A Supramolecularly Tunable Chiral Diphosphine Ligand: Application to Rh and Ir-Catalyzed Enantioselective Hydrogenation

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Supporting Information

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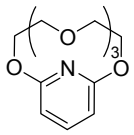
I. General Information

Unless otherwise noted, all experiments were carried out under an inert atmosphere of dry nitrogen by using standard Schlenk-type techniques. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded in CD_2Cl_2, $CDCl_3$ or CD_3COCD_3 on a Bruker advance spectrophotometer (400 or 500 MHz) at room temperature. Chemical shifts (δ) are given in ppm and are referenced to residual solvent peaks. Enantiomeric excesses of the asymmetric hydrogenation products were determined by chiral GC or HPLC. Gas chromatographic analyses were conducted on an Agilent 7820A with an FID detector. HPLC analyses were performed using an Agilent 1200 with a UV detector. Optical rotations were measured on a Perkin-Elmer Model 341 polarimeter in a 10 cm cell. The low resolution electrospray ionization mass [LRMS (ESI)] spectra were obtained with an Agilent Technologies 5975A or a Bruker Esquire 3000 plus mass spectrometer. The high resolution mass (HRMS) spectra were recorded on a Waters Micromass® GCT Premier™ orthogonal acceleration time-of-flight (oa-TOF) GC mass spectrometer with EI resource and are reported as *m*/*z* (relative intensity). IR absorption spectra (FT = diffuse reflectance spectroscopy) were performed on a Bruker TENSOR27 and only noteworthy absorptions (in cm^{-1}) are listed. Element analysis was performed on a Thermo Finnigan Italia S.P.A (EA 1112).

$[Rh(COD)_2]BF_4$,[1] $[Ir(COD)_2]BF_4$, $MBAr_F$ (M= Li, Na or K, BAr_F^- = $(3,5\text{-}(CF_3)_2C_6H_3)_4B^-$),[2] $[Rh(COD)_2]BAr_F$,[3] α-dehydroamino acid derivatives[4] and 2-alkyl-substituted quinoline derivatives[5] were prepared according to the known literature procedures. Optically pure Xyl-P-Phos, 2,6-dichloropyridine, tetraethylene glycol, and other reagents for the preparation of ligands, catalysts, and substrates were purchased from Strem, Aldrich, Alfa aesar or Acros organics and used as received without further purification unless otherwise stated. All solvents were purified and dried according to standard methods prior to use.

II. Synthetic Procedures for (–)-Xyl-P16C6-Phos, (+)-Xyl-P16C6-Phos, and the Self-assembled Catalysts

2,6-Pyrido-l6-crown-6 (2)[6]



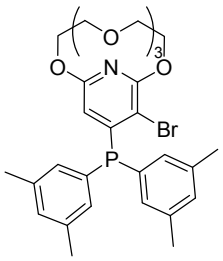
THF (200 mL) was added to a 500 mL three-necked flask equipped with a magnetic stirring bar, a reflux condenser and an addition funnel. Then NaH (1.92 g, 80.0 mmol) and KPF_6 (3.86 g, 21.0 mmol) was added and the mixture was heated under reflux. A solution of 2,6-dichloropyridine (2.96 g, 20.0 mmol) and tetraethylene glycol (3.88 g, 20.0 mmol) in THF (150 mL) was added dropwise to the above mixture over 12 h. The reaction mixture was refluxed for further 3 days before being quenched with MeOH/H_2O. The solvent was evaporated in vacuo and the residue was partitioned between CH_2Cl_2 (100 mL) and brine (50 mL). The organic layer was dried with anhydrous Na_2SO_4, filtered, and evaporated in vacuo to give the crude product, which was purified by column chromatography (silica gel, acetone/CH_2Cl_2 = 1:10) to afford 2,6-pyrido-l6-crown-6 (**2**, 3.50 g, 65% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (t, J = 8.0 Hz, 1H), 6.27 (d, J = 8.0 Hz, 2H), 4.59 (t, J = 5.6 Hz, 4H), 3.89 (t, J = 5.6 Hz, 4H), 3.63–3.65 (m, 4H), 3.52–3.54 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 161.97, 141.07, 101.96, 71.15, 70.12, 69.69, 64.56.

3-Bromo-2,6-pyrido-l6-crown-6 (3)[7]

To a stirred mixture of **2** (2.45 g, 9.10 mmol) and dichloromethane (50 mL), a solution of NBS (1.46 g, 8.20 mmol) in dichloromethane (20 mL) was slowly added at –70 °C over 12 h. The progress of the reaction was monitored by thin-layer chromatography. Upon completion, the reaction was quenched with a saturated Na_2CO_3 solution followed by thrice extraction with dichloromethane (30 mL each). The combined extracts were dried with anhydrous Na_2SO_4 and the solvent was removed in vacuo to give the crude product, which was purified by flash chromatography on silica gel (acetone:CH_2Cl_2 = 1:100) to furnish the desired monobrominated product (**3**) as a white solid (2.71 g, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J = 8.0 Hz, 1H), 6.24 (d, J = 8.0 Hz, 1H), 4.68 (t,

J = 5.7 Hz, 2H), 4.56 (t, *J* = 5.5 Hz, 2H), 3.92 (t, *J* = 5.5 Hz, 2H), 3.87 (t, *J* = 5.5 Hz, 2H), 3.61–3.66 (m, 4H), 3.51–3.54 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 161.07, 157.66, 143.91, 103.94, 95.40, 71.42, 70.86, 70.31, 70.18, 69.73, 69.64, 65.65, 65.51. HRMS (ESI) for $C_{13}H_{18}BrNO_5$ ($[M + H]^+$): calculated, 348.0441; found, 348.0437.

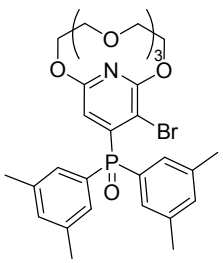
3-Bromo-4-di(3,5-dimethylphenyl)phosphino-2,6-pyrido-l6-crown-6 (4)[8]



To a mixture of *i*Pr_2NH (30.1 mL, 214 mmol) and THF (100 mL), which was placed in a 500 mL, three-necked flask equipped with a magnetic stirring bar and an addition funnel, a solution of *n*BuLi (84.5 mL, 186 mmol, 2.2 M in hexane) was added slowly at –78 °C. Upon completion of the addition, the reaction mixture was allowed to stir at –78 °C for 10 min, warm up by itself to –10 °C and stir at –10 °C for 30 min. The fresh prepared LDA solution was then cooled back to –78 °C, to which a solution of **3** (49.6 g, 142 mmol) in dried THF (100 mL) was added *via* cannula over a period of 20 minutes. The reaction mixture was stirred for further 30 min after the addition was completed. To the resulting red-brown suspension, a solution of $(3,5\text{-}Me_2C_6H_3)_2PCl$ (43.5 g, 157 mmol) in THF (30 mL) was added slowly at −78 °C. The reaction mixture was allowed to warm to room temperature spontaneously and stirred at room temperature overnight. The reaction was worked up with 50 mL water and the solvent was removed with a rotary evaporator. The organic product was extracted with CH_2Cl_2 (3 × 25 mL). The combined extract was washed with water (2 × 10 mL) and was dried with anhydrous Na_2SO_4 and concentrated in vacuo to give the crude product, which was purified by flash chromatography on silica gel (CH_2Cl_2:acetone = 100:1) to provide a white powder product (**4**, 61.2 g, 73% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.91–7.00 (m, 6H), 5.80 (d, *J* = 2.0 Hz, 1H), 4.72 (t, *J* = 5.6 Hz, 2H), 4.52 (t, *J* = 5.2 Hz, 2H), 3.96 (t, *J* = 5.2 Hz, 2H), 3.86 (t, *J* = 5.6 Hz, 2 H), 3.53–3.68 (m, 8H), 2.27 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.55, 157.91, 157.85, 155.10, 154.97, 138.29, 138.23, 134.31, 134.24, 132.18, 132.02, 131.62, 131.44, 108.18, 102.25, 102.03, 71.91, 70.83, 70.48, 70.28, 70.11, 69.91, 69.81, 65.93, 65.86, 21.55. ^{31}P NMR (202 MHz, $CDCl_3$,): δ –4.37. HRMS (EI) for $C_{29}H_{35}BrNO_5P$

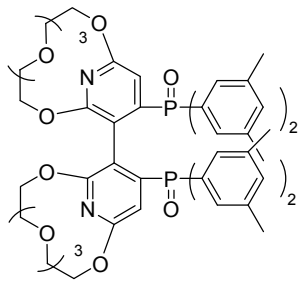
([M]$^+$): calculated, 587.1436; found, 587.1435.

