Electronic Supplementary Material (ESI) for ChemComm.
This journal is © The Royal Society of Chemistry 2019

Supporting Information

Unexpected multi-component one-pot cascade to access furanobenzodihydropyran-fused polycyclic heterocycles

Jiaomei Guo, Hongjie Miao, Yang Zhao, Xuguan Bai, Yanshuo Zhu, Qilin Wang* and Zhanwei Bu*

Institute of Functional Organic Molecular Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, China.

E-mail: wangqilin@henu.edu.cn; buzhanwei@henu.edu.cn

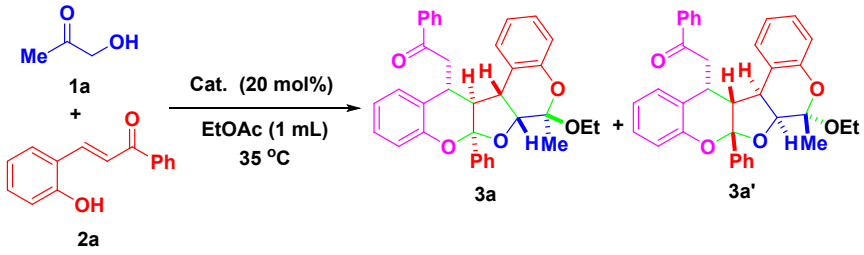
Table of Contents

1. General methods

NMR spectra were recorded with tetramethylsilane as the internal standard. ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 100 MHz (Bruker Avance). ^{1}H NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) with the solvent signal as the internal standard ($CDCl_3$ at 7.26 ppm, $(CD_3)_2SO$ at 2.50 ppm). ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.00 ppm, $(CD_3)_2SO$ at 39.52 ppm). Data are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet), br (broad) or m (multiplets), coupling constants (Hz) and integration. Flash column chromatography was carried out using silica gel eluting with ethyl acetate and petroleum ether. High resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer. Reactions were monitored by TLC and visualized with ultraviolet light. IR spectra were recorded on a Thermo Fisher Nicolet Avatar 360 FTIR spectrometer on a KBr beam splitter. All the solvents were used directly without any purification.

2. Optimization of reaction conditions

Table S1 The screening of catalysts[a]



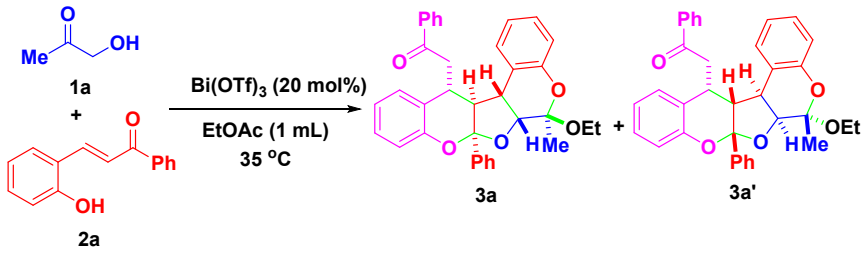
entry	Cat.	time (h)	yield[b]	**3a/3a'**[c]
1	TfOH	72	45	1:1
2	*p*-TSA	72	29	1:1
3	$Fe(OTf)_3$	72	45	1:1
4	$Bi(OTf)_3$	48	52	1:1
5	$In(OTf)_3$	72	23	1:1
6	$Sc(OTf)_3$	72	40	1:1
7	$Cu(OTf)_2$	72	--	--
8	$Yb(OTf)_3$	72	--	--
9	$Zn(OTf)_2$	72	--	--

[a] Unless otherwise noted, the reactions were conducted with 0.48 mmol of **1a** and 0.40 mmol **2a** with 20 mol% of catalyst in 1.0 mL of EtOAc at 35 °C. [b] Isolated yields obtained by silica gel column chromatography. [c] The two diastereoisomers could be separated by silica gel column chromatography, and the dr value was determined by ^{1}H NMR analysis of the crude reaction mixture.

To determine the optimal condition, reactions between hydroxyacetone **1a** and *ortho*-hydroxychalcone **2a** were conducted under the catalysis of different Brønsted acids and Lewis acids (Table S1). Among them, $Bi(OTf)_3$ turned out to be the best of choice, with which the corresponding products **3a**/**3a'** were afforded in 52% yield with 1:1 dr (Table S1, entry 4). Unfortunately, $Cu(OTf)_2$, $Yb(OTf)_3$ and $Zn(OTf)_2$ could not promote the reaction.

After the optimal catalyst established, we also evaluated the effect of substrate ratios (Table S2). The substrate ratio has an apparent influence on the yields. When the molar ratio of **1a** to **2a** was changed from 1.2:1 to 1:1, the yield was enhanced to 72% from 52%, and the reaction time was shortened to 24 h (Table S2, entries 1 vs 2). Further improvement of the amount of **1a** did not give better results (Table S2, entries 3 and 4). And it was not beneficial to the yields when excessive **2a** was employed.

Table S2 Optimization of the substrate ratio[a]

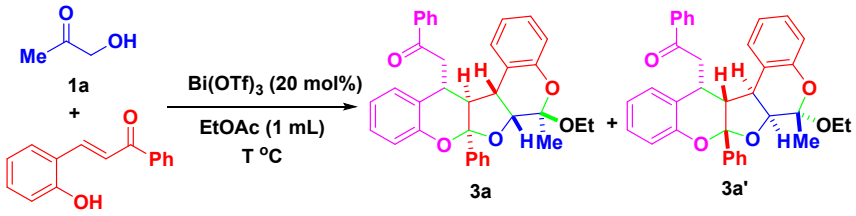


entry	**1a**/**2a**	time (h)	yield[b]	**3a**/**3a'**[c]
1	1:1	24	72	1:1
2	1.2:1	48	52	1:1
3	1.5:1	24	66	1:1
4	2:1	24	65	1:1
5	1:1.2	36	69	1:1
6	1:1.5	36	60	1:1
7	1:1.8	36	62	1:1

[a] Unless otherwise noted, the reaction was conducted on a 0.40 mmol scale of the starting materials in 1.0 mL of EtOAc. [b] Isolated yield obtained by column chromatography. [c] The two diastereoisomers could be separated by silica gel column chromatography, and the dr value was determined by ^{1}H NMR analysis of the crude reaction mixture.

We also investigated the effect of reaction temperatures (Table S3). When the reaction was conducted at 25 °C, it did not occur at all. Increasing the temperatures from 35 °C to 40 °C, the yield was improved to 76% with reduced reaction time (Table S3, entries 2 vs 3). Further increasing the temperatures gave inferior results. When the reaction was conducted at 80 °C, the desired product was obtained in only 12% yield (Table S3, entry 7).

Table S3 Optimization of reaction temperatures[a]



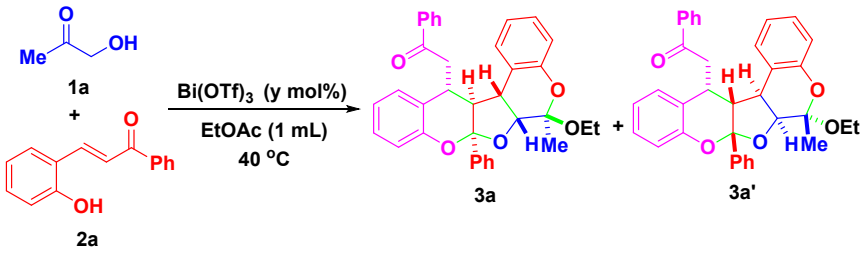
entry	T (°C)	time (h)	yield[b]	**3a/3a'**[c]
1	25	72	--	--
2	35	24	72	1:1
3	40	10	76	1:1
4	50	10	70	1:1
5	60	10	68	1:1
6	70	10	26	n.d.
7	80	10	12	n.d.

[a] Unless otherwise noted, the reactions were conducted with 0.40 mmol of **1a** and 0.40 mmol **2a** with 20 mol% of $Bi(OTf)_3$ in 1.0 mL of EtOAc at 40 °C. [b] Isolated yields obtained by silica gel column chromatography. [c] The two diastereoisomers could be separated by silica gel column chromatography, and the dr value was determined by ^{1}H NMR analysis of the crude reaction mixture. n.d. = not determined.

Then, we studied the effect of the catalyst loadings (Table S4). With the increase of the catalyst loadings, the yields increased. When 20 mol% of $Bi(OTf)_3$ was used, the desired products **3a/3a'** was obtained in 76% yield (Table S4, entry 4). However, the yield could not be further

improved by using 25 mol% of catalyst. Therefore, 20 mol% was the best of choice.

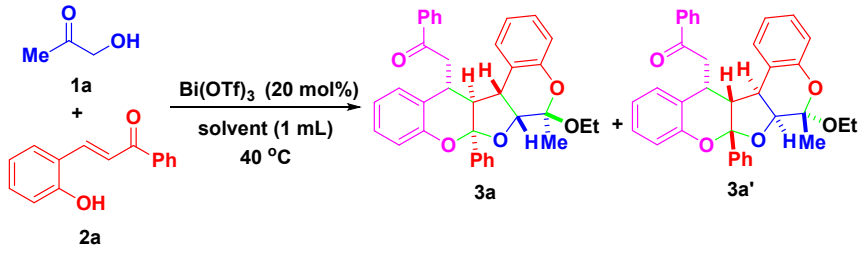
Table S4 Screening the catalyst loadings[a]



entry	y	time (h)	yield[b]	**3a/3a'**[c]
1	5	10	53	1:1
2	10	10	64	1:1
3	15	10	67	1:1
4	20	10	76	1:1
5	25	10	51	1:1

[a] Unless otherwise noted, the reactions were conducted with 0.40 mmol of **1a** and 0.40 mmol **2a** in 1.0 mL of EtOAc at 40 °C. [b] Isolated yields obtained by silica gel column chromatography. [c] The two diastereoisomers could be separated by silica gel column chromatography, and the dr value was determined by ^{1}H NMR analysis of the crude reaction mixture.

Table S5 The effect of the solvent[a]



entry	solvent	time (h)	yield[b]	**3a/3a'**[c]
1	EtOAc	10	76	1:1
2	CH_3CN	72	--	--
3	$CHCl_3$	72	--	--
4	THF	72	--	--
5	toluene	72	--	--
6	EtOH	72	40	1:1

7[d]	EtOAc	72	38	1:1
8[d]	CH_3CN	48	73	1.2:1
9[d]	$CHCl_3$	24	72	1.2:1
10[d]	THF	72	52	1:1
11[d]	toluene	72	58	1:1
12[e]	EtOAc	24	47	1:1
13[f]	EtOAc	24	43	1:1
14[g]	EtOAc	24	40	1:1

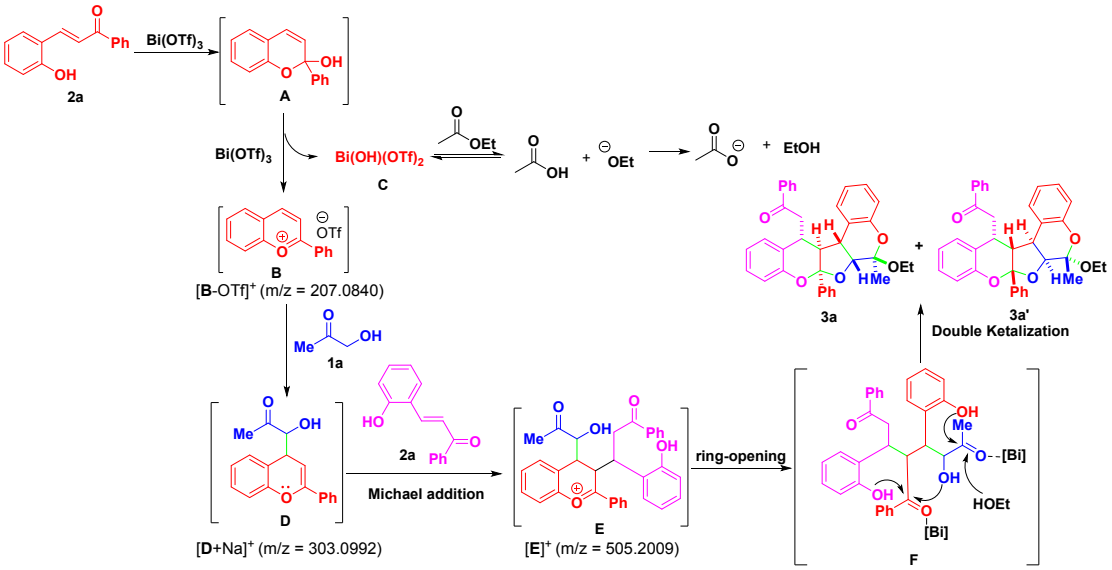
[a] Unless otherwise noted, the reactions were conducted with 0.40 mmol of **1a** and 0.40 mmol **2a** in 1.0 mL of specified solvent at 40 °C. [b] Isolated yields obtained by silica gel column chromatography. [c] The two diastereoisomers could be separated by silica gel column chromatography, and the dr value was determined by ^{1}H NMR analysis of the crude reaction mixture. [d] Adding 5.0 equivalents of EtOH to 1.0 mL of the specified solvent. [e] Adding 1.0 equivalents of EtOH to 1.0 mL of the specified solvent. [f] Adding 2.0 equivalents of EtOH to 1.0 mL of the specified solvent. [g] Adding 4.0 equivalents of EtOH to 1.0 mL of the specified solvent.

To further improve the yield, the reaction media were evaluated (Table S5). The solvents had significant influence on the reaction outcomes. By using solvents completely absent of EtO-sources, such as CH_3CN, $CHCl_3$, THF and toluene, the reaction was totally retarded (Table S5, entries 2-5). By addition of 0.1 mL of EtOH (5.0 equiv.) to EtOAc or performing the reaction in pure EtOH, the yields dropped sharply (Table S5, entries 6 and 7). Our reaction could proceed successfully in the combined solvent system, such as CH_3CN-EtOH, $CHCl_3$-EtOH, THF-EtOH and toluene-EtOH, albeit with relatively lower yields (Table S5, entries 8-11). Subsequently, we did some experiments by adding different equivalents of ethanol into the reaction systems (Table S5, entries 7 and 12-14). And the results showed that addition of ethanol was detrimental to the yields. As the amount of ethanol increased, the yields decreased with prolonged reaction time.

3. Mechanistic studies

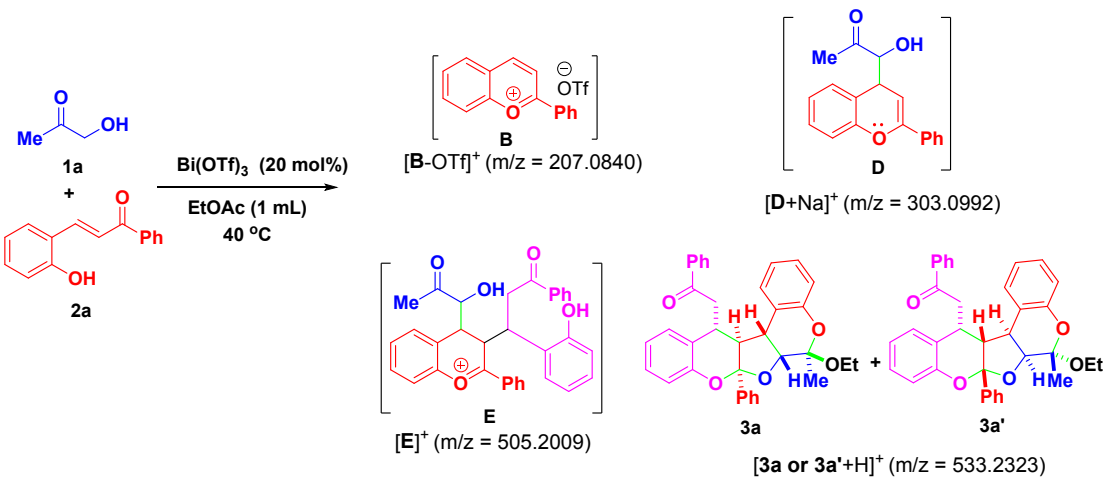
At this stage, the exact reaction mechanism is still unclear. Based on the experimental results and HRMS analysis (for details, see the following), a plausible reaction mechanism was proposed to explain the reaction pathway (Scheme S1). Initially, under the catalysis of $Bi(OTf)_3$, an intramolecular cyclization of **2a** occurred to give intermediate **A**, which

subsequently was converted into benzopyrylium intermediate **B** and **C**. A transesterification between *in situ* generated intermediate **C** and ethyl acetate took place to generate ethyoxyl group. Then, a 1,4-addition of intermediate **B** and **1a** took place to deliver intermediate **D**. Subsequently, another Michael addition between intermediate **D** and **2a** proceeded to generate benzopyrylium **E**. Followed by a ring-opening and double ketalization cascade process, the desired products **3a/3a'** were afforded in the end. We assumed that the excellent stereochemical outcome of this multi-component cascade reaction may result from the multiple hydrogen bonding sites of substrates together with other steric factors, which assisted in the fine-tuning of the transition state at each process. However, the concrete stereochemical model could not be deduced.



Scheme S1 Proposed mechanism

To get some evidences, we tried to detect the intermediate of the crude reaction mixture of **1a** and **2a** in the presence of 20 mol% $Bi(OTf)_3$ by HRMS analysis (Scheme S2). As shown in Figure S1, after the reaction proceeded for 4 h, we could obtain the signal peaks of intermediates **B**, **D** and **E**.



Scheme S2 Reaction between **1a** and **2a** for 4 h

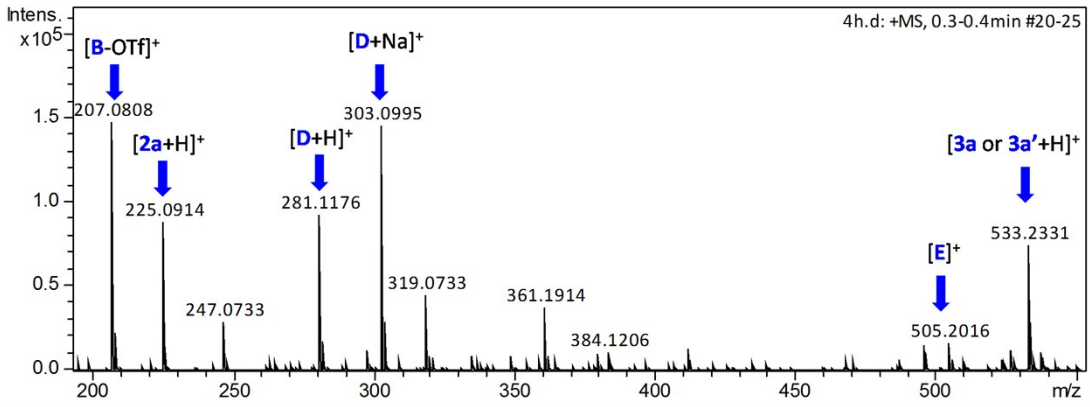
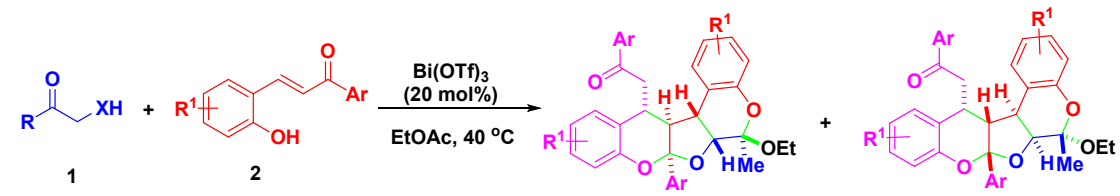


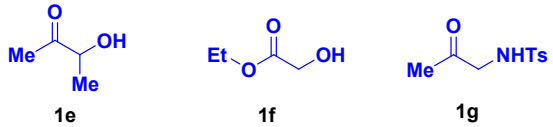
Figure S1 HRMS spectra of the reaction between **1a** and **2a** for 4 h

4. Experimental data for furanobenzopyran-fused heterocycles 3



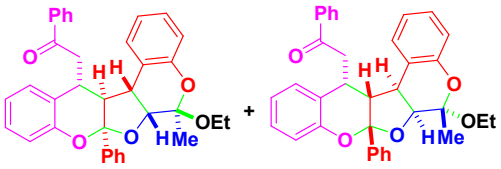
1a, R= Me, X= O
1b, R= Et, X= O
1c, R= Ph, X= O
1d, R= Ph, X= NTs

unsuccessful examples



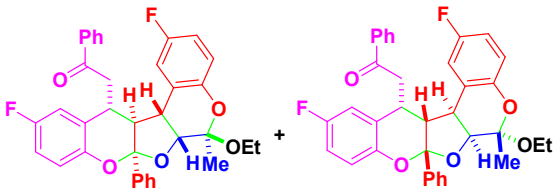
General procedure： To a 5.0 mL vial were successively added α-hydroxyl ketone **1** (0.40 mmol), *ortho*-hydroxychalcone **2** (0.40 mmol), $Bi(OTf)_3$ (0.08 mmol) and 1.0 mL EtOAc. The resulting mixture was stirred at 40 °C until almost full consumption of **2** as monitored by thin

layer chromatography, and then the reaction mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ ethyl acetate) to afford the corresponding products **3** and **3'**. For the reaction of **1b** with **2a**, in addition to **3s** and **3s'**, the bridged cyclic product **4** was also generated. While for **1c** and **1d**, only the bridged cyclic products **5** and **6** were afforded.



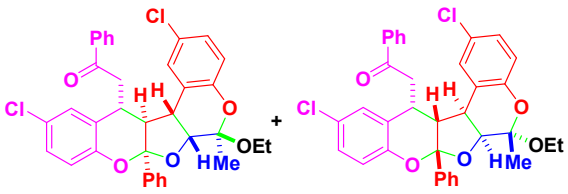
3a **3a'**

White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 80:1-70:1), 81.2 mg, 76% yield; Reaction time = 10 h; dr = 1:1 (**3a**/**3a'**, separable isomers); m. p. 173.7-174.9 °C (**3a**), 204.9-206.3 °C (**3a'**); ^{1}H NMR (400 MHz, $CDCl_3$) for **3a** δ 7.51 (d, J = 8.0 Hz, 2H), 7.43 (t, J = 8.0 Hz, 3H), 7.33 (d, J = 8.0 Hz, 1H), 7.29-7.20 (m, 7H), 7.16 (t, J = 8.0 Hz, 2H), 7.05-6.97 (m, 2H), 6.92 (d, J = 8.0 Hz, 1H), 4.27 (d, J = 8.0 Hz, 1H), 3.97 (t, J = 8.0 Hz, 1H), 3.56-3.46 (m, 1H), 3.41 (q, J = 8.0 Hz, 2H), 2.90 (dd, J_1 = J_2 = 4.0 Hz, 2H), 2.79 (d, J = 8.0 Hz, 1H), 1.63 (s, 3H), 0.77 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3a** δ 197.7, 154.3, 150.3, 141.3, 136.6, 132.9, 129.9, 128.7, 128.5, 128.4, 128.3, 127.8, 127.7, 127.6, 127.4, 126.0, 124.4, 122.5, 122.1, 118.0, 117.3, 108.4, 100.4, 81.5, 59.4, 56.1, 44.3, 43.4, 34.6, 19.6, 15.0. ^{1}H NMR (400 MHz, $CDCl_3$) for **3a'** δ 8.07 (d, J = 8.0 Hz, 2H), 7.61 (dd, J_1 = J_2 = 8.0 Hz, 3H), 7.53 (t, J = 8.0 Hz, 2H), 7.30-7.24 (m, 4H), 7.14 (d, J = 8.0 Hz, 1H), 7.07-7.00 (m, 3H), 6.87 (t, J = 8.0 Hz, 2H), 6.76 (t, J = 8.0 Hz, 1H), 4.01 (t, J = 4.0 Hz, 1H), 3.91 (dd, J_1 = J_2 = 8.0 Hz, 1H), 3.77 (d, J = 4.0 Hz, 1H), 3.50-3.33 (m, 4H), 3.10 (t, J = 4.0 Hz, 1H), 1.61 (s, 3H), 0.76 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3a'** δ 197.0, 155.6, 150.7, 141.5, 136.7, 133.5, 128.8, 128.3 (3C), 128.2, 128.0, 127.6, 127.4, 126.6, 125.5, 125.1, 122.5, 122.0, 118.0, 117.5, 111.8, 98.9, 82.1, 62.1, 56.2, 39.4, 39.1, 31.1, 20.1, 15.1. IR (KBr) for **3a** v 2927, 1687, 1489, 1234, 1105, 755 cm^{-1}; IR (KBr) for **3a'** v 2920, 1685, 1488, 1232, 1117, 757 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{33}O_5$ $[M+H]^+$: 533.2323, found: 533.2323.



3b **3b'**

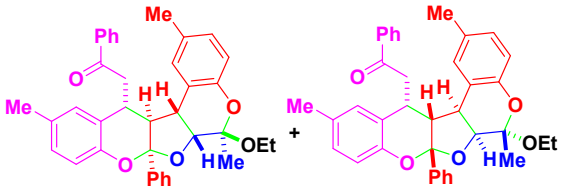
White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 60:1), 53.7 mg, 47% yield; Reaction time = 24 h; dr = 1.2:1 (**3b**/**3b'**, separable isomers); m. p. 174.9-176.3 °C (**3b**), 180.6-182.4 °C (**3b'**); ^{1}H NMR (400 MHz, $CDCl_3$) for **3b** δ 7.51-7.44 (m, 5H), 7.30 (t, J = 8.0 Hz, 2H), 7.25-7.23 (m, 3H), 7.11-7.07 (m, 2H), 7.00-6.93 (m, 2H), 6.87 (dd, $J_1 = J_2$ = 4.0 Hz, 2H), 4.16 (d, J = 8.0 Hz, 1H), 3.90 (t, J = 8.0 Hz, 1H), 3.54-3.50 (m, 1H), 3.43-3.35 (m, 2H), 2.98 (d, J = 8.0 Hz, 2H), 2.82 (d, J = 4.0 Hz, 1H), 1.60 (s, 3H), 0.80 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3b** δ 197.2, 157.9 (d, J = 252.0 Hz, 1C), 150.2, 146.3, 141.1, 136.4, 133.1, 128.6, 128.4 (d, J = 2.0 Hz, 1C), 127.7, 125.8, 118.9 (d, J = 8.0 Hz, 1C), 118.6 (d, J = 9.0 Hz, 1C), 116.2, 115.9, 115.6, 115.3, 114.5, 114.3 (2C), 114.1, 108.9, 100.3, 81.2, 59.2, 56.2, 44.1, 43.9, 35.3, 19.6, 15.0. ^{1}H NMR (400 MHz, $CDCl_3$) for **3a'** δ 8.08 (d, J = 8.0 Hz, 2H), 7.65 (t, J = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 4H), 7.29 (d, J = 4.0 Hz, 3H), 7.09 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 6.99-6.94 (m, 1H), 6.83-6.73 (m, 3H), 6,56 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 4.00 (q, J = 8.0 Hz, 1H), 3.84 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 3.66 (d, J = 8.0 Hz, 1H), 3.50-3.34 (m, 3H), 3.25 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.12 (t, J = 4.0 Hz, 1H), 1.59 (s, 3H), 0.79 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3b'** δ 196.5, 156.8 (d, J = 91.0 Hz, 1C), 151.3, 146.7, 141.3, 136.4, 133.8, 129.0, 128.5, 128.4, 128.1, 125.3, 119.0 (d, J = 8.0 Hz, 1C), 118.7 (d, J = 8.0 Hz, 1C), 1114.8, 114.6 (d, J = 2.0 Hz, 1C), 114.5, 114.3, 114.2, 112.6, 112.3, 112.0, 98.9, 81.8, 61.8, 56.3, 39.8, 38.8, 31.5, 20.0, 15.1. IR (KBr) for **3b** ν 2930, 1688, 1491, 1212, 1095, 757 cm^{-1}; IR (KBr) for **3a'** ν 2927, 1683, 1487, 1193, 1095, 759 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{31}F_2O_5$ $[M+H]^+$: 569.2134, found: 569.2138.



3c **3c'**

White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 70:1), 47.5 mg, 40% yield; Reaction time = 24 h; dr = 3.7:1 (**3c**/**3c'**, inseparable isomers); m. p. 124.1-

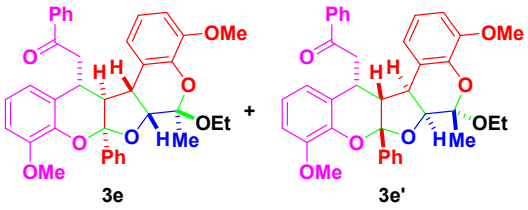
125.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, J = 8.0 Hz, 2H), 7.65 (t, J = 8.0 Hz, 1H), 7.55 (t, J = 8.0 Hz, 4H), 7.33-7.23 (m, 4H), 7.09-6.99 (m, 3H), 6.80 (dd, J_1 = J_2 = 4.0 Hz, 2H), 3.97 (q, J = 8.0 Hz, 1H), 3.81 (dd, J_1 = J_2 = 8.0 Hz, 2H), 3.53-3.45 (m, 2H), 3.40-3.30 (m, 1H), 3.26 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 1H), 3.08 (t, J = 8.0 Hz, 1H), 1.61 (s, 3H), 0.79 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 154.1, 150.2, 140.0, 139.6, 134.7, 134.5, 129.7, 129.0, 128.9, 128.7, 128.5, 128.4, 127.8, 127.5, 127.0, 124.3, 122.6, 122.5, 118.0, 117.4, 108.0, 100.1, 81.5, 59.2, 56.1, 43.9, 43.5, 35.0, 19.6, 15.0. IR (KBr) v 3432, 2931, 1683, 1489, 1234, 1098, 758 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{31}Cl_2O_5$ $[M+H]^+$: 601.1543, found: 601.1544.



3d **3d'**

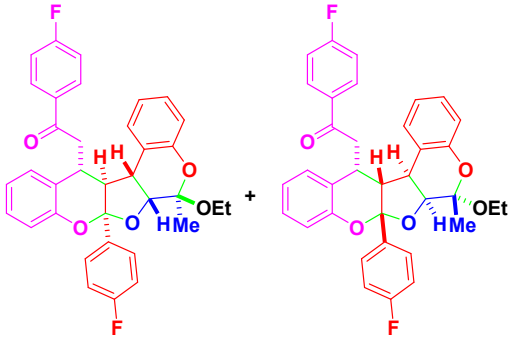
White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 70:1), 53.4 mg, 48% yield; Reaction time = 12 h; dr = 1:1 (**3d**/**3d'**, separable isomers); m. p. 95.3-96.6 °C (**3d**), 181.6-183.2 °C (**3d'**); ^{1}H NMR (400 MHz, $CDCl_3$) for **3d** δ 7.52 (dd, J_1 = J_2 = 4.0 Hz, 2H), 7.43 (dd, J_1 = J_2 = 8.0 Hz, 3H), 7.28-7.21 (m, 5H), 7.13 (s, 1H), 7.04 (d, J = 8.0 Hz, 3H), 6.95 (d, J = 8.0 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 4.21 (d, J = 8.0 Hz, 1H), 3.92 (t, J = 8.0 Hz, 1H), 3.53-3.48 (m, 1H), 3.44-3.37 (m, 1H), 3.33 (t, J = 8.0 Hz, 1H), 2.99-2.85 (m, 2H), 2.78 (dd, J_1 = J_2 = 4.0 Hz, 1H), 2.31 (d, J = 8.0 Hz, 6H), 1.60 (s, 3H), 0.79 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3d** δ 197.8, 152.2, 148.0, 141.6, 136.7, 132.9, 131.7, 131.3, 130.3, 129.2, 128.3 (2C), 128.2 (2C), 127.7, 127.0, 126.1, 124.3, 117.6, 117.0, 108.5, 100.2, 81.4, 59.9, 56.0, 44.3, 43.5, 35.0, 20.9, 20.7, 19.7, 15.1, one carbon missing in the aromatic region. ^{1}H NMR (400 MHz, $CDCl_3$) for **3d'** δ 8.13 (d, J = 12.0 Hz, 2H), 7.67-7.52 (m, 5H), 7.29 (d, J = 12.0 Hz, 3H), 7.04 (q, J = 8.0 Hz, 2H), 6.94 (s, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 6.51 (s, 1H), 3.99 (q, J = 8.0 Hz, 1H), 3.84 (dd, J_1 = J_2 = 8.0 Hz, 1H), 3.76 (d, J = 12.0 Hz, 1H), 3.63-3.31 (m, 3H), 3.23 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.10 (t, J = 4.0 Hz, 1H), 2.34 (s, 3H), 1.85 (s, 3H), 1.60 (s, 3H), 0.77 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3d'** δ 196.8, 153.4, 148.3, 141.8, 136.7, 133.5, 131.7, 131.1, 128.8, 128.7, 128.6, 128.2, 128.1, 127.9, 127.4, 126.3, 125.6, 125.5, 117.6, 117.2, 111.8, 98.9, 82.0, 61.4, 56.1, 39.2, 38.6, 31.0, 21.1, 20.2 (2C), 15.2, one carbon missing in the aromatic region. IR (KBr) for **3d** v 2921, 1688, 1496, 1233, 1115, 1002, 732 cm^{-1}; IR (KBr)

for **3d'** *v* 2920, 1686, 1494, 1235, 1115, 993, 753 cm^{-1}. HRMS (ESI) calcd. for $C_{37}H_{37}O_5$ $[M+H]^+$: 561.2636, found: 561.2639.



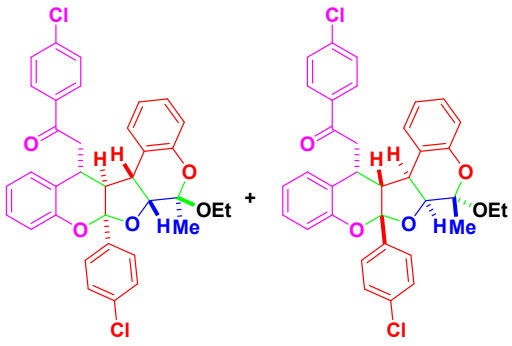
3e **3e'**

White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 40:1-10:1), 40.0 mg, 34% yield; Reaction time = 12 h; dr = 1.4:1 (**3e**/**3e'**, separable isomers); m. p. 100.2-101.4 °C (**3e**), 197.4-198.7 °C (**3e'**); ^{1}H NMR (400 MHz, $CDCl_3$) for **3e** δ 7.55 (dd, $J_1 = J_2$ = 4.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 8.0 Hz, 2H), 7.24-7.21 (m, 5H), 6.99 (t, J = 8.0 Hz, 1H), 6.92-6.81 (m, 5H), 4.35 (d, J = 8.0 Hz, 1H), 3.91 (d, J = 8.0 Hz, 7H), 3.53-3.37 (m, 3H), 2.84 (d, J = 8.0 Hz, 2H), 2.75 (d, J = 8.0 Hz, 1H), 1.69 (s, 3H), 0.75 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3e** δ 197.6, 149.3, 148.5, 143.4, 141.0, 139.5, 136.6, 132.8, 128.7, 128.4, 128.2 (2C), 127.7, 126.2, 124.8, 122.2, 121.6, 121.5, 119.7, 111.2, 109.9, 108.3, 101.7, 81.8, 58.6, 56.2 (2C), 55.8, 44.2, 43.2, 33.9, 19.5, 15.0. ^{1}H NMR (400 MHz, $CDCl_3$) for **3e'** δ 8.03 (d, J = 8.0 Hz, 2H), 7.67-7.59 (m, 3H), 7.51 (t, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 3H), 6.98-6.89 (m, 2H), 6.76-6.64 (m, 3H), 6.53 (d, J = 8.0 Hz, 1H), 4.02-3.95 (m, 1H), 3.90-3.82 (m, 8H), 3.55-3.30 (m, 4H), 3.02 (t, J = 8.0 Hz, 1H), 1.70 (s, 3H), 0.74 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3e'** δ 197.0, 149.3, 148.7, 144.5, 141.3, 140.1, 136.6, 133.4, 128.8, 128.4, 128.2, 128.1, 128.0, 125.8, 122.1, 121.6, 120.1, 117.4, 112.1, 112.0, 109.5, 100.0, 82.4, 61.5, 56.4, 56.2, 55.9, 39.5 (2C), 31.0, 20.1, 15.0, one carbon missing in the aromatic region. IR (KBr) for **3e** *v* 2924, 1681, 1484, 1217, 1079, 991, 763 cm^{-1}; IR (KBr) for **3e'** *v* 2936, 1686, 1479, 1270, 1092, 760 cm^{-1}. HRMS (ESI) calcd. for $C_{37}H_{37}O_7$ $[M+H]^+$: 593.2534, found: 593.2538.



3f **3f'**

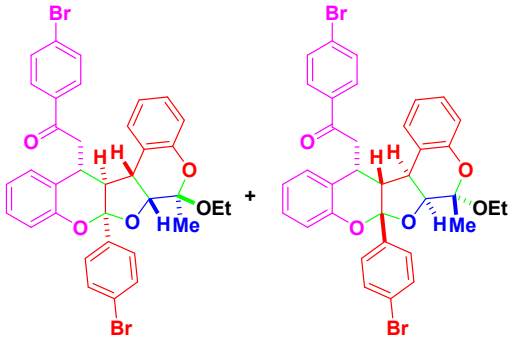
White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 70:1-60:1), 46.9 mg, 41% yield; Reaction time = 10 h; dr = 1:1 (**3f**/**3f'**, separable isomers); m. p. 157.2-158.9 °C (**3f**), 163.7-165.2 °C (**3f'**); ^{1}H NMR (400 MHz, $CDCl_3$) for **3f** δ 7.51-7.44 (m, 4H), 7.32-7.25 (m, 3H), 7.21-7.13 (m, 2H), 7.05-6.87 (m, 7H), 4.20 (d, *J* = 8.0 Hz, 1H), 3.95 (d, *J* = 8.0 Hz, 1H), 3.55-3.38 (m, 3H), 2.98-2.84 (m, 2H), 2.78 (d, *J* = 4.0 Hz, 1H), 1.60 (s, 3H), 0.77 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3f** δ 196.0, 165.6 (d, *J* = 254.0 Hz, 1C), 162.7 (d, *J* = 247.0 Hz, 1C), 154.2, 150.2, 137.4, 132.9, 130.3 (d, *J* = 9.0 Hz, 1C), 129.7, 128.8, 127.9 (d, *J* = 8.0 Hz, 1C), 127.7 (d, *J* = 4.0 Hz, 1C), 127.1, 124.5, 122.6, 122.4, 117.8 (d, *J* = 57.0 Hz, 1C), 115.6, 115.4, 115.3, 115.1, 108.2, 100.2, 81.4, 59.4, 56.1, 44.0, 43.5, 35.0, 19.6, 15.0. ^{1}H NMR (400 MHz, $CDCl_3$) for **3f'** δ 8.13-8.09 (m, 2H), 7.57-7.53 (m, 2H), 7.30-7.25 (m, 1H), 7.21 (t, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.08-7.03 (m, 3H), 6.99-6.94 (m, 2H), 6.83 (dd, $J_1 = J_2 = 8.0$ Hz, 2H), 6.75 (t, *J* = 8.0 Hz, 1H), 3.97 (q, *J* = 4.0 Hz, 1H), 3.87 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 3.72 (d, *J* = 8.0 Hz, 1H), 3.51-3.34 (m, 3H), 3.29 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 3.08 (t, *J* = 4.0 Hz, 1H), 1.59 (s, 3H), 0.75 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3f'** δ 195.4, 155.4, 150.7, 137.5, 133.1, 130.7 (d, *J* = 9.0 Hz, 1C), 128.5, 128.2, 127.6, 127.5, 127.4, 126.5, 125.0, 122.7, 122.1, 118.1, 117.7, 116.1, 115.9, 115.2, 115.0, 111.5, 98.9, 82.2, 62.0, 56.2, 39.4, 38.7, 31.1, 20.1, 15.1. IR (KBr) for **3f** *v* 2927, 1684, 1500, 1233, 1113, 758 cm^{-1}; IR (KBr) for **3f'** *v* 2920, 1685, 1498, 1230, 1115, 750 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{31}F_2O_5$ $[M+H]^+$: 569.2134, found: 569.2137.



3g **3g'**

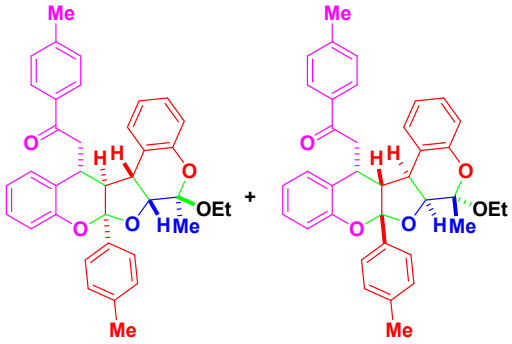
White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 80:1-70:1), 58.4 mg, 49% yield; Reaction time = 10 h; dr = 3:1 (**3g**/**3g'**, inseparable isomers); m. p. 167.4-168.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 8.0 Hz, 3H), 7.31-7.11 (m, 9H), 7.06-6.90 (m, 4H), 4.20 (d, *J* = 8.0 Hz, 1H), 3.93 (t, *J* = 4.0 Hz, 1H), 3.54-3.37 (m, 3H), 2.99-2.64 (m, 3H), 1.59 (s, 3H), 0.77 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for δ 196.4, 154.1, 150.2,

140.0, 139.6, 134.7, 134.5, 129.7, 129.0, 128.7, 128.6, 128.4, 128.1, 127.8, 127.5, 125.3, 124.3, 122.6, 122.5, 118.0, 117.4, 108.0, 100.1, 81.5, 59.2, 56.1, 43.9, 43.5, 35.0, 19.6, 15.0. IR (KBr) *v* 2976, 1683, 1488, 1237, 1093, 759 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{31}Cl_2O_5$ $[M+H]^+$: 601.1543, found: 601.1550.

