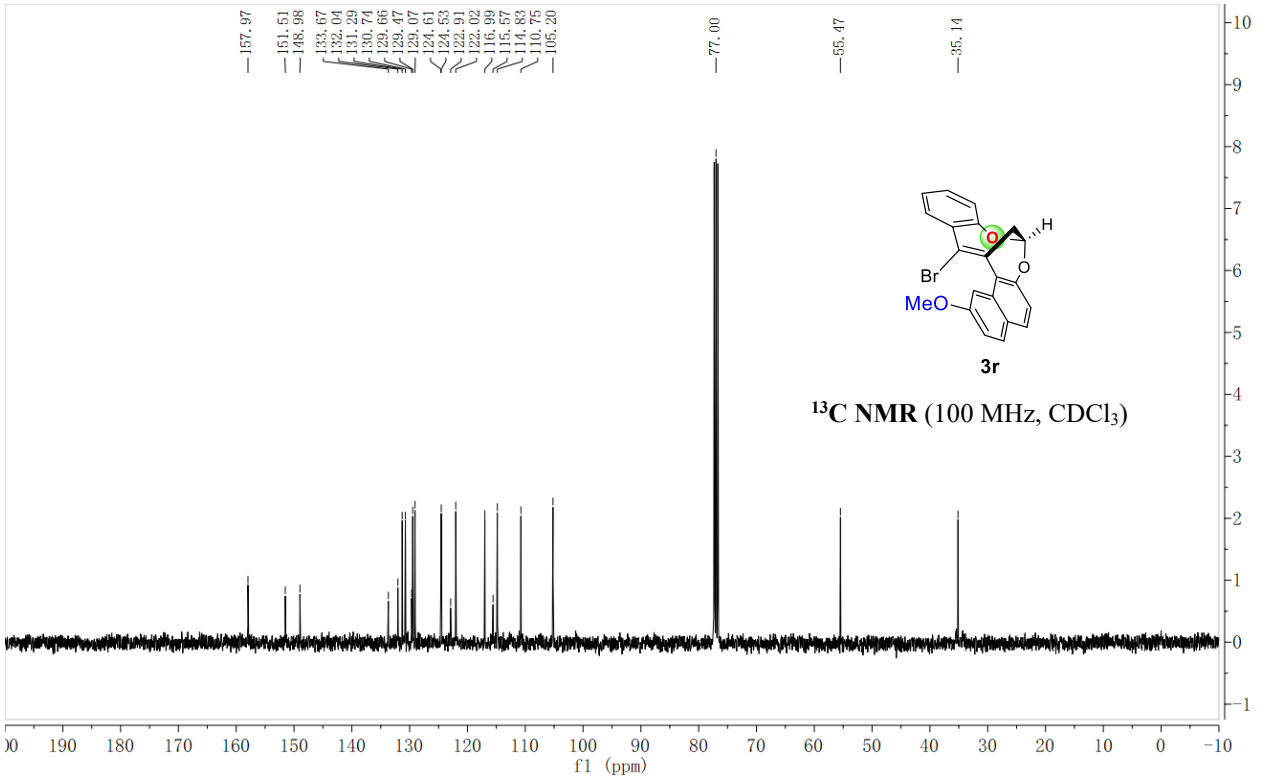
^{1}H NMR (400 MHz, $CDCl_3$)



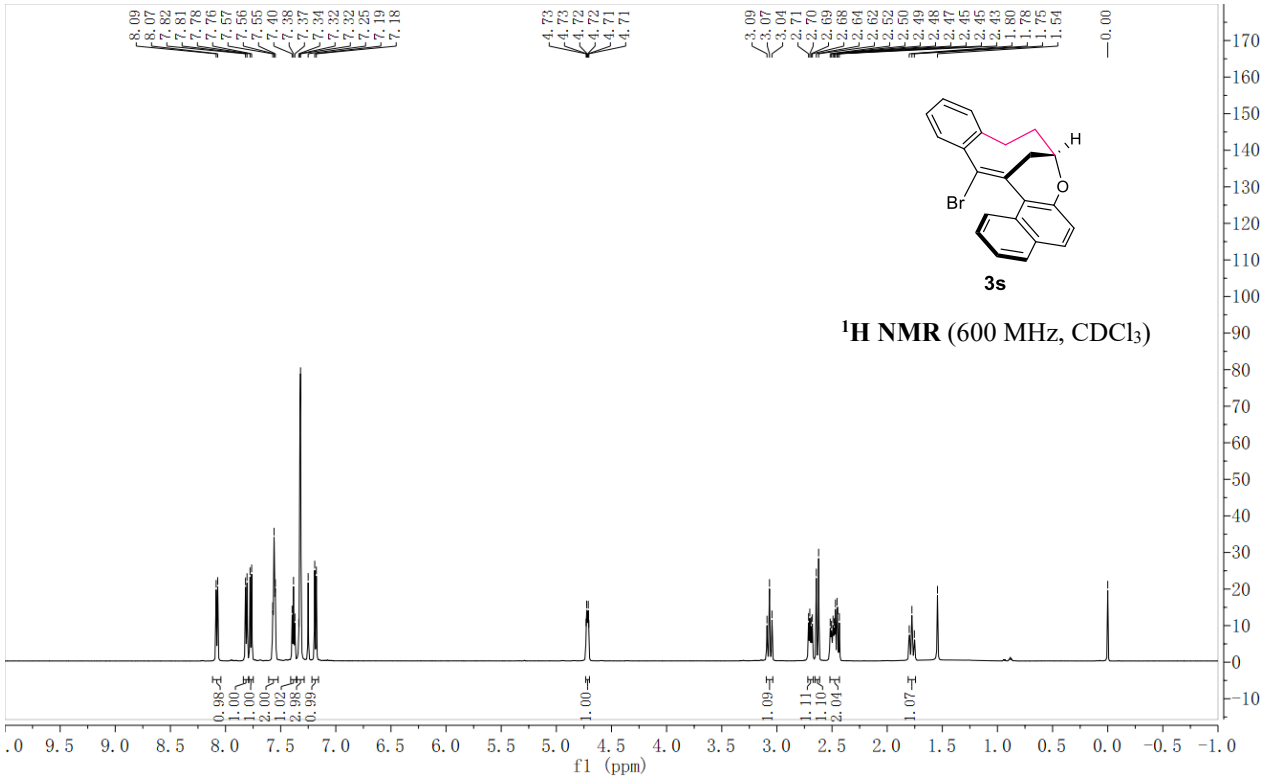
^{13}C NMR (100 MHz, $CDCl_3$)



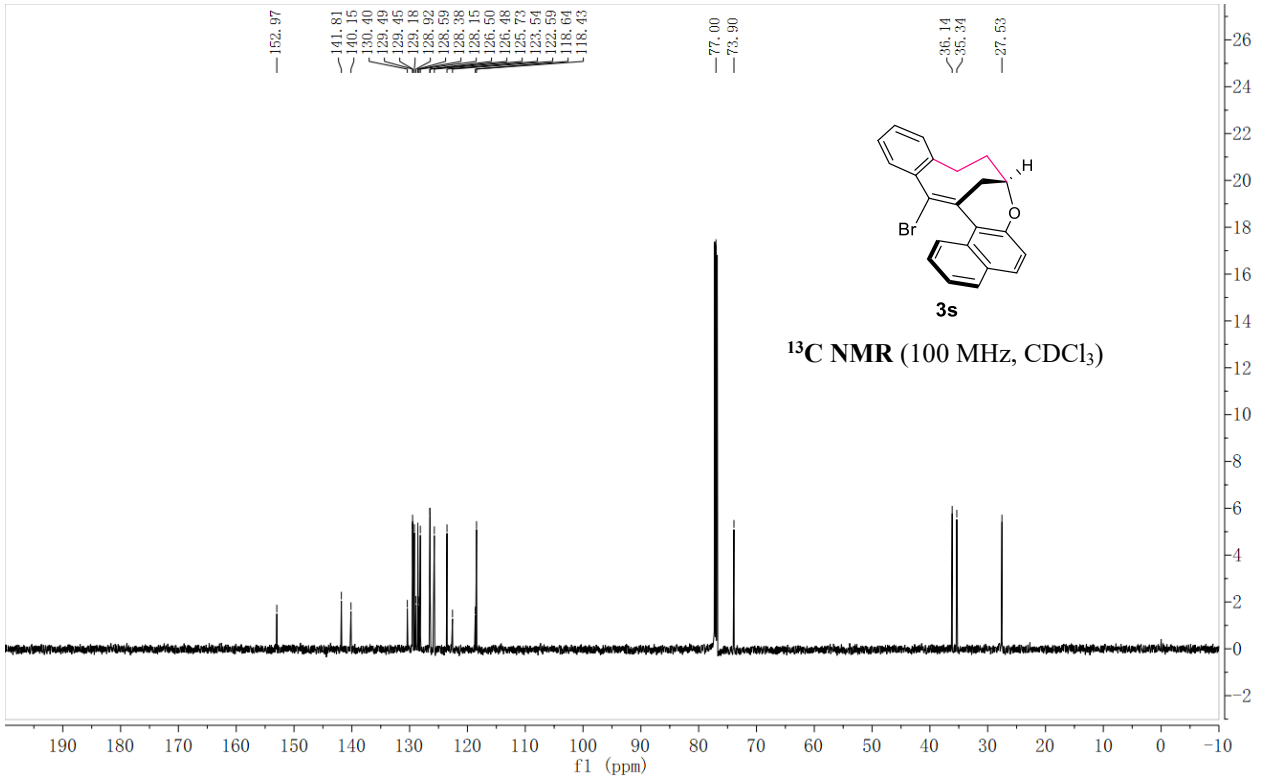
^{1}H NMR (400 MHz, $CDCl_3$)



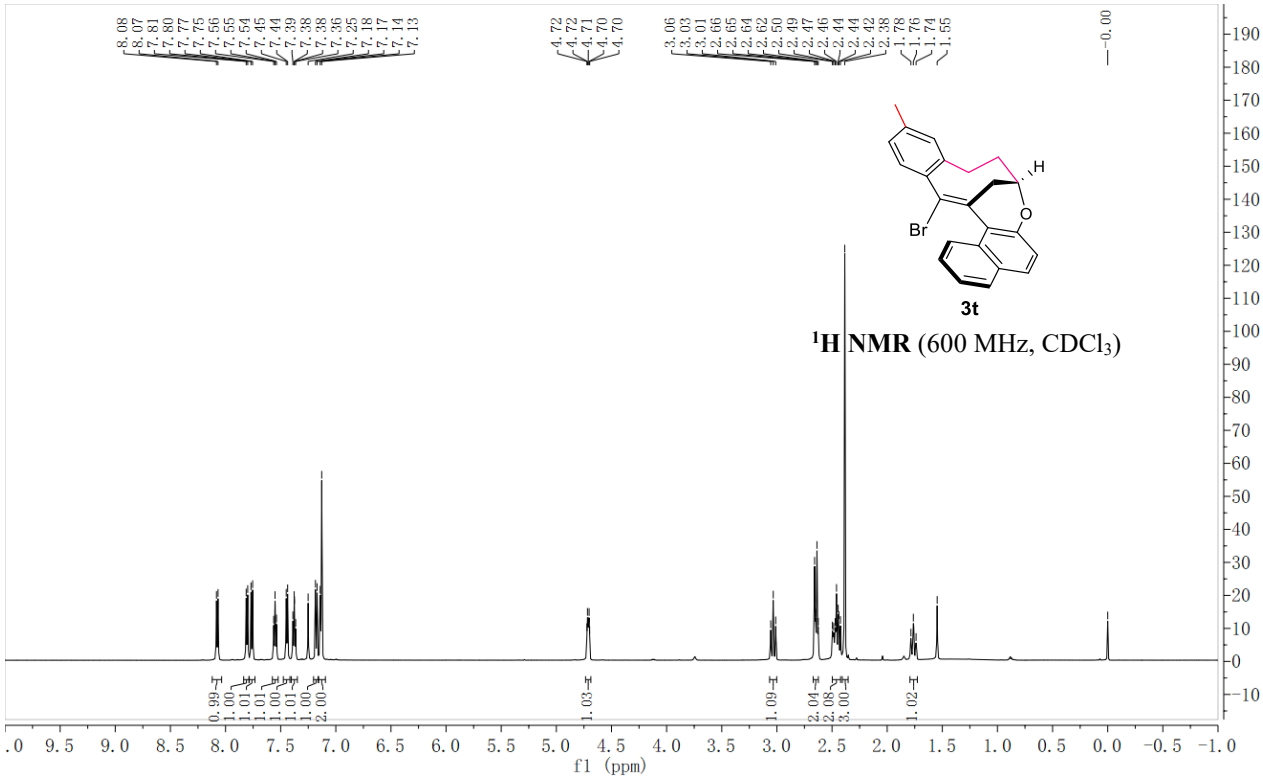
^{13}C NMR (100 MHz, $CDCl_3$)

