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Electronic Supplementary Information

New insights into the asymmetric Diels-Alder reaction: the *Endo*- and *S*-selective retro-Diels-Alder reaction

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Contents

General Experimental Details

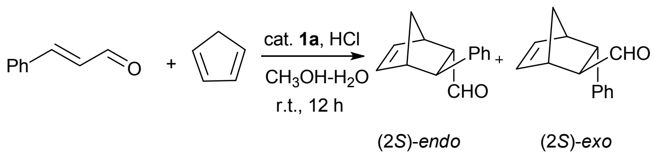
General Information:

All commercial solvents and reagents were used as obtained without further purification. Column chromatography was performed using silica-gel (200-400 mesh). High resolution Mass spectra were were obtained using Bruker micrOTOF-Q II. ^{1}H NMR and ^{13}C NMR spectra were recorded at VARIAN-400 operating at 400 MHz and 100 MHz respectively, the chemical shifts were referenced to internal tetramethylsilane (TMS, δ = 0.0 ppm) for ^{1}H, the central line of $CDCl_3$ (δ = 77.0 ppm) for ^{13}C. Enantiomeric excesses of products were determined by HPLC using a Daicel Chiralcel OD-H, OJ-H column and eluting with hexane/*i*-PrOH.

The synthesis of imidazolethione catalysts:

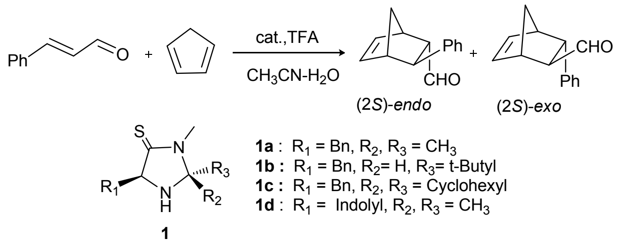
Catalysts **1a-d** were prepared according to the literatures.[1-4] ^{1}H NMR and ^{13}C NMR data were consistent with previously reported values. [1-4]

General procedure for the synthesis of 3-Phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde



To a solution of catalyst **1a** (0.012 g, 0.05 mmol) in CH_3OH/H_2O (1.9 mL/0.1 mL) was added concentrated hydrochloric acid (0.005 g, 0.05 mmol) and *trans*-cinnamaldehyde (0.132 g, 1 mmol). The solution was stirred for 1-2 minutes before the addition of freshly distilled cyclopentadiene (0.198 g, 3 mmol). The reaction was stirred at room temperature for 12 h until the reaction was judged to be complete by TLC. After removing CH_3OH under vacuo, the crude product dimethyl acetal was hydrolyzed in TFA: H_2O: $CHCl_3$ (1:1:2). The solution was stirred for 2 h at room temperature, followed by neutralization by sat. aq. $NaHCO_3$ and extraction with Et_2O. The organic solvent was removed with a rotary evaporator. The residue was purified silica-gel chromatography (petroleum ether/EtOAc: 15:1) to afford the desired product**.** ^{1}H NMR and ^{13}C NMR data were consistent with previously reported values. [5-12]

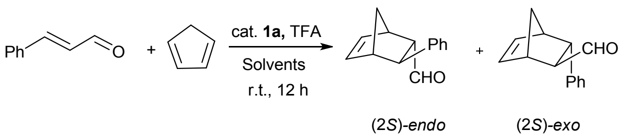
Table S1 Imidazolethione-catalyzed asymmetric Diels-Alder reactions



Entry	Catalyst	Yield[b] (%)	*exo*/*endo*[c]	*ee*[d] (%)	
				exo	*endo*
1	**1a**	92	1.3:1	59	56
2	**1b**	83	1.3:1	50	0
3	**1c**	80	1.3:1	40	23
4	**1d**	91	1.2:1	67	43

[a] Reaction condition: *trans*-cinnamaldehyde (1.0 mmol), cyclopentadiene (5.0 mmol), CH_3CN (1.9 mL), H_2O (0.1 mL), catalyst (10 mol%), TFA (10 mol%), r.t., 12 h. [b] Isolated yield. [c] *exo*/*endo* selectivity was determined by ^1H NMR analysis of a crude reaction mixture. [d] Enantiomeric excess was determined by HPLC analysis after conversion to the corresponding alcohol.

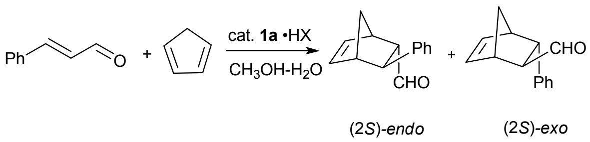
Table S2 Optimization of reaction conditions by using different solvents.



Entry	Solvent	Yield[b] (%)	*exo*/*endo*[c]	*ee*[d] (%)	
				exo	*endo*
1	CH_3CN/H_2O	92	1.3:1	59	56
2	CH_3CN	83	1.1:1	27	25
3	THF/H_2O	trace	n.d.[e]	n.d.	n.d.
4	CH_2Cl_2/H_2O	trace	n.d.	n.d.	n.d.
5	CH_3OH/H_2O	95	1.2:1	88	87
6	CH_3NO_2/H_2O	93	1.3:1	47	41

[a] Reaction condition: *trans*-cinnamaldehyde (1.0 mmol), cyclopentadiene (5.0 mmol), organic solvent (1.9 mL), H_2O (0.1 mL), catalyst **1a** (10 mol%), TFA (10 mol%), r.t., for 12 h. [b] Isolated yield. [c] *exo*/*endo* selectivity was determined by ^1H NMR analysis of a crude reaction mixture. [d] Enantiomeric excess determined by HPLC analysis. [e] Not determined.

Table S3 Optimization of reaction conditions by using different acid co-catalysts.



Entry	Acid	*T* (°C)	t (h)	Yield[b] (%)	*exo*/*endo*[c]	*ee*[d] (%)	
						exo	*endo*
1	TFA	25	12	92	1.2 : 1	88	87
2	TfOH	25	12	93	1.2 : 1	87	86
3	HBF_4	25	12	90	1.2 : 1	84	83
4	*p*-TSA	25	12	89	1.1 : 1	83	83
5	HCl	25	12	95	1.2 : 1	95	94
6	AcOH	25	12	20	1.1 : 1	n.d.	n.d.[e]
7	PhCOOH	25	12	23	1.1 : 1	n.d.	n.d.
8	HCl	0	48	73	1.2 : 1	95	95
9	HCl	-10	72	64	1.2 : 1	94	93
10[f]	HCl	25	12	95	1.2 : 1	95	94

[a] Reaction condition: *trans*-cinnamaldehyde (1.0 mmol), cyclopentadiene (5.0 mmol), CH_3OH (1.9 mL), H_2O (0.1 mL), catalyst **1a** (10 mol%), acid (10 mol%). [b] Isolated yield. [c] *exo/endo* selectivity was determined by ^1H NMR analysis of crude reaction mixture. [d] Enantiomeric excess determined by HPLC analysis. [e] Not determined. [f] catalyst **1a** (5 mol%), HCl (5 mol%), cyclopentadiene (3 equiv.).

Figure S1 The changes in *ee* of both adducts in Diels-Alder reaction over the time.

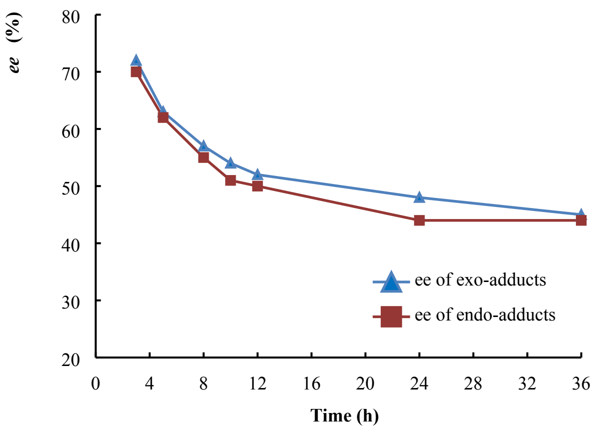


Fig. S1 The changes in *ee* of both adducts in Diels-Alder reaction over the time: *trans*-cinnamaldehyde (1.0 mmol), cyclopentadiene (3.0 mmol), 5% **1a**, 5% TFA, CH_3CN (1.9 mL), H_2O (0.1 mL), r.t.

Figure S2 The stability of isolated aldehyde adducts in CH_3OH-H_2O system.

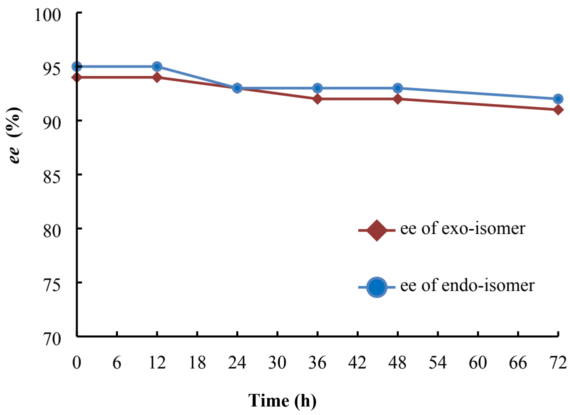
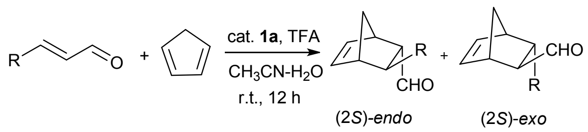


Fig. S2 The stability of isolated aldehyde adducts in CH_3OH-H_2O system：aldehyde products (1 mmol, 95% *ee* in *endo*-isomers, 94% *ee* in *exo*-isomer), 20 mol% **1a**, 100 mol% HCl, CH_3OH (1.9 mL), H_2O (0.1 mL), r.t., 72 h.

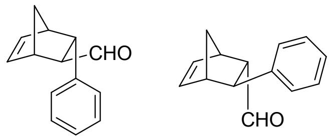
Table S4 Enantioselectivity of various substrates in CH_3CN-H_2O system.



Entry	R	Yield[b] (%)	*exo*/*endo*[c]	*ee*[d] (%)	
				exo	*endo*
1	Ph	92	1.3:1	59	56
2	*m*-MeC_6H_4	93	1.2:1	62	57
3	*o*-$OMeC_6H_4$	95	1.2:1	34	34
4	*p*-$OMeC_6H_4$	93	1.1:1	11	9
5	*p*-FC_6H_4	91	1.2:1	40	37
6	*p*-ClC_6H_4	90	1.1:1	34	32
7	*m*-ClC_6H_4	91	1:1	46	44
8[e]	Furyl	82	1.1:1	18	13
9	*n*-Pr	90	1.2:1	77	58

[a] Reaction condition: *α,β*-unsaturated aldehyde (1.0 mmol), cyclopentadiene (3.0 mmol), CH_3CN (1.9 mL), H_2O (0.1 mL), catalyst **1a** (5 mol%), HCl (5 mol%), [b] Isolated yield. [c] *exo*/*endo* selectivity was determined by ^1H NMR analysis of a crude reaction mixture. [d] Enantiomeric excess was determined by HPLC analysis. [e] 10 mol% catalyst, 24 h.

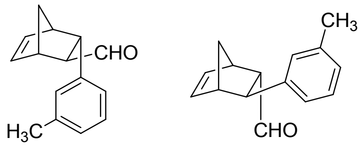
Experimental characterization data for compounds



3-Phenylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 1).

188.1 mg, 95% yield (colorless oil); 1.3/1.0 *exo*/*endo*, *exo* 95% *ee*, *endo* 94% *ee*. Enantioselectivity was determined by HPLC after reduction with $NaBH_4$/MeOH. [Chiralcel OJ-H (0.46 cm × 25 cm). (from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 70/30, 0.8 mL/min, 225 nm], t_r =11.0 min, 24.5 min, 31.4 min, 42.5 min. HRMS (ESI, m/z): $[M+Na]^+$, calcd. for $C_{14}H_{14}NaO$: 221.0929, found: 233.0937.

^{1}H NMR and ^{13}C NMR data were consistent with previously reported values. [5-12]

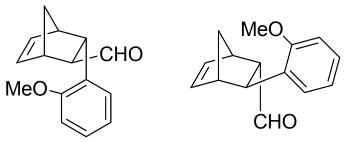


3-(m-tolyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 2).

201.5 mg, 95% yield (colorless oil); 1.1/1.0 *exo*/*endo*, *exo* 93% *ee*, *endo* 93% *ee*. Enantioselectivity was determined by HPLC after reduction with $NaBH_4$/MeOH. [Chiralcel OJ-H (0.46 cm × 25 cm). (from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 80/20, 0.8 mL/min, 210 nm], t_r =9.5 min, 15.8 min, 22.8 min, 27.0 min. HRMS (ESI, m/z): $[M+Na]^+$, calcd. for $C_{15}H_{16}NaO$: 235.1092, found: 235.1093.

^{1}H NMR (400 MHz, $CDCl_3$) (two isomers): δ 9.88 (d, J = 2.0 Hz, 1H), 9.56 (d, J = 2.2 Hz, 1H), 7.22-6.91 (m, 8H), 6.39 (dd, J = 5.6, 3.4 Hz, 1H), 6.31 (dd, J = 5.4, 3.4 Hz, 1H), 6.14 (dd, J = 5.6, 2.8 Hz, 1H), 6.06 (dd, J = 5.2, 2.8 Hz, 1H), 3.67 (t, J = 4.0, 1H), 3.31 (s, 1H), 3.20 (d, J = 1.6 Hz, 2H), 3.10-3.03 (m, 2H) , 2.98-2.96 (m, 2H), 2.59-2.57 (m, 1H), 2.33 (s, 3H), 2.30 (s, 3H), 1.80 (d, J = 8.6 Hz, 1H), 1.62-1.53 (m, 3H).

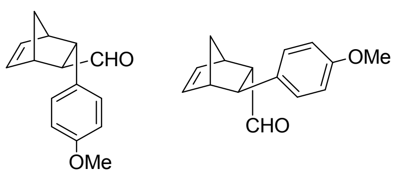
^{13}C NMR (100 MHz, $CDCl_3$) (two isomers): δ 202.4, 201.8, 143.5, 142.5, 139.0, 138.0, 137.5, 136.5, 136.1, 133.8, 128.6, 128.4, 128.2, 127.9, 126.9, 126.9, 124.7, 124.2, 60.9, 59.5, 48.9, 48.6, 47.8, 47.3, 46.3, 46.1, 45.8, 45.3, 21.4.



3-(2-Methoxyphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 3).

218.9 mg, 96% yield (colorless oil); 1.2/1.0 *exo*/*endo*, *exo* 96% ee, *endo* 94% ee. Enantioselectivity was determined by HPLC after reduction with $NaBH_4$/MeOH. [Chiralcel OJ-H (0.46 cm × 25 cm). (from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 95/5, 0.6 mL/min, 210 nm], t_r =19.9 min, 23.6 min, 25.7 min, 38.4 min. HRMS (ESI, m/z): $[M+Na]^+$, calcd. for $C_{15}H_{16}NaO_2$: 251.1034, found: 251.1043.

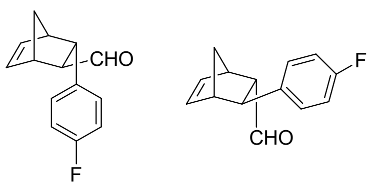
^{1}H NMR and ^{13}C NMR data were consistent with previously reported values. [5-12]



3-(4-methoxyphenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 4).

216.7 mg, 95% yield (colorless oil); 1.1/1.0 *exo*/*endo*, *exo* 95% *ee*, *endo* 94% *ee*. Enantioselectivity was determined by HPLC after reduction with $NaBH_4$/MeOH. [Chiralcel OJ-H (0.46 cm × 25 cm). (from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 85/15, 20min → 80/20, 0.8 mL/min, 210 nm], t_r =18.6 min, 27.7 min, 49.9 min, 67.1 min. HRMS (ESI, m/z): $[M+Na]^+$, calcd. for $C_{15}H_{16}NaO_2$: 251.1040, found: 251.1043.

^{1}H NMR and ^{13}C NMR data were consistent with previously reported values. [5-12]

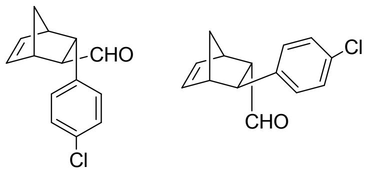


3-(4-fluorophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 5).

198.7 mg, 92% yield (colorless oil); 1.1/1.0 *exo*/*endo*, *exo* 93% *ee*, *endo* 93% *ee*. Enantioselectivity was determined by HPLC after reduction with $NaBH_4$/MeOH. [Chiralcel OJ-H (0.46 cm × 25 cm). (from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 85/15, 0.8 mL/min, 210 nm], t_r = 9.3 min, 16.1 min, 25.8 min, 44.2 min. HRMS (ESI, m/z): $[M+Na]^+$, calcd. for $C_{14}H_{13}FNaO$:239.0848, found: 239.0843.

^{1}H NMR (400 MHz, $CDCl_3$) (two isomers): δ 9.87 (d, J = 2.0 Hz, 1H), 9.56 (d, J = 2.2 Hz, 1H), 7.21-7.17 (m, 3H), 7.09-7.06 (m, 3H), 6.99-6.87 (m, 3H), 6.39 (dd, J = 5.6, 3.2 Hz, 1H), 6.33 (dd, J = 5.6, 3.2 Hz, 1H), 6.15 (dd, J = 5.6, 2.8 Hz, 1H), 6.03 (dd, J = 5.6, 2.9 Hz, 1H), 3.69 (t, J = 4.2Hz, 1H), 3.33 (s, 1H), 3.21-3.16 (m, 2H), 3.08-3.04 (m, 2H), 2.92-2.89 (m, 1H), 2.53-2.51 (m, 1H), 1.78-1.75 (m, 1H), 1.64-1.53 (m, 3H).

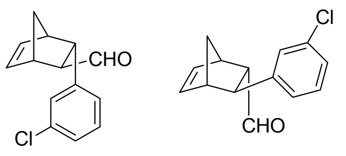
^{13}C NMR (100 MHz, $CDCl_3$) (two isomers): δ 202.8, 202.1, 162.3, 162.2, 159.9, 159.8, 138.9, 136.2, 136.1, 133.5, 129.0, 129.0, 128.5, 128.5, 115.2, 115.0, 114.8, 114.5, 61.0, 59.6, 48.4, 48.4, 47.5, 47.0, 45.4, 45.0, 45.0, 44.6.



3-(4-Chlorophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 6).

211.2 mg, 91% yield (colorless oil); 1.1/1.0 *exo*/*endo*, *exo* 93% *ee*, *endo* 92% *ee*. Enantioselectivity was determined by HPLC after reduction with $NaBH_4$/MeOH. [Chiralcel OJ-H (0.46 cm × 25 cm). (from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90/10, 10 min, →80/20, 0.6 mL/min, 210 nm], t_r = 15.1 min, 21.3 min, 36.7 min, 51.1 min. HRMS (ESI, m/z): $[M+Na]^+$, calcd. for $C_{14}H_{13}ClNaO$:255.0567, found: 255.0575.

^{1}H NMR and ^{13}C NMR data were consistent with previously reported values. [5-12]



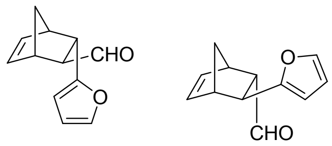
3-(3-Chlorophenyl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 7).