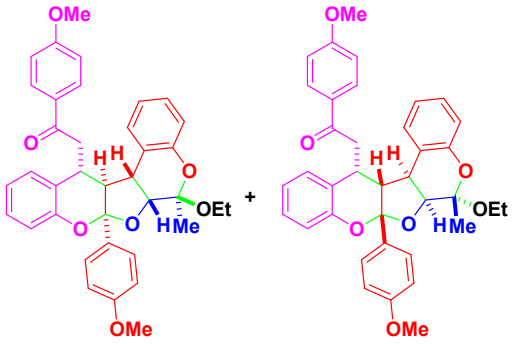


3h **3h'**

White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 80:1), 61.1 mg, 44% yield; Reaction time = 10 h; dr = 1.2:1 (**3h**/**3h'**, separable isomers); m. p. 164.5-165.9 °C (**3h**), 144.5-145.9 °C (**3h'**); ^{1}H NMR (400 MHz, $CDCl_3$) for **3h** δ 8.01 (d, J = 8.0 Hz, 2H), 7.50 (dd, J_1 = 4.0 Hz, J_2 = 8.0 Hz, 4H), 7.30-7.24 (m, 3H), 7.13 (d, J = 8.0 Hz, 1H), 7.08-7.04 (m, 3H), 6.85 (d, J = 8.0 Hz, 1H), 6.80-6.73 (m, 2H), 3.95 (q, J = 4.0 Hz, 1H), 3.86 (dd, J_1 = J_2 = 8.0 Hz, 1H), 3.68 (d, J = 8.0 Hz, 1H), 3.51-3.33 (m, 3H), 3.29 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.07 (t, J = 4.0 Hz, 1H), 1.58 (s, 3H), 0.75 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3h** δ 195.7, 155.3, 150.7, 140.2, 140.1, 135.0, 134.3, 129.5, 129.2, 128.5, 128.4, 128.2, 127.6, 127.5, 127.0, 126.3, 124.9, 122.8, 122.1, 118.1, 117.7, 111.5, 98.8, 82.2, 62.0, 56.2, 39.4, 38.7, 31.1, 20.1, 15.1. ^{1}H NMR (400 MHz, $CDCl_3$) for **3h'** δ 7.93 (d, J = 8.0 Hz, 2H), 7.68 (d, J = 8.0 Hz, 2H), 7.42 (q, J = 8.0 Hz, 4H), 7.29-7.25 (m, 1H), 7.13 (d, J = 8.0 Hz, 1H), 7.05 (d, J = 8.0 Hz, 3H), 6.85 (d, J = 8.0 Hz, 1H), 6.79-6.73 (m, 2H), 3.94 (q, J = 4.0 Hz, 1H), 3.85 (dd, J_1 = J_2 = 8.0 Hz, 1H), 3.70 (d, J = 8.0 Hz, 1H), 3.49-3.35 (m, 3H), 3.29 (dd, J_1 = J_2 = 4.0 Hz, 1H), 3.07 (t, J = 4.0 Hz, 1H), 1.58 (s, 3H), 0.75 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3h'** δ 195.9, 155.3, 150.7, 140.7, 135.3, 132.2, 131.4, 129.5, 128.8, 128.5, 128.1, 127.6, 127.4, 127.3, 126.3, 124.9, 122.8, 122.6, 122.1, 118.1, 117.7, 111.5, 98.8, 82.2, 62.0, 56.2, 39.3, 38.7, 31.1, 20.1, 15.1. IR (KBr) for **3h** *v* 2929, 1685, 1487, 1233, 1111, 758 cm^{-1}; IR (KBr) for **3h'** *v* 2931, 1681, 1486, 1233, 1117, 755 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{31}Br_2O_5$ $[M+H]^+$: 689.0533, found: 689.0527.

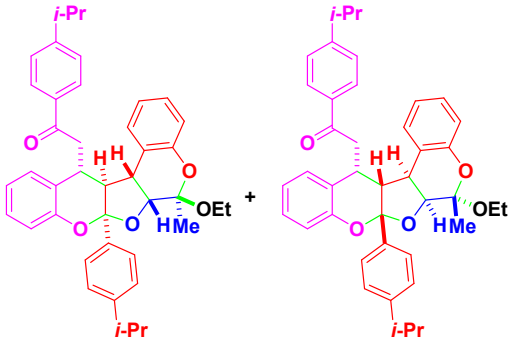


White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 70:1), 74.5 mg, 67% yield; Reaction time = 2 h; dr = 1.1:1 (**3i**/**3i'**, separable isomers); m. p. 177.2-179.0 ^{o}C (**3i**), 181.1-182.6 ^{o}C (**3i'**); ^{1}H NMR (400 MHz, $CDCl_3$) for **3i** δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.32-7.13 (m, 7H), 7.03 (t, *J* = 8.0 Hz, 5H), 6.99-6.91 (m, 2H), 4.26 (d, *J* = 8.0 Hz, 1H), 3.95 (d, *J* = 8.0 Hz, 1H), 3.55-3.46 (m, 1H), 3.44-3.37 (m, 2H), 2.94-2.76 (m, 3H), 2.31 (s, 3H), 2.24 (s, 3H), 1.62 (s, 3H), 0.76 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3i** δ 197.3, 154.4, 150.3, 143.5, 138.4, 138.1, 134.2, 129.8, 128.9, 128.8, 128.6, 127.8 (2C), 127.5, 127.4, 125.9, 124.4, 122.5, 121.9, 117.9, 117.2, 108.4, 100.4, 81.3, 59.1, 56.0, 44.1, 43.3, 34.7, 21.5, 21.0, 19.6, 15.0. ^{1}H NMR (400 MHz, $CDCl_3$) for **3i'** δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.13-6.99 (m, 6H), 6.87 (q, *J* = 8.0 Hz, 2H), 6.77 (t, *J* = 8.0 Hz, 1H), 4.02-3.98 (m, 1H), 3.88 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 3.75 (d, *J* = 8.0 Hz, 1H), 3.49-3.33 (m, 3H), 3.29 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 3.07 (t, *J* = 4.0 Hz, 1H), 2.45 (s, 3H), 2.29 (s, 3H), 1.60 (s, 3H), 0.76 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3i'** δ 196.6, 155.7, 150.8, 144.3, 138.7, 137.9, 134.3, 129.5, 128.9, 128.4, 128.2 (2C), 117.7, 127.4, 126.8, 125.4, 125.2, 122.4, 122.0, 118.0, 117.5, 111.9, 99.0, 82.0, 62.1, 56.1, 39.4, 39.0, 31.1, 21.7, 21.1, 20.1, 15.1. IR (KBr) for **3i** *v* 2927, 1673, 1490, 1237, 1113, 753 cm^{-1}; IR (KBr) for **3i'** *v* 2930, 1676, 1487, 1235, 1117, 753 cm^{-1}. HRMS (ESI) calcd. for $C_{37}H_{37}O_5$ $[M+H]^+$: 561.2636, found: 561.2639.



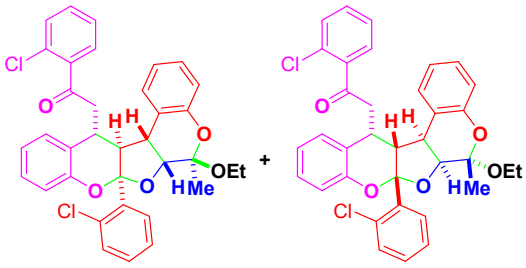
3j **3j'**

White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 30:1 to 10:1), 57.1 mg, 48% yield; Reaction time = 3 h; dr = 1.2:1 (**3j**/**3j'**, separable isomers); m. p. 124.5-125.8 °C (**3j**), 171.6-173.0 °C (**3j'**); ^{1}H NMR (400 MHz, $CDCl_3$) for **3j** δ 7.41 (dd, $J_1 = J_2 =$ 4.0 Hz, 4H), 7.32-7.12 (m, 5H), 7.06-6.90 (m, 3H), 6.73 (d, J = 8.0 Hz, 4H), 4.23 (d, J = 12.0 Hz, 1H), 3.95 (t, J = 8.0 Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 3.54-3.35 (m, 3H), 2.90-2.74 (m, 3H), 1.61 (s, 3H), 0.76 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3j** δ 196.3, 162.3, 159.5, 154.4, 150.3, 133.4, 130.0, 129.9, 129.7, 128.6, 127.8, 127.6, 127.5, 127.3, 124.4, 122.5, 122.0, 117.9, 117.1, 113.6, 113.3, 108.3, 100.4, 81.2, 59.0, 56.0, 55.3, 55.1, 43.7, 43.2, 34.8, 19.6, 15.0. ^{1}H NMR (400 MHz, $CDCl_3$) for **3j'** δ 8.06 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.29-7.23 (m, 1H), 7.13-6.99 (m, 6H), 6.92-6.72 (m, 5H), 4.01-3.97 (m, 1H), 3.91 (s, 3H), 3.89-3.80 (m, 1H), 3.76 (s, 3H), 3.73 (d, J = 12.0 Hz, 1H), 3.49-3.32 (m, 3H), 3.29 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 3.06 (t, J = 4.0 Hz, 1H), 1.60 (s, 3H), 0.76 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3j'** δ 195.5, 163.8, 159.6, 155.7, 150.8, 134.0, 130.4, 129.8, 128.4, 128.2, 127.8, 127.4, 126.8 (2C), 125.2, 122.4, 122.0, 118.0, 117.4, 114.0, 113.6, 111.9, 99.0, 81.9, 62.1, 56.2, 55.5, 55.2, 39.4, 38.8, 31.2, 20.1, 15.1. IR (KBr) for **3j** ν 2934, 1670, 1605, 1487, 1254, 1113, 757 cm^{-1}; IR (KBr) for **3j'** ν 2928, 1678, 1602, 1485, 1248, 1116, 756 cm^{-1}. HRMS (ESI) calcd. for $C_{37}H_{37}O_7$ $[M+H]^+$: 593.2534, found: 593.2534.



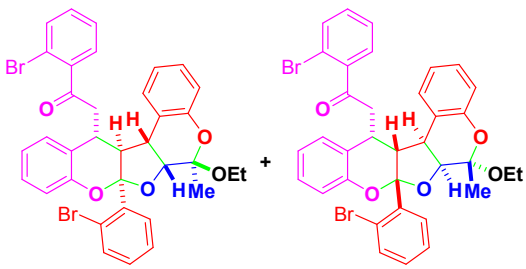
3k **3k'**

White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 70:1), 69.3 mg, 56% yield; Reaction time = 12 h; dr = 1:1 (**3k**/**3k'**, separable isomers); m. p. 188.4-189.2 ^{o}C (**3k**), 188.9-190.8 ^{o}C (**3k'**); ^{1}H NMR (400 MHz, $CDCl_3$) for **3k** δ 7.42 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.32-7.08 (m, 9H), 7.03 (t, J = 8.0 Hz, 1H), 6.96 (t, J = 8.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 4.28 (d, J = 8.0 Hz, 1H), 3.96 (t, J = 8.0 Hz, 1H), 3.56-3.37 (m, 3H), 2.92-2.76 (m, 5H), 1.62 (s, 3H), 1.19-1.14 (m, 12H), 0.77 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3k** δ 197.2, 154.5, 154.4, 150.5, 149.2, 138.6, 134.6, 130.0, 128.6, 128.0, 127.9, 127.6, 126.4 (2C), 126.1, 124.4, 122.6, 122.0, 118.1, 117.2, 108.3, 100.7, 100.0, 81.5, 59.1, 56.1, 44.4, 43.2, 34.2 (2C), 33.8, 24.0, 23.6, 19.6, 15.1. ^{1}H NMR (400 MHz, $CDCl_3$) for **3k'** δ 8.02 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.25-7.22 (m, 1H), 7.15-6.98 (m, 6H), 6.92 (d, J = 8.0 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.79 (t, J = 8.0 Hz, 1H), 4.04-4.00 (m, 1H), 3.90 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 3.76 (d, J = 4.0 Hz, 1H), 3.51-3.28 (m, 4H), 3.09 (t, J = 4.0 Hz, 1H), 3.05-2.98 (m, 1H), 2.89-2.82 (m, 1H), 1.60 (s, 3H), 1.31 (d, J = 8.0 Hz, 6H), 1.20 (d, J = 8.0 Hz, 6H), 0.76 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3k'** δ 196.7, 155.8, 155.1, 150.8, 148.9, 139.0, 134.7, 128.4, 128.3, 128.2, 127.7, 127.4, 126.9 (2C), 126.3, 125.5, 125.2, 122.4, 122.0, 118.0, 117.4, 111.9, 99.0, 82.0, 62.0, 56.1, 39.5, 39.3, 34.3, 33.8, 31.1, 23.9, 23.7, 20.1, 15.1. IR (KBr) for **3k** v 2964, 1676, 1600, 1487, 1228, 1113, 757 cm^{-1}; IR (KBr) for **3k'** v 2963, 1683, 1454, 1232, 1117, 760 cm^{-1}. HRMS (ESI) calcd. for $C_{41}H_{44}O_5$ $[M+H]^+$: 617.3262, found: 617.3263.



3l **3l'**

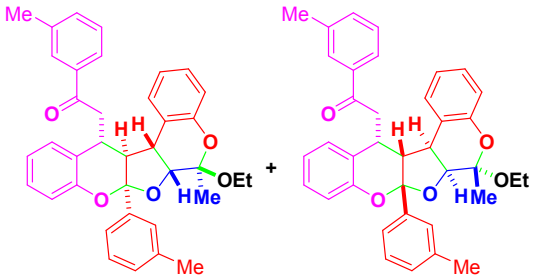
White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 80:1 to 70:1), 59.1 mg, 49% yield; Reaction time = 36 h; dr = 1.2:1 (**3l**/**3l'**, separable isomers); m. p. 161.4-162.4 °C (**3l**), 174.6-176.4 °C (**3l'**); ^{1}H NMR (400 MHz, $CDCl_3$) for **3l** δ 7.77 (dd, $J_1 = J_2 =$ 4.0 Hz, 1H), 7.32-7.21 (m, 5H), 7.16-7.09 (m, 6H), 7.02 (d, J = 8.0 Hz, 1H), 6.97 (q, J = 8.0 Hz, 2H), 6.85 (d, J = 8.0 Hz, 1H), 4.35 (d, J = 8.0 Hz, 1H), 3.92 (t, J = 8.0 Hz, 1H), 3.57-3.38 (m, 3H), 3.32 (d, J = 4.0 Hz, 1H), 2.90 (d, J = 8.0 Hz, 2H), 1.65 (s, 3H), 0.79 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3l** δ 200.6, 153.7, 150.6, 138.5, 136.6, 132.4, 131.9, 131.7, 131.0, 130.3, 129.9, 129.8, 129.3, 129.0, 128.8, 127.6, 127.4, 126.8, 126.6, 126.5, 123.4, 122.3, 122.1, 117.7, 117.0, 107.0, 100.0, 81.1, 56.1, 53.4, 49.5, 42.7, 35.0, 19.6, 15.1. ^{1}H NMR (400 MHz, $CDCl_3$) for **3l'** δ 7.77 (d, J = 8.0 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.43 (q, J = 8.0 Hz, 2H), 7.35 (t, J = 8.0 Hz, 1H), 7.26 (q, J = 8.0 Hz, 2H), 7.16-7.04 (m, 5H), 6.96 (s, 2H), 6.75 (q, J = 8.0 Hz, 2H), 4.29 (d, J = 8.0 Hz, 1H), 3.95 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 3.60-3.36 (m, 6H), 1.56 (s, 3H), 0.79 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3l'** δ 200.8, 155.0, 150.8, 138.6, 138.3, 132.3, 132.1, 131.2, 130.9, 130.8, 129.7, 129.6, 128.7, 128.4 (2C), 128.0, 127.4, 127.2, 126.3, 124.9, 124.6, 123.0, 121.9, 118.7, 117.3, 111.3, 98.0, 81.6, 59.6, 56.2, 43.4, 38.9, 32.5, 20.4, 15.2. IR (KBr) for **3l** ν 2916, 1682, 1487, 1232, 1118, 757 cm^{-1}; IR (KBr) for **3l'** ν 2904, 1709, 1484, 1219, 1120, 759 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{31}Cl_2O_5$ $[M+H]^+$: 601.1543, found: 601.1544.



3m **3m'**

White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 80:1 to 70:1), 46.1 mg, 33% yield; Reaction time = 48 h; dr = 1.3:1 (**3m**/**3m'**, separable isomers); m. p.

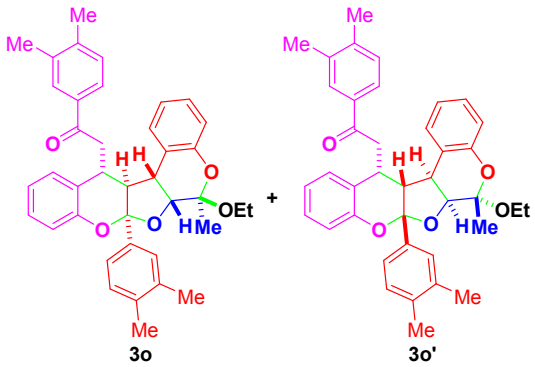
134.5-136.1 °C (**3m**), 192.8-194.3 °C (**3m'**); ^{1}H NMR (400 MHz, $CDCl_3$) for **3m** δ 7.77 (dd, J_1 = J_2 = 4.0 Hz, 1H), 7.43-7.40 (m, 2H), 7.32 (dd, J_1 = J_2 = 4.0 Hz, 1H), 7.28-7.24 (m, 2H), 7.18-7.11 (m, 5H), 7.05-6.94 (m, 3H), 6.86-6.81 (m, 2H), 4.39 (d, J = 8.0 Hz, 1H), 3.96 (t, J = 8.0 Hz, 1H), 3.56-3.50 (m, 1H), 3.46-3.40 (m, 2H), 3.35 (dd, J_1 = J_2 = 4.0 Hz, 1H), 2.86 (t, J = 4.0 Hz, 2H), 1.67 (s, 3H), 0.79 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3m** δ 201.4, 153.8, 150.6, 140.8, 137.8, 135.4, 133.5, 131.7, 130.1, 129.9, 129.4, 129.0, 128.8, 127.7, 127.5, 127.3, 127.2, 126.4, 122.8, 122.3, 122.1, 121.1, 118.8, 117.7, 116.9, 107.0, 100.0, 80.9, 56.0, 53.0, 49.2, 42.3, 34.8, 19.6, 15.1. ^{1}H NMR (400 MHz, $CDCl_3$) for **3m'** δ 7.76 (dd, J_1 = J_2 = 4.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.50 (t, J = 8.0 Hz, 2H), 7.39 (t, J = 8.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.27-7.23 (m, 1H), 7.18 (d, J = 8.0 Hz, 1H), 7.08 (d, J = 8.0 Hz, 3H), 7.03-6.94 (m, 3H), 6.78-6.71 (m, 2H), 4.01 (q, J = 8.0 Hz, 1H), 3.92 (dd, J_1 = J_2 = 8.0 Hz, 1H), 3.65-3.38 (m, 6H), 1.56 (s, 3H), 0.81 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3m'** δ 201.7, 154.9, 150.8, 140.9, 139.9, 134.5, 134.0, 132.1, 129.7, 129.3, 128.8, 128.7, 128.4, 128.0, 127.7, 127.5, 126.8, 124.6 (2C), 123.0, 121.9, 120.8, 119.1, 118.9, 117.3, 111.5, 98.0, 81.5, 59.4, 56.3, 43.0, 38.9, 32.8, 20.4, 15.2. IR (KBr) for **3m** v 2914, 1684, 1488, 1230, 1118, 757 cm^{-1}; IR (KBr) for **3m'** v 2922, 1692, 1487, 1231, 1118, 757 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{31}Br_2O_5$ $[M+H]^+$: 689.0533, found: 689.0532.



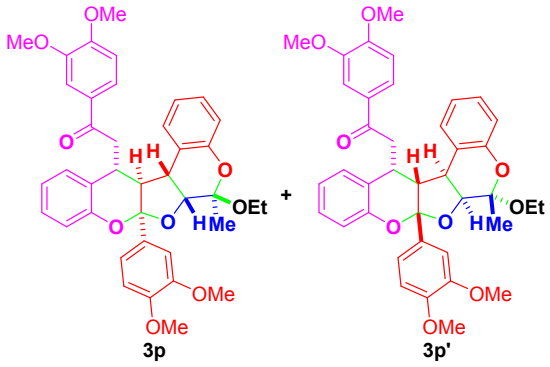
3n **3n'**

White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 70:1), 53.4 mg, 48% yield; Reaction time = 6 h; dr = 3.9:1 (**3n**/**3n'**, inseparable isomers); m. p. 132.9-134.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (t, J = 8.0 Hz, 4H), 7.23 (d, J = 8.0 Hz, 4H), 7.15 (q, J = 8.0 Hz, 4H), 7.06-6.92 (m, 4H), 4.26 (d, J = 8.0 Hz, 1H), 3.96 (t, J = 8.0 Hz, 1H), 3.55-3.38 (m, 3H), 3.30-2.66 (m, 3H), 2.26 (s, 3H), 2.18 (s, 3H), 1.63 (s, 3H), 0.77 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 154.3, 150.4, 141.2, 137.9 (2C), 136.6, 133.6, 129.8, 129.1, 128.6, 128.2, 128.1, 128.0, 127.8, 127.6, 127.3, 126.4, 124.8, 124.4, 123.1, 122.5, 122.0, 117.9, 117.2, 108.3, 100.4, 81.4, 59.0, 56.0, 44.3, 43.2, 34.5, 21.4, 21.1, 19.6, 15.0. IR (KBr) v 2921, 1679,

1487, 1235, 1121, 757 cm^{-1}. HRMS (ESI) calcd. for $C_{37}H_{37}O_5$ $[M+H]^+$: 561.2636, found: 561.2637.

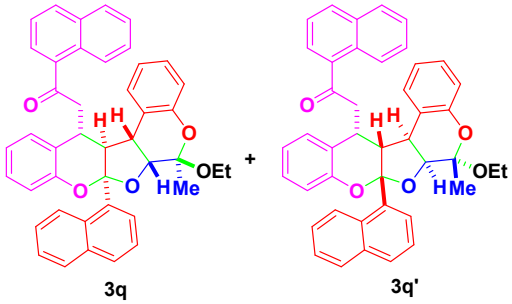


White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 70:1), 52.0 mg, 44% yield; Reaction time = 6 h; dr = 2.9:1 (**3o**/**3o'**, inseparable isomers); m. p. 171.2-172.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, J = 8.0 Hz, 3H), 7.14 (d, J = 12.0 Hz, 3H), 7.07 (t, J = 8.0 Hz, 2H), 6.94-6.85 (m, 6H), 4.16 (d, J = 12.0 Hz, 1H), 3.85 (t, J = 8.0 Hz, 1H), 3.42-3.27 (m, 3H), 2.82-2.70 (m, 3H), 2.12 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.53 (s, 3H), 0.68 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 154.4, 150.3, 142.2, 138.6, 136.6, 136.4, 136.3, 134.5, 129.8, 129.5, 129.3, 128.8, 128.5, 127.8, 127.5, 127.4, 126.9, 125.3, 124.4, 123.4, 122.4, 121.8, 117.9, 117.1, 108.3, 100.4, 81.3, 58.7, 56.0, 44.1, 43.0, 34.4, 19.8, 19.7, 19.6, 19.5, 19.3, 15.0. IR (KBr) ν 2925, 1677, 1489, 1240, 1118, 755 cm^{-1}. HRMS (ESI) calcd. for $C_{39}H_{41}O_5$ $[M+H]^+$: 589.2949, found: 589.2952.



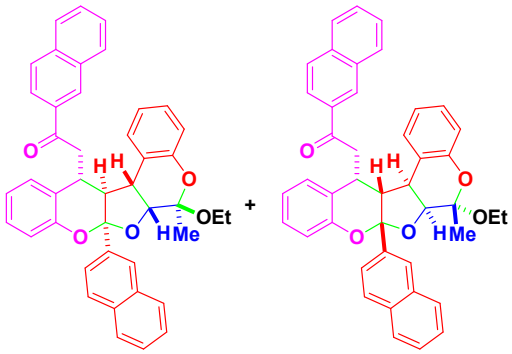
White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 10:1 to 2:1), 80.2 mg, 62% yield; Reaction time = 24 h; dr = 1.3:1 (**3p**/**3p'**, inseparable isomers); m. p. 159.5-161.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-6.96 (m, 10H), 6.91-6.77 (m, 3H), 6.68 (dd, J_1 = J_2 = 4.0 Hz, 1H), 4.03-3.78 (m, 11H), 3.66-3.39 (m, 7H), 3.17-2.91 (m, 2H), 1.58 (d, J = 4.0 Hz, 3H), 0.79 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 154.4, 153.2, 150.3, 148.8, 148.7, 134.5, 129.9, 129.6, 128.6, 128.1, 127.5, 127.2, 125.8, 122.6, 122.5, 122.3, 118.1,

117.7, 117.6, 112.0, 110.5, 110.2, 109.8, 109.2, 109.1, 99.8, 81.4, 60.2, 56.1, 56.0, 55.8, 55.7, 55.6, 44.0, 39.5, 36.0, 19.8, 15.0. IR (KBr) *v* 29237, 1671, 1516, 1267, 1115, 1023, 762 cm^{-1}. HRMS (ESI) calcd. for $C_{39}H_{41}O_9$ $[M+H]^+$: 653.2745, found: 653.2744.



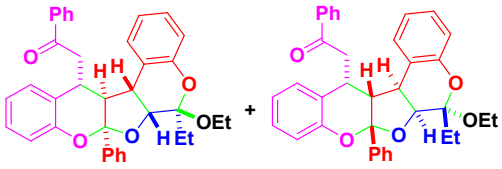
3q **3q'**

Light yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 70:1), 67.5 mg, 53% yield; Reaction time = 10 h; dr = 1.1:1 (**3q**/**3q'**, separable isomers); m. p. 213.1-214.8 °C (**3q**), 144.3-145.8 °C (**3q'**); ^{1}H NMR (400 MHz, $CDCl_3$) for **3q** δ 8.19 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 4.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 3H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 3H), 7.31-7.21 (m, 5H), 7.11-6.99 (m, 4H), 6.97-6.90 (m, 2H), 6.41 (d, *J* = 8.0 Hz, 1H), 4.59 (d, *J* = 8.0 Hz, 1H), 4.13 (t, *J* = 8.0 Hz, 1H), 3.57-3.46 (m, 3H), 3.17 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 2.67 (d, *J* = 8.0 Hz, 2H), 1.65 (s, 3H), 0.79 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3q** δ 201.7, 154.4, 150.3, 135.5, 134.5, 134.3, 133.5, 132.2, 130.2, 130.1, 129.7, 129.3, 128.8, 128.4, 128.0, 127.8, 127.7, 127.5, 126.6, 126.0, 125.9, 125.4, 125.2 (3C), 124.3, 123.7, 122.7, 122.0, 121.8, 118.0, 116.6, 107.6, 100.8, 81.3, 56.2, 55.7, 47.6, 42.3, 34.9, 19.4, 15.0, one carbon missing in the aromatic region. ^{1}H NMR (400 MHz, $CDCl_3$) for **3q'** δ 8.51 (d, *J* = 8.0 Hz, 1H), 8.41 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 7.99-7.94 (m, 3H), 7.85-7.75 (m, 3H), 7.51-7.44 (m, 3H), 7.40-7.33 (m, 2H), 7.30-7.23 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 7.07-6.99 (m, 3H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.72 (t, *J* = 8.0 Hz, 1H), 4.10-4.06 (m, 2H), 3.97 (dd, $J_1 = J_2$ = 8.0 Hz, 1H), 3.55-3.38 (m, 5H), 1.64 (s, 3H), 0.77 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3q'** δ 201.1, 155.6, 151.0, 135.4, 135.0, 134.5, 134.0, 133.1, 130.1, 130.0 (2C), 128.7, 128.5, 128.4 (2C), 128.1, 127.6, 127.4, 126.6 (2C), 126.5, 126.0, 125.9, 125.7, 125.6, 125.4, 125.2, 124.7, 124.2, 122.2, 122.1, 118.0, 117.1, 112.4, 99.3, 82.2, 59.1, 56.2, 43.1, 38.8, 32.0, 20.1, 15.1. IR (KBr) for **3q** *v* 2928, 1677, 1488, 1245, 1100, 1074, 767 cm^{-1}; IR (KBr) for **3q'** *v* 2931, 1683, 1486, 1233, 1116, 765 cm^{-1}. HRMS (ESI) calcd. for $C_{43}H_{37}O_5$ $[M+H]^+$: 633.2636, found: 633.2637.



3r **3r'**

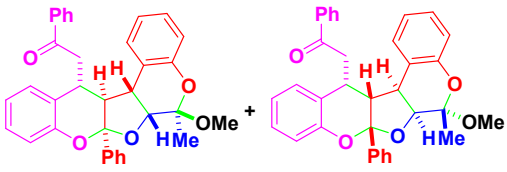
Light yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 70:1), 73.4 mg, 58% yield; Reaction time = 6 h; dr = 2.8:1 (**3r**/**3r'**, inseparable isomers); m. p. 124.5-126.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.62 (dd, $J_1 = J_2 = 12.0$ Hz, 4H), 7.47 (t, J = 8.0 Hz, 4H), 7.40-7.12 (m, 10H), 7.09-6.97 (m, 3H), 4.37 (d, $J = 8.0$ Hz, 1H), 4.05 (t, $J = 8.0$ Hz, 1H), 3.61-3.45 (m, 3H), 3.05-2.93 (m, 3H), 1.66 (s, 3H), 0.79 (t, $J = 8.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 154.4, 150.4, 138.5, 135.2, 133.6, 133.1, 132.8, 131.9, 130.0, 129.4, 129.3, 128.8, 128.5, 128.3, 128.2, 127.9, 127.8, 127.7, 127.5, 127.4 (2C), 126.3 (2C), 126.2, 125.2, 124.2, 123.9, 123.2, 122.6, 122.1, 118.1, 117.2, 108.3, 100.6, 81.6, 58.8, 56.1, 44.2, 43.1, 34.5, 19.6, 15.0. IR (KBr) ν 2930, 1682, 1484, 1235, 1118, 750 cm^{-1}. HRMS (ESI) calcd. for $C_{43}H_{37}O_5$ $[M+H]^+$: 633.2636, found: 633.2639.



3s **3s'**

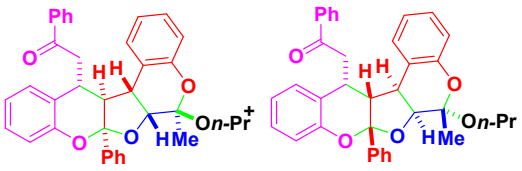
Light yellow solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 80:1), 30.7 mg, 28% yield; Reaction time = 10 h; dr = 1.6:1 (**3s**/**3s'**, inseparable isomers); m. p. 107.2-109.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, $J = 8.0$ Hz, 2H), 7.50-7.32 (m, 6H), 7.28-7.14 (m, 7H), 7.00 (q, $J = 8.0$ Hz, 1H), 6.91 (t, $J = 8.0$ Hz, 2H), 4.91 (s, 1H), 4.28 (d, $J = 8.0$ Hz, 0.5H), 3.97 (t, $J = 8.0$ Hz, 0.5H), 3.66 (d, $J = 4.0$ Hz, 1H), 3.44-3.37 (m, 1H), 3.01-2.89 (m, 1H), 2.73-2.51 (m, 2H), 2.40 (d, $J = 12.0$ Hz, 1H), 2.25 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 2.15-1.96 (m, 1H), 1.09 (t, $J = 8.0$ Hz, 3H), 0.90 (t, $J = 8.0$ Hz, 1.5H), 0.76 (t, $J = 8.0$ Hz, 1.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 154.5, 152.7, 141.6, 138.4, 132.9, 129.8, 128.9, 128.4, 128.3, 127.8, 127.7, 127.0, 126.4, 126.0, 124.9, 122.4, 121.0, 117.9, 116.6, 108.6, 102.4, 93.4, 78.4, 59.8, 44.2, 41.4, 36.5,

35.0, 24.5, 14.9, 7.5. IR (KBr) *v* 2933, 1722, 1487, 1236, 1106, 1029, 894, 758 cm^{-1}. HRMS (ESI) calcd. for $C_{36}H_{35}O_5$ $[M+H]^+$: 547.2479, found: 547.2476.



3t **3t'**

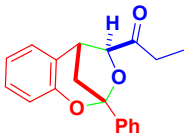
White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 80:1 to 70:1), 71.3 mg, 69% yield; Reaction time = 12 h; dr = 1:1 (**3t**/**3t'**, separable isomers); m. p. 123.1-125.0 °C (**3t**), 218.9-220.7 °C (**3t'**); ^{1}H NMR (400 MHz, $CDCl_3$) for **3t** δ 7.51-7.40 (m, 5H), 7.33-7.14 (m, 10H), 7.06-6.94 (m, 3H), 4.21 (d, *J* = 8.0 Hz, 1H), 3.98 (t, *J* = 8.0 Hz, 1H), 3.39 (t, *J* = 8.0 Hz, 1H), 3.11 (s, 3H), 2.95 (t, *J* = 8.0 Hz, 2H), 2.85 (d, *J* = 8.0 Hz, 1H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3t** δ 197.7, 154.4, 150.1, 141.3, 136.6, 132.9, 129.8, 128.7, 128.4, 128.3 (2C), 128.0, 127.8, 127.7, 126.9, 125.9, 124.7, 122.7, 122.3, 118.0, 117.4, 108.6, 100.2, 81.2, 59.6, 48.2, 44.1, 43.5, 35.0, 18.9. ^{1}H NMR (400 MHz, $CDCl_3$) for **3t'** δ 8.07 (d, *J* = 12.0 Hz, 2H), 7.63-7.48 (m, 5H), 7.30-7.21 (m, 4H), 7.13 (d, *J* = 12.0 Hz, 1H), 7.08-6.99 (m, 3H), 6.87 (t, *J* = 12.0 Hz, 2H), 6.75 (t, *J* = 8.0 Hz, 1H), 4.06-4.00 (m, 1H), 3.90 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 3.68 (d, *J* = 8.0 Hz, 1H), 3.41 (dd, $J_1 = J_2 = 8.0$ Hz, 1H), 3.29 (dd, $J_1 = J_2 = 4.0$ Hz, 1H), 3.16 (t, *J* = 4.0 Hz, 1H), 3.06 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3t'** δ 196.9, 155.6, 150.4, 141.6, 136.7, 133.5, 128.8, 128.4, 128.3, 128.2 (2C), 128.0, 127.9, 127.6, 126.0, 125.3, 125.0, 122.7, 122.2, 117.9, 117.6, 111.9, 98.5, 81.7, 62.3, 48.2, 39.2, 38.9, 31.2, 19.4. IR (KBr) for **3t** *v* 2905, 1676, 1590, 1488, 1230, 756 cm^{-1}; IR (KBr) for **3t'** 2908, 1681, 1487, 1231, 761 cm^{-1}. HRMS (ESI) calcd. for $C_{34}H_{31}O_5$ $[M+H]^+$: 519.2166, found: 519.2166.



3u **3u'**

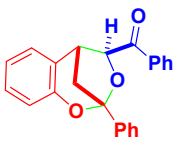
White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 80:1), 60.2 mg, 55% yield; Reaction time = 15 h; dr = 1:1 (**3u**/**3u'**, separable isomers); m. p. 185.6-186.7 °C (**3u**), 162.5-164.3 °C (**3u'**); ^{1}H NMR (400 MHz, $CDCl_3$) for **3u** δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 12.0 Hz, 3H), 7.34-7.14 (m, 10H), 7.04-6.91 (m, 3H), 4.27 (d, *J* = 12.0 Hz, 1H), 3.97 (d, *J*

= 8.0 Hz, 1H), 3.45-3.38 (m, 2H), 3.33-3.26 (m, 1H), 2.90 (d, *J* = 8.0 Hz, 2H), 2.79 (d, *J* = 8.0 Hz, 1H), 1.63 (s, 3H), 1.24-1.12 (m, 2H), 0.45 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3u** δ 197.7, 154.4, 150.3, 141.3, 136.6, 132.9, 129.9, 128.7, 128.4, 128.3 (2C), 128.1, 127.7, 127.6, 127.5, 126.0, 124.4, 122.5, 122.1, 118.1, 117.3, 108.4, 100.2, 81.5, 62.0, 59.4, 44.3, 43.4, 34.6, 22.6, 19.6, 10.0. ^{1}H NMR (400 MHz, $CDCl_3$) for **3u'** δ 8.06 (d, *J* = 8.0 Hz, 2H), 7.63-7.59 (m, 3H), 7.52 (t, *J* = 8.0 Hz, 2H), 7.29-7.23 (m, 4H), 7.13 (d, *J* = 12.0 Hz, 1H), 7.05 (t, *J* = 8.0 Hz, 3H), 6.87 (q, *J* = 8.0 Hz, 2H), 6.75 (t, *J* = 8.0 Hz, 1H), 4.04-3.99 (m, 1H), 3.91 (dd, J_1 = J_2 = 8.0 Hz, 1H), 3.77 (d, *J* = 8.0 Hz, 1H), 3.44-3.36 (m, 2H), 3.31-3.21 (m, 2H), 3.09 (t, *J* = 4.0 Hz, 1H), 1.61 (s, 3H), 1.20-1.08 (m, 2H), 0.43 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for **3u'** δ 197.0, 155.6, 150.8, 141.6, 136.7, 133.5, 128.8, 128.4, 128.3 (2C), 128.2, 127.6, 127.4, 126.8, 125.7, 125.5, 125.1, 122.5, 122.0, 118.2, 117.5, 111.8, 98.8, 82.2, 61.1 (2C), 39.4, 39.1, 31.1, 22.6, 20.1, 10.1. IR (KBr) for **3u** *v* 3042, 2932, 1688, 1589, 1489, 1234, 756 cm^{-1}; IR (KBr) for **3u'** 3062, 2962, 1688, 1489, 1452, 1167, 756 cm^{-1}. HRMS (ESI) calcd. for $C_{36}H_{35}O_5$ $[M+H]^+$: 547.2479, found: 547.2481.



4

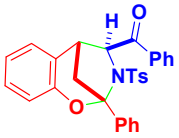
White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 80:1), 24.6 mg, 21% yield; Reaction time = 10 h; dr > 20:1; m. p. 117.8-119.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 3H), 7.19 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.85 (t, *J* = 8.0 Hz, 1H), 4.84 (s, 1H), 3.64 (s, 1H), 2.59-2.43 (s, 3H), 1.98-1.88 (m, 1H), 0.69 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.2, 152.5, 138.7, 129.2, 129.0, 128.4, 128.3, 125.8, 123.5, 121.0, 116.1, 108.4, 93.5, 42.5, 39.4, 32.9, 6.33. IR (KBr) *v* 2982, 1713, 1454, 1231, 1102, 885, 757 cm^{-1}. HRMS (ESI) calcd. for $C_{19}H_{19}O_3$ $[M+H]^+$: 295.1329, found: 295.1331.



5

White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 80:1 to 70:1), 41.2 mg, 30% yield; Reaction time = 10 h; dr > 20:1; m. p. 131.1-132.3 °C; ^{1}H NMR (400

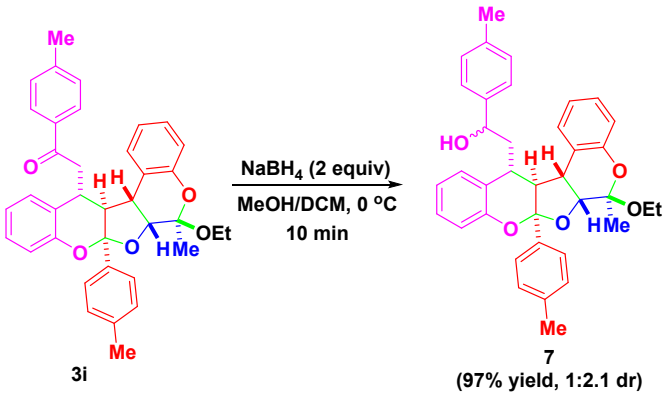
MHz, $CDCl_3$) δ 8.04 (d, J = 8.0 Hz, 2H), 7.84 (d, J = 8.0 Hz, 2H), 7.60 (t, J = 8.0 Hz, 1H), 7.49 (t, J = 8.0 Hz, 2H), 7.38 (q, J = 8.0 Hz, 3H), 7.23 (t, J = 8.0 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.95 (t, J = 8.0 Hz, 1H), 5.81 (s, 1H), 3.70 (d, J = 4.0 Hz, 1H), 2.46 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 2.34 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 152.8, 138.5, 134.4, 133.7, 129.0, 128.8, 128.7, 128.2, 127.1, 126.2, 126.1, 121.1, 116.9, 108.2, 90.3, 42.0, 37.0, one carbon missing in the aromatic region. IR (KBr) v 3063, 1697, 1232, 888, 756 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{19}O_3$ $[M+H]^+$: 343.1329, found: 343.1326.



