

Table of Contents

1. General information	S2
2. General procedure	S3
3. Additional experiments	S4
4. Characterization data of products	S12
5. Crystallographic data for compound 7a	S43
6. Copies of the ^1H , ^{19}F NMR and ^{13}C NMR spectra	S54
7. References	S116

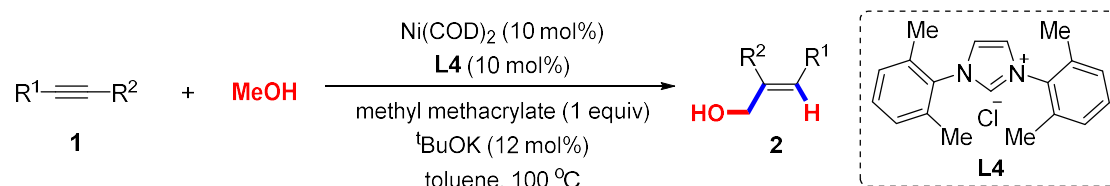
1. General information

^1H and ^{13}C NMR data were recorded with Bruker ADVANCE III (400 MHz) or JNM-ECZ400S/L1 (400 MHz) spectrometers. Chemical shifts are given in ppm. The spectra are calibrated to the residual ^1H and ^{13}C signals of the solvents. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), septet (sept), multiplet (m), and broad (b). ^{19}F NMR spectra were recorded using CFCl_3 as internal standard. Gas chromatography were determined with a SHIMADZU Nexis GC 2030 gas chromatography instrument with a FID detector. High-resolution mass spectra (HRMS) were recorded on Thermo Fisher Orbitrap Elite mass spectrometer. The photoreaction instrument (WPTEC-1020L) was purchased from WATTCAS, China.

Unless otherwise stated, starting materials were purchased from commercial suppliers (Energy Chemical, Alfa, Aldrich and so on). All reactions dealing with air- or moisture-sensitive compounds were performed in the argon-filled glove box or by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere. Solvents were purchased in HPLC quality, degassed by purging thoroughly with argon and dried over activated molecular sieves of appropriate size. More sensitive compounds were stored in a desiccator or in a glove-box if required. Reactions were monitored by thin layer chromatography (TLC) using glass 0.25 mm silica gel plates. Compounds were visualized by UV-light at 254 nm and by dipping the plates in an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (200-400 mesh).

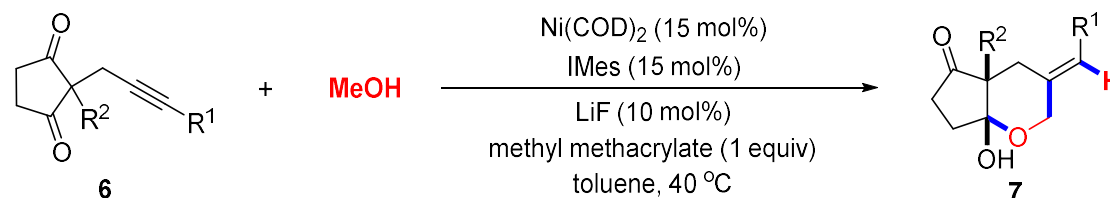
2. General procedures

2.1



A mixture of $Ni(COD)_2$ (10 mol%), **L4** (10 mol%), methyl methacrylate (0.2 mmol), $tBuOK$ (12 mol%), dry toluene (1 mL) and methanol (3 mL) were stirred in a sealed tube at room temperature for 30 min under argon. To the resulting solution was added alkyne substrate **1** (0.2 mmol), the reaction mixture was heated at 100 °C until the reaction was complete (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20~1:6 (v/v) to afford the allylic alcohol **2**.

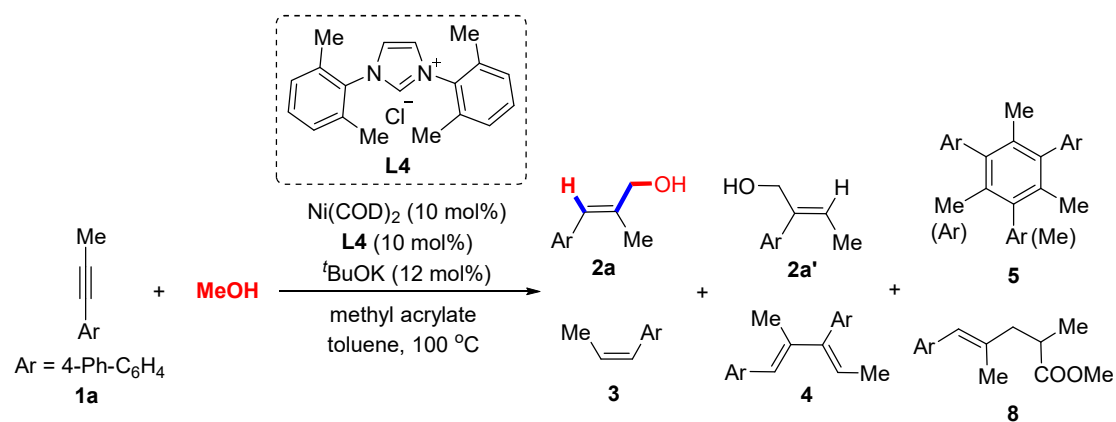
2.2



A mixture of $Ni(COD)_2$ (15 mol%), IMes (15 mol%), methyl methacrylate (0.2 mmol), LiF (10 mol%), dry toluene (1.5 mL) and methanol (0.5 mL) was stirred in a sealed tube at room temperature for 30 min under argon. To the resulting solution was added alkyne substrate **6** (0.2 mmol), the reaction mixture was heated at 40 °C until the reaction was complete (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:8~1:2 (v/v) to afford the allylic alcohol **7**.

3. Additional Experiments

3.1 Side Reactions

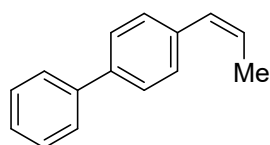


entry	ligand	additive	yield ^b (2 , %)	yield ^b (3 , %)	yield ^b (4 , %)	yield ^b (5 , %)	yield ^b (8 , %)
1	L4	0	40 (14/1)	9	22	23	0
2	L4	0.2 equiv	54 ^c (14/1)	8	6	7	13%
3	L4	1.0 equiv.	60 ^c (14/1)	6	< 2	< 2	18%

^aReactions conditions: **1a** (0.2 mmol), Ni(COD)₂ (10 mol%), ligand (20 mol%), ^tBuOK (12 mol%), additive (1 equiv) in toluene (1 mL) and MeOH (3 mL) in sealed tube at 100 °C.

^bDetermined by GC analysis using adamantane as the internal standard. ^cIsolated yield.

(*Z*)-4-(prop-1-en-1-yl)-1,1'-biphenyl (**3**)

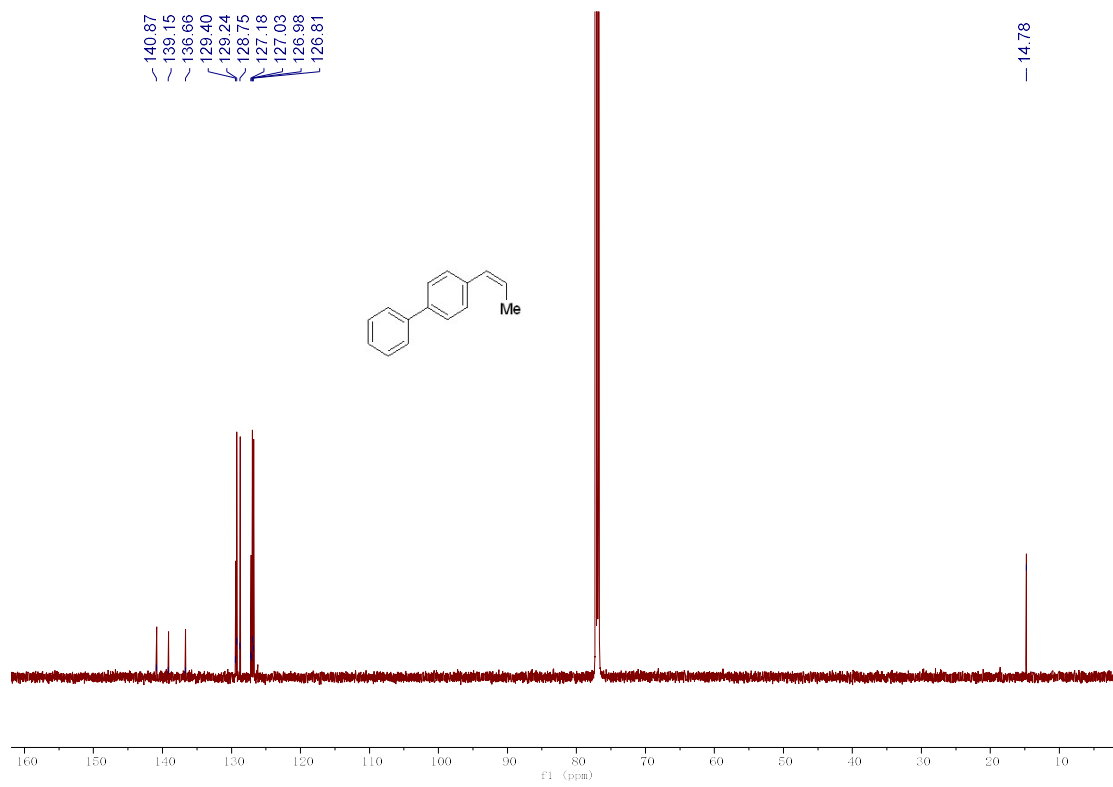
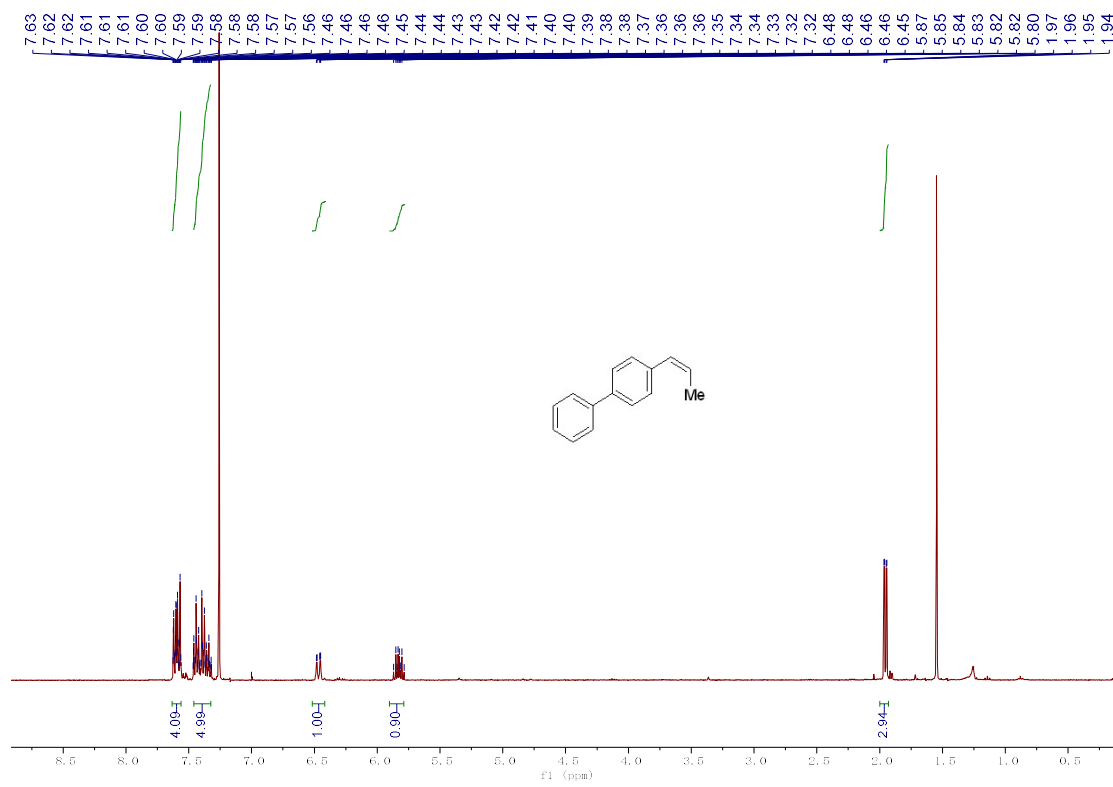


Chemical Formula: C₁₅H₁₄

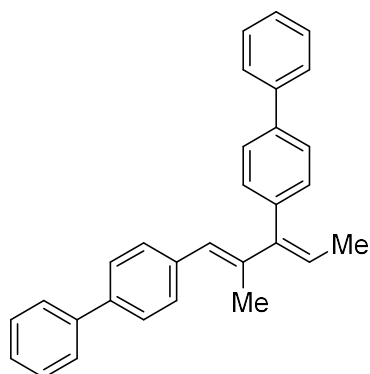
Exact Mass: 194.1096

¹H NMR (400 MHz, CDCl₃) δ 7.63 - 7.56 (m, 4H), 7.46 - 7.32 (m, 5H), 6.52 - 6.42 (m, 1H), 5.90 - 5.79 (m, 1H), 1.96 (dd, *J* = 7.19, 1.83 Hz, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 140.9, 139.1, 136.7, 129.4, 129.2, 128.8, 127.2, 127.03, 126.98, 126.8, 14.8.

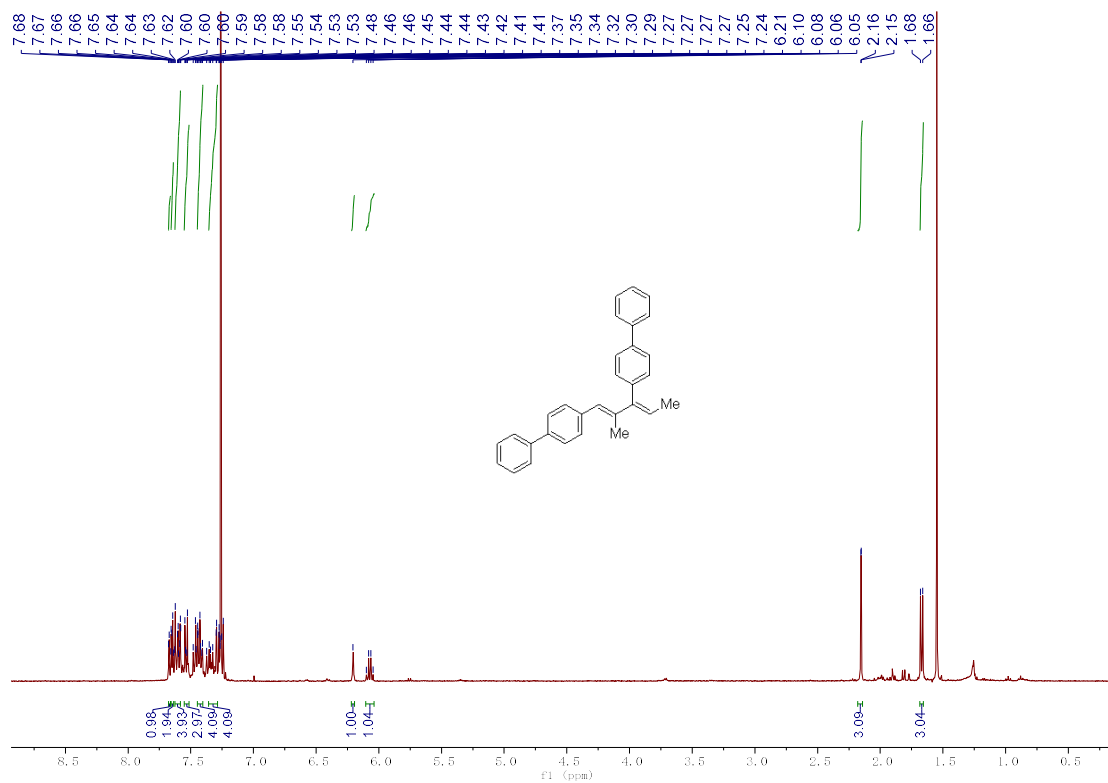


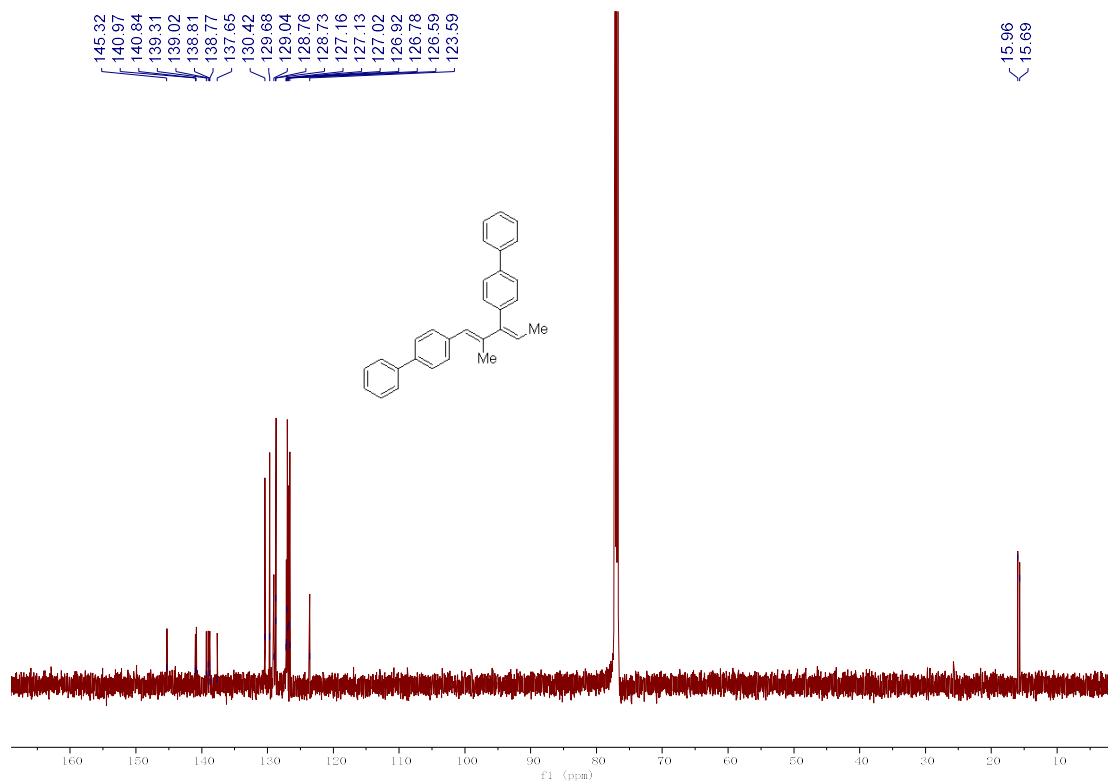
4,4''-(2,3-dimethylbuta-1,3-diene-1,4-diyl)di-1,1'-biphenyl (4)



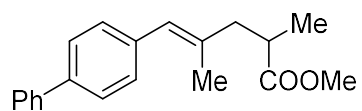
^1H NMR (400 MHz, CDCl_3) δ 7.68 - 7.66 (m, 1H), 7.66 - 7.64 (m, 2H), 7.63 - 7.58 (m, 4H), 7.55 - 7.51 (m, 3H), 7.45 - 7.40 (m, 4H), 7.36 - 7.29 (m, 4H), 6.21 (s, 1H), 6.07 (q, $J = 7.01$ Hz, 1H), 2.15 (d, $J = 1.21$ Hz, 3H), 1.67 (d, $J = 7.01$ Hz, 3H);

^{13}C NMR (151 MHz, CDCl_3) δ 145.3, 140.8, 139.3, 139.0, 138.8, 130.4, 129.7, 129.0, 128.8, 128.7, 127.2, 127.1, 127.0, 126.9, 126.8, 126.6, 123.6, 16.0, 15.7.





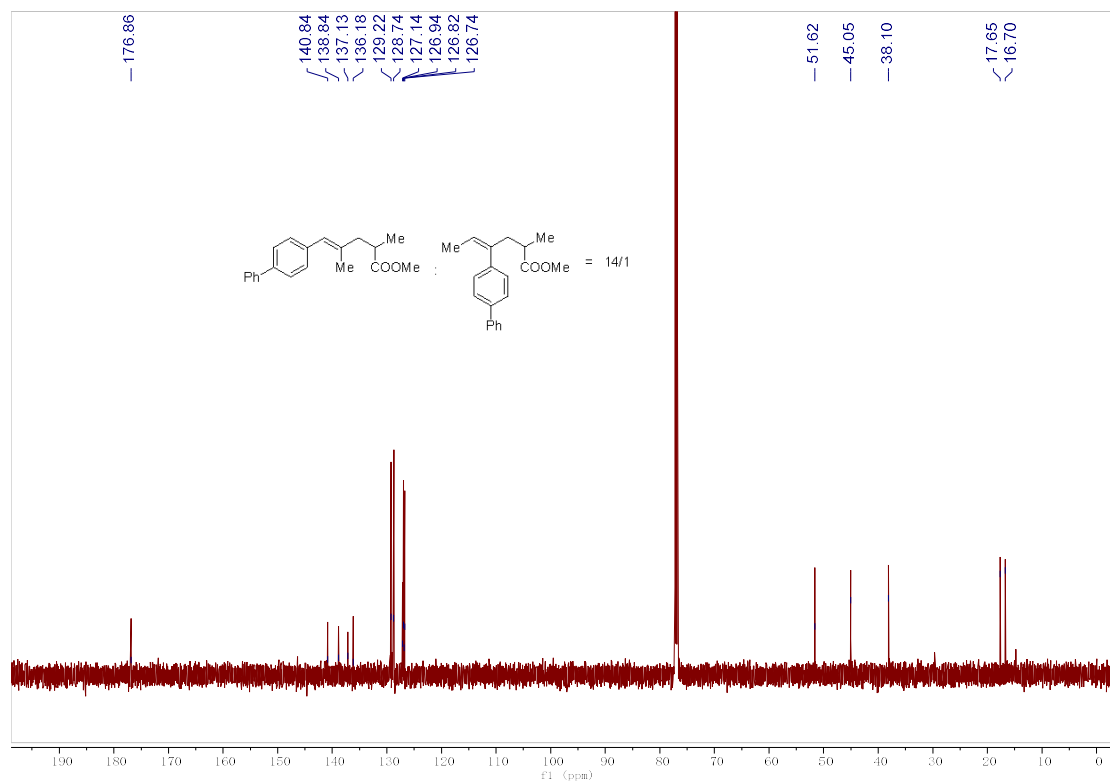
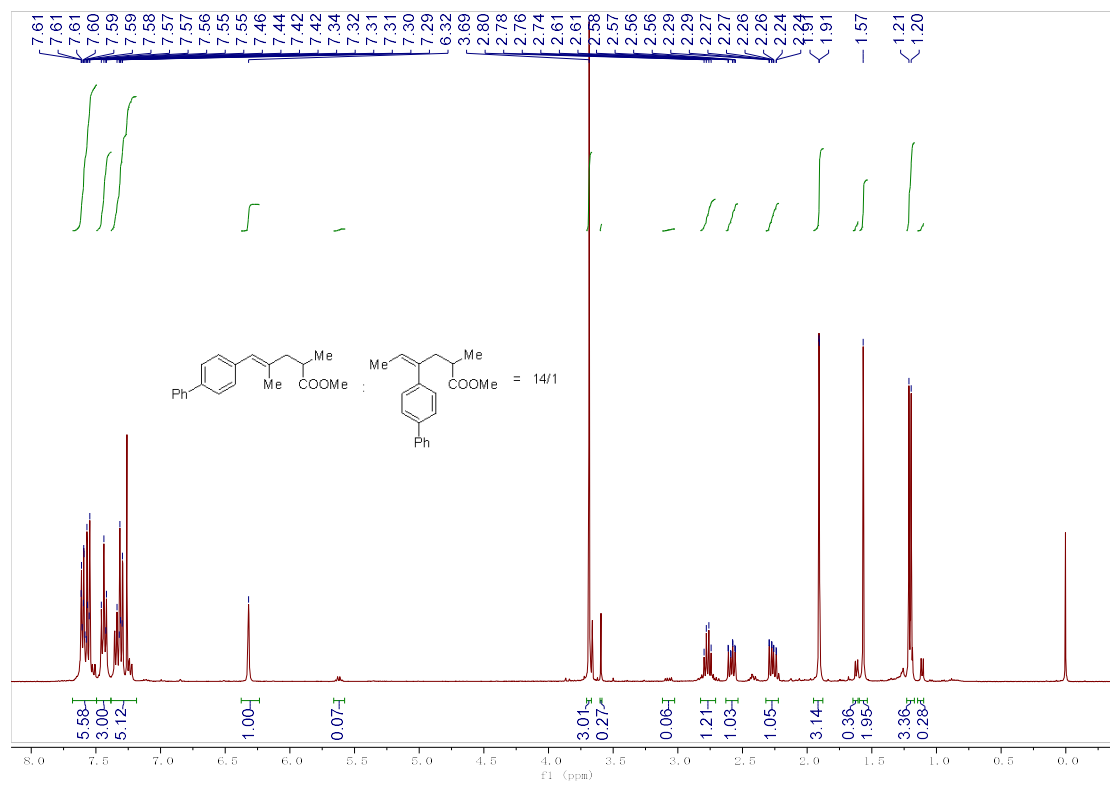
methyl (*E*)-5-([1,1'-biphenyl]-4-yl)-2,4-dimethylpent-4-enoate (8)



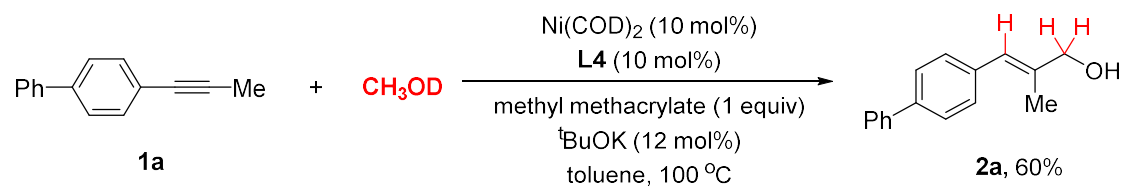
Chemical Formula: C₂₀H₂₂O₂
 Exact Mass: 294.1620

¹H NMR (400 MHz, CDCl₃) δ 7.64 - 7.54 (m, 5H), 7.43 (m, 2H), 7.34 - 7.30 (m, 2H), 6.32 (s, 1H), 3.69 (s, 3H), 2.81 - 2.73 (m, 1H), 2.62 - 2.55 (m, 1H), 2.30 - 2.23 (m, 1H), 1.91 (d, *J* = 1.4 Hz, 3H), 1.57 (s, 2H), 1.20 (d, *J* = 7.0 Hz, 3H);

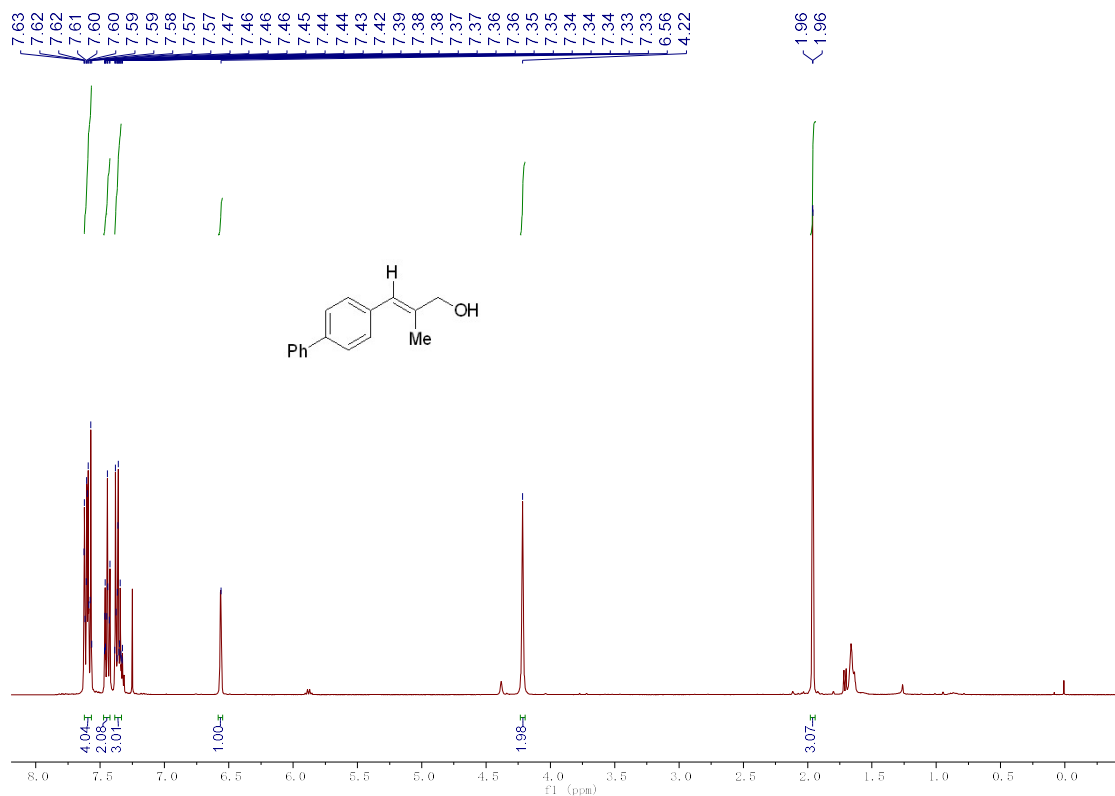
¹³C NMR (151 MHz, CDCl₃) δ 176.9, 140.8, 138.8, 137.1, 136.2, 129.2, 128.7, 127.1, 126.9, 126.8, 126.7, 51.6, 45.1, 38.1, 17.7, 16.7.

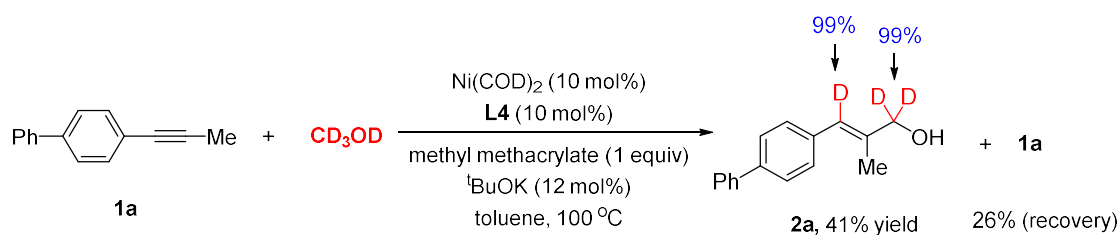


3.2 Mechanistic study

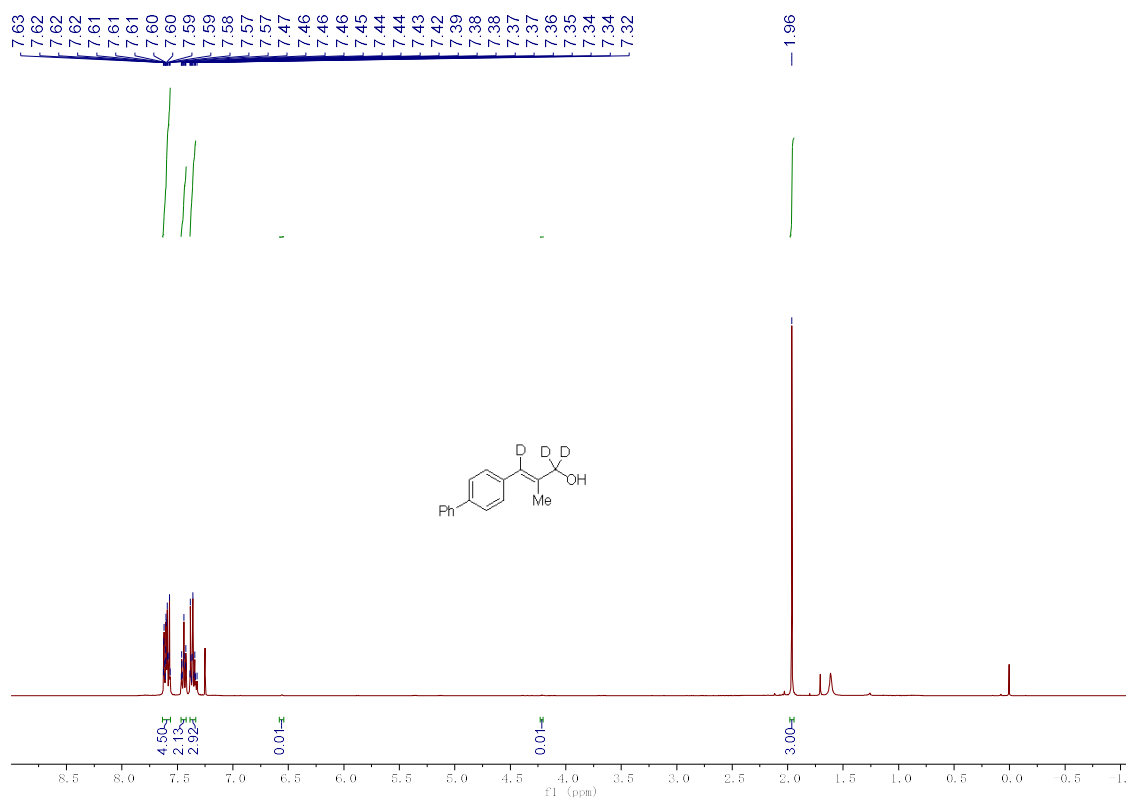


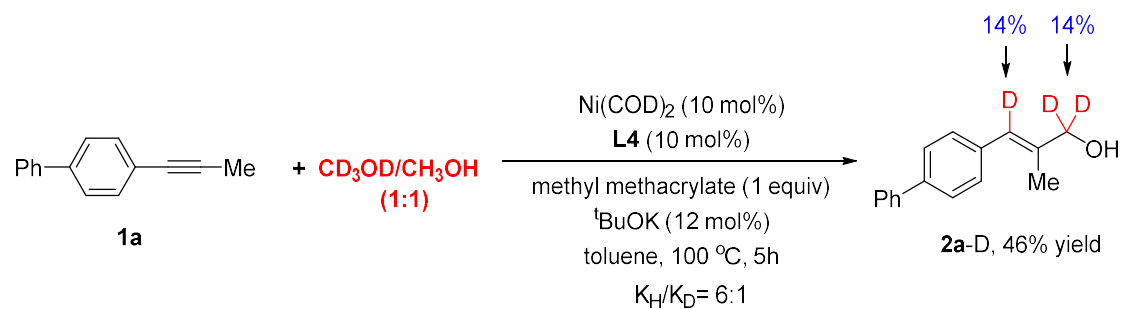
Experimental procedure: A mixture of Ni(COD)_2 (10 mol%, 5.4 mg), **L4** (10 mol%, 6.2 mg), methyl methacrylate (0.2 mmol, 20 mg), tBuOK (12 mol%, 2.7 mg), dry toluene (1 mL) and CH_3OD (3 mL) were stirred in a sealed tube at room temperature for 30 min under argon. To the resulting solution was added alkyne substrate **1a** (0.2 mmol, 38.4 mg), the reaction mixture was heated at 100 $^\circ\text{C}$ until the reaction was complete (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20~1:8 (v/v) to afford the allylic alcohol **2a** (27 mg, 60% yield) with 0% deuterium incorporation.



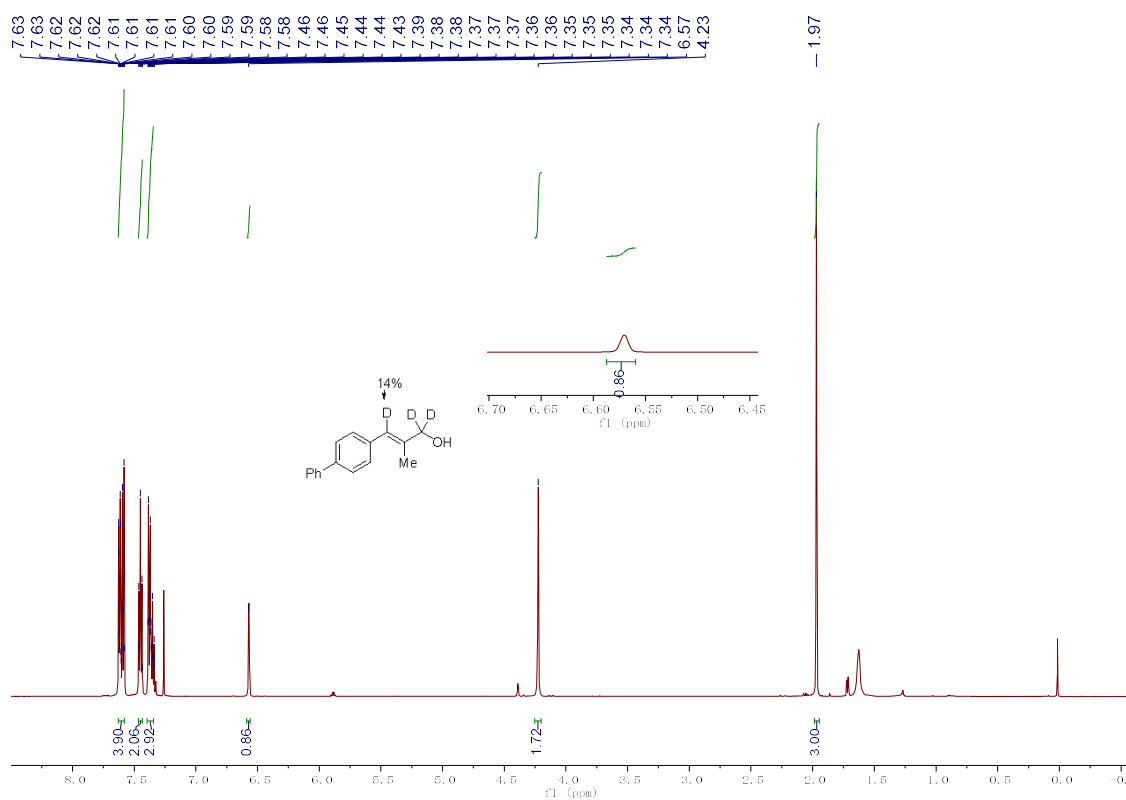


Experimental procedure: A mixture of $\text{Ni}(\text{COD})_2$ (10 mol%, 5.4 mg), **L4** (10 mol%, 6.2 mg), methyl methacrylate (0.2 mmol, 20 mg), $t\text{BuOK}$ (12 mol%, 2.7 mg), dry toluene (1 mL) and CD_3OD (3 mL) were stirred in a sealed tube at room temperature for 30 min under argon. To the resulting solution was added alkyne substrate **1a** (0.2 mmol, 38.4 mg), the reaction mixture was heated at 100 °C until the reaction was complete (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20~1:8 (v/v) to afford the allylic alcohol **2a-D** (18.4 mg, 41% yield) with 99% deuterium incorporation.



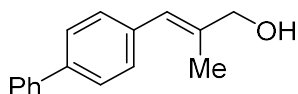


Experimental procedure: A mixture of Ni(COD)_2 (10 mol%, 5.4 mg), **L4** (10 mol%, 6.2 mg), methyl methacrylate (0.2 mmol, 20 mg), 'BuOK (12 mol%, 2.7 mg), dry toluene (1 mL), CD_3OD (1.5 mL) and CH_3OH (1.5 mL) were stirred in a sealed tube at room temperature for 30 min under argon. To the resulting solution was added alkyne substrate **1a** (0.2 mmol, 38.4 mg), the reaction mixture was heated at 100°C for 5 hours (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20~1:8 (v/v) to afford the allylic alcohol **2a-D** (20.6 mg, 46% yield) with 14% deuterium incorporation.



4. Characterization data of products

(*E*)-3-([1,1'-biphenyl]-4-yl)-2-methylprop-2-en-1-ol (**2a**)



Chemical Formula: C₁₆H₁₆O

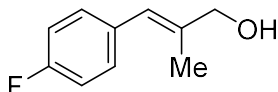
Exact Mass: 224.1201

2a was prepared according to general procedure 2.1 using **1a** (38.4 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2a** as colorless oil (26.9 mg, 60% yield, 14/1 r.r).

The NMR data matched those reported in the literature.¹ ¹H NMR (600 MHz, CDCl₃) δ 7.65 - 7.57 (m, 4H), 7.48 - 7.43 (m, 2H), 7.40 - 7.33 (m, 3H), 6.57 (s, 1H), 4.23 (d, *J* = 1.4 Hz, 2H), 1.97 (d, *J* = 1.4 Hz, 3H), 1.72 (bs, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 140.7, 139.1, 137.8, 136.5, 129.3, 128.7, 127.2, 126.9, 126.8, 124.6, 69.0, 15.4.

(*E*)-3-(4-fluorophenyl)-2-methylprop-2-en-1-ol (**2b**)



Chemical Formula: C₁₀H₁₁FO

Exact Mass: 166.0794

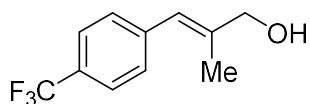
2b was prepared according to general procedure 2.1 using **1b** (26.8 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2b** as colorless oil (19.4 mg, 58% yield, 25/1 r.r).

The NMR data matched those reported in the literature.² ¹H NMR (600 MHz, CDCl₃) δ 7.25 - 7.21 (m, 2H), 7.04 - 6.99 (m, 2H), 6.49 (s, 1H), 4.18 (d, *J* = 1.5 Hz, 2H), 1.87 (d, *J* = 1.4 Hz, 3H), 1.60 (bs, 1H);

¹⁹F NMR (565 MHz, CDCl₃) δ -115.8 (m);

¹³C NMR (151 MHz, CDCl₃) δ 161.4 (d, *J* = 245.8 Hz), 137.5, 133.5 (d, *J* = 3.3 Hz), 130.4 (d, *J* = 7.8 Hz), 123.9, 115.0 (d, *J* = 21.3 Hz), 68.8, 15.2.

(*E*)-2-methyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-ol (**2c**)



Chemical Formula: $C_{11}H_{11}F_3O$

Exact Mass: 216.0762

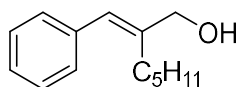
2c was prepared according to general procedure 2.1 using **1c** (36.8 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2c** as colorless oil (18.7 mg, 43% yield, 33/1 r.r).

The NMR data matched those reported in the literature.² 1H NMR (600 MHz, $CDCl_3$) δ 7.61 - 7.55 (m, 2H), 7.40 - 7.34 (m, 2H), 6.57 (s, 1H), 4.22 (s, 2H), 1.89 (d, $J = 1.4$ Hz, 3H), 1.67 (bs, 1H);

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.41;

^{13}C NMR (151 MHz, $CDCl_3$) δ 141.2, 139.9, 129.0, 128.4 (q, $J = 32.3$ Hz), 125.1 (q, $J = 3.8$ Hz), 124.3 (q, $J = 271.8$ Hz), 123.4, 68.4, 15.3.

(E)-2-benzylideneheptan-1-ol (2d)



Chemical Formula: $C_{14}H_{20}O$

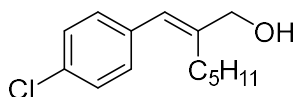
Exact Mass: 204.1514

2d was prepared according to general procedure 2.1 using **1d** (34.4 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2d** as colorless oil (22.9 mg, 56% yield, 13/1 r.r).

The NMR data matched those reported in the literature.³ 1H NMR (600 MHz, $CDCl_3$) δ 7.36 - 7.32 (m, 2H), 7.27 - 7.21 (m, 3H), 6.53 (s, 1H), 4.23 (d, $J = 1.4$ Hz, 2H), 2.34 - 2.27 (m, 2H), 1.62 (bs, 1H), 1.56 - 1.48 (m, 2H), 1.33 - 1.26 (m, 4H), 0.90 - 0.86 (m, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.4, 137.6, 128.6, 128.2, 126.4, 125.3, 67.0, 32.0, 28.7, 28.1, 22.4, 14.0.

(E)-2-(4-chlorobenzylidene)heptan-1-ol (2e)



Chemical Formula: $C_{14}H_{19}ClO$
Exact Mass: 238.1124

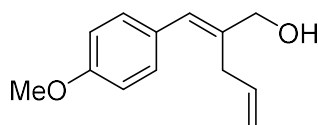
2e was prepared according to general procedure 2.1 using **1e** (41.2 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2e** as colorless oil (24.0 mg, 50% yield, 25/1 r.r).

1H NMR (600 MHz, $CDCl_3$) δ 7.36 - 7.32 (m, 2H), 7.26 - 7.21 (m, 2H), 6.53 (s, 1H), 4.23 (d, J = 1.4 Hz, 2H), 2.34 - 2.27 (m, 2H), 1.62 (bs, 1H), 1.56 - 1.48 (m, 2H), 1.33 - 1.26 (m, 4H), 0.90 - 0.86 (m, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 142.4, 137.6, 128.6, 128.2, 126.4, 125.3, 67.0, 32.0, 28.7, 28.1, 22.4, 14.0;

HRMS: (ESI) calcd for $C_{14}H_{18}Cl^+$ $[M-H_2O+H]^+$ 221.1092; found 221.1087.

(E)-2-(4-methoxybenzylidene)pent-4-en-1-ol (2f)



Chemical Formula: $C_{13}H_{16}O_2$
Exact Mass: 204.1150

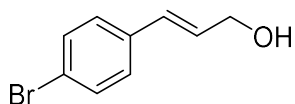
2f was prepared according to general procedure 2.1 using **1f** (mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2f** as colorless oil (24.5 mg, 60% yield).

1H NMR (400 MHz, $CDCl_3$) δ 7.25 - 7.22 (m, 2H), 6.89 - 6.86 (m, 2H), 6.59 (s, 1H), 5.99 - 5.88 (m, 1H), 5.18 - 5.10 (m, 2H), 4.20 (d, J = 1.4 Hz, 2H), 3.81 (s, 3H), 3.09 - 3.05 (m, 2H), 1.62 (bs, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 137.3, 135.7, 129.7, 129.5, 126.6, 116.2, 113.6, 67.1, 55.2, 33.0;

HRMS: (ESI) calcd for $C_{13}H_{15}O^+$ $[M-H_2O+H]^+$ 187.1117; found 187.1114.

(E)-3-(4-bromophenyl)prop-2-en-1-ol (2g)



Chemical Formula: C₉H₉BrO

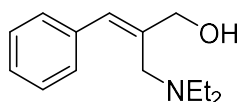
Exact Mass: 211.9837

2g was prepared according to general procedure 2.1 using **1g** (50.2 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2g** as colorless oil (19.1 mg, 45% yield).

The NMR data matched those reported in the literature.³ ¹H NMR (600 MHz, CDCl₃) δ 7.46 - 7.41 (m, 2H), 7.27 - 7.22 (m, 2H), 6.56 (d, *J* = 15.9 Hz, 1H), 6.35 (dt, *J* = 15.9, 5.6 Hz, 1H), 4.32 (dd, *J* = 5.6, 1.6 Hz, 2H), 1.5 (bs, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 135.6, 131.7, 129.8, 129.3, 128.0, 121.4, 63.5.

(E)-2-((diethylamino)methyl)-3-phenylprop-2-en-1-ol (2h)



Chemical Formula: C₁₄H₂₁NO

Exact Mass: 219.1623

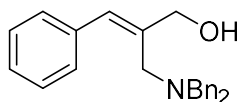
2h was prepared according to general procedure 2.1 using **1h** (37.4 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 4/1, Et₃N 1%) to obtain **2h** as colorless oil (30.2 mg, 69% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.28 - 7.22 (m, 2H), 7.20 - 7.16 (m, 1H), 7.12 - 7.05 (m, 2H), 6.61 (s, 1H), 5.43 (bs, 1H), 4.28 (d, *J* = 1.1 Hz, 2H), 3.35 (d, *J* = 1.3 Hz, 2H), 2.39 (q, *J* = 7.2 Hz, 4H), 0.91 (t, *J* = 7.1 Hz, 6H);

¹³C NMR (151 MHz, CDCl₃) δ 137.4, 136.7, 130.1, 128.9, 128.2, 126.9, 70.0, 53.0, 46.8, 11.5;

HRMS: (ESI) calcd for C₁₄H₂₂NO⁺ [M+H]⁺ 220.1696; found 220.1689.

(E)-2-((dibenzylamino)methyl)-3-phenylprop-2-en-1-ol (2i)



Chemical Formula: C₂₄H₂₅NO

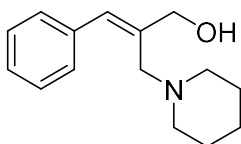
Exact Mass: 343.1936

2i was prepared according to general procedure 2.1 using **1i** (62.2 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **2i** as colorless oil (41.2 mg, 60% yield).

The NMR data matched those reported in the literature.⁴ ¹H NMR (600 MHz, CDCl₃) δ 7.37 - 7.33 (m, 2H), 7.32 - 7.28 (m, 5H), 7.27 - 7.23 (m, 6H), 7.19 - 7.16 (m, 2H), 6.73 (s, 1H), 4.61 (bs, 1H), 4.28 (d, *J* = 1.1 Hz, 2H), 3.46 (s, 4H), 3.37 (d, *J* = 1.3 Hz, 2H);

¹³C NMR (151 MHz, CDCl₃) δ 138.1, 137.9, 136.8, 130.2, 129.2, 129.0, 128.5, 128.2, 127.4, 127.0, 68.9, 58.5, 52.5.

(E)-3-phenyl-2-(piperidin-1-ylmethyl)prop-2-en-1-ol (2j)



Chemical Formula: C₁₅H₂₁NO
Exact Mass: 231.1623

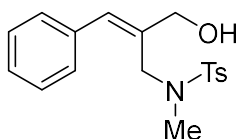
2j was prepared according to general procedure 2.1 using **1j** (40.0 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 4/1, Et₃N 1%) to obtain **2j** as colorless oil (25.0 mg, 54% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.34 - 7.30 (m, 2H), 7.26 - 7.22 (m, 1H), 7.18 - 7.15 (m, 2H), 6.68 (s, 1H), 5.89 (bs, 1H), 4.35 (d, *J* = 1.1 Hz, 2H), 3.31 (d, *J* = 1.2 Hz, 2H), 2.38 (s, 4H), 1.58 - 1.50 (m, 4H), 1.38 (s, 2H);

¹³C NMR (151 MHz, CDCl₃) δ 136.7, 136.6, 130.1, 128.8, 128.1, 126.8, 70.3, 58.5, 54.5, 25.9, 23.9;

HRMS: (ESI) calcd for C₁₅H₂₂NO⁺ [M+H]⁺ 232.1696; found 232.1689.

(E)-N-(2-(hydroxymethyl)-3-phenylallyl)-N,4-dimethylbenzenesulfonamide (2k)



Chemical Formula: C₁₈H₂₁NO₃S
Exact Mass: 331.1242

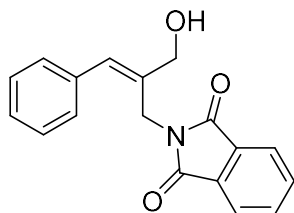
2k was prepared according to general procedure 2.1 using **1k** (59.8 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 4/1) to obtain **2k** as colorless oil (20.5 mg, 31% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.64 - 7.60 (m, 2H), 7.32 - 7.26 (m, 4H), 7.24 - 7.20 (m, 1H), 7.10 - 7.06 (m, 2H), 6.81 (s, 1H), 4.37 (s, 2H), 3.85 (s, 2H), 2.82 (bs, 1H), 2.57 (s, 3H), 2.42 (s, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 143.6, 136.3, 135.9, 134.1, 130.9, 129.8, 128.7, 128.3, 127.2, 127.1, 64.8, 46.9, 34.6, 21.5;

HRMS: (ESI) calcd for C₁₈H₂₂NO₃S⁺ [M+H]⁺ 332.1315; found 332.1296.

(E)-2-(2-(hydroxymethyl)-3-phenylallyl)isoindoline-1,3-dione (2l)



Chemical Formula: C₁₈H₁₅NO₃
Exact Mass: 293.1052

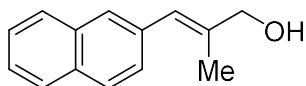
2l was prepared according to general procedure 2.1 using **1l** (52.2 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 3/1) to obtain **2l** as colorless oil (25.0 mg, 43% yield, 13/1 r.r).

¹H NMR (600 MHz, CDCl₃) δ 7.83 - 7.80 (m, 2H), 7.73 - 7.69 (m, 2H), 7.44 - 7.40 (m, 2H), 7.38 - 7.34 (m, 2H), 7.26 - 7.23 (m, 1H), 6.75 (s, 1H), 4.63 (d, *J* = 1.3 Hz, 2H), 4.15 (d, *J* = 5.7 Hz, 2H), 2.76 (t, *J* = 6.67 Hz, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 168.7, 136.1, 135.1, 134.1, 131.8, 130.9, 128.7, 128.3, 127.2, 123.4, 65.7, 36.0;

HRMS: (ESI) calcd for C₁₈H₁₆NO₃⁺ [M+H]⁺ 294.1125; found 294.1126.

(E)-2-methyl-3-(naphthalen-2-yl)prop-2-en-1-ol (2m)



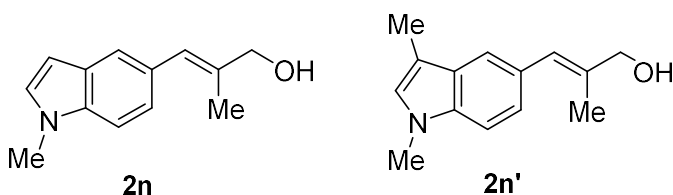
Chemical Formula: C₁₄H₁₄O
Exact Mass: 198.1045

2m was prepared according to general procedure 2.1 using **1m** (33.2 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2m** as colorless oil (24.6 mg, 62% yield, 17/1 r.r).

The NMR data matched those reported in the literature.³ ¹H NMR (600 MHz, CDCl₃) δ 7.85 - 7.79 (m, 3H), 7.75 - 7.73 (m, 1H), 7.50 - 7.41 (m, 3H), 6.75 - 6.63 (m, 1H), 4.25 (d, *J* = 1.6 Hz, 2H), 1.99 (d, *J* = 1.4 Hz, 3H), 1.75 (bs, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 138.1, 135.0, 133.3, 132.1, 127.8, 127.6, 127.55, 127.47, 127.3, 126.0, 125.7, 125.0, 69.0, 15.4.

(E)-2-methyl-3-(1-methyl-1H-indol-5-yl)prop-2-en-1-ol (2n)



Chemical Formula: C₁₃H₁₅NO
Exact Mass: 201.1154

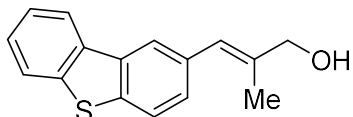
2n was prepared according to general procedure 2.1 using **1n** (33.8 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain a 5:1 mixture of **2n** and **2n'** as colorless oil (25.3 mg, 63% yield, 10/1 r.r).

¹H NMR (600 MHz, (CD₃)₂SO) δ 7.47 - 7.44 (m, 1H), 7.41 - 7.36 (m, 1H), 7.31 - 7.28 (m, 1H), 7.12 - 7.07 (m, 1H), 6.55 (s, 1H), 6.42 - 6.38 (m, 1H), 4.90 (t, *J* = 5.7 Hz, 1H), 3.99 (d, *J* = 5.4 Hz, 2H), 3.78 (s, 3H), 1.85 (d, *J* = 1.4 Hz, 3H);

¹³C NMR (151 MHz, (CD₃)₂SO) δ 135.8, 135.1, 129.9, 128.5, 128.0, 124.3, 122.6, 120.2, 109.3, 100.4, 67.1, 32.5, 15.4;

HRMS: (ESI) calcd for C₁₃H₁₆NO₃⁺[M+H]⁺ 202.1226; found 202.1221.

(E)-3-(dibenzo[*b,d*]thiophen-2-yl)-2-methylprop-2-en-1-ol (2o)



Chemical Formula: C₁₆H₁₄OS
Exact Mass: 254.0765

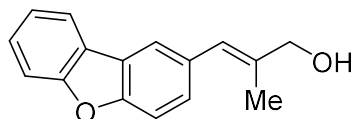
2o was prepared according to general procedure 2.1 using **1o** (44.4 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **2o** as colorless oil 20.3 mg, 40% yield, 14/1 r.r).

¹H NMR (600 MHz, CDCl₃) δ 8.16 - 8.11 (m, 1H), 8.07 - 8.04 (m, 1H), 7.88 - 7.83 (m, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.48 - 7.44 (m, 2H), 7.42 - 7.37 (m, 1H), 6.71 (s, 1H), 4.26 (s, 2H), 1.99 (d, *J* = 1.4 Hz, 3H), 1.68 (bs, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 139.8, 137.7, 137.5, 135.5, 135.4, 134.0, 127.8, 126.7, 124.9, 124.3, 122.9, 122.4, 121.6, 121.5, 69.0, 15.4;

HRMS: (ESI) calcd for C₁₆H₁₃S⁺ [M-H₂O+H]⁺ 237.0732; found 237.0725.

