Direct Asymmetric Aldol Reactions between Aldehydes and Ketones Catalyzed by L-Tryptophan in the Presence of Water

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Supporting Information

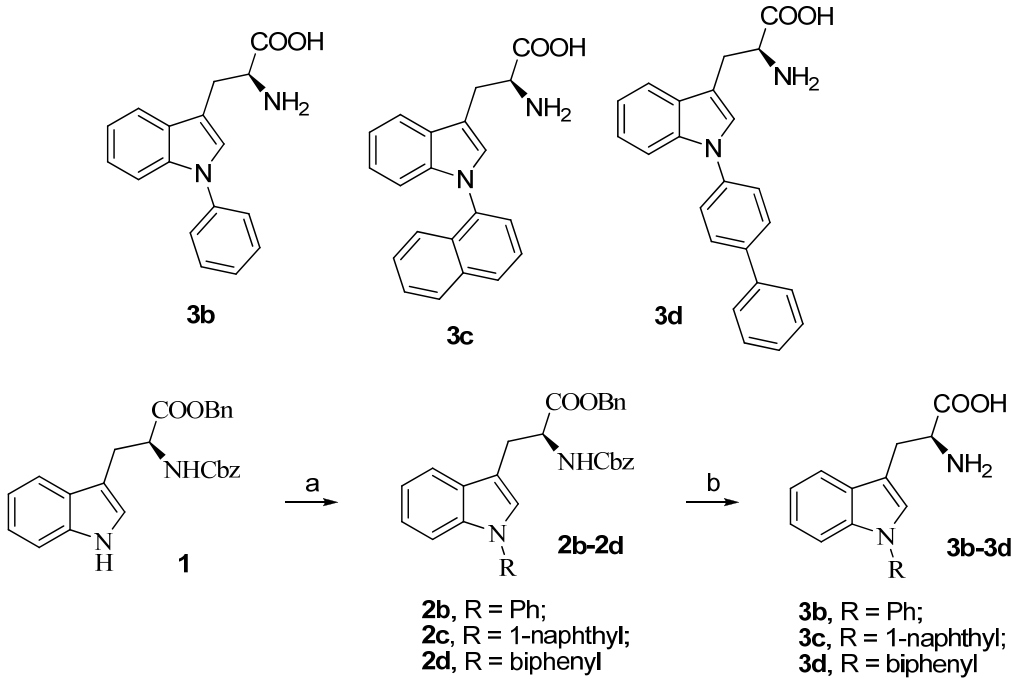
A. Preparation of tryptophan derivatives **3b-3d** S2

B. Analytical Data and HPLC spectra of the aldol Products S4

C. DFT calculations S19

A. Preparation of tryptophan derivatives 3b-3d

General synthetic scheme:



a: ArI, CuI, K_3PO_4, *trans*-1,2-cyclohexanediamine, toluene,microwave, 135 °C, 2 h;
b: H_2, Pd/C, MeOH, RT

Intermediates **2b**, **2c** and 2**d** were synthesized following the literature procedure on *N*-arylation.[1] Subsequent hydrogenolysis simultaneously remove Cbz protection on the nitrogen and cleave off benzyl ester, affording catalysts **3b**, **3c** and **3d**.

Benzyl (*S*)-1-((benzyloxy)carbonyl)-2-(1-phenyl-1H-indol-3-yl)ethylcarbamate (**2b**)

A white solid; 73% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.38-3.40 (m, 2H, CH_2), 4.81-4.88 (m, 1H, CH), 5.08-5.19 (m, 4H, $2CH_2$), 6.94 (s, 1H, ArH), 7.12-7.59 (m, 19H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 172.37, 156.44, 140.12, 136.98, 136.66, 135.81, 130.22, 129.74, 129.24, 129.19, 129.13, 127.07, 124.97, 123.34, 121.01, 119.72, 111.26, 67.95, 55.31, 28.56; MS (ESI): calcd for $[C_{32}H_{29}N_2O_4]^+$ M: 504.2; found *m/z* 504.3.

(*S*)-2-Amino-3-(1-phenyl-1H-indol-3-yl)propanoic acid (**3b**)

A grey solid; 86% yield; ^{1}H NMR (300 MHz, MeOD) δ = 3.13-3.18 (m, 1H, CH_2), 3.51-3.57 (m, 1H, CH_2), 3.82-3.86 (m, 1H, CH), 7.13-7.74 (m, 10H, ArH); ^{13}C NMR (75 MHz, MeOD) δ = 170.15, 138.60, 136.54, 128.81, 128.27, 128.22, 127.60, 127.44, 121.58, 119.18, 118.99, 110.35, 110.13, 55.04, 27.49; HRMS (ESI): calcd for $[C_{17}H_{17}N_2O_2]^+$ M: 281.1285; found *m/z* 281.1290.

Benzyl (*S*)-1-((benzyloxy)carbonyl)-2-(1-(naphthalen-1-yl)-1H-indol-3-yl)ethylcarbamate (**2c**)

A white solid; 77% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.43-3.47 (m, 2H, CH_2), 4.88-4.90 (m, 1H, CH), 5.06-5.22 (m, 4H, $2CH_2$), 6.83-6.85 (m, 1H, ArH), 6.99-7.52 (m, 21H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 172.30, 156.41, 138.79, 136.97, 136.35, 135.72, 135.09, 131.24, 131.11, 130.16, 129.20, 129.16, 129.14, 129.02, 128.99, 128.87, 128.84, 128.80, 128.76, 128.75, 127.67, 127.32, 127.28, 126.06, 125.75, 124.09, 123.95, 123.08, 120.76, 119.53, 111.56, 110.76, 67.94, 67.91, 55.63, 28.67.

(*S*)-2-Amino-3-(1-(naphthalen-1-yl)-1H-indol-3-yl)propanoic acid (**3c**)

A grey solid; 91% yield; ^{1}H NMR (300 MHz, DMSO) δ = 3.12-3.19 (m, 1H, CH_2), 3.34-3.50 (m, 1H, CH_2), 3.60-3.69 (m, 1H, CH), 6.86-7.79 (m, 12H, ArH); ^{13}C NMR (75 MHz, DMSO) δ = 171.01, 138.27, 135.84, 134.54, 130.10, 129.61, 129.54, 128.78, 128.72, 128.41, 128.32, 127.46, 127.13, 126.24, 125.57, 123.82, 122.55, 119.72, 110.71, 54.88, 27.25; HRMS (ESI) calcd for $[C_{21}H_{18}N_2O_2Na]^+$ M: 331.1245; found *m/z* 353.1260.

Benzyl (*S*)-1-((benzyloxy)carbonyl)-2-(1-(4'-phenyl)-phenyl-1H-indol-3-yl)ethylcarbamate (**2d**)

A white solid; 76% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 3.33-3.53 (m, 2H, CH_2), 4.87-4.92 (m, 1H, CH), 5.12-5.23 (m, 4H, $2CH_2$), 7.01 (s, 1H, ArH), 7.16-7.52 (m, 23H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 172.34, 156.43, 140.85, 139.92, 139.27, 136.95, 136.61, 135.79, 129.80, 129.60, 129.22, 129.17, 129.10, 128.82, 128.76, 128.20, 127.69, 127.14, 125.07, 123.40, 121.08, 119.75, 111.68, 111.32, 67.93, 67.61, 55.28, 28.55.

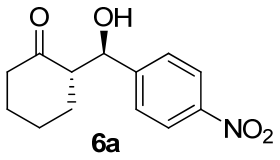
(*S*)-2-Amino-3-(1-(4'-phenyl)-phenyl-1H-indol-3-yl)propanoic acid (**3d**)

A grey solid; 89% yield; ^{1}H NMR (300 MHz, DMSO) δ = 3.17-3.32 (m, 1H, CH_2), 3.52-3.67 (m, 1H, CH_2), 3.86-4.01 (m, 1H, CH), 7.11-7.84 (m, 14H, ArH); ^{13}C NMR (75 MHz, DMSO) δ = 171.01, 139.68, 138.88, 138.24, 135.75, 129.23, 128.16, 127.76, 127.55, 126.86, 124.16, 122.78, 120.27, 119.65, 112.21, 110.56, 54.58, 26.92; HRMS (ESI) calcd for $[C_{23}H_{21}N_2O_2]^+$ M: 357.1598; found *m/z* 357.1594.

B. Analytical Data and HPLC spectra of the Aldol Products

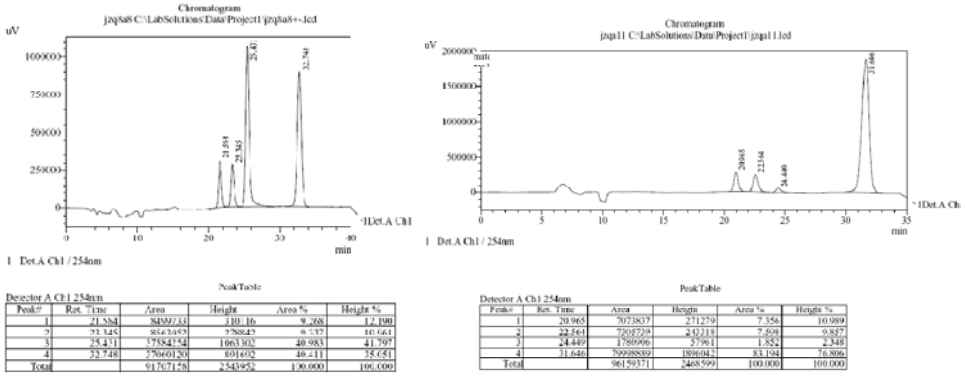
Compounds **6j**, **6n** and **6u** are new, all the other aldol products are known compounds.

(*S*)-2-((*R*)-Hydroxy(4-nitrophenyl)methyl)cyclohexanone (**6a**)[2]



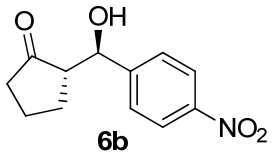
6a

Compound **6a**: a yellow solid; Chiralcel AD-H column, λ = 254 nm, *i*-PrOH:Hexane = 20:80, 0.5 mL/min, t_R = 24.45 min. (minor), t_R = 31.65 min. (major); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.58-1.85 (m, 6H, $3CH_2$), 2.09-2.14 (m, 1H, OH), 2.31-2.63 (m, 3H, CH, CH_2), 4.88-4.91 (d, *J* = 8.4 Hz, 0.84H, CH), 5.48 (s, 0.16H, CH), 7.49-7.52 (d, *J* = 8.7 Hz, 2H, ArH), 8.20-8.22 (d, *J* = 8.7 Hz, 2H, ArH).