6

White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 20:1 to 15:1), 61.3 mg, 31% yield; Reaction time = 72 h; dr > 20:1; m. p. 218.3-219.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (t, J = 8.0 Hz, 4H), 7.68 (t, J = 8.0 Hz, 1H), 7.59 (t, J = 8.0 Hz, 2H), 7.46-7.37 (m, 5H), 7.09 (q, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 6.89 (t, J = 8.0 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 5.82 (s, 1H), 2.31 (d, J = 4.0 Hz, 1H), 2.87 (dd, $J_1 = J_2$ = 4.0 Hz, 1H), 2.33 (s, 3H), 2.15 (d, J = 12.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 151.2, 143.0, 138.3, 136.5, 134.5, 133.9, 129.1, 128.8, 128.6, 128.3, 128.2, 127.8 (2C), 126.7, 126.1, 125.8, 121.2, 117.3, 96.0, 74.1, 40.8 (2C), 21.3. IR (KBr) v 3059, 2971, 1687, 1592, 1488, 756 cm^{-1}. HRMS (ESI) calcd. for $C_{30}H_{26}NO_4S$ $[M+H]^+$: 496.1577, found: 496.1577.

5. Experimental data for derivations of 3i, 3a' and 3h

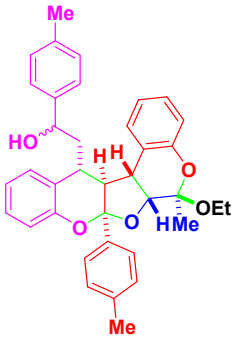


3i **7**

(97% yield, 1:2.1 dr)

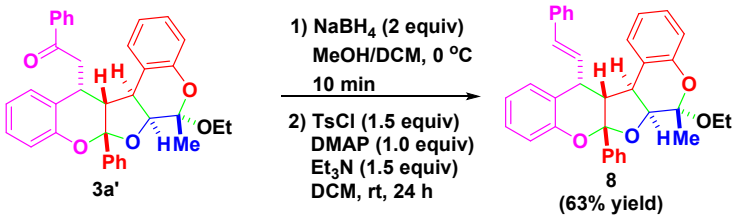
General procedure: A solution of **3i** (112.1 mg, 0.20 mmol) in 8.0 mL MeOH and 4.0 mL DCM was cooled to 0 °C, and then $NaBH_4$ (15.1 mg, 0.4 mmol) was added successively. The reaction mixture was stirred at 0 °C for 10 min until the complete consumption of **3i** as monitored

by thin layer chromatography. Then, saturated aq. NH_4Cl solution was added. The mixture was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, filtered, concentrated and purified with silica gel column chromatography to obtain **7** in 97% yield.



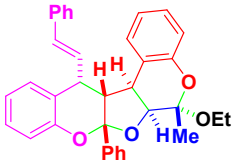
7

White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 60:1 to 20:1), 109.5.5 mg, 97% yield; Reaction time = 10 min; dr = 2.1:1 (separable isomers); m. p. 160.8-162.1 °C (major isomer), 166.6-168.2 °C (minor isomer); ^{1}H NMR (400 MHz, $CDCl_3$) for major isomer δ 7.36 (d, J = 8.0 Hz, 2H), 7.26-7.12 (m, 4H), 7.05-6.89 (m, 10H), 4.25 (s, 1H), 4.15 (d, J = 8.0 Hz, 1H), 3.54-3.36 (m, 2H), 3.30-3.23 (m, 2H), 2.85 (d, J = 4.0 Hz, 1H), 2.30 (s, 3H), 2.27 (s, 3H), 1.78-1.73 (m, 1H), 1.69-1.64 (m, 1H), 1.61 (s, 3H), 1.43 (s, 1H), 0.75 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for major isomer δ 154.3, 150.5, 140.8, 138.6, 138.0, 137.2, 129.9, 129.1, 128.9, 128.4, 127.7 (2C), 127.5, 125.9, 125.8, 125.3, 122.4, 121.8, 118.0, 117.5, 109.0, 100.6, 81.4, 71.6, 59.6, 56.1, 44.0, 43.9, 37.0, 21.1, 19.6, 15.0, one carbon missing in the aromatic region. ^{1}H NMR (400 MHz, $CDCl_3$) for minor isomer δ 7.41 (d, J = 8.0 Hz, 2H), 7.23-7.09 (m, 7H), 6.96-6.92 (m, 5H), 6.59 (d, J = 8.0 Hz, 2H), 4.31 (d, J = 12.0 Hz, 1H), 4.06 (d, J = 12.0 Hz, 1H), 3.55-3.28 (m, 4H), 2.91 (d, J = 8.0 Hz, 1H), 2.34 (s, 3H), 2.30 (d, J = 8.0 Hz, 1H), 2.24 (s, 3H), 1.65 (s, 3H), 1.51-1.47 (m, 2H), 0.75 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) for minor isomer δ 154.3, 150.4, 141.2, 138.4, 138.2, 136.7, 129.5, 129.1, 129.0, 128.8, 128.3, 128.2, 127.5, 127.3, 126.2, 125.1, 124.7, 122.3, 121.7, 118.2, 116.9, 107.9, 100.8, 81.1, 70.4, 56.8, 56.1, 44.6, 43.2, 35.9, 21.1, 19.5, 15.0. IR (KBr) for major isomer ν 3442, 2926, 1487, 1234, 1112, 759 cm^{-1}; IR (KBr) for minor isomer ν 3501, 2924, 1488, 1237, 1116, 759 cm^{-1}. HRMS (ESI) calcd. for $C_{37}H_{39}O_5$ $[M+H]^+$: 563.2795, found: 563.2792.



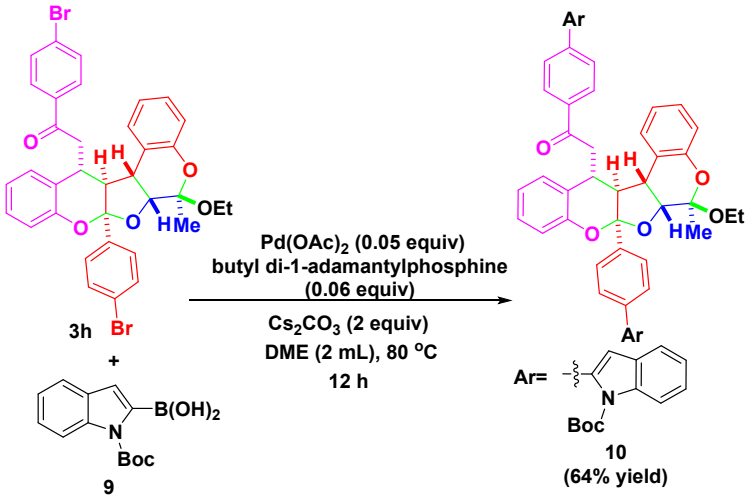
General procedure: (*Step 1*) A solution of **3a'** (106.5 mg, 0.20 mmol) in 8.0 mL MeOH and 4.0 mL DCM was cooled to 0 °C, and then $NaBH_4$ (15.1 mg, 0.4 mmol) was added successively. The reaction mixture was stirred at 0 °C for 10 min until the complete consumption of **3a'**, which was monitored by thin layer chromatography. Then, saturated NH_4Cl solution was added. The mixture was extracted with CH_2Cl_2. The combined organic phase was dried over $MgSO_4$, filtered and concentrated to give the reduction product, which was used directly without further purification.

(*Step 2*) To a solution of the reduction product in 5.0 mL DCM, TsCl (57.2 mg, 0.30 mmol), DMAP (24.4 mg, 0.20 mmol), and Et_3N (30.4 mg, 0.30 mmol) were successively added. The resulting mixture was stirred at room temperature for 24 h, then diluted with Et_2O, washed with saturated aq. $NaHCO_3$ and brine, dried over $MgSO_4$, filtered, concentrated and purified by silica gel column chromatography (petroleum ether/ ethyl acetate). The desired product **8** was obtained as a white solid in 63% overall yield.

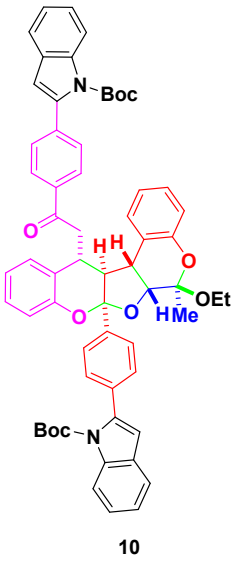


8

White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 80:1), 65.1 mg, 63% yield; Reaction time = 24 h; m. p. 202.8-204.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.0 Hz, 4H), 7.38 (t, J = 8.0 Hz, 2H), 7.32-7.28 (m, 6H), 7.15 (d, J = 12.0 Hz, 1H), 7.07-7.03 (m, 3H), 6.86 (d, J = 12.0 Hz, 1H), 6.78-6.63 (m, 3H), 3.96 (t, J = 8.0 Hz, 2H), 3.57-3.41 (m, 3H), 3.03 (t, J = 8.0 Hz, 1H), 1.64 (s, 3H), 0.82 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 150.4, 141.7, 136.7, 134.7, 128.8, 128.7 (2C), 128.3 (2C), 127.9, 127.5, 127.3, 127.0, 126.8, 126.7, 126.4, 125.5, 122.3, 122.2, 117.6, 117.0, 110.8, 98.5, 81.4, 63.4, 56.2, 39.8, 38.6, 20.3,15.2. IR (KBr) ν 3435, 2931, 1488, 1239, 1118, 758 cm^{-1}. HRMS (ESI) calcd. for $C_{35}H_{33}O_4$ $[M+H]^+$: 517.2373, found: 517.2371.



General procedure: Under nitrogen atmosphere, compound **3h** (138.1 mg, 0.20 mmol), 2-indolyl boronic acid **9** (156.6 mg, 0.6 mmol, 1.5 equiv), Cs_2CO_3 (2.0 equiv), $Pd(OAc)_2$ (0.05 equiv) and butyl di-1-adamantylphosphine (0.06 equiv) were successively added to a 15 mL dried tube, followed by adding 2.0 mL DME. The resulting mixture was stirred at 80 °C for 12 h, and then the reaction mixture was directly subjected to silica gel column chromatography (petroleum ether/ ethyl acetate as eluent) to afford the corresponding product **10** as a white solid in 64% yield.

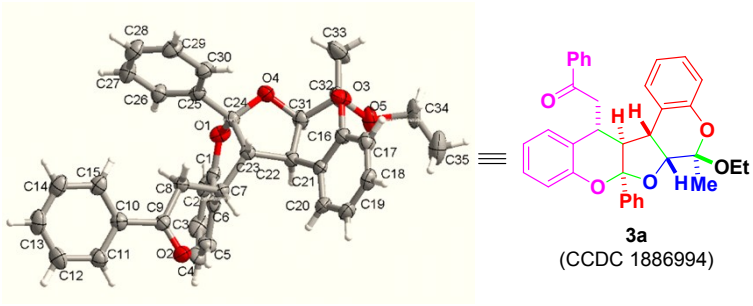


10

White solid obtained by silica gel column chromatography (petroleum ether/ethyl acetate = 60:1 to 40:1), 122.8 mg, 64% yield; Reaction time = 12 h; m. p. 169.1-170.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (t, J = 8.0 Hz, 2H), 7.61 (d, J = 12.0 Hz, 2H), 7.54 (d, J = 12.0 Hz, 2H), 7.47 (d, J = 12.0 Hz, 1H), 7.40-7.14 (m, 14H), 7.05 (q, J = 8.0 Hz, 2H), 6.94 (d, J = 12.0 Hz, 1H), 6.45 (s, 1H), 6.38 (s, 1H), 4.22 (d, J = 8.0 Hz, 1H), 4.01 (t, J = 8.0 Hz, 1H), 3.57-3.43 (m, 3H), 3.20-2.96 (m, 3H), 1.63 (s, 3H), 1.25 (s, 9H), 1.19 (s, 9H), 0.80 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$)

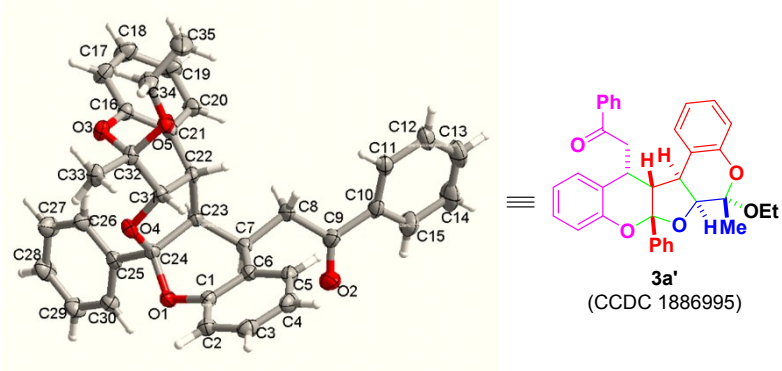
δ 197.1, 154.3, 150.3, 150.0, 149.8, 141.1, 139.8, 139.4, 139.0, 137.6, 137.4, 135.3, 135.0, 129.6, 128.9, 128.8, 128.6, 128.5, 128.0, 127.7, 127.3, 127.1, 125.3, 125.2, 124.8, 124.4, 123.1, 122.9, 122.6, 122.5, 120.8, 120.4, 117.9, 117.7, 115.2, 115.1, 111.2, 110.1, 108.9, 100.1, 83.8, 83.5, 81.7, 59.6, 56.1, 44.2, 43.9, 35.4, 27.5 (2C), 19.7, 15.0, one carbon missing in the aromatic region. IR (KBr) *v* 3063, 1697, 1232, 888, 756 cm^{-1}. HRMS (ESI) calcd. for $C_{23}H_{19}O_3$ $[M+H]^+$: 343.1329, found: 343.1326.

6. Crystal structures of 3a, 3a', 3s, 5 and 8



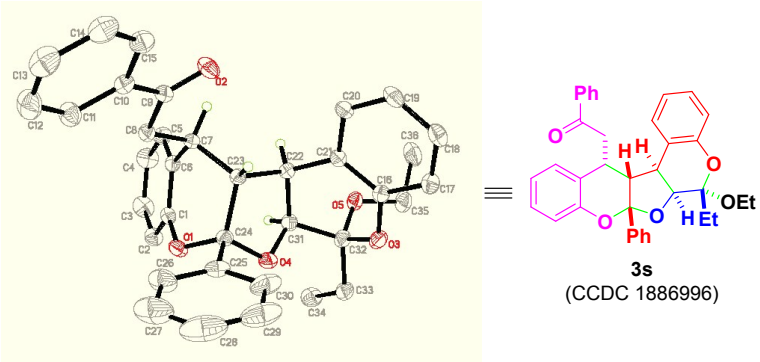
3a
(CCDC 1886994)

Displacement ellipsoids are drawn at the 30% probability level.



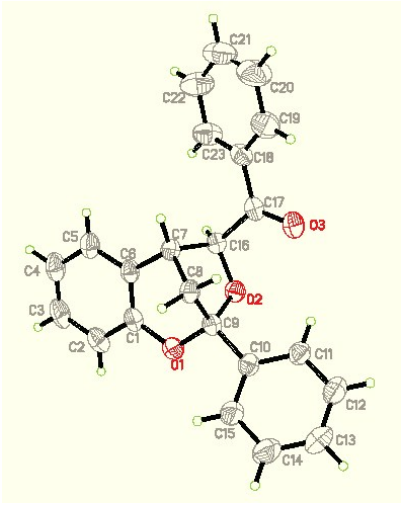
3a'
(CCDC 1886995)

Displacement ellipsoids are drawn at the 30% probability level.

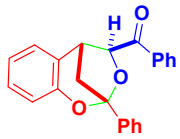


3s
(CCDC 1886996)

Displacement ellipsoids are drawn at the 30% probability level.

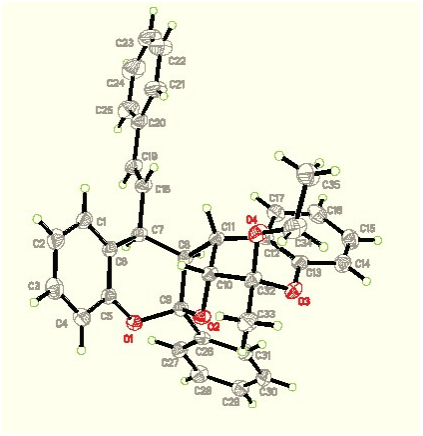


≡

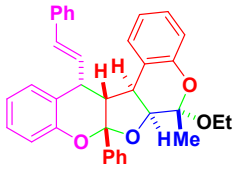


5
(CCDC 1886997)

Displacement ellipsoids are drawn at the 30% probability level.



≡

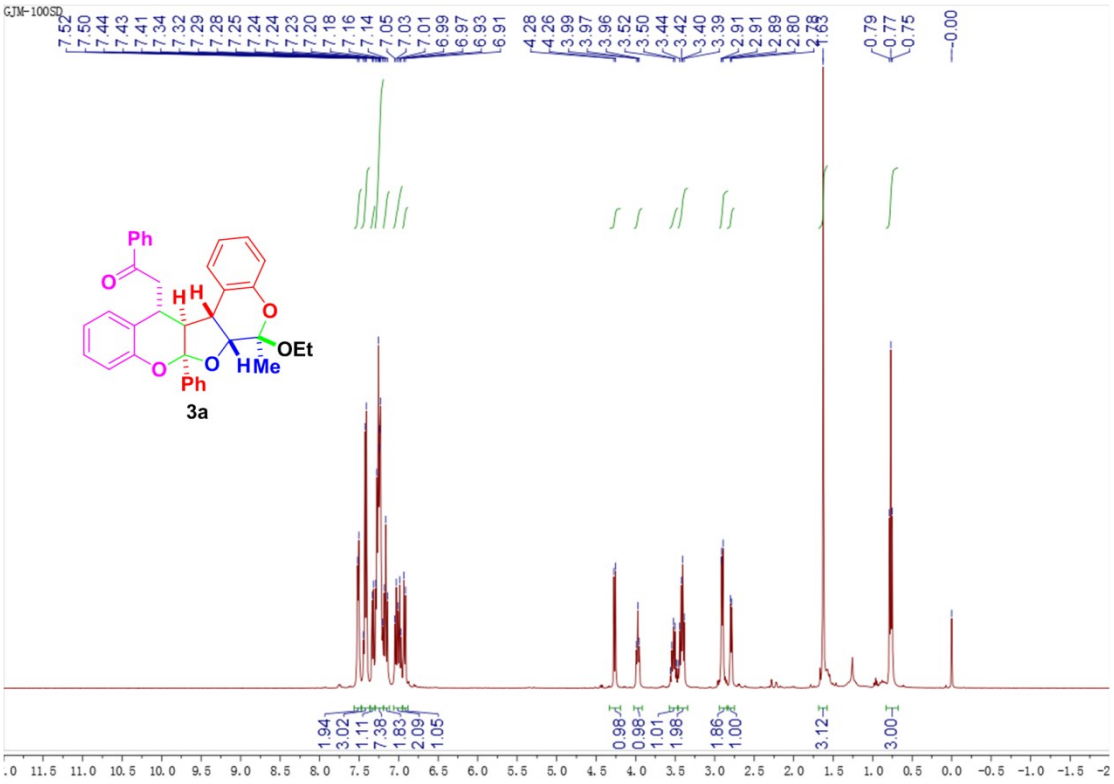


8
(CCDC 1886998)

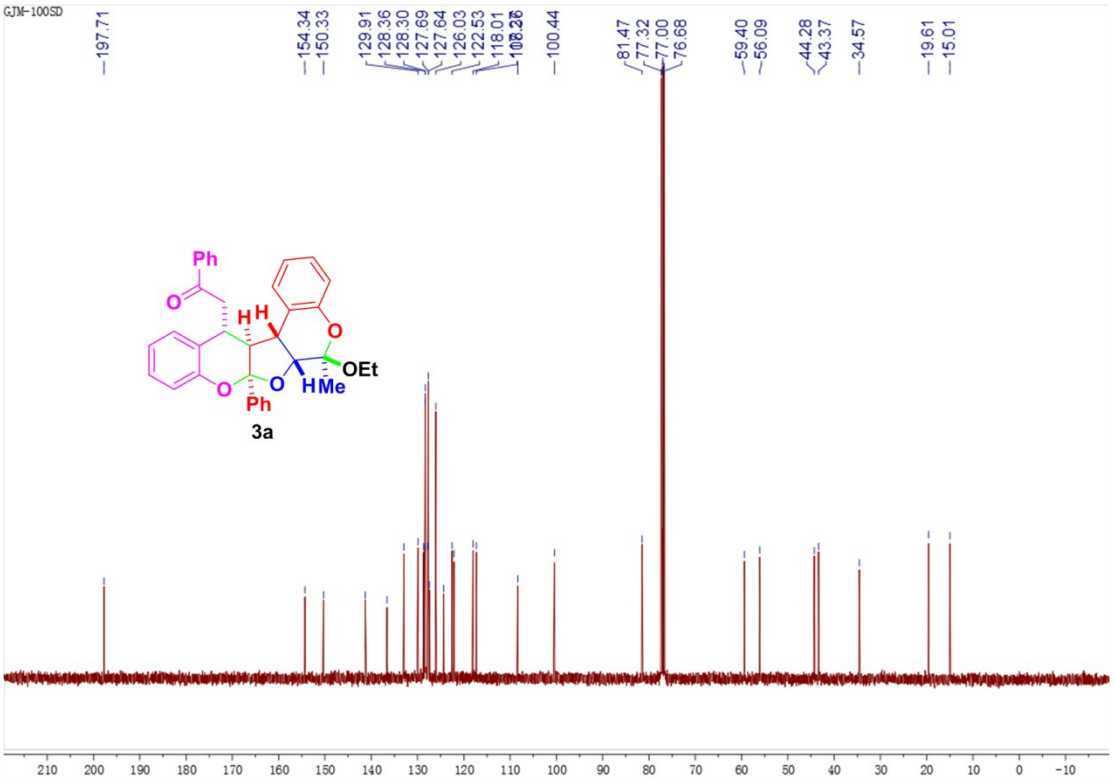
Displacement ellipsoids are drawn at the 30% probability level.

7. ^{1}H NMR and ^{13}C NMR spectra

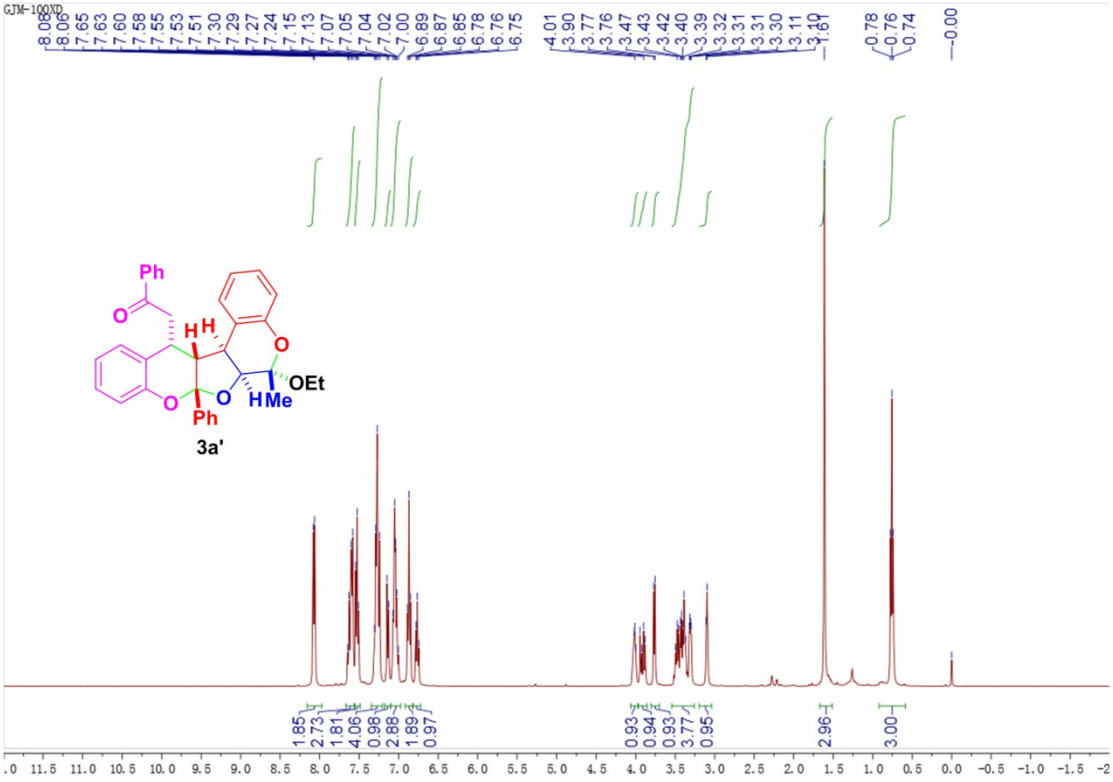
^{1}H NMR spectrum of 3a



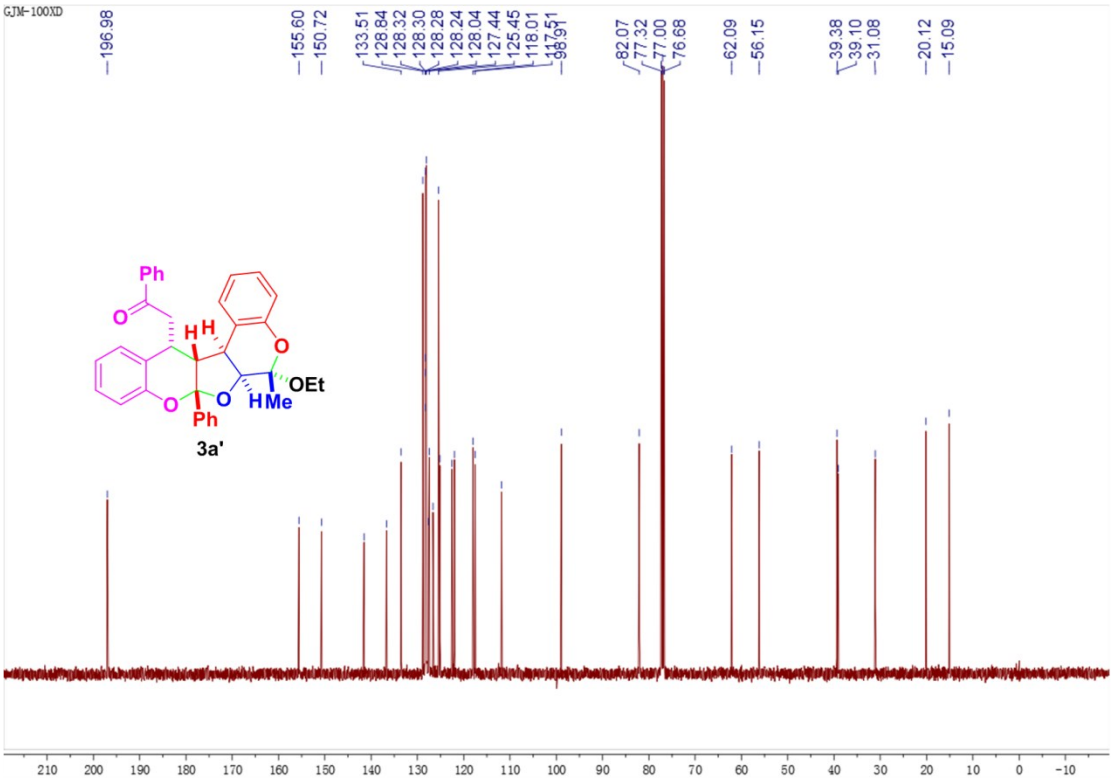
^{13}C NMR spectrum of 3a



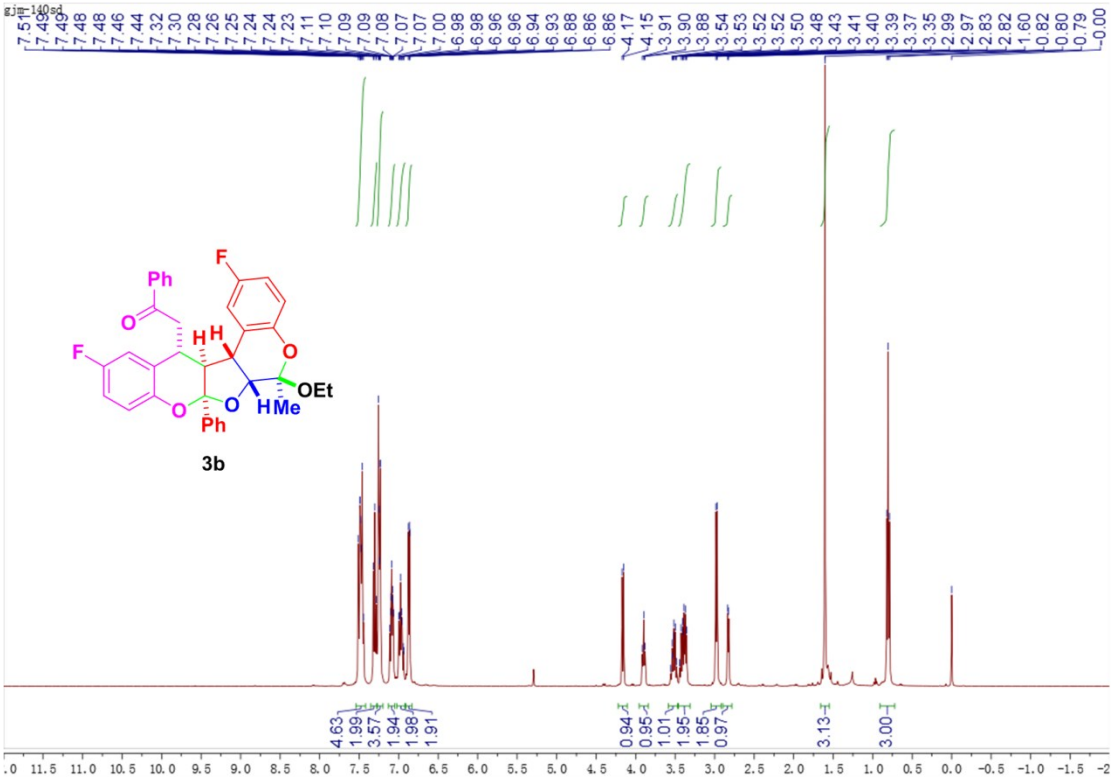
^{1}H NMR spectrum of 3a'



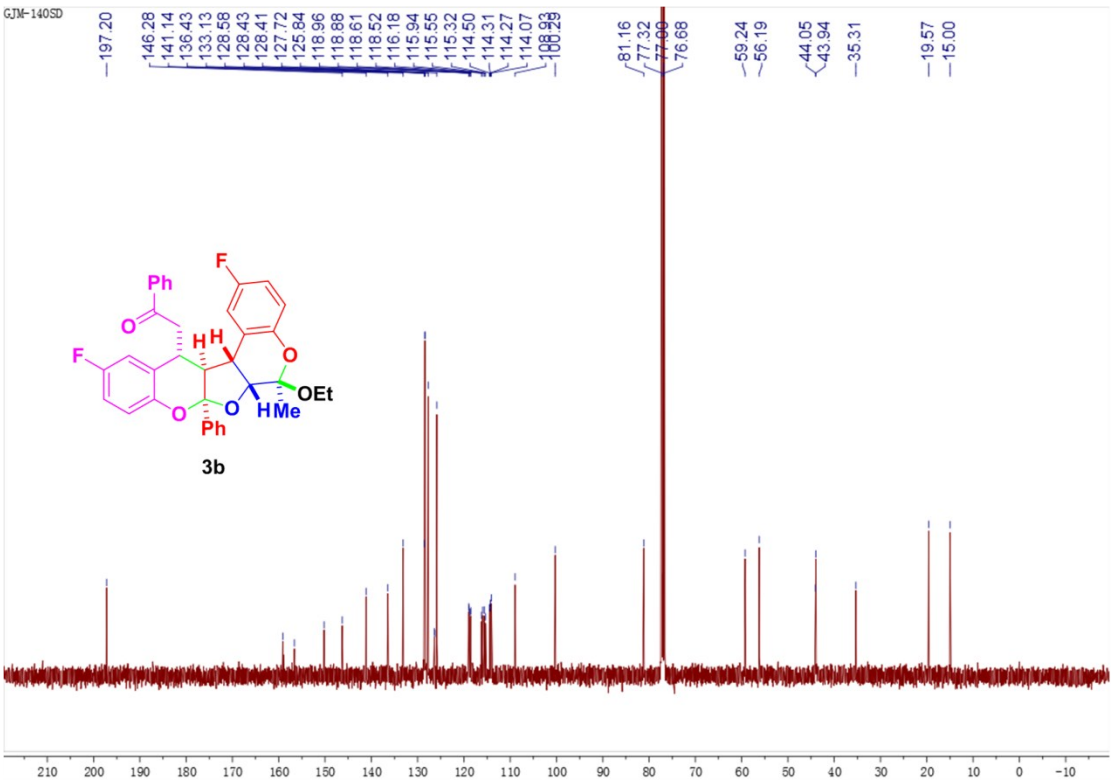
^{13}C NMR spectrum of 3a'



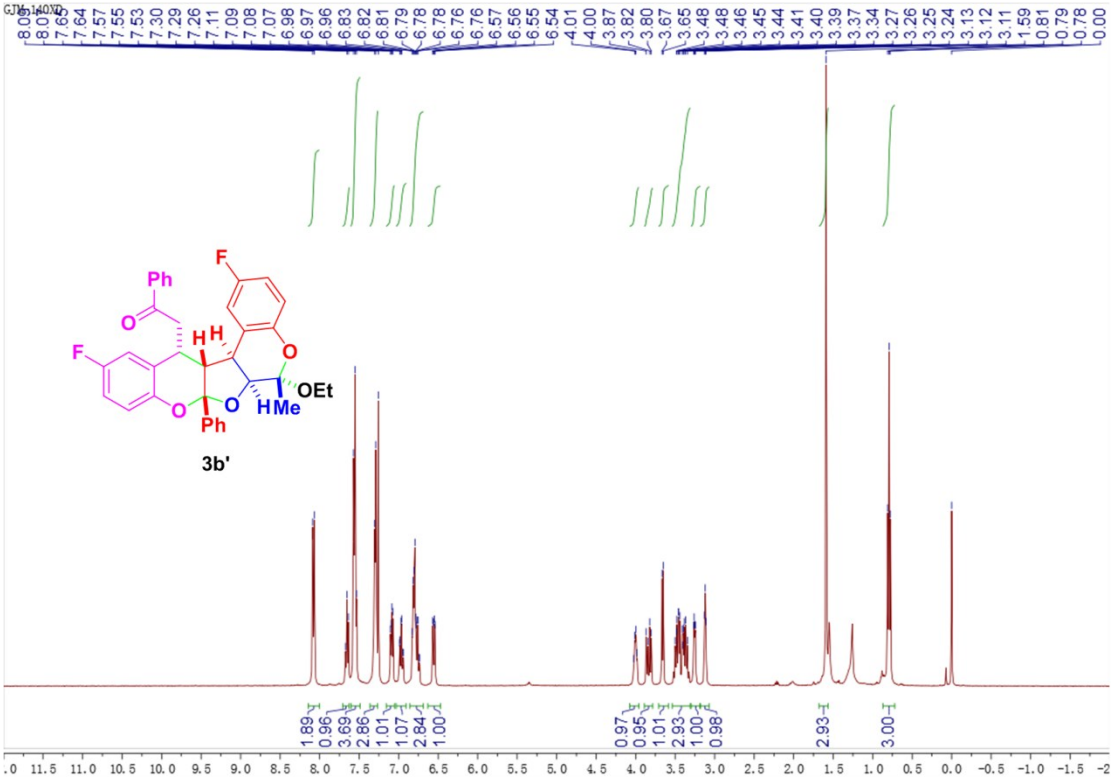
^{1}H NMR spectrum of 3b



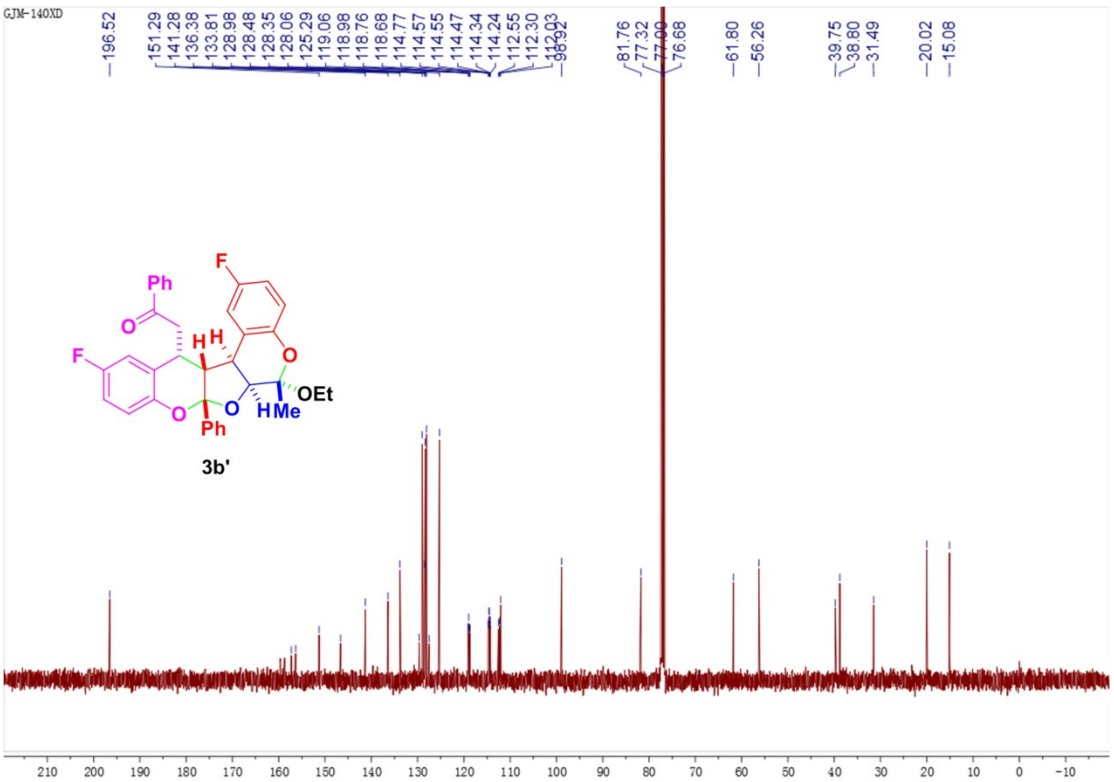
^{13}C NMR spectrum of 3b



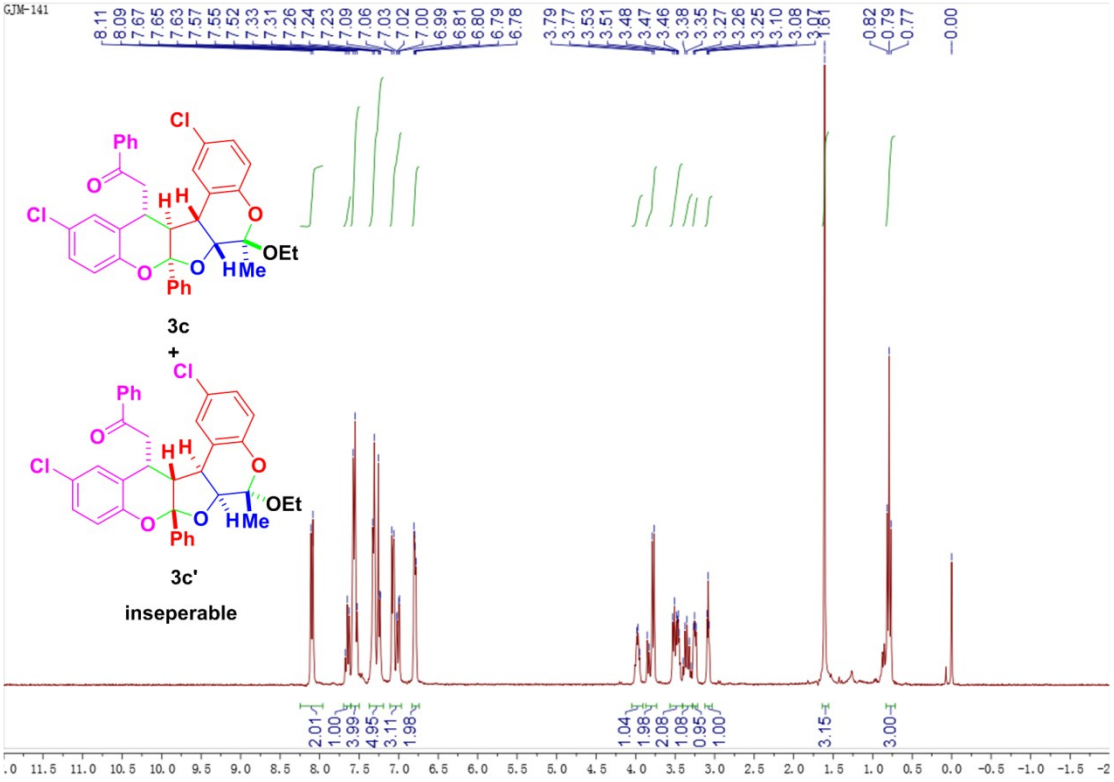
^{1}H NMR spectrum of 3b'



