Supporting Information for

Organocatalytic Cascade Reactions to Multi-functionalized Chiral Cyclic Ethers through Vinylidene *ortho*-Quinone Methides

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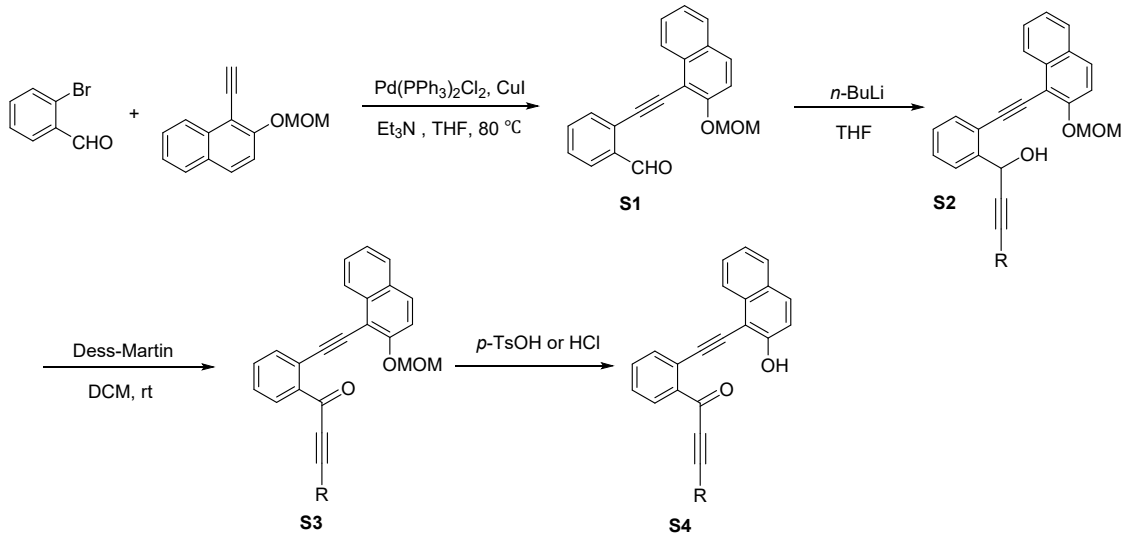
I. General information

^{1}H and ^{13}C NMR spectra were recorded on Agilent 400MR DD2 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and tetramethylsilane or the residual solvent peak was used as an internal reference: ^{1}H (tetramethylsilane δ 0.00 ppm, toluene δ 2.08 ppm), ^{13}C (chloroform δ 77.00 ppm, acetone δ 29.70 ppm, toluene δ 137.48 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. Enantiomeric excesses (*ee*) were determined by HPLC analysis on Hitachi Chromaster using DAICEL CHIRALCEL AD-H, 4.6 mm *Φ* × 250 mmL, DAICEL CHIRALCEL OD-H, 4.6 mm *Φ* × 250 mmL, DAICEL CHIRALCEL IA-H, 4.6 mm *Φ* × 250 mmL, DAICEL CHIRALCEL IB-H, 4.6 mm *Φ* × 250 mmL and DAICEL CHIRALCEL IC-H, 4.6 mm *Φ* × 250 mmL. High resolution mass spectra (HRMS) were performed on Bruker Solarix 7.0 T. X-ray crystallography analysis of single crystal was performed on an Agilent SuperNova-CCD X-Ray diffractometer. Optical rotations were measured on a Rudolph Autopol I polarimeter and are reported as follows: $[\alpha]_D^{20}$ (c in g per 100 mL solvent). Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification.

II. General procedure for the synthesis of substrate.

Method A:



Step1：1-ethynyl-2-(methoxymethoxy)naphthalene (1.0 eq. 10 mmol) was dropwised to a solution of the 2-bromobenzaldehyde (1.0 eq. 10 mmol), $PdCl_2(PPh_3)_2$ (0.02 eq. 0.2mmol), CuI (0.04 eq. 0.4 mmol), and Et_3N (20 mL) in THF (20 mL) at 80 ℃ under N_2. The mixture was stirred for 2 h. Then the mixture was filtered through a pad of celite. Removal of the solvent under reduced pressure. The crude product was purified by column chromatography on silica gel (PE: EA = 10:1) to afford **S1**.

Step2：An oven-dried 100 mL three-neck round-bottom flask quipped with a 100 mL pressure-equalizing addition funnel, N_2 gas inlet adaptor, septum, and magnetic stir bar was charged with THF (20 mL) and corresponding alkynes (1.1 eq. 11 mmol). The solution was cooled to -78 °C under N_2 and 2.5 M *n*-BuLi in hexane (1.1 eq. 11 mmol,) was added dropwise over 30 min. After 2 h stirring at -78 °C, a solution of benzaldehyde (1.0 eq. 10 mmol) in 20 mL THF was added dropwise over 35 min to the cloudy white reaction mixture at -78 °C. After stirring for 2 h at -78 °C, the homogeneous reaction

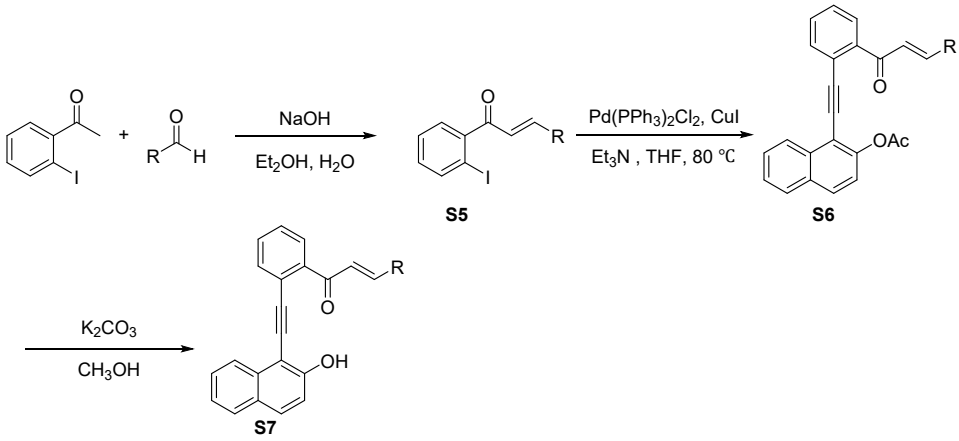
mixture was quenched by dropwise addition of saturated NH_4Cl in methanol (20 mL) to the reaction mixture at -78 °C over 15 min. After stirring an additional 5 min at -78 °C, the cooling bath was removed, and the reaction mixture was allowed to warm to room temperature (ca. 1 h). Once at room temperature, diethyl ether (20 mL) and water (20 mL) were added to the reaction mixture. The mixture was shaken, and the layers were separated. The aqueous layer was extracted with diethyl ether (2 × 10 mL), and the combined organic layers were washed with saturated NaCl (aq) (2 × 10 mL) and water (2 × 25 mL), dried over anhydrous MgSO4, and filtered. The solvent was removed in vacuo to afford a pale yellow liquid. The crude product was purified by column chromatography on silica gel (SiO_2, PE: EA = 10:1) to afford **S2**

Step3： Dissolve the propargylic alcohol (10 mmol) in DCM (50 mL) and cool to 0 °C. Add Dess-Martin periodinane (1.1 eq. 11 mmol) and allow the mixture to warm to room temperature. Monitor the reaction mixture by TLC and add aq. NaOH (1.1 equiv, 1M solution). Separate the layers and extract the aqueous layer with DCM (3 x). Combine the organic layers and dry over Na_2SO_4. Evaporate the solvent. Purify the crude product by flash column chromatography (SiO_2, PE: EA = 10:1) to obtain the product **S3**.

Step4： Dissolve **S3** (1.0 eq. 10 mmol) in tetrahydrofuran (50 mL), then add *p*-toluenesulfonic acid (2.0 eq. 20 mmol) or Concentrated hydrochloric acid (HCl). Stir the reaction mixture at room temperature for 2 hours. Quench the reaction mixture with brine (10 mL), extract with diethyl ether (3 x 10 mL). Combine the organic portions and dry over anhydrous MgSO4. Remove the solvents in vacuo and purify the residue by flash chromatography on silica gel (SiO_2, PE: EA = 10:1) to obtain **S4** as yellow

amorphous solid.

Method B:

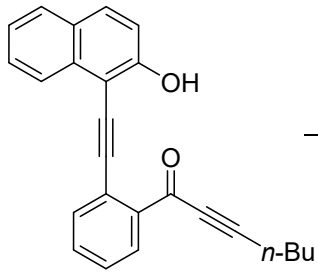


Step1： Cool a solution of NaOH (731 mg, 18.3 mmol) in H_2O (20.0 mL) and Et_2OH (20.0 mL) to 0 °C. Introduce 1-(2-iodophenyl)ethan-1-one (3.00 g) and benzaldehyde (1.20 mL, 12.2 mmol) slowly to the mixture. Allow the reaction mixture to warm to room temperature overnight. After 12 hours, dilute the reaction mixture with Et_2O. Separate the organic phase. Concentrate the organic layer in vacuo. Purify the residue by column chromatography (SiO_2, PE: DCM = 10:1) to obtain the product **S5** as yellow oil.

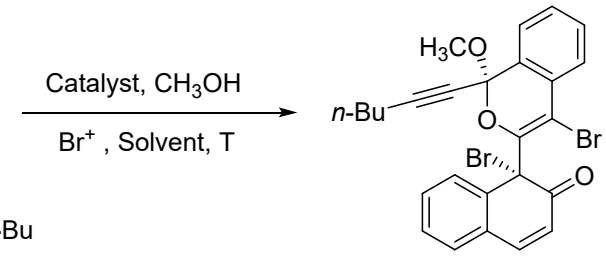
Step2： Ester-protected alkyne (1.0 eq. 10 mmol) was dropwised to a solution of the 2-bromobenzaldehyde (1.0 eq. 10 mmol), $Pd(PPh_3)_2Cl_2$ (0.02 eq. 0.2mmol), CuI (0.04 eq. 0.4 mmol), and Et_3N (20 mL) in THF (20 mL) at 80 ℃ under N_2. The mixture was stirred for 1 h. Then the mixture was filtered through a pad of celite. Removal of solvent under reduced pressure. The crude product was purified by column chromatography on silica gel (PE: EA = 10:1) to afford **S6** as yellow solid.

Step3： To a solution of the acetate (1.0 eq. 10 mmol) in MeOH at 0 °C was added anhydrous K_2CO_3 (1.1 eq. 11 mmol). After the solution was stirred for 0.5 h, the reaction was quenched with 1 M HCl and extracted with CH_2Cl_2. The organic layer was washed with brine and dried over Na_2SO_4, followed by filtration and concentration. The residue was chromatographed (SiO_2, PE: EA = 10:1) to yield **S7** as yellow solid.

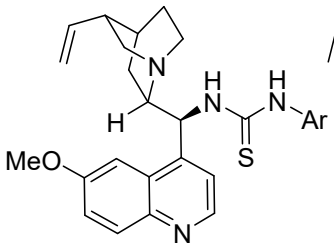
III. Optimization of the reaction conditions



1a

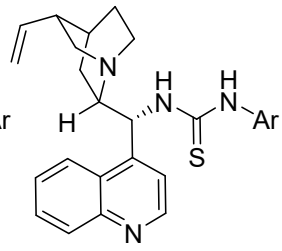


2a

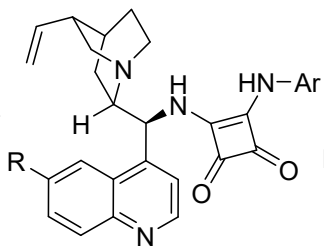


A

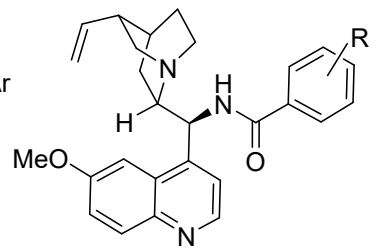
Ar=3,5-$(CF_3)_2C_6H_3$



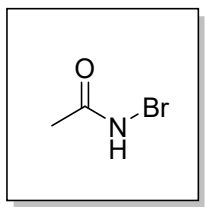
B



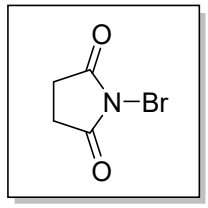
C, R=OMe
D, R=OH



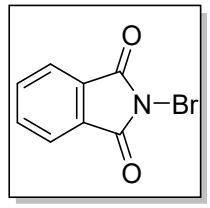
E, R=4-F **F**, R=4-Cl
G, R=4-CF_3 **H**, R=3,5-$(CF_3)_2$



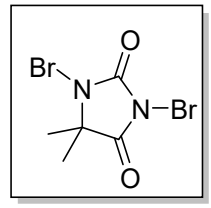
NBA



NBS



NBP

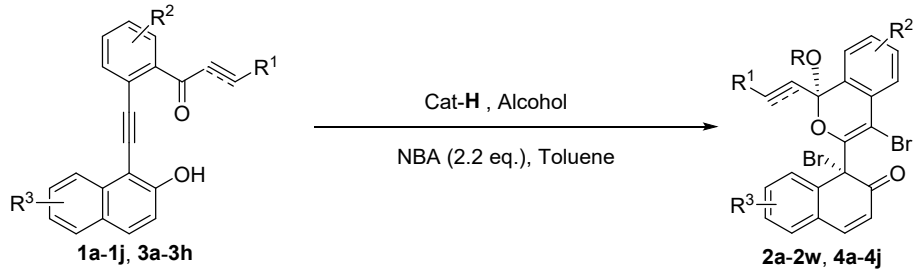


DBDMH

Entry	Catalyst	Solvent	*T* (°C)	Br^+	Yield (%)[a]	*ee* (%)[b]	d.r.[c]
1	**A**	toluene	rt.	NBA	80	37	>20:1
2	**B**	toluene	rt.	NBA	82	-25	>20:1
3	**C**	toluene	rt.	NBA	72	59	>20:1
4	**D**	toluene	rt.	NBA	65	7	>20:1
5	**E**	toluene	rt.	NBA	78	74	>20:1
6	**F**	toluene	rt.	NBA	79	77	>20:1
7	**G**	toluene	rt.	NBA	78	74	>20:1
8	**H**	toluene	rt.	NBA	88	91	>20:1
9	**H**	*o*-xylene	rt.	NBA	86	90	>20:1
10	**H**	*p*-xylene	rt.	NBA	89	84	>20:1
11	**H**	*m*-xylene	rt.	NBA	87	90	>20:1
12	**H**	mesitylene	rt.	NBA	84	90	>20:1
13	**H**	DCE	rt.	NBA	70	70	>20:1
14	**H**	DCM	rt.	NBA	68	74	>20:1
15	**H**	$CHCl_3$	rt.	NBA	72	79	>20:1
16	**H**	toluene	0	NBA	85	91	>20:1
17	**H**	toluene	-20	NBA	76	89	>20:1
18	**H**	toluene	-40	NBA	30	78	>20:1
19	**H**	toluene	rt.	NBS	80	5	>20:1
20	**H**	toluene	rt.	NBP	82	33	>20:1
21	**H**	toluene	rt.	DBDMH	89	65	>20:1
22[d]	**H**	toluene	rt.	NBA	81	83	>20:1
23[e]	**H**	toluene	rt.	NBA	89	90	>20:1

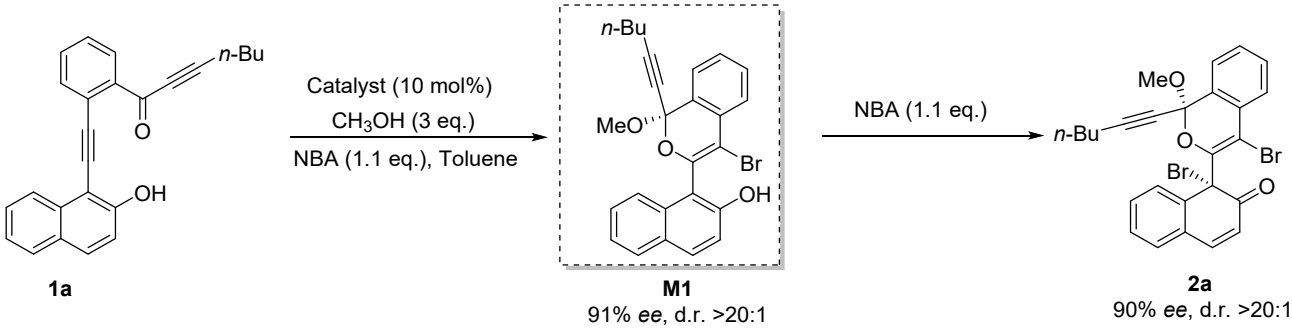
Reaction conditions: **1a** (0.05 mmol, 1.0 eq.), catalyst (10 mol%) and methanol (3.0 eq.) in solvent (1.0 mL) at corresponding temperature for 5 min, then brominating reagents (1.1 mmol, 2.2 eq.) were added at corresponding temperature. After the reaction was completed, monitored by TLC (about 3 min at rt, 30 min at 0 °C, 4 h at -20 °C, and 12 h at -40 °C). [a] Isolated yield. [b] Enantiomeric excess was (*ee*) determined by HPLC. [c] Diastereomeric ratio (d.r.) was determined by HPLC. [d] Reaction in toluene (0.5 mL). [e] Reaction in toluene (2.0 mL).

IV. General procedure for the asymmetric reaction



The substrate **1** (0.1 mmol), catalyst (10 mol%) were added to a 10 mL flame-dried schlenk tube (wrapped with aluminum foil) with a magnetic stirring bar. Toluene (2 mL) and alcohols (3 eq.) were injected into the tube. NBA was poured into reaction system，after stirring for 5 min, the mixture was evaporated and purified by flash column chromatography (SiO_2, PE: EA = 10:1) to afford the product. Racemic samples were prepared with Et_3N (1.0 eq.) as the additive base.

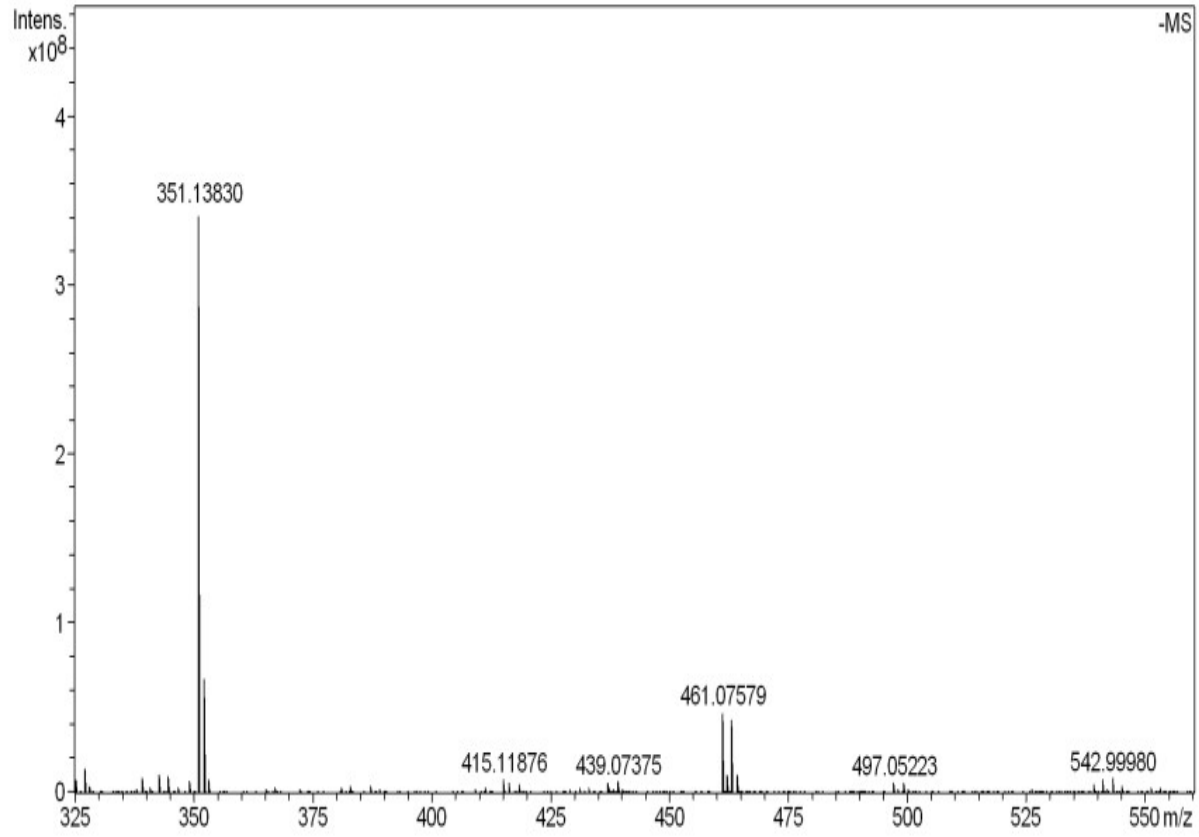
V. Mechanistic studies



The substrate **1** (0.1 mmol), catalyst (10 mol%) were added to a 10 mL flame-dried schlenk tube with a magnetic stirring bar. Toluene-d_8 (2 mL) and methanol (3 eq.) was injected into the tube at -10 ℃. NBA (2.2 eq.) was poured into reaction system, The intermediate **M1** were monitored by TLC, and detected by HRMS.

Acquisition Parameter

Polarity	Negative	n/a	n/a	No. of Laser Shots	200
n/a	n/a	No. of Cell Fills	1	Laser Power	20.0 lp
Broadband Low Mass	200.7 m/z	n/a	n/a	n/a	n/a
Broadband High Mass	1000.0 m/z	n/a	n/a	n/a	n/a
Acquisition Mode	Single MS	n/a	n/a		
Pulse Program	basic	n/a	n/a	Calibration Date	Tue Apr 13 03:01:48 2021
Source Accumulation	0.500 sec	n/a	n/a	Data Acquisition Size	1048576
Ion Accumulation Time	0.100 sec	n/a	n/a	Apodization	Sine-Bell Multiplication
Flight Time to Acq. Cell	0.001 sec				



Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
351.13830	1	C 25 H 19 O 2	100.00	351.13905	2.14	1.97	48.4	16.5	even	ok
461.07579	1	C 26 H 22 Br O 3	100.00	461.07578	-0.02	0.06	179.2	15.5	even	ok
538.98633	1	C 26 H 21 Br 2 O 3	100.00	538.98629	-0.06	0.34	145.7	15.5	even	ok

Figure 1：HRMS of reaction system

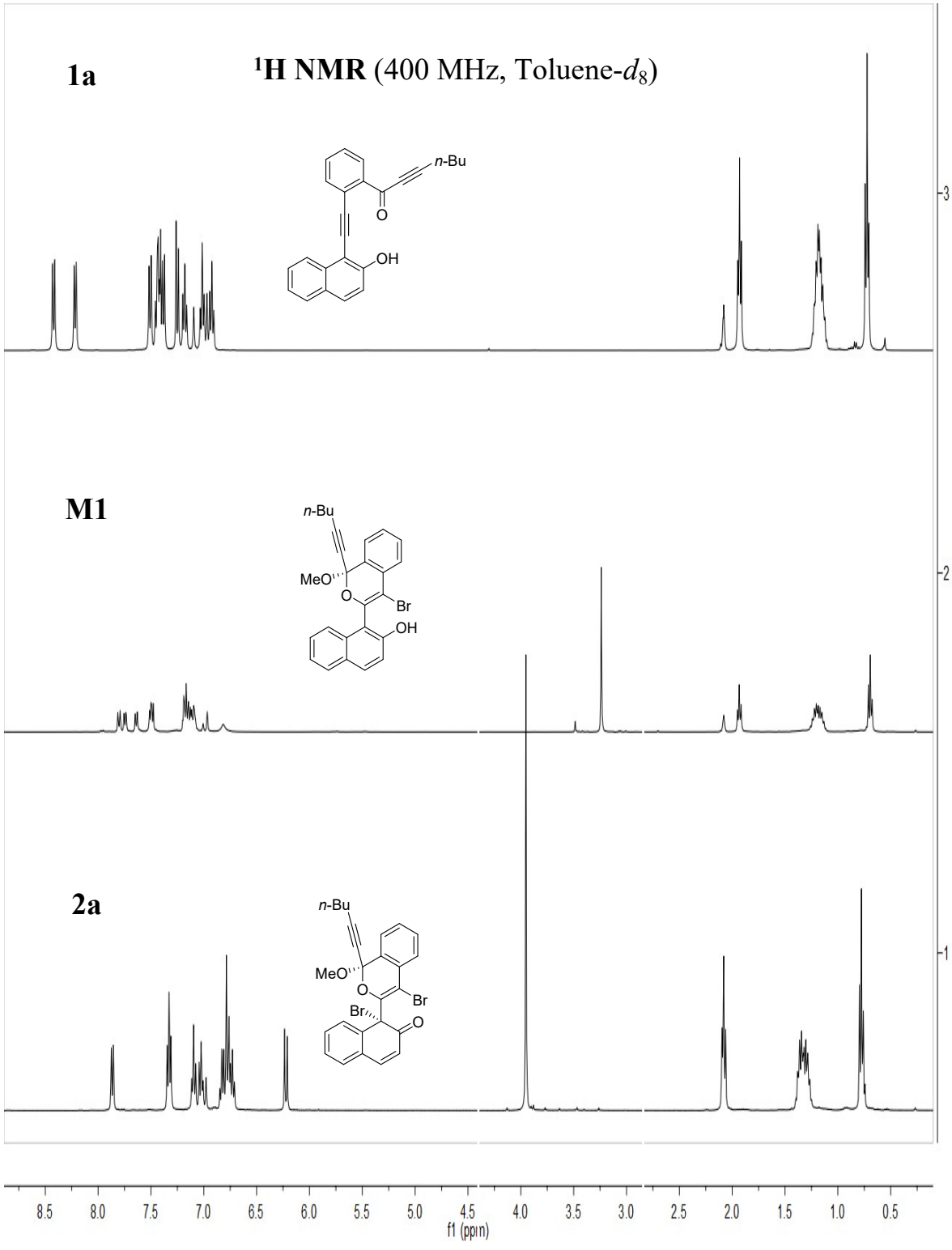


Figure 2：[1]H NMR of standard substance **1a**, **M1**, **2a**

Time (min)	Ratio (**1a**)%	Ratio (**M1**)%	Ratio (**2a**)%
0	100	0	0
5	26	62	12
15	19	65	16
20	10	57	33
40	0.1	53	37
60	0	11	88
70	0	0	100

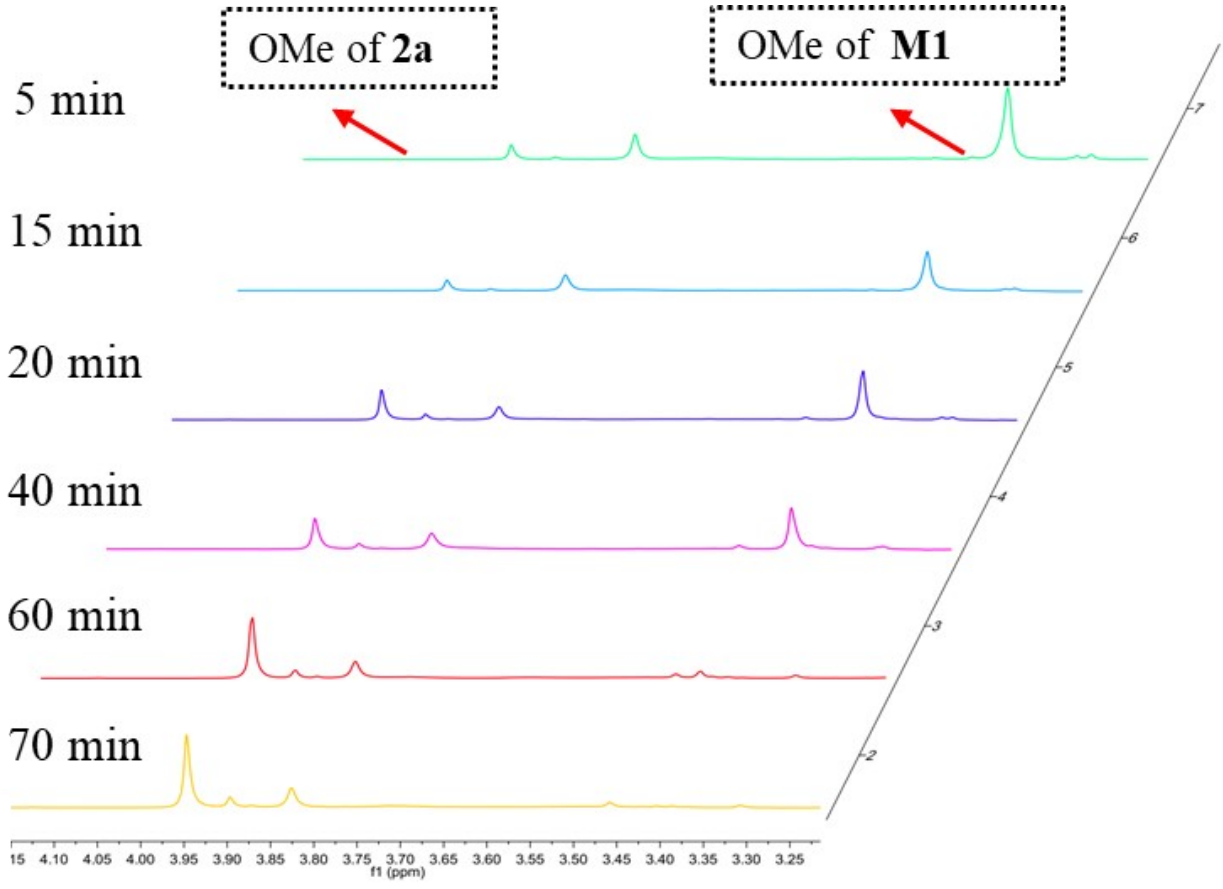


Figure 3：The reaction process is monitored by **^{1}H NMR** every 5 minutes at -10 ℃

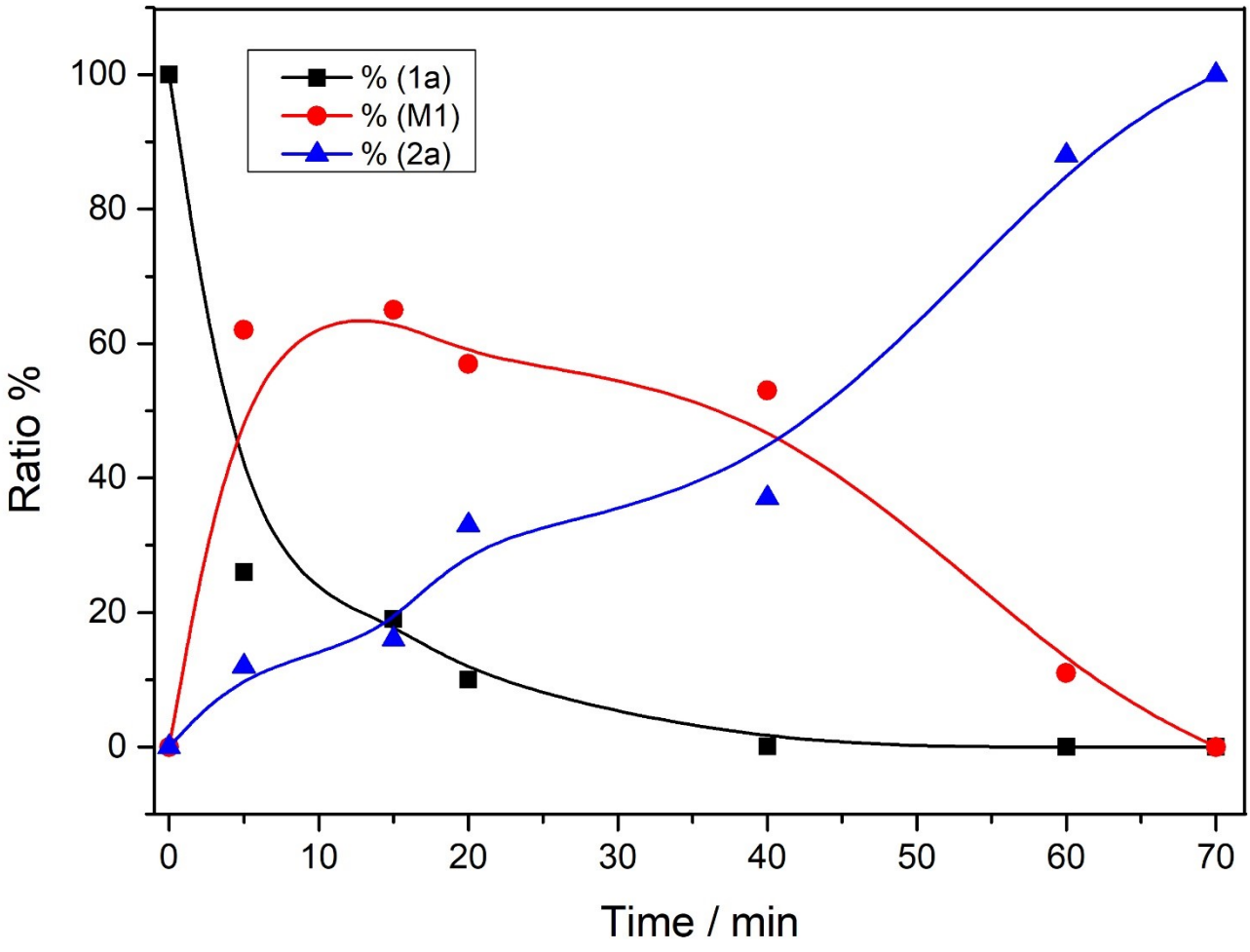
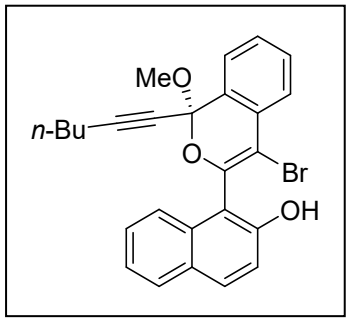
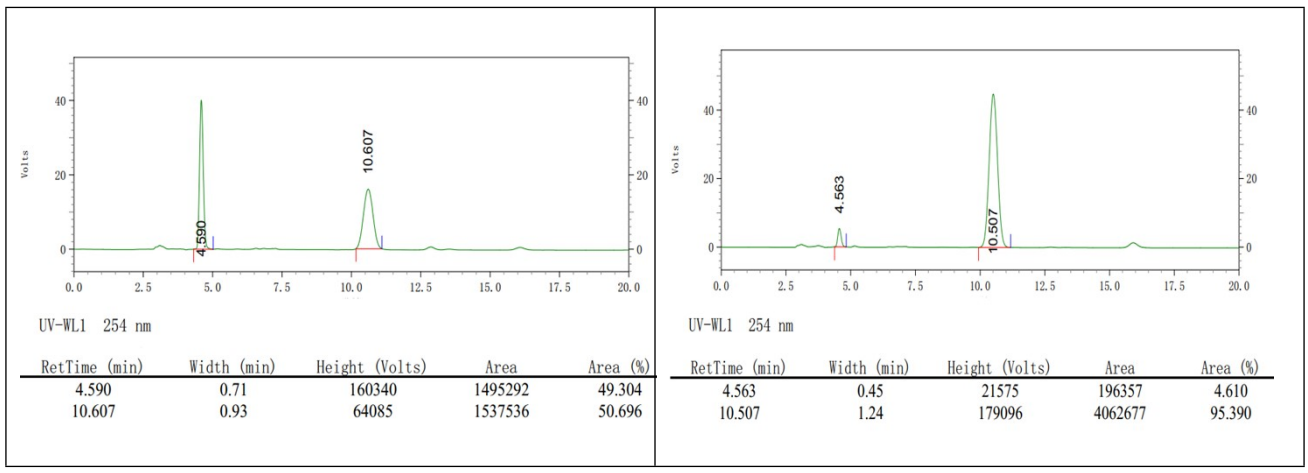


Figure 4：Equilibration process of the reaction

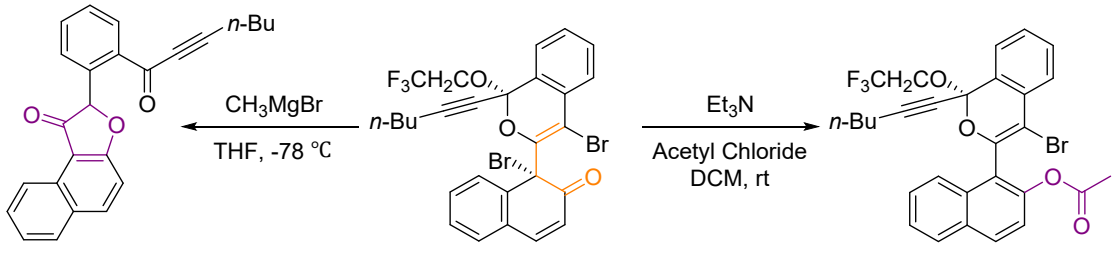
(*S*)-1-(4-bromo-1-(hex-1-yn-1-yl)-1-methoxy-1H-isochromen-3-yl)naphthalen-2-ol（M1）



^{1}H NMR (400 MHz, Toluene-d_8): δ 7.80 (d, J = 8.3 Hz, 1H), 7.77 – 7.72 (m, 1H), 7.66 – 7.62 (m, 1H), 7.50 (dd, J = 8.2, 5.6 Hz, 2H), 7.15 (m, 5H), 6.82 (s, 1H), 3.24 (s, 3H), 1.93 (t, J = 6.8 Hz, 2H), 1.23 (dd, J = 14.1, 6.5 Hz, 2H), 1.16 (dd, J = 14.6, 7.3 Hz, 2H), 0.69 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 154.23, 144.51, 132.36, 132.14, 132.08, 130.30, 130.05, 129.36, 129.02, 128.48, 127.41, 127.38, 126.53, 125.76, 125.72, 124.82, 123.74, 118.55, 118.52, 114.76, 107.05, 99.14, 91.01, 74.93, 52.06, 30.49, 22.29, 18.38, 13.57. **HRMS (ESI)** m/z Calcd for [$C_{26}H_{22}BrO_3$, M-H]$^-$: 461.0831, Found: 461.0758. **HPLC analysis**: Chiralcel AD-H (Hexane/*i*-PrOH) =90:10, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 4.563 min (minor), t_R = 10.507 min (major); **Physical properties:** yellow foam. (**Note:** The compound **M1** is unstable in silica gel column, which need scraper detection at -20 ℃)



VI. Synthetic transformation and continuous flow experiment:



5j
90% yield, 87% *ee*

2j

6j
88% yield, 93% *ee*, d.r. >20:1

To a Pyrex Schlenk tube was added **2j** (100 mg) in dry THF (3 mL) under an argon atmosphere. To the mixture was added methylmagnesium bromide (0.3 ml, 1M in THF) by syringe at -78°C, This mixture was stirred at that temperature for 2h. The resulting mixture was quenched by H_2O (3 mL) and extract by Et_2O (3×3 mL). The combined extracts were dried over MgSO4. The organic phase was concentrated under reduced pressure, and the resultant residue was purified by neutral silica gel column chromatography (eluent: hexane/EtOAc, 20:1) to give the desired product **5j** as yellow oil.

A round bottom flask was charged with the **2j** (100 mg) and dissolved with DCM (5 mL). Triethylamine (0.3 mL) were subsequently added to the reaction vessel at 20 °C after stirred 30 min, the acetyl chloride (0.1 mL) was added and stirred for 1 hours. The mixture was then quenched with 5% aq. HCl and extracted several times with CH_2Cl_2. The combined organic layers were washed with brine, dried over MgSO4, and concentrated under reduced pressure. The crude residue was purified by flash chromatography (hexanes/AcOEt 9/1) to give the desired product **7j** as yellow foam.

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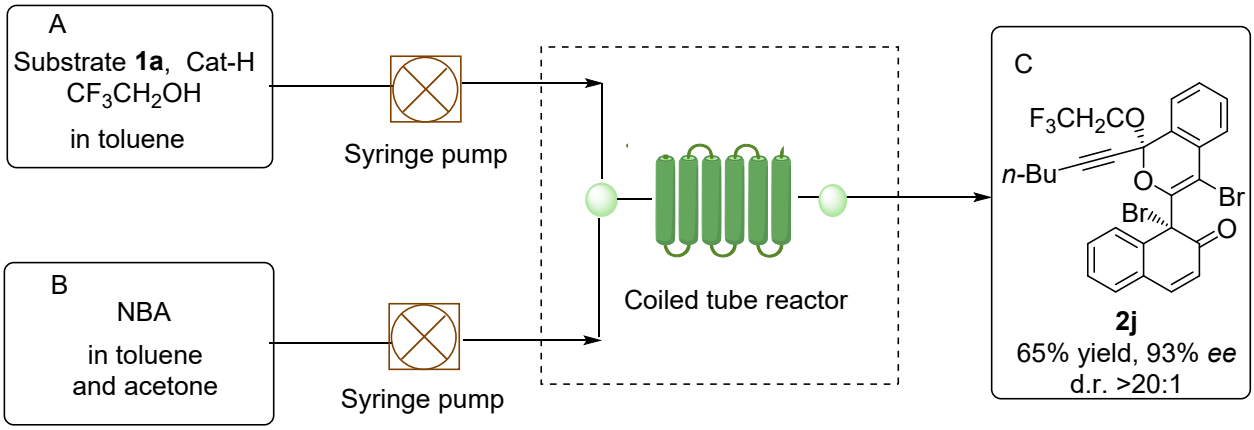
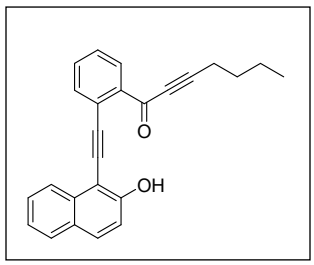


The microreactor system was placed in room temperature. A solution of CF_3CH_2OH (3.0 eq.), catalyst (0.1 eq.) and **1a** (10 g, 0.05 M in toluene) in toluene was carefully prepared and homogenized (flow rate: 1.0 mL/min). The solution of NBA (0.1 M in toluene/acetone=10:1) were introduced to coiled tube reactor by syringe pumps (flow rate: 2.0 mL/min). When finished, column chromatographic purification was carried out on silica gel (SiO_2) with mixtures of PE/EA=10:1 as eluent (Fast process). The reaction in flow at 20 °C provides the product with a good yield and enantioselectivity. (65%, 93% *ee*).

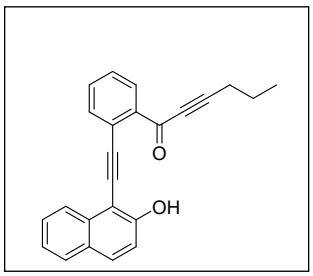
VII. ^{1}H, ^{13}C NMR and HRMS data of substrates (1a-1k, 3a-3h)

1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)hept-2-yn-1-one (1a)



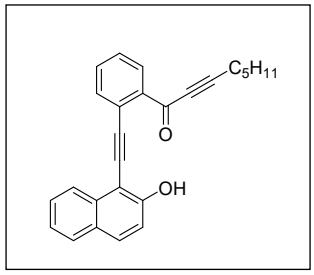
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.36 (d, *J* = 7.8 Hz, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 3H), 7.57 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 14.8 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 2.50 (t, *J* = 7.0 Hz, 2H), 1.65 (p, *J* = 7.3 Hz, 2H), 1.49 (h, *J* = 7.2 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.34, 159.61, 135.47, 134.11, 133.50, 133.42, 133.15, 131.46, 128.23, 128.04, 127.54, 127.21, 124.66, 123.72, 122.95, 117.41, 102.38, 100.66, 98.11, 89.75, 80.12, 29.71, 22.06, 18.95, 13.50. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{19}O_2, M - H]^-$: 351.1463, Found: 351.1391.

1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)hex-2-yn-1-one (1b)



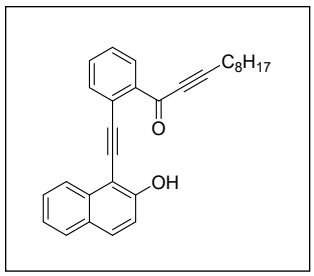
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.37 (d, *J* = 7.9 Hz, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.79 (d, *J* = 8.3 Hz, 3H), 7.62 – 7.52 (m, 2H), 7.47 – 7.42 (m, 1H), 7.39 – 7.33 (m, 1H), 7.28 (d, *J* = 9.0 Hz, 1H), 2.48 (t, *J* = 7.0 Hz, 2H), 1.70 (m, 2H), 1.07 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.34, 159.61, 135.45, 134.11, 133.49, 133.42, 133.16, 131.46, 128.23, 128.04, 127.55, 127.21, 124.66, 123.72, 122.95, 117.41, 102.38, 100.66, 97.93, 89.75, 80.24, 21.28, 21.18, 13.61. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{17}O_2, M - H]^-$: 337.1307, Found: 337.1287.

1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)oct-2-yn-1-one (1c)



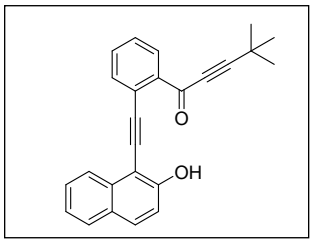
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.38 (d, *J* = 7.7 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 7.82 – 7.75 (m, 3H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 2.50 (t, *J* = 7.1 Hz, 2H), 1.68 (p, *J* = 7.2 Hz, 2H), 1.40 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.37, 159.63, 135.50, 134.14, 133.51, 133.44, 133.17, 131.48, 128.24, 128.05, 127.55, 127.22, 124.67, 123.73, 122.99, 117.43, 102.38, 100.66, 98.18, 89.77, 80.14, 31.10, 27.41, 22.10, 19.24, 13.91. **HRMS (ESI)** m/z Calcd for $[C_{26}H_{21}O_2, M - H]^-$: 365.1620, Found: 365.1610.

1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)undec-2-yn-1-one (1d)



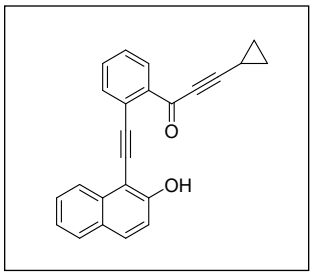
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (s, 1H), 8.38 (d, *J* = 7.9 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 7.78 (t, *J* = 7.6 Hz, 3H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.26 (d, *J* = 8.1 Hz, 1H), 2.50 (t, *J* = 7.1 Hz, 2H), 1.67 (p, *J* = 7.2 Hz, 2H), 1.53 – 1.22 (m, 10H), 0.89 (t, *J* = 6.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.37, 159.64, 135.53, 134.14, 133.52, 133.45, 133.17, 131.48, 128.25, 128.06, 127.54, 127.22, 124.68, 123.73, 123.00, 117.44, 102.38, 100.66, 98.21, 89.79, 80.16, 31.63, 28.93, 28.70, 27.72, 22.59, 19.28, 14.07. **HRMS (ESI)** m/z Calcd for $[C_{29}H_{27}O_2, M - H]^-$: 407.2089, Found: 407.2073.

1-(2-((2-hydroxynaphthalen-1-yl)ethyn yl)phenyl)-4,4-dimethylpent-2-yn-1-one (1e)



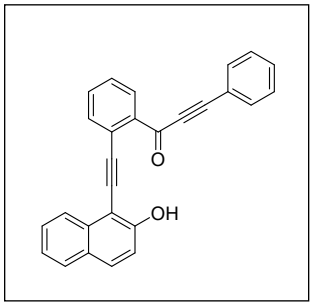
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (s, 1H), 8.34 (d, *J* = 7.9 Hz, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.82 – 7.74 (m, 3H), 7.62 – 7.52 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 14.9 Hz, 1H), 7.28 (d, *J* = 8.9 Hz, 1H), 1.38 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.48, 159.63, 135.60, 134.00, 133.49, 133.42, 133.12, 131.46, 128.23, 128.05, 127.55, 127.21, 124.67, 123.72, 122.96, 117.41, 105.03, 102.39, 100.69, 89.71, 78.66, 30.05, 28.09. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{19}O_2, M - H]^-$: 351.1463, Found: 351.1442.

3-cyclopropyl-1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)prop-2-yn-1-one (1f)



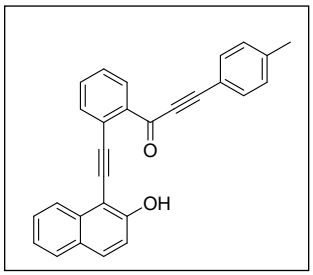
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (s, 1H), 8.32 (d, *J* = 7.8 Hz, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.81 – 7.74 (m, 3H), 7.57 (m, 2H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 9.0 Hz, 1H), 1.54 (p, *J* = 7.5 Hz, 1H), 1.05 (d, *J* = 8.0 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.04, 159.64, 135.61, 133.97, 133.52, 133.40, 133.05, 131.45, 128.24, 128.06, 127.52, 127.21, 124.68, 123.72, 122.89, 117.44, 102.47, 102.40, 100.64, 89.73, 76.13, 10.06, 0.12. **HRMS (ESI)** m/z Calcd for $[C_{24}H_{15}O_2, M - H]^-$: 335.1150, Found: 335.1123.

1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)-3-phenylprop-2-yn-1-one (1g)



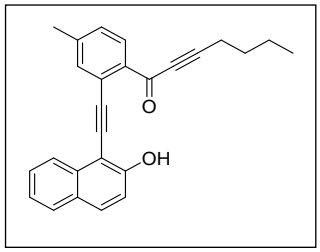
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 1H), 8.42 (d, *J* = 7.9 Hz, 1H), 8.22 (d, *J* = 8.3 Hz, 1H), 7.76 (t, *J* = 8.1 Hz, 3H), 7.65 (d, *J* = 7.9 Hz, 2H), 7.56 (dt, *J* = 15.3, 7.7 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.37 (dd, *J* = 13.7, 6.9 Hz, 3H), 7.28 (d, *J* = 9.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.02, 159.62, 135.28, 134.00, 133.50, 133.47, 133.36, 133.06, 131.53, 130.92, 128.62, 128.22, 128.02, 127.61, 127.24, 124.66, 123.74, 123.03, 119.79, 117.37, 102.39, 100.72, 94.17, 89.96, 87.34. **HRMS (ESI)** m/z Calcd for $[C_{27}H_{15}O_2, M - H]^-$: 371.1150, Found: 371.1123.

1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)-3-(p-tolyl)prop-2-yn-1-one (1h)



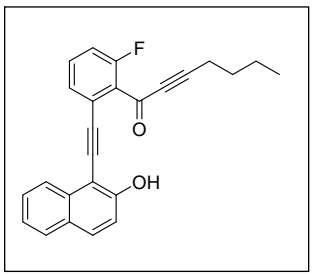
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 1H), 8.46 (d, *J* = 7.7 Hz, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 7.78 (t, *J* = 8.4 Hz, 3H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.55 (t, *J* = 8.4 Hz, 3H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 8.9 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 2H), 2.38 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.15, 159.70, 141.79, 135.56, 134.00, 133.52, 133.28, 133.16, 131.52, 129.48, 128.26, 128.08, 127.64, 127.25, 124.70, 123.75, 123.08, 117.44, 116.76, 102.43, 100.73, 94.99, 89.94, 87.37, 21.78. **HRMS (ESI)** m/z Calcd for $[C_{28}H_{17}O_2, M - H]^-$: 385.1307, Found: 385.1286

1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)-4-methylphenyl)hept-2-yn-1-one (1i)



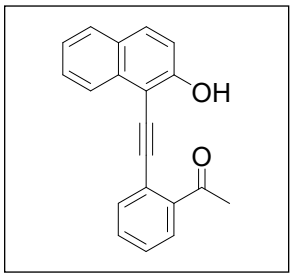
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.89 (s, 1H), 8.23 (dd, *J* = 8.1, 3.8 Hz, 2H), 7.77 (dd, *J* = 8.2, 5.5 Hz, 2H), 7.55 (d, *J* = 5.8 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 8.9 Hz, 1H), 7.23 (d, *J* = 9.6 Hz, 1H), 2.49 (t, *J* = 7.1 Hz, 2H), 2.44 (s, 3H), 1.65 (p, *J* = 7.0 Hz, 2H), 1.49 (h, *J* = 7.2 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 176.99, 159.66, 144.35, 134.36, 133.88, 133.52, 133.21, 131.35, 128.53, 128.21, 128.03, 127.15, 124.70, 123.67, 122.91, 117.45, 102.45, 100.84, 97.43, 89.29, 80.15, 29.75, 22.06, 21.47, 18.94, 13.52. **HRMS (ESI)** m/z Calcd for $[C_{26}H_{21}O_2, M - H]^-$: 365.1620, Found: 365.1598

1-(2-fluoro-6-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)hept-2-yn-1-one (1j)



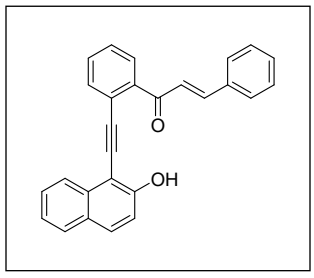
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 1H), 8.16 (d, *J* = 8.3 Hz, 1H), 7.99 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.80 – 7.69 (m, 3H), 7.56 – 7.49 (m, 1H), 7.37 – 7.32 (m, 1H), 7.31 – 7.23 (m, 2H), 2.50 (t, *J* = 7.1 Hz, 2H), 1.70 – 1.61 (m, 2H), 1.49 (dq, *J* = 14.4, 7.3 Hz, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 175.94 (d, *J* = 2.0 Hz), 161.07 (d, *J* = 249.0 Hz), 159.42, 137.08 (d, *J* = 6.0 Hz), 135.22 (d, *J* = 8.0 Hz), 133.41, 131.47, 128.24, 128.04, 127.23, 124.59, 123.75, 120.75 (d, *J* = 23.0 Hz), 120.39 (d, *J* = 24.0 Hz), 119.10 (d, *J* = 4.0 Hz), 117.35, 102.23, 99.63, 98.87, 89.38, 79.74, 29.63, 22.07, 18.95, 13.48. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{18}FO_2, M - H]^-$: 369.1369, Found: 369.1341

1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)ethan-1-one (1k)



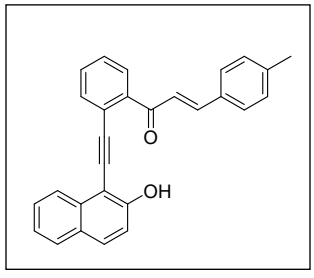
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (s, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 7.9 Hz, 1H), 7.77 (dd, *J* = 7.8, 5.1 Hz, 3H), 7.55 (t, *J* = 7.5 Hz, 2H), 7.42 – 7.33 (m, 2H), 7.28 (d, *J* = 8.9 Hz, 1H), 2.68 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.40, 159.50, 135.94, 133.74, 133.47, 132.49, 131.28, 130.92, 128.22, 128.05, 127.63, 127.18, 124.69, 123.71, 122.43, 117.34, 102.51, 101.04, 88.61, 28.18. **HRMS (ESI)** m/z Calcd for $[C_{20}H_{12}O_2, M - H]^-$: 286.0994, Found: 285.0972.

(E)-1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)-3-phenylprop-2-en-1-one (3a)



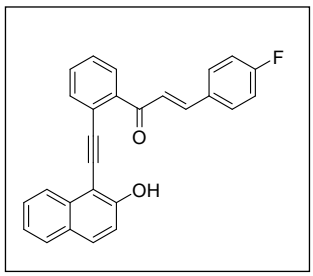
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (s, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 15.7 Hz, 1H), 7.80 – 7.73 (m, 3H), 7.62 – 7.56 (m, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.47 – 7.39 (m, 2H), 7.39 – 7.32 (m, 4H), 7.28 (d, *J* = 8.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 190.84, 159.29, 146.20, 138.01, 134.49, 133.44, 133.41, 131.89, 131.17, 130.76, 129.68, 128.90, 128.56, 128.19, 128.08, 127.56, 127.17, 124.75, 123.72, 123.28, 122.92, 117.32, 102.54, 100.34, 88.56. **HRMS (ESI)** m/z Calcd for $[C_{27}H_{17}O_2, M - H]^-$: 373.1307, Found: 373.1297

(E)-1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)-3-(p-tolyl)prop-2-en-1-one (3b)



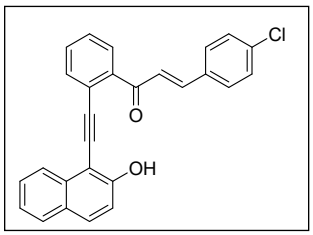
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (s, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 7.7 Hz, 1H), 7.87 – 7.73 (m, 4H), 7.53 (dt, *J* = 14.4, 7.6 Hz, 4H), 7.42 (dd, *J* = 15.6, 9.6 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.29 (d, *J* = 8.9 Hz, 1H), 7.19 (d, *J* = 7.8 Hz, 2H), 2.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 191.05, 159.32, 146.43, 141.44, 138.29, 133.45, 133.38, 131.80, 131.14, 129.69, 129.65, 128.64, 128.20, 128.09, 127.57, 127.16, 124.78, 123.72, 122.90, 122.34, 117.36, 102.56, 100.33, 88.50, 21.53. **HRMS (ESI)** m/z Calcd for $[C_{28}H_{19}O_2, M - H]^-$: 387.1463, Found: 387.1441

(E)-3-(4-fluorophenyl)-1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)prop-2-en-1-one (3c)



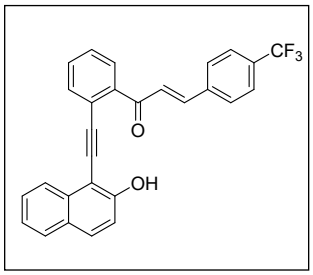
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 1H), 7.81 – 7.71 (m, 4H), 7.59 – 7.49 (m, 4H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 5.2 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.9 Hz, 1H), 7.04 (t, *J* = 8.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 190.54, 164.10 (d, *J* = 251.0 Hz), 159.26, 144.77, 137.90, 133.42, 131.93, 131.20, 130.77 (d, *J* = 3.0 Hz), 130.53, 130.45, 129.63, 128.21, 128.09, 127.57, 127.19, 124.72, 123.75, 122.91, 117.29, 116.18, 115.96, 102.51, 100.34, 88.59. **HRMS (ESI)** m/z Calcd for $[C_{27}H_{16}FO_2, M - H]^-$: 391.1213, Found: 391.1210

(E)-3-(4-chlorophenyl)-1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)prop-2-en-1-one (3d)



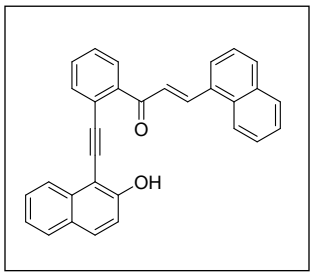
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (s, 1H), 8.19 (d, *J* = 8.3 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.79 – 7.71 (m, 4H), 7.52 (m, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.37 (m, 3H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 190.34, 159.26, 144.50, 137.71, 136.60, 133.45, 133.42, 132.97, 132.01, 131.23, 129.66, 129.15, 128.21, 128.08, 127.56, 127.20, 124.71, 123.75, 123.52, 122.95, 117.28, 102.50, 100.37, 88.66. **HRMS (ESI)** m/z Calcd for $[C_{27}H_{16}ClO_2, M - H]^-$: 407.0917, Found: 407.0911

(E)-1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (3e)



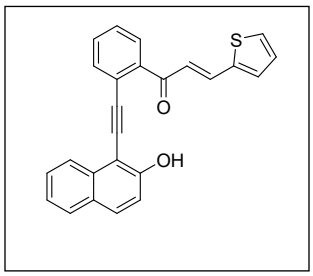
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 1H), 8.20 (d, *J* = 8.3 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.88 – 7.74 (m, 4H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.66 – 7.49 (m, 5H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 8.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 190.31, 159.29, 143.97, 137.75 (d, *J* = 34.0 Hz), 133.62, 133.48, 132.51, 132.28, 132.03 (d, *J* = 33.0 Hz), 131.54, 131.36, 129.81, 128.61, 128.27, 128.16, 127.67, 127.27, 125.89, 125.85, 125.46, 123.76 (q, *J* = 270.0 Hz), 124.73, 123.83, 123.17, 117.30, 102.47, 100.29, 88.88. **HRMS (ESI)** m/z Calcd for $[C_{28}H_{16}F_3O_2, M - H]^-$: 441.1181, Found: 441.1167

(E)-1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)-3-(naphthalen-1-yl)prop-2-en-1-one (3f)



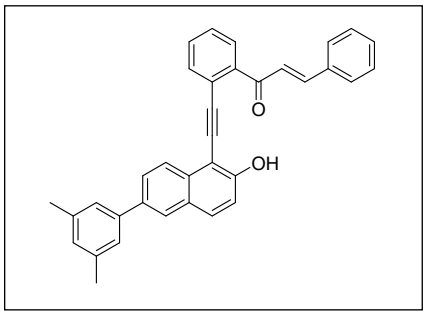
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 – 8.66 (m, 2H), 8.24 (d, *J* = 8.2 Hz, 2H), 8.00 (d, *J* = 6.8 Hz, 1H), 7.88 (dd, *J* = 15.5, 7.4 Hz, 4H), 7.81 – 7.74 (m, 2H), 7.62 – 7.42 (m, 7H), 7.35 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 8.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 190.69, 159.35, 143.07, 138.12, 133.69, 133.55, 133.52, 132.01, 131.70, 131.24, 131.10, 129.84, 128.73, 128.23, 128.16, 127.65, 127.22, 127.05, 126.33, 125.96, 125.38, 125.31, 124.80, 123.76, 123.48, 123.12, 117.37, 102.58, 100.38, 88.74. **HRMS (ESI)** m/z Calcd for $[C_{31}H_{19}O_2, M - H]^-$: 423.1463, Found: 423.1441

(E)-1-(2-((2-hydroxynaphthalen-1-yl)ethynyl)phenyl)-3-(thiophen-2-yl)prop-2-en-1-one (3g)



^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.99 (d, *J* = 15.3 Hz, 1H), 7.90 (d, *J* = 7.8 Hz, 1H), 7.81 – 7.72 (m, 3H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.45 – 7.31 (m, 4H), 7.31 – 7.20 (m, 2H), 7.04 (t, *J* = 4.3 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 190.13, 159.32, 140.04, 138.56, 137.97, 133.44, 133.39, 132.57, 131.88, 131.15, 129.52, 129.40, 128.41, 128.18, 128.07, 127.59, 127.16, 124.76, 123.71, 122.90, 121.87, 117.33, 102.56, 100.38, 88.58. **HRMS (ESI)** m/z Calcd for $[C_{25}H_{15}O_2S, M - H]^-$: 379.0871, Found: 379.0851

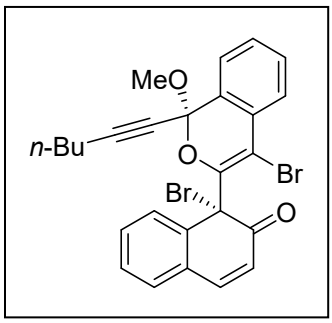
(E)-1-(2-((6-(3,5-dimethylphenyl)-2-hydroxynaphthalen-1-yl)ethynyl)phenyl)-3-phenylprop-2-en-1-one (3h)



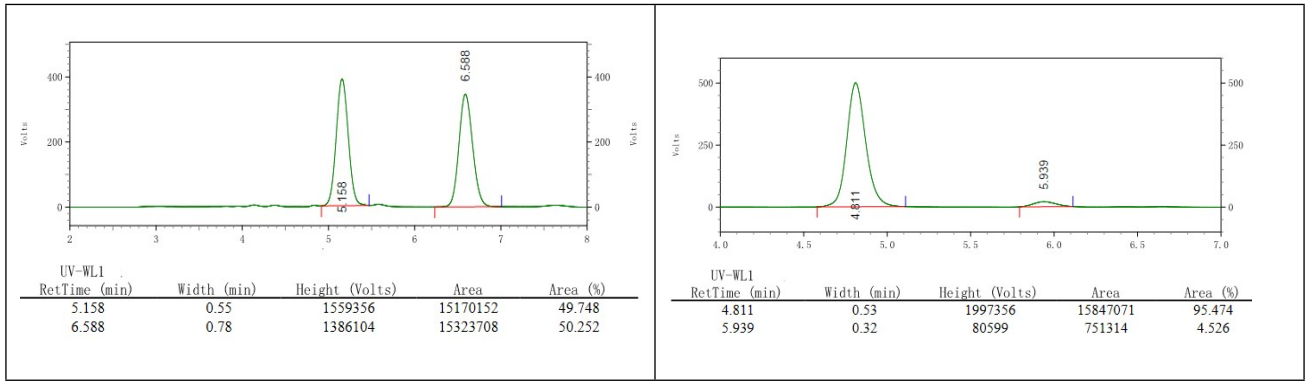
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.24 (d, *J* = 8.6 Hz, 1H), 7.97 – 7.73 (m, 6H), 7.63 – 7.51 (m, 3H), 7.48 – 7.35 (m, 5H), 7.29 (d, *J* = 8.0 Hz, 3H), 6.99 (s, 1H), 2.40 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 190.88, 159.31, 146.22, 140.89, 138.27, 138.11, 136.75, 134.56, 133.45, 132.59, 131.89, 131.42, 130.77, 129.68, 128.93, 128.79, 128.59, 128.36, 127.58, 126.91, 126.06, 125.18, 125.09, 123.36, 122.95, 117.67, 102.48, 100.31, 88.61, 21.42. **HRMS (ESI)** m/z Calcd for $[C_{35}H_{25}O_2, M - H]^-$: 477.1933, Found: 477.1910

VIII. ^{1}H, ^{13}C NMR, HRMS data and HPLC traces of products (2a-2w, 4a-4j, 5j, 6j)

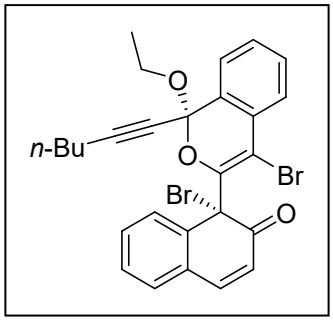
(*R*)-1-bromo-1-((*S*)-4-bromo-1-(hex-1-yn-1-yl)-1-methoxy-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2a)



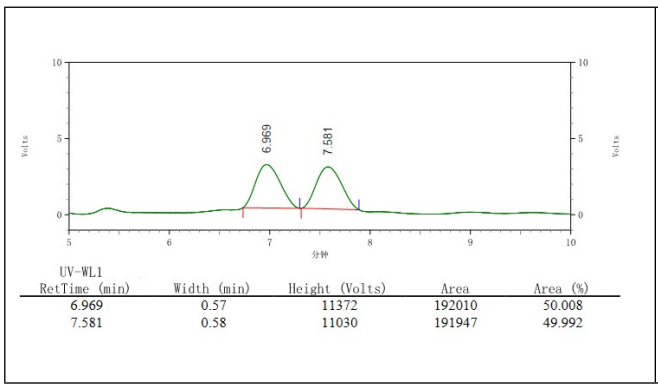
^{1}H NMR (400 MHz, Toluene-d_8) δ 7.87 (d, J = 7.5 Hz, 1H), 7.33 (t, J = 7.1 Hz, 2H), 7.10 (t, J = 7.5 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.78 (m, 4H), 6.22 (d, J = 10.0 Hz, 1H), 3.95 (s, 3H), 2.08 (t, J = 6.8 Hz, 2H), 1.32 (m, 4H), 0.78 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 188.99, 146.64, 142.76, 142.70, 131.09, 130.73, 129.86, 129.70, 129.49, 128.76, 128.71, 128.52, 128.43, 125.91, 124.50, 124.30, 102.55, 99.99, 89.93, 76.01, 63.28, 53.42, 30.68, 22.37, 18.54, 13.69. **HRMS (ESI)** m/z Calcd for $[C_{26}H_{22}Br_2NaO_3, M+Na]^+$: 562.9936, Found: 562.9828. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) =80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 4.811 min (major), t_R = 5.939 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 95° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 88%, 47.4 mg.



(*R*)-1-bromo-1-((*S*)-4-bromo-1-ethoxy-1-(hex-1-yn-1-yl)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2b)

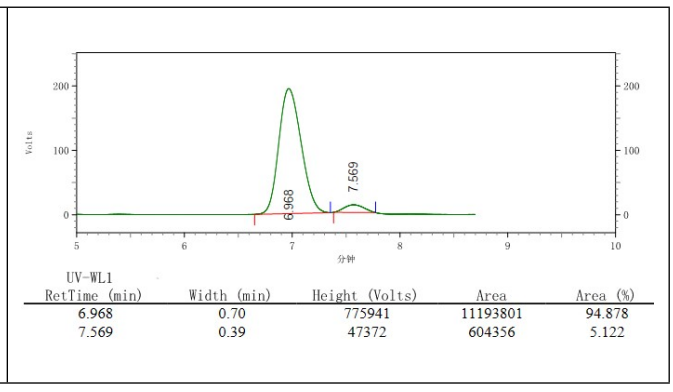


^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.76 – 7.72 (m, 2H), 7.61 – 7.58 (m, 1H), 7.51 – 7.39 (m, 6H), 6.44 (d, *J* = 10.0 Hz, 1H), 4.23 – 4.10 (m, 2H), 2.52 (t, *J* = 7.0 Hz, 2H), 1.71 – 1.63 (m, 2H), 1.59 – 1.50 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 189.80, 147.05, 144.21, 142.83, 131.69, 131.33, 130.63, 130.61, 130.07, 129.62, 129.37, 129.13, 128.85, 126.29, 124.59, 124.48, 102.16, 99.43, 90.76, 76.23, 63.56, 62.02, 31.06, 22.62, 18.66, 15.06, 13.85. **HRMS (ESI)** m/z Calcd for $[C_{27}H_{24}Br_2NaO_3, M + Na]^+$: 577.0092, Found: 577.0010. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 6.968 min (major), t_R = 7.569 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 99° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 75%, 41.6 mg.



UV-WL1

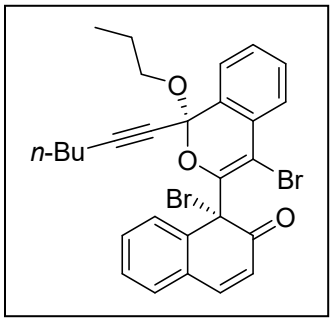
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.969	0.57	11372	192010	50.008
7.581	0.58	11030	191947	49.992



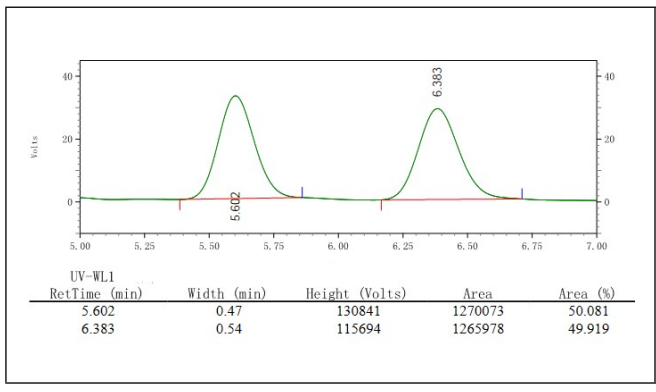
UV-WL1

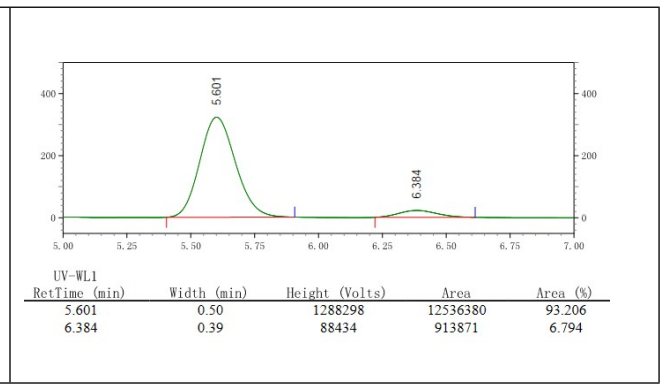
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.968	0.70	775941	11193801	94.878
7.569	0.39	47372	604356	5.122

(*R*)-1-bromo-1-((*S*)-4-bromo-1-(hex-1-yn-1-yl)-1-propoxy-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2c)

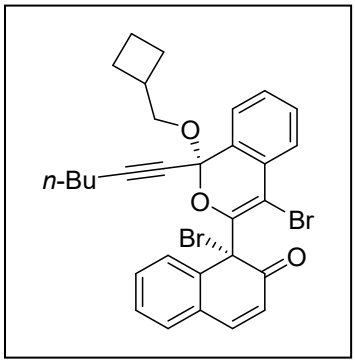


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 – 7.68 (m, 1H), 7.46 (m, 2H), 7.40 – 7.28 (m, 6H), 6.43 (d, *J* = 9.9 Hz, 1H), 4.12 – 4.01 (m, 2H), 2.44 (t, *J* = 6.9 Hz, 2H), 1.82 – 1.60 (m, 4H), 1.53 (dt, *J* = 14.4, 6.9 Hz, 2H), 0.97 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 189.50, 145.73, 142.96, 141.98, 130.69, 130.36, 129.46, 129.34, 128.91, 128.65, 128.38, 128.36, 127.88, 125.44, 124.14, 123.94, 101.71, 98.70, 89.55, 75.83, 67.75, 62.56, 30.31, 22.52, 22.02, 18.47, 13.59, 10.60. **HRMS (ESI)** m/z Calcd for $[C_{28}H_{26}Br_2NaO_3, M+ Na]^+$: 591.0249, Found: 591.0195. **HPLC analysis**: Chiralcel IC-H (Hexane/*i*-PrOH) = 90:10, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 5.601 min (major), t_R = 6.384 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 103° (c = 1.0, $CHCl_3$); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 77%, 43.7 mg.