(racemic **6a**) (enatiometric enriched **6a**)

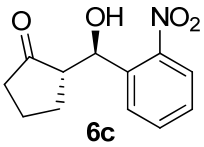
(*S*)-2-((*R*)-Hydroxy(4-nitrophenyl)methyl)cyclopentanone (**6b**)[3]



6b

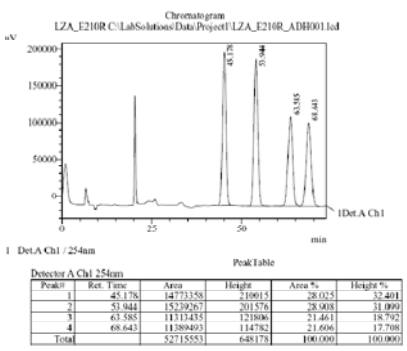
Compound **6b**: a yellow solid; Chiralcel AD-H column, λ = 254 nm, *i*-PrOH:Hexane = 3:97, 0.5 mL/min, t_R = 140.1 min. (minor), t_R = 145.9 min. (major); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.54-1.57 (m, 2H, CH_2), 1.66-2.47 (m, 5H, CH, $2CH_2$), 2.81 (br, 1H, OH), 4.82-4.85 (d, *J* = 9.03 Hz, 0.34H, CH), 5.41 (s, 0.66H, CH), 7.50-7.54 (m, 2H, ArH), 8.18-8.21 (m, 2H, ArH).

(*S*)-2-((*R*)-Hydroxy(2-nitrophenyl)methyl)cyclopentanone (**6c**)[4]

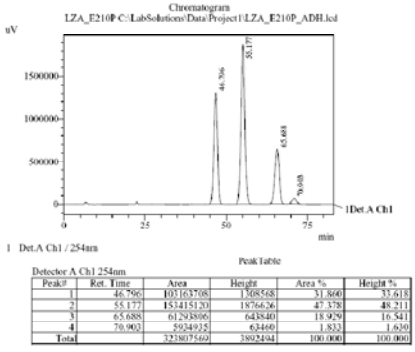


6c

Compound **6c**: a yellow oil; Chiralcel AD-H column, λ = 254 nm, *i*-PrOH:Hexane = 5:95, 0.5 mL/min, t_R = 65.69 min. (major), t_R = 70.90 min. (minor); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.71-1.73 (m, 2H, CH_2), 2.03-2.31 (m, 3H, $2CH_2$), 2.67-2.69 (m, 1H, CH), 5.40-5.43 (d, *J* = 8.37 Hz, 0.24H, CH), 5.88-5.89 (d, *J* = 2.79 Hz, 0.76H, CH), 7.42-7.97 (m, 4H, ArH).

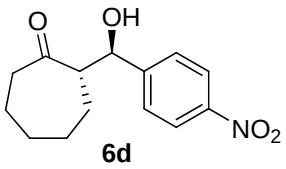


(racemic **6c**)



(enatiometric enriched **6c**)

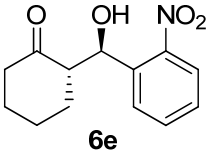
(*S*)-2-((*R*)-Hydroxy(4-nitrophenyl)methyl)cycloheptanone (**6d**)[3]



6d

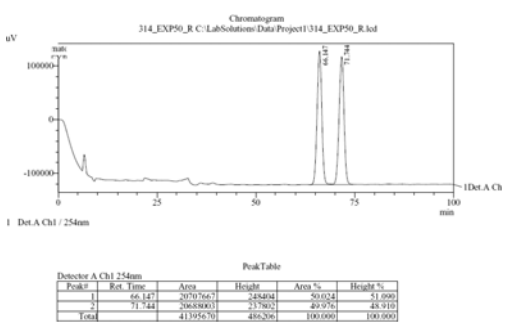
Compound **6d**: a yellow solid; Chiralcel AD-H column, λ = 254 nm, *i*-PrOH:Hexane = 10:90, 0.5 mL/min, t_R = 39.01 min. (major), t_R = 92.60 min. (minor); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.25-1.60 (m, 8H, $4CH_2$), 2.47-2.52 (m, 2H, CH_2), 2.84-2.97 (m, 1H, CH), 3.75 (br, 1H, OH), 4.90-4.93 (d, *J* = 7.56 Hz, 0.60H, CH), 5.30 (s, 0.40H, CH), 7.50-7.53 (d, *J* = 8.88 Hz, 2H, ArH), 8.19-8.22 (d, *J* = 8.55 Hz, 2H, ArH).

(*S*)-2-((*R*)-Hydroxy(2-nitrophenyl)methyl)cyclohexanone (**6e**)[3]

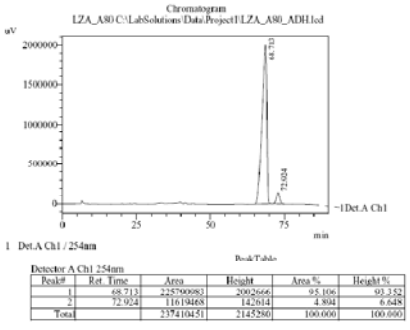


6e

Compound **6e**: a yellow oil; Chiralcel AD-H column, λ = 254 nm, *i*-PrOH:Hexane = 5:95, 0.5 mL/min, t_R = 68.71 min. (major), t_R = 72.92 min. (minor); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.56-2.12 (m, 6H, $3CH_2$), 2.28-2.47 (m, 2H, CH_2), 2.71-2.79 (m, 1H, CH), 5.43-5.45 (d, *J* = 6.9 Hz, 1H, CH), 7.40-7.45 (m, 1H, ArH), 7.61-7.66 (m, 1H, ArH), 7.75-7.82 (m, 1H, ArH), 7.83-7.85 (m, 1H, ArH).

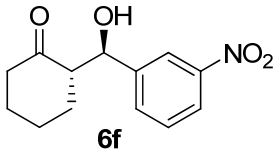


(racemic **6e**)



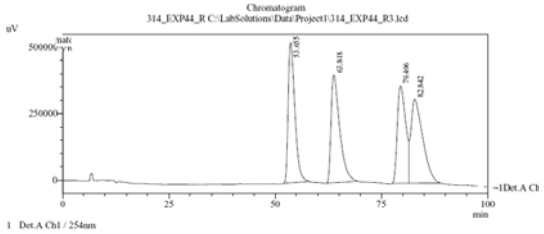
(enatiometric enriched **6e**)

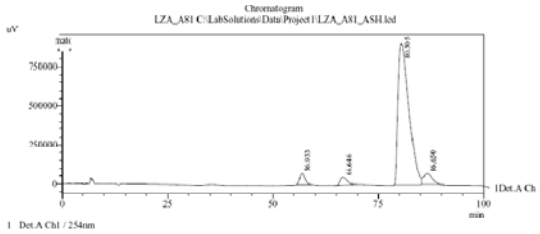
(*S*)-2-((*R*)-Hydroxy(3-nitrophenyl)methyl)cyclohexanone (**6f**)[3]



6f

Compound **6f**: a yellow oil; Chiralcel AS-H column, λ = 254 nm, *i*-PrOH:Hexane = 5:95, 0.5 mL/min, t_R = 80.51 min. (major), t_R = 86.65 min. (minor); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.36-2.10 (m, 6H, $3CH_2$), 2.30-2.61 (m, 3H, CH_2, CH), 4.87-4.90 (d, *J* = 8.55 Hz, 1H, CH), 7.49-7.54 (m, 1H, ArH), 7.65-7.67 (d, *J* = 6.9 Hz, 1H, ArH), 8.14-8.20 (m, 2H, ArH).





PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	53.655	57833568	527224	25.497	32.677
2	63.818	57378120	404462	25.296	25.068
3	79.496	50278541	366245	22.166	22.700
4	82.842	61335669	315511	27.041	19.555
Total		226825897	1613441	100.000	100.000

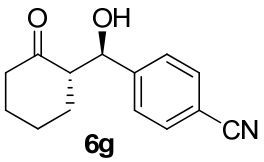
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	56.033	6347877	71507	3.452	6.511
2	66.646	5628325	50617	3.061	4.609
3	80.505	162249745	908095	88.227	82.687
4	86.650	5695361	68068	3.260	6.193
Total		183893307	1098227	100.000	100.000

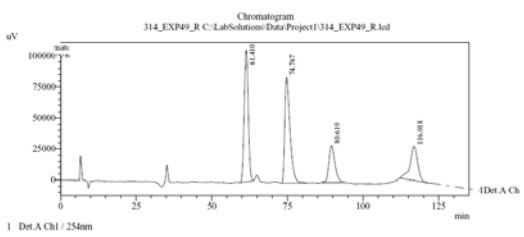
(racemic **6f**) (enatiometric enriched **6f**)

(*S*)-2-((*R*)-Hydroxy(4-cyanophenyl)methyl)cyclohexanone (**6g**)[4]



6g

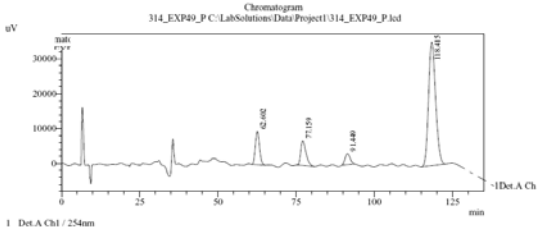
Compound **6g**: a yellow solid; Chiralcel AS-H column, λ = 254 nm, *i*-PrOH:Hexane = 5:95, 0.5 mL/min, t_R = 91.45 min. (minor), t_R = 118.42 min. (major); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.32-2.14 (m, 6H, $3CH_2$), 2.30-2.61 (m, 3H, CH_2, CH), 4.82-4.85 (d, *J* = 8.4 Hz, 1H, CH), 7.43-7.46 (m, 2H, ArH), 7.63-7.66 (m, 2H, ArH).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	61.410	9891586	106133	34.115	42.795
2	74.767	10180718	85000	35.112	34.274
3	89.619	4078640	29491	14.067	11.891
4	116.918	4844144	27379	16.707	11.040
Total		28995087	248004	100.000	100.000



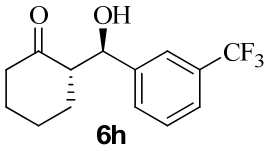
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	62.602	895713	9520	11.680	17.221
2	77.159	838271	7067	10.931	12.783
3	91.449	359201	3124	4.684	5.652
4	118.415	5575708	35569	72.706	64.344
Total		7668893	55279	100.000	100.000

