Supporting Information

Rhodium(III)-catalyzed asymmetric allylic cyclization of cyclohexa-dienone-tethered allenes

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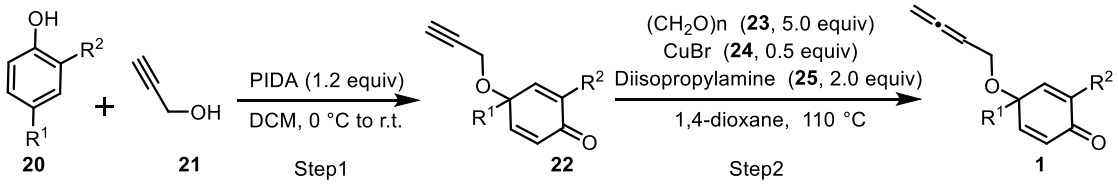
Contents

1. General Information

Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel (300-400 mesh). Chemical yields referred to pure isolated substances. Solvents were dried by Innovative Technology Solvent Purification System. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 MHz or 600 MHz NMR Spectrometer. Data for ^{1}H NMR spectra are reported relative to chloroform as an internal standard (7.26 ppm) and are reported as follows: (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; *J* = coupling constant in Hz, integration). Data for ^{13}C NMR spectra were reported relative to chloroform as an internal standard (77.0 ppm) and are reported in terms of chemical shift (ppm). High resolution mass spectra were acquired by Agilent 6545 Accurate-Mass Q-TOF LC/MS System. Specific Rotation was measured on Rudolph Research Analytical AUTOPOL IV Automatic Polarimeter. Enantiomeric excess was determined by chiral HPLC analysis on Agilent 1260 Infinity II LC System.

2. Substrate Preparation

General Procedures for the Preparation of Cyclohexadienone-Tethered Alkynes

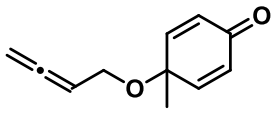


Step1: A stirring solution of phenol **20** (1.0 equiv) in DCM of propargyl alcohol (**21**, 10.0 equiv) was cooled to 0 ℃ and treated with phenyliodine (III) diacetate (PIDA, 1.2 equiv) in several portions. The resulting mixture was warmed to room temperature and stirred overnight. After that, the reaction mixture was extracted with DCM (3x). The organic layer was washed with brine, dried over Na_2SO_4, and concentrated by rotary evaporation. The residue was then purified by column chromatography to afford the desired products **22**.

Step2: To a well-stirred solution of **22** (1.0 equiv) in 1,4-dioxane was added paraformaldehyde **23** (5.0 equiv), CuBr (**24**, 0.5 equiv) and diisopropylamine **25** (2.0 equiv) under argon atmosphere. The resulting mixture was stirred at 110 ℃ for 1 h. After cooled

to room temperature, the reaction mixture was filtered and washed with DCM (10 mL ×3). The combined organic phases were desiccated with anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified through flash column chromatography employing hexane/ethyl acetate eluent to obtained the pure substrates **1**.

4-(Buta-2,3-dien-1-yloxy)-4-methylcyclohexa-2,5-dien-1-one (1a)[1-3]

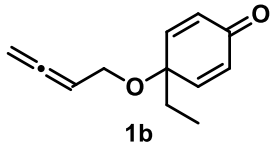


1a

R_f = 0.40 (PE/EA = 5/1), yellow oil (240 mg, 22.1% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 6.81 (d, *J* = 10.2 Hz, 2H), 6.37 – 6.20 (m, 2H), 5.28 – 5.14 (m, 1H), 4.83 – 4.66 (m, 2H), 3.99 – 3.79 (m, 2H), 1.45 (d, *J* = 1.5 Hz, 3H).

4-(Buta-2,3-dien-1-yloxy)-4-ethylcyclohexa-2,5-dien-1-one (1b)[1-3]

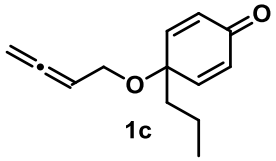


1b

R_f = 0.40 (PE/EA = 5/1), yellow oil (190 mg, 11.7% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.75 (d, *J* = 10.3 Hz, 2H), 6.35 (d, *J* = 10.2 Hz, 2H), 5.34 – 5.12 (m, 1H), 4.79 – 4.68 (m, 2H), 3.89 (dd, *J* = 7.0, 0.8 Hz, 2H), 1.79 (dd, *J* = 7.6, 0.8 Hz, 2H), 0.83 (t, *J* = 7.4 Hz, 3H).

4-(Buta-2,3-dien-1-yloxy)-4-propylcyclohexa-2,5-dien-1-one (1c)[1-3]

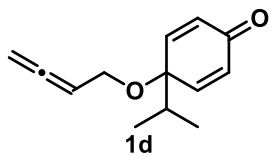


1c

R_f = 0.40 (PE/EA = 5/1), yellow oil (329 mg, 30.1% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.77 (d, *J* = 10.2 Hz, 2H), 6.32 (d, *J* = 10.2 Hz, 2H), 5.24 – 5.14 (m, 1H), 4.75 (d, *J* = 6.6 Hz, 2H), 3.87 (d, *J* = 7.0 Hz, 2H), 1.77 – 1.69 (m, 2H), 1.34 – 1.21 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

4-(Buta-2,3-dien-1-yloxy)-4-isopropylcyclohexa-2,5-dien-1-one (1d)[1-3]

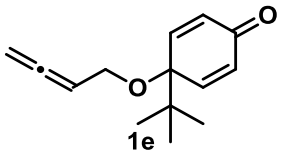


1d

R_f = 0.40 (PE/EA = 5/1), colorless oil (210 mg, 19.5% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.75 (d, *J* = 10.1 Hz, 2H), 6.37 (d, *J* = 10.2 Hz, 2H), 5.26 – 5.14 (m, 1H), 4.75 (dd, *J* = 6.6, 0.8 Hz, 2H), 3.96 – 3.81 (m, 2H), 2.12 – 1.95 (m, 1H), 0.93 (d, *J* = 6.6 Hz, 6H).

4-(Buta-2,3-dien-1-yloxy)-4-(tert-butyl)cyclohexa-2,5-dien-1-one (**1e**)[1-3]

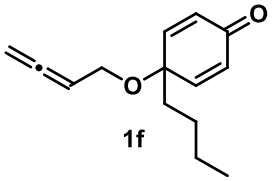


1e

R_f = 0.45 (PE/EA = 1/1), colorless oil (1.2 g, 27.3% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.91 (d, *J* = 10.4 Hz, 2H), 6.36 (d, *J* = 10.4 Hz, 2H), 5.27 – 5.09 (m, 1H), 4.81 – 4.69 (m, 2H), 3.89 – 3.80 (m, 2H), 1.00 (s, 9H).

4-(Buta-2,3-dien-1-yloxy)-4-butylcyclohexa-2,5-dien-1-one (**1f**)[1-3]

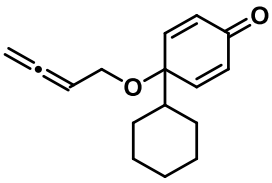


1f

R_f = 0.45 (PE/EA = 1/1), colorless solid (120 mg, 12.0% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.77 (d, *J* = 10.1 Hz, 2H), 6.33 (d, *J* = 10.2 Hz, 2H), 5.35 – 5.04 (m, 1H), 4.76 (d, *J* = 6.7 Hz, 2H), 3.88 (d, *J* = 7.0 Hz, 2H), 1.75 (d, *J* = 9.5 Hz, 2H), 1.34 – 1.19 (m, 4H), 0.86 (t, *J* = 7.1 Hz, 3H).

1-(Buta-2,3-dien-1-yloxy)-[1,1'-bi(cyclohexane)]-2,5-dien-4-one (**1g**)[1-3]

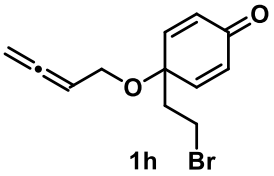


1g

R_f = 0.50 (PE/EA = 1/1), yellow oil (1.1 g, 33.0% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 6.76 (d, *J* = 10.3 Hz, 2H), 6.34 (d, *J* = 10.3 Hz, 2H), 5.25 – 5.10 (m, 1H), 4.80 – 4.73 (m, 2H), 3.90 – 3.71 (m, 2H), 1.88 (d, *J* = 11.8 Hz, 2H), 1.74 (d, *J* = 13.5 Hz, 2H), 1.71 – 1.64 (m, 2H), 1.24 – 1.16 (m, 2H), 1.12 – 1.04 (m, 1H), 0.92 (m, 2H).

4-(2-Bromoethyl)-4-(buta-2,3-dien-1-yloxy)cyclohexa-2,5-dien-1-one (1h)[1-3]

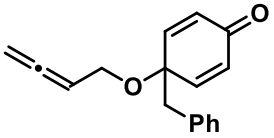


1h

R_f = 0.40 (PE/EA = 1/1), yellow oil (78 mg, 17.6% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.81 (d, *J* = 10.4 Hz, 2H), 6.38 (d, *J* = 10.4 Hz, 2H), 5.26 – 5.11 (m, 1H), 4.78 (dd, *J* = 6.7, 2.5 Hz, 2H), 3.87 (d, *J* = 6.9 Hz, 2H), 3.37 (t, *J* = 8.1 Hz, 2H), 2.33 (t, *J* = 8.1 Hz, 2H).

4-Benzyl-4-(buta-2,3-dien-1-yloxy)cyclohexa-2,5-dien-1-one (1i) [1-3]

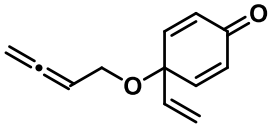


1i

R_f = 0.50 (PE/EA = 1/1), colorless oil (50 mg, 6.0% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.24 (m, 3H), 7.18 – 7.14 (m, 2H), 6.77 (d, *J* = 10.2 Hz, 2H), 6.26 (d, *J* = 10.2 Hz, 2H), 5.31 – 5.15 (m, 1H), 4.76 (d, *J* = 6.6 Hz, 2H), 3.88 (d, *J* = 6.8 Hz, 2H), 3.03 (s, 2H).

4-(Buta-2,3-dien-1-yloxy)-4-vinylcyclohexa-2,5-dien-1-one (1j) [1-3]

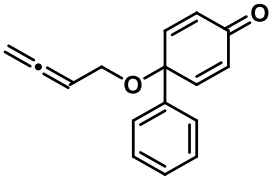


1j

R_f = 0.50 (PE/EA = 1/1), colorless solid (98 mg, 33.6% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 6.77 (d, *J* = 10.2 Hz, 2H), 6.32 (d, *J* = 10.1 Hz, 2H), 5.73 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.44 (m, 1H), 5.32 – 5.20 (m, 2H), 4.89 – 4.70 (m, 2H), 4.04 – 3.89 (m, 2H).

1-(Buta-2,3-dien-1-yloxy)-[1,1'-biphenyl]-4(1H)-one (1k)[1-3]

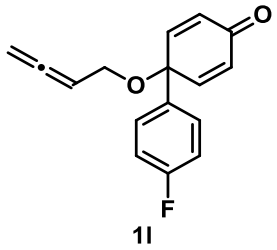


1k

R_f = 0.50 (PE/EA = 1/1), yellow oil (98 mg, 32.9% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.55 – 7.42 (m, 2H), 7.40 – 7.30 (m, 3H), 6.85 (d, *J* = 10.2 Hz, 2H), 6.38 (d, *J* = 10.1 Hz, 2H), 5.46 – 5.26 (m, 1H), 4.82 (d, *J* = 6.7 Hz, 2H), 4.12 (d, *J* = 6.8 Hz, 2H).

1-(Buta-2,3-dien-1-yloxy)-4'-fluoro-[1,1'-biphenyl]-4(1H)-one (**1l**)[1-3]

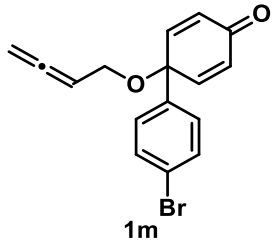


1l

R_f = 0.50 (PE/EA = 1/1), yellow oil (56 mg, 29.7% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.49 – 7.41 (m, 2H), 7.07 – 7.00 (m, 2H), 6.81 (d, *J* = 10.1 Hz, 2H), 6.38 (d, *J* = 10.1 Hz, 2H), 5.36 – 5.26 (m, 1H), 4.82 (d, *J* = 6.6 Hz, 2H), 4.10 (d, *J* = 6.8 Hz, 2H).

4'-Bromo-1-(buta-2,3-dien-1-yloxy)-[1,1'-biphenyl]-4(1*H*)-one (**1m**)[1-3]

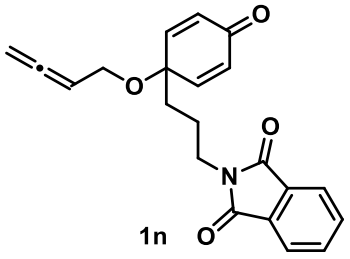


1m

R_f = 0.30 (PE/EA = 1/1), yellow oil (86 mg, 25.6% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.48 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 10.2 Hz, 2H), 6.38 (d, *J* = 10.2 Hz, 2H), 5.37 – 5.23 (m, 1H), 4.82 (d, *J* = 6.6 Hz, 2H), 4.10 (d, *J* = 6.8 Hz, 2H).

2-(3-(1-(Buta-2,3-dien-1-yloxy)-4-oxocyclohexa-2,5-dien-1-yl)propyl)isoindoline-1,3-dione (**1n**)



1n

R_f = 0.35 (PE/EA = 1/1), yellow oil (108 mg, 47.2% yield).

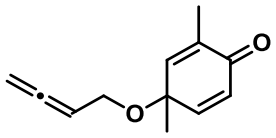
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.70 (dd, *J* = 5.5, 3.1 Hz, 2H), 6.76 (d, *J* = 10.1 Hz, 2H), 6.32 (d, *J* = 10.0 Hz, 2H), 5.16 (d, *J* = 6.7 Hz,

1H), 4.74 (d, *J* = 6.6 Hz, 2H), 3.85 (d, *J* = 7.0 Hz, 2H), 3.66 (t, *J* = 7.0 Hz, 2H), 1.84 – 1.75 (m, 2H), 1.68 (dd, *J* = 6.8, 4.0 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 209.19, 185.15, 168.24, 150.49, 133.97, 131.98, 131.24, 123.23, 88.44, 76.10, 75.23, 63.73, 37.70, 36.67, 22.84.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{21}H_{20}NO_4^{\oplus}$ 350.1387, found 350.1395.

4-(Buta-2,3-dien-1-yloxy)-2,4-dimethylcyclohexa-2,5-dien-1-one (1o)[1-3]

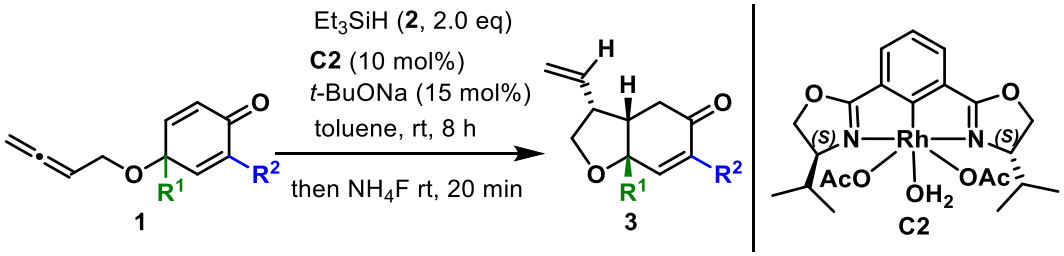


1o

R_f = 0.50 (PE/EA = 1/1), yellow oil (378 mg, 35.0% yield).

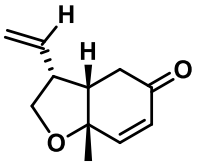
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 6.76 (dd, *J* = 10.0, 3.0 Hz, 1H), 6.56 (d, *J* = 1.5 Hz, 1H), 6.26 (d, *J* = 10.0 Hz, 1H), 5.28 – 5.15 (m, 1H), 4.74 (d, *J* = 6.5 Hz, 2H), 4.01 – 3.78 (m, 2H), 1.89 (s, 3H), 1.41 (s, 3H).

3. Scope of the Substrates



Under nitrogen, [Rh(Phebox-*i*-Pr)] (0.01 mmol, 5.4 mg), *t*-BuONa (0.015 mmol, 1.4 mg), substrate **1** (0.1 mmol), and 1.0 mL of toluene were added to a 10-mL Schlenk tube. The reaction was stirred at room temperature, after which Et_3SiH (**2**, 0.2 mmol, 23.3 mg) was added in two portions. After 8 hours, A solution of NH_4F in MeOH (0.2 M, 1.0 mL) was then added, and the reaction was stirred for 20 min. Finally, the reaction mixture was filtered, washed with EtOAc (10 mL × 3) and concentrated in vacuo. The residue was purified by flash silica gel chromatography to afford desired products **3**.

(3*R*,3a*S*,7a*S*)-7a-Methyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3aa)



3aa

R_f = 0.30 (PE/EA = 1/1), colorless oil (14.4 mg, 71% yield).

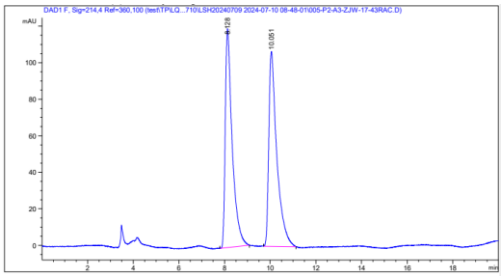
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.62 (dd, *J* = 10.3, 1.4 Hz, 1H), 5.98 (dd, *J* = 10.3, 0.8 Hz, 1H), 5.67 – 5.45 (m, 1H), 5.12 – 5.01 (m, 2H), 4.08 (dd, *J* = 9.1, 7.6 Hz, 1H), 3.56 (dd, *J* = 9.1, 6.7 Hz, 1H), 3.20 – 3.05 (m, 1H), 2.68 – 2.46 (m, 3H), 1.47 (s, 3H).

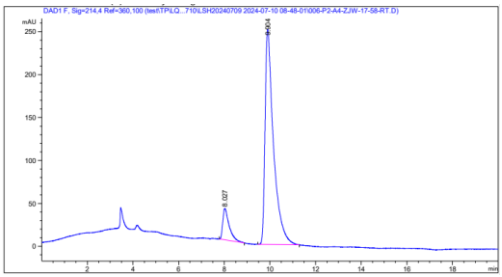
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.6, 152.7, 135.7, 129.6, 118.8, 78.8, 71.1, 47.6, 46.3, 35.7, 25.3.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{11}H_{15}O_2^{\oplus}$ 179.1067, found 179.1068.

Specific Rotation: $[\alpha]_D^{20.4}$ +3.6 (*c* 0.5, $CHCl_3$) for 90:10 er.

Chiral HPLC analysis: Chiralpak AD-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.5 mL/min; Retention time: 8.0 min (minor), 9.9 min (major).





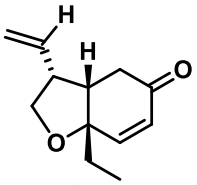
Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.128	VV R	0.2892	2523.79346	119.84834	49.2496
2	10.051	BV R	0.3154	2600.70264	106.69042	50.7504
Totals :				5124.49609	226.53876	

Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.027	BV R	0.2344	714.31451	36.72310	10.0267
2	9.904	VV R	0.3516	6409.77930	250.43301	89.9733
Totals :				7124.09381	287.15611	

(3*R*,3a*S*,7a*S*)-7a-Ethyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3ba)



3ba

R_f = 0.30 (PE/EA = 1/1), colorless oil (15.4 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.63 (dd, *J* = 10.4, 1.4 Hz, 1H), 6.04 (dd, *J* = 10.4, 0.9 Hz, 1H), 5.70 – 5.48 (m, 1H), 5.18 – 5.03 (m, 2H), 4.02 (dd, *J* = 9.0, 7.2 Hz, 1H),

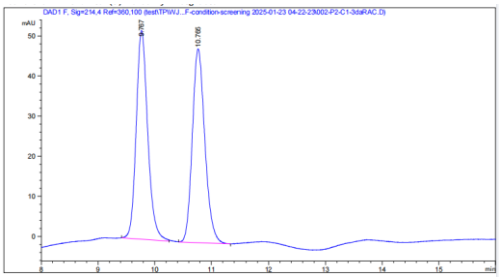
3.58 (dd, *J* = 9.0, 6.1 Hz, 1H), 3.16 – 3.00 (m, 1H), 2.69 – 2.46 (m, 3H), 1.89 – 1.67 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H).

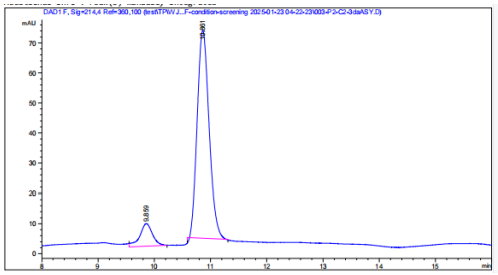
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.8, 151.8, 135.8, 130.2, 118.7, 81.2, 71.0, 48.1, 43.8, 36.0, 31.9, 8.3.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{12}H_{17}O_2^{\oplus}$ 193.1223, found 193.1224.

Specific Rotation: $[\alpha]_D^{20.6}$ +2.9 (*c* 0.5, $CHCl_3$) for 90:10 er.

Chiral HPLC analysis: Chiralpak AD-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol =90/10; flow rate = 0.5 mL/min; Retention time: 9.9 min (minor), 10.9 min (major).





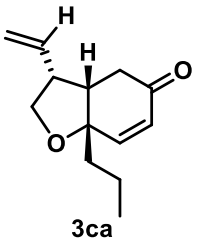
Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.767	MF R	0.2353	735.02222	52.05842	49.7514
2	10.765	BB	0.2278	742.36786	48.29585	50.2486
Totals :				1477.39008	100.35427	

Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.859	MM R	0.2605	117.29287	7.50293	10.3675
2	10.861	MM R	0.2449	1014.05914	69.01598	89.6325
Totals :				1131.35201	76.51891	

(3*R*,3a*S*,7a*S*)-7a-Propyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3ca)



3ca

R_f = 0.30 (PE/EA = 1/1), colorless oil (22.9 mg, 71% yield).

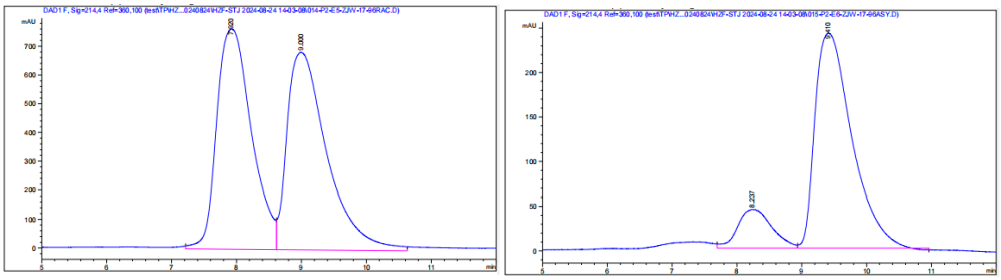
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.63 (dd, *J* = 10.2, 1.4 Hz, 1H), 6.02 (d, *J* = 10.3 Hz, 1H), 5.64 – 5.46 (m, 1H), 5.10 – 4.99 (m, 2H), 4.02 (dd, *J* = 9.4, 6.8 Hz, 1H), 3.56 (dd, *J* = 9.0, 6.1 Hz, 1H), 3.05 (m, 1H), 2.69 – 2.45 (m, 3H), 1.82 – 1.65 (m, 2H), 1.50 – 1.40 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.8, 152.1, 135.8, 130.0, 118.7, 80.9, 71.0, 48.0, 44.4, 41.5, 35.9, 17.3, 14.6.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{13}H_{19}O_2^{\oplus}$ 207.1380, found 207.1382.

Specific Rotation: $[\alpha]_D^{20.7}$ +17.6 (*c* 0.9, $CHCl_3$) for 86:14 er.

Chiral HPLC analysis: Chiralpak AD-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol = 97/3; flow rate = 0.5 mL/min; Retention time: 8.2 min (minor), 9.4 min (major).



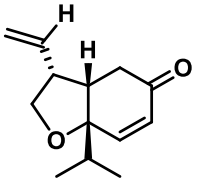
Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.920	MF R	0.6187	2.83655e4	764.16284	49.2908
2	9.000	FM R	0.7101	2.91817e4	684.93536	50.7092
Totals :				5.75472e4	1449.09821	

Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.237	MF R	0.6097	1581.54370	43.23181	14.2740
2	9.410	FM R	0.6561	9498.34082	241.26616	85.7260
Totals :				1.10799e4	284.49797	

(3*R*,3a*S*,7a*S*)-7a-Isopropyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3da)



3da

R_f = 0.30 (PE/EA = 1/1), colorless oil (15.0 mg, 73% yield).

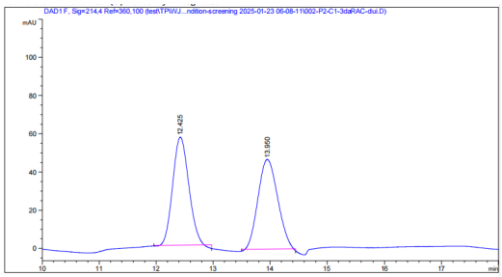
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 6.60 (dd, *J* = 10.5, 1.4 Hz, 1H), 6.10 (d, *J* = 10.4 Hz, 1H), 5.62 – 5.50 (m, 1H), 5.10 – 5.02 (m, 2H), 3.94 (dd, *J* = 8.9, 6.6 Hz, 1H), 3.56 (dd, *J* = 8.9, 5.6 Hz, 1H), 3.04 – 2.97 (m, 1H), 2.79 – 2.73 (m, 1H), 2.60 – 2.45 (m, 2H), 2.03 – 1.95 (m, 1H), 1.01 (dd, *J* = 6.9, 5.7 Hz, 6H).

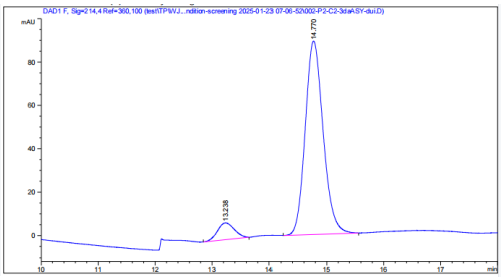
^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 198.1, 150.4, 135.7, 130.7, 118.6, 83.1, 70.7, 49.1, 41.6, 36.9, 36.6, 29.7, 17.7, 16.9.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{13}H_{19}O_2^{\oplus}$ 207.1380, found 207.1382.

Specific Rotation: $[\alpha]_D^{20.9}$ +10.4 (*c* 0.8, $CHCl_3$) for 93:7 er.

Chiral HPLC analysis: Chiralpak ID-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol = 97/3; flow rate = 0.5 mL/min; Retention time: 13.2 min (major), 14.8 min (minor).





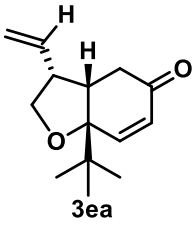
Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.425	MM R	0.3276	1110.78601	56.51940	49.7585
2	13.950	MM R	0.3987	1121.56653	46.88999	50.2415
Totals :				2232.35254	103.40939	

Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.238	BB	0.2496	157.87149	7.71793	7.4902
2	14.770	BB	0.3296	1949.82935	89.18498	92.5098
Totals :				2107.70084	96.90291	

(3*R*,3a*S*,7a*S*)-7a-(Tert-butyl)-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3ea)



3ea

R_f = 0.35 (PE/EA = 1/1), colorless oil (16.2 mg, 74% yield).

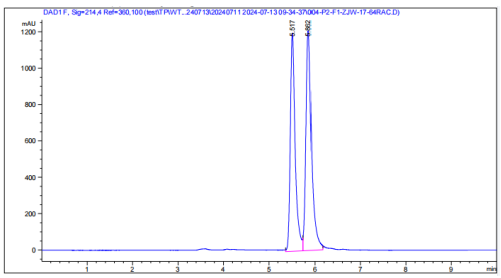
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.75 (dd, *J* = 10.6, 1.3 Hz, 1H), 6.10 (d, *J* = 10.6 Hz, 1H), 5.66 – 5.49 (m, 1H), 5.13 – 4.95 (m, 2H), 3.91 (dd, *J* = 8.8, 6.0 Hz, 1H), 3.56 (dd, *J* = 8.9, 4.2 Hz, 1H), 3.03 – 2.89 (m, 2H), 2.67 – 2.45 (m, 2H), 1.05 (s, 9H).

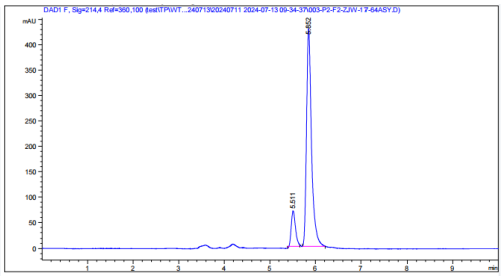
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.8, 150.5, 136.0, 130.5, 118.4, 84.6, 71.1, 49.6, 40.0, 38.5, 37.1, 25.4.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{14}H_{21}O_2^{\oplus}$ 221.1536, found 221.1538.

Specific Rotation: $[\alpha]_D^{21.0}$ +30.4 (*c* 0.5, $CHCl_3$) for 88:12 er.

Chiral HPLC analysis: Chiralpak OD-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.5 mL/min; Retention time: 5.5 min (minor), 5.9 min (major).





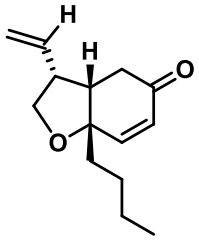
Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.517	MF R	0.1251	8992.52441	1197.63953	47.9516
2	5.862	FM R	0.1347	9760.79785	1207.59094	52.0484
Totals :				1.87533e4	2405.23047	

Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.511	MM R	0.1073	441.74792	68.59313	11.9835
2	5.852	MM R	0.1265	3244.55713	427.60492	88.0165
Totals :				3686.30505	496.19805	

(3*R*,3a*S*,7a*S*)-7a-Butyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3fa)



3fa

R_f = 0.35 (PE/EA = 1/1), colorless oil (17.6 mg, 80% yield).

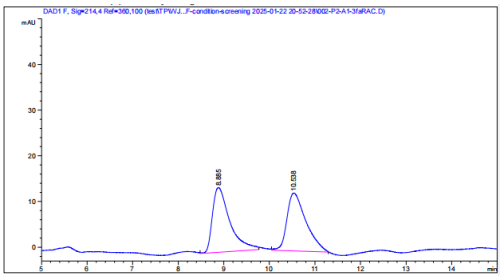
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.63 (dd, *J* = 10.4, 1.2 Hz, 1H), 6.02 (d, *J* = 10.4 Hz, 1H), 5.62 – 5.47 (m, 1H), 5.16 – 4.97 (m, 2H), 4.02 (dd, *J* = 9.1, 7.2 Hz, 1H), 3.56 (dd, *J* = 9.1, 6.2 Hz, 1H), 3.12 – 3.01 (m, 1H), 2.78 – 2.43 (m, 3H), 1.91 – 1.64 (m, 2H), 1.44 – 1.32 (m, 4H), 0.91 (t, *J* = 6.9 Hz, 3H).

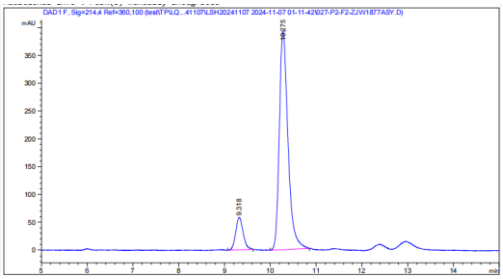
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.8, 152.1, 135.8, 130.0, 118.7, 80.9, 71.0, 48.0, 44.4, 39.0, 36.0, 26.1, 23.2, 13.9.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{14}H_{21}O_2^{\oplus}$ 221.1536, found 221.1539.

Specific Rotation: $[\alpha]_D^{21.3}$ +14.3 (*c* 1.1, $CHCl_3$) for 89:11 er.

Chiral HPLC analysis: Chiralpak IA-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.5 mL/min; Retention time: 9.3 min (minor), 10.3 min (major).





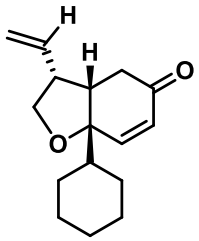
Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.885	MM R	0.4425	375.31830	14.13784	50.4494
2	10.538	MM R	0.4849	368.63181	12.66942	49.5506
Totals :				743.95010	26.80726	

Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.318	VV R	0.1402	654.27698	57.97693	11.1950
2	10.275	BV R	0.1801	5190.11475	394.25684	88.8050
Totals :				5844.39172	452.23376	

(3*R*,3a*S*,7a*S*)-7a-Cyclohexyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3ga)



3ga

R_f = 0.30 (PE/EA = 1/1), yellow oil (20.0 mg, 81% yield).

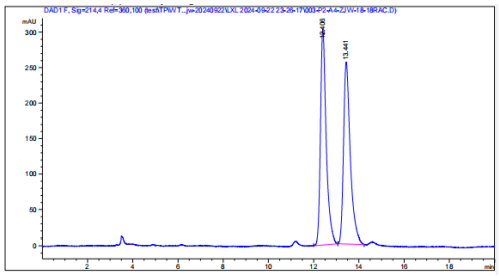
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.59 (dd, *J* = 10.5, 1.4 Hz, 1H), 6.07 (d, *J* = 10.4 Hz, 1H), 5.64 – 5.48 (m, 1H), 5.11 – 5.01 (m, 2H), 3.92 (dd, *J* = 9.0, 6.4 Hz, 1H), 3.56 (dd, *J* = 8.9, 5.4 Hz, 1H), 3.03 – 2.92 (m, 1H), 2.83 – 2.73 (m, 1H), 2.62 – 2.44 (m, 2H), 1.96 – 1.76 (m, 4H), 1.66 (m, 2H), 1.30 – 1.04 (m, 5H).

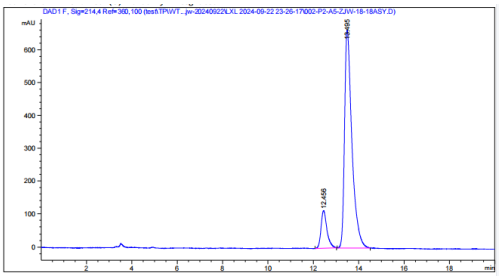
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.2, 151.0, 135.8, 130.3, 118.6, 82.8, 70.7, 49.1, 47.1, 41.7, 36.9, 27.9, 27.0, 26.5, 26.4, 26.3.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{16}H_{23}O_2^{\oplus}$ 247.1693, found 247.1695.

Specific Rotation: $[\alpha]_D^{21.8}$ +5.7 (*c* 0.7, $CHCl_3$) for 88:12 er.

Chiral HPLC analysis: Chiralpak IG-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.5 mL/min; Retention time: 12.5 min (minor), 13.5 min (major).





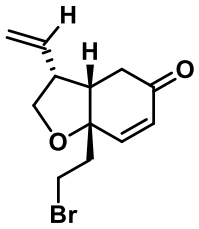
Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.406	VV R	0.2431	5317.40918	303.16962	50.1967
2	13.441	BV R	0.2522	5275.73730	255.14090	49.8033
Totals :				1.05931e4	558.31052	

Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.456	VV R	0.2197	2061.08887	112.78951	12.1849
2	13.495	VV R	0.2921	1.48540e4	662.55206	87.8151
Totals :				1.69151e4	775.34157	

(3*R*,3a*S*,7a*S*)-7a-(2-Bromoethyl)-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3ha)



3ha

R_f = 0.35 (PE/EA = 1/1), colorless oil (23.0 mg, 85% yield).