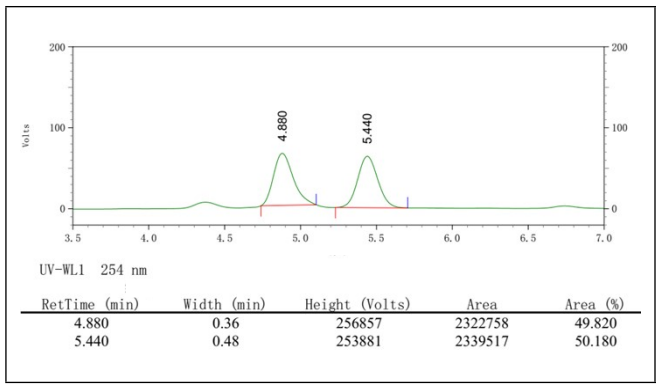


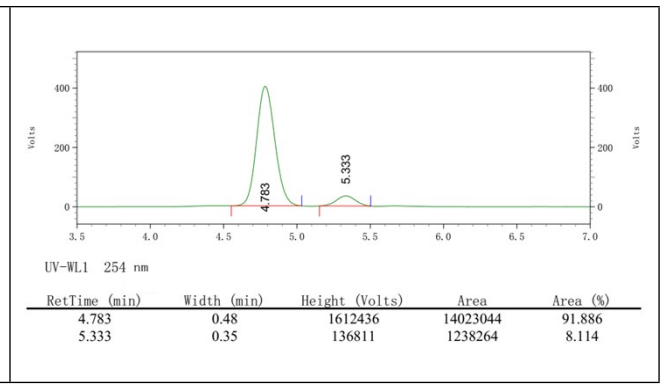


(*R*)-1-bromo-1-((*S*)-4-bromo-1-(cyclobutylmethoxy)-1-(hex-1-yn-1-yl)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2d)

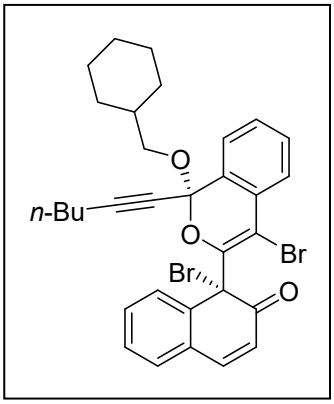


^{1}H NMR (400 MHz, Toluene-d_8): δ 8.01 (d, J = 7.6 Hz, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.41 (d, J = 7.7 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.15 – 7.10 (m, 1H), 6.97 – 6.91 (m, 1H), 6.91 – 6.81 (m, 3H), 6.32 (d, J = 10.0 Hz, 1H), 4.64 (dd, J = 9.1, 6.5 Hz, 1H), 4.59 – 4.53 (m, 1H), 3.00 (m, 1H), 2.26 – 2.15 (m, 5H), 2.12 – 1.97 (m, 2H), 1.97 – 1.89 (m, 1H), 1.56 – 1.38 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 188.83, 146.76, 142.71, 142.63, 131.20, 130.70, 129.78, 129.64, 129.45, 128.76, 128.73, 128.54, 128.40, 126.01, 124.51, 124.37, 102.30, 99.65, 89.68, 77.01, 70.80, 63.47, 35.37, 30.73, 25.69, 25.21, 22.38, 19.12, 18.60, 13.67. **HRMS (ESI)** m/z Calcd for $[C_{30}H_{28}Br_2NaO_3, M + Na]^+$: 617.0405, Found: 617.0428. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 90:10), flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 4.783 min (major), t_R =5.333 (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 122° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 75%, 44.6 mg.

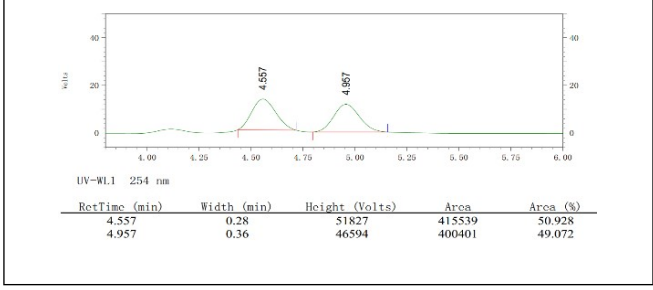


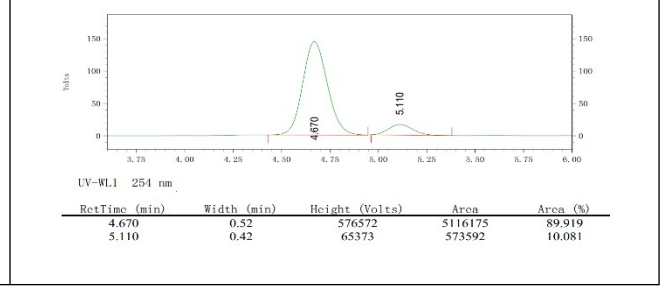


(*R*)-1-bromo-1-((*S*)-4-bromo-1-(cyclohexylmethoxy)-1-(hex-1-yn-1-yl)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2e)

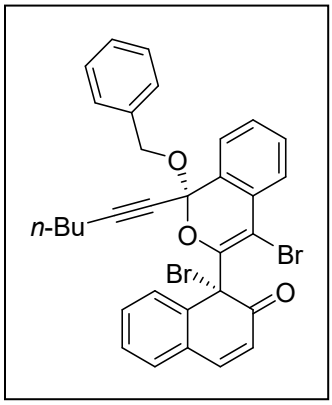


^{1}H NMR (400 MHz, Toluene-d_8): δ 7.91 (d, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.7 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 6.80 – 6.71 (m, 3H), 6.21 (d, *J* = 10.0 Hz, 1H), 4.38 (dd, *J* = 8.9, 5.2 Hz, 1H), 4.27 – 4.20 (m, 1H), 2.12 (t, *J* = 6.9 Hz, 2H), 2.02 (d, *J* = 11.5 Hz, 1H), 1.93 (d, *J* = 8.7 Hz, 2H), 1.67 (t, *J* = 12.1 Hz, 2H), 1.58 (d, *J* = 10.1 Hz, 1H), 1.37 (m, 4H), 1.16 (m, 5H), 0.80 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 188.77, 146.82, 142.76, 142.56, 131.33, 130.68, 129.75, 129.69, 129.41, 128.75, 128.74, 128.56, 128.39, 125.97, 125.38, 125.13, 124.89, 124.52, 124.39, 102.25, 99.69, 89.59, 77.08, 72.22, 63.46, 38.12, 30.87, 30.74, 30.38, 27.13, 26.46, 26.31, 22.37, 18.61, 13.67. **HRMS (ESI)** m/z Calcd for $[C_{32}H_{32}Br_2NaO_3, M + Na]^+$: 645.0718, Found: 645.0695. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 90:10), flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 4.670 min (major), t_R =5.110 (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 112° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 75% 46.5 mg.

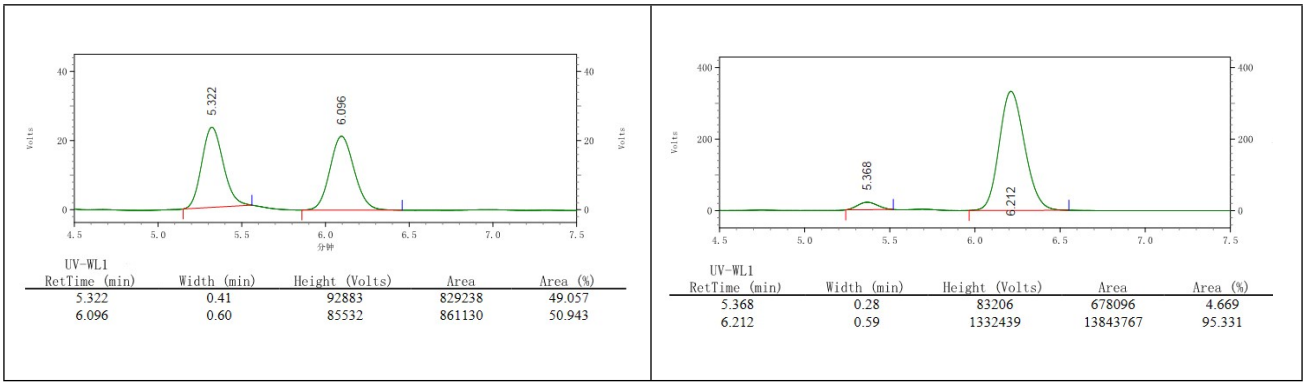




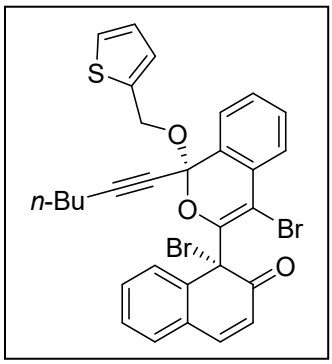
(*R*)-1-((*S*)-1-(benzyloxy)-4-bromo-1-(hex-1-yn-1-yl)-1H-isochromen-3-yl)-1-bromonaphthalen-2(1*H*)-one (2f)



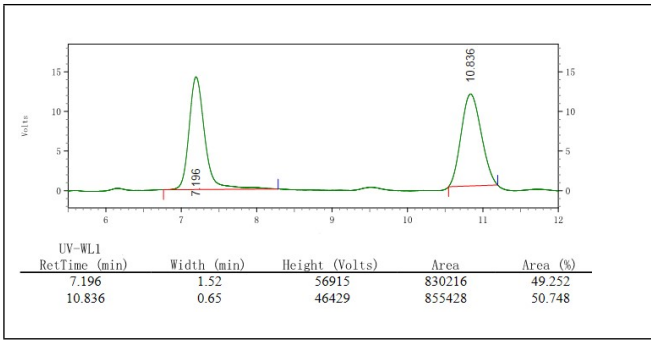
^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 7.80 (dd, *J* = 6.1, 2.7 Hz, 1H), 7.77 (d, *J* = 10.0 Hz, 1H), 7.61 (dd, *J* = 6.2, 3.0 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.40 (m, 6H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.31 – 7.25 (m, 1H), 6.48 (d, *J* = 10.0 Hz, 1H), 5.24 (d, *J* = 10.7 Hz, 1H), 5.14 (d, *J* = 10.7 Hz, 1H), 2.56 (t, *J* = 7.0 Hz, 2H), 1.69 (p, *J* = 6.9 Hz, 2H), 1.56 (dq, *J* = 14.2, 7.1 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 190.03, 146.90, 144.41, 142.76, 138.47, 131.79, 130.94, 130.80, 130.70, 130.15, 129.60, 129.57, 129.51, 129.15, 128.94, 128.88, 128.46, 126.49, 124.70, 124.46, 102.37, 99.67, 91.35, 76.25, 69.00, 63.59, 31.03, 22.66, 18.71, 13.87. **HRMS (ESI)** m/z Calcd for $[C_{32}H_{26}Br_2NaO_3, M+Na]^+$: 639.0249, Found: 639.0149. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 90:10, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 5.368 min (minor), t_R = 6.212 min (major). **Optical Rotation:** $[\alpha]_D^{20}$ = 144° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 76%, 46.8mg.

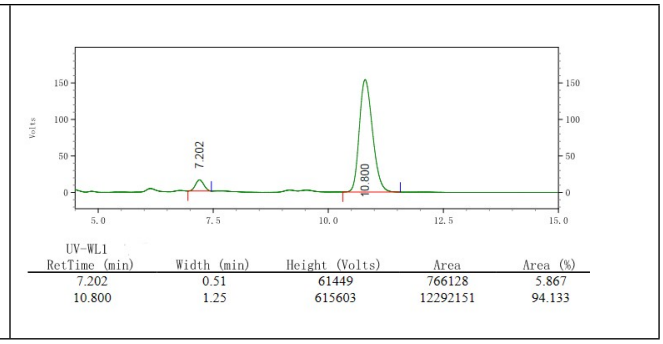


(*R*)-1-bromo-1-((*S*)-4-bromo-1-(hex-1-yn-1-yl)-1-(thiophen-2-ylmethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2g)

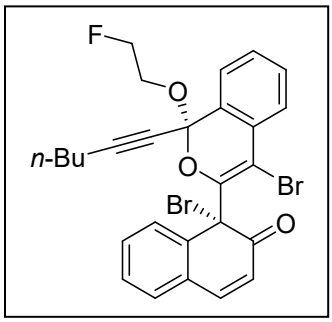


^{1}H NMR (400 MHz, Toluene-d_8): δ 7.89 – 7.85 (m, 1H), 7.36 – 7.31 (m, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.06 – 7.02 (m, 1H), 7.00 – 6.95 (m, 1H), 6.86 – 6.82 (m, 1H), 6.82 – 6.78 (m, 1H), 6.76 (d, *J* = 3.3 Hz, 1H), 6.75 – 6.68 (m, 3H), 6.23 (d, *J* = 10.0 Hz, 1H), 5.71 (s, 2H), 2.11 (t, *J* = 6.9 Hz, 2H), 1.40 (m, 2H), 1.35 – 1.28 (m, 2H), 0.79 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 189.19, 146.40, 142.94, 142.61, 140.41, 130.78, 130.69, 129.94, 129.56, 129.52, 128.80, 128.73, 128.57, 128.49, 128.30, 126.88, 126.12, 125.97, 124.53, 124.23, 102.80, 99.32, 90.29, 76.41, 63.48, 63.30, 30.64, 22.41, 18.61, 13.72. **HRMS (ESI)** m/z Calcd for $[C_{30}H_{24}Br_2O_3NaS, M+ Na]^+$: 644.9813, Found: 644.9780. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 7.202 min (minor), t_R = 10.800 min (major). **Optical Rotation:** $[\alpha]_D^{20}$ = 99° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 71%, 44.1 mg.

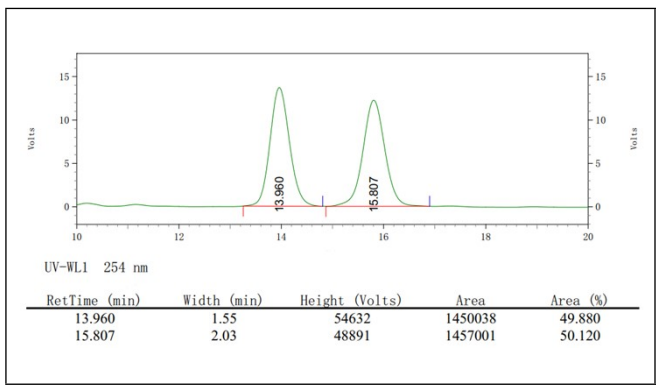




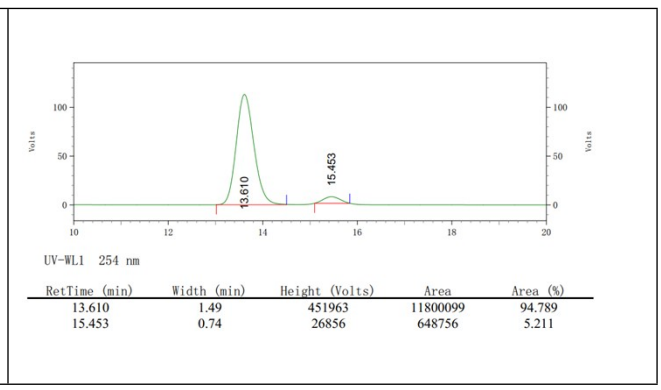
(*R*)-1-bromo-1-((*S*)-4-bromo-1-(2-fluoroethoxy)-1-(hex-1-yn-1-yl)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2h)



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 – 7.72 (m, 1H), 7.49 – 7.42 (m, 2H), 7.42 – 7.23 (m, 6H), 6.42 (d, *J* = 10.0 Hz, 1H), 4.92 – 4.58 (m, 2H), 4.48 – 4.21 (m, 2H), 2.45 (t, *J* = 7.1 Hz, 2H), 1.67 (p, *J* = 7.1 Hz, 2H), 1.52 (dq, *J* = 14.4, 7.2 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 190.18, 146.70, 144.55, 142.71, 131.83, 130.91, 130.78, 130.74, 130.17, 129.60, 129.54, 129.13, 128.89, 126.49, 124.75, 124.38, 102.60, 99.46, 91.46, 83.00 (d, *J* = 166.0 Hz), 75.58, 65.74 (d, *J* = 20.0 Hz), 63.43, 31.00, 22.64, 18.66, 13.85. **HRMS (ESI)** m/z Calcd for $[C_{27}H_{23}Br_2NaFO_3$, M+ Na$]^+$: 594.9998, Found: 594.9908. **HPLC analysis**: Chiralcel IC-H (Hexane/*i*-PrOH) =95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R =13.610 min (major), t_R = 15.453 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 99° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 74%, 42.3 mg.

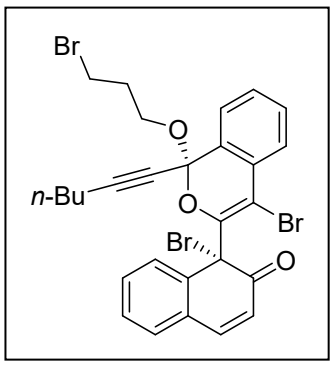


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
13.960	1.55	54632	1450038	49.880
15.807	2.03	48891	1457001	50.120

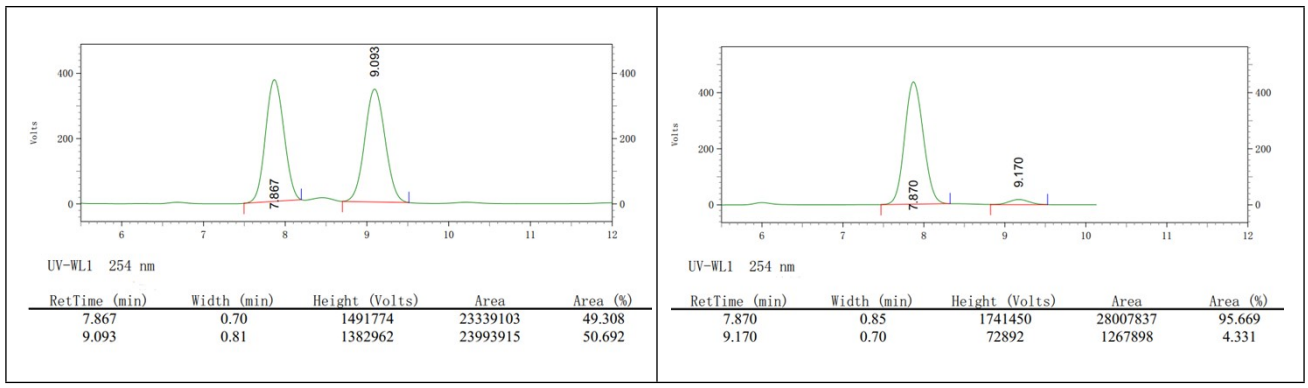


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
13.610	1.49	451963	11800099	94.789
15.453	0.74	26856	648756	5.211

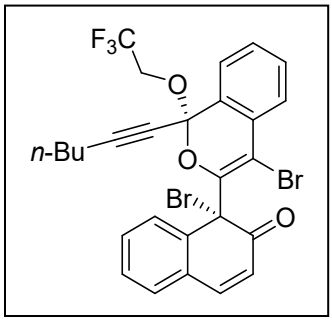
(*R*)-1-bromo-1-((*S*)-4-bromo-1-(3-bromopropoxy)-1-(hex-1-yn-1-yl)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2i)



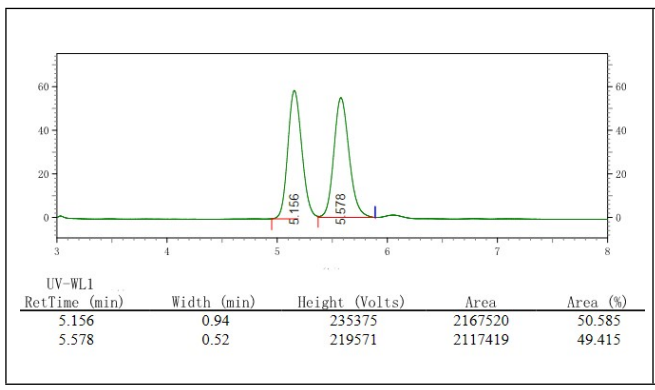
^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.79 – 7.74 (m, 1H), 7.70 (d, *J* = 10.1 Hz, 1H), 7.55 (m, 1H), 7.49 – 7.36 (m, 6H), 6.43 (d, *J* = 10.0 Hz, 1H), 4.30 (td, *J* = 8.7, 7.9, 5.1 Hz, 1H), 4.23 (dt, *J* = 9.6, 5.5 Hz, 1H), 3.55 (tt, *J* = 9.9, 5.4 Hz, 2H), 2.50 (t, *J* = 7.0 Hz, 2H), 2.35 – 2.26 (m, 1H), 2.25 – 2.15 (m, 1H), 1.66 (dt, *J* = 14.4, 6.9 Hz, 2H), 1.53 (dq, *J* = 14.1, 7.1 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $(CD_3)_2CO$): δ 189.90, 146.83, 144.31, 142.66, 131.70, 130.94, 130.74, 130.63, 130.07, 129.48, 129.43, 129.04, 128.79, 126.35, 124.65, 124.38, 102.25, 99.46, 91.24, 75.96, 64.44, 63.44, 33.35, 31.48, 30.97, 22.63, 18.71, 13.89. **HRMS (ESI)** m/z Calcd for $[C_{28}H_{25}Br_3NaO_3, M+ Na]^+$: 668.9354, Found: 668.9274. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 7.870 min (major), t_R = 9.170 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 102° (c = 1.0, CH_3OH); **Physical properties**: yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 77 %, 49.7 mg.

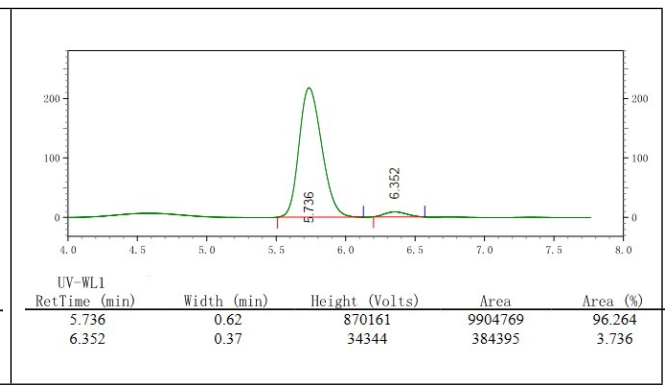


(*R*)-1-bromo-1-((*S*)-4-bromo-1-(hex-1-yn-1-yl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2j)

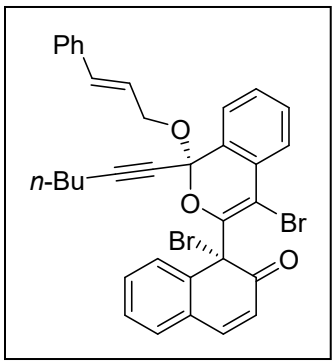


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 – 7.74 (m, 1H), 7.47 (d, *J* = 10.0 Hz, 1H), 7.42 (m, 4H), 7.38 – 7.28 (m, 3H), 6.44 (d, *J* = 10.0 Hz, 1H), 4.69 – 4.58 (m, 1H), 4.45 – 4.34 (m, 1H), 2.46 (t, *J* = 7.1 Hz, 2H), 1.67 (p, *J* = 7.1 Hz, 2H), 1.52 (dq, *J* = 14.3, 7.2 Hz, 2H), 0.98 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 189.75, 144.80, 143.43, 141.69, 130.85, 130.19, 129.54, 129.11, 128.78, 128.53, 128.37, 127.92, 125.89, 124.41, 123.84 (q, *J* = 276.0 Hz), 123.76, 102.72, 98.70, 91.01, 74.01, 63.43 (q, *J* = 35.0 Hz), 62.16, 30.12, 22.00, 18.40, 13.54. **HRMS (ESI)** m/z Calcd for $[C_{27}H_{21}Br_2F_3NaO_3, M+ Na]^+$: 630.9810, Found: 630.9710. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 5.736 min (major), t_R = 6.352 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 160° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 72%, 43.8 mg.

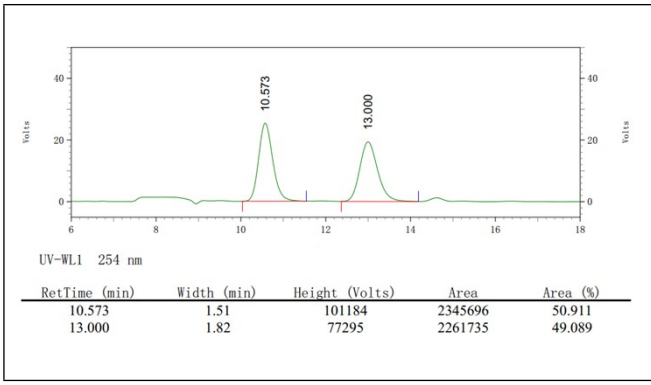




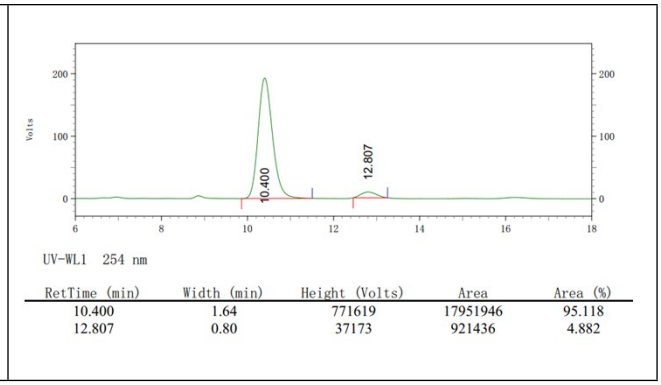
(*R*)-1-bromo-1-((*S*)-4-bromo-1-(cinnamyloxy)-1-(hex-1-yn-1-yl)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2k)



^{1}H NMR (400 MHz, Toluene-d_8): δ 7.94 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 8.2 Hz, 2H), 7.22 (d, J = 7.3 Hz, 2H), 7.12 (d, J = 7.5 Hz, 1H), 7.04 (t, J = 7.4 Hz, 3H), 6.97 (s, 1H), 6.80 (t, J = 7.3 Hz, 1H), 6.72 (td, J = 10.3, 9.4, 4.0 Hz, 5H), 6.23 (d, J = 10.0 Hz, 1H), 5.26 (dd, J = 11.6, 4.8 Hz, 1H), 5.07 (dd, J = 11.5, 5.9 Hz, 1H), 2.13 (t, J = 7.0 Hz, 2H), 1.45 – 1.36 (m, 2H), 1.36 – 1.29 (m, 2H), 0.79 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 189.18, 146.66, 142.88, 142.65, 137.60, 133.33, 131.04, 130.77, 129.94, 129.69, 129.51, 128.80, 128.74, 128.60, 128.52, 128.51, 127.53, 127.06, 126.38, 126.04, 124.60, 124.28, 102.71, 99.40, 90.00, 76.44, 67.64, 63.39, 30.72, 22.43, 18.64, 13.71. **HRMS (ESI)** m/z Calcd for $[C_{34}H_{28}Br_2NaO_3, M+Na]^+$: 665.0405, Found: 665.0385. **HPLC analysis**: Chiralcel IC-H (Hexane/*i*-PrOH) = 95:5, wave length = 254 nm, t_R = 10.400 min (major), t_R = 12.807 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 95° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 60%, 38.5 mg.

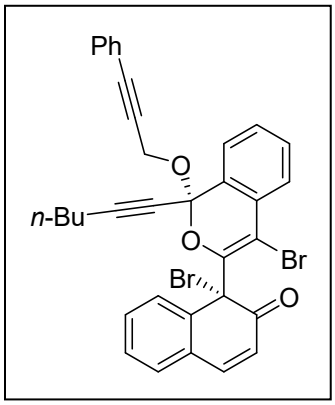


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
10.573	1.51	101184	2345696	50.911
13.000	1.82	77295	2261735	49.089

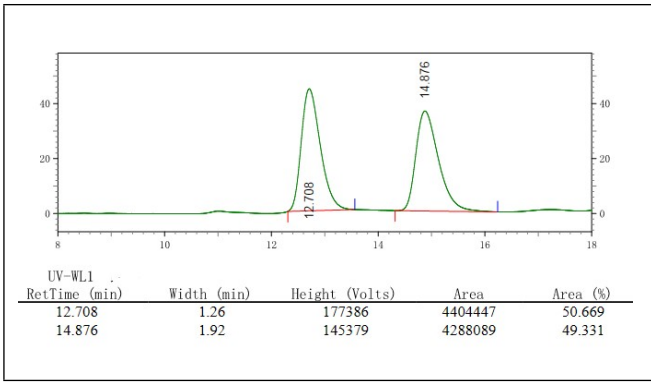


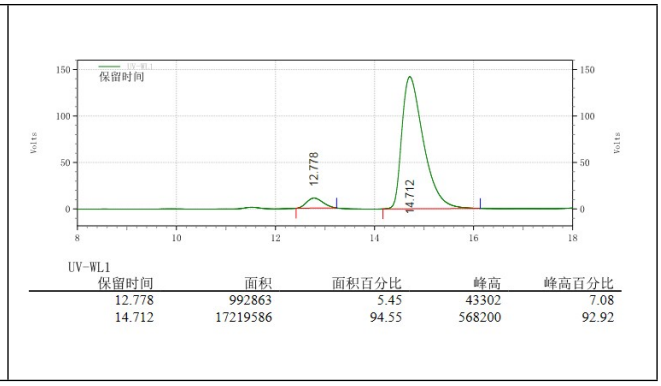
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
10.400	1.64	771619	17951946	95.118
12.807	0.80	37173	921436	4.882

(*R*)-1-bromo-1-((*S*)-4-bromo-1-(hex-1-yn-1-yl)-1-((3-phenylprop-2-yn-1-yl)oxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2l)

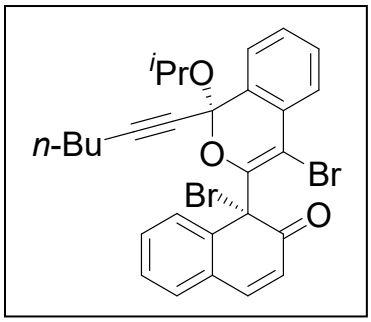


^{1}H NMR (400 MHz, Toluene-d_8): δ 7.92 (d, J = 7.4 Hz, 1H), 7.37 – 7.31 (m, 4H), 7.13 (d, J = 6.9 Hz, 1H), 7.09 – 7.04 (m, 1H), 6.99 – 6.92 (m, 3H), 6.90 – 6.81 (m, 3H), 6.77 (t, J = 7.4 Hz, 1H), 6.26 (d, J = 10.0 Hz, 1H), 5.54 (d, J = 15.2 Hz, 1H), 5.41 (d, J = 15.2 Hz, 1H), 2.13 (t, J = 6.9 Hz, 2H), 1.42 (dt, J = 14.3, 7.0 Hz, 2H), 1.33 (dt, J = 14.1, 7.0 Hz, 2H), 0.80 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 189.07, 146.25, 142.96, 142.54, 132.13, 130.75, 130.49, 130.10, 129.62, 129.59, 128.69, 128.55, 128.30, 126.20, 124.59, 124.24, 123.81, 102.94, 99.21, 90.73, 86.57, 86.36, 75.83, 63.19, 55.63, 30.60, 22.41, 18.63, 13.68. **HRMS (ESI)** m/z Calcd for [$C_{34}H_{26}Br_2NaO_3$, M+ Na]$^+$: 663.0249, Found: 663.0149. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 12.778 min (minor), t_R = 14.712 min (major). **Optical Rotation:** $[\alpha]_D^{20}$ = 105° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 60%, 38.4 mg.

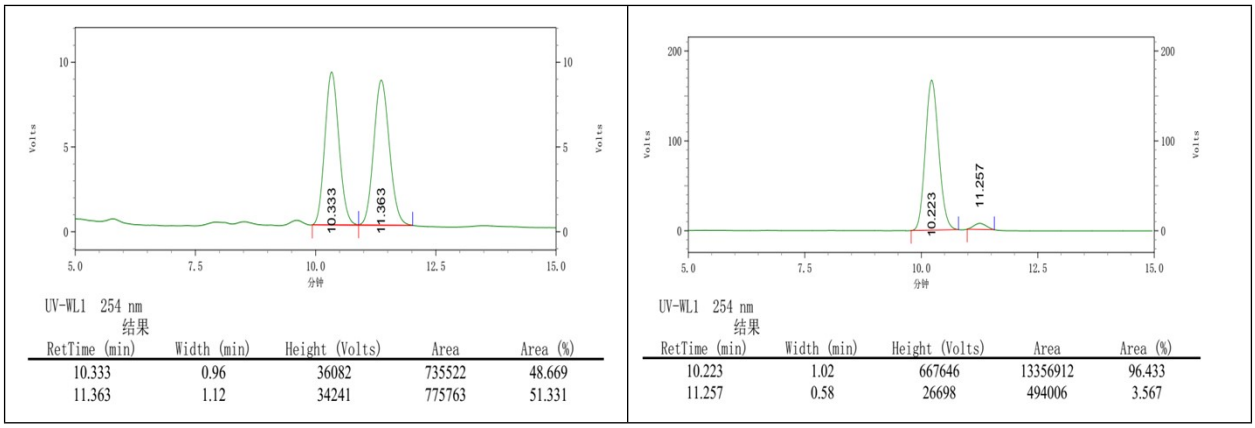




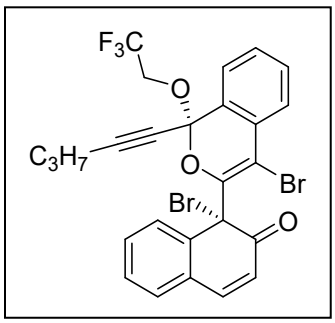
(*R*)-1-bromo-1-((*S*)-4-bromo-1-(hex-1-yn-1-yl)-1-propoxy-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2m)



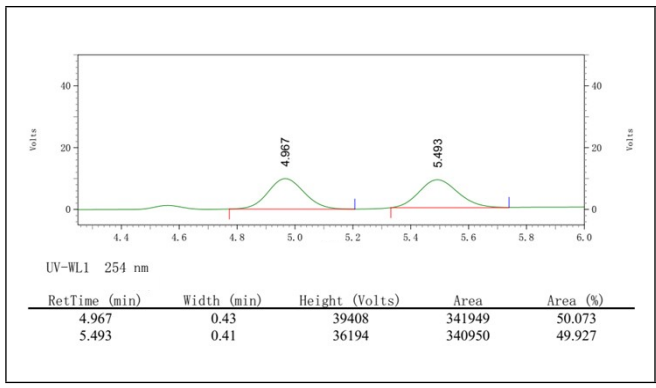
^{1}H NMR (400 MHz, Toluene-d_8) δ 7.80 (d, J = 7.7 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 7.8 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H), 6.99 – 6.95 (m, 1H), 6.84 (t, J = 7.8 Hz, 1H), 6.80 – 6.72 (m, 3H), 6.21 (d, J = 10.0 Hz, 1H), 5.09 (p, J = 6.2 Hz, 1H), 2.05 (t, J = 7.0 Hz, 2H), 1.60 (d, J = 6.2 Hz, 3H), 1.46 (d, J = 6.1 Hz, 3H), 1.36 (m, 2H), 1.31 – 1.23 (m, 2H), 0.77 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, Toluene-d_8) δ 188.31, 147.05, 142.64, 142.39, 131.25, 130.54, 129.57, 129.42, 129.24, 128.53, 128.31, 125.93, 124.44, 101.45, 98.96, 89.50, 78.13, 70.08, 63.67, 30.55, 23.96, 23.84, 22.32, 18.55, 13.62. **HRMS (ESI)** m/z Calcd for $[C_{28}H_{26}Br_2NaO_3, M+Na]^+$: 591.0249, Found: 591.0121. **HPLC analysis**: Chiralcel IC-H (Hexane/*i*-PrOH) =95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 10.223 min (major), t_R = 11.257 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 170 ° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 78%, 44.3 mg.



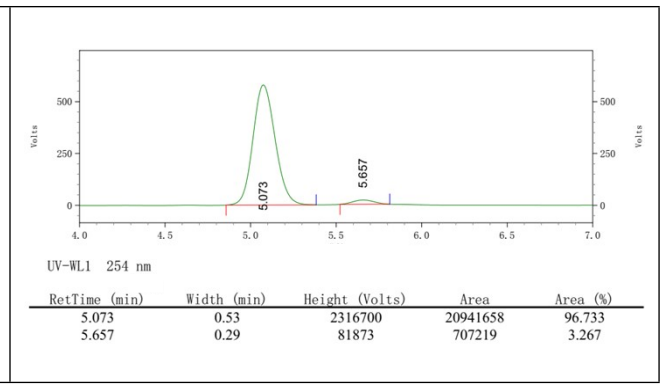
(*R*)-1-bromo-1-((*S*)-4-bromo-1-(pent-1-yn-1-yl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2n)



^{1}H NMR (400 MHz, Toluene-d_8): δ 7.85 – 7.81 (m, 1H), 7.24 (d, J = 7.6 Hz, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.07 – 7.02 (m, 1H), 7.02 – 6.97 (m, 1H), 6.83 (t, J = 7.3 Hz, 1H), 6.78 (d, J = 9.4 Hz, 2H), 6.72 (t, J = 7.5 Hz, 1H), 6.16 (d, J = 10.0 Hz, 1H), 4.97 (dt, J = 11.8, 8.8 Hz, 1H), 4.92 – 4.82 (m, 1H), 2.01 (t, J = 7.0 Hz, 2H), 1.37 (h, J = 7.2 Hz, 2H), 0.87 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 189.32, 145.69, 143.25, 142.24, 130.86, 130.49, 129.67, 129.46, 129.31, 128.95, 128.92, 128.59, 128.45, 126.21, 124.84 (q, J = 276.0 Hz), 124.73, 124.01, 103.27, 99.48, 91.10, 75.03, 64.25 (q, J = 35.0 Hz), 62.88, 21.90, 20.56, 13.48. **HRMS (ESI)** m/z Calcd for $[C_{26}H_{19}Br_2F_3NaO_3, M+Na]^+$: 616.9653, Found: 616.9583. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 95:2, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 5.073 min (major), t_R = 5.657 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 134° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 75%, 44.6 mg.

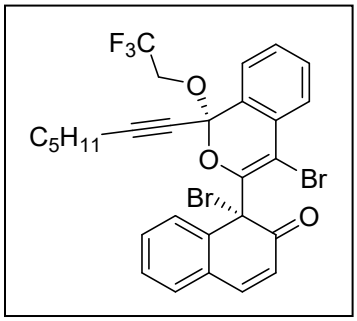


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
4.967	0.43	39408	341949	50.073
5.493	0.41	36194	340950	49.927

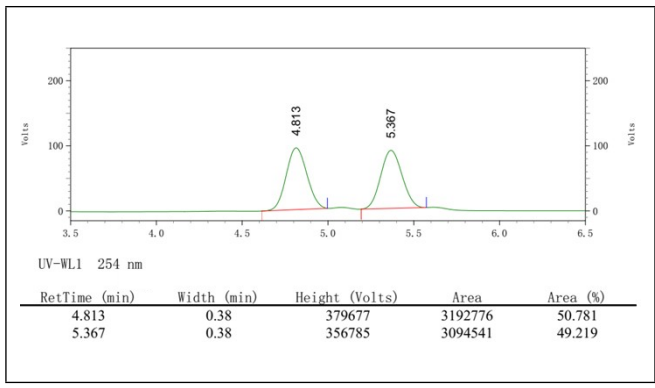


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
5.073	0.53	2316700	20941658	96.733
5.657	0.29	81873	707219	3.267

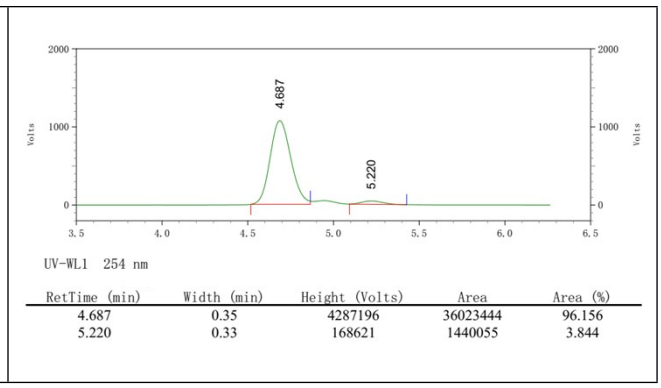
(*R*)-1-bromo-1-((*S*)-4-bromo-1-(hept-1-yn-1-yl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2o)



^{1}H NMR (400 MHz, Toluene-d_8) : δ 7.88 – 7.82 (m, 1H), 7.27 – 7.23 (m, 1H), 7.20 (d, J = 7.7 Hz, 1H), 7.03 (td, J = 7.5, 1.3 Hz, 1H), 6.98 (dd, J = 7.7, 1.5 Hz, 1H), 6.80 (td, J = 7.5, 1.2 Hz, 1H), 6.74 – 6.67 (m, 3H), 6.15 (d, J = 10.0 Hz, 1H), 4.99 (dq, J = 11.9, 8.8 Hz, 1H), 4.93 – 4.84 (dq, J = 11.9, 8.8 Hz, 1H), 2.08 – 2.04 (m, 2H), 1.39 (dt, J = 14.4, 6.7 Hz, 2H), 1.25 (m, 2H), 1.16 (m, 2H), 0.82 (t, J = 7.2 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.74, 144.81, 143.41, 141.72, 130.85, 130.19, 129.54, 129.11, 128.82, 128.77, 128.56, 128.40, 127.94, 125.91, 123.84 (q, J = 276.0 Hz), 124.42, 123.80, 102.72, 98.71, 91.07, 74.07, 63.44 (q, J = 35.0 Hz), 62.16, 31.05, 27.76, 22.13, 18.68, 13.96. **HRMS (ESI)** m/z Calcd for $[C_{28}H_{23}Br_2F_3NaO_3, M+ Na]^+$: 644.9966, Found: 644.9876. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 4.687 min (major), t_R = 5.220 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 211° (c = 1.0, $CHCl_3$); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 83%, 51.6 mg.

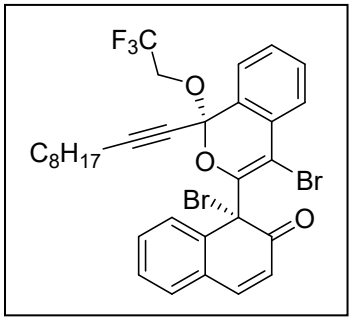


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
4.813	0.38	379677	3192776	50.781
5.367	0.38	356785	3094541	49.219

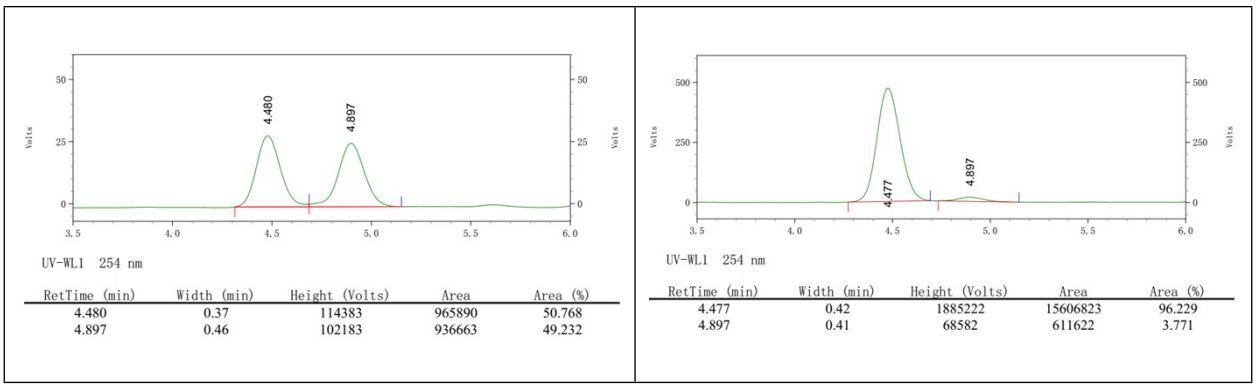


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
4.687	0.35	4287196	36023444	96.156
5.220	0.33	168621	1440055	3.844

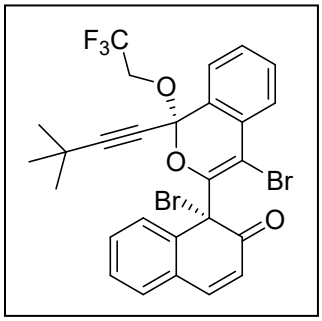
(*R*)-1-bromo-1-((*S*)-4-bromo-1-(dec-1-yn-1-yl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2p)



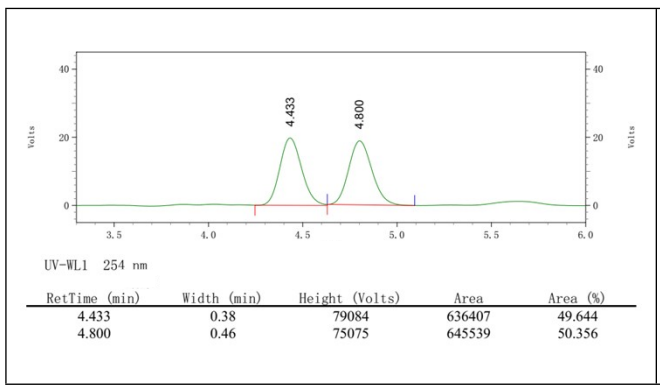
^{1}H NMR (400 MHz, Toluene-d_8) δ: 7.68 – 7.63 (m, 1H), 7.03 (d, J = 7.7 Hz, 1H), 6.98 (d, J = 7.7 Hz, 1H), 6.87 – 6.82 (m, 1H), 6.80 – 6.77 (m, 1H), 6.63 – 6.58 (m, 1H), 6.56 – 6.46 (m, 3H), 5.96 – 5.93 (d, 1H), 4.86 – 4.73 (m, 1H), 4.68 (dt, J = 11.8, 8.9 Hz, 1H), 1.88 (t, J = 7.0 Hz, 2H), 1.20 (dt, J = 14.2, 6.9 Hz, 2H), 1.13 – 0.89 (m, 10H), 0.66 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (100MHz, Toluene-d_8): δ 189.31, 145.70, 143.21, 142.27, 130.85, 130.49, 129.64, 129.48, 129.34, 128.45, 126.24, 124.86 (q, J = 275.0 Hz), 124.75, 124.02, 103.30, 99.51, 91.25, 74.95, 64.29 (q, J = 35.0 Hz), 62.87, 32.14, 29.19, 29.13, 28.47, 23.03, 18.72, 14.33. **HRMS (ESI)** m/z Calcd for $[C_{31}H_{29}Br_2F_3NaO_3, M + Na]^+$: 687.0436, Found: 687.0386. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 4.477 min (major), t_R = 4.897 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 200° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 87%, 57.7 mg.



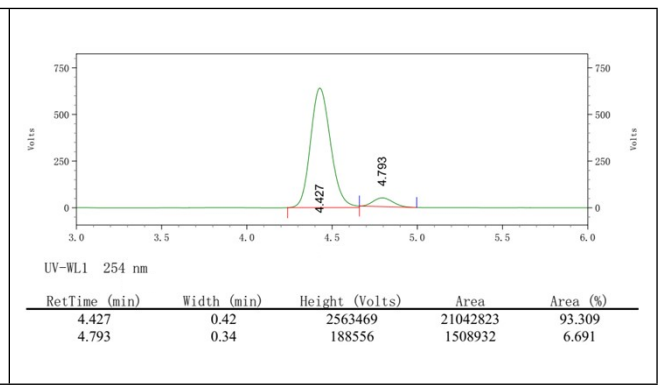
(*R*)-1-bromo-1-((*S*)-4-bromo-1-(3,3-dimethylbut-1-yn-1-yl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2q)



^{1}H NMR (400 MHz, Toluene-d_8) δ 7.88 – 7.83 (m, 1H), 7.24 (d, J = 7.6 Hz, 1H), 7.12 (d, J = 7.8 Hz, 1H), 7.07 – 7.02 (m, 1H), 7.00 – 6.96 (m, 1H), 6.79 (t, J = 7.2 Hz, 1H), 6.74 – 6.64 (m, 3H), 6.14 (d, J = 10.0 Hz, 1H), 4.99 (dq, J = 12.0, 8.9 Hz, 1H), 4.93 – 4.82 (m, 1H), 1.19 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 189.78, 144.84, 143.40, 141.76, 130.85, 130.17, 129.53, 129.10, 128.88, 128.78, 128.59, 128.43, 127.94, 125.87, 124.42, 123.81, 123.86 (q, J = 276.0 Hz), 102.74, 98.72, 98.59, 72.67, 63.43 (q, J = 35.0 Hz), 62.11, 30.47, 27.69. **HRMS (ESI)** m/z Calcd for $[C_{27}H_{21}Br_2F_3NaO_3, M+ Na]^+$: 630.9810, Found: 630.9750. **HPLC analysis**: Chiralcel IA -H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 4.427 min (major), t_R = 4.793 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 166° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 86%, 52.3 mg.

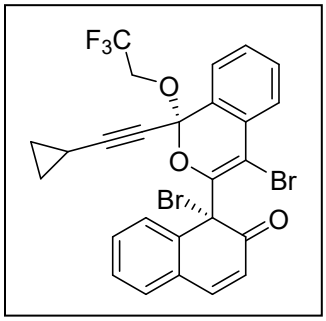


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
4.433	0.38	79084	636407	49.644
4.800	0.46	75075	645539	50.356

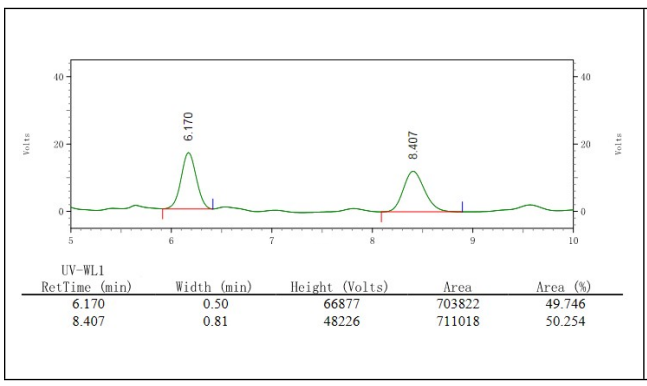


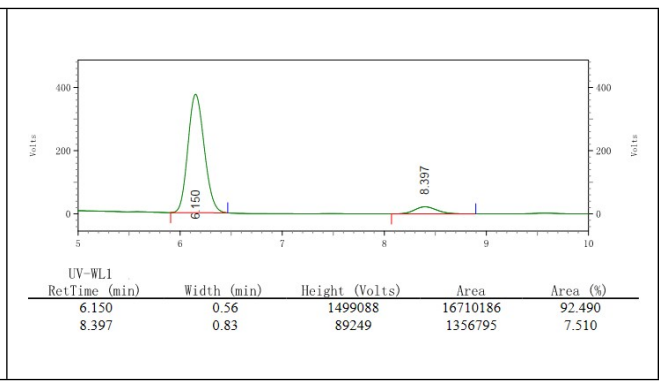
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
4.427	0.42	2563469	21042823	93.309
4.793	0.34	188556	1508932	6.691

(*R*)-1-bromo-1-((*S*)-4-bromo-1-(cyclopropylethynyl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2r)

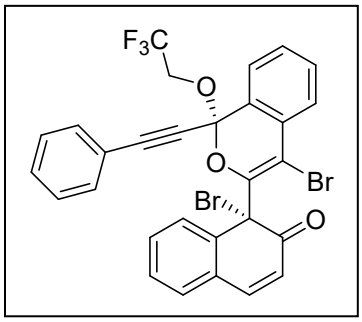


^{1}H NMR (400 MHz, Toluene-d_8): δ 7.80 – 7.75 (m, 1H), 7.25 – 7.20 (m, 1H), 7.16 (d, J = 7.7 Hz, 1H), 7.04 – 6.96 (m, 2H), 6.83 (t, J = 7.2 Hz, 1H), 6.77 (d, J = 9.8 Hz, 2H), 6.74 – 6.67 (m, 1H), 6.15 (d, J = 10.0 Hz, 1H), 4.99 – 4.77 (m, 2H), 1.05 (m, 1H), 0.68 – 0.62 (m, 2H), 0.44 (dq, J = 6.3, 3.4 Hz, 2H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 189.34, 145.67, 143.27, 142.18, 137.48, 130.87, 130.48, 129.67, 129.43, 129.25, 128.94, 128.56, 128.40, 124.81 (q, J = 276.0 Hz), 124.70, 123.97, 103.27, 99.45, 94.14, 69.67, 64.17 (q, J = 36.0 Hz), 62.81, 8.77, 8.68, -0.45. **HRMS (ESI)** m/z Calcd for $[C_{26}H_{17}Br_2F_3NaO_3, M + Na]^+$: 614.9497, Found: 614.9428. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 85:15), flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 6.150 min (major), t_R =8.397 (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 84° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 72%, 42.6 mg.

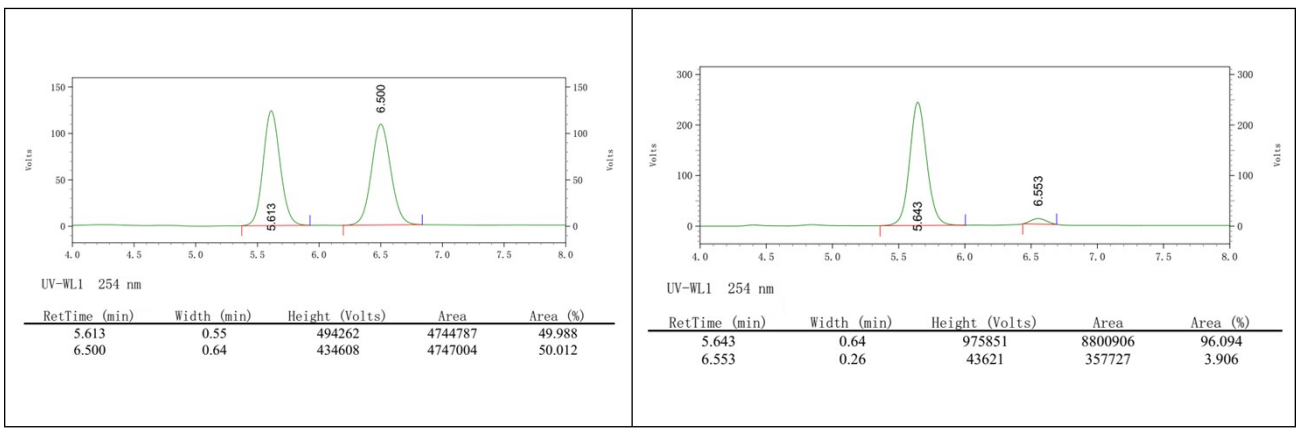




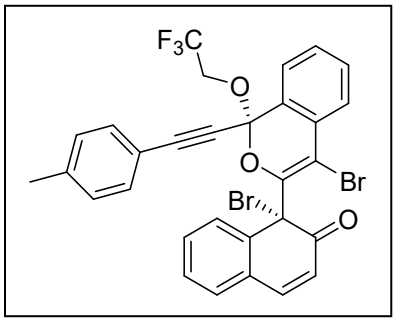
(*R*)-1-bromo-1-((*S*)-4-bromo-1-(phenylethynyl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2s)



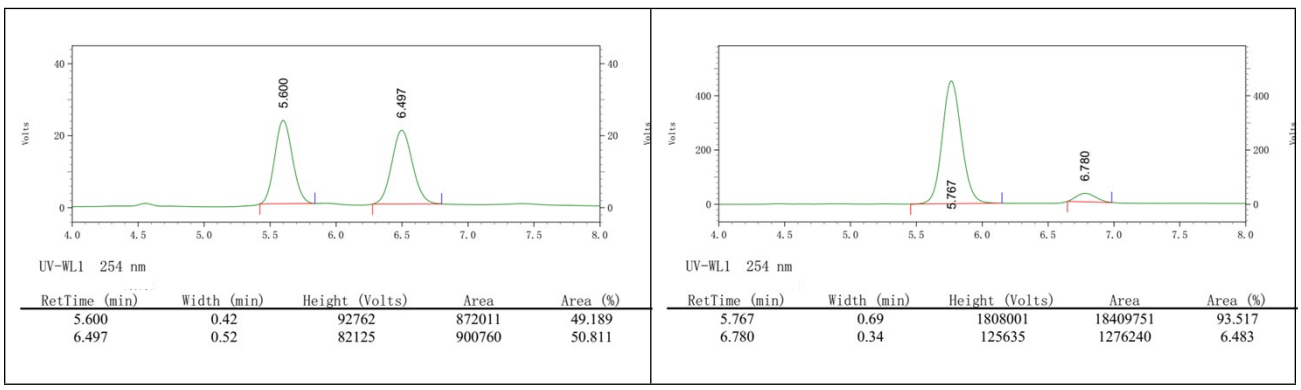
^{1}H NMR (400 MHz, Toluene-d_8)**:** δ 7.88 – 7.84 (m, 1H), 7.44 – 7.38 (m, 2H), 7.29 – 7.20 (m, 2H), 7.05 – 6.98 (m, 3H), 6.96 (d, *J* = 7.7 Hz, 2H), 6.85 – 6.80 (m, 1H), 6.73 (dd, *J* = 15.5, 8.8 Hz, 3H), 6.17 (d, *J* = 10.0 Hz, 1H), 5.06 (dq, *J* = 11.9, 8.7 Hz, 1H), 5.00 – 4.89 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 189.75, 144.76, 143.51, 141.64, 132.13, 130.91, 130.42, 129.80, 129.59, 129.15, 128.96, 128.56, 128.53, 128.48, 128.37, 127.92, 125.89, 124.56, 123.82 (q, *J* =276.0 Hz), 123.73, 120.57, 102.89, 99.08, 89.04, 82.28, 63.68 (q, *J* = 35.0 Hz), 62.11. **HRMS (ESI)** m/z Calcd for $[C_{29}H_{17}Br_2F_3NaO_3, M + Na]^+$: 650.9497, Found: 650.9397. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 5.643 min (major), t_R = 6.553 (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 170° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 72 %, 45.2 mg.



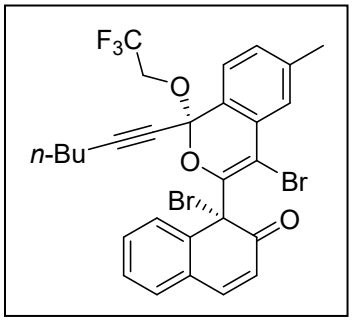
(*R*)-1-bromo-1-((*S*)-4-bromo-1-(p-tolylethynyl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2t)



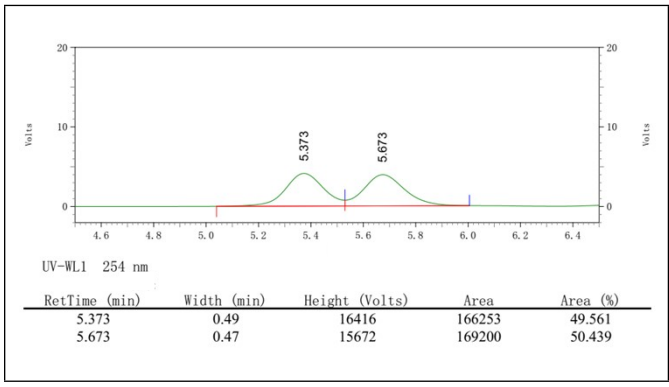
^{1}H NMR (400 MHz, Toluene-d_8): δ 7.92 – 7.87 (m, 1H), 7.38 (d, J = 8.0 Hz, 2H), 7.29 – 7.21 (m, 2H), 7.02 – 6.97 (m, 2H), 6.78 (t, J = 7.9 Hz, 3H), 6.75 – 6.68 (m, 3H), 6.16 (d, J = 10.0 Hz, 1H), 5.08 (dq, J = 11.9, 8.7 Hz, 1H), 5.00 – 4.89 (m, 1H), 1.98 (s, 3H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 189.23, 145.69, 143.08, 142.36, 140.17, 132.37, 130.85, 130.56, 129.58, 129.39, 129.37, 128.69, 128.49, 126.30, 124.86 (q, J =276.0 Hz), 124.83, 124.11, 118.13, 103.49, 100.00, 89.86, 82.62, 64.53 (q, J =35.0 Hz), 62.75, 21.30. **HRMS (ESI)** m/z Calcd for $[C_{30}H_{19}Br_2F_3NaO_3, M + Na]^+$: 664.9653, Found: 664.9547. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 5.767 min (major), t_R = 6.780 (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 171° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 79 %, 50.7 mg.

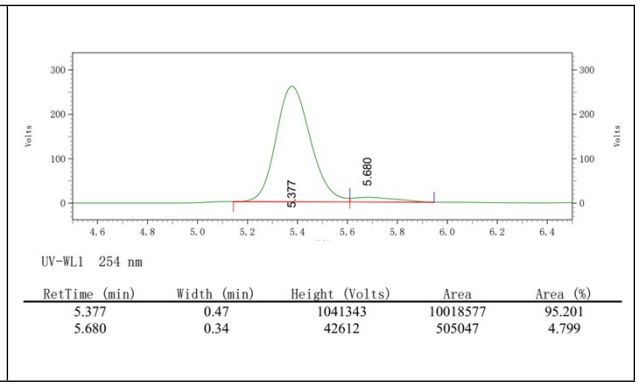


(*R*)-1-bromo-1-((*S*)-4-bromo-1-(hex-1-yn-1-yl)-6-methyl-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2u)

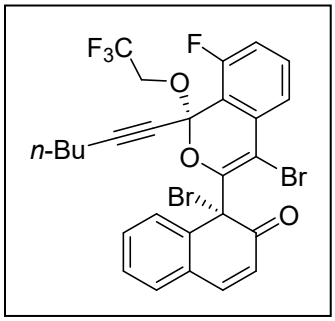


^{1}H NMR (400 MHz, Toluene-d_8): δ 7.78 (d, J = 7.8 Hz, 1H), 7.24 (d, J = 7.7 Hz, 1H), 7.13 (s, 1H), 6.86 (d, J = 7.8 Hz, 1H), 6.84 – 6.79 (m, 1H), 6.72 (m, 3H), 6.16 (d, J = 10.0 Hz, 1H), 5.06 – 4.86 (m, 2H), 2.05 (d, J = 7.0 Hz, 2H), 1.95 (s, 3H), 1.40 – 1.26 (m, 4H), 0.79 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 189.34, 145.65, 143.21, 142.36, 140.64, 130.81, 129.70, 129.66, 129.18, 128.90, 128.61, 128.48, 127.03, 126.31, 125.22, 124.91 (q, J = 275.0 Hz), 124.04, 103.40, 99.55, 90.93, 75.03, 64.24 (q, J = 35.0 Hz), 62.94, 30.47, 22.30, 21.14, 18.40, 13.60. **HRMS (ESI)** m/z Calcd for $[C_{28}H_{23}Br_2F_3NaO_3, M + Na]^+$: 644.9966, Found: 644.9866. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 5.377 min (major), t_R = 5.680 (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 160° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 74%, 46.0mg.

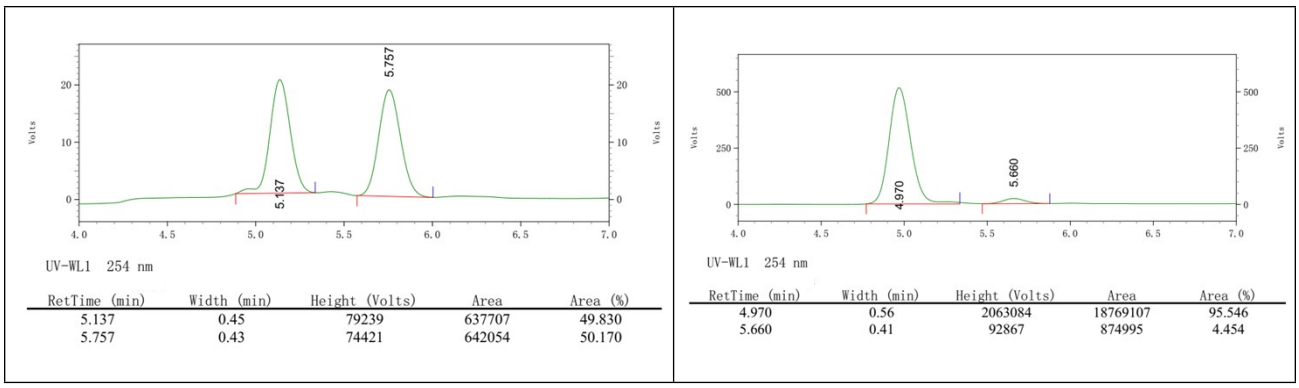




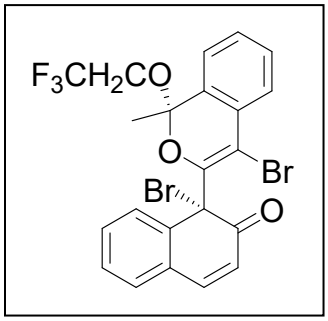
(*R*)-1-bromo-1-((*S*)-4-bromo-8-fluoro-1-(hex-1-yn-1-yl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2v)



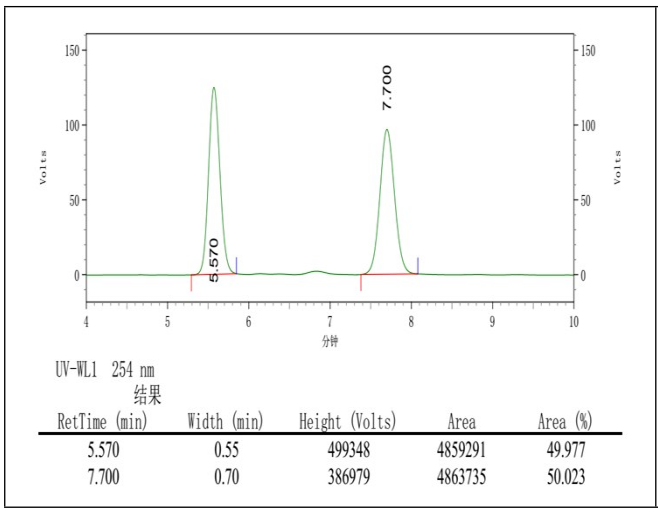
^{1}H NMR (400 MHz, Toluene-d_8) δ 7.64 (dd, J = 8.4, 2.5 Hz, 1H), 7.19 (d, J = 7.7 Hz, 1H), 7.06 (dd, J = 8.5, 5.1 Hz, 1H), 6.84 (d, J = 7.4 Hz, 1H), 6.76 (m, 3H), 6.62 (t, J = 8.4 Hz, 1H), 6.16 (d, J = 10.0 Hz, 1H), 4.87 (m, 2H), 2.00 (t, J = 6.8 Hz, 2H), 1.27 (m, 4H), 0.76 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, Toluene-d_8) δ: 189.28, 163.02 (d, J = 248.0 Hz), 145.20 (d, J = 2.0 Hz), 143.28, 142.15, 131.32 (d, J = 8.0 Hz), 131.28, 130.87, 129.71, 129.04, 128.54, 128.44, 127.07 (d, J = 8.0 Hz), 125.68 (d, J = 2.0 Hz), 124.71 (q, J = 276.0 Hz), 123.98, 117.46 (d, J = 22.0 Hz), 113.06 (d, J = 25.0 Hz), 102.36, 98.84, 91.82, 74.26, 64.31 (q, J = 36.0 Hz), 62.65, 30.30, 22.25, 18.25, 13.49. **HRMS (ESI)** m/z Calcd for $[C_{27}H_{20}Br_2F_4NaO_3, M + Na]^+$: 648.9715, Found: 648.9621. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 4.970 min (major), t_R = 5.660 (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 236° (c = 1.0, CH_2Cl_2); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 79%, 49.4 mg.

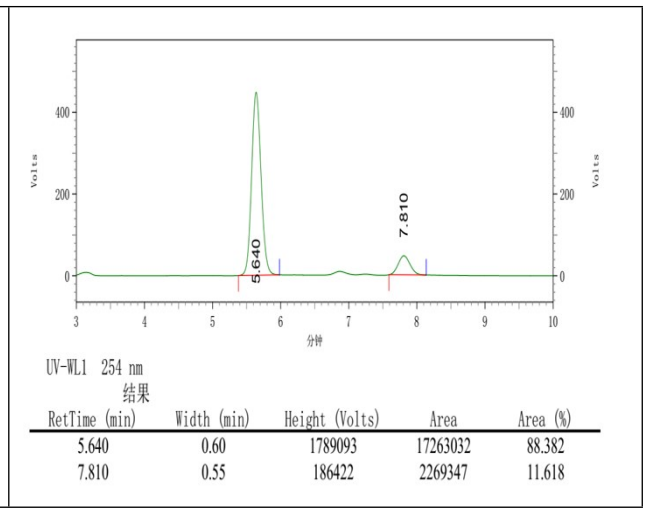


(*R*)-1-bromo-1-((*S*)-4-bromo-1-methyl-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (2w)

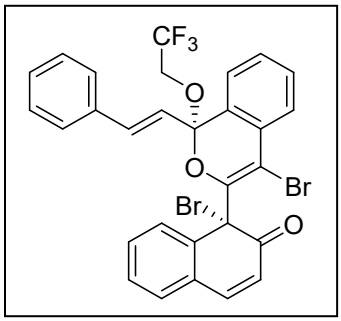


^{1}H NMR (400 MHz, Toluene-d_8) δ 7.30 – 7.24 (m, 2H), 7.08 – 7.04 (m, 1H), 6.98 – 6.93 (m, 2H), 6.88 – 6.80 (m, 2H), 6.80 – 6.73 (m, 2H), 6.17 (d, J = 9.9 Hz, 1H), 4.50 (dq, J = 12.0, 8.8 Hz, 1H), 4.10 (dq, J = 12.0, 8.9 Hz, 1H), 1.92 (s, 3H).**^{13}C NMR** (100 MHz, Toluene-d_8) δ 189.03, 146.98, 143.05, 142.27, 130.72, 129.91, 129.78, 129.74, 128.95, 128.50, 124.76, 124.74 (q, J = 275.0 Hz), 124.58, 124.13, 103.92, 101.39, 63.23, 62.36 (q, J = 35.0 Hz), 48.07, 25.37. **HRMS (ESI)** m/z Calcd for $[C_{22}H_{15}Br_2F_3NaO_3, M+ Na]^+$: 564.9340, Found: 564.9295. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 5.640 min (major), t_R = 7.810 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 109° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 86%, 46.5 mg.

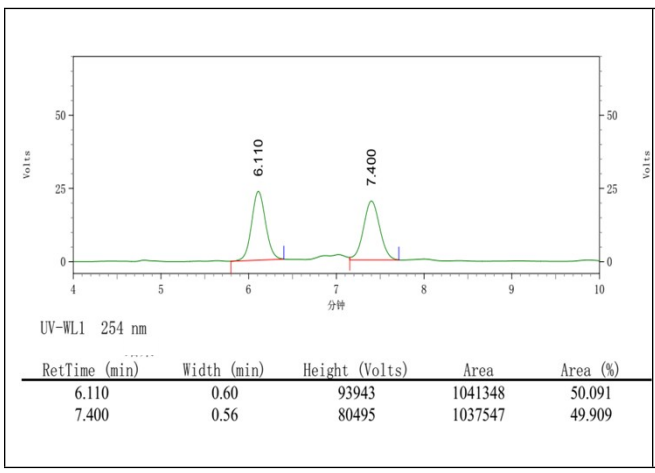




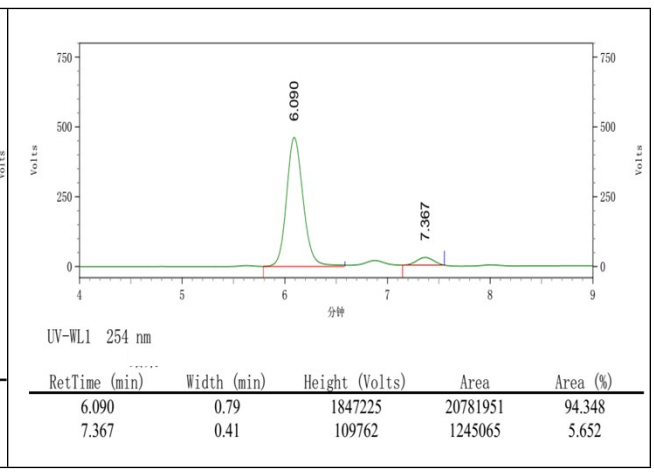
(*R*)-1-bromo-1-((*S*)-4-bromo-1-((*E*)-styryl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (4a)



^{1}H NMR (400 MHz, Toluene-d_8) δ: 7.37 (d, J = 7.5 Hz, 1H), 7.33 (dd, J = 7.1, 1.5 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.26 – 7.21 (m, 2H), 7.14 (d, J = 16.1 Hz, 1H), 7.12 – 7.05 (m, 3H), 7.01 – 6.96 (m, 2H), 6.83 (t, J = 7.4 Hz, 1H), 6.79 – 6.69 (m, 4H), 6.19 (d, J = 10.0 Hz, 1H), 4.59 – 4.49 (m, 1H), 4.44 (dq, J = 11.9, 8.8 Hz, 1H). **^{13}C NMR** (100 MHz, Toluene-d_8) δ: 189.09, 146.28, 143.10, 142.39, 136.18, 135.65, 130.79, 130.31, 130.14, 129.76, 129.26, 129.05, 128.97, 128.58, 128.36, 127.55, 125.85, 125.55, 124.91 (q, J = 276.0 Hz), 124.13, 104.17, 102.47, 63.30, 63.07 (q, J = 36.0 Hz). **HRMS (ESI)** m/z Calcd for [$C_{29}H_{19}Br_2F_3NaO_3$, M + Na]$^+$: 652.9653, Found: 652.9543. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 6.090 min (major), t_R = 7.367 (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 57° (c = 1.0, CH_2Cl_2); **Physical properties:** yellow foam; **Yield:** (Alumina N-neutral, PE:EA= 10:1) 85 %, 53.4 mg.