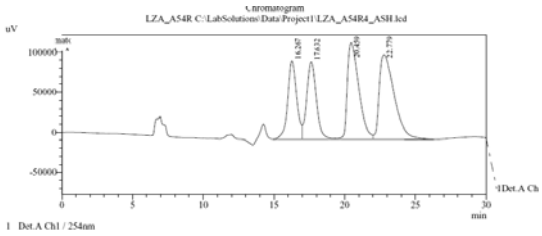
(racemic **6g**) (enatiometric enriched **6g**)

(*S*)-2-((*R*)-(3-(Trifluoromethyl)phenyl)(hydroxy)methyl)cyclohexanone (**6h**)[5]



6h

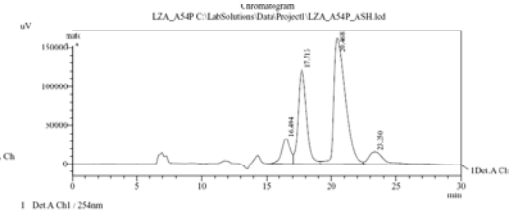
Compound **6h**: a white solid; Chiralcel AS-H column, λ = 254 nm, *i*-PrOH:Hexane = 5:95, 0.5 mL/min, t_R = 20.47 min. (major), t_R = 23.35 min. (minor); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.32-2.15 (m, 6H, $3CH_2$), 2.32-2.65 (m, 3H, CH_2, CH), 4.84-4.87 (d, *J* = 8.52 Hz, 1H, CH), 7.47-7.60 (m, 4H, ArH).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.267	4312648	97445	18.414	23.238
2	17.632	4553154	96103	19.441	22.918
3	20.459	6783929	120229	28.966	28.672
4	22.779	7709952	105553	33.180	25.172
Total		23429682	419330	100.000	100.000



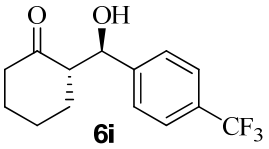
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.494	1479136	32222	8.048	9.917
2	17.713	5569148	121137	30.302	36.530
3	20.498	9897679	161692	53.854	48.680
4	23.350	1432611	16201	7.795	4.874
Total		18378523	332153	100.000	100.000

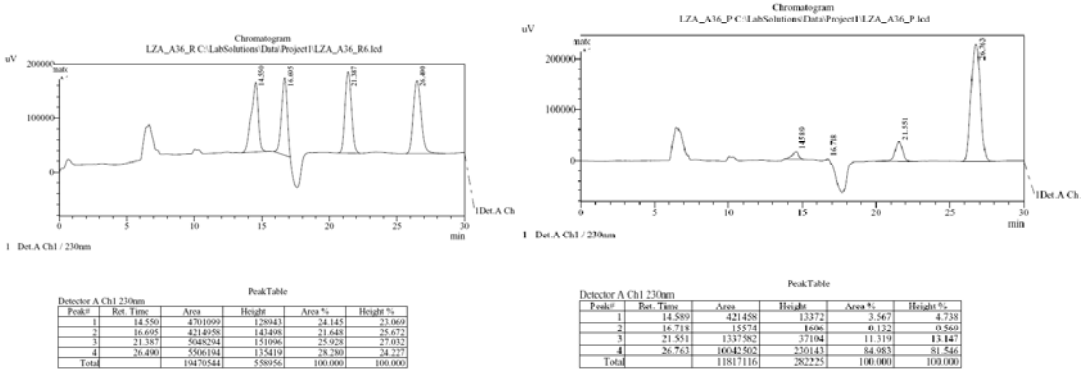
(racemic **6h**) (enatiometric enriched **6h**)

(*S*)-2-((*R*)-(4-(Trifluoromethyl)phenyl)(hydroxy)methyl)cyclohexanone (**6i**)[4]



6i

Compound **6i**: a white solid; Chiralcel AD-H column, λ = 230 nm, *i*-PrOH:Hexane = 10:90, 0.5 mL/min, t_R = 21.55 min. (minor), t_R = 26.76 min. (major); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.39-2.21 (m, 6H, $3CH_2$), 2.34-2.60 (m, 3H, CH_2, CH), 4.86-4.88 (d, *J* = 8.55 Hz,1H, CH), 7.33-7.57 (m, 1H, ArH), 7.58-7.83 (m, 1H, ArH), 8.02-8.18 (m, 1H, ArH).



PeakTable
Detector A Ch1 230nm

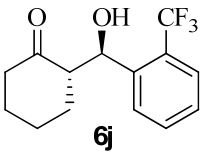
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.550	4701099	128943	24.145	23.069
2	16.695	4214958	143498	21.648	25.672
3	21.387	5048294	151996	25.928	27.032
4	26.490	5506194	135419	28.280	24.227
Total		19470544	558856	100.000	100.000

PeakTable
Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.589	421458	13372	3.567	4.738
2	16.718	15574	1606	0.132	0.569
3	21.551	1337582	37104	11.319	13.147
4	26.763	10042502	230143	84.983	81.546
Total		11817116	282225	100.000	100.000

(racemic **6i**) (enatiometric enriched **6i**)

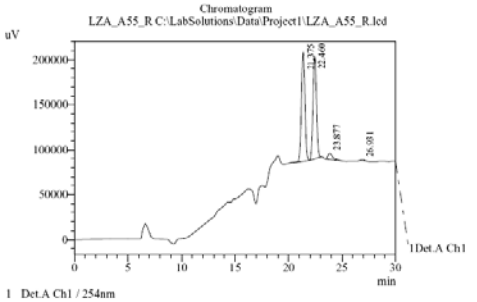
(*S*)-2-((*R*)-(2-(Trifluoromethyl)phenyl)(hydroxy)methyl)cyclohexanone (**6j**)



6j

Compound **6j**: a colorless oil; Chiralcel AD-H column, λ = 254 nm, *i*-PrOH:Hexane = 15:85, 0.5 mL/min, t_R = 19.92 min. (major), t_R = 20.91 min. (minor); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.37-2.08 (m, 6H, $3CH_2$), 2.36-2.50 (m, 2H, CH_2), 2.73-2.75 (m, 1H, CH), 5.28-5.32 (d, *J* = 7.41 Hz, 1H, CH), 7.39-7.41 (m, 1H, ArH), 7.60-7.70 (m, 3H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 214.8, 139.9, 132.4, 128.3, 127.9, 125.5, 125.4,

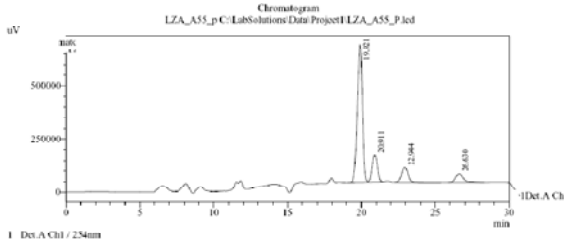
122.9, 69.1, 57.7, 42.6, 30.3, 27.7, 24.9; MS (ESI) calcd for $[C_{14}H_{15}O_2F_3Na]^+$ M: 295.1; found *m/z* 295.0; HRMS (ESI) calcd for $[C_{14}H_{15}O_2F_3Na]^+$ M: 295.0916; found *m/z* 295.0921.



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.375	2809753	121528	47.583	48.924
2	22.460	2575908	113665	43.623	45.759
3	23.877	206982	6745	3.505	2.716
4	26.931	27113	1112	0.461	0.448
5	43.805	285135	5350	4.829	2.154
Total		5904990	248400	100.000	100.000



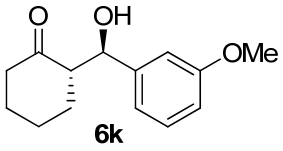
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.921	15399696	646452	69.593	73.207
2	20.911	3162246	127247	14.291	14.410
3	12.944	2108366	69384	9.528	7.857
4	26.830	1457900	39961	6.588	4.525
Total		22128208	883043	100.000	100.000

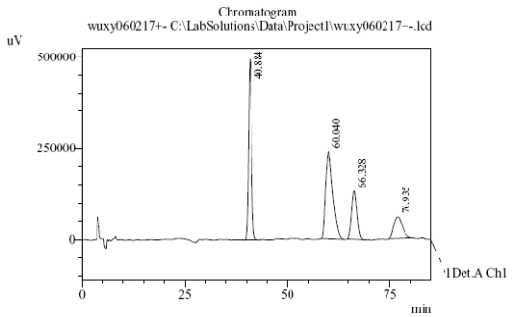
(racemic **6j**) (enatiometric enriched **6j**)

(*S*)-2-((*R*)-Hydroxy(3-methoxyphenyl)methyl)cyclohexanone (**6k**)[6]



6k

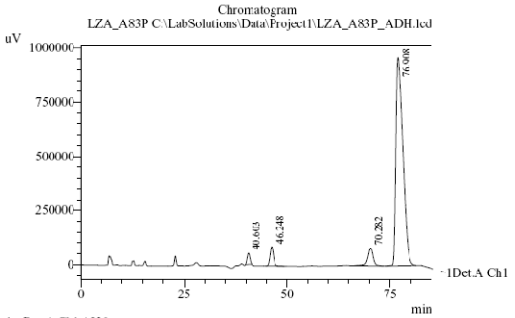
Compound **6k**: a colorless oil; Chiralcel AD-H column, λ = 230 nm, *i*-PrOH:Hexane = 5:95, 0.5 mL/min, t_R = 70.28 min. (minor), t_R = 76.91 min. (major); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.28-2.12 (m, 6H, $3CH_2$), 2.31-2.62 (m, 3H, CH_2, CH), 3.82 (s, 3H, OCH_3), 4.76-4.79 (d, *J* = 8.7 Hz, 1H, CH), 6.82-6.91 (m, 3H, ArH), 7.23-7.29 (m, 1H, ArH).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.884	25983363	403816	34.158	53.474
2	60.040	30244516	240383	39.760	26.030
3	66.328	11591788	131960	15.238	14.293
4	76.935	8248065	57284	10.843	6.203
Total		76067231	923472	100.000	100.000



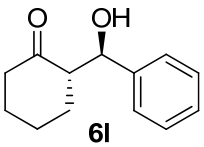
PeakTable

Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.603	2368666	51425	1.853	4.340
2	46.248	5200714	89246	4.069	7.533
3	70.282	7445946	82318	5.826	6.948
4	76.908	112790155	961823	88.251	81.179
Total		127805679	1184812	100.000	100.000

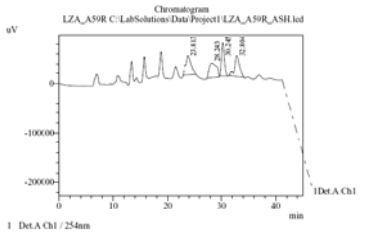
(racemic **6k**) (enatiometric enriched **6k**)