(E)-3-(dibenzo[*b,d*]furan-2-yl)-2-methylprop-2-en-1-ol (2p)



Chemical Formula: C₁₆H₁₄O₂
Exact Mass: 238.0994

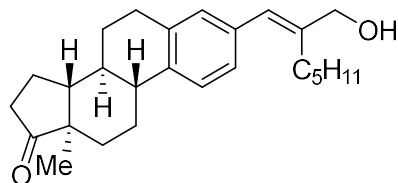
2p was prepared according to general procedure 2.1 using **1p** (41.2 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **2p** as colorless oil 23.8 mg, 50% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.96 - 7.92 (m, 1H), 7.86 - 7.83 (m, 1H), 7.58 - 7.55 (m, 1H), 7.54 - 7.51 (m, 1H), 7.48 - 7.44 (m, 1H), 7.39 - 7.31 (m, 2H), 6.69 (s, 1H), 4.25 (d, *J* = 1.5 Hz, 2H), 1.97 (d, *J* = 1.4 Hz, 3H), 1.67 (bs, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 156.5, 154.9, 137.1, 132.4, 128.3, 127.1, 125.0, 124.15, 124.13, 122.7, 120.64, 120.57, 111.7, 111.2, 69.0, 15.3;

HRMS: (ESI) calcd for C₁₆H₁₃O⁺ [M-H₂O+H]⁺ 221.0961; found 221.0956.

(8*S*,9*R*,13*R*,14*R*)-3-((*E*)-2-(hydroxymethyl)hept-1-en-1-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (2q)



Chemical Formula: C₂₆H₃₆O₂
Exact Mass: 380.2715

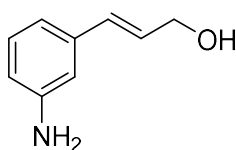
2q was prepared according to general procedure 2.1 using **1q** (69.6 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **2q** as colorless oil (47.2 mg, 62% yield, 13/1 r.r).

¹H NMR (600 MHz, CDCl₃) δ 7.26 - 7.24 (m, 1H), 7.08 - 7.04 (m, 1H), 7.01 - 6.98 (m, 1H), 6.45 (s, 1H), 4.21 (d, *J* = 1.4 Hz, 2H), 2.93 - 2.89 (m, 2H), 2.53 - 2.48 (m, 1H), 2.45 - 2.41 (m, 1H), 2.32 - 2.27 (m, 3H), 2.18 - 2.12 (m, 1H), 2.08 - 2.01 (m, 2H), 1.99 - 1.95 (m, 1H), 1.69 - 1.59 (m, 3H), 1.56 - 1.45 (m, 6H), 1.34 - 1.28 (m, 4H), 0.92 (s, 3H), 0.91 - 0.88 (m, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 221.0, 142.0, 138.0, 136.1, 135.0, 129.3, 126.0, 125.1, 124.9, 67.2, 50.5, 48.0, 44.3, 38.1, 35.8, 32.0, 31.5, 29.4, 28.8, 28.1, 26.5, 25.6, 22.4, 21.5, 14.0, 13.8;

HRMS: (ESI) calcd for C₂₆H₃₇O₂⁺ [M+H]⁺ 381.2788; found 381.2786.

(*E*)-3-(3-aminophenyl)prop-2-en-1-ol (2r)



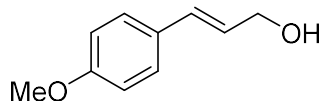
Chemical Formula: C₉H₁₁NO
Exact Mass: 149.0841

2r was prepared according to general procedure 2.1 using **1r** (23.4 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 1/2, Et₃N 1%) to obtain **2r** as colorless oil (15.0 mg, 50% yield).

The NMR data matched those reported in the literature.⁵ ¹H NMR (400 MHz, CDCl₃) δ 7.15 - 7.09 (m, 1H), 6.82 - 6.79 (m, 1H), 6.74 - 6.70 (m, 1H), 6.61 - 6.49 (m, 2H), 6.36 - 6.27 (m, 1H), 4.31 (dd, *J* = 5.8, 1.5 Hz, 2H), 3.67 (bs, 2H), 1.25 (bs, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 146.5, 137.7, 131.3, 129.5, 128.3, 117.1, 114.7, 113.0, 63.8.

(E)-3-(4-methoxyphenyl)prop-2-en-1-ol (2s)



Chemical Formula: C₁₀H₁₂O₂

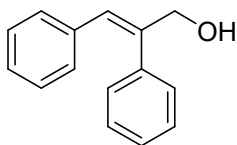
Exact Mass: 164.0837

2s was prepared according to general procedure 2.1 using **1s** (26.4 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2s** as colorless oil (10.9 mg, 33% yield).

The NMR data matched those reported in the literature.⁶ ¹H NMR (600 MHz, CDCl₃) δ 7.35 - 7.30 (m, 2H), 6.88 - 6.84 (m, 2H), 6.56 (dt, *J* = 15.8, 1.6 Hz, 1H), 6.24 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.30 (d, *J* = 4.7 Hz, 2H), 3.81 (s, 3H), 1.43 (bs, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 159.3, 131.0, 129.4, 127.7, 126.2, 114.0, 64.0, 55.3.

(E)-2,3-diphenylprop-2-en-1-ol (2t)



Chemical Formula: C₁₅H₁₄O

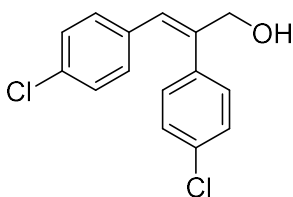
Exact Mass: 210.1045

2t was prepared according to general procedure 2.1 using **1t** (35.6 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2t** as colorless oil (25.2 mg, 60% yield).

The NMR data matched those reported in the literature.⁷ ¹H NMR (600 MHz, CDCl₃) δ 7.37 - 7.29 (m, 3H), 7.25 - 7.21 (m, 2H), 7.15 - 7.09 (m, 3H), 7.03 - 6.98 (m, 2H), 6.70 (s, 1H), 4.47 (s, 2H), 1.79 (bs, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 141.4, 138.5, 136.4, 129.2, 128.8, 128.7, 127.9, 127.5, 126.8, 126.4, 68.5.

(E)-2,3-bis(4-chlorophenyl)prop-2-en-1-ol (2u)



Chemical Formula: C₁₅H₁₂Cl₂O

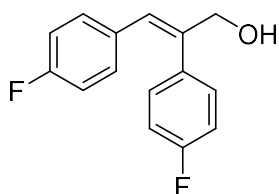
Exact Mass: 278.0265

2u was prepared according to general procedure 2.1 using **1u** (49.2 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2u** as colorless oil (27.3 mg, 49% yield).

The NMR data matched those reported in the literature.⁸ ¹H NMR (600 MHz, CDCl₃) δ 7.33 - 7.29 (m, 2H), 7.16 - 7.09 (m, 4H), 6.93 - 6.89 (m, 2H), 6.66 (s, 1H), 4.43 (d, *J* = 1.6 Hz, 2H), 1.76 (bs, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 140.9, 136.5, 134.6, 133.7, 132.7, 130.4, 130.1, 129.1, 128.3, 125.9, 68.0.

(E)-2,3-bis(4-fluorophenyl)prop-2-en-1-ol (2v)



Chemical Formula: C₁₅H₁₂F₂O

Exact Mass: 246.0856

2v was prepared according to general procedure 2.1 using **1v** (42.8 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2v** as colorless oil (27.6 mg, 56% yield).

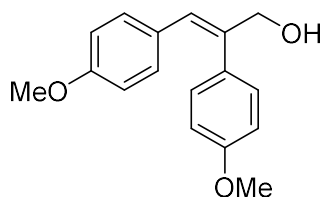
¹H NMR (600 MHz, CDCl₃) δ 7.20 - 7.15 (m, 2H), 7.06 - 7.00 (m, 2H), 6.97 - 6.92 (m, 2H), 6.86 - 6.79 (m, 2H), 6.66 (s, 1H), 4.43 (d, *J* = 1.5 Hz, 2H), 1.77 (bs, 1H);

¹⁹F NMR (565 MHz, CDCl₃) δ -114.10 (m), -114.63 (m);

¹³C NMR (151 MHz, CDCl₃) δ 162.3 (d, *J* = 246.9 Hz), 161.7 (d, *J* = 247.0 Hz), 140.2 (d, *J* = 1.8 Hz), 134.1 (d, *J* = 3.7 Hz), 132.3 (d, *J* = 3.5 Hz), 130.8 (d, *J* = 7.8 Hz), 130.5 (d, *J* = 7.8 Hz), 125.9, 116.0 (d, *J* = 21.3 Hz), 115.0 (d, *J* = 21.3 Hz), 68.3.

HRMS: (ESI) calcd for C₁₅H₁₁F₂⁺ [M-H₂O+H]⁺ 229.0823; found 229.0816.

(E)-2,3-bis(4-methoxyphenyl)prop-2-en-1-ol (2w)



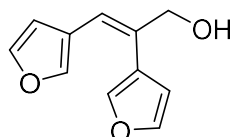
Chemical Formula: C₁₇H₁₈O₃
Exact Mass: 270.1256

2w was prepared according to general procedure 2.1 using **1w** (47.6 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2w** as colorless oil (34.0 mg, 63% yield).

The NMR data matched those reported in the literature.⁹ ¹H NMR (600 MHz, CDCl₃) δ 7.18 - 7.15 (m, 2H), 6.98 - 6.95 (m, 2H), 6.89 - 6.86 (m, 2H), 6.69 - 6.66 (m, 2H), 6.58 (s, 1H), 4.42 (d, *J* = 1.2 Hz, 2H), 3.82 (s, 3H), 3.74 (s, 3H), 1.7 (bs, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 158.9, 158.3, 139.0, 130.7, 130.4, 129.9, 129.2, 125.92, 125.90, 114.2, 68.8, 55.2, 55.1.

(E)-2,3-di(furan-3-yl)prop-2-en-1-ol (2x)



Chemical Formula: C₁₁H₁₀O₃
Exact Mass: 190.0630

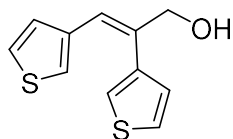
2x was prepared according to general procedure 2.1 using **1x** (31.6 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2x** as colorless oil (20.1 mg, 53% yield).

¹H NMR (600 MHz, (CD₃)₂SO) δ 7.75 - 7.63 (m, 2H), 7.63 - 7.56 (m, 1H), 7.54 - 7.48 (m, 1H), 6.48 - 6.42 (m, 1H), 6.40 - 6.36 (m, 1H), 6.17 - 6.15 (m, 1H), 5.15 (bs, 1H), 4.10 (d, *J* = 2.4 Hz, 2H);

¹³C NMR (151 MHz, (CD₃)₂SO) δ 143.6, 143.5, 142.1, 140.8, 133.1, 122.7, 122.6, 115.5, 111.5, 110.5, 65.8;

HRMS: (ESI) calcd for C₁₁H₉O₂⁺[M-H₂O+H]⁺ 173.0597; found 173.0593.

(E)-2,3-di(thiophen-3-yl)prop-2-en-1-ol (2y)



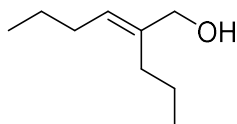
Chemical Formula: C₁₁H₁₀OS₂
Exact Mass: 222.0173

2y was prepared according to general procedure 2.1 using **1y** (38 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2y** as colorless oil (22.2 mg, 50% yield).

¹H NMR (600 MHz, CDCl₃) δ 7.36 - 7.32 (m, 1H), 7.21 - 7.20 (m, 1H), 7.11 - 7.08 (m, 1H), 6.99 - 6.93 (m, 2H), 6.69 (s, 1H), 6.66 - 6.63 (m, 1H), 4.40 (d, *J* = 1.4 Hz, 2H), 1.75 (bs, 1H);
¹³C NMR (151 MHz, CDCl₃) δ 138.7, 137.9, 135.2, 128.2, 127.9, 125.9, 124.8, 124.0, 123.1, 121.8, 68.3;

HRMS: (ESI) calcd for C₁₁H₁₀OS₂ Na⁺[M+Na]⁺ 245.0065; found 245.0061.

(E)-2-propylhex-2-en-1-ol (2z)



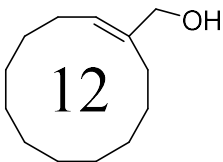
Chemical Formula: C₉H₁₈O
Exact Mass: 142.1358

2z was prepared according to general procedure 2.1 using **1z** (33.0 mg, 0.3 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 10/1) to obtain **2z** as colorless oil (37.1 mg, 87% yield).

The NMR data matched those reported in the literature.¹⁰ ¹H NMR (400 MHz, CDCl₃) δ 5.41 (t, *J* = 7.3 Hz, 1H), 4.02 (d, *J* = 1.1 Hz, 2H), 2.08 - 1.99 (m, 4H), 1.45 - 1.33 (m, 5H), 0.90 (t, *J* = 7.4 Hz, 6H);

¹³C NMR (151 MHz, CDCl₃) δ 139.0, 127.1, 67.2, 30.0, 29.5, 22.9, 21.7, 14.2, 13.9.

(E)-cyclododec-1-en-1-ylmethanol (2aa)



Chemical Formula: C₁₃H₂₄O

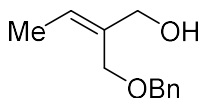
Exact Mass: 196.1827

2aa was prepared according to general procedure 2.1 using **1aa** (32.8 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2aa** as colorless oil (21.2 mg, 54% yield).

The NMR data matched those reported in the literature.¹¹ ¹H NMR (400 MHz, CDCl₃) δ 5.42 (t, *J* = 7.8 Hz, 1H), 4.05 (s, 2H), 2.20 (t, *J* = 7.0 Hz, 2H), 2.10 (q, *J* = 7.2 Hz, 2H), 1.56 - 1.50 (m, 2H), 1.47 - 1.42 (m, 2H), 1.40 - 1.32 (m, 9H), 1.28 - 1.22 (m, 4H);

¹³C NMR (151 MHz, CDCl₃) δ 138.9, 127.9, 66.8, 26.9, 25.1, 24.9, 24.7, 24.5, 24.2, 24.1, 23.9, 22.4, 22.3.

(Z)-2-((benzyloxy)methyl)but-2-en-1-ol (2ab)



Chemical Formula: C₁₂H₁₆O₂

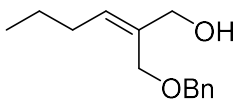
Exact Mass: 192.1150

2ab was prepared according to general procedure 2.1 using **1ab** (32.0 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2ab** as colorless oil (18.8 mg, 49% yield).

The NMR data matched those reported in the literature.¹² ¹H NMR (400 MHz, CDCl₃) δ 7.37 - 7.29 (m, 5H), 5.73 (q, *J* = 7.0 Hz, 1H), 4.53 (s, 2H), 4.19 (s, 2H), 4.15 (s, 2H), 2.18 (bs, 1H), 1.67 (d, *J* = 6.9 Hz, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 137.9, 135.7, 128.4, 127.76, 127.75, 126.3, 72.6, 67.1, 66.7, 13.2.

(Z)-2-((benzyloxy)methyl)hex-2-en-1-ol (2ac)



Chemical Formula: C₁₄H₂₀O₂
Exact Mass: 220.1463

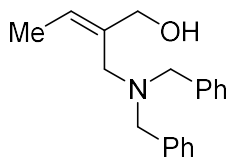
2ac was prepared according to general procedure 2.1 using **1ac** (37.6 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2ac** as colorless oil (25.1 mg, 57% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.36 - 7.33 (m, 4H), 7.32 - 7.28 (m, 1H), 5.64 (tt, *J* = 7.5, 1.1 Hz, 1H), 4.52 (s, 2H), 4.16 (d, *J* = 6.2 Hz, 4H), 2.23 (bs, 1H), 2.03 (q, *J* = 7.5 Hz, 2H), 1.39 (q, *J* = 7.4 Hz, 2H), 0.90 (t, *J* = 7.4 Hz, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 137.9, 134.9, 131.9, 128.4, 127.74, 127.72, 72.5, 67.1, 67.0, 29.5, 22.7, 13.7;

HRMS: (ESI) calcd for C₁₄H₂₁O₂⁺[M+H]⁺ 221.1536; found 221.1532.

(E)-2-((dibenzylamino)methyl)but-2-en-1-ol (2ad)



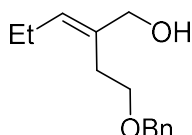
Chemical Formula: C₁₉H₂₃NO
Exact Mass: 281.1780

2ad was prepared according to general procedure 2.1 using **1ad** (49.8 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2ad** as colorless oil (28.1 mg, 50% yield).

The NMR data matched those reported in the literature.⁴ ¹H NMR (400 MHz, CDCl₃) δ 7.35 - 7.32 (m, 8H), 7.29 - 7.27 (m, 1H), 7.26 - 7.24 (m, 1H), 5.72 (q, *J* = 6.9 Hz, 1H), 4.62 (bs, 1H), 4.06 (s, 2H), 3.55 (s, 4H), 3.17 (s, 2H), 1.69 (d, *J* = 6.8 Hz, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 138.4, 135.2, 129.1, 128.5, 127.3, 125.9, 69.6, 58.5, 52.5, 13.1.

(E)-2-(2-(benzyloxy)ethyl)pent-2-en-1-ol (2ae)



Chemical Formula: C₁₄H₂₀O₂
 Exact Mass: 220.1463

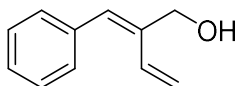
2ae was prepared according to general procedure 2.1 using **1ae** (49.8 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2ae** as colorless oil (26.9 mg, 61% yield, 1/1 r.r).

¹H NMR (400 MHz, CDCl₃) δ 7.36 - 7.27 (m, 5H), 5.54 - 5.37 (m, 1H), 4.57 - 4.51 (m, 2H), 4.07 - 3.93 (m, 2H), 3.58 - 3.48 (m, 2H), 2.47 - 2.35 (m, 2H), 2.16 - 2.01 (m, 2H), 1.84 - 1.45 (m, 1H), 1.02 - 0.94 (m, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 142.6, 138.3, 137.6, 135.7, 131.7, 128.4, 128.3, 127.73, 127.70, 127.6, 127.5, 121.7, 73.1, 72.9, 69.9, 69.5, 68.4, 66.5, 29.3, 27.9, 21.1, 20.9, 14.1, 13.2;

HRMS: (ESI) calcd for C₁₄H₂₀O₂⁺[M+H]⁺ 221.1536; found 221.1532.

(E)-2-benzylidenebut-3-en-1-ol (**2af**)



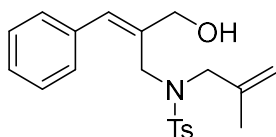
Chemical Formula: C₁₁H₁₂O
 Exact Mass: 160.0888

2af was prepared according to general procedure 2.1 using **1af** (25.6 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 8/1) to obtain **2af** as colorless oil (13.5 mg, 42% yield, 10/1 r.r).

The NMR data matched those reported in the literature.¹² ¹H NMR (400 MHz, CDCl₃) δ 7.38 - 7.33 (m, 2H), 7.31 - 7.26 (m, 3H), 6.84 - 6.75 (m, 1H), 6.75 (s, 1H), 5.54 - 5.44 (m, 1H), 5.28 - 5.22 (m, 1H), 4.49 (s, 2H), 1.62 (bs, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 137.3, 136.6, 132.5, 129.6, 129.4, 128.1, 127.2, 115.8, 64.5.

(E)-N-(2-(hydroxymethyl)-3-phenylallyl)-4-methyl-N-(2-methylallyl)benzenesulfonamide (**2ag**)



Chemical Formula: $C_{21}H_{25}NO_3S$
Exact Mass: 371.1555

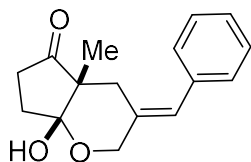
2ag was prepared according to general procedure 2.1 using **1ag** (25.6 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 4/1) to obtain **2ag** as colorless oil (32.0 mg, 43% yield).

1H NMR (600 MHz, $CDCl_3$) δ 7.64 - 7.60 (m, 2H), 7.31 - 7.25 (m, 2H), 7.27 - 7.20 (m, 3H), 7.09 - 7.05 (m, 2H), 6.74 (s, 1H), 4.56 - 4.52 (m, 1H), 4.39 - 4.35 (m, 1H), 4.32 (d, J = 1.1 Hz, 2H), 4.03 - 4.00 (m, 2H), 3.54 (s, 2H), 3.06 (bs, 1H), 2.41 (s, 3H), 1.43 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 143.5, 139.2, 136.8, 136.2, 136.1, 131.3, 129.7, 128.8, 128.1, 127.2, 127.0, 114.7, 64.9, 54.6, 44.7, 21.5, 19.9;

HRMS: (ESI) calcd for $C_{21}H_{24}NO_2S^+$ $[M-H_2O+H]^+$ 354.1522 ; found 354.1523.

(E)-3-benzylidene-7a-hydroxy-4a-methylhexahydrocyclopenta[b]pyran-5(2H)-one (7a)



Chemical Formula: $C_{16}H_{18}O_3$
Exact Mass: 258.1256

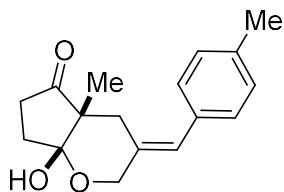
7a was prepared according to general procedure 2.2 using **6a** (45.6 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7a** as white solid (37.2 mg, 63% yield).

1H NMR (600 MHz, $CDCl_3$) δ 7.38 - 7.33 (m, 4H), 7.25 - 7.21 (m, 1H), 6.35 (s, 1H), 4.56 (dt, J = 12.3, 1.6 Hz, 1H), 3.91 (dd, J = 12.2, 2.0 Hz, 1H), 3.19 (dd, J = 14.6, 2.0 Hz, 1H), 2.69 (bs, 1H), 2.46 - 2.38 (m, 2H), 2.24 - 2.07 (m, 3H), 1.05 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 216.4, 136.3, 132.6, 128.8, 128.2, 126.8, 125.6, 103.1, 66.6, 53.0, 35.1, 32.9, 29.8, 20.7;

HRMS: (ESI) calcd for $C_{16}H_{19}O_3^+$ $[M+H]^+$ 259.1329; found 259.1337.

(E)-7a-hydroxy-4a-methyl-3-(4-methylbenzylidene)hexahydrocyclopenta[b]pyran-5(2H)-one (7b)



Chemical Formula: C₁₇H₂₀O₃
Exact Mass: 272.1412

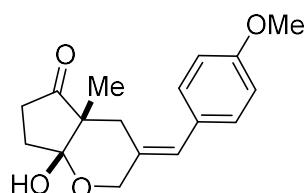
7b was prepared according to general procedure 2.2 using **6b** (48 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7b** as colorless oil (32.7 mg, 60% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.26 - 7.22 (m, 2H), 7.19 - 7.13 (m, 2H), 6.32 (s, 1H), 4.55 (dt, *J* = 12.2, 1.6 Hz, 1H), 3.89 (dd, *J* = 12.2, 2.0 Hz, 1H), 3.19 (dd, *J* = 14.6, 2.0 Hz, 1H), 2.90 (bs, 1H), 2.46 - 2.39 (m, 2H), 2.35 (s, 3H), 2.20 - 2.11 (m, 3H), 1.04 (s, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 216.5, 136.4, 133.4, 131.9, 128.9, 128.7, 125.5, 103.1, 66.6, 53.0, 35.1, 32.8, 29.8, 21.2, 20.6;

HRMS: (ESI) calcd for C₁₇H₂₁O₃⁺[M+H]⁺ 273.1485; found 273.1481.

(E)-7a-hydroxy-3-(4-methoxybenzylidene)-4a-methylhexahydrocyclopenta[b]pyran-5(2H)-one (7c)



Chemical Formula: C₁₇H₂₀O₄
Exact Mass: 288.1362

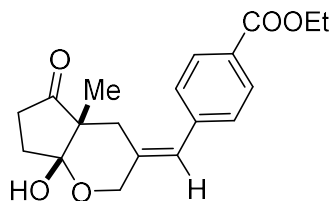
7c was prepared according to general procedure 2.2 using **6c** (51.2 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7c** as colorless oil (45.0 mg, 78% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.34 - 7.26 (m, 2H), 6.94 - 6.85 (m, 2H), 6.29 (s, 1H), 4.61 - 4.50 (m, 1H), 3.97 - 3.83 (m, 1H), 3.81 (s, 3H), 3.28 - 3.06 (m, 1H), 2.74 (bs, 1H), 2.53 - 2.31 (m, 2H), 2.24 - 2.08 (m, 3H), 1.05 (s, 3H);

^{13}C NMR (151 MHz, CDCl_3) δ 216.6, 158.4, 131.2, 130.0, 128.9, 125.1, 113.7, 103.1, 66.7, 55.2, 53.0, 35.1, 32.9, 29.7, 20.7;

HRMS: (ESI) calcd for $\text{C}_{17}\text{H}_{20}\text{O}_4\text{Na}^+[\text{M}+\text{Na}]^+$ 311.1254; found 311.1253.

ethyl **(E)-4-((7a-hydroxy-4a-methyl-5-oxohexahydrocyclopenta[b]pyran-3(2H)-ylidene)methyl)benzoate (7d)**



Chemical Formula: $\text{C}_{19}\text{H}_{22}\text{O}_5$
Exact Mass: 330.1467

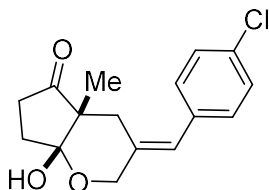
7d was prepared according to general procedure 2.2 using **6d** (59.6 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7d** as colorless oil (37.0 mg, 56% yield).

^1H NMR (600 MHz, CDCl_3) δ 8.05 - 8.01 (m, 2H), 7.44 - 7.40 (m, 2H), 6.37 (s, 1H), 4.57 (dt, J = 12.2, 1.6 Hz, 1H), 4.38 (q, J = 7.2 Hz, 2H), 3.92 - 3.89 (m, 1H), 3.15 (dd, J = 14.6, 2.0 Hz, 1H), 2.46 (bs, 1H), 2.46 - 2.37 (m, 2H), 2.21 - 2.11 (m, 3H), 1.39 (t, J = 7.1 Hz, 3H), 1.05 (s, 3H);

^{13}C NMR (151 MHz, CDCl_3) δ 216.2, 166.6, 141.0, 134.7, 129.6, 128.78, 128.77, 124.9, 103.1, 66.5, 60.9, 53.1, 35.1, 32.9, 29.8, 20.7, 14.4;

HRMS: (ESI) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_5^+[\text{M}+\text{H}]^+$ 331.1540; found 331.1541.

(E)-3-(4-chlorobenzylidene)-7a-hydroxy-4a-methylhexahydrocyclopenta[b]pyran-5(2H)-one (7e)



Chemical Formula: $\text{C}_{16}\text{H}_{17}\text{ClO}_3$
Exact Mass: 292.0866

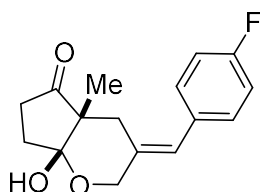
7e was prepared according to general procedure 2.2 using **6e** (52 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7e** as colorless oil (45.0 mg, 77% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.36 - 7.24 (m, 4H), 6.28 (s, 1H), 4.54 (d, *J* = 12.1 Hz, 1H), 3.87 (dd, *J* = 12.2, 2.1 Hz, 1H), 3.11 (dd, *J* = 14.5, 2.1 Hz, 1H), 2.87 (bs, 1H), 2.51 - 2.37 (m, 2H), 2.23 - 2.01 (m, 3H), 1.04 (s, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 216.5, 134.7, 133.4, 132.5, 130.1, 128.4, 124.4, 103.0, 66.4, 53.1, 35.1, 32.8, 29.6, 20.6;

HRMS: (ESI) calcd for C₁₆H₁₇ClO₃Na⁺[M+Na]⁺ 315.0758; found 315.0763.

(E)-3-(4-fluorobenzylidene)-7a-hydroxy-4a-methylhexahydrocyclopenta[b]pyran-5(2H)-one (7f)



Chemical Formula: C₁₆H₁₇FO₃
Exact Mass: 276.1162

7f was prepared according to general procedure 2.2 using **6f** (48.8 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7f** as colorless oil (33.2 mg, 60% yield).

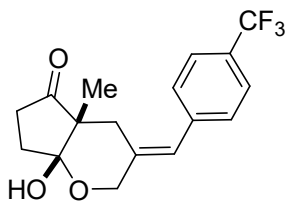
¹H NMR (400 MHz, CDCl₃) δ 7.36 - 7.29 (m, 2H), 7.09 - 7.00 (m, 2H), 6.30 (s, 1H), 4.55 (dt, *J* = 12.2, 1.5 Hz, 1H), 3.88 (dd, *J* = 12.2, 2.0 Hz, 1H), 3.12 (dd, *J* = 14.5, 1.9 Hz, 1H), 2.70 (bs, 1H), 2.53 - 2.34 (m, 2H), 2.24 - 2.06 (m, 3H), 1.05 (s, 3H);

¹⁹F NMR (376 MHz, CDCl₃) δ - 115.27 (m);

¹³C NMR (151 MHz, CDCl₃) δ 216.5, 161.7 (d, *J* = 245.9 Hz), 132.7, 132.3 (d, *J* = 3.2 Hz), 130.4 (d, *J* = 8.1 Hz), 124.5, 115.1 (d, *J* = 21.2 Hz), 103.1, 66.5, 53.1, 35.1, 32.8, 29.6, 20.7;

HRMS: (ESI) calcd for C₁₆H₁₇FO₃Na⁺[M+Na]⁺ 299.1054; found 299.1054.

(E)-7a-hydroxy-4a-methyl-3-(4-(trifluoromethyl)benzylidene)hexahydrocyclopenta[b]pyran-5(2H)-one (7g)



Chemical Formula: C₁₇H₁₇F₃O₃

Exact Mass: 326.1130

7g was prepared according to general procedure 2.2 using **6g** (58.8 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7g** as colorless oil (35.2 mg, 54% yield).

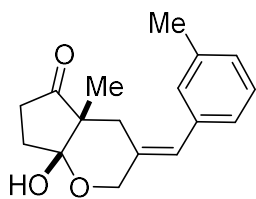
¹H NMR (600 MHz, CDCl₃) δ 7.63 - 7.59 (m, 2H), 7.48 - 7.45 (m, 2H), 6.35 (s, 1H), 4.57 (dt, *J* = 12.3, 1.5 Hz, 1H), 3.90 (dd, *J* = 12.3, 2.0 Hz, 1H), 3.12 (dd, *J* = 14.6, 2.0 Hz, 1H), 2.63 (bs, 1H), 2.48 - 2.40 (m, 2H), 2.21 - 2.12 (m, 3H), 1.05 (s, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 216.4, 140.0, 134.9, 129.1, 128.8 (q, *J* = 31.7 Hz), 125.2 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 273.3 Hz), 124.4, 103.1, 66.4, 53.2, 35.1, 32.8, 29.7, 20.7;

¹⁹F NMR (376 MHz, CDCl₃) δ - 62.32;

HRMS: (ESI) calcd for C₁₇H₁₈F₃O₃⁺ [M+H]⁺ 327.1203; found 327.1213.

(E)-7a-hydroxy-4a-methyl-3-(3-methylbenzylidene)hexahydrocyclopenta[b]pyran-5(2H)-one (7h)



Chemical Formula: C₁₇H₂₀O₃

Exact Mass: 272.1412

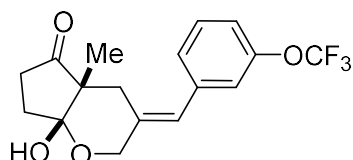
7h was prepared according to general procedure 2.2 using **6h** (48.1 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7h** as colorless oil (40.3 mg, 74% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.29 - 7.20 (m, 1H), 7.21 - 7.11 (m, 2H), 7.09 - 7.03 (m, 1H), 6.32 (s, 1H), 4.56 (dt, *J* = 12.3, 1.6 Hz, 1H), 3.89 (dd, *J* = 12.2, 2.0 Hz, 1H), 3.19 (dd, *J* = 14.7, 2.0 Hz, 1H), 2.86 (bs, 1H), 2.48 - 2.38 (m, 2H), 2.37 (s, 3H), 2.22 - 2.09 (m, 3H), 1.05 (s, 3H);

^{13}C NMR (151 MHz, CDCl_3) δ 216.5, 137.7, 136.2, 132.4, 129.5, 128.1, 127.6, 125.8, 125.7, 103.1, 66.6, 53.0, 35.1, 32.8, 29.8, 21.4, 20.6;

HRMS: (ESI) calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3\text{Na}^+[\text{M}+\text{Na}]^+$ 295.1305; found 295.1306.

(*E*)-7a-hydroxy-4a-methyl-3-(3-(trifluoromethoxy)benzylidene)hexahydrocyclopenta[*b*]pyran-5(2*H*)-one (7i)



Chemical Formula: $\text{C}_{17}\text{H}_{17}\text{F}_3\text{O}_4$

Exact Mass: 342.1079

7i was prepared according to general procedure 2.2 using **6i** (62 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7i** as colorless oil (41.1 mg, 60% yield).

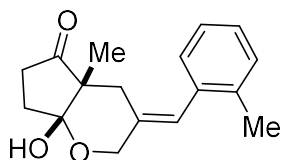
^1H NMR (600 MHz, CDCl_3) δ 7.40 - 7.35 (m, 1H), 7.32 - 7.30 (m, 1H), 7.23 (s, 1H), 7.12 - 7.08 (m, 1H), 6.31 (s, 1H), 4.56 (dt, $J = 12.3, 1.5$ Hz, 1H), 3.89 (dd, $J = 12.4, 2.1$ Hz, 1H), 3.12 (dd, $J = 14.6, 2.1$ Hz, 1H), 2.59 (bs, 1H), 2.48 - 2.40 (m, 2H), 2.22 - 2.11 (m, 3H), 1.06 (s, 3H);

^{13}C NMR (151 MHz, CDCl_3) δ 216.3, 149.2, 138.3, 134.3, 129.6, 127.2, 124.2, 121.3, 120.5 (q, $J = 257.3$ Hz), 119.2, 103.0, 66.4, 53.1, 35.0, 32.8, 29.6, 20.6;

^{19}F NMR (376 MHz, CDCl_3) δ - 57.58;

HRMS: (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{F}_3\text{O}_4\text{Na}^+[\text{M}+\text{Na}]^+$ 365.0971; found 365.0985.

(*E*)-7a-hydroxy-4a-methyl-3-(2-methylbenzylidene)hexahydrocyclopenta[*b*]pyran-5(2*H*)-one (7j)



Chemical Formula: $\text{C}_{17}\text{H}_{20}\text{O}_3$

Exact Mass: 272.1412

7j was prepared according to general procedure 2.2 using **6j** (48.1 mg, 0.2 mmol) and was

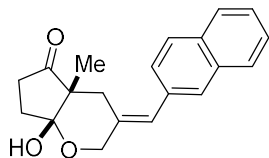
purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7j** as colorless oil (30.5 mg, 56% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.29 - 7.24 (m, 1H), 7.23 - 7.14 (m, 3H), 6.32 (s, 1H), 4.57 (d, J = 12.2 Hz, 1H), 3.95 (d, J = 12.2 Hz, 1H), 2.89 (d, J = 14.5 Hz, 1H), 2.61 (bs, 1H), 2.47 - 2.38 (m, 2H), 2.19 - 2.05 (m, 6H), 0.99 (s, 3H);

^{13}C NMR (151 MHz, CDCl_3) δ 216.0, 136.5, 135.4, 132.6, 129.7, 129.1, 127.2, 125.5, 124.9, 103.1, 66.3, 53.0, 35.1, 32.8, 29.8, 20.5, 19.8;

HRMS: (ESI) calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 295.1305; found 295.1302.

(E)-7a-hydroxy-4a-methyl-3-(naphthalen-2-ylmethylene)hexahydrocyclopenta[b]pyran-5(2H)-one (7k)



Chemical Formula: $\text{C}_{20}\text{H}_{20}\text{O}_3$
Exact Mass: 308.1412

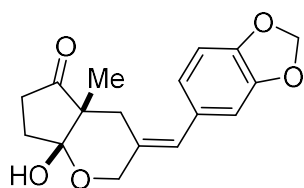
7k was prepared according to general procedure 2.2 using **6k** (55.2 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7k** as colorless oil (37.6 mg, 61% yield).

^1H NMR (400 MHz, CDCl_3) δ 7.91 - 7.78 (m, 4H), 7.54 - 7.41 (m, 3H), 6.50 (s, 1H), 4.61 (dt, J = 12.1, 1.6 Hz, 1H), 3.96 (dd, J = 12.3, 2.1 Hz, 1H), 3.28 (dd, J = 14.5, 2.1 Hz, 1H), 2.88 (bs, 1H), 2.50 - 2.40 (m, 2H), 2.29 - 2.09 (m, 3H), 1.06 (s, 3H);

^{13}C NMR (151 MHz, CDCl_3) δ 216.5, 133.8, 133.3, 133.1, 132.3, 128.0, 127.7, 127.64, 127.57, 127.1, 125.9, 125.72, 125.67, 103.1, 66.6, 53.1, 35.1, 32.8, 29.8, 20.7;

HRMS: (ESI) calcd for $\text{C}_{20}\text{H}_{20}\text{O}_3\text{Na}^+$ $[\text{M}+\text{Na}]^+$ 331.1305; found 331.1302.

(E)-3-(benzo[d][1,3]dioxol-5-ylmethylene)-7a-hydroxy-4a-methylhexahydrocyclopenta[b]pyran-5(2H)-one (7l)



Chemical Formula: C₁₇H₁₈O₅

Exact Mass: 302.1154

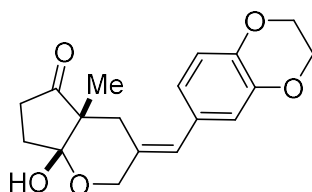
7l was prepared according to general procedure 2.2 using **6l** (54 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7l** as colorless oil (46.0 mg, 76% yield).

¹H NMR (400 MHz, CDCl₃) δ 6.88 (s, 1H), 6.83 - 6.76 (m, 2H), 6.25 (s, 1H), 5.98 - 5.93 (m, 2H), 4.53 (dd, *J* = 12.2, 1.6 Hz, 1H), 3.86 (dd, *J* = 12.3, 2.0 Hz, 1H), 3.17 (dd, *J* = 14.5, 2.0 Hz, 1H), 2.68 (bs, 1H), 2.47 - 2.38 (m, 2H), 2.21 - 2.07 (m, 3H), 1.05 (s, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 216.5, 147.4, 146.3, 131.7, 130.3, 125.3, 122.6, 109.1, 108.2, 103.1, 100.9, 66.6, 53.0, 35.1, 32.8, 29.7, 20.6;

HRMS: (ESI) calcd for C₁₇H₁₈O₅Na⁺ [M+Na]⁺ 325.1046; found 325.1057.

(E)-3-((2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)methylene)-7a-hydroxy-4a-methylhexahydrocyclopenta[*b*]pyran-5(2H)-one (7m)



Chemical Formula: C₁₈H₂₀O₅

Exact Mass: 316.1311

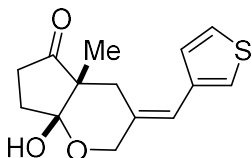
7m was prepared according to general procedure 2.2 using **6m** (56.8 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7m** as colorless oil (41.7 mg, 66% yield).

¹H NMR (400 MHz, CDCl₃) δ 6.91 - 6.87 (m, 1H), 6.85 - 6.81 (m, 2H), 6.21 (s, 1H), 4.53 (dt, *J* = 12.3, 1.5 Hz, 1H), 4.25 (s, 4H), 3.85 (dd, *J* = 12.3, 1.9 Hz, 1H), 3.20 (dd, *J* = 14.6, 1.9 Hz, 1H), 3.04 (bs, 1H), 2.45 - 2.36 (m, 2H), 2.21 - 2.08 (m, 3H), 1.04 (s, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 216.5, 143.1, 142.5, 131.6, 129.8, 125.0, 122.2, 117.6, 117.0, 103.1, 66.6, 64.4, 64.3, 52.9, 35.1, 32.8, 29.8, 20.6;

HRMS: (ESI) calcd for $C_{18}H_{20}O_5Na^+[M+Na]^+$ 339.1203; found 339.1193.

(E)-7a-hydroxy-4a-methyl-3-(thiophen-3-ylmethylene)hexahydrocyclopenta[b]pyran-5(2H)-one (7n)



Chemical Formula: $C_{14}H_{16}O_3S$
Exact Mass: 264.0820

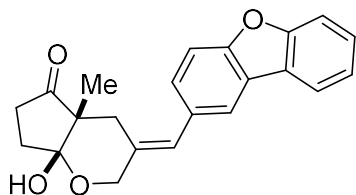
7n was prepared according to general procedure 2.2 using **6n** (46.4 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7n** as colorless oil (35.4 mg, 67% yield).

1H NMR (400 MHz, $CDCl_3$) δ 7.41 - 7.35 (m, 1H), 7.32 - 7.27 (m, 1H), 7.20 - 7.15 (m, 1H), 6.26 (s, 1H), 4.53 (dt, $J = 12.2, 1.5$ Hz, 1H), 3.86 (dd, $J = 12.1, 2.1$ Hz, 1H), 3.27 (dd, $J = 14.5, 2.1$ Hz, 1H), 2.83 (bs, 1H), 2.49 - 2.37 (m, 2H), 2.25 - 2.06 (m, 3H), 1.08 (s, 3H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 216.8, 137.1, 132.2, 128.5, 125.1, 123.3, 119.9, 103.1, 66.6, 53.2, 35.1, 32.9, 30.2, 20.7;

HRMS: (ESI) calcd for $C_{14}H_{17}O_3S^+[M+H]^+$ 265.0893, found 265.0894.

(E)-3-(dibenzo[b,d]furan-2-ylmethylene)-7a-hydroxy-4a-methylhexahydrocyclopenta[b]pyran-5(2H)-one (7o)



Chemical Formula: $C_{22}H_{20}O_4$
Exact Mass: 348.1362

7o was prepared according to general procedure 2.2 using **6o** (63.2 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7o** as colorless oil (42.0 mg, 60% yield).

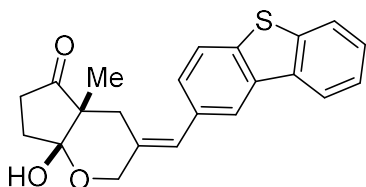
1H NMR (400 MHz, $CDCl_3$) δ 8.03 - 7.97 (m, 2H), 7.60 - 7.52 (m, 2H), 7.49 - 7.41 (m, 2H),

7.37 - 7.32 (m, 1H), 6.56 - 6.42 (m, 1H), 4.61 (dt, $J = 12.2, 1.5$ Hz, 1H), 3.95 (dd, $J = 12.2, 2.0$ Hz, 1H), 3.26 (dd, $J = 14.5, 2.0$ Hz, 1H), 2.61 (bs, 1H), 2.53 - 2.41 (m, 2H), 2.28 - 2.04 (m, 3H), 1.07 (s, 3H);

^{13}C NMR (151 MHz, CDCl_3) δ 216.6, 156.5, 155.1, 132.4, 131.1, 128.1, 127.1, 125.6, 124.3, 124.2, 122.7, 120.9, 120.8, 111.6, 111.3, 103.2, 66.7, 53.1, 35.2, 32.9, 29.7, 20.7;

HRMS: (ESI) calcd for $\text{C}_{22}\text{H}_{21}\text{O}_4^+[\text{M}+\text{H}]^+$ 349.1434; found 349.1428.

(*E*)-3-(dibenzo[*b,d*]thiophen-2-ylmethylene)-7a-hydroxy-4a-methylhexahydro-cyclopenta[*b*]pyran-5(2*H*)-one (7p)



Chemical Formula: $\text{C}_{22}\text{H}_{20}\text{O}_3\text{S}$

Exact Mass: 364.1133

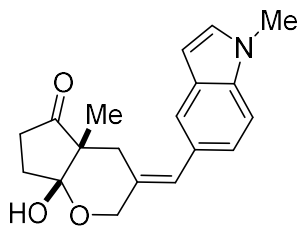
7p was prepared according to general procedure 2.2 using **6p** (66.4 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7p** as colorless oil (54.6 mg, 75% yield).

^1H NMR (400 MHz, CDCl_3) δ 8.33 - 8.28 (m, 2H), 7.87 - 7.81 (m, 2H), 7.49 - 7.44 (m, 2H), 7.43 - 7.39 (m, 1H), 6.53 (s, 1H), 4.62 (dt, $J = 12.1, 1.5$ Hz, 1H), 3.97 (dd, $J = 12.3, 2.0$ Hz, 1H), 3.31 (dd, $J = 14.5, 2.1$ Hz, 1H), 2.55 - 2.38 (m, 3H), 2.25 - 2.14 (m, 3H), 1.08 (s, 3H);

^{13}C NMR (151 MHz, CDCl_3) δ 216.7, 139.7, 137.8, 135.74, 135.68, 132.9, 132.7, 127.5, 126.7, 125.5, 124.4, 122.7, 122.5, 121.95, 121.91, 103.2, 66.8, 53.2, 35.2, 33.0, 29.7, 20.8;

HRMS: (ESI) calcd for $\text{C}_{22}\text{H}_{20}\text{O}_3\text{SNa}^+[\text{M}+\text{Na}]^+$ 387.1025; found 387.1020.

(*E*)-7a-hydroxy-4a-methyl-3-((1-methyl-1*H*-indol-5-yl)methylene)hexahydrocyclopenta[*b*]pyran-5(2*H*)-one (7q)



Chemical Formula: C₁₉H₂₁NO₃
Exact Mass: 311.1521

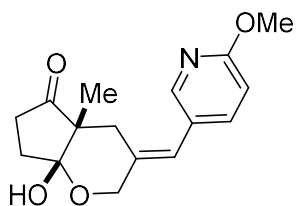
7q was prepared according to general procedure 2.2 using **6q** (55.8 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7q** as colorless oil (34.8 mg, 56% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.61 (s, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.24 (d, *J* = 8.5 Hz, 1H), 7.04 (d, *J* = 3.1 Hz, 1H), 6.50 (d, *J* = 2.8 Hz, 2H), 4.60 (d, *J* = 12.2 Hz, 1H), 3.95 (d, *J* = 12.1 Hz, 1H), 3.84 - 3.45 (m, 3H), 3.29 (d, *J* = 14.5 Hz, 1H), 2.87 (bs, 1H), 2.51 - 2.38 (m, 2H), 2.28 - 1.96 (m, 3H), 1.05 (s, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 216.6, 135.7, 130.4, 129.0, 128.4, 127.5, 126.8, 122.9, 121.1, 108.9, 103.2, 101.1, 66.8, 52.9, 35.1, 32.83, 32.82, 29.9, 20.6;

HRMS: (ESI) calcd for C₁₉H₂₂NO₃⁺[M+H]⁺ 312.1594, found 312.1594.

(E)-7a-hydroxy-3-((6-methoxypyridin-3-yl)methylene)-4a-methylhexahydrocyclopenta[b]pyran-5(2H)-one (7r)



Chemical Formula: C₁₆H₁₉NO₄
Exact Mass: 289.1314

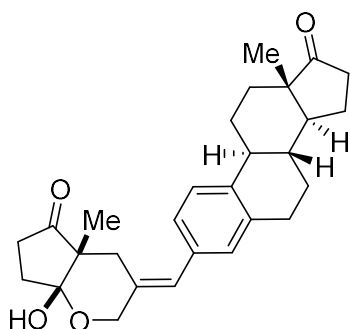
7r was prepared according to general procedure 2.2 using **6r** (51.4 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7r** as colorless oil (40.5 mg, 70% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.10 (s, 1H), 7.71 - 7.60 (m, 1H), 6.79 - 6.71 (m, 1H), 6.21 (s, 1H), 4.55 (d, *J* = 12.2 Hz, 1H), 3.94 (s, 3H), 3.87 (dd, *J* = 12.3, 2.0 Hz, 1H), 3.20 (bs, 1H), 3.09 (d, *J* = 14.4 Hz, 1H), 2.45 - 2.35 (m, 2H), 2.22 - 2.07 (m, 3H), 1.04 (s, 3H);

^{13}C NMR (151 MHz, CDCl_3) δ 216.5, 162.8, 146.8, 139.2, 133.5, 125.4, 121.7, 110.4, 103.0, 66.3, 53.5, 53.1, 35.0, 32.8, 29.7, 20.6;

HRMS: (ESI) calcd for $\text{C}_{16}\text{H}_{20}\text{NO}_4^+$ $[\text{M}+\text{H}]^+$ 290.1387; found 290.1397.

(E)-7a-hydroxy-4a-methyl-3-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[*a*]phenanthren-3-yl)methylene)hexahydrocyclopenta[*b*]pyran-5(2H)-one (7s)



Chemical Formula: $\text{C}_{28}\text{H}_{34}\text{O}_4$

Exact Mass: 434.2457

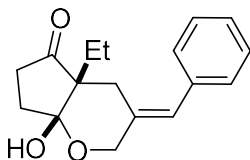
7s was prepared according to general procedure 2.2 using **6s** (80.4 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7s** as colorless oil (56.5 mg, 65% yield).

^1H NMR (600 MHz, CDCl_3) δ 7.29 - 7.26 (m, 1H), 7.19 - 7.13 (m, 1H), 7.09 - 7.04 (m, 1H), 6.28 (s, 1H), 4.56 (d, $J = 12.2$ Hz, 1H), 3.88 (d, $J = 12.0$ Hz, 1H), 3.20 (d, $J = 14.6$ Hz, 1H), 3.05 (s, 1H), 2.96 - 2.91 (m, 2H), 2.51 (dd, $J = 19.1, 8.6$ Hz, 1H), 2.45 - 2.40 (m, 3H), 2.33 - 2.28 (m, 1H), 2.20 - 2.11 (m, 4H), 2.07 - 1.96 (m, 3H), 1.65 - 1.59 (m, 2H), 1.56 - 1.45 (m, 4H), 1.05 (s, 3H), 0.92 (s, 3H);

^{13}C NMR (101 MHz, CDCl_3) δ 221.2, 216.7, 216.6, 138.28, 138.27, 136.2, 133.8, 132.2, 132.1, 129.40, 129.38, 126.23, 126.17, 125.3, 125.2, 103.0, 66.5, 52.94, 52.92, 50.5, 48.0, 44.4, 44.3, 38.08, 38.06, 35.8, 35.1, 32.8, 31.5, 29.8, 29.35, 29.33, 26.5, 25.60, 25.58, 21.6, 20.7, 13.8;

HRMS: (ESI) calcd for $\text{C}_{28}\text{H}_{35}\text{O}_4^+$ $[\text{M}+\text{H}]^+$ 435.2530; found 435.2546.

(E)-3-benzylidene-4a-ethyl-7a-hydroxyhexahydrocyclopenta[*b*]pyran-5(2H)-one (7t)



Chemical Formula: C₁₇H₂₀O₃

Exact Mass: 272.1412

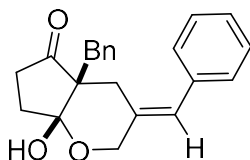
7t was prepared according to general procedure 2.2 using **6t** (48 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7t** as colorless oil (28.3 mg, 52% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.41 - 7.33 (m, 4H), 7.26 - 7.21 (m, 1H), 6.35 (s, 1H), 4.55 (dt, *J* = 12.2, 1.6 Hz, 1H), 3.89 (dd, *J* = 12.3, 2.0 Hz, 1H), 3.32 (d, *J* = 15.1 Hz, 1H), 2.42 - 2.37 (m, 2H), 2.29 - 2.20 (m, 1H), 2.13 - 2.01 (m, 2H), 1.73 - 1.64 (m, 1H), 1.58 - 1.51 (m, 2H), 0.79 (t, *J* = 7.5 Hz, 3H);

¹³C NMR (151 MHz, CDCl₃) δ 214.9, 136.4, 132.5, 128.8, 128.2, 126.7, 125.6, 103.3, 66.4, 56.2, 35.2, 33.1, 26.6, 26.4, 7.4;

HRMS: (ESI) calcd for C₁₇H₂₀O₃Na⁺ [M+Na]⁺ 295.1305; found 295.1302.

(E)-4a-benzyl-3-benzylidene-7a-hydroxyhexahydrocyclopenta[b]pyran-5(2H)-one (7u)



Chemical Formula: C₂₂H₂₂O₃

Exact Mass: 334.1569

7u was prepared according to general procedure 2.2 using **6u** (60.4 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7u** as colorless oil (30.1 mg, 45% yield).

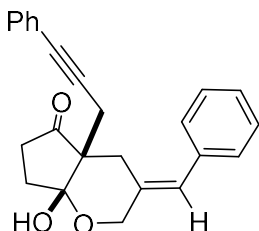
¹H NMR (600 MHz, CDCl₃) δ 7.35 - 7.29 (m, 4H), 7.25 - 7.18 (m, 4H), 7.14 - 7.09 (m, 2H), 6.33 (s, 1H), 4.56 (dd, *J* = 12.1, 1.5 Hz, 1H), 3.88 (dd, *J* = 12.2, 2.0 Hz, 1H), 3.20 (dd, *J* = 14.6, 2.0 Hz, 1H), 2.94 (d, *J* = 13.5 Hz, 1H), 2.80 (d, *J* = 13.6 Hz, 1H), 2.72 (bs, 1H), 2.38 - 2.27 (m, 1H), 2.27 - 2.19 (m, 1H), 2.13 - 2.05 (m, 1H), 1.99 - 1.92 (m, 1H), 1.77 - 1.68 (m, 1H);

¹³C NMR (151 MHz, CDCl₃) δ 216.4, 136.2, 132.3, 130.4, 128.8, 128.2, 128.0, 126.9, 126.8,

125.5, 103.1, 66.2, 57.8, 41.6, 36.3, 33.3, 29.7;

HRMS: (ESI) calcd for $C_{22}H_{23}O_3^+$ $[M+H]^+$ 335.1642; found 335.1643.

(E)-3-benzylidene-7a-hydroxy-4a-(3-phenylprop-2-yn-1-yl)hexahydrocyclopenta[*b*]pyran-5(2*H*)-one (7v)



Chemical Formula: $C_{24}H_{22}O_3$
Exact Mass: 358.1569

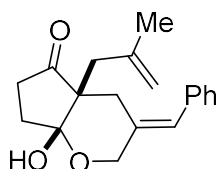
7v was prepared according to general procedure 2.2 using **6v** (65.2 mg, 0.2 mmol) and was purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7v** as colorless oil (22.2 mg, 31% yield).

1H NMR (600 MHz, $CDCl_3$) δ 7.42 - 7.39 (m, 2H), 7.37 - 7.33 (m, 4H), 7.30 - 7.27 (m, 3H), 7.26 - 7.22 (m, 1H), 6.39 (s, 1H), 4.56 (dt, $J = 12.3, 1.5$ Hz, 1H), 3.93 (dd, $J = 12.4, 2.0$ Hz, 1H), 3.44 (dd, $J = 14.6, 2.0$ Hz, 1H), 2.95 (d, $J = 2.8$ Hz, 1H), 2.67 (d, $J = 17.1$ Hz, 1H), 2.58 (d, $J = 17.1$ Hz, 1H), 2.51 - 2.44 (m, 3H), 2.29 - 2.25 (m, 1H), 2.23 - 2.19 (m, 1H);

^{13}C NMR (151 MHz, $CDCl_3$) δ 214.2, 136.2, 132.0, 131.5, 128.8, 128.25, 128.22, 128.1, 126.9, 126.0, 102.8, 84.7, 83.6, 66.3, 55.2, 35.9, 33.6, 28.6, 25.1;

HRMS: (ESI) calcd for $C_{24}H_{23}O_3^+$ $[M+H]^+$ 359.1642; found 359.1636.

(E)-3-benzylidene-7a-hydroxy-4a-(2-methylallyl)hexahydrocyclopenta[*b*]pyran-5(2*H*)-one (7w)



Chemical Formula: $C_{19}H_{22}O_3$
Exact Mass: 298.1569

7w was prepared according to general procedure 2.2 using **6w** (53.2 mg, 0.2 mmol) and was

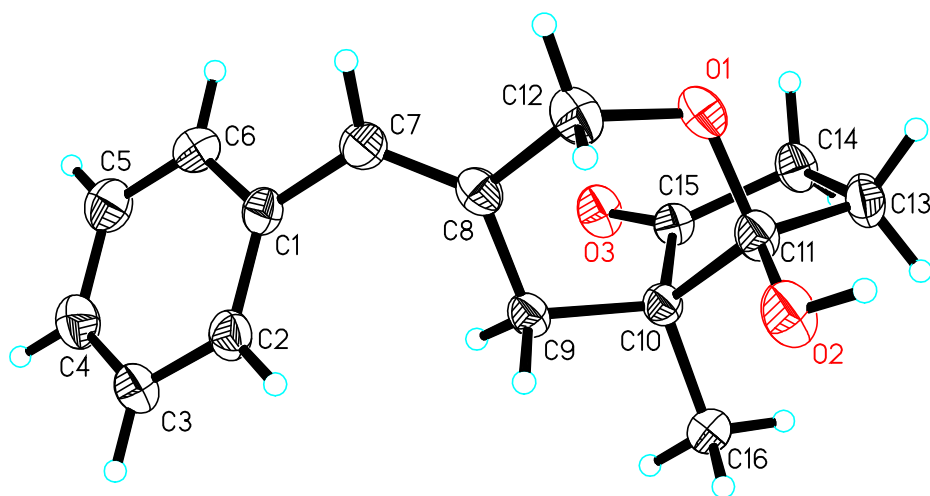
purified by silica gel column chromatography (PE/EtOAc = 6/1) to obtain **7w** as colorless oil (25.2 mg, 42% yield).