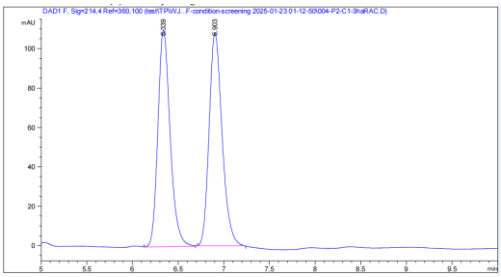
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.63 (dd, *J* = 10.4, 1.5 Hz, 1H), 6.06 (dd, *J* = 10.4, 0.8 Hz, 1H), 5.65 – 5.43 (m, 1H), 5.16 – 5.02 (m, 2H), 4.06 (dd, *J* = 9.1, 7.3 Hz, 1H), 3.59 (dd, *J* = 9.1, 6.0 Hz, 1H), 3.55 – 3.43 (m, 2H), 3.13 – 3.03 (m, 1H), 2.78 – 2.70 (m, 1H), 2.65 – 2.49 (m, 2H), 2.46 – 2.25 (m, 2H).

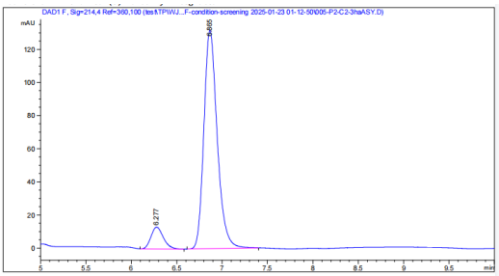
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 196.9, 150.1, 135.4, 130.6, 119.2, 80.5, 71.3, 47.6, 44.5, 42.3, 35.5, 26.3.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{12}H_{16}{}^{79}BrO_2{}^{\oplus}$ 271.0328, found 271.0326.

Specific Rotation: $[\alpha]_D^{21.9}$ +2.2 (*c* 0.2, $CHCl_3$) for 91.5:8.5 er.

Chiral HPLC analysis: Chiralpak OD-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol = 85/15; flow rate = 0.5 mL/min; Retention time: 6.3 min (minor), 6.9 min (major).





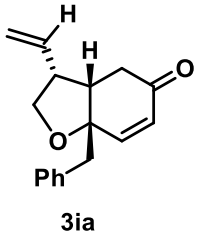
Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.339	MM R	0.1555	1027.78137	110.14160	49.1665
2	6.903	MM R	0.1642	1062.62830	107.84949	50.8335
Totals :				2090.40967	217.99110	

Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.277	BB	0.1393	124.89715	13.21199	8.5038
2	6.865	BB	0.1558	1343.82361	131.91660	91.4962
Totals :				1468.72076	145.12858	

(3*R*,3a*S*,7a*S*)-7a-Benzyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3ia)



3ia

R_f = 0.35 (PE/EA = 1/1), colorless oil (20.0 mg, 77% yield).

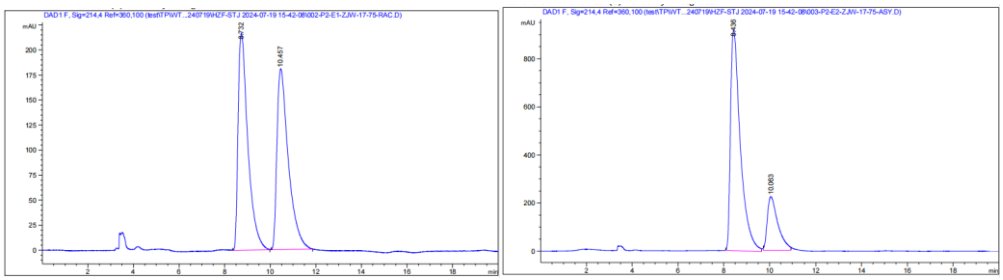
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.33 – 7.27 (m, 2H), 7.26 – 7.15 (m, 3H), 6.58 (dd, *J* = 10.4, 1.5 Hz, 1H), 6.00 (dd, *J* = 10.3, 0.9 Hz, 1H), 5.63 – 5.45 (m, 1H), 5.15 – 4.96 (m, 2H), 3.96 (dd, *J* = 9.0, 6.9 Hz, 1H), 3.57 (dd, *J* = 9.0, 5.5 Hz, 1H), 3.03 (d, *J* = 5.1 Hz, 2H), 3.00 – 2.92 (m, 1H), 2.73 – 2.64 (m, 1H), 2.58 – 2.38 (m, 1H), 2.15 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.6, 151.5, 135.9, 135.7, 130.3, 130.0, 128.3, 127.0, 118.7, 80.9, 71.0, 48.0, 45.2, 43.9, 35.7, 29.7.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{17}H_{19}O_2^{\oplus}$ 255.1380, found 255.1385.

Specific Rotation: $[\alpha]_D^{21.9}$ +1.4 (*c* 0.8, $CHCl_3$) for 79:21 er.

Chiral HPLC analysis: Chiralpak AD-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.5 mL/min; Retention time: 8.4 min (major), 10.1 min (minor).



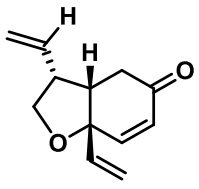
Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.732	VV R	0.3515	6458.43115	216.52341	50.6961
2	10.457	BV R	0.4151	6281.07861	180.43974	49.3039
Totals :				1.27395e4	396.96315	

Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.436	MM R	0.4997	2.74349e4	915.10620	79.2914
2	10.063	MM R	0.5360	7165.21484	222.77895	20.7086
Totals :				3.46002e4	1137.88515	

(3*R*,3a*S*,7a*S*)-3,7a-Divinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3ja)



3ja

R_f = 0.25 (PE/EA = 1/1), colorless oil (15.2 mg, 75% yield).

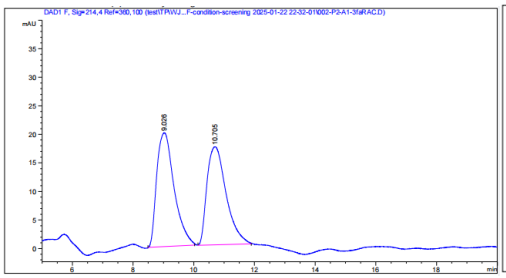
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.56 (d, *J* = 10.2 Hz, 1H), 6.10 (d, *J* = 10.3 Hz, 1H), 5.95 (m, 1H), 5.58 (m, 1H), 5.37 – 5.22 (m, 2H), 5.13 – 5.03 (m, 2H), 4.13 (dd, *J* = 9.0, 7.5 Hz, 1H), 3.70 (dd, *J* = 9.0, 6.3 Hz, 1H), 3.17 – 3.04 (m, 1H), 2.72 – 2.63 (m, 1H), 2.61 – 2.44 (m, 2H).

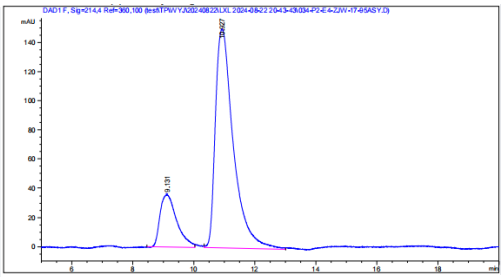
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.7, 149.2, 139.1, 135.4, 130.6, 118.9, 115.8, 81.3, 71.5, 47.1, 45.9, 35.0.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{12}H_{15}O_2^{\oplus}$ 191.1067, found 191.1065.

Specific Rotation: $[\alpha]_D^{21.5}$ −0.4 (*c* 0.2, $CHCl_3$) for 82:18 er.

Chiral HPLC analysis: Chiralpak AD-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol = 97/3; flow rate = 0.5 mL/min; Retention time: 9.1 min (minor), 10.9 min (major).





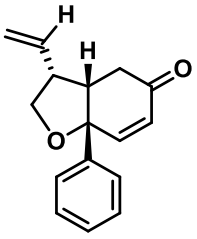
Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.026	MM R	0.6634	793.68445	19.93878	51.2687
2	10.705	MM R	0.7317	754.40363	17.18324	48.7313
Totals :				1548.08807	37.12202	

Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.131	MM R	0.6363	1367.46570	35.81712	18.2599
2	10.927	MM R	0.6799	6121.41992	150.06665	81.7401
Totals :				7488.88562	185.88377	

(3*R*,3a*S*,7a*S*)-7a-Phenyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3ka)



3ka

R_f = 0.35 (PE/EA = 1/1), colorless oil (24.0 mg, 83% yield).

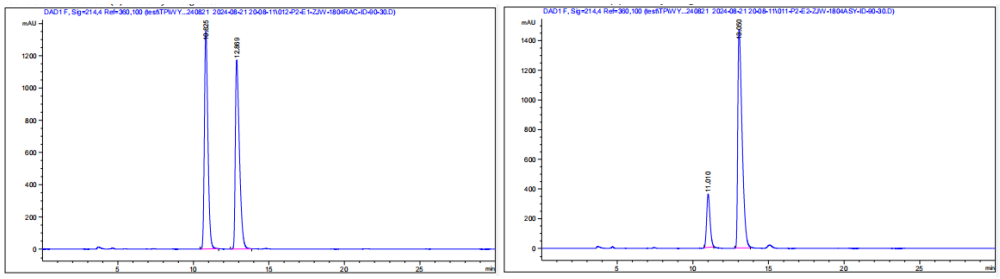
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.45 – 7.35 (m, 4H), 7.34 – 7.29 (m, 1H), 6.64 (dd, *J* = 10.1, 1.2 Hz, 1H), 6.18 (dd, *J* = 10.1, 1.5 Hz, 1H), 5.81 – 5.54 (m, 1H), 5.14 – 5.06 (m, 2H), 4.37 – 4.20 (m, 1H), 4.00 – 3.85 (m, 1H), 3.22 – 3.08 (m, 1H), 2.93 – 2.80 (m, 1H), 2.64 – 2.55 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.0, 149.4, 142.9, 134.8, 129.7, 128.7, 127.8, 124.9, 118.9, 82.6, 71.7, 48.7, 47.3, 35.4.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{16}H_{17}O_2^{\oplus}$ 241.1223, found 241.1226.

Specific Rotation: $[\alpha]_D^{22.1}$ +0.2 (*c* 0.7, $CHCl_3$) for 84:16 er.

Chiral HPLC analysis: Chiralpak ID-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.5 mL/min; Retention time: 11.0 min (minor), 13.1 min (major).



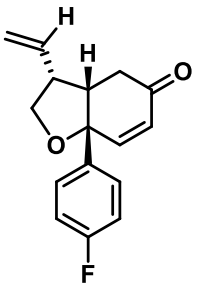
Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.825	VV R	0.1966	2.19185e4	1355.72070	49.8264
2	12.869	VV R	0.2518	2.20712e4	1171.72754	50.1736
Totals :				4.39897e4	2527.44824	

Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.010	MM R	0.2590	5577.51025	358.93594	16.0966
2	13.050	MM R	0.3294	2.90728e4	1470.97388	83.9034
Totals :				3.46503e4	1829.90982	

(3*R*,3*aS*,7a*S*)-7a-(4-Fluorophenyl)-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3la)



3la

R_f = 0.35 (PE/EA = 1/1), yellow oil (20.0 mg, 77% yield).

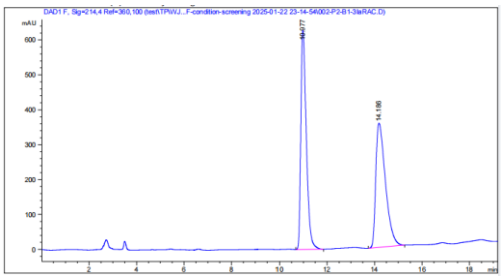
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.07 (t, *J* = 8.7 Hz, 2H), 6.62 (dd, *J* = 10.3, 1.0 Hz, 1H), 6.18 (d, *J* = 10.2 Hz, 1H), 5.79 – 5.54 (m, 1H), 5.15 – 5.05 (m, 2H), 4.29 (dd, *J* = 8.9, 7.5 Hz, 1H), 3.90 (dd, *J* = 8.9, 6.8 Hz, 1H), 3.12 (t, *J* = 8.0 Hz, 1H), 2.86 – 2.76 (m, 1H), 2.66 – 2.50 (m, 2H).

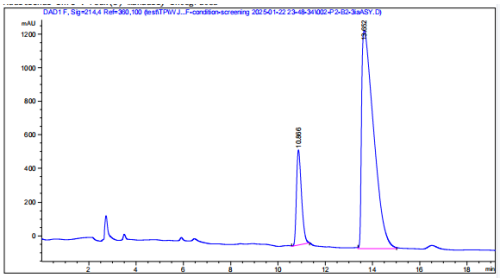
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.7, 163.6, 161.1, 149.2, 138.6, 138.6, 134.7, 129.9, 126.8, 126.7, 119.1, 115.7, 115.5, 82.3, 71.7, 48.8, 47.2, 35.3.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{16}H_{16}FO_2^{\oplus}$ 259.1129, found 259.1132.

Specific Rotation: $[\alpha]_D^{22.0}$ −46.3 (*c* 1.1, $CHCl_3$) for 85:15.

Chiral HPLC analysis: Chiralpak ID-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.7 mL/min; Retention time: 10.9 min (minor), 13.7 min (major).





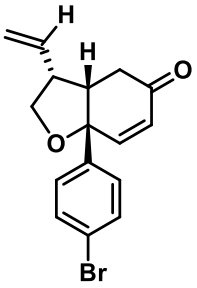
Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.977	BB	0.2426	1.00713e4	628.10815	50.0580
2	14.186	BB	0.4141	1.00479e4	356.20514	49.9420
Totals :				2.01192e4	984.31329	

Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.866	MM R	0.2463	8319.21094	562.98615	15.3011
2	13.652	MM R	0.5916	4.60506e4	1297.40320	84.6989
Totals :				5.43699e4	1860.38934	

(3*R*,3a*S*,7a*S*)-7a-(4-Bromophenyl)-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3ma)



3ma

R_f = 0.35 (PE/EA = 1/1), yellow oil (28.4 mg, 89% yield).

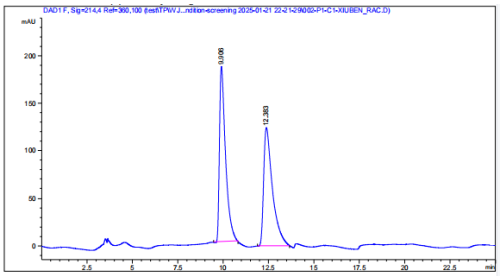
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.51 (d, *J* = 8.6 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 6.60 (dd, *J* = 10.2, 1.0 Hz, 1H), 6.19 (d, *J* = 10.2 Hz, 1H), 5.63 (dd, *J* = 17.5, 9.8 Hz, 1H), 5.15 – 5.06 (m, 2H), 4.28 (dd, *J* = 8.9, 7.5 Hz, 1H), 3.91 (dd, *J* = 8.9, 6.8 Hz, 1H), 3.18 – 3.06 (m, 1H), 2.85 – 2.78 (m, 1H), 2.65 – 2.47 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.6, 148.8, 142.0, 134.6, 131.8, 130.1, 126.8, 122.0, 119.2, 82.3, 71.8, 48.8, 47.2, 35.3.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{16}H_{16}{}^{79}BrO_2{}^{\oplus}$ 319.0328, found 319.0325.

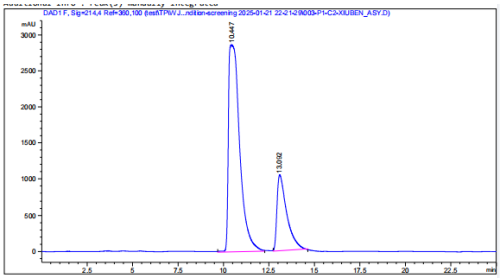
Specific Rotation: $[\alpha]_D^{21.9}$ −52.5 (*c* 0.4, $CHCl_3$) for 76:24 er.

Chiral HPLC analysis: Chiralpak AD-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.5 mL/min; Retention time: 10.4 min (major), 13.1 min (minor).



Signal 1: DAD1 F, Sig=214,4 Ref=360,100

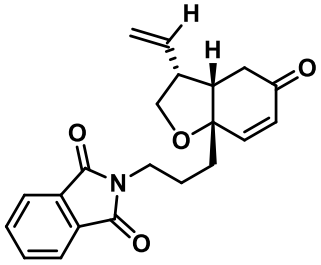
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.906	MM R	0.3871	4271.68994	183.91985	50.5691
2	12.383	MM R	0.5617	4175.55176	123.89445	49.4309
Totals :				8447.24170	307.81430	



Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.447	MM R	0.7158	1.23410e5	2873.39429	75.9351
2	13.092	MM R	0.6254	3.91105e4	1042.22058	24.0649
Totals :				1.62520e5	3915.61487	

2-(3-((3*R*,3a*S*,7a*S*)-5-Oxo-3-vinyl-3,3a,4,5-tetrahydrobenzofuran-7a(2*H*)-yl)propyl)isoindoline-1,3-dione (3na)



3na

R_f = 0.25 (PE/EA = 1/1), yellow oil (18.0 mg, 65% yield).

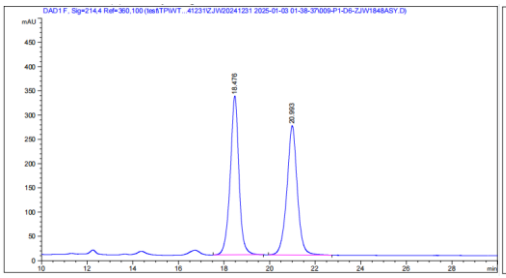
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.85 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.62 (d, *J* = 10.3 Hz, 1H), 6.01 (d, *J* = 10.3 Hz, 1H), 5.62 – 5.40 (m, 1H), 5.12 – 4.97 (m, 2H), 4.00 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.74 (t, *J* = 6.6 Hz, 2H), 3.55 (dd, *J* = 9.1, 6.0 Hz, 1H), 3.14 – 2.97 (m, 1H), 2.74 – 2.62 (m, 1H), 2.61 – 2.40 (m, 2H), 1.89 – 1.72 (m, 4H).

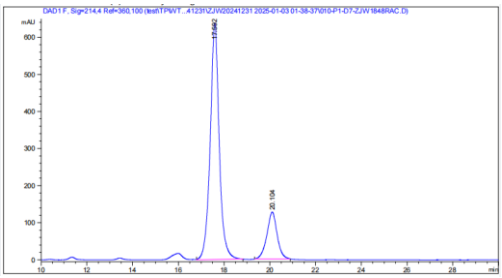
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.4, 168.4, 151.3, 135.6, 134.0, 132.1, 130.3, 123.3, 118.8, 80.4, 71.1, 47.9, 44.4, 38.0, 36.2, 35.8, 23.3.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{21}H_{22}NO_4^{\oplus}$ 352.1543, found 352.1547.

Specific Rotation: $[\alpha]_D^{22.1}$ +0.3 (*c* 0.7, $CHCl_3$) for 82:18 er.

Chiral HPLC analysis: Chiralpak IA-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol = 80/20; flow rate = 0.5 mL/min; Retention time: 17.6 min (major), 20.1 min (minor).





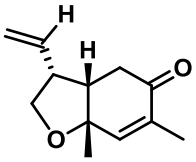
Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.476	BB	0.3934	8711.47363	327.41434	50.7441
2	20.993	BB	0.4482	8456.00098	266.49042	49.2559
Totals :				1.71675e4	593.90475	

Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.592	MM R	0.4561	1.74508e4	637.68585	81.6214
2	20.104	MM R	0.5181	3929.38086	126.40710	18.3786
Totals :				2.13802e4	764.09295	

(3*R*,3a*S*,7a*R*)-6,7a-Dimethyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (3oa)



3oa

R_f = 0.25 (PE/EA = 1/1), yellow oil (7.7 mg, 40% yield).

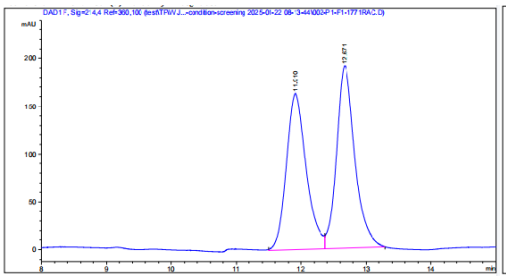
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.38 (s, 1H), 5.60 – 5.40 (m, 1H), 5.20 – 5.00 (m, 2H), 4.06 (dd, *J* = 9.1, 7.7 Hz, 1H), 3.55 (dd, *J* = 9.1, 6.9 Hz, 1H), 3.12 (t, *J* = 8.2 Hz, 1H), 2.66 – 2.42 (m, 3H), 1.77 (s, 3H), 1.44 (s, 3H).

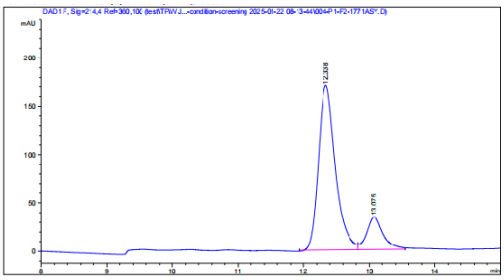
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.0, 147.7, 136.0, 135.8, 118.5, 79.4, 70.9, 47.5, 46.6, 35.9, 25.5, 15.7.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{12}H_{17}O_2^{\oplus}$ 193.1223, found 193.1225.

Specific Rotation: $[\alpha]_D^{22.2}$ +0.8 (*c* 0.4, $CHCl_3$) for 84:16 er.

Chiral HPLC analysis: Chiralpak IG-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol = 97/3; flow rate = 0.5 mL/min; Retention time: 12.3 min (major),13.1 min (minor).





Signal 1: DAD1 F, Sig=214,4 Ref=360,100

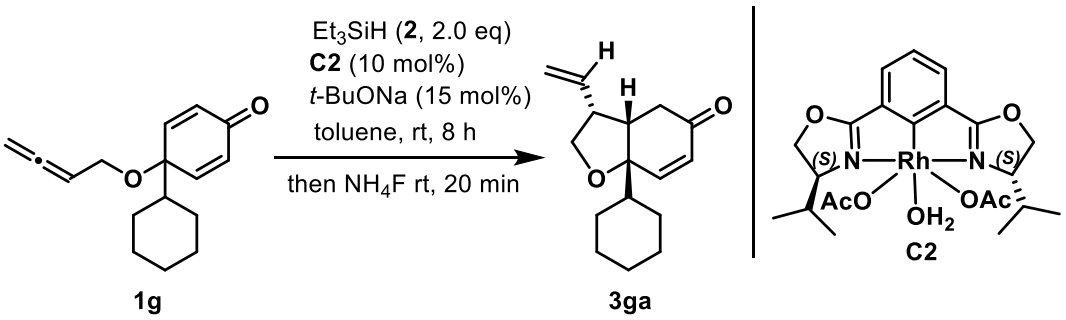
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.910	MF R	0.3570	3565.31665	163.62910	48.4506
2	12.671	FM R	0.3260	3729.50562	190.67442	51.5494
Totals :				7234.82227	354.30353	

Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.338	MF R	0.2970	3029.50146	170.00897	83.7070
2	13.075	FM R	0.2910	589.67126	33.77160	16.2930
Totals :				3619.17273	203.78057	

4. Subgram-Scale Reaction and Product Transformation

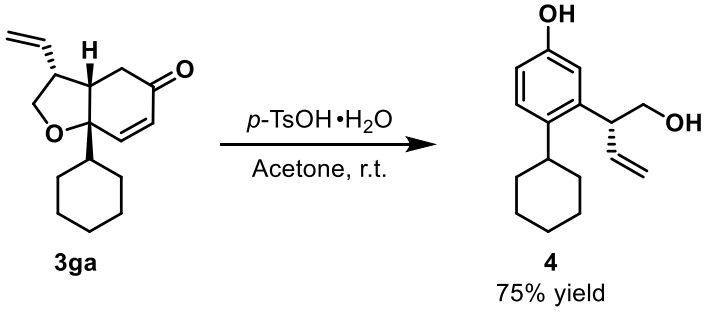
4.1 Subgram-Scale Reaction



Standard condition: under nitrogen, [Rh(Phebox-*i*-Pr)] (0.4 mmol, 220.4 mg), *t*-BuONa (0.6 mmol, 58.9 mg), substrate **1g** (4.1 mmol, 1.0 g), and 20.0 mL of toluene were added to a 50-mL Schlenk tube. The reaction was stirred at room temperature, after which Et_3SiH (**2**, 8.2 mmol, 952.1 mg,) was added in two portions. After 8 hours, A solution of NH_4F in MeOH (0.2 M, 20.0 mL) was then added, and the reaction was stirred for 20 min. Finally, the reaction mixture was filtered, washed with EtOAc (50 mL × 3) and concentrated in vacuo. The residue was purified by flash silica gel chromatography to afford desired products **3ga**. The residue was purified by silica gel flash column chromatography to afford the product **3ga** as a colorless oil (eluent: PE/EA = 1/1, 709 mg, 70% yield, 71% ee).

4.2 Product Transformation

(*R*)-4-Cyclohexyl-3-(1-hydroxybut-3-en-2-yl)phenol (4)



To a solution of **3ga** (10.0 mg, 0.04 mmol, 1.0 equiv) in acetone (1.0 mL), *p*-TsOH·H_2O (14 mg, 0.08 mmol, 2.0 equiv) was added, and the resulting mixture was stirred at room temperature for 1 h. the reaction mixture was evaporated under reduced pressure and purified by flash column chromatography (PE/EA = 1/1) to afford **4**.

R_f = 0.20 (PE/EA = 1/1), colorless oil (7.6 mg, 75% yield).

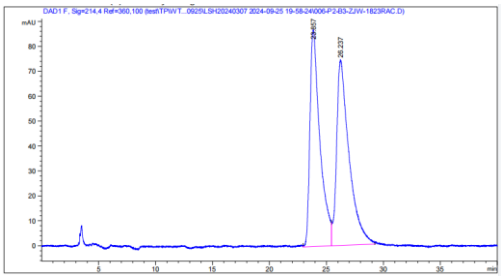
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.14 (d, *J* = 8.9 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 2H), 6.03 – 5.85 (m, 1H), 5.27 – 5.11 (m, 2H), 4.94 (br, 1H), 3.93 – 3.77 (m, 3H), 2.73 (t, *J* = 11.4 Hz, 1H), 1.91 – 1.71 (m, 5H), 1.51 – 1.22 (m, 6H).

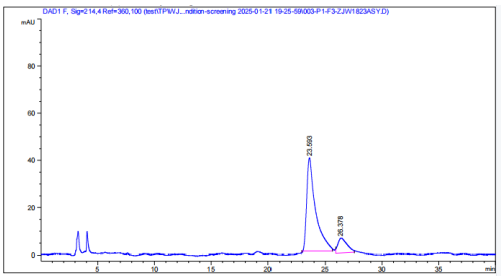
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 153.5, 138.8, 138.7, 138.6, 127.6, 117.0, 113.8, 113.6, 65.8, 46.7, 38.7, 34.9, 34.4, 27.1, 27.1, 26.2.

HRMS (ESI-TOF): $[M+NH_4]^{\oplus}$ calcd for $C_{16}H_{26}NO_2^{\oplus}$ 264.1958, found 264.1959.

Specific Rotation: $[\alpha]_D^{22.3}$ −30.5 (*c* 0.6, $CHCl_3$) for 86:14 er.

Chiral HPLC analysis: Chiralpak AD-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol = 90/10; flow rate = 0.5 mL/min; Retention time: 23.6 min (major), 26.4 min (minor).





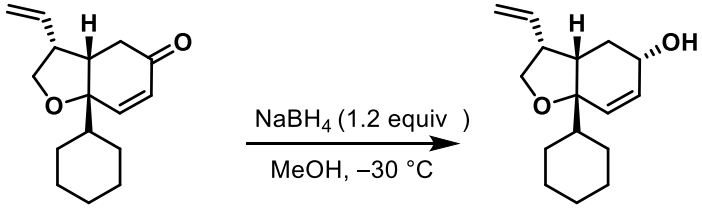
Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.857	MF R	1.0167	5309.31104	87.03562	48.3677
2	26.237	FM R	1.2668	5667.67529	74.56694	51.6323
Totals :				1.09770e4	161.60256	

Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.593	MM R	0.9037	2140.93726	39.48260	85.8301
2	26.378	MM R	0.9301	353.45264	6.33332	14.1699
Totals :				2494.38989	45.81593	

(3*R*,3a*S*,7a*S*)-7a-Cyclohexyl-3-vinyl-2,3,3a,7a-tetrahydrobenzofuran-5(4*H*)-one (5)



3ga **5** 45% yield

A solution of **3ga** (0.10 mmol, 24.6 mg) in 1.0 mL of MeOH was cooled to −30 ℃. After the addition of $NaBH_4$ (0.12 mmol, 3.4 mg), the reaction was stirred for 5 hours.

The reaction was then quenched with H_2O, and the mixture was extracted with DCM. The organic layer was concentrated under reduced pressure, and product **5** was obtained by column chromatography.

R_f = 0.20 (PE/EA = 1/1), colorless oil (11.1 mg, 45% yield).

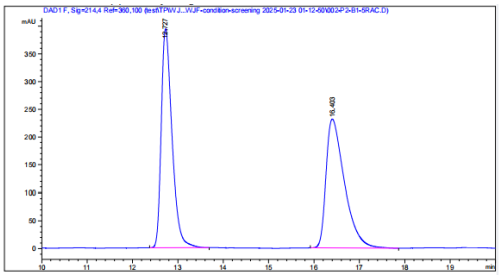
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.92 (d, *J* = 10.2 Hz, 1H), 5.85 – 5.70 (m, 1H), 5.61 (dd, *J* = 10.2, 2.3 Hz, 1H), 5.20 – 5.06 (m, 2H), 4.04 (d, *J* = 10.1 Hz, 1H), 3.89 (t, *J* = 7.9 Hz, 1H), 3.67 (dd, *J* = 10.8, 8.4 Hz, 1H), 3.27 – 3.03 (m, 1H), 2.41 – 2.23 (m, 1H), 1.95 – 1.86 (m, 2H), 1.81 – 1.61 (m, 4H), 1.38 (t, *J* = 12.0 Hz, 1H), 1.29 (d, *J* = 4.8 Hz, 1H), 1.24 – 1.03 (m, 4H), 1.00 – 0.84 (m, 2H).

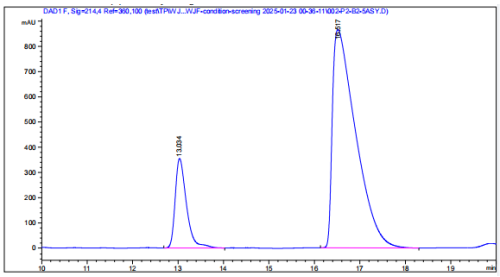
^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 135.1, 134.5, 129.5, 117.4, 84.6, 69.0, 67.0, 47.2, 47.0, 40.7, 32.6, 28.7, 27.1, 26.6, 26.6.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{16}H_{25}O_2^{\oplus}$ 249.1849, found 249.1849.

Specific Rotation: $[\alpha]_D^{22.3}$ +0.5 (*c* 0.7, $CHCl_3$) for 83:17 er.

Chiral HPLC analysis: Chiralpak ID-3 Column; detected at 214 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.6 mL/min; Retention time: 13.0 min (minor), 16.5 min (major).





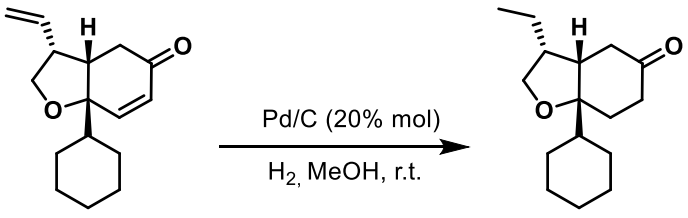
Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.727	BB	0.2512	6485.20654	393.62753	49.9270
2	16.403	BB	0.4127	6504.17334	231.22125	50.0730
Totals :				1.29894e4	624.84879	

Signal 1: DAD1 F, Sig=214,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.034	BB	0.2592	6094.57520	355.17703	16.5145
2	16.517	BB	0.4958	3.08098e4	865.51379	83.4855
Totals :				3.69044e4	1220.69083	

(3*R*,3a*S*,7a*R*)-7a-Cyclohexyl-3-ethylhexahydrobenzofuran-5(4*H*)-one (6)



3ga **6**

64% yield

Compound **3ga** (0.1 mmol, 24.6 mg) was dissolved in MeOH, and 20% mol Pd/C (0.02 mmol, 2.1 mg) was added. The mixture was then stirred at room temperature for 5 hours, filtered, and evaporated. The product **6** was obtained by column chromatography.

R_f = 0.30 (PE/EA = 1/1), colorless oil (16.0 mg, 64% yield).

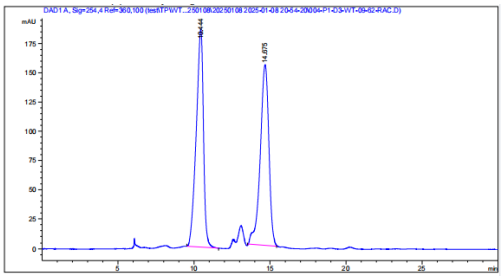
^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 3.97 (t, *J* = 8.2 Hz, 1H), 3.31 (dd, *J* = 10.4, 8.6 Hz, 1H), 2.58 – 2.50 (m, 1H), 2.47 – 2.37 (m, 2H), 2.36 – 2.26 (m, 2H), 2.24 – 2.18 (m, 1H), 2.07 (dd, *J* = 14.4, 10.5 Hz, 1H), 1.99 – 1.93 (m, 1H), 1.88 (d, *J* = 16.3 Hz, 1H), 1.85 – 1.76 (m, 3H), 1.74 – 1.67 (m, 2H), 1.48 – 1.35 (m, 2H), 1.31 – 1.26 (m, 1H), 1.21 (t, *J* = 6.4 Hz, 1H), 1.16 – 1.12 (m, 1H), 1.11 – 1.01 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 214.5, 86.7, 71.9, 46.8, 44.9, 41.8, 39.0, 35.1, 28.8, 28.1, 27.0, 26.9, 26.6, 26.6, 20.7, 13.0.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{16}H_{27}O_2^{\oplus}$ 251.2006, found 251.2006.

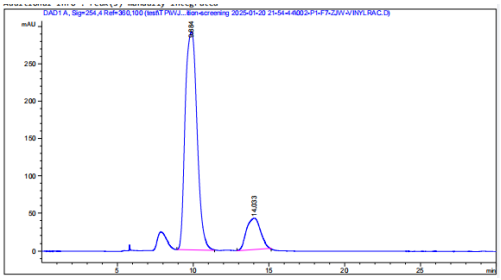
Specific Rotation: $[\alpha]_D^{22.3}$ +28.2 (*c* 0.7, $CHCl_3$). for 86:14 er.

Chiral HPLC analysis: Chiralpak OD-3 Column; detected at 254 nm; *n*-hexane/*i*-propanol = 95/5; flow rate = 0.5 mL/min; Retention time: 9.9 min (major), 14.0 min (minor).



Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.444	BB	0.4722	6108.38916	185.70737	50.4170
2	14.675	MM R	0.6510	6007.34521	153.80923	49.5830
Totals :				1.21157e4	339.51660	

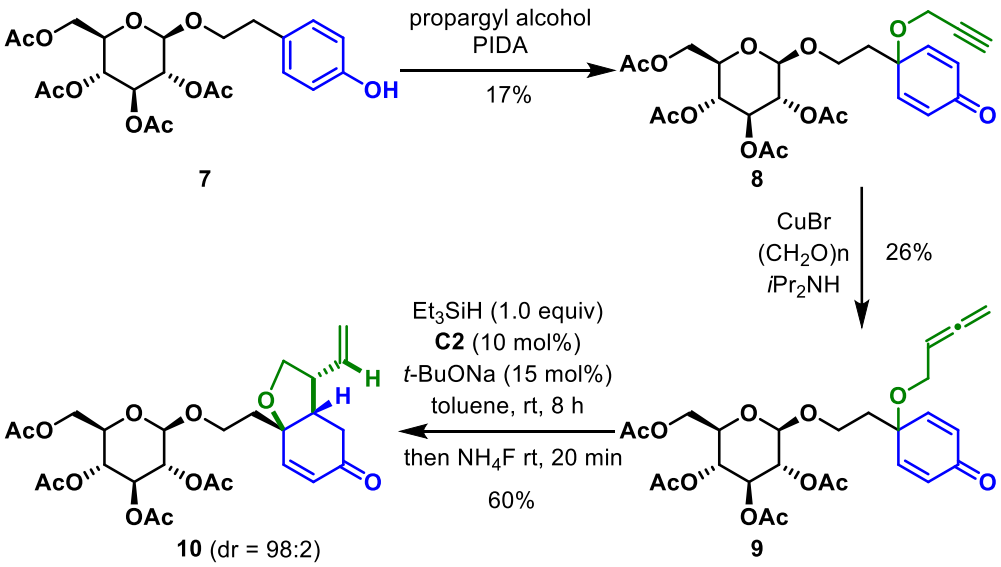


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.884	MF R	0.9030	1.57682e4	291.02060	85.8560
2	14.033	MM R	1.0608	2597.67700	40.81280	14.1440
Totals :				1.83659e4	331.83340	

5 Asymmetric Dearomatization Modification of 10, 14 and 15

5.1 Asymmetric Dearomatization Modification of 10



(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(Acetoxymethyl)-6-(2-(4-oxo-1-(prop-2-yn-1-yloxy)cyclohexa-2,5-dien-1-yl)ethoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (8)[1]

Salidroside tetraacetate **7** (1.5 mmol, 1.0 equiv) was dissolved in 1 mL of DCM. Subsequently, 0.8 mL of propargyl alcohol (10 equiv) was added to the solution. The mixture was cooled to 0 °C and treated with phenyliodine (III) diacetate (PIDA; 722 mg, 1.5 equiv), introduced in portions. The reaction mixture was then allowed to warm to room temperature and stirred for 15 hours. After completion of the reaction, water (10 mL) was added to dilute the mixture, followed by extraction with DCM (10 mL×3). The combined organic extracts were washed with brine (10 mL), dried over anhydrous sodium sulfate (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford product **8**.

R_f = 0.20 (PE/EA = 1/1), colorless oil (136.0 mg, 17% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.95 – 6.70 (m, 2H), 6.53 – 6.26 (m, 2H), 5.16 (t, *J* = 9.5 Hz, 1H), 5.06 (t, *J* = 9.6 Hz, 1H), 4.94 (dd, *J* = 9.6, 8.0 Hz, 1H), 4.44 (d, *J* = 7.9 Hz, 1H), 4.23 (dd, *J* = 12.3, 4.7 Hz, 1H), 4.14 – 4.09 (m, 1H), 4.03 – 3.88 (m, 3H), 3.70 – 3.53 (m, 2H), 2.45 (t, *J* = 2.5 Hz, 1H), 2.09 – 1.95 (m, 14H).

(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(Acetoxymethyl)-6-(2-((3*R*,3a*S*,7a*S*)-5-oxo-3-vinyl-3,3a,4,5-tetrahydrobenzofuran-7a(2*H*)-yl)ethoxy)tetrahydro-2*H*-pyran-3,4,5-triyl-triacetate (9)[1]

To a well-stirred solution of **8** (0.3 mmol, 1.0 equiv) in dioxane (2 mL) was added paraformaldehyde (45 mg, 1.5 mmol, 5.0 equiv), CuBr (21.5 mg, 0.15 mmol, 0.5 equiv) and diisopropylamine (84 ul, 0.6 mmol, 2.0 equiv) under argon atmosphere. The resulting mixture was stirred at 110 ℃ for 30min. After cooled to room temperature, the reaction mixture was filtered and washed with DCM (10 mL ×3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography.

R_f = 0.20 (PE/EA = 1/1), yellow oil (40.0 mg, 26% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.84 – 6.75 (m, 2H), 6.31 (dd, *J* = 10.3, 4.5 Hz, 2H), 5.17 (t, *J* = 8.3 Hz, 2H), 5.07 (t, *J* = 9.6 Hz, 1H), 4.95 (dd, *J* = 9.5, 7.9 Hz, 1H), 4.77 (d, *J* = 6.7 Hz, 2H), 4.44 (d, *J* = 7.9 Hz, 1H), 4.24 (dd, *J* = 12.3, 4.8 Hz, 1H), 4.12 (dd, *J* = 12.3, 2.5 Hz, 1H), 3.97 – 3.91 (m, 1H), 3.86 (d, *J* = 7.0 Hz, 2H), 3.70 – 3.64 (m, 1H), 3.62 – 3.55 (m, 1H), 2.08 (s, 3H), 2.05 – 1.98 (m, 11H).

(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(Acetoxymethyl)-6-(2-((3*R*,3a*S*,7a*S*)-5-oxo-3-vinyl-3,3a,4,5-tetrahydrobenzofuran-7a(2*H*)-yl)ethoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (10)

The reaction was carried out in 0.01mmol accroding to standard condition to afford **10**.

R_f = 0.25 (PE/EA = 1/2), yellow oil (6.0 mg, 60% yield).

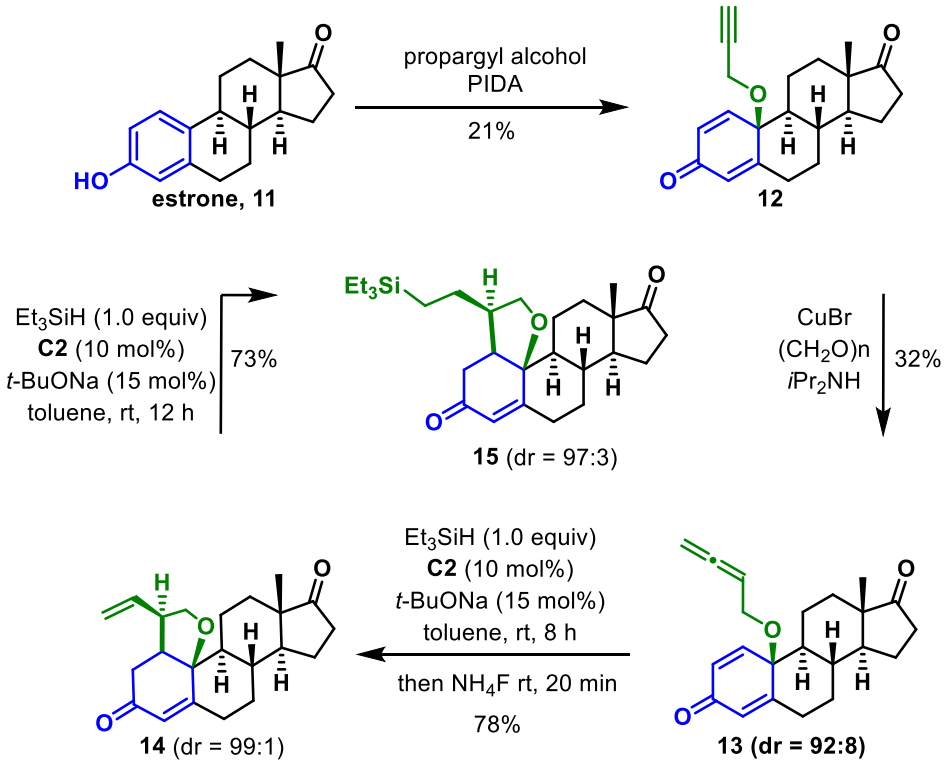
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.57 (d, *J* = 10.3 Hz, 1H), 6.00 (d, *J* = 10.4 Hz, 1H), 5.62 – 5.47 (m, 1H), 5.18 (d, *J* = 9.5 Hz, 1H), 5.12 – 5.03 (m, 3H), 4.97 (t, *J* = 8.8 Hz, 1H), 4.51 (d, *J* = 7.9 Hz, 1H), 4.30 – 4.21 (m, 1H), 4.18 – 4.13 (m, 1H), 4.09 – 3.99 (m, 2H), 3.73 – 3.64 (m, 2H), 3.56 (d, *J* = 9.0 Hz, 1H), 3.05 (d, *J* = 8.1 Hz, 1H), 2.79 (d, *J* = 4.9 Hz, 1H), 2.54 (s, 2H), 2.09 (s, 3H), 2.05 – 1.97 (m, 11H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.6, 170.6, 170.3, 169.4, 169.2, 151.2, 135.7, 130.1, 118.8, 100.6, 79.8, 72.8, 71.9, 71.3, 71.1, 68.4, 65.2, 61.9, 47.8, 44.4, 38.5, 35.50, 29.7, 29.3, 20.6.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{26}H_{35}O_{12}^{\oplus}$ 539.2123, found 539.2128.

Specific Rotation: $[\alpha]_D^{21.7}$ −0.6 (*c* 0.4, $CHCl_3$).

5.2 Asymmetric Dearomatization Modification of 14



(8*S*,9*S*,10*S*,13*S*,14*S*)-13-methyl-10-(prop-2-yn-1-yloxy)-7,8,9,10,11,12,13,14,15,16-decahydro-3*H*-cyclop enta[a]phenanthrene-3,17(6*H*)-dione (12)[1]

Estrone **13** (8.0 mmol, 1.0 equiv) was dissolved in 5 mL of DCM. Subsequently,4.7 mL of propargyl alcohol (10 equiv) was added to the solution. The mixture was cooled to 0 °C and treated with phenyliodine (III) diacetate (PIDA, 3.92 g, 1.5 equiv), introduced in portions. The reaction mixture was then allowed to warm to room temperature and stirred for 15 hours. After completion of the reaction, water (10 mL) was added to dilute the mixture, followed by extraction with DCM (30 mL×3). The combined organic extracts were washed with brine (30 mL), dried over anhydrous sodium sulfate (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by flash column chromatography to afford product **12**.

R_f = 0.25 (PE/EA = 2/1), colorless oil (540.0 mg, 21% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.05 (d, *J* = 10.3 Hz, 1H), 6.35 (dd, *J* = 10.4, 2.1 Hz, 1H), 6.19 (d, *J* = 2.0 Hz, 1H), 3.85 (d, *J* = 2.5 Hz, 2H), 2.68 – 2.55 (m, 1H), 2.47 – 2.32 (m, 3H), 2.23 – 2.02 (m, 4H), 1.97 – 1.91 (m, 1H), 1.84 (dd, *J* = 7.8, 5.3 Hz, 1H), 1.76 (dd, *J* = 13.7, 3.0 Hz, 1H), 1.69 – 1.60 (m, 1H), 1.24 – 1.12 (m, 4H), 0.97 (s, 3H).

(8*S*,9*S*,10*S*,13*S*,14*S*)-10-(buta-2,3-dien-1-yloxy)-13-methyl-7,8,9,10,11,12,13,-14,15,16-decahydro-3*H*-cyclopenta[a]phenanthrene-3,17(6*H*)-dione (13)[1]

To a well-stirred solution of **12** (1.1 mmol, 1.0 equiv) in dioxane (5 mL) was added paraformaldehyde (165 mg, 5.5 mmol, 5.0 equiv), CuBr (78.9 mg, 0.55 mmol, 0.5 equiv) and diisopropylamine (355 ul, 2.2 mmol, 2.0 equiv) under argon atmosphere. The resulting mixture was stirred at 110 ℃ for 30min. After cooled to room temperature, the reaction mixture was filtered and washed with DCM (30 mL ×3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography.

R_f = 0.35 (PE/EA = 2/1), yellow oil (116.0 mg, 32% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.03 (d, *J* = 10.3 Hz, 1H), 6.34 (dd, *J* = 10.3, 2.0 Hz, 1H), 6.18 (t, *J* = 1.8 Hz, 1H), 5.19 (d, *J* = 6.5 Hz, 1H), 4.78 (dd, *J* = 6.6, 2.8 Hz, 2H), 3.78 – 3.64 (m, 2H), 2.55 (dd, *J* = 5.3, 1.7 Hz, 1H), 2.51 – 2.43 (m, 1H), 2.41 – 2.35 (m, 1H), 2.25 – 2.18 (m, 1H), 2.13 – 2.05 (m, 3H), 1.97 – 1.92 (m, 1H), 1.88 – 1.82 (m, 1H), 1.75 (dd, *J* = 13.7, 2.6 Hz, 1H), 1.62 – 1.55 (m, 1H), 1.24 – 1.10 (m, 4H), 0.95 (s, 3H).

(3a*S*,5a*S*,5b*R*,8*R*,8a*S*,13a*S*,13b*S*)-3a-methyl-8-vinyl-1,2,3a,4,5,5a,7,8,8a,9,12,13,-13a,13b-tetradecahydrocyclopenta[7,8]phenanthro[4a,4-b]furan-3,10-dione (14)

The reaction was carried out in 0.1 mmol accroding to standard condition (Et_3SiH was used in 1.0 equiv) to afford **14**.

R_f = 0.25 (PE/EA = 1/1), yellow oil (26.6 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.88 (s, 1H), 5.62 – 5.46 (m, 1H), 5.13 – 4.96 (m, 2H), 4.00 (dd, *J* = 9.0, 7.2 Hz, 1H), 3.46 (dd, *J* = 9.0, 6.1 Hz, 1H), 3.07 – 3.00 (m, 1H), 2.97 – 2.87 (m, 1H), 2.80 – 2.71 (m, 1H), 2.56 (dd, *J* = 17.5, 2.4 Hz, 1H), 2.52 – 2.35 (m, 2H), 2.23 (d, *J* = 12.3 Hz, 1H), 2.15 – 2.02 (m, 3H), 1.98 – 1.93 (m, 1H), 1.88 (d, *J* = 13.2 Hz, 1H), 1.79 (d, *J* = 14.9 Hz, 1H), 1.73 – 1.66 (m, 1H), 1.43 – 1.27 (m, 4H), 1.18 – 1.09 (m, 1H), 0.95 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.3, 166.4, 136.2, 125.5, 118.7, 82.7, 70.9, 50.8, 50.4, 47.9, 47.9, 40.0, 36.6, 35.9, 35.8, 32.1, 32.1, 31.1, 21.8, 21.2, 13.9.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{22}H_{29}O_3^{\oplus}$ 341.2111, found 341.2115.

Specific Rotation: $[\alpha]_D^{22.3}$ +65.8 (*c* 0.4, $CHCl_3$).

(3a*S*,5a*S*,5b*R*,8*R*,8a*S*,13a*S*,13b*S*)-3a-methyl-8-(2-(triethylsilyl)ethyl)-1,2,3a,4,5,-5a,7,8,8a,9,12,13,13a,13b-tetradecahydrocyclopenta[7,8]phenanthro[4a,4-b]furan-3,10-dione (15)

The reaction was carried out in 0.1 mmol accroding to standard condition (Et_3SiH was used in 1.0 equiv) to afford **15**.

R_f = 0.25 (PE/EA = 4/1), yellow oil (33.3 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.85 (d, *J* = 1.4 Hz, 1H), 3.99 (dd, *J* = 8.8, 7.2 Hz, 1H), 3.30 (dd, *J* = 8.7, 7.5 Hz, 1H), 2.88 – 2.78 (m, 1H), 2.73 – 2.64 (m, 1H), 2.60 – 2.38 (m, 3H), 2.31 – 2.19 (m, 2H), 2.14 – 1.99 (m, 3H), 1.97 – 1.85 (m, 2H), 1.77 – 1.64 (m, 3H), 1.59 – 1.52 (m, 1H), 1.37 – 1.30 (m, 3H), 1.13 – 1.01 (m, 2H), 0.94 (s, 3H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.45 (q, *J* = 7.9 Hz, 6H), 0.41 – 0.31 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 220.5, 198.0, 166.2, 124.7, 83.0, 71.7, 51.0, 50.8, 47.8, 46.3, 39.3, 36.4, 36.1, 35.8, 32.2, 32.0, 31.1, 23.6, 21.8, 21.3, 13.9, 10.7, 7.4, 3.2.

HRMS (ESI-TOF): $[M+H]^{\oplus}$ calcd for $C_{28}H_{45}NO_3Si^{\oplus}$ 457.3132, found 457.3139.

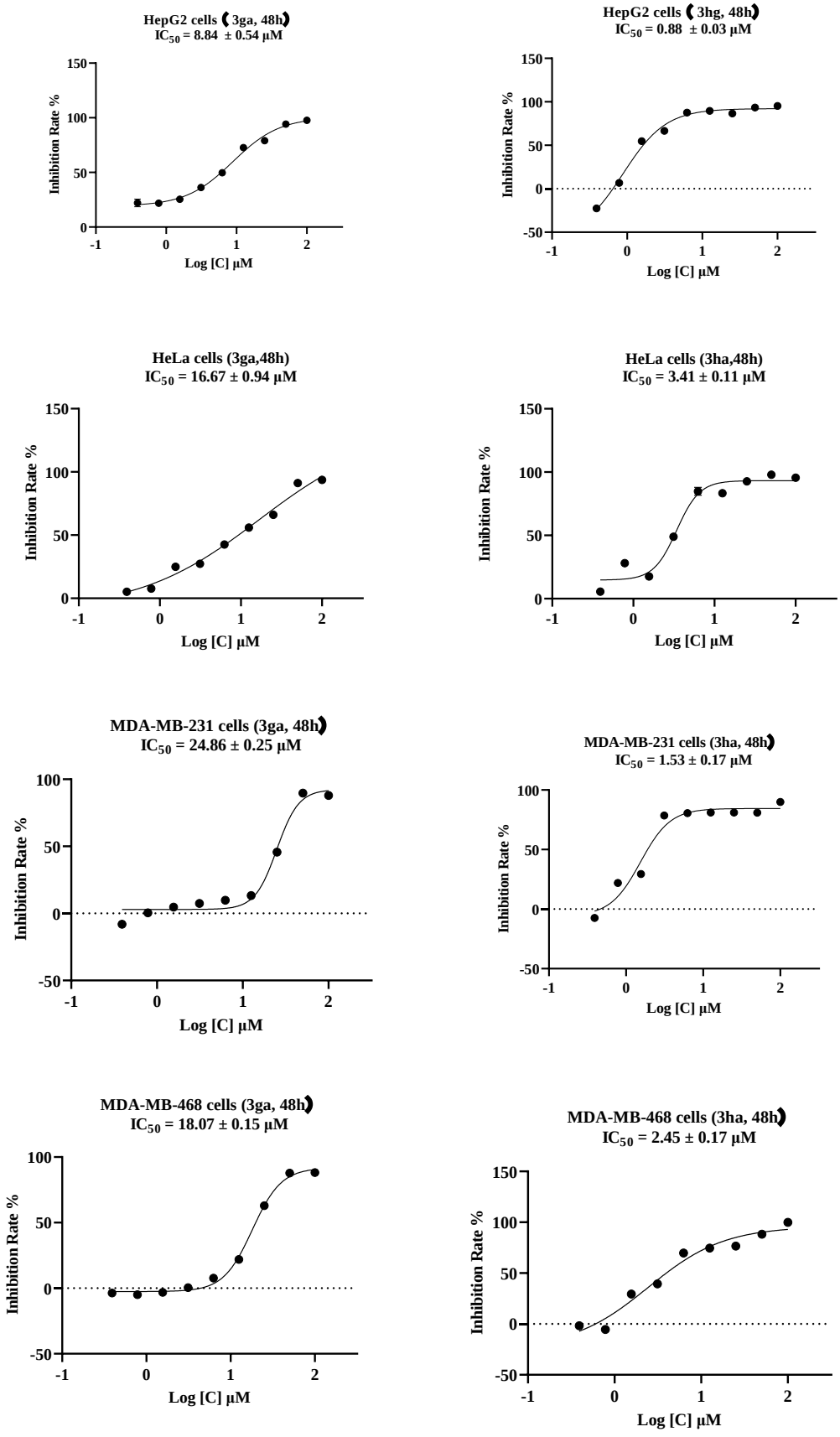
Specific Rotation: $[\alpha]_D^{22.3}$ +65.5 (*c* 1.6, $CHCl_3$).

6. In Vitro Inhibiting Activity Against HepG2 Cells

Human liver carcinoma HepG2 cells were purchased from the Cell Bank of Shanghai Institute of Biochemistry and Cell Biology, Chinese Academy of Sciences (Shanghai, China). Cells were maintained in Dulbecco Modified Eagle Medium (DMEM, Biological Industries, Beit Haemek, Israel) containing 10% fetal bovine serum (FBS, Gibco) and 1% penicillin/streptomycin at 37 ℃ with 5% CO_2 in a humidified atmosphere. Culture medium was changed every 2 days. Cells were subcultured at a 1:1 ratio when they were 80–90% confluent. Cells in the logarithmic growth phase were employed for further experiments. All tested compounds were solubilized in dimethyl sulfoxide (DMSO) (Alfa Aesar, China) to make a 10 mM stock solution.

Human liver carcinoma HepG2 cells were seeded at a density of 5000 cells per well in 96-well plates. The plates were incubated overnight and then treated with various concentrations of compounds for 48 h at 37 ℃. The final concentration of DMSO in medium was less than 0.1%. After removing the medium, 10% Cell Counting Kit-8 (CCK-8, APExBIO, Houston, USA) solution (100 μL) was added into the 96-well plates and incubated at 37 ℃ for 3 h. Absorbance was measured at 450 nm with a microplate spectrophotometer (MK3, Thermo, Germany). The inhibitory activity was expressed as the IC_{50} value and all experiments were performed in triplicate.

Figure S1. The IC_{50} values of **3ga** and **3ha** in different cell lines.



7. Computational Details

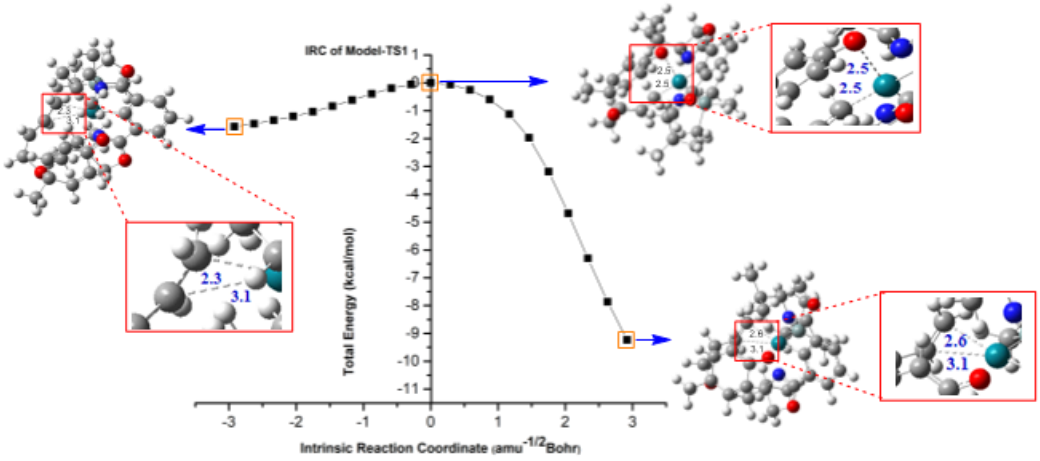
All density functional theory (DFT) calculations were carried out using Gaussian09 software package.[4] All geometry optimizations were performed with B3LYP-D3 (Becke−Johnson damping function) functional using def2-SVP basis set for all atoms.[5-8] The vibrational frequencies were computed at the same level of theory as for the geometry optimizations, and to evaluate the zero-point vibrational energy (ZPVE) and thermal corrections at 298 K. The single-point energies were computed based on the gas-phase optimized structures, using B3LYP functional, and def2-TZVPP basis set for all atoms, with the inclusion of solvation energy correc-tions using a self-consistent reaction field (SCRF) based on SMD implicit solvent model with toluene as solvent.[9-10]

7.1 Table of Energies

Zero-point correction (*ZPE*), thermal correction to enthalpy (*TCH*), thermal correction to Gibbs free energy (*TCG*), energies (*E*), enthalpies (*H*), and Gibbs free energies (*G*) (in Hartree) of the structures calculated at the B3LYP/def2-TZVPP-SMD(toluene)//B3LYP-D3(BJ)/def2-SVP level of theory.

Structures	*ZPE*	*TCH*	*TCG*	*E*		*H*	*H*	*G*		Imaginary Frequency
				6-31g(d)	6-311+g(d,p)		6-311+g(d,p)	6-31g(d)	6-311+g(d,p)	
Rh(III)-π-allyl intermediate	0.713500	0.757588	0.639979	-2055.944860	-2057.942625	-2055.187272	-2057.185037	-2055.304881	-2057.302646	
TS	0.713118	0.756054	0.643247	-2055.928807	-2057.920746	-2055.172754	-2057.164692	-2055.285561	-2057.277499	-240.5i
1a	0.200808	0.214385	0.161584	-576.354369	-577.018505	-576.139984	-576.804120	-576.192785	-576.856921	
3aa	0.227856	0.240666	0.190180	-577.632765	-578.293296	-577.392099	-578.052630	-577.442585	-578.103116	

7.2 Figure of IRC Pathway



7.3 Cartesian Coordinates of the Structures

Rh(III)-π-allyl intermediate

O	1.65960800	-2.86187000	-1.90121100
O	-4.54298600	0.53373300	-0.60042900
N	1.03014700	-1.40739900	-0.31106400
N	-2.47560900	0.68773600	0.25035000
C	-1.45237400	-1.28479000	-1.01248500
C	-2.80057900	-1.05783200	-1.32586000
C	-3.43370100	-1.84041000	-2.30057000
H	-4.48559800	-1.67761600	-2.54674100
C	-2.69141800	-2.82469300	-2.97176100
H	-3.17897100	-3.43465400	-3.73473400
C	-1.32803000	-3.02139100	-2.70159000
H	-0.75553900	-3.76447900	-3.26167800
C	-0.71074300	-2.24523800	-1.71220900
C	0.67995300	-2.19255200	-1.29344900
C	2.90670000	-2.34323200	-1.36438200
H	3.36336400	-1.70987100	-2.13715000
H	3.56509000	-3.19527100	-1.15651900
C	2.48626500	-1.54203200	-0.11114500
C	-3.29432400	0.06848400	-0.55267700
C	-4.63529600	1.56807200	0.41497200
H	-5.23892300	1.16843200	1.24344100
H	-5.14917400	2.43085500	-0.02673700
C	-3.16713600	1.84804300	0.82270300
Rh	-0.56043900	-0.12782400	0.27424500
C	1.05556000	2.68075000	-0.95247400
C	2.00546000	0.87225300	-2.33984800
C	2.31516600	2.98880200	-0.47256400
H	0.19437000	3.28583300	-0.67007300
C	3.25511100	1.21458500	-1.99733300
H	1.80011300	0.08617200	-3.07141600
H	2.49108500	4.00703500	-0.11910200
C	0.81730800	1.51166800	-1.72759100
O	-0.32647900	1.02837200	-1.94859200
C	3.56840000	2.25051600	-0.94539200
C	4.59321600	3.26086600	-1.48276600

H	5.49976900	2.73575000	-1.81878100
H	4.17572100	3.83065000	-2.32699200
H	4.87919200	3.97416800	-0.69397900
O	4.18078600	1.49677500	0.12528500
C	3.96579100	2.07372700	1.42400200
H	4.56357000	2.99776300	1.53682200
H	4.38054700	1.32149600	2.11556100
C	2.51639000	2.34438200	1.65875300
H	2.20990200	3.35768300	1.92277900
C	1.63516900	1.30689900	1.99091700
H	2.07805100	0.31483500	2.13871000
C	0.24501600	1.39498000	2.09472100
Si	-1.22732200	-1.58392400	1.99111000
C	-2.78412200	-0.93275200	2.87470500
H	-3.64978500	-0.88095500	2.19724600
H	-3.04491800	-1.61809000	3.69904900
H	-2.62593600	0.06608300	3.31111400
C	0.03325100	-1.87390500	3.39162200
H	0.78558100	-2.62120200	3.11036000
H	0.55768100	-0.96668300	3.72447300
H	-0.51734600	-2.27660900	4.25927400
C	-1.69167700	-3.31699400	1.36601900
H	-0.87311200	-3.78864200	0.80199900
H	-1.92881700	-3.96626800	2.22628400
H	-2.57083200	-3.28712600	0.70479800
H	4.12352200	0.71288400	-2.43671600
H	2.93797200	-0.54192400	-0.11999600
H	-3.05781200	1.82754700	1.91701000
C	2.85862200	-2.22136000	1.21931000
H	2.33807100	-1.64670300	1.99881600
C	2.38684100	-3.67332400	1.31504000
H	2.56388100	-4.07223000	2.32581500
H	2.92636200	-4.32775500	0.61142500
H	1.31175800	-3.76500200	1.10568600
C	4.36503000	-2.09001400	1.46312700
H	4.68959700	-1.04043300	1.39201300
H	4.94455800	-2.66654500	0.72180000
H	4.63709600	-2.47396300	2.45853300

C	-2.59302800	3.18064000	0.30029300
H	-1.52670200	3.15782700	0.57303100
C	-2.67669800	3.30631000	-1.22178800
H	-3.71966900	3.29318400	-1.58054100
H	-2.11529700	2.49639600	-1.70961200
H	-2.23536700	4.26147600	-1.54749900
C	-3.24262600	4.36196100	1.02551000
H	-3.14300000	4.27288500	2.11980200
H	-4.31786100	4.44433300	0.79122700
H	-2.77282000	5.30978600	0.72101100
H	-0.26881500	0.73925200	2.79488600
H	-0.21246400	2.38378300	1.98843800

TS

O	3.12539300	1.41275200	-1.67181000
O	-3.35298400	-1.72531100	-1.38112700
N	2.05798600	0.19986500	-0.11009600
N	-1.74424900	-1.33537700	0.13762500
C	-0.04454500	-0.28036900	-1.45038300
C	-1.26837800	-0.60996200	-2.06883400
C	-1.46498900	-0.36175200	-3.43232100
H	-2.41522800	-0.61319100	-3.90833900
C	-0.43159100	0.23125000	-4.17587100
H	-0.58257300	0.43086700	-5.23843300
C	0.78944400	0.58150800	-3.57494800
H	1.57713500	1.05586900	-4.16549000
C	0.98043600	0.31939900	-2.21409200
C	2.09321000	0.62628700	-1.34384200
C	3.84657200	1.68708900	-0.44362800
H	3.69773500	2.74844600	-0.20037800
H	4.91284600	1.49855500	-0.62530500
C	3.20723700	0.75148200	0.61499900
C	-2.15475400	-1.21238200	-1.09730800
C	-3.80877600	-2.40746900	-0.18846600
H	-3.79205400	-3.48789600	-0.39287800
H	-4.84111200	-2.09149300	0.00857600
C	-2.80321400	-1.99046600	0.91672800
Rh	0.26241100	-0.73646700	0.41700900

C	-2.71248300	3.33278100	0.38996400
C	-1.29544500	2.71111100	-1.58438700
C	-1.62831500	3.78406900	1.03666500
H	-3.71182600	3.39290300	0.82722600
C	-0.21420400	3.15719200	-0.93116800
H	-1.22843400	2.27131500	-2.57931900
H	-1.73486100	4.24950800	2.02040300
C	-2.62703200	2.70280100	-0.95168400
O	-3.60174100	2.18363400	-1.47815400
C	-0.23971600	3.77063300	0.44490200
C	0.25365300	5.22830600	0.34793200
H	1.28037300	5.23744600	-0.04730700
H	-0.39145100	5.82674300	-0.31270000
H	0.26712400	5.68229200	1.35049900
O	0.73795000	3.07734700	1.24100600
C	0.35062600	2.34925700	2.41778200
H	-0.32653900	2.97435800	3.02534700
H	1.29367800	2.28051700	2.98341200
C	-0.21928600	0.96858600	2.25391500
H	-1.30304500	0.87375900	2.17713500
C	0.57195300	-0.13014200	2.62258900
H	1.61919000	0.11205400	2.84473100
C	0.28032900	-1.50844400	2.57990500
Si	0.99018100	-2.86723200	-0.33649700
C	-0.44115200	-4.10128600	-0.58343400
H	-1.15342400	-3.76046700	-1.35108600
H	-0.03301700	-5.07013300	-0.91885500
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C	2.19349600	-3.75175000	0.84645400
H	3.01358000	-3.10160400	1.18277600
H	1.66374500	-4.11137200	1.74227700
H	2.64019800	-4.62688300	0.34306100
C	1.85039700	-2.82393300	-2.03699800
H	2.67465100	-2.09744700	-2.09393800
H	2.26641800	-3.82105400	-2.26179800
H	1.13456200	-2.56582700	-2.83237700
H	0.77830500	3.09209600	-1.38540400
H	2.82355000	1.35609300	1.44815500

H	-2.38078700	-2.88152600	1.40614400
C	4.12586600	-0.34082200	1.19052200
H	3.45934100	-0.99490800	1.77731100
C	4.78637800	-1.19690000	0.10952600
H	5.32643700	-2.04248500	0.56207100
H	5.51909300	-0.62037400	-0.47878800
H	4.04213200	-1.61136800	-0.58299700
C	5.15565800	0.27233900	2.14254700
H	4.66985500	0.84375400	2.94999800
H	5.83813600	0.95758000	1.61094300
H	5.77580500	-0.50924500	2.60780600
C	-3.39649600	-1.07783800	2.01020400
H	-2.55504200	-0.81395400	2.67016500
C	-3.96173900	0.22064000	1.43897700
H	-4.81715200	0.04941600	0.76635400
H	-3.19914800	0.75894300	0.86427100
H	-4.30528500	0.88279700	2.24864900
C	-4.42091300	-1.84282900	2.85224500
H	-3.98750600	-2.76085200	3.28164100
H	-5.30361800	-2.13304600	2.25779400
H	-4.78198800	-1.22033400	3.68532300
H	1.05585500	-2.19439300	2.92062400
H	-0.74039400	-1.87124600	2.70371700

1a

C	-1.29436000	0.33801300	-1.25557600
C	-1.96379100	-0.36189800	1.06116900
C	-0.13664400	-0.32592900	-1.12457200
H	-1.54048900	0.89707100	-2.16156900
C	-0.81604700	-1.04229000	1.18049900
H	-2.68850700	-0.29758100	1.87620400
H	0.58296900	-0.33215100	-1.94731100
C	-2.30734600	0.37927900	-0.17481800
O	-3.35030300	1.00350000	-0.29061400
C	0.20685400	-1.17279500	0.08069500
C	0.29003300	-2.64668100	-0.37101300
H	0.54663800	-3.27967300	0.49114000
H	-0.66663300	-2.98300800	-0.79648500

H	1.07157600	-2.76893800	-1.13713700
O	1.44666800	-0.81883100	0.72128100
C	2.53226900	-0.40206900	-0.06482900
H	2.61955100	-0.98416600	-1.00451700
H	3.43922600	-0.63681400	0.52016700
C	2.51490900	1.07746400	-0.38657400
H	3.29196300	1.43814300	-1.07378000
C	1.64617400	1.91909600	0.11921300
C	0.73684300	2.72065900	0.60858500
H	-0.55171500	-1.55503000	2.11015400
H	0.88688100	3.25359100	1.55383100
H	-0.21574400	2.87411000	0.08728400

3aa

C	-0.89057500	0.66669900	1.30613300
C	-0.81874200	1.52046000	-1.09439800
C	0.40785800	-0.08028700	1.00639400
H	-0.66116400	1.55747600	1.91907100
C	0.49521400	1.25489000	-1.15883800
H	-1.35521200	1.98019000	-1.92879700
C	-1.64146900	1.18867300	0.09032200
O	-2.84172300	1.37874000	0.10946600
C	1.29969600	0.58673000	-0.06892000
C	2.31146100	1.57025700	0.52074700
H	2.93815300	2.00178400	-0.27391200
H	1.80050900	2.39233500	1.04582500
H	2.96889000	1.04698500	1.23174100
O	2.01240900	-0.49621200	-0.69957300
C	1.67371900	-1.73443800	-0.09305000
H	2.39889500	-1.99071400	0.70417900
H	1.71639000	-2.52107200	-0.86167100
C	0.27253000	-1.54303100	0.50221000
H	1.06991000	1.50250600	-2.05784100
H	0.99652600	-0.13074700	1.93645500
H	0.10420100	-2.21201900	1.36059300
C	-0.81849400	-1.76269900	-0.50969300
C	-1.98466500	-2.35704500	-0.24619200
H	-2.21921000	-2.73807200	0.75350300

H	-2.75290800	-2.47695000	-1.01416900
H	-0.62339000	-1.38667100	-1.51941100
H	-1.58626600	0.05348700	1.89699700

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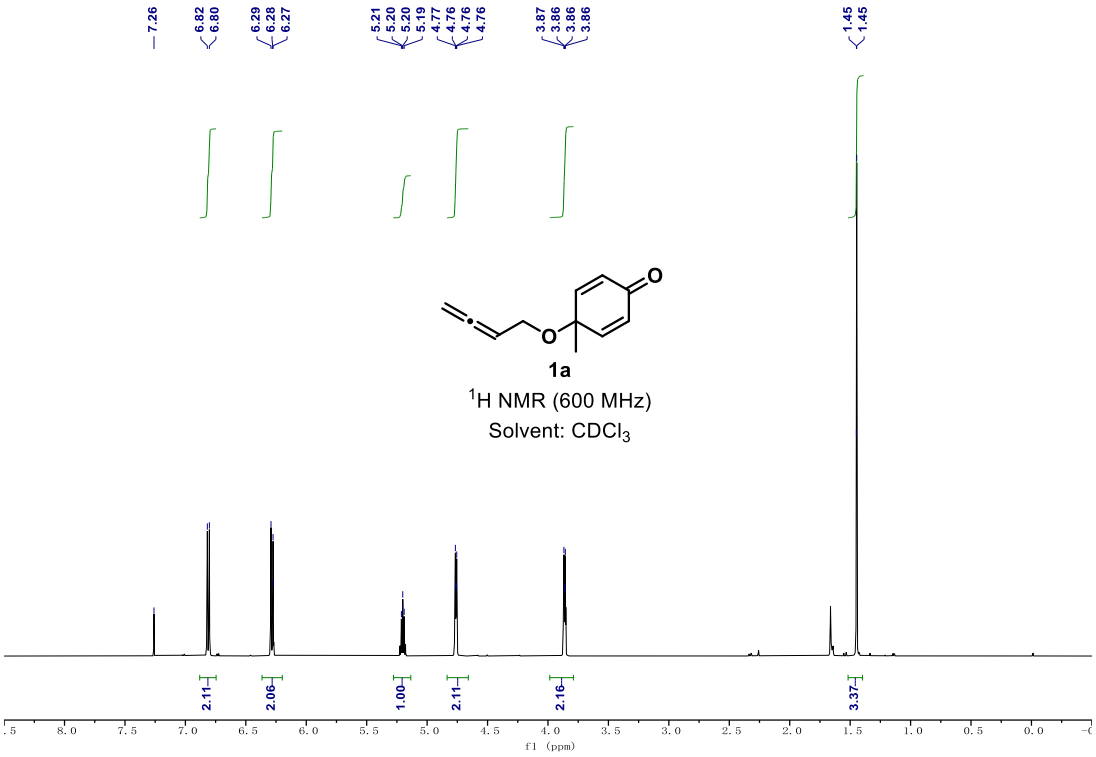
10. M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.* **2003**, *24*, 669−681.

