Supporting Information

A Highly Efficient Kinetic Resolution of Morita-Baylis-Hillman Adducts Achieved by N-Ar Axially Chiral Pd-Complexes Catalyzed Asymmetric Allylation

Feijun Wang,[1,*] Shengke Li,[1] Mingliang Qu,[1] Mei-Xin Zhao,[1] Lian-Jun Liu,[1] and Min Shi[1,2,*]

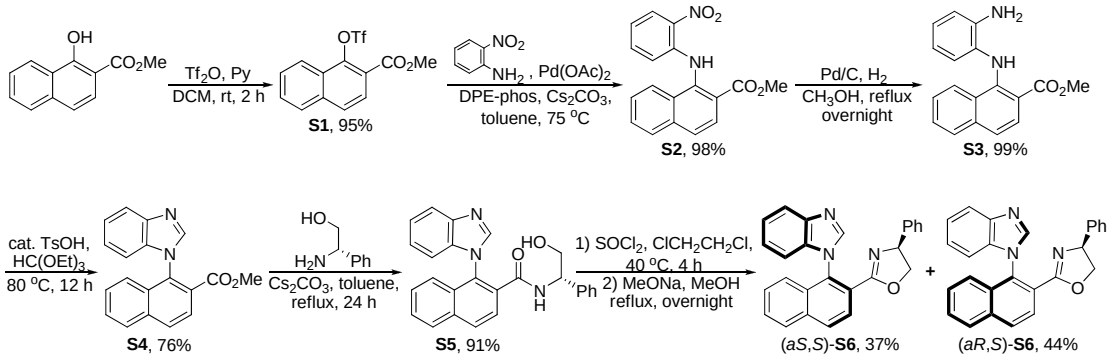
[1]*Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, and 130 MeiLong Road, Shanghai 200237, People's Republic of China, and* [2]*State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Road, Shanghai 200032, People's Republic of China*

feijunwang@ecust.edu.cn, *Mshi@mail.sioc.ac.cn*

CONTENTS

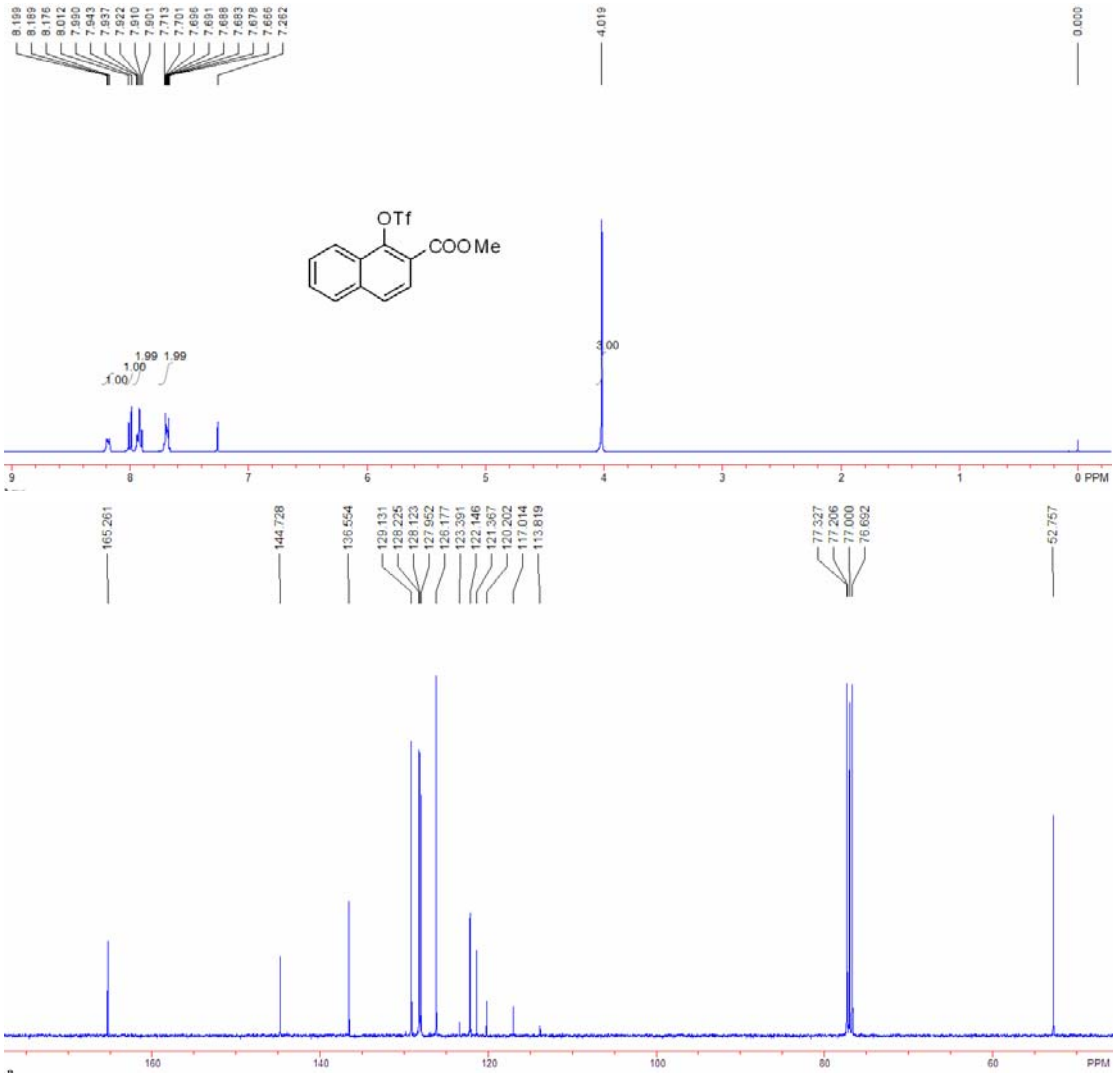
General remarks. Dichloromethane was freshly distilled from calcium hydride; THF and toluene were distilled from sodium (Na) under argon (Ar) atmosphere. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrophotometers. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF_{254}) were used. Elementary analysis was taken on a Carlo-Erba 1106 analyzer. Mass spectra were recorded by EI and ESI, and HRMS were measured on a HP-5989 instrument. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$-values are given in unit of 10 deg^{-1} cm_2 g^{-1}. Chiral HPLC was performed on a SHIMADZU SPD-10A *vp* series with chiral columns (Chiralpak AD-H, OD-H and OJ-H columns 4.6 × 250 mm, Daicel Chemical Ind., Ltd.).

Synthesis of axially chiral ligands (a*S*,*S*)-S6 and (a*R*,*S*)-S6.



Methyl 1-(trifluoromethylsulfonyloxy)-2-naphthoate **S1**.[1]

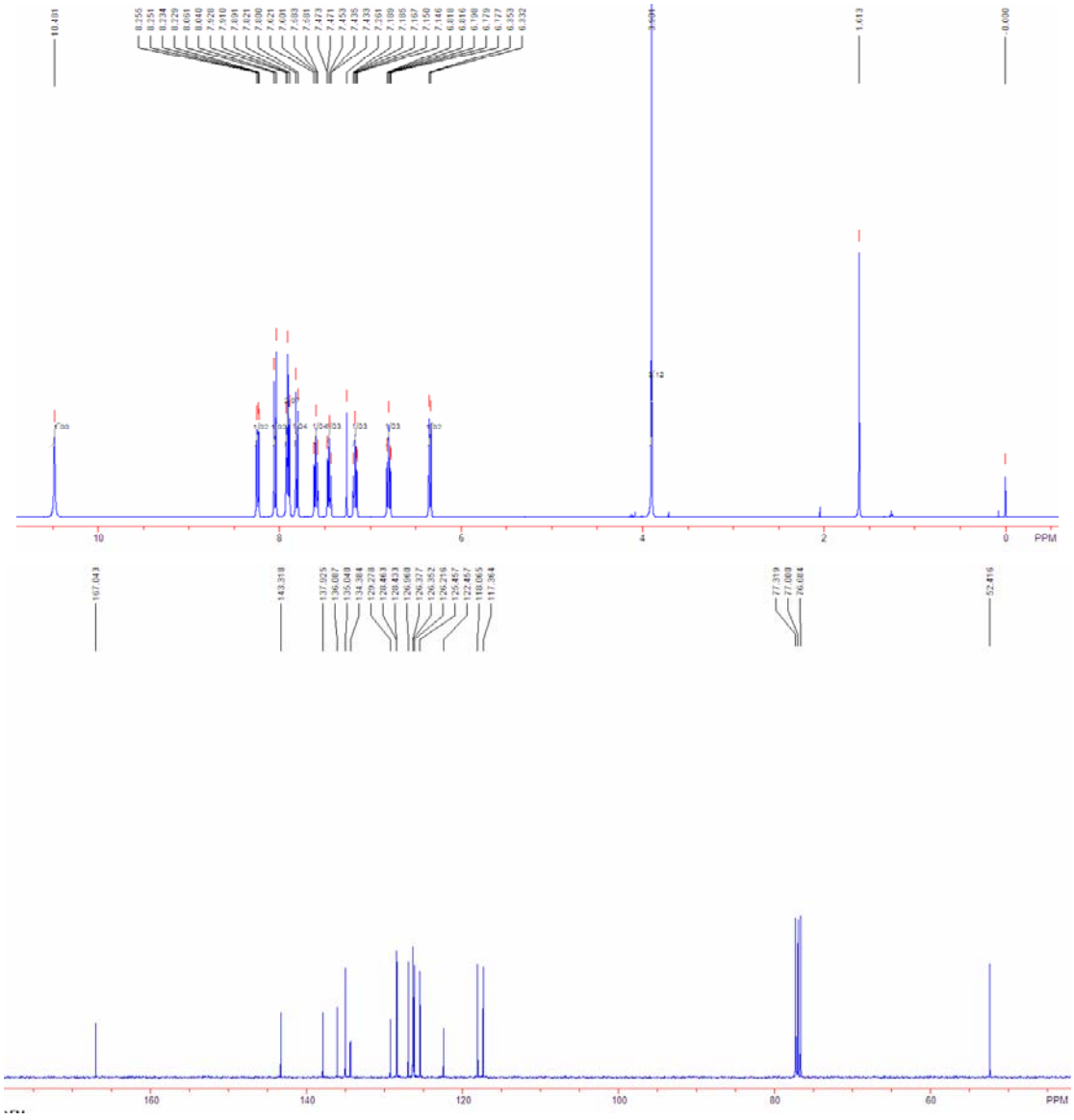
Trifluoromethanesulfonic anhydride (1.1 mL, 6.5 mmol) was added dropwise to the solution of methyl 1-hydroxy-2-naphthoate (1.01 g, 5.0 mmol) and pyridine (0.5 mL, 6.2 mol) in dried CH_2Cl_2 (12 mL) at 0 °C, and the resulting solution was stirred for 2 h at room temperature. The reaction mixture was diluted with CH_2Cl_2, and washed with water and saturated sodium bicarbonate solution. The organic layer was dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (ethyl acetate/petroleum ether = 1/16) to afford **S1** as light yellow solid in 95% yield (1.59 g, 4.75 mmol). ^{1}H NMR(400 MHz, $CDCl_3$) δ 4.02 (s, 3H), 7.67-7.71 (m, 2H), 7.90-7.94 (m, 2H), 8.00 (d, *J* = 8.8 Hz, 1H), 8.18-8.20 (m, 1H). ^{13}C NMR(100 MHz, $CDCl_3$) δ 52.8, 113.8, 117.0, 120.2, 121.4, 122.1, 123.4, 126.2, 128.0, 128.1, 128.2, 129.1, 136.6, 144.7, 165.3. ^{19}F NMR(470 MHz, $CDCl_3$) δ -73.0; MS (ESI) *m/z* (%): 333.0 (M-H, 100); HRMS (Micromass LCT) Calcd. for $C_{13}H_8O_5SF_3$: 333.0045; Found: 333.0044.



Methyl 1-(2-nitrophenylamino)-2-naphthoate **S2**.

Methyl 1-(trifluoromethylsulfonyloxy)-2-naphthoate **S1** (0.67 g, 2.0 mmol), 2-nitroaniline (0.30 g, 2.2 mmol), $Pd(OAc)_2$ (22.5 mg, 0.1 mmol), DPE-phos (108.0 mg, 0.2 mmol), and Cs_2CO_3 (0.98 g, 3.0 mmol) were stirred in anhydrous toluene (10 mL) at 75 ^oC until the reaction was completed. The reaction mixture was cooled to room temperature, and was filtrated by diatomite. The filtrate was washed with water, extracted with DCM (3 x 20 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (ethyl acetate/petroleum ether = 1/10) to afford the desired product **S2** as orange solid in 98% yield (0.63 g, 1.96 mmol). Mp. 141.6-142.9 ^oC; IR (direct irradiation) ν 630, 760, 810, 890, 962, 1034, 1135, 1205, 1284, 1344, 1422,

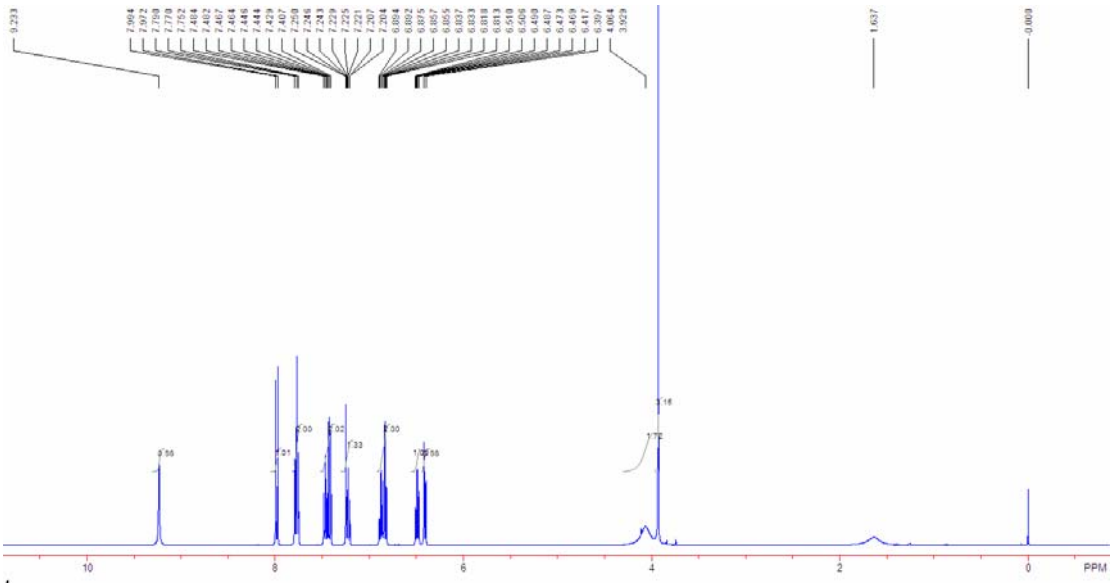
1728, 2960, 3082 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 3.90 (s, 3H), 6.34 (d, *J* = 8.4 Hz, 1H), 6.78-6.82 (m, 1H), 7.15-7.19 (m, 1H), 7.43-7.47 (m, 1H), 7.58-7.62 (m, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.91 (t, *J* = 7.2 Hz, 2H), 8.05 (d, *J* = 8.4 Hz, 1H), 8.24 (dd, *J* = 1.6, 8.4 Hz, 1H), 10.48 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 52.4, 117.4, 118.1, 122.5, 125.5, 126.2, 126.35, 126.37, 127.0, 128.4, 128.5, 129.3, 134.4, 135.0, 136.1, 137.9, 143.3, 167.0; MS (ESI) *m/z* (%): 323.1 (M + H, 21); HRMS (Micromass LCT) Calcd. for $C_{18}H_{15}N_2O_4$: 323.1032; Found: 323.1036.

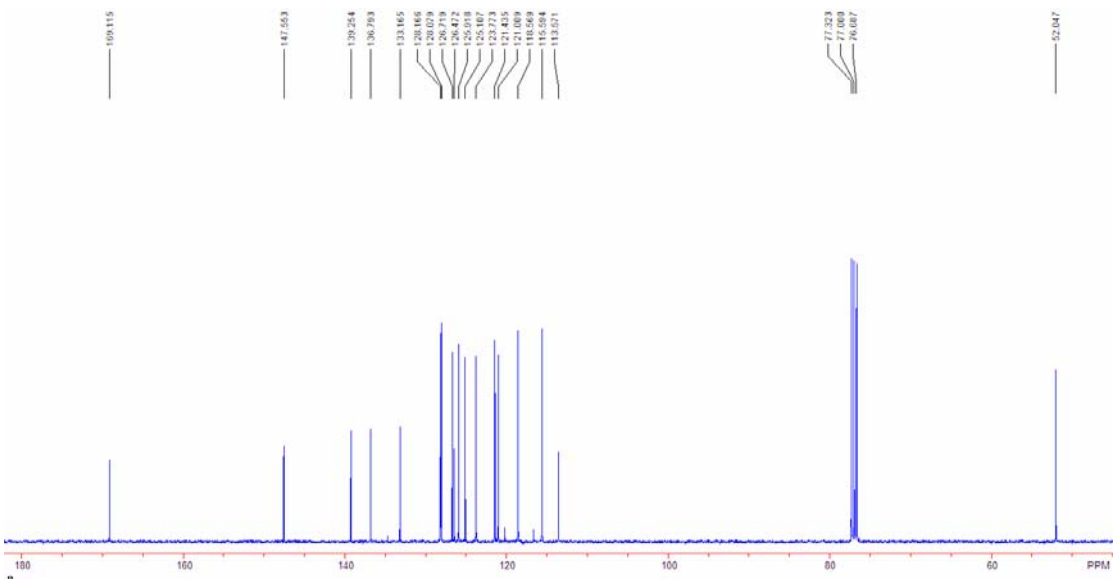


Methyl 1-(2-aminophenylamino)-2-naphthoate **S3**.

A mixture of **S2** (0.97 g, 3.0 mmol), 10% Pd-C (0.32 g) in a solution of MeOH (14 mL) were stirred overnight under reflux in 1 atm of H_2. After cooling to room

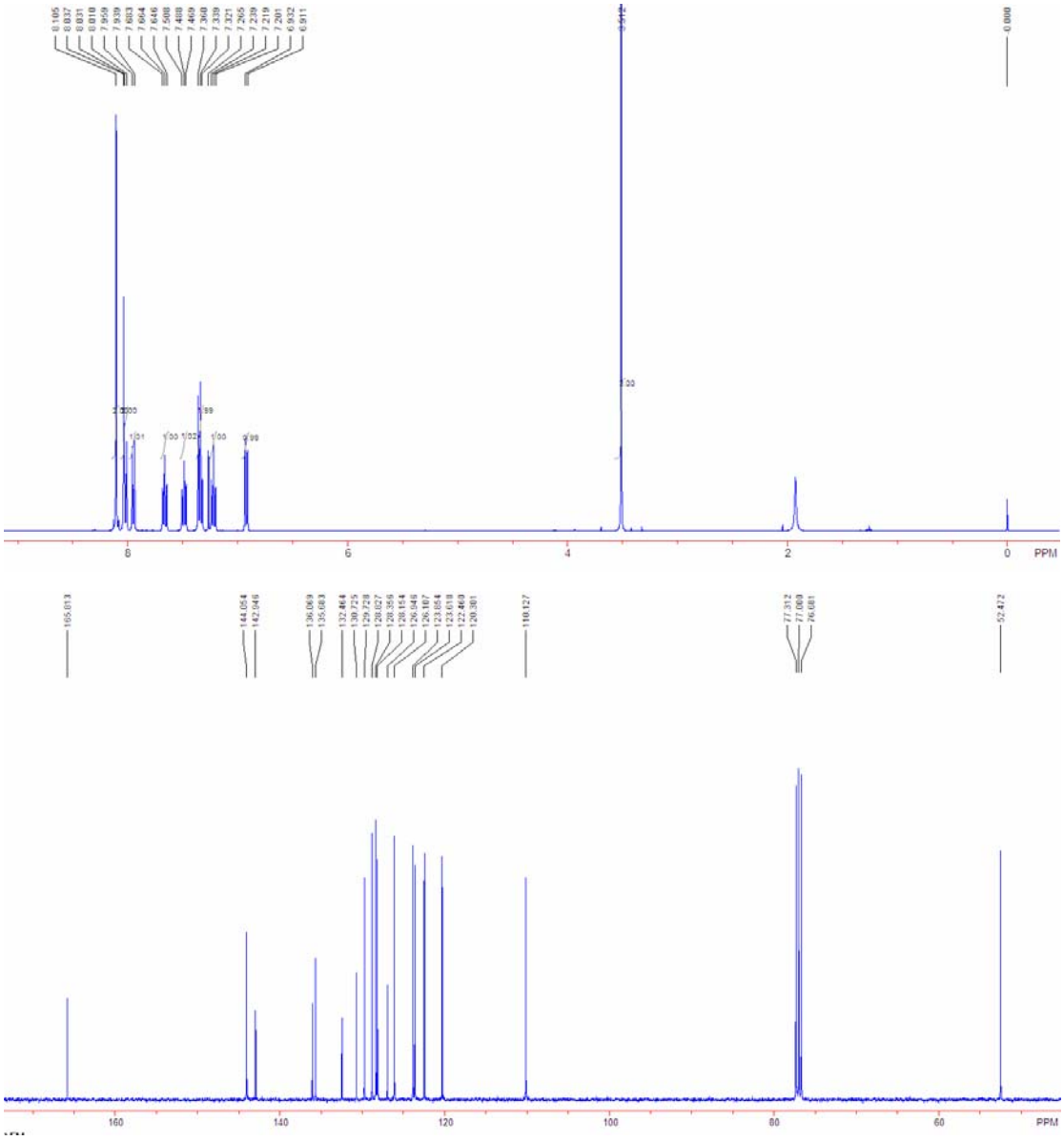
temperature, Pd-C was removed by filtration, and the resulting solution was evaporated to remove solvent under reduced pressure. The residue was purified by a silica gel flash column chromatography (ethyl acetate/petroleum ether = 1/10, 1% NEt_3 added) to afford the desired product **S3** as yellow solid in 99% yield (0.87 g, 2.97 mmol). Mp. 134.3-136.1 ^oC; IR (direct irradiation) ν 713, 740, 760, 788, 1138, 1208, 1243, 1270, 1341, 1496, 1569, 1669, 3337, 3440 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.93 (s, 3H), 4.06 (br s, 2H), 6.41 (d, J = 8.0 Hz, 1H), 6.47-6.51 (m, 1H), 6.81-6.89 (m, 2H), 7.20-7.25 (m, 1H), 7.41-7.48 (m, 2H), 7.77 (t, J = 8.0 Hz, 2H), 7.98 (d, J = 8.8 Hz, 1H), 9.23 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 52.0, 113.6, 115.6, 118.6, 121.0, 121.4, 123.8, 125.1, 125.9, 126.5, 126.7, 128.1, 128.2, 133.2, 136.8, 139.3, 147.6, 169.1; MS (ESI) *m/z* (%): 293.1 (M + H, 100); HRMS (Micromass LCT) Calcd. for $C_{18}H_{17}N_2O_2$: 293.1290; Found: 293.1294.





Methyl 1-(1*H*-benzo[d]imidazol-1-yl)-2-naphthoate **S4**.

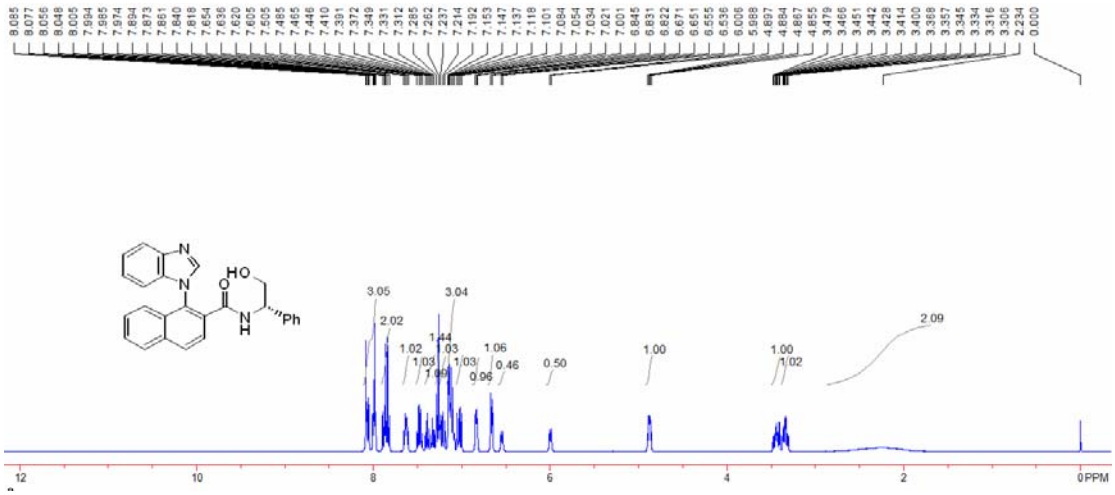
The compound **S3** (0.88 g, 3.0 mmol) and triethyl orthoformate [$HC(OC_2H_5)_3$] (8.0 mL) containing a catalytic amount of TsOH were heated at 80 ^oC until the compound **S3** was consumed. After cooling to room temperature, ethyl acetate was added to form an azeotropic solution in order to remove the excess amount of triethyl orthoformate under reduced pressure. The residue was purified by a silica gel flash column chromatography (ethyl acetate/petroleum ether = 1/3) to afford the desired product **S4** in 76% yield (0.69 g, 2.28 mmol). Viscous brown solid; Mp. 115.0-116.7 ^oC; IR (direct irradiation) ν 683, 750, 766, 1138, 1161, 1190, 1223, 1237, 1270, 1431, 1454, 1486, 1718, 2951 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.51 (s, 3H), 6.92 (d, J = 8.4 Hz, 1H), 7.22 (t, J = 8.0 Hz, 1H), 7.34 (t, J = 8.0 Hz, 2H), 7.49 (t, J = 8.0 Hz, 1H), 7.66 (t, J = 7.6 Hz, 1H), 7.95 (d, J = 8.0 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 8.04 (s, 1H), 8.11 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 52.5, 110.1, 120.3, 122.5, 123.6, 123.9, 126.1, 126.9, 128.2, 128.4, 128.8, 129.7, 130.7, 132.5, 135.7, 136.1, 143.0, 144.1, 165.8; MS (ESI) *m/z* (%): 303.1 (M + H, 100); HRMS (Micromass LCT) Calcd. for $C_{19}H_{15}N_2O_2$: 303.1134; Found: 303.1134.

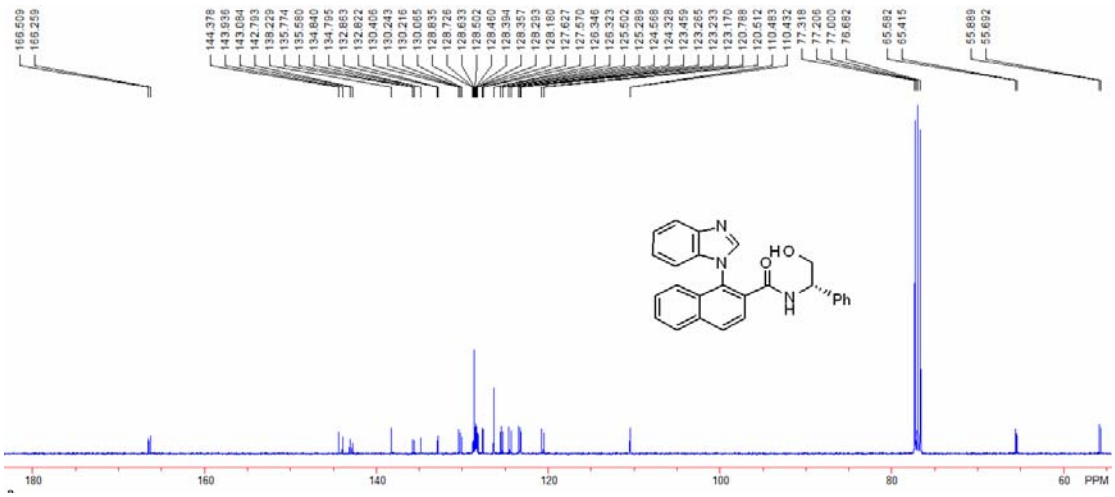


1-(1*H*-benzo[d]imidazol-1-yl)-*N*-((*S*)-2-hydroxy-1-phenylethyl)-2-naphthamide **S5**.

A solution of (*S*)-2-amino-2-phenylethanol (1.10 g, 8.0 mmol), compound **S4** (1.21 g, 4.0 mmol), Cs_2CO_3 (2.61 g, 8.0 mmol), and toluene (20 mL) was stirred at 85 ^oC until the compound **S4** was consumed. After cooling to room temperature, The mixture was diluted with DCM, and washed with cold water, and brine. The organic layer was dried over $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by a silica gel flash column chromatography (petroleum ether/ethyl acetate, 1/1-0/1) to afford the diastereomeric mixture **S5** in 91% yield (1.48 g, 3.63 mmol). Pale red solid; Mp. 226.7-228.4 ^oC; IR (direct irradiation) ν 700, 742, 752, 763, 1045,

1136, 1231, 1306, 1270, 1491, 1455, 1649, 1721, 3055, 3194 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.23 (br s, 2H), 3.31-3.37 (m, 1H), 3.40-3.48 (m, 1H), 4.86-4.90 (m, 1H), 6.00 (d, *J* = 7.2 Hz, 0.50H), 6.55 (d, *J* = 7.6 Hz, 0.46H), 6.65-6.67 (m, 1H), 6.82-6.85 (m, 1H), 7.01 (d, *J* = 8.0 Hz, 0.54H), 7.04 (d, *J* = 8.0 Hz, 0.50H), 7.08-7.15 (m, 3H), 7.19-7.25 (m, 1H), 7.33 (t, *J* = 7.2 Hz, 0.52H), 7.39 (t, *J* = 7.6 Hz, 0.56H), 7.46 (d, *J* = 7.6 Hz, 0.50H), 7.50 (d, *J* = 8.0 Hz, 0.53H), 7.61-7.65 (m, 1H), 7.82-7.89 (m, 2H), 7.97-8.09 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 55.7, 55.9, 65.4, 65.6, 110.4, 110.5, 120.5, 120.8, 123.17, 123.23, 123.3, 123.5, 124.3, 124.6, 125.3, 125.5, 126.32, 126.35, 127.57, 127.63, 128.2, 128.29, 128.36, 128.39, 128.46, 128.50, 128.6, 128.7, 128.8, 130.1, 130.22, 130.24, 130.41, 132.83, 132.86, 134.80, 134.84, 135.6, 135.8, 138.2, 142.8, 143.1, 143.9, 144.4, 166.3, 166.5; MS (ESI) *m/z* (%): 408.2 (M + H, 100); HRMS (Micromass LCT) Calcd. for $C_{26}H_{22}N_3O_2$: 408.1712; Found: 408.1715.



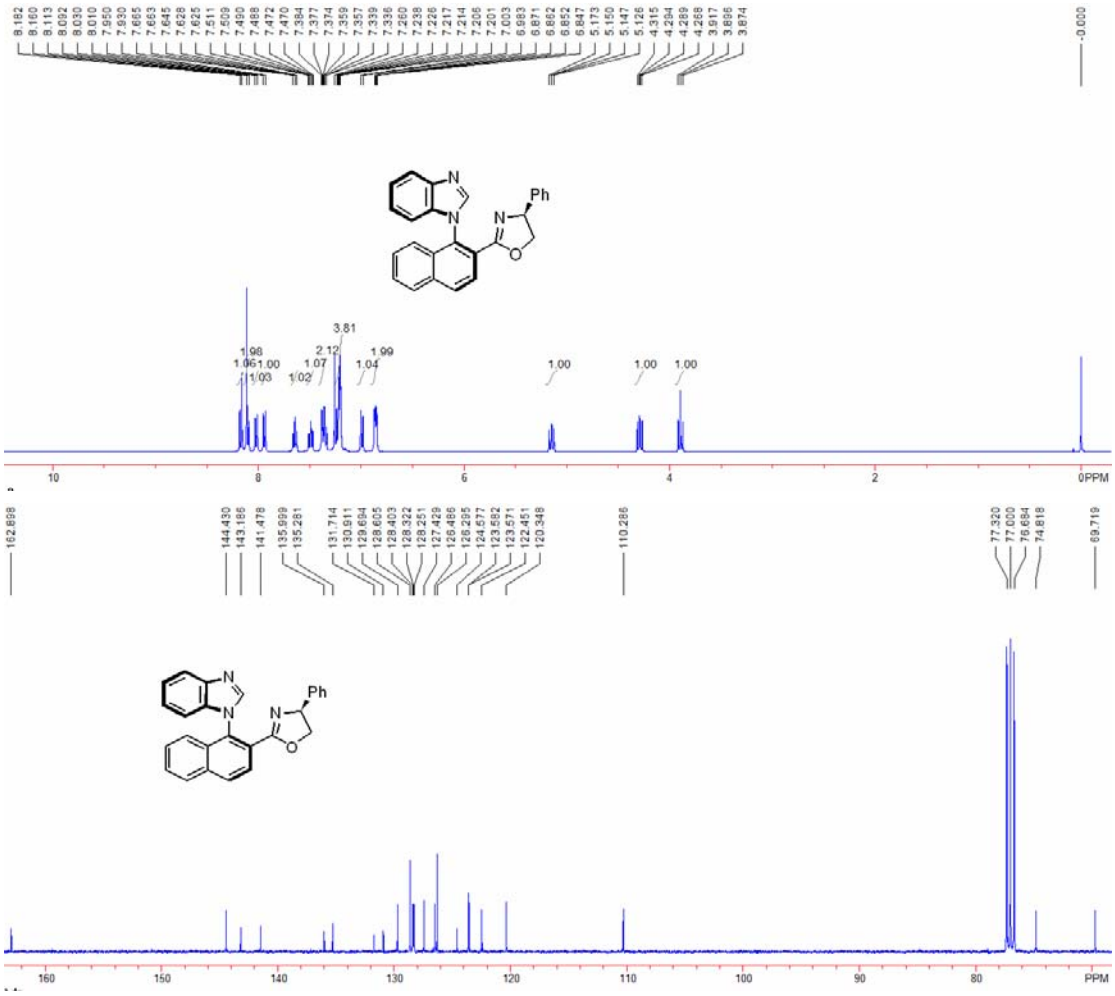


(*S*)-2-((*S*)-1-(1*H*-benzo[d]imidazol-1-yl)naphthalen-2-yl)-4-phenyl-4,5-dihydrooxazole (a*S*,*S*)-**S6** and (*S*)-2-((*R*)-1-(1H-benzo[d]imidazol-1-yl)naphthalen-2-yl)-4-phenyl-4,5-dihydrooxazole (a*R*,*S*)-**S6**.

$SOCl_2$ (0.36 mL, 5.1 mol) was slowly added to a solution of diastereomeric mixture **S5** (0.41 g, 1.0 mol) and dried 1,2-dichloroethane (10 mL) at 0 °C. The resulting solution was stirred at 40 °C for 4 h, and then the solvent was removed under reduced pressure. Subsequently, the residue was treated with sodium methoxide (0.43 g, 8.0 mol) in CH_3OH (15 mL), and stirred overnight under reflux. The resulting mixture was diluted with cold water, and extracted with DCM **(**3 x 20 mL). The organic layer was washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by a silica gel flash column chromatography (ethyl acetate/petroleum ether = 1/2) to afford (a*S*,*S*)-**S6** (144.1 mg, 0.37 mmol) and (a*R*,*S*)-**S6** (171.4 mg, 0.44 mmol).

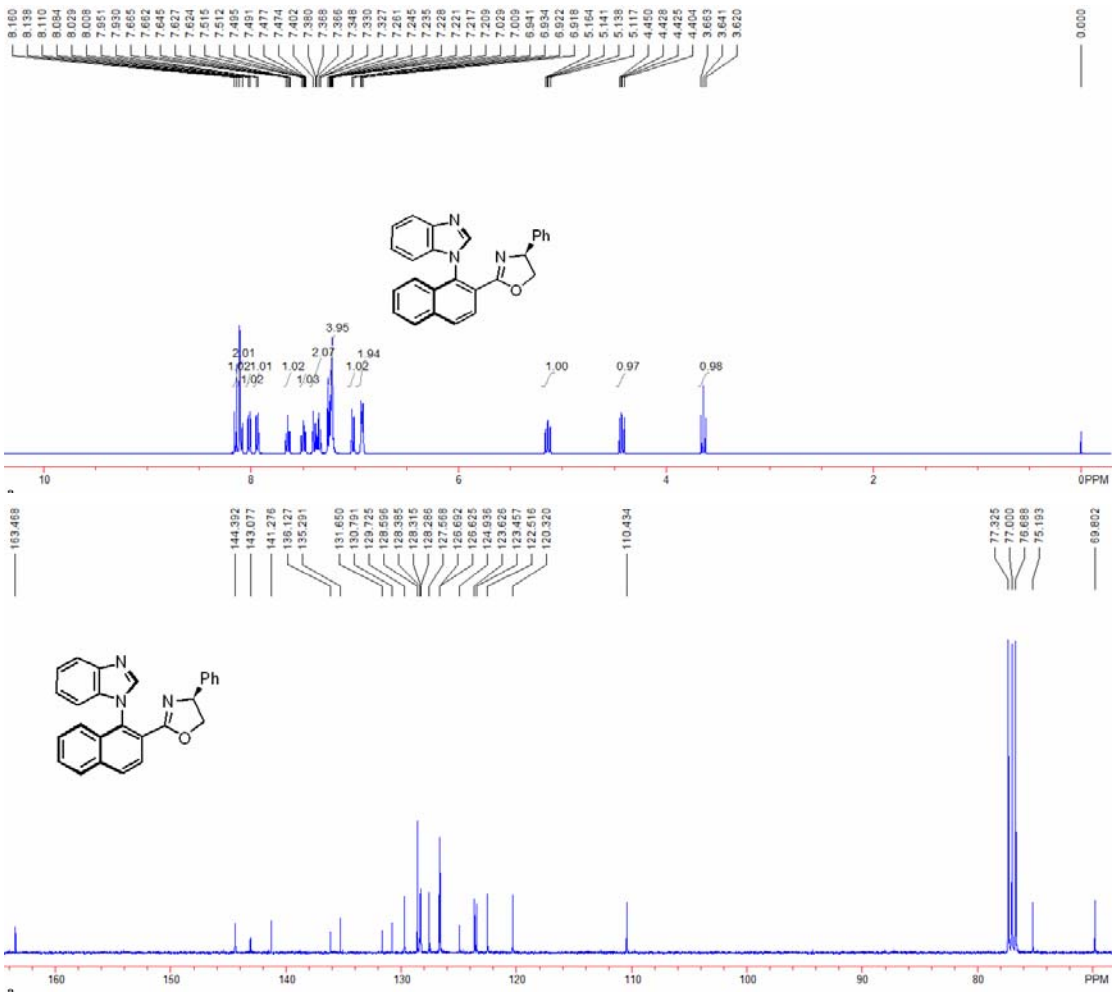
(a*S*,*S*)-**S6**: White solid, 37% yield; Mp. 186.1-187.9 ^{o}C; IR (direct irradiation) ν 683, 698, 748, 759, 831, 971, 1008, 1106, 1224, 1454, 1471, 1645, 2898, 3073 cm^{-1}; $[\alpha]^{20}_{D}$ = +112.1 (c 0.70, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.90 (t, *J* = 8.8 Hz, 1H), 4.29 (dd, *J* = 8.4, 10.4 Hz, 1H), 5.15 (dd, *J* = 8.8, 10.4 Hz, 1H), 6.85-6.87 (m, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 7.19-7.24 (m, 4H), 7.34-7.38 (m, 2H), 7.47-7.51 (m, 1H), 7.63-7.67 (m, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 2H), 8.17 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 69.7, 74.8, 110.3, 120.3, 122.5, 123.57, 123.58, 124.6, 126.3, 126.5, 127.4, 128.25, 128.32, 128.4,

128.6, 129.7, 130.9, 131.7, 135.3, 136.0, 141.5, 143.2, 144.4, 162.9; MS (ESI) *m/z* (%): 390.2 (M + H, 71); HRMS (Micromass LCT) Calcd. for $C_{16}H_{20}N_3O$: 390.1606; Found: 390.1611.

