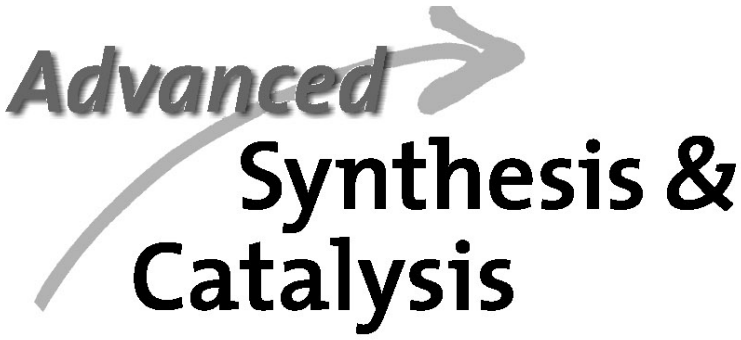


Supporting Information

Catalytic Asymmetric Addition of Diethylzinc to Diphenylphosphinoyl Imines Catalyzed by Copper(II) Trifluoromethanesulfonate—Chiral (2'-Ethylamino-[1,1']binaphthalenyl-2-yl)-thiophosphoramidic Acid O,O'-Diaryl Ester Ligands

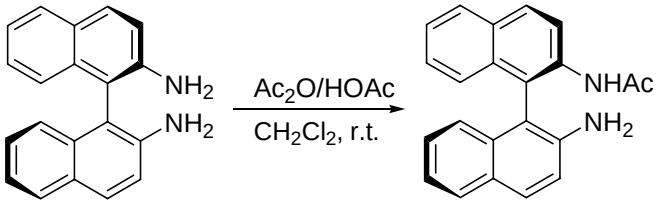
Min Shi, Zhi-Yu Lei, Qin Xu*

School of Chemistry & Pharmaceutics, East China University of Science and Technology, 130 MeiLong Road, Shanghai 200237 China, Fax: 86-21-64166128, Mshi@pub.sioc.ac.cn

Supporting Information

General Remarks. MPs were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; J-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer or HRMS. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash column chromatography was carried out using 200-300 mesh silica gel at increased pressure. Enantiomeric ratios were determined by chiral HPLC analysis. Racemic products were synthesized by addition of substrates with ethylmagnesium bromide (1.0 M in THF) at 0 ^{o}C.

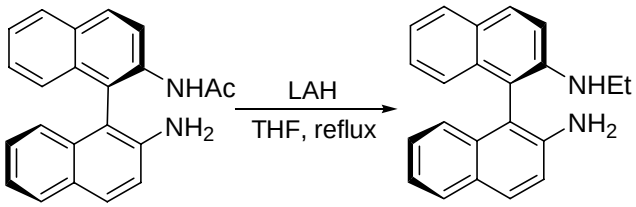
Synthesis of (*R*)-(+)-*N*-acetyl-1,1'-binaphthyl-2,2'-diamine.



Acetic anhydride (208 μL, 2.2 mmol) was added to a mixture of (*R*)-(+)-binaphthyldiamine (568 mg, 2.0 mmol), acetic acid (1.2 mL, 20 mmol) and dichloromethane (20.0 mL) with ice-cooling. The mixture was stirred at room temperature over night, and 2.0 N NaOH was

added until pH > 7. After extraction with dichloromethane, the combined organic layers were dried over $MgSO_4$. The residue obtained upon evaporation was purified by column chromatography to afford (*R*)-(+)-*N*-acetyl-1,1'-binaphthyl-2,2'-diamine as a colorless solid (509 mg, 78%). mp: 240-241 ^oC; $[\alpha]^{25}_D$ = +40.0 (c 0.55, $CHCl_3$); IR (KBr) ν 3400, 1675, 1595, 1500, 1445, 1270, 1040, 965, 670 cm^{-1}; ^1H NMR ($CHCl_3$, TMS, 300 MHz) δ 1.85 (s, 3H, Me), 6.91-7.42 (m, 8H, ArH and NHCO), 7.81-8.03 (m, 4H, ArH), 8.58 (d, *J* = 9.0 Hz, 2H, ArH); ^{13}C NMR ($(CD_3)_2SO$, TMS, 75 MHz) δ 23.98, 110.31, 119.39, 121.93, 123.77, 124.48, 125.01, 125.03, 125.68, 126.18, 126.92, 127.91, 128.66, 128.71, 129.97, 130.03, 132.06, 133.14, 134.51, 136.16, 144.98, 169.53; MS (EI) *m/e* 326 (M^+, 43.47), 284 (M^+-42, 25.13), 267 (M^+-59, 100); Anal. Calcd. for $C_{22}H_{18}ON_2$ requires C 80.98, H 5.52, N 8.59%; found: C 80.66, H 5.61, N 8.48%.

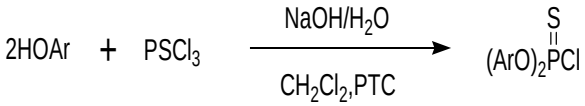
Synthesis of (*R*)-(+)-*N*-ethyl-1,1'-binaphthyl-2,2'-diamine.



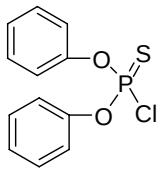
To a stirred suspension of $LiAlH_4$ (280 mg, 7.37 mmol) in 30.0 mL of anhydrous THF was added dropwise a solution of (*R*)-(+)-*N*-ethyl-1,1'-binaphthyl-2,2'-diamine (509 mg, 1.56 mmol) in 10.0 mL of THF. The mixture was heated under reflux for 4 h. The reaction mixture was cooled in an ice-bath and the remaining hydride was carefully quenched by dropwise addition of water (5.0 mL) and then 10% NaOH (5.0 mL). A white precipitate was filtered off and thoroughly washed with ethyl acetate. The combined filtrate and ethyl acetate washings were washed with brine and dried over $MgSO_4$. After the solvents were evaporated under reduced pressure, the product was purified by flash chromatography to afford product (*R*)-(+)-*N*-ethyl-1,1'-binaphthyl-2,2'-diamine (470 mg, 97%) as a colorless solid. mp: 123-124 ^oC; $[\alpha]^{25}_D$ = +175.2 (c 0.63, $CHCl_3$); IR(KBr) ν 3385, 3060, 2985, 2910, 1645, 1598, 1510, 1425, 1350, 1150, 915, 820cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.99 (t, *J* = 7.5 Hz, 3H, Me), 3.18 (q, *J* = 7.5 Hz, 2H, CH_2), 3.60 (br, 3H, amino-H), 6.96-7.25 (m, 8H, ArH), 7.75-7.87 (m, 4H, ArH); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 15.57, 39.02, 112.62, 112.84,

114.69, 118.71, 122.28, 122.79, 124.15, 124.36, 127.09, 127.19, 128.03, 128.50, 128.54, 128.80, 129.86, 129.96, 134.01, 134.30, 143.35, 144.73; MS (EI) *m/e* 313 (M^++1, 100.00), 297 (M^+-15, 34.21), 280 (M^+-32, 42.91), 267 (M^+-45, 25.99); Anal. Calcd. for $C_{22}H_{20}N_2$ requires C 84.62, H 6.41, N 8.97%; found: C 84.53, H 6.56, N 8.95%.

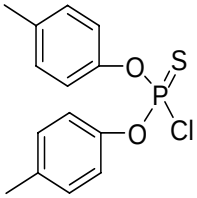
Representative Experimental Procedure for the Synthesis of O,O-Diaryl Chlorothiophosphate.[1]



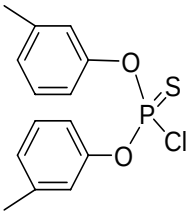
To a solution of thiophosphoryl chloride (8.5 g, 0.05 mol) and tetrabutylammonium bromide (2.5 g, 0.008 mol) in CH_2Cl_2 (150 mL) was added dropwise 25.0 mL aqueous solution of phenol (9.4 g, 0.1 mol) and sodium hydroxide (4.0 g, 0.1 mol), and the mixture was heated under reflux for 2 h. Then reaction mixture was poured into water. The organic layer was collected and the aqueous phase was extracted once with CH_2Cl_2. The combined organic layers were washed with brine and then was dried over anhydrous Na_2SO_4, filtered and concentrated under reduce pressure. Most of the products were sufficiently pure but if necessary they can be purified by recrystallization.



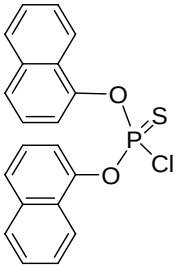
8.52 g, 60% yield. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.24-7.33 (m, 6H, ArH), 7.37-7.44 (m, 4H, ArH); MS (EI) *m/e* 284 (M^+,100), 155 (M^+-129, 22.17).



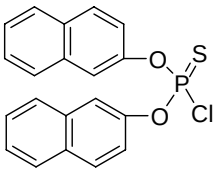
8.89 g, 57% yield. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.35 (s, 3H, Me), 2.36 (s, 3H, Me), 7.19 (s, 8H, Me).



8.27 g, 53% yield. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 2.39 (s, 3H, Me), 7.08-7.13 (m, 6H, ArH), 7.25-7.31 (m, 2H, ArH).

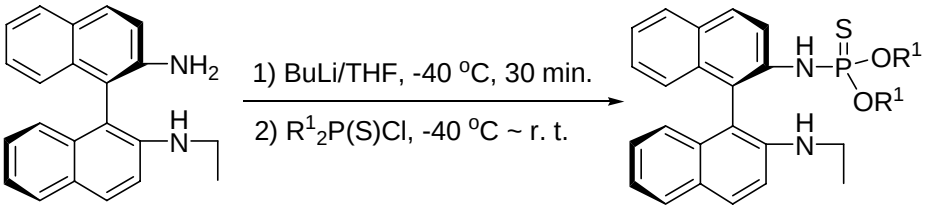


10.56 g, 55% yield. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.45-7.58 (m, 6H, ArH), 7.63-7.67 (m, 2H, ArH), 7.78-7.81 (m, 2H, ArH), 7.88-7.91 (m, 2H, ArH), 8.12-8.15 (m, 2H, ArH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85%H_3PO_4) δ +59.16; MS (EI) *m/e* 384 (M^+,100), 205 (M^+-179, 19.95).



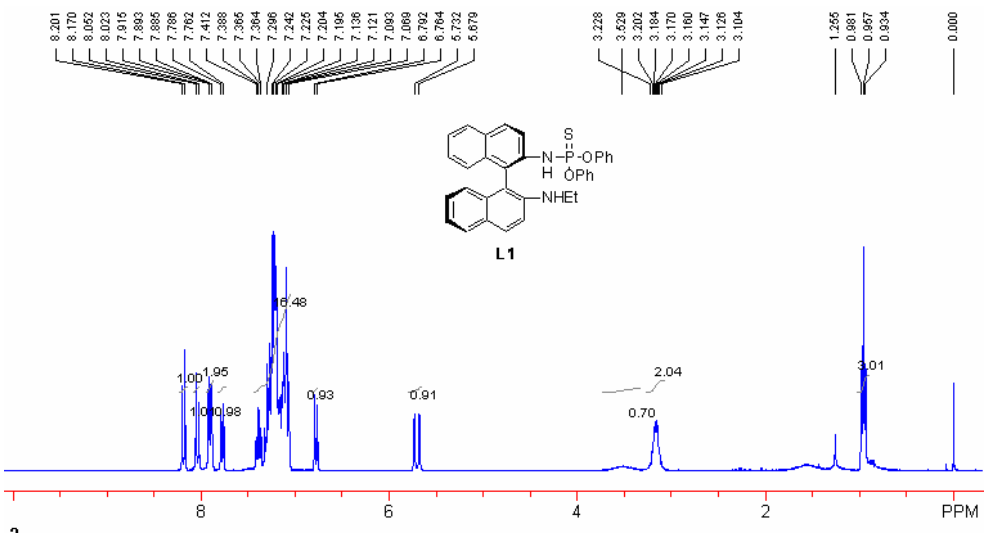
9.22 g, 48% yield. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 7.46-7.57 (m, 6H, ArH), 7.80-7.92 (m, 8H, ArH).

