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Supporting Information

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Cobalt-catalyzed enantioselective alkynylation of oxabicyclic alkenes

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Supporting Information

Contents:

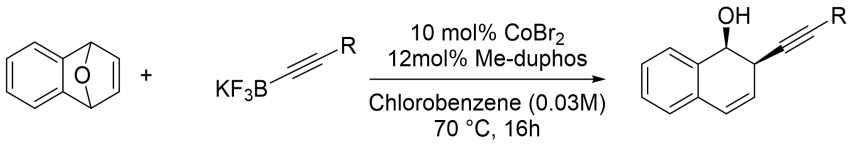
1. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received. **^{1}H and ^{13}C NMR** spectra were recorded on a JEOL JNM-ECZ400S/L1 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.16) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode, and a Finnigan/MAT 95XL-T mass spectrometer in EI mode. All high resolution mass spectra (**HRMS**) were obtained on a Finnigan/MAT 95XL-T or WATERS I-Class VION IMS QT spectrometer. For thin layer chromatography (**TLC**), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine, or potassium permanganate solution followed by heating using a heat gun. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel. The enantiomeric ratios (**er**) of products were determined by chiral phase HPLC analysis on SHIMAZU HPLC units, including the following instruments: pump, LC-20AD; detector, SPD-20A; column, Chiralcel OD-H **Optical rotations** were recorded on an MRC AP81 automatic polarimeter.

All reactions were carried out under nitrogen atmosphere. All commercially available reagents listed below were used as received for the reactions without any purification. Alkynyl trifluoroborates were synthesized according to reported procedure [1]. Heterobicyclic alkenes were synthesized according to reported procedure[2-4].

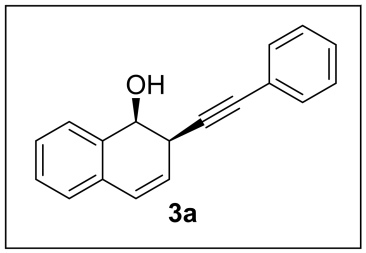
2. General procedure for cobalt-catalyzed alkynylation of oxabicylic alkenes

1) cobalt-catalyzed enantioselective alkynylylation of oxabicyclic alkenes



To a 10 mL vial equipped with a dried stir bar was added cobalt bromide (4.4 mg, 0.020 mmol), (*S*, *S*)-Me-duphos (7.4 mg, 0.024 mmol), anhydrous chlorobenzene (6.0 mL) in the glovebox. The reaction mixture was then allowed to stir for 30 mins, followed by addition of alkynl trifluoroborates (0.30 mmol) and oxabicyclic alkene **1a** (0.20 mmol). The reaction mixture was taken outside the glovebox and allowed to stir at 70 ^{o}C for 16 h. The reaction was monitored by TLC (R_f = 0.3; ethyl acetate: petroleum ether = 1:10). The crude reaction mixture was concentrated under reduced pressure. The products **3a** were directly purified by silica gel chromatography (ethyl acetate: petroleum ether = 1:20). The enantiopurity of the purified products was analyzed by chiral HPLC (Chiralcel OD-H).

3. Analytical data of alkynylation products



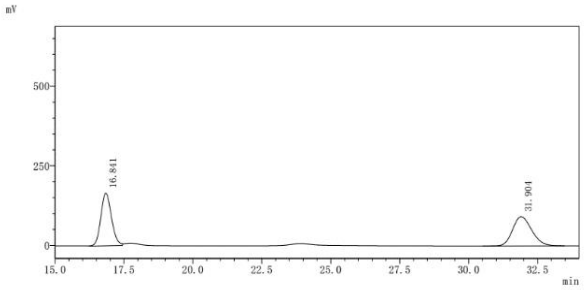
Viscous oil, 31mg, 63% yield. The reaction was monitored by TLC (R_f = 0.3; ethyl acetate: petroleum ether = 1:10).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.48 (dd, *J* = 6.4, 2.5 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.33 – 7.28 (m, 5H), 7.19 – 7.14 (m, 1H), 6.62 (dd, *J* = 9.4, 2.2 Hz, 1H), 6.02 (dd, *J* = 9.5, 3.9 Hz, 1H), 4.88 (d, *J* = 5.4 Hz, 1H), 3.83 (ddd, *J* = 5.8, 3.8, 2.2 Hz, 1H), 2.40 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 135.4, 132.0, 132.0(2C), 128.8, 128.4(3C), 128.3, 128.0, 127.3, 126.9, 125.9, 122.9, 86.1, 84.3, 69.4, 35.5.

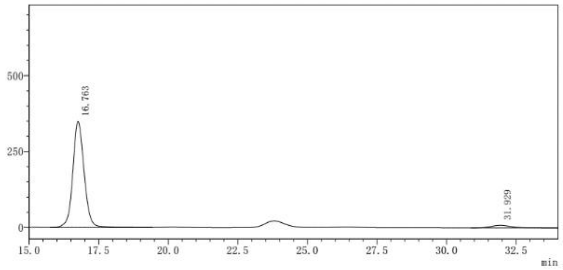
Optical Rotation: $[\alpha]^{22}_D$ = +417.33 (c = 3, MeOH). The absolute configuration was assigned by literature[5].

96:4 er. HPLC condition: Chiralpark OD-H column, n-hexane/i-PrOH = 95:5, flow rate = 1 ml/min, wavelength = 254nm, t_R = 31.929 min for minor isomer, t_R = 16.763 min for major isomer.



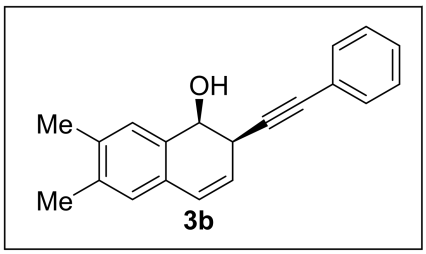
Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	16.841	4429808	165314	50.111
2	31.904	4410162	91681	49.889
Total		8839970	256994	



Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	16.763	9895574	349218	95.871
2	31.929	426184	8454	4.129
Total		10321758	357672	



Viscous oil, 33mg, 59% yield. The reaction was monitored by TLC (R_f = 0.3; ethyl acetate: petroleum ether = 1:10).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.44 (dt, *J* = 7.4, 3.7 Hz, 3H), 7.34 – 7.27 (m, 3H), 7.22 (s, 1H), 6.94 (s, 1H), 6.56 (dd, *J* = 9.5, 2.4 Hz, 1H), 5.93 (dt, *J* = 9.3, 4.7 Hz, 1H), 4.80 (d, *J* = 5.0 Hz, 1H), 3.85 – 3.75 (m, 1H), 2.29 (s, 3H), 2.26 (s, 3H).

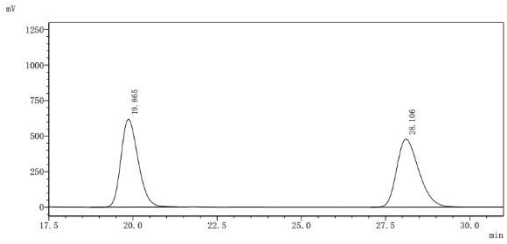
^{13}C NMR (101 MHz, Chloroform-d) δ 137.1, 136.7, 132.6, 132.0(3C), 129.6, 129.0, 128.4, 128.3, 128.2, 127.8, 124.8, 123.0, 86.7, 84.1, 69.2, 35.8, 19.8, 19.6.

HRMS (ESI) m/z Calcd. for [$C_{20}H_{19}O$, M+H]: 275.14304; Found: 275.14679.

Optical Rotation: $[\alpha]^{22}_D$ = +53.33 (c = 0.3, MeOH). The absolute configuration was assigned by analogy to that of **3a**.

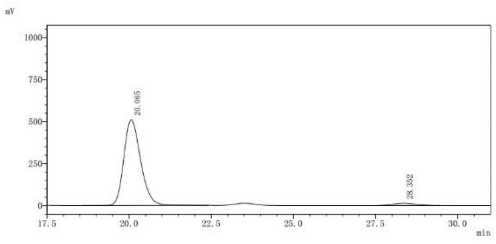
96:4 er. HPLC condition: Chiralpark OD-H column, n-hexane/i-PrOH = 95:5, flow rate = 1 ml/min,

wavelength = 254nm, t_R = 28.352 min for minor isomer, t_R = 20.065 min for major isomer.



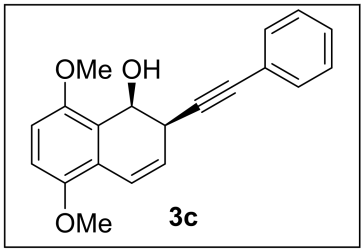
Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	19.865	21872528	617238	49.890
2	28.106	21969390	478426	50.110
Total		43841918	1095664	



Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	20.065	18131671	509742	96.452
2	28.352	667059	12695	3.548
Total		18798730	522437	



3c

Viscous oil, 41mg, 67% yield. The reaction was monitored by TLC (R_f = 0.3; ethyl acetate: petroleum ether = 1:10).

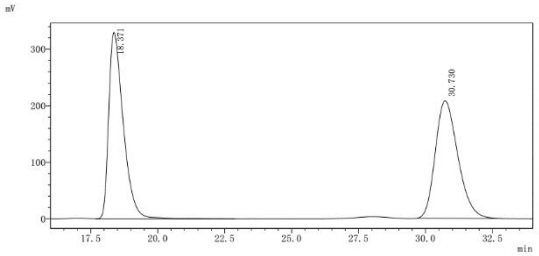
^{1}H NMR (400 MHz, Chloroform-d) δ 7.52 – 7.47 (m, 2H), 7.33 – 7.30 (m, 3H), 7.00 (dd, *J* = 9.7, 3.3 Hz, 1H), 6.82 (d, *J* = 2.9 Hz, 2H), 5.98 (ddd, *J* = 9.7, 2.4, 1.5 Hz, 1H), 5.24 (dd, *J* = 4.4, 1.6 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.74 (ddd, *J* = 5.8, 4.2, 2.1 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 150.9, 149.7, 131.9(2C), 128.4(2C), 128.2, 125.8, 123.4, 123.2, 122.0, 121.5, 111.8, 111.2, 87.7, 83.9, 62.2, 56.3(2C), 35.6.

HRMS (ESI) m/z Calcd. for [$C_{20}H_{19}O_3$, M+H]: 307.13287; Found: 307.13255.

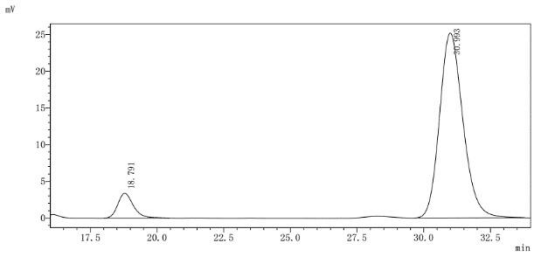
Optical Rotation: $[\alpha]^{22}_D$ = +220.00 (c = 0.1, MeOH). The absolute configuration was assigned by analogy to that of **3a**.

91:9 er. HPLC condition: Chiralpark OD-H column, n-hexane/i-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 254nm, t_R = 18.791 min for minor isomer, t_R = 30.993 min for major isomer.



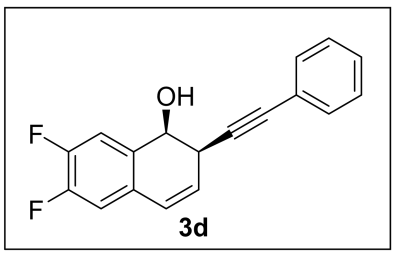
Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	18.371	12509257	329891	50.687
2	30.730	12170255	207754	49.313
Total		24679512	537645	



Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	18.791	136215	3365	8.150
2	30.993	1535201	25173	91.850
Total		1671416	28538	



3d

Viscous oil, 31mg, 55% yield. The reaction was monitored by TLC (R_f = 0.6; ethyl acetate: petroleum ether = 1:10).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.37 (dt, *J* = 4.9, 2.2 Hz, 2H), 7.35 – 7.27 (m, 4H), 6.95 (dd, *J* = 10.5, 7.6 Hz, 1H), 6.48

(dd, *J* = 9.5, 1.8 Hz, 1H), 6.05 (dd, *J* = 9.5, 4.6 Hz, 1H), 4.83 (t, *J* = 6.3 Hz, 1H), 3.85 – 3.70 (m, 1H), 2.39 (d, *J* = 8.0 Hz, 1H).

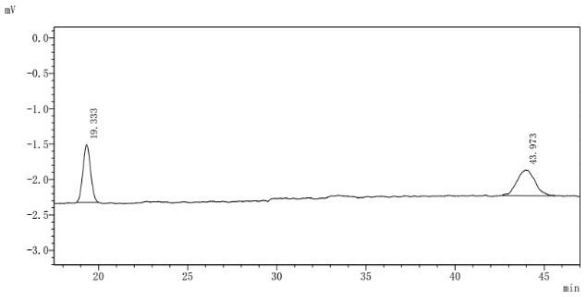
^{13}C NMR (101 MHz, Chloroform-d) δ 132.0(2C), 128.6, 128.4(2C), 126.6(2C), 126.5, 126.4, 122.6, 116.3 (d, *J* = 18.9 Hz)(2C), 115.5 (d, *J* = 18.0 Hz)(2C), 84.8, 84.6, 68.6, 34.8.

^{19}F NMR (376 MHz, Chloroform-d) δ -137.75 (dt, *J* = 19.5, 9.8 Hz), -139.01 (dt, *J* = 19.3, 10.4 Hz).

HRMS (ESI) m/z Calcd. for [$C_{18}H_{12}F_2NaO$, M+Na]: 305.07484; Found: 305.07352.

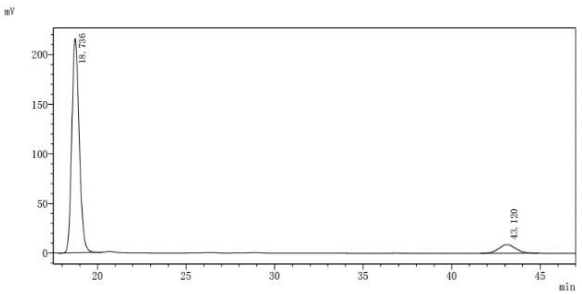
Optical Rotation: $[\alpha]^{22}_D$ = +60.00 (c = 0.3, MeOH). The absolute configuration was assigned by analogy to that of **3a**.