(*S*)-2-((*R*)-Hydroxy(phenyl)methyl)cyclohexanone (**6l**)[3]



6l

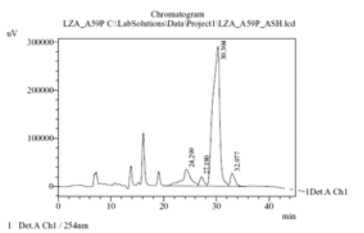
Compound **6l**: a colorless oil; Chiralcel AS-H column, λ = 254 nm, *i*-PrOH:Hexane = 5:95, 0.5 mL/min, t_R = 30.30 min. (major), t_R = 32.98 min. (minor); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.26-2.09 (m, 6H, $3CH_2$), 2.29-2.62 (m, 3H, CH_2, CH), 4.77-4.80 (d, *J* = 8.7 Hz, 0.51H, CH), 5.38-5.39 (d, *J* = 2.13 Hz, 0.49H, CH), 7.28-7.34 (m, 5H, ArH).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.813	2856530	39686	26.090	22.010
2	28.243	2832230	29526	25.877	16.375
3	30.245	2550037	68132	23.299	37.786
4	32.804	2707849	42067	24.733	23.329
Total		10948646	180312	100.000	100.000



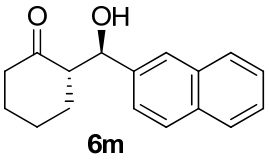
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.299	4035485	34691	12.112	9.336
2	27.180	1075750	19457	3.229	5.236
3	30.304	26691960	296854	79.842	78.166
4	32.977	1605091	26991	4.817	7.263
Total		33318286	376125	100.000	100.000

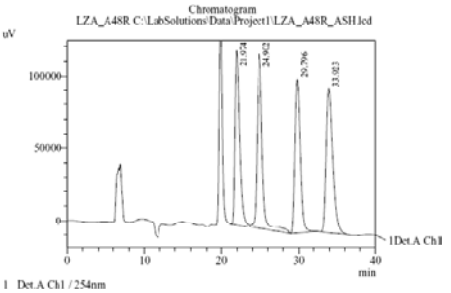
(racemic **6l**) (enatiometric enriched **6l**)

(*S*)-2-((*R*)-Hydroxy(naphthalen-3-yl)methyl)cyclohexanone (**6m**)[7]



6m

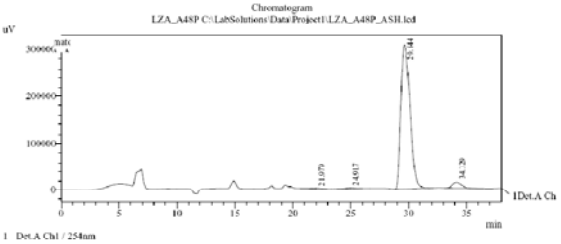
Compound **6m**: a white solid; Chiralcel AS-H column, λ = 254 nm, *i*-PrOH:Hexane = 10:90, 0.5 mL/min, t_R = 21.98 min. (minor), t_R = 29.64 min. (major); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.32-2.10 (m, 6H, $3CH_2$), 2.32-2.53 (m, 2H, CH_2), 2.68-2.76 (m, 1H, CH), 4.95-4.98 (d, *J* = 8.7 Hz, 1H, CH), 7.46-7.49 (m, 3H, ArH), 7.75 (s, 1H, ArH), 7.81-7.86 (m, 3H, ArH).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.974	5028092	120607	22.988	26.934
2	24.902	5777446	120503	26.414	26.910
3	29.796	5132399	106648	23.465	23.816
4	33.923	5934526	100038	27.132	22.340
Total		21872463	447796	100.000	100.000



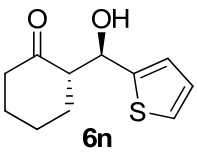
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.979	91438	1516	0.516	0.464
2	24.917	117680	2498	0.635	0.799
3	29.644	16793751	308809	94.692	94.626
4	34.129	737290	13415	4.157	4.111
Total		17735159	326348	100.000	100.000

(racemic **6m**) (enatiometric enriched **6m**)

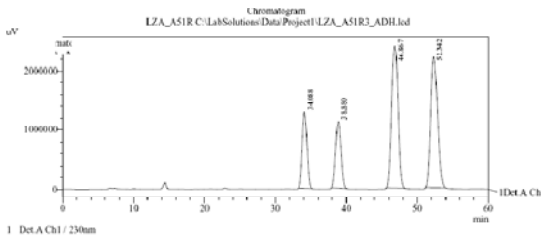
(S)-2-((*R*)-Hydroxy(thiophen-2-yl)methyl)cyclohexanone (**6n**)



6n

Compound **6n**: a colorless oil; Chiralcel AD-H column, λ = 230 nm, *i*-PrOH:Hexane = 5:95, 0.5 mL/min, t_R = 47.27 min. (major), t_R = 52.95 min. (minor); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.60-1.88 (m, 6H, $3CH_2$), 2.45-2.65 (m, 3H, CH_2, CH), 5.05-5.08 (d, *J* = 8.37 Hz, 0.73H, CH), 5.52-5.53 (d, *J* = 2.6 Hz, 0.27H, CH), 6.93-6.95

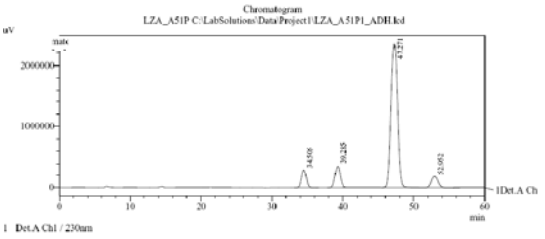
(m, 2H, ArH), 7.20-7.26 (m, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 214.5, 133.5, 127.6, 126.3, 125.1, 70.8, 57.9, 42.6, 30.9, 27.7, 24.7; MS (ESI) calcd for $[C_{11}H_{14}O_2SNa]^+$ M: 233.1; found *m/z* 233.0; HRMS (ESI) calcd for $[C_{11}H_{14}O_2SNa]^+$ M: 223.0607; found *m/z* 223.0617.



PeakTable

Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.088	61703136	1278080	14.521	18.260
2	38.880	60135595	1120035	14.147	16.031
3	46.867	153664276	2398115	36.164	34.262
4	52.342	149429893	2201054	35.167	31.447
Total		424910884	6999284	100.000	100.000



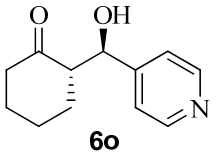
PeakTable

Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.505	14048919	290084	7.127	9.122
2	39.285	18977310	356064	9.627	11.197
3	47.271	151961761	2340563	77.092	73.886
4	52.952	12128472	184280	6.153	5.795
Total		197117561	3180001	100.000	100.000

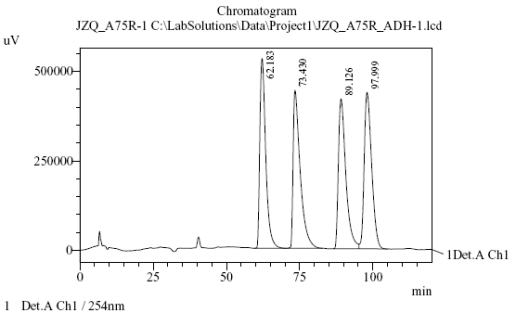
(racemic **6n**) (enatiometric enriched **6n**)

(*S*)-2-((*R*)-Hydroxy(pyridin-4-yl)methyl)cyclohexanone (**6o**)[7]



6o

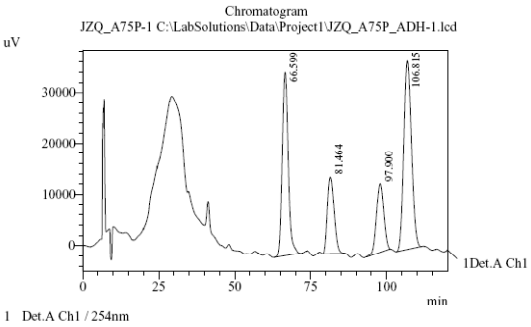
Compound **6o**: a white solid; Chiralcel AD-H column, λ = 254 nm, *i*-PrOH:Hexane = 5:95, 0.5 mL/min, t_R = 97.90 min. (minor), t_R = 106.82 min. (major); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.41-2.09 (m, 6H, $3CH_2$), 2.34-2.59 (m, 3H, CH_2, CH), 4.77-4.79 (d, *J* = 8.04 Hz, 0.6H, CH), 5.37-5.38 (d, *J* = 1.8 Hz, 0.4H, CH), 7.25-7.29 (m, 2H, ArH), 8.56-8.59 (m, 2H, ArH).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	62.183	74562909	530355	24.819	29.025
2	73.430	74352167	441251	24.749	24.148
3	89.126	74067219	418550	24.654	22.906
4	97.999	77439789	437093	25.777	23.921
Total		300422084	1827249	100.000	100.000



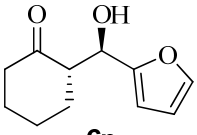
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	66.599	4937855	35887	30.813	35.494
2	81.464	2323625	14897	14.500	14.734
3	97.900	2254961	13377	14.071	13.231
4	106.815	6508860	36945	40.616	36.541
Total		16025301	101106	100.000	100.000

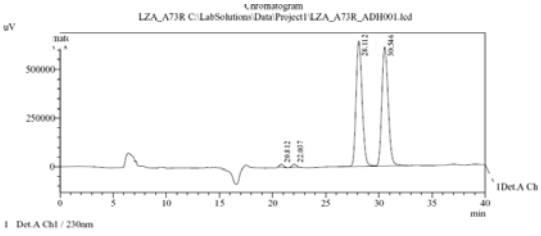
(racemic **6o**) (enatiometric enriched **6o**)

(*S*)-2-((*R*)-(Furan-2-yl)(hydroxy)methyl)cyclohexanone (**6p**)[7]



6p

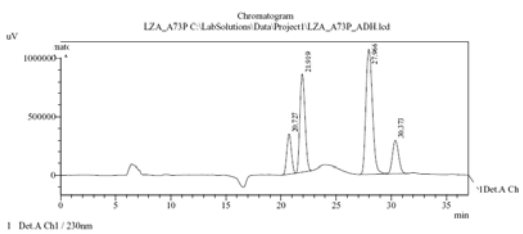
Compound **6p**: a colorless oil; Chiralcel AD-H column, λ = 230 nm, *i*-PrOH:Hexane = 10:90, 0.5 mL/min, t_R = 27.97 min. (major), t_R = 30.37 min. (minor); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.25-2.10 (m, 6H, $3CH_2$), 2.44-2.45 (m, 2H, CH_2), 2.83-3.03 (m, 1H, CH), 4.81-4.84 (d, *J* = 8.22 Hz, 0.6H, CH), 5.27-5.29 (d, *J* = 6.09 Hz, 0.4H, CH), 6.27-6.33 (m, 2H, CH), 7.34-7.38 (m, 1H, CH).