215.8 mg, 93% yield (colorless oil); 1.0/1.0 *exo*/*endo*, *exo* 92% *ee*, *endo* 90% *ee*. Enantioselectivity was determined by HPLC after reduction with $NaBH_4$/MeOH. [Chiralcel OJ-H (0.46 cm × 25 cm). (from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99.9/0.1, 20 min, → 98/2, 0.6 mL/min, 210 nm], t_r = 46.3 min, 50.1 min, 53.9 min, 55.9 min. HRMS (ESI, m/z): $[M+Na]^+$, calcd. for $C_{14}H_{13}ClNaO$:255.0548, found: 255.0547.

^{1}H NMR (400 MHz, $CDCl_3$) (two isomers): δ 9.87 (d, J = 2.0 Hz, 1H), 9.56 (d, J = 2.1 Hz, 1H), 7.24-7.19 (m, 2H), 7.16-7.09 (m, 5H), 7.01-6.99 (m, 1H), 6.39 (dd, J = 5.6, 3.2 Hz, 1H), 6.33 (dd, J = 5.6, 3.2 Hz, 1H), 6.15 (dd, J = 5.8, 2.8 Hz, 1H), 6.02 (dd, J = 5.6, 2.8 Hz, 1H), 3.69 (dd, J = 5.2, 3.6 Hz, 1H), 3.35 (s, 1H), 3.23-3.19 (m, 2H), 3.10-3.05 (m, 2H), 2.94-2.92 (m, 1H), 2.55 (d, J

= 5.2 Hz, 1H), 1.77-1.75 (m, 1H), 1.64-1.56 (m, 3H).

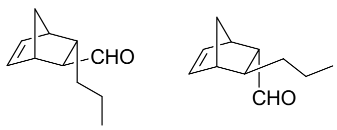
^{13}C NMR (100 MHz, $CDCl_3$) (two isomers): δ 202.2, 201.6, 145.5, 144.5, 138.8, 136.3, 136.0, 134.1, 133.7, 133.6, 129.6, 129.1, 127.7, 127.2, 126.2，126.1，125.9，125.5，60.8 59.3, 48.3, 48.2, 48.1, 47.5, 47.1, 45.4, 45.0



3-(furan-2-yl)bicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 8).

157.9 mg, 84% yield (colorless oil); 1.0/1.0 *exo*/*endo*, *exo* 93% *ee*, *endo* 90% *ee*. Enantioselectivity was determined by HPLC after reduction with $NaBH_4$/MeOH. [Chiralcel OJ-H (0.46 cm × 25 cm). (from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 90/10, 0.8 mL/min, 220 nm], t_r = 11.5 min, 23.2 min, 25.2 min, 29.0 min. HRMS (ESI, m/z): $[M+Na]^+$, calcd. for $C_{12}H_{12}NaO_2$: 211.0723, found: 211.0730.

^{1}H NMR and ^{13}C NMR data were consistent with previously reported values. [5-12]



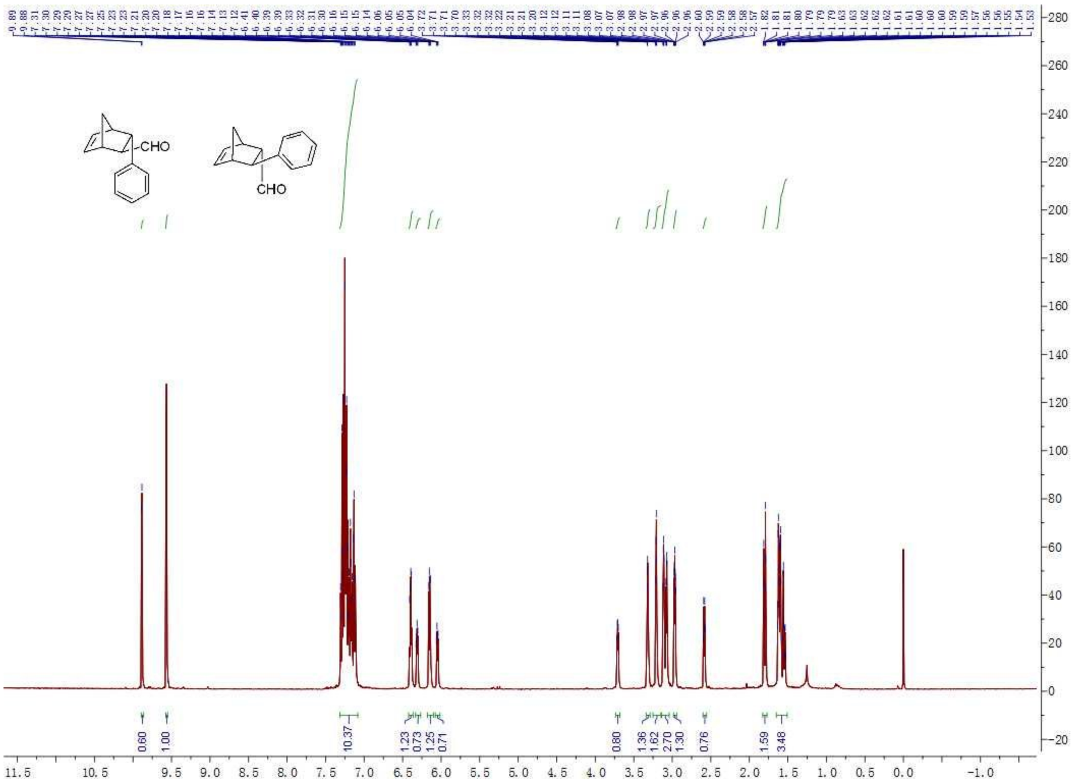
3-propylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde (Table 4, entry 9).

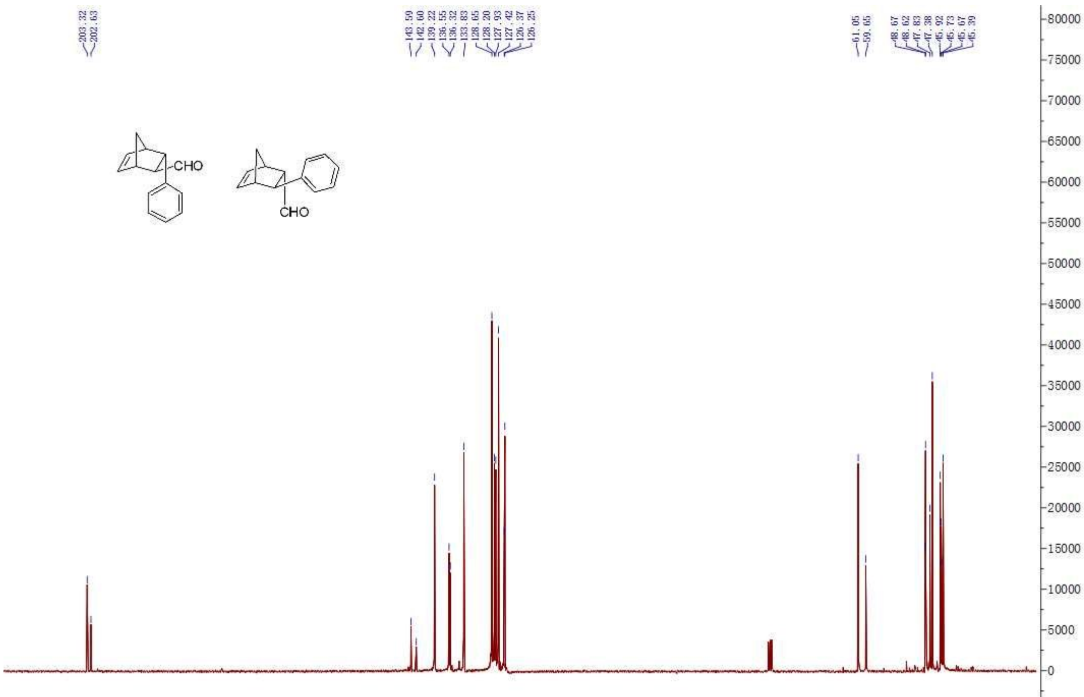
152.7 mg, 92% yield (colorless oil); 1.2/1.0 *exo*/*endo*, *exo* 93% *ee*, *endo* 92% *ee*. Enantioselectivity was determined by HPLC after reduction with $NaBH_4$/MeOH. [Chiralcel OD-H (0.46 cm × 25 cm). (from Daicel Chemical Ind., Ltd.) hexane/*i*-PrOH, 99.5/0.5, 0.6 mL/min, 210 nm], t_r = 28.7 min, 29.9 min, 32.0 min, 33.9 min. This compound was identified by corresponding alcohol due to the instability of aldehyde products. HRMS (ESI, m/z): $[M+H]^+$, calcd. for $C_{11}H_{19}O$: 167.1423, found: 167.1430.

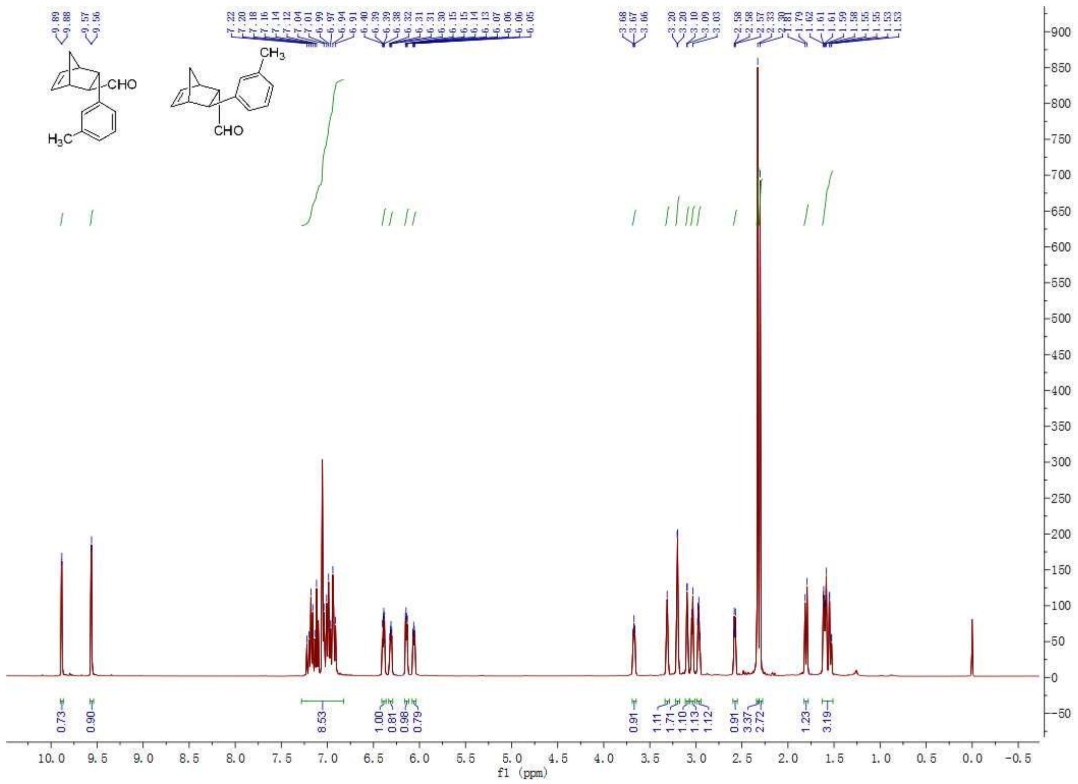
^{1}H NMR and ^{13}C NMR data were consistent with previously reported values. [5-12]

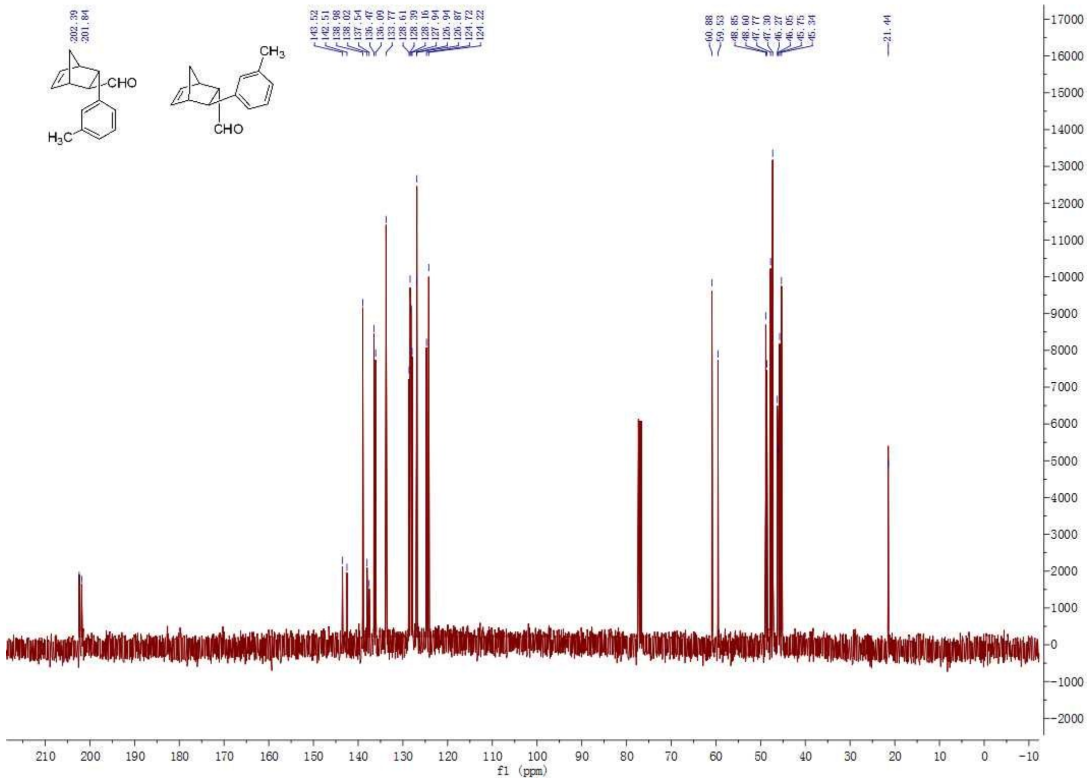
NMR spectra and HPLC analyses for products

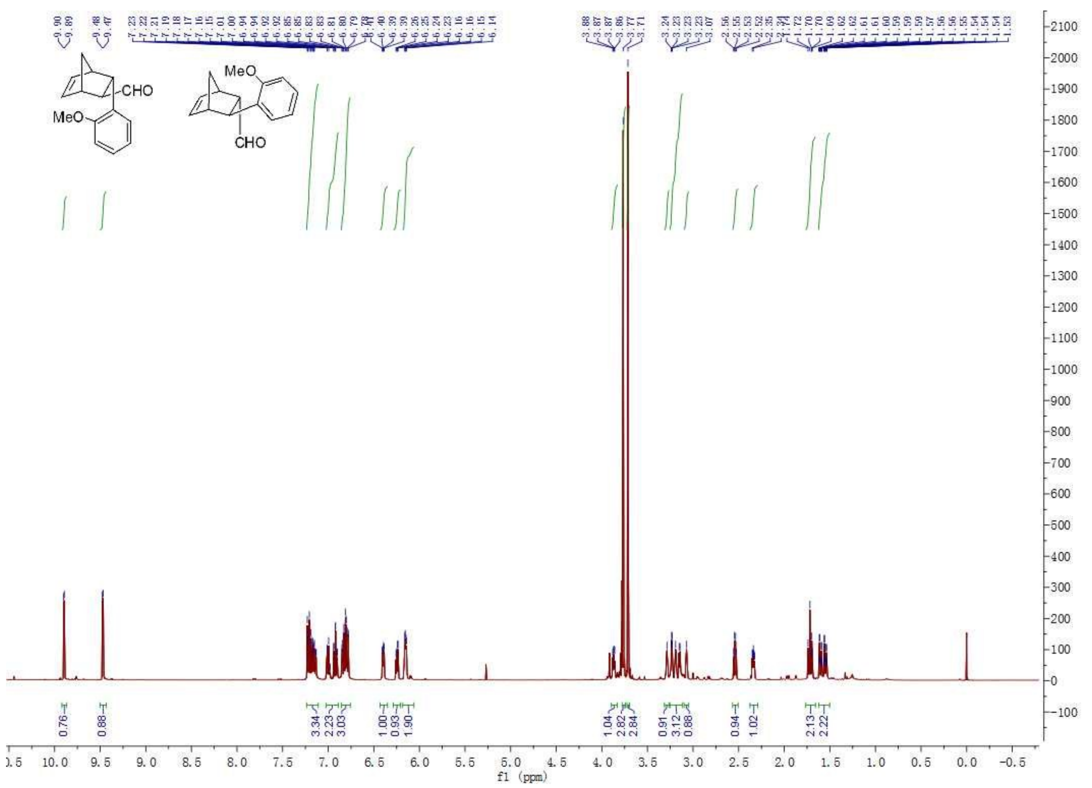
NMR spectra of products



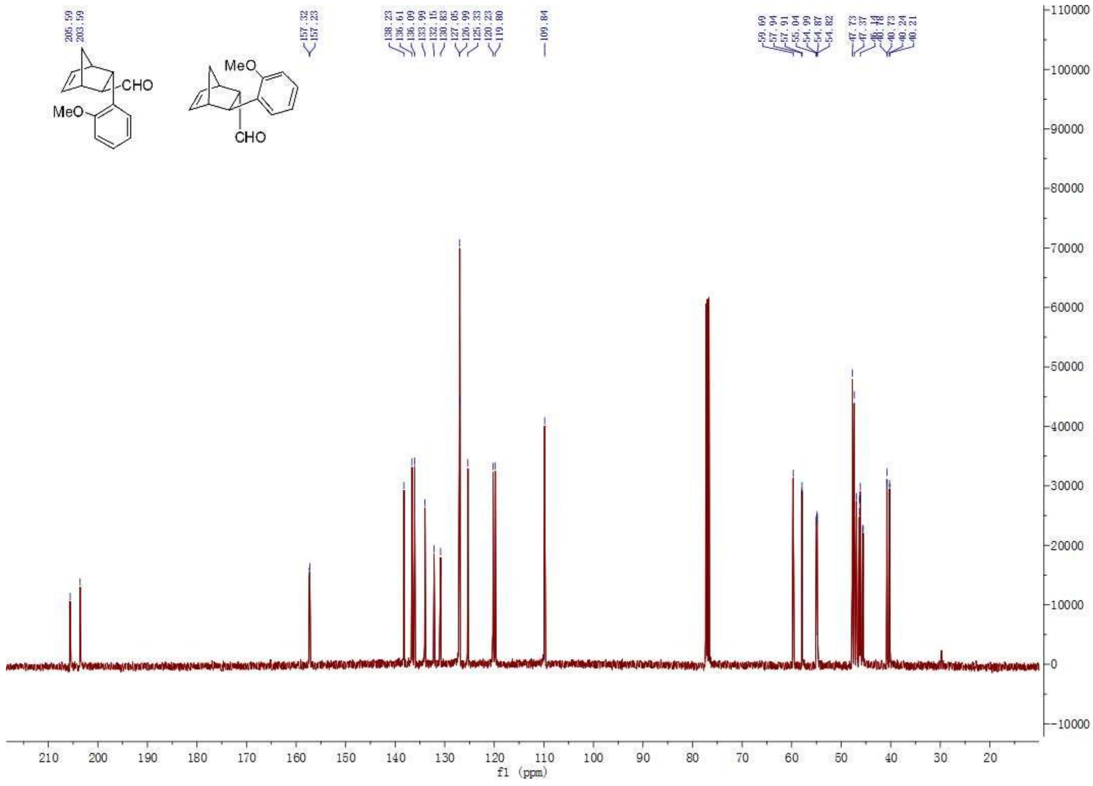








CHO
MeO
MeO
CHO
f1 (ppm)