3-Bromo-4-di(3,5-dimethylphenyl)phosphino-2,6-pyridoyl-l6-crown-6 (5)[8]



To a magnetically stirred solution of **4** (61.5 g, 105 mmol) in acetone (150 mL), 76 mL of ca. 30% hydrogen peroxide was added slowly at 0 °C. The reaction was monitored by thin-layer chromatography and the product was extracted with CH_2Cl_2 (3 × 50 mL). The combined extract was washed with 10% aq. Na_2SO_3 (3 × 20 mL) and water (2 × 20 mL) and dried with anhydrous Na_2SO_4. The filtrate was concentrated in vacuo to give a white powder (**5**, 53.8 g, 85% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30–7.41 (m, 6H), 6.27 (d, J = 13.0 Hz, 1H), 4.86 (t, J = 5.1 Hz, 2H), 4.67 (t, J = 4.9 Hz, 2H), 4.09 (t, J = 5.1 Hz, 2H), 3.94 (t, J = 4.9 Hz, 2H), 3.77–3.79 (m, 2H), 3.63–3.70 (m, 6H), 2.46 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 160.67, 160.53, 159.24, 159.14, 147.31, 146.54, 138.54, 138.44, 134.19, 131.11, 130.26, 129.65, 129.56, 109.59, 109.50, 99.28, 99.25, 72.06, 70.85, 70.51, 70.24, 70.07, 69.77, 66.35, 66.27, 21.55. ^{31}P NMR (202 MHz, $CDCl_3$,): δ 31.47. HRMS (EI) for $C_{29}H_{35}BrNO_6P$ ([M]$^+$): calculated, 603.1385; found, 603.1379.

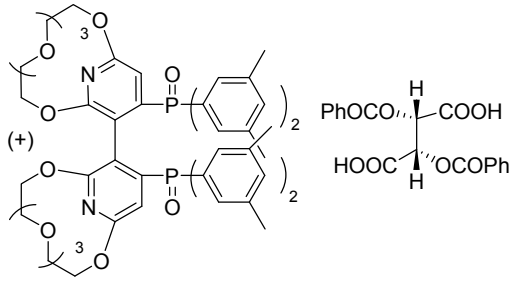
Compound (±)-6[9]



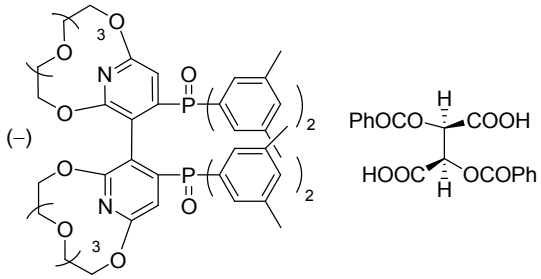
A mixture of **5** (34.4 g, 56.8 mmol), Cu powder (36.1 g, 568 mmol) and dried DMF (60 mL) was stirred at 145 °C for 48 h. The mixture was evaporated to dryness, then $CHCl_3$ (50 mL) was added and the mixture was refluxed for a few minutes. Insoluble solid was removed by filtration and was washed with $CHCl_3$ (60 mL). The combined filtrate was dried with anhydrous Na_2SO_4 and the solvent was evaporated under vacuum. The solid residue was purified by flash chromatography on silica gel (ethyl acetate:methanol = 10:1) and the desired product (±)-**6** was obtained as a white solid (14.9 g, 50% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, J = 12.0 Hz, 4H), 7.07–7.13 (m, 6H), 6.94 (s, 2H), 6.32 (d, J = 13.0 Hz, 2H), 4.78–4.83 (m, 2H), 4.54–4.57 (m, 2H), 4.14–4.19 (m, 2H), 3.97–4.01 (m, 2H), 3.33–3.71 (m, 24H), 2.32 (s, 12H), 2.08 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$):

δ 160.49, 160.35, 160.29, 160.15, 145.27, 144.51, 137.94, 137.84, 137.69, 137.58, 134.08, 133.85, 133.51, 133.27, 133.03, 130.30, 130.23, 130.05, 129.98, 129.79, 113.54, 106.23, 106.12, 71.42, 70.87, 70.49, 70.10, 69.55, 69.33, 69.23, 65.06, 64.57, 21.54, 21.22. ^{31}P NMR (202 MHz, $CDCl_3$): δ 29.92. HRMS (ESI) for $C_{58}H_{70}N_2O_{12}P_2$ ($[M + H]^+$): calculated, 1049.4482; found, 1049.4477.

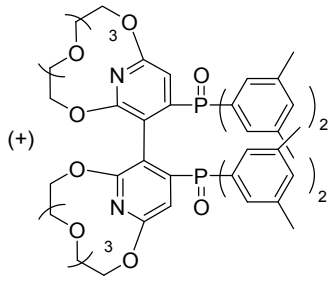
Optical resolution of (±)-6[10]



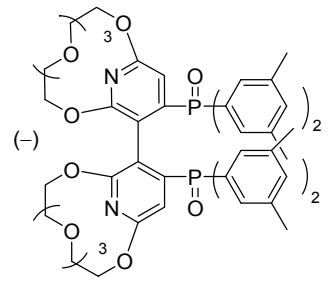
To a refluxing solution of (±)- **6** (5.68 g, 5.41 mmol) in $CHCl_3$ (10 mL), a solution of (–)-2,3-*O*,*O*′-dibenzoyltartaric acid monohydrate [(*L*)-(–)-DBTA monohydrate, 1.94 g, 5.41 mmol] in ethyl acetate (30 mL) was added slowly. The mixture was stirred under reflux for 3 h and then allowed to stand at room temperature overnight. The crystals formed were collected on a glass funnel and the filtrate was stored for recovery of the other enantiomer. The white solid product was dried in vacuo at room temperature for 2 h to give a 1:1 complex (+)-**6**-(–)-DBTA. Decomposition of a small amount of complex (+)-**6**-(–)-DBTA with 10% aq. NaOH in $CHCl_3$ provided enantiomerically enriched **6** ($[\alpha]_D^{20}$ = +147.5, c = 1.00, $CHCl_3$). Recrystallization of the above complex (+)-**6**-(–)-DBTA from the same solvent system for several times till no substantial changes in optical rotation occurred for enantiomeric **6**, which indicated that (+)-**6** was optically pure enough. Finally the optically pure 1:1 complexes of (+)-**6** and (*L*)-DBTA was obtained as white needles [2.28 g, 60% yield, $[\alpha]_D^{20}$ = +225.9 (c = 1.00, $CHCl_3$) for (+)-**6**]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.0 Hz, 4H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 4H), 7.19 (d, *J* = 12.5 Hz, 8H), 7.05 (s, 2H), 6.97 (s, 2H), 6.40 (d, *J* = 14.0 Hz, 2H), 5.90 (s, 2H), 4.69–4.73 (3m, 2H), 4.41–4.68 (m, 2H), 4.23–4.27 (m, 2H), 3.97–4.02 (m, 2H), 3.21–3.78 (m, 26H), 2.23 (s, 12H), 2.16 (s, 12H). ^{31}P NMR (202 MHz, $CDCl_3$) δ 30.90.



The optically pure 1:1 complex (–)-**6**-(*D*)-DBTA ($[\alpha]_D^{20}$ = –220.3 for (–)-**6** (c = 1.03, $CHCl_3$)) was obtained in 61 % yield according to the same procedure as in the preparation of complex (+)-**6**-(*L*)-DBTA. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.0 Hz, 4H), 7.52 (t, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 4H), 7.18 (t, *J* = 11.5 Hz, 8H), 7.05 (s, 2H), 6.96 (s, 2H), 6.38 (d, *J* = 14.5 Hz, 2H), 5.89 (s, 2H), 4.68–4.72 (m, 2H), 4.41–4.45 (m, 2H), 4.22–4.26 (m, 2H), 3.97–4.01 (m, 2H), 3.20–3.76 (m, 26H), 2.23 (s, 12H), 2.14 (s, 12H). ^{31}P NMR (202 MHz, $CDCl_3$): δ 31.64.

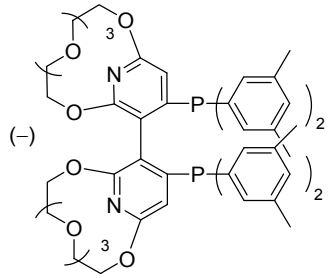


The complex (+)-**6**-(*L*)-DBTA (1.73 g, 1.23 mmol) was dissolved in $CHCl_3$ (15 mL) and treated with 10% aq. NaOH (15 mL) overnight. The mixture was extracted with $CHCl_3$ (3 × 30 mL). The combined organic layer was washed with 10% aq. NaOH (15 mL), water (2 × 10 mL) and dried over anhydrous Na_2SO_4. The filtrate was concentrated in vacuo to furnish a white solid (+)-**6** [1.18 g, 91 % yield based on (+)-**6**-(*L*)-DBTA initially used, $[\alpha]_D^{20}$ = +225.9 (c = 1.00, $CHCl_3$)]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, *J* = 11.5 Hz, 4H), 7.07–7.12 (m, 6H), 6.93 (s, 2H), 6.32 (d, *J* = 12.5 Hz, 2H), 4.78–4.83 (m, 2H), 4.55–4.57 (m, 2H), 4.14–4.18 (m, 2H), 3.96–4.00 (m, 2H), 3.32–3.81 (m, 24H), 2.32 (s, 12H), 2.08 (s, 12H). ^{31}P NMR (202 MHz, $CDCl_3$): δ 29.02.



