

Electronic Supplementary Information (ESI)

**Study on the coupling of acyclic esters with alkene - the synthesis
of 2-(2-hydroxyalkyl)cyclopropanols via cascade cyclization using
allylsamarium bromide**

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1. General Information.

THF was distilled from sodium/benzophenone. Metallic samarium and other solvents were obtained from commercial sources, and used without further purification, if not stated otherwise. Unless otherwise noted, all the cascade reactions were carried out under a nitrogen atmosphere in oven-dried flasks. All melting points are uncorrected. The ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on a 400 MHz instrument with TMS as internal standard. Recorded shifts are reported in parts per million (δ) downfield from TMS. Data are represented as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad), coupling constant (J , Hz) and integration. TLC was carried out with 0.2 mm thick silica gel plates (GF254). Visualization was accomplished by UV light. The columns were hand packed with silica gel 60 (300–400 mesh) or basic alumina (200–300 mesh). Unknown compounds were additionally confirmed by HRMS. Mass spectra were obtained using ESI ionization.

2. General Procedure.

General procedure for the synthesis of the homoallyl alcohols^[1-2]

To a mixture of aldehyde or ketone (10 mmol) in $aq\text{NH}_4\text{Cl}$ (10 mL)/THF (2.0 mL) were added allyl bromide (15 mmol) and Zn dust (15 mmol) subsequently. The mixture was allowed to stir at room temperature until the reaction was deemed complete (monitored by TLC). The reaction mixture was extracted by Et_2O (4×10 mL). The organic phase was dried over Na_2SO_4 . Removing the solvent under reduced pressure gave the corresponding homoallyl alcohol, which was used directly without further purification.

General procedure for the synthesis of the homoallyl esters.

Method A (for the synthesis of *1a-1k, 1m-1p* and *1s-1t*)^[1-2]: To a solution of the homoallyl alcohol (10 mmol) in CH_2Cl_2 (50 mL), was added Ac_2O (30 mmol) and pyridine (50 mmol) subsequently. The reaction mixture was allowed to stir at 34–37 °C until the reaction was deemed complete (monitored by TLC) (about 24 h). The reaction was quenched by the addition of $aq\text{HCl}$ (10%). The organic phase was washed with brine (30 mL), dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (300–400 mesh) using petrol/EtOAc (15/1, v:v) as the eluent to afford the corresponding products.

Method B (for the synthesis of *1l, 1q*)^[3]: To a solution of the homoallyl alcohol (10 mmol) in CH_2Cl_2 (50 mL), was added Ac_2O (30 mmol), TEA (30 mmol), and DMAP (2 mmol) subsequently. The reaction mixture was allowed to stir at 40 °C until the

reaction was deemed complete (monitored by TLC) (about 24 h). The organic phase was washed with brine (30 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (300–400 mesh) using petrol/EtOAc (20/1, v:v) as the eluent to afford the corresponding products.

Method C (for the synthesis of *Ir*)^[4]: In an oven-dried Schlenk flask, a solution of aldehyde (1.3 mmol, 1.0 equiv) in THF (1.8 mL) was prepared under an inert atmosphere at 0 °C. To the solution, the vinylic Grignard reagent (1.4 mmol, 1.1 equiv) was added and the reaction was stirred for 2 h. The reaction was allowed to warm up to room temperature, quenched with a saturated aqueous NH₄Cl solution, and extracted with diethyl ether (20 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and evaporated to give the crude allylic alcohol. Then solution the crude allylic alcohols (0.5 mmol) in anhydrous dichloromethane (5 mL), acetic anhydride (102 mg, 1 mmol) and a catalytic amount of DMAP in pyridine (5 mL; 1% solution) were added. After stirring for 2 hours at room temperature the solvent was evaporated *in vacuo* and the crude product was purified by flash chromatography on silica gel using petrol/EtOAc (30/1, v:v) as eluent to afford the corresponding products.

General procedure for the cascade synthesis of the diol 2.

To a two-necked flask containing samarium powder (2.5 mmol), was added THF (18 mL) and ally bromide (2.2 mmol) under nitrogen. The mixture was allowed to stir at room temperature for 1 h (the color would turn into purple). HMPA (2 mL) and H₂O (1 mmol) was then added in sequence *via* a syringe. A solution of substrate **1** (1 mmol) in THF (5 mL) was subsequently added. The color would fade out in 3 h (monitored by TLC). The reaction mixture was quenched with aq. sodium-potassium tartrate and extracted with diethyl ether (3×20 mL). The organic phase was washed with brine (30 mL), dried over Na₂SO₄, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (300–400 mesh) using petrol/EtOAc (5/1, v:v) as the eluent to afford the corresponding products.

Typical procedures for attempts to isolate 4 and 5.

Method A: To a two-necked flask containing samarium powder (1.25 mmol), was added THF (9 mL) and ally bromide (1.1 mmol) under nitrogen. The mixture was allowed to stir at room temperature for 1 h (the color would turn into purple). HMPA (1 mL) and H₂O (0.5 mmol) was then added in sequence *via* a syringe. A solution of substrate **1a** (1 mmol) in THF (5 mL) was subsequently added. The mixture was stirred at r.t. and the purple color faded in 1 h. Usual work-up afforded *cis*- and *trans*-**3a** in 33% overall yields (63 mg) and also the recovery of starting material **1a** in 58% yield (110 mg). The desired **4** or **5** could not be obtained.

Method B: To a two-necked flask containing samarium powder (2.5 mmol), was added THF (18 mL) and ally bromide (2.2 mmol) under nitrogen. The mixture was allowed to stir at room temperature for 1 h (the color would turn into purple). HMPA (2 mL) and H₂O (1 mmol) was then added in sequence *via* a syringe. A mixture of substrate **1a** (1 mmol) and 1,4-cyclohexadiene (0.24 g, 3 mmol) in THF (5 mL) was subsequently added. After being stirred at r.t. for 3 h, usual work-up afforded *cis*- and

trans-3a in 65% overall yield (0.125g) and also the deprotected product *2a* in 16% yield (23.7 mg). Attempt to isolate *4* or *5* again failed.

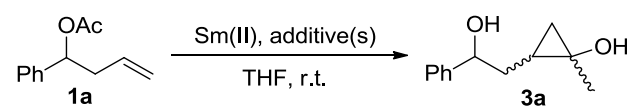
Method C: To a two-necked flask containing samarium powder (3.75 mmol), was added THF (25 mL) and allyl bromide (3.3 mmol) under nitrogen. The mixture was allowed to stir at room temperature for 1 h (the color would turn into purple). HMPA (3 mL) and H₂O (1.5 mmol) was then added in sequence *via* a syringe. A solution of substrate **1** (1 mmol) in THF (5 mL) was subsequently added. After being stirred at r.t. for 3 h, usual work-up afforded *cis*- and *trans-3a* (0.3g) in 78% overall yield (0.15g), and **5a** in 8% yield (15.5mg).

General Procedure for cyclic voltammetry experiments.

Cyclic voltammetry was performed with a BAS 100B electrochemical analyzer. A platinum wire as was used as the auxiliary electrode, glassy carbon as the working electrode and Ag/AgNO₃ was employed for the reference electrode. Glassy carbon electrode was polished with polishing alumina and cleansed with solvent before use. The scan rate for all experiments was 100 mV/s. The electrolyte used was tetrabutylammoniumhexafluorophosphate. All solutions were prepared in the glovebox and transferred under argon for analysis.

3. Optimization of the Reaction Conditions

Table S1. Optimization of the reaction conditions^a

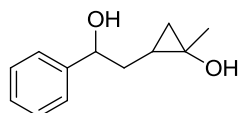


Entry	Sm(II) (equiv)	Additive (s) (equiv)	Temp. (°C)	Reaction time	Yield (%) ^b (<i>cis:trans</i>)
1	allylSmBr (2.2)	HMPA (10)	r.t.	Overnight	- ^c
2	allylSmBr (4.4)	HMPA (20)	r.t.	Overnight	trace
3	allylSmBr (2.2)	HMPA (10)/H ₂ O (0.5)	r.t.	3h	55(1.1: 1)
4	allylSmBr (2.2)	H ₂ O (1.0)	r.t.	Overnight	- ^d
5	allylSmBr (3.3)	HMPA (15)/H₂O (0.75)	r.t.	3h	62 (6.1: 1)
6	allylSmBr (4.4)	HMPA (20)/H ₂ O (1.0)	r.t.	3h	65(4.3: 1)
7	allylSmBr (2.2)	HMPA (10)/H₂O (1.0)	r.t.	3h	73 (1.5:1)
8	allylSmBr (2.2)	HMPA (10)/H ₂ O (1.0)	40 °C	Overnight	28(2.3:1)
9	allylSmBr (2.2)	HMPA (10)/H ₂ O (1.0)	0 °C	Overnight	34(2.9:1)
10	SmI ₂ (2.2)	HMPA (10)/H ₂ O (1.0)	r.t.	Overnight	- ^c
11	allylSmBr (2.2)	HMPA (10)/H ₂ O (3.0)	r.t.	Overnight	- ^d

^a Reaction conditions: a mixture of substrate **1** (1 mmol), Sm (II) reagent, and additive(s) in dry THF (20 mL) under nitrogen. ^b Isolated yield; the ratio of was given in parentheses. ^c Complex mixture. ^d No reaction.

4. Spectra Data for the Products.

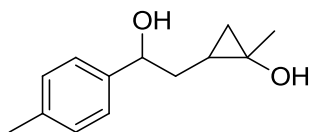
2-(2-Hydroxy-2-phenylethyl)-1-methylcyclopropanol (3a):



trans-isomer: Yellow oil^[5]; ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 4.3 Hz, 4H), 7.29–7.27 (m, 1H), 4.80–4.77 (m, 1H), 3.56 (s, 1H), 2.98 (s, 1H), 2.18–2.15 (m, 1H), 1.71–1.62 (m, 1H), 1.41 (s, 3H), 0.84–0.79 (m, 1H), 0.65–0.61 (m, 1H), 0.42 (t, *J* = 5.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 145.0, 128.5, 127.5, 125.6, 74.9, 54.4, 38.8, 26.0, 23.2, 20.0. HRMS (ESI) *m/z*: calcd. for C₁₂H₁₆O₂Na [M + Na]⁺: 215.10425; found: 215.10416.

cis-isomer: White solid, mp 88–90 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.35 (d, *J* = 4.4 Hz, 4H), 7.30–7.27 (m, 1H), 4.75–4.72 (m, 1H), 2.78 (s, 2H), 1.84–1.77 (m, 1H), 1.56–1.54 (m, 1H), 1.34 (s, 3H), 1.10–1.07 (m, 1H), 0.87–0.83 (m, 1H), 0.05 (t, *J* = 6.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 144.6, 128.4, 127.5, 125.9, 74.4, 55.4, 39.4, 22.4, 20.8, 19.7. HRMS (ESI) *m/z*: calcd. for C₁₂H₁₆O₂Na [M + Na]⁺: 215.10425; found: 215.10452.

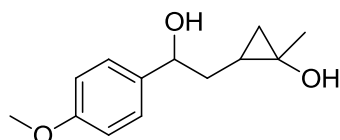
2-(2-Hydroxy-2-(4-methoxyphenyl)ethyl)-1-methylcyclopropanol (3b)



trans-isomer: Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.76–4.74 (m, 1H), 3.75 (s, 1H), 2.96 (s, 1H), 2.35 (s, 3H), 2.16–2.12 (m, 1H), 1.69–1.63 (m, 1H), 1.41 (s, 3H), 0.83–0.77 (m, 1H), 0.64–0.61 (m, 1H), 0.42 (t, *J* = 5.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 142.0, 137.2, 129.1, 125.6, 74.8, 54.3, 38.8, 26.0, 23.2, 21.1, 20.0. HRMS (ESI) *m/z*: calcd. for C₁₃H₁₈O₂Na [M + Na]⁺: 229.11990; found: 229.11967.

cis-isomer: White solid, mp 102–104 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 7.9 Hz, 2H), 4.73–4.70 (m, 1H), 2.49 (s, 1H), 2.46 (s, 1H), 2.34 (s, 3H), 1.84–1.77 (m, 1H), 1.56–1.54 (m, 1H), 1.35 (s, 3H), 1.09–1.06 (m, 1H), 0.87–0.83 (m, 1H), 0.05 (t, *J* = 6.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 141.6, 137.3, 129.1, 125.8, 74.2, 55.4, 39.3, 22.5, 21.1, 20.8, 19.7. HRMS (ESI) *m/z*: calcd. for C₁₃H₁₈O₂Na [M + Na]⁺: 229.11990; found: 229.11980.

2-(2-Hydroxy-2-(4-methoxyphenyl)ethyl)-1-methylcyclopropanol (3c)

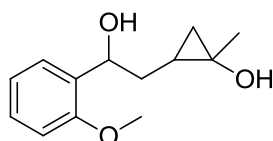


trans-isomer: White solid, mp 76–78 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, *J* = 8.3 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.75–4.73 (m, 1H), 3.80 (s, 3H), 3.62 (s, 1H),

2.78 (s, 1H), 2.14 – 2.11 (m, 1H), 1.71– 1.62 (m,1H), 1.41 (s, 3H), 0.82 – 0.76 (m, 1H), 0.64 – 0.61 (m, 1H), 0.42 (t, $J = 5.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.0, 137.2, 126.9, 113.8, 74.6, 55.3, 54.3, 38.7, 26.0, 23.2, 20.0.HRMS (ESI) m/z : calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_3\text{Na}$ $[\text{M} + \text{Na}]^+$: 245.11482; found: 245.11432.

cis-isomer: Pale yellow solid, mp 78 – 80 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.24 (d, $J = 8.4$ Hz, 2H), 6.86 (d, $J = 8.4$ Hz, 2H), 4.66 – 4.63 (m,1H), 3.78 (s, 3H), 3.17 (s, 2H), 1.81– 1.73 (m, 1H), 1.49 – 1.46 (m,1H), 1.34 (s, 3H), 1.05 – 1.02 (m, 1H), 0.84 – 0.80 (m, 1H), 0.00 (t, $J = 5.7$ Hz,1H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.9, 136.8, 127.1, 113.8, 73.9, 55.29, 55.27, 39.3, 22.5, 20.7, 19.6.HRMS (ESI) m/z : calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_3\text{Na}$ $[\text{M} + \text{Na}]^+$: 245.11482; found: 245.11453.

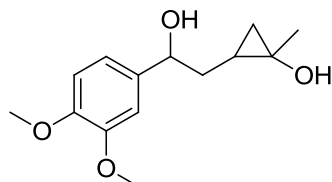
2-(2-Hydroxy-2-(2-methoxyphenyl)ethyl)-1-methylcyclopropanol (3d)



trans-isomer: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.40 (d, $J = 7.1$ Hz, 1H), 7.28–7.26 (m, 1H), 6.98 (t, $J = 7.4$ Hz,1H), 6.88 (d, $J = 8.2$ Hz, 1H), 5.13– 5.10 (m, 1H), 3.86 (s, 3H),2.28 – 2.24 (m, 1H), 1.71 – 1.62 (m,1H), 1.42 (s, 3H), 0.85 – 0.83 (m, 1H), 0.65 – 0.61 (m, 1H), 0.44 (t, $J = 5.5$ Hz,1H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.2, 132.6, 128.4, 126.1, 120.8, 110.3, 55.3, 36.1, 26.1, 23.4, 20.0, 18.6.HRMS (ESI) m/z : calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_3\text{Na}$ $[\text{M} + \text{Na}]^+$: 245.11482; found: 245.11468.

cis-isomer: White solid, mp 116 – 118°C; ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, $J = 7.5$ Hz, 1H), 7.26 (d, $J = 6.6$ Hz, 1H), 6.98 (t, $J = 7.5$ Hz,1H), 6.89 (d, $J = 8.2$ Hz, 1H), 4.99 – 4.95 (m, 1H), 3.86 (s, 3H),2.76 (s, 1H), 2.20 (s, 1H), 1.86 – 1.81 (m,1H), 1.65 – 1.61 (m, 1H), 1.35 (s, 3H), 1.12 – 1.09 (m, 1H), 0.88 – 0.84 (m, 1H), 0.08 (t, $J = 6.4$ Hz,1H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.4, 132.3, 128.4, 126.9, 120.8, 110.6, 70.8, 55.5, 55.4, 37.4, 22.7, 20.8, 19.7.HRMS (ESI) m/z : calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_3\text{Na}$ $[\text{M} + \text{Na}]^+$: 245.11482; found: 245.11455.

2-(2-(3,4-Dimethoxyphenyl)-2-hydroxyethyl)-1-methylcyclopropanol (3e)

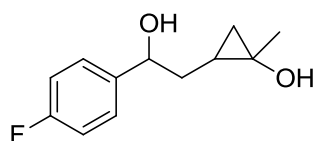


trans-isomer: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 6.90 (d, $J = 5.6$ Hz, 1H), 6.87 (d, $J = 1.7$ Hz, 1H),6.83 (d, $J = 8.0$ Hz, 1H), 4.76 – 4.74 (m, 1H), 3.89 (s, 3H),3.87 (s, 3H), 3.53 (s, 1H), 2.64 (s, 1H), 2.17 – 2.12 (m, 1H), 1.73 – 1.67 (m,1H), 1.42 (s, 3H), 0.83 – 0.78 (m, 1H), 0.66 – 0.62 (m, 1H), 0.44 (t, $J = 5.6$ Hz,1H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.9,148.5, 137.7, 117.8, 110.9, 108.6, 75.0, 55.95, 55.89, 54.4, 38.7,

26.1, 23.3, 20.1.HRMS (ESI) m/z : calcd. for $C_{14}H_{20}O_4Na$ $[M + Na]^+$: 275.12538; found: 275.12561.

cis-isomer: White solid, mp 74 – 78 °C; 1H NMR (400 MHz, $CDCl_3$) δ 6.93 (s, 1H), 6.89 (d, $J = 8.6$ Hz, 1H), 6.84 (d, $J = 8.2$ Hz, 1H), 4.73 – 4.70 (m, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 1.89 – 1.83 (m, 3H), 1.56 – 1.51 (m, 1H), 1.38 (s, 3H), 1.13 – 1.05 (m, 1H), 0.89 – 0.83 (m, 1H), 0.08 (t, $J = 5.8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 148.4, 137.1, 118.1, 110.9, 109.0, 74.3, 55.94, 55.90, 55.5, 39.2, 22.3, 20.8, 19.9.HRMS (ESI) m/z : calcd. for $C_{14}H_{20}O_4Na$ $[M + Na]^+$: 275.12538; found: 275.12532.

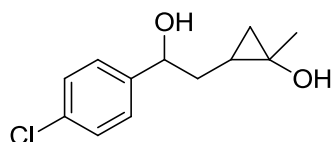
2-(2-(4-Fluorophenyl)-2-hydroxyethyl)-1-methylcyclopropanol (3f)



trans-isomer: Pale yellow solid, mp 86 – 88 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 2H), 7.01 (t, $J = 8.6$ Hz, 2H), 4.77 – 4.74 (m, 1H), 3.63 (s, 1H), 3.24 (s, 1H), 2.15 – 2.07 (m, 1H), 1.67 – 1.60 (m, 1H), 1.41 (s, 3H), 0.81 – 0.75 (m, 1H), 0.65 – 0.61 (m, 1H), 0.41 (t, $J = 5.7$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, $J_{C-F} = 243.5$ Hz, 1C), 140.8 (d, $J_{C-F} = 3.04$ Hz, 1C), 127.2 (d, $J_{C-F} = 8.2$ Hz, 1C), 115.2 (d, $J_{C-F} = 21.3$ Hz, 1C), 74.3, 54.4, 40.0, 25.9, 23.2, 20.0.HRMS (ESI) m/z : calcd. for $C_{12}H_{15}FO_2Na$ $[M + Na]^+$: 233.09483; found: 233.09505.

cis-isomer: White solid, mp 106 – 108 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, $J = 7.7$ Hz, 2H), 7.03 (t, $J = 8.6$ Hz, 2H), 4.73 (m, 1H), 2.57 (s, 1H), 2.43 (s, 1H), 1.84 – 1.76 (m, 1H), 1.55 – 1.49 (m, 1H), 1.36 (s, 3H), 1.10 – 1.03 (m, 1H), 0.86 – 0.82 (m, 1H), 0.03 (t, $J = 5.8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, $J_{C-F} = 244.1$ Hz, 1C), 140.2 (d, $J_{C-F} = 2.9$ Hz, 1C), 127.5 (d, $J_{C-F} = 8.1$ Hz, 1C), 115.2 (d, $J_{C-F} = 21.3$ Hz, 1C), 73.7, 55.4, 39.4, 22.2, 20.8, 19.8; HRMS (ESI) m/z : calcd. for $C_{12}H_{15}FO_2Na$ $[M + Na]^+$: 233.09483; found: 233.09516.

2-(2-(4-Chlorophenyl)-2-hydroxyethyl)-1-methylcyclopropanol (3g)

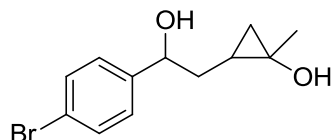


trans-isomer: Yellow oil; 1H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 4H), 4.79 – 4.77 (m, 1H), 3.23 (s, 1H), 2.80 (s, 1H), 2.16 – 2.09 (m, 1H), 1.68 – 1.59 (m, 1H), 1.43 (s, 3H), 0.83 – 0.78 (m, 1H), 0.67 – 0.63 (m, 1H), 0.43 (t, $J = 5.7$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 133.1, 128.6, 127.0, 74.4, 54.5, 38.9, 26.0, 23.2, 20.1.HRMS (ESI) m/z : calcd for $C_{12}H_{15}ClO_2Na$ $[M + Na]^+$: 249.06528; found: 249.06586.

cis-isomer: White solid, mp 122 – 124 °C; 1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28

(m, 4H), 4.75 – 4.72 (m, 1H), 2.28 (s, 2H), 1.84 – 1.77 (m, 1H), 1.53 – 1.50 (m, 1H), 1.36 (s, 3H), 1.11– 1.03 (m, 1H), 0.87 – 0.83 (m, 1H), 0.05 (t, $J = 5.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.9, 133.2, 128.6, 127.3, 73.7, 55.5, 39.3, 22.1, 20.8, 19.9; HRMS (ESI) m/z : calcd for $\text{C}_{12}\text{H}_{15}\text{ClO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 249.06528; found: 249.06598.

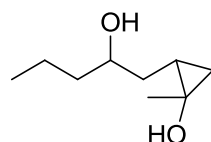
2-(2-(4-Bromophenyl)-2-hydroxyethyl)-1-methylcyclopropanol (3h)



trans-isomer: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (d, $J = 8.1$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 4.77– 4.74 (m, 1H), 3.30 (s, 1H), 2.93 (s, 1H), 2.15 – 2.11 (m, 1H), 1.64 – 1.60 (m, 1H), 1.43 (s, 3H), 0.82 – 0.78 (m, 1H), 0.67 – 0.63 (m, 1H), 0.43 (t, $J = 5.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.1, 131.5, 127.4, 121.2, 74.4, 54.5, 38.9, 26.0, 23.2, 20.1. HRMS (ESI) m/z : calcd for $\text{C}_{12}\text{H}_{15}\text{BrO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 293.01476; found: 293.01413.

cis-isomer: White solid, mp 124 – 126 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, $J = 8.0$ Hz, 2H), 7.24 (d, $J = 8.1$ Hz, 2H), 4.75 – 4.72 (m, 1H), 2.05 (s, 2H), 1.83 – 1.80 (m, 1H), 1.53 – 1.50 (m, 1H), 1.36 (s, 3H), 1.11 – 1.03 (m, 1H), 0.88 – 0.84 (m, 1H), 0.06 (t, $J = 5.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.5, 131.5, 127.6, 121.3, 73.8, 55.5, 39.3, 22.1, 20.8, 19.9; HRMS (ESI) m/z : calcd for $\text{C}_{12}\text{H}_{15}\text{BrO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 293.01476; found: 293.01429.

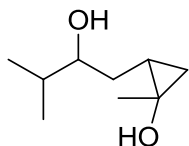
2-(2-Hydroxypentyl)-1-methylcyclopropanol (3i)



trans-isomer: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 3.81 (s, 1H), 3.73– 3.72 (m, 1H), 2.60 (s, 1H), 1.99– 1.95 (m, 1H), 1.45 – 1.43 (m, 3H), 1.39 (s, 3H), 1.33 – 1.25 (m, 2H), 0.93 (t, $J = 6.4$ Hz, 3H), 0.71 – 0.63 (m, 1H), 0.62 – 0.58 (m, 1H), 0.39 (t, $J = 5.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 72.4, 54.2, 40.3, 36.2, 26.1, 23.3, 20.1, 18.9, 14.1. HRMS (ESI) m/z : calcd for $\text{C}_9\text{H}_{18}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 181.11990; found: 181.11972.

cis-isomer: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 3.70 – 3.66 (m, 1H), 1.50 – 1.45 (m, 3H), 1.40 (s, 3H), 1.34 – 1.30 (m, 1H), 1.28 – 1.25 (m, 1H), 1.10 – 1.02 (m, 1H), 0.94 – 0.87 (m, 4H), 0.08 (t, $J = 6.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 71.7, 55.3, 39.4, 37.4, 22.4, 20.9, 19.7, 18.9, 14.1. HRMS (ESI) m/z : calcd for $\text{C}_9\text{H}_{18}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 181.11990; found: 181.12034.

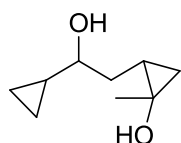
2-(2-Hydroxy-3-methylbutyl)-1-methylcyclopropanol (3j)



trans-isomer: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 4.05 (s, 1H), 3.51 – 3.48 (m, 1H), 2.75 (s, 1H), 2.02– 1.96 (m, 1H), 1.66 – 1.64 (m, 1H), 1.38 (s, 3H), 1.28 – 1.24 (m, 1H), 0.92 (d, $J = 3.4$ Hz, 3H), 0.90 (d, $J = 3.4$ Hz, 3H), 0.69 – 0.58 (m, 2H), 0.39 (t, $J = 5.1$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 76.7, 54.2, 34.2, 32.7, 26.1, 23.5, 20.0, 18.5, 17.4. HRMS (ESI) m/z : calcd for $\text{C}_9\text{H}_{18}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 181.11990; found: 181.11979.

cis-isomer: Yellow solid, mp 72–74 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.45 – 3.40 (m, 1H), 3.24 (s, 1H), 2.39 (s, 1H), 1.72 – 1.64 (m, 1H), 1.49 – 1.42 (m, 1H), 1.40 (s, 3H), 1.29 – 1.24 (m, 1H), 1.11 – 1.04 (m, 1H), 0.92 (d, $J = 3.4$ Hz, 3H), 0.90 (d, $J = 3.4$ Hz, 3H), 0.88 – 0.85 (m, 1H), 0.06 (t, $J = 5.7$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 76.7, 55.4, 34.0, 33.4, 22.8, 21.0, 19.5, 18.9, 17.3. HRMS (ESI) m/z : calcd for $\text{C}_9\text{H}_{18}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 181.11990; found: 181.11968.

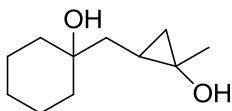
2-(2-Cyclopropyl-2-hydroxyethyl)-1-methylcyclopropanol (3k)



trans-isomer: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 2.98 – 2.93 (m, 1H), 2.18 – 2.13 (m, 1H), 1.52 – 1.44 (m, 1H), 1.37 (s, 3H), 0.96 – 0.83 (m, 2H), 0.69 – 0.58 (m, 2H), 0.54 – 0.50 (m, 2H), 0.42 (t, $J = 5.2$ Hz, 1H), 0.32 – 0.27 (m, 1H), 0.24 – 0.20 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 76.7, 54.2, 36.0, 26.0, 23.2, 20.1, 18.2, 2.9, 2.6. HRMS (ESI) m/z : calcd for $\text{C}_9\text{H}_{16}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 179.10425; found: 179.10476.

cis-isomer: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 2.95 – 2.90 (m, 1H), 1.67 – 1.60 (m, 1H), 1.50 – 1.44 (m, 1H), 1.42 (s, 3H), 1.17 – 1.10 (m, 1H), 0.98 – 0.87 (m, 3H), 0.57 – 0.48 (m, 2H), 0.33 – 0.28 (m, 1H), 0.26 – 0.20 (m, 1H), 0.10 (t, $J = 6.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 76.7, 55.4, 37.1, 22.4, 20.9, 19.9, 17.7, 3.0, 2.8. HRMS (ESI) m/z : calcd for $\text{C}_9\text{H}_{16}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 179.10425; found: 179.10463.

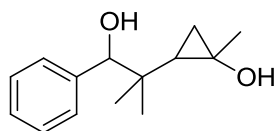
1-(2-Hydroxy-2-methylcyclopropyl)cyclohexanol (3l)



trans-isomer: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 4.26 (s, 1H), 2.80 (s, 1H), 2.03 – 1.98 (m, 1H), 1.62 – 1.41 (m, 9H), 1.36 – 1.31 (m, 5H), 0.72 – 0.65 (m, 1H), 0.61 – 0.58 (m, 1H), 0.38 (t, $J = 5.3$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 72.1, 54.0, 40.2, 39.4, 36.0, 26.0, 25.8, 22.7, 22.3, 20.6, 20.0; HRMS (ESI) m/z : calcd for $\text{C}_{11}\text{H}_{20}\text{NO}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 207.13555; found: 207.13597.

cis-isomer: White solid, mp 118 – 122 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.48 (s, 1H), 1.86 (s, 1H), 1.67 – 1.54 (m, 7H), 1.47 – 1.45 (m, 4H), 1.40 (s, 3H), 1.28 – 1.22 (m, 2H), 1.15 – 1.09 (m, 1H), 0.95–0.91 (m, 1H), 0.13 (t, *J* = 5.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 71.8, 54.8, 42.2, 37.6, 37.1, 25.8, 22.14, 22.11, 21.0, 20.4, 20.2; HRMS (ESI) *m/z*: calcd for C₁₁H₂₀NO₂Na [M+ Na]⁺: 207.13555; found: 207.13589.

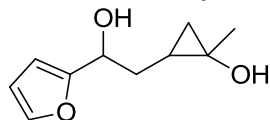
2-(1-Hydroxy-2-methyl-1-phenylpropan-2-yl)-1-methylcyclopropanol (3m)



trans-isomer: White solid, mp 104–108 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.37 – 7.29 (m, 5H), 4.69 (s, 1H), 3.69 (s, 1H), 2.76 (s, 1H), 1.41 (s, 3H), 0.87 (s, 3H), 0.81 (s, 3H), 0.78 – 0.75 (m, 1H), 0.70 – 0.66 (m, 1H), 0.58 – 0.54 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 141.8, 127.8, 127.7, 127.6, 83.0, 55.8, 39.4, 35.6, 29.0, 27.4, 17.0, 16.0; HRMS (ESI) *m/z*: calcd for C₁₄H₂₀O₂Na [M+ Na]⁺: 243.13555; found: 243.13550.

cis-isomer: White solid, mp 102–105 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.28 (m, 5H), 4.53 (s, 1H), 2.30 (s, 1H), 2.07 (s, 1H), 1.35 (s, 3H), 1.12 – 1.07 (m, 1H), 0.91 (s, 3H), 0.83 (s, 3H), 0.73 – 0.69 (m, 1H), 0.29 – 0.26 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 142.0, 127.8, 127.6, 127.4, 82.4, 56.0, 38.8, 33.6, 24.3, 22.0, 20.9, 16.0; HRMS (ESI) *m/z*: calcd for C₁₄H₂₀O₂Na [M+ Na]⁺: 243.13555; found: 243.13532

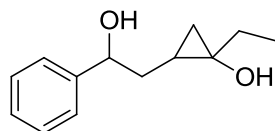
2-(2-(Furan-2-yl)-2-hydroxyethyl)-1-methylcyclopropanol (3n)



trans-isomer: Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.38 (s, 1H), 6.34 (d, *J* = 1.7 Hz, 1H), 6.25 (d, *J* = 3.1 Hz, 1H), 4.83 – 4.80 (m, 1H), 3.33 (s, 1H), 2.90 (s, 1H), 2.33 – 2.28 (m, 1H), 1.87 – 1.78 (m, 1H), 1.43 (s, 3H), 0.80 – 0.75 (m, 1H), 0.68 – 0.65 (m, 1H), 0.49 – 0.46 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 156.9, 141.9, 110.2, 105.5, 68.1, 54.4, 34.6, 25.9, 22.7, 20.0; HRMS (ESI) *m/z*: calcd for C₁₀H₁₄O₃Na [M+ Na]⁺: 205.08352; found: 205.08325.

cis-isomer: Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.38 (s, 1H), 6.34 (d, *J* = 3.0 Hz, 1H), 6.27 (d, *J* = 3.1 Hz, 1H), 4.76 (t, *J* = 7.4 Hz, 1H), 2.15 (s, 2H), 1.99 – 1.92 (m, 1H), 1.70 – 1.66 (m, 1H), 1.42 (s, 3H), 1.13 – 1.09 (m, 1H), 0.90 – 0.86 (m, 1H), 0.12 – 0.07 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 156.4, 141.9, 110.2, 106.1, 67.8, 55.4, 35.7, 22.0, 20.8, 19.7. HRMS (ESI) *m/z*: calcd for C₁₀H₁₄O₃Na [M+ Na]⁺: 205.08352; found: 205.08337.

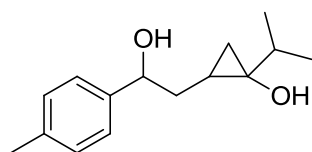
2-(2-Hydroxy-2-phenylethyl)-1-ethylcyclopropanol (3o)



trans-isomer: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.40 – 7.32 (m, 4H), 7.30 – 7.25 (m, 1H), 4.79 – 4.76 (m, 1H), 3.67 (s, 1H), 2.94 (s, 1H), 2.19 – 2.14 (m, 1H), 1.69 – 1.62 (m, 2H), 1.50 – 1.41 (m, 1H), 1.05 (t, $J = 7.4$ Hz, 3H), 0.86 – 0.79 (m, 1H), 0.65 – 0.62 (m, 1H), 0.41 (t, $J = 5.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.1, 128.5, 127.5, 125.6, 75.2, 58.7, 38.9, 32.4, 22.4, 19.2, 9.8. HRMS (ESI) m/z : calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 229.11990; found: 229.12013.

cis-isomer: White solid, mp 94 – 96 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.34 (m, 4H), 7.29 – 7.27 (m, 1H), 4.75 – 4.71 (m, 1H), 2.31 (s, 2H), 2.05 – 1.97 (m, 1H), 1.62 – 1.40 (m, 3H), 1.20 – 1.12 (m, 1H), 1.06 (t, $J = 7.2$ Hz, 3H), 0.84 – 0.80 (m, 1H), 0.08 – 0.01 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.6, 128.4, 127.6, 125.9, 77.2, 74.5, 39.0, 27.2, 22.8, 19.0, 10.0. HRMS (ESI) m/z : calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 229.11990; found: 229.11976.