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MeO
MeO
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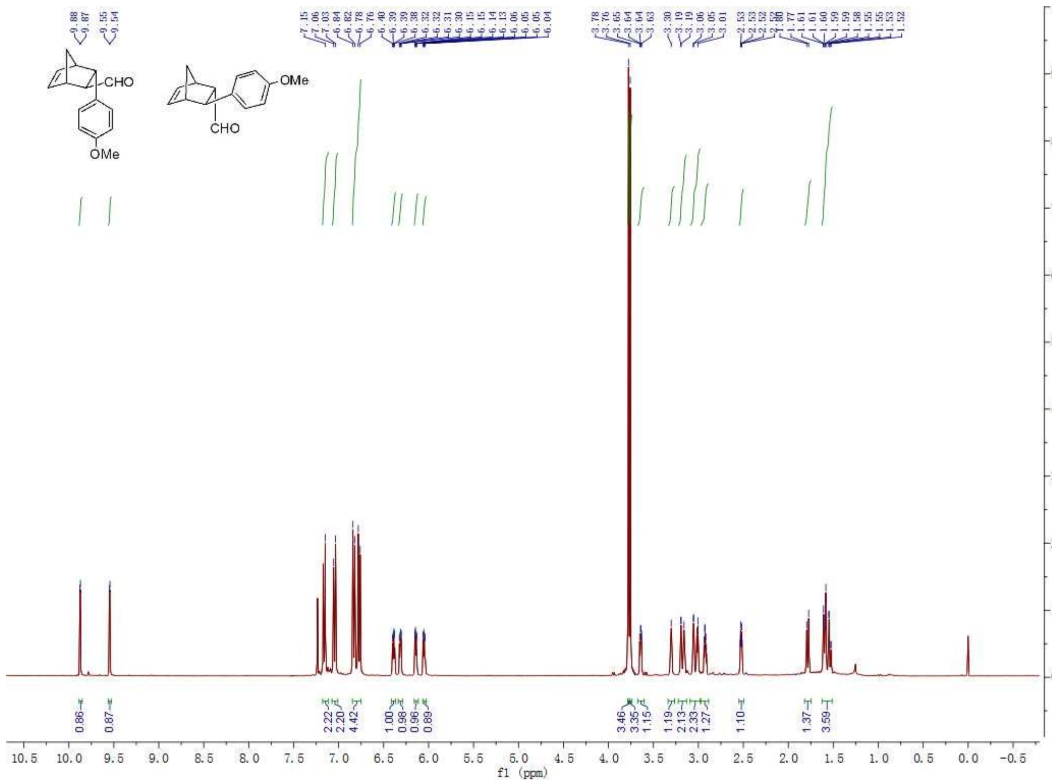
f1 (ppm)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OMe
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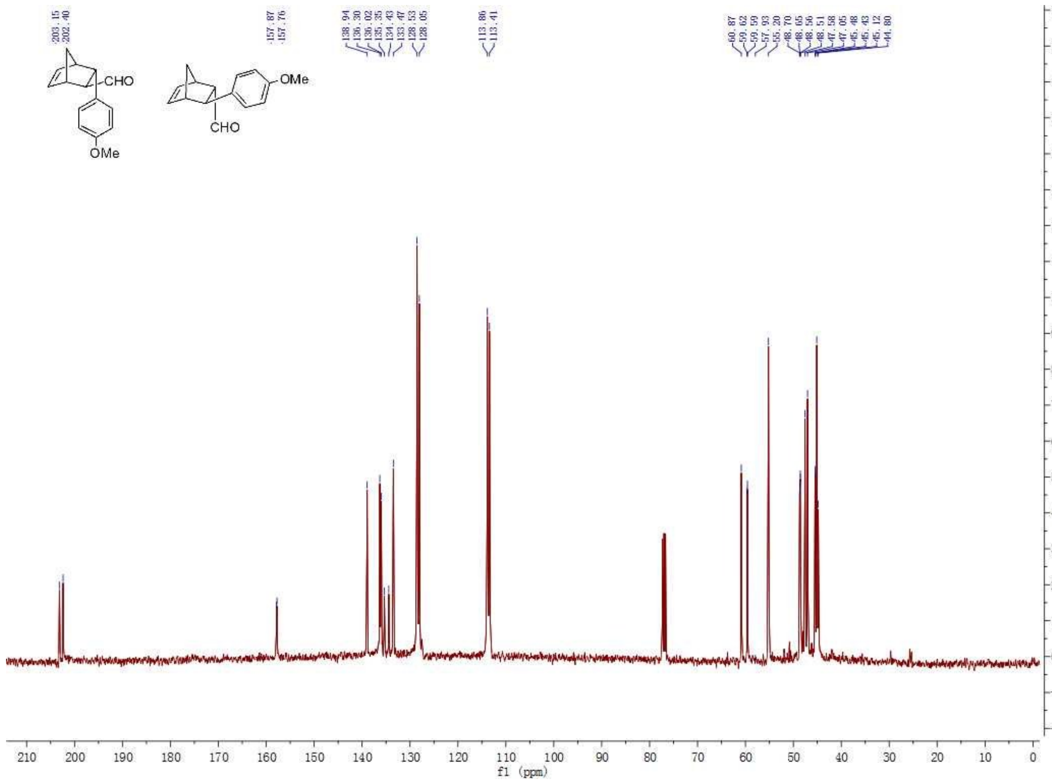
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OMe
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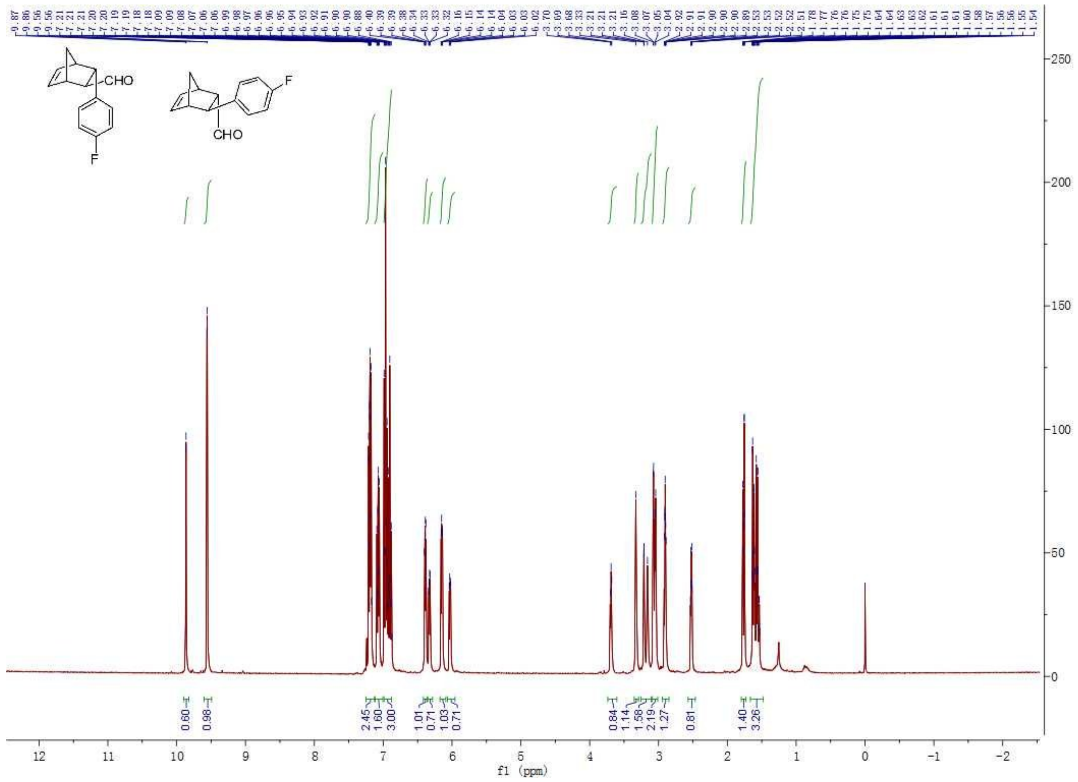
f1 (ppm)



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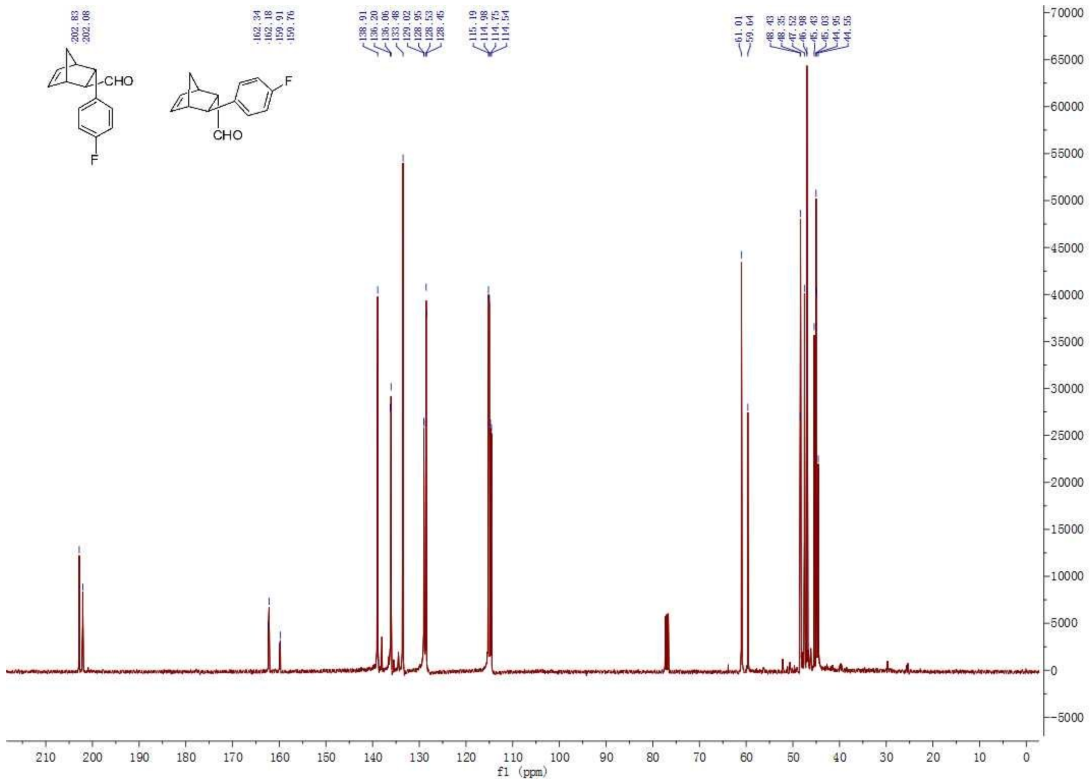
CHO
F
f1 (ppm)



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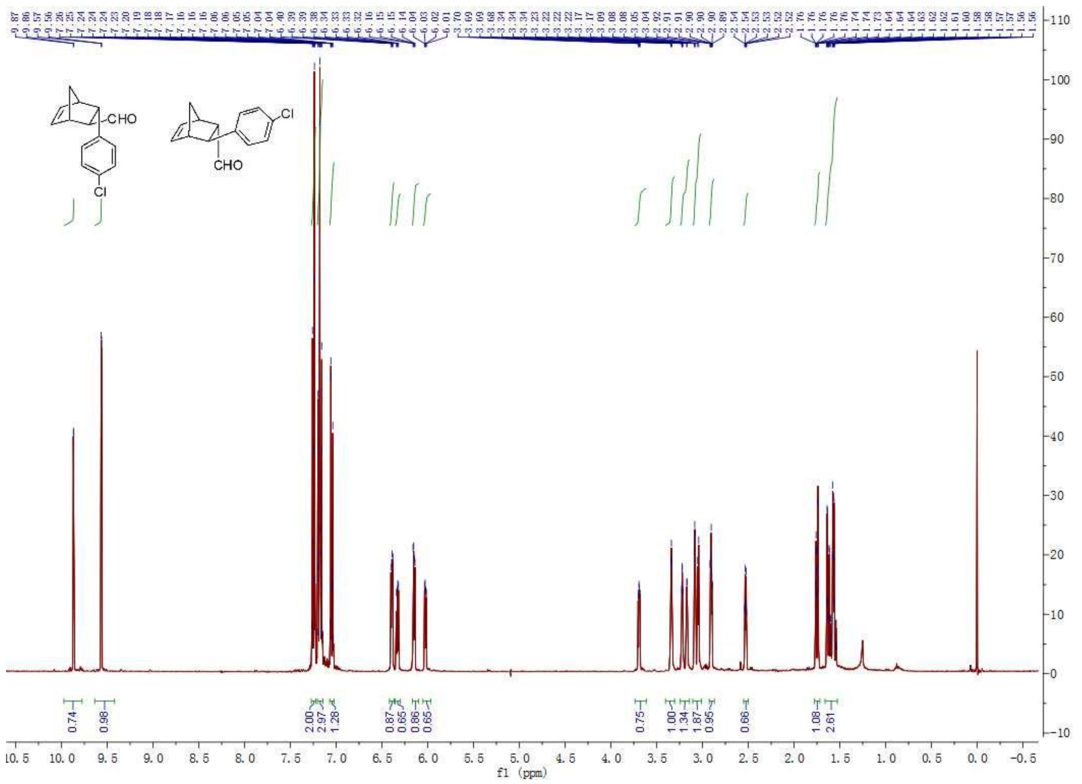
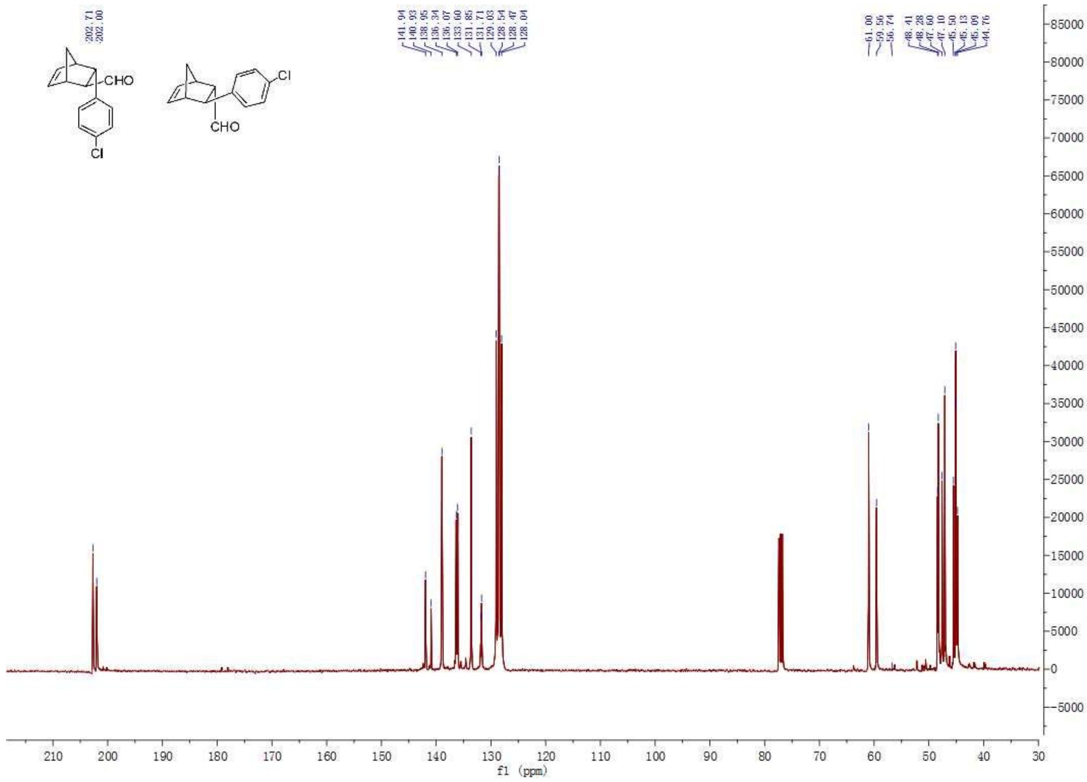
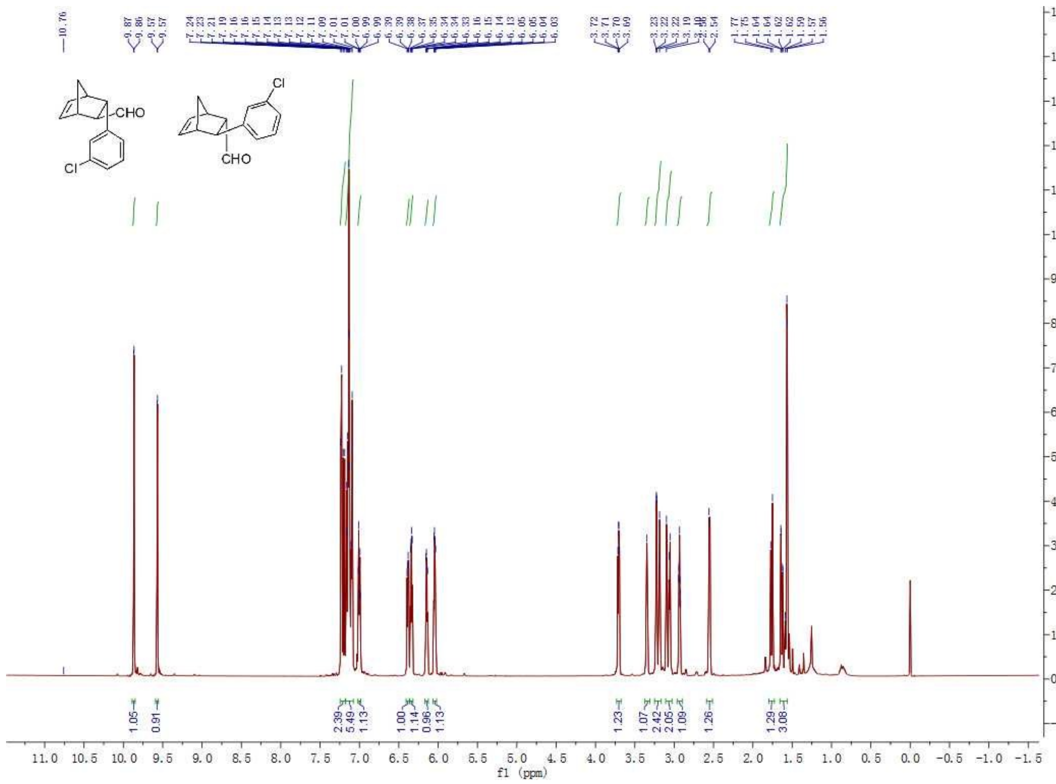
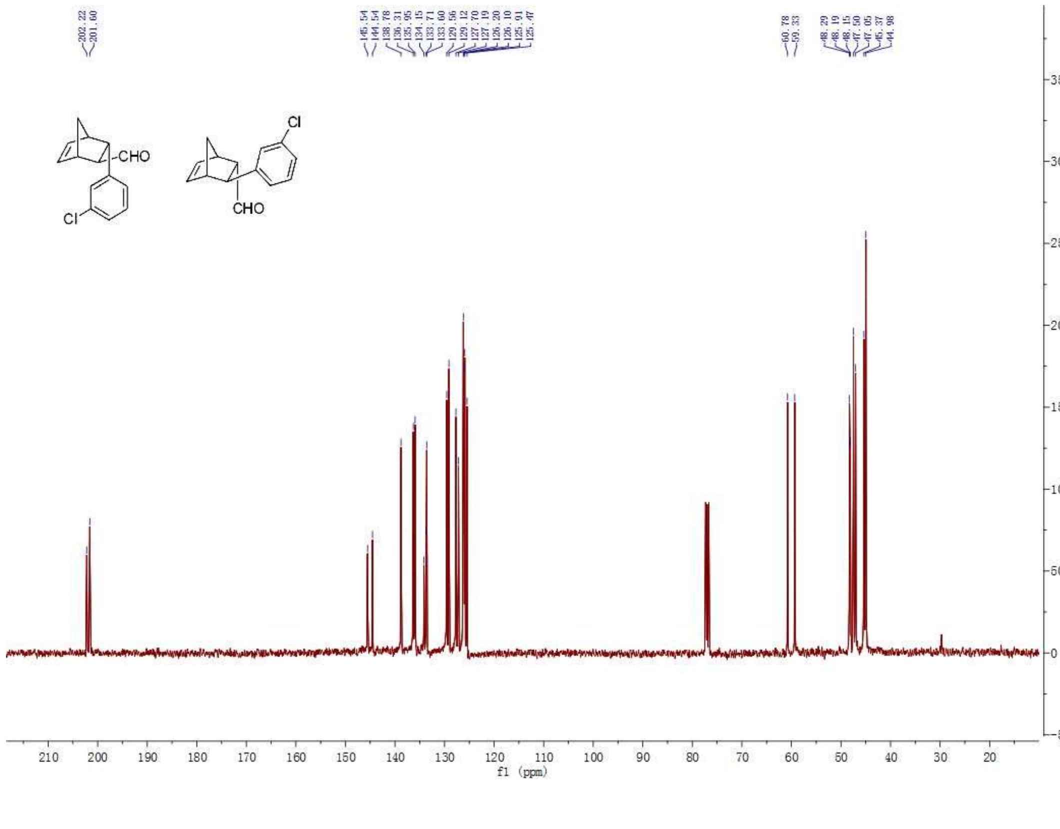
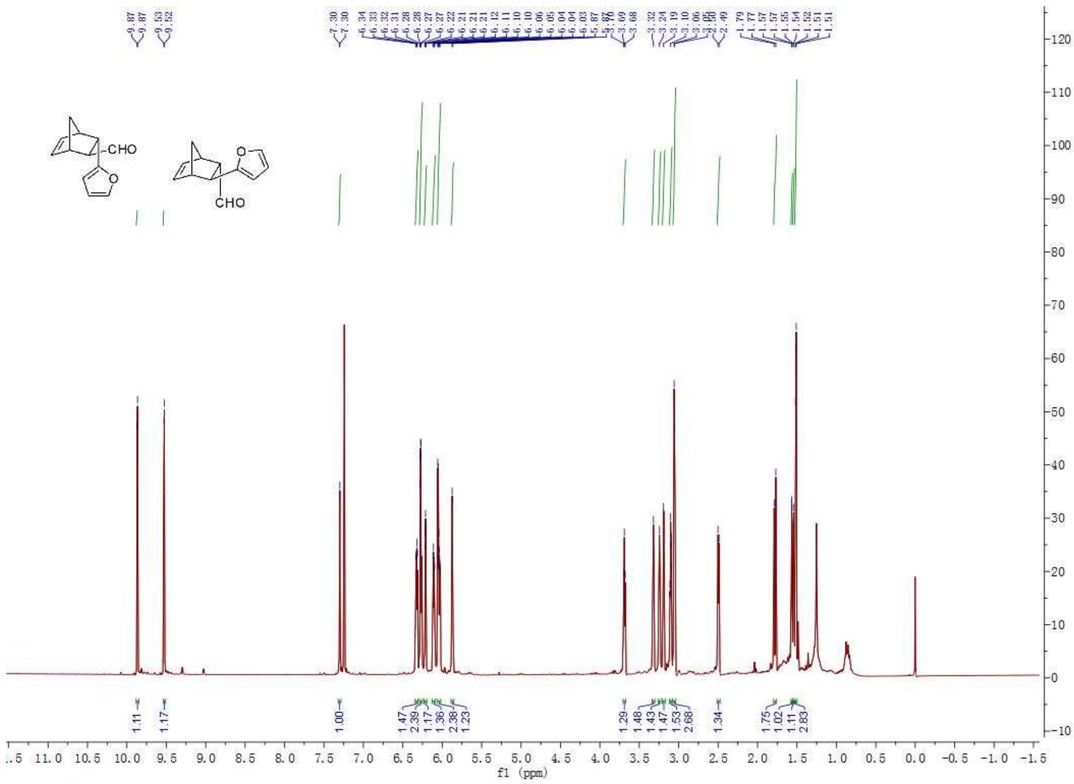
F
CHO
F
f1 (ppm)

