Electronic Supplementary Information

One-step Assembly of MacMillan Catalyst-Based Phenolic-Type Polymer

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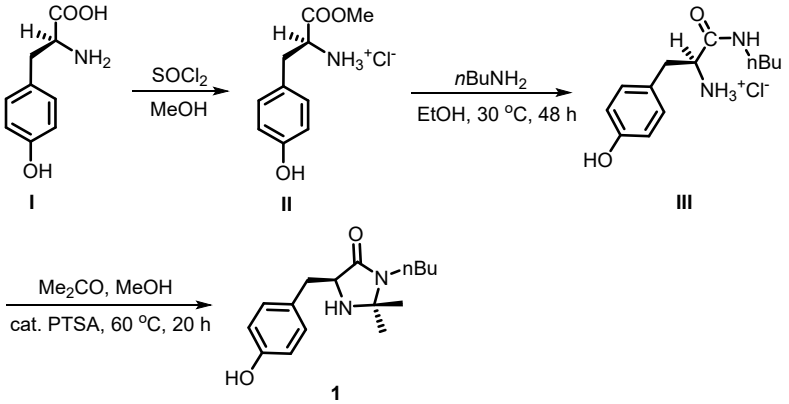
1. Experiment Information and Product Data

1.1 General Information.

Unless otherwise noted, all reagents were purchased from commercial sources and used as received without further purification. Racemic standard products were prepared using *DL*-proline as catalyst in order to establish HPLC conditions. The silica gel (200−300 meshes) was used for column chromatography and TLC inspections were taken on silica gel GF254 plates. Elemental analysis was carried out on an Elementar Analysensysteme GmbH Vario EL V3.00 elemental analyzer. Liquid ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer. High resolution mass spectra (HRMS) were obtained on a mass spectrometer by using electrospray ionization (ESI) analyzed by quadrupole time-of-flight (QTof). High performance liquid chromatography (HPLC) analysis was performed on a Waters 1525 Delta or an Agilent 1260 equipment, using Daicel Chiralpak OJ-H or OD-H columns and with *i*-PrOH/hexane as the eluent. Solid-state NMR spectra were obtained on a WB 400 MHz Bruker Avance II spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with the contact time of 3 ms (ramp 100) and the recycle delay of 2 s with a 4-mm double-resonance probe. FT-IR spectra were recorded on a Nicolet NEXUS 670 instrument. The morphology and size of the obtained sample was characterized by a JEOL-6701F field-emission scanning electron microscope (SEM, operated at 10 kV).

1.2 Synthesis of chiral precursor 1.[1]



To a suspension of *L*-tyrosine (10.0 g, 55.2 mmol) in ice-cooled dry methanol (30 mL), thionyl chloride (16.0 mL, 220.0 mmol) was added dropwise under argon. After the addition was complete, the cooling bath was removed and the mixture was stirred at room temperature for 24 h. Then the solvent was removed under reduced pressure to give (S)-tyrosine methyl ester hydrochloride (**II**) as a yellow solid quantitatively, which was directly used in the next step without further purification. (S)-tyrosine

methyl ester hydrochloride (**II**) was added in one portion to a solution of *n*-butylamine (35 mL) in dry ethanol (20 mL), and the resulting solution was stirred at room temperature until the amino ester was judged to be consumed as determined by TLC (ca. 48 h). After removal of the organic solvents under vacuum, the residue was suspended in Et_2O and then concentrated under vacuum. This Et_2O addition–removal cycle was repeated several times to remove excess *n*-butylamine. The product was directly used for the next step without further purification. Dry MeOH (50 mL), dry acetone (100 mL) and PTSA (0.199 g) was added to the crude product (**III**). The resulting solution was heated to 60 °C for 24 h and concentrated under vacuum to afford a crude product, which was purified by silica gel chromatography (petroleum ether/EtOAc = 3:2) to provide chiral precursor **1** as a white solid (10.5 g) in 70% overall yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06-7.03 (m, 2H), 6.76-6.73 (m, 2H), 3.74 (t, J = 5.2 Hz, 1H), 3.35-3.28 (m, 1H), 3.10-2.87 (m, 3H), 1.53-1.45 (m, 2H), 1.31-1.25 (m, 5H), 1.18 (s, 3H), 0.93-0.88 (m, 3H); ^{13}CNMR (100 MHz, $CDCl_3$): δ 174.1, 155.7, 130.7, 127.0, 115.7, 76.4, 58.8, 40.4, 35.4, 31.3, 27.7, 26.2, 20.3, 13.7.

1.3 Synthesis of Mac-CP.

To a suspension of chiral precursor **1** (276 mg, 1.0 mmol) and formaldehyde (37% aqueous solution; 243 mg, 3.0 mmol) in water (0.2 mL), 20% NaOH solution (0.1 mmol) was added dropwise. The mixture was stirred at 45 °C for 10 min, then heated to 75 °C and stirred at this temperature for 3 h. After cooling, the solution was neutralized with 0.6 M HCl, the resulting solid was crushed, then filtered and washed with water, hexane and Et_2O in turn (3 times each). After dried under vacuum for 12 h, **Mac-CP** was obtained as a light-pink solid (265 mg). Elemental analysis calcd (%) for $C_{17}H_{26}N_2O_2$: C 70.31, H 9.02, N 9.65; found: C 66.49, H 7.64, N 8.56.

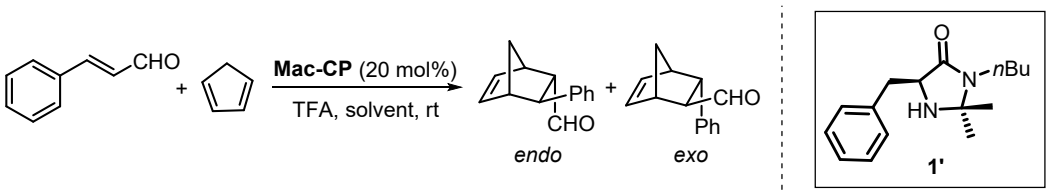
1.4 General procedure for the asymmetric Diels-Alder reaction.

To a solution of catalyst **Mac-CP** (6.5 mg, 0.02 mmol) in CH_3CN/H_2O (0.05 mL, 95/5 v/v) was added α, β-unsaturated aldehyde (0.1 mmol) and cyclopentadiene (0.042 mL, 0.5 mmol, 5 eq). The solution was stirred for 2 minutes before the addition of TFA (1.5 μL, 0.02 mmol). The reaction was then stirred at room temperature for 48 h. After completion of the reaction, hexane (2.0 mL) was added and stirred for 10 minutes, the catalyst was isolated via centrifugation, and thoroughly washed with hexane (4 times). The combined organic phase was evaporated under vacuum. The corresponding products were obtained by column chromatography with ethyl

acetate/petroleum ether as eluent.

1.5 Optimization of the Reaction Conditions.

Table S1. Optimization of the Reaction Conditions for the Asymmetric Diels–Alder Reaction Catalyzed by **Mac-CP**.[a]



Entry	Solvent	Yield (%)[b]	*exo/endo*[c]	*exo* ee (%)[d]	*endo* ee (%)[d]
1	CH_3CN/H_2O (95:5, v/v)	71	1.2/1	91	91
		(89	1.0/1	95	94)[e]
		(71	2.1/1	90	89)[f]
2	CH_3OH/H_2O	46	1.2/1	92	95
		(74	1.8/1	95	93)[e]
3[g]	**CH_3CN/H_2O**	**95**	**1.2/1**	**92**	**93**
4[g, h]	CH_3CN/H_2O	20	1.3/1	91	94
5[g, i]	CH_3CN/H_2O	80	1.2/1	93	92
6[j]	H_2O	91	1.2/1	78	83

[a] Unless otherwise noted, all reactions were performed on a 0.1 mmol scale using **Mac-CP** (0.02 mmol), TFA (0.02 mmol), (*E*)-cinnamaldehyde (0.1 mmol), and cyclopentadiene (0.5 mmol) at r.t. in 0.2 mL of solvent for 48 h. [b] Yield of the isolated product. [c] Determined by ^{1}H NMR spectroscopy. [d] The ee values were determined by HPLC with a Daicel chiral OJ-H column after reduction of the product to the corresponding alcohol with $NaBH_4$. [e] Precursor **1** (20 mol%) was used as the catalyst, and the obtained results are presented in parentheses. [f] Precursor **1'** (20 mol%) was used as the catalyst, and the obtained results are presented in parentheses. [g] 50 μL of solvent was used. [h] 0.02 mmol of HCl was used instead of TFA as additive. [i] 10 mol% of **Mac-CP** and 10 mol% of TFA were used. [j] 0.4 mL of water was used as the solvent, and 0.02 mmol of HBF_4 was used instead of TFA as additive.

1.6 Catalytic activity at different reaction times.

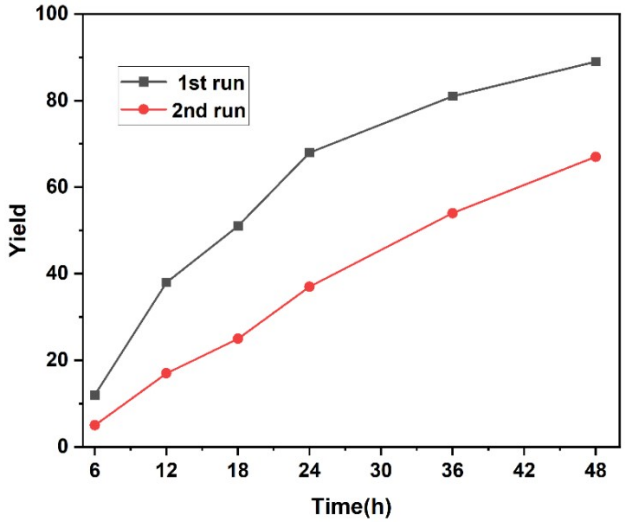


Fig. S1 Catalytic activity at different, shorter reaction times.

1.7 ^{13}C CP/MAS NMR and FT-IR spectra of recycled Mac-CP catalyst.

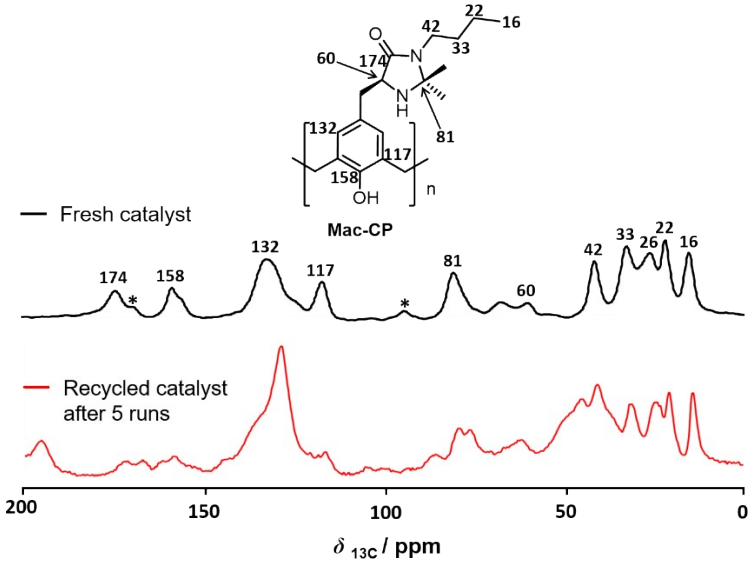


Fig. S2 ^{13}C CP/MAS NMR spectra of fresh (black) and recycled **Mac-CP** catalyst after 5 times of catalytic reactions (red).

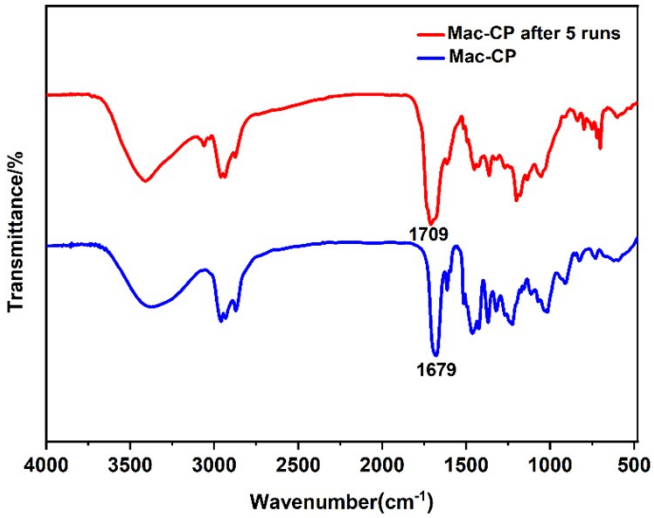
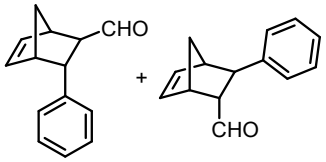
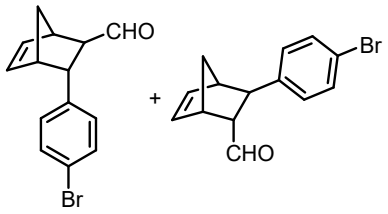


Fig. S3 FT-IR spectra of fresh (black) and recycled **Mac-CP** catalyst after 5 times of catalytic reactions (red).

1.8 Product Data.

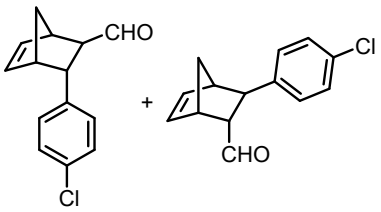


3-Phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde. The product was obtained in 95% yield. Colourless liquid, *exo*/*endo* = 1.15/1.0. The Product was converted to the corresponding alcohol with $NaBH_4$, and the enantiomers were separated by HPLC using a Chiralcel OJ-H column (70/30 hexane/*i*-PrOH; flow rate 1.0 mL/min; *exo* 92% ee, *endo* 93% ee): *endo* isomer (t_R (major) = 19.9 min, t_R (minor) = 9.2 min), *exo* isomer (t_R (major) = 33.8 min, t_R (minor) = 25.1 min). ^{1}H NMR (400 MHz, $CDCl_3$) ***exo*** isomer: δ 9.91 (d, J = 2.0 Hz, 1H), 7.31-7.13 (m, 5H), 6.33 (dd, J = 5.4, 3.2 Hz, 1H), 6.07 (dd, J = 5.6, 2.8 Hz, 1H), 3.73-3.71 (m, 1H), 3.22-3.21 (m, 2H), 2.60-2.58 (m, 1H), 1.63-1.61 (m, 1H), 1.60-1.56 (m, 1H); ***endo*** isomer: δ 9.59 (d, J = 2.0 Hz, 1H), 7.31-7.13 (m, 5H), 6.41 (dd, J = 5.6, 3.2 Hz, 1H), 6.17 (dd, J = 5.6, 2.8 Hz, 1H), 3.33 (s, 1H), 3.12-3.08 (m, 2H), 2.98-2.97 (m, 1H), 1.82-1.79 (m, 1H), 1.63-1.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): (two isomers) δ 203.4, 202.7, 143.5, 142.5, 139.2, 136.5, 136.2, 133.7, 128.5, 128.1, 127.8, 127.3, 126.3, 126.1, 60.8, 59.4, 48.4, 48.3, 47.5, 47.1, 45.6, 45.44, 45.38, 45.1. Spectroscopic data are in agreement with the published data.[2,3]

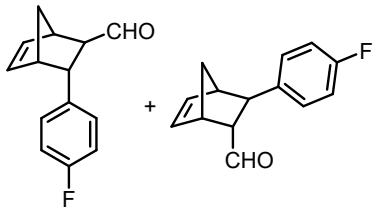


3-(4-Bromophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde. The desired product was obtained in 97% yield. Colourless liquid, 1.15/1.0 *exo*/*endo*. The Product was converted to the corresponding alcohol with $NaBH_4$ and enantiomers were separated by HPLC using a Chiralcel OJ-H column (70/30 hexane/*i*-PrOH; flow rate 1.0 mL/min; *exo* 91% ee, *endo* 84% ee, *endo* isomer (t_R (major) = 9.5 min, t_R (minor) = 4.9 min), *exo* isomer (t_R (major) = 12.7 min, t_R (minor) = 5.6 min). ^{1}H NMR (400 MHz, $CDCl_3$) ***exo*** isomer: δ 9.90 (d, J = 1.92 Hz, 1H), 7.36 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 8.4 Hz, 2H), 6.35 (dd, J = 5.6, 3.2 Hz, 1H), 6.04 (dd, J = 5.6, 2.8 Hz, 1H), 3.69 (t, J = 4.4 Hz, 1H), 3.24-3.18 (m, 2H), 2.54-2.53 (m, 1H), 1.58-1.57 (m, 2H); ***endo*** isomer: δ 9.59 (d, J = 2.0 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H),

6.41 (dd, *J* = 5.6, 3.2 Hz, 1H), 6.17 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.35 (s, 1H), 3.09-3.04 (m, 2H), 2.93-2.91 (m, 1H), 1.75 (d, *J* = 8.8 Hz, 1H), 1.65-1.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): (two isomers) δ 203.0, 202.3, 142.6, 141.6, 139.1, 136.5, 136.2, 133.8, 131.6, 131.1, 129.6, 129.1, 120.1, 119.9, 61.0, 59.5, 48.3, 48.1, 47.5, 47.0, 45.4, 45.1, 45.0, 44.7. Spectroscopic data are in agreement with the published data.[3-5]

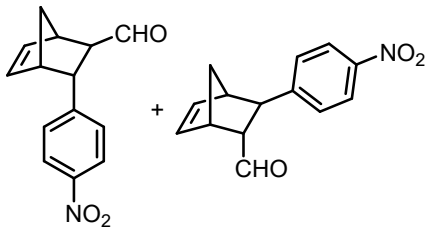


3-(4-Chlorophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde. The desired product was obtained in 90% yield. Colourless liquid, 1.16/1.0 *exo*/*endo*. The Product was converted to the corresponding alcohol with $NaBH_4$ and enantiomers were separated by HPLC using a Chiralcel OJ-H column (80/20 hexane/*i*-PrOH; flow rate 1.0 mL/min; *exo* 90% ee, *endo* 88% ee, *endo* isomer (t_R (major) = 10.7 min, t_R (minor) = 5.2 min), *exo* isomer (t_R (major) = 16.1 min, t_R (minor) = 6.3 min). ^{1}H NMR (400 MHz, $CDCl_3$) ***exo*** isomer: δ 9.90 (d, *J* = 2.0 Hz, 1H), 7.23-7.15 (m, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.35 (dd, *J* = 5.2, 3.2 Hz, 1H), 6.05 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.71 (t, *J* = 4.2 Hz, 1H), 3.23-3.18 (m, 1H), 3.10-3.05 (m, 1H), 2.55-2.53 (m, 1H), 1.58-1.57 (m, 2H); ***endo*** isomer: δ 9.59 (d, *J* = 2.0 Hz, 1H), 7.26-7.18 (m, 4H), 6.41 (dd, *J* = 5.6, 3.2 Hz, 1H), 6.17 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.35 (s, 1H), 3.23-3.18 (m, 2H), 2.93-2.92 (m, 1H), 1.76 (d, *J* = 8.8 Hz, 1H), 1.65-1.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): (two isomers) δ 203.0, 202.3, 142.1, 141.1, 139.1,136.5, 136.3, 133.7, 132.1, 131.9, 129.2, 128.7, 128.6, 128.2, 61.0, 59.6, 48.4, 48.2, 47.5, 47.0, 45.4, 45.1, 45.0, 44.7. Spectroscopic data are in agreement with the published data.[3a,6,7]