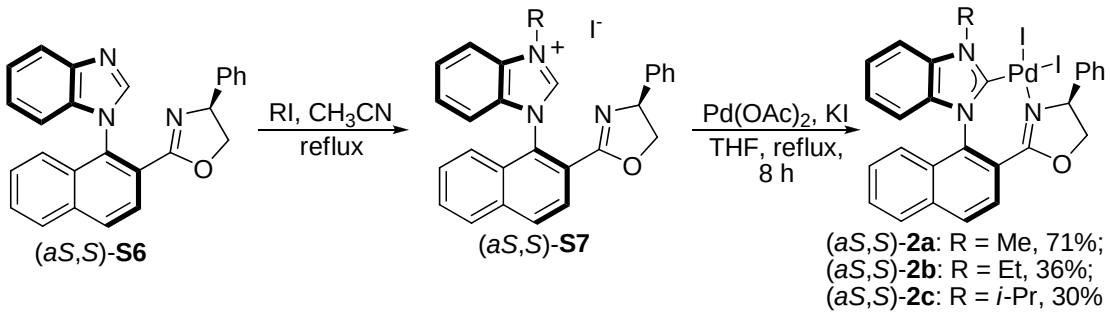


(a*R*,*S*)-**S6**: White solid, 44% yield; Mp. 153.6-155.4 ^{o}C; $[\alpha]^{20}_{D}$ = -62.5 (c 0.80, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.64 (t, *J* = 8.8 Hz, 1H), 4.43 (dd, *J* = 8.8, 10.0 Hz, 1H), 5.14 (dd, *J* = 9.2, 10.4 Hz, 1H), 6.92-6.94 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 1H), 7.21-7.25 (m, 4H), 7.33-7.37 (m, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.47-7.52 (m, 1H), 7.62-7.67 (m, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 10.4 Hz, 2H), 8.15 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 69.8, 75.2, 110.4, 120.3, 122.5, 123.5, 123.6, 124.9, 126.6, 126.7, 127.6, 128.28, 128.32, 128.4, 128.6, 129.7, 130.8, 131.7, 135.3, 136.1, 141.3, 143.1, 144.4, 163.5; MS (ESI)

m/z (%): 390.2 (M + H, 71); HRMS (Micromass LCT) Calcd. for $C_{16}H_{20}N_3O$: 390.1606; Found: 390.1611.



Synthesis of axially chiral Pd complexes (a*S*,*S*)-2.



(a*S*,*S*)-**S6**

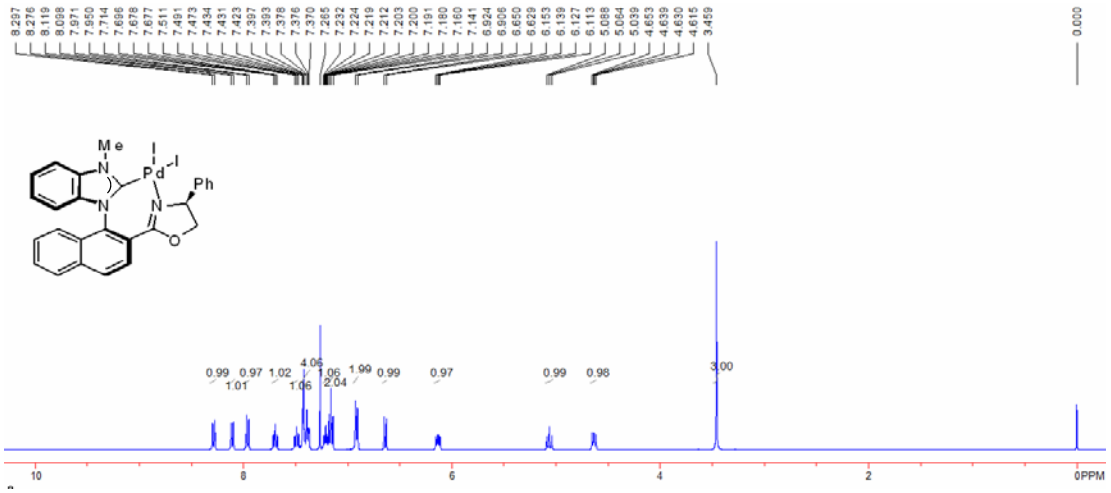
(a*S*,*S*)-**S7**

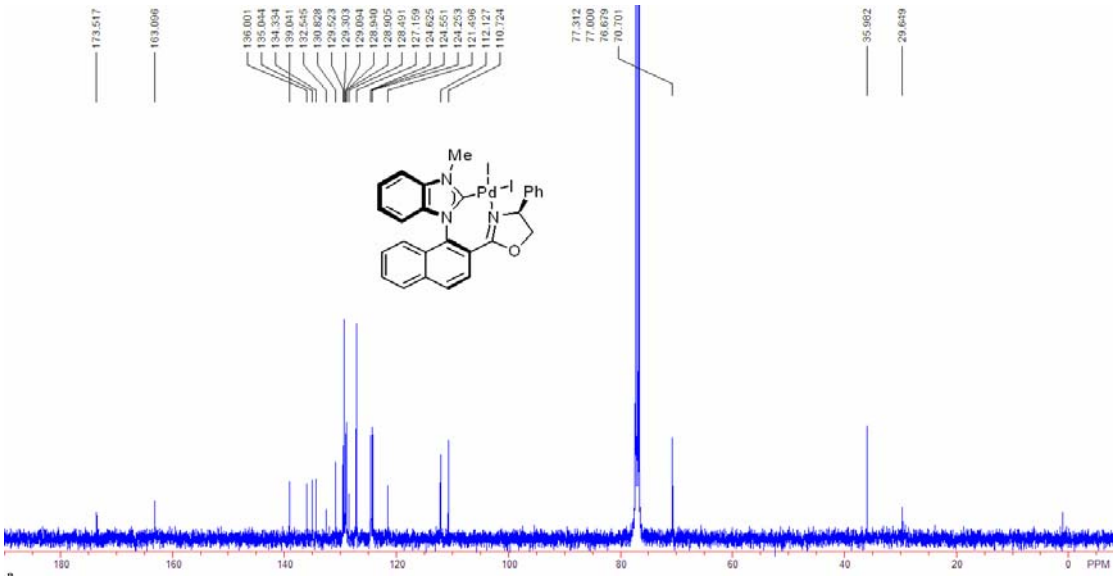
(a*S*,*S*)-**2a**: R = Me, 71%;
(a*S*,*S*)-**2b**: R = Et, 36%;
(a*S*,*S*)-**2c**: R = *i*-Pr, 30%

The compound (a*S*,*S*)-**S6** (0.58 g, 1.49 mmol) and RI (15 mmol) in CH_3CN (10 mL) were stirred under reflux until the compound (a*S*,*S*)-**S6** was consumed. After

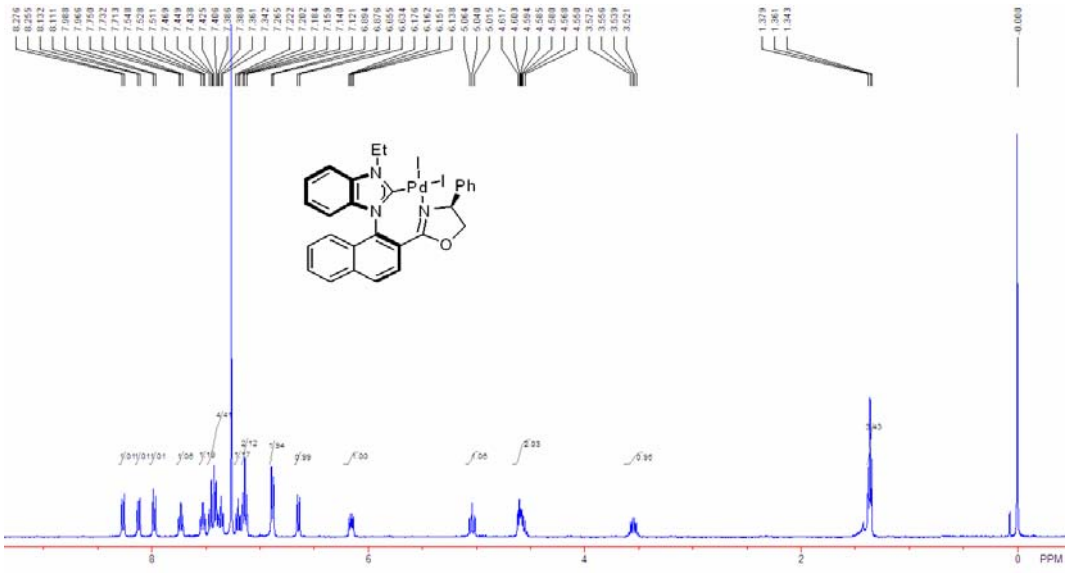
cooling to room temperature, volatiles were removed under reduced pressure to obtain the crude benzimidazolium salt (a*S*,*S*)-**S7**. Salt (a*S*,*S*)-**S7**, $Pd(OAc)_2$ (0.33 g, 1.47 mmol) and KI (0.50 g, 3.0 mmol) were refluxed in THF (25 mL) for 8 h. The volatiles were then removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (dichloromethane/petroleum ether = 6/1-1/0) to give (a*S*,*S*)-**2** as earth yellow solid.

Complex (a*S*,*S*)-**2a** (R = Me, 806.7 mg, 71% yield): Mp. > 250 ^{o}C; $[\alpha]^{20}_{D}$ = +65.8 (c 0.50, $CHCl_3$); A single crystal of (a*S*,*S*)-**2a** suitable for X-ray crystal analysis was obtained by recrystallization from a saturated solution of CH_2Cl_2/petroleum ether (1/1, v/v). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.46 (s, 3H), 4.63 (dd, *J* = 5.6, 9.2 Hz, 1H), 5.06 (t, *J* = 9.6 Hz, 1H), 6.13 (dd, *J* = 5.6, 10.4 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 2H), 7.16 (t, *J* = 8.0 Hz, 2H), 7.18-7.23 (m, 1H), 7.37-7.43 (m, 4H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.2 Hz, 1H), 7.96 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 29.6, 36.0, 70.7, 110.7, 112.1, 121.5, 124.3, 124.55, 124.63, 127.2, 128.5, 128.91, 128.94, 129.1, 129.3, 129.5, 130.8, 132.5, 134.3, 135.0, 136.0, 139.0, 163.1, 173.5; MS (ESI) *m/z* (%): 636.0 (M-I, 100); HRMS (Micromass LCT) Calcd. for $C_{27}H_{21}IN_3OPd$: 635.9764; Found: 635.9764.





Complex (a*S*,*S*)-**4b** (R = Et, 417.6 mg, 36% yield): Mp. > 250 ^{o}C; $[\alpha]^{20}_{D}$ +20.8 (*c* 0.74, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (t, *J* = 7.2 Hz, 3 H), 3.50-3.59 (m, 1H), 4.53-4.62 (m, 2H), 5.04 (t, *J* = 9.6 Hz, 1 H), 6.16 (dd, *J* = 5.6, 10.0 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1 H), 6.89 (d, *J* = 7.2 Hz, 2 H), 7.14 (t, *J* = 7.6 Hz, 2 H), 7.20 (t, *J* = 8.0 Hz, 1 H), 7.34-7.47 (m, 4H), 7.53 (t, *J* = 8.0 Hz, 1 H), 7.73 (t, *J* = 7.2 Hz, 1 H), 7.98 (d, *J* = 8.8 Hz, 1 H), 8.12 (d, *J* = 8.4 Hz, 1 H), 8.27 (d, *J* = 8.4 Hz, 1 H). MS (ESI) *m/z* (%): 650.0 (M-I, 100); HRMS (Micromass LCT) Calcd. for $C_{28}H_{23}IN_3OPd$: 649.9921; Found: 649.9905.



Complex (a*S*,*S*)-**4c** (R = *i*-Pr, 355.2 mg, 30% yield): Mp. > 250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75 (d, *J* = 7.2 Hz, 3H), 1.65 (d, *J* = 7.2 Hz, 3H), 4.57 (dd, *J* = 5.2, 8.8 Hz, 1H), 5.03 (t, *J* = 10.0 Hz, 1H), 5.73-5.80 (m, 1H), 6.25 (dd, *J* = 5.2, 9.2 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 20.8, 29.7, 55.9, 70.8, 112.7, 113.2, 121.4, 123.9, 124.4, 125.1, 126.9, 128.5, 128.8, 128.9, 129.2, 129.4, 129.5, 130.8, 131.9, 132.6, 136.2, 136.3, 138.8, 164.0, 172.5, 207.1. MS (ESI) *m/z* (%): 636.0 (M-I, 100); HRMS (Micromass LCT) Calcd. for $C_{29}H_{25}IN_3OPd$: 664.0077; Found: 664.0073.

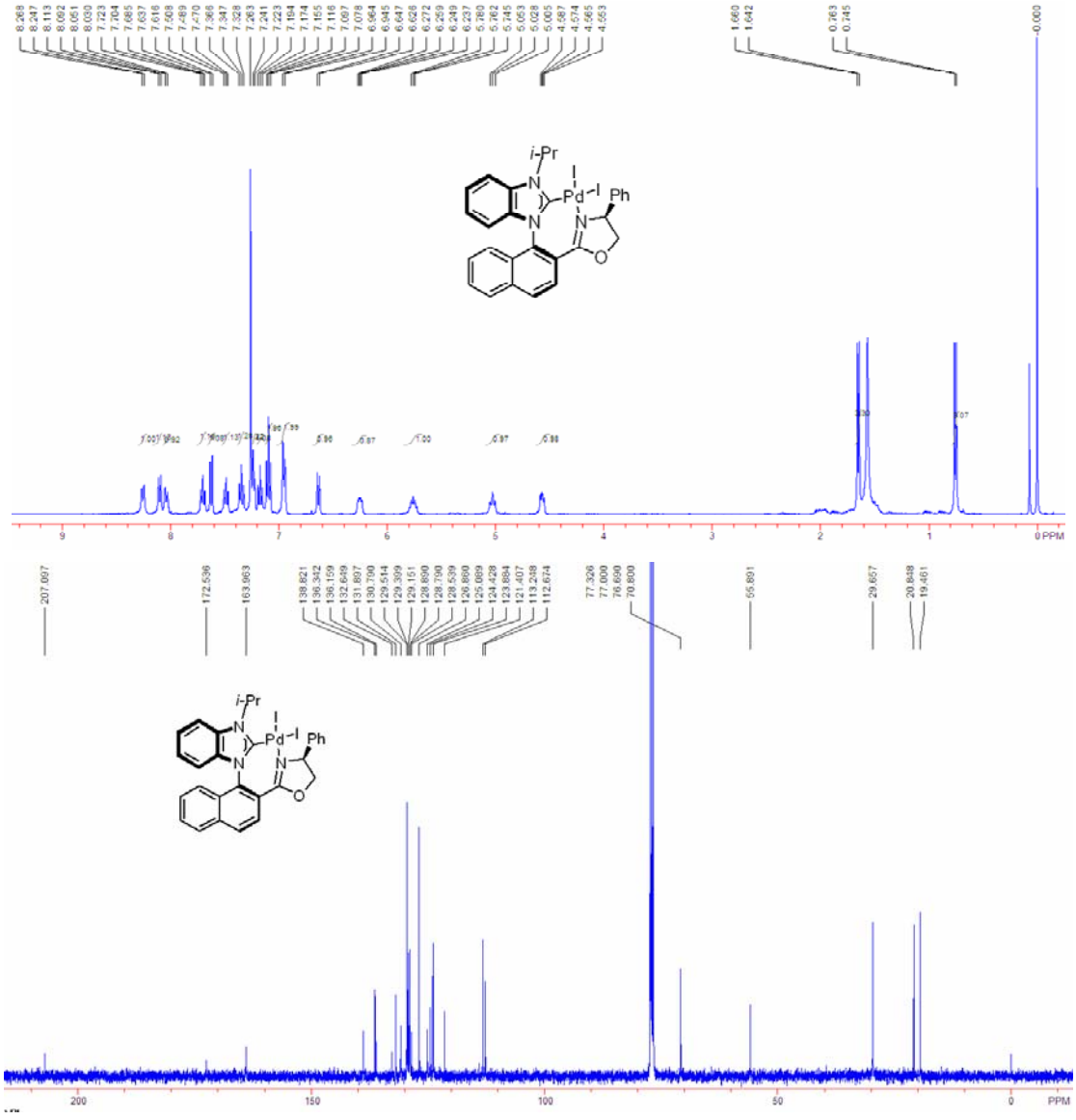
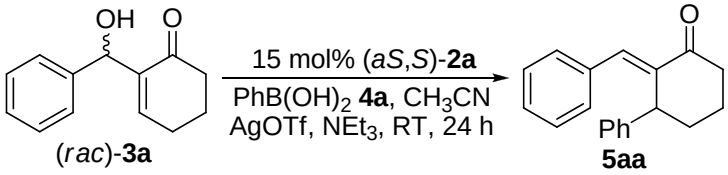


Table S1 Screening of the amount of $PhB(OH)_2$ and NEt_3.[a]



(*rac*)-**3a** **5aa**

Entry	amount of $PhB(OH)_2$	amount of NEt_3	Conv.[b] [%]	**5aa** Yield[c] [%]	**5aa** ee[d] [%]	Recovered **3a** Yield[c] [%]	Recovered **3a** ee[e] [%]
1	0.5 equiv	0.5 equiv	35	34	97	63	41
2	1.0 equiv	0.5 equiv	40	39	93	58	73
3	3.0 equiv	0.5 equiv	43	40	94	55	53
4	1.0 equiv	0.25 equiv	40	35	93	56	70
5	3.0 equiv	1.5 equiv	20	38	96	68	16

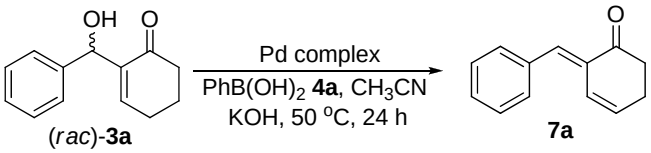
[a] Reaction conditions: 1.0 mL CH_3CN, 0.1 mmol **3a**, 153 mol% Pd complex, 15 mol% AgOTf, RT, 24 h. [b] Determined by crude ^1H NMR spectra. [c] Isolated yields. [d] The enantioselectivity of (*E*)-**5aa** was determined by chiral HPLC analysis. [e] Determined by chiral HPLC analysis.

General procedure for the Pd(II)-catalyzed asymmetric allylic alkylation of 4 with 3.

(a*S*,*S*)-**2a** (15 mol%, 11.5 mg, 0.015 mmol) and AgOTf (15 mol%, 3.9 mg, 0.015 mmol) were stirred in CH_3CN (1.0 mL) for 10 minutes. Then, racemic allylic alcohol **3** (0.1 mmol), arylboronic acid **4** (0.2 mmol), and triethylamine (0.05 mmol) were added and the reaction mixture was stirred at room temperature for 24 h. The solvent was evaporated under reduced pressure and the residue was purified by chromatography on silica gel to obtain the allylic alkylation product **5** and recovered alcohol **3**. The enantioselectivities of compound (*E*)-**5** and recovered alcohol **3** were determined by HPLC on a chiral stationary phase.

(*R*,*E*)-2-Benzylidene-3-phenylcyclohexanone **5aa**[2] (Table 1, entry 5): $[\alpha]_D^{20}$ +149.4 (*c* 0.38, $CHCl_3$) for 98 % ee. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.69-1.76 (m, 2H), 2.08-2.13 (m, 2H), 2.41-2.50 (m, 1H), 2.65-2.67 (m, 1H), 4.51 (t, *J* = 3.6 Hz, 1H), 7.16-7.28 (m, 8H), 7.33-7.36 (m, 2H), 7.59 (s, 1H). Chiralcel OJ, hexane/*i*-PrOH = 97/3, 0.8 mL/min, 230 nm, t_{major} = 12.74 min, t_{minor} = 20.11 min.

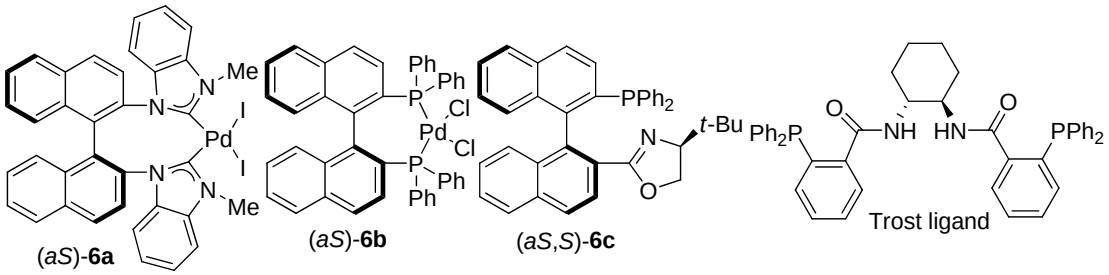
Table S2 Screening of chiral Pd-complexes.[a]



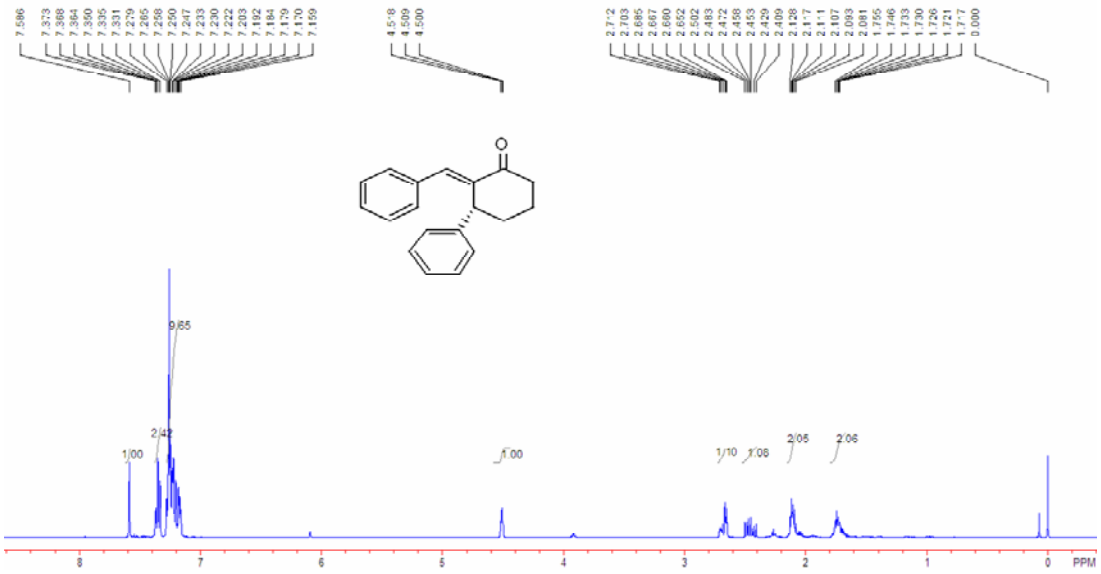
(*rac*)-**3a** **7a**

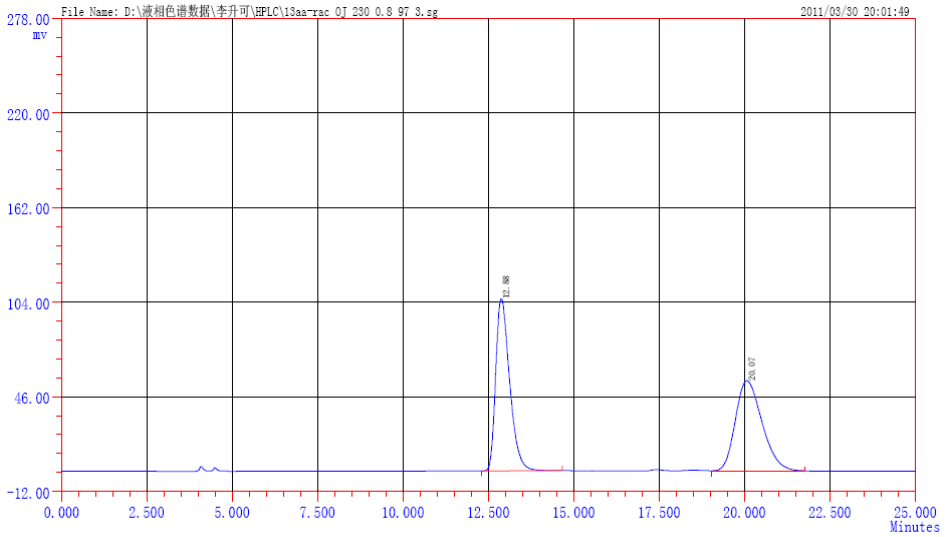
Entry	Pd complex	**7a**, Yield[b] [%]
1[c]	(*aS*,*S*)-**6a**, AgOTf	11
2[c]	(*aS*,*S*)-**6b**, AgOTf	55
3	(*aS*,*S*)-**6c**, $Pd(OTf)_2$	13
4[d]	Trost ligand, $Pd(OTf)_2$	trace

[a] Reaction conditions: 1.0 mL CH_3CN, 0.1 mmol **3a**, 0.2 mmol **4a**, 3 mol% Pd complex, 0.05 mmol KOH, 50 °C, 24 h. [b] Isolated yields. [c] 3 mol% AgOTf. [d] 15 mol% Pd complex, 15 mol% AgOTf.



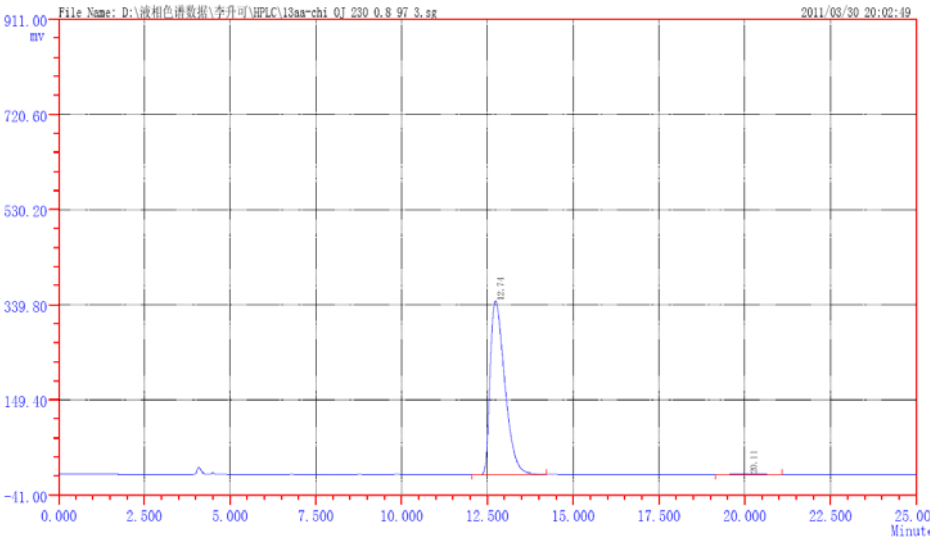
(*aS*)-**6a** (*aS*)-**6b** (*aS*,*S*)-**6c** Trost ligand





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		12.878	105544	2999090.6	49.6643	1.45	4094
2		20.073	55519	3039628.7	50.3357	1.27	2679
	Σ:		161063	6038719.4	100.0000		

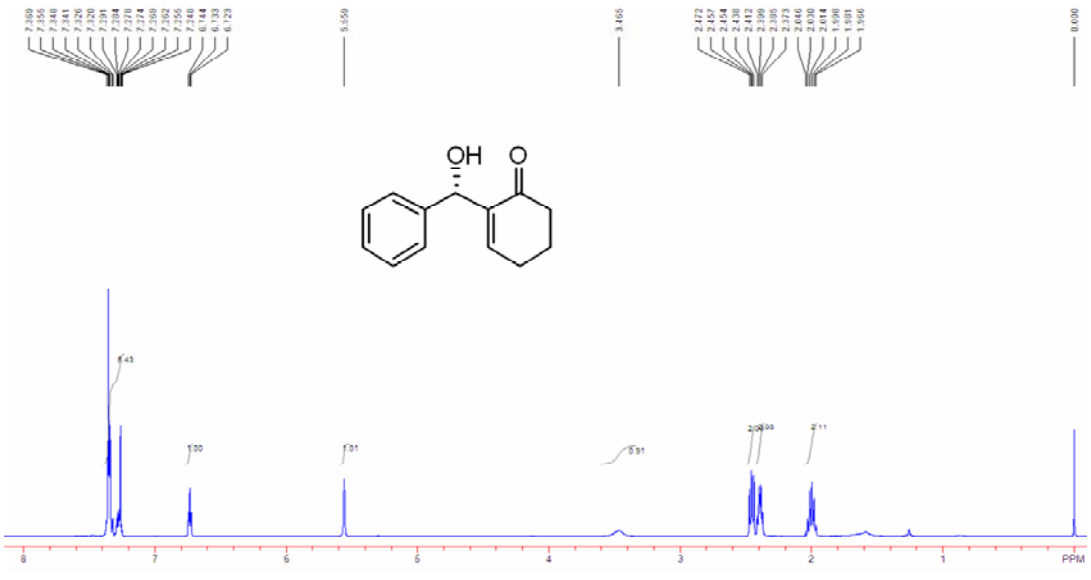
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

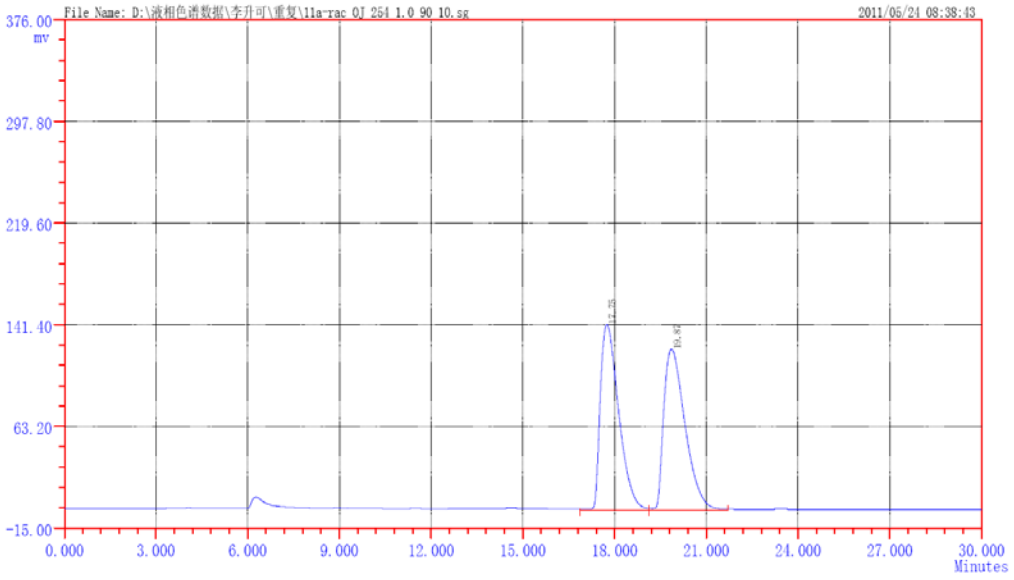


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		12.738	347188	10347175.2	99.0297	1.65	3641
2		20.113	1776	101377.2	0.9703	0.97	2475
	Σ:		348964	10448552.4	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

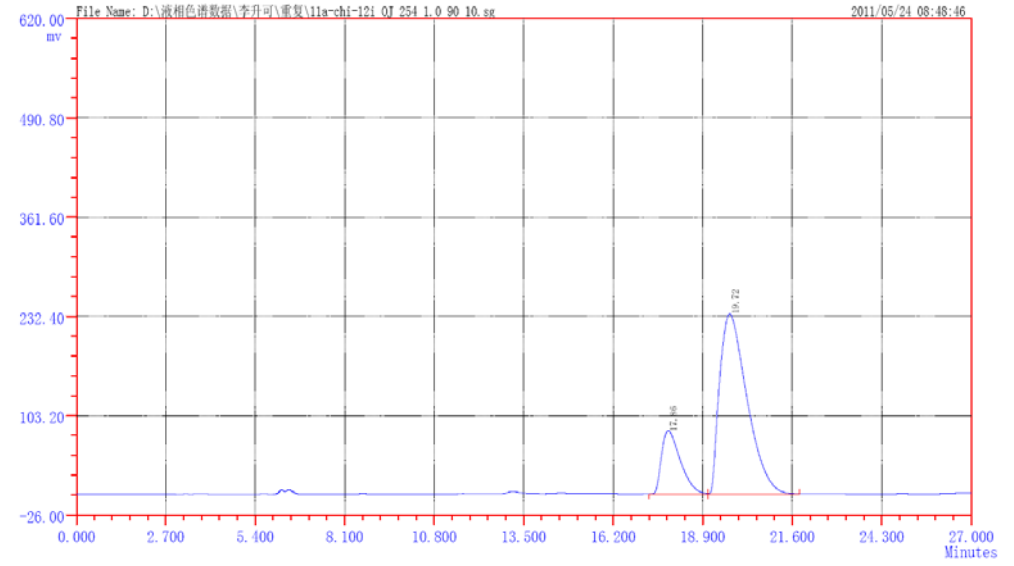
(*S*)-2-(hydroxy(phenyl)methyl)cyclohex-2-enone **3a**.[3] $[\alpha]_D^{20}$ +9.3 (*c* 0.80, CH_2Cl_2) for 61 % ee (Fig. 2, entry 8). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.97-2.05 (m, 2H), 2.37-2.41 (m, 2H), 2.44-2.47 (m, 2H), 3.47 (br s, 1H), 5.56 (s, 1H), 6.73 (t, *J* = 4.4 Hz, 1H), 7.25-7.37 (m, 5H). Chiralcel OJ, hexane/*i*-PrOH = 90/10, 1.0 mL/min, 254 nm, t_{major} = 19.72 min, t_{minor} = 17.86 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		17.750	142905	5985020.4	49.8226	1.75	3580
2		19.870	123993	6027629.6	50.1774	1.71	3330
	Σ:		266898	12012650.0	100.0000		

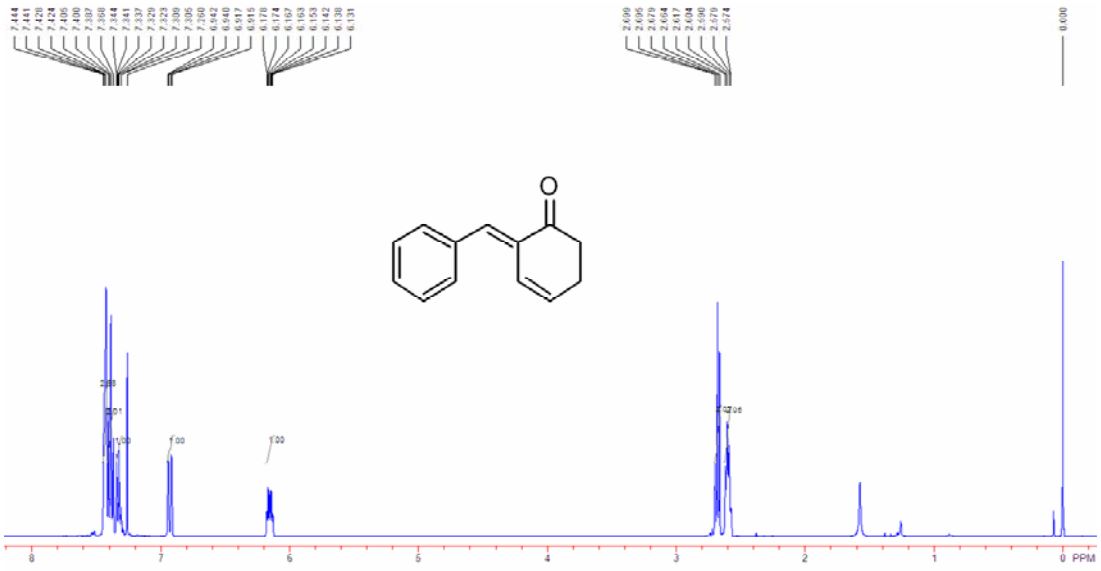
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)



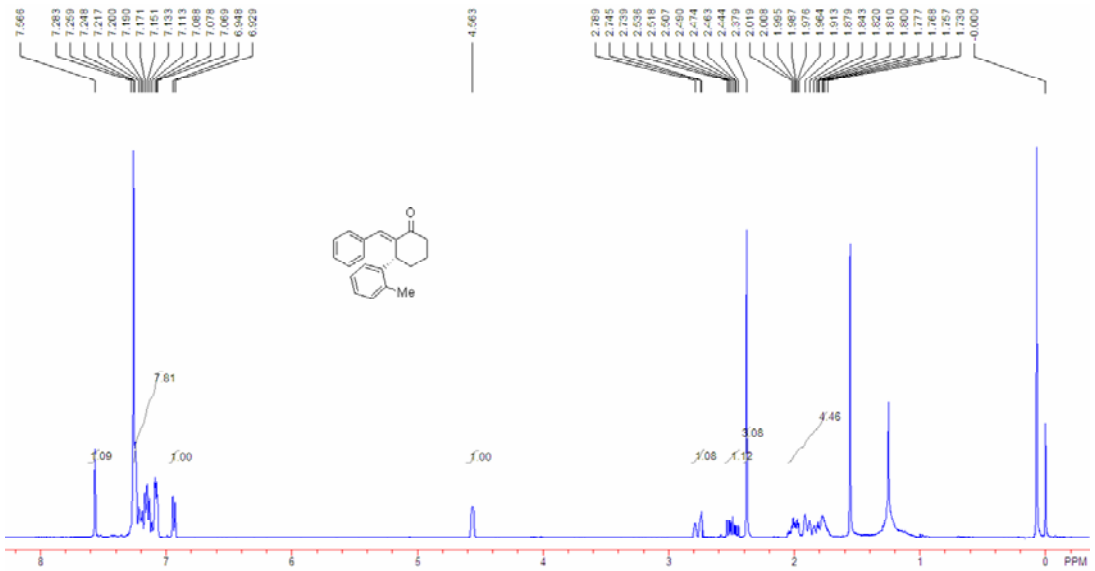
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		17.858	82396	3270826.8	19.5487	1.72	4034
2		19.722	234695	13460860.2	80.4513	1.73	2357
	Σ:		317091	16731687.0	100.0000		

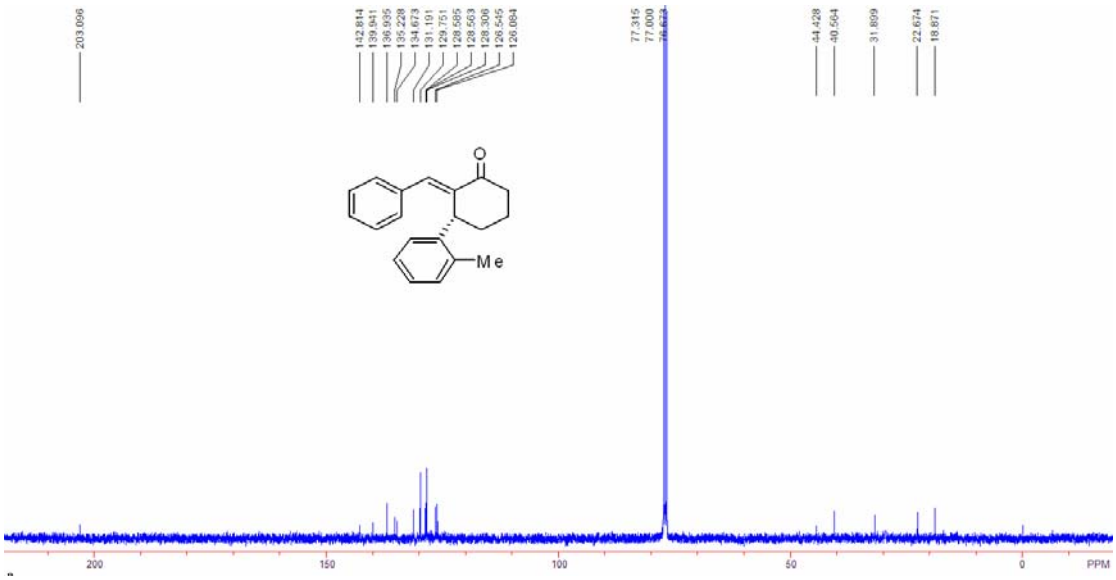
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

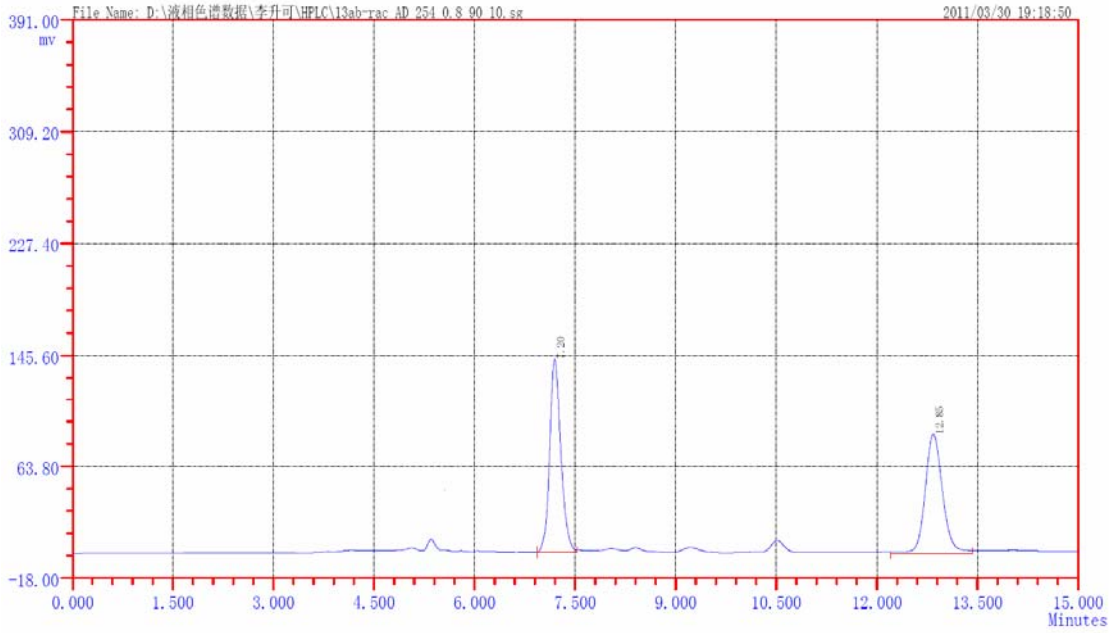
(*E*)-2-benzylidenecyclohex-3-enone **7a** (Table 1, entries 6-8):[4] ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.57-2.62 (m, 2H), 2.66-2.70 (m, 2H), 6.13-6.18 (m, 1H), 6.93 (dd, *J* = 0.8, 10.0 Hz, 1H), 7.31-7.34 (m, 1H), 7.37-7.41 (m, 2H), 7.42-7.44 (m, 3H).