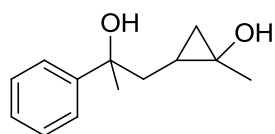
2-(2-Hydroxy-2-phenylethyl)-1-isopropylcyclopropanol (3p):



trans-isomer: White solid, mp 78 – 80 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.23 (d, $J = 8.0$ Hz, 2H), 7.15 (d, $J = 7.9$ Hz, 2H), 4.73 – 4.70 (m, 1H), 3.81 (s, 1H), 2.91 (s, 1H), 2.35 (s, 3H), 2.15 – 2.11 (m, 1H), 1.69 – 1.60 (m, 1H), 1.23 – 1.13 (m, 1H), 1.05 (d, $J = 6.9$ Hz, 3H), 1.03 (d, $J = 6.8$ Hz, 3H), 0.88 – 0.78 (m, 1H), 0.63 – 0.60 (m, 1H), 0.39 (t, $J = 5.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.2, 137.1, 129.1, 125.6, 75.1, 61.7, 38.9, 36.6, 22.8, 21.1, 19.2, 18.2, 18.1; HRMS (ESI) m/z : calcd for $\text{C}_{14}\text{H}_{20}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 243.13555; found: 243.13592.

cis-isomer: White solid, mp 89 – 92 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.24 (d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 7.9$ Hz, 2H), 4.71 – 4.67 (m, 1H), 2.35 (s, 3H), 2.22 – 2.15 (m, 1H), 1.94 (s, 1H), 1.78 (s, 1H), 1.34 – 1.19 (m, 3H), 1.06 (d, $J = 6.8$ Hz, 3H), 1.04 (d, $J = 6.8$ Hz, 3H), 0.85 – 0.81 (m, 1H), 0.03 – 0.00 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.8, 137.2, 129.1, 125.8, 74.4, 62.5, 38.4, 31.6, 23.5, 21.1, 19.6, 18.5, 18.0. HRMS (ESI) m/z : calcd for $\text{C}_{14}\text{H}_{20}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 243.13555; found: 243.13580.

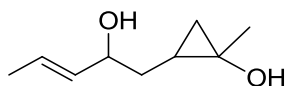
2-(2-hydroxy-2-phenylpropyl)-1-methylcyclopropanol (3q):



trans-isomers (dr = 1:1): Yellow oil; One pair of isomers: ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.46 (m, 2H), 7.38 – 7.33 (m, 2H), 7.27 – 7.23 (m, 1H), 3.86 (s, 1H), 3.23 (s, 1H), 2.20 – 2.16 (dd, $J = 3.8$ Hz, $J = 3.8$ Hz, 1H), 1.76–1.69 (m, 1H), 1.66 (s, 3H), 1.33 (s, 3H), 0.88 – 0.81 (m, 1H), 0.50 – 0.47 (m, 1H), 0.40 – 0.37 (t, $J = 5.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.4, 128.2, 126.7, 125.0, 74.8, 54.3, 43.6, 31.4, 25.8, 20.9, 20.1. The other pair of isomers: ^1H NMR (400 MHz, CDCl_3) δ 7.49 – 7.46 (m, 2H), 7.38 – 7.33 (m, 2H), 7.27 – 7.23 (m, 1H), 3.23 (br, s, 1 H), 2.87 (br, s, 1H), 2.36 – 2.32 (dd, $J = 3.5$ Hz, $J = 3.6$ Hz, 1H), 1.76 – 1.69 (m, 1H), 1.61 (s, 3H), 1.26 (s, 3H), 0.66 – 0.62 (m, 1H), 0.40 – 0.37 (t, $J = 5.8$ Hz, 1H), 0.21 – 0.14 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.1, 128.1, 126.4, 124.6, 75.1, 54.4, 43.6, 28.2, 25.7, 20.8, 20.2. HRMS (ESI) m/z : calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 229.11990; found: 229.11964.

cis-isomers (dr = 3:1): Yellow oil; The major pair of isomers: ^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.45 (m, 2H), 7.36 – 7.32 (m, 2H), 7.27 – 7.22 (m, 1H), 2.52 (br, s, 2H), 2.02 – 1.97 (dd, $J = 5.4$ Hz, $J = 5.4$ Hz, 1H), 1.59 (s, 3H), 1.53 – 1.48 (m, 1H), 1.23 (s, 3H), 1.01 – 0.91 (m, 1H), 0.89 – 0.86 (m, 1H), 0.08 (t, $J = 5.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.1, 128.1, 126.7, 124.9, 75.0, 54.4, 43.9, 29.5, 20.8, 20.2. The minor pair of isomers: ^1H NMR (400 MHz, CDCl_3) δ 7.50 – 7.45 (m, 2H), 7.36 – 7.32 (m, 2H), 7.27 – 7.22 (m, 1H), 2.52 (br, s, 2H), 1.80 – 1.60 (m, 2H), 1.59 (s, 3H), 1.29 – 1.24 (m, 1H), 1.23 (s, 3H), 0.82 – 0.75 (m, 1H), 0.02 – 0.01 (t, $J = 1.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.0, 128.2, 126.7, 125.0, 74.8, 60.5, 43.8, 29.6, 21.0, 20.0, 14.2. HRMS (ESI) m/z : calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 229.11990; found: 229.11987.

2-(2-hydroxypent-3-en-1-yl)-1-methylcyclopropanol (3s):



trans-isomer: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 5.72 – 5.64(m, 1H), 5.54 – 5.48 (m, 1H), 4.18 – 4.14 (m, 1H), 3.66 (br, s, 1H), 2.30 (br, s, 1H), 2.00 – 1.96 (m, 1H), 1.70 – 1.68 (dd, $J = 1.0$ Hz, $J = 0.8$ Hz, 3H), 1.46 – 1.37 (m, 4H), 0.73 – 0.66 (m, 1H), 0.62 – 0.59 (m, 1H), 0.42 – 0.39 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 134.3, 126.6, 73.6, 54.2, 36.5, 26.0, 22.9, 20.1, 17.6. HRMS (ESI) m/z : calcd for $\text{C}_9\text{H}_{16}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 179.10425; found: 179.10437.

cis-isomer: Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 5.73–5.64 (m, 1H), 5.57 – 5.49 (m, 1H), 4.15 – 4.10 (m, 1H), 2.30 (br, s, 2H), 1.71–1.69(d, $J = 0.68$ Hz, 3H), 1.60 – 1.53 (m, 1H), 1.41 – 1.31 (m, 4H), 1.10 – 1.01 (m, 1H), 0.90 – 0.86 (m, 1H), 0.11–0.07 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 134.0, 126.8, 72.9, 55.3, 37.4, 22.1, 20.8, 19.8, 17.7. HRMS (ESI) m/z : calcd for $\text{C}_9\text{H}_{16}\text{O}_2\text{Na}$ $[\text{M} + \text{Na}]^+$: 179.10425; found: 179.10409.

5. References:

1. S. R. Wilson and M. E. Guazzaroni, *J. Org. Chem.* 1989, **54**, 3087-3091.
2. F. A. Khan, K. S. Krishnakumar, and C. Sudheer, *Synthesis*. 2007, 1054–1060.
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4. Chen, P, Xiang, P, *Tetrahedron Lett.* 2011, **52**, 5758–5760.
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6.X-Ray Crystallographic Information of Product 3m.

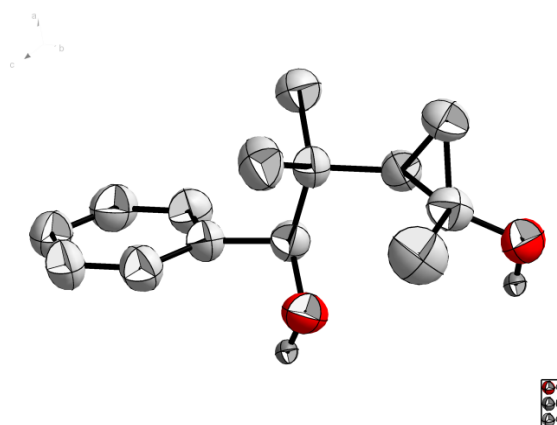
Single crystals of product **3m** (*cis*- or *trans*-isomer) was obtained through slow evaporation at room temperature of a solution in ethyl acetate – petroleum ether. A single crystal of **3m** was attached to a glass fiber with epoxy glue and transferred to a X-ray diffractometer equipped with a graphite-monochromator. Diffraction data of the product **3m** were measured with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 296(2) K. The structure was solved by direct methods using the SHELXS-97 program. Refinements were carried out with a full matrix least squares method against F^2 using SHELXL-97. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atoms to which they were attached. The important crystal data of product **3m** are given below.

Important X-Ray Crystallographic Data of cis-3m (see Table S1)

Table S2 Crystallographic Data of *cis-3m* (from the CIF Data Importer)

Compound reference	<i>cis-3m</i>
Chemical formula	C ₁₄ H ₂₀ O ₂
Formula Mass	220.30
Crystal system	Monoclinic
<i>a</i> /Å	25.307(9)
<i>b</i> /Å	6.060(3)
<i>c</i> /Å	17.759(7)
α /°	90.00
β /°	109.21(3)
γ /°	90.00
Unit cell volume/Å ³	2571.6(18)
Temperature/K	296(2)
Space group	<i>C2/c</i>
No. of formula units per unit cell, Z	8
No. of reflections measured	9527
No. of independent reflections	2899
R_{int}	0.1107
Final R_I values ($I > 2\sigma(I)$)	0.0773
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2006
Final R_I values (all data)	
Final $wR(F^2)$ values (all data)	0.2485

X-Ray Crystal Structure of cis-3m:



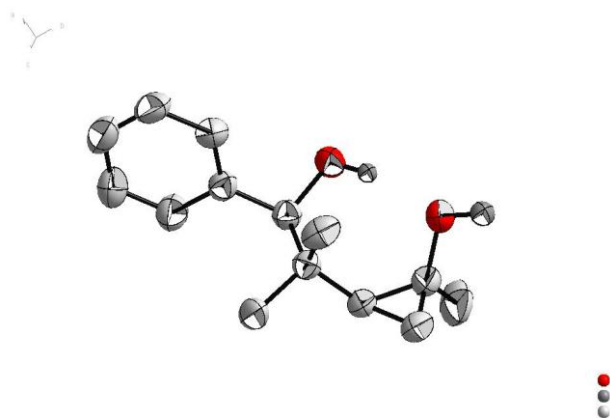
For more details please see the CIF file attached with ESI. The crystal data of the product has already been deposited at Cambridge Crystallographic Data Center, UK, and the CCDC reference number is **876387**.

Important X-Ray Crystallographic Data of trans-3m (see Table S2)

Table S3 Crystallographic Data of *trans-3m* (from the CIF Data Importer)

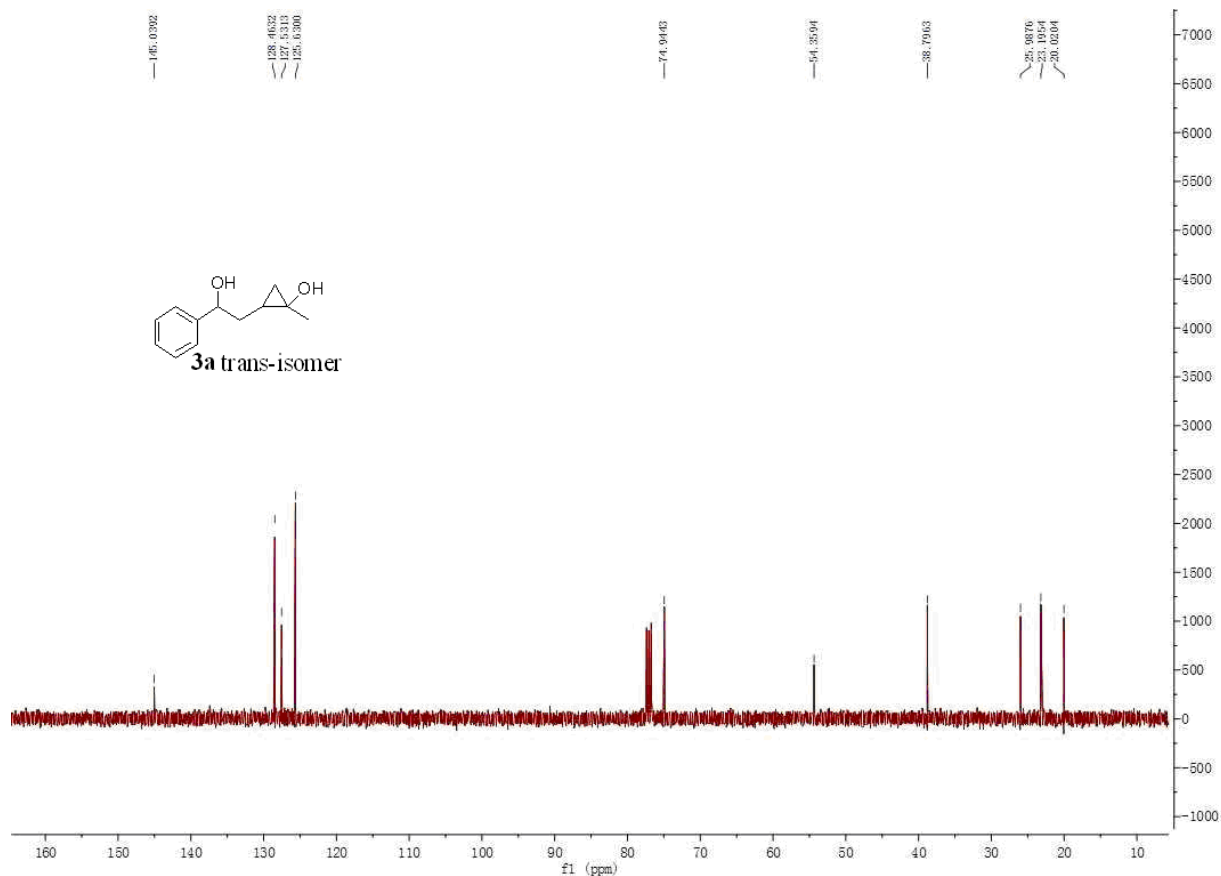
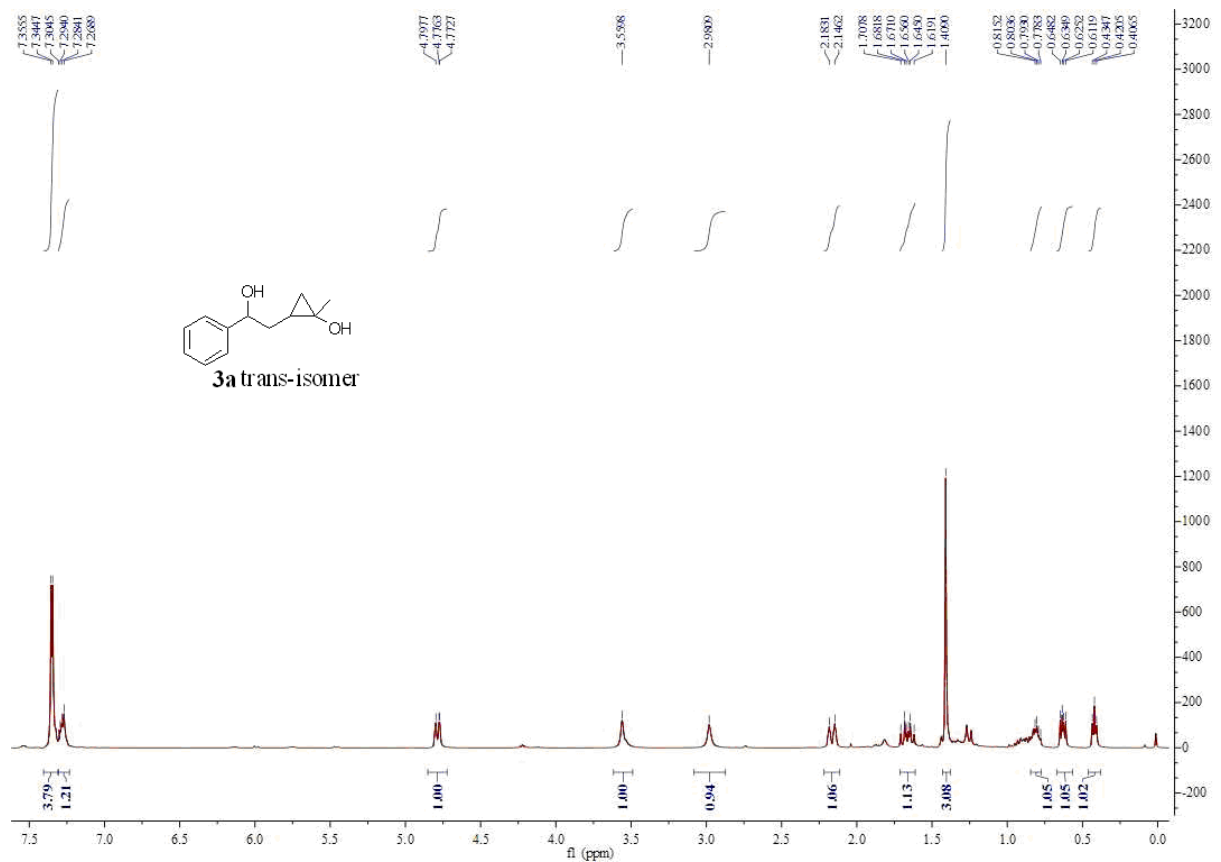
Compound reference	<i>trans-3m</i>
Chemical formula	C ₁₄ H ₂₀ O ₂
Molecular Weight	220.30
Crystal system	Orthorhombic
<i>a</i> /Å	16.351(3)
<i>b</i> /Å	51.476(9)
<i>c</i> /Å	6.0436(10)
α /°	90.00
β /°	90.00
γ /°	90.00
Unit cell volume/Å ³	5086.8(15)
Temperature/K	296(2)
Space group	Fdd2
No. of formula units per unit cell, <i>Z</i>	16
No. of reflections measured	5556
No. of independent reflections	2518
<i>R</i> _{int}	0.0299
Final <i>R</i> ₁ values (<i>I</i> > 2σ(<i>I</i>))	0.0557
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2σ(<i>I</i>))	0.1373
Final <i>R</i> ₁ values (all data)	
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.1551

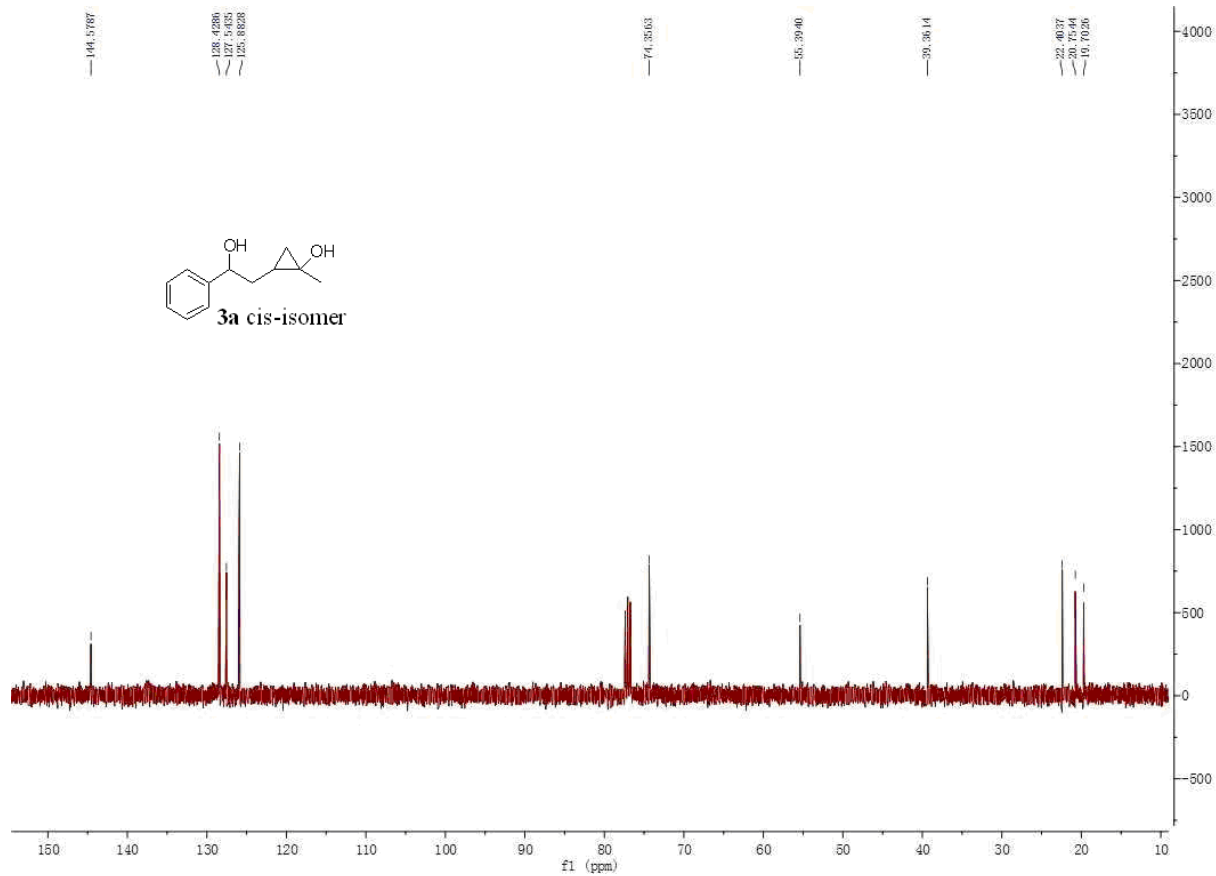
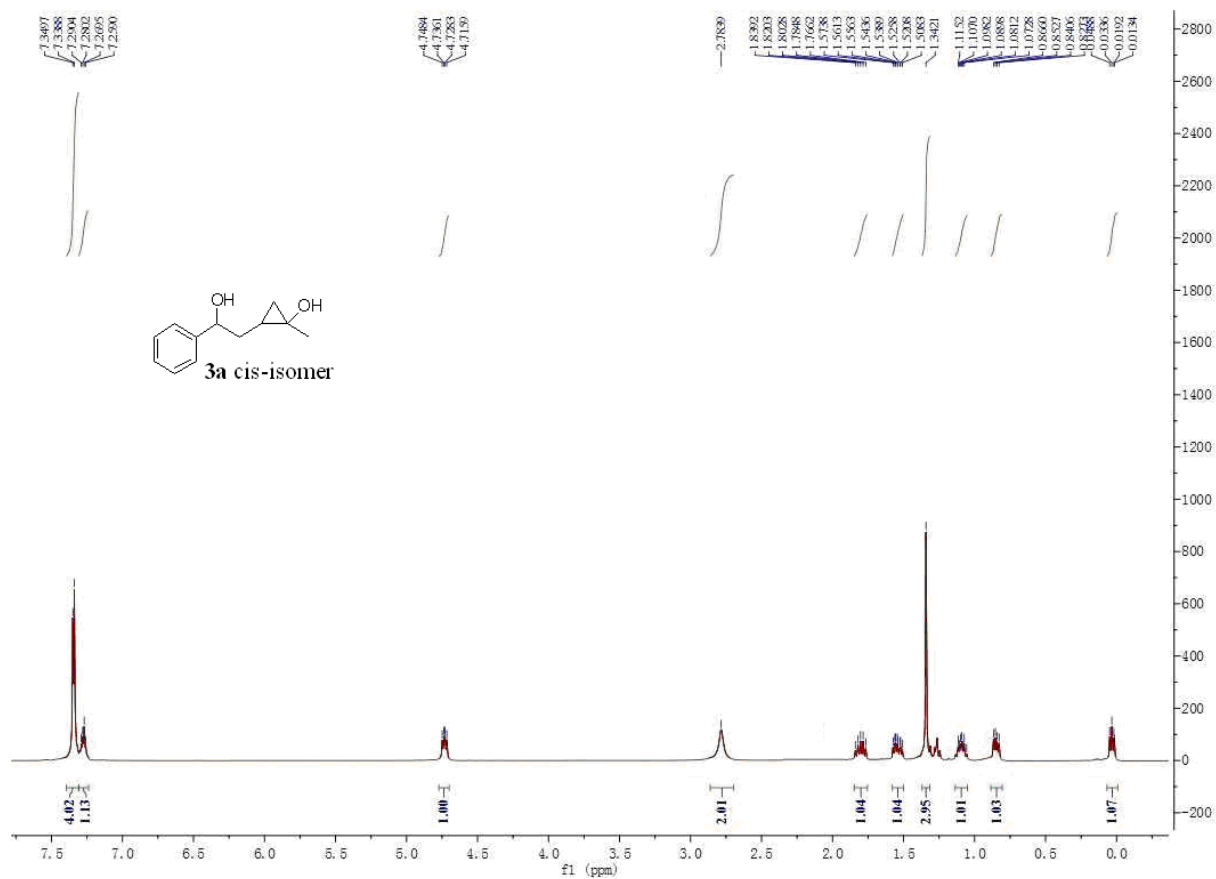
X-Ray Crystal Structure of trans-3m:

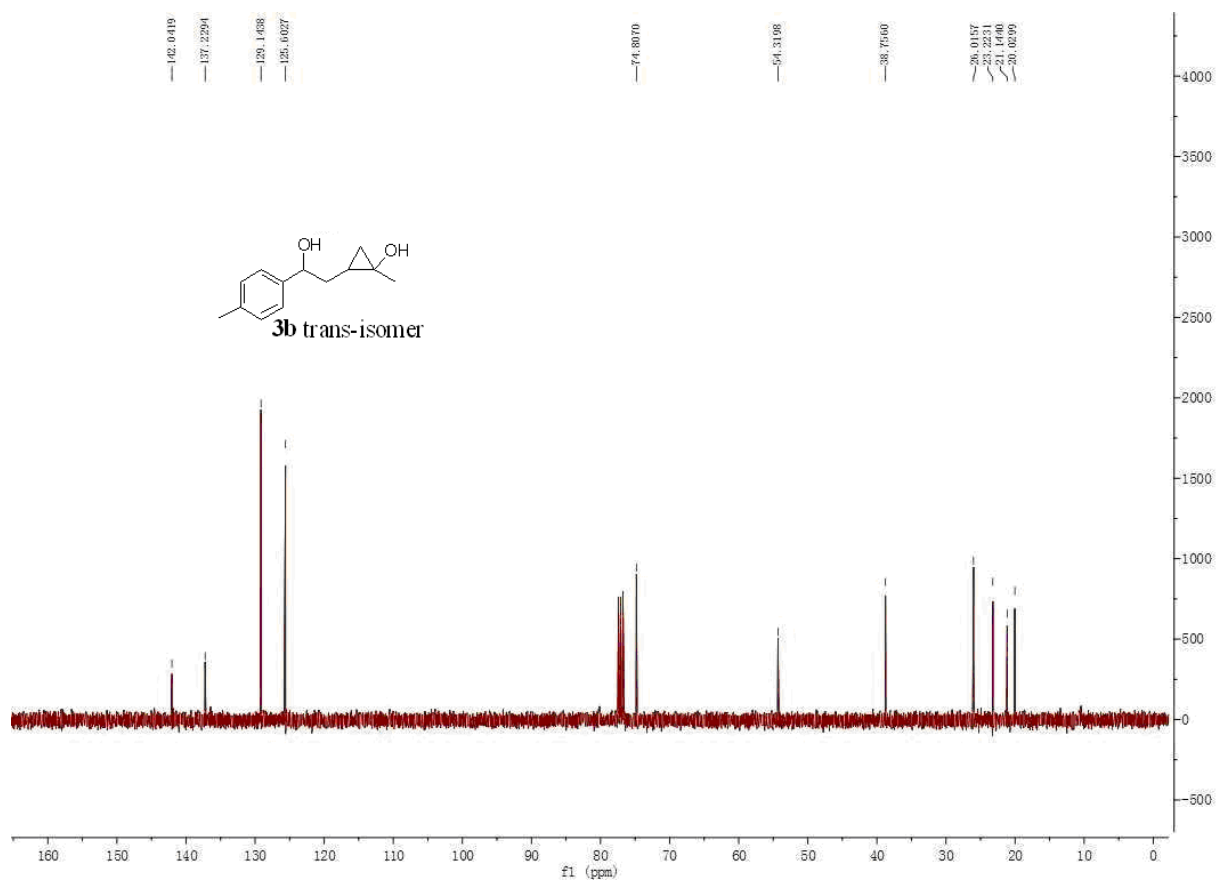
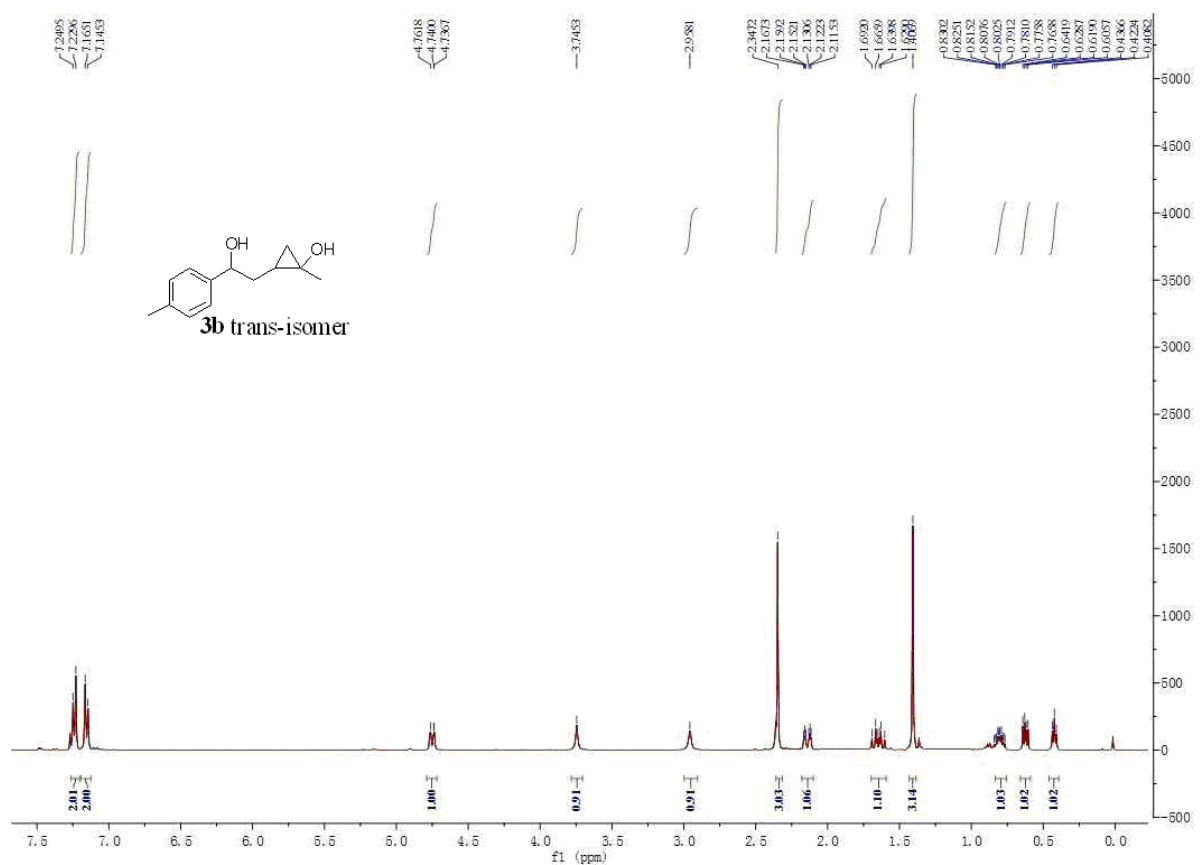


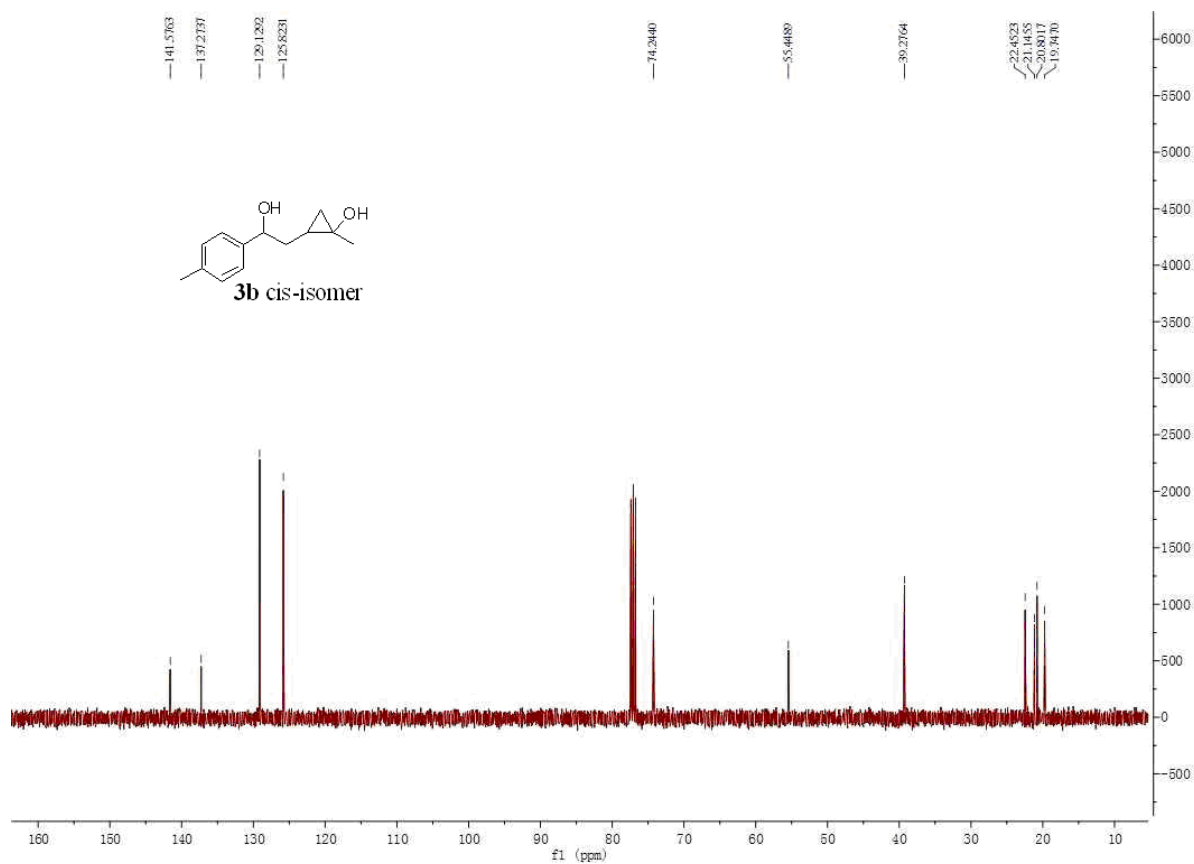
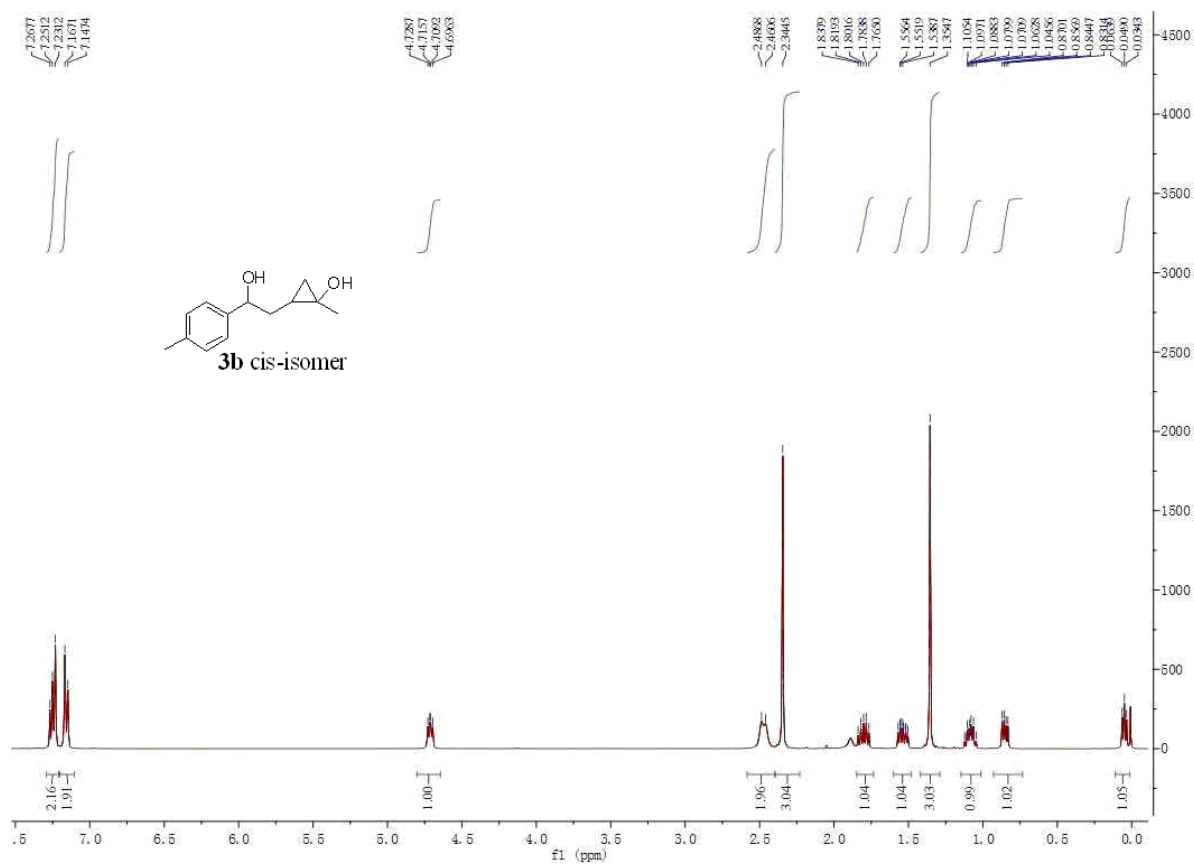
For more details please see the CIF file attached with ESI. The crystal data of the product has already been deposited at Cambridge Crystallographic Data Center, UK, and the CCDC reference number is **876386**.