Representative Experimental Procedure for the Synthesis of Ligands L1-L5.

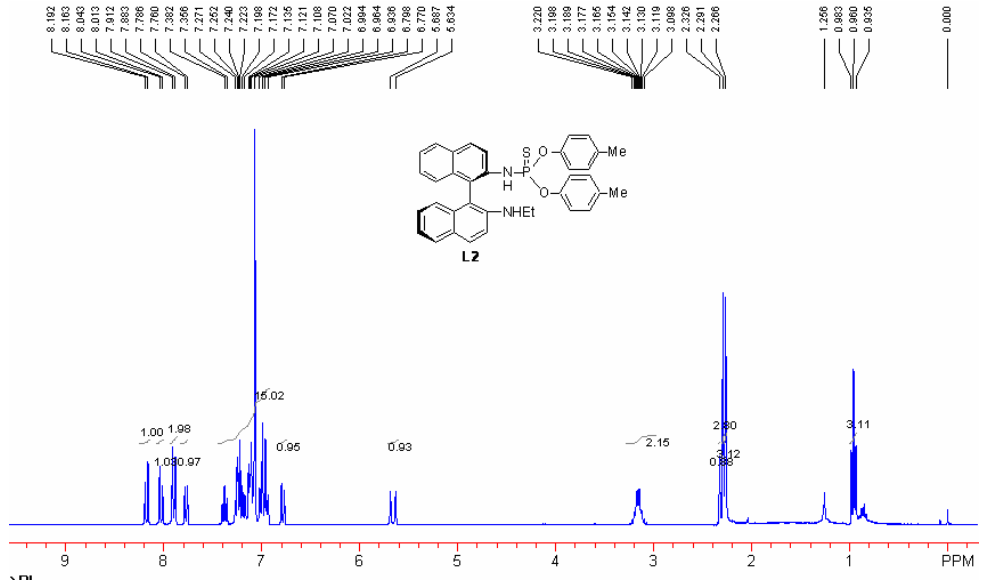


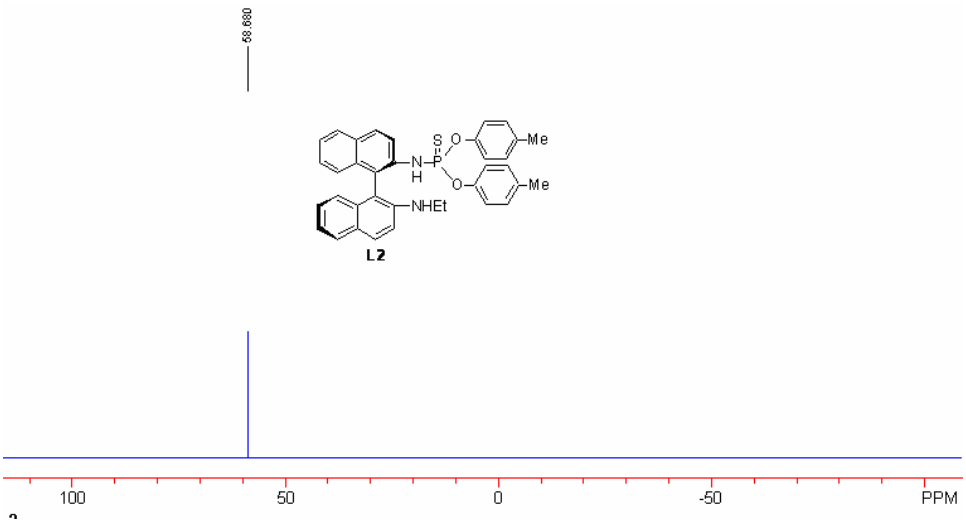
To a solution of (*R*)-(+)-*N*-ethyl-1,1'-binaphthyl-2,2'-diamine (200 mg, 0.64 mmol) in THF (10.0 mL) was added dropwise n-butyllithium (1.12 mL, 1.8 mmol, 1.6 M solution in hexane) at –40 ^{o}C over 40 min, and the reaction mixture was stirred for 1 h at the same temperature. Then O,O-diphenyl chlorothiophosphate (365 mg, 1.28 mmol) in 5.0 mL of THF was added dropwise and the reaction solution was slowly warmed to room temperature. After 2 h, THF was removed in vacuo. The residue was purified by alumina column chromatography to give the corresponding **ligand 1** (**L1**) as a colorless solid (316 mg, 88%).

Ligand 1 (L1): 316 mg, 88% yield. a colorless solid; mp: 49-51 ^{o}C; $[\alpha]^{25}_{D}$ = +9.0 (c 0.19, $CHCl_3$); IR (CH_2Cl_2) ν 3409, 3350, 3057, 2969, 2926, 2869, 1619, 1597, 1513, 1427, 1150, 1070, 1027, 1010, 897, 867 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.96 (t, *J* = 6.9 Hz, 3H, Me), 3.17 (m, 2H, CH_2), 3.53 (br, 1H, NH), 5.70 (d, *J* = 15.9 Hz, 1H, NH), 6.78 (d, *J* = 8.4 Hz, 1H, ArH), 7.07-7.41 (m, 16H, ArH), 7.77 (d, *J* = 7.5 Hz, 1H, ArH), 7.88-7.92 (m, 2H, ArH), 8.04 (d, *J* = 9.0 Hz, 1H, ArH), 8.19 (d, *J* = 9.3 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 14.9, 38.2, 109.2, 113.9, 118.2, 118.7, 118.9, 121.0, 121.11, 121.19, 122.0, 123.2, 124.58, 124.61, 125.30, 125.37, 125.4, 126.9, 127.1, 127.4, 128.1, 128.2, 129.47, 129.49, 129.50, 129.67, 130.2, 130.6, 133.3, 133.6, 136.1 (d, *J* = 9.6 Hz), 144.3, 150.2 (d, *J* = 27.6 Hz), 150.4 (d, *J* = 24.3 Hz); ^{31}P NMR ($CDCl_3$, 121 MHz, 85%H_3PO_4) δ +58.03; HRMS(EI) Calcd. For $C_{34}H_{29}N_2O_2PS$ (M^+): 560.1687, found: 560.1687.

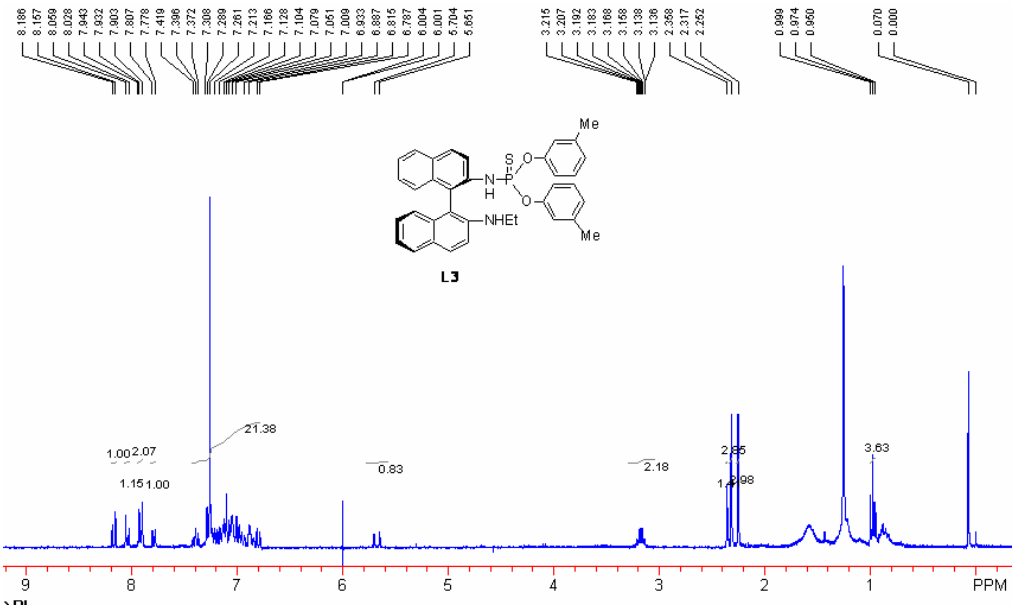


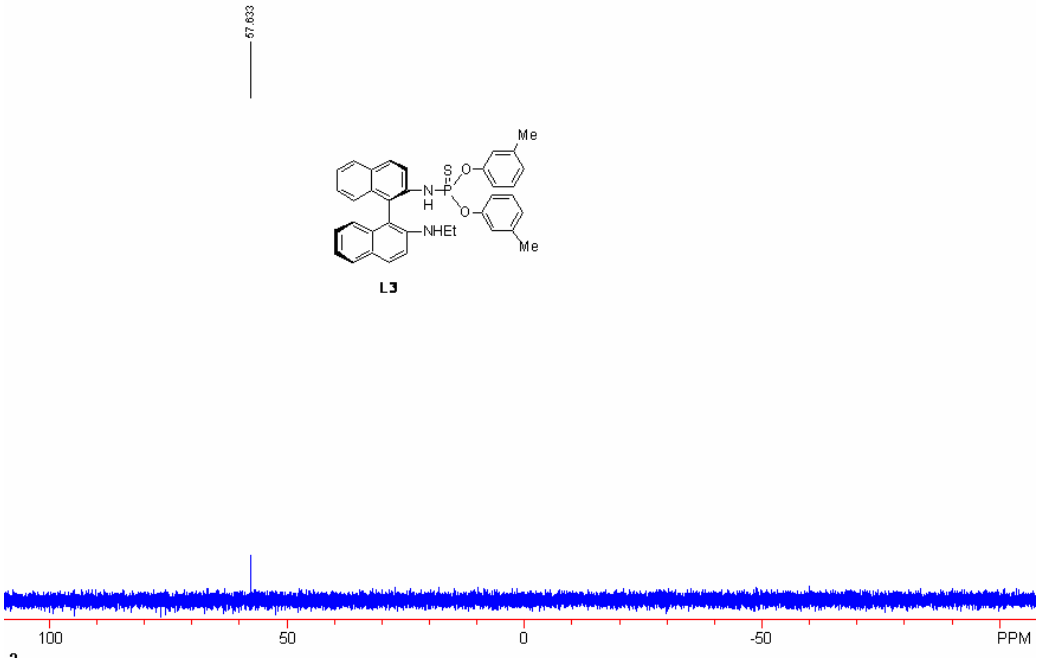
Ligand 2 (L2): 280 mg, 75% yield. a colorless solid; mp: 136.9-138.1 ^{o}C; $[\alpha]^{25}_{D}$ = +8.7 (c 1.96, $CHCl_3$); IR (CH_2Cl_2) ν 3405, 3355, 3053, 2967, 2924, 2868, 1619, 1597, 1511, 1472, 1390, 1337, 1161, 1004, 918, 821 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.96 (t, *J* = 6.9 Hz, 3H, Me), 2.27 (s, 3H, Me), 2.29 (s, 3H, Me), 2.33 (s, 1H, NH), 3.16 (m, 2H, CH_2), 5.66 (d, *J* = 15.6 Hz, 1H, NH), 6.78 (d, *J* = 8.4 Hz, 1H, ArH), 6.93-7.38 (m, 14H, ArH), 7.77 (d, *J* = 8.1 Hz, 1H, ArH), 7.90 (d, *J* = 9.0 Hz, 2H, ArH), 8.03 (d, *J* = 9.0 Hz, 1H, ArH), 8.18 (d, *J* = 8.7 Hz, 1H, ArH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85%H_3PO_4) δ +58.68; HRMS(EI) Calcd. For $C_{36}H_{33}N_2O_2PS$ (M^+): 588.2000, found: 588.1997.