(*R*,*E*)-2-benzylidene-3-o-tolylcyclohexanone **5ab** (Fig. 2, entry 1): $[\alpha]_D^{20}$ +16.8 (*c* 0.25, $CHCl_3$) for 93 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.73-2.02 (m, 4H), 2.38 (s, 3H), 2.44-2.54 (m, 1H), 2.74-2.79 (m, 1H), 4.56 (br s, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 7.07-7.25 (m, 8H), 7.57 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.9, 22.7, 31.9, 40.6, 44.4, 126.1, 126.5, 128.3, 128.56, 128.59, 129.8, 131.2, 134.7, 135.2, 136.9, 139.9, 142.8, 203.1. Chiralcel AD, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, t_{major} = 12.95 min, t_{minor} = 7.29 min.

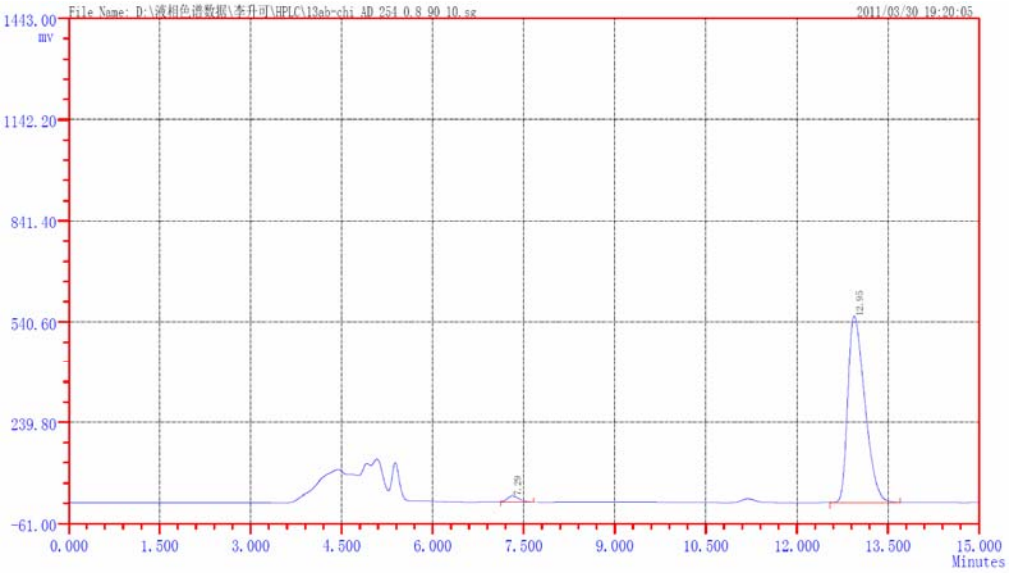






ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		7.195	142131	1616025.2	50.5612	1.27	7981
2		12.847	87322	1580154.1	49.4388	1.14	10045
	Σ:		229453	3196179.3	100.0000		

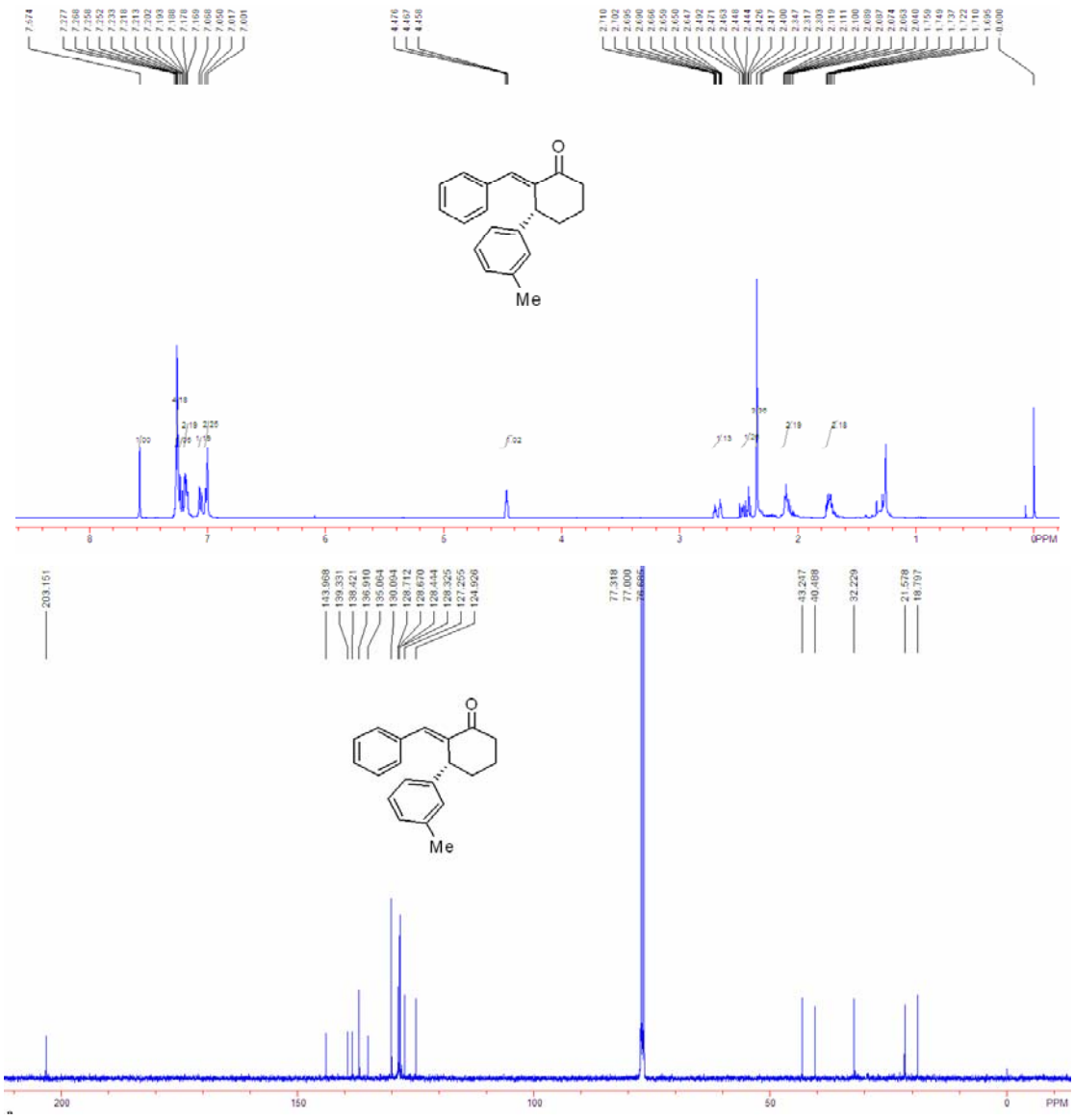
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

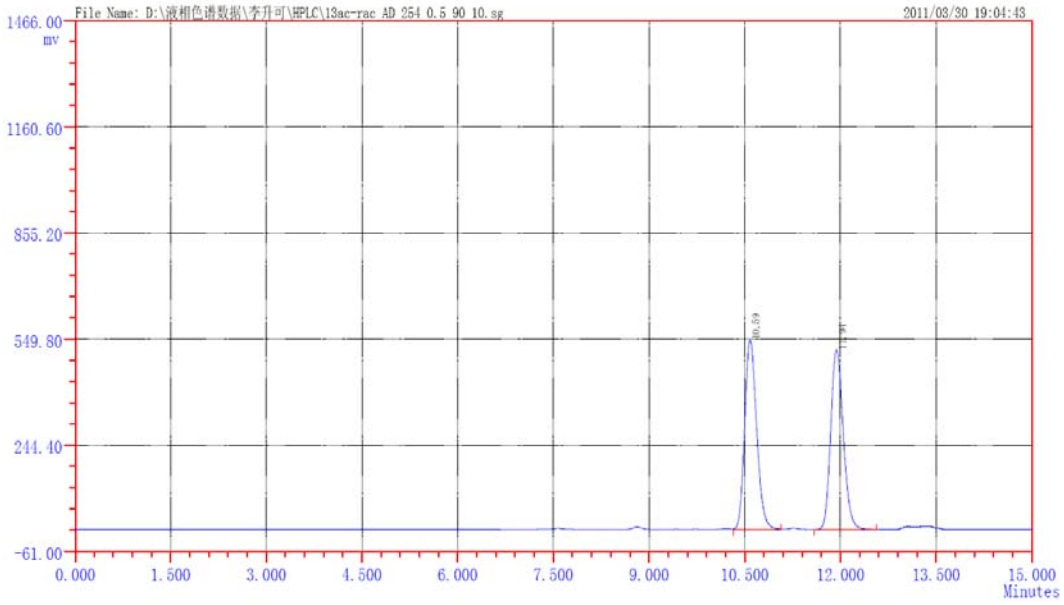


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		7.287	26760	387510.5	3.4405	2.59	5046
2		12.948	557486	10875659.0	96.5595	1.48	8780
	Σ:		584246	11263169.5	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

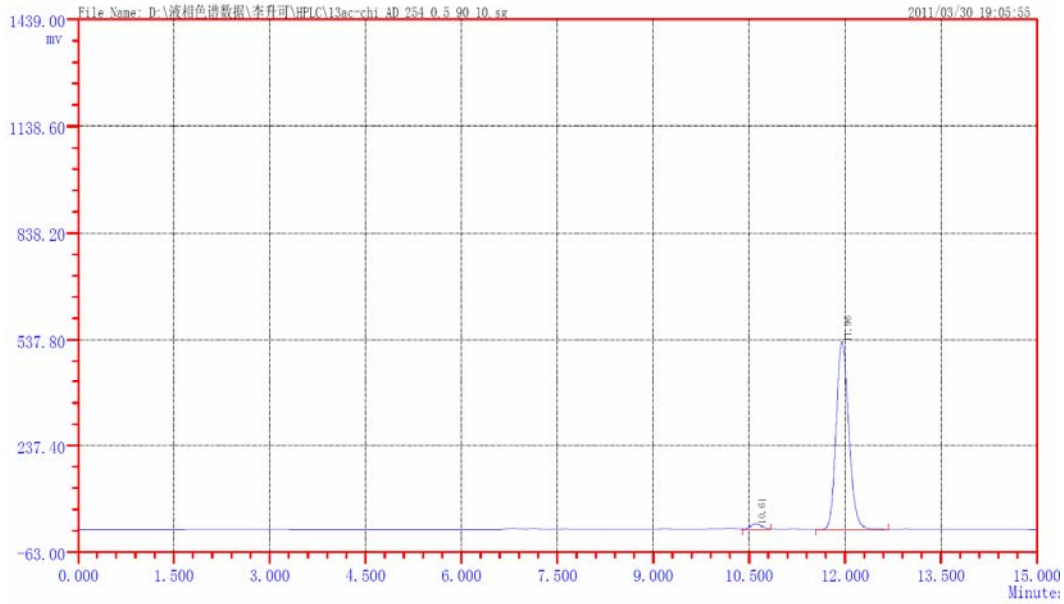
(*R*,*E*)-2-Benzylidene-3-*m*-tolylcyclohexanone **5ac** (Fig. 2, entry 2): $[\alpha]_D^{20}$ +152.4 (*c* 0.50, $CHCl_3$) for 95 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.70-1.76 (m, 2H), 2.04-2.12 (m, 2H), 2.35 (s, 3H), 2.40-2.49 (m, 1H), 2.65-2.71 (m, 1H), 4.47 (t, *J* = 3.6 Hz, 1H), 7.00-7.02 (m, 2H), 7.06 (d, *J* = 7.2 Hz, 1H), 7.17-7.20 (m, 2H), 7.21-7.23 (m, 1H), 7.25-7.28 (m, 3H), 7.57 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.8, 21.6, 32.2, 40.5, 43.2, 124.9, 127.3, 128.3, 128.4, 128.67, 128.71, 130.1, 135.1, 136.9, 138.4, 139.3, 144.0, 203.2. MS (ESI) *m/z* (%): 277.2 (M+H, 17.8); HRMS (Micromass LCT) Calcd. for $C_{20}H_{21}O$: 277.1592; Found: 277.1597. Chiralcel AD, hexane/*i*-PrOH = 90/10, 0.5 mL/min, 254 nm, t_{major} = 11.96 min, t_{minor} = 10.61 min.


Me
PPM
Me
PPM



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		10.587	546405	7161455.0	50.0953	1.20	13004
2		11.940	517680	7134200.3	49.9047	1.18	14961
	Σ:		1064085	14295655.3	100.0000		

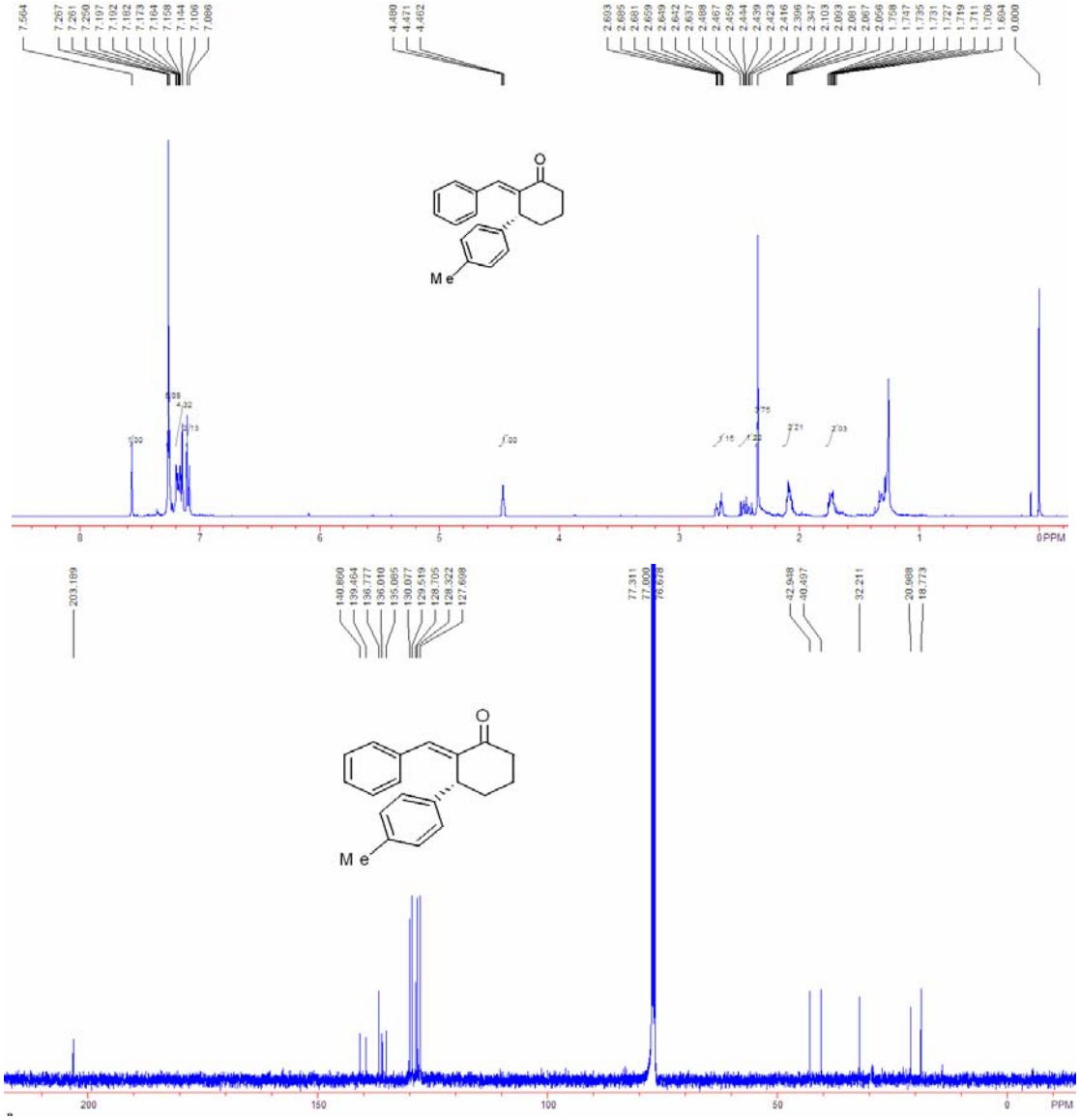
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

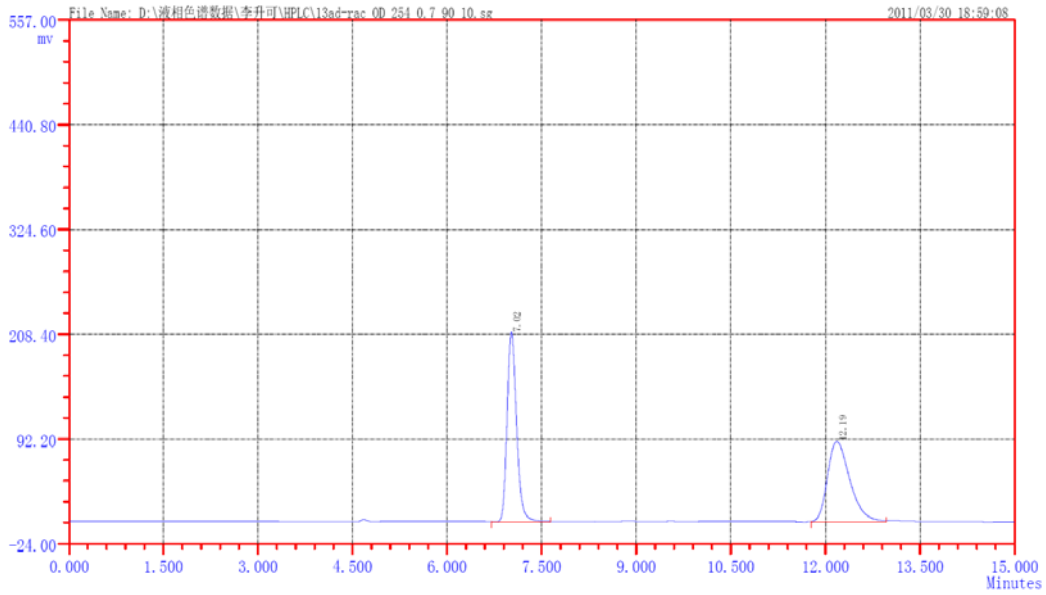


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		10.607	14573	180755.0	2.4097	1.13	14575
2		11.955	530777	7320247.3	97.5903	1.17	14976
	Σ:		545350	7501002.3	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

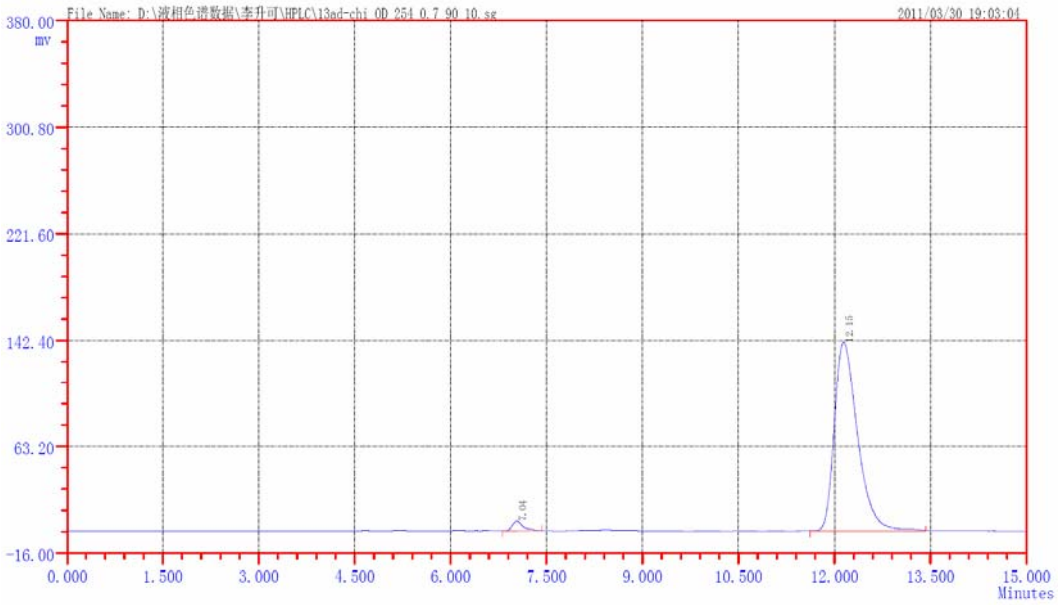
(*R*,*E*)-2-Benzylidene-3-*p*-tolylcyclohexanone **5ad**[2] (Fig. 2, entry 3): $[\alpha]_D^{20}$ +67.1 (*c* 0.35, $CHCl_3$) for 95 % ee. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.69-1.76 (m, 2H), 2.06-2.10 (m, 2H), 2.35 (s, 3H), 2.40-2.49 (m, 1H), 2.64-2.69 (m, 1H), 4.47 (t, *J* = 3.6 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.14-7.20 (m, 4H), 7.25-7.27 (m, 3H), 7.56 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.8, 21.0, 32.2, 40.5, 42.9, 127.7, 128.3, 128.7, 129.5, 130.1, 135.1, 136.0, 136.8, 139.5, 140.9, 203.2. MS (ESI) *m/z* (%): 277.2 (M+H, 100); HRMS (Micromass LCT) Calcd. for $C_{20}H_{21}O$: 277.1592; Found: 277.1588. Chiralcel OD, hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm, t_{major} = 12.15 min, t_{minor} = 7.04 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		7.020	210789	2231957.4	50.0003	1.23	8760
2		12.187	89701	2231929.4	49.9997	1.37	4781
	Σ:		300490	4463886.7	100.0000		

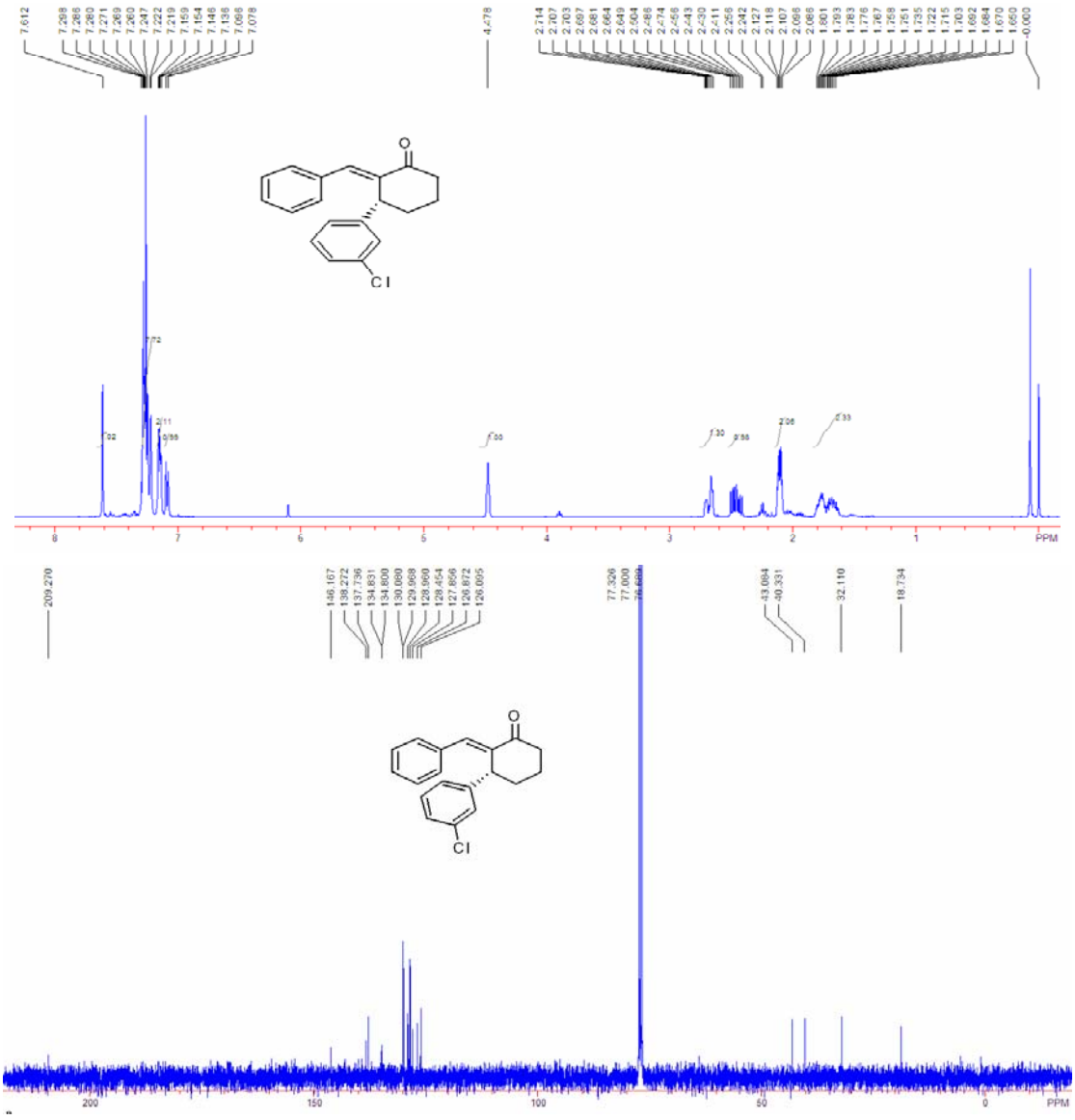
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

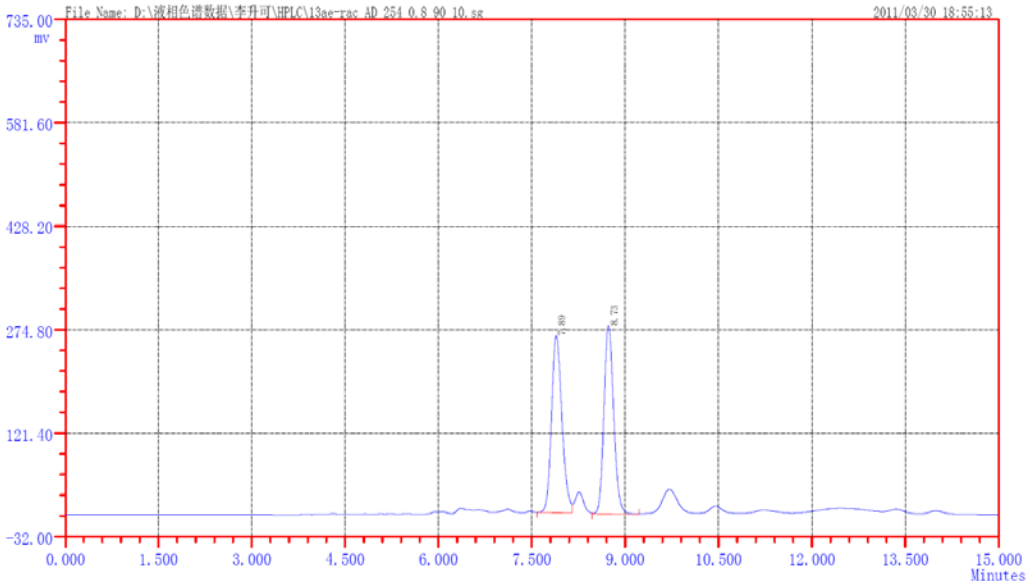


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		7.035	7641	92004.1	2.5179	1.59	6804
2		12.147	140689	3562002.1	97.4821	1.44	4587
	Σ:		148330	3654006.2	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

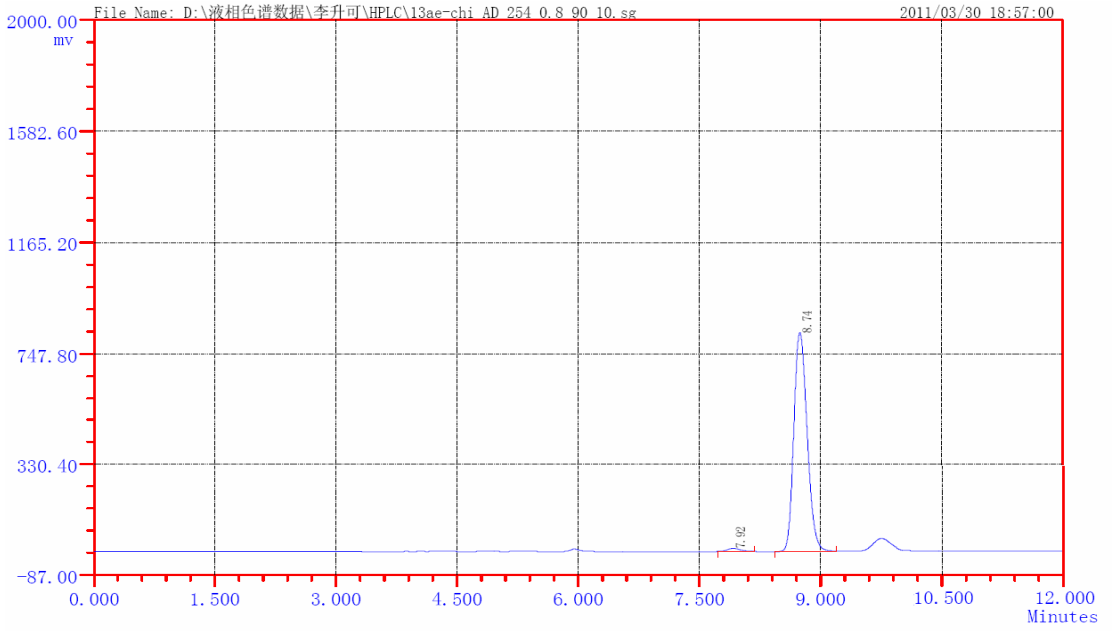
(*R*,*E*)-2-Benzylidene-3-(3-chlorophenyl)cyclohexanone **5ae**. (Fig. 2, entry 4): $[\alpha]_D^{20}$ +47.1 (*c* 0.39, $CHCl_3$) for 97 % ee. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.64-1.80 (m, 2H), 2.09-2.13 (m, 2H), 2.41-2.50 (m, 1H), 2.65-2.71 (m, 1H), 4.48 (br s, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.14-7.16 (m, 2H), 7.22-7.30 (m, 6H), 7.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.7, 32.1, 40.3, 43.1, 126.1, 126.9, 127.9, 128.5, 129.0, 130.0, 130.1, 134.80, 134.83, 137.7, 138.3, 146.2, 209.3. MS (ESI) *m/z* (%): 297.1 (M+H, 100); HRMS (Micromass LCT) Calcd. for $C_{19}H_{18}ClO$: 297.1046; Found: 297.1049. Chiralcel AD, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, t_{major} = 8.74 min, t_{minor} = 7.92 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		7.893	263082	3058241.8	50.1847	1.23	9189
2		8.732	279663	3035733.5	49.8153	1.15	12896
	Σ:		542745	6093975.3	100.0000		

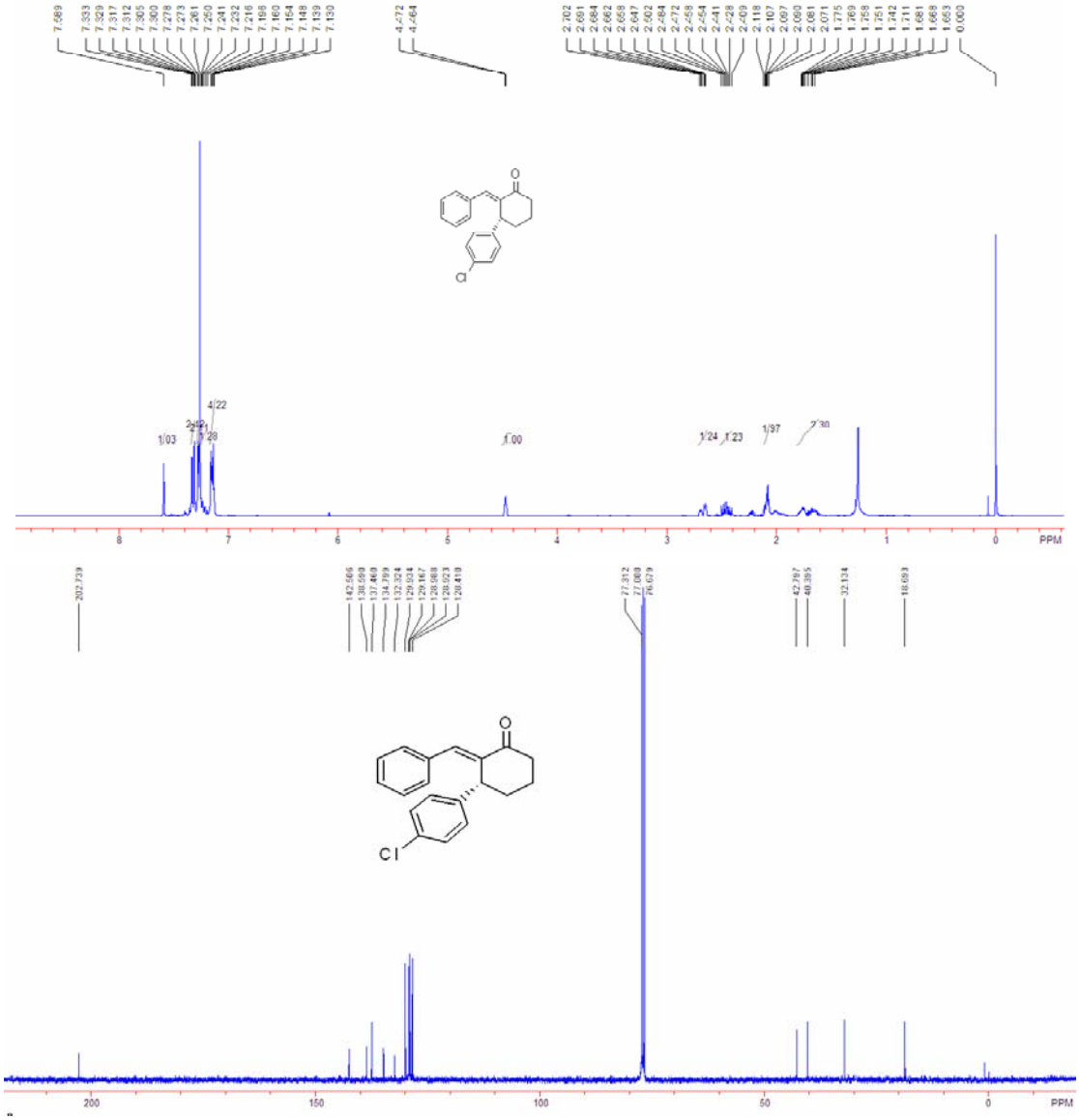
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

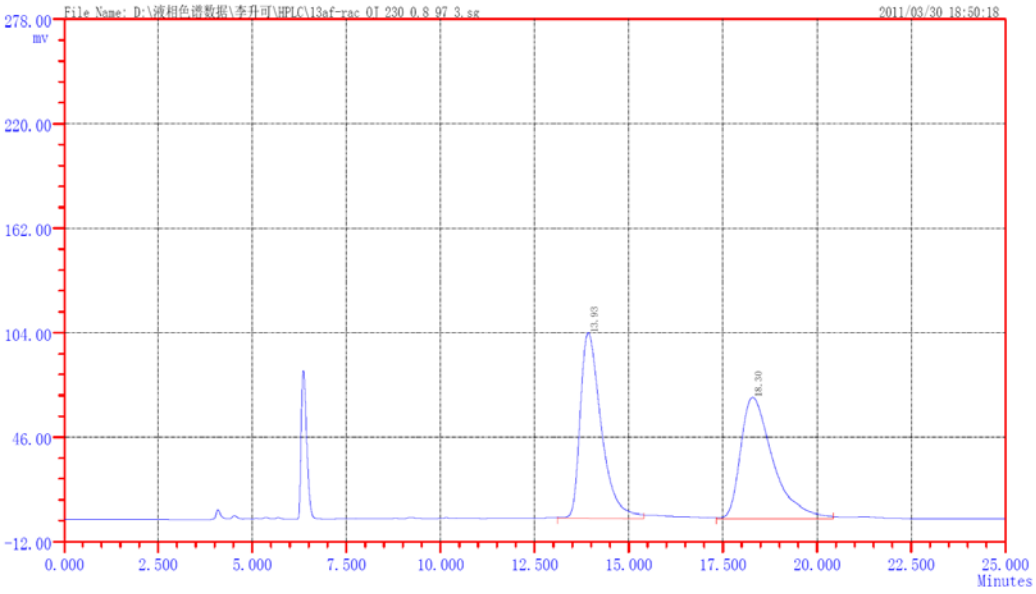


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		7.918	11371	131407.3	1.3678	1.21	9357
2		8.743	826046	9475694.6	98.6322	1.20	11579
	Σ:		837417	9607101.8	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