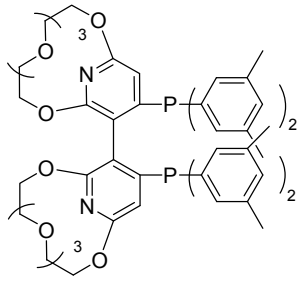
The white solid (–)-**6** was obtained according to the same procedure as in the preparation of (+)-**6** [1.02 g, 89 % yield based on (–)-**6**-(*D*)-DBTA initially used, $[\alpha]_D^{20}$ = –220.3 (c = 1.03, $CHCl_3$)]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35 (d, *J* = 12.5 Hz, 4H), 7.07–7.13 (m, 6H), 6.93 (s, 2H), 6.32 (d, *J* = 13.0 Hz, 2H), 4.79–4.81 (m, 2H), 4.55–4.56 (m, 2H), 4.15–4.18 (m, 2H), 3.97–3.99 (m, 2H), 3.33–3.80 (m, 24H), 2.32 (s, 12H), 2.08 (s, 12H). ^{31}P NMR (202 MHz, $CDCl_3$): δ 29.81.

(–)-Xyl-P16C6-Phos ((–)-7)[10]



A 250 mL three-necked flask, fitted with a magnetic stirring bar, a thermometer and a reflux condenser, was filled with (–)-**6** (1.02 g, 0.97 mmol) and followed by the addition of dry, degassed toluene (40 mL), triethylamine (1.3 mL, 9.3 mmol) and trichlorosilane (1.0 mL, 9.3 mmol). The mixture was stirred and heated at 100 °C for 1 h and finally at reflux overnight. After the solution was cooled to room temperature, 40 mL of 10% aqueous NaOH solution was carefully added. The mixture was then stirred at 80 °C until the organic and aqueous layers were clear. The aqueous layer was separated and extracted with warm toluene (2 × 25mL). The combined organic layer was washed with 40 mL of 10% NaOH solution and brine (2 × 40 mL) and then dried over anhydrous sodium sulfate. The organic layer was concentrated under reduced pressure to dryness, and then degassed methanol (2 × 10 mL) was added. The precipitates were collected and dried at reduced pressure overnight to give the desired product (–)-**7** [0.86 g, 87 % yield, $[\alpha]_D^{20}$ = –83.3 (c = 1.07, $CHCl_3$)] as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.82 (d, *J* = 10.0 Hz, 4H), 6.73–6.76 (m, 8H), 5.98 (s, 2H), 4.50–4.55 (m, 2H), 4.28–4.33 (m, 2H), 4.09–4.13 (m, 2H), 3.76–3.88 (m, 6H), 3.37–3.62 (m, 18H), 3.17–3.22 (m, 2H), 2.16 (s, 12H), 2.14 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$): *δ* 161.18, 159.61, 159.57, 159.53, 154.82, 154.76, 154.71, 137.69, 137.67, 137.64, 137.25, 137.22, 137.20, 136.76, 136.70, 136.65, 135.56, 135.52, 135.48, 132.44, 132.36, 132.27, 131.57, 131.48, 131.40, 130.55, 130.38, 115.14, 114.99, 114.85, 106.67, 71.35, 70.60, 70.54, 69.88, 69.72, 68.68, 64.98, 64.10, 21.53, 21.49. ^{31}P NMR (202 MHz, $CDCl_3$): *δ* –13.79 HRMS (ESI) for $C_{58}H_{71}N_2O_{10}P_2$ ($[M + H]^+$): calculated, 1017.4584; found, 1017.4692.

(+)-Xyl-P16C6-Phos ((+)-7)[10]



The white solid (+)-**7** was obtained according to the same procedure as in the preparation of (–)-**7** [1.22 g, 91% yield, $[\alpha]_D^{20}$ = +78.7 (c = 1.00, $CHCl_3$)]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.82 (d, J = 9.5 Hz, 4H), 6.74–6.76 (m, 8H), 5.98 (s, 2H), 4.50–4.55 (m, 2H), 4.28–4.33 (m, 2H), 4.09–4.13 (m, 2H), 3.76–3.88 (m, 6H), 3.37–3.62 (m, 18H), 3.18–3.22 (m, 2H), 2.16 (s, 12H), 2.14 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.20, 159.63, 159.58, 159.54, 154.84, 154.79, 154.74, 137.72, 137.68, 137.67, 137.28, 137.25, 137.21, 136.77, 136.71, 136.66, 135.57, 135.54, 135.50, 132.46, 132.37, 132.28, 131.58, 131.49, 131.42, 130.57, 130.40, 115.15, 115.01, 114.87, 106.68, 71.35, 70.61, 70.56, 69.89, 69.74, 68.70, 65.00, 64.11, 21.54, 21.51. ^{31}P NMR (202 MHz, $CDCl_3$): δ –13.79. HRMS (ESI) for $C_{58}H_{71}N_2O_{10}P_2$ ($[M + H]^+$): calculated, 1017.4584; found, 1017.4574.

Preparation of a Stock Solution of Rh Catalyst Based on (–)-Xyl-P16C6-Phos and $[Rh(COD)_2]BF_4$ (1:1 molar ratio)[11]

Under nitrogen atmosphere, $[Rh(COD)_2]BF_4$ (2.1 mg, 5.2×10^{-3} mmol) was dissolved in CH_2Cl_2 (1.5 mL). A solution of (–)-Xyl-P16C6-Phos ((–)-**7**, 5.5 mg, 5.4×10^{-3} mmol) in CH_2Cl_2 (1.5 mL) was added dropwise to the above solution with stirring. The reaction mixture was stirred overnight to give a solution of Rh catalyst based on (–)-Xyl-P16C6-Phos and $Rh(COD)_2BF_4$ (1:1 molar ratio, 1.7×10^{-3} mol•L^{-1}). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 23.85 (d, $J_{Rh–P}$ = 143.6 Hz).

Preparation of a Stock Solution of Rh Catalyst Based on (–)-Xyl-P16C6-Phos, $[Rh(COD)_2]BF_4$ and $NaBAr_F$ (1:1:10 molar ratio)[12]

Under nitrogen atmosphere, a solution of (–)-Xyl-P16C6-Phos ((–)-**7**, 9.5 mg, 9.3×10^{-3} mmol) and $NaBAr_F$ (82.5 mg, 9.3×10^{-2} mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 2 hours. Then to the mixture, a solution of $[Rh(COD)_2]BF_4$ (3.6 mg, 8.9×10^{-3} mmol) in CH_2Cl_2 (2 mL) was added dropwise. The reaction mixture was stirred overnight to give a solution of Rh catalyst based on (–)-Xyl-P16C6-Phos, $Rh(COD)_2BF_4$ and $NaBAr_F$ (1:1:10 molar ratio, 2.2×10^{-3}

mol•L^{-1}). ^{31}P NMR (202 MHz, $CDCl_3$): δ 24.42 (d, J_{Rh-P} = 143.0 Hz).

The catalyst derived from (–)-Xyl-P16C6-Phos, $[Rh(COD)_2]BF_4$, and $LiBAr_F$ [1:1:10 molar ratio, ^{31}P NMR (202 MHz, $CDCl_3$): δ 24.41 (d, J_{Rh-P}=143.8 Hz)] and the catalyst based on (–)-Xyl-P16C6-Phos, $[Rh(COD)_2]BF_4$ and $KBAr_F$ [1:1:10 molar ratio, ^{31}P NMR (202 MHz, $CDCl_3$): δ 24.05 (d, J_{Rh-P} = 143.6 Hz)] were prepared with the same procedure as above.

Preparation of a Stock Solution of Ir Catalyst Based on (+)-Xyl-P16C6-Phos and $[Ir(COD)_2]BF_4$ (1:1 molar ratio)[12]

Under nitrogen atmosphere, $[Ir(COD)_2]BF_4$ (2.2 mg, 0.0045 mmol) was dissolved in CH_2Cl_2 (1.0 mL). A solution of (+)-Xyl-P16C6-Phos (4.8 mg, 0.0047 mmol) in CH_2Cl_2 (1.0 mL) was added dropwise to the above solution with stirring. The reaction mixture was stirred overnight to give a solution of Ir catalyst based on (+)-Xyl-P16C6-Phos and $[Ir(COD)_2]BF_4$ (1:1 molar ratio, 2.3×10^{-3} mol•L^{-1}). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 13.45.