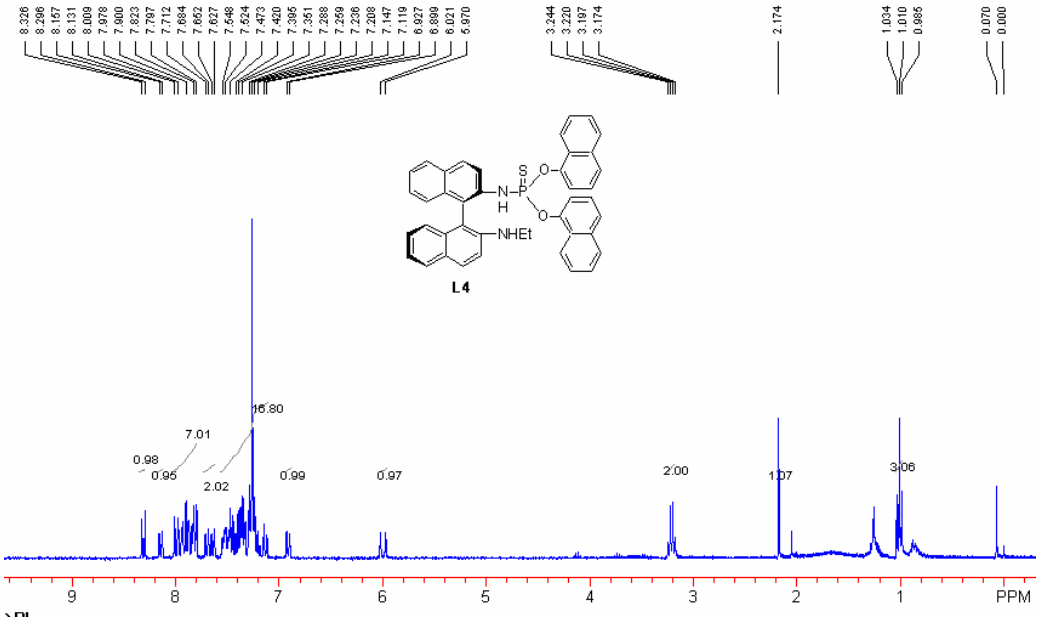


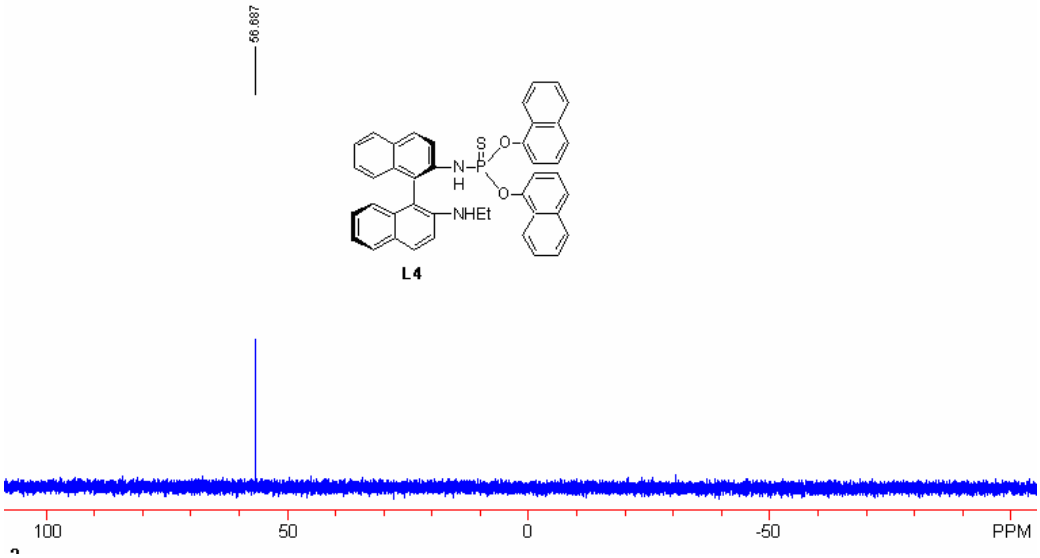
Ligand 3 (L3): 209 mg, 56% yield. a colorless oil; $[\alpha]^{25}_{D}$ = +3.8 (c 0.73, $CHCl_3$); IR (CH_2Cl_2) ν 3405, 3355, 3504, 2961, 2923, 2853, 1611, 1585, 1510, 1487, 1240, 1138, 1010, 957, 865 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.97 (t, *J* = 7.2 Hz, 3H, Me), 2.25 (s, 3H, Me), 2.32 (s, 3H, Me), 2.36 (s, 1H, NH), 3.17 (m, 2H, CH_2), 5.68 (d, *J* = 15.9 Hz, 1H, NH), 6.79-7.45 (m, 15H, ArH), 7.79 (d, *J* = 8.7 Hz, 1H, ArH), 7.92 (d, *J* = 8.7 Hz, 2H, ArH), 8.04 (d, *J* = 8.4 Hz, 1H, ArH), 8.17 (d, *J* = 8.7 Hz, 1H, ArH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85%H_3PO_4) δ +57.63; HRMS(EI) Calcd. For $C_{36}H_{33}N_2O_2PS$ (M^+): 588.2000, found: 588.2000.



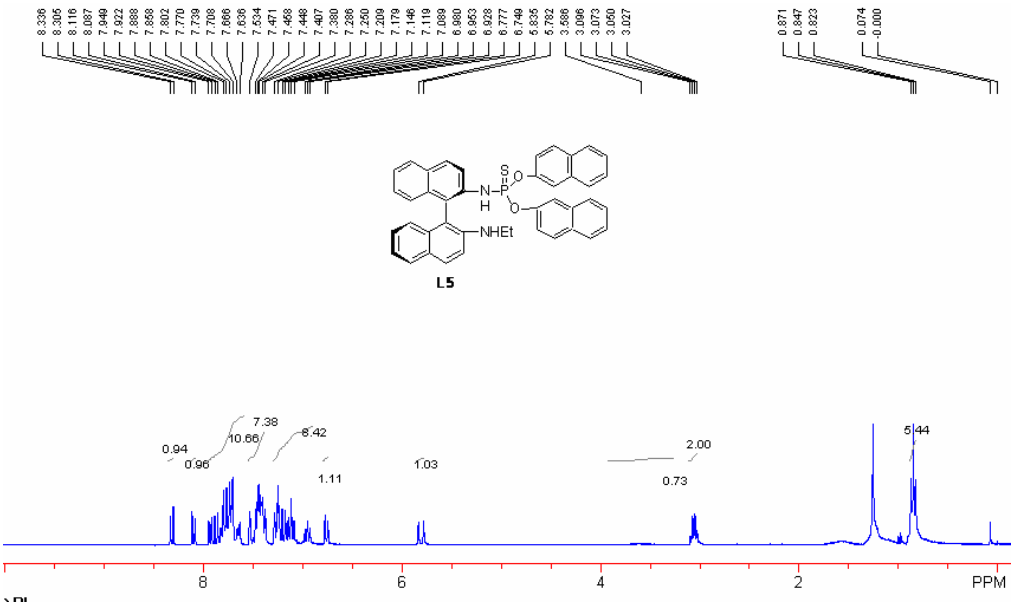


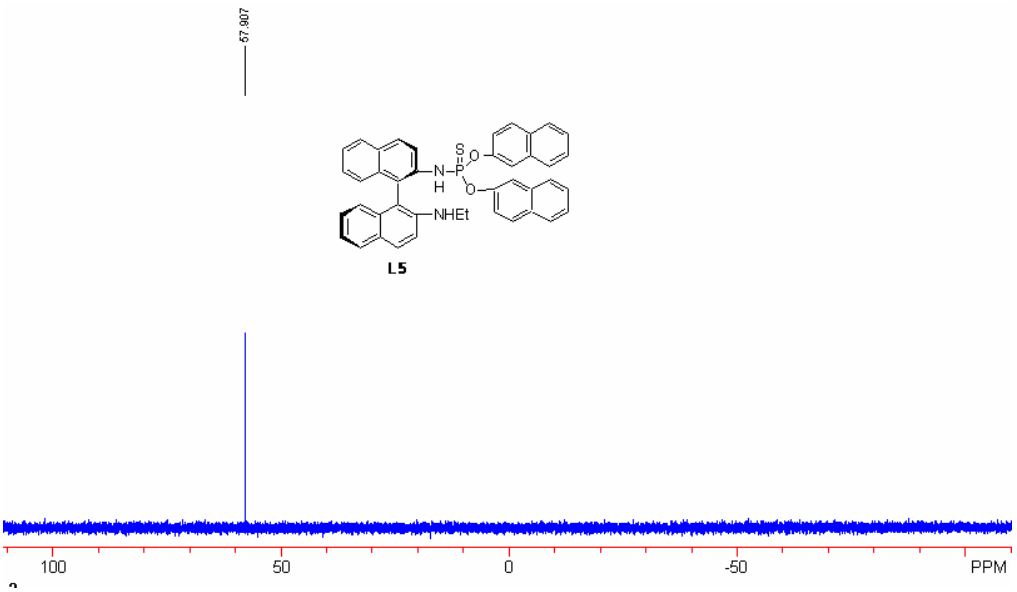
Ligand 4 (L4): 334 mg, 79% yield. a colorless solid; mp: 196.7-197.0 ^{o}C; $[\alpha]^{25}_{D}$ = -25.3 (c 0.73, $CHCl_3$); IR (CH_2Cl_2) ν 3347, 3054, 1618, 1597, 1573, 1508, 1470, 1426, 1389, 1257, 1222, 1153, 1078, 1038, 1004, 822 cm^{-1}; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 1.01 (t, *J* = 7.2 Hz, 3H, Me), 2.17 (s, 1H, NH), 3.21 (q, *J* = 7.2 Hz, 2H, CH_2), 5.99 (d, *J* = 15.3 Hz, 1H, NH), 6.91 (d, *J* = 8.4 Hz, 1H, ArH), 7.12-7.60 (m, 14H, ArH), 7.61-7.73 (m, 2H, ArH), 7.78-8.04 (m, 7H, ArH), 8.14 (d, *J* = 8.4 Hz, 1H, ArH), 8.31 (d, *J* = 8.7 Hz, 1H, ArH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85%H_3PO_4) δ +56.69; MS (EI) *m/e* 660.2 (M^+,100); Anal Calcd. for $C_{42}H_{33}N_2O_2PS$ requires: C, 76.34; H, 5.03; N, 4.24%. found: C, 76.27; H, 4.88; N, 4.14%.



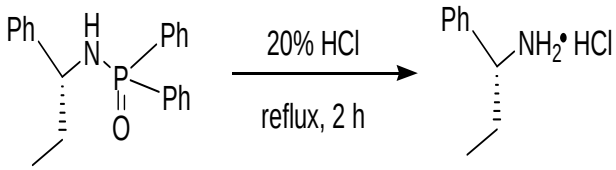


Ligand 5 (L5): 304 mg, 72% yield. a colorless oil; $[\alpha]^{25}_{D}$ = -0.2 (c 1.15,$CHCl_3$); IR (CH_2Cl_2) ν 3388, 3351, 3056, 2965, 2925, 2853, 1618, 1598, 1510, 1463, 1241, 1207, 1152, 1119, 1004, 963, 929, 861, 810 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.85 (t, *J* = 7.2 Hz, 3H, Me), 3.06 (q, *J* = 7.2 Hz, 2H, CH_2), 3.59 (br, 1H, NH), 5.81 (d, *J* = 15.9 Hz, 1H, NH), 6.76 (d, *J* = 8.4 Hz, 1H, ArH), 6.93-7.29 (m, 5H, ArH), 7.38-7.53 (m, 7H, ArH), 7.64-7.95 (m, 11H, ArH), 8.10 (d, *J* = 9.0 Hz, 1H, ArH) , 8.32 (d, *J* = 9.0 Hz, 1H, ArH); ^{31}P NMR ($CDCl_3$, 121 MHz, 85%H_3PO_4) δ +57.91; HRMS(EI) Calcd. For $C_{42}H_{33}N_2O_2PS(M^+)$: 660.2000, found: 660.2010.