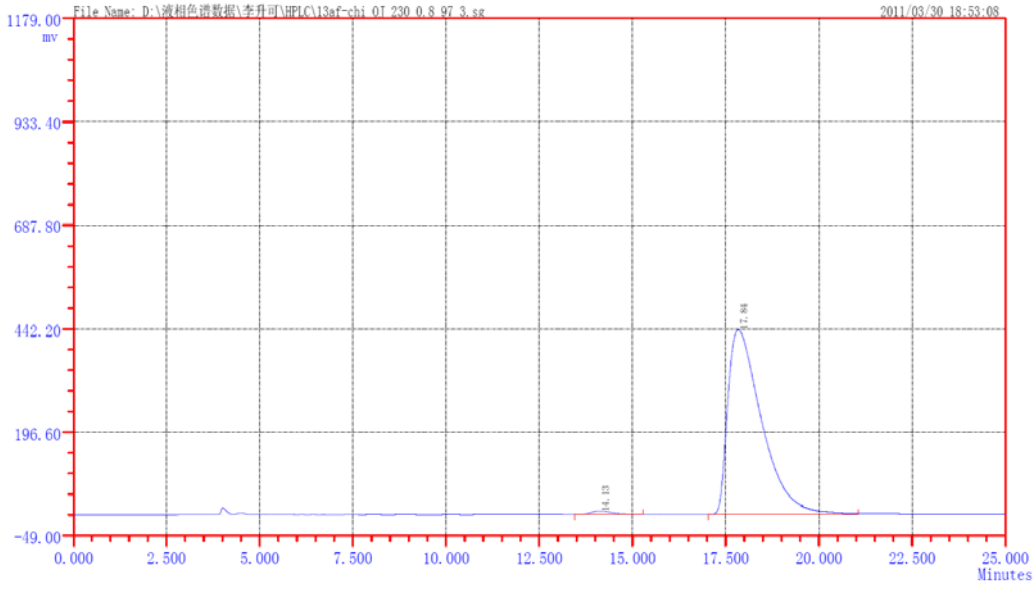
(*R*,*E*)-2-benzylidene-3-(4-chlorophenyl)cyclohexanone **5af**. (Fig. 2, entry 5): $[\alpha]_D^{20}$ +267.9 (*c* 0.47, $CHCl_3$) for 98 % ee. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.62-1.79 (m, 2H), 2.07-2.12 (m, 2H), 2.41-2.48 (m, 1H), 2.65-2.70 (m, 1H), 4.47 (t, *J* = 3.2 Hz, 1H), 7.13-7.16 (m, 4H), 7.20-7.25 (m, 1H), 7.27-7.28 (m, 2H), 7.32 (dd, *J* = 1.6, 6.4 Hz, 2H), 7.59 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.7, 32.1, 40.4, 42.8, 128.4, 128.9, 129.0, 129.2, 129.9, 132.3, 134.8, 137.5, 138.6, 142.5, 202.7. MS (ESI) *m/z* (%): 297.1 (M+H, 38); HRMS (Micromass LCT) Calcd. for $C_{19}H_{18}ClO$: 297.1046; Found: 297.1049. Chiralcel OJ, hexane/*i*-PrOH = 97/3, 0.8 mL/min, 230 nm, t_{major} = 17.84 min, t_{minor} = 14.13 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		13.928	103035	4013871.6	50.0523	1.61	2548
2		18.302	67311	4005475.5	49.9477	1.68	1885
	Σ:		170346	8019347.1	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

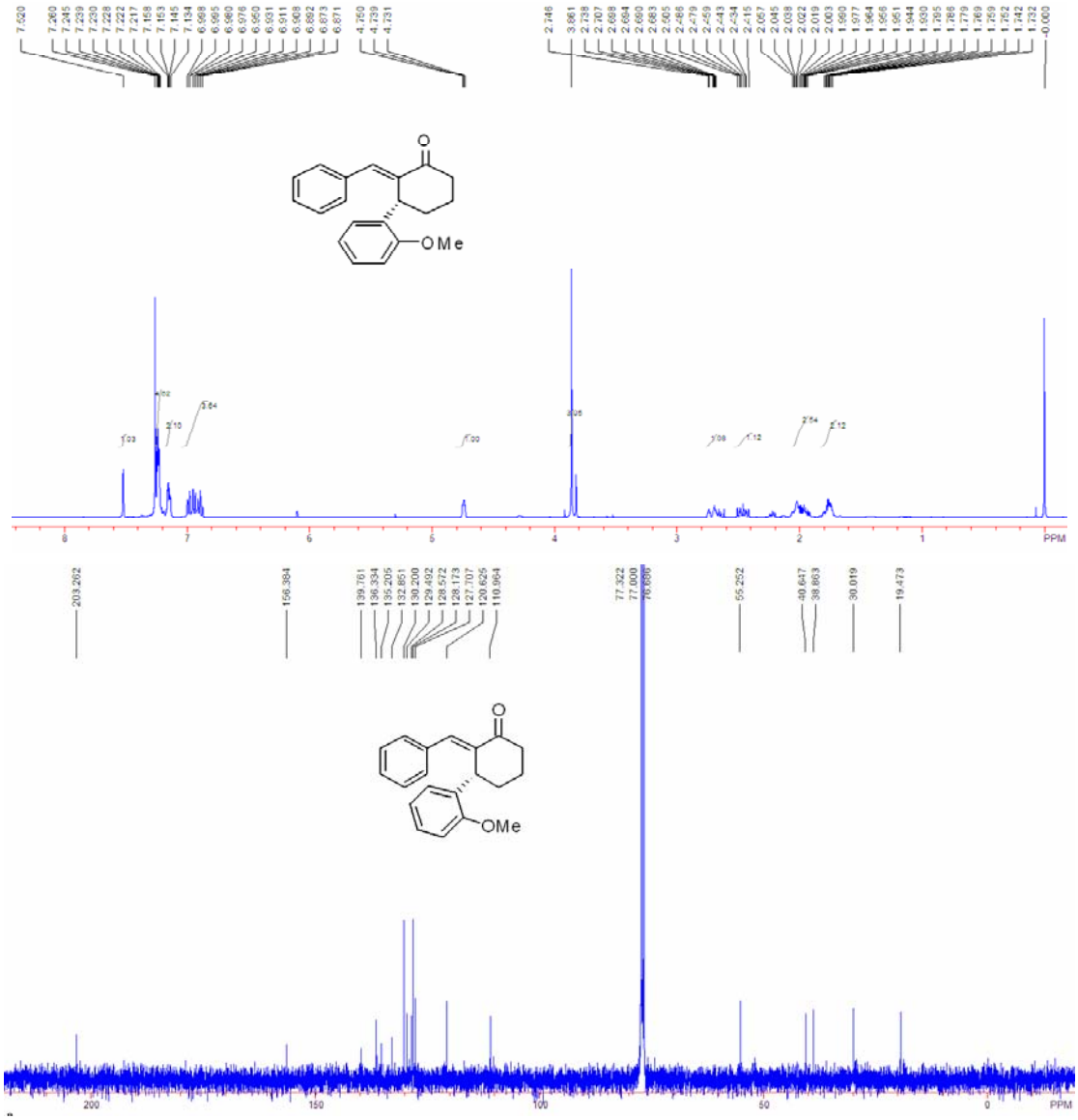


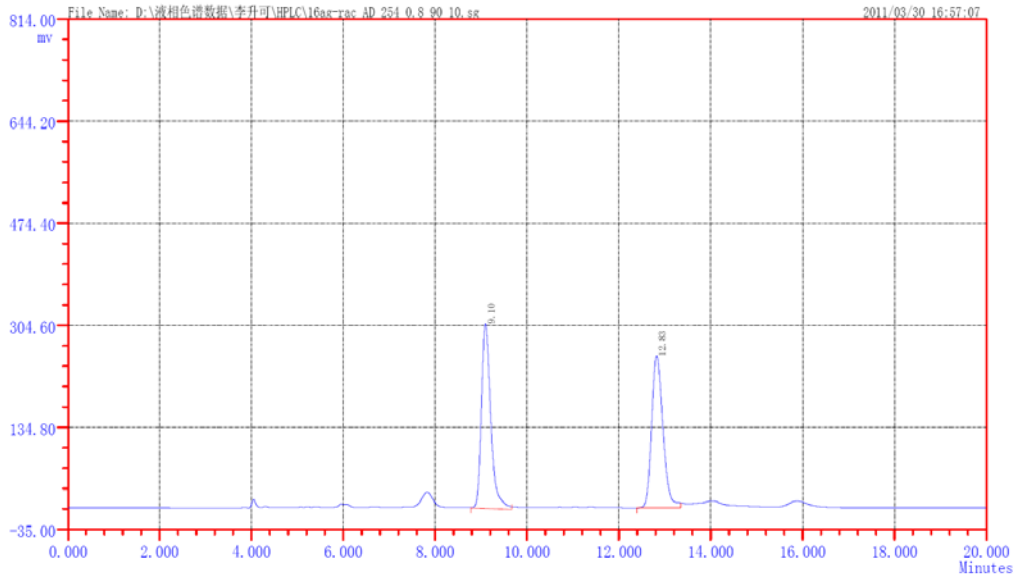
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		14.132	8302	317994.2	1.1300	1.50	2713
2		17.842	439421	27823594.6	98.8700	2.12	1582
	Σ:		447723	28141588.8	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

(*R*,*E*)-2-Benzylidene-3-(2-methoxyphenyl)cyclohexanone **5ag**. (Fig. 2, entry 6): $[\alpha]_D^{20}$ +37.2 (*c* 0.52, $CHCl_3$) for 94 % ee. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.73-1.81

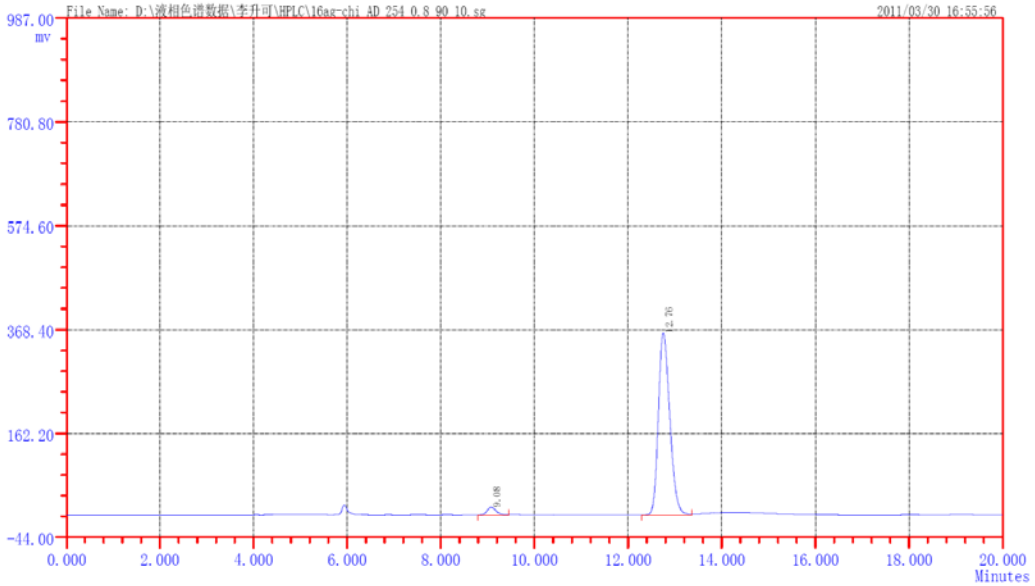
(m, 2H), 1.93-2.06 (m, 2H), 2.42-2.51 (m, 1H), 2.64-2.75 (m, 1H), 3.86 (s, 3H), 4.74 (t, J = 4.4 Hz, 1H), 6.87-7.00 (m, 3H), 7.13-7.16 (m, 2H), 7.22-7.25 (m, 4H), 7.52 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.5, 30.0, 38.9, 40.6, 55.3, 111.0, 120.6, 127.7, 128.2, 128.6, 129.5, 130.2, 132.9, 135.2, 136.3, 139.8, 156.4, 203.3. MS (ESI) *m/z* (%): 297.1 (M, 100); HRMS (Micromass LCT) Calcd. for $C_{20}H_{20}O_2$: 292.1463; Found: 292.1467. Chiralcel AD, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, t_{major} = 12.76 min, t_{minor} = 9.08 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		9.097	306894	4362069.4	49.9876	1.37	8164
2		12.825	253365	4364233.0	50.0124	1.24	11049
	Σ:		560259	8726302.4	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

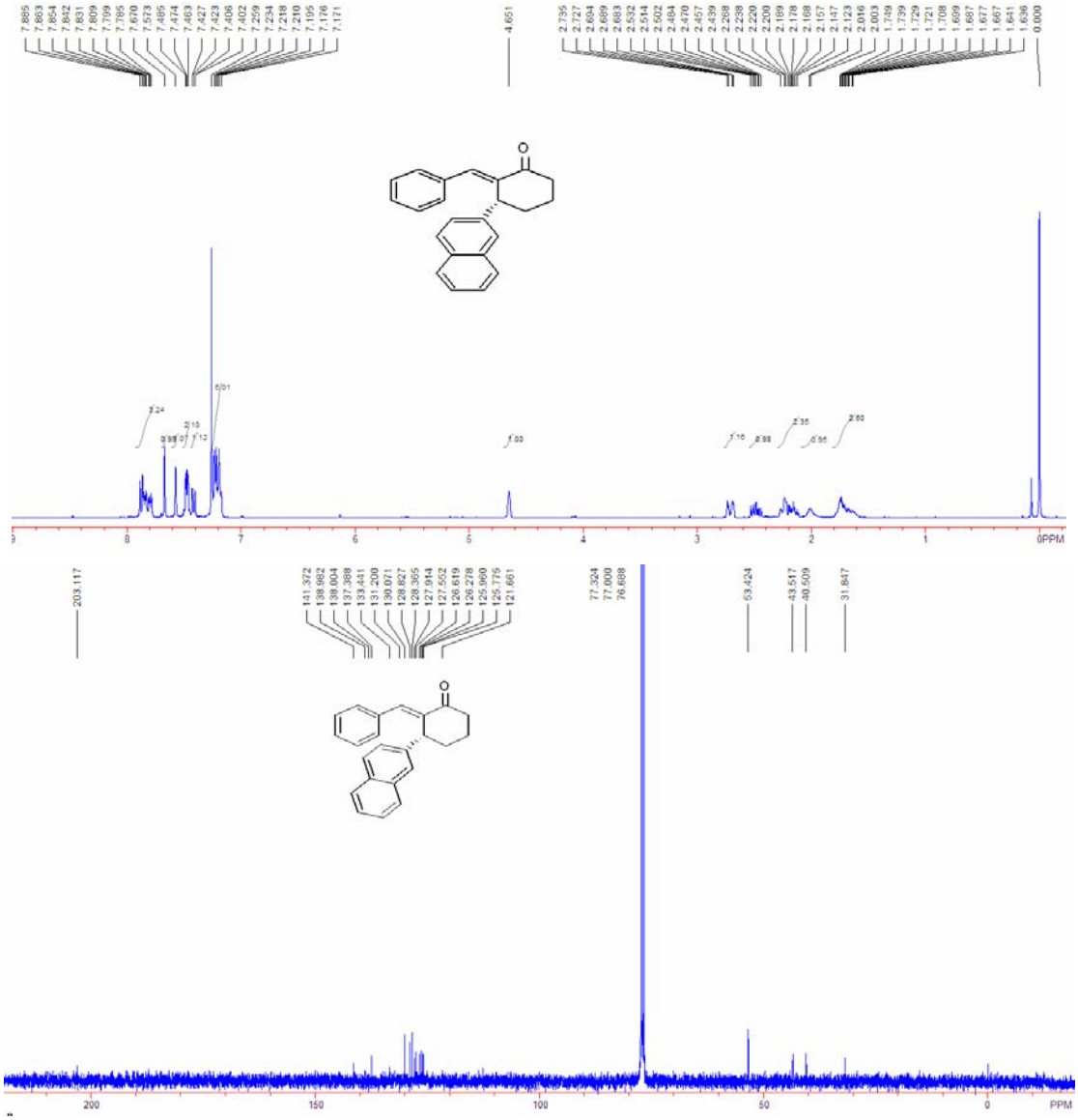


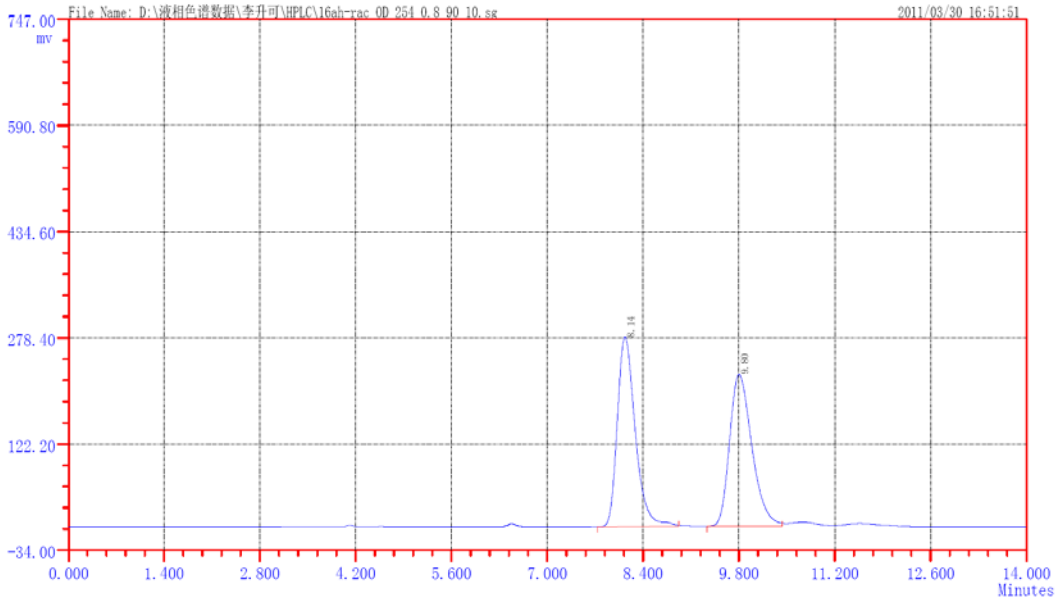
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		9.075	14895	201283.8	3.1800	1.27	8988
2		12.755	361174	6128310.8	96.8200	1.23	11263
	Σ:		376069	6329594.7	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

(*R*,*E*)-2-Benzylidene-3-(naphthalen-2-yl)cyclohexanone **5ah**. (Fig. 2, entry 7): $[\alpha]_D^{20}$ +25.4 (*c* 1.20, $CHCl_3$) for 98 % ee. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.62-1.75

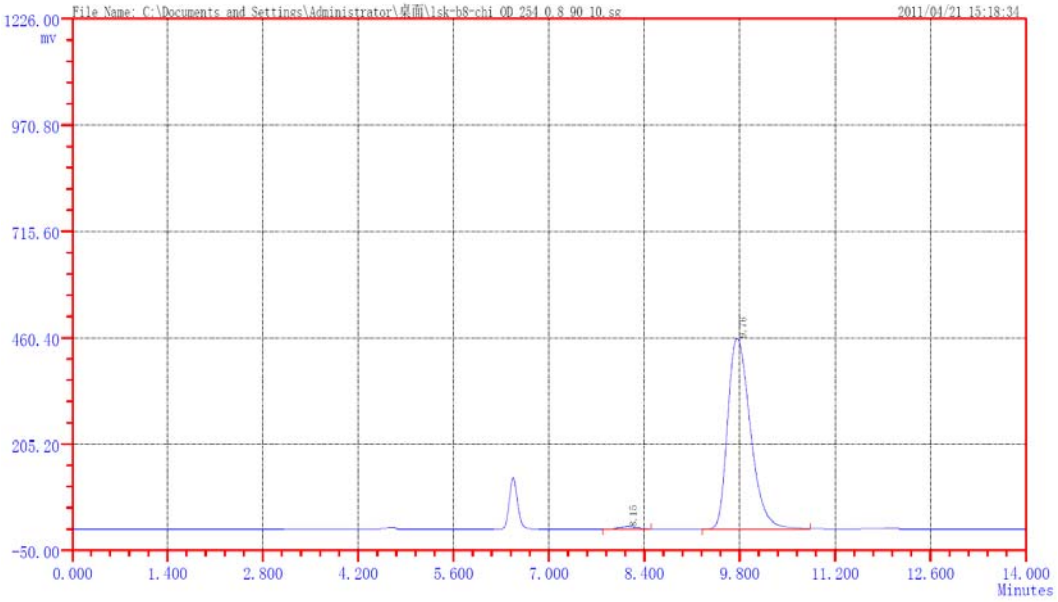
(m, 2H), 2.15-2.27 (m, 2H), 2.44-2.53 (m, 1H), 2.68-2.74 (m, 1H), 4.65 (br s, 1H), 7.17-7.23 (m, 5H), 7.41 (dd, J = 1.6, 8.4 Hz, 1H), 7.45-7.50 (m, 2H), 7.57 (s, 1H), 7.67 (s, 1H), 7.79-7.89 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 31.8, 40.5, 43.5, 53.4, 121.7, 125.8, 126.0, 126.3, 126.6, 127.6, 127.9, 128.4, 128.8, 130.1, 131.2, 133.4, 137.4, 138.0, 139.0, 141.4, 203.1. MS (ESI) *m/z* (%): 313.2 (M+H, 62); HRMS (Micromass LCT) Calcd. for $C_{23}H_{21}O$: 313.1592; Found: 313.1594. Chiralcel OD, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, t_{major} = 9.76 min, t_{minor} = 8.15 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		8.137	278771	5094116.7	50.0385	1.34	3952
2		9.805	223386	5086279.5	49.9615	1.33	3696
	Σ:		502157	10180396.2	100.0000		

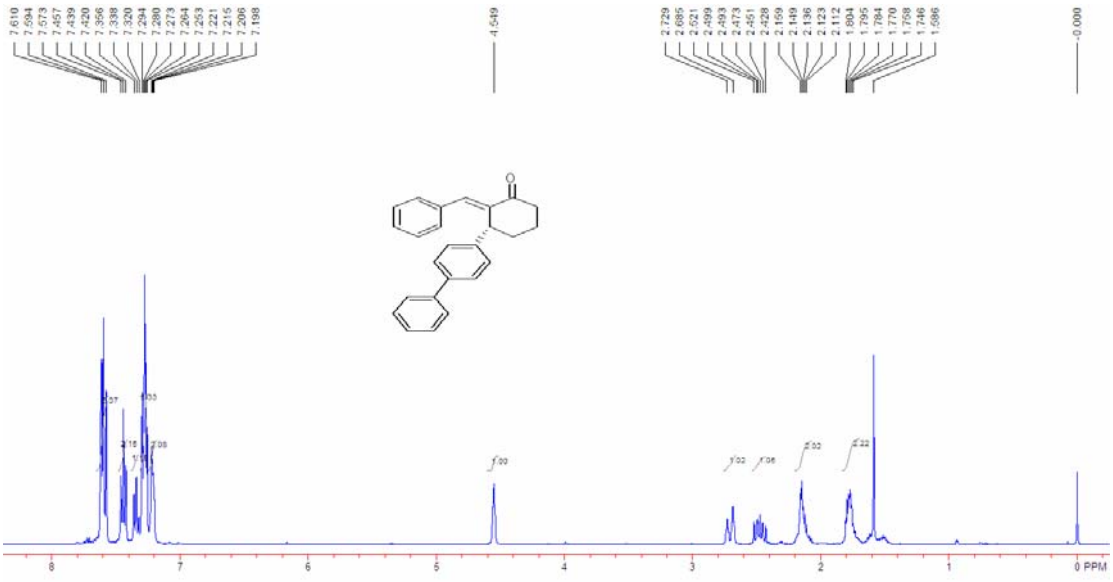
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

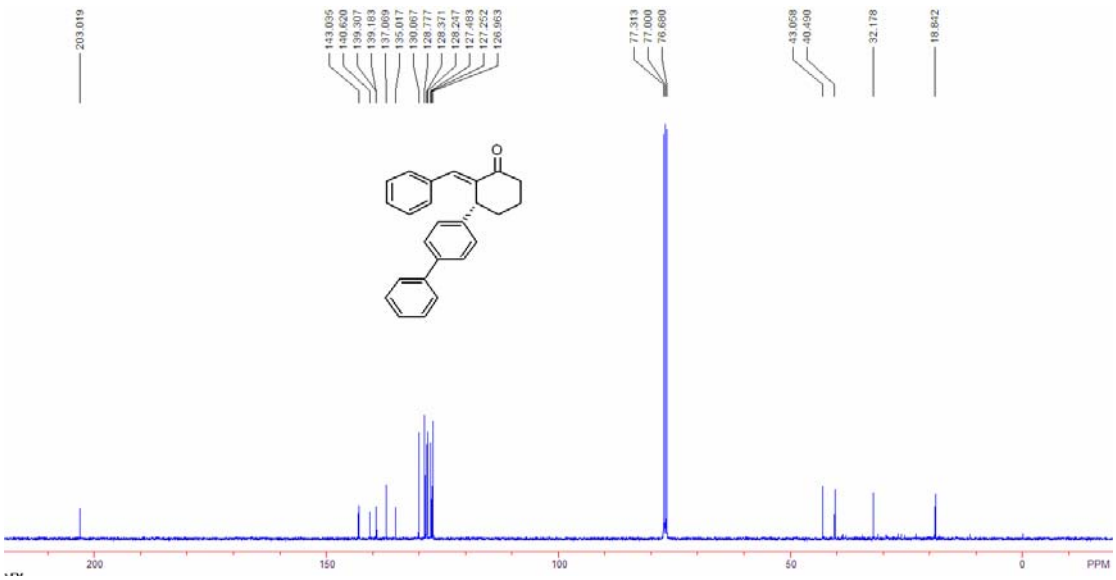


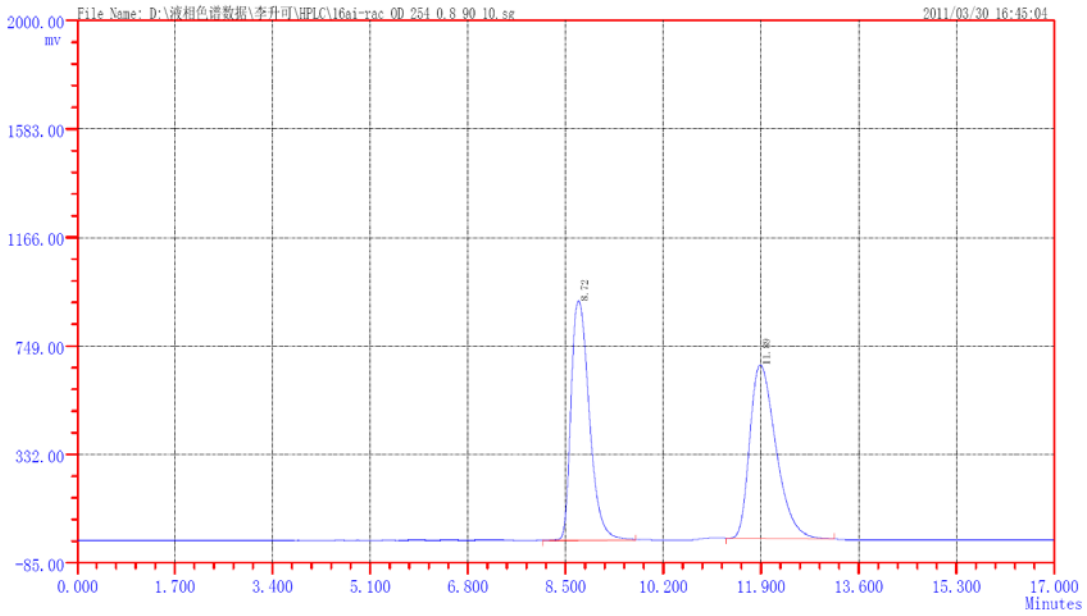
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		8.152	6089	110059.8	1.0225	1.16	4054
2		9.763	458217	10653888.8	98.9775	1.37	3514
	Σ:		464306	10763948.6	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

(*R*,*E*)-2-benzylidene-3-(biphenyl-4-yl)cyclohexanone **5ai**. (Fig. 2, entry 8): $[\alpha]_D^{20}$ +134.8 (*c* 0.77, $CHCl_3$) for 99 % ee. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.75-1.80 (m, 2H), 2.11-2.16 (m, 2H), 2.43-2.52 (m, 1H), 2.68-2.73 (m, 1H), 4.55 (br s, 1H), 7.20-7.22 (m, 2H), 7.25-7.29 (m, 5H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 2H), 7.57-7.61 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.8, 32.2, 40.5, 43.1, 127.0, 127.3, 127.5, 128.2, 128.4, 128.8, 130.1, 135.0, 137.1, 139.2, 139.3, 140.6, 143.0, 203.0. MS (ESI) *m/z* (%): 377.1 (M+K, 20); HRMS (Micromass LCT) Calcd. for $C_{25}H_{22}KO$: 377.1308; Found: 377.1329. Chiralcel OD, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, t_{major} = 12.02 min, t_{minor} = 8.83 min.

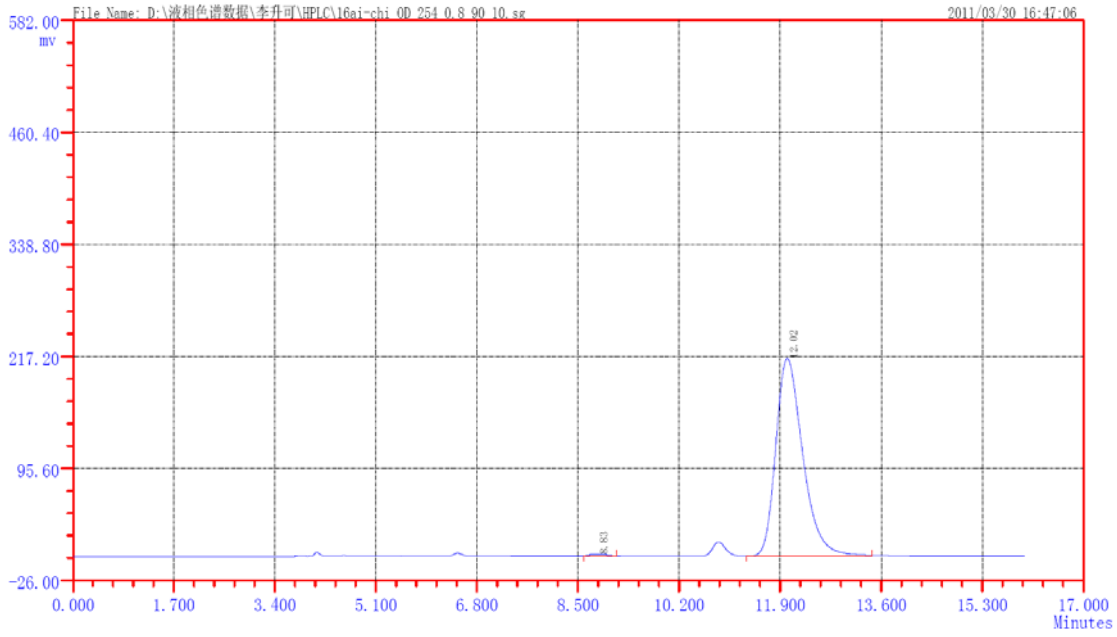






ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		8.725	920113	20427642.4	49.0233	1.43	3078
2		11.892	667948	21241594.7	50.9767	1.42	2787
	Σ:		1588061	41669237.1	100.0000		

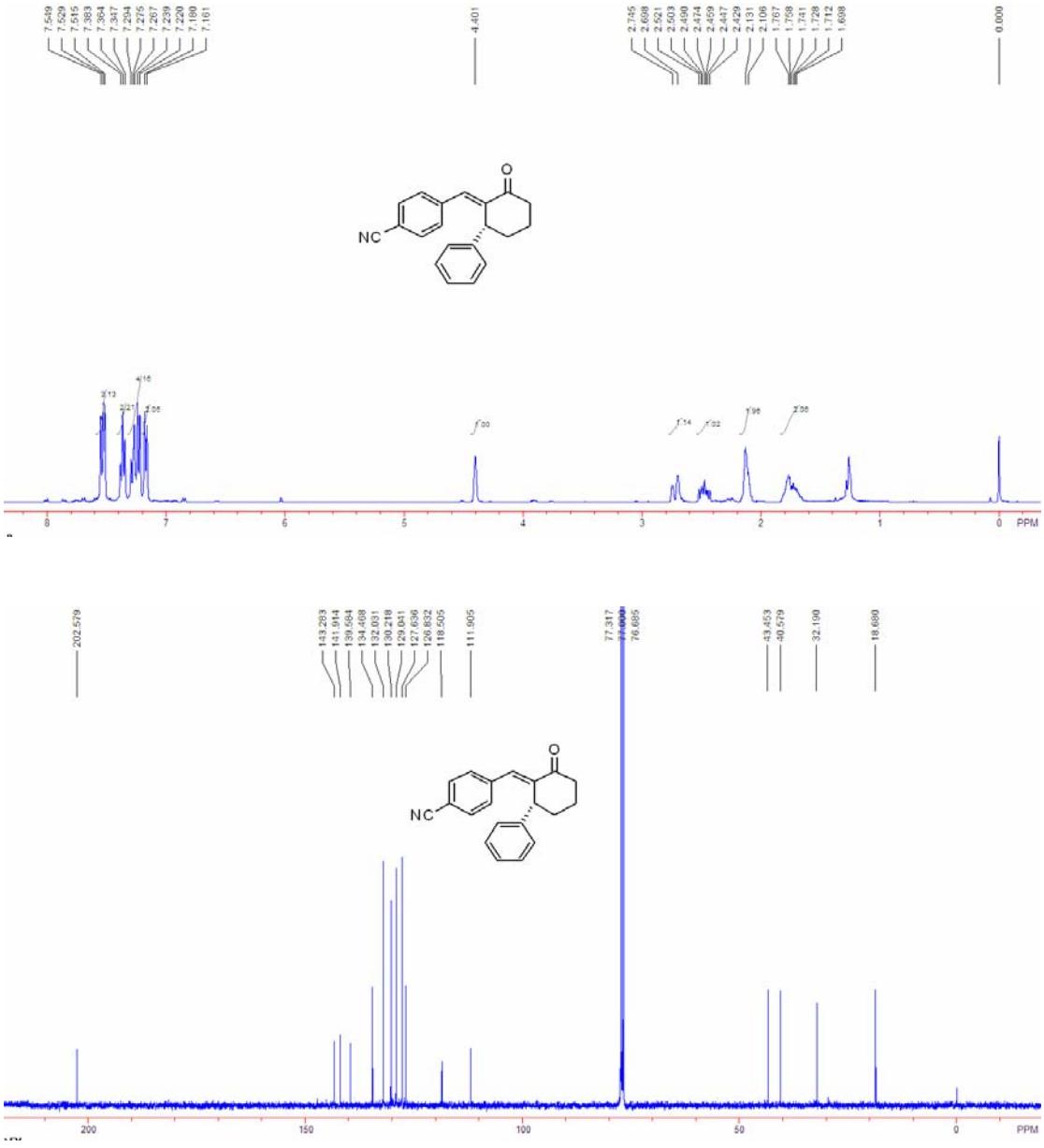
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

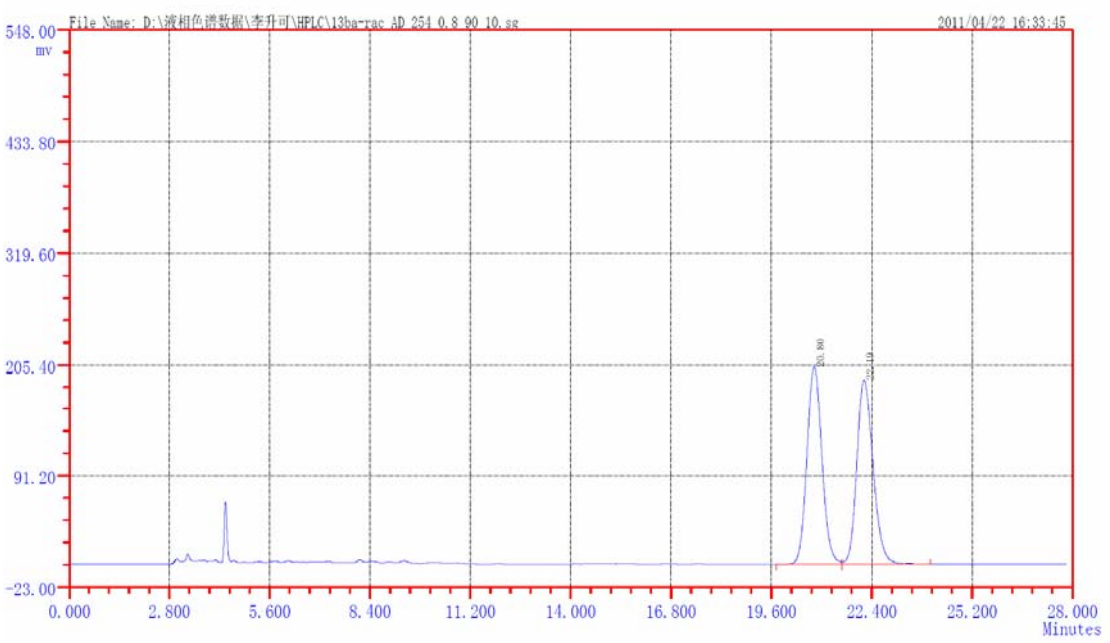


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		8.832	2145	41703.1	0.6098	1.19	4113
2		12.022	214738	6797289.8	99.3902	1.35	2875
	Σ:		216883	6838992.9	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