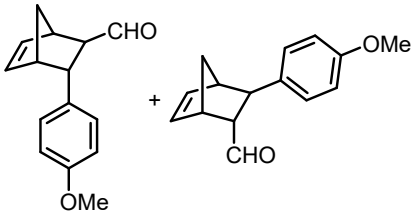


3- (4-Fluorophenyl) bicyclo [2.2.1] hept-5-ene-2-carbaldehyde. The desired product was obtained in 81% yield. Colourless liquid, 1.18/1.0 *exo*/*endo*. The Product was converted to the corresponding alcohol with $NaBH_4$ and enantiomers were separated by HPLC using a Chiralcel OJ-H column (95/5 hexane/*i*-PrOH; flow rate 1.0 mL/min; *exo* 89% ee, *endo* 90% ee, *endo* isomer (t_R (major) = 43.3 min, t_R (minor) = 14.1 min), *exo* isomer (t_R (major) = 65.0 min, t_R (minor) = 25.2 min). ^{1}H NMR (400 MHz,

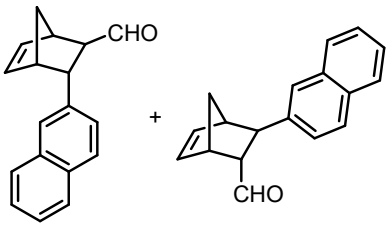
$CDCl_3$) ***exo*** isomer: δ 9.90 (d, J = 2.0 Hz, 1H), 7.08-7.11 (m, 2H), 6.90-6.96 (m, 2H), 6.35 (dd, J = 5.6, 3.2 Hz, 1H), 6.05 (dd, J = 5.6, 2.8 Hz, 1H), 3.70 (t, J = 4.2 Hz, 1H), 3.18-3.23 (m, 2H), 2.53 (dt, J = 5.2, 1.8 Hz, 1H), 1.55-1.65 (m, 2H); ***endo*** isomer: δ 9.59 (d, J = 2.0 Hz, 1H), 7.20-7.23 (m, 2H), 6.97-7.02 (m, 2H), 6.41 (dd, J = 5.6, 3.2 Hz, 1H), 6.17 (dd, J = 5.8, 2.6 Hz, 1H), 3.34 (s, 1H), 3.05-3.09 (m, 2H), 2.90-2.93 (m, 1H), 1.79-1.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): (two isomers) δ 203.2, 202.5, 162.7, 162.5, 160.2, 160.1, 139.2, 138.22, 138.19, 136.4, 136.3, 133.7, 129.23, 129.15, 128.73, 128.66, 115.4, 115.2, 115.0, 114.8, 61.1, 59.7, 48.5, 48.4, 47.6, 47.0, 45.5, 45.1, 45.0, 44.6; HRMS (ESI) calcd for $C_{14}H_{13}FONa$ $[M+Na]^+$ 239.0843, found 239.0839. Spectroscopic data are in agreement with the published data.[3b]



3-(4-Nitrophenylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde. Prepared according to the general procedure using *trans*-3-(4-nitrophenyl)acrylaldehyde (17.7 mg, 0.1 mmol) and cyclopentadiene (0.042 mL, 0.5 mmol) in CH_3NO_2/H_2O (0.05 mL, 95/5 v/v), the desired product was obtained in 82% yield. Colourless liquid, 1.54/1.0 *exo*/*endo*. The enantiomeric excess was determined by reduction of the formyl group followed by conversion of the resulting alchol to the benzoyl ester (3.0 eq Et_3N, 0.1 eq DMAP and 1.1 eq BzCl, CH_2Cl_2 (0.2 M)) and HPLC analysis. Enantiomers were separated by HPLC using a Chiralcel OD-H column (96/4 hexane/*i*-PrOH; flow rate 1.0 mL/min; *exo* 88% ee, *endo* 90% ee, *endo* isomer (t_R (major) = 19.8 min, t_R (minor) = 14.9 min), *exo* isomer (t_R (major) = 23.9 min, t_R (minor) = 17.9 min). ^{1}H NMR (400 MHz, $CDCl_3$) ***exo*** isomer: δ 9.92 (d, J = 1.6 Hz, 1H), 8.12-8.10 (m, 2H), 7.31-7.29 (m, 2H), 6.41 (dd, J = 5.6, 3.2 Hz, 1H), 6.05 (dd, J = 5.6, 2.8 Hz, 1H), 3.90-3.87 (m, 1H), 3.30 (s, 1H), 3.25 (s, 1H), 2.62 (d, J = 4.4 Hz, 1H), 1.62 (s, 2H); ***endo*** isomer: δ 9.64 (d, J = 1.6 Hz, 1H), 8.18-8.16 (m, 2H), 7.44-7.42 (m, 2H), 6.44 (dd, J = 5.6, 3.2 Hz, 1H), 6.20 (dd, J = 5.8, 2.6 Hz, 1H), 3.43 (s, 1H), 3.22-3.19 (m, 2H), 2.97-2.94 (m, 1H), 1.78-1.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): (two isomers) δ 202.1, 201.5, 151.6, 150.5, 146.5, 146.4, 139.1, 136.9, 136.0, 133.9, 128.7, 128.2, 123.8, 123.4, 61.2, 59.6, 48.4, 47.9, 47.6, 47.1, 45.53, 45.45, 45.1, 45.0. Spectroscopic data are in agreement with the published data.[5]

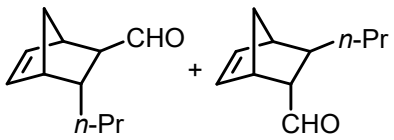


3-(4-Methoxyphenylbicyclo[2,2,1]hept-5-ene-2-carboxaldehyde. Prepared according to the general procedure using *trans*-3-(4-methoxyphenyl)acrylaldehyde (16.2 mg, 0.1 mmol) and cyclopentadiene (0.042 mL, 0.5 mmol) in CH_3NO_2/H_2O (0.05 mL, 95/5 v/v), the desired product was obtained in 86% yield. Colourless liquid, 1.28/1.0 *exo*/*endo*. The Product was converted to the corresponding alcohol with $NaBH_4$ and enantiomers were separated by HPLC using a Chiralcel OJ-H column (70/30 hexane/*i*-PrOH; flow rate 1.0 mL/min; *exo* 85% ee, *endo* 92% ee, *endo* isomer (t_R (major) = 32.7 min, t_R (minor) = 8.2 min), *exo* isomer (t_R (major) = 22.8 min, t_R (minor) = 11.7 min). ^{1}H NMR (400 MHz, $CDCl_3$) ***exo*** isomer: δ 9.91 (d, J = 2.1 Hz, 1H), 7.08-7.06 (m, 2H), 6.80-6.78 (m, 2H), 6.34 (dd, J = 5.6, 3.2 Hz, 1H), 6.07 (dd, J = 5.6, 2.8 Hz, 1H), 3.77 (s, 3H), 3.66 (dd, J = 4.8, 4.0 Hz, 1H), 3.21 and 3.17 (two brs, 2H), 2.54-2.53 (m, 1H), 1.60 (brd, J = 9.0 Hz, 1H), 1.54 (dd, J = 9.0, 1.5 Hz, 1H); ***endo*** isomer: δ 9.58 (d, J = 2.3 Hz, 1H), 7.20-7.17 (m, 2H), 6.86-6.84 (m, 2H), 6.41 (dd, J = 5.6, 3.2 Hz, 1H), 6.16 (dd, J = 5.6, 2.8 Hz, 1H), 3.79 (s, 3H), 3.32 (s, 1H), 3.06 (s, 1H), 3.02 (d, J = 4.4 Hz, 1H), 2.95-2.92 (m, 1H), 1.79 (d, J = 8.8 Hz, 1H), 1.62 (brd, J = 8.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): (two isomers) δ 203.7, 202.9, 158.1, 158.0, 139.2, 136.5, 136.3, 135.5, 134.6, 133.7, 128.8, 128.3, 113.9, 113.5, 60.9, 59.7, 55.3, 55.2, 48.7, 48.6, 47.6, 47.1, 45.5, 45.1, 45.0, 44.7. Spectroscopic data are in agreement with the published data.[3,5]

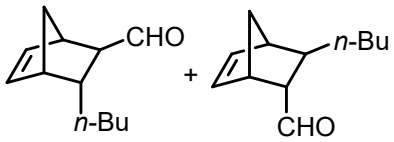


3-(Naphthalen-2-yl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde. Prepared according to the general procedure using *trans*-3-(naphthalen-1-yl)acrylaldehyde (18.2 mg, 0.1 mmol) and cyclopentadiene (0.042 mL, 0.5 mmol) in CH_3CN/H_2O (0.1 mL, 95/5 v/v), the desired product was obtained in 86% yield. Colourless liquid, 1.32/1.0 *exo*/*endo*. The Product was converted to the corresponding alcohol with $NaBH_4$ and enantiomers

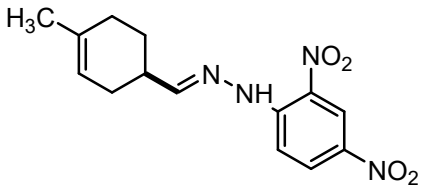
were separated by HPLC using a Chiralcel OJ-H column (95/5 hexane/*i*-PrOH; flow rate 1.0 mL/min; *exo* 92% ee, *endo* 94% ee, *endo* isomer (t_R (major) = 63.9 min, t_R (minor) = 34.6 min), *exo* isomer (t_R (major) = 108.4 min, t_R (minor) = 49.5 min). ^{1}H NMR (400 MHz, $CDCl_3$) ***exo*** isomer: δ 9.96 (d, J = 2.0 Hz, 1H), 7.81-7.72 (m, 3H), 7.54 (brs, 1H), 7.47-7.37 (m, 2H), 7.30 (dd, J = 8.4, 2.0 Hz, 1H), 6.37 (dd, J = 5.6, 3.2 Hz, 1H), 6.08 (dd, J = 5.6, 2.8 Hz, 1H), 3.89 (t, J = 4.2 Hz, 1H), 3.31 and 3.26 (two brs, 2H), 2.74-2.72 (m, 1H), 1.65 (brd, J = 8.5 Hz, 1H), 1.61 (dd, J = 8.5, 1.5 Hz, 1H); ***endo*** isomer: δ 9.65 (d, J = 2.4 Hz, 1H), 7.81-7.72 (m, 3H), 7.68 (brs, 1H), 7.47-7.37 (m, 3H), 6.46 (dd, J = 5.6, 3.6 Hz, 1H), 6.20 (dd, J = 5.6, 2.8 Hz, 1H), 3.38 (s, 1H), 3.31 and 3.26 (two brs, 2H), 3.09-3.06 (m, 1H), 1.88 (d, J = 8.4 Hz, 1H), 1.66-1.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): (two isomers) δ 203.5, 202.8, 141.1, 140.0, 139.2, 136.5, 136.3, 133.8, 133.5, 133.2, 132.1, 132.0, 128.2, 127.7, 127.63, 127.59, 127.51, 127.47, 126.8, 126.6, 126.1, 126.0 , 125.9, 125.5, 125.4, 124.7, 60.8, 59.2, 48.5, 48.2, 47.6, 47.2, 45.8, 45.54, 45.48, 45.2. Spectroscopic data are in agreement with the published data.[5]



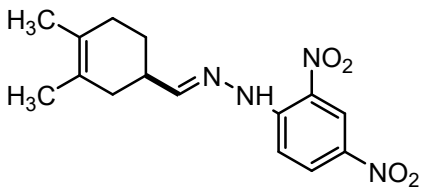
3-Propylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde. The desired product was obtained in 88% yield. Colourless liquid, 1.0/1.08 *exo*/*endo*. The Product was converted to the corresponding phenyl hydrazone derivatives with 2,4-dinitrophenylhydrazine and enantiomers were separated by HPLC using a Chiralcel OJ-H column (97/3 hexane/*i*-PrOH, flow rate 0.5 mL/min, *endo* 91% ee, *endo* isomer (t_R (major) = 67.8 min, t_R (minor) = 77.5 min); 87/13 hexane/*i*-PrOH, flow rate 1.0 mL/min, *exo* 81% ee, *exo* isomer (t_R (major) = 19.9 min, t_R (minor) = 31.7 min). ^{1}H NMR (400 MHz, $CDCl_3$) ***exo*** isomer: δ 9.78 (d, J = 2.8 Hz, 1H), 6.21 (dd, J = 5.6, 3.2 Hz, 1H), 6.13 (dd, J = 5.6, 3.2 Hz, 1H), 3.02 (s, 1H), 2.87 (s, 1H), 1.77-1.75 (m, 2H), 1.49-1.18 (m, 6H), 0.86 (t, J = 7.2 Hz, 3H); ***endo*** isomer: δ 9.37 (d, J = 3.6 Hz, 1H), 6.28 (dd, J = 5.6, 3.2 Hz, 1H), 6.06 (dd, J = 5.8, 2.6 Hz, 1H), 3.12 (s, 1H), 2.66 (s, 1H), 2.38-2.37 (m, 2H),1.55-1.18 (m, 6H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (two isomers) δ 205.1, 204.1, 138.8, 136.1, 135.9, 132.8, 60.0, 58.8, 47.2, 47.0, 46.5, 45.7, 45.1, 44.8, 41.9, 41.6, 38.0, 36.4, 21.6, 21.5, 14.2. Spectroscopic data are in agreement with the published data.[2,8]



3-Butylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde. The desired product was obtained in 83% yield. Colourless liquid, 1.0/1.04 *exo*/*endo*. The Product was converted to the corresponding phenyl hydrazone derivatives with 2,4-dinitrophenylhydrazine and enantiomers were separated by HPLC using a Chiralcel OJ-H column (99/1 hexane/*i*-PrOH, flow rate 0.5 mL/min, *endo* 89% ee, *endo* isomer (t_R (major) = 124.0 min, t_R (minor) = 112.8 min); 95/5 hexane/*i*-PrOH, flow rate 1.0 mL/min, *exo* 71% ee, *exo* isomer (t_R (major) = 28.4 min, t_R (minor) = 41.5 min). ^{1}H NMR (400 MHz, $CDCl_3$) ***exo*** isomer: δ 9.78 (d, J = 2.8 Hz, 1H), 6.21 (dd, J = 5.6, 3.2 Hz, 1H), 6.14 (dd, J = 5.6, 2.8 Hz, 1H), 3.02 (s, 1H), 2.88 (s, 1H), 2.29-2.23 (m, 1H), 1.77-1.75 (m, 1H), 1.49-1.17 (m, 8H), 0.87-0.84 (m, 3H); ***endo*** isomer: δ 9.37 (d, J = 3.6 Hz, 1H), 6.27 (dd, J = 5.6, 3.2 Hz, 1H), 6.06 (dd, J = 6.0, 2.8 Hz, 1H), 3.12 (s, 1H), 2.67 (s, 1H), 2.37 (q, J = 3.6 Hz, 1H), 1.69-1.64 (m, 1H), 1.49-1.17 (m, 8H), 0.91-0.89 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): (two isomers) δ 205.2, 204.1, 138.8, 136.1, 135.9, 132.8, 60.0, 58.8, 47.2, 47.0, 46.5, 45.7, 45.1, 44.9, 42.1, 41.8, 35.5, 33.9, 30.7, 30.6, 22.8, 22.7, 14.0. Spectroscopic data are in agreement with the published data.[4]



(R,E)-1-(2,4-dinitrophenyl)-2-((4-methylcyclohex-3-en-1-yl)methylene)hydrazine. The product was obtained in 94% yield. The enantiomers were separated by HPLC using a Chiralcel AS-H column (90/10 hexane/*i*-PrOH; flow rate 1.0 mL/min; 65% ee): enantiomer (t_R (major) = 14.5 min, t_R (minor) = 15.1 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.98 (s, 1H), 9.10 (d, J = 2.6 Hz, 1H), 8.28 (dd, J = 9.6, 2.6 Hz, 1H), 7.91 (s, 1H), 7.49 (d, J = 5.2 Hz, 1H), 5.46–5.38 (m, 1H), 2.62 (d, J = 5.3 Hz, 1H), 2.35–2.01 (m, 4H), 2.02–1.93 (m, 1H), 1.67 (d, J = 2.0 Hz, 3H), 1.66–1.58 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 145.2, 134.3, 130.0, 123.5, 119.0, 116.6, 36.8, 28.9, 28.61, 26.4, 23.6.



(R,E)-1-((3,4-dimethylcyclohex-3-en-1-yl)methylene)-2-(2,4-dinitrophenyl) hydrazine. The product was obtained in 85% yield. The enantiomers were separated by HPLC using a Chiralcel AS-H column (90/10 hexane/*i*-PrOH; flow rate 1.0 mL/min; 69% ee): enantiomer (t_R (major) = 11.3 min, t_R (minor) = 12.4 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.98 (s, 1H), 9.09 (d, J = 2.6 Hz, 1H), 8.26 (d, J = 2.5 Hz, 1H), 7.91 (s, 1H), 7.49 (d, J = 5.2 Hz, 1H), 2.70–2.59 (m, 1H), 2.12 (s, 4H), 1.93 (ddt, J = 12.7, 7.1, 4.0 Hz, 1H), 1.65 (s, 6H), 1.57 (d, J = 12.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.8, 145.2, 137.7, 130.0, 128.8, 125.8, 123.7, 123.5, 116.6, 37.8, 34.7, 30.6, 26.8, 19.2, 19.0.

Table S2. Comparison of Catalytic Efficiency and Enantioselectivity for the Asymmetric Diels–Alder Reaction of (*E*)-Cinnamaldehyde and Cyclopentadiene with Various Recoverable MacMillan Catalysts.

