Electronic Supplementary Information for

An Iron Variant of the Noyori Hydrogenation Catalyst for the Asymmetric Transfer Hydrogenation of Ketones

Shangfei Huo, Qingwei Wang*, Weiwei Zuo*

State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, College of materials science and engineering, Donghua University.
*Corresponding author. E-mail: wqwq888@dhu.edu.cn, zuoweiwei@dhu.edu.cn

Contents

1. General considerations

Manipulations and procedures involving air-sensitive compounds were performed under an inert atmosphere with argon or nitrogen using Schlenk techniques or an inert gas protected glove-box. Solvents were dried and degassed using standard procedures before manipulations and reactions. The amino(imino)diphosphino carbonyl iron chloride tetrafluoroborate (**A**) was prepared using our previous procedure.[1] Ketone substrates were distilled under inert atmosphere and stored in a glovebox prior to catalytic reactions. Deuterated solvents were purchased from Cambridge Isotope Laboratories, INC and some of them were distilled and dried over activated molecular sieves if necessary. All of the other chemicals were purchased from commercial sources and used without further purification. NMR spectra were recorded at ambient temperature and pressure using BRUKER AVANCE III, HD 600 MHz spectrometers [^{1}H (600 MHz),^{11}B{^{1}H} (193MHz), ^{13}C{^{1}H} (151 MHz) and ^{31}P{^{1}H} (242 MHz). The ^{31}P NMR spectra were referenced to 85% H_3PO_4 (0 ppm). The electrospray ionization mass spectrometry (ESI-MS) data were collected on an Xevo G2 XS QTOFMS mass spectrometer with an ESI source at Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences and a Waters Xevo G2-XS QT of mass spectrometer with an ESI source at the Instrumental Analysis Center of Shanghai Jiao Tong University. Single-crystal X-ray diffraction data were collected using a Nonius Kappa-CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) at Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences. The structures were solved and refined using SHELXTL V6.1. Crystallographic data for **6a** (1873096) was deposited at Cambridge Crystallographic Data Centre and are available free of charge from website https://www.ccdc.cam.ac.uk/.

Synthesis of 1a

In an argon protected glovebox, (s)-2,2'-dibromo-1,1'-binaphthyl (5.00g, 12.13mmol) was dissolved in 120 ml of THF in a flask and the solution was stirred for around 10 min until all the solid was dissolved. The flask was immersed in a cooling bath equipped by the glovebox at -90 ^{o}C that was achieved by solidifying a medium mixture of toluene and heptane in a volume ratio of 1:3 by liquid nitrogen, which was placed outside the cooling bath. The solution was stirred at -90 ^{o}C for 5 min to completely cool the solution. *N*-butyl lithium in hexane (8.34 mL, 1.6 M, 1.1 equiv.) was added dropwise and the slightly yellow solution was stirred at -90 ^{o}C for further 15 minutes. Chlorodiphenylphosphine (2.95g, 13.23 mmol) was dissolved in THF (5 mL) and then added dropwise. The solution was stirred at -90 ^{o}C for 10 min, during which if the cooling medium started to melt, slightly more liquid nitrogen was added to the medium mixture. The flask was then taken out of the glovebox, and H_2O_2 (30 wt%, 50 mL, 36.3 equiv.) was added with stirring into solution after the temperature rose to room temperature. The solution was poured into a separating funnel and the organic compound was washed with H_2O (200 mL) and extracted by dichloromethane (300 mL). The organic phase was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporators. Pure product of **1a** was obtained by running column chromatography (silica gel, CH_2Cl_2:EtOAc = 5 :1) to obtain a white solid (5.82 g, 90 % yield).^{31}P{^{1}H} NMR (242 MHz, $CDCl_3$) δ: 28.22 (s). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.04 (d, *J* = 7.7 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.84 (dd, *J* = 11.4, 8.7 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.61–7.56 (m, 2H), 7.52 (dd, *J* = 13.0, 8.3 Hz, 3H), 7.45–7.37 (m, 4H), 7.35–7.31 (m, 1H), 7.27 (tt, *J* = 7.9, 3.8 Hz, 3H), 7.14 (dt, *J* = 13.0, 8.0 Hz, 4H), 7.01 (d,

J = 8.5 Hz, 1H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ: 142.8 (d, J_{CP} = 9.1 Hz), 135.2 (d, J_{CP} = 4.5 Hz), 134.7 (d, J_{CP} = 1.5 Hz), 134.6 (s), 133.7 (s), 133.03 (d, J_{CP} = 10.8 Hz), 132.36 (t, J_{CP} = 6.0 Hz), 131.93 (d, J_{CP} = 10.8 Hz), 131.9 (s), 131.6 (d, J_{CP} = 10.8 Hz), 131.3 (d, J_{CP} = 3.0Hz), 131.1 (d, J_{CP} = 3.0 Hz), 130.0 (s), 129.7 (s), 129.5 (s), 129.1 (s), 129.0 (s), 128.2 (s), 128.2 (s), 128.2 (s), 128.1 (s), 127.9 (d, J_{CP} = 12.1 Hz), 127.8 (s), 127.6 (d, J_{CP} = 12.1 Hz), 127.4 (s), 126.7 (d, J_{CP} = 4.5 Hz), 126.6 (s), 125.9 (s), 123.7 (s). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{32}H_{22}BrOP)+H]^+$: 533.0681, found: 533.0670. FTIR (ATR, cm^{-1}): 607s, 611s, 636s, 667m, 679s, 695s, 721s, 747s, 752s, 774s, 784m, 814s, 821s, 836s, 854m, 876m, 1026m, 1055m, 1071m, 1101s, 1115s, 1137m, 1160m, 1169m, 1199s, 1259m, 1308s, 1435s, 1484m, 1503s, 1557m, 1580m, 1589m, 2923m, 3056s.

Synthesis of borane adduct of 2a

In an argon glovebox, compound **1a** (5.00g, 9.37 mmol) was dissolved in 100 ml of THF in a flask of 200ml, and the solution was immersed in the cooling bath and further stirred at -90 °C for 10 min. *N*-butyl lithium in hexane (6.44 mL, 1.6 M, 1.1 equiv.) was added dropwise and the slightly yellow solution was stirred at -90 °C for further 15 minutes. Dichlorophenylphosphine (1.85 g, 10.34 mmol) was added dropwise into the solution, and the solution was stirred for 10 min at -90 °C. After that, 1.3 equivalent of methylmagnesium bromide (1 M in THF, 12.19 mL) was added dropwise and the solution was stirred for 10min at this temperature. 1.5 equivalent of borane - tetrahydrofuran complex (0.9 M in THF, 15.62 mL) was added into solution with stirring after the temprature rose up to room temperature. The flask was then taken out of the glovebox. The product was washed with H_2O (200 mL) and extracted by dichloromethane (400 mL). The organic phase was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporators. Pure borane adduct of **2a** was obtained by running column chromatography (silica gel, petroleum ether:EtOAc = 2:1) to obtain a white solid (3.95 g, 71 % yield). $^{31}P\{^1H\}$ NMR (242 MHz, $CDCl_3$) δ: 27.82 (s), 16.85 (m). ^1H NMR (600 MHz, $CDCl_3$) δ: 8.08 (td, *J* = 9.2, 6.0 Hz, 2H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.79 (t, *J* = 8.9 Hz, 3H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.63–7.53 (m, 3H), 7.52–7.42 (m, 6H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.33– 7.27 (m, 1H), 7.21 (ddd, *J* = 19.0, 12.0, 7.3 Hz, 4H), 7.03 (t, *J* = 7.2 Hz, 2H), 6.61 (t, *J* = 7.6 Hz, 1H), 6.46 (d, *J* = 8.5 Hz, 1H), 1.56 (d, J_{HP} = 10.5 Hz, 3H, PCH_3), 0.74–0.15 (m, 3H, BH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ: 142.6 (dd, J_{CP} = 4.5 Hz, 1.5Hz), 139.8 (dd, J_{CP} = 4.5 Hz), 134.4 (d, J = 1.5 Hz), 134.4 (t, J_{CP} = 4.5 Hz), 133.6 (d, J_{CP} = 7.6 Hz), 133.3 (d, J_{CP} = 15.1 Hz), 132.7 (d, J_{CP} = 9.1 Hz), 132.2 (d, J_{CP} = 9.1 Hz), 131.7 (d, J_{CP} = 3.0 Hz), 133. 3 (d, J_{CP} = 10.6 Hz), 131.3 (s), 130.9 (d, J_{CP} = 1.5 Hz), 130.7 (s), 130.7 (s), 130.0 (s), 129.5 (s), 129.2 (s), 128.7 (s), 128.6 (s), 128.6 (s), 128.6 (s), 128.5 (s), 128.4 (s), 128.4 (d, J_{CP} = 3.0 Hz), 128.3 (s), 128.2 (s), 128.1 (s), 127.8 (s), 127.7(d, J_{CP} = 12.1 Hz), 127.5 (s), 127.3 (s), 126.8 (d, J_{CP} = 21.1 Hz), 125.7 (s), 13.3 (d, J_{CP} = 39.3 Hz, *C*H_3). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{39}H_{33}BOP_2)+Na]^+$: 613.2015, found: 613.2004. FTIR (ATR, cm^{-1}): 693s, 700s, 725s, 745s, 750s, 810s, 824m, 875m, 889m, 905s, 1061s, 1100s, 1118s, 1166m, 1184m, 1200s, 1307m, 1436s, 1737s, 2327s, 2392s, 3048s, 3068m.

Synthesis of (S_A, R_P)-2-methylphenylphosphino-2'-diphenylphosphino-1,1'-binapthyl

The borane adduct of **2a** (3.50 g, 5.93 mmol) was dissolved in 100 ml of THF in a 150 ml of high pressure-resistant glass bottle. Triethyl amine (3.00 g , 29.65 mmol, dried and degassed) and trichlorosilane (16.06 g, 118.58 mmol) were added by syringe at room temperature. The solution was then stirred at 80 °C for 3h. After reaction ceased and the temperature dropped to room

temperature, the solution was poured into a solution mixture of cool dichloromethane (600 mL) and sodium hydroxide in H_2O (10 wt%, 100 mL) with stirring. The organic phase was washed with H_2O (100 mL) and was then dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporators. Pure product was obtained by running column chromatography (silica gel, petroleum ether: EtOAc = 10 :1) to obtain a white solid (3.00 g, 90 % yield). $^{31}P\{^1H\}$ NMR (242 MHz, $CDCl_3$) δ: -15.11 (d, J = 13.9 Hz), -37.79 (d, J = 13.9 Hz). ^1H NMR (600 MHz, $CDCl_3$) δ: 7.95 (td, J = 10.3, 5.3 Hz, 2H), 7.88 (dd, J = 15.4, 8.2 Hz, 2H), 7.65–7.60 (m, 1H), 7.57–7.52 (m, 1H), 7.45 (dd, J = 10.9, 4.0 Hz, 1H), 7.42–7.33 (m, 6H), 7.21 (dd, J = 13.4, 6.8 Hz, 1H), 7.19–7.12 (m, 8H), 7.12–7.05 (m, 3H), 7.00 (t, J = 7.6 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 1.39 (m, 3H, PCH_3). ^{13}C NMR$\{^1H\}$ (151 MHz, $CDCl_3$) δ: 145.7 (d, J_{CP} = 7.6 Hz), 145.5 (d, J_{CP} =7.6 Hz), 144.4 (d, J_{CP} = 7.6 Hz), 144.2 (d, J_{CP} = 7.6Hz), 141.1 (d, J_{CP} = 13.6 Hz), 137.9 (d, J_{CP} = 12.1 Hz), 137.5 (d, J_{CP} = 13.6 Hz), 135.6 (d, J_{CP} = 6.0 Hz), 134.0 (d, J_{CP} = 21.1 Hz), 133.4 (s), 133.3 (s), 133.2 (dd, J_{CP} = 1.5Hz, 18.1 Hz), 131.3 (d, J_{CP} = 16.6 Hz), 130.3 (s), 128.5 (d, J_{CP} = 18.1Hz), 128.3 (s), 128.3 (s), 128.2 (d, J_{CP} = 4.5 Hz), 128.1 (s), 128.0 (s), 127.9 (s), 127.9 (s), 127.8 (s), 127.8 (s), 127.7 (s), 127.5 (s), 127.3 (d, J_{CP} = 3.0 Hz), 126.7 (s), 126.4 (s), 126.2 (s), 126.0 (s), 11.9 (d, J_{CP} = 15.1 Hz, CH_3). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{39}H_{30}P_2)+H]^+$: 561.1907, found: 561.1901. FTIR (ATR, cm^{-1}): 638m, 694s, 741s, 815s, 879s, 1026s, 1038s, 1433s, 1480s, 1502s, 1584s, 2162m, 2904m, 2963m, 3000m, 3013m, 3049s.

Synthesis of borane adduct of 4a and 4a

In an argon glovebox, (S_A, R_P)-2-methylphenylphosphino-2'-diphenylphosphino-1,1'-binapthyl (3.00 g, 5.35 mmol) was dissolved in 100 ml of THF in a 200ml of Schlenk flask, and 1.0 equivalent of borane-tetrahydrofuran complex (0.9 M in THF, 5.95 mL) was added into solution with stirring at room temperature. The solution was further stirred at 45 °C for 12 h to afford **3a** [$^{31}P\{^1H\}$ NMR (242 MHz, THF) δ: -15.77 (s), 18.38 (m), $^{11}B\{^1H\}$ NMR (193 MHz, $CDCl_3$) δ: -35.97 (s)], 81% conversion. The mono-phosphine protection of **3** was crucial for the following reaction, because the *bis*(boranato) adduct do not give the target product but affords unknown side products instead. The introduction of a BH_3 group is to activate the methyl group for the following deprotonation. The lack of success in the *bis*(boranato) analogue could be due to the relative weak bonding between the BH_3 group and the phosphorus atom that bears two phenyl groups, so that *sec*-butyl lithium will first react with this BH_3 group instead of deprotonating the acidic methyl group. A balloon was connected to the neck of the Schlenk flask and the flask together with the balloon was then pressured (See **Fig. S1** for details). The valve between the flask and the balloon was closed and the flask was sealed with a rubber stopper. The valve was then opened to maintain the same pressure of flask and the balloon. The flask was taken out of glovebox and immersed in a cooling bath at -70 °C that was produced by a mixture of ethanol and dry ice (**Fig. S1**). After the solution was stirred at -70 °C for 15 min, 1.2 equivalent of *sec*-butyl lithium (1.3 M in hexane, 4.94 mL) was added *via* syringe. The dark brown solution was stirred at -70 °C for 30s and tributyltin chloride (2.09 g, 6.42 mmol) was immediately added *via* syringe. The resulting slightly yellow solution was then stirred at -70 °C for further 5 minutes. The function of the pressured balloon was to prevent the pressure decreasing when the solution was cooled, so as to avoid the suck of the air which may otherwise destroy the active lithium intermediates. Crude product was obtained by removing THF with rotary evaporators. Pure borane adduct of **4a** was obtained by running column chromatography (silica gel, petroleum ether:EtOAc = 20:1) to obtain a white solid (1.39 g, 38% yield). $^{31}P\{^1H\}$ NMR (242 MHz, $CDCl_3$) δ: 26.01 (m), -16.35 (s). ^1H NMR (600 MHz, $CDCl_3$) δ: 7.97

(d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.84 (dd, *J* = 20.4, 9.5 Hz, 3H), 7.74 (d, *J* = 8.1 Hz, 1H), 7.59 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.56–7.47 (m, 2H), 7.43–7.33 (m, 8H), 7.30 (t, *J* = 14.7, 7.4 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.18 (q, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 2H), 6.98 (t, *J* = 7.7 Hz, 2H), 6.68 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 8.6 Hz, 1H), 1.33– 0.45 (m, 27H), 0.96 (m, 1H, PCH_2, overlapping with CH_2 of butyl group), 0.044 (m, 1H, PCH_2, overlapping with solvent). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ: 143.7 (dd, J_{CP} = 4.5 Hz, 33.2 Hz), 140.6 (dd, J_{CP} = 4.5 Hz, 73.0 Hz), 137.9 (d, J_{CP} = 13.6 Hz), 136.4 (d, J_{CP} = 12.1 Hz), 136.1 (d, J_{CP} = 12.1 Hz), 134.5 (d, J_{CP} = 22.7 Hz), 134.2 (s), 133.8 (d, J_{CP} = 7.6 Hz), 133.3 (s), 133.2 (d, J_{CP} = 18.1 Hz), 133.1 (d, J_{CP} = 3.0 Hz), 133.0 (d, J_{CP} = 4.5 Hz), 131.2 (s), 130.9 (s), 130.7 (d, J_{CP} = 1.5Hz), 129.8 (s), 129.4 (d, *J* = 15.1 Hz), 128.7 (s), 128.6 (s), 128.5 (s), 128.5 (s), 128.5 (s), 128.3 (d, J_{CP} = 3.0 Hz), 128.3 (s), 128.2 (d, J_{CP} = 7.6 Hz), 127.8 (d, J_{CP} = 10.6 Hz), 127.4 (s), 127.3 (d, J_{CP} = 9.1 Hz), 127.0 (s), 126.8 (s), 125.8 (s), 28.5 (m, *C*H_2), 27.2 (m, *C*H_2), 13.6 (s, *C*H_3), 10.9 (m, Sn*C*H_2), 4.8 (d, J_{CP} = 24.2 Hz, P*C*H_2). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{51}H_{59}BSnP_2)+H]^+$:865.3300, found: 865.3304. FTIR (ATR, cm^{-1}): 672s, 694s, 775m, 800s, 815s, 868m, 1001m, 1026s, 1063s, 1092s, 1260s, 1304m, 1375m, 1435s, 1463m, 1480m, 1502m, 2162m, 2184m, 2257m, 2341s, 2382s, 2851s, 2869s, 2921s, 2955s, 3052s.

In the argon glovebox, the borane adduct of **4a** (1.20 g, 1.39 mmol) was dissolved in 100 mL of THF in a flask of 200 mL, and diethyl amine (50 mL) was added into solution at room temperature. The solution was further stirred at 40 °C for 12 h. Crude product was obtained by removing solvent with rotary evaporator. Pure product of **4a** was obtained by running a flash column with Al_2O_3 (petroleum ether : EtOAc = 60 :1) to obtain a liquid (0.91 g, 77 % yield). $^{31}P\{^1H\}$ NMR (242 MHz, $CDCl_3$) δ: -13.49 (d, J_{PP} = 38.1 Hz), -27.27 (d, J_{PP} = 38.1 Hz).

Synthesis of 5a

In an argon glovebox, **4a** (0.91 g, 1.07 mmol) was dissolved in 50 mL of THF in a flask of 100 mL, and was then stirred at -90 °C for 10 min. 5 equivalents of *n*-butyl lithium (1.6 M in hexane, 3.35 mL) was added and the solution was stirred at -90 °C for 1.5h. After that, excess of ethyl formate (2 mL) was added and the solution was further stirred for 10 min before it being taken out of the glovebox. The solution was poured into H_2O (100 mL) with stirring. The product was washed with H_2O (100 mL) and extracted by dichloromethane (300 mL). The organic phase was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporators. Pure product of **5a** was obtained by running column chromatography (silica gel, petroleum ether: EtOAc = 5:1) to obtain a white solid (0.29 g, 46 % yield). $^{31}P\{^1H\}$ NMR (242 MHz, $CDCl_3$) δ: -15.31 (d, *J* = 16.2 Hz), -38.06 (d, *J* = 16.2 Hz). ^1H NMR (600 MHz, $CDCl_3$) δ: 9.28 (m, 1H, C*H*O), 7.98 (dd, *J* = 8.4, 5.0 Hz, 2H), 7.90 (d, *J* = 8.2 Hz, 2H), 7.59 (ddd, *J* = 18.5, 8.5, 2.6 Hz, 2H), 7.50–7.33 (m, 7H), 7.25–7.10 (m, 9H), 7.05 (dt, *J* = 16.4, 9.4 Hz, 4H), 6.90 (d, *J* = 8.5 Hz, 1H), 3.27 (dd, J_{HP} = 13.2 Hz, J_{HH} = 5.0 Hz, 1H, PCH_2), 2.88 (d, J_{HP} = 13.1 Hz, 1H, PCH_2). ^{13}C NMR$\{^1H\}$ (151 MHz, $CDCl_3$) δ: 199.0 (d, J_{CP} = 18.1 Hz, *C*HO), 144.9 (td, J_{CP} = 42.3, 34.4, 8.4 Hz), 137.5– 137.2 (m), 135.4 (dd, J_{CP} = 3.0, 9.1 Hz), 134.1 (d, J_{CP} = 3.0 Hz), 134.0 (d, J_{CP} = 1.5 Hz), 133.8 (d, J_{CP} = 21.1 Hz), 133.5 (d, J_{CP} = 4.5 Hz), 133.4 (s), 133.4 (s), 133.3 (d, J_{CP} = 3.0 Hz), 133.2 (d, J_{CP} = 1.5 Hz), 133.2 (d, J_{CP} = 1.5 Hz), 131.8 (d, J_{CP} = 19.6 Hz), 130.3 (s), 128.8 (s), 128.6 (s), 128.6 (s), 128.4 (s), 128.3 (d, J_{CP} = 3.0 Hz), 128.3 (s), 128.3 (s), 128.2 (s), 128.1 (s), 127.9 (s), 127.5 (d, J_{CP} = 3.0Hz), 127.1 (d, J_{CP} = 3.0 Hz), 126.9 (d, J_{CP} = 6.0 Hz), 126.4 (s), 44.8 (dd, J_{CP} = 22.8, 3.0 Hz, P*C*H_2). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{40}H_{30}OP_2)+H]^+$: 589.1854, found: 589.1850. FTIR (ATR, cm^{-1}): 638m, 694s, 741s, 815s, 1025s, 1158m, 1307m, 1433s, 1479s, 1501m, 1584m, 1712s, 1980m, 2162m, 2822m, 2849m, 2925s, 2953s, 3000m, 3013m, 3050s.

Synthesis of 6a

In an argon glovebox, compound **5a** (0.2900 g, 0.493 mmol) was dissolved in 20 mL of dichloromethane in a Schlenk flask of 100 mL. Iron(II) tetrafluoroborate hexahydrate (0.1662 g, 0.493 mmol) and (1*S*,2*S*)-1,2-diphenylethylenediamine (0.1047 g, 0.493 mmol) were dissolved in 20 mL of acetonitrile, respectively. The above solutions were mixed with stirring to afford a dark pink solution, which was further stirred at room temperature for additional 2 h. After reaction, part of the solution was transfer into an NMR tube for analysis using a C_6D_6 insert for locking and shimming. After reaction, the solution was concentrated to 2 mL and diethyl ether (10 mL) was let to slowly diffuse into the solution to afford pink crystals after 2 days. The crystals were collected and were further dried under vacuum to afford pure **6a**, 0.3828 g, 71% yield. ^{31}P NMR{^{1}H} (242 MHz, CH_3CN, C_6D_6 insert) δ: 63.34 (d, J = 35.4 Hz), 52.49 (d, J = 35.4 Hz). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{54}H_{42}N_2P_2Fe)]^{2+}$: 419.1158, found: 419.1165. FTIR (ATR, cm^{-1}): 613m, 623w, 646w, 669m, 698s, 745s, 819m, 847w, 873w, 1001s, 1224w, 1259w, 1283w, 1310w, 1371w, 1436s, 1456m, 1482w, 1499m, 1586m, 1639w, 2932w, 3061m, 3267m, 3325w, 3551w, 3627w.

To get the ^{1}H and ^{13}C {^{1}H} NMR data of the iron complex, the bis(d_3-acetonotrile) analogue of **6a** was prepared by utilizing d_3-acetonotrile as the solvent without the use of dichloromethane. ^{31}P{^{1}H} NMR (242 MHz, CD_3CN) δ: 62.44 (d, J = 35.7 Hz), 51.52 (d, J = 35.7 Hz). ^{1}H NMR (600 MHz, CD_3CN) δ: 7.96 (d, J = 8.1 Hz, 1H), 7.88 (t, J = 5.8 Hz, 2H), 7.82 (t, J = 7.7 Hz, 1H), 7.77–7.68 (m, 1H), 7.70 (*H*CN, determined by HSQC, COSY), 7.57 (ddd, J = 44.4, 23.7, 13.6 Hz, 6H), 7.47 (dd, J = 19.4, 11.8 Hz, 2H), 7.45–7.29 (m, 12H), 7.20 (t, J = 9.4 Hz, 1H), 7.14 (t, J = 9.2 Hz, 1H), 7.04 (t, J = 6.7 Hz, 1H), 6.85 (dd, J = 19.9, 10.1 Hz, 3H), 6.80 (t, J = 6.5 Hz, 2H), 6.73 (d, J = 6.7 Hz, 1H), 6.66 (d, J = 6.3 Hz, 2H), 6.32 (d, J = 8.5 Hz, 1H), 5.22 (d, J_{HH} = 11.8 Hz, 1H, C*H*(Ph)N=C), 5.01 (d, J = 9.8 Hz, 1H, NH_2), 4.63 (dd, J_{HP} = 19.1 Hz, J_{HH} = 6.0 Hz, 1H, PCH_2), 4.46–4.34 (m, 1H, C*H*(Ph)NH_2), 3.72 (m, NH_2), 3.67 (m, 1H, PCH_2). ^{13}C{^{1}H} NMR (151 MHz, CD_3CN) δ: 176.0 (d, J_{CP} = 6.0 Hz, H*C*N), 140.7 (s), 140.4 (d, J_{CP} =13.6 Hz), 138.8 (s), 137.9 (s), 135.6 (d, J_{CP} = 39.3 Hz), 134.5 (d, J_{CP} = 10.6 Hz), 134.2 (s), 134.2 (s), 134.0 (d, J_{CP} = 10.6 Hz), 133.7 (s), 133.6 (s), 132.3 (d, J_{CP} = 30.2 Hz), 131.5 (d, J_{CP} = 6.0 Hz), 131.1 (s), 129.8 (s), 129.6–129.2 (m), 128.8–128.5 (m), 128.3 (d, J_{CP} = 9.1Hz), 128.0 (d, J_{CP} = 9.1Hz), 127.9 (s), 127.6 (s), 127.4 (s), 127.2 (s), 127.1 (s), 126.9 (s), 126.7 (d, J_{CP} = 33.2 Hz), 124.1 (s), 75.0 [s, *C*H(Ph)N=C], 65.5 [s, *C*H(Ph)NH_2], 41.9 (d, J_{CP} = 22.7 Hz, P*C*H$_2$).

Synthesis of 6a'

Complex **6a'** was synthesized by the similar procedure to **6a** except that (1*R*,2*R*)-1,2-diphenylethylenediamine was used, 0.3936 g of **6a'** obtained, 73 % yield. Two sets of phosphorus resonances were observed for **6a'**. The major: ^{31}P NMR (242 MHz, CH_3CN, C_6D_6 insert) δ: 55.35 (d, J = 54.6 Hz), 52.97 (d, J = 54.6 Hz). The minor: ^{31}P{^{1}H} NMR (242 MHz, CH_3CN, C_6D_6 insert) δ: 68.49 (d, J = 39.6 Hz), 53.73 (d, J = 39.6 Hz). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{54}H_{42}N_2P_2Fe)]^{2+}$: 419.1153, found: 419.1165. FTIR(ATR, cm^{-1}): 612w, 622w, 635w, 668m, 698s, 745s, 818m, 846w, 872w, 1058s, 1161m, 1223w, 1283w, 1309w, 1283w, 1309w, 1371w, 1436s, 1455m, 1481w, 1498m, 1553w, 1586m, 2934w, 3061m, 3168w, 3263m, 3311m, 3543w, 3626w.