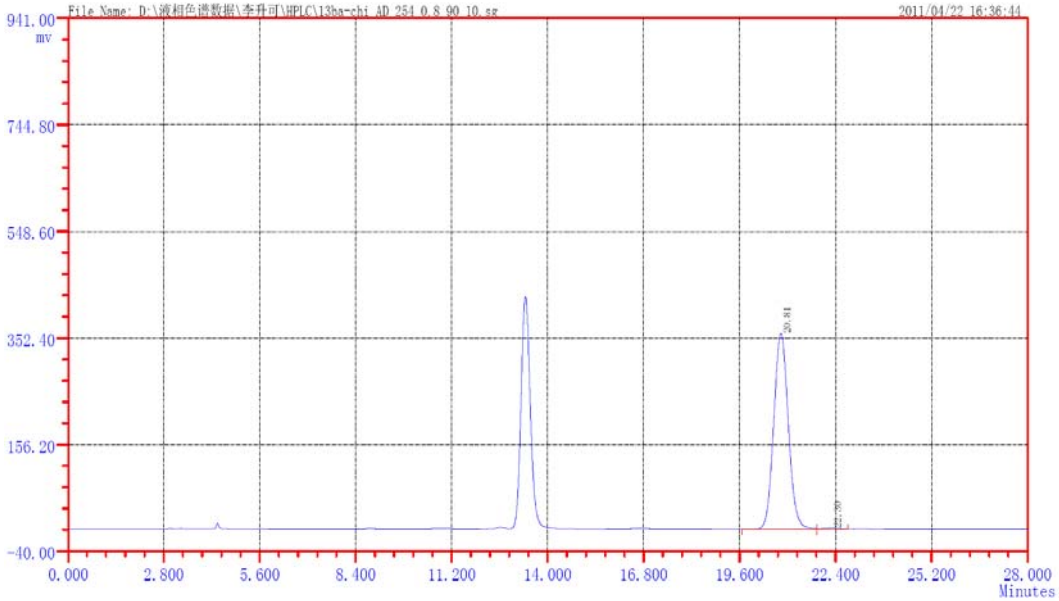
(*R*,*E*)-4-((2-oxo-6-phenylcyclohexylidene)methyl)benzonitrile **5ba** (Fig. 2, entry 9): $[\alpha]_D^{20}$ +127.6 (*c* 0.30, $CHCl_3$) for 99 % ee. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.70-1.77 (m, 2H), 2.10-2.13 (m, 2H), 2.43-2.52 (m, 1H), 2.70-2.75 (m, 1H), 4.40 (br s, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.22-7.29 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 5.6 Hz, 2H), 7.55 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.7, 32.2, 40.6, 43.5, 111.9, 118.5, 126.8, 127.6, 129.0, 130.2, 132.0, 134.5, 139.6, 141.9, 143.3, 202.6. MS (EI) *m/z* (%): 288.1 (M+H, 100); HRMS (Micromass LCT) Calcd. for $C_{20}H_{18}NO$: 288.1388; Found: 288.1376. Chiralcel AD, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, t_{major} = 20.81 min, t_{minor} = 22.30 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		20.798	203602	5936662.4	49.8539	1.10	10141
2		22.193	189496	5971469.1	50.1461	1.20	9886
	Σ:		393098	11908131.5	100.0000		

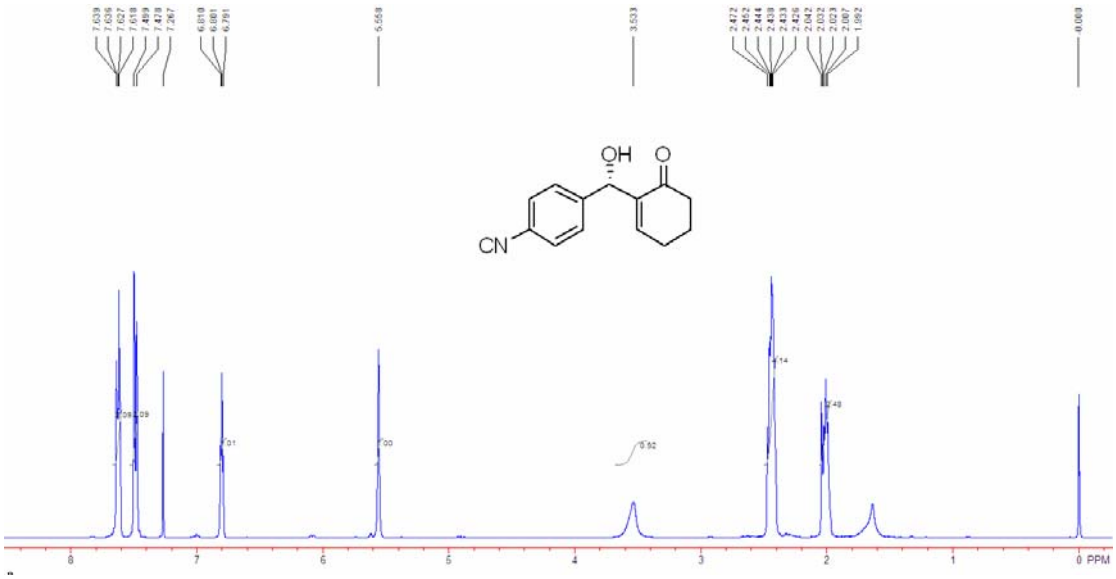
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

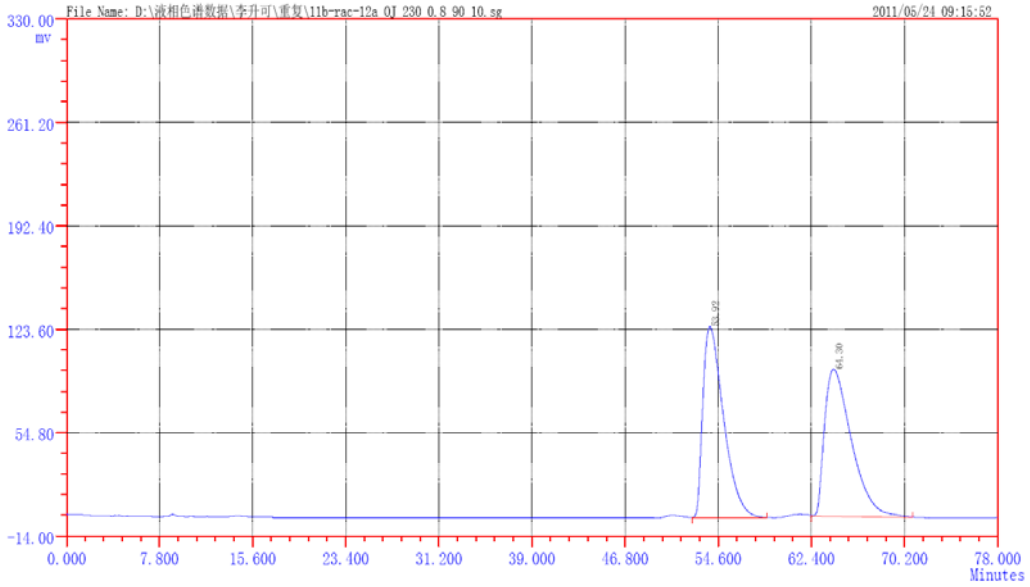


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		20.810	360397	10668925.9	99.2816	1.08	9849
2		22.302	2296	77204.6	0.7184	1.02	8767
	Σ:		362693	10746130.5	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

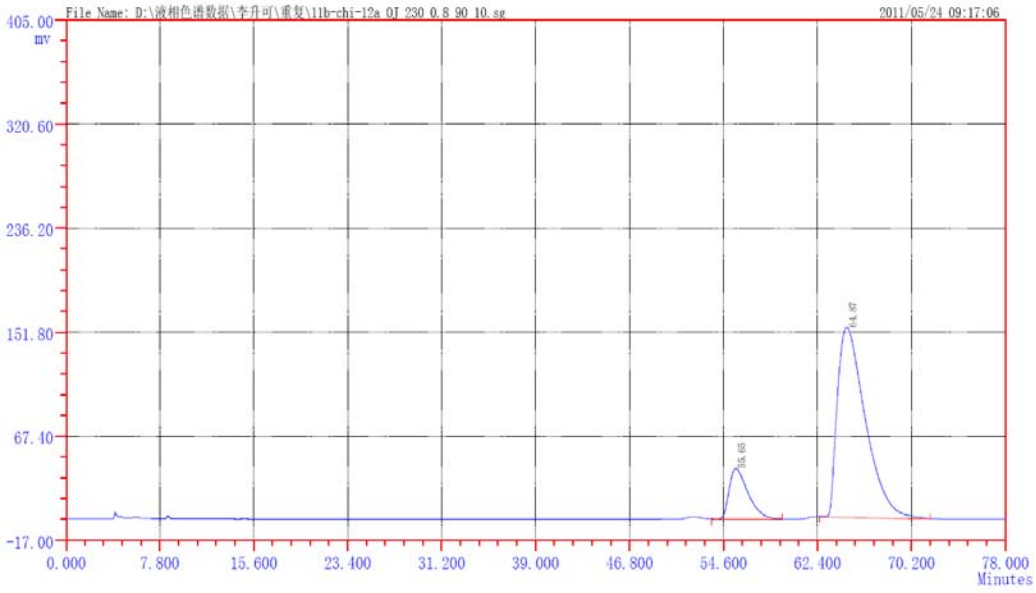
(*S*)-2-(hydroxy(4-isocyanophenyl)methyl)cyclohex-2-enone **3b**.[5] $[\alpha]_D^{20}$ +31.3 (*c* 0.60, CH_2Cl_2) for 70 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.99-2.04 (m, 2H), 2.43-2.47 (m, 4H), 3.53 (br s, 1H), 5.56 (s, 1H), 6.80 (t, *J* = 4.0 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H). Chiralcel OJ, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 230 nm, t_{major} = 64.87 min, t_{minor} = 55.65 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		53.917	127212	15405059.5	49.9979	1.86	3951
2		64.295	98230	15406337.1	50.0021	1.88	3349
	Σ:		225442	30811396.6	100.0000		

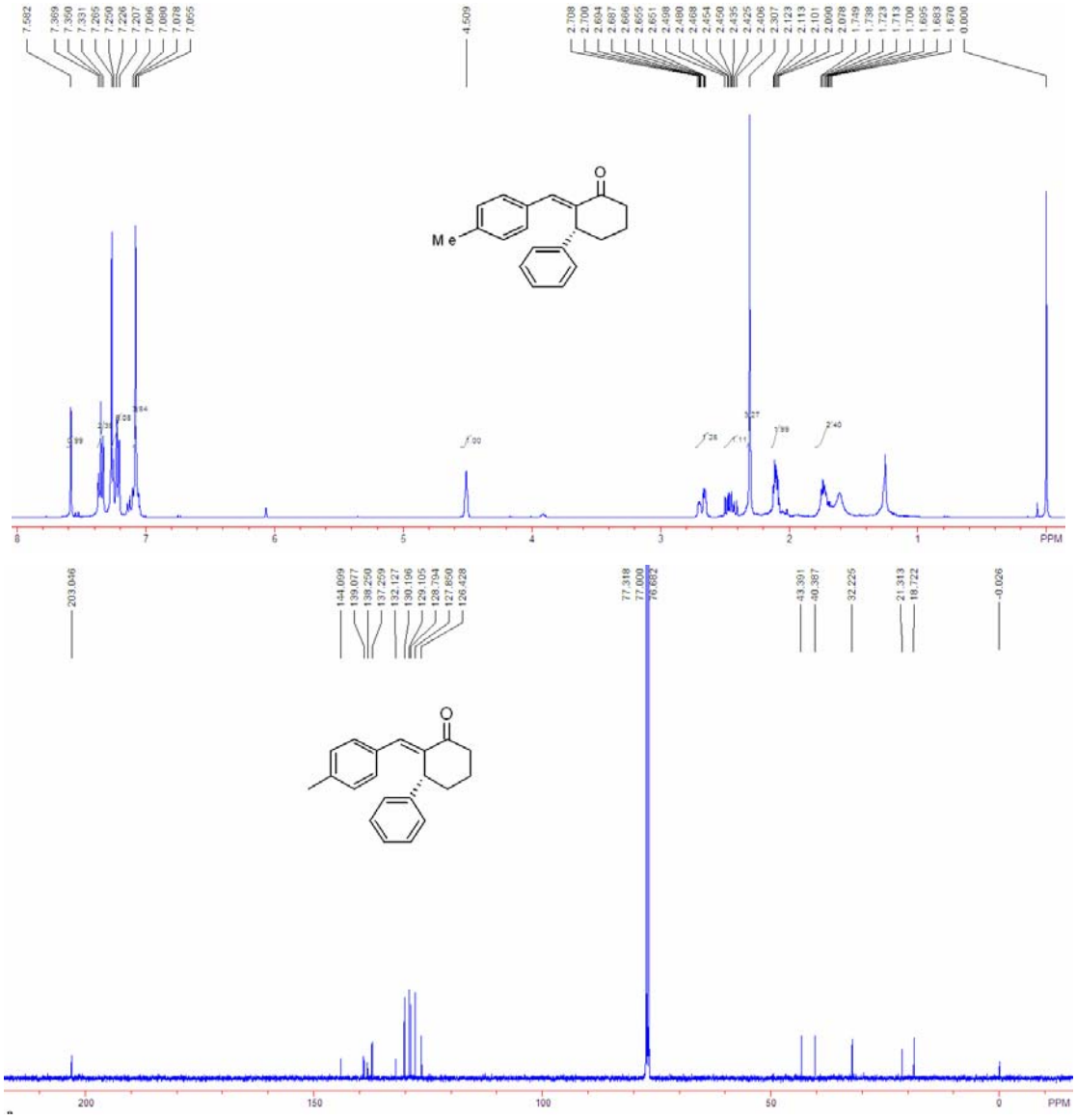
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

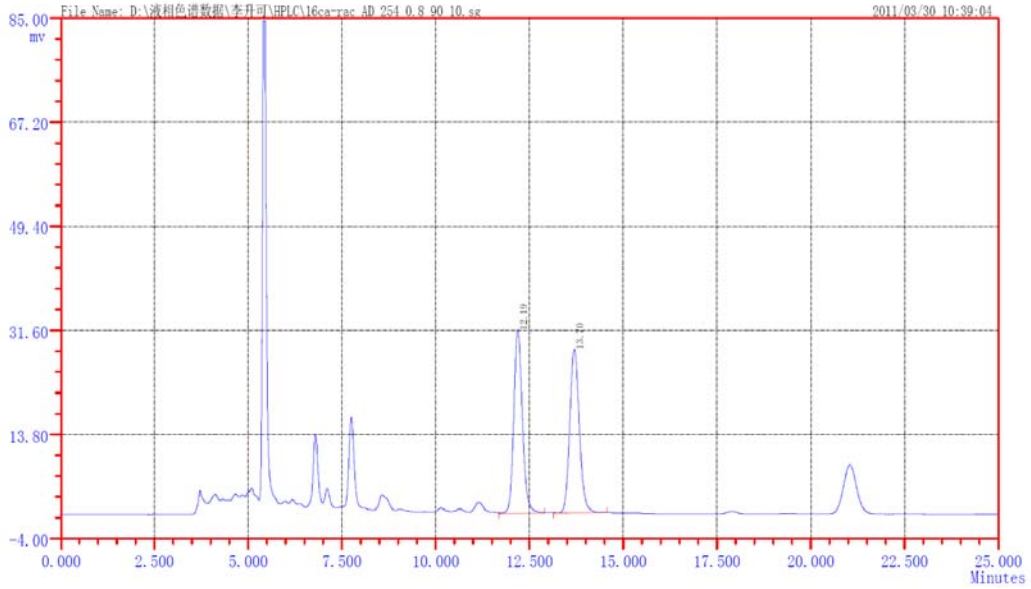


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		55.645	41105	4481956.5	15.2194	1.69	5191
2		64.867	154435	24967037.1	84.7806	1.91	3209
	Σ:		195540	29448993.7	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

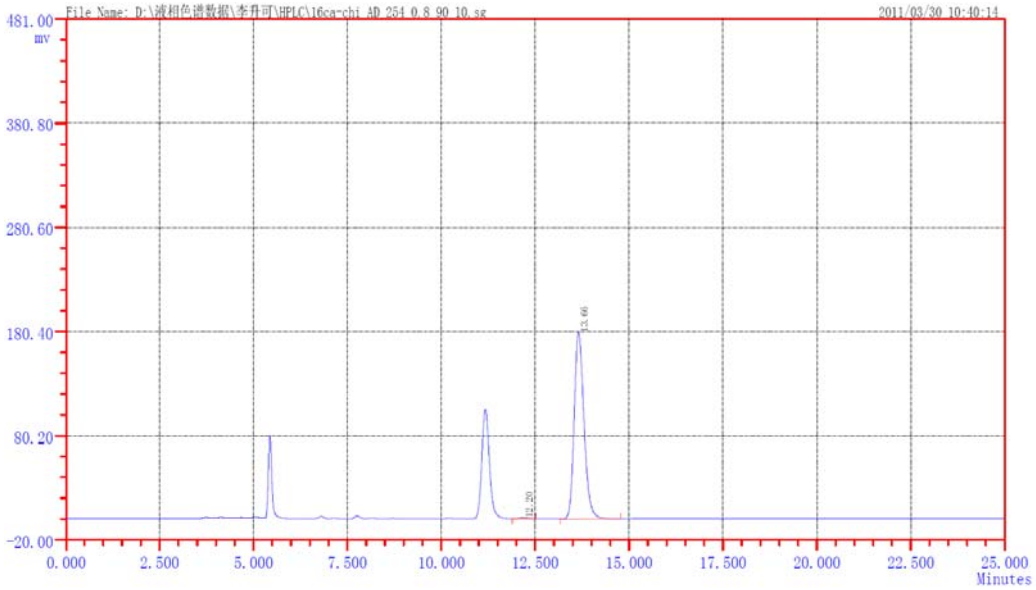
(*R*,*E*)-2-(4-methylbenzylidene)-3-phenylcyclohexanone **5ca** (Fig. 2, entry 10): $[\alpha]_D^{20}$ +167.9 (*c* 0.41, $CHCl_3$) for 99 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.68-1.75 (m, 2H), 2.08-2.12 (m, 2H), 2.31 (s, 3H), 2.41-2.50 (m, 1H), 2.65-2.70 (m, 1H), 4.51 (br s, 1H), 7.06-7.12 (m, 4H), 7.21-7.27 (m, 3H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.58 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.7, 21.3, 32.2, 40.4, 43.4, 126.4, 127.9, 128.8, 129.1, 130.2, 132.1, 137.3, 138.3, 139.1, 144.1, 203.0. MS (EI) *m/z* (%): 276.2 (M, 100); HRMS (Micromass LCT) Calcd. for $C_{20}H_{20}O$: 276.1514; Found: 276.1513. Chiralcel AD, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, t_{major} = 13.66 min, t_{minor} = 12.20 min.


Me
PPM
PPM



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		12.188	31421	501437.2	50.1913	1.17	11626
2		13.700	28005	497614.9	49.8087	1.12	11848
	Σ:		59426	999052.1	100.0000		

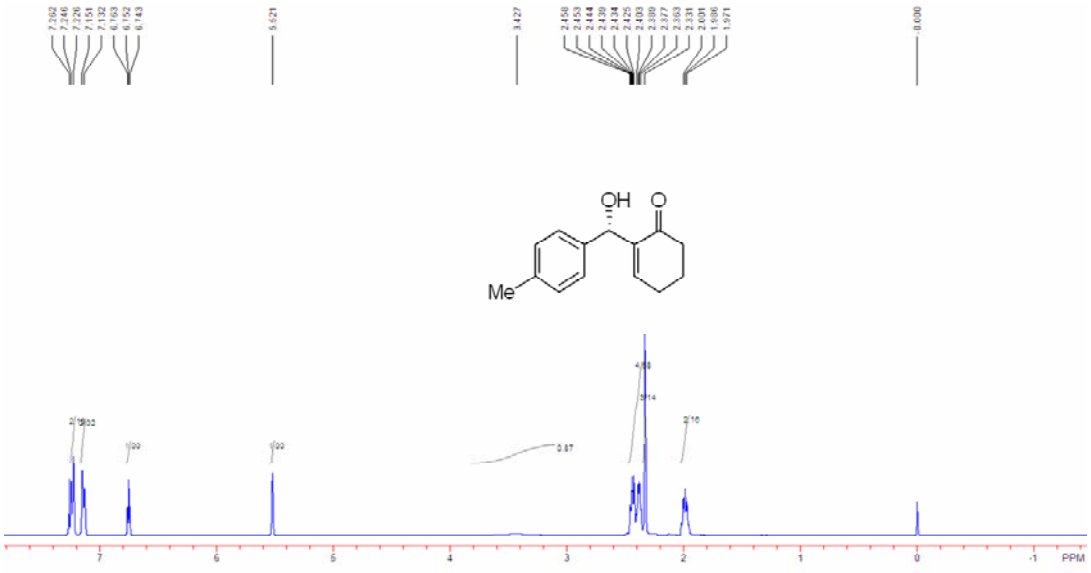
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

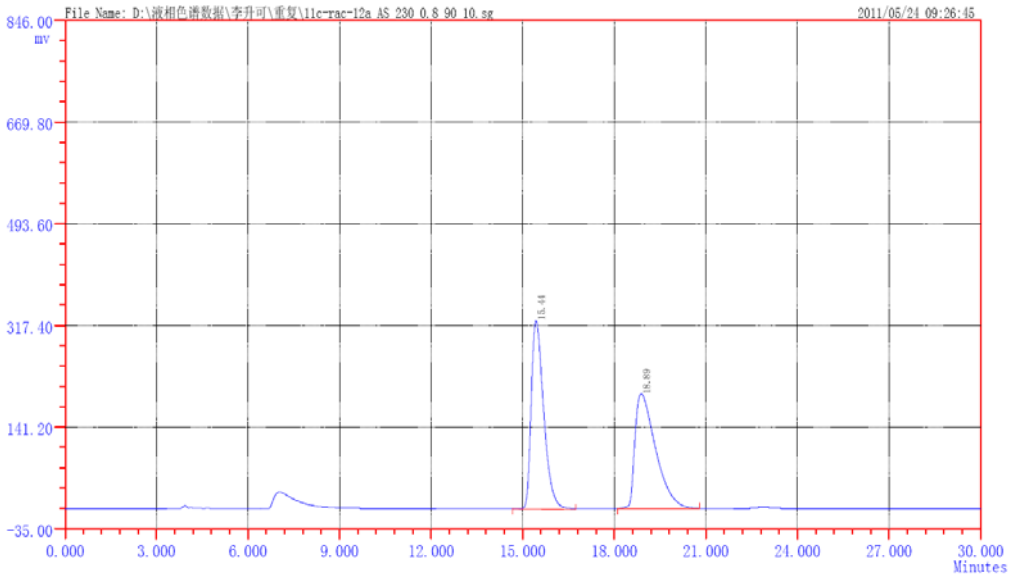


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		12.198	1067	17820.7	0.5451	0.95	10632
2		13.657	179635	3251340.9	99.4549	1.22	11347
	Σ:		180702	3269161.6	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

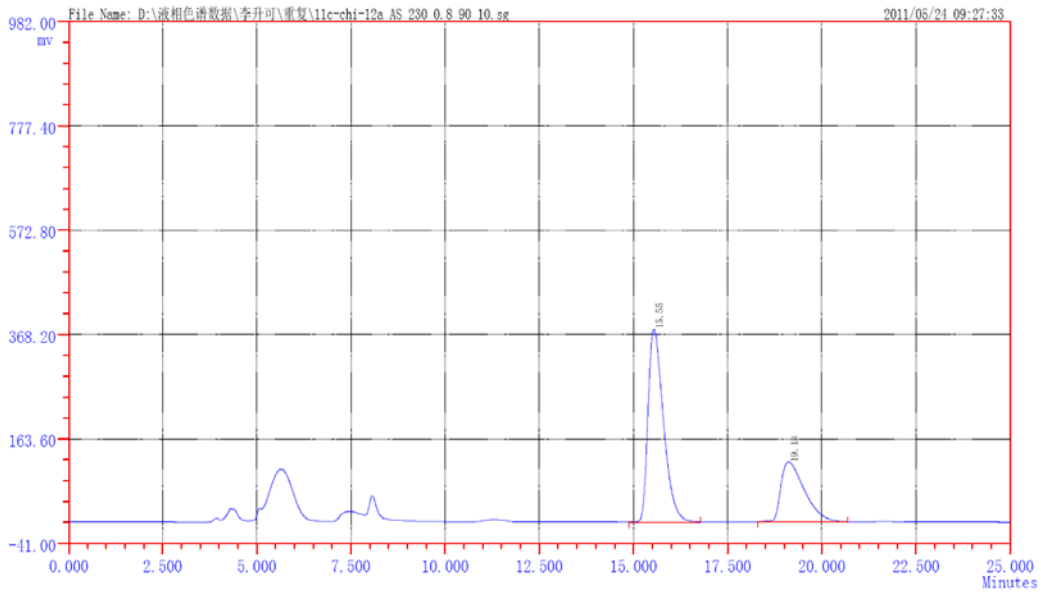
(*S*)-2-(hydroxy(p-tolyl)methyl)cyclohex-2-enone **3c**.[6] $[\alpha]_D^{20}$ +2.7 (*c* 1.0, CH_2Cl_2) for 36 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.97-2.00 (m, 2H), 2.33 (s, 3H), 2.36-2.46 (m, 4H), 3.43 (br s, 1H), 5.52 (s, 1H), 6.75 (t, *J* = 4.4 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H). Chiralcel AS, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 230 nm, t_{major} = 15.55 min, t_{minor} = 19.13 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		15.438	326426	9269329.6	49.7683	1.52	5891
2		18.893	198770	9355633.8	50.2317	2.07	3211
	Σ:		525196	18624963.4	100.0000		

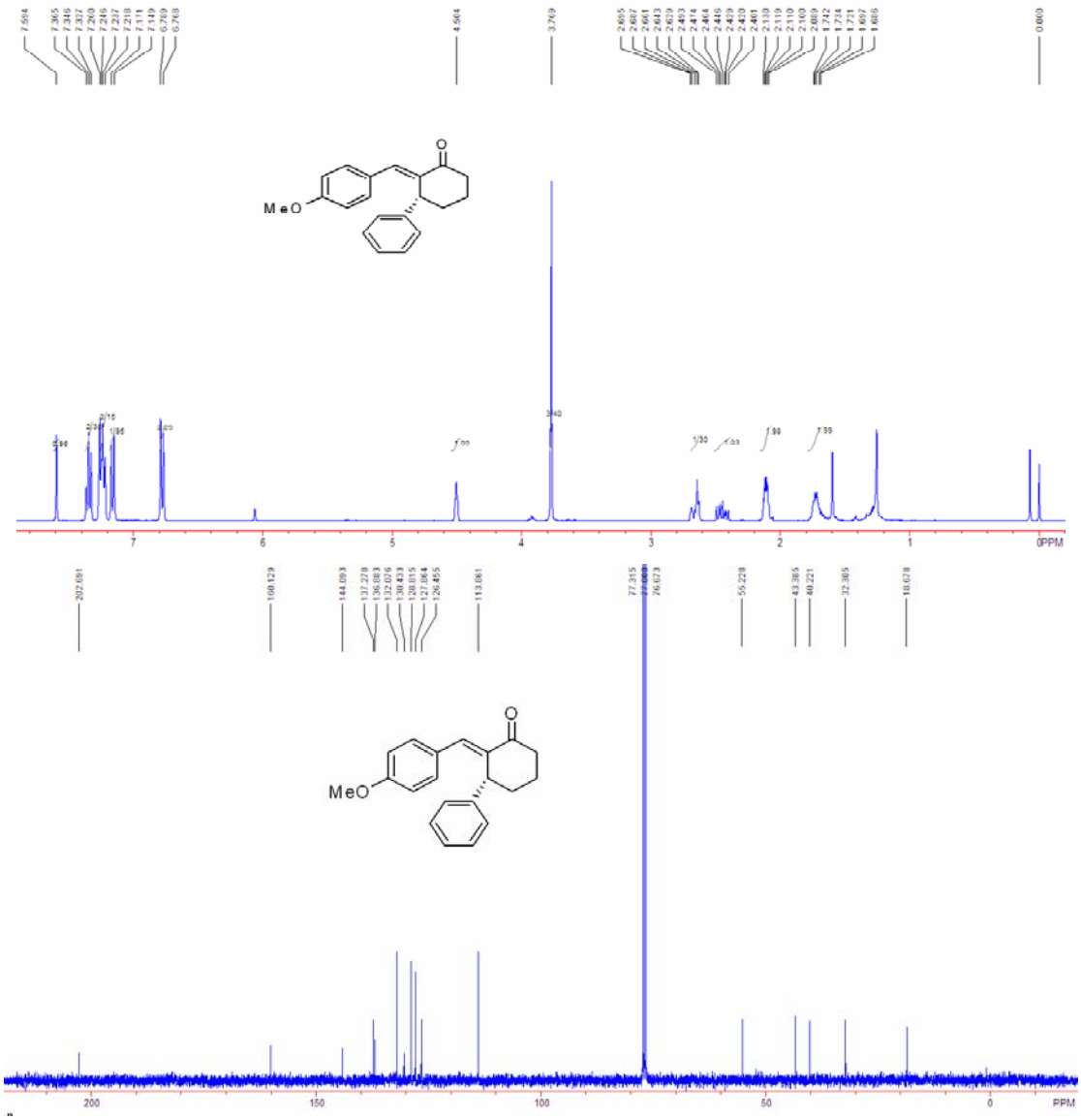
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

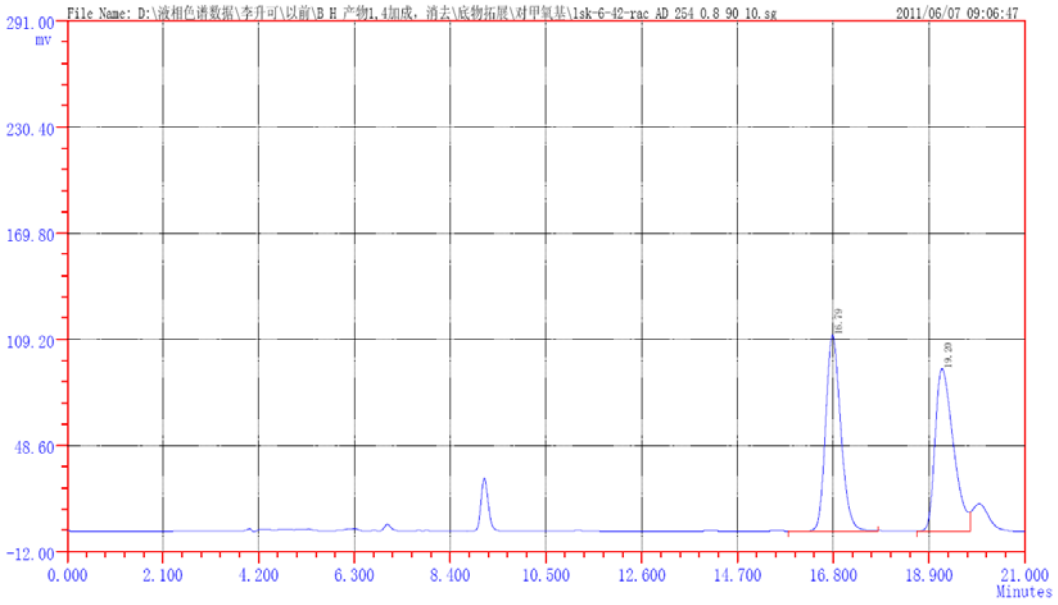


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		15.547	379351	10887409.0	67.7475	1.54	5848
2		19.128	118002	5183159.1	32.2525	1.87	3780
	Σ:		497353	16070568.1	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

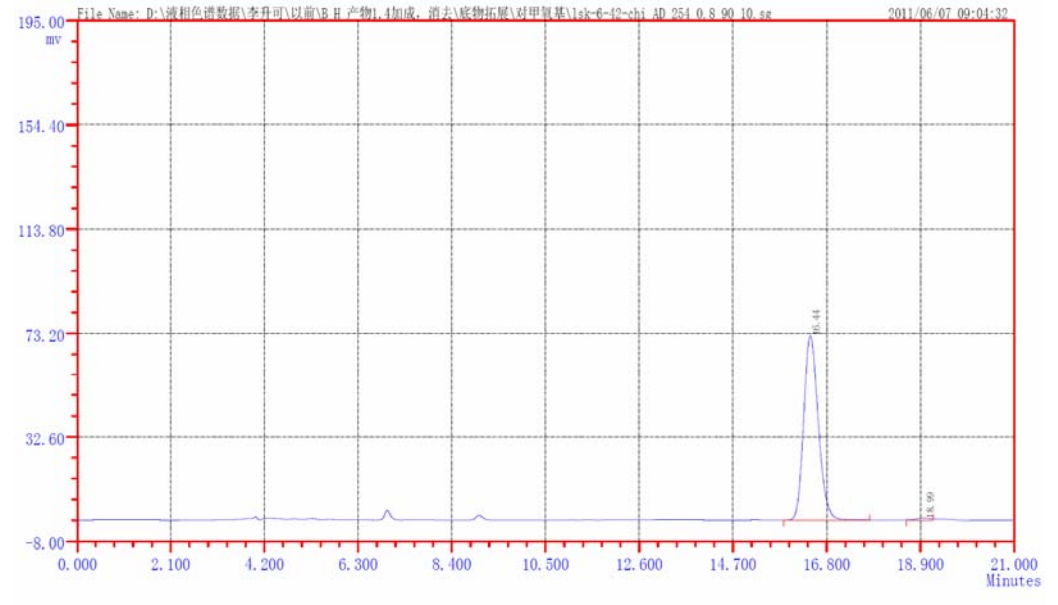
(*R*,*E*)-2-(4-methoxybenzylidene)-3-phenylcyclohexanone **5da** (Fig. 2, entry 11). $[\alpha]_D^{20}$ +323.4 (*c* 1.0, $CHCl_3$) for 98 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.69-1.74 (m, 2H), 2.09-2.13 (m, 2H), 2.40-2.49 (m, 1H), 2.63-2.70 (m, 1H), 3.77 (s, 3H), 4.50 (br s, 1H), 6.78 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.22-7.25 (m, 3H), 7.33-7.37 (m, 2H), 7.59 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.7, 32.3, 40.2, 43.4, 55.2, 113.9, 126.5, 127.9, 128.8, 130.4, 132.1, 136.9, 137.3, 144.1, 160.1, 202.7. MS (EI) *m/z* (%): 292.1 (M, 100); HRMS (Micromass LCT) Calcd. for $C_{20}H_{20}O_2$: 292.1463; Found: 292.1465. Chiralcel AD, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, t_{major} = 16.44 min, t_{minor} = 18.99 min.


MeO
PPM
MeO
PPM



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		16.790	112212	2612570.5	50.0183	1.20	10365
2		19.195	93012	2610655.4	49.9817	1.46	9321
	Σ:		205224	5223226.0	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

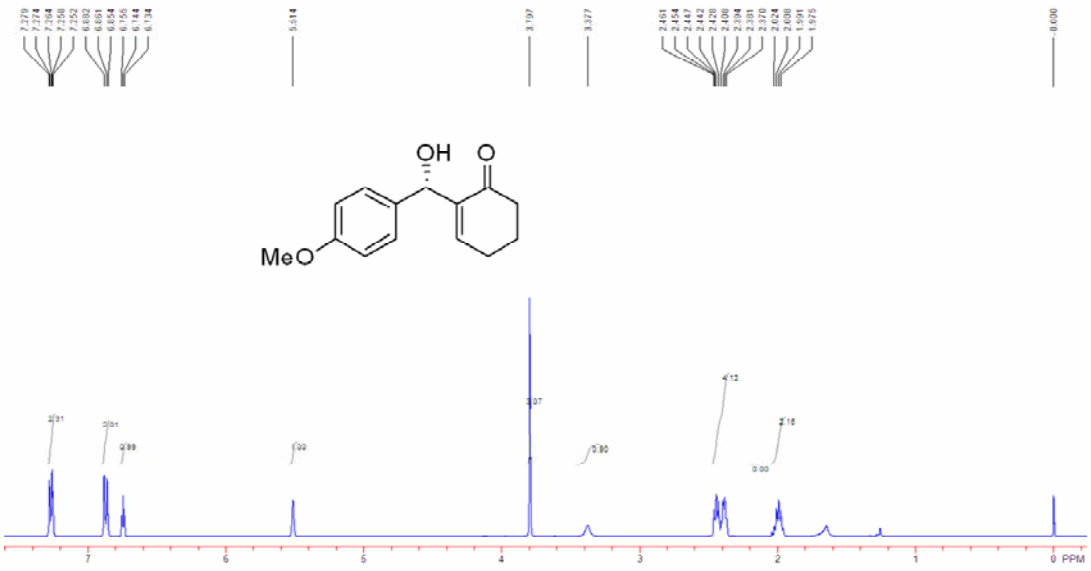


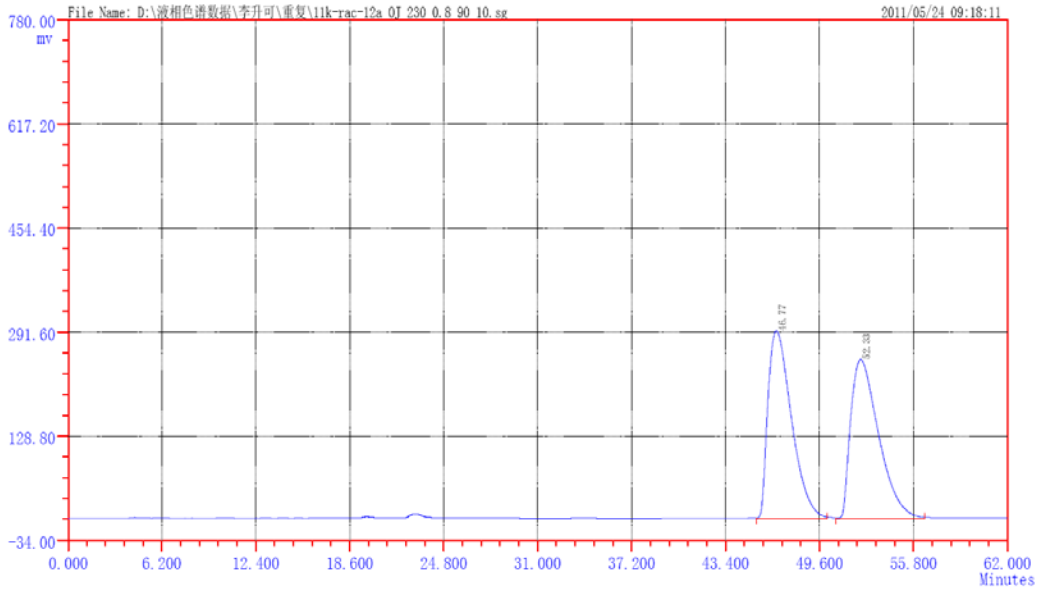
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		16.437	72297	1635186.1	98.7954	1.20	10526
2		18.993	902	19936.8	1.2046	0.75	14717
	Σ:		73199	1655122.9	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

(*S*)-2-(hydroxy(4-methoxyphenyl)methyl)cyclohex-2-enone **3d**.[7] $[\alpha]_D^{20}$ +0.4 (*c* 1.2, CH_2Cl_2) for 32 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.98-2.02 (m, 2H),

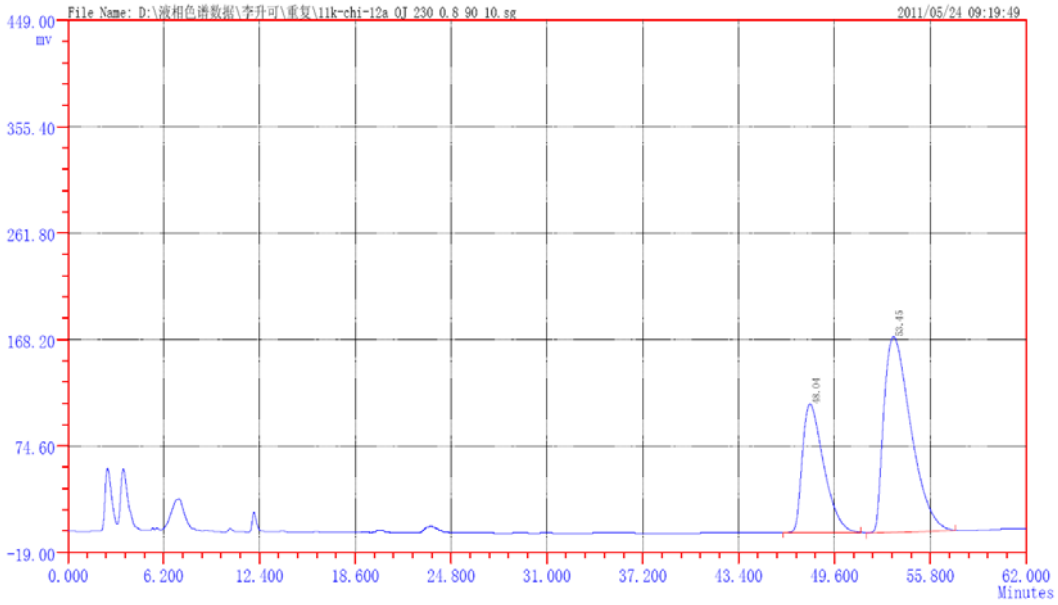
2.37-2.46 (m, 4H), 3.38 (br s, 1H), 3.80 (s, 3H), 5.51 (s, 1H), 7.74 (t, J = 4.4 Hz, 1H), 6.85-6.88 (m, 2H), 7.25-7.28 (m, 2H). Chiralcel AS, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 230 nm, t_{major} = 53.45 min, t_{minor} = 48.04 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		46.772	293174	31630164.8	49.8808	1.75	3746
2		52.333	248374	31781322.9	50.1192	1.81	3334
	Σ:		541548	63411487.6	100.0000		