92:8 er. HPLC condition: Chiralpark OD-H column, n-hexane/i-PrOH = 95:5, flow rate = 1 ml/min, wavelength = 254nm, t_R = 43.120 min for minor isomer, t_R = 18.736 min for major isomer.



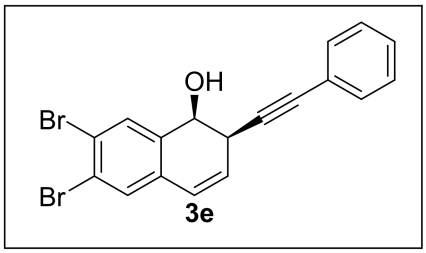
Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	19.333	24178	813	48.546
2	43.973	25626	363	51.454
Total		49804	1176	



Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	18.736	6299079	215696	91.557
2	43.120	580874	8638	8.443
Total		6879954	224333	



3e

Viscous oil, 44mg, 54% yield. The reaction was monitored by TLC (R_f = 0.5; ethyl acetate: petroleum ether = 1:10).

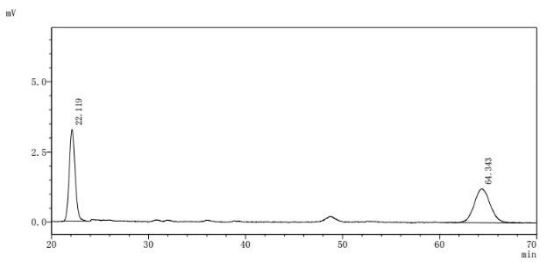
^{1}H NMR (400 MHz, Chloroform-d) δ 7.76 (s, 1H), 7.41 – 7.35 (m, 3H), 7.33 – 7.27 (m, 3H), 6.48 (dd, *J* = 9.5, 1.7 Hz, 1H), 6.10 (dd, *J* = 9.5, 4.7 Hz, 1H), 4.84 (d, *J* = 5.1 Hz, 1H), 3.78 (ddd, *J* = 6.2, 4.6, 1.8 Hz, 1H), 2.37 (d, *J* = 8.1 Hz, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 136.5, 132.8, 132.0 (2C), 131.9, 131.4, 128.6, 128.4 (2C), 127.7, 126.4, 124.5, 123.9, 122.4, 84.9, 84.2, 68.5, 34.9.

HRMS (ESI) m/z Calcd. for [$C_{18}H_{12}Br_2KO$, M+K]: 440.88865; Found: 440.88071.

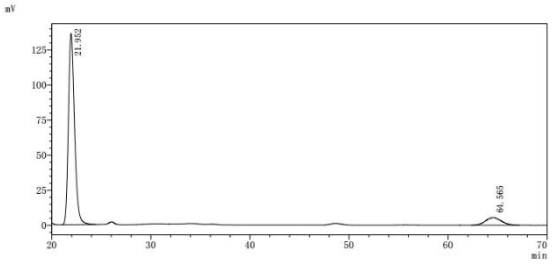
Optical Rotation: $[\alpha]^{22}_D$ = +66.67 (c = 0.3, MeOH). The absolute configuration was assigned by the analogue **3a**.

91:9 er. HPLC condition: Chiralpark OD-H column, n-hexane/i-PrOH = 95:5, flow rate = 1 ml/min, wavelength = 254nm, t_R = 21.952 min for minor isomer, t_R = 64.565 min for major isomer.



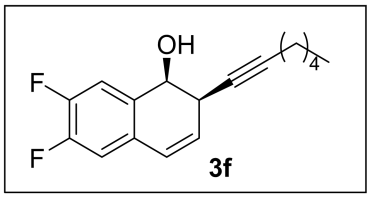
Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	22.119	137701	3259	49.708
2	64.343	139320	1207	50.292
Total		277021	4466	



Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	21.952	5840129	136502	90.694
2	64.565	599239	5425	9.306
Total		6439368	141927	



Viscous oil, 31mg, 56% yield. The reaction was monitored by TLC (R_f = 0.5; ethyl acetate: petroleum ether = 1:15).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.31 (dd, *J* = 10.6, 7.9 Hz, 1H), 6.91 (dd, *J* = 10.5, 7.6 Hz, 1H), 6.40 (dd, *J* = 9.5, 1.7 Hz, 1H), 5.95 (dd, *J* = 9.6, 4.7 Hz, 1H), 4.70 (t, *J* = 5.3 Hz, 1H), 3.51 (ddq, *J* = 6.6, 4.4, 2.1 Hz, 1H), 2.33 (d, *J* = 7.7 Hz, 1H), 2.14 (td, *J* = 7.1, 2.4 Hz, 2H), 1.48 – 1.40 (m, 2H), 1.28 (q, *J* = 3.7 Hz, 4H), 0.89 – 0.84 (m, 3H).

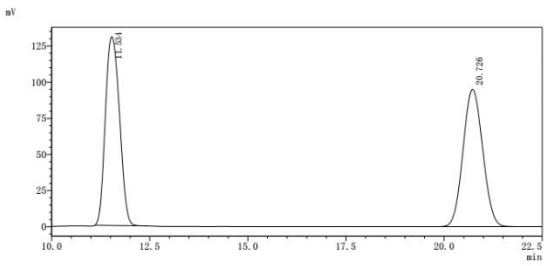
^{13}C NMR (101 MHz, Chloroform-d) δ 132.8, 128.9, 127.2, 125.9, 116.2 (d, *J* = 17.8 Hz), 115.3 (d, *J* = 18.8 Hz) , 85.5, 74.7, 68.4, 34.1, 31.0, 28.4, 22.2, 18.7, 14.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -138.18 (dd, *J* = 20.3, 9.4 Hz), -139.51 (dd, *J* = 20.4, 9.8 Hz).

HRMS (ESI) m/z Calcd. for [$C_{17}H_{18}F_2KO$, M+K]: 315.09573; Found: 315.09128.

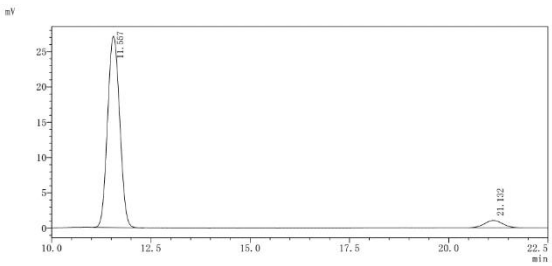
Optical Rotation: $[\alpha]^{22}_D$ = +186.67 (c = 0.3, MeOH). The absolute configuration was assigned by analogy to that of **3a**.

95:5 er. HPLC condition: Chiralpark OD-H column, n-hexane/i-PrOH = 99:1, flow rate = 1 ml/min, wavelength = 254nm, t_R = 21.132 min for minor isomer, t_R = 11.557 min for major isomer.



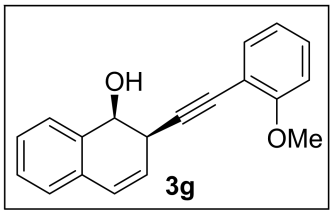
Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	11.534	3268286	130559	49.700
2	20.726	3307737	94938	50.300
Total		6576023	225497	



Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	11.557	574839	27092	94.670
2	21.132	32362	1027	5.330
Total		607201	28119	



3g

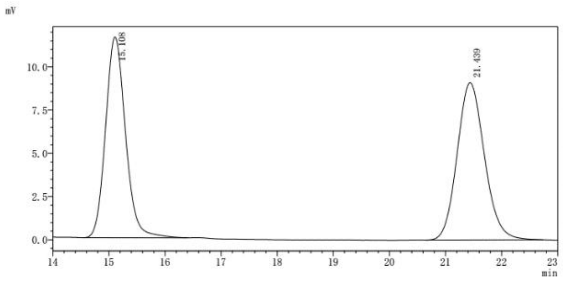
Viscous oil, 32mg, 58% yield. The reaction was monitored by TLC (R_f = 0.3; ethyl acetate: petroleum ether = 1:10).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.52 – 7.47 (m, 1H), 7.34 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.29 (ddt, *J* = 5.2, 3.6, 1.8 Hz, 3H), 7.16 – 7.12 (m, 1H), 6.91 – 6.83 (m, 2H), 6.59 (dd, *J* = 9.6, 2.2 Hz, 1H), 6.00 (dd, *J* = 9.5, 3.9 Hz, 1H), 4.90 (d, *J* = 5.4 Hz, 1H), 3.86 (s, 3H), 3.85 – 3.81 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 160.4, 135.3, 132.8, 132.1, 129.7, 128.7, 128.1, 127.9, 127.5, 126.8, 125.6, 120.5, 112.1, 110.5, 90.7, 80.9, 69.2, 55.8, 35.8.

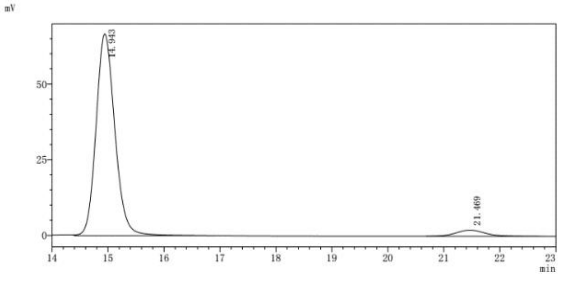
Optical Rotation: $[\alpha]^{22}_D$ = +78.00 (c = 1.0, MeOH). The absolute configuration was assigned by analogy to that of **3a**.

95.5:4.5 er. HPLC condition: Chiralpark OD-H column, n-hexane/i-PrOH = 90:10, flow rate = 1 ml/min, wavelength = 254nm, t_R = 21.469 min for minor isomer, t_R = 14.943 min for major isomer.



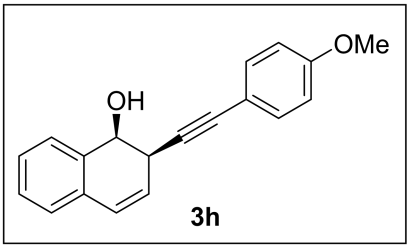
Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	15.108	287047	11607	48.230
2	21.439	308121	9090	51.770
Total		595168	20697	



Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	14.943	1557783	66664	95.482
2	21.469	73708	2029	4.518
Total		1631492	68693	



3h

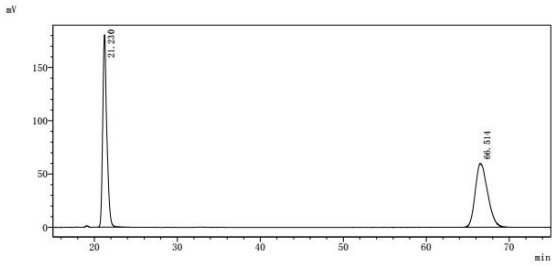
Viscous oil, 35mg, 63% yield. The reaction was monitored by TLC (R_f = 0.3; ethyl acetate: petroleum ether = 1:10).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.47 (dd, *J* = 6.7, 2.2 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.18 – 7.12 (m, 1H), 6.84 – 6.77 (m, 2H), 6.59 (dd, *J* = 9.5, 2.2 Hz, 1H), 6.00 (dd, *J* = 9.5, 3.8 Hz, 1H), 4.88 – 4.81 (m, 1H), 3.80 (s, 4H), 2.35 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-d) δ 159.6, 135.3, 133.3(2C), 132.0, 128.7, 128.1, 127.8, 127.3, 126.8, 126.0, 114.9, 113.9(2C), 84.3, 84.1, 69.3, 55.3, 35.5.

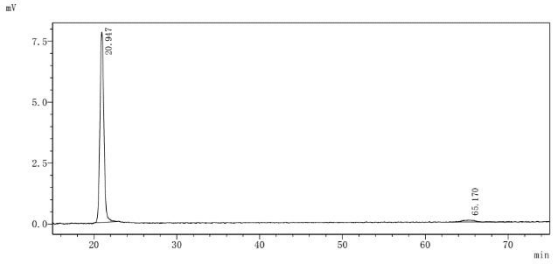
Optical Rotation: $[\alpha]^{22}_D$ = +232.00 (c = 0.5, MeOH). The absolute configuration was assigned by the analogue **3a**.

97:3 er. HPLC condition: Chiralpark OD-H column, n-hexane/i-PrOH = 95:5, flow rate = 1 ml/min, wavelength = 254nm, t_R = 65.170 min for minor isomer, t_R = 20.947 min for major isomer.



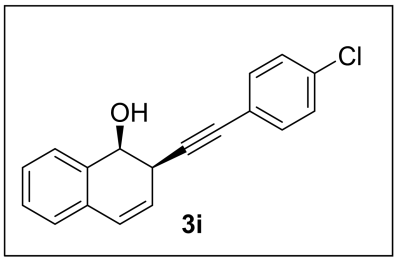
Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	21.230	6216514	180496	50.082
2	66.514	6196205	59722	49.918
Total		12412718	240218	



Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	20.947	256324	7793	97.308
2	65.170	7090	79	2.692
Total		263414	7872	



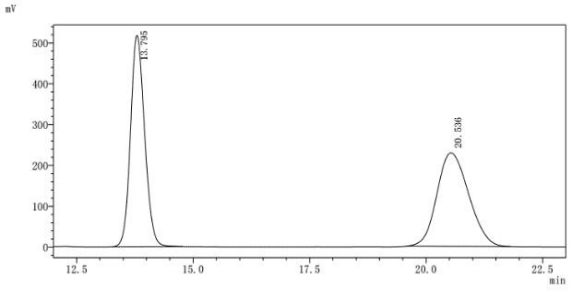
Viscous oil, 29mg, 52% yield. The reaction was monitored by TLC (R_f = 0.4; ethyl acetate: petroleum ether = 1:10).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.46 (dd, *J* = 6.4, 2.4 Hz, 1H), 7.34 (d, *J* = 1.9 Hz, 1H), 7.32 (d, *J* = 2.1 Hz, 2H), 7.30 (d, *J* = 3.0 Hz, 1H), 7.26 (s, 1H), 7.25 (d, *J* = 1.9 Hz, 1H), 7.15 (dd, *J* = 6.7, 2.1 Hz, 1H), 6.61 (dd, *J* = 9.5, 2.2 Hz, 1H), 5.99 (dd, *J* = 9.4, 3.9 Hz, 1H), 4.86 (d, *J* = 5.2 Hz, 1H), 3.81 (ddd, *J* = 5.7, 3.9, 2.2 Hz, 1H), 2.28 (s, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.6, 134.3, 133.1(2C), 131.9, 128.8(2C), 128.6, 128.3, 128.1, 127.2, 126.9, 125.5, 121.4, 87.2, 83.0, 69.4, 35.5.