The major bis(d_3-acetonotrile) analogue of **6a'**: ^{31}P{^{1}H} NMR (242 MHz, CD_3CN) δ: 54.49 (d, J = 54.7 Hz), 52.06 (d, J = 54.7 Hz). ^{1}H NMR (600 MHz, CD_3CN), the aromatic protons were overlapped with those of the minor, δ: 8.11 (m, 2H), 8.04–7.67 (m), 7.72 (m, 1H, *H*CN),7.62 (m, 3H), 7.52 (m, 5H), 7.41–7.28 (m), 7.20 (m, 3H), 7.10 (m, 2H), 7.04–6.85 (m), 6.68 (m, 3H), 6.50 (m), 6.31 (d, J = 8.2 Hz,

1H), 6.20 (m), 5.98 (d, J = 8.2 Hz, 1H), 5.09 (m, 1H, NH_2), 4.78 (dd, 1H, J_{HP} = 14.9 Hz, PCH_2), 4.49 (d, J_{HH} = 11.1 Hz, 1H, CH(Ph)N=C), 4.03 (m, 1H, CH(Ph)NH_2), 3.84 (m, PCH_2), 3.04 (m, 1H, NH_2). $^{13}C\{^1H\}$ NMR (151 MHz, CD_3CN) δ: 177.9 (s, H*C*N), 143.1 (d, J_{CP} = 4.5 Hz), 140.8 (s), 139.9 (s), 138.1 (s), 137.6 (s), 137.2 (s), 136.9 (s), 135.8 (s), 135.1 (d, J_{CP} = 37.8 Hz), 134.6–134.5 (m), 134.1–134.0 (m), 133.6–132.7 (m), 132.4 (d, J_{CP} = 10.6 Hz), 131.8 (s), 131.5–131.4 (m), 131.2 (s), 130.7 (d, J_{CP} = 7.6 Hz), 129.9–129.1 (m), 128.9–128.6 (m), 128.4–127.5 (m), 127.3 (d, J_{CP} = 7.6 Hz), 127.0 (s), 126.7–126.5 (m), 126.1 (d, J_{CP} = 13.6 Hz), 125.7 (d, J_{CP} = 4.5 Hz), 125.6 (s), 125.3 (s), 124.3 (s), 123.8 (s), 81.0 [s, *C*H(Ph)N=C], 62.8 [s, *C*H(Ph)NH_2], 40.3 (d, J_{CP} = 27.2 Hz, P*C*H$_2$). The minor bis(d_3-acetonotrile) analogue of **6a'**: $^{31}P\{^1H\}$ NMR (242 MHz, CD_3CN) δ: 67.56 (d, J = 39.6 Hz), 52.88 (d, J = 39.6 Hz). ^1H NMR (600 MHz, CD_3CN), the aromatic protons were overlapped with those of the major, δ: 7.91 (m, 1H, *H*CN), 4.93 (d, J_{HH} = 12.0 Hz, CH(Ph)N=C), 4.70 (m, 1H, PCH_2), 4.63 (m, 1H, CH(Ph)NH_2), 4.39 (d, J_{HH} = 10.4 Hz, 1H, NH_2), 3.95 (dd, J_{HH} = 10.3, 10.4 Hz, 1H, NH_2), 3.82 (m, 1H, PCH_2). $^{13}C\{^1H\}$ NMR (151 MHz, CD_3CN) δ: 179.0 (s, H*C*N), 74.8 [s, *C*H(Ph)N=C], 66.8 [s, *C*H(Ph)NH_2], 42.7 (d, J_{CP} = 24.2 Hz, P*C*H$_2$).

Synthesis of 7a

The solvent for the synthesis of compound **6a** (0.3828 g, 0.350mmol) was removed and sodium chloride (0.102 g, 1.750 mmol) was added and the solid mixture was exposed to a carbon monoxide atmosphere at 1 atm. Anhydrous and degassed acetone (20 mL) was injected with stirring *via* syringe to afford an orange solution immediately. The solution was stirred for additional 30 min under the atmosphere of CO at room temperature. After reaction, acetone was removed under vacuum and the Schlenk flask was brought inside the glovebox. Dichloromethane (10 mL) was added and the solution was filtered through a syringe filter with PTFE membrane (pore size 0.225 μm). The filtrate was condensed to around 2 mL, and diethyl ether was added slowly with stirring to cause yellow precipitate. The solvent of the solution was discarded and the yellow solid was dried under vacuum to afford **7a** (0.1901 g, 55% yield). Due to the less stability of **7a**, further purification was not fulfilled, and the precatalyst sample was directly prepared by equally dividing the acetone solution followed by removing acetone under vacuum. $^{31}P\{^1H\}$ NMR (242 MHz, acetone) δ: 62.01 (d, J = 55.7 Hz), 58.18 (d, J = 55.7 Hz). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{55}H_{44}N_2P_2FeClO)]^+$: 901.1970, found: 901.1968. FTIR (ATR, cm^{-1}): 622w, 641w, 698s, 745s, 814s, 871m, 1025s, 1082s, 1222w, 1261s, 1310m, 1374m, 1436s, 1454m, 1480m, 1498m, 1585m, 1616m, 1639m, 1683w, 1706w, 1980s, 2926m, 2962s, 3057m, 3307w.

Synthesis of 7a'

The same procedure to the synthesis of **7a** was employed to synthesize **7a'** using 0.3936 g of **6a'**, 0.1777 g of **7a'** obtained, 50% yield. $^{31}P\{^1H\}$ NMR (242 MHz, acetone) δ: 59.14 (d, J = 53.5 Hz), 58.22 (d, J = 53.5 Hz). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{55}H_{44}N_2P_2FeClO)]^+$: 901.1970, found: 901.1968. FTIR (ATR, cm^{-1}): 622w, 641w, 698s, 745s, 816s, 871m, 1026s, 1067s, 1221m, 1258w, 1279w, 1310m, 1376m, 1435s, 1455s, 1480m, 1498m, 1585s, 1634s, 1982s, 2852s, 2923s, 3057s, 3201m, 3308m, 3356m.

Synthesis of 1b

In an argon protected glovebox, (s)-2,2'-dibromo-1,1'-binaphthyl (3.00 g, 7.27 mmol) was dissolved in 100 mL of THF in a flask and the solution was stirred for around 10 min until all the

solid was dissolved. The flask was immersed in a cooling bath equipped by the glovebox at -90 °C. The solution was stirred at -90 °C for 10 min to completely cool the solution. *N*-butyl lithium in hexane (5.00 mL, 1.6 M, 1.1 equiv.) was added dropwise and the slightly yellow solution was stirred at -90 °C for further 15 minutes. Chlorobis(4-methoxyphenyl)phosphine (2.25 g, 8.01 mmol) was dissolved in THF (5 mL) and then added dropwise. The solution was stirred at -90 °C for 10 min, during which if the cooling medium started to melt, slightly more liquid nitrogen was added to solidify the medium mixture. The flask was then taken out of the glovebox, and H_2O_2 (30 wt%, 40 mL, 48.5 equiv.) was added into solution with stirring after the temperature rose to room temperature. The solution was poured into a separating funnel and the organic compound was washed with H_2O (200 mL) and extracted by dichloromethane (300 mL). The organic phase was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporator. Pure product of **1b** was obtained by running column chromatography (silica gel, CH_2Cl_2: EtOAc = 5:1) to obtain a white solid (3.97 g, 92 % yield). $^{31}P\{^1H\}$ NMR (242 MHz, $CDCl_3$) δ: 28.78 (s). ^1H NMR (600 MHz, $CDCl_3$) δ: 8.08–8.03 (m, 1H), 7.96 (dd, J = 14.1, 5.8 Hz, 2H), 7.72 (d, J = 8.1 Hz, 1H), 7.60–7.54 (m, 2H), 7.52 (d, J = 8.8 Hz, 1H), 7.47–7.37 (m, 3H), 7.34–7.23 (m, 3H), 7.18 (t, J = 7.6 Hz, 1H), 7.03 (dd, J = 17.2, 8.5 Hz, 2H), 6.76 (dd, J = 8.7, 2.0 Hz, 2H), 6.53 (dd, J = 8.7, 2.0 Hz, 2H), 3.80 (s, 3H, H_3CO),3.77 (s, 3H, H_3CO). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ: 161.9 (d, J_{CP} = 3.0 Hz), 161.5 (d, J_{CP} = 3.0 Hz), 142.0 (d, J_{CP} = 9.1 Hz), 135.4 (d, J_{CP} = 4.5Hz), 134.7–134.6 (m), 133.8 (d, J_{CP} = 12.1 Hz), 133.4 (d, J_{CP} = 12.1 Hz), 132.3 (d, J_{CP} = 12.1 Hz), 131.9 (s), 130.4 (s), 129.7 (d, J_{CP} = 19.6 Hz), 129.2 (d, J_{CP} = 12.1 Hz), 128.24 (s), 128.16 (s), 128.1 (s), 127.7 (s), 127.3 (s), 126.8 (d, J_{CP} = 3.0 Hz), 126.6 (s), 126.0 (s), 125.1 (s), 124.3 (d, J_{CP} = 42.3 Hz), 123.6 (s), 123.4 (s), 113.5 (d, J_{CP} = 13.6 Hz), 113.0 (d, J_{CP} = 13.6 Hz), 55.3 (s, H_3CO), 55.2 (s, H_3CO). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{34}H_{26}BrO_3P)+H]^+$: 593.0889, found: 593.0881. FTIR (ATR, cm^{-1}): 646m, 669s, 681s, 693s, 745s, 803s, 826s, 1025s, 1116s, 1178s, 1202s, 1253s, 1292s, 1306s, 1437s, 1460s, 1501s, 1569s, 1595s, 2930s, 3057s.

Synthesis of borane adduct of 2b

In an argon glovebox, compound **1b** (3.50 g, 5.90 mmol) was dissolved in 100 mL of THF in a flask of 200mL, and the solution was immersed in the cooling bath and further stirred at -90 °C for 10 min. *N*-butyl lithium in hexane (4.05 mL, 1.6 M, 1.1 equiv.) was added dropwise and the slightly yellow solution was stirred at -90 °C for further 15 minutes. Dichlorophenylphosphine (1.16 g, 6.48 mmol) was added dropwise into the solution, and the solution was stirred for 10 min at -90 °C. After that, 1.3 equivalent of methylmagnesium bromide (1 M in THF, 7.67 mL) was added dropwise and the solution was stirred for 10 min at this temperature. 1.5 equivalent of borane-tetrahydrofuran complex (0.9 M in THF, 9.83 mL) was added into solution with stirring after the temprature rose up to room temperature. The flask was then taken out of the glovebox. The product was washed with H_2O (200 mL) and extracted by dichloromethane (400 mL). The organic phase was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporator. Pure borane adduct of **2b** was obtained by running column chromatography (silica gel, petroleum ether: EtOAc = 2 :1) to obtain a white solid (3.02 g, 79% yield). $^{31}P\{^1H\}$ NMR (242 MHz, $CDCl_3$) δ: 27.55 (s), 17.23 (m). ^1H NMR (600 MHz, $CDCl_3$) δ: 8.16 (ddd, J = 10.1, 6.8, 3.2 Hz, 2H), 8.02 (dd, J = 8.6, 1.8 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.79–7.71 (m, 3H), 7.69 (d, J = 8.1 Hz, 1H), 7.62–7.56 (m, 2H), 7.51–7.47 (m, 3H), 7.45 (dd, J = 10.6, 8.8 Hz, 1H), 7.36 (dd, J = 11.2, 4.1 Hz, 1H), 7.32–7.28 (m, 1H), 7.25 (t, J = 7.3 Hz, 1H), 7.07 (dd, J = 11.3, 8.7 Hz, 2H), 7.01 (dd, J = 8.8, 1.9 Hz, 2H), 6.73–6.68 (m, 1H), 6.52–6.45 (m, 3H), 3.85 (s, 3H, H_3CO), 3.73 (s, 3H, H_3CO), 1.52 (d, J_{HP} = 10.6 Hz,

3H, PCH_3), 0.81–0.18 (m, 3H, BH_3). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ: 162.2 (d, J_{CP} = 3.0 Hz), 161.5 (d, J_{CP} = 3.0 Hz), 142.1 (dd, J_{CP} = 3.0, 4.1 Hz), 139.8 (dd, J_{CP} = 3.0, 4.5Hz), 134.4 (s), 134.2 (d, J_{CP} = 10.6 Hz), 134.0 (d, J_{CP} = 10.6 Hz), 133.4 (d, J_{CP} = 9.1 Hz), 133.3 (d, J_{CP} = 16.6 Hz), 133.0 (s), 132.9 (s), 132.8 (s), 132.4 (d, J_{CP} = 10.6 Hz), 131.4 (d, J_{CP} = 102.7 Hz), 130.7 (d, J_{CP} = 1.5 Hz), 129.5 (d, J_{CP} = 54.4 Hz), 128.7 (d, J_{CP} =10.6 Hz), 128.7 (d, J_{CP} = 10.6 Hz), 128.5–128.3 (m), 128.2 (s), 127.8 (s), 127.5 (s), 127.2 (s), 127.0 (s), 126.6 (s), 125.5 (d, J_{CP} = 110.2 Hz), 125.7 (s), 122.5 (d, J_{CP} = 108.7 Hz), 114.2 (s), 114.1 (s), 113.3 (s), 113.3 (s), 55.4 (s, H_3CO), 55.2 (s, H_3CO), 13.1 (d, J_{CP} = 39.3 Hz, PCH_3). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{41}H_{37}BO3P_2)+Na]^+$: 673.2225, found: 673.2216. FTIR (ATR, cm^{-1}): 649s, 673m, 685s, 695s, 722m, 747s, 777m, 802s, 815s, 874m, 1026s, 1059s, 1116s, 1140m, 1154m, 1179s, 1195s, 1224m, 1254s, 1293s, 1407m, 1437s, 1462s, 1501s, 1553m, 1569s, 1596s, 2162m, 2257m, 2336s, 2380s, 2850s, 2919s, 2958s, 3008m, 3055s.

Synthesis of
(S_A, R_P)-2-methylphenylphosphino-2'-di(4-methoxyphenyl)phosphino-1,1'-binapthyl

The borane adduct of **2b** (3.00 g, 4.61 mmol) was dissolved in 100 mL of THF in a 150 mL of high pressure-resistant glass bottle. Triethyl amine (2.33g, 23.03mmol, dried and degassed) and trichlorosilane (12.49 g, 92.22 mmol) were added by syringe at room temperature. The solution was then stirred at 80 °C for 3h. After reaction ceased and the solution temperature dropped to room temperature, the solution was poured into a solution mixture of cool dichloromethane (600 mL) and sodium hydroxide in H_2O (10 wt%, 100 mL) with stirring. The organic phase was washed with H_2O (100 mL) and was then dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporator. Pure product was obtained by running column chromatography (silica gel, petroleum ether: EtOAc = 10 :1) to obtain a white solid (2.63g, 92% yield). $^{31}P\{^1H\}$ NMR (242 MHz, $CDCl_3$) δ: -17.79 (d, J = 17.0 Hz), -37.73 (d, J = 17.0 Hz). ^1H NMR (600 MHz, $CDCl_3$) δ: 7.89 (dd, J = 8.3, 6.5 Hz, 2H), 7.83 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.1 Hz, 1H), 7.57 (dd, J = 8.5, 2.9 Hz, 1H), 7.48 (dd, J = 7.4, 3.7 Hz, 1H), 7.37 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 7.26 (dd, J = 8.6, 6.5 Hz, 2H), 7.12–7.07 (m, 6H), 7.05–7.01 (d, 12 Hz, 1H), 6.96–6.90 (m, 3H), 6.87 (d, J = 7.7 Hz, 2H), 6.76 (d, J = 8.5 Hz, 1H), 6.61 (d, J = 8.4 Hz, 2H), 3.79 (s,3H, H_3CO),3.71 (s, 3H, H_3CO), 1.40 (d, J_{HP} = 4.8 Hz, 3H, PCH_3). ^{13}C NMR$\{^1H\}$ (151 MHz, $CDCl_3$) δ: 159.8 (d, J_{CP} = 52.9 Hz), 145.0–144.1 (m), 141.4 (d, J_{CP} = 15.1 Hz), 137.6 (d, J_{CP} = 3.0 Hz), 137.5 (d, J_{CP} = 1.5 Hz), 136.7 (d, J_{CP} = 3.0 Hz), 136.6 (d, J_{CP} = 3.0 Hz), 135.5 (d, J_{CP} = 22.7 Hz), 134.6 (dd, J_{CP} = 1.5 Hz, 18.1 Hz), 133.5–133.1 (m), 131.3 (d, J_{CP} = 16.6 Hz), 129.9 (s), 128.9 (d, J_{CP} = 9.1 Hz), 128.6 (d, J_{CP} = 6.0 Hz), 128.5 (s), 128.4 (d, J_{CP} = 1.5 Hz), 128.0 (s), 127.9 (t, J_{CP} = 6.0 Hz), 127.7 (s), 127.5 (d, J_{CP} = 1.5 Hz), 127.4 (s), 127.2 (d, J_{CP} = 1.5 Hz), 126.5 (s), 126.3 (s), 126.1 (s), 125.8 (s), 114.1 (d, J_{CP} = 6.0 Hz), 113.8 (d, J_{CP} = 7.6 Hz), 55.2 (s, H_3CO), 55.1 (s, H_3CO), 12.0 (dd, J_{CP} = 3.0 ,15.1 Hz, PCH_3). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{41}H_{34}O_2P_2)+H]^+$: 621.2110, found: 621.2112. FTIR (ATR, cm^{-1}): 692s, 746s, 895s, 1032s, 1059s, 1114s, 1174s, 1249s, 1290s, 1433s, 1495s, 1590s, 2379s, 2549m, 2849s, 2924s, 3053s, 3659w.

Synthesis of borane adduct of 4b and 4b

In the argon glovebox, (S_A, R_P)-2-methylphenylphosphino-2'-di(4-methoxyphenyl)phosphino-1,1'-binapthyl (2.50 g, 4.03 mmol) was dissolved in 100 mL of THF in a 200 mL of Schlenk flask, and 1.0 equivalent of borane-tetrahydrofuran complex (0.9 M in THF, 4.48 mL) was added into solution with stirring at room temperature. The solution was further stirred at 45 °C for 12 h to afford **3b** [$^{31}P\{^1H\}$ NMR (242 MHz, $CDCl_3$) δ: -19.06 (s), 17.06 (m), $^{11}B\{^1H\}$ NMR (193 MHz, $CDCl_3$) δ: -36.13

(s)], 80% conversion. A balloon was connected to the neck of the Schlenk flask and the flask together with the balloon was then pressured (See **Fig. S1** for details). The valve between the flask and the balloon was closed and the flask was sealed with a rubber stopper. The valve was then opened to maintain the same pressure of flask and the balloon. The flask was taken out of glovebox and immersed in a cooling bath at -70 °C that was produced by a mixture of ethanol and dry ice (**Fig. S1**). After the solution was stirred at -70 °C for 15 min, 1.2 equivalent of *sec*-butyl lithium (1.3 M in hexane, 3.72 mL) was added via syringe. The dark brown solution was stirred at -70 °C for 2 min and tributyltin chloride (1.58 g, 4.85 mmol) was immediately added *via* syringe. The resulting slightly yellow solution was then stirred at -70 °C for further 5 minutes. Crude product was obtained by removing THF with rotary evaporator. Pure borane adduct of **4b** was obtained by running column chromatography (silica gel, petroleum ether:EtOAc = 20:1) to obtain a white solid (1.49 g, 50% yield). $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) δ: 25.99 (m), -19.46 (s). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.90 (d, J = 6.7 Hz, 1H), 7.89–7.84 (m, 3H), 7.75 (t, J = 10.8 Hz, 1H), 7.68 (d, J = 8.1 Hz, 1H), 7.53–7.41 (m, 3H), 7.41–7.35 (m, 1H), 7.32–7.24 (m, 6H), 7.24–7.18 (m, 1H), 6.87 (t, J = 10.2 Hz, 2H), 6.83 (t, J = 8.2 Hz, 2H), 6.65 (q, J = 7.9 Hz, 1H), 6.54 (d, J = 8.5 Hz, 2H), 6.45 (t, J = 8.2 Hz, 1H), 3.79 (s, 3H, H_3CO), 3.71 (s, 3H, H_3CO), 1.10–0.39 (m, 27H), 1.08 (m, 1H, PC*H*2, overlapping with CH_3), 0.099 (m, 1H, PCH_2). $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ: 160.2 (s), 159.9 (s), 142.8 (dd, J_{CP} = 3.0, 33.2 Hz), 140.7–140.6 (m), 137.3 (d, J_{CP} = 12.1 Hz), 136.0 (d, J_{CP} = 24.2 Hz), 134.7 (d, J_{CP} = 19.5 Hz), 134.5 (d, J_{CP} = 58.9 Hz), 133.8 (d, J_{CP} = 7.6 Hz), 133.3–133.1 (m), 130.9 (dd, J_{CP} = 1.5, 46.8 Hz), 130.7 (d, J_{CP} = 1.5 Hz), 129.4 (d, J_{CP} = 15.1 Hz), 129.3 (s), 128.7 (d, J_{CP} = 7.6 Hz), 128.5 (d, J_{CP} = 10.6 Hz), 128.4 (s), 128.2 (d, J_{CP} = 3.0 Hz), 127.8 (d, J_{CP} = 10.6 Hz), 127.4 (s), 127.3 (d, J_{CP} = 6.0 Hz), 127.3 (s), 127.2 (s), 126.9 (s), 126.7 (s), 125.6 (s), 114.3 (d, J_{CP} = 6.0 Hz), 113.9 (d, J_{CP} = 9.1 Hz), 55.21 (s, H_3CO), 55.16 (s, H_3CO), 28.5 (m, CH_2), 27.2 (m, CH_2), 13.6 (s,CH_3), 10.9 (m, SnCH_2), 4.8 (d, J_{CP} = 24.2 Hz, PCH_2). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{53}H_{63}BO_2SnP_2)+H]^+$: 925.3508, found: 925.3516. FTIR (ATR, cm^{-1}): 673m, 684m, 695s, 743s, 751s, 776m, 798s, 812s, 821s, 1031s, 1060s, 1093s, 1115m, 1135m, 1161m, 1175s, 1225m, 1247s, 1283s, 1303m, 1438s, 1462s, 1497s, 1568s, 1594s, 2343m, 2351m, 2391s, 2850s, 2871s, 2920s, 2956s, 3048m.

In an argon glovebox, the borane adduct of **4b** (1.00 g, 1.08 mmol) was dissolved in 100 mL of THF in a flask of 200 mL, and diethyl amine (50 mL) was added into solution at room temperature. The solution was further stirred at 40 °C for 12 h. Crude product was obtained by removing solvent with rotary evaporator. Pure product of **4b** was obtained by running a flash column with Al_2O_3 (petroleum ether : EtOAc = 60 :1) to obtain an oil (0.81 g, 82 % yield). $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) δ: -16.33 (d, J_{PP} = 41.1 Hz), -26.97 (d, J_{PP} = 41.1 Hz).

Synthesis of 5b

In an argon glovebox, **4b** (0.81 g, 0.89 mmol) was dissolved in 50 mL of THF in a flask of 100 mL, and was then stirred at -90 °C for 10 min. 5 equivalents of *n*-butyl lithium (1.6 M in hexane, 2.78 mL) was added and the solution was stirred at -90 °C for 1.5h. After that, excess of ethyl formate (2 mL) was added and the solution was further stirred for 10 min before it was taken out of the glovebox. The solution was poured into H_2O (100 mL) with stirring. The product was washed with H_2O (100 mL) and extracted by dichloromethane (300 mL). The organic phase was dried over anhydrous sodium sulfate and the solvent was removed by rotary evaporators. Pure product of **5b** was obtained by running column chromatography (silica gel, petroleum ether:EtOAc = 5:1) to obtain a white solid (0.27 g, 47 % yield). ^{31}P NMR (242 MHz, $CDCl_3$) δ: -17.86 (d, J = 19.4 Hz), -37.49

(d, J = 19.4 Hz). ^{1}H NMR (600 MHz, $CDCl_3$) δ: 9.41 (m, 1H, C*H*O), 7.96 (dd, J = 8.5, 4.6 Hz, 2H), 7.90 (d, J = 8.2 Hz, 1H), 7.86 (d, J = 8.2 Hz, 1H), 7.60 (dd, J = 8.5, 2.6 Hz, 1H), 7.54 (dd, J = 8.5, 2.9 Hz, 1H), 7.42 (dt, J = 14.5, 7.5 Hz, 2H), 7.31 (dt, J = 16.4, 8.2 Hz, 2H), 7.21–7.10 (m, 6H), 7.03 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 8.5 Hz, 1H), 6.96–6.90 (m, 4H), 6.81 (d, J = 8.5 Hz, 1H), 6.65 (d, J = 8.4 Hz, 2H), 3.83 (s, 3H, H_3CO), 3.75 (s, 3H, H_3CO), 3.30 (dd, J_{HP} = 13.2 Hz, J_{HH} = 4.9 Hz, 1H, PCH_2), 3.00 (d, J_{HP} = 13.1 Hz, 1H, PCH_2). ^{13}C NMR{^{1}H} (151 MHz, $CDCl_3$) δ: 199.1 (d, J_{CP} = 18.1 Hz, *C*HO), 160.1 (s), 159.9 (s), 144.8–143.9 (m), 137.6 (d, J_{CP} = 16.6 Hz), 136.6 (dd, J_{CP} = 1.5, 9.1 Hz), 135.4 (d, J_{CP} = 22.7 Hz), 134.7 (d, J_{CP} = 21.1 Hz), 133.9–133.1 (m), 131.8 (d, J_{CP} = 19.6 Hz), 129.8 (s), 128.7 (s), 128.6 (d, J_{CP} = 1.5 Hz), 128.3 (s), 128.25 (s), 128.2 (s), 128.1 (s), 128.0 (s), 127.8 (s), 127.5 (d, J_{CP} = 3.0 Hz), 126.9 (d, J_{CP} = 1.5 Hz), 126.7 (d, J_{CP} = 19.6 Hz), 126.2 (d, J_{CP} = 9.1 Hz), 114.3 (d, J_{CP} = 6.0Hz), 113.9 (d, J_{CP} = 7.6 Hz), 55.3 (s, H_3*C*O), 55.1 (s, H_3*C*O), 44.8 (dd, J_{CP} = 3.0, 22.7 Hz, P*C*H_2). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{42}H_{34}O_3P_2)+H]^+$: 649.2061, found: 649.2061. FTIR (ATR, cm^{-1}): 694s, 745s, 797s, 819s, 1028s, 1094s, 1177s, 1248s, 1284s, 1306m, 1435s, 1462s, 1497s, 1568s, 1593s, 1712s, 2835m, 2869m, 2928s, 2957s, 3052m.

Synthesis of 6b

In an argon glovebox, compound **5b** (0.2700 g, 0.416 mmol) was dissolved in 10 mL of dichloromethane in a Schlenk flask of 100 mL. Iron(II) tetrafluoroborate hexahydrate (0.1404 g, 0.416 mmol) and (1*S*,2*S*)-1,2-diphenylethylenediamine (0.0883 g, 0.416 mmol) were dissolved in 20 mL of acetonitrile, respectively. The above solutions were mixed with stirring to afford a dark pink solution, which was further stirred at room temperature for additional 2 h. After reaction, part of the solution was transfer into an NMR tube for analysis using a C_6D_6 insert for locking and shimming. After reaction, the solution was concentrated to 2 mL and diethyl ether (10 mL) was let to slowly diffuse into the solution to afford pink crystals after 2 days. The crystals were collected and were further dried under vacuum to afford pure **6b**, 0.3603 g, yield 75 %. ^{31}P NMR{^{1}H} (242 MHz, CH_3CN, C_6D_6 insert) δ: 63.45 (d, J = 37.2 Hz), 48.33 (d, J = 37.2 Hz). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{56}H_{46}N_2O_2P_2Fe)]^{2+}$: 449.1265, found: 449.1271. FTIR (ATR, cm^{-1}): 611w, 624m, 671m, 698s, 746s, 801s, 820s, 873m, 1025s, 1058s, 1184s, 1256s, 1288s, 1307m, 1372w, 1406w, 1438m, 1456s, 1499s, 1570m, 1594s, 1640w, 2945m, 3060m, 3266m, 3323w, 3627w.