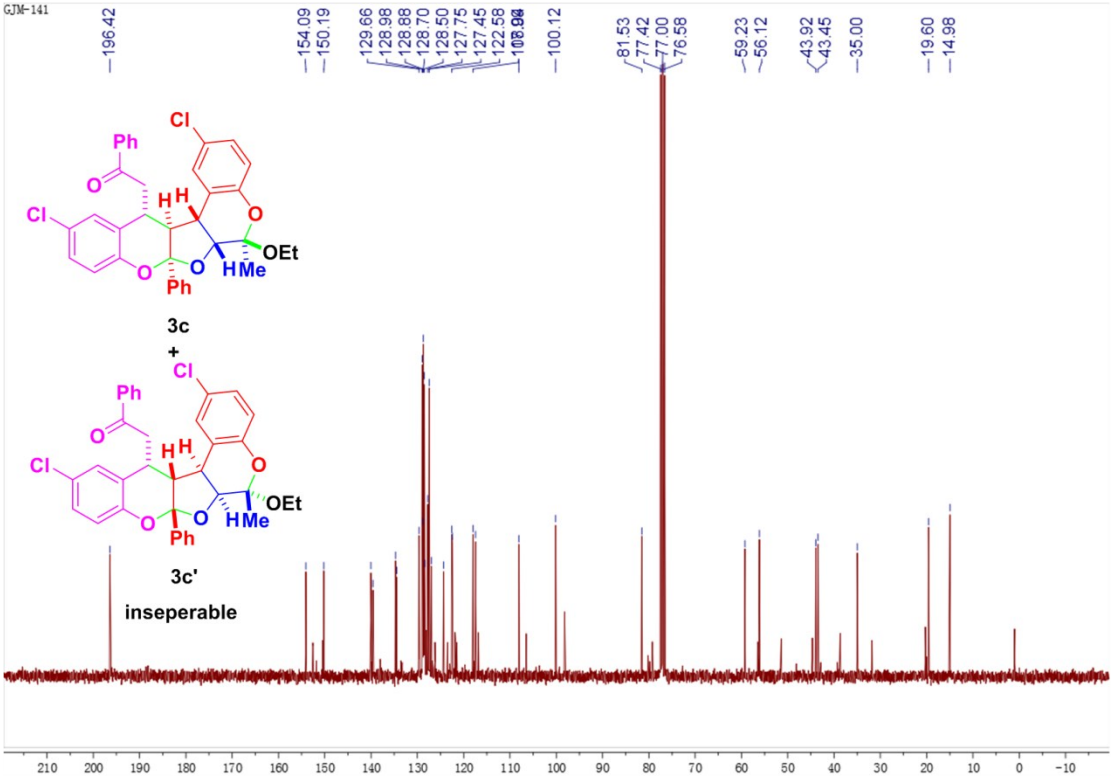
^{13}C NMR spectrum of 3b'



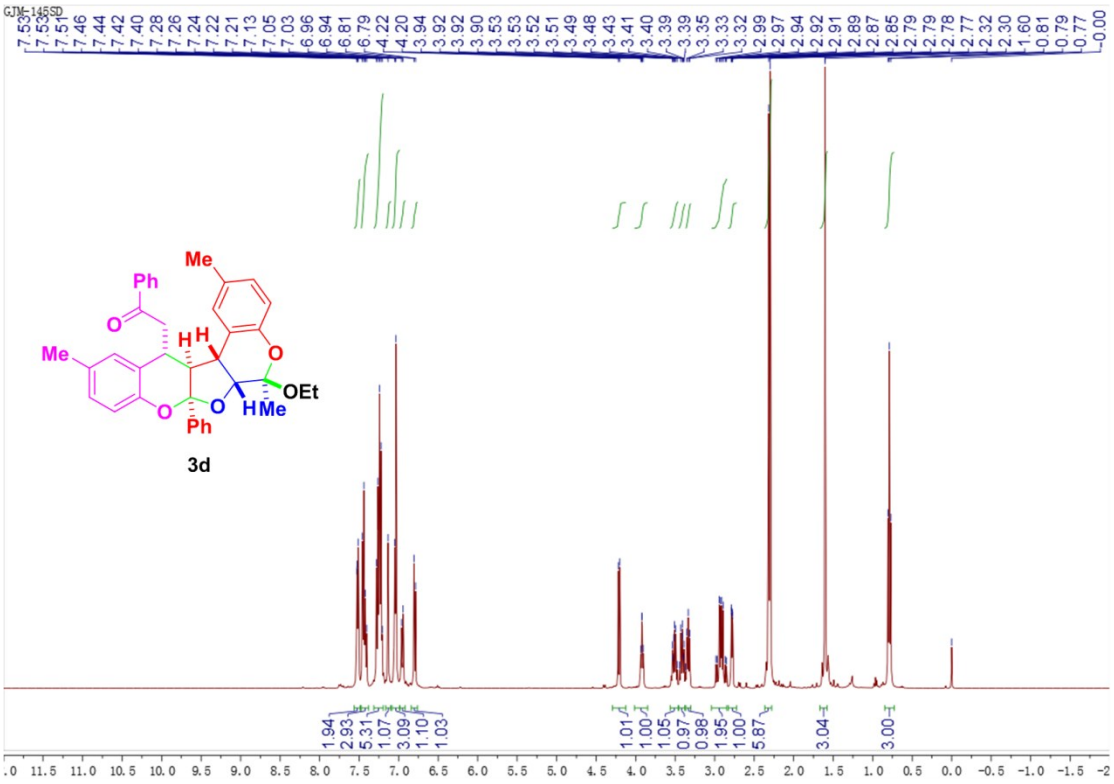
^{1}H NMR spectrum of 3c and 3c'



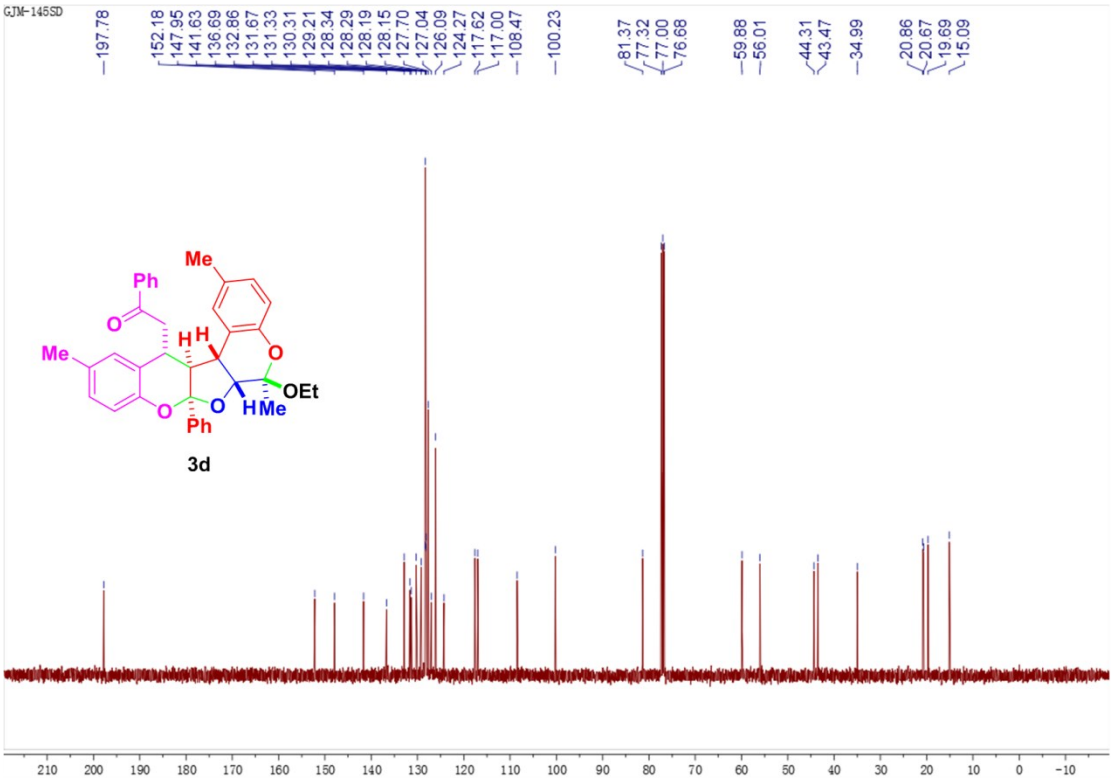
^{13}C NMR spectrum of 3c and 3c'



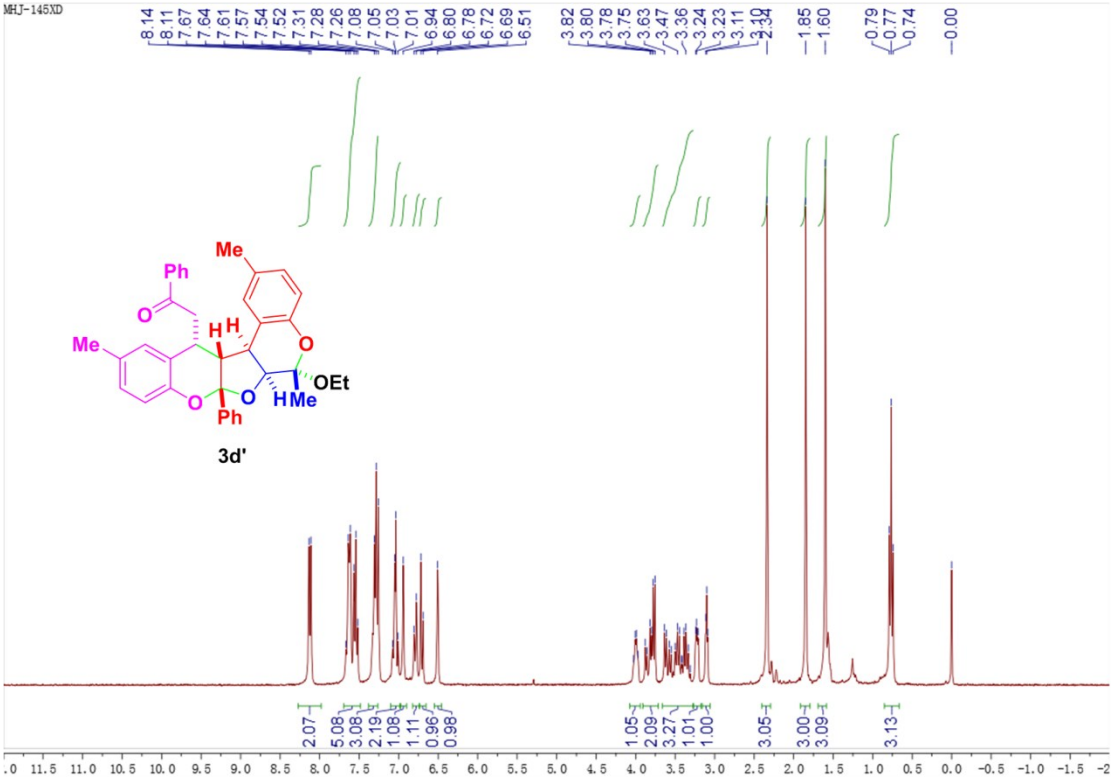
^{1}H NMR spectrum of 3d



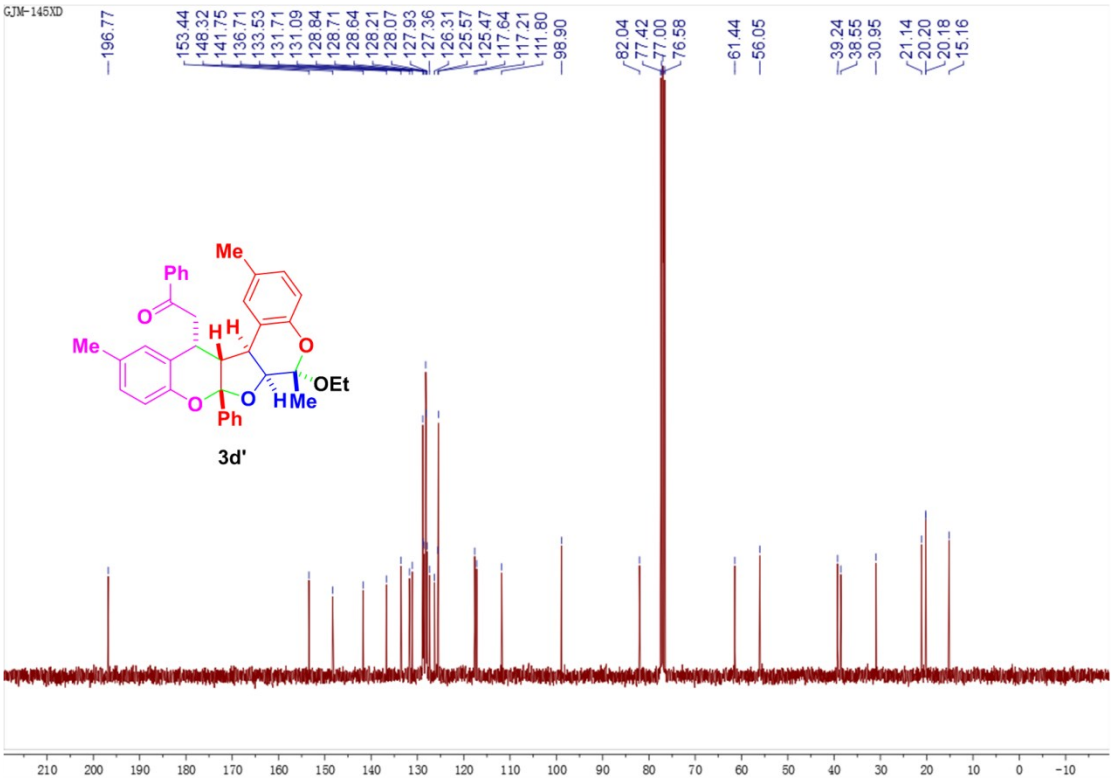
^{13}C NMR spectrum of 3d



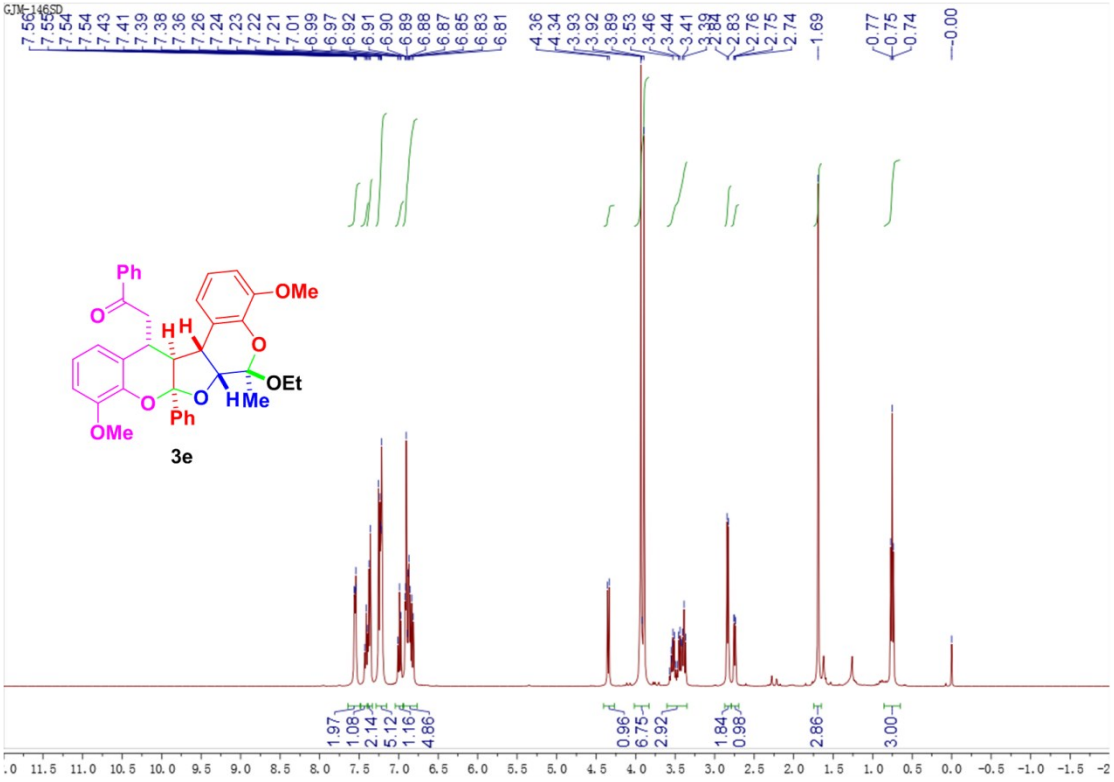
^{1}H NMR spectrum of 3d'



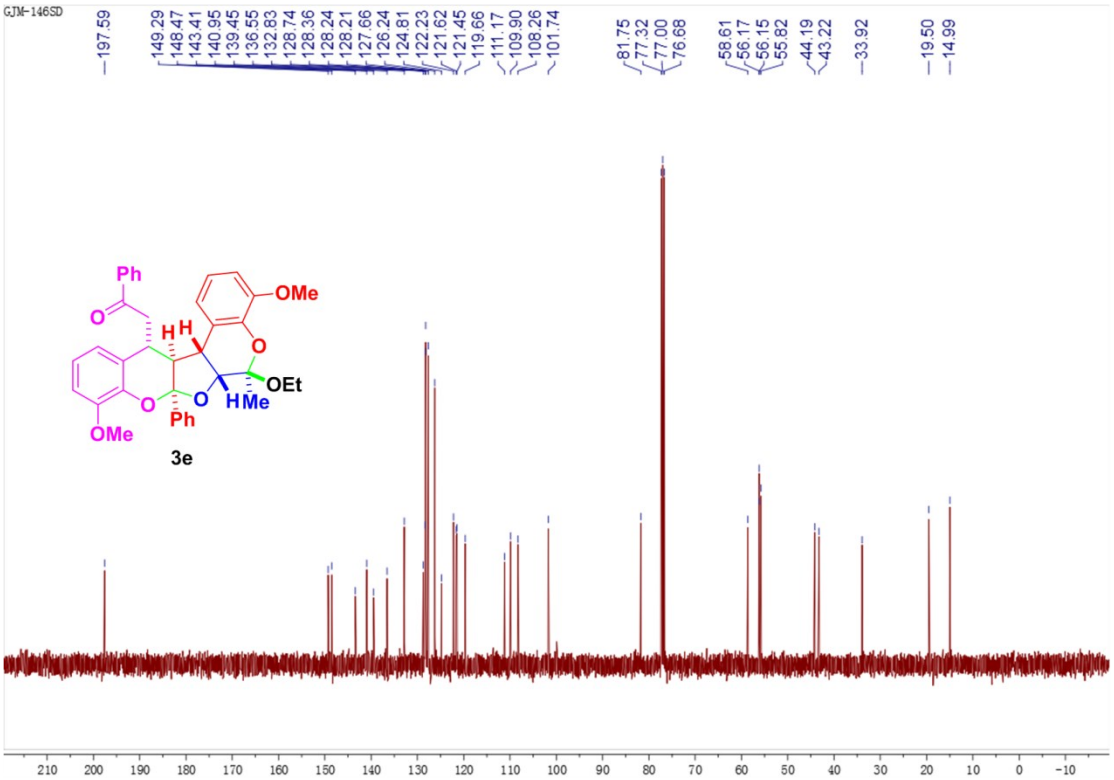
^{13}C NMR spectrum of 3d'



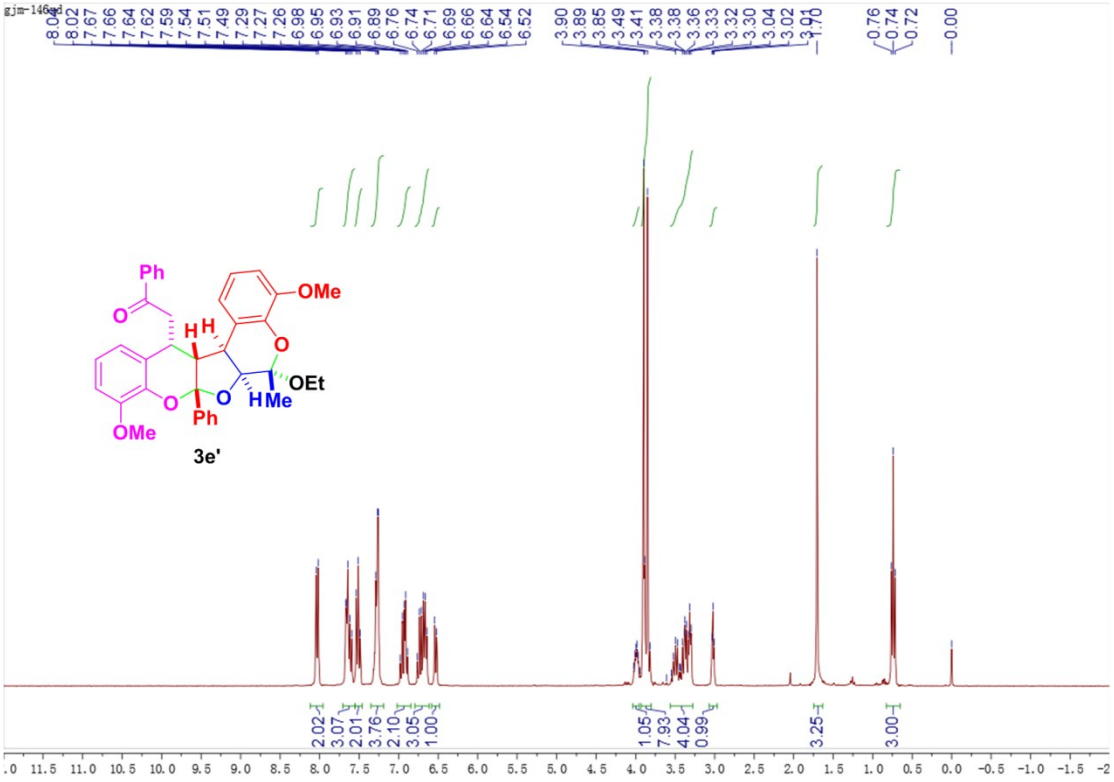
^{1}H NMR spectrum of 3e



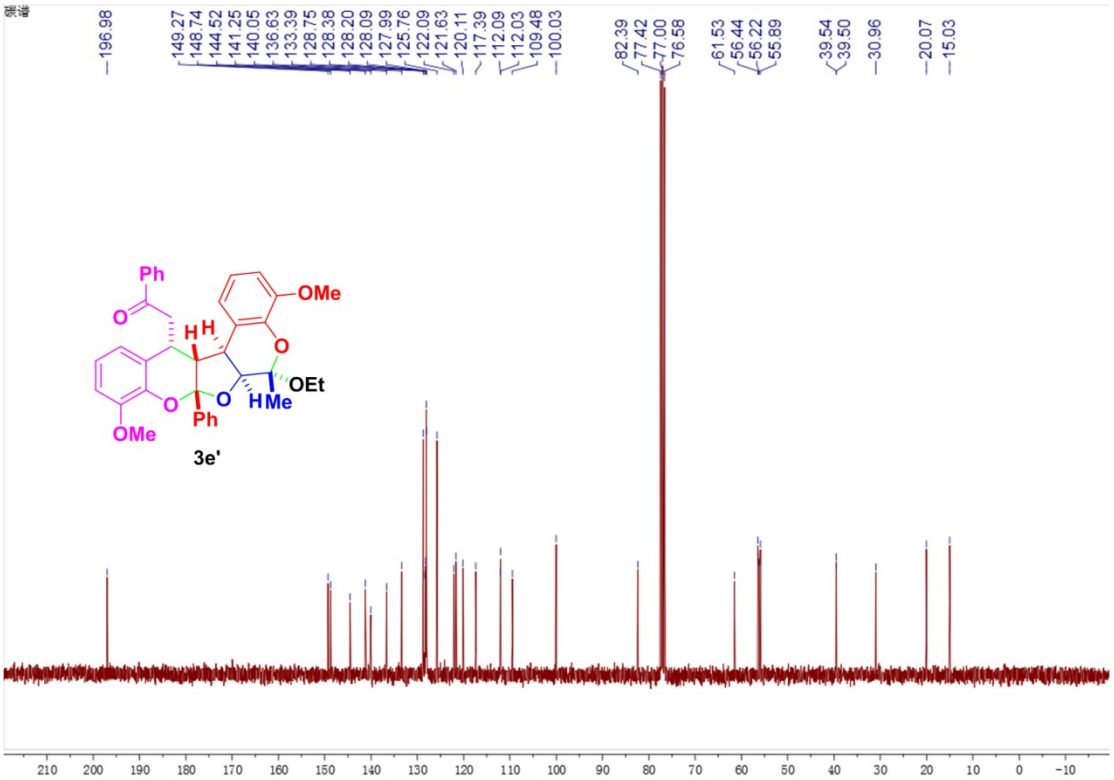
^{13}C NMR spectrum of 3e



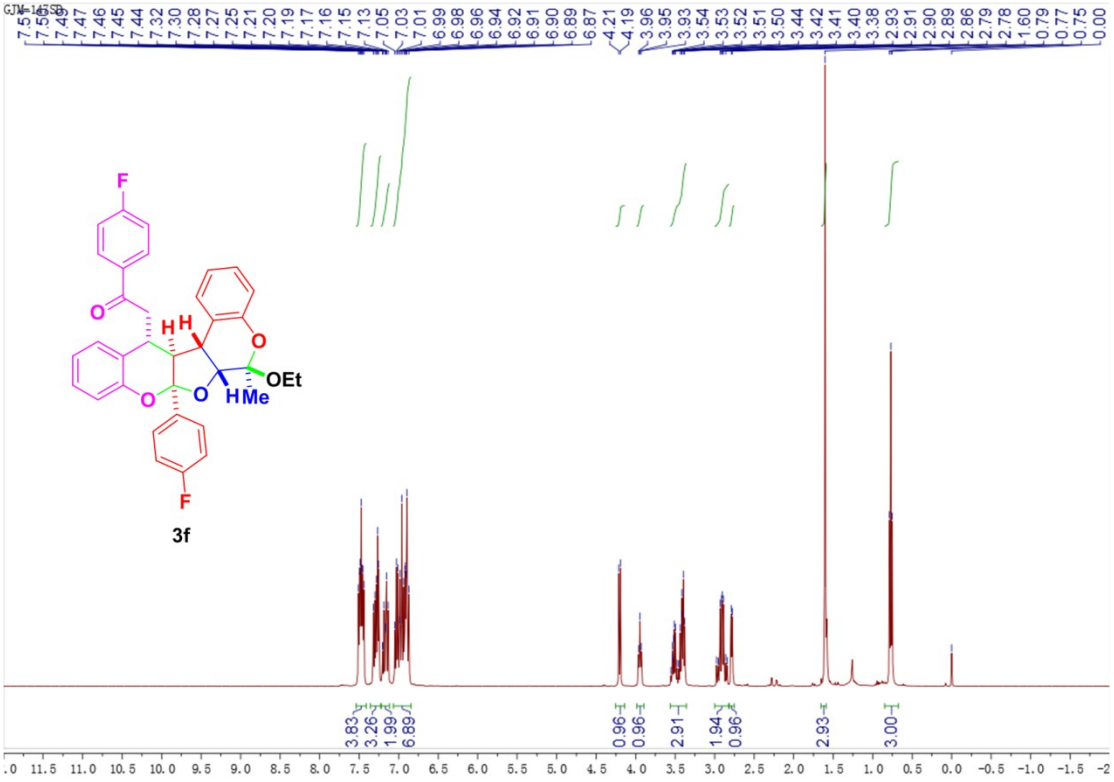
^{1}H NMR spectrum of 3e'



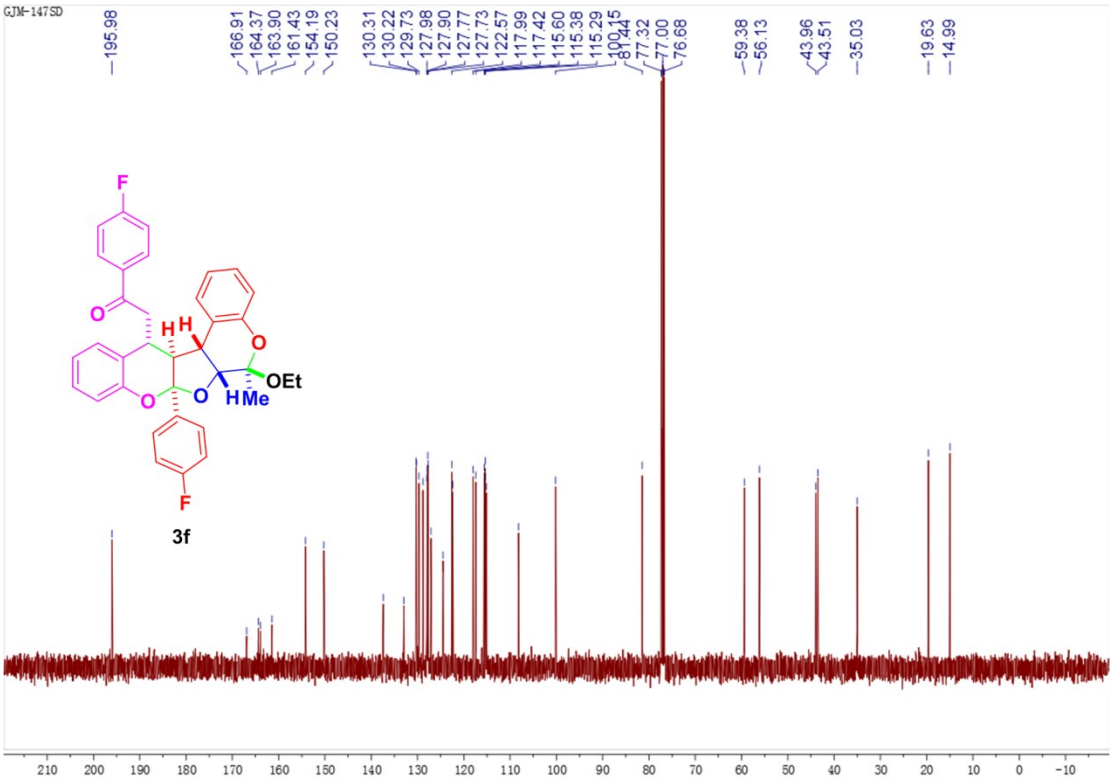
^{13}C NMR spectrum of 3e'



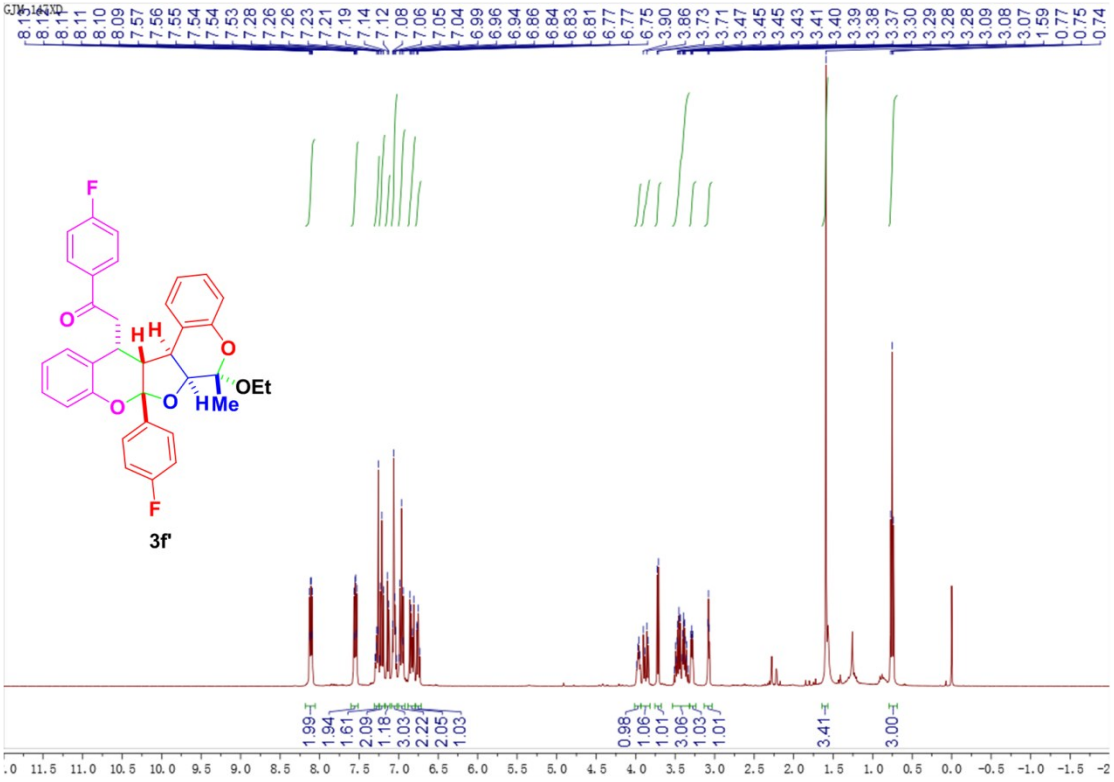
^{1}H NMR spectrum of 3f



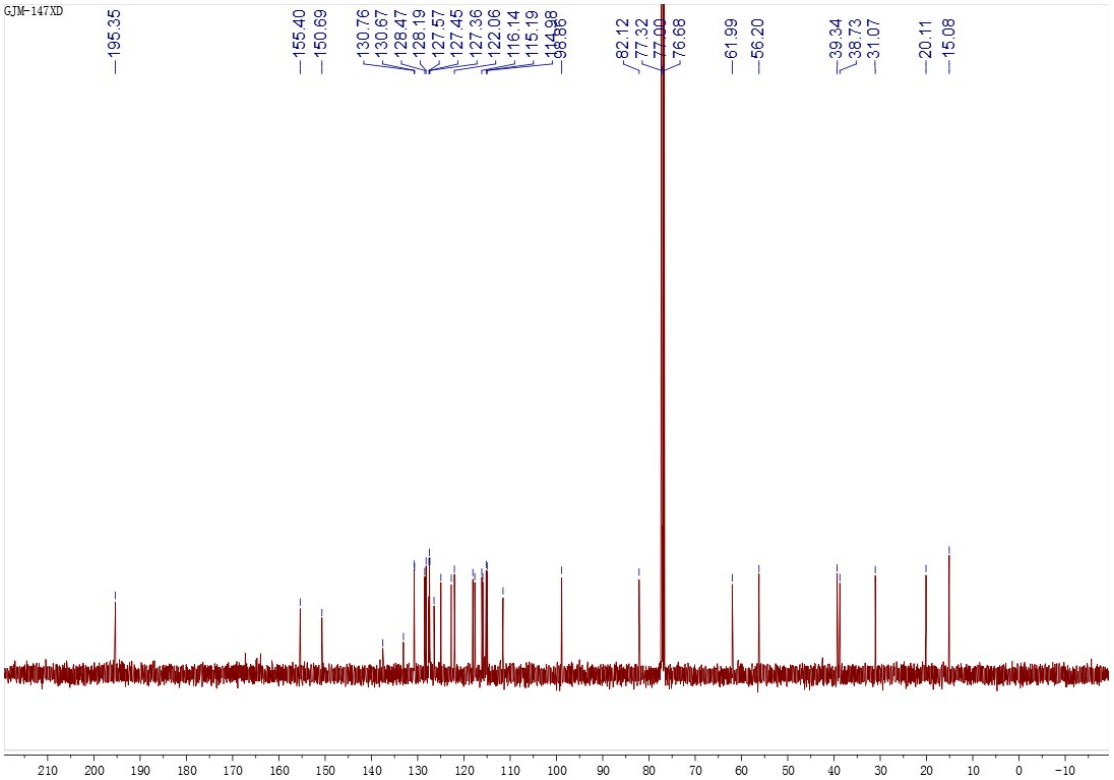
^{13}C NMR spectrum of 3f



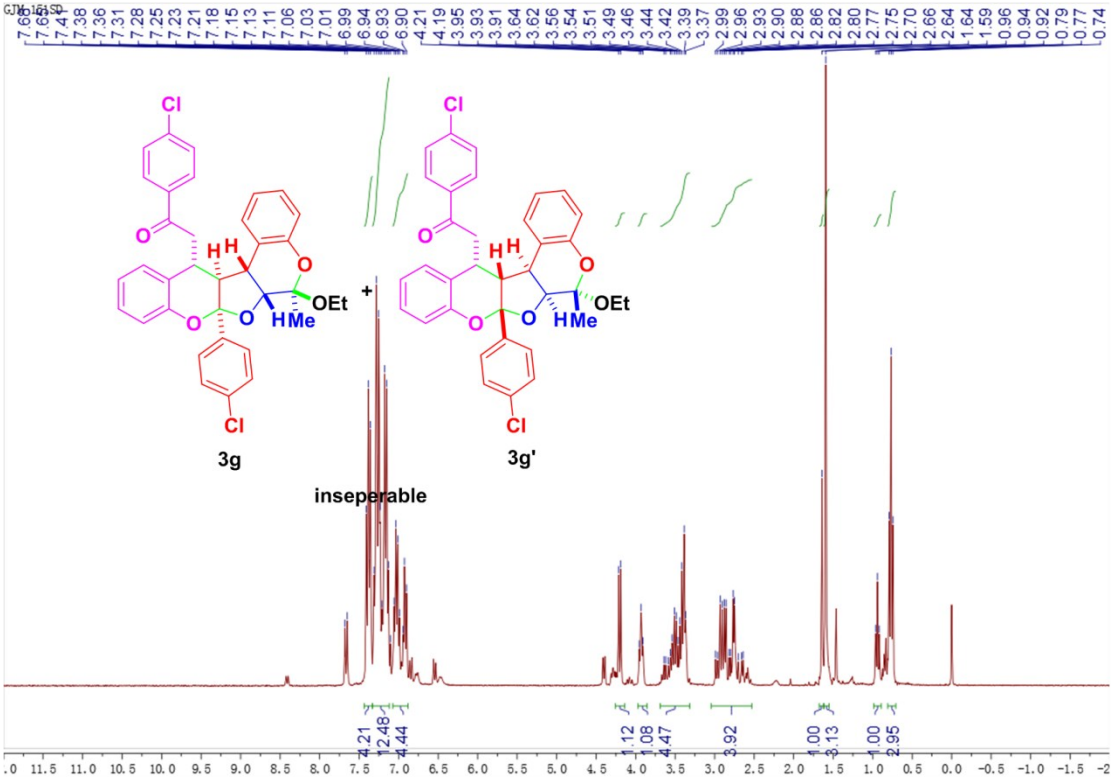
^{1}H NMR spectrum of 3f'



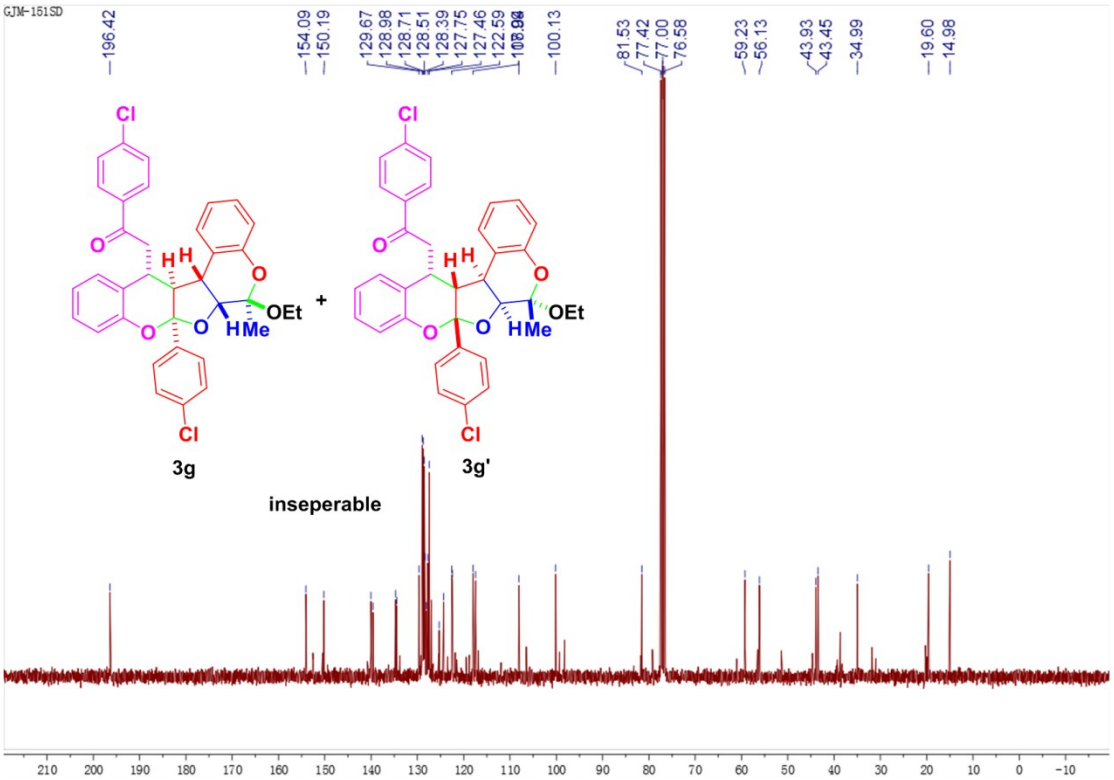
^{13}C NMR spectrum of 3f'