Preparation of a Stock Solution of Ir Catalyst Based on (+)-Xyl-P16C6-Phos, $[Ir(COD)_2]BF_4$ and $NaBAr_F$ (1:1:10 molar ratio)[11]

Under nitrogen atmosphere, a solution of (+)-Xyl-P16C6-Phos (9.6 mg, 9.5×10^{-3} mmol) and $NaBAr_F$ (79.8 mg, 9.0×10^{-2} mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 2 hours. Then to the mixture, a solution of $[Ir(COD)_2]BF_4$ (4.5 mg, 9.0×10^{-3} mmol) in CH_2Cl_2 (2 mL) was added dropwise. The reaction mixture was stirred overnight to give a solution of Ir catalyst based on (+)-Xyl-P16C6-Phos, $[Ir(COD)_2]BF_4$ and $NaBAr_F$ (1:1:10 molar ratio, 2.3×10^{-3} mol•L^{-1}). ^{31}P NMR (202 MHz, $CDCl_3$): δ 14.65.

III. Stacked ^{1}H and ^{31}P NMR Spectra of Ligands and Self-Assembled Catalysts

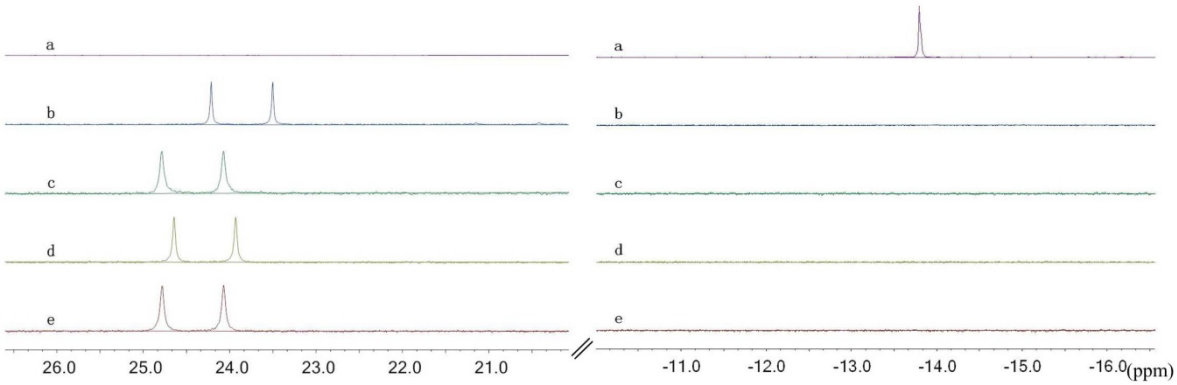


Fig S1 $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) Spectra of [a] (–)-**7**; [b] (–)-**7** + $[Rh(COD)_2]BF_4$ (1:1 molar ratio); [c] (–)-**7** + $[Rh(COD)_2]BF_4$ + $LiBAr_F$ (1:1:2 molar ratio); [d] (–)-**7** + $[Rh(COD)_2]BF_4$ + $NaBAr_F$ (1:1:2 molar ratio); [e] (–)-**7** + $[Rh(COD)_2]BF_4$ + $KBAr_F$ (1:1:2 molar ratio).

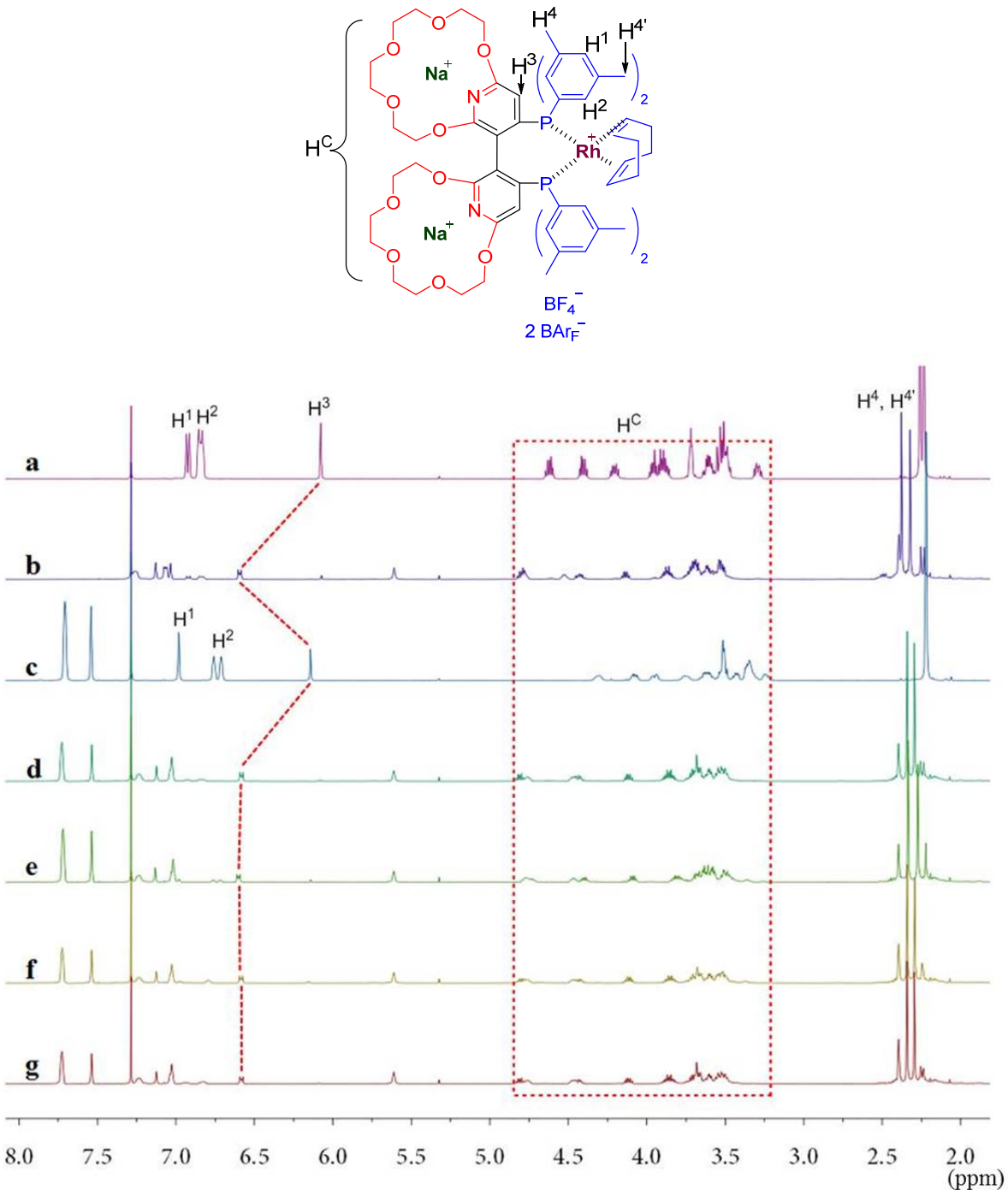


Fig S2 Stacked ^{1}H NMR (400 MHz, $CDCl_3$) spectra of [a] (–)-**7**; [b] (–)-**7** + $[Rh(COD)_2]BF_4$ (1:1 molar ratio); [c] (–)-**7** + $NaBAr_F$ (1:2 molar ratio); [d] (–)-**7** + $[Rh(COD)_2]BF_4$ + $NaBAr_F$ (1:1:1 molar ratio); [e] (–)-**7** + $[Rh(COD)_2]BF_4$ + $NaBAr_F$ (1:1:2 molar ratio); [f] (–)-**7** + $[Rh(COD)_2]BF_4$ + $NaBAr_F$ (1:1:5 molar ratio); [g] (–)-**7** + $[Rh(COD)_2]BF_4$ + $NaBAr_F$ (1:1:10 molar ratio).