To get the ^{1}H and ^{13}C {^{1}H} NMR data of the iron complex, the bis(d_3-acetonotrile) analogue of **6b** was prepared by utilizing d_3-acetonotrile as the solvent without the use of dichloromethane. ^{31}P{^{1}H} NMR (242 MHz, CD_3CN) δ: 62.60 (d, J = 36.2 Hz), 47.49 (d, J = 36.22.49 Hz). ^{1}H NMR (600 MHz, CD_3CN) δ: 7.97 (d, J = 8.4 Hz, 1H), 7.89 (t, J = 8.2 Hz, 2H), 7.81 (t, J = 8.0 Hz, 1H), 7.76–7.67 (m, 1H), 7.73 (m, 1H, *H*CN),7.59 (t, J = 7.2 Hz, 3H), 7.44–7.29 (m, 12H), 7.25 (t, J = 9.1 Hz, 2H), 7.22–7.13(m, 2H), 7.06 (d, J = 8.1 Hz, 2H), 6.86 (dd, J = 17.7, 9.6 Hz, 3H), 6.74 (t, J = 7.2 Hz, 1H), 6.66 (t, J = 6.8 Hz, 2H), 6.32 (m, 3H), 5.22 [d, J_{HH} = 11.7 Hz, 1H, C*H*(Ph)N=C)], 4.98 (d, J = 8.3 Hz, 1H, NH_2), 4.60 (dd, J_{HP} = 19.4 Hz, J_{HH} = 6.1 Hz, 1H, PCH_2), 4.43–4.30 [ddd, J_{HH} = 3.8, 12.5, 12.5 Hz, 1H, C*H*(Ph)NH_2], 3.85 (s, 3H, H_3CO), 3.67 (m, 1H, PCH_2), 3.61(dd, J_{HH} = 11.1, 12.3 Hz, 1H, NH_2), 3.56 (s, 3H, H_3CO). ^{13}C{^{1}H} NMR (151 MHz, CD_3CN) δ: 175.7 (d, J_{CP} = 7.6 Hz, H*C*N), 161.7 (s), 160.6 (s), 140.6 (s), 140.5 (s), 138.7 (s), 138.3 (dd, J_{CP} = 6.0, 4.5 Hz), 138.0 (s), 136.8 (s), 136.6 (s), 136.0 (d, J_{CP} = 12.1 Hz), 135.7 (d, J_{CP} = 12.1 Hz), 134.3–134.2 (m), 133.9 (s), 133.6 (s), 133.6 (s), 131.5 (d, J_{CP} = 9.1 Hz), 129.8 (s), 129.4–129.2 (m), 129.0 (s), 128.7 (s), 128.6 (s), 128.4 (d, J_{CP} = 7.6 Hz),128.2 (d, J_{CP} = 9.1 Hz), 127.9 (t, J_{CP} = 9.1 Hz), 127.6 (d, J_{CP} = 19.6 Hz), 127.2 (d, J_{CP} = 22.7 Hz), 126.8 (s), 126.5 (s), 124.1 (s), 123.2 (d, J_{CP} = 33.2 Hz), 117.6 (s), 117.3 (s), 114.9 (d, J_{CP} = 9.1 Hz), 123.2 (d, J_{CP} = 10.6 Hz),

75.1 [s, *C*H(Ph)N=C], 65.5 [s, *C*H(Ph)NH_2], 55.2 (s, H_3CO), 54.9 (s, H_3CO), 41.8 (d, J_{CP} = 25.7 Hz, P*C*H_2).

Synthesis of 6b'

Complex **6b'** was synthesized by the similar procedure to **6b** except that (1*R*,2*R*)-1,2-diphenylethylenediamine was used, 0.3747 g, yield 78 %. Two sets of phosphorus resonances were observed for **6b'**. The major: ^{31}P NMR (242 MHz, CH_3CN, C_6D_6 insert) δ: 53.29 (d, J = 55.3 Hz), 52.12 (d, J = 55.3 Hz). The minor: $^{31}P\{^1H\}$ NMR (242 MHz, CH_3CN, C_6D_6 insert) δ: 68.61 (d, J = 41.1 Hz), 50.05 (d, J = 41.1 Hz). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{56}H_{46}N_2O_2P_2Fe)]^{2+}$: 449.1254, found: 449.1271. FTIR (ATR, cm^{-1}): 635w, 670m, 697s, 746s, 801m, 821m, 872w, 1025s, 1058s, 1186s, 1257s, 1287s, 1307m, 1406w, 1438m, 1456s, 1499s, 1569m, 1593s, 2840w, 2942m, 3060m, 3264m, 3308m, 3545w, 3626w.

The major bis(d_3-acetonotrile) analogue of **6b'**: ^{31}P NMR (242 MHz, CD_3CN) δ: 52.41 (d, J = 55.2 Hz), 51.23 (d, J = 55.2 Hz). ^{1}H NMR (600 MHz, CD_3CN), the aromatic protons were overlapped with those of the minor, δ: 8.07 (m, 2H), 7.97 (m), 7.93 (d, J = 8.3 Hz, 1H), 7,87 (m), 7.80 (m, 1H, *H*CN), 7.82–7.70 (m, 1H), 7.54–7.45 (m, 3H), 7.45–7.31 (m), 7.25 (m, 2H), 7.23–7.11 (m, 4H), 7.09–6.94 (m, 4H), 6.91 (d, J = 7.0 Hz, 1H), 6.89–6.82 (m), 6.71 (m), 6.58 (m), 6.47 (m), 6.32 (d, J = 8.6 Hz, 1H), 6.17 (m), 6.00 (d, J = 8.6 Hz, 1H), 5.06 (m, 1H, N*H*$_2$), 4.94 (1H, NH_2), 4.77 (dd, J_{HP} = J_{HH} = 15.6 Hz, 1H, PC*H*$_2$), 4.50 [d, J = 11.9 Hz, 1H, C*H*(Ph)N=C], 4.06 [m, C*H*(Ph)NH_2], 3.88 (s, H_3CO), 3.80 (m, 1H, PC*H*$_2$), 3.58 (s, 3H, H_3CO), 3.09 (dd, J_{HH} = 11.4, 10.0 Hz). $^{13}C\{^1H\}$ NMR (151 MHz, CD_3CN) δ: 177.6 (s, H*C*N), 162.2 (s), 160.5 (s), 143.1 (d, J_{CP} = 15.1 Hz), 138.2 (s), 137.7 (s), 136.7–136.4 (m), 135.9 (s), 135.0–134.0 (m), 133.5 (s), 132.4 (d, J_{CP} = 10.6 Hz), 131.6 (d, J_{CP} = 4.5 Hz), 131.1 (s), 129.9–129.1 (m), 128.1–128.7 (m), 128.6–127.6 (m), 127.4 (s), 127.2–127.0 (m), 126.6–126.3 (m), 126.0 (s), 125.7 (d, J_{CP} = 4.5 Hz), 124.5 (s), 123.9 (s), 118.5 (s), 118.3 (s), 116.7 (s), 116.4 (s), 116.1 (d, J_{CP} = 9.1 Hz), 115.1 (d, J_{CP} = 9.1 Hz), 114.9 (s), 113.4–113.1 (m), 80.9 [s, *C*H(Ph)N=C], 62.8 [s, *C*H(Ph)NH_2], 55.6 (s, H_3CO), 54.9 (s, H_3CO), 40.4 (d, J_{CP} = 25.7 Hz, P*C*H_2). The minor bis(d_3-acetonotrile) analogue of **6b'**: $^{31}P\{^1H\}$ NMR (242 MHz, CD_3CN) δ: 67.75 (d, J = 41.0 Hz), 49.16 (d, J = 41.0 Hz). ^{1}H NMR (600 MHz, CD_3CN), the aromatic protons were overlapped with those of the major, δ: 7.87 (m, 1H, *H*CN), 4.94 [d, J_{HH} = 14.2 Hz, 1H, C*H*(Ph)N=C] 4.68 (m, 1H, PC*H*$_2$), 4.60 [m, 1H, C*H*(Ph)NH_2], 4.27 (m, 1H, N*H*$_2$), 3.94 (dd, J_{HH} = 11.2, 12.5 Hz, 1H, N*H*$_2$), 3.84 (H_3CO), 3.59 (H_3CO),3.81 (m, 1H, PC*H*$_2$,). $^{13}C\{^1H\}$ NMR (151 MHz, CD_3CN) δ: 178.8 (s, H*C*N), 161.8 (s), 160.7 (s), 74.8 [s, *C*H(Ph)N=C], 66.8 [s, *C*H(Ph)NH_2], 55.3 (s, H_3CO), 55.8 (s, H_3CO), 42.7 (d, J_{CP} = 22.7 Hz, P*C*H_2).

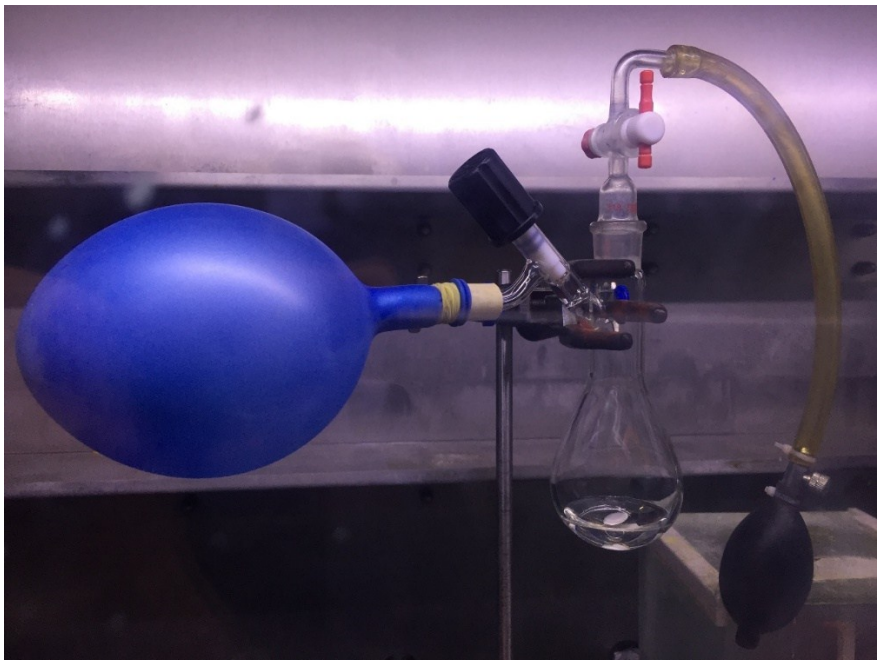
Synthesis of 7b

The solvent for the synthesis of compound **6b** (0.312 mmol) was removed and sodium chloride (0.0912 g, 1.56 mmol) was added and the solid mixture was exposed to a carbon monoxide atmosphere at 1 atm. Anhydrous and degassed acetone (20 mL) was injected with stirring *via* syringe to afford an orange solution immediately. The solution was stirred for additional 30 min under the atmosphere of CO at room temperature. After reaction, acetone was removed under vacuum and the Schlenk flask was brought inside the glovebox. Dichloromethane (10 mL) was added and the solution was filtered through a syringe filter with PTFE membrane (pore size 0.45 μm). The filtrate was condensed to around 2 mL, and diethyl ether was added slowly with stirring

to cause yellow precipitate. The solvent of the solution was discarded and the yellow solid was dried under vacuum to afford **7b** (0.1865 g, 57 % yield). Due to the less stability of **7b**, further purification was not fulfilled, and the precatalyst sample was directly prepared by equally dividing the acetone solution followed by removing acetone under vacuum. $^{31}P\{^{1}H\}$ NMR (242 MHz, acetone) δ: 62.50 (d, J = 56.2 Hz), 54.90 (d, J = 56.2 Hz). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{57}H_{48}N_2P_2FeClO_4)]^+$: 961.2183, found: 961.2180. FTIR (ATR, cm^{-1}): 696s, 745s, 798s, 821s, 923m, 1025s, 1066s, 1094s, 1133s, 1178s, 1250s, 1285s, 1306s, 1375m, 1439s, 1455s, 1498s, 1568s, 1593s, 1616m, 1639s, 1979s, 2929s, 2961s, 3030m, 3058s.

Synthesis of 7b'

The same procedure to the synthesis of **7b** was employed to synthesize **7b'** using 0.3747 g of **6b'**, 0.1871 g of **7b'** obtained, 55 % yield. $^{31}P\{^{1}H\}$ NMR (242 MHz, acetone) δ: 61.03 (d, J = 53.4 Hz), 56.46 (d, J = 53.4 Hz). HRMS (ESI-TOF, CH_2Cl_2) m/z calculated for $[(C_{57}H_{48}N_2P_2FeClO_4)]^+$: 961.2170, found: 961.2180. FTIR (ATR, cm^{-1}): 697s, 746s, 800s, 821s, 923m, 1025s, 1062s, 1179s, 1222m, 1252s, 1286s, 1306s, 1376m, 1405m, 1439s, 1455s, 1498s, 1568s, 1593s, 1615m, 1638m, 1981s, 2850s, 2871m, 2924s, 2956s, 3009m, 3032m, 3058s.



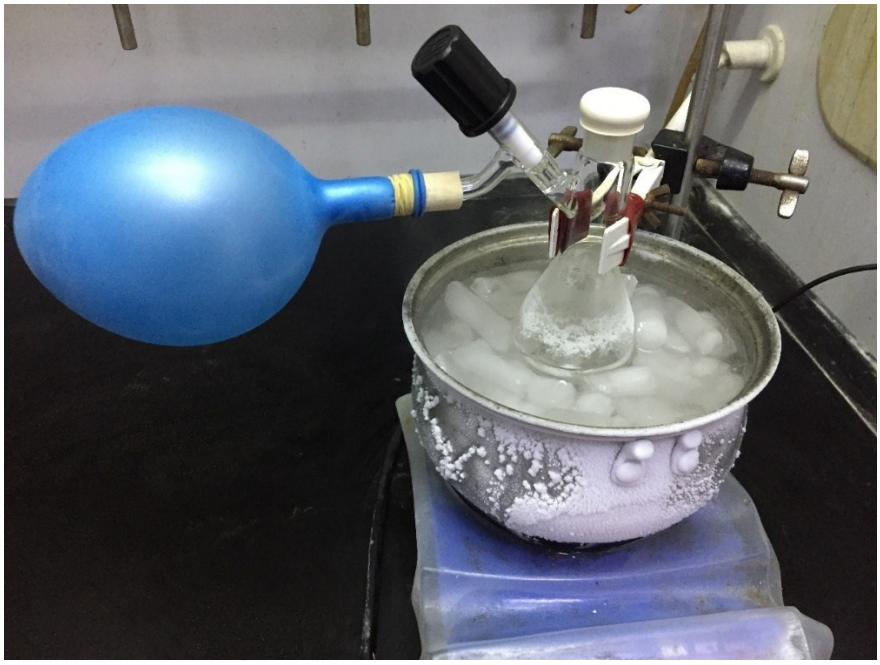
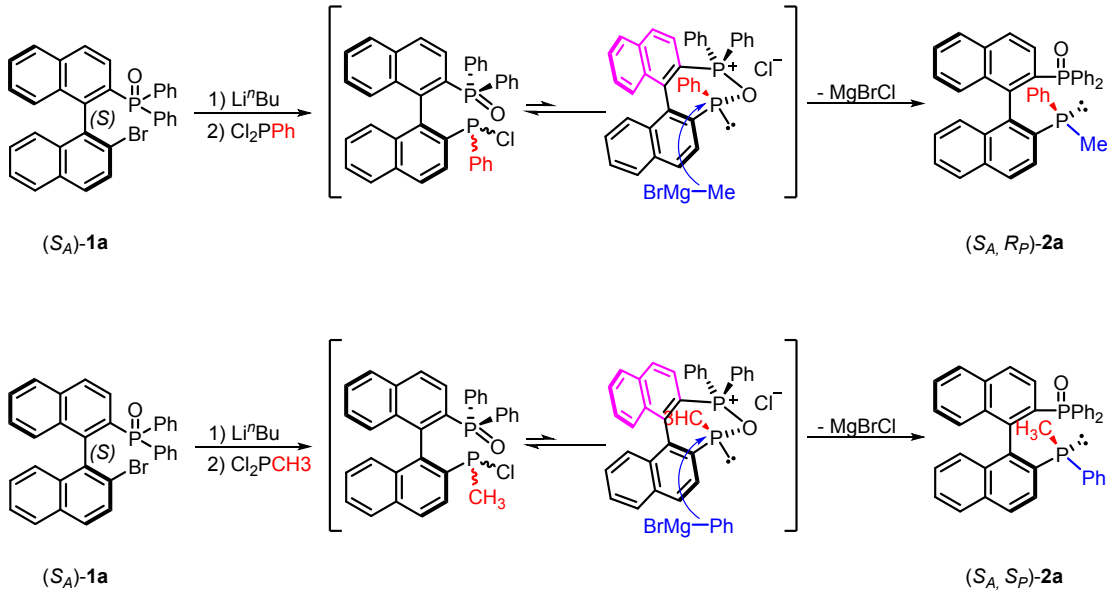


Fig. S1 The reaction setup in the synthesis of the borane adducts of **4a** and **4b**.

2. The postulated mechanism of our chiral induction reaction.



Scheme S1. The proposed mechanism for the 7-membered chiral cycle induced P-chirality recognition process.

The high diastereoselectivity in the synthesis of (S_A, R_P)-**2a** is rationalized by the intramolecular formation of binaphthyl-based 7-membered chiral cyclic POP intermediate, which guides the attacking direction of the methylmagnesium bromide.[2] In this putative phosphacycle the phenyl group (red) derived from dicholorophenyl phosphine is preferentially positioned in parallel to the upper napthyl moiety (pink) that is bonded to the phosphinyl group, in order to minimize the otherwise steric interactions with the other napthyl fragment. The methyl anion attacks the electrophilic phosphorus center from opposite side of oxygen atom, leading to inversion

of configuration at the central phosphine atom and affording the final product. The (S_A, S_P) epimer of **2a** that has an opposite configuration on the P-chiral center is also easily accessible simply by reversing the order of introducing P-substituents. An alternative mechanism of this diastereoselectivity could be an internal assistance of the phosphine oxide in the organometallic attack, particularly Grignard, in the anti-position of the P-Cl bond. It is possible that one chlorophosphine epimer reacts, when the second quickly epimerizes in the presence of lithium halide salt.[3]

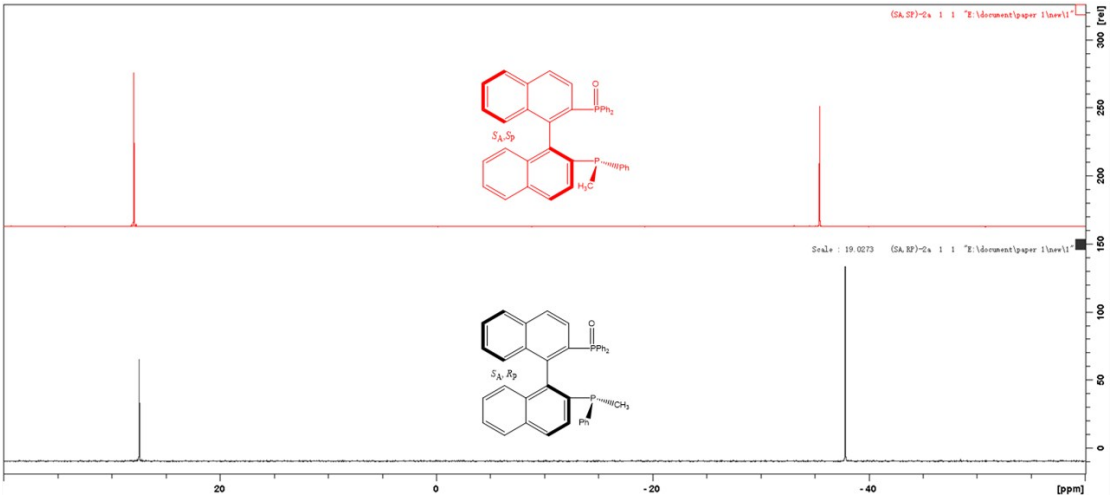


Fig. S2.1 $^{31}P\{^1H\}$ NMR (242 MHz, $CDCl_3$) spectrum of (S_A, S_P)- 2a and (S_A, R_P)- 2a.

The $^{31}P\{^1H\}$ NMR analysis of these two epimers shows a distinct difference between the chemical shifts of the centrally chiral phosphorus nucleus. The (S_A, S_P) isomer **2a** presents resonances at 27.97 and -35.46 ppm, while the opposite epimer (S_A, R_P)-**2a** shows signals at 27.47 and -37.82 ppm, respectively. This has also demonstrated that in each reaction a single diastereomer was obtained.

The same single-diastereomer-formation reaction was seen in the synthesis of free P-chirogenic diphosphine BINAP derivatives (S_A, R_P)-2-methylphenylphosphino-2'-diphenylphosphino-1,1'-binapthyl and (S_A, S_P)-2-methylphenylphosphino-2'-diphenylphosphino-1,1'-binapthyl. These two epimers exhibit distinct $^{31}P\{^1H\}$ chemical shifts. (S_A, R_P)-2-methylphenylphosphino-2'-diphenylphosphino-1,1'-binapthyl: δ -15.11 (d, J = 13.9 Hz), -37.79 (d, J = 13.9 Hz). (S_A, S_P)-2-methylphenylphosphino-2'-diphenylphosphino-1,1'-binapthyl: δ -15.71 (d, J = 12.1 Hz), -35.43 (d, J = 12.1 Hz).

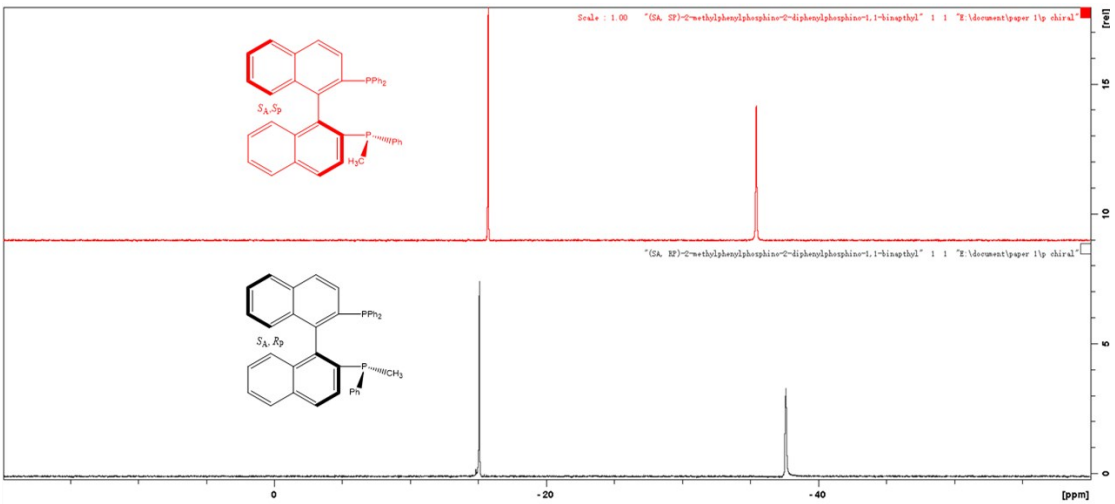
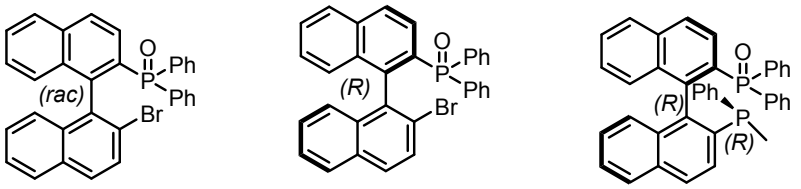


Fig. S2.2 $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) spectrum of (S_A, S_P)- 2-methylphenylphosphino-2'-diphenylphosphino-1,1'-binapthyl and (S_A, R_P)- 2-methylphenylphosphino-2'-diphenylphosphino-1,1'-binapthyl**.**

3. HPLC analyses of the 2-bromo-2'-phosphinyl-1,1'-binapthyl (1) and 2-phosphino-2'-phosphinyl-1,1'-binapthyl (2) to demonstrate no axial chirality racemization during the lithium-bromide exchange process and in the following C-P bond formation step.

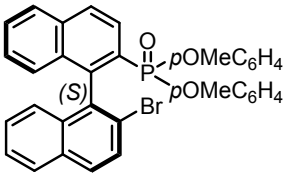
The (*rac*)-2-bromo-2'-diphenylphosphinyl-1,1'-binapthyl (titled as "**racemate**") was first analyzed to gain the right condition for the separation of diastereomers caused by the axial chirality. The analysis condition was listed in Table S1. The other 4 compounds (**S1** - **S4**, **Chart S1**) that were prepared from chiral 2,2'-dibromo-1,1'-binathyl were next analyzed under the same conditions to detect the otherwise diastereomer that was proposed to be derived from the racemization of the axial chirality during the lithium-bromide exchange process and in following C-P bond formation steps. The results were shown in Figure S3, from which it was found that only one single isomer was detected in each case. This means that all the reactions proceed with full retention of the binapthyl stereochemistry.



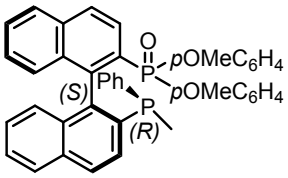
racemate
rac-1a

S3
(R_A)-1a

S4
(R_A, R_P)-2a



S1
(S_A)-1b



S2
(S_A, R_P)-2b

Chart S1 The 2'-phosphinyl-1,1'-binapthyls for HPLC analysis.

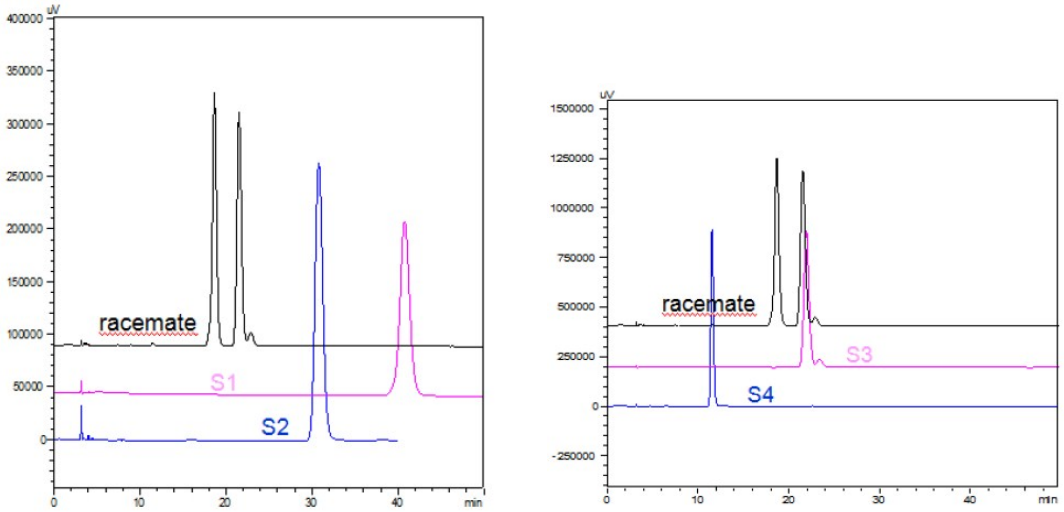


Fig. S3 HPLC analysis results.

Table S1 The conditions for HPLC analysis.

