Electronic Supplementary Material (ESI) for Polymer Chemistry.

[*Supporting Information*]

"Bottom-Up" Construction of Chiral Porous Organic Polymers for Heterogeneous Asymmetric Organocatalysis: MacMillan Catalyst Built-in Nanoporous Organic Frameworks

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A. General information

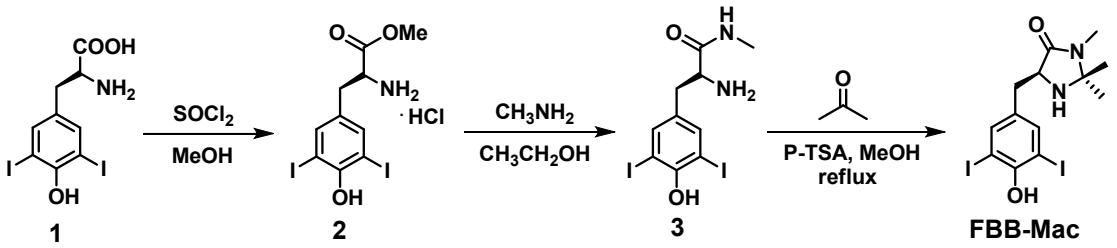
Chemicals and solvents were purchased from commercial suppliers and, if necessary, purified before use by standard techniques. All equipment was thoroughly oven-dried. Chemicals and solvents were purchased from commercial suppliers and, if necessary, purified before use by standard techniques. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light and/or immersion in a solution of phosphomolybdic acid in methanol followed by heating on a hot plate. Flash column chromatography (FCC) was carried out with silica gel (200–300 mesh). ^{1}H and ^{13}C liquid NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. The chemical shifts δ are given in ppm (parts per million) relative to tetramethylsilane (TMS) and the coupling constants J are given in Hz. All the spectra were recorded in $CDCl_3$ as solvent at room temperature. TMS served as the internal standard (δ = 0.00 ppm) for ^{1}H NMR while $CDCl_3$ as the internal standard (δ = 77.0 ppm) for ^{13}C NMR. HRMS data were obtained ESI ionization sources. Enantiomeric excess (ee) values were determined by HPLC on a Agilent Technologies 1200 Series and Waters 1525 Delta system with Daicel chiral OJ-H and AD-H columns and with *i*-PrOH/*n*-hexane as the eluent. Elemental analysis was performed on an Elementar Analysensysteme GmbH VarioEL V3.00 elemental analyzer. FT-IR spectra were recorded on a Nicolet NEXUS 670 instrument. The nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020M system. Solid-state NMR experiments were performed on a Bruker Avance II WB 400 MHz spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with the contact time of 2 ms (ramp 100) and the pulse delay of 3 s. Surface morphologies and microstructures of the synthesized materials were examined with a Hitachi S-4800 scanning electron microscope (SEM) and with a JEOL JEM-2010 transmission electron microscope (TEM) operated at 200 KV. Thermal properties of the synthesized materials were evaluated on a STA PT1600 Linseis thermogravimetric analysis (TGA) instrument in

the temperature range of 25 to 800 °C under nitrogen atmosphere with a heating rate of 10 °C/min. Powder X-ray diffraction (PXRD) data were collected with a Rigaku D/MAX-2400 X-ray diffractometer operated at 40 kV and 100 mA with Cu Kα radiation at a scan rate of 15°/min.

B. Materials and synthesis

Materials. All reagents were purchased from commercial sources and used as received without further purification. THF and toluene were dried over Na-benzophenone prior to distillation. DMF was dried by calcium hydride and used after distillation. $[Pd(PPh_3)_2Cl_2]$ and 1,3,5-triethynylbenzene was prepared and purified according to the literature procedures. All anhydrous reactions were carried out under dry nitrogen by using Schlenk tube techniques. All catalytic reactions were performed in a 5 mL centrifuge tube.

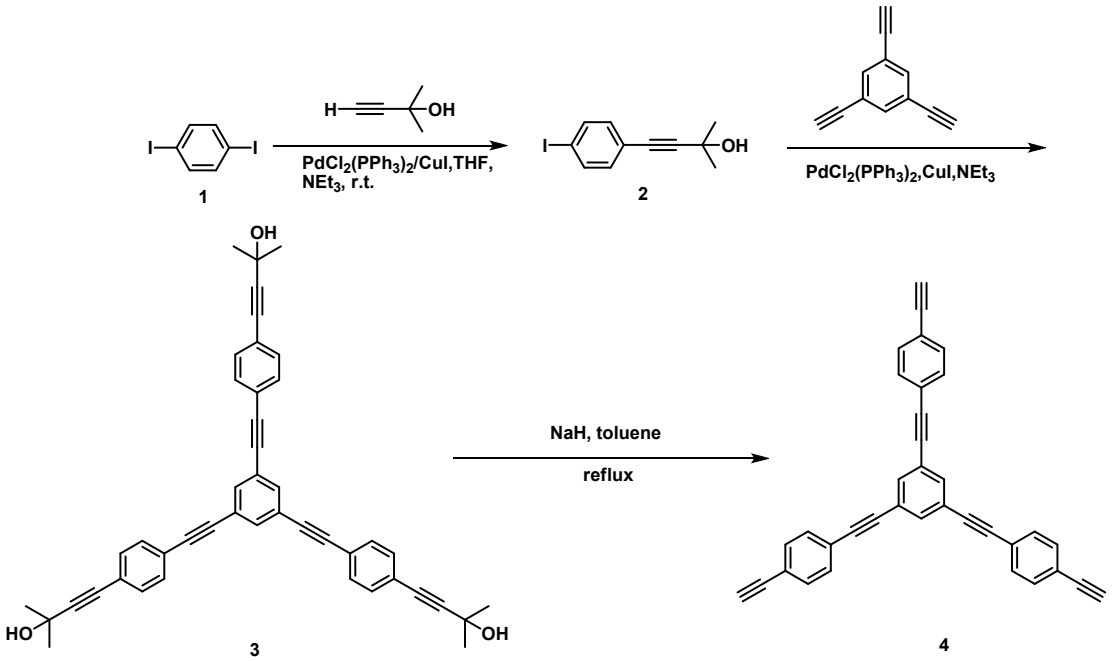
(I) Synthesis of the chiral functional building block (FBB-Mac)[1]



To a suspension of 3,5-diiodo-(L)-tyrosine dehydrate **1** (4.69 g, 10 mmol) in ice-cooled dry methanol (30 mL) was added dropwise thionyl chloride (2.38 g, 20 mmol). After the solution was stirred at room temperature overnight, the solvent was removed under reduced pressure to give quantitatively 3,5-diiodo-(L)-tyrosine methyl ester hydrochloride **2** as colorless crystalline solid, which was directly used in the next step without further purification. To a solution of 33% ethanolic $MeNH_2$ (1.53 g, 15 mmol) was added **2** (2.42 g, 5 mmol) and the resulting solution was stirred at room temperature until the amino ester was consumed as determined by TLC. After removal of the organic solvents under vacuum, the residue was then suspended in Et_2O and concentrated. The Et_2O addition–removal cycle was repeated several times

to remove excess $MeNH_2$. The obtained amide hydrochloride **3** was treated with saturated aqueous $NaHCO_3$ (20 mL) and stirred for 30 min. The resulting mixture was filtered and the residue was desiccated under vacuum. To this residue was added MeOH (25 mL), acetone (40 mL) and *p*TSA (50 mg). The resulting solution was heated to reflux for 24 h and concentrated under vacuum to afford the crude product, which was recrystallized further from MeOH to provide **FBB-Mac** as white solid in 70% overall yield. ^{1}H NMR (400 MHz, d_6-DMSO): δ (ppm) 9.31 (s, 1H), 7.64 (s, 2H), 3.57 (d, J = 7.3 Hz, 2H), 3.34 (s, 1H), 2.87 (d, J = 13.7 Hz, 2H), 2.64 (s, 3H), 1.20 (s, 3H), 1.18 (s, 3H). 13C NMR (100 MHz, d6-DMSO): δ (ppm) 172.5, 153.5, 139.7, 135.2, 86.8, 75.1, 58.9, 35.7, 27.1, 24.9, 24.7. RMS m/z calcd for $C_{13}H_{16}I_2N_2O_2$ (M+H): 486.9374, found: 486.9360.

(II) Synthesis of 1,3,5-tris((4-ethynylphenyl)ethynyl)benzene[2]

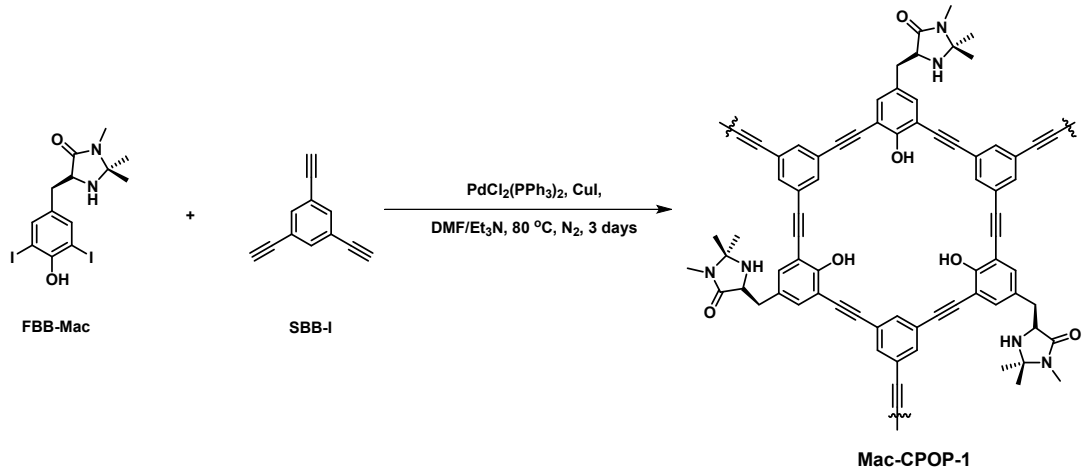


To a solution of 1,4-diiodobenzene **1** (2.00 g, 6.06 mmol) in THF (10 mL) and NEt_3 (6 mL) was added $PdCl_2(PPh_3)_2$ (255 mg, 0.36 mmol) and CuI (72 mg, 0.36 mmol). The solution was degassed with argon for 30 min. 2-Methyl-3-butyn-2-ol (510 mg, 60.06 mmol) was then added dropwise and the solution was stirred overnight at room temperature. The solvent was removed by rotary evaporation and the residue was treated with water and extracted with dichloromethane. The organic extracts were washed with water, brine, and dried over magnesium sulfate. The solvent was then

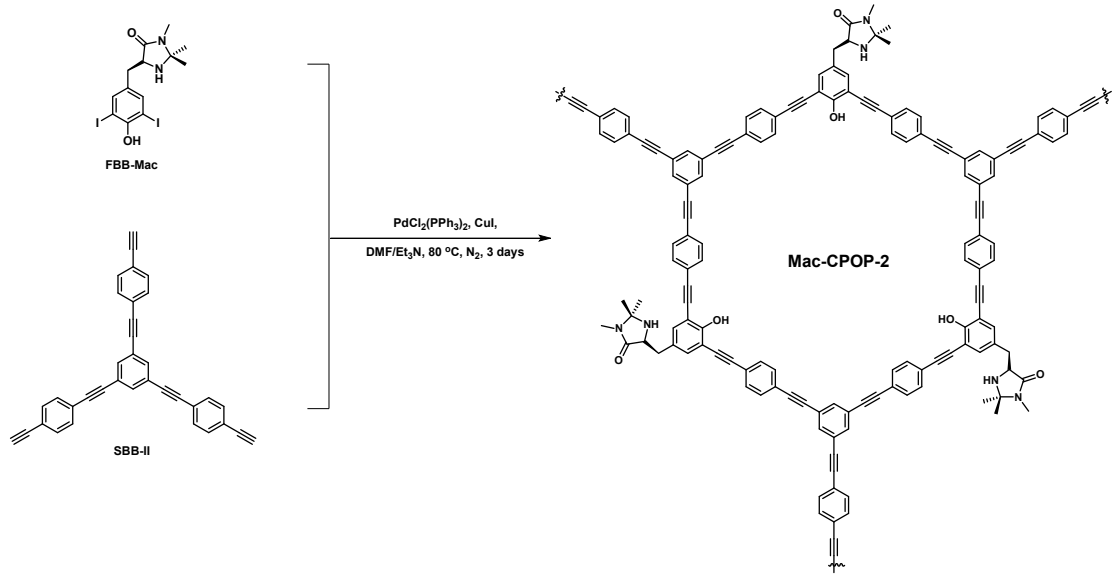
removed by rotary evaporation and the residue was purified by column chromatography on silica gel, eluting with ethyl acetate-petroleum ether (v/v 10/60) to give **2** (820 mg, 47 % yield)**.** $PdCl_2(PPh_3)_2$ (22 mg, 0.0315 mmol) and CuI (30 mg, 0.16 mmol) were added to a solution of 1,3,5-triethynylbenzene (95 mg, 0.63 mmol) and **2** (540 mg, 1.89 mmol) in NEt_3 (35 mL). The mixture was stirred for 2 h and then filtered through a glass sinter. The filtrate was reduced to dryness *in vacuo*. The residue was purified by column chromatography on silica gel, eluting with ethyl acetate-petroleum ether (v/v 10/10) Removal of the solvent afforded **3** as brown solid (318 mg, 81 % yield). To a solution of **3** (318 mg, 0.51 mmol) in anhydrous toluene (10 mL) was added sodium hydride (48 mg, 2.04 mmol). The solution was refluxed for 3 h at 130 °C. The solvent was then removed by rotary evaporation and the residue was treated with NH_4Cl and extracted with dichloromethane. The organic extracts were washed with water, and then brine, and dried over magnesium sulfate. The solvent was removed by rotary evaporation And the residue was purified by column chromatography on silica gel, eluting with ethyl acetate-petroleum ether (v/v 10/60) to give 1,3,5-tris((4-ethynylphenyl)ethynyl)benzene **4** (172 mg, 75 % yield) as light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.65 (s, 3H); 7.48 (s, 12H); 3.19 (s, 3H). ^{13}CNMR (100 MHz, $CDCl_3$): δ (ppm) 134.2, 132.1, 131.6, 123.9, 123.2, 122.4, 90.1, 89.6, 83.2, 79.2.

(III) Synthesis of MacMillan catalyst-based porous organic polymers (Mac-CPOP-1 and Mac-CPOP-2)[3]

The Mac-CPOPs frameworks were synthesized via palladium catalyzed Sonogashira-Hagihara coupling reaction of functional building block (FBB-Mac) with different structural building blocks: (1,3,5-triethynylbenzene (SBB-I) or 1,3,5-tris((4-ethynylphenyl)ethynyl)benzene (SBB-II).



SBB-I (100 mg, 0.67 mmol), **FBB-Mac** (486 mg, 1.00 mmol), bis-(triphenylphosphine)palladium(II) dichloride (75 mg), and copper iodide (45 mg) were dissolved in a mixture of dried dimethylformamide (5 mL) and Et_3N (5 mL). The reaction mixture was heated to 80 °C and stirred for 72 h under nitrogen atmosphere. The mixture was then cooled to room temperature, and the precipitated **Mac-CPOP-1** polymer was filtered and washed four times (once each) with chloroform, water, methanol, and acetone to remove any unreacted substrates or catalyst residues. Further purification of the **Mac-CPOP-1** polymer was carried out by Soxhlet extraction with methanol for 48 h. The product was dried in vacuum for 24 h at 70 °C (308 mg, yield: 93%). Elemental analysis (%) Found: C 68.59, H 4.72, N 6.25. Solid-state ^{13}C CP/MAS NMR: δ 173, 155, 130, 123, 107, 90, 75, 59, 35, 25 ppm. IR (KBr): 3440, 3065, 2205, 1610, 1538, 1500, 1409, 826 cm^{-1}.



SBB-II (63 mg, 0.14 mmol), **FBB-Mac** (102 mg, 0.21 mmol), bis-(triphenylphosphine)palladium(II) dichloride (30 mg), and copper iodide (15 mg) were dissolved in a mixture of dried dimethylformamide (2 mL) and Et_3N (2 mL). The reaction mixture was heated to 80 °C and stirred for 72 h under nitrogen atmosphere. The mixture was then cooled to room temperature, and the precipitated **Mac-CPOP-2** polymer was filtered and washed four times (once each) with chloroform, water, methanol, and acetone to remove any unreacted substrates or catalyst residues. Further purification of the **Mac-CPOP-2** polymer was carried out by Soxhlet extraction with methanol for 48 h. The product was dried in vacuum for 24 h at 70 °C (105 mg, yield: 95%). Elemental analysis (%) Found: C 71.11, H 4.27, N 3.39. Solid-state ^{13}C CP/MAS NMR: δ 173, 155, 139, 131, 123, 90, 75, 59, 35, 31, 24 ppm. IR (KBr): 3434, 3035, 2922, 2858, 2205, 1676, 1575, 1390, 833 cm^{-1}.

C. Physical properties for Mac-CPOP-1 and Mac-CPOP-2

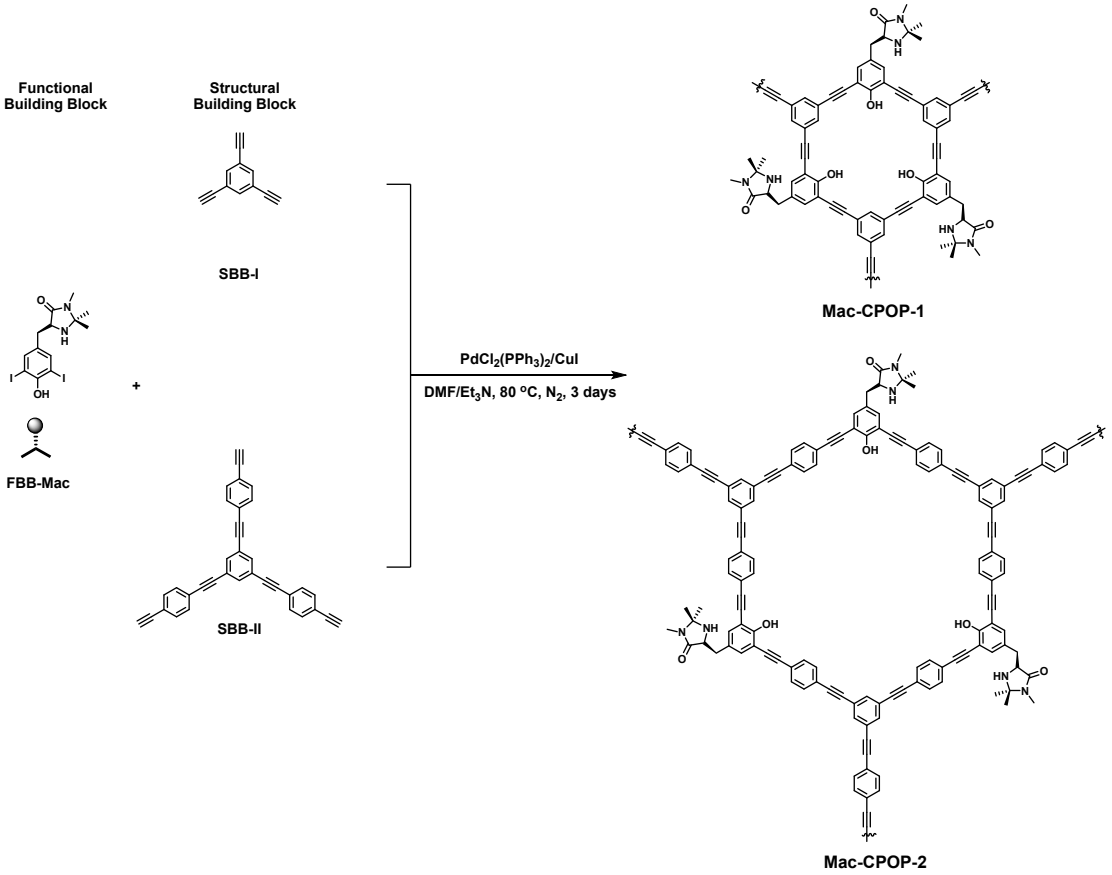


Table S1. Physical properties for the synthesized CPOPs polymers

Polymer	Building Blocks		Molar Ratio	SA_{BET}	V_{total}	Catalyst Loading
	Functional	Structural		$(m^2\ g^{-1})$[a]	$(cm^3\ g^{-1})$[b]	$(mmol\ g^{-1})$[c]
Mac-CPOP-1	FBB-Mac	SBB-I	3:2	5.9	0.19	2.23
Mac-CPOP-2	FBB-Mac	SBB-II	3:2	468	0.62	1.21

[a] Surface area (SA) calculated from the N_2 adsorption isotherm using the BET method. [b] Total pore volume at $P/P_o = 0.99$. [c] Catalyst loading calculated from elemental analysis.