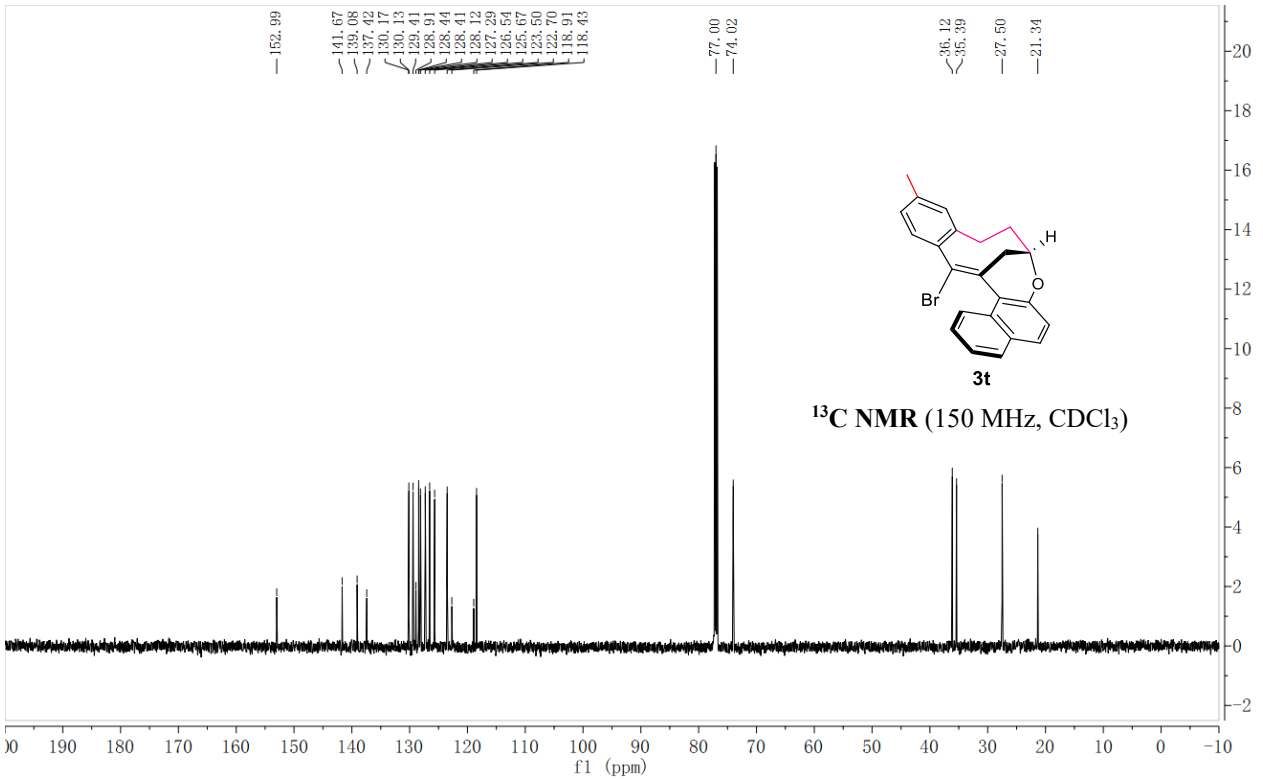


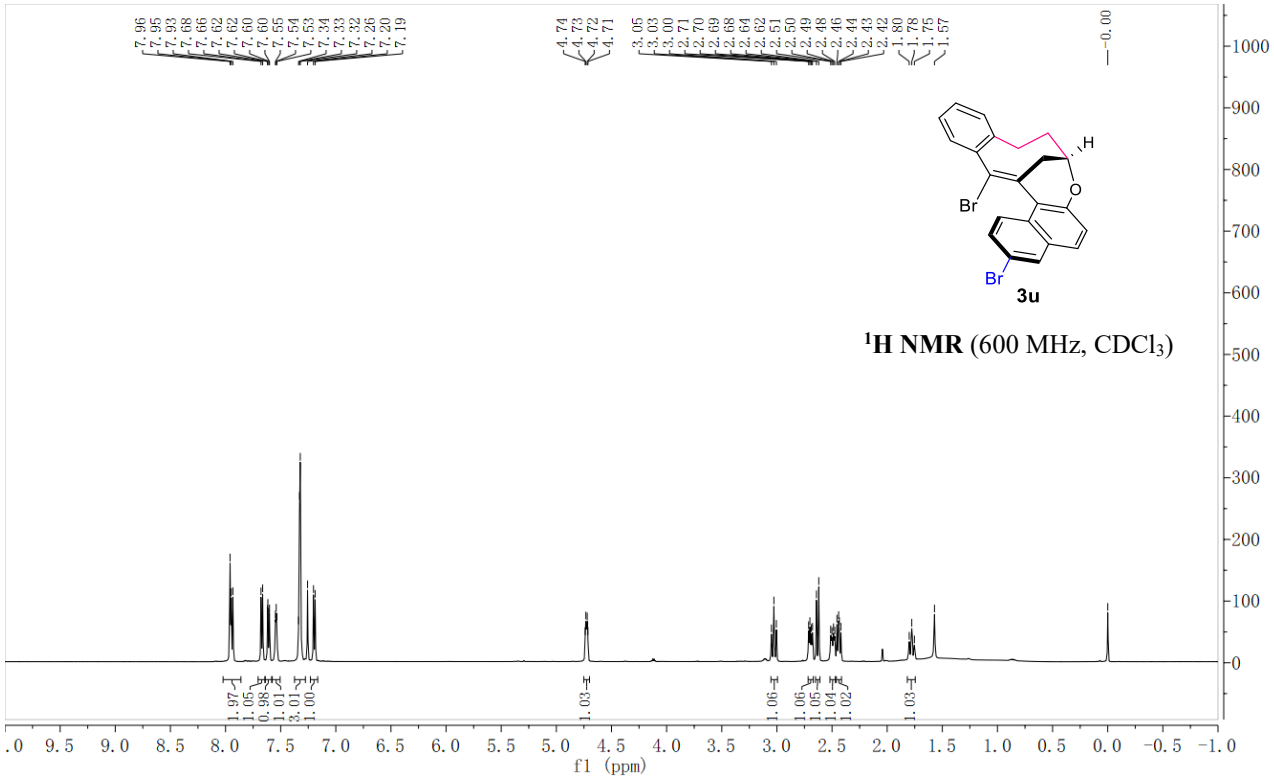
^{1}H NMR (600 MHz, $CDCl_3$)



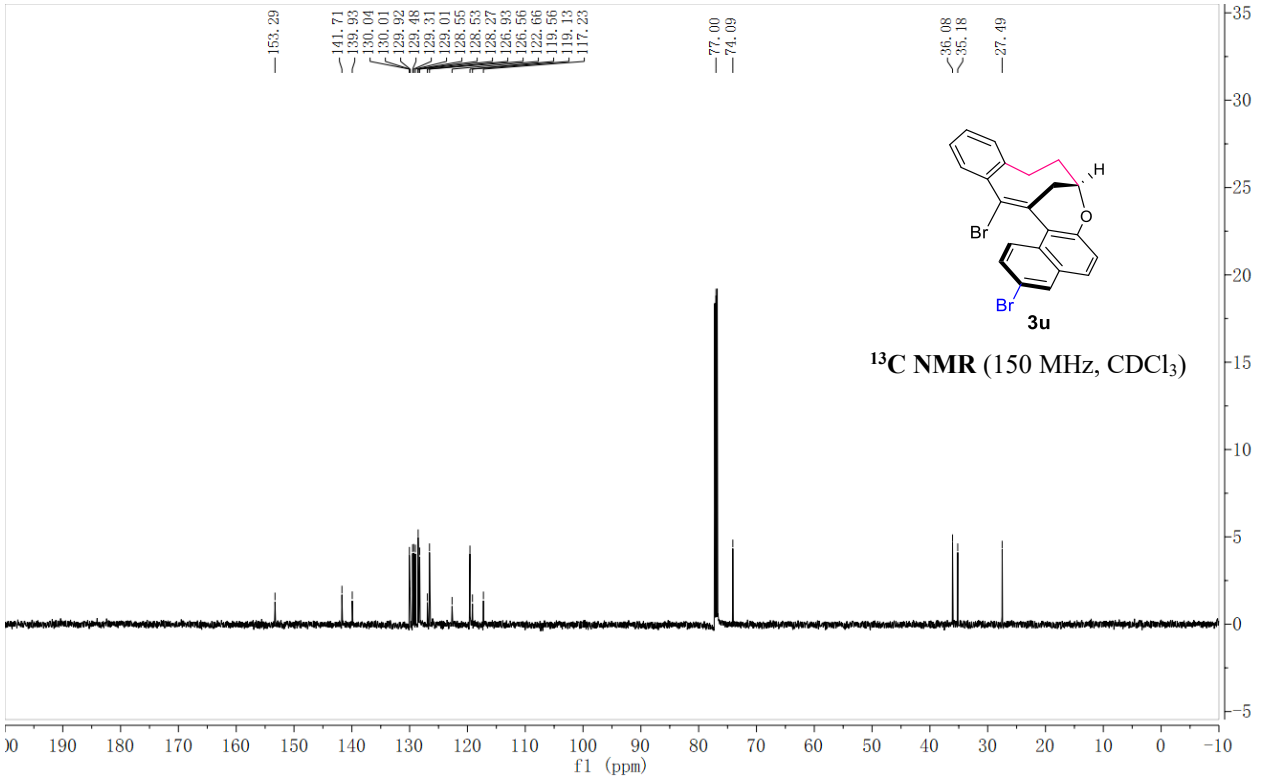
^{13}C NMR (100 MHz, $CDCl_3$)


Br
H
O
3t
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)

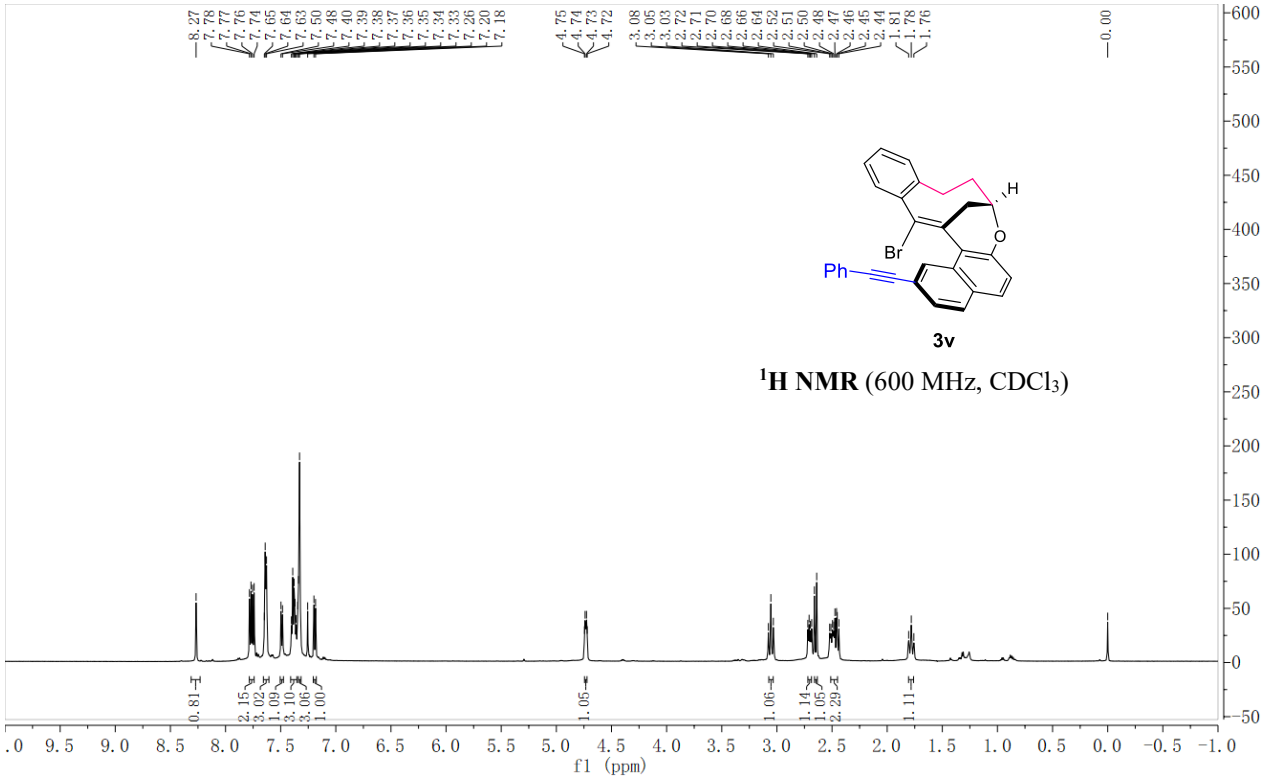

Br
H
O
3t
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)



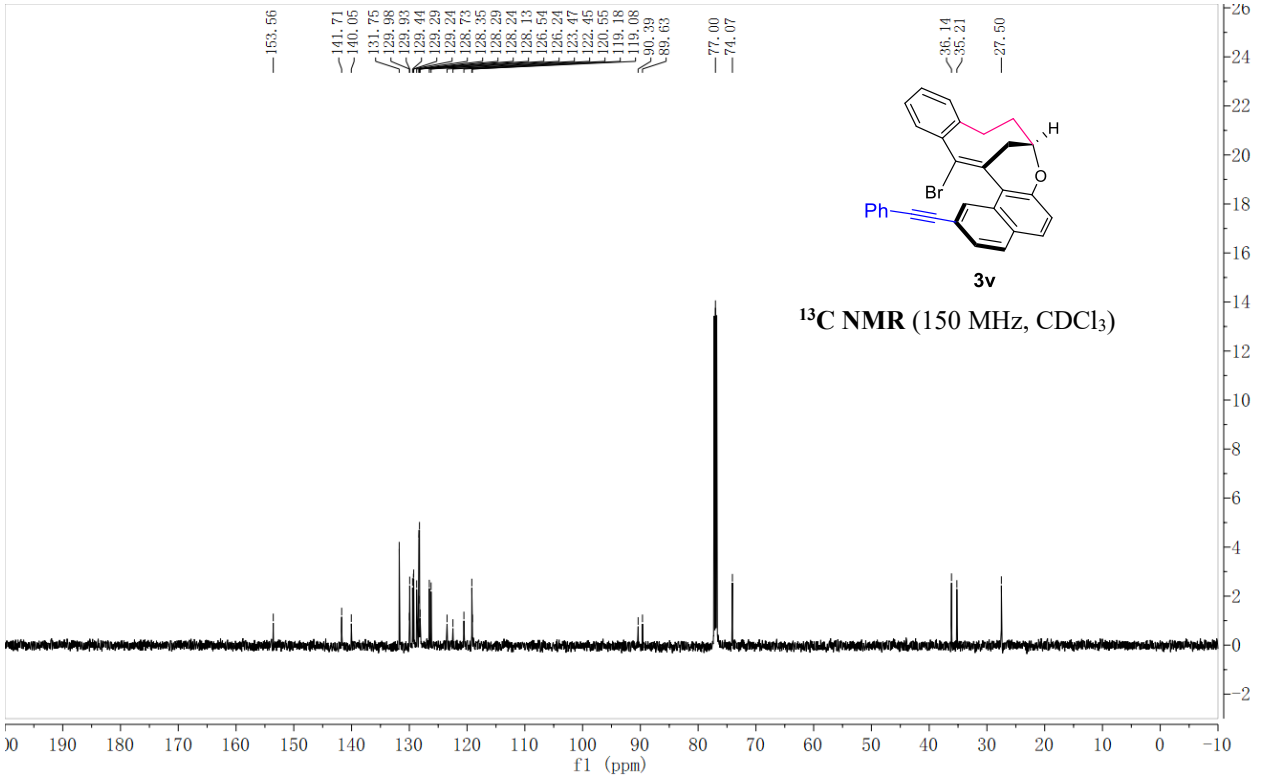
^{1}H NMR (600 MHz, $CDCl_3$)