^1H NMR (600 MHz, CD_3OD) δ 7.41 - 7.35 (m, 2H), 7.34 - 7.29 (m, 2H), 7.23 - 7.18 (m, 1H), 6.31 (s, 1H), 4.80 (dd, $J = 2.2, 1.4$ Hz, 1H), 4.66 (dd, $J = 2.2, 1.0$ Hz, 1H), 4.55 (dt, $J = 12.3, 1.6$ Hz, 1H), 3.82 (dd, $J = 12.4, 2.0$ Hz, 1H), 3.26 (dd, $J = 14.7, 2.0$ Hz, 1H), 2.47 - 2.40 (m, 1H), 2.35 (s, 2H), 2.31 - 2.24 (m, 2H), 2.14 - 2.03 (m, 2H), 1.62 (dd, $J = 1.5, 0.9$ Hz, 3H);

^{13}C NMR (151 MHz, CD_3OD) δ 218.2, 142.6, 138.1, 134.8, 129.9, 129.1, 127.6, 125.9, 116.0, 103.7, 66.7, 57.7, 43.2, 36.1, 33.0, 28.9, 24.1;

HRMS: (ESI) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_3^+$ $[\text{M}+\text{H}]^+$ 299.1642; found 299.1656.

5. Crystallographic data for compound 7a



CCDC: 2058189

Table 1. Crystal data and structure refinement for **7a**.

Identification code	cu_190522c_0m	
Empirical formula	C ₁₆ H ₁₈ O ₃	
Formula weight	258.30	
Temperature	296(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 2 ₁ /c 1	
Unit cell dimensions	a = 8.8774(4) Å	a = 90°.
	b = 11.4152(4) Å	b = 95.989(2)°.
	c = 13.2381(5) Å	g = 90°.
Volume	1334.19(9) Å ³	
Z	4	
Density (calculated)	1.286 Mg/m ³	
Absorption coefficient	0.708 mm ⁻¹	
F(000)	552	
Crystal size	0.12 x 0.12 x 0.1 mm ³	
Theta range for data collection	5.009 to 64.990°.	
Index ranges	-8<=h<=9, -13<=k<=13, -13<=l<=15	
Reflections collected	7918	
Independent reflections	2166 [R(int) = 0.0279]	
Completeness to theta = 64.990°	95.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7533 and 0.6584	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2166 / 0 / 175	
Goodness-of-fit on F ²	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0329, wR2 = 0.0869	
R indices (all data)	R1 = 0.0372, wR2 = 0.0901	
Extinction coefficient	0.0102(6)	
Largest diff. peak and hole	0.193 and -0.126 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **7a**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3779(2)	6875(1)	766(1)	42(1)
C(2)	2685(2)	7610(1)	1101(1)	45(1)
C(3)	2245(2)	8620(1)	579(1)	50(1)
C(4)	2869(2)	8917(1)	-296(1)	56(1)
C(5)	3955(2)	8196(2)	-644(1)	61(1)
C(6)	4411(2)	7194(1)	-115(1)	53(1)
C(7)	4316(2)	5823(1)	1344(1)	45(1)
C(8)	3481(2)	5042(1)	1779(1)	39(1)
C(9)	1785(1)	5004(1)	1663(1)	37(1)
C(10)	1163(2)	3757(1)	1539(1)	35(1)
C(11)	1973(2)	2893(1)	2308(1)	41(1)
C(12)	4207(2)	4107(1)	2464(1)	50(1)
C(13)	1572(2)	1684(1)	1876(1)	49(1)
C(14)	1625(2)	1848(1)	737(1)	45(1)
C(15)	1463(2)	3154(1)	556(1)	36(1)
C(16)	-562(2)	3765(1)	1570(1)	50(1)
O(1)	3561(1)	2971(1)	2251(1)	45(1)
O(2)	1585(2)	3131(1)	3281(1)	63(1)
O(3)	1551(1)	3637(1)	-249(1)	50(1)

Table 3. Bond lengths [Å] and angles [°] for **7a**.

C(1)-C(2)	1.391(2)
C(1)-C(6)	1.395(2)
C(1)-C(7)	1.475(2)
C(2)-H(2A)	0.9300
C(2)-C(3)	1.380(2)
C(3)-H(3)	0.9300
C(3)-C(4)	1.377(2)
C(4)-H(4)	0.9300
C(4)-C(5)	1.383(2)
C(5)-H(5)	0.9300
C(5)-C(6)	1.380(2)
C(6)-H(6)	0.9300
C(7)-H(7)	0.9300
C(7)-C(8)	1.3288(19)
C(8)-C(9)	1.4986(19)
C(8)-C(12)	1.5019(19)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(9)-C(10)	1.5284(17)
C(10)-C(11)	1.5405(18)
C(10)-C(15)	1.5206(17)
C(10)-C(16)	1.5357(19)
C(11)-C(13)	1.522(2)
C(11)-O(1)	1.4228(17)
C(11)-O(2)	1.3947(16)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(12)-O(1)	1.4339(17)
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(13)-C(14)	1.526(2)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(14)-C(15)	1.5148(18)
C(15)-O(3)	1.2097(15)
C(16)-H(16A)	0.9600

C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600
O(2)-H(2)	0.8200
C(2)-C(1)-C(6)	117.65(13)
C(2)-C(1)-C(7)	121.65(13)
C(6)-C(1)-C(7)	120.64(13)
C(1)-C(2)-H(2A)	119.5
C(3)-C(2)-C(1)	121.02(14)
C(3)-C(2)-H(2A)	119.5
C(2)-C(3)-H(3)	119.7
C(4)-C(3)-C(2)	120.61(15)
C(4)-C(3)-H(3)	119.7
C(3)-C(4)-H(4)	120.3
C(3)-C(4)-C(5)	119.33(15)
C(5)-C(4)-H(4)	120.3
C(4)-C(5)-H(5)	119.9
C(6)-C(5)-C(4)	120.13(15)
C(6)-C(5)-H(5)	119.9
C(1)-C(6)-H(6)	119.4
C(5)-C(6)-C(1)	121.26(15)
C(5)-C(6)-H(6)	119.4
C(1)-C(7)-H(7)	116.4
C(8)-C(7)-C(1)	127.29(13)
C(8)-C(7)-H(7)	116.4
C(7)-C(8)-C(9)	125.14(12)
C(7)-C(8)-C(12)	121.02(13)
C(9)-C(8)-C(12)	113.83(12)
C(8)-C(9)-H(9A)	109.0
C(8)-C(9)-H(9B)	109.0
C(8)-C(9)-C(10)	112.73(10)
H(9A)-C(9)-H(9B)	107.8
C(10)-C(9)-H(9A)	109.0
C(10)-C(9)-H(9B)	109.0
C(9)-C(10)-C(11)	112.77(11)
C(9)-C(10)-C(16)	110.01(10)
C(15)-C(10)-C(9)	114.80(10)
C(15)-C(10)-C(11)	99.42(10)
C(15)-C(10)-C(16)	106.81(11)

C(16)-C(10)-C(11)	112.57(11)
C(13)-C(11)-C(10)	104.97(11)
O(1)-C(11)-C(10)	108.76(10)
O(1)-C(11)-C(13)	103.36(11)
O(2)-C(11)-C(10)	110.03(11)
O(2)-C(11)-C(13)	116.94(12)
O(2)-C(11)-O(1)	112.22(11)
C(8)-C(12)-H(12A)	109.1
C(8)-C(12)-H(12B)	109.1
H(12A)-C(12)-H(12B)	107.8
O(1)-C(12)-C(8)	112.70(11)
O(1)-C(12)-H(12A)	109.1
O(1)-C(12)-H(12B)	109.1
C(11)-C(13)-H(13A)	111.1
C(11)-C(13)-H(13B)	111.1
C(11)-C(13)-C(14)	103.32(10)
H(13A)-C(13)-H(13B)	109.1
C(14)-C(13)-H(13A)	111.1
C(14)-C(13)-H(13B)	111.1
C(13)-C(14)-H(14A)	110.7
C(13)-C(14)-H(14B)	110.7
H(14A)-C(14)-H(14B)	108.8
C(15)-C(14)-C(13)	105.31(11)
C(15)-C(14)-H(14A)	110.7
C(15)-C(14)-H(14B)	110.7
C(14)-C(15)-C(10)	109.48(10)
O(3)-C(15)-C(10)	125.50(11)
O(3)-C(15)-C(14)	125.02(12)
C(10)-C(16)-H(16A)	109.5
C(10)-C(16)-H(16B)	109.5
C(10)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(11)-O(1)-C(12)	115.12(11)
C(11)-O(2)-H(2)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **7a**. The anisotropic displacement

factor exponent takes the form: $-2p^2[h^2 a^*2U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
C(1)	40(1)	36(1)	50(1)	-4(1)	2(1)	-8(1)
C(2)	54(1)	37(1)	46(1)	-5(1)	10(1)	-6(1)
C(3)	56(1)	38(1)	58(1)	-5(1)	7(1)	1(1)
C(4)	65(1)	43(1)	60(1)	9(1)	5(1)	-2(1)
C(5)	66(1)	58(1)	60(1)	12(1)	19(1)	-6(1)
C(6)	46(1)	52(1)	65(1)	2(1)	17(1)	-2(1)
C(7)	38(1)	42(1)	54(1)	-4(1)	-1(1)	-2(1)
C(8)	45(1)	35(1)	37(1)	-6(1)	-2(1)	2(1)
C(9)	46(1)	31(1)	33(1)	-1(1)	7(1)	4(1)
C(10)	42(1)	33(1)	31(1)	3(1)	9(1)	2(1)
C(11)	58(1)	38(1)	29(1)	5(1)	10(1)	4(1)
C(12)	56(1)	42(1)	47(1)	-1(1)	-10(1)	2(1)
C(13)	63(1)	34(1)	51(1)	9(1)	10(1)	0(1)
C(14)	57(1)	34(1)	45(1)	-4(1)	3(1)	-1(1)
C(15)	39(1)	36(1)	32(1)	0(1)	2(1)	0(1)
C(16)	48(1)	44(1)	59(1)	6(1)	18(1)	0(1)
O(1)	54(1)	36(1)	42(1)	3(1)	-4(1)	8(1)
O(2)	105(1)	55(1)	32(1)	10(1)	22(1)	13(1)
O(3)	75(1)	46(1)	30(1)	2(1)	8(1)	3(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for

7a.

	x	y	z	U(eq)
H(2A)	2243	7418	1686	54
H(3)	1520	9105	820	60
H(4)	2564	9596	-648	67
H(5)	4378	8387	-1237	73
H(6)	5154	6723	-351	64
H(7)	5356	5693	1410	54
H(9A)	1407	5463	1074	44
H(9B)	1415	5359	2255	44
H(12A)	5282	4078	2389	60
H(12B)	4095	4311	3164	60
H(13A)	570	1447	2026	59
H(13B)	2304	1103	2147	59
H(14A)	2580	1567	532	54
H(14B)	804	1425	356	54
H(16A)	-1012	4328	1092	74
H(16B)	-790	3969	2241	74
H(16C)	-961	3001	1397	74
H(2)	1727	2544	3637	94

Table 6. Torsion angles [°] for **7a**.

C(1)-C(2)-C(3)-C(4)	0.8(2)
C(1)-C(7)-C(8)-C(9)	7.6(2)
C(1)-C(7)-C(8)-C(12)	-171.39(13)
C(2)-C(1)-C(6)-C(5)	-0.8(2)
C(2)-C(1)-C(7)-C(8)	43.6(2)
C(2)-C(3)-C(4)-C(5)	-0.5(2)
C(3)-C(4)-C(5)-C(6)	-0.4(3)
C(4)-C(5)-C(6)-C(1)	1.0(3)
C(6)-C(1)-C(2)-C(3)	-0.1(2)
C(6)-C(1)-C(7)-C(8)	-139.49(16)
C(7)-C(1)-C(2)-C(3)	176.90(12)
C(7)-C(1)-C(6)-C(5)	-177.83(14)
C(7)-C(8)-C(9)-C(10)	138.81(13)
C(7)-C(8)-C(12)-O(1)	-134.31(14)
C(8)-C(9)-C(10)-C(11)	45.77(14)
C(8)-C(9)-C(10)-C(15)	-67.16(14)
C(8)-C(9)-C(10)-C(16)	172.35(11)
C(8)-C(12)-O(1)-C(11)	-57.23(16)
C(9)-C(8)-C(12)-O(1)	46.62(17)
C(9)-C(10)-C(11)-C(13)	-163.01(11)
C(9)-C(10)-C(11)-O(1)	-52.93(14)
C(9)-C(10)-C(11)-O(2)	70.36(15)
C(9)-C(10)-C(15)-C(14)	148.79(12)
C(9)-C(10)-C(15)-O(3)	-31.56(18)
C(10)-C(11)-C(13)-C(14)	39.02(14)
C(10)-C(11)-O(1)-C(12)	59.42(13)
C(11)-C(10)-C(15)-C(14)	28.20(14)
C(11)-C(10)-C(15)-O(3)	-152.15(13)
C(11)-C(13)-C(14)-C(15)	-20.39(15)
C(12)-C(8)-C(9)-C(10)	-42.16(15)
C(13)-C(11)-O(1)-C(12)	170.59(10)
C(13)-C(14)-C(15)-C(10)	-5.40(16)
C(13)-C(14)-C(15)-O(3)	174.95(13)
C(15)-C(10)-C(11)-C(13)	-40.95(13)
C(15)-C(10)-C(11)-O(1)	69.14(12)
C(15)-C(10)-C(11)-O(2)	-167.57(11)

C(16)-C(10)-C(11)-C(13)	71.79(14)
C(16)-C(10)-C(11)-O(1)	-178.13(10)
C(16)-C(10)-C(11)-O(2)	-54.84(15)
C(16)-C(10)-C(15)-C(14)	-88.97(13)
C(16)-C(10)-C(15)-O(3)	90.69(15)
O(1)-C(11)-C(13)-C(14)	-74.91(12)
O(2)-C(11)-C(13)-C(14)	161.27(12)
O(2)-C(11)-O(1)-C(12)	-62.55(14)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **7a** [\AA and $^\circ$].

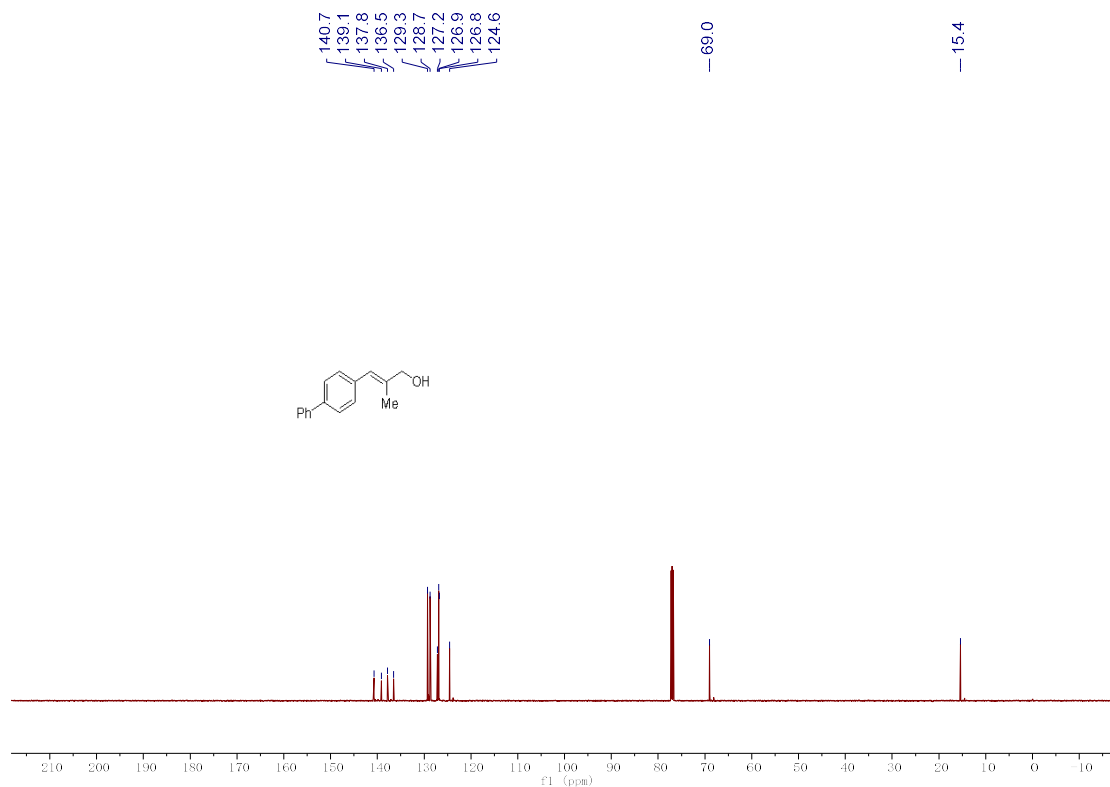
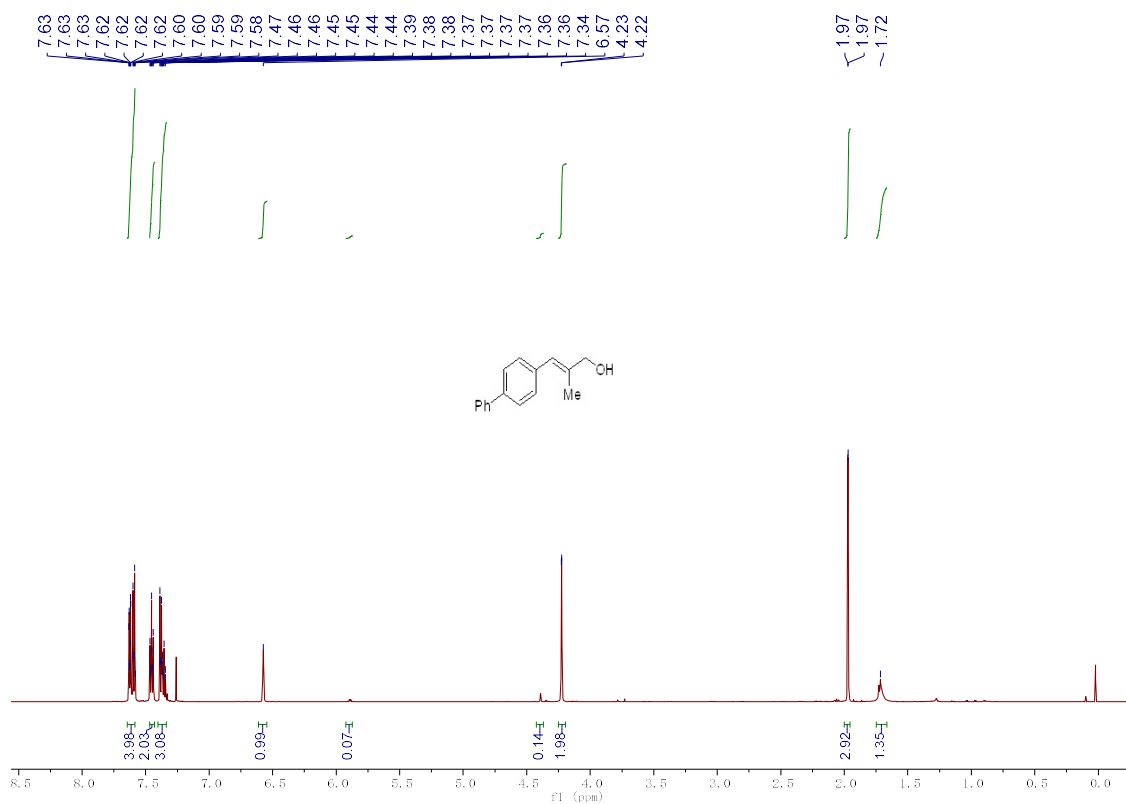
D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
O(2)-H(2)...O(3)#1	0.82	2.02	2.8055(14)	161.1

Symmetry transformations used to generate equivalent atoms:

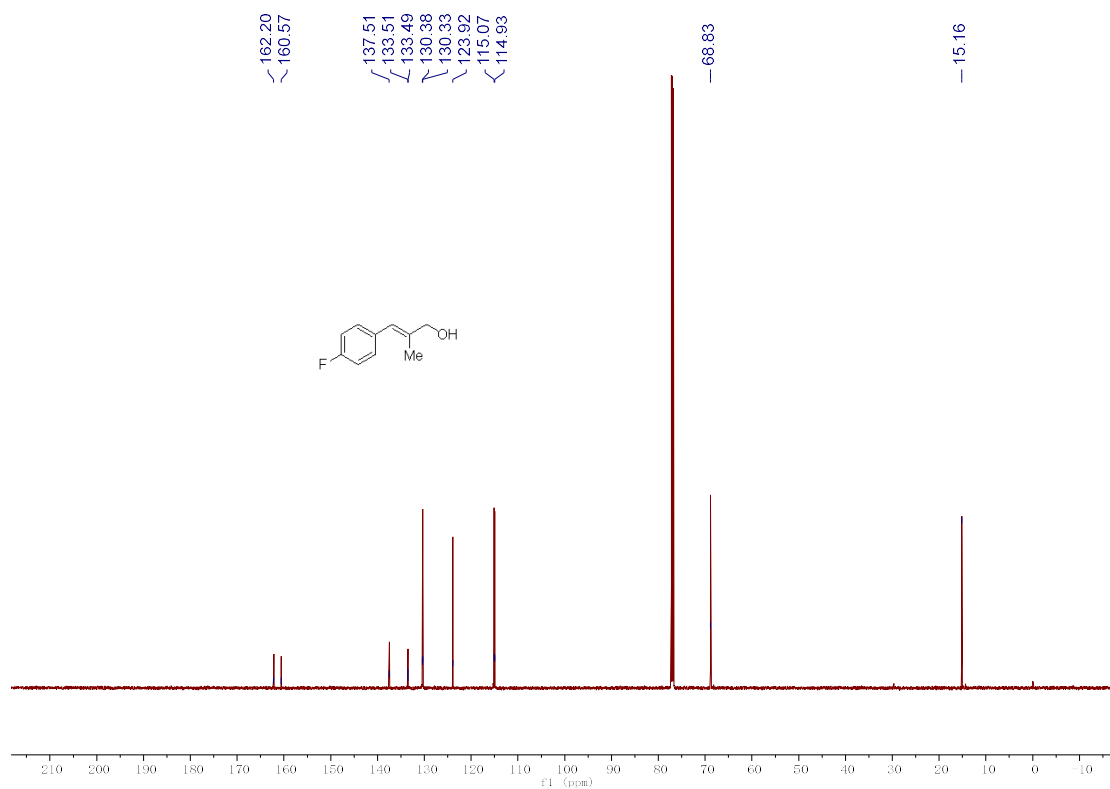
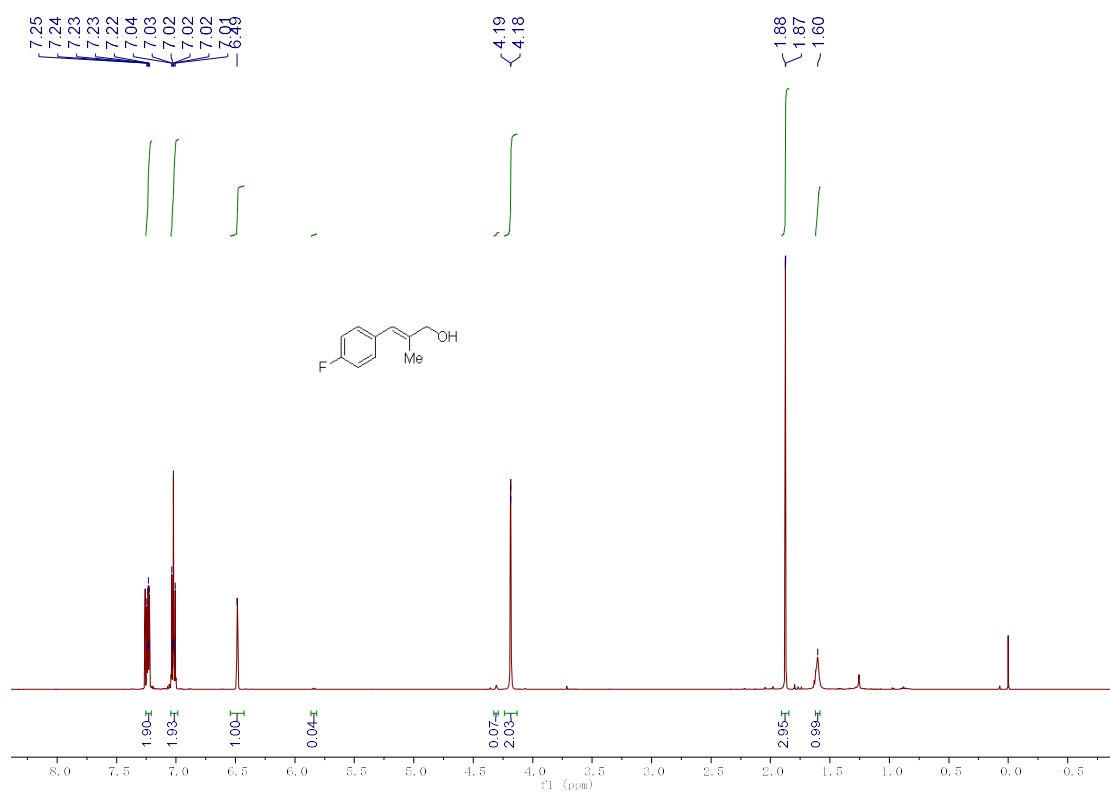
#1 $x, -y+1/2, z+1/2$

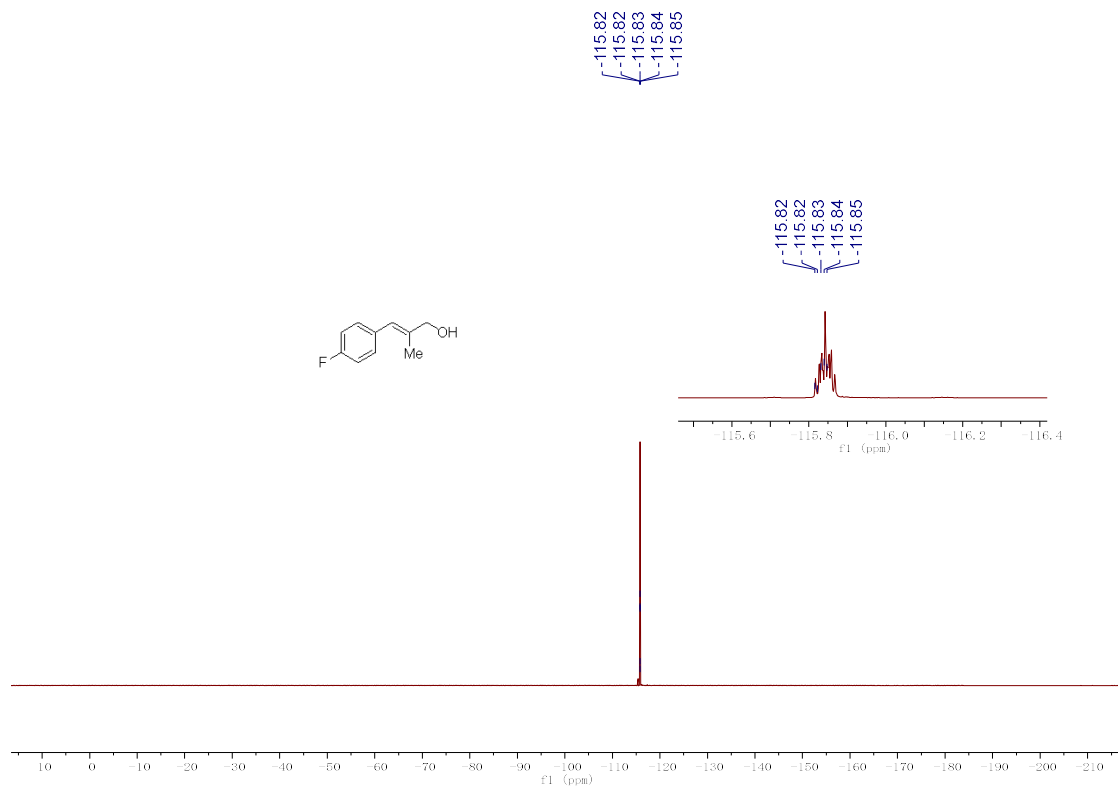
6. Copies of the ^1H and ^{13}C NMR spectra

2a

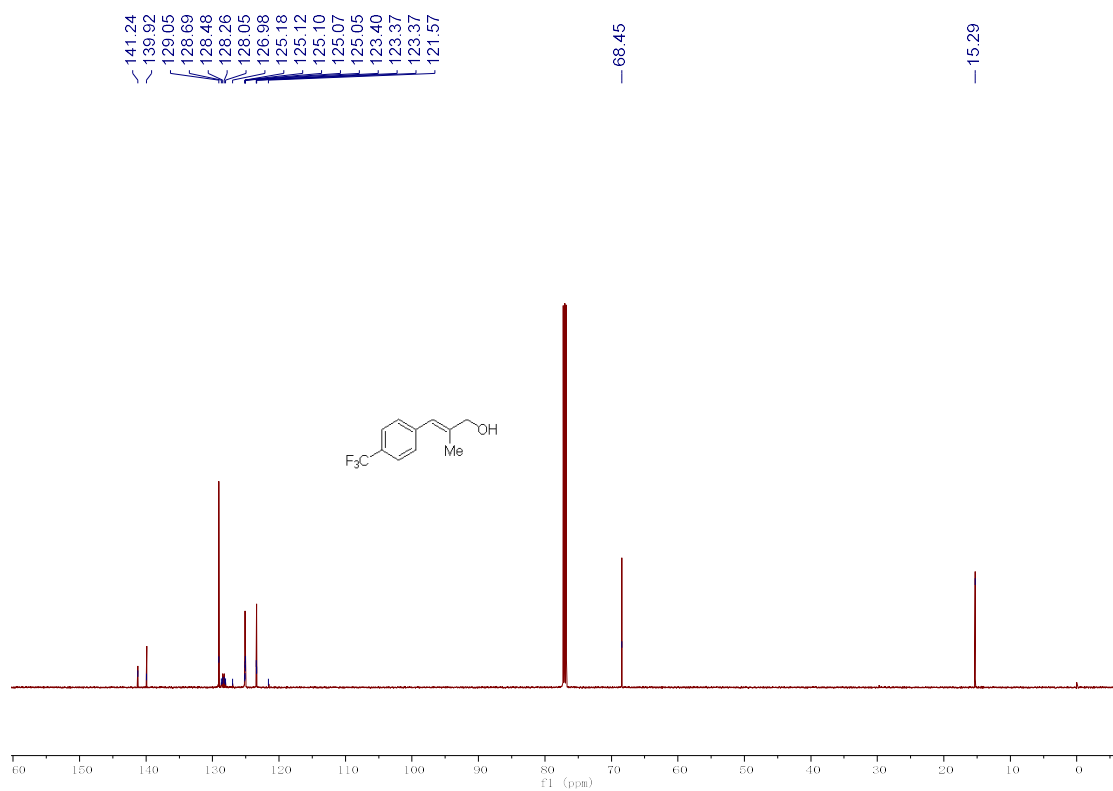
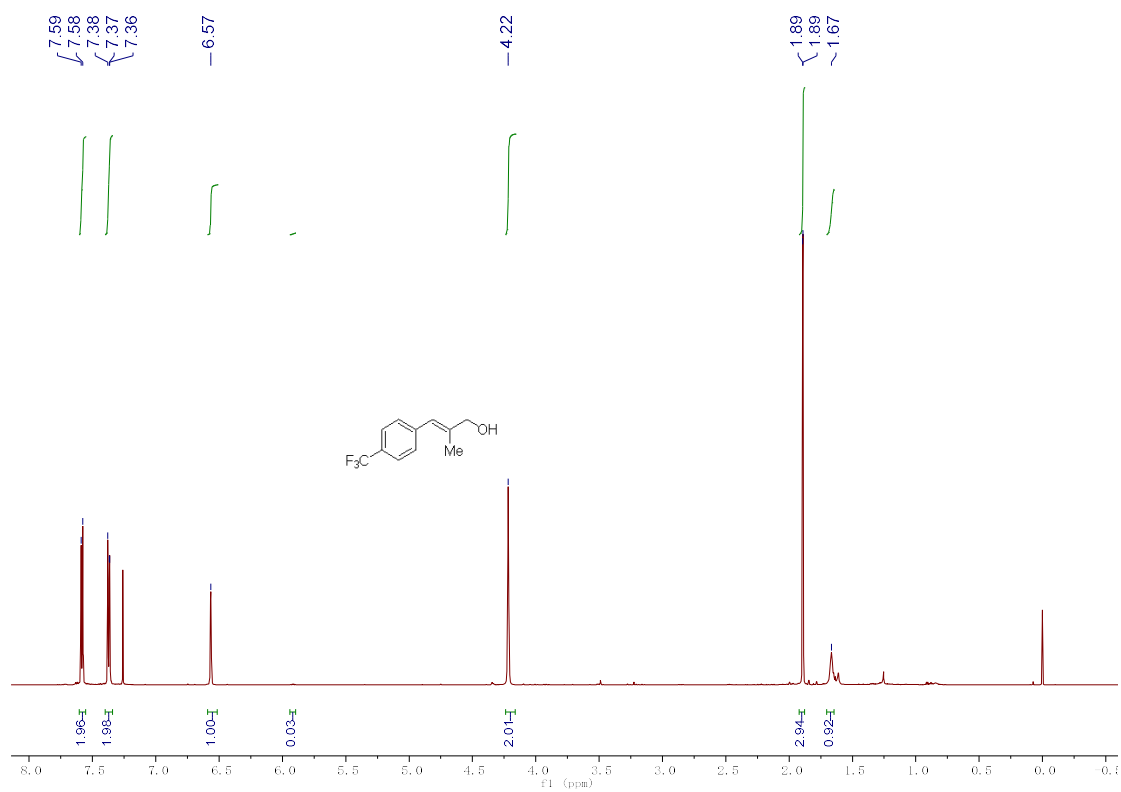


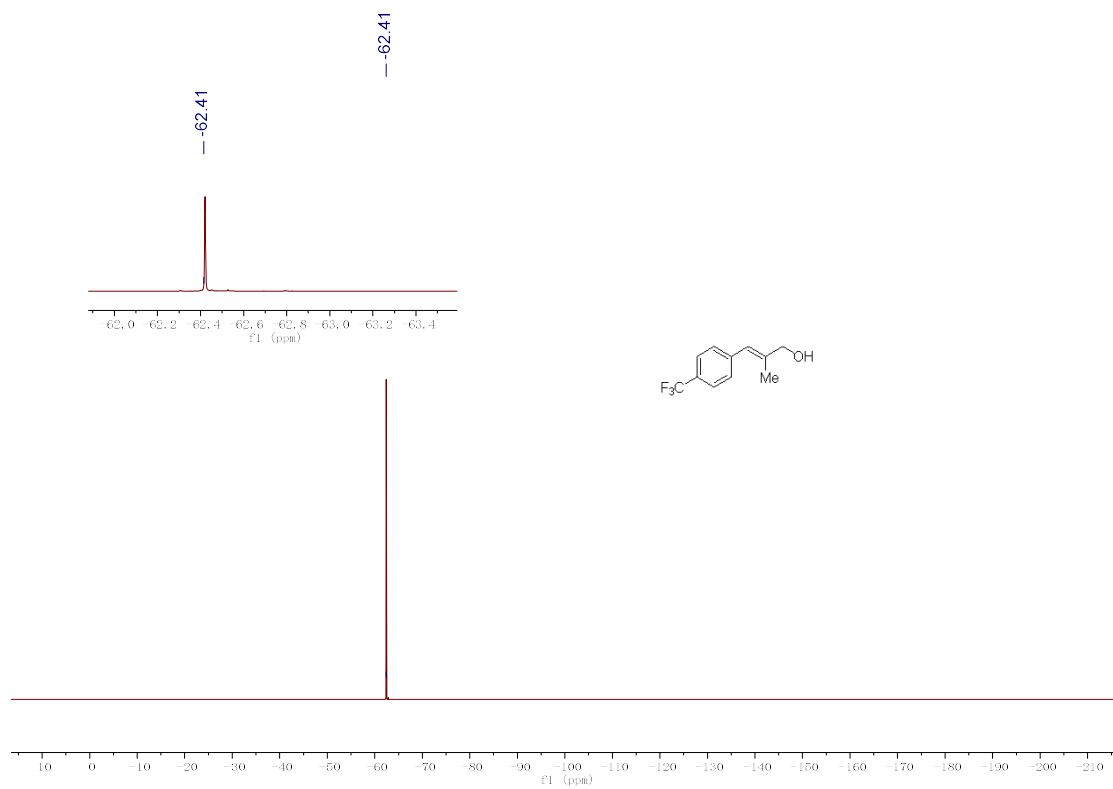
2b



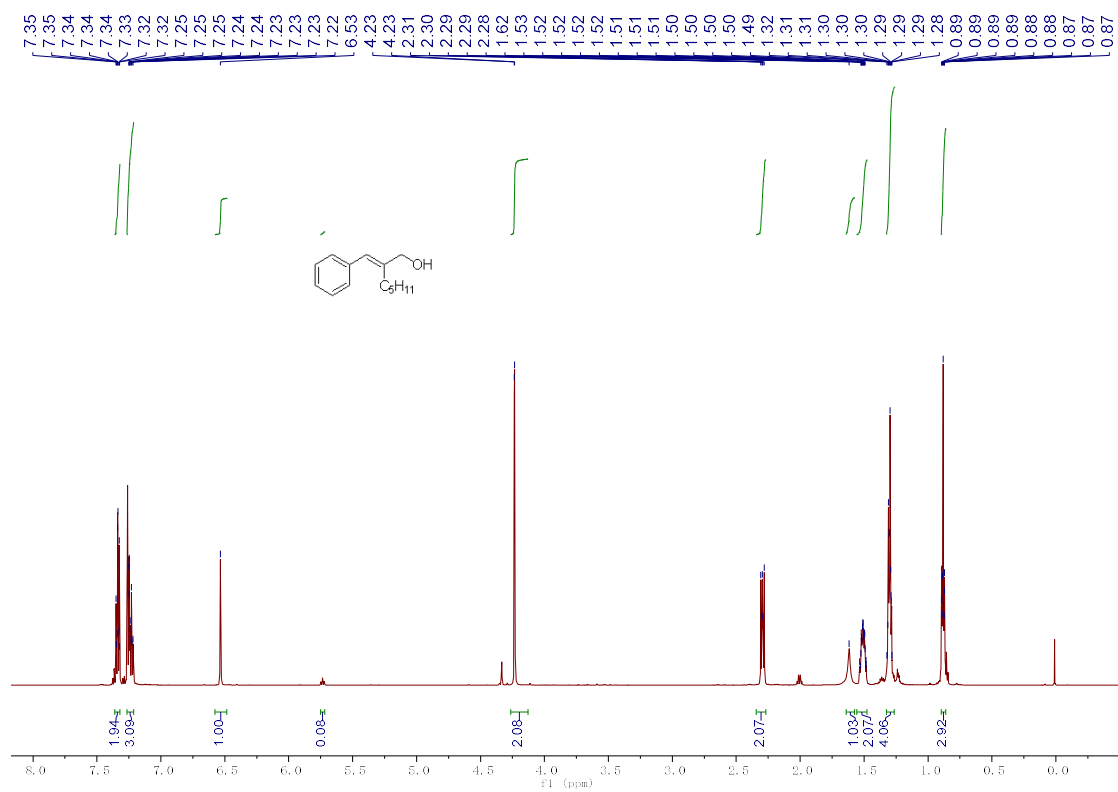


2c





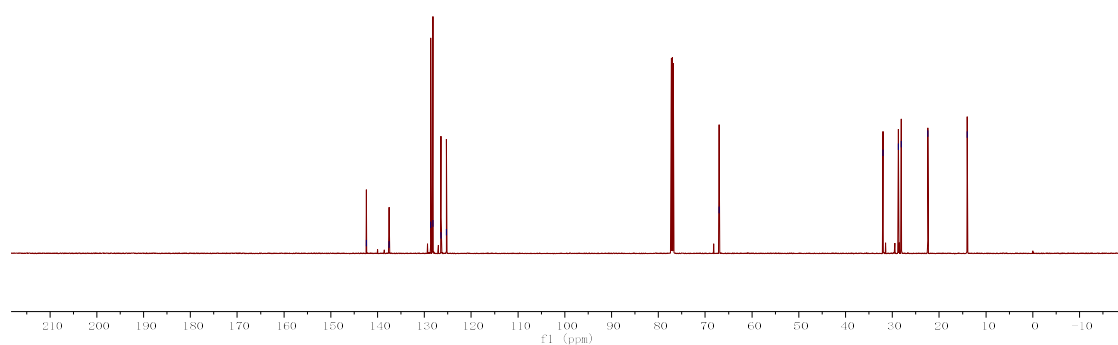
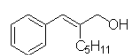
2d



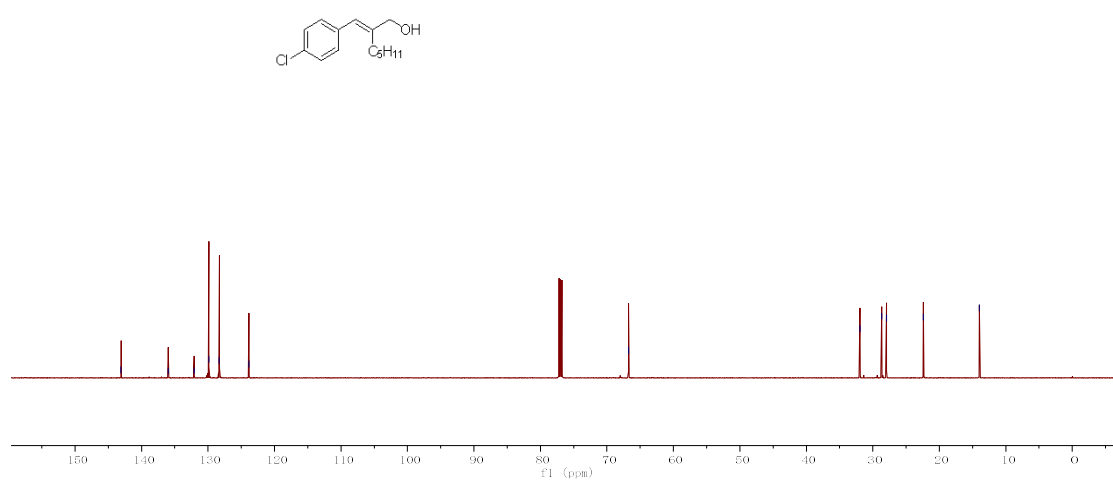
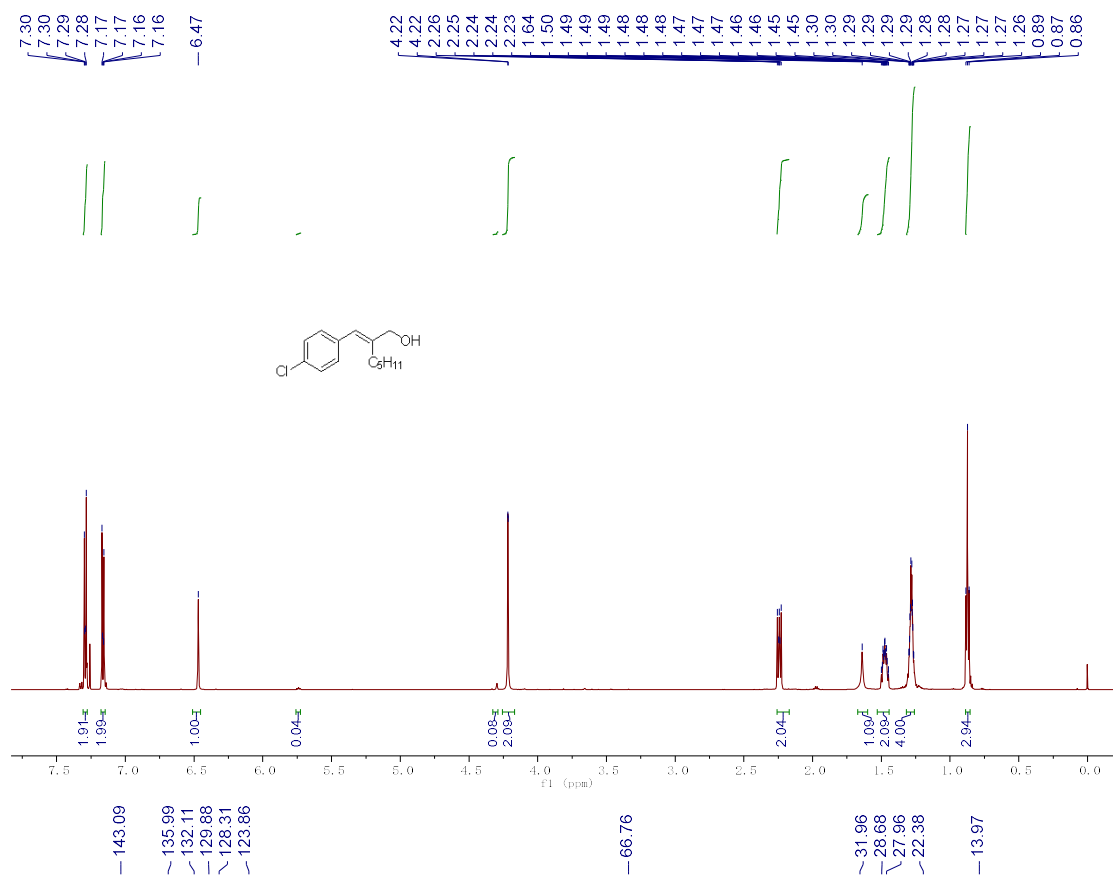
142.42
137.57
128.63
128.18
126.45
125.28

67.05

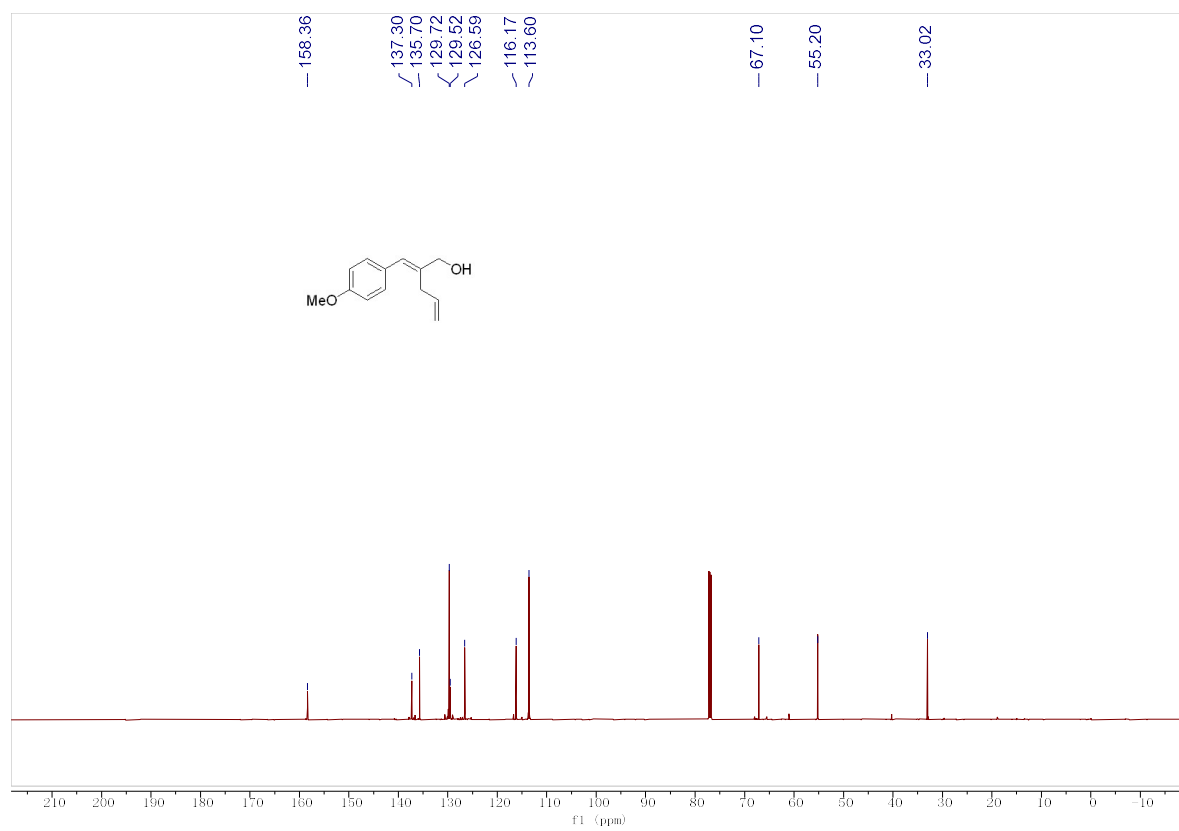
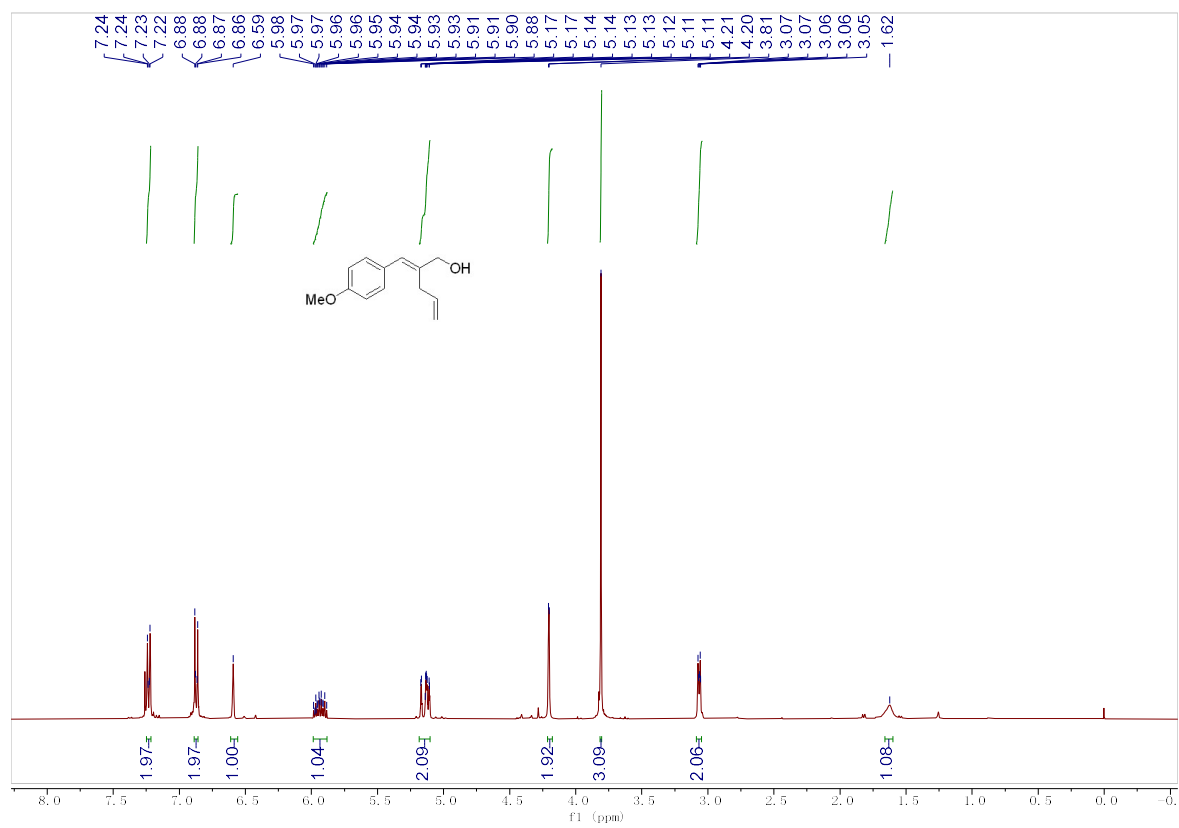
32.03
28.73
28.07
22.44
14.03



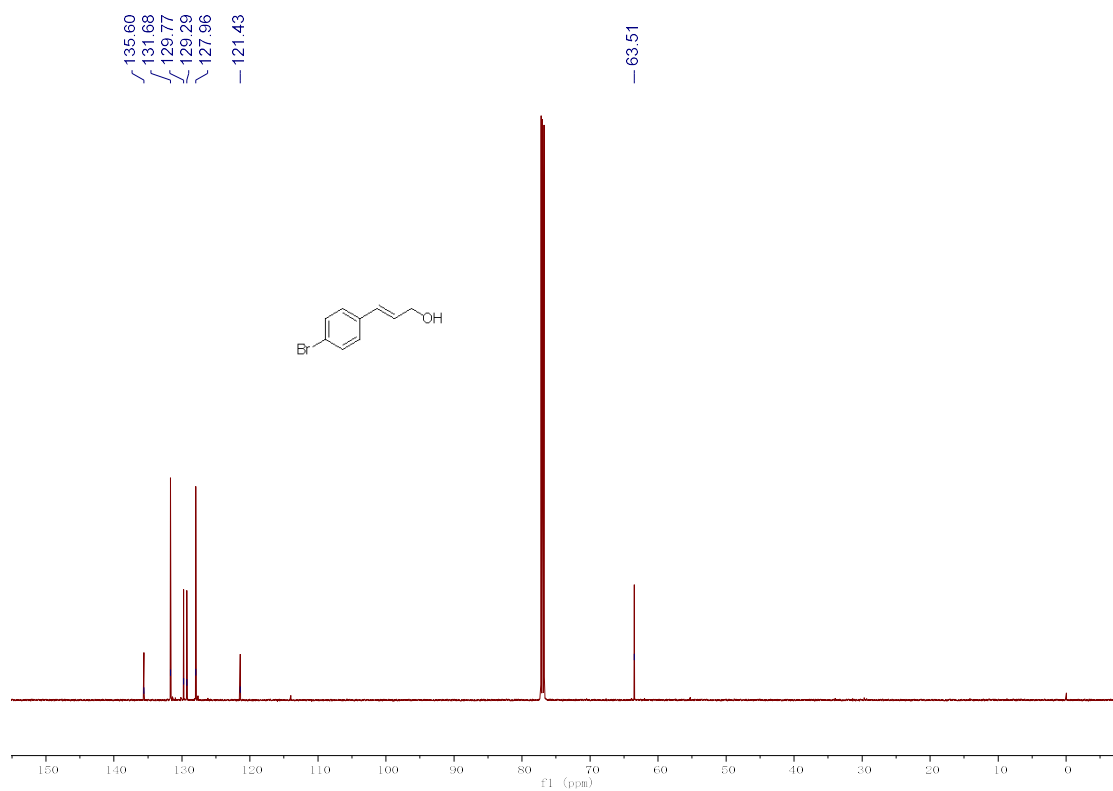
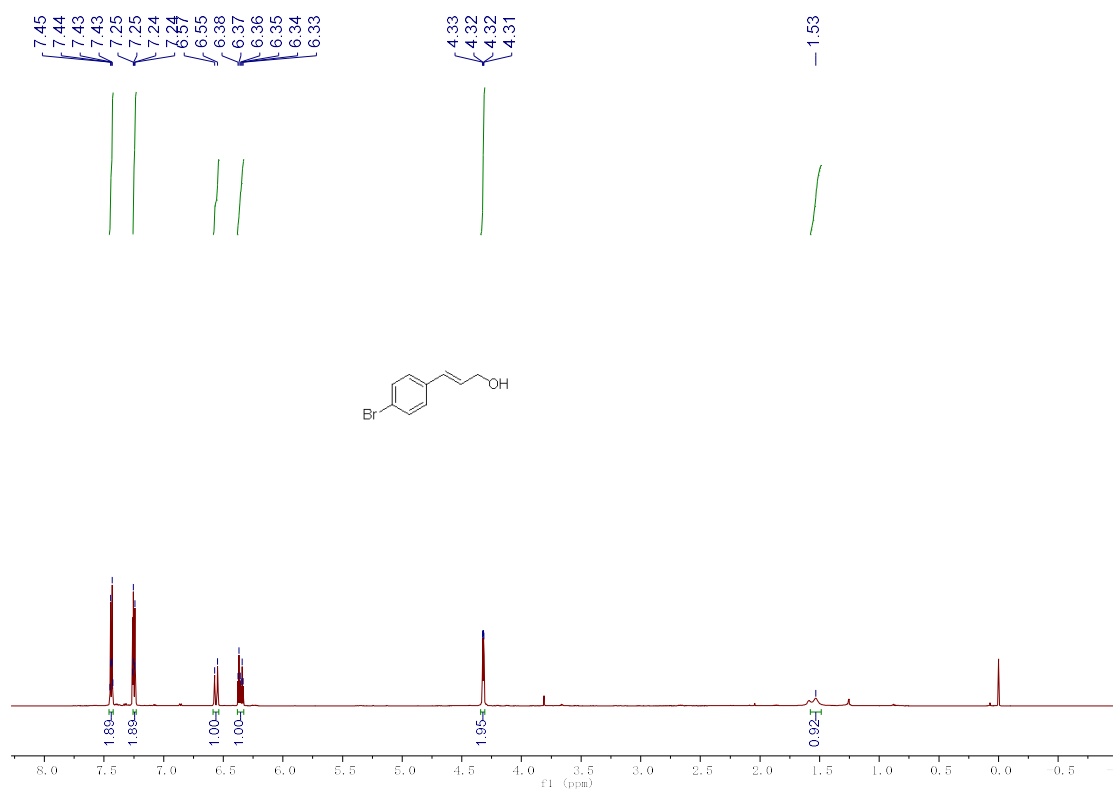
2e