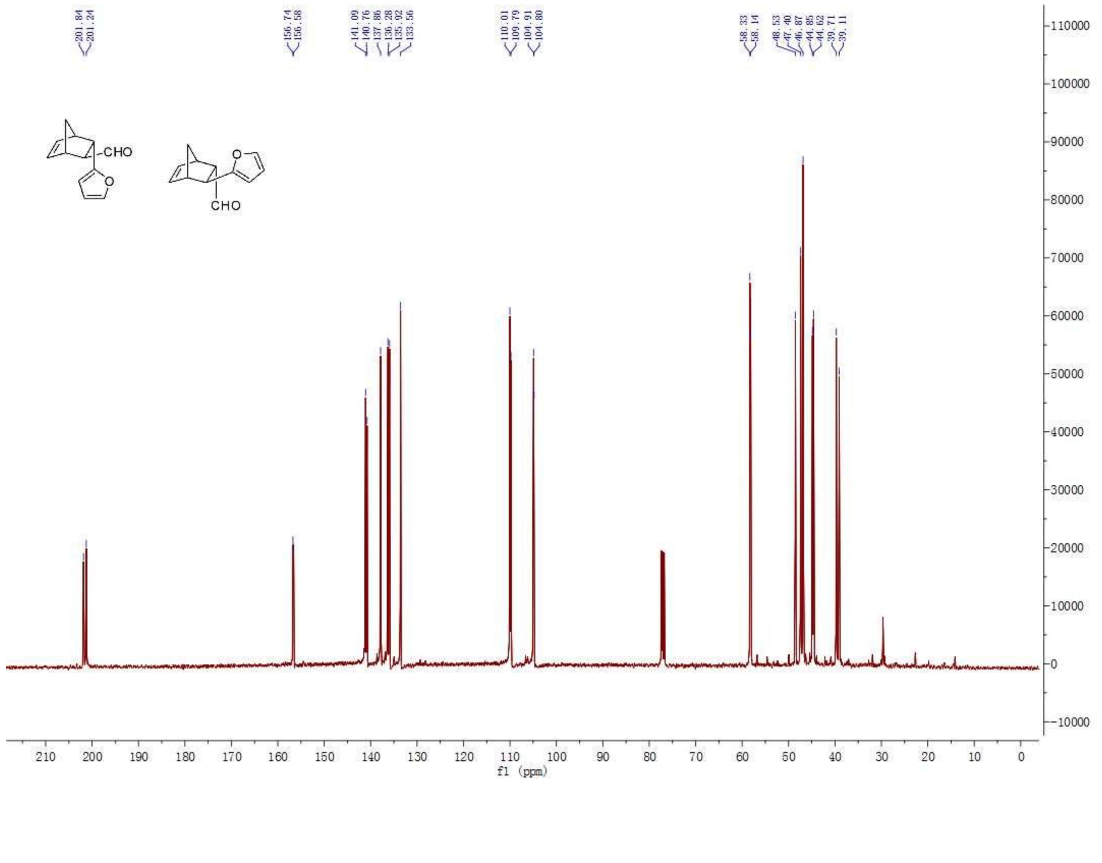


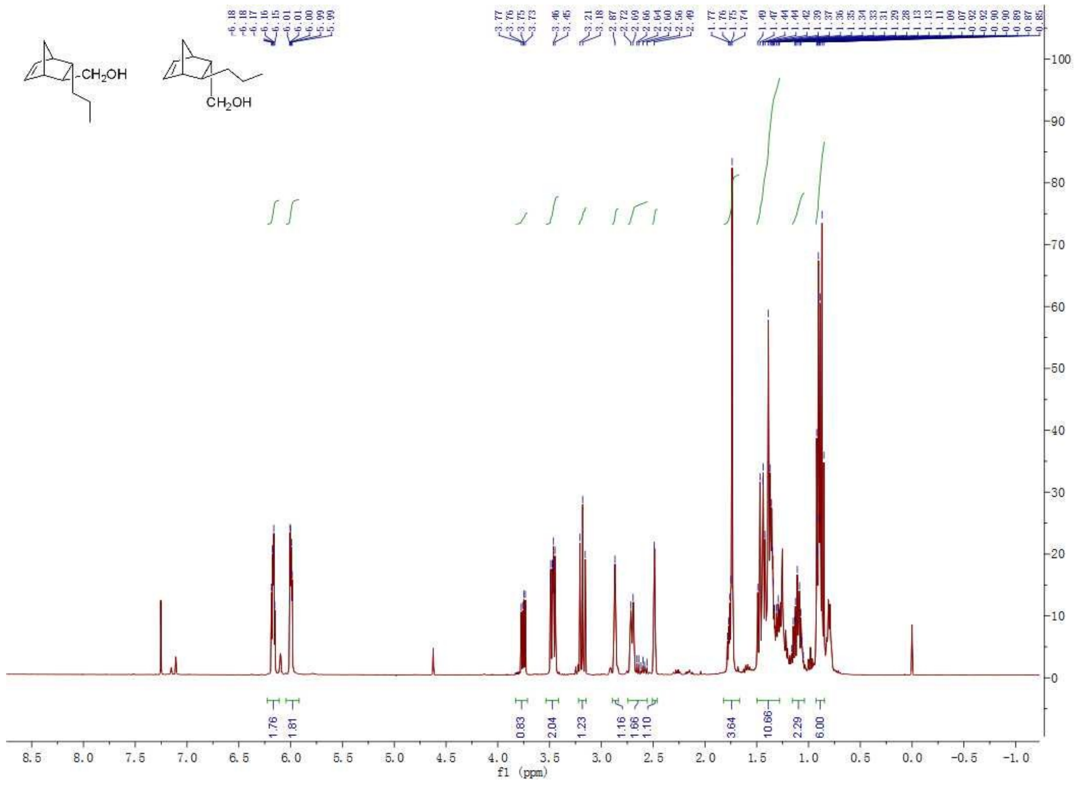




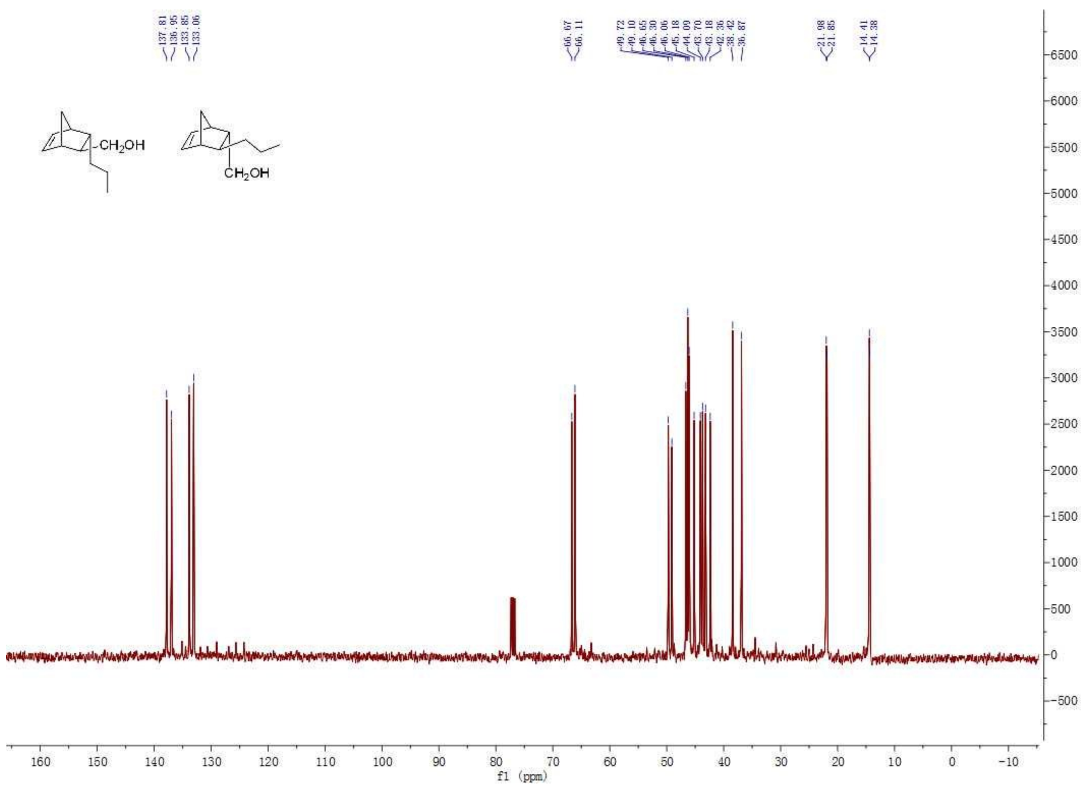






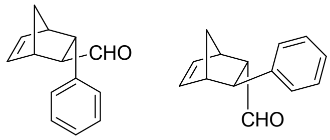


CH2OH
CH2OH
1.76
1.81
0.83
2.04
1.23
1.16
1.66
1.10
3.64
10.66
2.29
6.00
f1 (ppm)

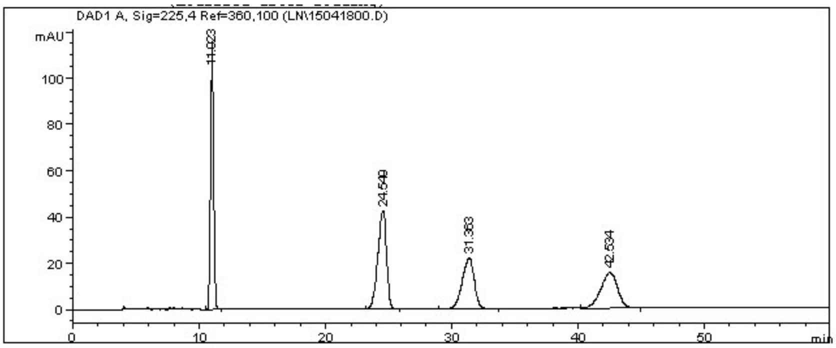


137.81
136.95
133.85
133.06
66.67
66.11
49.72
49.10
CH2OH
CH2OH
f1 (ppm)

HPLC spectra of products



Chiralcel OJ-H, 225 nm, hexane/*i*-PrOH = 70/30, 0.8 mL/min



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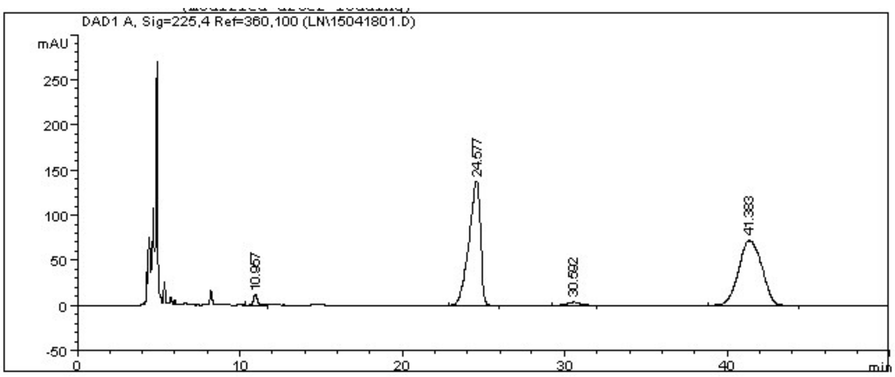
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.023 VV    0.2625 1968.80566  115.69119  29.0553
   2  24.549 VV    0.7113 1996.00671   42.23825  29.4568
   3  31.363 BB    1.0047 1405.90088   21.79185  20.7481
   4  42.534 BP    1.2930 1405.34131   15.33701  20.7398
```



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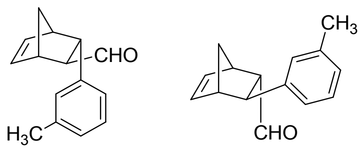
                        Area Percent Report
=====================================================================

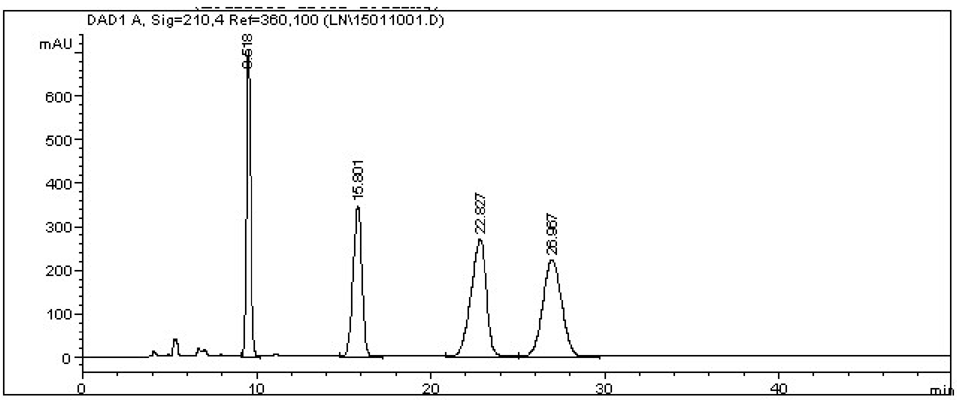
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.957 VV    0.2823  214.68037   11.47553   1.4916
   2  24.577 BB    0.7412 6815.63818  137.76959  47.3552
   3  30.592 BP    0.8364  222.85541    3.75500   1.5484
   4  41.383 BB    1.5953 7139.40479   71.84971  49.6048
```



Chiralcel OJ-H, 210 nm, hexane/*i*-PrOH = 80/20, 0.8 mL/min

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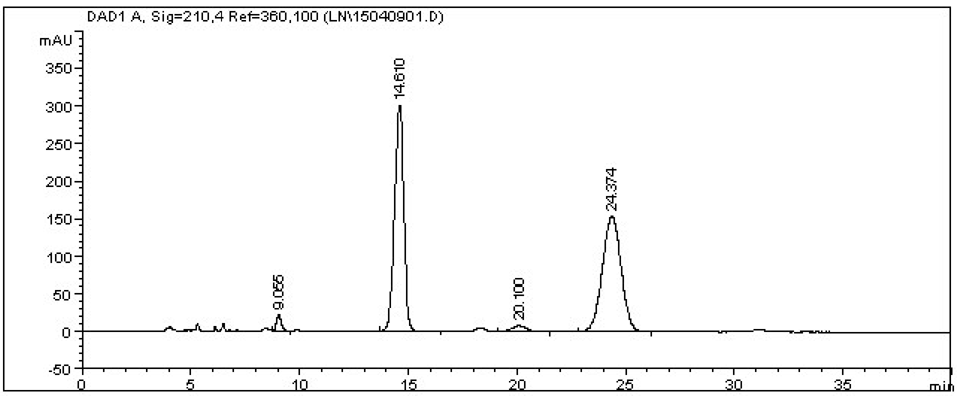
=====================================================================
                          Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=210,4 Ref=360,100
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.518	VV	0.2710	1.22995e4	706.70410	20.8441
2	15.801	VV	0.5665	1.25042e4	345.25137	21.1910
3	22.827	VV	0.9905	1.71871e4	270.05005	29.1273
4	26.967	VB	1.1874	1.70161e4	223.70053	28.8376

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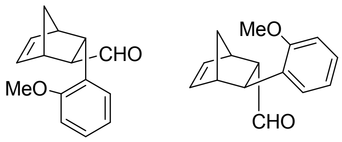
=====================================================================
                          Area Percent Report
=====================================================================