Column	:	CHIRALCEL® OZ-H
Column size	:	0.46 cm I.D. ×25 cm L ×5 μm
Injection	:	10 μl
Mobile phase	:	n-Hexane/ Ethanol = 90/10 (v/v)
Flow rate	:	1.0 ml/min
Wave length	:	UV 220 nm
Temperature	:	35℃
Sample solution	:	0.2mg/ml in MeOH20% EtOH20% Hexane60%(超声)
HPLC equipment	:	Shimadzu LC 20A QA&QC-HPLC-01

4. NMR spectra of compounds

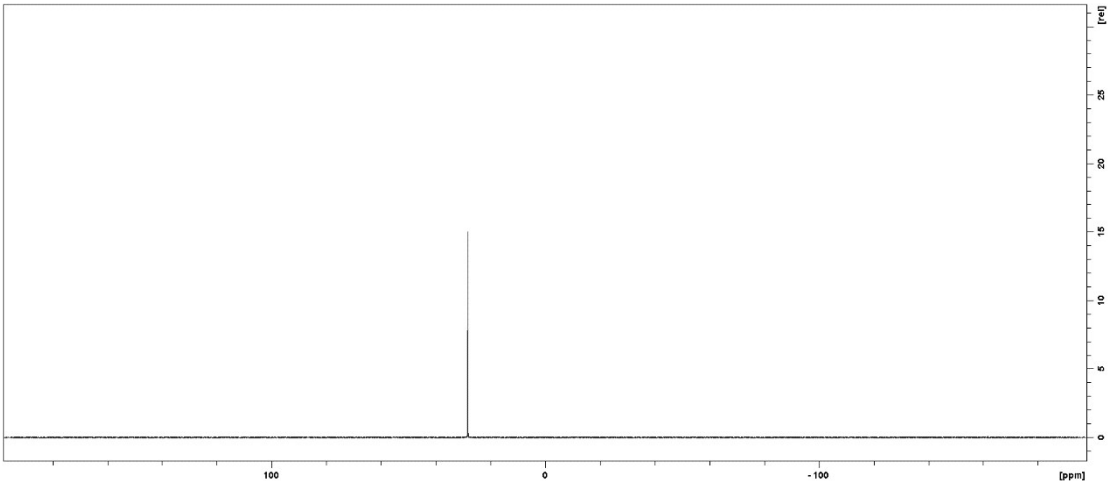


Fig. S4 $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) spectrum of **1a.**

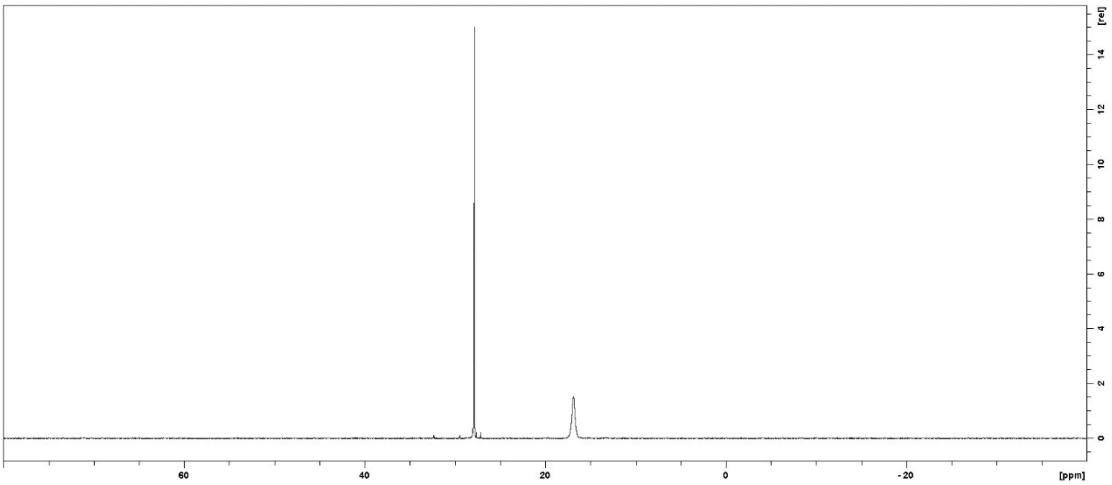


Fig. S5 $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) spectrum of borane adduct of **2a.**

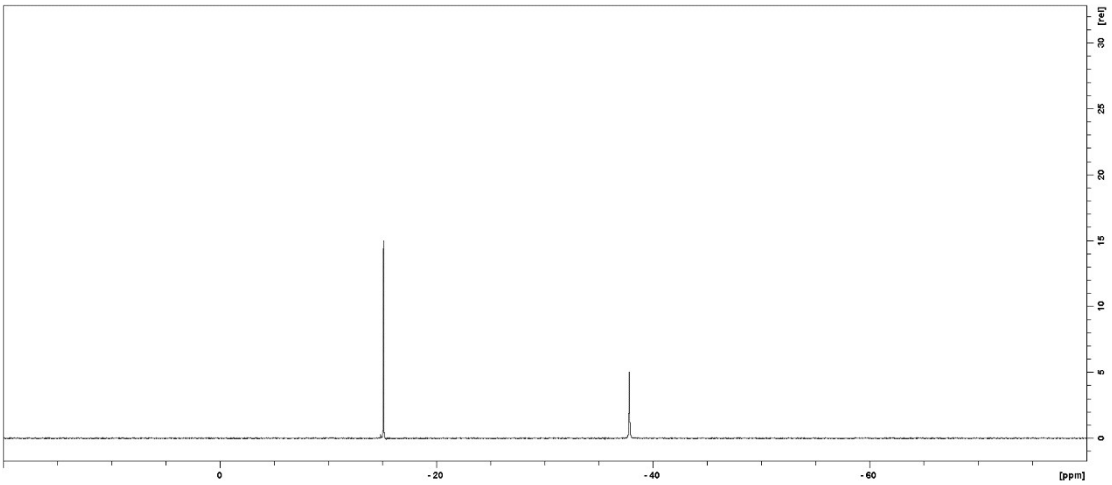


Fig. S6 $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) spectrum of (S_A, R_P)-**2-methylphenylphosphino-2'-diphenylphosphino-1,1'-binapthyl.**

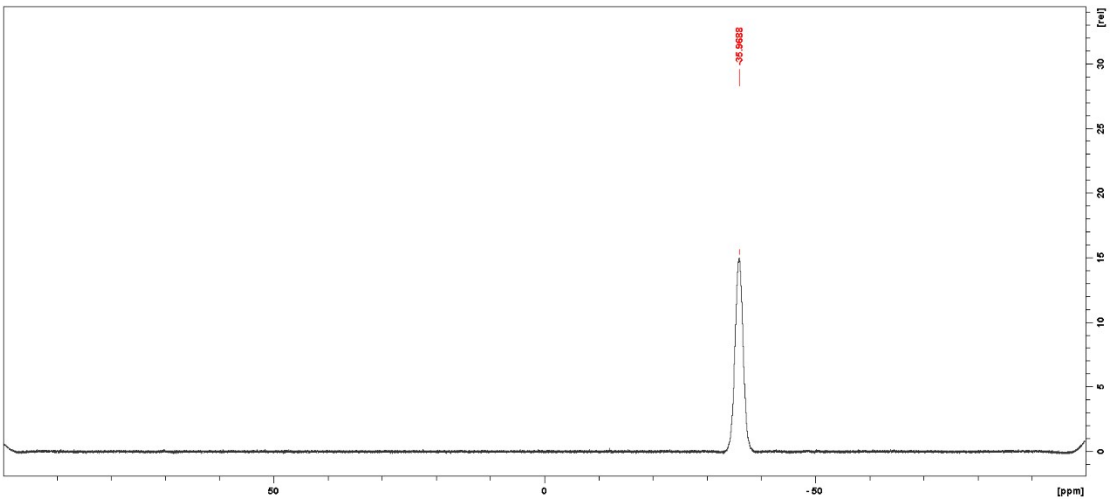


Fig. S7 $^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$) spectrum of **3a.**

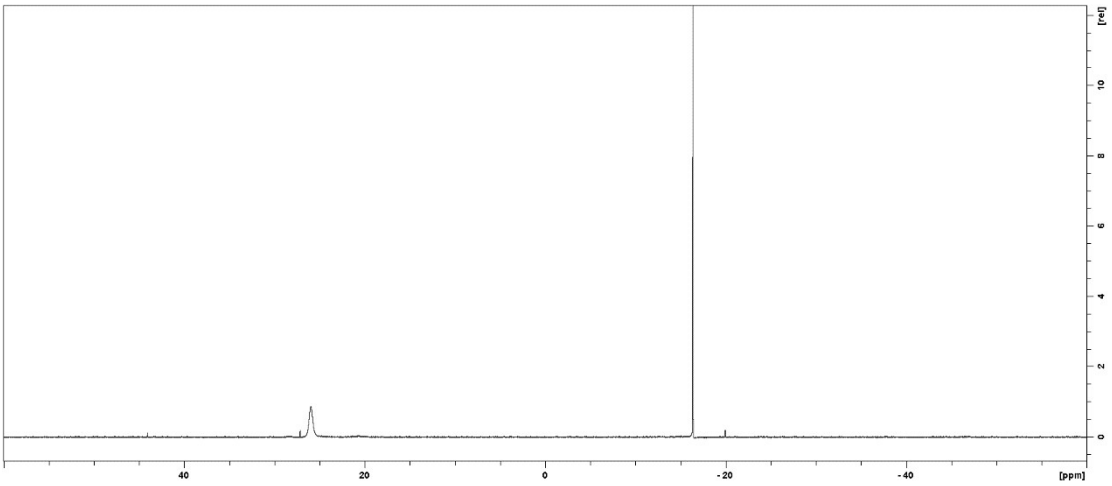


Fig. S8 $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) spectrum of borane adduct of **4a.**

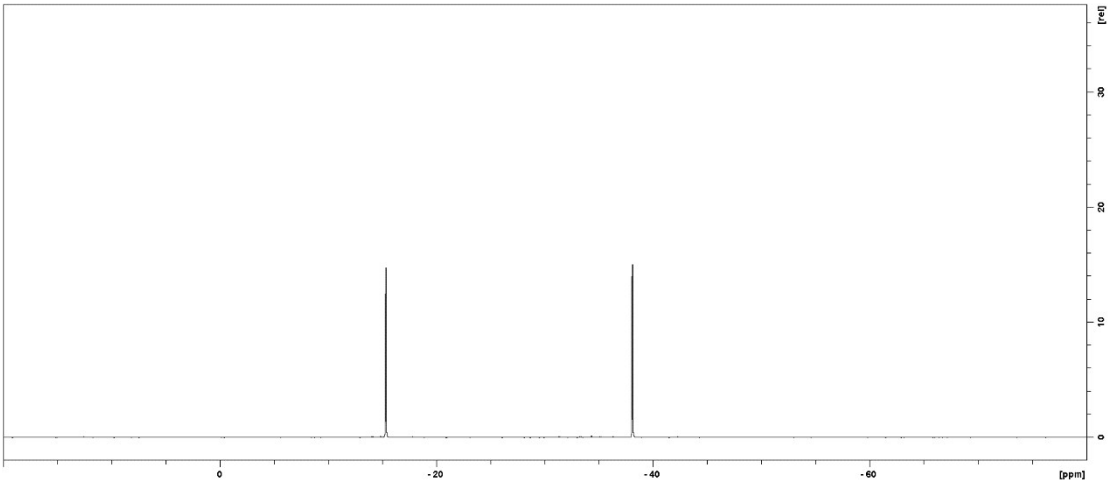


Fig. S9 $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) spectrum of **5a.**

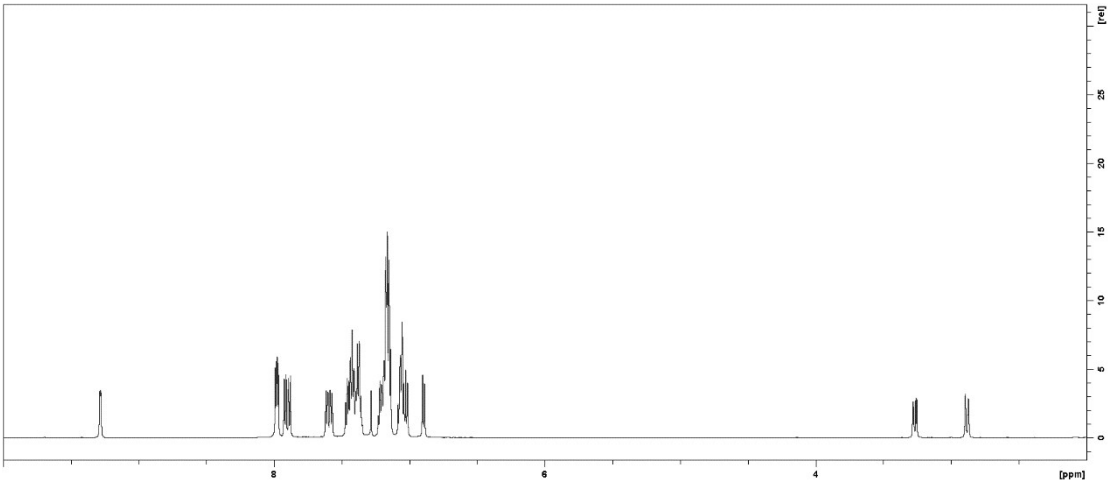


Fig. S10 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **5a.**

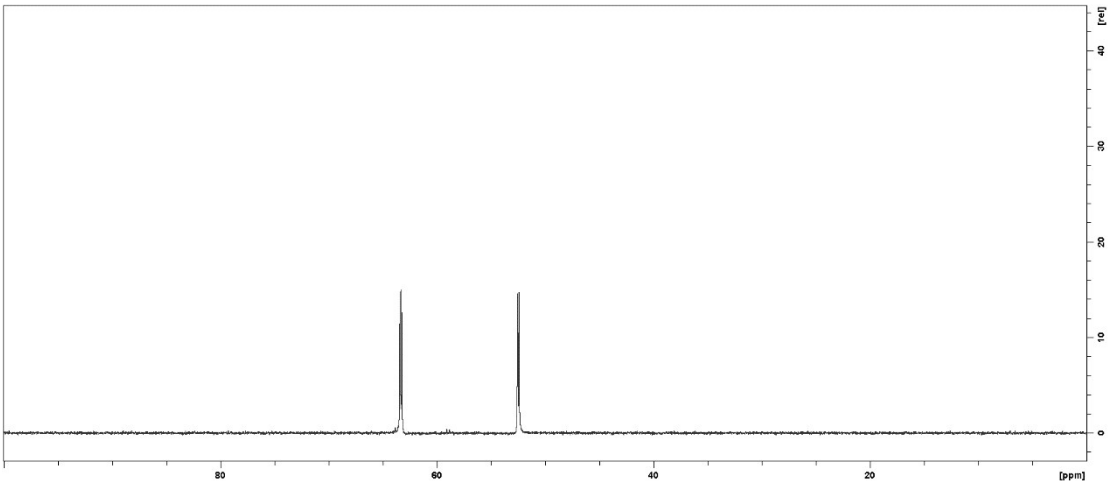


Fig. S11 $^{31}P\{^{1}H\}$ NMR (242 MHz, CH_3CN, C_6D_6 insert for lock and shimming) spectrum of **6a.**

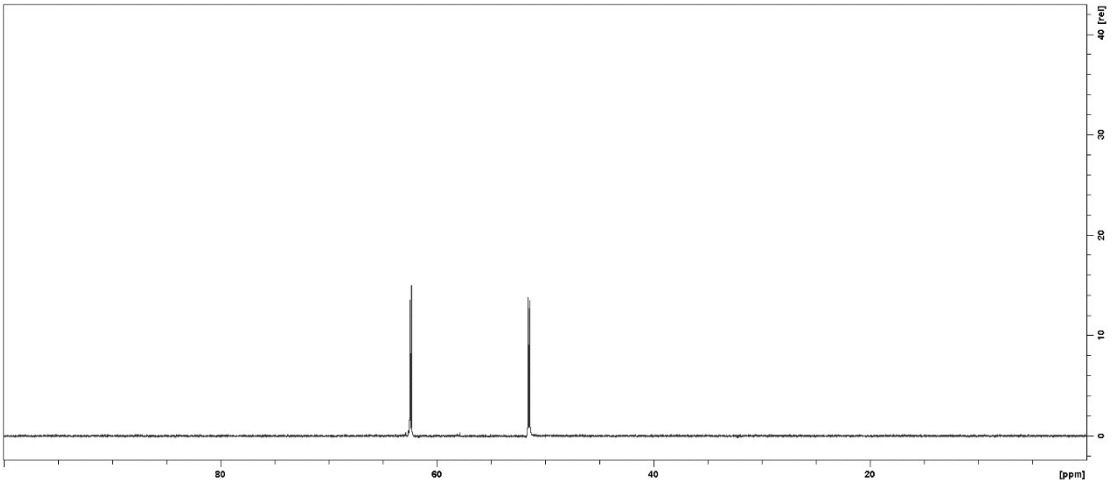


Fig. S12 $^{31}P\{^{1}H\}$ NMR (242 MHz, CD_3CN) spectrum of bis(d_3-acetonotrile) analogue of **6a.**

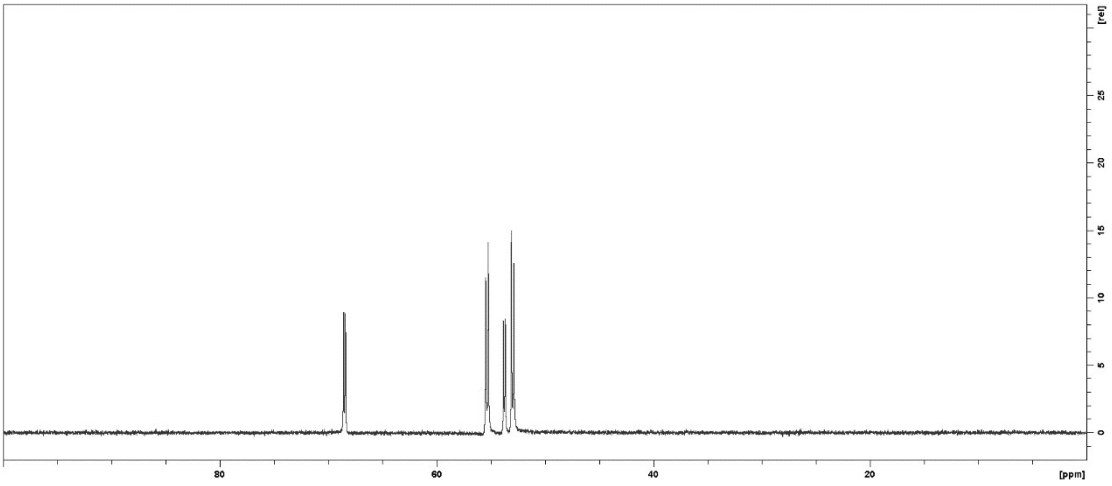


Fig. S13 $^{31}P\{^{1}H\}$ NMR (242 MHz, CH_3CN, C_6D_6 insert for lock and shimming) spectrum of **6a'.**

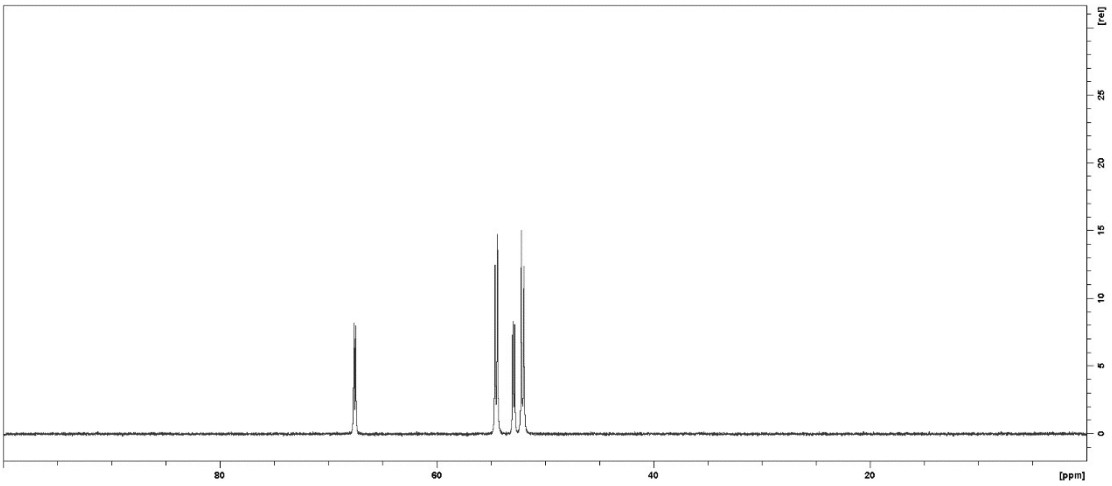


Fig. S14 $^{31}P\{^{1}H\}$ NMR (242 MHz, CD_3CN) spectrum of bis(d_3-acetonotrile) analogue of **6a'.**

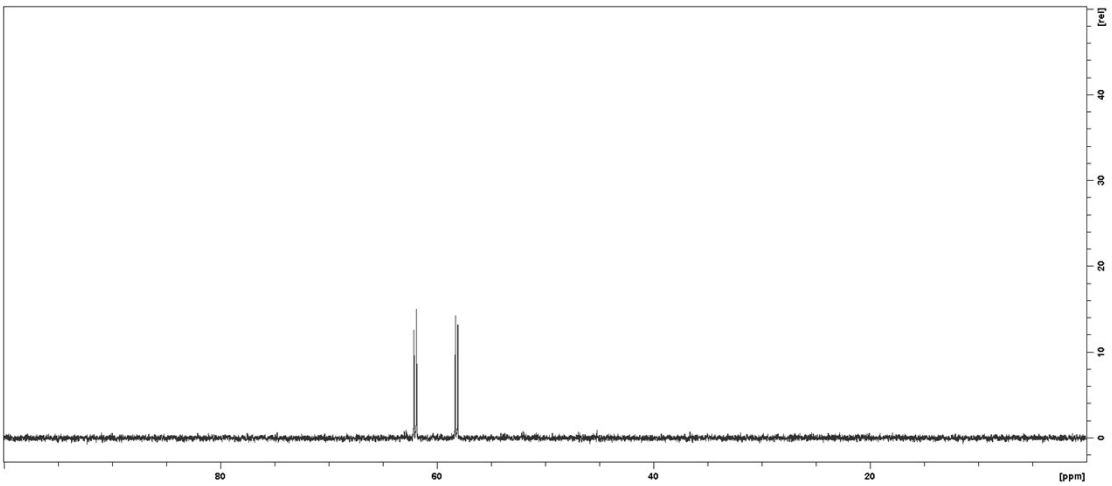


Fig. S15 $^{31}P\{^{1}H\}$ NMR (242 MHz, acetone) spectrum of **7a.**

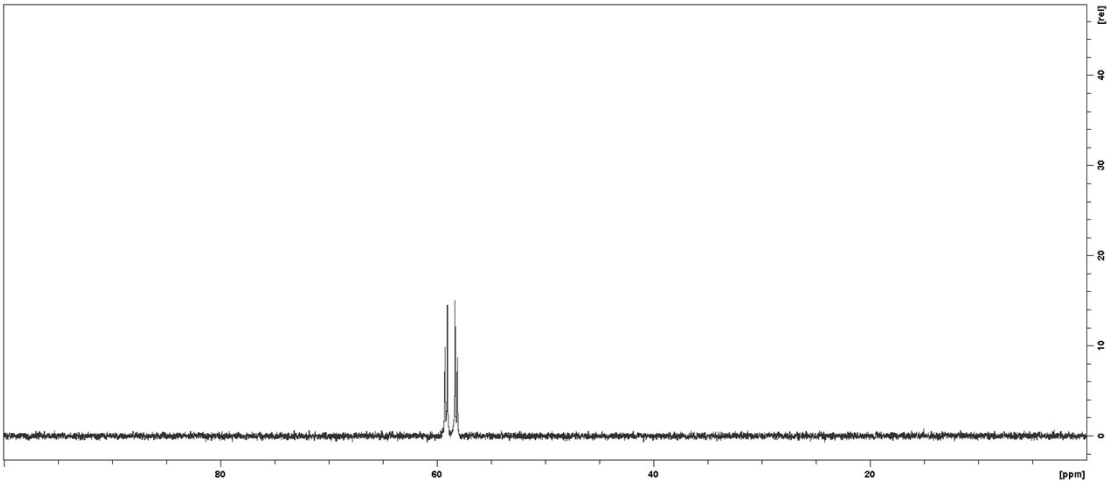


Fig. S16 $^{31}P\{^{1}H\}$ NMR (242 MHz, acetone) spectrum of **7a'.**

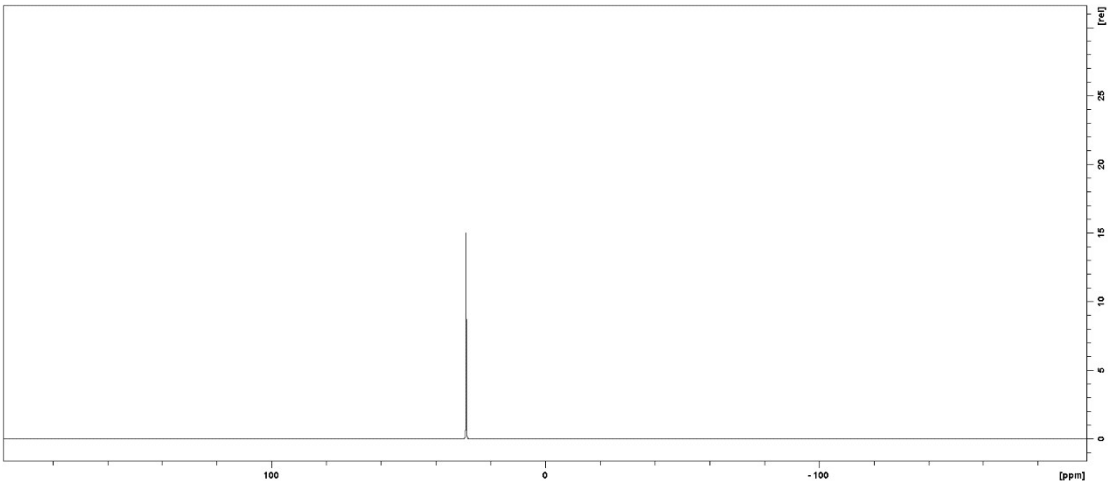


Fig. S17 $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) spectrum of **1b.**

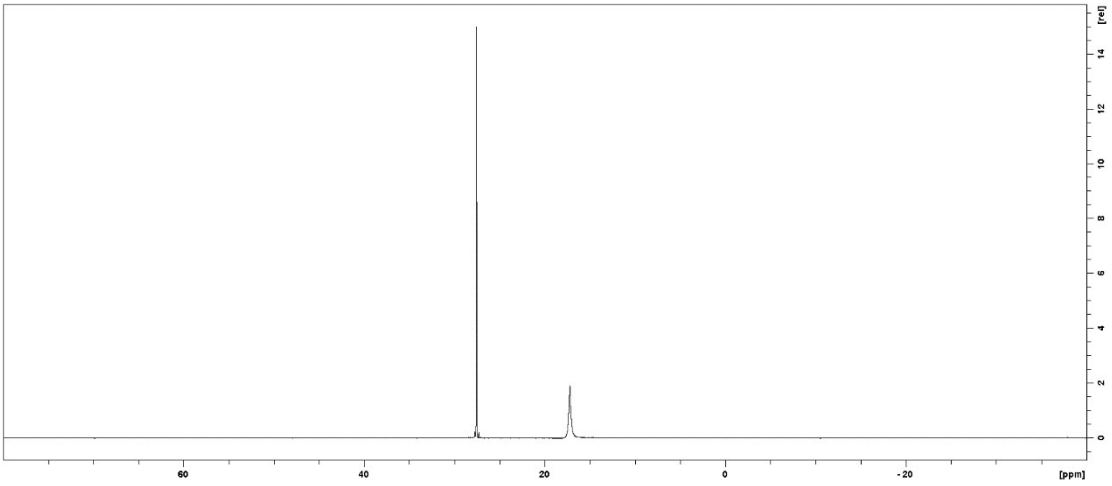


Fig. S18 $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) spectrum of the borane adduct of **2b.**

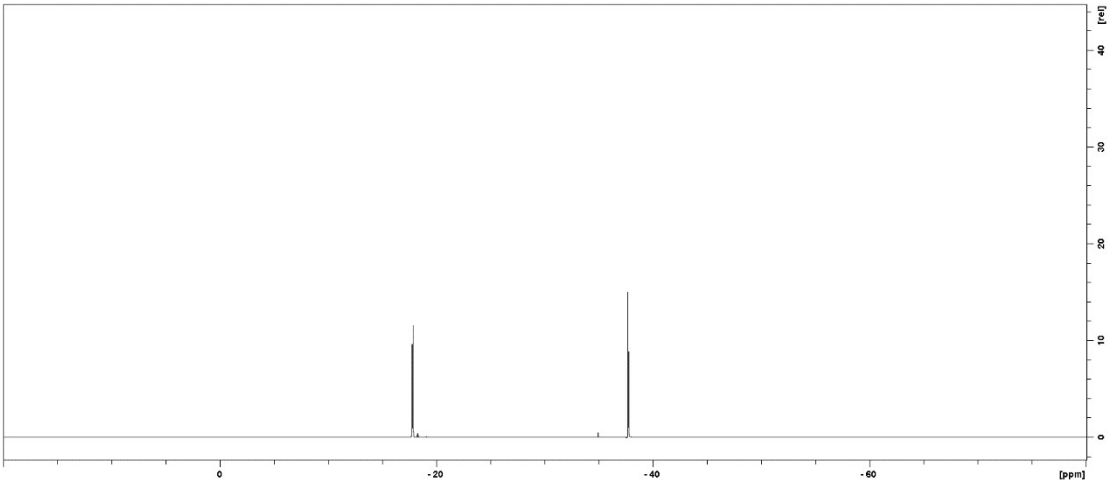


Fig. S19 $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) spectrum of (S_A, R_P)-**2-methylphenylphosphino-2'-di(*p*-methoxyphenyl)phosphino-1,1'-binapthyl.**