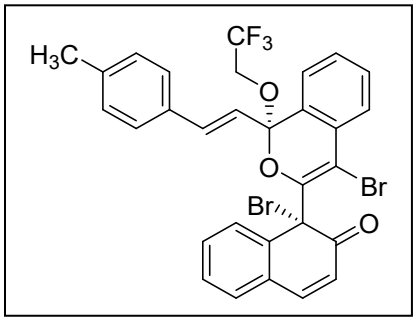


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.110	0.60	93943	1041348	50.091
7.400	0.56	80495	1037547	49.909

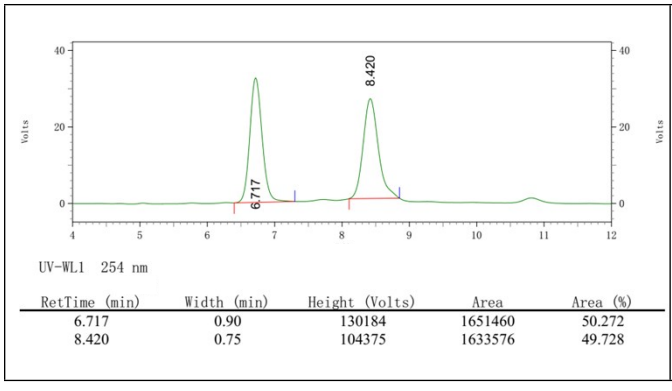


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.090	0.79	1847225	20781951	94.348
7.367	0.41	109762	1245065	5.652

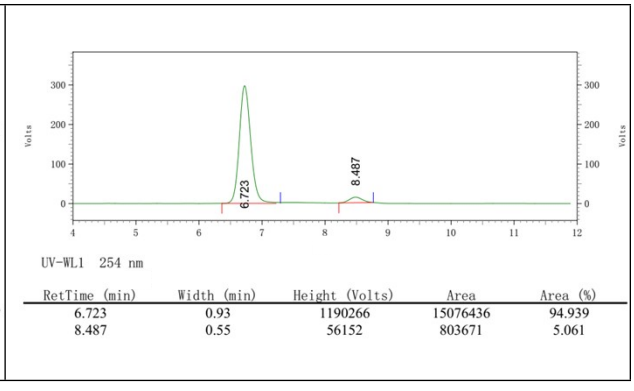
(*R*)-1-bromo-1-((*S*)-4-bromo-1-((*E*)-4-methylstyryl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (4b)



^{1}H NMR (400 MHz, Toluene-d_8) δ 7.38 (d, J = 7.5 Hz, 1H), 7.35 – 7.28 (m, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 16.1 Hz, 1H), 6.97 (d, J = 5.4 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 6.85 – 6.79 (m, 1H), 6.79 – 6.70 (m, 4H), 6.18 (d, J = 10.0 Hz, 1H), 4.61 – 4.50 (m, 1H), 4.50 – 4.39 (m, 1H), 2.11 (s, 3H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 189.07, 146.32, 143.03, 142.45, 138.95, 136.13, 133.01, 130.78, 130.36, 130.08, 129.80, 129.72, 129.41, 128.93, 128.40, 127.55, 125.89, 124.95 (q, J = 275.0 Hz), 124.82, 124.56, 124.17, 104.33, 102.46, 63.30, 63.07 (q, J = 34.0 Hz), 21.18. **HRMS (ESI)** m/z Calcd for $[C_{30}H_{21}Br_2F_3NaO_3, M + Na]^+$: 666.9810, Found: 666.9710. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 6.723 min (major), t_R = 8.487 (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 83° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (Alumina N-neutral, PE:EA= 10:1) 86%, 55.3 mg.

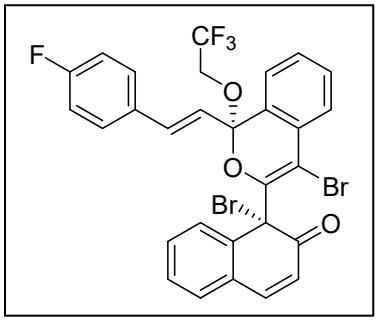


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.717	0.90	130184	1651460	50.272
8.420	0.75	104375	1633576	49.728

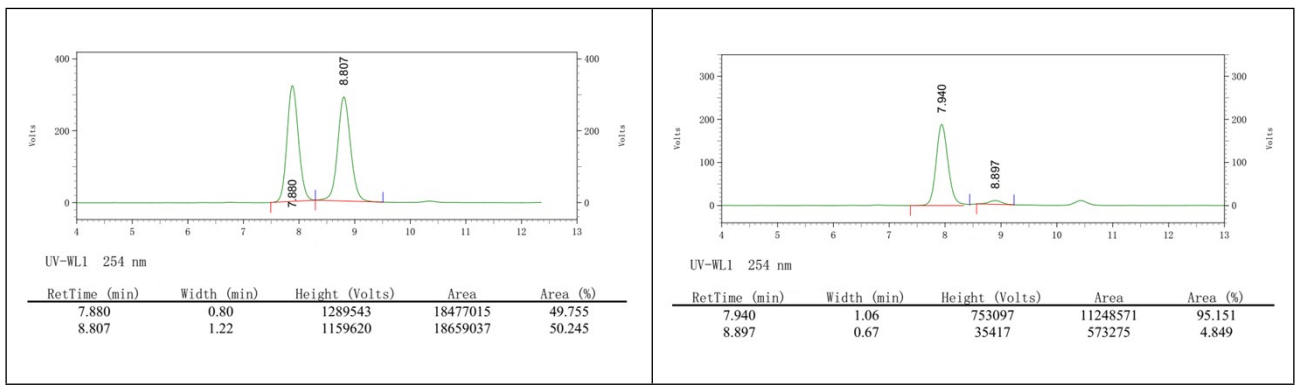


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.723	0.93	1190266	15076436	94.939
8.487	0.55	56152	803671	5.061

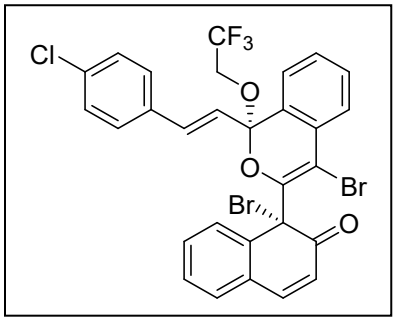
(*R*)-1-bromo-1-((*S*)-4-bromo-1-((*E*)-4-fluorostyryl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (4c)



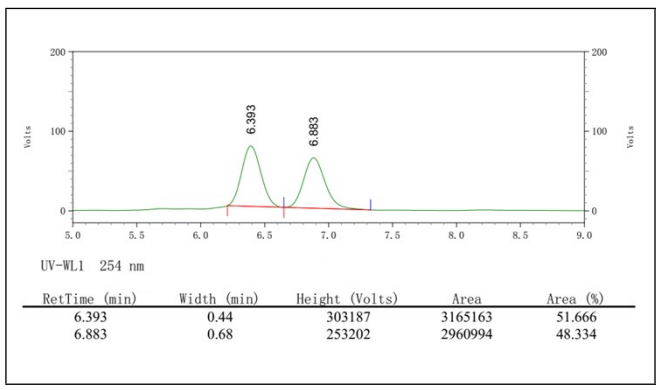
^{1}H NMR (400 MHz, Toluene-d_8): δ 7.40 – 7.31 (m, 2H), 7.26 (dd, J = 6.1, 2.7 Hz, 1H), 6.98 (m, 5H), 6.85 – 6.80 (m, 1H), 6.74 (m, 5H), 6.57 (d, J = 16.1 Hz, 1H), 6.18 (d, J = 10.0 Hz, 1H), 4.52 (dq, J = 11.6, 8.7 Hz, 1H), 4.45 – 4.35 (m, 1H). **^{13}C NMR** (100 MHz, Toluene-d_8) δ: 189.00, 163.44 (d, J = 248.0 Hz), 146.34, 143.03, 142.41, 134.74, 131.81, 131.78 (d, J = 3.0 Hz), 130.71, 130.39, 130.20, 129.78, 129.26, 129.18, 128.97, 128.95, 128.31, 125.83, 125.55, 124.88 (q, J = 275.0 Hz), 124.19, 116.04, 115.82, 104.17, 102.37, 63.28, 63.06 (q, J = 35.0 Hz). **HRMS (ESI)** m/z Calcd for $[C_{29}H_{18}Br_2F_4NaO_3, M + Na]^+$: 670.9559, Found: 670.9478. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 7.940 min (major), t_R = 8.897 (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 300° (c = 1.0, CH_3OH). **Physical properties:** yellow foam; **Yield:** (Alumina N-neutral, PE:EA= 10:1) 90 %, 58.3 mg.

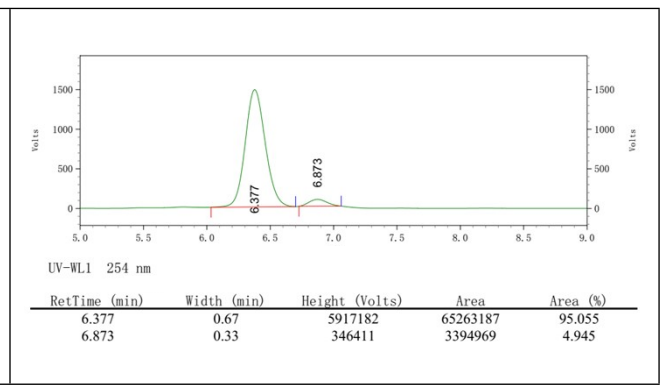


(*R*)-1-bromo-1-((*S*)-4-bromo-1-((*E*)-4-chlorostyryl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (4d)

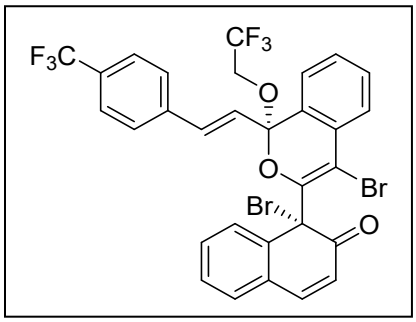


^{1}H NMR (400 MHz, Toluene-d_8) δ 7.38 – 7.32 (m, 2H), 7.27 – 7.24 (m, 1H), 7.05 – 6.97 (m, 5H), 6.94 (d, J = 8.5 Hz, 2H), 6.88 – 6.83 (m, 1H), 6.82 – 6.76 (m, 3H), 6.63 (d, J = 16.1 Hz, 1H), 6.19 (d, J = 10.0 Hz, 1H), 4.52 (dq, J = 11.8, 8.7 Hz, 1H), 4.46 – 4.35 (m, 1H). **^{13}C NMR** (100 MHz, Toluene-d_8) δ 189.10, 146.27, 143.18, 142.30, 134.87, 134.66, 134.05, 130.77, 130.29, 129.85, 129.22, 129.01, 128.95, 128.71, 128.27, 126.33, 125.81, 124.92, 124.85 (q, J = 276.0 Hz), 124.11, 104.02, 102.40, 63.30, 63.04 (q, J = 35.0 Hz). **HRMS (ESI)** m/z Calcd for $[C_{29}H_{18}Br_2ClF_3NaO_3$, M+ Na$]^+$: 686.9263, Found: 686.9185. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) =90:10, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 6.377 min (major), t_R = 6.873 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 110° (c = 1.0, CH_2Cl_2); **Physical properties:** (Alumina N-neutral, PE:EA= 10:1) yellow foam; **Yield:** 81%, 53.7 mg.

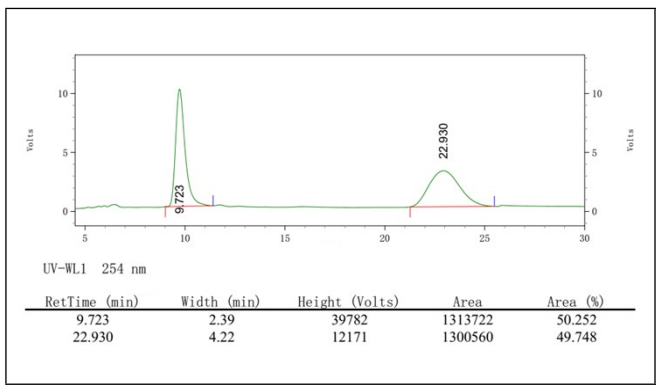


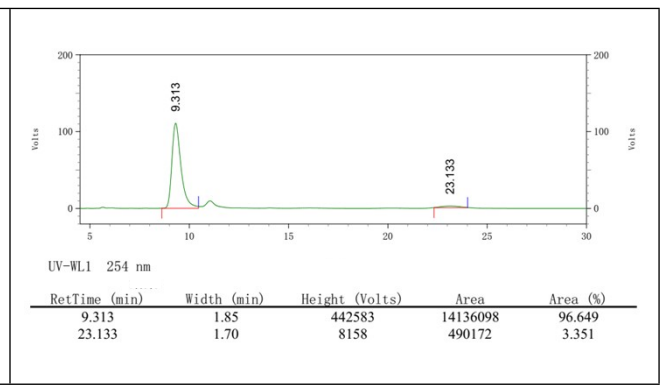


(*R*)-1-bromo-1-((*S*)-4-bromo-1-(2,2,2-trifluoroethoxy)-1-((*E*)-4-(trifluoromethyl)styryl)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (4e)

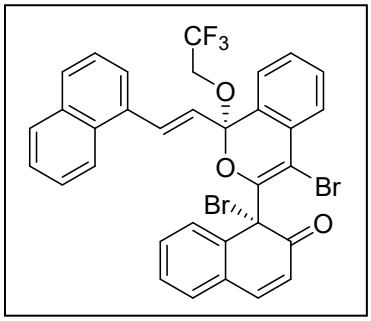


^{1}H NMR (400 MHz, Toluene-d_8): δ 7.39 – 7.33 (m, 2H), 7.32 – 7.24 (m, 3H), 7.10 – 7.01 (m, 5H), 6.86 – 6.82 (m, 1H), 6.81 – 6.68 (m, 4H), 6.20 (d, J = 10.0 Hz, 1H), 4.60 – 4.49 (m, 1H), 4.48 – 4.37 (m, 1H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 189.10, 146.25, 143.21, 142.27, 138.94, 134.38, 130.76, 130.67 (q, J = 32.0 Hz), 130.39, 130.26, 129.89, 128.85, 128.73, 128.35, 126.19, 126.12, 125.88, 124.81 (q, J = 276.0 Hz), 125.87, 125.81, 125.00, 124.10, 123.43, 120.67, 103.77, 102.43, 63.30, 63.10 (q, J = 35.0 Hz). **HRMS (ESI)** m/z Calcd for $[C_{30}H_{18}Br_2F_6NaO_3, M+Na]^+$: 720.9527, Found: 720.9487. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) =95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 9.313 min (major), t_R = 23.133 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 83° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (Alumina N-neutral, PE:EA= 10:1) 84%, 58.6 mg.

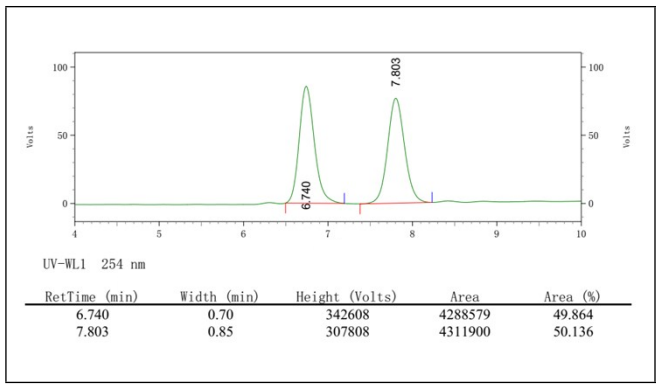




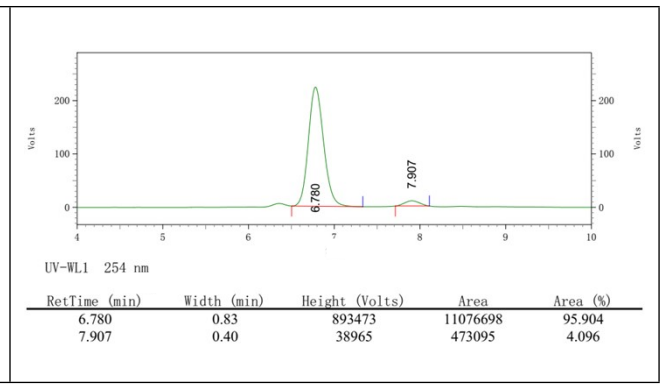
(*R*)-1-bromo-1-((*S*)-4-bromo-1-((*E*)-2-(naphthalen-1-yl)vinyl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (4f)



^{1}H NMR (400 MHz, Toluene-d_8) δ 8.15 – 8.10 (m, 1H), 8.02 (d, J = 15.8 Hz, 1H), 7.59 (dd, J = 9.3, 4.9 Hz, 3H), 7.40 (d, J = 7.7 Hz, 1H), 7.35 (ddt, J = 9.6, 6.8, 3.5 Hz, 2H), 7.27 – 7.22 (m, 1H), 7.22 – 7.17 (m, 2H), 7.02 – 6.98 (m, 2H), 6.83 – 6.68 (m, 5H), 6.19 (d, J = 10.0 Hz, 1H), 4.65 (dq, J = 11.8, 8.7 Hz, 1H), 4.59 – 4.48 (m, 1H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 189.12, 146.24, 143.12, 142.39, 134.24, 133.53, 133.36, 131.98, 130.84, 130.35, 130.18, 129.75, 129.53, 129.29, 129.03, 128.98, 128.94, 128.58, 128.37, 126.89, 126.25, 125.87, 125.84, 124.96 (q, J = 276.0 Hz), 124.91, 124.64, 124.13, 123.70, 104.07, 102.48, 63.39, 63.15 (q, J = 34.0 Hz). **HRMS (ESI)** m/z Calcd for $[C_{33}H_{21}Br_2F_3NaO_3, M+Na]^+$: 702.9810, Found: 702.9759. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) =95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 6.780 min (major), t_R = 7.907 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 126° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (Alumina N-neutral, PE:EA= 10:1) 90%, 61.2 mg.

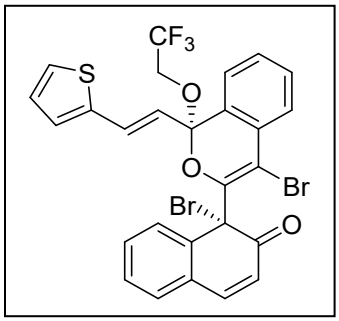


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.740	0.70	342608	4288579	49.864
7.803	0.85	307808	4311900	50.136

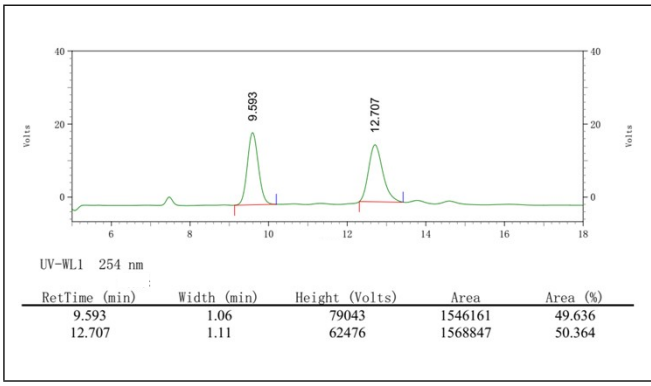


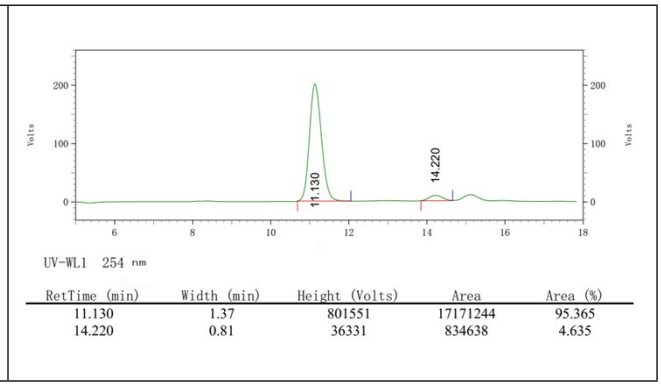
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
6.780	0.83	893473	11076698	95.904
7.907	0.40	38965	473095	4.096

(*R*)-1-bromo-1-((*S*)-4-bromo-1-((*E*)-2-(thiophen-2-yl)vinyl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (4g)

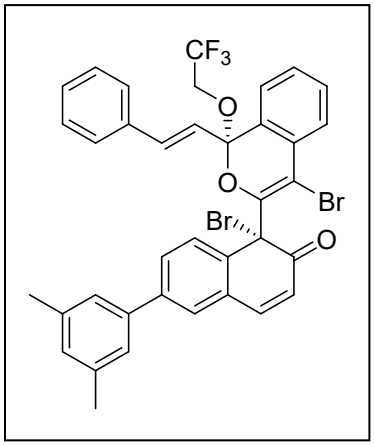


^{1}H NMR (400 MHz, Toluene-d_8): δ 7.36 – 7.23 (m, 4H), 6.96 – 6.89 (m, 2H), 6.85 – 6.80 (m, 1H), 6.79 – 6.65 (m, 6H), 6.64 – 6.59 (m, 1H), 6.16 (d, J = 10.0 Hz, 1H), 4.59 – 4.48 (m, 1H), 4.47 – 4.36 (m, 1H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 189.05, 146.22, 143.04, 142.38, 140.44, 130.80, 130.23, 130.12, 129.71, 129.19, 129.02, 128.38, 127.86, 126.25, 125.80, 124.76 (q, J = 255.0 Hz), 124.71, 124.14, 123.48, 103.86, 102.51, 63.26, 63.06 (q, J = 29.0 Hz). **HRMS (ESI)** m/z Calcd for $[C_{27}H_{17}Br_2F_3O_3NaS, M+Na]^+$: 658.9217, Found: 658.9177. **HPLC analysis**: Chiralcel AD-H (Hexane/*i*-PrOH) =80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 11.130 min (major), t_R = 14.220 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 126° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (Alumina N-neutral, PE:EA= 10:1) 75%, 47.7 mg.

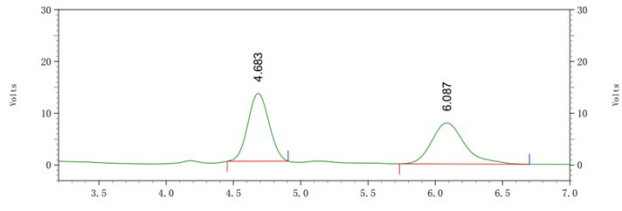




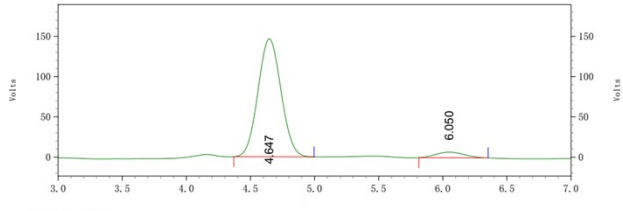
(*R*)-1-bromo-1-((*S*)-4-bromo-1-((*E*)-styryl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)-6-(3,5-dimethylphenyl)naphthalen-2(1*H*)-one (4h)



^{1}H NMR (400 MHz, Toluene-d_8) δ 7.47 (d, J = 8.1 Hz, 1H), 7.39 (dd, J = 7.5, 1.5 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.22 (d, J = 16.1 Hz, 1H), 7.18 (d, J = 1.6 Hz, 1H), 7.13 – 7.06 (m, 4H), 7.00 (td, J = 6.8, 1.4 Hz, 2H), 6.97 (s, 2H), 6.87 (d, J = 10.1 Hz, 1H), 6.81 – 6.75 (m, 2H), 6.26 (d, J = 10.0 Hz, 1H), 4.58 (dq, J = 10.2, 7.9, 7.3 Hz, 1H), 4.49 (dq, J = 11.9, 8.9, 7.9 Hz, 1H), 2.19 (s, 6H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 189.10, 146.30, 143.28, 142.65, 140.75, 139.70, 138.40, 136.22, 135.72, 130.36, 130.16, 130.00, 129.60, 129.35, 128.97, 128.50, 128.48, 127.59, 125.90, 125.58, 125.36, 125.12, 124.95 (q, J = 276.0 Hz), 124.88, 124.42, 104.17, 102.53, 63.58, 63.15 (q, J = 35.0 Hz), 21.37. **HRMS (ESI)** m/z Calcd for $[C_{37}H_{27}Br_2F_3NaO_3, M+Na]^+$: 757.0279, Found: 757.0189. **HPLC analysis**: Chiralcel AD-H (Hexane/*i*-PrOH) =95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 4.647 min (major), t_R = 6.050 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 11° (c = 1.0, CH_3OH); **Physical properties:** yellow foam; **Yield:** (Alumina N-neutral, PE:EA= 10:1) 70%, 51.4 mg.

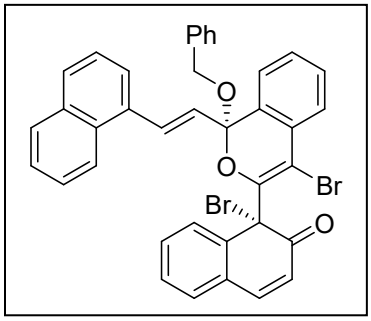


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
4.683	0.45	52340	570245	51.205
6.087	0.97	31741	543407	48.795

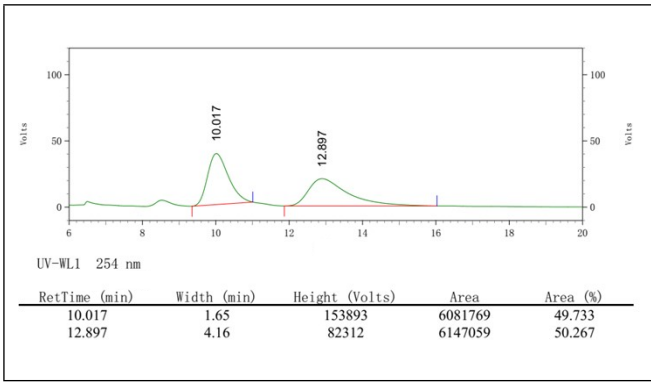


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
4.647	0.63	585509	7323793	94.461
6.050	0.54	27822	429470	5.539

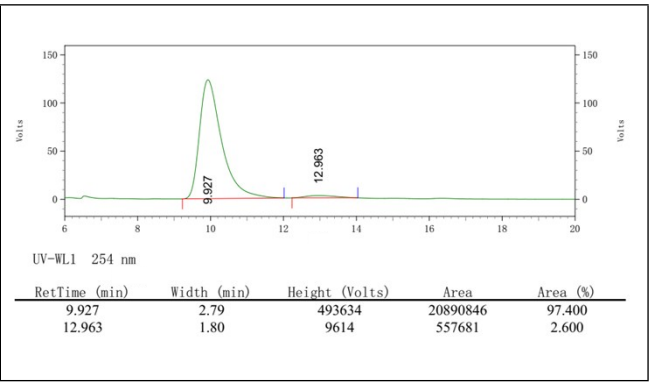
(*R*)-1-((*S*)-1-(benzyloxy)-4-bromo-1-((*E*)-2-(naphthalen-1-yl)vinyl)-1H-isochromen-3-yl)-1-bromonaphthalen-2(1*H*)-one (4i)



^{1}H NMR (400 MHz, Toluene-d_8): δ 7.99 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 15.8 Hz, 1H), 7.58 (dd, J = 8.2, 3.6 Hz, 2H), 7.55 – 7.50 (m, 3H), 7.45 – 7.38 (m, 2H), 7.22 (dd, J = 15.1, 7.4 Hz, 2H), 7.18 – 7.12 (m, 3H), 7.06 (d, J = 2.8 Hz, 1H), 7.05 – 7.00 (m, 2H), 6.97 (s, 1H), 6.85 (d, J = 15.8 Hz, 1H), 6.82 – 6.72 (m, 3H), 6.69 (td, J = 8.7, 7.9, 1.5 Hz, 1H), 6.24 (d, J = 10.0 Hz, 1H), 5.27 (d, J = 11.5 Hz, 1H), 5.11 (d, J = 11.5 Hz, 1H). **^{13}C NMR** (100 MHz, Toluene-d_8): δ 188.98, 147.36, 142.88, 142.70, 138.75, 134.22, 133.85, 132.31, 132.00, 130.86, 130.80, 130.44, 129.74, 129.68, 129.17, 128.77, 128.51, 128.45, 127.88, 127.65, 126.72, 126.15, 126.08, 125.85, 125.74, 124.69, 124.56, 124.33, 123.96, 105.13, 101.58, 67.80, 63.94. **HRMS (ESI)** m/z Calcd for $[C_{38}H_{26}Br_2NaO_3, M+ Na]^+$: 711.0249, Found: 711.0139. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) =80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 9.927 min (major), t_R = 12.963 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 25° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** (Alumina N-neutral, PE:EA= 10:1) 83%, 57.1 mg.

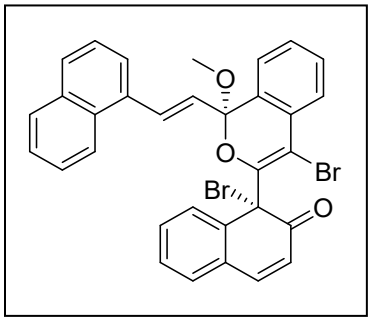


RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
10.017	1.65	153893	6081769	49.733
12.897	4.16	82312	6147059	50.267

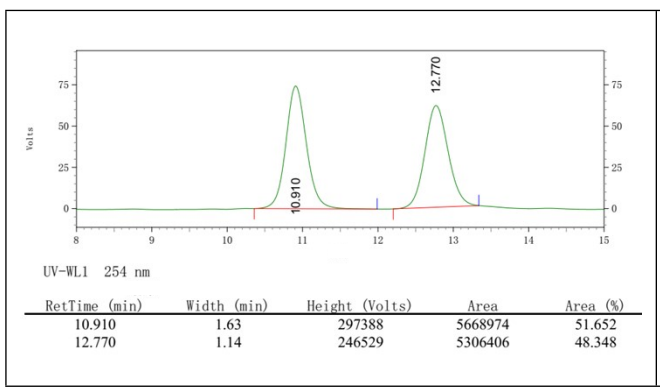


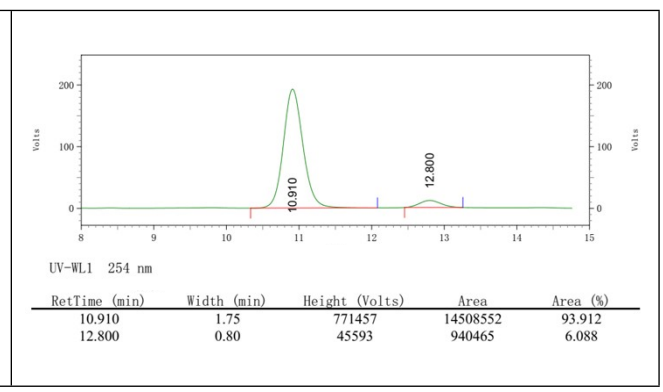
RetTime (min)	Width (min)	Height (Volts)	Area	Area (%)
9.927	2.79	493634	20890846	97.400
12.963	1.80	9614	557681	2.600

(*R*)-1-bromo-1-((*S*)-4-bromo-1-methoxy-1-((*E*)-2-(naphthalen-1-yl)vinyl)-1H-isochromen-3-yl)naphthalen-2(1*H*)-one (4j)

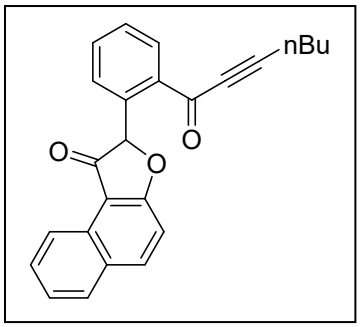


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 – 8.06 (m, 1H), 7.85 (d, *J* = 8.2 Hz, 2H), 7.78 (dd, *J* = 11.3, 3.5 Hz, 2H), 7.56 – 7.44 (m, 7H), 7.38 (dt, *J* = 14.2, 7.4 Hz, 3H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 6.75 (d, *J* = 15.8 Hz, 1H), 6.47 (d, *J* = 9.9 Hz, 1H), 3.68 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 189.61, 146.25, 143.17, 142.05, 133.61, 133.57, 132.30, 131.29, 130.84, 129.92, 129.75, 129.51, 129.46, 128.96, 128.82, 128.59, 128.43, 128.15, 128.01, 126.44, 125.97, 125.57, 125.39, 124.42, 124.18, 123.96, 123.64, 104.11, 101.02, 63.04, 52.42. **HRMS (ESI)** m/z Calcd for $[C_{32}H_{22}Br_2NaO_3, M+ Na]^+$: 634.9936, Found: 634.9857. **HPLC analysis**: Chiralcel IA-H (Hexane/*i*-PrOH) =95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 10.910 min (major), t_R = 12.800 min (minor). **Optical Rotation:** $[\alpha]_D^{20}$ = 141° (c = 1, CH_2Cl_2); **Physical properties:** (Alumina N-neutral, PE:EA= 10:1) yellow solid; **Yield:** 88%, 53.8 mg.

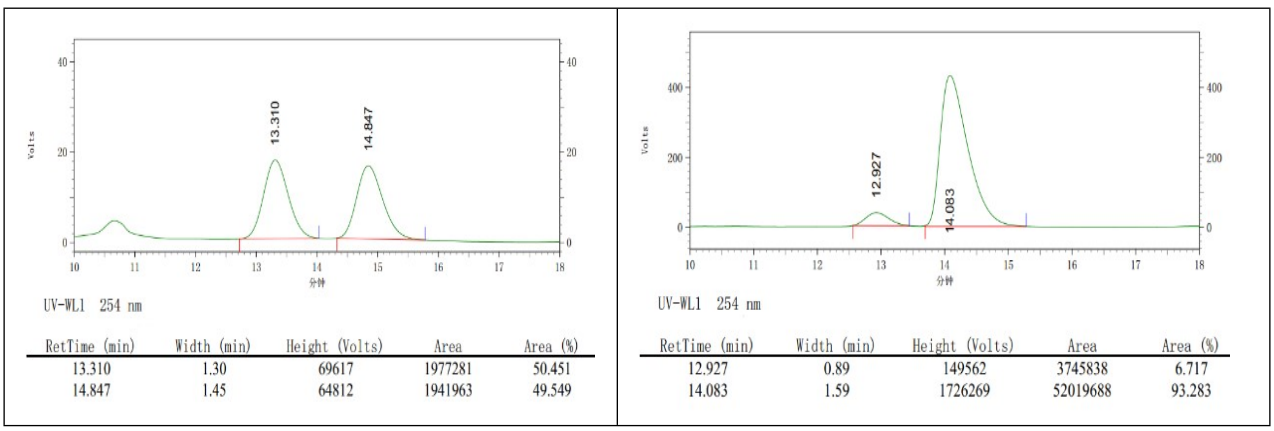




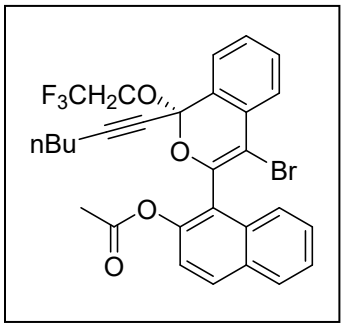
2-(2-(hept-2-ynoyl)phenyl)naphtho[2,1-b]furan-1(2*H*)-one (5j)



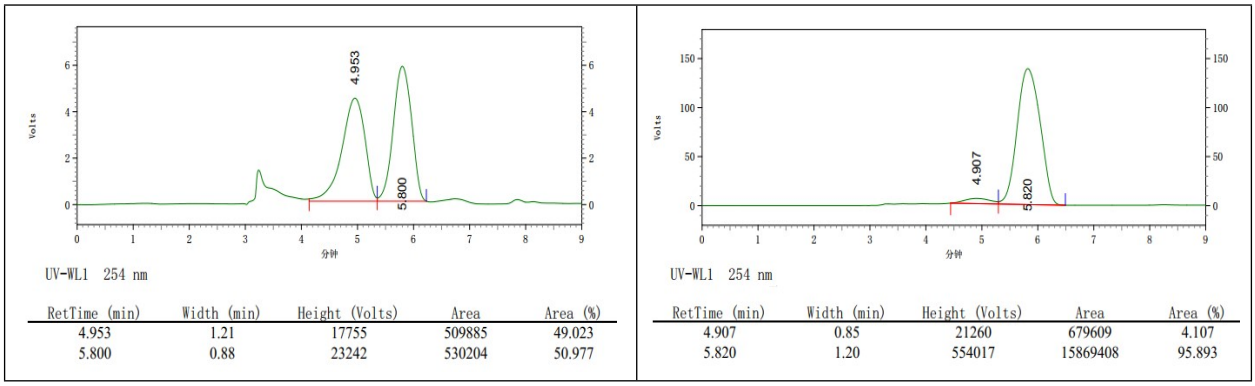
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.2 Hz, 1H), 8.37 – 8.31 (m, 1H), 8.12 (d, *J* = 9.0 Hz, 1H), 7.85 (d, *J* = 8.1 Hz, 1H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.38 (d, *J* = 9.0 Hz, 2H), 7.15 (s, 1H), 2.52 (t, *J* = 7.1 Hz, 2H), 1.73 – 1.63 (m, 2H), 1.52 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.68, 179.77, 175.23, 139.87, 135.43, 134.42, 133.63, 133.06, 129.82, 129.45, 129.42, 128.47, 128.41, 126.06, 125.40, 123.13, 113.76, 112.21, 96.97, 83.58, 80.90, 29.75, 22.09, 18.99, 13.52. **HRMS (ESI)** m/z Calcd for [$C_{25}H_{20}NaO_3$, M+Na]$^+$: 391.1412, Found: 391.1285. **HPLC analysis**: Chiralcel OD-H (Hexane/*i*-PrOH) = 90:10, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 12.927 min (minor), t_R = 14.083 min (major). **Physical properties:** yellow oil; **Yield:** (SiO_2, PE:EA= 10:1) 90%.



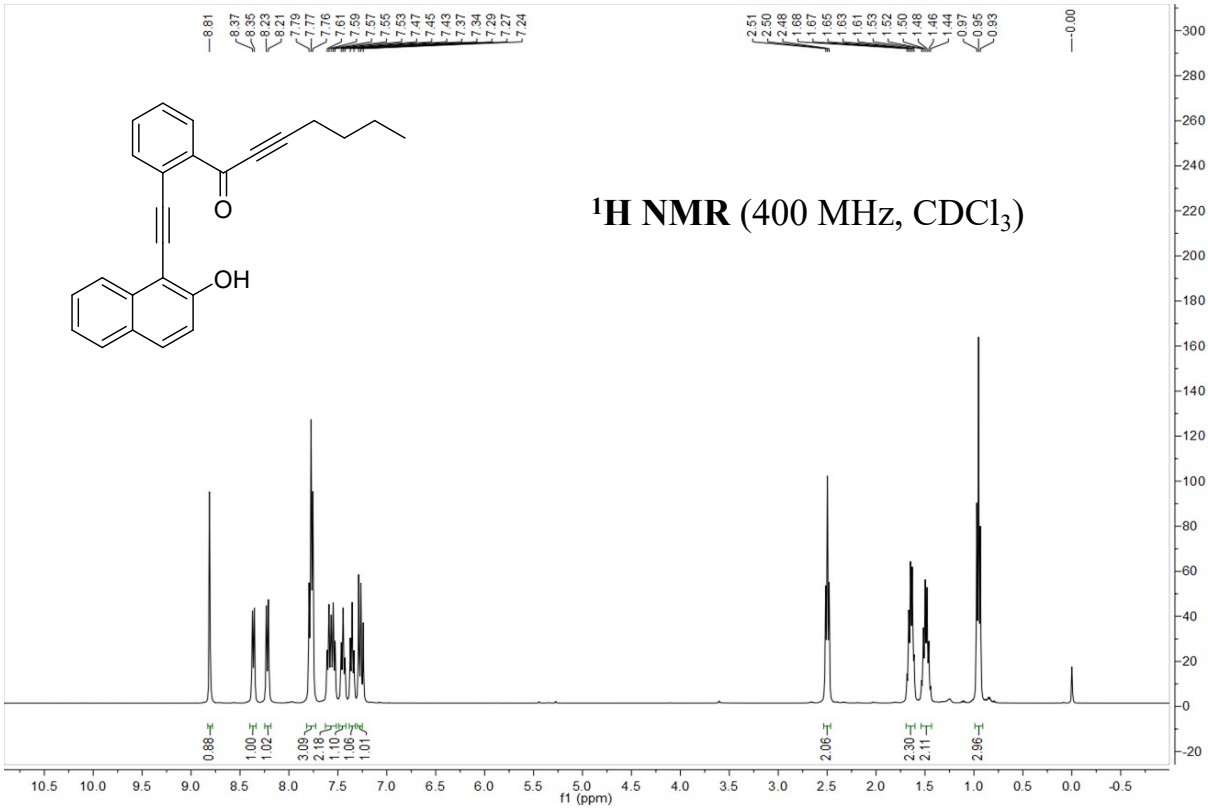
1-(4-bromo-1-(hex-1-yn-1-yl)-1-(2,2,2-trifluoroethoxy)-1H-isochromen-3-yl)naphthalen-2-yl acetate (6j)

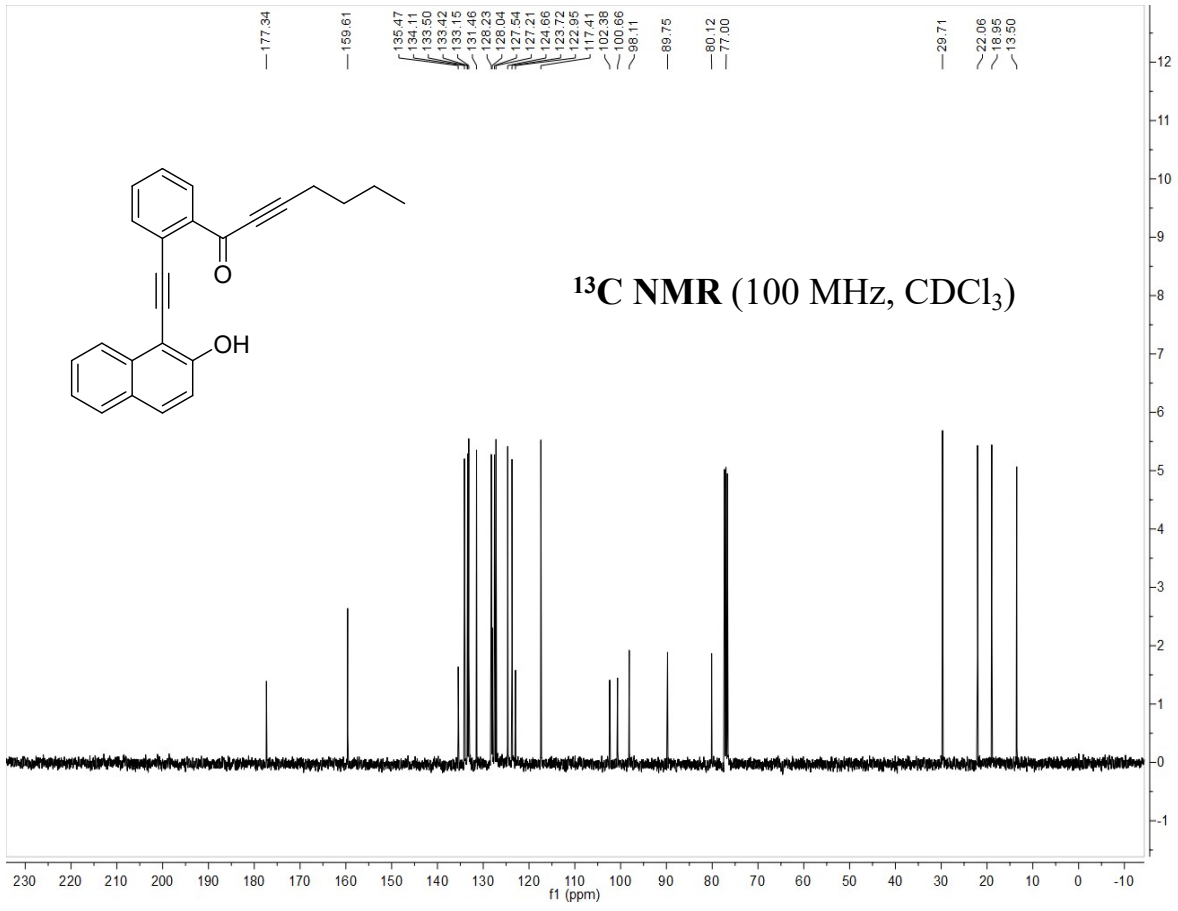


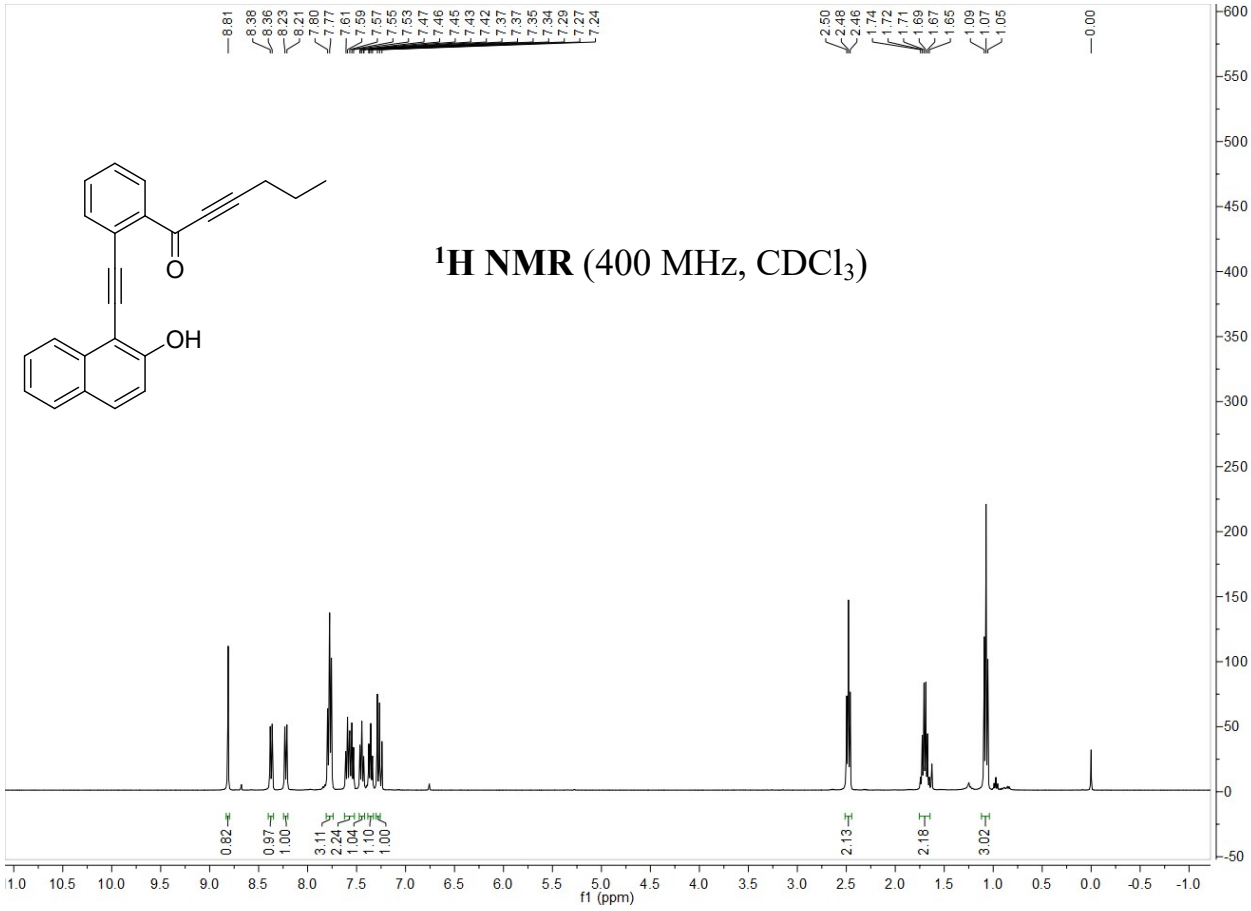
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 9.0 Hz, 1H), 7.87 (dd, *J* = 6.7, 2.6 Hz, 1H), 7.83 (dd, *J* = 6.7, 2.8 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.51 – 7.44 (m, 3H), 7.41 (d, *J* = 9.0 Hz, 1H), 4.49 (dq, *J* = 11.5, 8.9 Hz, 1H), 4.13 (dq, *J* = 11.7, 8.6 Hz, 1H), 2.33 (t, *J* = 7.1 Hz, 2H), 2.26 (s, 3H), 1.55 (p, *J* = 7.0 Hz, 2H), 1.42 (h, *J* = 7.1 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.14, 146.73, 142.60, 131.57, 131.46, 130.81, 130.29, 128.70, 128.22, 128.16, 127.30, 126.34, 126.03, 125.26, 124.92, 122.82, 122.47, 121.76, 104.57, 98.02, 91.43, 77.00, 74.53, 62.59 (*J* = 34.0 Hz), 30.02, 21.93, 20.81, 18.30, 13.45. **HRMS (ESI)** m/z Calcd for $[C_{29}H_{24}BrF_3NaO_4$, M+Na]$^+$: 595.0801, Found: 595.0707. **HPLC analysis**: Chiralcel AD-H (Hexane/*i*-PrOH) = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 4.907 min (minor), t_R = 5.820 min (major). **Physical properties:** yellow foam; **Yield:** (SiO_2, PE:EA= 10:1) 88%



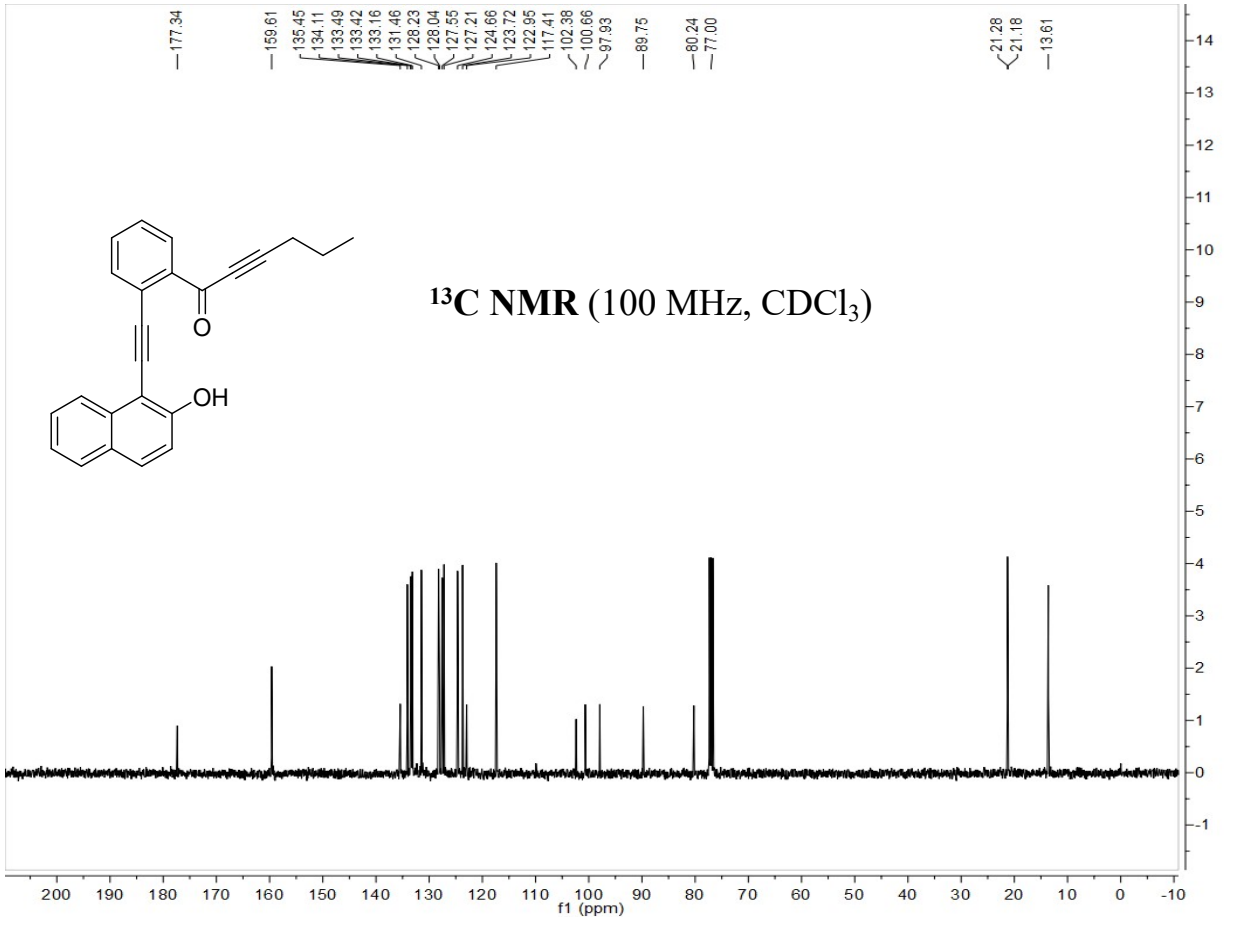
IX. ^{1}H and ^{13}C NMR spectra of substrates (1a-1k, 3a-3g)



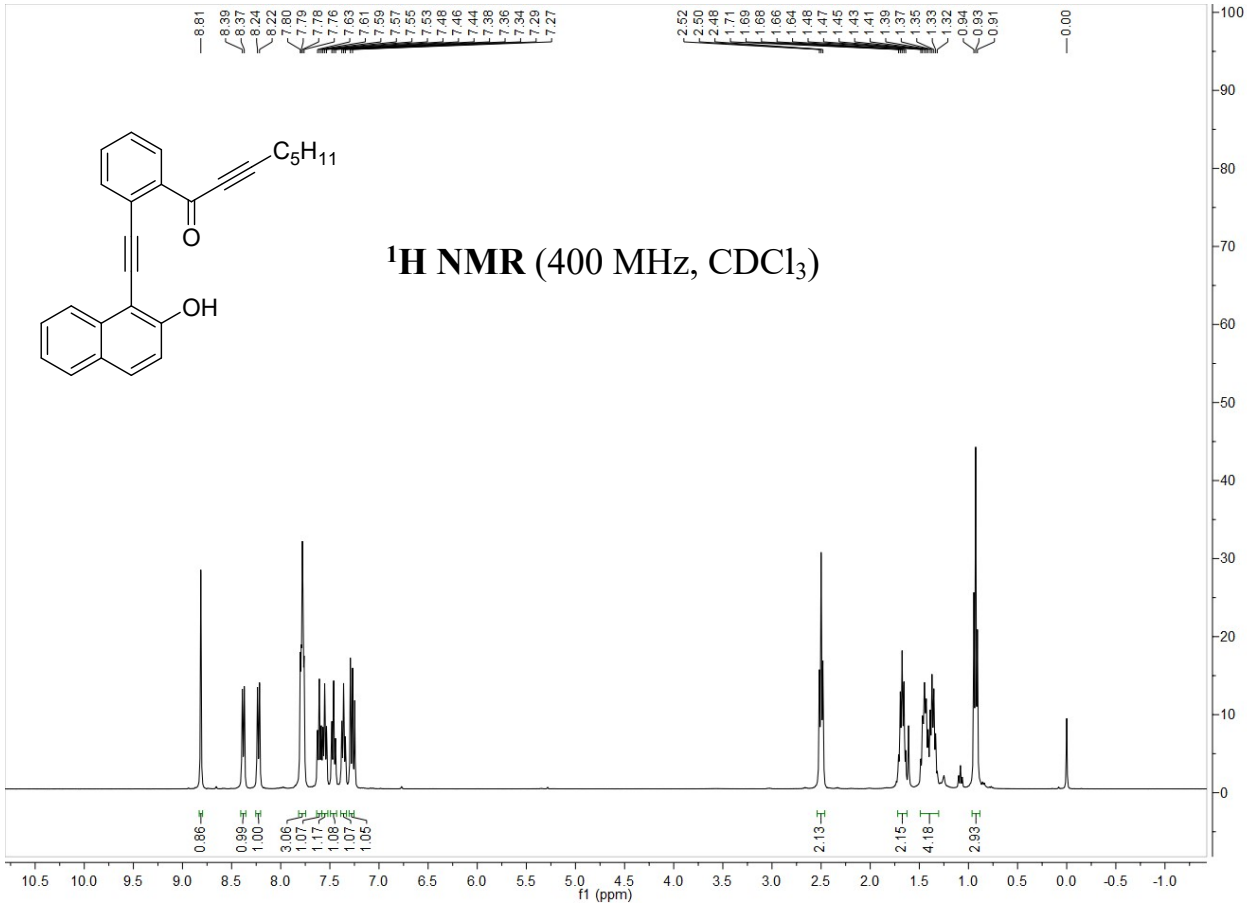


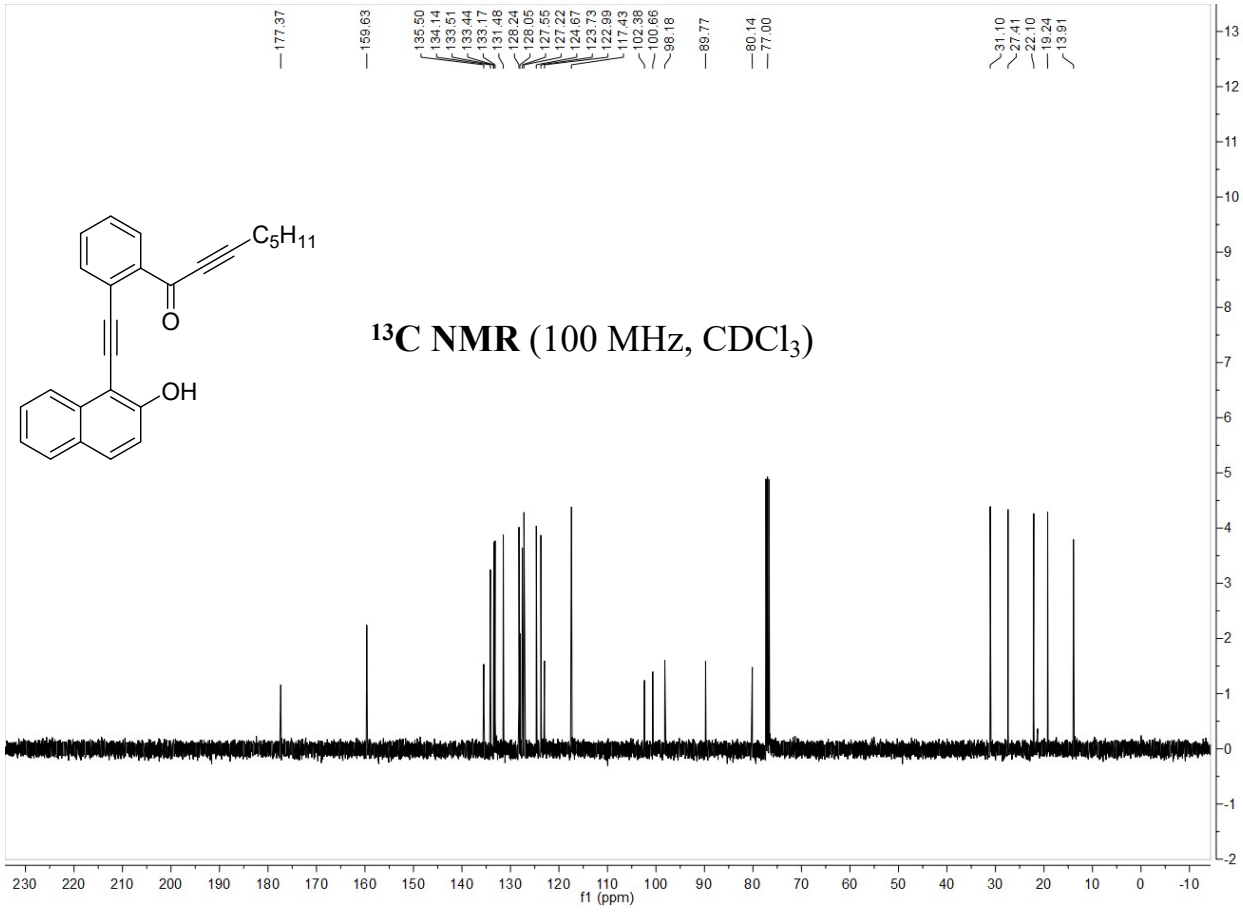


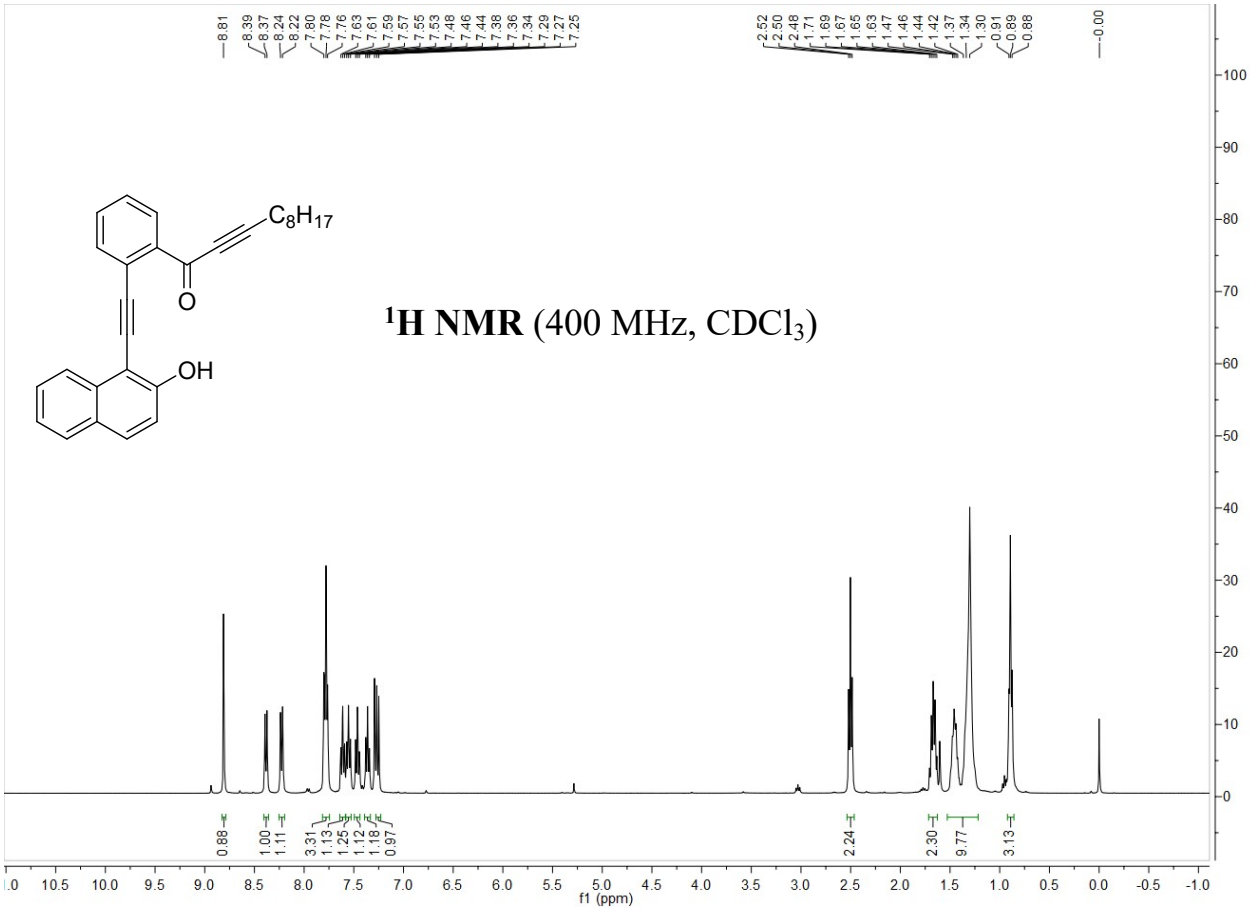
^{1}H NMR (400 MHz, $CDCl_3$)



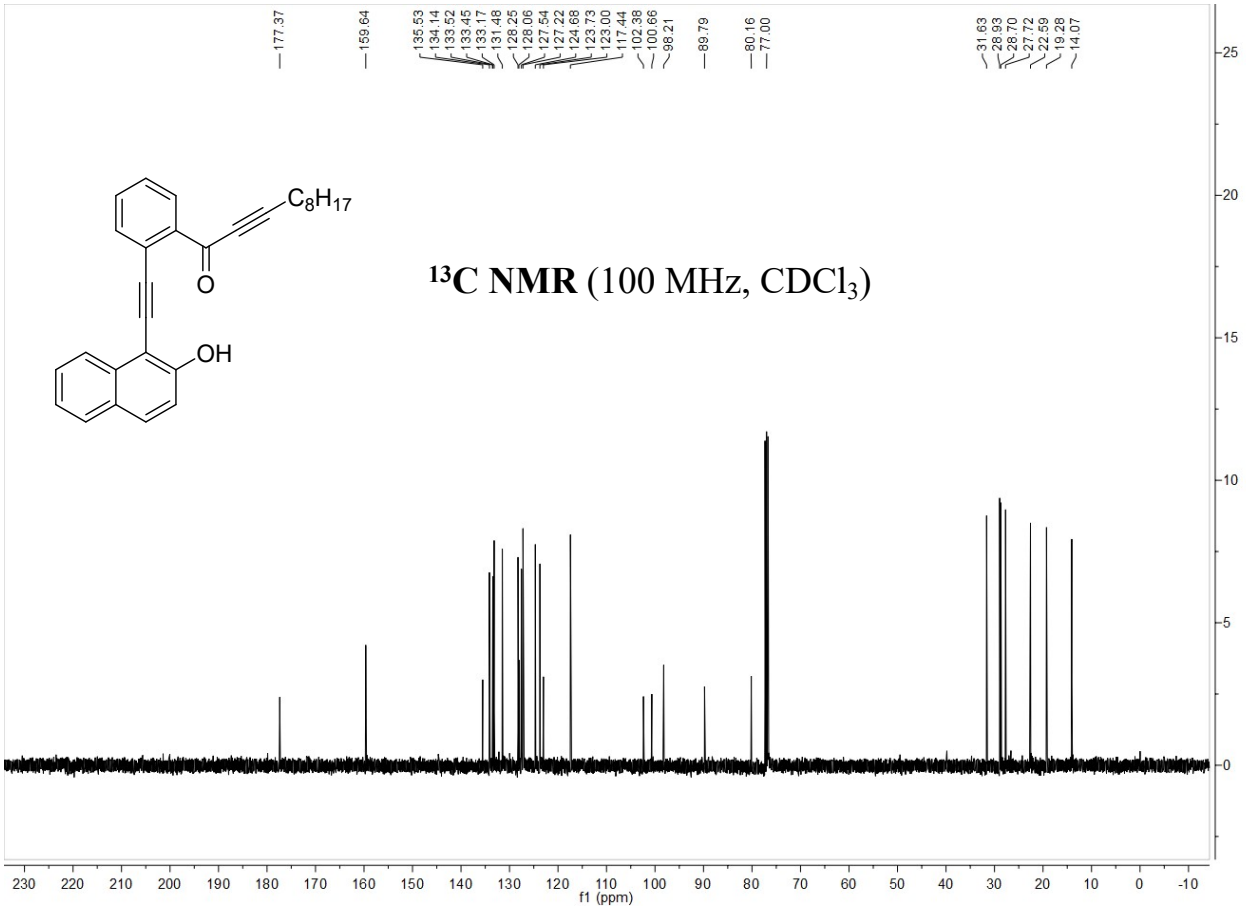
^{13}C NMR (100 MHz, $CDCl_3$)


C5H11
O
OH
1H NMR (400 MHz, CDCl3)
f1 (ppm)

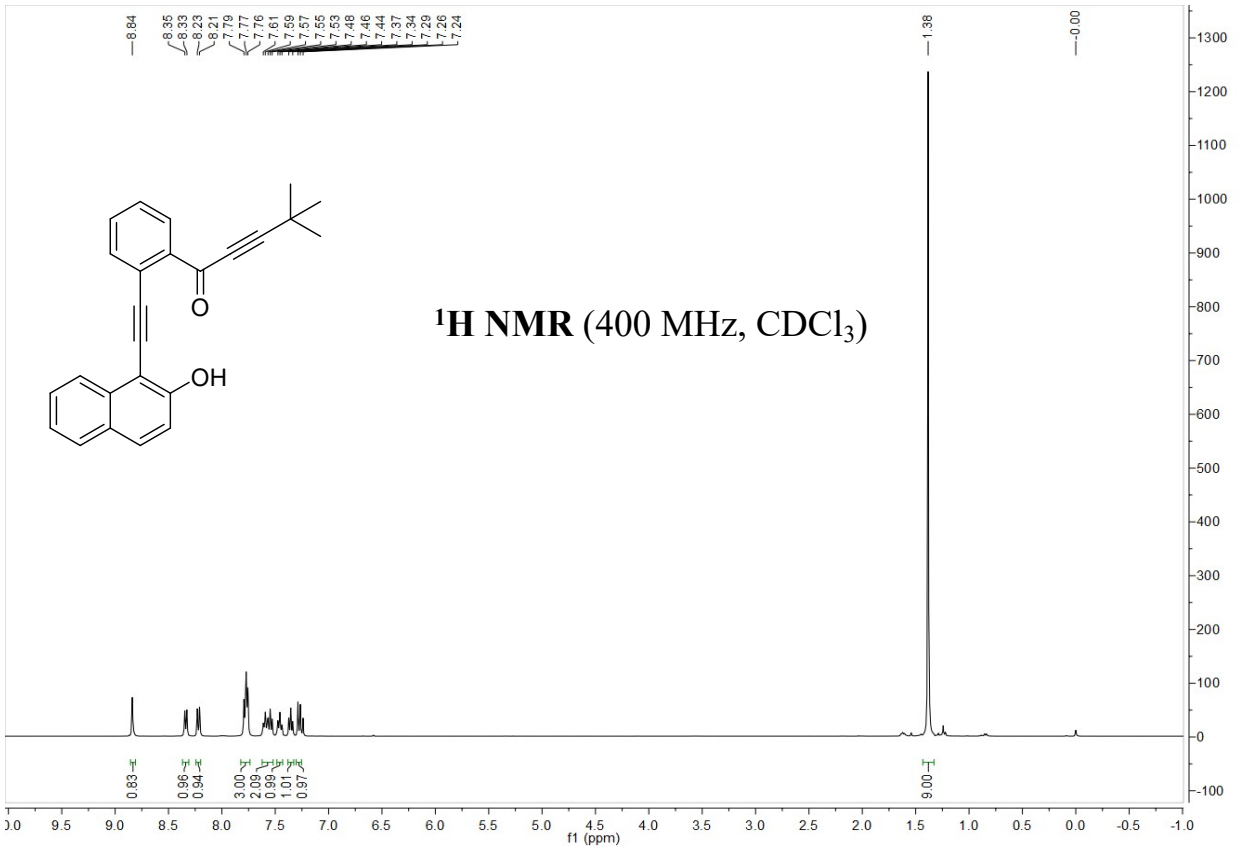

C5H11
O
OH
13C NMR (100 MHz, CDCl3)
f1 (ppm)