D. N_2 adsorption-desorption isotherms of Mac-CPOP-1

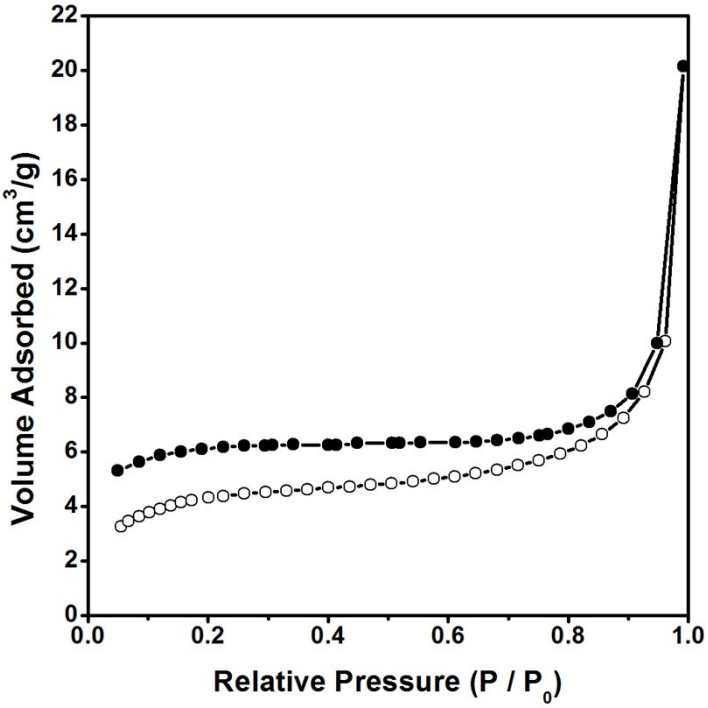


Figure S1. N_2 adsorption–desorption isotherms for Mac-CPOP-1 measured at 77 K.

E. The geometries of the reactants and products

The geometries of the reactants and products of the the Diels-Alder reaction were optimized with the Gaussian 09 package[4], using a B3LYP density function and the 6-31G(d, p) method. The three dimensional sizes of the reactants and products were approximately measured based the optimized geometries, such as 7.1 × 9.1 × 1.0 Å for (*E*)-cinnamaldehyde, 5.4 × 4.8 × 2.8 Å for cyclopentadiene, 10.2 × 6.4 × 5.2 Å for *endo* cycloaddition product, and 9.3 × 6.6 × 5.2 Å for *exo* cycloaddition product.

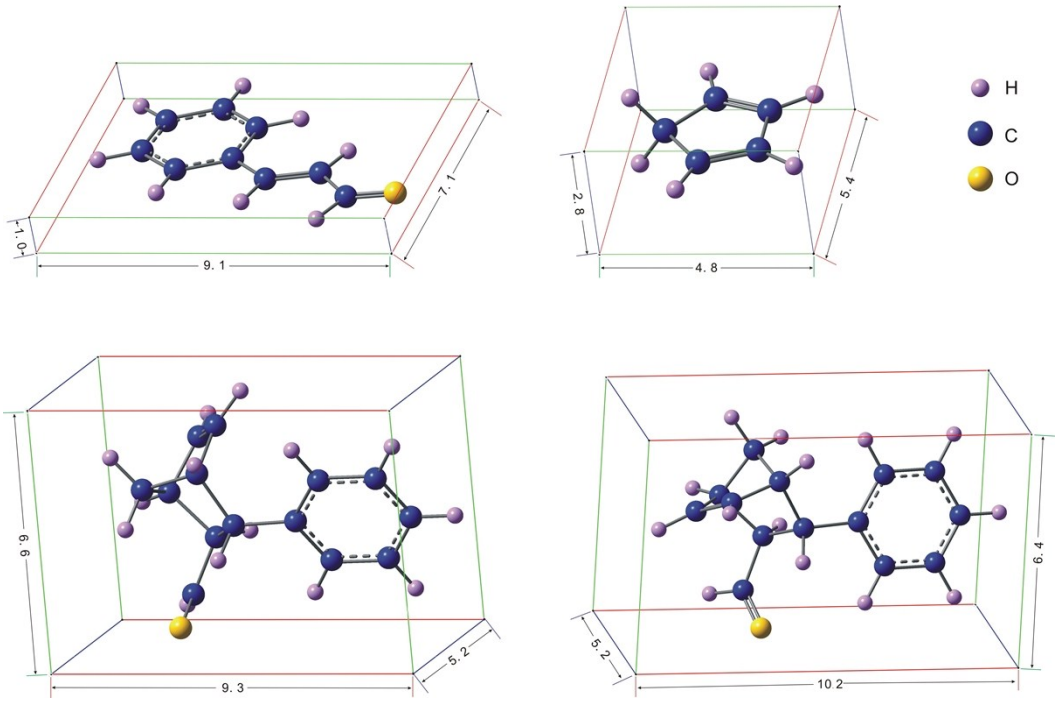


Figure S2. The geometries of the reactants and products

F. ^{13}C CP/MAS NMR spectrum for Mac-CPOP-1

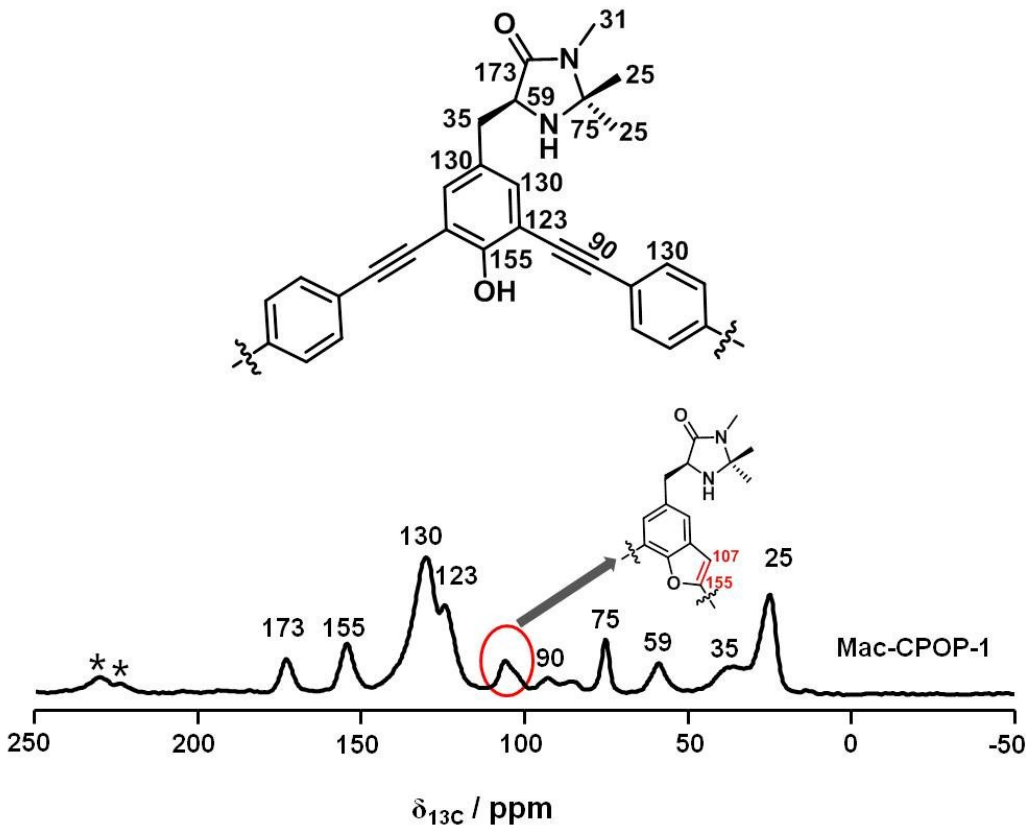


Figure S3. ^{13}C CP/MAS NMR spectra of **Mac-CPOP-1**. The spectrum was recorded at an MAS rate of 10 kHz. Asterisks denote spinning sidebands. the peak at ca. 102 ppm and 107 ppm corresponds to the carbon atoms of phenylbenzo[b]furan structure, which was formed under Pd/Cu catalytic conditions.

G. FT-IR spectra for fresh and recycled catalysts

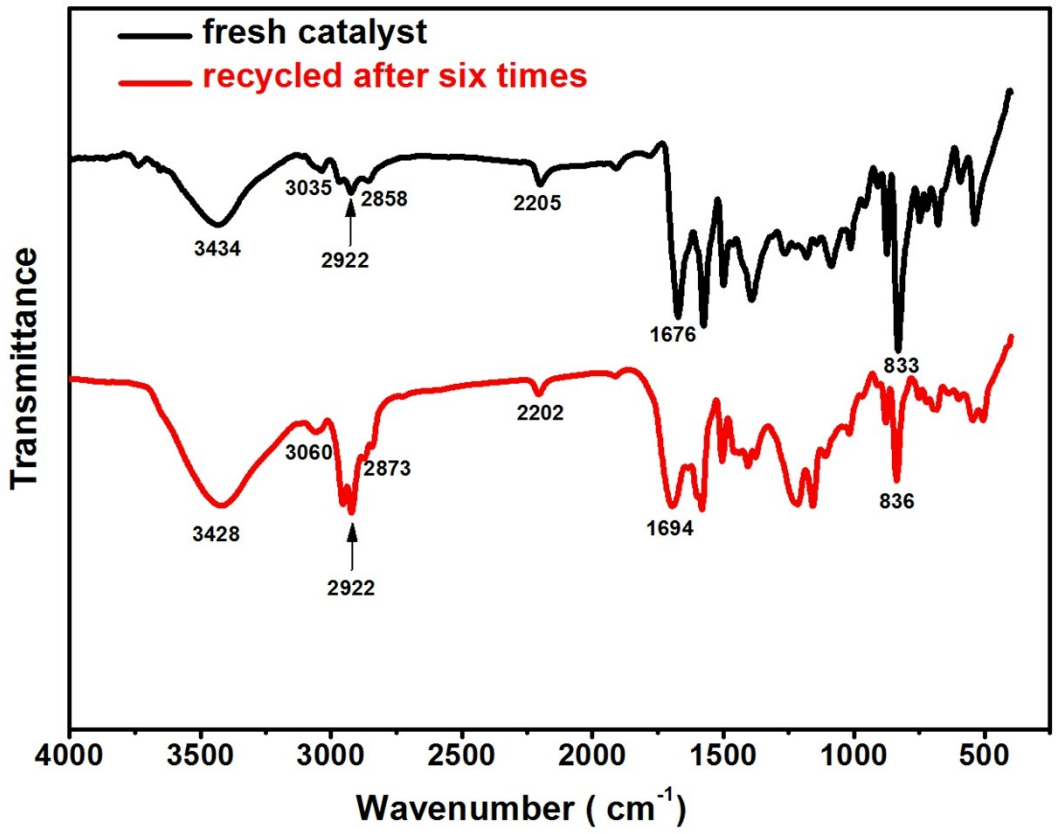


Figure S4. FT-IR spectra of **Mac-CPOP-2** as the fresh catalyst (in black) and as the recycled catalyst after six-time catalytic reactions (in red).

H. SEM images for Mac-CPOP-1

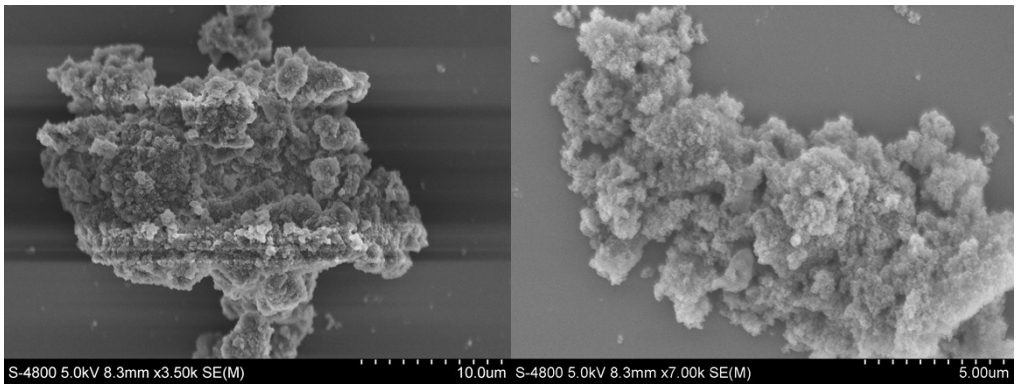


Figure S5. SEM images for Mac-CPOP-1

I. Powder X-Ray diffraction for Mac-CPOP-2

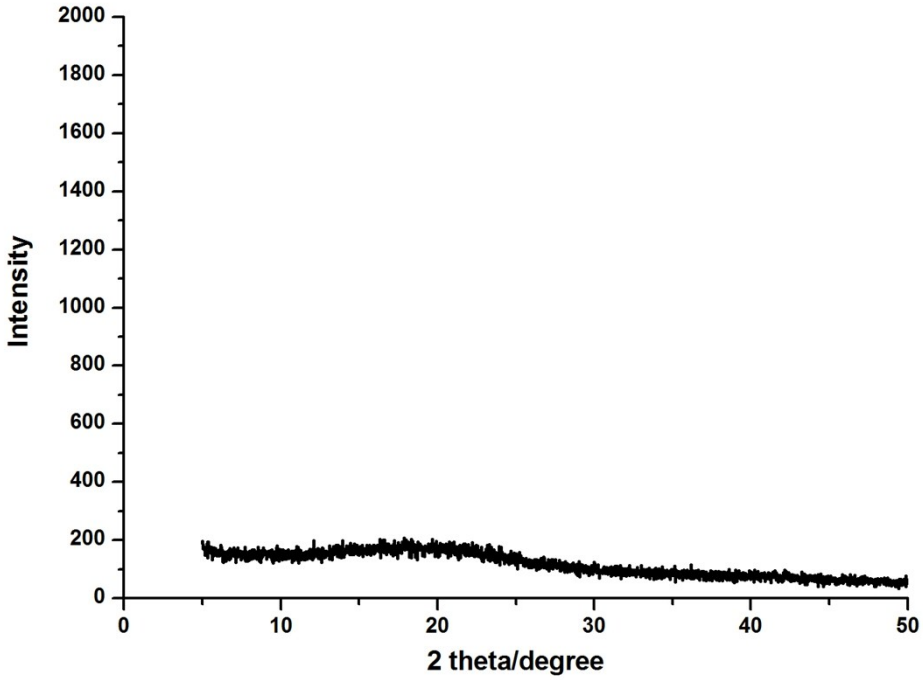


Figure S6. Powder X-ray diffraction pattern of **Mac-CPOP-2**. No intensive diffraction peaks were observable.

J. TGA for Mac-CPOP-1 and Mac-CPOP-2

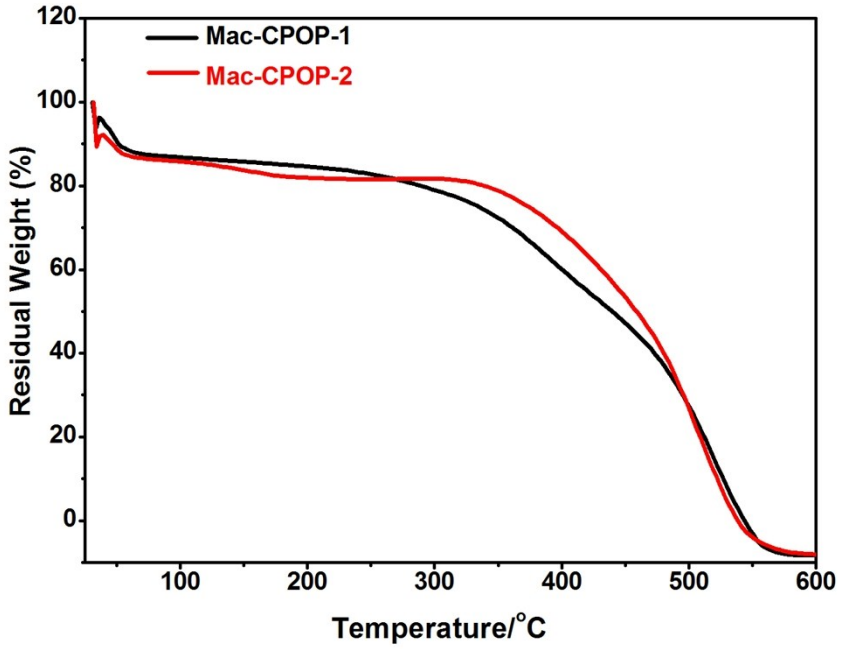


Figure S7. TGA analysis of **Mac-CPOP-2** and Mac-CPOP-2 under nitrogen atmosphere.

K. ^{13}C CP/MAS NMR spectra for fresh and recycled catalysts

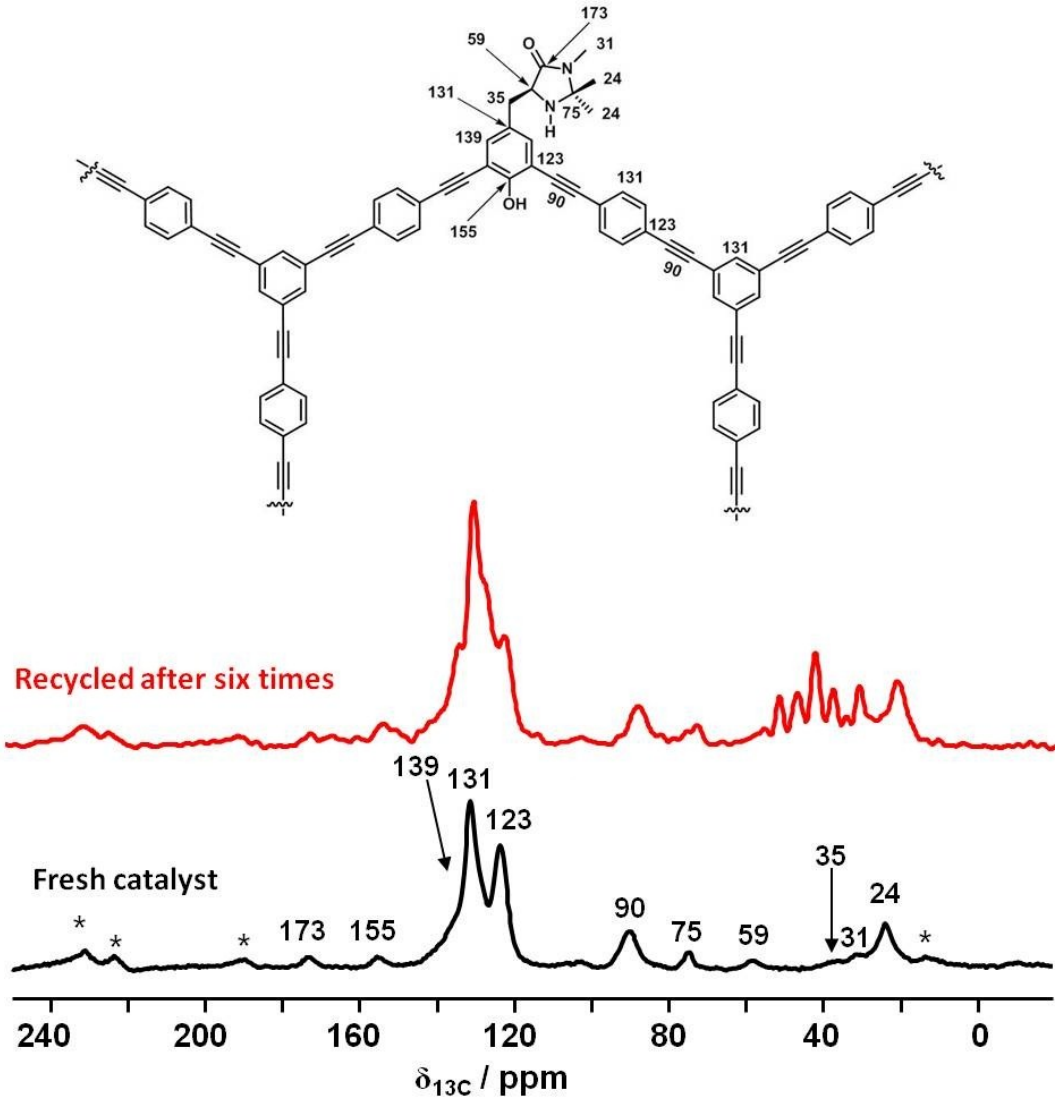


Figure S8. Solid-state ^{13}C CP/MAS NMR spectra of **Mac-CPOP-2** as fresh catalyst (in black), and as recycled catalysts after six-time catalytic reactions (in red). Each ^{13}C CP/MAS spectra was recorded at an MAS rate of 10.0 kHz and reported relative to Me_4Si. Asterisks denote spinning sidebands. It was evident that the structure of **Mac-CPOP-2** catalyst was not destroyed after catalytic reactions. However, little change in the high-field region (0 to 50 ppm) of ^{13}C solid-state NMR spectra should not be overlooked.