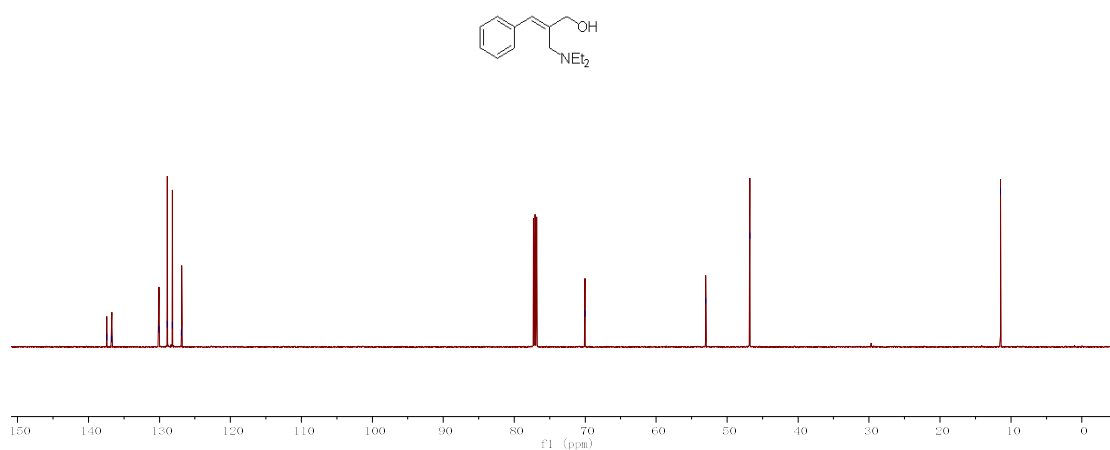
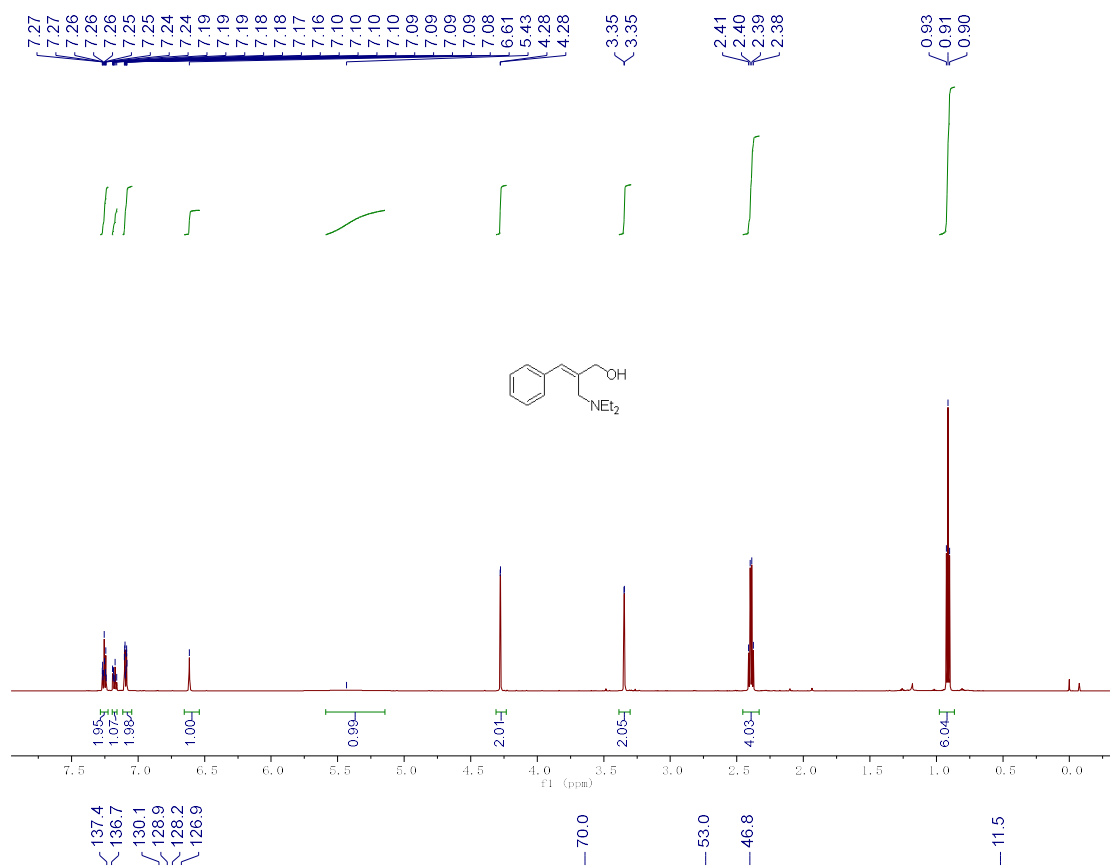
2f



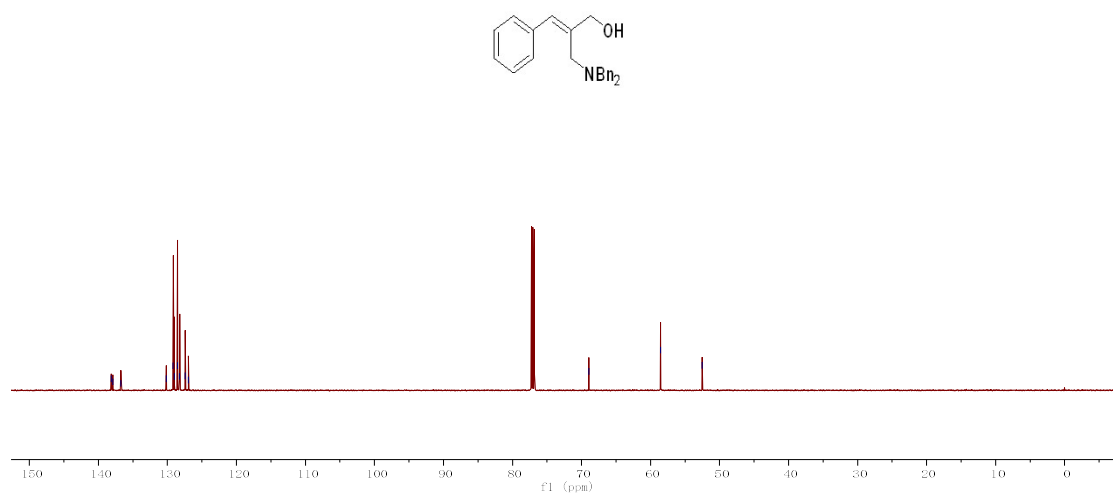
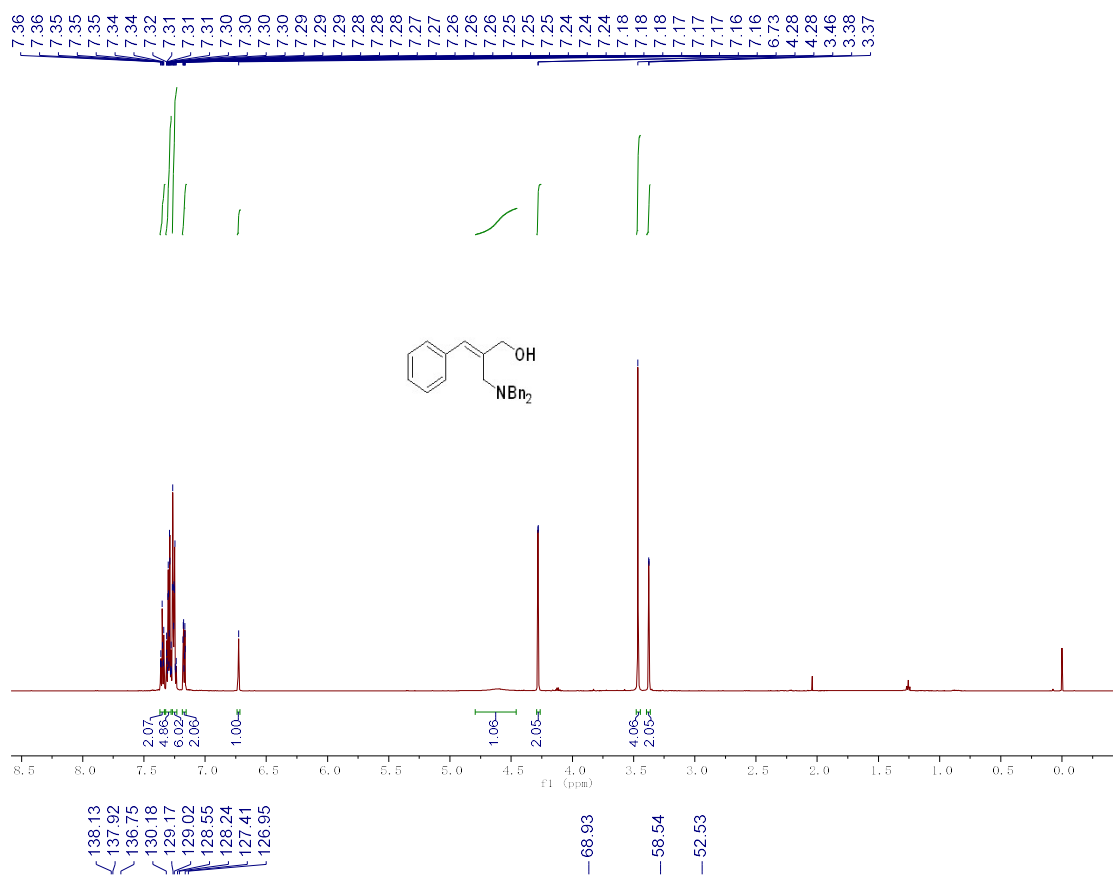
2g



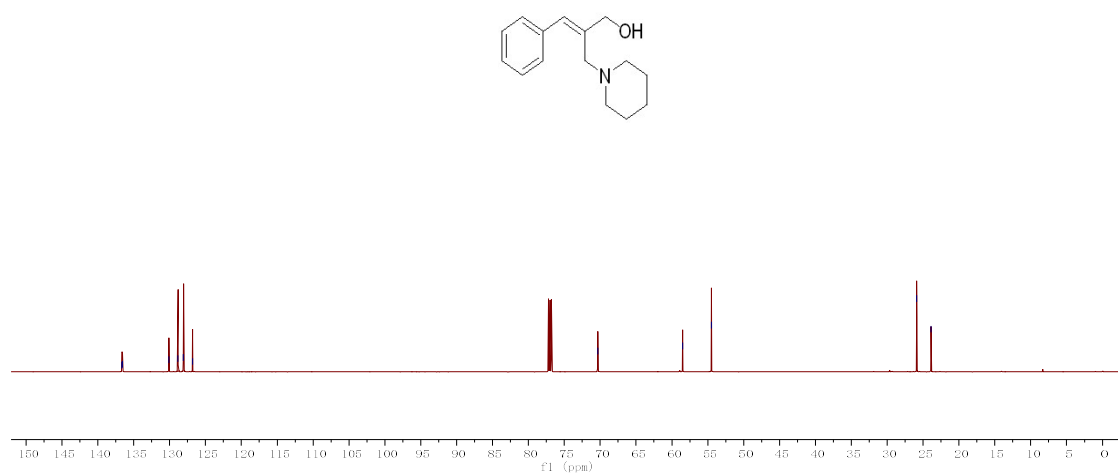
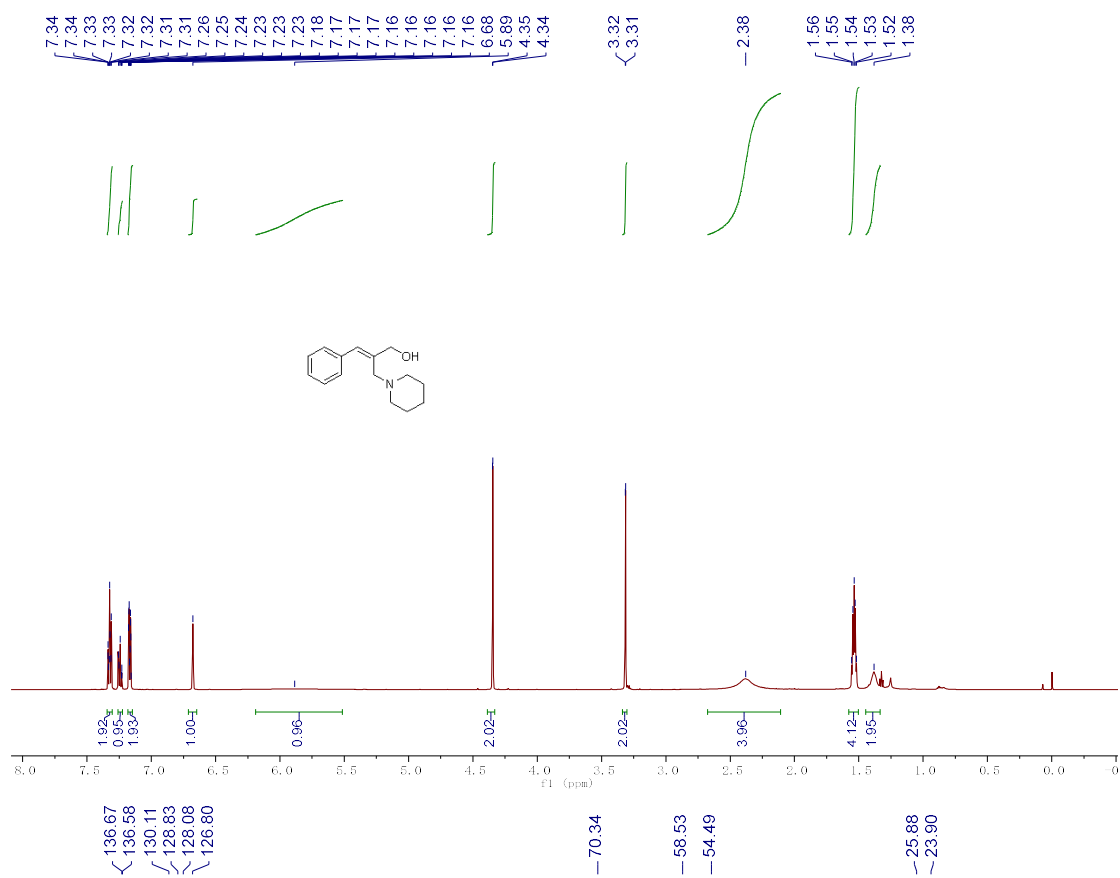
2h



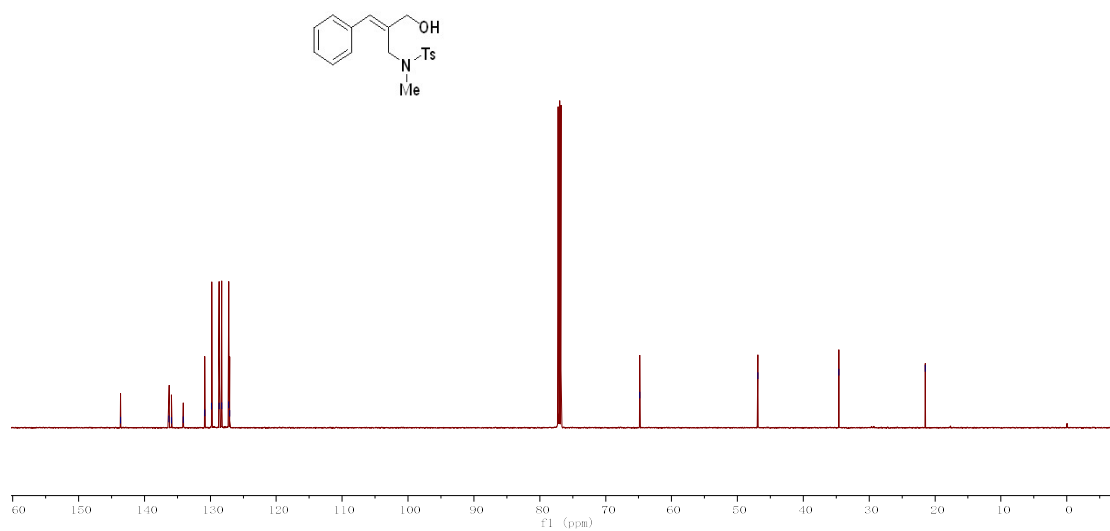
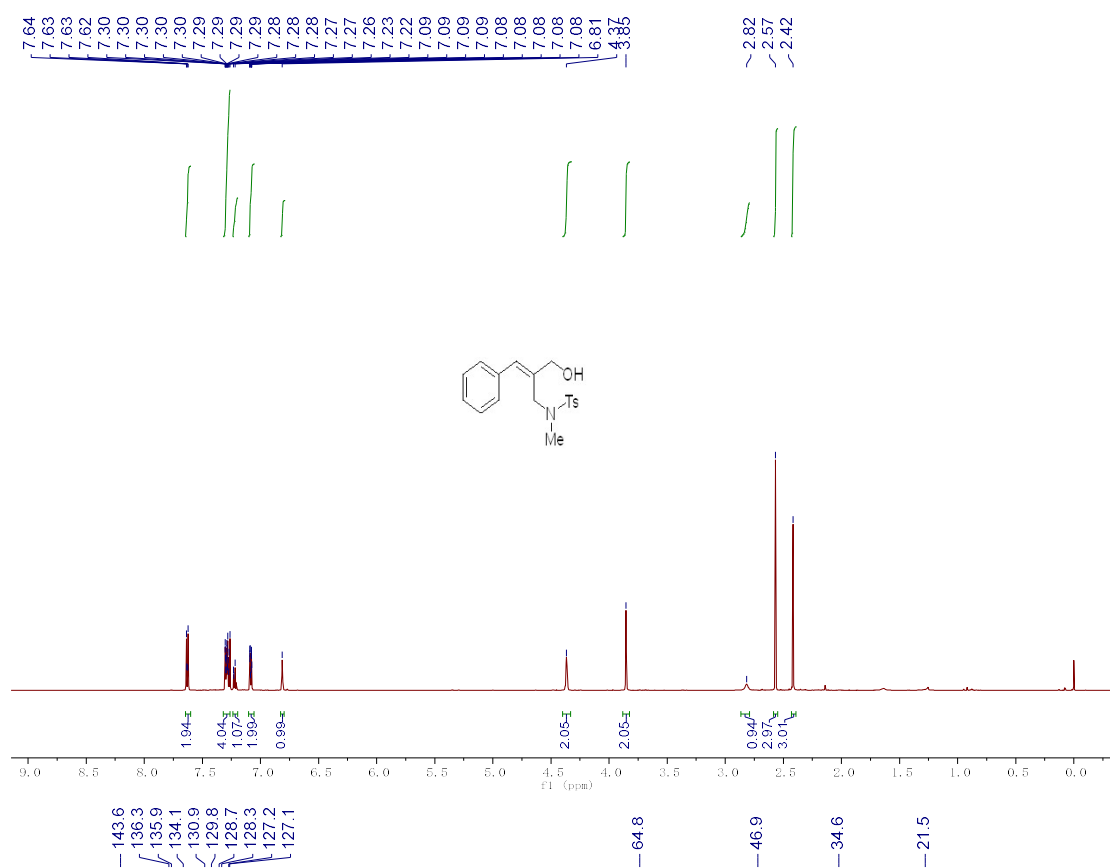
2i



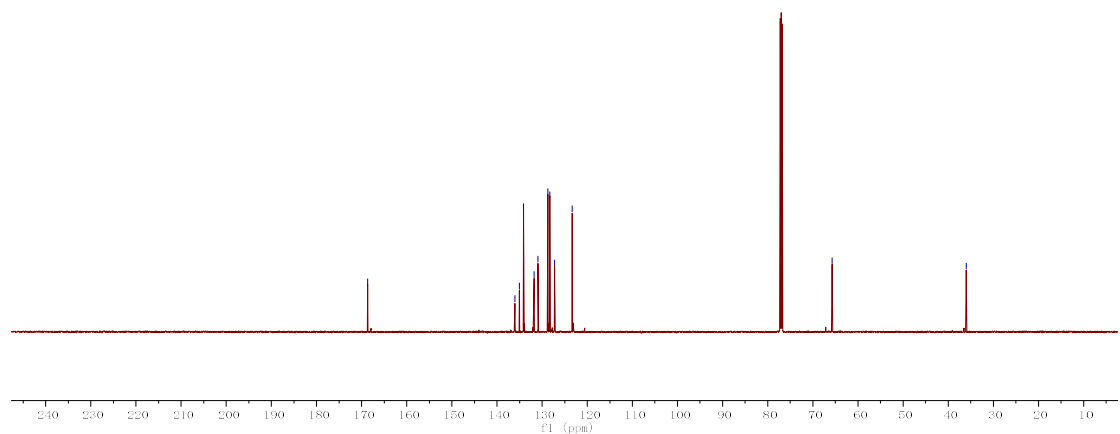
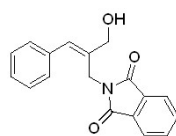
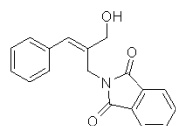
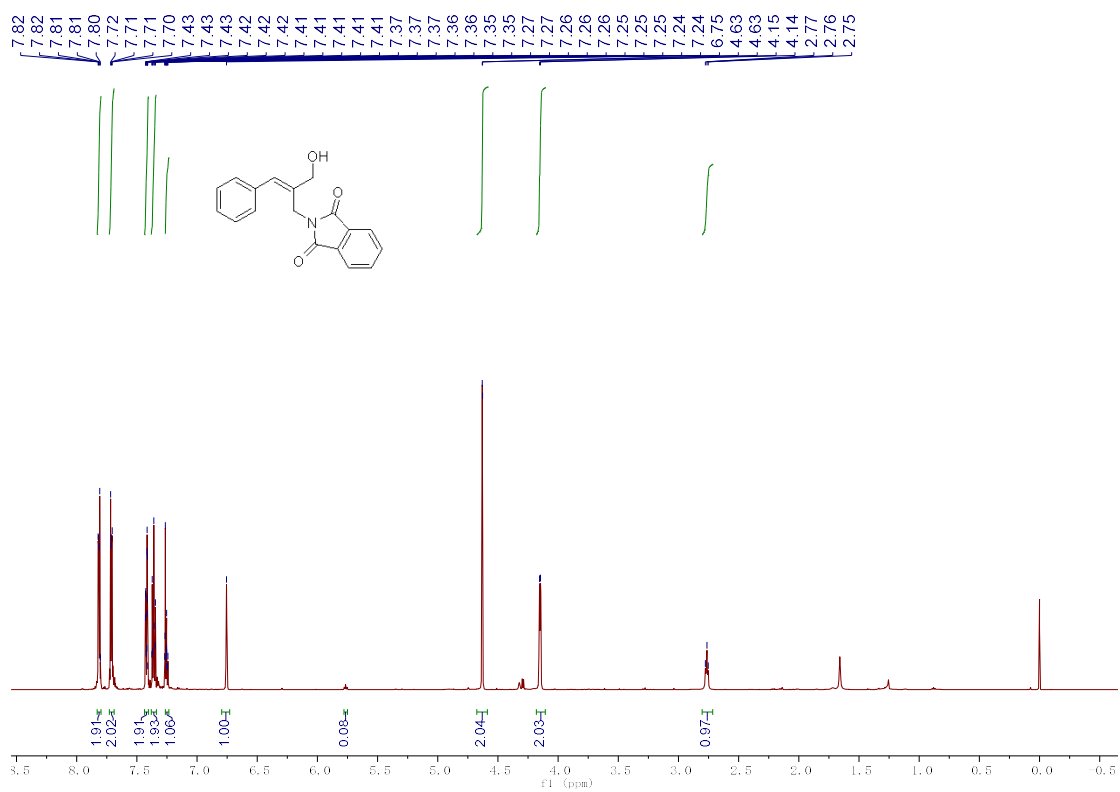
2j



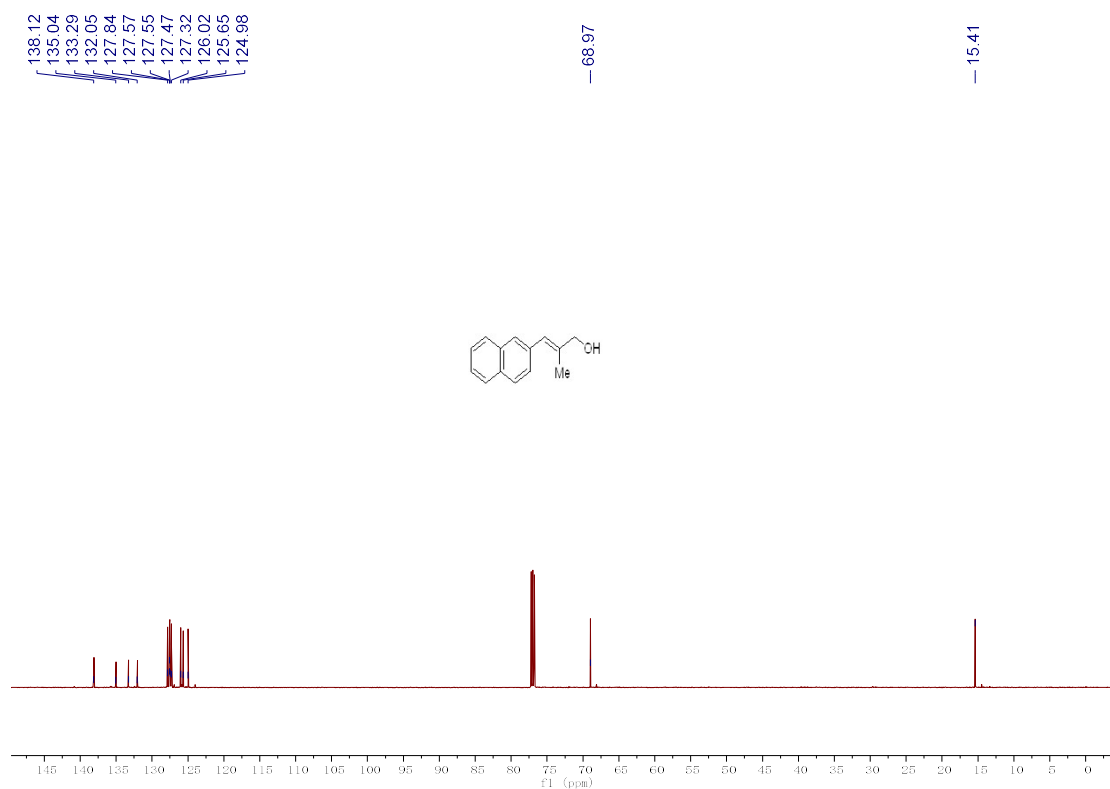
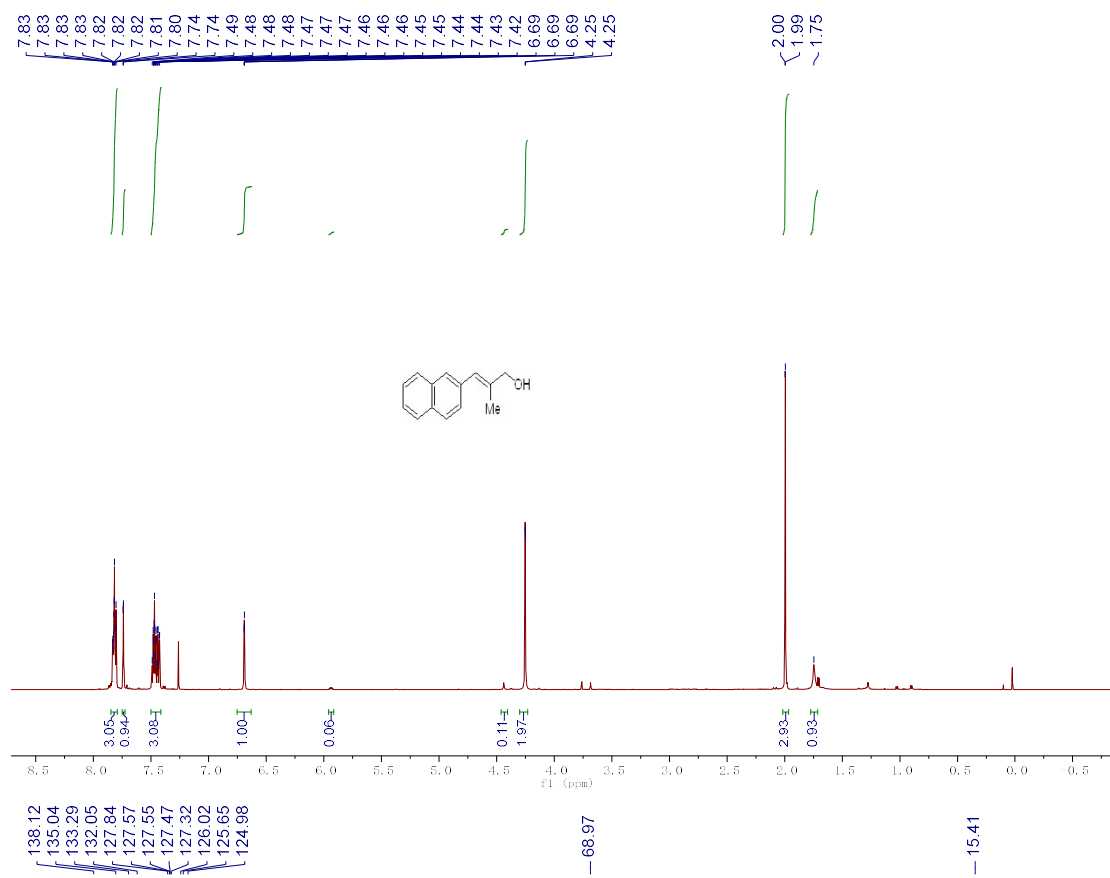
2k



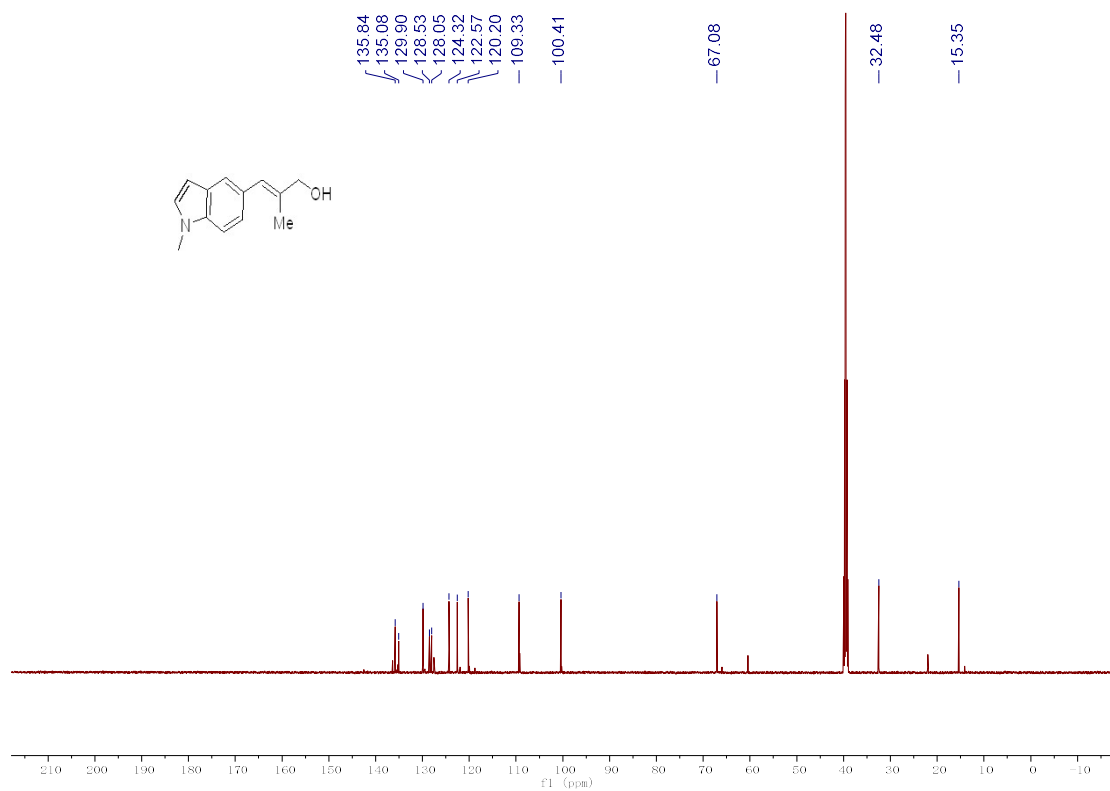
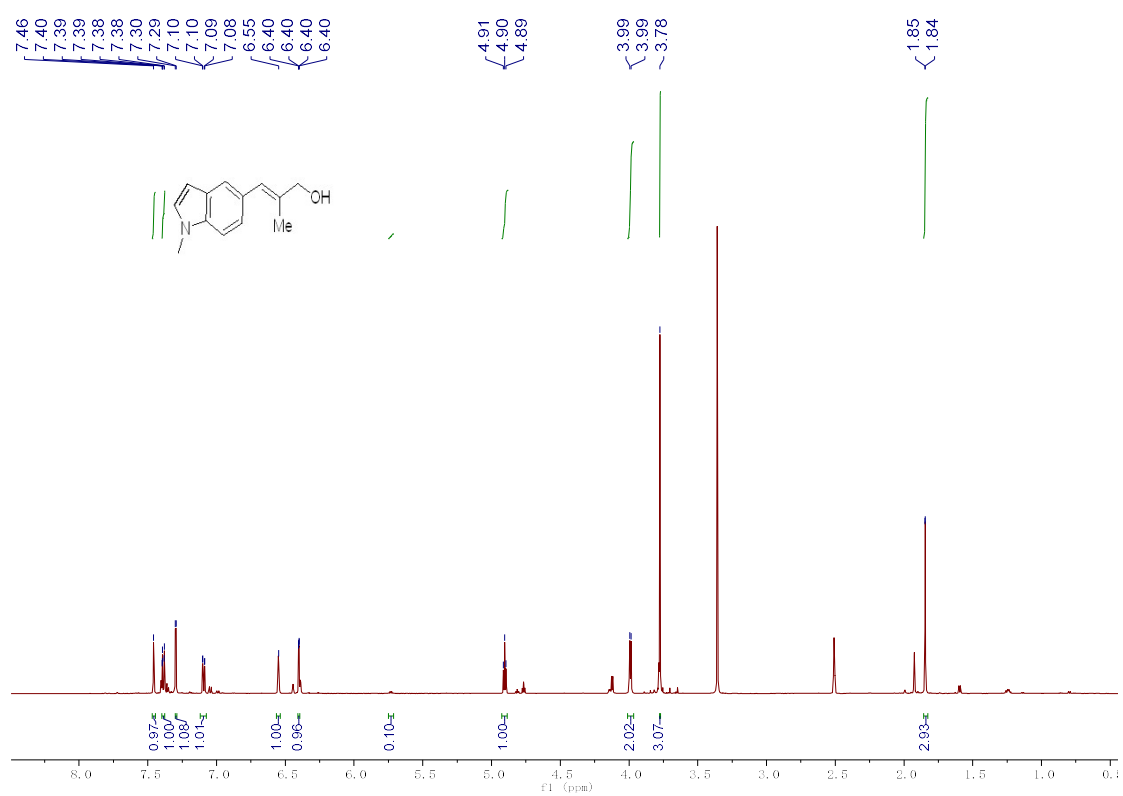
2I



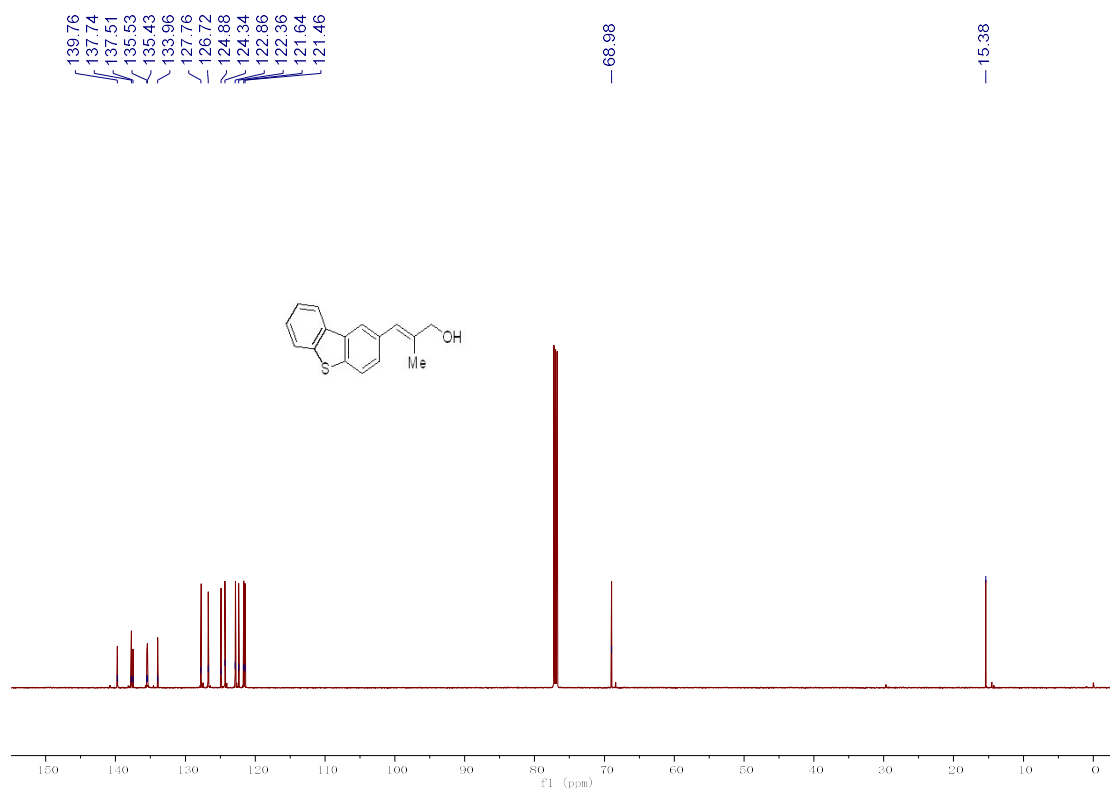
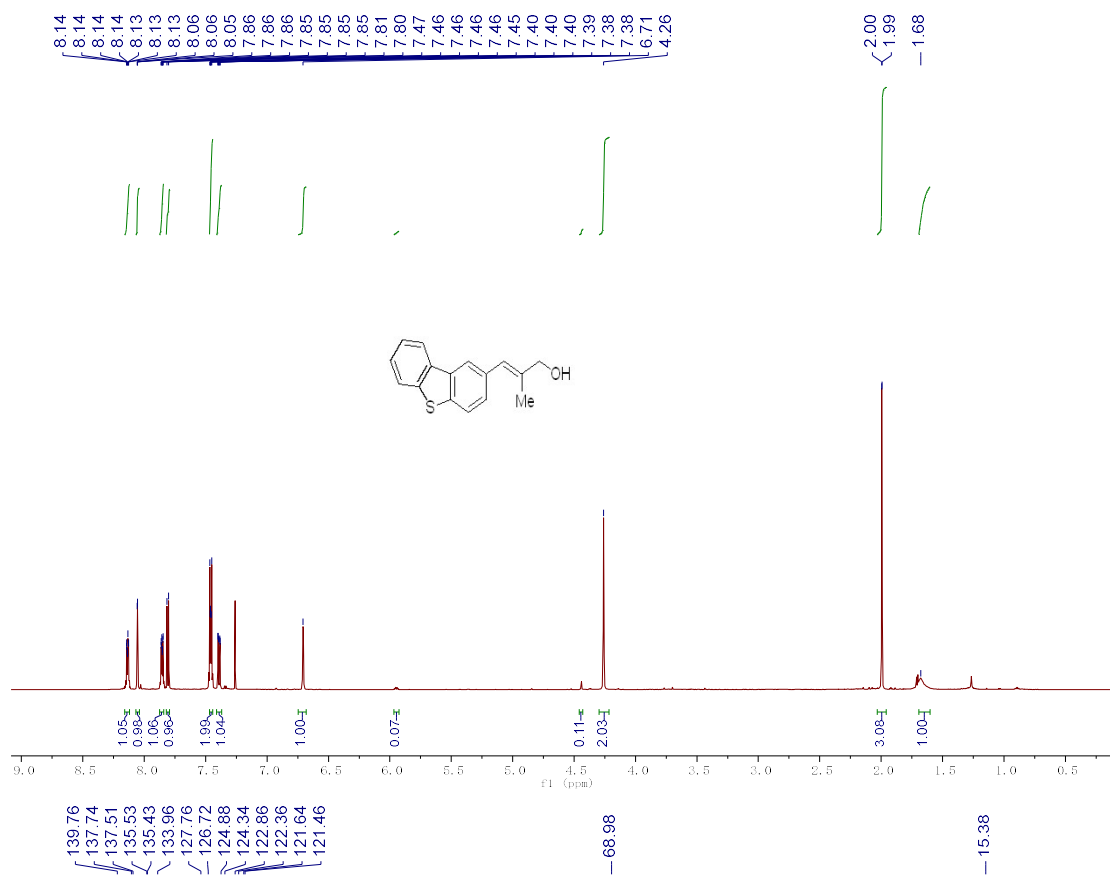
2m



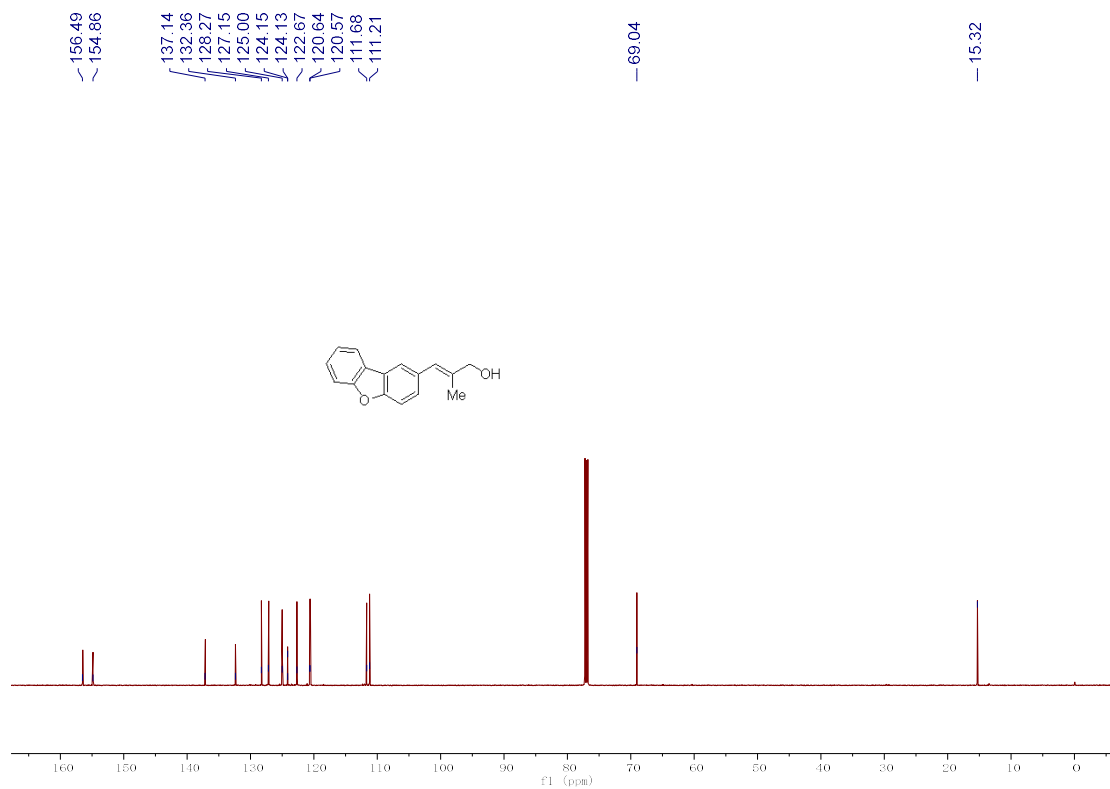
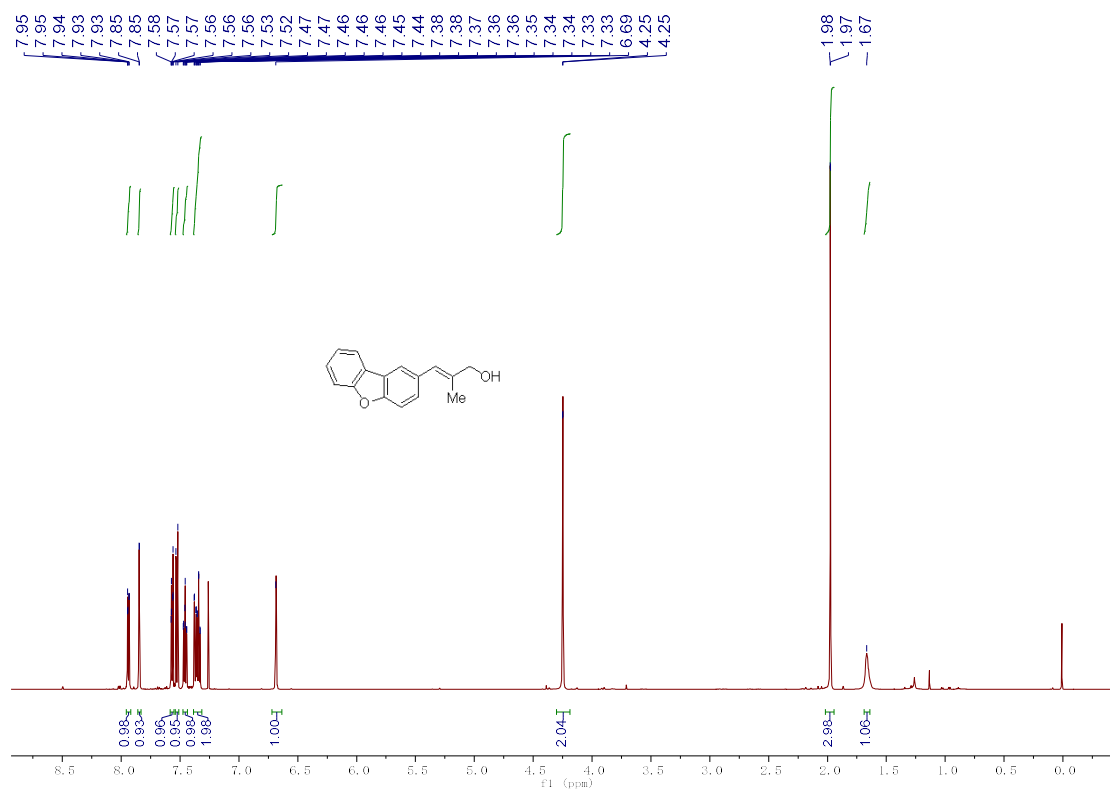
2n



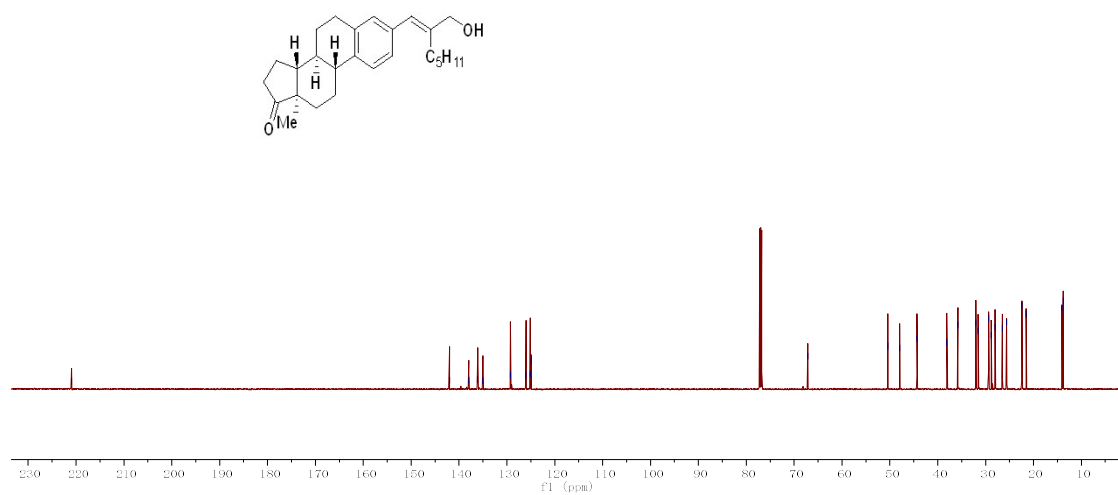
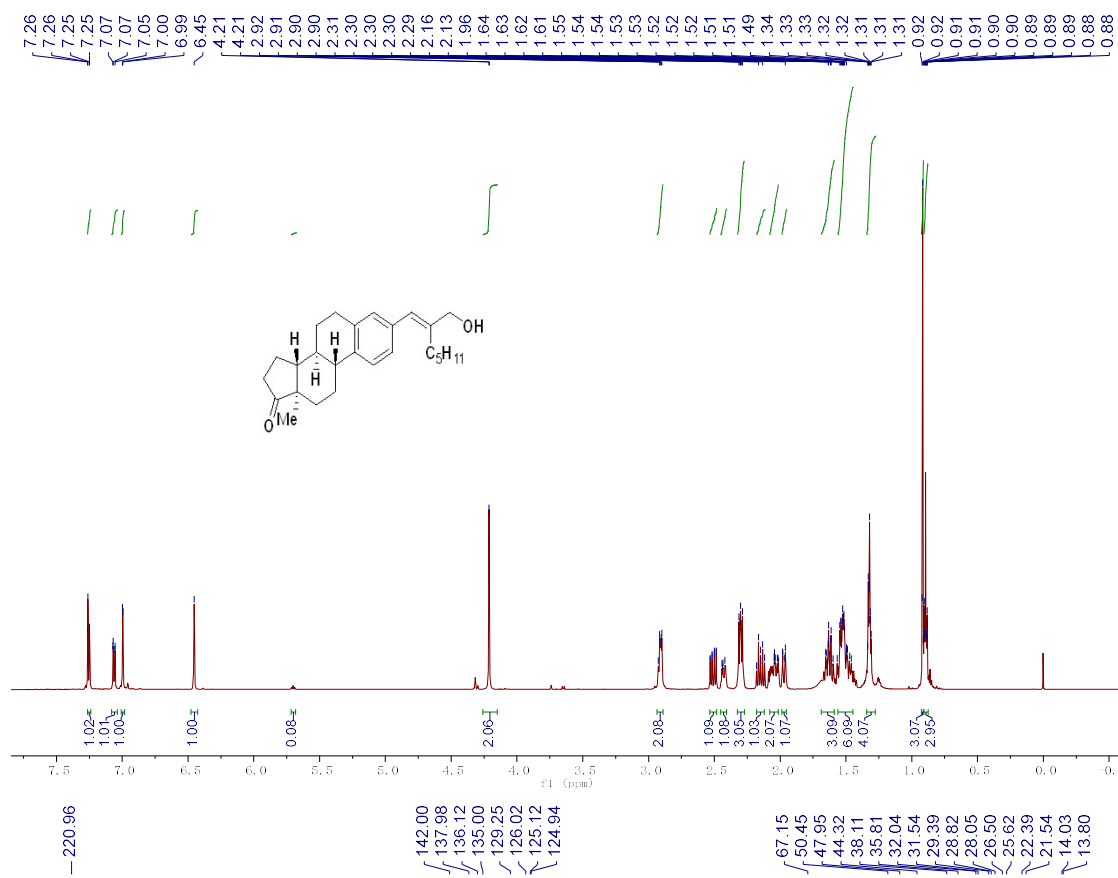
20



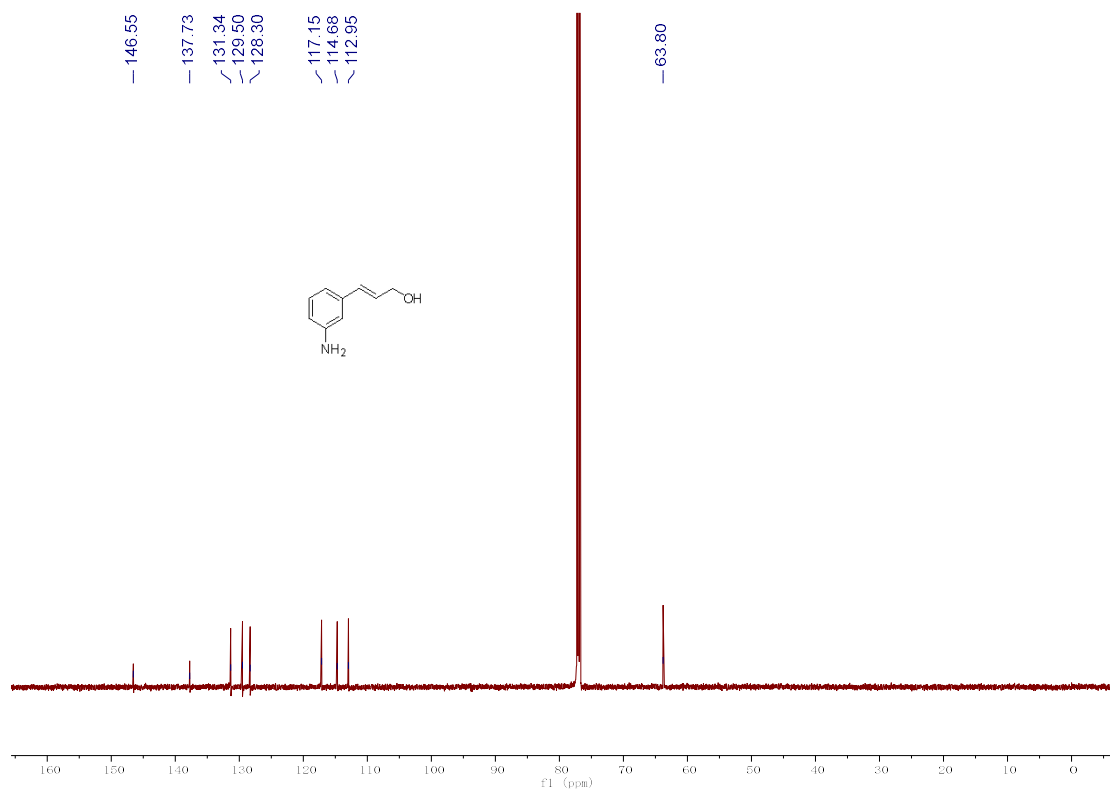
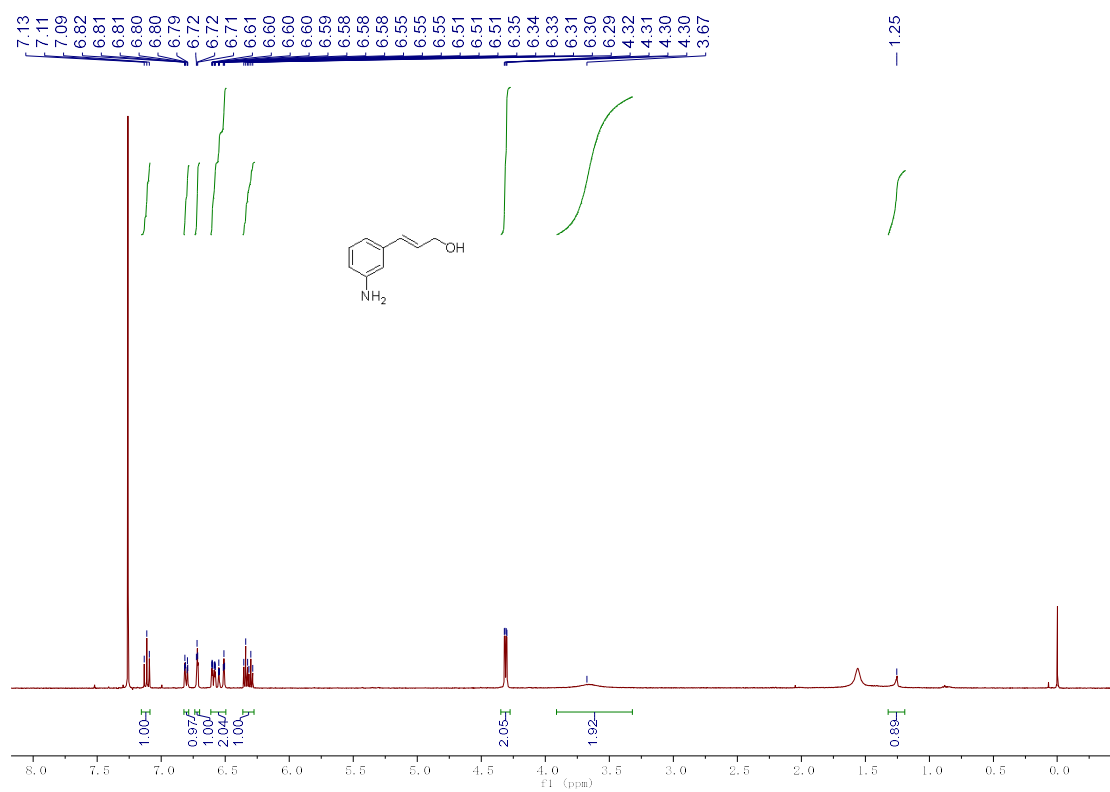
2p