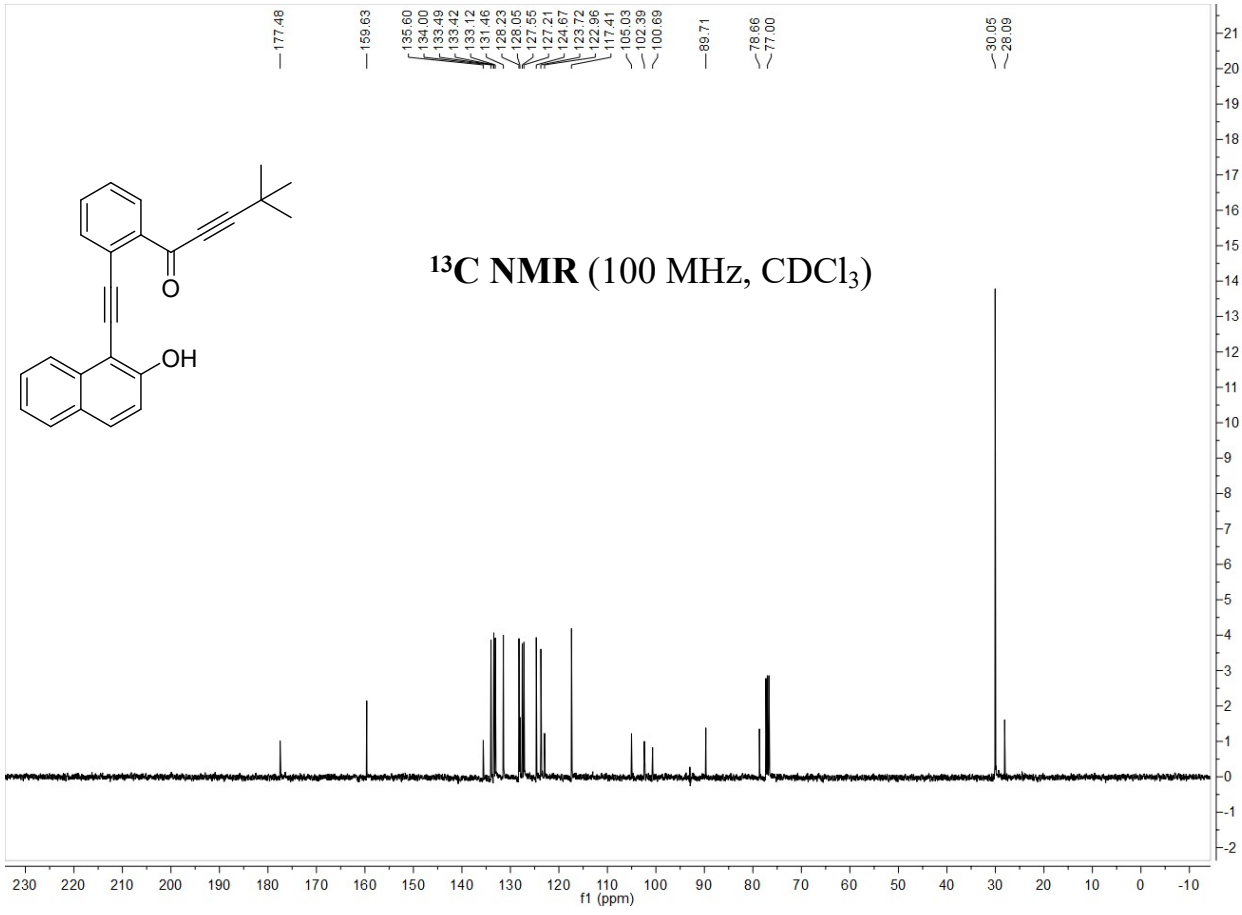
^{1}H NMR (400 MHz, $CDCl_3$)



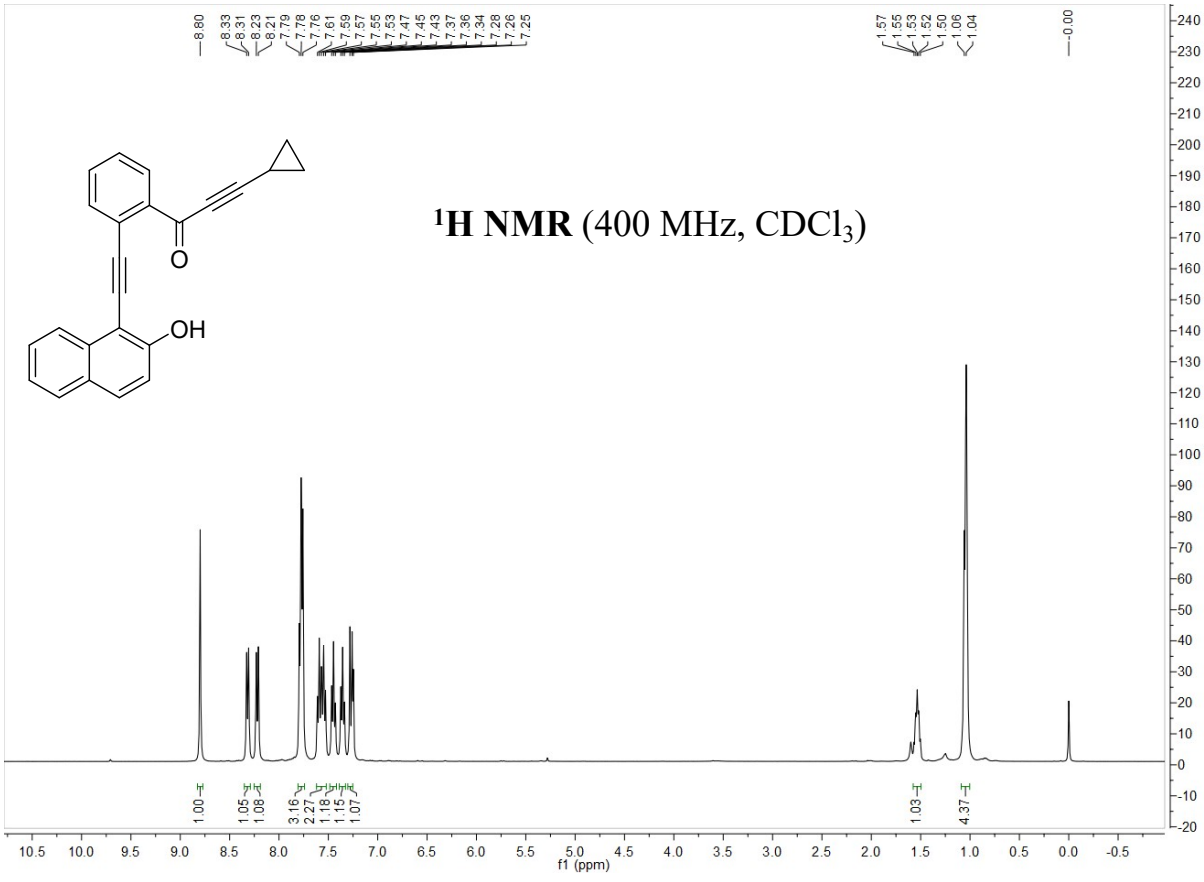
^{13}C NMR (100 MHz, $CDCl_3$)



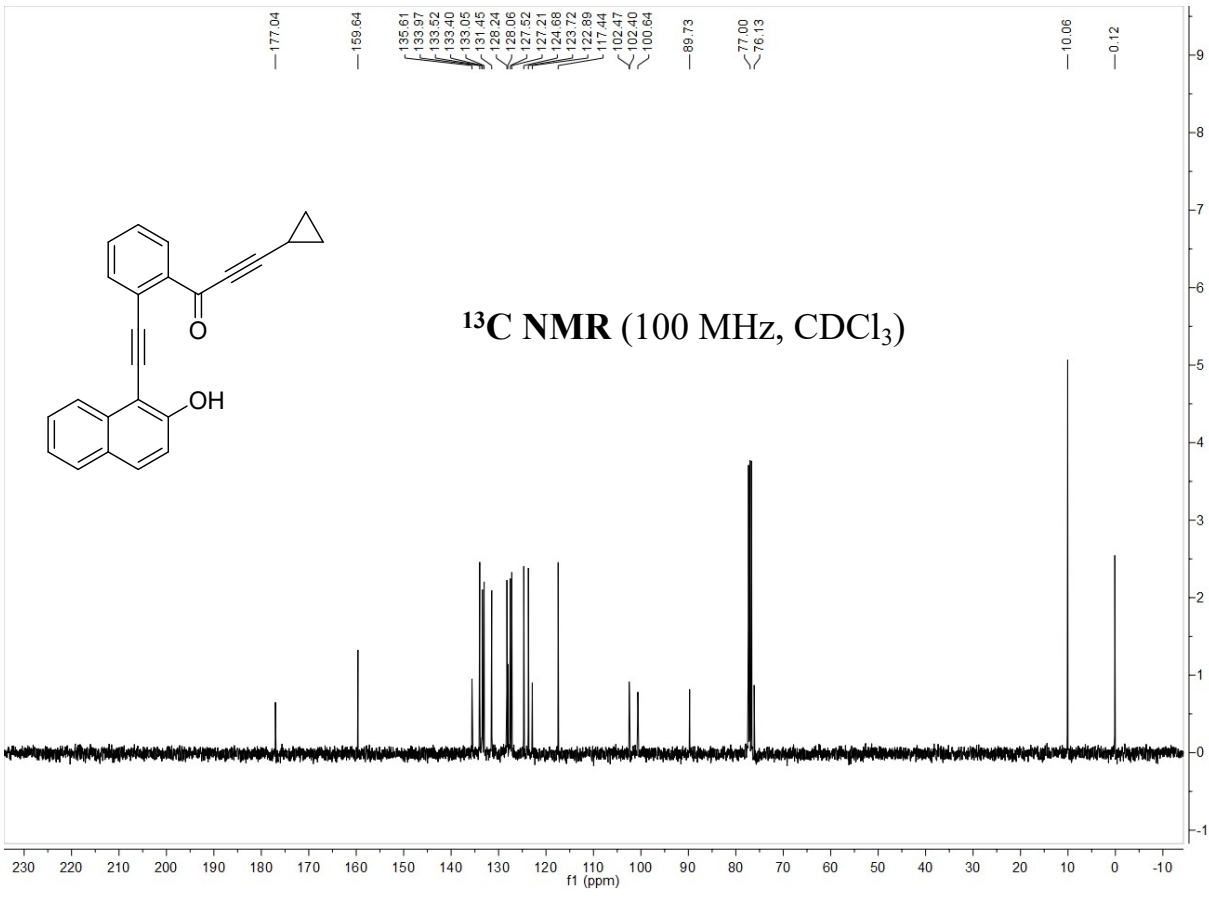
^{1}H NMR (400 MHz, $CDCl_3$)



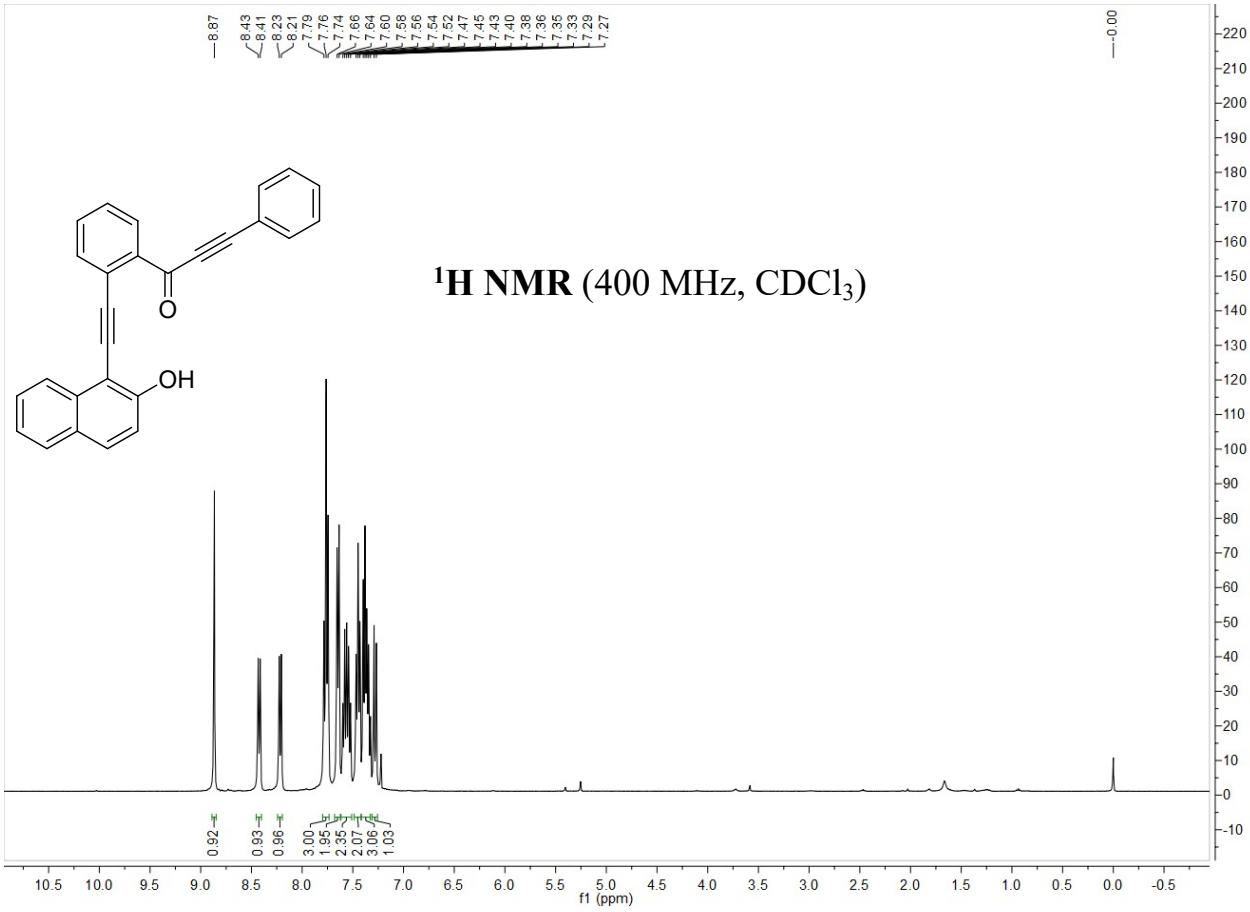
^{13}C NMR (100 MHz, $CDCl_3$)



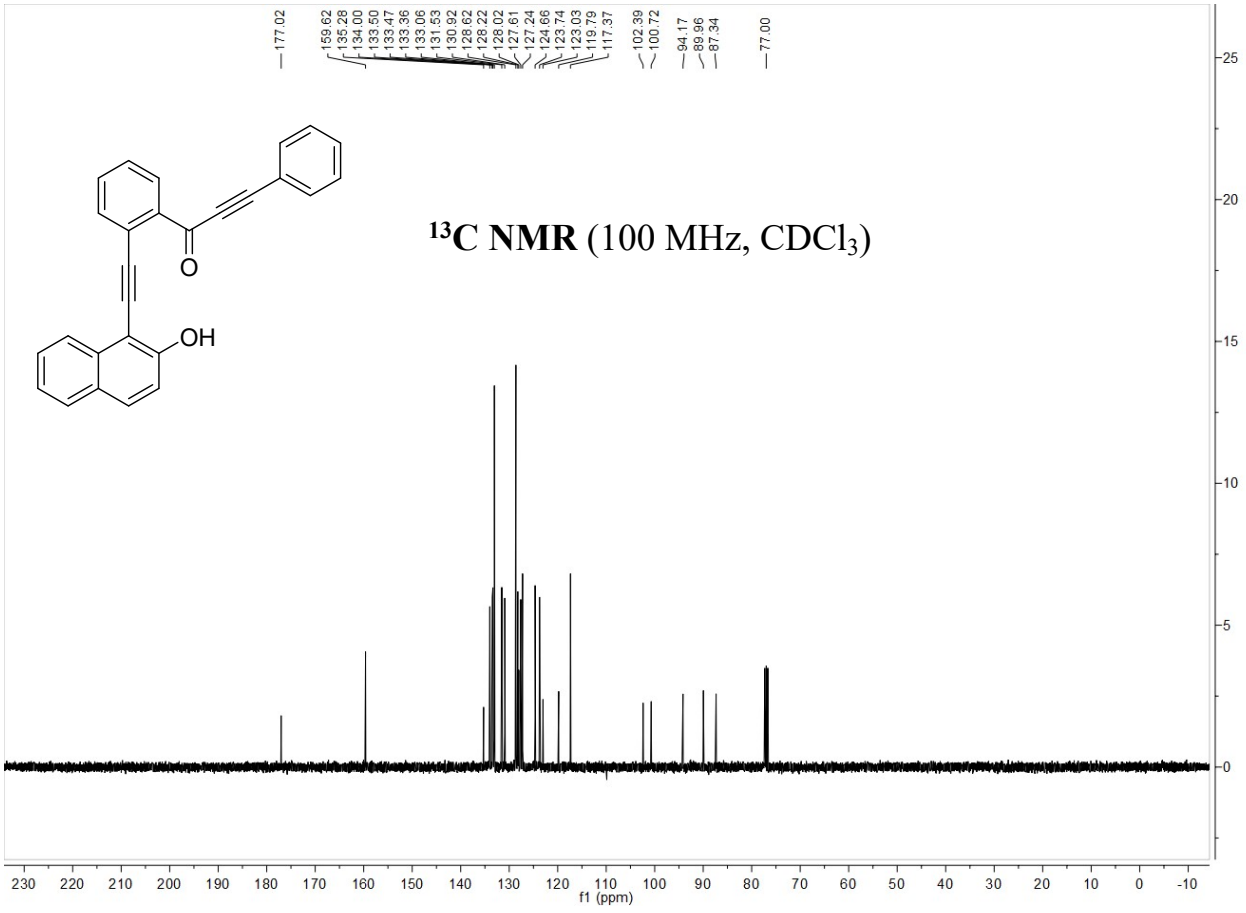
^{1}H NMR (400 MHz, $CDCl_3$)



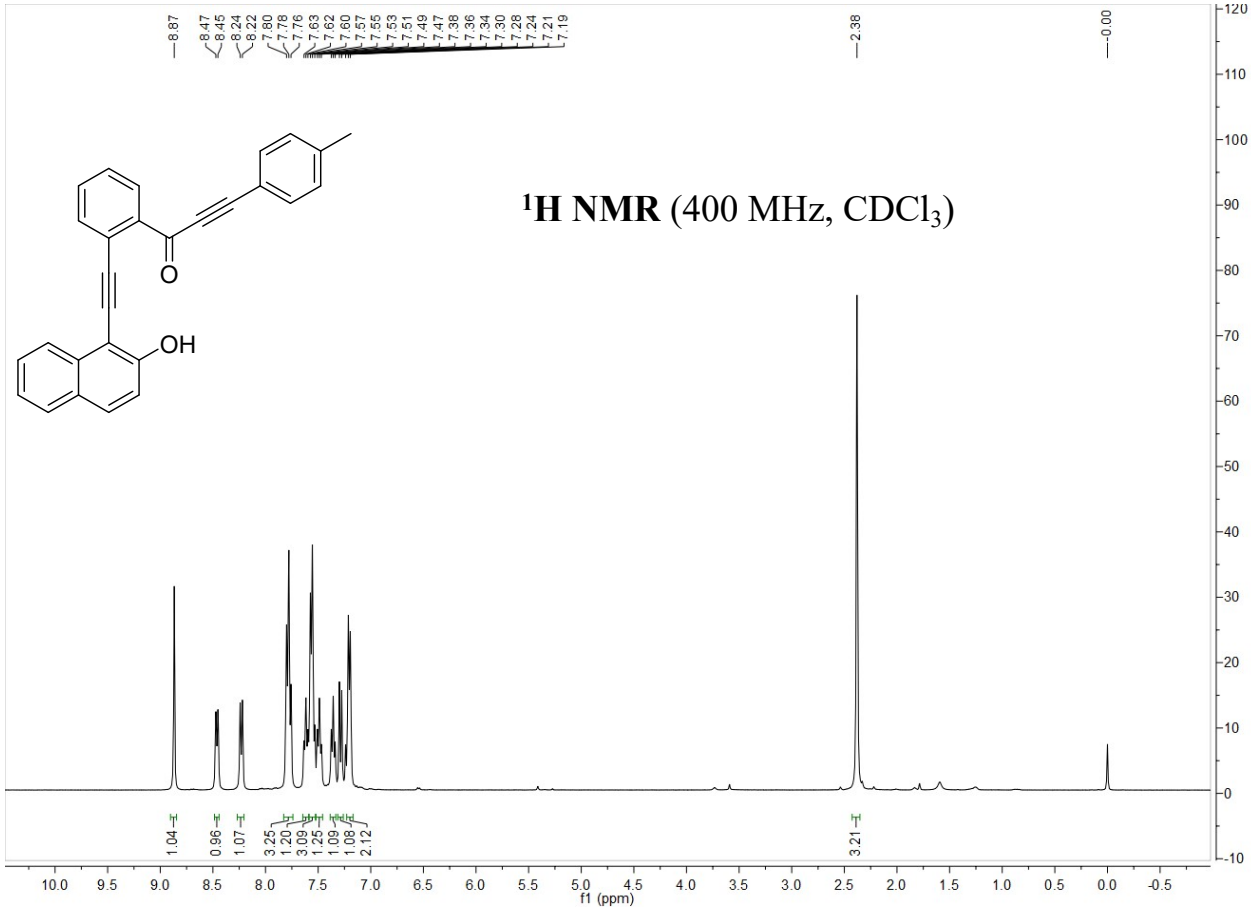
^{13}C NMR (100 MHz, $CDCl_3$)



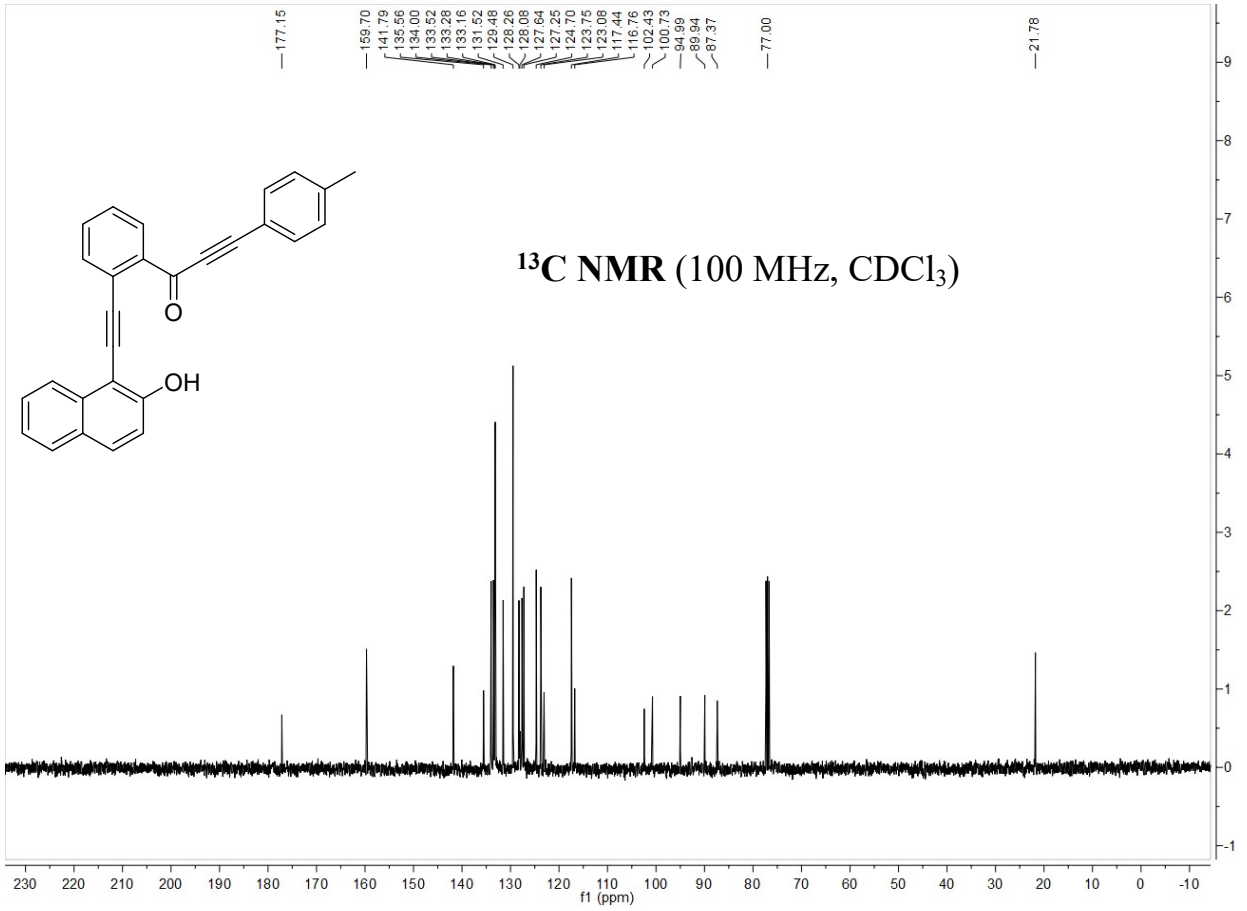
^{1}H NMR (400 MHz, $CDCl_3$)



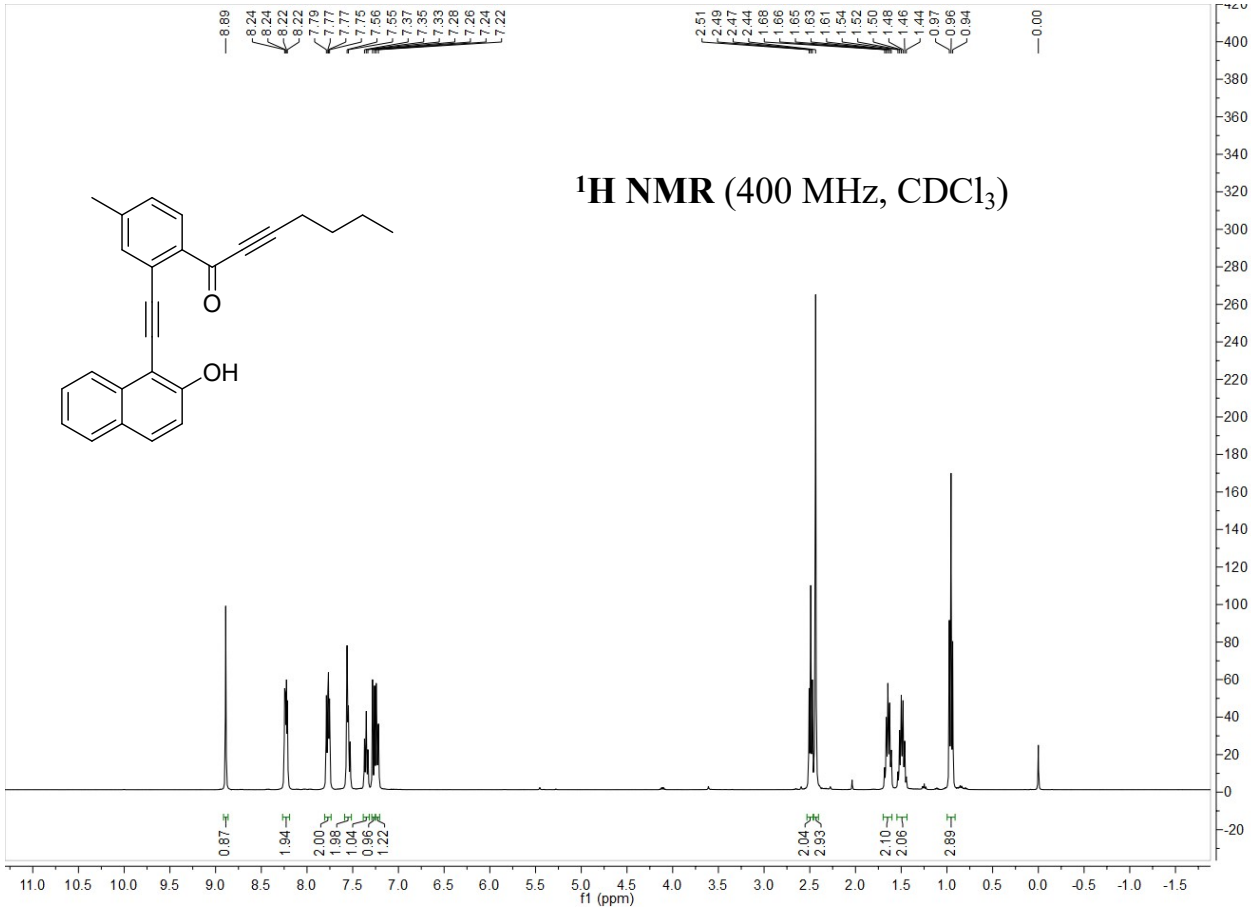
^{13}C NMR (100 MHz, $CDCl_3$)



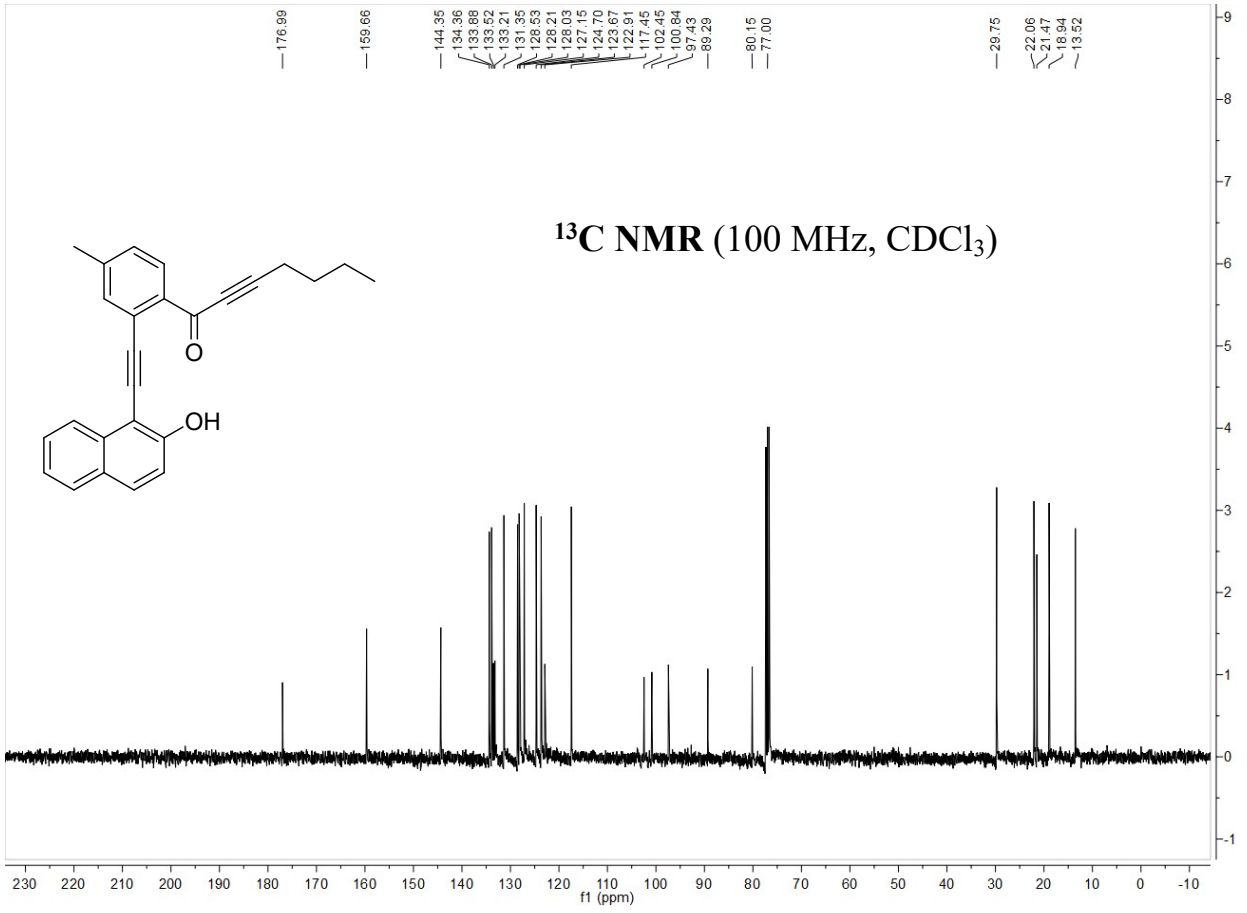
^{1}H NMR (400 MHz, $CDCl_3$)



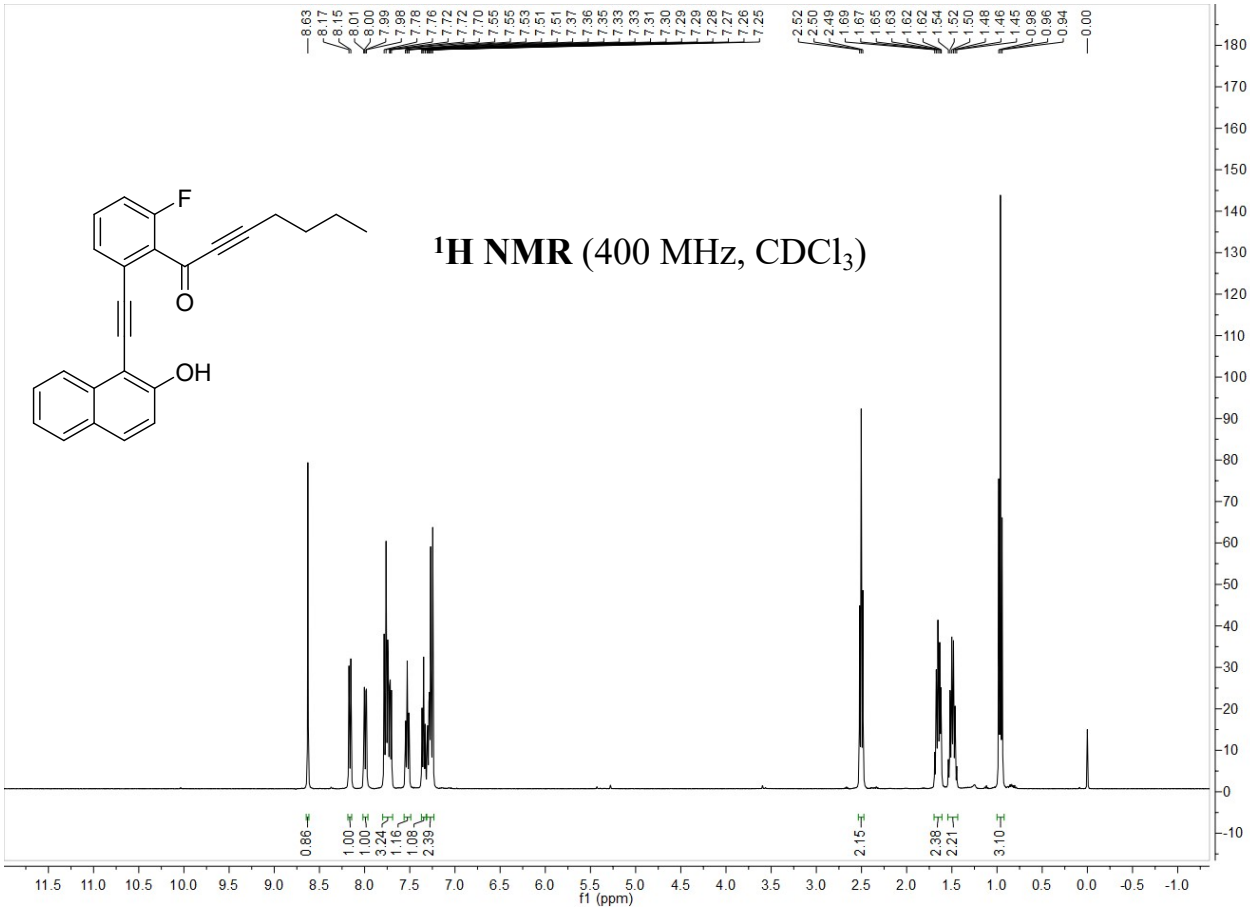
^{13}C NMR (100 MHz, $CDCl_3$)

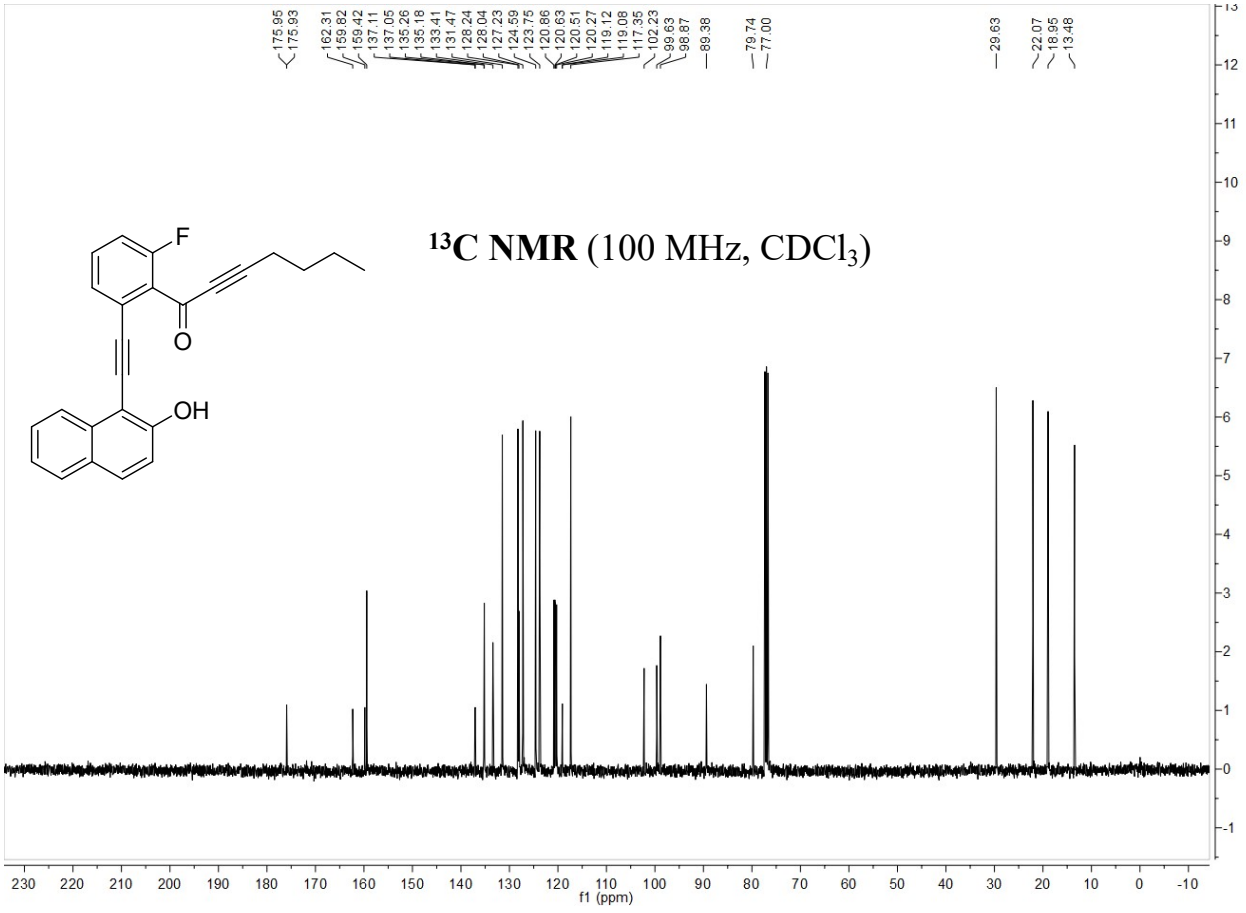


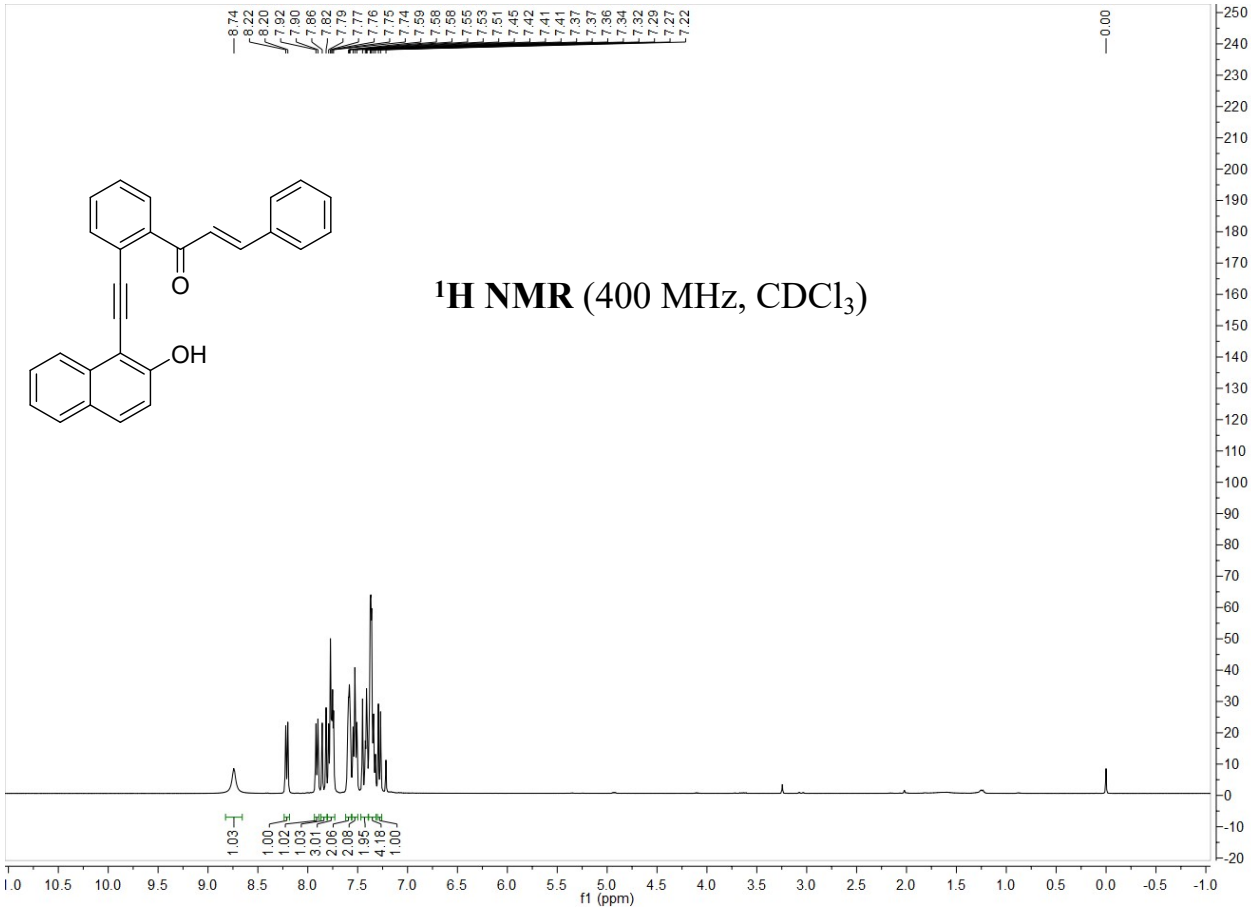
^{1}H NMR (400 MHz, $CDCl_3$)



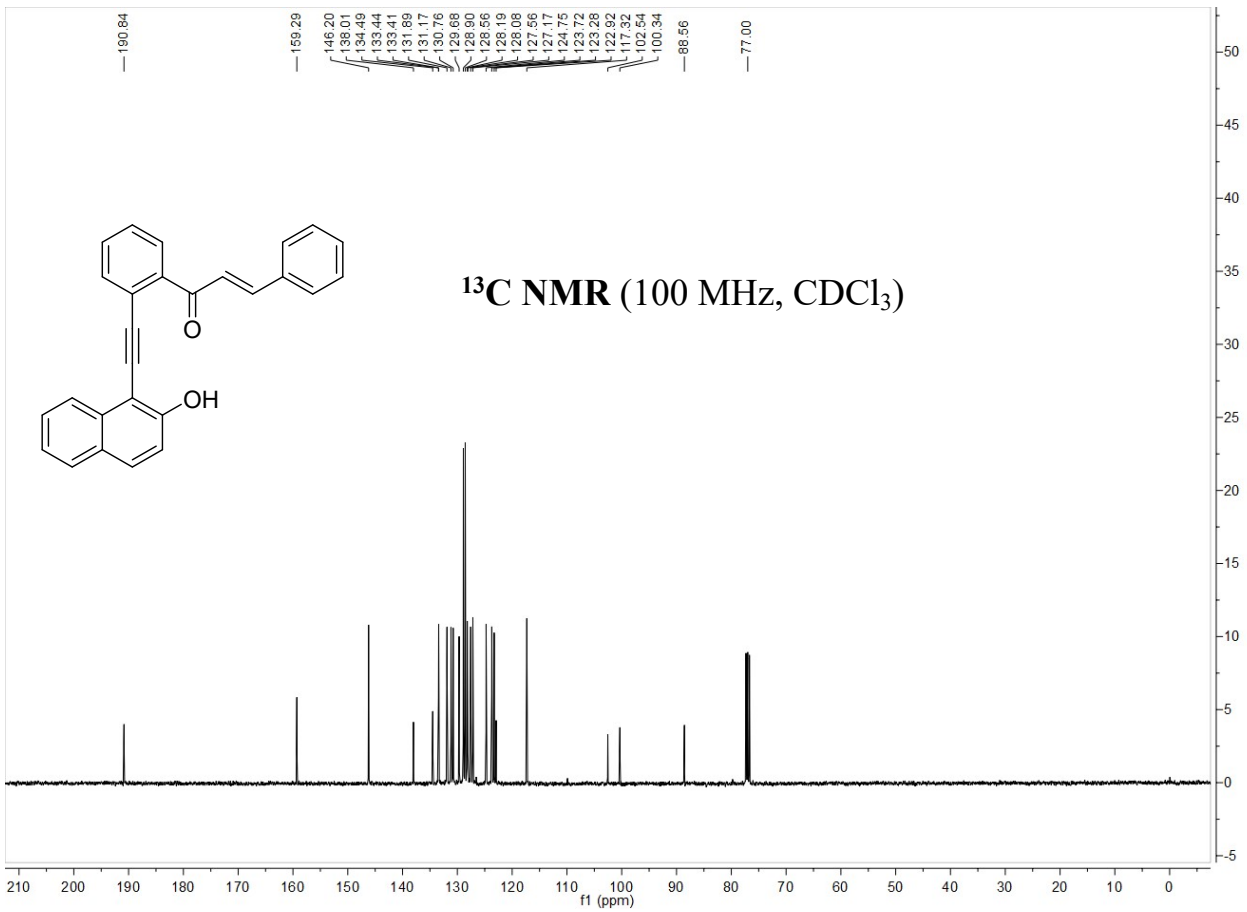
^{13}C NMR (100 MHz, $CDCl_3$)


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

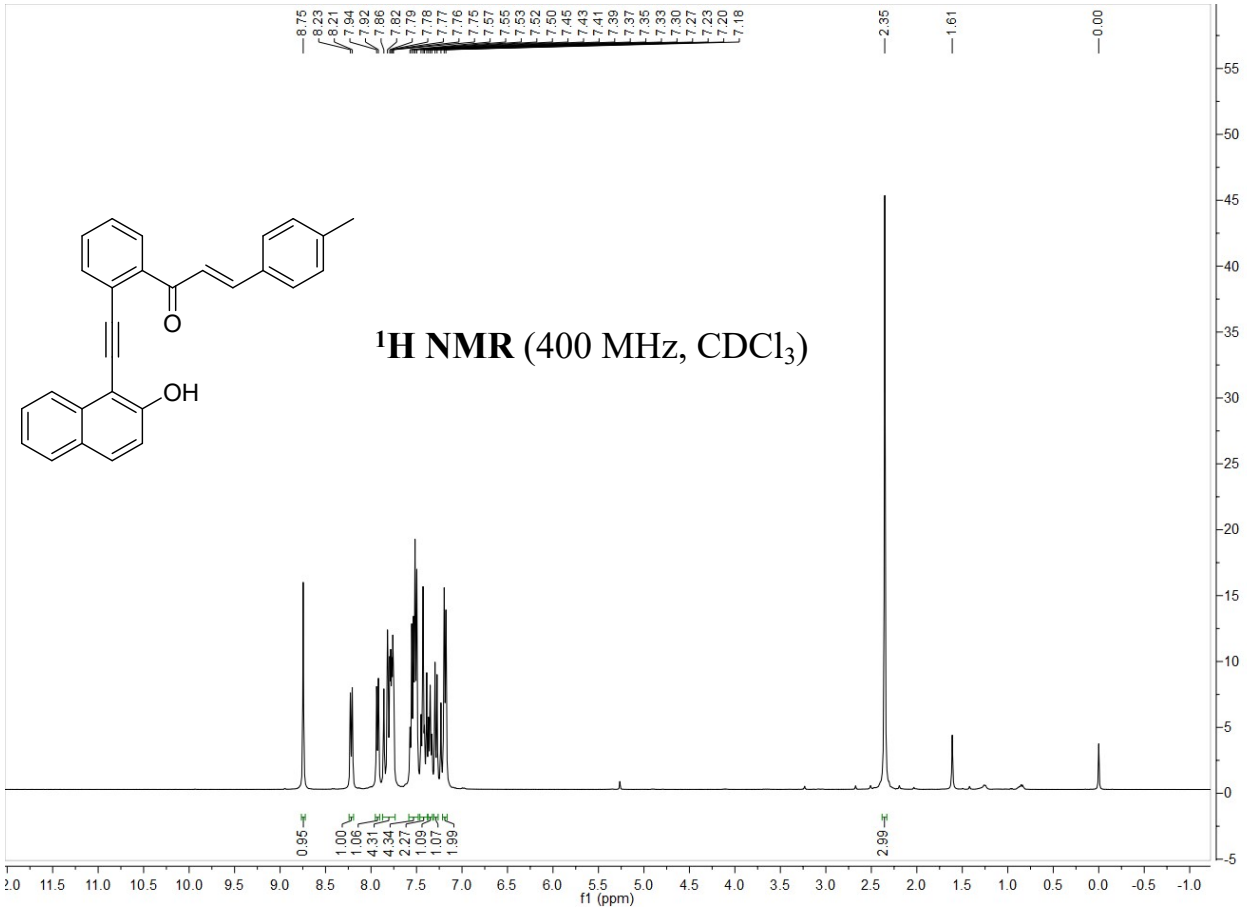

F
O
OH
¹³C NMR (100 MHz, CDCl3)
f1 (ppm)



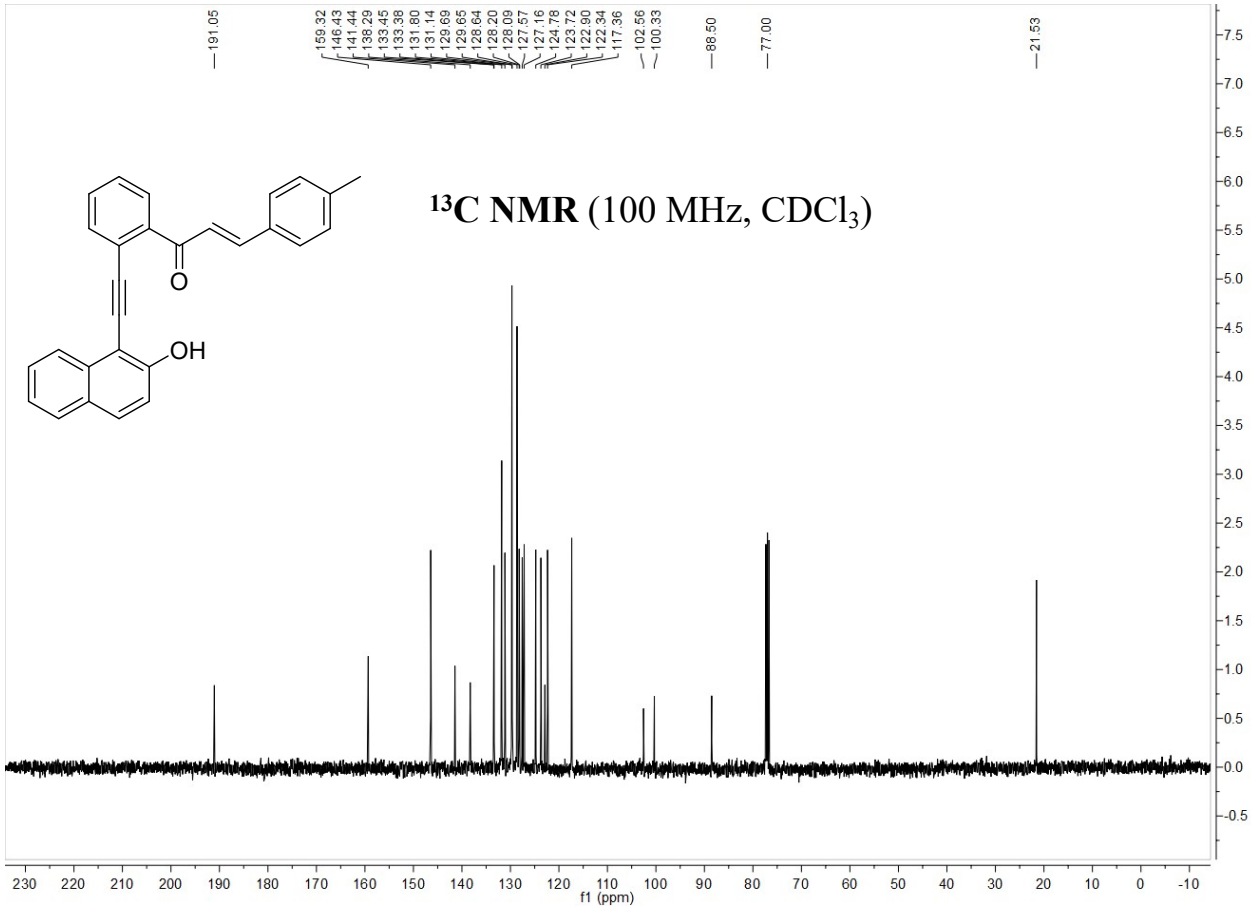
^{1}H NMR (400 MHz, $CDCl_3$)



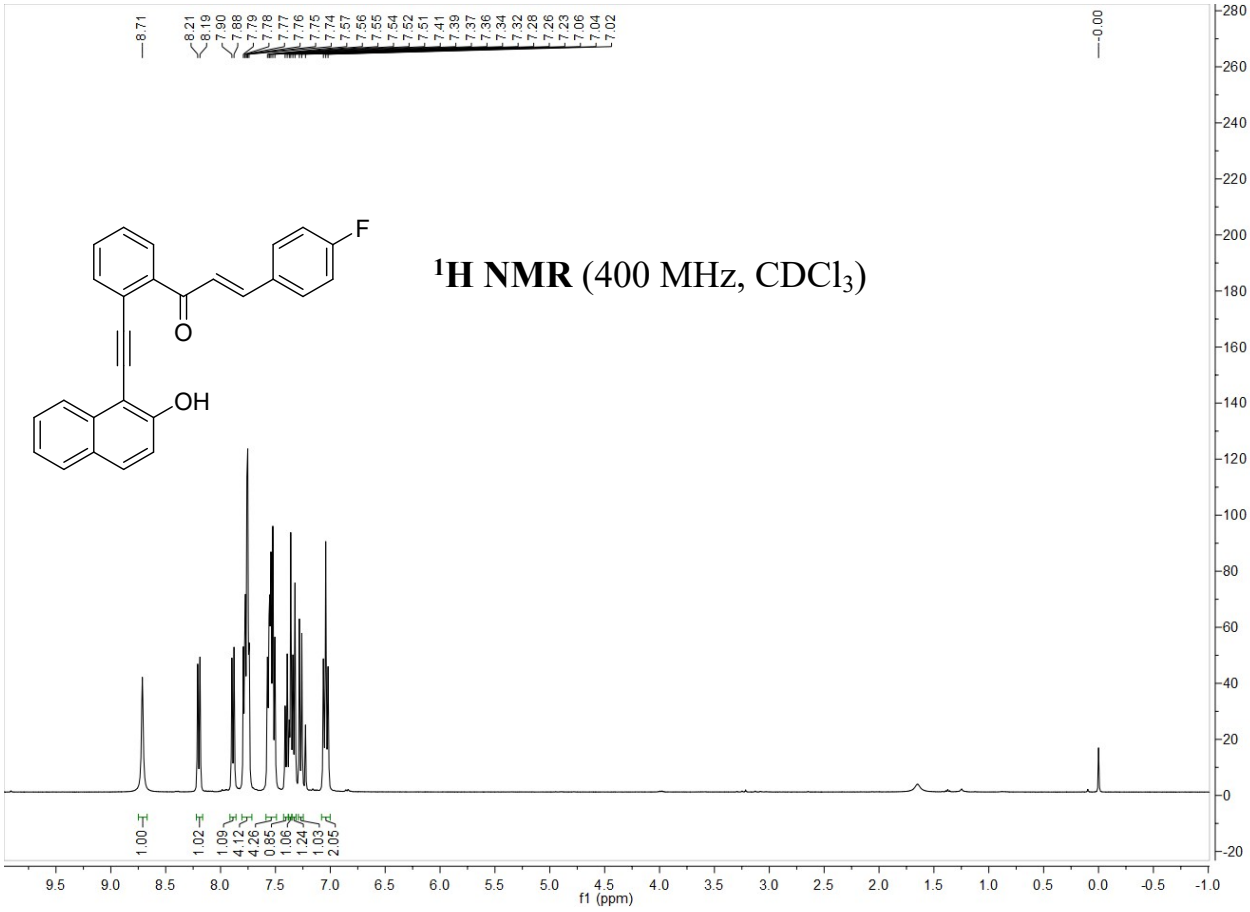
^{13}C NMR (100 MHz, $CDCl_3$)



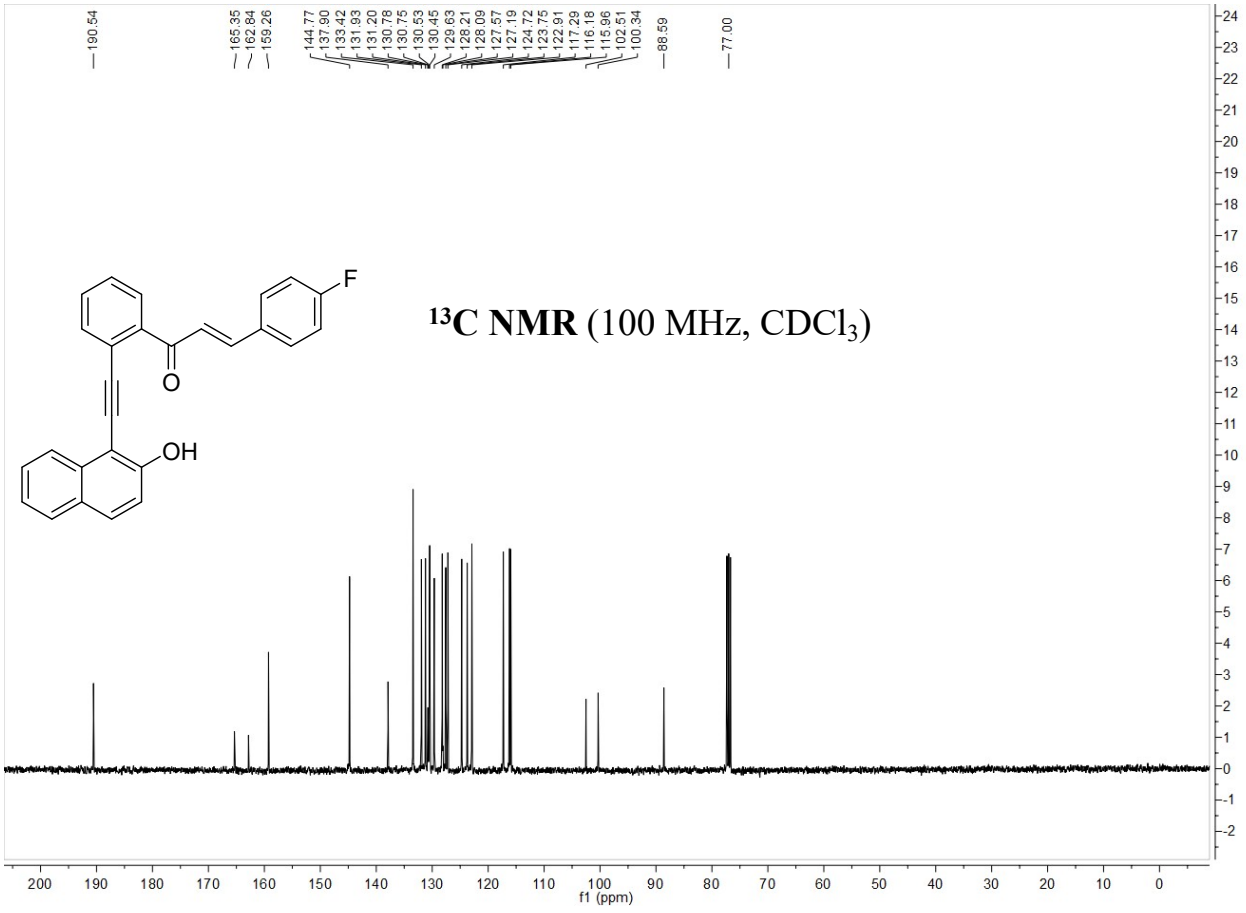
^{1}H NMR (400 MHz, $CDCl_3$)



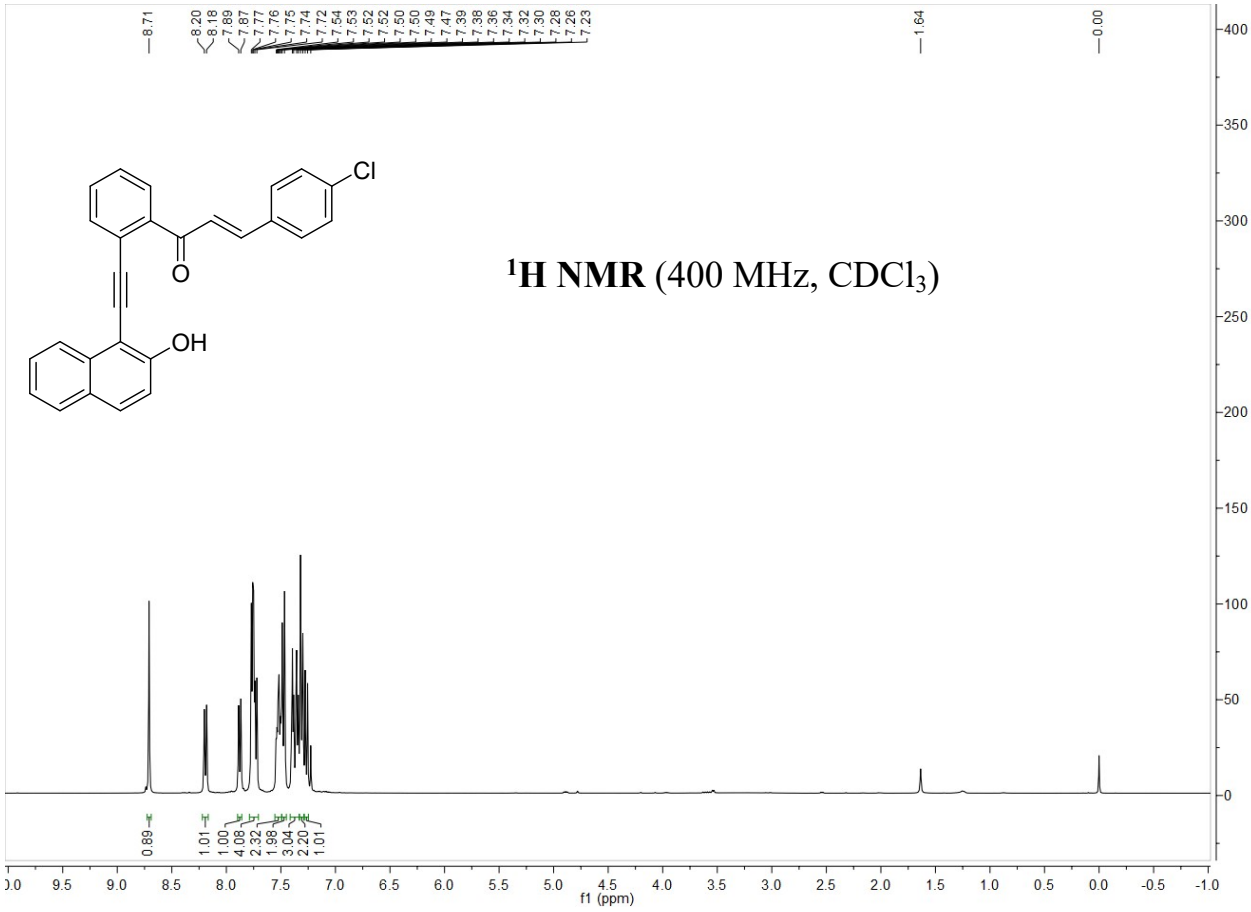
^{13}C NMR (100 MHz, $CDCl_3$)



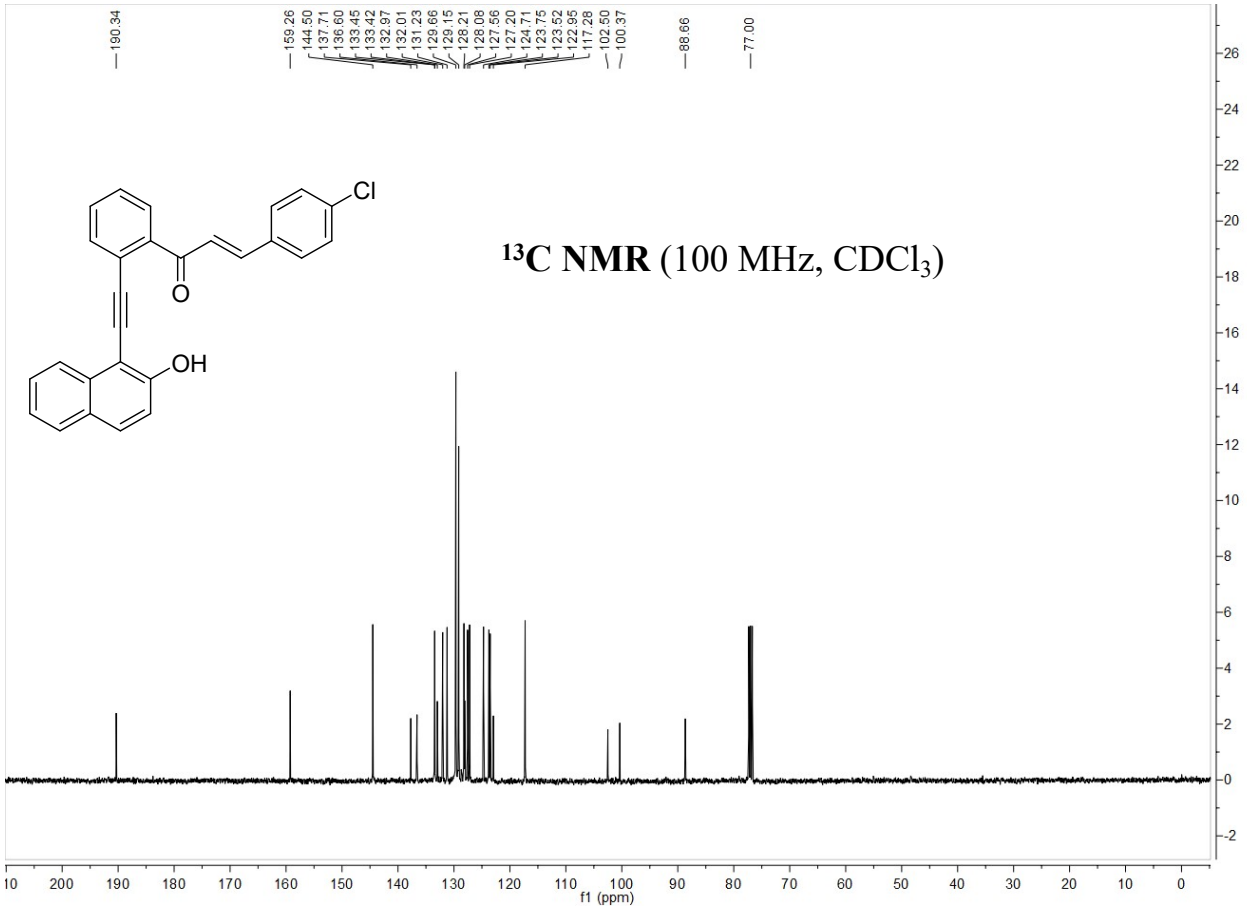
^{1}H NMR (400 MHz, $CDCl_3$)



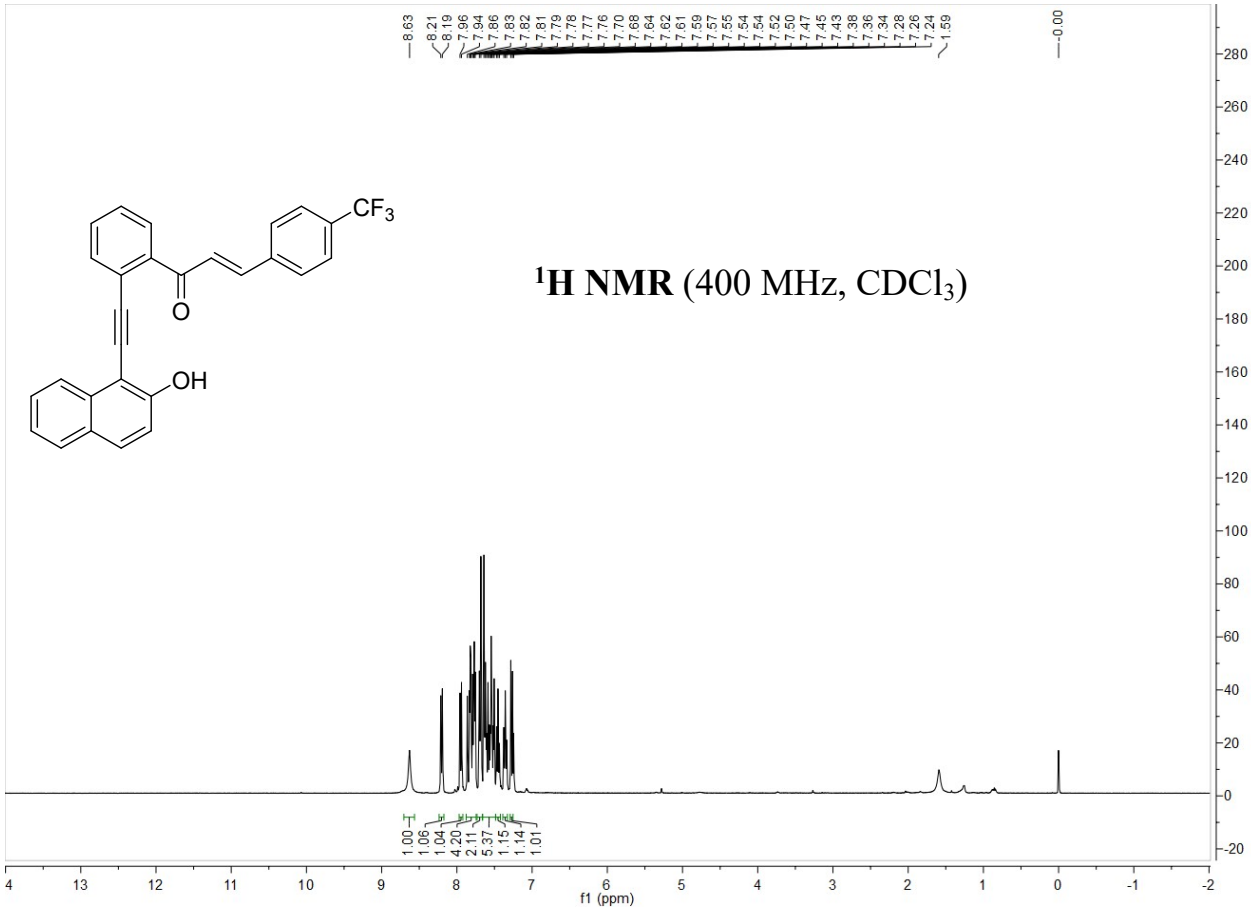
^{13}C NMR (100 MHz, $CDCl_3$)



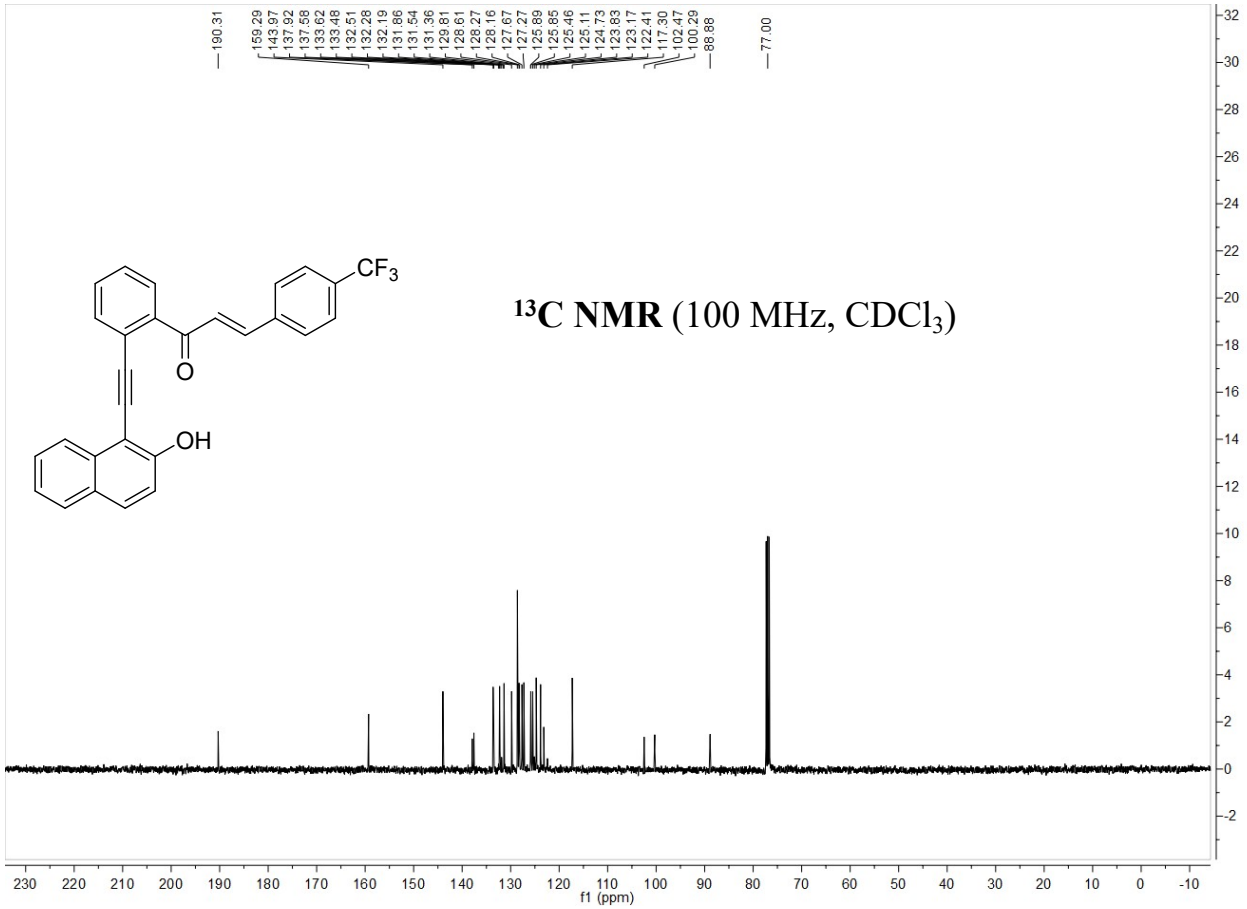
^{1}H NMR (400 MHz, $CDCl_3$)