Conversion of (*R*)-(+)-*N*-(1-phenylpropyl)-*P,P*-diphenylphosphinoylamide 1a to (R)-1-phenylpropylamine hydrochloride.[2]



A solution of **1a** (35 mg, 0.1 mmol, 92% ee) in 20% HCl (2.0 mL) was refluxed for 2 h. The reaction mixture was washed with Et_2O and AcOEt and evaporated. The residue was lyophilized to dryness to give (R)-1-phenylpropylamine hydrochloride (16.8 mg, 98% yield) as a colorless solid, which was sufficiently pure. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.81 (t, J = 7.5 Hz, 3H, Me), 1.96 (m, 2H, CH_2), 4.21 (t, J = 7.5 Hz, 3H, CH), 7.38-7.47 (m, 5H, ArH); $[\alpha]^{25}_D$ = +4.6 (c 0.55, absolute C_2H_5OH) (lit.[3] $[\alpha]^{25}_D$ = +5.1 (c 2.0, absolute C_2H_5OH) for (R)-1-phenylpropylamine hydrochloride).

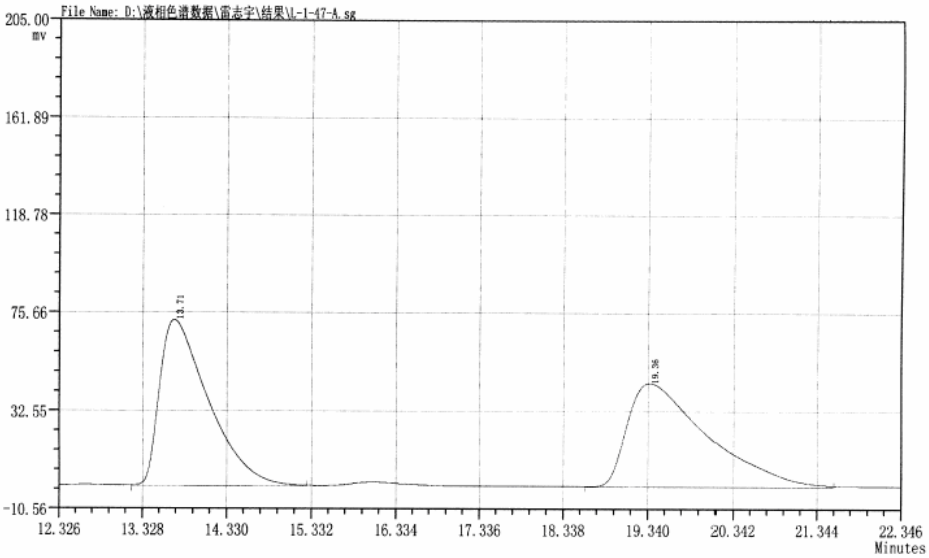
General Procedure for the Cu(II)-catalyzed asymmetric addition of diethylzinc to diphenylphosphinoylimines:

A solution of $Cu(OTf)_2$ (5.4 mg, 0.015 mmol) and ligand **L1** (12.6 mg, 0.0225 mmol) in dry toluene (3.0 mL) was stirred for 1 h at room temperature under an argon atmosphere. Diphenylphosphinoylimine of benzaldehyde (47 mg, 0.15 mmol) was added and the solution

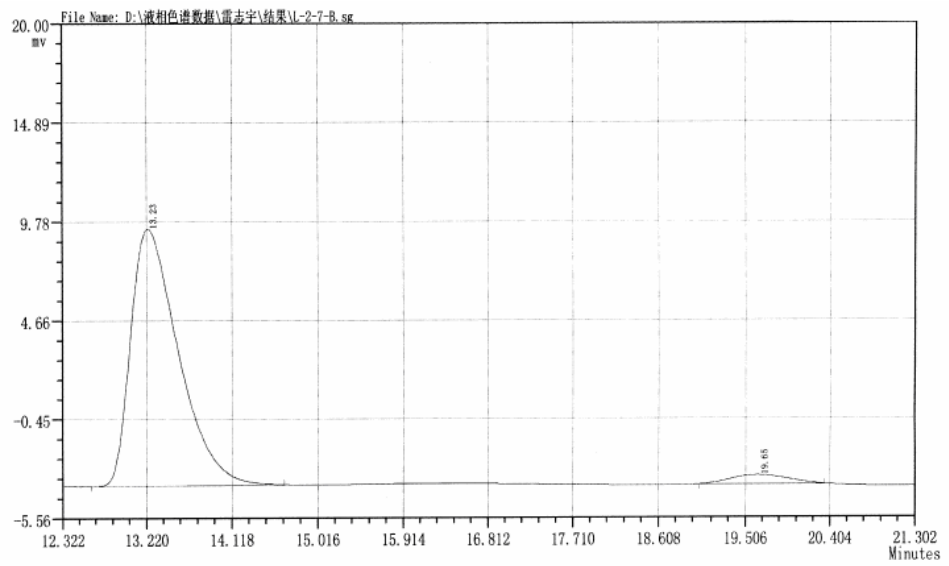
was stirred for a further 10 min, then Et_2Zn (0.45 mL, 0.45 mmol, 1.0 M solution in hexane) was added dropwise at -20 ^oC. The resulting mixture was stirred for 48 h at the same temperature, saturated NH_4Cl (10.0 mL) was added. After extraction with ethyl acetate (3 x 10.0 mL), the combined organic layers were dried over $MgSO_4$. The residue obtained upon removal of volatiles in vacuo was purified by column chromatography on silica gel (eluent: petroleum/ethyl acetate = 1/1) to afford the addition product *N*-(1-phenylpropyl)-*P,P*-diphenylphosphinoylamide **1a** (43.5 mg, 87%) as a colorless solid.

(*R*)-(+)-*N*-(1-phenylpropyl)-*P,P*-diphenylphosphinoylamide 1a (Table 3, entry 1).

43.5 mg, 87% yield. ^1H NMR ($CHCl_3$, TMS, 300 MHz) δ 0.79 (t, J = 7.5 Hz, 3H, Me), 1.83 (m, 1H, CH), 2.05 (m, 1H, CH), 3.24 (br, 1H, NH), 4.10 (m, 1H, CH), 6.96 (m, 2H, ArH), 7.33 (m, 11H, ArH), 7.74 (m, 2H, ArH), 7.83 (m, 2H, ArH); $[\alpha]^{25}_D$ = +41.5 (c 1.31, $CHCl_3$) for 92% ee; Chiralcel OD, hexane/i-PrOH = 95/5, 0.85 mL/min, 254 nm, t_{major} = 13.233 min, t_{minor} = 19.650 min.



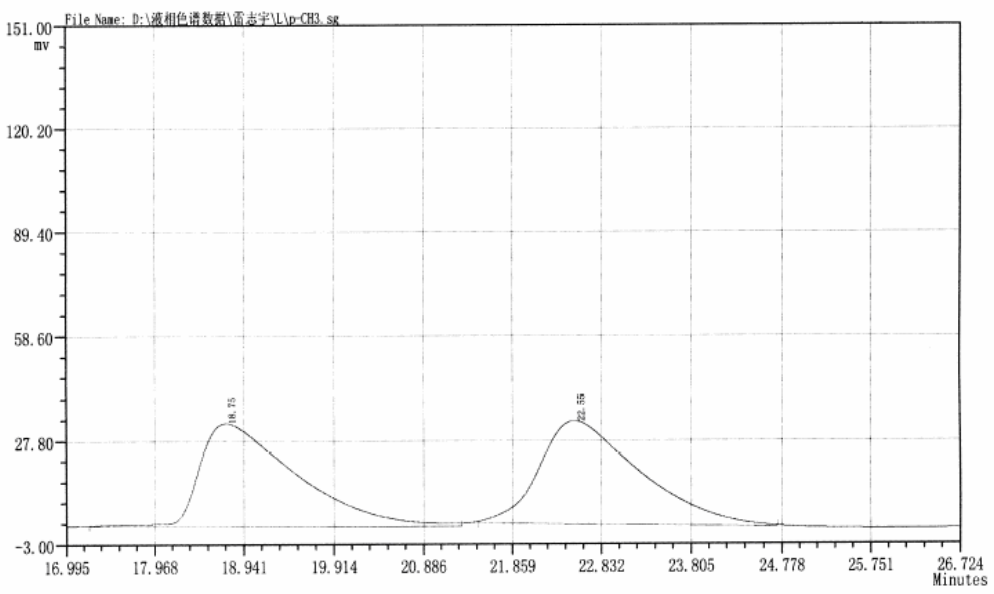
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因了	理论塔板
1		13.708	73149	2959576.0	49.8996	2.06	2288
2		19.362	45650	2971488.4	50.1004	2.26	1763
	Σ:		118799	5931064.4	100.0000		



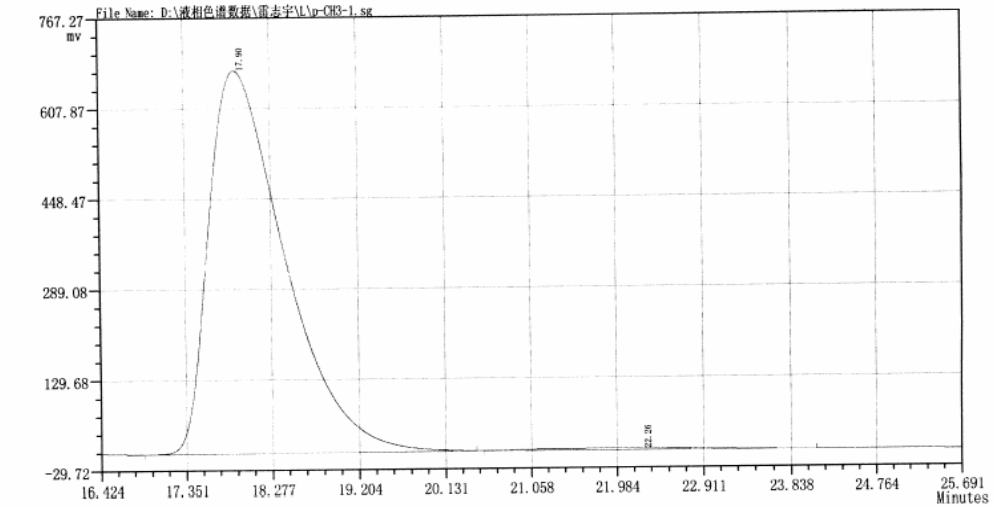
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		13.233	13309	466331.0	95.9239	1.66	2843
2		19.650	465	19816.0	4.0761	1.10	4238
	Σ:		13774	486147.0	100.0000		

(*R*)-(+)-*N*-(1-tolylpropyl)-*P,P*-diphenylphosphinoylamide 1b (Table 3, entry 2).