PeakTable

Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.812	375705	15647	0.722	1.216
2	22.037	440854	16614	0.847	1.291
3	28.112	25715834	644438	49.394	50.068
4	30.546	25530054	610426	49.037	47.426
Total		52062446	1287126	100.000	100.000



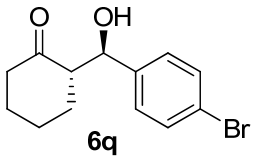
PeakTable

Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.727	9893329	339419	10.695	13.440
2	21.919	27132579	835589	29.332	33.078
3	27.966	44153651	1064153	47.729	42.138
4	30.373	11121874	286491	12.024	11.344
Total		92501134	2525413	100.000	100.000

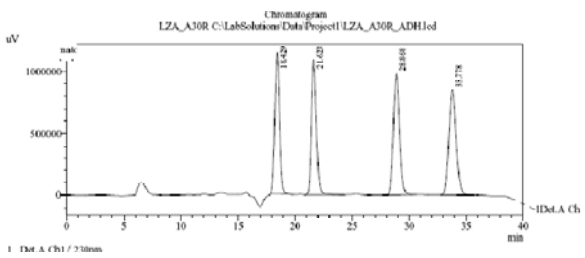
(racemic **6p**) (enatiometric enriched **6p**)

(*S*)-2-((*R*)-(4-Bromophenyl)(hydroxy)methyl)cyclohexanone (**6q**)[7]



6q

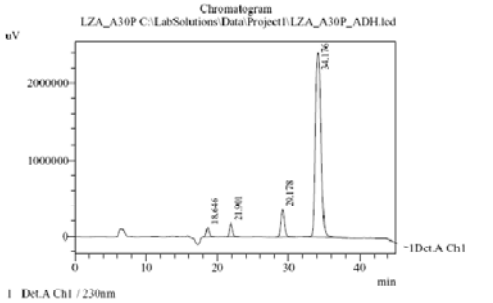
Compound **6-q**: a yellow solid; Chiralcel AD-H column, λ = 230 nm, *i*-PrOH: Hexane = 10:90, 0.5 mL/min, t_R = 29.18 min. (minor), t_R = 34.18 min. (major); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.27-2.08 (m, 6H, $3CH_2$), 2.33-2.55 (m, 3H, CH_2, CH), 4.73-4.76 (d, *J* = 8.7 Hz, 0.54H, CH), 5.33-5.34 (d, *J* = 1.95 Hz, 0.46H, CH), 7.18-7.21 (m, 2H, ArH), 7.45-7.48 (m, 2H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 215.2, 140.0, 131.5, 128.6, 121.7, 74.2, 57.3, 42.7, 30.8, 27.7, 24.7.



PeakTable

Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.429	33372044	1143292	23.552	28.101
2	21.623	33551557	1090266	23.678	26.798
3	28.868	36878429	984232	26.026	24.188
4	33.778	37894895	852716	26.744	20.963
Total		141696826	4068527	100.000	100.000



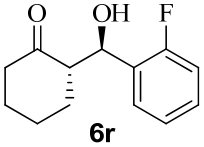
PeakTable

Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.646	3374439	122420	2.128	3.992
2	21.901	5080333	174430	3.204	5.688
3	29.178	13336079	333905	8.409	11.606
4	34.176	136795519	2413878	86.259	78.714
Total		158586370	3066632	100.000	100.000

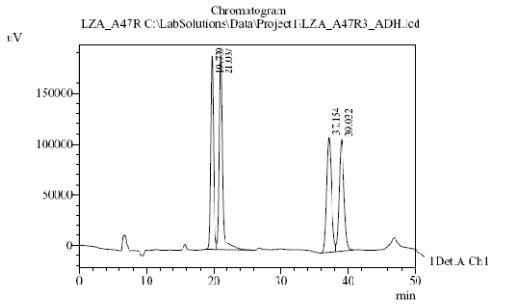
(racemic **6q**) (enatiometric enriched **6q**)

(*S*)-2-((*R*)-(2-Fluorophenyl)(hydroxy)methyl)cyclohexanone (**6r**)[8]



6r

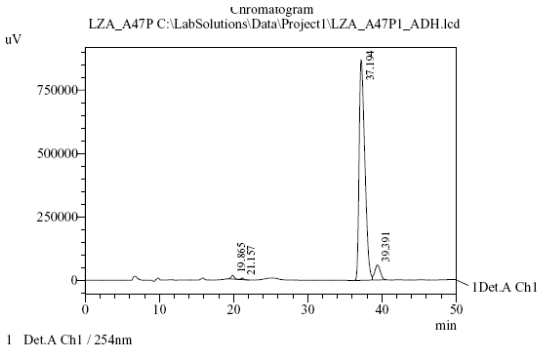
Compound **6r**: a colorless oil; Chiralcel AD-H column, λ = 254 nm, *i*-PrOH:Hexane = 5:95, 0.5 mL/min, t_R = 37.19 min. (major), t_R = 39.39 min. (minor); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.32-2.08 (m, 6H, $3CH_2$), 2.29-2.50 (m, 2H, CH_2), 2.63-2.72 (m, 1H, CH), 5.16-5.19 (d, *J* = 8.88 Hz, 1H, CH), 6.98-7.04 (m, 1H, ArH), 7.14-7.19 (m, 1H, ArH), 7.23-7.30 (m, 1H, ArH), 7.45-7.47 (m, 1H, ArH).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.739	5439907	189788	23.708	31.469
2	21.037	6269367	190996	27.283	31.674
3	37.154	5635045	112716	24.558	18.689
4	39.032	5610844	109692	24.452	18.188
Total		22946253	603192	100.000	100.000



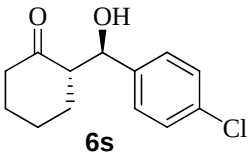
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.865	426854	14557	0.849	1.531
2	21.157	157183	6285	0.313	0.661
3	37.194	46600371	871061	92.660	91.589
4	39.391	3107612	59153	6.179	6.220
Total		50292020	951056	100.000	100.000

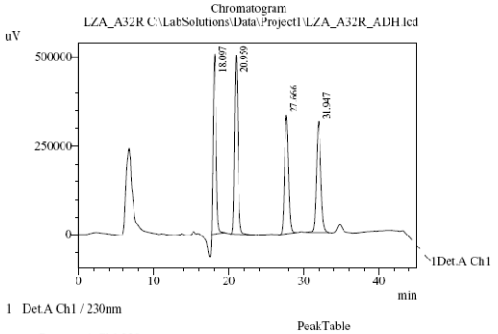
(racemic **6r**) (enatiometric enriched **6r**)

(*S*)-2-((*R*)-(4-Chlorophenyl)(hydroxy)methyl)cyclohexanone (**6s**)[3]



6s

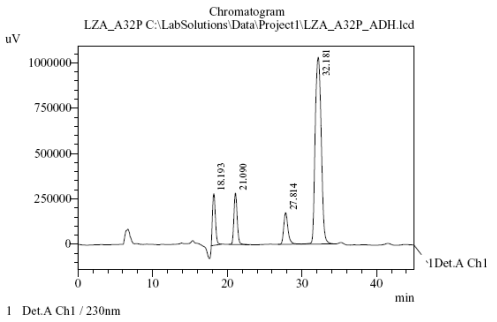
Compound **6s**: a white solid; Chiralcel AD-H column, λ = 230 nm, *i*-PrOH:Hexane = 10:90, 0.5 mL/min, t_R = 27.81 min. (minor), t_R = 32.18 min. (major); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.30-2.12 (m, 6H, $3CH_2$), 2.32-2.62 (m, 3H, CH_2, CH), 4.77-4.80 (d, *J* = 8.7 Hz, 1H, CH), 7.28-7.36 (m, 4H, ArH).



PeakTable

Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.097	14854376	507360	26.400	30.606
2	20.959	15714185	504589	27.928	30.439
3	27.666	12512632	333632	22.238	20.126
4	31.947	13185381	312130	23.434	18.829
Total		56266575	1657711	100.000	100.000



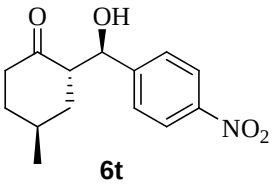
PeakTable

Detector A Ch1 230nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.193	7826777	284576	9.622	16.056
2	21.090	8702914	283844	10.699	16.015
3	27.814	6931725	173948	8.521	9.814
4	32.181	57883166	1029991	71.158	58.114
Total		81344582	1772359	100.000	100.000

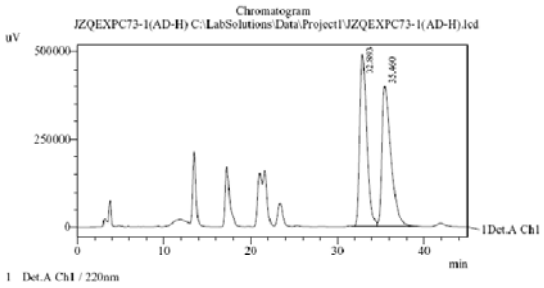
(racemic **6s**) (enatiometric enriched **6s**)

(2*S*)-2-((*R*)-Hydroxy(4-nitrophenyl)methyl)-4-methylcyclohexanone (**6t**)[9]



6t

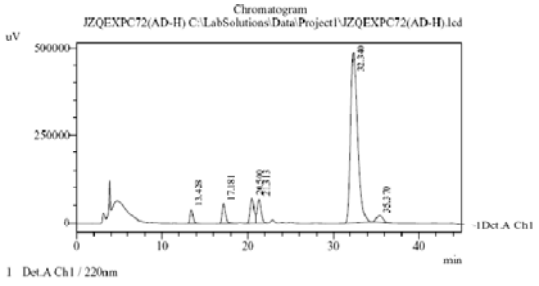
Compound **6t**: a yellow solid; Chiralcel AD-H column, λ = 220 nm, *i*-PrOH:Hexane = 10:90, 1.0 mL/min, t_R = 32.80 min. (major), t_R = 35.85 min. (minor); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.01-1.05 (m, 3H, CH_3), 1.25-1.33 (m, 2H, CH_2), 1.64-2.04 (m, 3H, CH_2, CH), 2.41-2.78 (m, 3H, CH_2, CH), 4.91-4.94 (d, *J* = 8.55 Hz, 0.79H, CH), 5.48 (s, 1H, CH), 7.48-7.51 (d, *J* = 8.73 Hz, 2H, ArH), 8.19-8.22 (d, *J* = 8.7 Hz, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 214.9, 148.4, 127.8, 126.6, 123.6, 74.1, 52.8, 38.1, 36.0, 32.9, 26.6, 18.2.