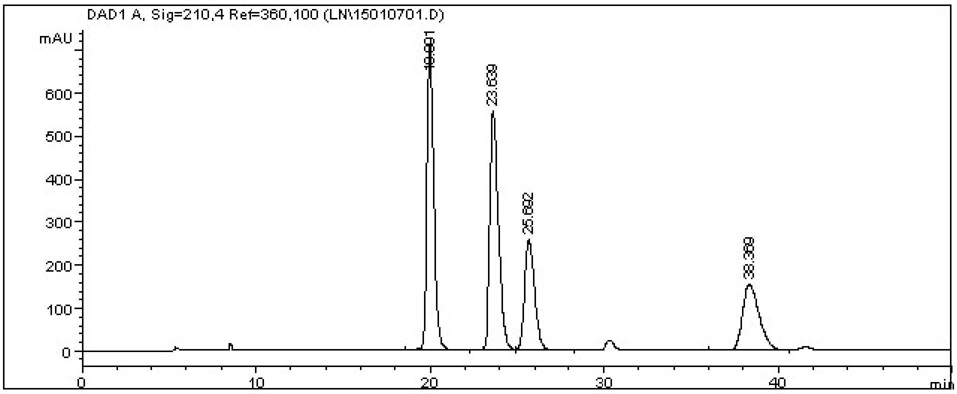
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=210,4 Ref=360,100
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.055	VV	0.2440	351.77438	22.30621	1.8695
2	14.610	VB	0.4636	8968.58398	301.03000	47.6636
3	20.100	VP	0.7306	360.64194	7.75366	1.9166
4	24.374	PV	0.9361	9135.41309	153.10680	48.5502



Chiralcel OJ-H, 210 nm, hexane/*i*-PrOH = 95/5, 0.6 mL/min

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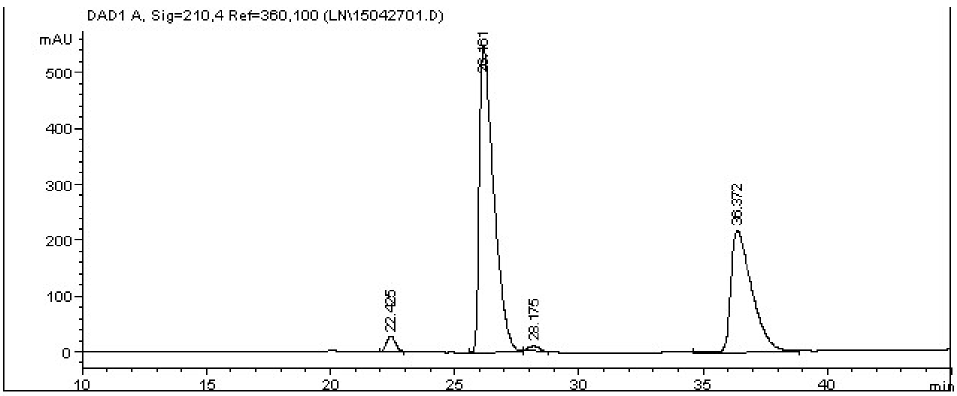
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=210,4 Ref=360,100
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.991	VV	0.4283	1.98084e4	712.51587	33.2035
2	23.639	VV	0.5397	1.93996e4	555.16254	32.5182
3	25.692	VB	0.6173	1.02672e4	257.44525	17.2102
4	38.369	VV	1.0236	1.01824e4	153.16229	17.0680

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=====================================================================
                         Area Percent Report
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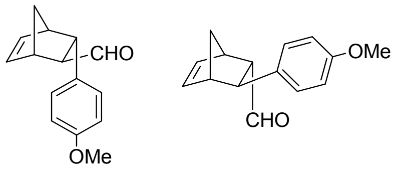
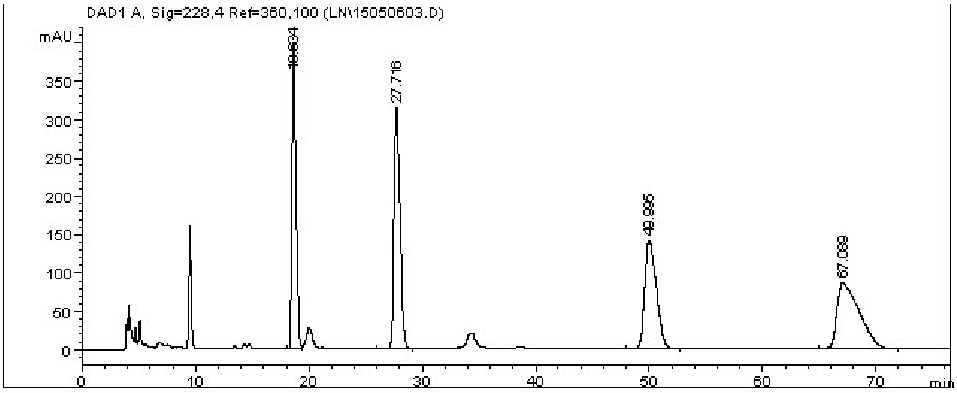
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=210,4 Ref=360,100
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.425	MM R	0.4333	731.34241	28.12763	2.0153
2	26.161	MM R	0.6692	2.20911e4	550.18604	60.8742
3	28.175	MM R	0.5419	301.87396	9.28492	0.8318
4	36.372	VV	0.8959	1.31654e4	219.44533	36.2787



Chiralcel OJ-H, 210 nm, hexane/*i*-PrOH = 85/15, 20min → 80/20, 0.8 mL/min.

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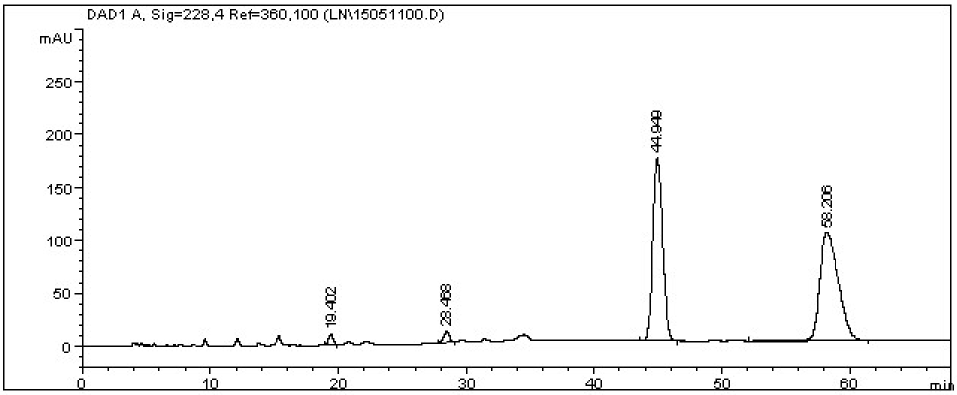
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=228,4 Ref=360,100
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.634	VV	0.3866	9953.17090	399.63657	23.0775
2	27.716	VV	0.5811	1.16550e4	313.95361	27.0234
3	49.995	BB	1.1162	9889.44824	139.98567	22.9298
4	67.089	VB	1.8879	1.16317e4	85.24593	26.9693

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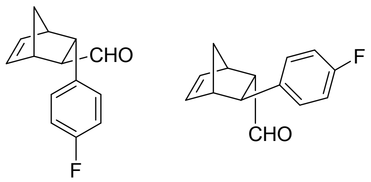
=====================================================================
                         Area Percent Report
=====================================================================

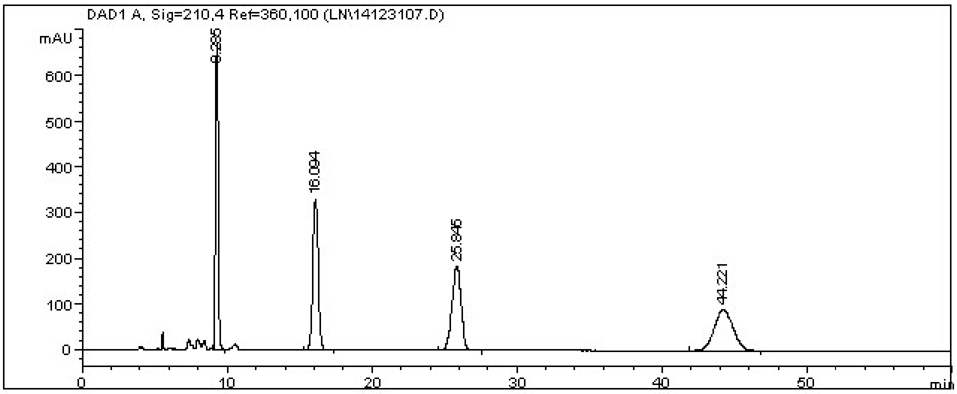
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=228,4 Ref=360,100
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.402	MM R	0.4224	256.65192	10.12667	1.2846
2	28.468	MM R	0.5111	306.85623	10.00722	1.5359
3	44.949	MM R	0.8749	9089.86621	173.16736	45.4980
4	58.206	VV	1.5232	1.03252e4	102.50018	51.6814



Chiralcel OJ-H, 210 nm, hexane/*i*-PrOH = 85/15, 0.8 mL/min



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                         Area Percent Report
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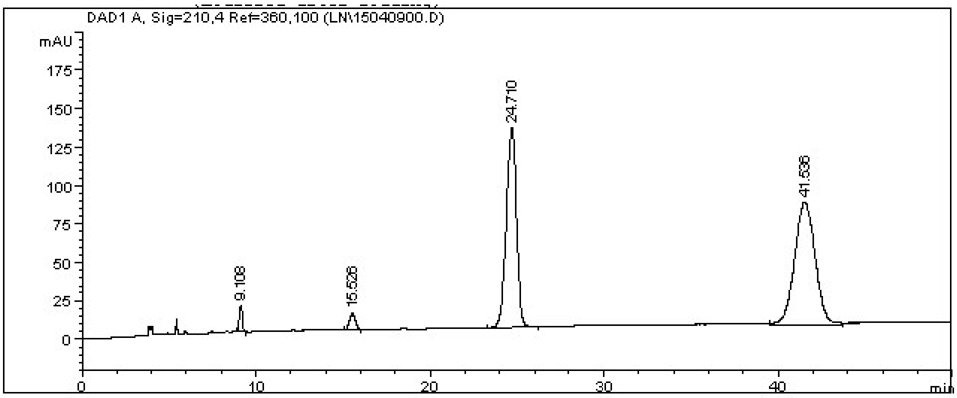
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=210,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.285 VV    0.1906 8183.82080  669.33771  24.7882
   2  16.094 VV    0.3942 8334.52051  330.55728  25.2446
   3  25.845 BB    0.6977 8136.25635  183.34978  24.6441
   4  44.221 VV    1.4420 8360.44531   91.15469  25.3231
```



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=====================================================================
                         Area Percent Report
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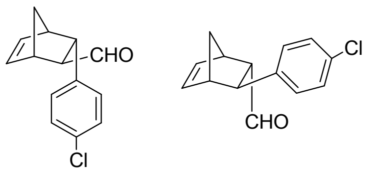
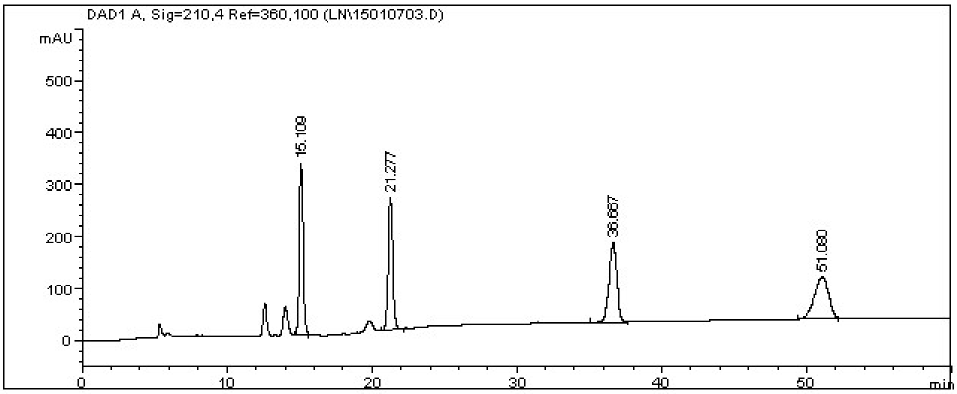
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=210,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1   9.108 MM R  0.1913  188.97432   16.45993   1.5491
   2  15.526 MM R  0.3932  255.14880   10.81443   2.0915
   3  24.710 MM R  0.6816 5314.94873  129.96785  43.5675
   4  41.536 MM R  1.3550 6440.27539   79.21528  52.7920
```



Chiralcel OJ-H, 210 nm, hexane/*i*-PrOH = 90/10, 10min → 80/20, 0.6 mL/min.

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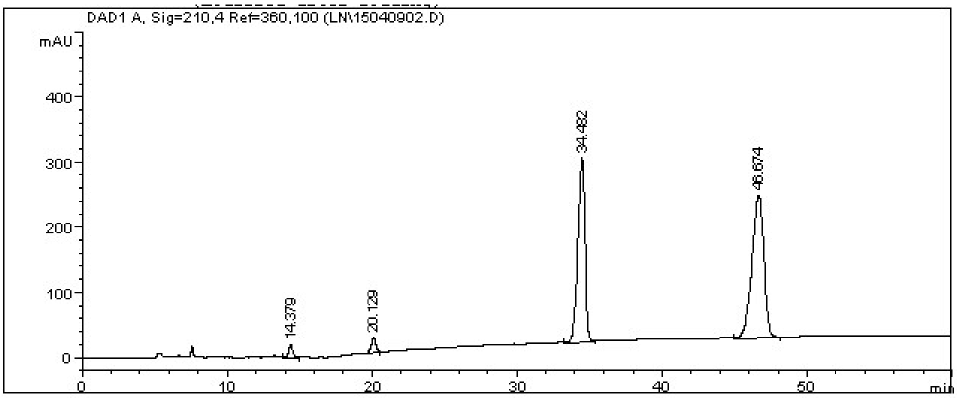
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=210,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  15.109 MM R  0.3096 6140.45117  330.60858  26.5849
   2  21.277 MM R  0.3656 5582.66064  254.47655  24.1700
   3  36.667 MM R  0.6422 5989.88770  155.44403  25.9330
   4  51.080 MM R  1.1178 5384.50879   80.28416  23.3121
```

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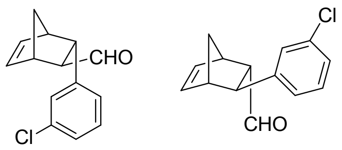
=====================================================================
                        Area Percent Report
=====================================================================

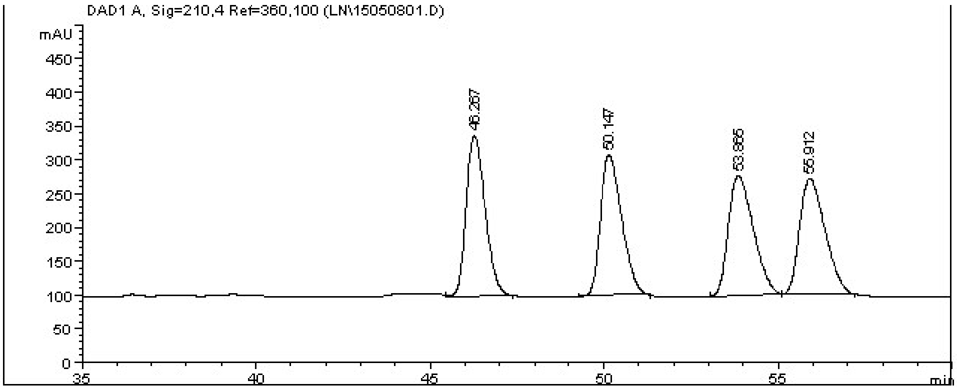
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=210,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  14.379 VV    0.2798  376.92023   20.76600   1.6347
   2  20.129 MM R  0.3552  530.77844   24.90523   2.3020
   3  34.482 MM R  0.5667 9638.06348  283.47128  41.8008
   4  46.674 MM R  0.9564 1.25113e4  218.03403  54.2624
```



Chiralcel OJ-H, 210 nm, hexane/*i*-PrOH = 99.9/0.1, 20min → 98/2, 0.6 mL/min.



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Area Percent Report

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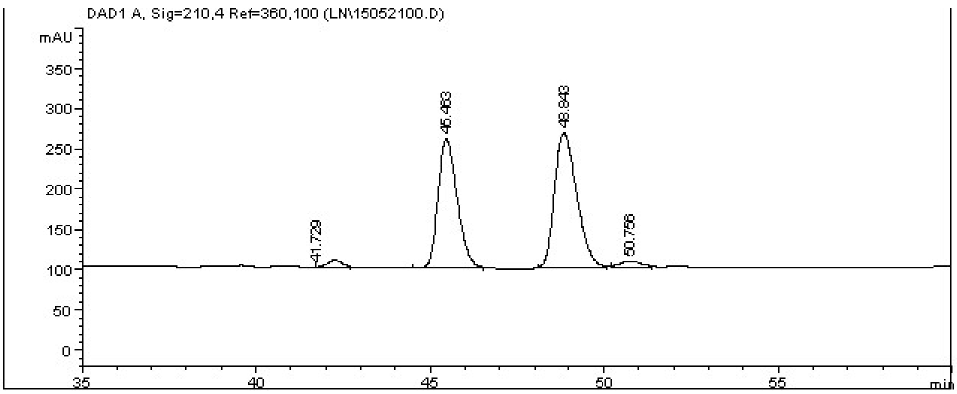
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	46.267	MM R	0.6309	8963.94336	236.82074	25.4444
2	50.147	MM R	0.7065	8758.95313	206.61642	24.8626
3	53.865	MM R	0.8259	8818.11426	177.96025	25.0305
4	55.912	MM R	0.8458	8688.49121	171.21066	24.6625



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Area Percent Report

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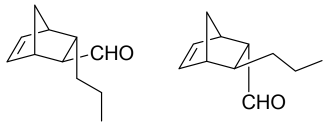
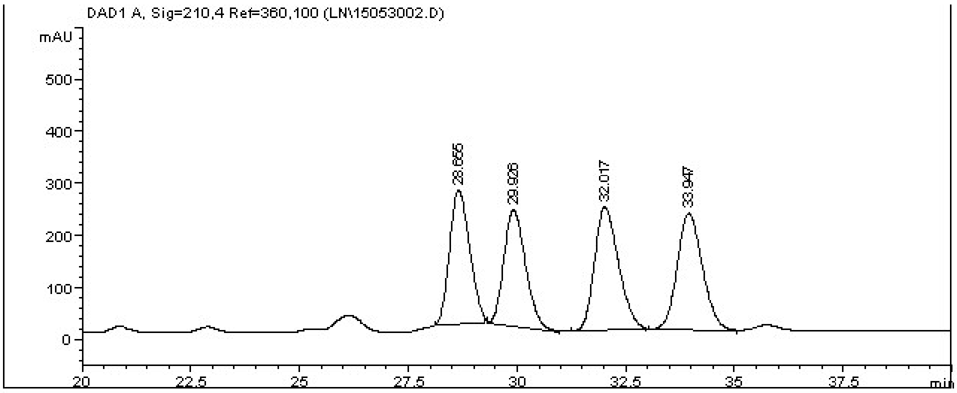
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	41.729	MM R	0.4855	238.03937	8.47672e-2	1.7144
2	45.463	MM R	0.6255	5970.71387	159.10014	43.0013
3	48.843	MM R	0.7361	7372.66699	166.93918	53.0982
4	50.756	MM R	0.6871	303.54443	7.36335	2.1861



Chiralcel OD-H, 210 nm, hexane/*i*-PrOH = 99.5/0.5, 0.6 mL/min.