L. N_2 adsorption-desorption isotherms of the recycled Mac-CPOP-2

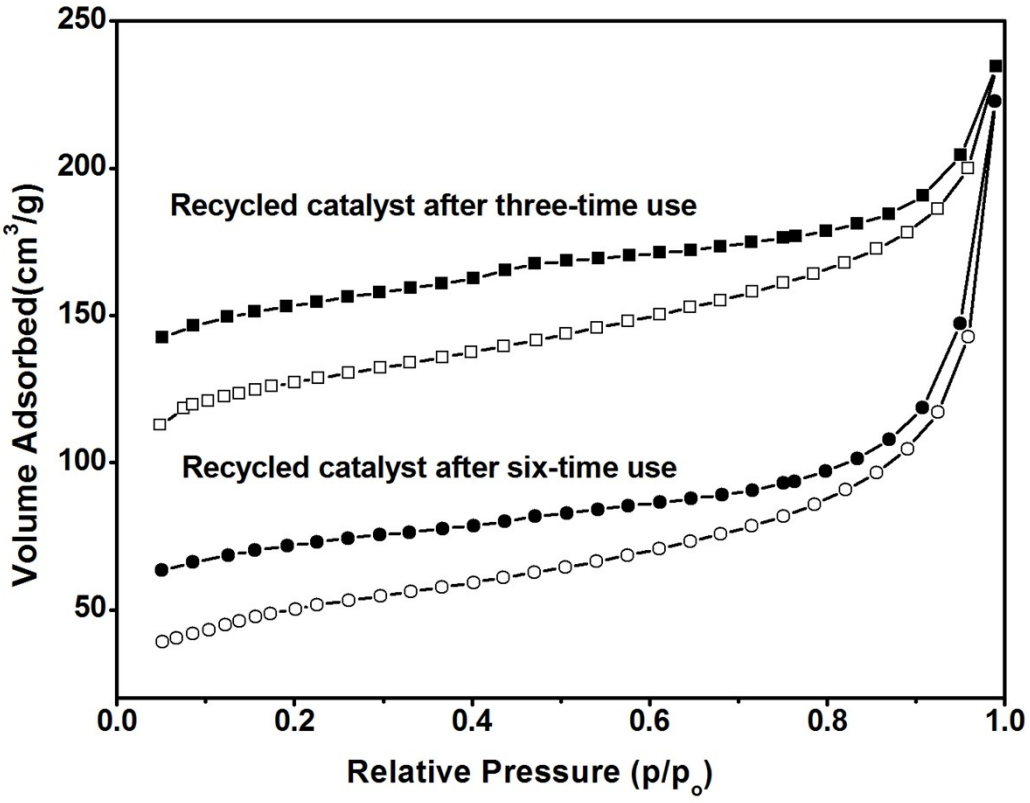
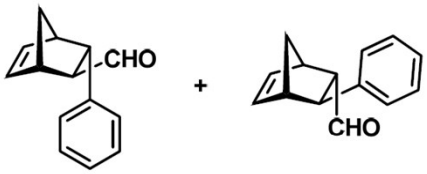


Figure S9. N_2 adsorption-desorption isotherms of **Mac-CPOP-2** as recycled catalyst after three-time catalytic reactions and six-time catalytic reactions. We found that the BET surface of **Mac-CPOP-2** had decreased 180 m^2g^{-1} after the sixth recycled used, which could be due to the partial blocking of the polymeric nanopores.

M. General procedure for the asymmetric Diels-Alder reaction[1]

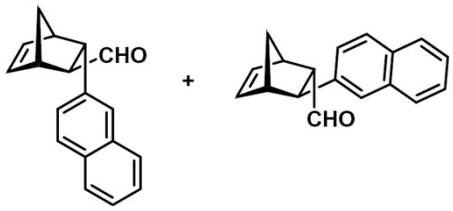
To a stirred solution of **Mac-CPOP-2** (0.04 mmol, 33 mg, 20 mol%) in a 3/1 H_2O/MeOH mixture (1.0 mL), trifluoroacetic acid (0.05 mmol) was added and the mixture was stirred for 5 min at room temperature. α, β-Unsaturated aldehyde (0.2 mmol, 1.0 eq) used soon after purification and cyclopentadiene (1.0 mmol, 5.0 eq) were added in this order. The mixture was then stirred at ambient temperature in open air. After the reaction was completed (monitored by TLC), the mixture was centrifugated and the solid catalyst was washed with MeOH (2 x 5.0 mL) and EtOAc (3 x 5.0 mL). After the evaporation of the combined organic phase under vacuum, the residue was purified by flash column chromatography with petroleum ether/ethyl acetate mixture as eluent to give the product as oil. Ratio of *endo* and *exo* was determined by 400 MHz ^{1}H liquid NMR. The products were converted to the corresponding alcohols with $NaBH_4$ and the enantiomers were separated by HPLC using a Daicel chiral OJ-H or AD-H column.

(1S, 2S, 3S, 4R)-3-Phenylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde and (1R, 2S, 3S, 4S)-3-Phenylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Table 2, entry 1).



Prepared according to the general procedure with (*E*)-cinnamaldehyde and cyclopentadiene. The products were collected as a colorless oil in 95% yield after silica gel chromatography (hexane:ethyl acetate = 10:1); *endo* 81% ee, *exo* 75% ee. The products were converted to the corresponding alcohols with $NaBH_4$ and the enantiomers were separated by HPLC using a Daicel chiral OJ-H column at 230 nm (70/30 hexane/i-PrOH; flow rate 0.75 ml/min) *endo* isomer [T_R1 = 14.69 min (major), T_R2 = 9.27 min (minor)], *exo* isomer [T_R1 = 23.18 min (major), T_R2 = 18.03 min (minor)]. Spectroscopic data are in agreement with the published data.[1]

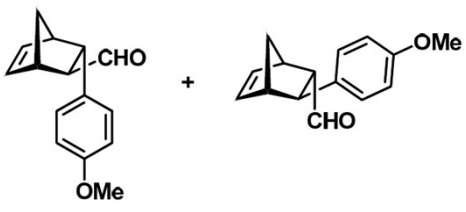
(1S, 2S, 3S, 4R)-3-(2-Naphtyl)-bicyclo[2.2.1]hex-5-ene-2-carboxaldehyde and (1R, 2S, 3S, 4S)-3-(2-Naphtyl)-bicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Table 2, entry 2).[5]



Prepared according to the general procedure with 3-naphthalen-2-yl-propenal, and cyclopentadiene. The products were collected as a colorless oil in 70% yield after silica gel chromatography (hexane:ethyl acetate=10:1); *endo* 73% ee, *exo* 75% ee. The products were converted to the corresponding alcohols with $NaBH_4$ and the enantiomers were separated by HPLC using a Daicel chiral OJ-H column at 230 nm (70/30 hexane/i-PrOH; flow rate 0.75 ml/min); endo isomer [T_R1= 12.24 min (major), T_R2 = 9.03 min (minor)], exo isomer [T_R1 = 16.97 min (major), T_R2 = 10.96 min (minor)].

^{1}H NMR (400 MHz, $CDCl_3$) ***exo*** isomer: δ 9.99 (d, J = 2.0 Hz, 1H), 7.83–7.32 (m, 7H), 6.39 (dd, J = 5.6, 3.2 Hz, 1H), 6.11 (dd, J = 5.6, 2.9 Hz, 1H), 3.93–3.90 (m, 1H), 3.33 (s, 1H), 3.28-3.27 (m, 1H), 2.75–2.74(m, 1H), 1.92-1.61 (m, 2H). ***endo*** isomer: δ 9.67 (d, J = 2.1 Hz, 1H), 7.83–7.32 (m, 7H), 6.49 (dd, J = 5.6, 3.3 Hz, 1H), 6.23 (dd, J = 5.6, 2.8 Hz, 1H), 3.40 (s, 1H), 3.28-3.27 (m, 2H), 3.10–3.09 (m, 1H), 1.92-1.61 (m, 2H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 202.7, 141.1, 140.0, 139.2, 136.6, 136.3, 133.8, 133.5, 133.2, 132.2, 132.1, 128.2, 127.7, 127.7, 127.6, 127.5, 127.5, 126.7, 126.6, 126.1, 126.0, 125.9, 125.5, 125.4, 124.8, 60.8, 59.2, 48.5, 48.3, 47.6, 47.2, 45.9, 45.6, 45.5, 45.2.

(1S, 2S, 3S, 4R)-3-o-Methoxyphenylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde and (1R, 2S, 3S, 4S)-3-o-Methoxyphenylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Table 2, entry 3).[6]

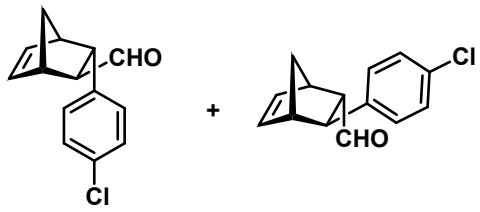


Prepared according to the general procedure with 3-(4-methoxyphenyl)propenal, and cyclopentadiene. The products were collected as a pale yellow oil in 64% yield after silica gel chromatography (hexane:ethyl acetate=10:1); *endo* 91% ee, *exo* 88% ee. The products were converted to the corresponding alcohols with $NaBH_4$ and the enantiomers were separated by HPLC

using a Daicel chiral OJ-H column at 230 nm (90/10 hexane/i-PrOH; flow rate 0.75 ml/min); endo isomer [T_R1= 22.78 min (major), T_R2 = 18.97 min (minor)], exo isomer [T_R1 = 30.59 min (major), T_R2 = 20.12 min (minor)].

^{1}H NMR (400 MHz, $CDCl_3$) ***exo*** isomer: δ 9.91 (d, J = 2.1 Hz, 1H), 7.07 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.8 Hz, 2H), 6.34 (dd, J = 5.6, 3.2 Hz, 1H), 6.08 (dd, J = 5.6, 2.8 Hz, 1H), 3.78 (s, 3H), 3.67–3.65 (m, 1H), 3.21–3.18 (m, 1H), 3.02 (t, J = 6.1 Hz, 1H), 2.54-2.53 (m, 1H), 1.63-1.54 (m, 2H). ***endo*** isomer: δ 9.58 (d, J = 2.3 Hz, 1H), 7.19 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), , 6.42 (dd, J = 5.6, 3.2 Hz, 1H), 6.17 (dd, J = 5.6, 2.7 Hz, 1H), 3.80 (s, 3H), 3.32 (s, 1H), 3.21–3.18 (m, 1H), 3.07 (s, 1H), 2.95–2.93 (m, 1H), 1.79 (d, J = 8.7 Hz, 1H), 1.63-1.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.7, 202.9, 158.1, 158.0, 139.2, 136.5, 136.3, 135.6, 134.6, 133.7, 128.8, 128.3, 114.0, 113.5, 60.9, 59.7, 55.3, 55.2, 48.7, 48.6, 47.6, 47.1, 45.5, 45.1, 45.1, 44.8.

(1S, 2S, 3S, 4R)-3-p-Chlorophenylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde and (1R, 2S, 3S, 4S)-3-p-Chlorophenylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Table 2, entry 4).[6]

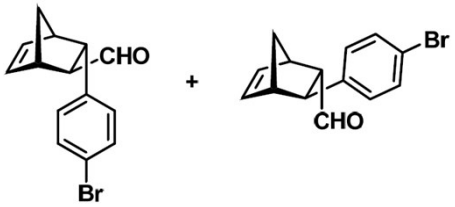


Prepared according to the general procedure with 3-(4-chlorophenyl)propenal, and cyclopentadiene. The products were collected as a pale yellow oil in 76% yield after silica gel chromatography (hexane:ethyl acetate=6:1); *endo* 95% ee, *exo* 93% ee. The products were converted to the corresponding alcohols with $NaBH_4$ and the enantiomers were separated by HPLC using a Daicel chiral OJ-H column at 230 nm (90/10 hexane/i-PrOH; flow rate 0.75 ml/min); endo isomer [T_R1= 21.18 min (major), T_R2 = 26.19 min (minor)], exo isomer [T_R1 = 30.12 min (major), T_R2 = 47.91 min (minor)].

^{1}H NMR (400 MHz, $CDCl_3$) ***exo*** isomer: δ 9.91 (d, J = 2.0 Hz, 1H), 7.30-7.06 (m, 4 H), 6.36 (dd, J = 5.6, 3.2 Hz, 1H), 6.05 (dd, J = 5.6, 2.8 Hz, 1H), 3.71–3.68 (m, 1H), 3.24–3.10 (m, 1H), 3.05 (d, J = 4.8 Hz, 1H), 2.54 (d, J = 5.2 Hz, 1H), 1.65–1.55 (m, 2H). ***endo*** isomer: δ 9.60 (d, J = 2.0 Hz, 1H), 7.30-7.06 (m, 4 H), 6.42 (dd, J = 5.6,

3.3 Hz, 1H), 6.18 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.36 (s, 1H), 3.24-3.10 (m, 2H), 2.93–2.91 (m, 1H), 1.76 (d, *J* = 8.8 Hz, 1H), 1.65–1.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 202.4, 142.1, 141.2, 139.1, 136.5, 136.3, 133.8, 132.1, 131.9, 129.2, 129.1, 128.6, 128.2, 61.0, 59.6, 48.4, 48.2, 47.6, 47.1, 45.5, 45.1, 45.0, 44.7.

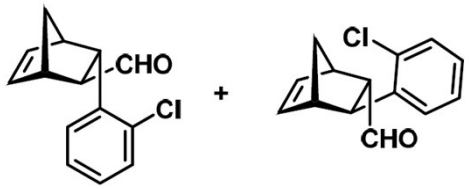
(1S, 2S, 3S, 4R)-3-p-Bromophenylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde and (1R, 2S, 3S, 4S)-3-p-Bromophenylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Table 2, entry 5).[5]



Prepared according to the general procedure with 3-(4-bromophenyl)propenal, and cyclopentadiene. The products were collected as a pale yellow oil in 80% yield after silica gel chromatography (hexane:ethyl acetate=6:1); *endo* 80% ee, *exo* 74% ee. The products were converted to the corresponding alcohols with $NaBH_4$ and the enantiomers were separated by HPLC using a Daicel chiral OJ-H column at 230 nm (90/10 hexane/i-PrOH; flow rate 0.75 ml/min); endo isomer [T_R1= 20.42 min (major), T_R2 = 9.94 min (minor)], exo isomer [T_R1 = 27.55 min (major), T_R2 = 11.81 min (minor)].

^{1}H NMR (400 MHz, $CDCl_3$) ***exo*** isomer: δ 9.91 (d, *J* = 2.0 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 3H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.36 (dd, *J* = 5.6, 3.2 Hz, 1H), 6.05 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.71–3.68 (m, 1H), 3.24–3.10 (m, 1H), 3.05 (d, *J* = 4.8 Hz, 1H), 2.54 (d, *J* = 5.2 Hz, 1H), 1.65–1.55 (m, 2H). ***endo*** isomer: δ 9.60 (d, *J* = 2.0 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.42 (dd, *J* = 5.6, 3.3 Hz, 1H), 6.18 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.36 (s, 1H), 3.24-3.10 (m, 2H), 2.93–2.91 (m, 1H), 1.76 (d, *J* = 8.8 Hz, 1H), 1.65–1.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.9, 202.2, 142.6, 141.6, 139.1, 136.5, 136.2, 133.8, 131.6, 131.2, 129.6, 129.1, 120.1, 120.0, 60.9, 59.5, 48.3, 48.2, 47.6, 47.0, 45.4, 45.2, 45.0, 44.8.

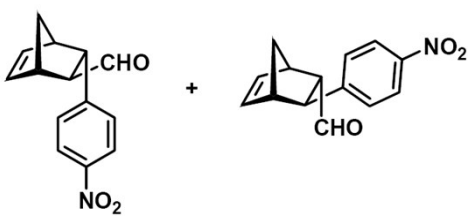
(1S, 2S, 3S, 4R)-3-o-Chlorophenylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde and (1R, 2S, 3S, 4S)-3-o-Chlorophenylbicyclo [2.2.1]hex-5-ene-2-carboxaldehyde (Table 4, entry 6).



Prepared according to the general procedure with 3-(*o*-Chlorophenyl)propenal, and cyclopentadiene. The products were collected as a pale yellow oil in 88% yield after silica gel chromatography (hexane:ethyl acetate=6:1); *endo* 93% ee, *exo* 55% ee. The Products were converted to the corresponding alcohols with $NaBH_4$ and the enantiomers were separated by HPLC using a Daicel chiral AD-H column (90/10 hexane/i-PrOH; flow rate 0.5 mL/min; endo isomer [T_R1= 14.72 min (major), T_R2 = 11.98 min (minor)], exo isomer (T_R1 = 13.72 min (major), T_R2 = 12.64 min (minor)].

^{1}H NMR (400 MHz, $CDCl_3$) ***exo*** isomer: δ 9.88 (d, J = 1.6 Hz, 1H), 7.38–6.97 (m, 5H), 6.40 (dd, J = 5.3, 3.2 Hz, 1H), 5.93 (dd, J = 5.3, 2.7 Hz, 1H), 4.18–4.16 (m, 1H), 3.30–3.26 (m, 2H), 2.63 (d, J = 5.2 Hz, 1H), 1.69 (d, J = 8.8 Hz, 1H), 1.56 (d, J = 8.8 Hz, 1H). ***endo*** isomer: δ 9.55 (d, J = 3.4 Hz, 1H), 7.38–6.97 (m, 5H), 6.47 (dd, J = 5.2, 3.4 Hz, 2H), 6.19 (dd, J = 5.5, 2.5 Hz, 1H), 3.37 (d, J = 4.4 Hz, 1H), 3.30–3.26 (m, 1H), 3.12 (s, 1H), 2.86 (dt, J = 10.0, 4.9 Hz, 1H), 1.77 (d, J = 8.8 Hz, 1H), 1.62 (d, J = 8.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.5, 202.3, 140.7, 139.3, 138.8, 136.4, 136.4, 135.0, 134.9, 134.2, 129.8, 129.4, 128.0, 127.5, 127.5, 127.1, 126.9, 126.2, 58.5, 58.1, 48.2, 47.8, 47.4, 47.3, 46.7, 46.1, 43.2, 42.0.

(1S, 2S, 3S, 4R)-3-p-Nitrophenylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde and (1R, 2S, 3S, 4S)-3-p-Nitrophenylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Table 2, entry 7).[5]

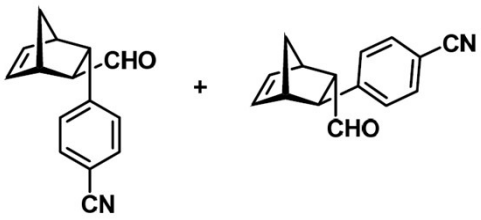


Prepared according to the general procedure

with 3-(4-nitrophenyl)propenal, and cyclopentadiene. The products were collected as a pale yellow oil in 90% yield after silica gel chromatography (hexane:ethyl acetate=6:1); *endo* 80% ee, *exo* 68% ee. The products were converted to the corresponding alcohols with $NaBH_4$ and the enantiomers were separated by HPLC using a Daicel chiral AD-H column (90/10 hexane/i-PrOH; flow rate 0.5 mL/min; endo isomer [T_R1= 35.25 min (major), T_R2 = 33.81 min (minor)], exo isomer (T_R1 = 38.20 min (major), T_R2 = 47.06 min (minor)] .