Catalyst	**Yield (%)**	***exo/endo***	***exo* ee (%)**	***endo* ee (%)**	**Ref.**
PEG-supported Mac	67	1/15.7	86	92	9
Polymer-supported Mac	70	1.2/1	99	99	10
MCF-supported Mac	93	1.3/1	83	87	11
Mac-SILC	67	1/1.1	92	95	12
Polymer-supported Mac	92	1.3/1	85	89	13
H-PhPMO-Mac	98	1/1.1	81	81	14
PMHS-supported Mac	95	1.1/1	92	91	15
Main-chain polymeric Mac	92	1.2/1	91	95	16
Ionic liquid-supported Mac	97	1.3/1	88	93	8
Mac-ChiOSP	94	1/1.1	90	86	5
SiO_2-Mac	94	1.1/1	85	85	17
Silica-supported Mac	91	1/1.2	90	92	18
Polymer-supported Mac	75	1.1/1	91	92	19
Ionic liquid-modified Mac	92	1.2/1	82	78	20
Ionic liquid-supported Mac	90	1/4.6	-	66	21
Polymeric Mac	94	1.5/1	93	97	22
POM–imidazolidinium	38	4.0/1	88	72	23
Main-chain polymeric Mac	87	1.1/1	92	96	24
Phosphonylated Mac	98	1.9/1	99	98	25
Main-chain polymeric Mac	99	1.5/1	93	98	26
Silica-supported Mac	65	1/1.1	82	78	27
Sulfated-Chitin-supported Mac	91	1.2/1	91	93	28
Mac-CPOP	95	1.2/1	75	81	7
Mac-CP	95	1.2/1	92	93	This Work

2. References

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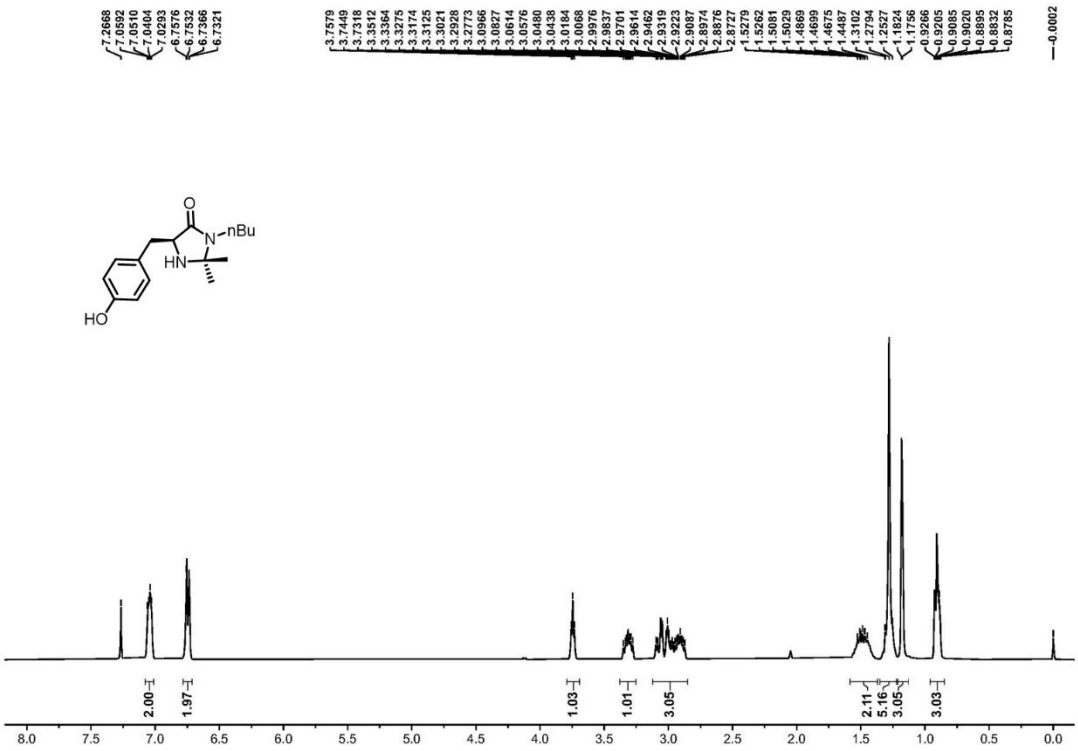
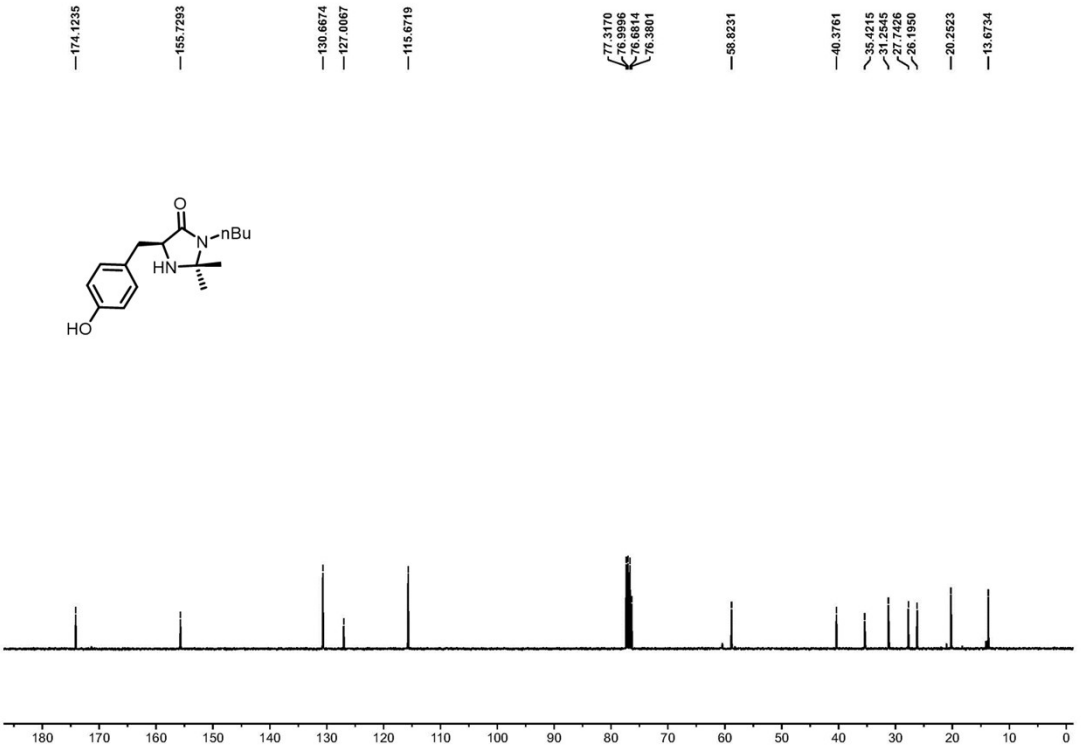
3. Copies of ^{1}H and ^{13}C NMR spectra

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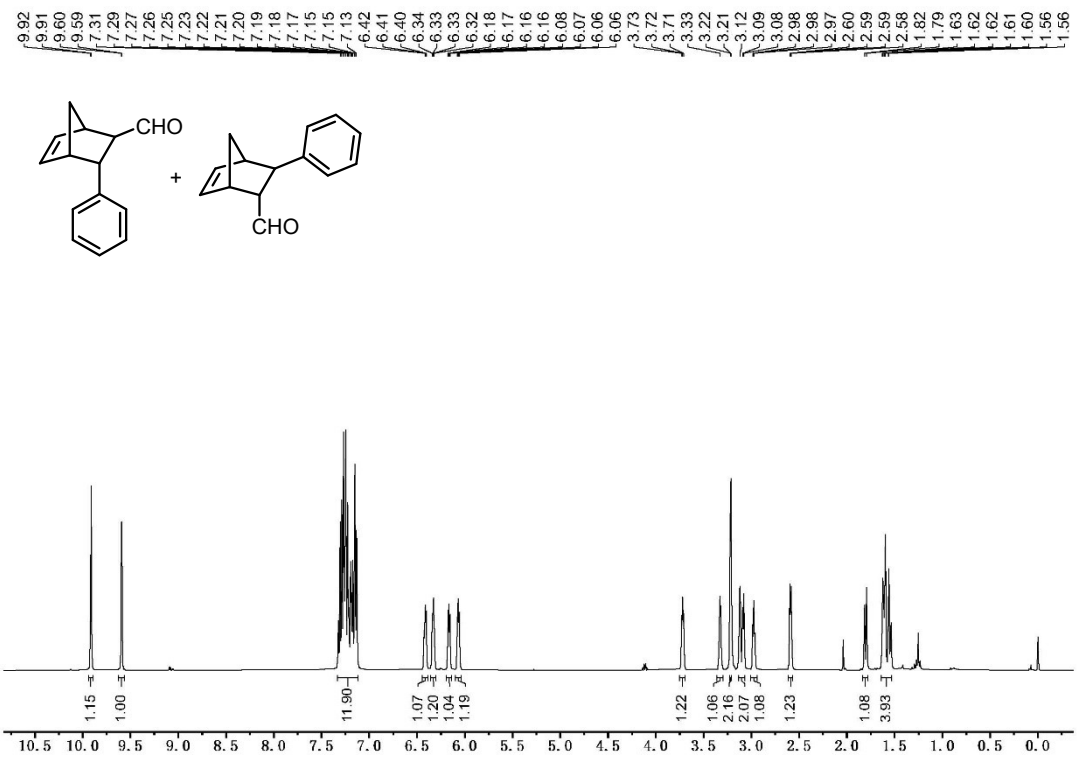
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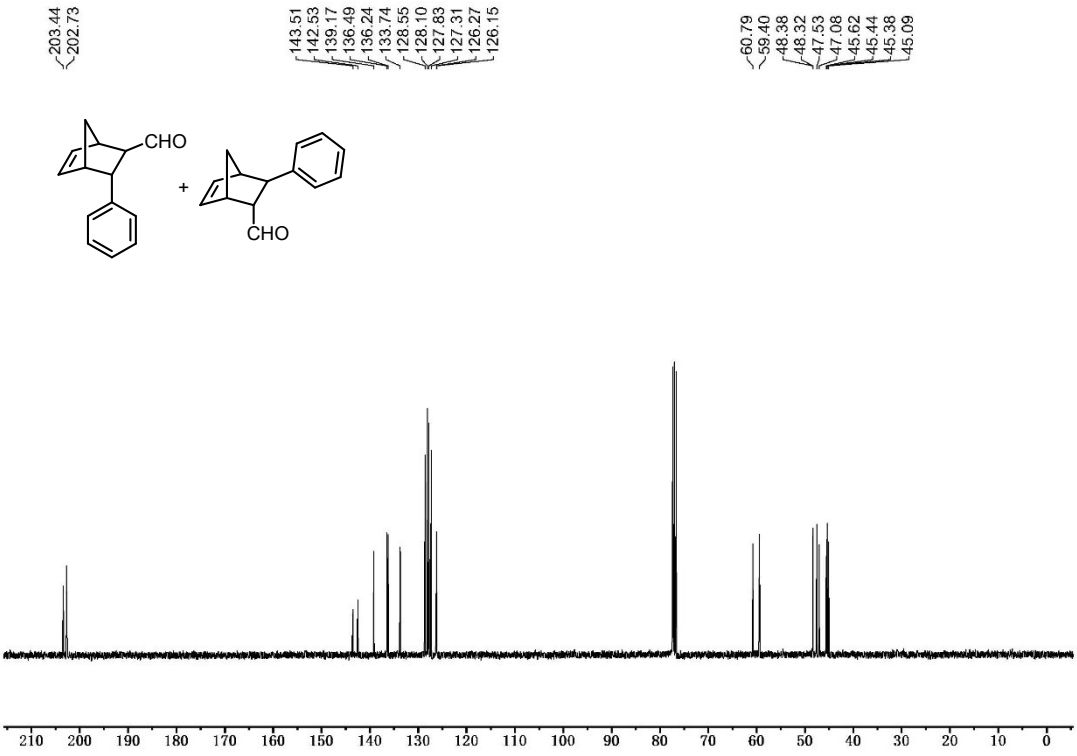
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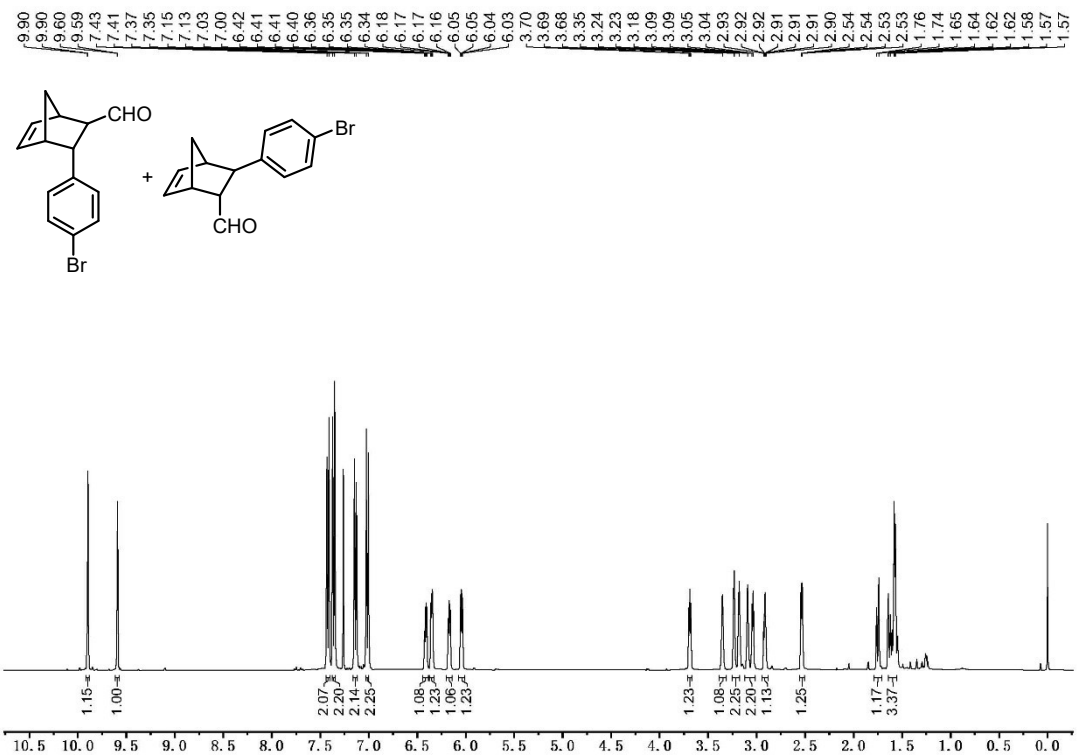
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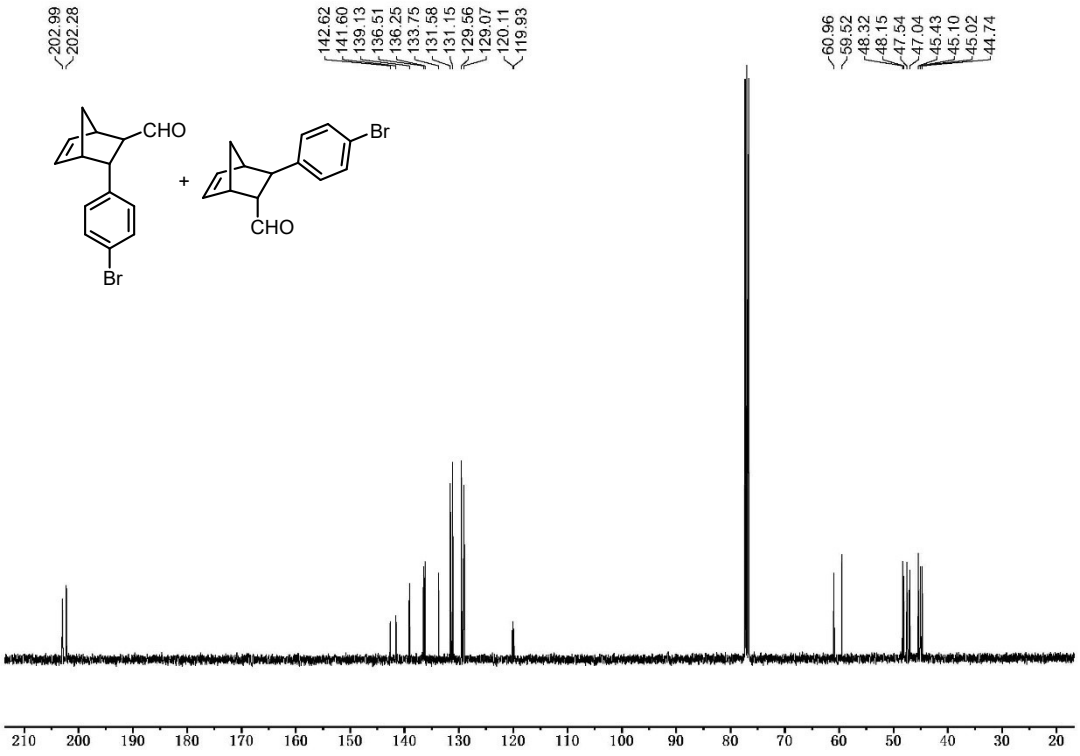
3.37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120.11
119.93
60.96
59.52
48.32
48.15
47.54
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45.02
44.74
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+
Br
CHO
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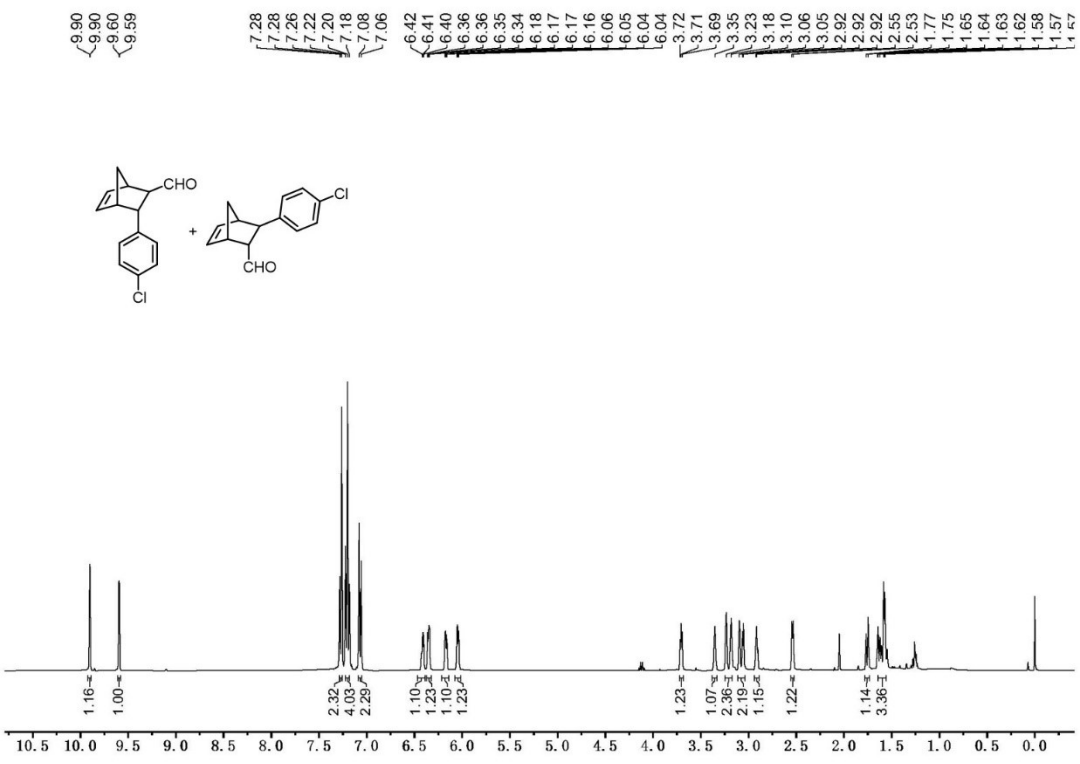
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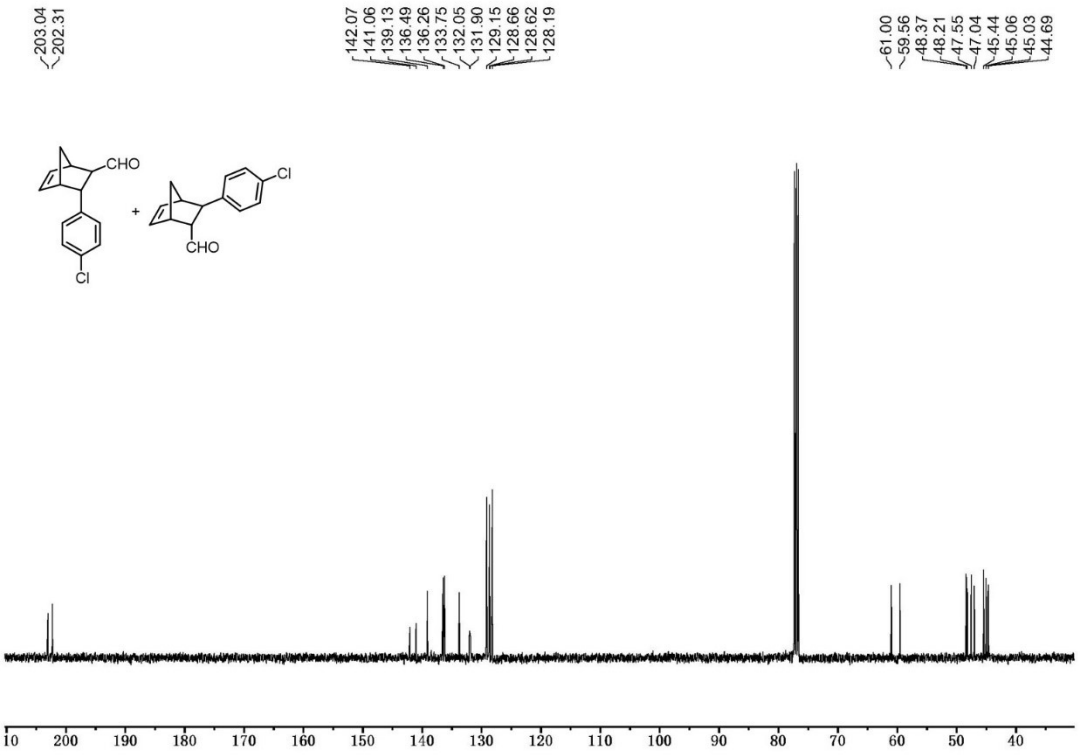
6.42
6.41
6.40
6.36
6.36
6.35
6.34
6.18
6.17
6.16
6.06
6.05
6.04
6.04
3.72
3.71
3.69
3.35
3.23
3.18
3.10
3.06
3.05
2.92
2.92
2.92
2.55
2.53
1.77
1.75
1.65
1.64
1.63
1.62
1.58
1.57
CHO
Cl
+
Cl
CHO
1.16
1.00
2.32
4.03
2.29
1.10
1.23
1.10
1.23
1.23
1.07
2.36
2.19
1.15
1.22
1.14
3.36
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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61.00
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45.03
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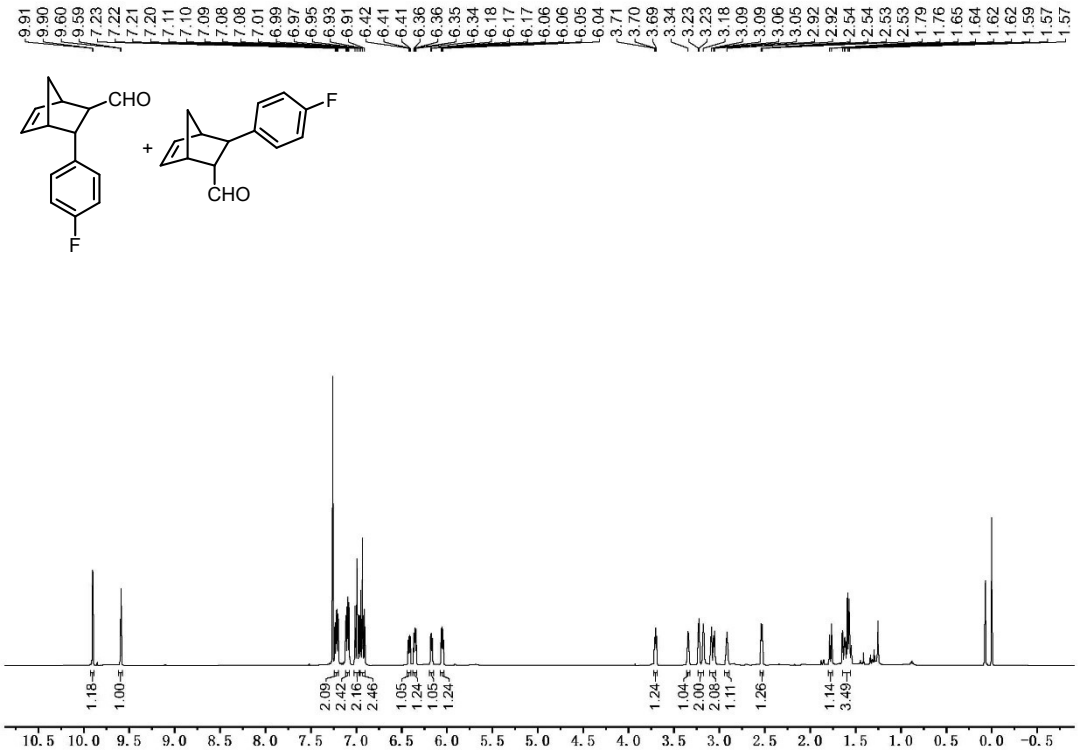
Cl
+
Cl
CHO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6.95
6.93
6.91
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6.34
6.18
6.17
6.17
6.06
6.06
6.05
6.04
3.71
3.70
3.69
3.34
3.23
3.23
3.18
3.09
3.09
3.06
3.05
2.92
2.92
2.54
2.54
2.53
2.53
1.79
1.76
1.65
1.64
1.62
1.62
1.59
1.57
1.57
CHO
F
+
F
CHO