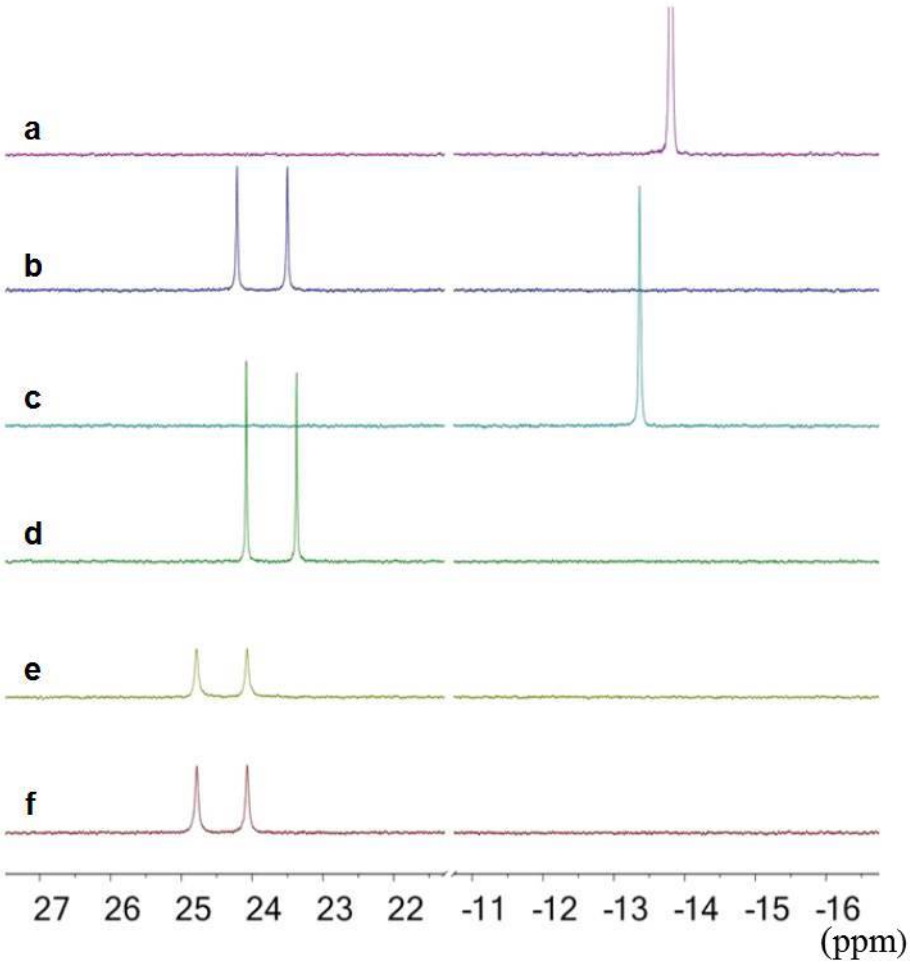


Fig S3 Stacked $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$) spectra of [a] (–)-**7**; [b] (–)-**7** + $[Rh(COD)_2]BF_4$ (1:1 molar ratio); [c] (–)-**7** + $NaBAr_F$ (1:2 molar ratio); [d] (–)-**7** + $[Rh(COD)_2]BF_4$ + $NaBAr_F$ (1:1:1 molar ratio); [e] (–)-**7** + $[Rh(COD)_2]BF_4$ + $NaBAr_F$ (1:1:2 molar ratio); [f] (–)-**7** + $[Rh(COD)_2]BF_4$ + $NaBAr_F$ (1:1:10 molar ratio).

IV. The Job Plots of the Complexes between (±)-7 or (±)-6 and $MBAr_F$ (M = Li, Na, or K)

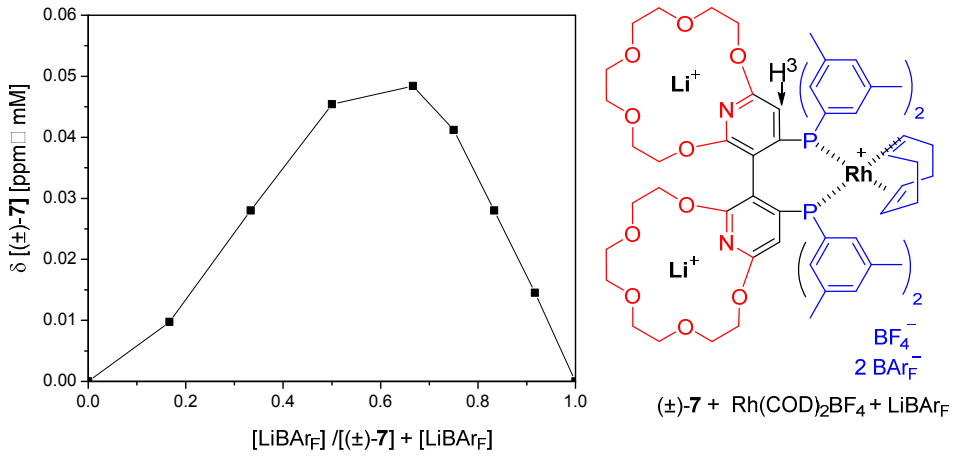


Fig S4 Job plot showing the 2:1 stoichiometry of the complex between (±)-**7** and $LiBAr_F$ in $CDCl_3$ using NMR data for H^3. Delta (δ) is the chemical shift change corresponding to H^3. [(±)-**7** + $[Rh(COD)]BF_4]_0$ + $[LiBAr_F]_0$ = 0.012 mM.

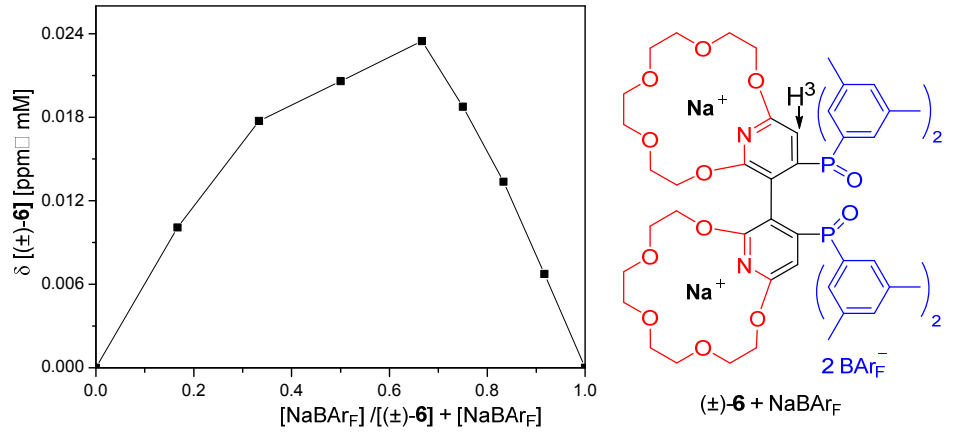


Fig S5 Job plot showing the 2:1 stoichiometry of the complex between (±)-**6** and $NaBAr_F$ in acetone-d_6 using NMR data for H^3. Delta (δ) is the chemical shift change corresponding to H^3. $[(\pm)\text{-}\mathbf{6}]_0$ + $[NaBAr_F]_0$ = 0.012 mM.

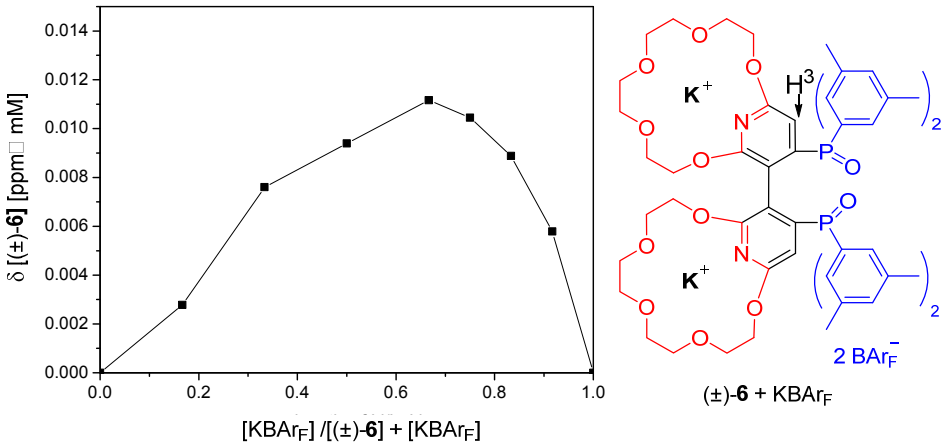


Fig S6 Job plot showing the 2:1 stoichiometry of the complex between (±)-**6** and $KBAr_F$ in acetone-d_6 using NMR data for H^3. Delta (δ) is the chemical shift change corresponding to H^3. $[(\pm)\text{-}\mathbf{6}]_0 + [KBAr_F]_0 = 0.012$ mM.

V. The ESI-MS Spectra of the Complexes between (±)-7and $MBAr_F$ (M = Li, Na, or K)

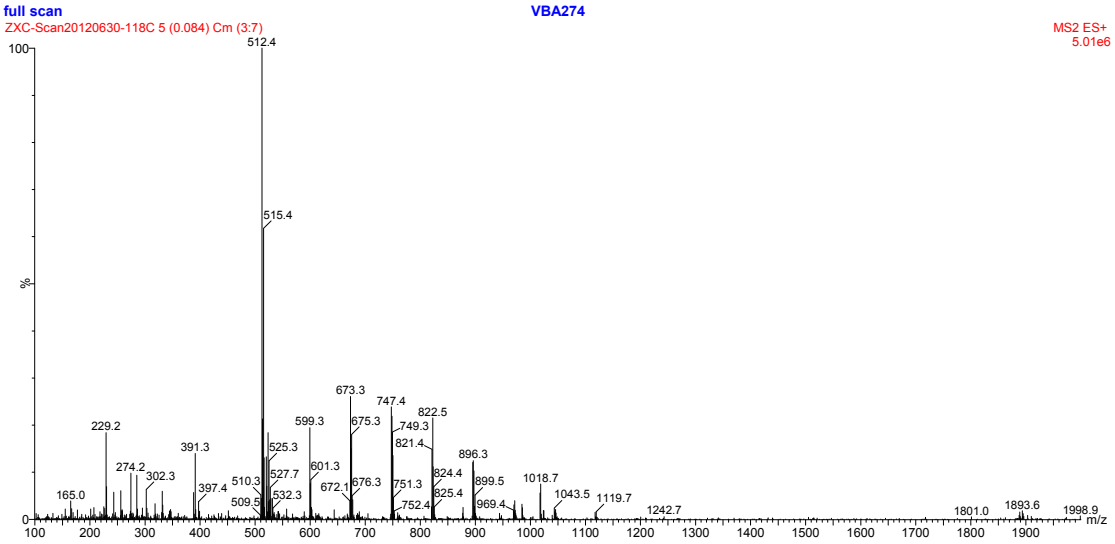


Fig S7 Electrospray mass spectrum of a solution of (±)-**7** and $LiBAr_F$ (2 equiv) in CH_2Cl_2. $[(\pm)\text{-}\mathbf{7} + 2\ Li + BAr_F]^+$: calculated, 1894.2; found, 1893.6. $[(\pm)\text{-}\mathbf{7} + 2\ Li]^{2+}$: calculated, 515.5; found, 515.4.