^{1}H NMR (400 MHz, $CDCl_3$) ***exo*** isomer: δ 9.92 (d, J = 1.5 Hz, 1H), 8.09 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.8 Hz, 2H), 6.40 (dd, J = 5.6, 3.2 Hz, 1H), 6.05 (dd, J = 5.6, 2.8 Hz, 1H), 3.89–3.87 (m, 1H), 3.30 (s, 1H), 3.25 (s, 1H), 2.62 (d, J = 4.8 Hz, 1H), 1.62 (d, J = 5.2 Hz, 2H). ***endo*** isomer: δ 9.64 (d, J = 1.5 Hz, 1H), 8.15 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 6.44 (dd, J = 5.6, 3.3 Hz, 1H), 6.20 (dd, J = 5.6, 2.8 Hz, 1H), 3.43 (s, 1H), 3.21–3.18 (m, 2H), 2.98–2.94 (m, 1H), 1.77 (d, J = 8.8 Hz, 1H), 1.70 (dd, J = 8.9, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 201.5, 151.6, 150.5, 146.5, 146.4, 139.0, 136.9, 135.9, 133.9, 128.6, 128.2, 123.8, 123.3, 61.1, 59.5, 48.4, 47.9, 47.6, 47.1, 45.6, 45.5, 45.2, 45.0.

(1S, 2S, 3S, 4R)-3-p-Cyanophenylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde and (1R, 2S, 3S, 4S)- 3-p-Cyanophenylbicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Table 2, entry 8).



Prepared according to the general procedure with 3-(4-cyanophenyl)propenal, and cyclopentadiene. The products were collected as a pale yellow oil in 80% yield after silica gel chromatography (hexane:ethyl acetate=6:1); *endo* 86% ee, *exo* 63% ee. The Products were converted to the corresponding alcohols with $NaBH_4$ and the enantiomers were separated by HPLC using a Daicel chiral OJ-H column at 230 nm (90/10 hexane/i-PrOH; flow rate 0.75 ml/min); endo isomer [T_R1= 23.76 min (major), T_R2 = 16.74 min (minor)], exo isomer [T_R1 = 33.28 min (major), T_R2 = 19.67 min (minor)].

^{1}H NMR (400 MHz, $CDCl_3$) ***exo*** isomer: δ 9.91 (d, J = 1.6 Hz, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 6.39 (dd, J = 5.6, 3.2 Hz, 1H), 6.04 (dd, J = 5.6, 2.8 Hz, 1H), 3.83–3.81 (m, 1H), 3.28 (s, 1H), 3.23 (s, 1H), 2.59 (d, J = 5.2 Hz, 1H), 1.62 (d, J = 14.0 Hz, 2H). ***endo*** isomer: δ 9.62 (d, J = 1.6 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H), 6.43 (dd, J = 5.5, 3.3 Hz, 1H), 6.19 (dd, J = 5.6, 2.8 Hz, 1H), 3.41 (s, 1H), 3.16 (d, J = 3.2 Hz, 2H), 2.96–2.88 (m, 1H), 1.75 (d, J = 8.8 Hz, 1H), 1.68 (dd, J = 8.8, 1.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.2, 201.6, 149.4, 148.3, 139.0, 136.8, 136.0, 133.9, 132.4, 131.9, 128.6, 128.1, 118.8, 110.2, 110.1, 61.0, 59.4, 48.3, 47.8, 47.6, 47.1, 45.7, 45.4, 45.3, 44.9.

(1S, 2S, 3S, 4R)-3-(2-Furyl)bicyclo[2.2.1]hex-5-ene-2-carboxaldehyde and (1R, 2S, 3S, 4S)-3-(2-Furyl)bicyclo[2.2.1]hex-5-ene-2-carboxaldehyde (Table 2, entry 9).[5]

Prepared according to the general procedure with 3-(2-furyl)propenal, and cyclopentadiene. The products were collected as a pale yellow oil in 66% yield after silica gel chromatography (hexane:ethyl acetate=6:1); *endo* 73% ee, *exo* 73% ee. The Products were converted to the corresponding alcohols with $NaBH_4$ and the enantiomers were separated by HPLC using a Daicel chiral OJ-H column at 230 nm (90/10 hexane/i-PrOH; flow rate 0.75 ml/min); endo isomer [T_R1= 18.67 min (major), T_R2 = 10.58 min (minor)], exo isomer [T_R1 = 21.61 min (major), T_R2 = 17.59 min (minor)]. Spectroscopic data are in agreement with the published data.[1]

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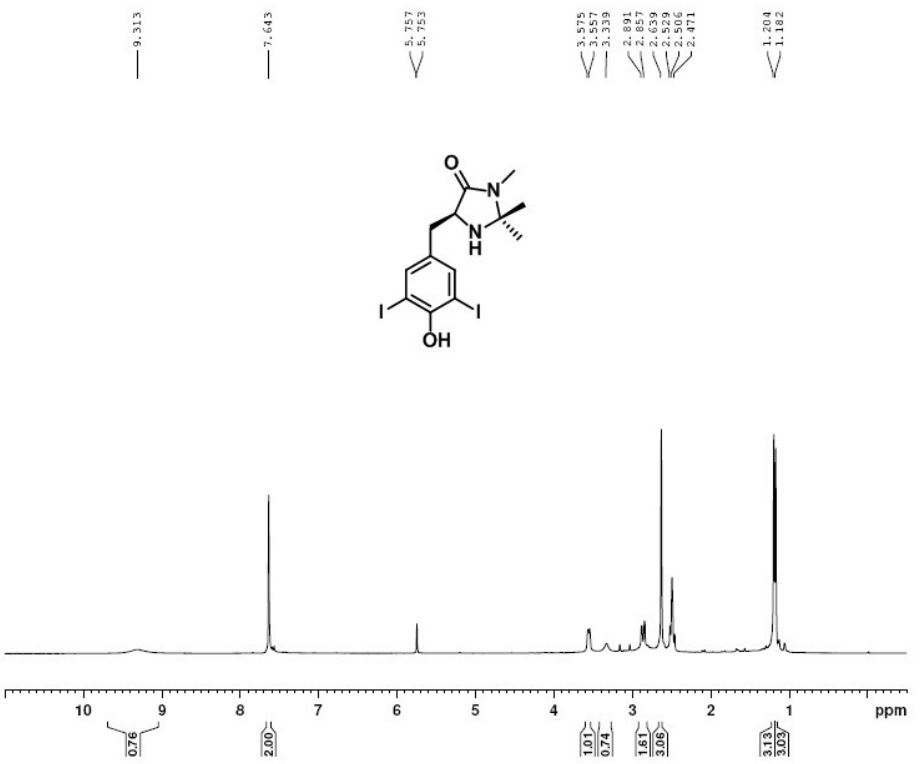
N. NMR and HPLC spectra for products

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NS                         16
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FIDRES           0.125483 Hz
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RG                        128
DW                  60.800 usec
DE                   6.50 usec
TE                  293.3 K
D1               1.00000000 sec
TD0                         1

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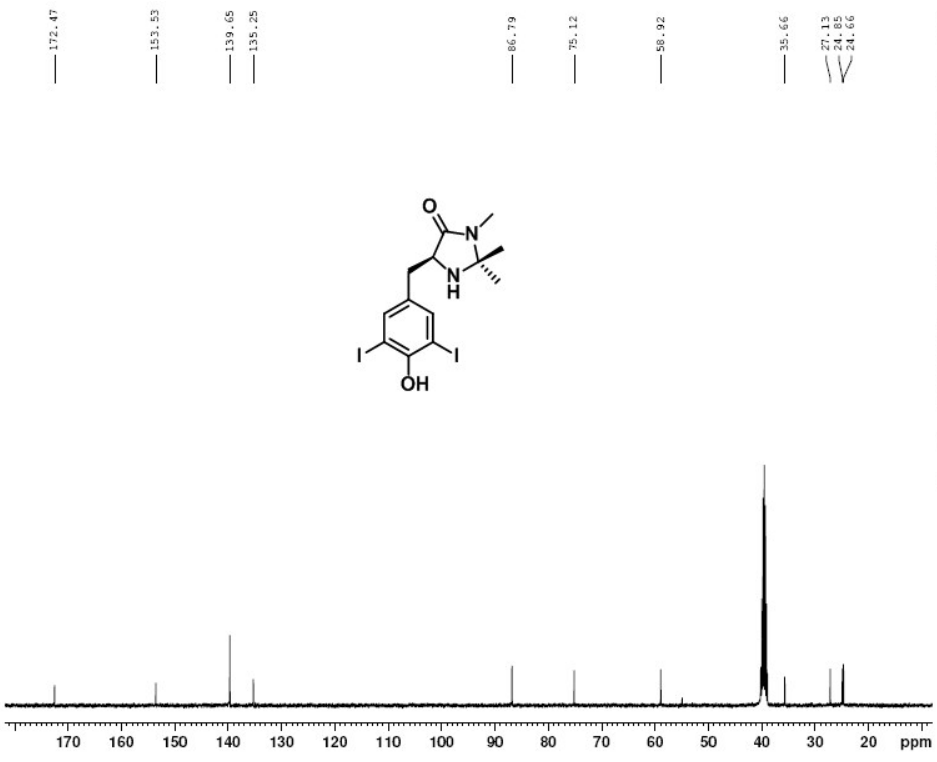


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TD0                         1

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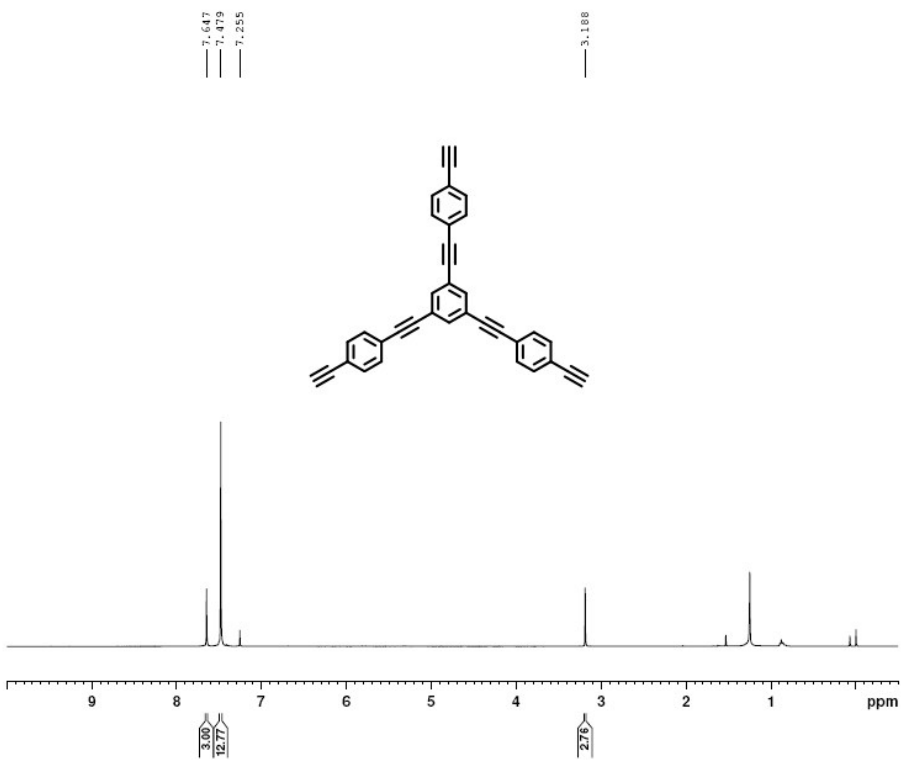


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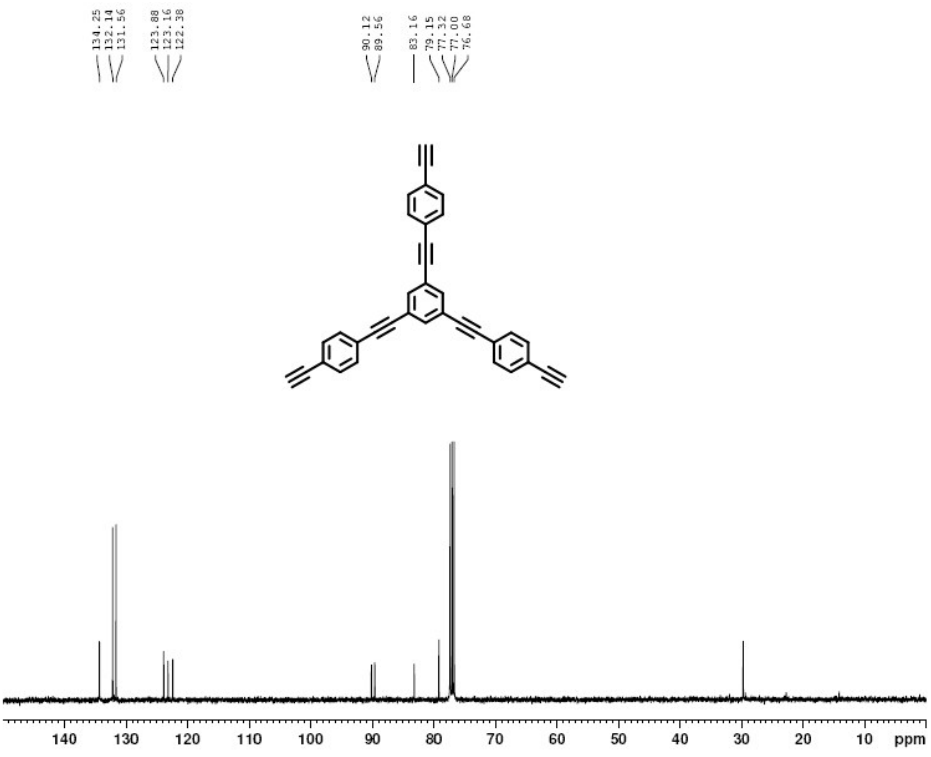


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TD0                         1

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PLW3             0.44513249 W
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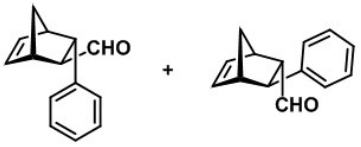


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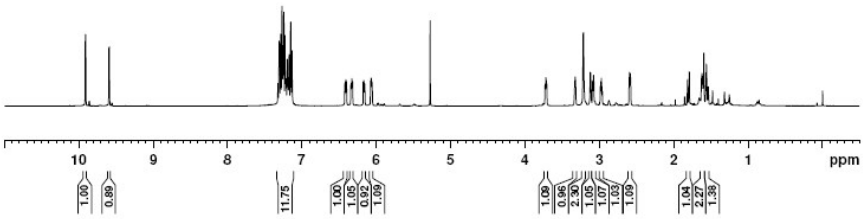
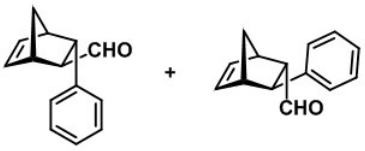
FIDRES                 0.125483 Hz
AQ                     3.9846387 sec
RG                          71.8
DW                        60.800 usec
DE                         6.50 usec
TE                        293.4 K
D1                     1.00000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         1H
P1                        14.70 usec
PL1                       -1.00 dB
PL1W                13.75599801 W
SFO1                400.1324710 MHz
SI                        32768
SF                  400.1300118 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```

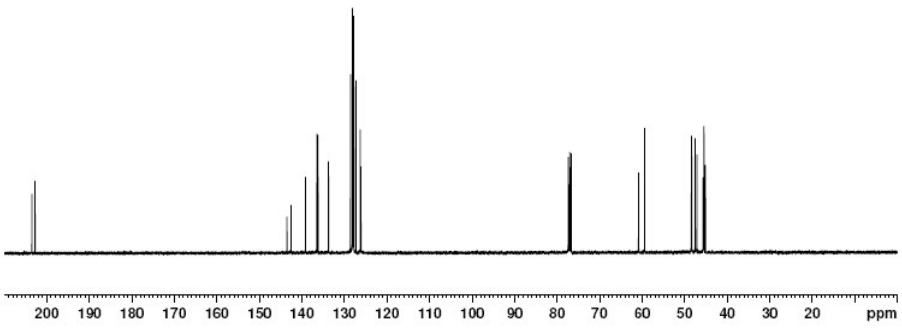


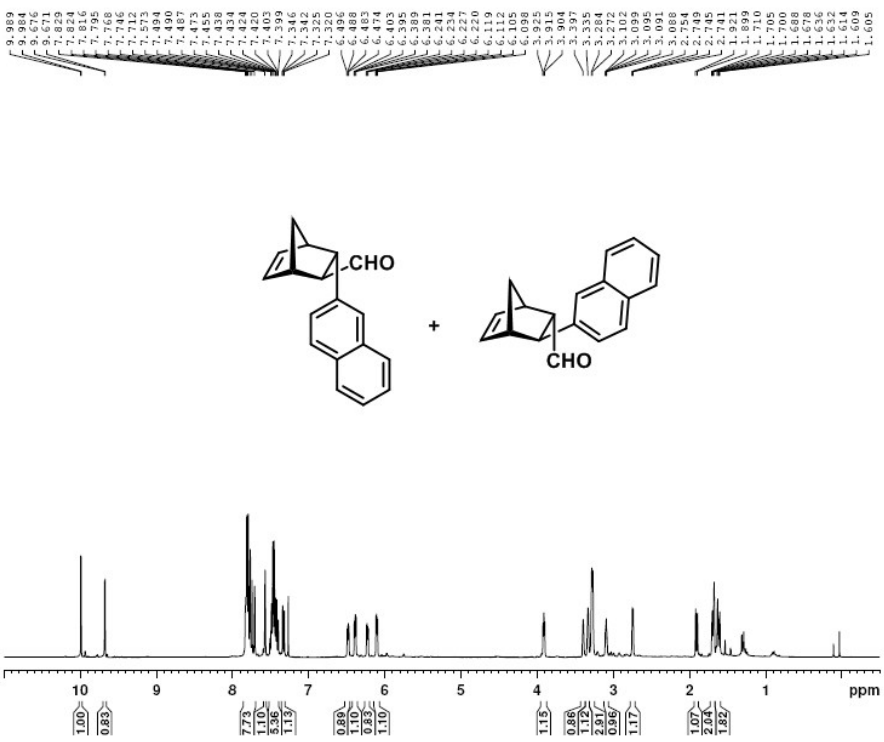



```
NAME          wangcha100106
EXPNO                        11
PROCNO                        1
Date_                  20100109
Time                       2.11
INSTRUM                    spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                        65536
SOLVENT                   CDCl3
NS                          256
DS                            4
SWH                24038.461 Hz
FIDRES                 0.366798 Hz
AQ                     1.3631988 sec
RG                          71.8
DW                        20.800 usec
DE                         6.50 usec
TE                        293.6 K
D1                     2.00000000 sec
D11                    0.03000000 sec
TD0                            1

======== CHANNEL f1 ========
NUC1                         13C
P1                         9.70 usec
PL1                       -2.00 dB
PL1W                56.13111005 W
SFO1                100.6228298 MHz

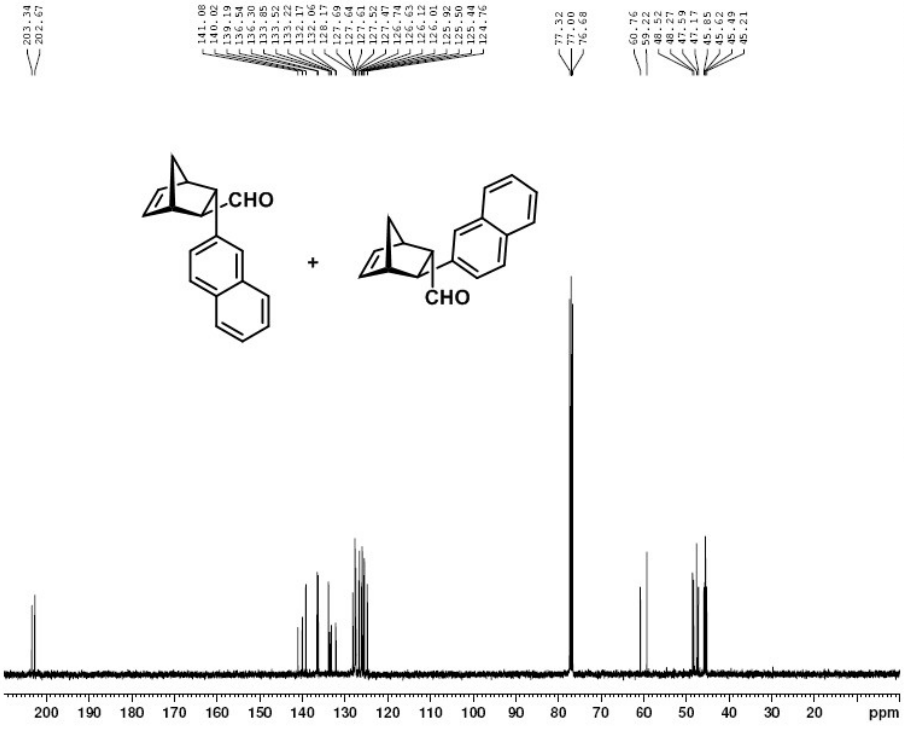
======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                     80.00 usec
PL2                       -2.10 dB
PL12                      13.90 dB
PL13                      13.90 dB
PL2W                17.72104263 W
PL12W                0.44513249 W
PL13W                0.44513249 W
SFO2                400.1316005 MHz
SI                        32768
SF                  100.6127766 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```