1.18
1.00
2.09
2.42
2.16
2.46
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1.05
1.24
1.24
1.04
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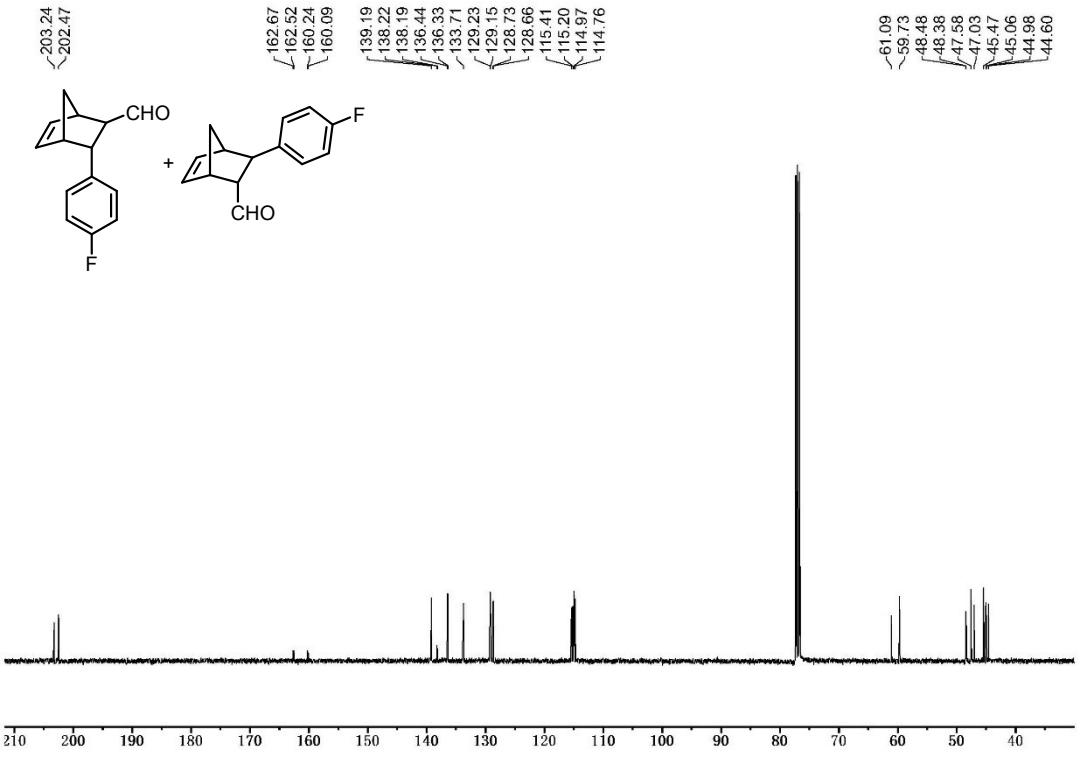
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128.73
128.66
115.41
115.20
114.97
114.76
61.09
59.73
48.48
48.38
47.58
47.03
45.47
45.06
44.98
44.60
CHO
F
+
F
CHO
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200
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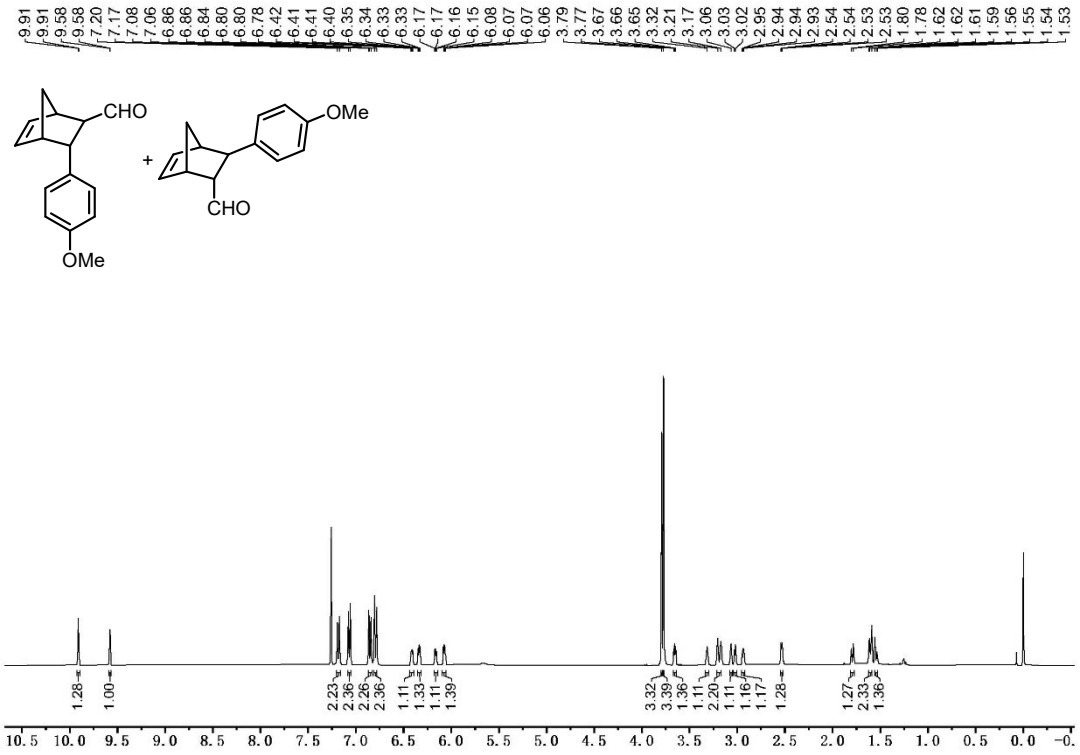
40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6.15
6.08
6.07
6.07
6.06
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3.66
3.65
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3.21
3.17
3.06
3.03
3.02
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2.94
2.94
2.93
2.54
2.54
2.53
2.53
1.80
1.78
1.62
1.62
1.61
1.59
1.56
1.55
1.54
1.53
CHO
OMe
+
OMe
CHO
1.28
1.00
2.23
2.36
2.26
2.36
1.11
1.33
1.11
1.39
3.32
3.39
1.36
1.11
2.20
1.11
1.16
1.17
1.28
1.27
2.33
1.36
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
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0.0
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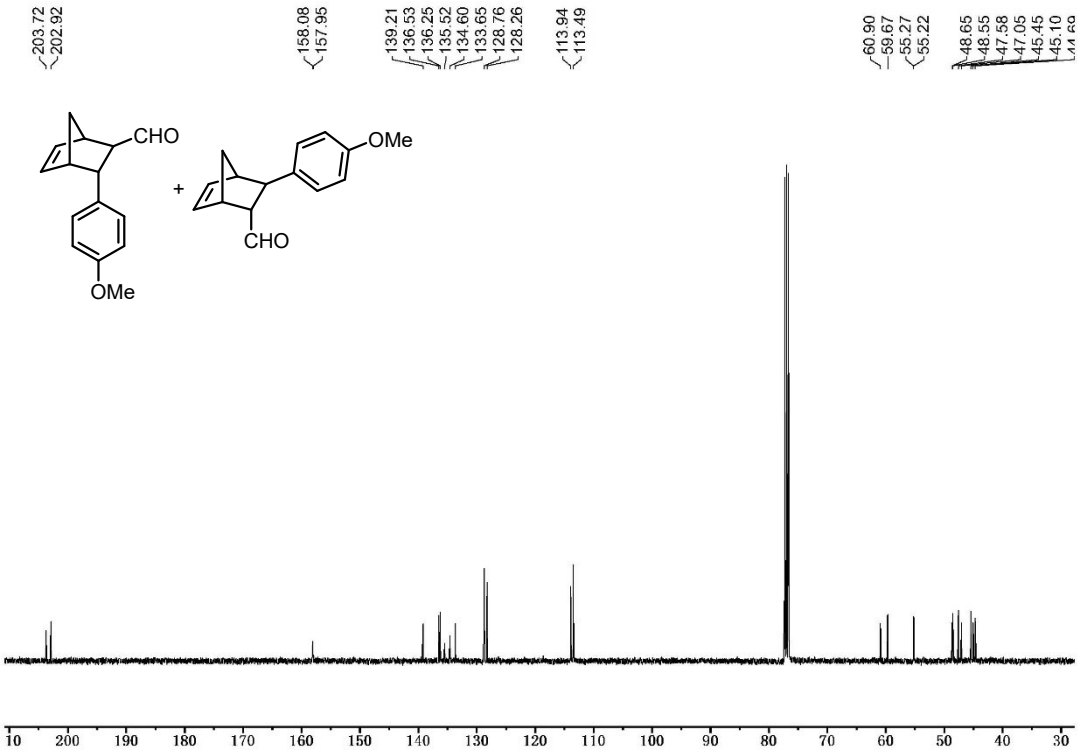
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128.26
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113.49
60.90
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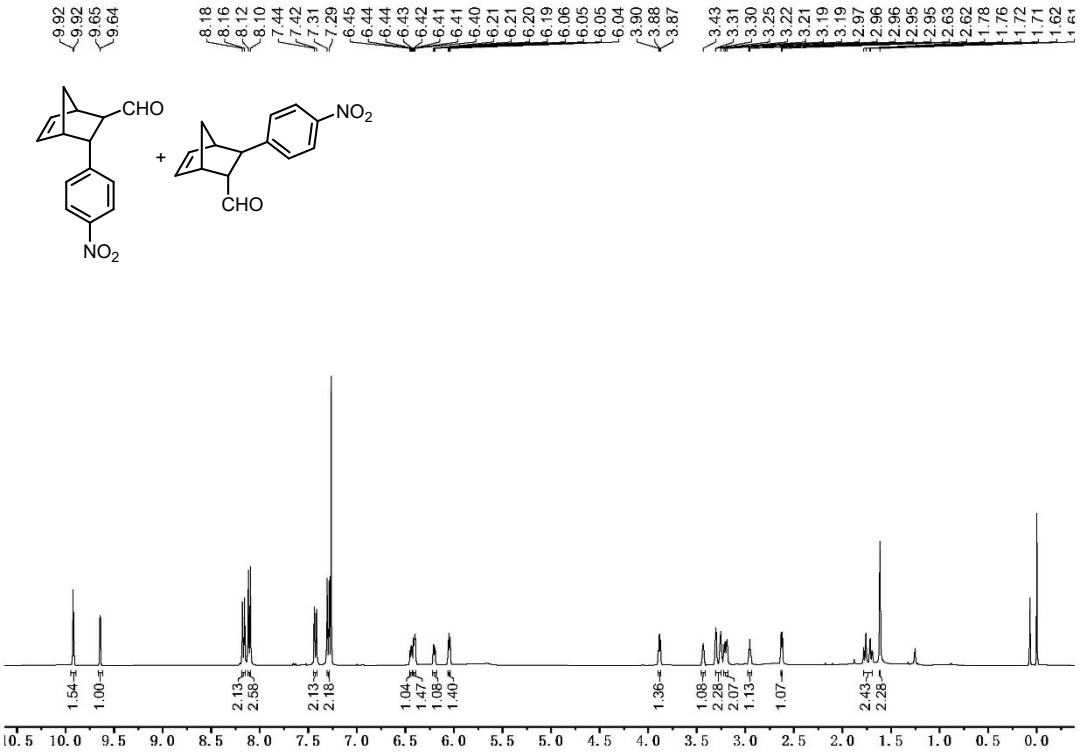
48.65
48.55
47.58
47.05
45.45
45.10
CHO
OMe
+
OMe
CHO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9.92
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9.64
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8.10
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7.42
7.31
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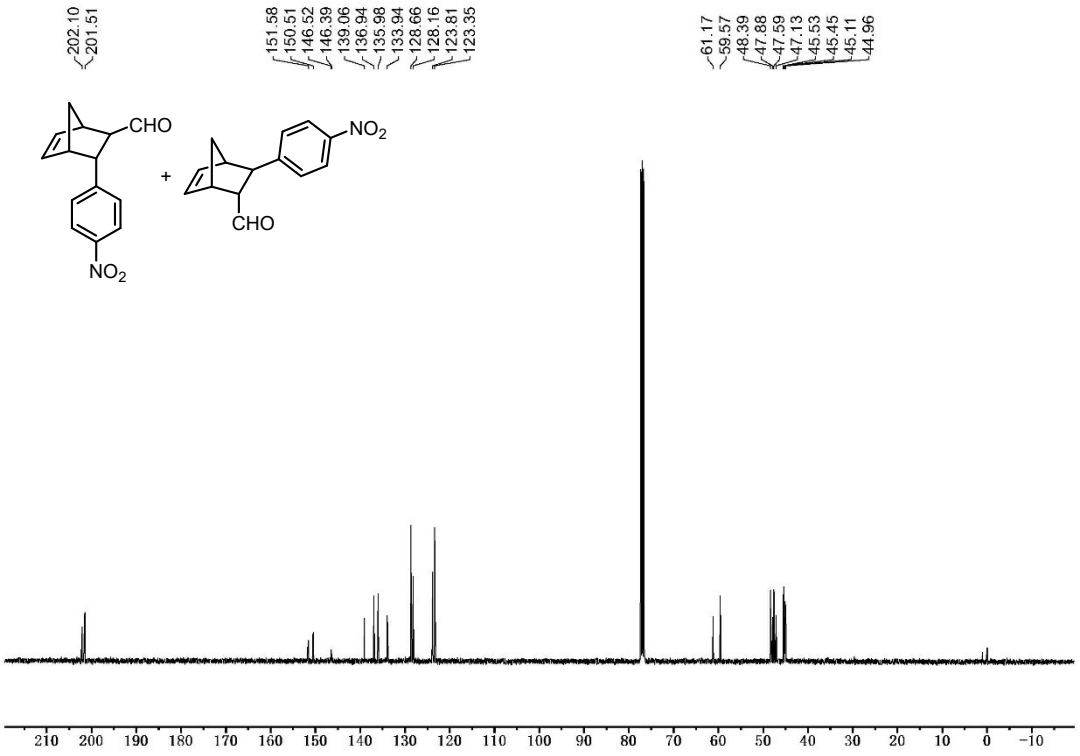
6.45
6.44
6.44
6.43
6.42
6.41
6.41
6.40
6.21
6.21
6.20
6.19
6.06
6.05
6.05
6.04
3.90
3.88
3.87
3.43
3.31
3.30
3.25
3.22
3.21
3.19
3.19
2.97
2.96
2.96
2.95
2.95
2.63
2.62
1.78
1.76
1.72
1.71
1.62
CHO
NO2
+
NO2
CHO
1.54
1.00
2.13
2.58
2.13
2.18
1.04
1.47
1.08
1.40
1.36
1.08
2.28
2.07
1.13
1.07
2.43
2.28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128.16
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123.35
61.17
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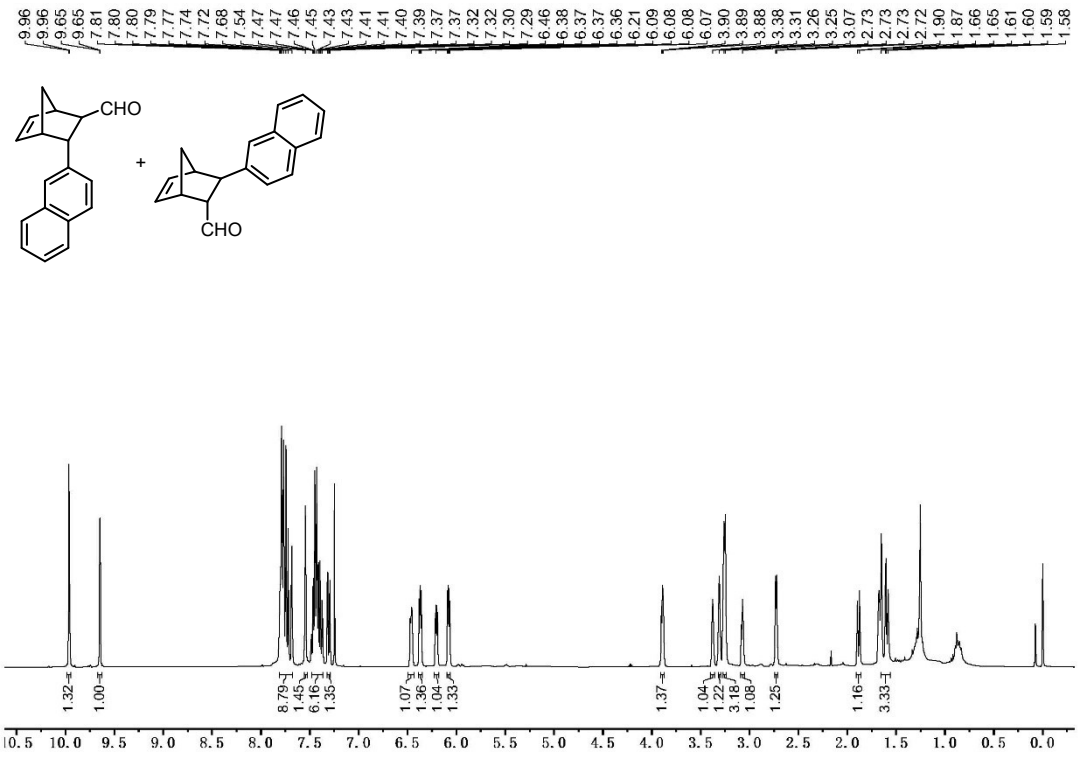
47.59
47.13
45.53
45.45
45.11
44.96
CHO
NO2
+
NO2
CHO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7.54
7.47
7.47
7.46
7.45
7.43
7.43
7.41
7.41
7.40
7.39
7.37
7.37
7.32
7.32
7.30
7.29
6.46
6.38
6.37
6.37
6.36
6.21
6.09
6.08
6.08
6.07
3.90
3.89
3.88
3.38
3.31
3.26
3.25
3.07
2.73
2.73
2.73
2.72
1.90
1.87
1.66
1.65
1.61
1.60
1.59
1.58
CHO
+
CHO
1.32
1.00
8.79
1.45
6.16
1.35
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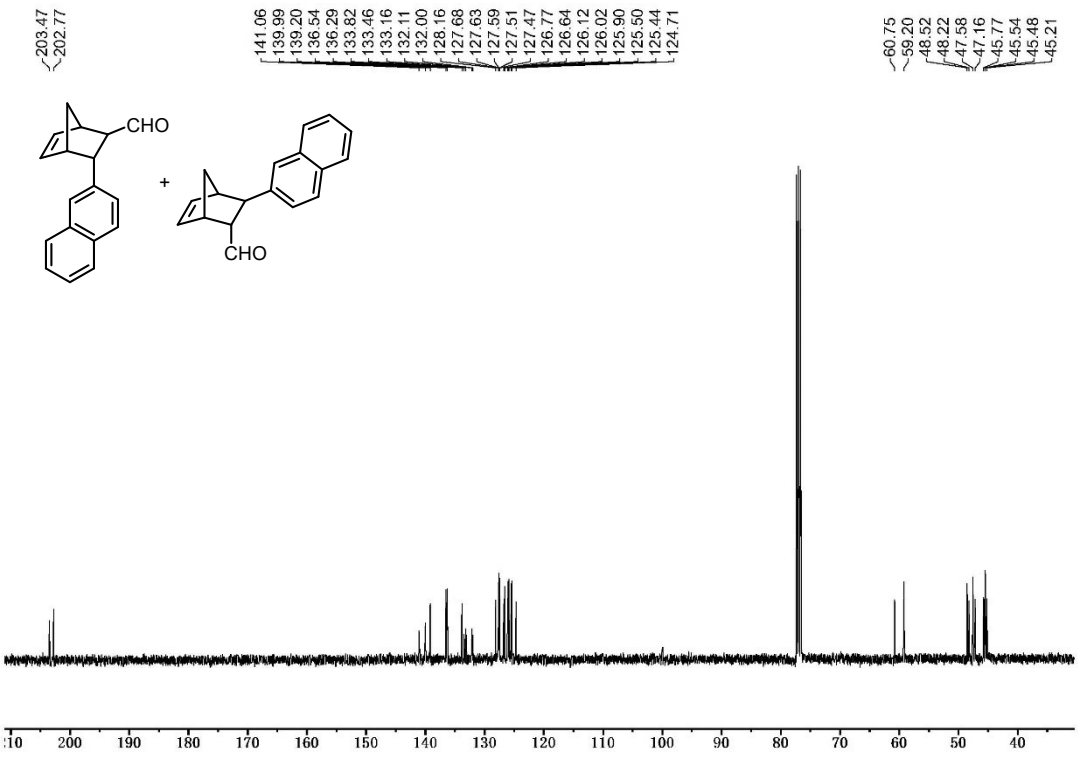
1.04
1.33
1.37
1.04
1.22
3.18
1.08
1.25
1.16
3.33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127.59
127.51
127.47
126.77
126.64
126.12
126.02
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125.50
125.44
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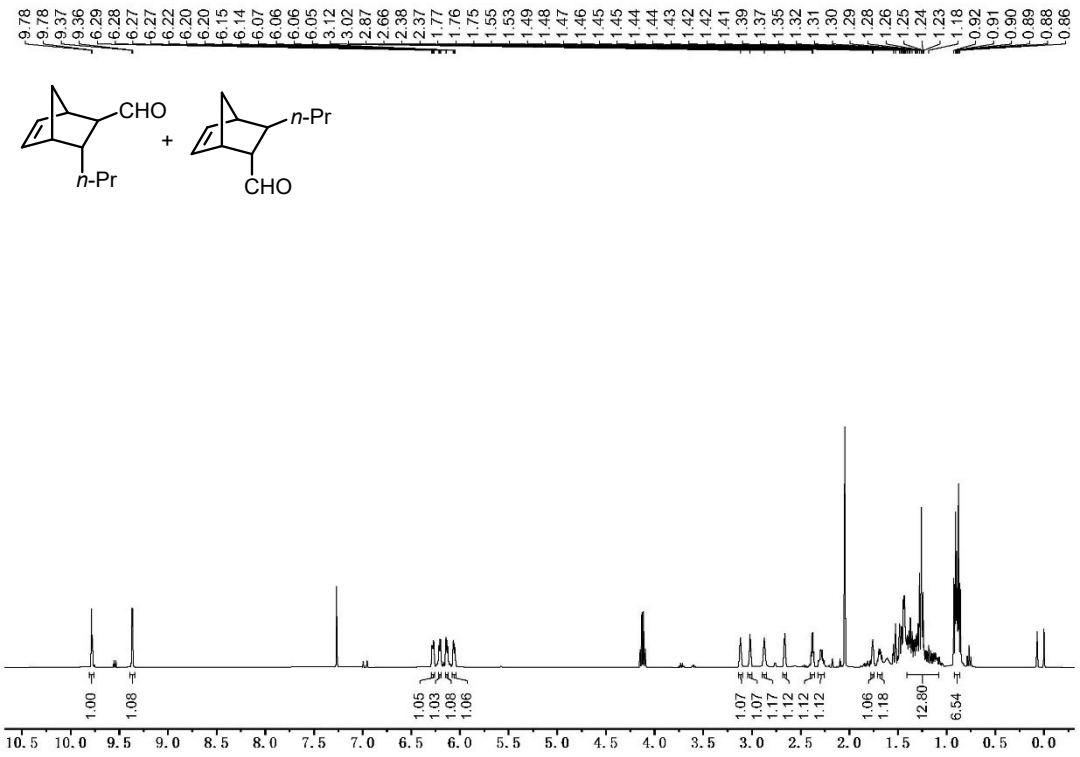
CHO
+
CHO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6.14
6.07
6.06
6.06
6.05
3.12
3.02
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2.66
2.38
2.37
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1.76
1.75
1.55
1.53
1.49
1.48
1.47
1.46
1.45
1.45
1.44
1.44
1.43
1.42
1.42
1.41
1.39
1.37
1.35
1.32
1.31
1.30
1.29
1.28
1.26
1.25
1.24
1.23
1.18
0.92
0.91
0.90
0.89
0.88
0.86
CHO
n-Pr
+
n-Pr
CHO