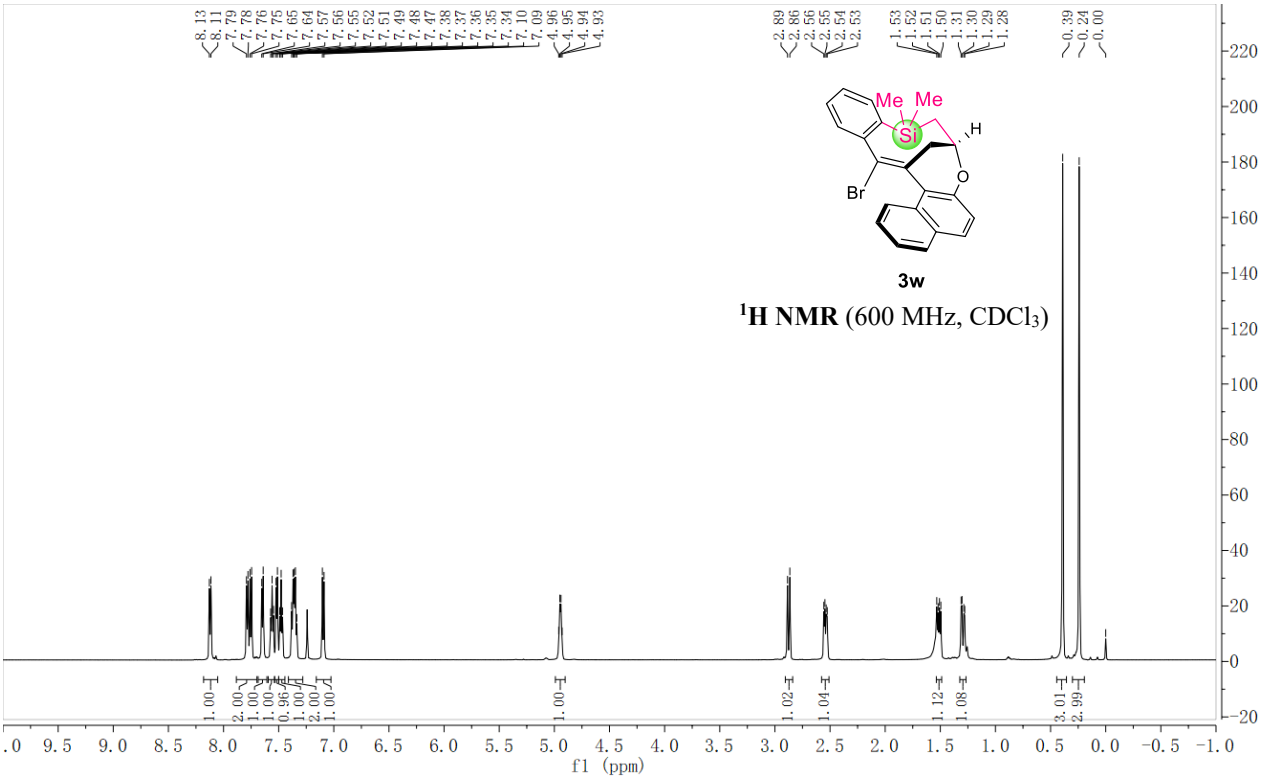
^{13}C NMR (150 MHz, $CDCl_3$)

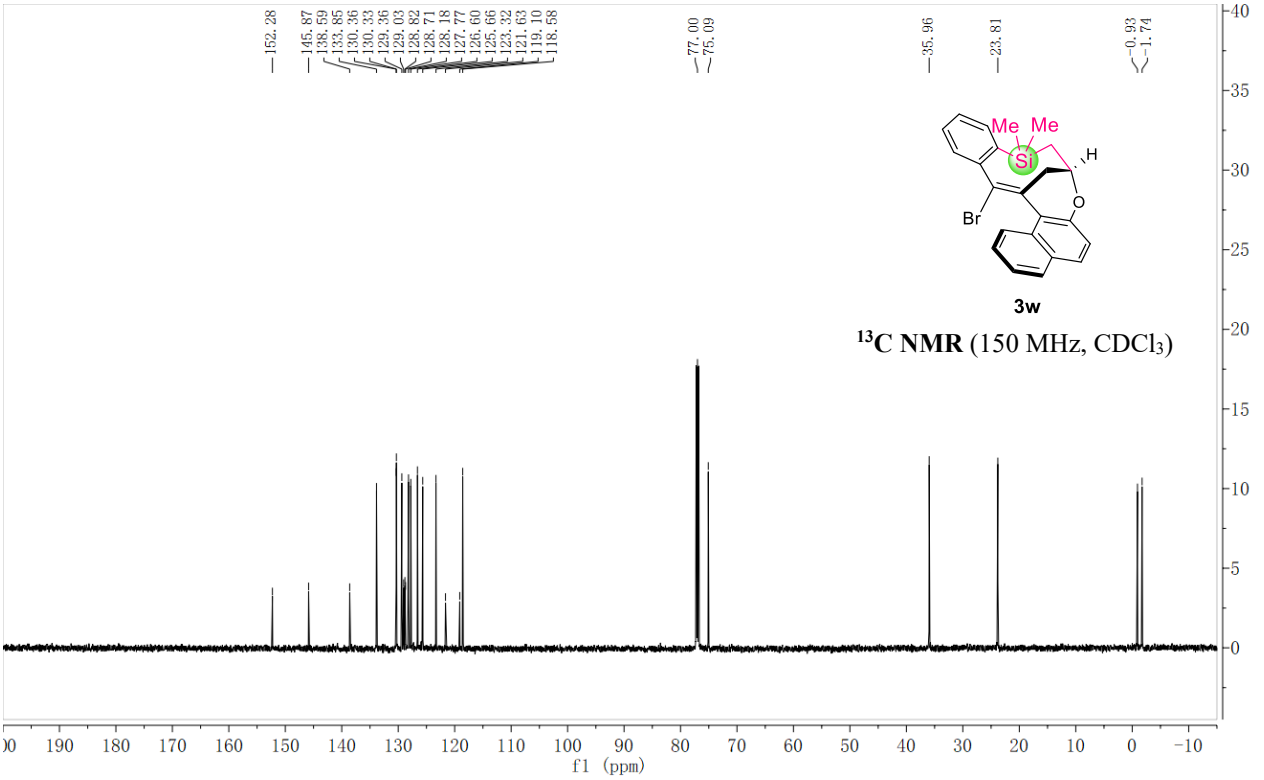


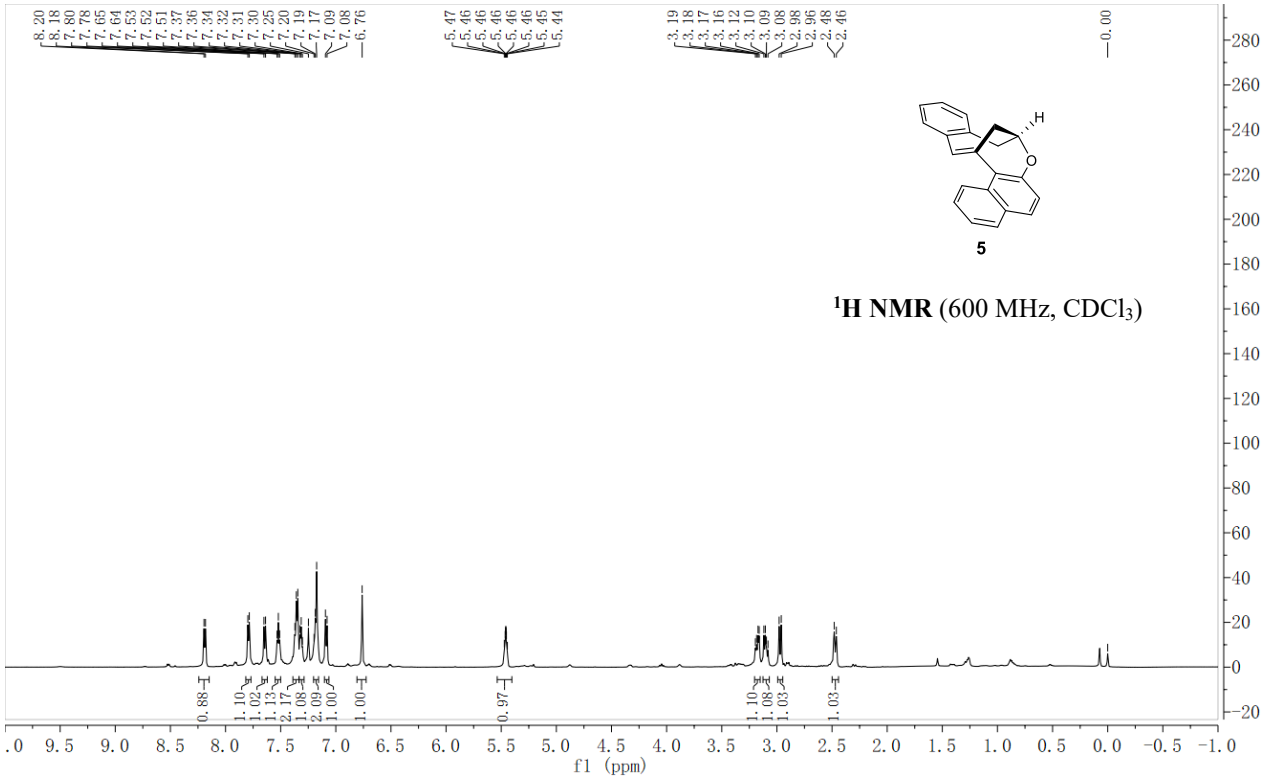
^{1}H NMR (600 MHz, $CDCl_3$)



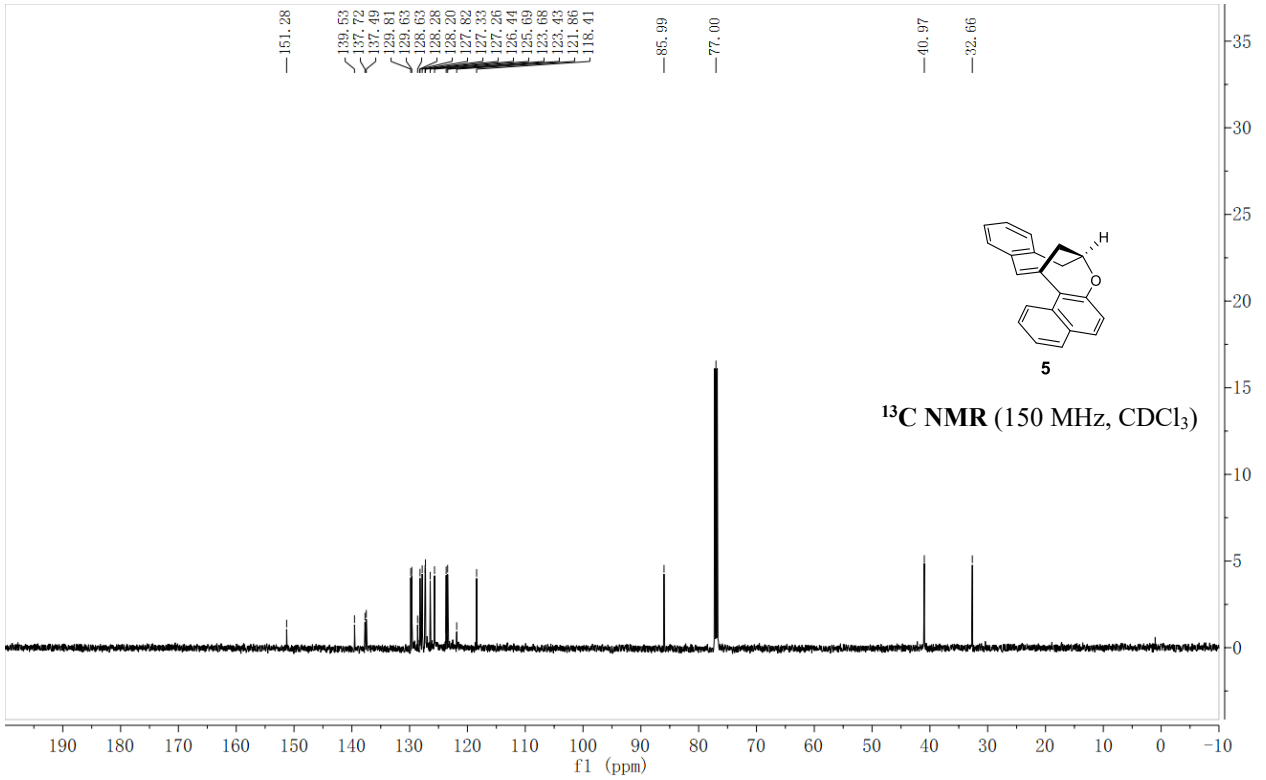
^{13}C NMR (150 MHz, $CDCl_3$)


Me Me
Si
H
O
Br
3w
1H NMR (600 MHz, CDCl3)
f1 (ppm)

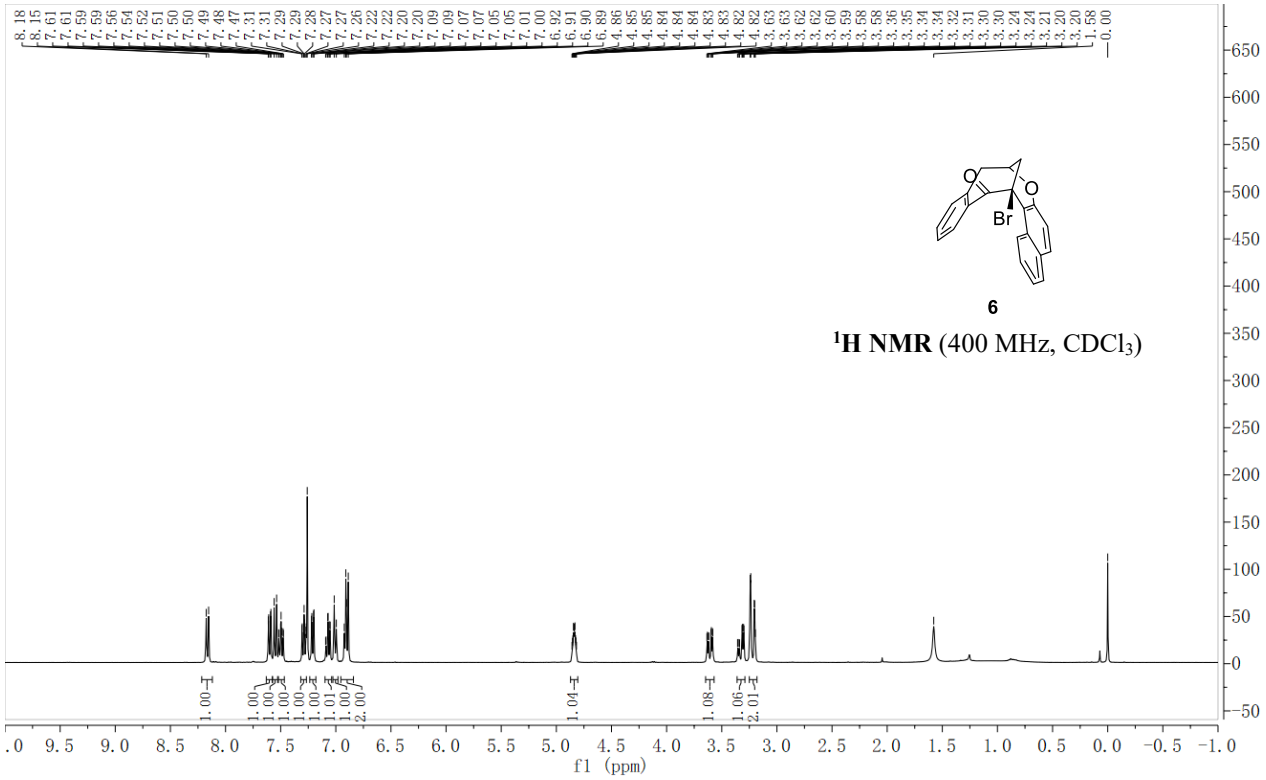

Me Me
Si
H
O
Br
3w
13C NMR (150 MHz, CDCl3)
f1 (ppm)