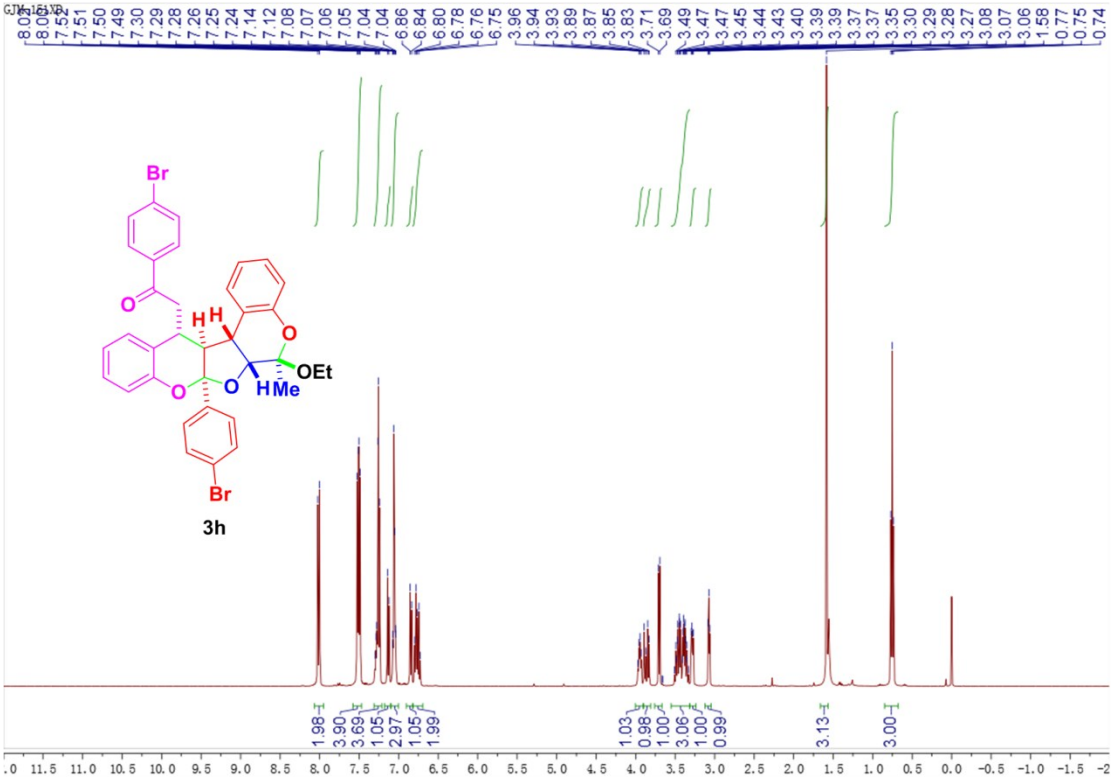
^{1}H NMR spectrum of 3g and 3g'



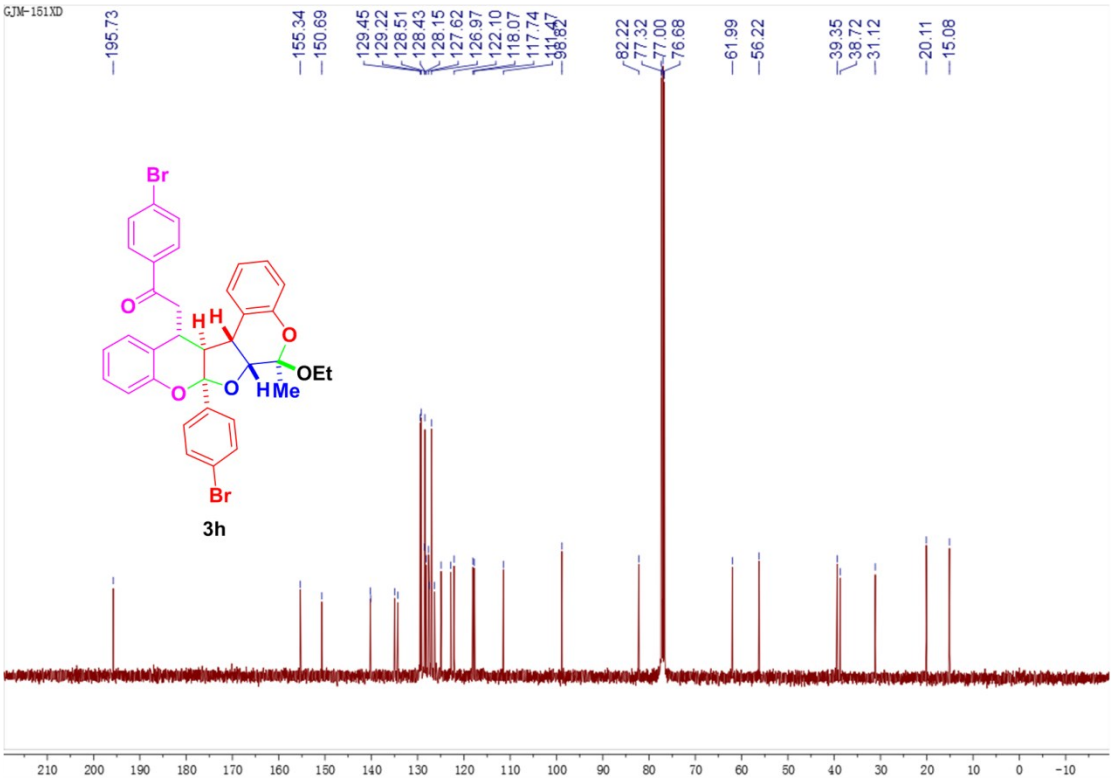
^{13}C NMR spectrum of 3g and 3g'



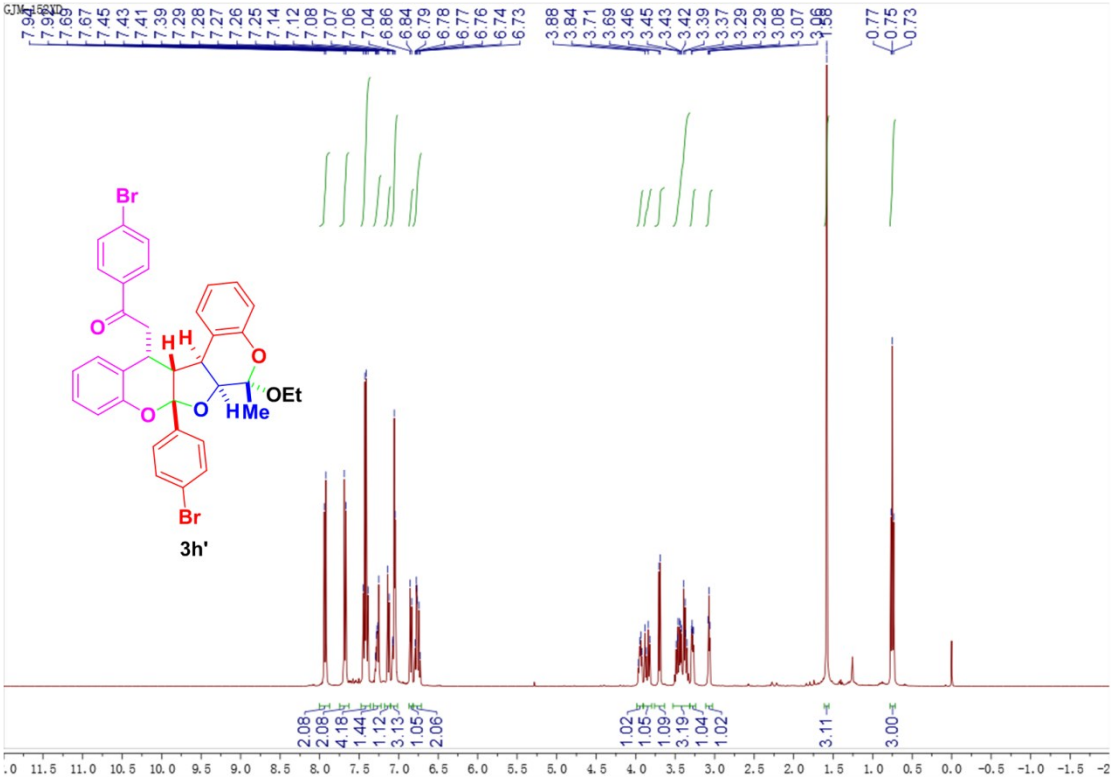
^{1}H NMR spectrum of 3h



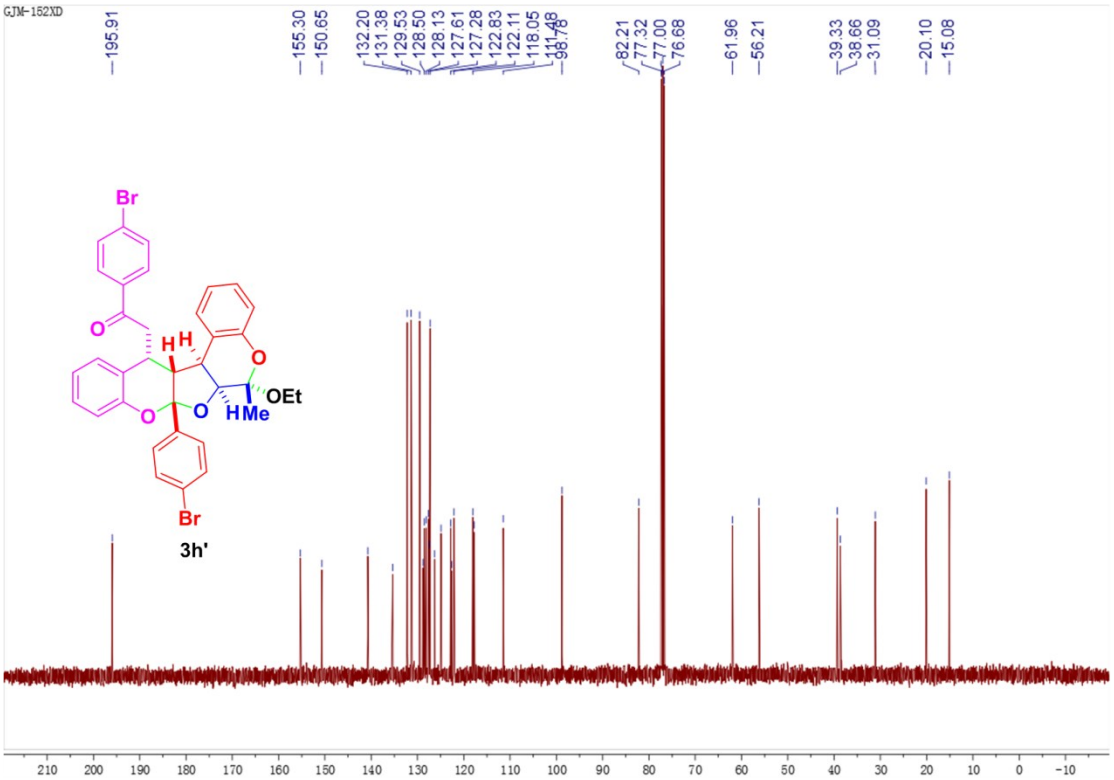
^{13}C NMR spectrum of 3h



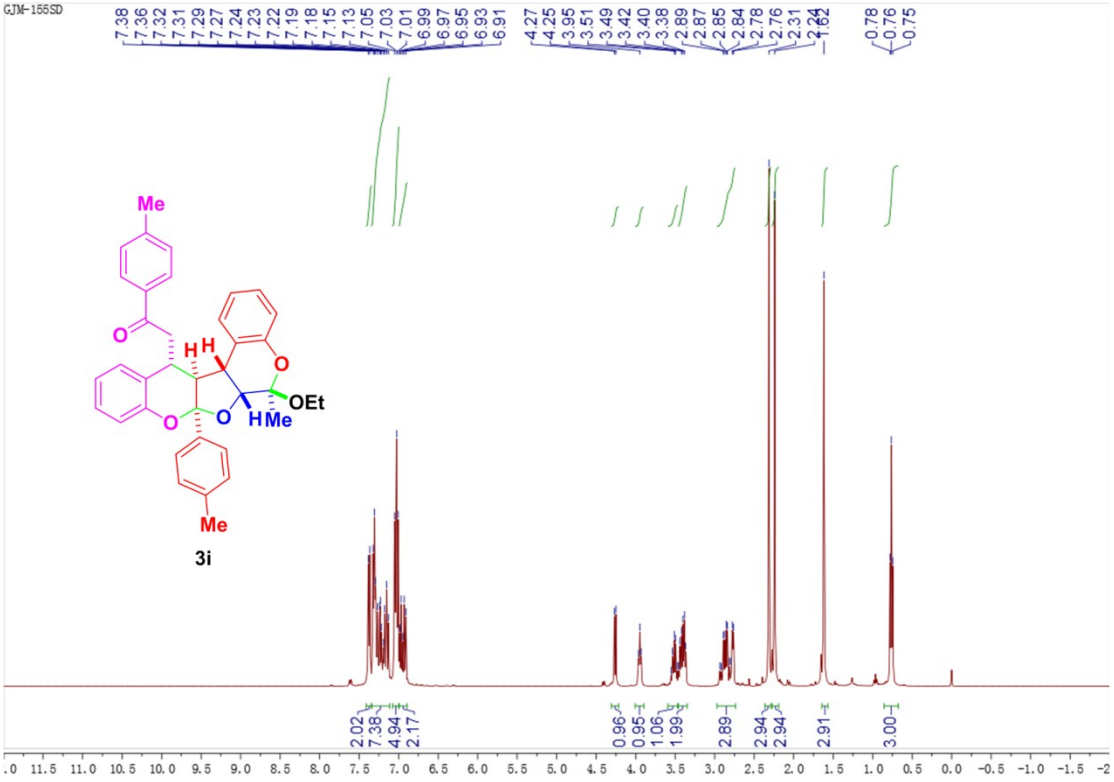
^{1}H NMR spectrum of 3h'



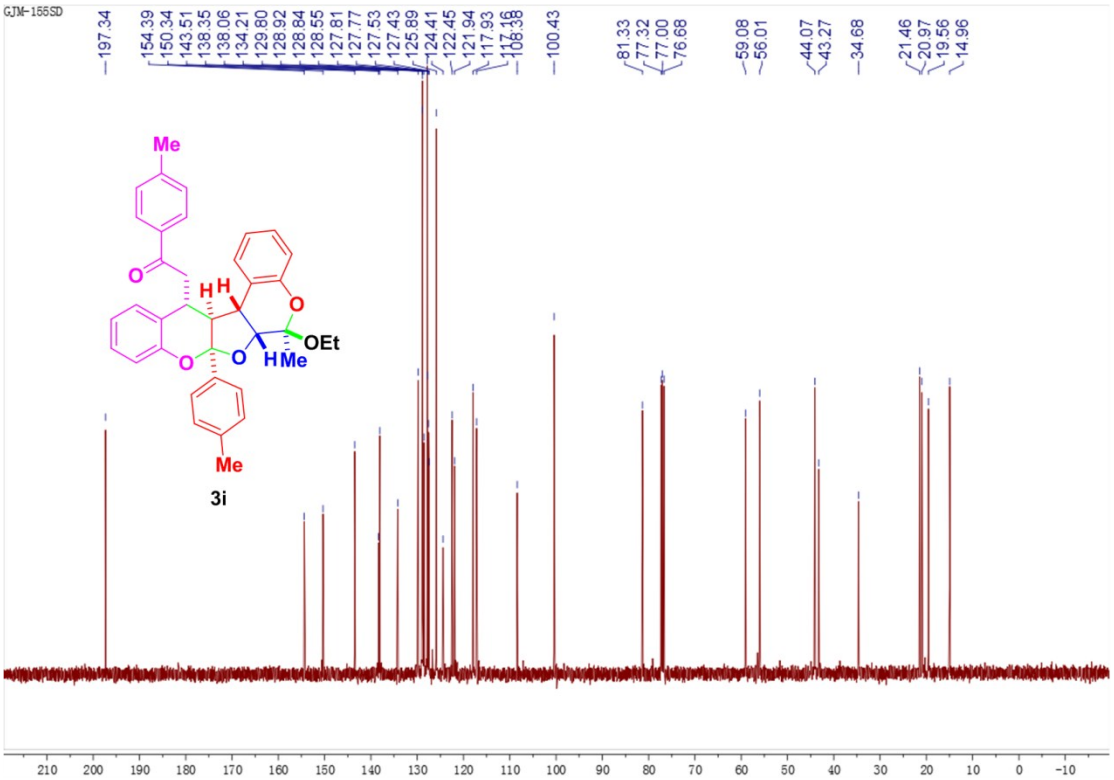
^{13}C NMR spectrum of 3h'



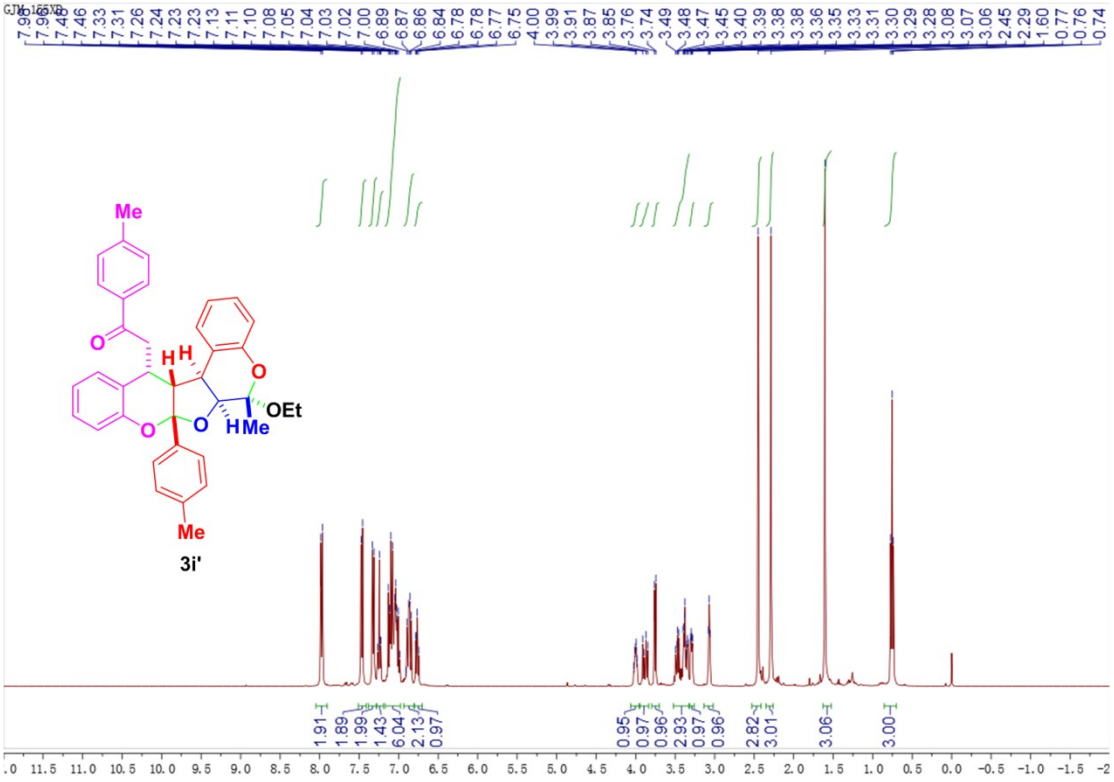
^{1}H NMR spectrum of 3i



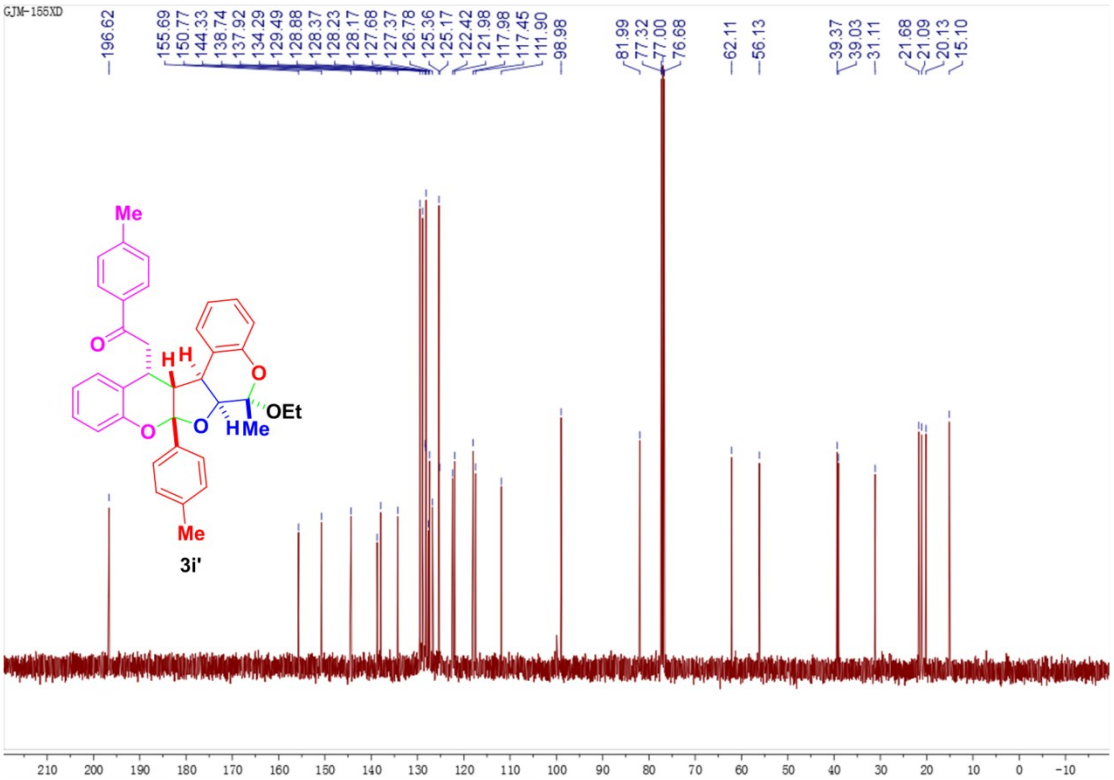
^{13}C NMR spectrum of 3i



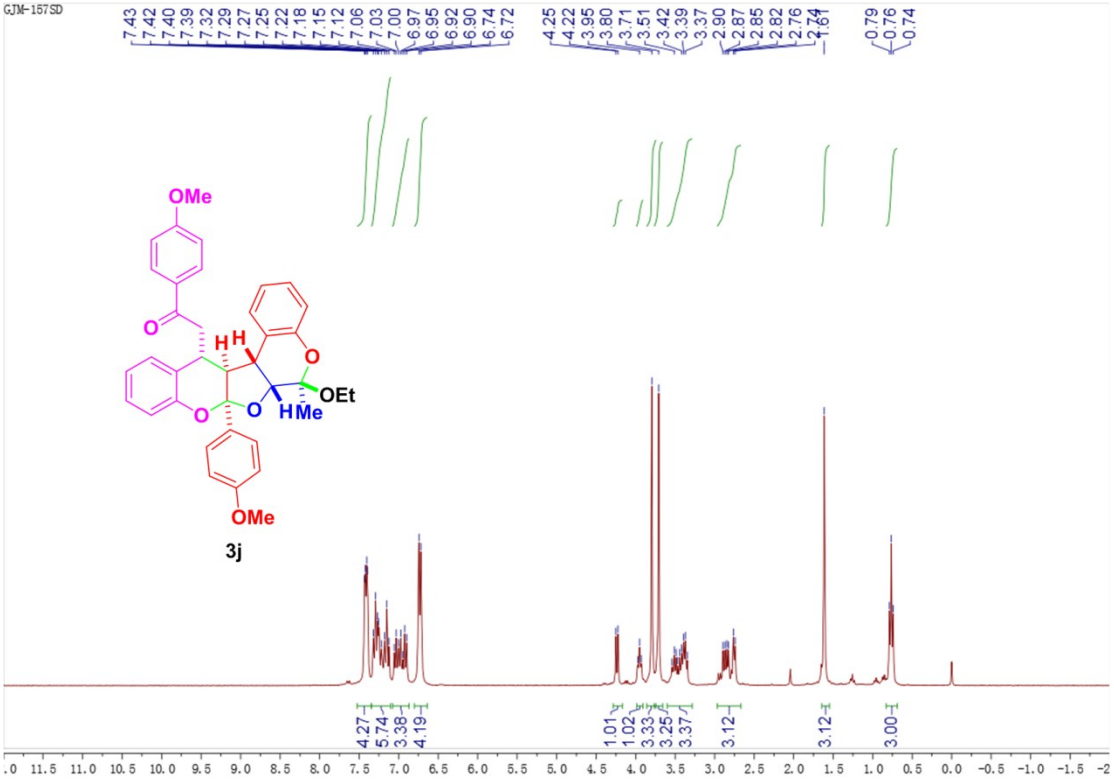
^{1}H NMR spectrum of 3i'



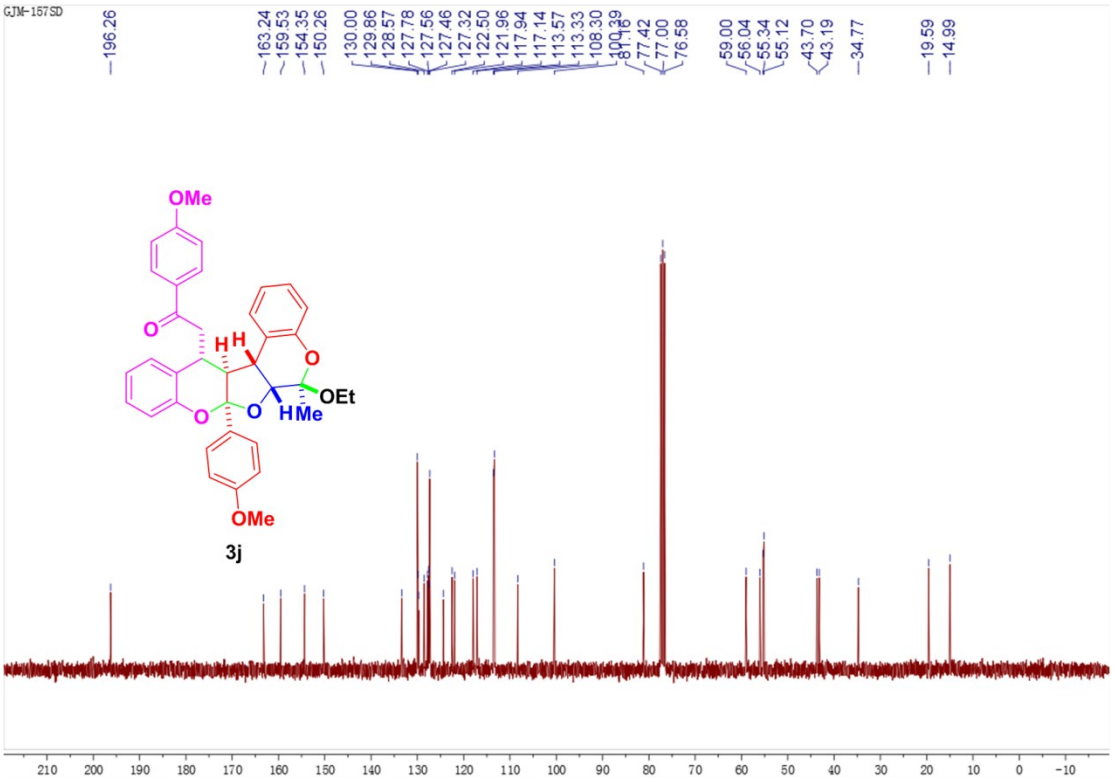
^{13}C NMR spectrum of 3i'



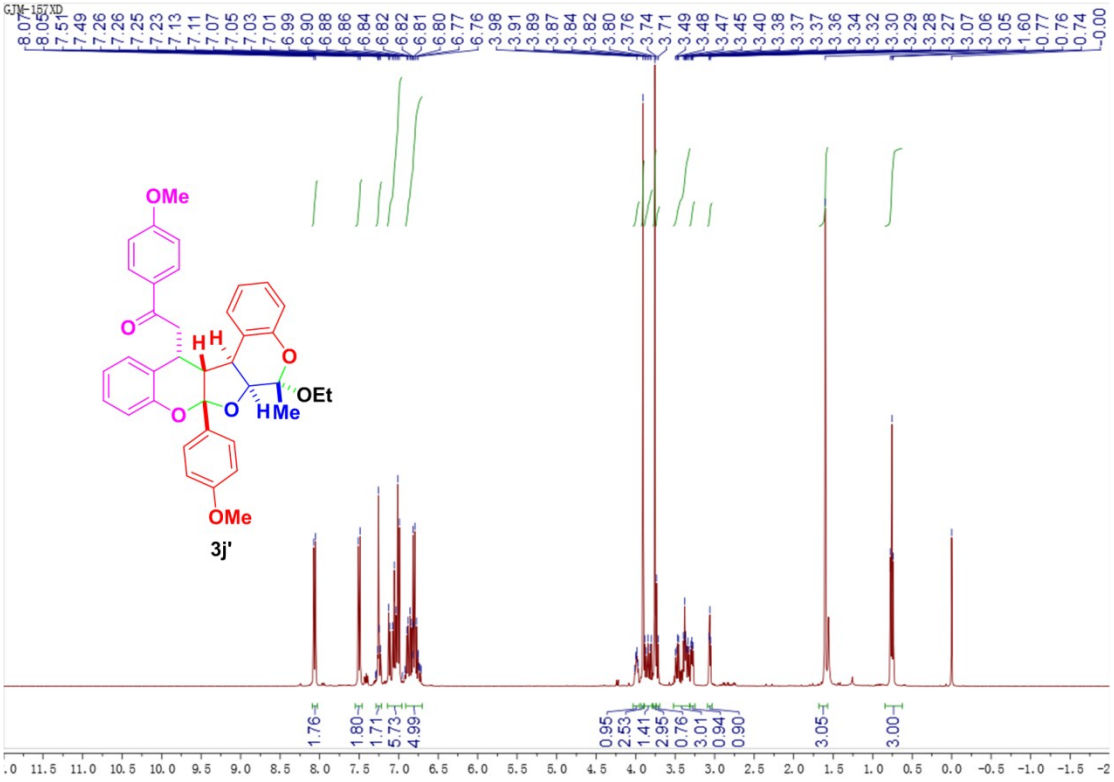
^{1}H NMR spectrum of 3j



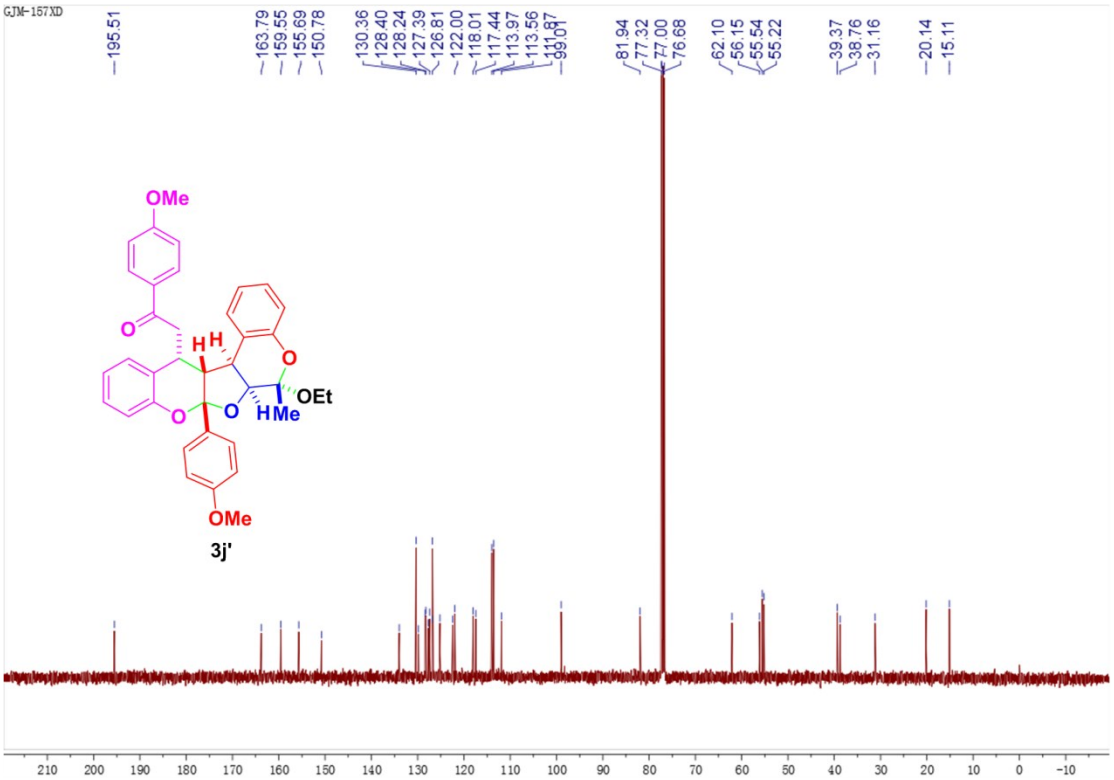
^{13}C NMR spectrum of 3j



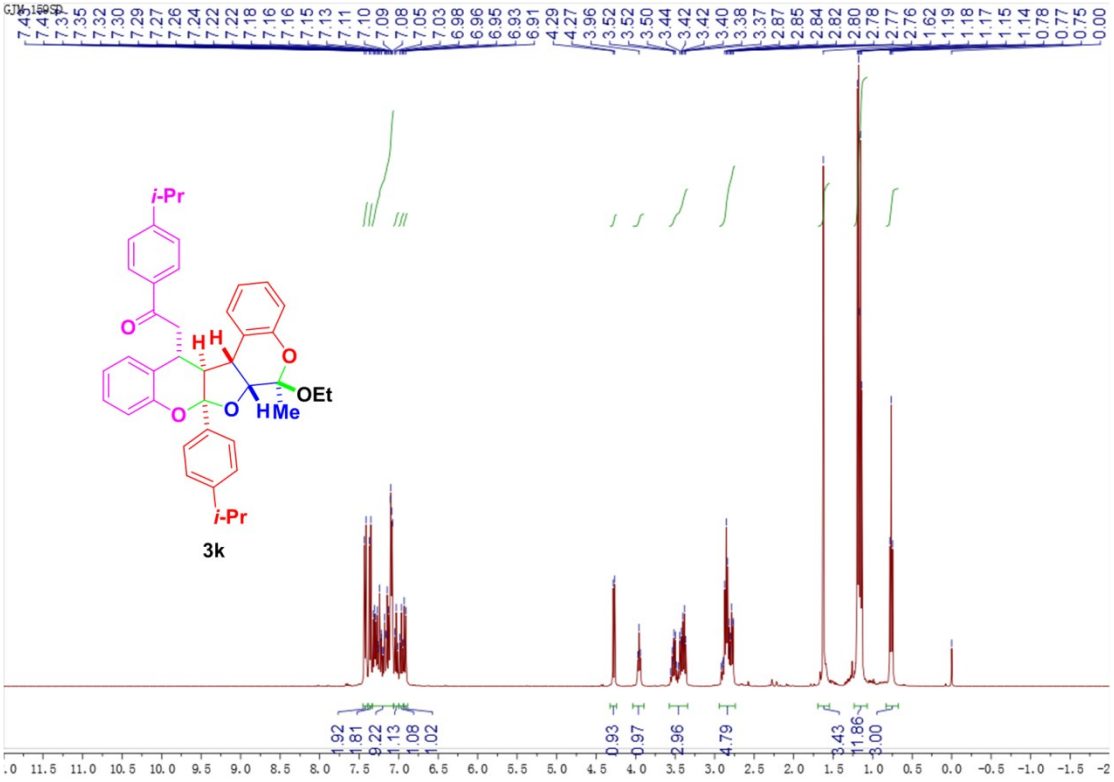
^{1}H NMR spectrum of 3j'



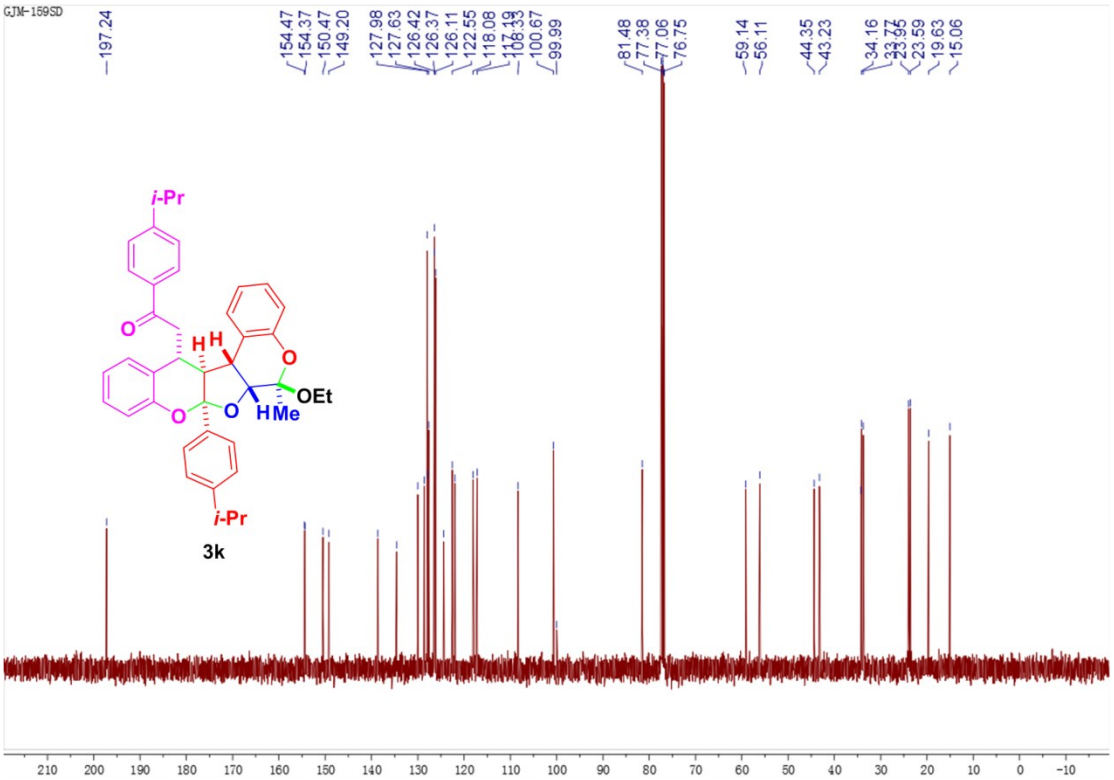
^{13}C NMR spectrum of 3j'