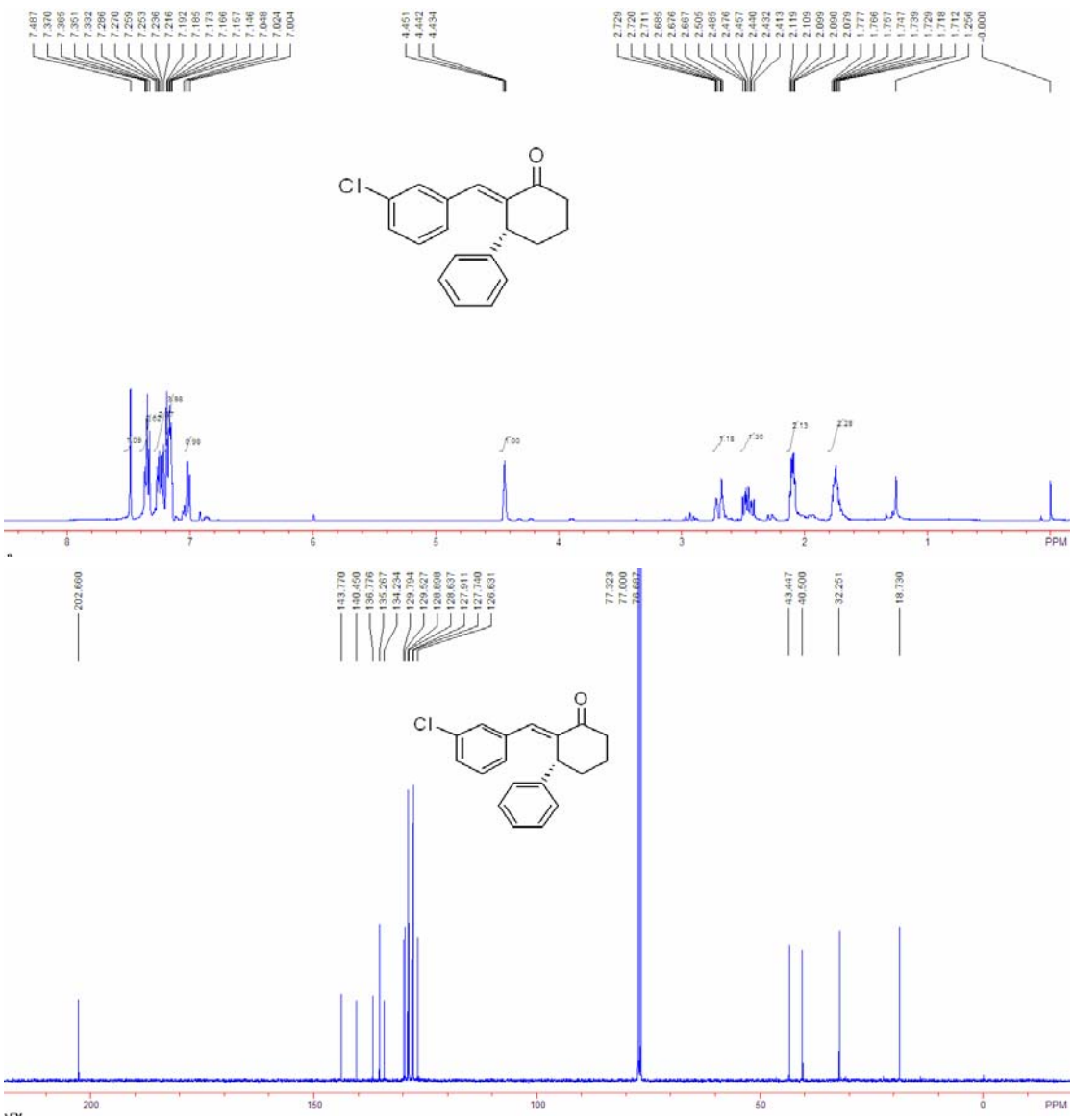
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

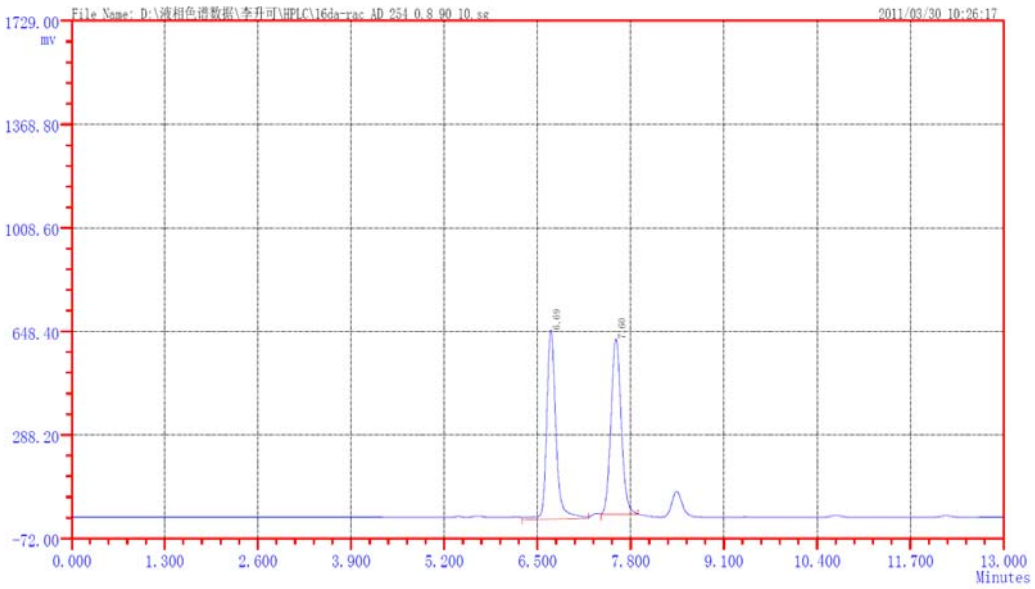


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		48.043	113121	10936061.8	34.1966	1.66	4922
2		53.450	172195	21043930.1	65.8034	1.79	3812
	Σ:		285316	31979991.9	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

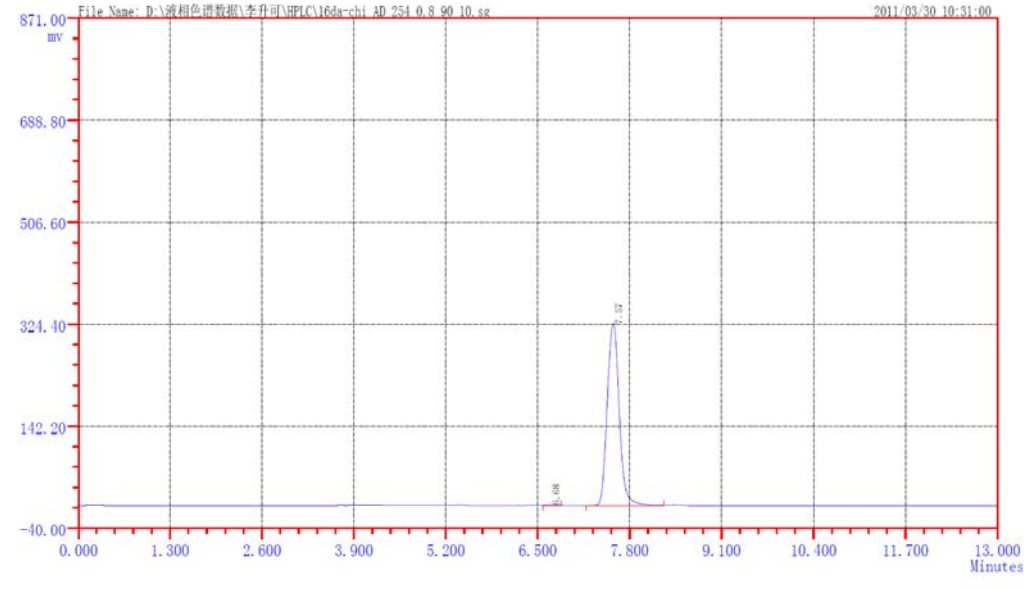
(*R*,*E*)-2-(3-chlorobenzylidene)-3-phenylcyclohexanone **5ea** (Fig. 2, entry 12): $[\alpha]_D^{20}$ +106.0 (*c* 0.37, $CHCl_3$) for 99 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.71-1.78 (m, 2H), 2.08-2.12 (m, 2H), 2.41-2.51 (m, 1H), 2.67-2.73 (m, 1H), 4.44 (t, *J* = 3.6 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 7.15-7.19 (m, 4H), 7.22-7.27 (m, 2H), 7.33-7.37 (m, 2H), 7.49 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.7, 32.3, 40.5, 43.4, 126.6, 127.7, 127.9, 128.6, 128.9, 129.5, 129.8, 134.2, 135.3, 136.8, 140.5, 143.8, 202.7. MS (EI) *m/z* (%): 297.1 (M+H, 100); HRMS (Micromass LCT) Calcd. for $C_{19}H_{18}ClO$: 297.1046; Found: 297.0949. Chiralcel AD, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, t_{major} = 7.57 min, t_{minor} = 6.68 min.


7.487
7.370
7.365
7.351
7.332
7.286
7.270
7.259
7.253
7.236
7.216
7.192
7.185
7.173
7.166
7.157
7.146
7.048
7.024
7.004
4.451
4.442
4.434
2.729
2.720
2.711
2.685
2.676
2.667
2.505
2.485
2.476
2.457
2.440
2.432
2.413
2.119
2.109
2.099
2.090
2.079
1.777
1.766
1.757
1.747
1.739
1.729
1.718
1.712
1.256
0.000
Cl
O
PPM
202.660
143.770
140.450
136.776
135.267
134.234
129.704
129.527
128.698
128.637
127.911
127.740
126.631
77.323
77.000
76.682
43.447
40.500
32.251
18.739
Cl
O
200
150
100
50
0
PPM



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		6.688	656872	5868468.0	49.1067	1.27	11170
2		7.595	611250	6081974.0	50.8933	1.10	11613
	Σ:		1268122	11950442.1	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

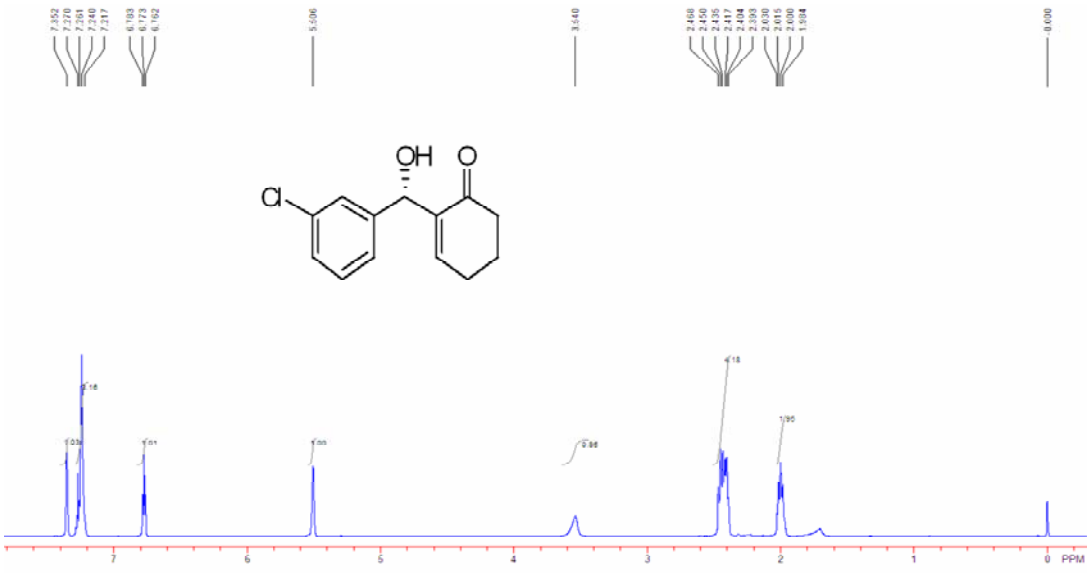


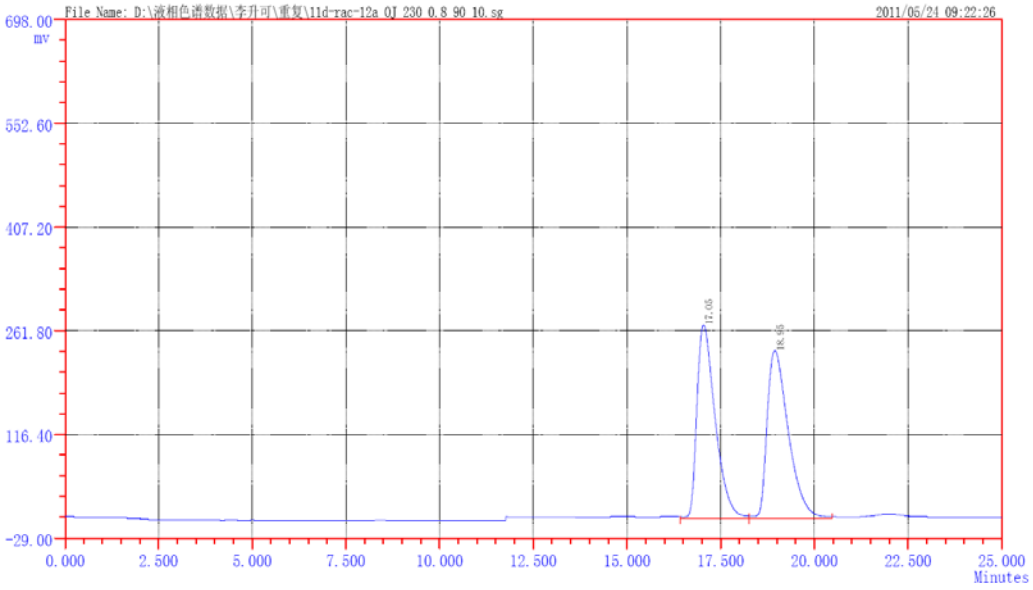
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		6.682	1823	15275.2	0.3972	1.20	12674
2		7.568	325166	3830607.7	99.6028	1.13	8226
	Σ:		326989	3845882.9	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

(*S*)-2-((3-chlorophenyl)(hydroxy)methyl)cyclohex-2-enone **3e**.[6] $[\alpha]_D^{20}$ +10.7 (*c* 1.1, CH_2Cl_2) for 48 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.98-2.03 (m, 2H),

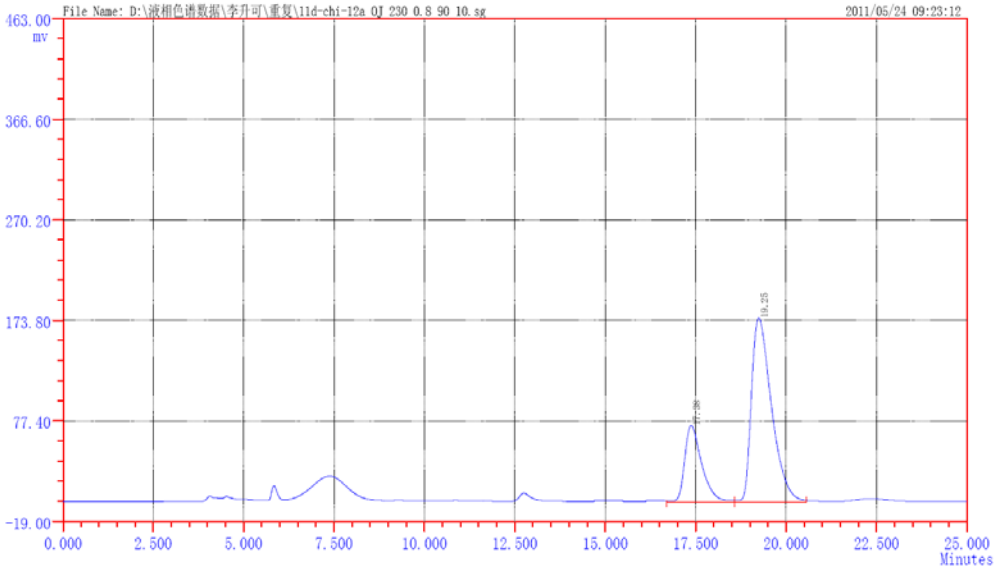
2.39-2.47 (m, 4H), 3.54 (br s, 1H), 5.51 (s, 1H), 6.77 (t, J = 4.0 Hz, 1H), 7.22-7.27 (m, 3H), 7.35 (s, 1H). Chiralcel OJ, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 230 nm, t_{major} = 19.25 min, t_{minor} = 17.38 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		17.050	271288	9204496.3	49.7579	1.64	5033
2		18.950	235320	9294057.7	50.2421	1.68	4588
	Σ:		506608	18498554.0	100.0000		

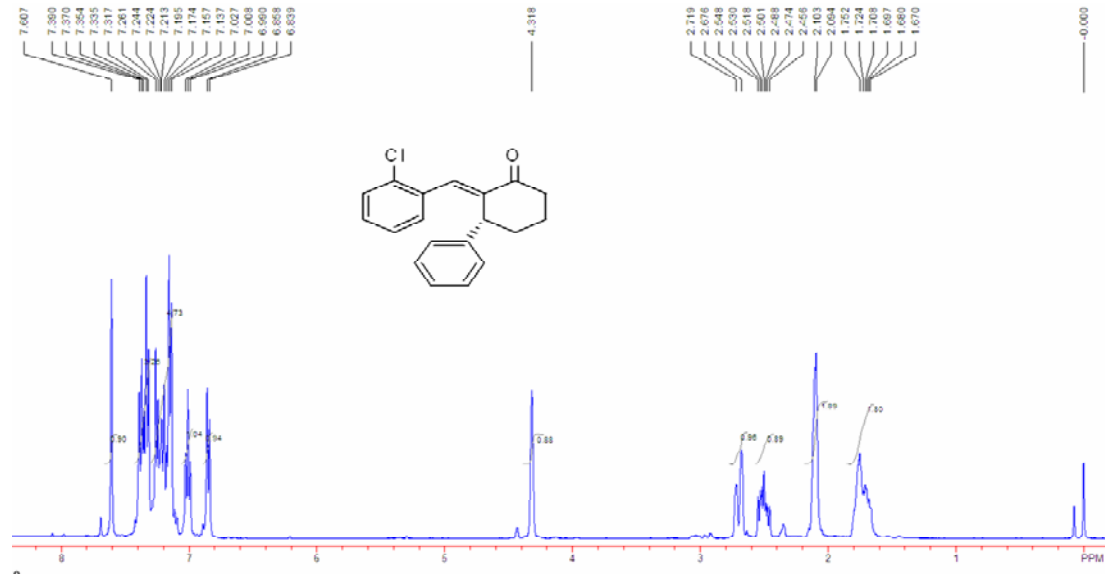
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

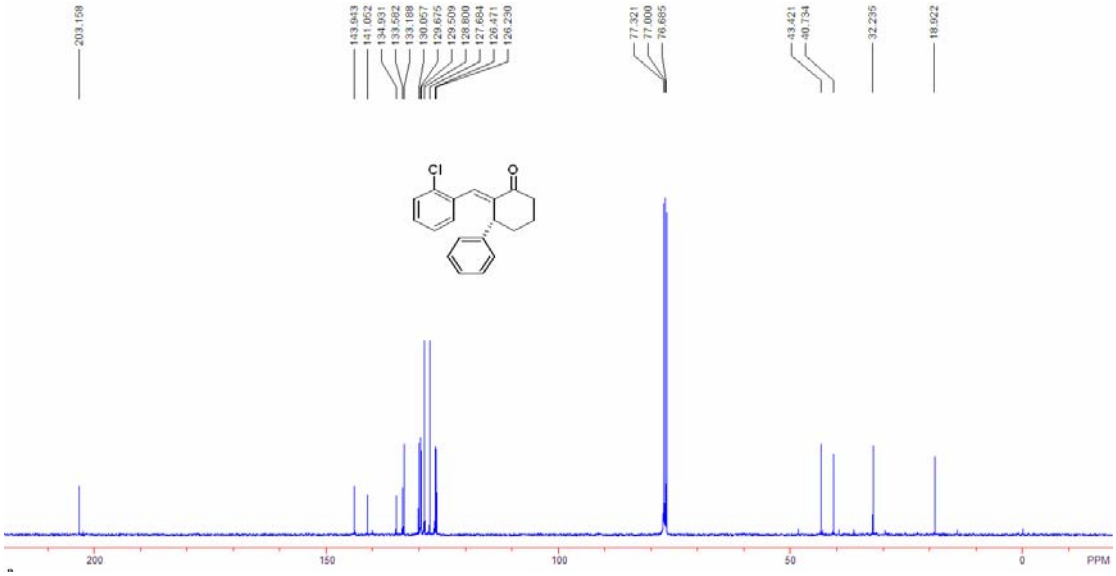


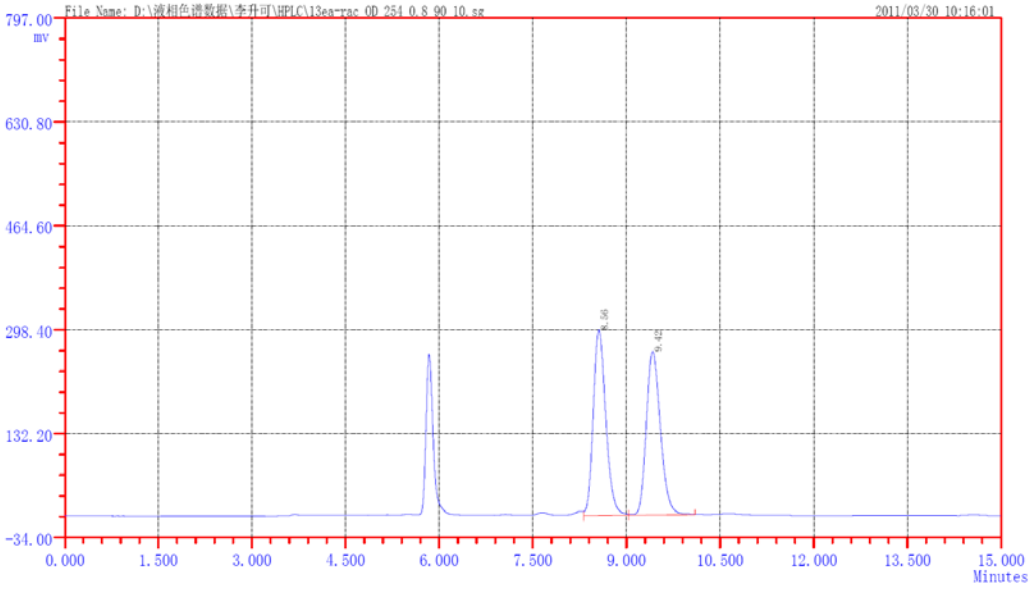
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		17.383	73155	2358604.2	25.8349	1.51	5794
2		19.250	176067	6770907.9	74.1651	1.64	4994
	Σ:		249222	9129512.0	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

(*R*,*E*)-2-(2-chlorobenzylidene)-3-phenylcyclohexanone **5fa** (Fig. 2, entry 13): $[\alpha]_D^{20}$ +78.8 (*c* 0.10, $CHCl_3$) for 98 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.71-1.75 (m, 2H), 2.09-2.10 (m, 2H), 2.46-2.55 (m, 1H), 2.68-2.72 (m, 1H), 4.32 (br s, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 7.14-7.25 (m, 4H), 7.32-7.39 (m, 3H), 7.61 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.9, 32.2, 40.7, 43.4, 126.2, 126.5, 127.7, 128.8, 129.5, 129.7, 130.1, 133.2, 133.6, 134.9, 141.1, 143.9, 203.2. MS (EI) *m/z* (%): 297.1 (M+H, 100); HRMS (Micromass LCT) Calcd. for $C_{19}H_{17}ClO$: 296.0968; Found: 296.0981. Chiralcel OD, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, t_{major} = 8.53 min, t_{minor} = 9.42 min.

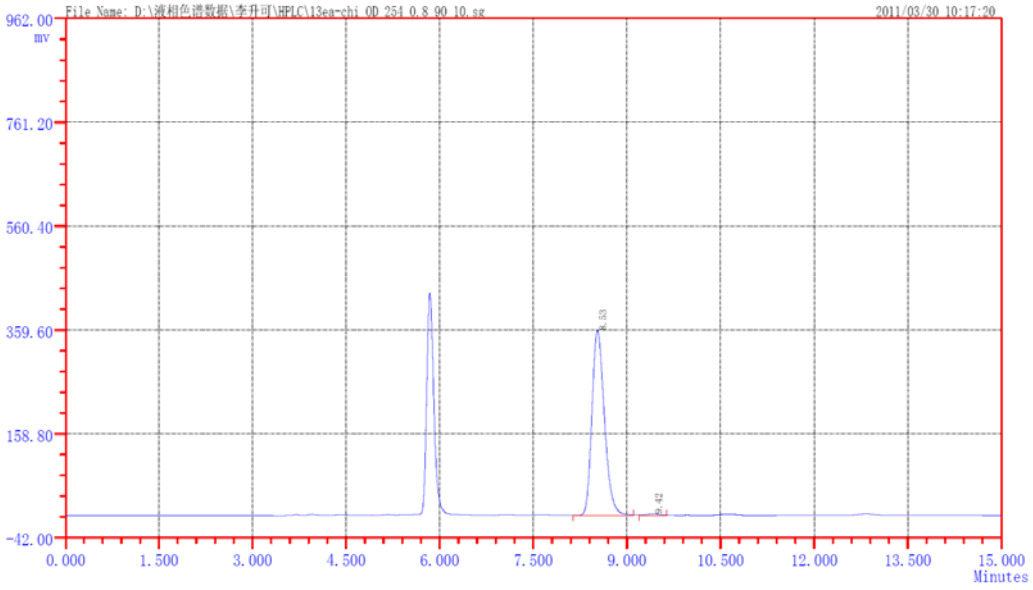

7.607
7.390
7.370
7.354
7.335
7.317
7.261
7.244
7.224
7.213
7.195
7.174
7.157
7.137
7.027
7.008
6.990
6.858
6.839
4.318
2.719
2.676
2.648
2.630
2.618
2.601
2.488
2.474
2.456
2.103
2.084
1.752
1.724
1.708
1.697
1.680
1.670
-0.000
Cl
O
PPM


203.158
143.943
141.052
134.931
133.562
133.188
130.057
129.675
129.509
128.600
127.664
126.471
126.230
77.321
77.000
76.685
43.421
40.734
32.235
18.922
Cl
O
200
150
100
50
0
PPM



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		8.558	296880	4173280.4	50.2074	1.22	7388
2		9.422	261930	4138801.6	49.7926	1.23	7086
	Σ:		558810	8312082.0	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

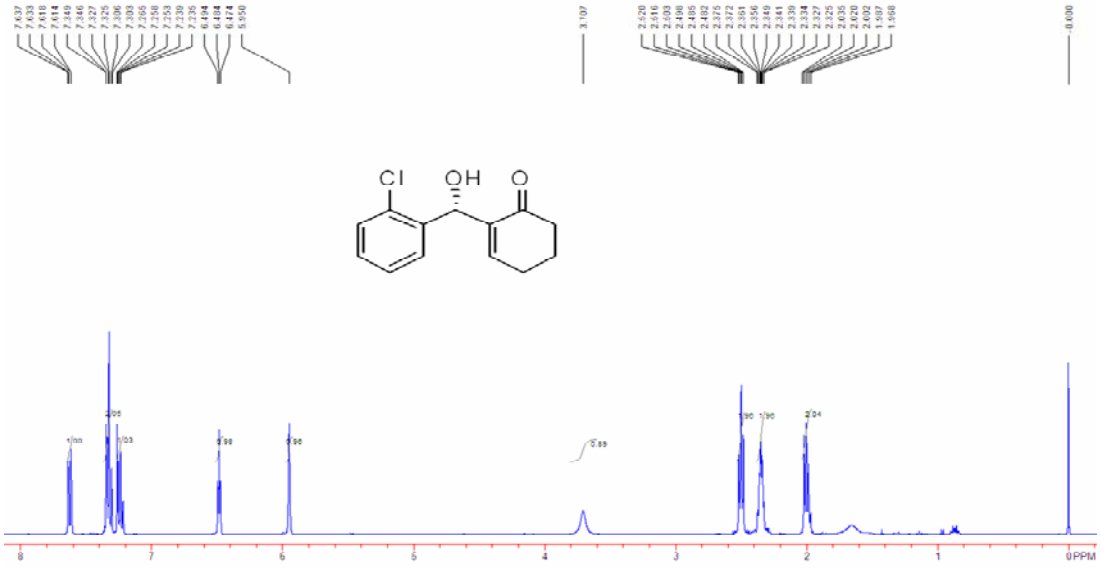


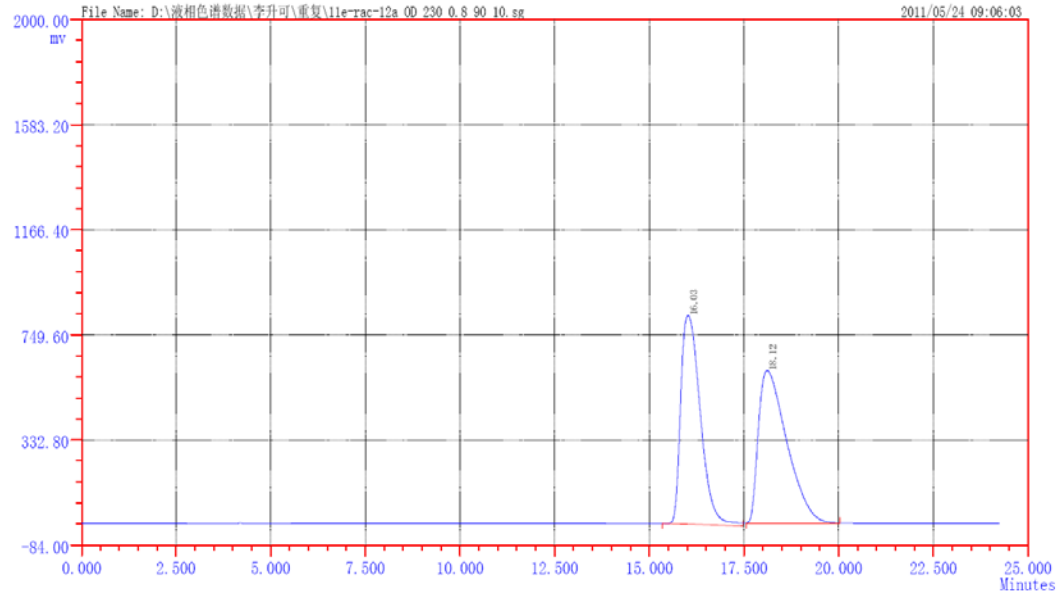
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		8.528	357172	5002151.2	99.0600	1.25	7391
2		9.422	2953	47467.6	0.9400	0.97	6847
	Σ:		360125	5049618.8	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

(*R*)-2-((2-chlorophenyl)(hydroxy)methyl)cyclohex-2-enone **3f**.[4] $[\alpha]_D^{20}$ -5.6 (*c* 1.0, CH_2Cl_2) for 30 % ee. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.97-2.04 (m, 2H),

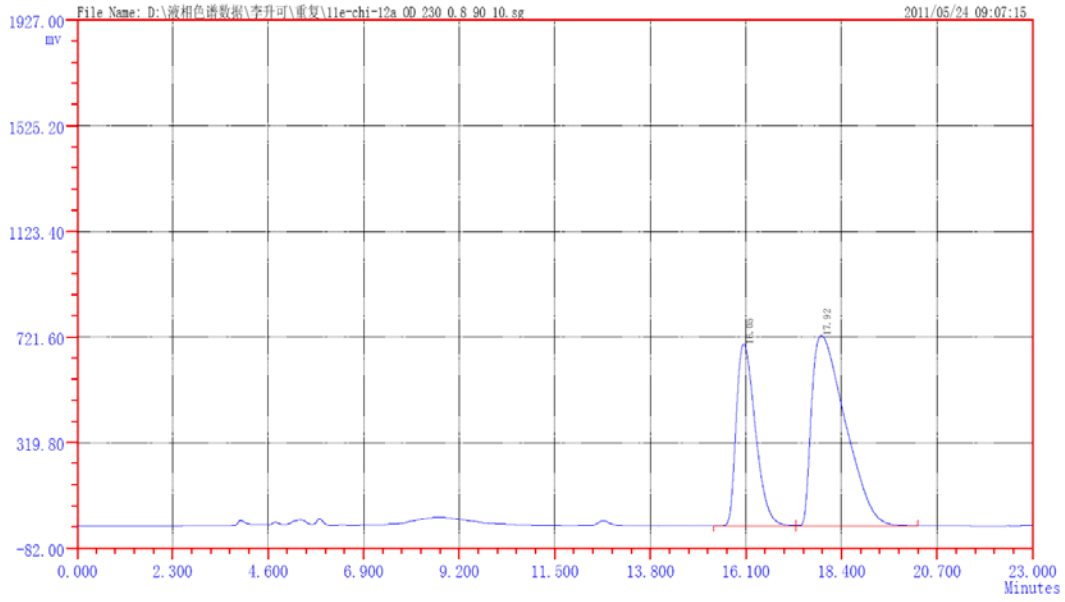
2.33-2.38 (m, 2H), 2.48-2.52 (m, 2H), 3.71 (br s, 1H), 5.95 (s, 1H), 6.48 (t, J = 4.0 Hz, 1H), 7.22-7.26 (m, 1H), 7.30-7.35 (m, 2H), 7.62 (dd, J = 1.6, 7.6 Hz, 1H). Chiralcel OD, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 230 nm, t_{major} = 17.92 min, t_{minor} = 16.05 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		16.027	827840	29746850.7	48.5753	1.55	3965
2		18.120	604042	31491788.8	51.4247	1.96	2408
	Σ:		1431882	61238639.6	100.0000		

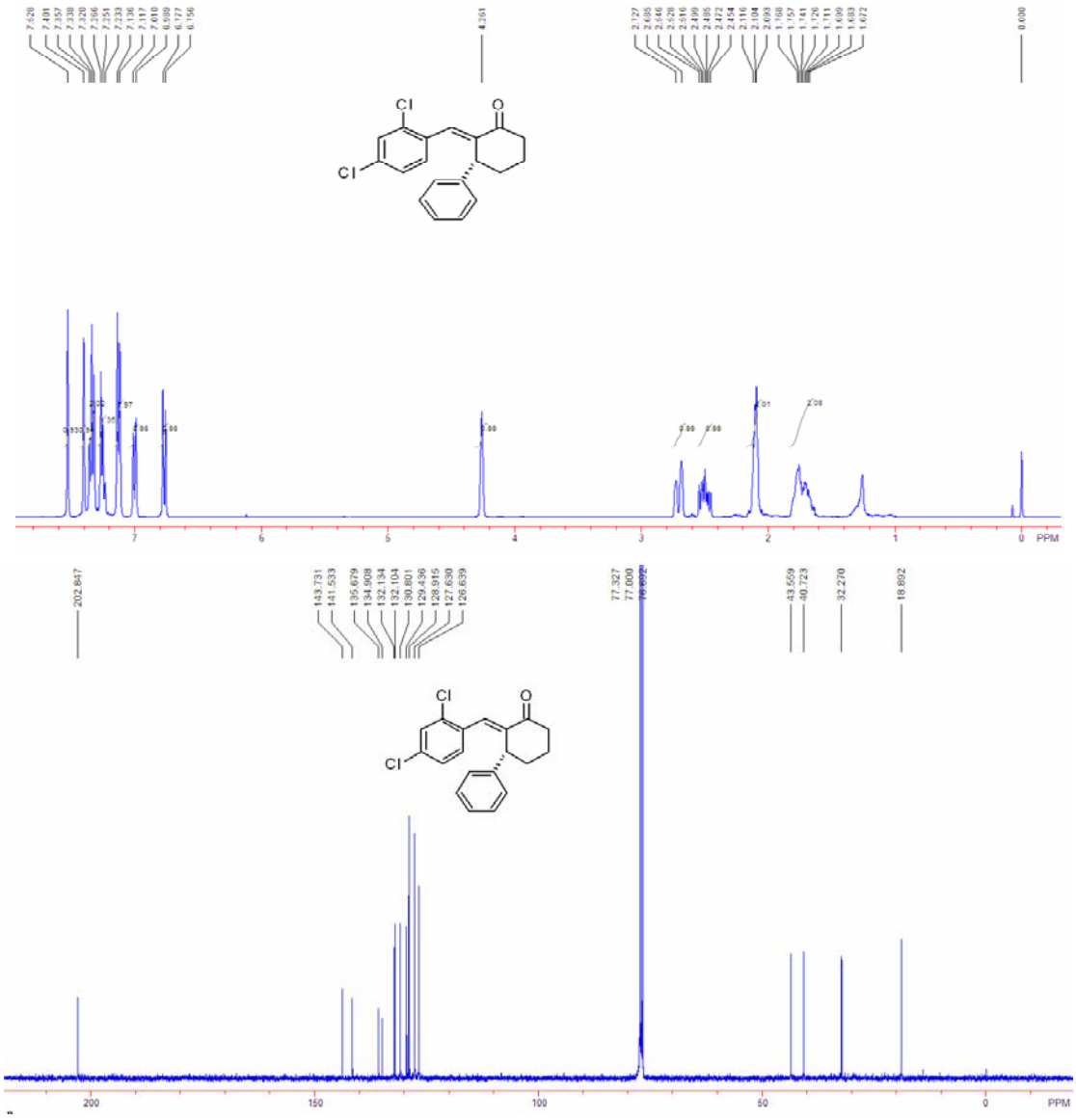
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

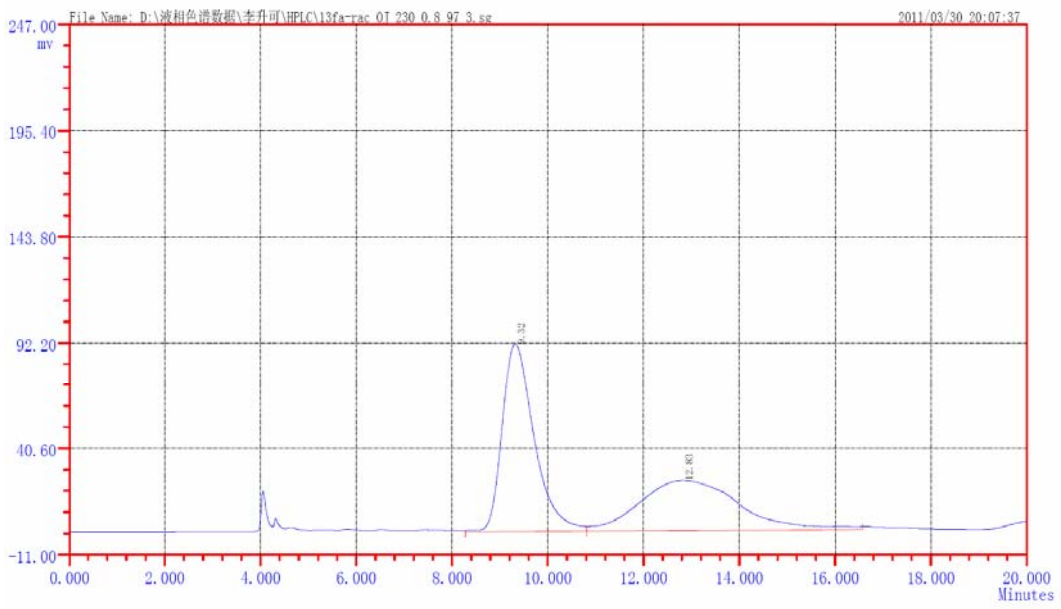


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		16.050	692624	22198577.7	35.2423	1.49	4998
2		17.918	724719	40789941.8	64.7577	2.14	2020
	Σ:		1417343	62988519.5	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

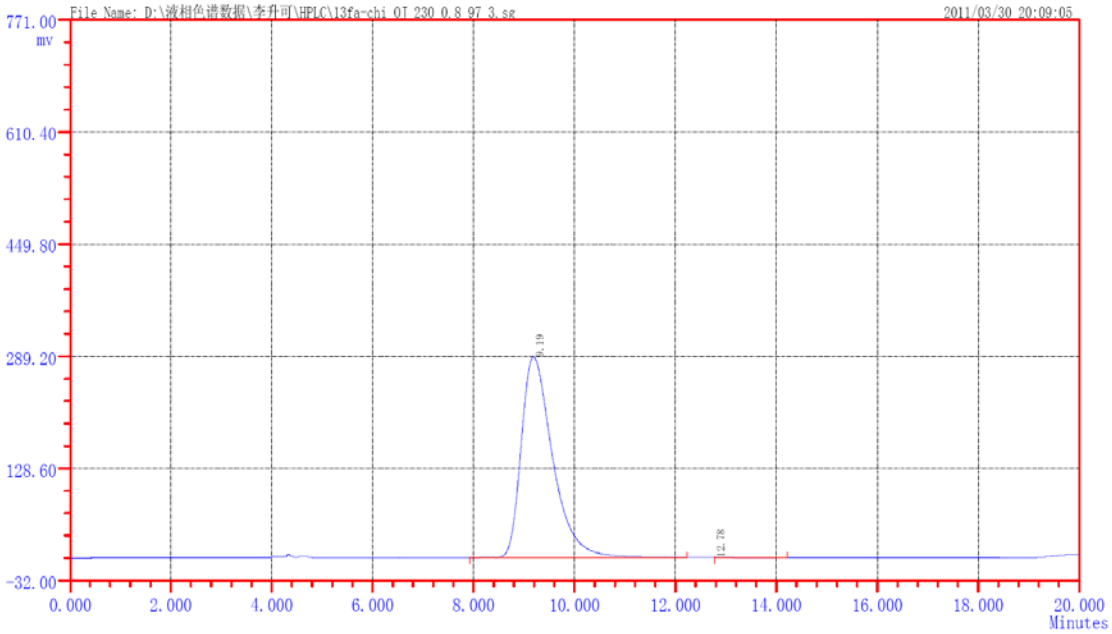
(*R*,*E*)-2-(2,4-dichlorobenzylidene)-3-phenylcyclohexanone **5ga** (Fig. 2, entry 14): $[\alpha]_D^{20}$ +51.6 (*c* 0.2, $CHCl_3$) for 99 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.67-1.77 (m, 2H), 2.09-2.12 (m, 2H), 2.45-2.55 (m, 1H), 2.68-2.73 (m, 1H), 4.26 (br s, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 2H), 7.23-7.27 (m, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.40 (s, 1H), 7.53 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.9, 32.3, 40.7, 43.6, 126.6, 127.6, 128.9, 129.4, 130.8, 132.10, 132.13, 134.9, 135.7, 141.5, 143.7, 202.8. MS (EI) *m/z* (%): 331.0 (M+H, 100); HRMS (Micromass LCT) Calcd. for $C_{19}H_{17}Cl_2O$: 331.0656; Found: 331.0477. Chiralcel OJ, hexane/*i*-PrOH = 97/3, 0.8 mL/min, 230 nm, t_{major} = 9.19 min, t_{minor} = 12.78 min.