43.4 mg, 83% yield. ^{1}H NMR ($CHCl_3$, TMS, 300 MHz) δ 0.86 (t, *J* = 7.2 Hz, 3H, Me), 1.92 (m, 1H, CH), 2.11 (m, 1H, CH), 2.44 (s, 3H, Me), 3.29 (br, 1H, NH), 4.15 (m, 1H, CH), 7.14 (d, *J* = 7.8 Hz, 2H, ArH), 7.21 (d, *J* = 7.8 Hz, 2H, ArH), 7.46 (m, 6H, ArH), 7.85 (m, 2H, ArH), 7.96 (m, 2H, ArH); $[\alpha]^{25}_D$ = +56.1 (c 1.21, $CHCl_3$) for 98% ee; Chiralcel OD, hexane/i-PrOH = 95/5, 0.6 mL/min, 254 nm, t_{major} = 17.902 min, t_{minor} = 22.258 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		18.752	30585	2214353.7	48.7687	2.29	1337
2		22.553	30734	2326170.4	51.2313	1.36	1770
	Σ:		61319	4540524.1	100.0000		

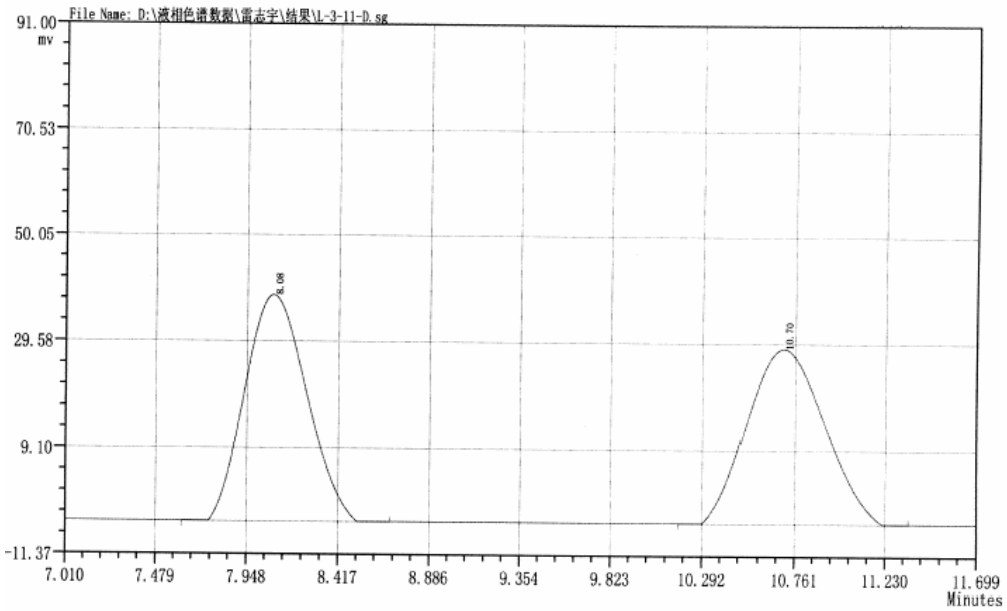


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		17.902	674081	38065982.7	99.1211	1.75	2003
2		22.258	3107	337530.7	0.8789	0.82	837
	Σ:		677188	38403513.4	100.0000		

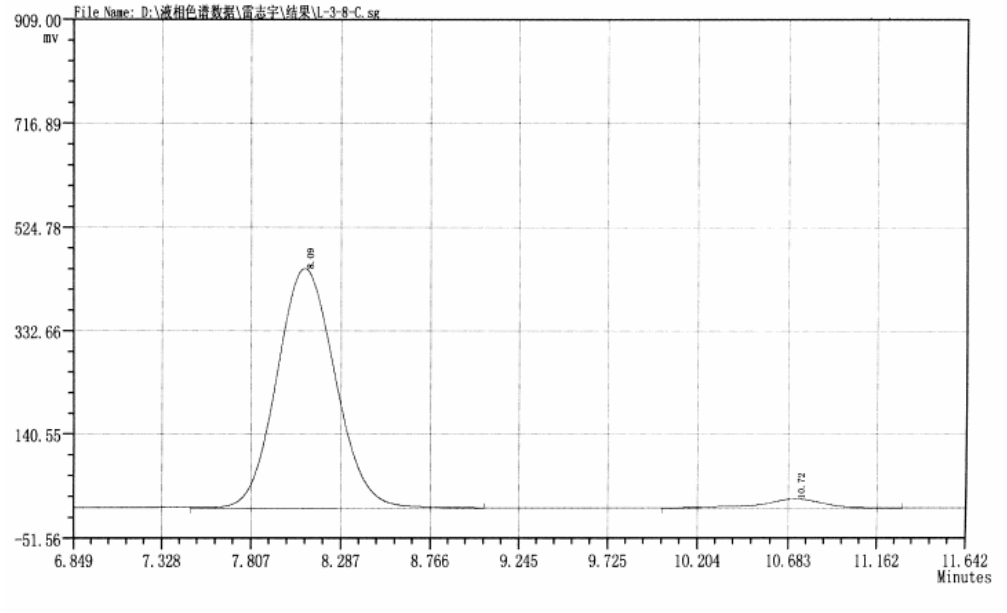
(*R*)-(+)-*N*-(1-*m*-tolylpropyl)-*P,P*-diphenylphosphinoylamide 1c (Table 3, entry 3).

45.1 mg, 87% yield. ^{1}H NMR ($CHCl_3$, TMS, 300 MHz) δ 0.78 (t, *J* = 7.2 Hz, 3H, Me), 1.86 (m, 1H, CH), 2.05 (m, 1H, CH), 2.32 (s, 3H, Me), 3.24 (br, 1H, NH), 4.05 (m, 1H, CH), 6.92 (s, 1H, ArH), 7.04 (m, 2H, ArH), 7.21 (m, 1H, ArH), 7.43 (m, 6H, ArH), 7.78 (m, 2H, ArH), 7.88 (m, 2H, ArH); $[\alpha]^{25}_D$ = +26.6 (c 0.81, $CHCl_3$) for 91% ee; Chiralcel AD, hexane/i-PrOH

= 80/20, 1.0 mL/min, 254 nm, t_{major} = 8.093 min, t_{minor} = 10.723 min.



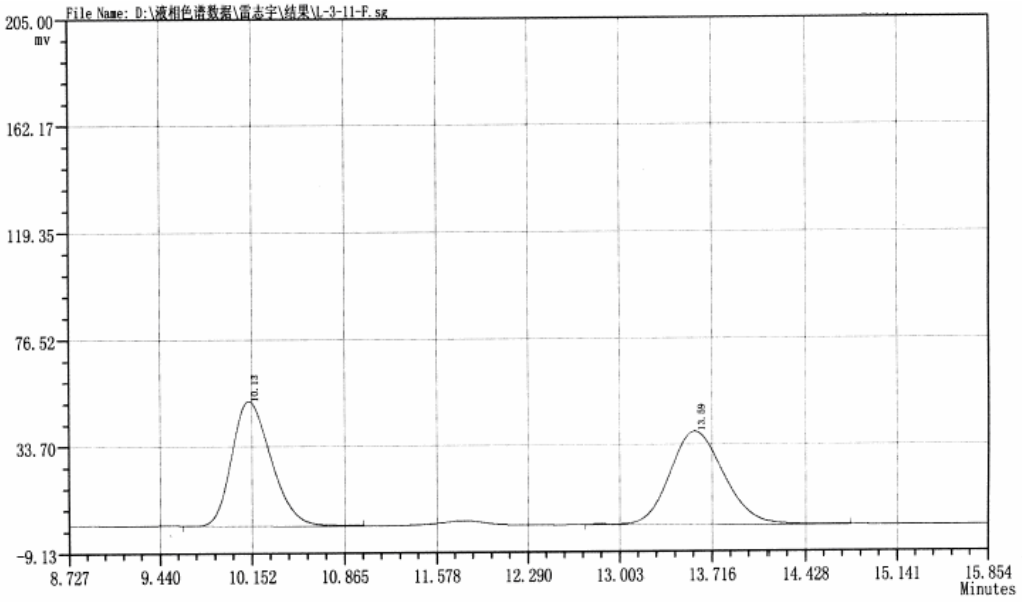
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		8.082	43532	955888.4	50.7227	1.15	2700
2		10.700	33740	928647.6	49.2773	1.13	3012
	Σ:		77272	1884536.0	100.0000		



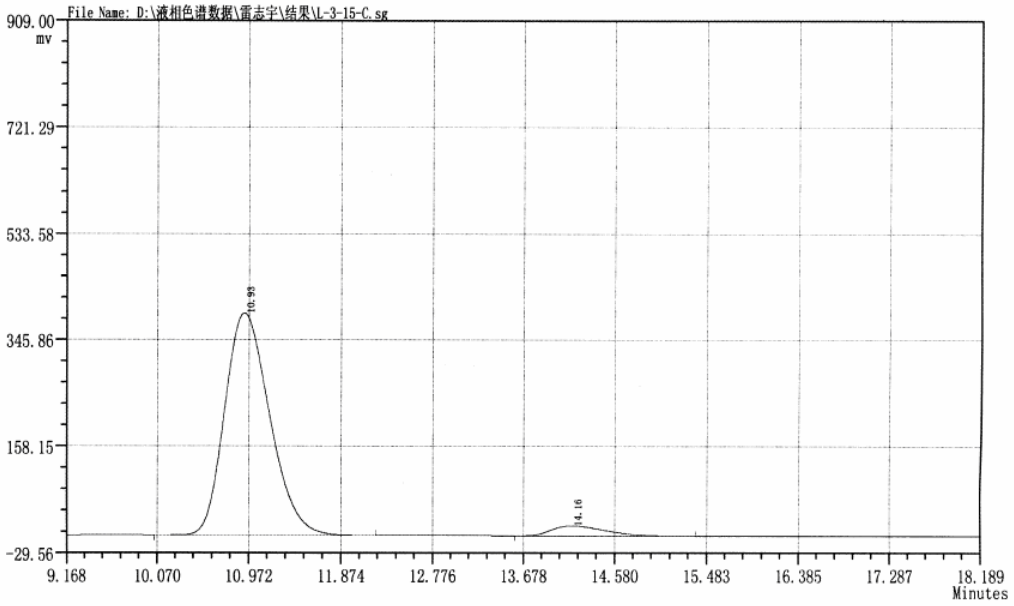
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		8.093	444400	9618701.8	95.6223	1.10	2787
2		10.723	17560	440359.0	4.3777	0.91	3644
	Σ:		461960	10059060.7	100.0000		

(*R*)-(+)-*N*-[1-(4-methoxyphenyl)propyl]-*P,P*-diphenylphosphinoylamide 1d (Table 3, entry 4).

40.5 mg, 75% yield. ^{1}H NMR ($CHCl_3$, TMS, 300 MHz) δ 0.77 (t, J = 7.5 Hz, 3H, Me), 1.82 (m, 1H, CH), 1.99 (m, 1H, CH), 3.20 (br, 1H, NH), 3.81 (s, 3H, Me), 4.06 (m, 1H, CH), 6.83 (d, J = 8.7 Hz, 2H, ArH), 7.08 (d, J = 8.7 Hz, 2H, ArH), 7.42 (m, 6H, ArH), 7.77 (m, 2H, ArH), 7.86 (m, 2H, ArH); $[\alpha]^{25}_D$ = +44.0 (c 0.17, $CHCl_3$) for 90% ee; Chiralpak AD, hexane/i-PrOH = 80/20, 1.0 mL/min, 254 nm, t_{major} = 10.930 min, t_{minor} = 14.162 min.