1.00
1.08
1.05
1.03
1.08
1.06
1.07
1.07
1.17
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1.12
1.12
1.06
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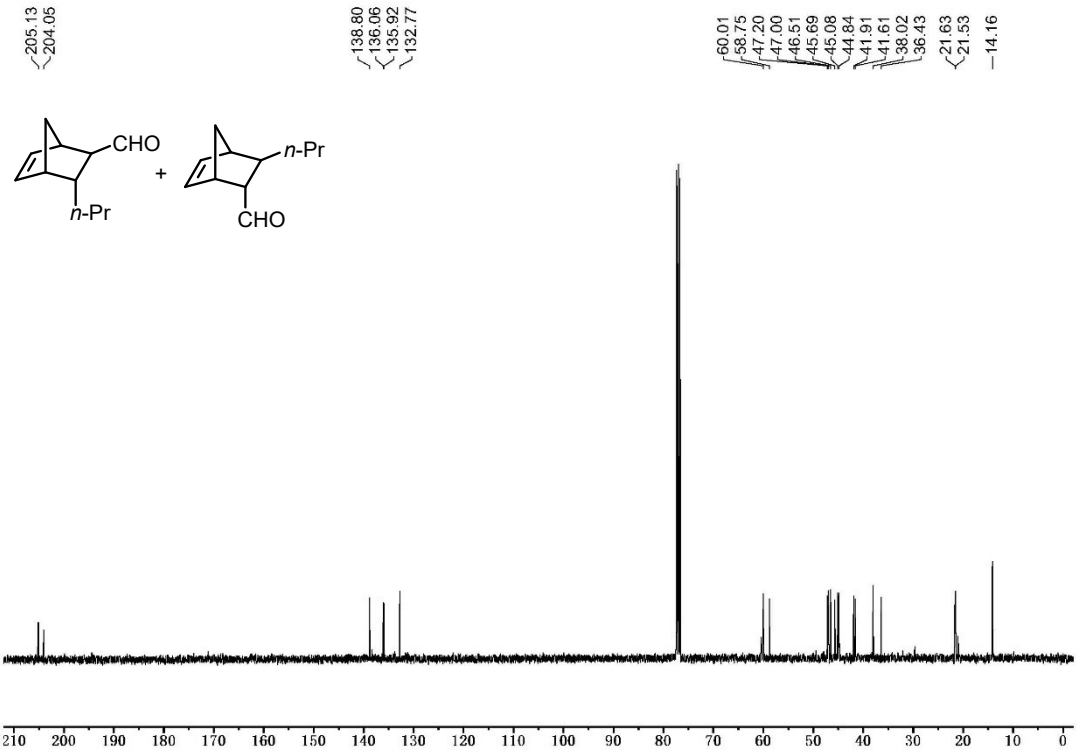
6.54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58.75
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47.00
46.51
45.69
45.08
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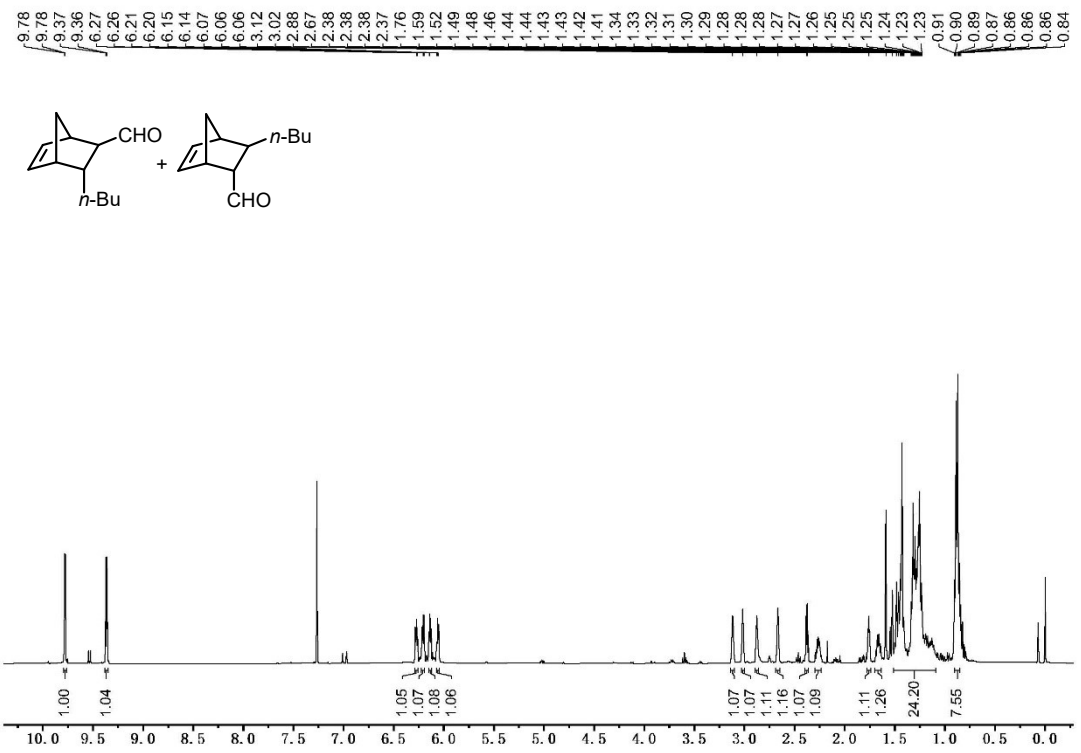
41.61
38.02
36.43
21.63
21.53
14.16
CHO
n-Pr
+
n-Pr
CHO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9.78
9.37
9.36
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6.26
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6.20
6.15
6.14
6.07
6.06
6.06
3.12
3.02
2.88
2.67
2.38
2.38
2.38
2.37
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1.59
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1.46
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1.44
1.43
1.43
1.42
1.41
1.34
1.33
1.32
1.31
1.30
1.29
1.28
1.28
1.28
1.27
1.27
1.26
1.25
1.25
1.25
1.24
1.23
1.23
0.91
0.90
0.89
0.87
0.86
0.86
0.86
0.84
CHO
n-Bu
+
n-Bu
CHO
1.00
1.04
1.05
1.07
1.08
1.06
1.07
1.07
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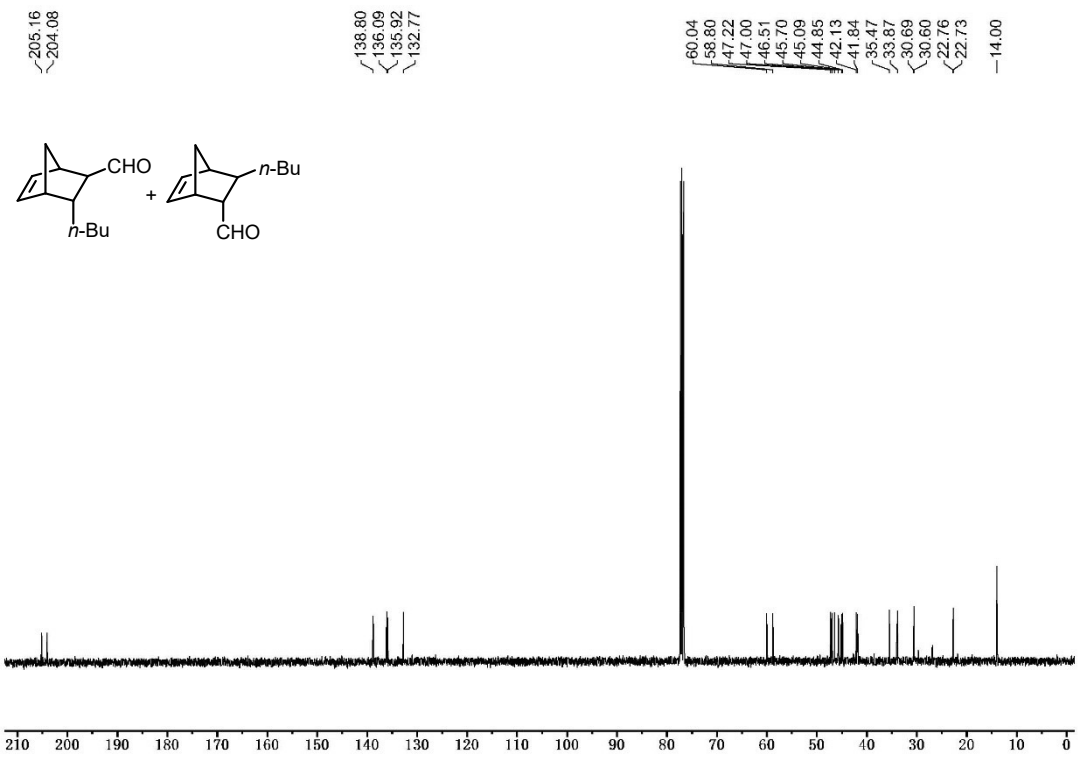
1.07
1.09
1.11
1.26
24.20
7.55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58.80
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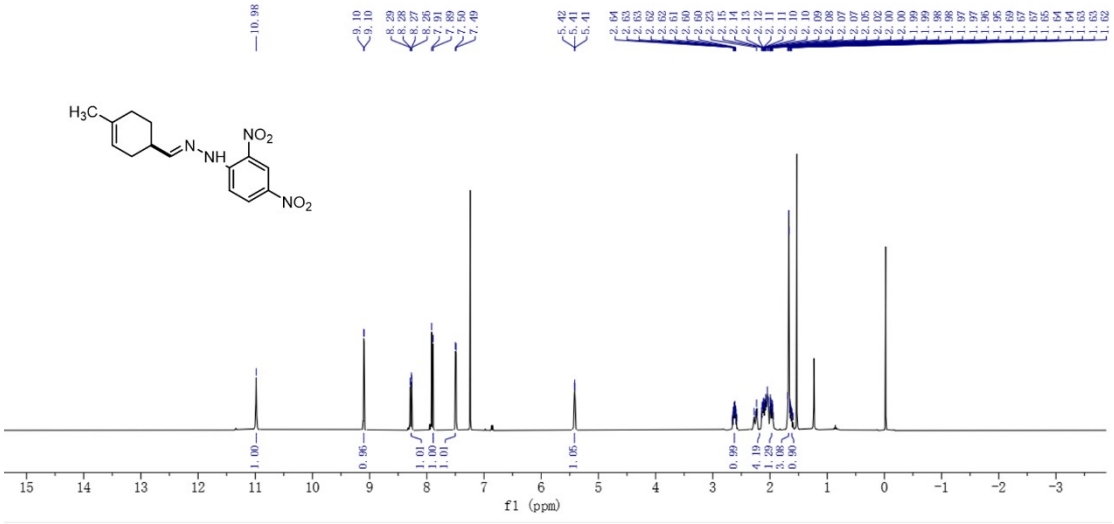
46.51
45.70
45.09
44.85
42.13
41.84
35.47
33.87
30.69
30.60
22.76
22.73
14.00
CHO
n-Bu
+
n-Bu
CHO
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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8.28
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8.26
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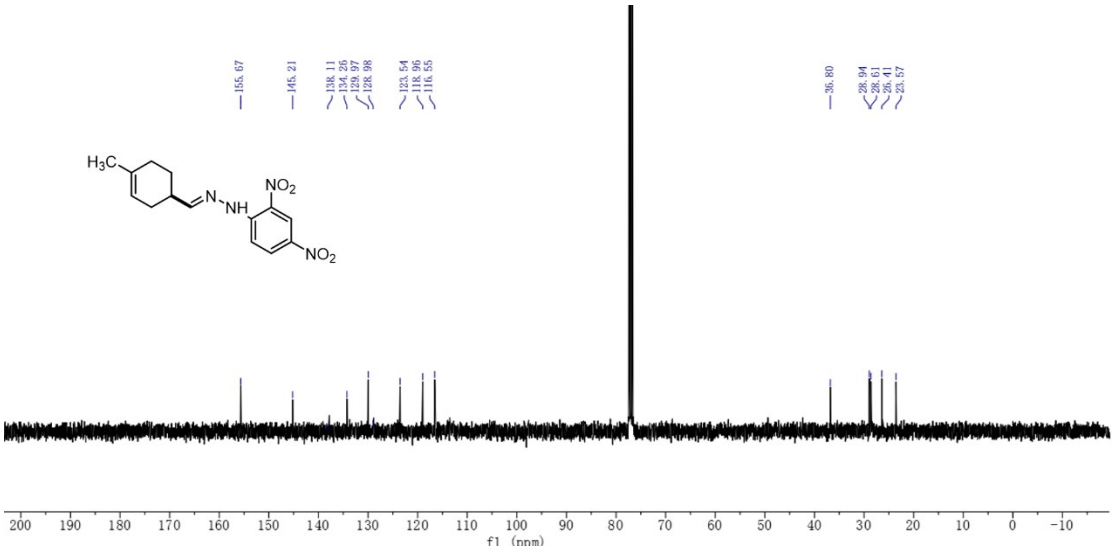
7.59
7.49
5.42
5.41
5.41
H3C
N
NH
NO2
NO2
1.00
0.96
1.01
1.00
1.01
1.05
0.99
4.19
1.29
3.08
0.90
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)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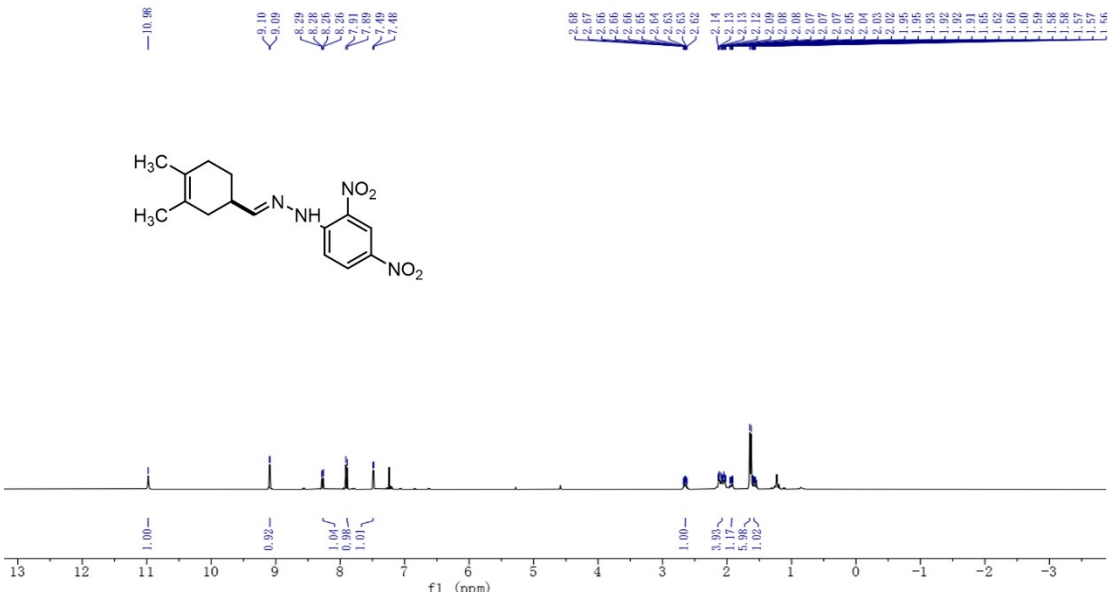
145.21
138.11
134.26
129.97
128.98
123.54
118.96
116.55
36.80
28.94
28.61
26.41
23.57
H3C
N
NH
NO2
NO2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.26
7.91
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7.49
7.48
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2.66
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2.65
2.64
2.63
2.63
2.62
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2.13
2.12
2.09
2.08
2.08
2.07
2.07
2.07
2.05
2.04
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1.91
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1.62
1.60
1.60
1.59
1.58
1.57
1.57
1.56
H3C
H3C
N
NH
NO2
NO2
1.00
0.92
1.04
0.98
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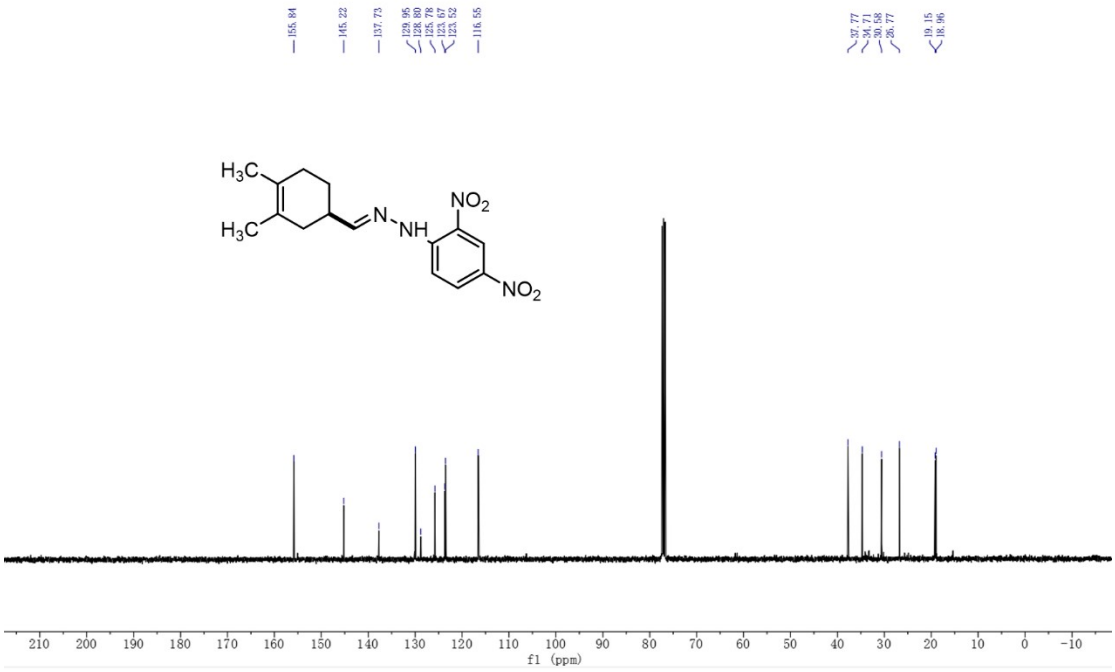
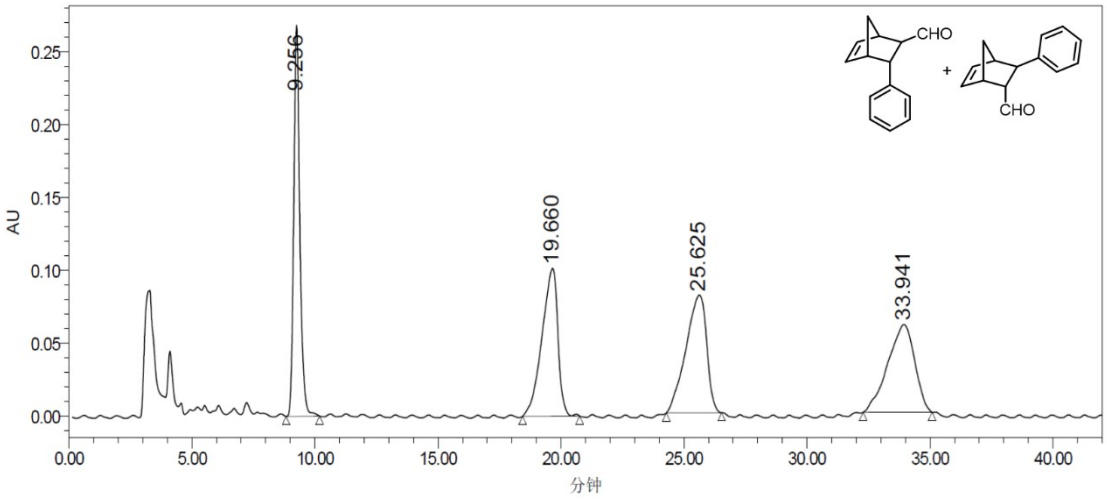
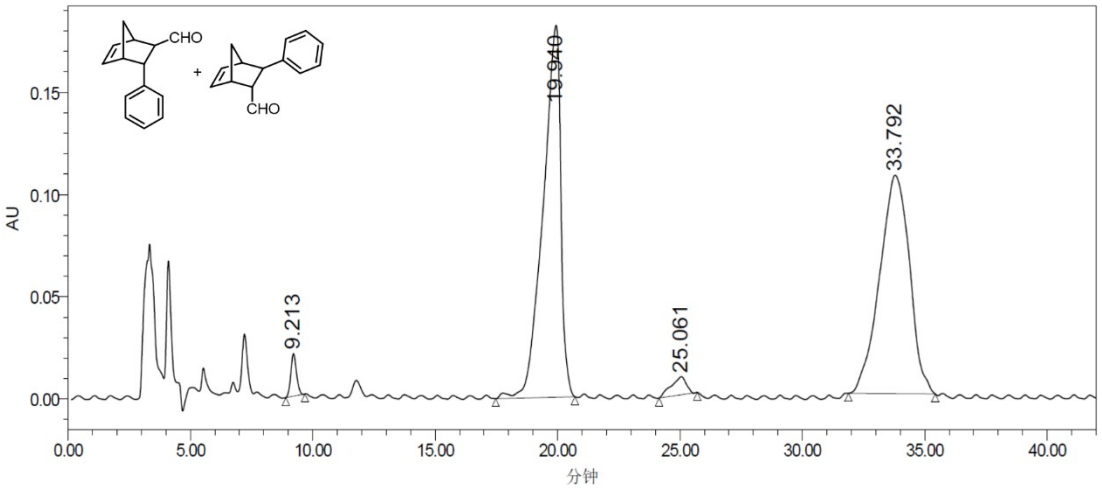
1.00
3.03
1.17
5.08
1.02
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)