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Area Percent Report
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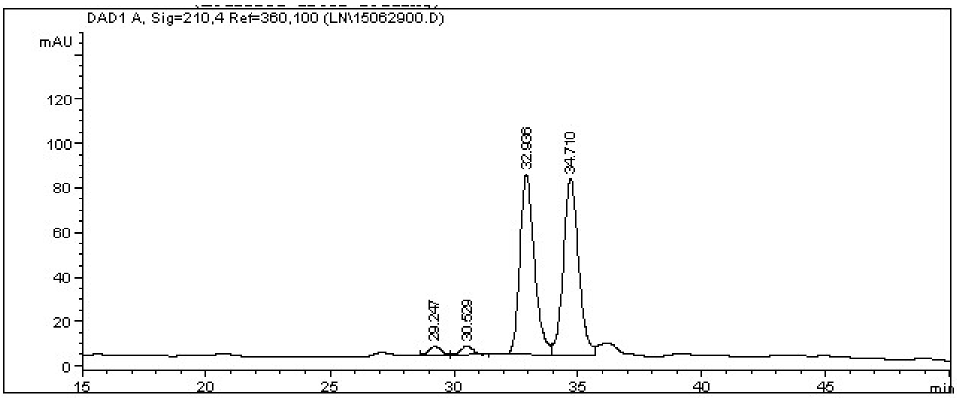
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.655	MM R	0.5343	8225.18262	256.58316	24.1793
2	29.926	MM R	0.5821	7791.08008	223.05606	22.9031
3	32.017	MM R	0.6422	9095.52539	236.06430	26.7378
4	33.947	MM R	0.6647	8905.73047	223.31462	26.1798



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Area Percent Report
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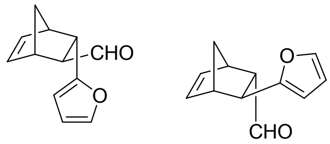
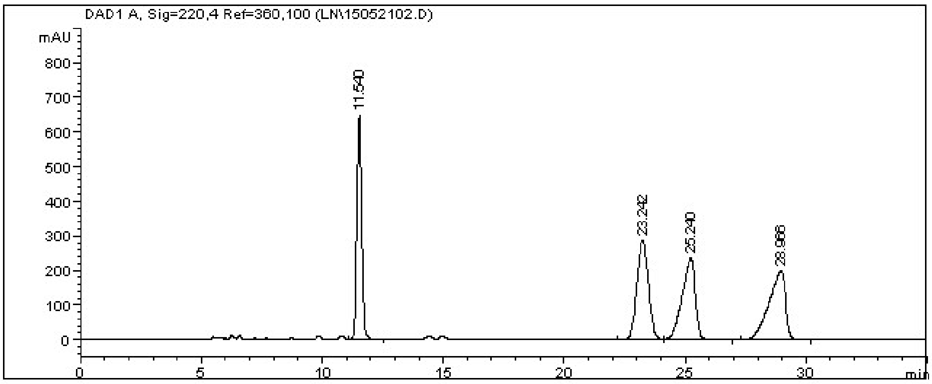
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.247	BV	0.5056	129.28737	3.99423	1.8700
2	30.529	VB	0.5149	128.85657	3.96733	1.8637
3	32.936	BV	0.6155	3263.65039	80.75188	47.2040
4	34.710	VV	0.6545	3392.12891	79.38487	49.0623



Chiralcel OJ-H, 220 nm, hexane/*i*-PrOH = 90/10, 0.8 mL/min

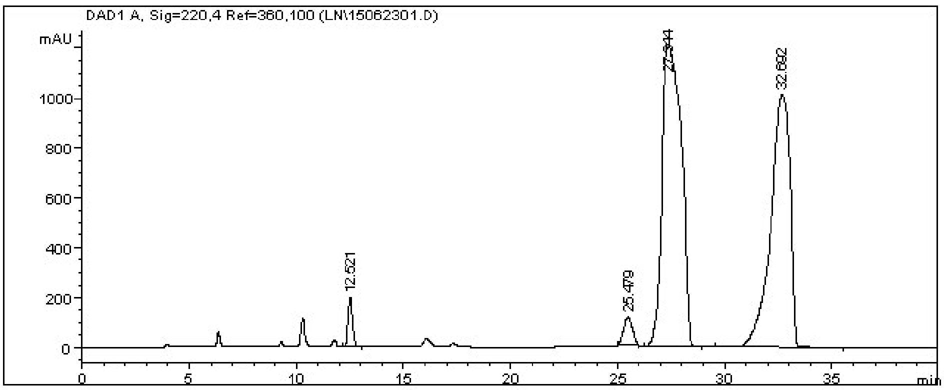



```
=====================================================================
                       Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  11.540 VV    0.2162 8921.57324  649.54095  24.1866
   2  23.242 VV    0.5227 9497.28711  286.53726  25.7473
   3  25.240 VB    0.5769 8957.12598  234.90878  24.2830
   4  28.966 BV    0.7132 9510.47949  199.12978  25.7831
```




```
=====================================================================
                       Area Percent Report
=====================================================================

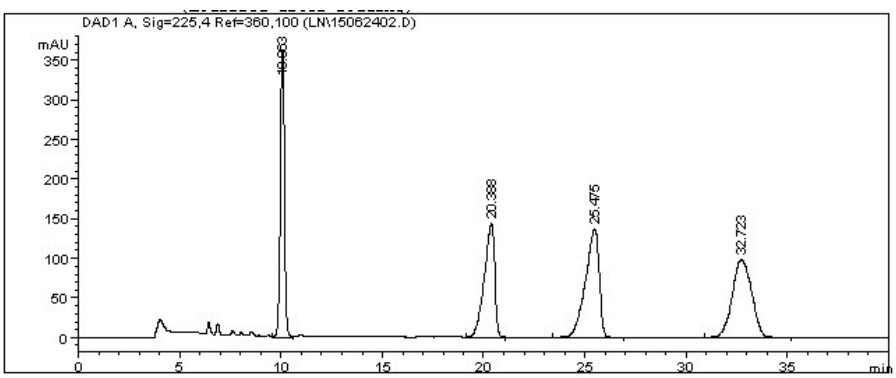
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  12.521 MM R  0.2413 2888.04102  199.46106   1.9791
   2  25.479 MM R  0.4782 3245.23193  113.09546   2.2239
   3  27.344 MM R  0.9322 7.60324e4  1213.88928  52.1026
   4  32.692 MM R  1.6963 6.37626e4  1014.15051  43.6945
```

HPLC spectra for Table 2 in manuscript

Table 2, entry 1:



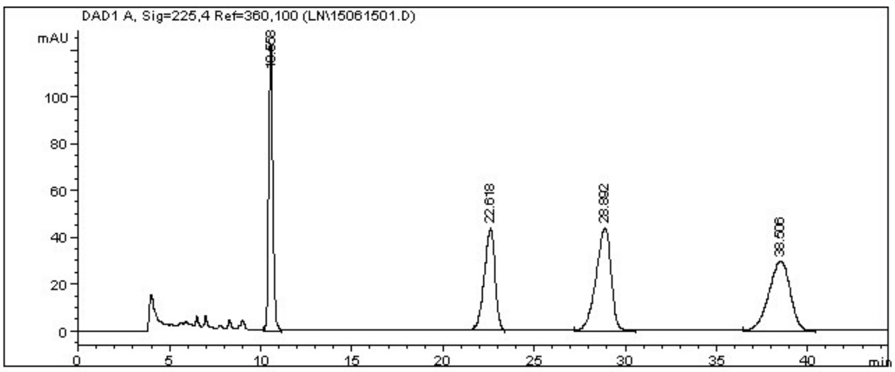
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.063	VV	0.2222	5162.26758	362.43411	22.0111
2	20.388	VV	0.5418	5223.04736	144.48164	22.2703
3	25.475	VB	0.7153	6511.12402	136.79135	27.7624
4	32.723	VV	1.0680	6556.56396	98.06458	27.9562

Table 2, entry 2:



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.558	VV	0.2506	1962.42896	122.69833	22.5436
2	22.618	MM R	0.6742	1752.06702	43.31303	20.1271
3	28.892	VV	0.8815	2552.80713	43.95701	29.3257
4	38.506	VV	1.0006	2437.71973	29.73178	28.0036

Table 2, entry 3:

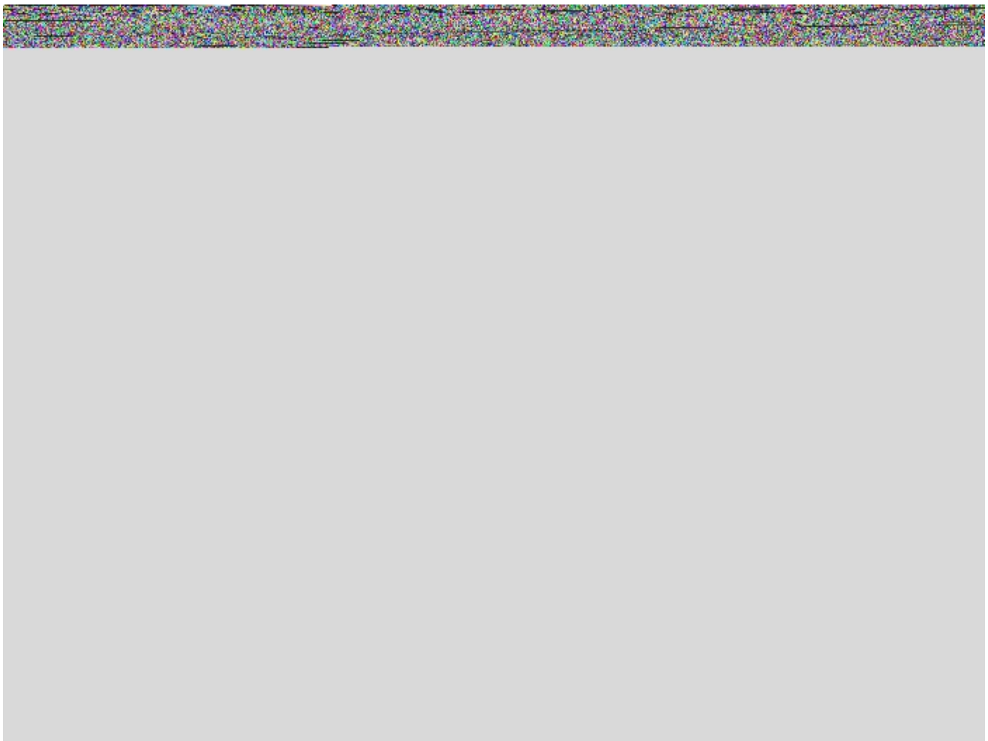
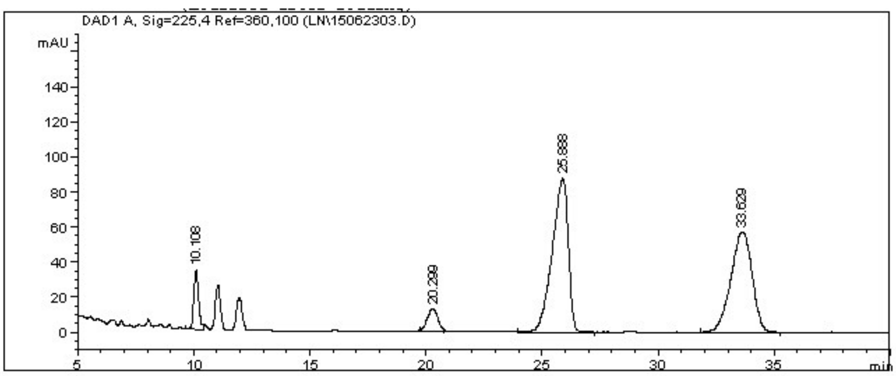


Table 2, entry 4:

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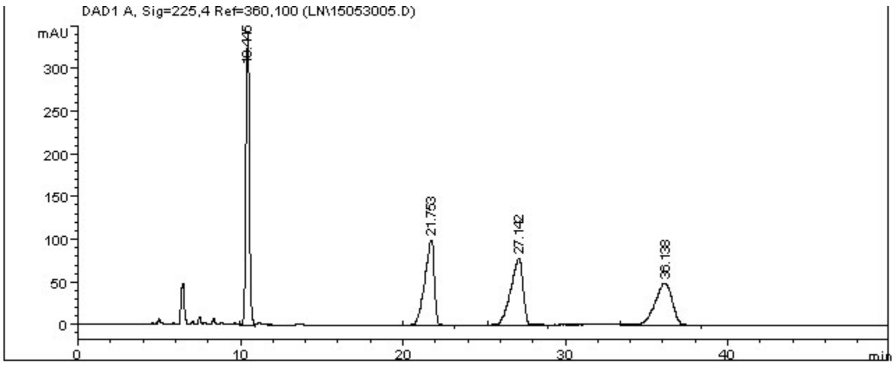
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.108	MM R	0.2392	483.60764	33.69835	5.5173
2	20.299	MM R	0.5269	402.28970	12.72617	4.5896
3	25.888	BV	0.7370	4220.09766	87.76259	48.1457
4	33.629	VV	0.9740	3659.27051	57.22977	41.7474

Table 2, entry 5:



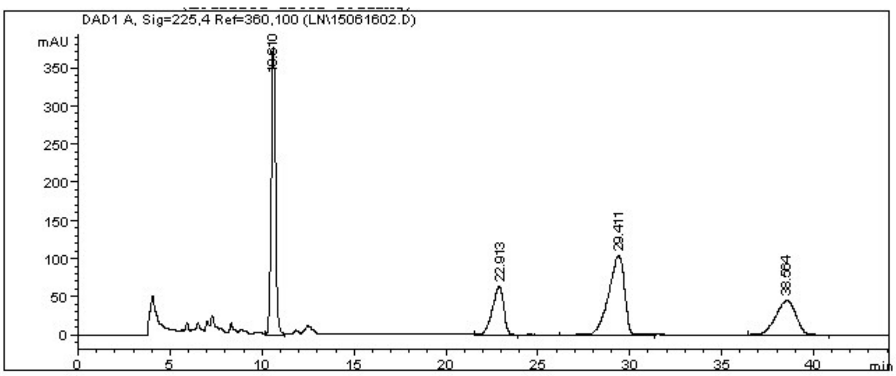

```
====================================================================
                         Area Percent Report
====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.445 VV    0.2374 5094.49902  335.07294  30.1132
   2  21.753 BB    0.6162 4081.69849  100.00665  24.1266
   3  27.142 BB    0.8016 4134.53857   77.60605  24.4389
   4  36.138 BV    1.1429 3607.09668   48.99744  21.3213
```

Table 2, entry 6:



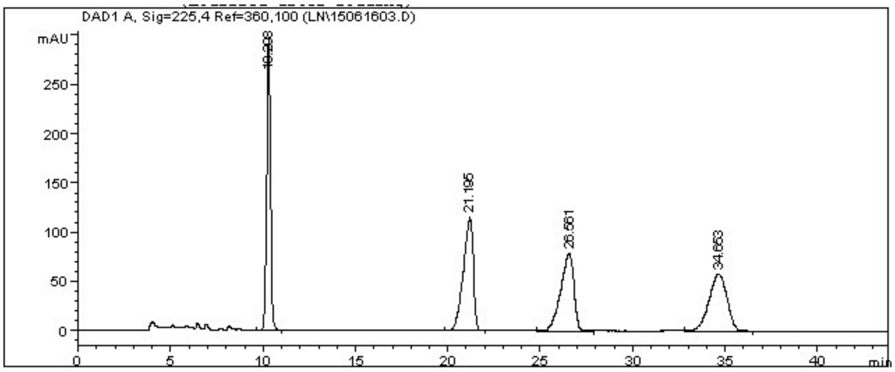

```
====================================================================
                         Area Percent Report
====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.610 VV    0.2567 6216.33398  376.27350  33.5594
   2  22.913 VV    0.6635 2701.79761   63.10043  14.5859
   3  29.411 VB    0.9136 6188.60596  104.09145  33.4097
   4  38.564 BP    1.2104 3416.62183   44.76526  18.4449
```

Table 2, entry 7:




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.298 VV    0.2299 4332.47314  290.60303  26.2605
   2  21.195 VV    0.5736 4312.05127  114.95724  26.1368
   3  26.561 VV    0.7553 3913.38818   78.81629  23.7203
   4  34.653 VB    1.0503 3940.11768   57.87358  23.8824
```

HPLC spectra for Figure1 in manuscript

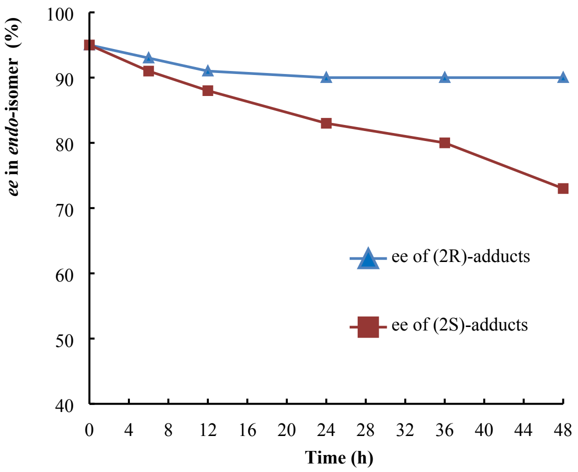
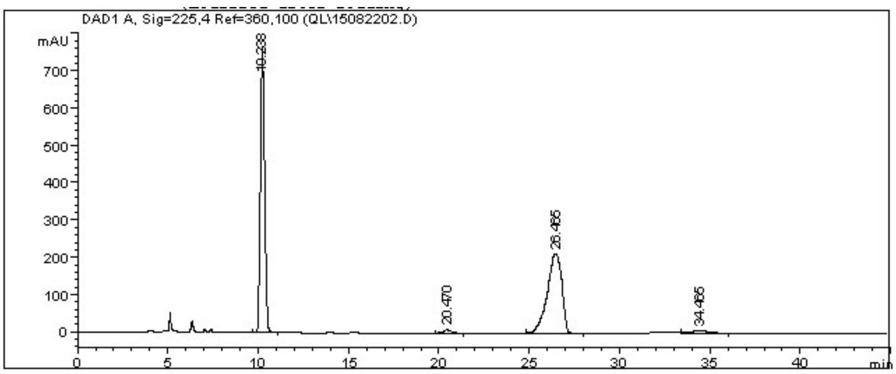


Fig.1 Different reversion reactivity between (2*S*)-adducts and (2*R*)-adducts in CH_3CN-H_2O system: (2*S*)-adducts (95% *ee* in *endo*-isomers) and the (2*R*)-adducts (95% *ee* in *endo*-isomers), 20 mol% **1a**, 50 mol% TFA, CH_3CN (1.9 mL), H_2O (0.1 mL), 40 °C, 48h.

T= 0 h , *ee* values in *2R-endo-isomer :* 95 %



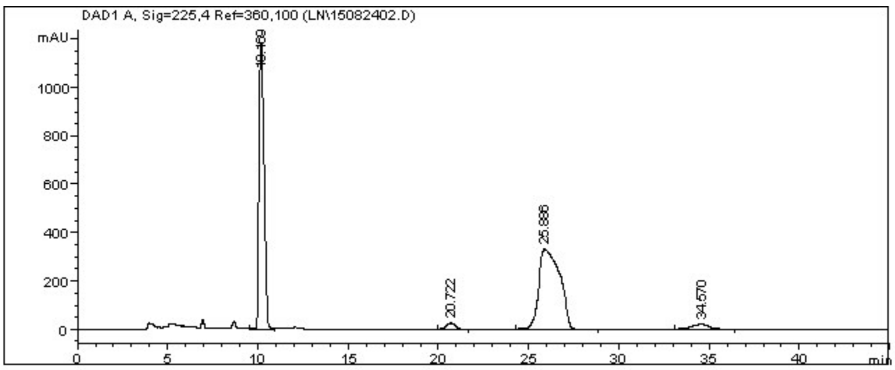

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.238 BV    0.2529 1.24207e4  767.14288  49.5628
   2  20.470 PB    0.5190  305.03113    9.19471   1.2172
   3  26.465 BB    0.8732 1.18672e4  213.24927  47.3541
   4  34.465 VP    0.9104  467.61353    7.08101   1.8659
```