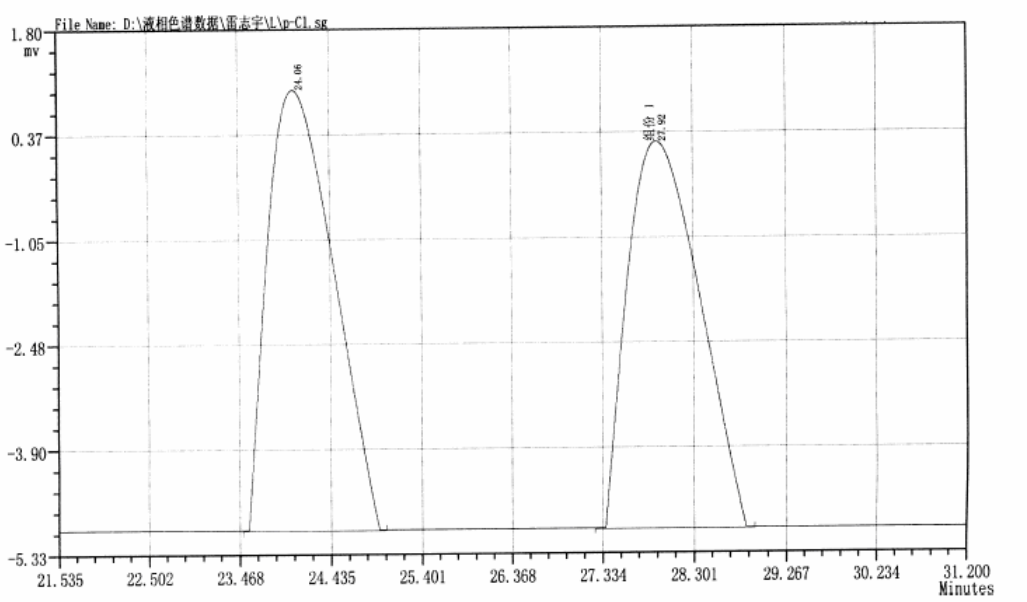
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		10.132	50091	1058085.0	49.5483	1.23	4585
2		13.590	37370	1077375.9	50.4517	1.11	4429
	Σ:		87461	2135460.9	100.0000		



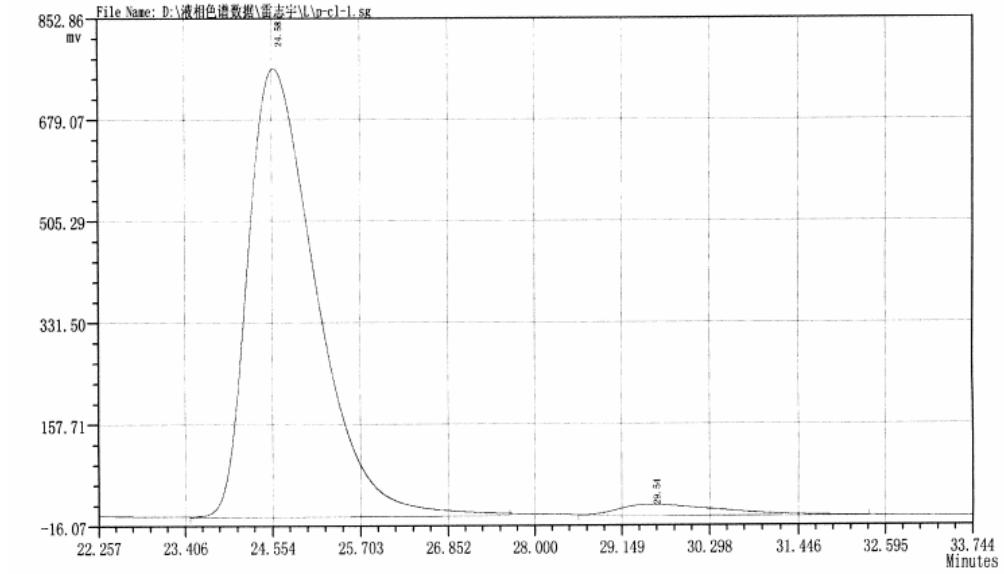
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		10.930	391314	11949922.9	94.6829	1.24	2553
2		14.162	18180	671075.8	5.3171	1.44	2934
	Σ:		409494	12620998.8	100.0000		

(*R*)-(+)-*N*-[1-(4-chlorophenyl)propyl]-*P,P*-diphenylphosphinoylamide 1e (Table 3, entry 5).

47.3 mg, 87% yield. ^{1}H NMR ($CHCl_3$, TMS, 300 MHz) δ 0.80 (t, *J* = 7.5 Hz, 3H, Me), 1.80 (m, 1H, CH), 1.97 (m, 1H, CH), 3.23 (br, 1H, NH), 4.07 (m, 1H, CH), 7.08 (d, *J* = 8.4 Hz, 2H, ArH), 7.26 (d, *J* = 8.4 Hz, 2H, ArH), 7.49 (m, 6H, ArH), 7.72 (m, 2H, ArH), 7.88 (m, 2H, ArH); $[\alpha]^{25}_D$ = +58.1 (c 1.18, $CHCl_3$) for 93% ee; Chiralcel OD, hexane/i-PrOH = 95/5, 0.6 mL/min, 254 nm, t_{major} = 24.578 min, t_{minor} = 29.537 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		24.057	5981	288948.5	51.0413	1.39	4942
1	组份 1	27.923	5248	277158.4	48.9587	1.32	5572
	Σ:		11229	566106.9	100.0000		

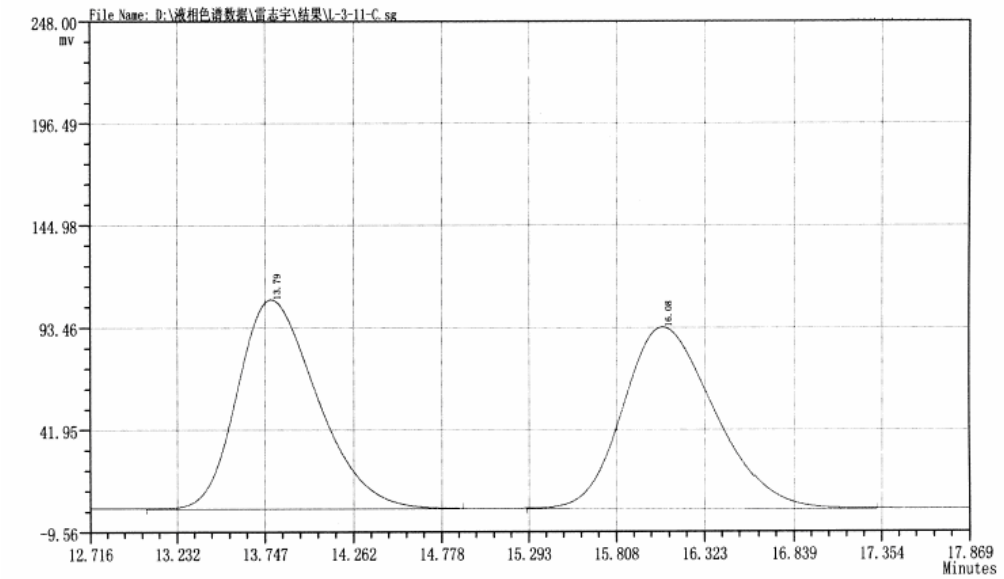


ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		24.578	767044	47372263.6	96.5846	1.57	3157
2		29.537	17959	1675149.1	3.4154	1.54	1999
	Σ:		785003	49047412.7	100.0000		

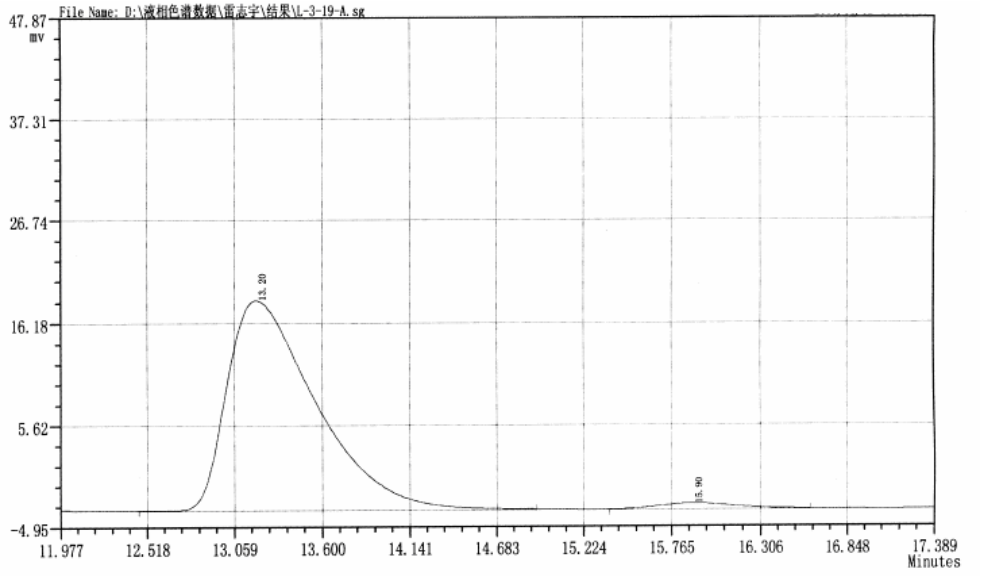
(*R*)-(+)-*N*-[1-(4-bromophenyl)propyl]-*P,P*-diphenylphosphinoylamide 1f (Table 3, entry 6).

49.8 mg, 82% yield. ^{1}H NMR ($CHCl_3$, TMS, 300 MHz) δ 0.81 (t, *J* = 7.5 Hz, 3H, Me), 1.81 (m, 1H, CH), 2.01 (m, 1H, CH), 3.25 (br, 1H, NH), 4.11 (m, 1H, CH), 7.04 (d, *J* = 8.1 Hz, 2H,

ArH), 7.42 (m, 8H, ArH), 7.76 (m, 2H, ArH), 7.85 (m, 2H, ArH); $[\alpha]^{25}_{D}$ = +65.1 (c 0.33, $CHCl_3$) for 95% ee; Chiralcel AD, hexane/i-PrOH = 80/20, 1.0 mL/min, 254 nm, t_{major} = 13.200 min, t_{minor} = 15.900 min.



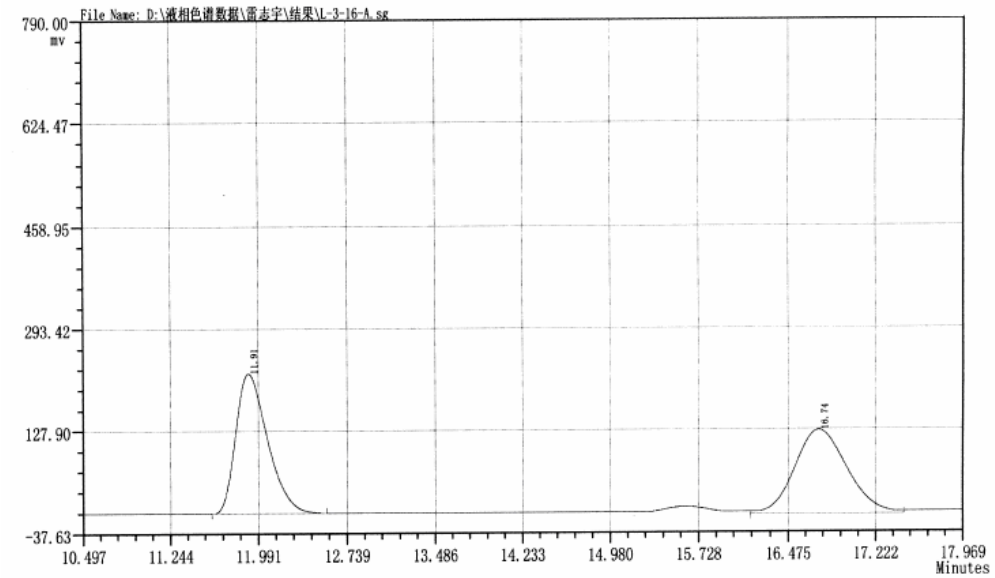
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		13.785	105181	3403877.6	49.9772	1.28	3616
2		16.078	91651	3406979.8	50.0228	1.21	3729
	Σ:		196832	6810857.4	100.0000		



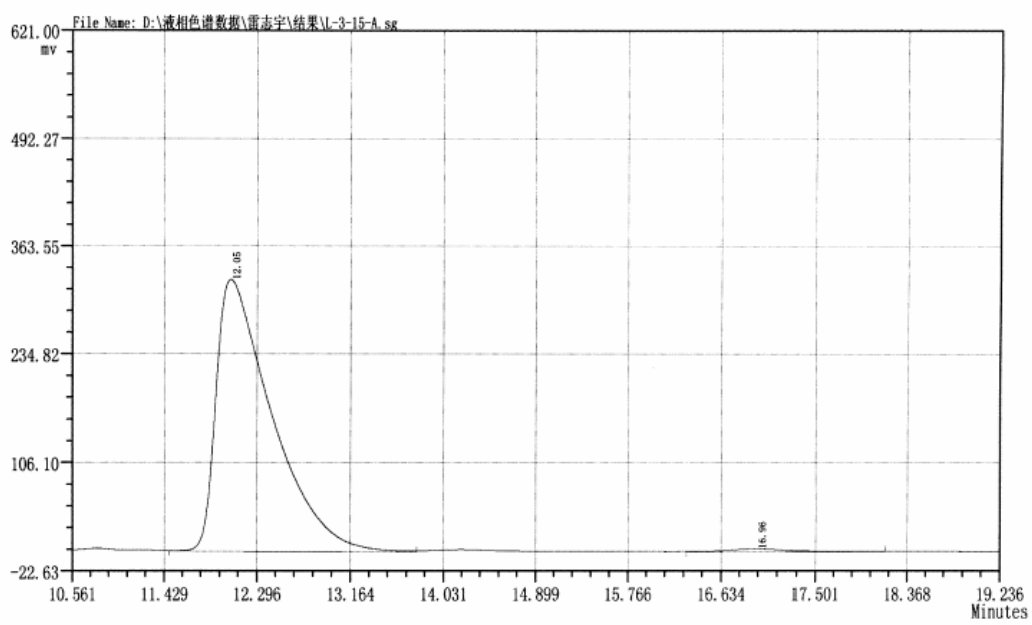
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		13.200	21822	840377.0	97.4508	1.85	2342
2		15.900	636	21983.0	2.5492	1.23	4218
	Σ:		22458	862360.0	100.0000		

(*R*)-(+)-*N*-[1-(2-chlorophenyl)propyl]-*P*,*P*-diphenylphosphinoylamide 1g (Table 3, entry 7).