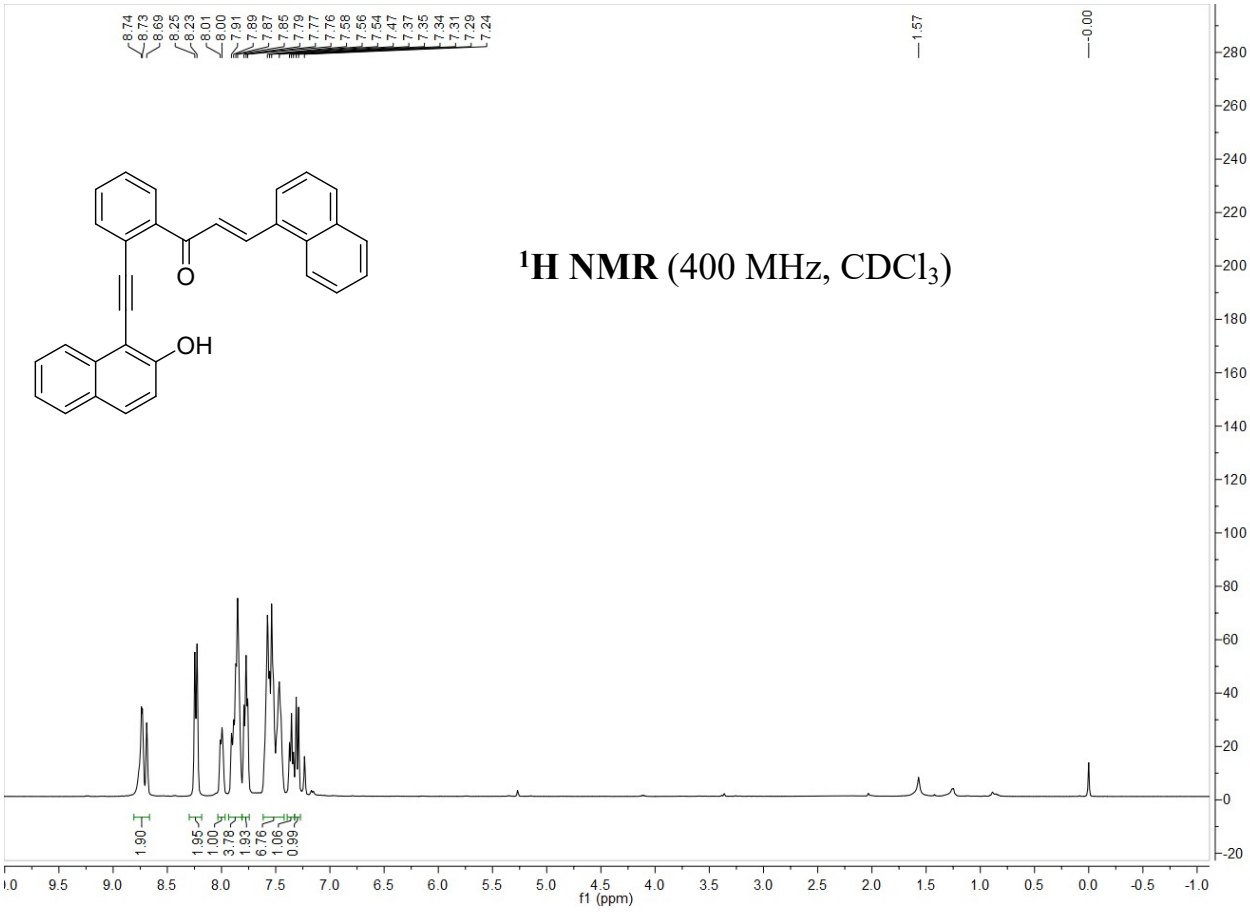
^{13}C NMR (100 MHz, $CDCl_3$)



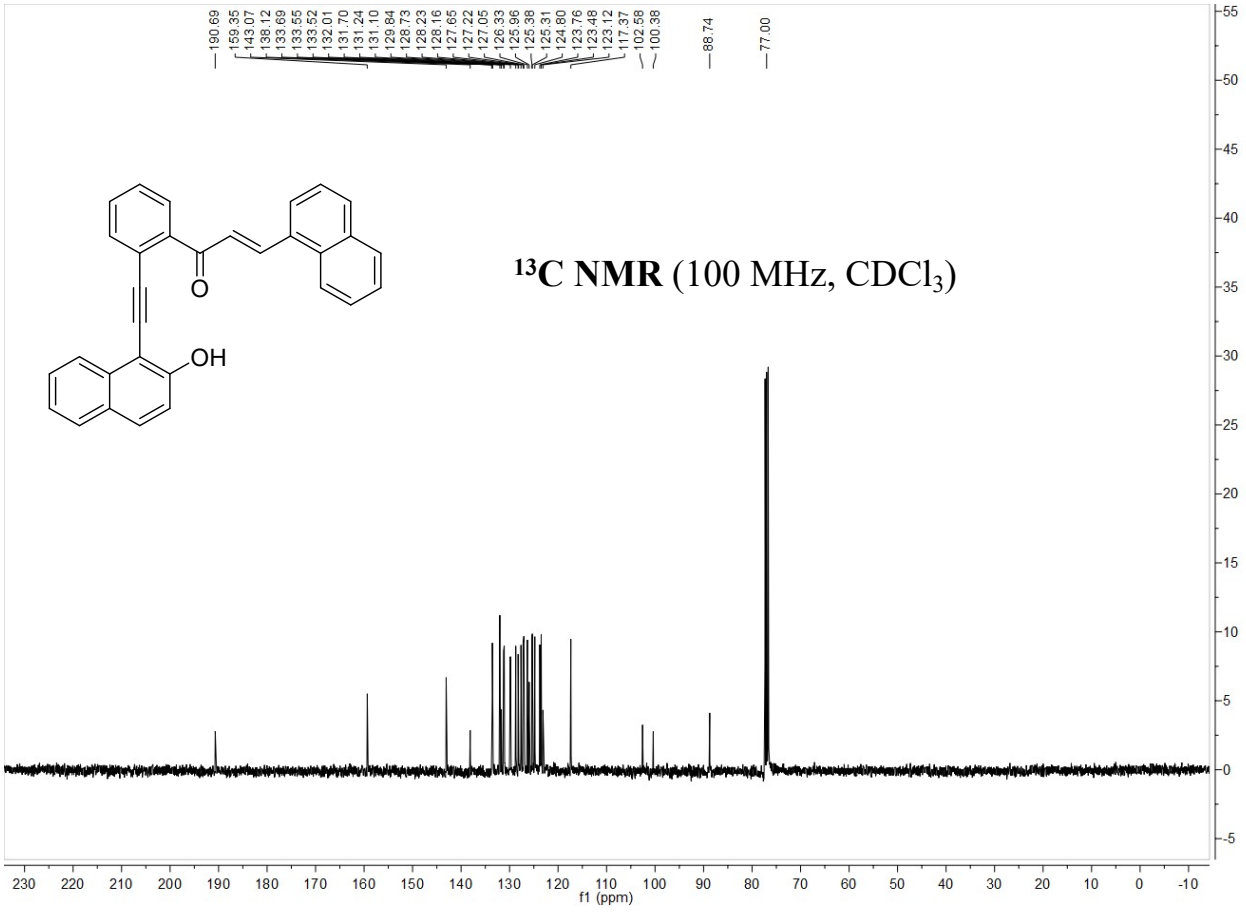
^{1}H NMR (400 MHz, $CDCl_3$)



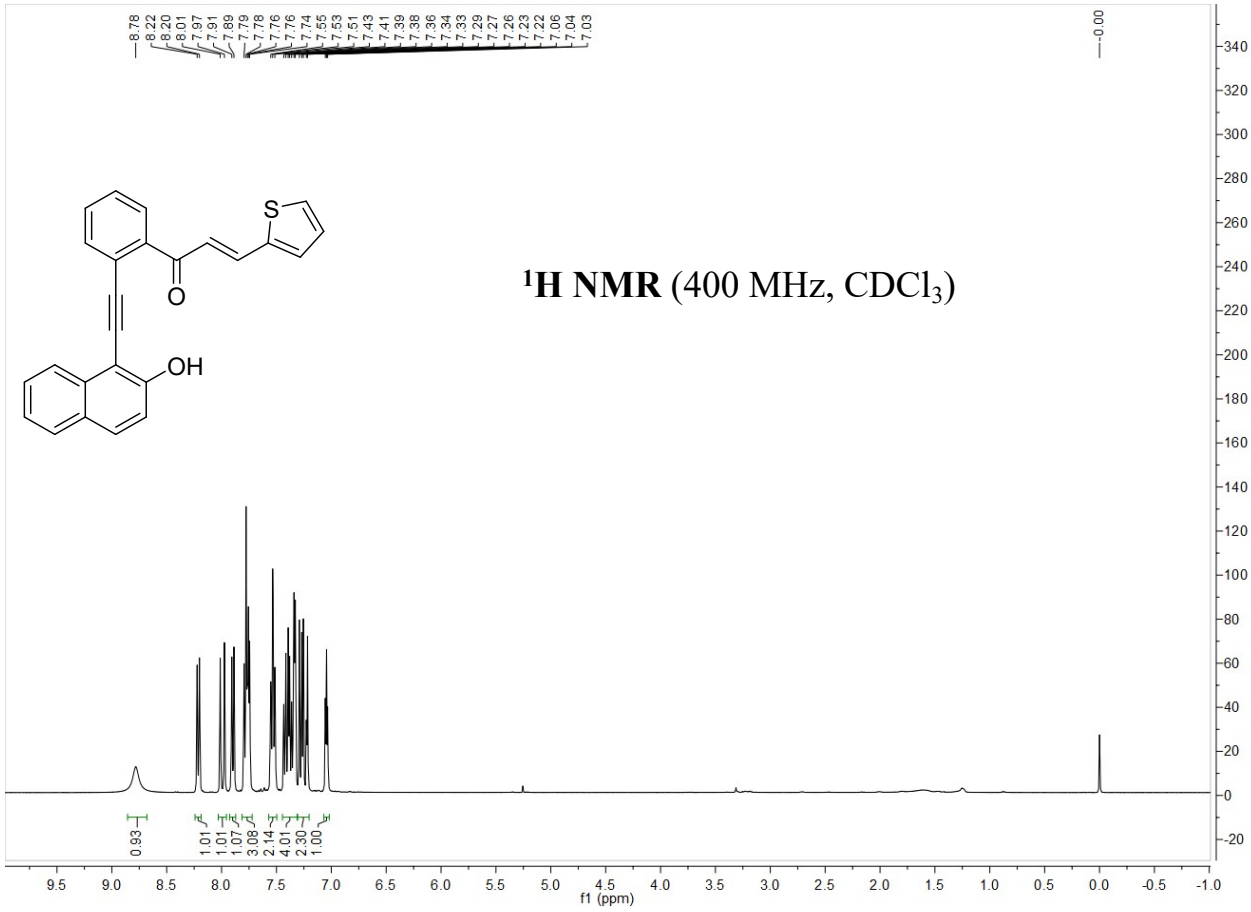
^{13}C NMR (100 MHz, $CDCl_3$)



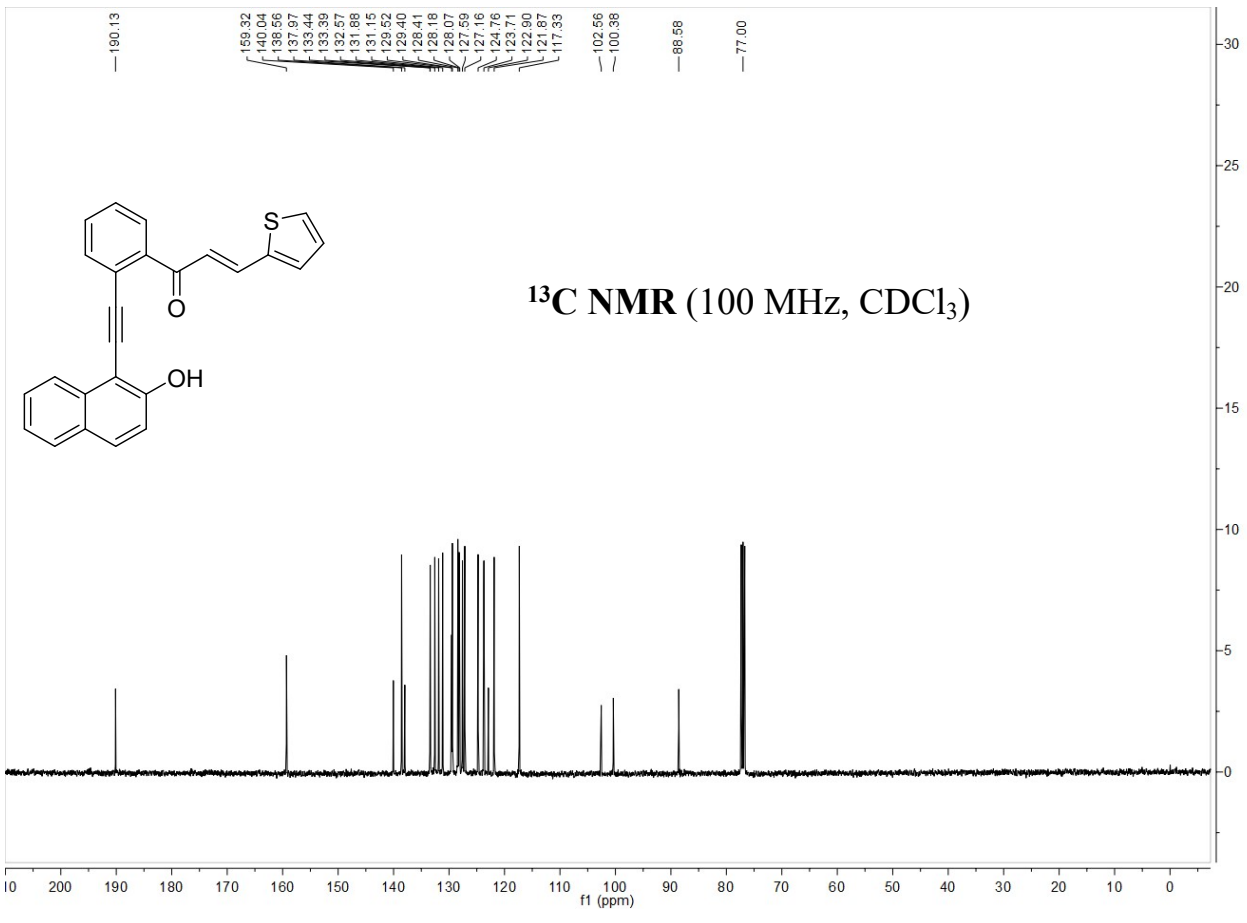
^{1}H NMR (400 MHz, $CDCl_3$)



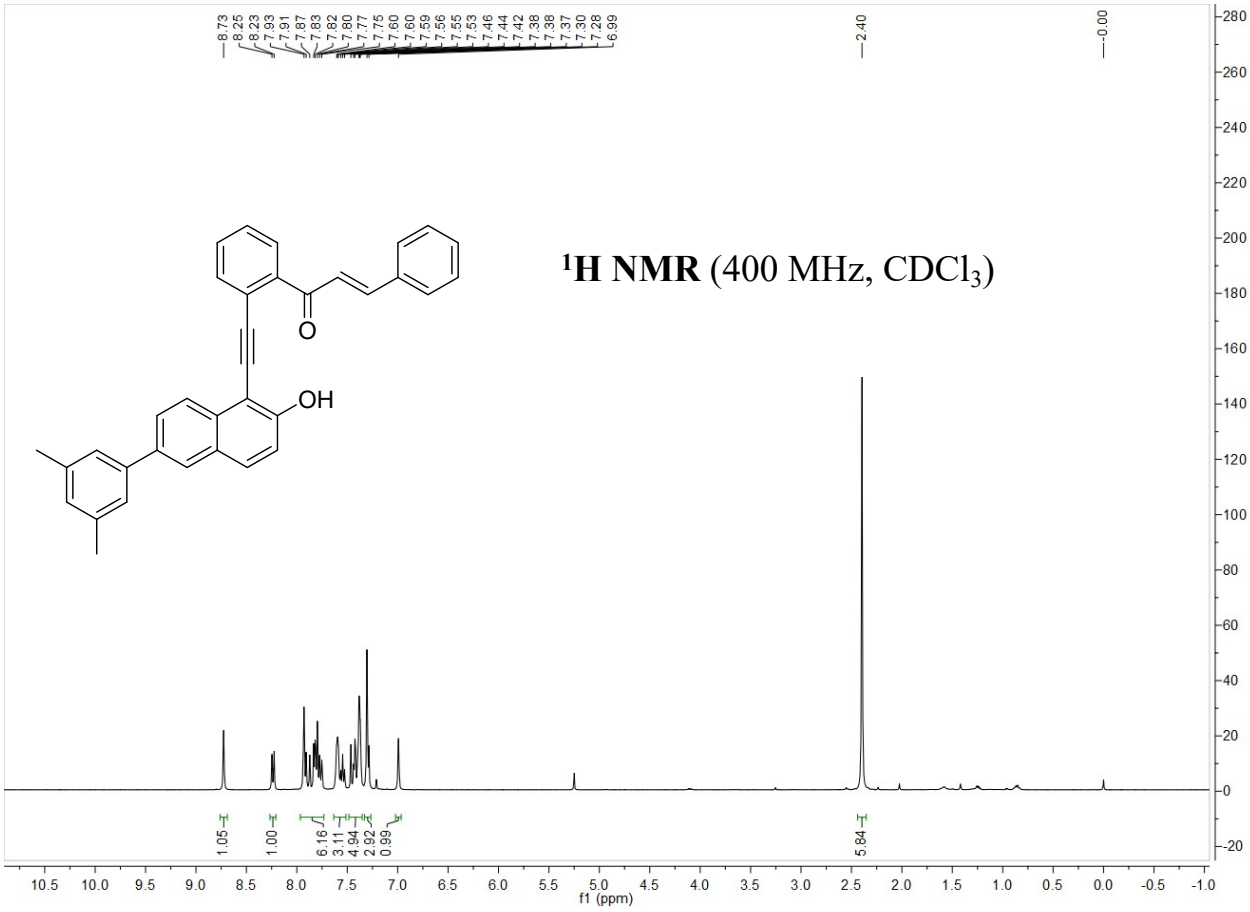
^{13}C NMR (100 MHz, $CDCl_3$)



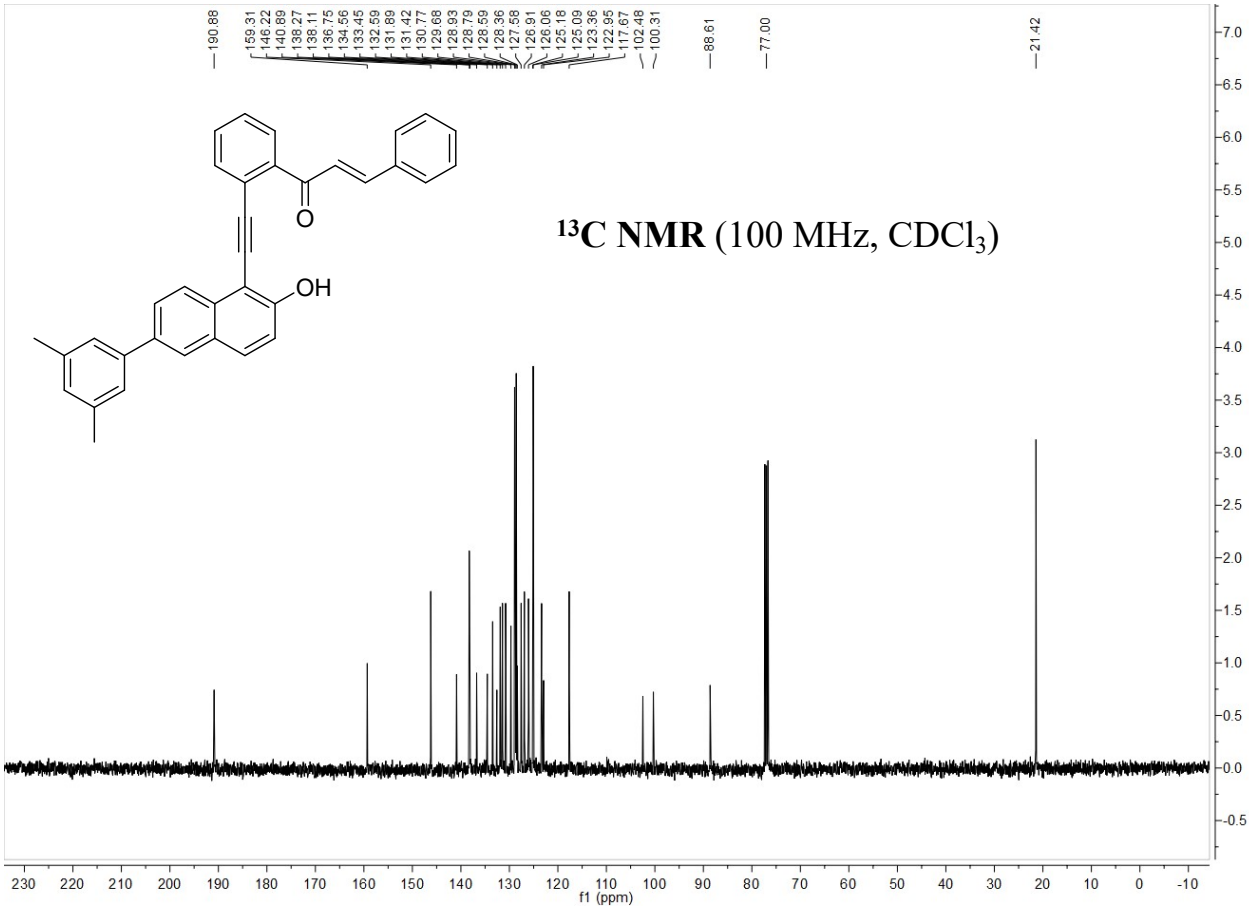
^{1}H NMR (400 MHz, $CDCl_3$)



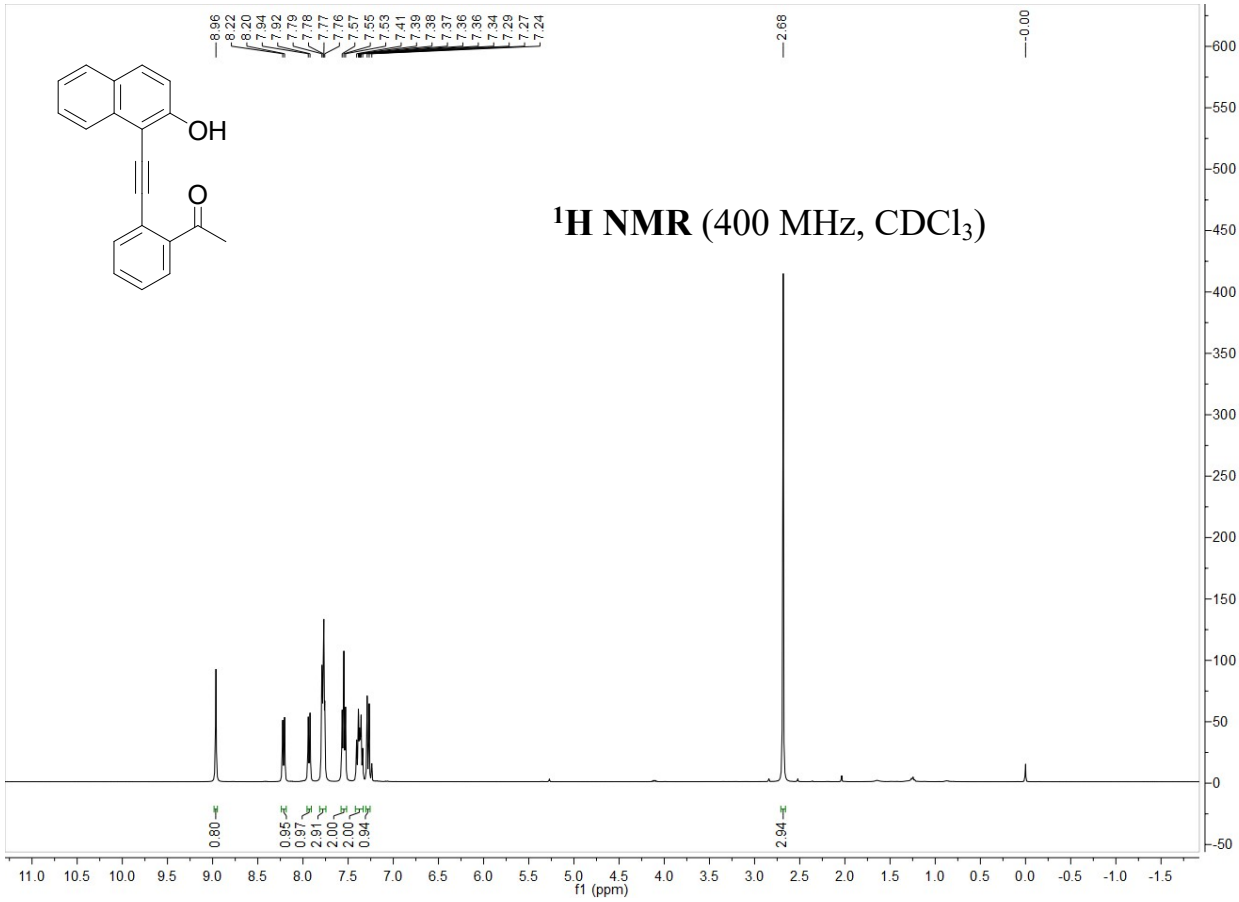
^{13}C NMR (100 MHz, $CDCl_3$)



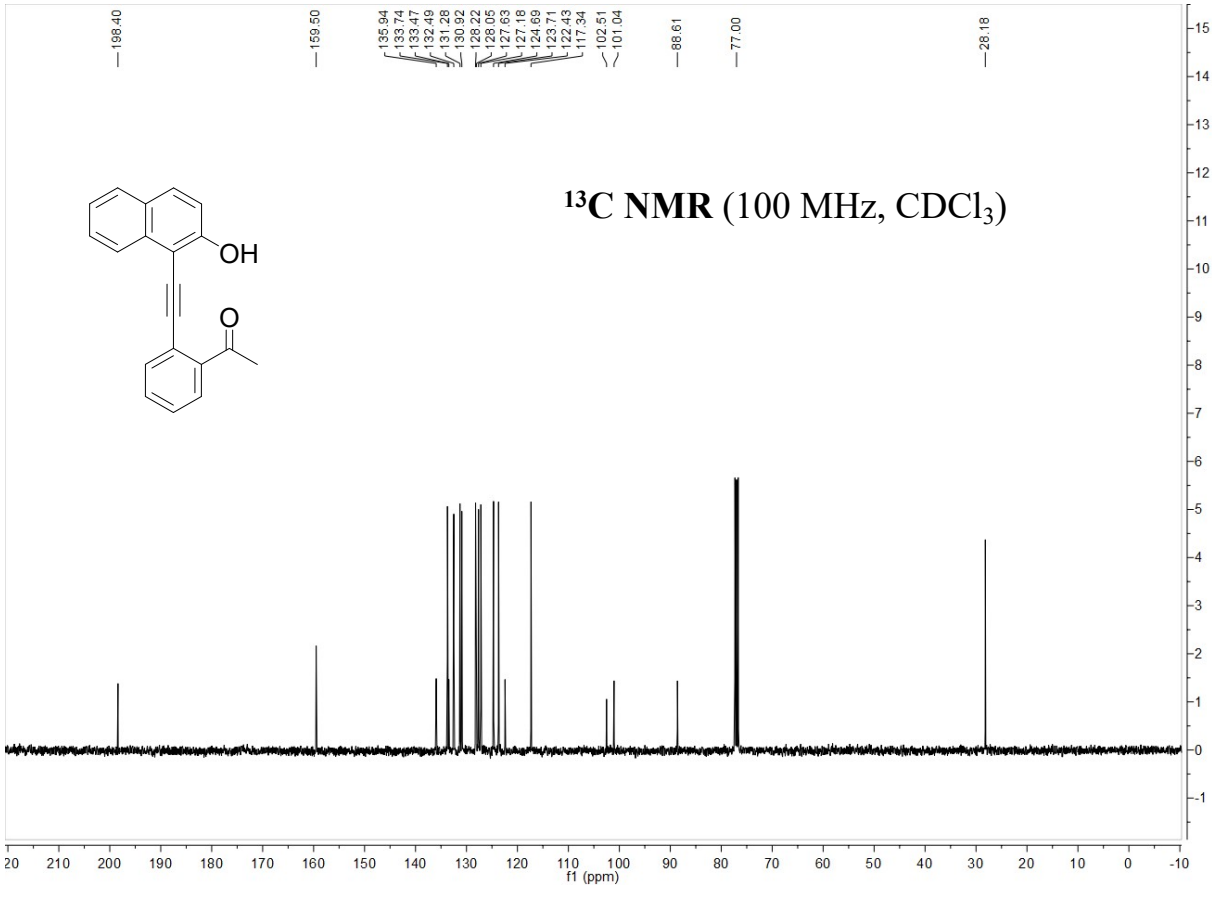
^{1}H NMR (400 MHz, $CDCl_3$)



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

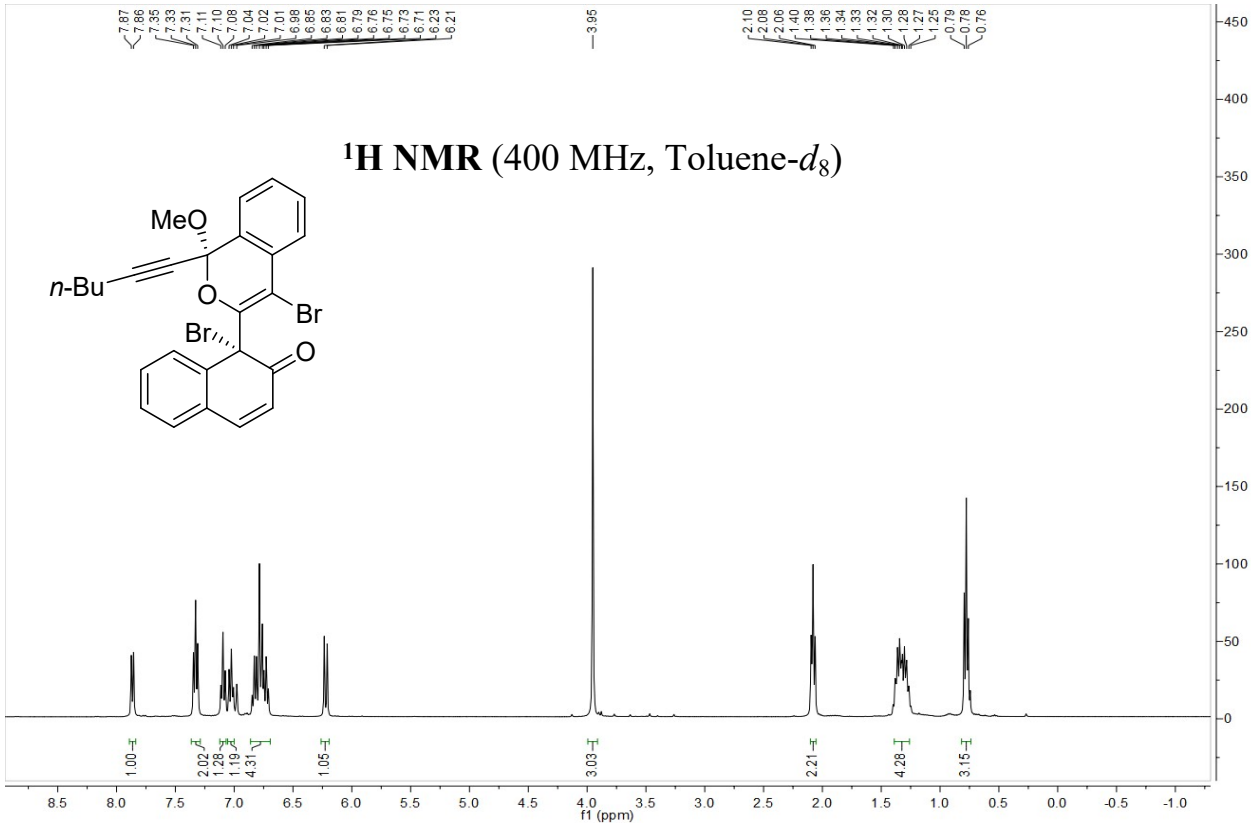


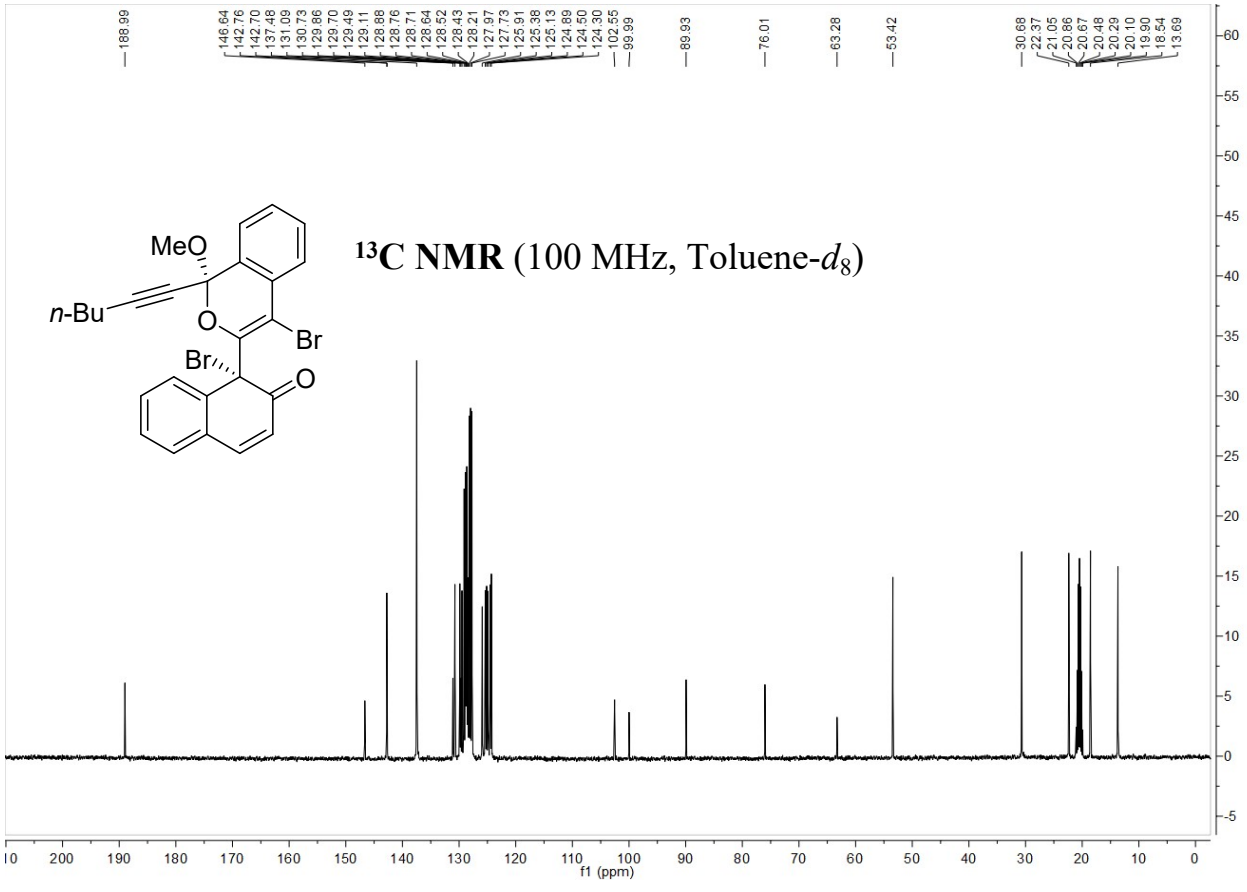
^{1}H NMR (400 MHz, $CDCl_3$)

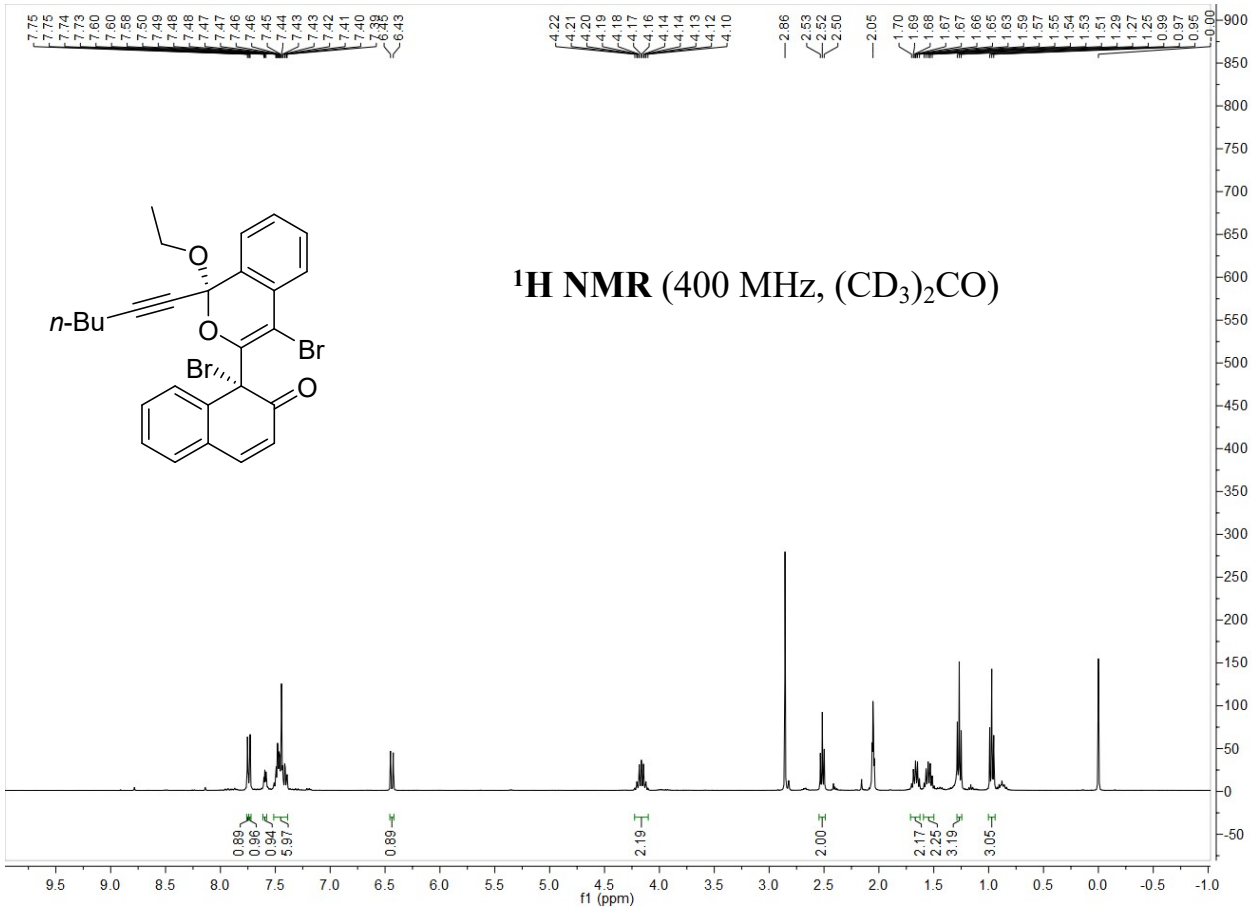


^{13}C NMR (100 MHz, $CDCl_3$)

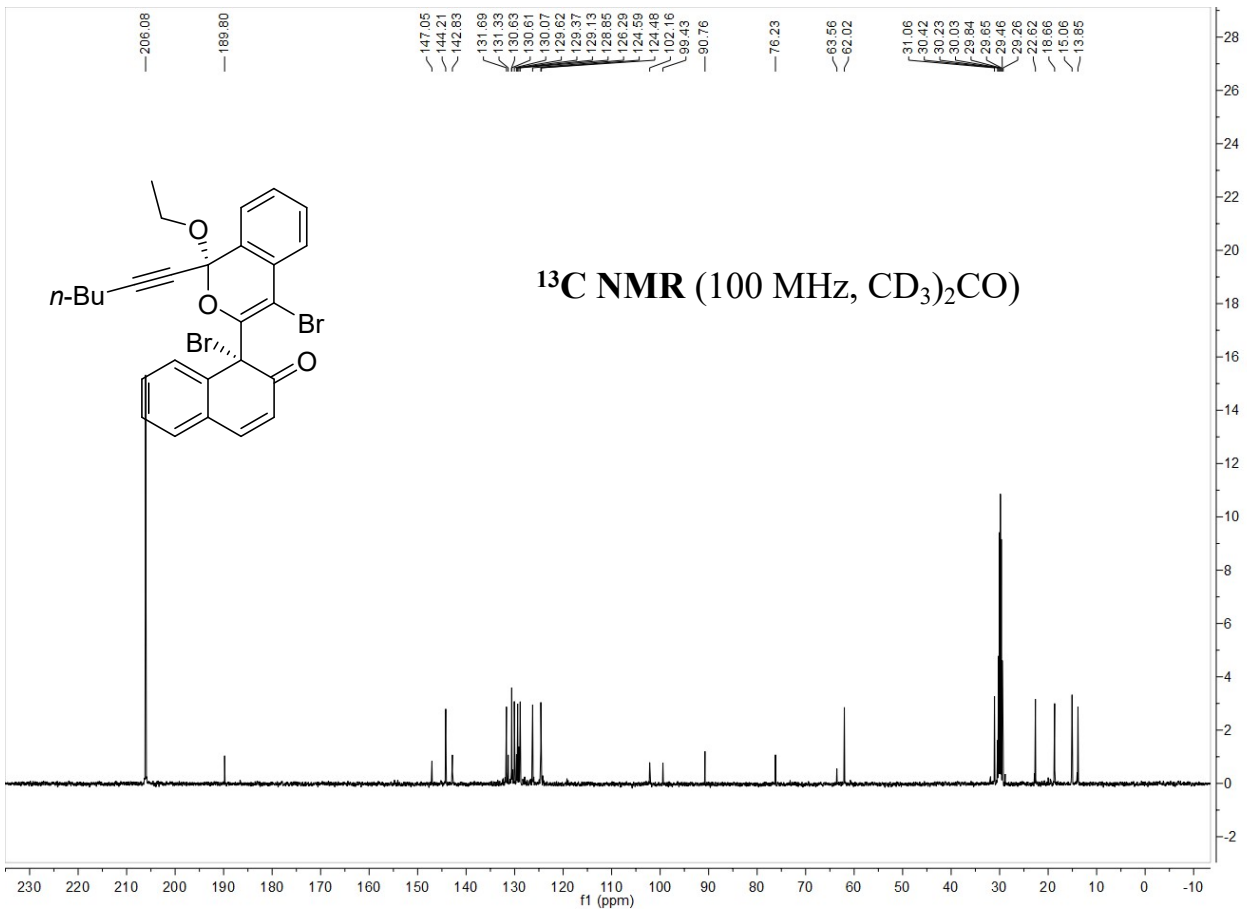
X. ^{1}H and ^{13}C NMR spectra of substrates (2a-2w, 4a-4j, M1, 5j-6j)



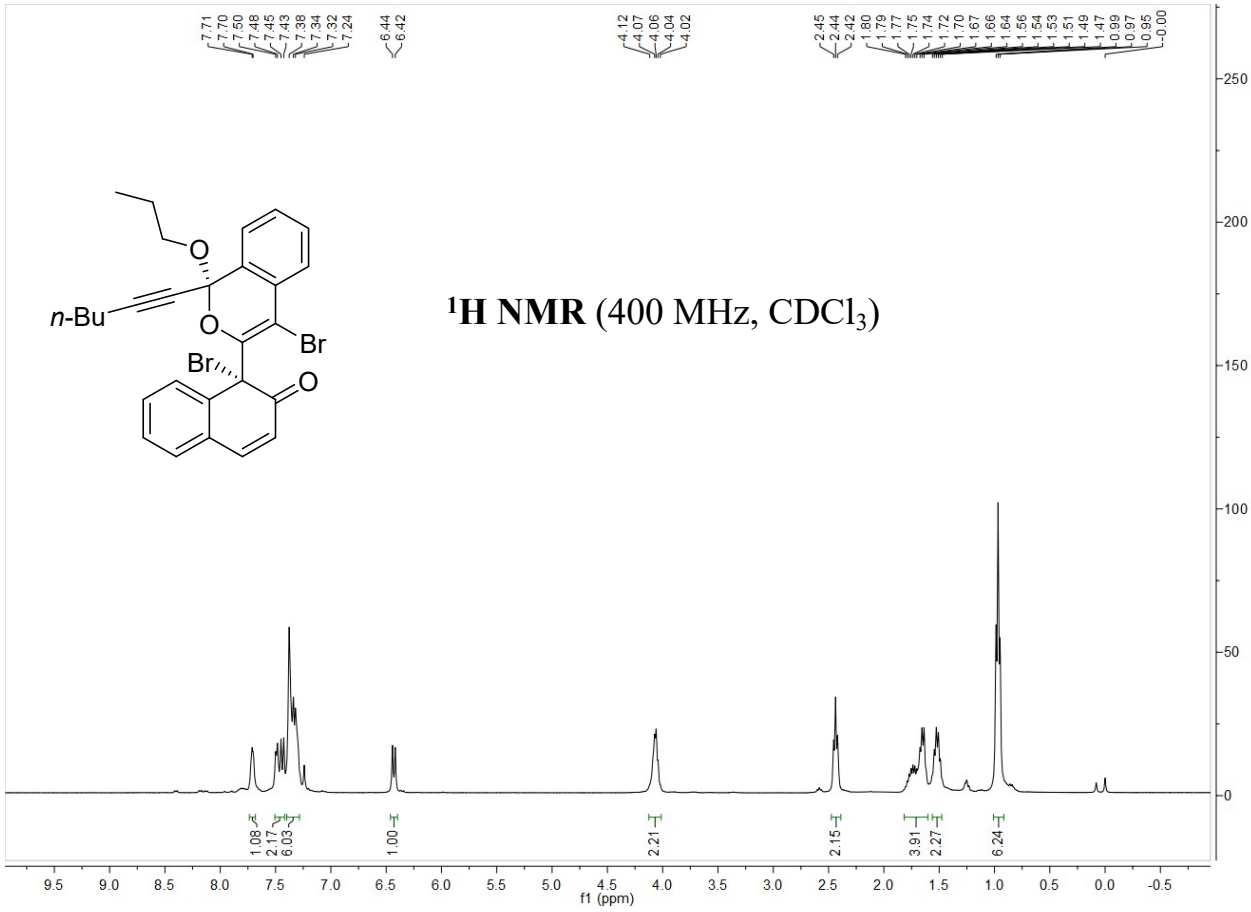




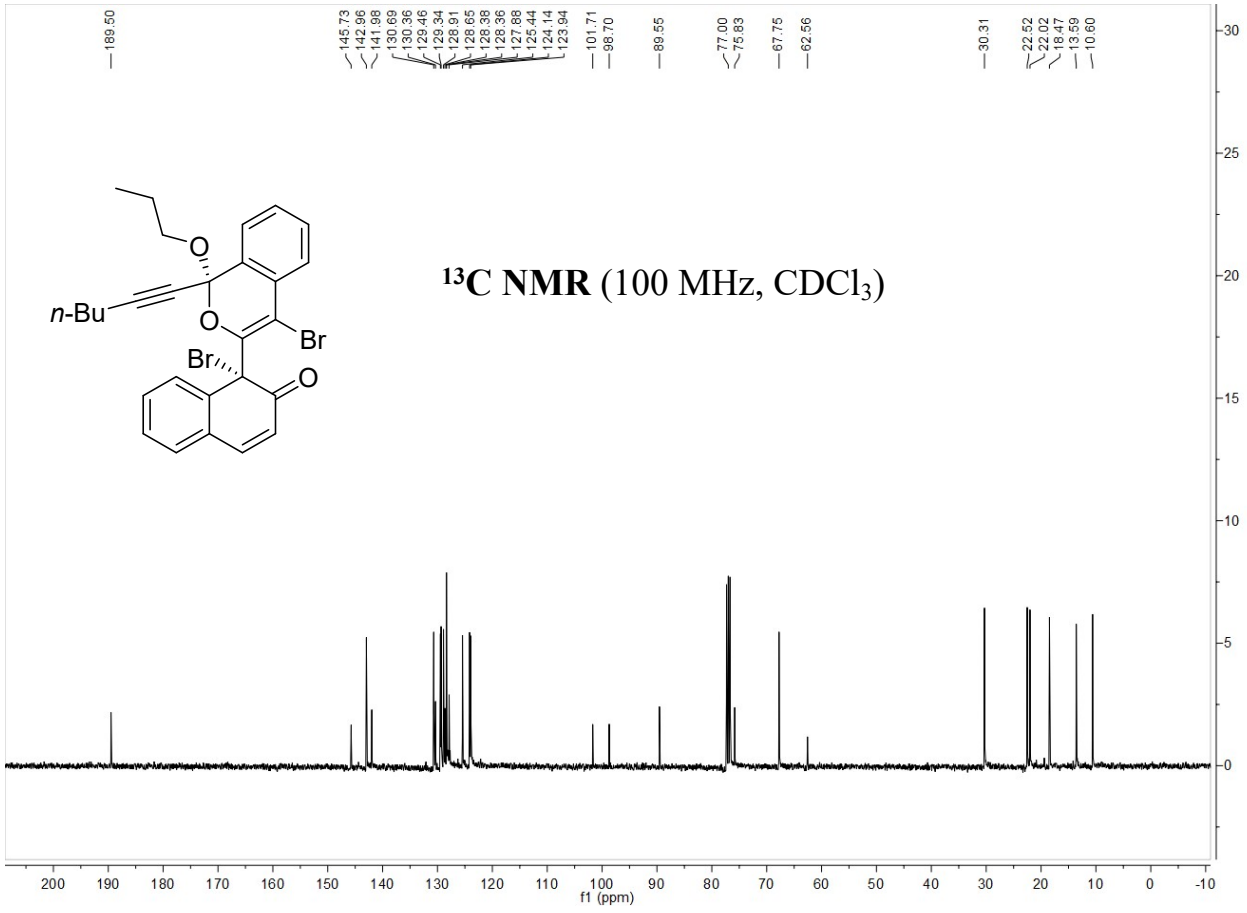
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



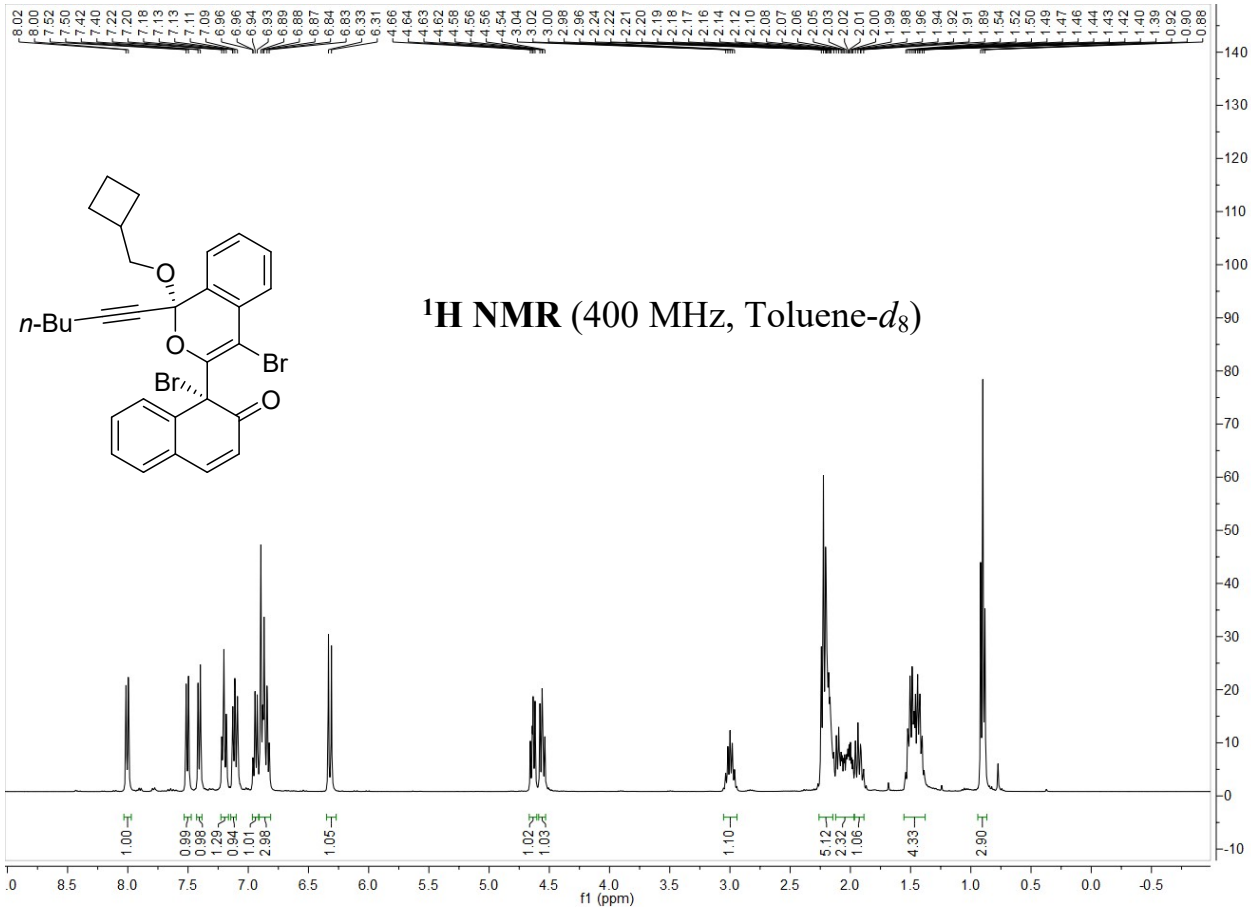
^{13}C NMR (100 MHz, $CD_3)_2CO$)

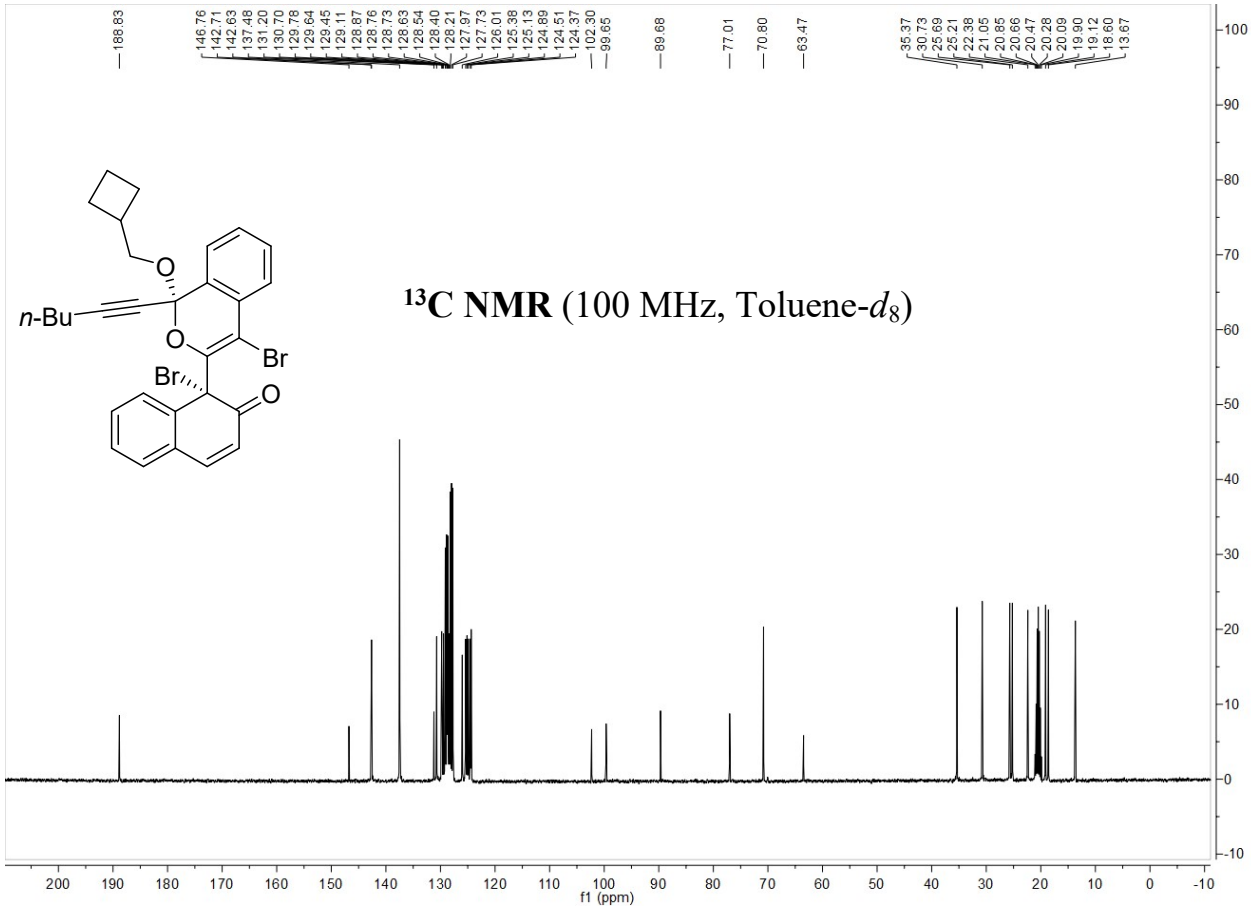


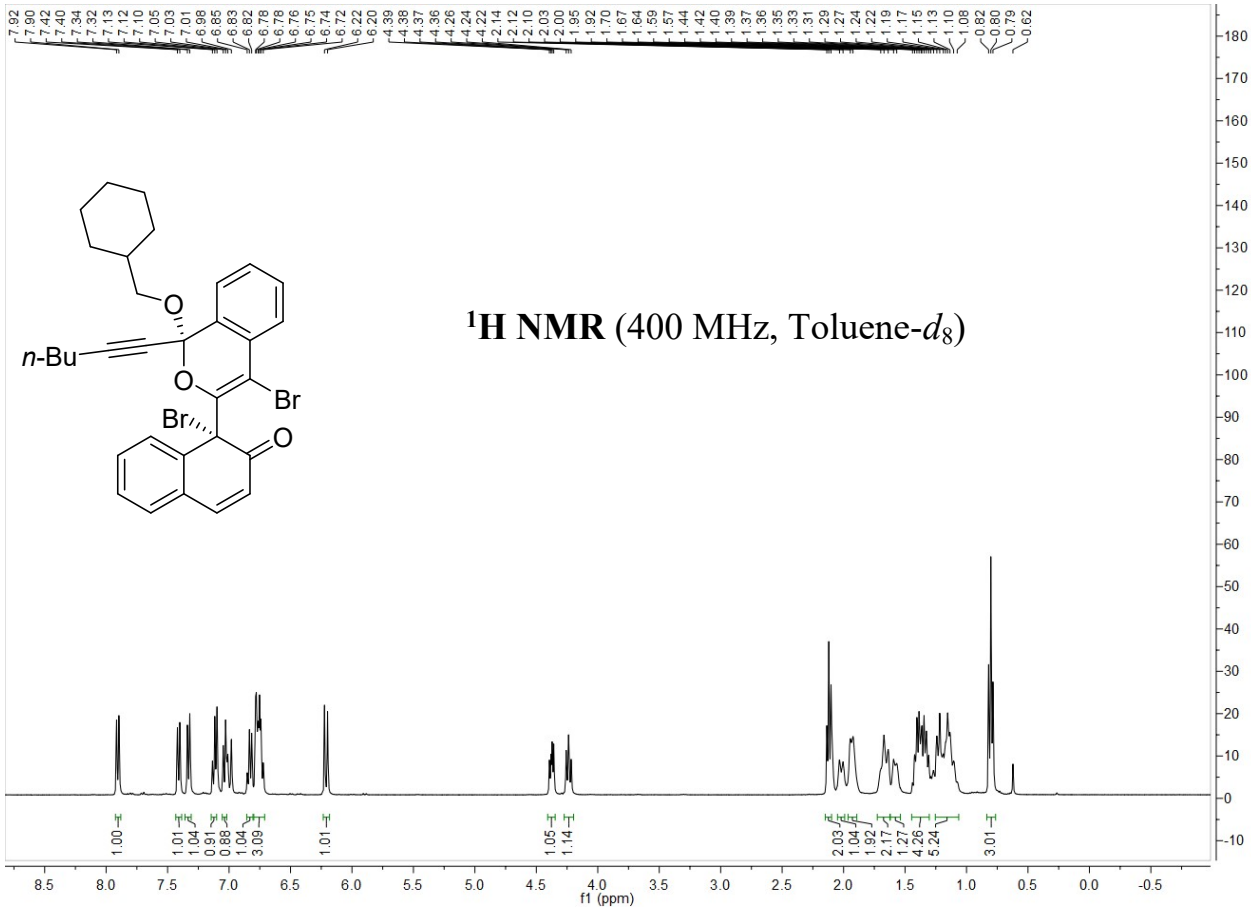
^{1}H NMR (400 MHz, $CDCl_3$)



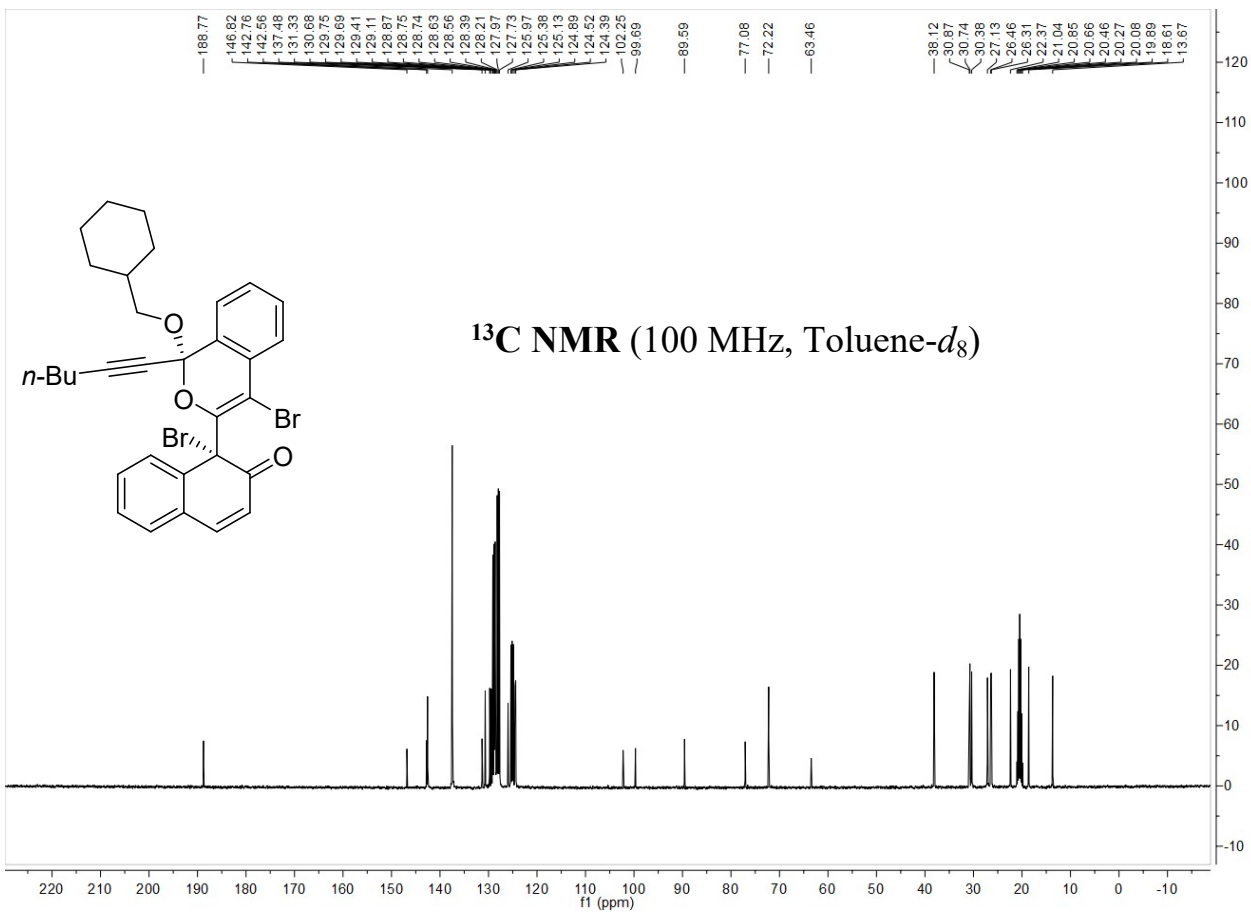
^{13}C NMR (100 MHz, $CDCl_3$)


n-Bu
O
O
Br
Br
O
¹H NMR (400 MHz, Toluene-d8)
f1 (ppm)

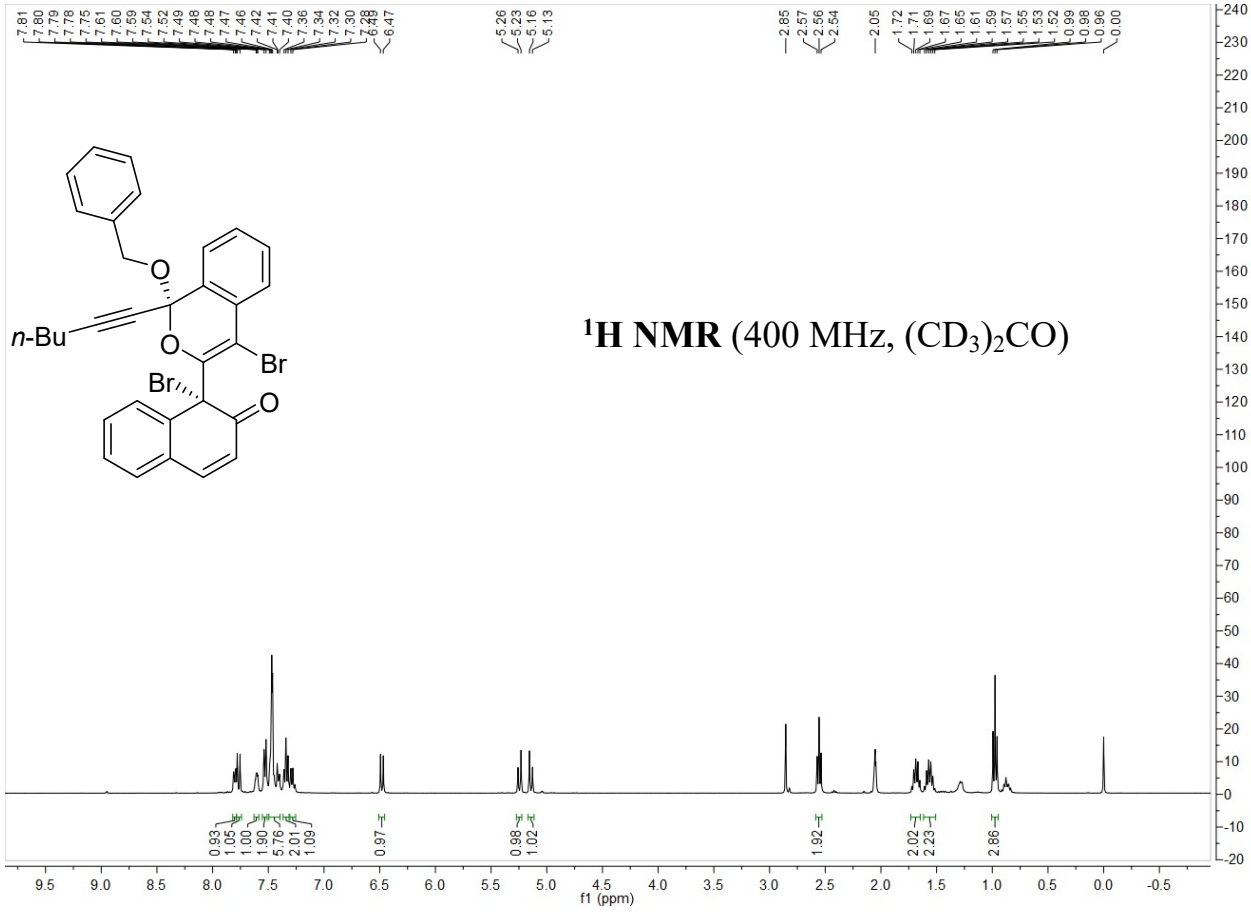

n-Bu
O
O
Br
Br
O
¹³C NMR (100 MHz, Toluene-d8)
f1 (ppm)



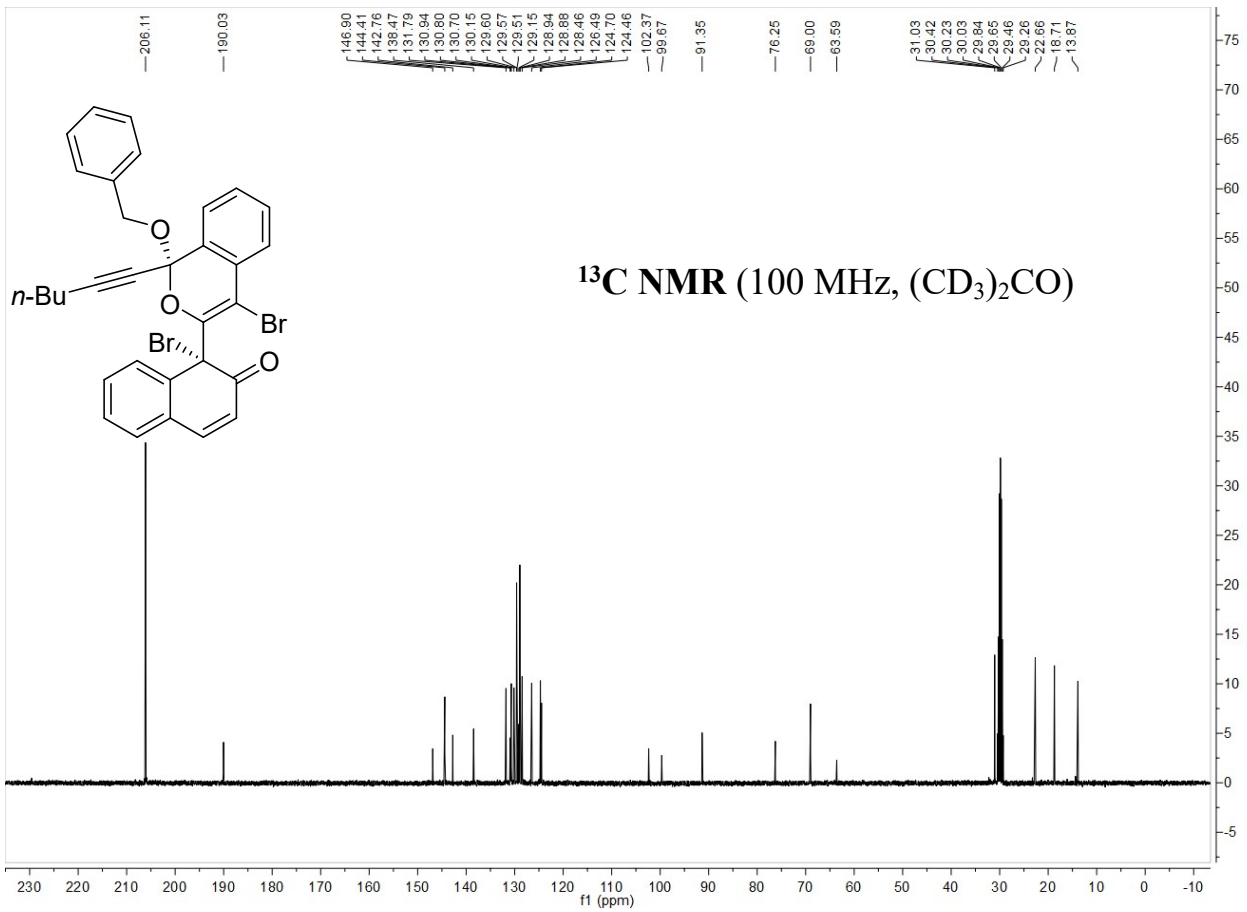
^{1}H NMR (400 MHz, Toluene-d_8)