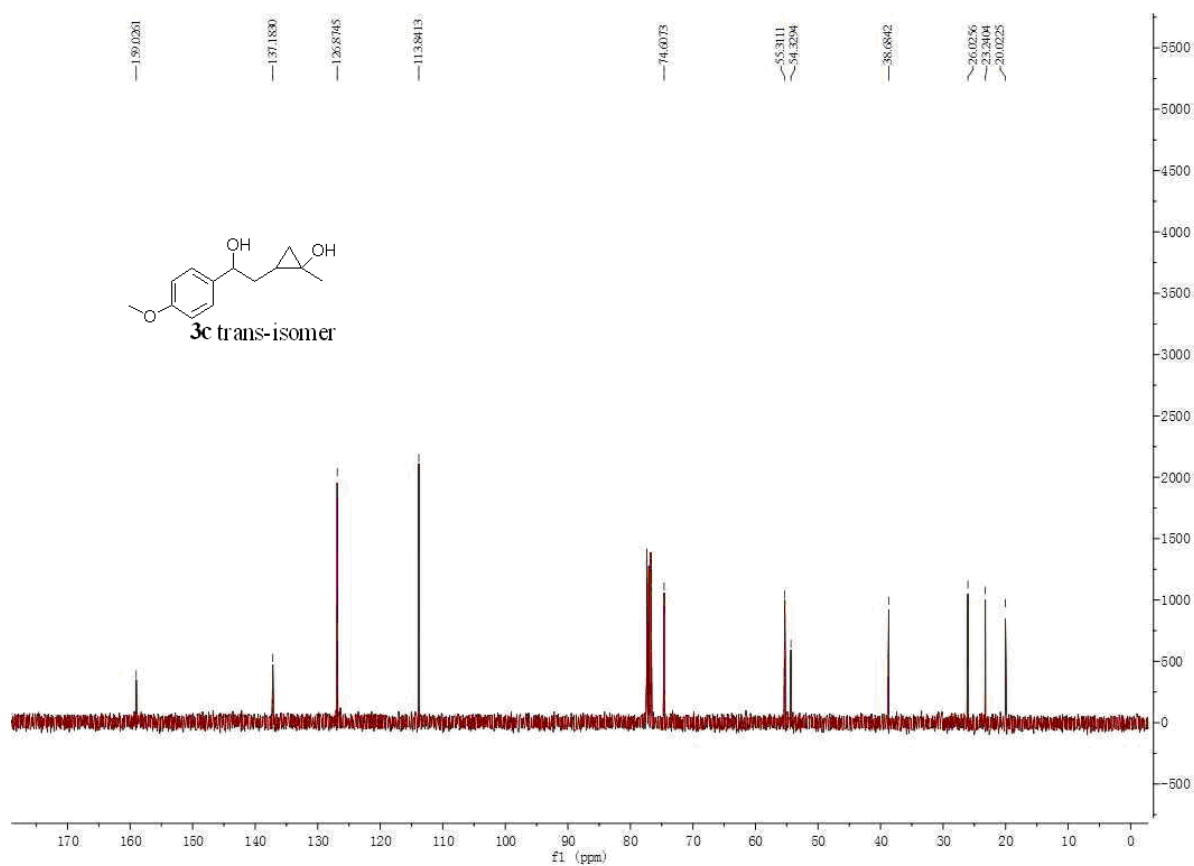
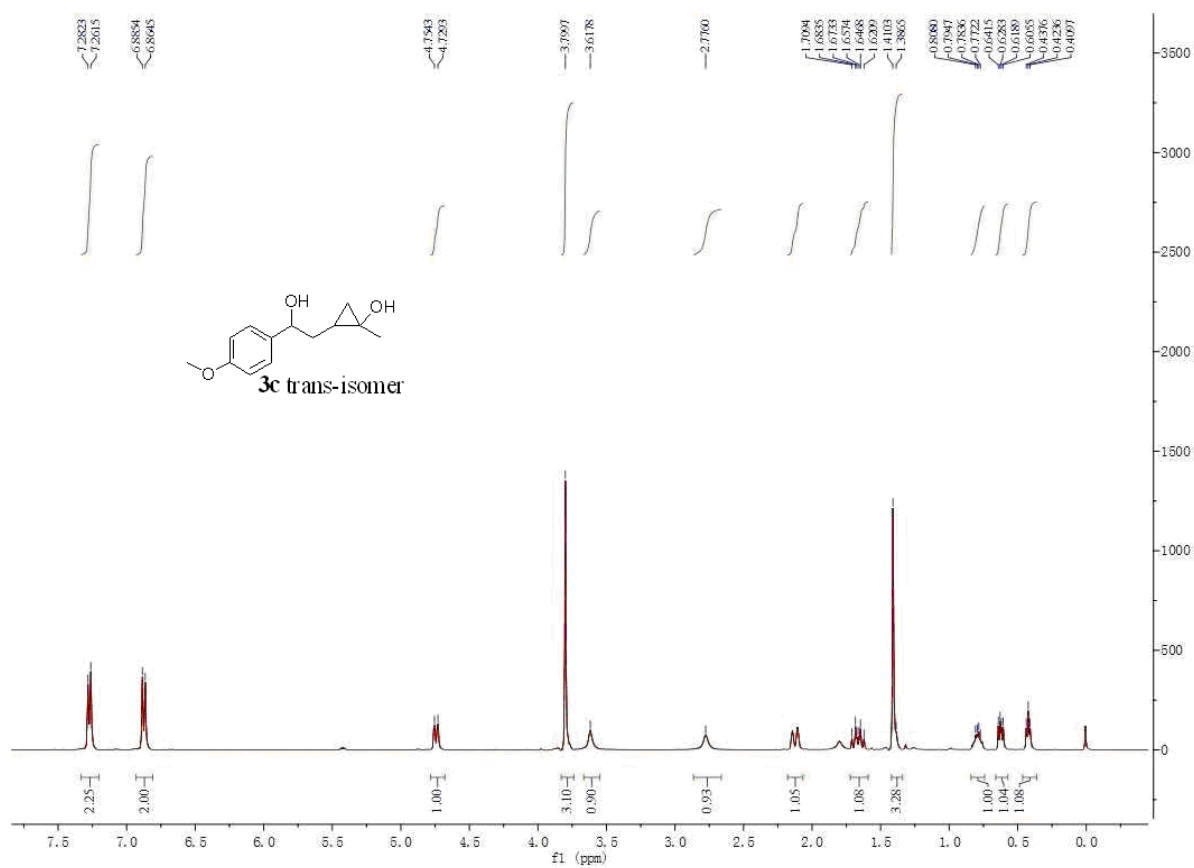
7. Spectra for the Compounds.

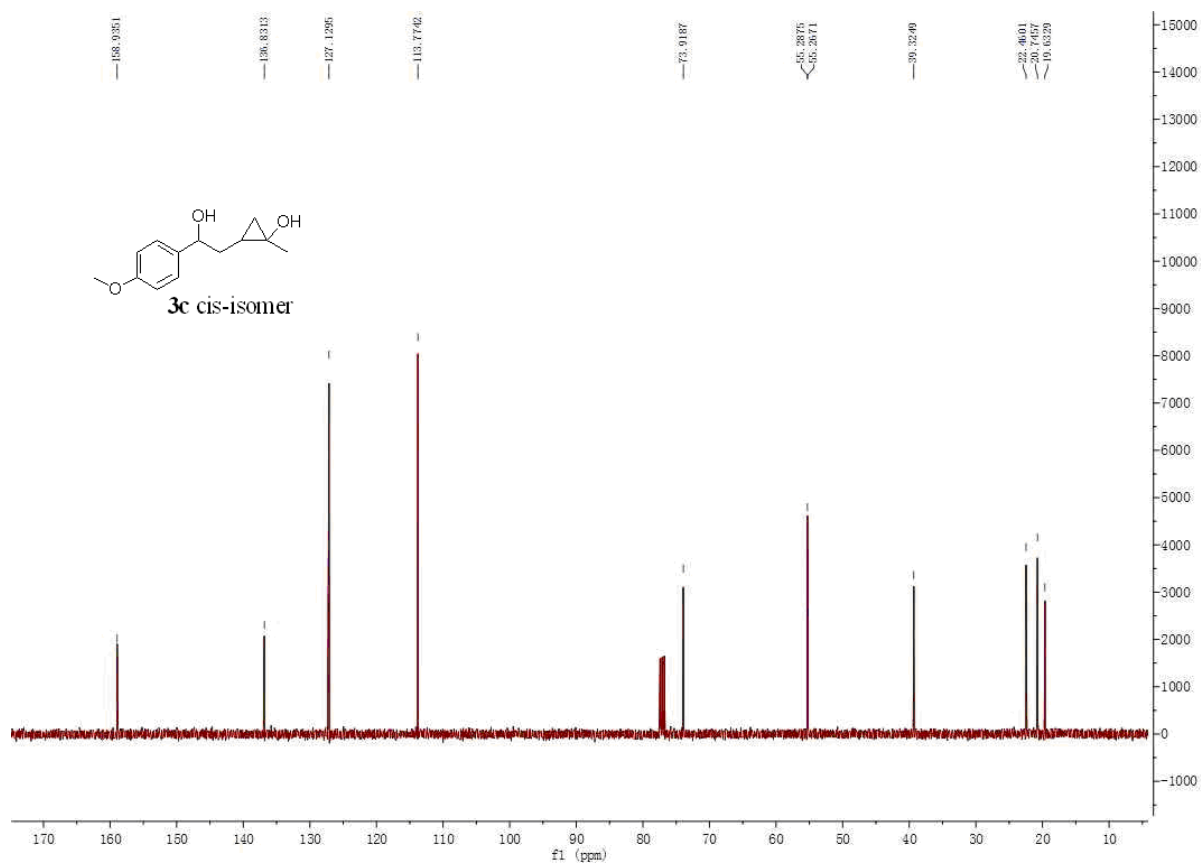
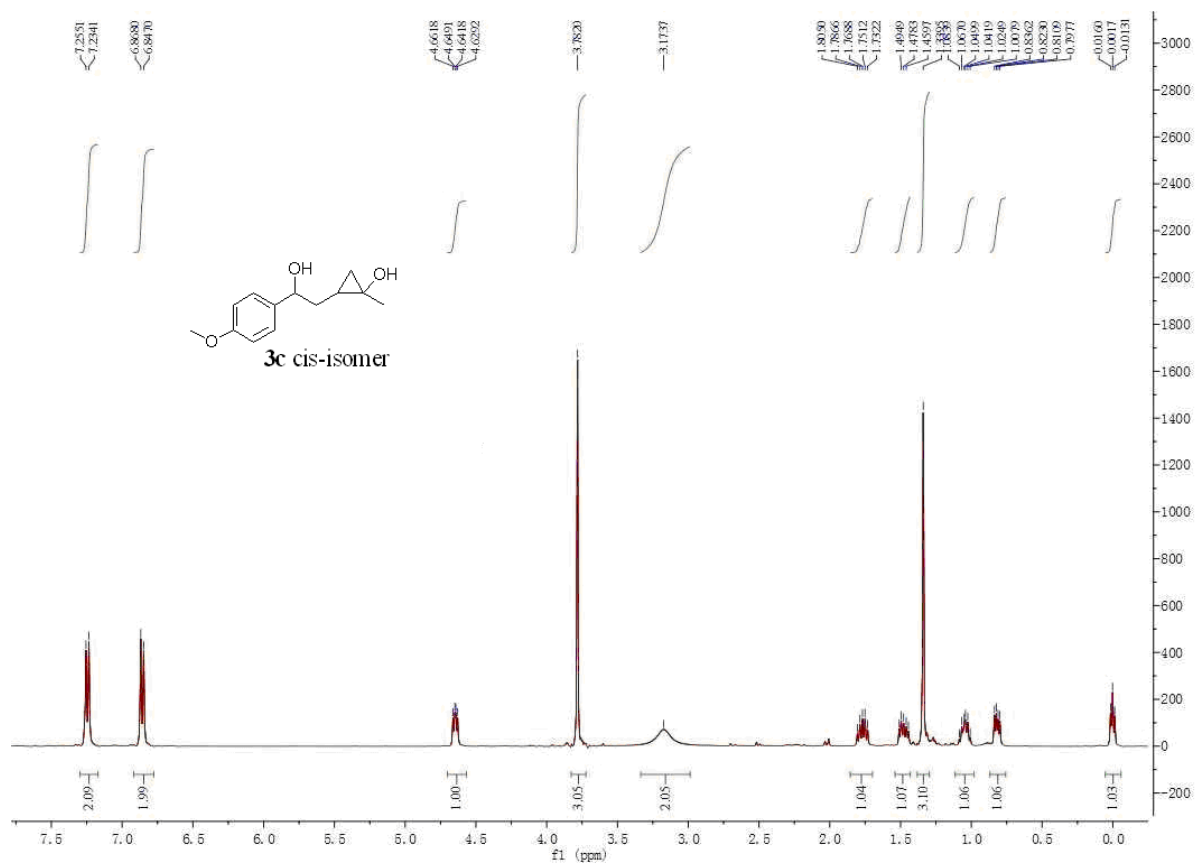


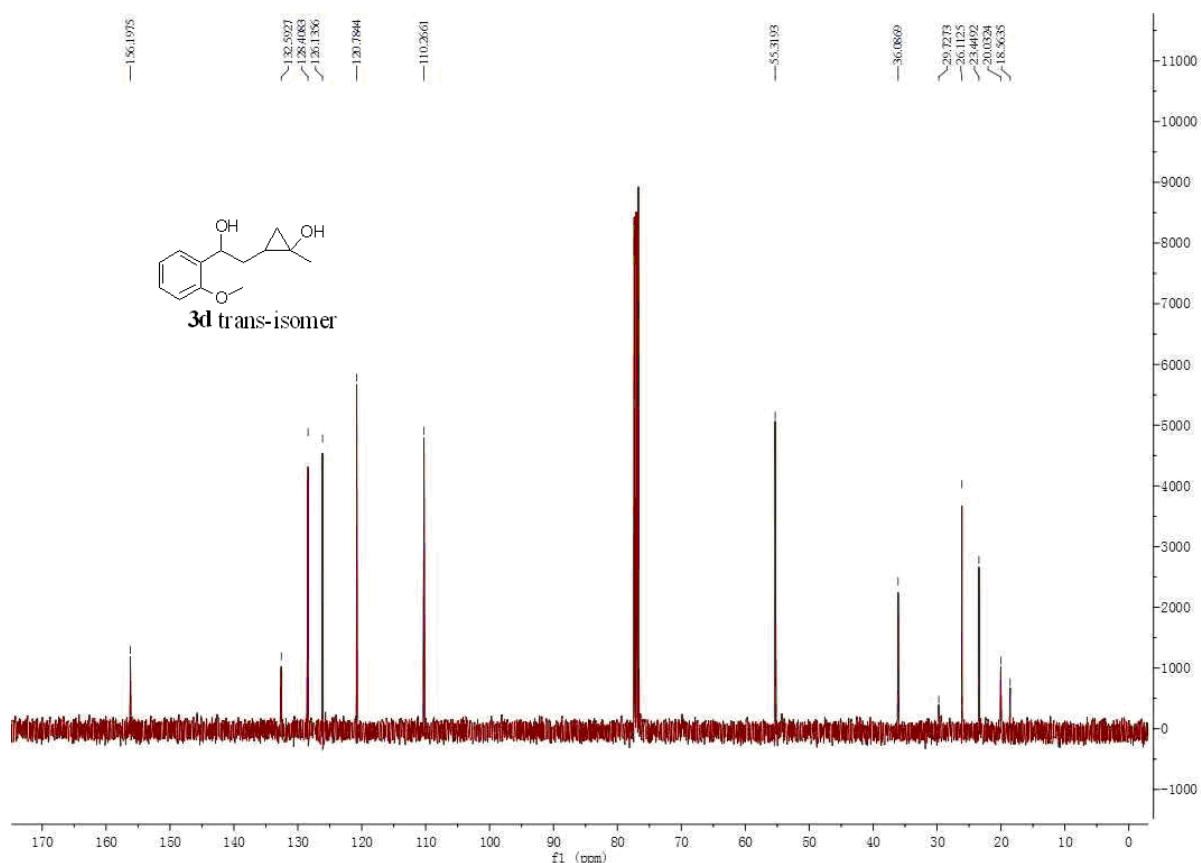
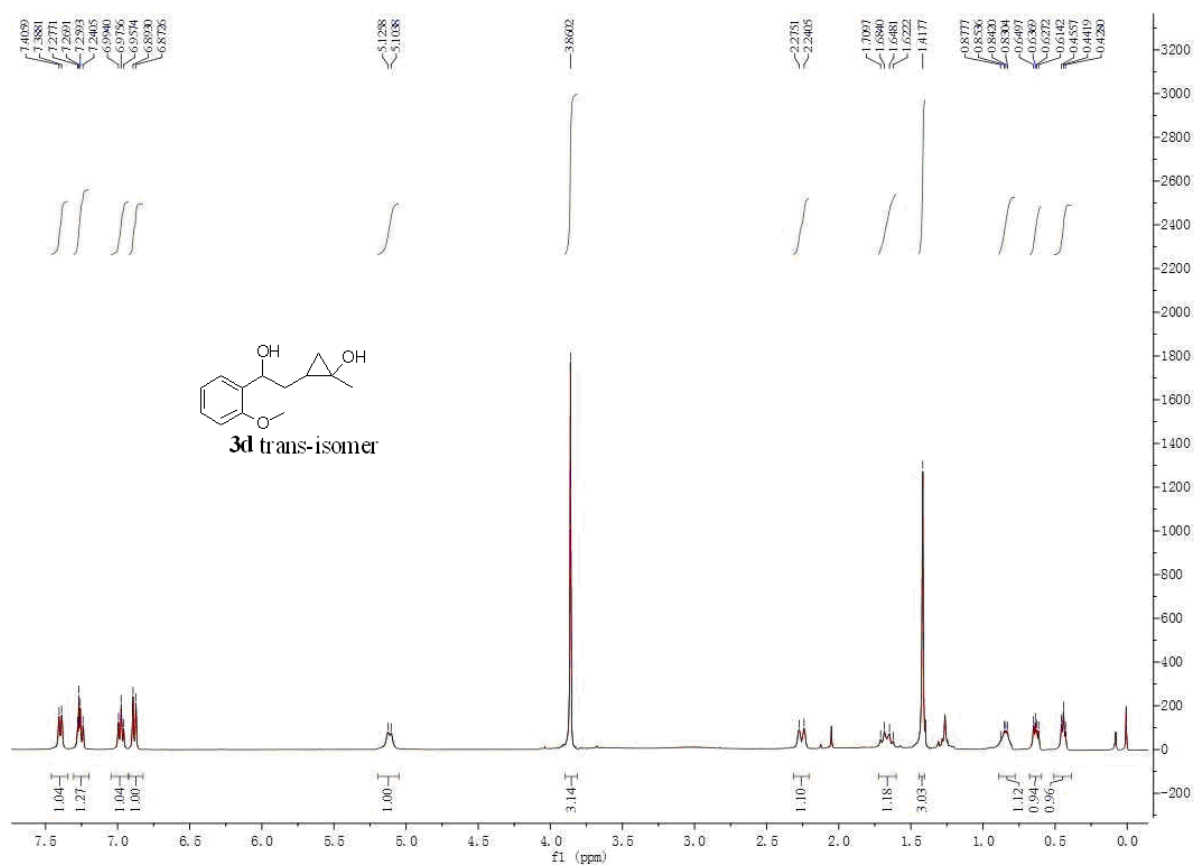


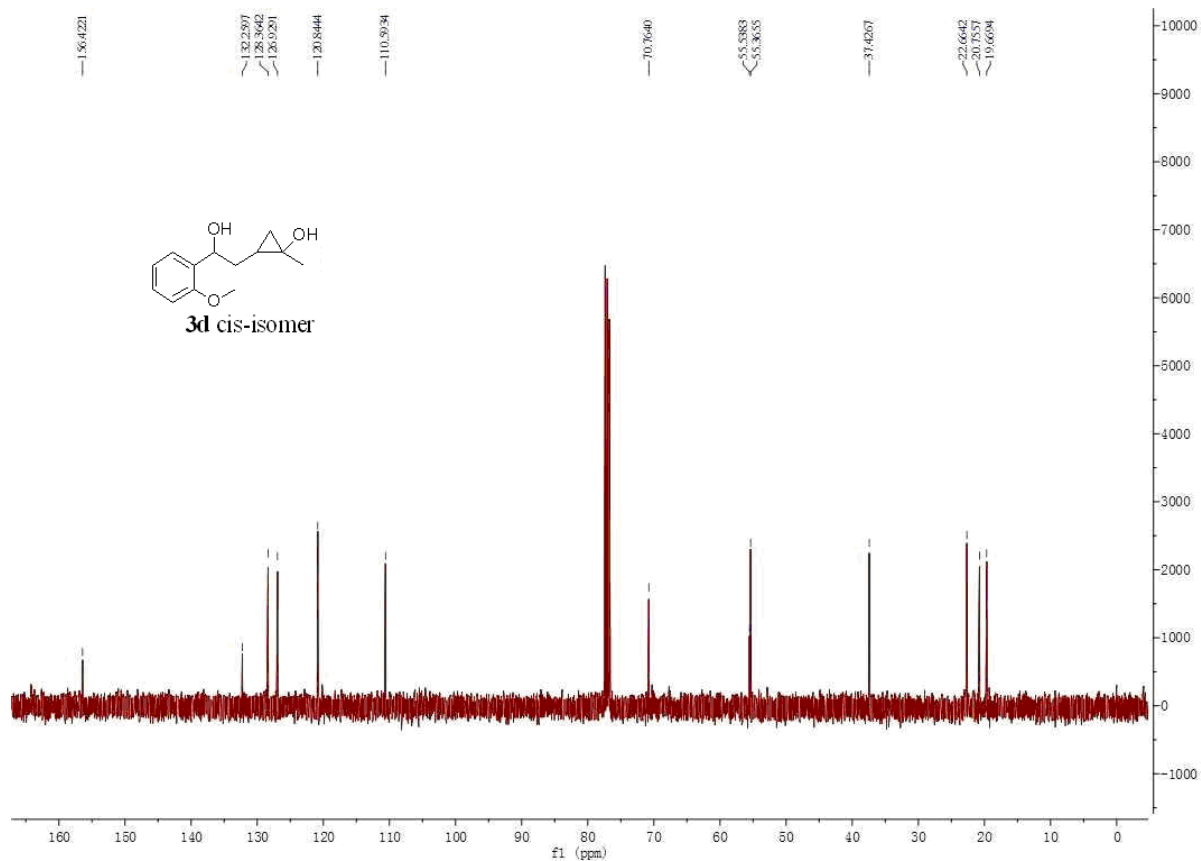
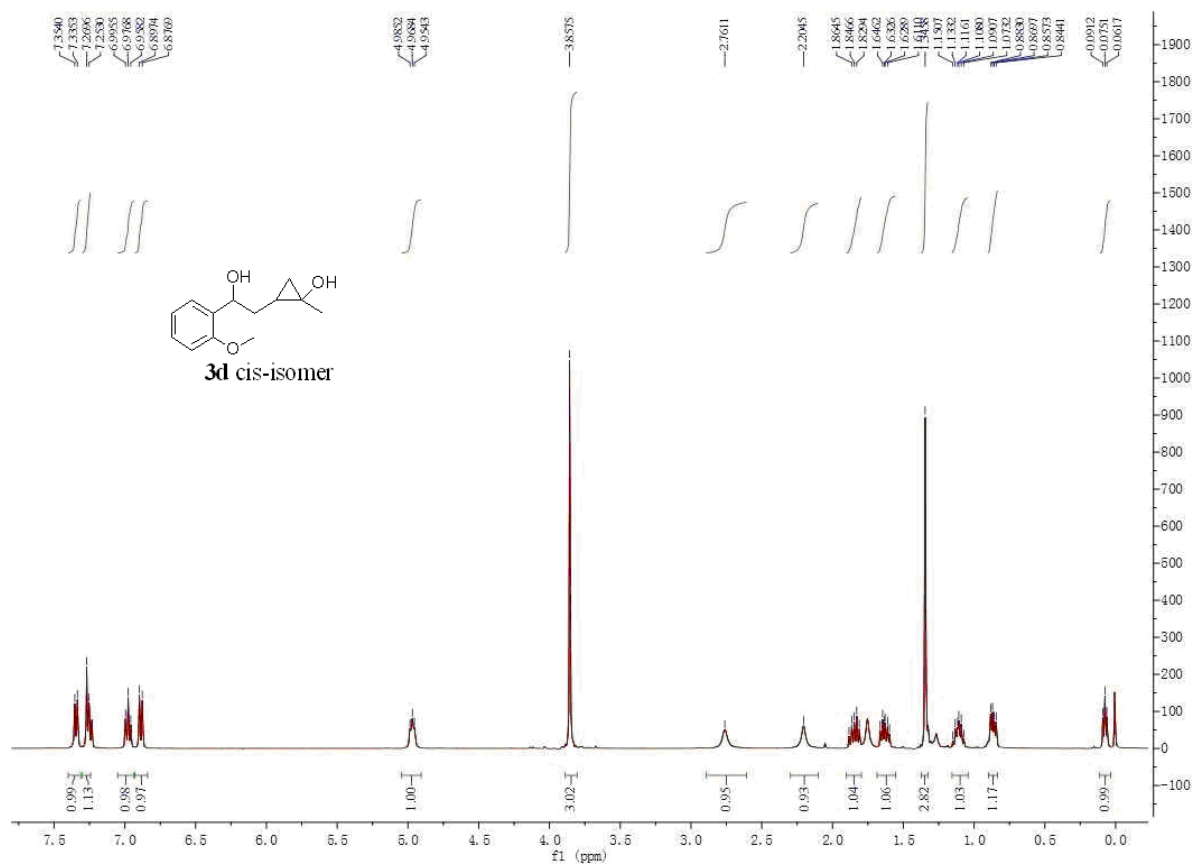


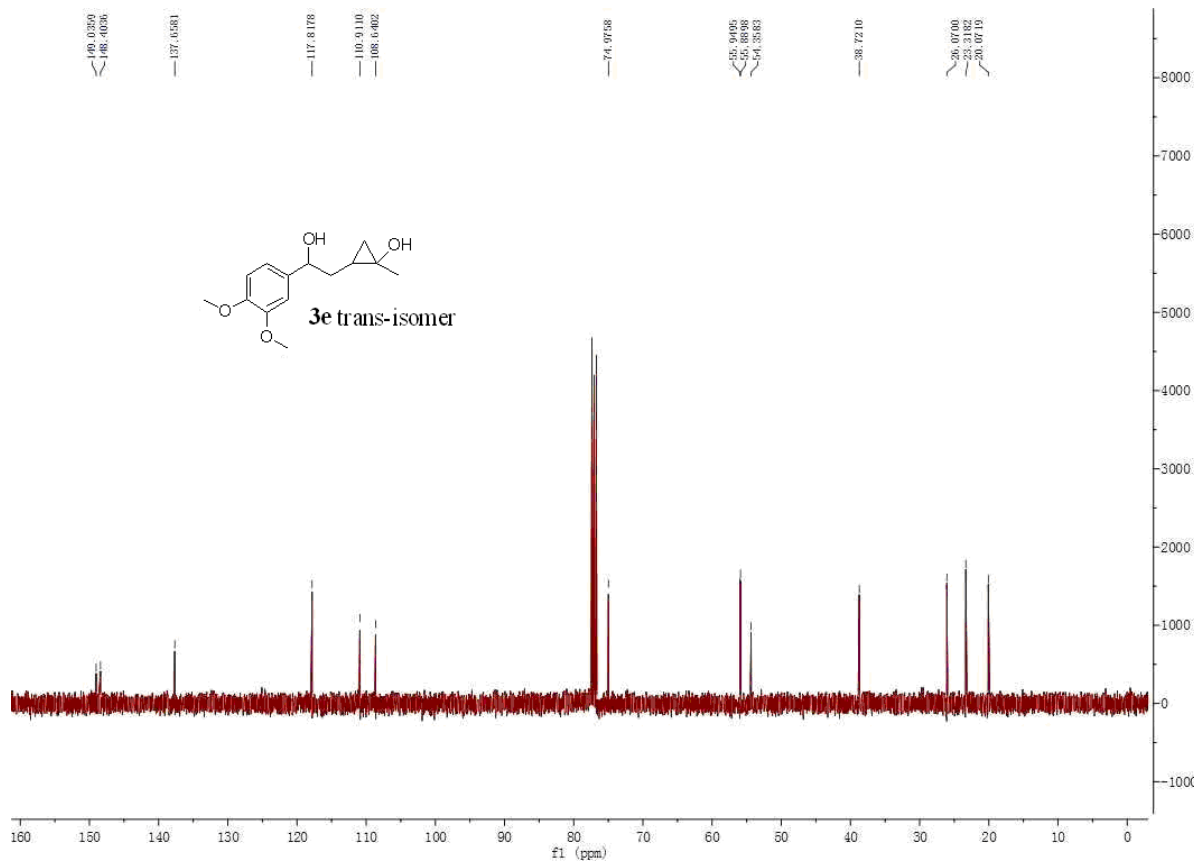
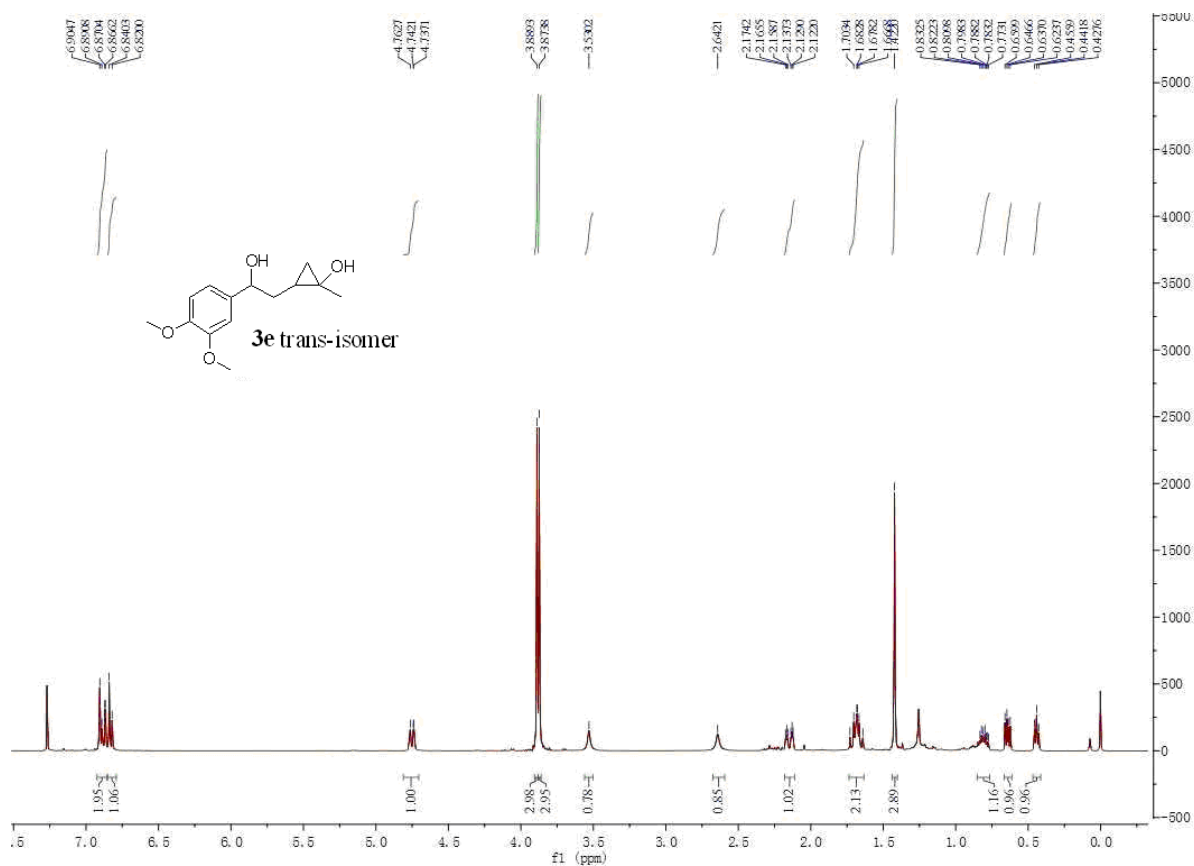