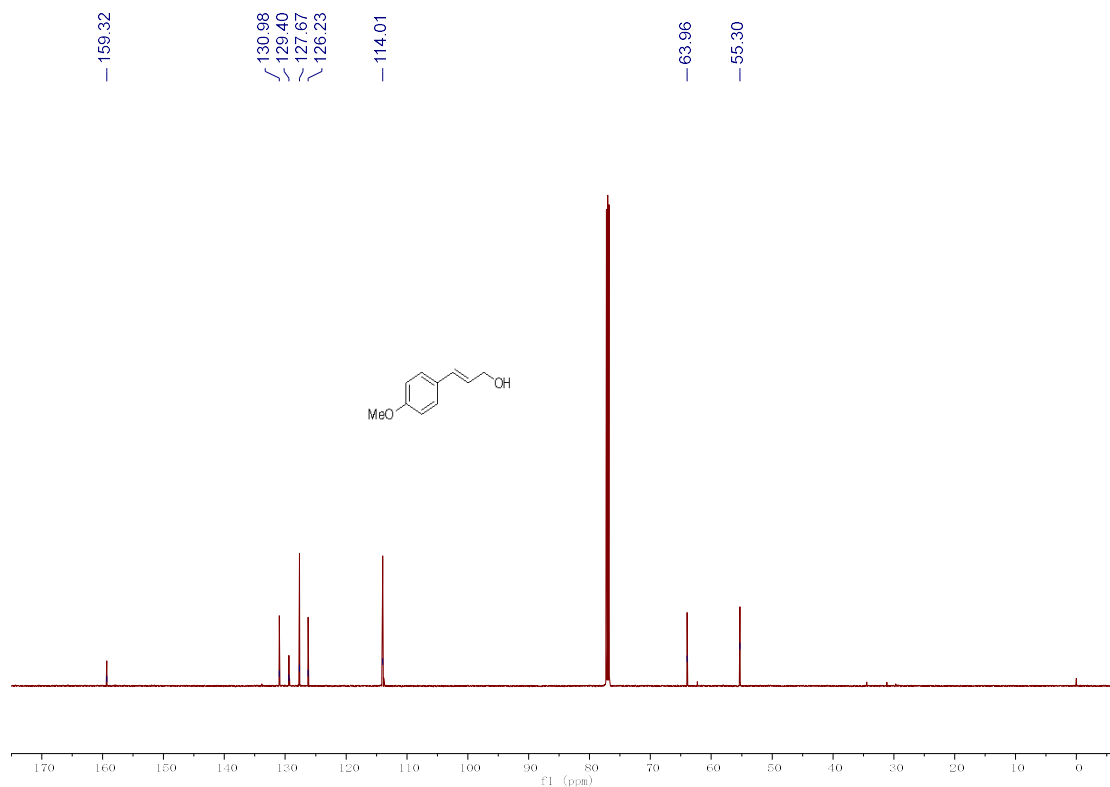
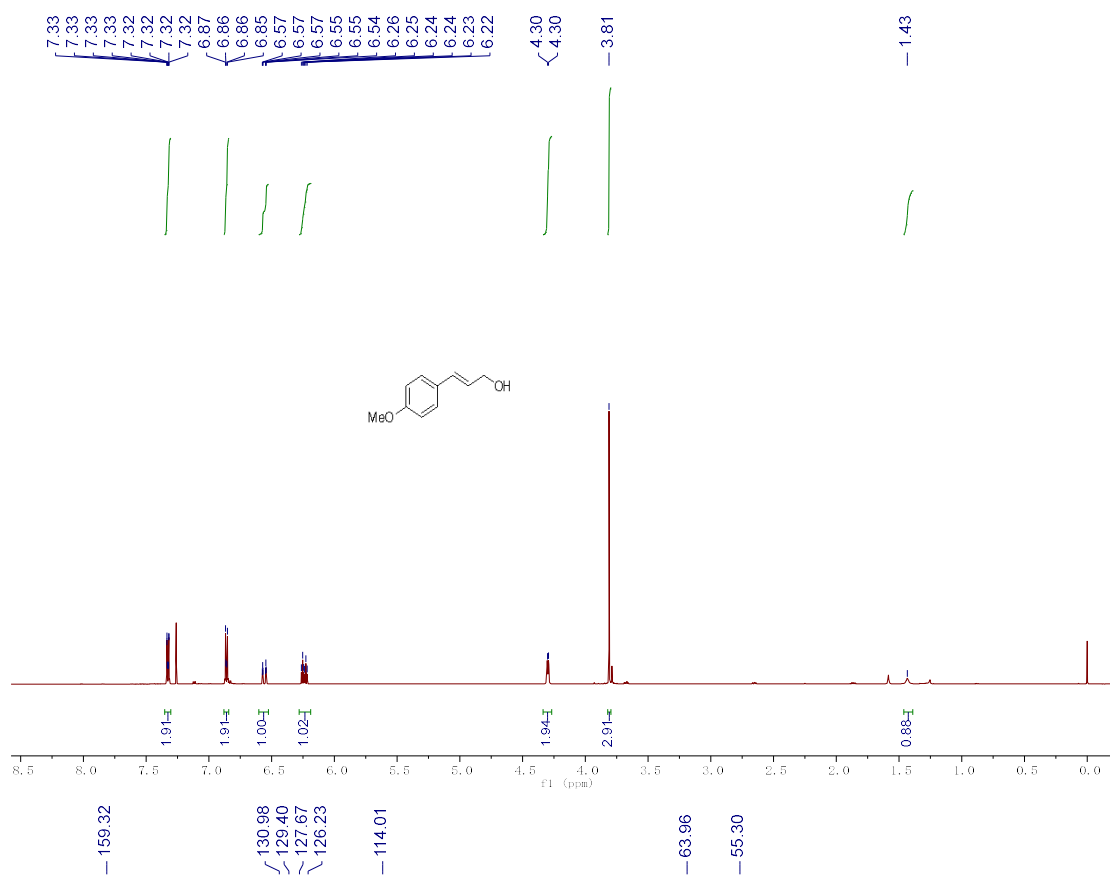
2q



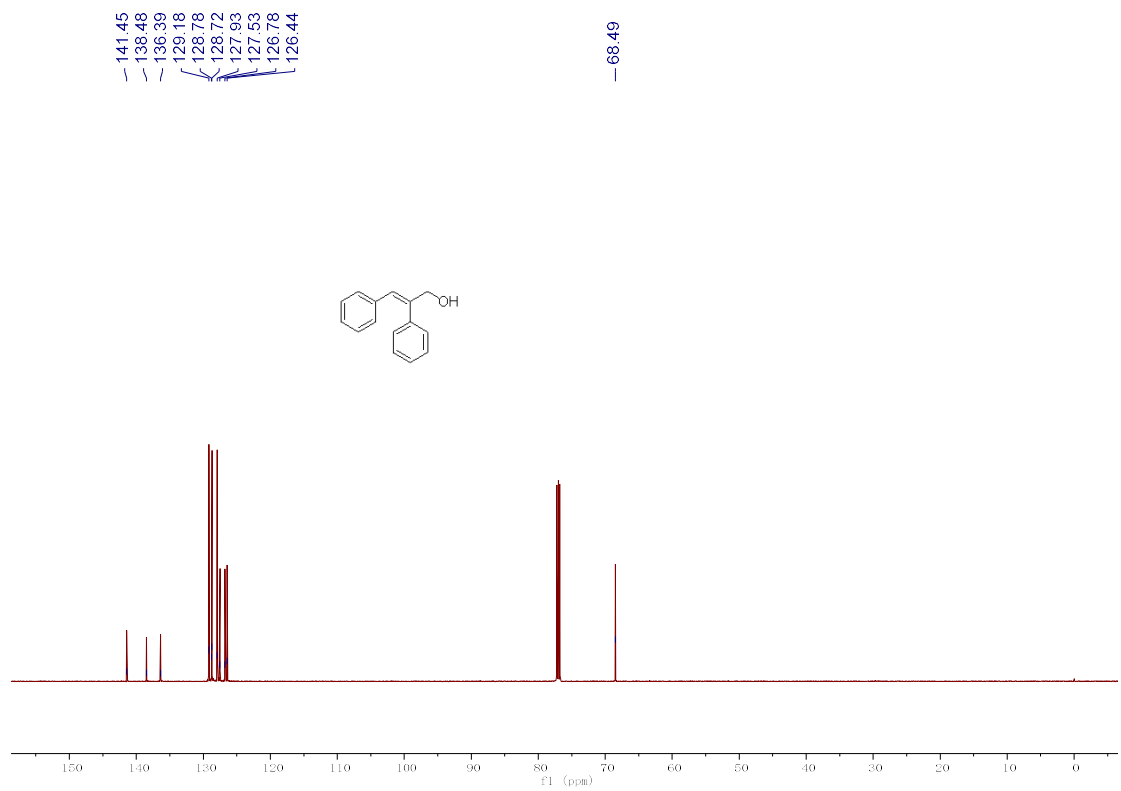
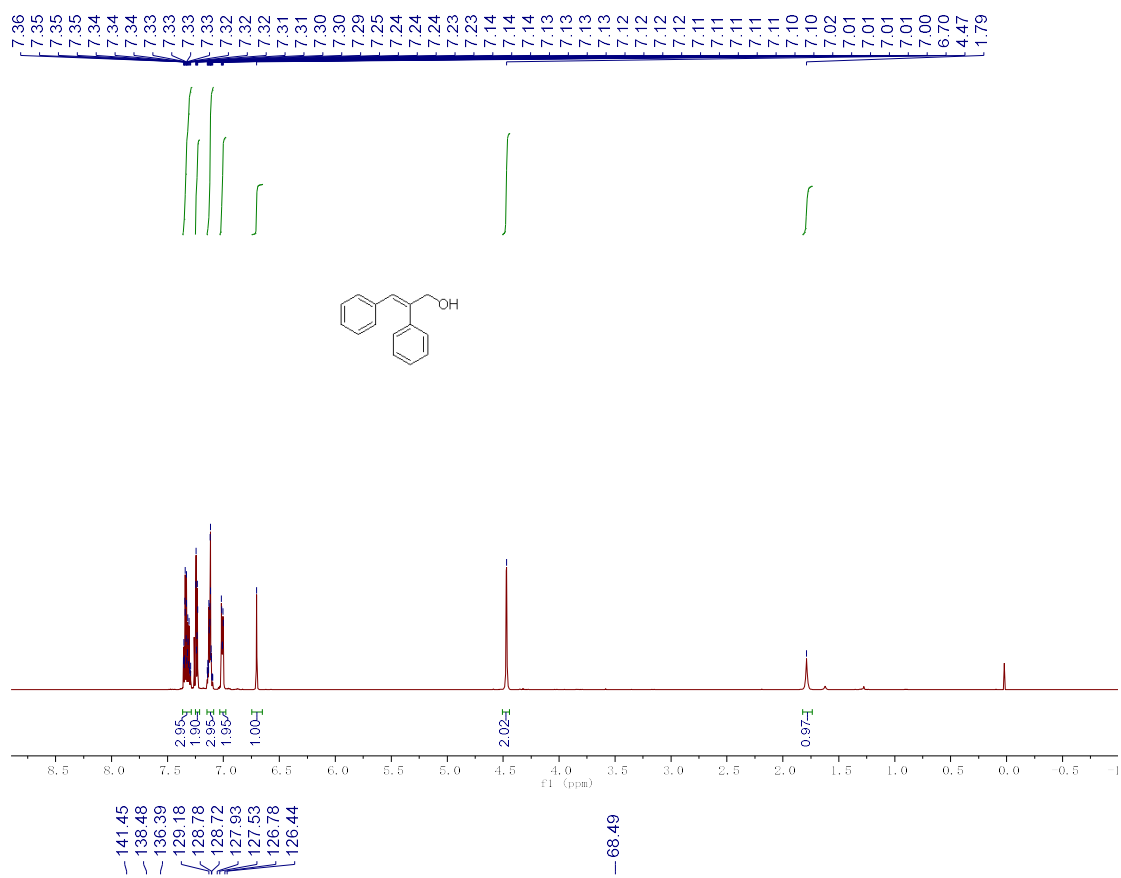
2r



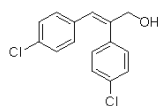
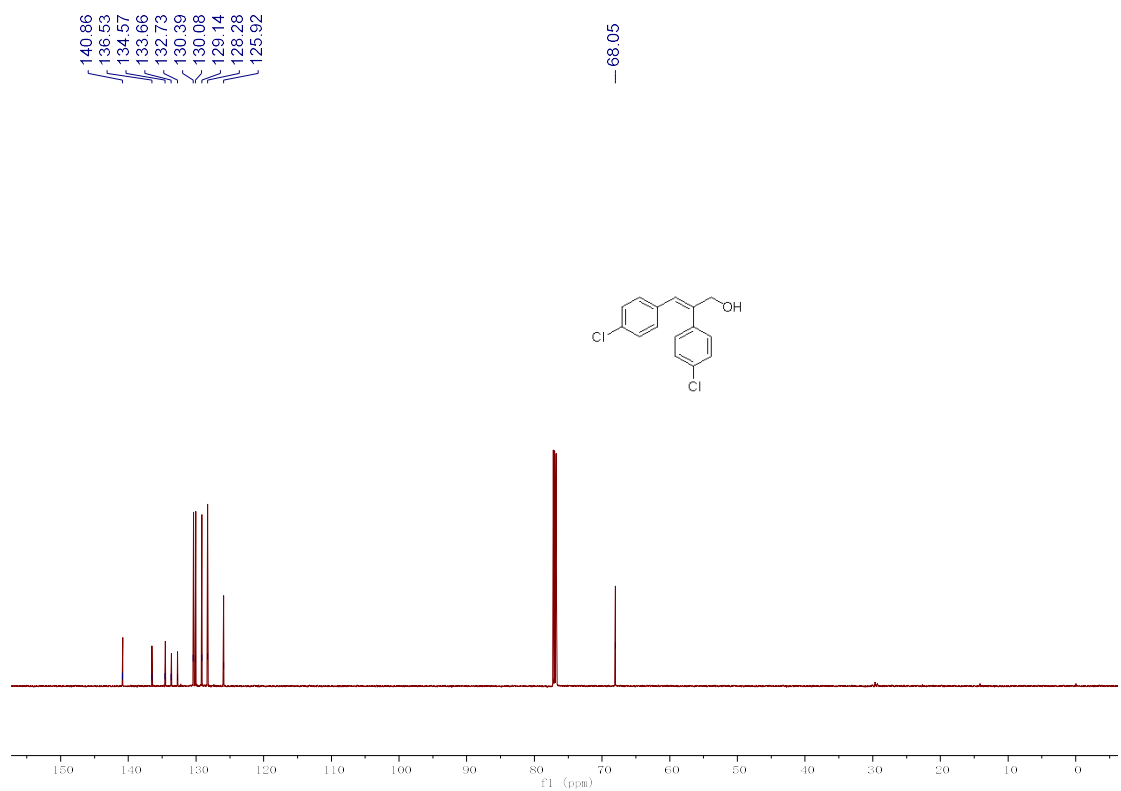
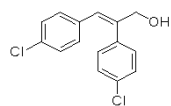
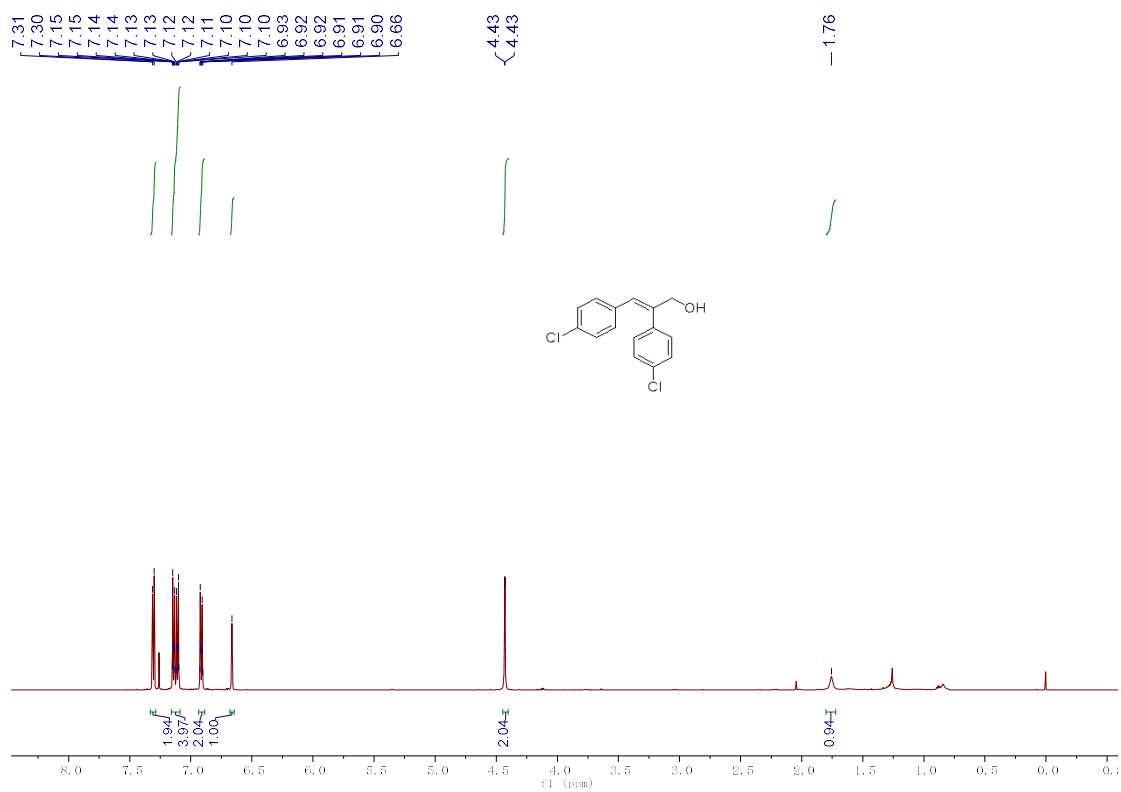
2s



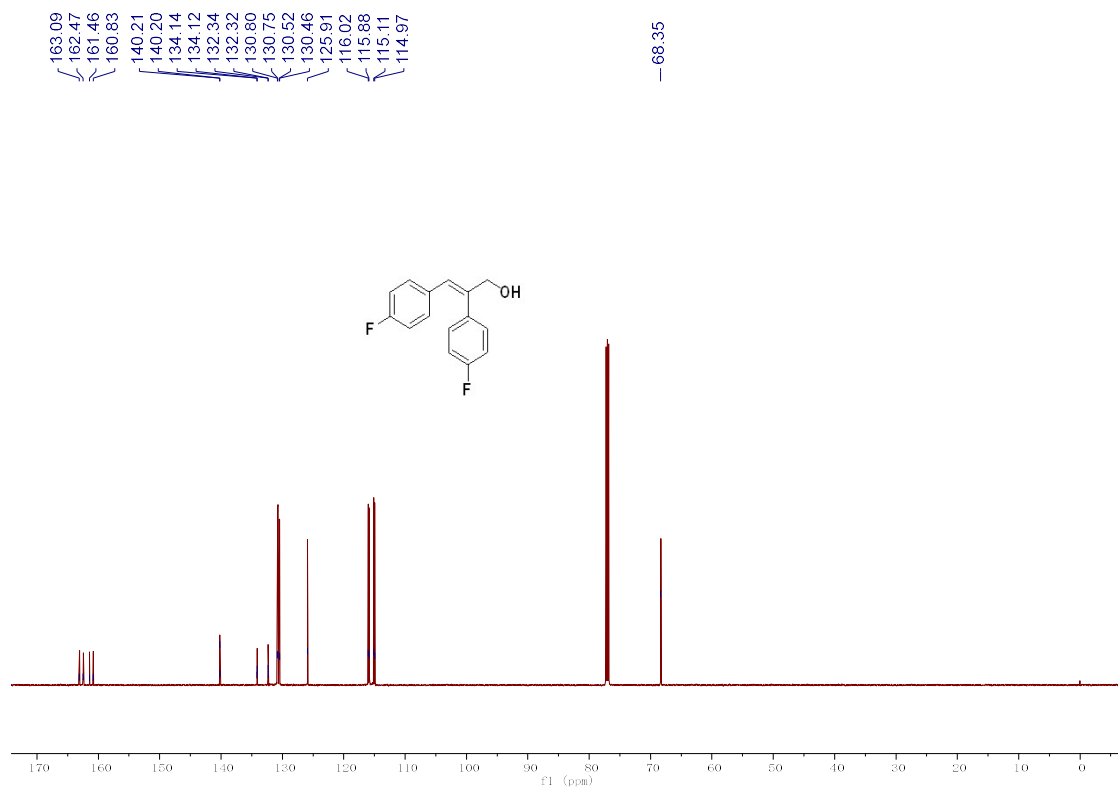
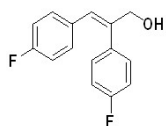
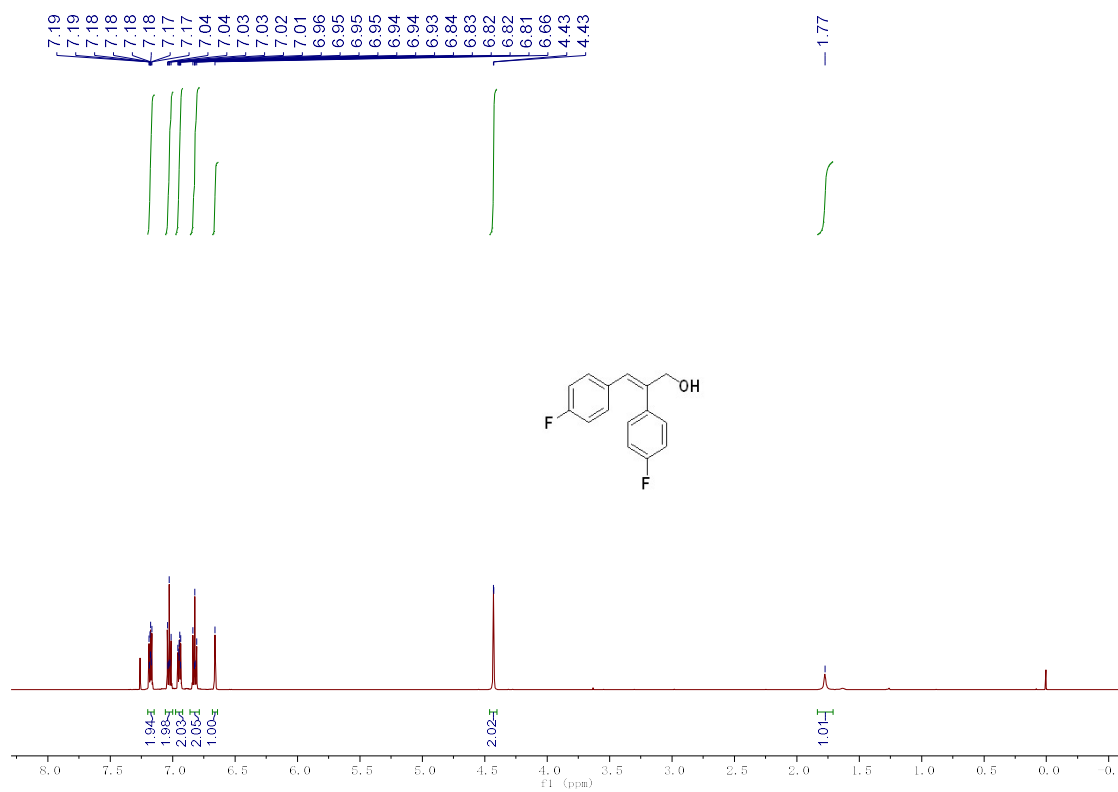
2t



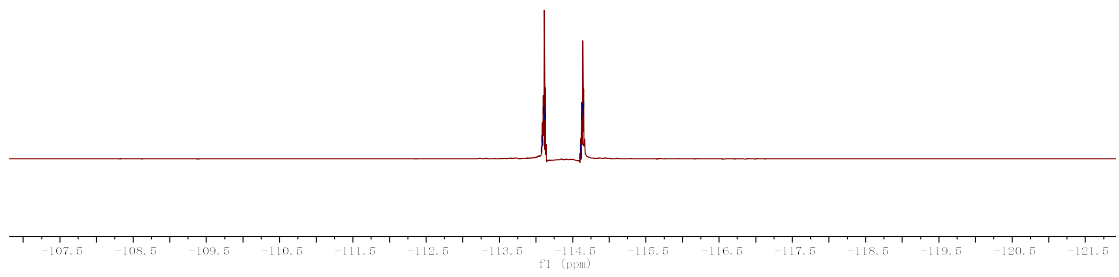
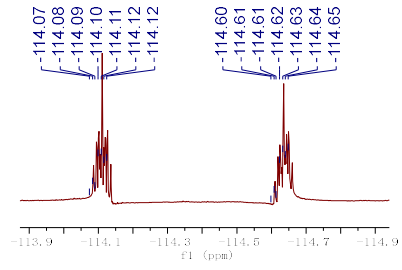
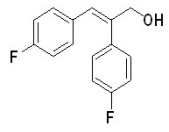
2u



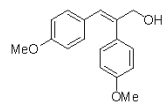
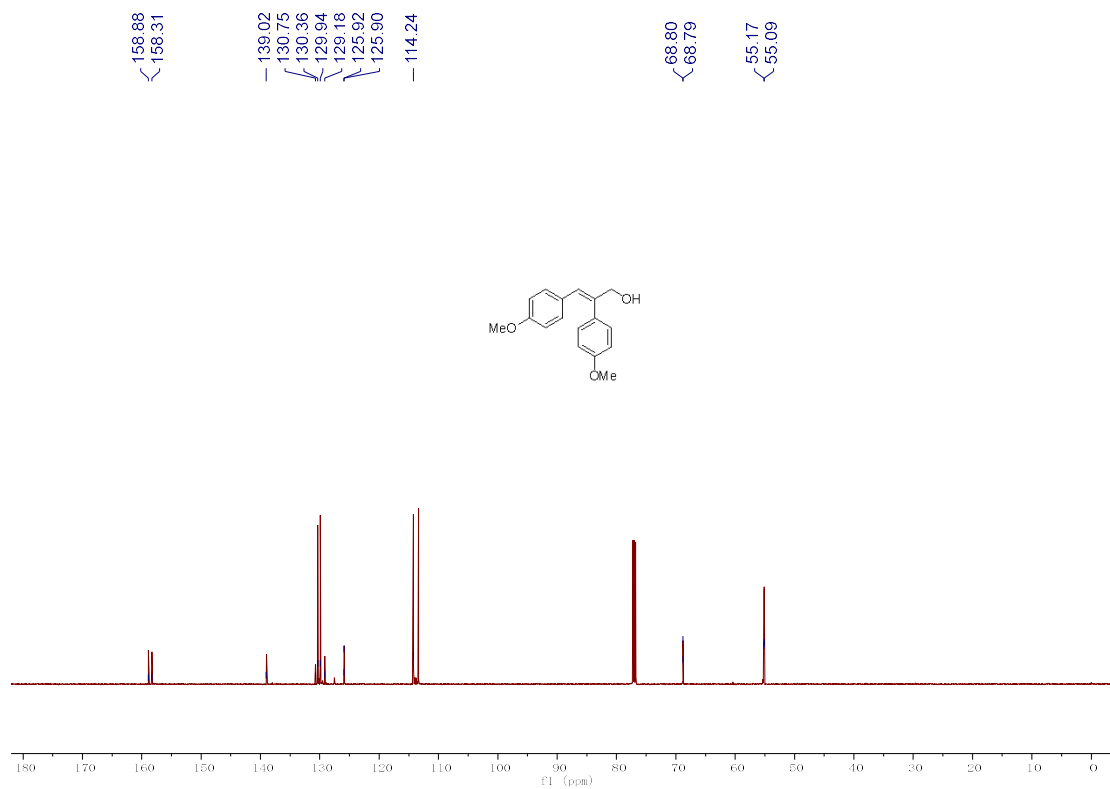
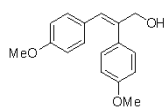
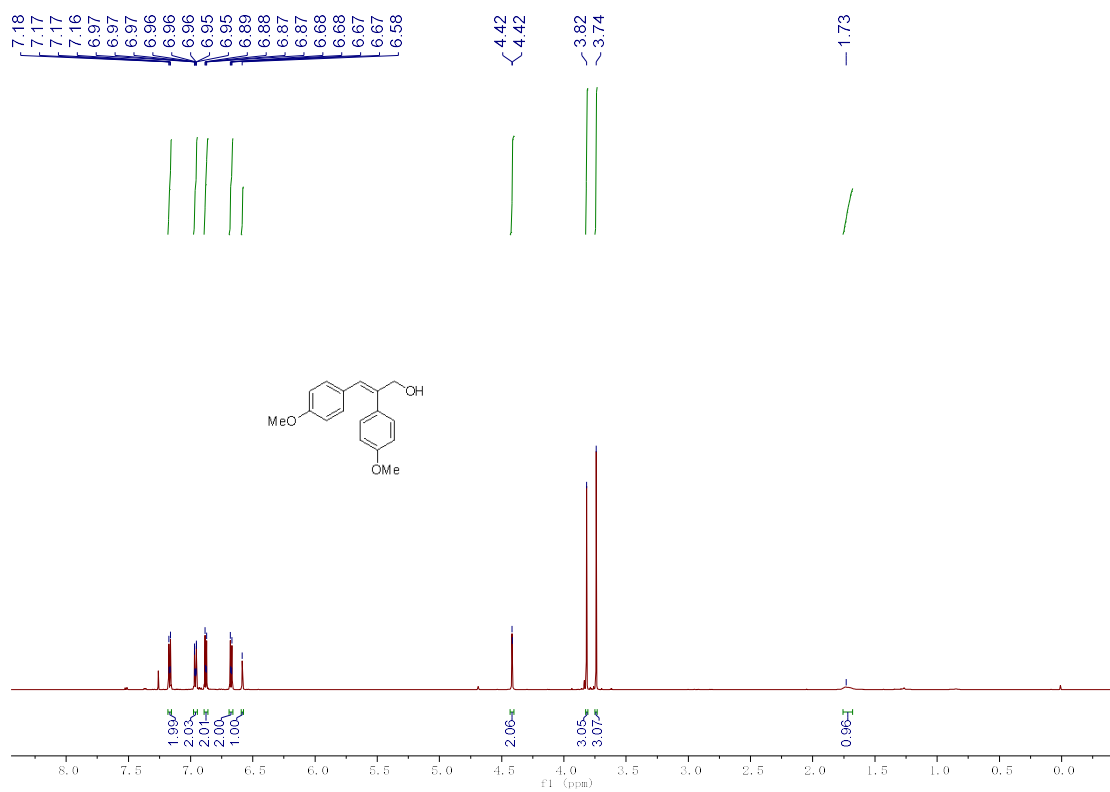
2v



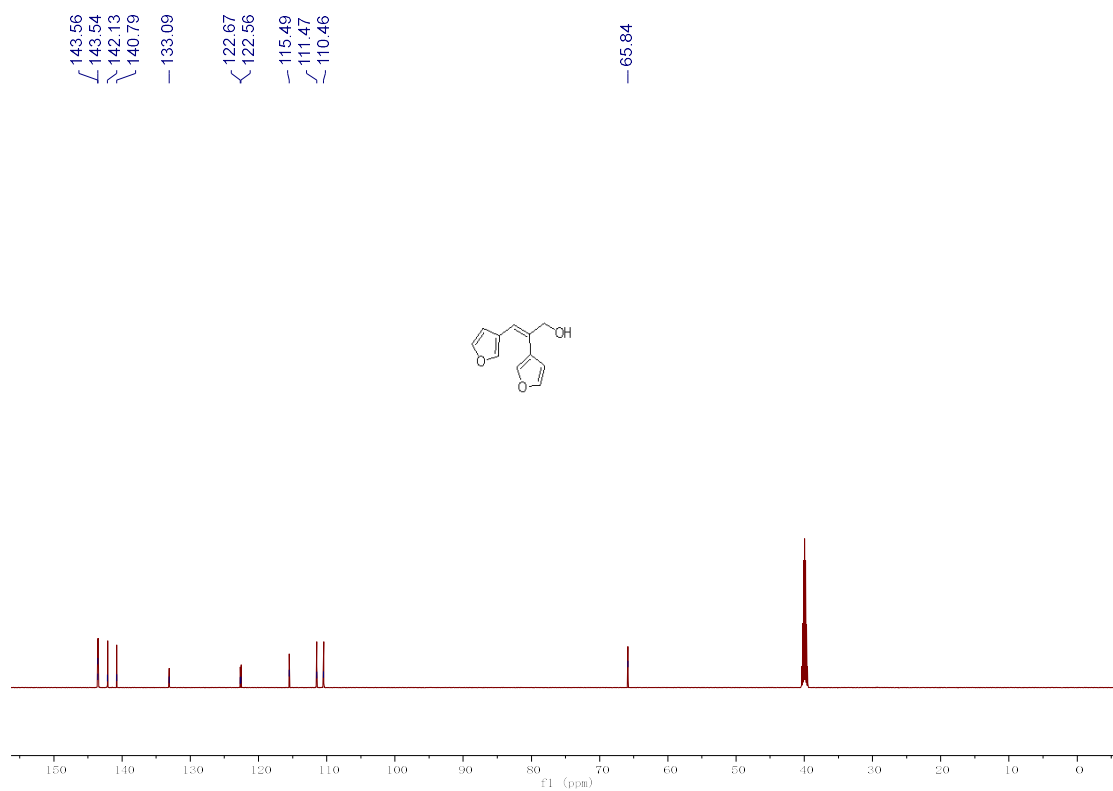
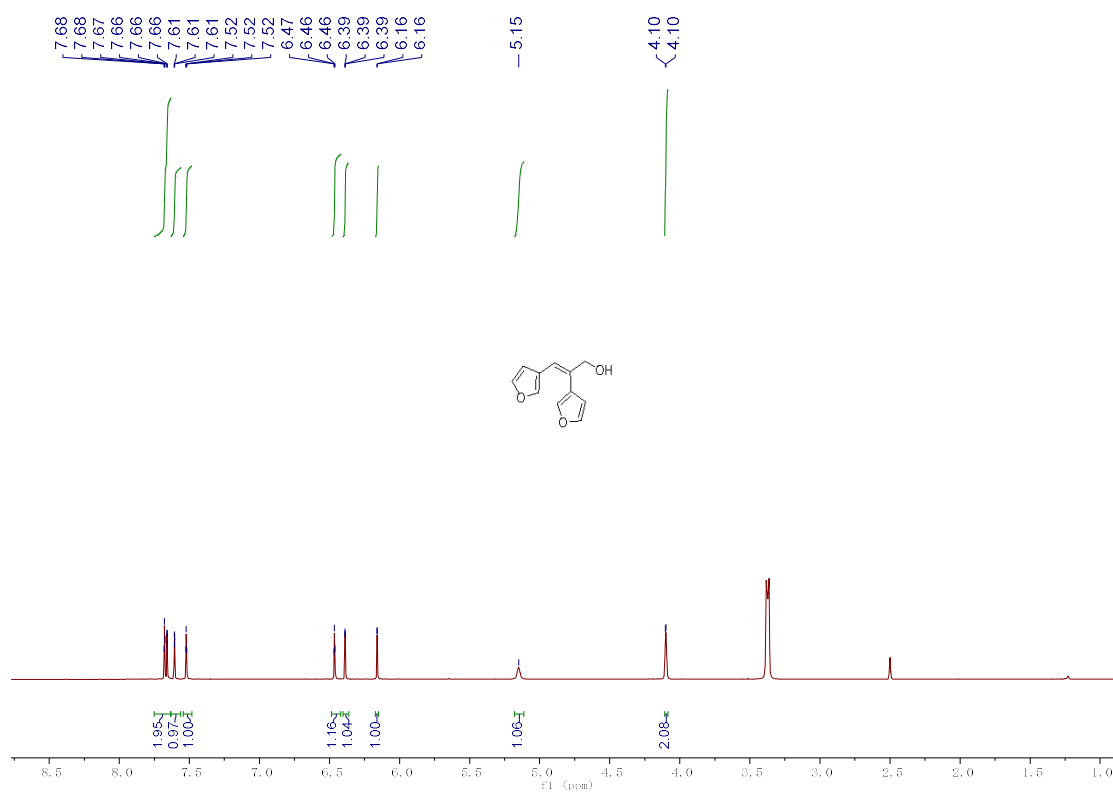
-114.07
-114.08
-114.09
-114.10
-114.11
-114.12
-114.12
-114.60
-114.61
-114.61
-114.62
-114.63
-114.64
-114.65



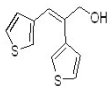
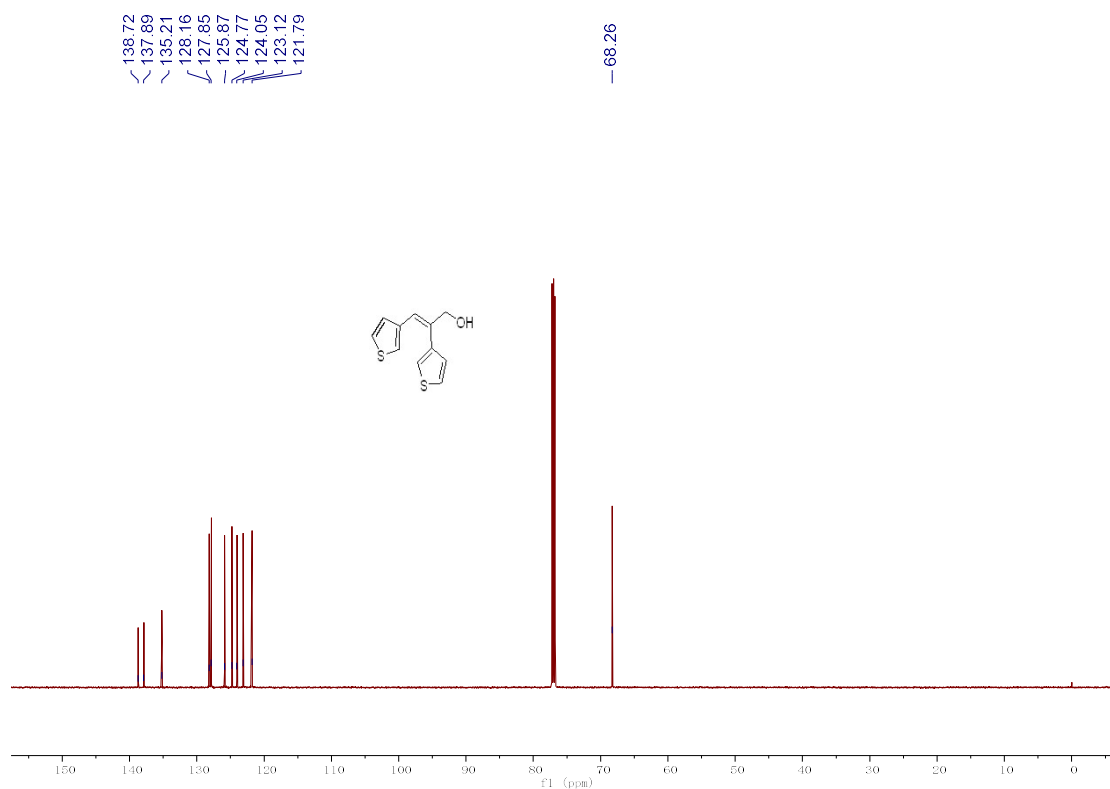
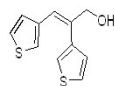
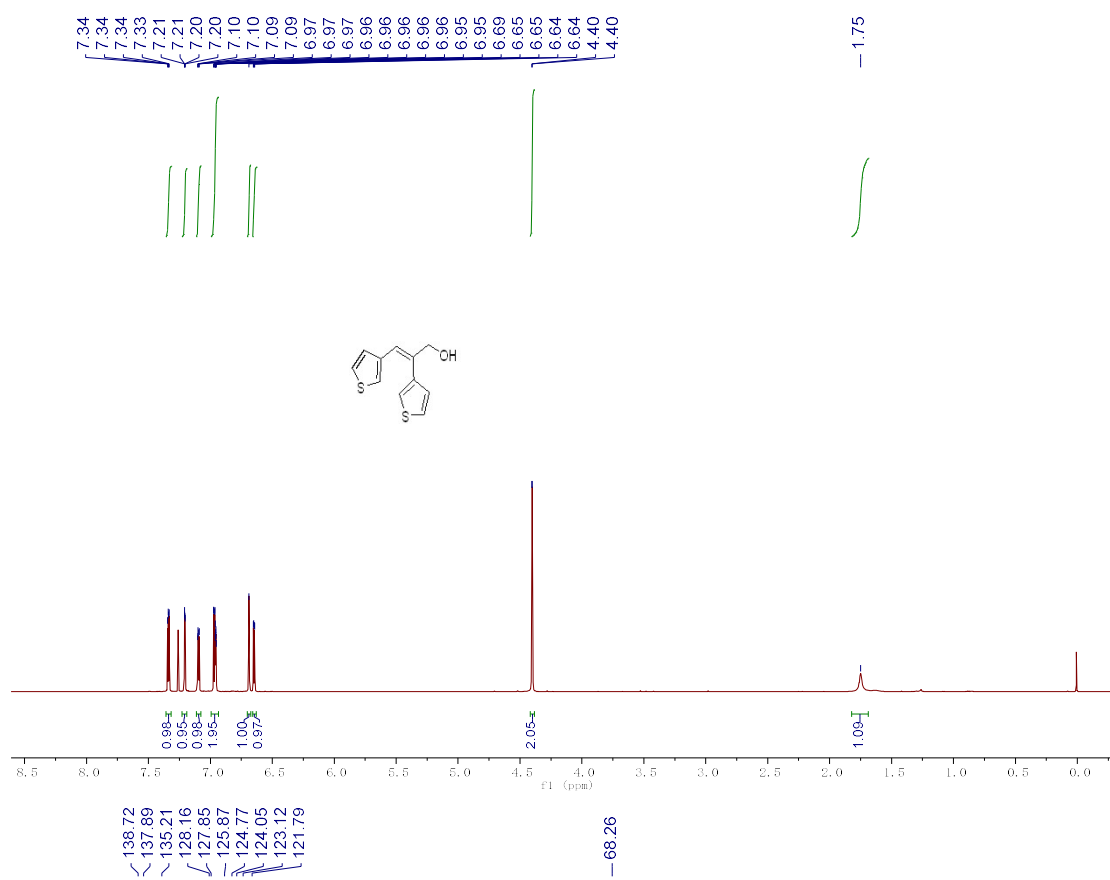
2w



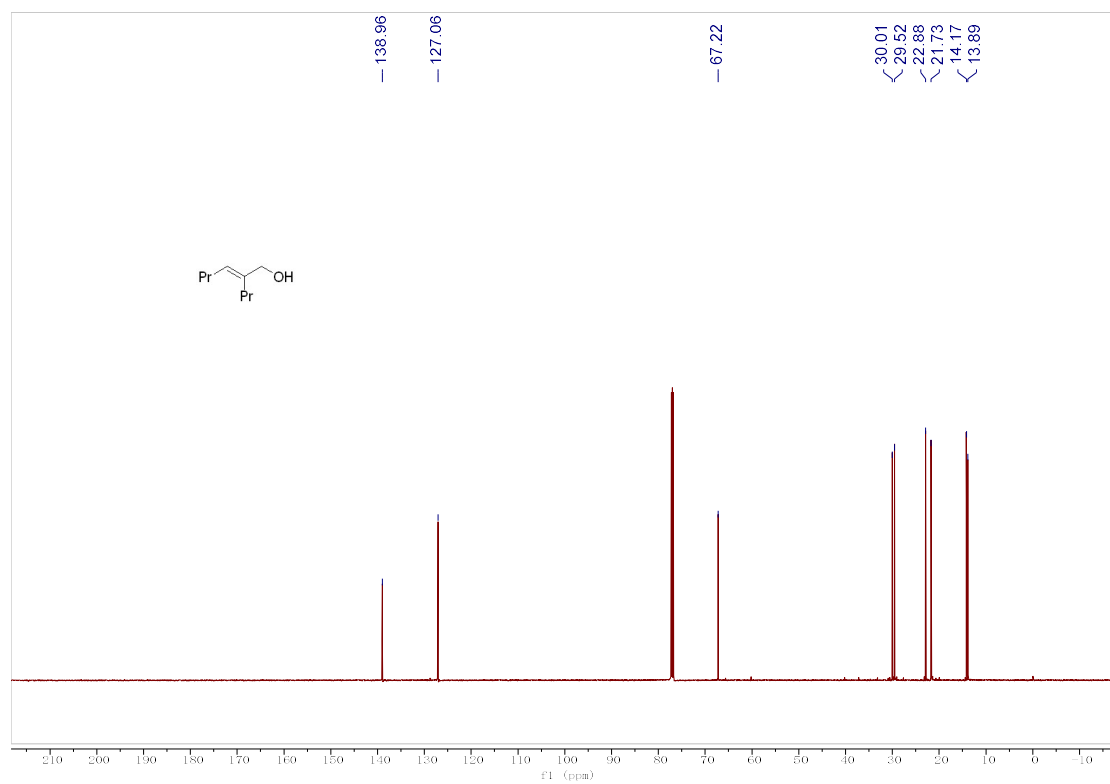
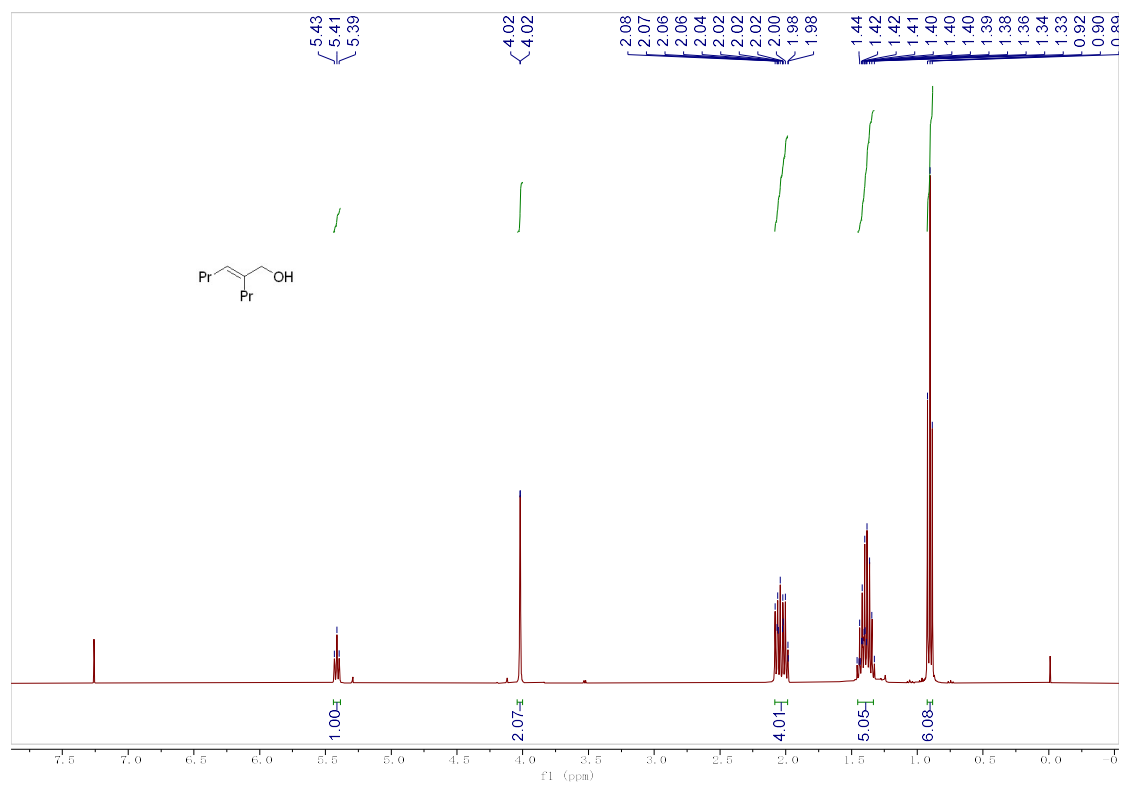
2x



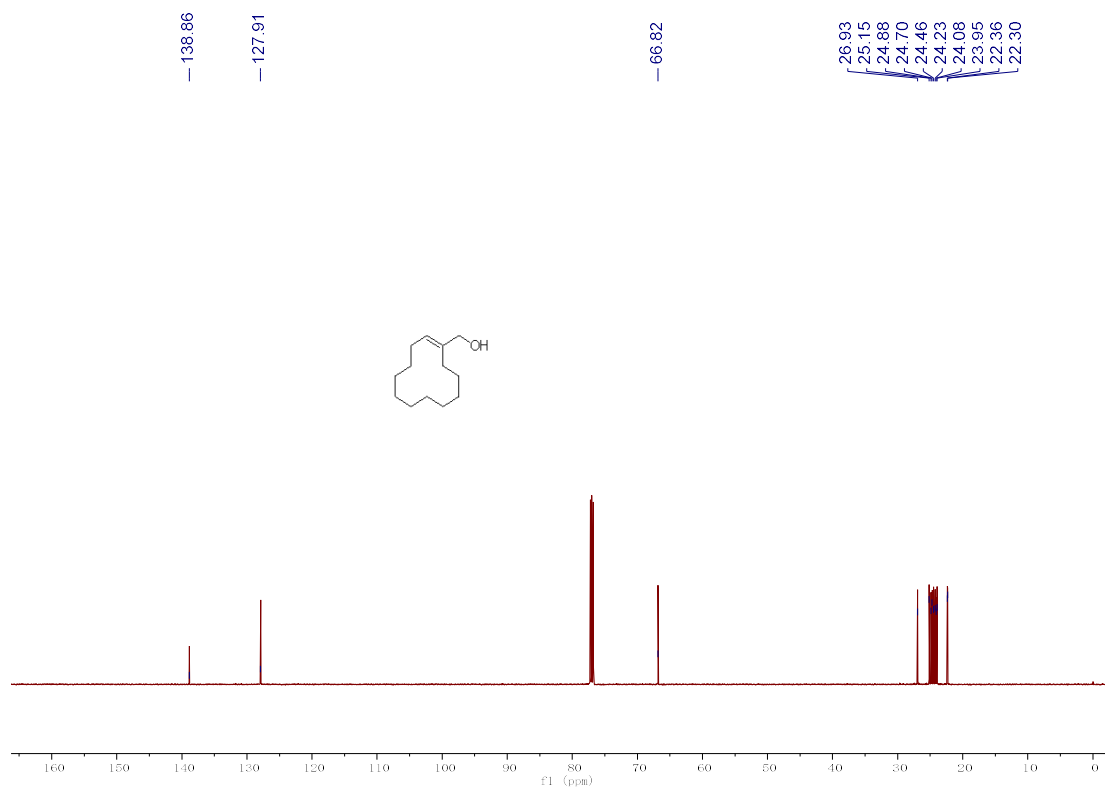
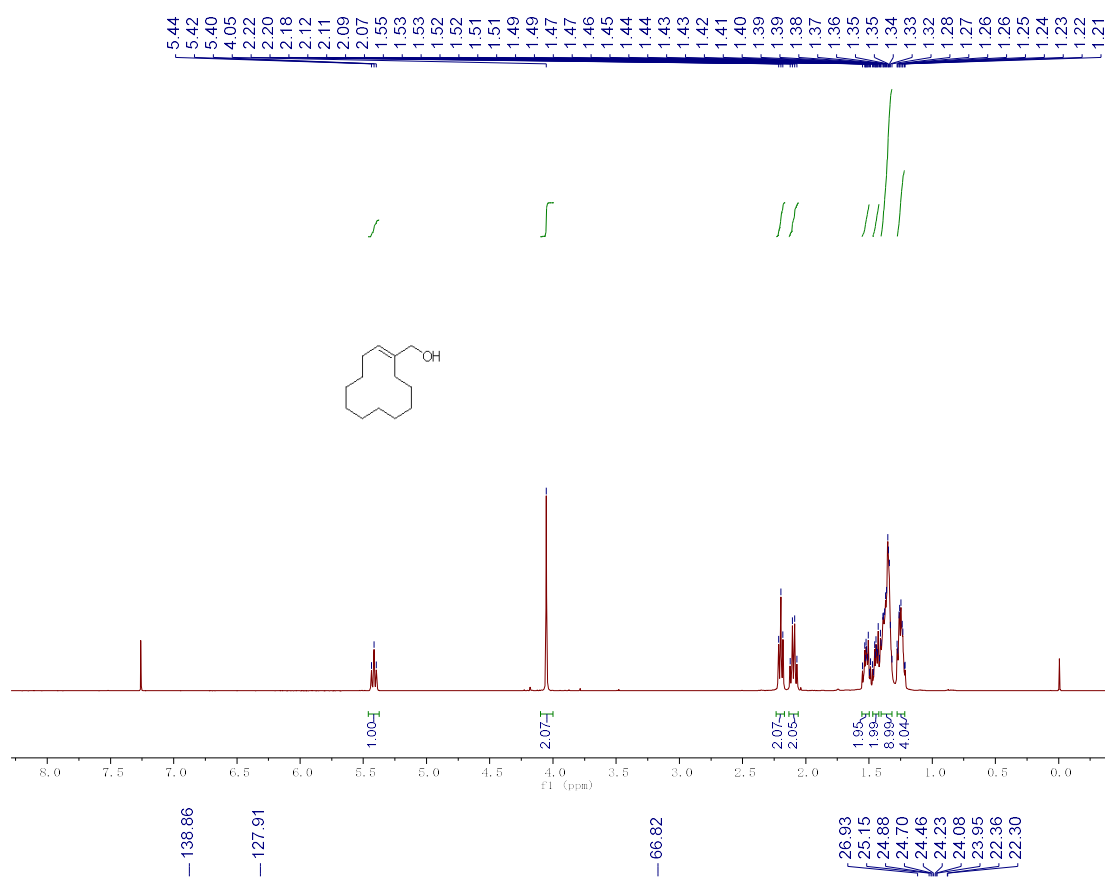
2y