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

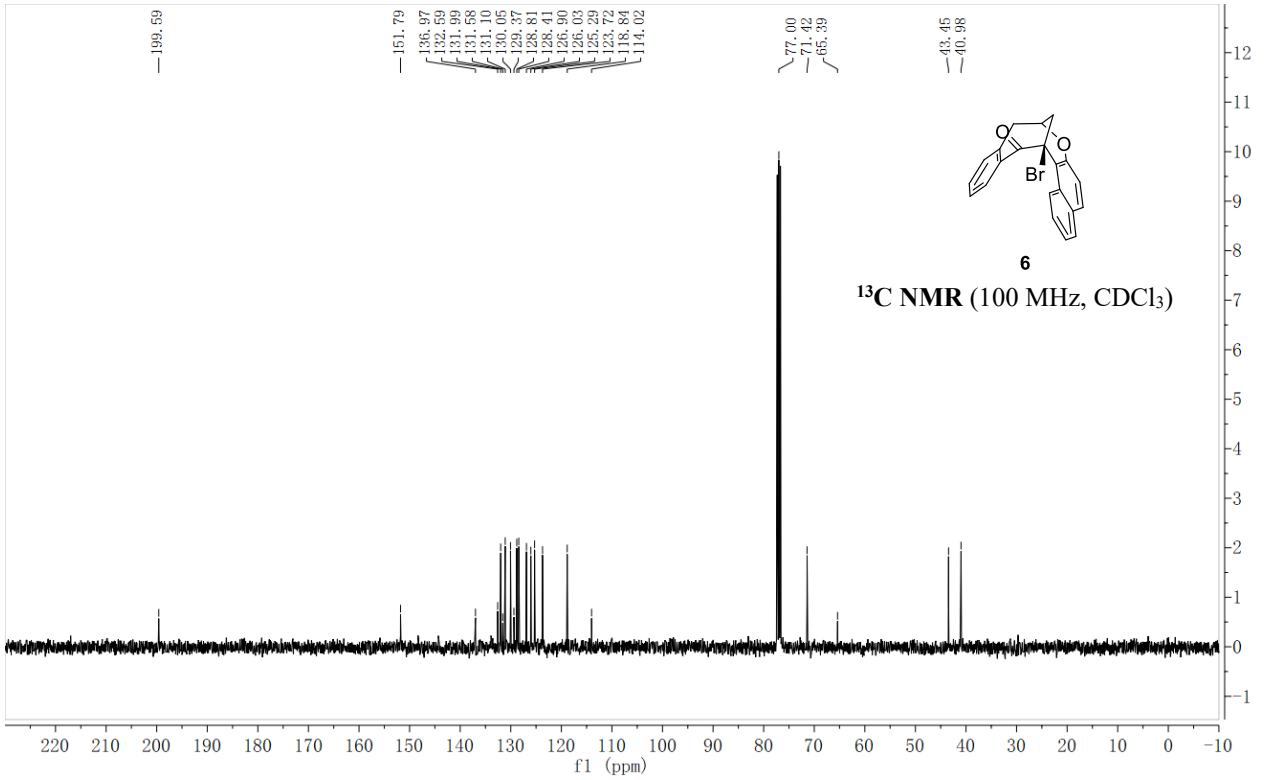


^{13}C NMR (150 MHz, $CDCl_3$)



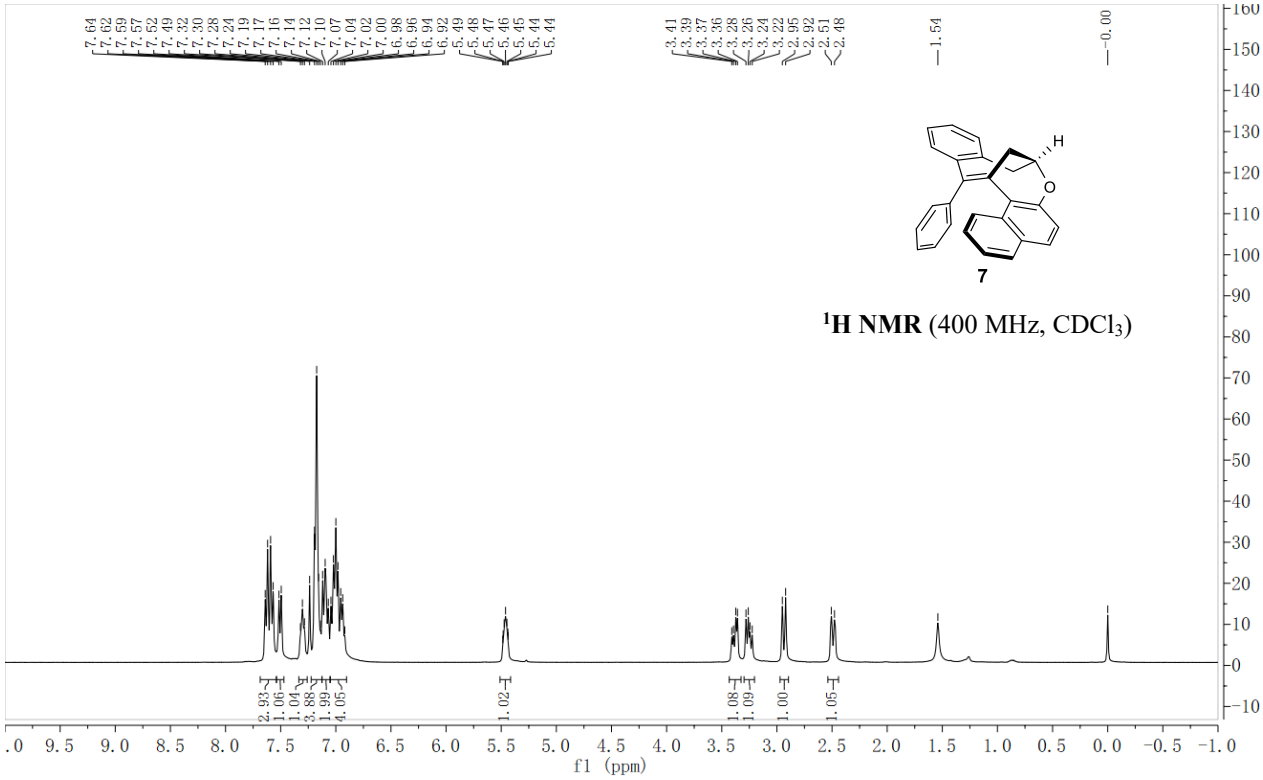
6

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

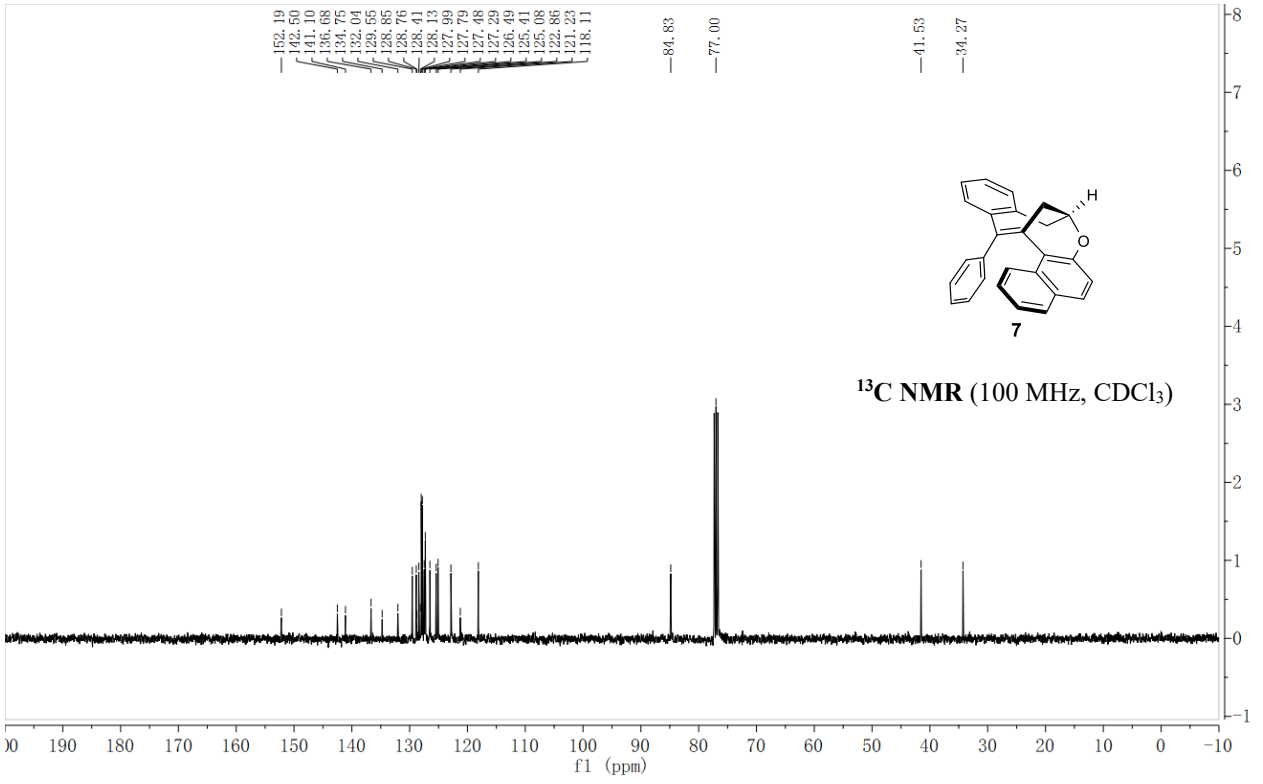


6

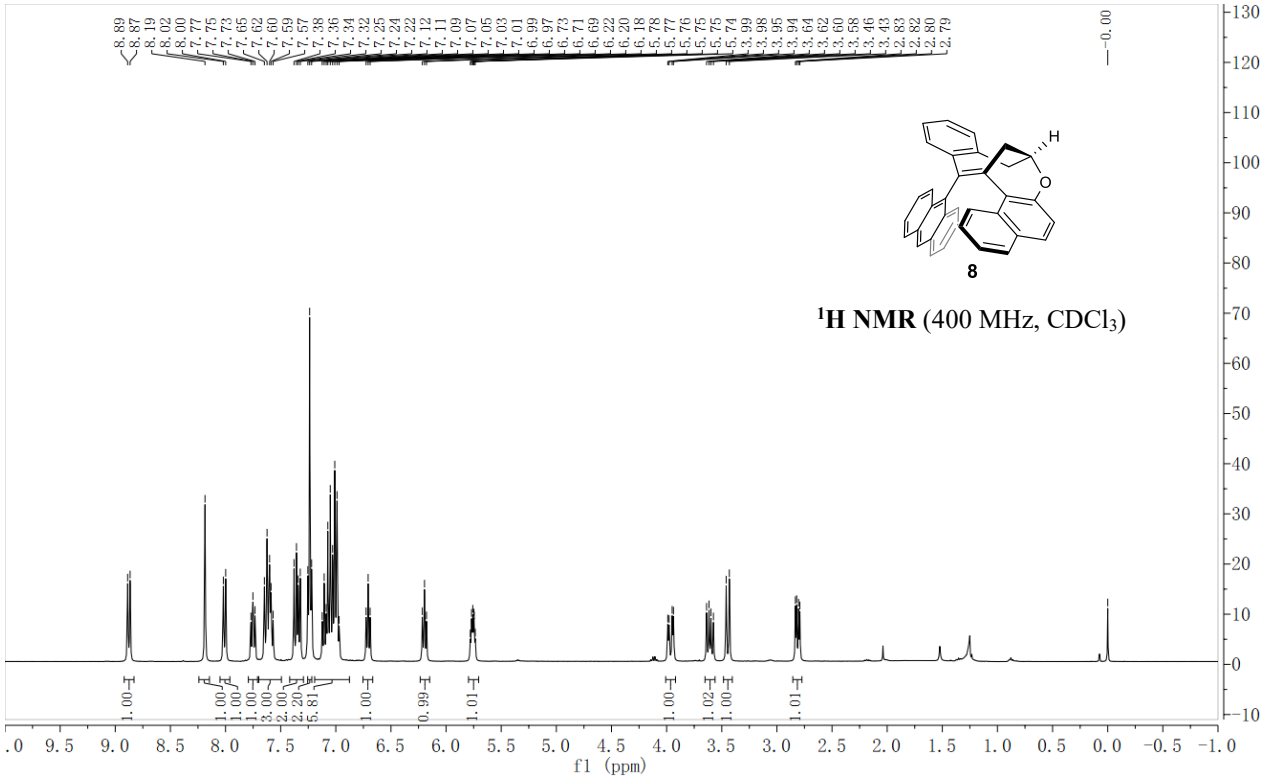
^{13}C NMR (100 MHz, $CDCl_3$)