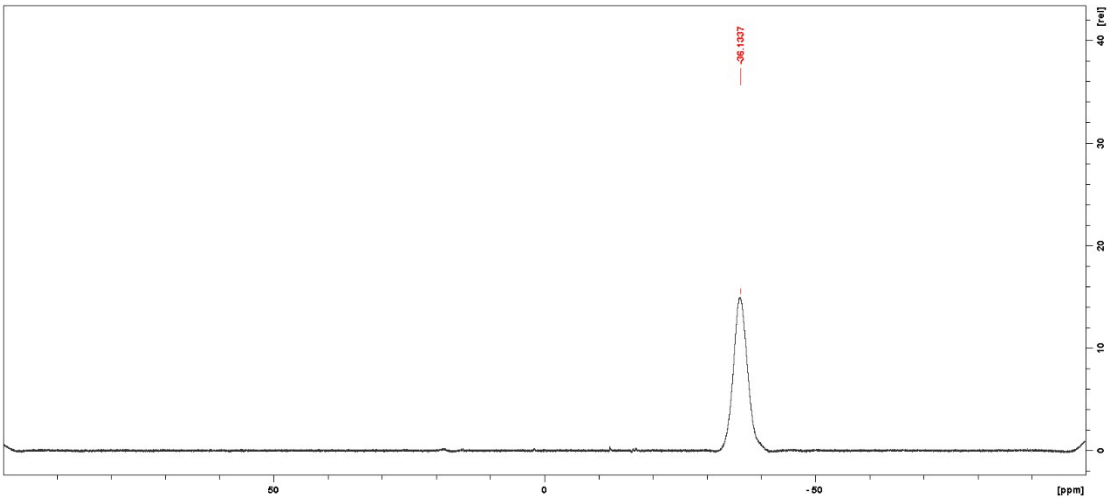


Fig. S20 $^{11}B\{^{1}H\}$ NMR (193 MHz, $CDCl_3$) spectrum of **3b.**

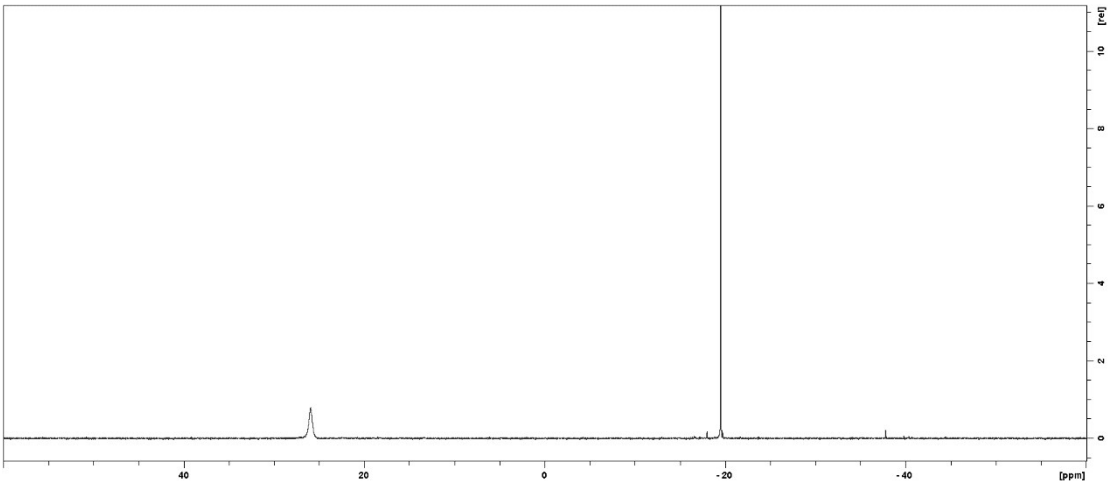


Fig. S21 $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) spectrum of borane adduct of **4b.**

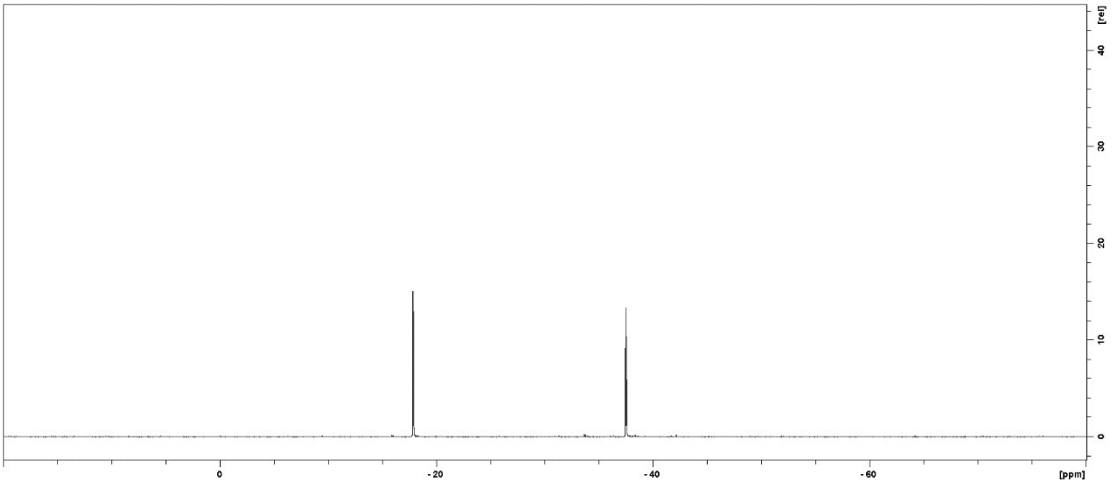


Fig. S22 $^{31}P\{^{1}H\}$ NMR (242 MHz, $CDCl_3$) spectrum of **5b.**

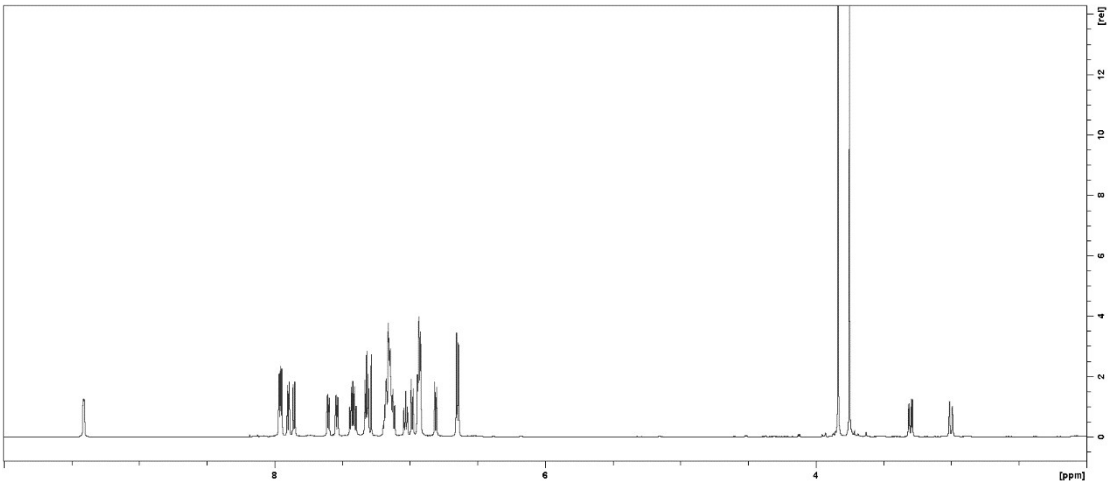


Fig. S23 ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **5b.**

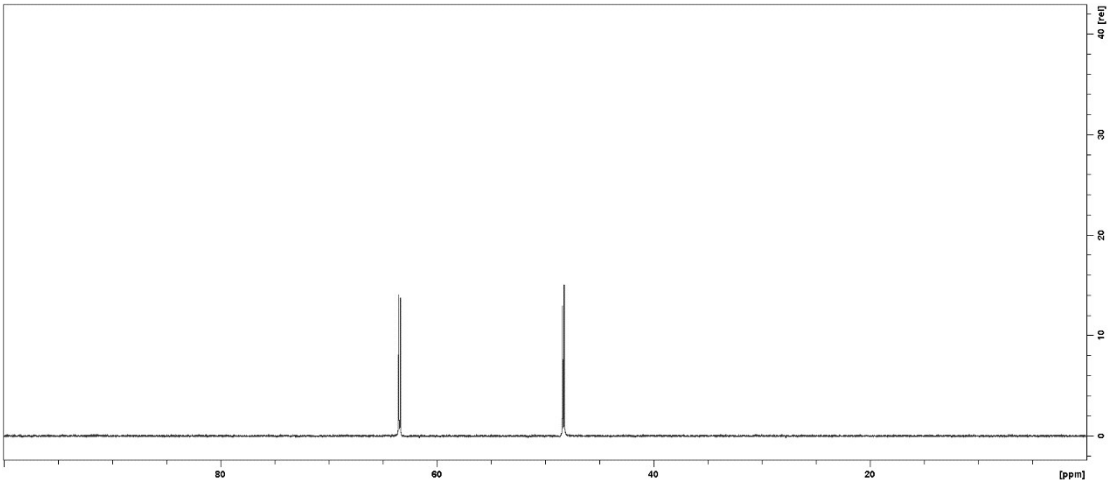


Fig. S24 $^{31}P\{^{1}H\}$ NMR (242 MHz, CH_3CN, C_6D_6 insert for lock and shimming) spectrum of **6b.**

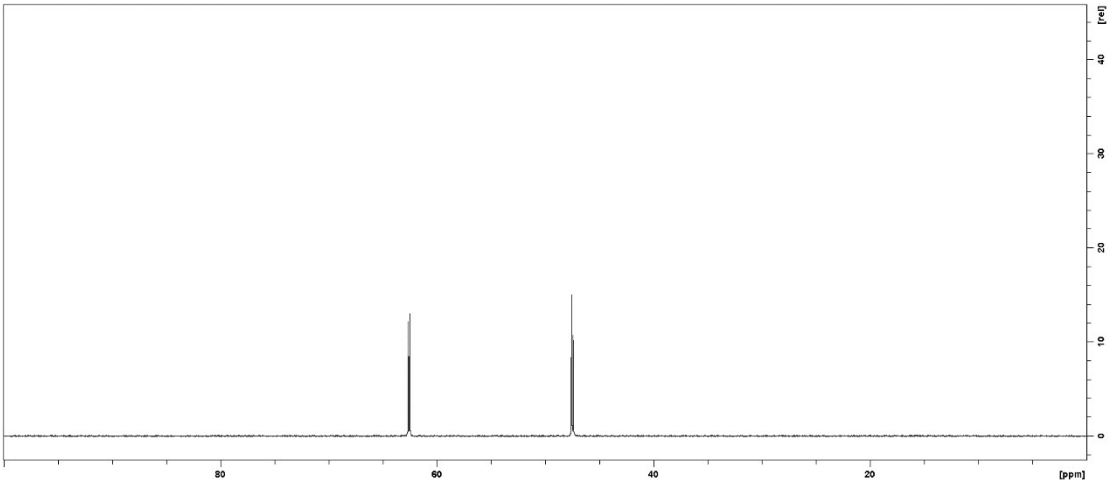


Fig. S25 $^{31}P\{^{1}H\}$ NMR (242 MHz, CD_3CN) spectrum of bis(d_3-acetonotrile) analogue of **6b.**

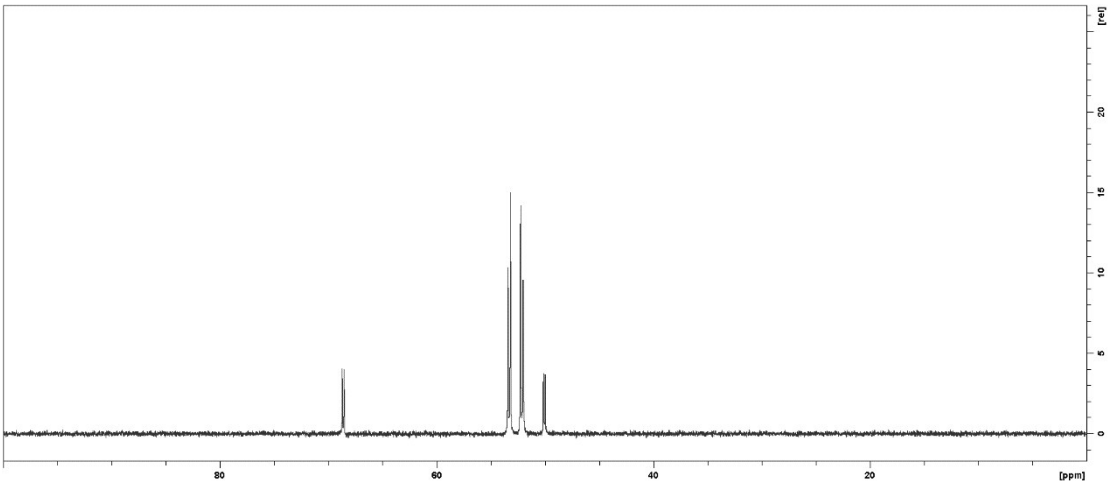


Fig. S26 $^{31}P\{^{1}H\}$ NMR (242 MHz, CH_3CN, C_6D_6 insert for lock and shimming) spectrum of **6b'.**

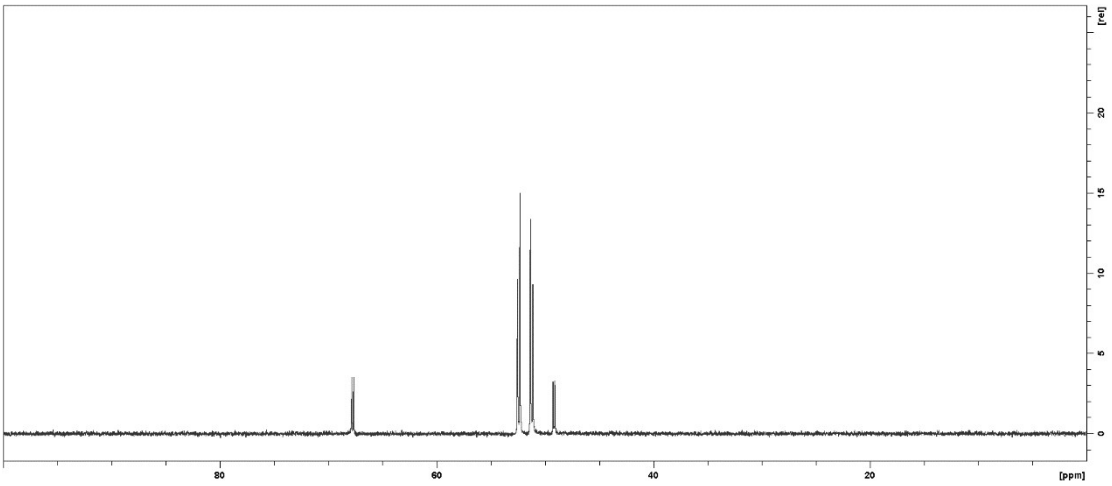


Fig. S27 $^{31}P\{^{1}H\}$ NMR (242 MHz, CD_3CN) spectrum of bis(d_3-acetonotrile) analogue of **6b'.**

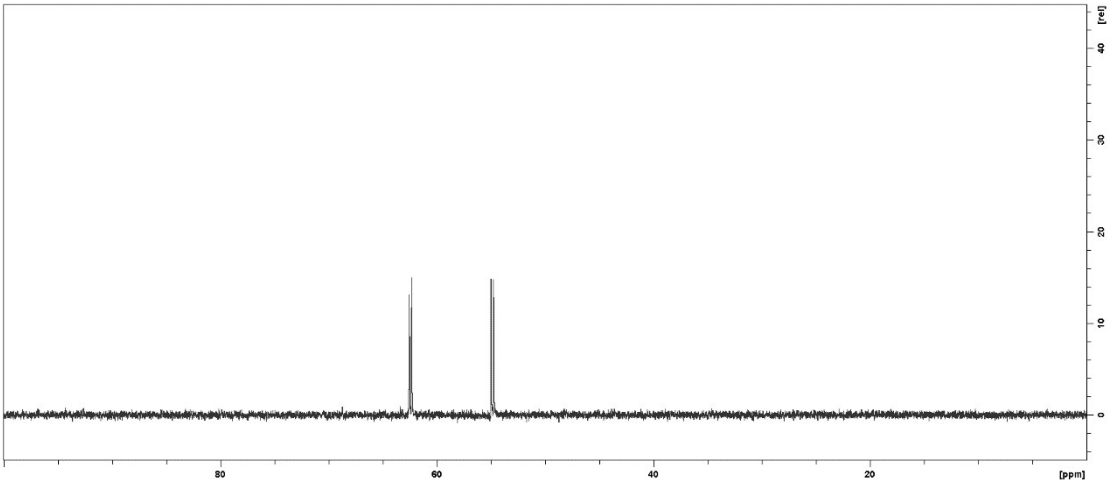


Fig. S28 $^{31}P\{^{1}H\}$ NMR (242 MHz, acetone) spectrum of **7b.**

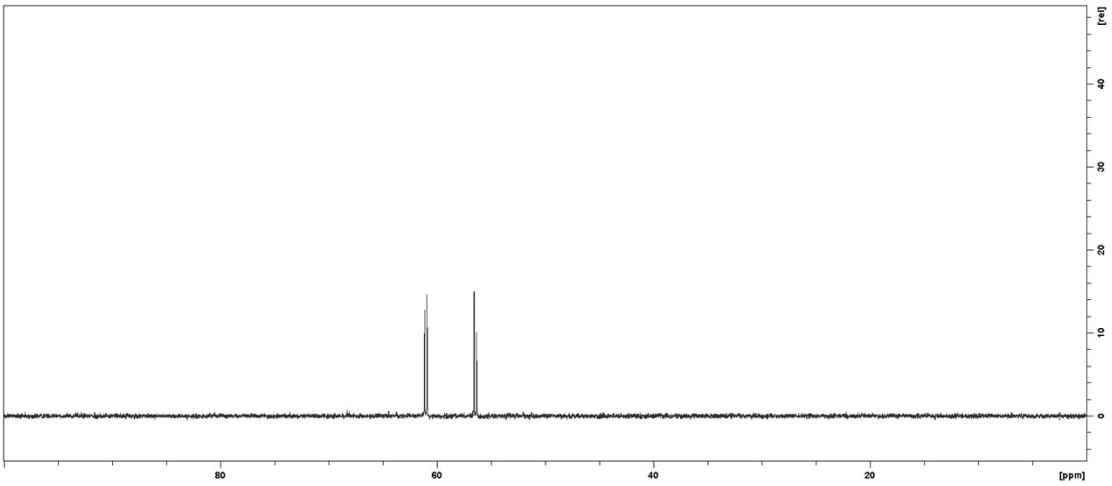


Fig. S29 $^{31}P\{^{1}H\}$ NMR (242 MHz, acetone) spectrum of **7b'.**

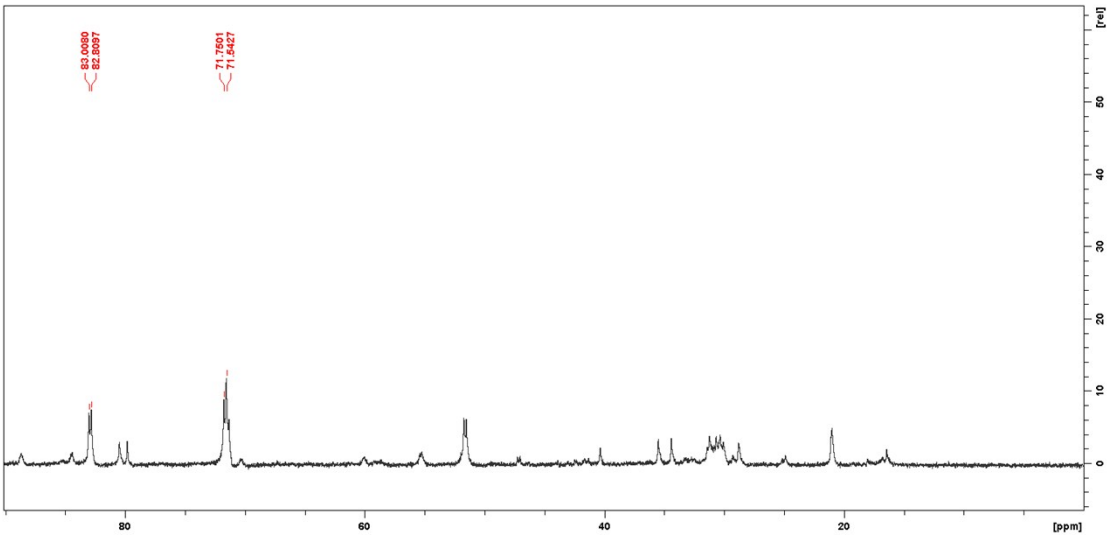


Fig. S30 $^{31}P\{^{1}H\}$ NMR (242 MHz, isopropanol) spectrum of the one-hour catalytic reaction on **7a'.**

5. General procedure to the catalytic asymmetric transfer hydrogenation of ketones

Contrary to the precatalyst preparation of **A** which is more stable, the precatalysts of complex **7a**–**7b'** were prepared directly from the reaction solution of the corresponding bis(acetonitrile) complexes in acetone after the ligand substitution reaction has finished. Therefore, the ligand substitution reaction of **6a**–**7b'** (1.50×10^{-4} mol) was conducted in acetone (10 mL) for 30 min, during which the reaction has reached completion based on $^{31}P\{^{1}H\}$ NMR analysis. The reaction flask was then brought inside the glovebox and the solution was transferred to a vial with known weight. More cool acetone was added to the solution to have a total solution weight of 14.1 g. After being kept still for 5 minutes, the solution was sucked into a syringe and was then equally divided into 46 portions to individual vials so that each vial contains 3.21×10^{-6} mol of the precatalyst. The solvent was removed for each vial to get yellow solid which was further dried under vacuum for 2 h. The base stock solution was prepared as before, by dissolving 49.0mg (4.37×10^{-4} mol) potassium *tert*-butoxide in 1.02g isopropanol.

For each catalytic reaction, the substrate with pre-calculated amount was prepared in a vial, to which isopropanol (7.13 g, 9.08 mL) and base stock solution (0.06 g, 2.57×10^{-5} mol, 8 equivalents relative to the precatalyst) were added. The solution was stirred for 1 min and then poured into the vial containing the precatalyst with rigorous stirring. The conversion of the substrate at intervals were monitored by analyzing the samples using a Shimadzu GC-2014 gas chromatograph with a chiral column (InertCap CHIRAMIX, 30 m × 0.25 mm, df = 2.5 µm). The samples were prepared by injecting the reaction solution into septa-sealed GC vials which contains aerated isopropanol for efficient quenching of the catalysis. Hydrogen gas was used as a mobile phase at a column pressure of 5 psi. The injector and the FID temperature were 275 °C. For the catalytic reactions that use higher amount of catalyst, the precatalyst solution in acetone was divided into the corresponding reduced amounts of portions. The calculation of conversion was conducted based on the ratio of area of the ketone and alcohol peaks. The accuracy of this method was calibrated by a standard curve of 1-Phenylethanol /(1-Phenylethanol + acetophenone) (**Fig. S31**). It was found that the calculated composition of a ketone/alcohol mixture based on the ratio of area of the peaks equals almost to real value.

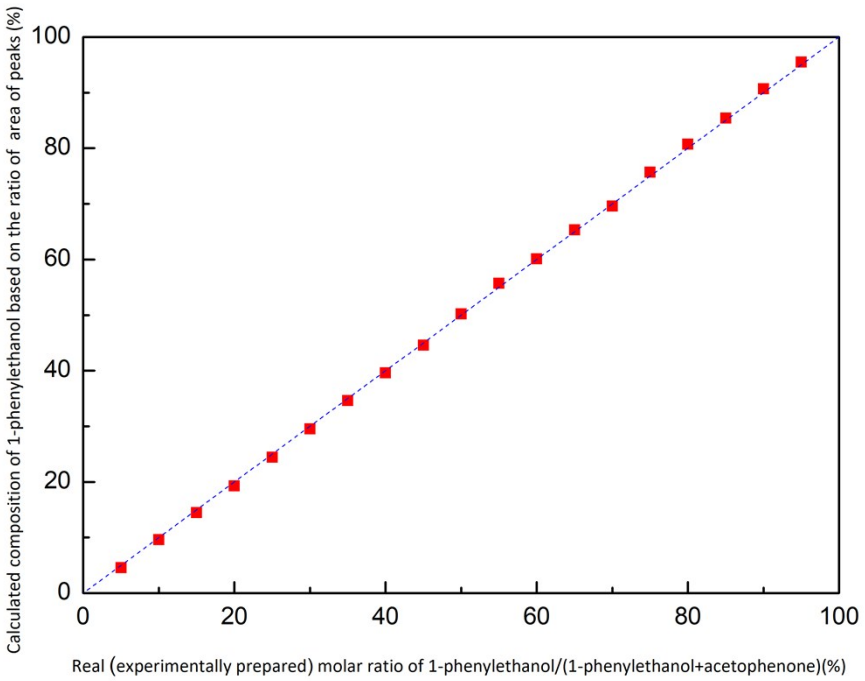
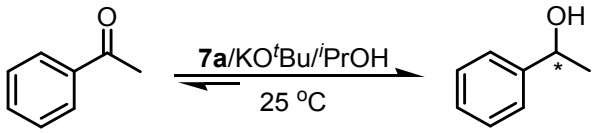
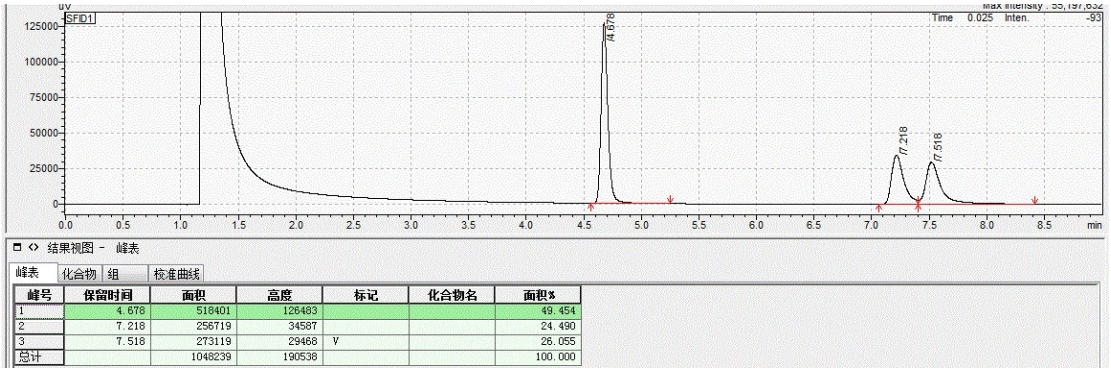


Fig. S31 Standard curve of 1-Phenylethanol /(1-Phenylethanol + acetophenone) in GC test.



General conditions: [**7a**] = 6.02 × 10^{-5} M, [KO^{t}Bu] = 4.82 × 10^{-4} M, [isopropanol] = 11.1 M, 25 °C, substrate/precatalyst = 21300:1. GC analysis conditions: Oven temperature (130 °C), SPL1 temperature (275 °C). Retention time: product isomer (*R*) = 7.24 min, product isomer (*S*) = 7.52 min, starting material = 4.68 min.