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.803	27408506	487839	49.408	55.120
2	35.460	28157757	397203	50.592	44.880
Total		55656263	885042	100.000	100.000



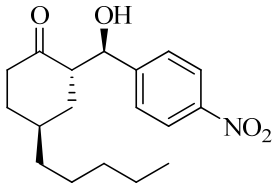
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.428	842733	38346	2.448	5.234
2	17.181	1573509	55022	4.570	7.511
3	20.500	2095553	69807	6.086	9.529
4	21.313	2217581	66966	6.441	9.141
5	32.340	26791835	485097	77.812	66.218
6	35.370	910364	17341	2.644	2.367
Total		34431576	732578	100.000	100.000

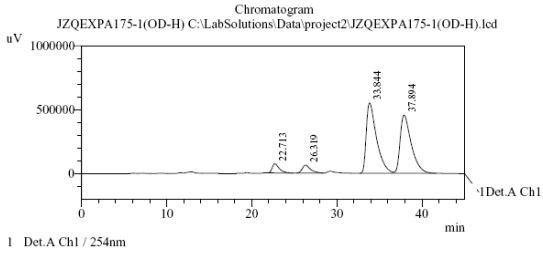
(racemic **6t**) (enatiometric enriched **6t**)

(2*S*)-2-((*R*)-Hydroxy(4-nitrophenyl)methyl)-4-pentylcyclohexanone (**6u**)



6u

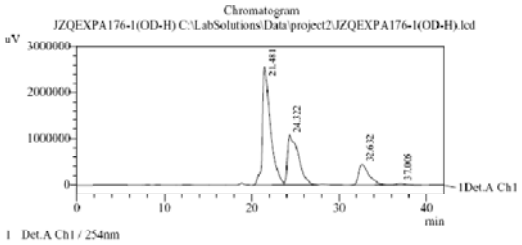
Compound **6u**: a yellow solid; Chiralcel OD-H column, λ = 254 nm, *i*-PrOH:Hexane = 10:90, 0.5 mL/min, t_R = 21.48 min. (major), t_R = 24.32 min. (minor); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 0.79-81 (m, 3H, CH_3), 1.18-1.33 (m, 8H, $4CH_2$), 1.42-1.63 (m, 5H, CH, $2CH_2$), 2.43-2.44 (m, 2H, CH_2), 2.64-2.65 (m, 1H, CH), 4.85-4.87 (d, *J* = 8.2 Hz, 1H, CH), 7.46-7.48 (d, *J* = 8.9 Hz, 2H, ArH) , 8.17-8.19 (d, *J* = 8.9 Hz, 2H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 214.1, 148.3, 146.9, 126.5, 123.3, 73.9, 56.0, 41.8, 36.2, 31.9, 31.8, 31.7, 26.6, 22.4, 13.9; MS (ESI) calcd for $[C_{18}H_{24}NO_4]^-$ M: 318.2; found *m/z* 318.2; HRMS (ESI) calcd for $[C_{18}H_{24}NO_4]^-$ M: 318.1711; found *m/z* 318.1714.



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.713	4178389	71725	4.356	6.295
2	26.319	4185625	62578	4.364	5.493
3	33.844	46077614	550190	48.038	48.290
4	37.894	41477546	454842	43.242	39.922
Total		95919174	1139336	100.000	100.000



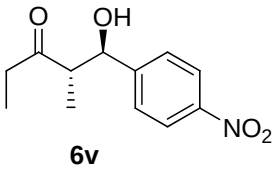
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.481	161910981	2552606	55.499	62.725
2	24.322	91742109	1054310	31.447	25.907
3	32.632	35420738	430016	12.141	10.567
4	37.005	2660761	32608	0.912	0.801
Total		291734589	4069540	100.000	100.000

(racemic **6u**) (enatiometric enriched **6u**)

(1*R*,2*S*)-1-Hydroxy-2-methyl-1-(4-nitrophenyl)pentan-3-one (**6v**)[10]



6v

Compound **6v**: a yellow solid; Chiralcel D-OJ-H column, λ = 220 nm, *i*-PrOH:Hexane = 10:90, 0.5 mL/min, t_R = 72.62 min. (major), t_R = 94.02 min. (minor); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 1.02-1.06 (m, 6H, $2CH_3$), 2.46-2.58 (m, 2H, CH_2), 3.35-3.36 (d, *J* = 5.0 Hz, 0.21H, CH), 3.56-3.57 (d, *J* = 2.55 Hz, 0.79H, CH), 4.87-4.89 (m, 0.22H, CH), 5.22 (s, 0.78H, CH), 7.49-7.51 (d, *J* = 8.85 Hz, 2H, ArH), 8.18-8.21 (d, *J* = 8.85 Hz, 2H, ArH).

C. DFT Calculations

The total energies and atomic coordinates of all optimized structures (B3LYP/6-31G**).

enam1 (-919.85139)				**enam2 (-919.85120)**			
N	-1.120013	0.641660	-0.496470	N	-1.014303	0.348673	-0.165128
C	-0.704157	1.633098	0.515180	C	-0.643802	1.517878	0.635297

C	-0.336459	2.957531	-0.191928	C	-0.435235	2.758165	-0.264128
O	0.269257	3.852254	0.355825	O	-0.046241	3.820255	0.169015
C	-2.198234	-0.254218	-0.222506	C	-2.288698	-0.264766	-0.066210
O	-0.778062	3.038387	-1.452924	O	-0.713128	2.555043	-1.557884
H	-0.300768	0.122133	-0.807527	H	-0.259800	-0.326539	-0.228255
H	-1.572676	1.872155	1.138038	H	-1.463635	1.765879	1.317456
C	0.438708	1.168369	1.447058	C	0.622848	1.288796	1.497303
C	1.691158	0.755870	0.720763	C	1.828459	0.854815	0.710891
H	0.068170	0.334953	2.052984	H	0.386812	0.544698	2.265638
H	0.649236	1.996652	2.129605	H	0.822236	2.233035	2.011004
C	2.627531	1.596186	0.163115	C	2.685255	1.671292	0.011210
C	2.143162	-0.589655	0.452184	C	2.286695	-0.497228	0.492533
H	2.647656	2.676236	0.148862	H	2.674828	2.747857	-0.083221
N	3.627111	0.856045	-0.434761	N	3.644216	0.910611	-0.627172
C	3.362343	-0.487775	-0.275871	C	3.429048	-0.423343	-0.354148
H	4.427349	1.242418	-0.908068	H	4.388253	1.278171	-1.197316
C	1.652137	-1.870751	0.767817	C	1.855504	-1.762436	0.935591
C	4.079912	-1.612031	-0.697373	C	4.129600	-1.561668	-0.765671
H	5.007985	-1.513168	-1.253299	H	4.999486	-1.486018	-1.411907
C	3.563400	-2.861640	-0.376683	C	3.672891	-2.795514	-0.317305
H	4.096265	-3.754852	-0.688421	H	4.194657	-3.698550	-0.619198
C	2.362221	-2.989523	0.350813	C	2.548272	-2.895294	0.526938
H	0.731517	-1.984683	1.333158	H	1.000146	-1.852852	1.600426
H	1.991057	-3.981276	0.591566	H	2.224577	-3.874687	0.866195
C	-3.179259	-2.574515	-0.246119	C	-4.765823	-0.295715	0.374185

C	-4.552707	-1.896939	-0.352749	C	-3.581135	-2.444875	-0.199921
C	-3.544482	0.387661	0.034224	C	-4.816747	-1.579086	-0.465348
C	-2.044590	-1.583922	-0.330817	C	-2.298703	-1.691582	-0.576349
H	-3.069139	-3.329797	-1.035464	C	-3.404007	0.357261	0.353120
H	-5.343795	-2.593571	-0.053838	H	-5.055975	-0.522393	1.412474
H	-3.459008	1.192434	0.774715	H	-3.547206	-2.710118	0.864910
H	-3.876529	0.878159	-0.892820	H	-4.848928	-1.316379	-1.531062
H	-1.049233	-1.985211	-0.516969	H	-2.175394	-1.679331	-1.669404
H	-3.111778	-3.131840	0.701313	H	-1.420733	-2.224624	-0.184944
H	-4.745668	-1.627912	-1.399719	H	-3.361822	1.391637	0.683423
H	-1.177692	2.150988	-1.626500	H	-5.518709	0.416298	0.011677
C	-4.594666	-0.629144	0.505820	H	-3.634000	-3.385933	-0.758485
H	-5.588778	-0.169816	0.477021	H	-5.733911	-2.138367	-0.248829
H	-4.399523	-0.894686	1.553201	H	-0.951859	1.600635	-1.611457

TS1 (-1469.93379)

N	2.011208	0.956266	0.684124
C	3.380555	0.918936	0.173704
C	3.497114	1.169726	-1.365799
O	4.623736	1.279751	-1.814501
C	1.236505	2.021452	0.842819
O	2.401112	1.269846	-2.076747
H	1.515540	0.067139	0.621597
H	3.953427	1.724825	0.639482
C	4.049319	-0.429844	0.537853

prod1 (-1469.94838)

N	-2.008751	-1.123174	0.561506
C	-3.320864	-1.325612	-0.034183
C	-3.140228	-1.604513	-1.622646
O	-4.182135	-1.460934	-2.261944
C	-1.071077	-2.005407	0.749431
O	-1.982867	-1.968775	-1.978903
H	-1.696959	-0.150868	0.510140
H	-3.769679	-2.233900	0.377672
C	-4.230263	-0.112929	0.231728