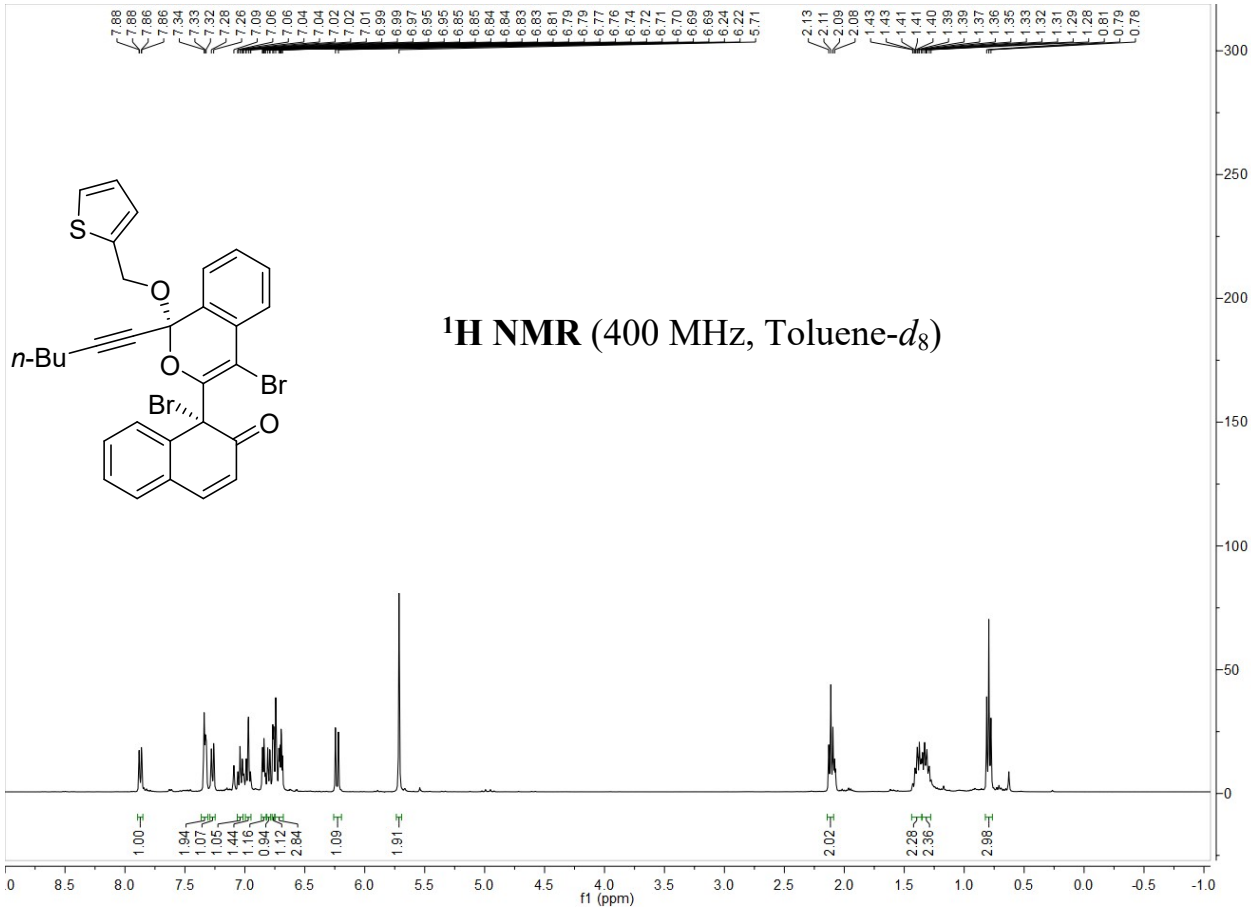
^{13}C NMR (100 MHz, Toluene-d_8)



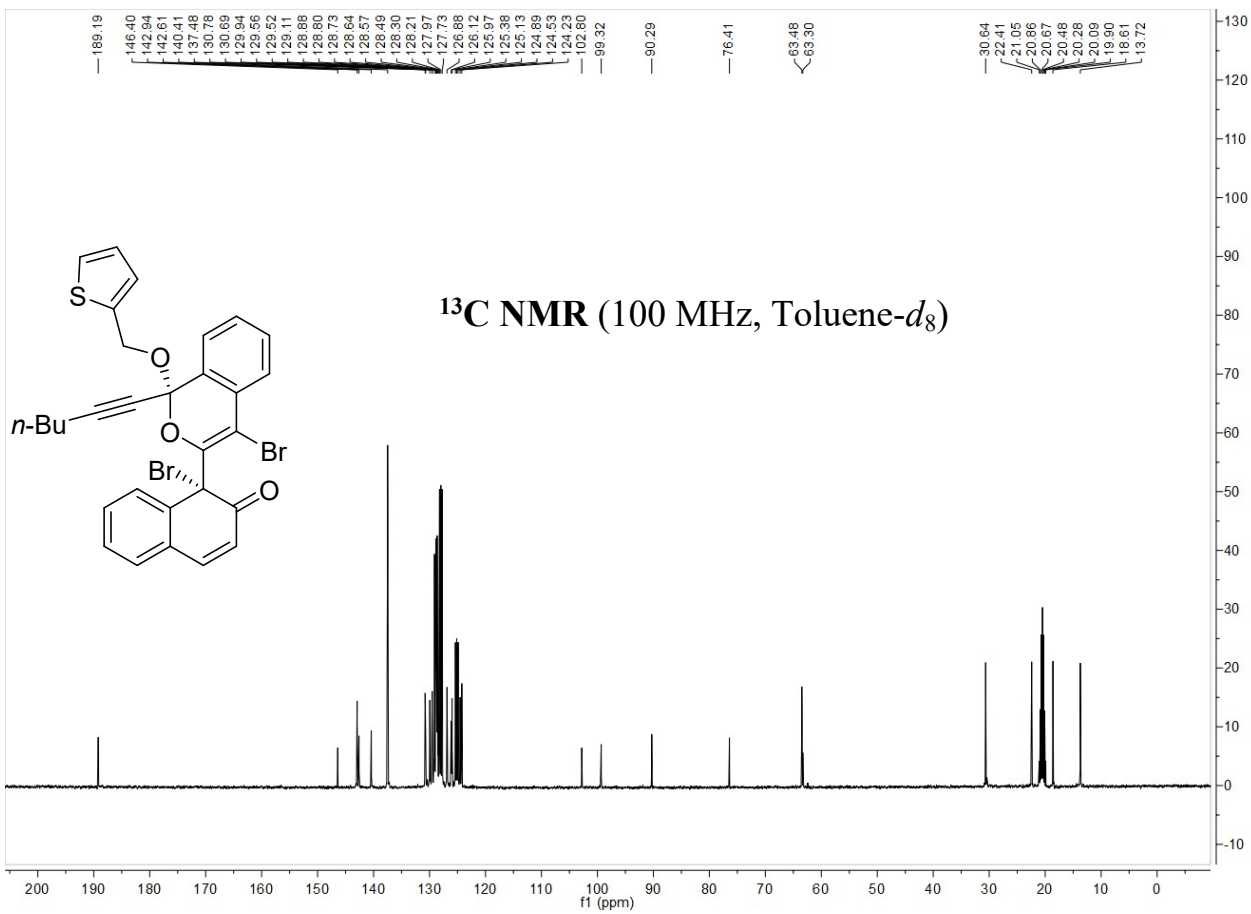
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



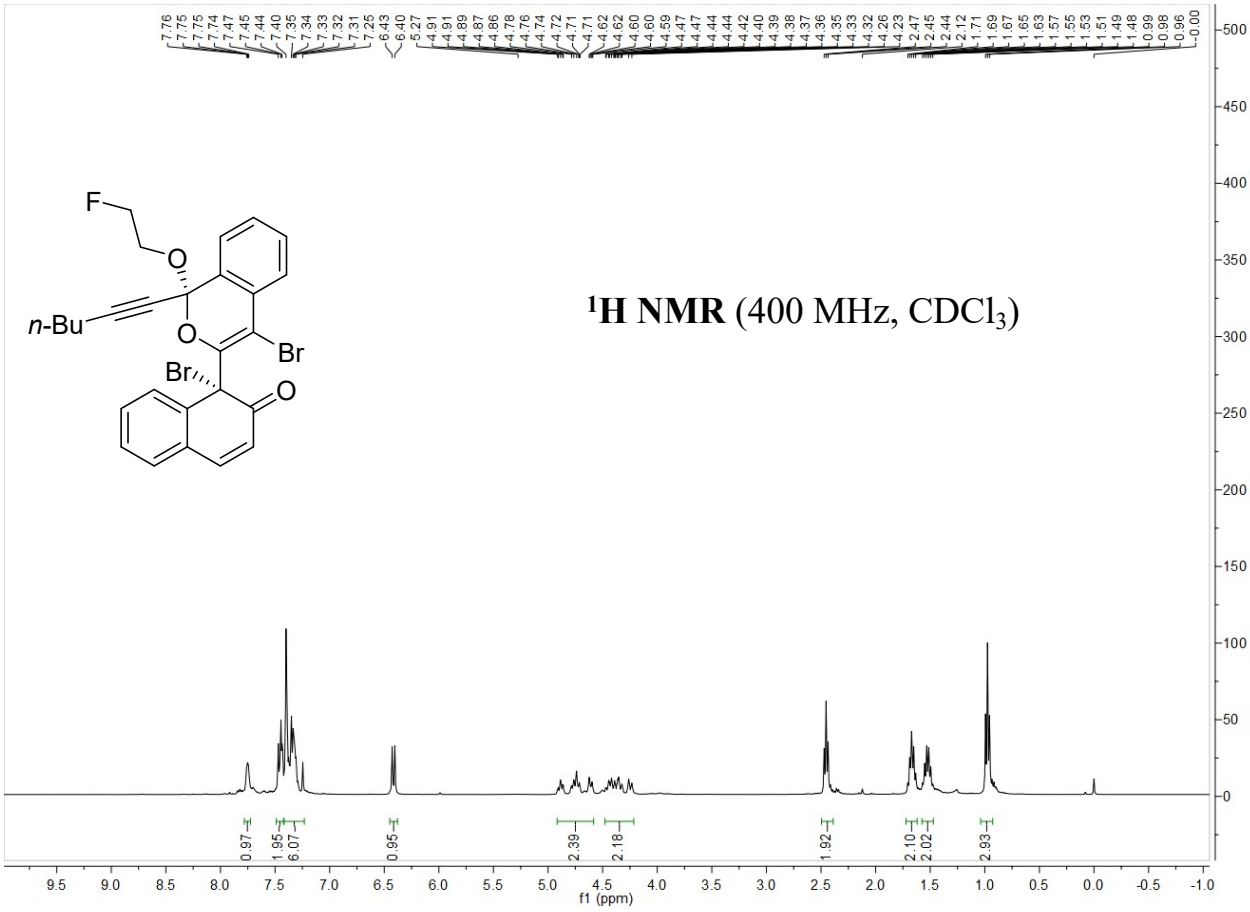
^{13}C NMR (100 MHz, $(CD_3)_2CO$)



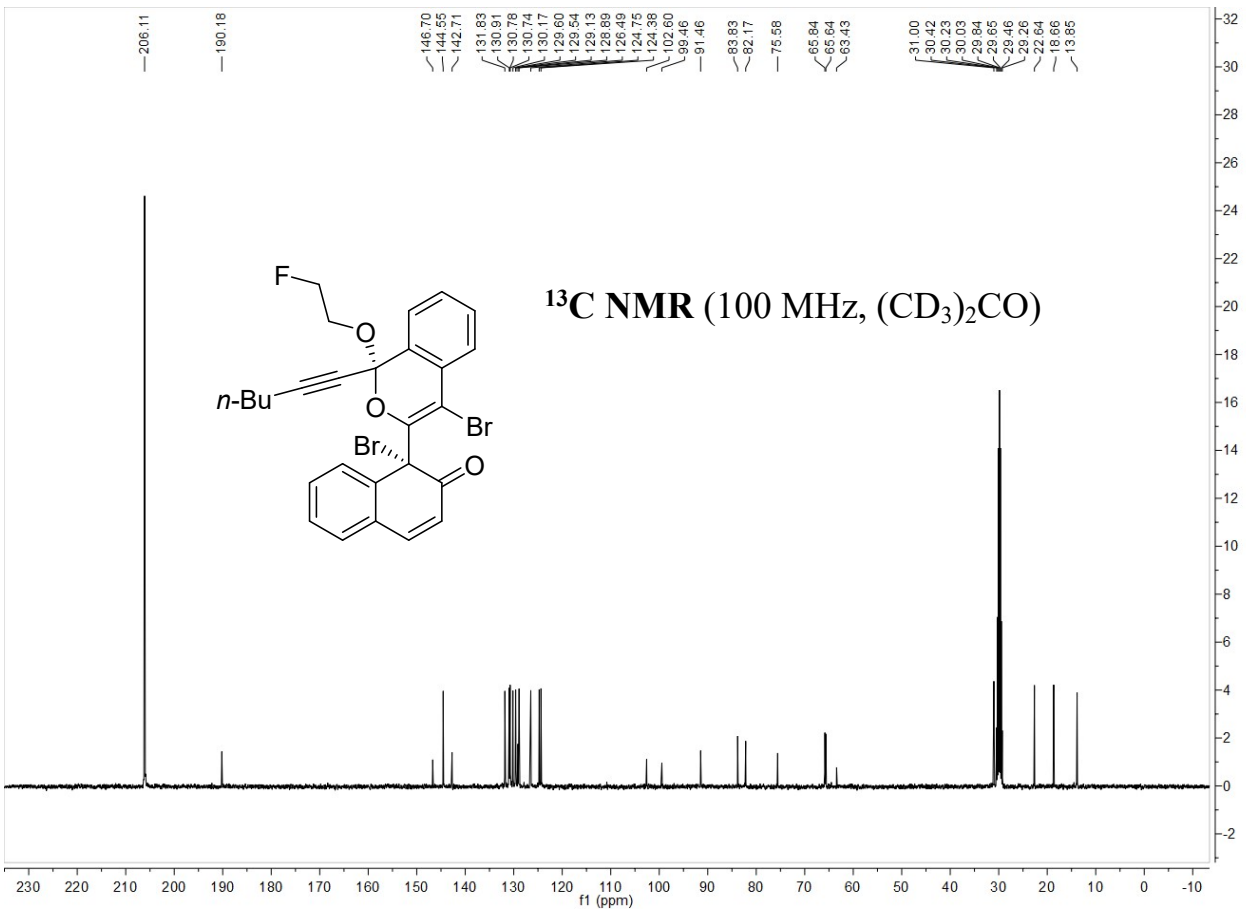
^{1}H NMR (400 MHz, Toluene-d_8)



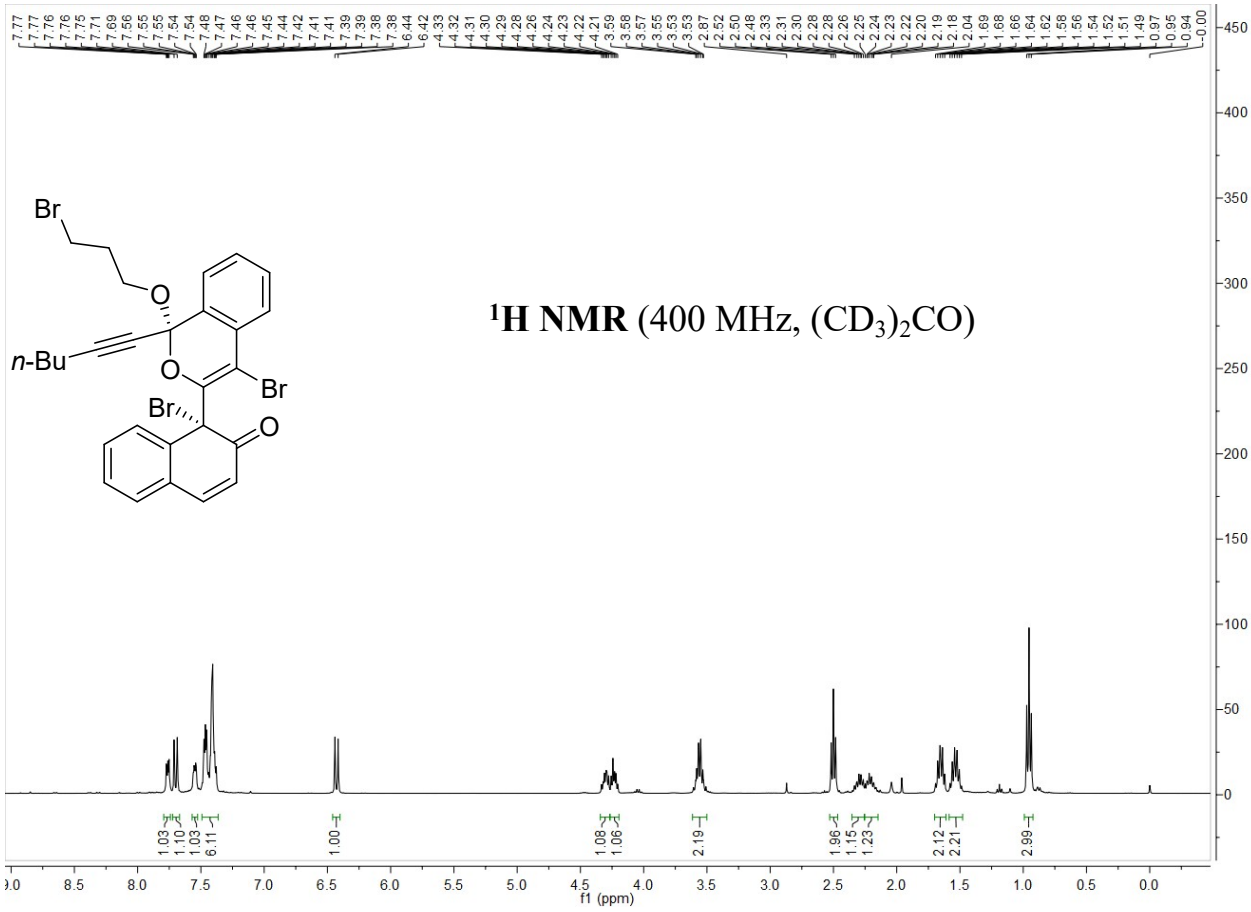
^{13}C NMR (100 MHz, Toluene-d_8)



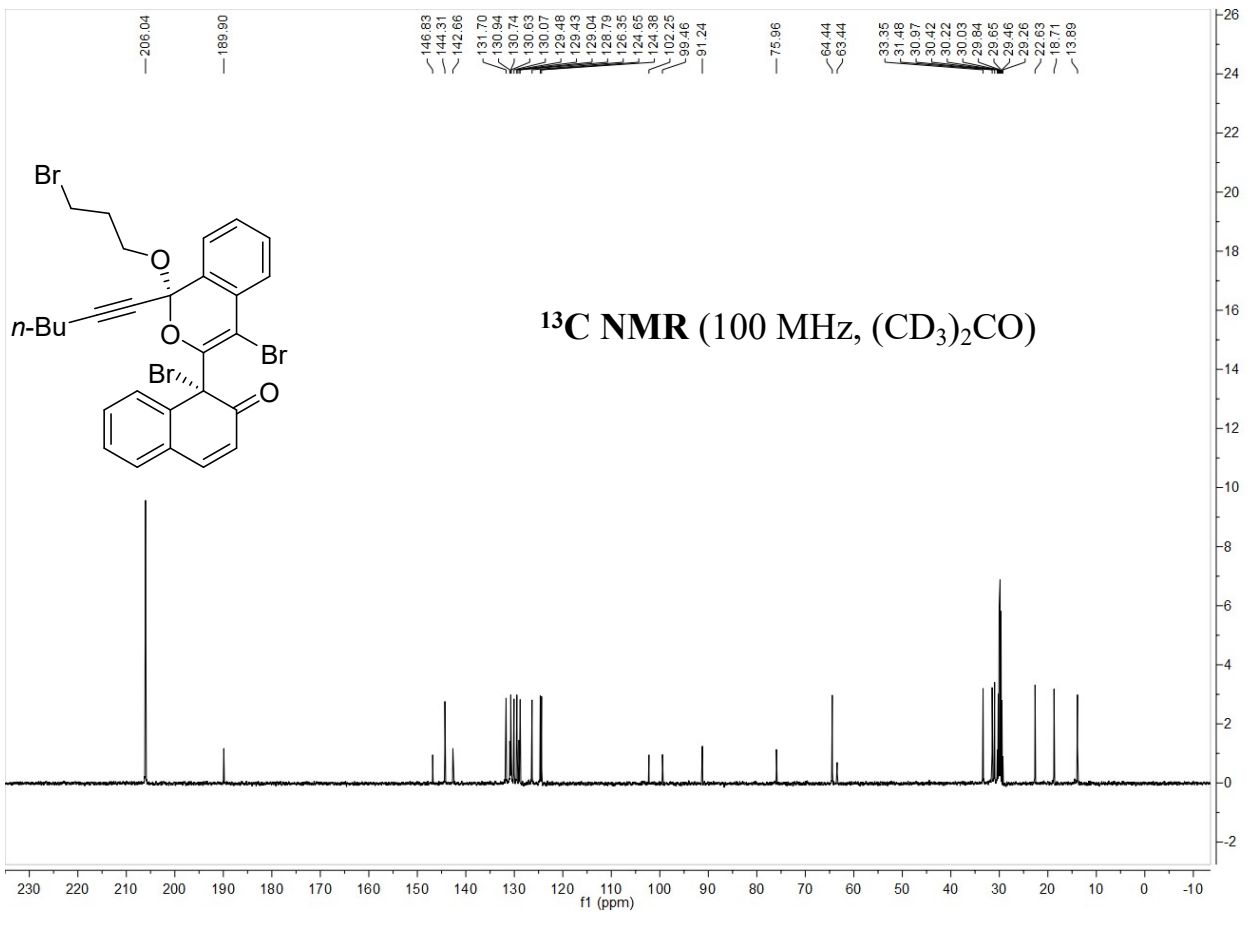
^{1}H NMR (400 MHz, $CDCl_3$)



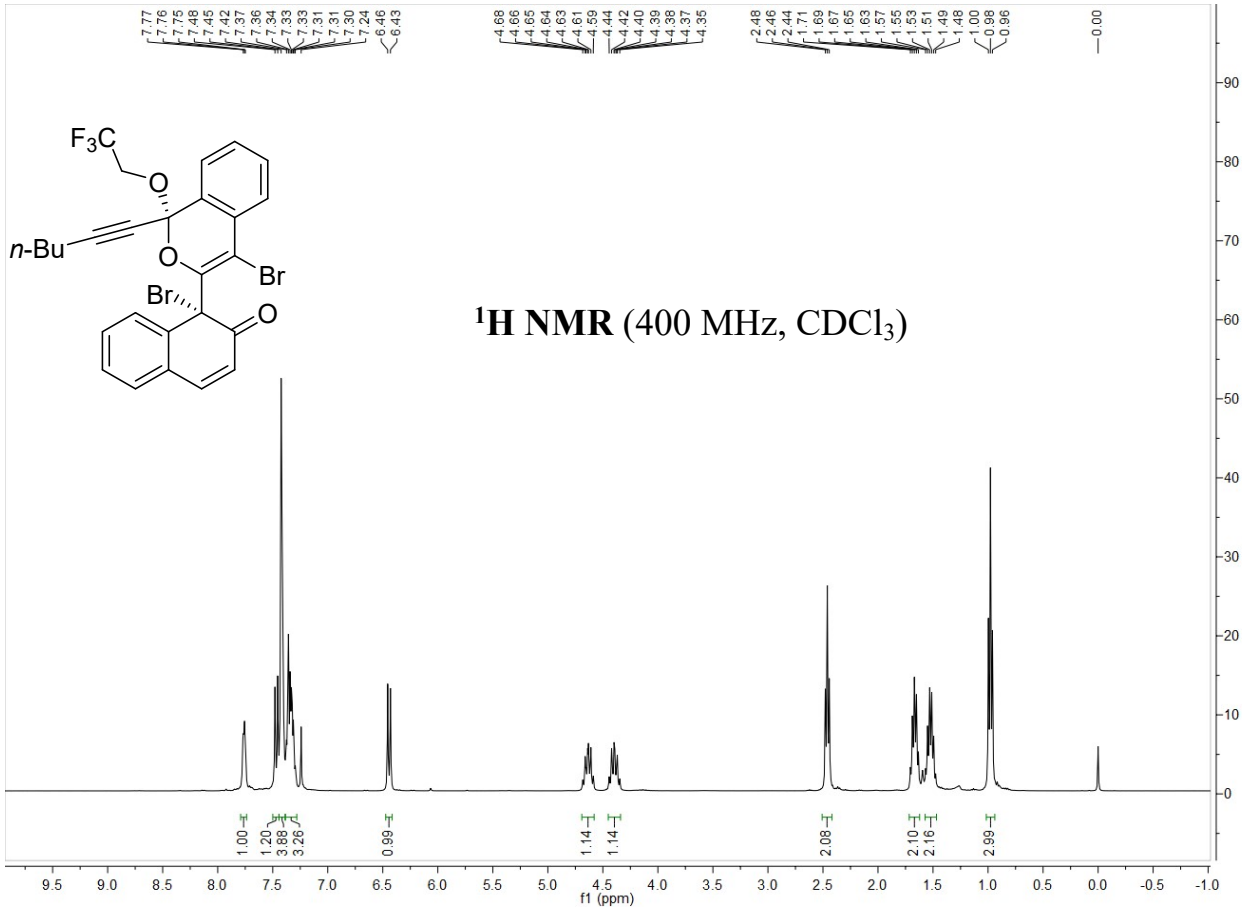
^{13}C NMR (100 MHz, $(CD_3)_2CO$)

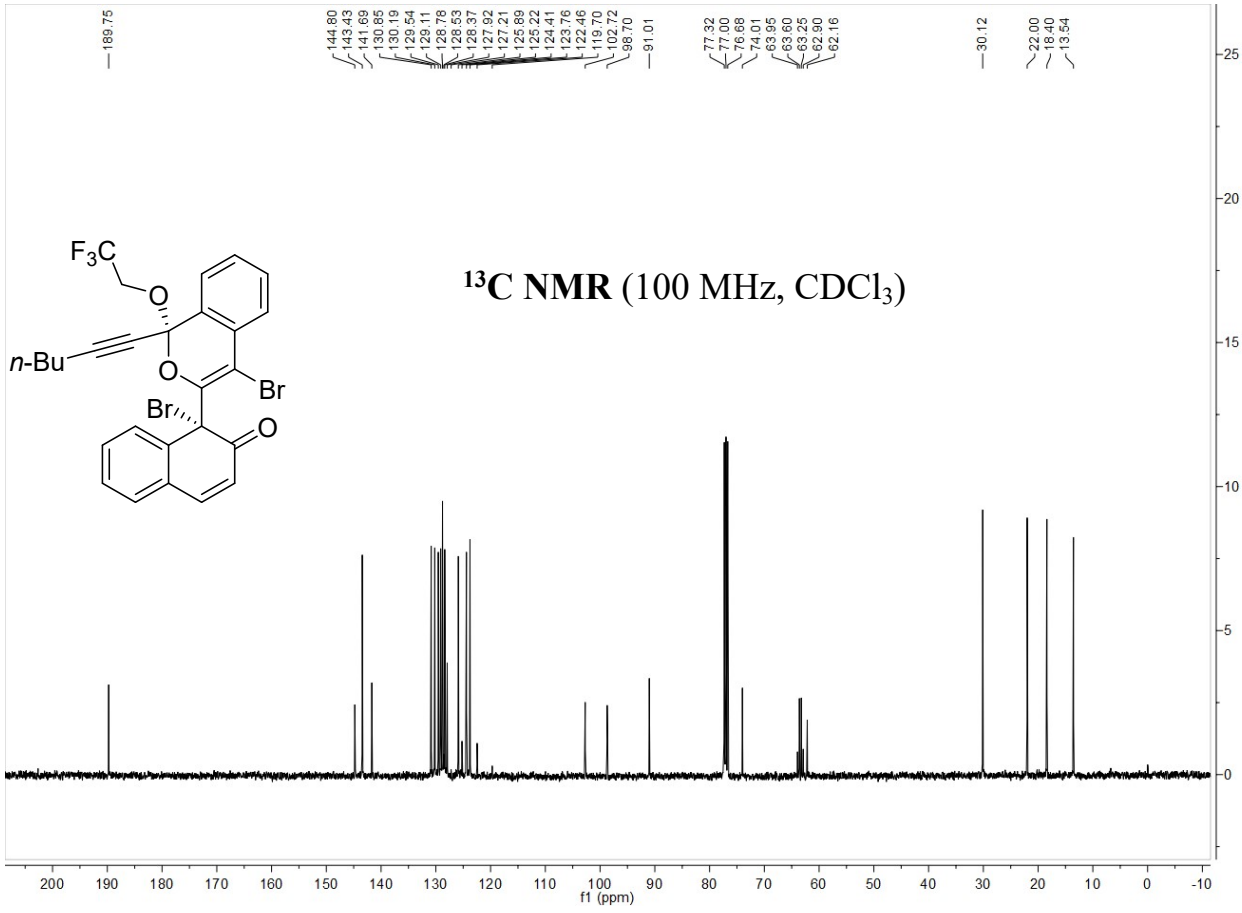


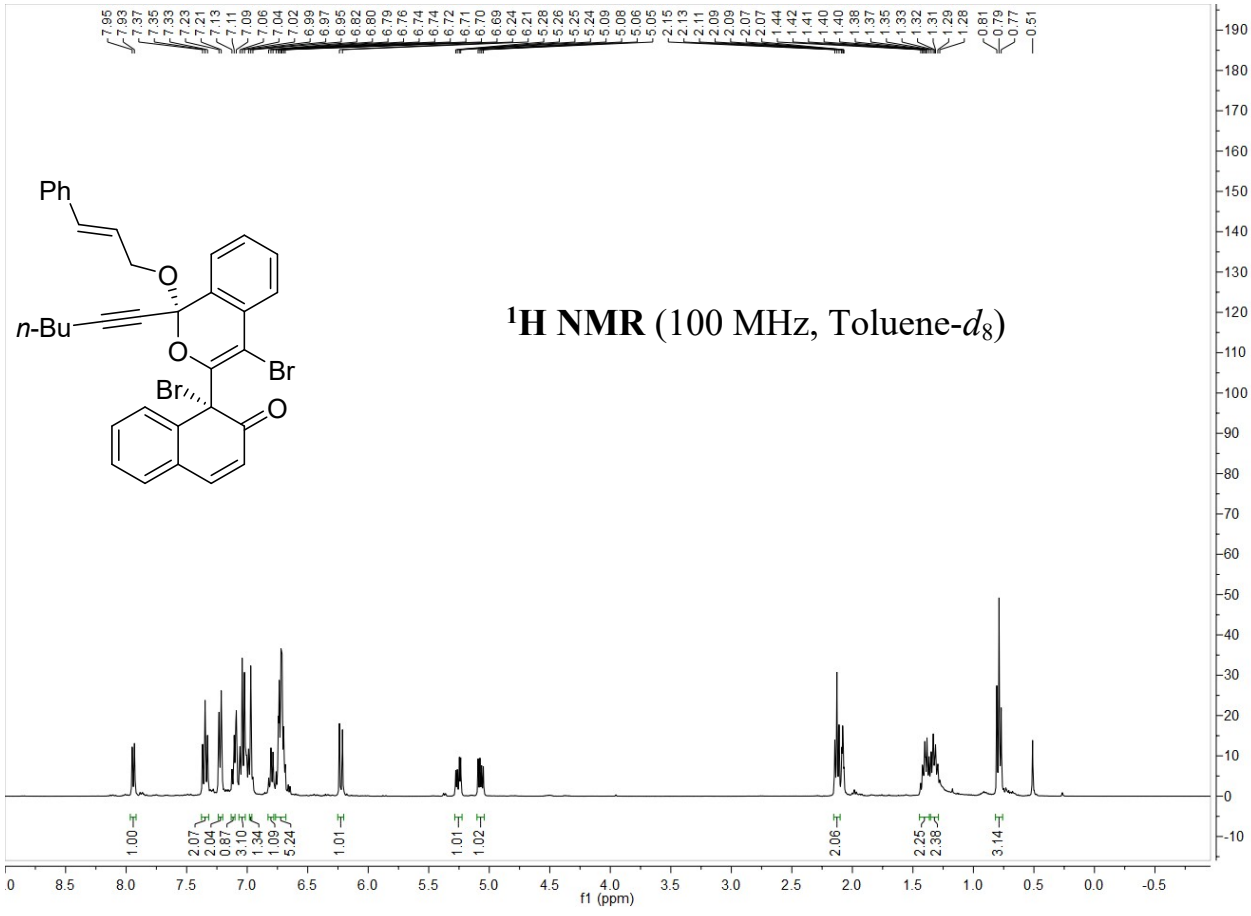
^{1}H NMR (400 MHz, $(CD_3)_2CO$)



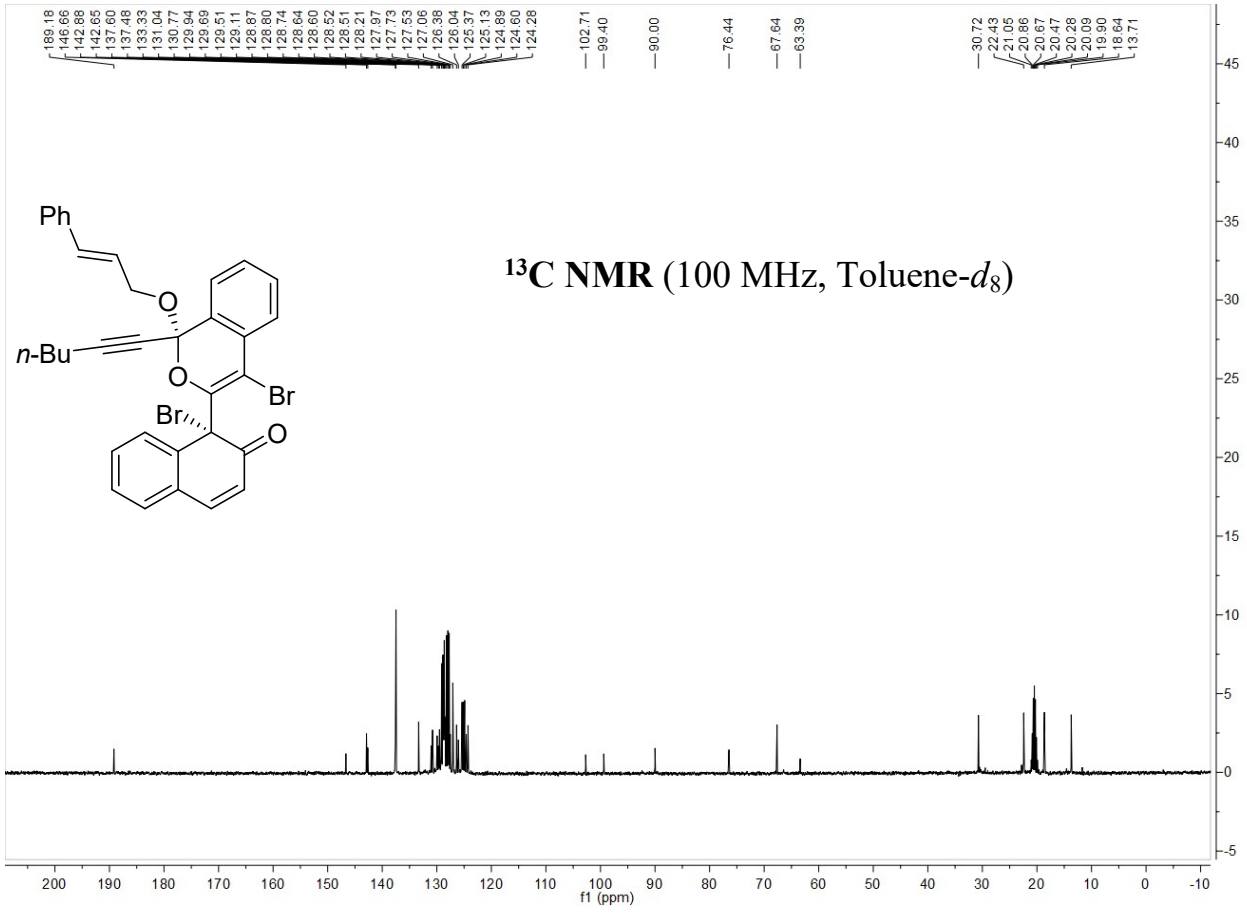
^{13}C NMR (100 MHz, $(CD_3)_2CO$)


F3C
O
n-Bu
O
Br
Br
O
1H NMR (400 MHz, CDCl3)
f1 (ppm)

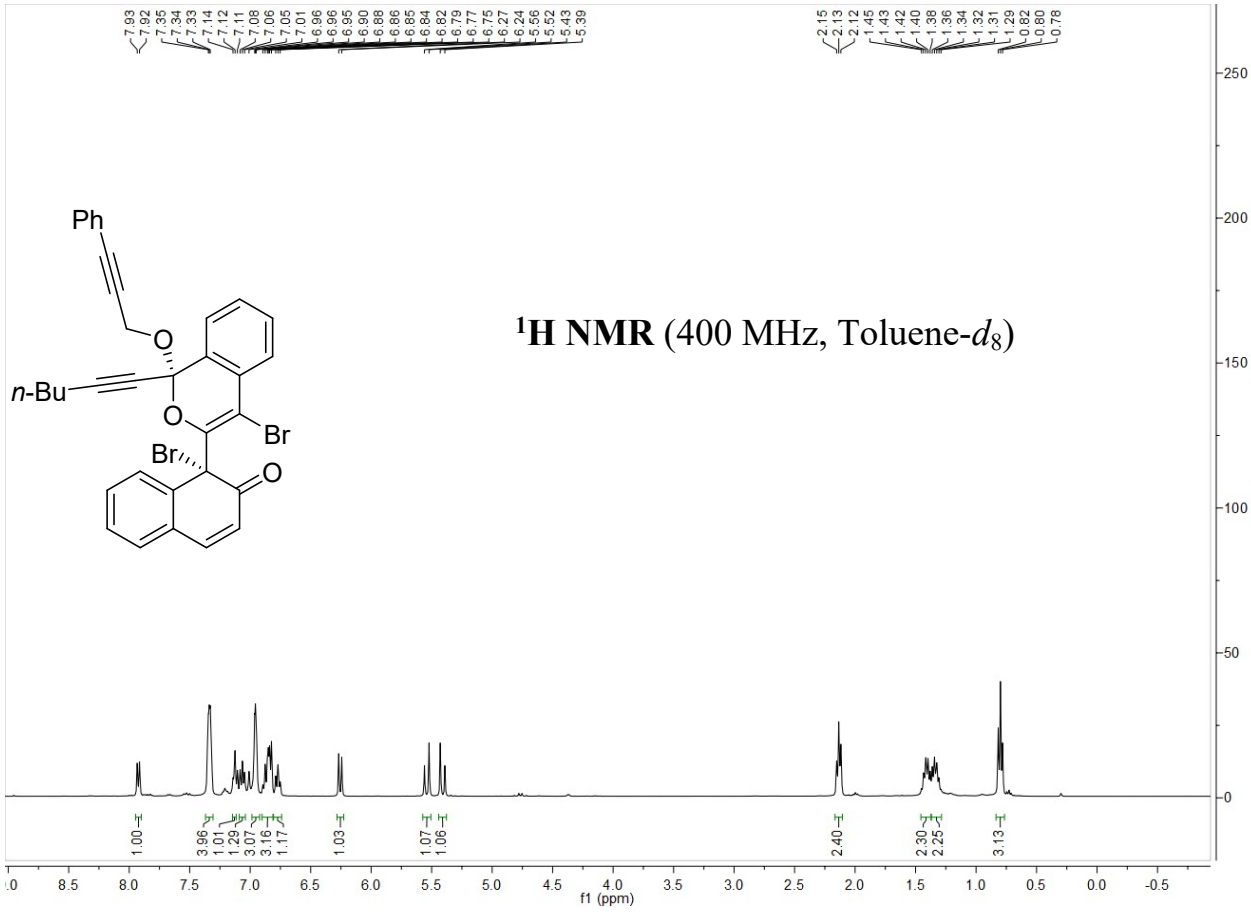

F3C
O
n-Bu
O
Br
Br
O
13C NMR (100 MHz, CDCl3)
f1 (ppm)



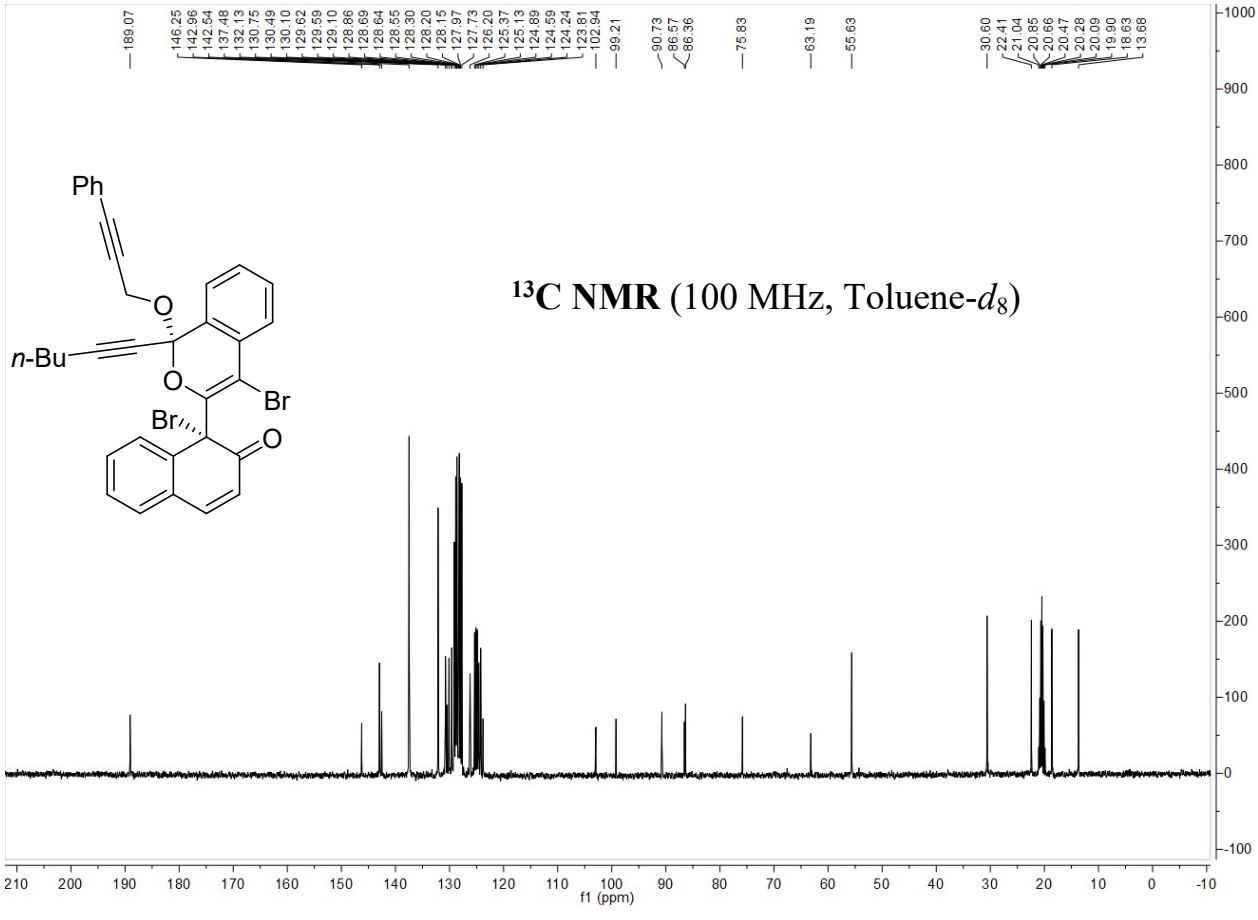
^{1}H NMR (100 MHz, Toluene-d_8)



^{13}C NMR (100 MHz, Toluene-d_8)

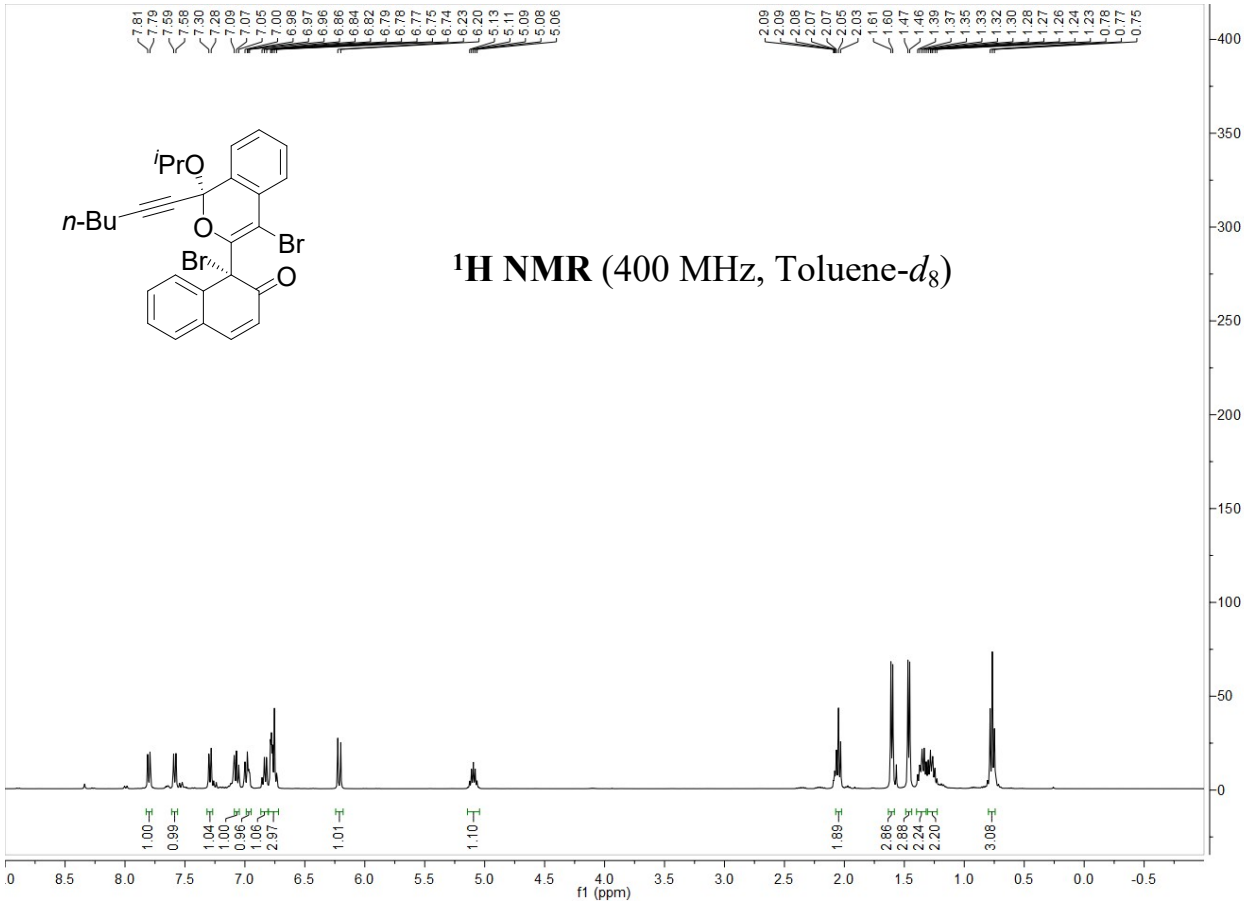


^{1}H NMR (400 MHz, Toluene-d_8)

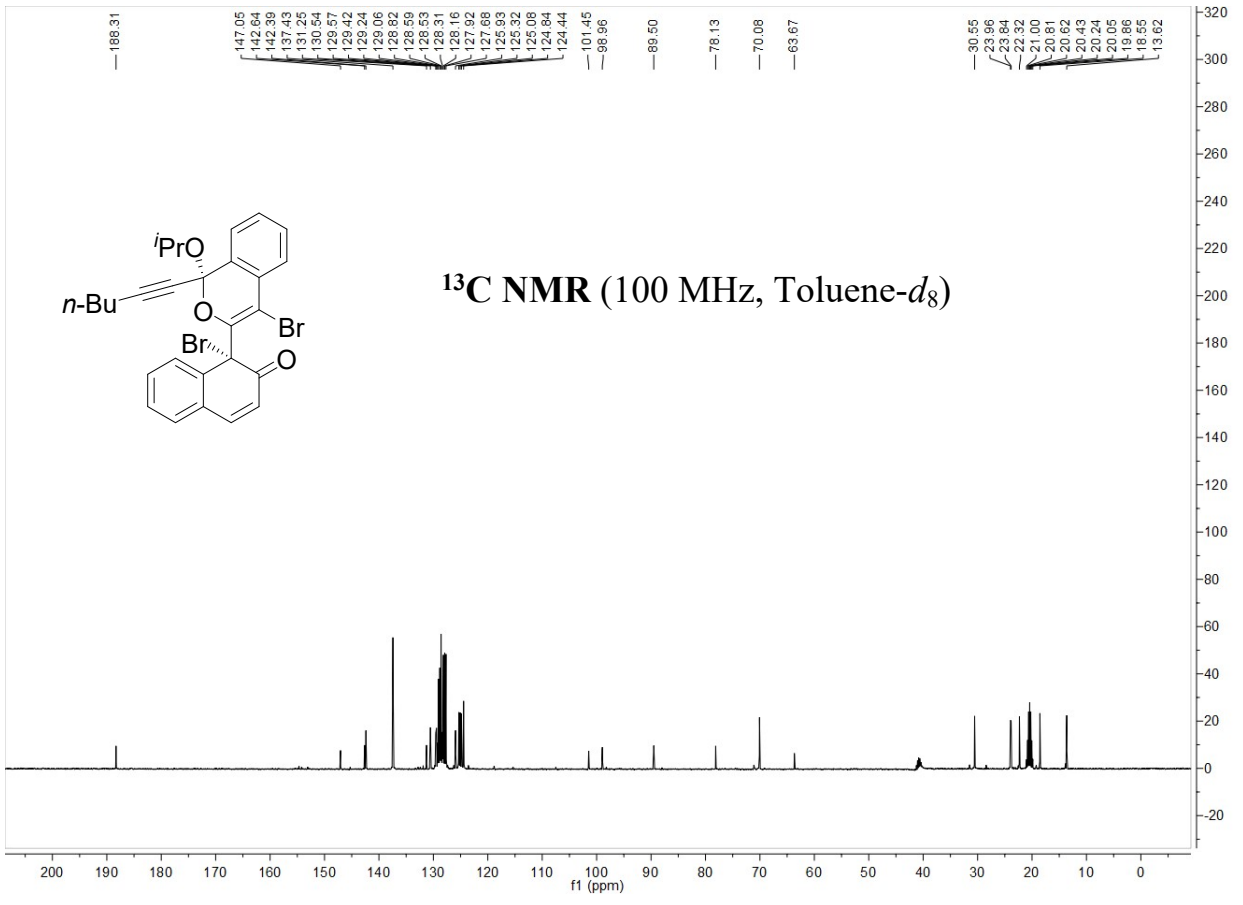


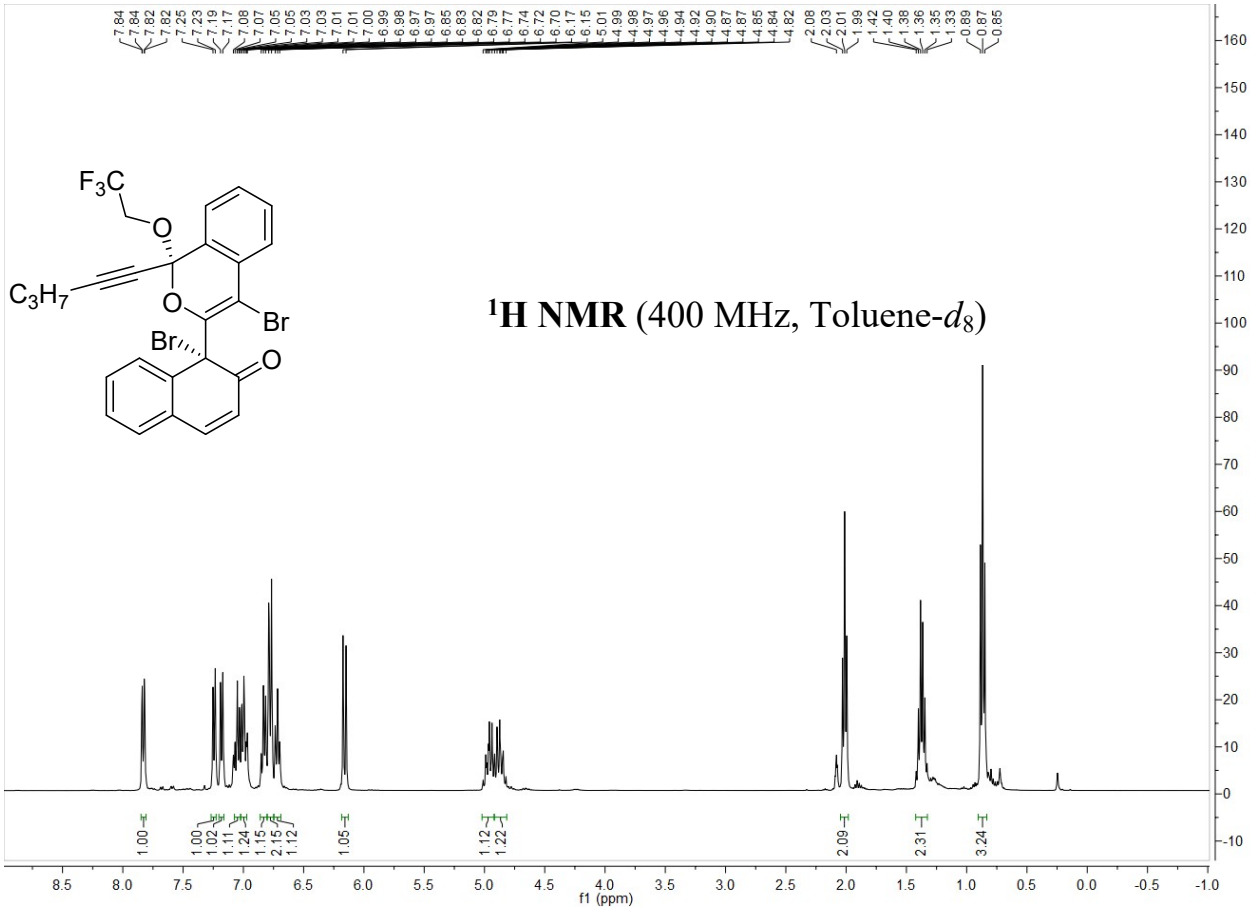
^{13}C NMR (100 MHz, Toluene-d_8)

^{1}H NMR (400 MHz, Toluene-d_8)

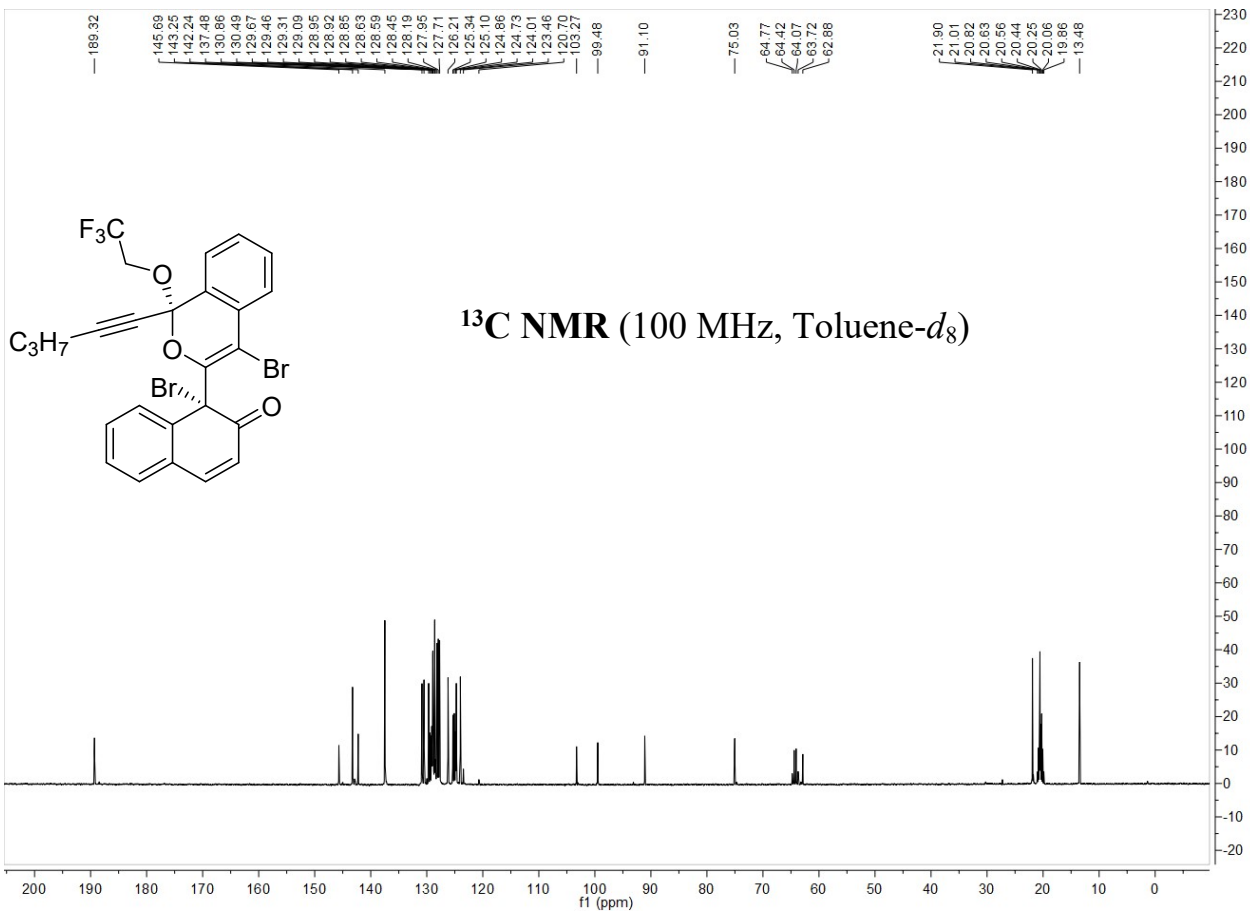


^{13}C NMR (100 MHz, Toluene-d_8)

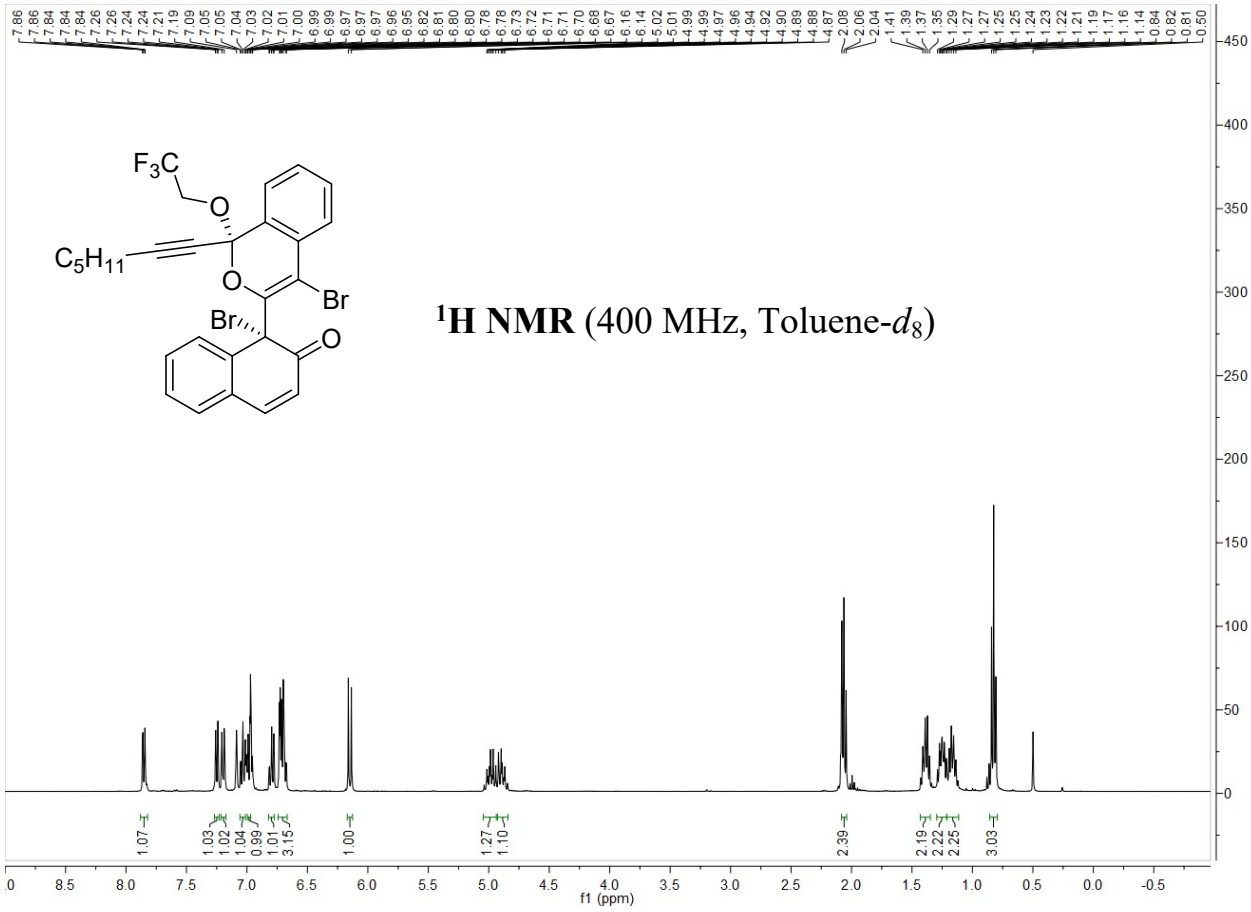


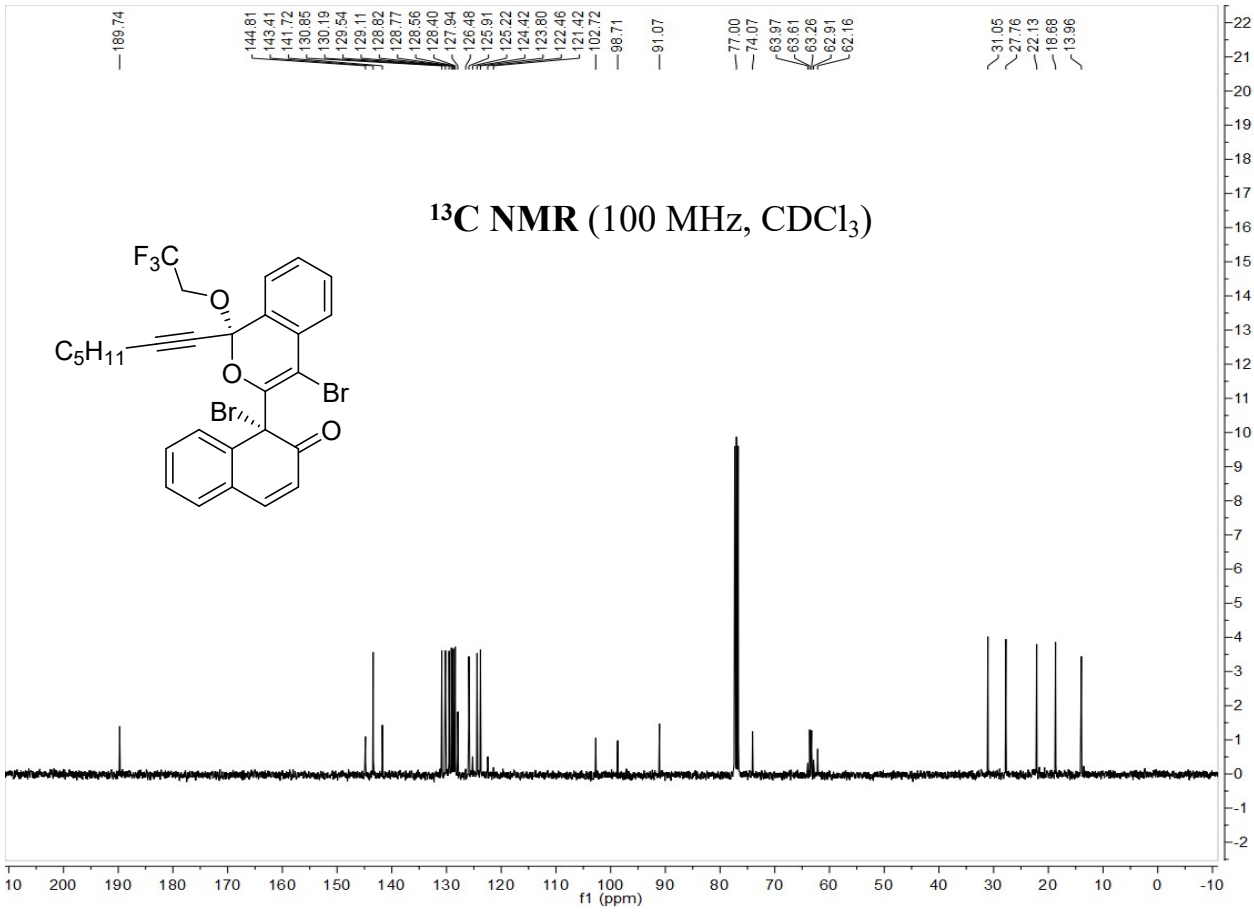


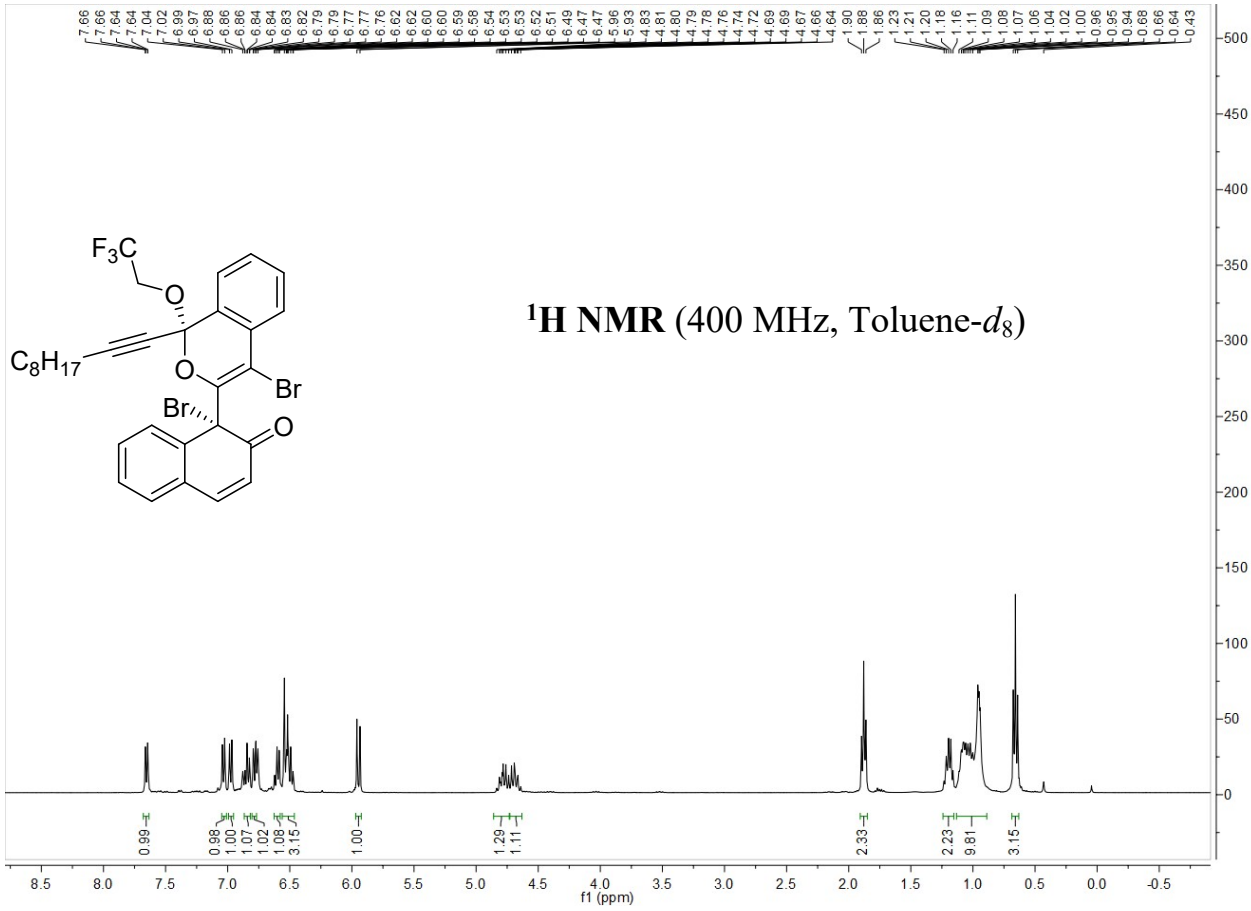
^{1}H NMR (400 MHz, Toluene-d_8)



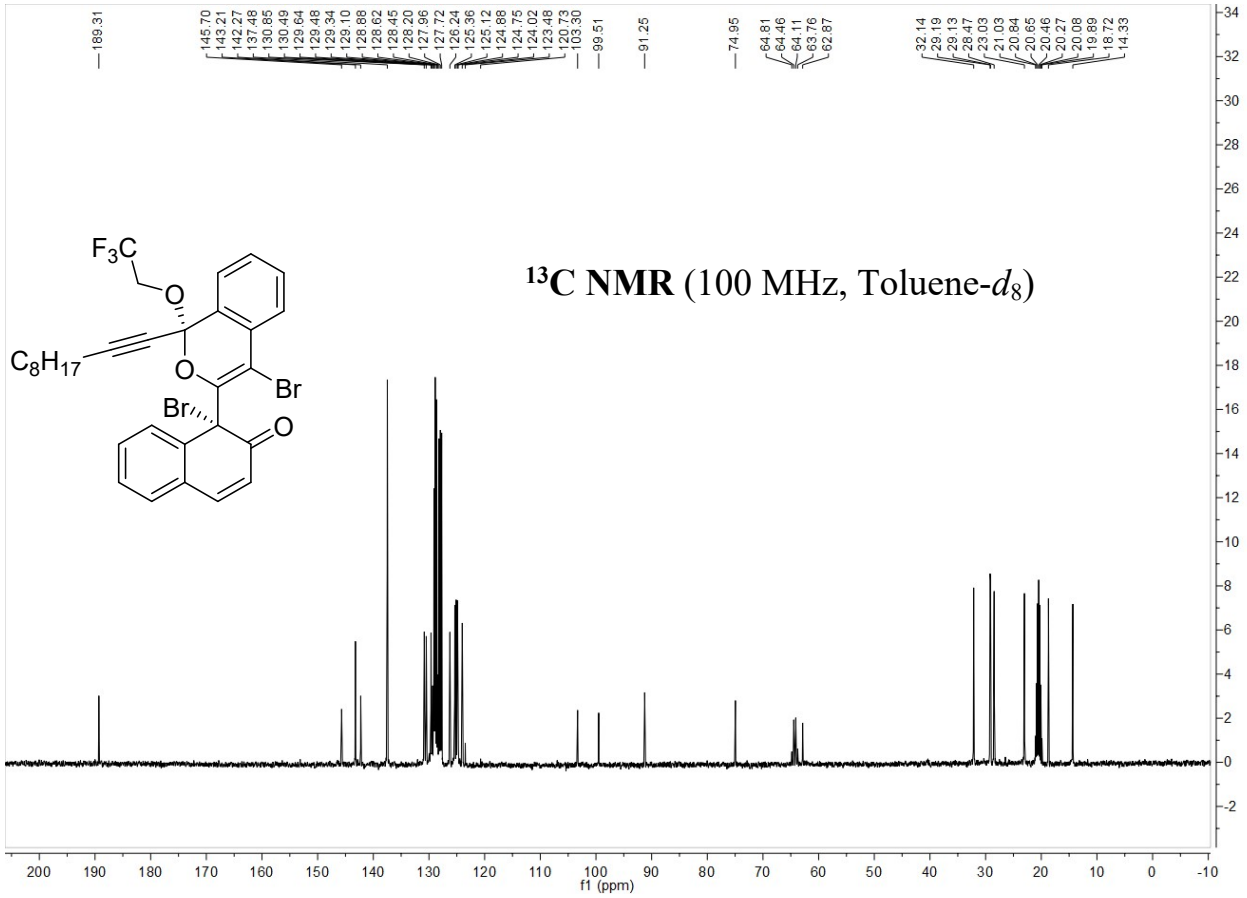
^{13}C NMR (100 MHz, Toluene-d_8)


F3C
O
C5H11
O
Br
Br
O
1H NMR (400 MHz, Toluene-d8)
f1 (ppm)