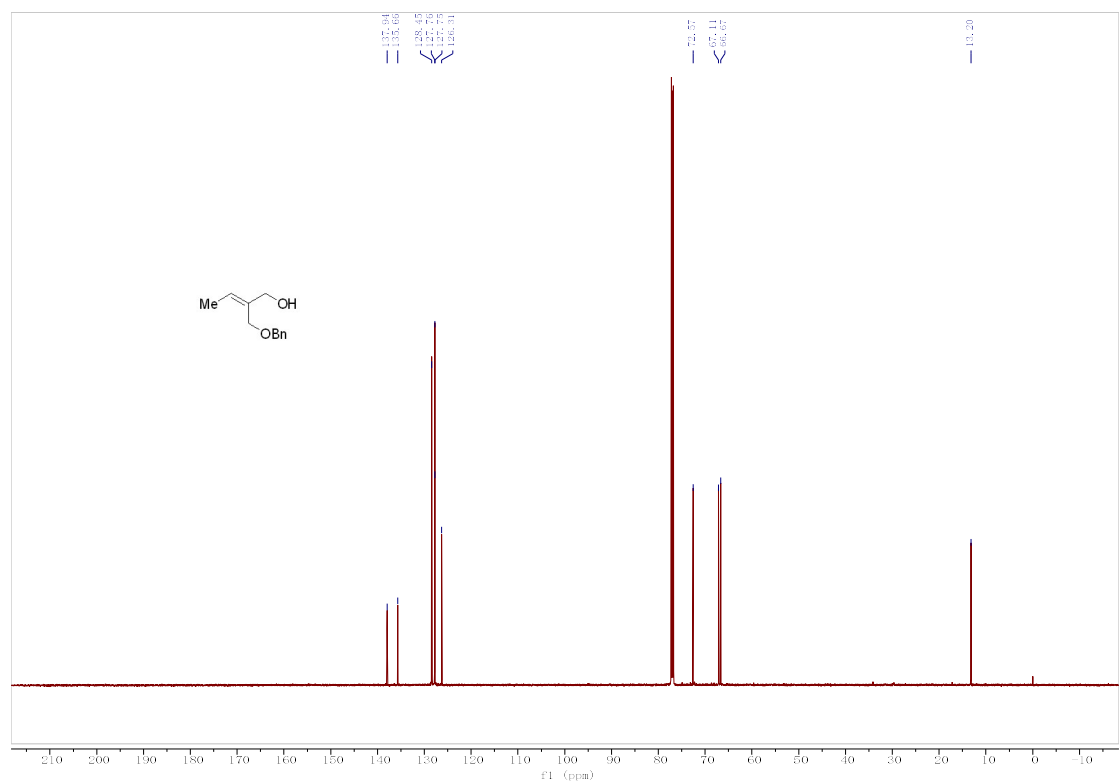
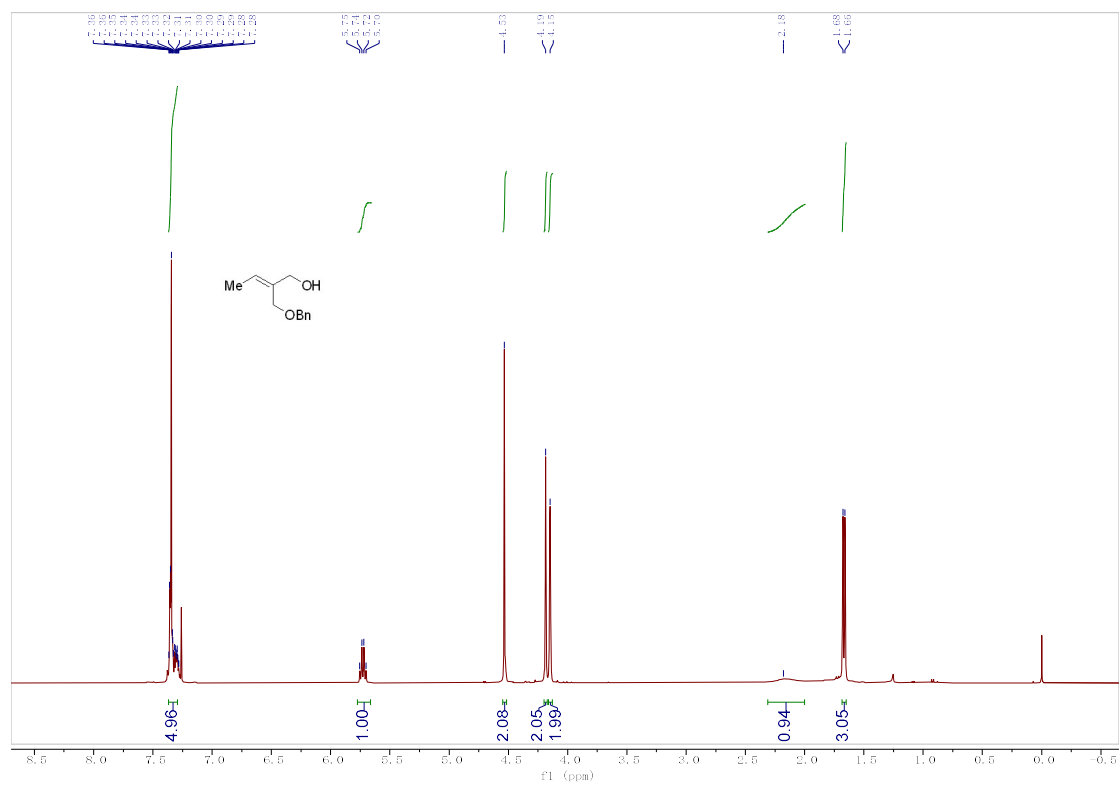
2z



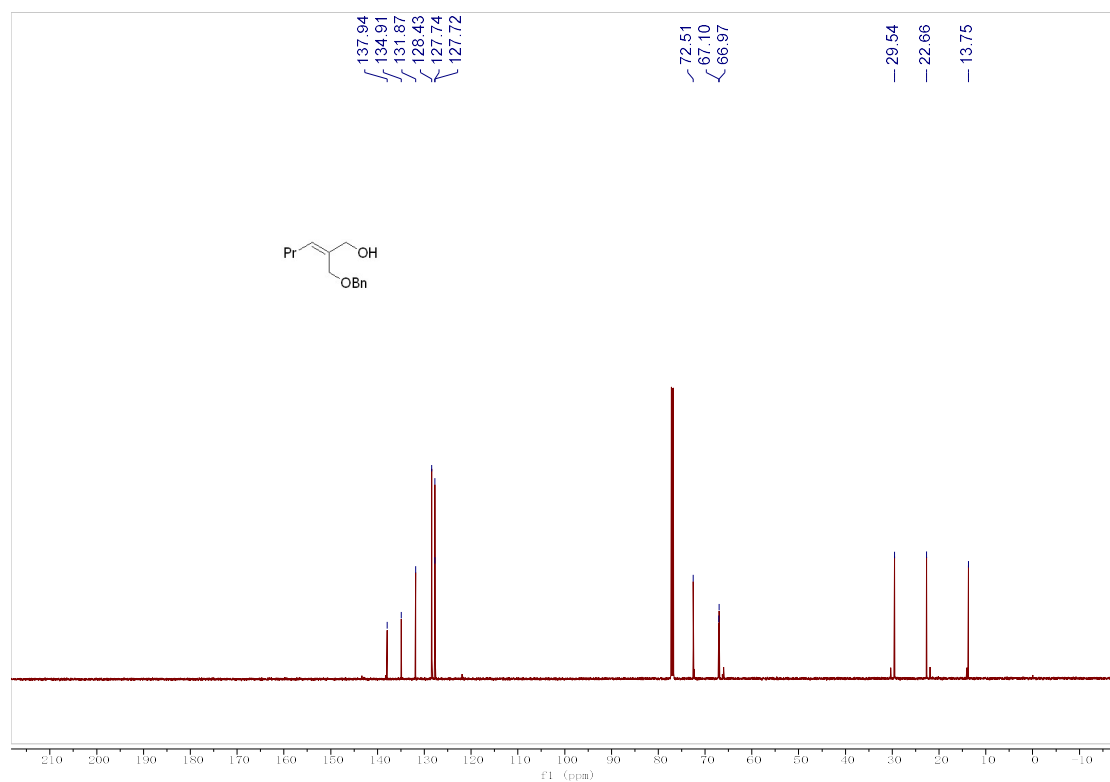
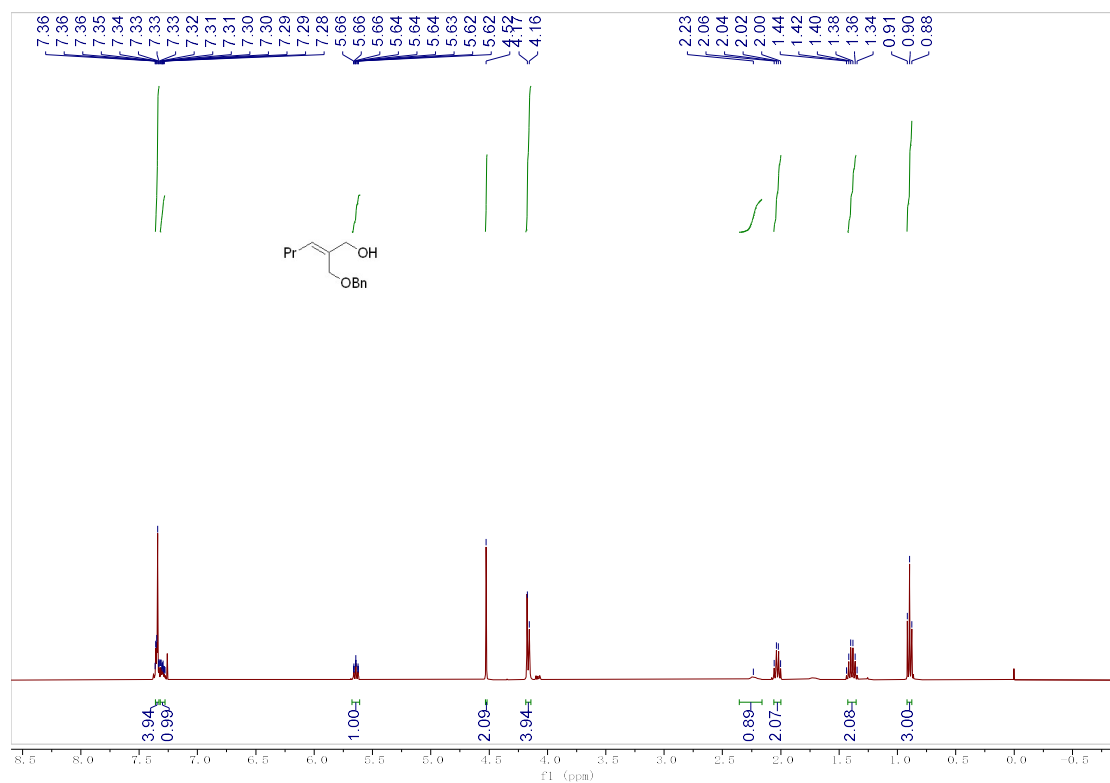
2aa



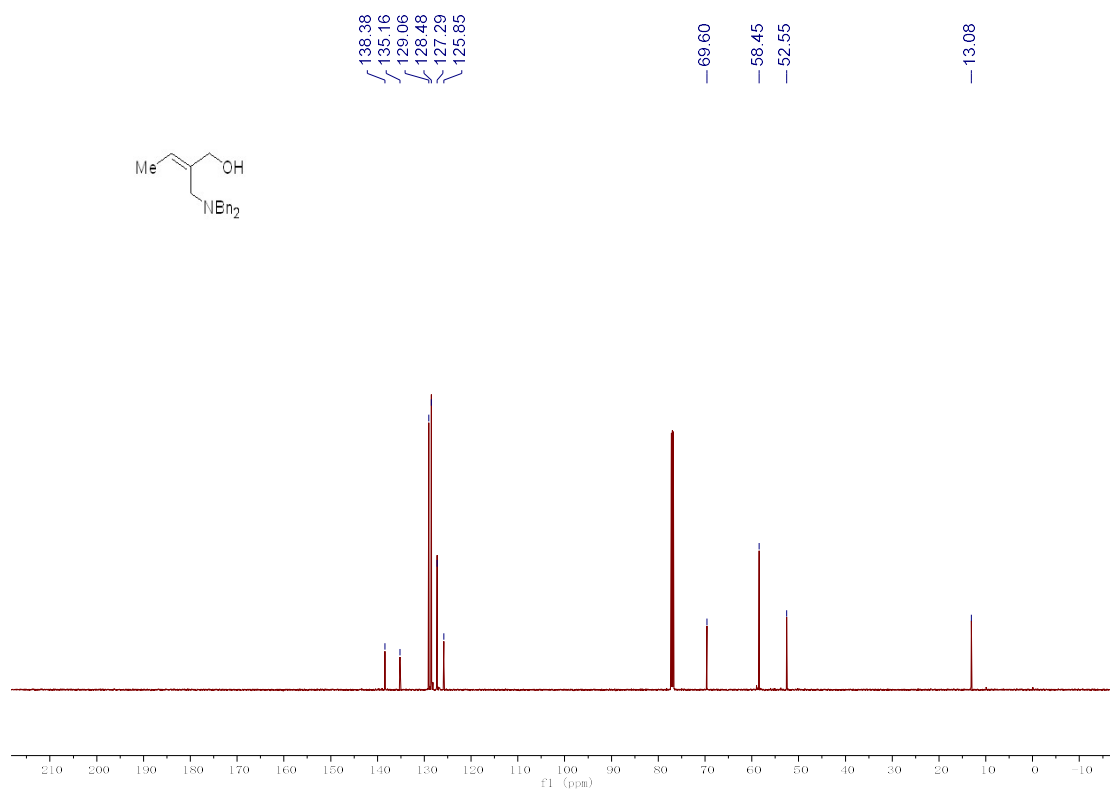
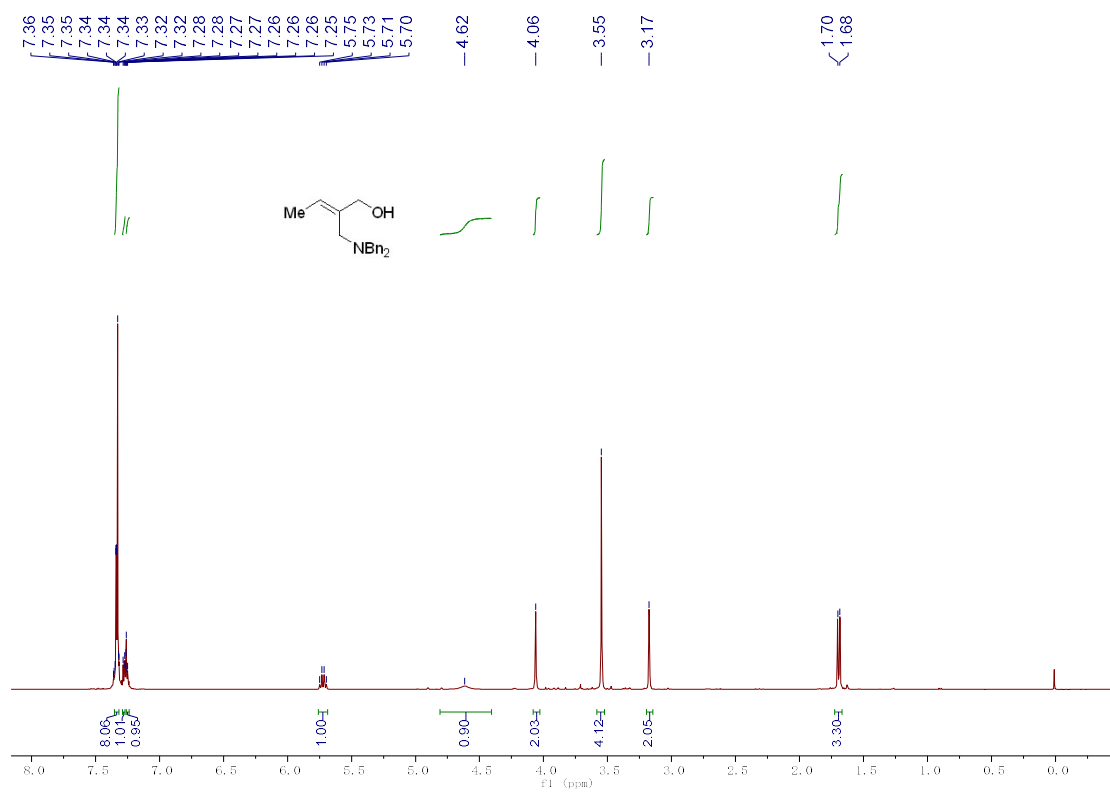
2ab



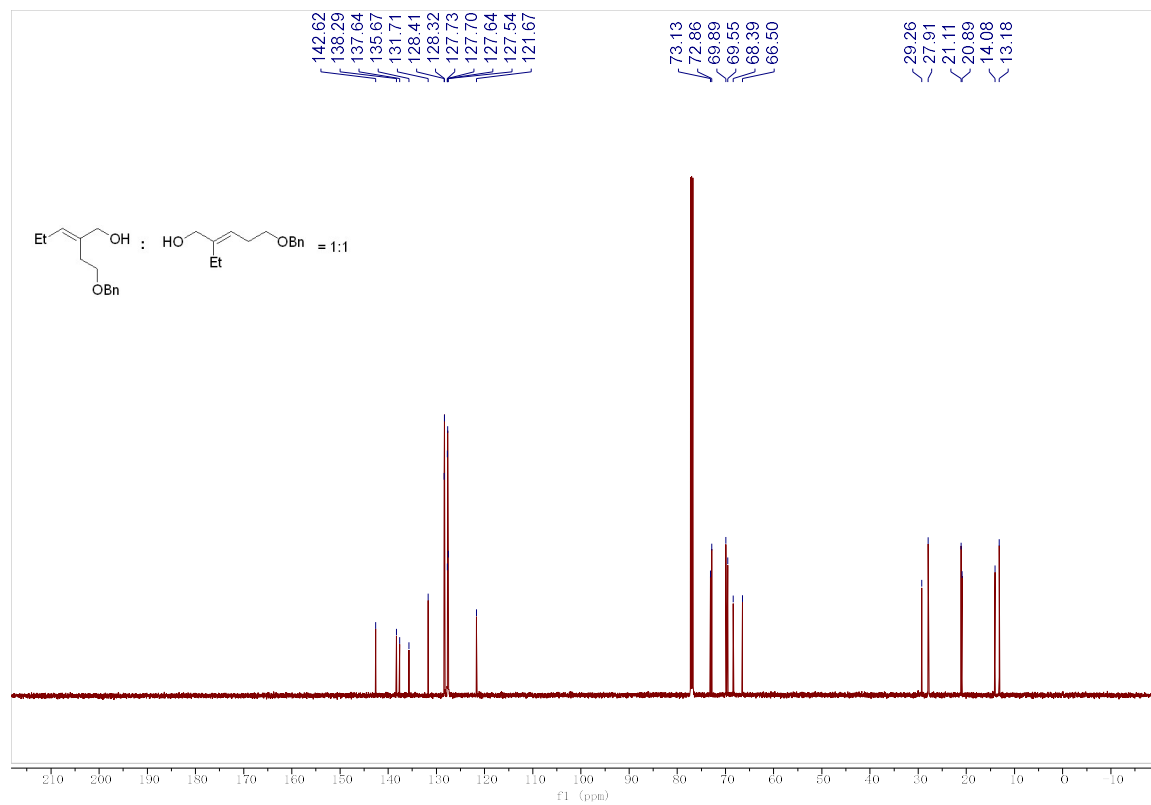
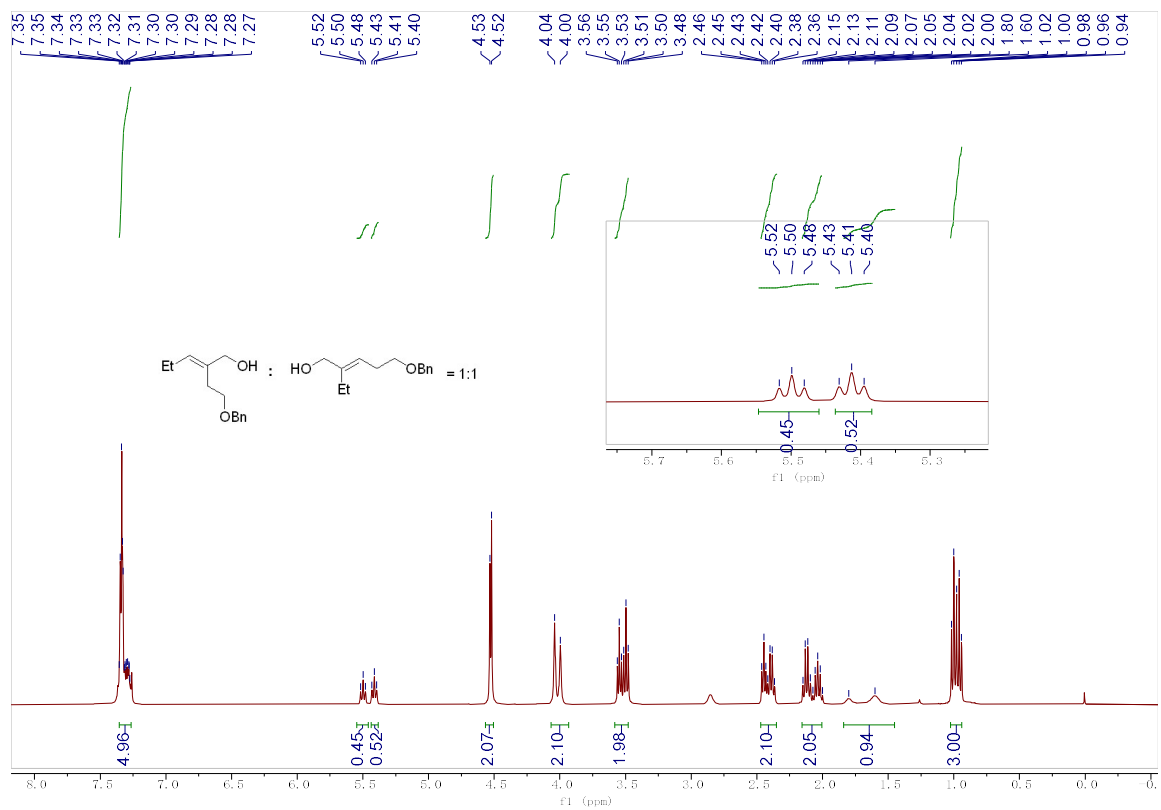
2ac



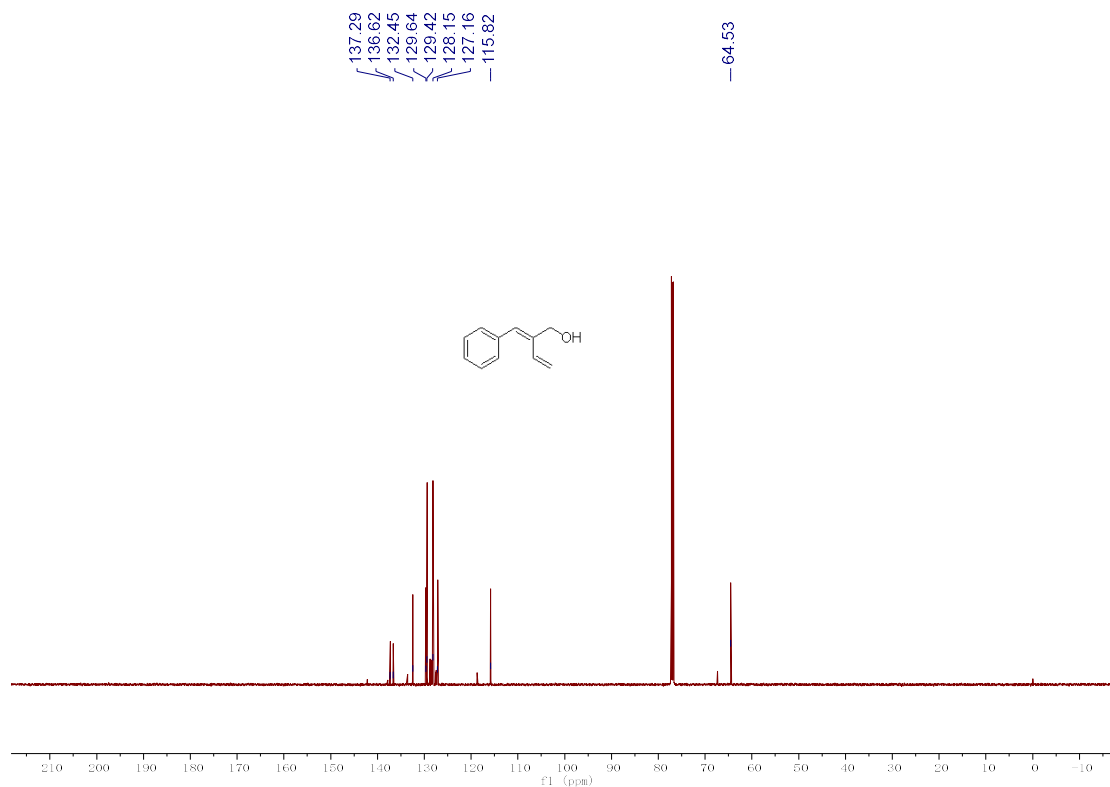
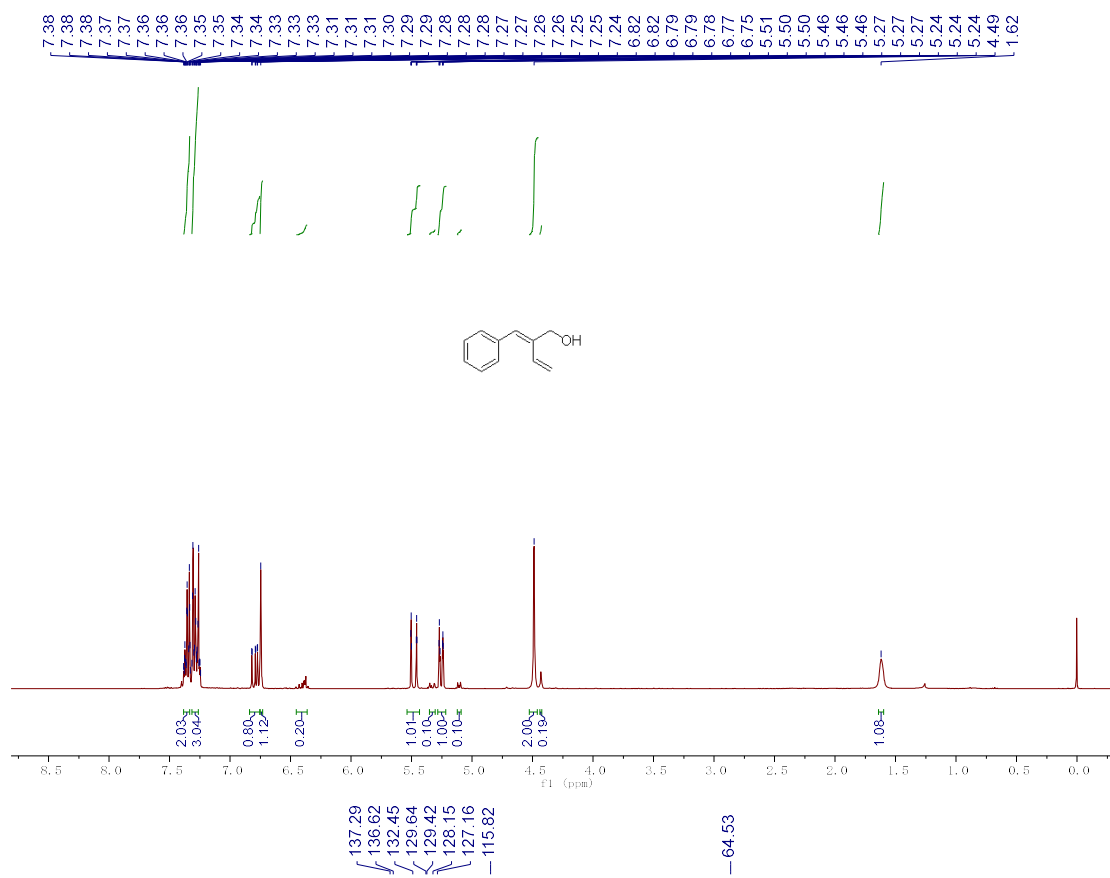
2ad



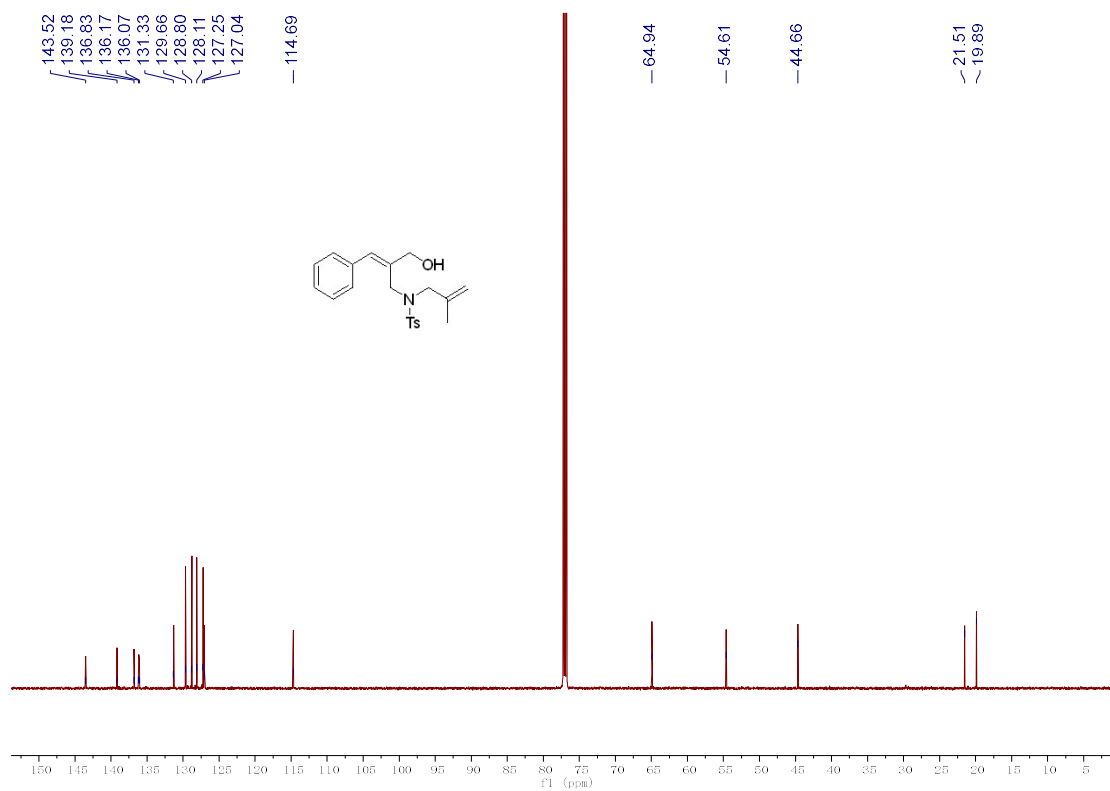
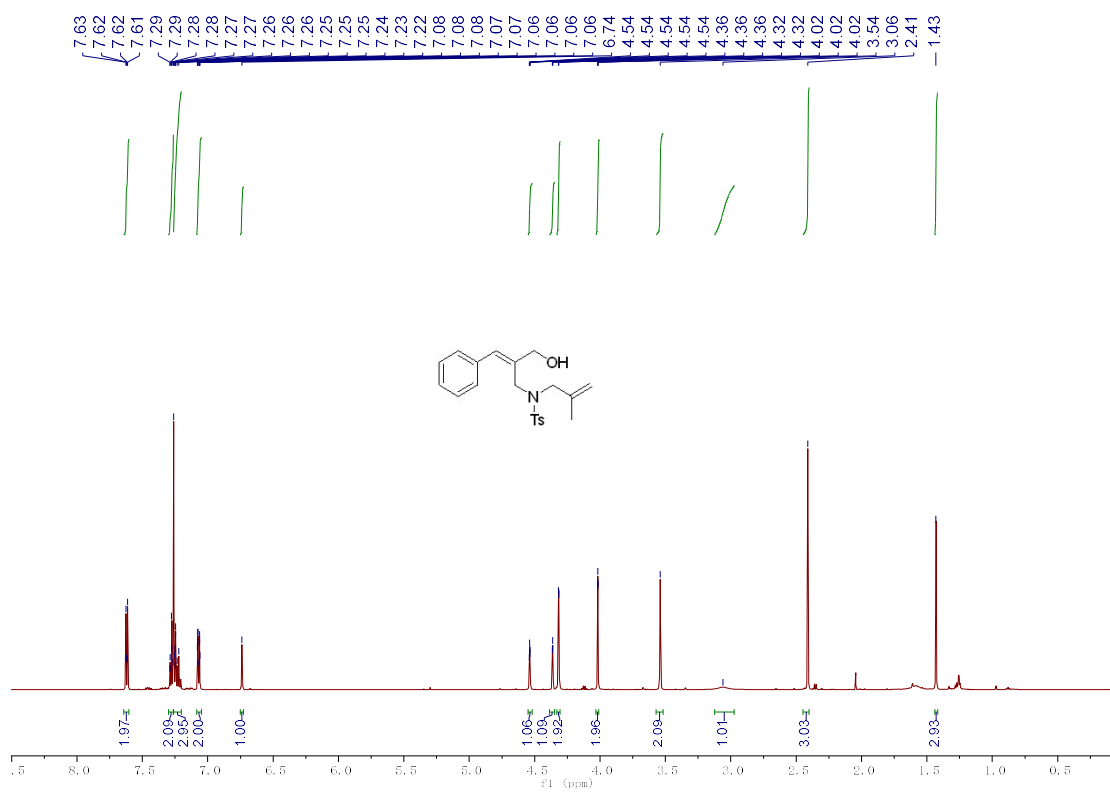
2ae



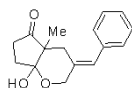
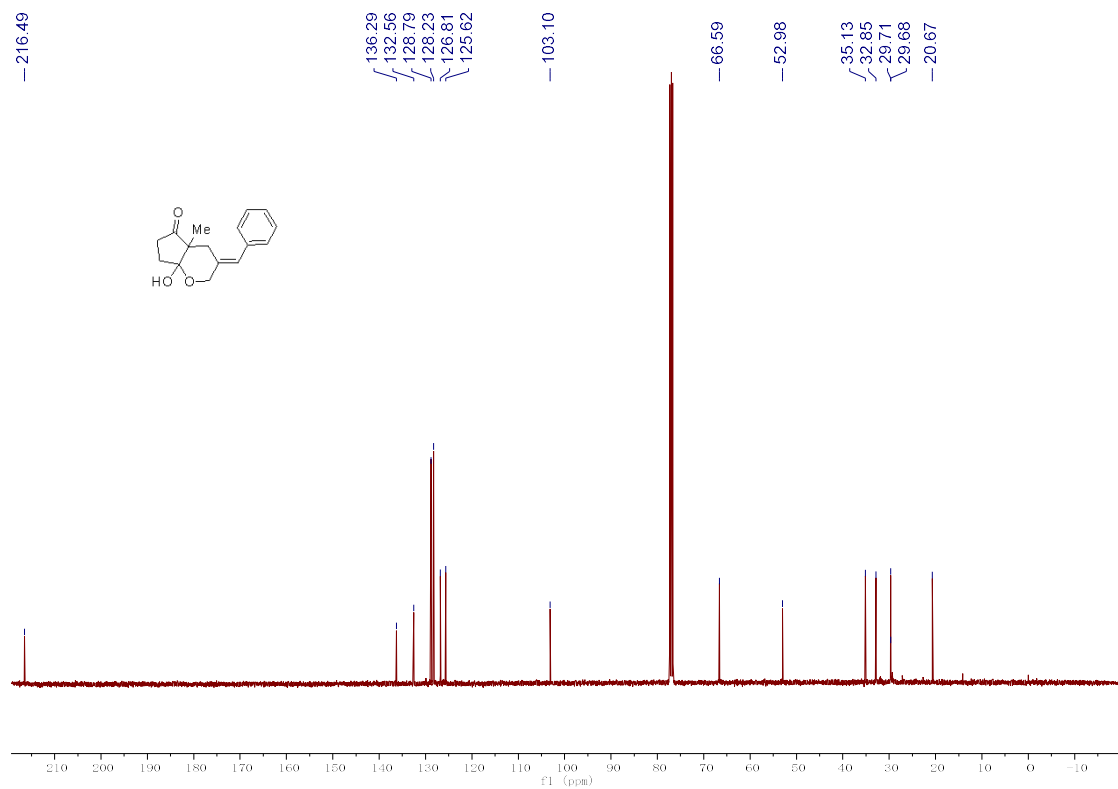
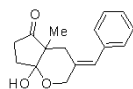
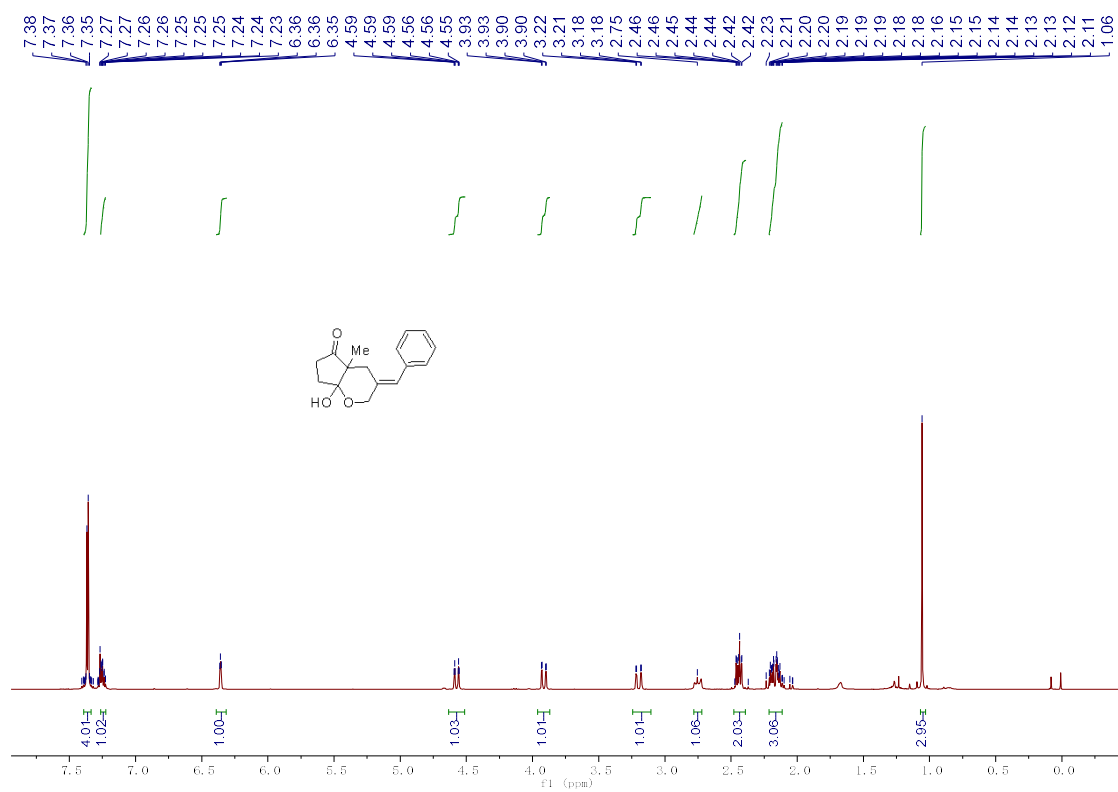
2af



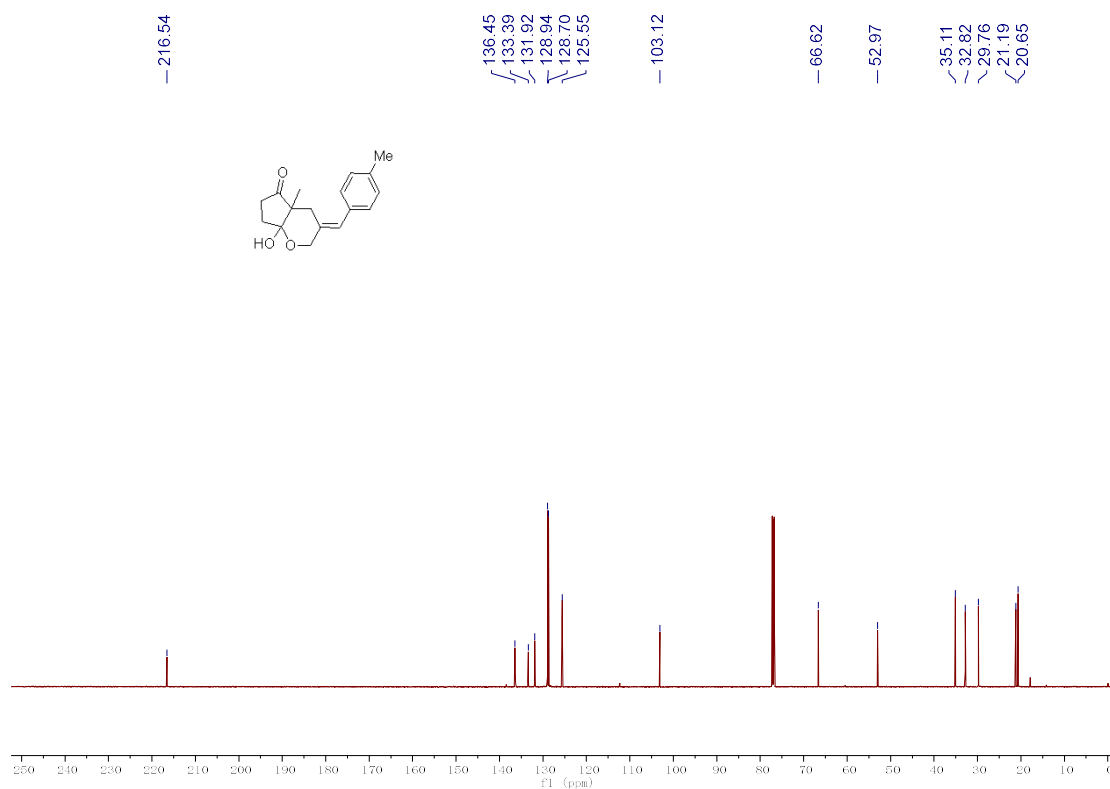
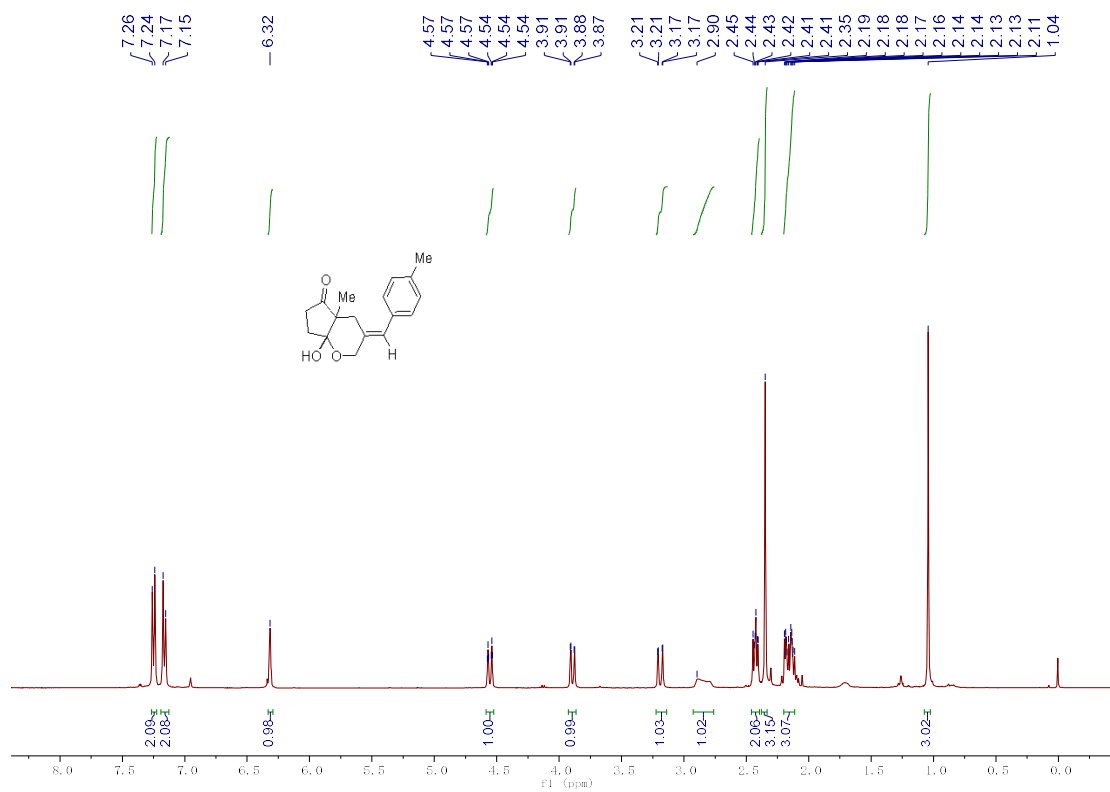
2ag



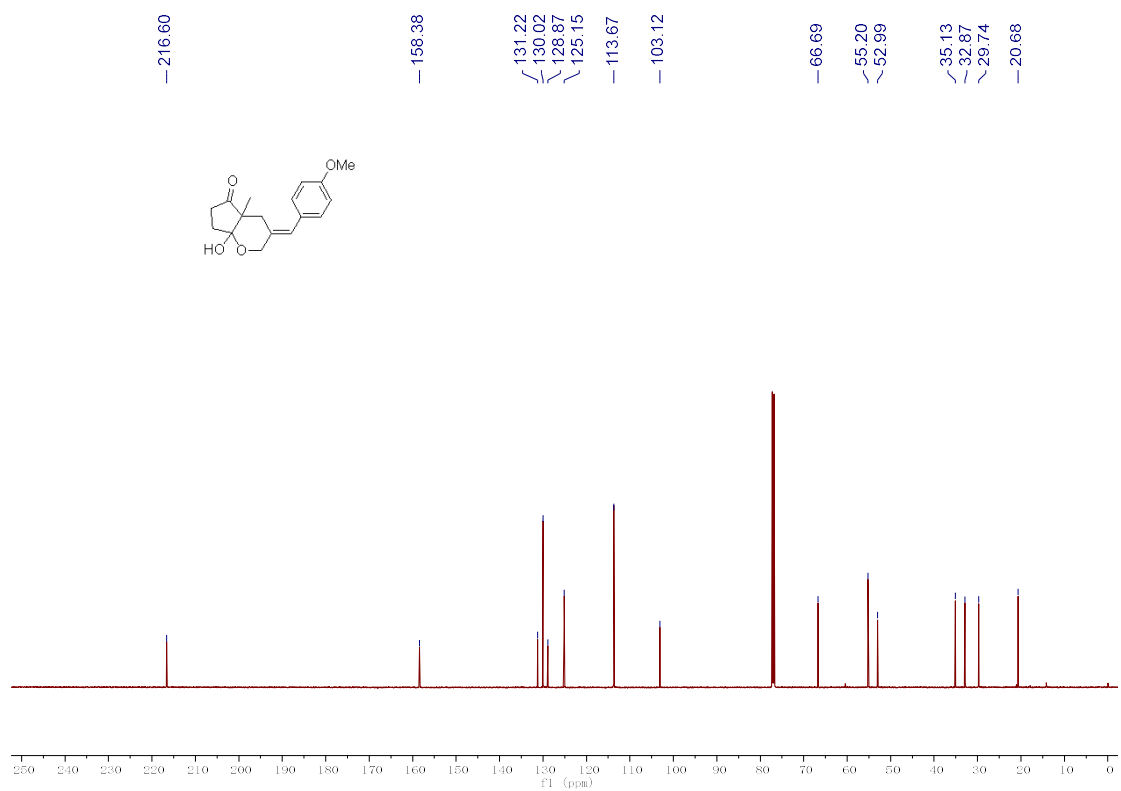
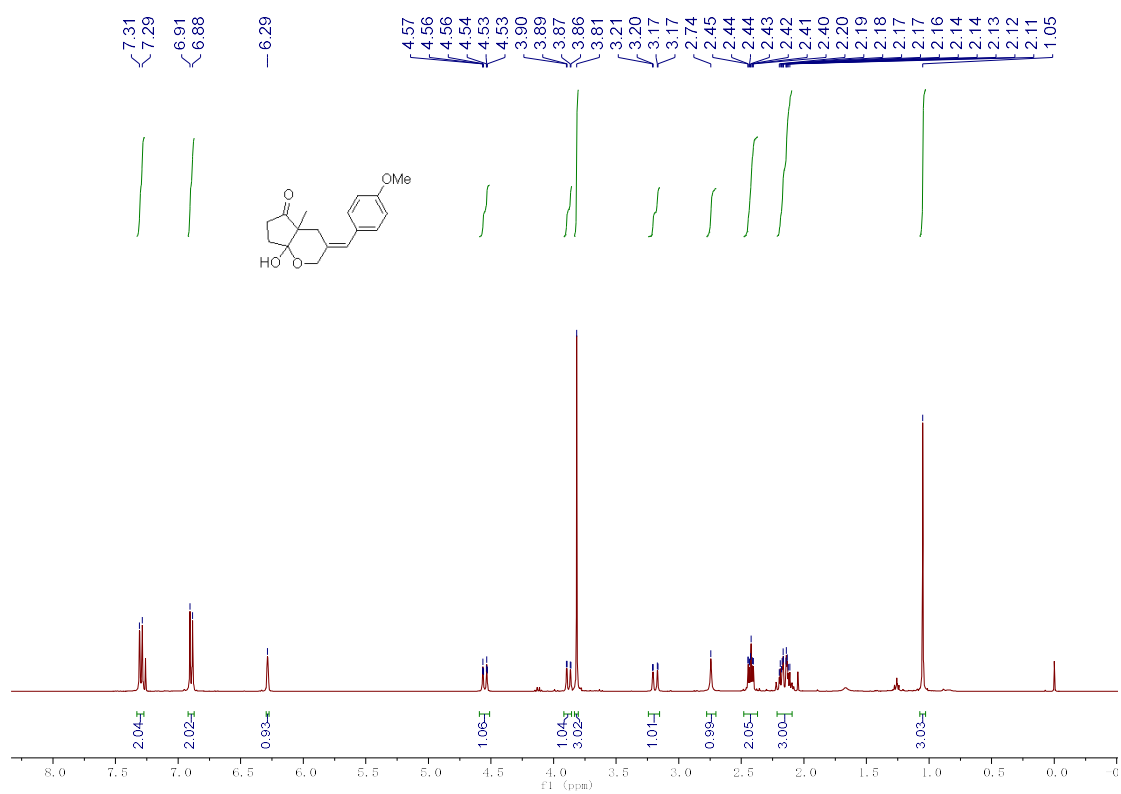
7a



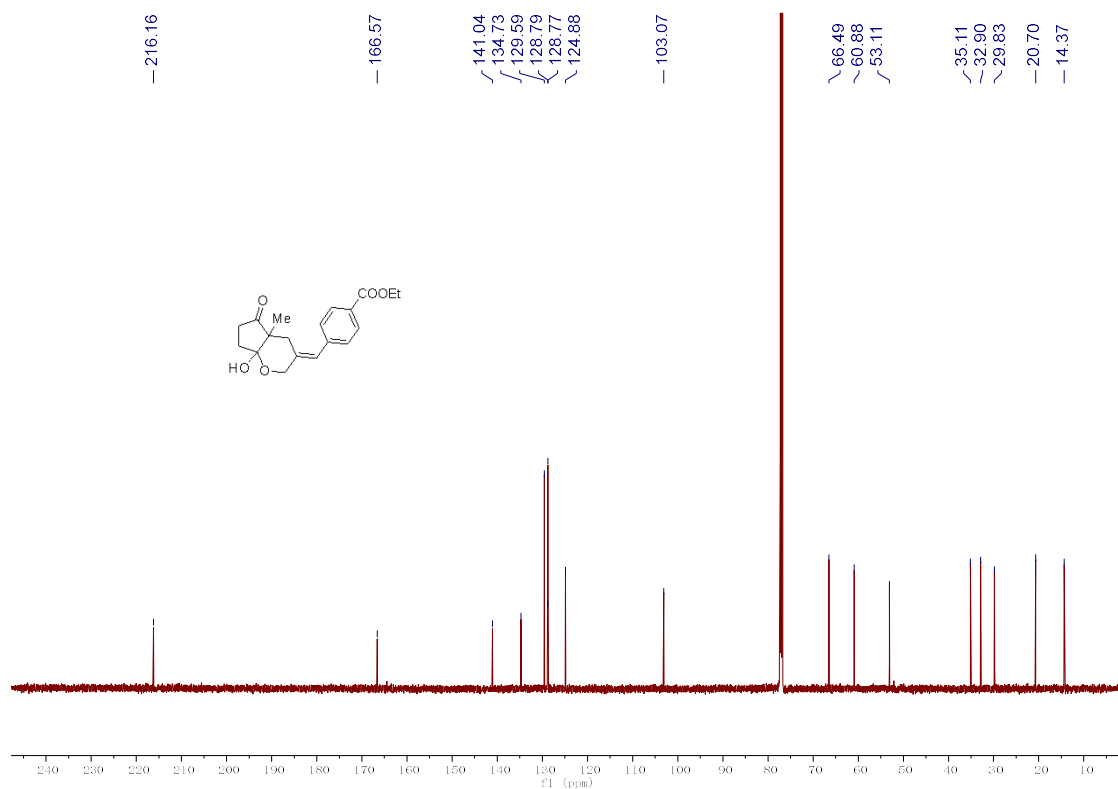
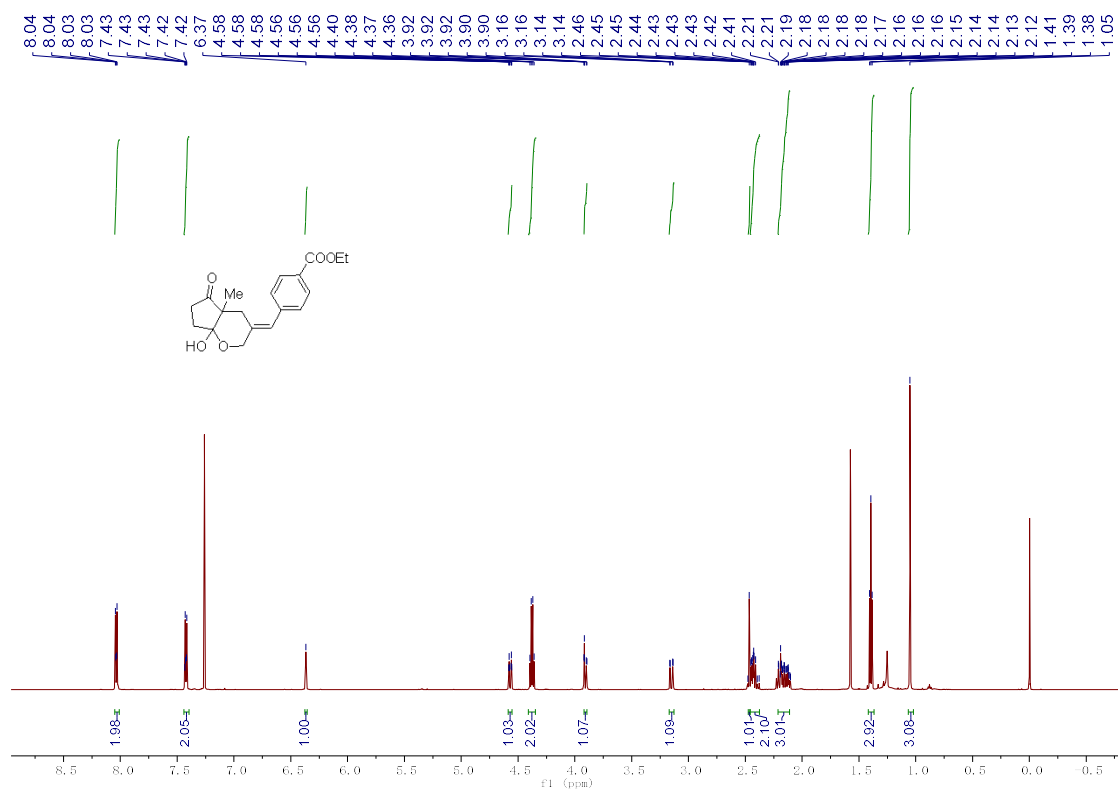
7b