T= 6 h , *ee* values in *2R-endo-isomer :* 93%



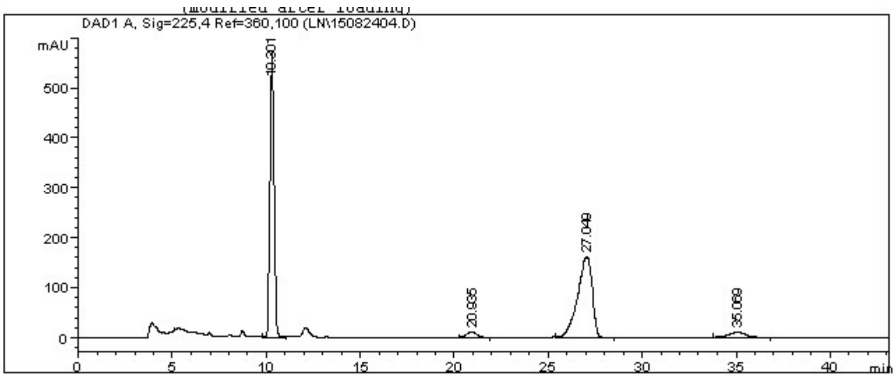

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.169 BV    0.3168 2.27853e4 1182.68140  43.9224
   2  20.722 BB    0.5243  890.17065   26.47439   1.7159
   3  25.886 BP    1.3901 2.68358e4  330.92719  51.7303
   4  34.570 BP    1.0873 1365.08118   19.43820   2.6314
```

T= 12 h , *ee* values in *2R-endo-isomer :* 91%



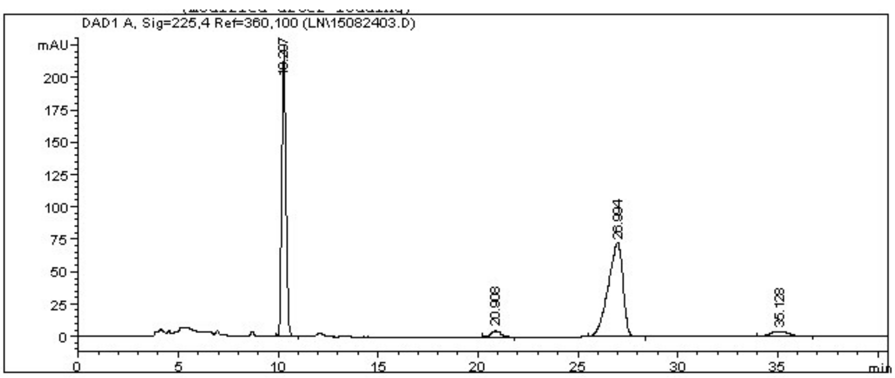

```
===================================================================
                      Area Percent Report
===================================================================

Sorted By            :      Signal
Multiplier           :      1.0000
Dilution             :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=225,4 Ref=360,100
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.301	BB	0.2405	8873.85937	573.49976	47.7755
2	20.935	BB	0.5315	422.69302	12.22247	2.2757
3	27.049	BB	0.8233	8645.78516	160.79494	46.5476
4	35.069	BP	0.9498	631.74329	9.57410	3.4012

T= 24 h , *ee* values in *2R-endo-isomer :* 90%



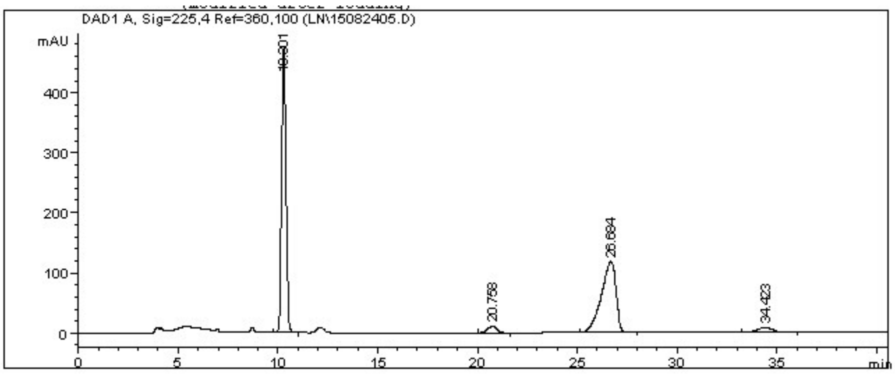

```
===================================================================
                      Area Percent Report
===================================================================

Sorted By            :      Signal
Multiplier           :      1.0000
Dilution             :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=225,4 Ref=360,100
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.297	BB	0.2319	3252.47974	220.79329	43.8346
2	20.908	BP	0.4988	170.93530	4.90281	2.3037
3	26.994	BB	0.7940	3732.11963	72.33378	50.2988
4	35.128	BB	0.8292	264.36237	4.09474	3.5629

T= 36 h , *ee* values in *2R-endo-isomer :* 90%



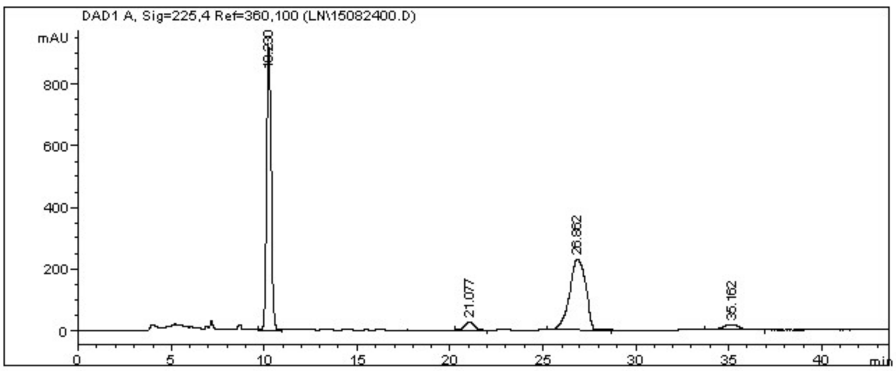

```
=====================================================================
                          Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.301	BB	0.2321	7176.20117	475.54129	51.2866
2	20.758	BB	0.5245	392.94409	11.67997	2.8083
3	26.684	BB	0.7718	5955.08936	117.38891	42.5596
4	34.423	BB	0.9683	468.12747	7.45820	3.3456

T= 48 h , *ee* values in *2R-endo-isomer :* 90%



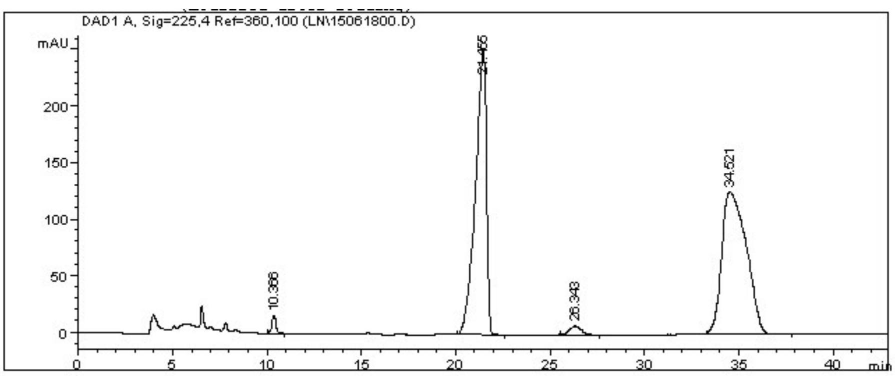

```
=====================================================================
                          Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.230	BV	0.2775	1.60925e4	931.71936	50.1626
2	21.077	BP	0.5509	913.76117	26.20192	2.8483
3	26.862	BB	0.9773	1.39495e4	230.76067	43.4825
4	35.162	BP	1.0470	1124.94214	16.59127	3.5066

T= 0 h , *ee* values in *2S-endo-isomer :* 95%



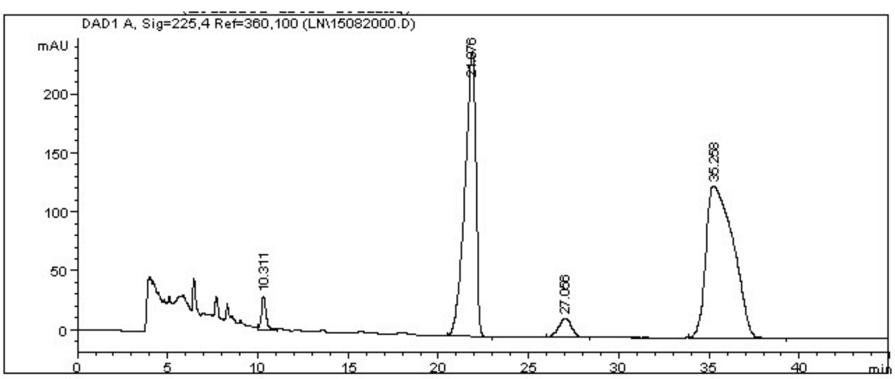
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.366	BP	0.2378	251.03027	16.11035	1.1263
2	21.455	PP	0.6014	1.02592e4	252.83867	46.0290
3	26.343	BB	0.7175	348.31900	7.67479	1.5628
4	34.521	BP	1.5473	1.14299e4	126.35559	51.2819

T= 6 h , *ee* values in *2S-endo-isomer :* 91%



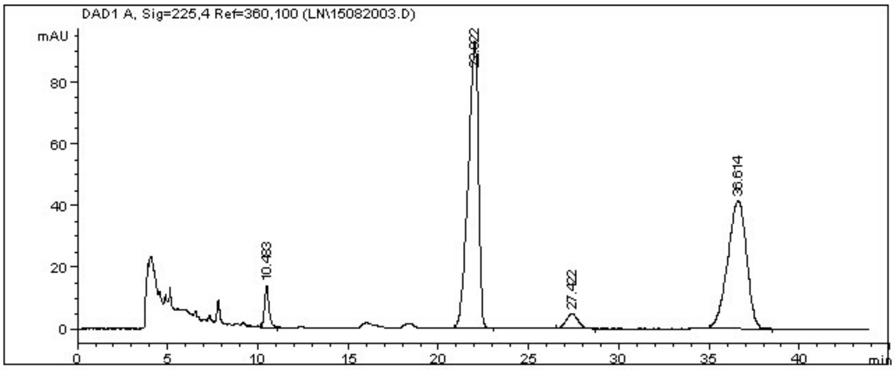
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.311	VB	0.2641	507.50729	28.45744	2.0261
2	21.876	BP	0.6369	1.02009e4	241.46463	40.7245
3	27.056	BP	0.7597	794.83325	15.99607	3.1732
4	35.258	BP	1.8231	1.35453e4	128.77971	54.0762

T= 12 h , *ee* values in *2S-endo-isomer :* 88%

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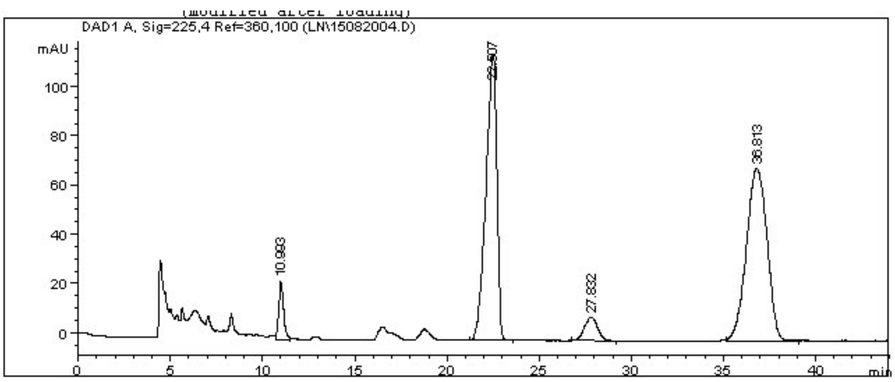
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.483	BB	0.2560	227.04349	13.51404	3.1623
2	22.022	BP	0.6067	3694.70728	93.16764	51.4599
3	27.422	BB	0.7632	230.55415	4.70892	3.2112
4	36.614	BP	1.1255	3027.47534	41.57715	42.1667

T= 24 h , *ee* values in *2S-endo-isomer :* 83%



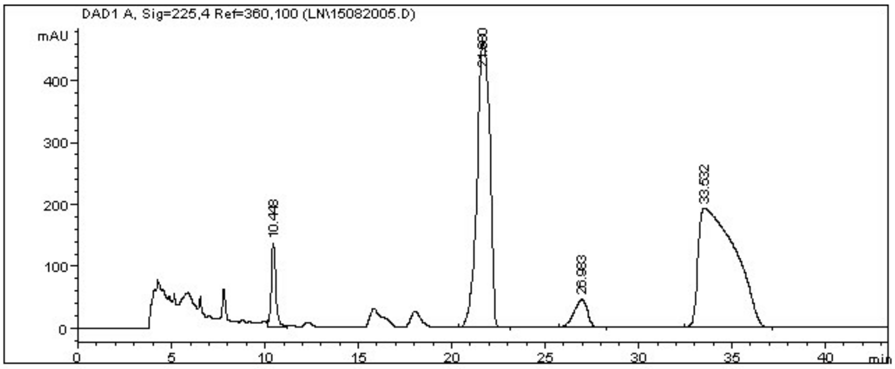

```
=====================================================================
                         Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.993	MM R	0.3117	441.55316	23.61311	3.9588
2	22.507	BP	0.6390	4796.51611	115.85979	43.0033
3	27.832	BP	0.7816	476.02811	9.61577	4.2678
4	36.813	BB	1.2470	5439.72949	69.66243	48.7701

T=36 h , *ee* values in *2S-endo-isomer :* 80%



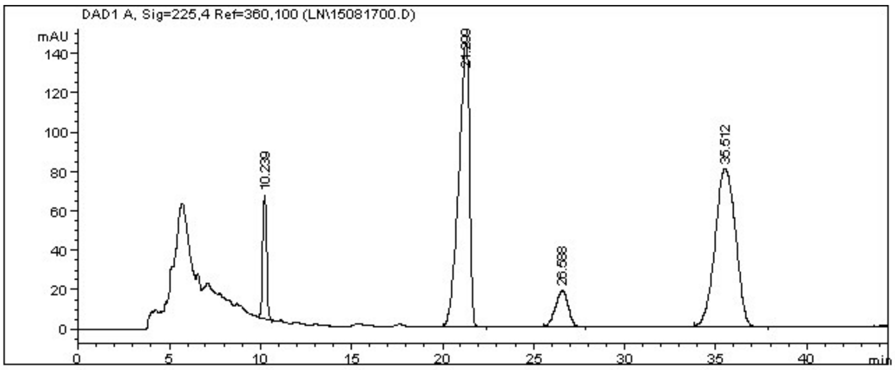

```
====================================================================
                       Area Percent Report
====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.448 VB    0.2625 2407.61743  136.01732   4.5097
   2  21.680 PB    0.7810 2.22346e4   462.38345  41.6476
   3  26.983 BP    0.7806 2271.18848   45.63766   4.2542
   4  33.532 BB    1.9326 2.64741e4   192.96602  49.5886
```

T=48 h , *ee* values in *2S-endo-isomer :* 73%




```
====================================================================
                       Area Percent Report
====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.239 MM R  0.2374  897.29095   62.98620   6.4569
   2  21.299 BP    0.6134 5859.77637  144.42162  42.1667
   3  26.588 BP    0.7450  894.77893   18.34726   6.4388
   4  35.512 BP    1.2574 6244.83594   80.11901  44.9376
```

HPLC spectra for Figure2 in manuscript

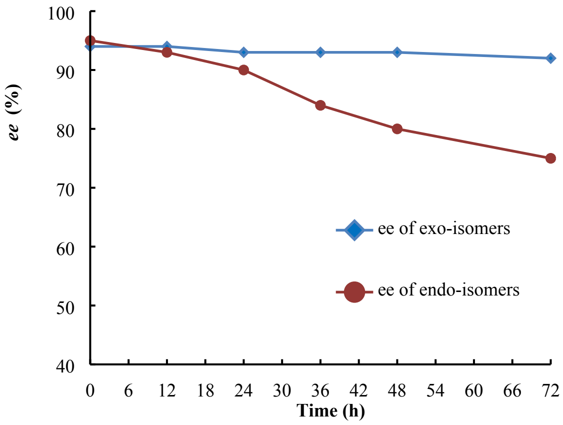
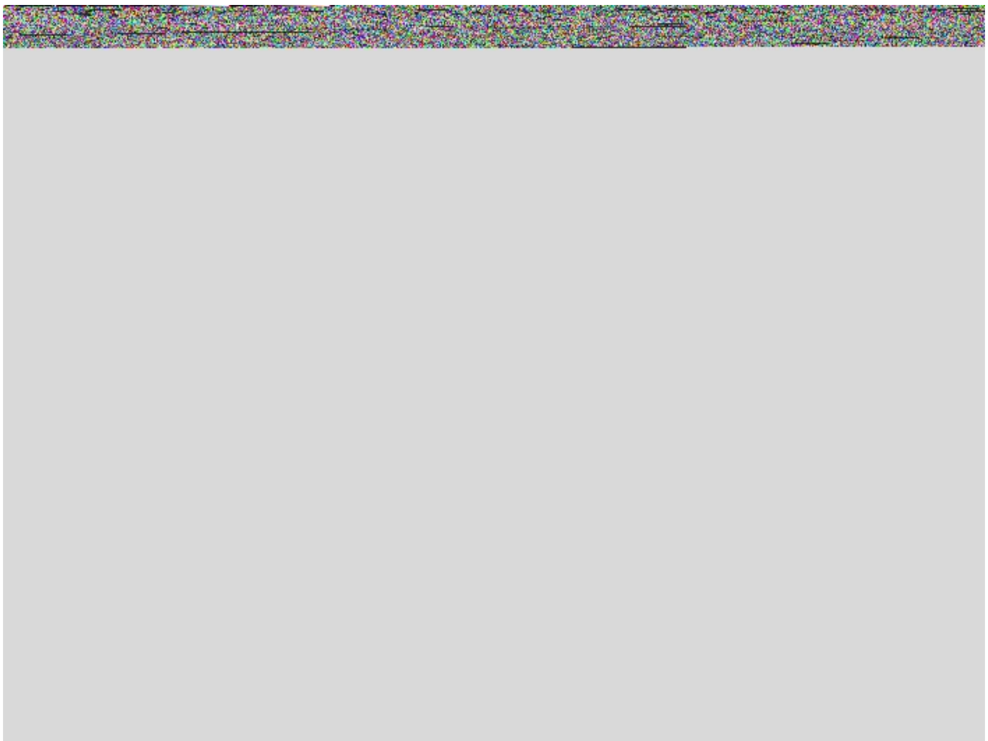
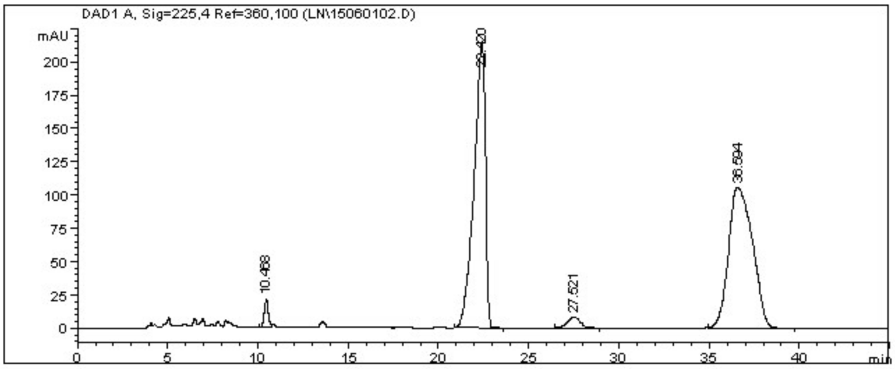


Fig. 2 The stability of isolated aldehyde adducts in CH_3CN-H_2O system：aldehyde products (1 mmol, 94% *ee* in 2*S*-*endo*-isomers, 95% *ee* in 2*S*-*exo*-isomers), 20 mol% **1a**, 100 mol% TFA, CH_3CN (1.9 mL), H_2O (0.1 mL), r.t..