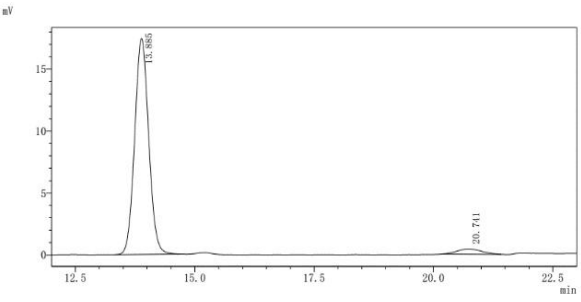
Optical Rotation: $[\alpha]^{22}_D$ = +200.00 (c = 0.3, MeOH). The absolute configuration was assigned by analogy to that of **3a**.

97:3 er. HPLC condition: Chiralpark OD-H column, n-hexane/i-PrOH = 95:5, flow rate = 1 ml/min, wavelength = 254nm, t_R = 20.741 min for minor isomer, t_R = 13.885 min for major isomer.



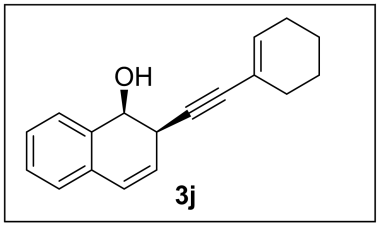
Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	13.795	10925696	516797	50.150
2	20.536	10860309	228833	49.850
Total		21786005	745630	



Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	13.885	356341	17436	95.983
2	20.741	14914	419	4.017
Total		371255	17855	



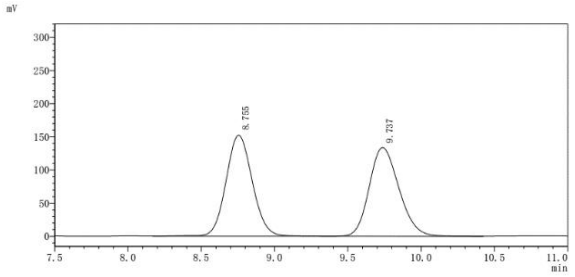
Viscous oil, 30mg, 60% yield. The reaction was monitored by TLC (R_f = 0.3; ethyl acetate: petroleum ether = 1:15).

^{1}H NMR (400 MHz, Chloroform-d) δ 7.46 – 7.42 (m, 1H), 7.32 – 7.26 (m, 2H), 7.15 – 7.08 (m, 1H), 6.55 (dd, *J* = 9.4, 2.2 Hz, 1H), 6.07 (tt, *J* = 3.8, 1.7 Hz, 1H), 5.92 (dd, *J* = 9.4, 3.8 Hz, 1H), 4.77 (t, *J* = 5.8 Hz, 1H), 3.74 – 3.65 (m, 1H), 2.30 (d, *J* = 6.8 Hz, 1H), 2.08 (tq, *J* = 8.3, 2.6 Hz, 4H), 1.63 – 1.54 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-d) δ 135.3, 135.2, 132.0, 128.6, 128.0, 127.6, 127.3, 126.7, 126.2, 120.2, 86.2, 82.8, 69.2, 35.3, 29.4, 25.6, 22.3, 21.5.

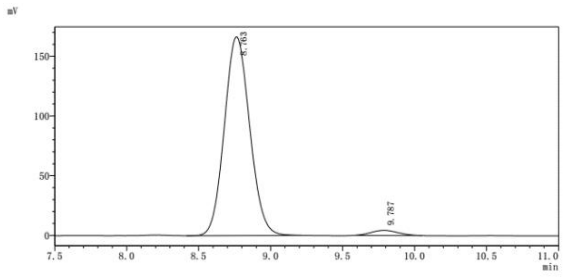
Optical Rotation: $[\alpha]^{22}_D$ = +148.00 (c = 0.3, MeOH). The absolute configuration was assigned by analogy to that of **3a**.

97:3 er. HPLC condition: Chiralpark OD-H column, n-hexane/i-PrOH = 95:5, flow rate = 1 ml/min, wavelength = 254nm, t_R = 9.787 min for minor isomer, t_R = 8.763 min for major isomer.



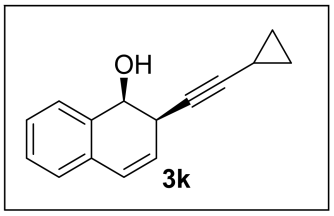
Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	8.755	1910909	152399	50.235
2	9.737	1893008	133740	49.765
Total		3803917	286139	



Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	8.763	2040648	166362	97.294
2	9.787	56762	4314	2.706
Total		2097410	170676	



Viscous oil, 29mg, 69% yield. The reaction was monitored by TLC (R_f = 0.3; ethyl acetate: petroleum ether = 1:15).

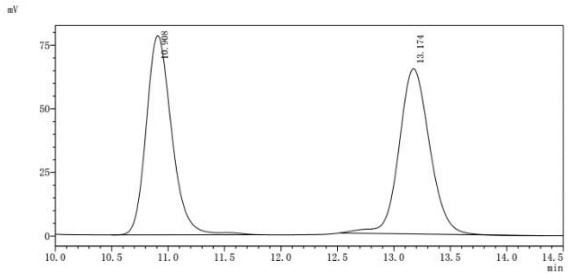
^{1}H NMR (400 MHz, Chloroform-d) δ 7.45 – 7.41 (m, 1H), 7.31 – 7.26 (m, 2H), 7.14 – 7.09 (m, 1H), 6.52 (dd, *J* = 9.6, 2.2 Hz, 1H), 5.87 (dd, *J* = 9.4, 3.8 Hz, 1H), 4.71 (t, *J* = 5.9 Hz, 1H), 3.53 (ddt, *J* = 5.9, 4.1, 2.2 Hz, 1H), 2.31 (dd, *J* = 7.0, 2.8 Hz, 1H), 1.25 – 1.20 (m, 1H), 0.77 – 0.70 (m, 2H), 0.68 – 0.60 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 135.3, 131.9, 128.5, 128.0, 127.4, 127.3, 126.7, 126.4, 87.7, 71.4, 69.2, 34.8, 8.3(2C), -0.4.

Optical Rotation: $[\alpha]^{22}_D$ = +73.33 (c = 1.5, MeOH). The absolute configuration was assigned by analogy to that of **3a**.

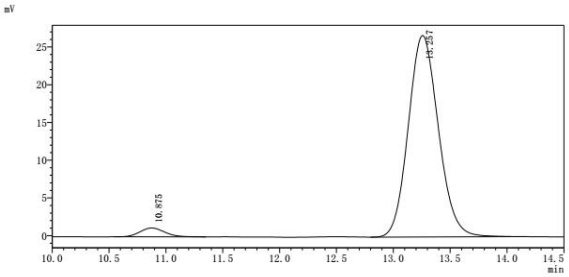
96.5:3.5 er. HPLC condition: Chiralpark OD-H column, n-hexane/i-PrOH = 95:5, flow rate = 1 ml/min, wavelength = 254nm, t_R = 10.875 min for minor isomer, t_R = 13.257 min for major

isomer.



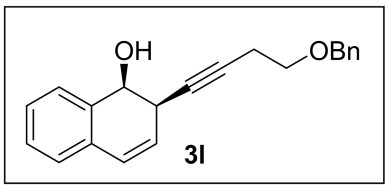
Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	10.908	1231646	78360	50.061
2	13.174	1228647	64988	49.939
Total		2460292	143348	



Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	10.875	17733	1172	3.479
2	13.257	491932	26700	96.521
Total		509664	27872	



3l

Viscous oil, 36mg, 59% yield. The reaction was monitored by TLC (R_f = 0.2; ethyl acetate: petroleum ether = 1:10).

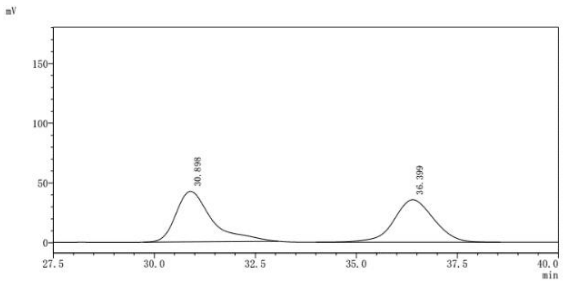
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (dd, *J* = 6.5, 2.6 Hz, 1H), 7.39 – 7.33 (m, 4H), 7.31 (dd, *J* = 6.4, 2.4 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.15 – 7.08 (m, 1H), 6.54 (dd, *J* = 9.6, 2.2 Hz, 1H), 5.90 (dd, *J* = 9.5, 4.0 Hz, 1H), 4.75 (d, *J* = 5.4 Hz, 1H), 4.54 (s, 2H), 3.56 (ddq, *J* = 9.1, 4.4, 2.3 Hz, 3H), 2.50 (td, *J* = 6.8, 2.5 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 138.1, 135.4, 132.0, 128.5, 128.5(2C), 128.1, 127.8(3C), 127.6, 127.2, 126.7, 126.2, 81.4, 77.6, 73.0, 69.2, 68.4, 34.8, 20.3.

HRMS (ESI) m/z Calcd. for [$C_{21}H_{21}O_2$, M+H]: 305.15361; Found: 305.15395.

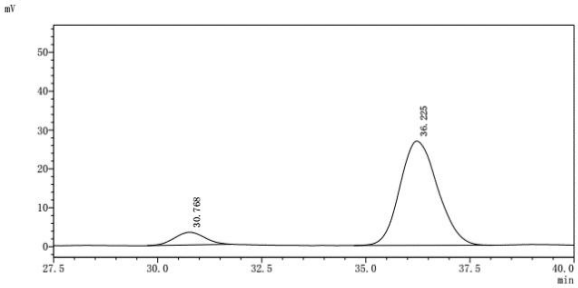
Optical Rotation: $[\alpha]^{22}_D$ = +13.33 (c = 0.3, MeOH). The absolute configuration was assigned by analogy to that of **3a**.

91:9 er. HPLC condition: Chiralpark OD-H column, n-hexane/i-PrOH = 95:5, flow rate = 1 ml/min, wavelength = 254nm, t_R = 30.768 min for minor isomer, t_R = 36.225 min for major isomer.



Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	30.898	2617816	42236	51.766
2	36.399	2439242	35569	48.234
Total		5057058	77806	



Detector A 254nm

Peak	Ret.Time(min)	Area	Height	Conc.
1	30.768	164578	3258	8.863
2	36.225	1692375	26812	91.137
Total		1856953	30070	

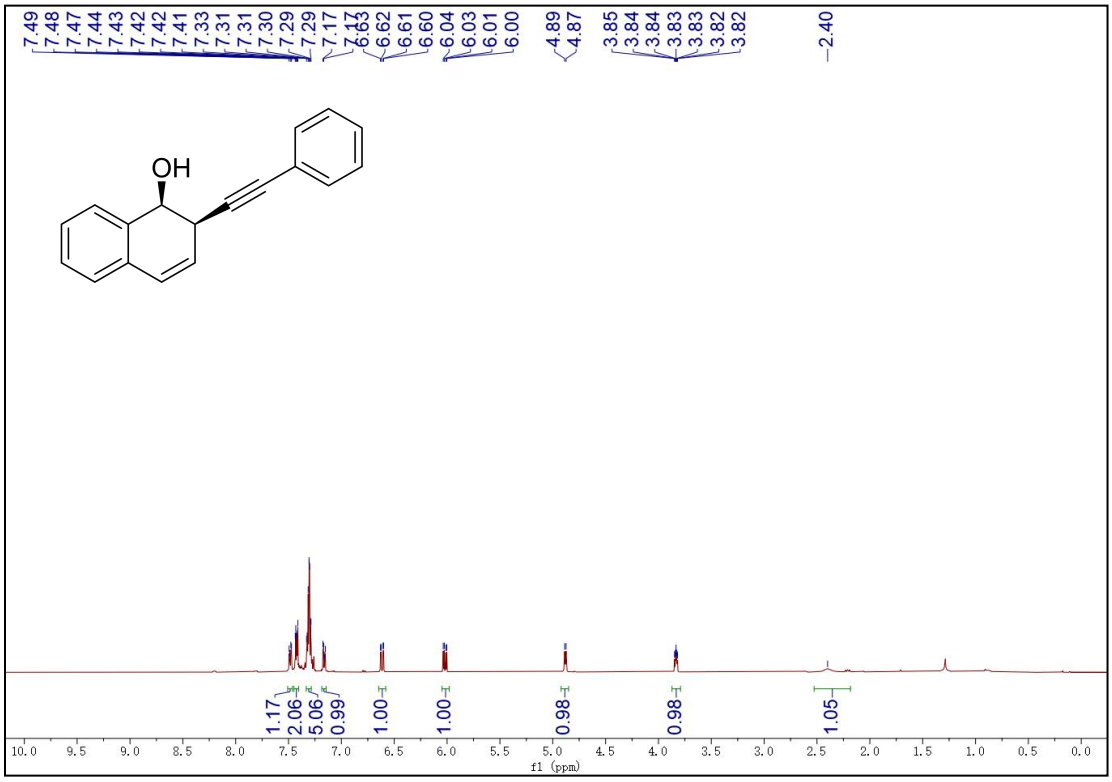
5. Reference

1. Nguyen, T. N.; May, J. A. *Org. Lett.* **2018**, *20*, 3618-3621.
2. Zhu, J.; Tsui, G. C.; Lautens, M. *Angew. Chem., Int. Ed.* **2012**, *51*, 12353-12356.
3. Yoshida, K.; Toyoshima, T.; Akashi, N.; Imamoto, T.; Yanagisawa, A. *Chem. Commun.* **2009**, 2923-2925.
4. R Luo, R.; Liao, J.; Xie, L.; Tang, W.; Chan, A. S. C. *Chem. Commun.* **2013**, *49*, 9959-9961.
5. Liu, S.; Li, S.; Chen, H.; Yang, Q.; Xu, J.; Zhou, Y.; Yuan, M.; Zeng, W.; Fan, B. *Adv.*