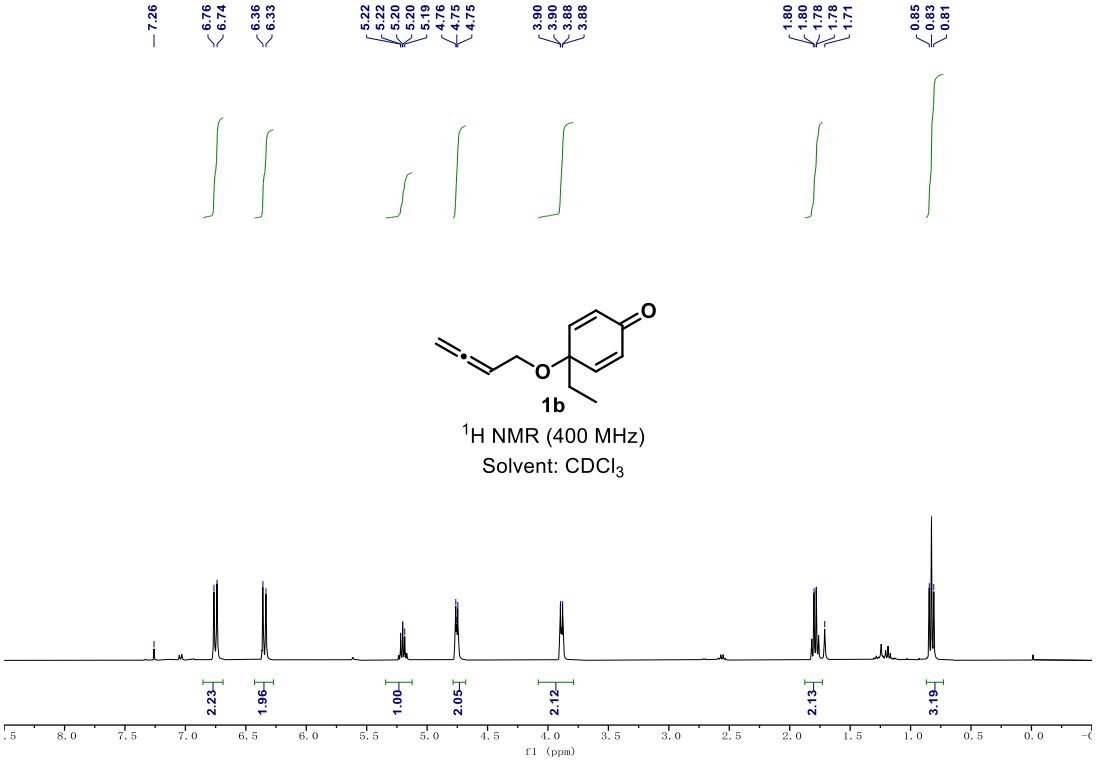
9. ^{1}H NMR and ^{13}C NMR Spectra Copies



1a

^{1}H NMR (600 MHz)

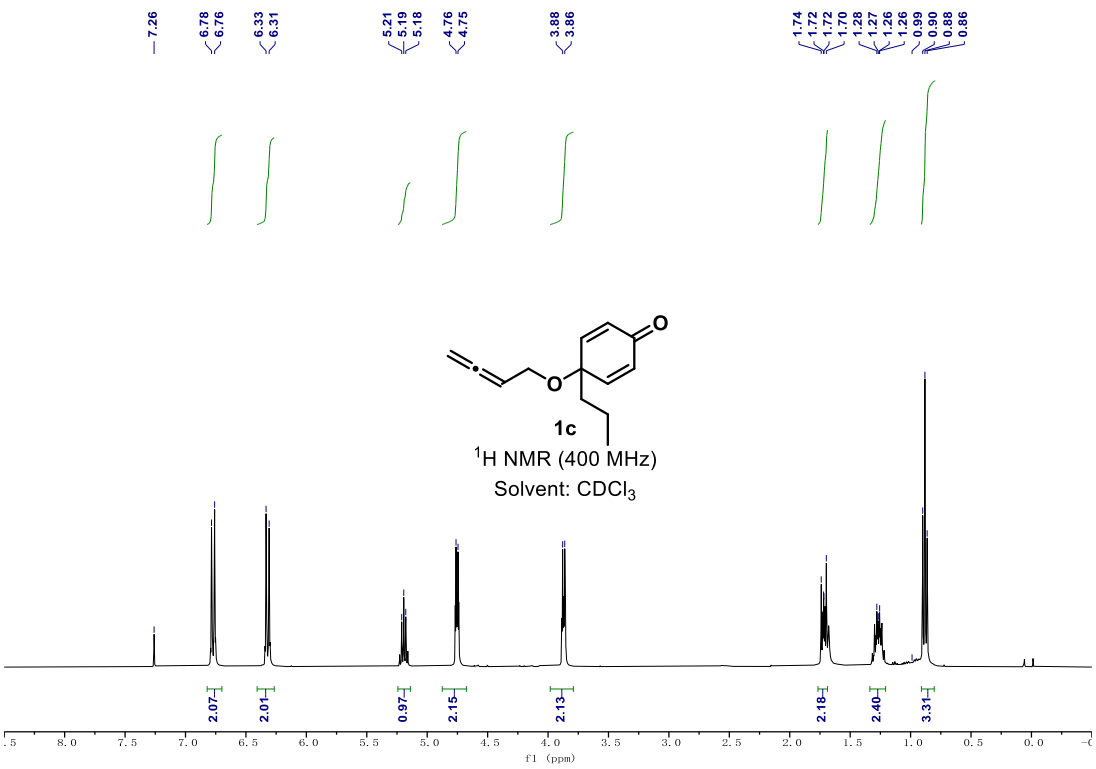
Solvent: $CDCl_3$

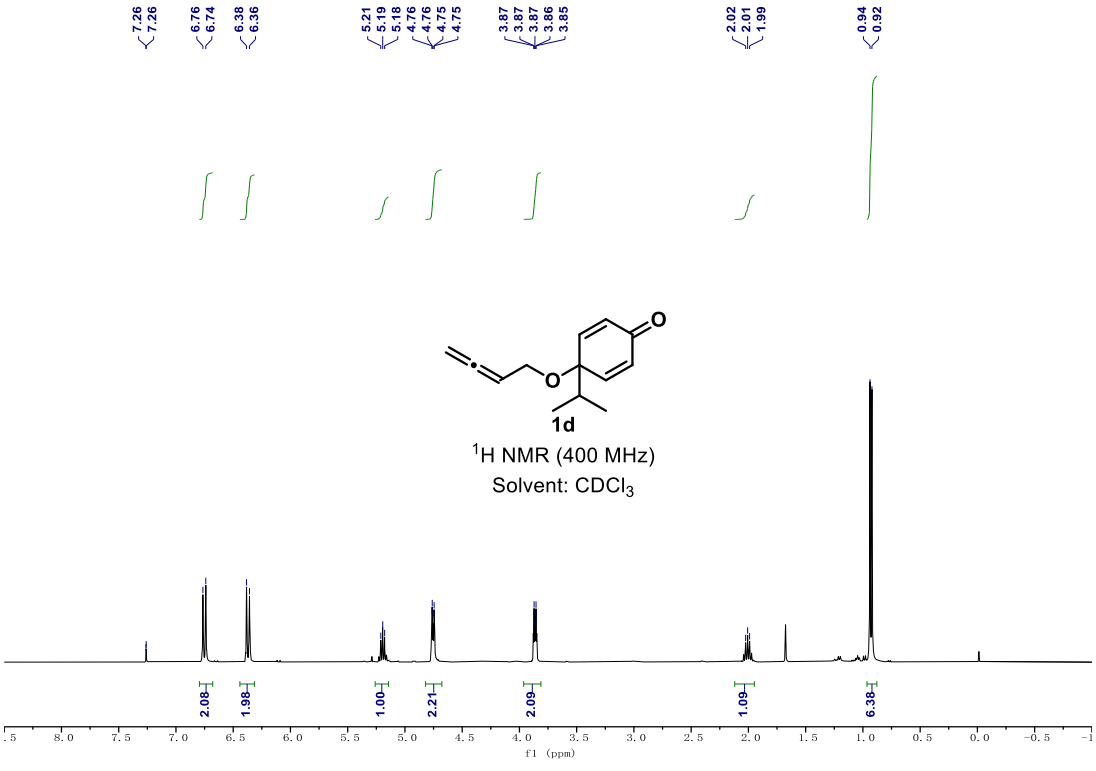


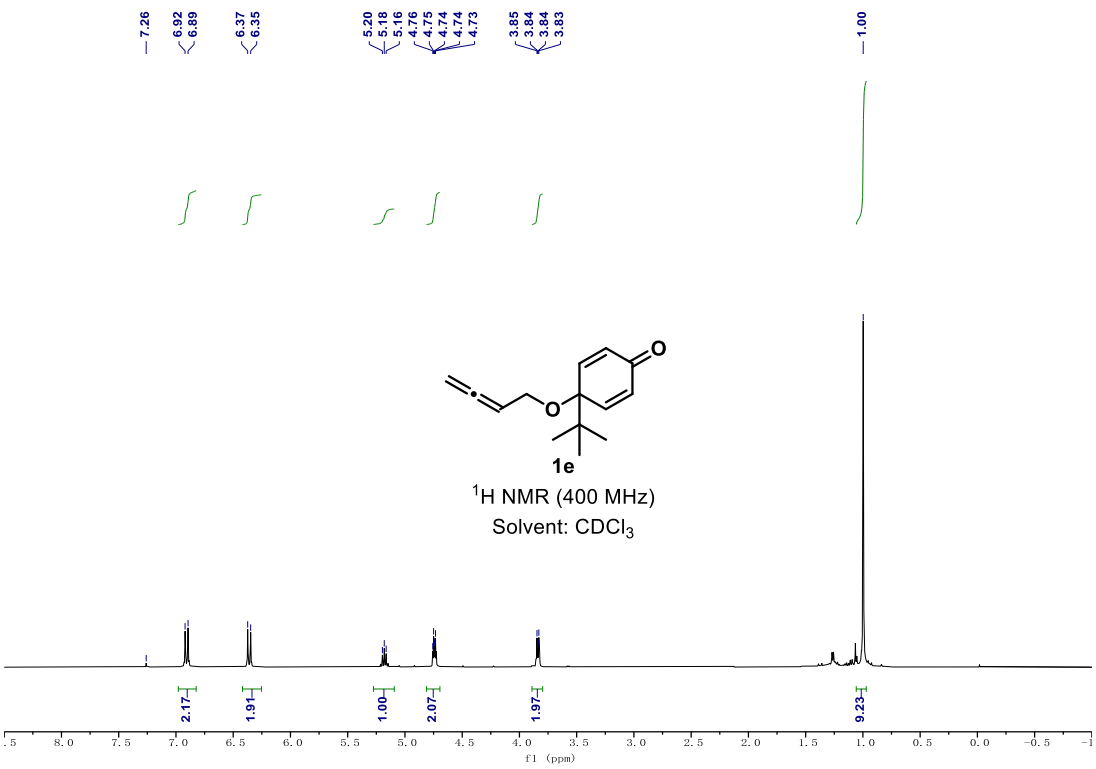
1b

^{1}H NMR (400 MHz)

Solvent: $CDCl_3$


7.26
6.78
6.76
6.33
6.31
5.21
5.19
5.18
4.76
4.75
3.88
3.86
1.74
1.72
1.72
1.70
1.28
1.27
1.26
1.26
0.99
0.90
0.88
0.86
O
O
1c
1H NMR (400 MHz)
Solvent: CDCl3
2.07
2.01
0.97
2.15
2.13
2.18
2.40
3.31
f1 (ppm)


7.26
7.26
6.76
6.74
6.38
6.36
5.21
5.19
5.18
4.76
4.76
4.75
4.75
3.87
3.87
3.87
3.86
3.85
2.02
2.01
1.99
0.94
0.92
O
O
1d
1H NMR (400 MHz)
Solvent: CDCl3
2.08
1.98
1.00
2.21
2.09
1.09
6.38
f1 (ppm)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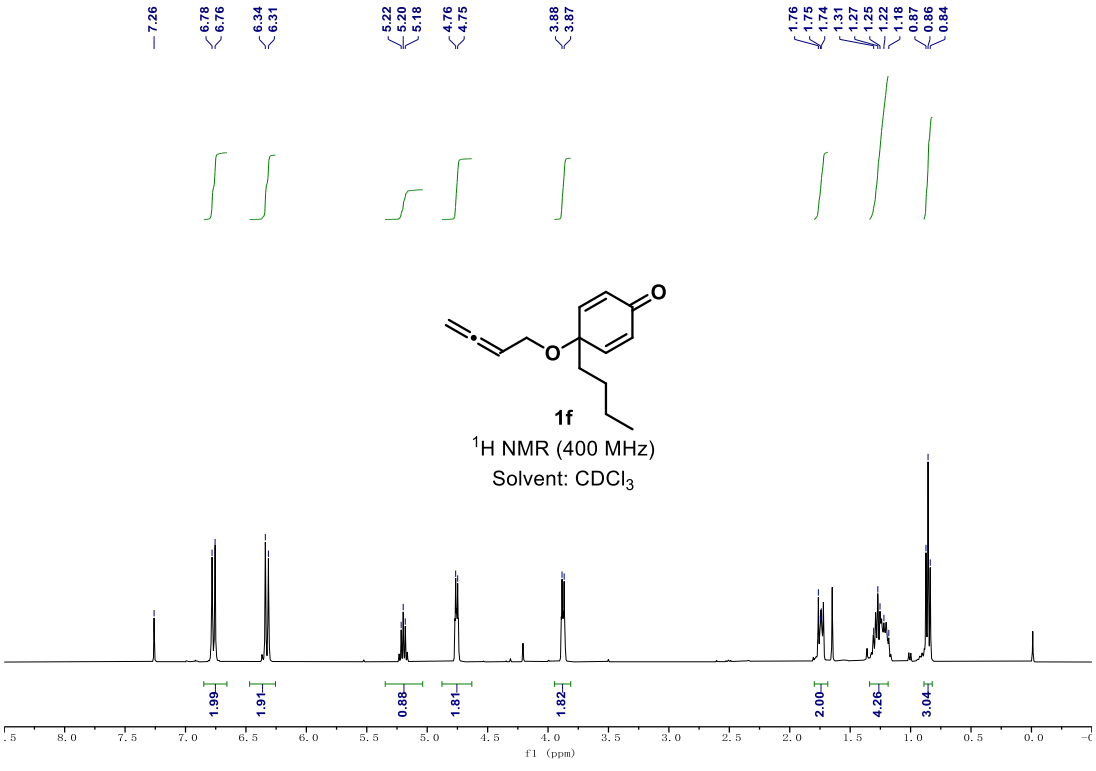
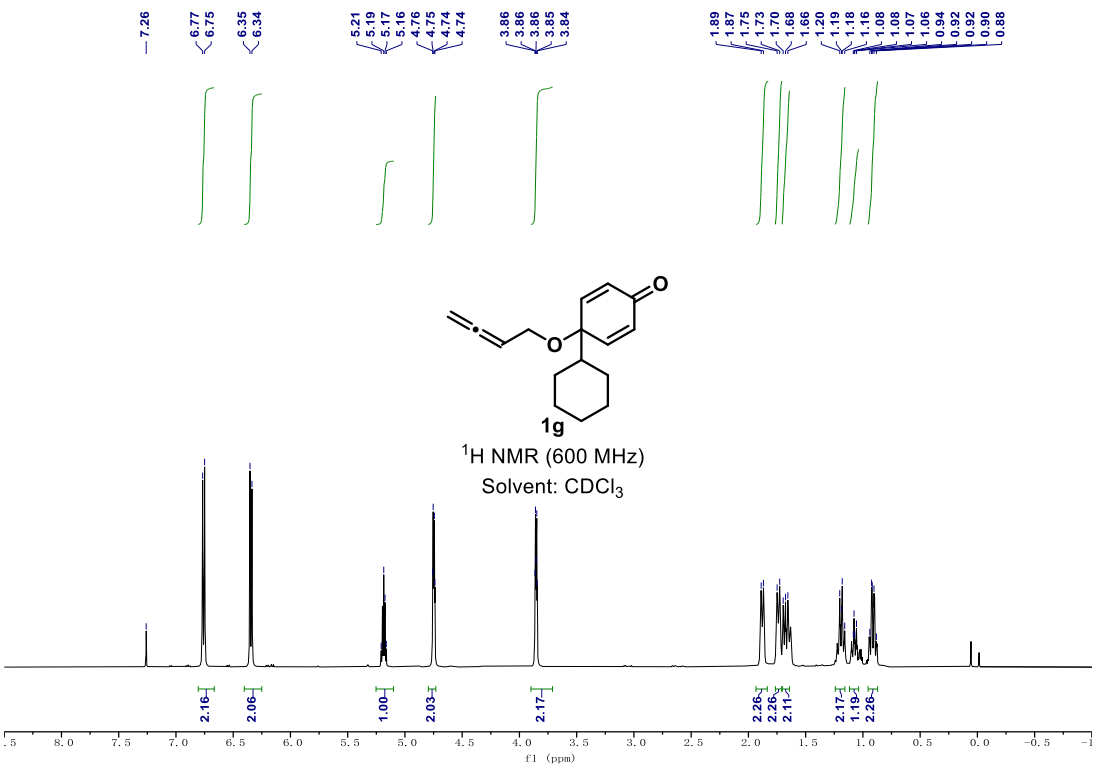
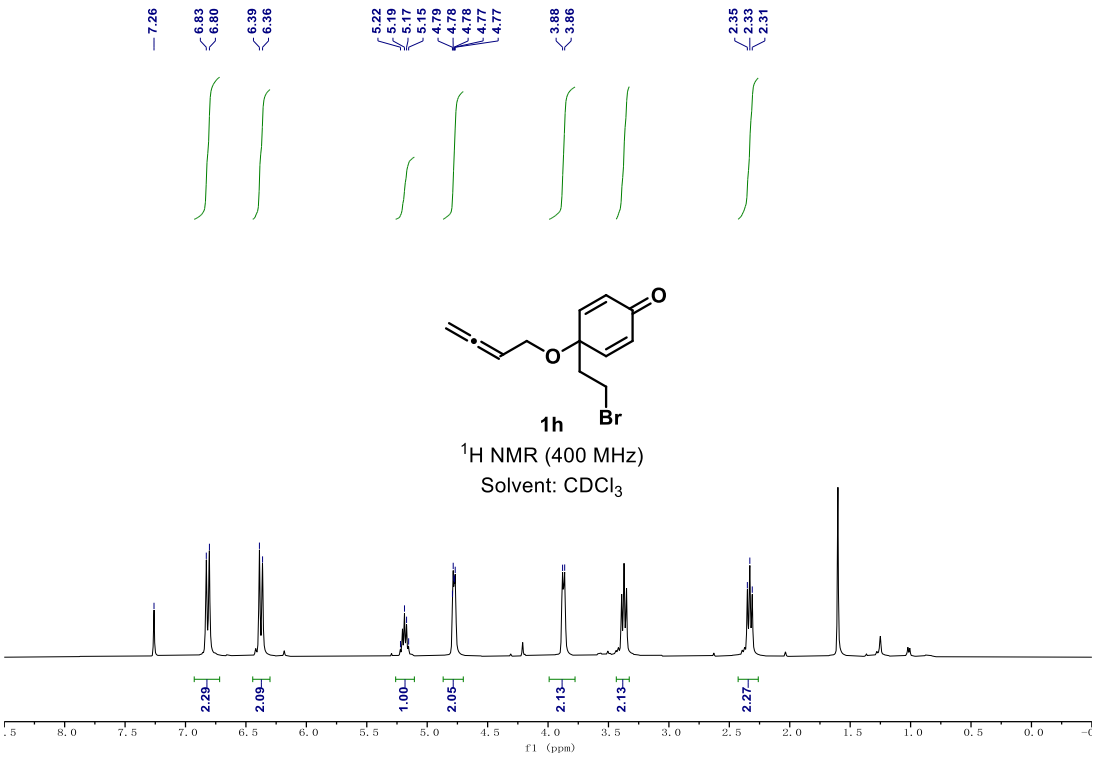
6.89
6.37
6.35
5.20
5.18
5.16
4.76
4.75
4.74
4.74
4.73
3.85
3.84
3.84
3.83
1.00
O
O
1e
1H NMR (400 MHz)
Solvent: CDCl3
2.17
1.91
1.00
2.07
1.97
9.23
f1 (ppm)


7.26
6.78
6.76
6.34
6.31
5.22
5.20
5.18
4.76
4.75
3.88
3.87
1.76
1.75
1.74
1.31
1.27
1.25
1.22
1.18
0.87
0.86
0.84
O
O
1f
1H NMR (400 MHz)
Solvent: CDCl3
1.99
1.91
0.88
1.81
1.82
2.00
4.26
3.04
f1 (ppm)


7.26
6.77
6.75
6.35
6.34
5.21
5.19
5.17
5.16
4.76
4.75
4.74
4.74
3.86
3.86
3.86
3.85
3.84
1.89
1.87
1.75
1.73
1.70
1.68
1.66
1.20
1.19
1.18
1.16
1.08
1.08
1.07
1.06
0.94
0.92
0.92
0.90
0.88
O
O
1g
1H NMR (600 MHz)
Solvent: CDCl3
2.16
2.06
1.00
2.03
2.17
2.26
2.26
2.11
2.17
1.19
2.26
f1 (ppm)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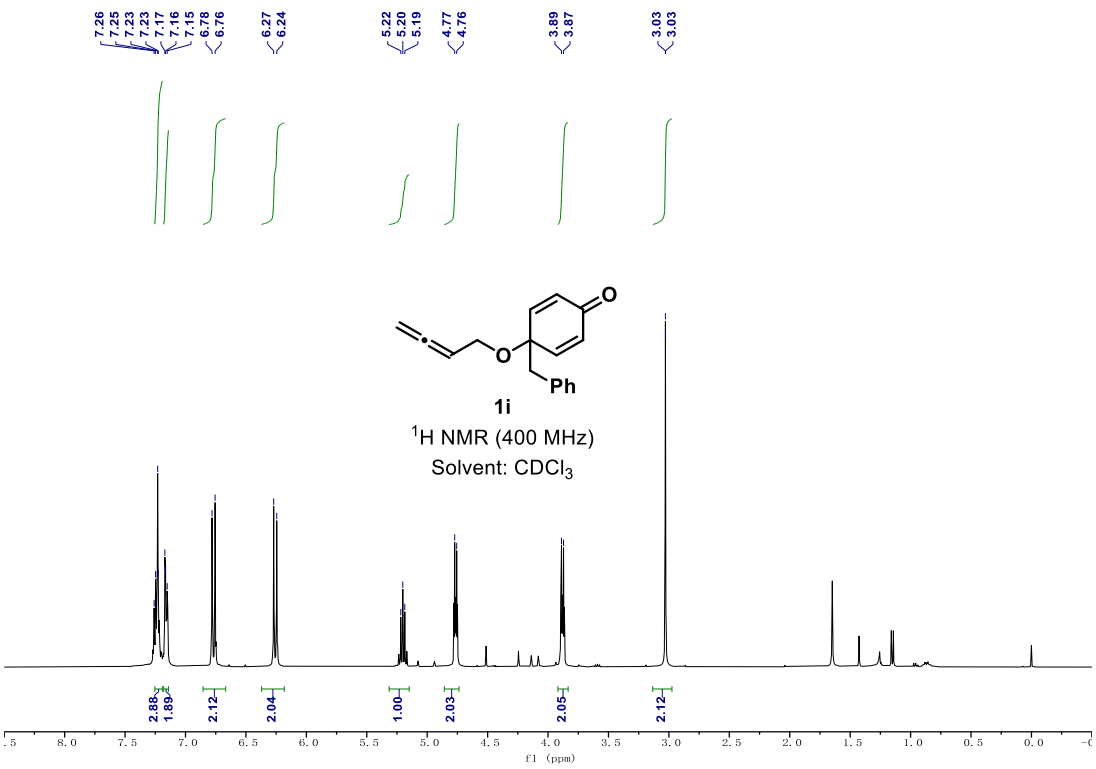
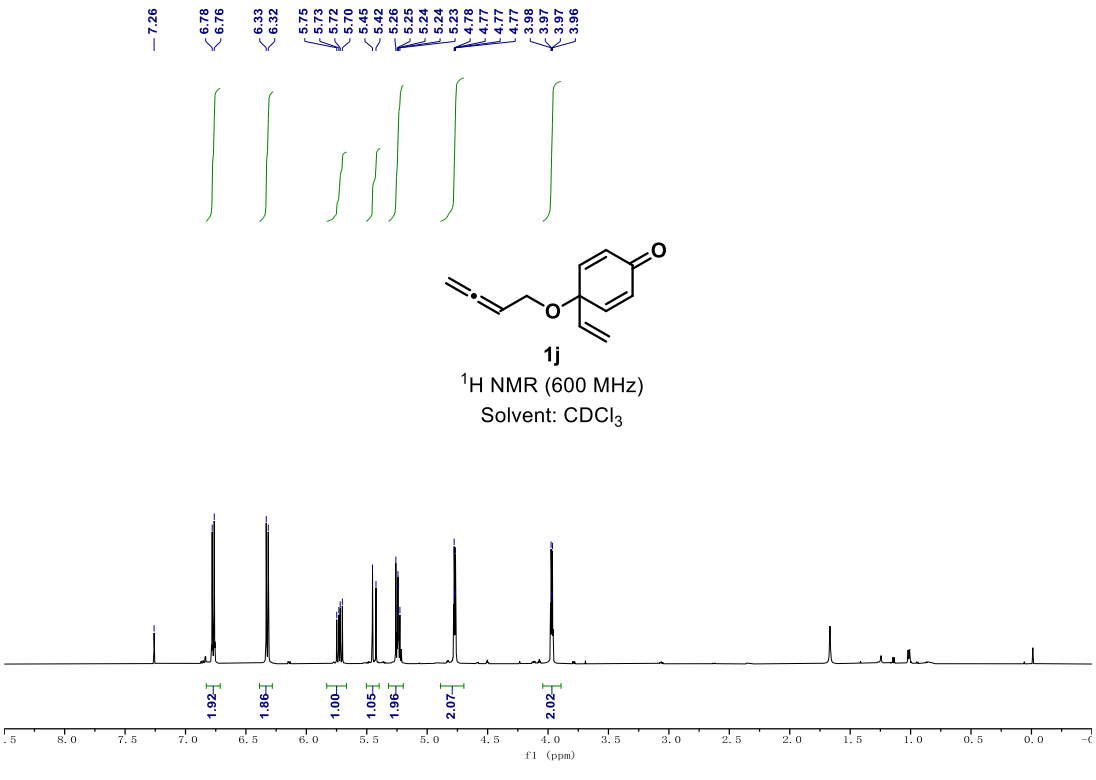
6.83
6.80
6.39
6.36
5.22
5.19
5.17
5.15
4.79
4.78
4.78
4.77
4.77
3.88
3.86
2.35
2.33
2.31
O
O
Br
1h
1H NMR (400 MHz)
Solvent: CDCl3
2.29
2.09
1.00
2.05
2.13
2.13
2.27
f1 (ppm)



1i

^{1}H NMR (400 MHz)

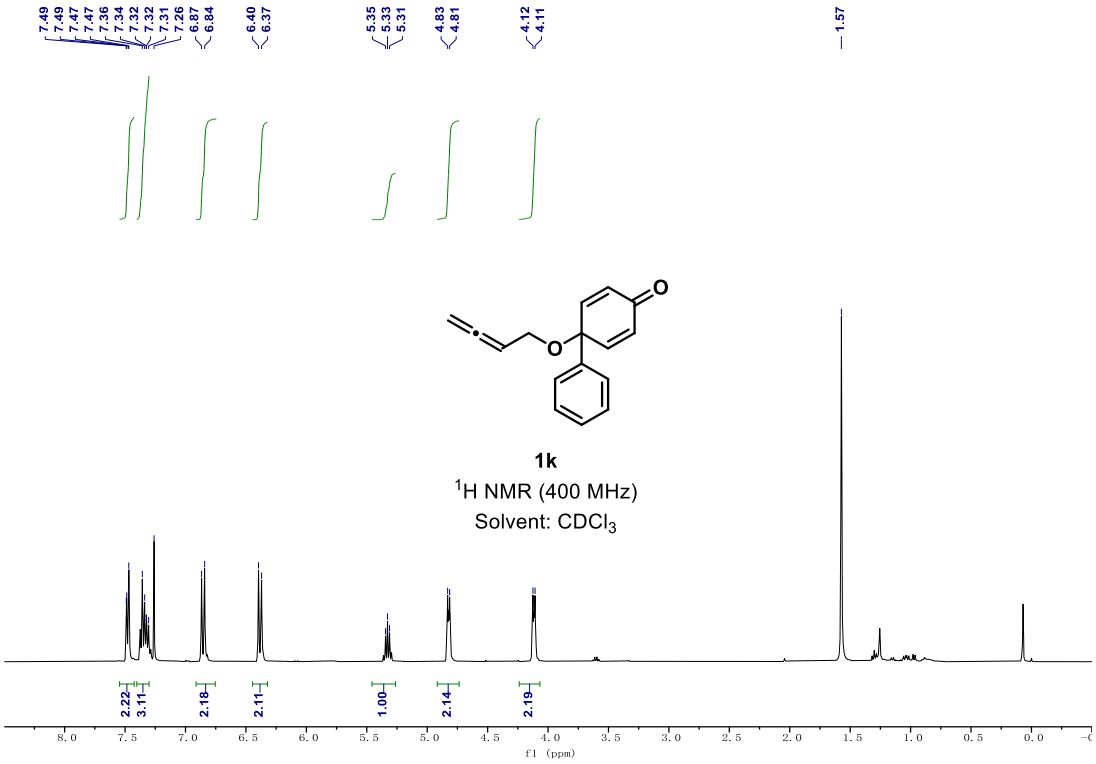
Solvent: $CDCl_3$

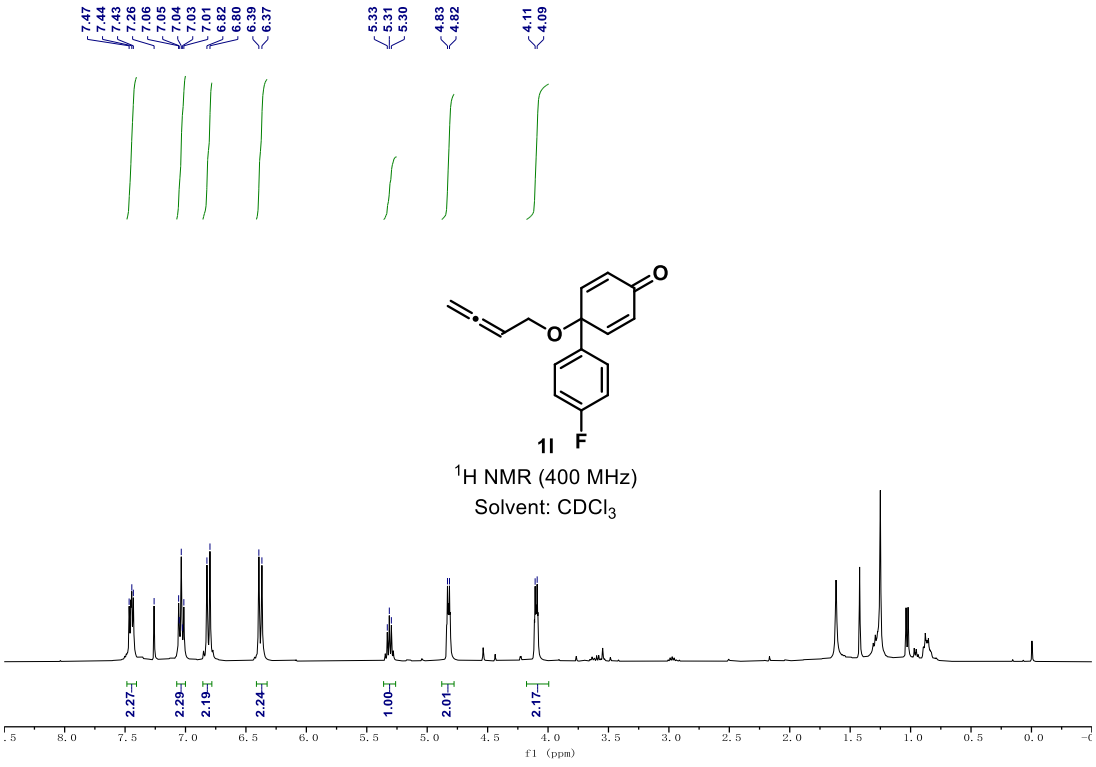


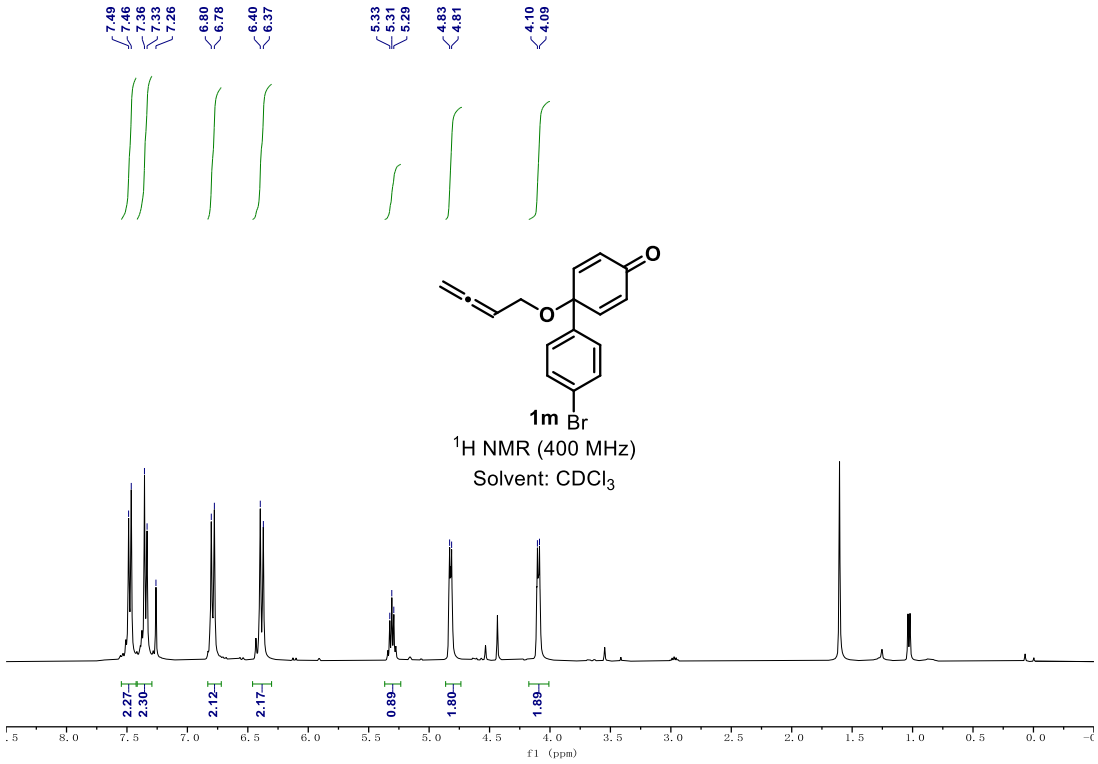
1j

^{1}H NMR (600 MHz)