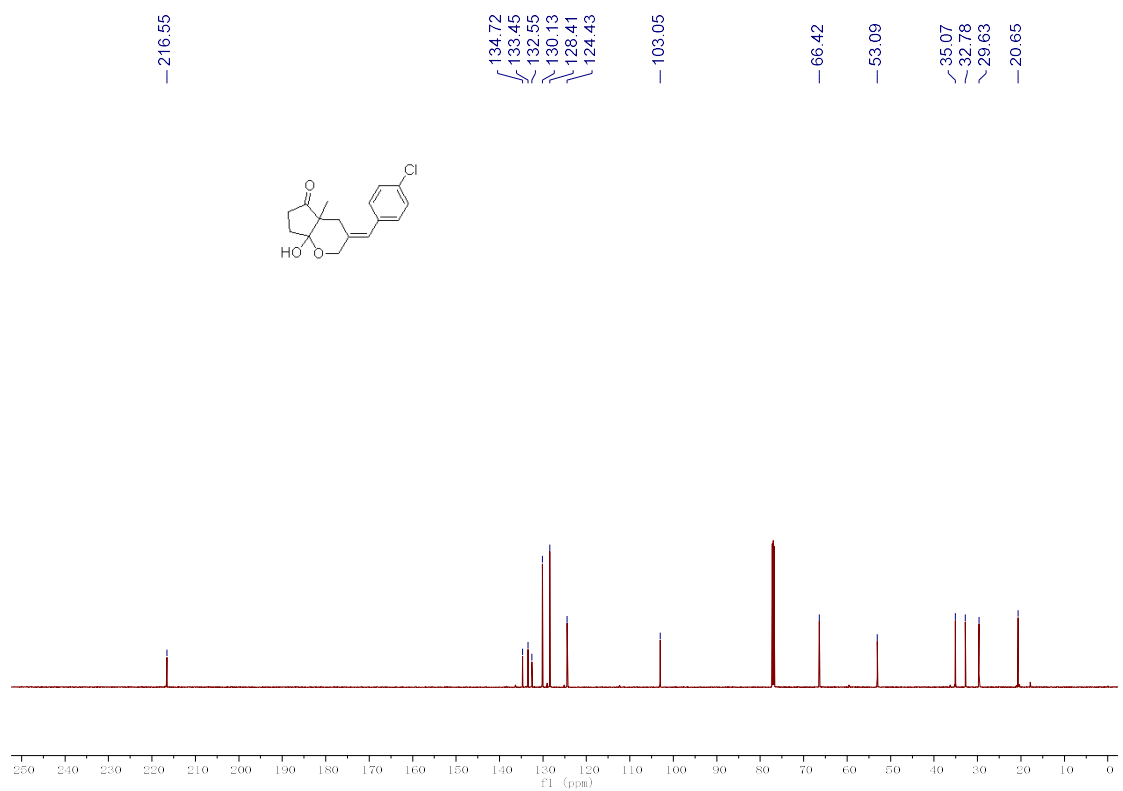
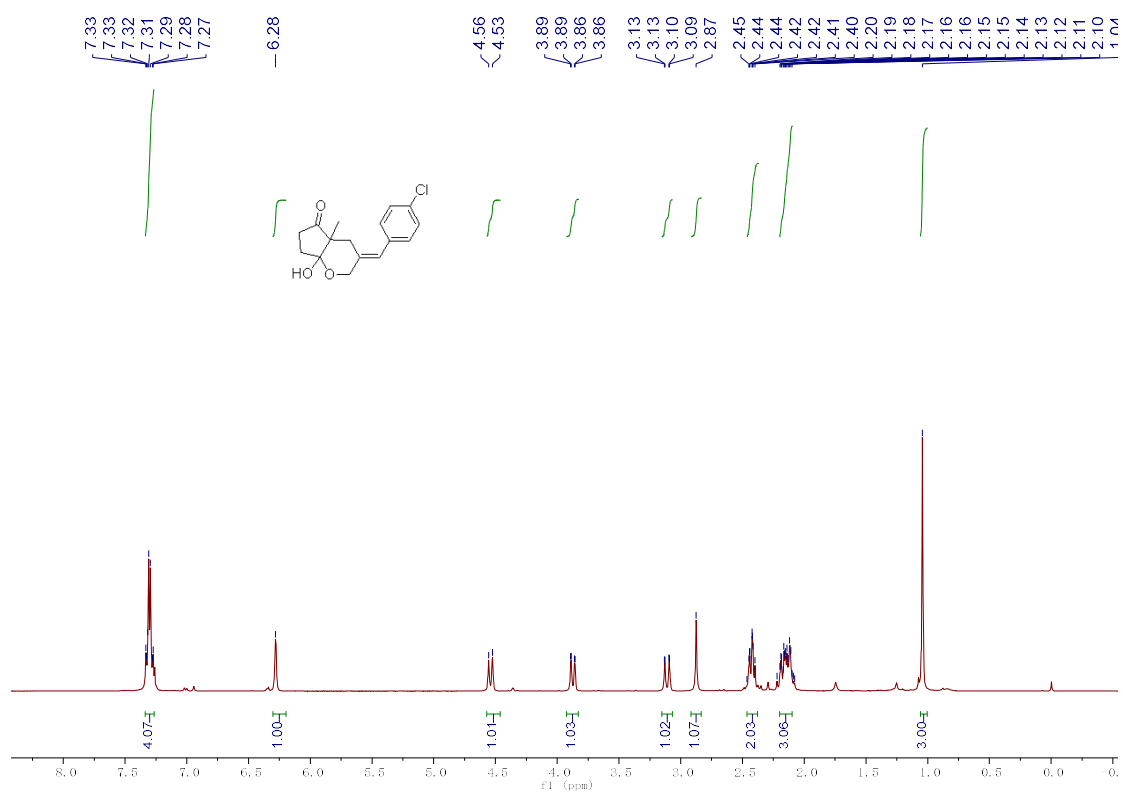
7c



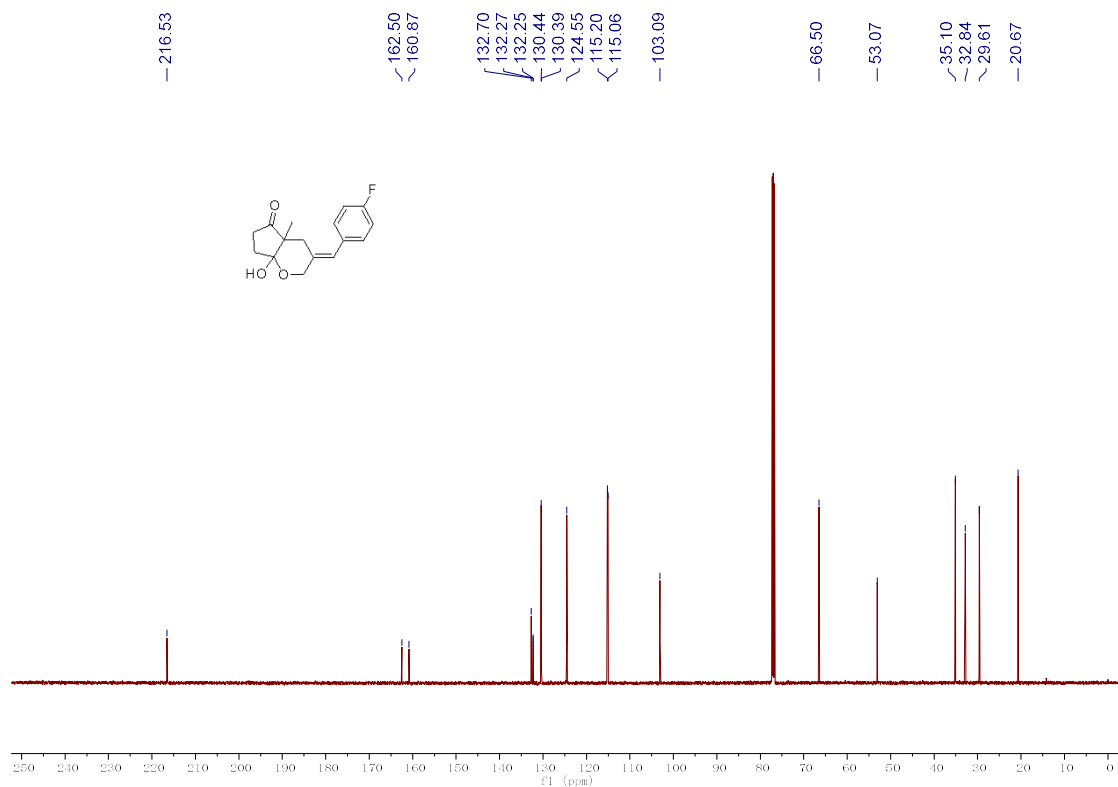
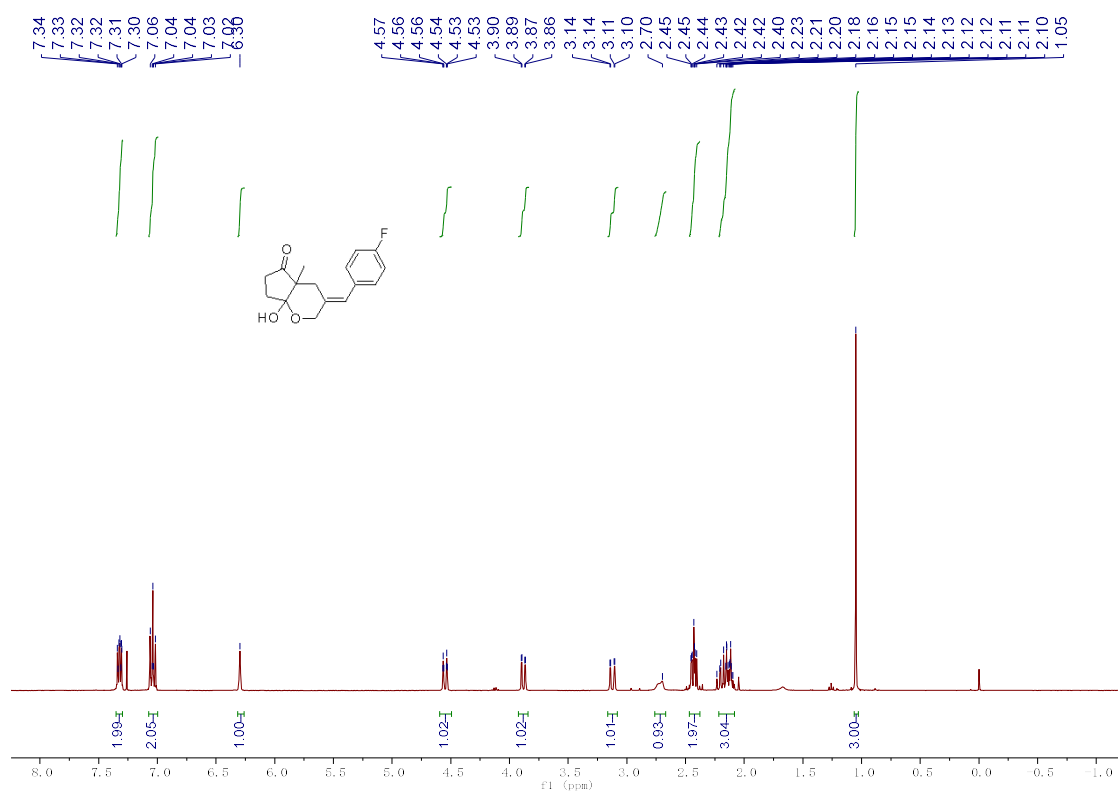
7d

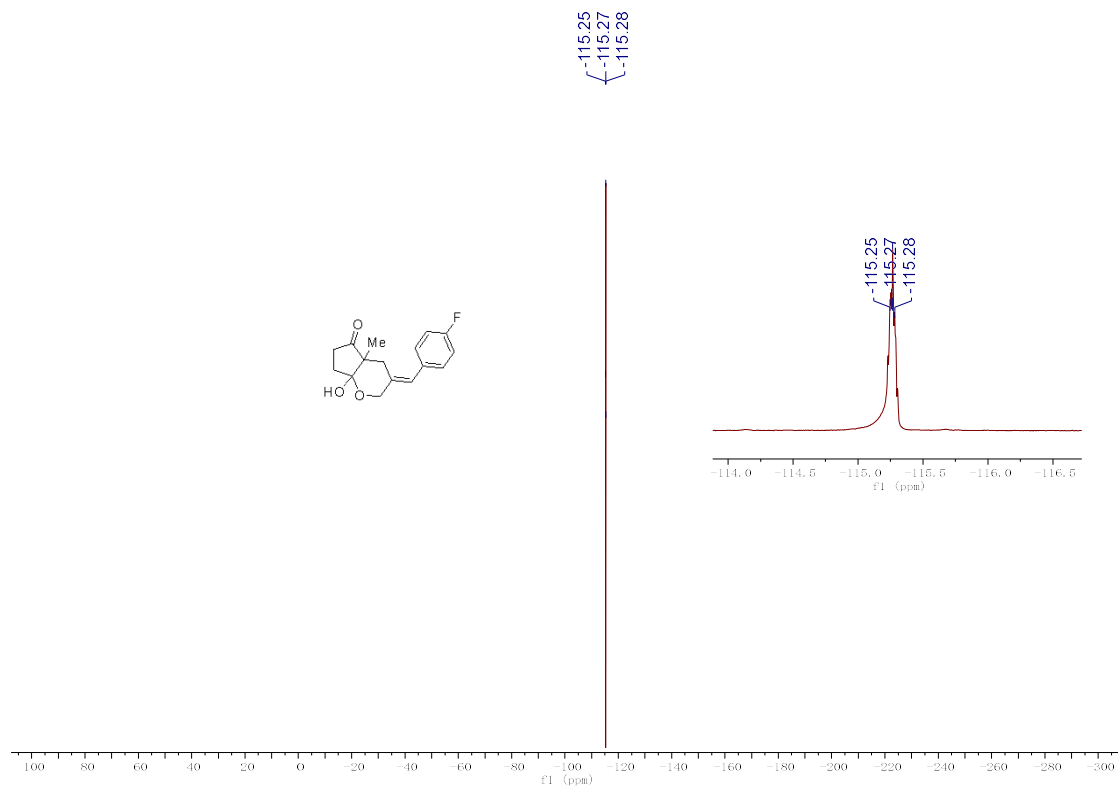


7e

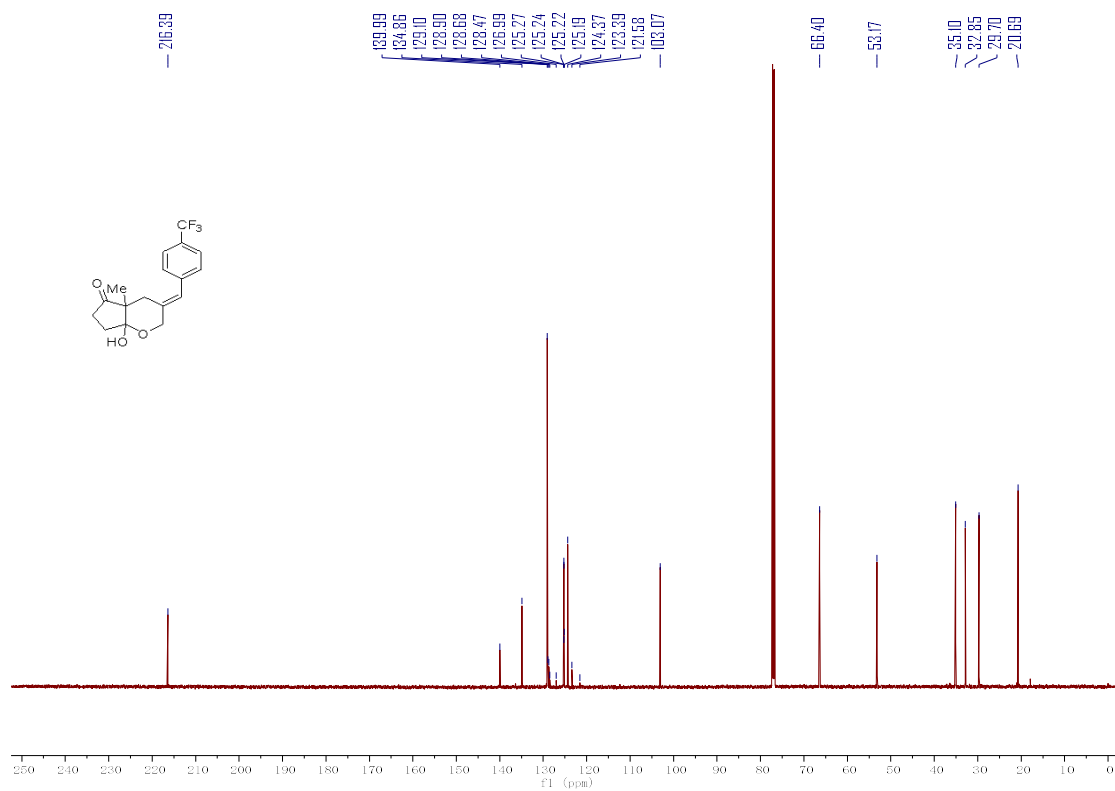
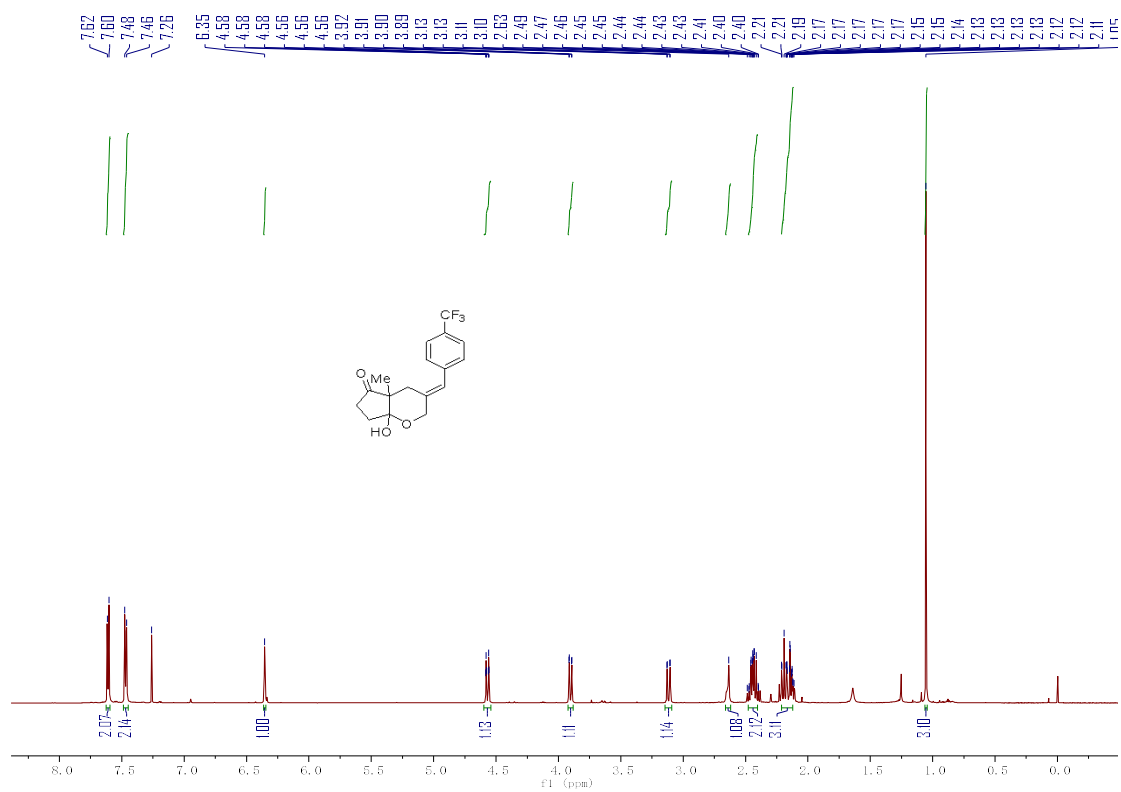


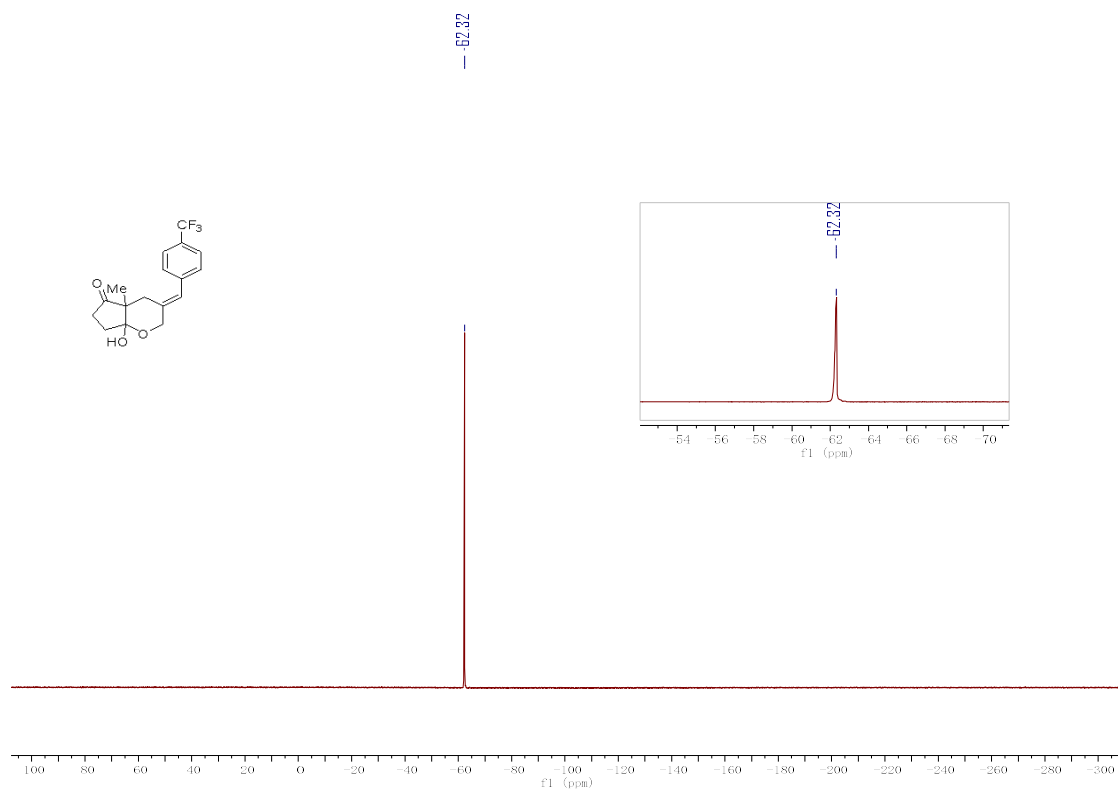
7f



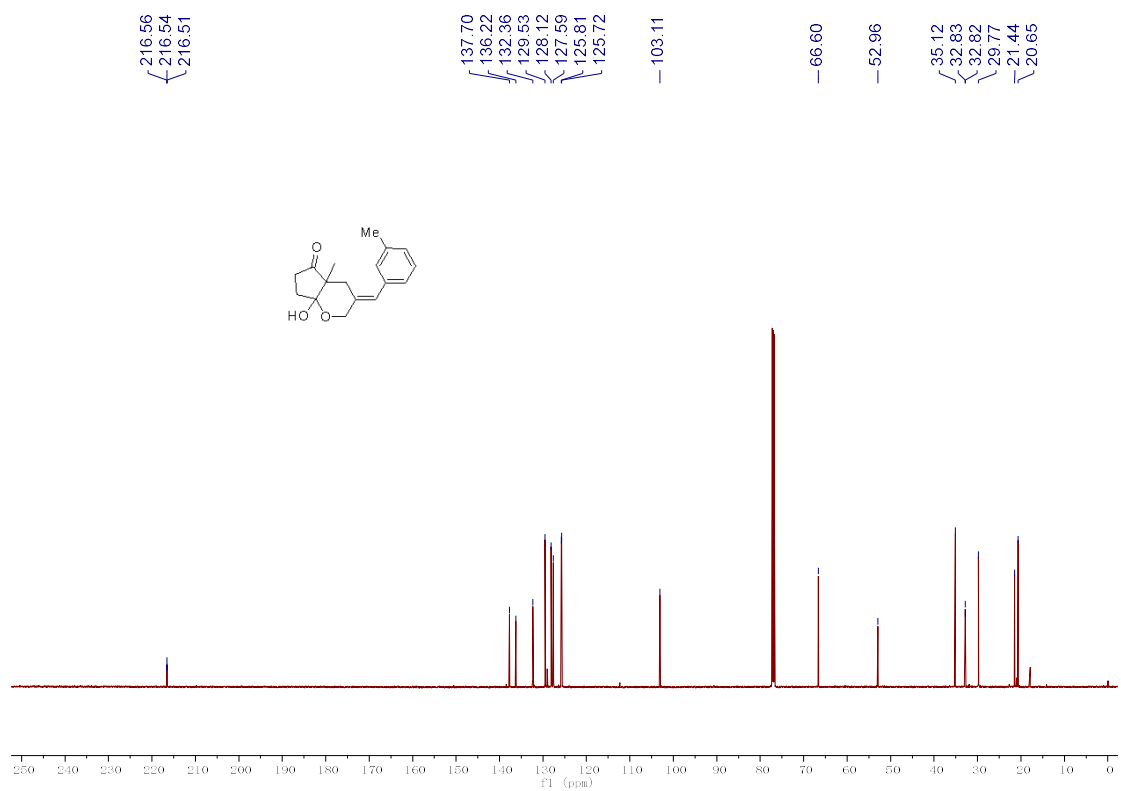
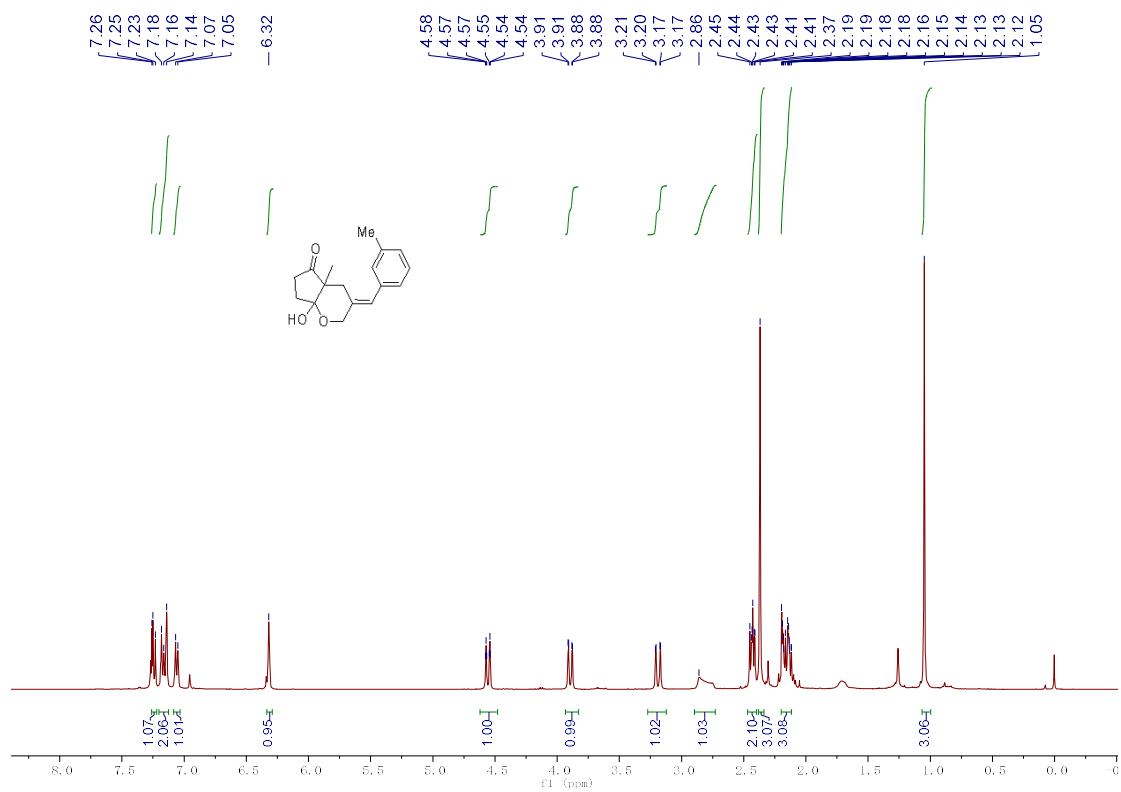


7g

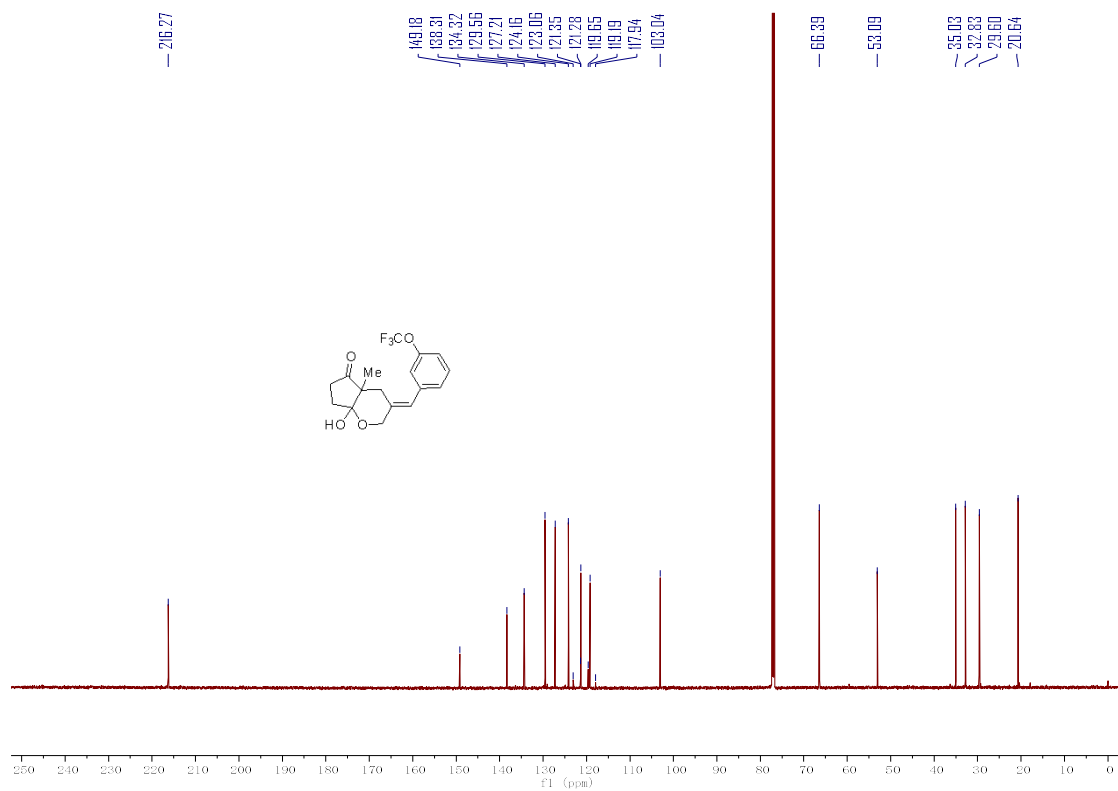
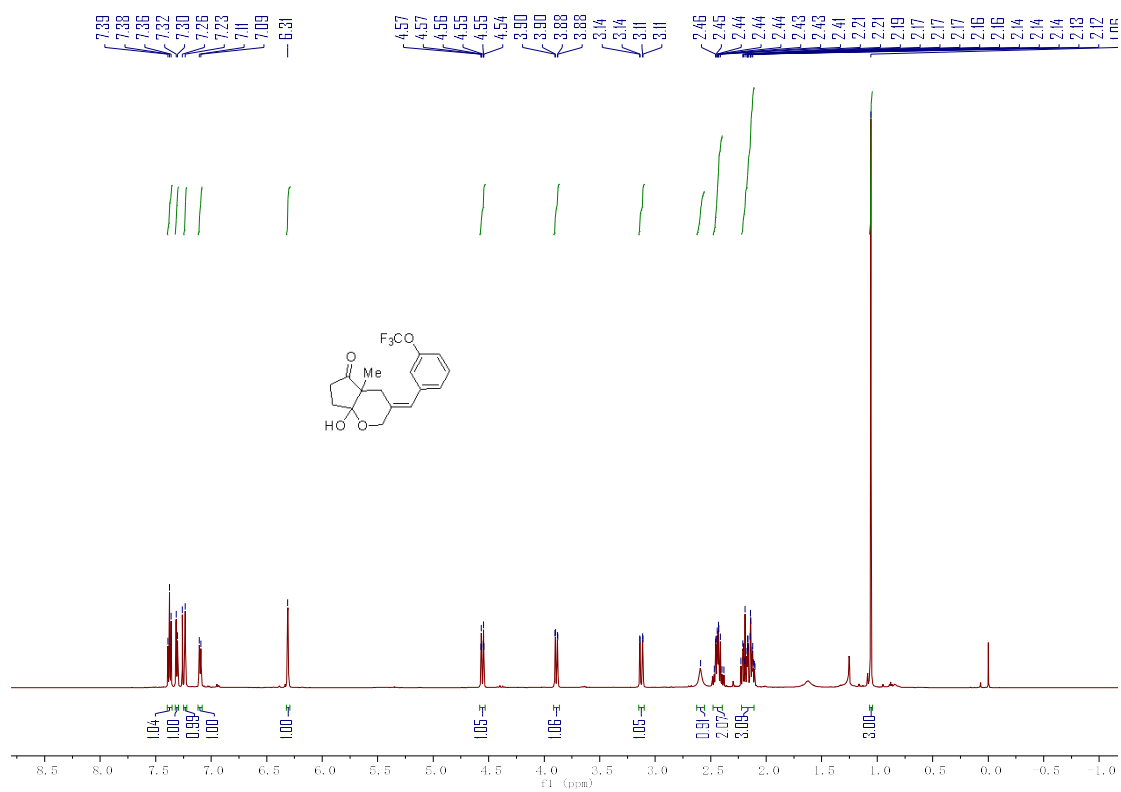


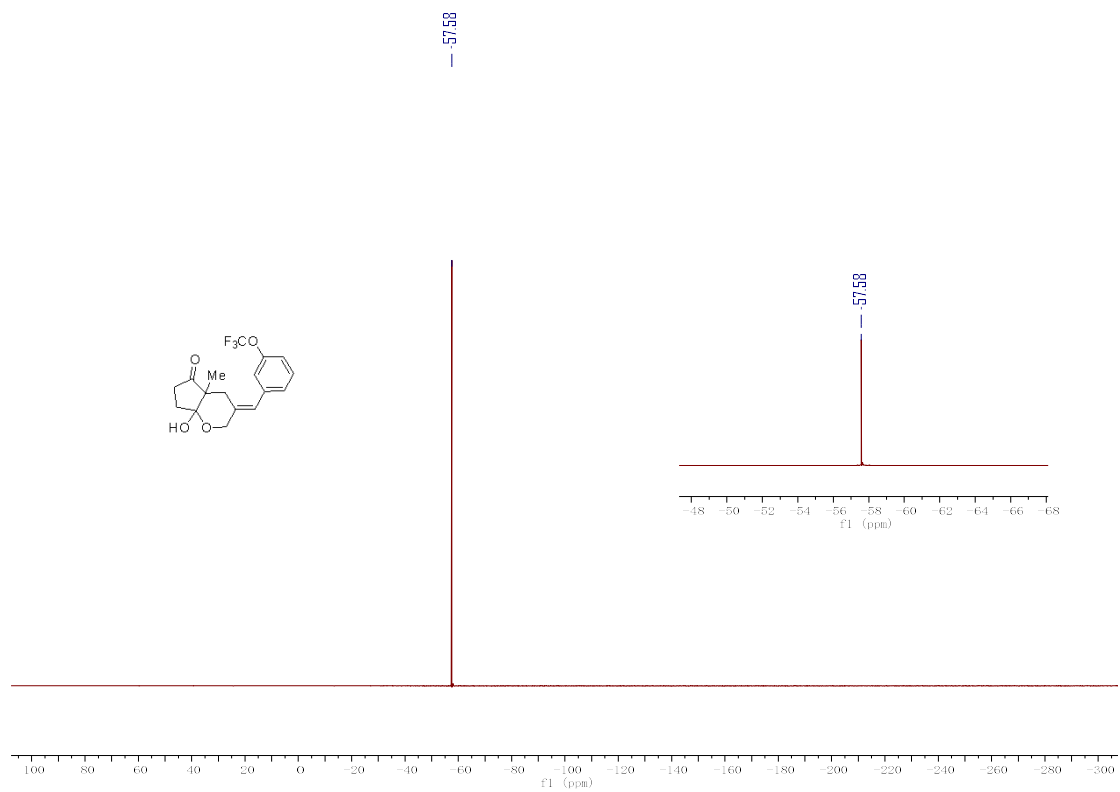


7h

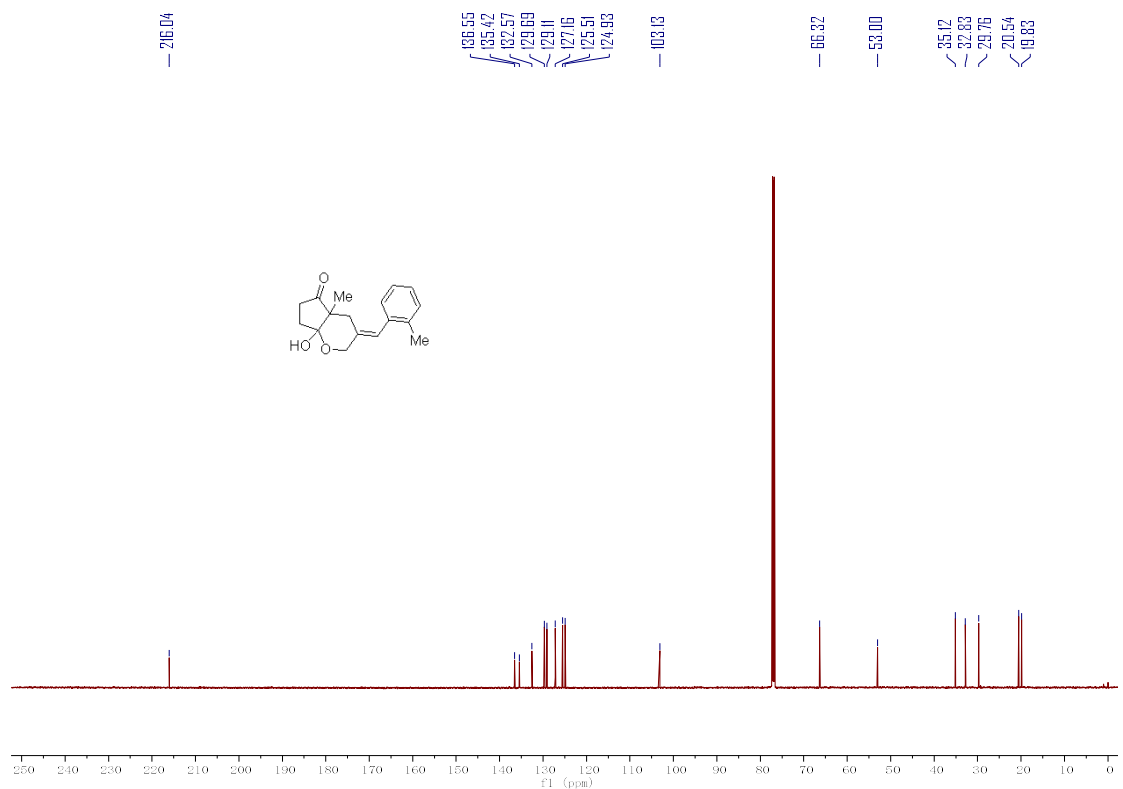
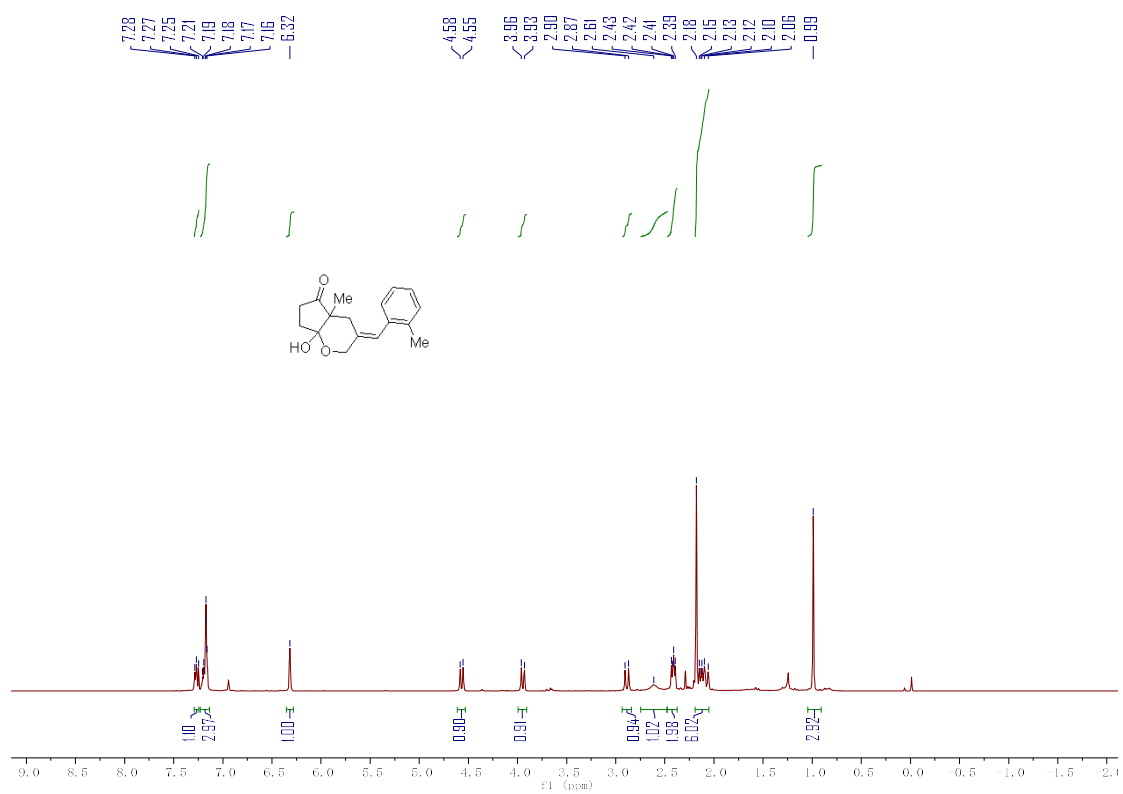


7i

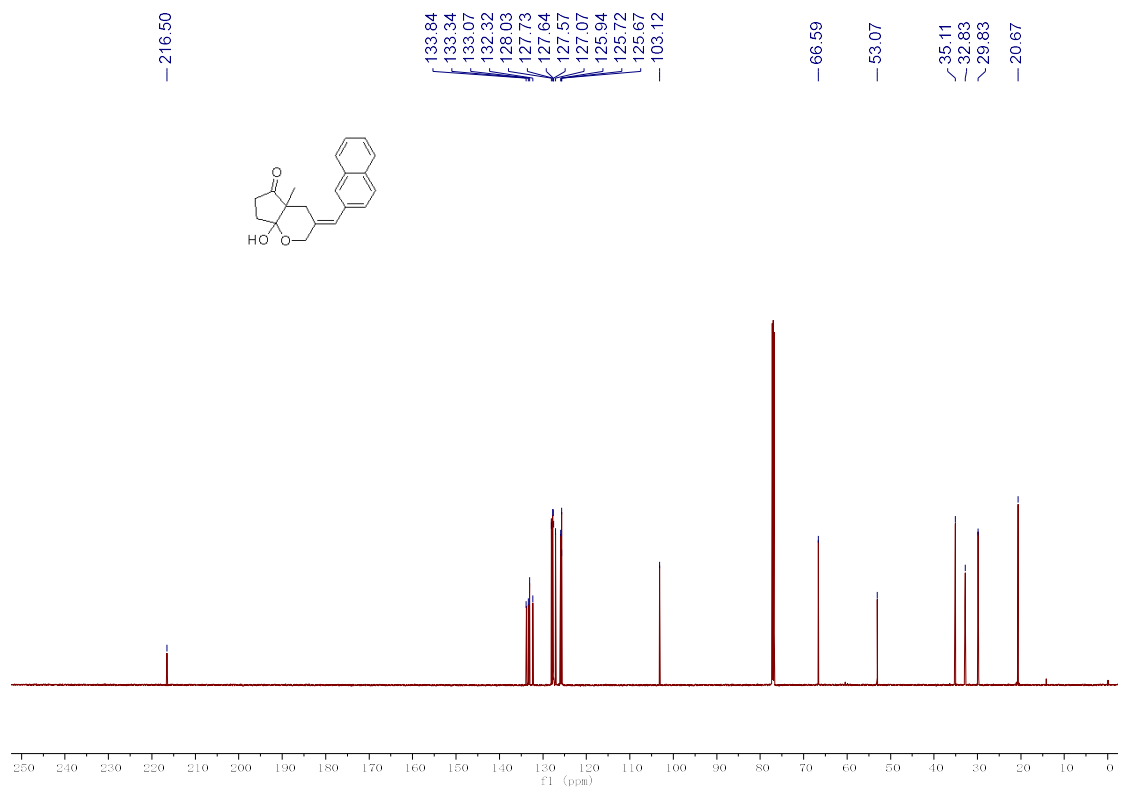
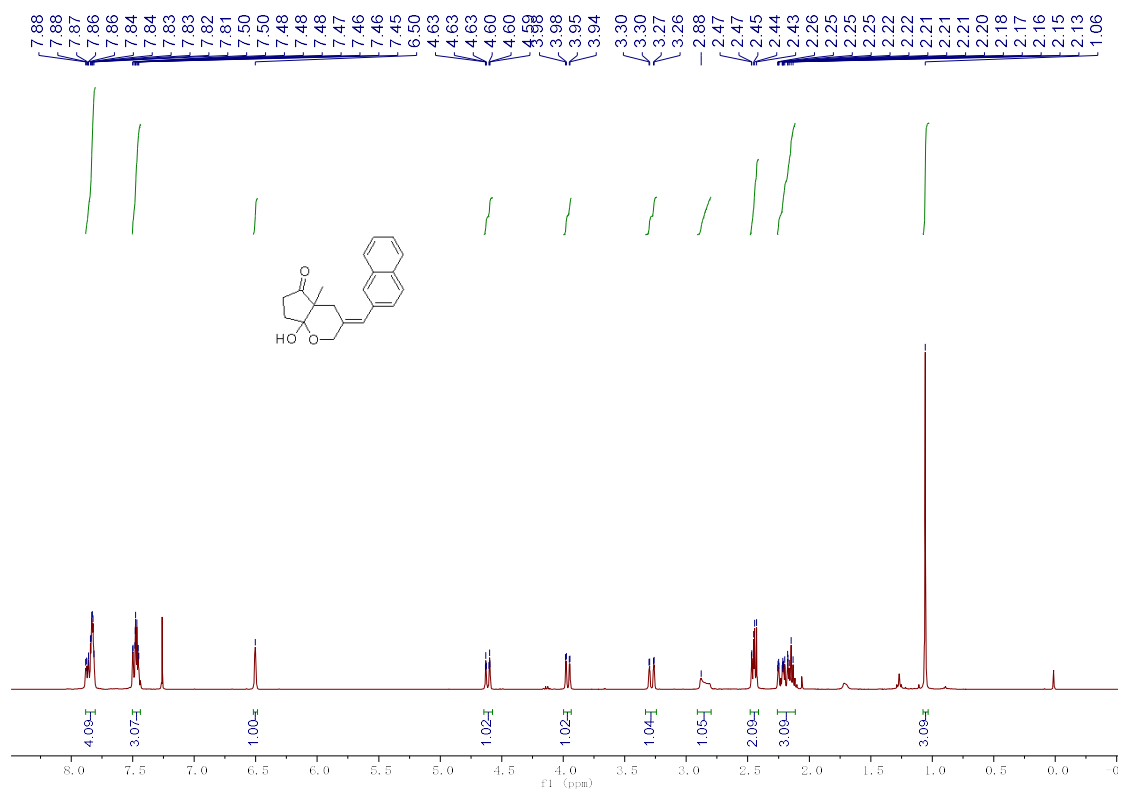


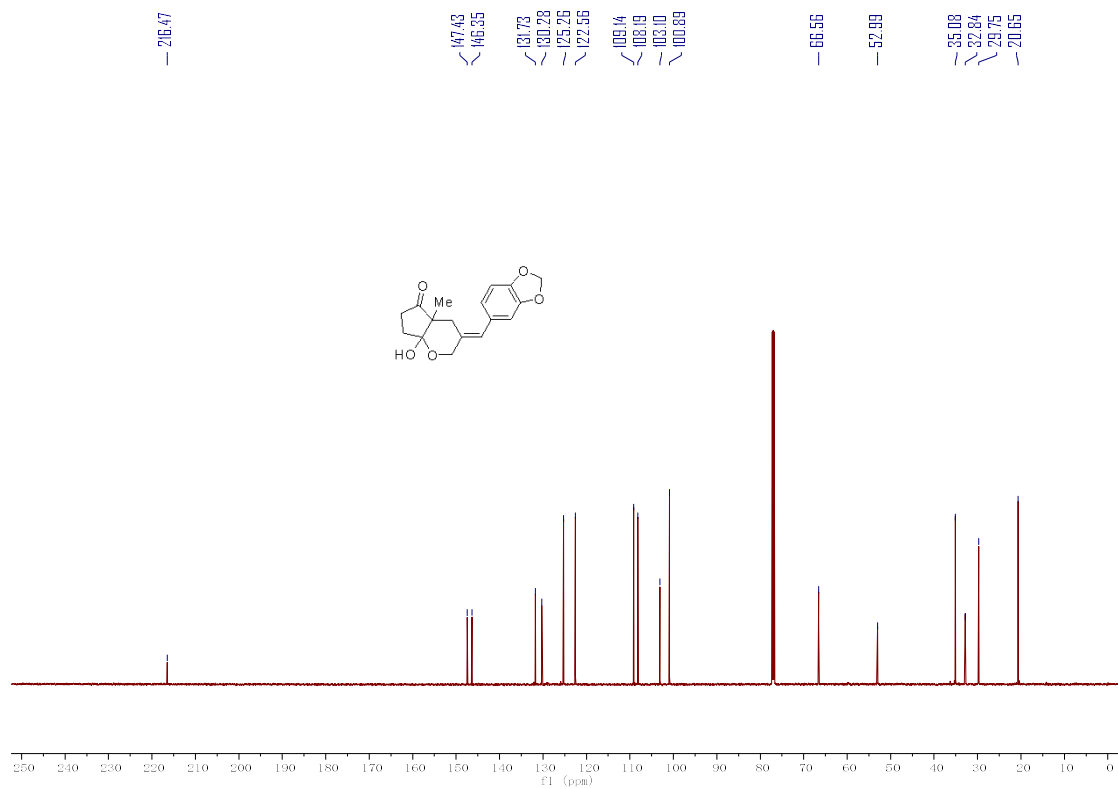
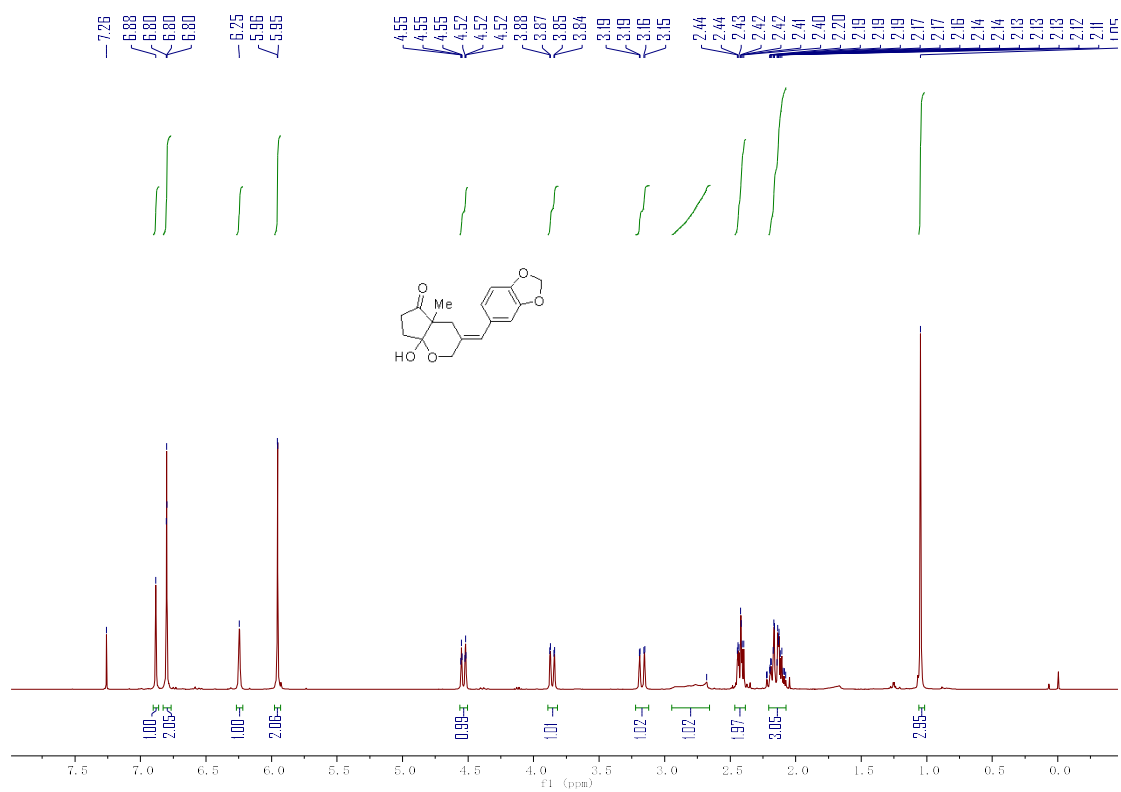


7j

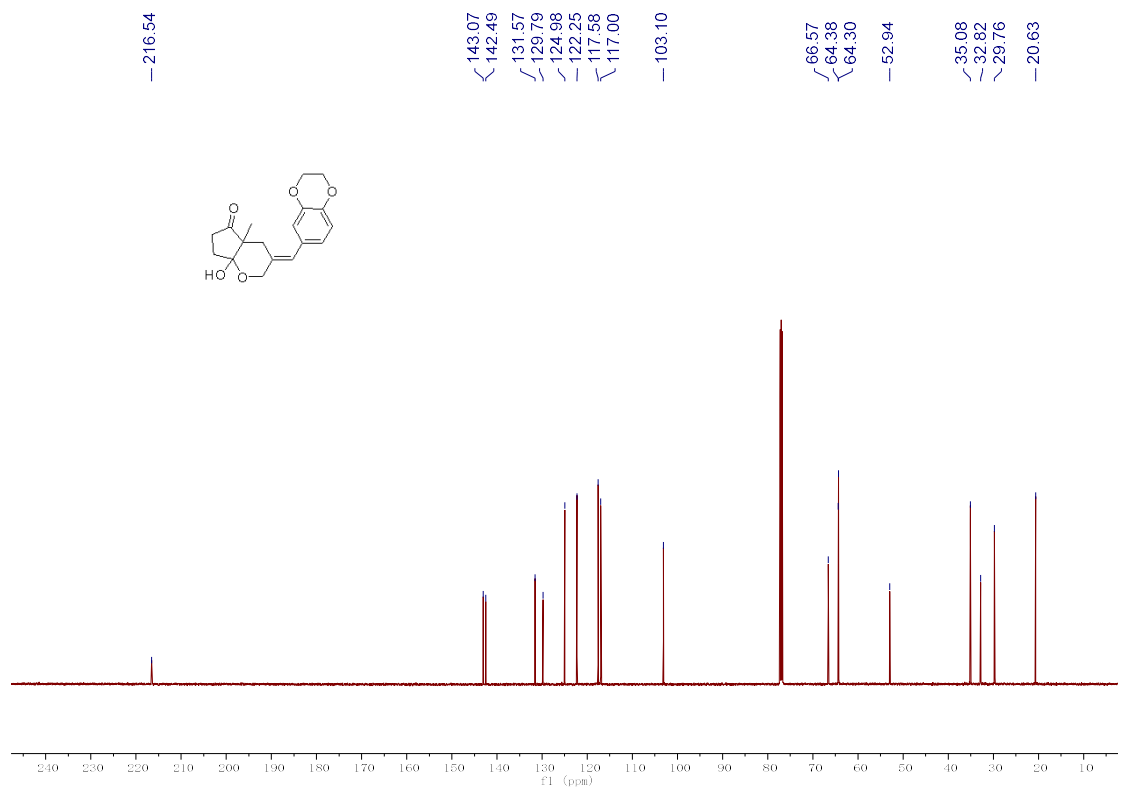
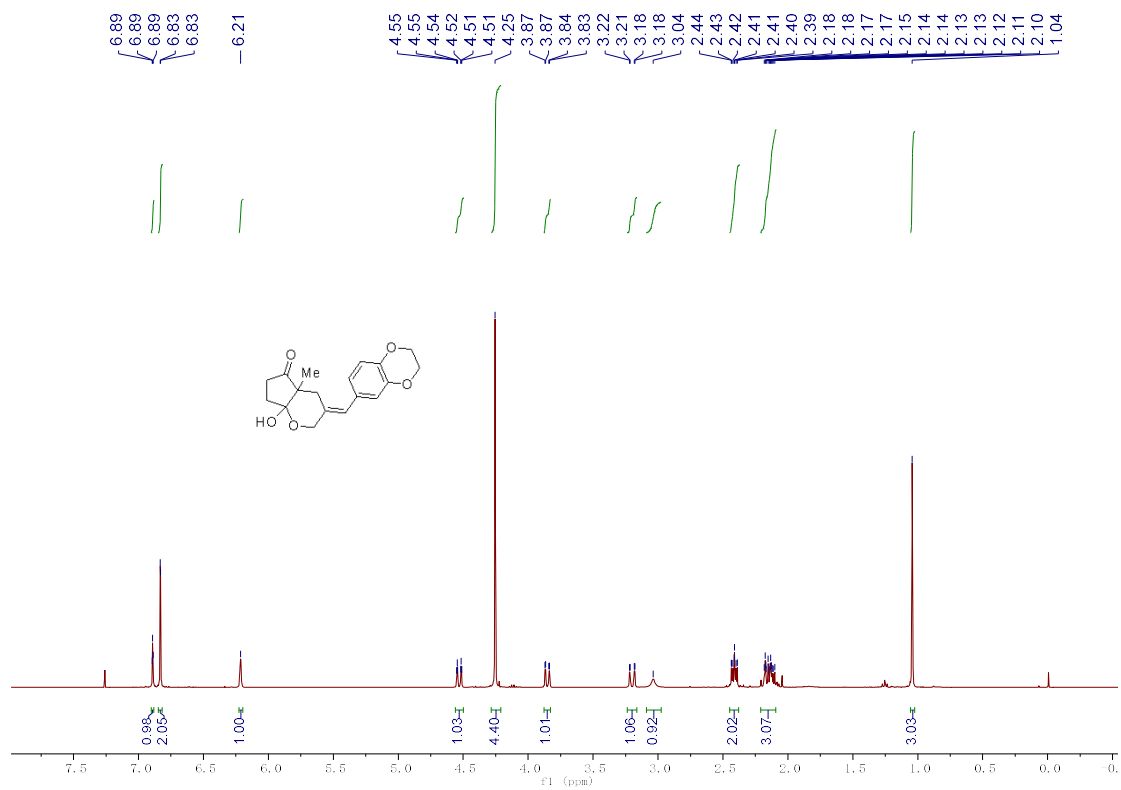