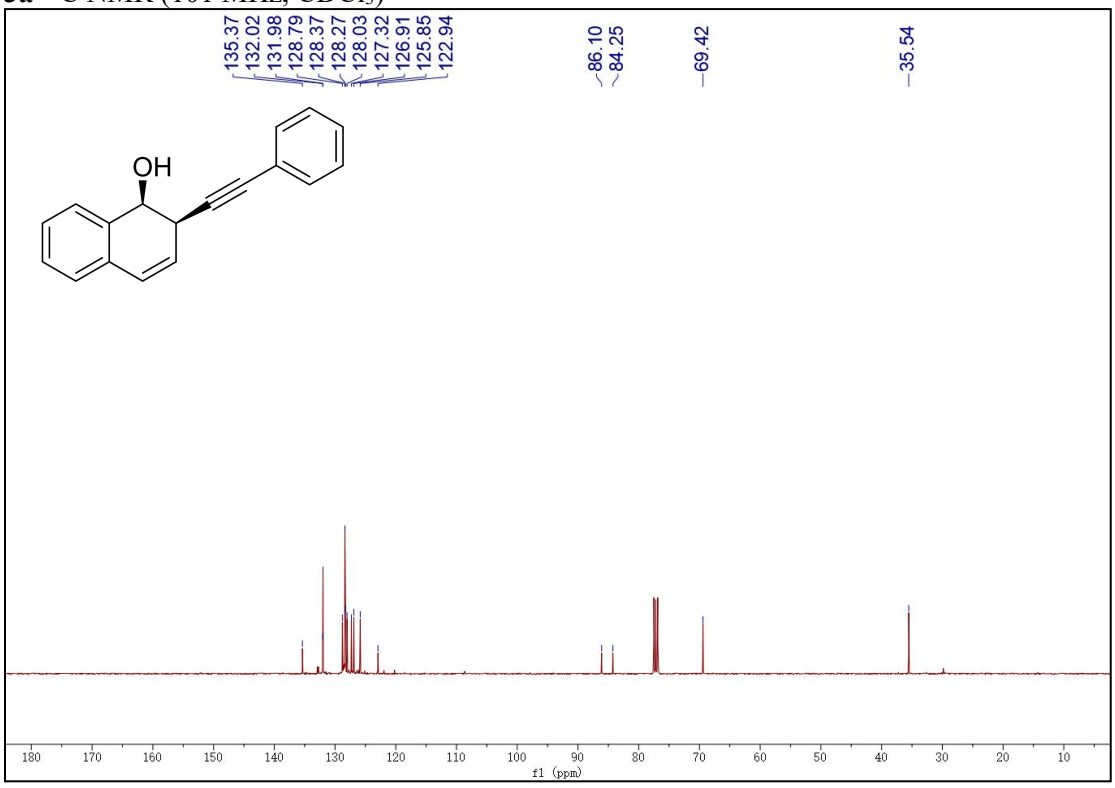
Synth. Catal. **2014**, *365*, 2960-2964.

5. NMR spectra of the products

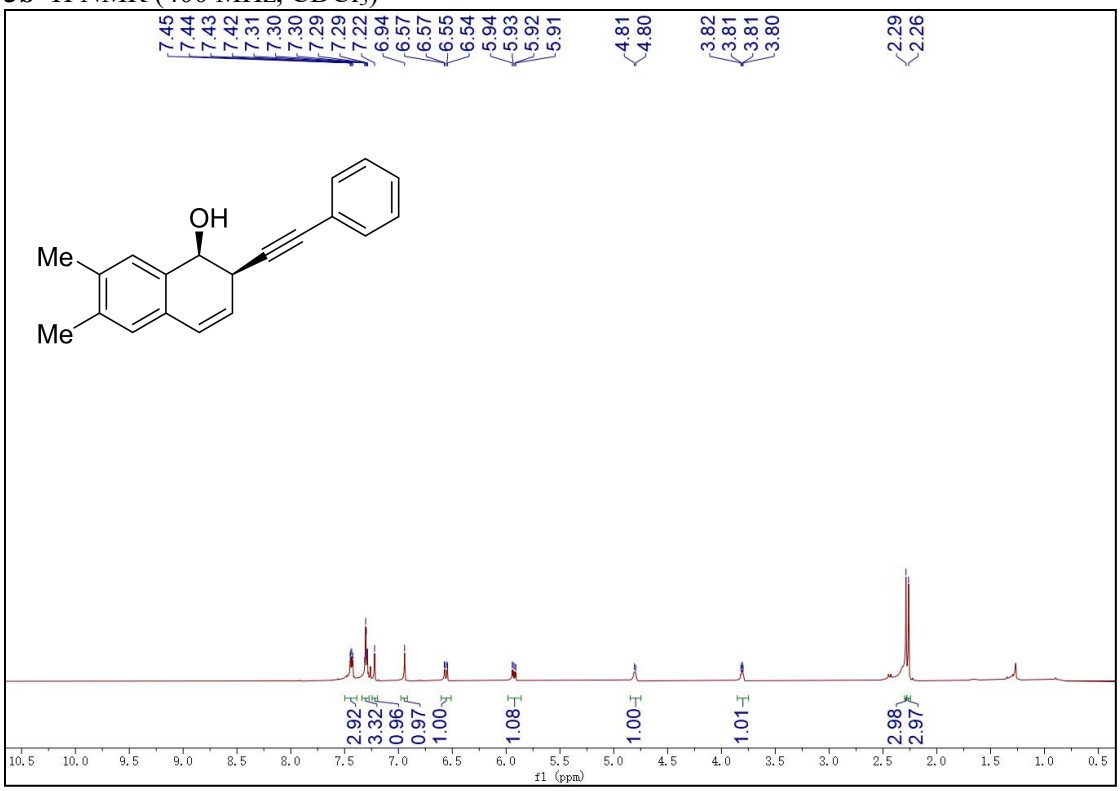
3a ^{1}H NMR (400 MHz, $CDCl_3$)



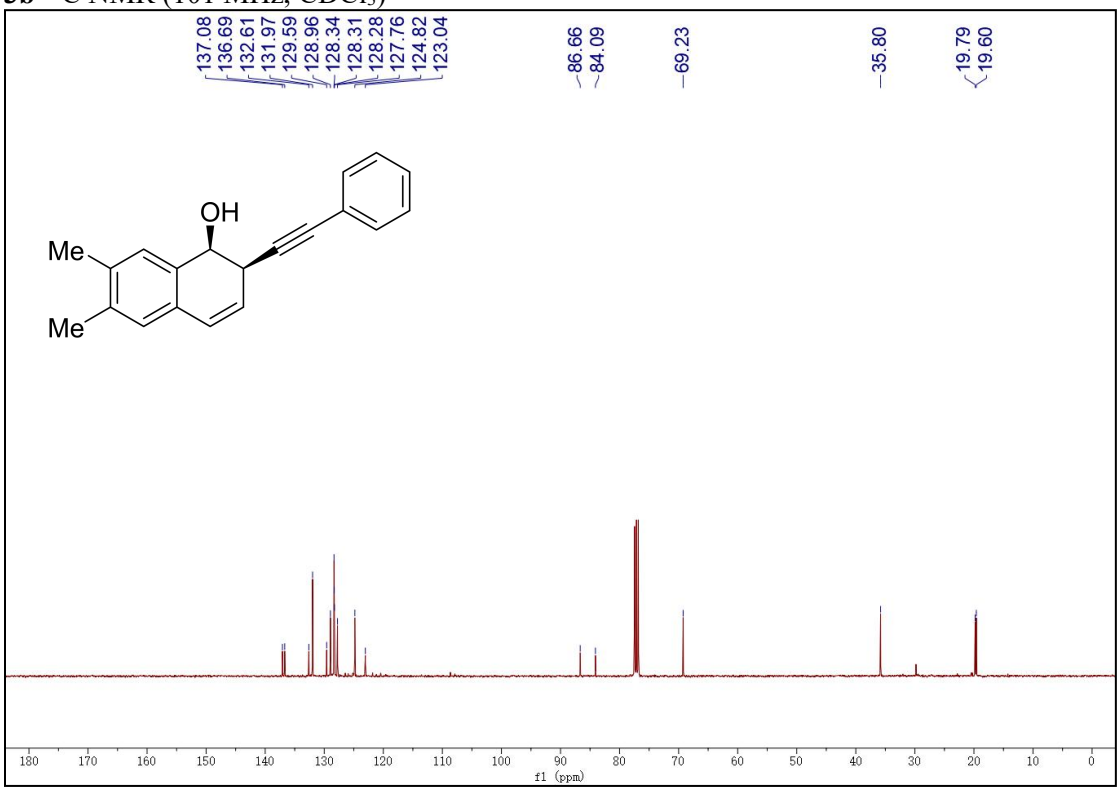
3a ^{13}C NMR (101 MHz, $CDCl_3$)



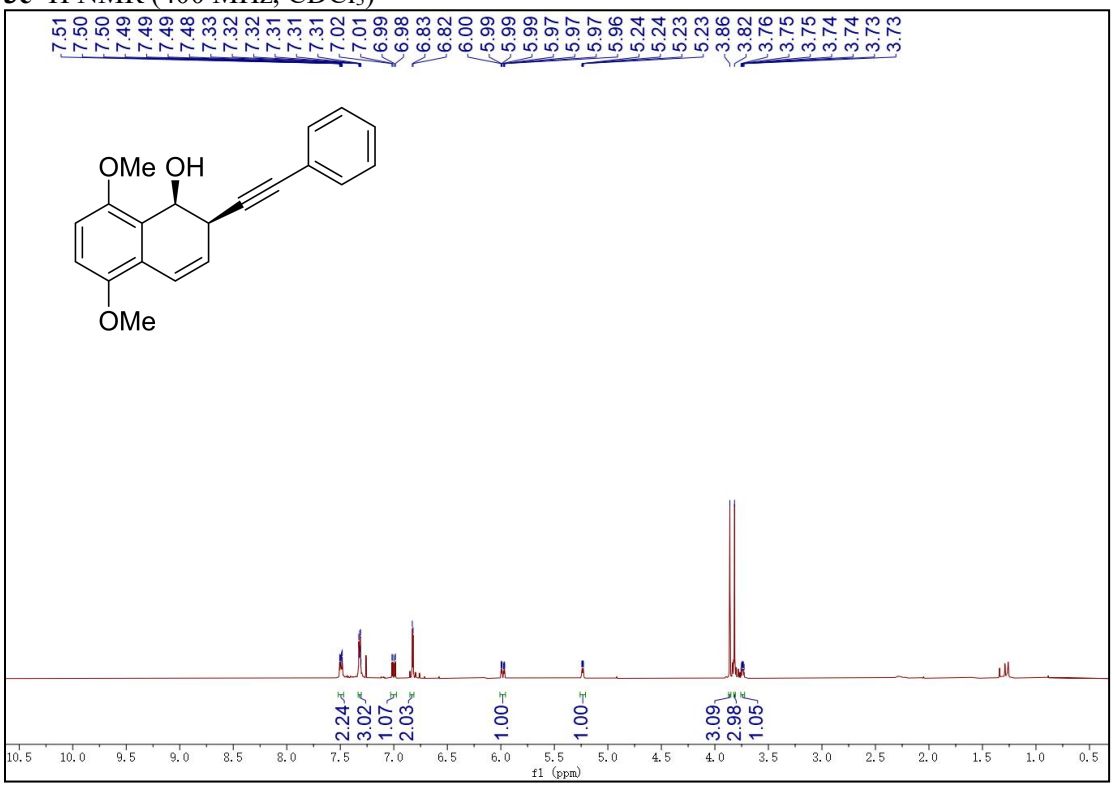
3b ^{1}H NMR (400 MHz, $CDCl_3$)



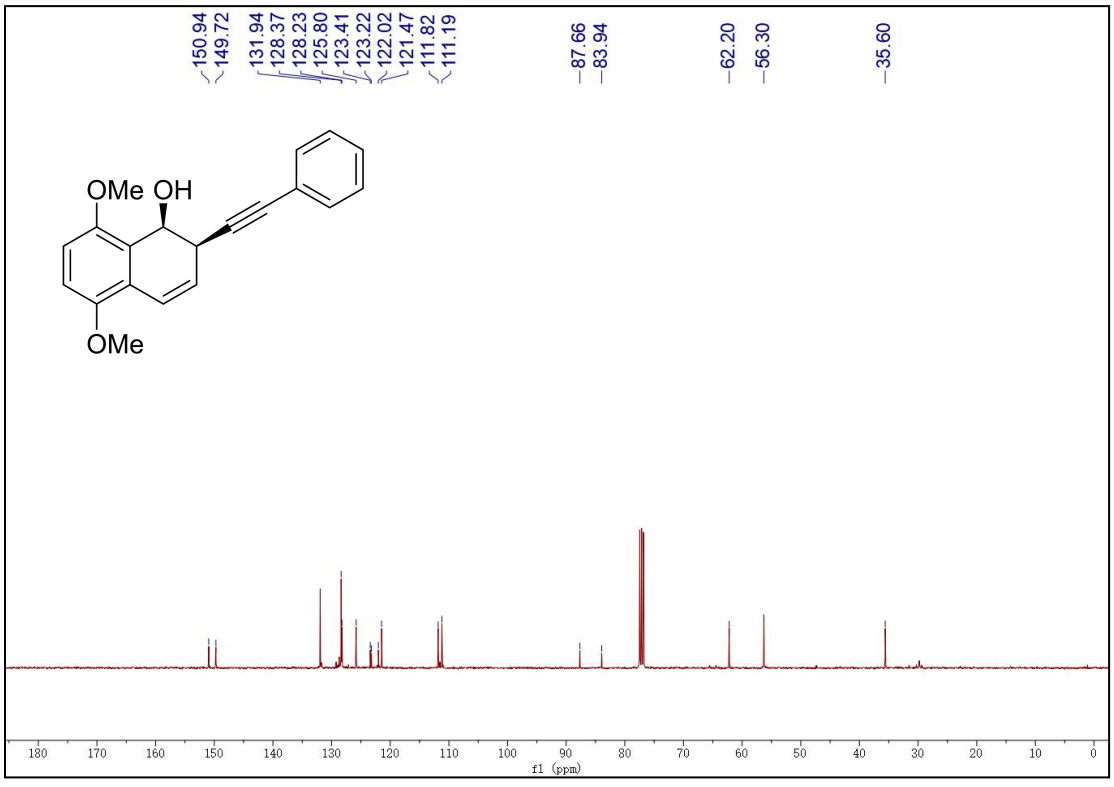
3b ^{13}C NMR (101 MHz, $CDCl_3$)