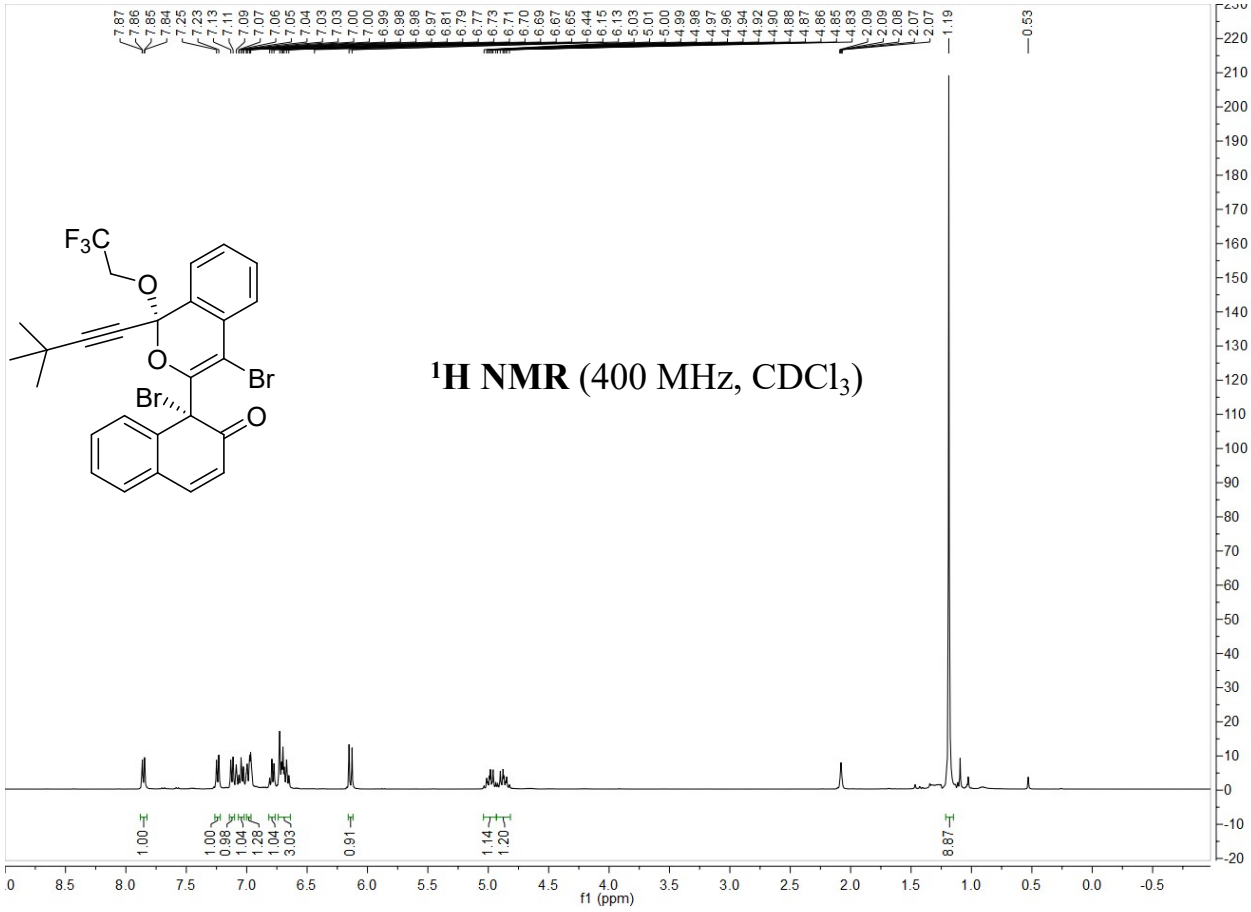

189.74
144.81
143.41
141.72
130.85
130.19
129.54
129.11
128.82
128.77
128.56
128.40
127.94
126.48
125.91
125.22
124.42
123.80
122.46
121.42
102.72
98.71
91.07
77.00
74.07
63.97
63.61
63.26
62.91
62.16
31.05
27.76
22.13
18.68
13.96
13C NMR (100 MHz, CDCl3)
F3C
O
C5H11
O
Br
Br
O
f1 (ppm)



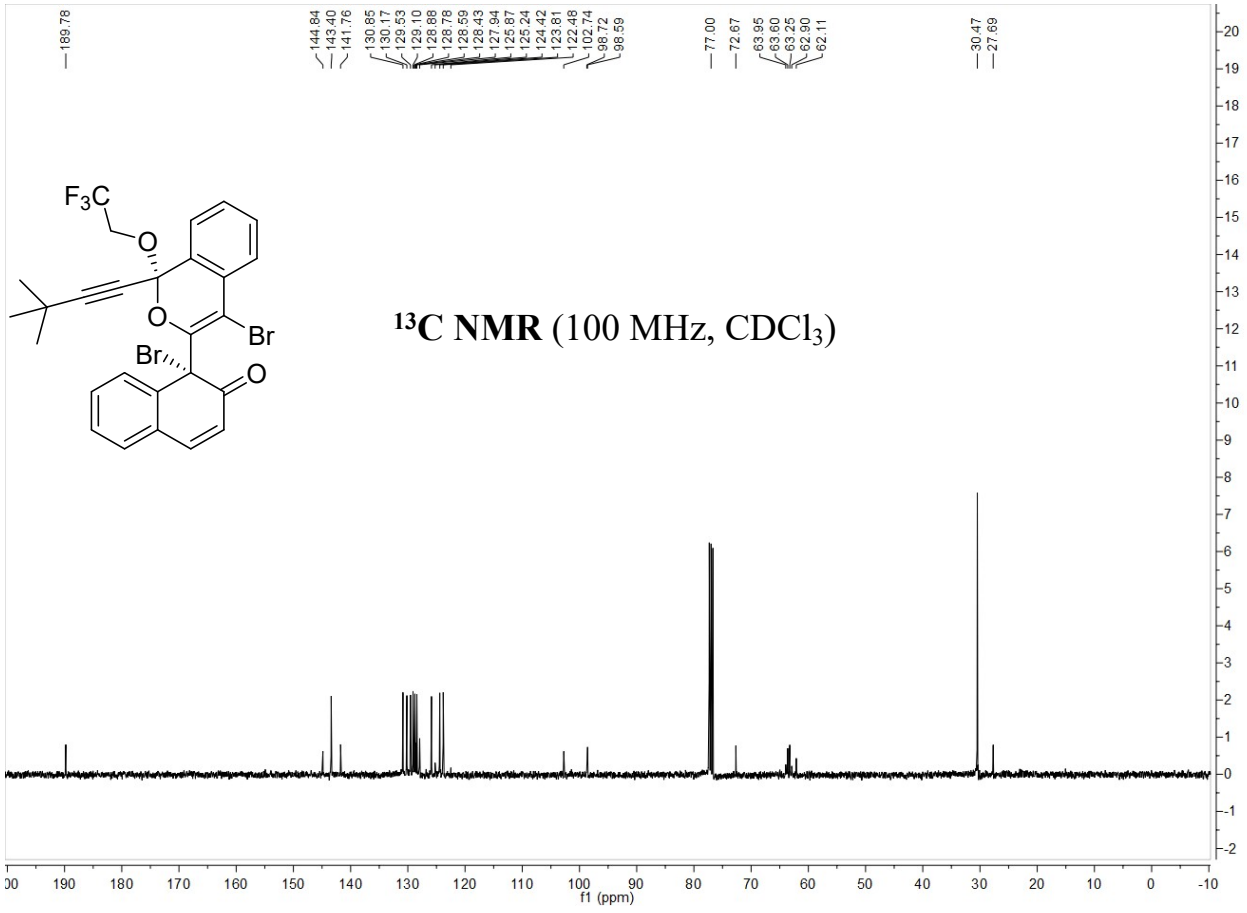
^{1}H NMR (400 MHz, Toluene-d_8)



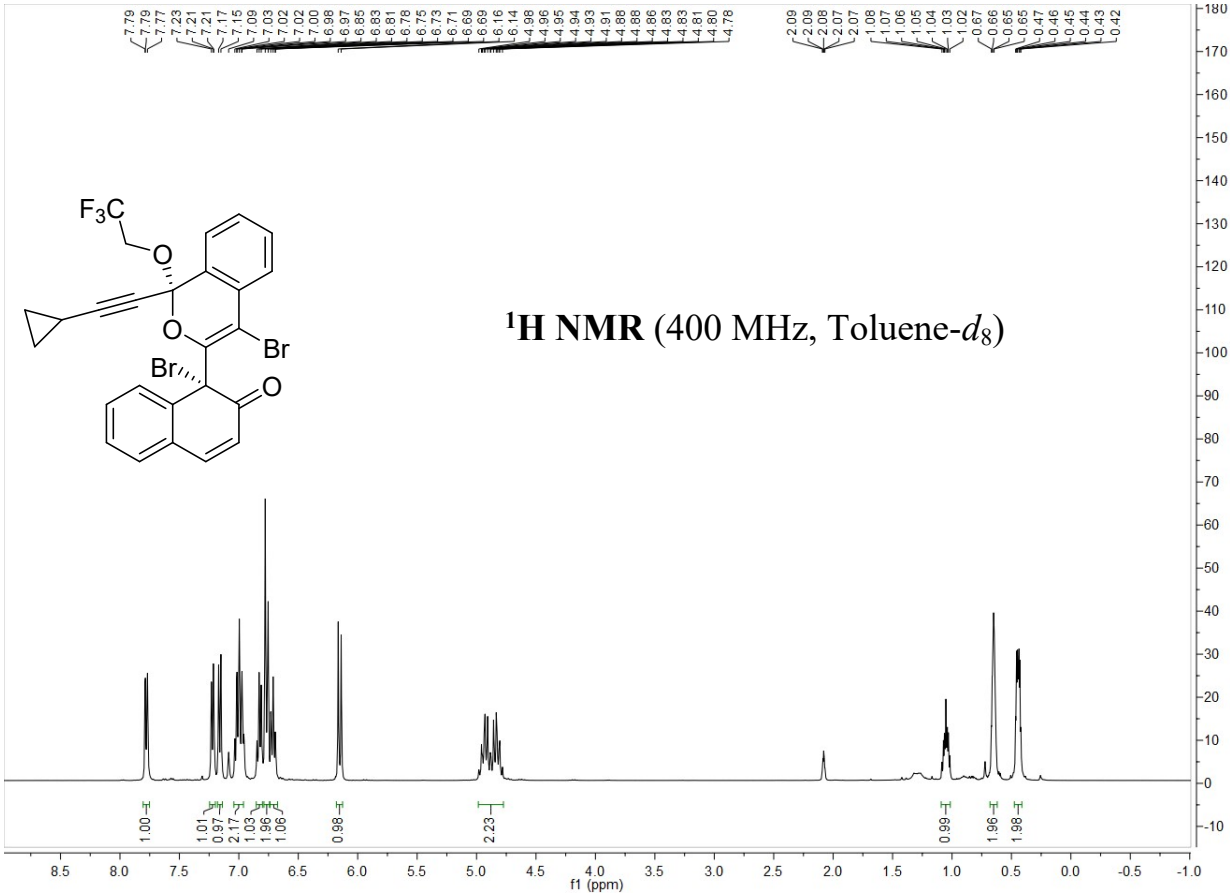
^{13}C NMR (100 MHz, Toluene-d_8)

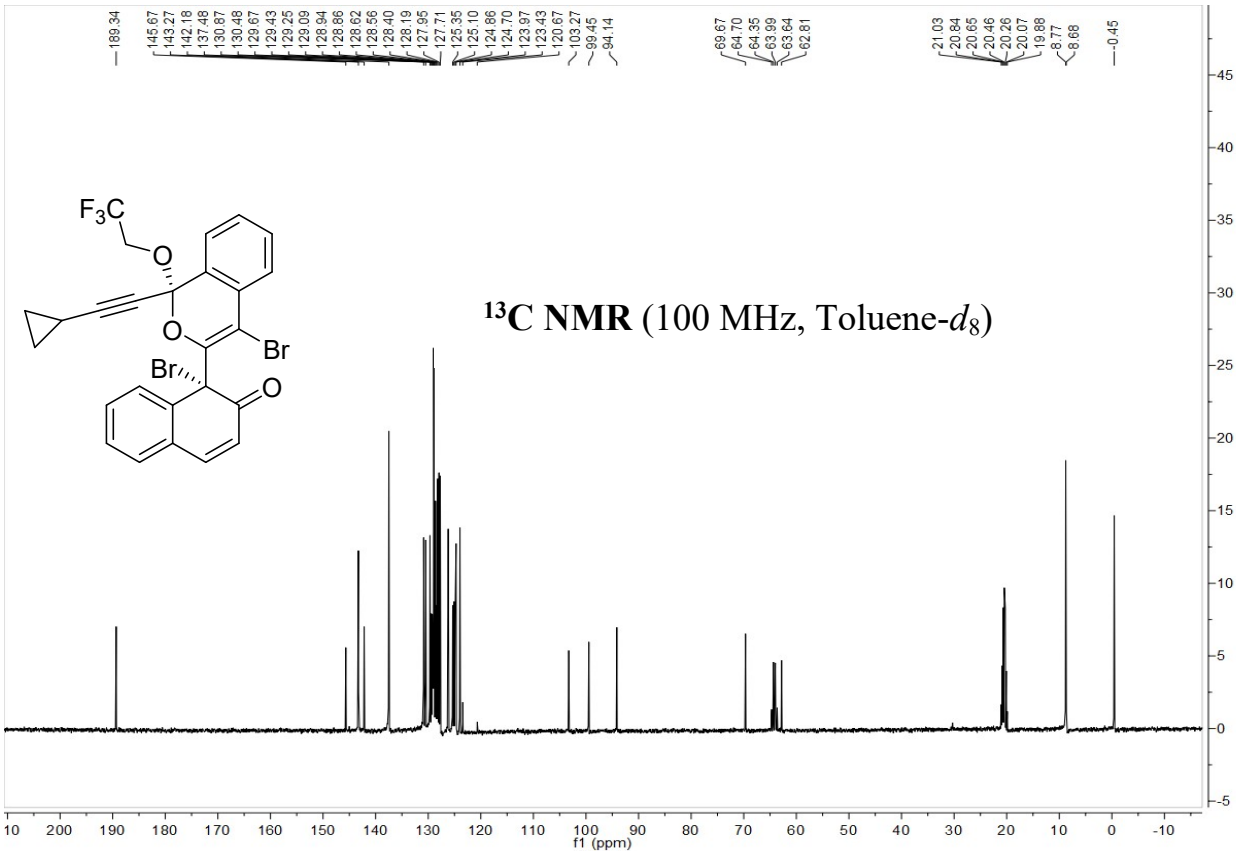


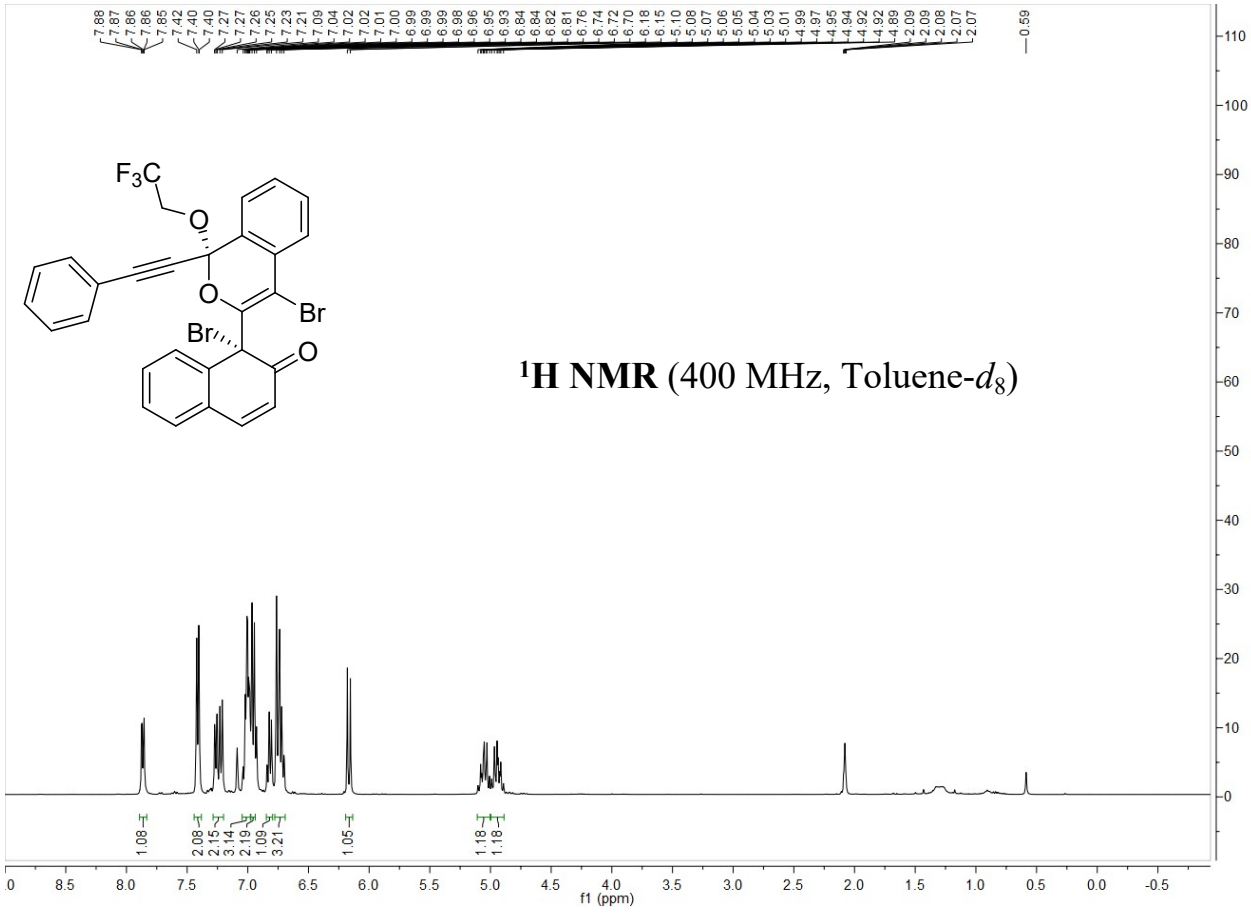
^{1}H NMR (400 MHz, $CDCl_3$)



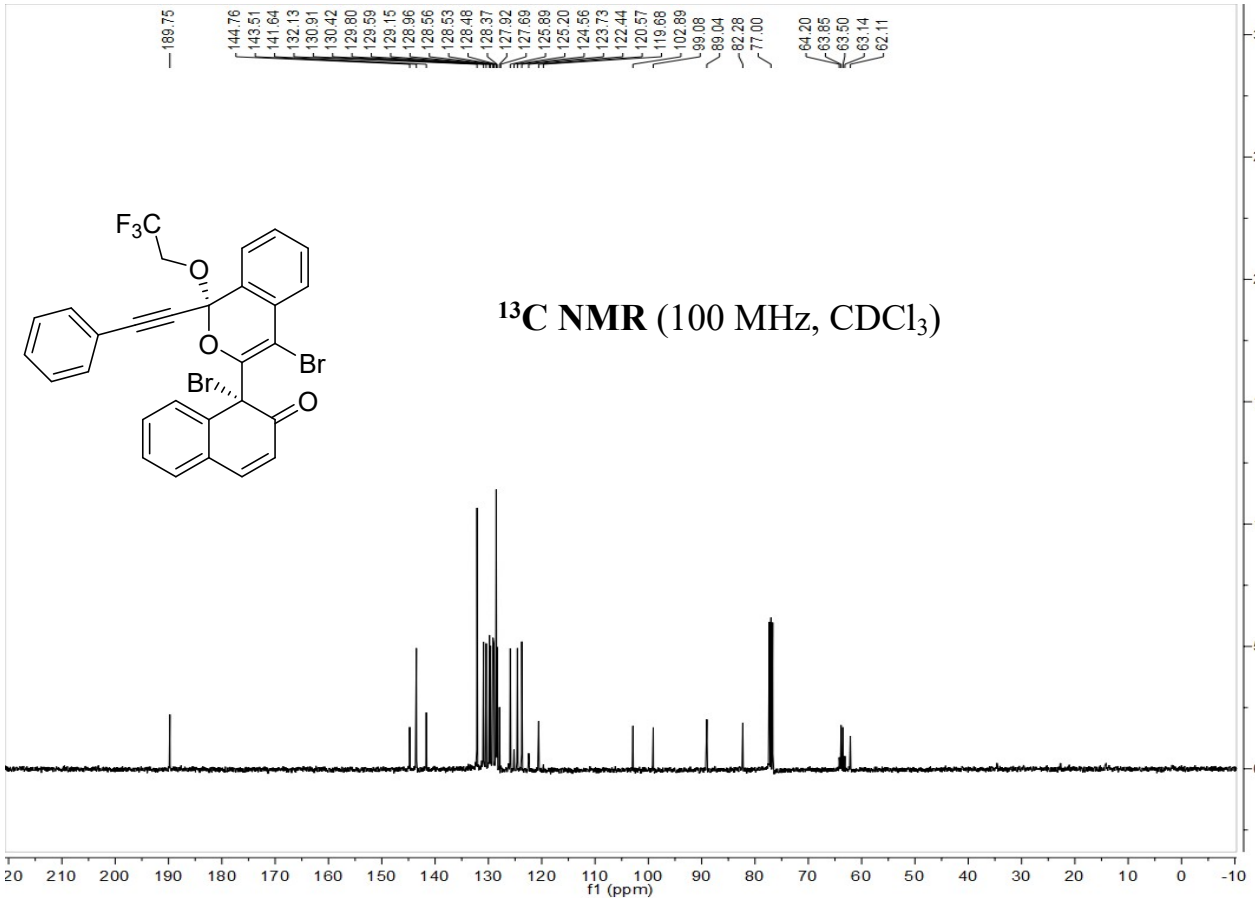
^{13}C NMR (100 MHz, $CDCl_3$)


F3C
O
O
Br
Br
O
1H NMR (400 MHz, Toluene-d8)
f1 (ppm)

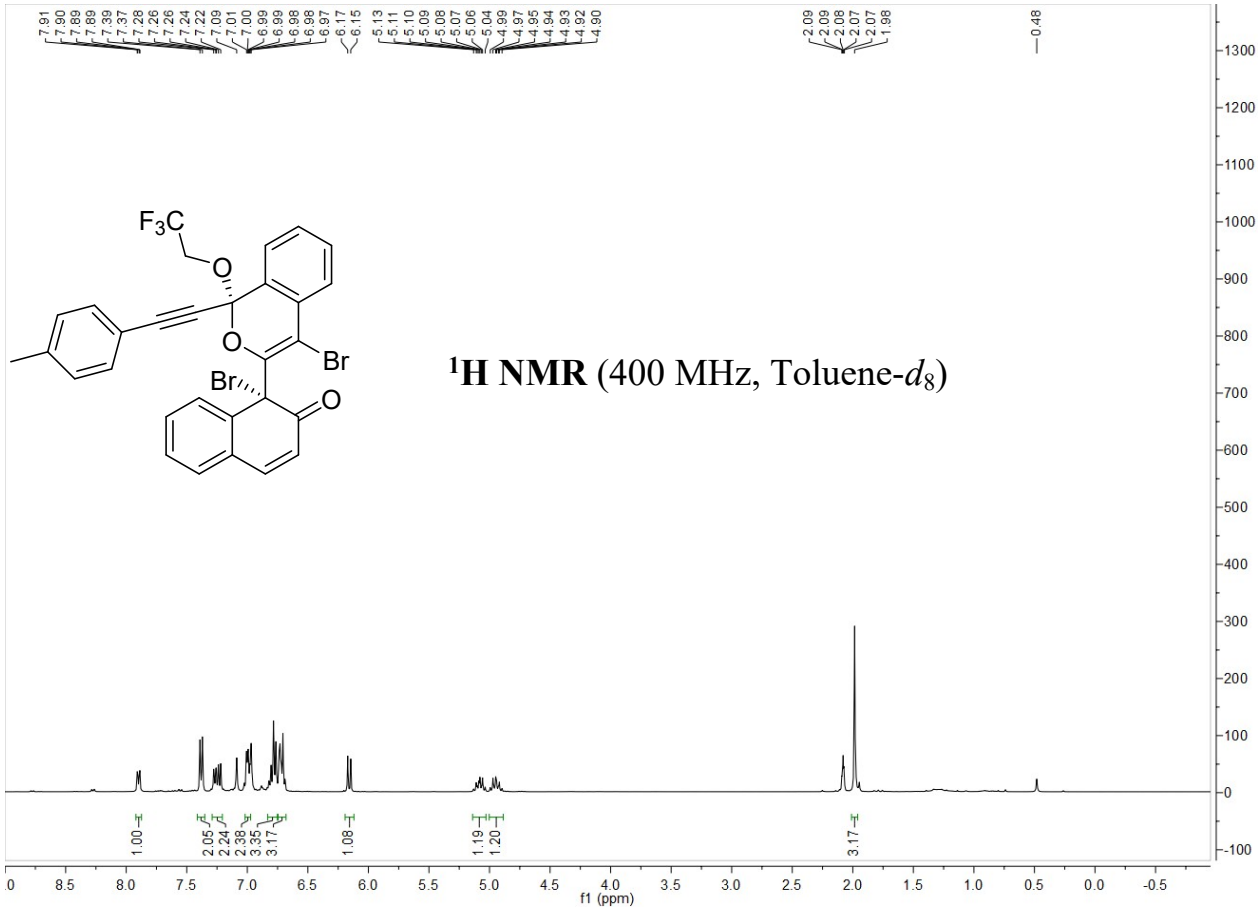

F3C
O
O
Br
Br
O
13C NMR (100 MHz, Toluene-d8)
f1 (ppm)



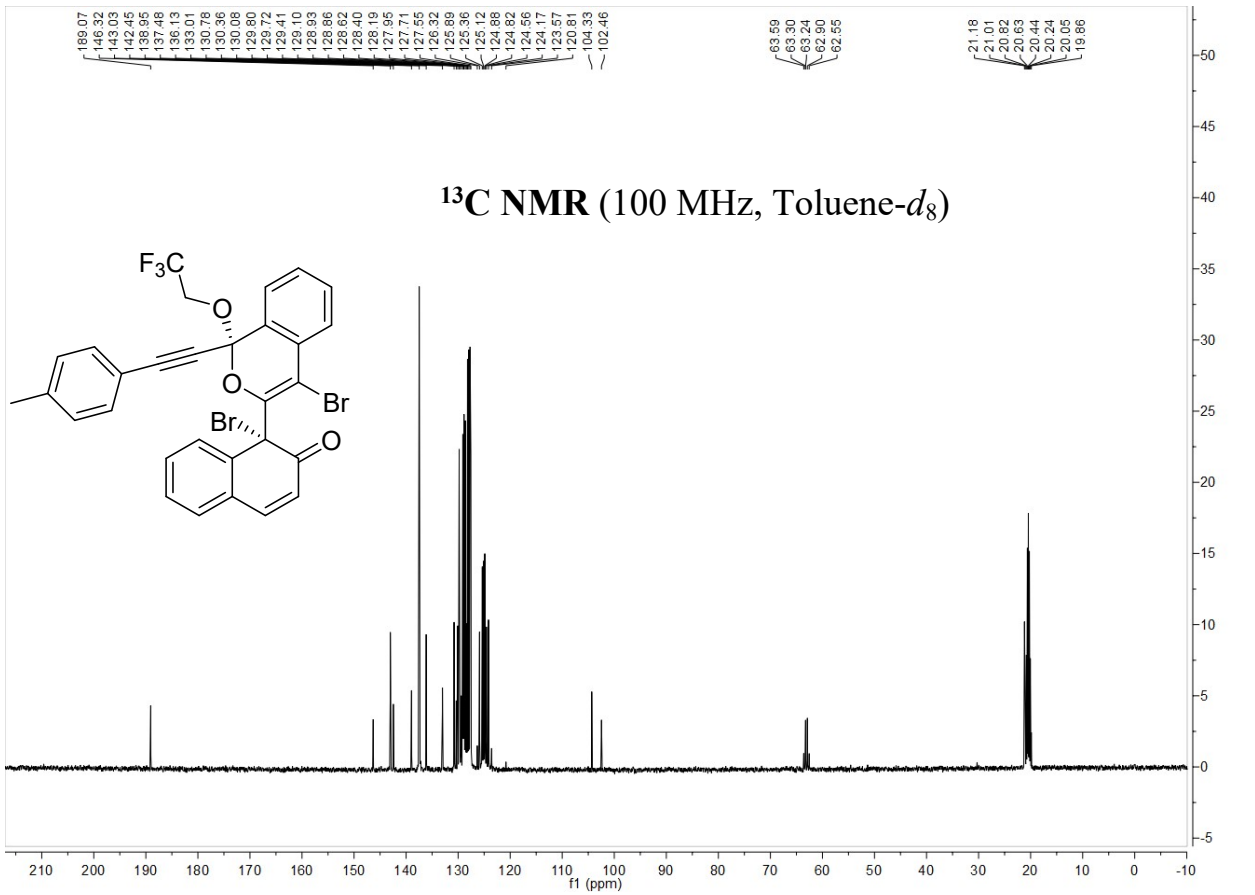
^{1}H NMR (400 MHz, Toluene-d_8)



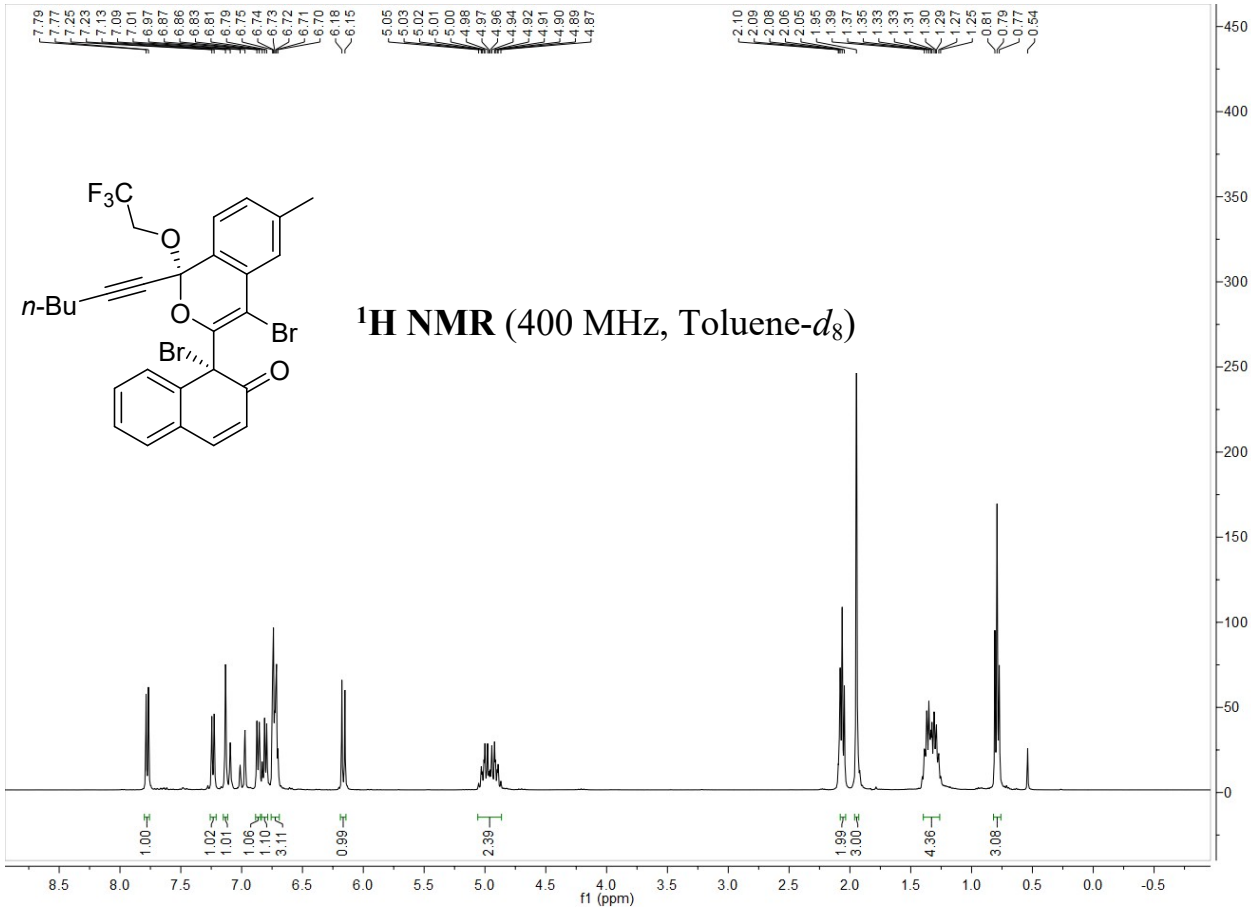
^{13}C NMR (100 MHz, $CDCl_3$)

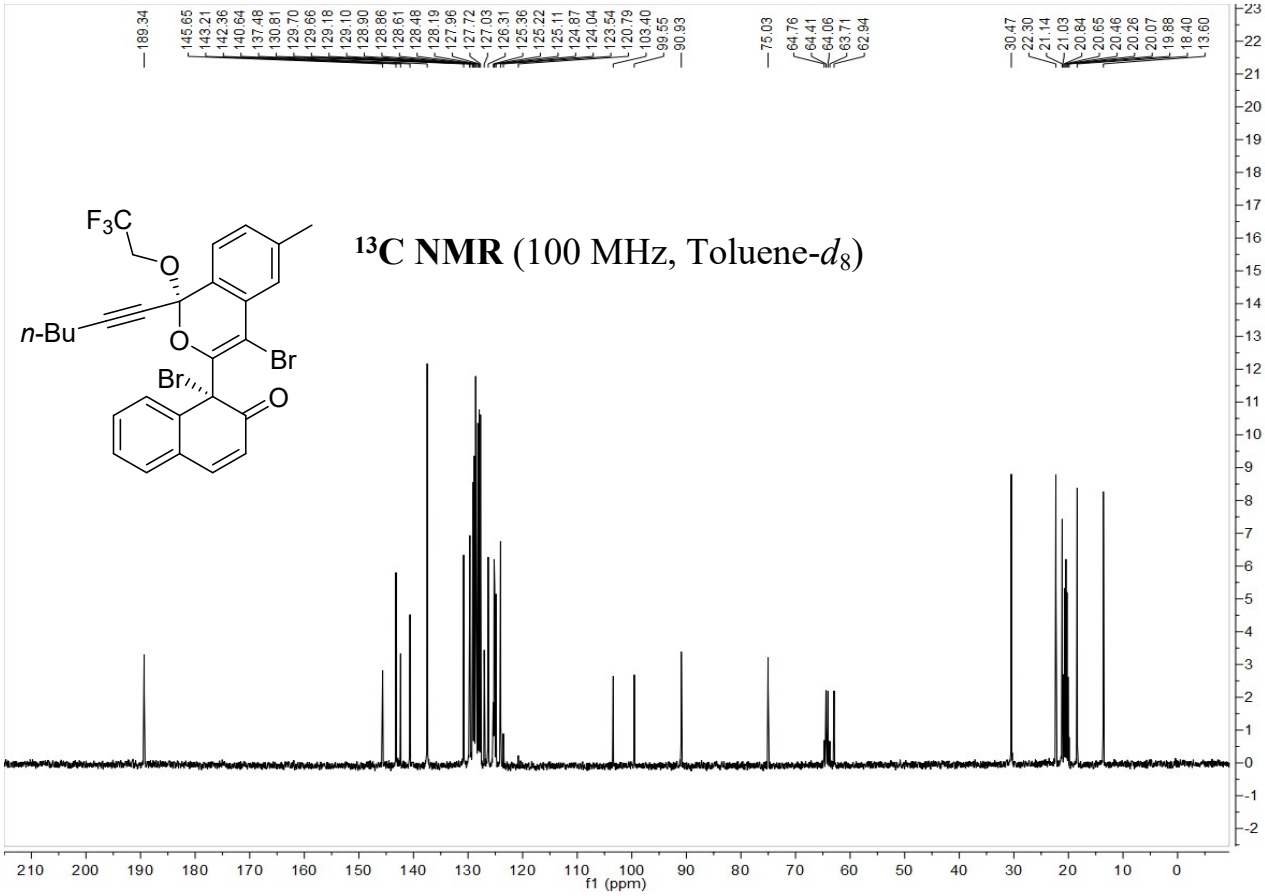


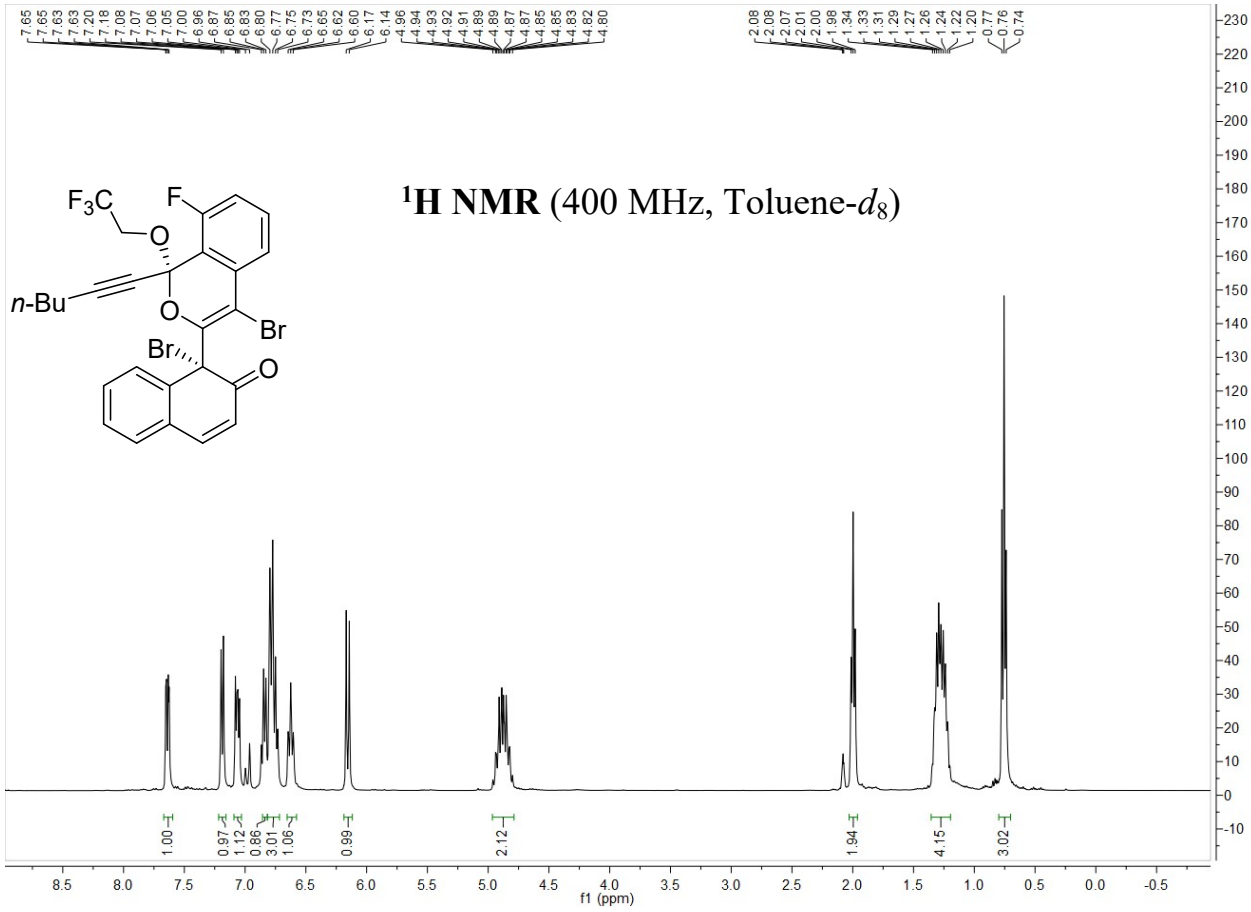
^{1}H NMR (400 MHz, Toluene-d_8)



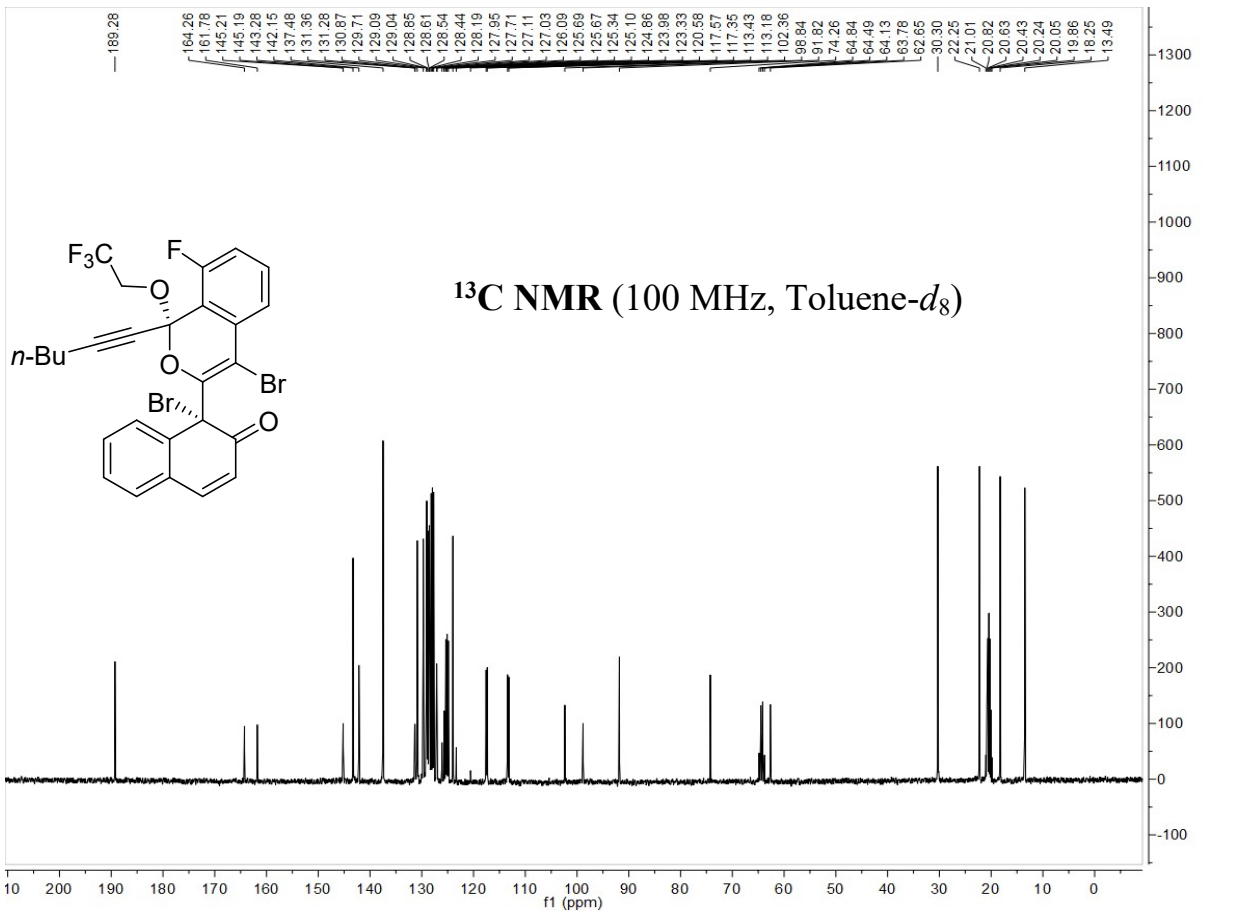
^{13}C NMR (100 MHz, Toluene-d_8)


F3C
O
n-Bu
O
Br
Br
O
1H NMR (400 MHz, Toluene-d8)
f1 (ppm)

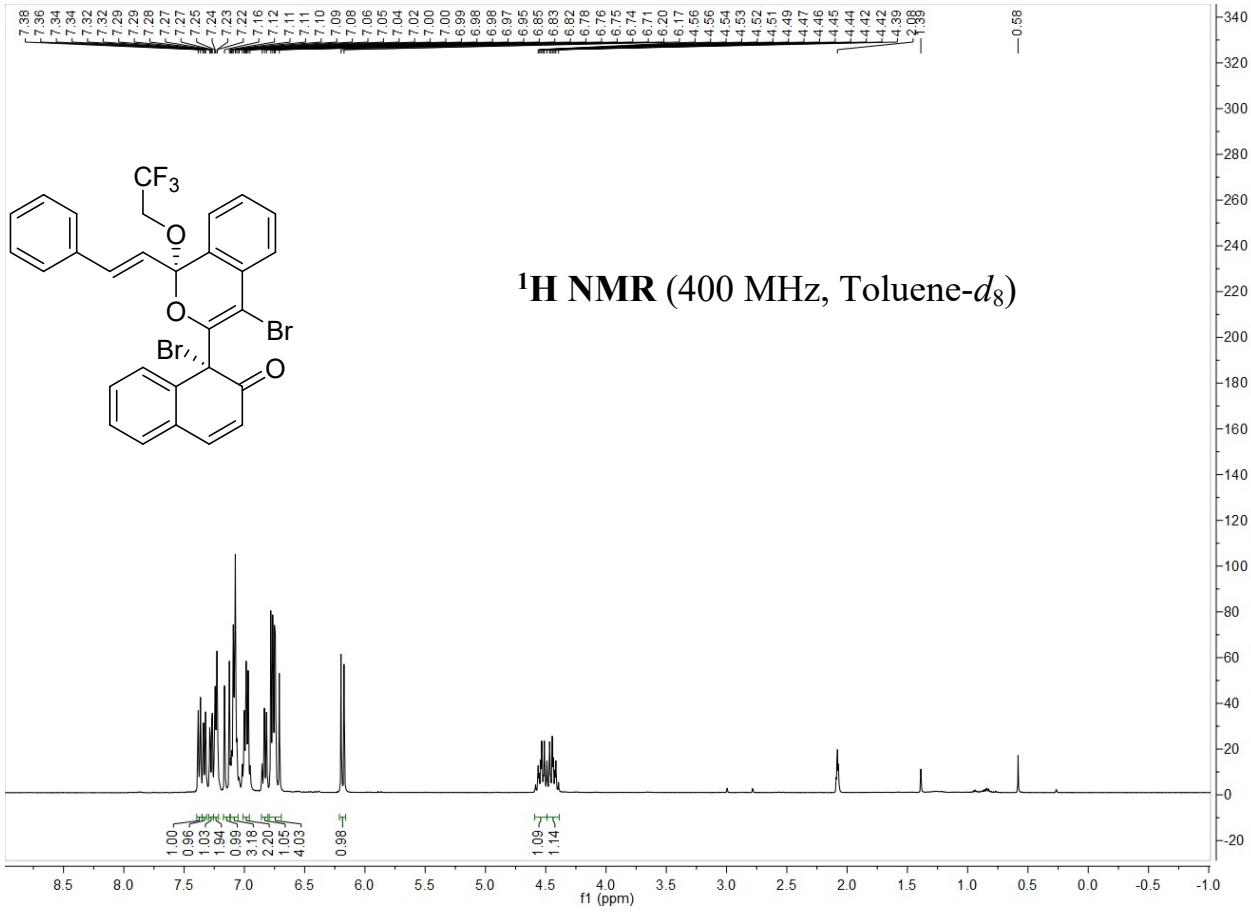

189.34
145.65
143.21
142.36
140.64
137.48
130.81
129.70
129.66
129.18
129.10
128.90
128.86
128.61
128.48
128.19
127.96
127.72
127.03
126.31
125.36
125.22
125.11
124.87
124.04
123.54
120.79
103.40
99.55
90.93
75.03
64.76
64.41
64.06
63.71
62.94
30.47
22.30
21.14
21.03
20.84
20.65
20.46
20.26
20.07
19.88
18.40
13.60
F3C
O
n-Bu
O
Br
Br
O
13C NMR (100 MHz, Toluene-d8)
f1 (ppm)



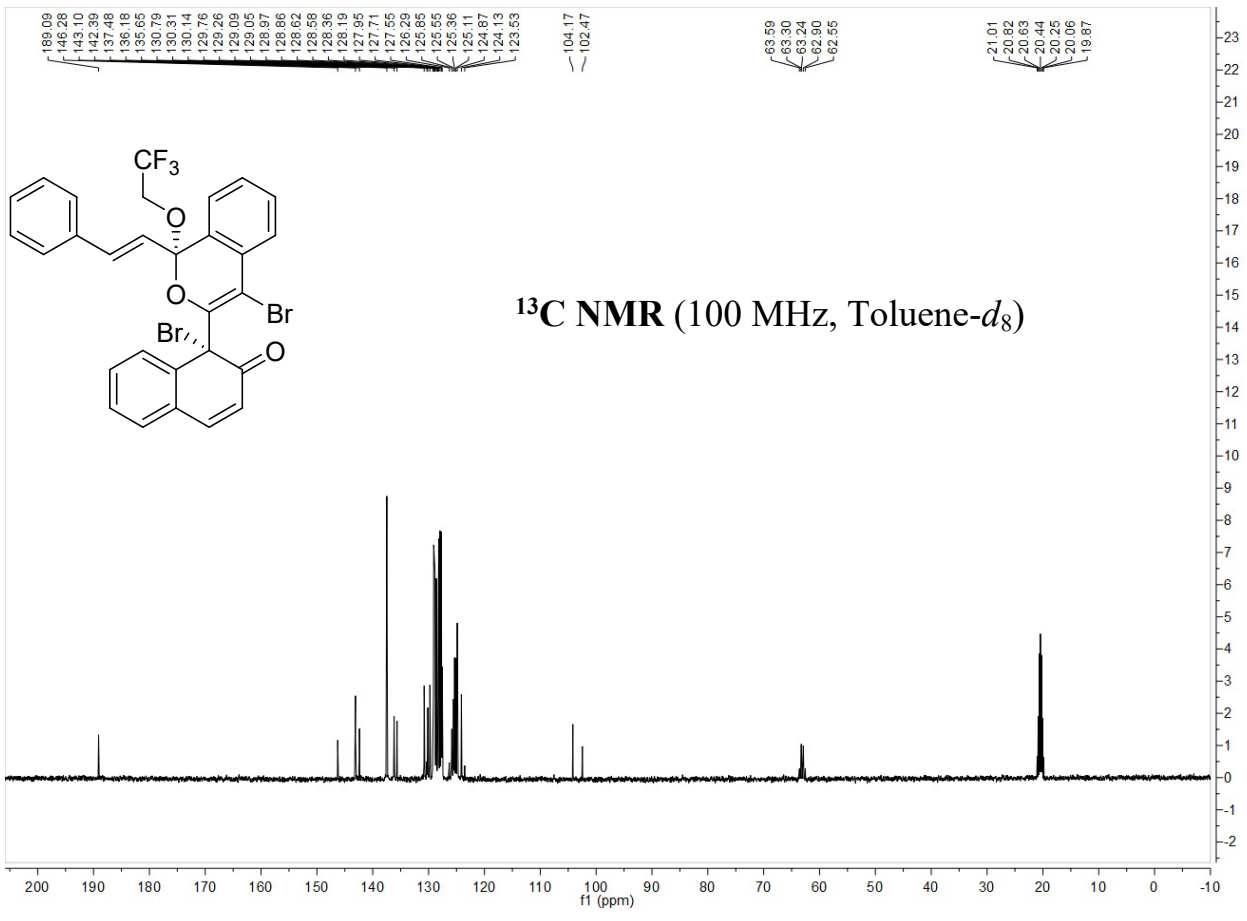
^{1}H NMR (400 MHz, Toluene-d_8)



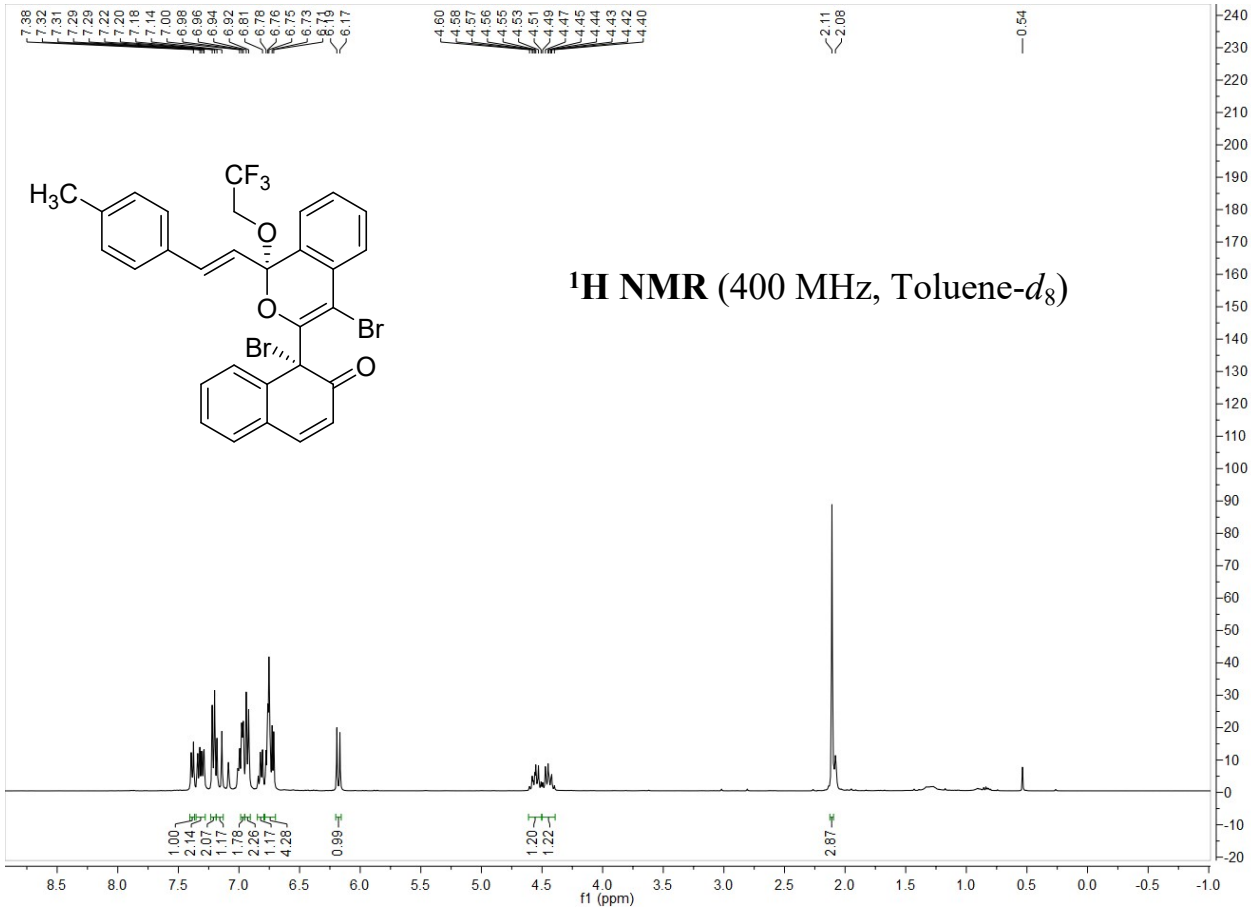
^{13}C NMR (100 MHz, Toluene-d_8)



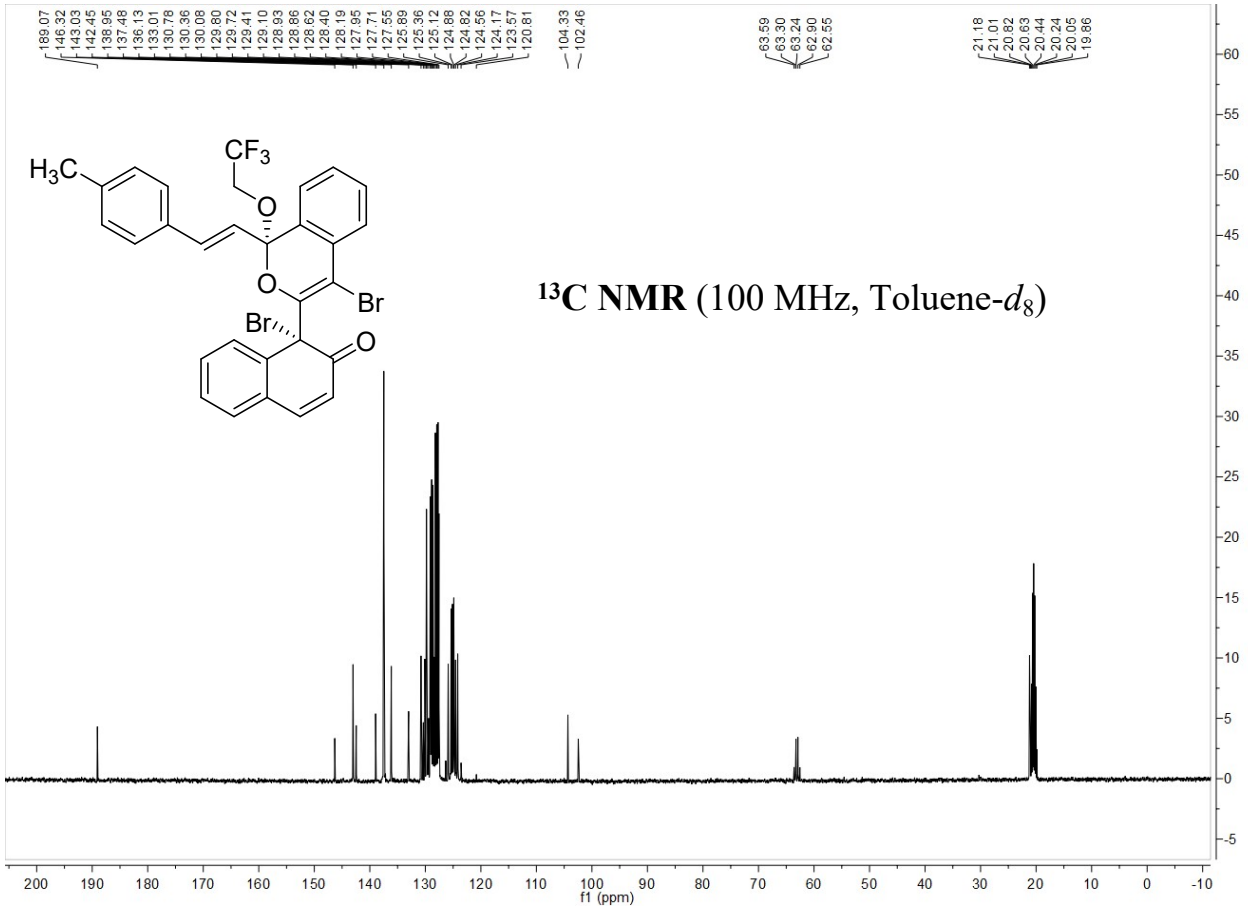
^{1}H NMR (400 MHz, Toluene-d_8)



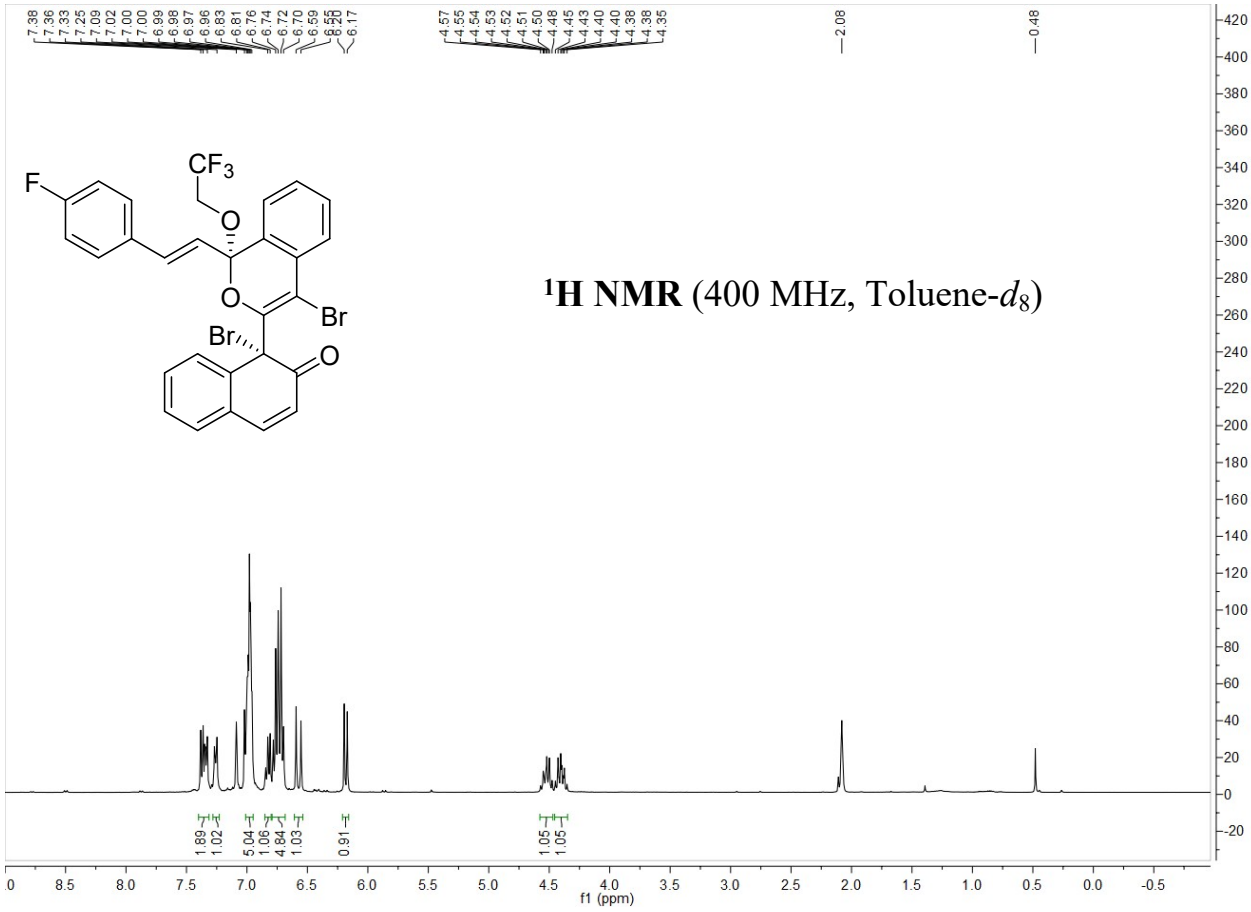
^{13}C NMR (100 MHz, Toluene-d_8)

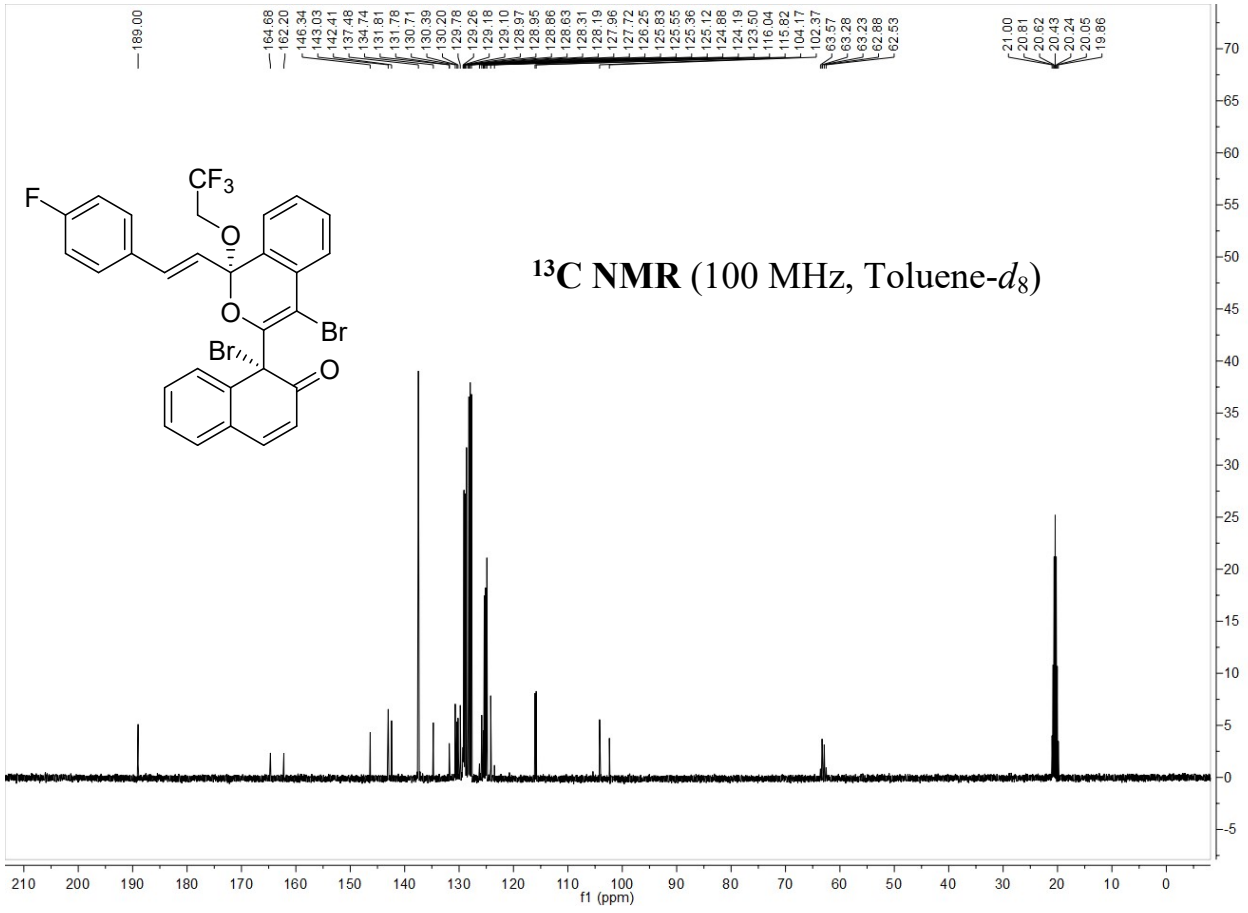


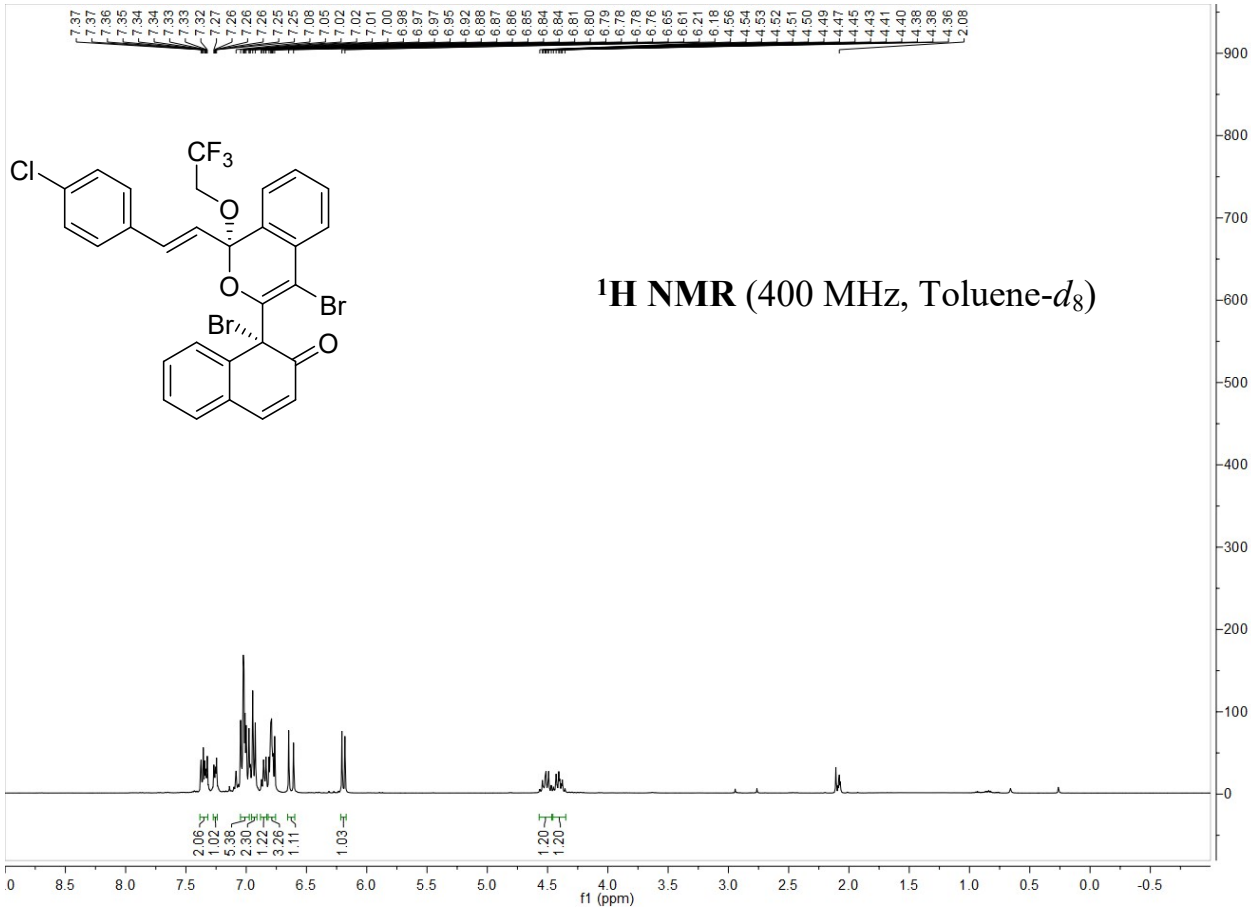
^{1}H NMR (400 MHz, Toluene-d_8)



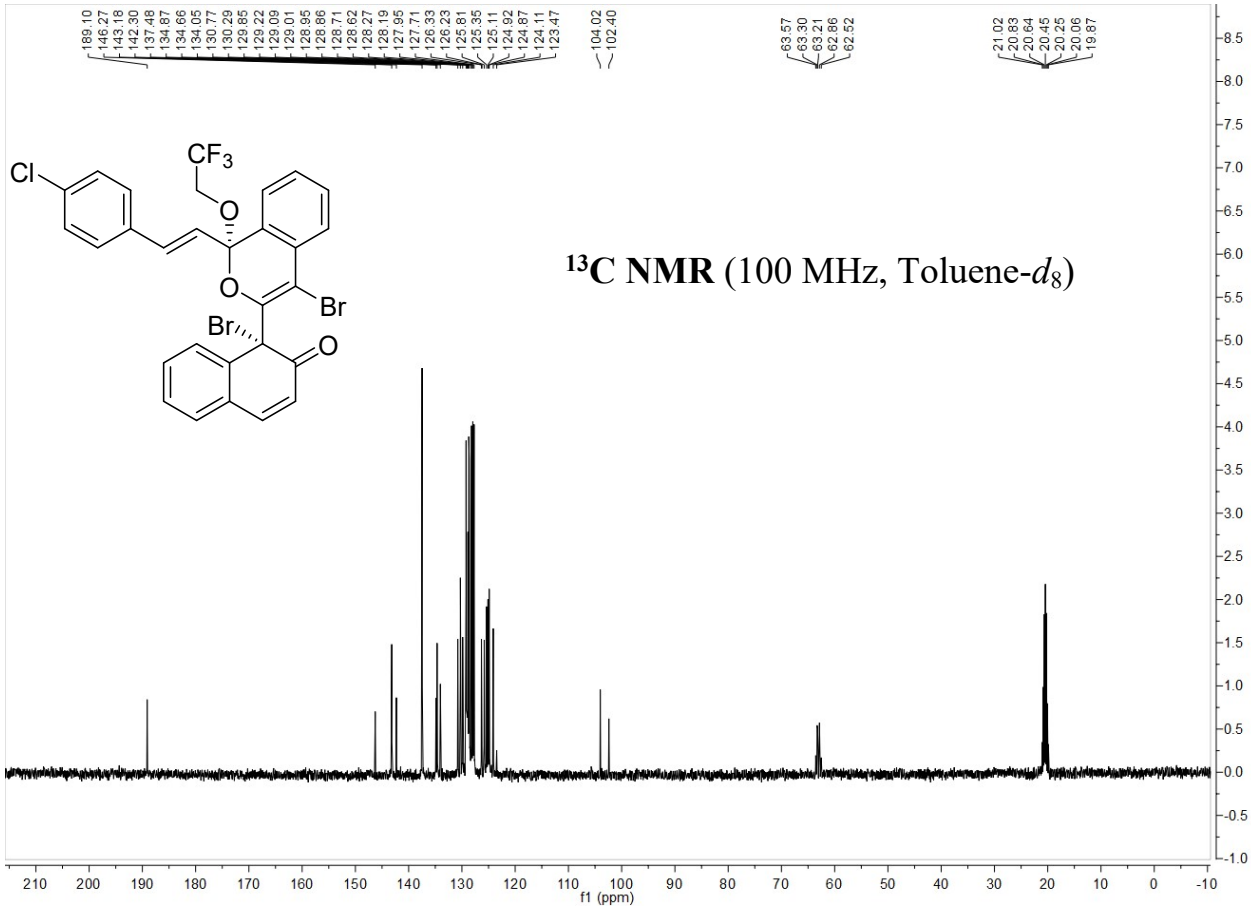
^{13}C NMR (100 MHz, Toluene-d_8)


F
CF3
O
O
Br
Br
O
1H NMR (400 MHz, Toluene-d8)
f1 (ppm)