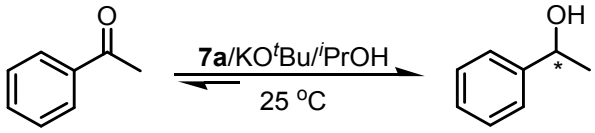


The table in the graph is as follow:

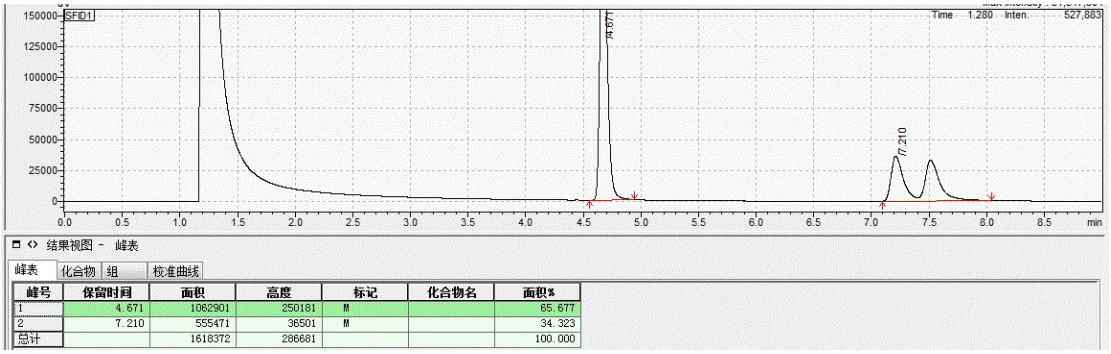
Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage

1	4.678	518401	126483			49.454
2	7.218	256719	34587			24.490
3	7.518	273119	29468			26.055
Total		1048239	190538			100.000

Fig. S32 3 min, 50% conversion.



General conditions: [**7a**] = 6.02 × 10^{-5} M, [KO^{t}Bu] = 4.82 × 10^{-4} M, [isopropanol] = 11.1 M, 25 °C, substrate/precatalyst = 42600:1. GC analysis conditions: Oven temperature (130 °C). Retention time: product isomer (*R*) = 7.23 min, product isomer (*S*) = 7.54 min, starting material = 4.68 min.

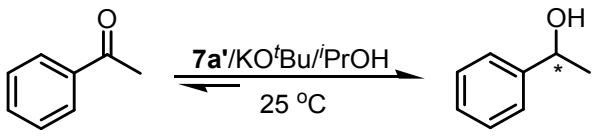


峰号	保留时间	面积	高度	标记	化合物名	面积%
1	4.671	1062901	250181	M		65.677
2	7.210	555471	36501	M		34.323
总计		1618372	286681			100.000

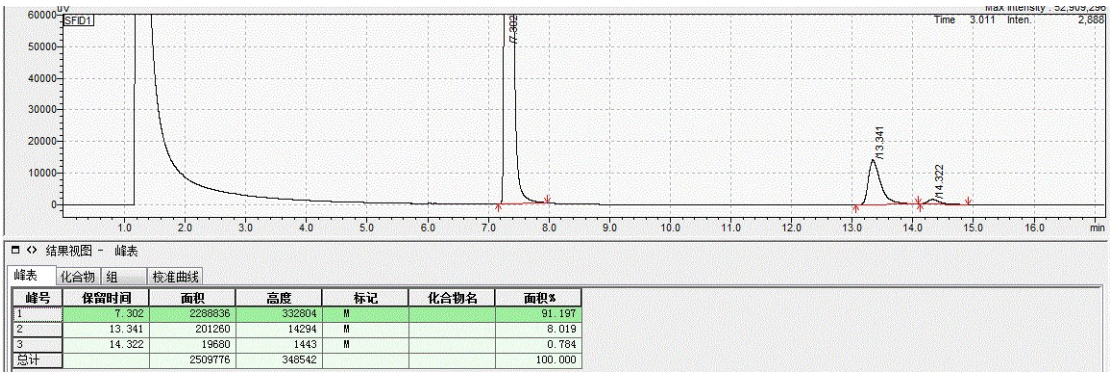
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	4.671	1062910	250181			65.677
2	7.210	555471	36501			34.323
Total		1618372	286681			100.000

Fig. S33 3 min, 34% conversion.



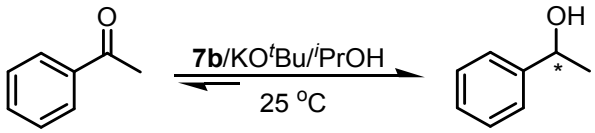
General conditions: [**7a'**] = 6.02 × 10^{-5} M, [KO^{t}Bu] = 4.82 × 10^{-4} M, [isopropanol] = 11.1 M, 25 °C, substrate/precatalyst = 21300:1. GC analysis conditions: Oven temperature (110 °C). Retention time: product isomer (*R*) = 13.36 min, product isomer (*S*) = 14.33 min, starting material = 7.30 min. For better separation of the enantiomers, a lower oven temperature of 110 °C was employed.



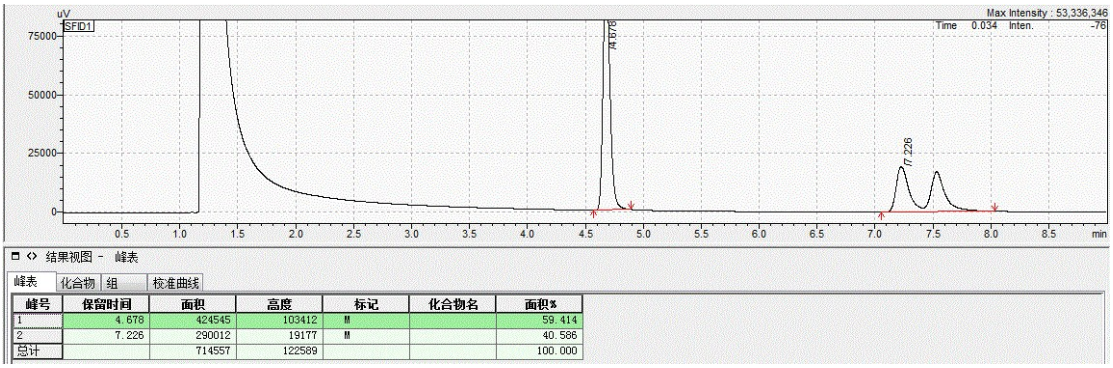
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	7.302	2288836	332804			91.197
2	13.341	201260	14294			8.019
3	14.322	19680	1443			0.784
Total		2509776	348542			100.000

Fig. S34 3h, 9% conversion, 82% ee.



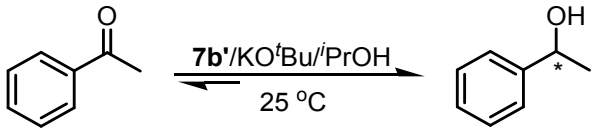
General conditions: [**7b**] = 6.02 × 10^{-5} M, [KO^{t}Bu] = 4.82 × 10^{-4} M, [isopropanol] = 11.1 M, 25 °C, substrate/precatalyst = 21300:1. GC analysis conditions: Oven temperature (130 °C). Retention time: product isomer (*R*) = 7.22 min, product isomer (*S*) = 7.52 min, starting material = 4.68 min.



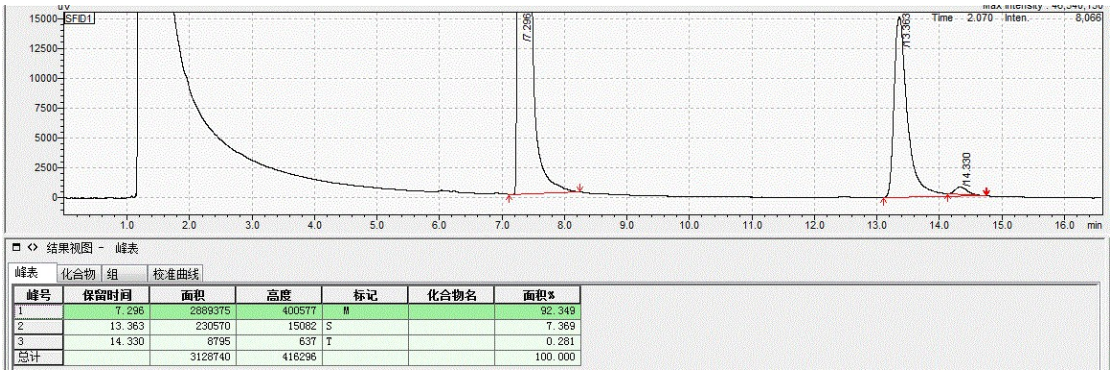
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	4.678	424545	103412			59.414
2	7.226	290012	19177			40.586
Total		714557	122589			100.000

Fig. S35 3 min, 41% conversion.



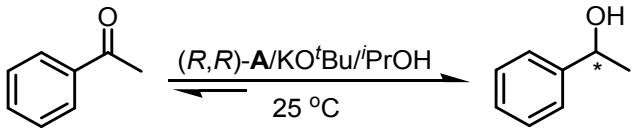
General conditions: [**7b'**] = 6.02 × 10^{-5} M, [KO^{t}Bu] = 4.82 × 10^{-4} M, [isopropanol] = 11.1 M, 25 °C, substrate/precatalyst = 21300:1. GC analysis conditions: Oven temperature (110 °C). Retention time: product isomer (*R*) = 13.36 min, product isomer (*S*) = 14.33 min, starting material = 7.30 min. For better separation of the enantiomers, a lower oven temperature of 110 °C was employed.



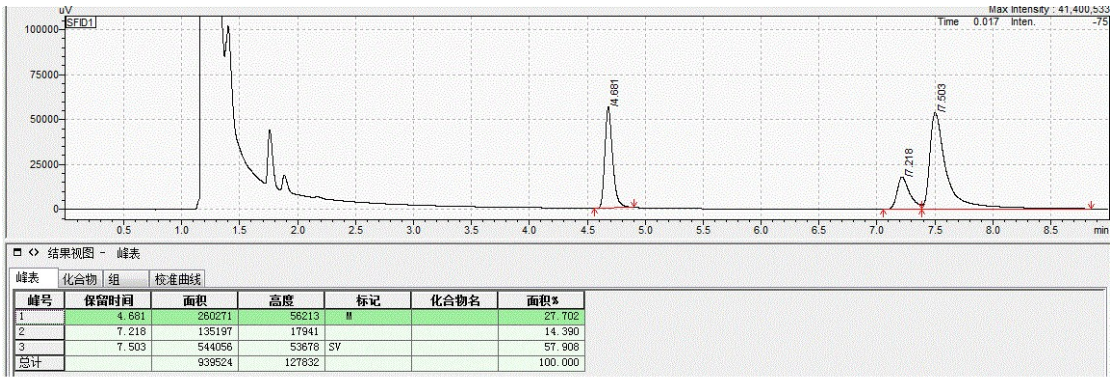
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	7.296	2889375	400577			92.349
2	13.363	230570	15082			7.369
3	14.330	8795	637			0.281
Total		3128740	416296			100.000

Fig. S36 3h, 8% conversion, 93% ee.



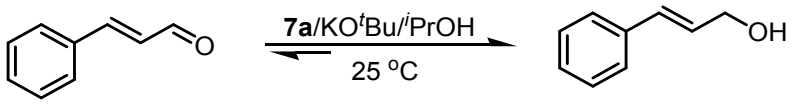
General conditions: [**A**] = 6.02 × 10^{-5} M, [KO^{t}Bu] = 4.82 × 10^{-4} M, [isopropanol] = 11.1 M, 25 °C, substrate/precatalyst = 21300:1. GC analysis conditions: Oven temperature (130 °C). Retention time: product isomer (*R*) = 7.24 min, product isomer (*S*) = 7.54 min, starting material = 4.68 min.



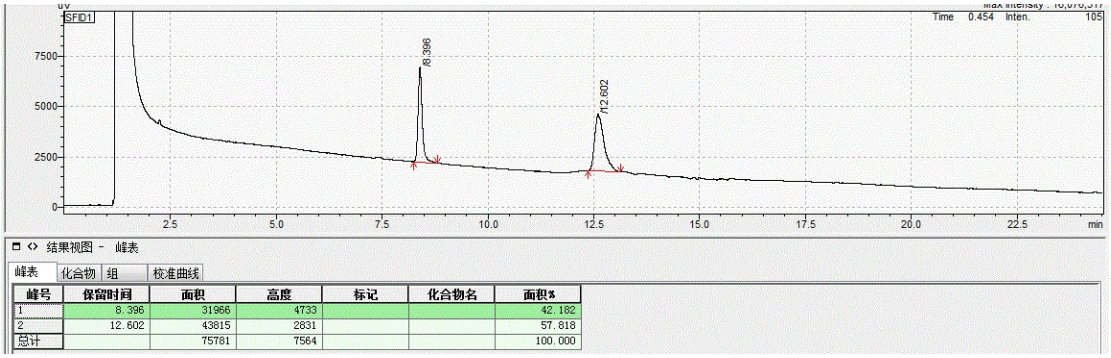
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	4.681	260271	56213			27.702
2	7.218	135197	17941			14.390
3	7.503	544056	53678			57.908
Total		939524	127832			100.000

Fig. S37 10min, 72% conversion, 60% ee.



General conditions: [7**a**] = 5.95 × 10^{-5} M, [KO^{t}Bu] = 4.76 ×10^{-4} M, [ketone] = 1.27 M, [^{i}PrOH] = 11.1 M, 25°C. GC analysis conditions: Oven temperature (150 °C), SPL1 temperature (275 °C). Retention time: product = 12.06 min, starting material = 8.40 min.



The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	8.396	31966	4733			42.182
2	12.62	43815	2831			57.818
Total		75781	7564			100.000

Fig. S38.1 3min, 58% conversion.

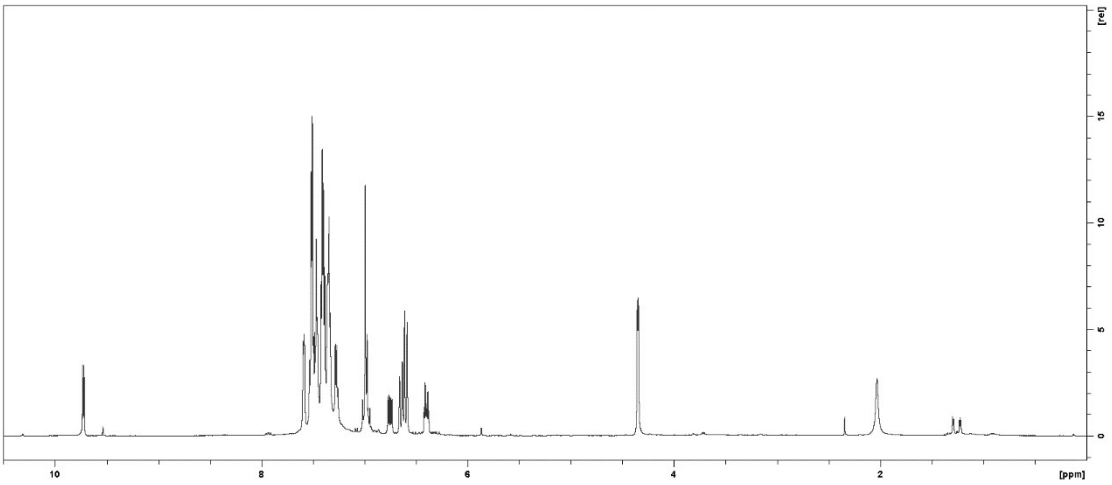
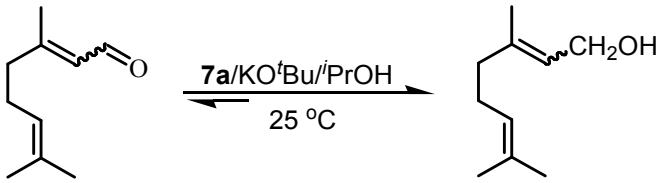
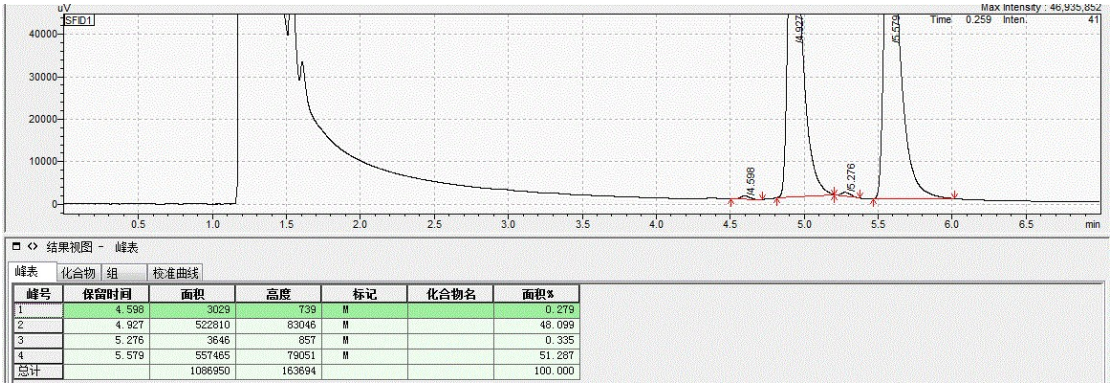


Fig. S38.2 The ^{1}H NMR ($CDCl_3$, 600MHz) spectrum of the reaction mixture of transfer hydrogenation of cinnamaldehyde (58% yield), after removing the solvent isopropanol.



General conditions: [7**a**] = 6.67 × 10^{-5} M, [KO^{t}Bu] = 5.34 ×10^{-4} M, [ketone] = 0.33 M, [^{i}PrOH] = 12.4 M, 25°C. GC analysis conditions: Oven temperature (150 °C), SPL1 temperature (275 °C). Retention time: product = 4.93 and 5.58 min (*E* and *Z*), starting material = 4.60 and 5.28 min (*E* and *Z*).



峰号	保留时间	面积	高度	标记	化合物名	面积%
1	4.598	3029	739	M		0.279
2	4.927	522810	83046	M		48.099
3	5.276	3646	857	M		0.335
4	5.579	557465	79051	M		51.287
总计		1086950	163694			100.000

The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	4.598	3029	739			0.279
2	4.927	522810	83046			48.099
3	5.276	3646	857			0.335
4	5.579	557465	79051			51.287
Total		1086950	163694			100.000

Fig. S39.1 3min, >99% conversion.

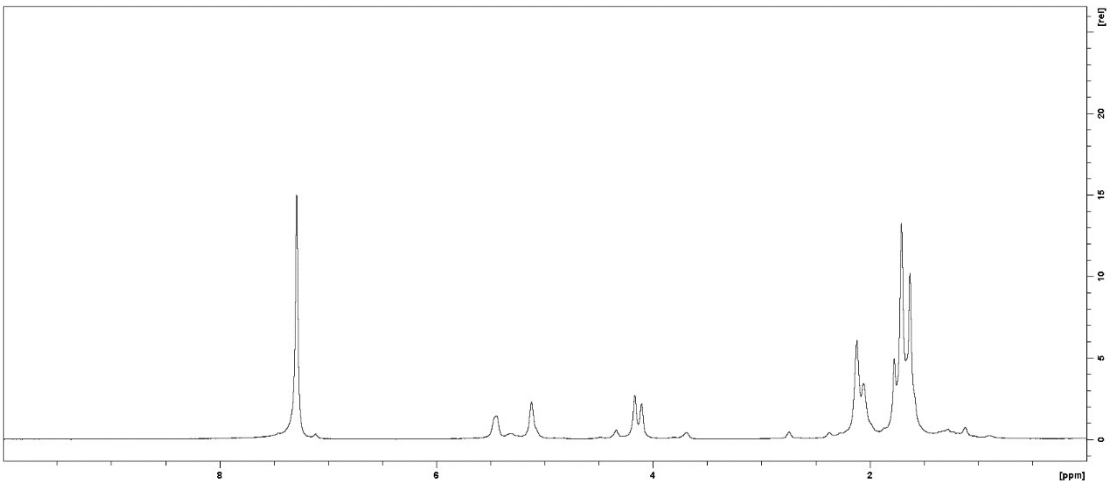
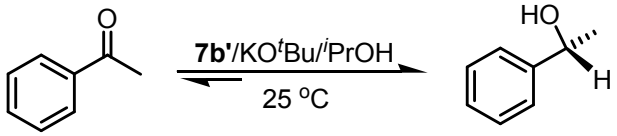
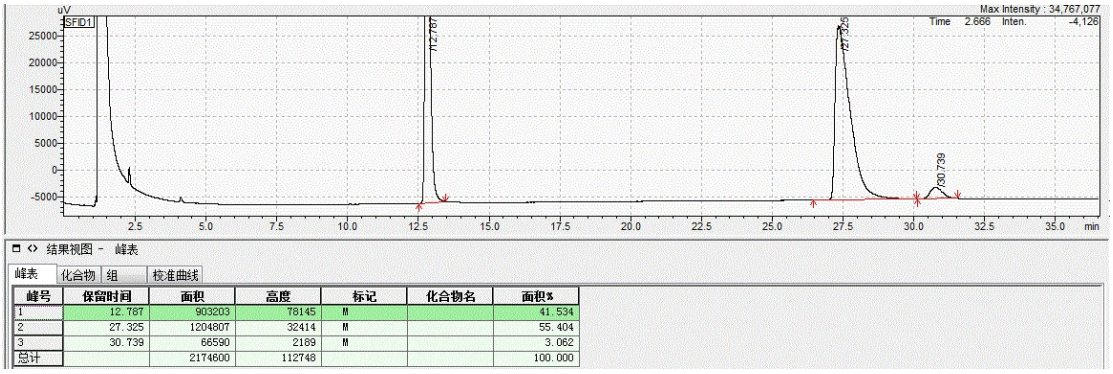


Fig. S39.2 ^{1}H NMR ($CDCl_3$, 600MHz) spectrum of the crude product of transfer hydrogenation of citral (*E* and *Z*), after removing the solvent isopropanol.



General conditions: [7**b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 1.28 M, [^{i}PrOH] = 11.1 M, 25°C. GC analysis conditions: Oven temperature (100 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 27.33 min, product minor isomer (*S*) = 30.74 min, starting material = 12.79 min.

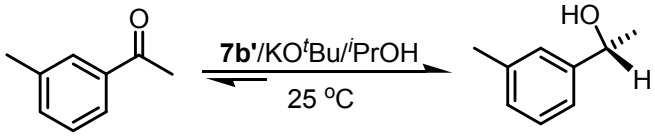


峰号	保留时间	面积	高度	标记	化合物名	面积%
1	12.787	903203	78145	M		41.534
2	27.325	1204807	32414	M		55.404
3	30.739	66590	2189	M		3.062
总计		2174600	112748			100.000

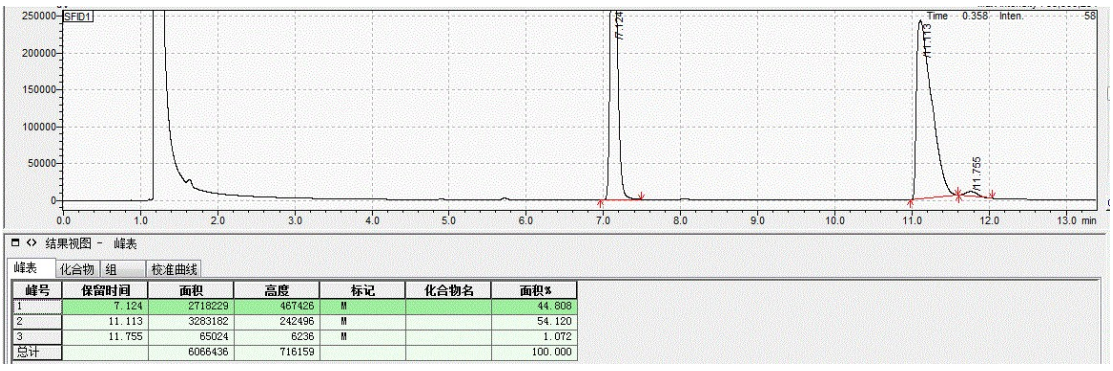
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	12.787	903203	78145			41.534
2	27.325	1204807	32414			55.404
3	30.739	66590	2189			3.062
Total		2174600	112748			100.000

Fig. S40 3h, 59% conversion, 90% ee.



General conditions: [7**b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 1.28 M, [^{i}PrOH] = 11.1 M, 25°C. GC analysis conditions: Oven temperature (130 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 11.11 min, product minor isomer (*S*) = 11.76 min, starting material = 7.12 min.

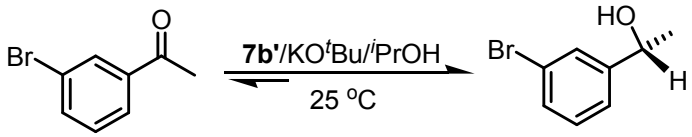


峰号	保留时间	面积	高度	标记	化合物名	面积%
1	7.124	2718229	467426	M		44.808
2	11.113	3283182	242496	M		54.120
3	11.755	65024	6236	M		1.072
总计		6066436	716159			100.000

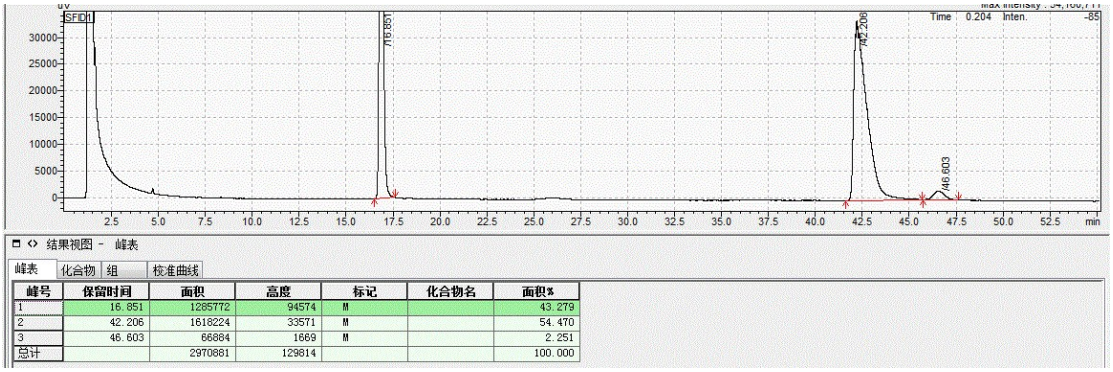
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	7.124	2718229	467426			44.808
2	11.113	3283182	242496			54.120
3	11.755	65024	6236			1.072
Total		6066436	716159			100.000

Fig. S41 3h, 55% conversion, 96% ee.



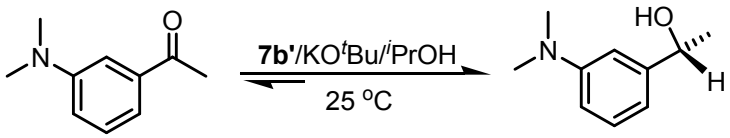
General conditions: [**7b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 1.28 M, [^{i}PrOH] = 11.1M, 25°C. GC analysis conditions: Oven temperature (130 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 42.21 min, product minor isomer (*S*) = 46.60 min, starting material = 16.85 min.



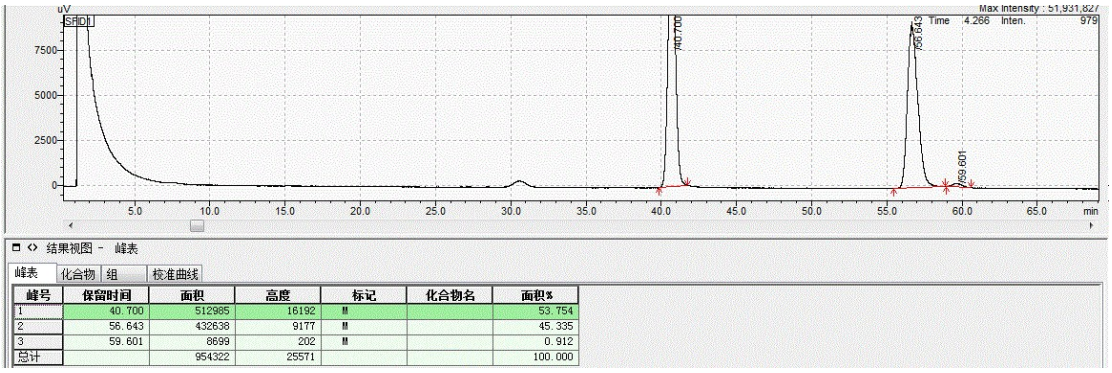
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	16.851	1285772	94574			43.279
2	42.206	1618224	33571			54.470
3	46.603	66884	1669			2.251
Total		2970881	129814			100.000

Fig. S42 3h, 57% conversion, 92% ee.