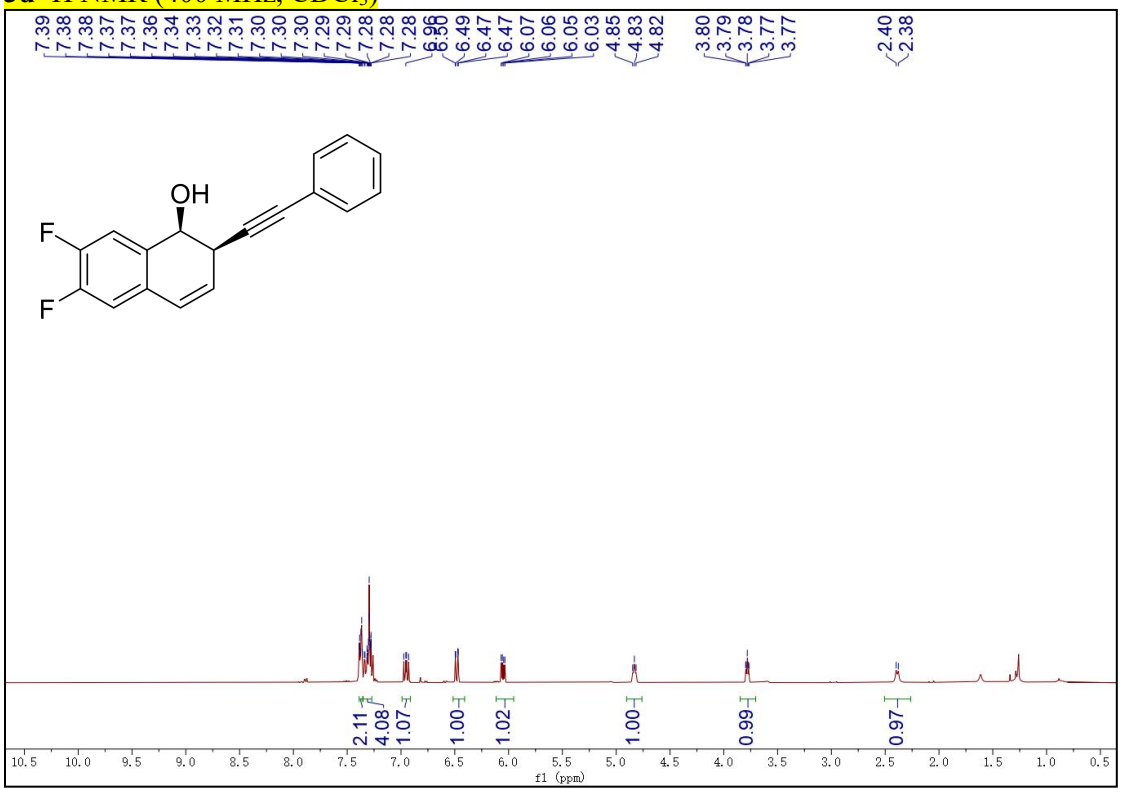
3c ^{1}H NMR (400 MHz, $CDCl_3$)



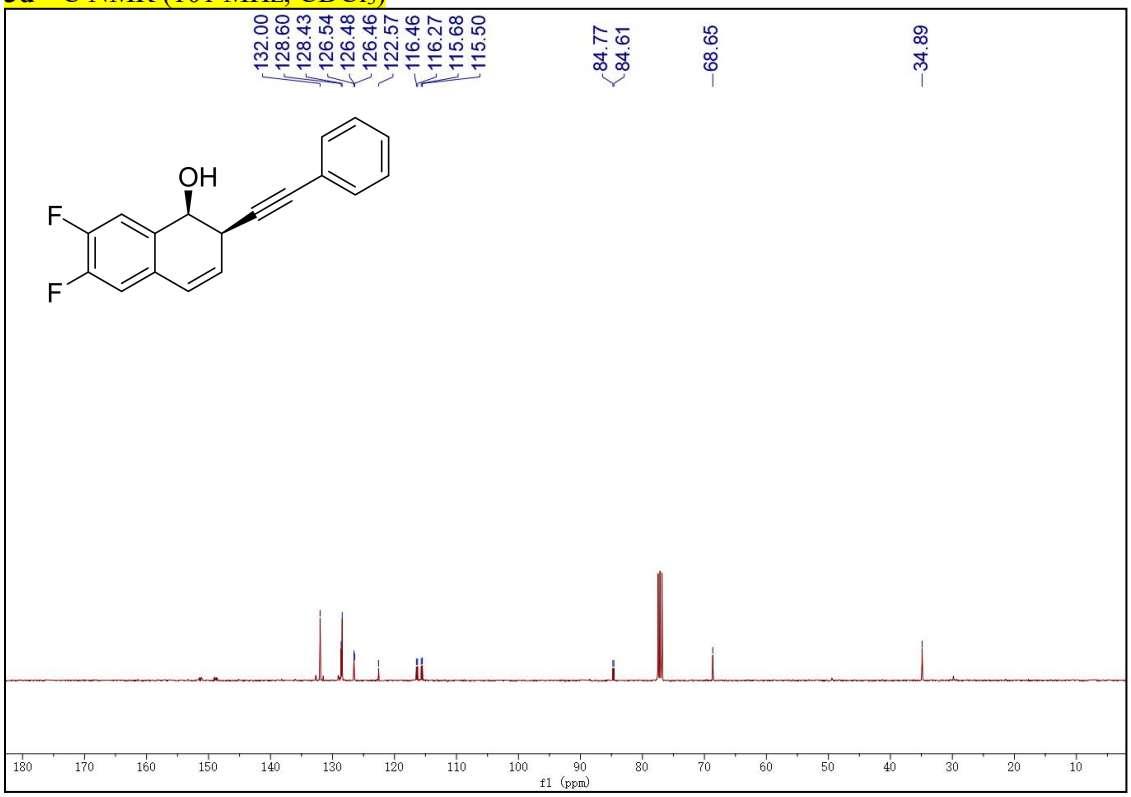
3c ^{13}C NMR (101 MHz, $CDCl_3$)



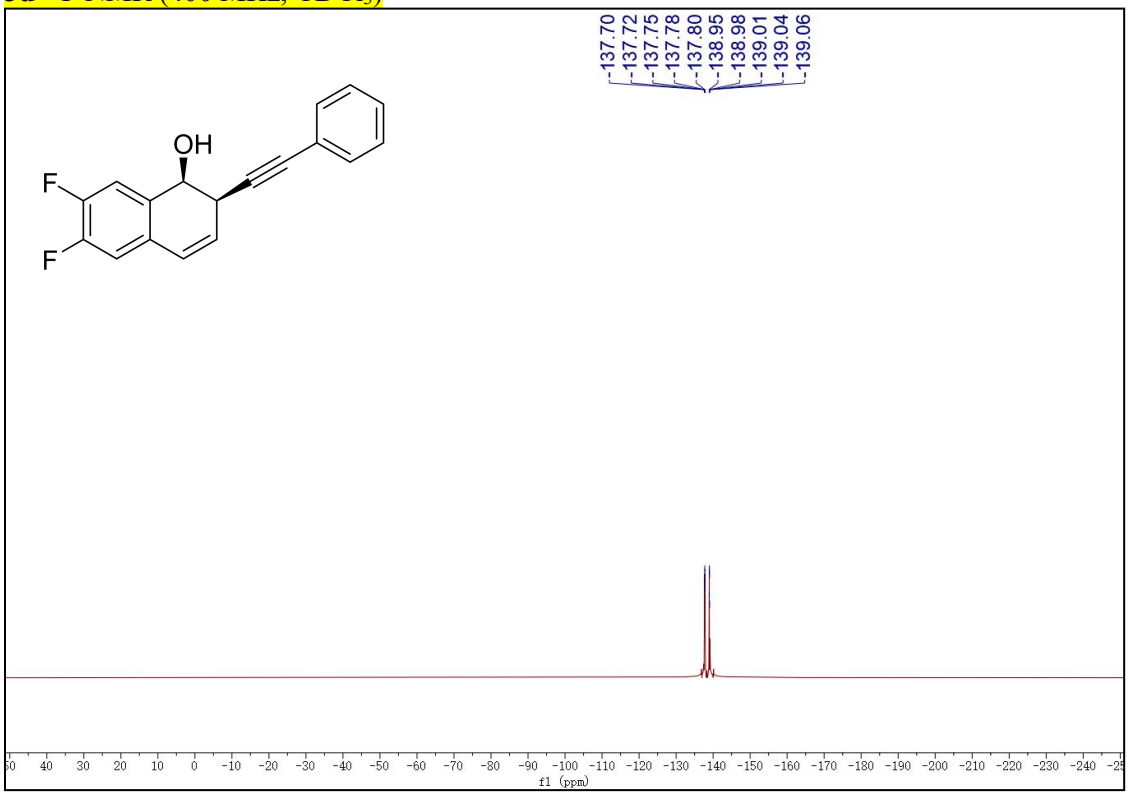
3d ^{1}H NMR (400 MHz, $CDCl_3$)



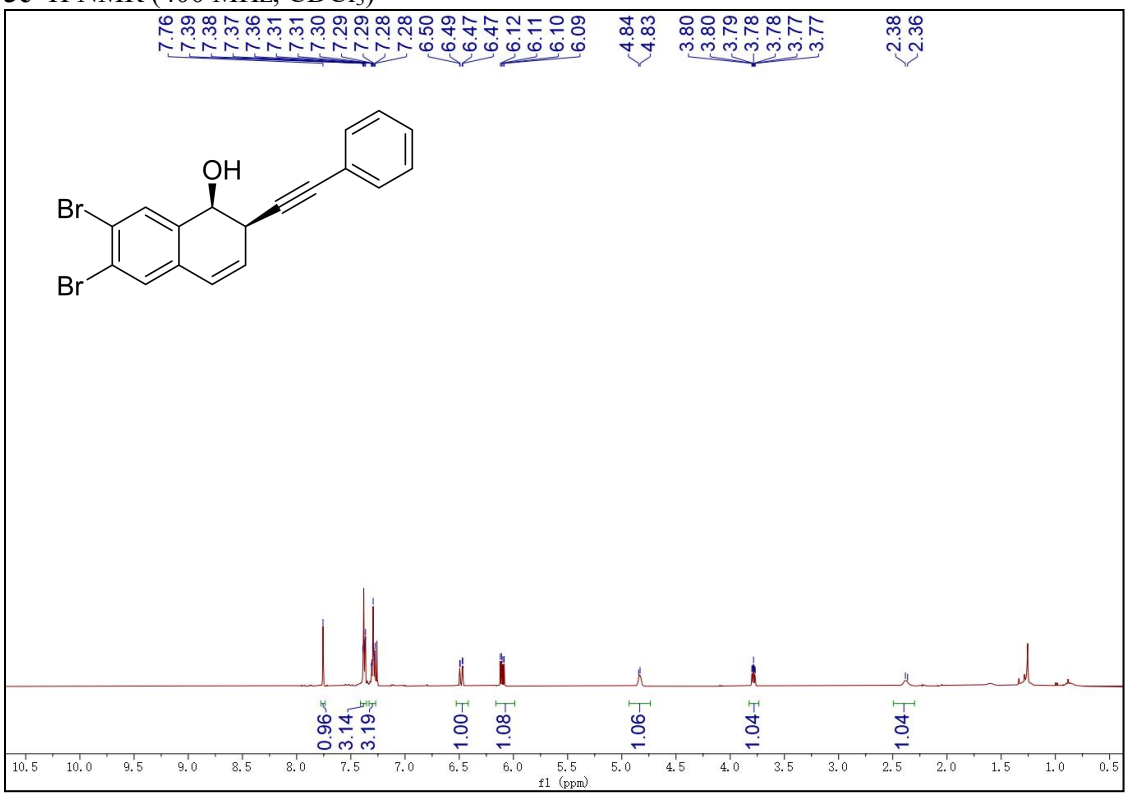
3d ^{13}C NMR (101 MHz, $CDCl_3$)



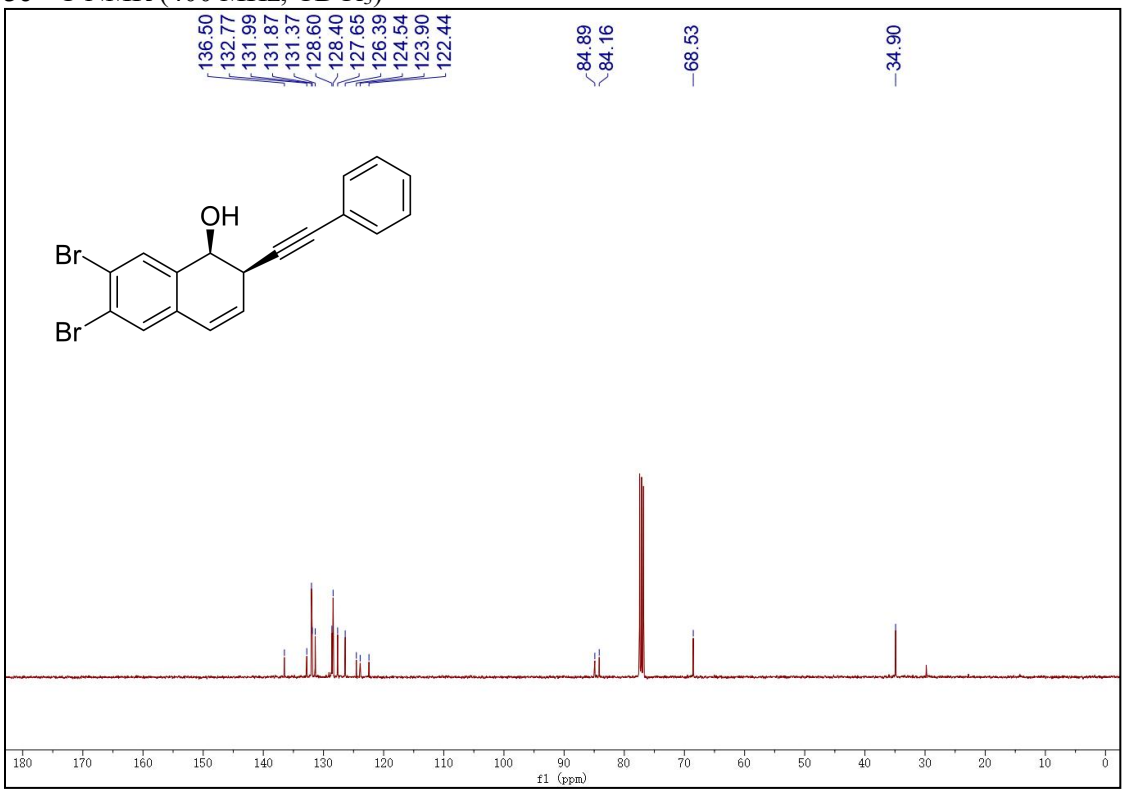
3d ^{19}F NMR (400 MHz, $CDCl_3$)