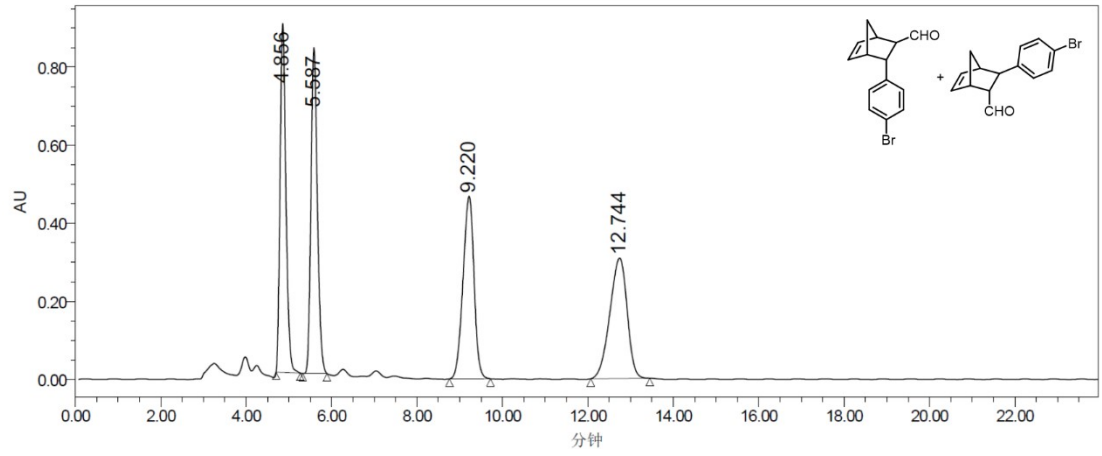
4. Copies of HPLC spectra of product



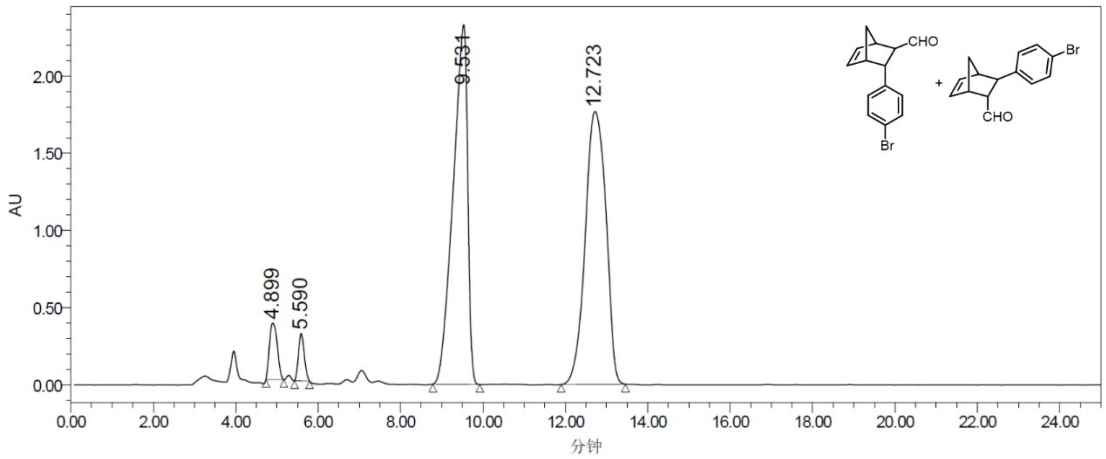
Peak	**Retention Time** [min]	**Area** [microvolt*s]	**Height** [microvolt]	**Relative Area** [%]
1	9.256	4602011	268449	24.88
2	19.660	4571487	101411	24.71
3	25.625	4742273	80755	25.64
4	33.941	4583357	60305	24.78



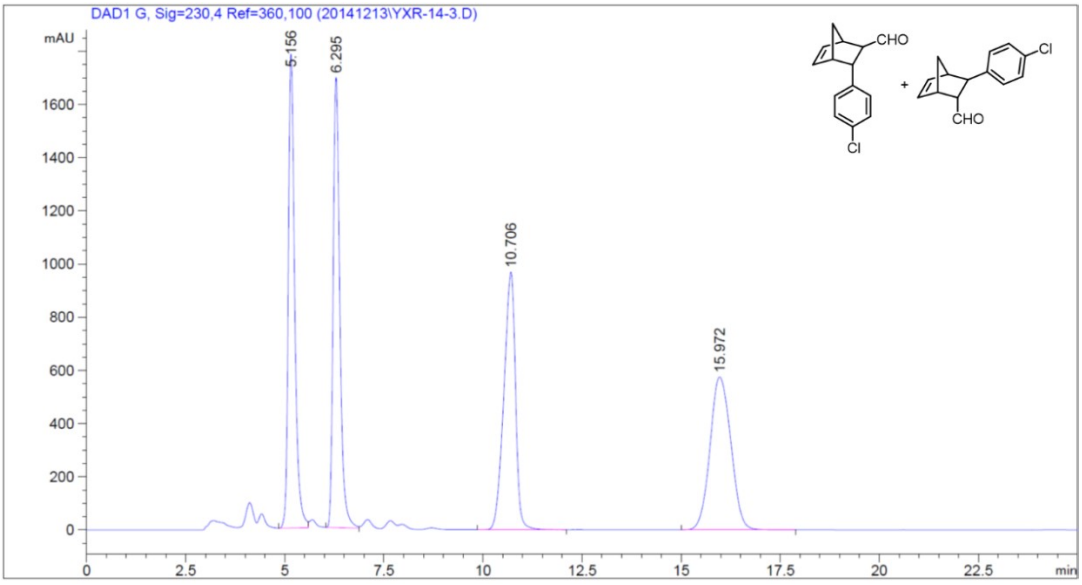
Peak	**Retention Time** [min]	**Area** [microvolt*s]	**Height** [microvolt]	**Relative Area** [%]
1	9.213	334977	20856	1.77
2	19.940	9166881	181928	48.32
3	25.061	381710	8854	2.01
4	33.792	9088323	106909	47.90



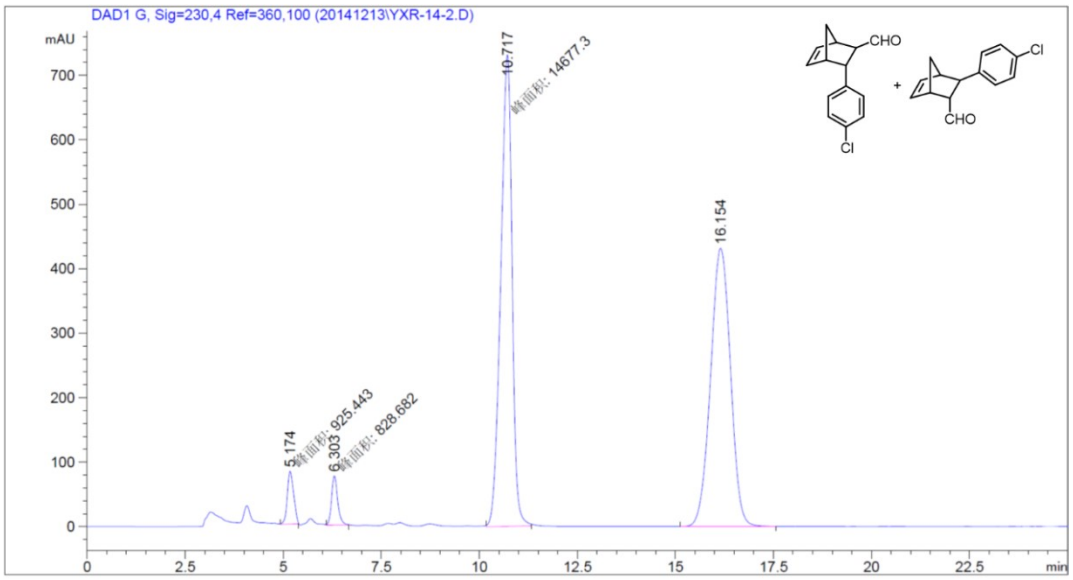
Peak	**Retention Time** [min]	**Area** [microvolt*s]	**Height** [microvolt]	**Relative Area** [%]
1	4.856	8478910	894679	24.78
2	5.587	8680399	836494	25.37
3	9.220	8396427	467631	24.54
4	12.744	8665909	308544	25.32