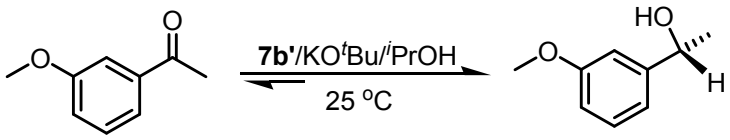
General conditions: [**7b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 1.28 M, [^{i}PrOH] = 11.1 M, 25°C. GC analysis conditions: Oven temperature (130 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 56.64 min, product minor isomer (*S*) = 59.60 min, starting material = 40.70 min.



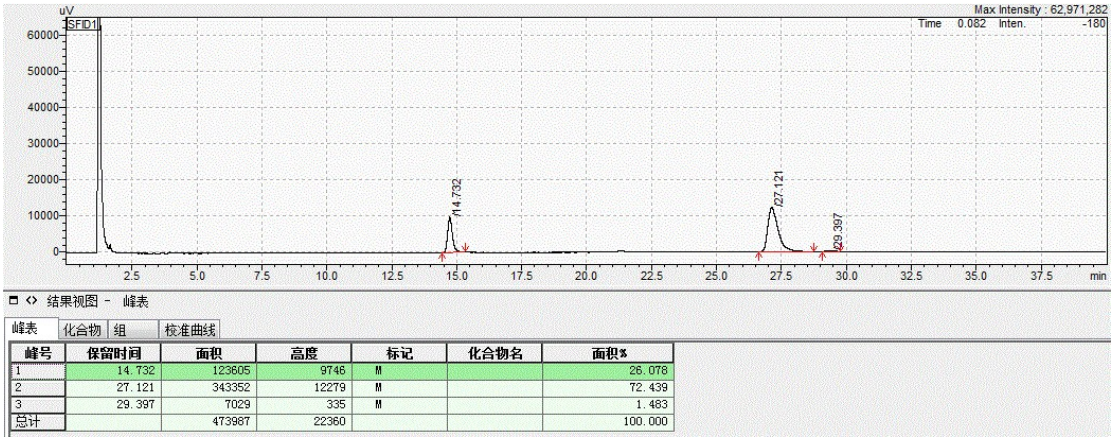
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	40.700	512985	16192			53.754
2	56.643	432638	9177			45.335
3	59.601	8699	202			0.912
Total		954322	25571			100.000

Fig. S43 3h, 46% conversion, 96% ee.



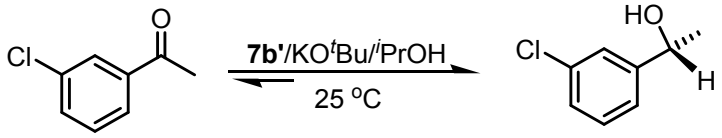
General conditions: [**7b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 0.03 M, [^{i}PrOH] = 11.1M, 25°C. GC analysis conditions: Oven temperature (130 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 27.12 min, product minor isomer (*S*) = 29.40 min, starting material = 14.73 min.



The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	14.732	123605	9746			26.078
2	27.121	343352	12279			72.439
3	29.397	7029	335			1.483
Total		473987	22360			100.000

Fig. S44 3h, 74% conversion, 98% ee.



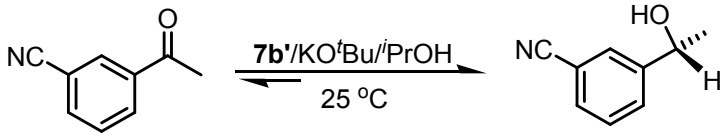
General conditions: [7**b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 1.28 M, [^{i}PrOH] = 11.1 M, 25°C. GC analysis conditions: Oven temperature (120 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 42.09 min, product minor isomer (*S*) = 47.68 min, starting material = 15.25 min.

峰号	保留时间	面积	高度	标记	化合物名	面积%
1	15.248	563877	45237	M		28.316
2	42.094	1355044	26342	M		68.046
3	47.679	72450	1769	M		3.638
总计		1991372	73348			100.000

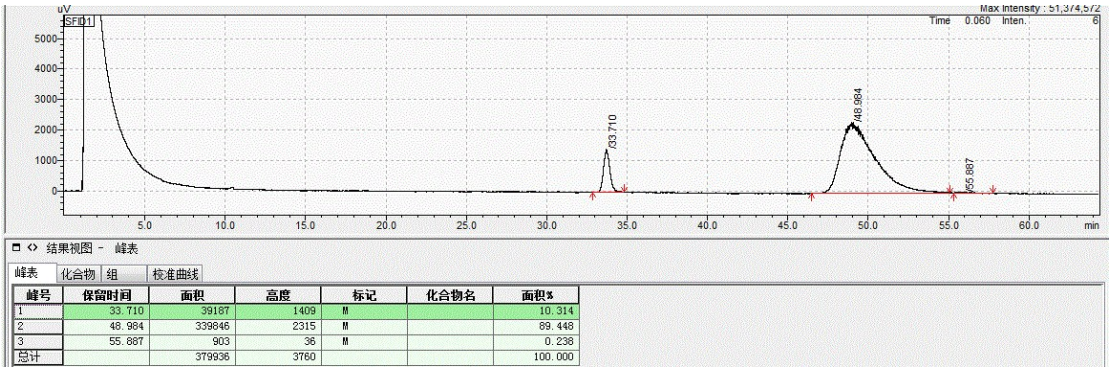
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	15.248	563877	45237			28.316
2	42.094	1355044	26342			68.046
3	47.679	72450	1769			3.638
Total		1991372	73348			100.000

Fig. S45 3h, 72% conversion, 90% ee.



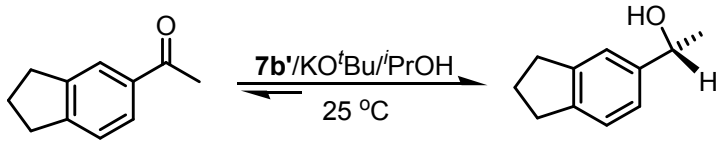
General conditions: [7**b'**] = 3.54 × 10^{-4} M, [KO^{t}Bu] = 2.83 ×10^{-3} M, [ketone] = 3.54 × 10^{-1} M, [^{i}PrOH] = 12.4 M, 25°C. GC analysis conditions: Oven temperature (130 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 48.98 min, product minor isomer (*S*) = 55.89 min, starting material = 33.71 min.



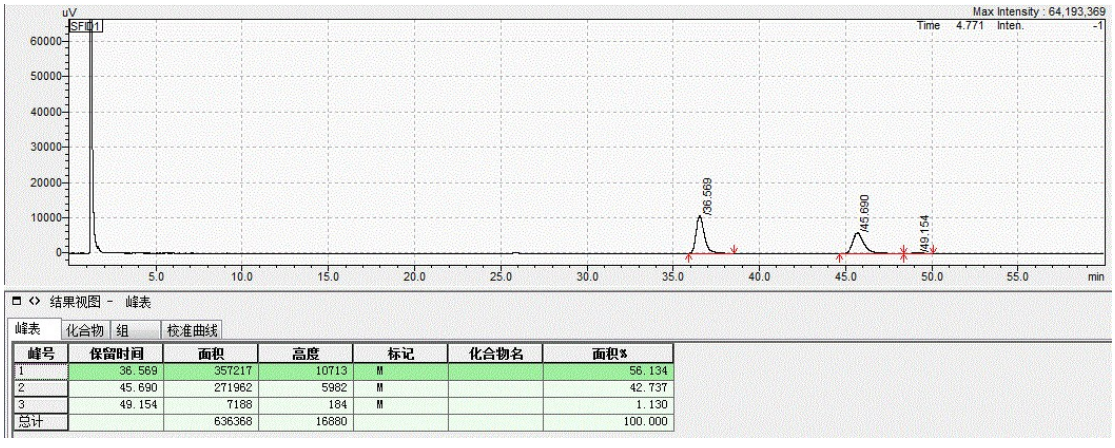
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	33.710	39187	1409			10.314
2	48.984	339846	2315			89.448
3	55.887	903	36			0.238
Total		379936	3760			100.000

Fig. S46 3h, 90% conversion, 99% ee.



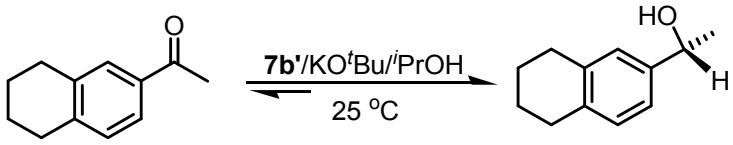
General conditions: [7**b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 0.03 M, [^{i}PrOH] = 11.1 M, 25°C. GC analysis conditions: Oven temperature (130 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 45.69 min, product minor isomer (*S*) = 49.15 min, starting material = 36.57 min.



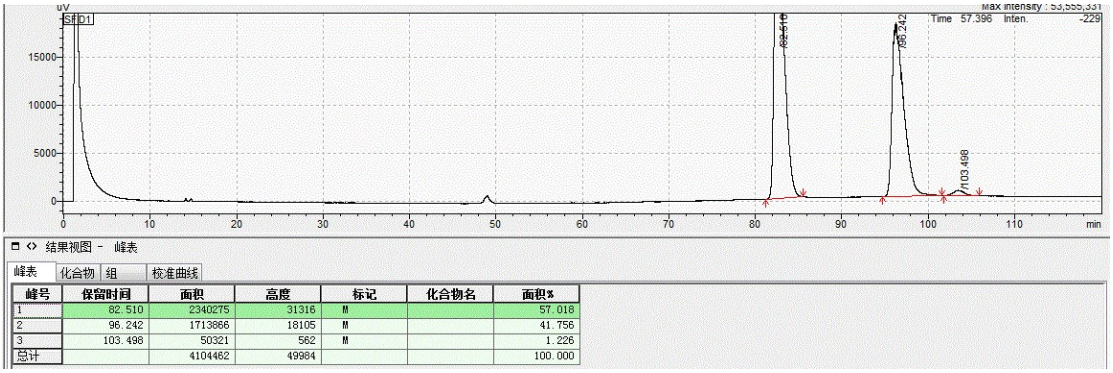
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	36.569	357217	10713			56.134
2	45.690	271962	5982			42.737
3	49.154	7188	184			1.130
Total		636368	16880			100.000

Fig. S47 3h, 44% conversion, 97% ee.



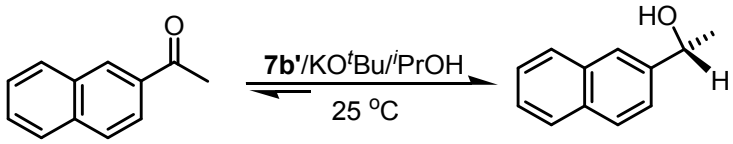
General conditions: [7**b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 1.28 M, [^{i}PrOH] = 11.1 M, 25°C. GC analysis conditions: Oven temperature (130 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 96.24 min, product minor isomer (*S*) = 103.50 min, starting material = 82.51 min.



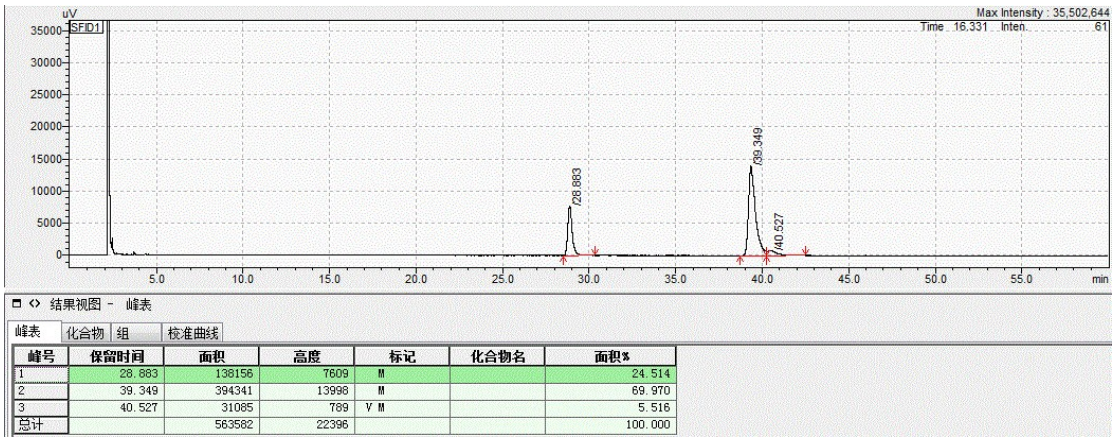
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	82.510	2340275	142377			89.019
2	96.242	36335	4731			5.232
3	103.498	39925	4646			5.749
Total		694492	151754			100.000

Fig. S48 3h, 43% conversion, 94% ee.



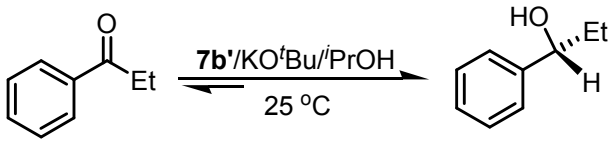
General conditions: [7**b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 0.03 M, [^{i}PrOH] = 11.1 M, 25°C. GC analysis conditions: Oven temperature (150 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 39.35 min, product minor isomer (*S*) = 40.53 min, starting material = 28.88 min.



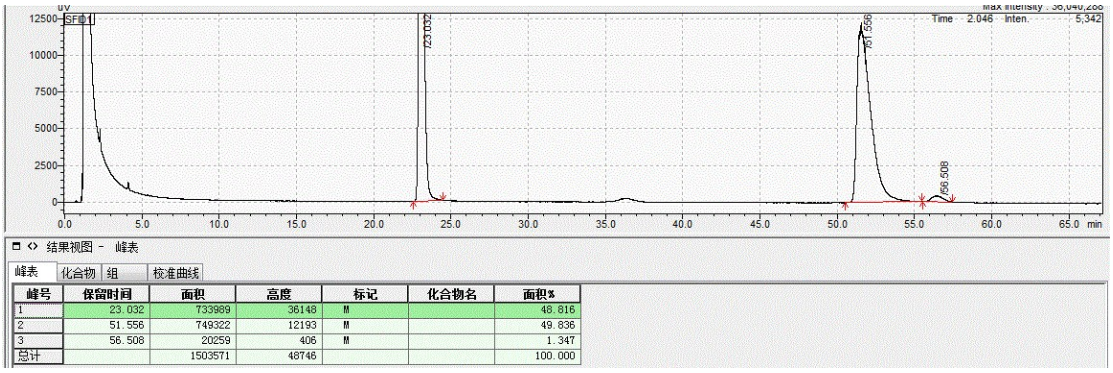
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	28.883	138156	7609			24.514
2	39.349	394341	13998			69.970
3	40.527	31085	789			5.516
Total		563582	22396			100.000

Fig. S49 3h, 75% conversion, 93% ee.



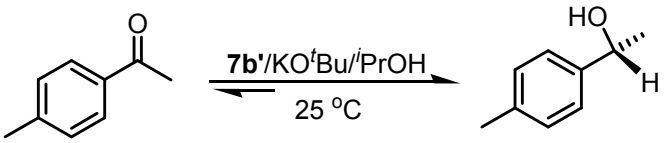
General conditions: [7**b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3}M, [ketone] = 1.28 M, [^{i}PrOH] = 11.1 M, 25°C. GC analysis conditions: Oven temperature (100 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 51.56 min, product minor isomer (*S*) = 56.51 min, starting material = 23.03 min.



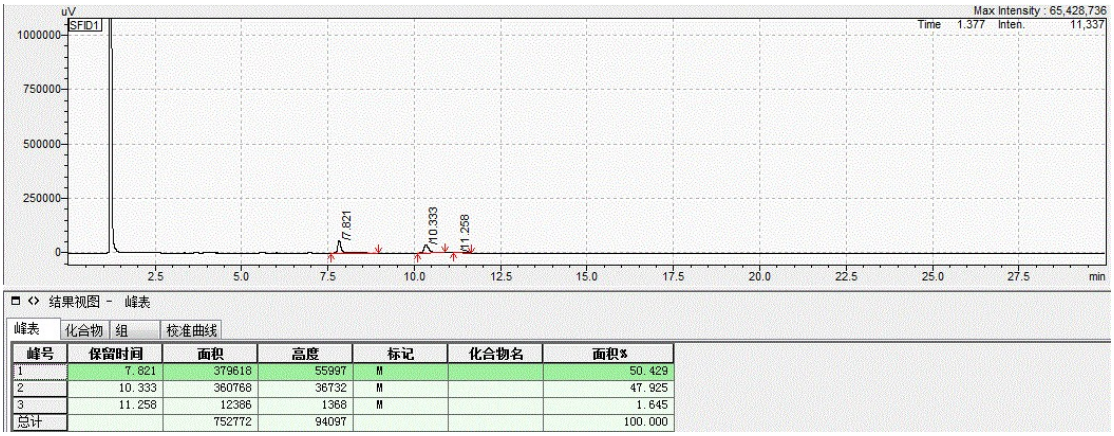
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	23.032	733989	36148			48.816
2	51.556	749322	12193			49.836
3	56.508	20259	406			1.347
Total		1503571	48746			100.000

Fig. S50 3h, 51% conversion, 94% ee.



General conditions: [7**b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 0.03 M, [^{i}PrOH] = 11.1 M, 25°C. GC analysis conditions: Oven temperature (130 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 10.33 min, product minor isomer (*S*) = 11.26 min, starting material = 7.82 min.

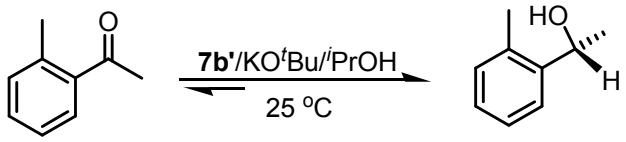


峰号	保留时间	面积	高度	标记	化合物名	面积%
1	7.821	379618	55997	M		50.429
2	10.333	360768	36732	M		47.925
3	11.258	12386	1368	M		1.645
总计		752772	94097			100.000

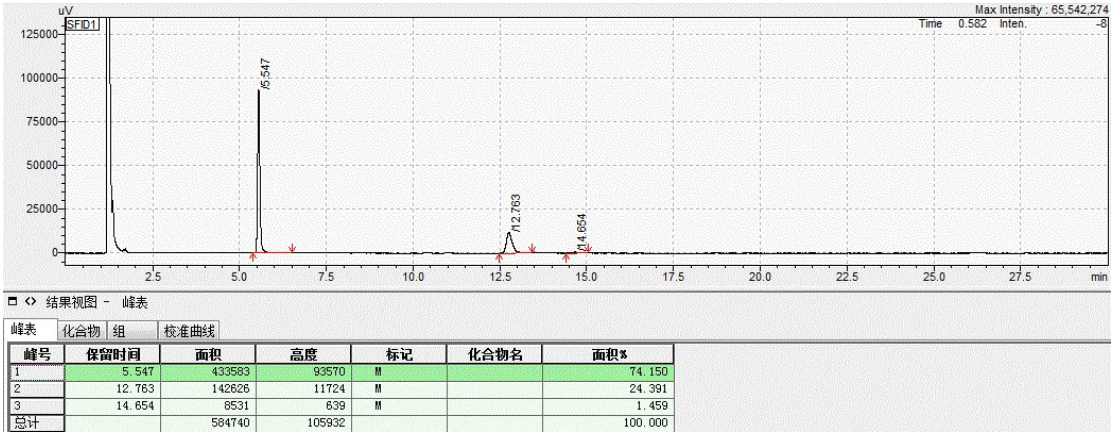
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	7.821	379618	55997			50.429
2	10.333	360768	36732			47.925
3	11.258	12386	1368			1.645
Total		752772	94097			100.000

Fig. S51 3h, 50% conversion, 97% ee.



General conditions: [7**b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 0.03 M, [^{i}PrOH] = 11.1 M, 25°C. GC analysis conditions: Oven temperature (130 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 12.76 min, product minor isomer (*S*) = 14.65 min, starting material = 5.55 min.

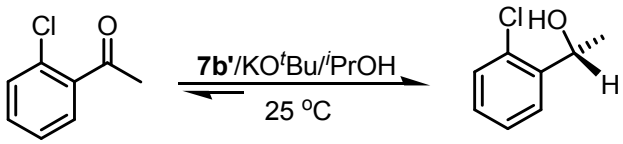


峰号	保留时间	面积	高度	标记	化合物名	面积%
1	5.547	433583	93570	M		74.150
2	12.763	142626	11724	M		24.391
3	14.654	8531	639	M		1.459
总计		584740	105932			100.000

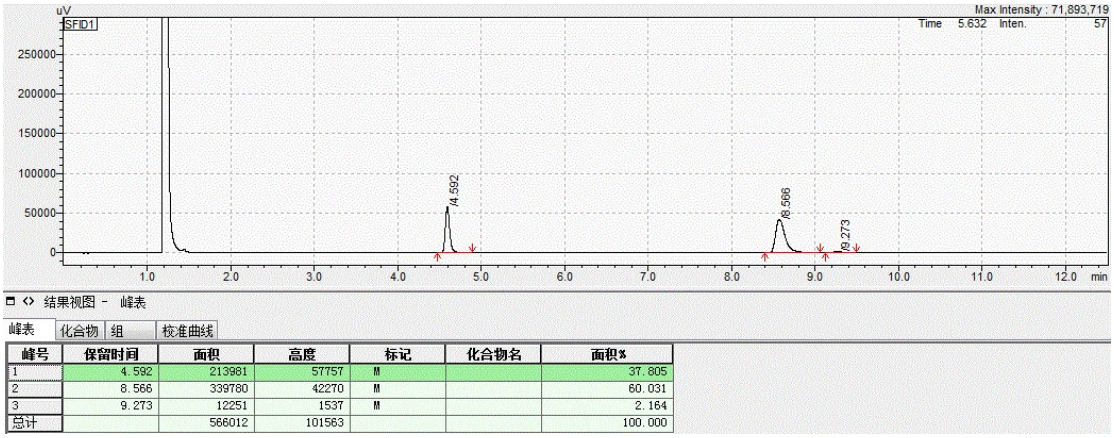
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	5.547	433583	93570			74.150
2	12.763	142626	11724			24.391
3	14.654	8531	639			1.459
Total		584740	105932			100.000

Fig. S52 3h, 26% conversion, 95% ee.



General conditions: [7**b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 0.03 M, [^{i}PrOH] = 11.1 M, 25°C. GC analysis conditions: Oven temperature (150 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 8.57 min, product minor isomer (*S*) = 9.27 min, starting material = 4.59 min.



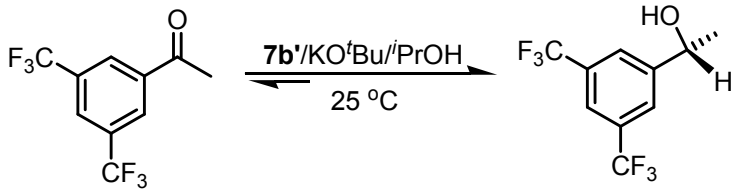
峰号	保留时间	面积	高度	标记	化合物名	面积%
1	4.592	213981	57757	M		37.805
2	8.566	339780	42270	M		60.031
3	9.273	12251	1537	M		2.164
总计		566012	101563			100.000

The table in the graph is as follow:

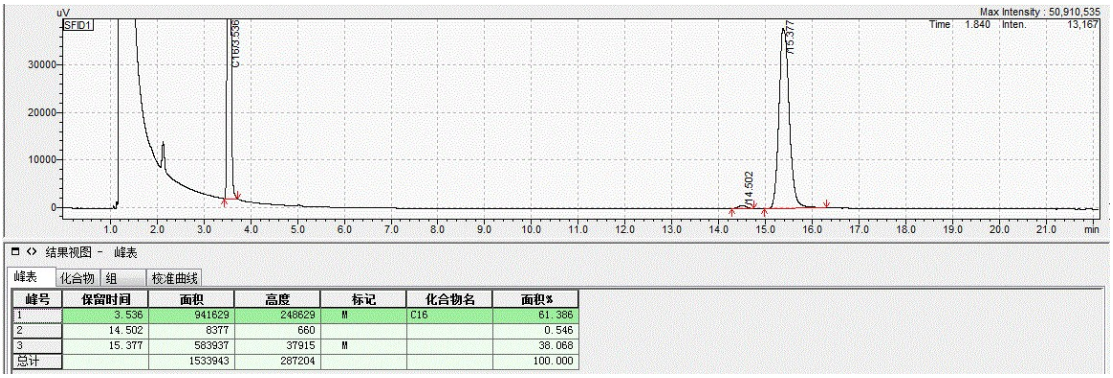
Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	4.592	213981	57757			37.805
2	8.566	339780	42270			60.031
3	9.273	12251	1537			2.164

Total		566012	101563			100.000

Fig. S53 3h, 62% conversion, 97% ee.



General conditions: [7**b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 1.28 M, [^{i}PrOH] = 11.1 M, 25°C. GC analysis conditions: Oven temperature (110 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 15.38 min, product minor isomer (*S*) = 14.50 min, starting material = 3.54 min.

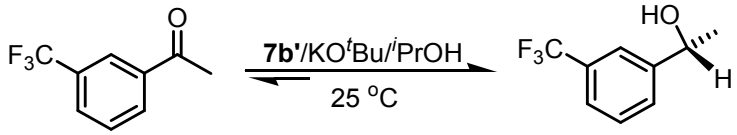


峰号	保留时间	面积	高度	标记	化合物名	面积%
1	3.536	941629	248629	M	C16	61.386
2	14.502	8377	660			0.546
3	15.377	583937	37915	M		38.068
总计		1533943	287204			100.000

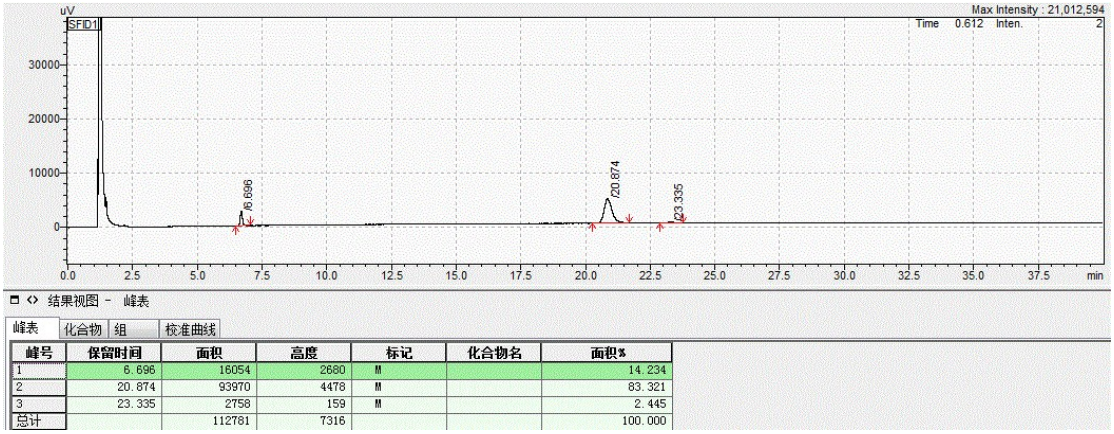
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	3.536	941629	248629			61.386
2	14.502	8377	660			0.546
3	15.377	583937	37915			38.068
Total		1533943	287204			100.000

Fig. S54 3h, 39% conversion, 97% ee.



General conditions: [7**b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 0.03 M, [^{i}PrOH] = 11.1 M, 25°C. GC analysis conditions: Oven temperature (110 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 20.87 min, product minor isomer (*S*) = 23.34 min, starting material = 6.70 min.