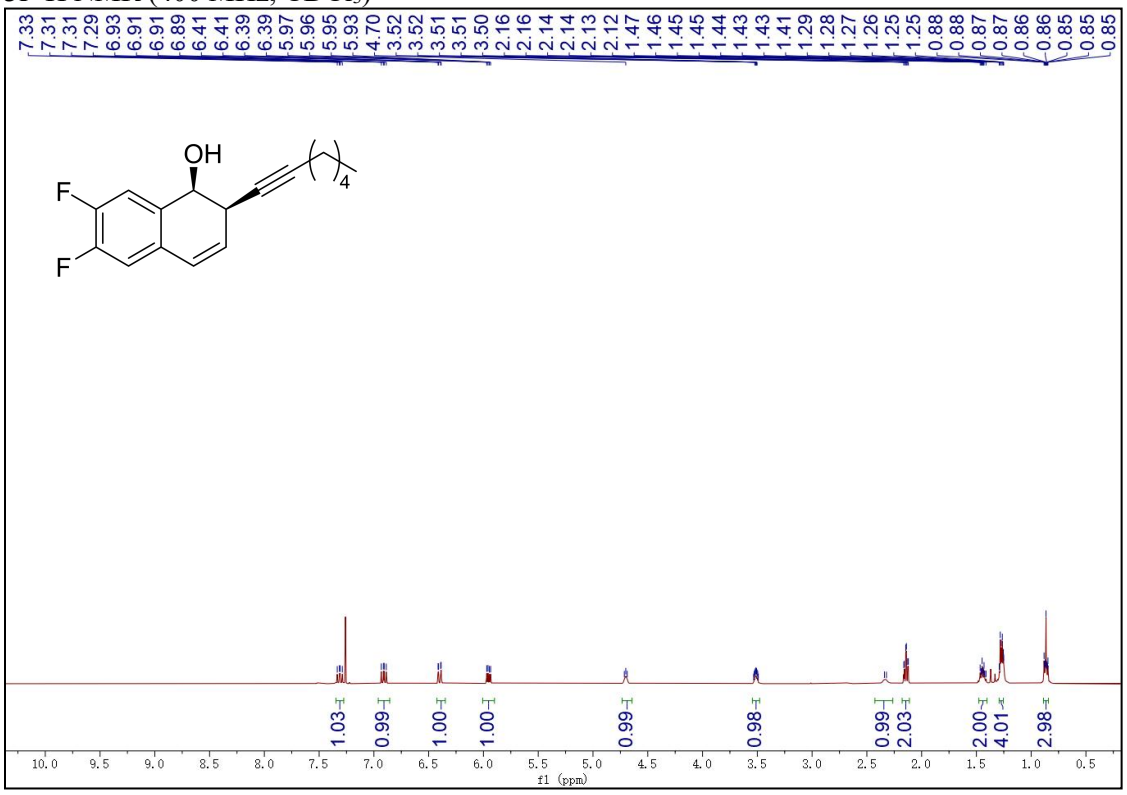
3e ^{1}H NMR (400 MHz, $CDCl_3$)



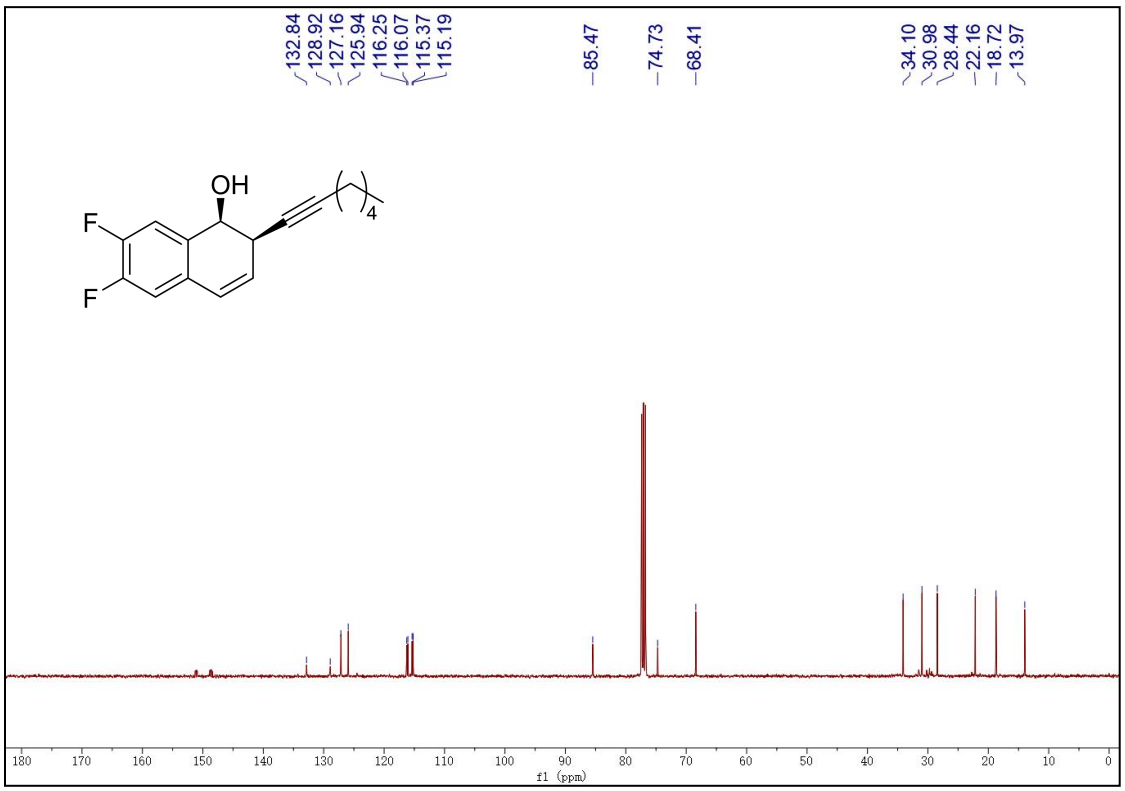
3e ^{13}C NMR (400 MHz, $CDCl_3$)



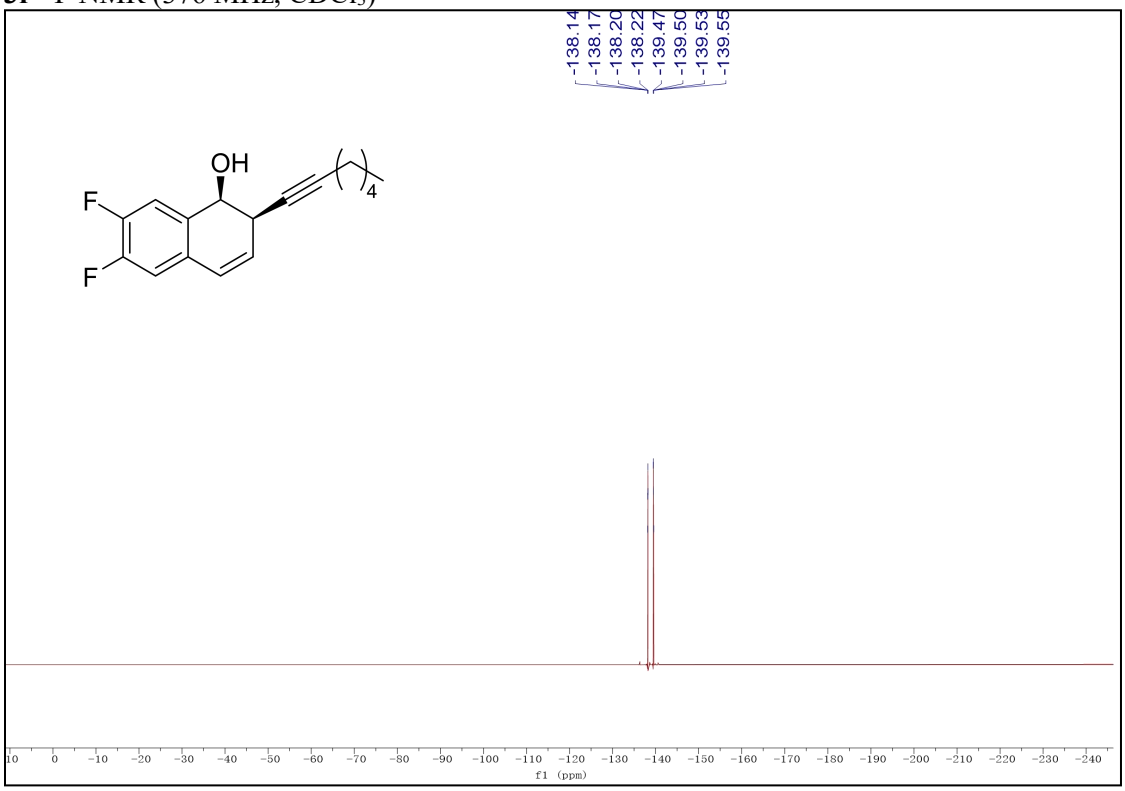
3f ^{1}H NMR (400 MHz, $CDCl_3$)



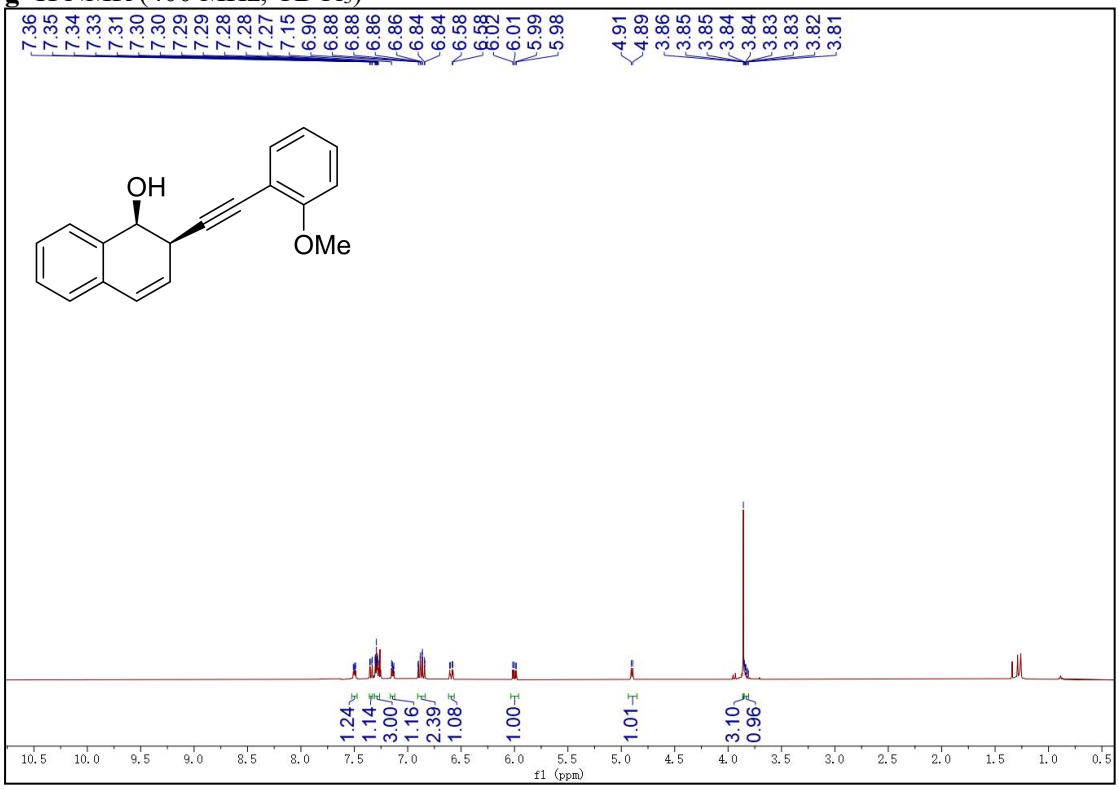
3f ^{13}C NMR (400 MHz, $CDCl_3$)