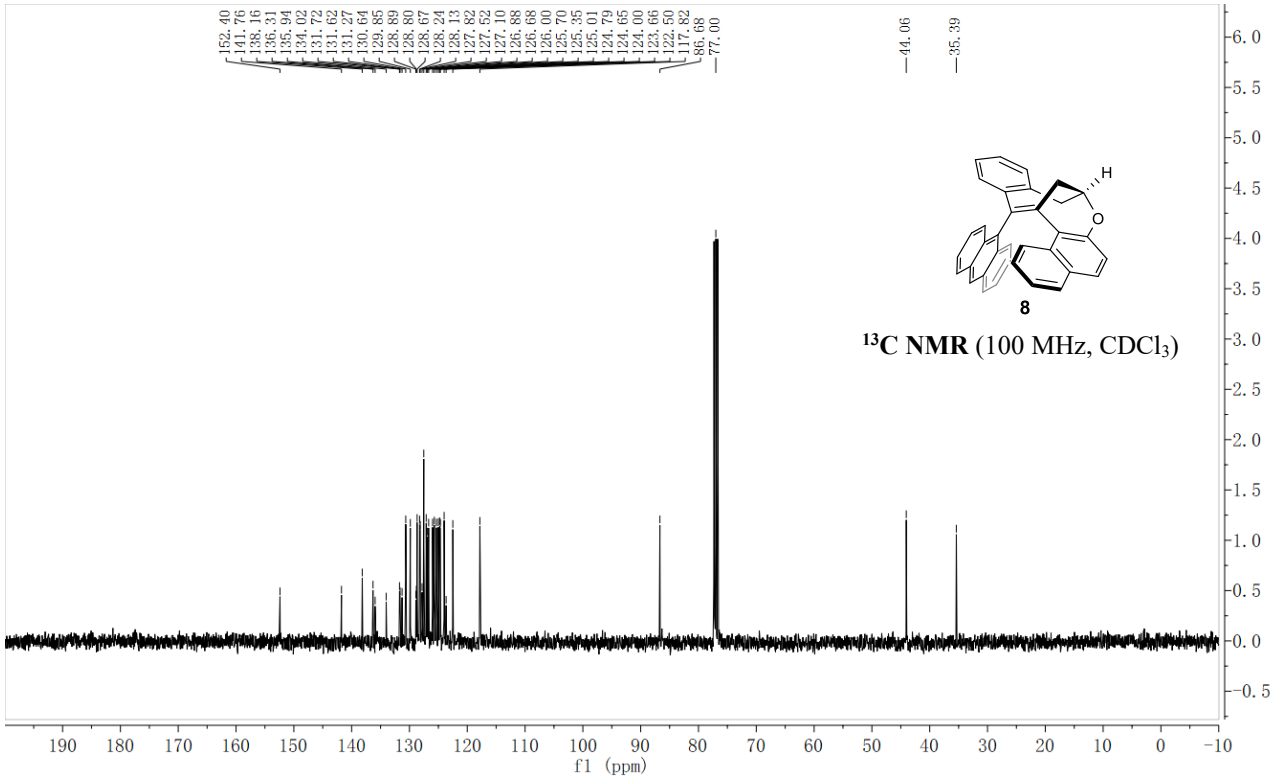


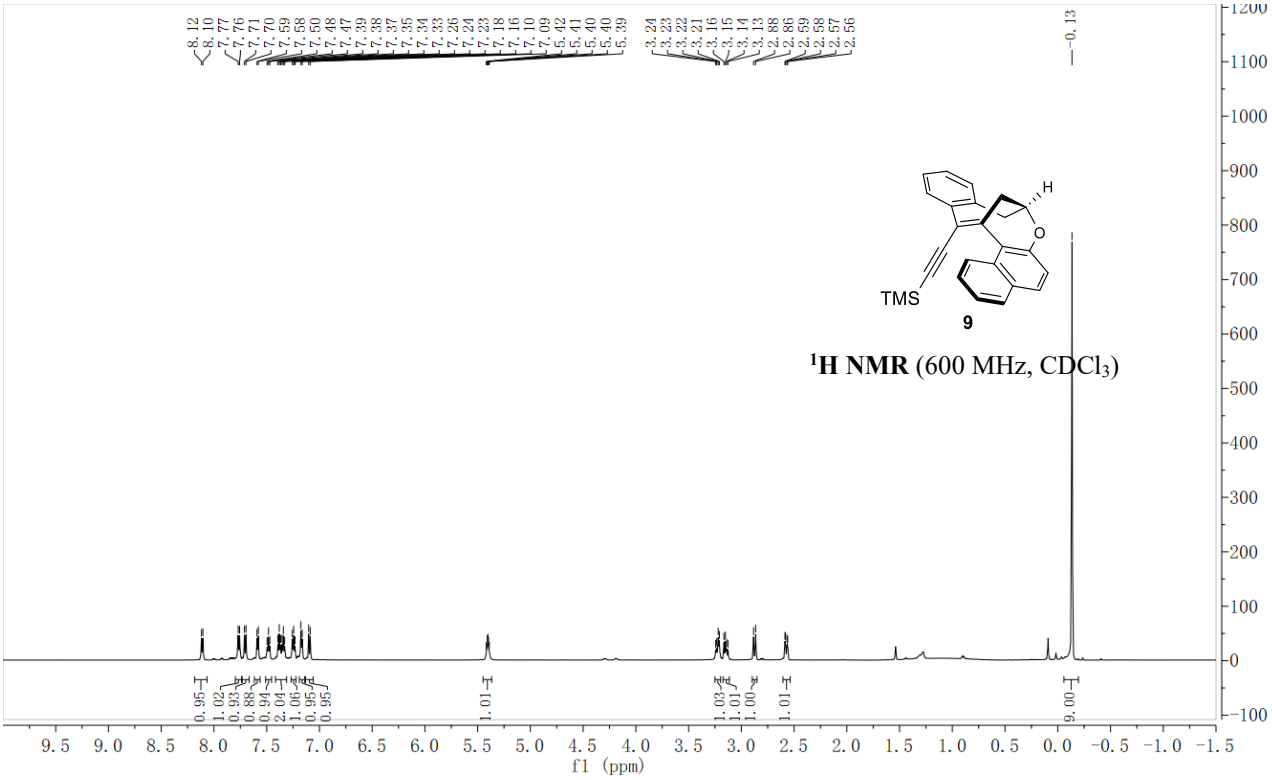
^{1}H NMR (400 MHz, $CDCl_3$)



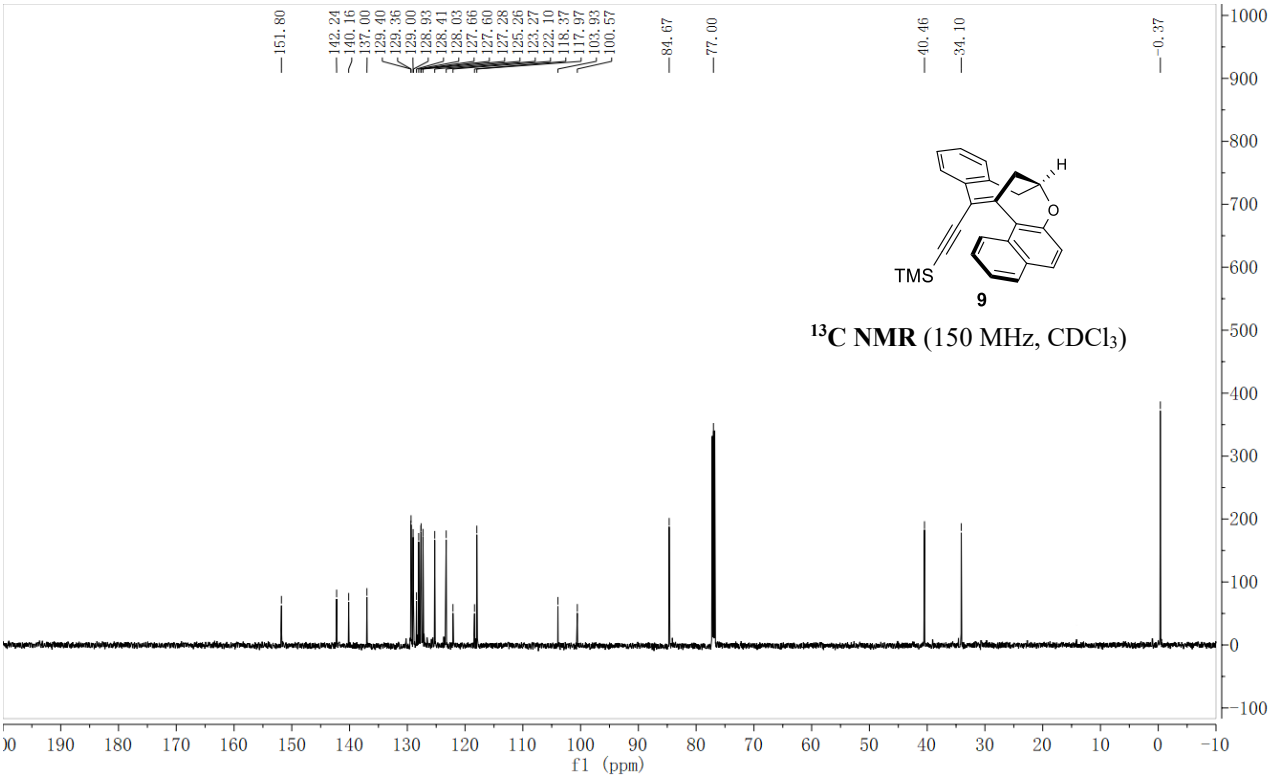
^{13}C NMR (100 MHz, $CDCl_3$)


8.89
8.87
8.19
8.02
8.00
7.77
7.75
7.73
7.65
7.62
7.60
7.59
7.57
7.38
7.36
7.34
7.32
7.25
7.24
7.22
7.12
7.11
7.09
7.07
7.05
7.03
7.01
6.99
6.97
6.73
6.71
6.69
6.22
6.20
6.18
5.78
5.77
5.76
5.75
5.75
5.74
3.99
3.98
3.95
3.94
3.64
3.62
3.60
3.58
3.46
3.43
2.83
2.82
2.80
2.79
0.00
H
O
8
1H NMR (400 MHz, CDCl3)
1.00
1.00
1.00
3.00
2.00
2.20
5.81
1.00
0.99
1.01
1.00
1.02
1.00
1.01
f1 (ppm)

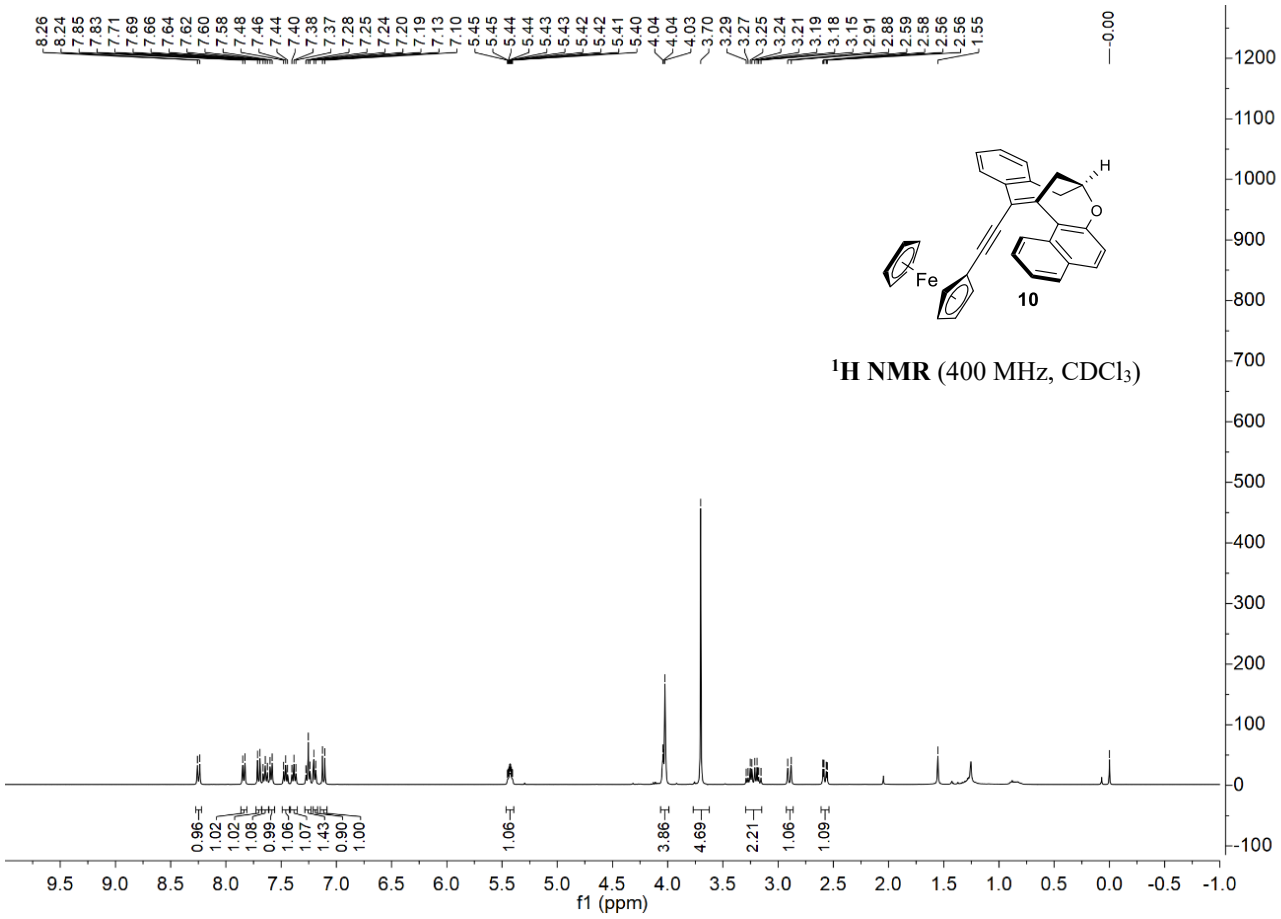

152.40
141.76
138.16
136.31
135.94
134.02
131.72
131.62
131.27
130.64
129.85
128.89
128.80
128.67
128.24
128.13
127.82
127.52
127.10
126.88
126.68
126.00
125.70
125.35
125.01
124.79
124.65
124.00
123.66
122.50
117.82
86.68
77.00
44.06
35.39
H
O
8
13C NMR (100 MHz, CDCl3)
f1 (ppm)