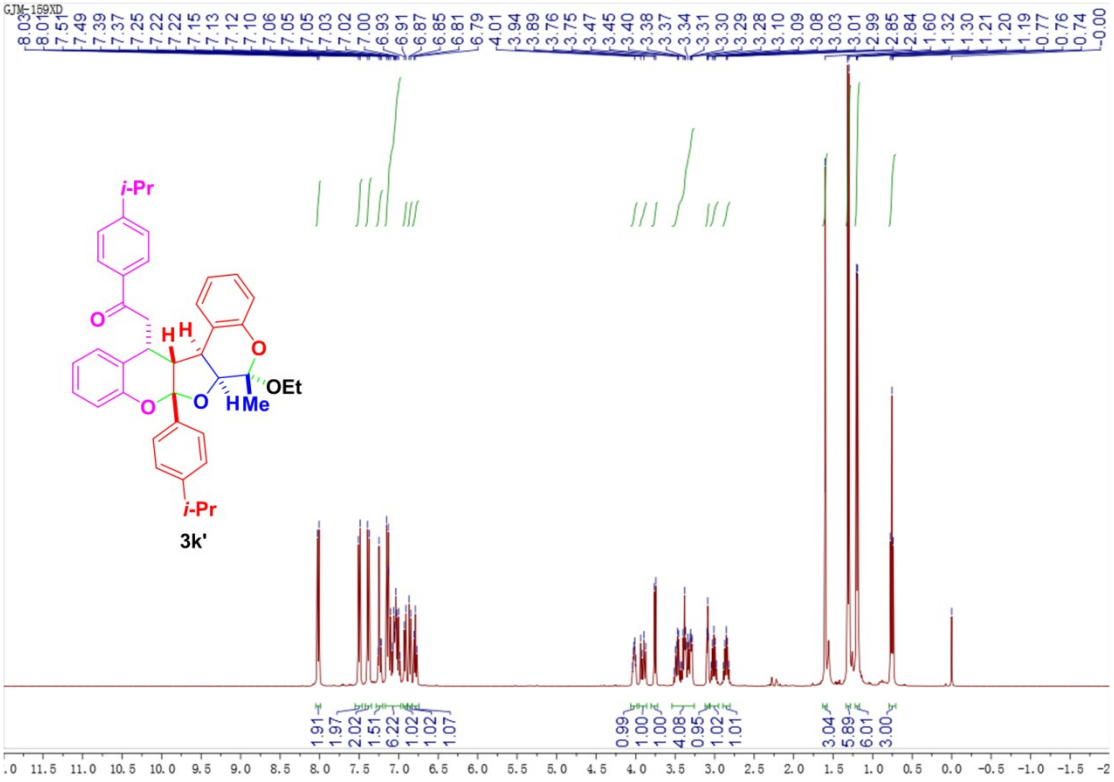
^{1}H NMR spectrum of 3k



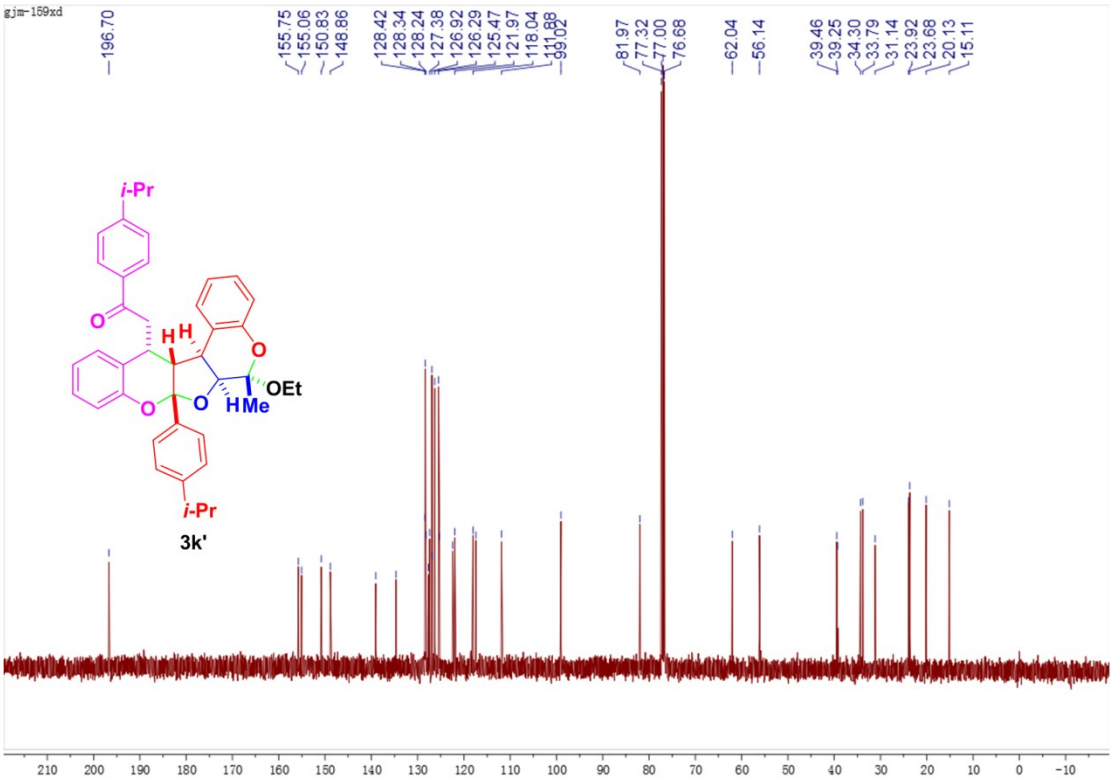
^{13}C NMR spectrum of 3k



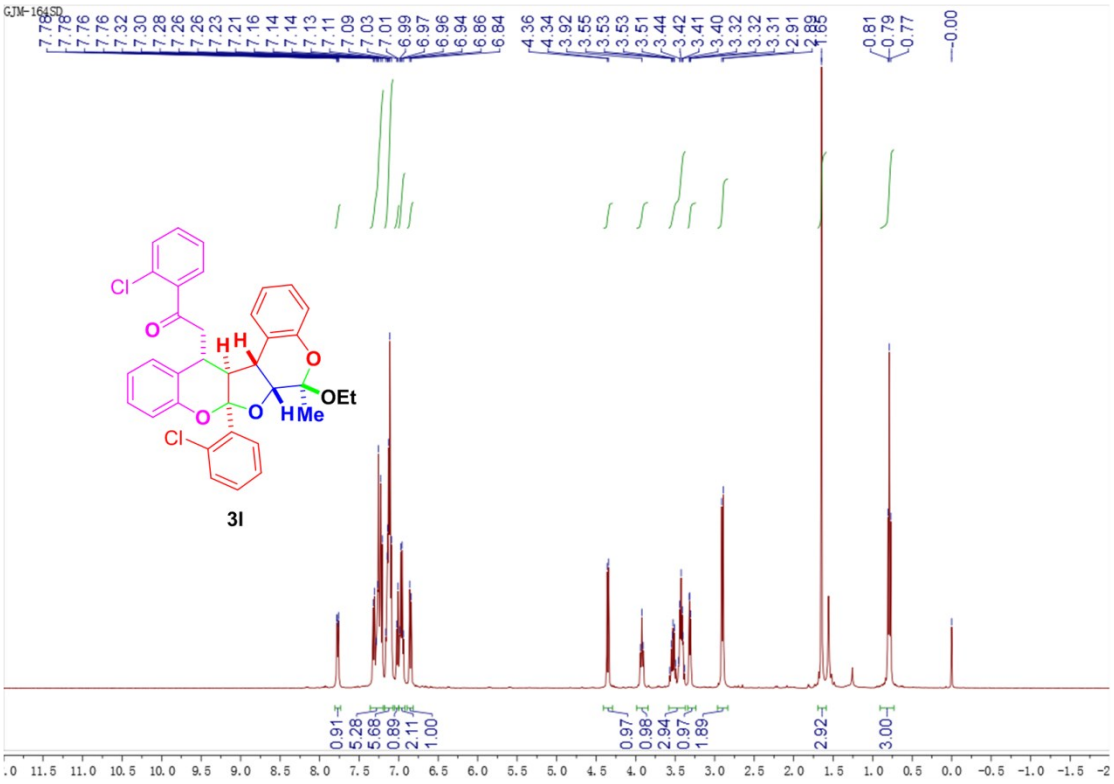
^{1}H NMR spectrum of 3k'



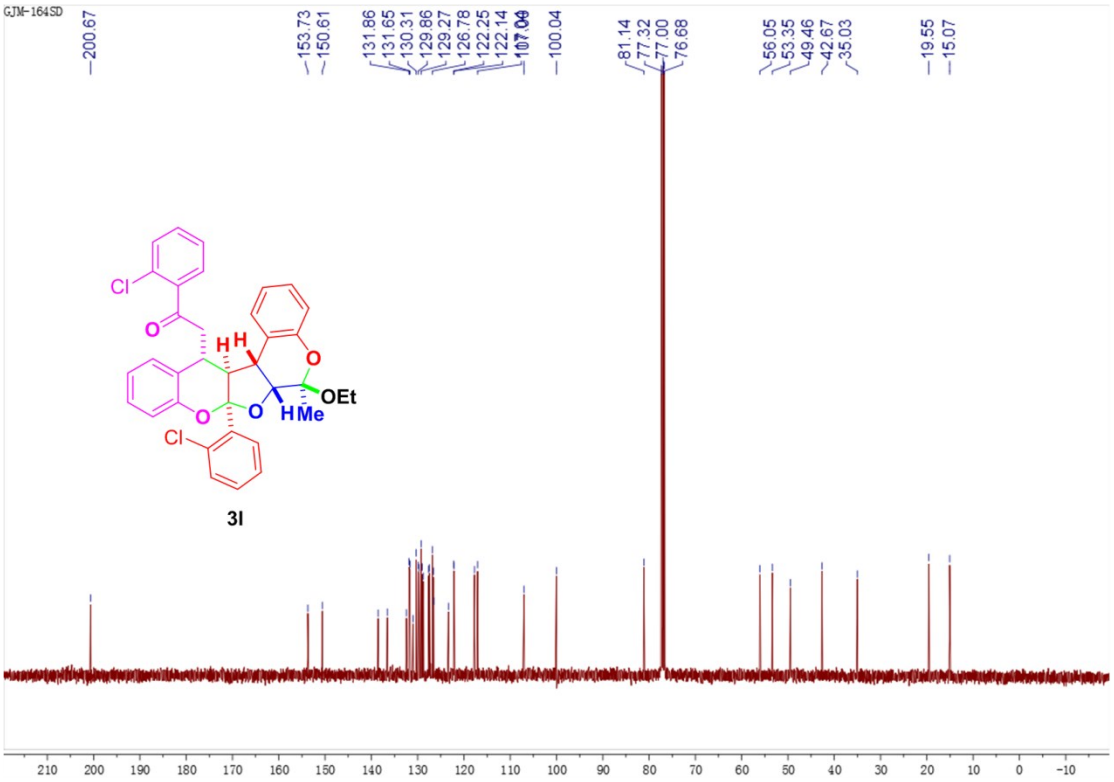
^{13}C NMR spectrum of 3k'



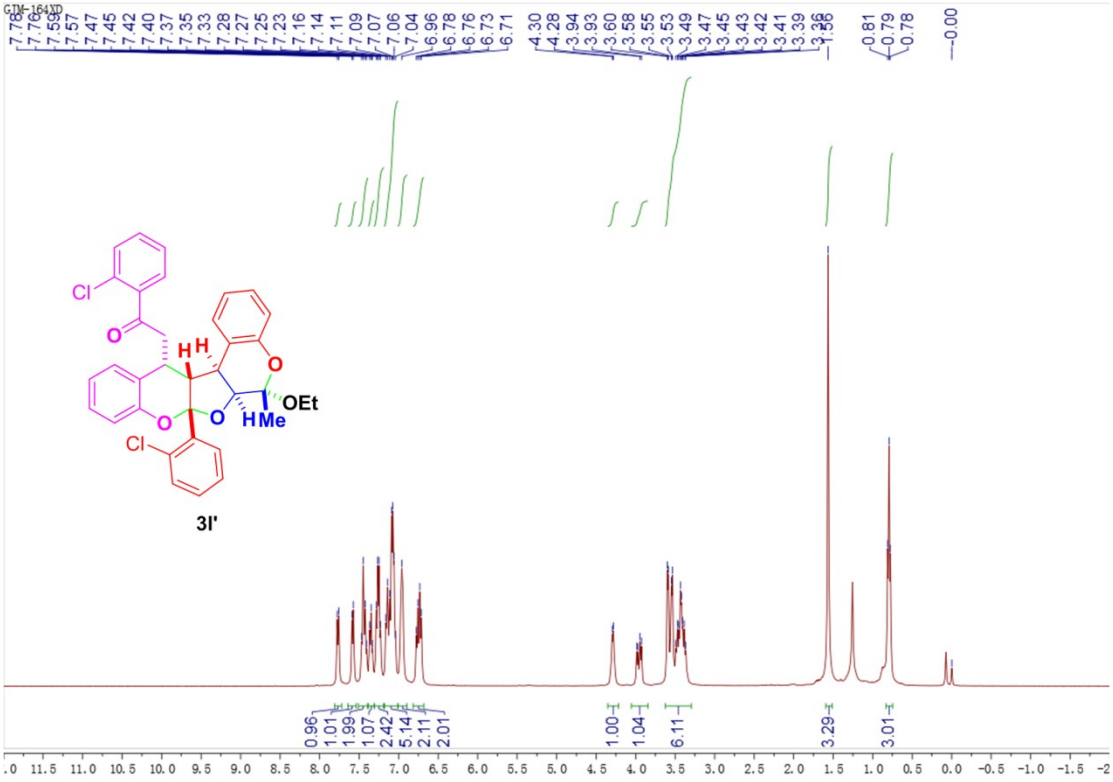
^{1}H NMR spectrum of 3l



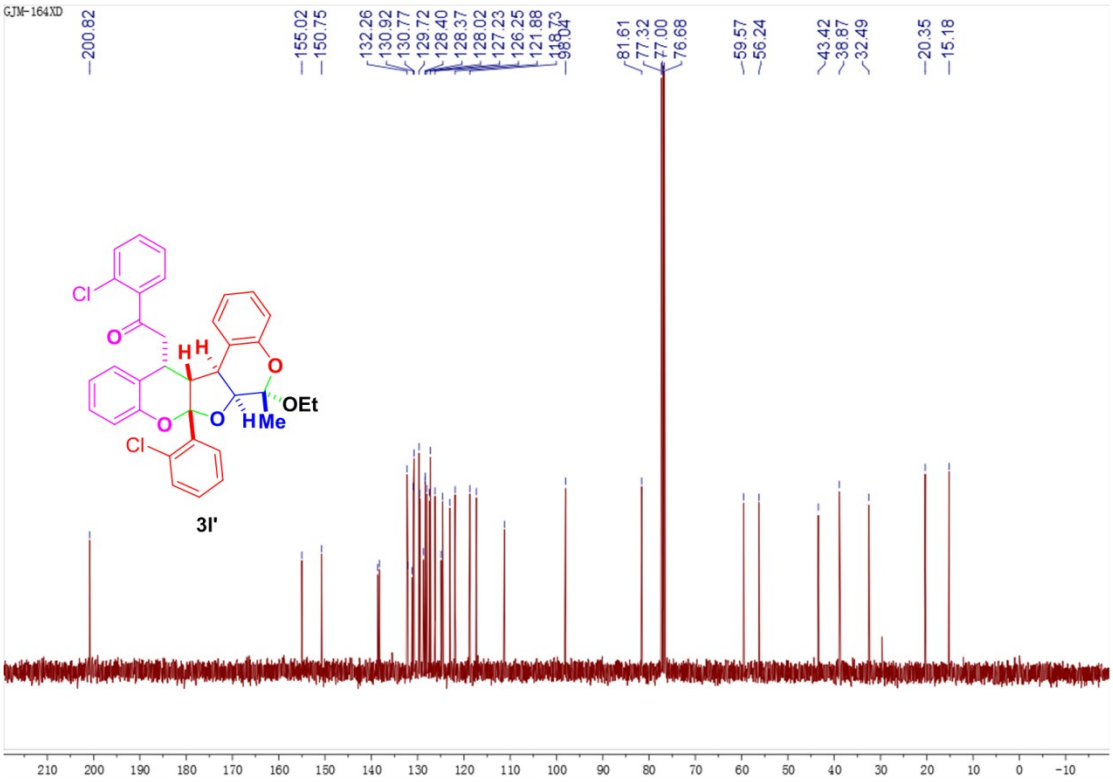
^{13}C NMR spectrum of 3l



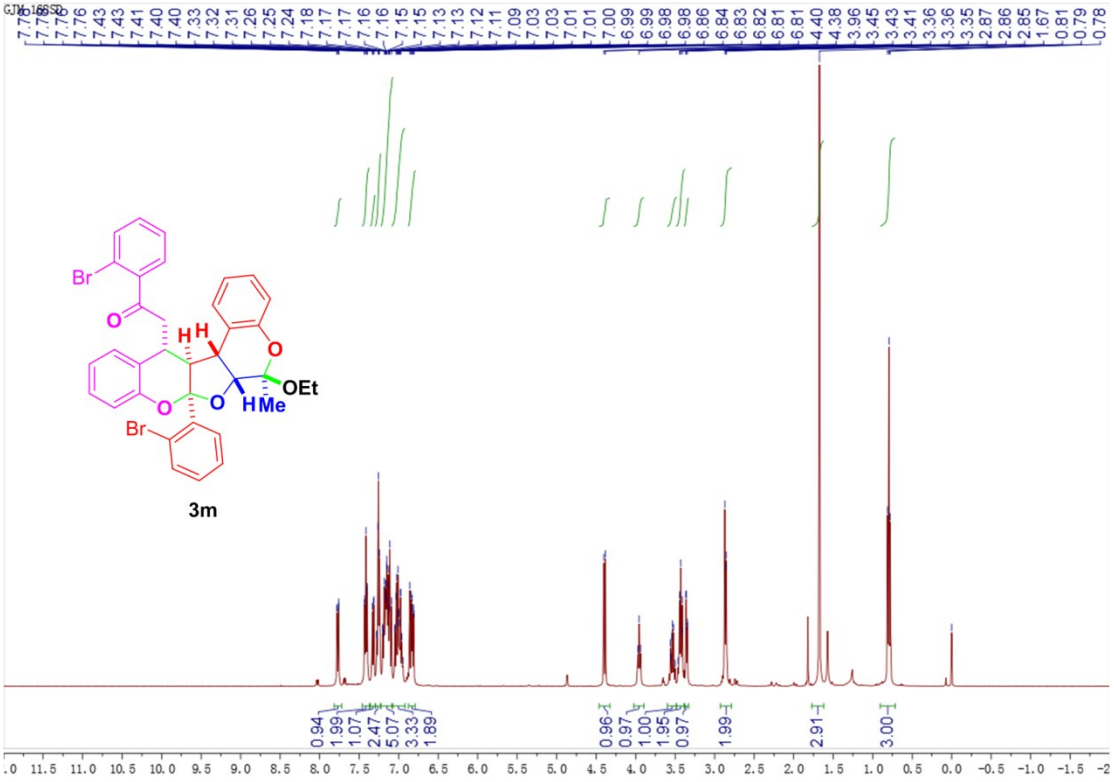
^{1}H NMR spectrum of 3l'



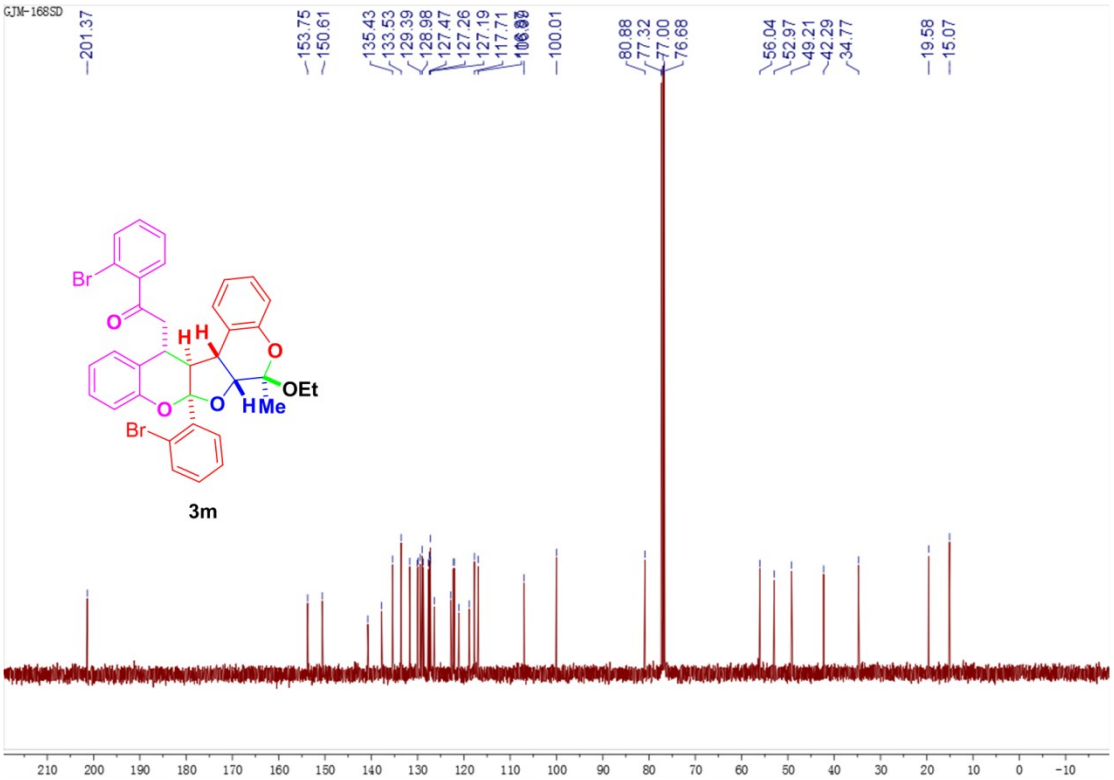
^{13}C NMR spectrum of 3l'



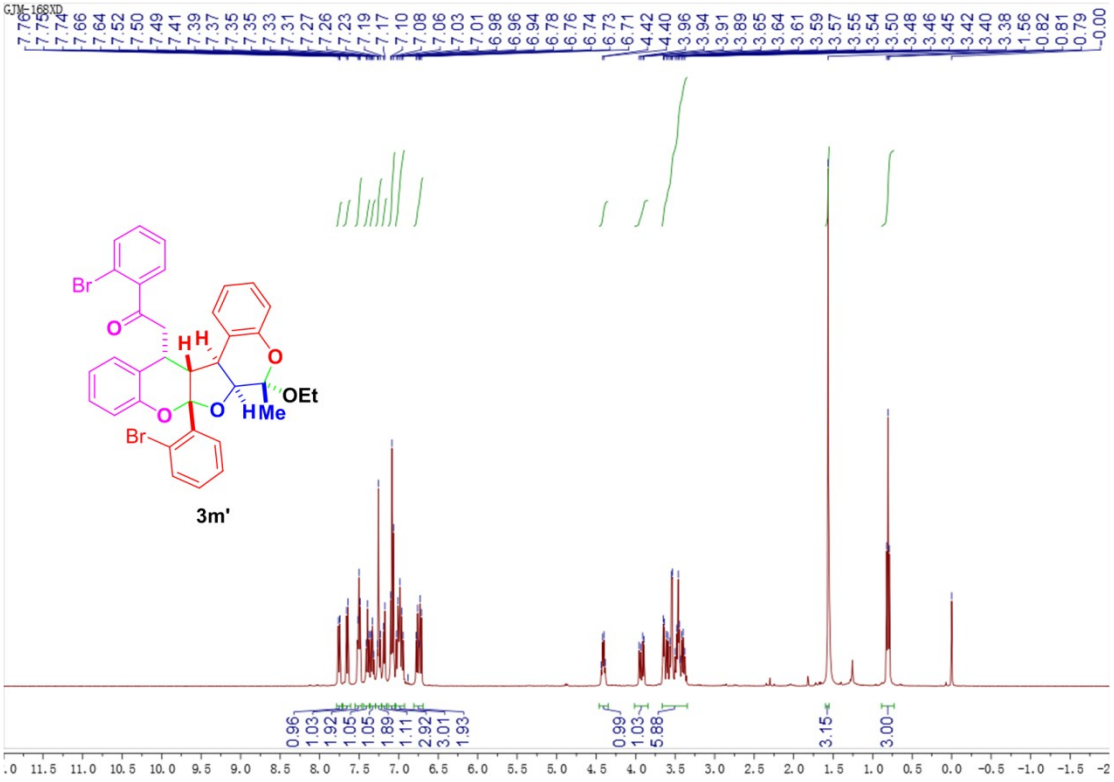
^{1}H NMR spectrum of 3m



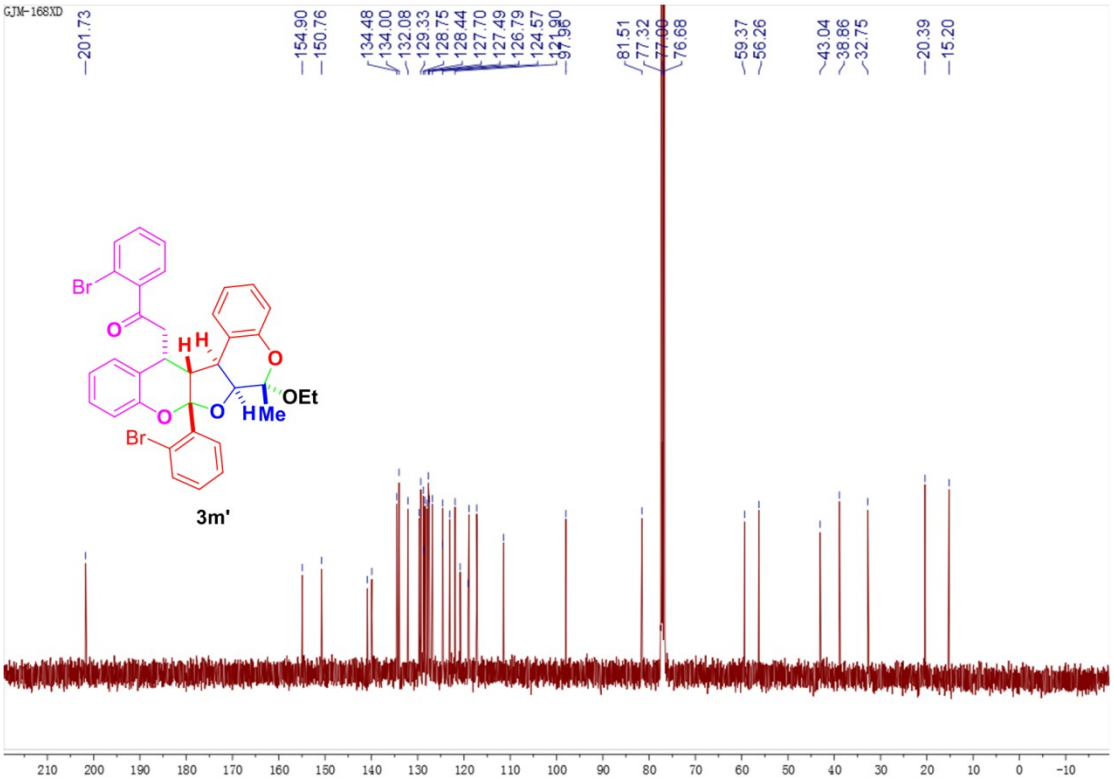
^{13}C NMR spectrum of 3m



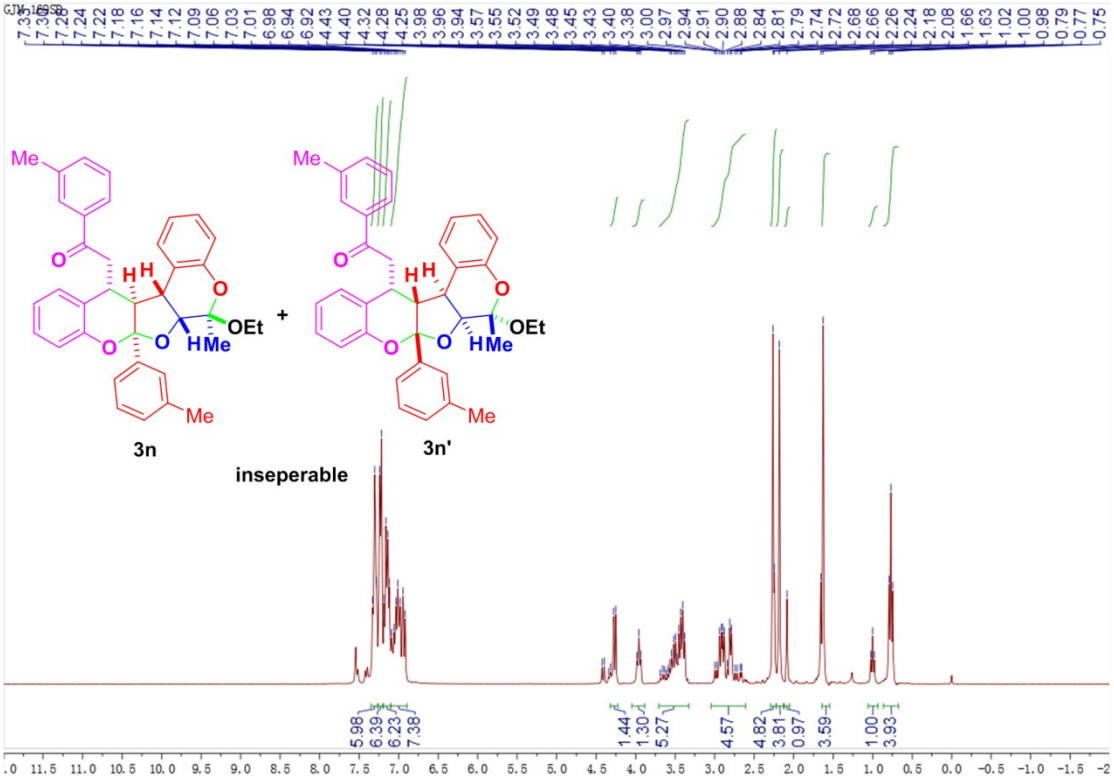
^{1}H NMR spectrum of 3m'



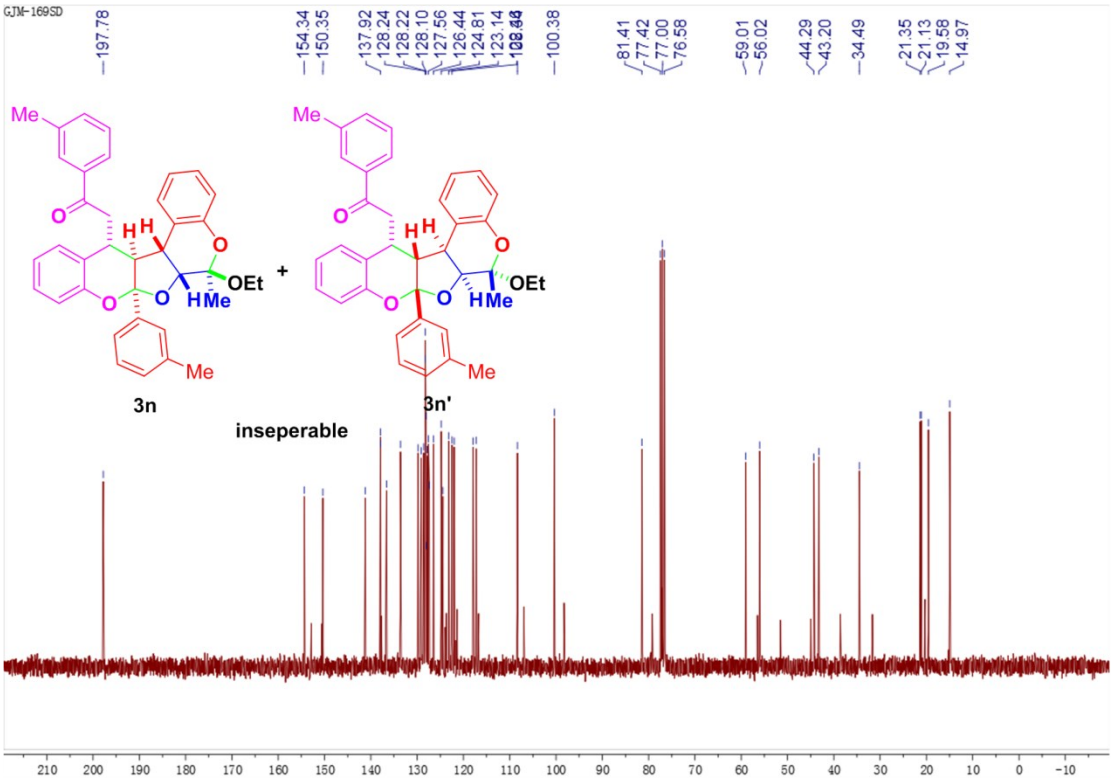
^{13}C NMR spectrum of 3m'



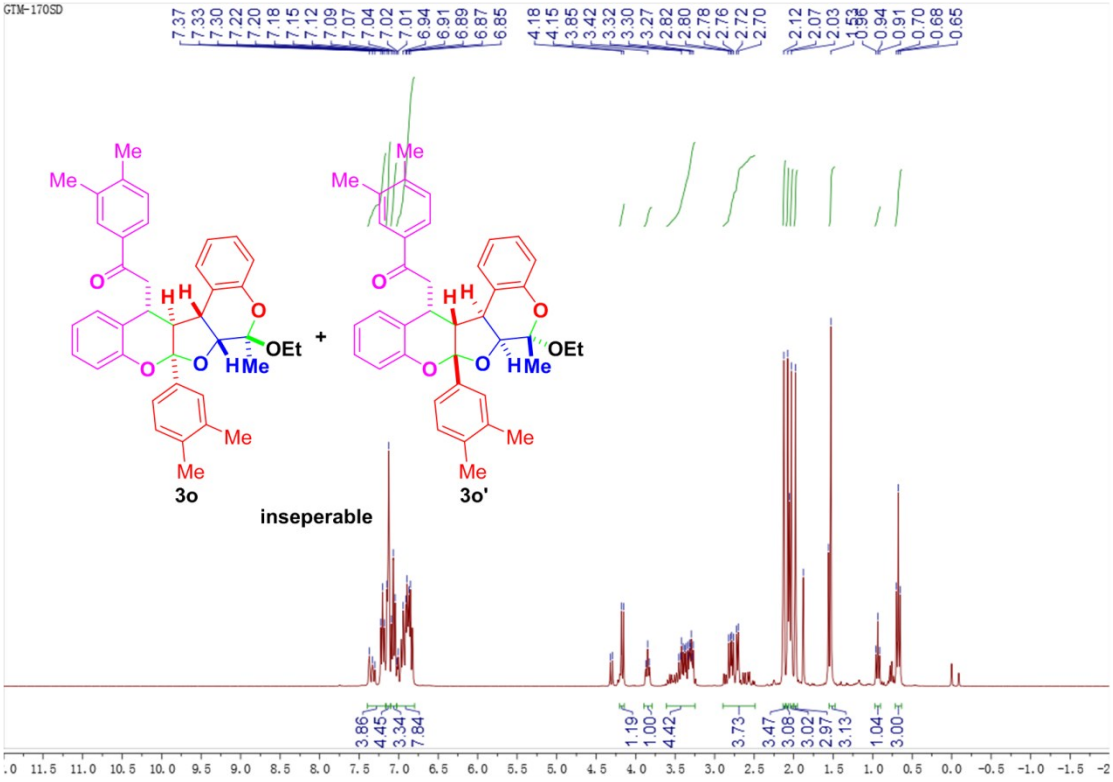
^{1}H NMR spectrum of 3n and 3n'



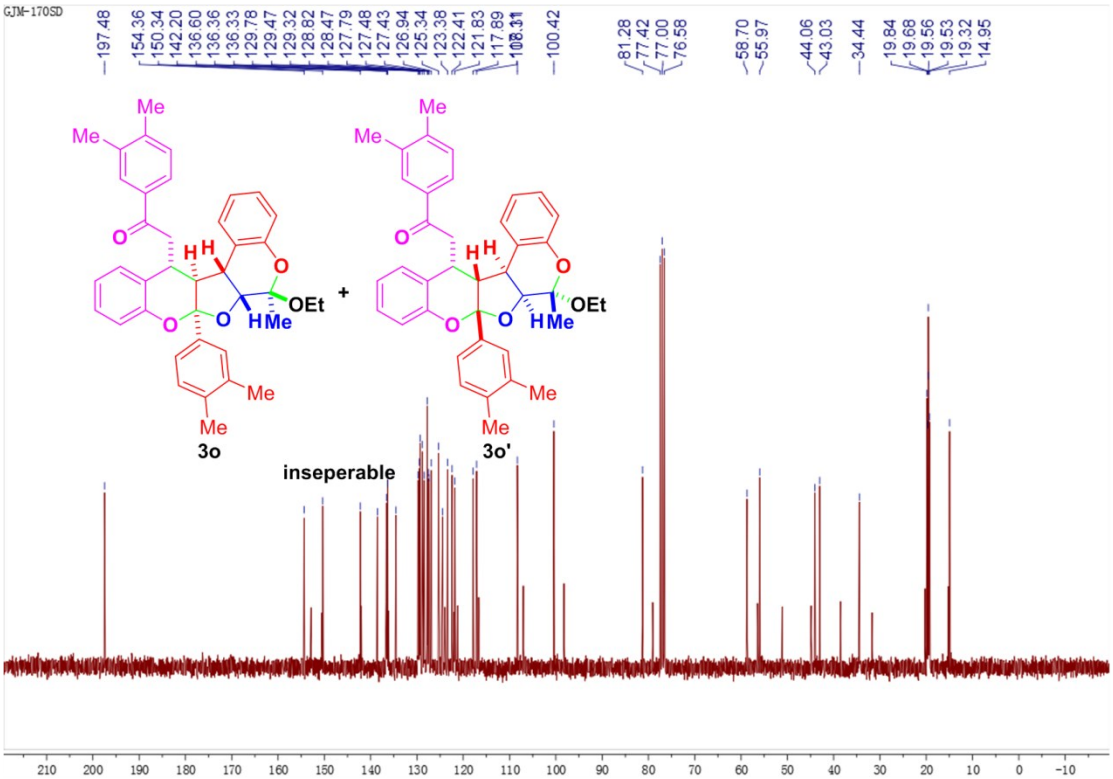
^{13}C NMR spectrum of 3n and 3n'



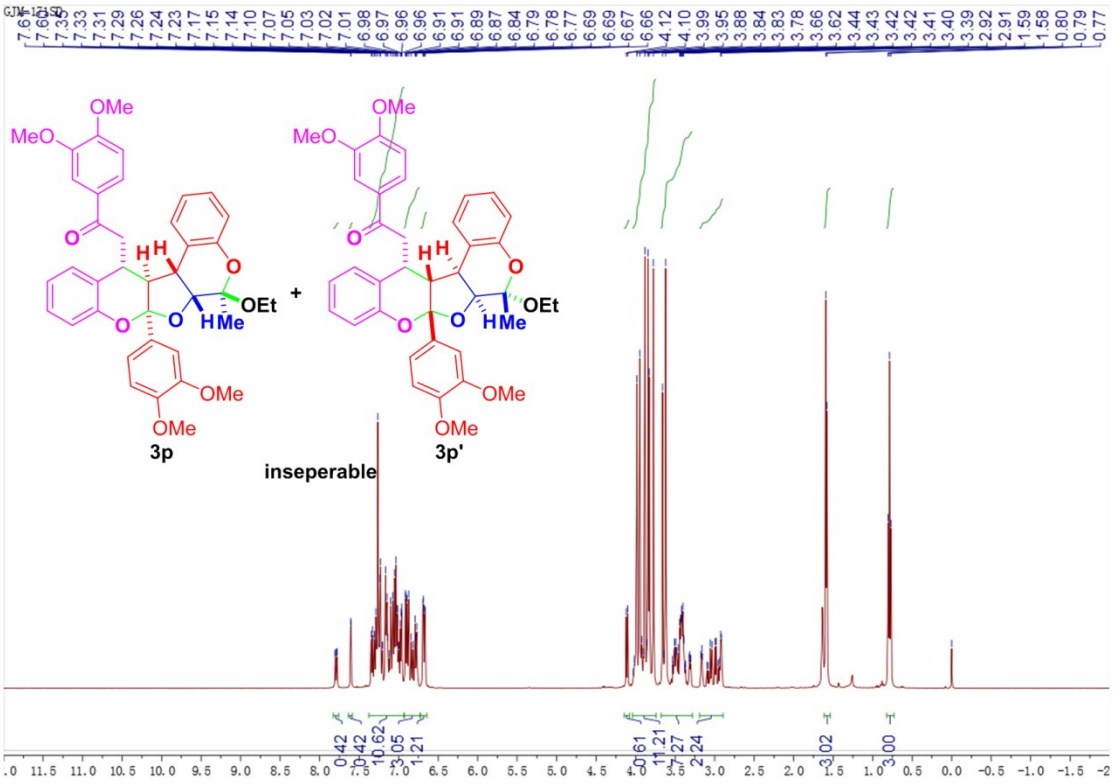
^{1}H NMR spectrum of 3o and 3o'