```
NAME          wangcha-cmp-1-2-Np
EXPNO                         10
PROCNO                         1
Date_               20100508
Time                      12.39
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG                   zg30
TD                       65536
SOLVENT                  CDCl3
NS                            16
DS                             2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                   3.9846387 sec
RG                          114
DW                     60.800 usec
DE                      6.50 usec
TE                      297.1 K
D1                  1.00000000 sec
TD0                            1

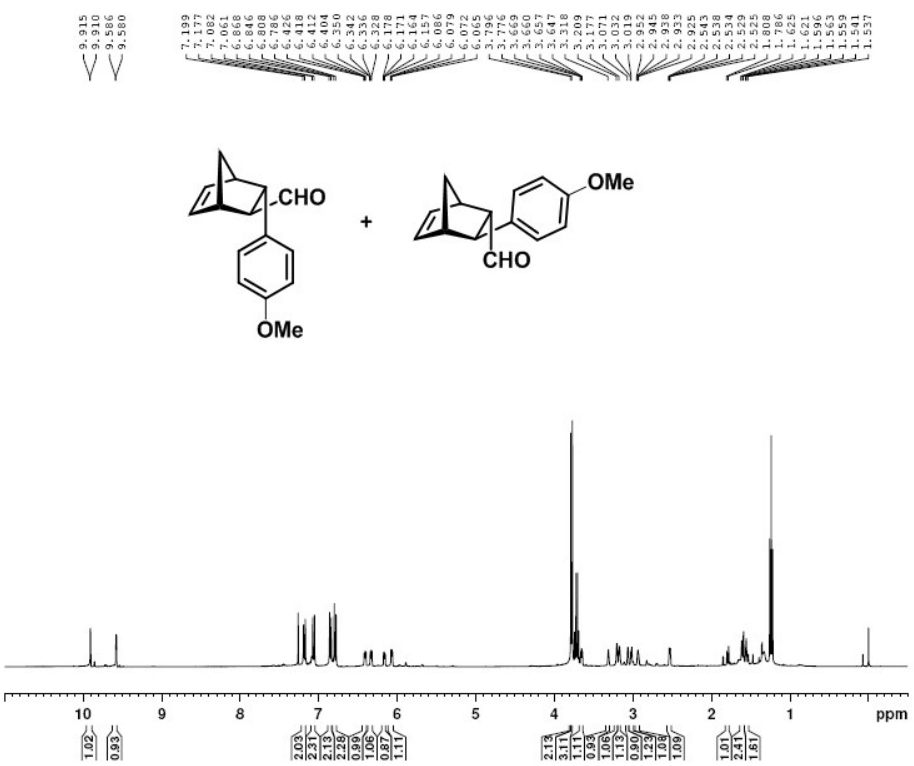
======== CHANNEL f1 ========
NUC1                       1H
P1                      14.70 usec
PL1                     -1.00 dB
PLW                13.75590801 W
SFO1               400.1324710 MHz
SI                        32768
SF                 400.1300009 MHz
WDW                          EM
SSB                           0
LB                         0.30 Hz
GB                            0
PC                         1.00
```




```
NAME          wangcha-cmp-1-2-Np
EXPNO                         11
PROCNO                         1
Date_               20100508
Time                      12.56
INSTRUM                   spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                           256
DS                             4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                          71.8
DW                     20.800 usec
DE                      6.50 usec
TE                      298.7 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                            1

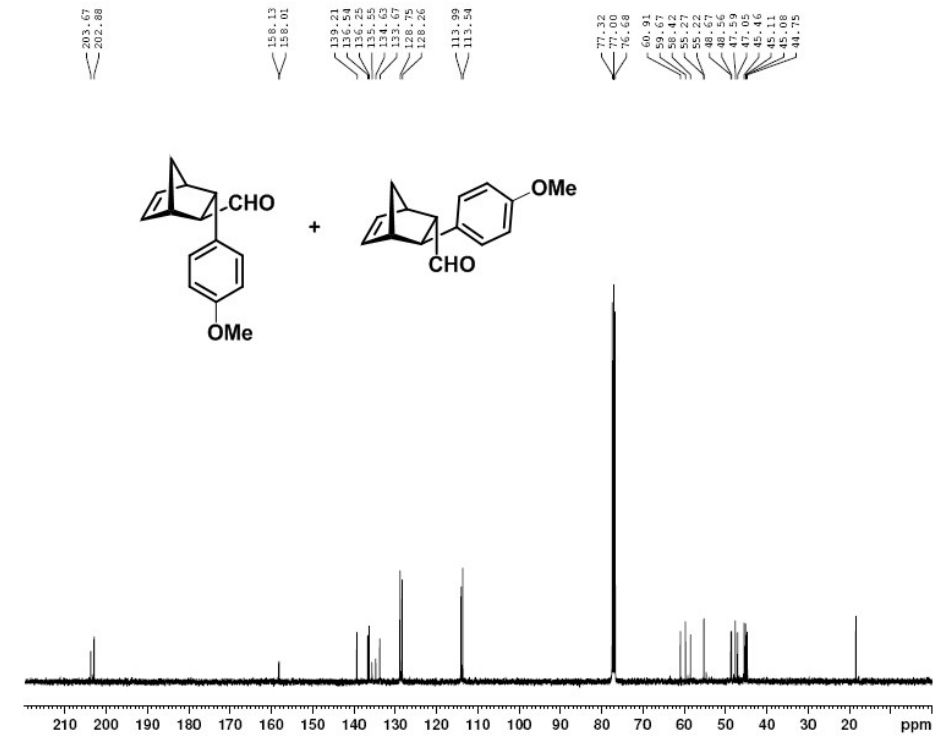
======== CHANNEL f1 ========
NUC1                       13C
P1                       9.70 usec
PL1                     -2.00 dB
PLW                56.13311005 W
SFO1               100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   80.00 usec
PL2                     -2.10 dB
PL12                    13.90 dB
PL13                    13.90 dB
PL2W               17.72104263 W
PL12W               0.44513249 W
PL13W               0.44513249 W
SFO2               400.1316005 MHz
SI                        32768
SF                 100.6127721 MHz
WDW                          EM
SSB                           0
LB                         1.00 Hz
GB                            0
PC                         1.40
```




```
NAME          wangcha-cmp-1-p-OMe
EXPNO                          10
PROCNO                          1
Date_                    20100516
Time                         8.57
INSTRUM                      spect
PROBHD    5 mm PABBO BB-
PULPROG                      zg30
TD                          65536
SOLVENT                     CDCl3
NS                             16
DS                              2
SWH                     8223.685 Hz
FIDRES                  0.125483 Hz
AQ                      3.9846387 sec
RG                            144
DW                       60.800 usec
DE                        6.50 usec
TE                        297.1 K
D1                    1.00000000 sec
TD0                             1

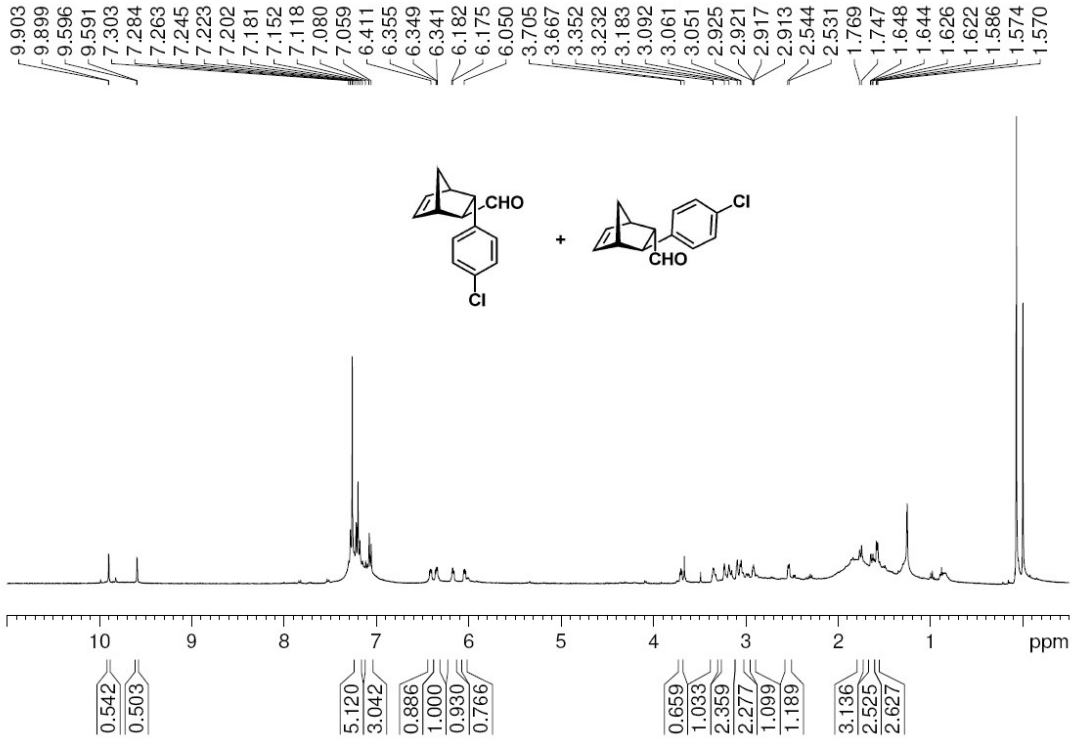
======== CHANNEL f1 ========
NUC1                         1H
P1                        14.70 usec
PL1                       -1.00 dB
PLW1                13.75590801 W
SFO1                400.1324710 MHz
SI                         32768
SF                  400.1300048 MHz
WDW                           EM
SSB                            0
LB                          0.30 Hz
GB                             0
PC                          1.00
```

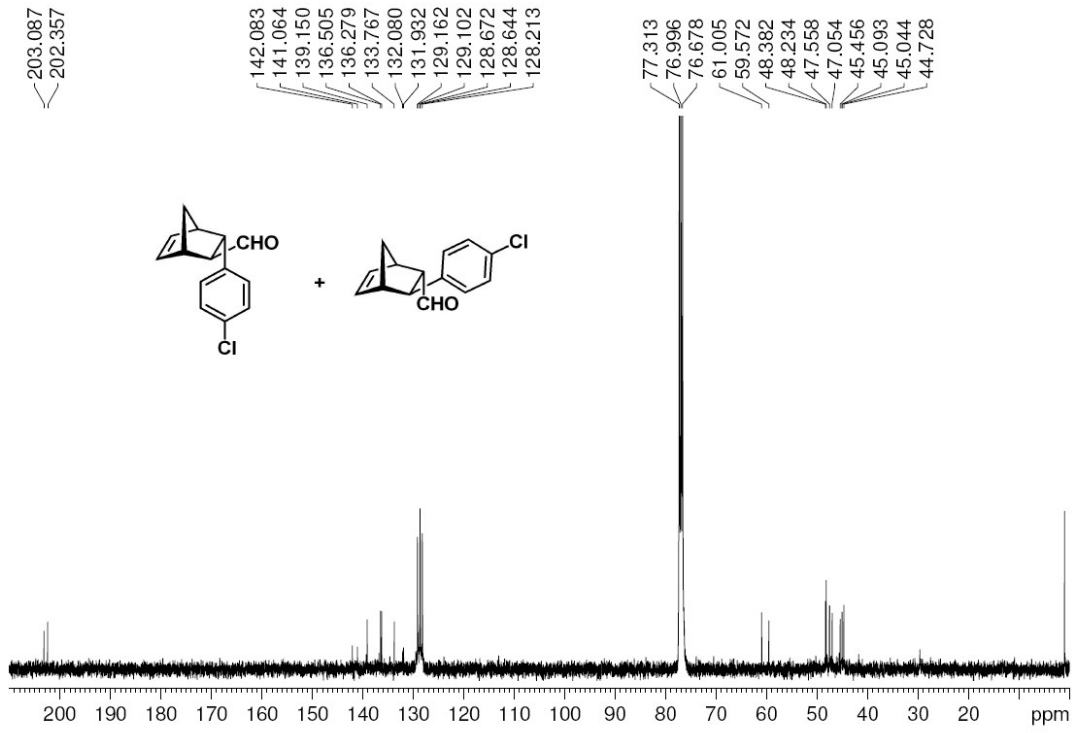



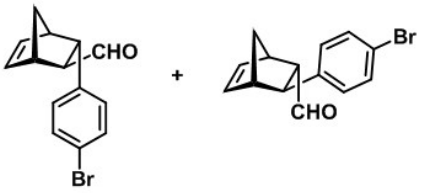

```
NAME          wangcha-cmp-1-p-OMe
EXPNO                          11
PROCNO                          1
Date_                    20100516
Time                         9.29
INSTRUM                      spect
PROBHD    5 mm PABBO BB-
PULPROG                  zgpg30
TD                          65536
SOLVENT                     CDCl3
NS                            512
DS                              4
SWH                    24038.461 Hz
FIDRES                  0.366798 Hz
AQ                      1.3631988 sec
RG                           71.8
DW                       20.800 usec
DE                        6.50 usec
TE                        298.7 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                             1

======== CHANNEL f1 ========
NUC1                        13C
P1                         9.70 usec
PL1                       -2.00 dB
PLW1                56.13311905 W
SFO1                100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                         1H
PCPD2                     80.00 usec
PL2                       -2.10 dB
PL12                      13.90 dB
PL13                      13.90 dB
PLW2                17.72119263 W
PLW12                0.44513249 W
PLW13                0.44513249 W
SFO2                400.1316005 MHz
SI                         32768
SF                  100.6127692 MHz
WDW                           EM
SSB                            0
LB                          1.00 Hz
GB                             0
PC                          1.40
```

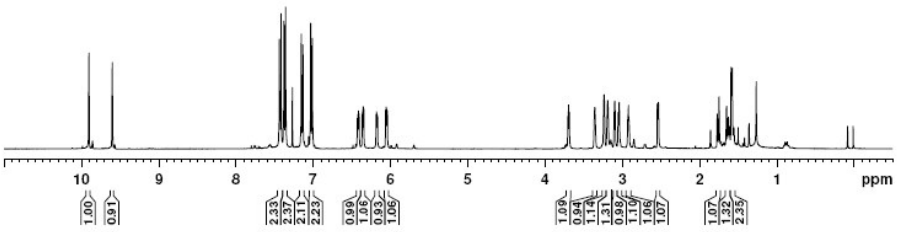

9.903
9.899
9.596
9.591
7.303
7.284
7.263
7.245
7.223
7.202
7.181
7.152
7.118
7.080
7.059
6.411
6.355
6.349
6.341
6.182
6.175
6.050
3.705
3.667
3.352
3.232
3.183
3.092
3.061
3.051
2.925
2.921
2.917
2.913
2.544
2.531
1.769
1.747
1.648
1.644
1.626
1.622
1.586
1.574
1.570
CHO
Cl
+
Cl
CHO
10
9
8
7
6
5
4
3
2
1
ppm
0.542
0.503
5.120
3.042
0.886
1.000
0.930
0.766
0.659
1.033
2.359
2.277
1.099
1.189
3.136
2.525
2.627

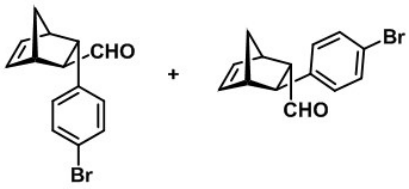

203.087
202.357
142.083
141.064
139.150
136.505
136.279
133.767
132.080
131.932
129.162
129.102
128.672
128.644
128.213
77.313
76.996
76.678
61.005
59.572
48.382
48.234
47.558
47.054
45.456
45.093
45.044
44.728
CHO
Cl
+
Cl
CHO
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm




```
NAME          wangcha-cmp-1-Br
EXPNO                       10
PROCNO                       1
Date_              20100508
Time                      6.01
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                          16
DS                           2
SWH                 8223.685 Hz
FIDRES              0.125483 Hz
AQ                  3.9846387 sec
RG                         144
DW                    60.800 usec
DE                     6.50 usec
TE                    296.1 K
D1                  1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       1H
P1                      12.00 usec
PL1                     -3.00 dB
PL1W               22.90425682 W
SFO1              400.1324710 MHz
SI                       32768
SF                400.1300010 MHz
WDW                         EM
SSB                          0
LB                        0.30 Hz
GB                           0
PC                        1.00
```

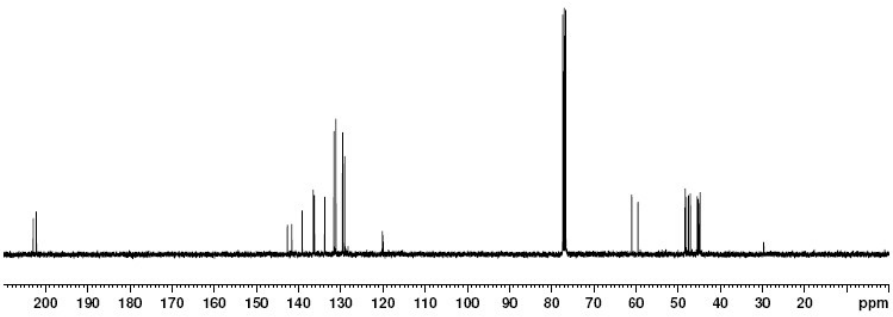





```
NAME          wangcha-cmp-1-Br
EXPNO                       11
PROCNO                       1
Date_              20100508
Time                      6.17
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                 zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                         256
DS                           4
SWH                24038.461 Hz
FIDRES              0.366798 Hz
AQ                  1.3631988 sec
RG                        2050
DW                    20.800 usec
DE                     6.50 usec
TE                    297.1 K
D1                  2.00000000 sec
D11                 0.03000000 sec
TD0                          1

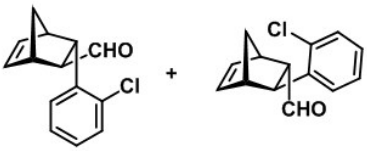
======== CHANNEL f1 ========
NUC1                       13C
P1                       9.40 usec
PL1                     -2.00 dB
PL1W               57.32743073 W
SFO1              100.6228298 MHz