Solvent: $CDCl_3$


7.49
7.49
7.47
7.47
7.36
7.34
7.32
7.32
7.31
7.26
6.87
6.84
6.40
6.37
5.35
5.33
5.31
4.83
4.81
4.12
4.11
1.57
O
O
1k
1H NMR (400 MHz)
Solvent: CDCl3
2.22
3.11
2.18
2.11
1.00
2.14
2.19
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

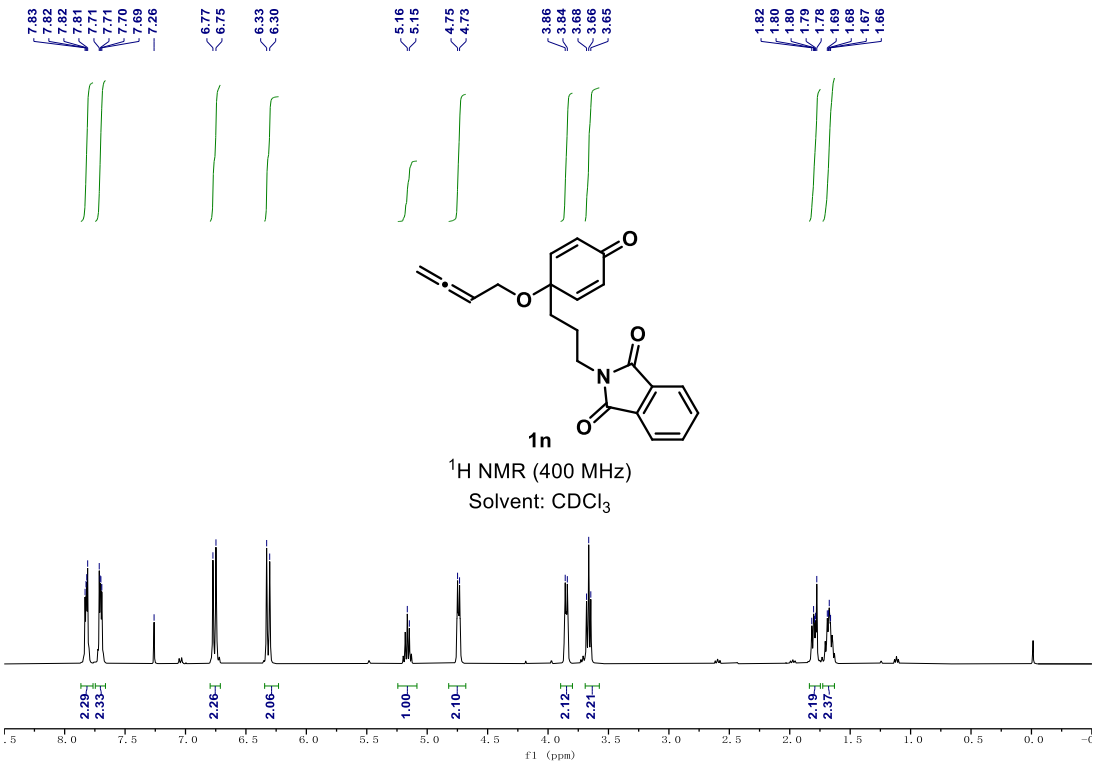

7.47
7.44
7.43
7.26
7.06
7.05
7.04
7.03
7.01
6.82
6.80
6.39
6.37
5.33
5.31
5.30
4.83
4.82
4.11
4.09
O
O
F
1l
1H NMR (400 MHz)
Solvent: CDCl3
2.27
2.29
2.19
2.24
1.00
2.01
2.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



1m

^{1}H NMR (400 MHz)

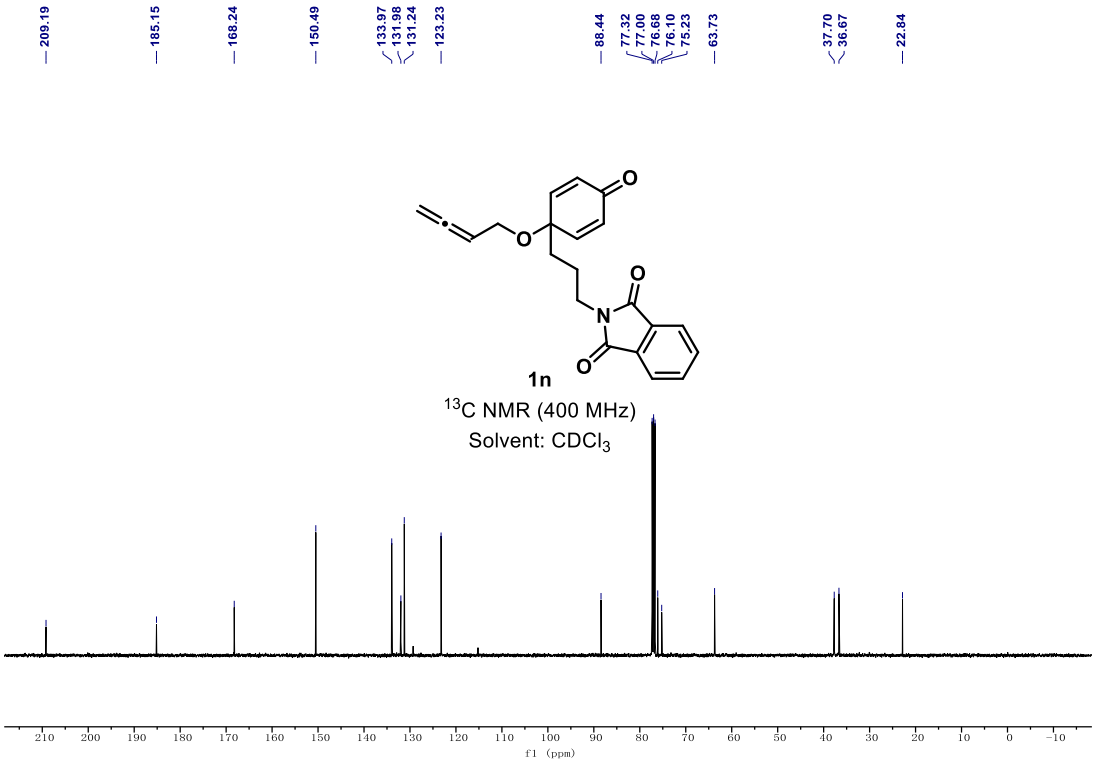
Solvent: $CDCl_3$



1n

^{1}H NMR (400 MHz)

Solvent: $CDCl_3$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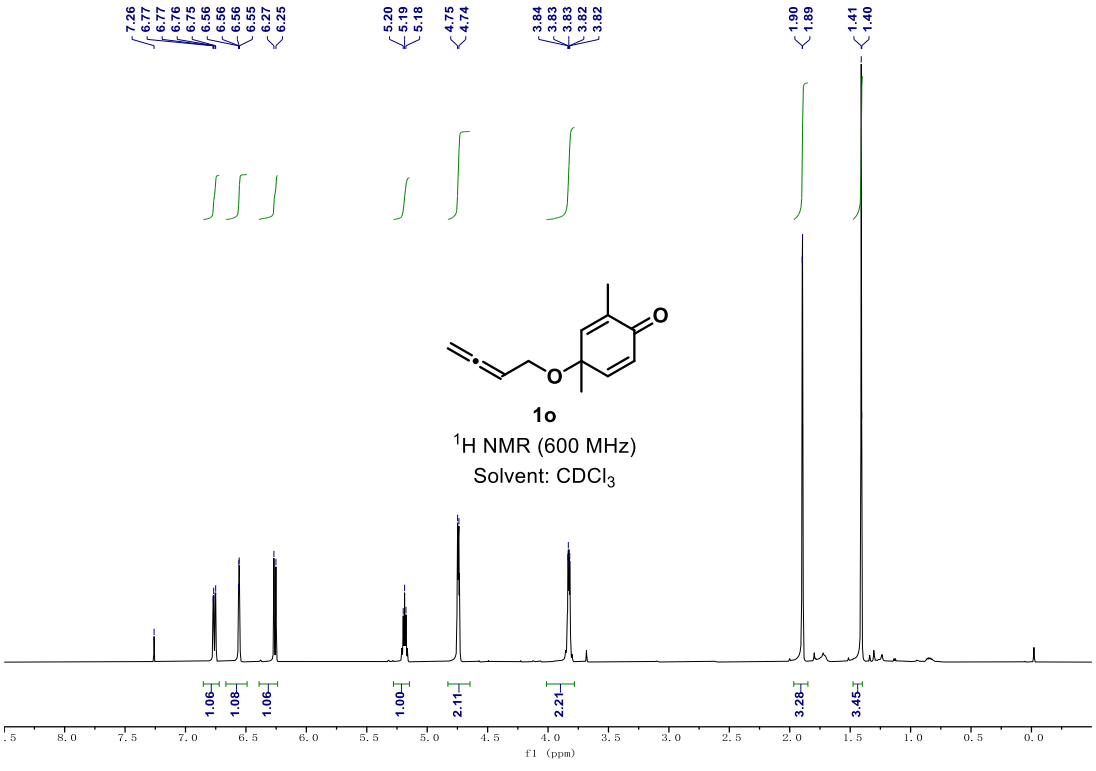
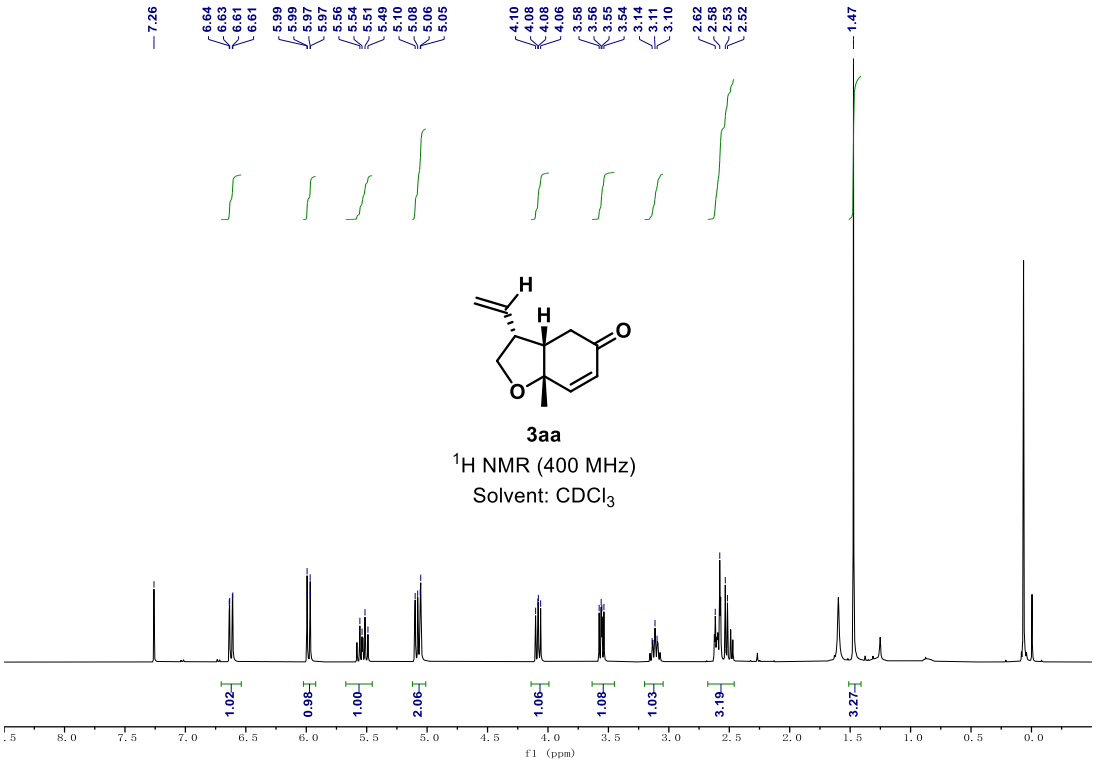
185.15
168.24
150.49
133.97
131.98
131.24
123.23
88.44
77.32
77.00
76.68
76.10
75.23
63.73
37.70
36.67
22.84
O
O
N
O
O
1n
13C NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)

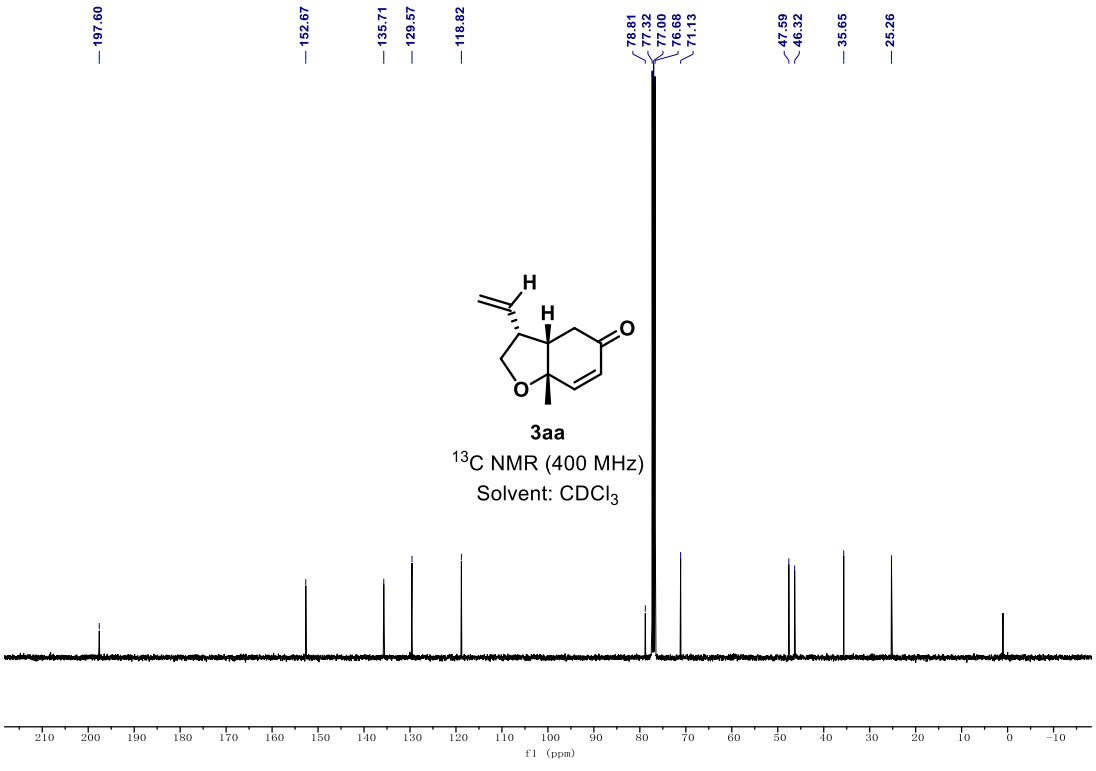

7.26
6.77
6.77
6.76
6.75
6.56
6.56
6.56
6.55
6.27
6.25
5.20
5.19
5.18
4.75
4.74
3.84
3.83
3.83
3.82
3.82
1.90
1.89
1.41
1.40
O
O
1o
1H NMR (600 MHz)
Solvent: CDCl3
1.06
1.08
1.06
1.00
2.11
2.21
3.28
3.45
f1 (ppm)



3aa

^{1}H NMR (400 MHz)

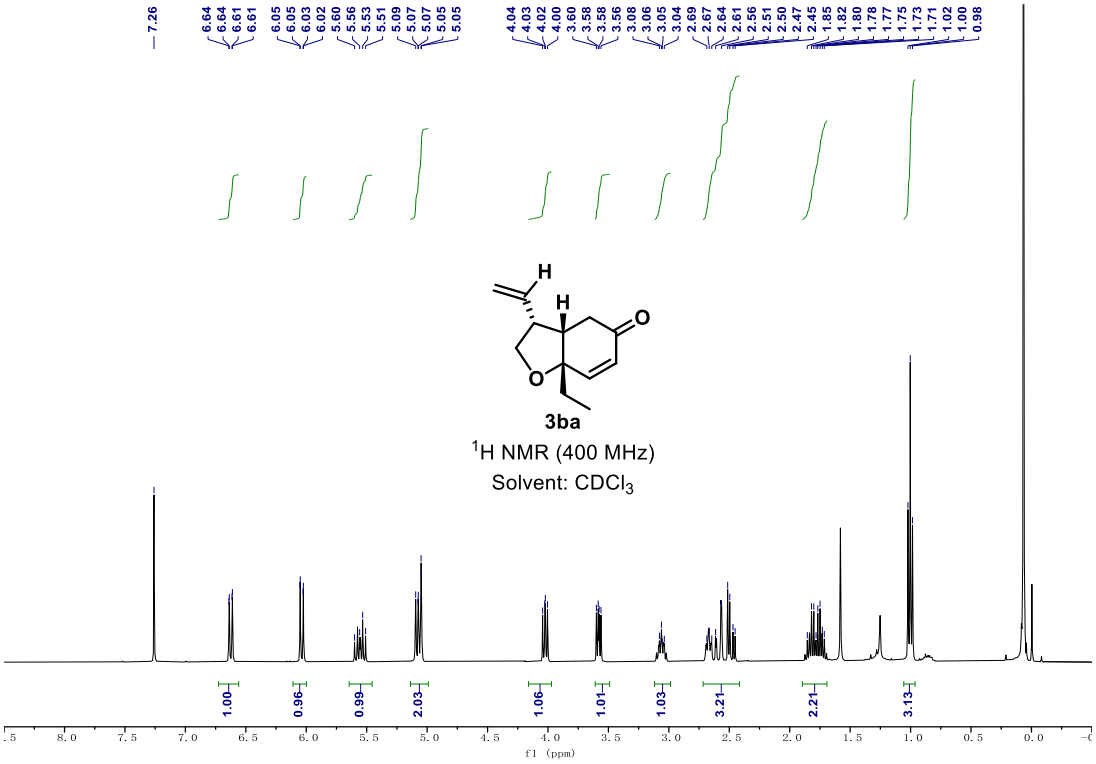
Solvent: $CDCl_3$

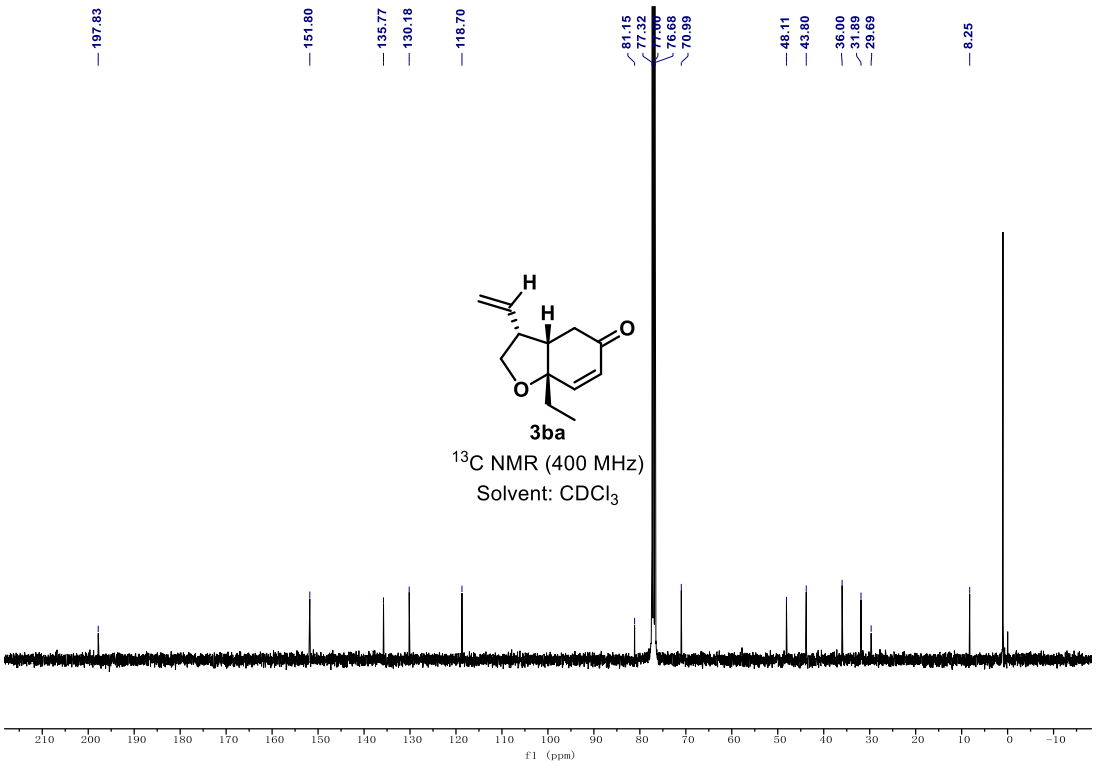


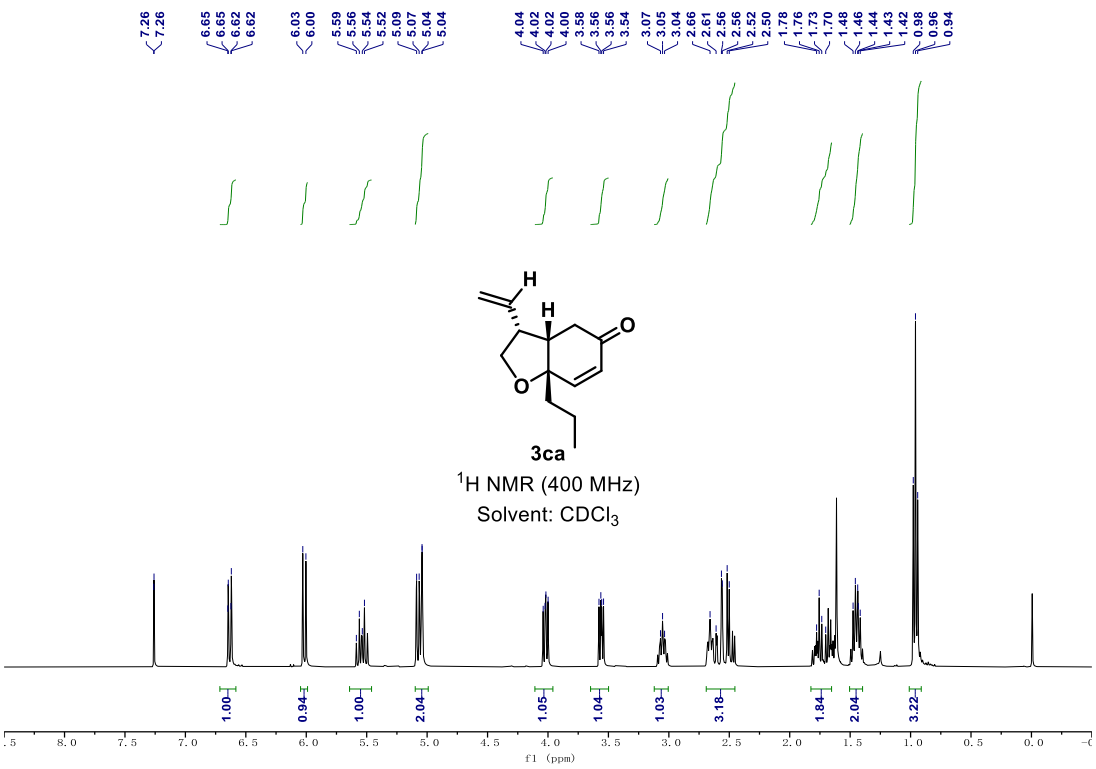
3aa

^{13}C NMR (400 MHz)

Solvent: $CDCl_3$


7.26
6.64
6.64
6.61
6.61
6.05
6.05
6.03
6.02
5.60
5.56
5.53
5.51
5.09
5.07
5.05
5.05
4.04
4.03
4.02
4.00
3.60
3.58
3.58
3.56
3.08
3.06
3.05
3.04
2.69
2.67
2.64
2.61
2.56
2.51
2.50
2.47
2.45
1.85
1.82
1.80
1.78
1.77
1.75
1.73
1.71
1.02
1.00
0.98
H
H
O
O
3ba
1H NMR (400 MHz)
Solvent: CDCl3
1.00
0.96
0.99
2.03
1.06
1.01
1.03
3.21
2.21
3.13
f1 (ppm)


197.83
151.80
135.77
130.18
118.70
81.15
77.32
77.00
76.68
70.99
48.11
43.80
36.00
31.89
29.69
8.25
H
H
O
O
3ba
13C NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)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6.65
6.62
6.03
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5.56
5.54
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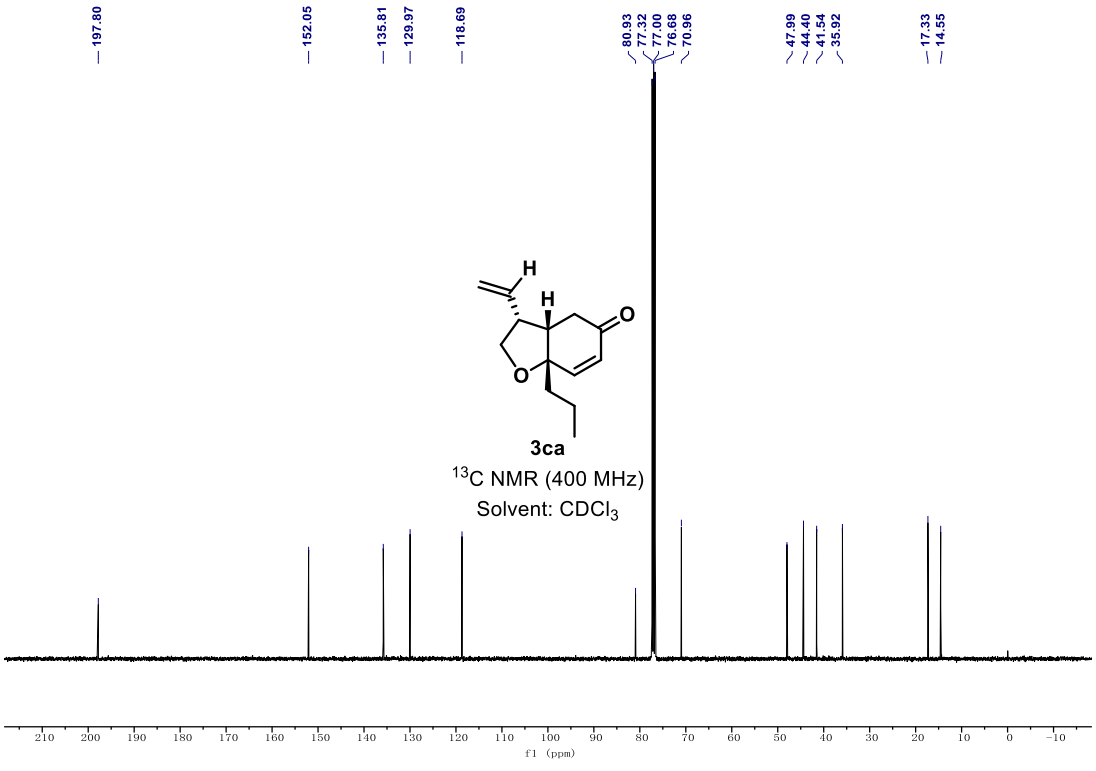
5.09
5.07
5.04
4.04
4.02
4.00
3.58
3.56
3.54
3.07
3.05
3.04
2.66
2.61
2.56
2.52
2.50
1.78
1.76
1.73
1.70
1.48
1.46
1.44
1.43
1.42
0.98
0.96
0.94
H
H
O
O
3ca
1H NMR (400 MHz)
Solvent: CDCl3
1.00
0.94
1.00
2.04
1.05
1.04
1.03
3.18
1.84
2.04
3.22
f1 (ppm)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80.93
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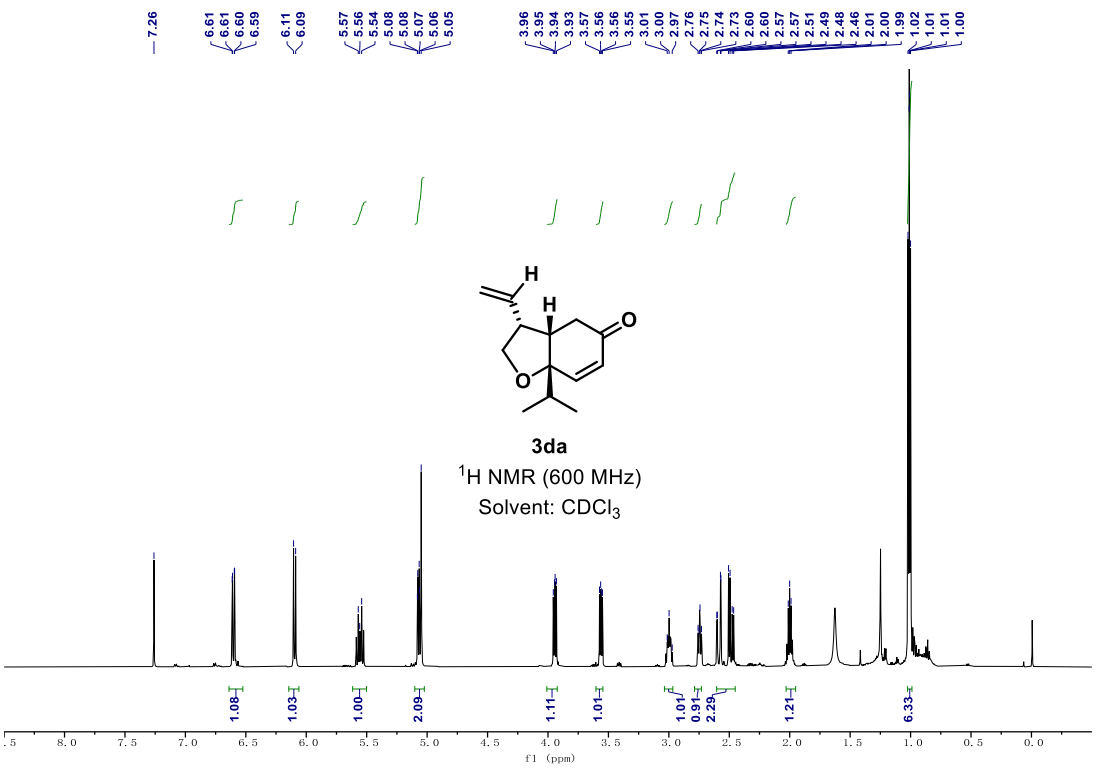
77.00
76.68
70.96
47.99
44.40
41.54
35.92
17.33
14.55
H
H
O
O
3ca
13C NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)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6.61
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6.60
6.59
6.11
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5.57
5.56
5.54
5.08
5.08
5.07
5.06
5.05
3.96
3.95
3.94
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3.57
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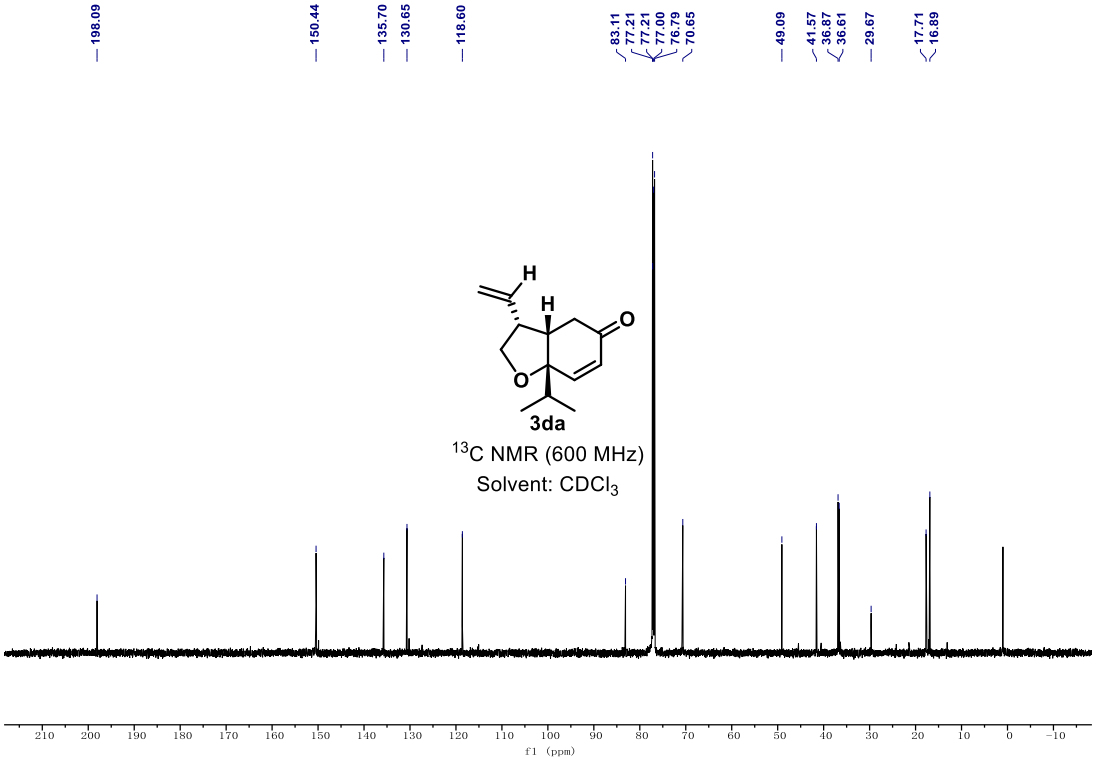
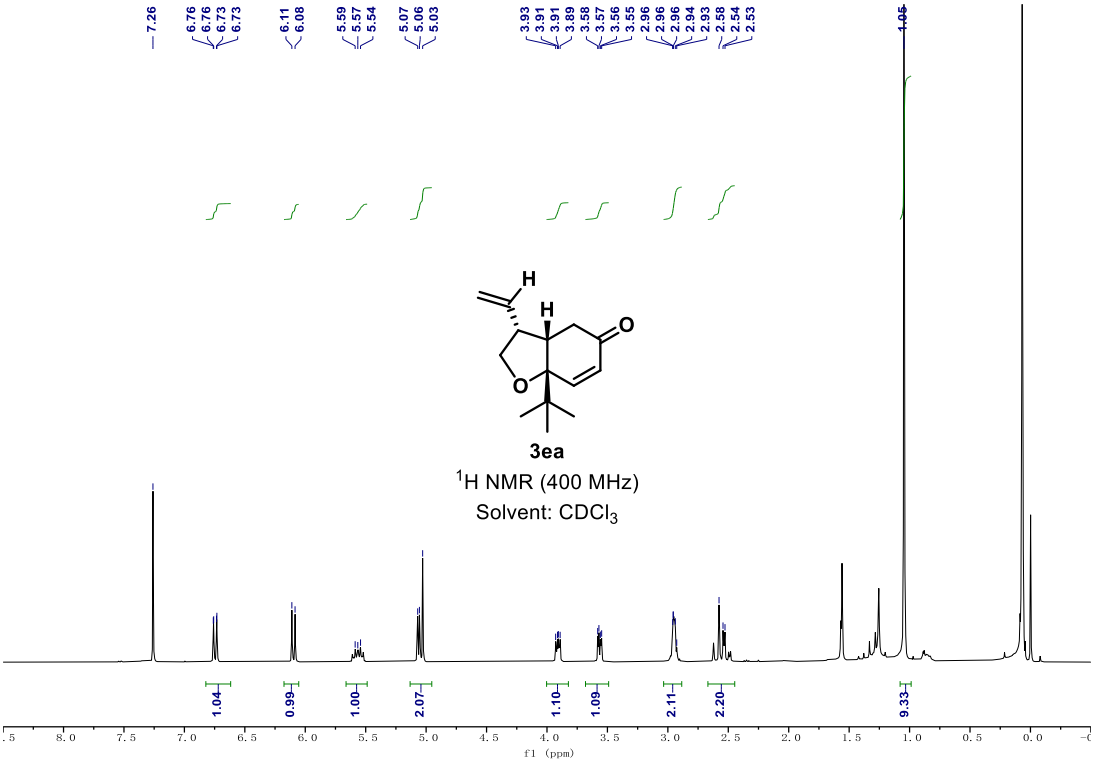
2.57
2.57
2.51
2.49
2.48
2.46
2.01
2.00
1.99
1.02
1.01
1.01
1.00
H
H
O
O
3da
1H NMR (600 MHz)
Solvent: CDCl3
1.08
1.03
1.00
2.09
1.11
1.01
1.01
0.91
2.29
1.21
6.33
f1 (ppm)