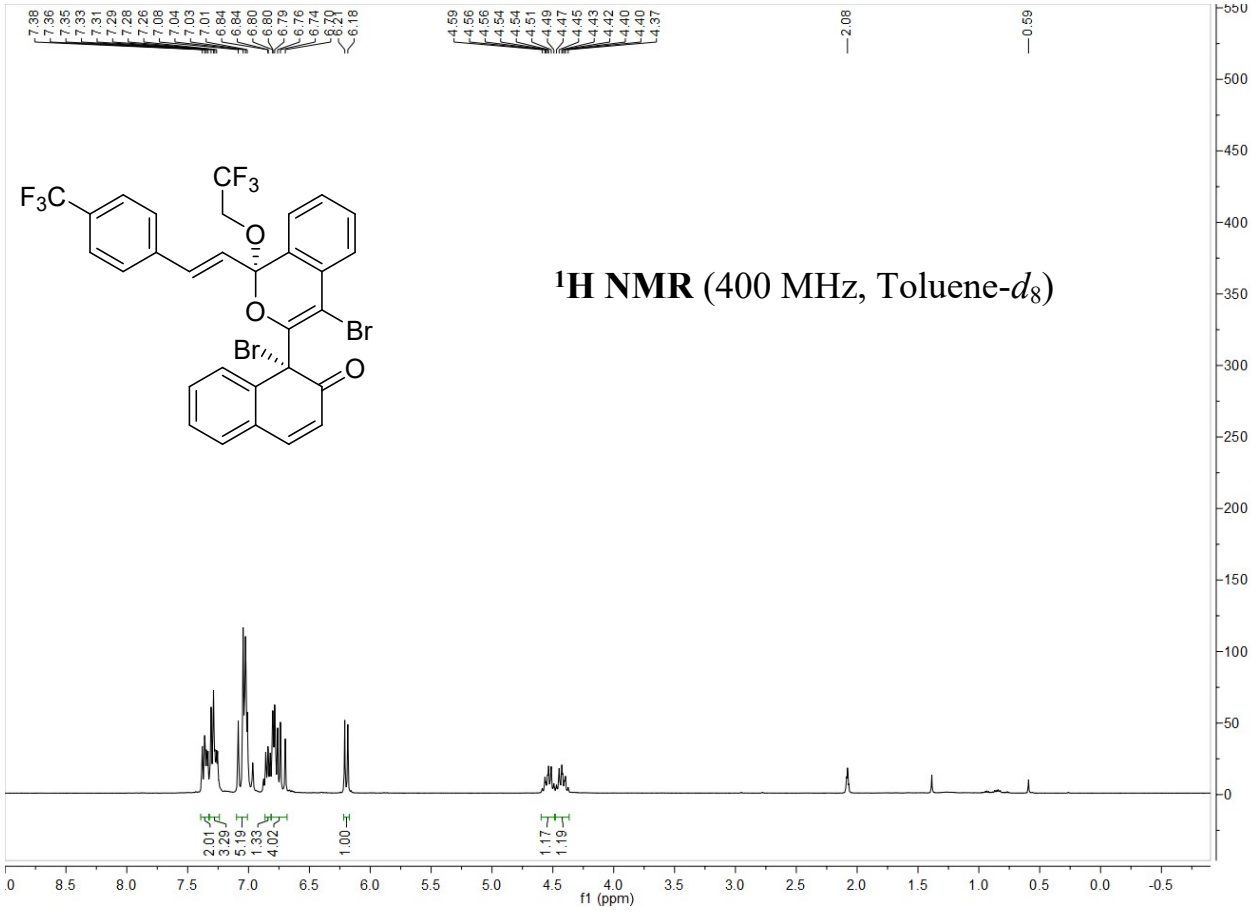

F
CF3
O
O
Br
Br
O
13C NMR (100 MHz, Toluene-d8)
f1 (ppm)



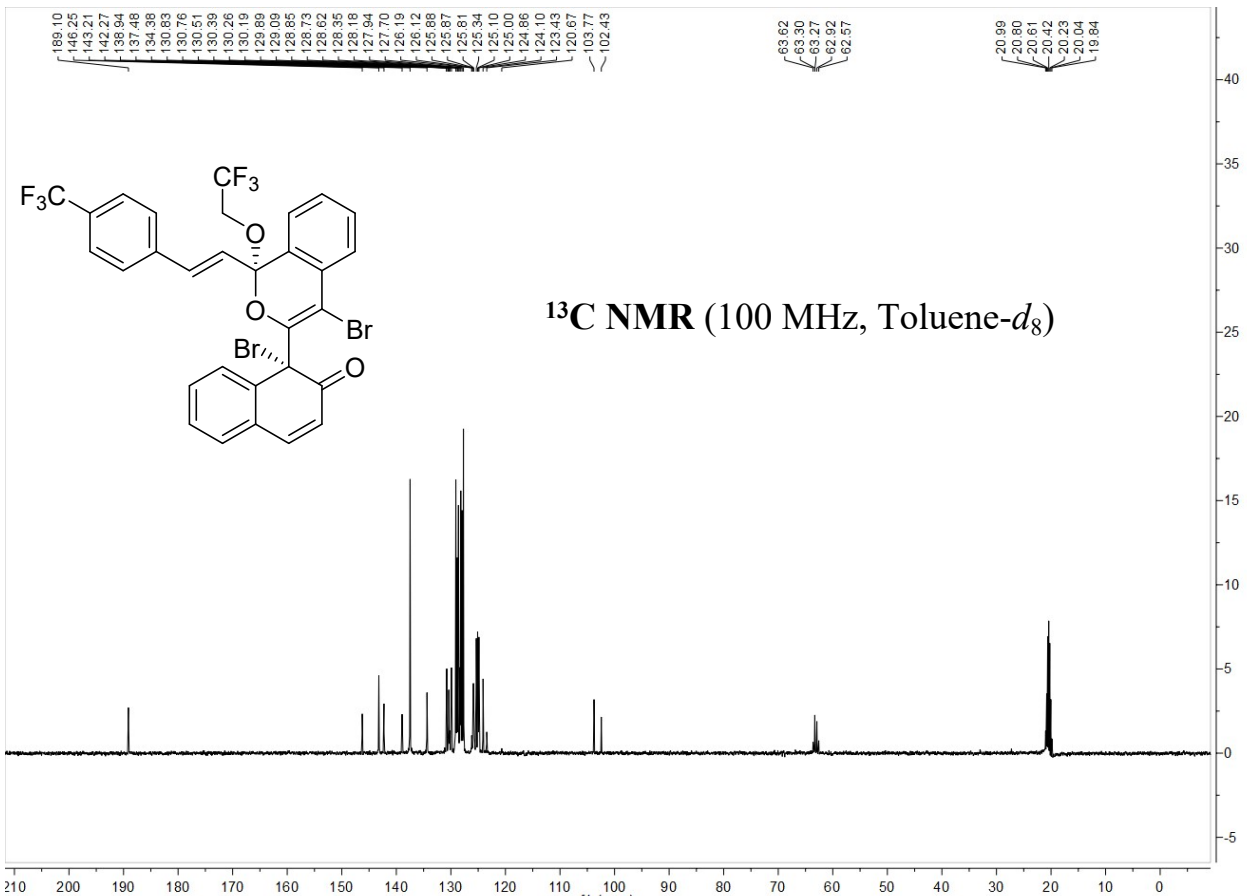
^{1}H NMR (400 MHz, Toluene-d_8)



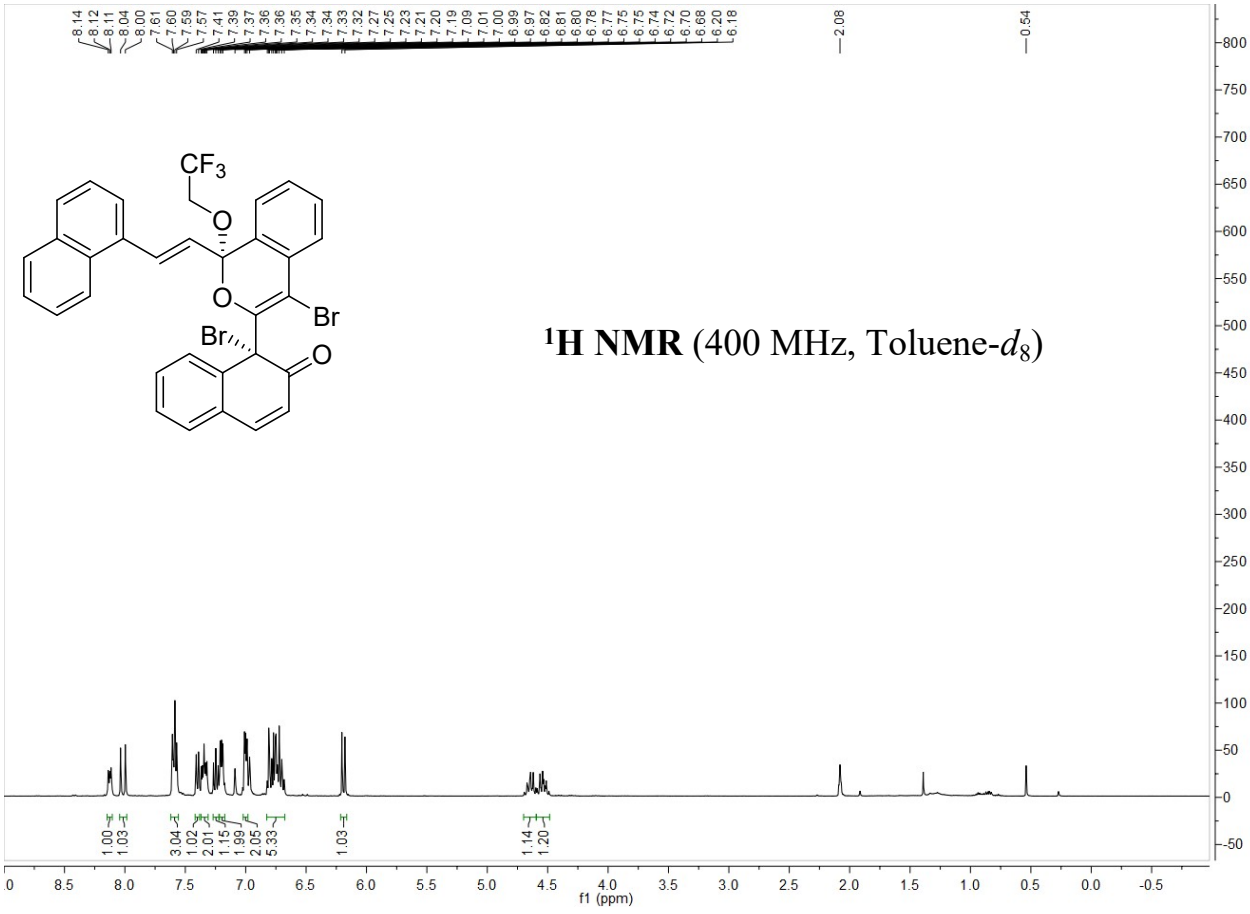
^{13}C NMR (100 MHz, Toluene-d_8)



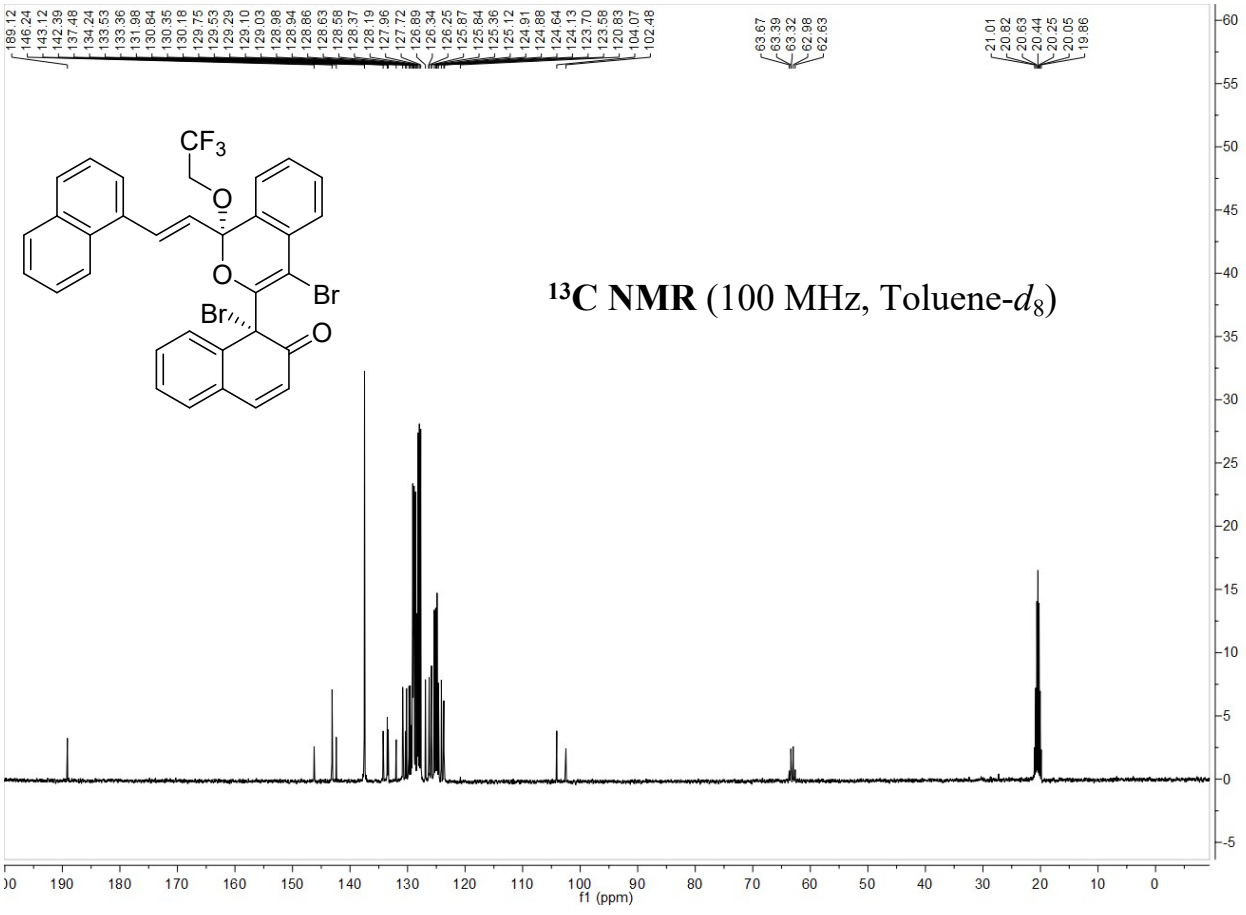
^{1}H NMR (400 MHz, Toluene-d_8)



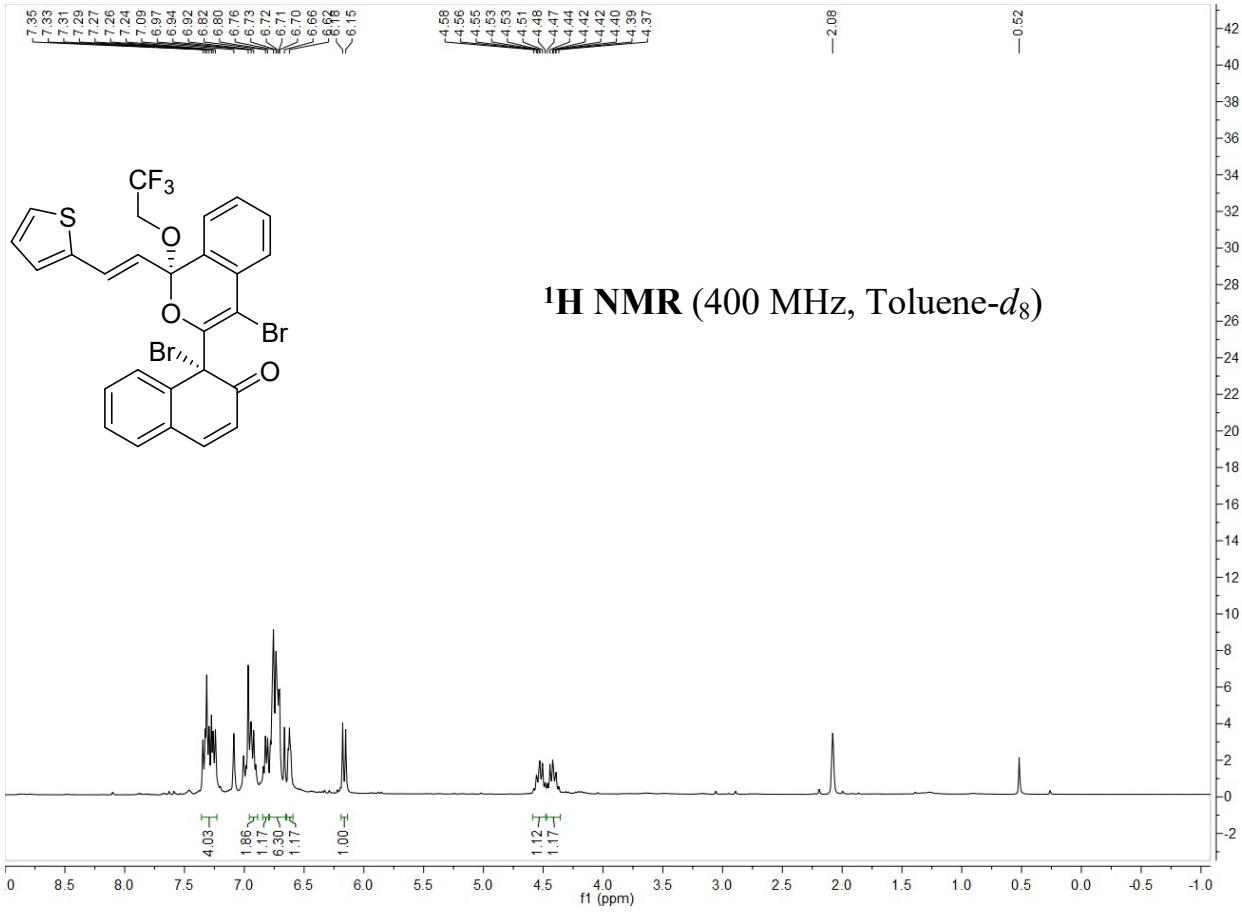
^{13}C NMR (100 MHz, Toluene-d_8)



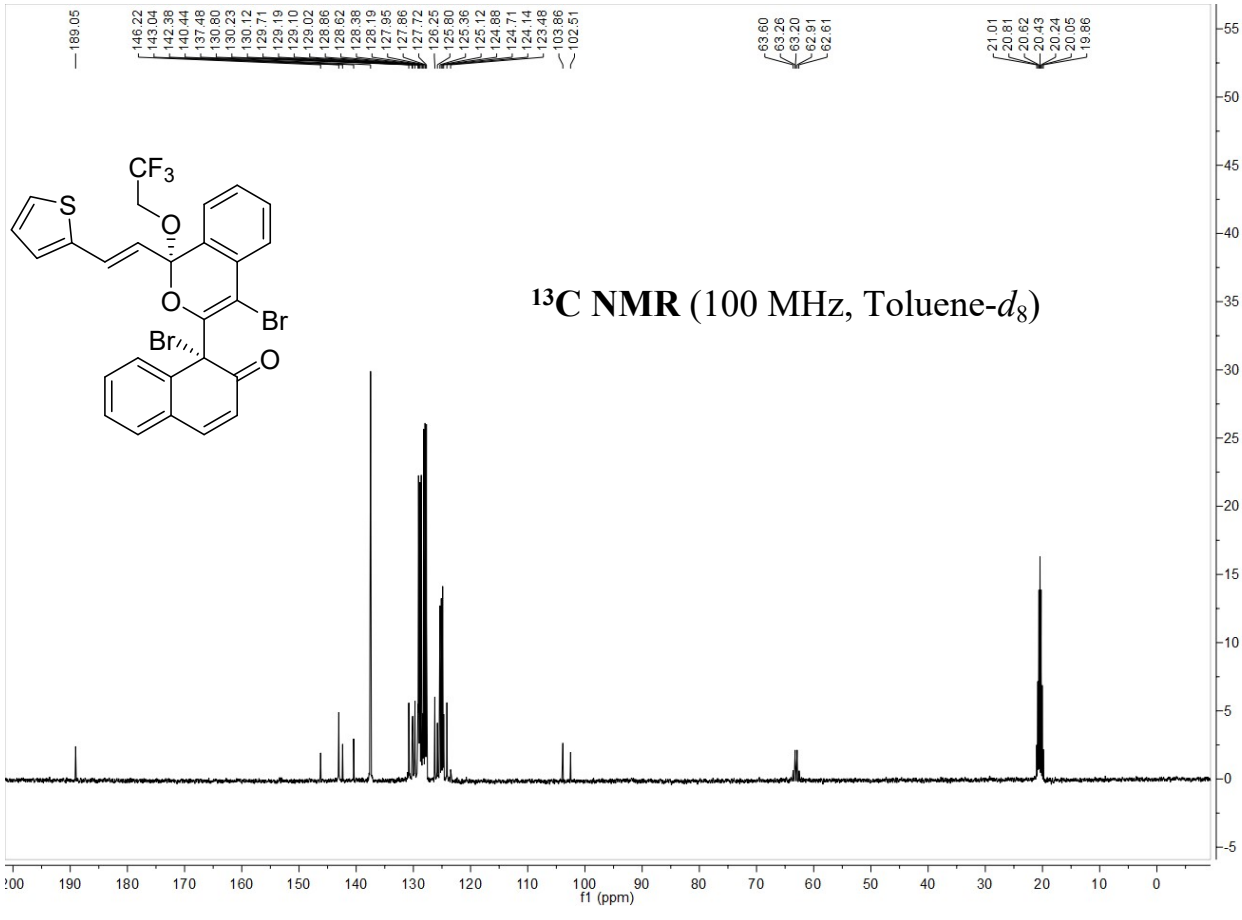
^{1}H NMR (400 MHz, Toluene-d_8)



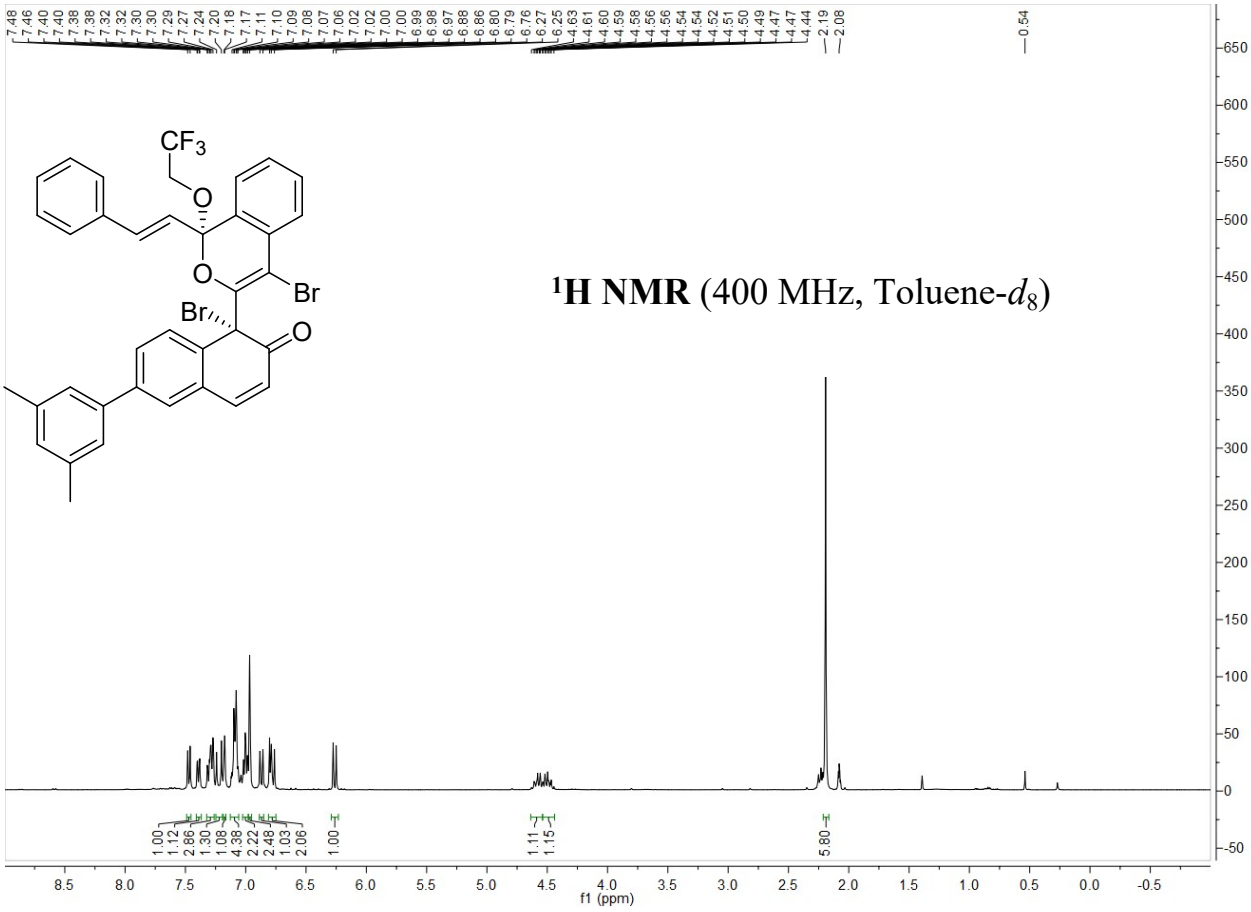
^{13}C NMR (100 MHz, Toluene-d_8)

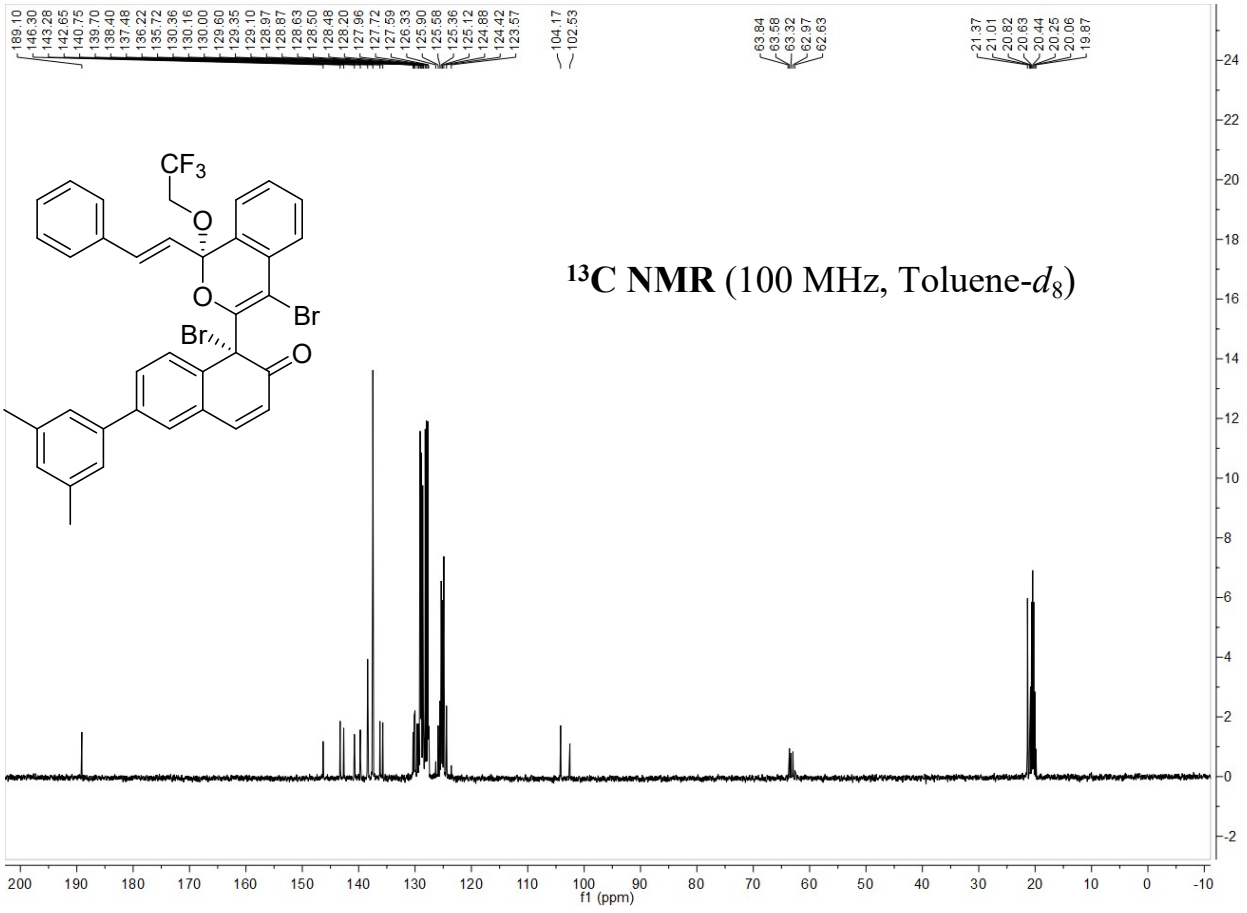


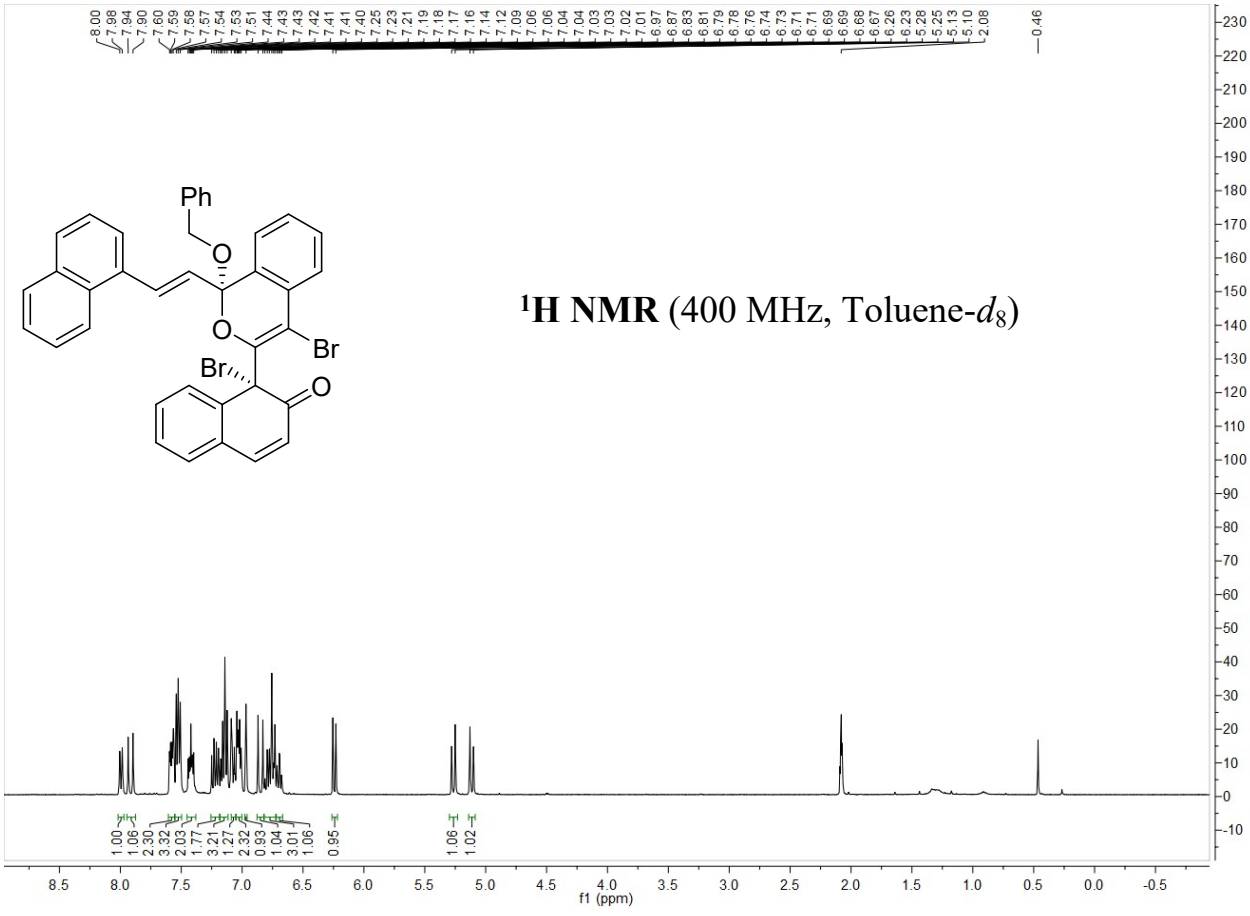
^{1}H NMR (400 MHz, Toluene-d_8)



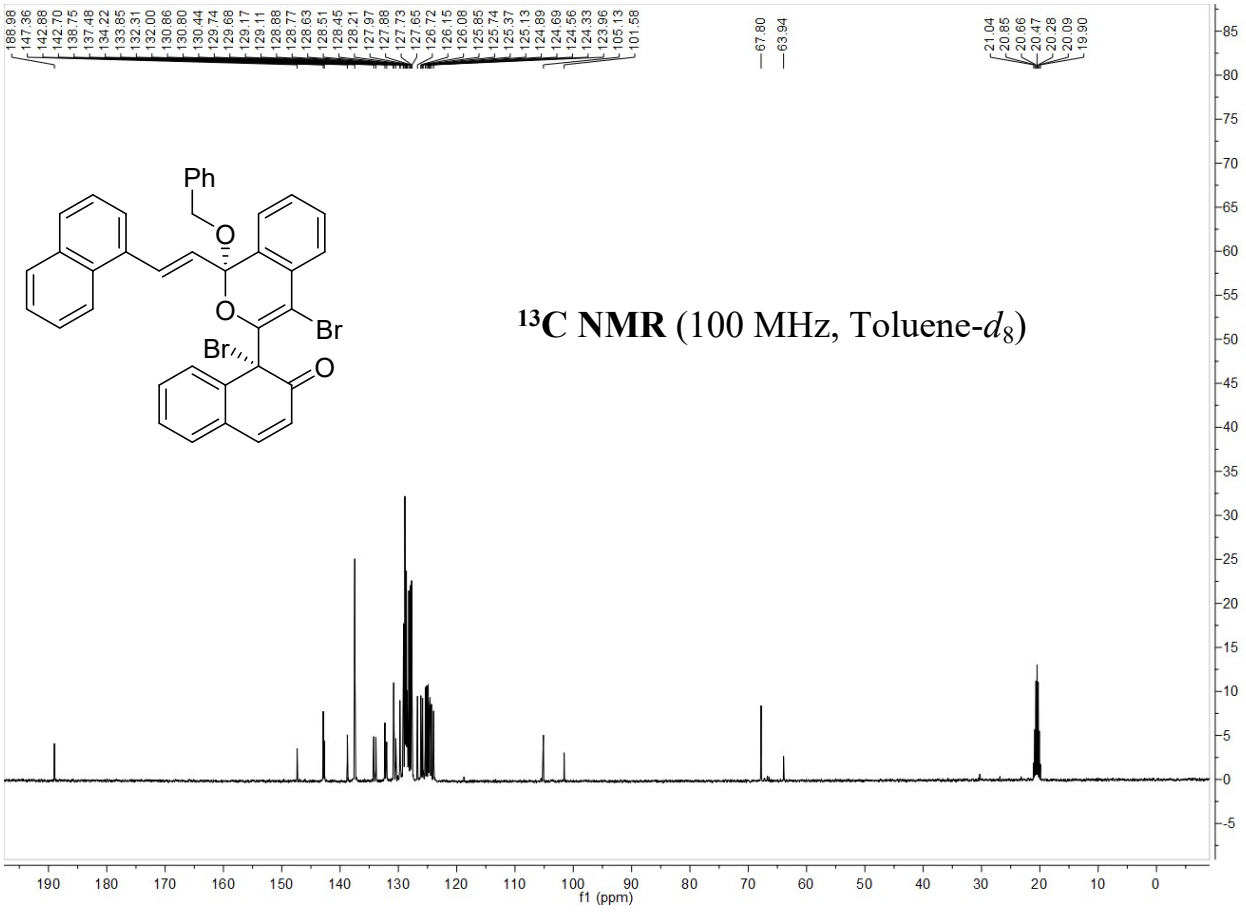
^{13}C NMR (100 MHz, Toluene-d_8)


CF3
O
O
Br
Br
O
¹H NMR (400 MHz, Toluene-d8)
f1 (ppm)

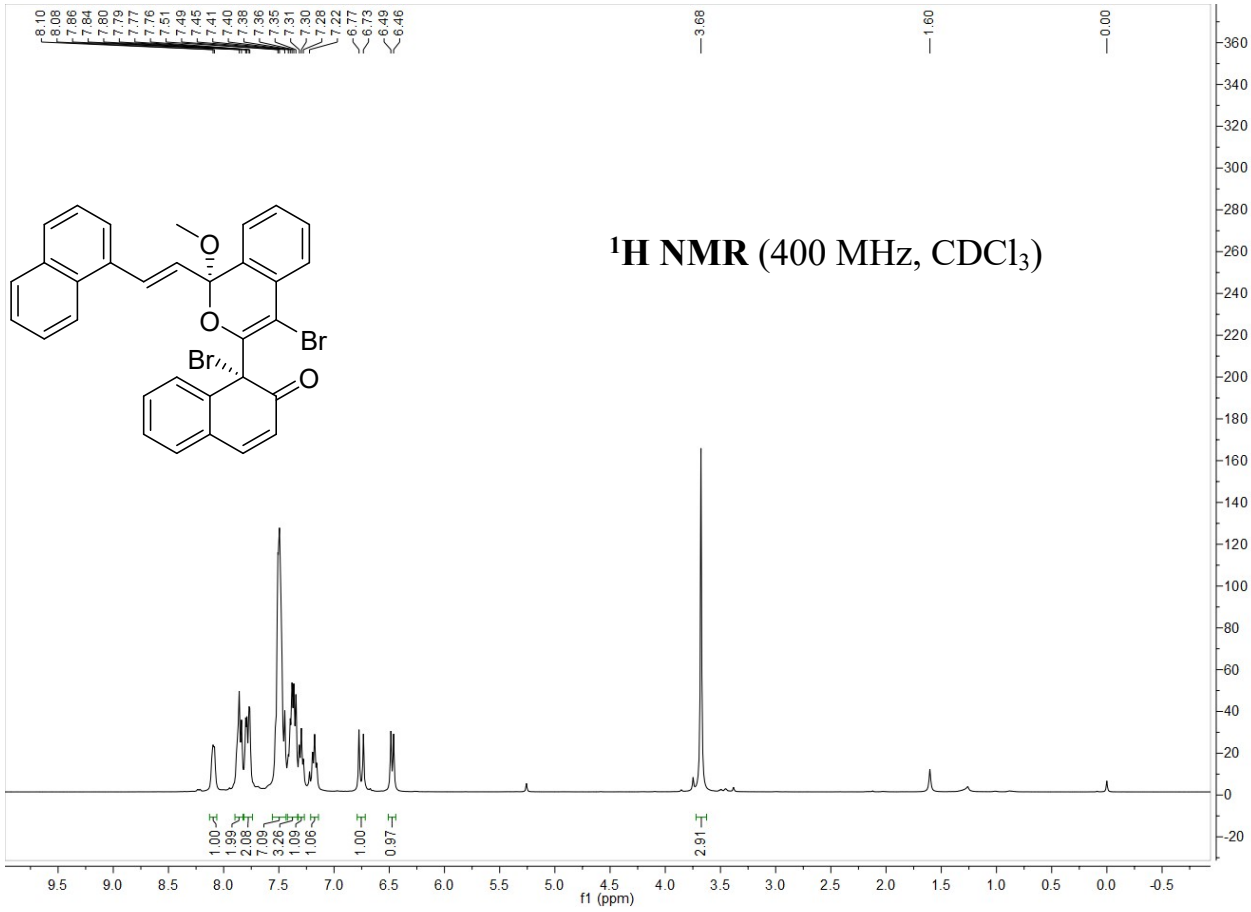

CF3
O
O
Br
Br
O
¹³C NMR (100 MHz, Toluene-d8)
f1 (ppm)



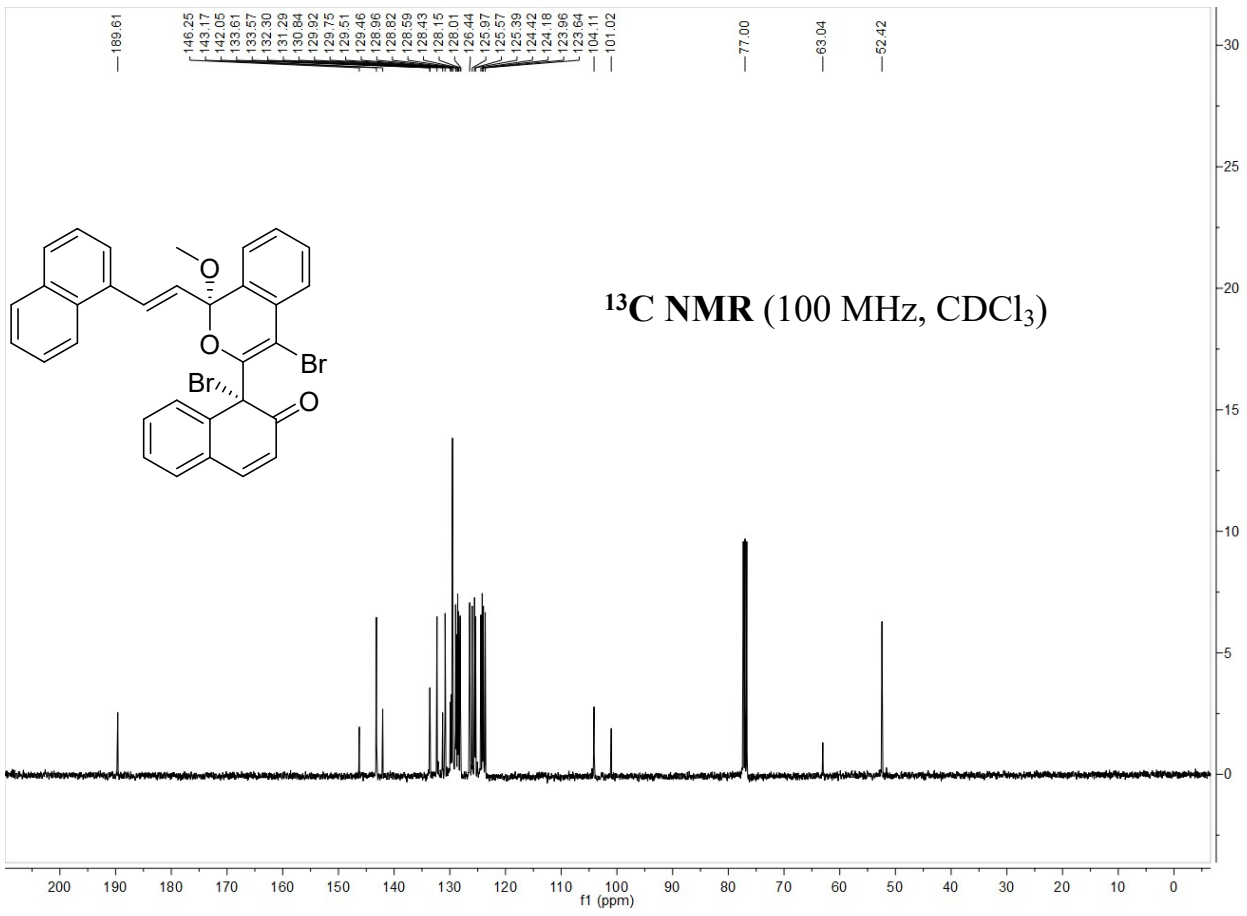
^{1}H NMR (400 MHz, Toluene-d_8)



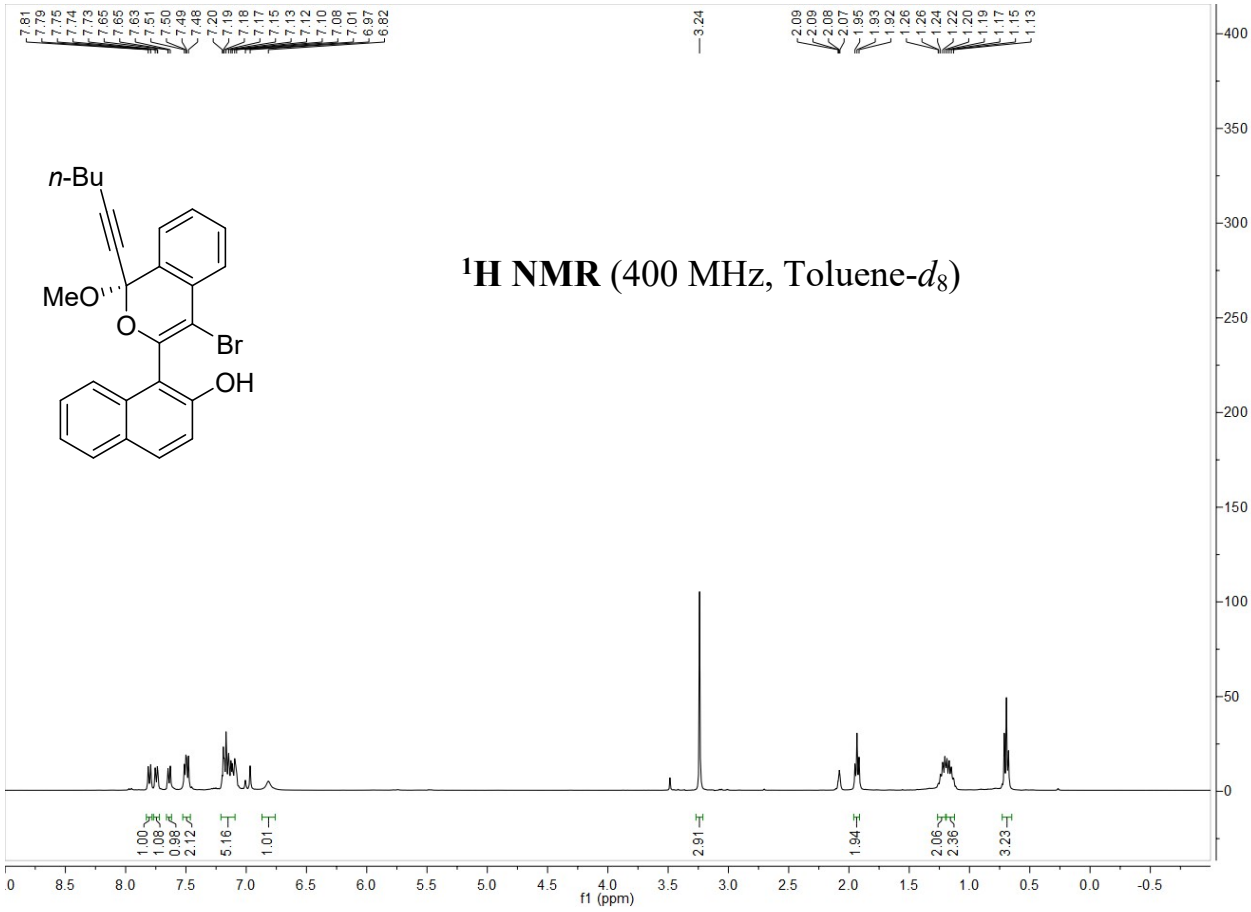
^{13}C NMR (100 MHz, Toluene-d_8)

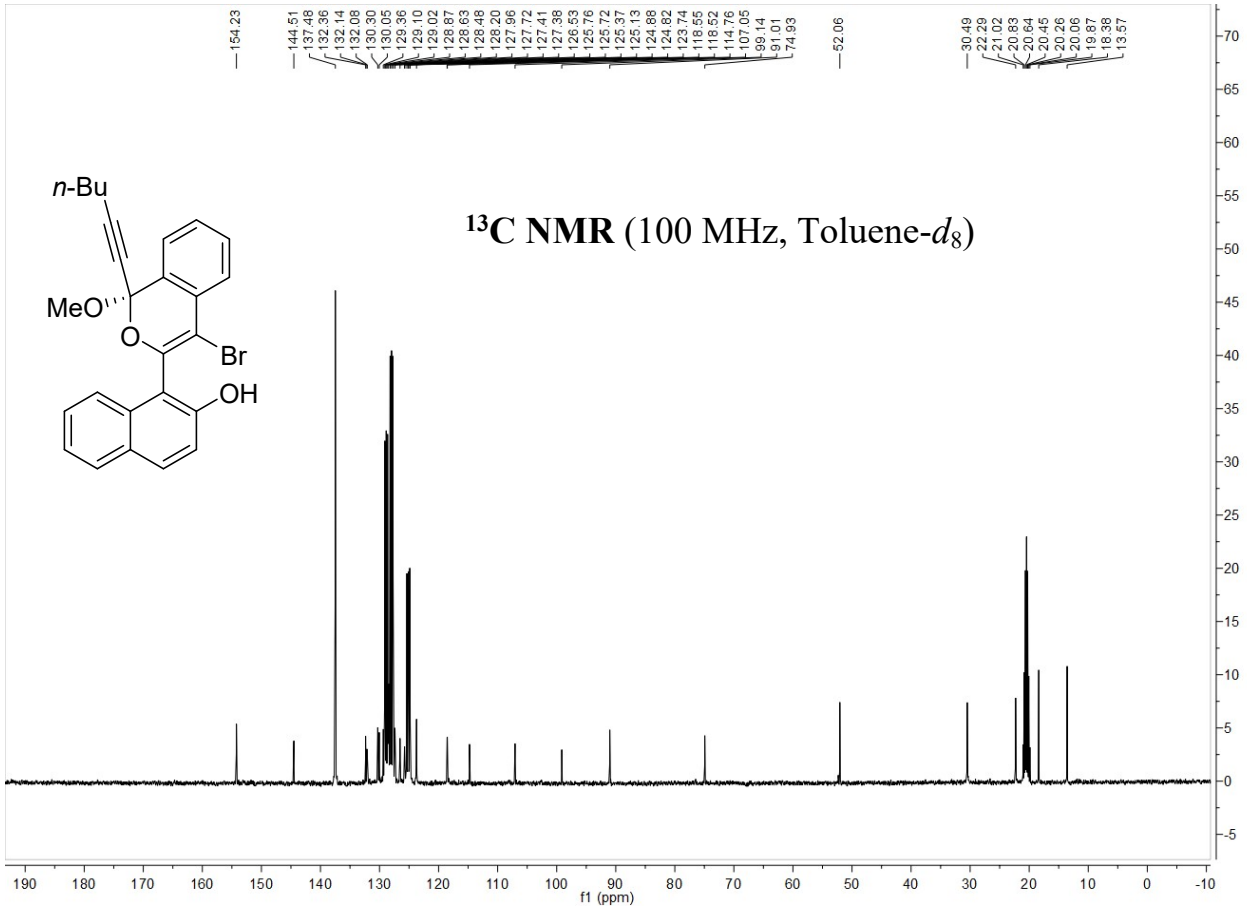


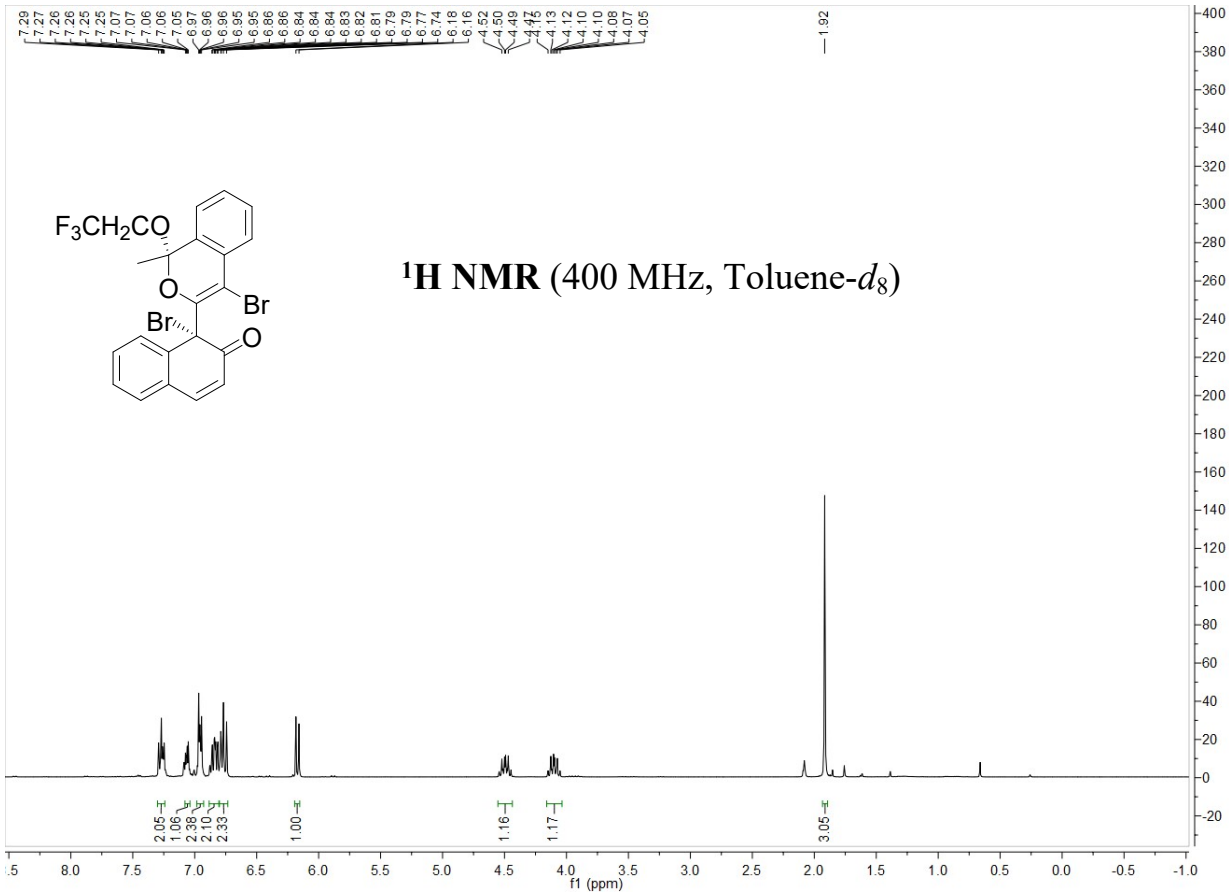
^{1}H NMR (400 MHz, $CDCl_3$)

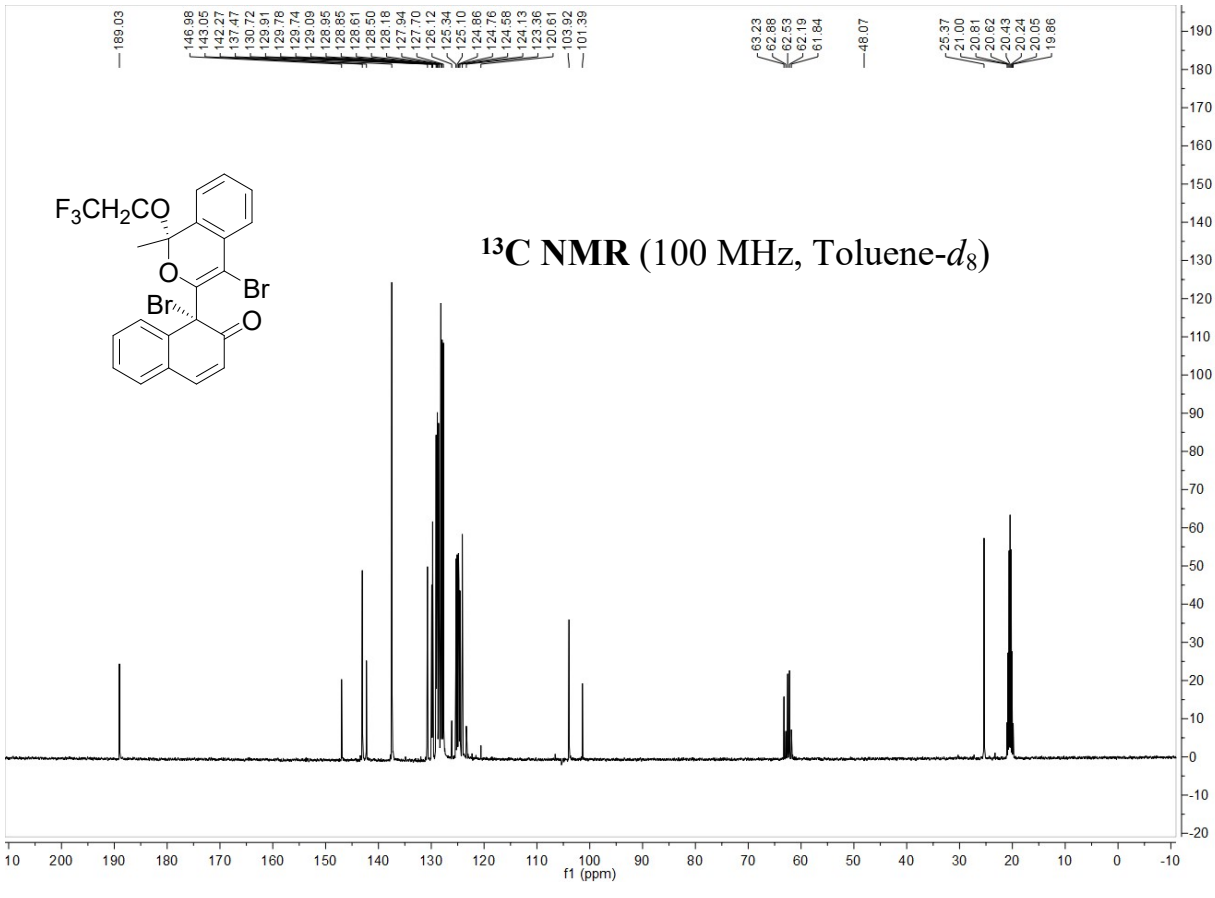


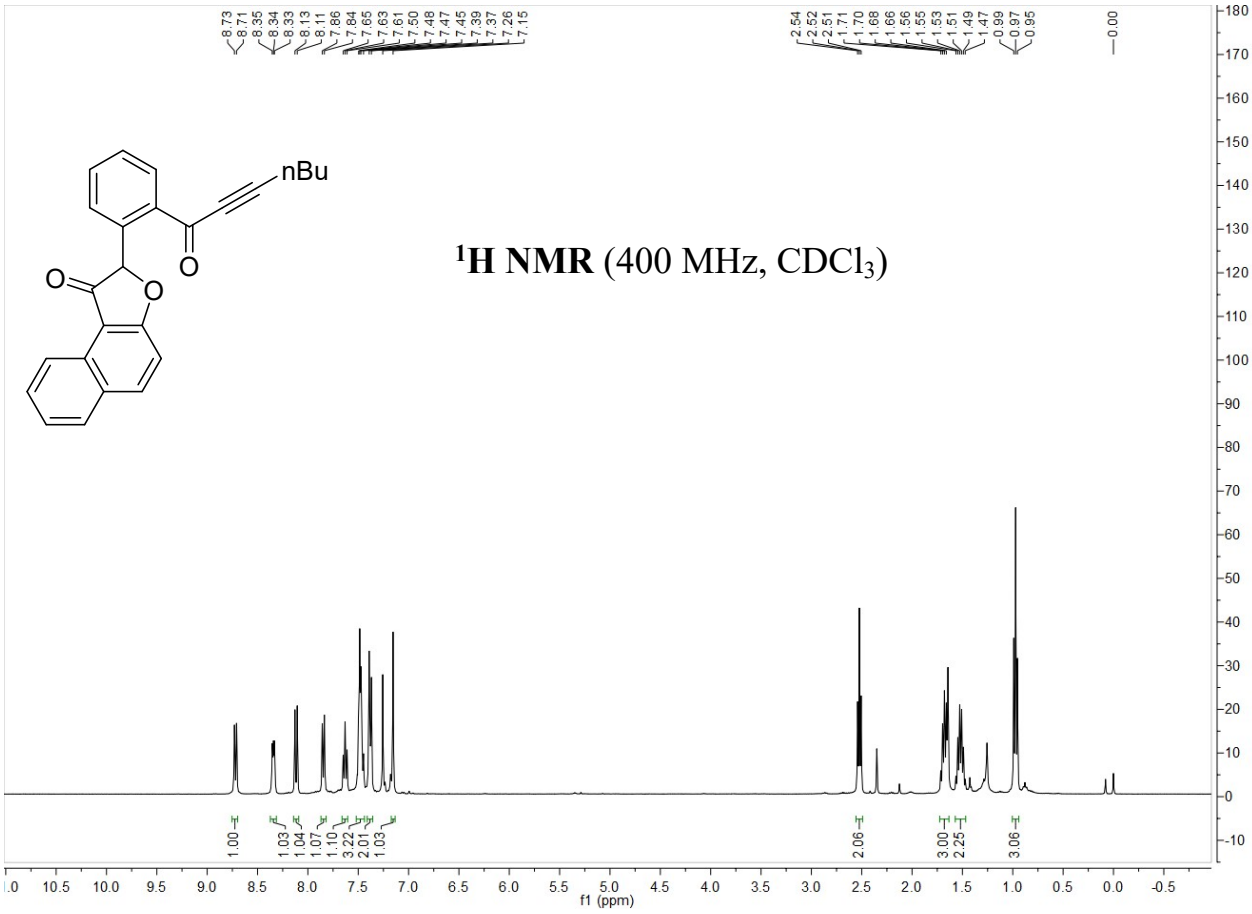
^{13}C NMR (100 MHz, $CDCl_3$)


n-Bu
MeO
O
Br
OH
1H NMR (400 MHz, Toluene-d8)
f1 (ppm)

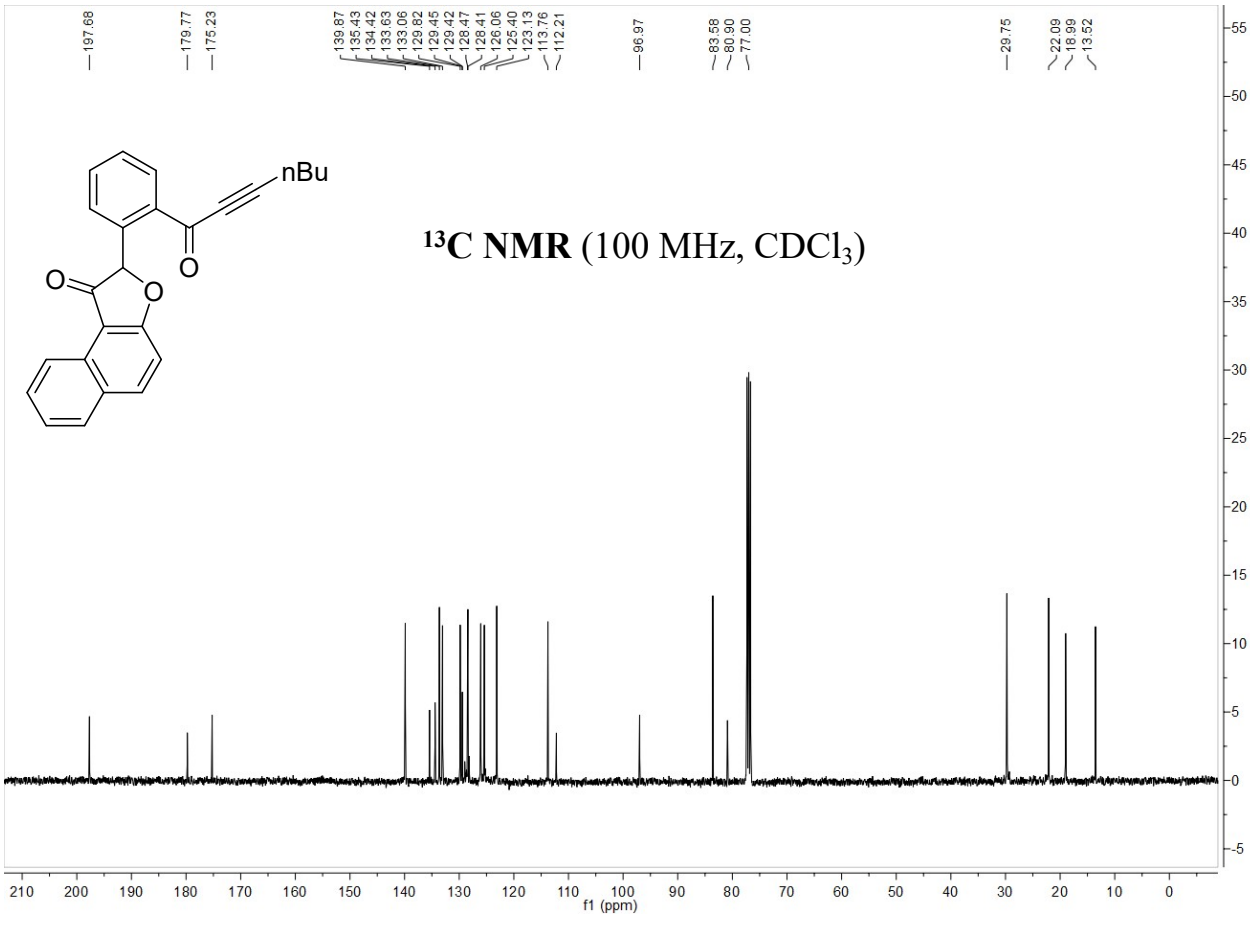

n-Bu
MeO
O
Br
OH
13C NMR (100 MHz, Toluene-d8)
f1 (ppm)


F3CH2CO
O
Br
Br
O
1H NMR (400 MHz, Toluene-d8)
f1 (ppm)

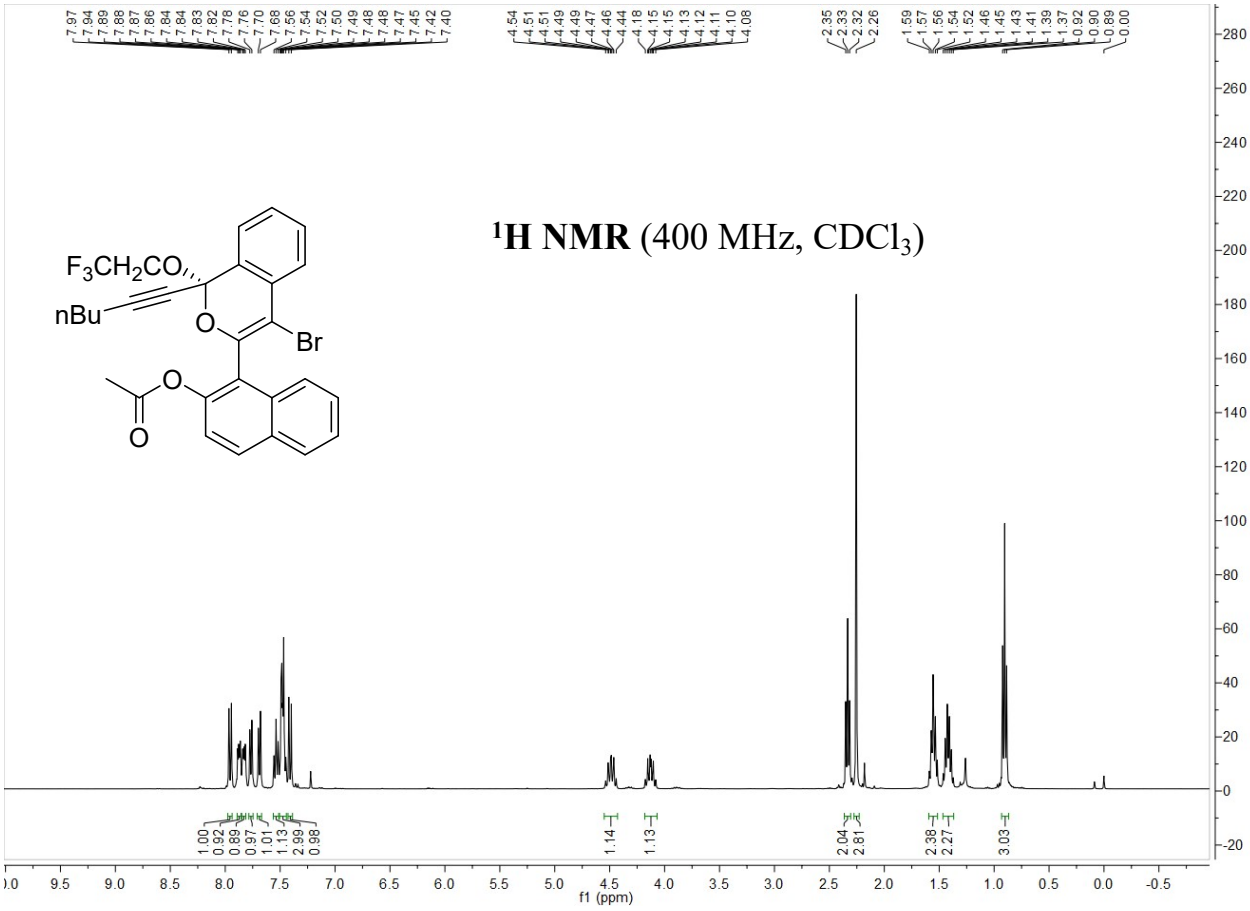

F3CH2CO
O
Br
Br
O
13C NMR (100 MHz, Toluene-d8)
f1 (ppm)

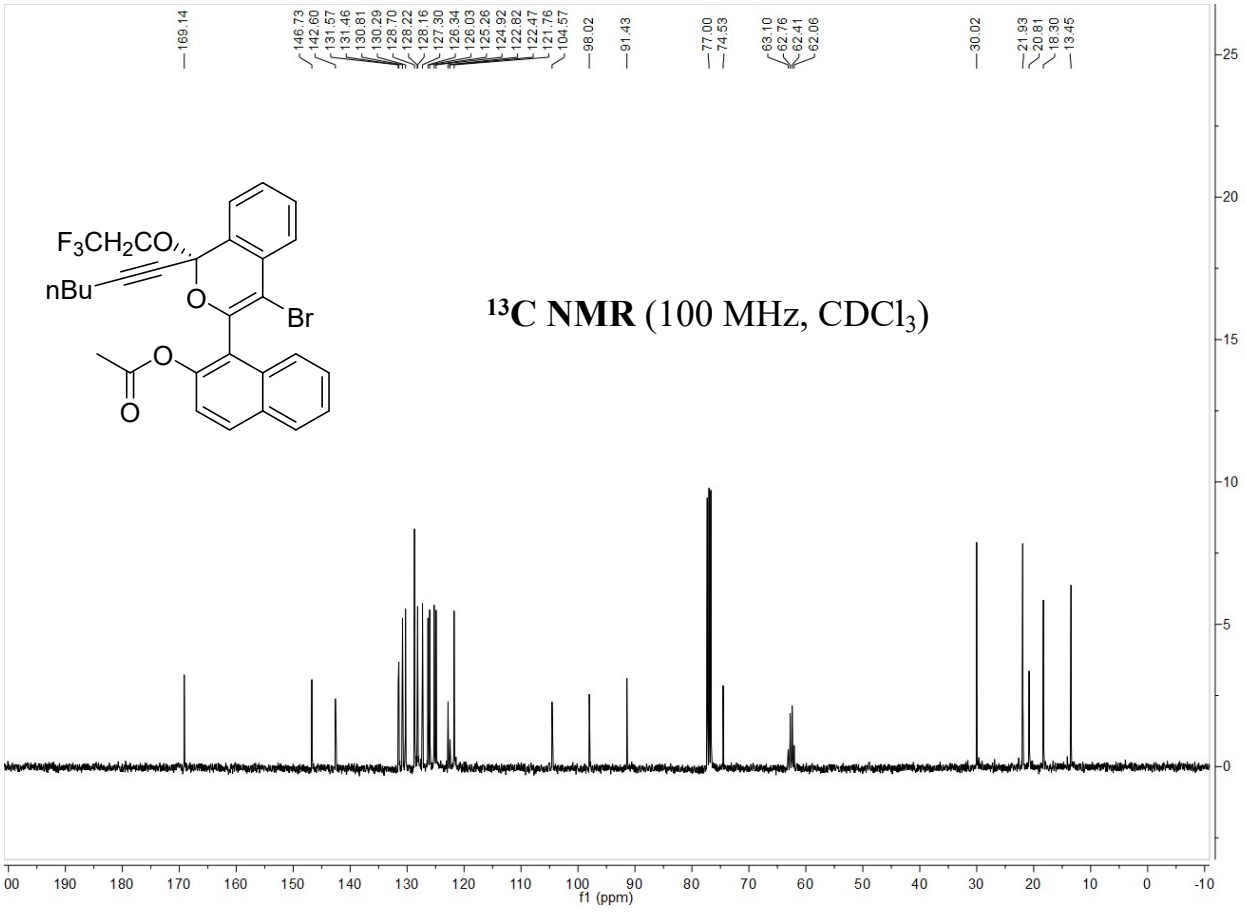


^{1}H NMR (400 MHz, $CDCl_3$)

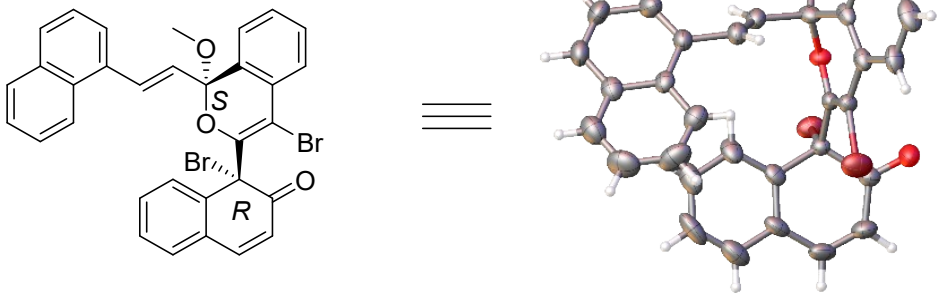


^{13}C NMR (100 MHz, $CDCl_3$)


F3CH2CO
nBu
O
Br
O
O
1H NMR (400 MHz, CDCl3)
f1 (ppm)


F3CH2CO
nBu
O
Br
O
O
13C NMR (100 MHz, CDCl3)
f1 (ppm)

XI. Crystallographic details of 4j.



4j **CCDC: 2077845**

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Cell:	a=7.8735(3)	b=13.6168(5)	c=24.1689(10)
	alpha=90	beta=90	gamma=90
Temperature:	295 K		
	Calculated		Reported
Volume	2591.19(17)		2591.18(19)
Space group	P 21 21 21		P 21 21 21
Hall group	P 2ac 2ab		P 2ac 2ab
Moiety formula	C32 H22 Br2 O3		C32 H22 Br2 O3
Sum formula	C32 H22 Br2 O3		C32 H22 Br2 O3
Mr	614.30		614.31
Dx,g cm-3	1.575		1.575
Z	4		4
Mu (mm-1)	3.161		
F000	1232.0		
F000’	1230.22		
h,k,lmax	10,18,33		10,18,32
Nref	6928[3907]		5957
Tmin,Tmax	0.457,0.483		0.717,1.000
Tmin’	0.423		

Correction method= # Reported T Limits: Tmin=0.717 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 1.52/0.86 Theta(max)= 29.042
R(reflections)= 0.0421(4360) wR2(reflections)= 0.0779(5957)
S = 1.049 Npar= 335