45.1 mg, 82% yield. ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.87 (t, J = 7.5 Hz, 3H, Me), 1.93 (m, 2H, CH_2), 3.54 (br, 1H, NH), 4.50 (m, 1H, CH), 7.14-7.33 (m, 6H, ArH), 7.40-7.52 (m, 4H, ArH), 7.69-7.75 (m, 2H, ArH), 7.83-7.91 (m, 2H, ArH); $[\alpha]^{25}_D$ = +21.0 (c 1.23, $CHCl_3$) for 98% ee; Chiralcel AD, hexane/i-PrOH = 80/20, 1.0 mL/min, 254 nm, t_{major} = 12.053 min, t_{minor} = 16.963 min.



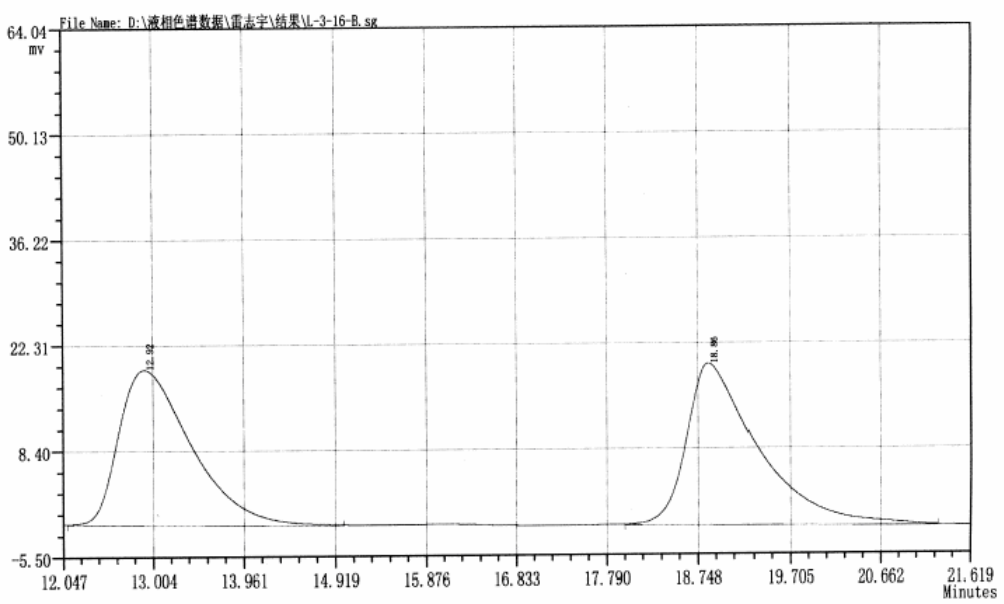
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		11.912	225736	4231305.1	50.4023	1.38	8049
2		16.738	134990	4163750.6	49.5977	1.13	5869
	Σ:		360726	8395055.7	100.0000		



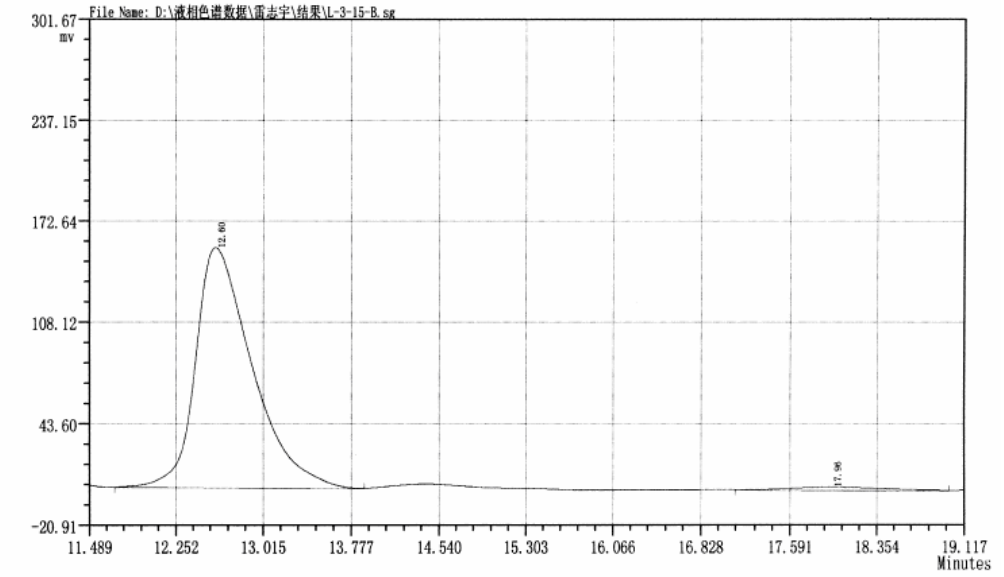
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		12.053	322495	11615992.0	98.8752	2.34	2232
2		16.963	3440	132138.1	1.1248	1.65	3887
	Σ:		325935	11748130.1	100.0000		

(*R*)-(+)-*N*-[1-(2,4-dichlorophenyl)propyl]-*P,P*-diphenylphosphinoylamide 1h (Table 3, entry 8).

48.6 mg, 82% yield. Mp 140.3-142.7 ^{o}C; ^{1}H NMR ($CDCl_3$, TMS, 300 MHz) δ 0.87 (t, J = 7.5 Hz, 3H, Me), 1.90 (m, 2H, CH_2), 3.49 (br, 1H, NH), 4.47 (m, 1H, CH), 7.21-7.35 (m, 5H, ArH), 7.41-7.56 (m, 4H, ArH), 7.68-7.75 (m, 2H, ArH), 7.82-7.90 (m, 2H, ArH); $[\alpha]^{25}_{D}$ = +35.2 (c 0.38, $CHCl_3$) for 95% ee; Chiralcel AD, hexane/i-PrOH = 80/20, 1.0 mL/min, 254 nm, t_{major} = 12.603 min, t_{minor} = 17.963 min.



ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	埋论塔板
1		12.920	20341	1085810.1	49.6708	1.62	1168
2		18.860	21248	1100202.2	50.3292	1.83	2644
	Σ:		41589	2186012.3	100.0000		



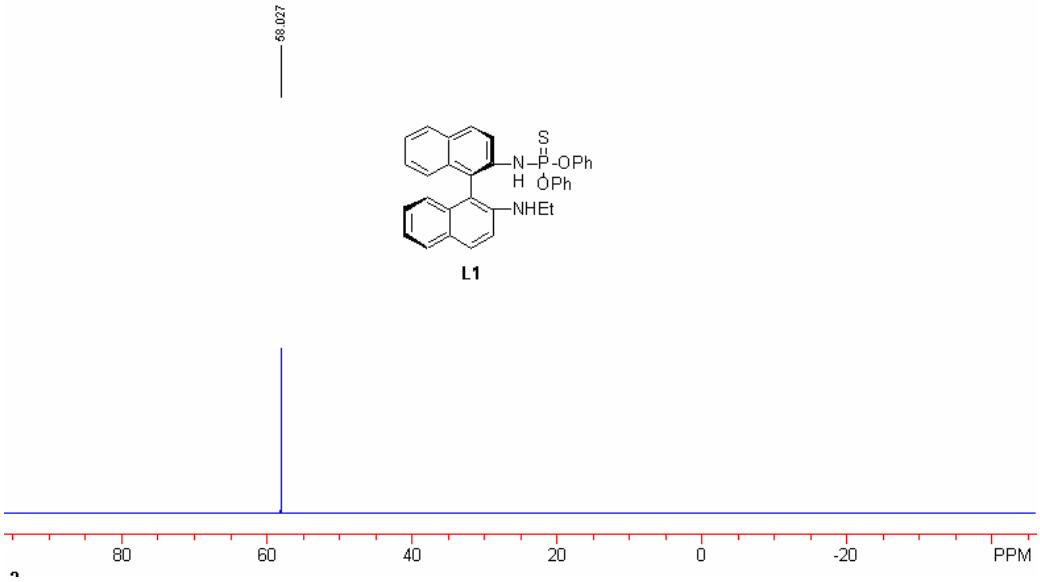
ID	组分名	保留时间	峰高	峰面积	浓度	拖尾因子	理论塔板
1		12.603	152751	5247165.5	97.5553	1.46	2683
2		17.963	2156	131491.4	2.4447	1.08	1729
	Σ:		154907	5378656.9	100.0000		

^{31}P NMR and ^{13}C NMR Spectroscopic Data of L1 in $CDCl_3$.

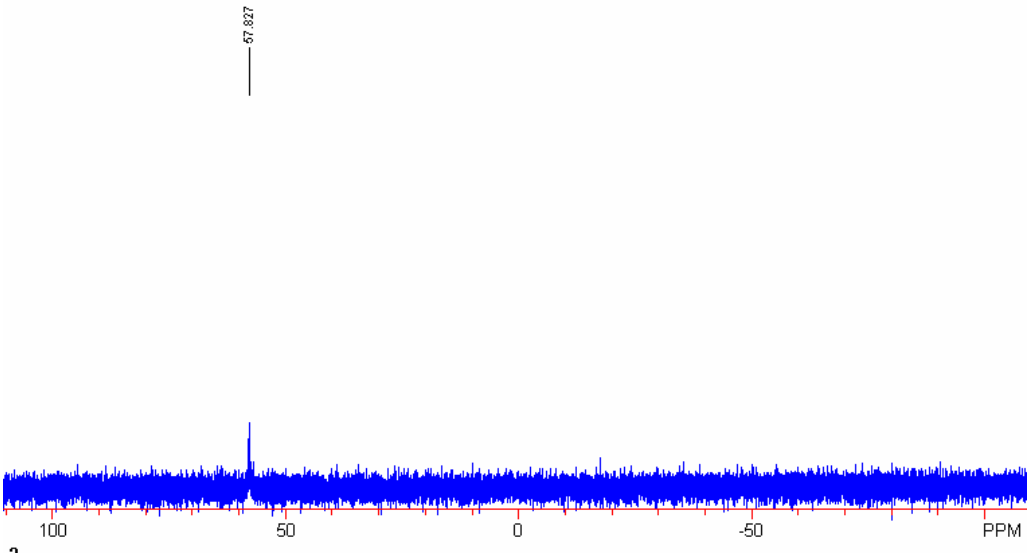
^{31}P NMR ($CDCl_3$, 121 MHz, 85%H_3PO_4) δ +58.03; ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 14.9, 38.2, 109.2, 113.9, 118.2, 118.7, 118.9, 121.0, 121.11, 121.19, 122.0, 123.2, 124.58, 124.61, 125.30, 125.37, 125.4, 126.9, 127.1, 127.4, 128.1, 128.2, 129.47, 129.49, 129.50, 129.67, 130.2, 130.6, 133.3, 133.6, 136.1 (d, *J* = 9.6 Hz), 144.3, 150.2 (d, *J* = 27.6 Hz), 150.4 (d, *J* = 24.3 Hz).