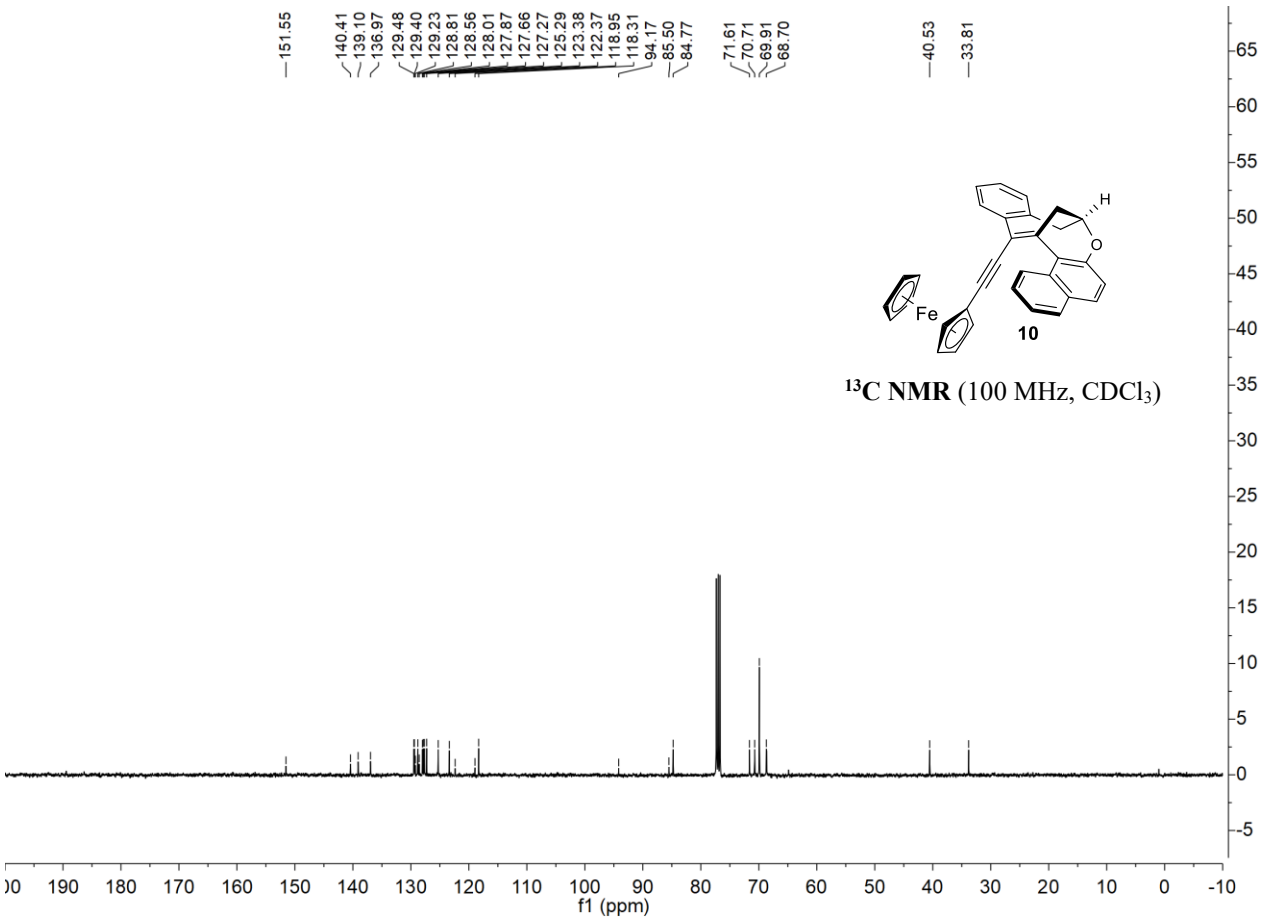
^{1}H NMR (600 MHz, $CDCl_3$)



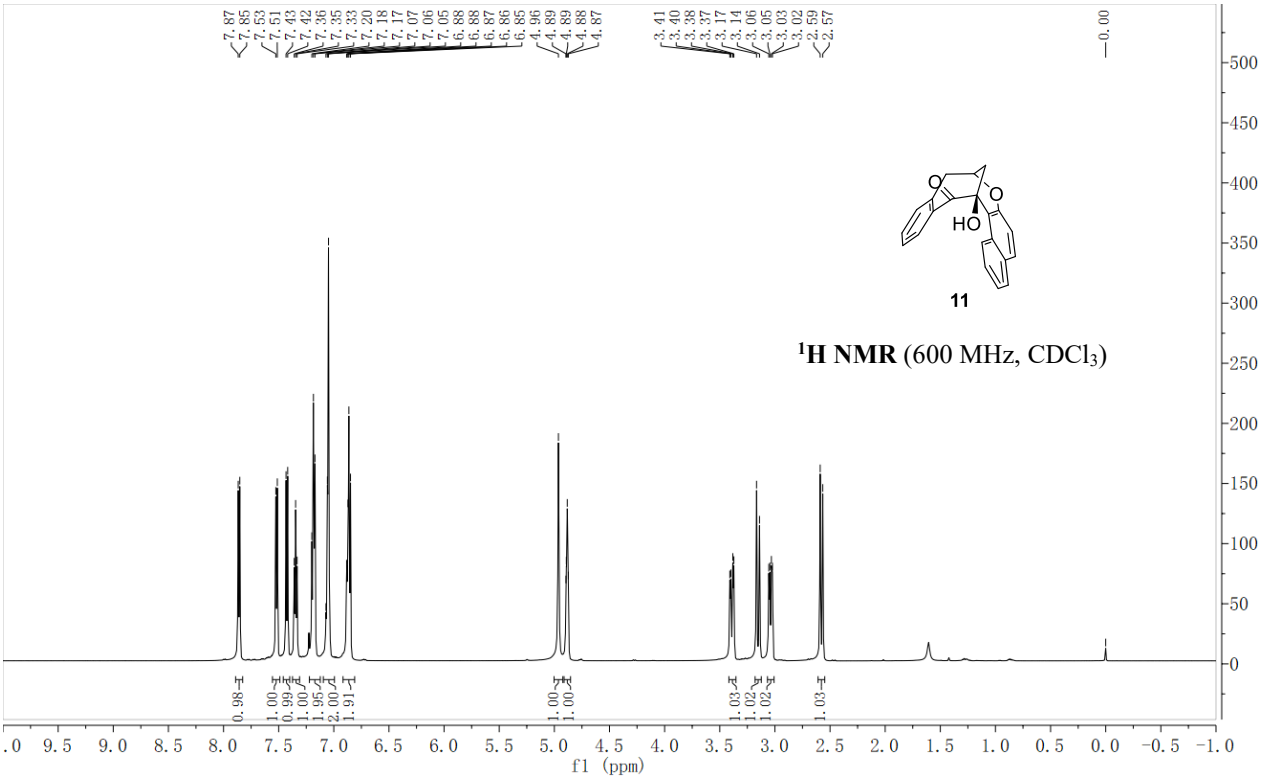
^{13}C NMR (150 MHz, $CDCl_3$)

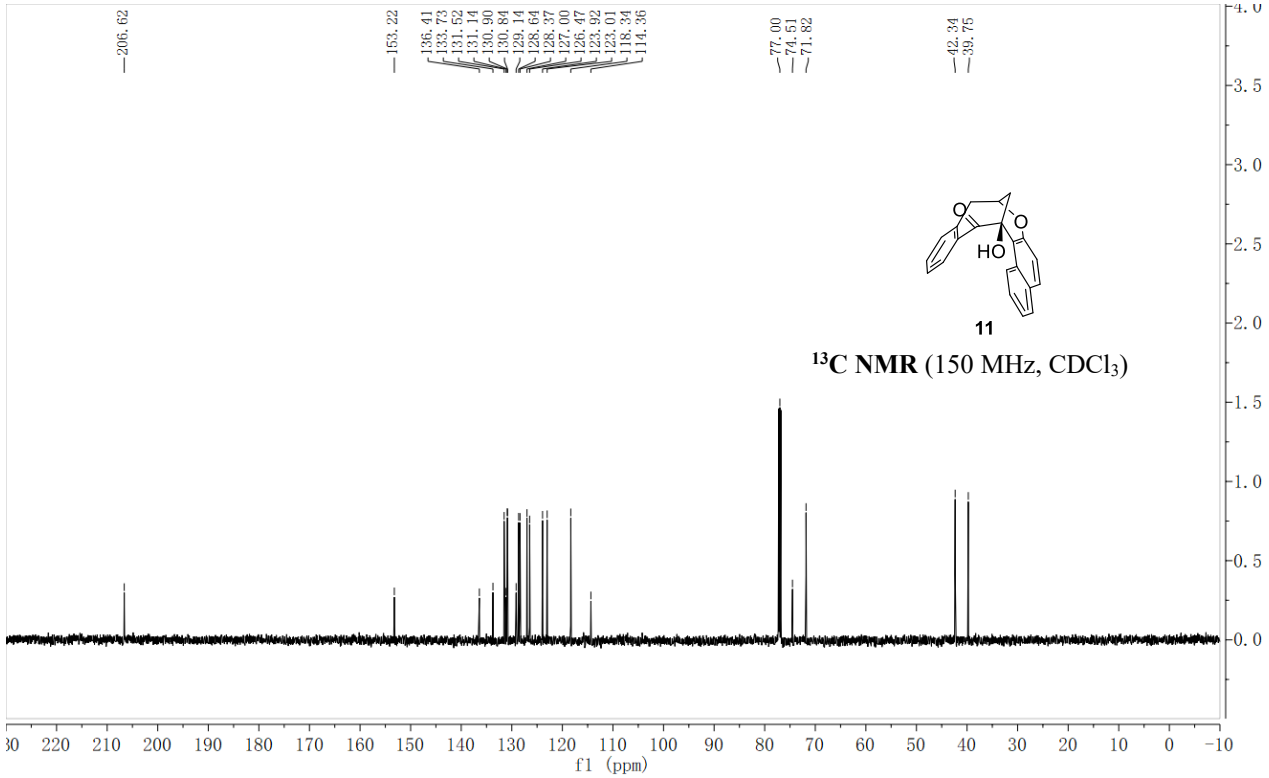


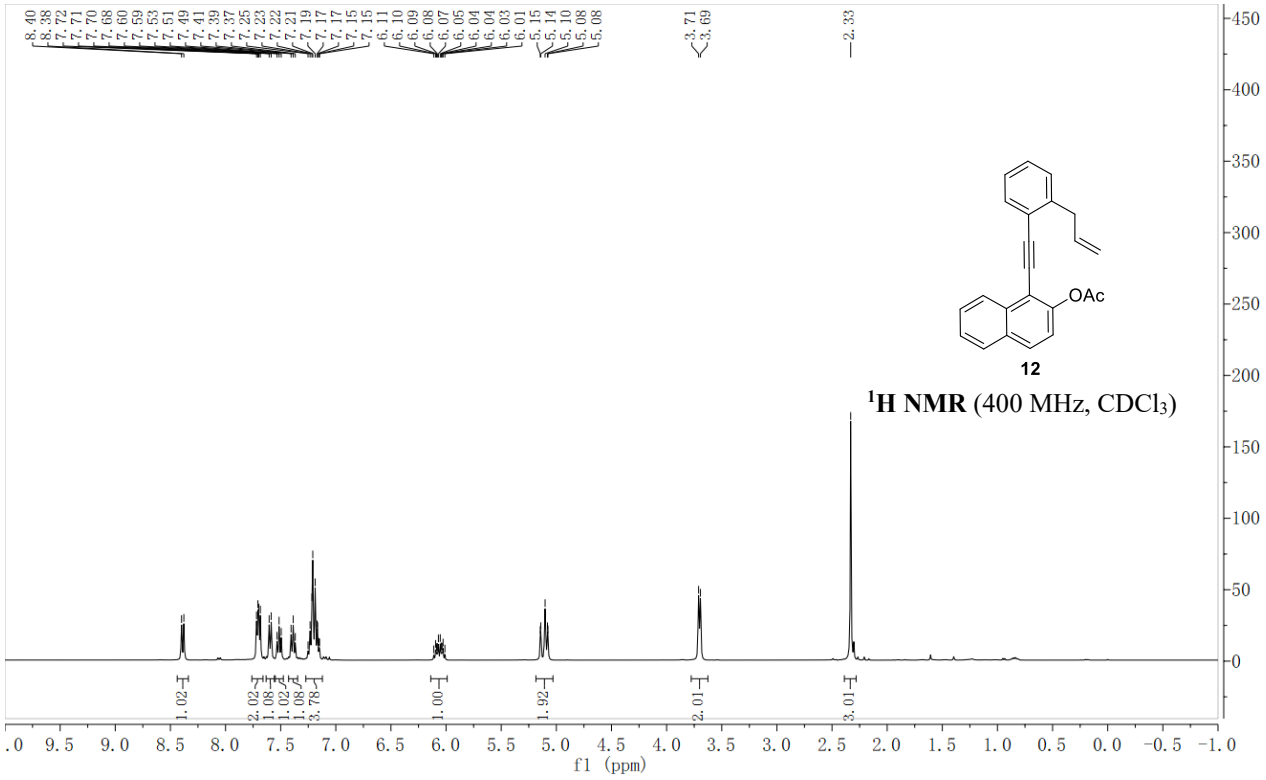
^{1}H NMR (400 MHz, $CDCl_3$)



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

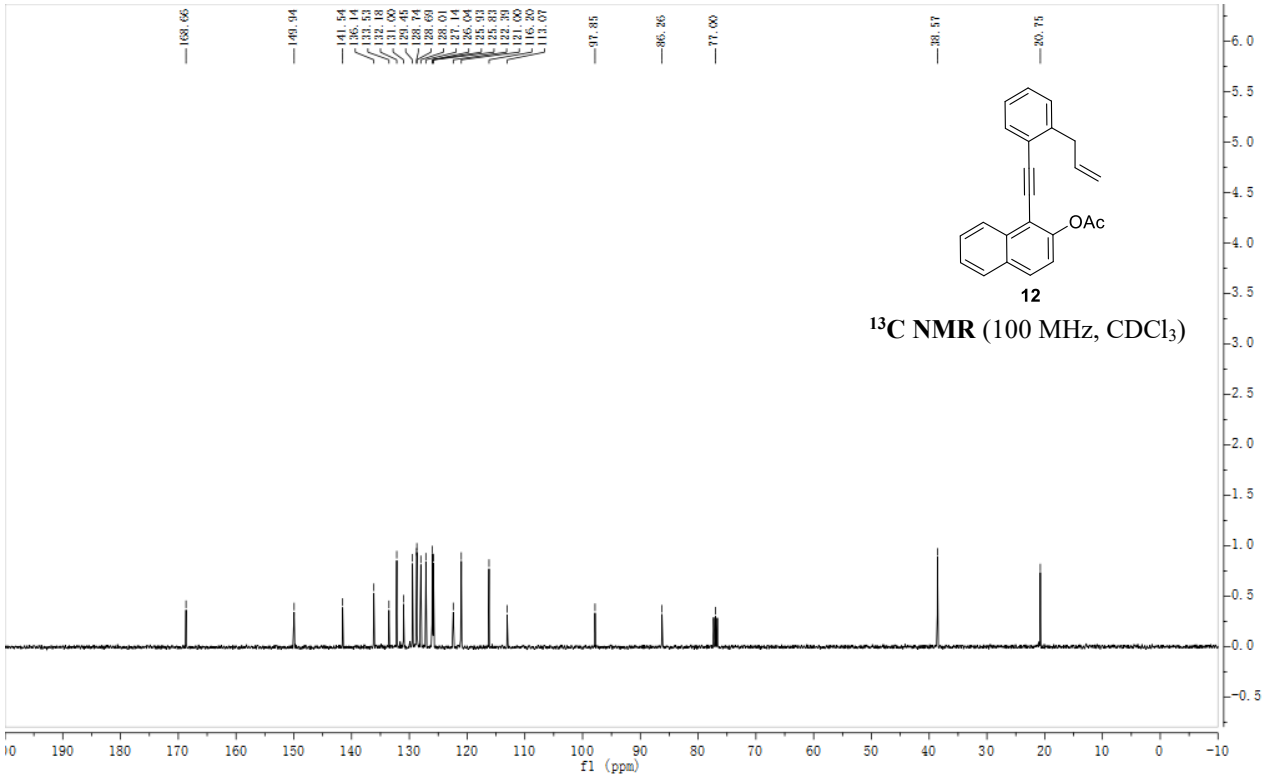

HO
11
^{1}H NMR (600 MHz, CDCl$_3$)
f1 (ppm)