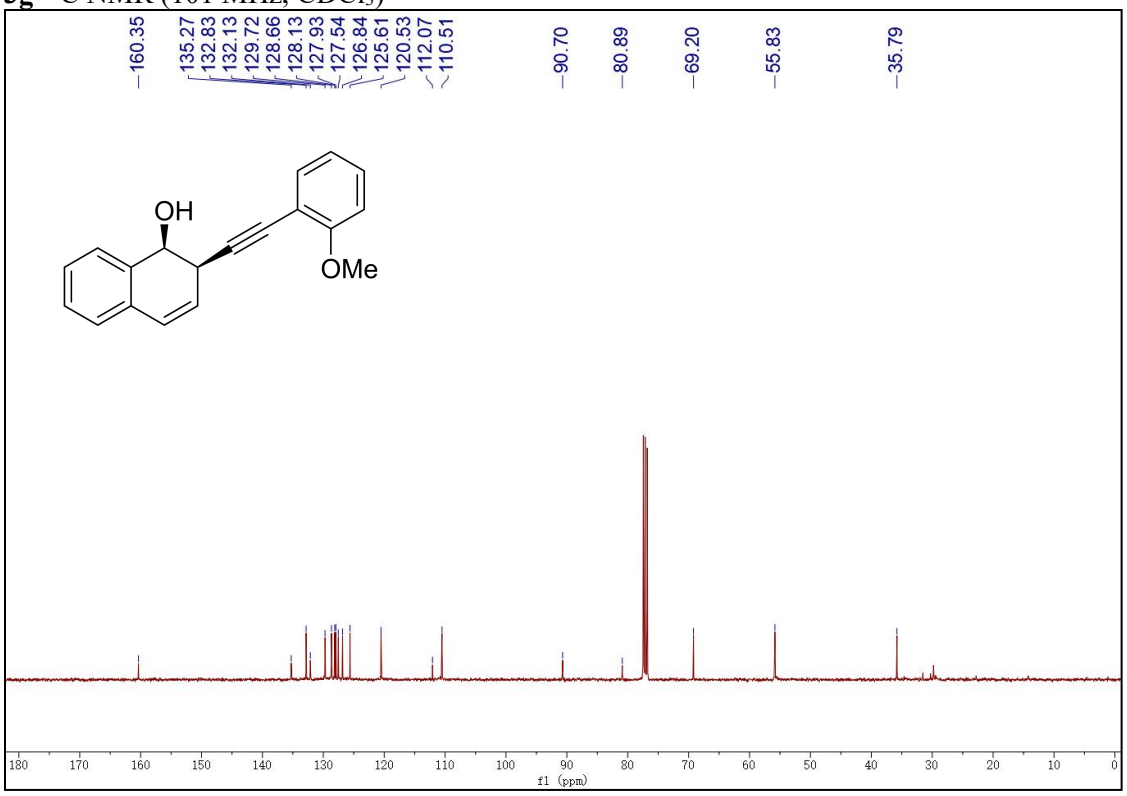
3f ^{19}F NMR (376 MHz, $CDCl_3$)



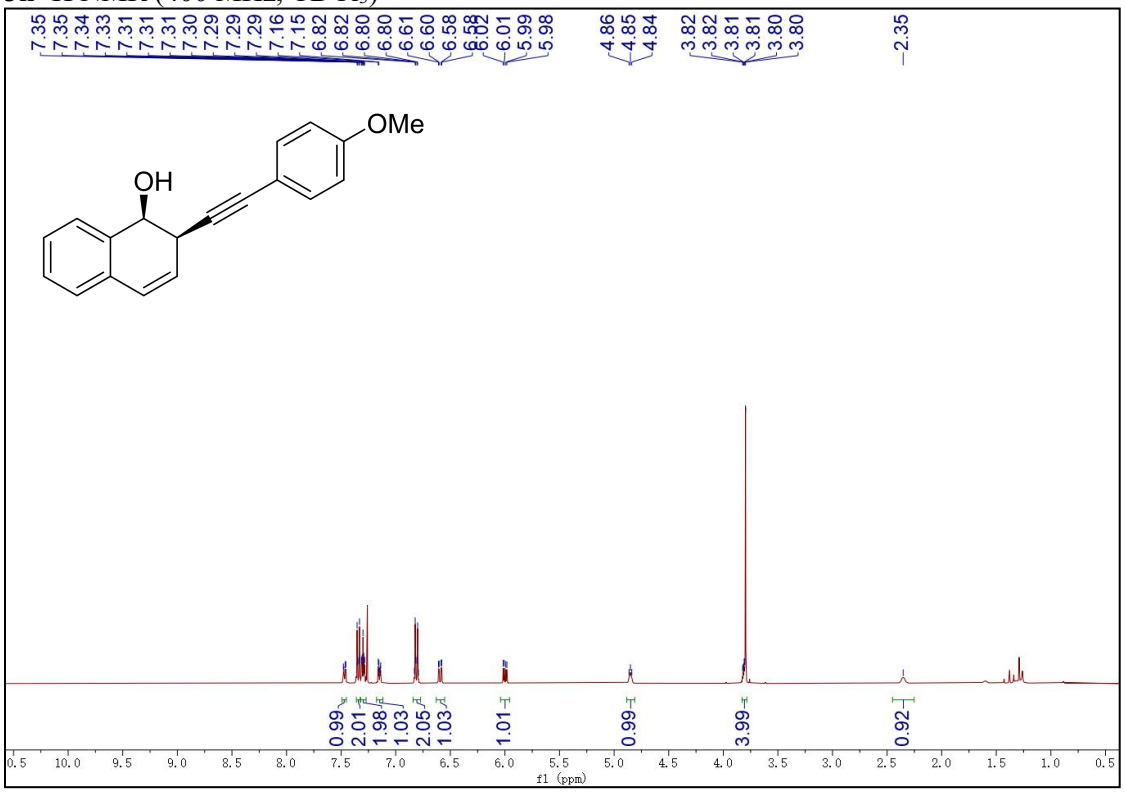
3g ^{1}H NMR (400 MHz, $CDCl_3$)



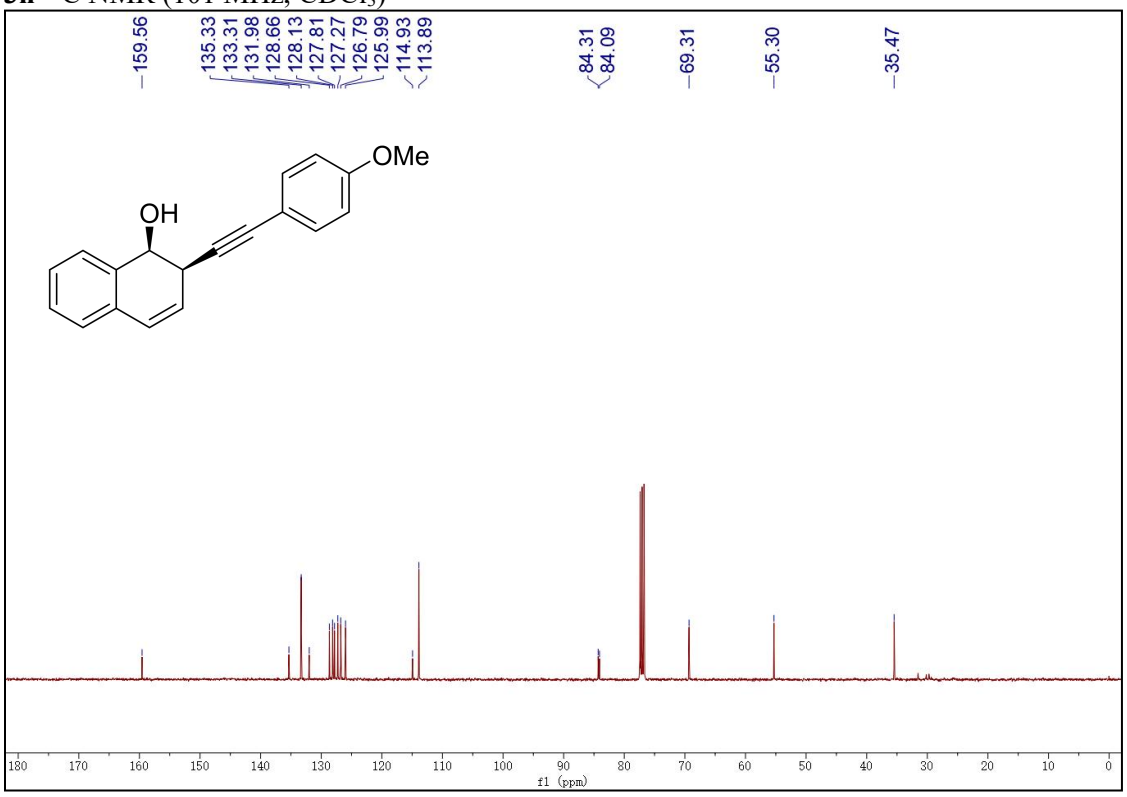
3g ^{13}C NMR (101 MHz, $CDCl_3$)



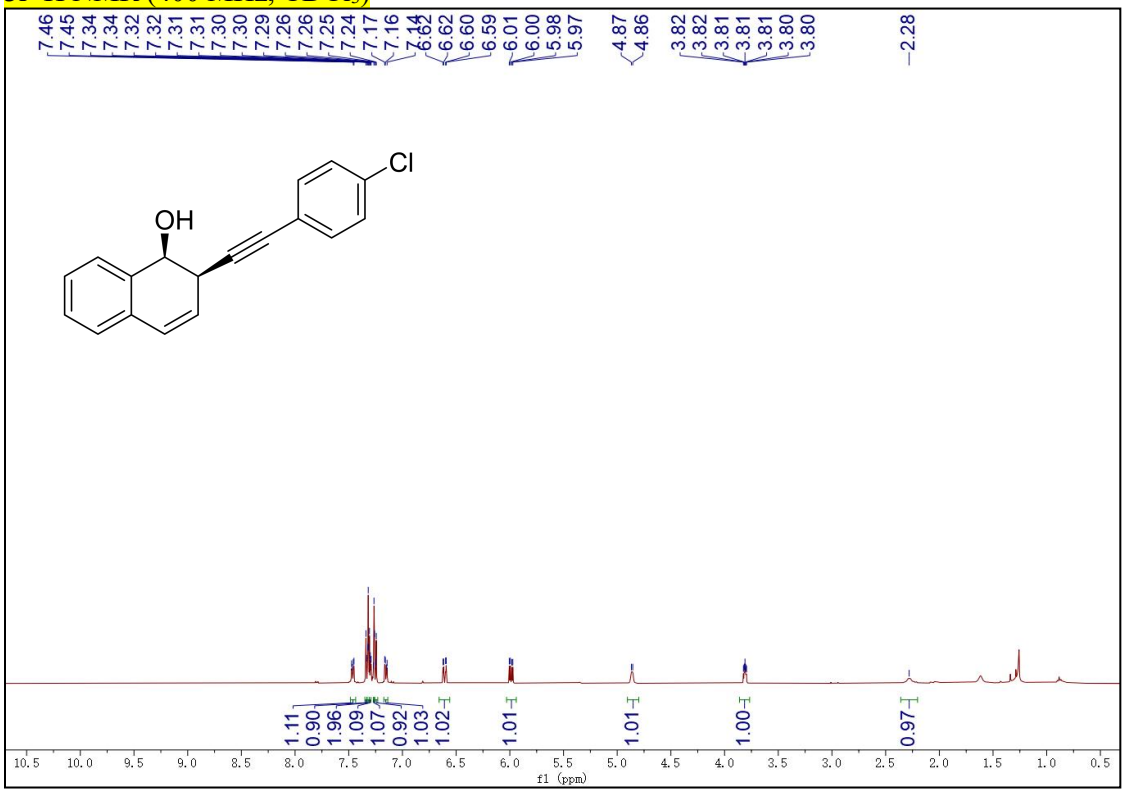
3h ^{1}H NMR (400 MHz, $CDCl_3$)



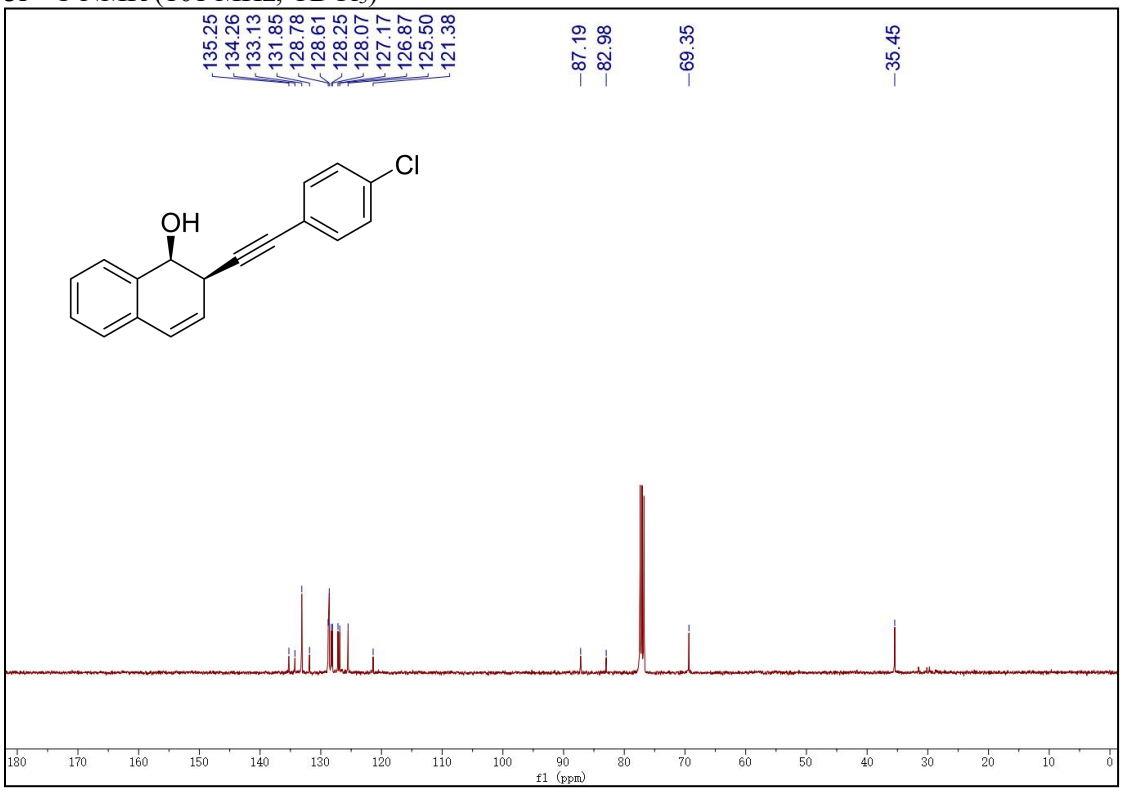
3h ^{13}C NMR (101 MHz, $CDCl_3$)