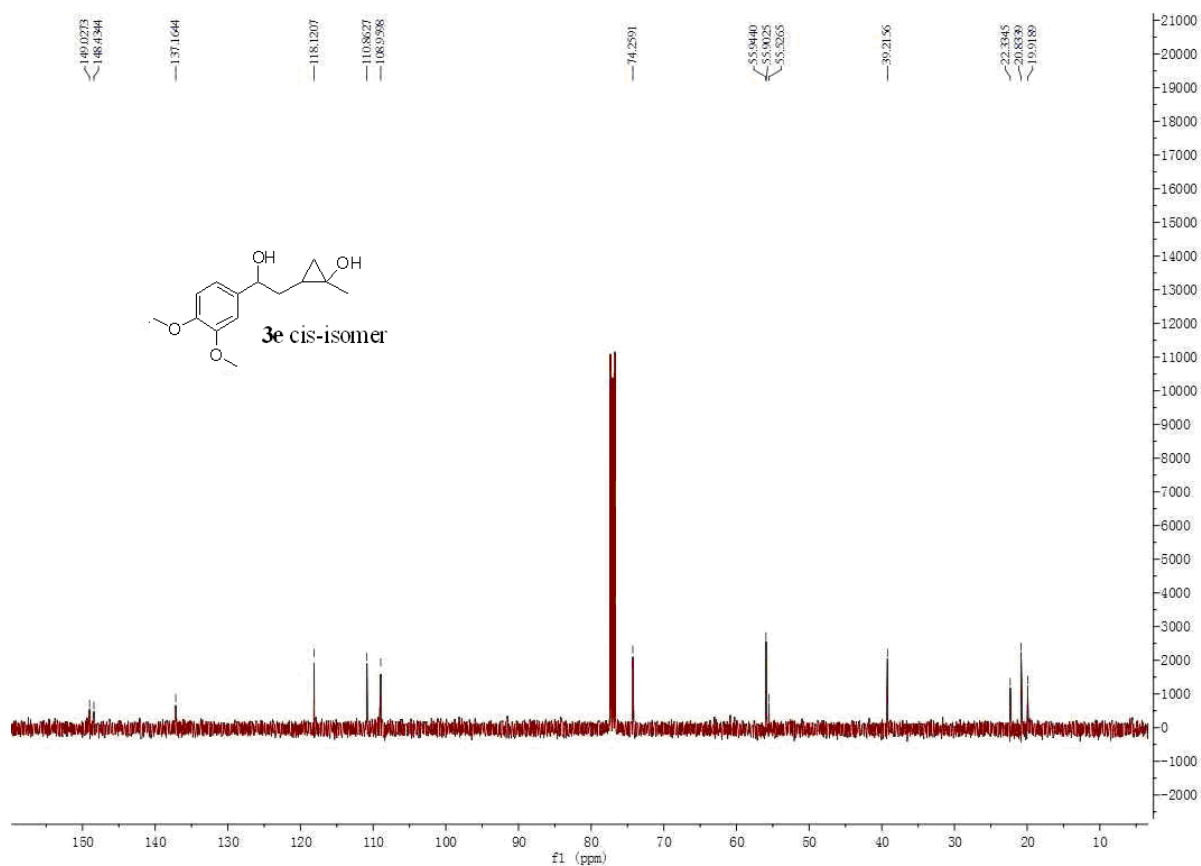
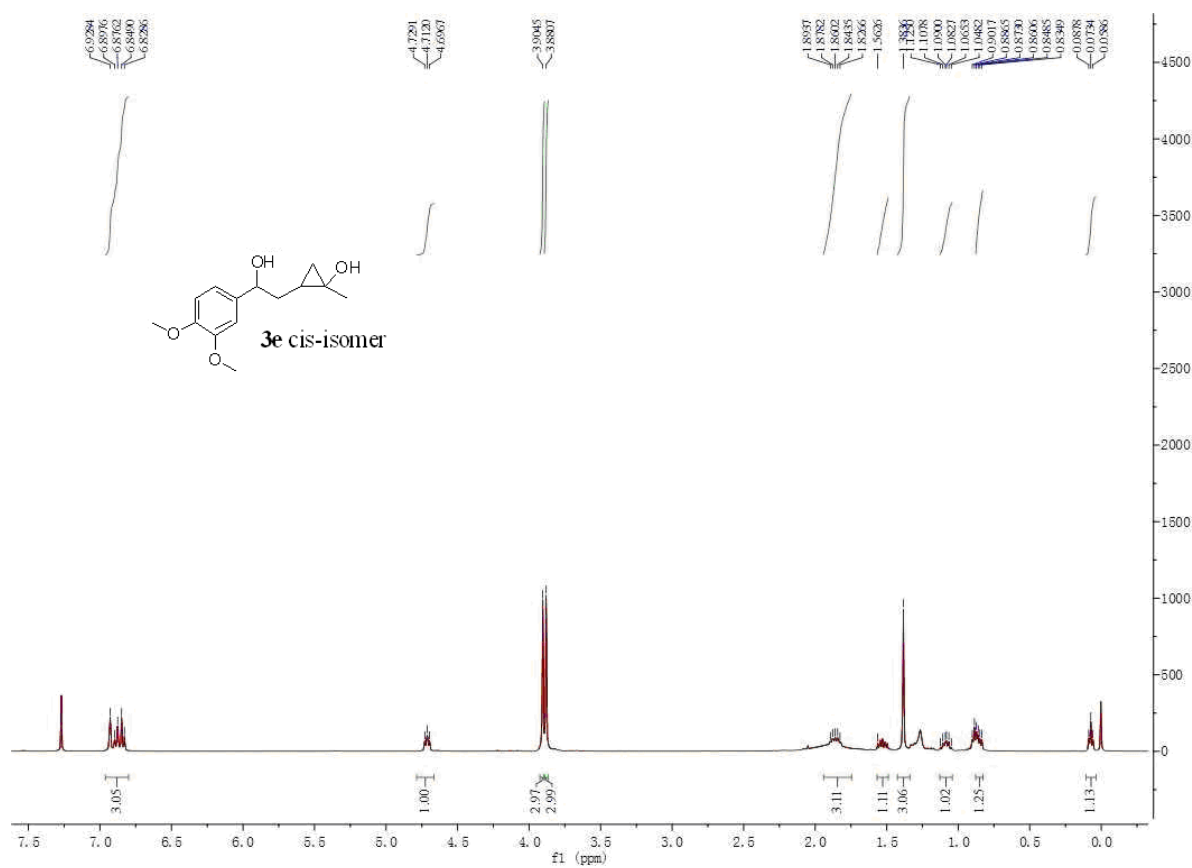


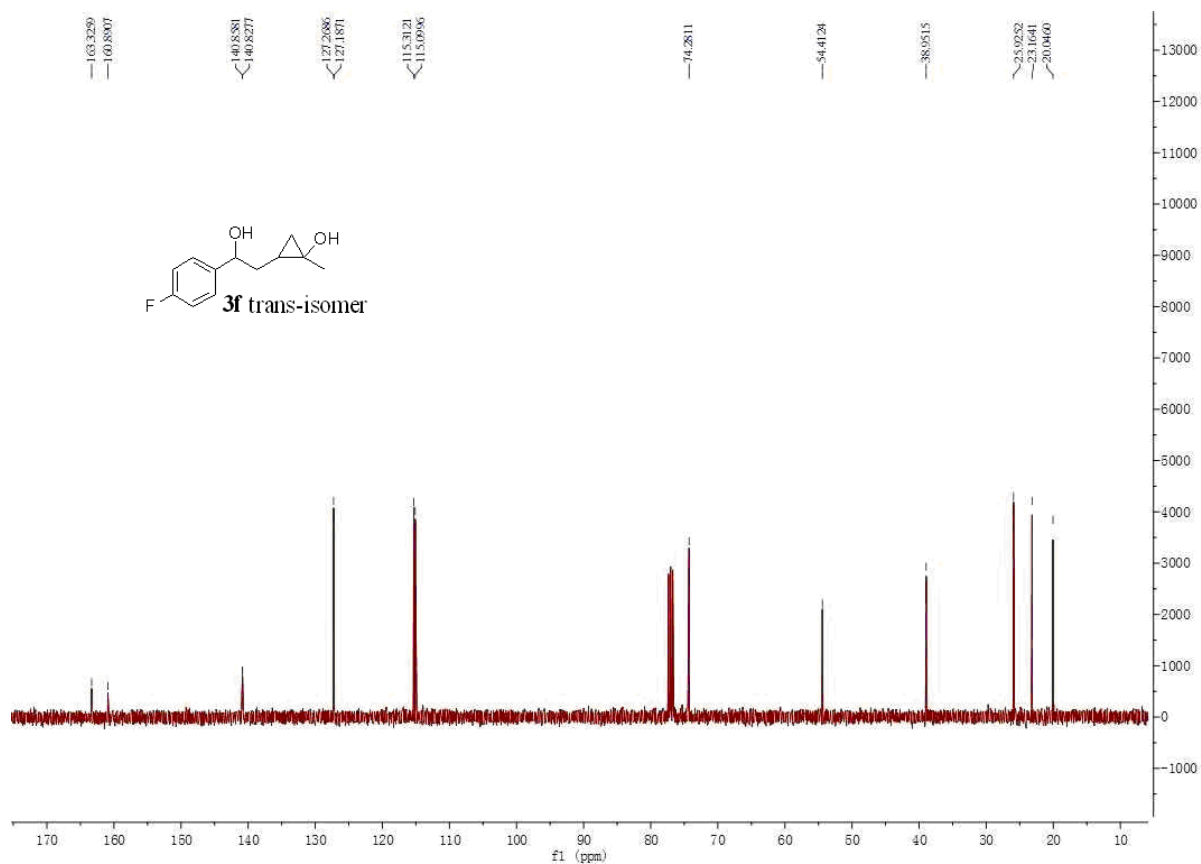
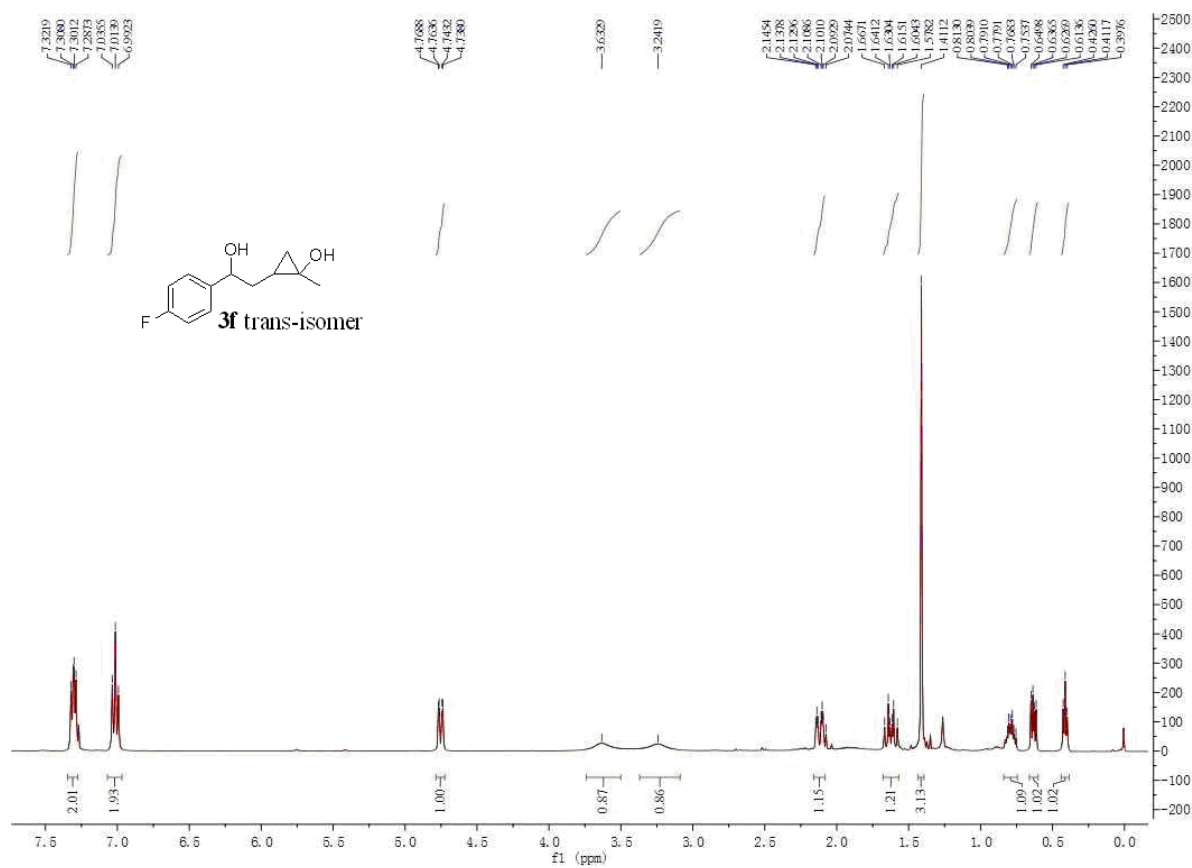


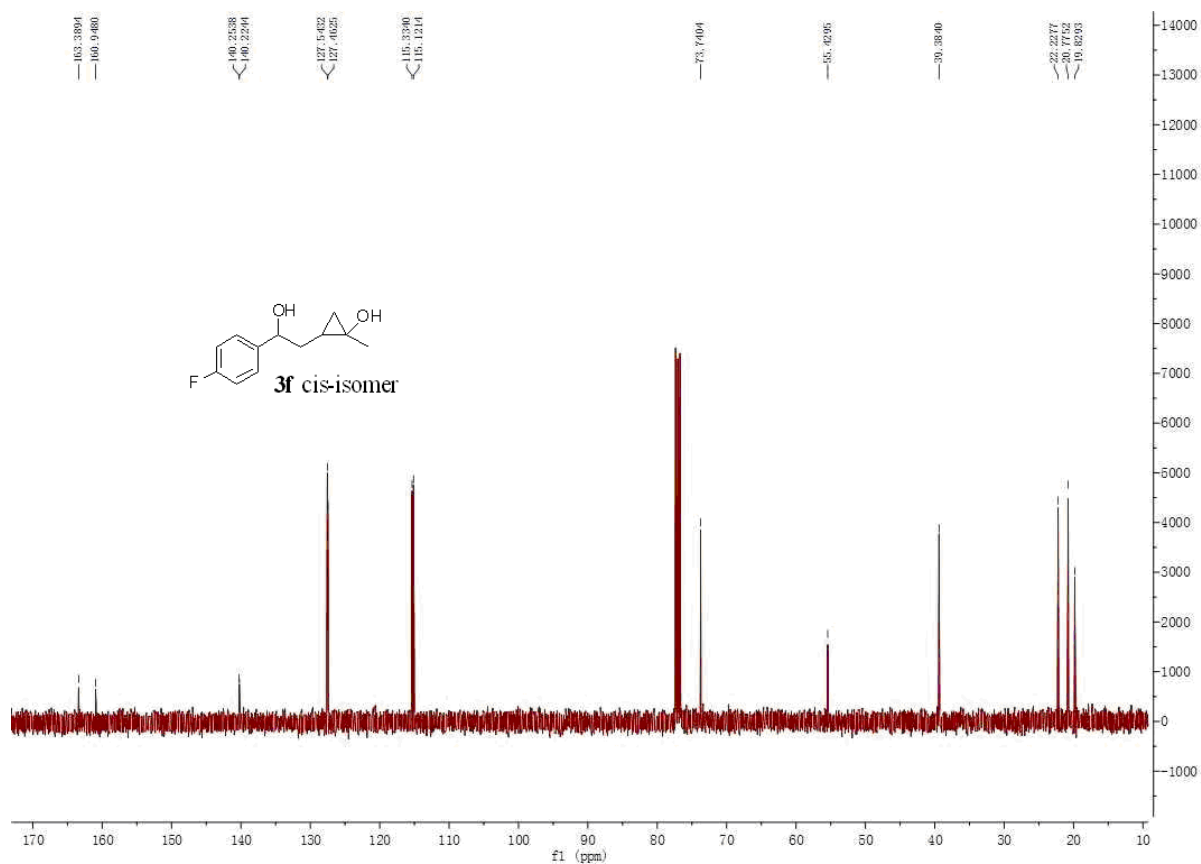
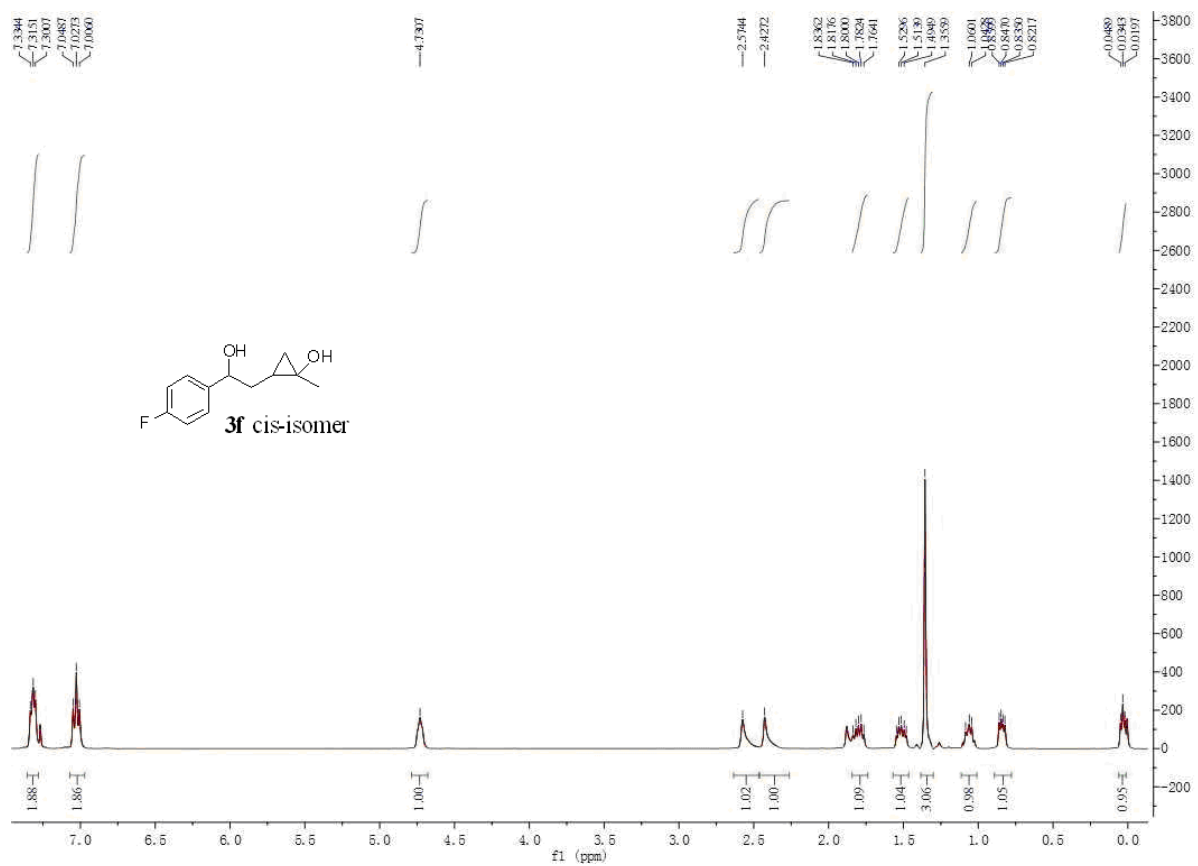


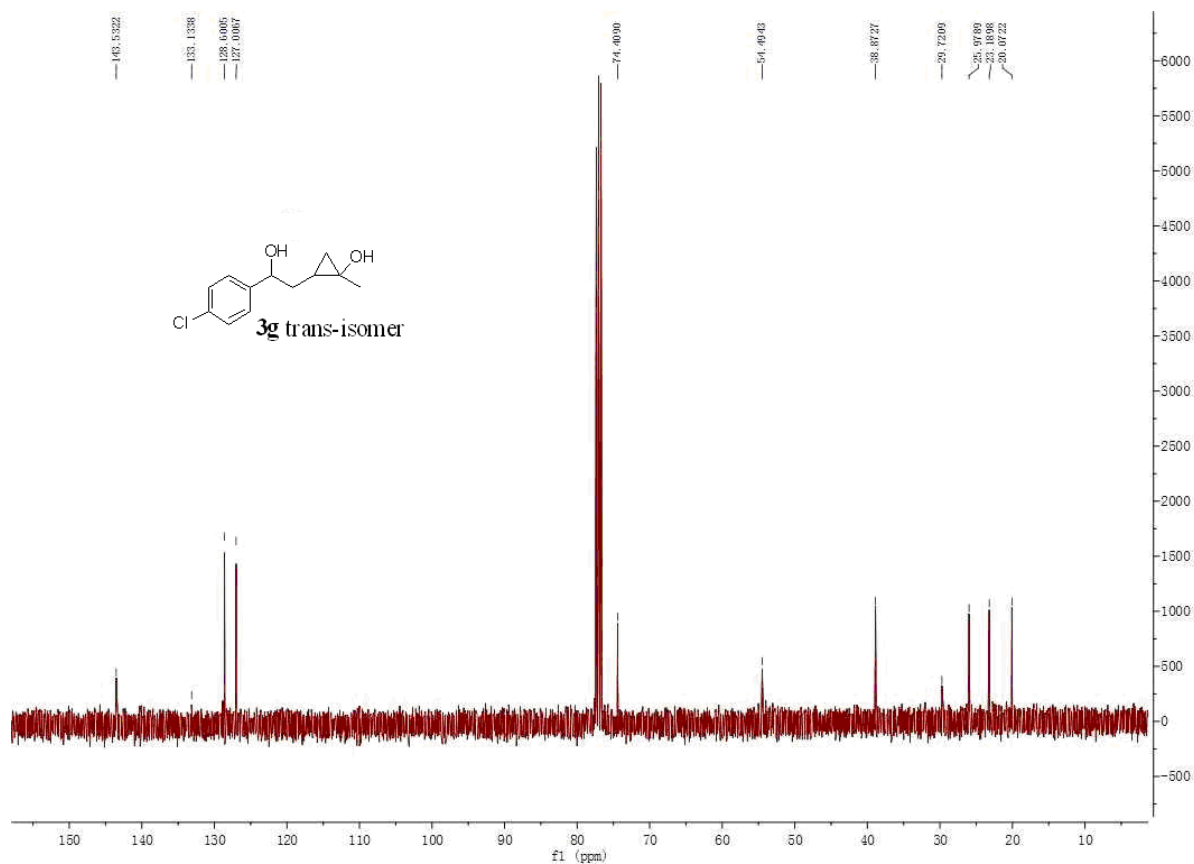
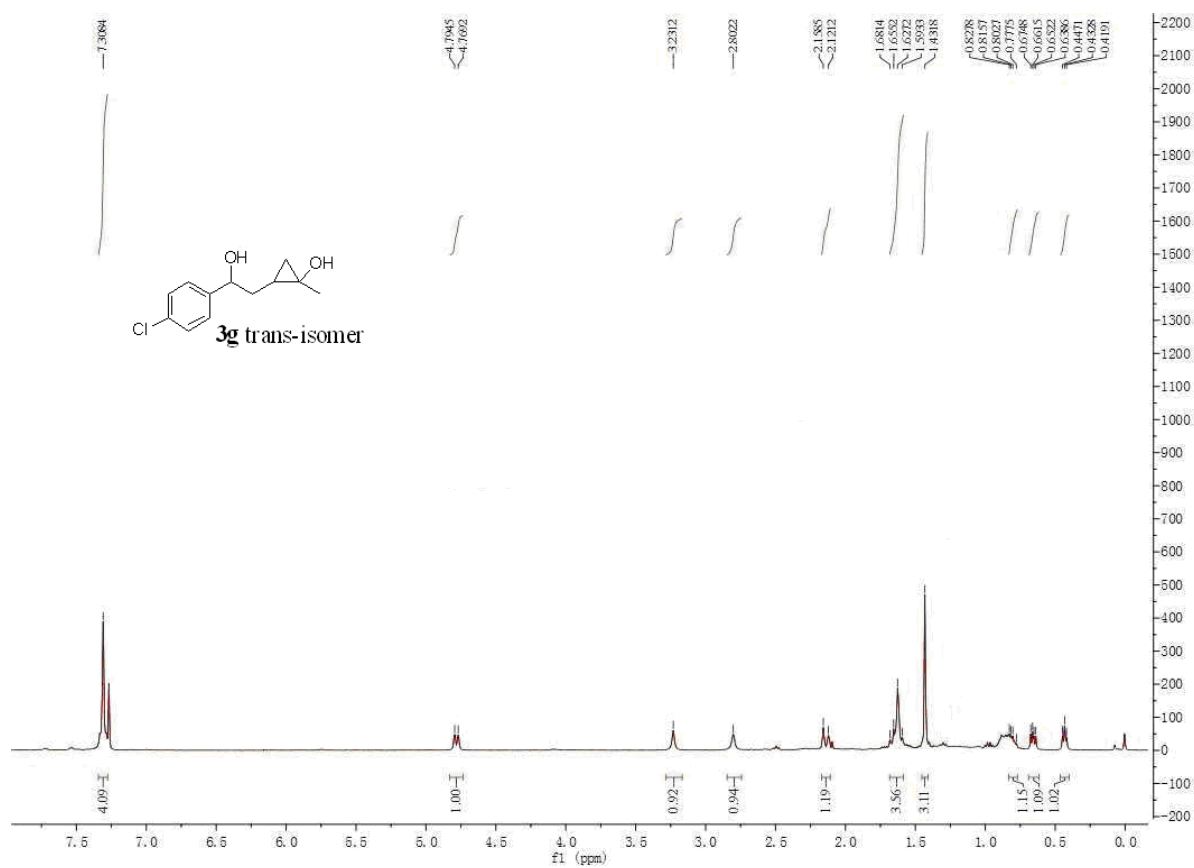


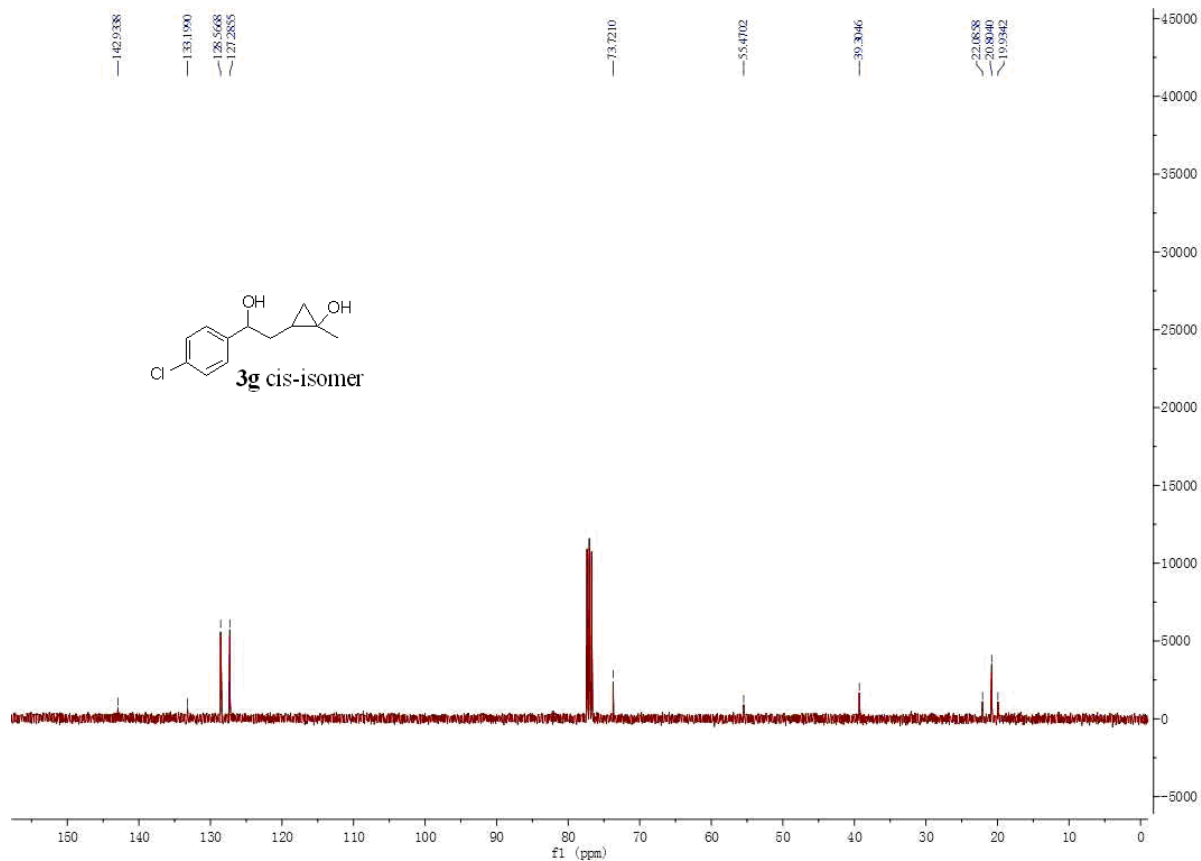
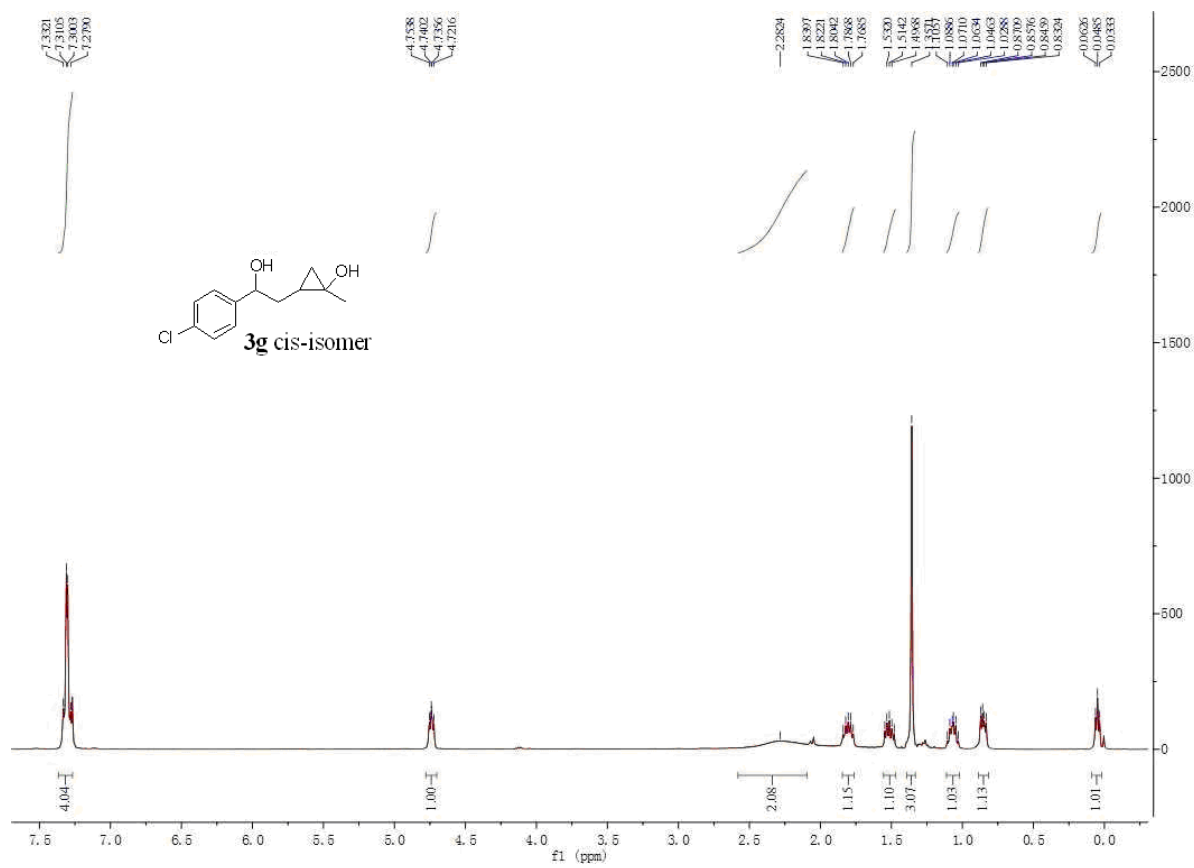


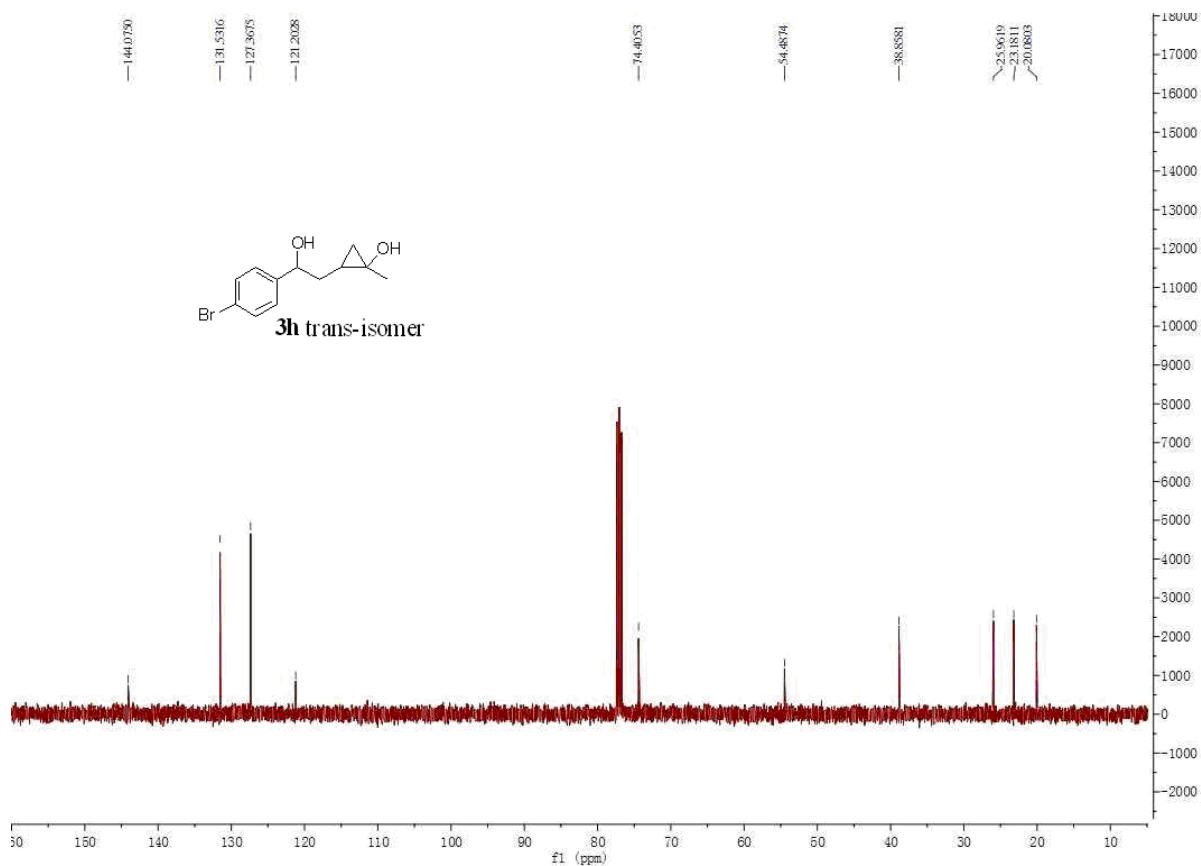
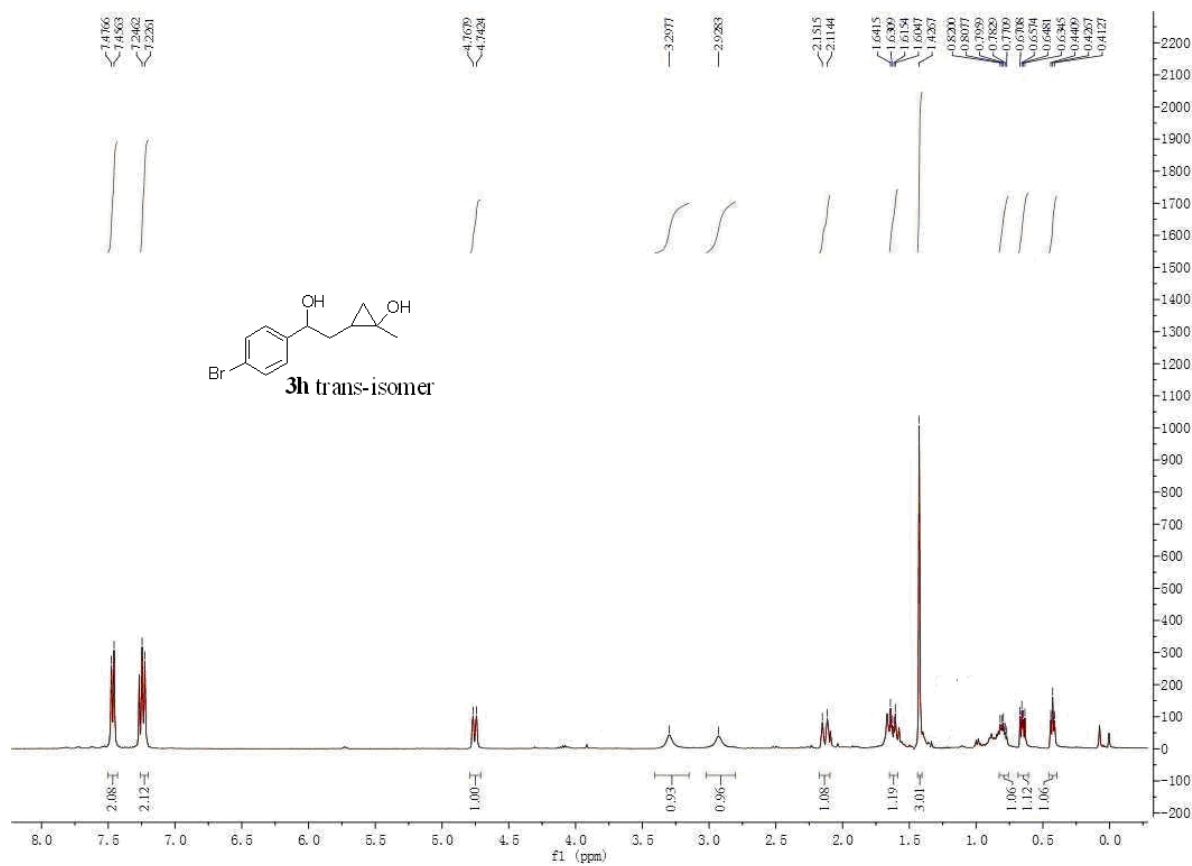