HO
11
^{13}C NMR (150 MHz, CDCl$_3$)
f1 (ppm)



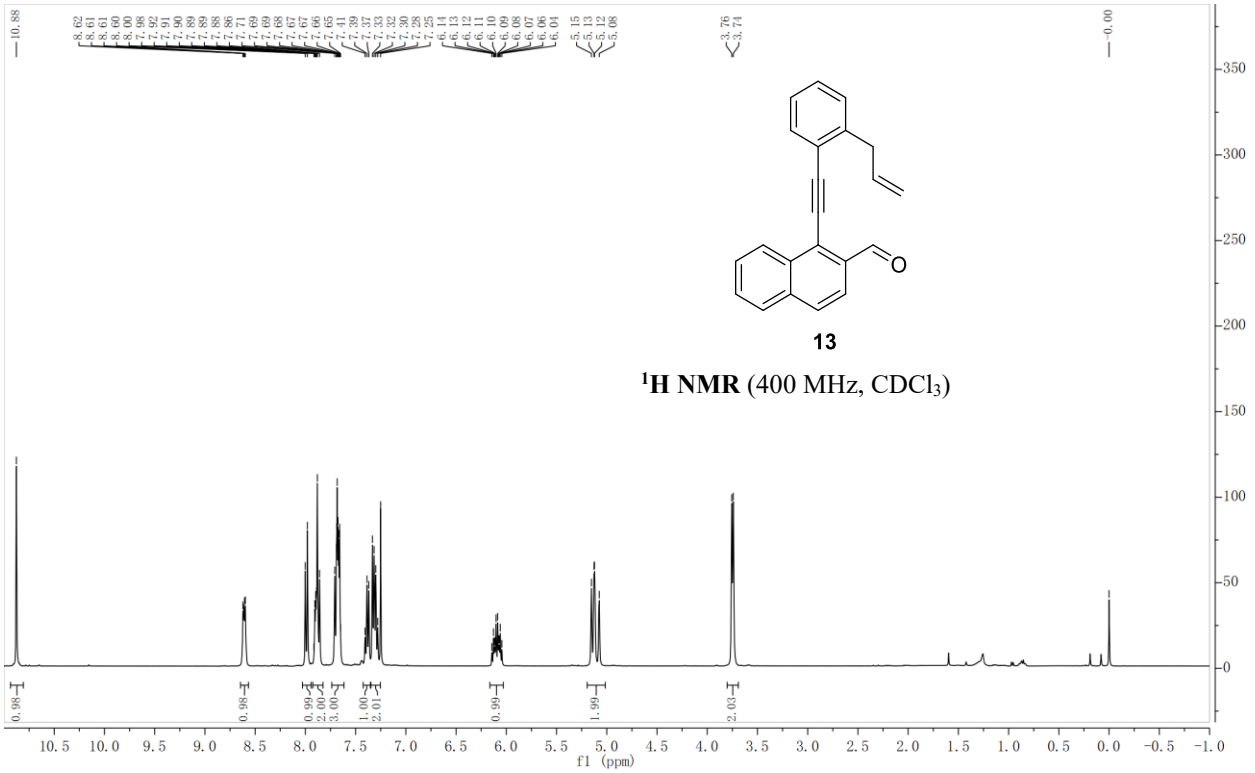
12

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

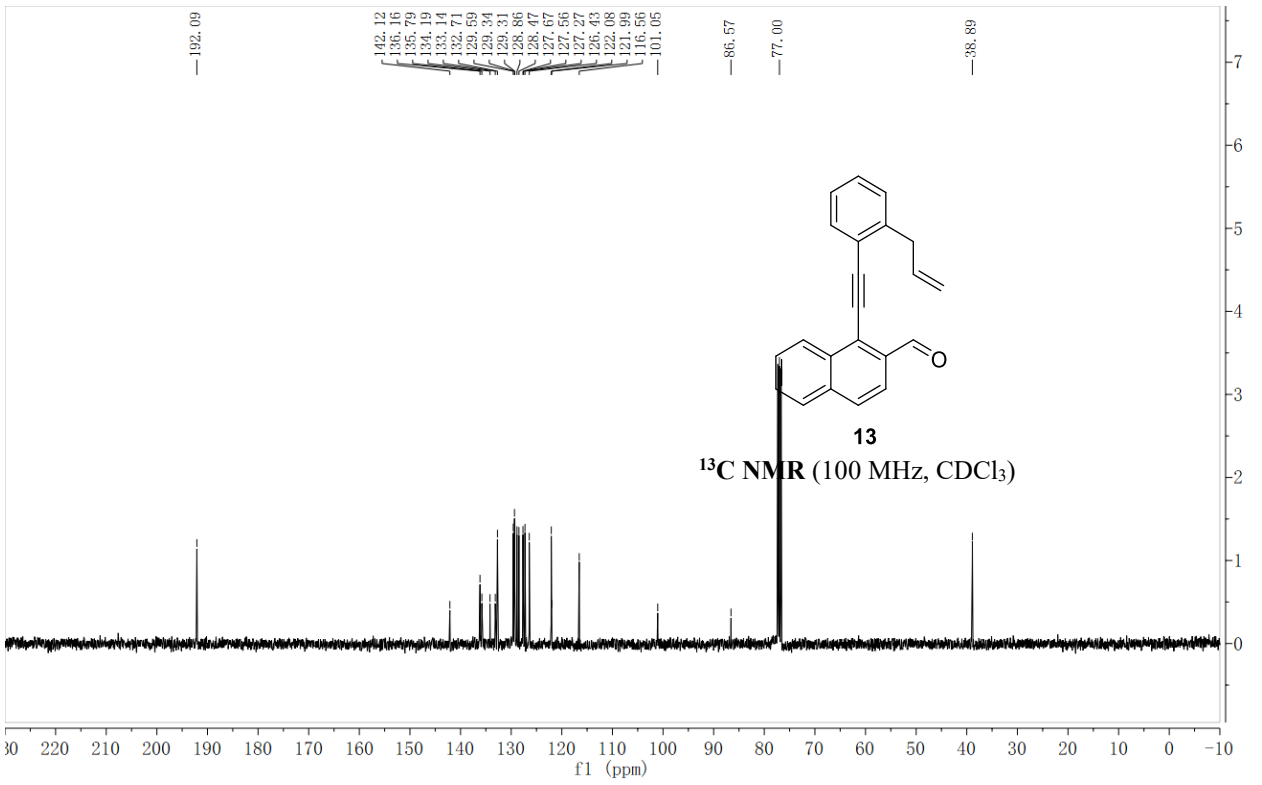


12

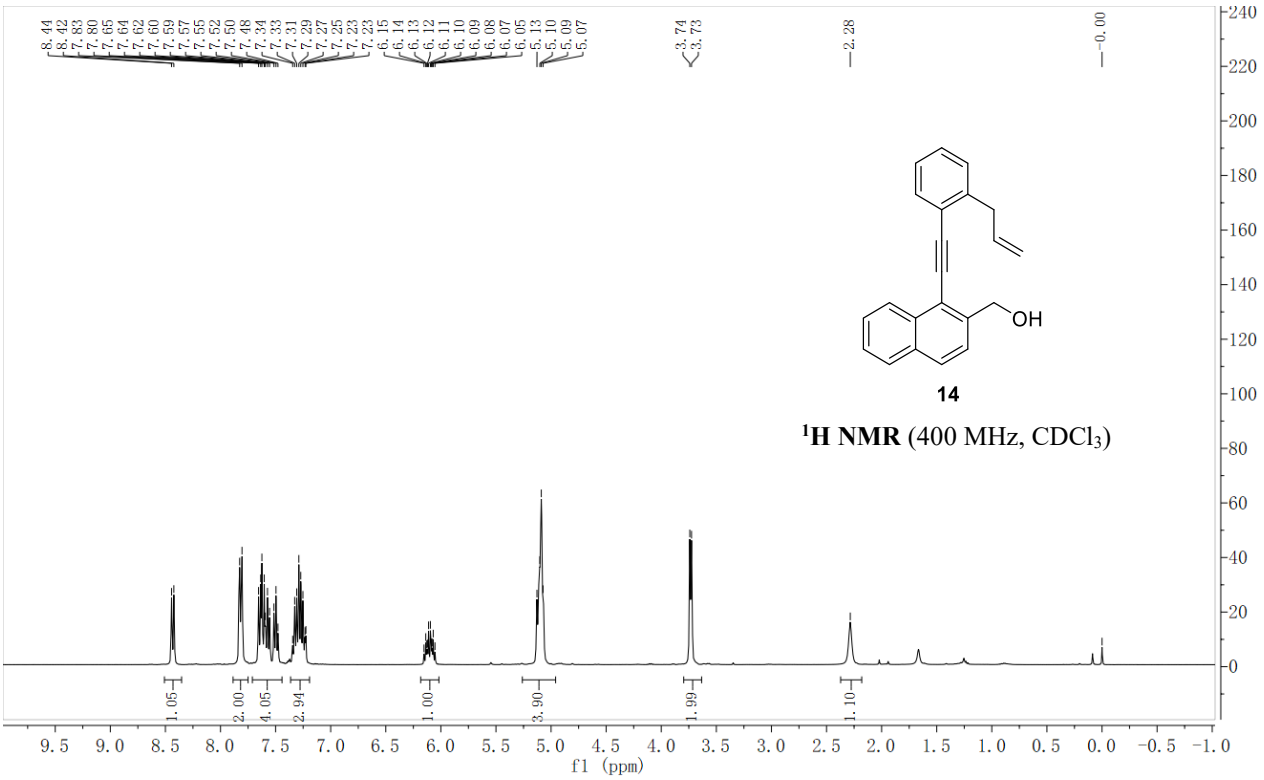
^{13}C NMR (100 MHz, $CDCl_3$)



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

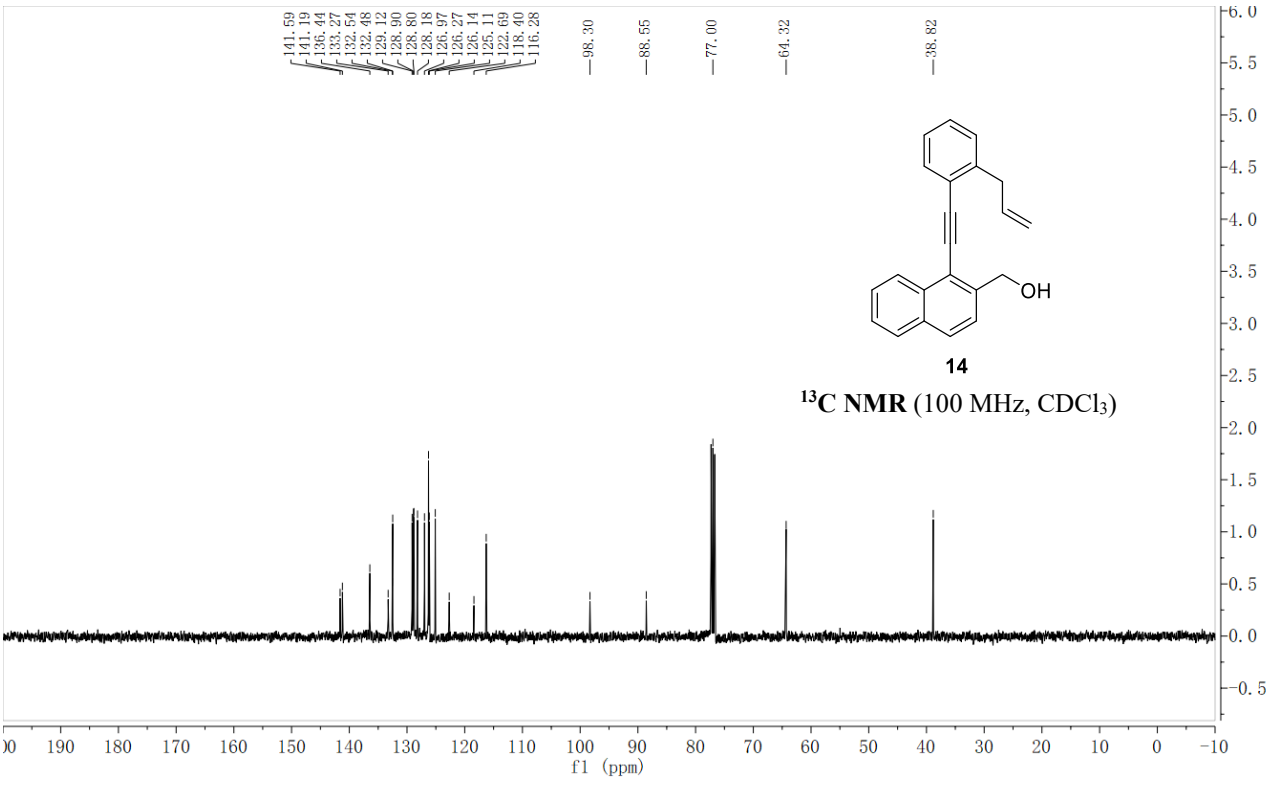


^{13}C NMR (100 MHz, $CDCl_3$)



14

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

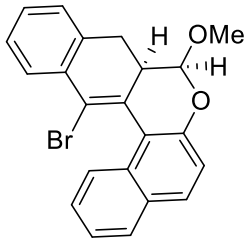


14

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

XII. X-ray crystallographic information

The authors thank Mr. Xiangnan Gong (Analytical and Testing Center of Chongqing University) for spectroscopic measurements.