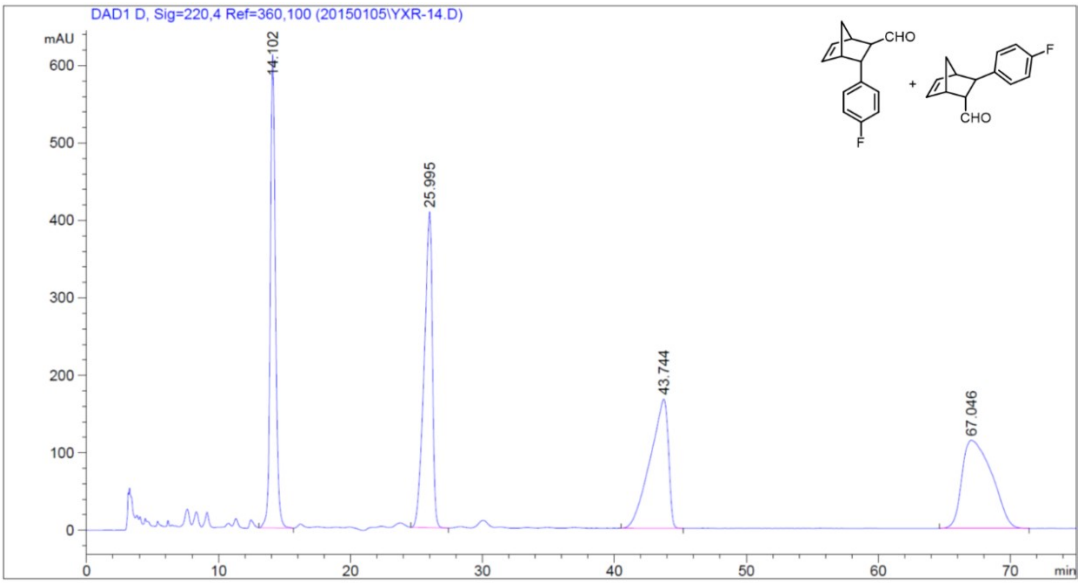
Peak	**Retention Time** [min]	**Area** [microvolt*s]	**Height** [microvolt]	**Relative Area** [%]
1	4.899	4847647	365408	3.83
2	5.590	3000439	306801	2.37
3	9.531	56954630	2327793	44.99
4	12.723	61788914	1765911	48.81



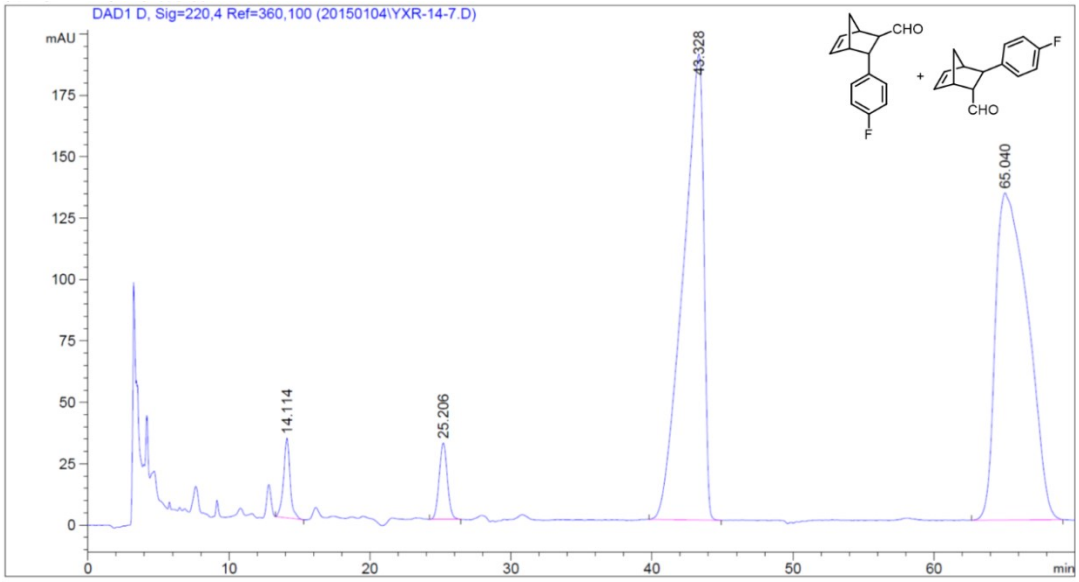
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	5.156	1.99959e4	1783.97327	24.8167
2	6.295	1.97281e4	1694.29089	24.4843
	10.706	1.98124e4	969.28064	24.5889
	15.972	2.10381e4	574.78815	26.1101



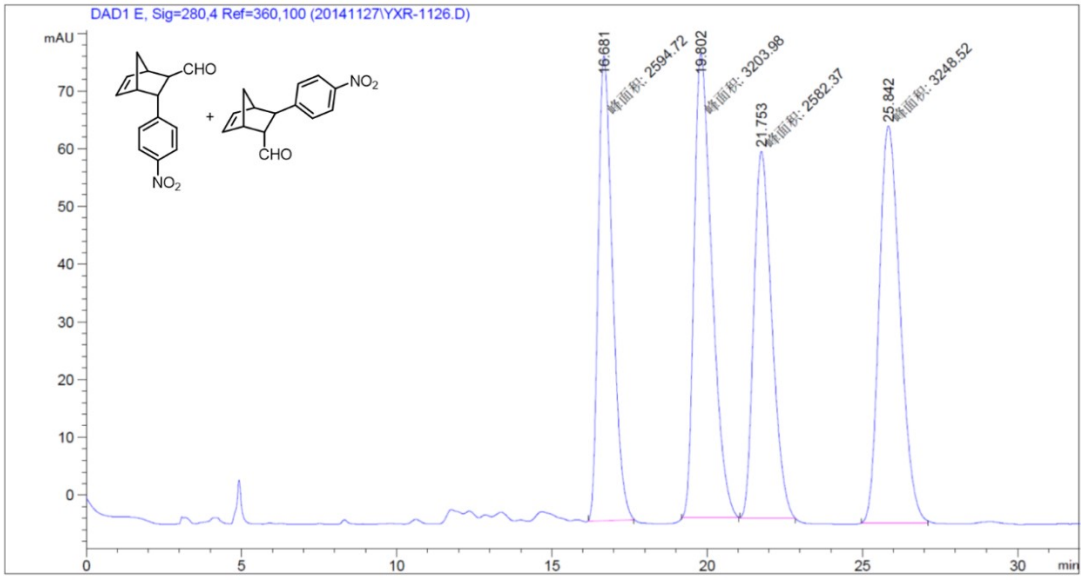
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	5.174	925.44299	82.06293	2.9226
2	6.303	828.68219	76.42378	2.6171
3	10.717	1.46773e4	731.51764	46.3525
4	16.154	1.52331e4	431.43854	48.1078



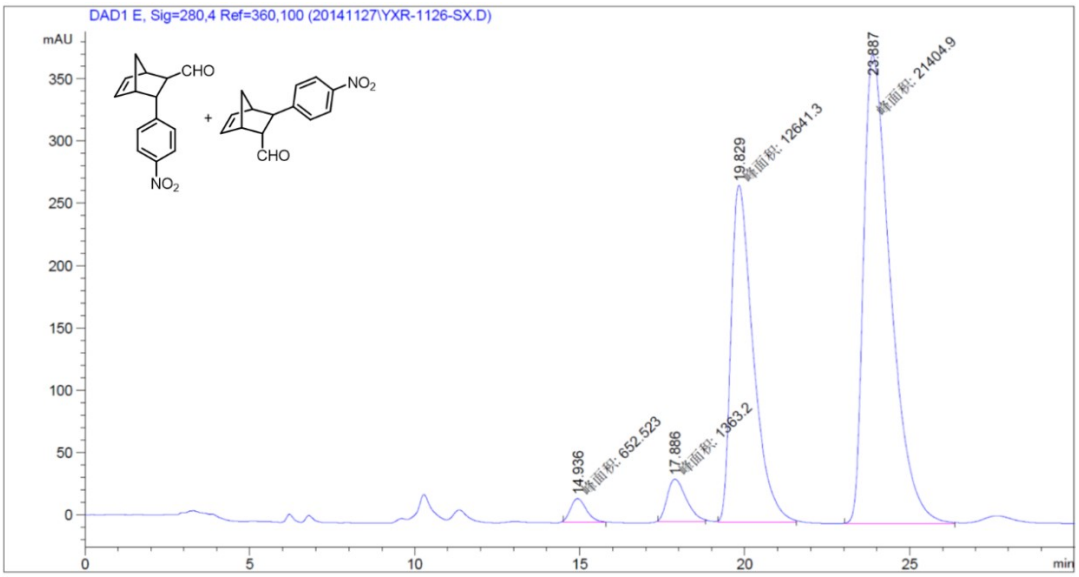
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	14.102	1.65701e4	611.34021	24.3042
2	25.995	1.76448e4	408.06799	25.8806
3	43.744	1.60629e4	166.75073	23.5603
4	67.046	1.79001e4	114.00917	26.2549



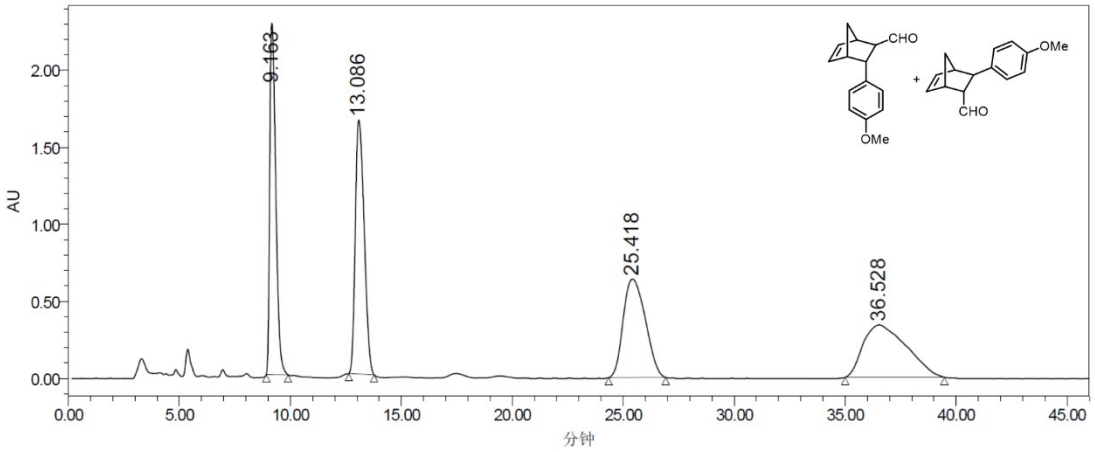
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	14.114	1045.77380	32.47417	2.4355
2	25.206	1253.16882	31.11964	2.9185
3	43.328	1.92307e4	189.71445	44.7861
4	65.040	2.14093e4	133.20595	49.8599



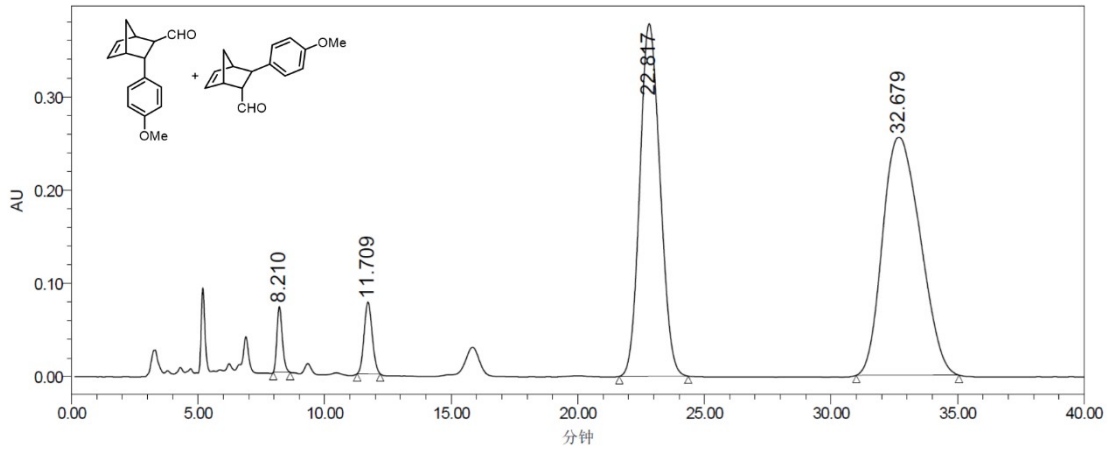
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	16.681	2594.71582	80.53811	22.3113
2	19.802	3203.98193	80.37839	27.5503
3	21.753	2582.36890	63.46484	22.2052
4	25.842	3248.52466	68.80418	27.9333



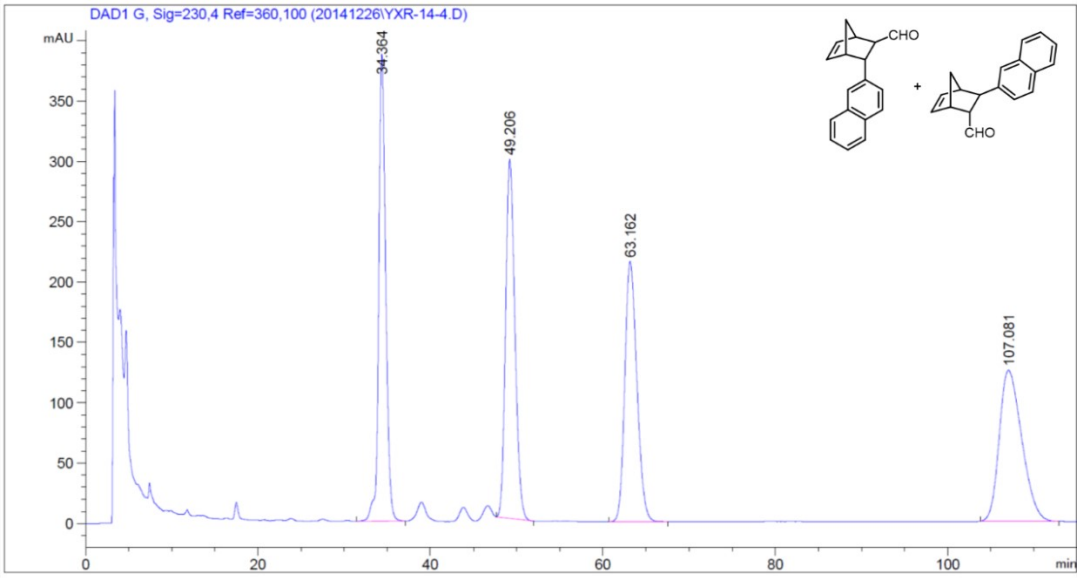
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	14.936	652.52313	19.20616	1.8094
2	17.886	1363.19727	33.92844	3.7801
3	19.829	1.26413e4	270.41690	35.0545
4	23.887	2.14049e4	376.10620	59.3559



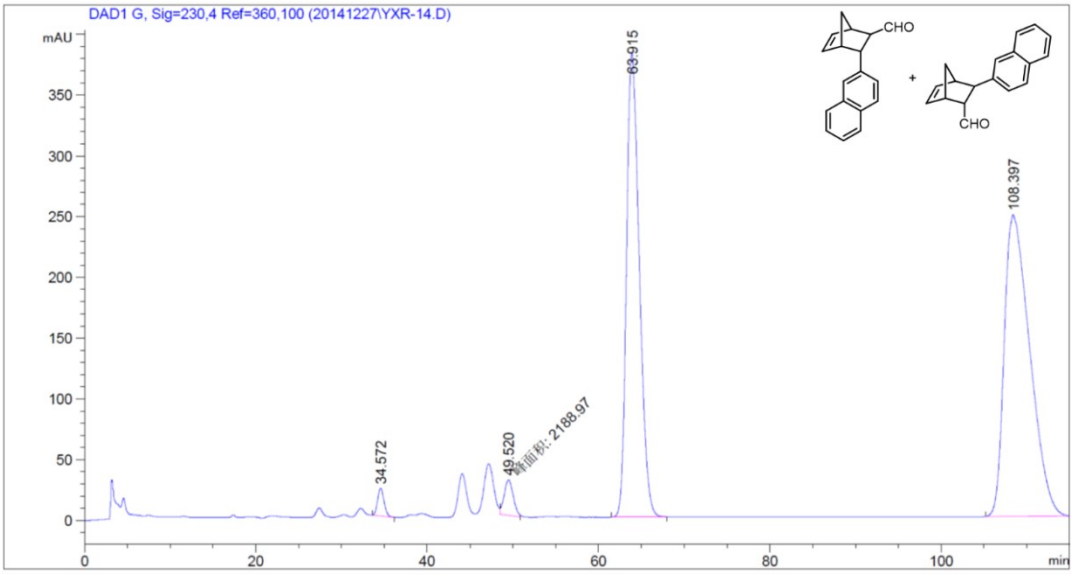
Peak	**Retention Time** [min]	**Area** [microvolt*s]	**Height** [microvolt]	**Relative Area** [%]
1	9.163	43035059	2281249	24.03
2	13.086	43035059	1648518	25.57
3	25.418	44293951	639461	24.74
4	36.528	45950716	340337	25.66



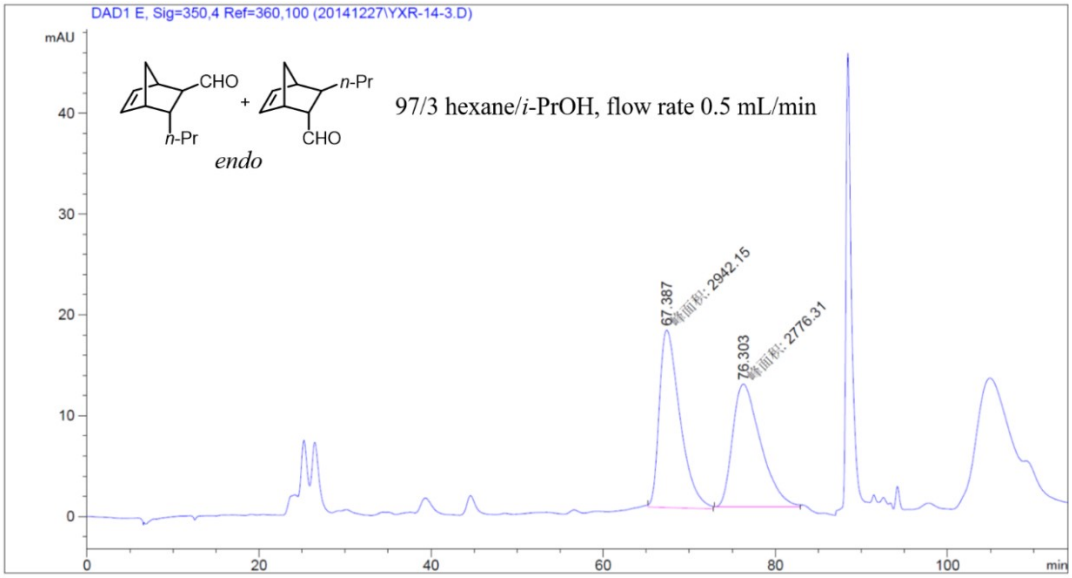
Peak	**Retention Time** [min]	**Area** [microvolt*s]	**Height** [microvolt]	**Relative Area** [%]
1	8.210	1046721	70643	2.09
2	11.709	1706167	76596	3.40
3	22.817	20988777	377795	41.84
4	32.679	26420142	254787	52.67