7k

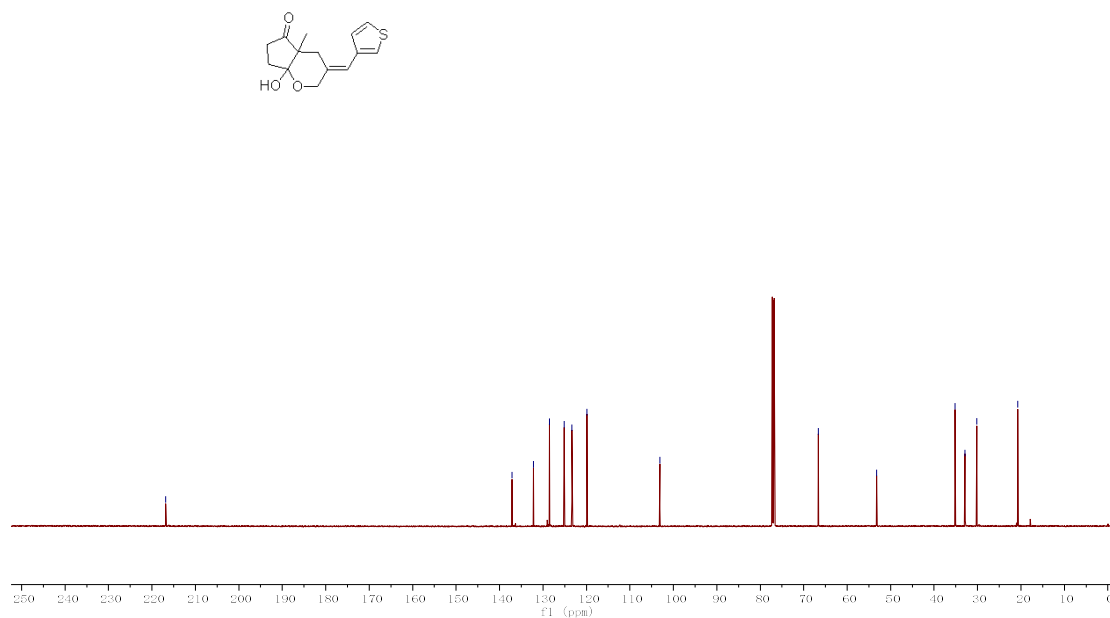
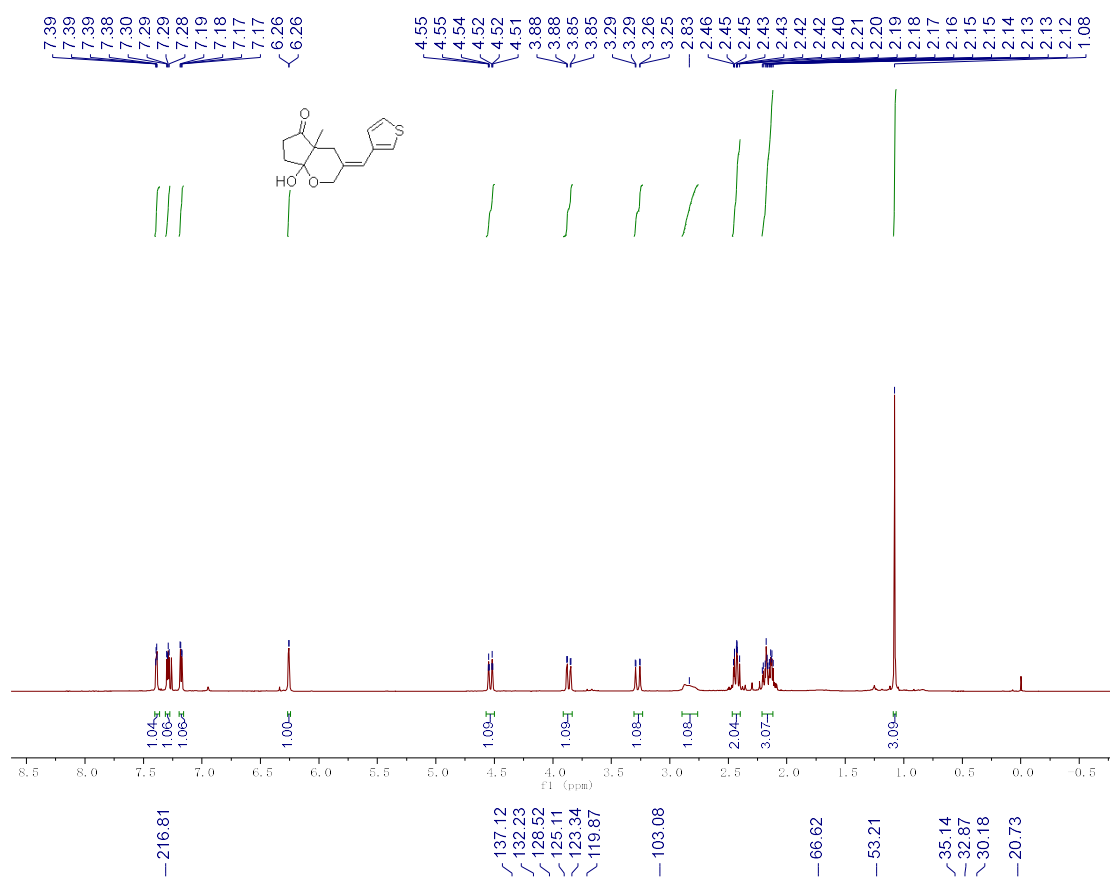




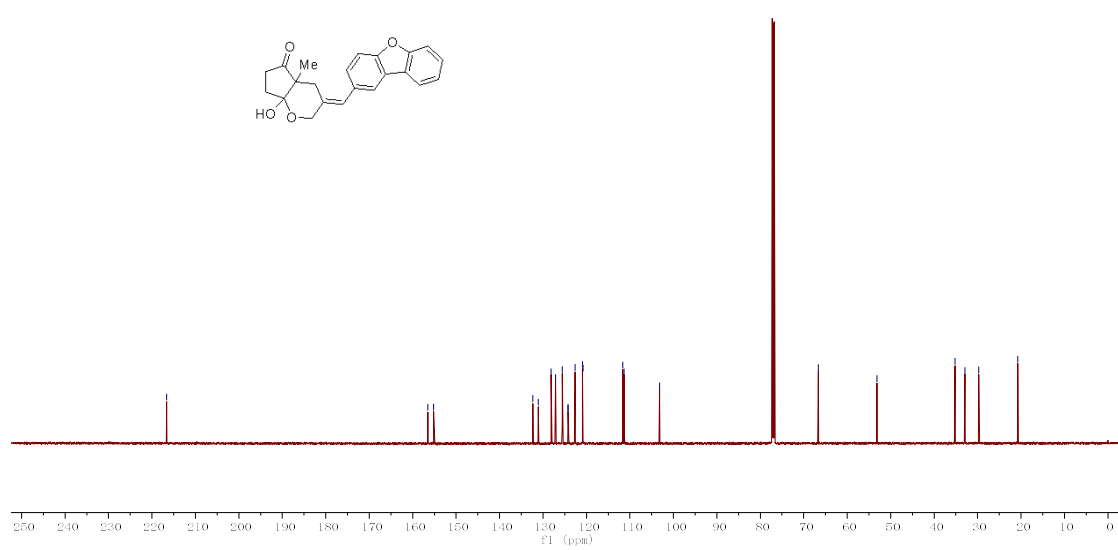
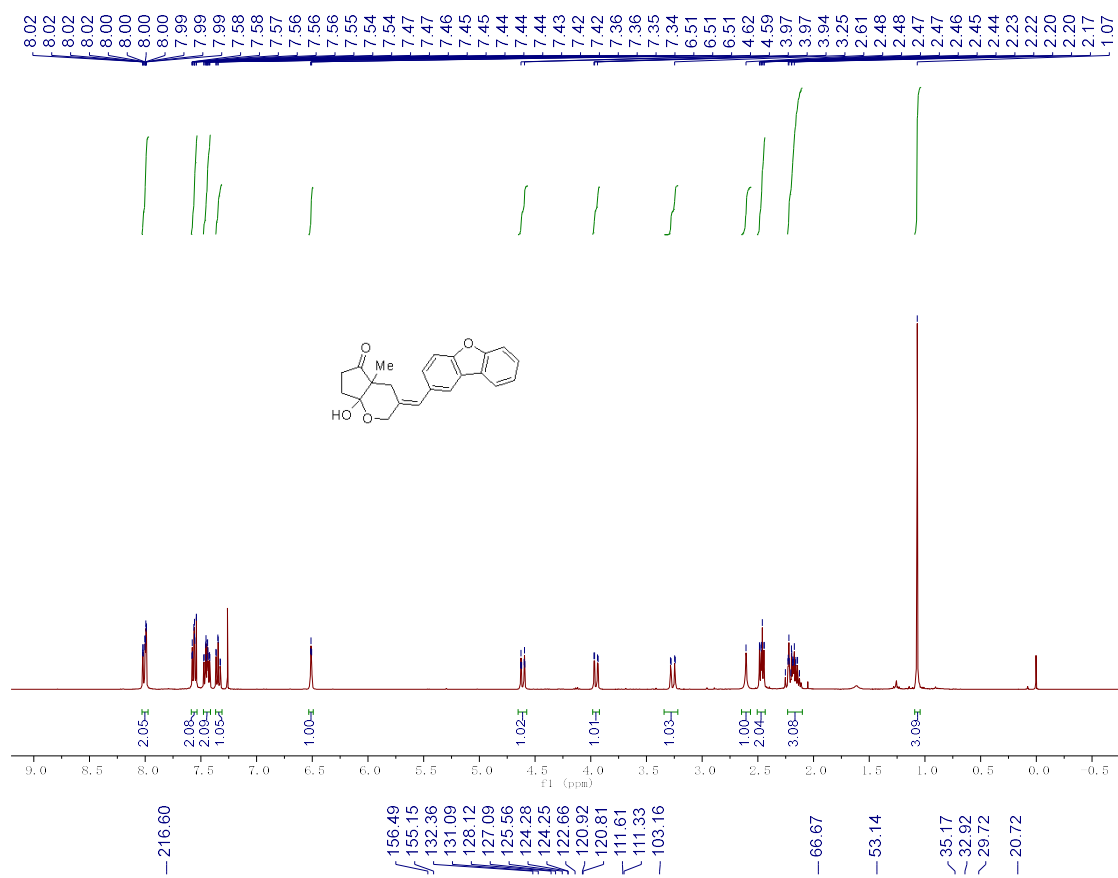
7m



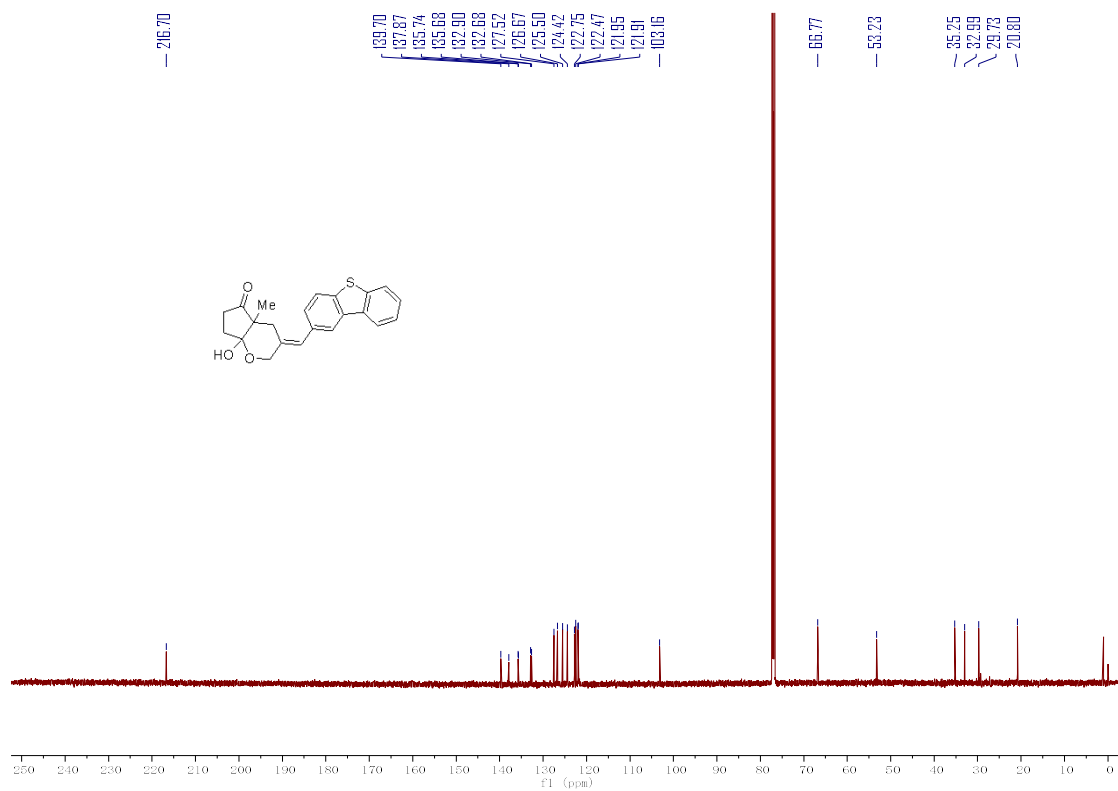
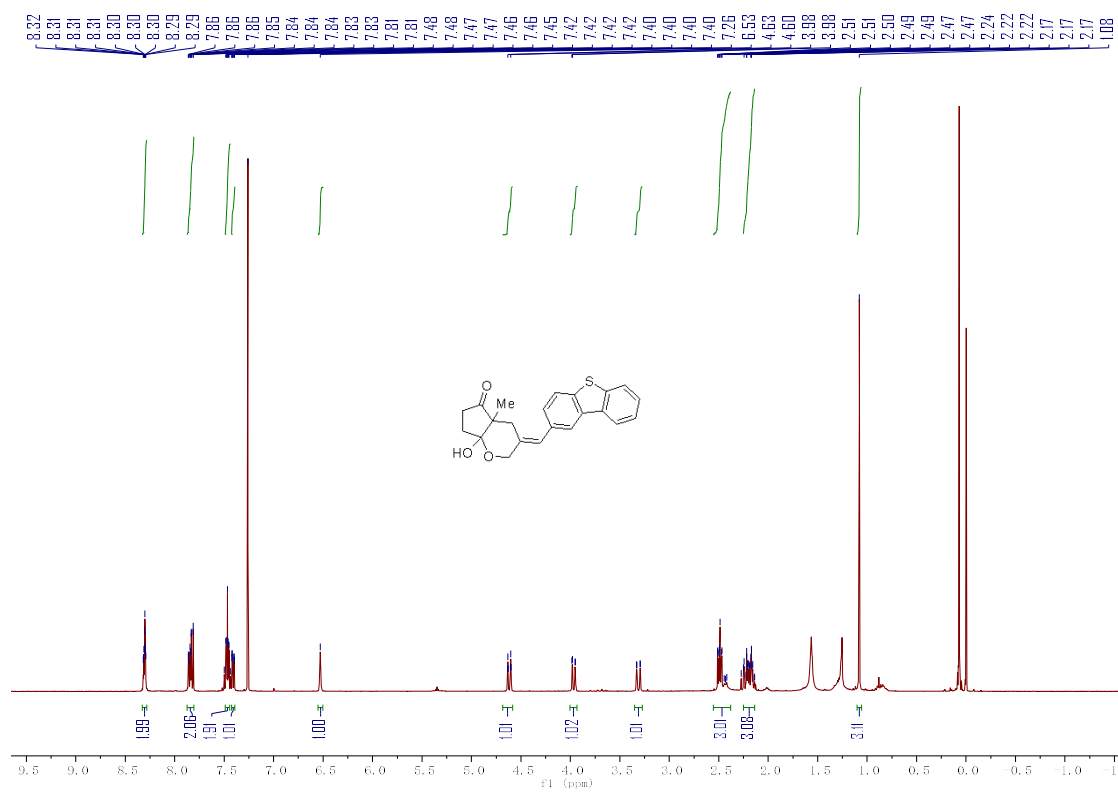
7n



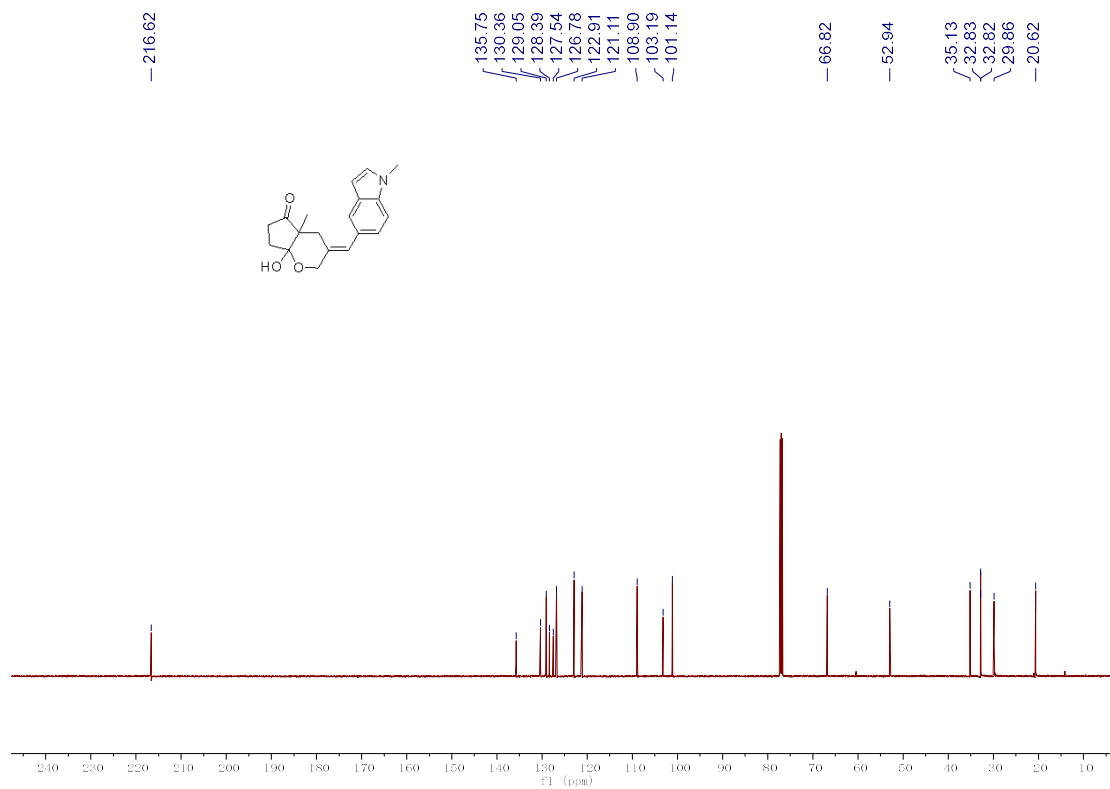
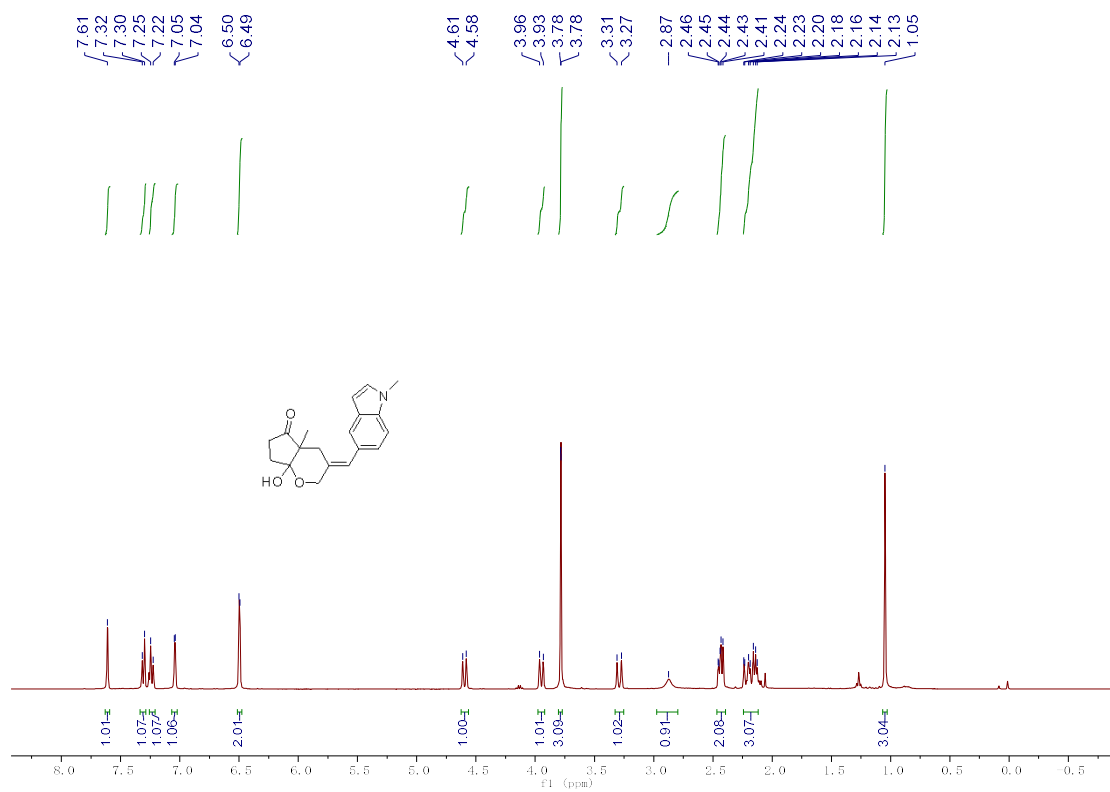
7o



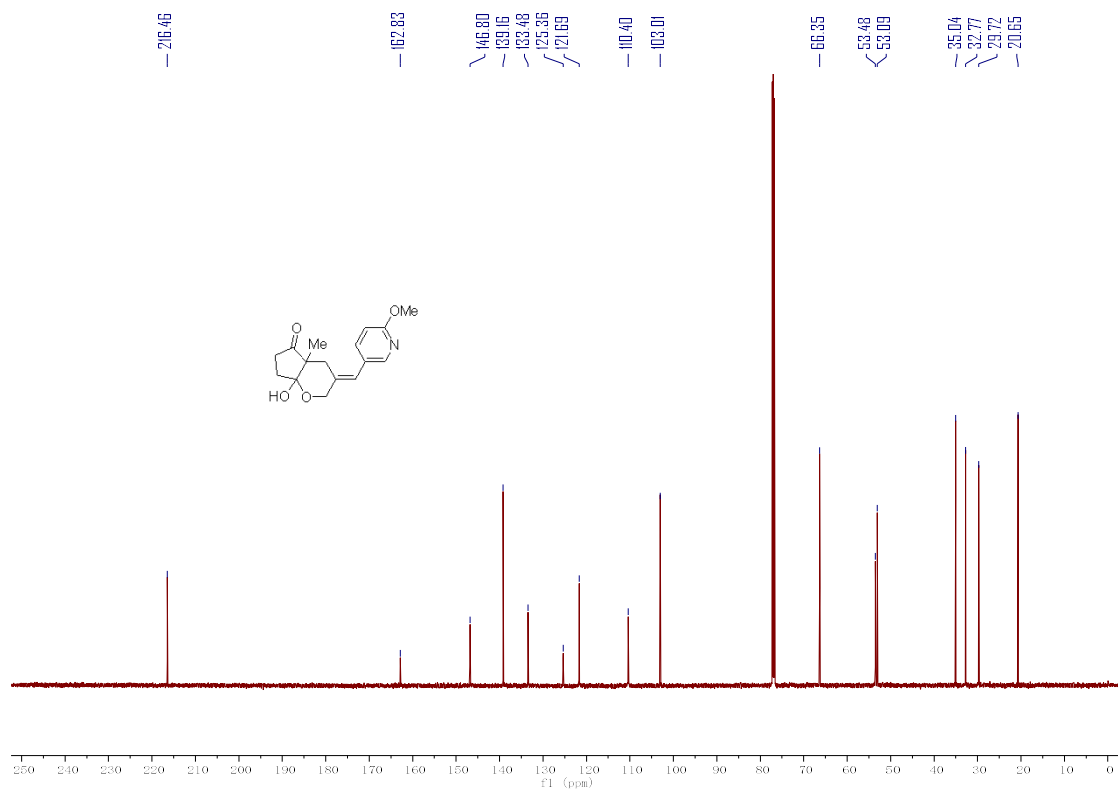
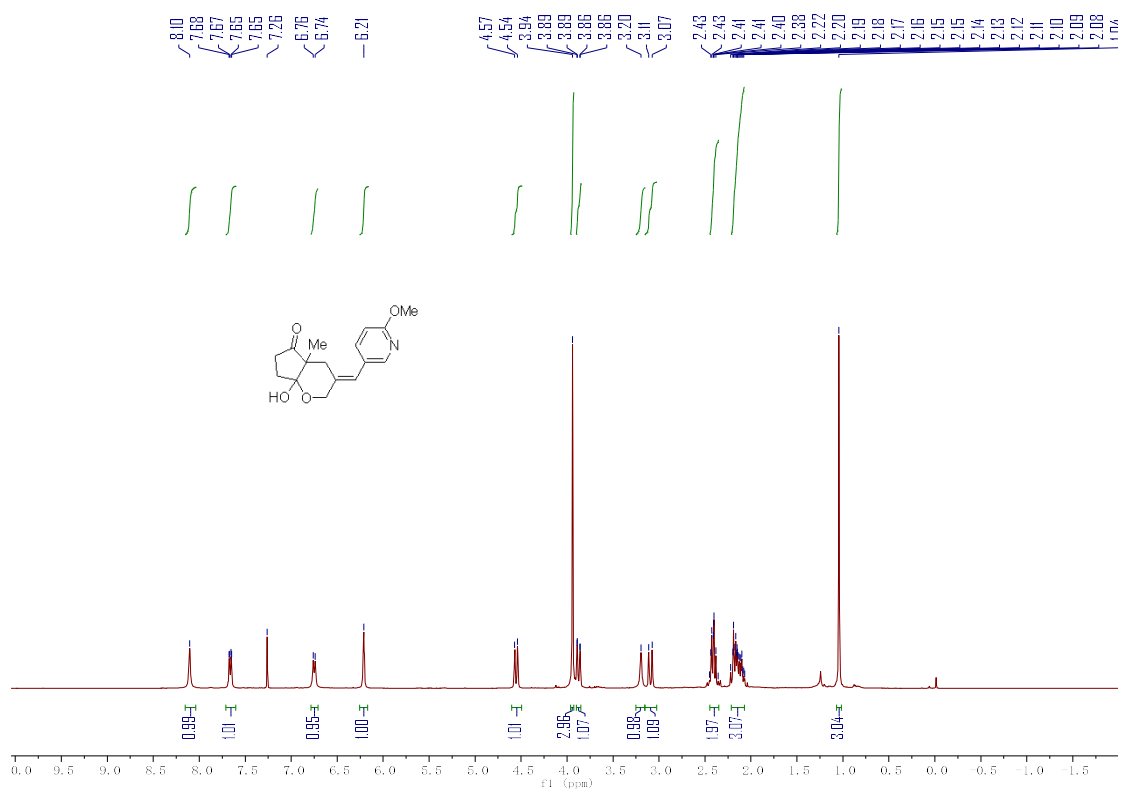
7p



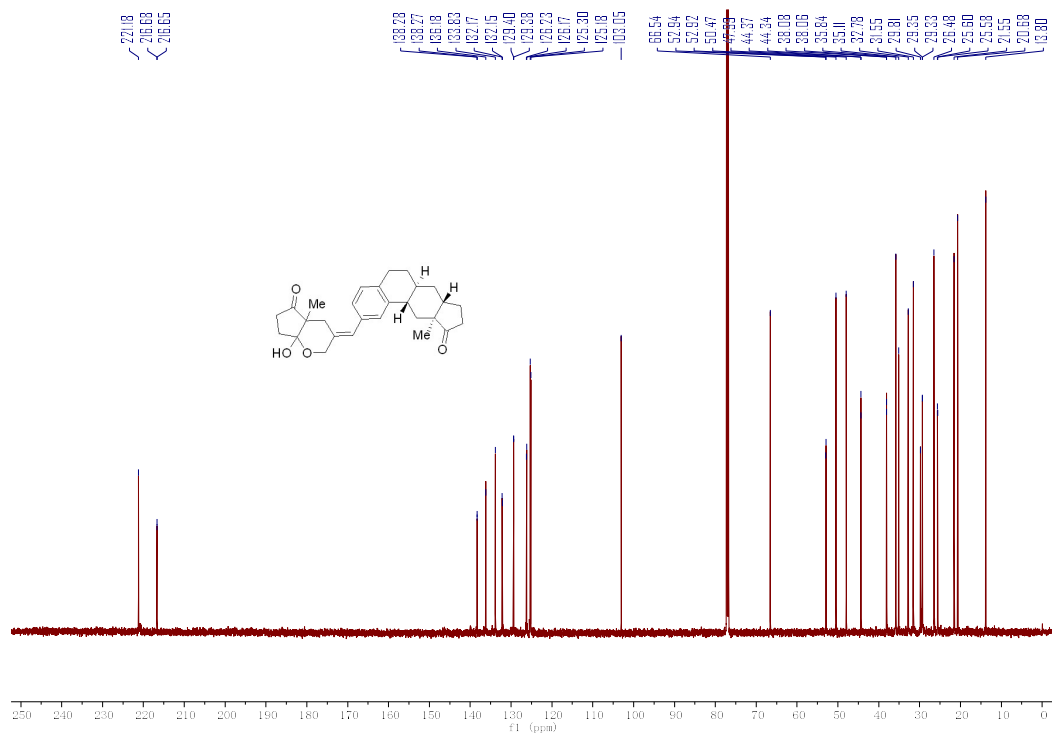
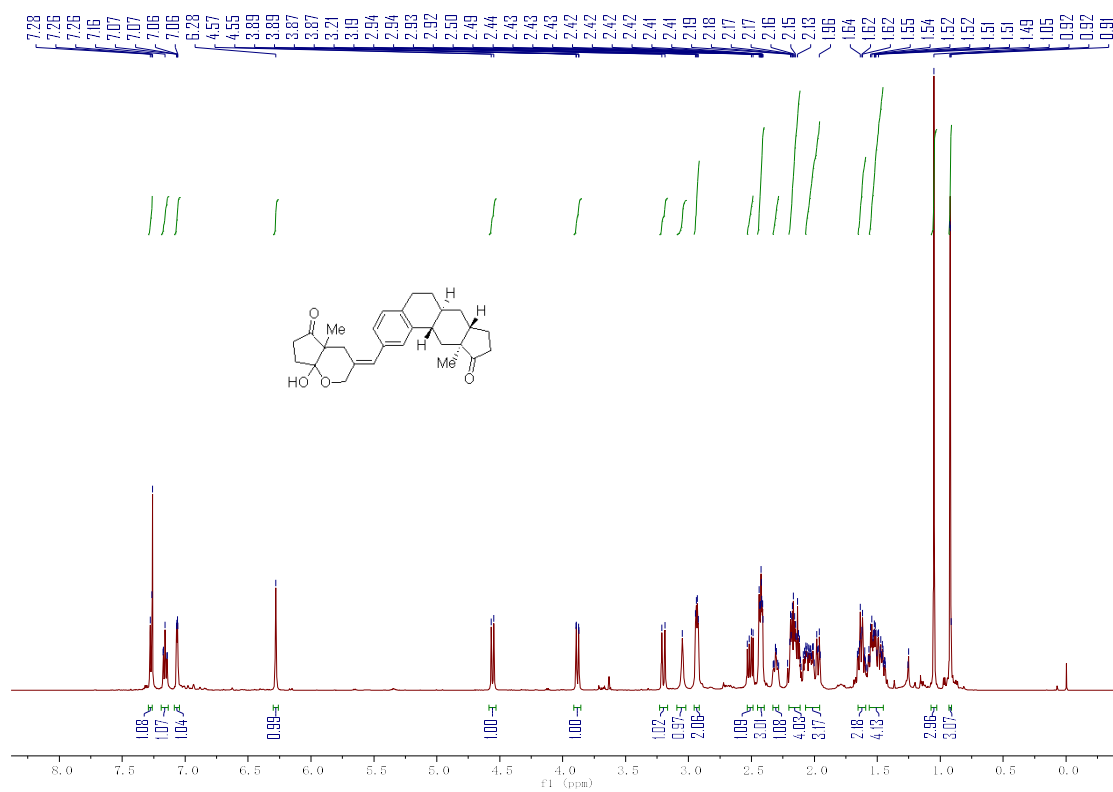
7q



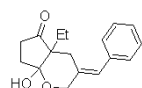
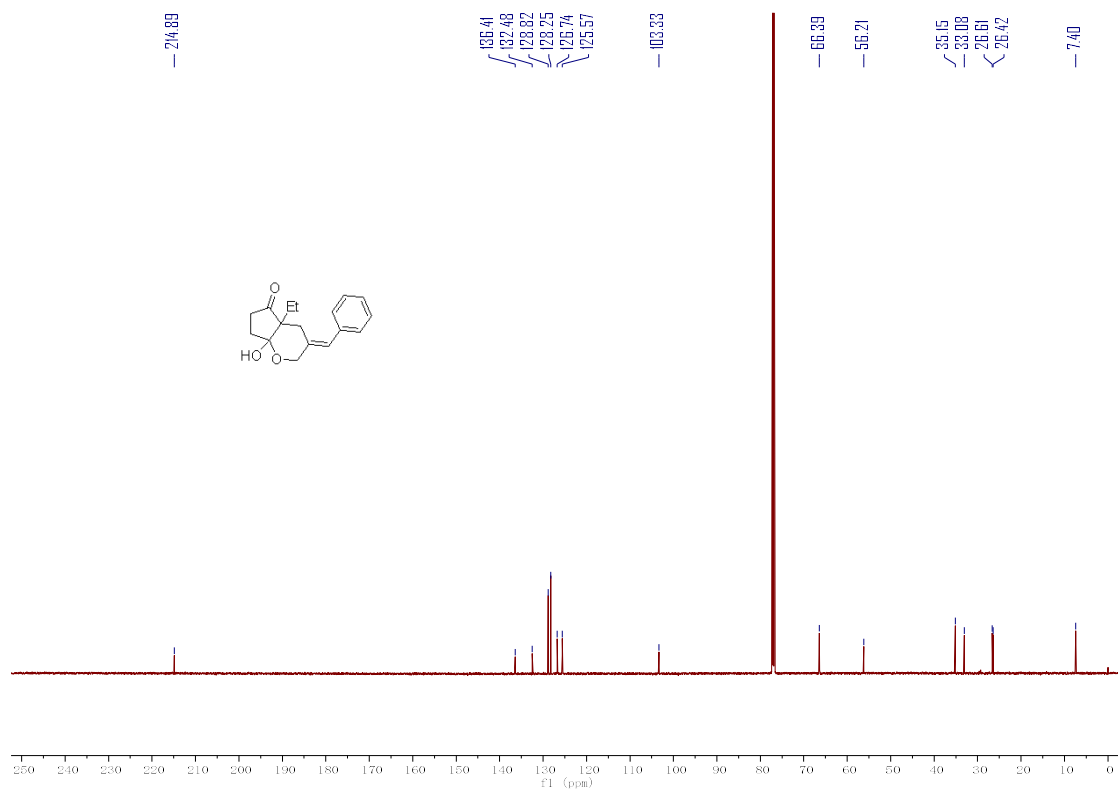
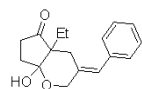
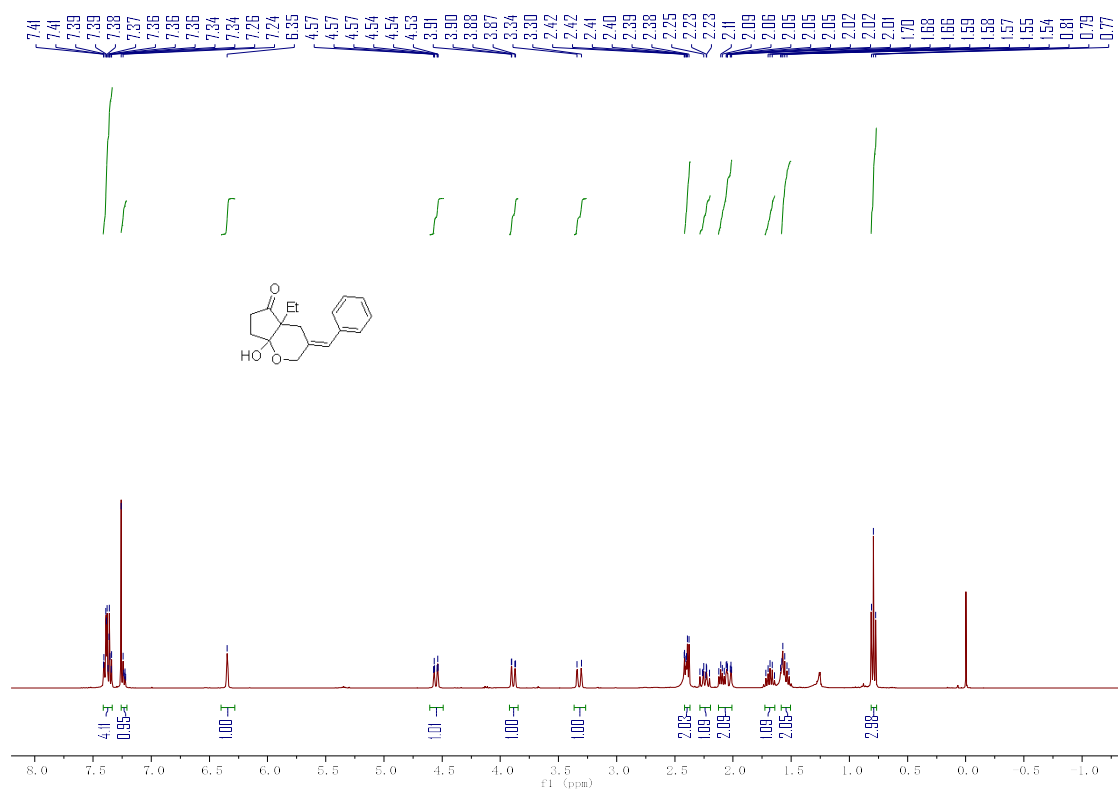
7r



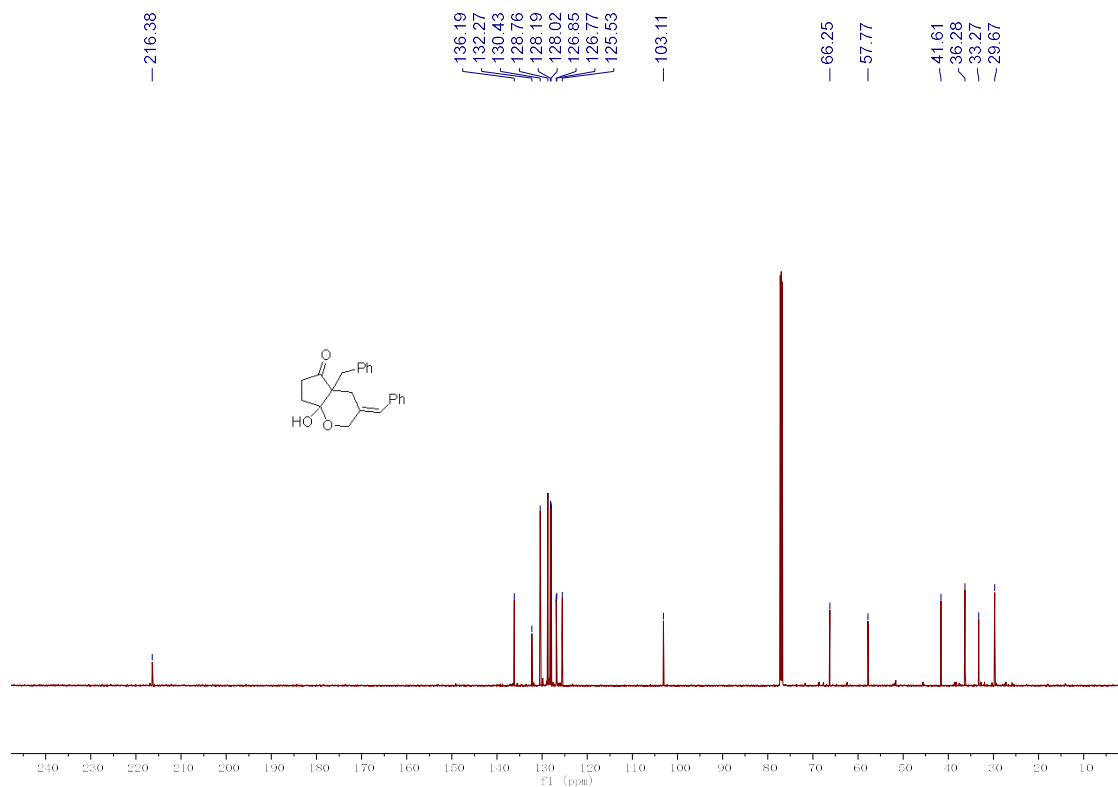
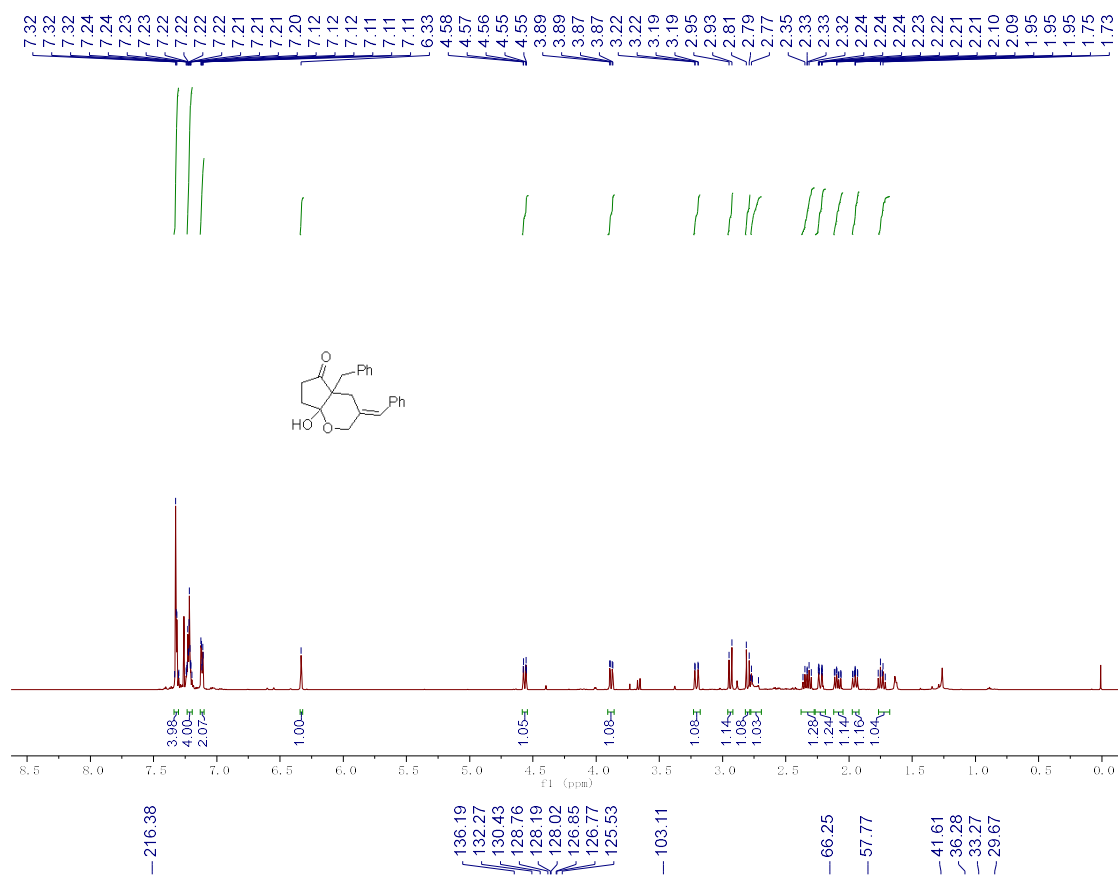
7s



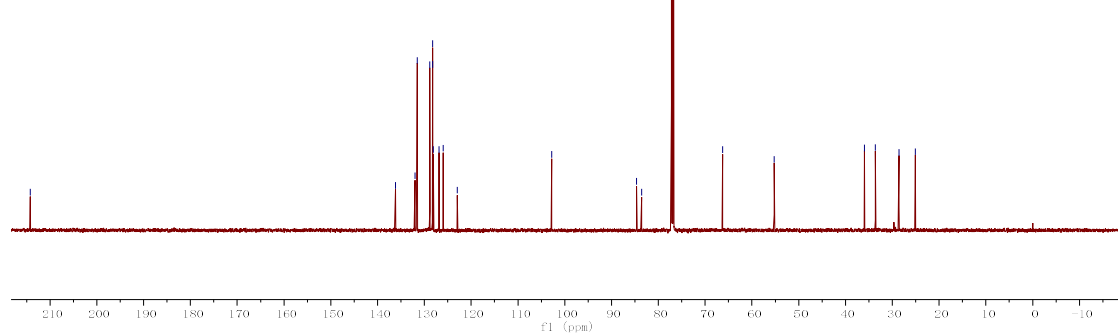
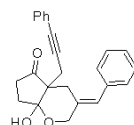
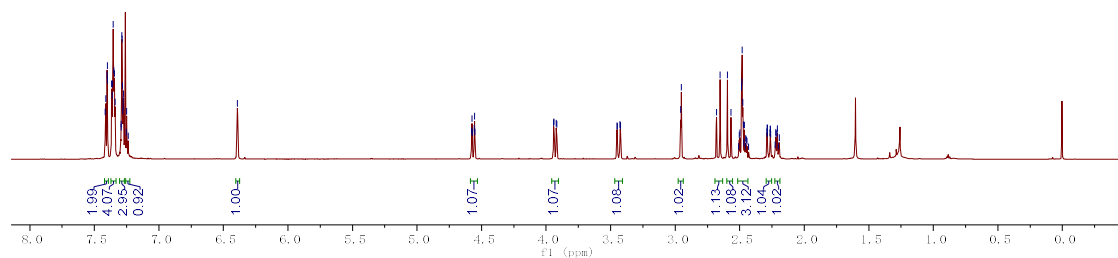
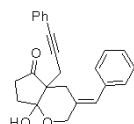
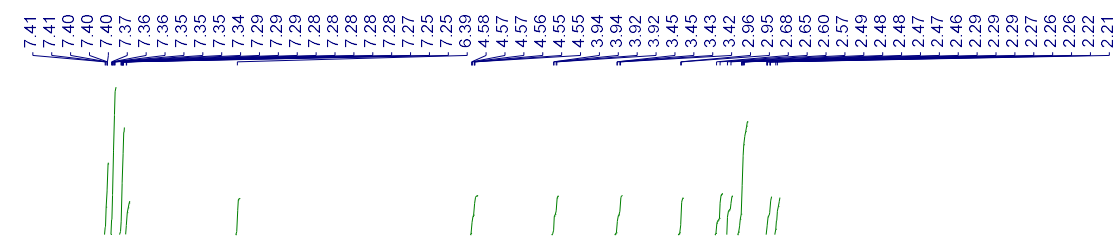
7t



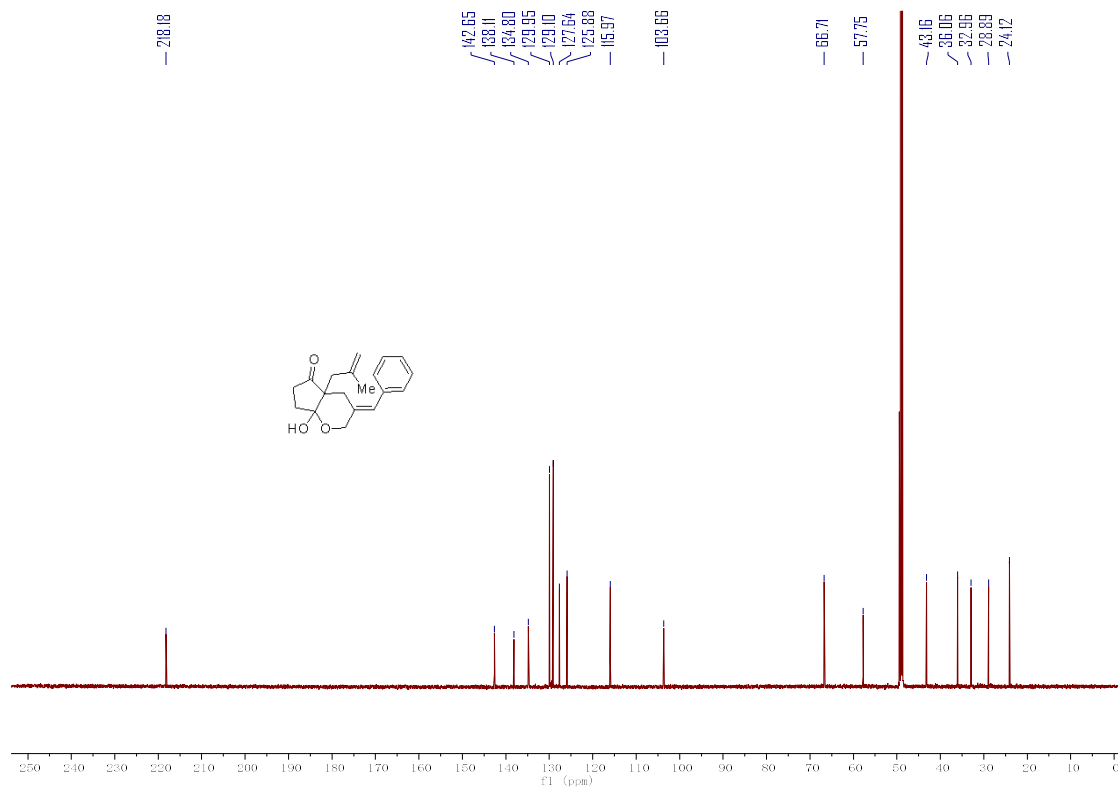
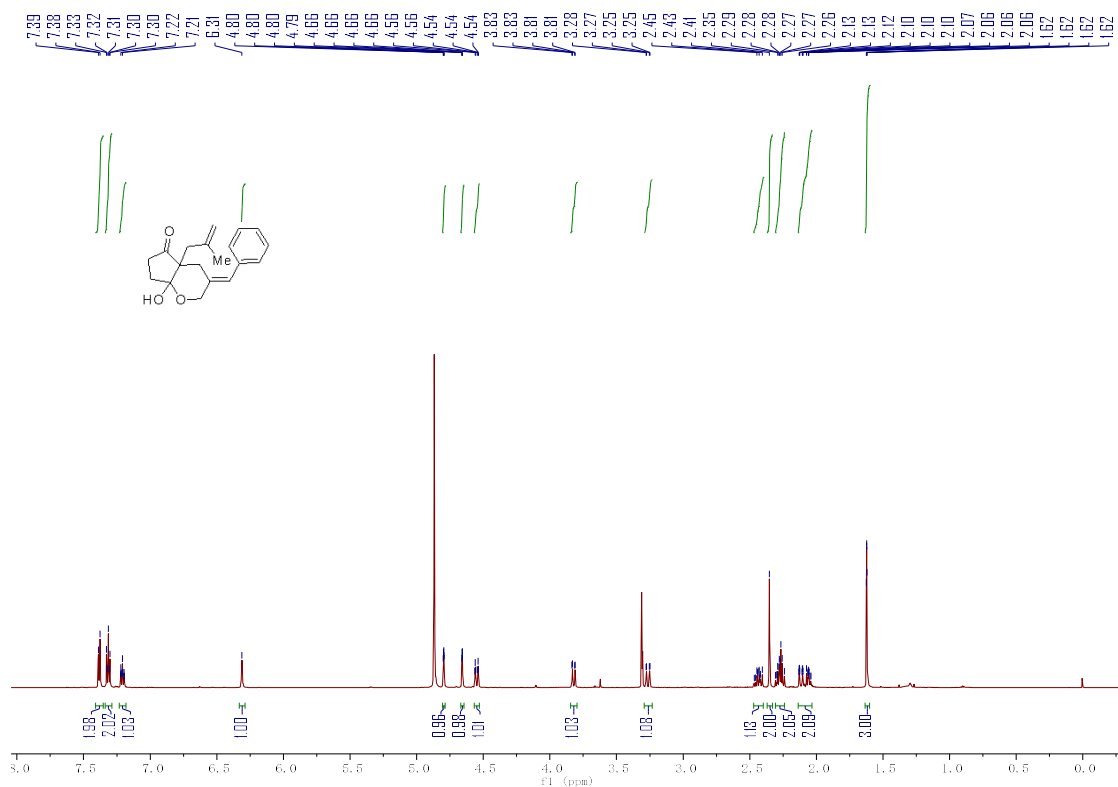
7u



7v



7w



7. References

- [1] S. Ni, H. Wei, B. Li, F. Chen, Y. Liu, W. Chen, Y. Xu, X. Qiu, X. Li, Y. Lu, W. Liu, L. Hu, D. Lin, M. Wang, X. Zheng, F. Mao, J. Zhu, L. Lan and J. Li, *J. Med. Chem.* **2017**, *60*, 8145.
- [2] A. V. Malkov, L. Czemerzys and D. A. Malyshev, *J. Org. Chem.* **2009**, *74*, 3350.
- [3] R. Wang, Y. Tang, M. Xu, C. Meng and F. Li, *J. Org. Chem.* **2018**, *83*, 2274.
- [4] P. V. Ramachandran, T. E. Burghardt and M. V. R. Reddy, *Tetrahedron Let.* **2005**, *46*, 2121.
- [5] J. Deng, E. Feng, S. Ma, Y. Zhang, X. Liu, H. Li, H. Huang, J. Zhu, W. Zhu, X. Shen, L. Miao, H. Liu, H. Jiang and J. Li, *J. Med. Chem.* **2011**, *54*, 4508.
- [6] W. Lölsberg, S. Y. Hans and G. Schmalz, *Adv. Synth. Catal.* **2010**, *352*, 2023.
- [7] M. H. Babu, G. R. Kumar, R. Kantc and M. S. Reddy, *Chem. Commun.* **2017**, *53*, 3894.
- [8] T. Fujihara, T. H. Xu, K. Semba, J. Terao and Y. Tsuji, *Angew. Chem. Int. Ed.* **2011**, *50*, 523.
- [9] F. Habib and A. G. B. Reza, *Chem. Soc. Jpn.* **1995**, *68*, 2595-2602.
- [10] M. R. Unroe and B. A. Reinhardt, *Synthesis* **1987**, *11*, 981.
- [11] M. Kitamura, Y. Hirokawa and N. Maezaki, *Chem. Eur. J.* **2009**, *15*, 9911.
- [12] B. N. Hemric, A. W. Chen and Q. Wang, *ACS Catal.* **2019**, *9*, 10070.