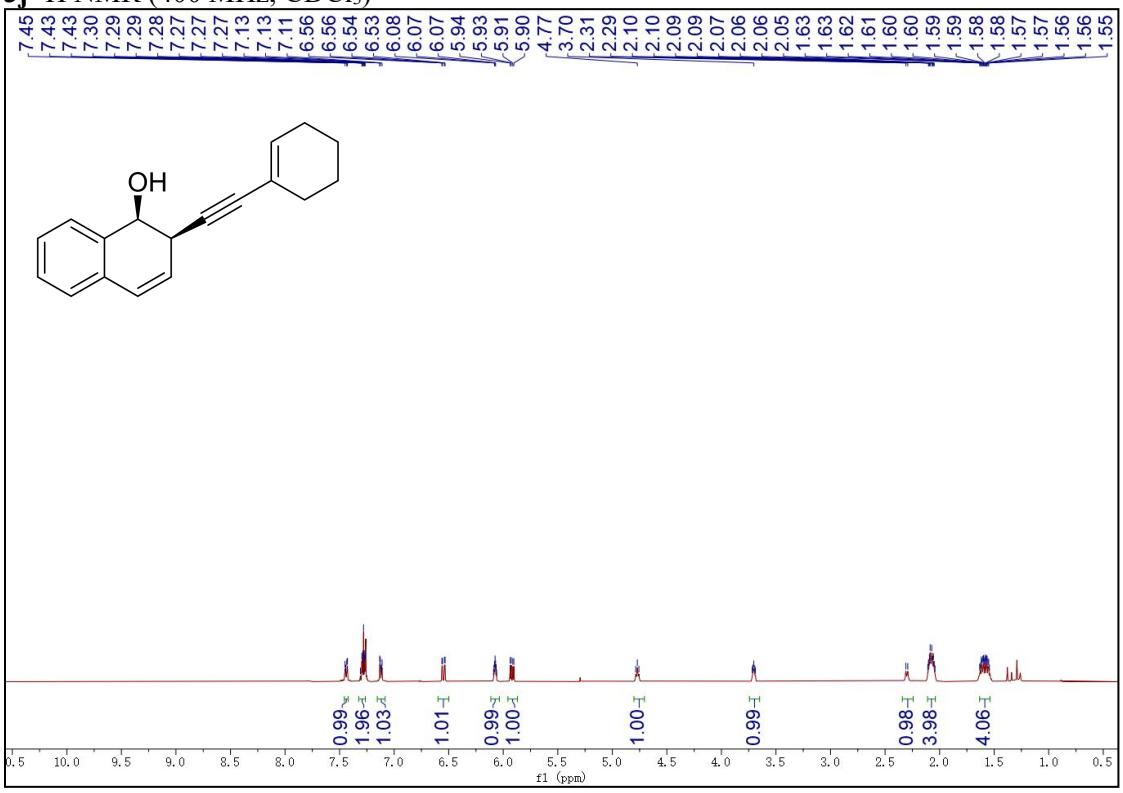
3i ^{1}H NMR (400 MHz, $CDCl_3$)



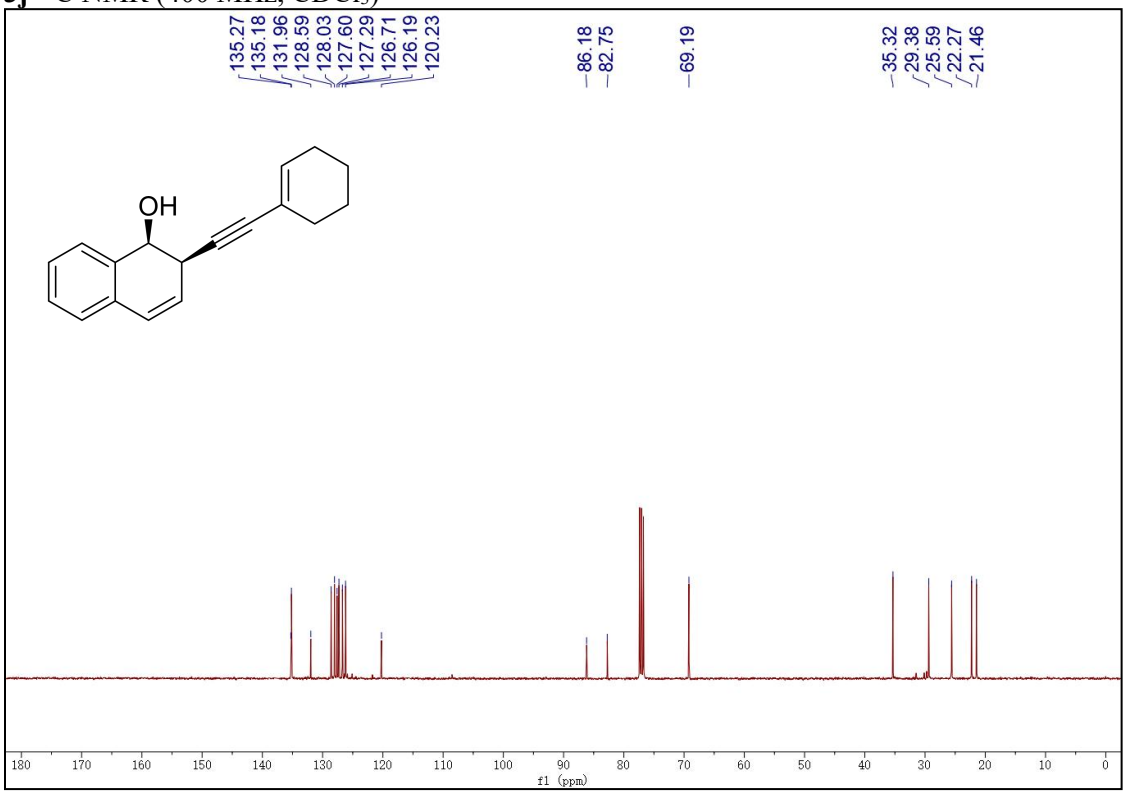
3i ^{13}C NMR (101 MHz, $CDCl_3$)



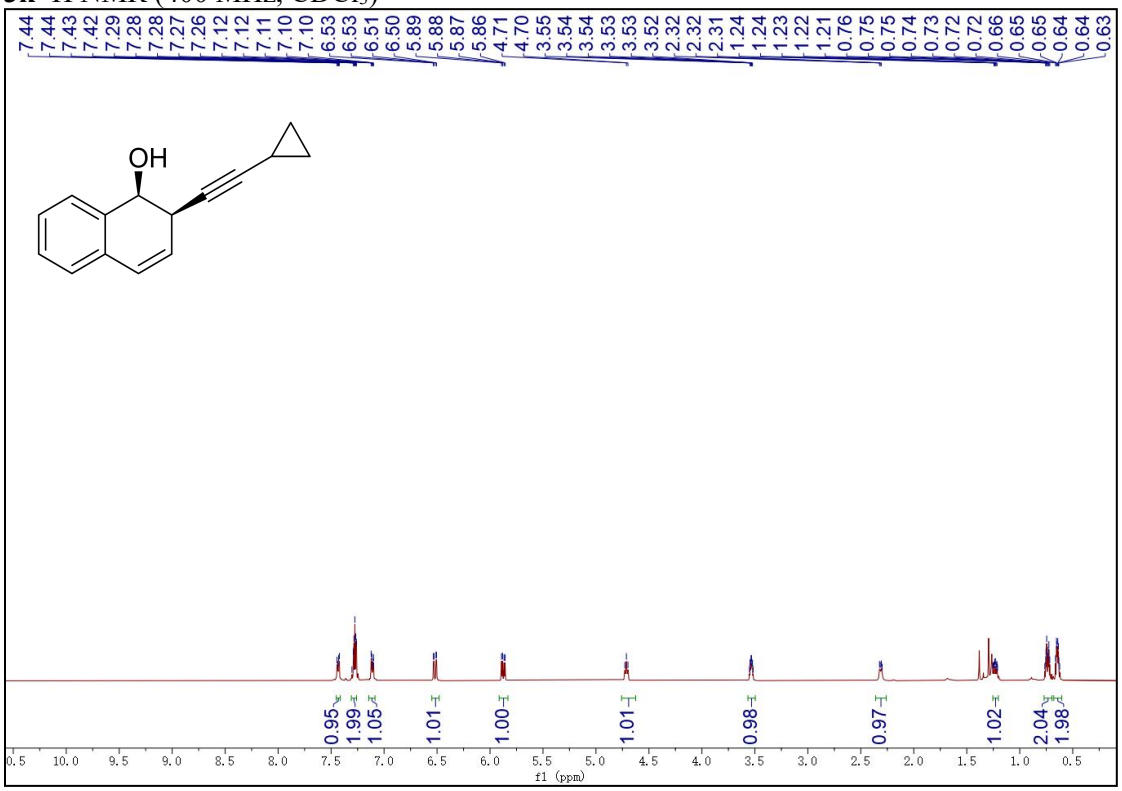
3j ^{1}H NMR (400 MHz, $CDCl_3$)



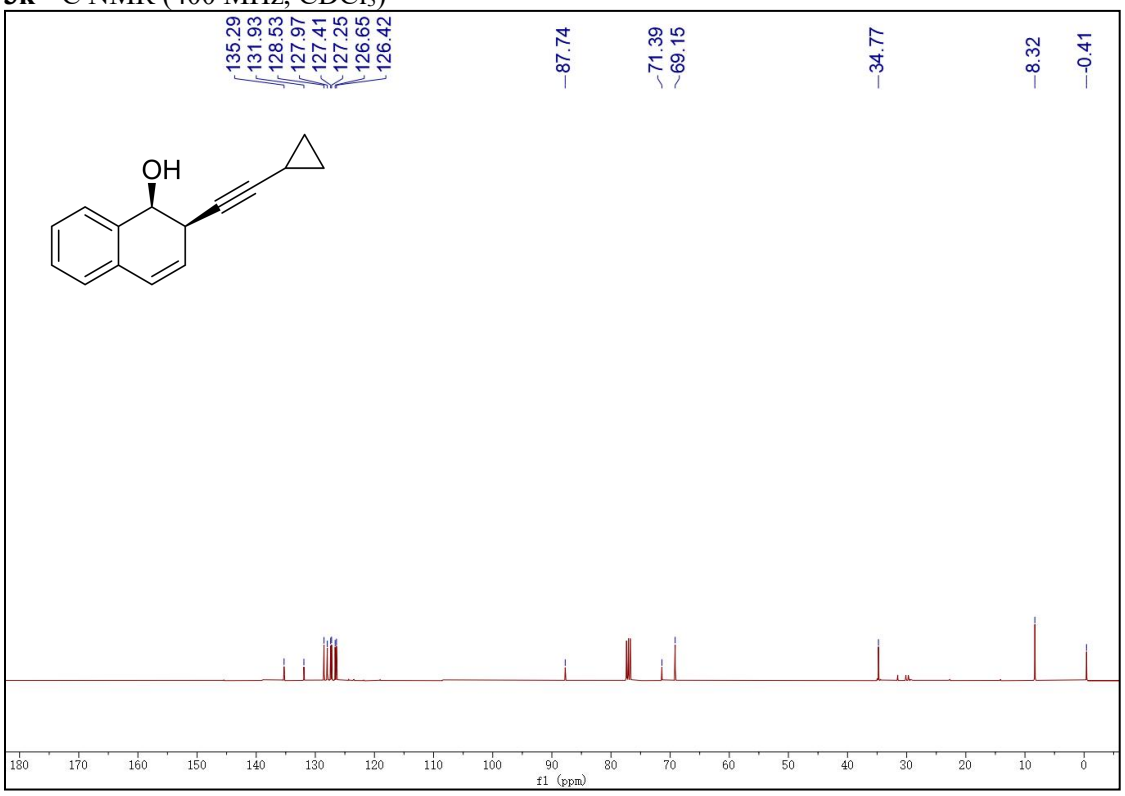
3j ^{13}C NMR (400 MHz, $CDCl_3$)



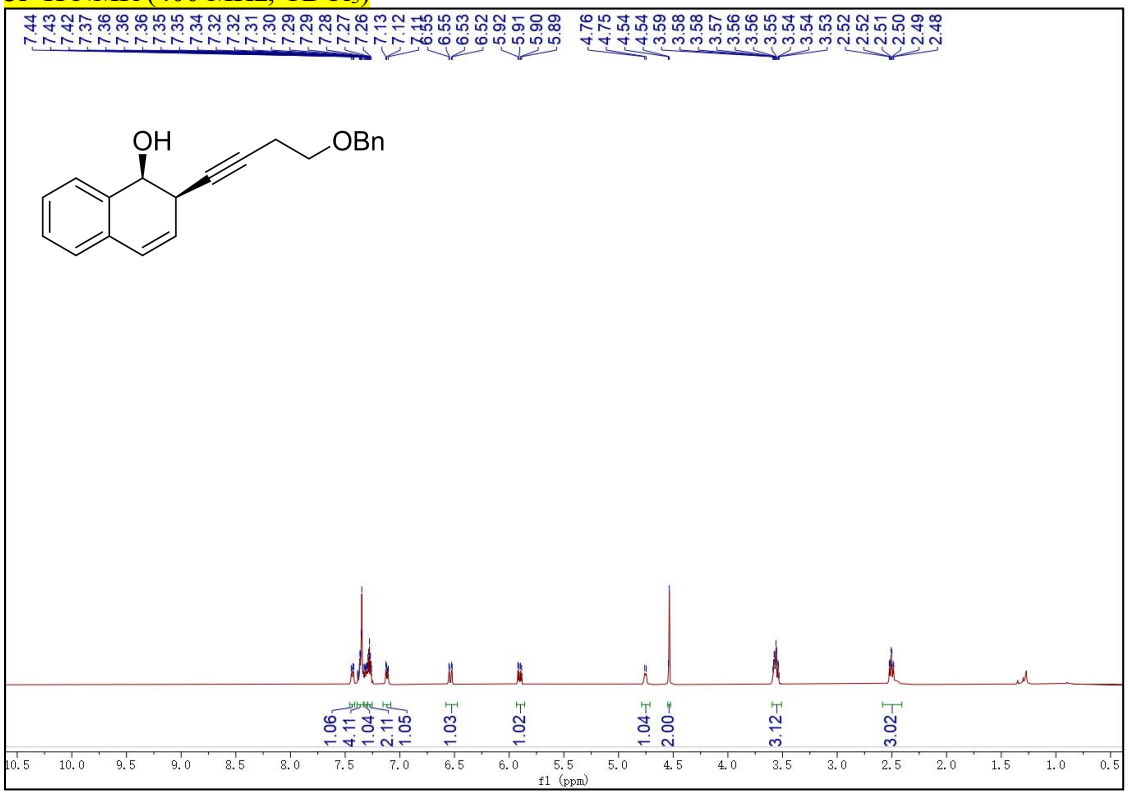
3k ^{1}H NMR (400 MHz, $CDCl_3$)



3k ^{13}C NMR (400 MHz, $CDCl_3$)



3l ^{1}H NMR (400 MHz, $CDCl_3$)



3l ^{13}C NMR (400 MHz, $CDCl_3$)