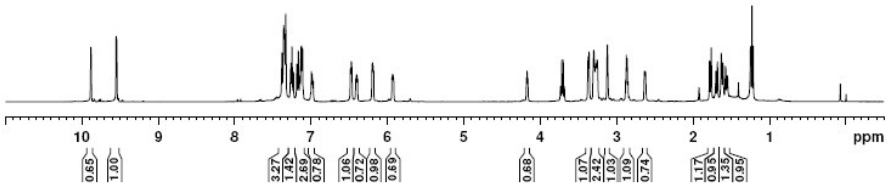
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   90.00 usec
PL2                     -2.00 dB
PL12                    15.50 dB
PL13                    15.50 dB
PL2W               18.19349861 W
PL12W               0.32353121 W
PL13W               0.32353121 W
SFO2              400.1316005 MHz
SI                       32768
SF                100.6127711 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```




```
NAME        WANGCHA-CMP-1-o-Cl
EXPNO                       10
PROCNO                       1
Date_                 20100512
Time                      6.32
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
TD                      65536
SOLVENT                 CDCl3
NS                         16
DS                          2
SWH                  8223.685 Hz
FIDRES               0.125483 Hz
AQ                   3.9846387 sec
RG                        80.6
DW                    60.800 usec
DE                     6.50 usec
TE                     297.5 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                    14.70 usec
PL1                   -1.00 dB
PLW             13.75580801 W
SFO1            400.1324710 MHz
SI                       32768
SF              400.1300048 MHz
WDW                         EM
SSB                          0
LB                    0.30 Hz
GB                           0
PC                    1.00
```

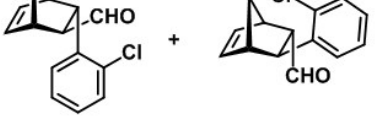


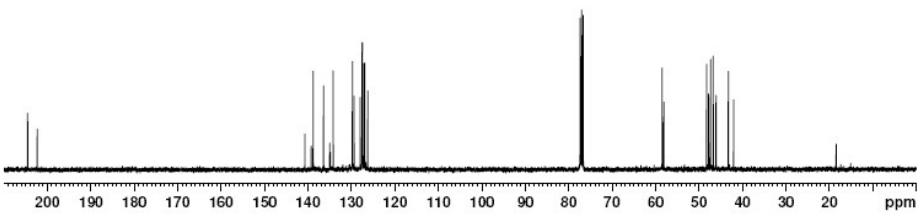


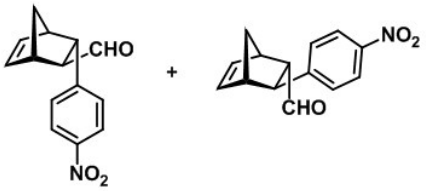

```
NAME        WANGCHA-CMP-1-o-Cl
EXPNO                       11
PROCNO                       1
Date_                 20100512
Time                      6.49
INSTRUM                  spect
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
TD                      65536
SOLVENT                 CDCl3
NS                         256
DS                           4
SWH                 24038.461 Hz
FIDRES               0.366798 Hz
AQ                   1.3631988 sec
RG                         724
DW                    20.800 usec
DE                     6.50 usec
TE                     298.8 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                     9.70 usec
PL1                   -2.00 dB
PLW             56.13311005 W
SFO1            100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                 80.00 usec
PL2                   -2.10 dB
PL12                  13.90 dB
PL13                  13.90 dB
PL2W            17.72104263 W
PL12W            0.44513249 W
PL13W            0.44513249 W
SFO2            400.1316005 MHz
SI                       32768
SF              100.6127722 MHz
WDW                         EM
SSB                          0
LB                    1.00 Hz
GB                           0
PC                    1.40
```

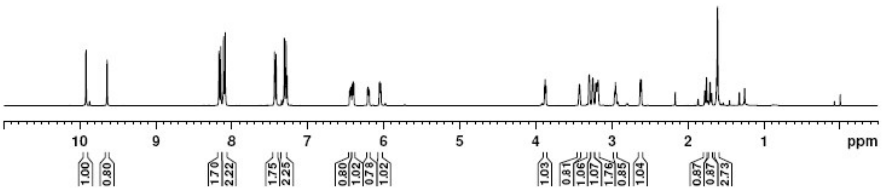


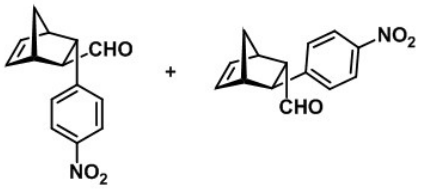





```
NAME        wangcha-cmp-1-NO2
EXPNO                      10
PROCNO                      1
Date_             20100623
Time                   13.11
INSTRUM                spect
PROBHD     5 mm PABBO BB-
PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8223.685 Hz
FIDRES            0.125483 Hz
AQ                 3.9846387 sec
RG                      128
DW                 60.800 usec
DE                   6.50 usec
TE                  297.7 K
D1                1.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                   12.00 usec
PL1                  -3.00 dB
PL1W            22.90425682 W
SFO1           400.1324710 MHz
SI                       32768
SF             400.1300011 MHz
WDW                      EM
SSB                       0
LB                     0.30 Hz
GB                        0
PC                     1.00
```

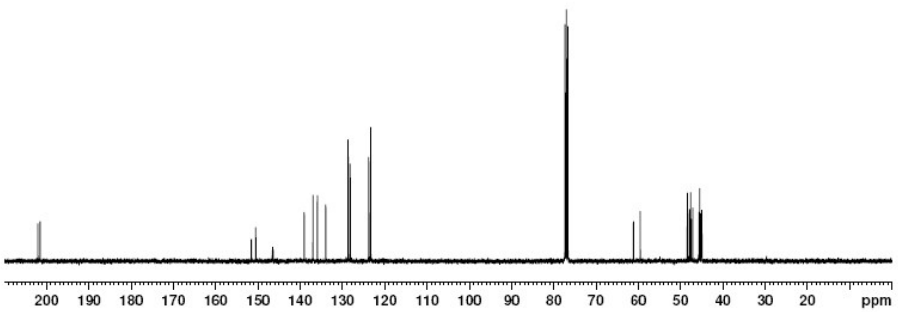


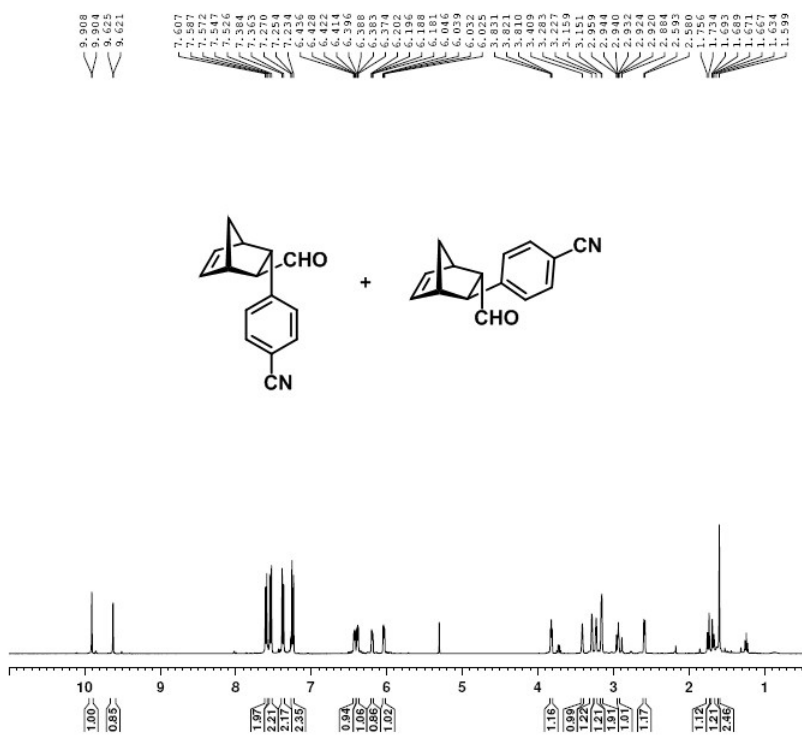



```
NAME        wangcha-cmp-1-NO2
EXPNO                      11
PROCNO                      1
Date_             20100623
Time                   13.27
INSTRUM                spect
PROBHD     5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      256
DS                        4
SWH               24038.461 Hz
FIDRES            0.366798 Hz
AQ                 1.3631988 sec
RG                     2050
DW                 20.800 usec
DE                   6.50 usec
TE                  298.7 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      13C
P1                    9.40 usec
PL1                  -2.00 dB
PL1W            57.32743073 W
SFO1           100.6228298 MHz

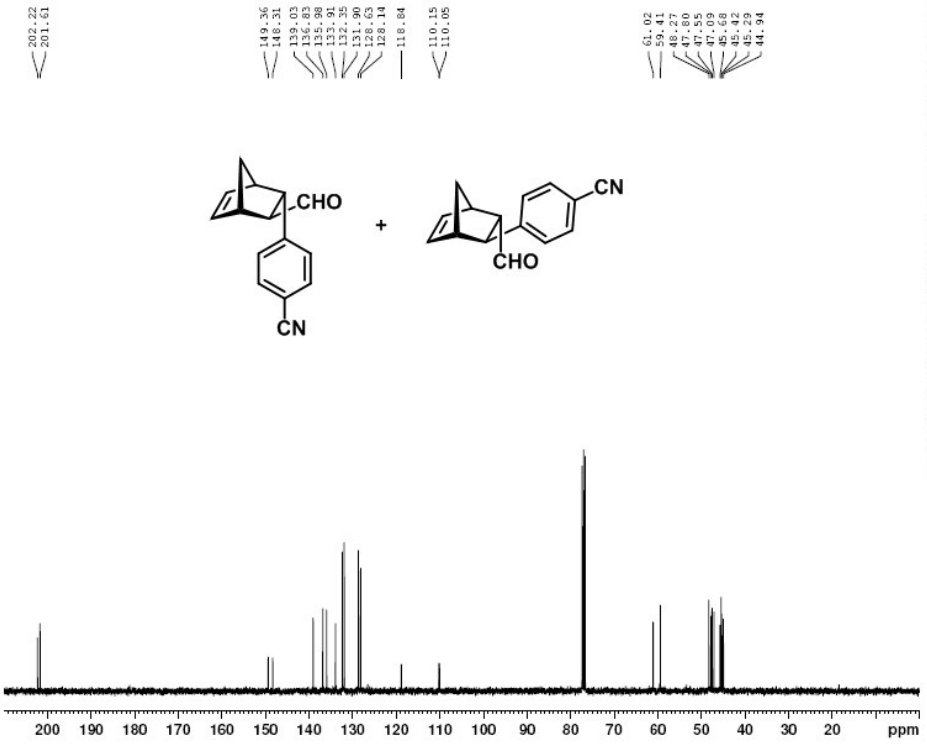
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                      1H
PCPD2                90.00 usec
PL2                  -2.00 dB
PL12                 15.50 dB
PL13                 15.50 dB
PL2W            18.19349861 W
PL12W            0.32353121 W
PL13W            0.32353121 W
SFO2           400.1316005 MHz
SI                       32768
SF             100.6127715 MHz
WDW                      EM
SSB                       0
LB                     1.00 Hz
GB                        0
PC                     1.40
```






```
NAME        wangcha100322-CN
EXPNO                 10
PROCNO                 1
Date_           20100322
Time                19.25
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ               3.9846387 sec
RG                   128
DW                60.800 usec
DE                 6.50 usec
TE                293.3 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 14.70 usec
PL1                -1.00 dB
PL1W          13.75590801 W
SFO1          400.1324710 MHz
SI                 32768
SF            400.1300011 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




```
NAME        wangcha100322-CN
EXPNO                 11
PROCNO                 1
Date_           20100322
Time                19.42
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   256
DS                     4
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                  71.8
DW                20.800 usec
DE                 6.50 usec
TE                294.9 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                  9.70 usec
PL1                -2.00 dB
PL1W          56.13311005 W
SFO1          100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                -2.10 dB
PL12               13.90 dB
PL13               13.90 dB
PL2W          17.72134243 W
PL12W          0.44513249 W
PL13W          0.44513249 W
SFO2          400.1316005 MHz
SI                 32768
SF            100.6127713 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
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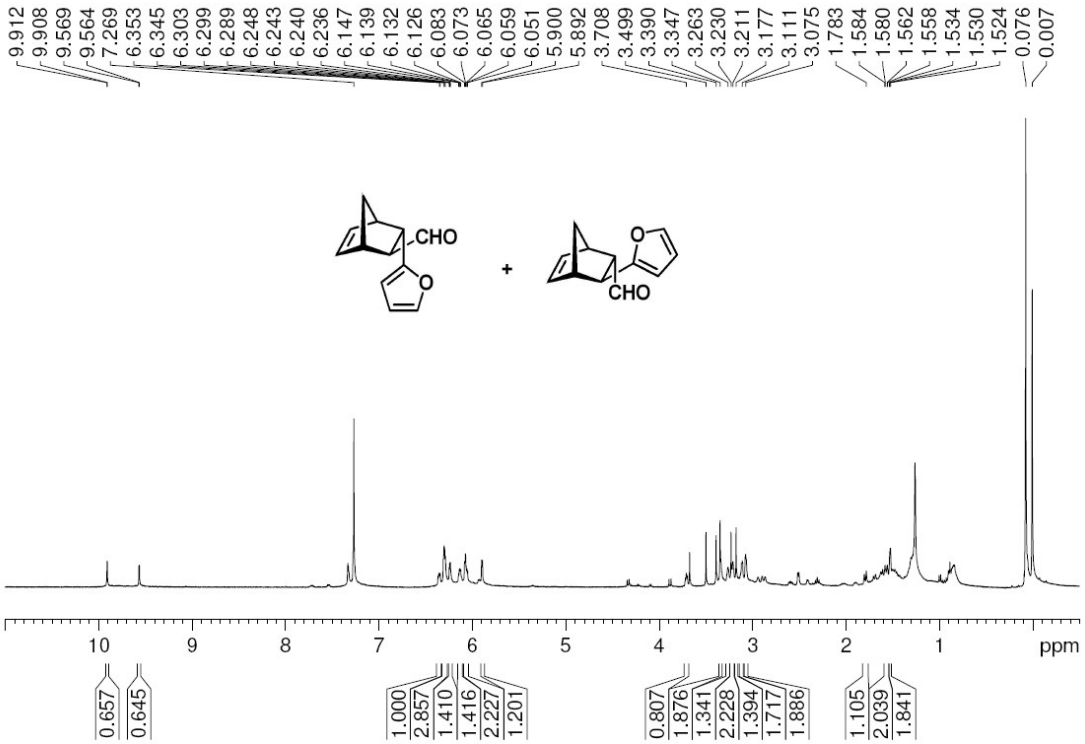
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9.569
9.564
7.269
6.353
6.345
6.303
6.299
6.289
6.248
6.243
6.240
6.236
6.147
6.139
6.132
6.126
6.083
6.073
6.065
6.059
6.051
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1.783
1.584
1.580
1.562
1.558
1.534
1.530
1.524
0.076
0.007
CHO
O
+
O
CHO
10
9
8
7
6
5
4
3
2
1
ppm
0.657
0.645
1.000
2.857
1.410
1.416
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0.807
1.876
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1.394
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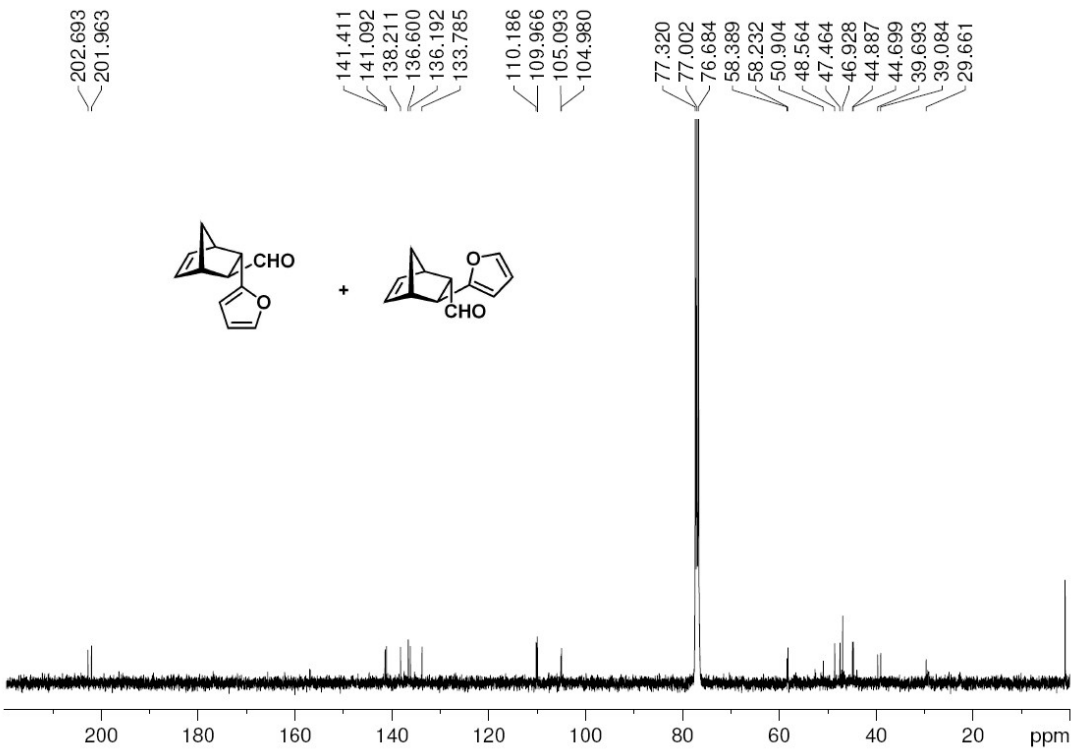
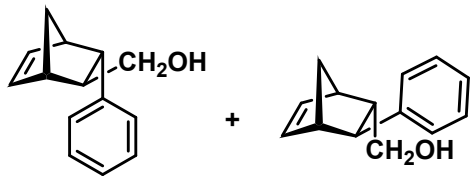
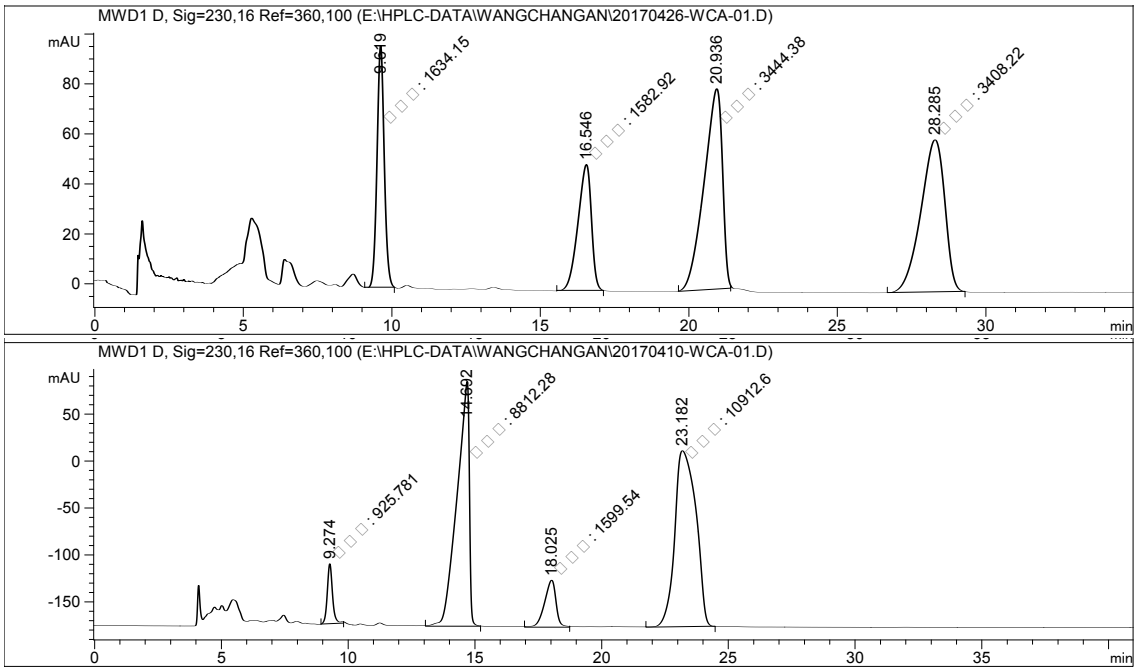
1.886
1.105
2.039
1.841

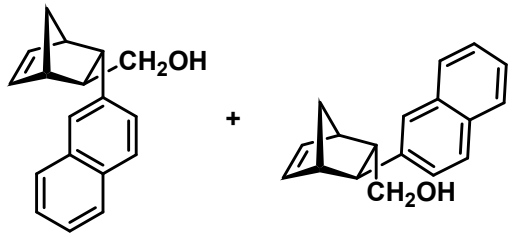

202.693
201.963
141.411
141.092
138.211
136.600
136.192
133.785
110.186
109.966
105.093
104.980
77.320
77.002
76.684
58.389
58.232
50.904
48.564
47.464
46.928
44.887
44.699
39.693
39.084
29.661
CHO
O
+
O
CHO
200
180
160
140
120
100
80
60
40
20
ppm