C	3.292997	-1.621735	0.022775	C	-3.598008	1.186695	-0.185064
H	4.157025	-0.488344	1.626528	H	-4.511894	-0.076244	1.290561
H	5.054641	-0.388789	0.111779	H	-5.135254	-0.303340	-0.348474
C	3.366002	-2.148033	-1.245366	C	-3.531545	1.681356	-1.466942
C	2.272862	-2.372602	0.716751	C	-2.860691	2.109967	0.646553
H	3.997250	-1.852654	-2.071547	H	-3.936897	1.256956	-2.374188
N	2.461920	-3.179782	-1.378910	N	-2.813382	2.857934	-1.479124
C	1.766833	-3.337571	-0.199570	C	-2.377530	3.146276	-0.203819
H	2.302294	-3.701420	-2.225282	H	-2.603312	3.396297	-2.303844
C	1.732874	-2.326236	2.016441	C	-2.555841	2.167004	2.020491
C	0.748891	-4.232831	0.144051	C	-1.609970	4.211292	0.278068
H	0.374515	-4.962024	-0.568566	H	-1.250908	4.993118	-0.385054
C	0.230968	-4.155060	1.432055	C	-1.321288	4.233836	1.637946
H	-0.560086	-4.836390	1.730066	H	-0.727226	5.047354	2.043049
C	0.719867	-3.212923	2.360313	C	-1.790770	3.222566	2.501024
H	2.106901	-1.611985	2.745481	H	-2.922248	1.401448	2.699912
H	0.299095	-3.186292	3.360961	H	-1.553656	3.276204	3.559432
C	-1.035866	2.965271	1.442815	C	1.215527	-2.416208	1.758541
C	0.948462	4.506710	1.285093	C	-0.424574	-4.316429	1.584209
C	1.809318	3.402391	0.652800	C	-1.345876	-3.478261	0.680674
C	-0.171311	1.803792	0.966994	C	0.334388	-1.498212	0.888049
H	-2.072250	2.800713	1.132158	H	2.260607	-2.111724	1.658024
H	1.315005	5.481198	0.946878	H	-0.563679	-5.374399	1.340804
H	-0.415394	0.855089	1.445733	H	0.301616	-0.495960	1.332015
H	-1.052863	2.974250	2.541949	H	0.949077	-2.254485	2.810938

H	1.072651	4.484703	2.375468	H	-0.728203	-4.192847	2.631876
H	1.498128	0.864658	-1.659458	H	-0.741555	-0.953964	-1.663145
C	-1.987091	0.692302	-0.664664	C	2.248068	-0.585851	-0.542527
C	-0.580390	1.213011	-0.822639	C	0.880351	-1.242002	-0.601794
O	0.308714	0.331894	-1.180523	O	0.003171	-0.399118	-1.287043
H	-0.563138	2.191079	-1.334451	H	0.974629	-2.218260	-1.097664
C	-4.563541	-0.312169	-0.412477	C	4.734661	0.642903	-0.405558
C	-3.096842	1.516463	-0.897943	C	3.421409	-1.341831	-0.660112
C	-2.192305	-0.653619	-0.322529	C	2.343591	0.802943	-0.369591
C	-3.478227	-1.161372	-0.188893	C	3.585022	1.424976	-0.298654
C	-4.392855	1.022241	-0.772586	C	4.673491	-0.735526	-0.590787
H	-2.947207	2.549060	-1.200690	H	3.358965	-2.414276	-0.821604
H	-1.328831	-1.295273	-0.184106	H	1.434982	1.392335	-0.317370
H	-3.658925	-2.195419	0.076261	H	3.680409	2.495495	-0.168214
H	-5.262324	1.641323	-0.953538	H	5.590694	-1.302958	-0.683711
N	-5.926809	-0.843018	-0.274539	N	6.051866	1.293453	-0.328538
O	-6.051863	-2.027078	0.040000	O	6.078679	2.513935	-0.171046
O	-6.865922	-0.072631	-0.478804	O	7.049663	0.578419	-0.423050
H	2.831076	3.443031	1.043181	H	-2.397366	-3.679052	0.903010
H	1.898096	3.562909	-0.432601	H	-1.211075	-3.748826	-0.376543
C	-0.532538	4.325000	0.941524	C	1.042643	-3.905717	1.433204
H	-1.127483	5.129308	1.387224	H	1.672444	-4.503321	2.100775
H	-0.667201	4.400974	-0.145750	H	1.382516	-4.118393	0.411133

TS2 (-1469.92930) **prod2 (-1469.94416)**

N	1.119751	-0.039743	1.058754	N	1.328557	0.222356	1.221262
C	1.533645	1.235476	1.634141	C	1.780415	1.565089	1.548240
C	1.054258	2.477294	0.810457	C	1.021411	2.608417	0.570562
O	1.368440	3.568825	1.249337	O	1.578010	3.701633	0.479669
C	0.058695	-0.778953	1.332684	C	0.167342	-0.316272	1.458547
O	0.342011	2.295279	-0.272747	O	-0.055020	2.171189	0.070641
H	1.583981	-0.269816	0.178489	H	1.863345	-0.192789	0.454662
H	1.075094	1.344925	2.618835	H	1.459752	1.820811	2.561938
C	3.073501	1.285087	1.791240	C	3.310405	1.671218	1.429720
C	3.810627	1.092325	0.496244	C	3.831880	1.162107	0.113769
H	3.377292	0.525803	2.520224	H	3.790329	1.137943	2.258349
H	3.296773	2.263935	2.221800	H	3.531050	2.734412	1.544596
C	4.096928	2.070180	-0.427668	C	3.810669	1.837564	-1.084919
C	4.302682	-0.147818	-0.056876	C	4.382215	-0.144615	-0.164533
H	3.877525	3.127773	-0.389633	H	3.448577	2.834752	-1.290184
N	4.741027	1.516389	-1.512998	N	4.325695	1.037939	-2.082510
C	4.879097	0.157692	-1.321972	C	4.678402	-0.186889	-1.557291
H	5.028950	2.023292	-2.324013	H	4.386789	1.296145	-3.053960
C	4.320194	-1.483098	0.388503	C	4.655676	-1.282453	0.618851
C	5.457007	-0.820917	-2.136676	C	5.227367	-1.317320	-2.170533
H	5.890881	-0.568930	-3.099984	H	5.447081	-1.331351	-3.234167
C	5.453740	-2.129891	-1.670069	C	5.480339	-2.425134	-1.369999
H	5.893551	-2.913688	-2.279165	H	5.906125	-3.318759	-1.816080
C	4.892348	-2.457854	-0.418973	C	5.198450	-2.407685	0.011424
H	3.898590	-1.748678	1.354436	H	4.454570	-1.278902	1.687141

H	4.913254	-3.490155	-0.082482	H	5.415981	-3.288345	0.608524
C	-1.266955	-2.882044	0.793227	C	-1.078224	-2.532882	1.378432
C	-1.615574	-1.688122	2.989963	C	-1.469548	-0.909961	3.273898
C	-0.846301	-0.453346	2.490682	C	-0.775052	0.221795	2.490433
C	-0.283320	-1.792065	0.366891	C	-0.218363	-1.497884	0.618487
H	-1.773915	-3.283917	-0.091133	H	-1.559476	-3.200673	0.656462
H	-2.348564	-1.370624	3.738336	H	-2.214235	-0.467124	3.942530
H	-0.275106	-0.001339	3.306766	H	-0.261942	0.912248	3.163220
H	-1.559631	0.312557	2.151453	H	-1.522778	0.816918	1.951146
H	0.613261	-2.214385	-0.090265	H	0.714447	-1.984925	0.310887
H	-0.694536	-3.720343	1.213776	H	-0.400815	-3.163381	1.968283
H	-0.919147	-2.367588	3.498387	H	-0.734362	-1.417063	3.912466
H	0.242684	1.305241	-0.693775	H	0.011971	0.789293	-0.926669
H	-0.690853	-1.688510	-1.817014	H	-0.732243	-1.924520	-1.406425
C	-0.754949	-0.822232	-1.135380	C	-0.804929	-1.012567	-0.800928
O	0.161228	0.091308	-1.343289	O	0.063785	-0.090471	-1.386443
C	-2.208480	-0.399047	-1.025473	C	-2.276821	-0.607535	-0.819353
C	-4.896797	0.320294	-0.875240	C	-4.984838	0.037769	-0.915180
C	-3.213457	-1.268164	-1.481359	C	-3.243454	-1.590864	-1.088329
C	-2.583736	0.860278	-0.527542	C	-2.697385	0.719840	-0.632629
C	-3.924998	1.222428	-0.444880	C	-4.051764	1.044077	-0.677023
C	-4.558965	-0.923140	-1.405247	C	-4.599390	-1.283102	-1.129713
H	-2.936563	-2.223062	-1.918775	H	-2.931413	-2.612928	-1.283629
H	-1.824775	1.574786	-0.230163	H	-1.970894	1.508277	-0.464270
H	-4.228924	2.189503	-0.064128	H	-4.391767	2.062409	-0.535912

H	-5.341518	-1.585331	-1.753536	H	-5.351777	-2.033783	-1.335541
N	-6.314817	0.695010	-0.783107	N	-6.415598	0.377536	-0.954828
O	-6.586606	1.796600	-0.305275	O	-6.731056	1.550944	-0.760599
O	-7.149133	-0.117517	-1.184354	O	-7.213683	-0.534129	-1.175817
C	-2.299221	-2.418139	1.830941	C	-2.120449	-1.920772	2.325714
H	-2.855271	-3.284304	2.205476	H	-2.599050	-2.721369	2.900048
H	-3.032085	-1.752043	1.363061	H	-2.912256	-1.427091	1.753648

TS3 (-1469.92594)

N	1.404190	0.492069	-0.418231
C	1.490871	1.662229	0.467489
C	1.628048	2.941932	-0.424955
O	2.579709	3.689880	-0.286649
C	0.511864	-0.479417	-0.516471
O	0.677032	3.110680	-1.308271
H	2.247708	0.374016	-0.971904
H	0.544542	1.749691	1.004321
C	2.679202	1.498085	1.440241
C	3.946920	0.990920	0.802141
H	2.376283	0.807457	2.235124
H	2.846953	2.474309	1.901228
C	4.876898	1.727271	0.104872
C	4.422964	-0.374079	0.797388
H	4.863632	2.782123	-0.124059
N	5.899321	0.906400	-0.324491

prod3 (-1469.94025)

N	-1.487123	-0.217819	-0.160715
C	-1.576287	-1.468806	0.572565
C	-1.583519	-2.657963	-0.544869
O	-2.341387	-3.594711	-0.292374
C	-0.466778	0.496210	-0.528265
O	-0.796912	-2.448362	-1.506752
H	-2.378953	0.002099	-0.607381
H	-0.664228	-1.613236	1.156295
C	-2.833366	-1.482476	1.457907
C	-4.081262	-1.035669	0.740778
H	-2.671816	-0.856132	2.342828
H	-2.940279	-2.516374	1.792215
C	-4.831261	-1.784661	-0.138203
C	-4.720176	0.259003	0.821042
H	-4.655367	-2.797080	-0.471160
N	-5.895647	-1.038696	-0.598561