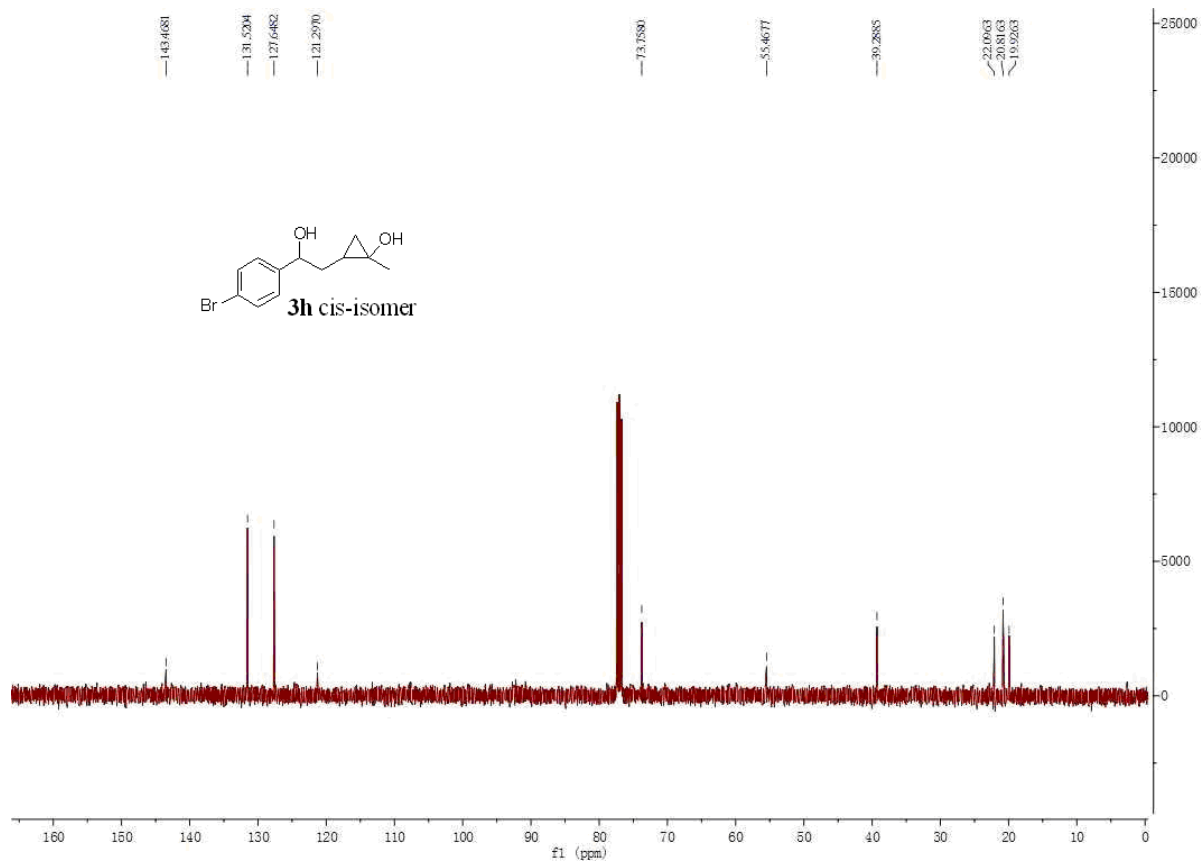
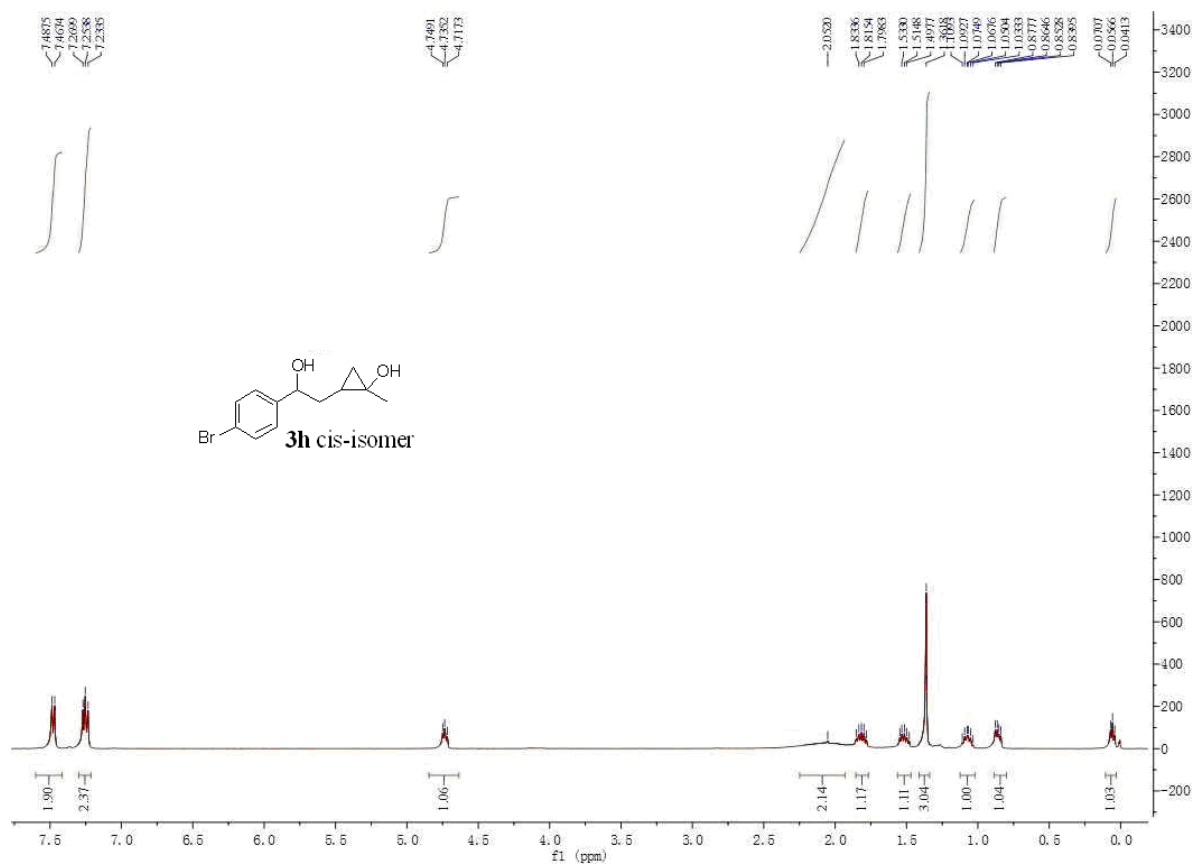


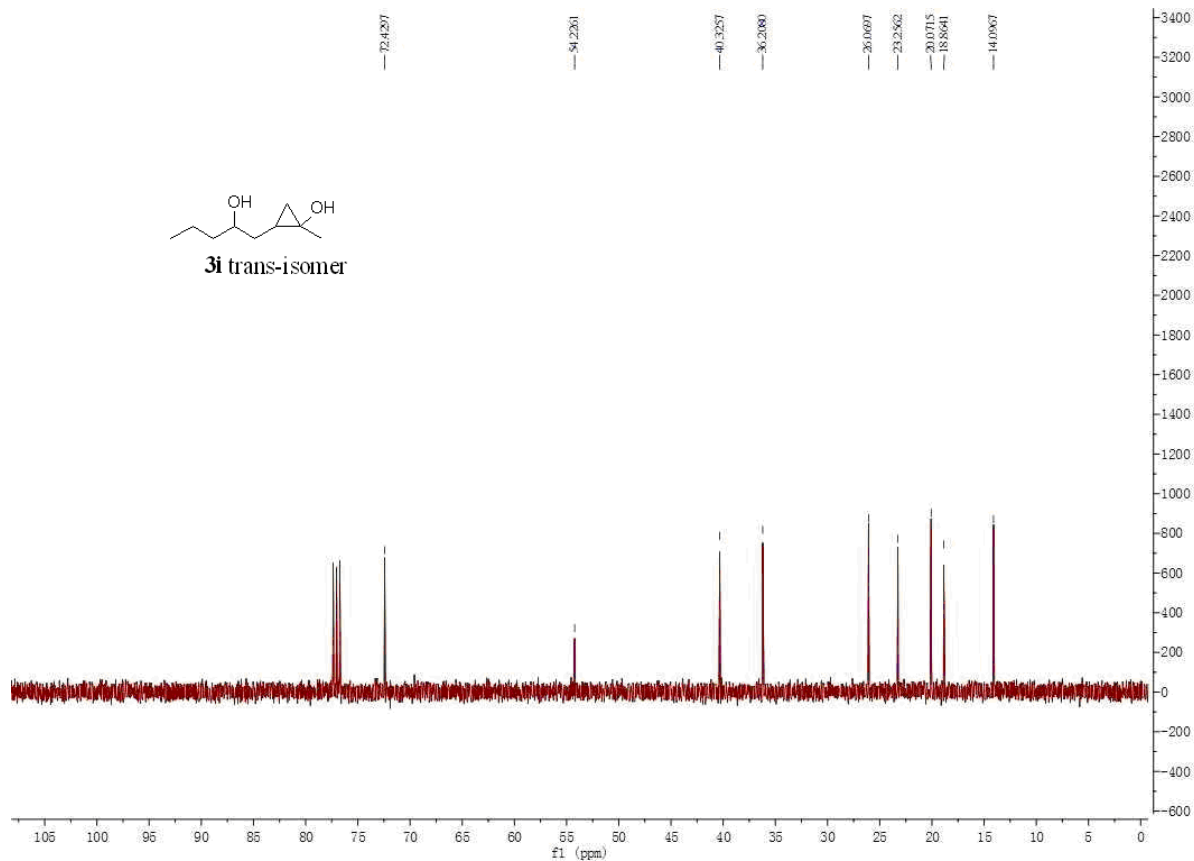
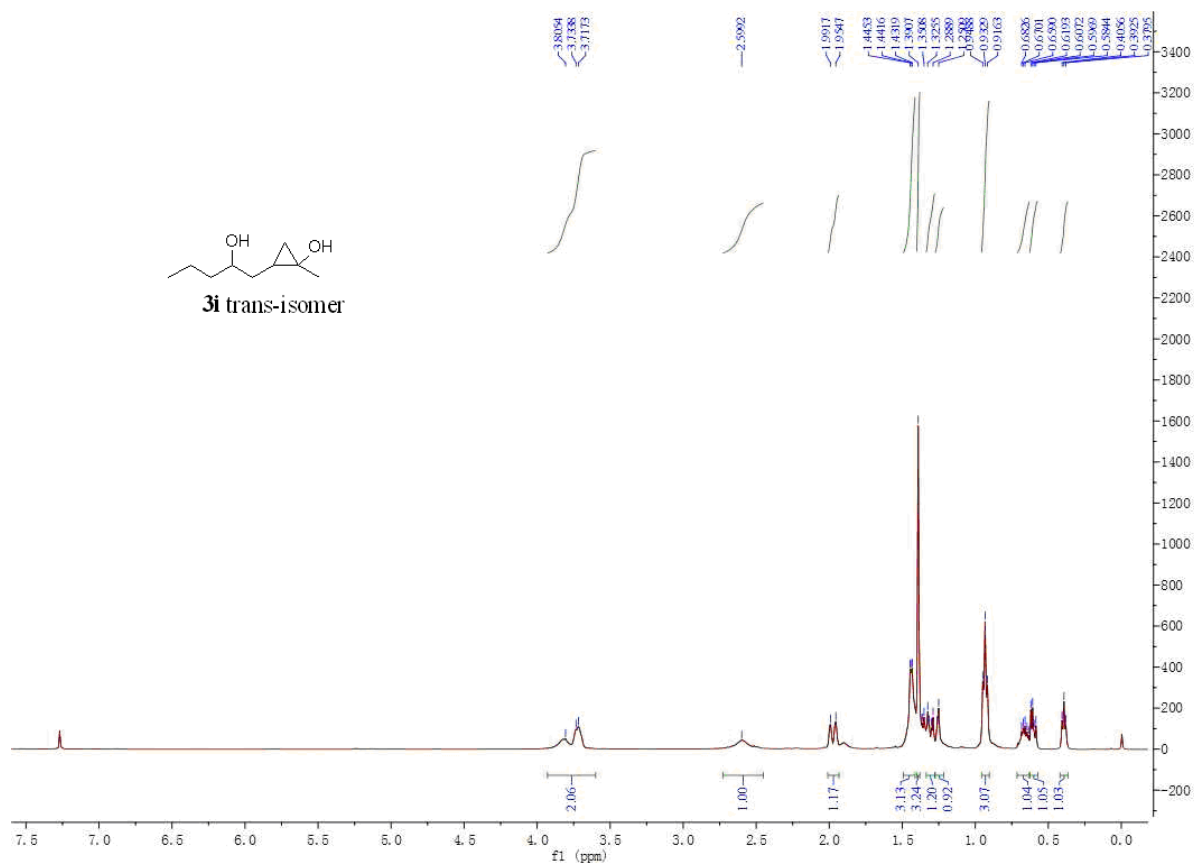


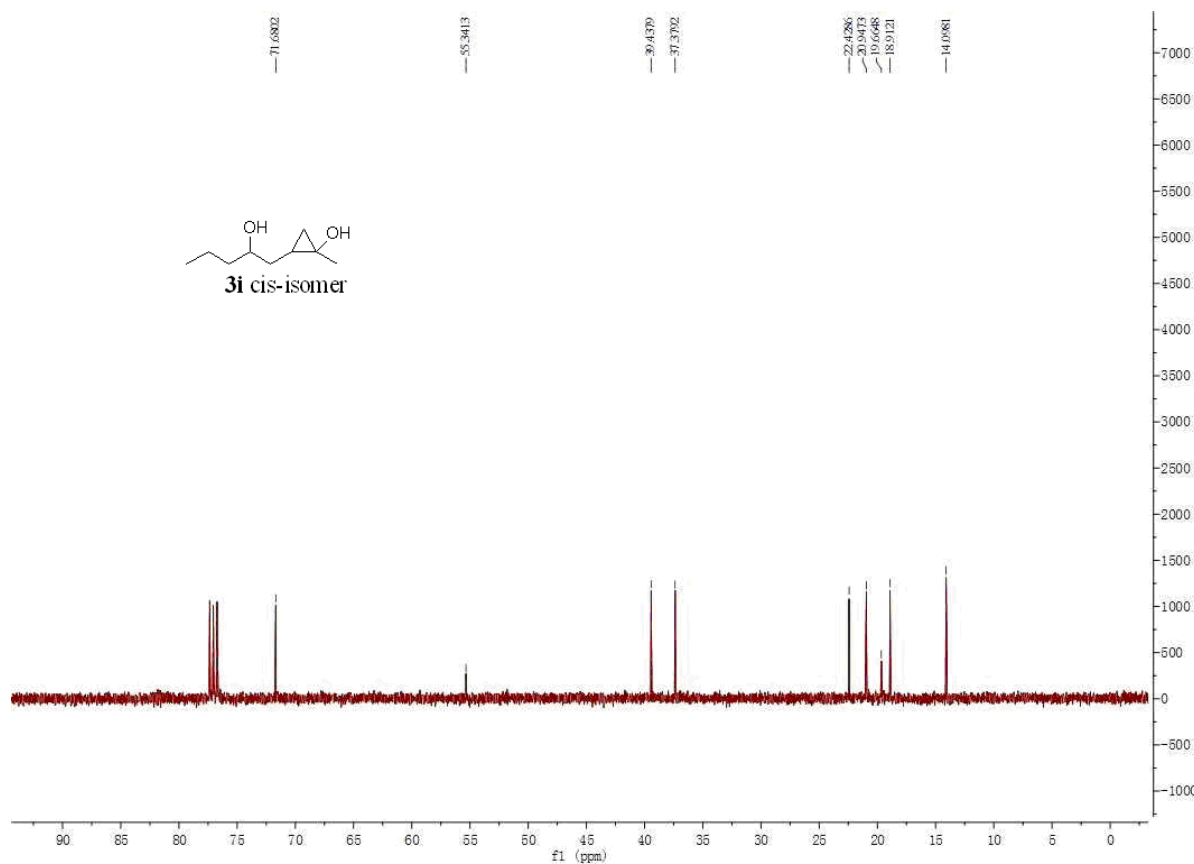
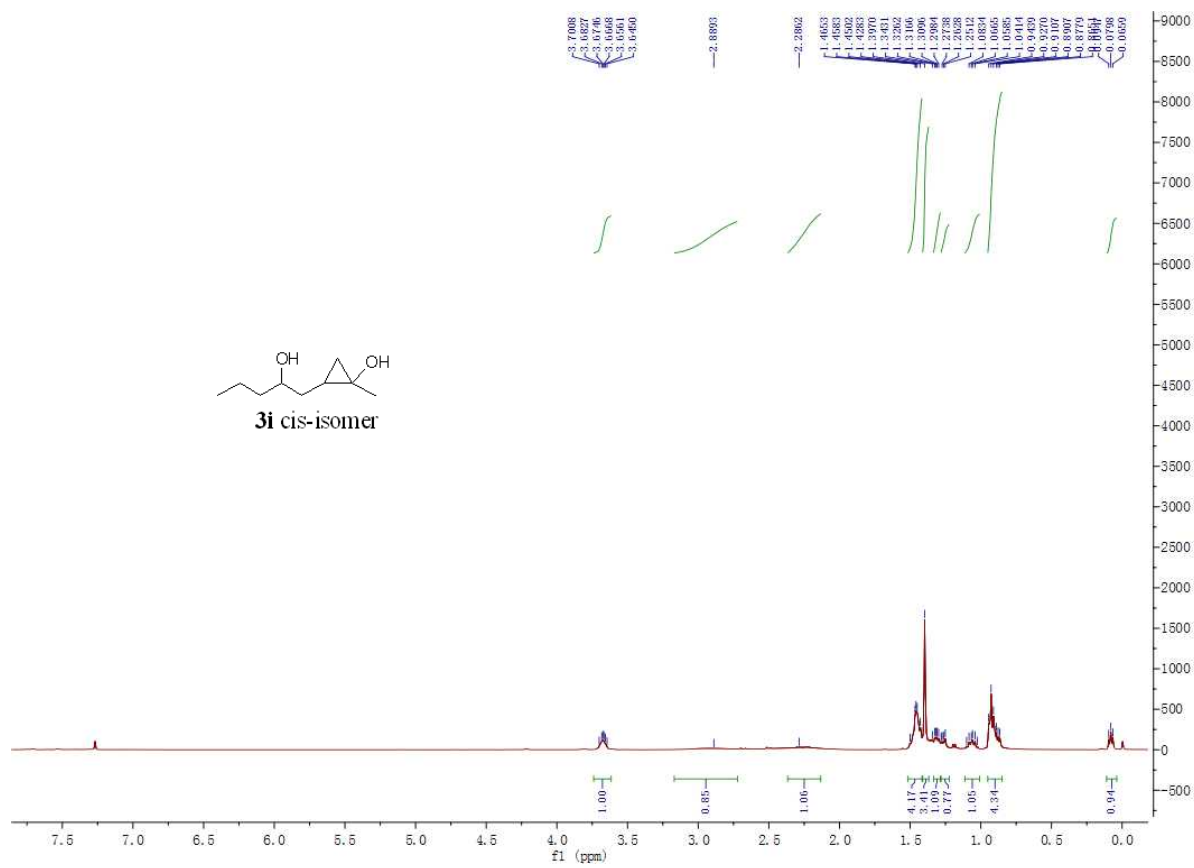


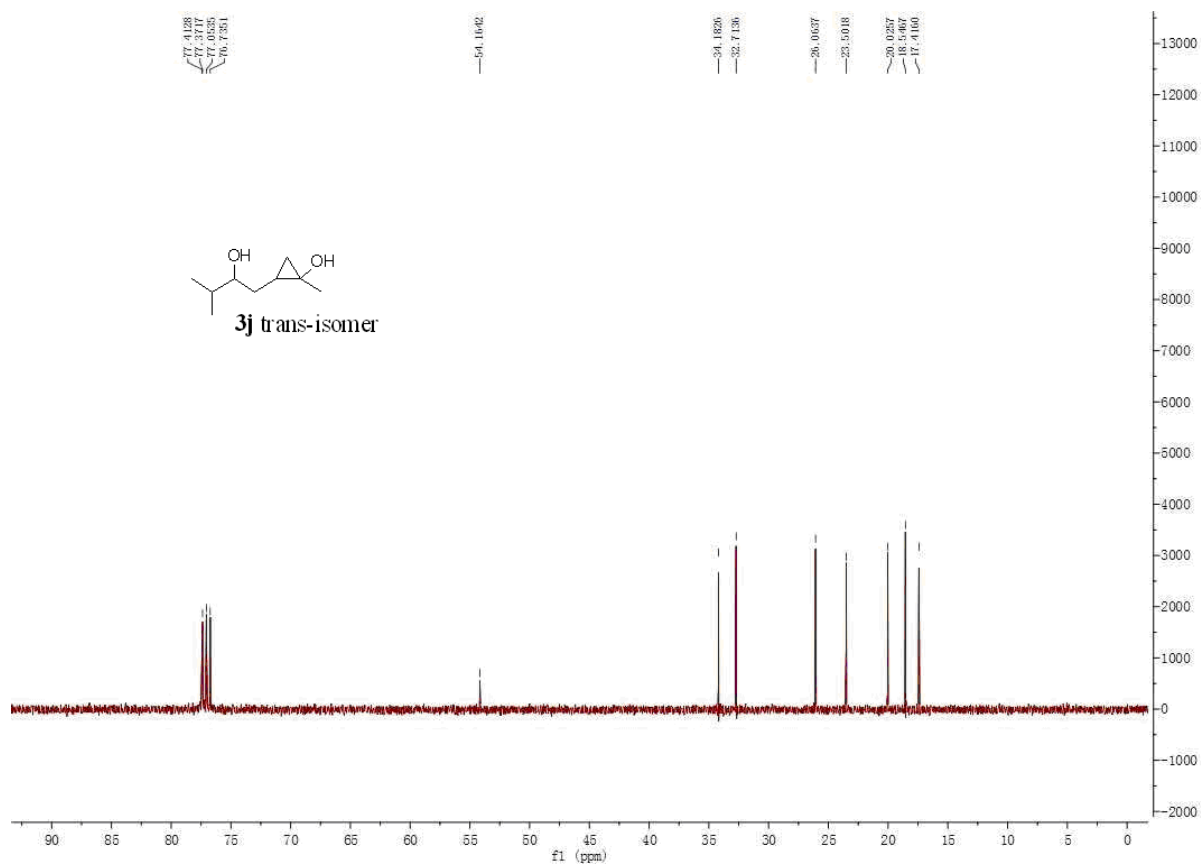
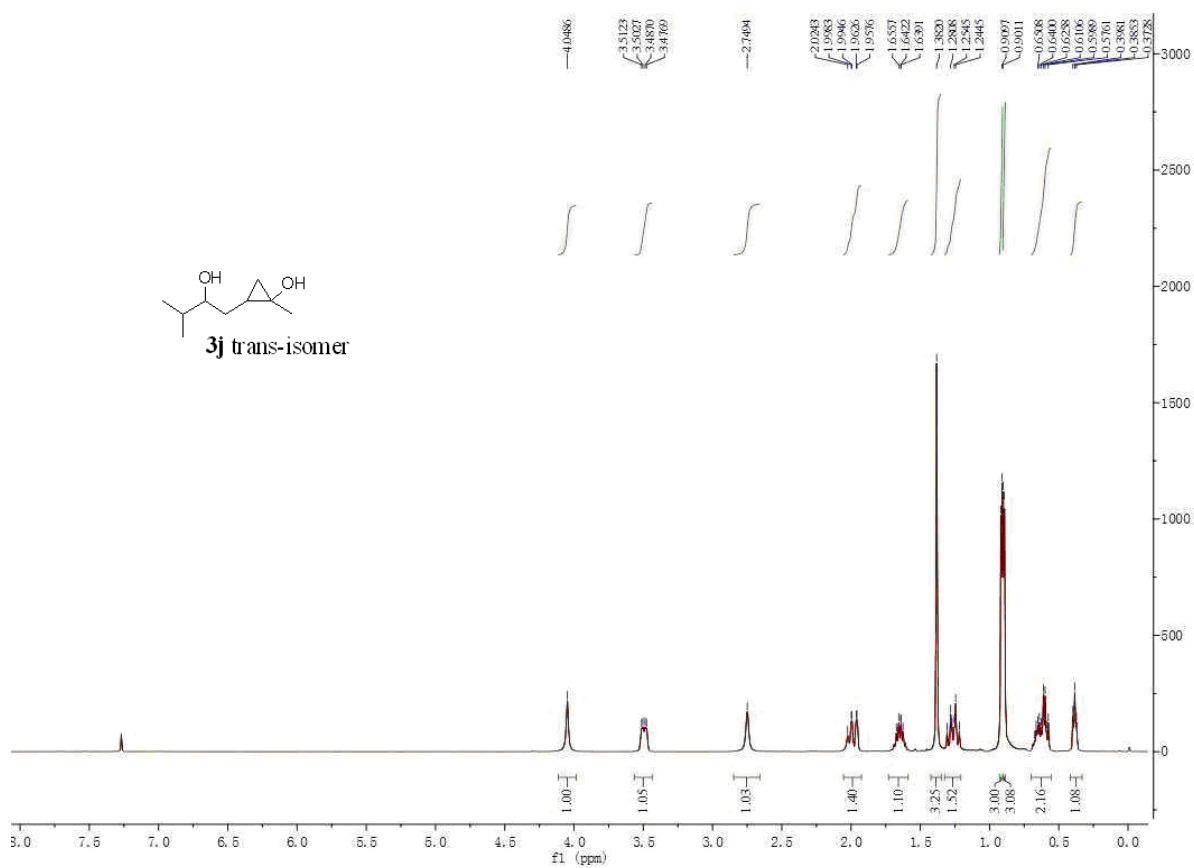


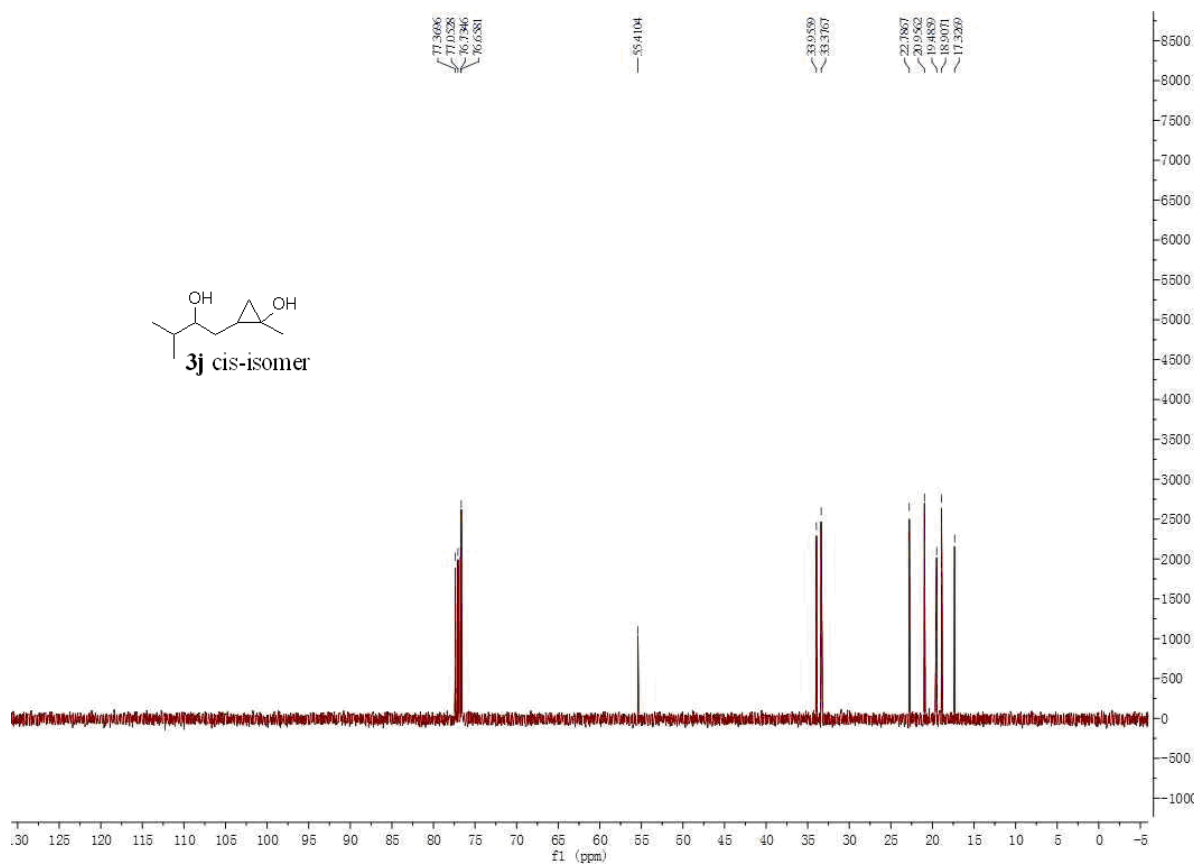
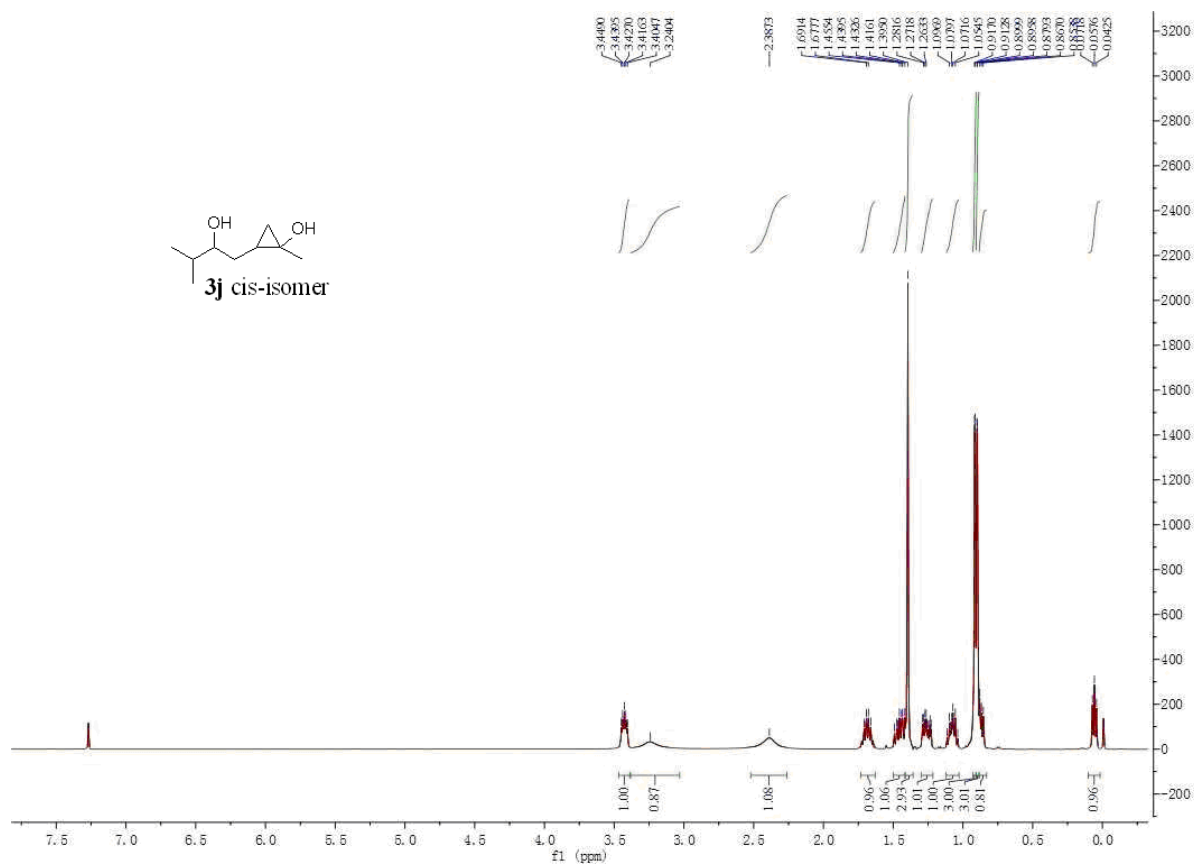