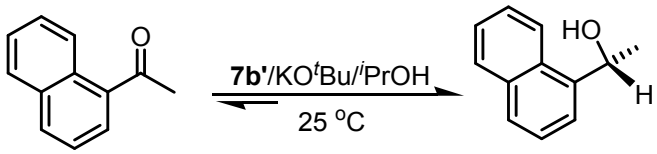


峰号	保留时间	面积	高度	标记	化合物名	面积%
1	6.696	16054	2680	M		14.234
2	20.874	93970	4478	M		83.321
3	23.335	2758	159	M		2.445
总计		112781	7316			100.000

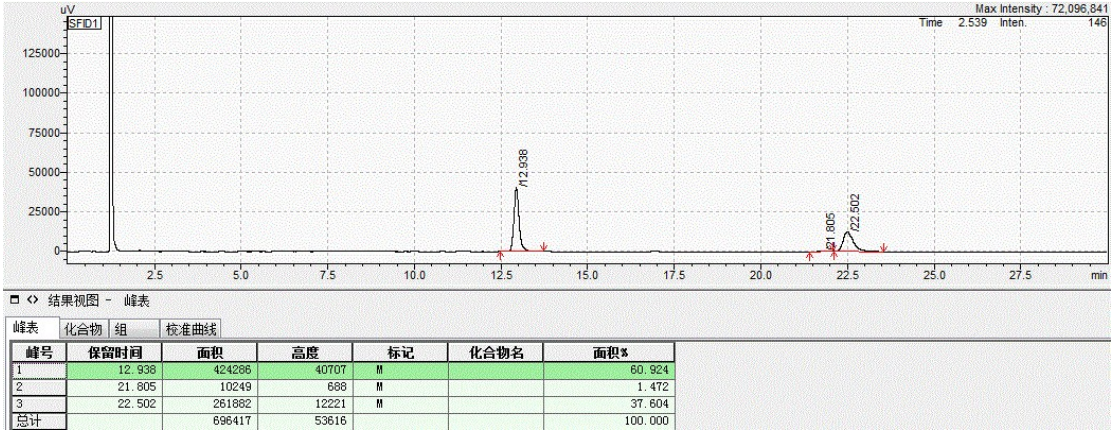
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	6.696	16054	2680			14.234
2	20.874	93970	4478			83.321
3	23.335	2758	159			2.445
Total		112781	7316			100.000

Fig. S55 3h, 86% conversion, 97% ee.



General conditions: [**7b'**] = 3.00 × 10^{-4} M, [KO^{t}Bu] = 2.40 ×10^{-3} M, [ketone] = 0.03 M, [^{i}PrOH] = 11.1 M, 25°C. GC analysis conditions: Oven temperature (170 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 21.81 min, product minor isomer (*S*) = 22.50 min, starting material = 12.94 min.



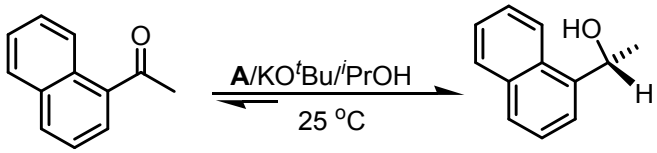
峰号	保留时间	面积	高度	标记	化合物名	面积%
1	12.938	424286	40707	M		60.924
2	21.805	10249	688	M		1.472
3	22.502	261882	12221	M		37.604
总计		696417	53616			100.000

The table in the graph is as follow:

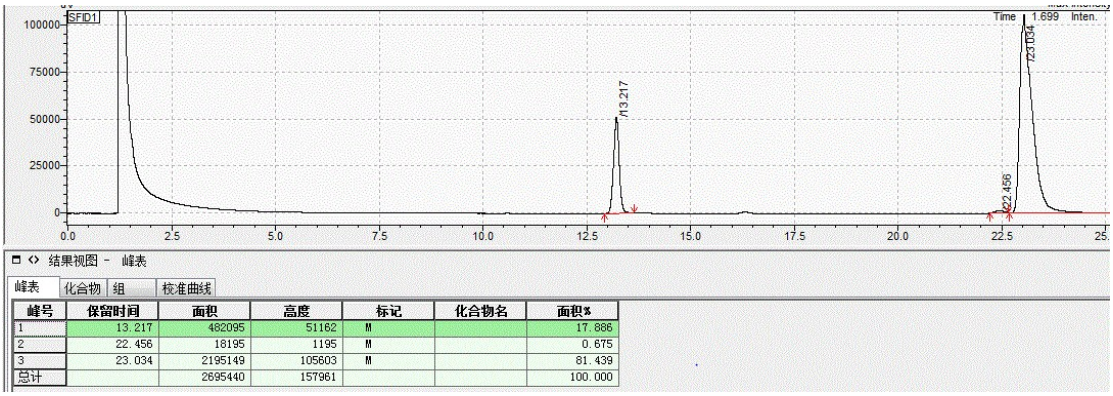
Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	12.938	424286	40707			60.924
2	21.805	10249	688			1.472
3	22.502	261882	12221			37.604

Total		696417	53616			100.000

Fig. S56.1 3h, 39% conversion, 96% ee.



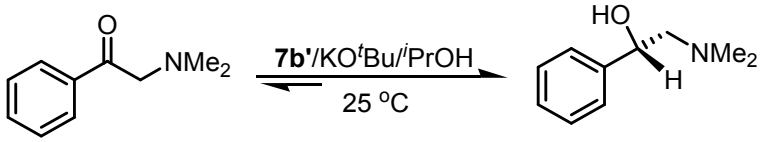
General conditions: [**A**] = 7.08 × 10^{-5} M, [KO^{t}Bu] = 5.66 × 10^{-4} M, [ketone] = 1.51 M, [^{i}PrOH] = 12.4 M, 25°C. GC analysis conditions: Oven temperature (170 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*R*) = 23.03 min, product minor isomer (*S*) = 22.46 min, starting material = 13.21 min.



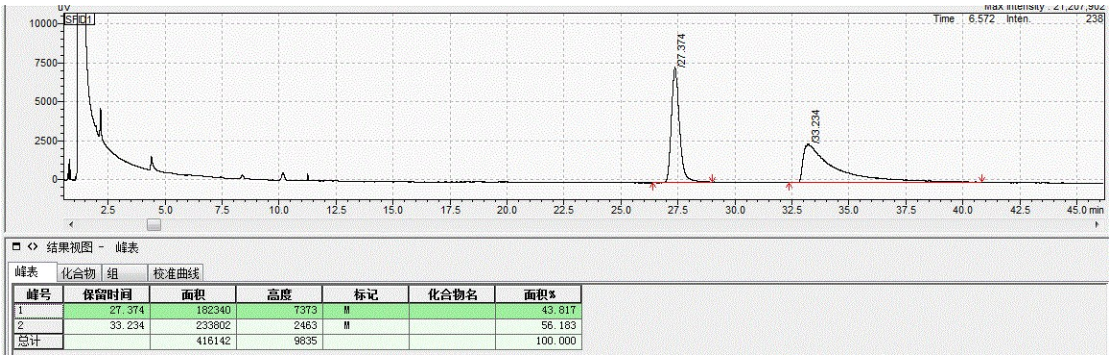
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	13.217	482095	51162			17.886
2	22.456	18195	1195			0.675
3	23.034	2195149	105603			81.439
Total		2695440	157961			100.000

Fig. S56.2 50 min, 82% conversion, 98% ee.



General conditions: [**7b'**] = 2.55 × 10^{-4} M, [KO^{t}Bu] = 2.04 × 10^{-3} M, [ketone] = 0.26 M, [^{i}PrOH] = 12.4 M, 25°C. GC analysis conditions: Oven temperature (115 °C), SPL1 temperature (275 °C). Retention time: product isomer mixture = 33.23 min, starting material = 27.37 min.



The table in the graph is as follow:

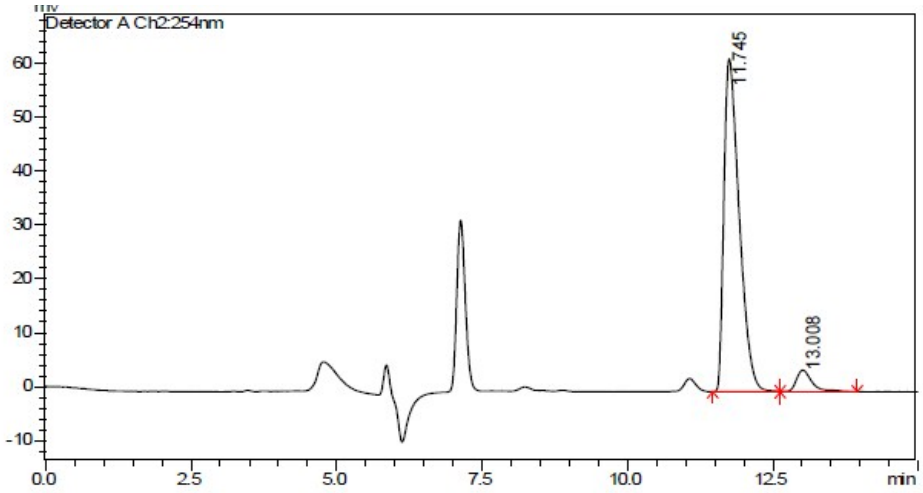
Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	27.374	182340	7373			43.817
2	33.234	233802	2463			56.183
Total		416142	9835			100.000

Fig. S57.1 3h, 56% conversion.

The crude product was separated by silica chromatography and the amino alcohol was further analyzed by chiral HPLC to determine the enantioselectivity at 87% ee.

Table S2. HPLC analysis conditions.

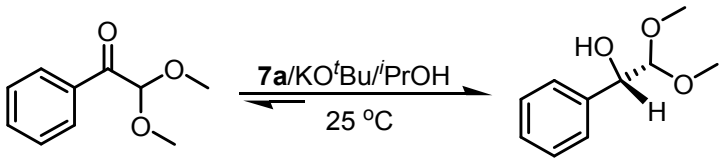
Column	:	CHIRALPAK® AD-H
Column size	:	0.46 cm I.D. ×25 cm L ×5 μm
Injection	:	5 μl
Mobile phase	:	n-Hexane/ Ethanol / Diethylamine = 99/1/0.1 (v/v/v)
Flow rate	:	1.0 ml/min
Wave length	:	UV 254 nm
Temperature	:	35℃
Sample solution	:	5.0 mg/ml in EtOH10% Hexane90%
HPLC equipment	:	Shimadzu LC 20A QA&QC-HPLC-01



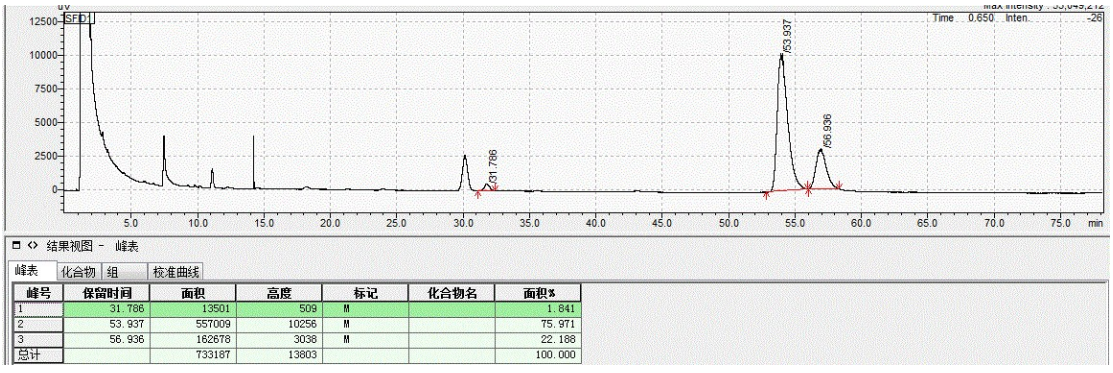
<Column Performance Report>

Peak No.	Time	Area	Area %	Plate number	Tailing	Resolution
1	11.745	1132751	93.6884	8951.571	1.737	--
2	13.008	76311	6.3116	12720.873	1.884	2.636

Fig. S57.2 87% ee.



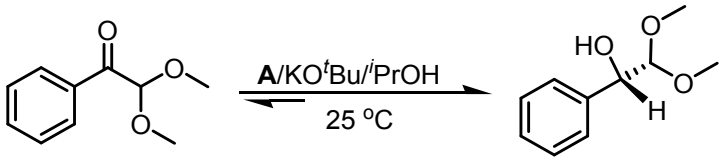
General conditions: [**7a**] = 2.55 × 10^{-4} M, [KO^{t}Bu] = 2.04 ×10^{-3} M, [ketone] = 0.10 M, [^{i}PrOH] = 12.4 M, 25°C. GC analysis conditions: Oven temperature (115 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*S*) = 53.94 min, product minor isomer (*R*) = 56.94 min, starting material = 31.79 min, impurity = 30.01 min.



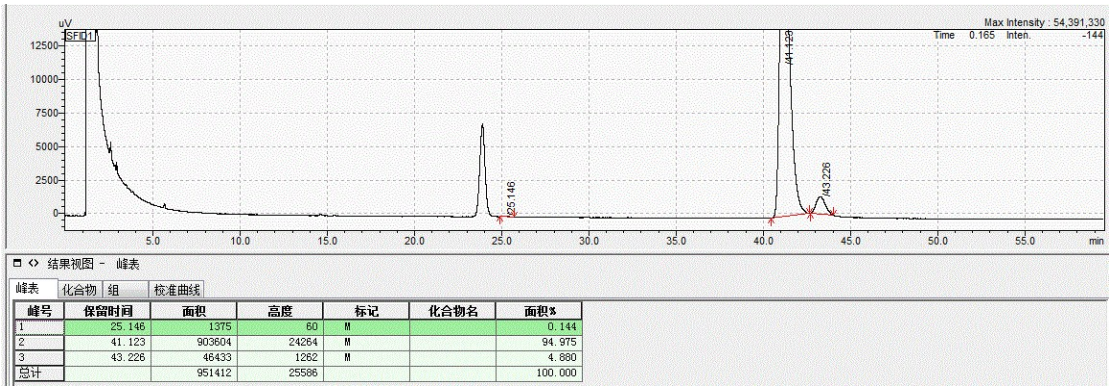
The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	31.786	13501	509			1.841
2	53.937	557009	10256			75.971
3	56.936	162678	3038			22.188
Total		733187	13803			100.000

Fig. S58.1 3 min, 98% conversion, 54% ee.



General conditions: [**A**] = 2.55 × 10^{-4} M, [KO^{t}Bu] = 2.04 ×10^{-3} M, [ketone] = 0.10 M, [^{i}PrOH] = 12.4 M, 25°C. GC analysis conditions: Oven temperature (120 °C), SPL1 temperature (275 °C). Retention time: product major isomer (*S*) = 41.12 min, product minor isomer (*R*) = 43.22 min, starting material = 25.15 min, impurity = 23.85 min.



峰号	保留时间	面积	高度	标记	化合物名	面积%
1	25.146	1375	60	M		0.144
2	41.123	903604	24264	M		94.975
3	43.226	46433	1262	M		4.880
总计		951412	25586			100.000

The table in the graph is as follow:

Peaks number	Retention time	Area	Height of peaks	Mark	Name of compounds	Area percentage
1	25.146	1375	60			0.144
2	41.123	903604	24264			94.975
3	43.226	46433	1262			4.880
Total		951412	25586			100.000

Fig. S58.2 3 min, >99% conversion, 90% ee.

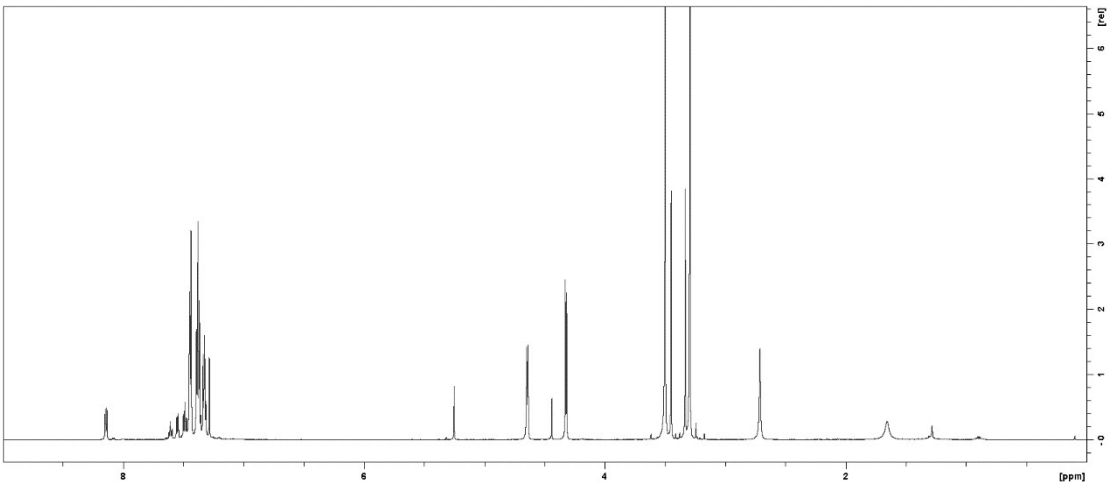


Fig. S58.3 The ^{1}H NMR ($CDCl_3$, 600MHz) spectrum of the crude product of [(*R*)-2-(dimethoxy)-1-phenylethanol by asymmetric transfer hydrogenation of 2,2-dimethoxyacetophenone, after removing the solvent isopropanol.

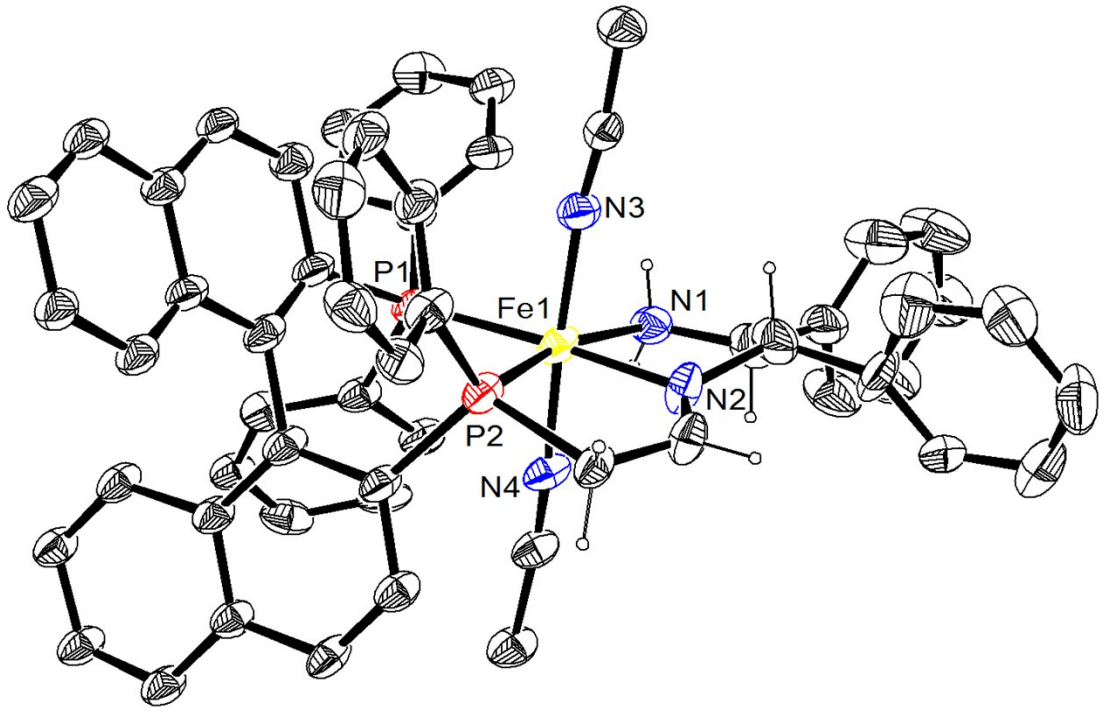
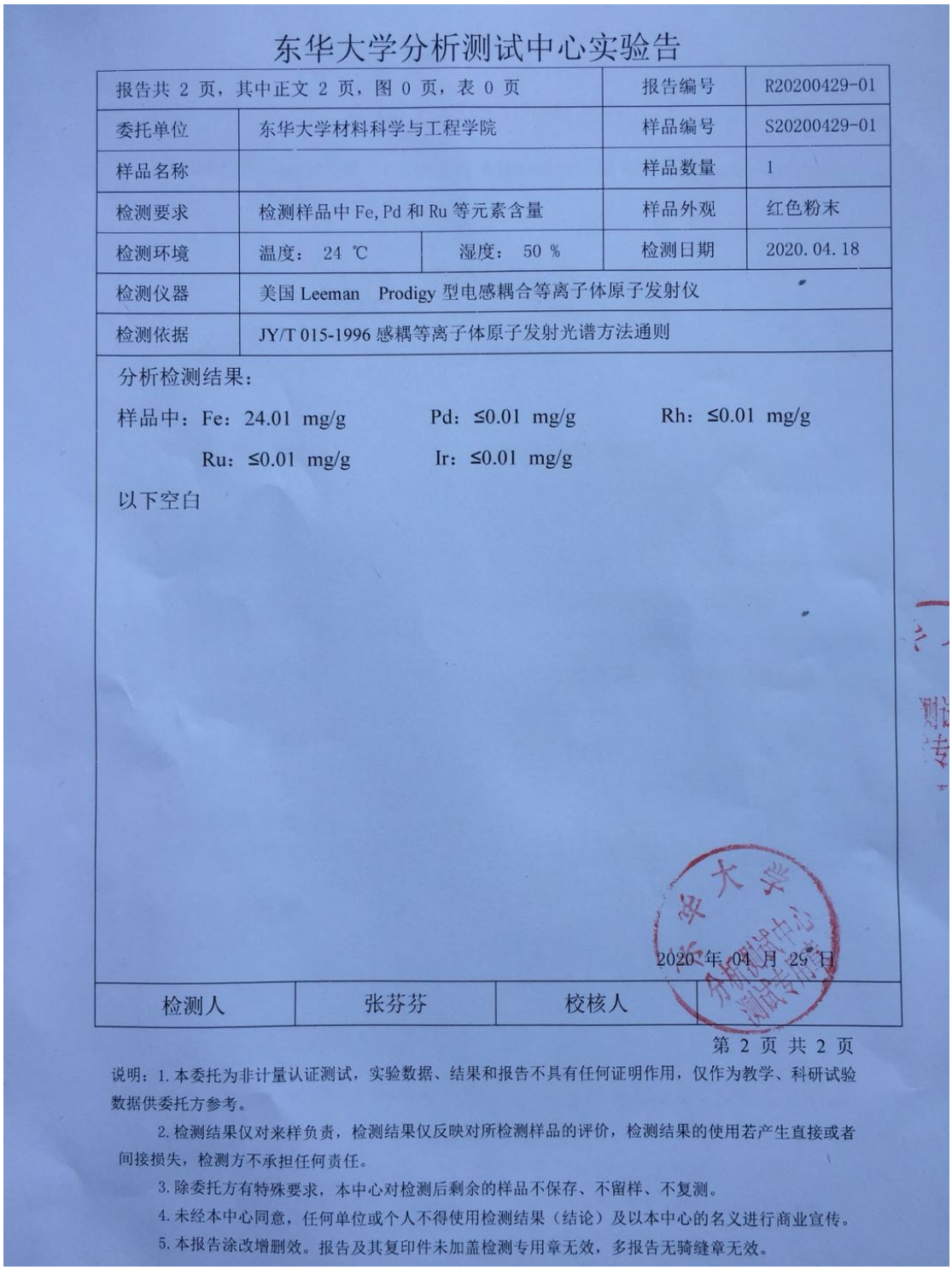


Fig. S59 The molecular structure of (S_A, R_P, *SS*)-**6a** with the thermal ellipsoids set at 10% probability. Aromatic ring protons and the two BF_4 counteranions were omitted for clarity.

Table S3. Crystal data and structure refinement for **6a**

Compound reference	**6a**
Empirical formula	$C_{58}H_{50}B_2F_8FeN_4P_2$
Formula weight	1094.43
Temperature/K	170.0
Crystal system	monoclinic
Space group	C2/c
a/Å	36.052(7)
b/Å	10.495(2)
c/Å	35.315(6)
α/°	90
β/°	113.603(10)
γ/°	90
Volume/Å^3	12244(4)
Z	8
ρ_{calc}g/cm^3	1.187
μ/mm^{-1}	1.983
F(000)	4512.0
Crystal size/mm^3	0.1 × 0.06 × 0.05
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	8.32 to 110.44
Index ranges	-44 ≤ h ≤ 43, -12 ≤ k ≤ 9, -43 ≤ l ≤ 43
Reflections collected	59640
Independent reflections	10825 [R_{int} = 0.1273, R_{sigma} = 0.1477]
Data/restraints/parameters	10825/80/673
Goodness-of-fit on F^2	0.700
Final R indexes [I>=2σ (I)]	R_1 = 0.0989, wR_2 = 0.2082
Final R indexes [all data]	R_1 = 0.1906, wR_2 = 0.2778
Largest diff. peak/hole / e Å^{-3}	0.59/-0.26



东华大学分析测试中心实验告

报告共 2 页，其中正文 2 页，图 0 页，表 0 页			报告编号	R20200429-01
委托单位	东华大学材料科学与工程学院		样品编号	S20200429-01
样品名称			样品数量	1
检测要求	检测样品中 Fe, Pd 和 Ru 等元素含量		样品外观	红色粉末
检测环境	温度： 24 ℃	湿度： 50 %	检测日期	2020. 04. 18
检测仪器	美国 Leeman Prodigy 型电感耦合等离子体原子发射仪			
检测依据	JY/T 015-1996 感耦等离子体原子发射光谱方法通则			

分析检测结果：

样品中：Fe：24.01 mg/g　　Pd：≤0.01 mg/g　　Rh：≤0.01 mg/g

Ru：≤0.01 mg/g　　Ir：≤0.01 mg/g

以下空白

2020 年 04 月 29 日

检测人	张芬芬	校核人	

第 2 页 共 2 页

说明：1. 本委托为非计量认证测试，实验数据、结果和报告不具有任何证明作用，仅作为教学、科研试验数据供委托方参考。

2. 检测结果仅对来样负责，检测结果仅反映对所检测样品的评价，检测结果的使用若产生直接或者间接损失，检测方不承担任何责任。

3. 除委托方有特殊要求，本中心对检测后剩余的样品不保存、不留样、不复测。

4. 未经本中心同意，任何单位或个人不得使用检测结果（结论）及以本中心的名义进行商业宣传。

5. 本报告涂改增删效。报告及其复印件未加盖检测专用章无效，多报告无骑缝章无效。

The table in the graph is as follow:

Test Report of Analysis and Test Center of Donghua University

The report contains two pages, including two pages of main text, no graph, no sheet		Report number	R20200429-01
Client	College of materials science and engineering	Sample number	R20200429-01
Sample name		Sample quantity	1

Test requirement	Detect elements content in the sample, i.e., Fe, Pd, Rh, Ru, Ir.		The sample appearance	Brown powder
Test environment	Temperature: 24 °C	Humidity: 50%	Test date	2020.04.18
Machine	Inductively coupled plasma atomic emission spectrometer, Leeman Prodigy from USA			
Test standard	JY/T 015-1996 General principles of inductively coupled plasma atomic emission spectrometry			
Test results: Sample: Fe: 24.01 mg/g Pd: ≤0.01 mg/g Rh: ≤ 0.01 mg/g Ru: ≤ 0.01 mg/g Ir: ≤ 0.01 mg/g 2020.04.29				
Tester	Fenfen Zhang		Checker	

Fig. S60 ICP analysis of **7a**.

6.Reference

1. W. Zuo and R. H. Morris, *Nature Protocols*, 2015, **10**, 241-257.
2. W. P. Chen, W. Mbafor, S. M. Roberts and J. Whittall, *Journal of the American Chemical Society*, 2006, **128**, 3922-3923.
3. S. Humbel, C. Bertrand, C. Darcel, C. Bauduin and S. Juge, *Inorganic Chemistry*, 2003, **42**, 420-427.