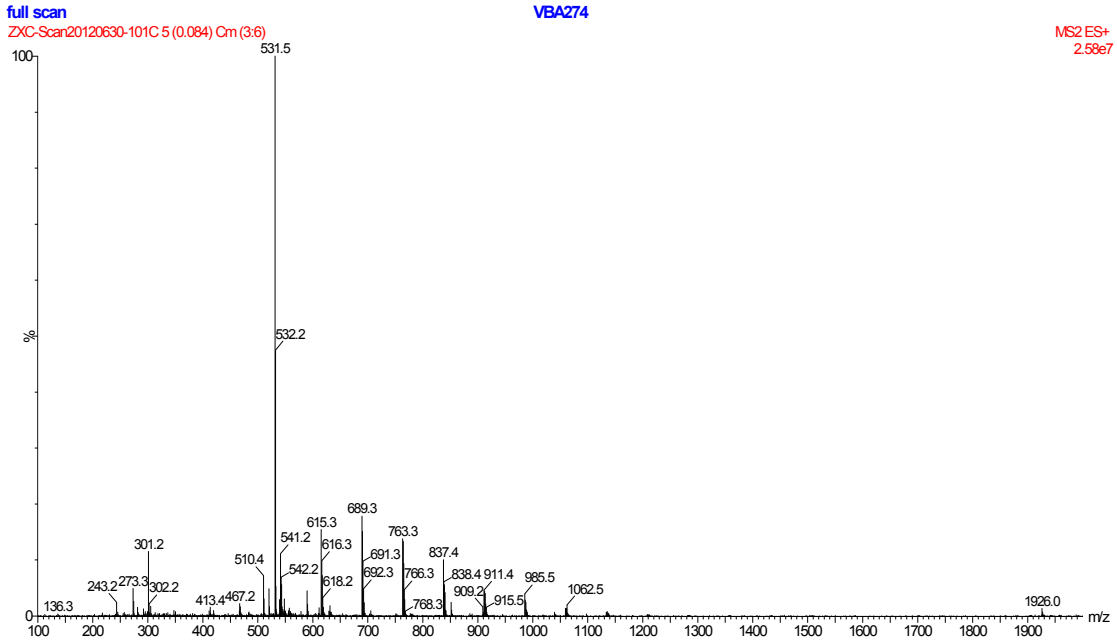


Fig S8 Electrospray mass spectrum of a solution of (±)**7** and $NaBAr_F$ (2 equiv) in CH_2Cl_2. [(±)-**7** + 2 Na + BAr_F]$^+$: calculated, 1926.3; found, 1926.0. [(±)-**7** + 2 Na]$^{2+}$: calculated, 531.6; found, 531.5.

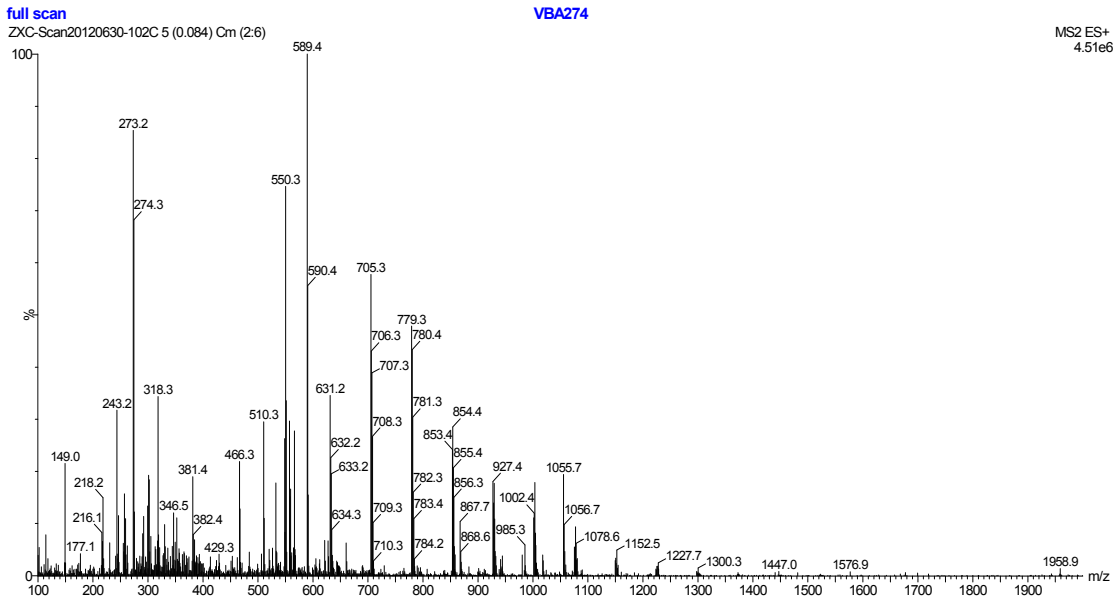


Fig S9 Electrospray mass spectrum of a solution of (±)-**7** and $KBAr_F$ (2 equiv) in CH_2Cl_2. [(±)-**7** + 2 K + BAr_F]$^+$: calculated, 1958.5; found, 1958.9. [(±)-**7** + K]$^+$: calculated, 1056.2; found, 1056.7.

VI. Stacked ^{1}H and ^{31}P NMR Spectra of Self-Assembled Ir Catalysts

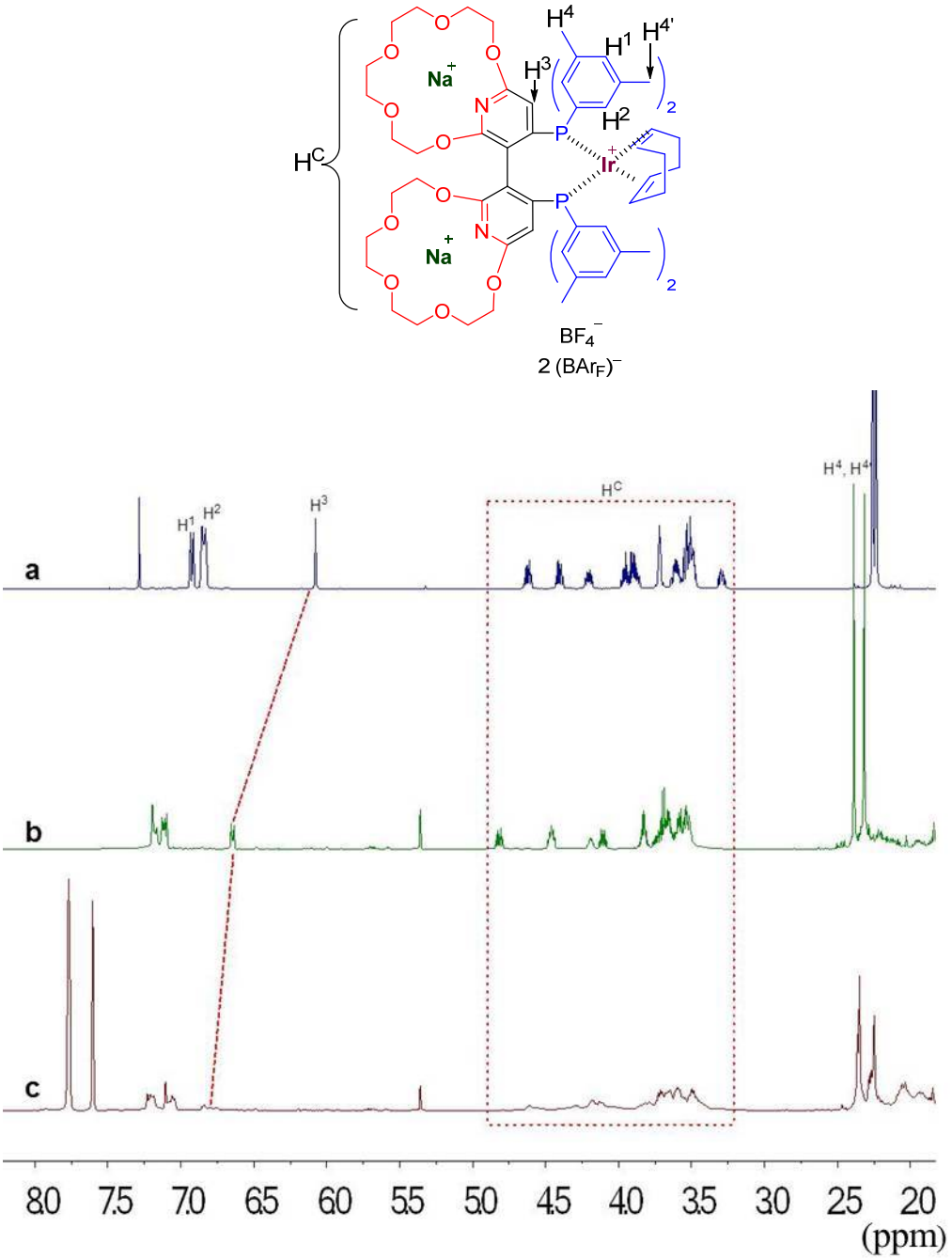


Fig S10 Stacked ^{1}H NMR (500 MHz, CD_2Cl_2) spectra of [a] (+)-**7**; [b] (+)-**7** + $[Ir(COD)_2]BF_4$ (1:1 molar ratio); [c] (+)-**7** + $[Ir(COD)_2]BF_4$ + $NaBAr_F$ (1:1:10 molar ratio).