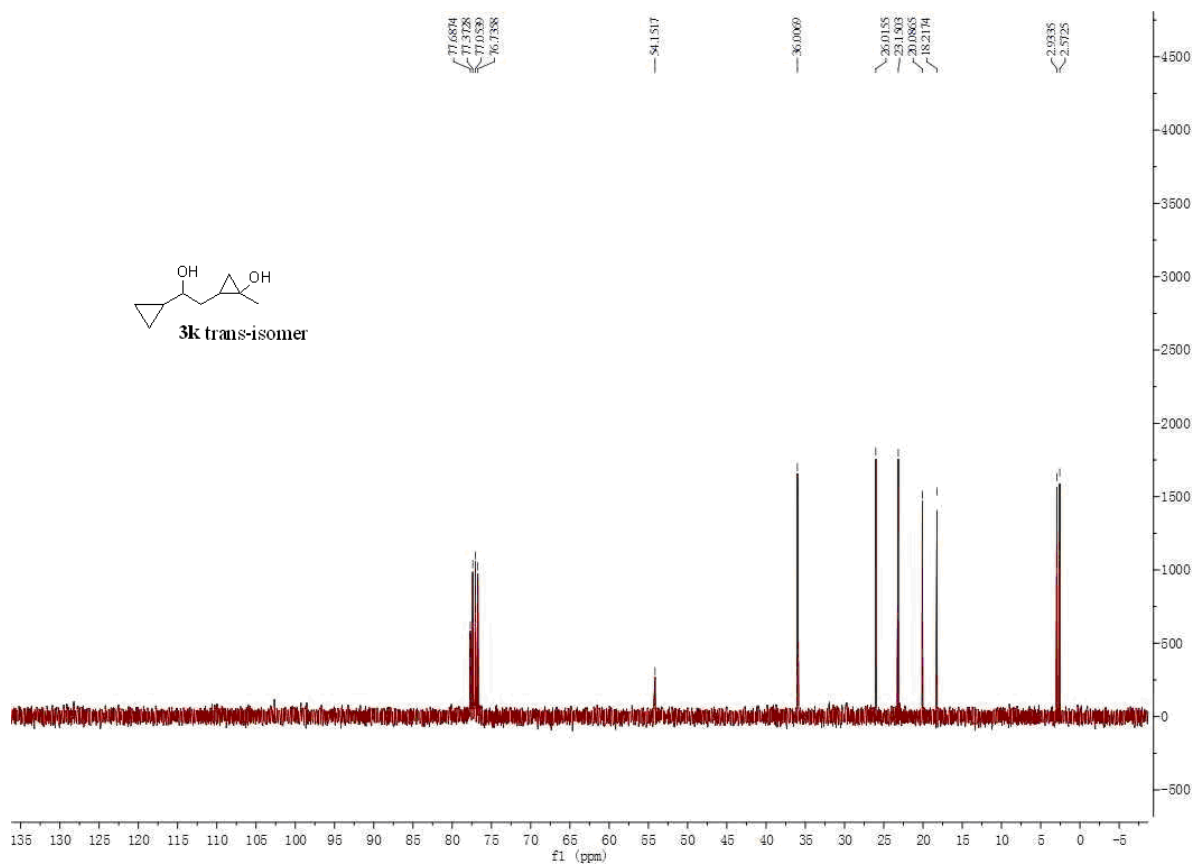
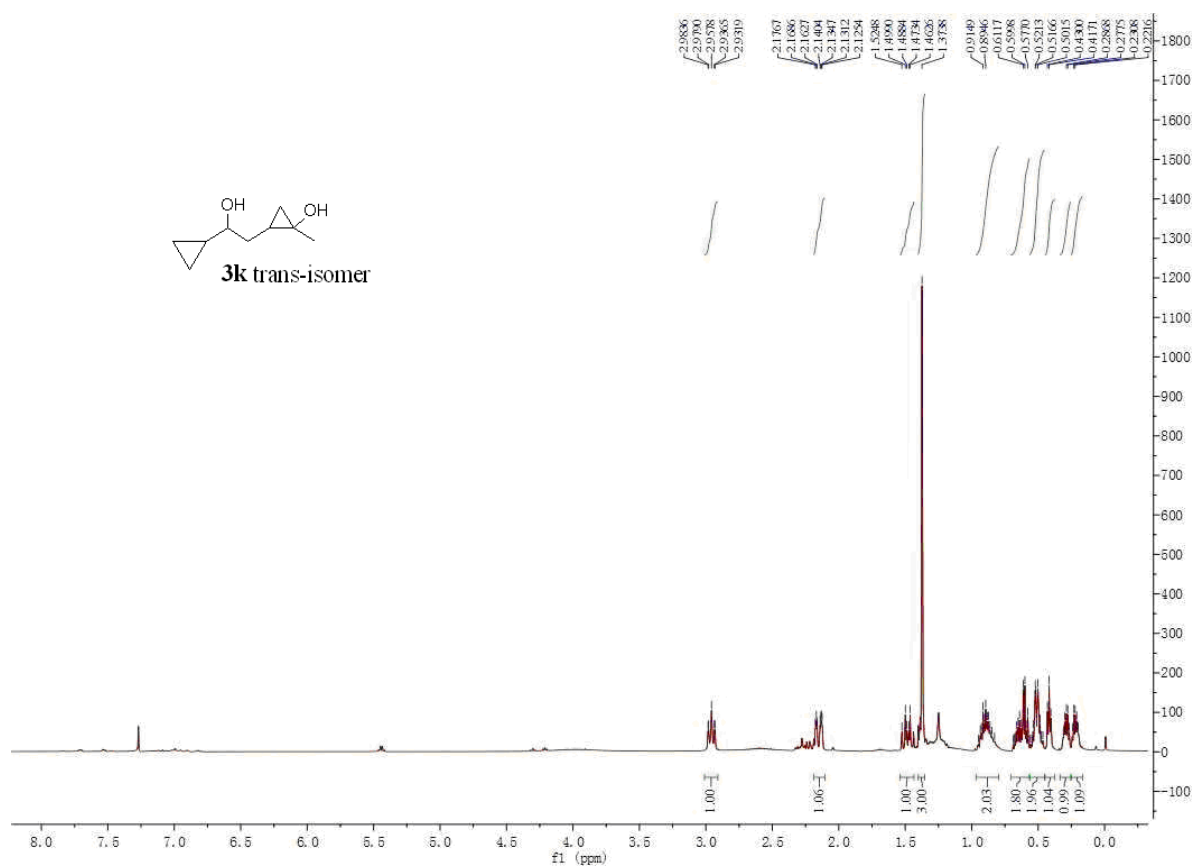


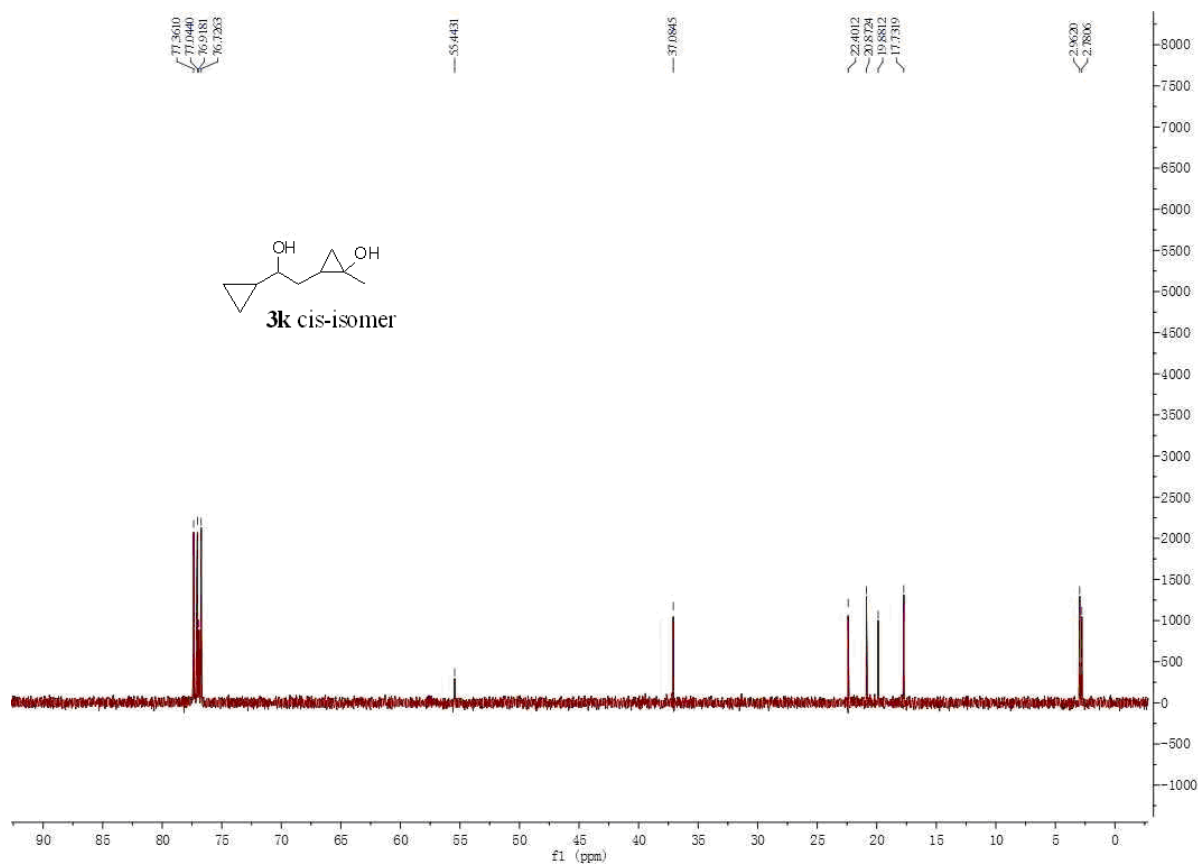
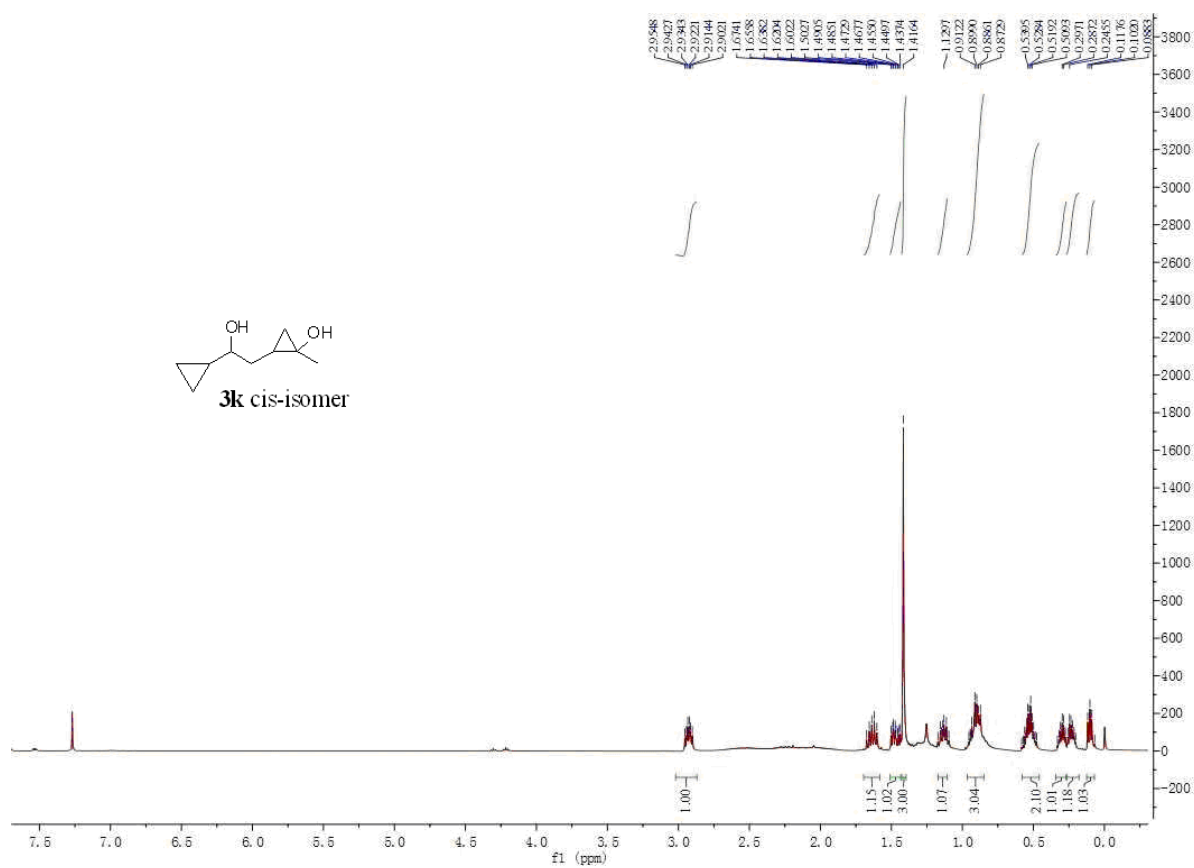


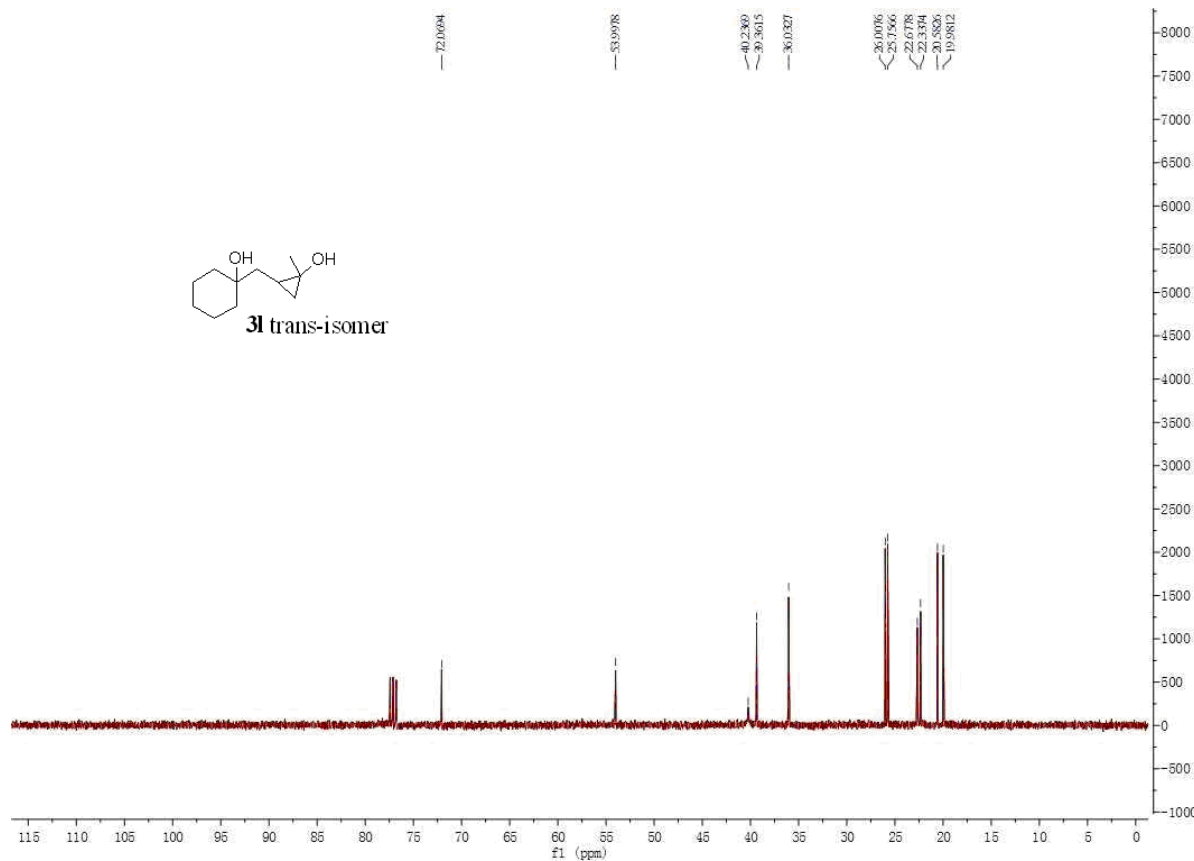
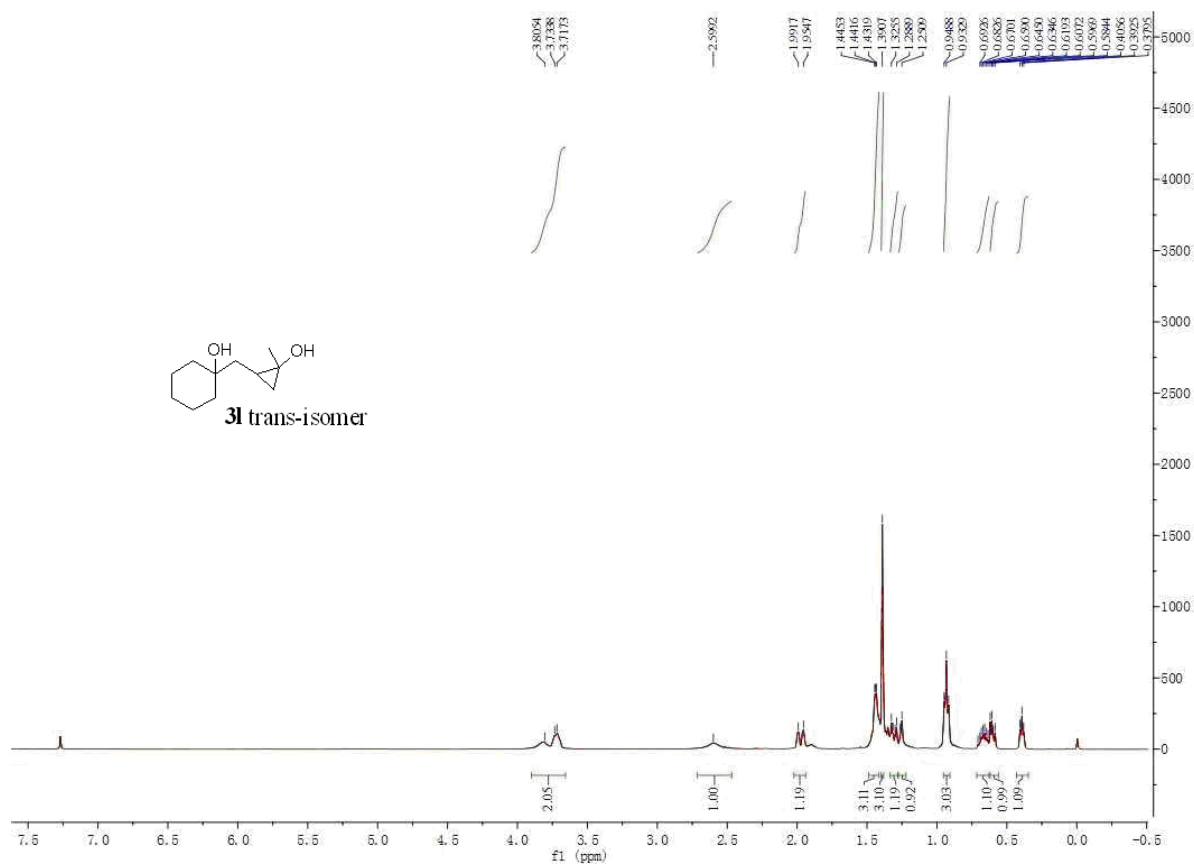


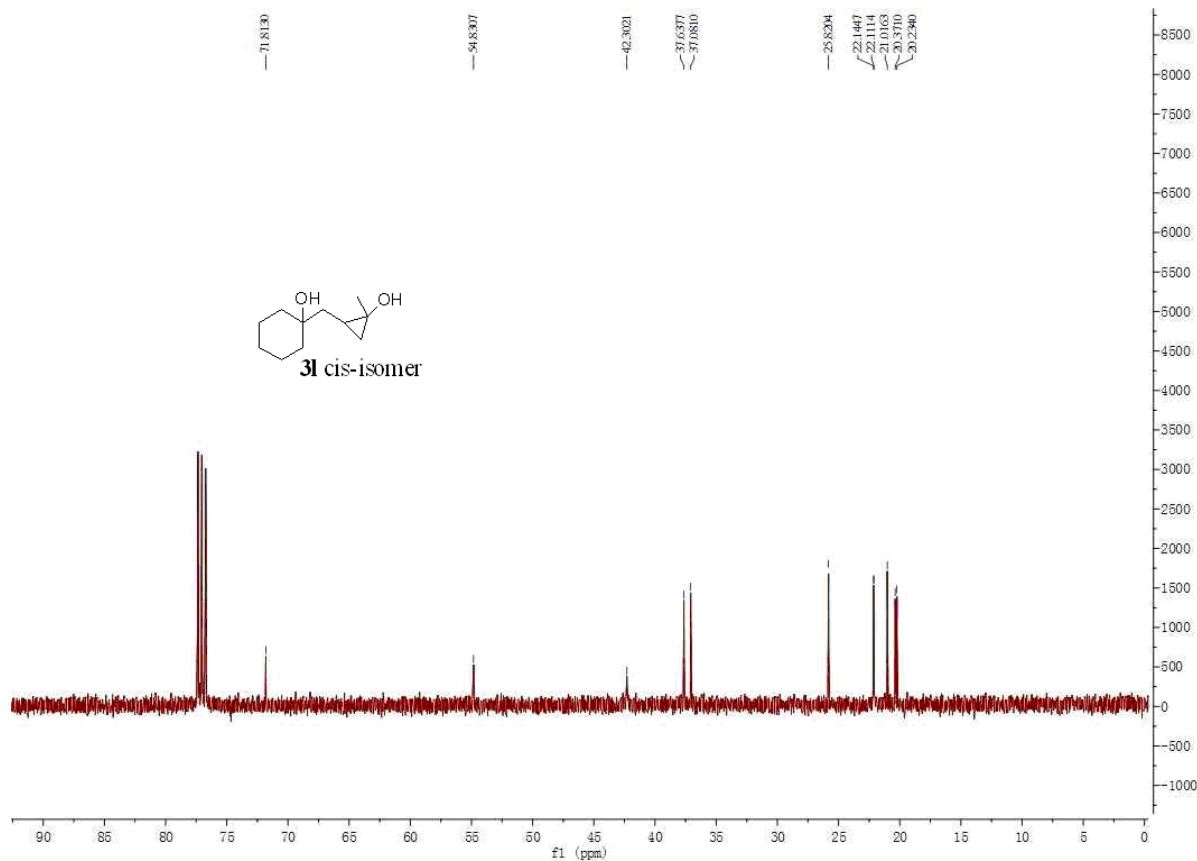
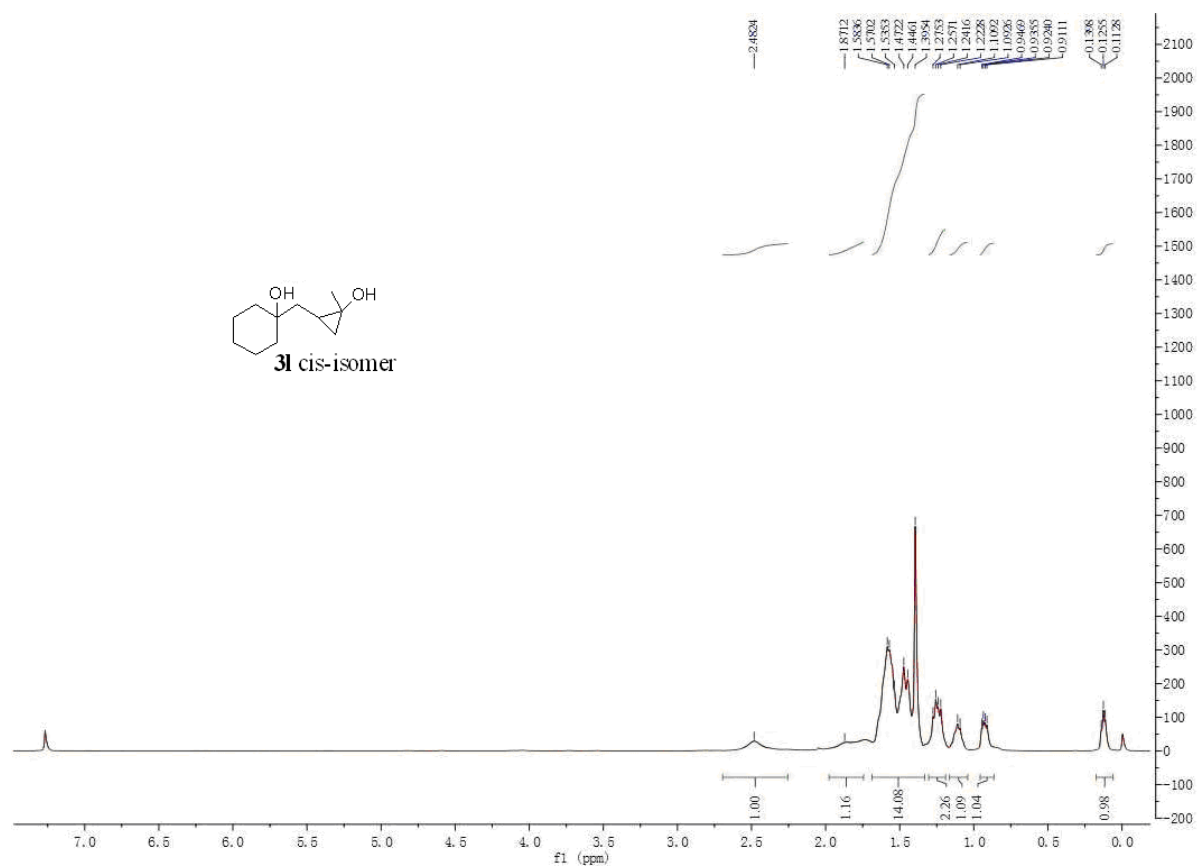


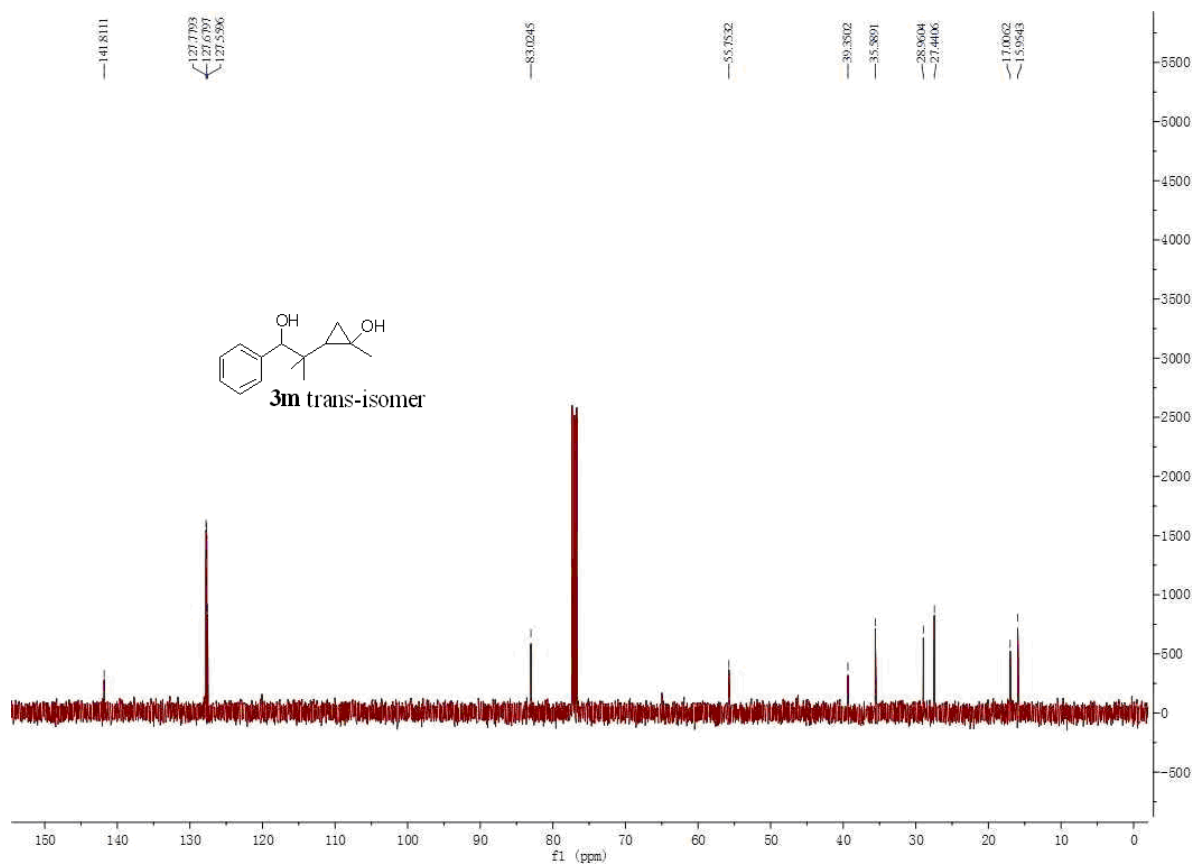
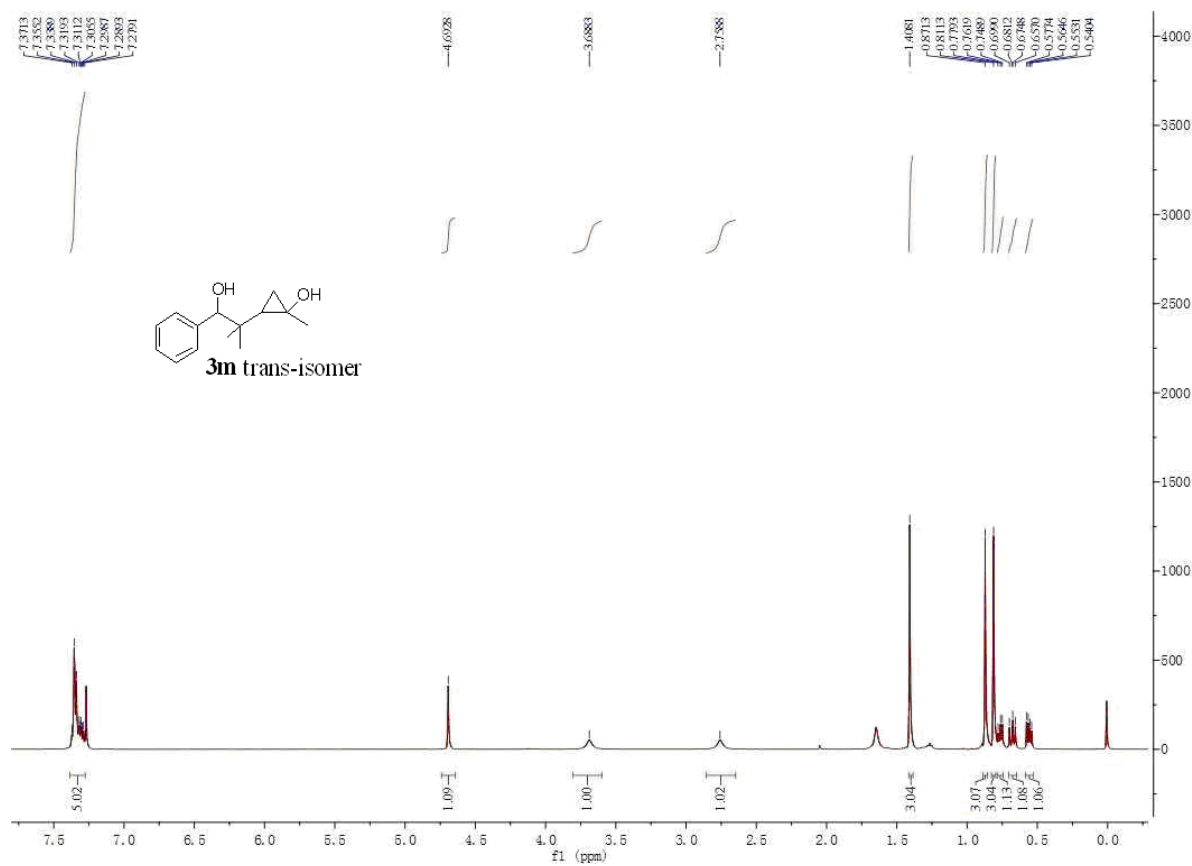


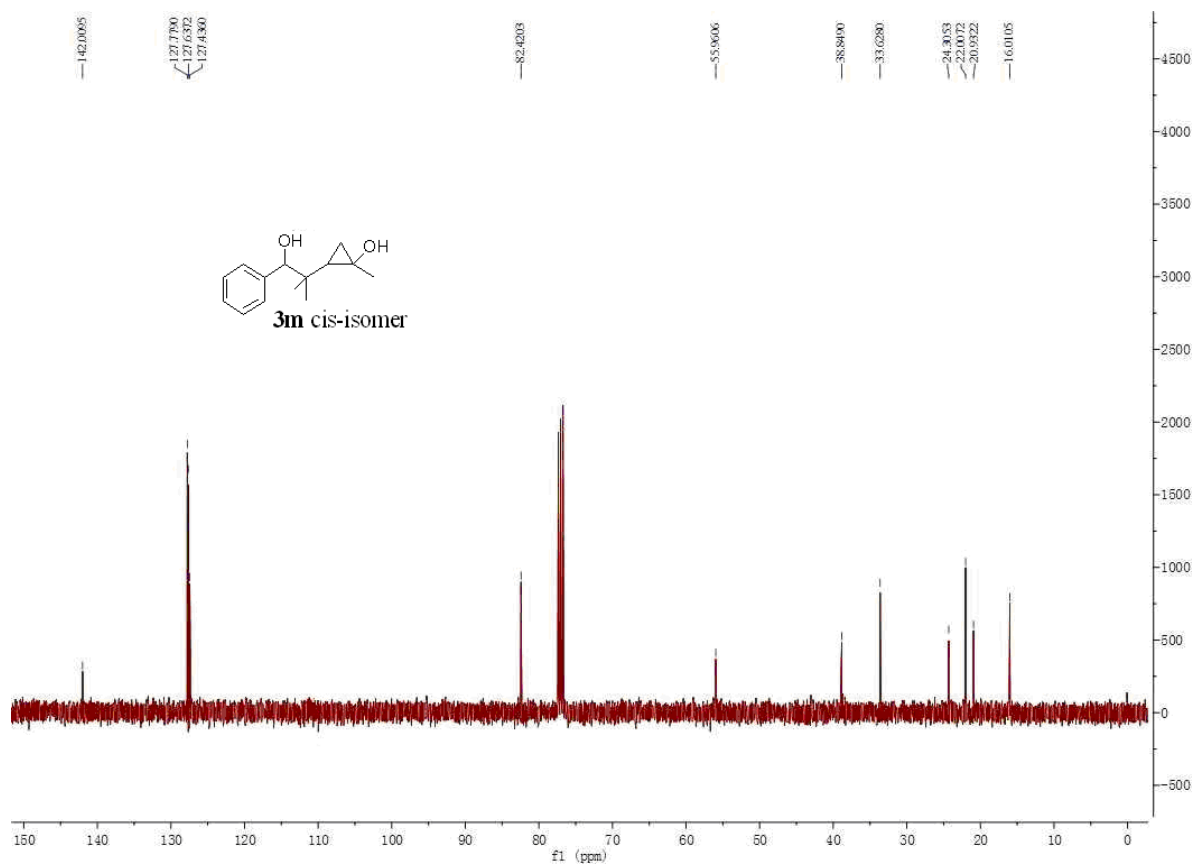
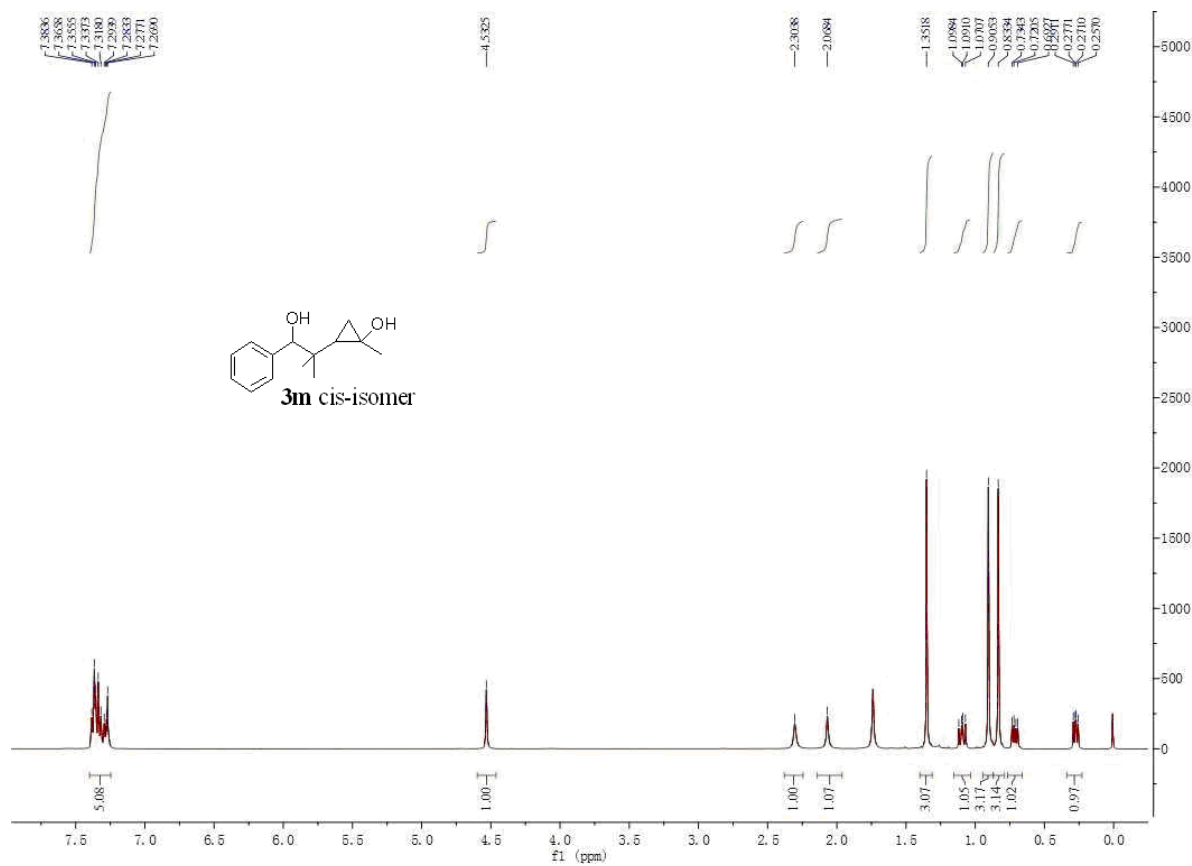