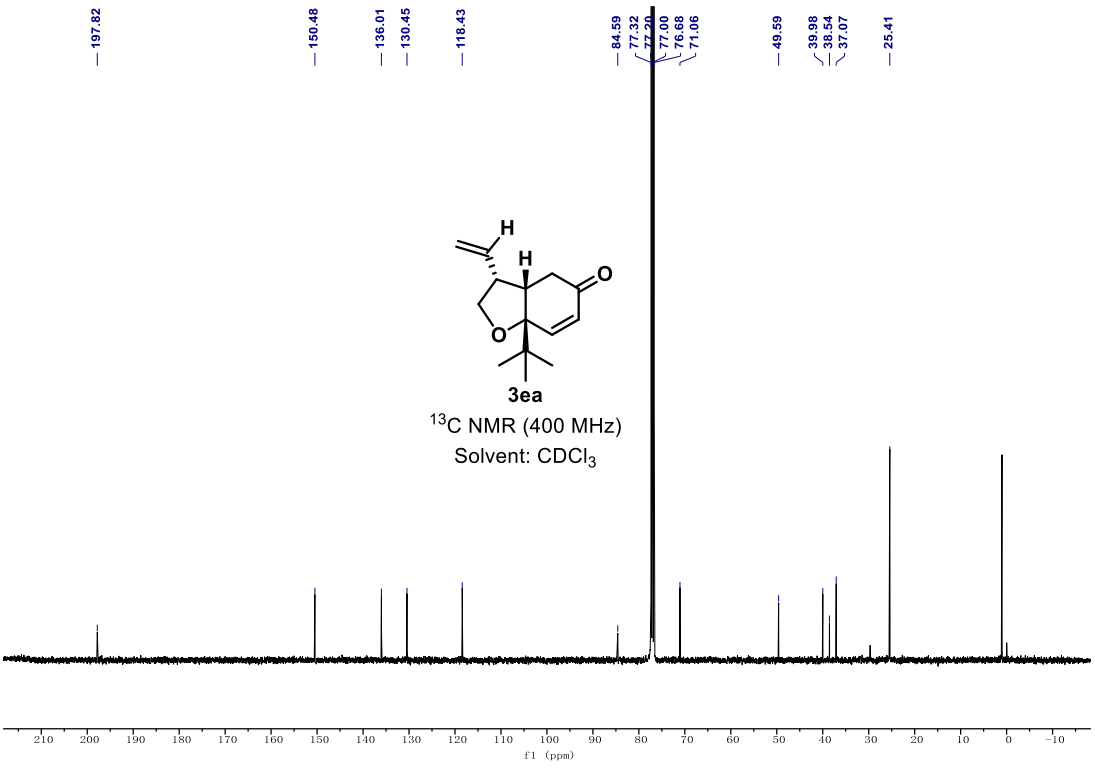

198.09
150.44
135.70
130.65
118.60
83.11
77.21
77.21
77.00
76.79
70.65
49.09
41.57
36.87
36.61
29.67
17.71
16.89
H
H
O
O
3da
13C NMR (600 MHz)
Solvent: CDCl3
f1 (ppm)



3ea

^{1}H NMR (400 MHz)

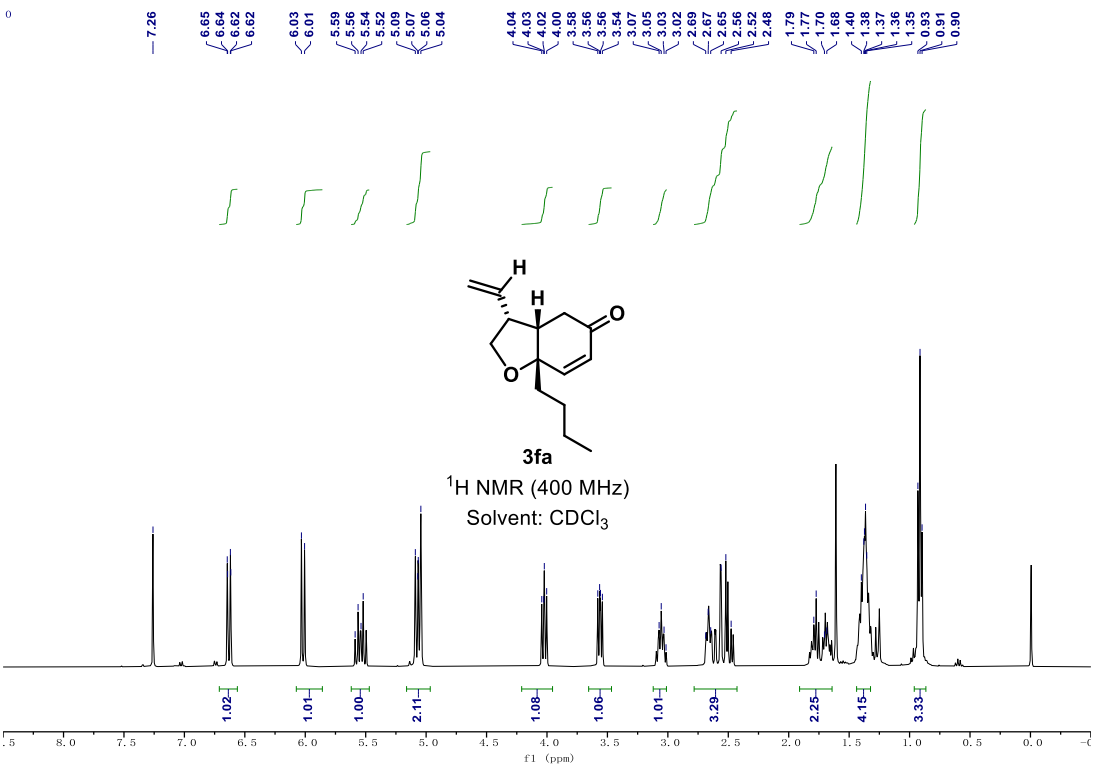
Solvent: $CDCl_3$



3ea

^{13}C NMR (400 MHz)

Solvent: $CDCl_3$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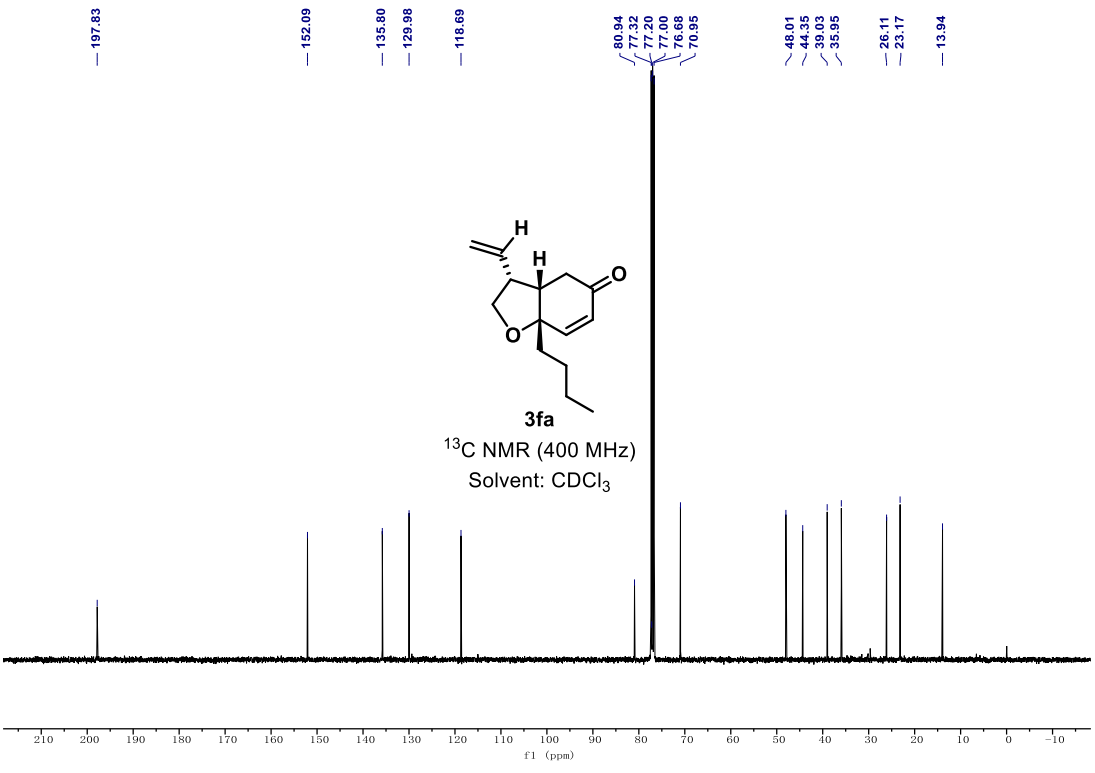
6.62
6.62
6.03
6.01
5.59
5.56
5.54
5.52
5.09
5.07
5.06
5.04
4.04
4.03
4.02
4.00
3.58
3.56
3.56
3.54
3.07
3.05
3.03
3.02
2.69
2.67
2.65
2.56
2.52
2.48
1.79
1.77
1.70
1.68
1.40
1.38
1.37
1.36
1.35
0.93
0.91
0.90
H
H
O
O
3fa
1H NMR (400 MHz)
Solvent: CDCl3
1.02
1.01
1.00
2.11
1.08
1.06
1.01
3.29
2.25
4.15
3.33
f1 (ppm)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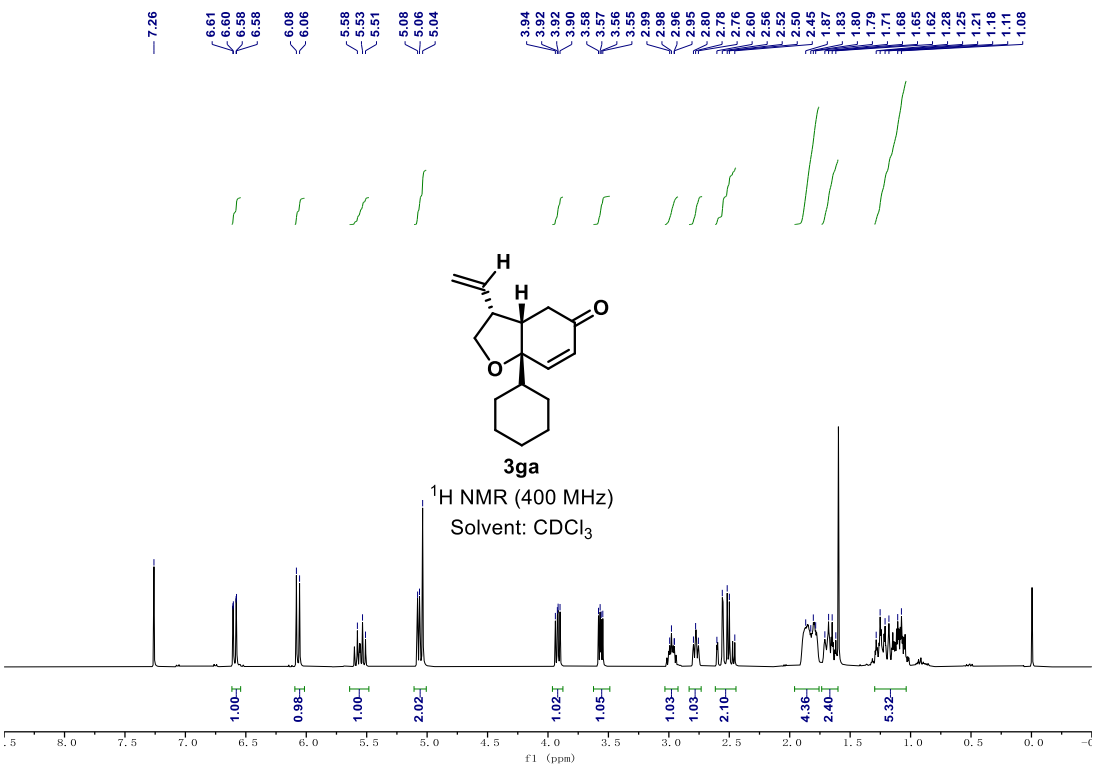
77.32
77.20
77.00
76.68
70.95
48.01
44.35
39.03
35.95
26.11
23.17
13.94
H
H
O
O
3fa
13C NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)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6.06
5.58
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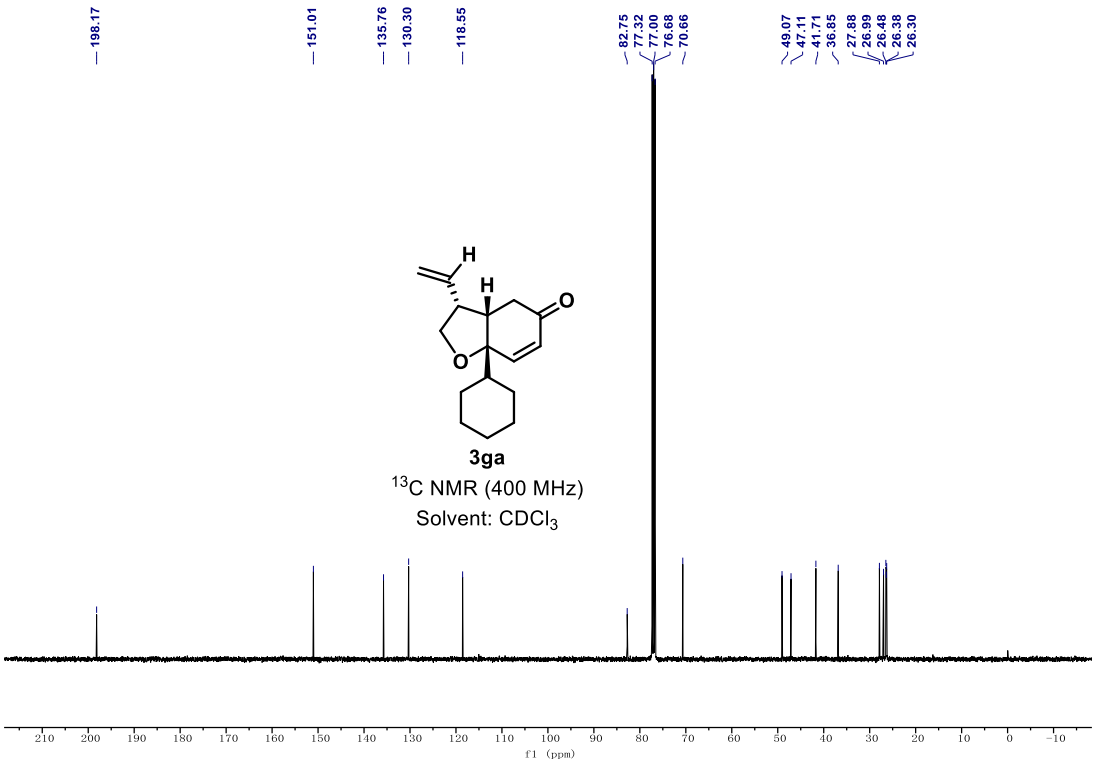
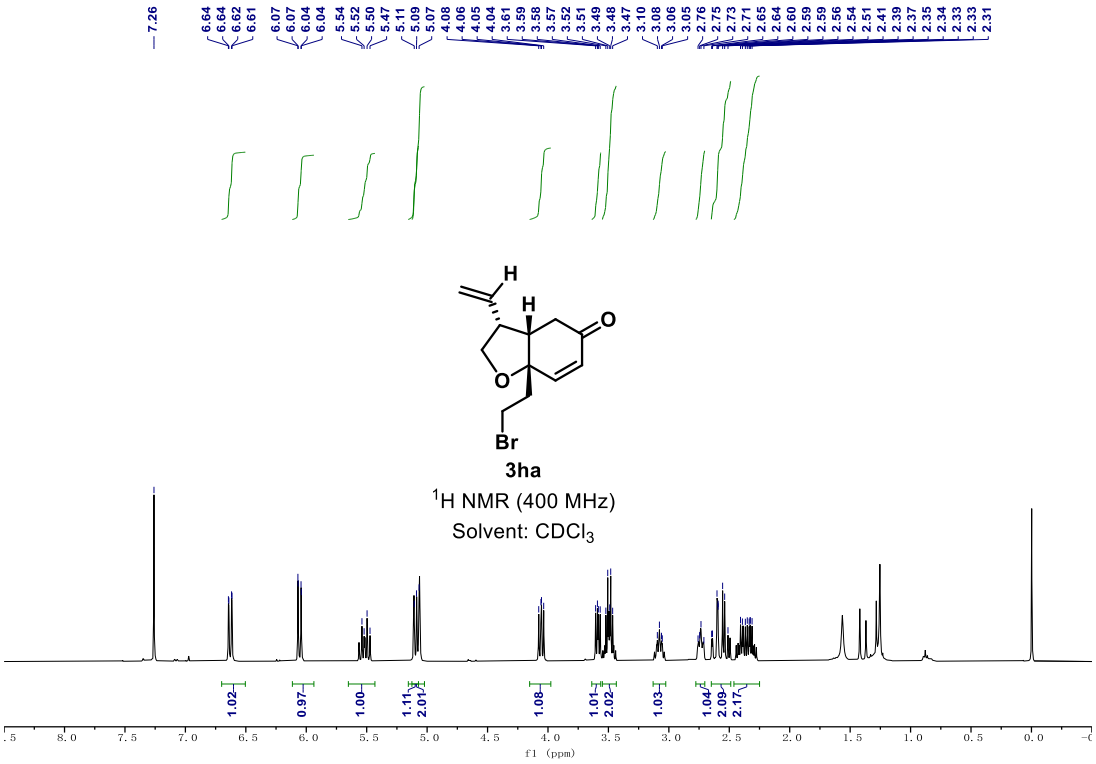
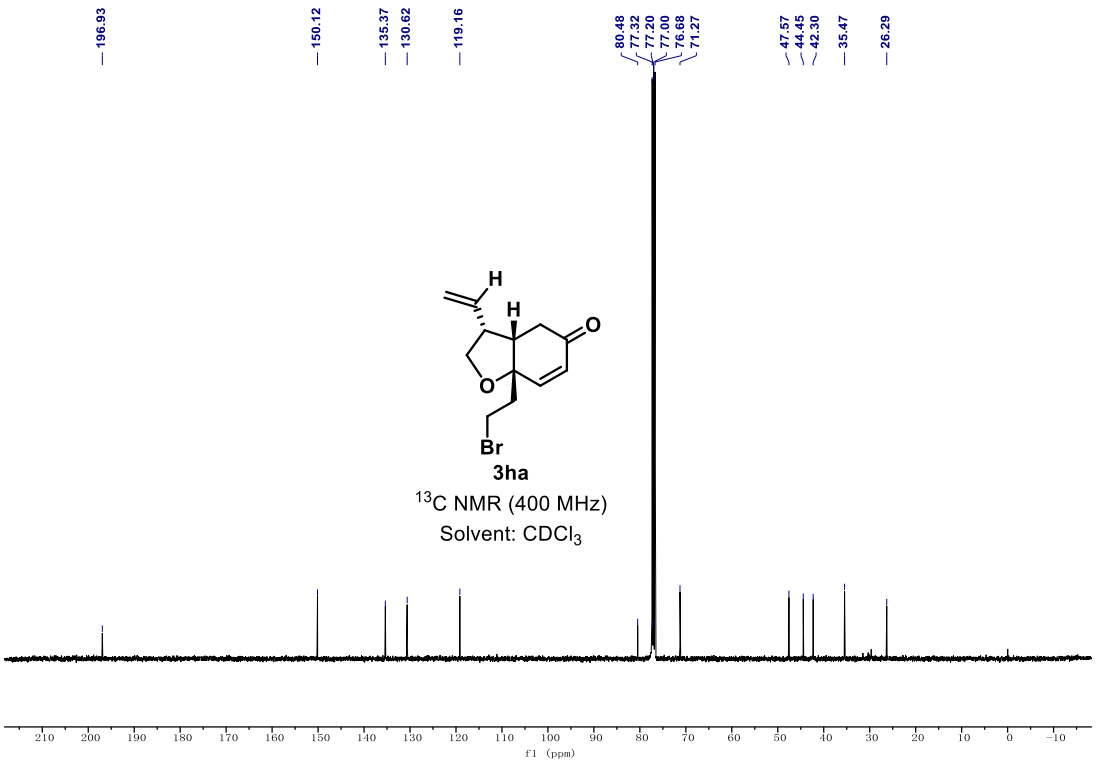
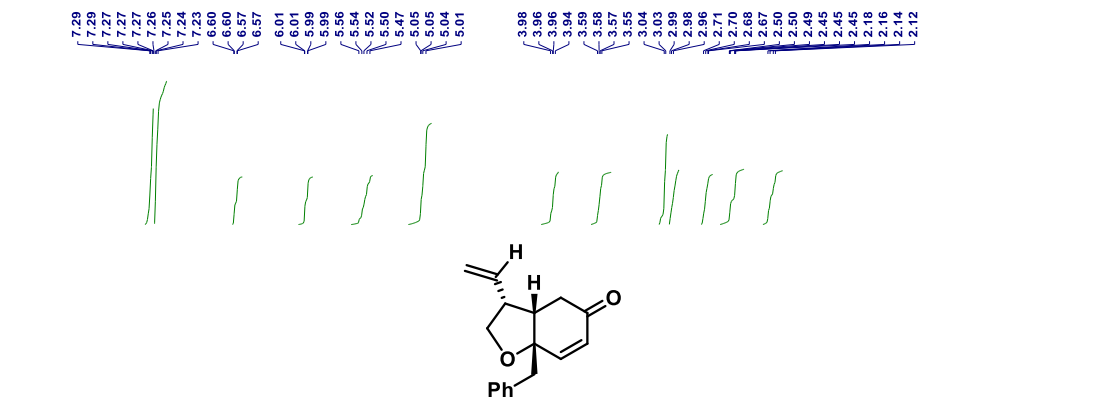
2.76
2.60
2.56
2.52
2.50
2.45
1.87
1.83
1.80
1.79
1.71
1.68
1.65
1.62
1.28
1.25
1.21
1.18
1.11
1.08
H
H
O
O
3ga
1H NMR (400 MHz)
Solvent: CDCl3
1.00
0.98
1.00
2.02
1.02
1.05
1.03
1.03
2.10
4.36
2.40
5.32
f1 (ppm)


198.17
151.01
135.76
130.30
118.55
82.75
77.32
77.00
76.68
70.66
49.07
47.11
41.71
36.85
27.88
26.99
26.48
26.38
26.30
H
H
O
O
3ga
13C NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)


7.26
6.64
6.64
6.62
6.61
6.07
6.07
6.04
6.04
5.54
5.52
5.50
5.47
5.11
5.09
5.07
4.08
4.06
4.05
4.04
3.61
3.59
3.58
3.57
3.52
3.51
3.49
3.48
3.47
3.10
3.08
3.06
3.05
2.76
2.75
2.73
2.71
2.65
2.64
2.60
2.59
2.59
2.56
2.54
2.51
2.41
2.39
2.37
2.35
2.34
2.33
2.33
2.31
H
H
O
O
Br
3ha
1H NMR (400 MHz)
Solvent: CDCl3
1.02
0.97
1.00
1.11
2.01
1.08
1.01
2.02
1.03
1.04
2.09
2.17
f1 (ppm)

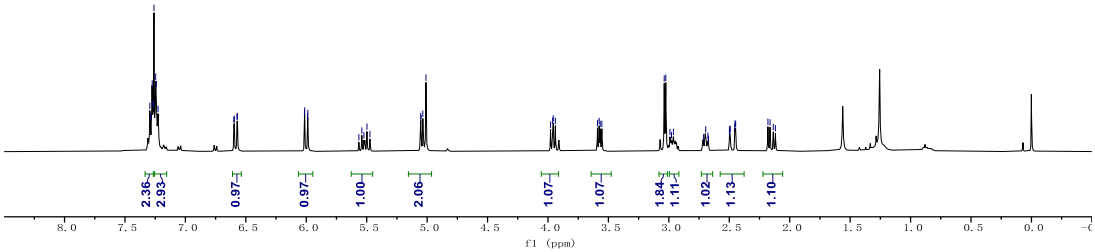

196.93
150.12
135.37
130.62
119.16
80.48
77.32
77.20
77.00
76.68
71.27
47.57
44.45
42.30
35.47
26.29
H
H
O
O
Br
3ha
13C NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)

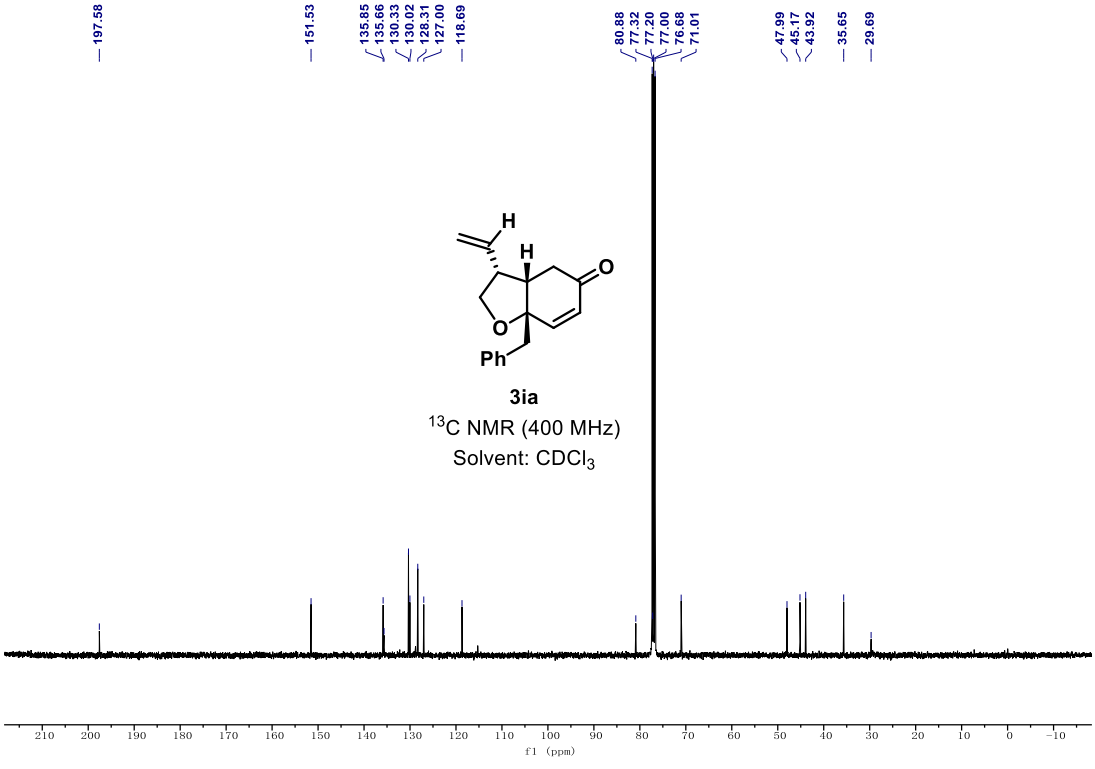


3ia

^{1}H NMR (400 MHz)

Solvent: $CDCl_3$

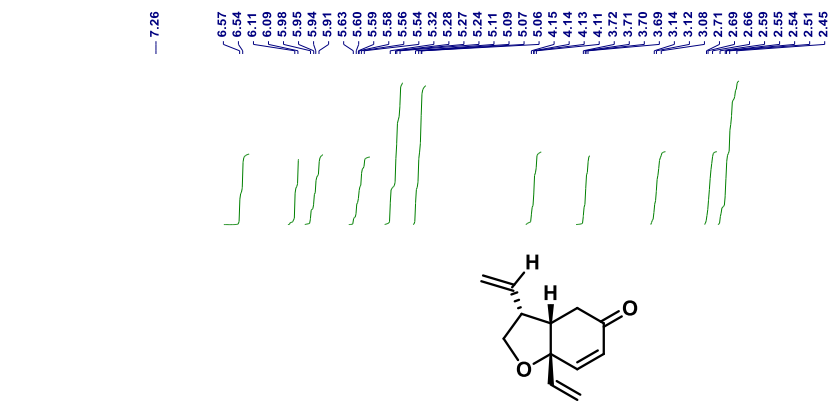




3ia

^{13}C NMR (400 MHz)

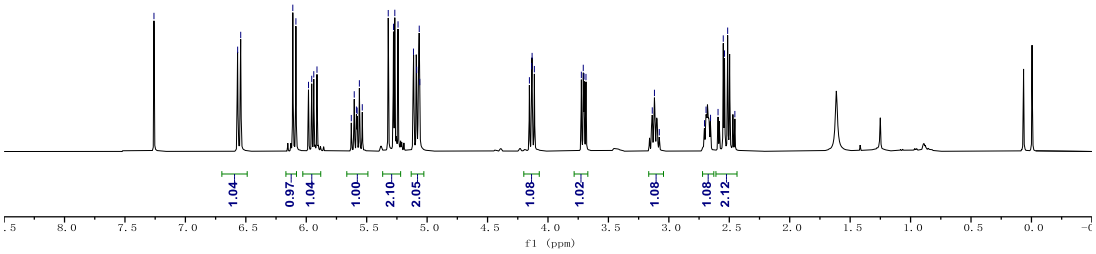
Solvent: $CDCl_3$

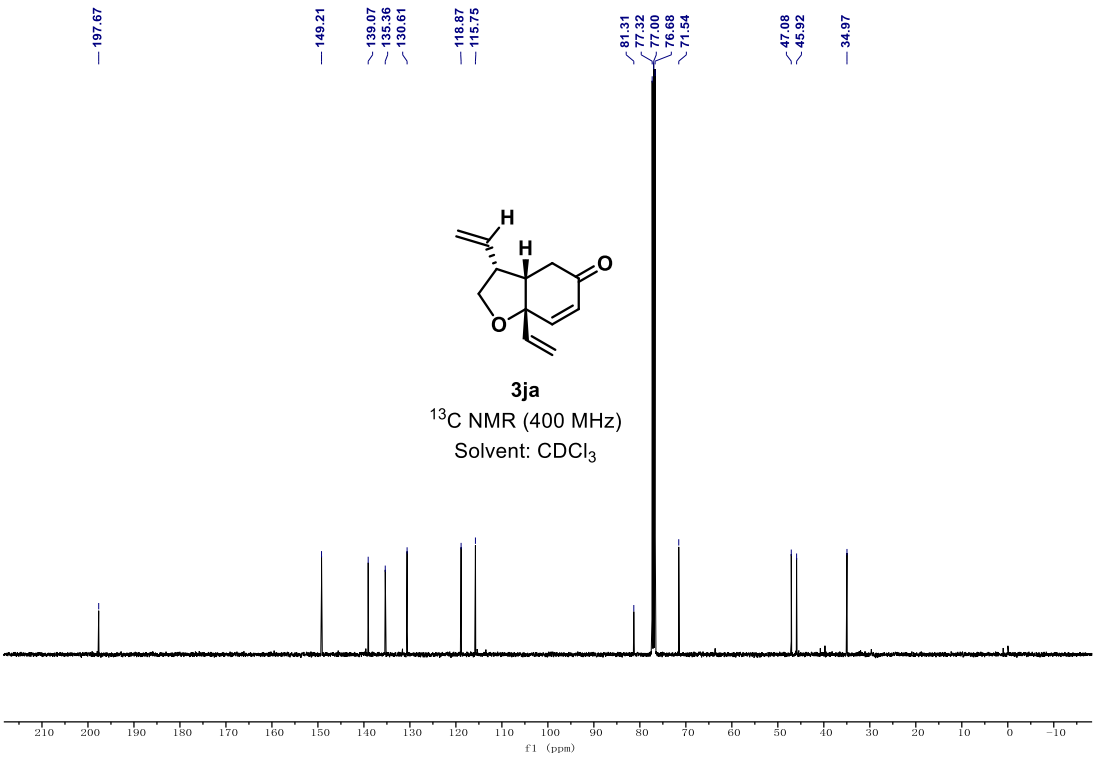


3ja

^{1}H NMR (400 MHz)