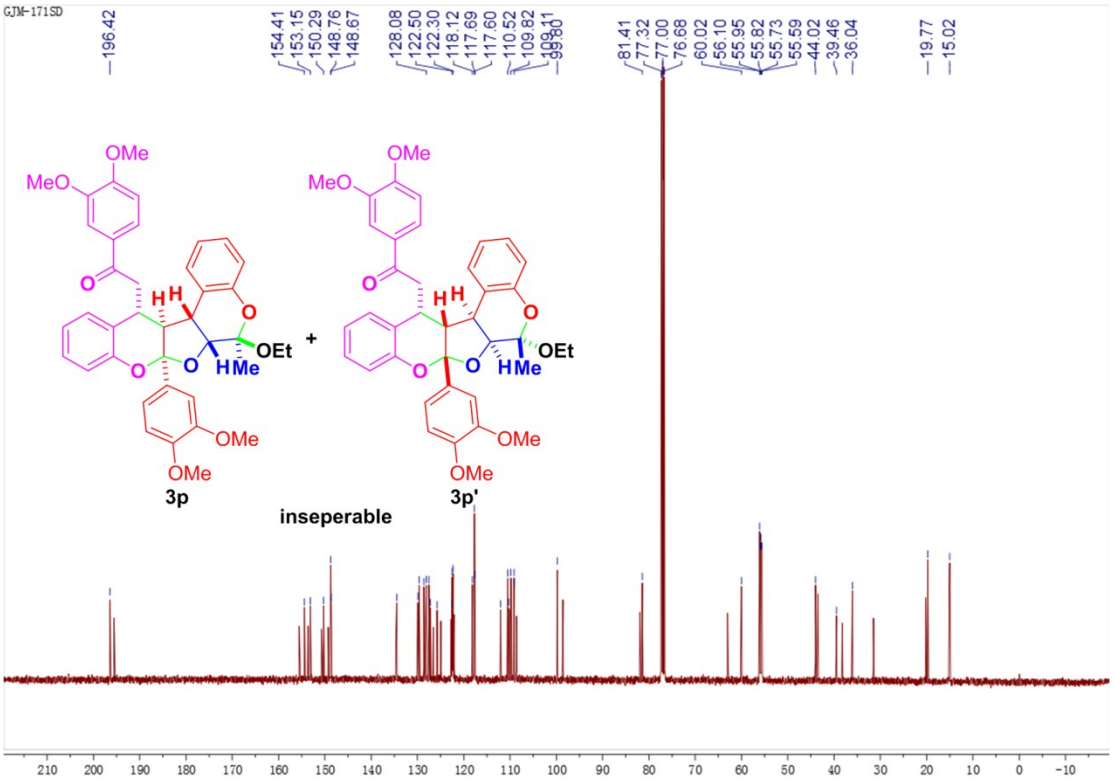
^{13}C NMR spectrum of 3o and 3o'



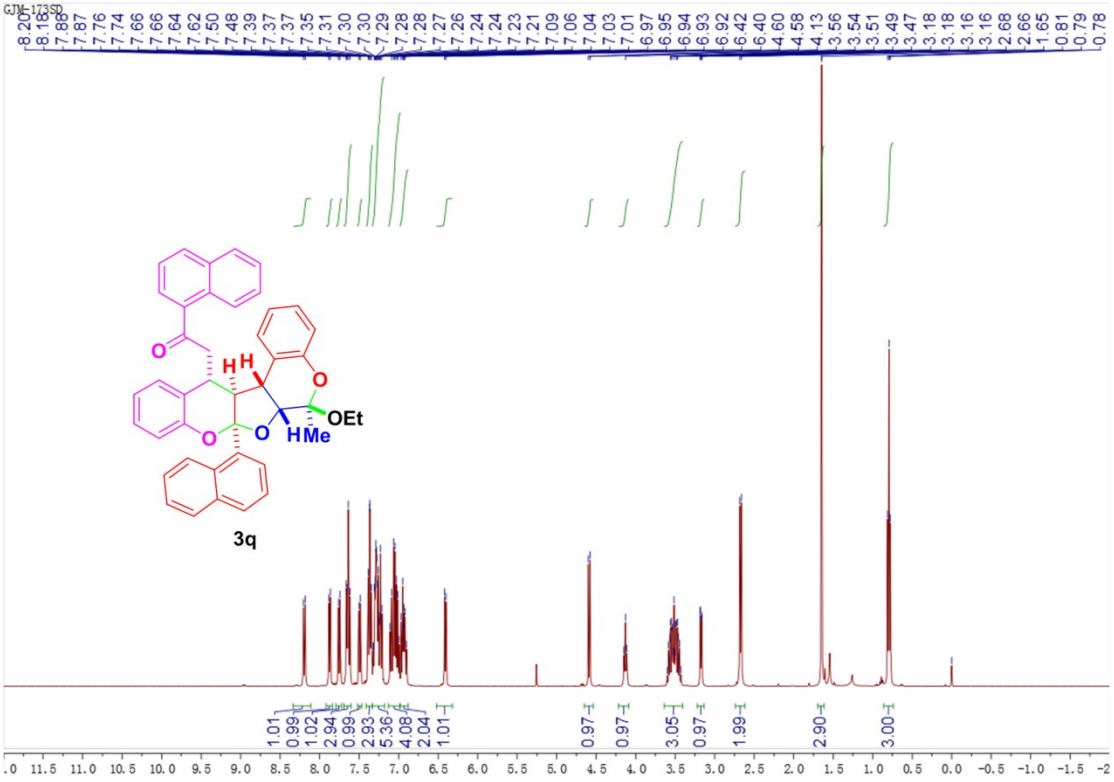
^{1}H NMR spectrum of 3p and 3p'



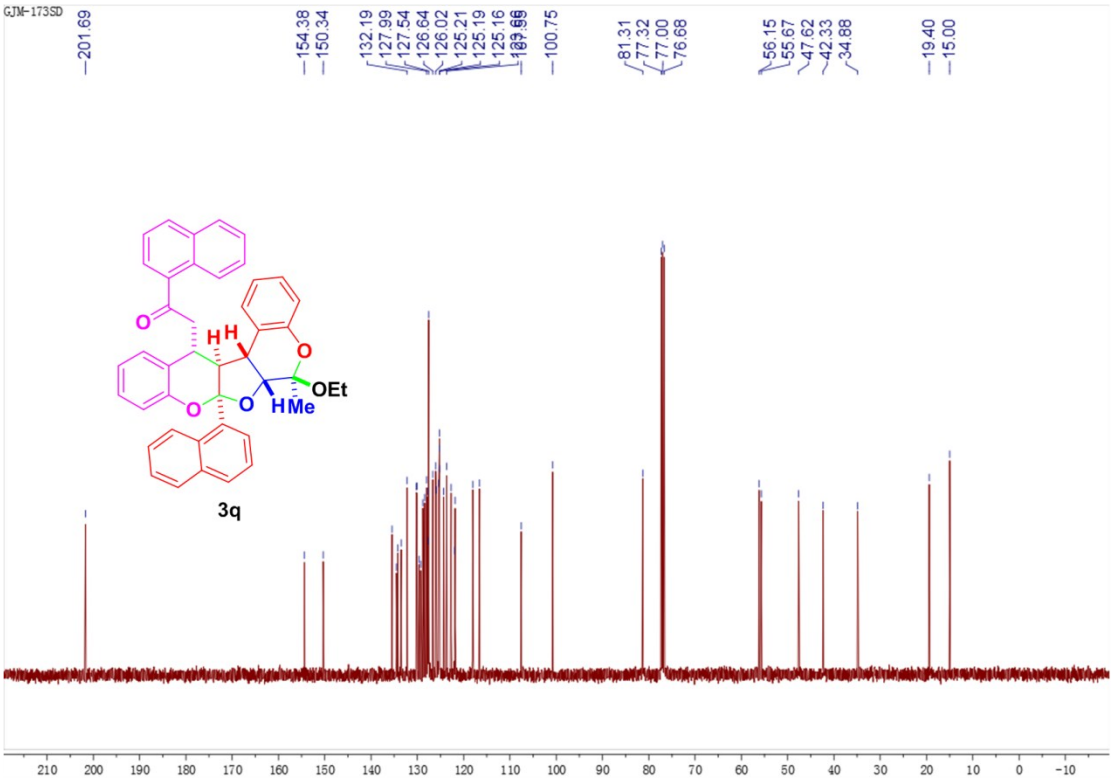
^{13}C NMR spectrum of 3p and 3p'



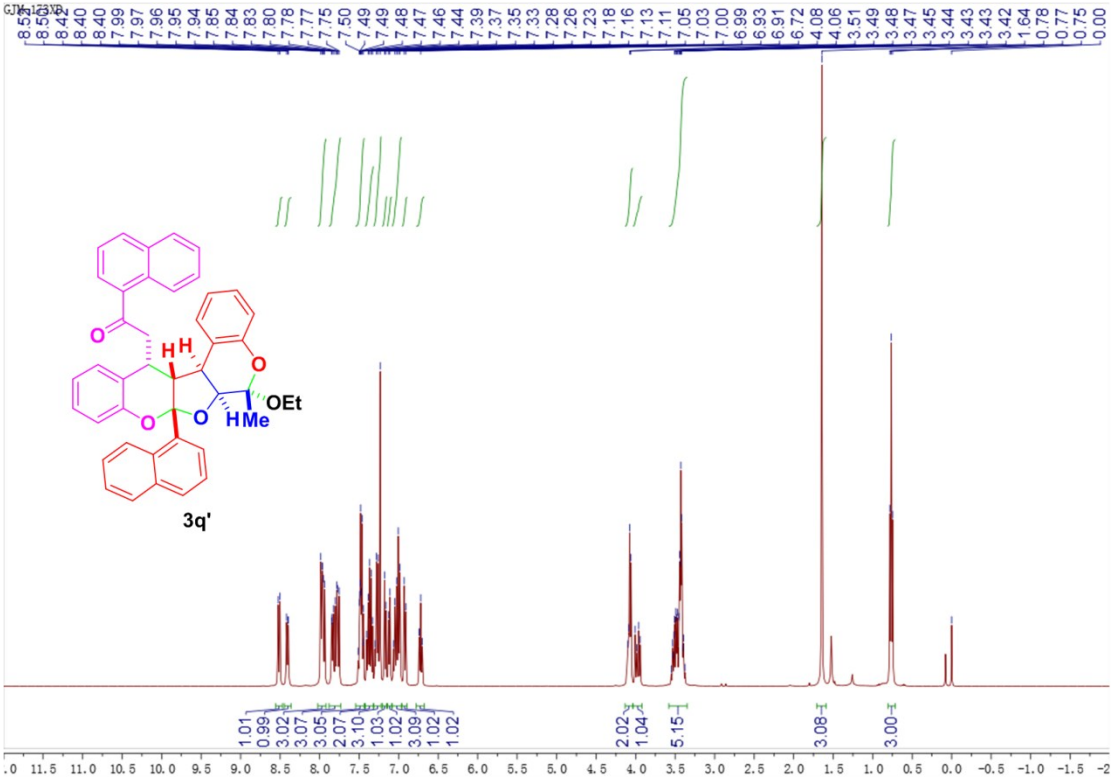
^{1}H NMR spectrum of 3q



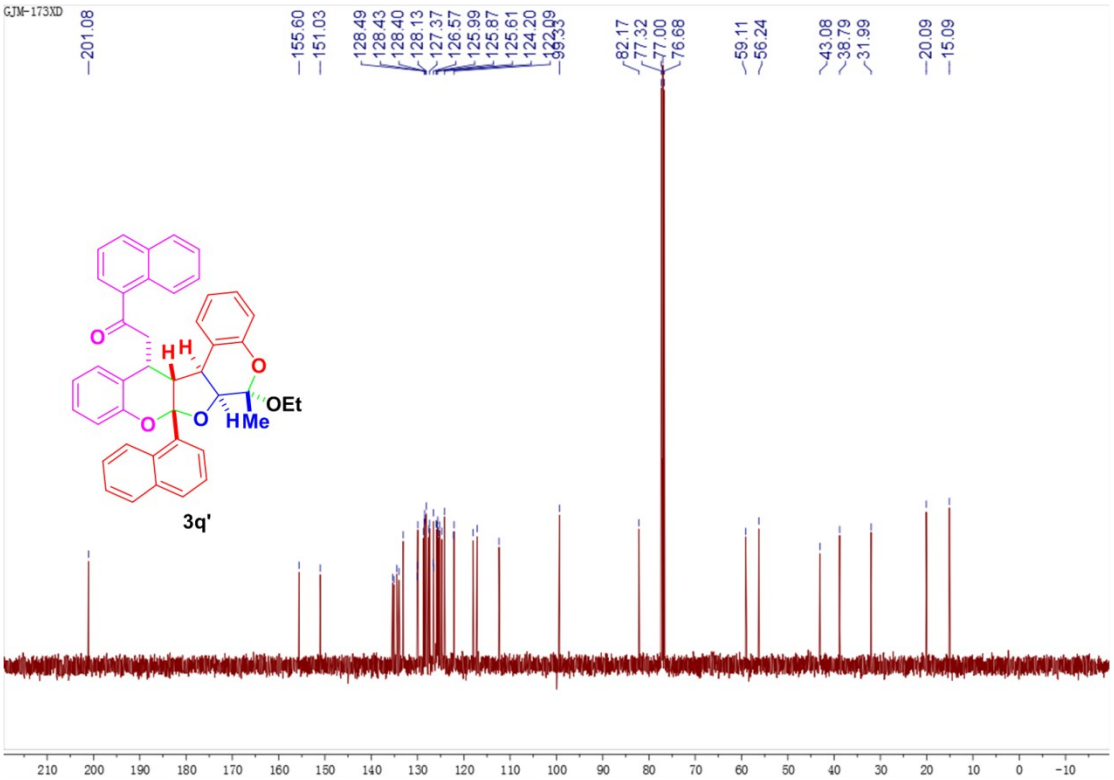
^{13}C NMR spectrum of 3q



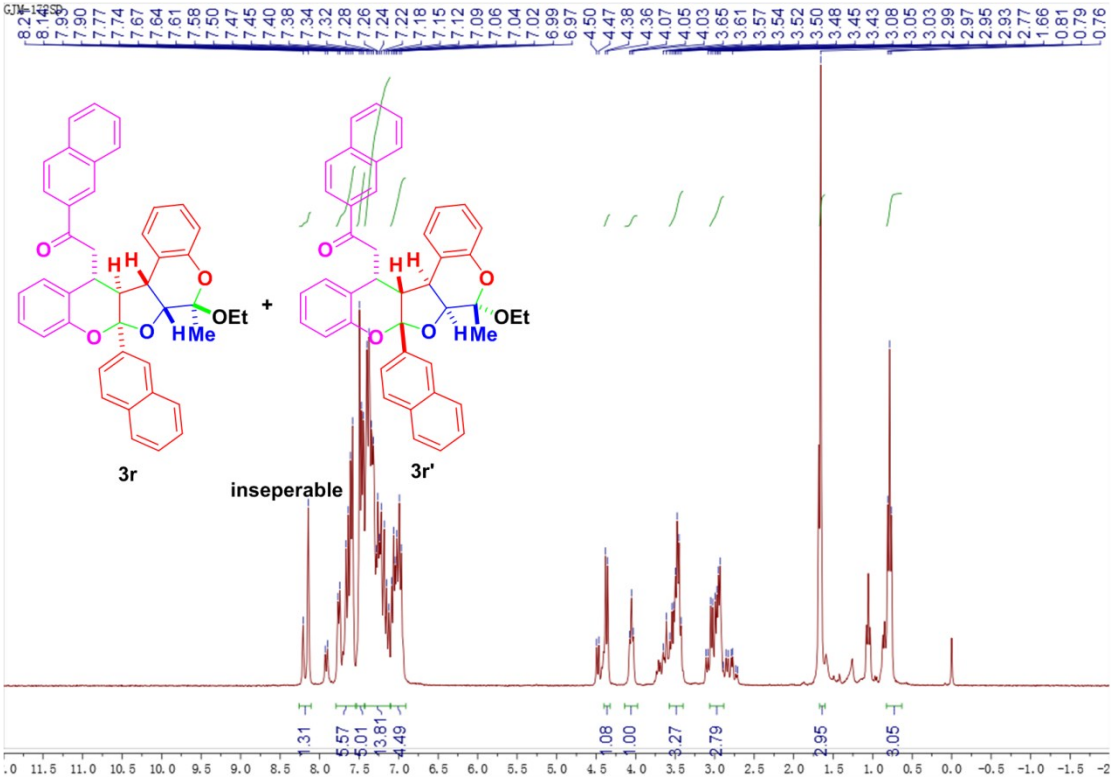
^{1}H NMR spectrum of 3q'



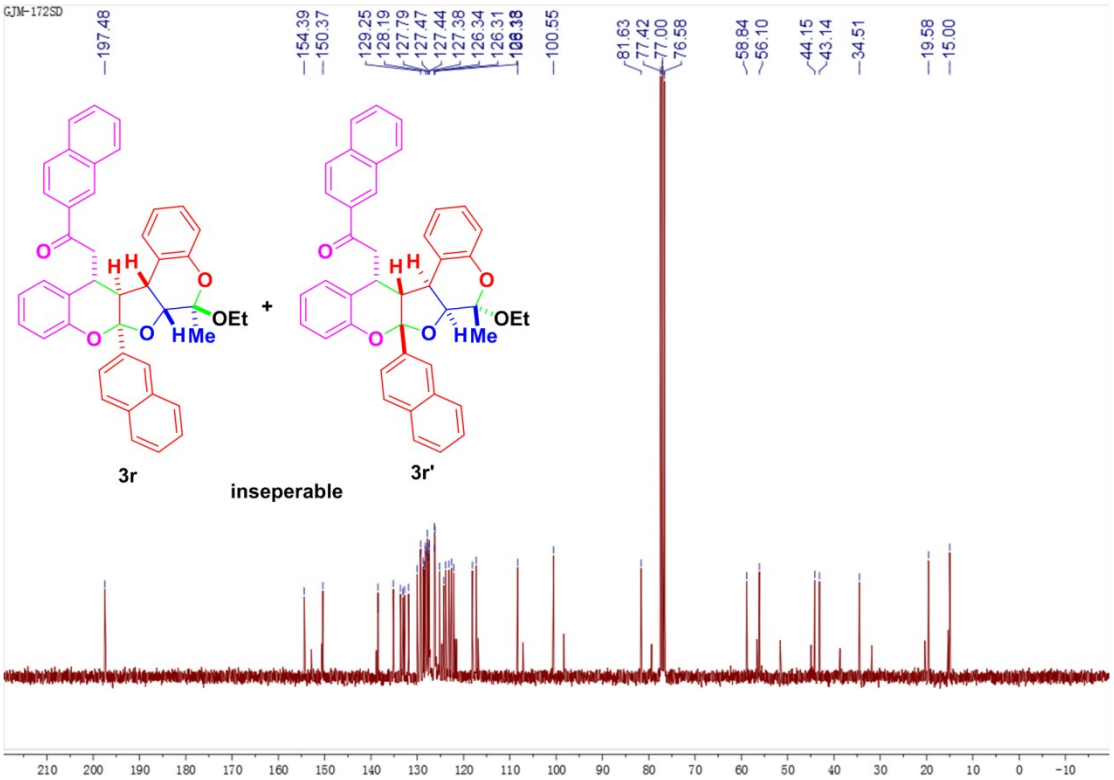
^{13}C NMR spectrum of 3q'



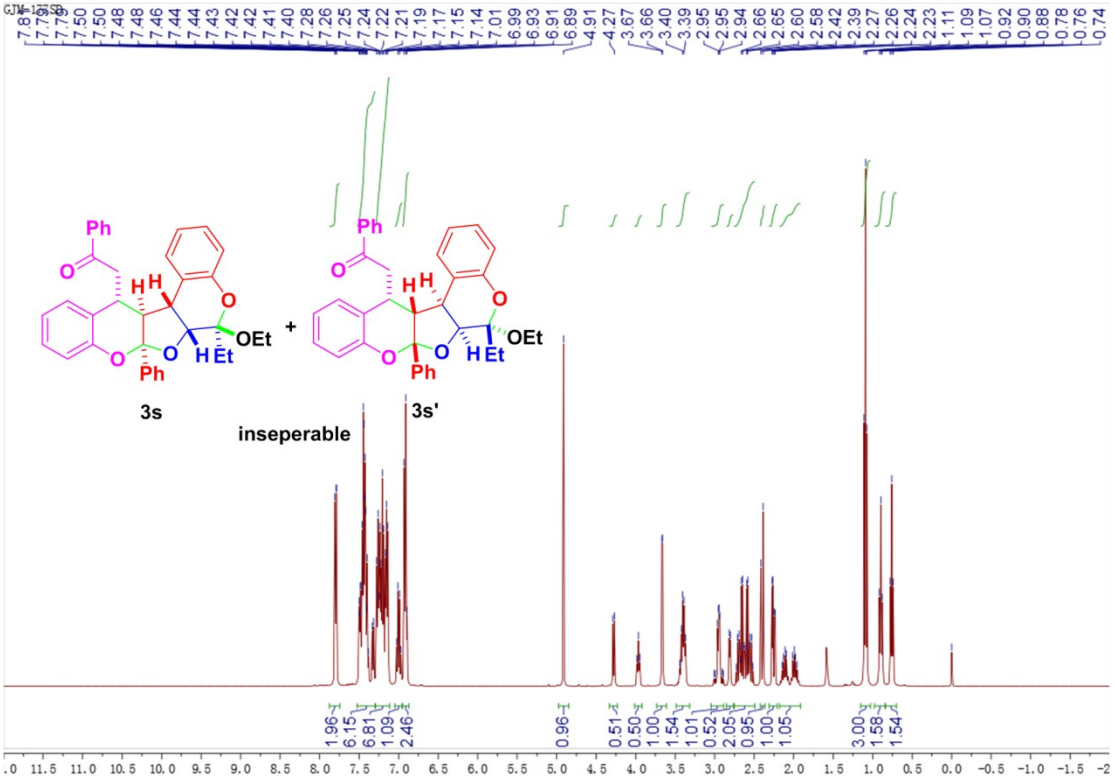
^{1}H NMR spectrum of 3r and 3r'



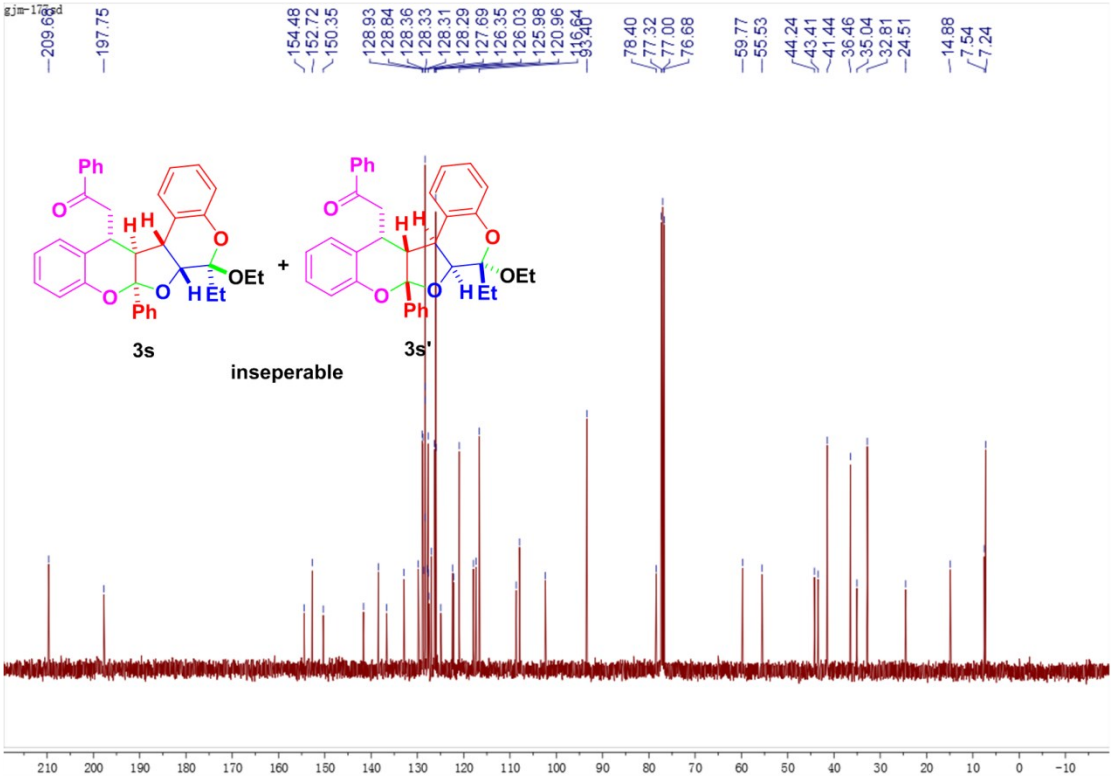
^{13}C NMR spectrum of 3r and 3r'



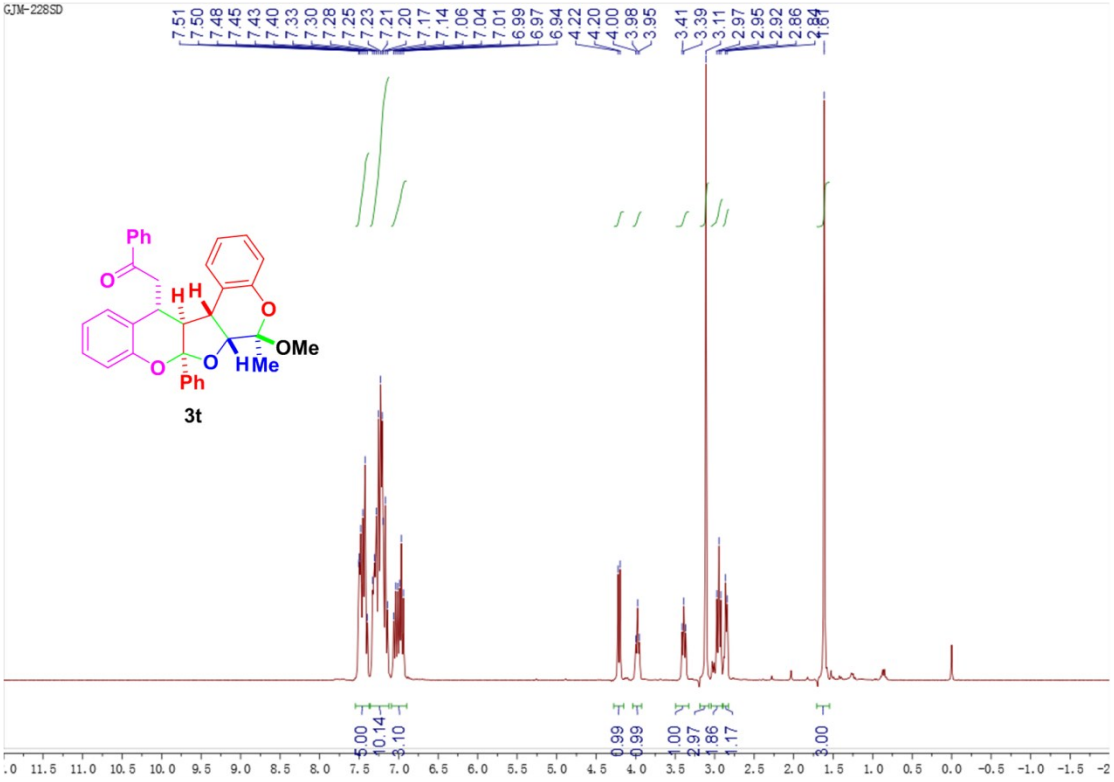
^{1}H NMR spectrum of 3s and 3s'



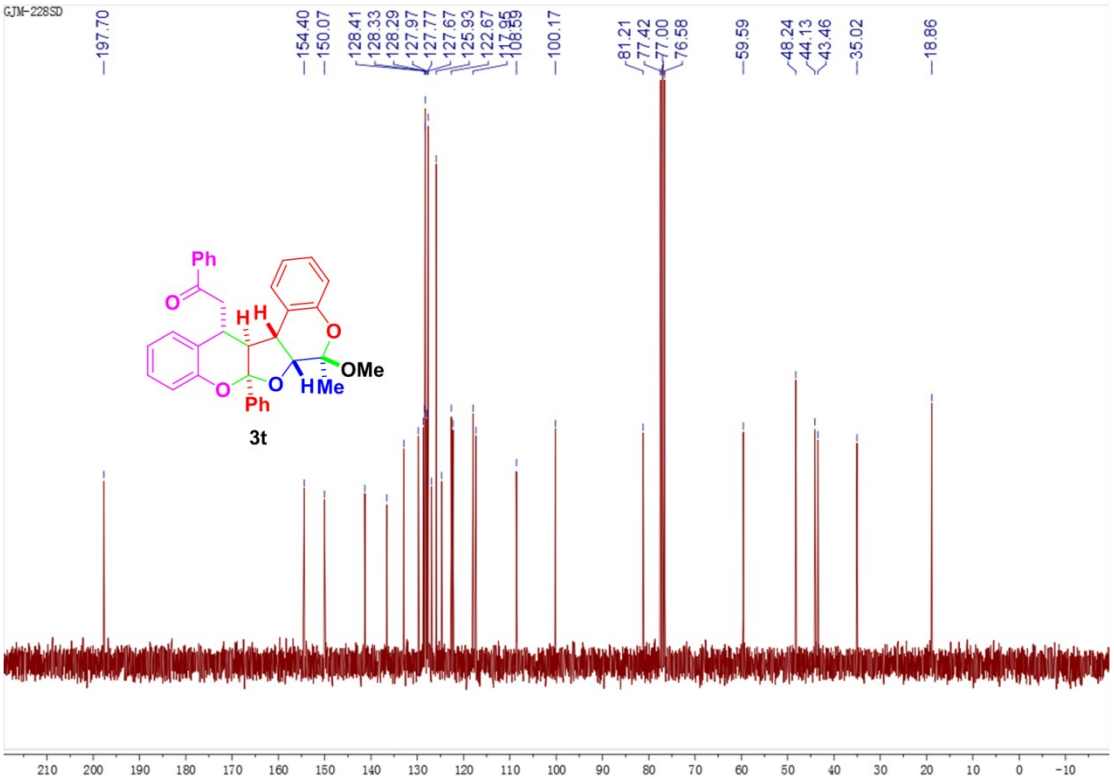
^{13}C NMR spectrum of 3s and 3s'



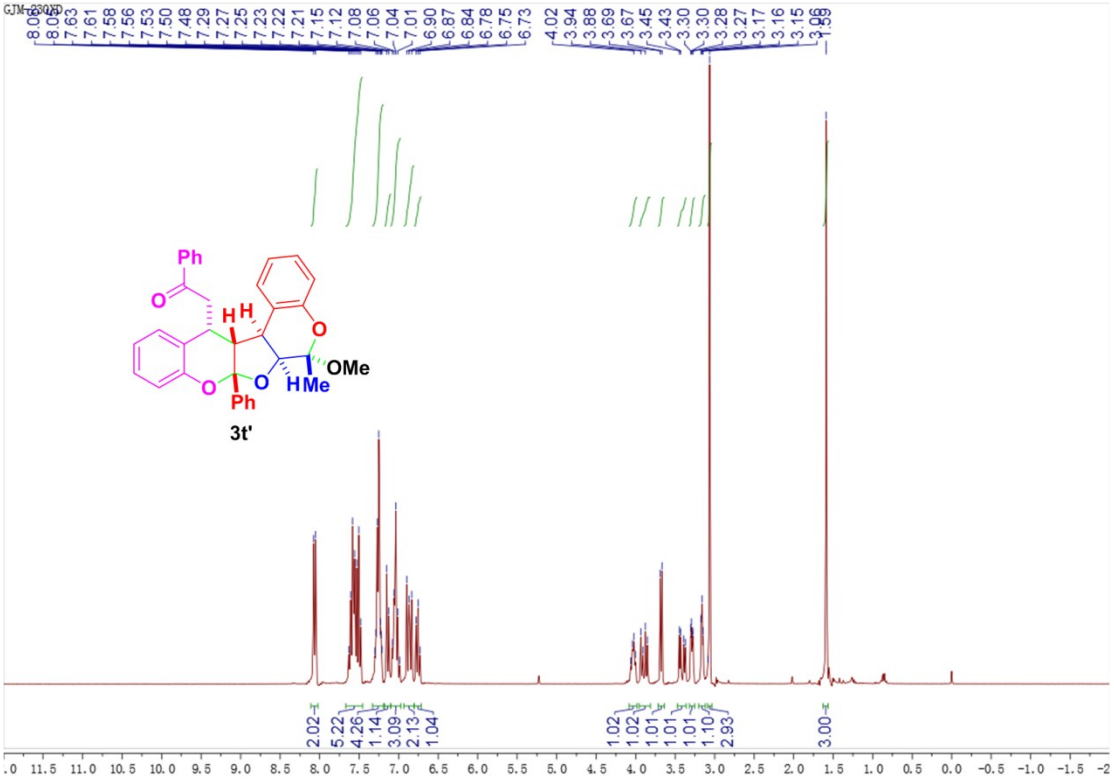
^{1}H NMR spectrum of 3t



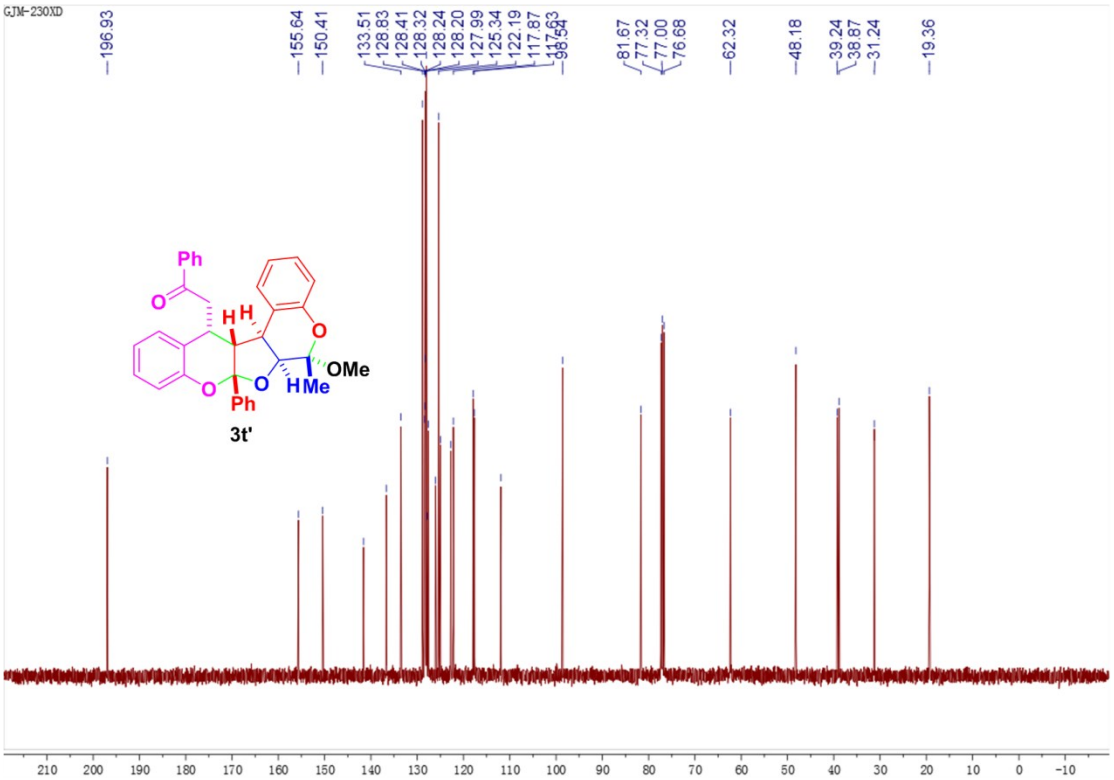
^{13}C NMR spectrum of 3t



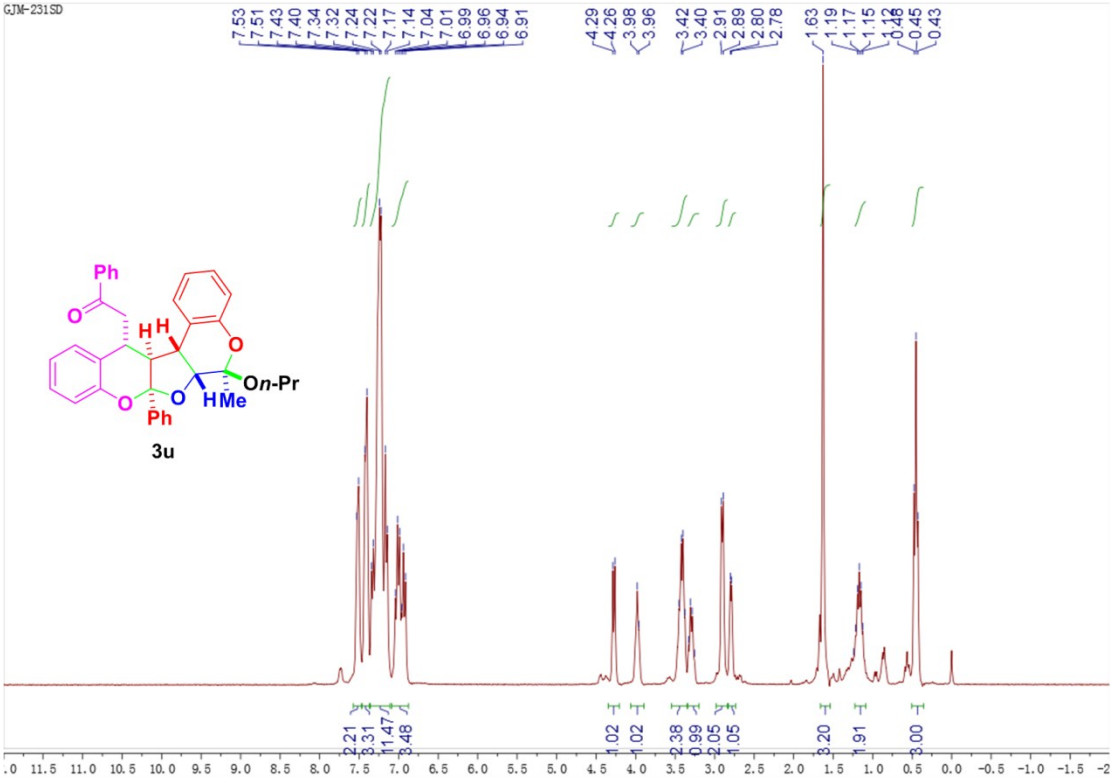
^{1}H NMR spectrum of 3t'



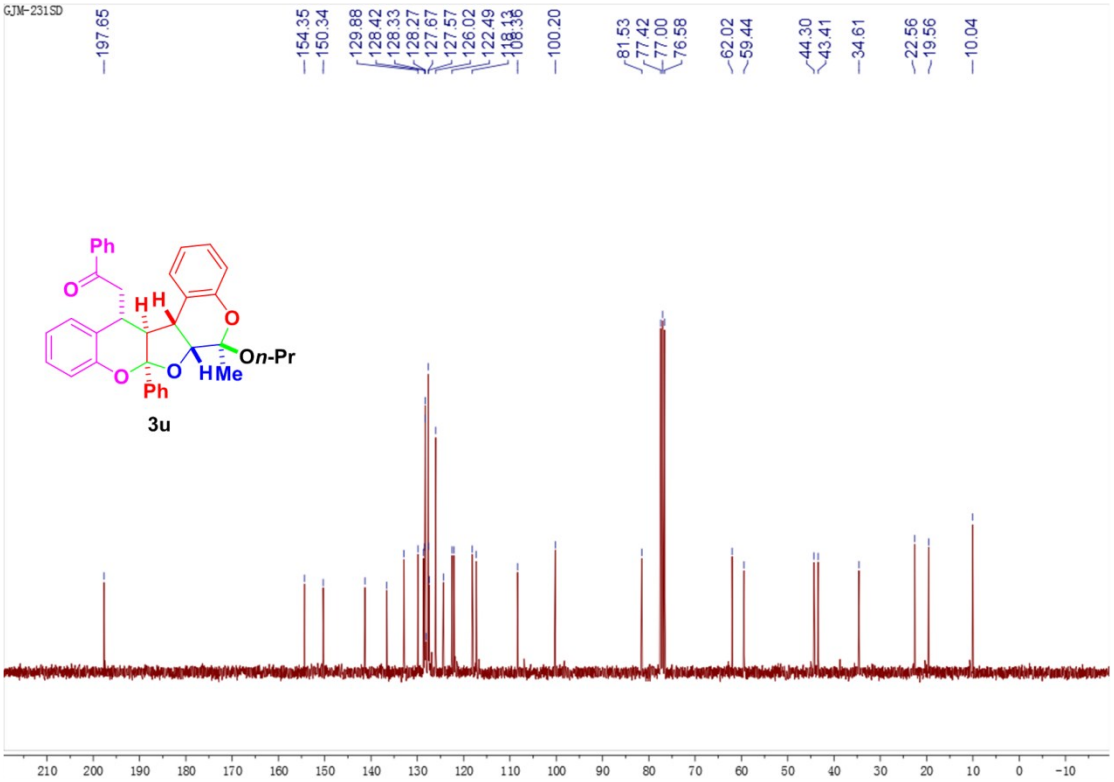
^{13}C NMR spectrum of 3t'