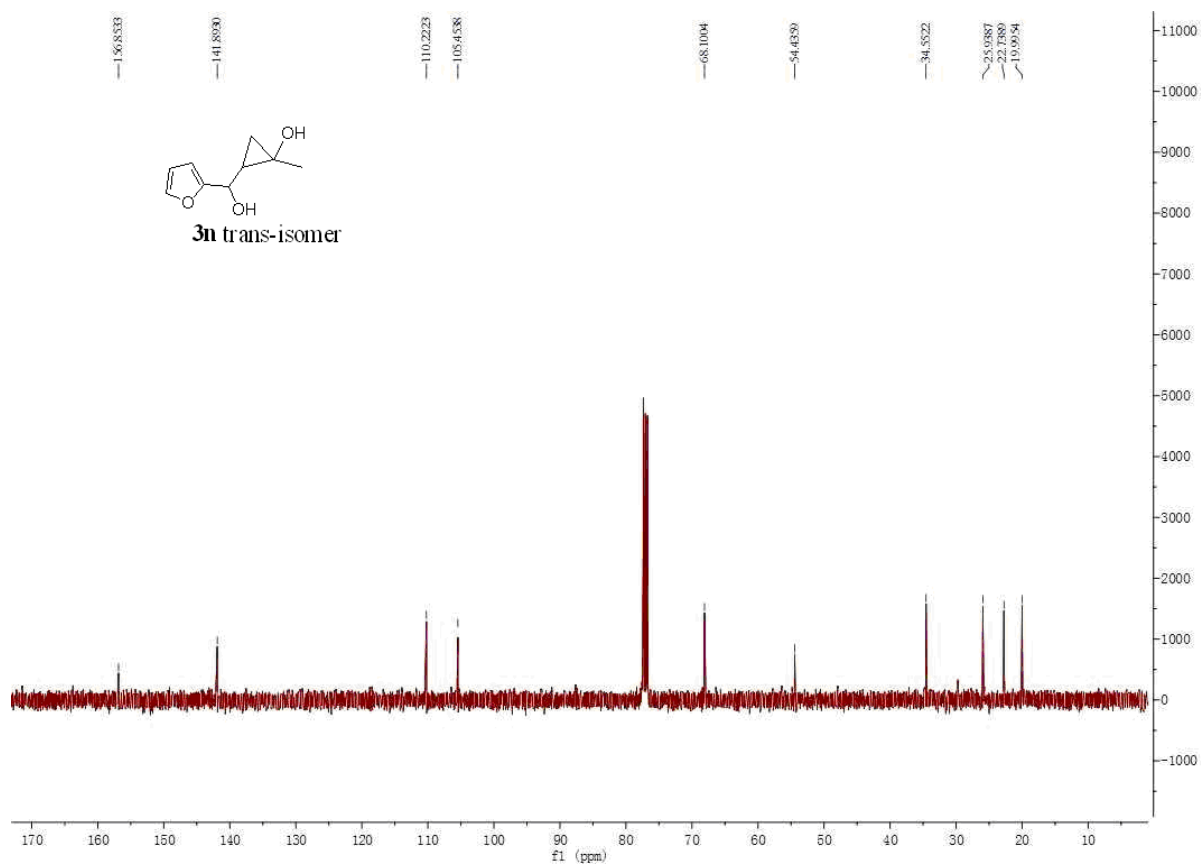
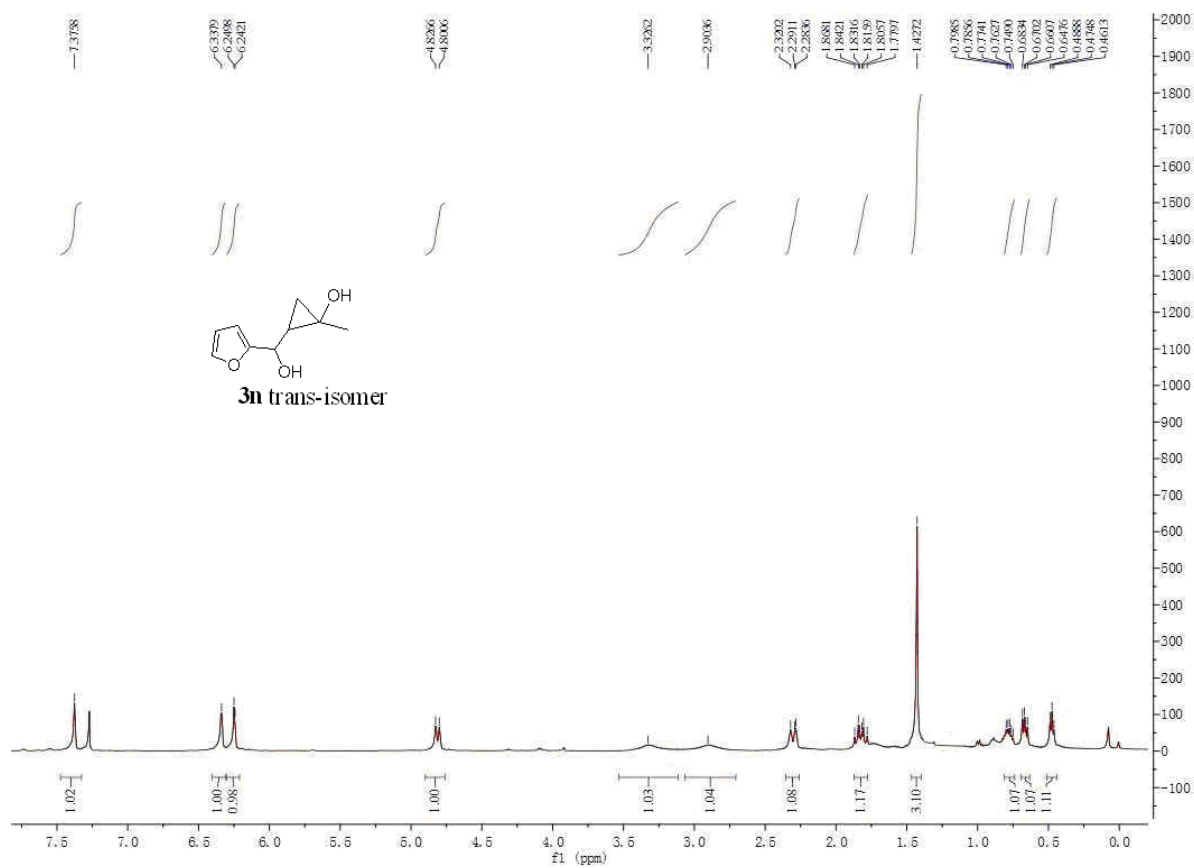


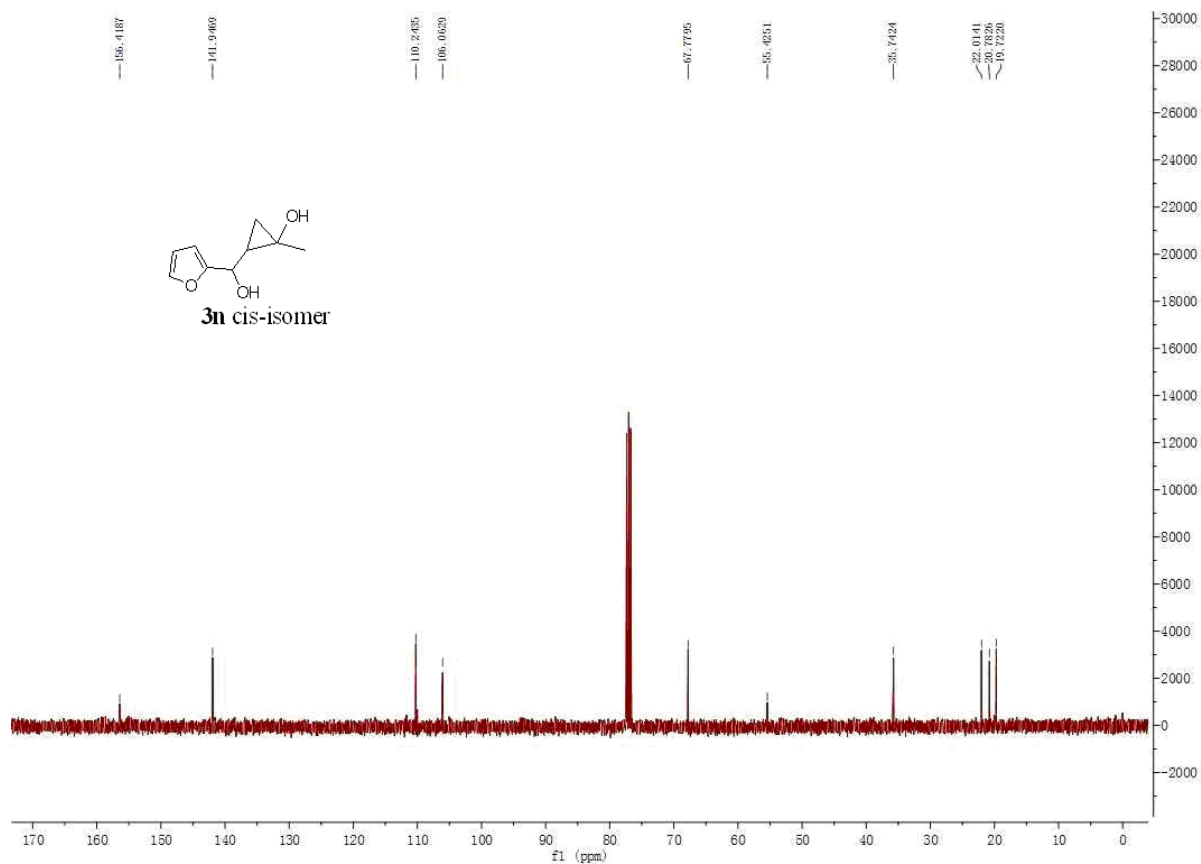
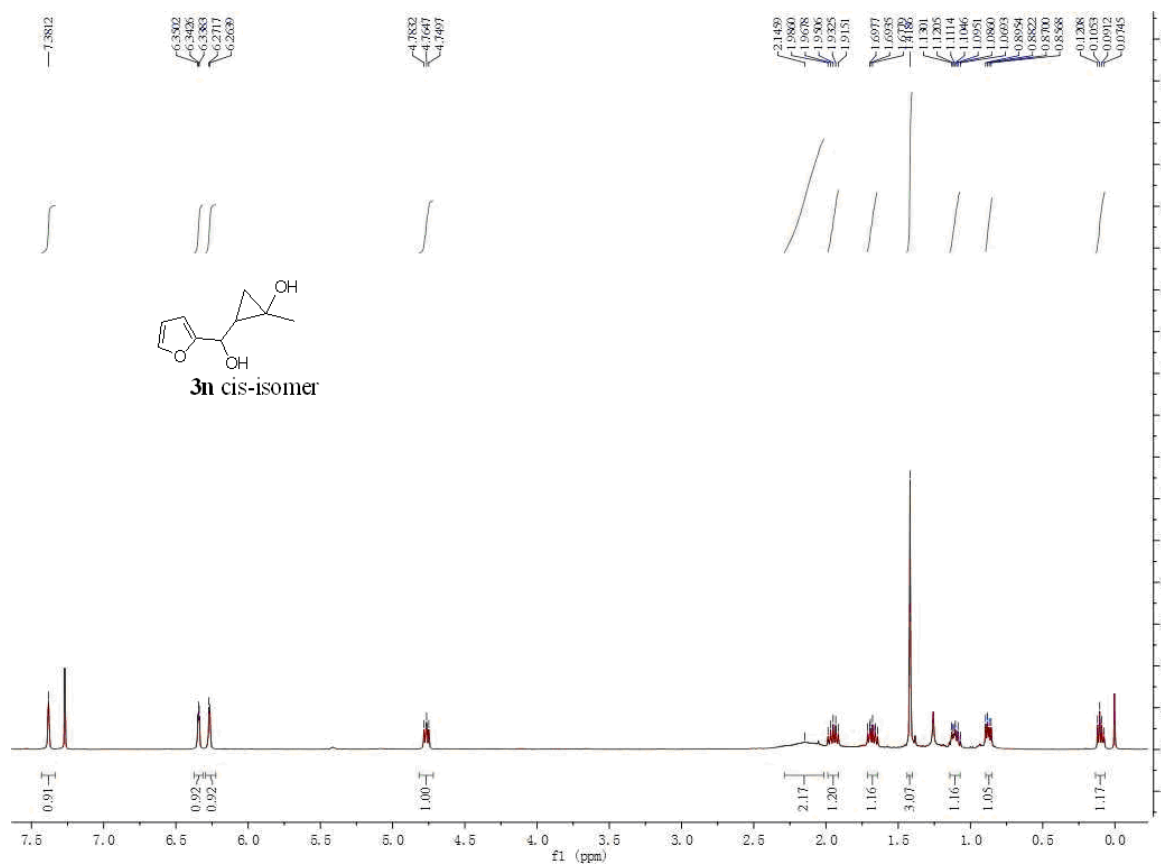


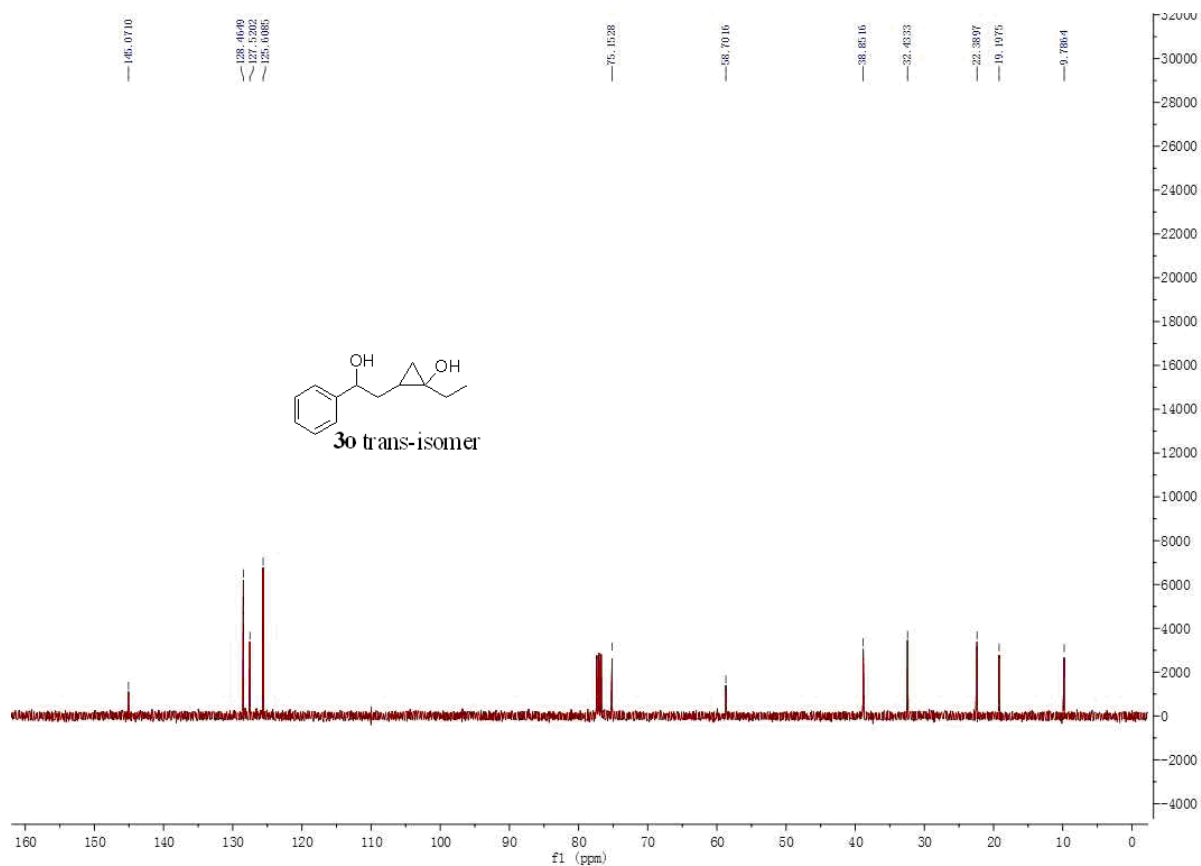
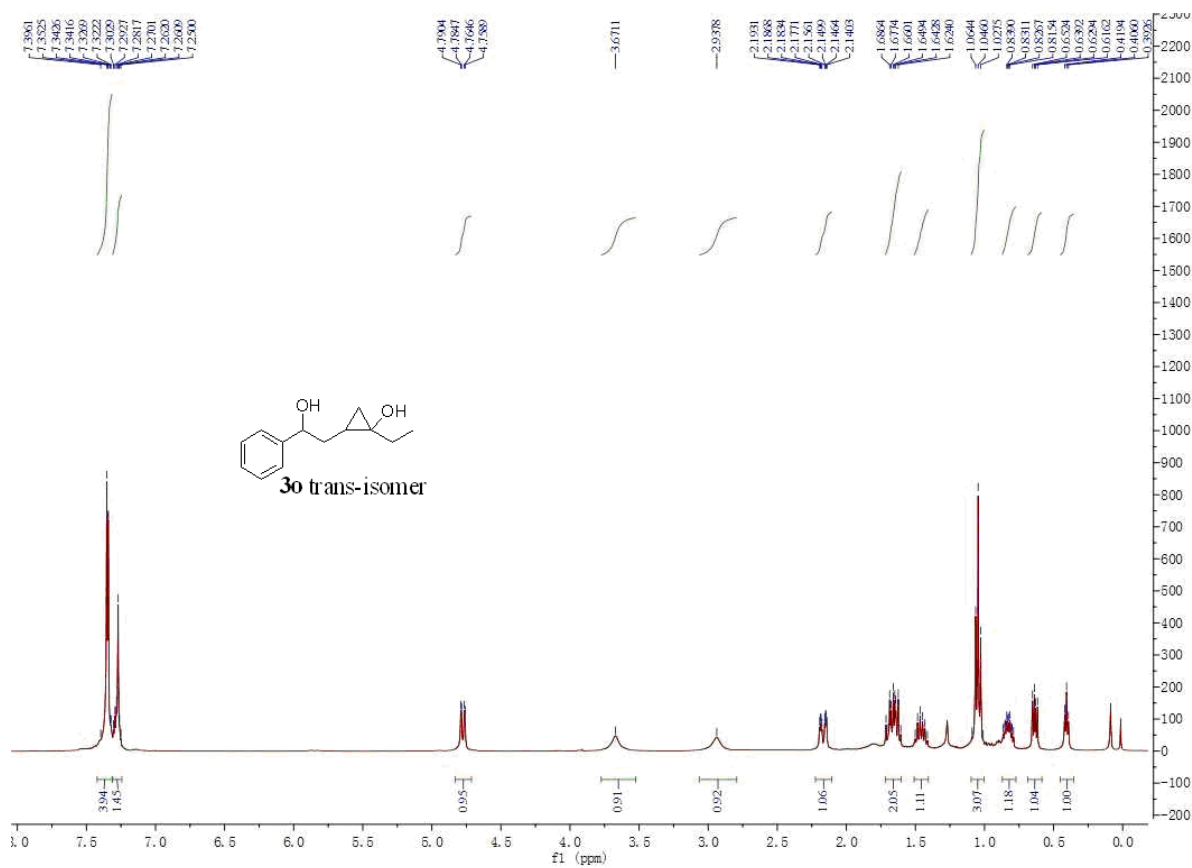


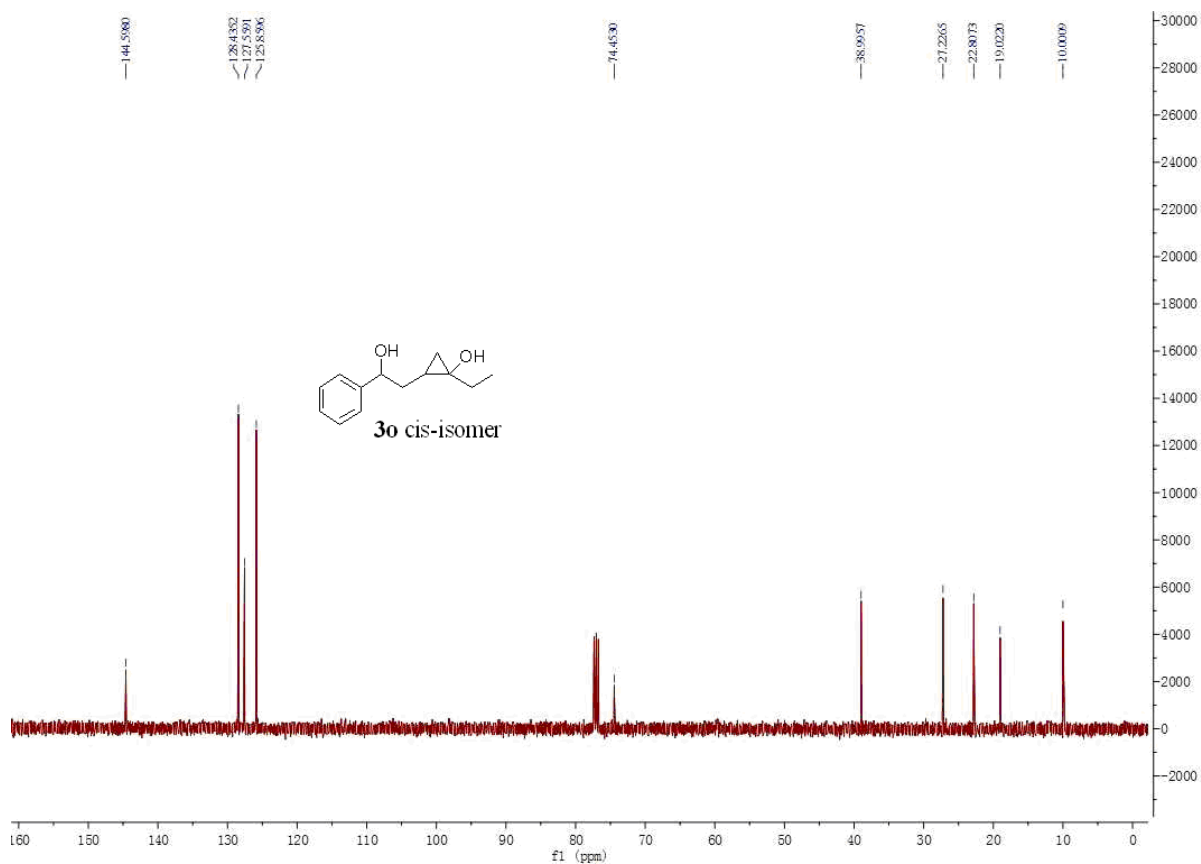
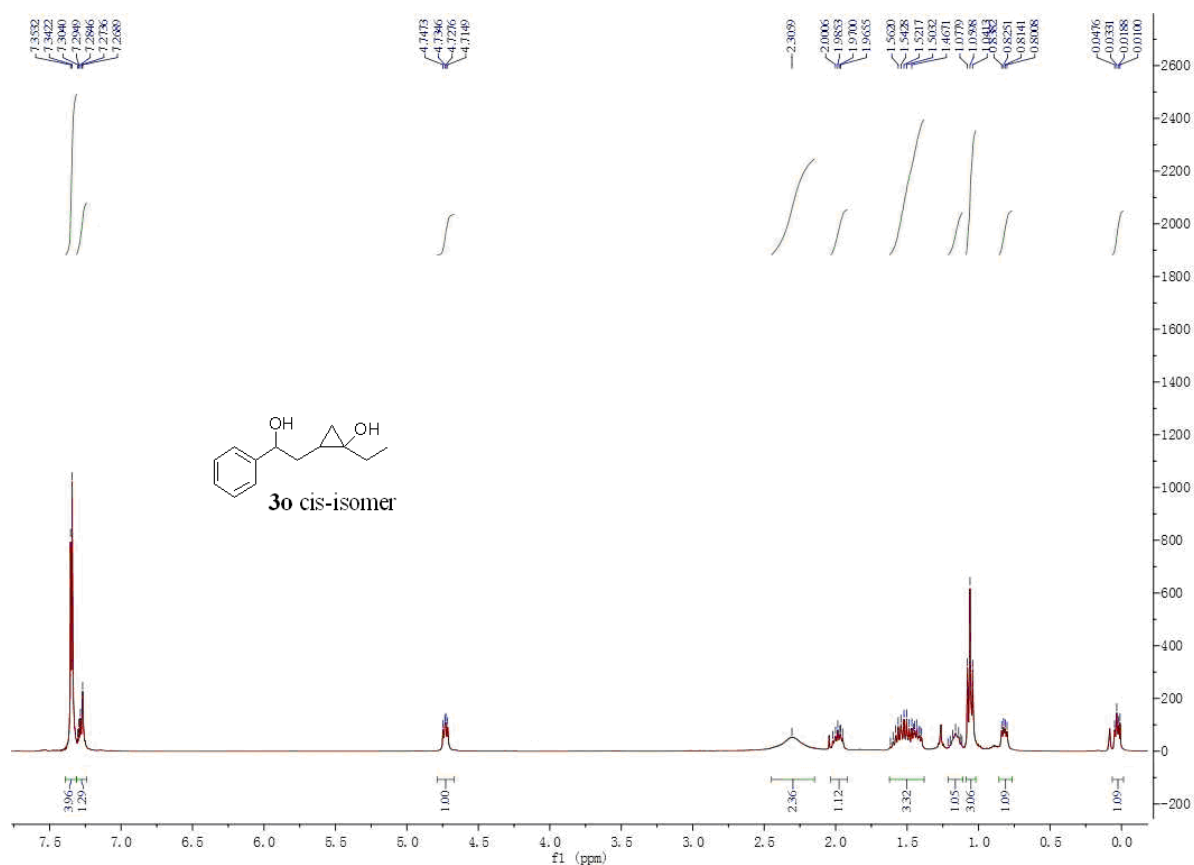


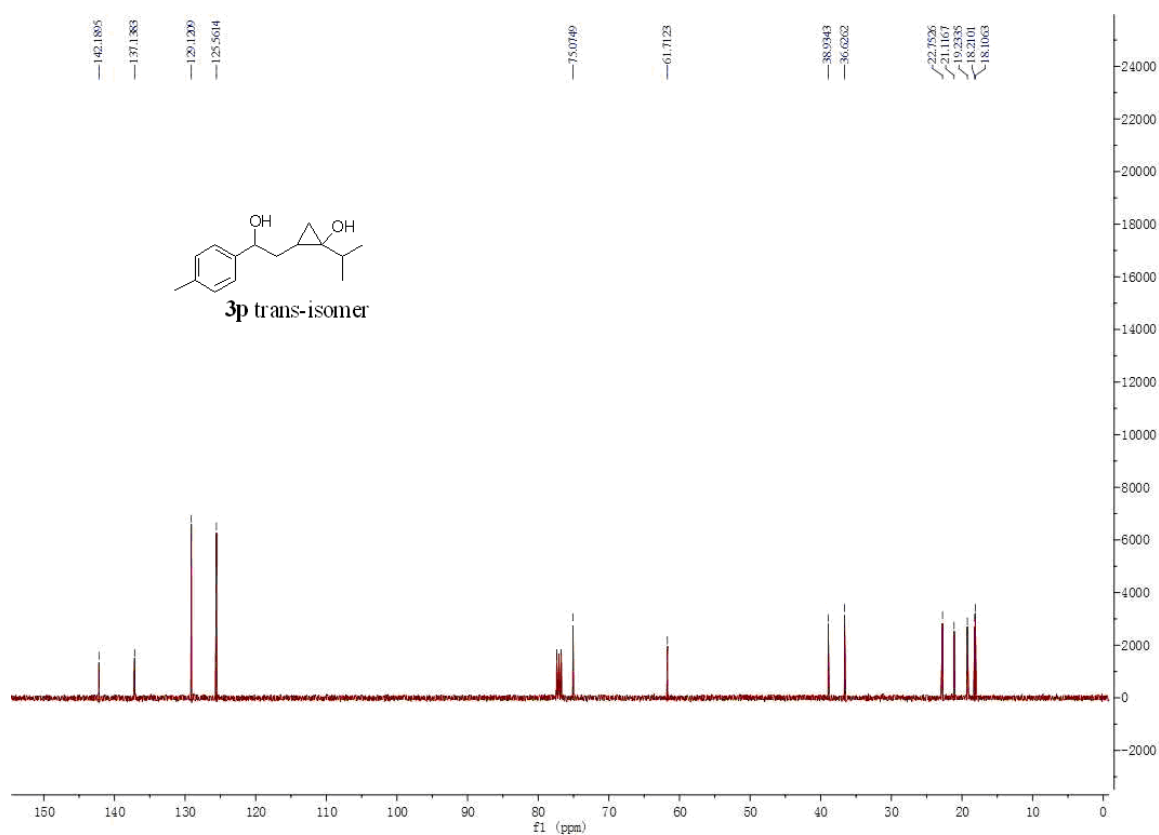
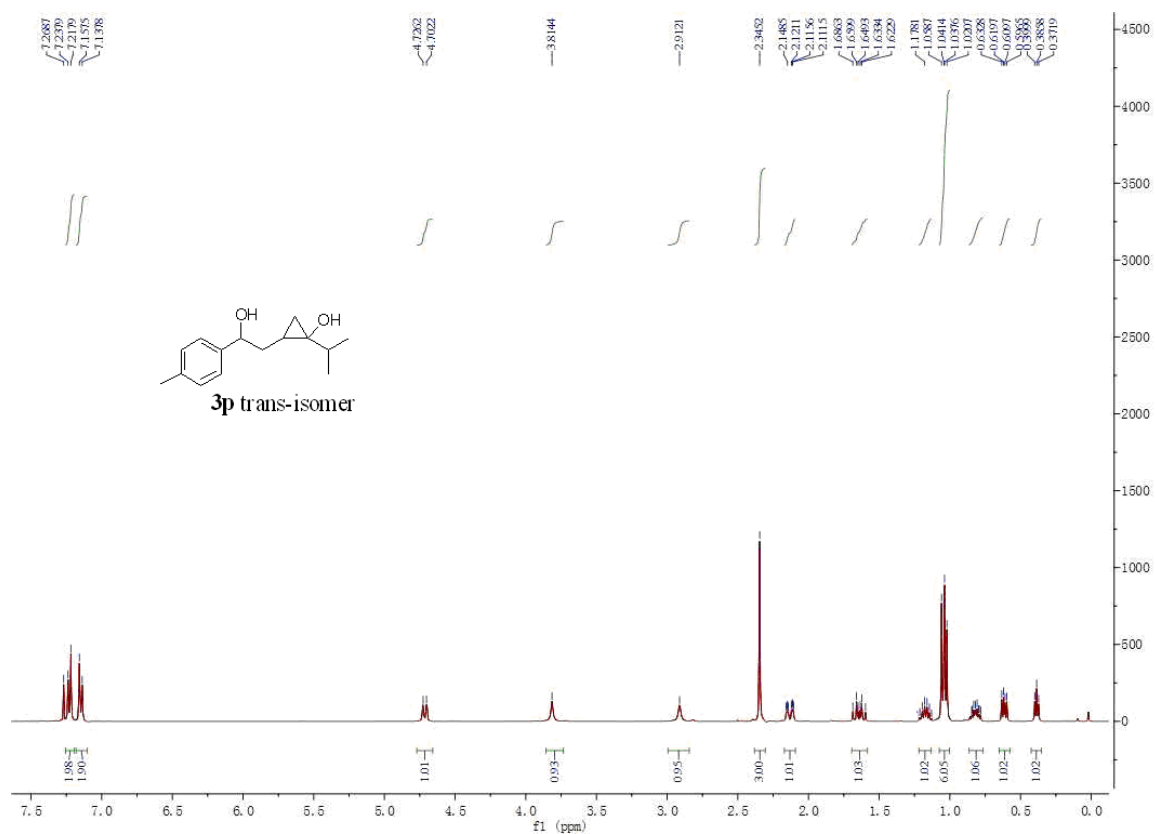


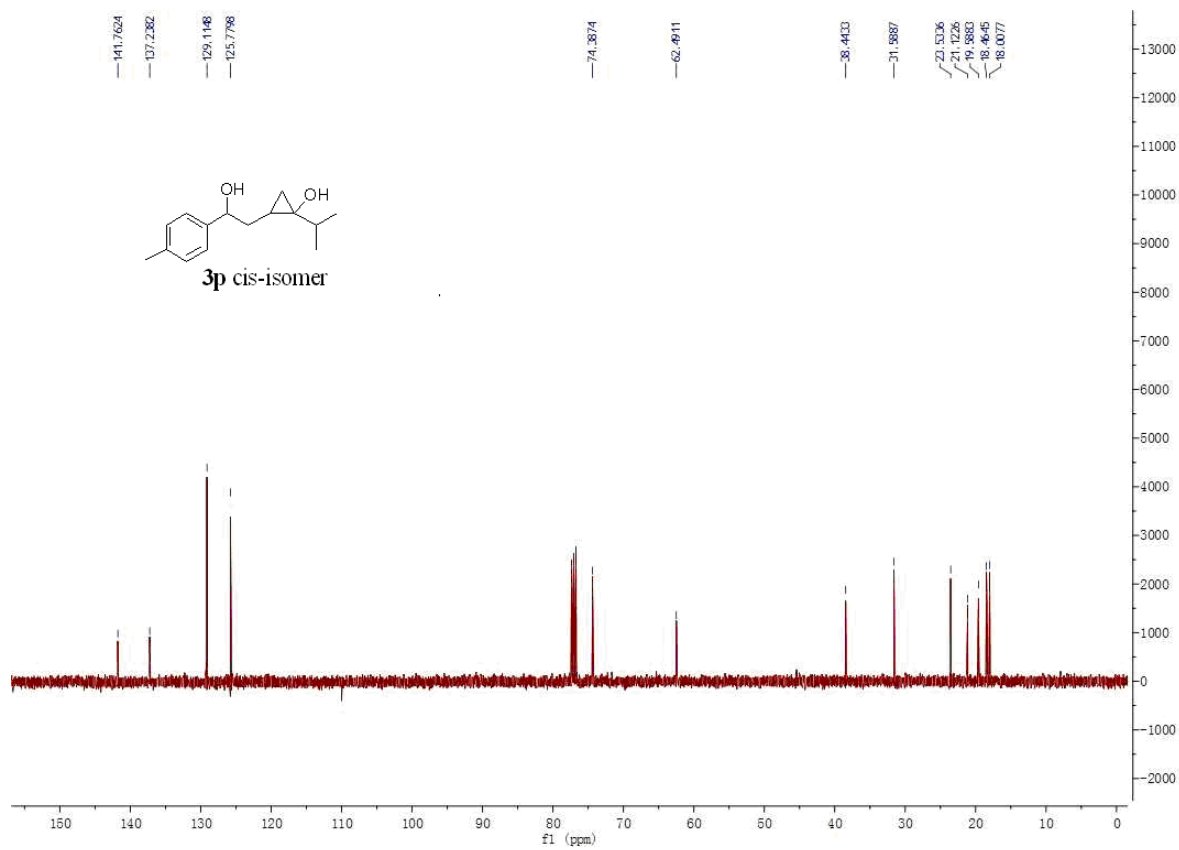
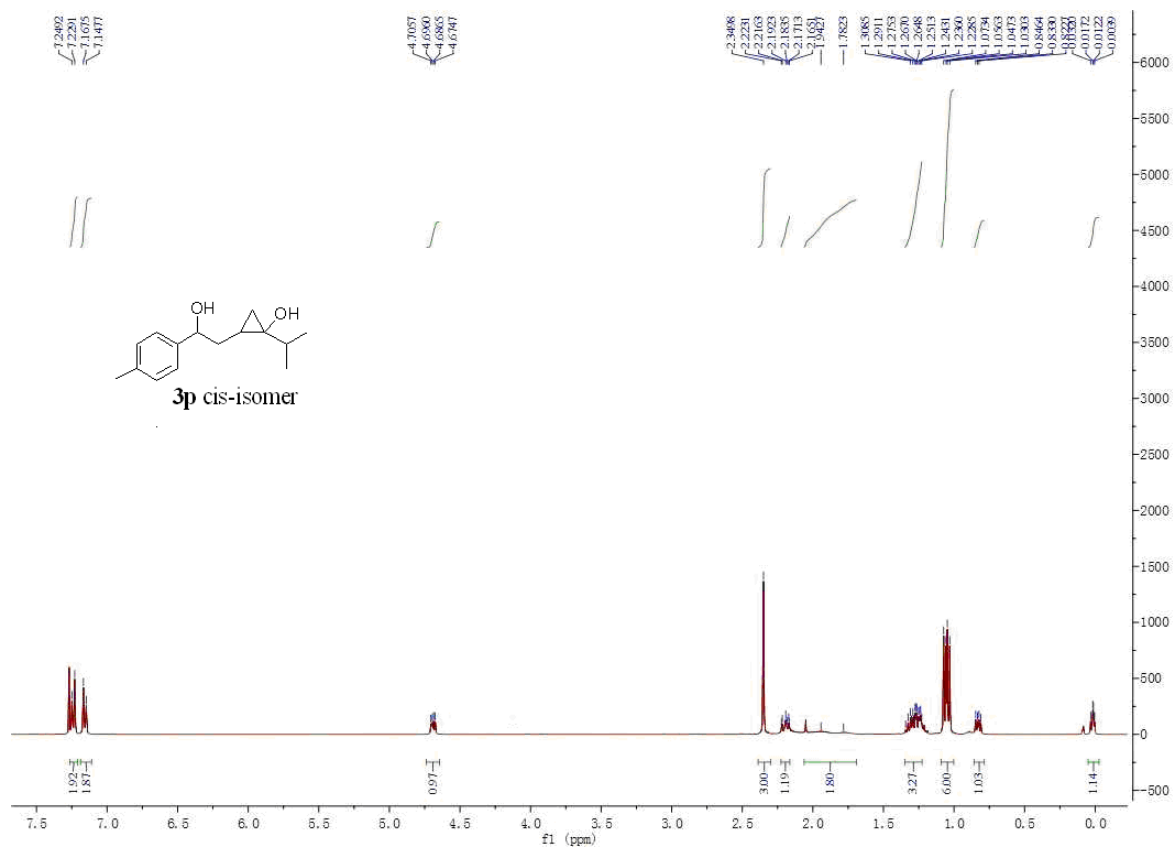