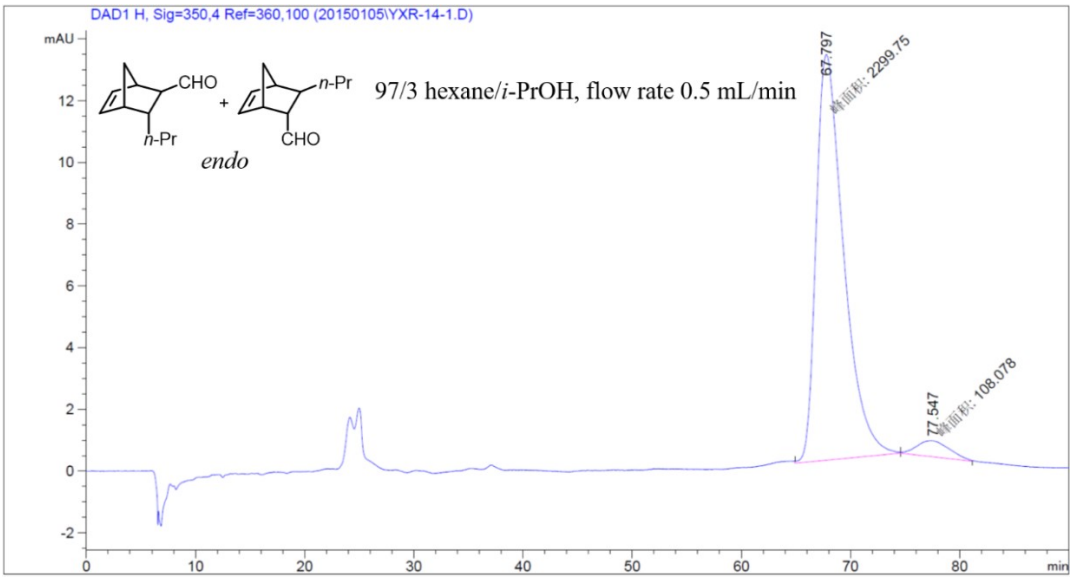
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	34.364	2.16306e4	387.35880	24.7017
2	49.206	2.22556e4	297.55243	25.4154
3	63.162	2.09928e4	216.05513	23.9733
4	107.081	2.26884e4	125.53026	25.9097



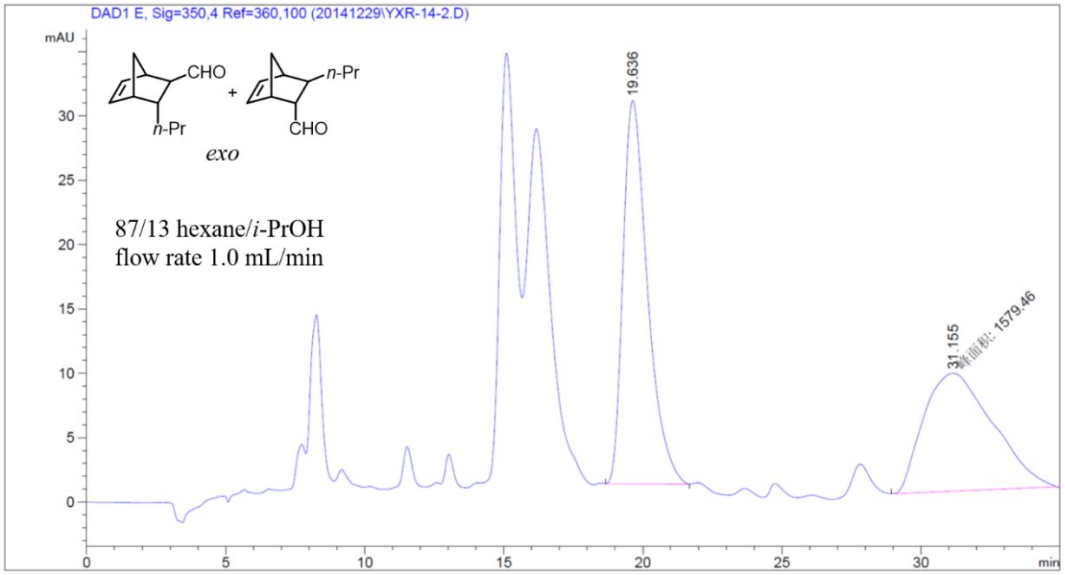
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	34.572	1177.30334	22.65335	1.2465
2	49.520	2188.96729	29.36175	2.3177
3	63.915	3.96087e4	381.54727	41.9383
4	108.397	5.14701e4	248.37175	54.4974



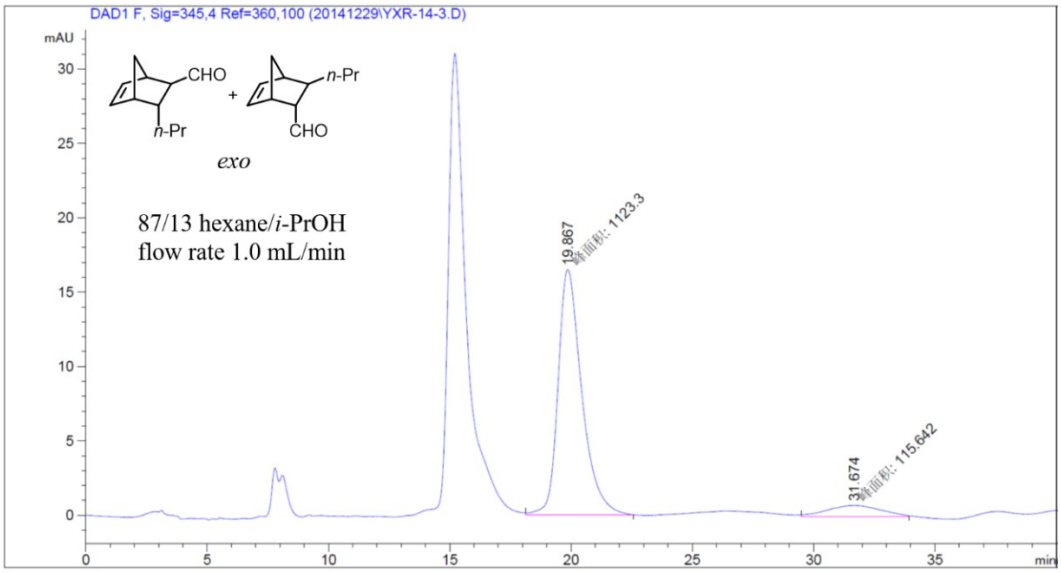
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	67.387	2942.15308	17.60140	51.4501
2	76.303	2776.31152	12.20779	48.5499



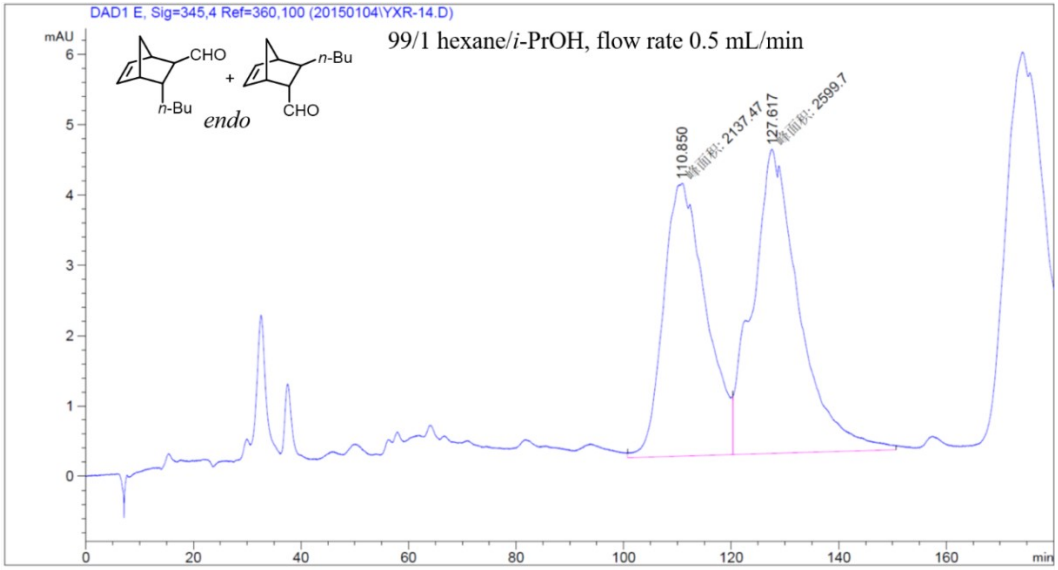
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	67.797	2299.74780	13.14571	95.5114
2	77.547	108.07756	5.22665e-1	4.4886



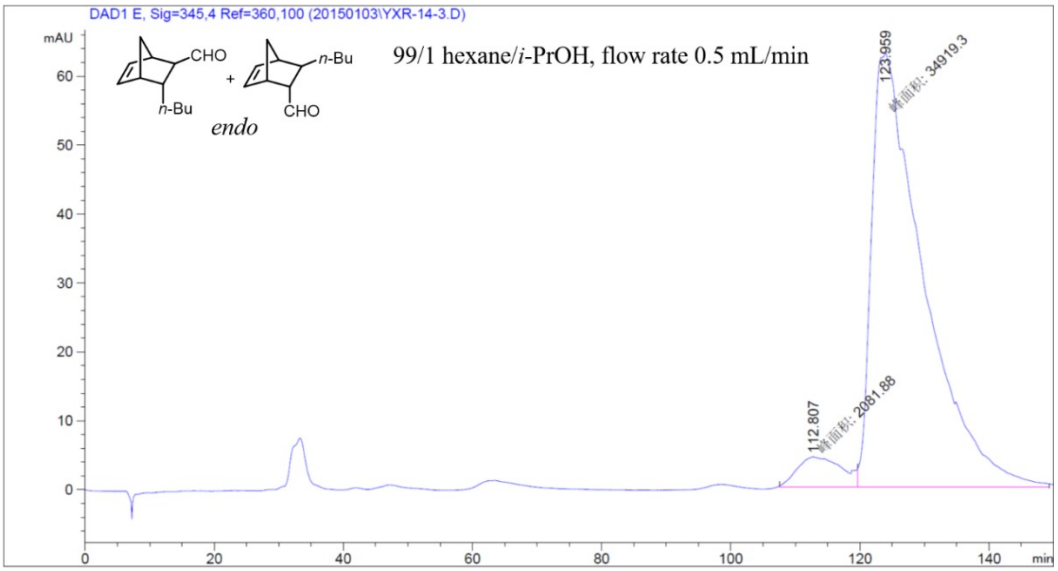
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	19.636	1824.40112	29.78798	53.5980
2	31.155	1579.45642	9.16245	46.4020



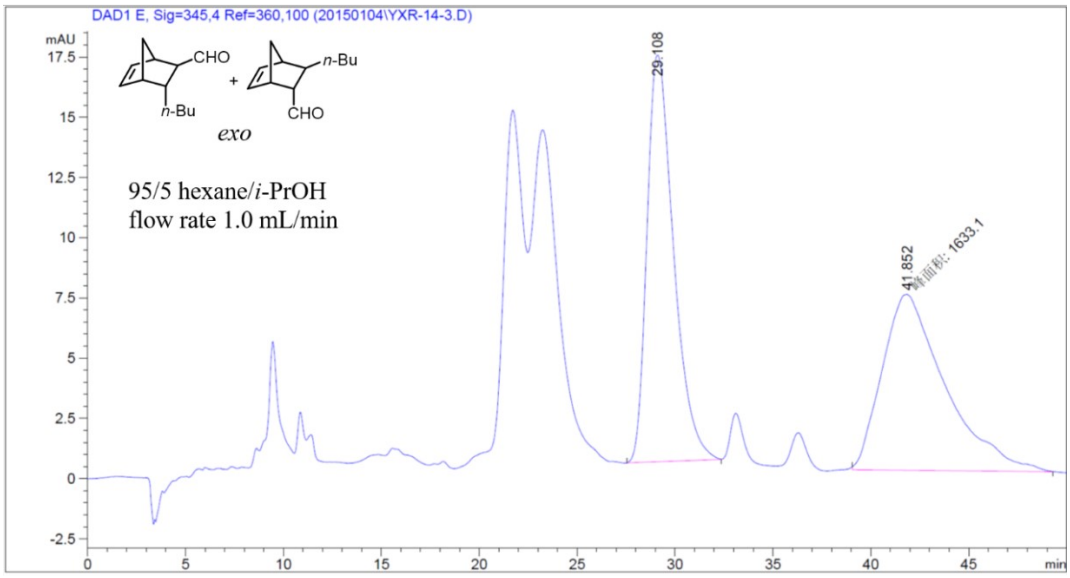
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	19.867	1123.30151	16.49524	90.6661
2	31.674	115.64172	7.53940e-1	9.3339



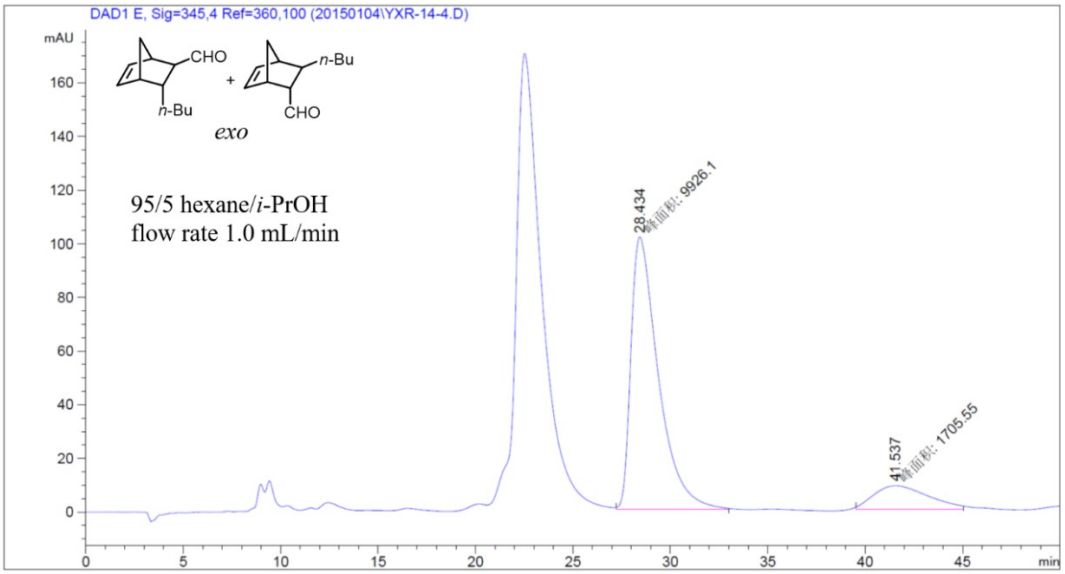
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	110.850	2137.46533	3.87987	45.1212
2	127.617	2599.70020	4.32672	54.8788



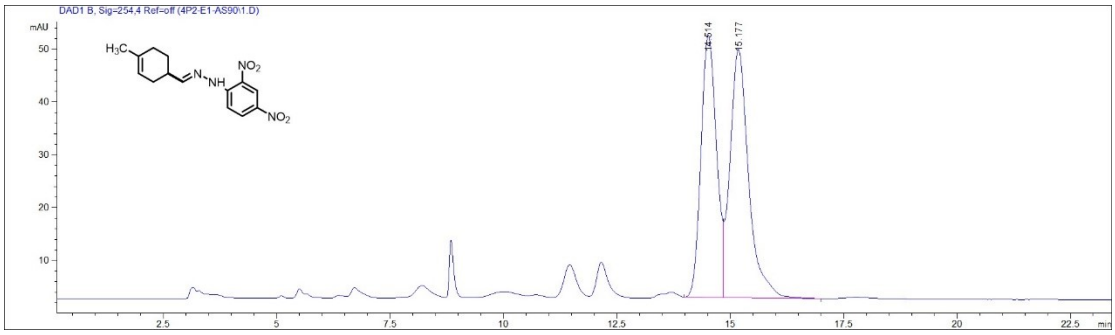
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	112.807	2081.88257	4.32419	5.6265
2	123.959	3.49193e4	62.86743	94.3735



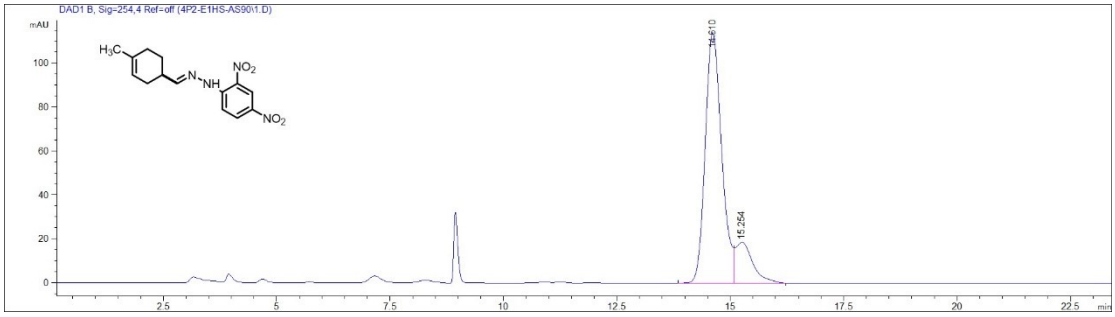
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	29.108	1597.34082	16.88131	49.4465
2	41.852	1633.10291	7.30475	50.5535



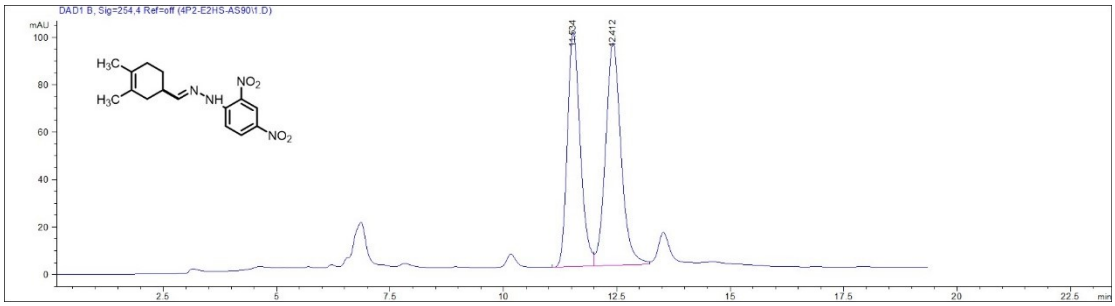
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	28.434	9926.09668	101.51617	85.3370
2	41.537	1705.55115	8.82788	14.6630



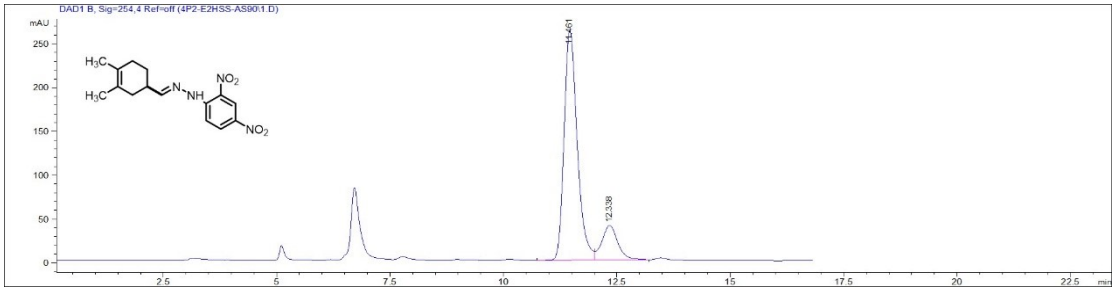
Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	14.514	1184.17883	49.65815	40.5741
2	15.117	1343.25098	46.99037	46.0245



Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	14.610	3448.31396	135.23485	51.6369
2	15.254	727.62213	24.74633	10.8958



Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	11.334	1948.85571	98.70258	39.6378
2	12.412	2220.75342	93.76180	45.1679



Peak	**Retention Time** [min]	**Area** [mAU*s]	**Height** [mAU]	**Relative Area** [%]
1	11.361	5259.41699	262.37720	67.9523
2	12.338	956.60291	39.48647	12.3594