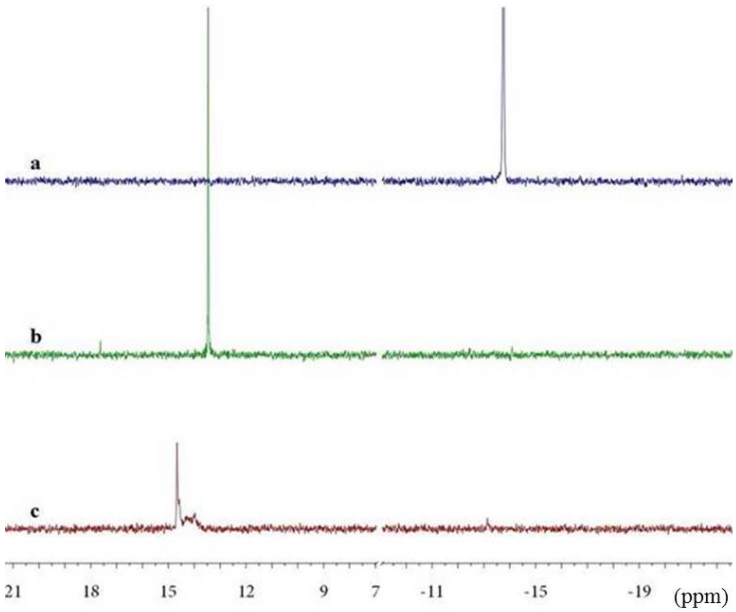


Fig S11 Stacked ^{31}P NMR (202 MHz, CD_2Cl_2) spectra of [a] (+)-**7**; [b] (+)-**7** + $[Ir(COD)_2]BF_4$ (1:1 molar ratio); [c] (+)-**7** + $[Ir(COD)_2]BF_4$ + $NaBAr_F$ (1: 1: 10 molar ratio).

VII. General Procedure for the Rh-catalyzed Asymmetric Hydrogenation of *α*-Dehydroamino Acid Esters[10,11]

Typical procedure for the asymmetric hydrogenation of methyl-(*Z*)-2-acetamidocinnamate 8a (Table 2, entry 8)

A solution of 2.2×10^{-3} mol•L^{-1} catalyst based on (–)-**7**, $Rh(COD)_2BF_4$ and $NaBAr_F$ (1:1:10 molar ratio) in CH_2Cl_2 (428 μL, 9.5×10^{-4} mmol), methyl-(*Z*)-2-acetamidocinnamate (20.8 mg, 9.5×10^{-2} mmol) and *c*-hexane (2 mL) were charged to a 25 mL glass-lined stainless steel reactor equipped with a magnetic stirring bar under nitrogen atmosphere. Hydrogen was initially introduced into the autoclave at a pressure of 8 atm before being reduced to 1 atm by carefully releasing the stop valve. After this procedure was repeated for three times, the vessel was pressurized to 1 atm. The reaction mixture was stirred at ambient temperature for 6 h. The conversion and the enantiomeric excess of the hydrogenation product, (*R*)-2-acetamido-3-phenylpropanoste ((*R*)-**9a**) were determined by NMR and chiral GC analysis to be >99% and 97%, respectively (column, Chrompack Chirasil-L-Val, 25 m × 0.25 mm, carrier gas, N_2). The isolated product (19.6 mg, 94% yield) was obtained by column chromatography on silica gel (ethyl acetate: petroleum ether =

1:10).

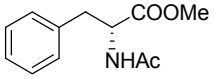
VIII. General Procedure for the Ir-catalyzed Asymmetric Hydrogenation of 2-Alkyl-Substituted Quinoline Derivatives[13]

Typical procedure for the Ir-catalyzed asymmetric hydrogenation of 2-methylquinoline 10a (Table 3, entry 3)

2-Methylquinoline (57.3 mg, 0.40 mmol) and a solution of 2.3×10^{-3} mol•L^{-1} catalyst based on (+)-**7**, $[Ir(COD)_2]BF_4$ and $NaBAr_F$ (1:1:10 molar ratio) in CH_2Cl_2 (1.7 mL, 4.0×10^{-3} mmol) were charged to a 25 mL glass-lined stainless steel reactor with a magnetic stirring bar under nitrogen atmosphere. The solvent was removed, then ethyl acetate (2 mL) and I_2 (10.2 mg, 4.0×10^{-2} mmol) were added. Hydrogen was initially introduced into the autoclave at a pressure of 50 atm before being reduced to 1 atm. After this procedure was repeated for three times, the autoclave was pressurized with H_2 to 50 atm. The hydrogenation was performed under this H_2 pressure at room temperature for 24 h. After carefully releasing the hydrogen, the reaction mixture was diluted with CH_2Cl_2 (2 mL), then saturated $NaHCO_3$ aqueous solution (2 mL) was added. After stirring for 15 min, the aqueous layer was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated to afford the crude product, which was purified by flash chromatography on silica gel (petroleum ether:ethyl acetate = 10:1 to give the pure product (*R*)-2-methyl-1,2,3,4-tetrahydroquinoline ((*R*)-**11a**, 56.6 mg, 96% yield). The enantiomeric excess of (*R*)-**11a** was determined to be 97% by chiral HPLC with a 25 cm × 4.6 mm Daicel Chiralcel OJ-H columns (eluent, hexanes/*i*-PrOH = 95/5, flow rate: 0.5 mL•min^{-1}; detection: 254 nm light).

IX. Analytical Data and Spectra for 9a–t and 11a–e

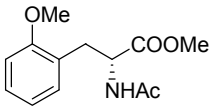
(*R*)-*N*-acetyl-phenylalanine methyl ester (9a)[14]



^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23–7.31 (m, 3H), 7.09 (d, J = 7.0 Hz, 2H), 5.92 (d, J = 6.5 Hz, 1H), 4.87–4.91 (m, 1H), 3.73 (s, 3H), 3.08–3.17 (m, 2H), 1.98 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.10, 169.59, 135.83, 129.25, 128.61, 127.16, 53.12, 52.35, 37.87, 23.17. IR (thin film): ν_{max} (cm^{-1}) = 3253, 3002, 2953, 1724, 1668, 1436, 1205, 986, 842, 770, 693.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 170 °C, isothermal; t_R (**8a**) = 18.28 min; t_R (*S*) = 7.16 min; t_R (*R*) = 7.72 min.

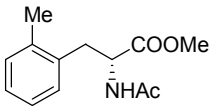
(*R*)-*N*-acetyl-*o*-methoxylphenylalanine methyl ester (9b)[15]



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–7.27 (m, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.86–6.92 (m, 2H), 6.26 (d, J = 6.4 Hz, 1H), 4.75 (q, J = 6.9 Hz, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 3.10 (d, J = 6.4 Hz, 2H), 1.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.50, 169.79, 157.52, 131.20, 128.62, 124.58, 120.85, 110.55, 55.42, 53.13, 52.18, 32.36, 23.04. IR (thin film): ν_{max} (cm^{-1}) = 3262, 3004, 2952, 1726, 1668, 1248, 1199, 1165, 986, 845, 757.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 150 °C, isothermal; t_R (**8b**) = 85.07 min; t_R (*S*) = 29.22 min; t_R (*R*) = 32.49 min.

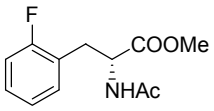
(*R*)-*N*-acetyl-*o*-methylphenylalanine methyl ester (9c)[16]



^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95–7.05 (m, 4H), 6.55 (br, 1H), 4.74 (q, J = 7.3 Hz, 1H), 3.56 (s, 3H), 2.87–3.06 (m, 2H), 2.23 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.74, 170.11, 136.63, 134.53, 130.53, 129.71, 127.14, 125.91, 52.58, 52.20, 35.58, 22.85, 19.28. IR (thin film): ν_{max} (cm^{-1}) = 3263, 3020, 2953, 1728, 1667, 1436, 1225, 986, 849, 753.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 165 °C, isothermal; t_R (**8c**) = 27.30 min; t_R (*S*) = 11.99 min; t_R (*R*) = 13.24 min.