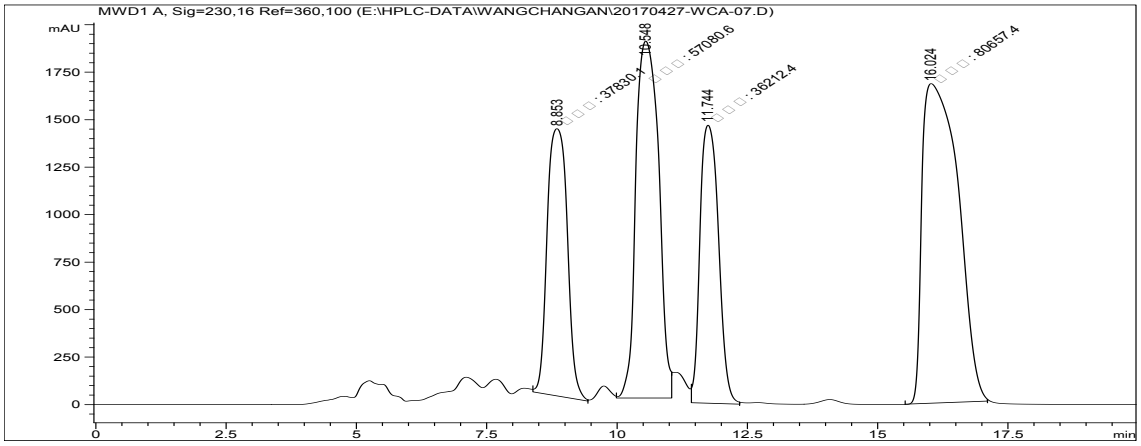
HPLC spectra

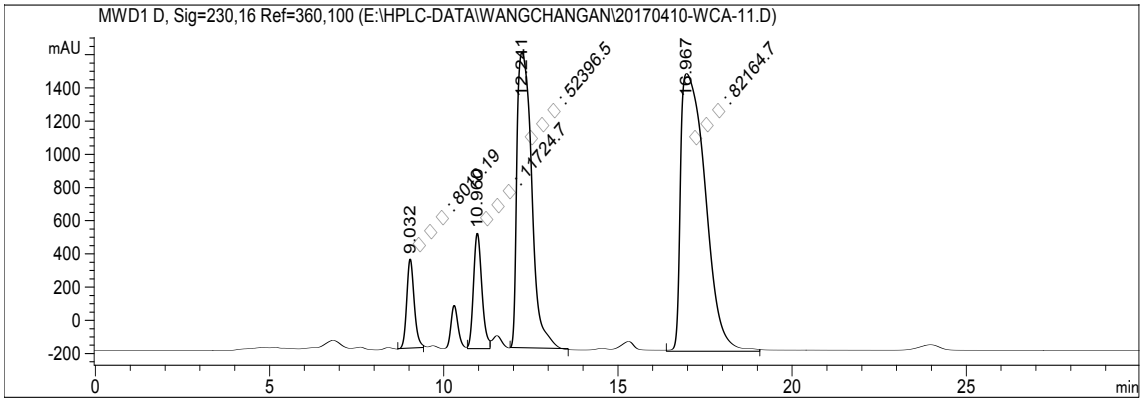




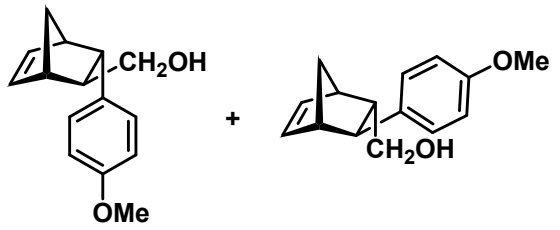
	Retention Time (minute)	Area (microvolt*sec.)	Height (microvolt)	% Area
1	9.274	926	64.06	4.16
2	14.692	8812	260.79	39.61
3	18.025	1599	50.40	7.19
4	23.182	10913	187.73	49.04

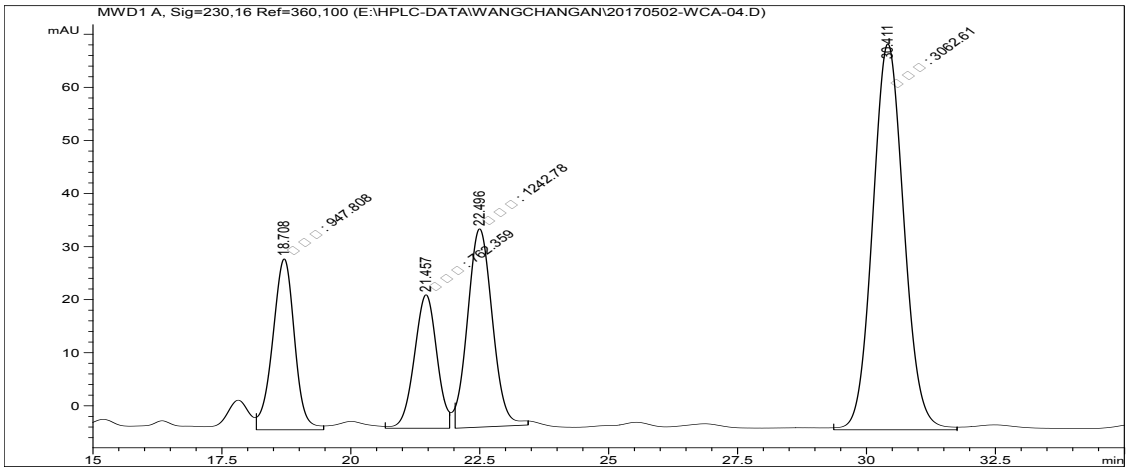


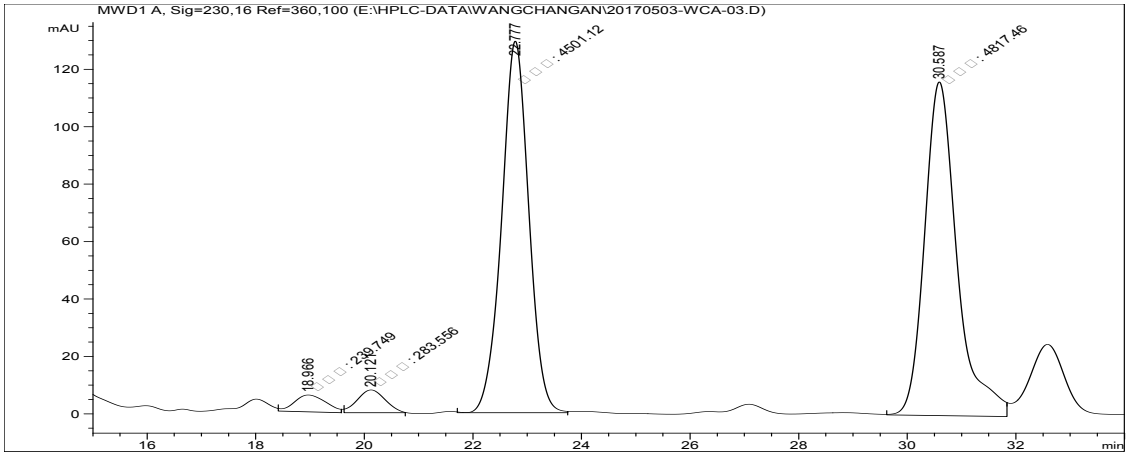




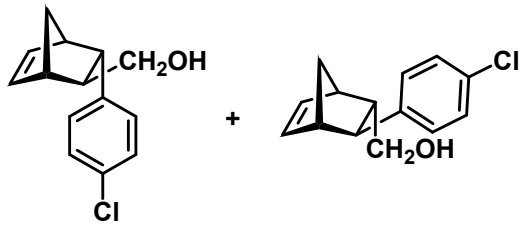
	Retention Time (minute)	Area (microvolt*sec.)	Height (microvolt)	% Area
1	9.032	8010	538.01	5.19
2	10.960	11725	696.67	7.60
3	12.241	52397	1779.38	33.96
4	16.967	82165	1672.96	53.25

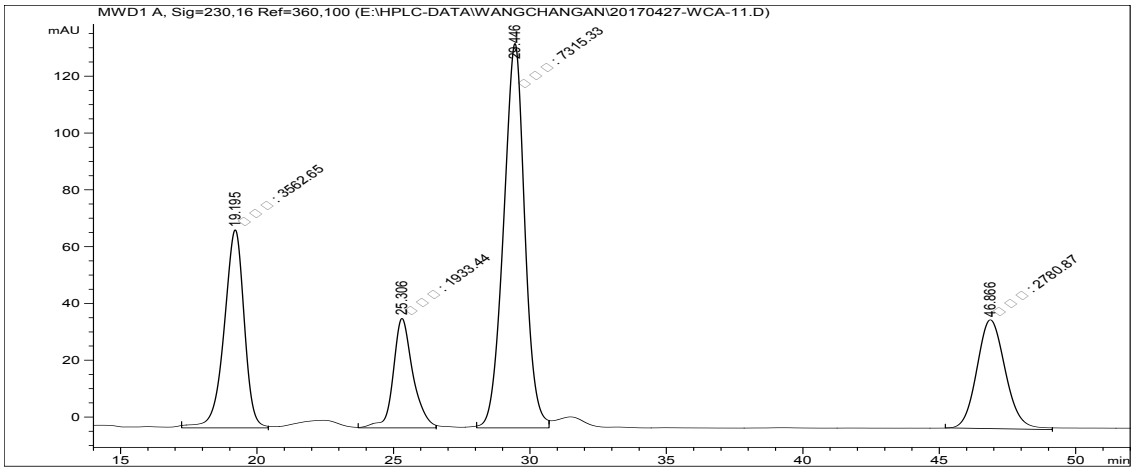


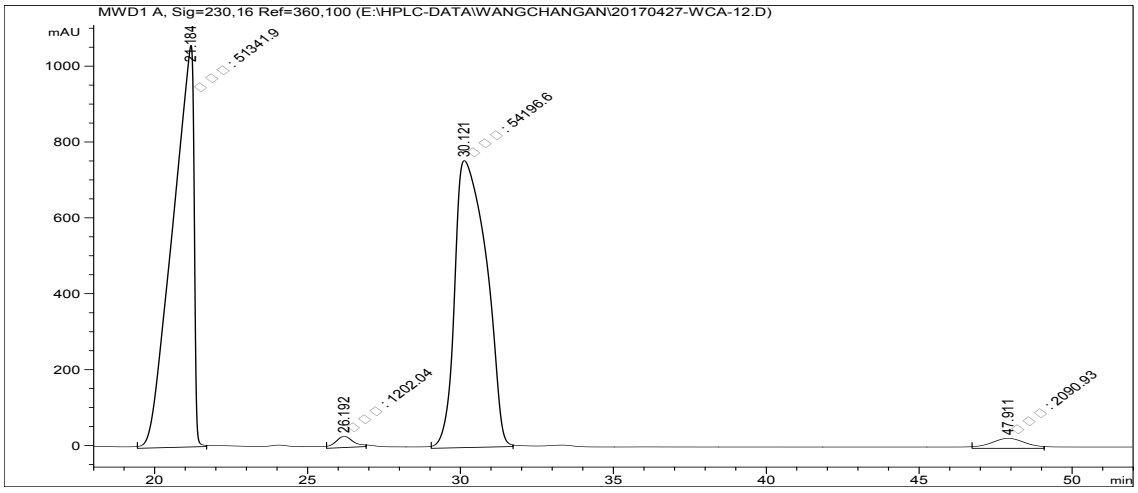




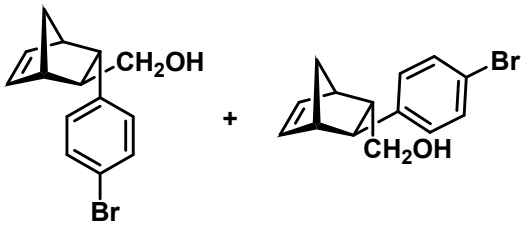
	Retention Time (minute)	Area (microvolt*sec.)	Height (microvolt)	% Area
1	18.966	239	5.90	2.43
2	20.121	283	7.96	2.88
3	22.777	4501	129.46	45.73
4	30.587	4817	116.24	48.95

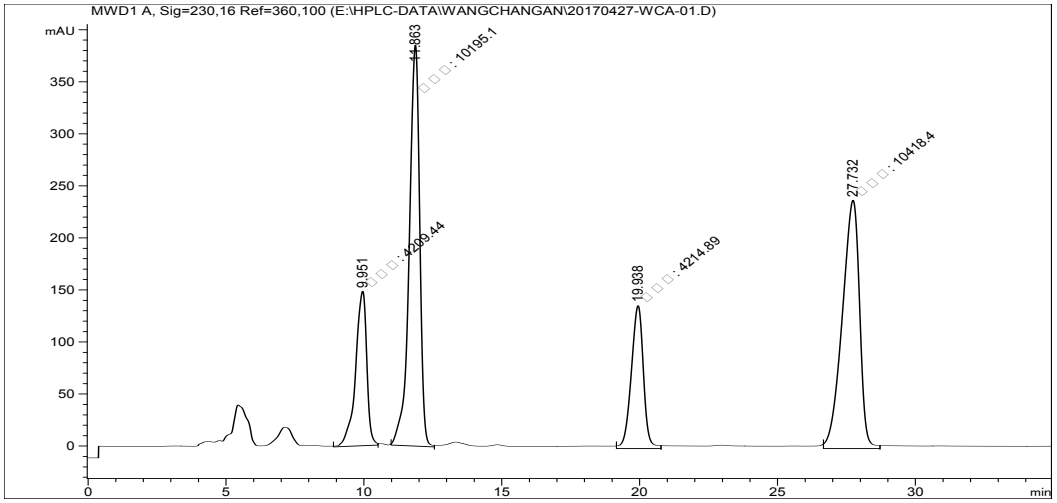


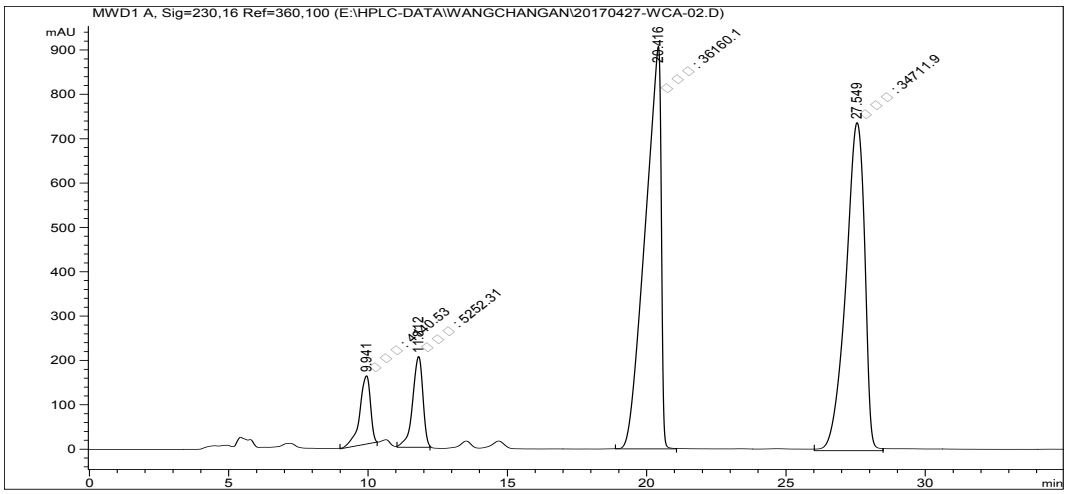




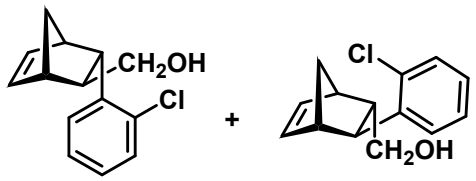
	Retention Time (minute)	Area (microvolt*sec.)	Height (microvolt)	% Area
1	21.184	51342	1058.76	47.18
2	26.192	1202	29.82	1.10
3	30.121	54197	756.89	49.80
4	47.911	2090	26.48	1.92

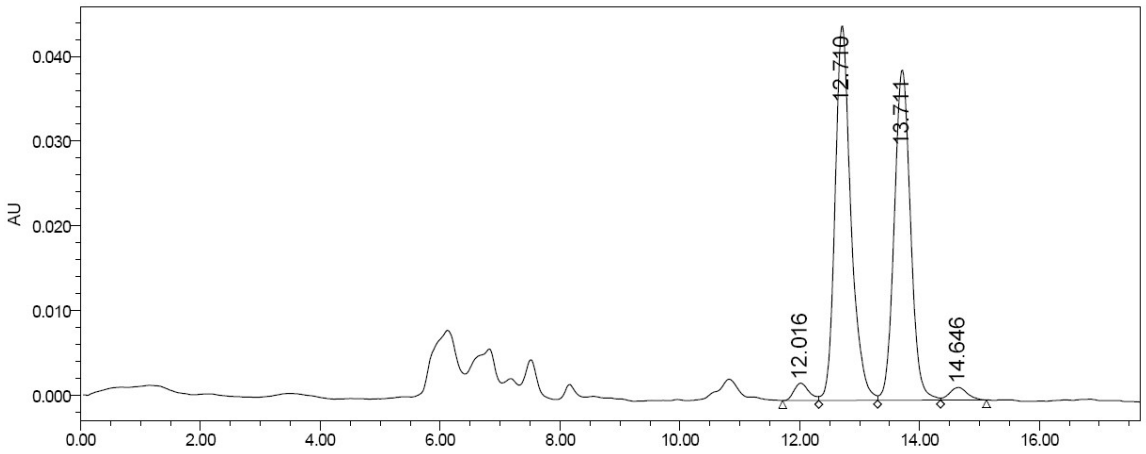


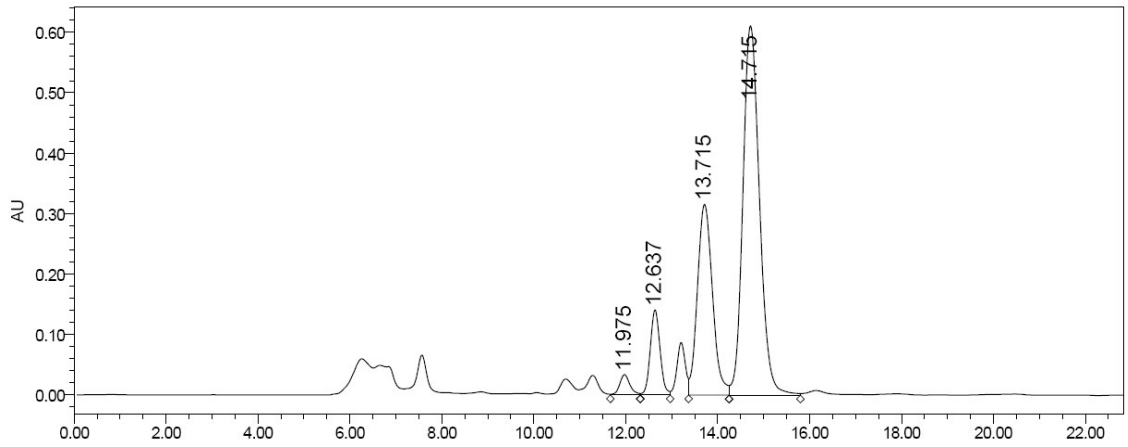




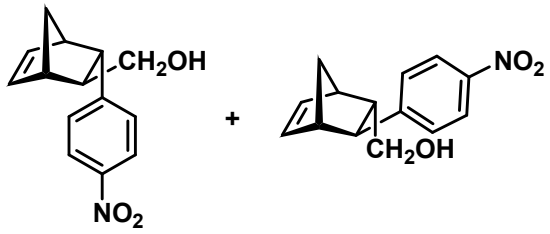
	Retention Time (minute)	Area (microvolt*sec.)	Height (microvolt)	% Area
1	9.941	4140	154.29	5.16
2	11.812	5252	204.81	6.54
3	20.416	36160	907.93	45.05
4	27.549	34712	739.83	43.25