Solvent: $CDCl_3$

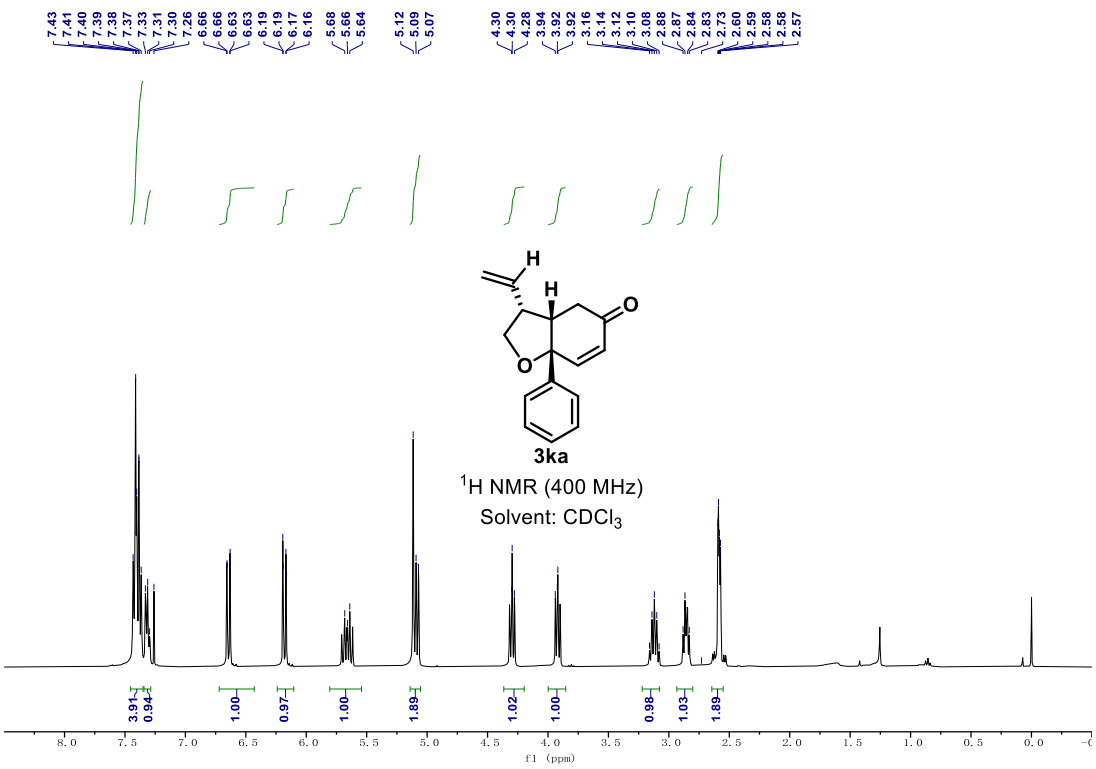


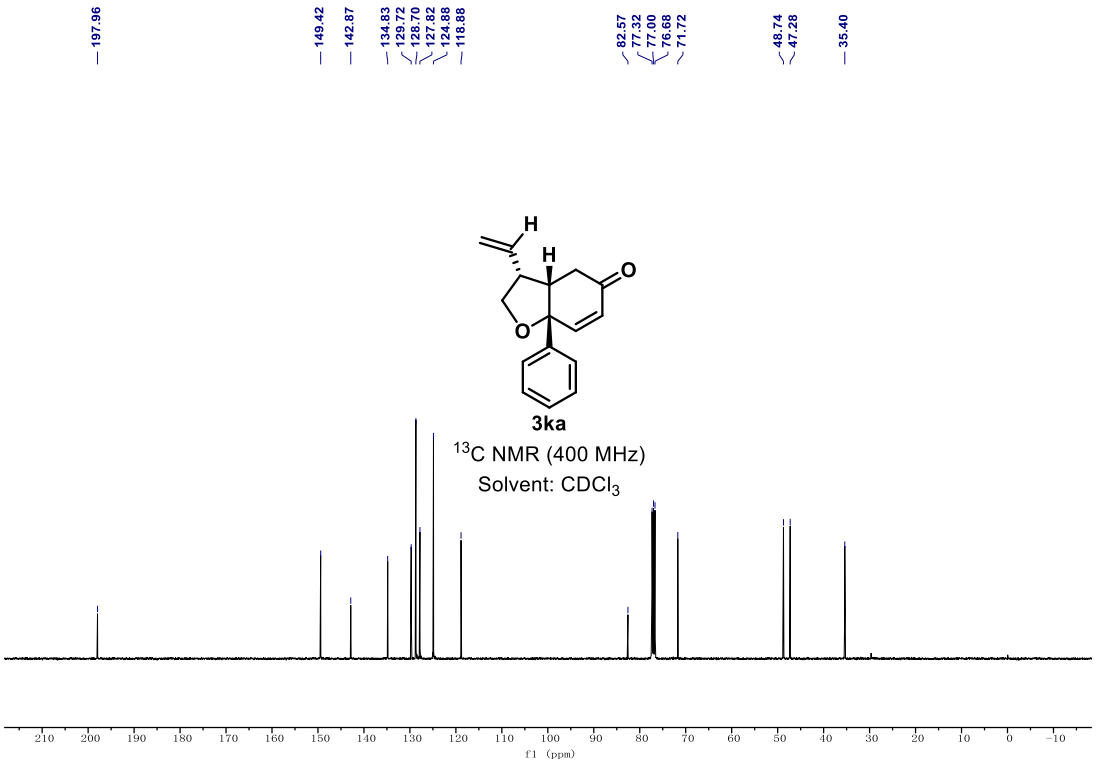


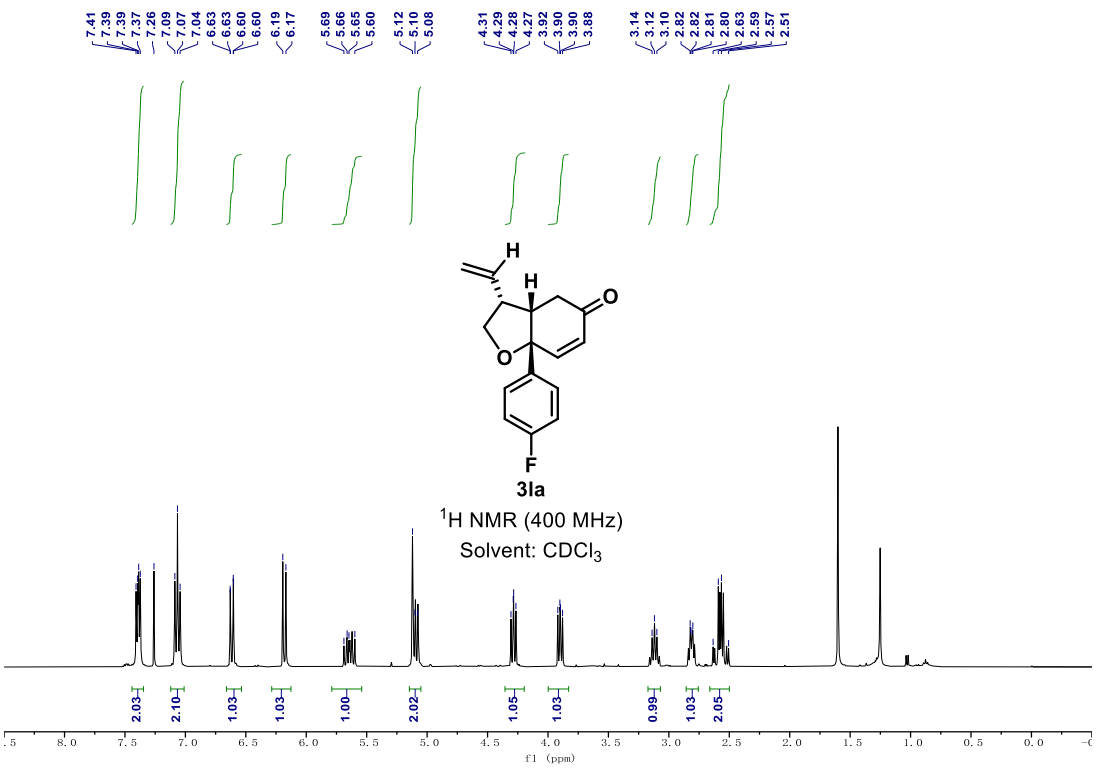
3ja

^{13}C NMR (400 MHz)

Solvent: $CDCl_3$


7.43
7.41
7.40
7.39
7.38
7.37
7.33
7.31
7.30
7.26
6.66
6.66
6.63
6.63
6.19
6.19
6.17
6.16
5.68
5.66
5.64
5.12
5.09
5.07
4.30
4.30
4.28
3.94
3.92
3.92
3.16
3.14
3.12
3.10
3.08
2.88
2.87
2.84
2.83
2.73
2.60
2.59
2.58
2.58
2.57
H
H
O
O
3ka
1H NMR (400 MHz)
Solvent: CDCl3
3.91
0.94
1.00
0.97
1.00
1.89
1.02
1.00
0.98
1.03
1.89
f1 (ppm)

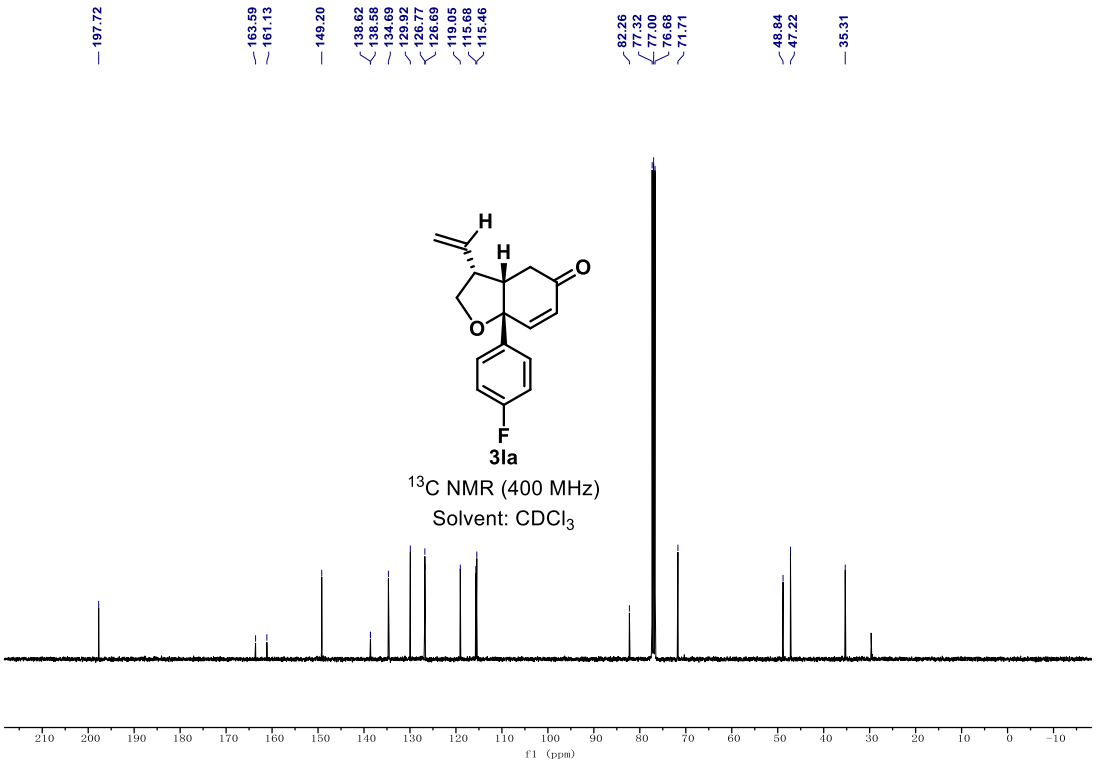

197.96
149.42
142.87
134.83
129.72
128.70
127.82
124.88
118.88
82.57
77.32
77.00
76.68
71.72
48.74
47.28
35.40
H
H
O
O
3ka
13C NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)



3la

^{1}H NMR (400 MHz)

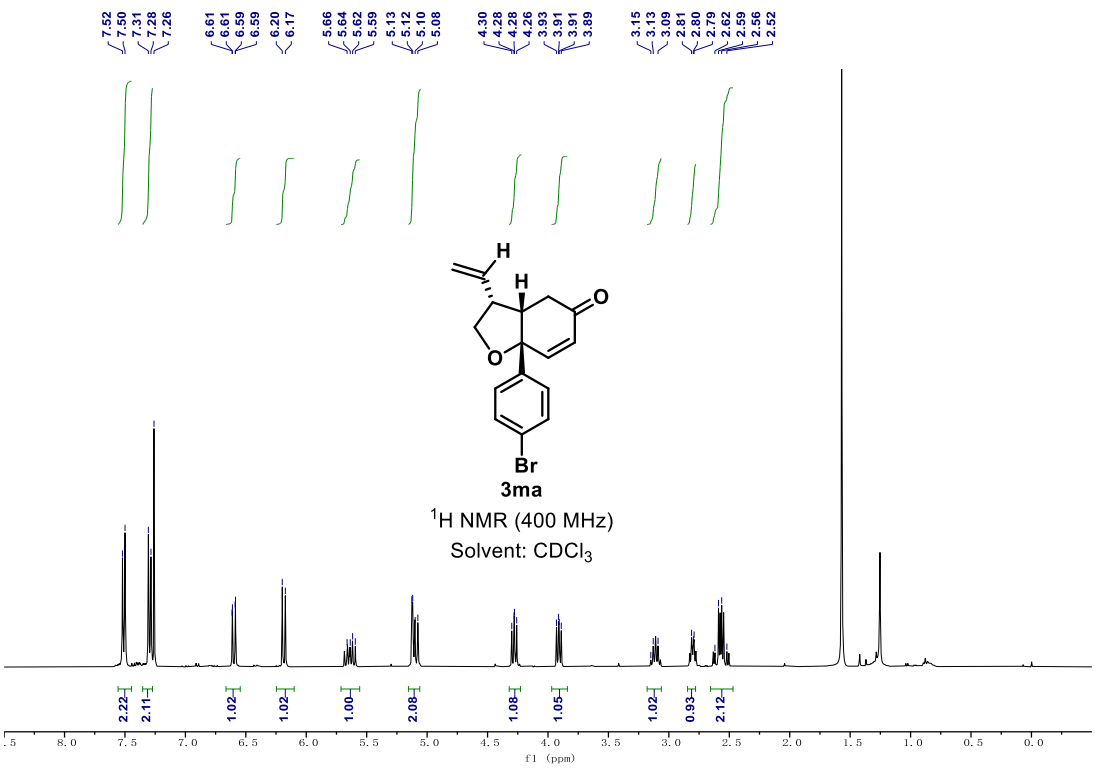
Solvent: $CDCl_3$

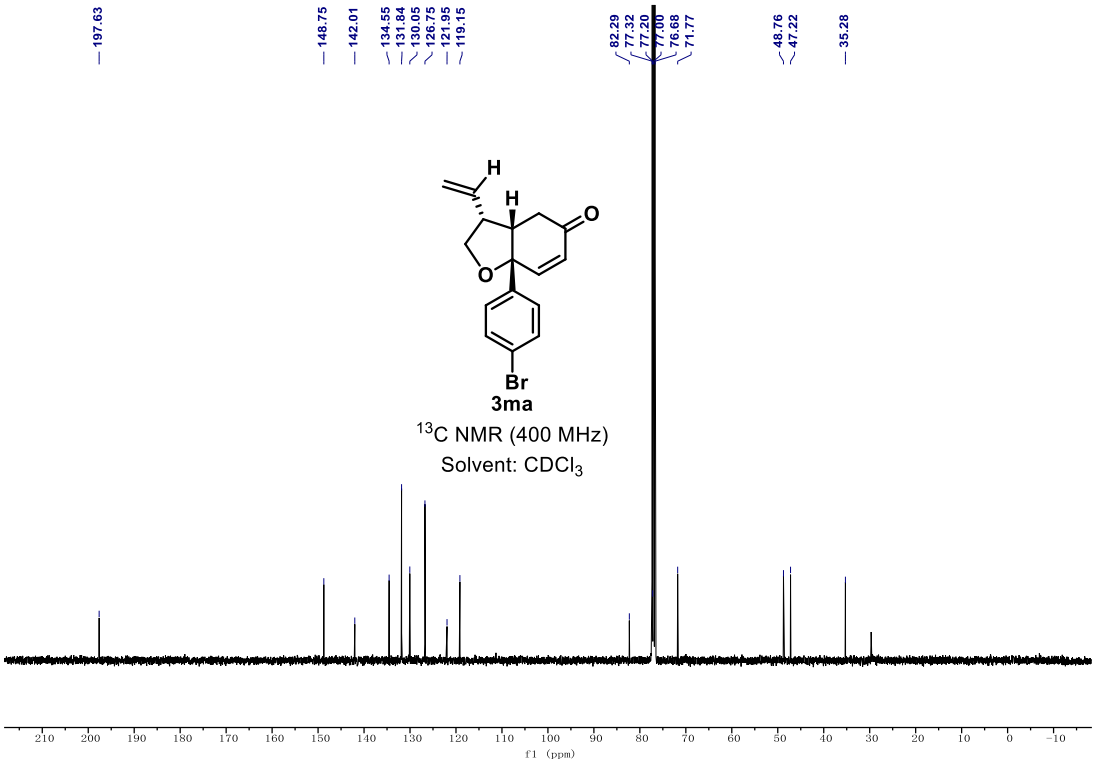


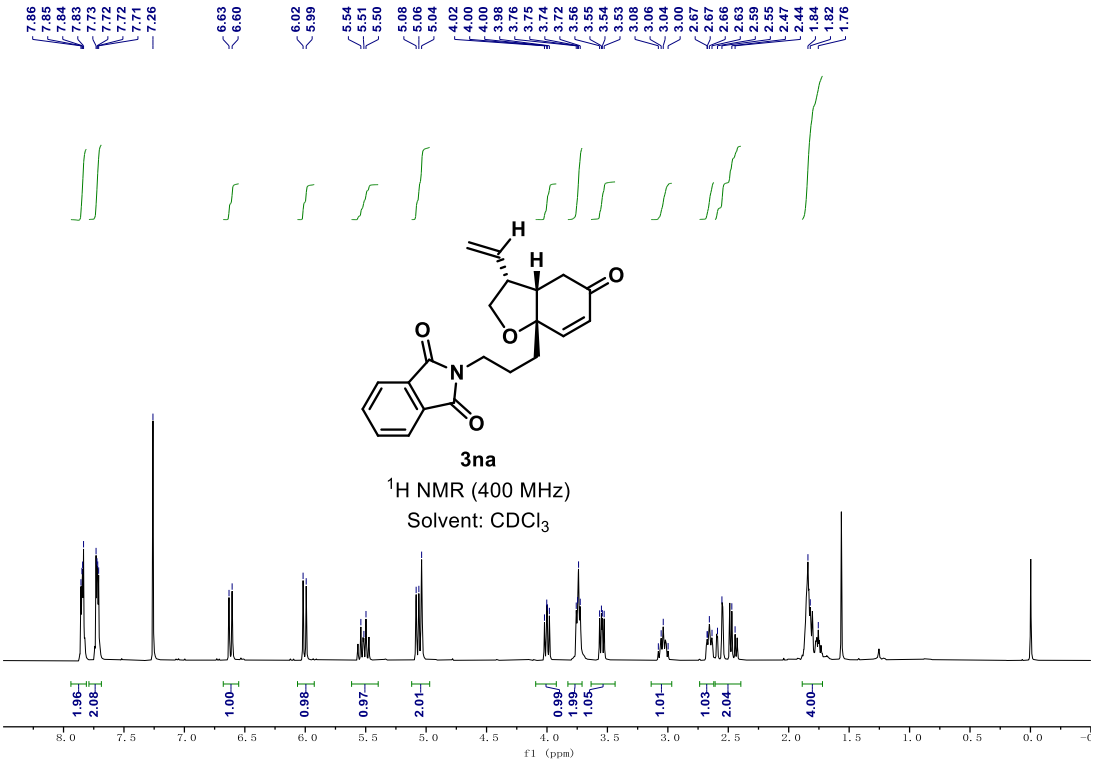
3la

^{13}C NMR (400 MHz)

Solvent: $CDCl_3$


7.52
7.50
7.31
7.28
7.26
6.61
6.61
6.59
6.59
6.20
6.17
5.66
5.64
5.62
5.59
5.13
5.12
5.10
5.08
4.30
4.28
4.28
4.26
3.93
3.91
3.91
3.89
3.15
3.13
3.09
2.81
2.80
2.79
2.62
2.59
2.56
2.52
H
H
O
O
Br
3ma
1H NMR (400 MHz)
Solvent: CDCl3
2.22
2.11
1.02
1.02
1.00
2.08
1.08
1.05
1.02
0.93
2.12
f1 (ppm)

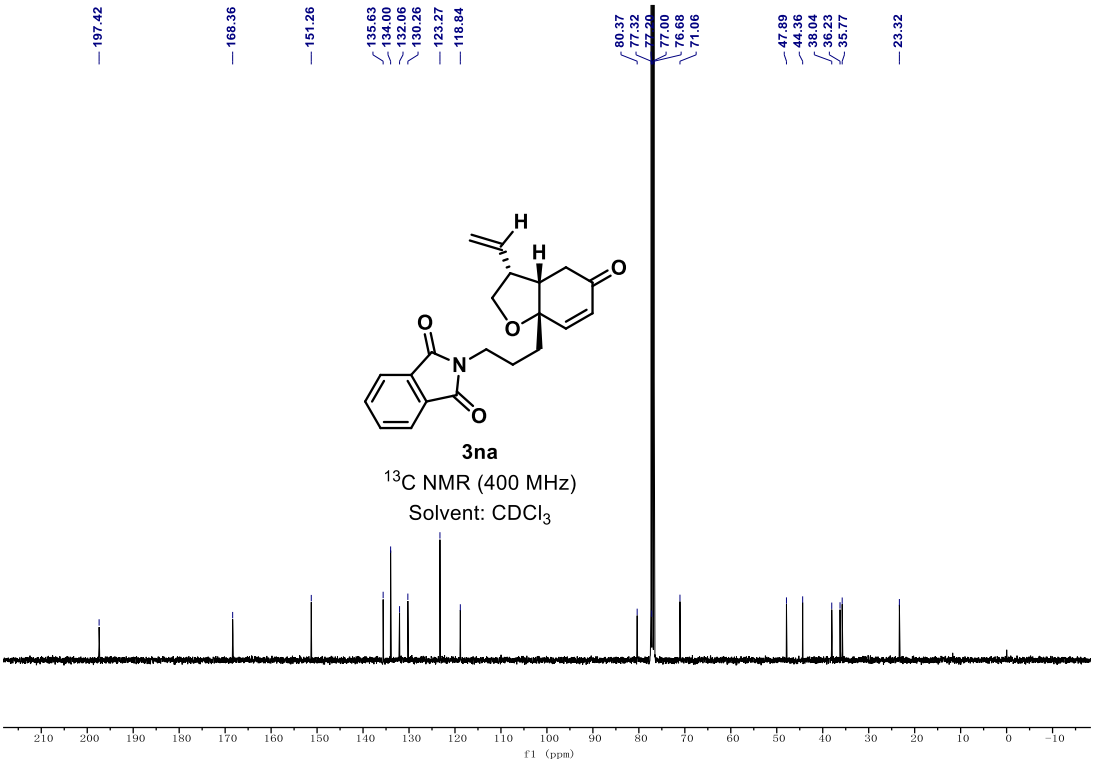

197.63
148.75
142.01
134.55
131.84
130.05
126.75
121.95
119.15
82.29
77.32
77.20
77.00
76.68
71.77
48.76
47.22
35.28
H
H
O
O
Br
3ma
13C NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)



3na

^{1}H NMR (400 MHz)

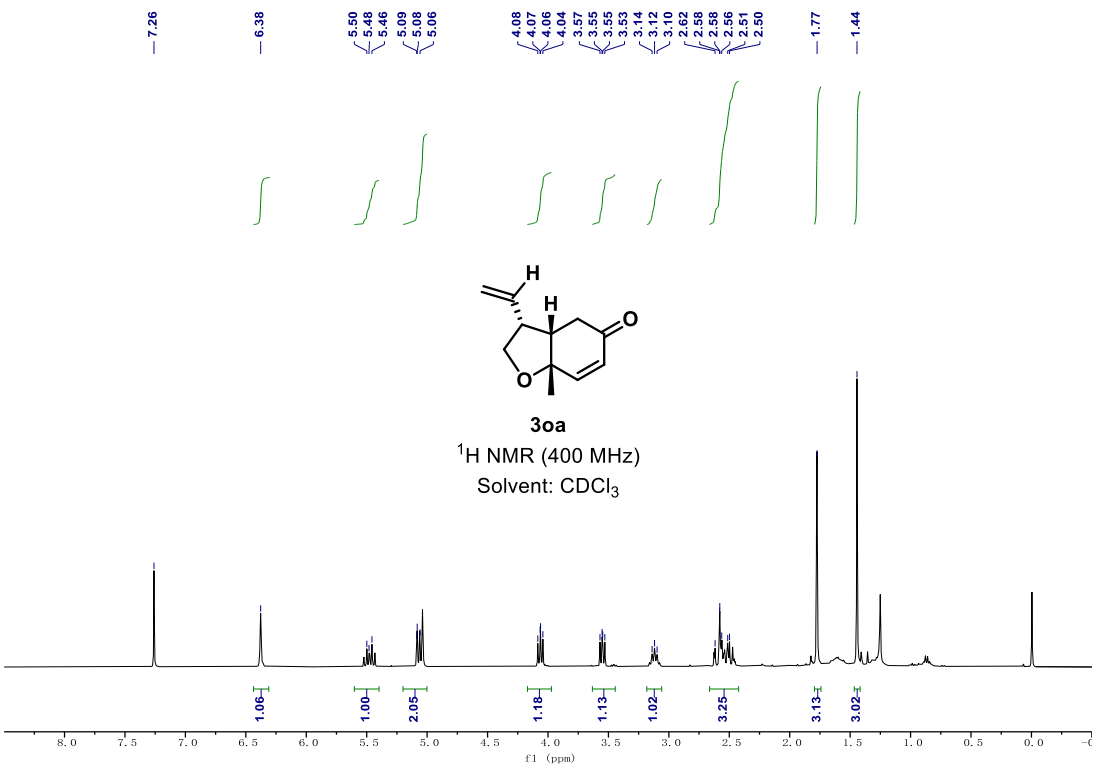
Solvent: $CDCl_3$



3na

^{13}C NMR (400 MHz)

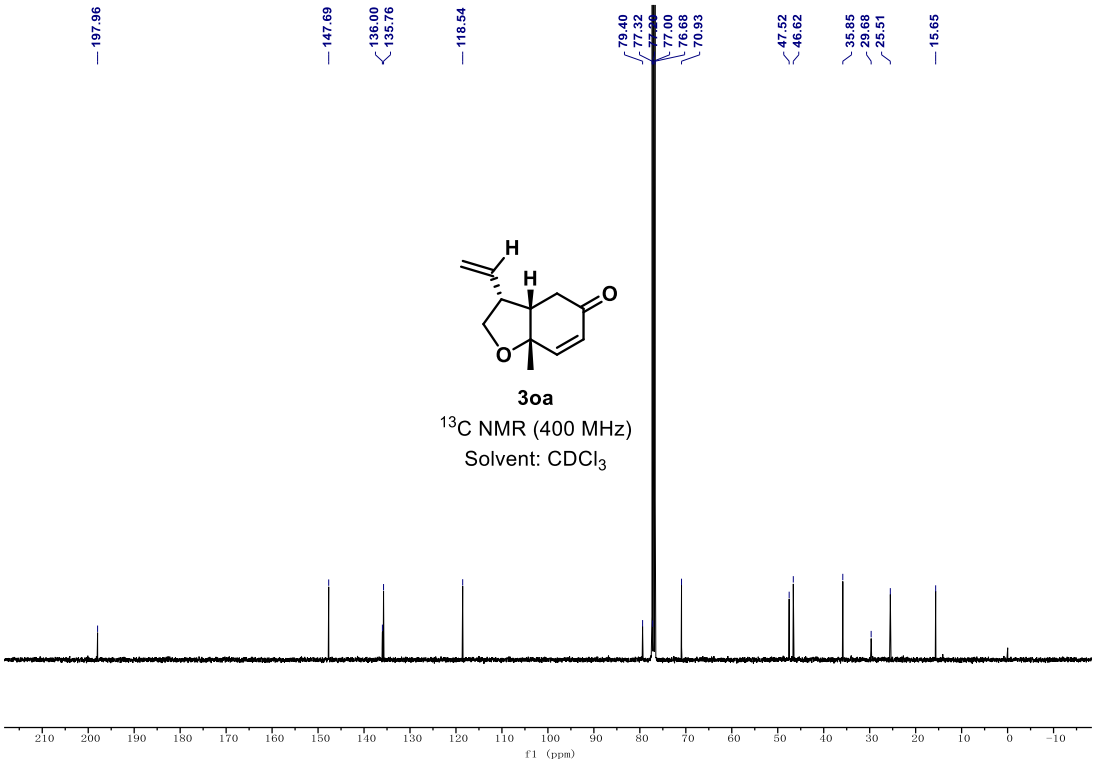
Solvent: $CDCl_3$



3oa

^{1}H NMR (400 MHz)

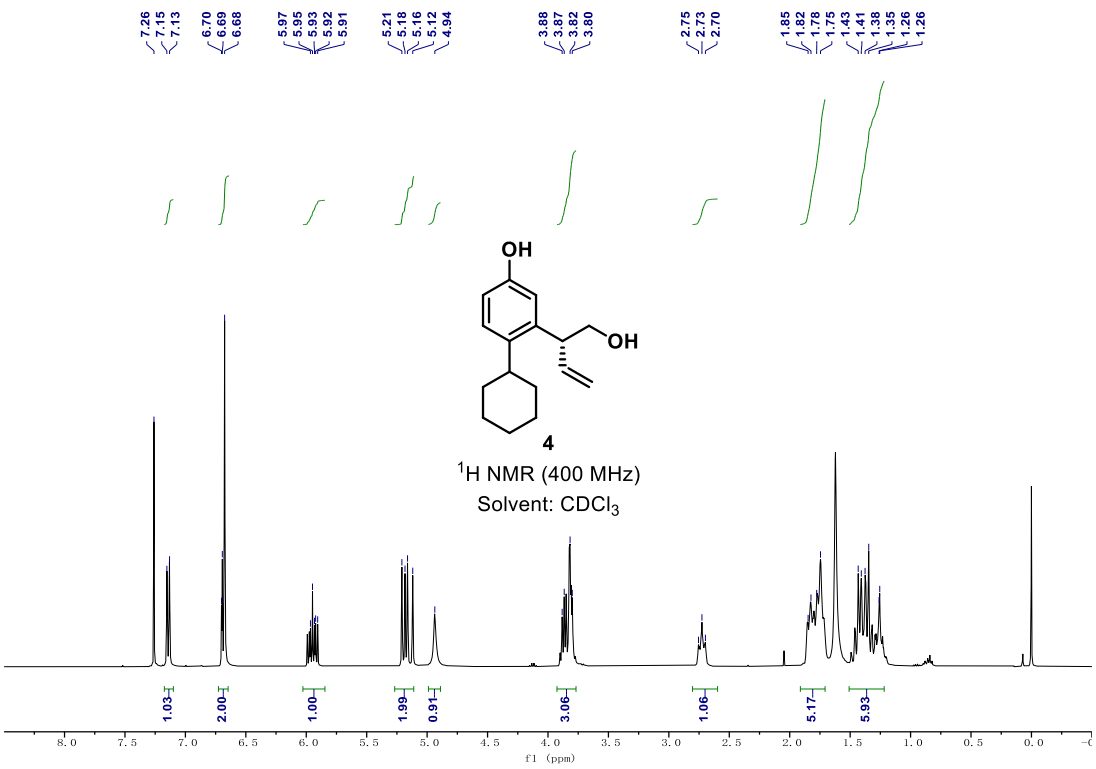
Solvent: $CDCl_3$

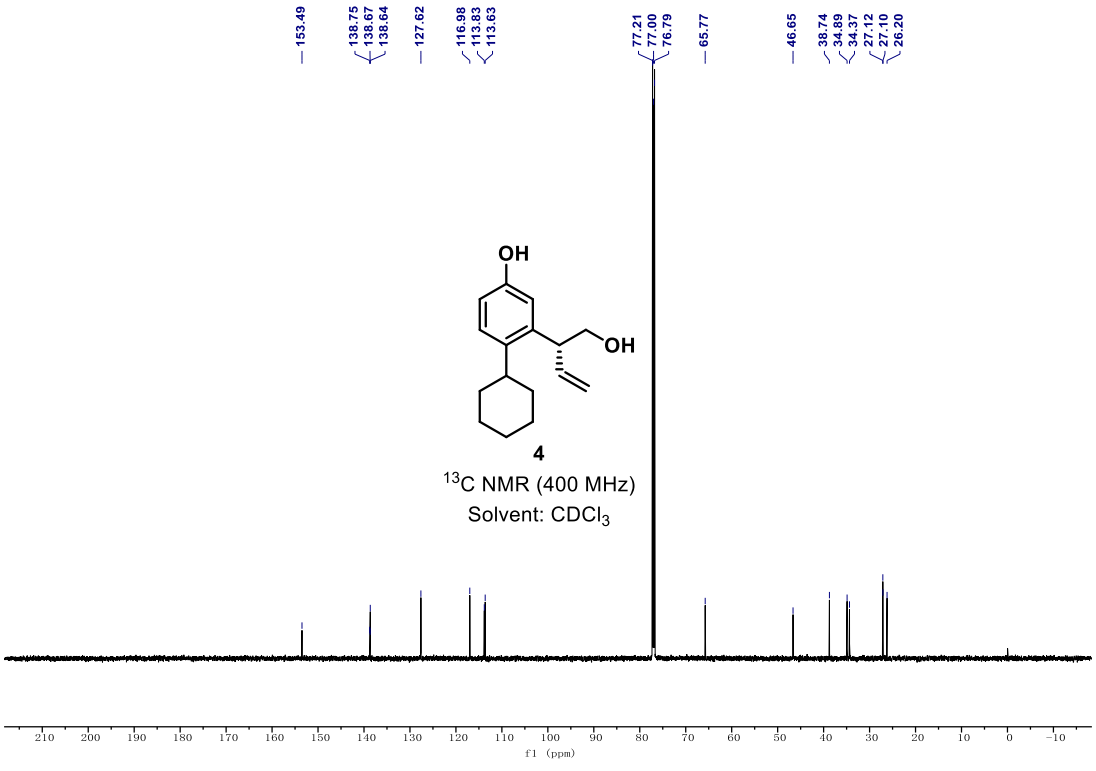


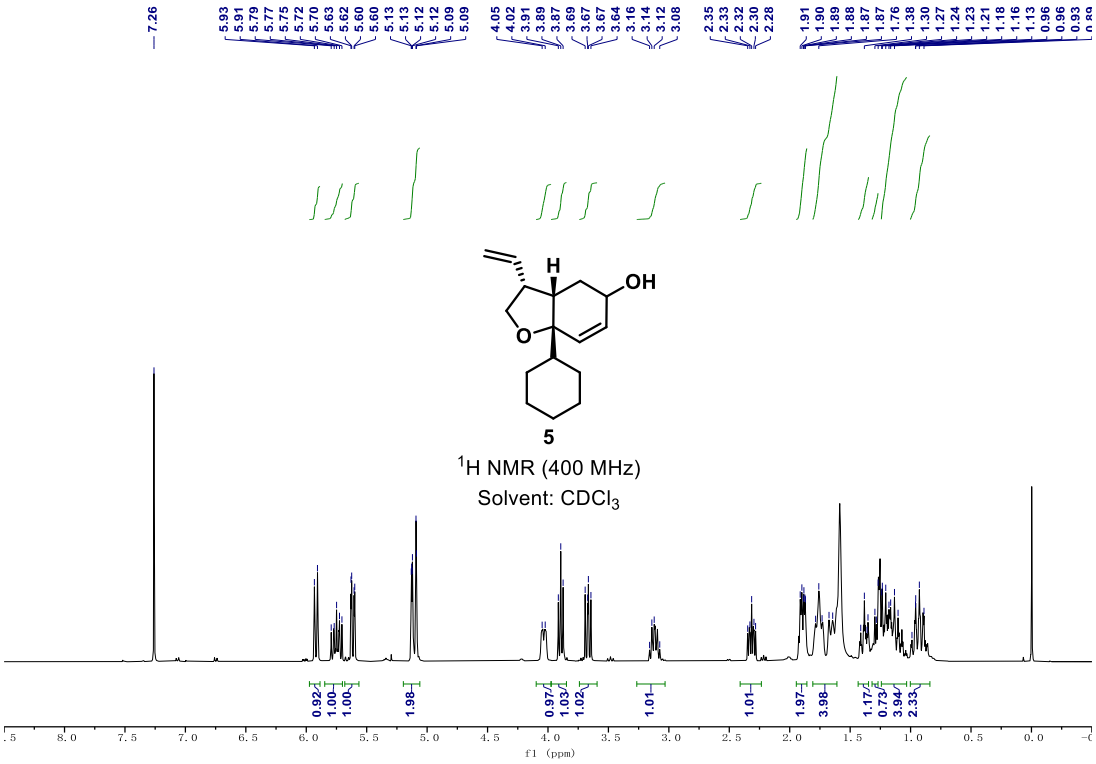
3oa

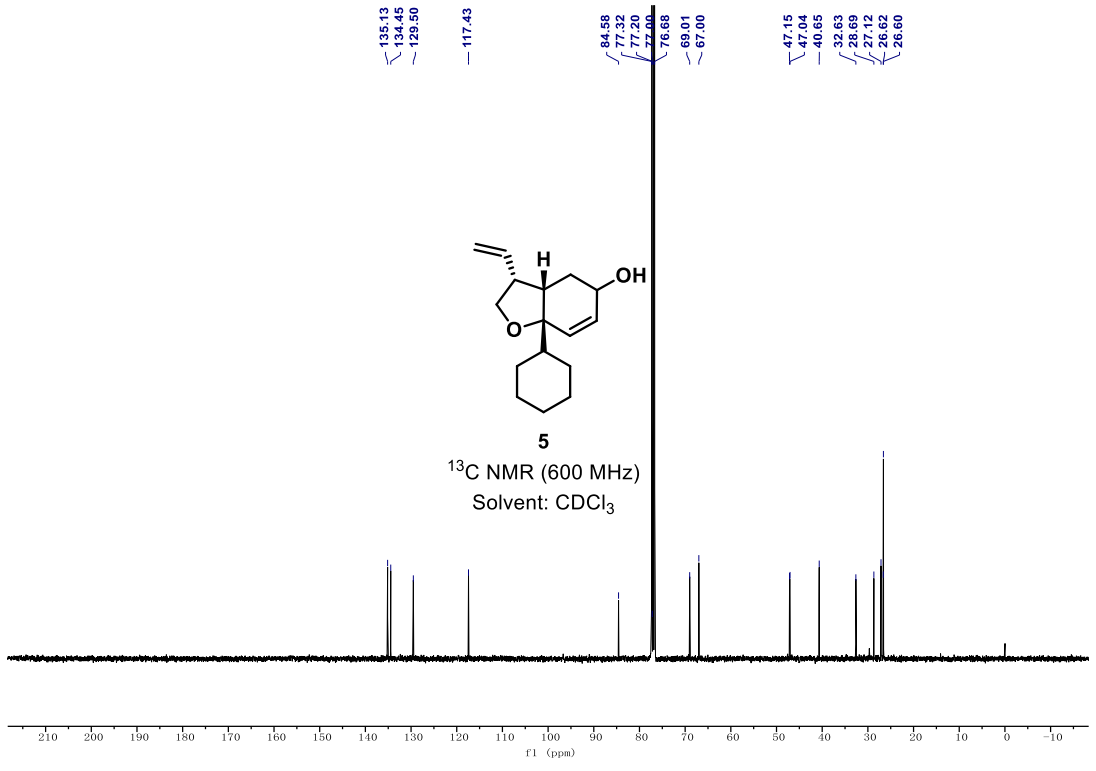
^{13}C NMR (400 MHz)