^{31}P NMR and ^{13}C NMR Spectroscopic Data of L1/$Cu(OTf)_2$ complex (1:1 mixture) in $CDCl_3$.

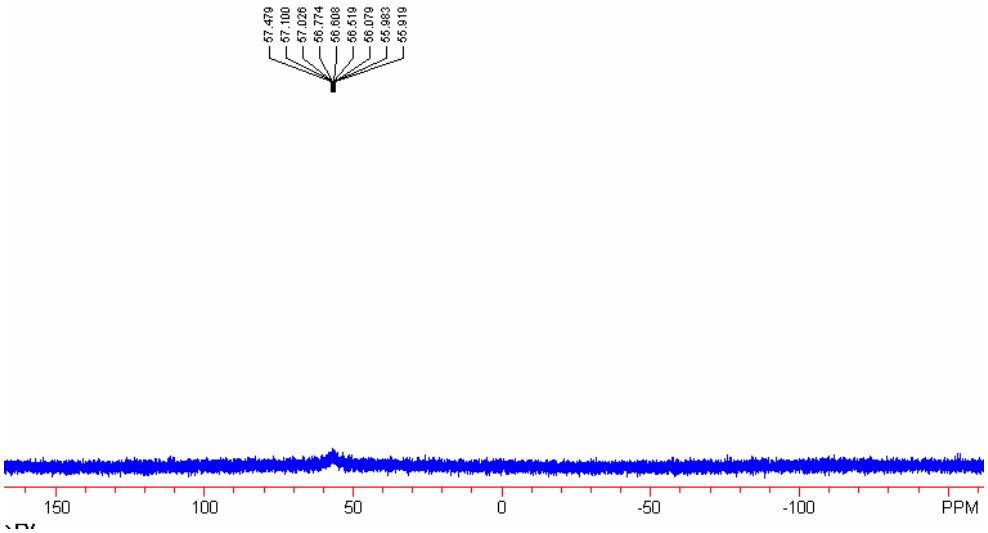
^{31}P NMR ($CDCl_3$, 121 MHz, 85%H_3PO_4) δ +57.83; ^{13}C NMR ($CDCl_3$, TMS, 75 MHz) δ 14.8, 38.9, 114.4, 118.4, 118.6, 118.7, 121.05, 121.13, 121.15, 121.2, 122.5, 123.4, 124.8, 125.30, 125.45, 125.46, 125.51, 125.53, 127.1, 127.3, 128.2, 128.3, 129.52, 129.54, 129.57, 129.59, 129.9, 130.3, 130.8, 133.3, 133.5, 136.1 (d, *J* = 10.2 Hz), 143.4, 150.2 (d, *J* = 28.2 Hz), 150.4 (d, *J* = 29.7 Hz).



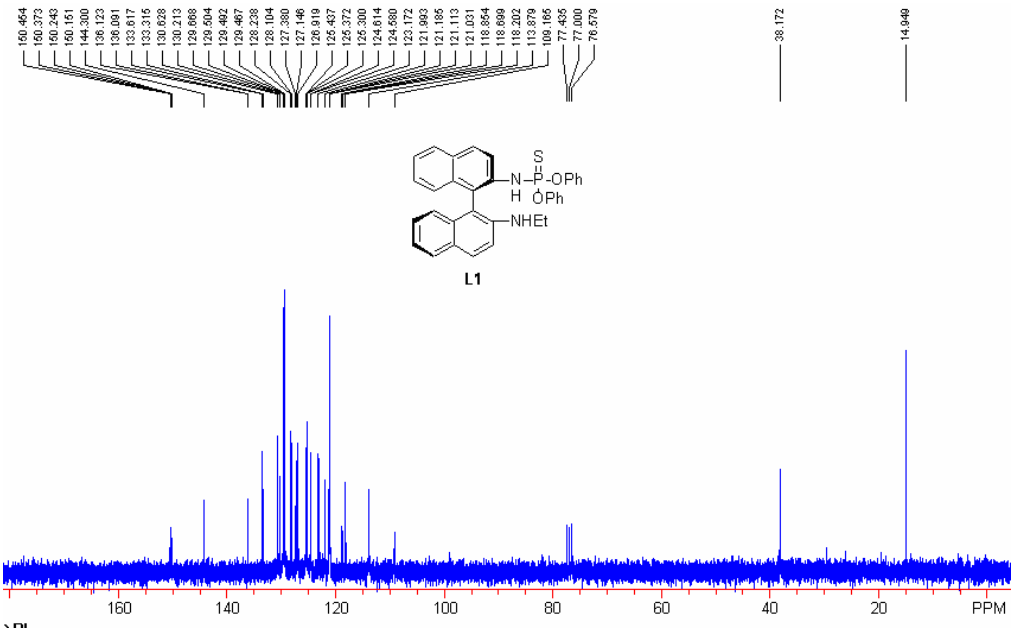
^{31}P NMR spectrum of **L1** in $CDCl_3$.



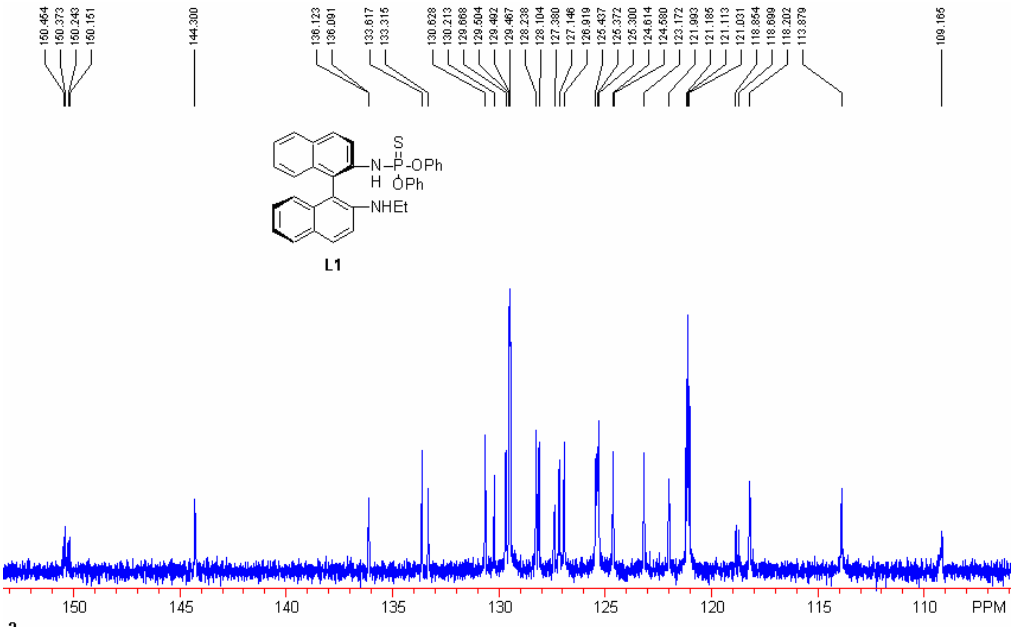
^{31}P NMR spectrum of **L1**/Cu(OTf)$_2$ (1:1 mixture) in $CDCl_3$.



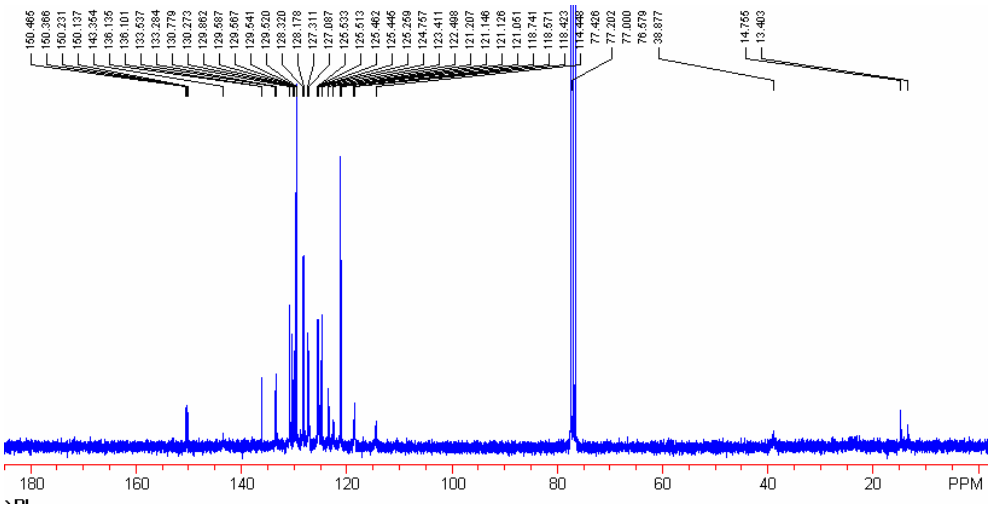
^{31}P NMR spectrum of **L1**/Cu(OTf)$_2$ (1:1 mixture) in $CDCl_3$ after 12 hours.



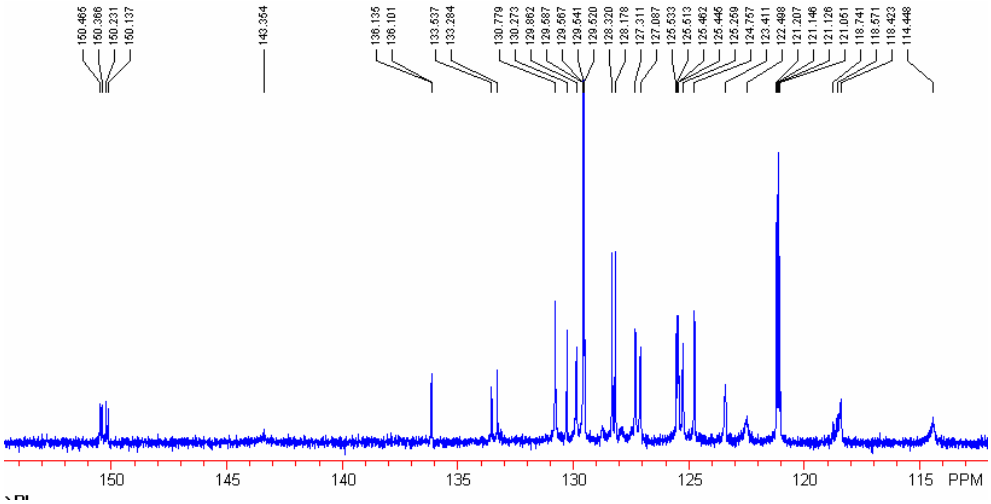
^{13}C NMR spectrum of **L1** in $CDCl_3$.



Enlargement of ^{13}C NMR spectrum of **L1** in $CDCl_3$.



^{13}C NMR spectrum of **L1**/Cu(OTf)$_2$ (1:1 mixture) in $CDCl_3$.



Enlargement of ^{13}C NMR spectrum of **L1**/Cu(OTf)$_2$ (1:1 mixture) in $CDCl_3$.

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(1) R.-R. Tang, Q.-X. Zhang, *HECHENG HUAXUE,* **1999**, *7*, 4-5.

(2) S. Kawahara, A. Nakano, T. Esumi, Y. Iwabuchi, S. Hatakeyama, *Org. Lett.* **2003**, *5*, 3103-3105.

(3) H. E. Smith, A. W. Gordon, A. F. Bridges, *J. Org. Chem.* **1974**, *39*, 2309-2311.