T=0 h , *ee* values in *endo-isomer* (95%) and *exo-isomer* (94%)



T=12 h , *ee* values in *endo-isomer* (93%) and *exo-isomer* (94%)



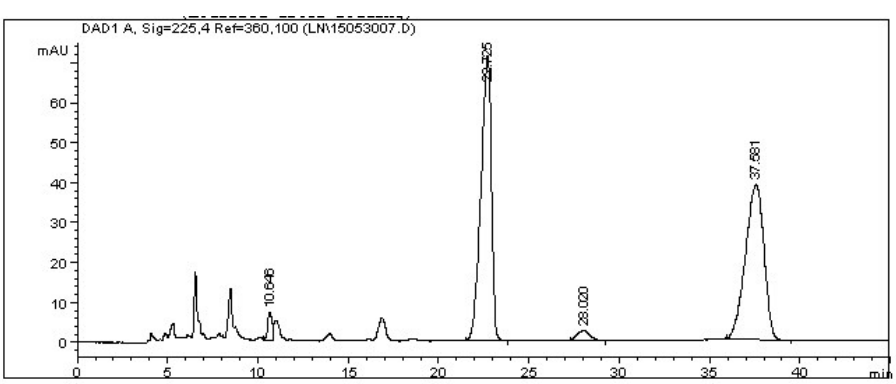
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.468	MM R	0.2589	323.99570	20.86004	1.6193
2	22.420	BB	0.6494	9476.46973	215.33949	47.3630
3	27.521	BB	0.7965	424.82736	8.47954	2.1233
4	36.594	BP	1.5509	9782.88770	105.78684	48.8944

T=24 h , *ee* values in *endo-isomer* (90%) and *exo-isomer* (93%)



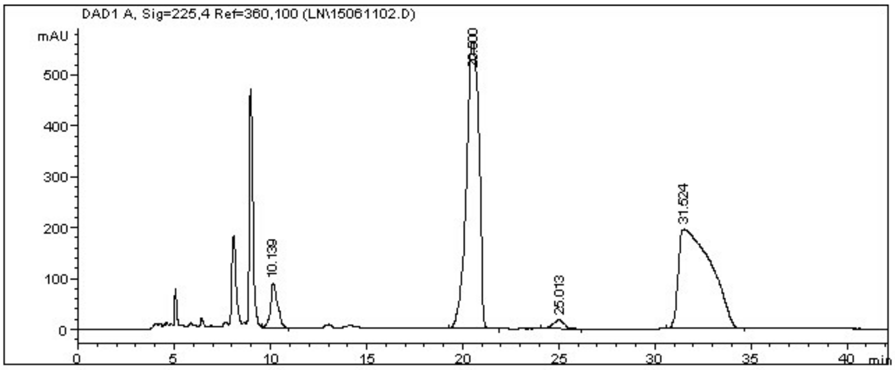
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.646	VV	0.2468	113.75322	6.81216	1.9251
2	22.725	BP	0.6132	2890.74951	71.26836	48.9217
3	28.020	BP	0.6795	121.38595	2.54951	2.0543
4	37.581	BP	1.1037	2783.04175	38.85152	47.0989

T=36 h , *ee* values in *endo-isomer* (84%) and *exo-isomer* (93%)

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                     Area Percent Report
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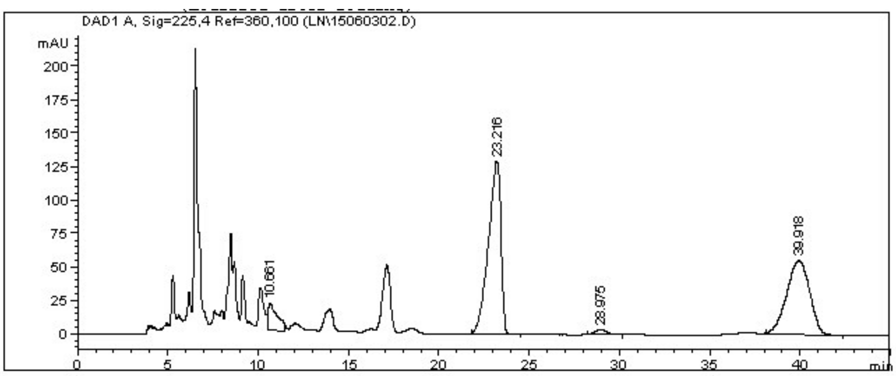
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.139 VB    0.3726 2246.44702   87.19568   4.3398
   2  20.500 BB    0.7392 2.56956e4   564.35150  49.6394
   3  25.013 BB    0.6759  730.62921   16.78360   1.4115
   4  31.524 BP    1.5542 2.30918e4   195.47653  44.6094
```

T=48 h , *ee* values in *endo-isomer* (80%) and *exo-isomer* (93%)

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                     Area Percent Report
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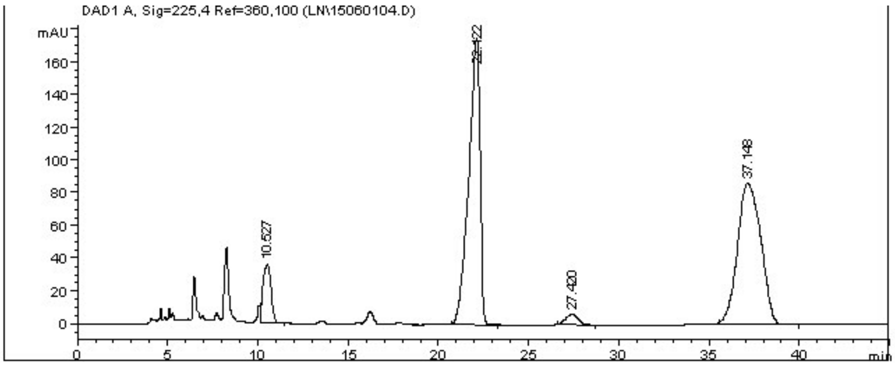
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.661 MM R  0.5892  681.72711   19.28439   5.7350
   2  23.216 BP    0.7190 6193.94971  129.28271  52.1067
   3  28.975 BP    0.7432  187.75990    3.58406   1.5795
   4  39.918 BP    1.3925 4823.62451   54.71772  40.5788
```

T=72 h , *ee* values in *endo-isomer* (75%) and *exo-isomer* (92%)



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                         Area Percent Report
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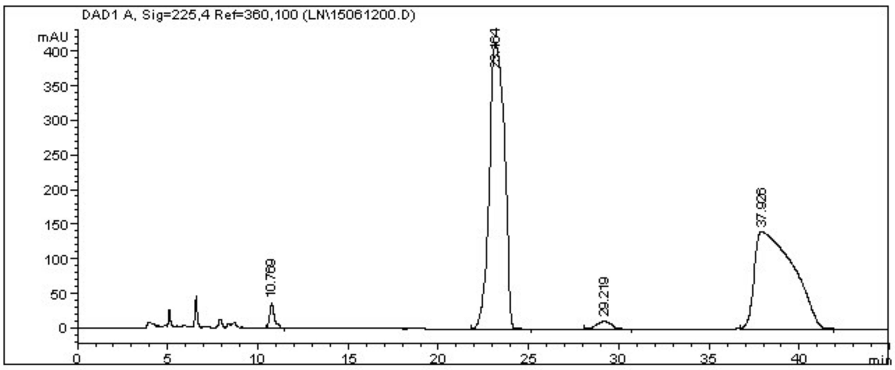
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.527 VB    0.4916 1083.85425   35.55757   6.4483
   2  22.122 BB    0.6467 7660.56445  174.99257  45.5761
   3  27.420 BB    0.7525  327.71350    6.49726   1.9497
   4  37.148 BP    1.4734 7736.14648   86.00327  46.0258
```

HPLC spectra for Figure S1 in ESI

T=0 h , *ee* values in *endo-isomer* (95%) and *exo-isomer* (94%)



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                         Area Percent Report
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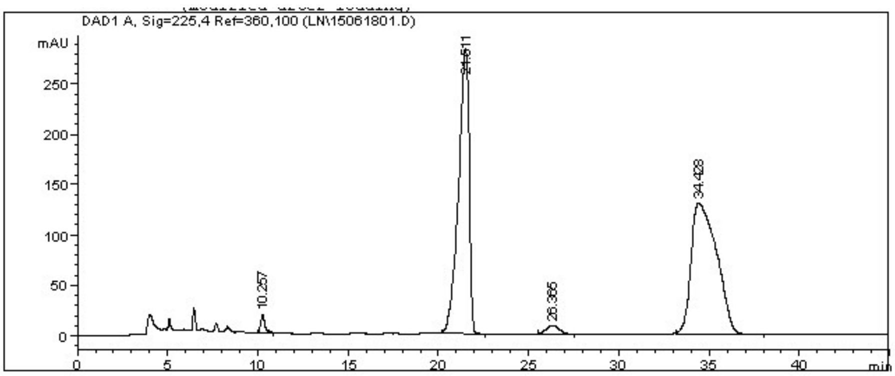
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.769 BP    0.2707  660.67389   36.58621   1.4249
   2  23.164 BB    0.9649 2.40303e4  414.16150  51.8271
   3  29.219 BB    0.7539  649.87408   11.11955   1.4016
   4  37.926 BB    1.9235 2.10254e4  140.69432  45.3464
```

T=12 h , *ee* values in *endo-isomer* (95%) and *exo-isomer* (94%)

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                         Area Percent Report
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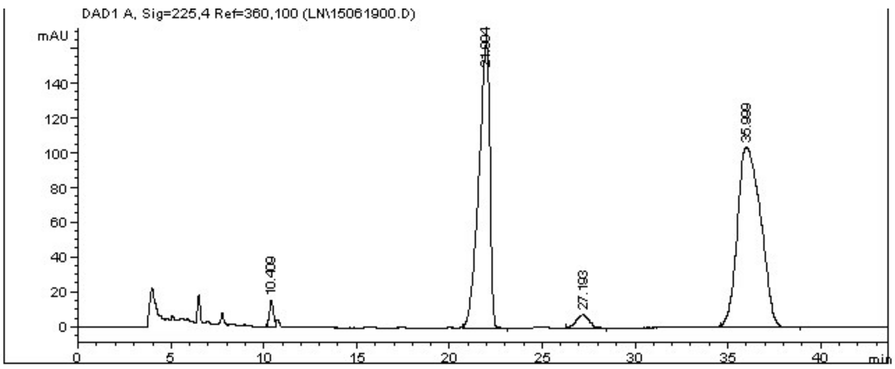
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.257 BP    0.2472  299.94528   18.69756   1.2056
   2  21.511 BB    0.6148 1.15243e4  283.14890  46.3192
   3  26.365 BB    0.7042  379.44745    8.19518   1.5251
   4  34.428 BB    1.6879 1.26765e4  129.73596  50.9501
```

T=24 h , *ee* values in *endo-isomer* (93%) and *exo-isomer* (93%)

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                         Area Percent Report
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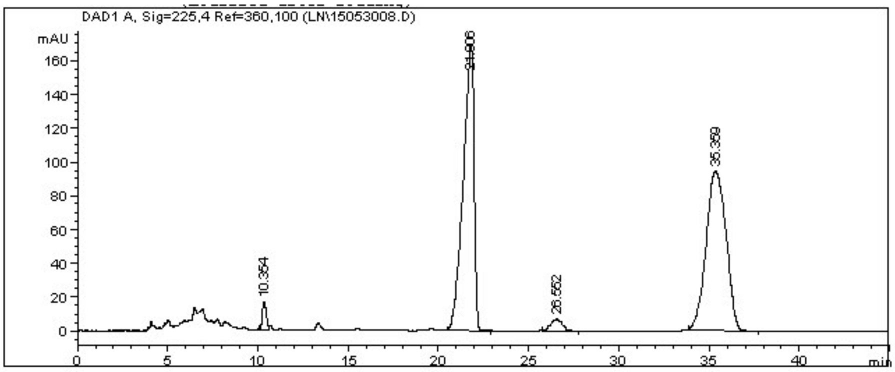
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]        %
----|-------|----|-------|----------|----------|--------|
   1  10.409 BV    0.2291  230.93750   15.56846   1.4033
   2  21.994 BP    0.6167 6839.79785  164.61702  41.5630
   3  27.193 BP    0.7579  362.34909    7.41724   2.2019
   4  35.999 BB    1.4476 9023.38574  103.65433  54.8318
```

T=36 h , *ee* values in *endo-isomer* (93%) and *exo-isomer* (92%)

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                         Area Percent Report
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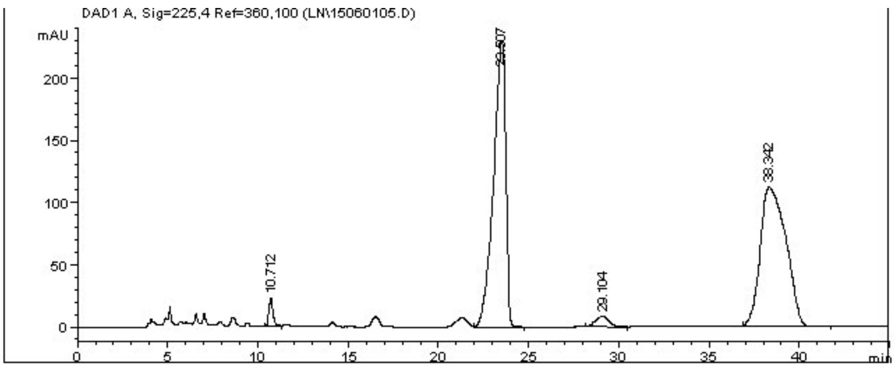
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.354 MM R  0.2536  252.15631   16.57029   1.6953
   2  21.806 BB    0.6161 7021.85059  169.23514  47.2102
   3  26.552 BB    0.7112  313.98285    6.89637   2.1110
   4  35.359 BP    1.2566 7285.59766   94.37815  48.9835
```

T=48 h , *ee* values in *endo-isomer* (93%) and *exo-isomer* (92%)

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                         Area Percent Report
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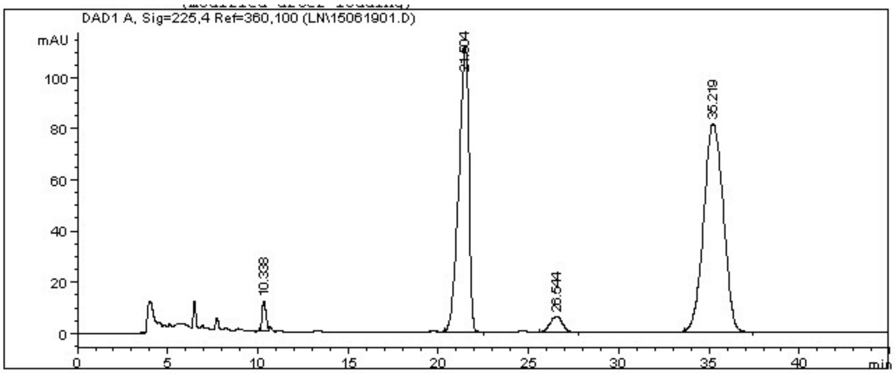
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.712 BB    0.2698  400.14087   22.68261   1.7611
   2  23.507 VB    0.7116 1.07883e4  229.83121  47.4817
   3  29.104 BP    0.8117  459.72009    8.76844   2.0233
   4  38.342 BB    1.6673 1.10728e4  111.82038  48.7338
```

T=72 h , *ee* values in *endo-isomer* (92%) and *exo-isomer* (91%)

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                        Area Percent Report
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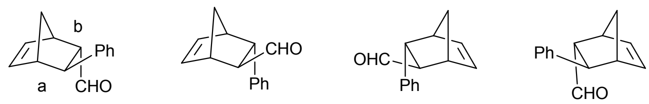
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=225,4 Ref=360,100
```

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.338	BV	0.2267	172.87318	11.81619	1.5913
2	21.504	BB	0.5711	4285.38428	111.81972	39.4464
3	26.544	BB	0.7042	278.78607	6.06531	2.5662
4	35.219	BP	1.2104	6126.76270	81.37682	56.3961

The molecular models and the calculation results:

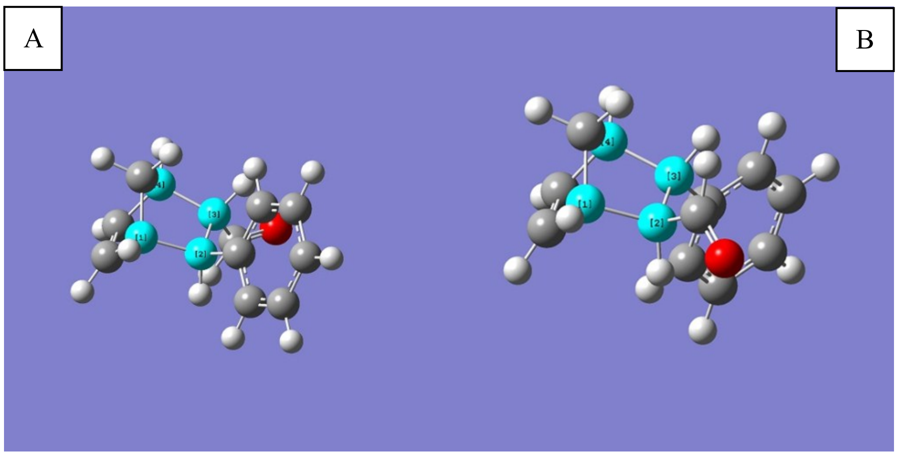


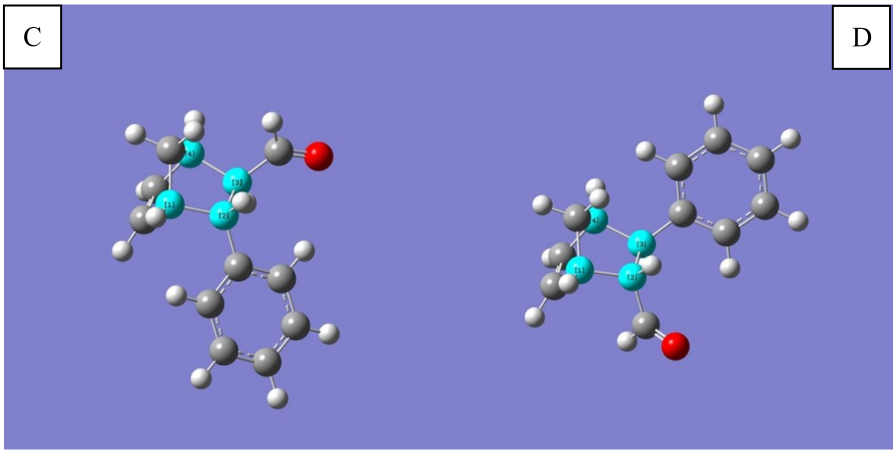
A (2*S*)-*endo*

B (2*S*)-*exo*

C (2*R*)-*exo*

D (2*R*)-*endo*





化合物	a 键长（Å）	b 键长（Å）	平均键长（Å）
A	1.60215	1.59614	1.599145
B	1.60458	1.59671	1.600645
C	1.58403	1.58876	1.586395
D	1.58886	1.58371	1.586285

References:

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