C	5.653344	-0.388912	0.081327	C	-5.859237	0.219152	-0.033146
H	6.702936	1.212551	-0.848409	H	-6.591649	-1.368015	-1.247614
C	3.938205	-1.584429	1.327460	C	-4.451017	1.445168	1.529369
C	6.391060	-1.560626	-0.116893	C	-6.713205	1.314845	-0.194526
H	7.328575	-1.551137	-0.665555	H	-7.578064	1.264223	-0.849861
C	5.882124	-2.739164	0.415849	C	-6.416570	2.471778	0.516523
H	6.431358	-3.666028	0.281384	H	-7.060793	3.339839	0.415249
C	4.667845	-2.750639	1.132612	C	-5.296813	2.535587	1.371091
H	3.009097	-1.607416	1.890983	H	-3.597173	1.506460	2.199137
H	4.303624	-3.687626	1.543551	H	-5.098735	3.452969	1.917553
C	-1.348890	-1.890049	0.411985	C	1.414856	1.812463	0.407569
C	0.334955	-2.932292	-1.146583	C	-0.123636	2.906510	-1.257494
C	-1.138950	-2.881998	-0.737395	C	1.321077	2.796133	-0.763410
C	0.823289	-1.535173	-1.554908	C	-0.683879	1.517045	-1.613167
C	-0.750498	-0.498229	0.162347	C	0.900127	0.380877	0.085864
H	-0.886021	-2.302797	1.319799	H	0.818887	2.204047	1.242581
H	0.944121	-3.297528	-0.310098	H	-0.748802	3.356428	-0.476072
H	-1.747122	-2.590676	-1.603420	H	1.970948	2.472144	-1.585565
H	0.318703	-1.232169	-2.484803	H	-0.162316	1.134825	-2.503480
H	1.897803	-1.541982	-1.767353	H	-1.745666	1.570295	-1.876162
H	-0.775970	0.113992	1.062164	H	0.824870	-0.169018	1.028232
H	-2.413520	-1.789335	0.637966	H	2.441911	1.736638	0.771826
H	0.492412	-3.625638	-1.979136	H	-0.196155	3.556831	-2.134924
H	-1.485061	-3.875879	-0.434102	H	1.687515	3.778795	-0.447733
H	-0.182283	2.524529	-1.097108	H	0.682316	-2.112293	-1.028613

C	-3.187496	0.415926	-0.471488	C	3.320831	-0.332951	-0.416641
C	-1.759001	0.703359	-0.881430	C	1.864190	-0.535785	-0.801902
O	-1.331265	1.895004	-0.591868	O	1.555636	-1.876583	-0.592214
H	-1.569168	0.317545	-1.902321	H	1.746799	-0.241766	-1.857453
C	-5.820333	-0.038835	0.282001	C	5.977650	0.014109	0.319616
C	-3.986364	-0.482744	-1.190850	C	4.175677	0.461169	-1.190873
C	-3.739628	1.100664	0.620684	C	3.830820	-0.970790	0.724134
C	-5.054542	0.874109	1.008783	C	5.157786	-0.798867	1.101816
C	-5.307817	-0.718214	-0.821056	C	5.508579	0.643444	-0.829980
H	-3.576951	-0.991867	-2.059110	H	3.804361	0.929908	-2.097650
H	-3.123698	1.829357	1.135736	H	3.182350	-1.626871	1.293300
H	-5.500811	1.390813	1.849167	H	5.569568	-1.283629	1.977938
H	-5.943305	-1.404224	-1.366585	H	6.184089	1.249912	-1.419736
N	-7.212268	-0.285227	0.685035	N	7.381843	0.205555	0.714164
O	-7.642554	0.326757	1.662869	O	7.771482	-0.361613	1.734575
O	-7.866301	-1.092686	0.023600	O	8.083101	0.925338	0.002671

TS4 (-1469.92480)

N	-0.940491	0.562611	-0.374984
C	-1.525446	1.778830	-0.959209
C	-1.126348	2.996679	-0.060060
O	-1.975178	3.619927	0.551673
C	-0.136781	-0.362342	-0.877460
O	0.156965	3.260484	-0.014154
H	-1.344329	0.350145	0.533214

prod4 (-1469.93983)

N	-1.140804	0.391415	-0.612087
C	-1.661547	1.704919	-0.959867
C	-1.123927	2.759464	0.148088
O	-1.953695	3.578221	0.541146
C	-0.088366	-0.267713	-0.997520
O	0.095450	2.605808	0.437889
H	-1.667427	-0.012262	0.164980

H	-1.062960	1.940612	-1.934712	H	-1.226728	2.025095	-1.910126
C	-3.058096	1.615223	-1.077565	C	-3.199169	1.650390	-1.025801
C	-3.722096	0.963069	0.108268	C	-3.831964	0.963761	0.156843
H	-3.265272	1.018420	-1.972785	H	-3.512179	1.154573	-1.951990
H	-3.472662	2.611598	-1.248867	H	-3.523895	2.691493	-1.074696
C	-4.077848	1.559343	1.296400	C	-4.046617	1.511396	1.401823
C	-4.112760	-0.424671	0.217273	C	-4.313369	-0.398481	0.222846
H	-3.931738	2.583618	1.603852	H	-3.794309	2.503047	1.747399
N	-4.668638	0.631210	2.128608	N	-4.637935	0.579406	2.227624
C	-4.705348	-0.596370	1.500095	C	-4.814290	-0.603631	1.540506
H	-5.020520	0.826347	3.051742	H	-4.894526	0.741527	3.187934
C	-4.025024	-1.538766	-0.638196	C	-4.375792	-1.464462	-0.694764
C	-5.197107	-1.829825	1.939627	C	-5.359385	-1.823682	1.952963
H	-5.646573	-1.940381	2.922359	H	-5.737016	-1.960345	2.962281
C	-5.091446	-2.910415	1.071967	C	-5.401539	-2.856597	1.023760
H	-5.464872	-3.881633	1.381880	H	-5.819694	-3.816215	1.311960
C	-4.512089	-2.765872	-0.205455	C	-4.915454	-2.678135	-0.287738
H	-3.589889	-1.441015	-1.629375	H	-4.015902	-1.338338	-1.712761
H	-4.453071	-3.629283	-0.861548	H	-4.971366	-3.504098	-0.990672
C	0.961474	-1.562193	-2.812424	C	1.091392	-1.119712	-3.037311
C	0.324157	-2.844529	-0.731507	C	0.493279	-2.724341	-1.190099
C	1.364011	-2.681770	-1.842409	C	1.533996	-2.360022	-2.252023
C	0.163986	-1.525438	0.039008	C	0.246966	-1.530167	-0.248524
C	0.513216	-0.250030	-2.151114	C	0.741170	0.133762	-2.182459
H	0.135508	-1.923892	-3.440031	H	0.199423	-1.383366	-3.620104

H	-0.644927	-3.137898	-1.154890	H	-0.451527	-3.010229	-1.669887
H	2.337291	-2.461164	-1.390694	H	2.502233	-2.187122	-1.770341
H	1.100361	-1.294440	0.565871	H	1.164905	-1.330306	0.319652
H	-0.619905	-1.608097	0.799781	H	-0.539361	-1.755477	0.479844
H	-0.044011	0.368483	-2.853169	H	0.135073	0.793146	-2.809864
H	1.784357	-1.347524	-3.505423	H	1.854974	-0.830014	-3.767518
H	0.617077	-3.634618	-0.032733	H	0.819816	-3.582788	-0.594951
H	1.479172	-3.618892	-2.397877	H	1.672040	-3.195665	-2.946879
H	0.712913	2.758508	-0.775986	H	1.076547	2.510231	-0.847948
H	2.289380	0.774613	-2.976235	H	2.540885	1.060347	-2.827437
C	1.866640	1.005787	-1.980205	C	1.993913	1.083167	-1.876186
O	1.317903	2.178646	-1.878645	O	1.580043	2.398991	-1.704261
C	2.847648	0.573313	-0.904252	C	2.958832	0.595805	-0.797380
C	4.698401	-0.178932	1.034910	C	4.777938	-0.264418	1.126904
C	3.930438	-0.258117	-1.230326	C	4.127867	-0.085927	-1.168080
C	2.730014	1.045396	0.413492	C	2.733233	0.864292	0.563848
C	3.647902	0.666983	1.388909	C	3.638969	0.431407	1.529071
C	4.859822	-0.643423	-0.268893	C	5.042438	-0.525781	-0.214730
H	4.056736	-0.594036	-2.255794	H	4.335527	-0.264321	-2.219663
H	1.927545	1.727357	0.671956	H	1.853958	1.424998	0.868630
H	3.572053	1.021181	2.409404	H	3.481377	0.630438	2.581764
H	5.702286	-1.280229	-0.507624	H	5.948952	-1.050414	-0.488764
N	5.668837	-0.584263	2.061616	N	5.732009	-0.730351	2.144983
O	6.592694	-1.322192	1.716818	O	6.732045	-1.335446	1.757259
O	5.498145	-0.167647	3.207526	O	5.471640	-0.493701	3.324280

cyclohexanone (-309.90369)

C	-1.160466	0.000000	0.064969
C	1.018467	1.265967	-0.282404
C	1.018468	-1.265967	-0.282403
C	1.791720	0.000000	0.111297
C	-0.392695	-1.287120	0.341755
C	-0.392695	1.287120	0.341755
O	-2.307259	0.000000	-0.340948
H	-0.990539	-2.130180	-0.014228
H	-0.297443	-1.383608	1.433758
H	1.567974	-2.164732	0.019045
H	0.927464	-1.308375	-1.375938
H	1.967040	0.000000	1.196586
H	2.779322	0.000000	-0.364089
H	1.567973	2.164733	0.019045
H	0.927463	1.308376	-1.375938
H	-0.990539	2.130180	-0.014226
H	-0.297441	1.383607	1.433759

p-nitrobenzaldehyde (-550.09551)

C	-1.036086	-1.111191	0.000000
C	1.275757	0.486131	0.000000
C	0.236662	-1.702311	0.000000
C	-1.162113	0.271690	0.000000
C	0.000000	1.045527	0.000000
C	1.385798	-0.901336	0.000000
C	0.367814	-3.183155	0.000000
O	-0.573828	-3.949476	0.000000
N	-0.127082	2.516828	0.000000
O	0.910312	3.177265	0.000000
O	-1.262269	2.988937	0.000000
H	1.414408	-3.557674	0.000000
H	2.367745	-1.366928	0.000000
H	2.142446	1.134558	0.000000
H	-1.908544	-1.755866	0.000000
H	-2.127192	0.762181	0.000000

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