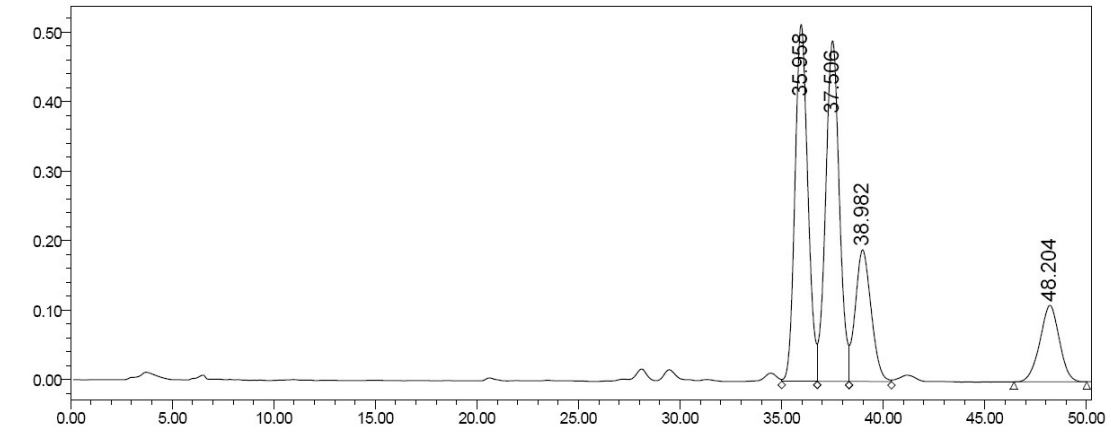


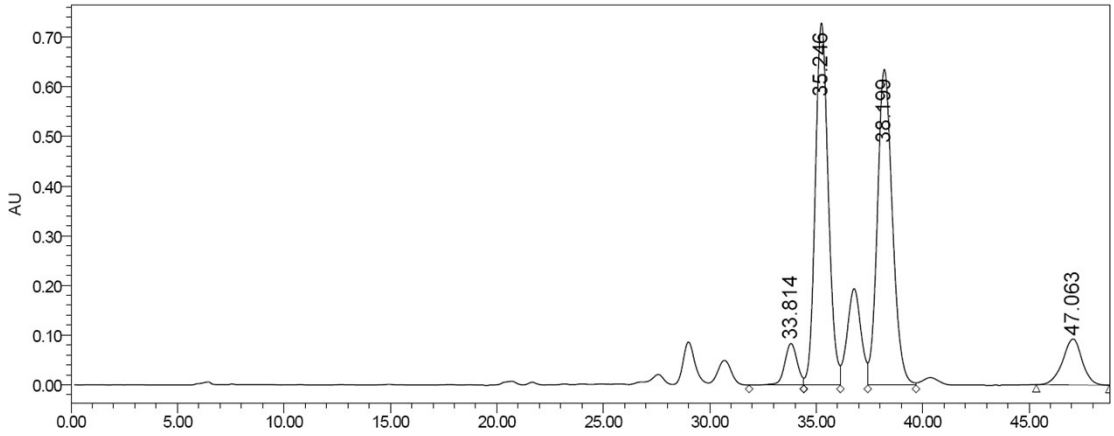




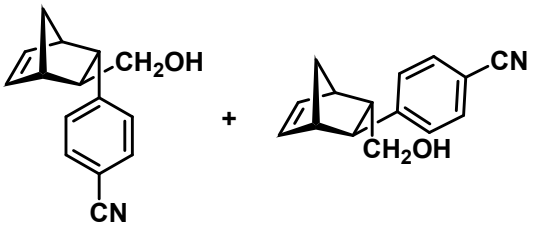
	Retention Time (minute)	Area (microvolt*sec.)	Height (microvolt)	% Area
1	11.975	526636	33827	2.09
2	12.637	2078794	141081	8.25
3	13.715	7247752	315944	28.77
4	14.715	15337777	611528	60.89

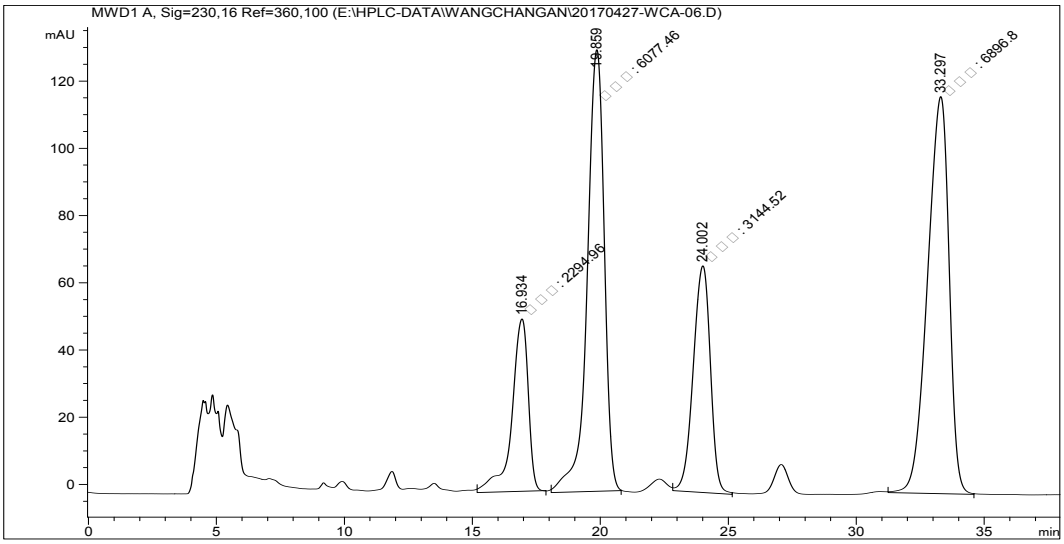


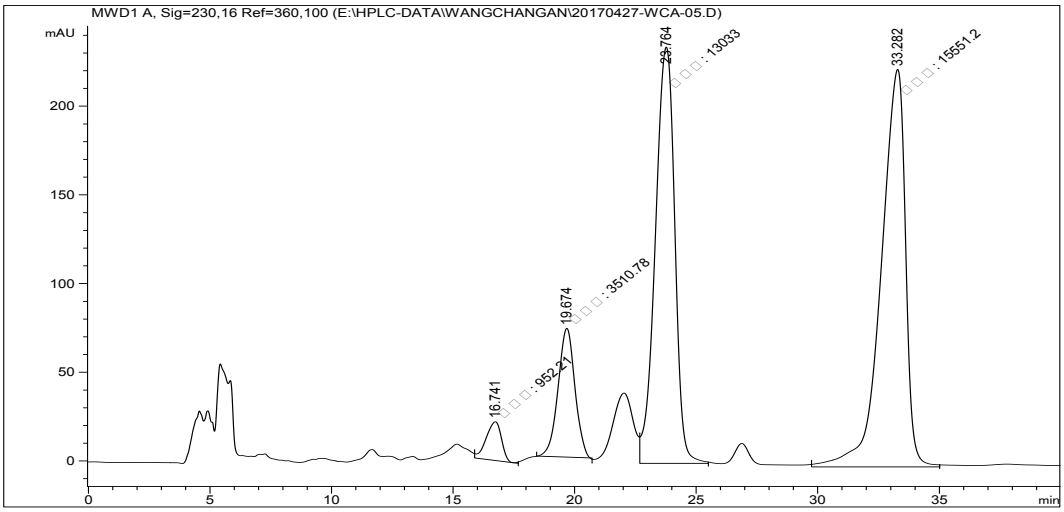




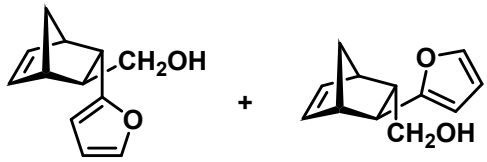
	Retention Time (minute)	Area (microvolt*sec.)	Height (microvolt)	% Area
1	33.814	3451714	83878	4.82
2	35.246	30960900	729467	43.20
3	38.199	31351674	635806	43.75
4	47.063	5902902	92527	8.24

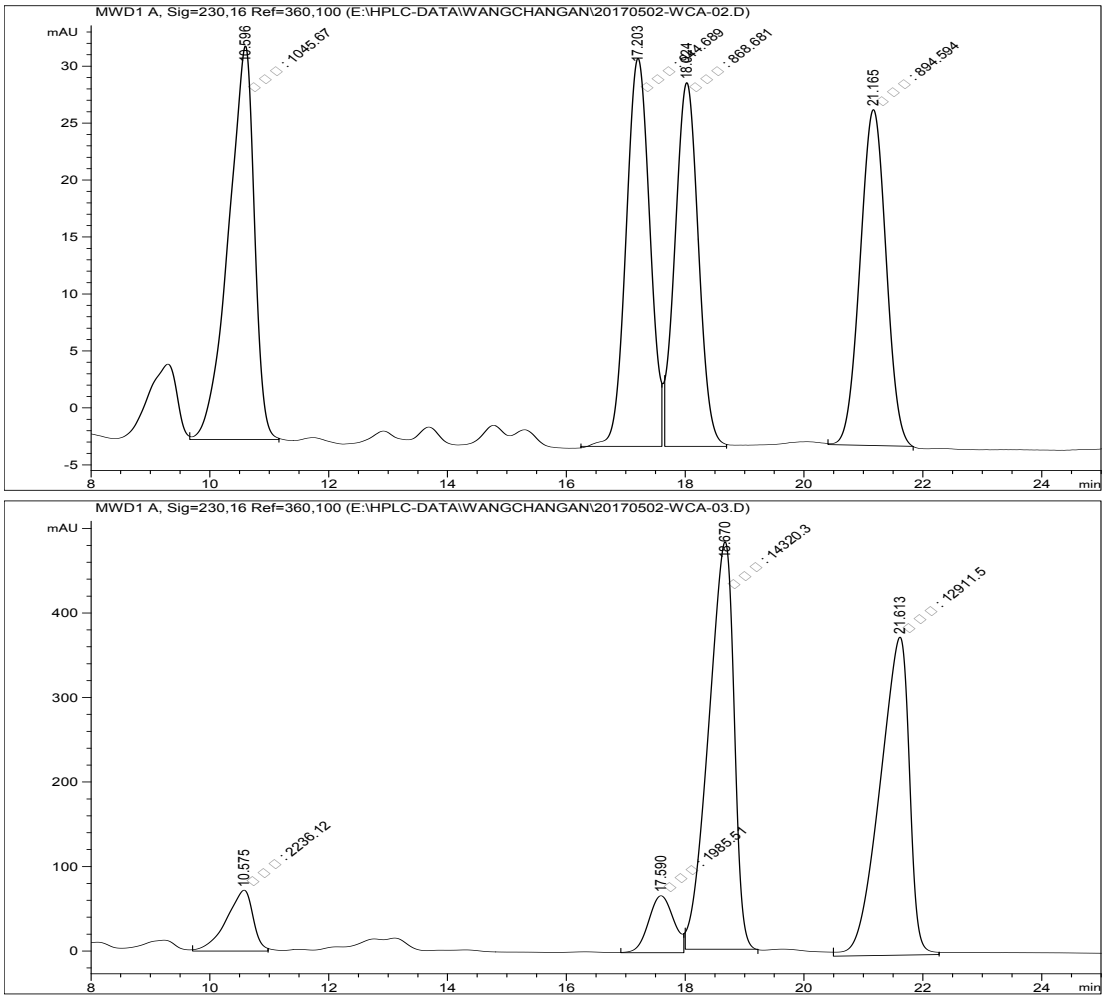






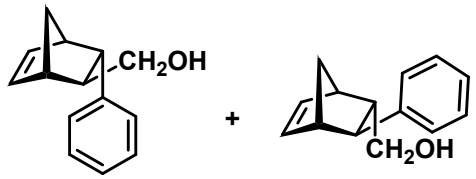
	Retention Time (minute)	Area (microvolt*sec.)	Height (microvolt)	% Area
1	16.741	952	21.88	2.88
2	19.674	3511	72.65	10.62
3	23.764	13033	234.69	39.44
4	33.282	15551	224.10	47.06

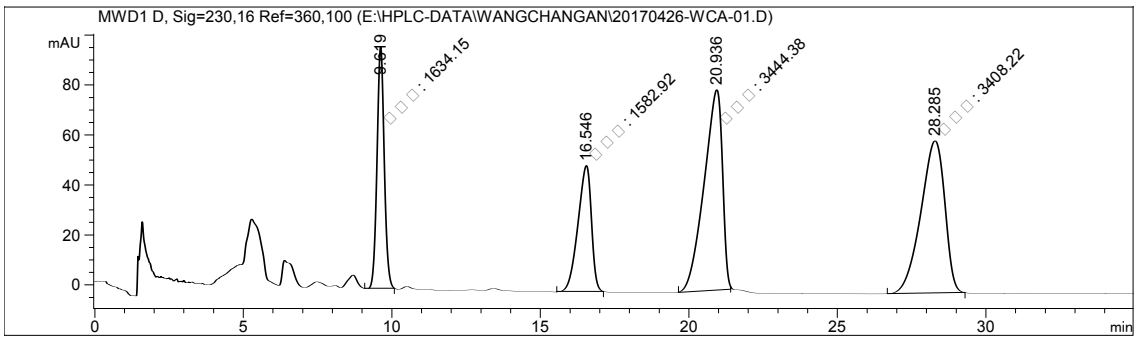




	Retention Time (minute)	Area (microvolt*sec.)	Height (microvolt)	% Area
1	10.575	2236	72.09	7.11
2	17.590	1985	67.54	6.31
3	18.670	114320	482.39	45.53
4	21.613	12912	376.53	41.05

The recyclability of Mac-CPOP-2:





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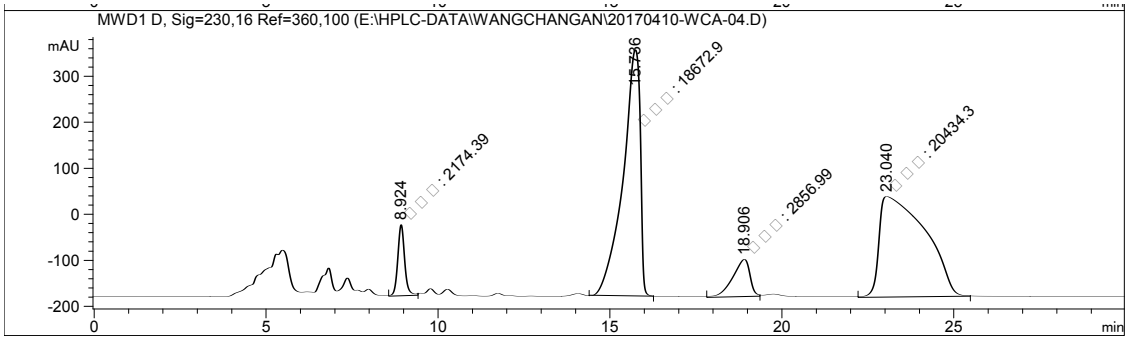
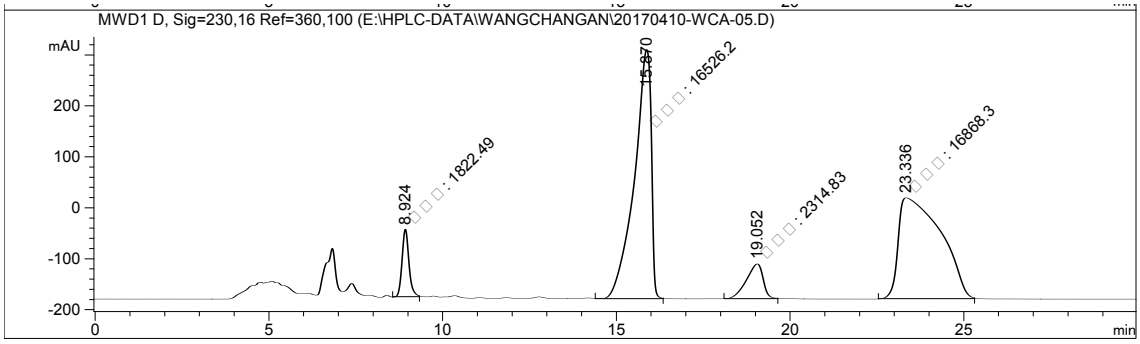
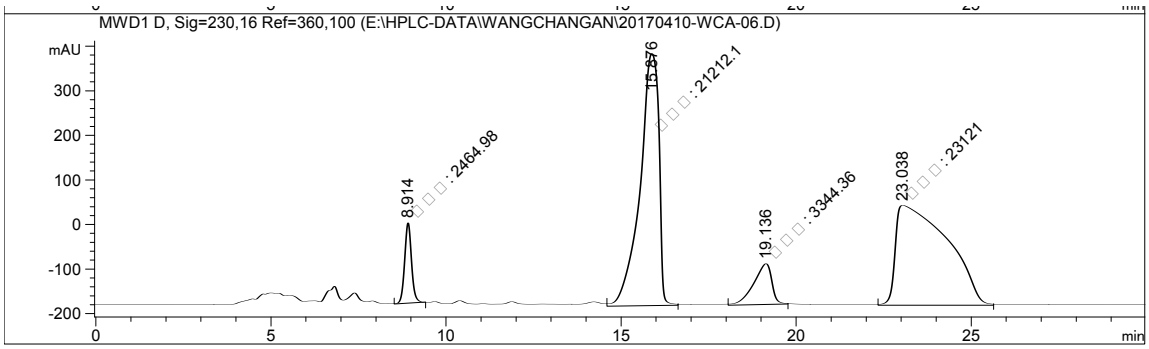


Run 2



Run 3



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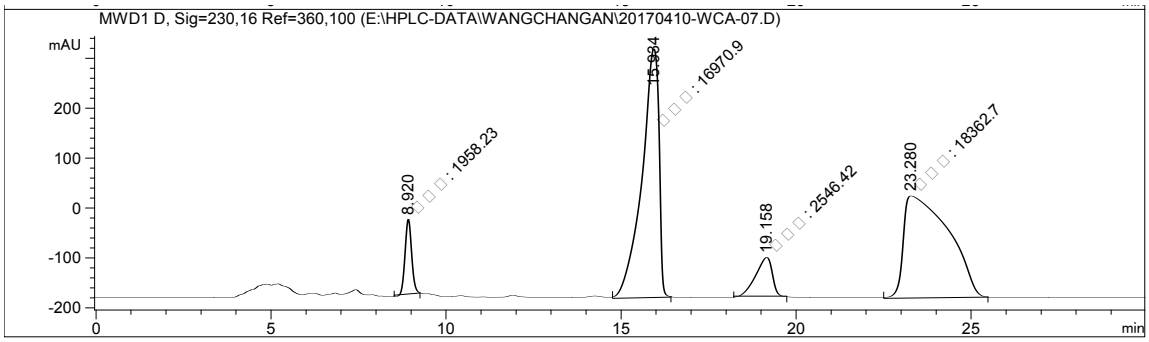
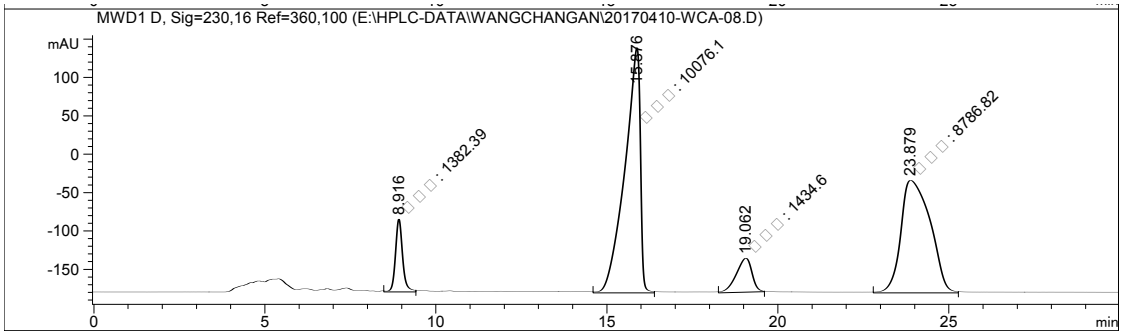


Run 5



Run 6