2a

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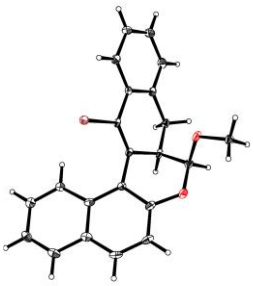


CCDC 2151481

Bond precision:	C-C = 0.0096 A	Wavelength=0.71073	
Cell:	a=28.1188(8)	b=7.6926(2)	c=15.6637(5)
alpha=90	beta=92.223(3)	gamma=90	
Temperature:	200 K		
	Calculated	Reported	
Volume	3385.61(17)	3385.61(17)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C22 H17 Br O2	2(C22 H17 Br O2)	
Sum formula	C22 H17 Br O2	C44 H34 Br2 O4	
Mr	393.26	786.53	
Dx,g cm-3	1.543	1.543	
Z	8	4	
Mu (mm-1)	2.441	2.441	
F000	1600.0	1600.0	
F000’	1598.34		
h,k,lmax	38,10,21	37,10,21	
Nref	9036	8072	
Tmin,Tmax	0.500,0.584	b 0.758,1.000	
Tmin’	0.465		

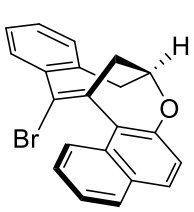
Correction method= # Reported T Limits: Tmin=0.758 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.893 Theta(max)= 29.036

R(reflections)= 0.0781(6205) wR2(reflections)=0.1771(8072)

S = 1.151 Npar= 453



3a

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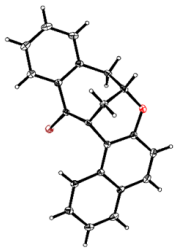


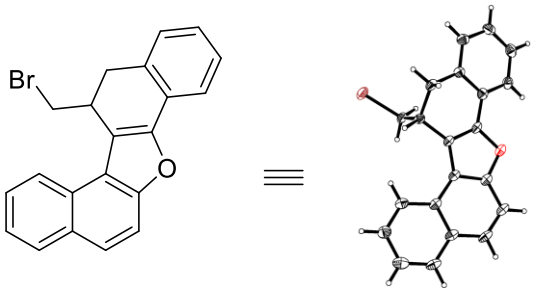
CCDC 2151484

Bond precision:	C-C = 0.0040 A	Wavelength=0.71073	
Cell:	a=15.1076(5)	b=10.0376(5)	c=20.6682(10)
alpha=90	beta=90	gamma=90	
Temperature:	293 K		
	Calculated	Reported	
Volume	3134.2(2)	3134.2(2)	
Space group	P b c a	P b c a	
Hall group	-P 2ac 2ab	-P 2ac 2ab	
Moiety formula	C21 H15 Br O	C21 H15 Br O	
Sum formula	C21 H15 Br O	C21 H15 Br O	
Mr	363.23	363.24	
Dx,g cm-3	1.540	1.540	
Z	8	8	
Mu (mm-1)	2.625	2.625	
F000	1472.0	1472.0	
F000’	1470.26		
h,k,lmax	20,13,28	20,13,27	
Nref	4202	3707	
Tmin,Tmax	0.437,0.467	0.970,1.000	
Tmin’	0.404		

Correction method= # Reported T Limits: Tmin=0.970 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 0.882	Theta(max)= 29.094
R(reflections)= 0.0391(2444)	wR2(reflections) = 0.0899(3707)
S = 1.038	Npar= 208



4a **CCDC 2151483**

Bond precision:	C-C = 0.0083 A	Wavelength=0.71073	
Cell:	a=7.8805(4)	b=11.2373(4)	c=17.8564(12)
alpha=90	beta=90	gamma=90	
Temperature:	293 K		
	Calculated	Reported	
Volume	1581.28(14)	1581.28(14)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C21 H15 Br O	C21 H15 Br O	
Sum formula	C21 H15 Br O	C21 H15 Br O	
Mr	363.23	363.24	
Dx,g cm-3	1.526	1.526	
Z	4	4	
Mu (mm-1)	2.601	2.601	
F000	736.0	736.0	
F000’	735.13		
h,k,lmax	10,15,24	10,15,22	
Nref	4242[2425]	3598	
Tmin,Tmax	0.358,0.424	0.770,1.000	
Tmin’	0.331		

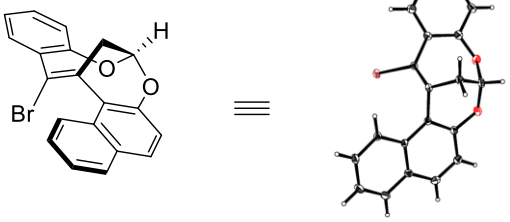
Correction method= # Reported T Limits: Tmin=0.770 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.48/0.85 Theta(max)= 29.096

R(reflections)= 0.0487(2126) wR2(reflections) = 0.1007(3598)

S = 0.981 Npar= 208



3o (3a-3) ≡ **CCDC 2151485**

Bond precision:	C-C = 0.0076 A	Wavelength=0.71073
Cell:	a=8.0085(3)	b=8.9848(6) c=21.0224(11)
alpha=90	beta=90	gamma=90
Temperature:	295 K	
	Calculated	Reported
Volume	1512.66(14)	1512.66(15)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C20 H13 Br O2	C20 H13 Br O2
Sum formula	C20 H13 Br O2	C20 H13 Br O2
Mr	365.20	365.21
Dx,g cm-3	1.604	1.604
Z	4	4
Mu (mm-1)	2.725	2.725
F000	736.0	736.0
F000’	735.16	
h,k,lmax	10,12,28	10,11,28
Nref	4032[2317]	3463
Tmin,Tmax	0.435,0.596	0.776,1.000
Tmin’	0.402	

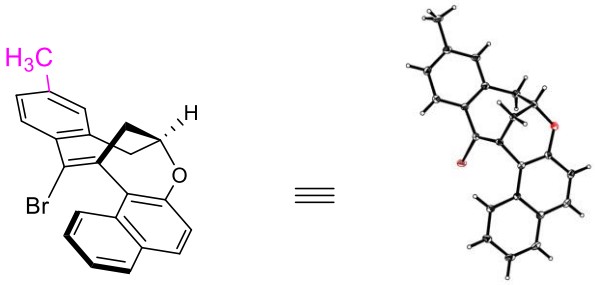
Correction method= # Reported T Limits: Tmin=0.776 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.49/0.86 Theta(max)= 29.044

R(reflections)= 0.0439(2759) wR2(reflections) = 0.0823(3463)

S = 1.035 Npar= 208



3b **CCDC 2151486**

Bond precision:	C-C = 0.0063 A	Wavelength=0.71073	
Cell:	a=5.5950(3)	b=10.2307(4)	c=29.7158(12)
alpha=90	beta=90	gamma=90	
Temperature:	293 K		
	Calculated	Reported	
Volume	1700.96(13)	1700.96(13)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C22 H17 Br O	C22 H17 Br O	
Sum formula	C22 H17 Br O	C22 H17 Br O	
Mr	377.26	377.26	
Dx,g cm-3	1.473	1.473	
Z	4	4	
Mu (mm-1)	2.421	2.421	
F000	768.0	768.0	
F000’	767.13		
h,k,lmax	7,13,40	7,13,37	
Nref	4531[2634]	3859	
Tmin,Tmax	0.551,0.559	0.831,1.000	
Tmin’	0.541		

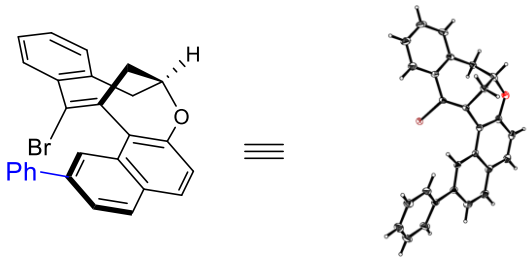
Correction method= # Reported T Limits: Tmin=0.831 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.47/0.85 Theta(max)= 29.010

R(reflections)= 0.0436(2981) wR2(reflections) = 0.0772(3859)

S = 1.065 Npar= 218



3i **CCDC 2151487**

Bond precision:	C-C = 0.0082 A		Wavelength=0.71073
Cell:	a=8.7121(3)	b=8.8820(4)	c=13.2952(6)
alpha=90	beta=98.023(4)	gamma=90	
Temperature:	293 K		
	Calculated		Reported
Volume	1018.73(7)		1018.72(7)
Space group	P 21		P 1 21 1
Hall group	P 2yb		P 2yb
Moiety formula	C27 H19 Br O		C27 H19 Br O
Sum formula	C27 H19 Br O		C27 H19 Br O
Mr	439.32		439.33
Dx,g cm-3	1.432		1.432
Z	2		2
Mu (mm-1)	2.033		2.033
F000	448.0		448.0
F000’	447.59		
h,k,lmax	11,12,18		11,12,17
Nref	5421[2878]		4625
Tmin,Tmax	0.443,0.462		0.981,1.000
Tmin’	0.409		

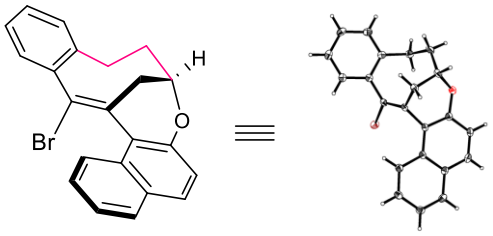
Correction method= # Reported T Limits: Tmin=0.981 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.61/0.85 Theta(max)= 29.047

R(reflections)= 0.0420(3735) wR2(reflections) = 0.0842(4625)

S = 1.053 Npar= 262

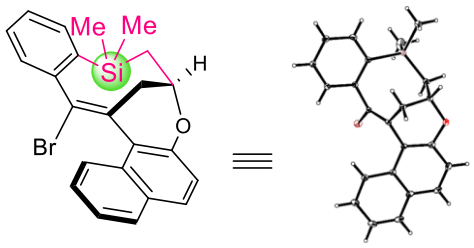


3s **CCDC 2151488**

Bond precision: C-C = 0.0070 A Wavelength=0.71073
Cell: a=7.6693(2) b=13.0042(5) c=17.0867(8)
alpha=90 beta=90 gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1704.11(11)	1704.11(11)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C22 H17 Br O	C22 H17 Br O
Sum formula	C22 H17 Br O	C22 H17 Br O
Mr	377.26	377.26
Dx,g cm-3	1.470	1.470
Z	4	4
Mu (mm-1)	2.417	2.417
F000	768.0	768.0
F000’	767.13	
h,k,lmax	10,17,23	10,17,23
Nref	4526[2582]	3886
Tmin,Tmax	0.386,0.440	0.824,1.000
Tmin’	0.357	

Correction method= # Reported T Limits: Tmin=0.824 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 1.51/0.86 Theta(max)= 28.983
R(reflections)= 0.0458(2775) wR2(reflections) = 0.0841(3886)
S = 1.040 Npar= 217



3w **CCDC 2151489**

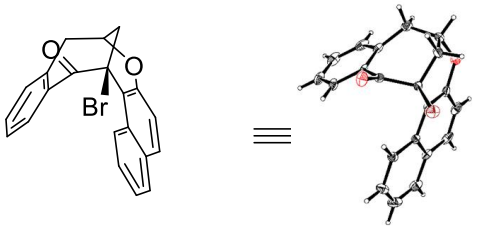
Bond precision:	C-C = 0.0058 A		Wavelength=0.71073
Cell:	a=8.6383(3)	b=12.6159(5)	c=17.6123(7)
alpha=90	beta=90	gamma=90	
Temperature:	293 K		

	Calculated	Reported
Volume	1919.39(13)	1919.39(13)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C23 H21 Br O Si	C23 H21 Br O Si
Sum formula	C23 H21 Br O Si	C23 H21 Br O Si
Mr	421.39	421.40
Dx,g cm-3	1.458	1.458
Z	4	4
Mu (mm-1)	2.213	2.213
F000	864.0	864.0
F000’	863.46	
h,k,lmax	11,17,24	11,16,23
Nref	5099[2887]	4349
Tmin,Tmax	0.449,0.482	0.806,1.000
Tmin’	0.415	

Correction method= # Reported T Limits: Tmin=0.806 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.51/0.85	Theta(max)= 28.995
R(reflections)= 0.0398(3532)	wR2(reflections) = 0.0805(4349)
S = 1.039	Npar= 237



6 **CCDC 2151482**

Bond precision:	C-C = 0.0104 A		Wavelength=0.71073
Cell:	a=8.8697(4)	b=22.6968(7)	c=8.9630(5)
alpha=90	beta=114.336(6)	gamma=90	
Temperature:	293 K		
	Calculated	Reported	
Volume	1644.05(15)	1644.05(15)	
Space group	P 21	P 1 21 1	
Hall group	P 2yb	P 2yb	
Moiety formula	C21 H15 Br O2	C21 H15 Br O2	
Sum formula	C21 H15 Br O2	C21 H15 Br O2	
Mr	379.23	379.24	
Dx,g cm-3	1.532	1.532	
Z	4	4	
Mu (mm-1)	2.510	2.510	
F000	768.0	768.0	
F000’	767.16		
h,k,lmax	12,30,12	12,30,12	
Nref	8758[4487]	7480	
Tmin,Tmax	0.526,0.547	0.664,1.000	

Tmin’ 0.516

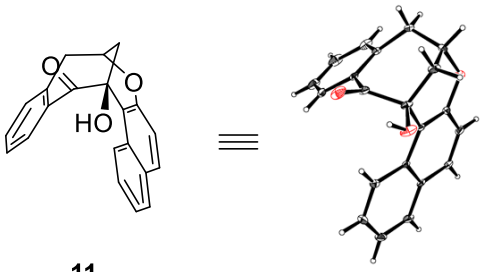
Correction method= # Reported T Limits: Tmin=0.664 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.67/0.85 Theta(max)= 29.012

R(reflections)= 0.0472(5045) wR2(reflections) = 0.0867(7480)

S = 1.010 Npar= 433



11 **CCDC 2151449**

Bond precision:	C-C = 0.0041 A		Wavelength=1.54184
Cell:	a=7.48375(11)	b=23.7768(5)	c=8.95801(13)
alpha=90	beta=94.0554(14)	gamma=90	
Temperature:	180 K		
	Calculated	Reported	
Volume	1589.99(5)	1589.99(5)	
Space group	P 21	P 1 21 1	
Hall group	P 2yb	P 2yb	
Moiety formula	C21 H16 O3 [+ solvent]	C21 H16 O3	
Sum formula	C21 H16 O3 [+ solvent]	C21 H16 O3	
Mr	316.34	316.34	
Dx,g cm-3	1.321	1.321	
Z	4	4	
Mu (mm-1)	0.707	0.707	
F000	664.0	664.0	
F000’	666.03		
h,k,lmax	9,29,11	9,28,10	
Nref	6209[3184]	5126	
Tmin,Tmax	0.775,0.770	0.334,1.000	
Tmin’	0.703		

Correction method= # Reported T Limits: Tmin=0.334 Tmax=1.000

AbsCorr = MULTI-SCAN

Data completeness= 1.61/0.83	Theta(max)= 71.700
R(reflections)= 0.0354(5051)	wR2(reflections) = 0.0924(5126)
S = 1.057	Npar= 435

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