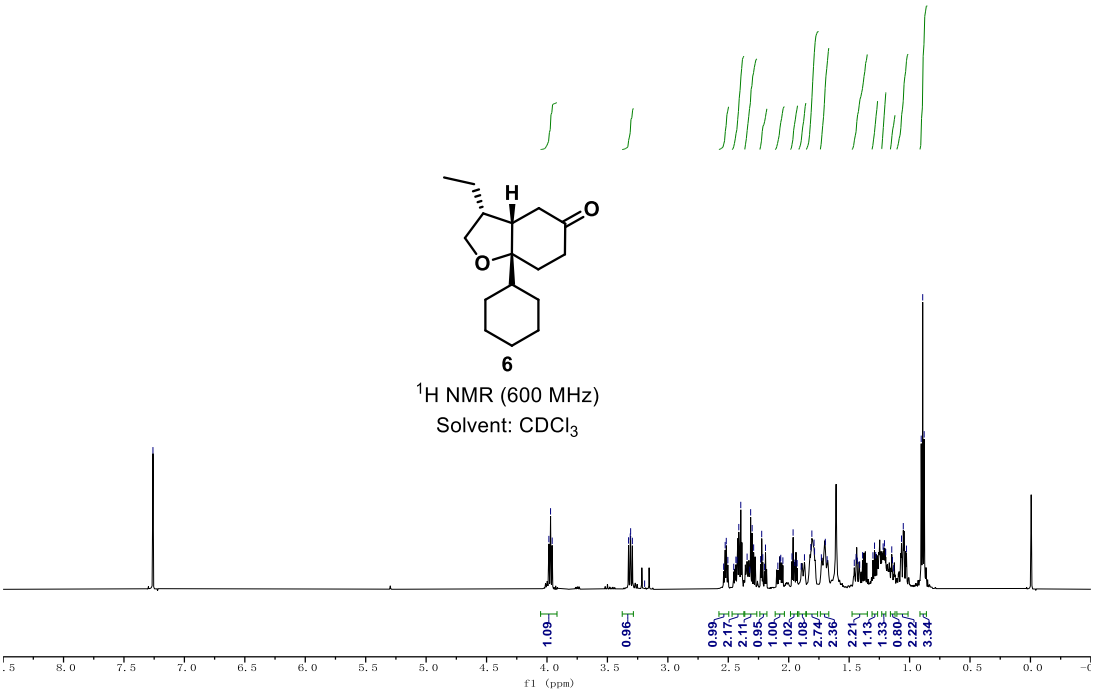
Solvent: $CDCl_3$


7.26
7.15
7.13
6.70
6.69
6.68
5.97
5.95
5.93
5.92
5.91
5.21
5.18
5.16
5.12
4.94
3.88
3.87
3.82
3.80
2.75
2.73
2.70
1.85
1.82
1.78
1.75
1.43
1.41
1.38
1.35
1.26
1.26
OH
OH
4
1H NMR (400 MHz)
Solvent: CDCl3
1.03
2.00
1.00
1.99
0.91
3.06
1.06
5.17
5.93
f1 (ppm)


153.49
138.75
138.67
138.64
127.62
116.98
113.83
113.63
77.21
77.00
76.79
65.77
46.65
38.74
34.89
34.37
27.12
27.10
26.20
OH
OH
4
13C NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)


7.26
5.93
5.91
5.79
5.77
5.75
5.72
5.70
5.63
5.62
5.60
5.60
5.13
5.13
5.12
5.12
5.09
5.09
4.05
4.02
3.91
3.89
3.87
3.69
3.67
3.67
3.64
3.16
3.14
3.12
3.08
2.35
2.33
2.32
2.30
2.28
1.91
1.90
1.89
1.88
1.87
1.87
1.76
1.38
1.30
1.27
1.24
1.23
1.21
1.18
1.16
1.13
0.96
0.96
0.93
H
OH
O
5
1H NMR (400 MHz)
Solvent: CDCl3
0.92
1.00
1.00
1.98
0.97
1.03
1.02
1.01
1.01
1.97
3.98
1.17
0.73
3.94
2.33
f1 (ppm)

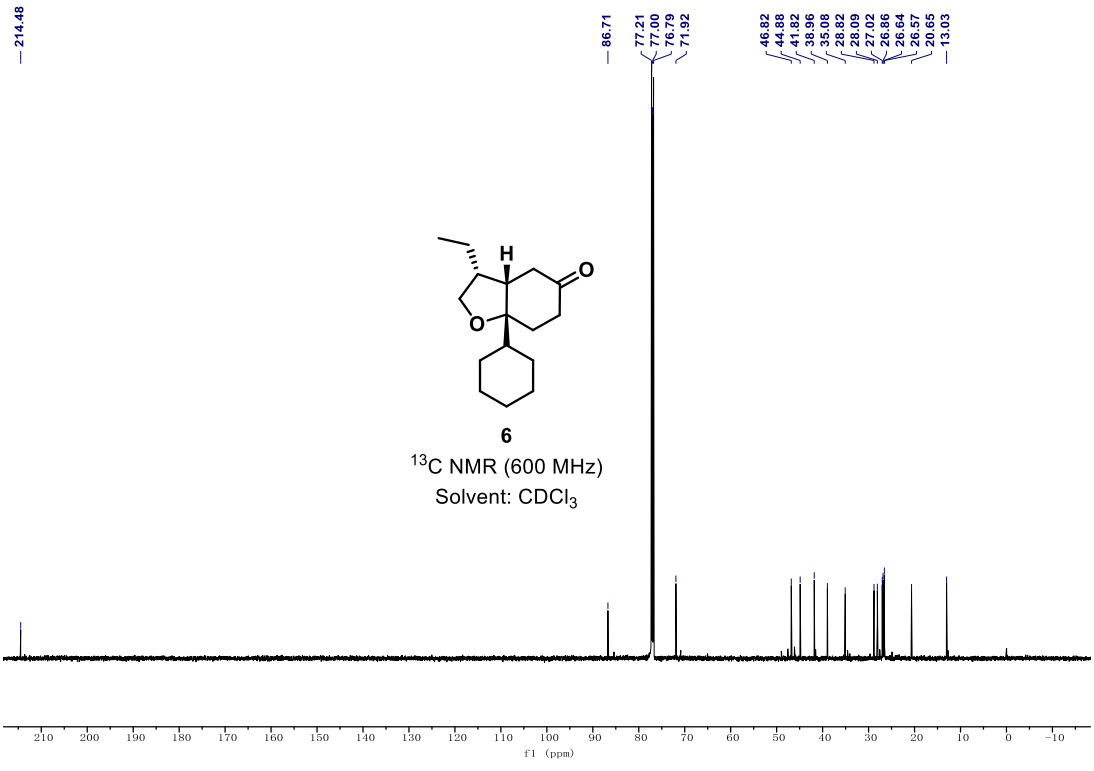

135.13
134.45
129.50
117.43
84.58
77.32
77.20
77.00
76.68
69.01
67.00
47.15
47.04
40.65
32.63
28.69
27.12
26.62
26.60
H
OH
O
5
13C NMR (600 MHz)
Solvent: CDCl3
f1 (ppm)



6

^{1}H NMR (600 MHz)

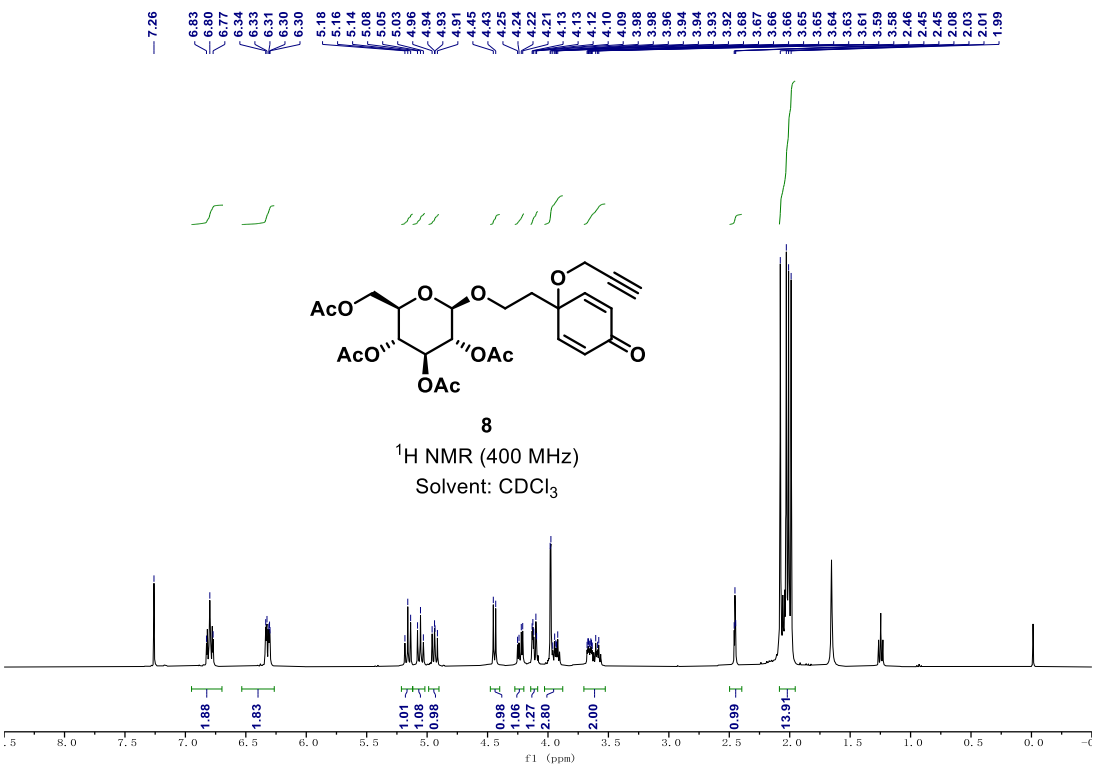
Solvent: $CDCl_3$

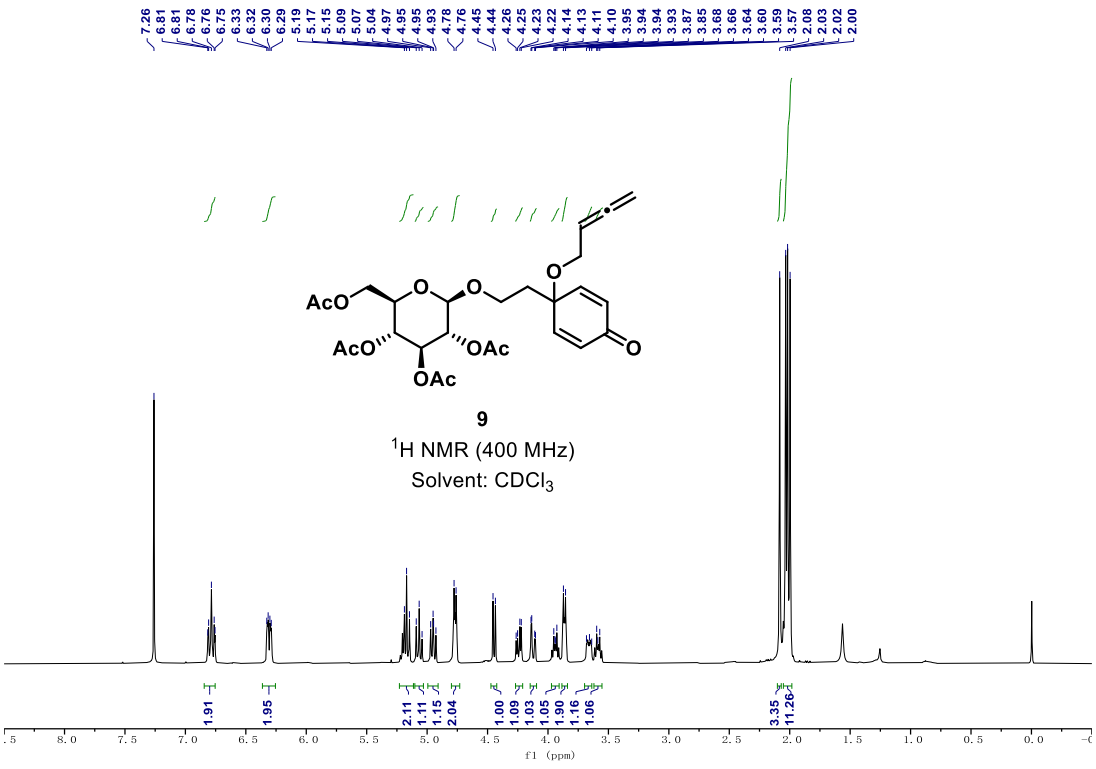


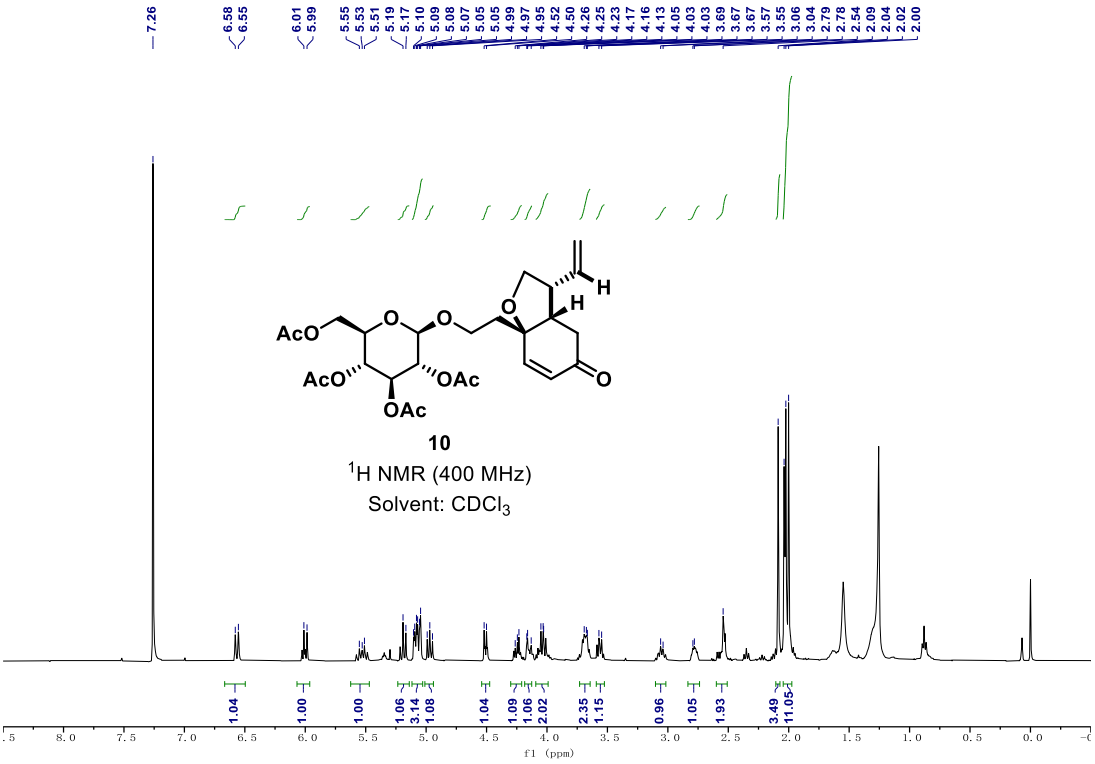
6

^{13}C NMR (600 MHz)

Solvent: $CDCl_3$


AcO
AcO
OAc
OAc
O
O
O
O
8
1H NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)

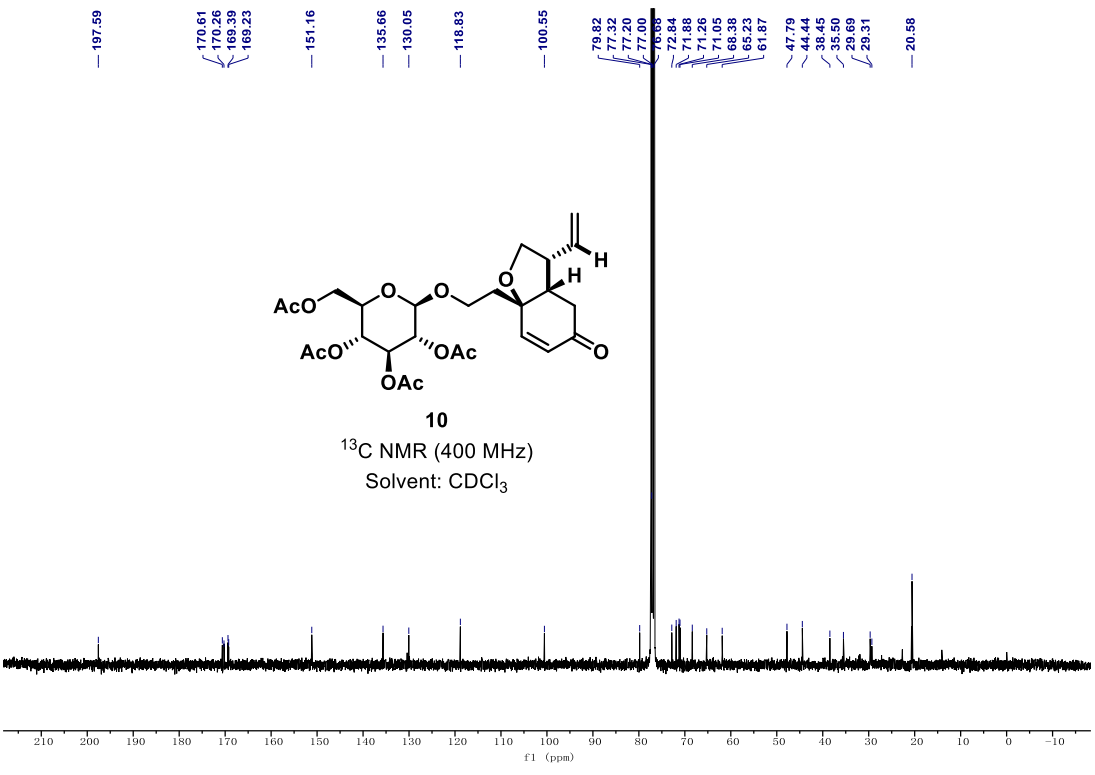

AcO
AcO
OAc
OAc
O
O
O
O
9
1H NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)



10

^{1}H NMR (400 MHz)

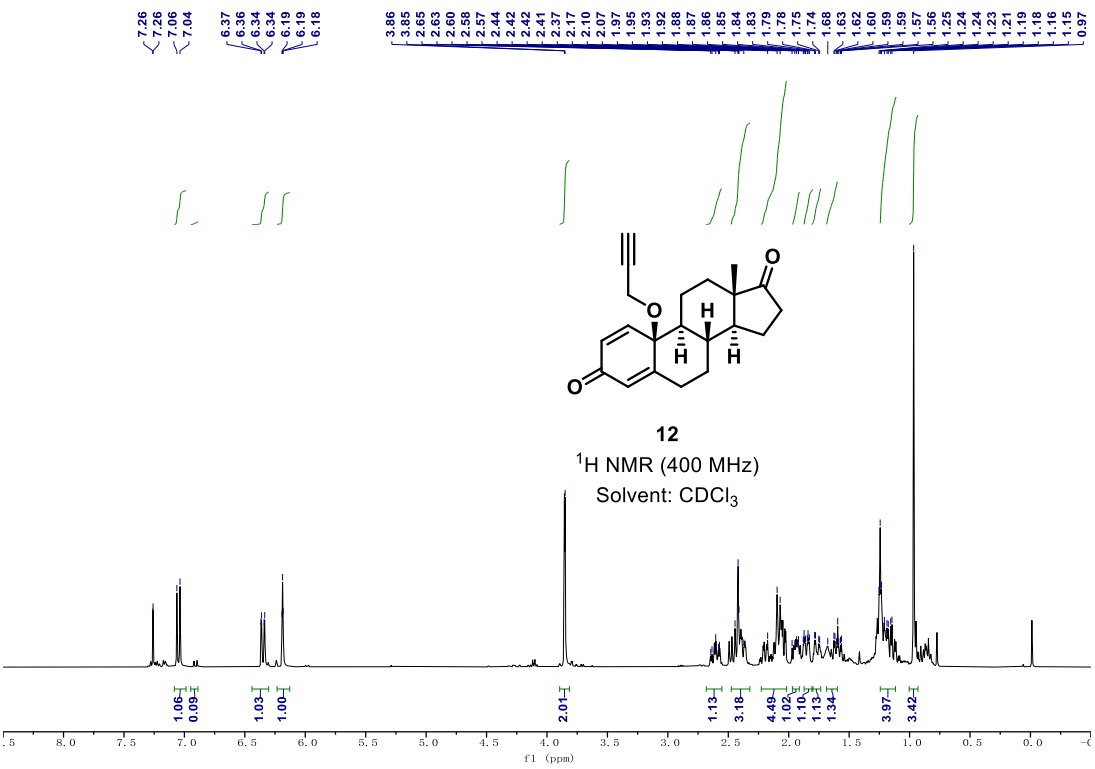
Solvent: $CDCl_3$

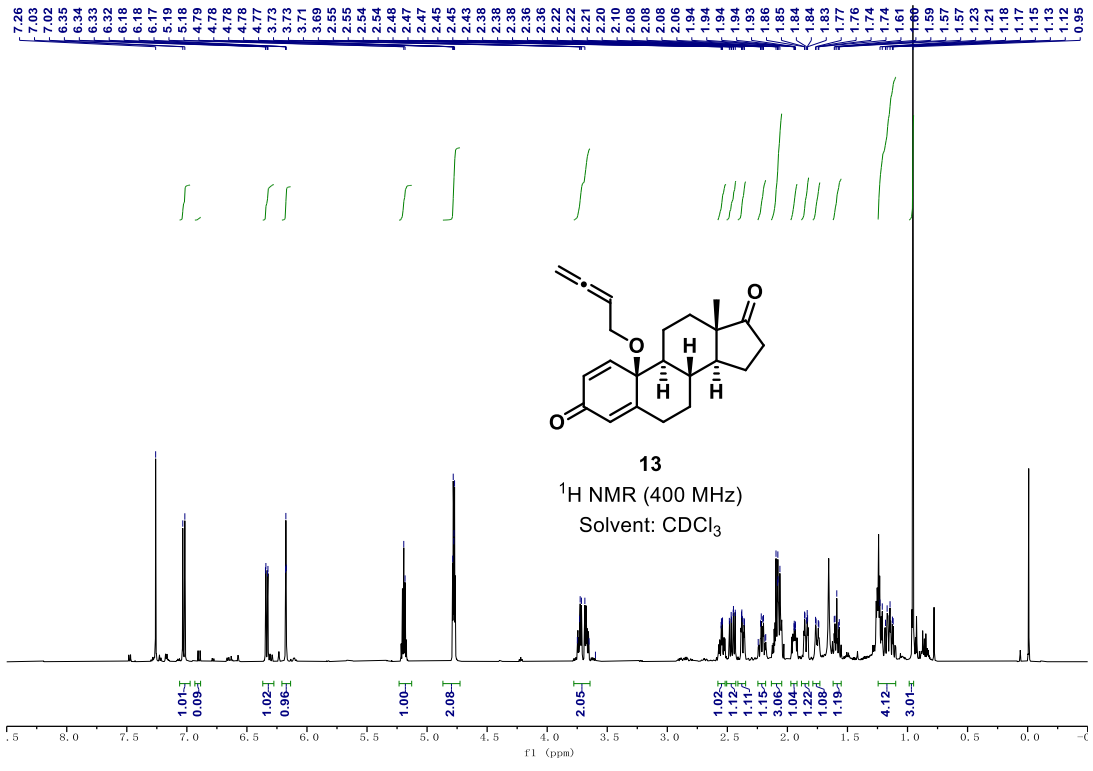


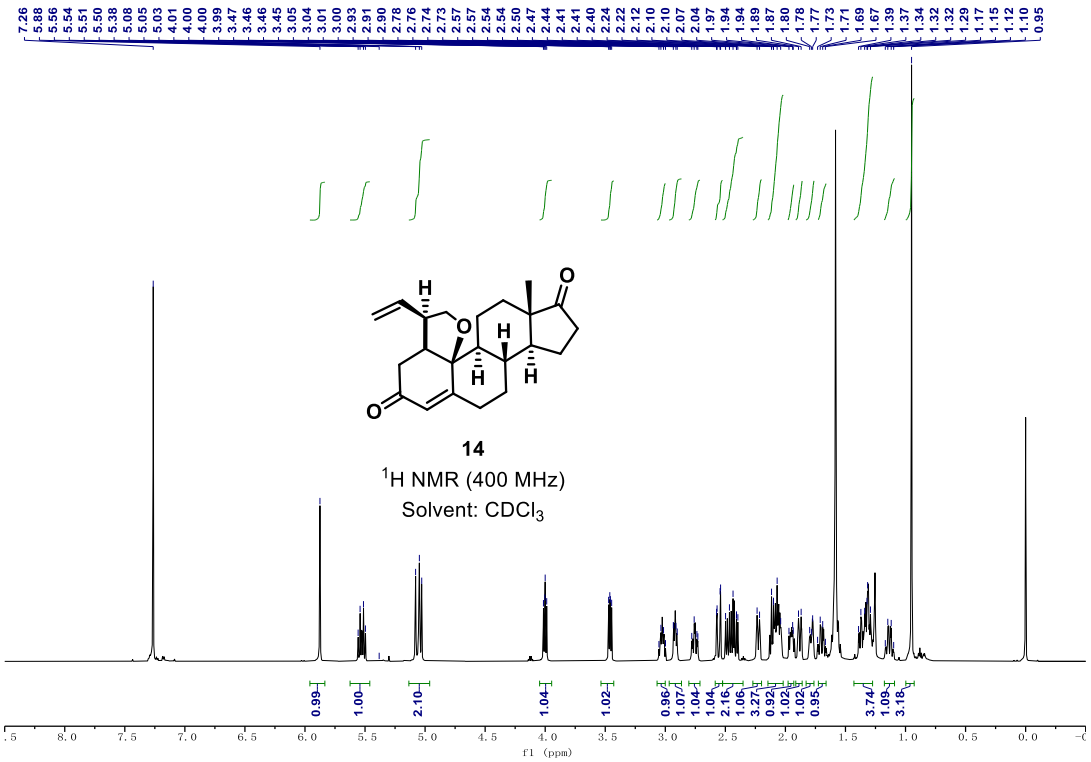
10

^{13}C NMR (400 MHz)

Solvent: $CDCl_3$


12
1H NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)

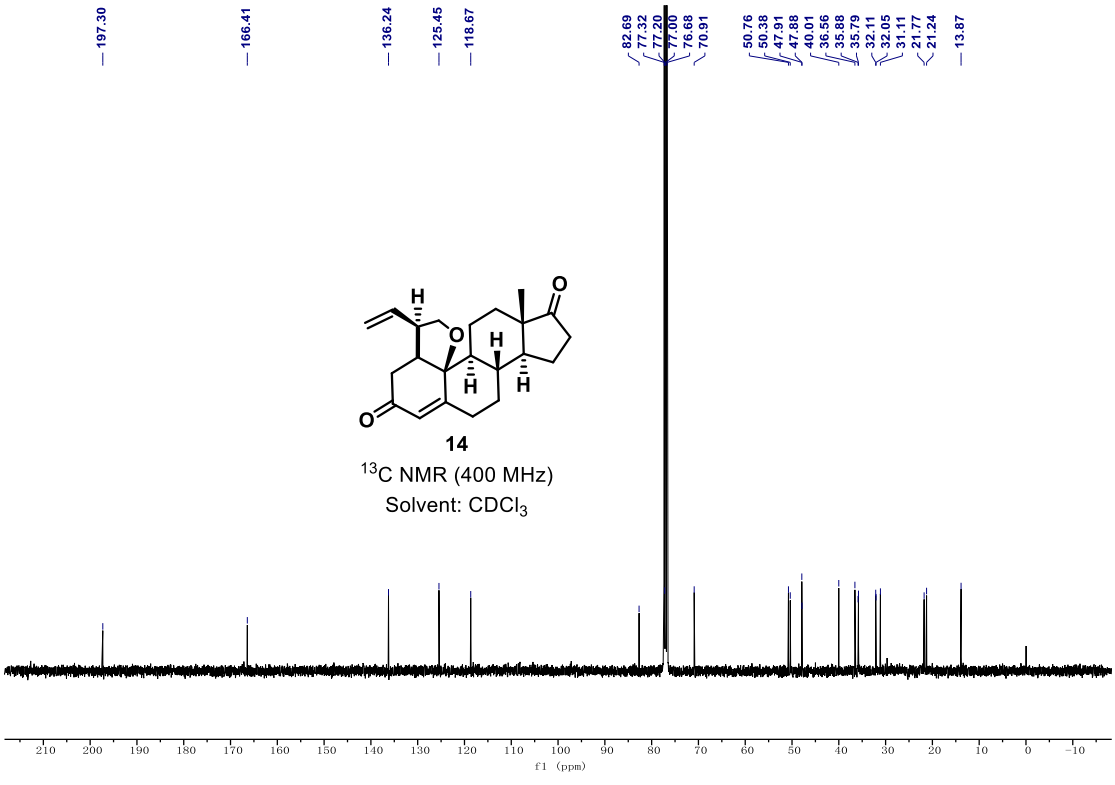

13
1H NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)



14

^{1}H NMR (400 MHz)

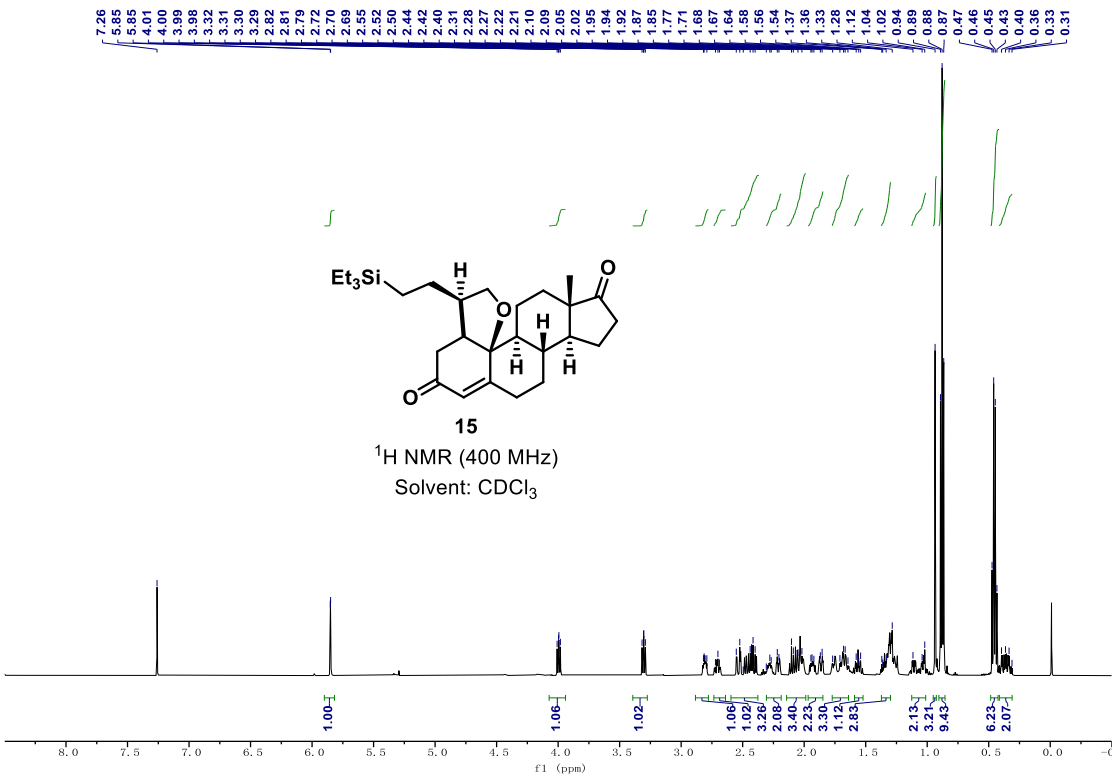
Solvent: $CDCl_3$

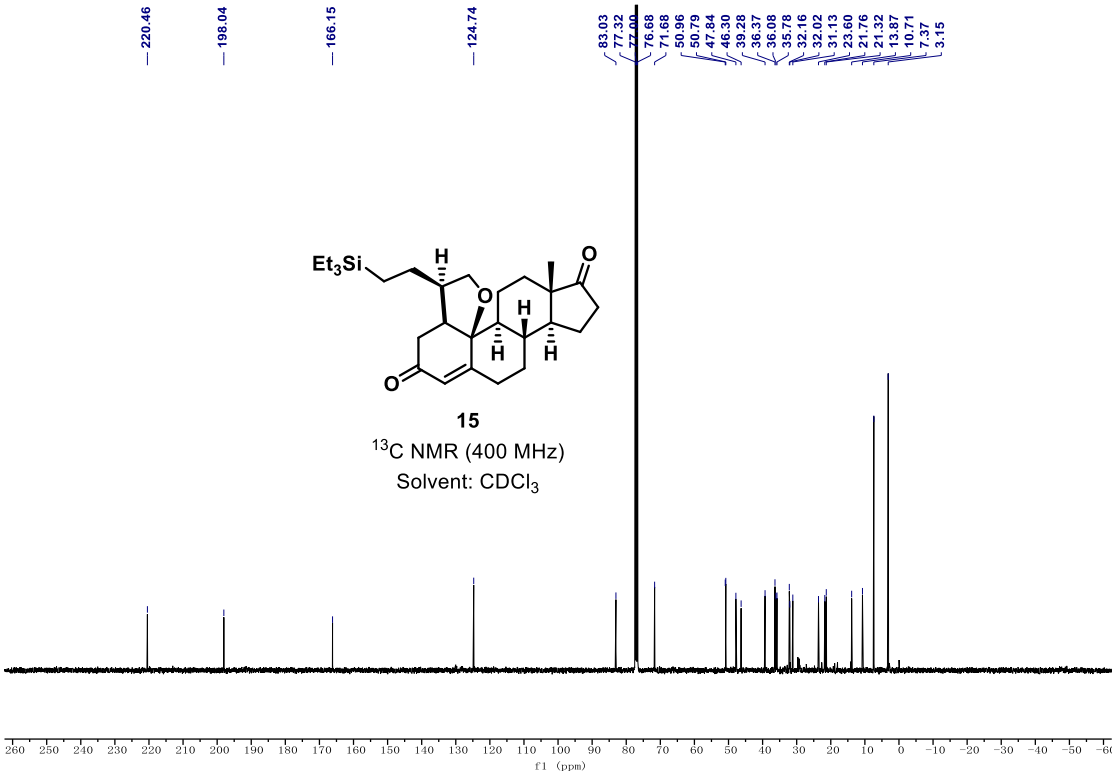


14

^{13}C NMR (400 MHz)

Solvent: $CDCl_3$


Et3Si
H
O
O
H
H
H
O
15
1H NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)


Et3Si
H
O
O
H
H
H
O
15
13C NMR (400 MHz)
Solvent: CDCl3
f1 (ppm)