Cl
O
Cl
PPM
Cl
O
Cl
200
150
100
50
0
PPM



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		9.322	91493	4232072.6	50.0652	1.48	809
2		12.830	24352	4221043.0	49.9348	1.43	109
	Σ:		115845	8453115.6	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

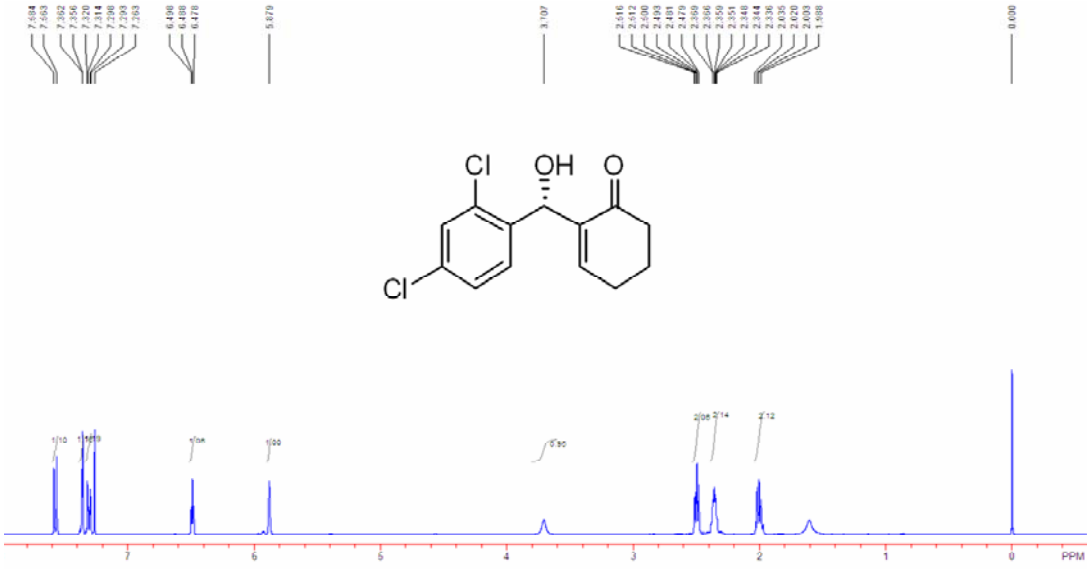


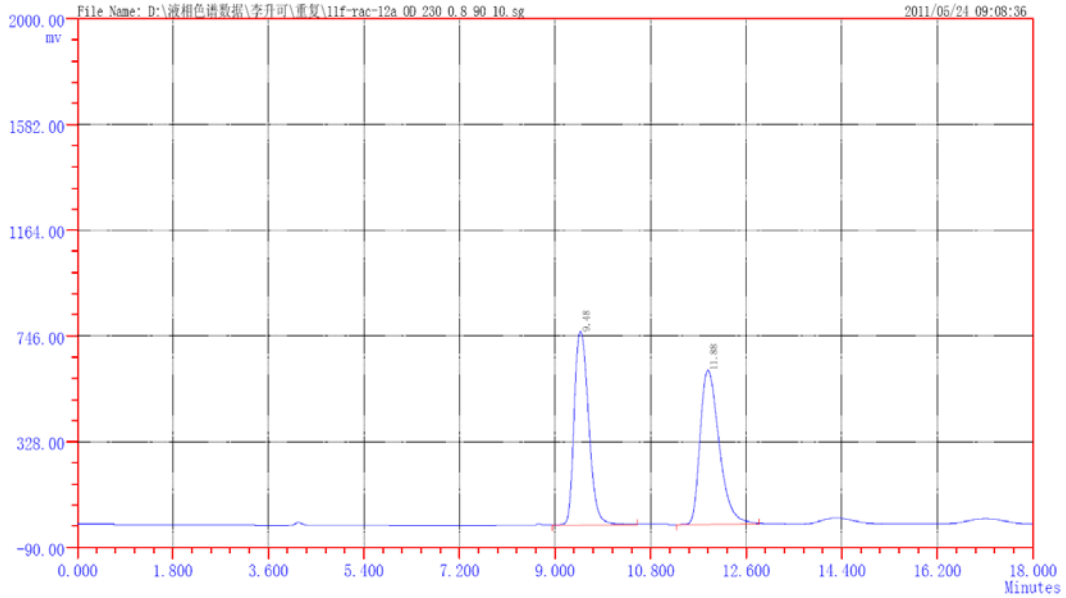
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		9.190	287787	12536771.6	99.5637	1.53	887
2		12.783	791	54935.6	0.4363	429.50	675
	Σ:		288578	12591707.1	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

(*R*)-2-((2,4-dichlorophenyl)(hydroxy)methyl)cyclohex-2-enone **3g**.[6] $[\alpha]_D^{20}$ -5.4 (*c* 1.0, CH_2Cl_2) for 34 % ee. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.99-2.04 (m, 2H),

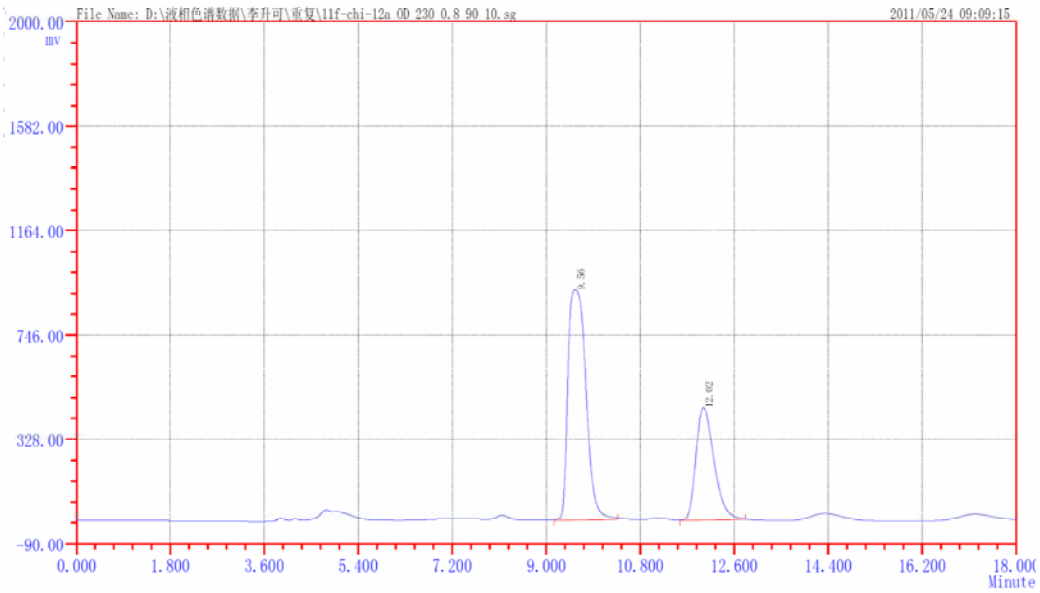
2.34-2.37 (m, 2H), 2.48-2.52 (m, 2H), 3.71 (br s, 1H), 5.88 (s, 1H), 6.49 (t, J = 4.0 Hz, 1H), 7.31 (dd, J = 2.4, 8.8 Hz, 1H), 7.36 (d, J = 2.4 Hz, 1H), 7.57 (d, J = 8.8 Hz, 1H). Chiralcel OD, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 230 nm, t_{major} = 9.56 min, t_{minor} = 12.02 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		9.480	765215	14569189.9	48.6842	1.29	4941
2		11.883	608884	15356742.6	51.3158	1.44	4425
	Σ:		1374099	29925932.5	100.0000		

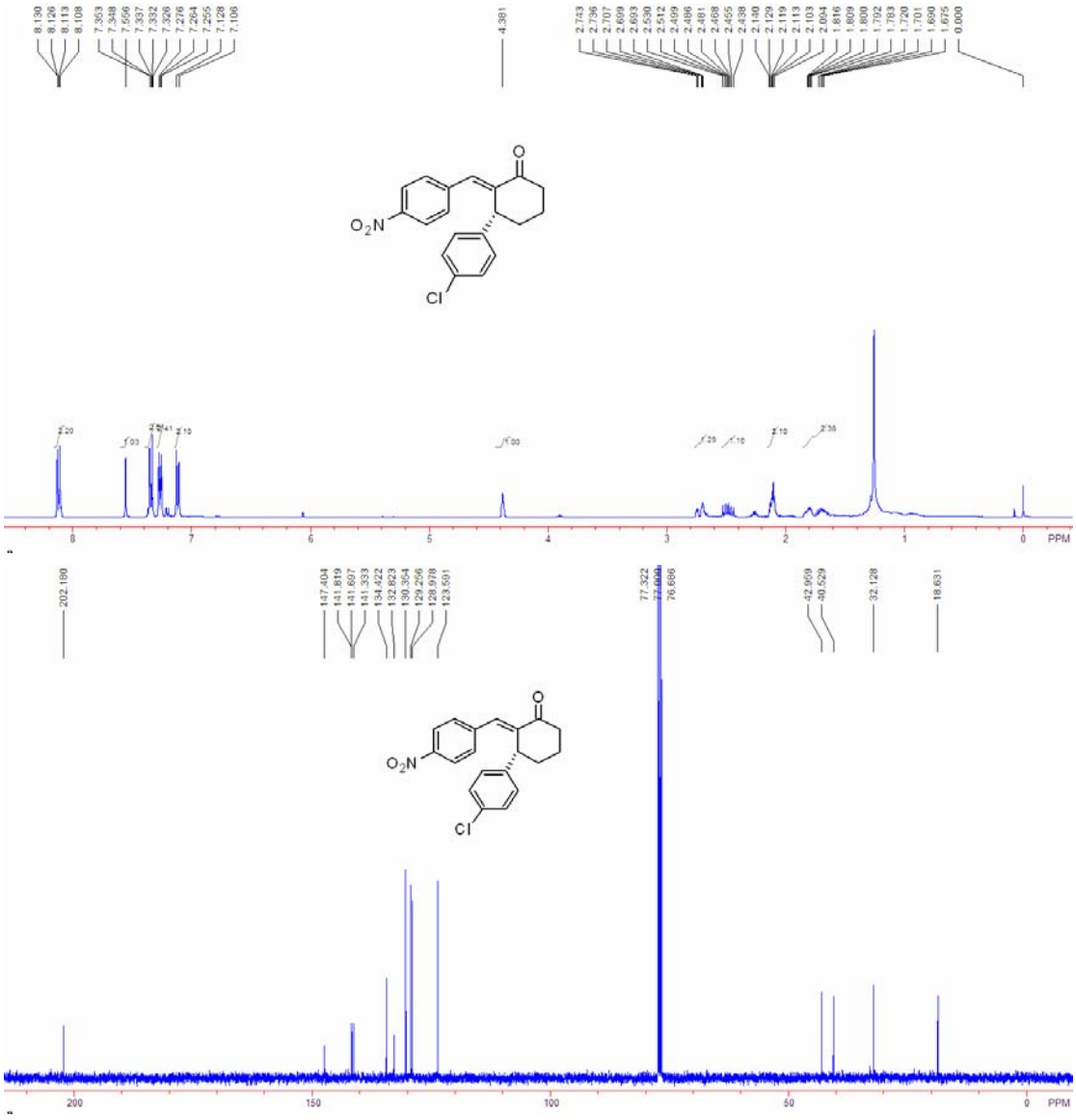
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

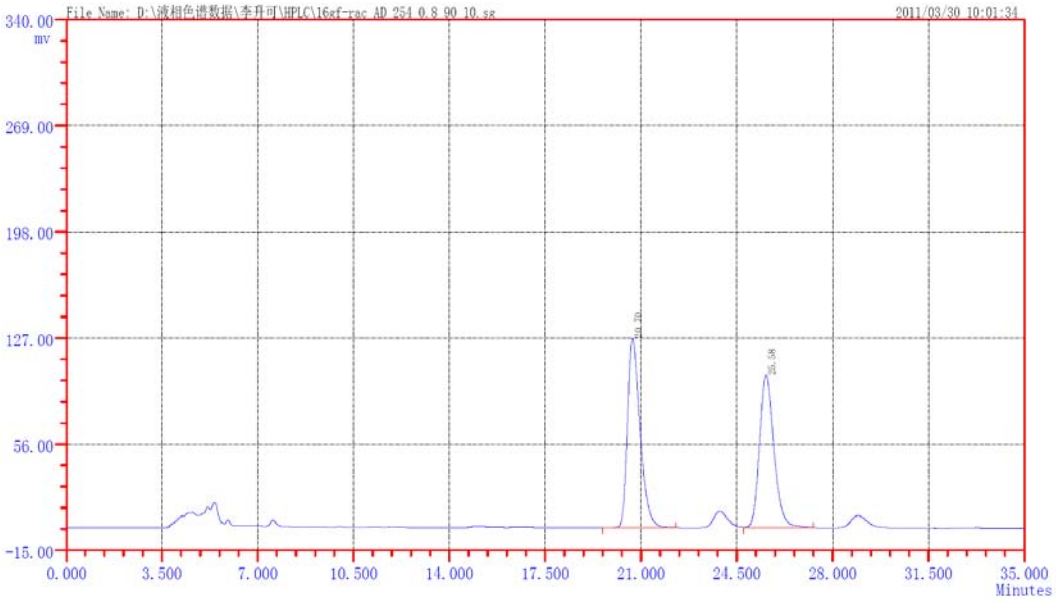


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		9.557	925898	22150081.6	66.8462	1.43	3181
2		12.015	452420	10985815.5	33.1538	1.40	4880
	Σ:		1378318	33135897.2	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

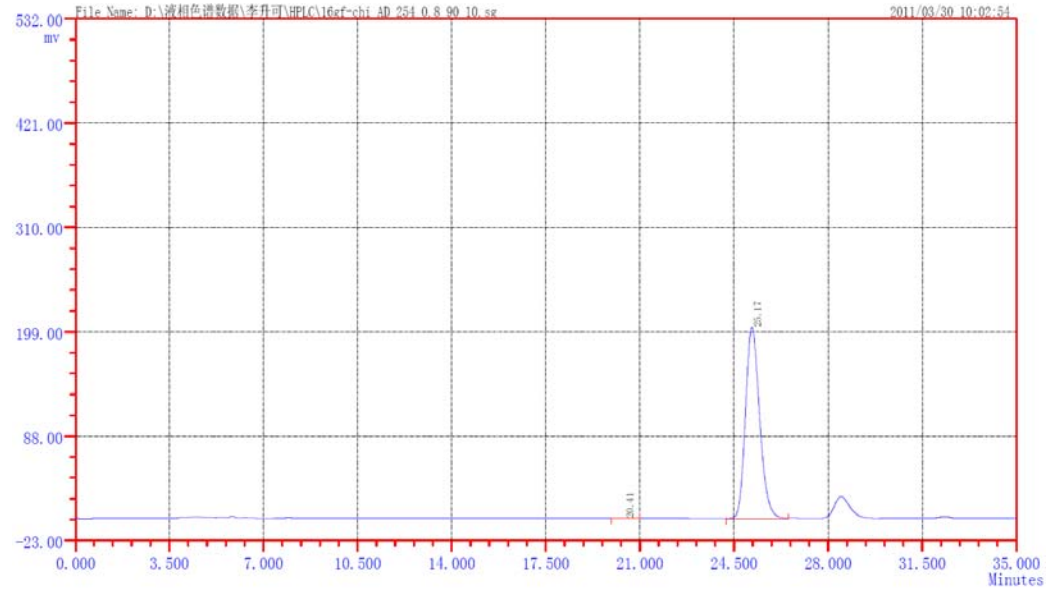
(*R*,*E*)-3-(4-chlorophenyl)-2-(4-nitrobenzylidene)cyclohexanone **5hf** (Fig. 2, entry 15): A pale yellow solid; $[\alpha]_D^{20}$ +815.0 (*c* 0.28, $CHCl_3$) for 99 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.66-1.84 (m, 2H), 2.09-2.14 (m, 2H), 2.44-2.53 (m, 1H), 2.68-2.75 (m, 1H), 4.38 (br s, 1H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.33-7.36 (m, 2H), 7.56 (s, 1H), 8.11-8.13 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.6, 32.1, 40.5, 43.0, 123.6, 129.0, 129.3, 130.4, 132.8, 134.4, 141.3, 141.7, 141.8, 147.4, 202.2. MS (EI) *m/z* (%): 342.1 (M+H, 100); HRMS (Micromass LCT) Calcd. for $C_{19}H_{17}ClNO_3$: 342.0897; Found: 342.0900. Chiralcel AD, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, t_{major} = 25.17 min, t_{minor} = 20.41 min.


8.130
8.126
8.113
8.108
7.353
7.348
7.596
7.337
7.332
7.326
7.276
7.264
7.255
7.128
7.106
4.381
2.743
2.736
2.707
2.609
2.603
2.530
2.512
2.499
2.486
2.481
2.468
2.455
2.438
2.140
2.129
2.119
2.113
2.103
2.004
1.816
1.809
1.800
1.792
1.783
1.720
1.701
1.690
1.675
0.000
O
O2N
Cl
PPM
202.180
147.404
141.819
141.697
141.333
134.422
132.823
130.364
129.256
128.978
123.591
77.322
77.000
76.686
42.969
40.529
32.128
18.631
O
O2N
Cl
200
150
100
50
0
PPM



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		20.697	126848	4127749.3	52.0656	1.41	8062
2		25.575	102309	3800230.9	47.9344	1.21	9449
	Σ:		229157	7927980.2	100.0000		

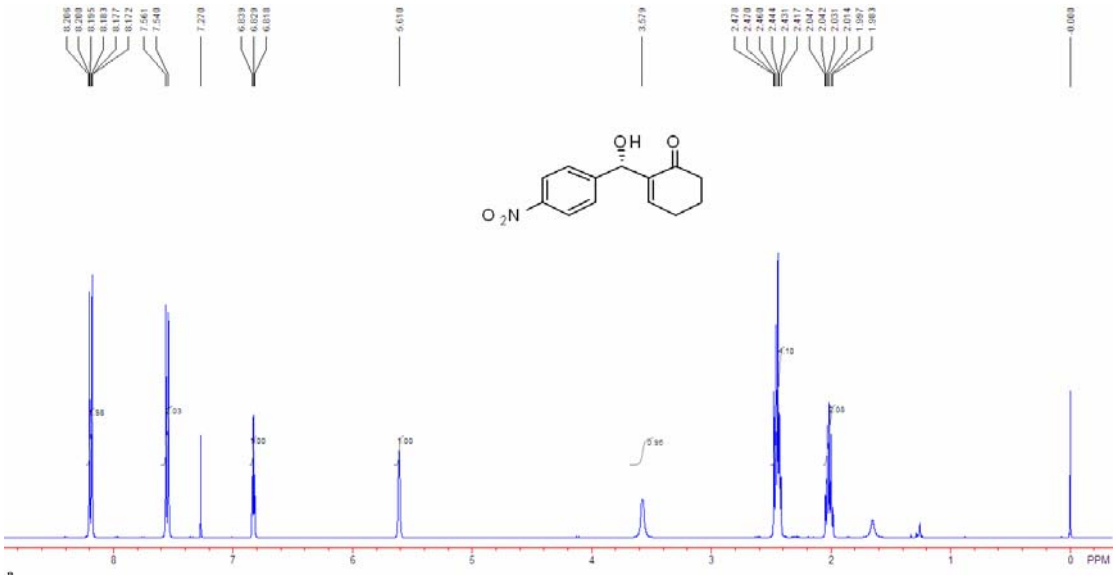
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

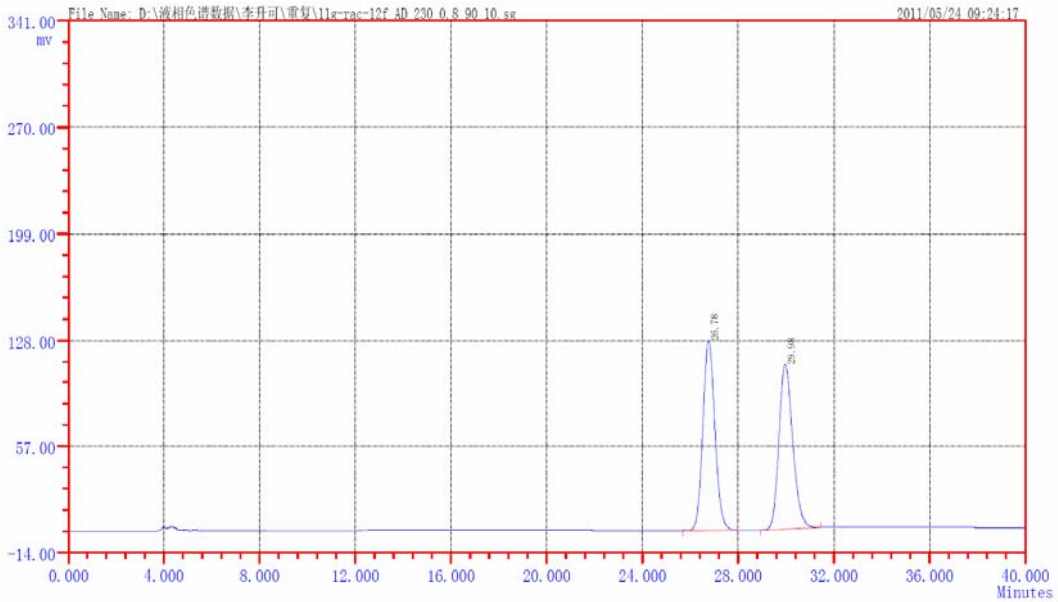


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		20.410	721	26288.3	0.3484	1.11	6245
2		25.172	204076	7518141.9	99.6516	1.20	9305
	Σ:		204797	7544430.3	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

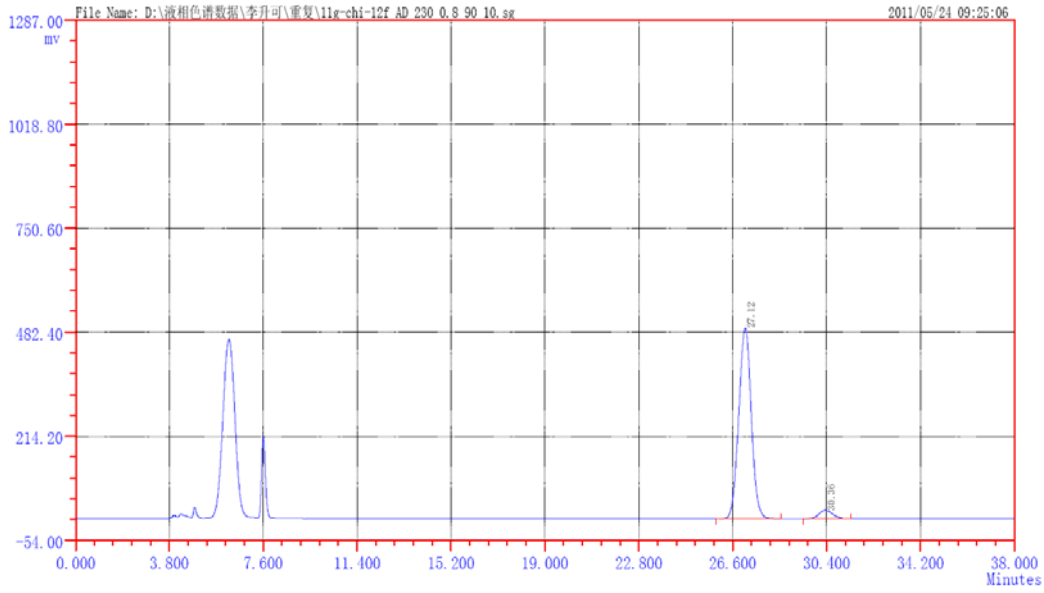
(*S*)-2-(hydroxy(4-nitrophenyl)methyl)cyclohex-2-enone **3h**.[8] $[\alpha]_D^{20}$ +36.4 (*c* 0.8, CH_2Cl_2) for 90 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.98-2.05 (m, 2H), 2.42-2.48 (m, 4H), 3.58 (br s, 1H), 5.61 (s, 1H), 6.83 (t, *J* = 4.0 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 2H), 8.17-8.21 (m, 2H). Chiralcel AD, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 230 nm, t_{major} = 27.12 min, t_{minor} = 30.36 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		26.775	127229	4453270.6	50.0751	1.10	11663
2		29.975	110635	4439913.9	49.9249	1.22	11119
	Σ:		237864	8893184.5	100.0000		

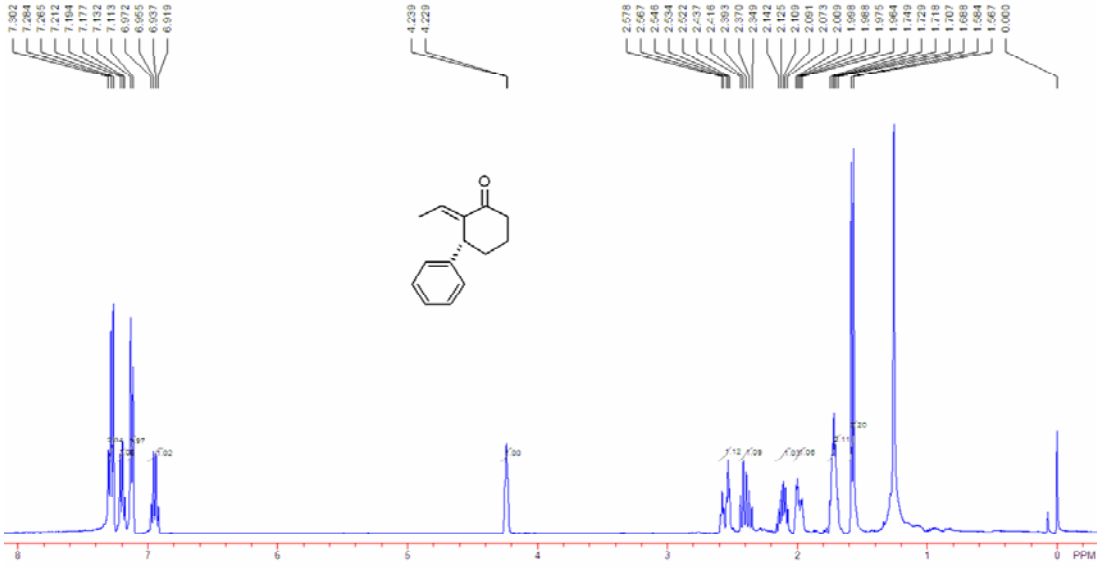
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

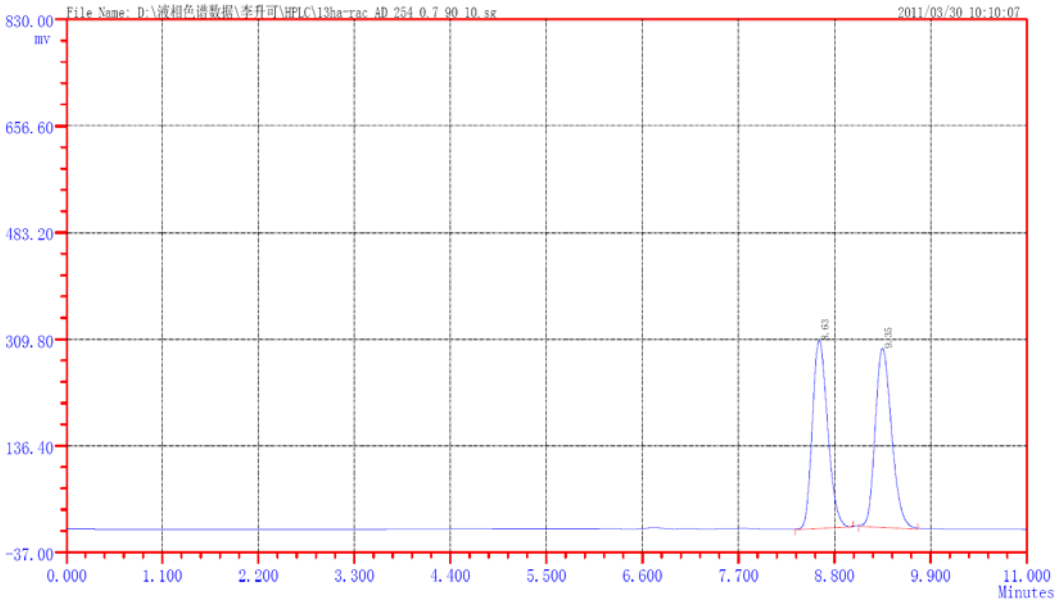


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		27.115	492370	17474677.6	94.9929	1.01	11633
2		30.357	22451	921099.6	5.0071	1.18	10912
	Σ:		514821	18395777.2	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

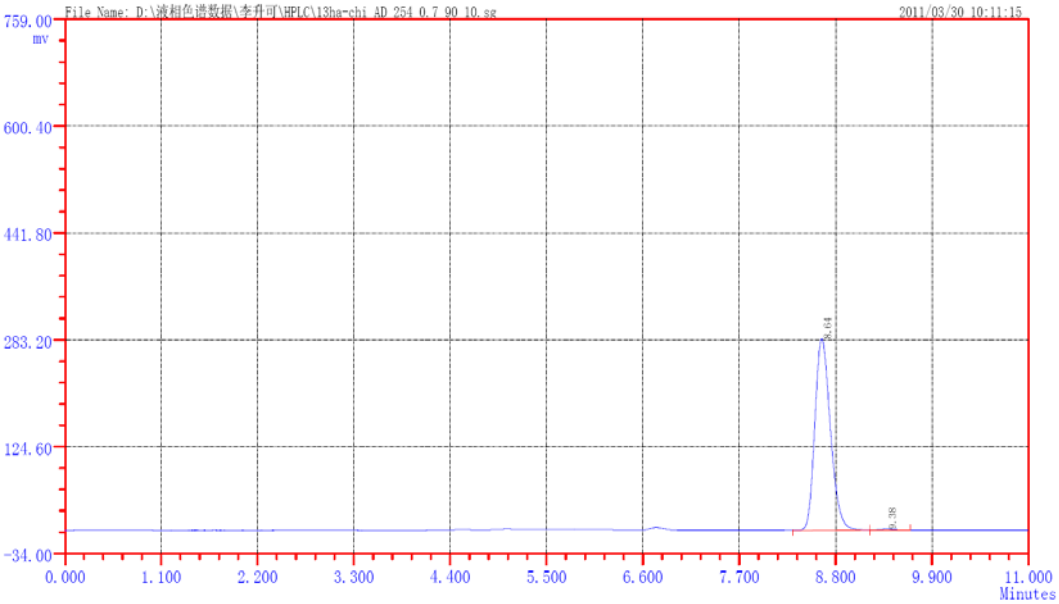
(*R*,*E*)-2-ethylidene-3-phenylcyclohexanone **5ia**[2] (Fig. 2, entry 16): $[\alpha]_D^{20}$ +38.0 (*c* 0.60, $CHCl_3$) for 99 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.58 (d, *J* = 6.8 Hz, 3H), 1.69-1.75 (m, 2H), 1.96-2.01 (m, 1H), 2.07-2.14 (m, 1H), 2.35-2.44 (m, 1H), 2.52-2.58 (m, 1H), 4.74 (br s, 1H), 6.95 (q, *J* = 7.2 Hz, 1H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 2H). Chiralcel AD, hexane/*i*-PrOH = 90/10, 0.7 mL/min, 254 nm, t_{major} = 8.64 min, t_{minor} = 9.38 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		8.627	306593	3743278.9	49.5520	1.24	9950
2		9.353	291601	3810961.6	50.4480	1.20	10209
	Σ:		598194	7554240.6	100.0000		

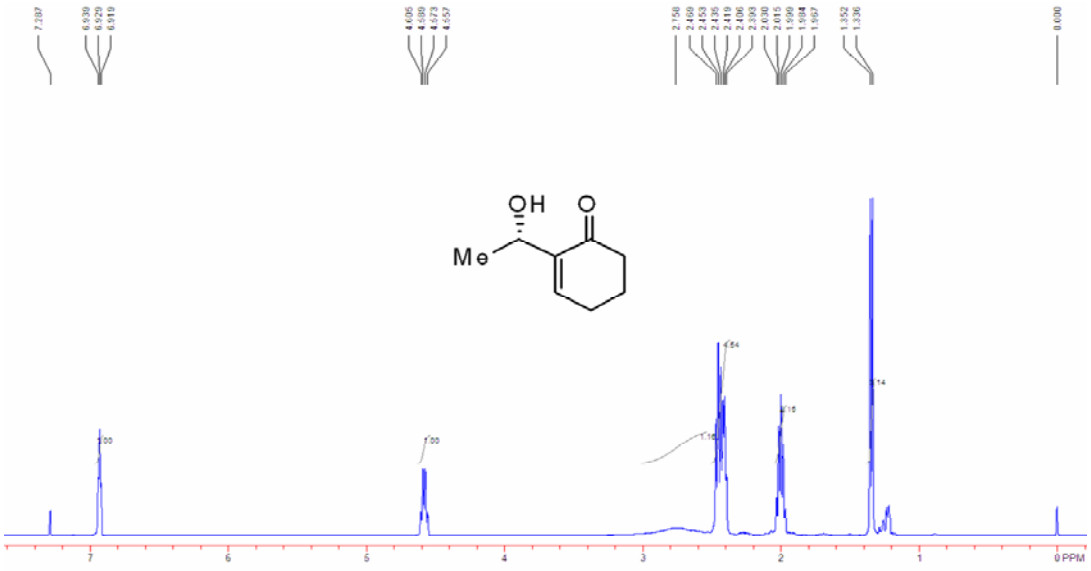
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

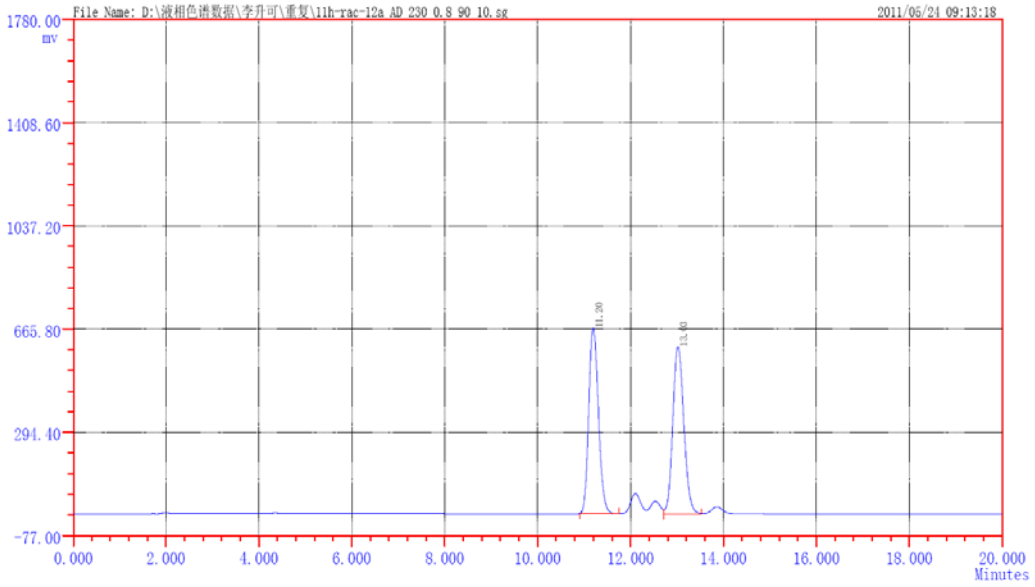


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		8.643	284236	3517722.2	99.4232	1.25	9721
2		9.383	1556	20408.7	0.5768	1.21	10201
	Σ:		285792	3538130.9	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