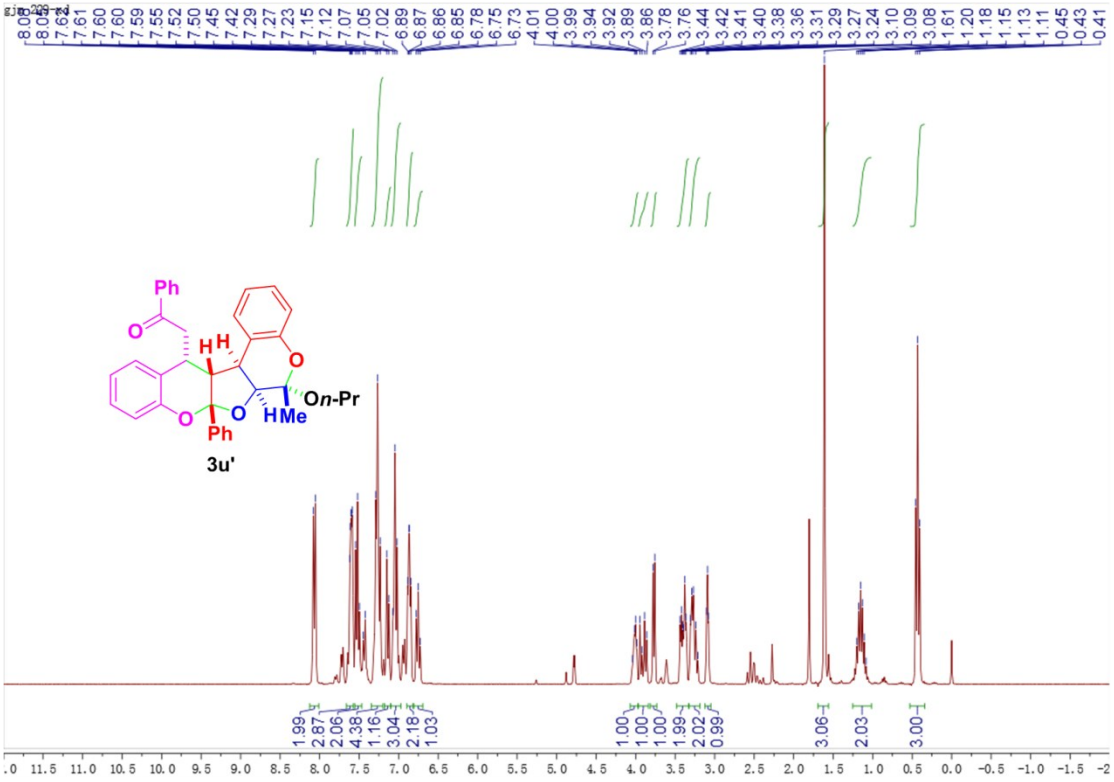
^{1}H NMR spectrum of 3u



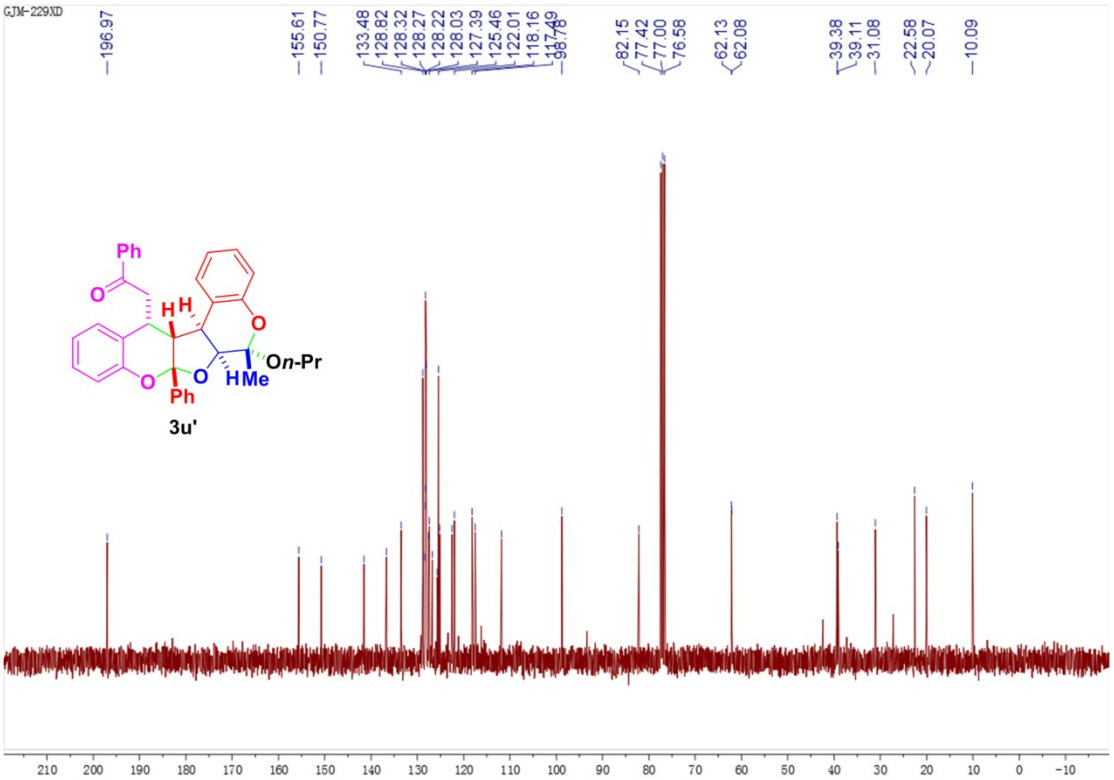
^{13}C NMR spectrum of 3u



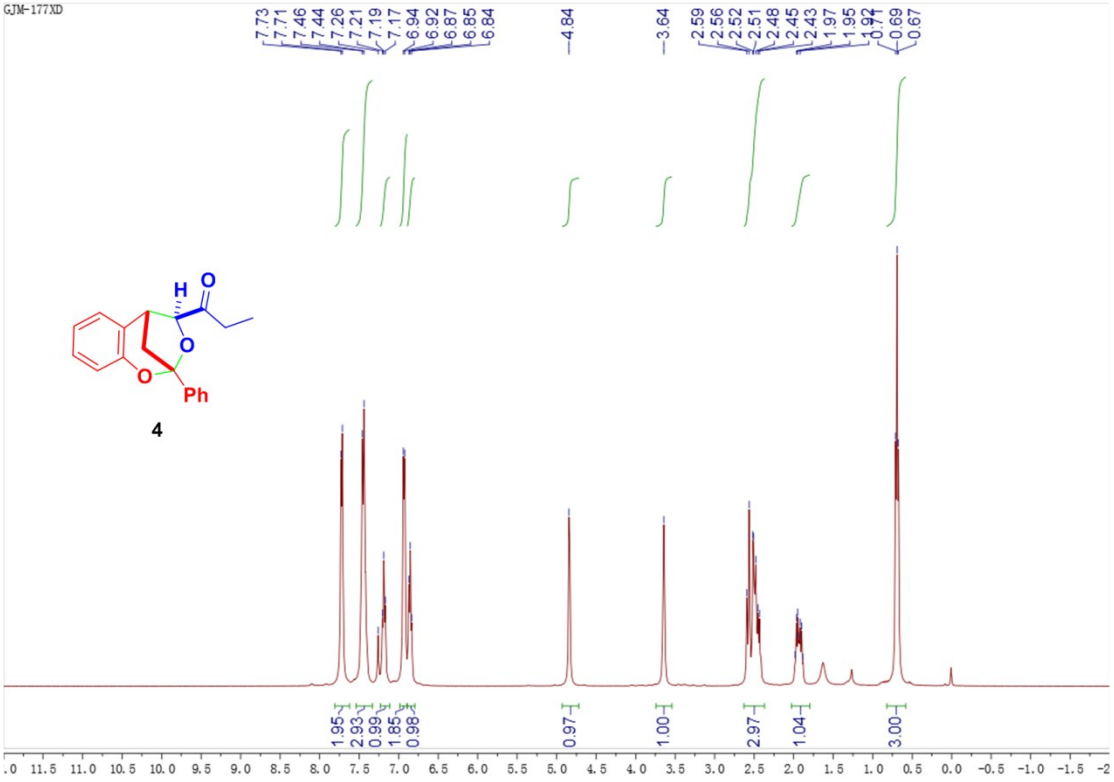
^{1}H NMR spectrum of 3u'



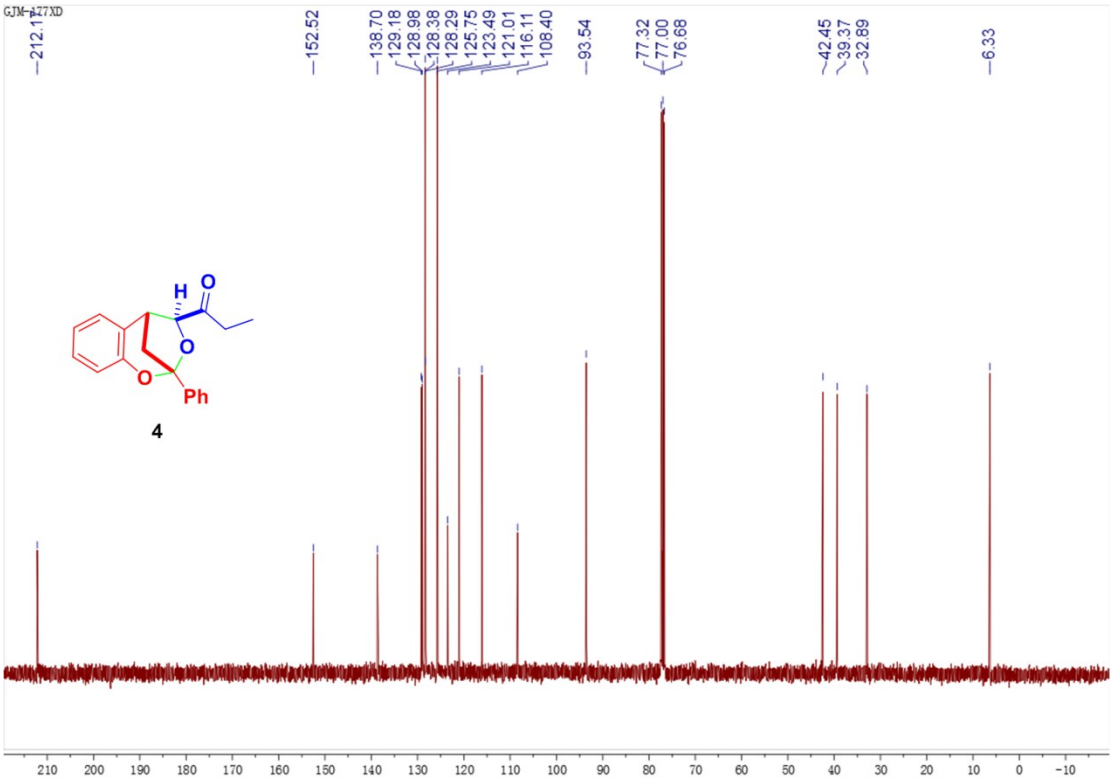
^{13}C NMR spectrum of 3u'



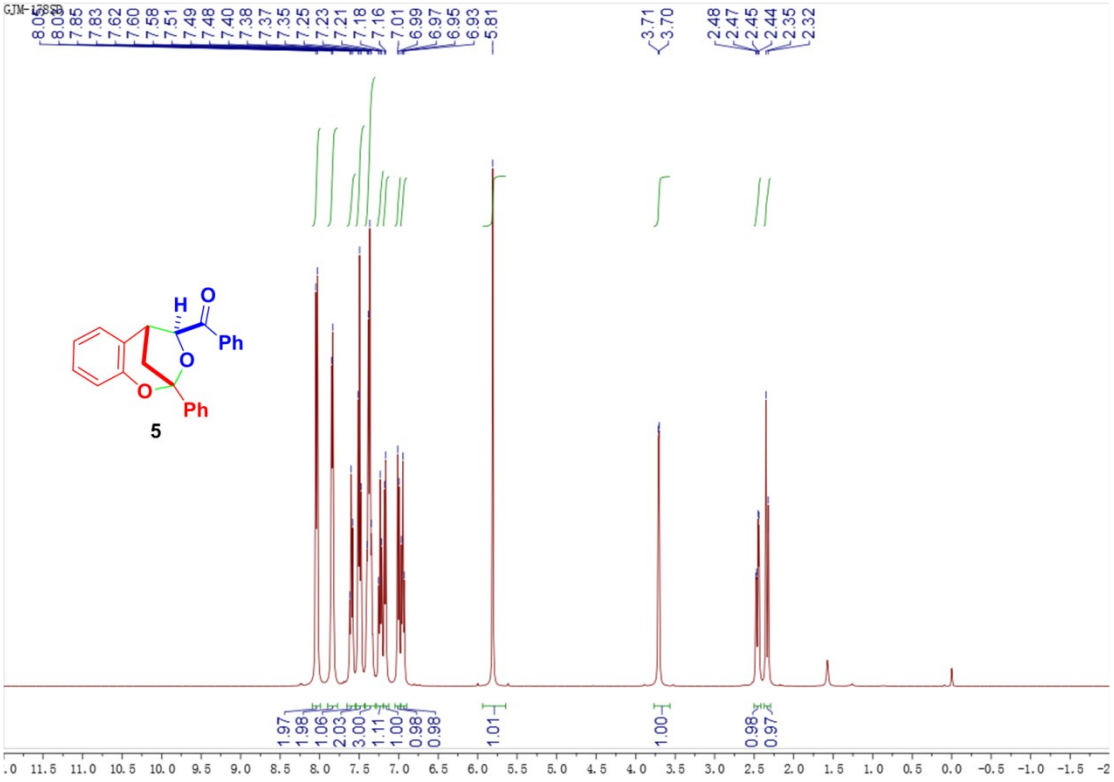
^{1}H NMR spectrum of 4



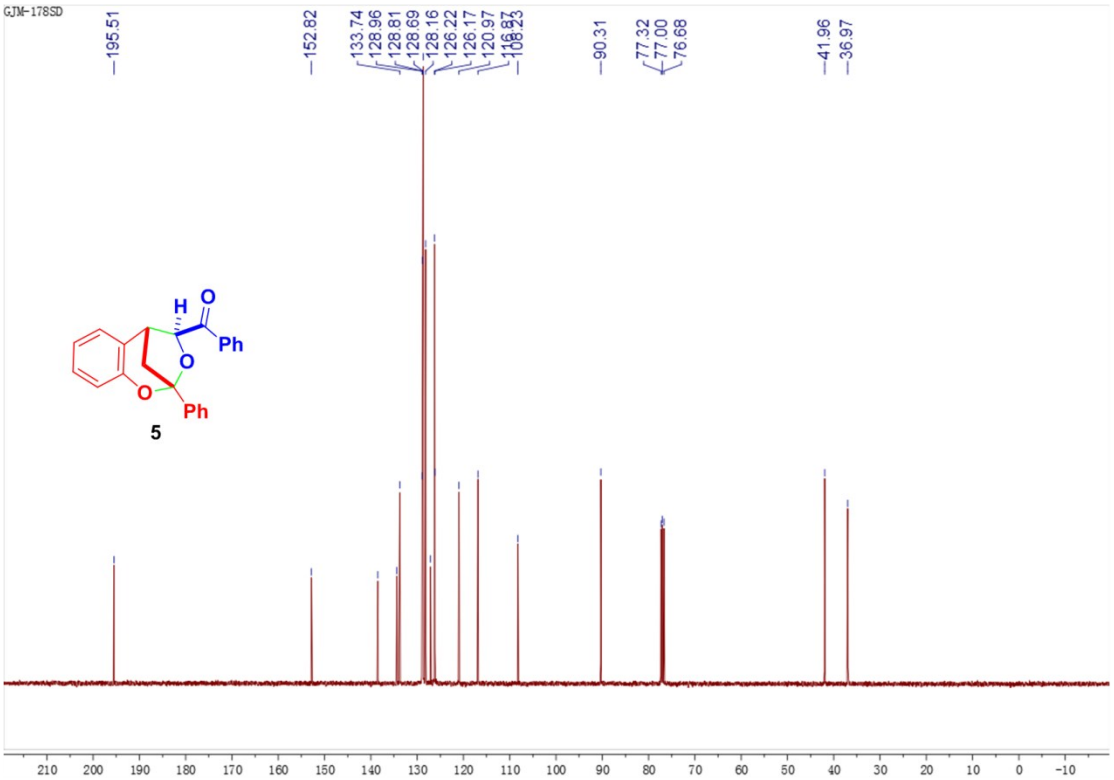
^{13}C NMR spectrum of 4



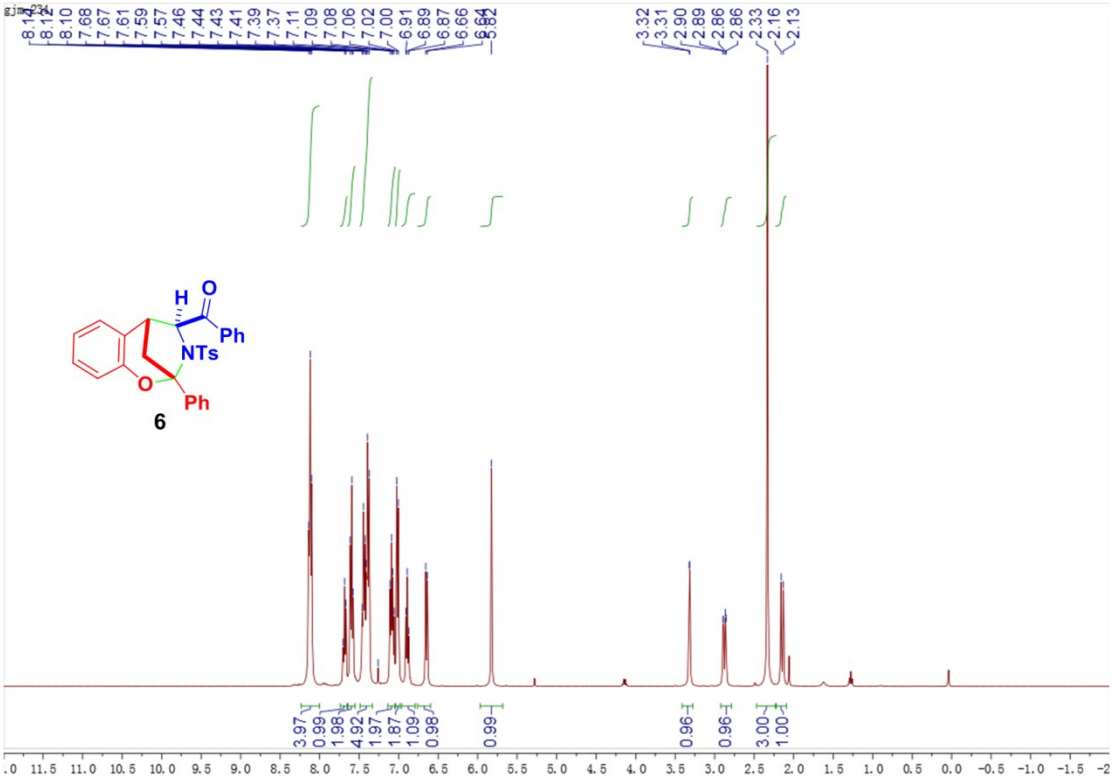
^{1}H NMR spectrum of 5



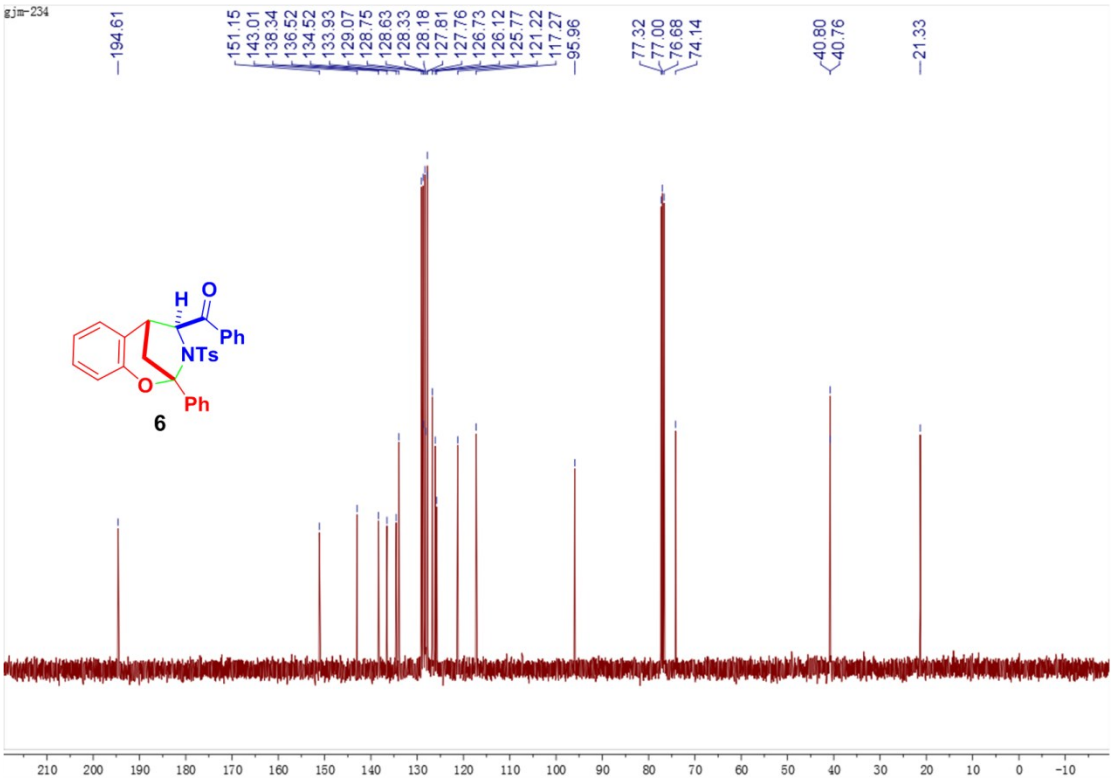
^{13}C NMR spectrum of 5



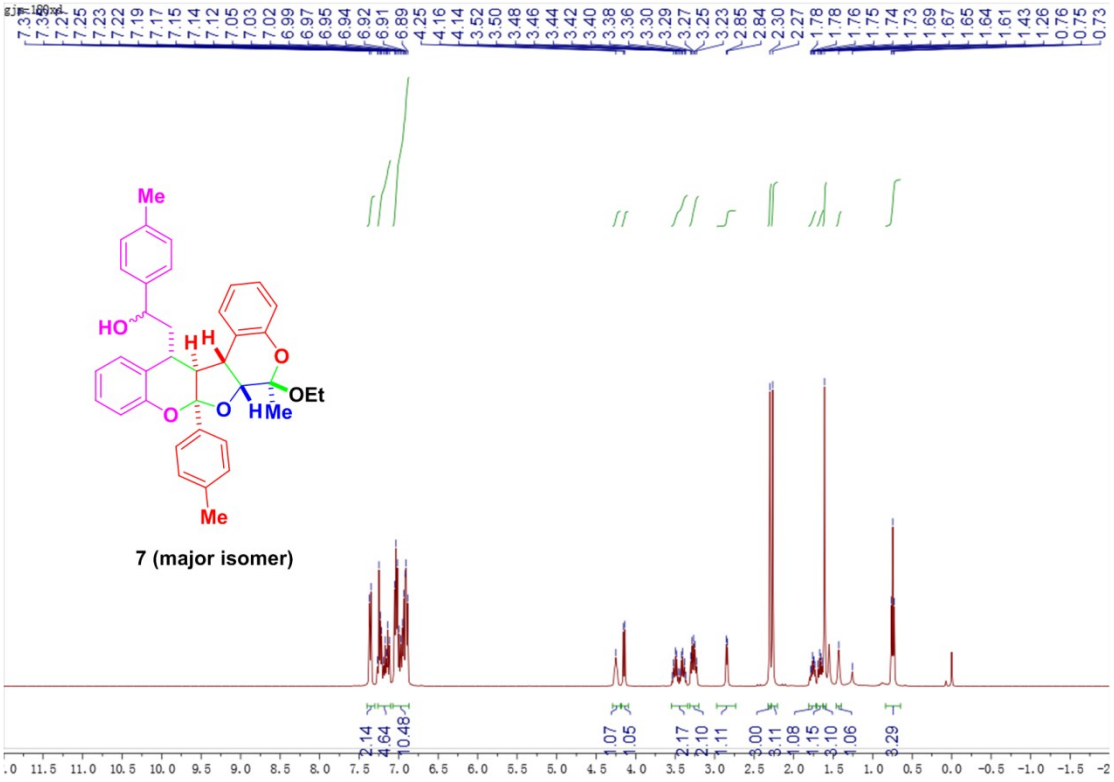
^{1}H NMR spectrum of 6



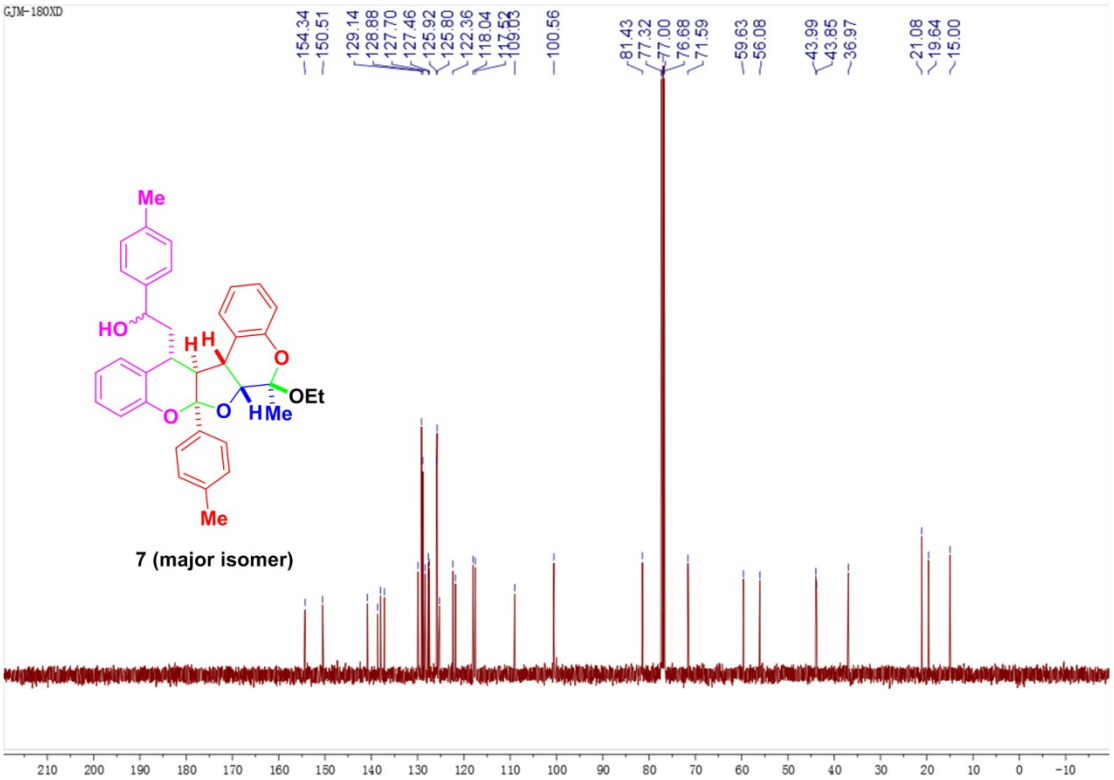
^{13}C NMR spectrum of 6



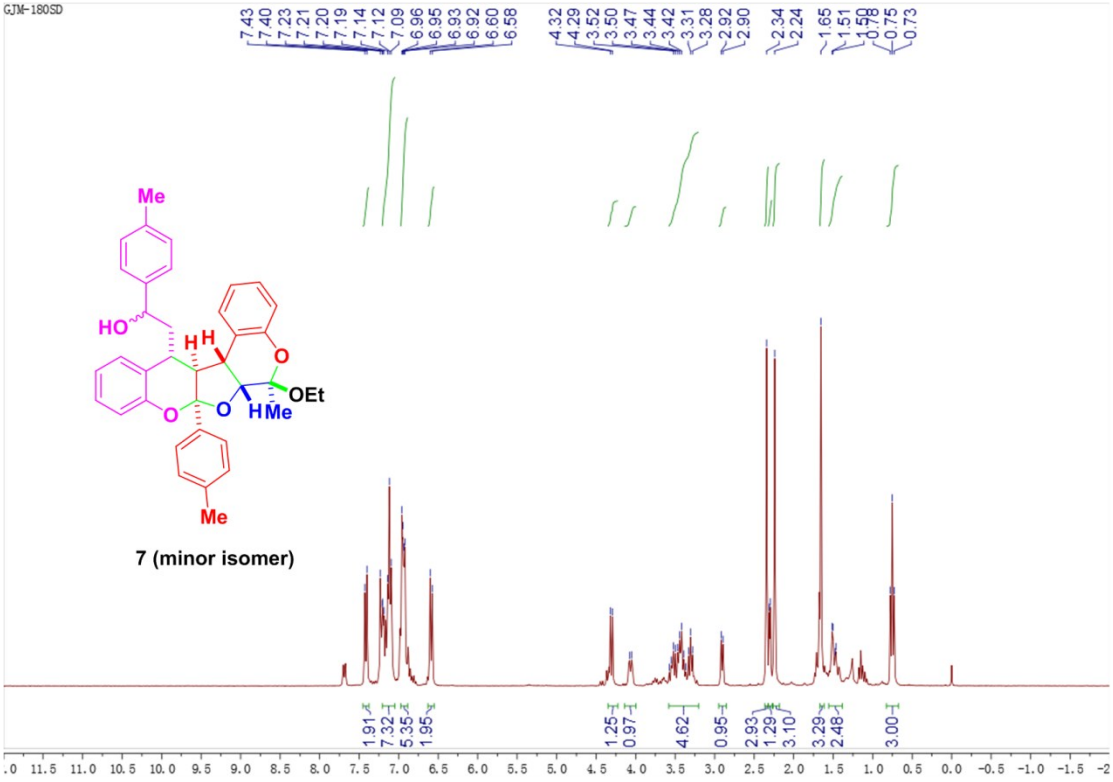
^{1}H NMR spectrum of 7 (major isomer)



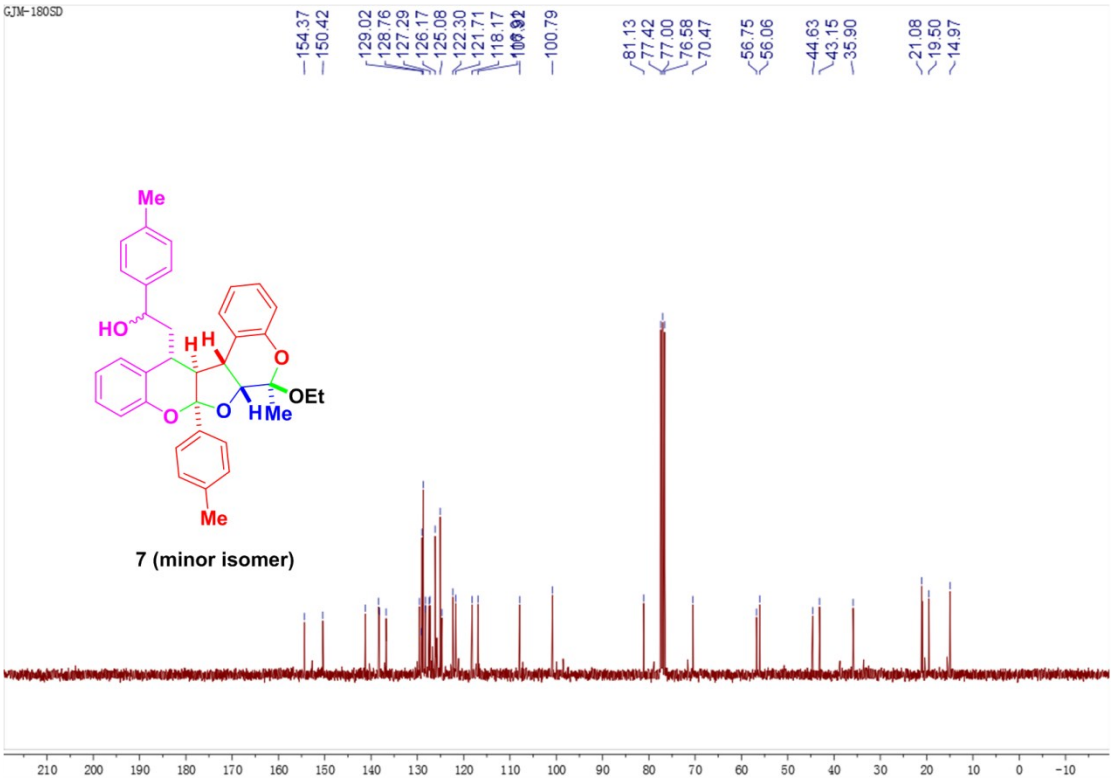
^{13}C NMR spectrum of 7 (major isomer)



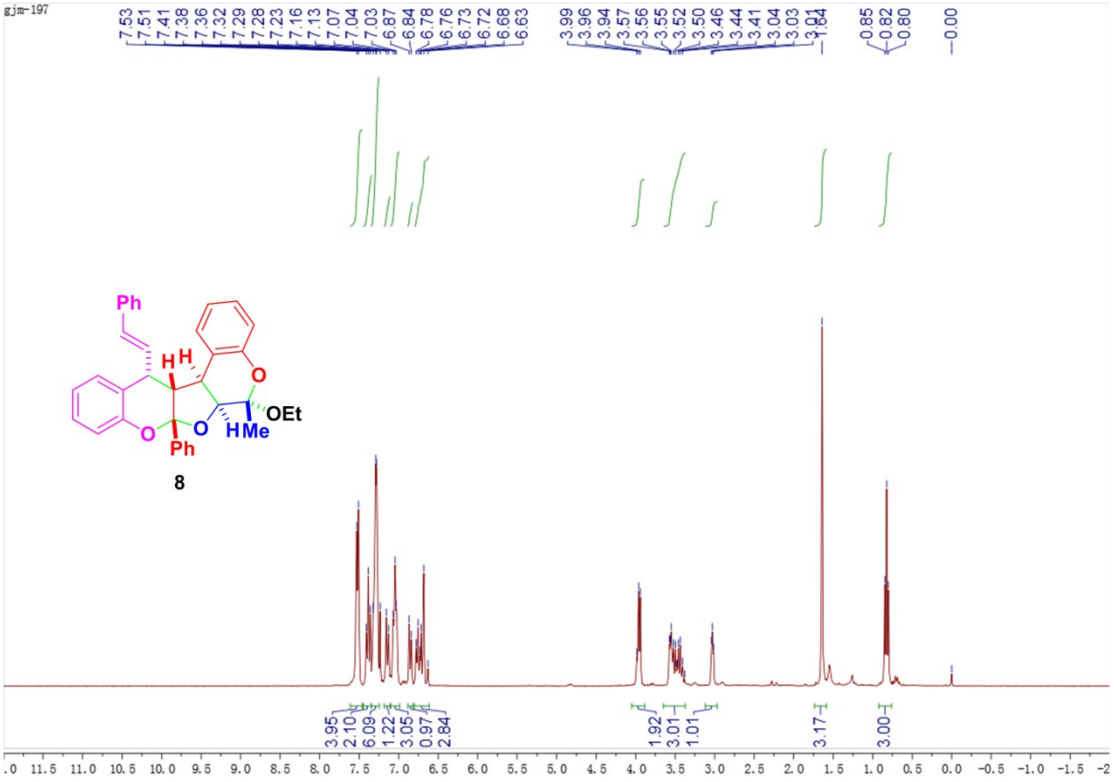
^{1}H NMR spectrum of 7 (minor isomer)



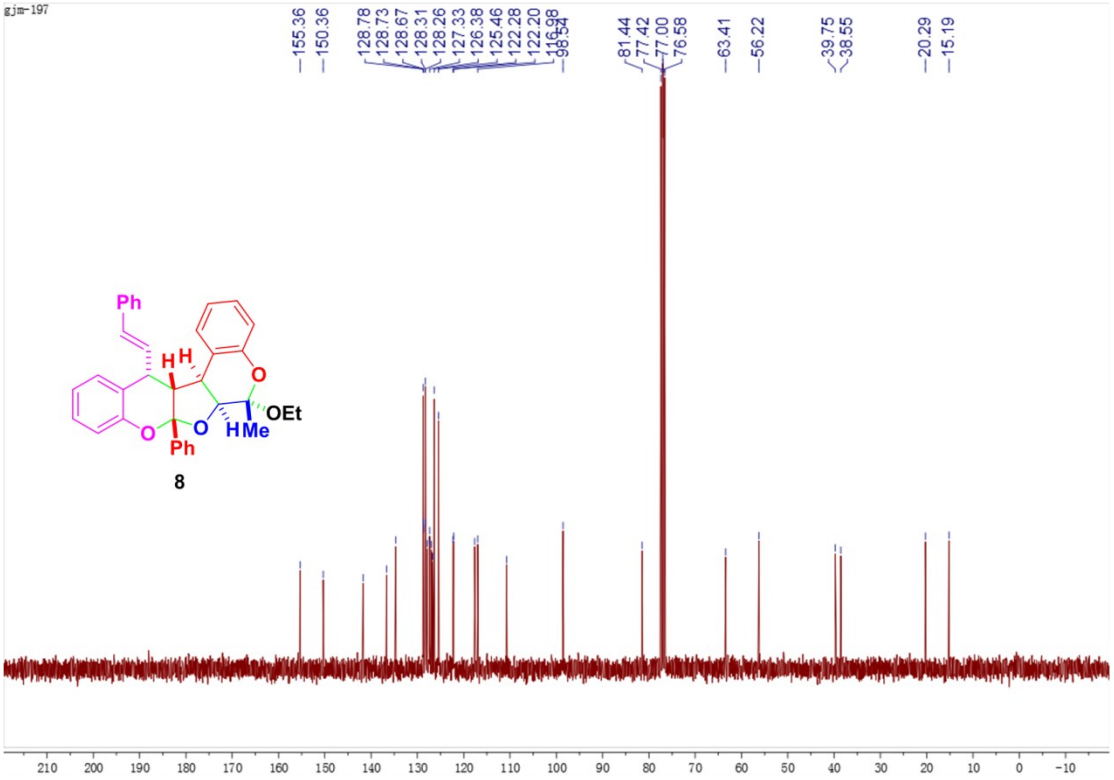
^{13}C NMR spectrum of 7 (minor isomer)



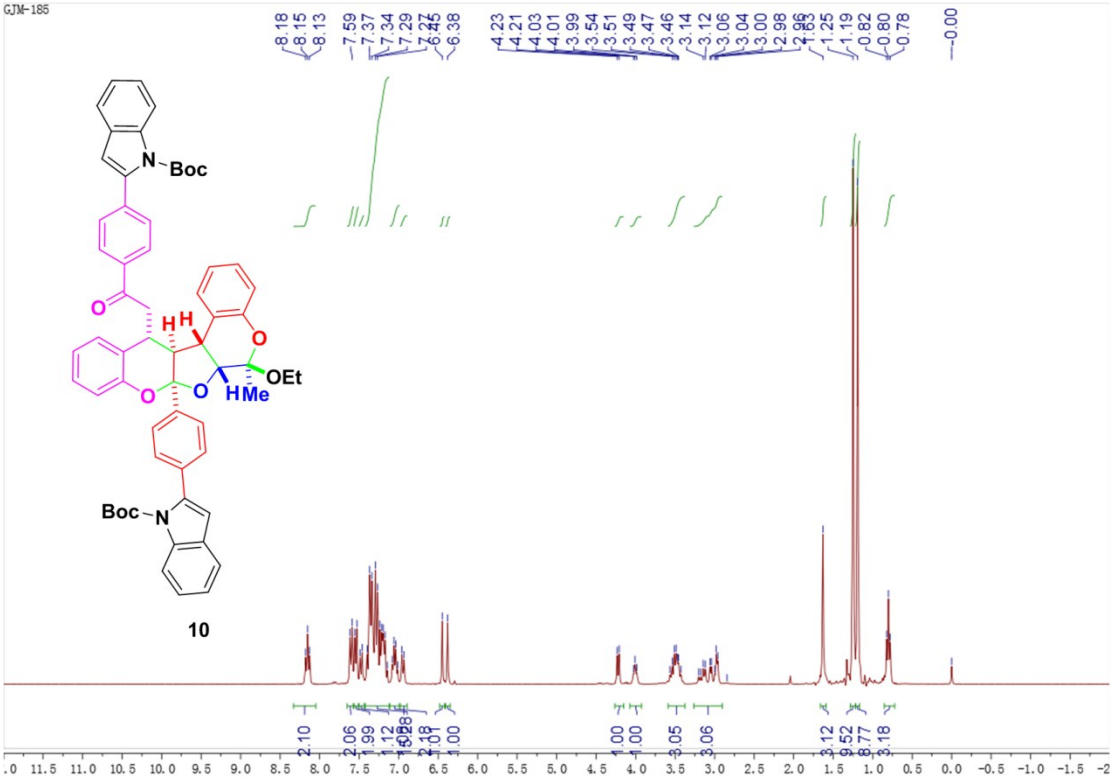
^{1}H NMR spectrum of 8



^{13}C NMR spectrum of 8



^{1}H NMR spectrum of 10



^{13}C NMR spectrum of 10