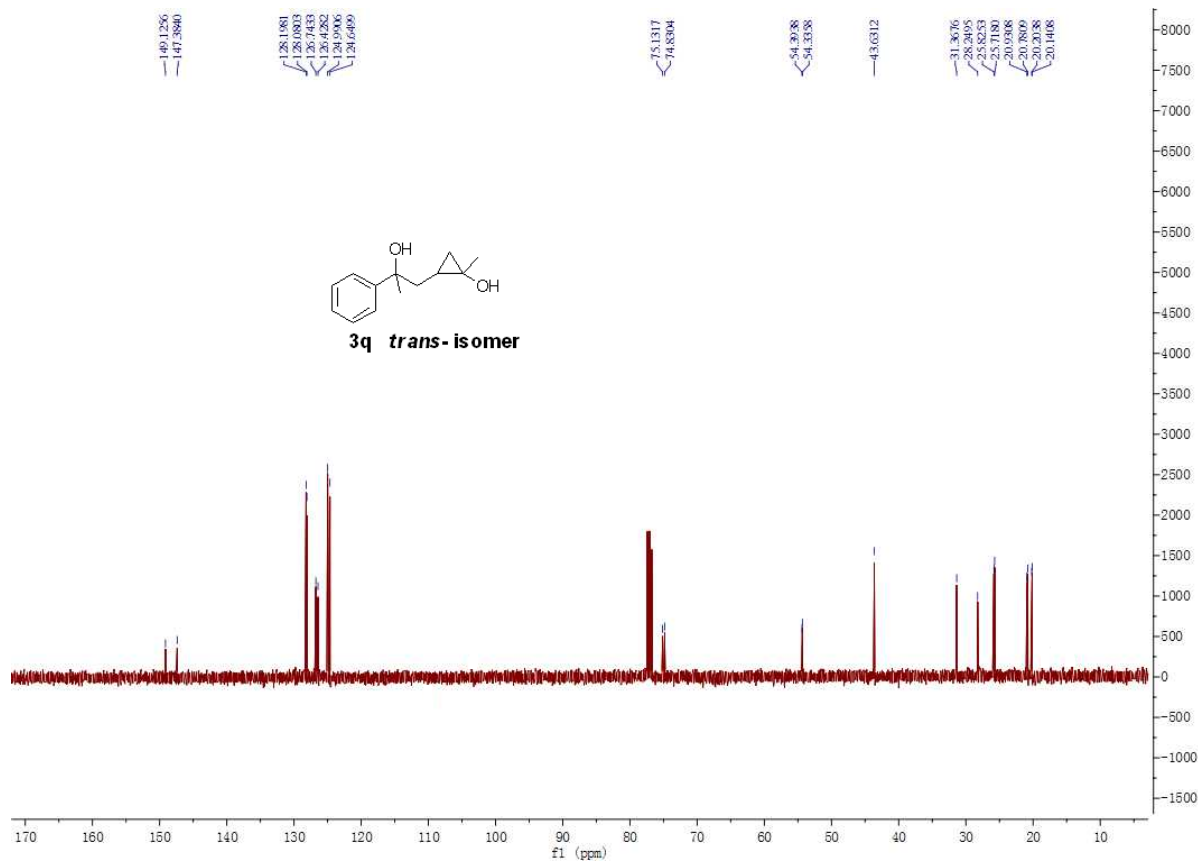
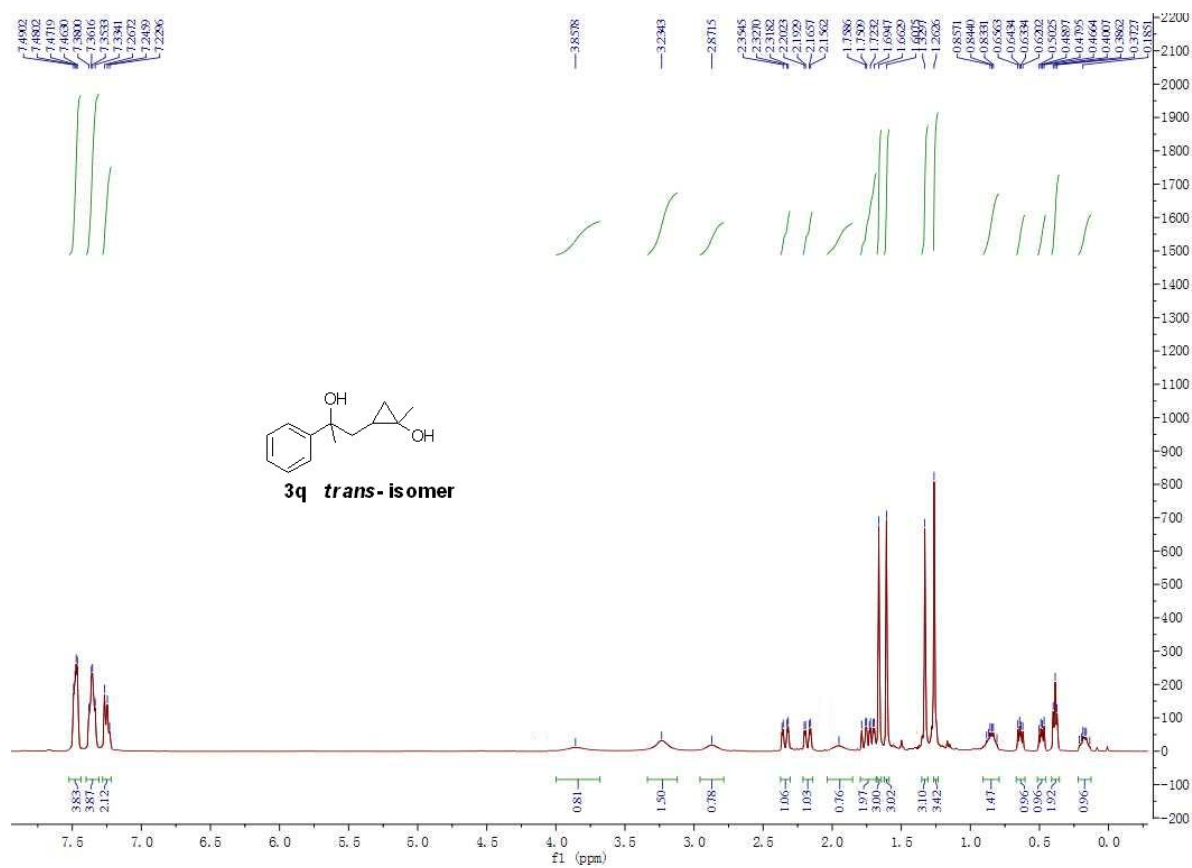


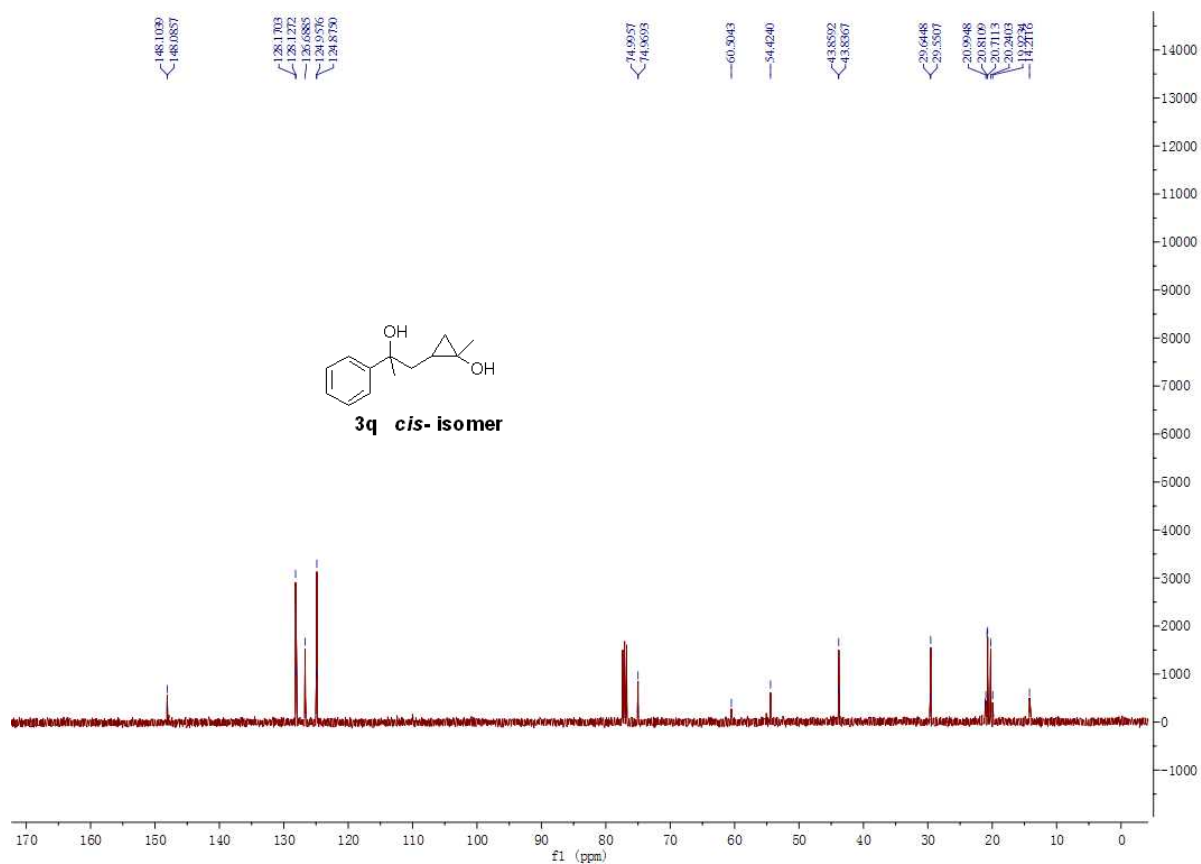
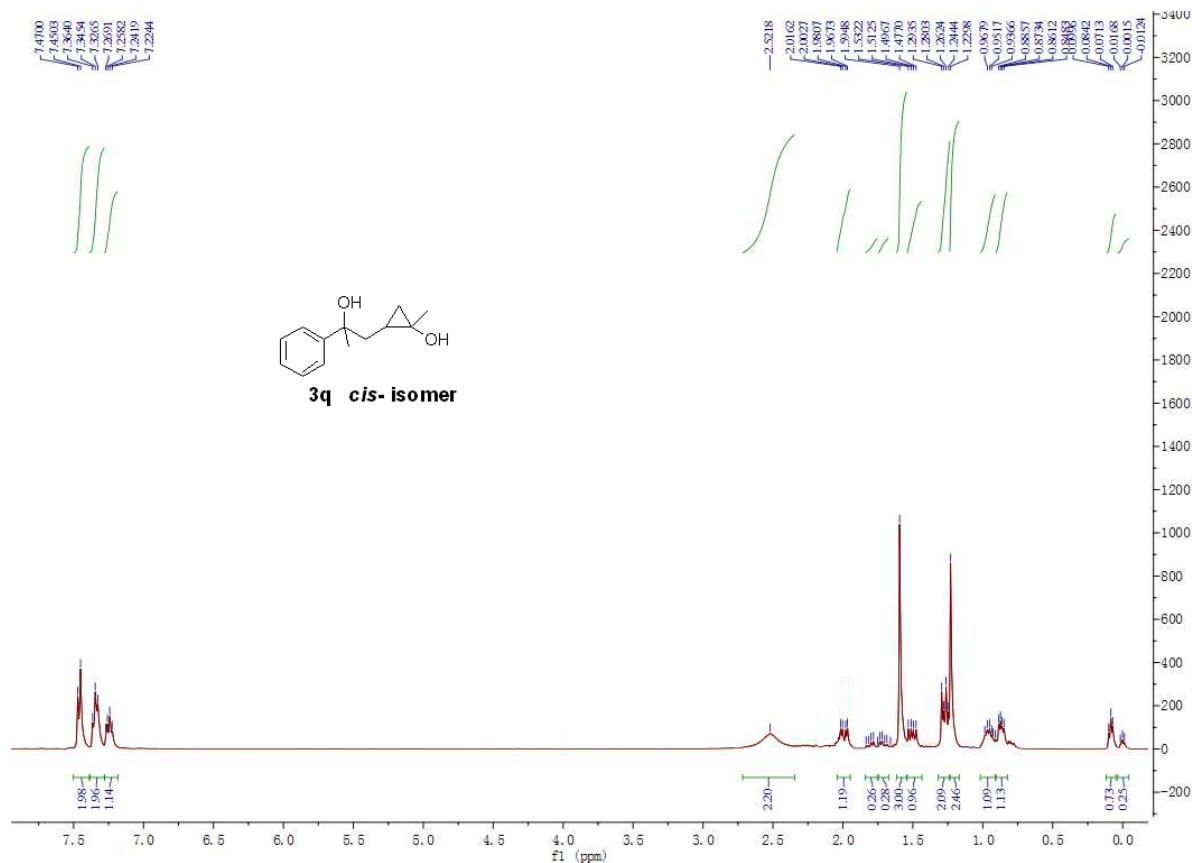


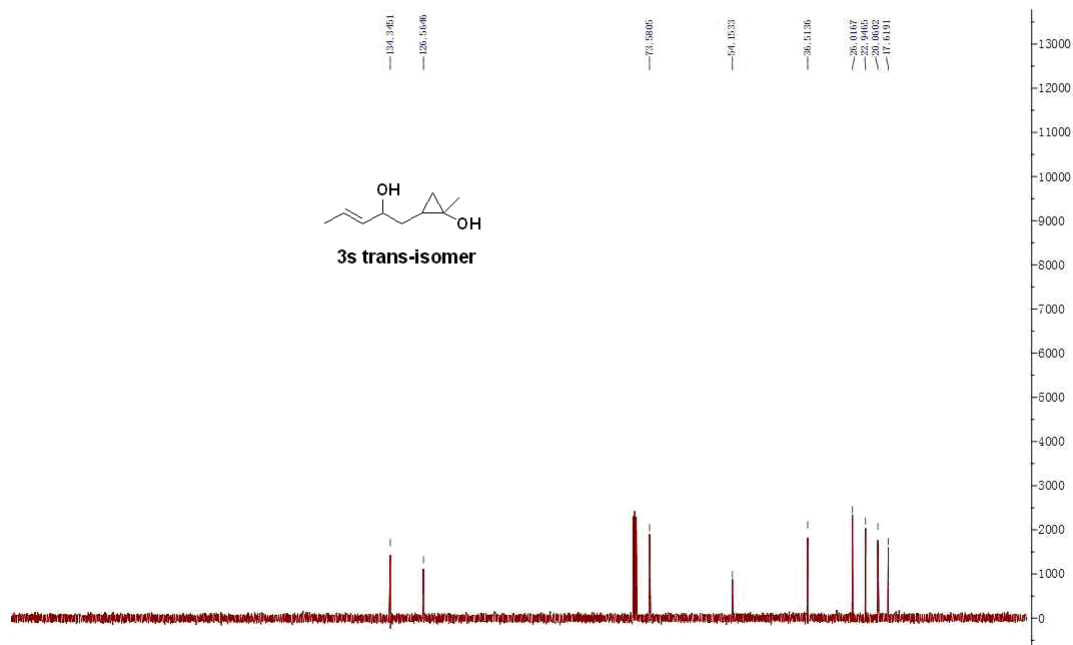
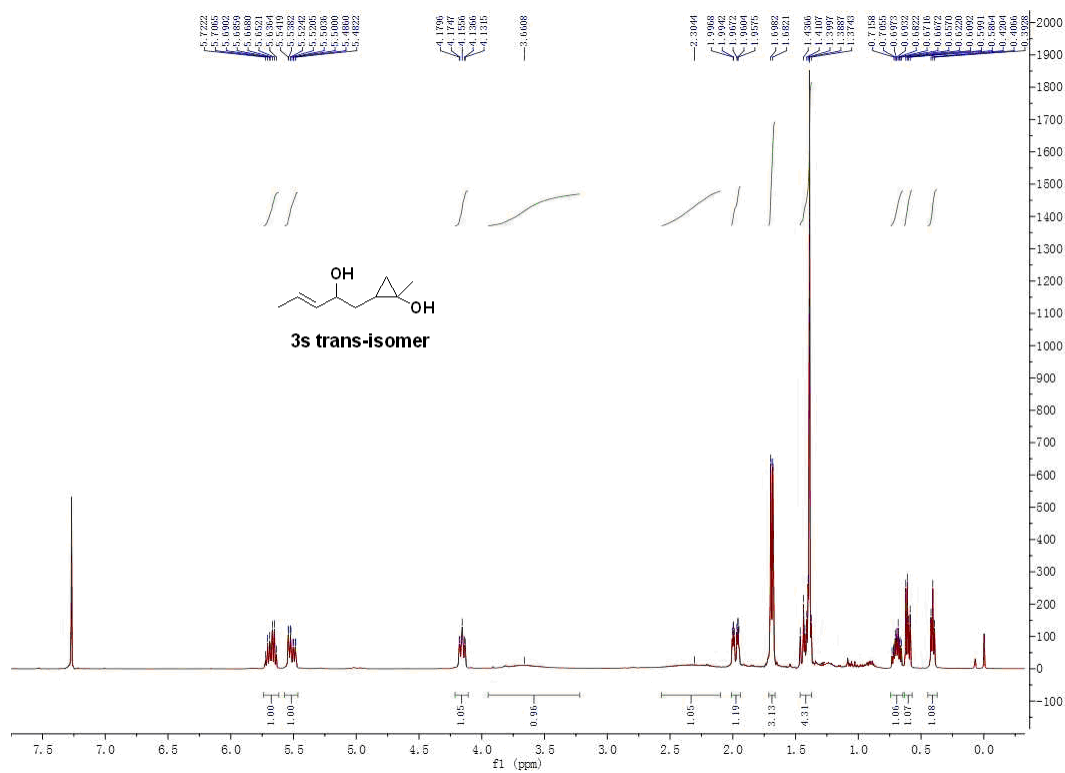


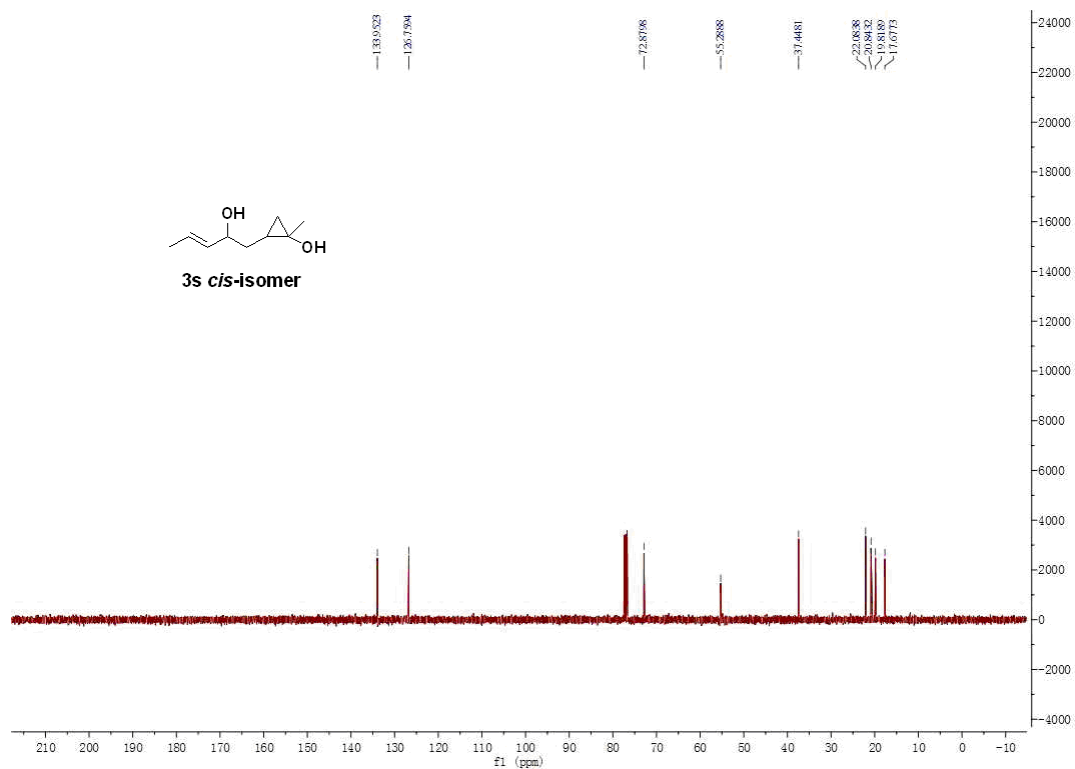
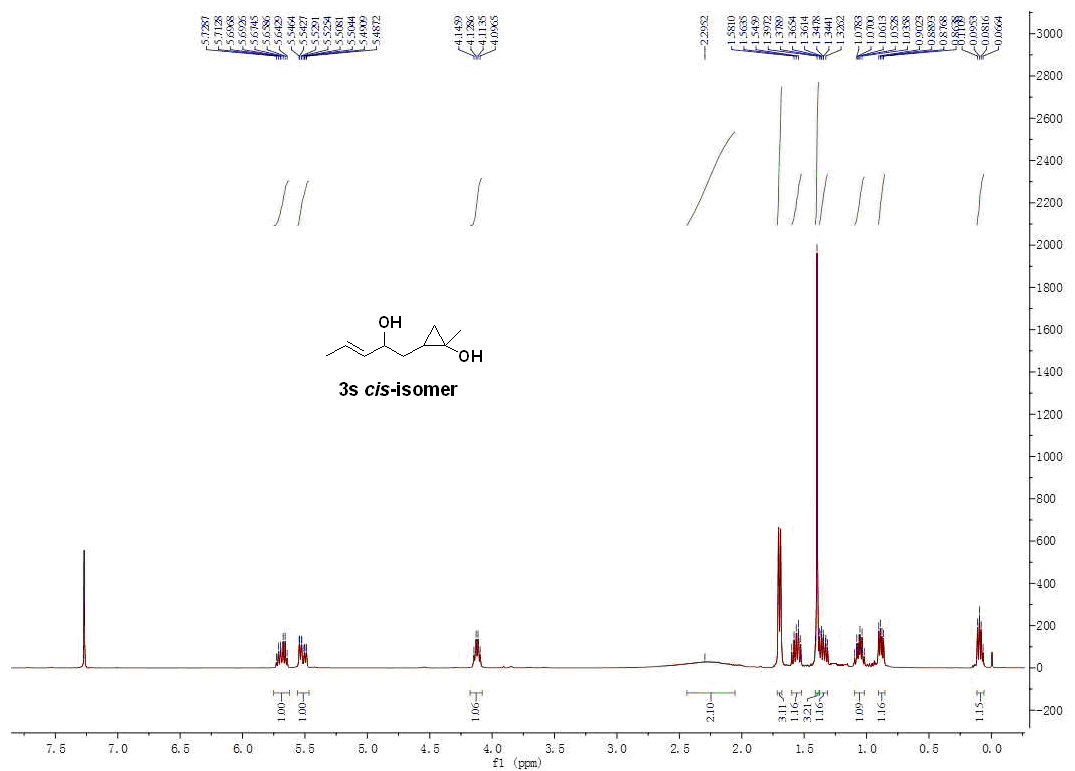


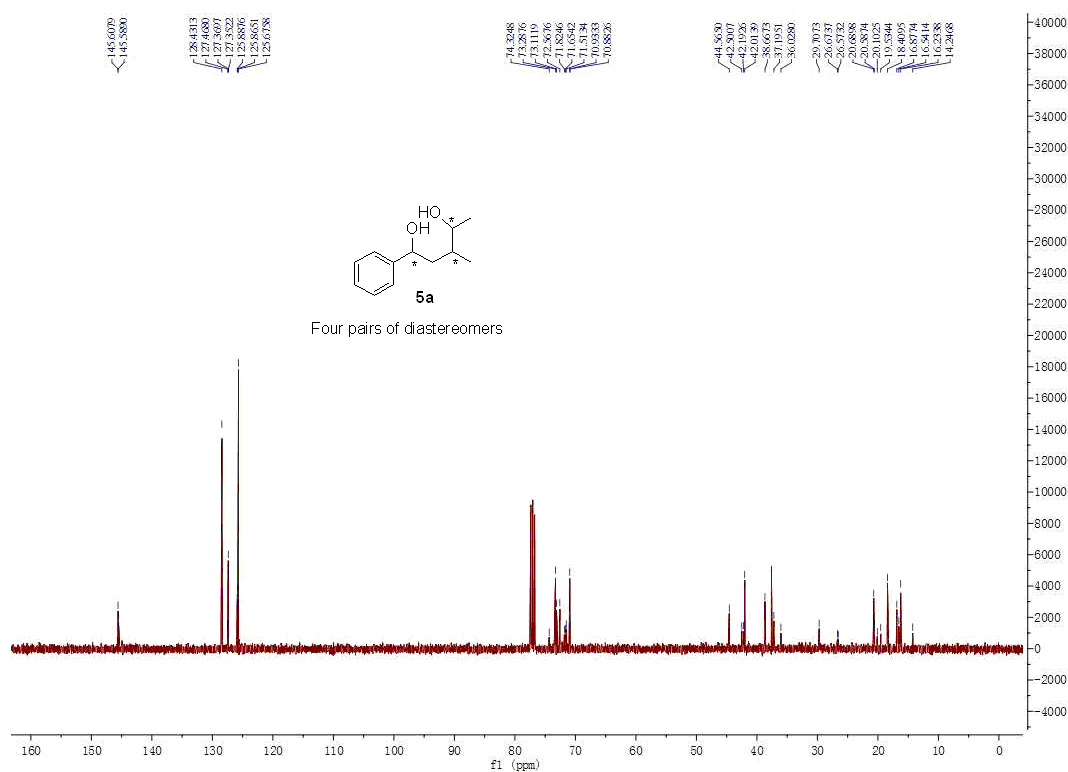
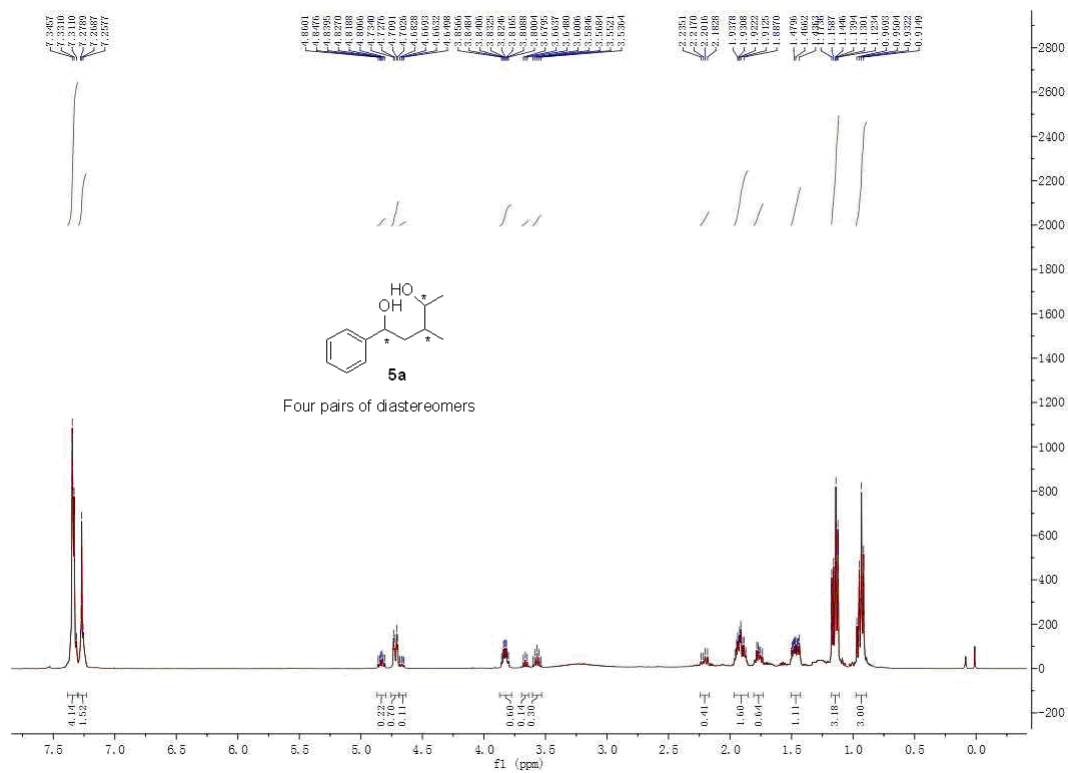












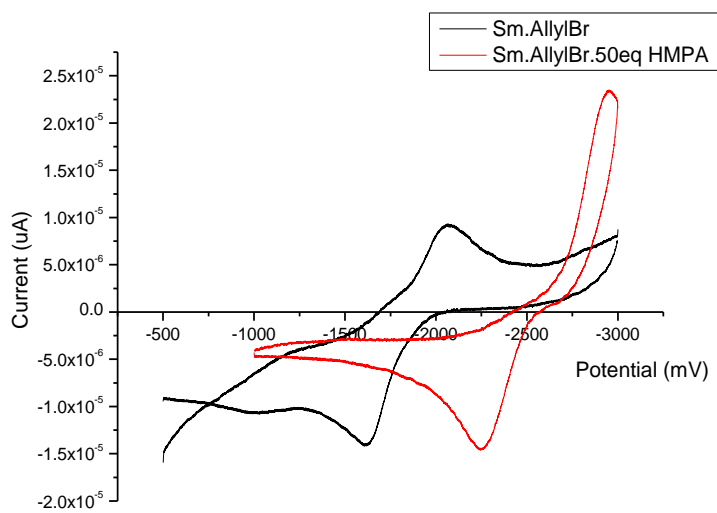
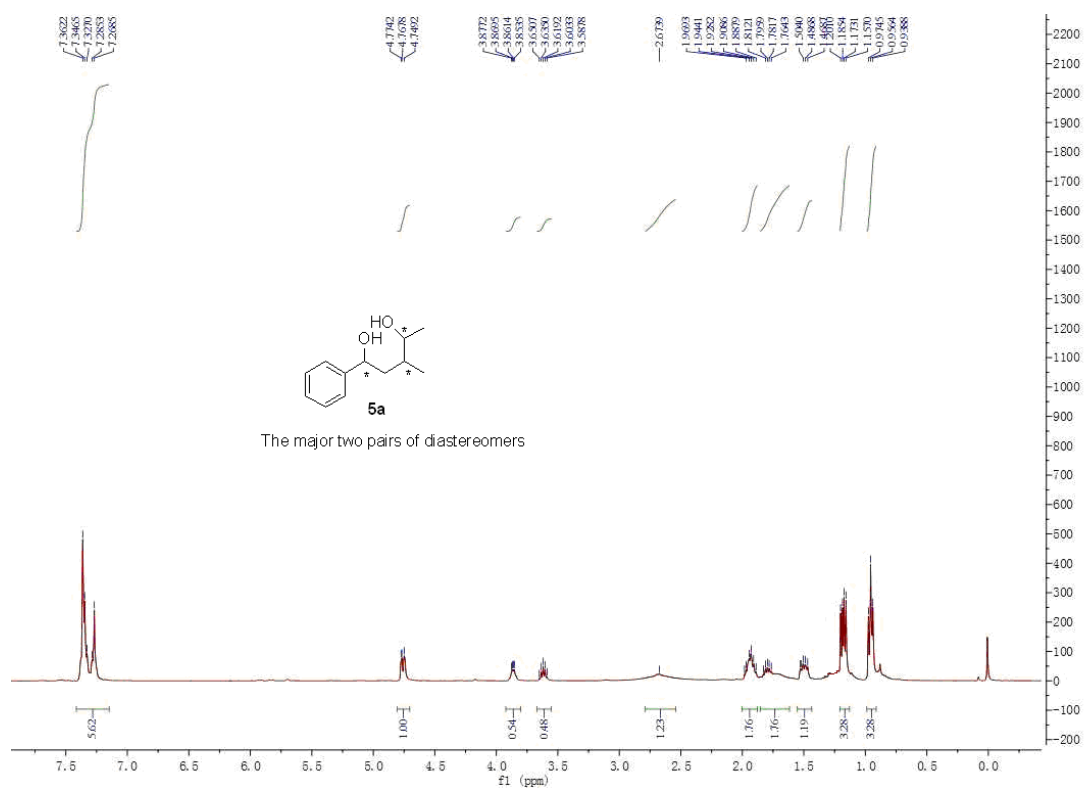


Figure S1 Cyclic voltammograms of AllylSmBr and AllylSmBr/HMPA
Sm and allyl bromide (1.14:1) in THF with Ag/AgNO₃ reference with
tetrabutylammoniumhexafluorophosphate