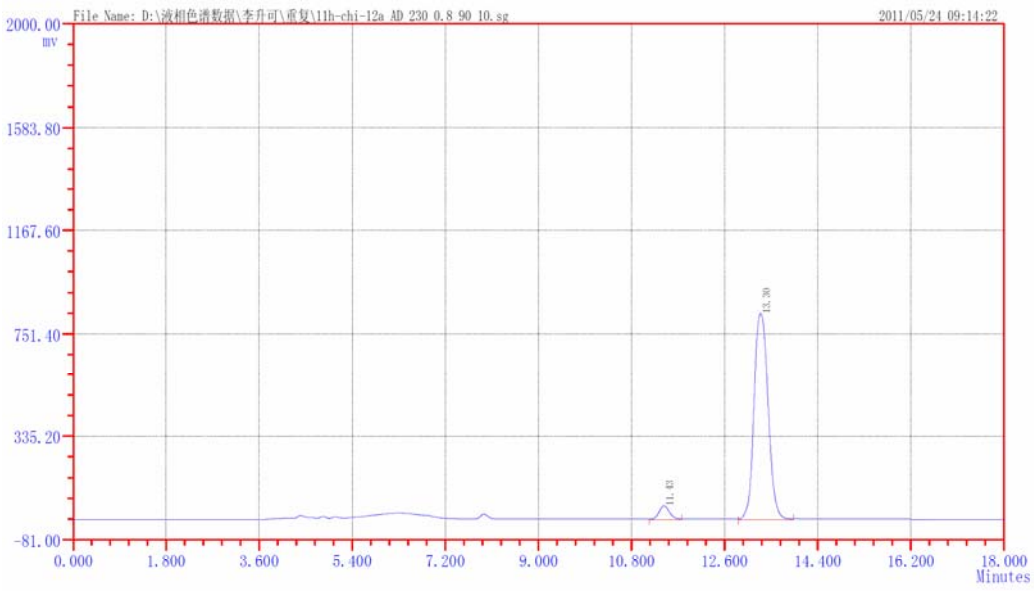
(*R*)-2-(1-hydroxyethyl)cyclohex-2-enone **3i**.[9] $[\alpha]_D^{20}$ +0.7 (*c* 0.6, CH_2Cl_2) for 91 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.34 (d, *J* = 5.6 Hz, 3H), 1.97-2.03 (m, 2H), 2.39-2.47 (m, 4H), 2.76 (br s, 1H), 4.58 (dd, *J* = 6.4, 12.8 Hz, 1H), 6.93 (t, *J* = 4.0 Hz, 1H). Chiralcel AD, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 230 nm, t_{major} = 13.30 min, t_{minor} = 11.43 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		11.200	666318	9696383.1	49.2581	1.15	11806
2		13.025	601643	9988482.6	50.7419	1.12	12268
	Σ:		1267961	19684865.7	100.0000		

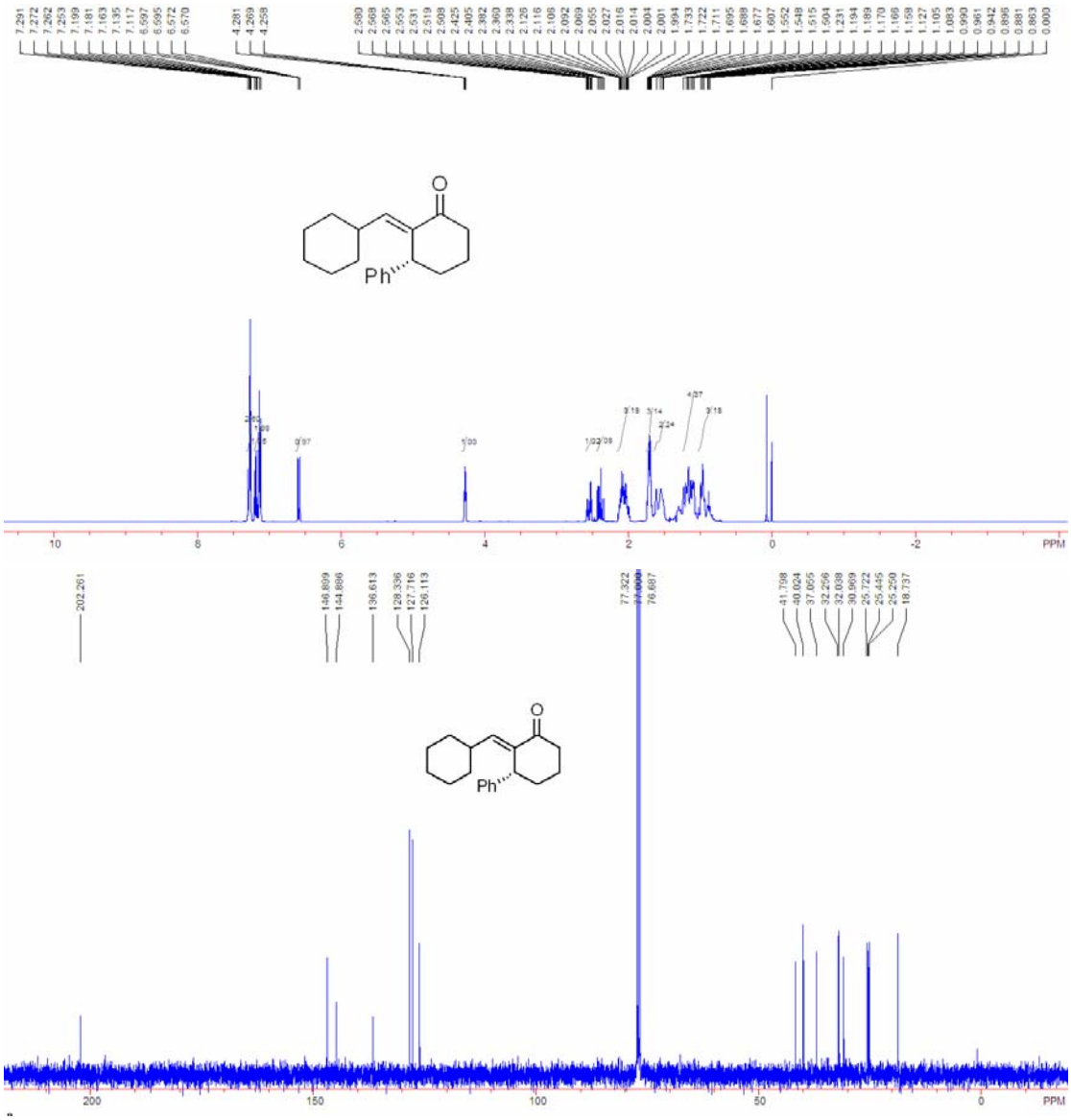
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

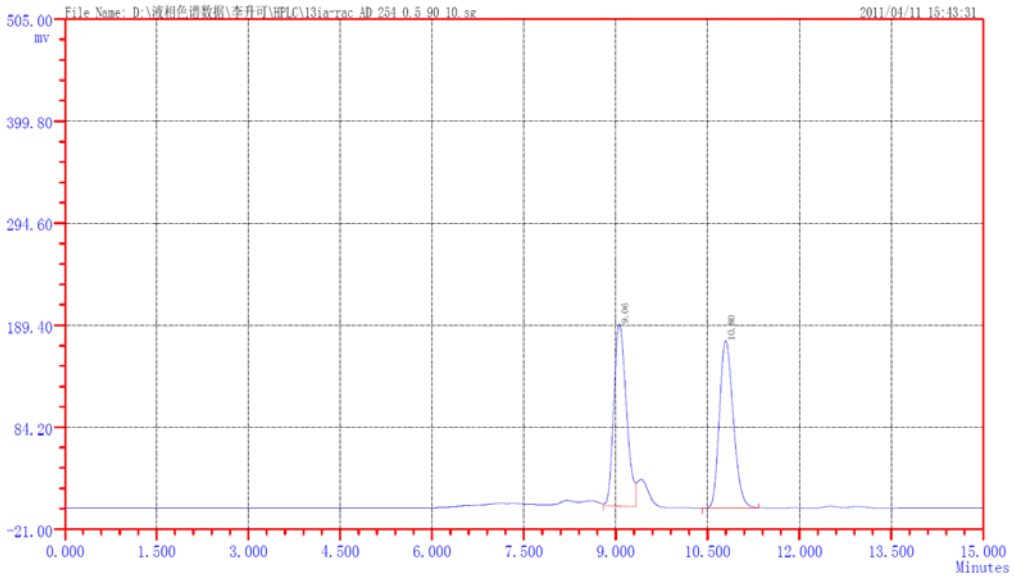


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		11.432	54315	762320.1	4.6505	1.13	13222
2		13.298	832597	15629921.3	95.3495	1.07	10002
	Σ:		886912	16392241.4	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

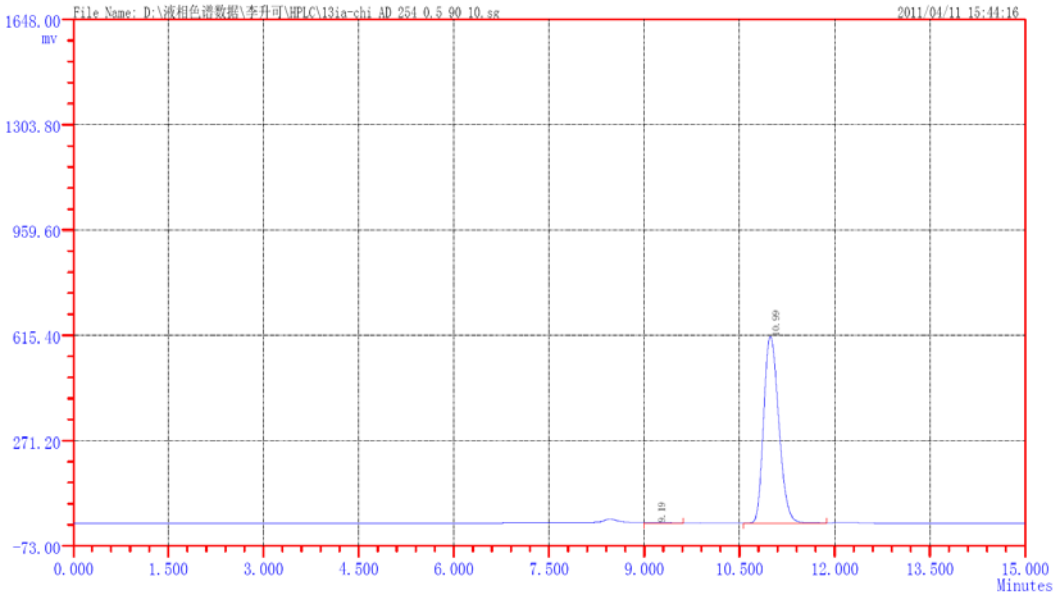
(*R*,*E*)-2-(cyclohexylmethylene)-3-phenylcyclohexanone **5ja** (Fig. 2, entry 17): $[\alpha]_D^{20}$ +104.3 (*c* 0.50, $CHCl_3$) for 99 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.86-0.99 (m, 3H), 1.08-1.23 (m, 4H), 1.50-1.61 (m, 2H), 1.68-1.73 (m, 3H), 1.99-2.13 (m, 3H), 2.34-2.43 (m, 1H), 2.51-2.58 (m, 1H), 4.27 (t, *J* = 4.8 Hz, 1H), 6.58 (dd, *J* = 0.8, 10.0 Hz, 1H), 7.13 (d, *J* = 7.2 Hz, 2H), 7.16-7.20 (m, 1H), 7.25-7.29 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.7, 25.3, 25.4, 25.7, 31.0, 32.0, 32.3, 37.1, 40.0, 41.8, 126.1, 127.7, 128.3, 136.6, 144.9, 146.9, 202.3. MS (EI) *m/z* (%): 268.2 (M+H, 100); HRMS (Micromass LCT) Calcd. for $C_{19}H_{24}O$: 268.1827; Found: 268.1838. Chiralcel AD, hexane/*i*-PrOH = 90/10, 0.5 mL/min, 254 nm, t_{major} = 10.99 min, t_{minor} = 9.19 min.


Ph
Ph
PPM
PPM



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		9.060	188157	2705002.5	49.8448	1.21	7916
2		10.800	172797	2721842.9	50.1552	1.21	9370
	Σ:		360954	5426845.4	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

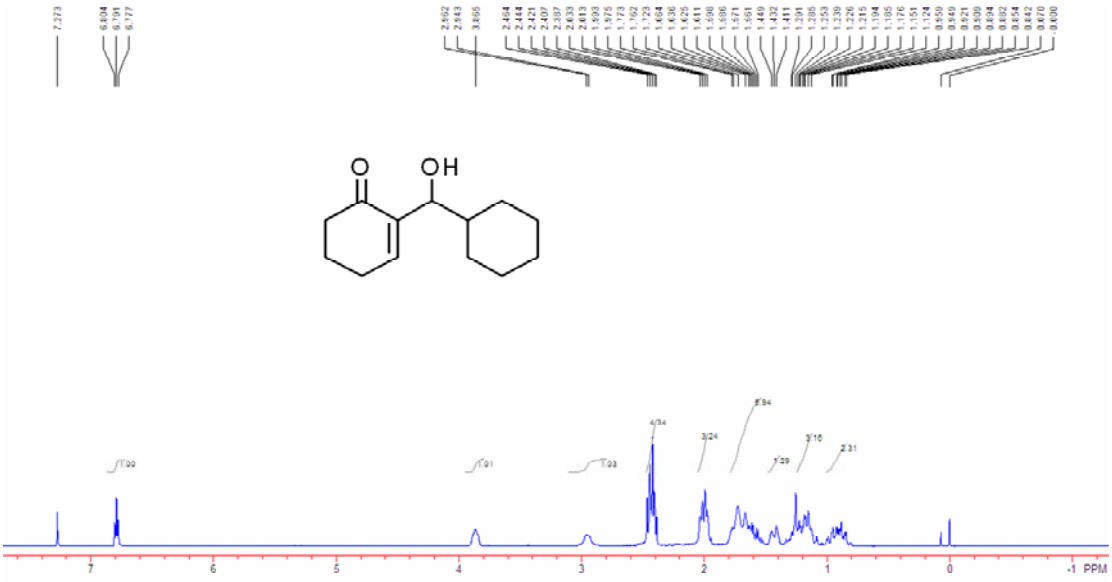


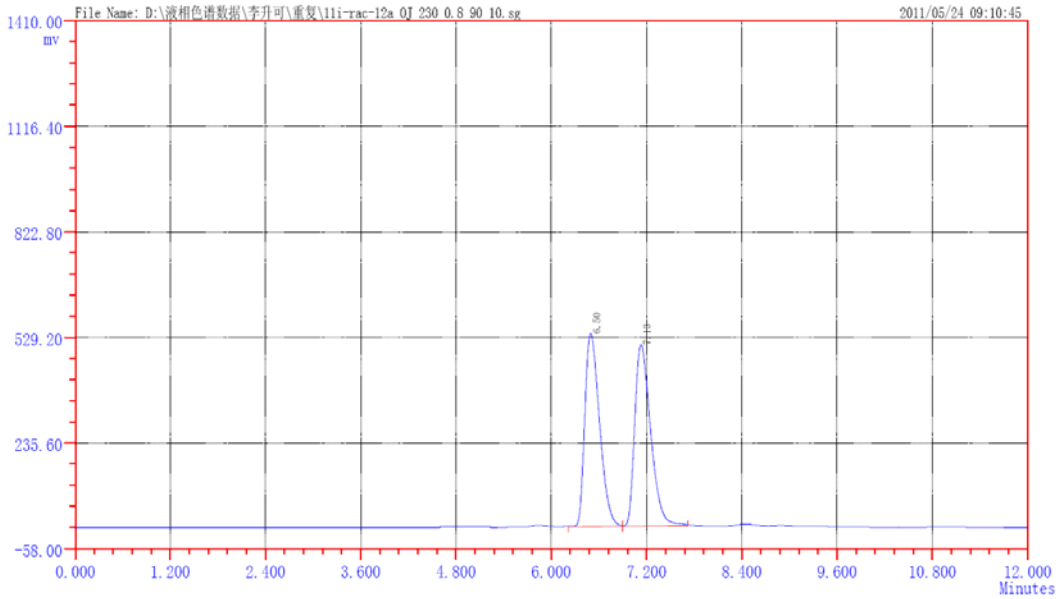
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		9.188	2560	56874.3	0.5584	1.64	3409
2		10.988	610482	10128416.2	99.4416	1.23	8743
	Σ:		613042	10185290.5	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

(*R*)-2-(cyclohexyl(hydroxy)methyl)cyclohex-2-enone **3j**.[3,10] $[\alpha]_D^{20}$ +32.6 (*c* 0.5, CH_2Cl_2) for 92 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.84-1.77 (m, 10H),

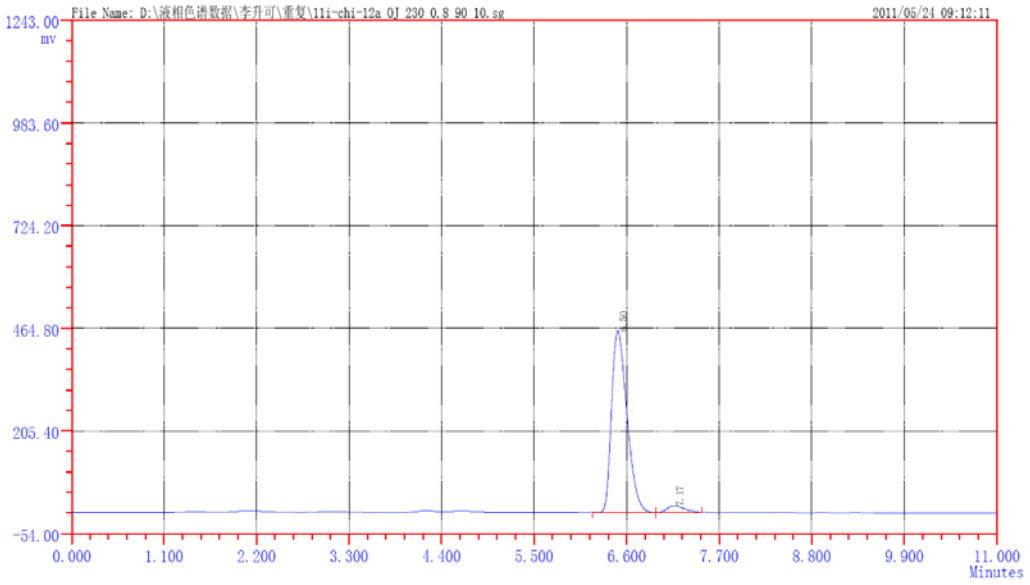
1.98-2.03 (m, 3H), 2.39-2.46 (m, 4H), 2.95 (br s, 1H), 3.87 (br s, 1H), 6.79 (t, J = 4.2 Hz, 1H). Chiralcel OJ, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 230 nm, t_{major} = 6.50 min, t_{minor} = 7.17 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		6.498	536710	6916485.3	49.6328	1.43	5068
2		7.133	504172	7018830.8	50.3672	1.46	5233
	Σ:		1040882	13935316.1	100.0000		

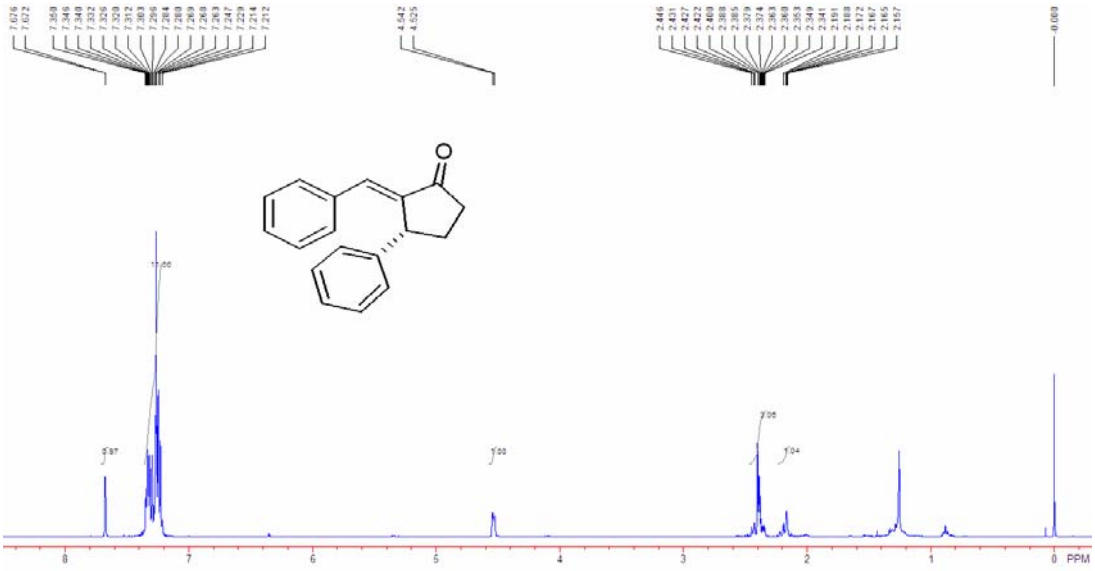
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

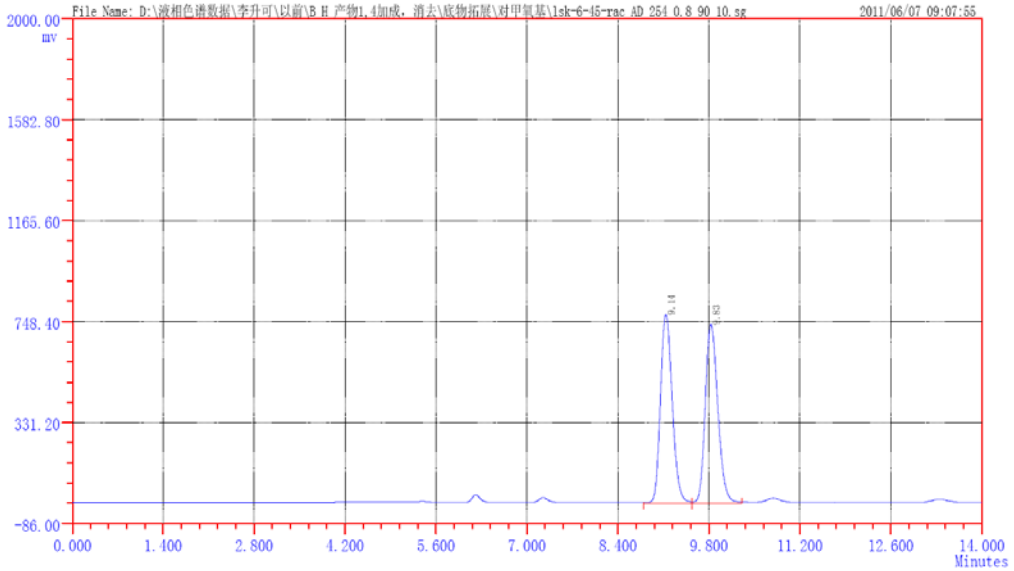


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		6.495	457961	5830130.0	95.8731	1.41	5188
2		7.168	16604	250961.2	4.1269	1.23	4483
	Σ:		474565	6081091.2	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

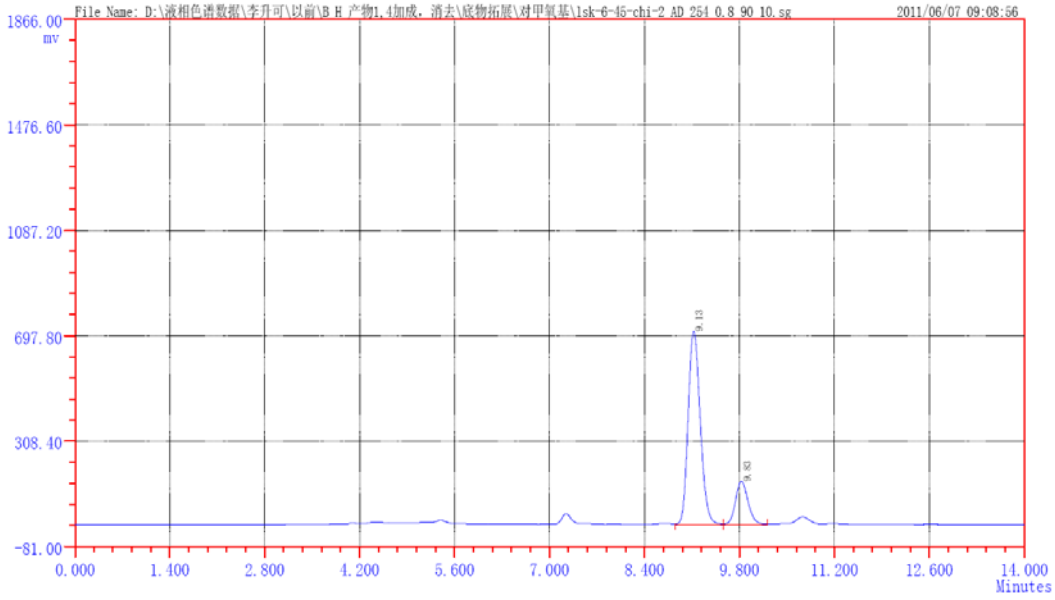
(*R*,*E*)-2-benzylidene-3-phenylcyclopentanone **5ka**[2] (Fig. 2, entry 18). $[\alpha]_D^{20}$ +182.4 (*c* 0.60, $CHCl_3$) for 62 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.16-2.19 (m, 1H), 2.34-2.45 (m, 3H), 4.53 (d, *J* = 6.8 Hz, 1H), 7.21-7.35 (m, 10H), 7.268 (d, *J* = 1.6 Hz, 1H). MS (EI) *m/z* (%): 249.1 (M+H, 100); HRMS (Micromass LCT) Calcd. for $C_{18}H_{17}O$: 249.1279; Found: 249.1283. Chiralcel AD, hexane/*i*-PrOH = 90/10, 0.8 mL/min, 254 nm, t_{major} = 9.13 min, t_{minor} = 9.83 min.





ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		9.140	780325	9867804.1	49.7504	1.18	10412
2		9.833	737573	9966829.3	50.2496	1.21	10554
	Σ:		1517898	19834633.4	100.0000		

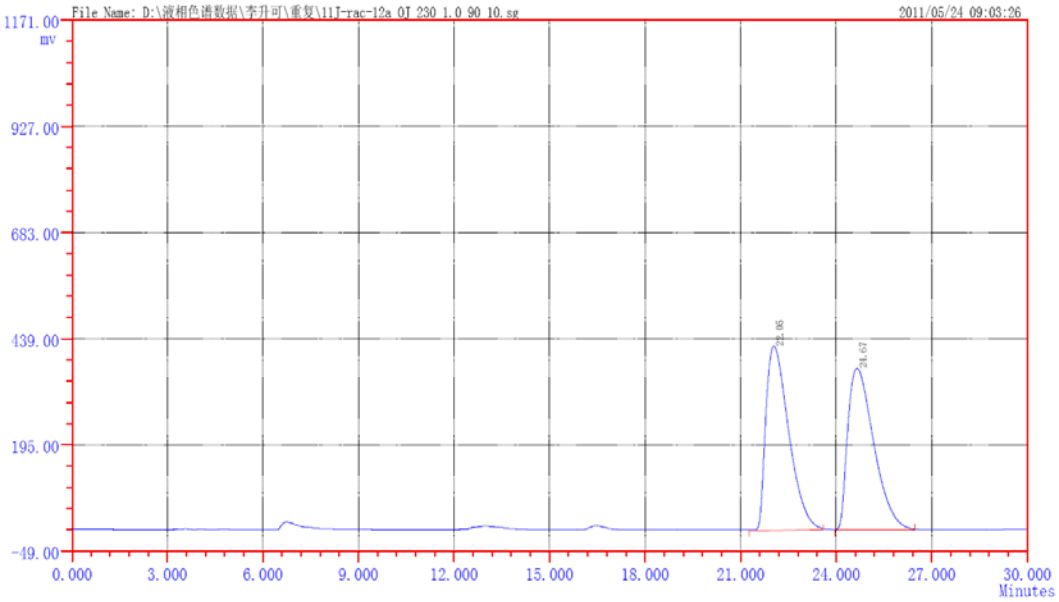
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		9.128	714281	8854272.9	81.1960	1.17	10808
2		9.832	159785	2050545.0	18.8040	1.14	11698
	Σ:		874066	10904817.9	100.0000		

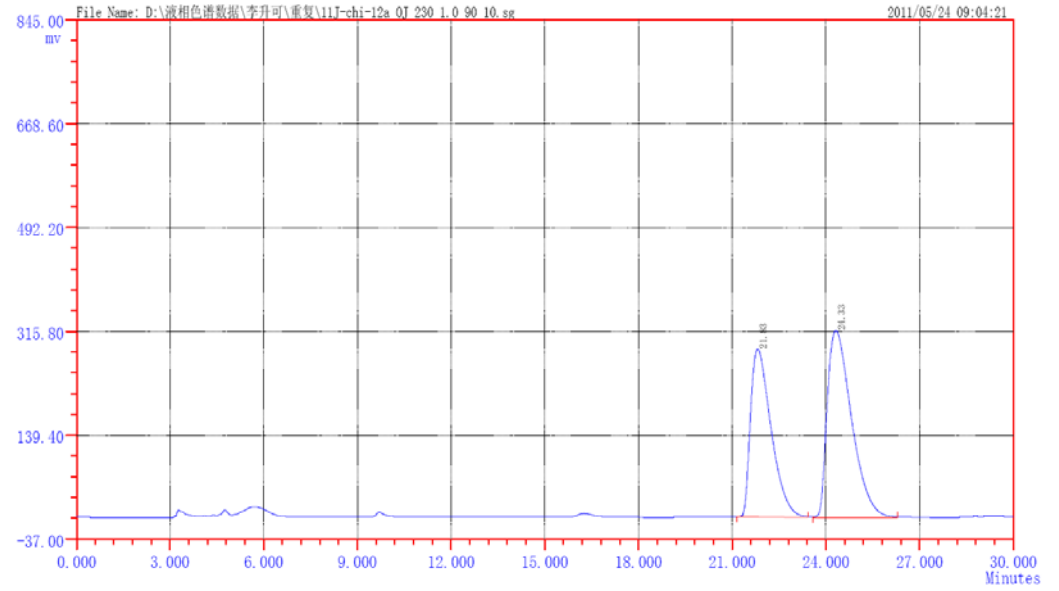
Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

(*R*)-2-(hydroxy(phenyl)methyl)cyclopent-2-enone **3k**.[11] $[\alpha]_D^{20}$ -7.8 (*c* 0.70, CH_2Cl_2) for 13 % ee. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.45-2.47 (m, 2H), 2.58-2.60 (m, 2H), 3.48 (br s, 1H), 5.57 (s, 1H), 7.26-7.40 (m, 6H). Chiralcel OJ, hexane/*i*-PrOH = 90/10, 1.0 mL/min, 230 nm, t_{major} = 24.33 min, t_{minor} = 21.83 min.



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		22.052	423743	21244118.6	50.1703	1.80	3856
2		24.667	371384	21099901.6	49.8297	1.74	3757
	Σ:		795127	42344020.2	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		21.827	285360	13051870.0	43.3254	1.74	4539
2		24.327	316985	17073319.3	56.6746	1.75	4066
	Σ:		602345	30125189.3	100.0000		

Sample	RetTime (min)	Hight	Area	Area (%)	Tailing factor	Theoretical plates (N)

References

1. P. Wessig, G. Müller, *Australian Journal of Chemistry* **61**, 569 (2008).

2. T. Gendrineau, J. –P. Genet, S. Darses, *Org. Lett*. **12**, 308 (2010).

3. N. T. McDougal, S. E. Schaus, *J. Am. Chem. Soc.* **125**, 12094 (2003).

4. Z. Shafiq, L. Liu, Z. Liu, D. Wang, Y. Chen, *Org*. *Lett*. **9**, 2525 (2007).

5. C. K.-W. Kwong, R. Huang, M. Zhang, M. Shi, P. H. Toy, *Chem. Eur. J*. **13**, 2369 (2007).

6. M. Shi, X.-G. Liu, *Org*. *Lett*. **10**, 1043 (2008).

7. (a) A. Berkessel, K. Roland, J. M. Neudoerfl, *Org*. *Lett*. **8**, 4195 (2006). (b) A. Lattanzi, *Synlett* 2106 (2007).

8. T. Kataoka, T. Iwama, S. Tsujiyama, T. Iwamura, S. Watanabe, *Tetrahedron* **54**, 11813 (1998).

9. (a) M. Bailey, I. Staton, P. R. Ashton, I. E. Marko, W. D. Ollis, *Tetrahedron*: *Asymmetry* **2**, 495 (1991). (b) M. Bailey, I. E. Marko, W. D. Ollis, *Tetrahedron Lett* **32**, 2687 (1991).

10. V. K. Aggarwal, A. Mereu, *Chem*. *Commun*. 2311 (1999).

11. A. Bugarin, B. T. Connell, *Chem*. *Commun*. 2644 (2010).

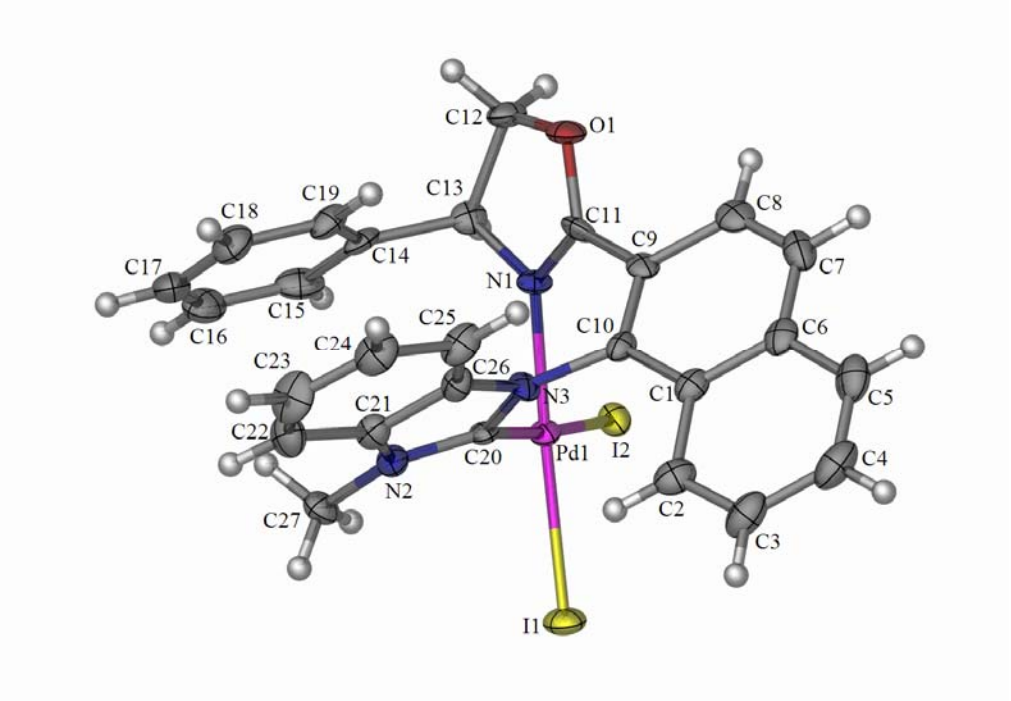


Fig. S1. X-ray crystal data of product (a*S*,*S*)-**2a**.

The crystal data of (a*S*,*S*)-**2a** have been deposited in CCDC with number 798781. Empirical formula: $C_{27}H_{21}I_2N_3OPd$; Formula weight: 763.67; Temperature: 296(2) K; Wavelength: 0.71073 Å: Crystal system, space group: Orthorhombic, P2(1)2(1)2(1); Unit cell dimensions: a = 9.0426(5) Å, alpha = 90 deg. b = 15.0498(9) Å, beta = 90 deg. c = 19.5924(11) Å, gamma = 90 deg. Volume: 2666.3(3) $Å^3$; Z, Calculated density: 4, 1.902 Mg/m^3; F(000): 1456; Crystal size: 0.39 x 0.23 x 0.09 mm; Final R indices [I>2sigma(I)], R1 = 0.0496, wR2 = 0.1067; R indices (all data) R1 = 0.0645, wR2 = 0.1171. Selected bond distances (Å) and angles (^{o}): I1-Pd1 2.5771(12), I2-Pd1 2.6709(+11), N1-Pd1 2.068(8), C20-Pd1 1.935(11), N2-C20 1.341(14), N3-C20 1.376(14), N1-C11 1.283(14), I1-Pd1-I2 96.67(4), N1-Pd1-C20 84.7(4), Pd1-C20-N3 122.8(8), C20-N3-C10-C1 -116.9(13), C20-N3-C10-C9 66.9(16), C10-C9-C11-N1 -45.1(18).

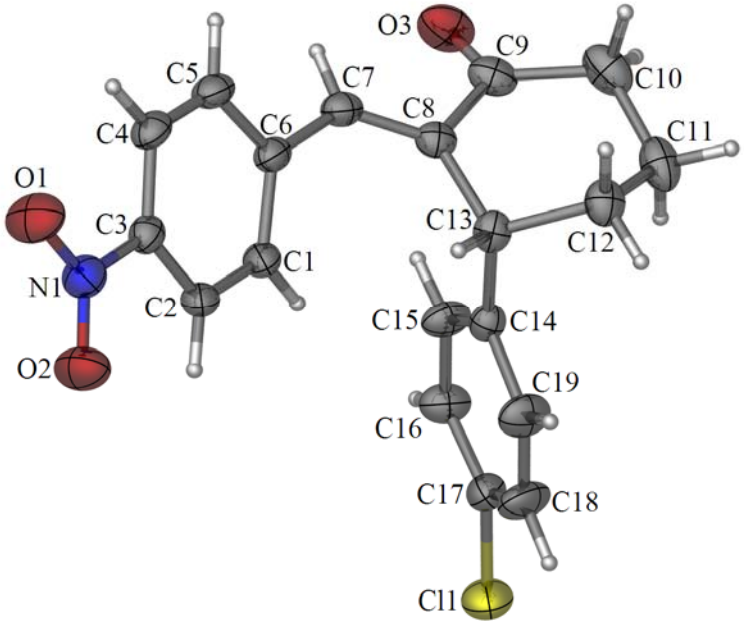


Fig. S2. X-ray crystal data of product (*R*)-**5hf**.

The crystal data of (*R*)-**5hf** have been deposited in CCDC with number 822886. Empirical formula: $C_{19}H_{16}ClNO_3$; Formula weight: 341.78; Temperature: 296(2) K; Wavelength: 0.71073 Å: Crystal system, space group: Monoclinic, P2(1); Unit cell dimensions: a = 11.1242(5) Å, alpha = 90 deg. b = 6.2039(3) Å, beta = 111.5220(10), c = 13.0579(6) Å, gamma = 90 deg. Volume: 838.34(7) $Å^3$; Z, Calculated density: 2, 1.354 Mg/m^3; F(000): 356; Crystal size: 0.46 x 0.38 x 0.32 mm; Final R indices [I>2sigma(I)], R1 = 0.0337, wR2 = 0.0818; R indices (all data) R1 = 0.0394, wR2 = 0.0855.

A possible catalytic cycled for the kinetic resolution.