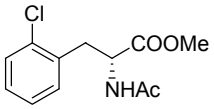
(*R*)-*N*-acetyl-*o*-fluorophenylalanine methyl ester (9d)[17]



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.00–7.27 (m, 4H), 6.08 (d, J = 6.8 Hz, 1H), 4.86 (q, J = 6.4 Hz, 1H), 3.73 (s, 3H), 3.09–3.24 (m, 2H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.00, 169.70, 162.67, 160.14, 131.67, 131.62, 129.09, 129.00, 128.22, 125.30, 124.22, 124.18, 123.07, 122.92, 115.49, 115.26, 52.49, 52.45, 31.41, 23.04. IR (thin film): ν_{max} (cm^{-1}) = 3225, 3004, 2955, 2850, 1729, 1667, 1484, 1455, 1439, 1374, 1305, 1263, 1235, 758.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 150 °C, isothermal; t_R (**8d**) = 29.73 min; t_R (*S*) = 13.28 min; t_R (*R*) = 14.78 min.

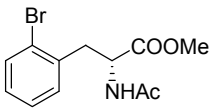
(*R*)-*N*-acetyl-*o*-chlorophenylalanine methyl ester (9e)[14]



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19–7.36 (m, 4H), 6.12 (d, J = 7.2 Hz, 1H), 4.90 (q, J = 7.1 Hz, 1H), 3.72 (s, 3H), 3.15–3.33(m, 2H), 1.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.12, 169.69, 134.48, 134.11, 131.29, 129.67, 128.60, 126.96, 52.49, 52.48, 35.41, 23.09. IR (thin film): ν_{max} (cm^{-1}) = 3220, 3002, 2953, 2849, 1726, 1663, 1467, 1438, 1371, 1294, 1254, 1212, 1128, 780, 689.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 170 °C, isothermal; t_R (**8e**) = 35.61 min; t_R (*S*) = 13.85 min; t_R (*R*) = 15.14 min.

(*R*)-*N*-acetyl-*o*-bromophenylalanine methyl ester (9f)[18]

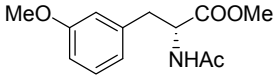


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09–7.55 (m, 4H), 6.21 (d, J = 7.6 Hz, 1H), 4.91 (q, J = 7.2 Hz, 1H), 3.71 (s, 3H), 3.14–3.34 (m, 2H), 1.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.14, 169.79, 135.96, 132.99, 131.19, 128.80, 127.59, 124.98, 52.53, 52.50, 37.86, 23.06. IR (thin film): ν_{max} (cm^{-1}) = 3255, 3002, 2952, 1727, 1670, 1465, 1436, 1370, 1294, 1256, 1207, 745, 665.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 170 °C,

isothermal; t_R (**8f**) = 36.63 min; t_R (*S*) = 19.50 min; t_R (*R*) = 21.32 min.

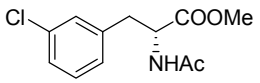
(*R*)-*N*-acetyl-*m*-methoxyphenylalanine methyl ester (9g)[15,17]



^{1}H NMR (400 MHz, $CDCl_3$): δ 6.57–7.20 (m, 4H), 5.94 (d, *J* = 6.8 Hz, 1H), 4.80 (q, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 2.97–3.07 (m, 2H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.09, 169.66, 159.71, 137 .37, 129.58, 121.54, 115.03, 112.43, 55.15, 53.07, 52.36, 37.83, 23.15. IR (thin film): ν_{max} (cm^{-1}) = 3261, 2953, 1723, 1667, 1435, 1372, 1298, 1240, 1194, 1162, 1119, 787, 730.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 170 °C, isothermal; t_R (**8g**) =41.74 min; t_R (*S*) = 15.37 min; t_R (*R*) = 16.67 min.

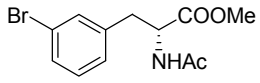
(*R*)-*N*-acetyl-*m*-chlorophenylalanine methyl ester (9h)[14]



^{1}H NMR (400 MHz, $CDCl_3$): δ 6.98–7.23 (m, 4H), 6.13 (d, *J* = 6.8 Hz, 1H), 4.87 (q, *J* = 6.5 Hz, 1H), 3.74 (s, 3H), 3.02–3.16 (m, 2H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.86, 169.75, 138.01, 134.30, 129.80, 129.43, 127.39, 127.33, 53.06, 52.45, 37.53, 23.09. IR (thin film): ν_{max} (cm^{-1}) = 3255, 3003, 2953, 1724, 1668, 1489, 1436, 1372, 1311, 1286, 1256, 1204, 1114, 766, 684.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 170 °C, isothermal; t_R (**8h**) = 37.34 min; t_R (*S*) = 14.47 min; t_R (*R*) = 15.95 min.

(*R*)-*N*-acetyl-*m*-bromophenylalanine methyl ester (9i)[18]

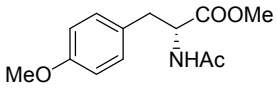


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07–7.44 (m, 4H), 6.09 (d, *J* = 7.2 Hz, 1H), 4.91 (q, *J* = 6.4 Hz, 1H), 3.78 (s, 3H), 3.07–3.20 (m, 2H), 2.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.82, 169.70, 138.26, 132.38, 130.27, 130.10, 129.04, 128.22, 127.85, 125.31, 122.55, 53.07, 52.47, 37.51, 23.14. IR (thin film): ν_{max} (cm^{-1}) = 3263, 3001, 2951, 1725, 1668, 1435, 1371, 1291, 1203, 1123, 899, 887, 788, 738.

The conversion and ee value were determined by Capillary GC with a

Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 170 °C, isothermal; t_R (**8i**) = 56.23 min; t_R (*S*) = 20.68 min; t_R (*R*) = 22.88 min.

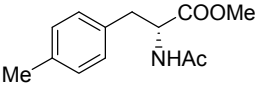
(*R*)-*N*-acetyl-*p*-methoxyphenylalanine methyl ester (9j)[14,15]



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (d, J = 7.6 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 5.95 (d, J = 7.2 Hz, 1H), 4.87 (q, J = 6.3 Hz, 1H), 3.74 (s, 3H), 3.03–3.13 (m, 2H), 2.32 (s, 3H), 1.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.24, 169.78, 136.74, 132.66, 129.31, 129.11, 53.19, 52.38, 37.36, 23.16, 21.12. IR (thin film): ν_{max} (cm^{-1}) = 3258, 2953, 2841, 1719, 1667, 1436, 1372, 1255, 1208, 1177, 1119, 831, 788.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 170 °C, isothermal; t_R (**8j**) = 57.18 min; t_R (*S*) = 17.43 min; t_R (*R*) = 18.92 min.

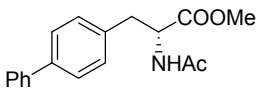
(*R*)-*N*-acetyl-*p*-methylphenylalanine methyl ester (9k)[16,20]



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, J = 7.6 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.02 (d, J = 7.2 Hz, 1H), 4.85 (q, J = 6.4 Hz, 1H), 3.72 (s, 3H), 3.01–3.12 (m, 2H), 2.31 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.21, 169.66, 136.72, 132.69, 129.30, 129.10, 53.19, 52.30, 37.40, 23.13, 21.07. IR (thin film): ν_{max} (cm^{-1}) = 3256, 2952, 1723, 1667, 1259, 1205, 1185, 814, 736.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 170 °C, isothermal; t_R (**8k**) = 12.72 min; t_R (*S*) = 8.22 min; t_R (*R*) = 8.85 min.

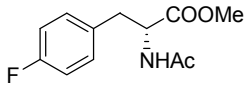
(*R*)-*N*-acetyl-*p*-phenylphenylalanine methyl ester (9l)[17]



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15–7.58 (m, 9H), 6.03 (br, 1H), 4.92 (q, J = 6.3 Hz, 1H), 3.75 (s, 3H), 3.11–3.22 (m, 2H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.13, 169.71, 169.68, 140.63, 140.03, 134.90, 129.70, 128.81, 127.34, 127.29, 127.00, 53.13, 52.41, 37.48, 23.19. IR (thin film): ν_{max} (cm^{-1}) = 3255, 3029, 2952, 1722, 1666, 1434, 1372, 1320, 1272, 1193, 1120, 834, 770, 718, 697.

The conversion was determined by ^{1}H NMR [^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker advance 400 spectrophotometer (400 MHz)]. The ee value was determined by chiral HPLC analysis with a 25 cm × 4.6 mm Daicel Chiralcel AD column (eluent, 2-propanol/hexane 30/70; flow rate: 1.0 mL•min^{-1}; detection: 254 nm light, 20 °C); t_R (*S*) = 5.39 min; t_R (*R*) = 7.26 min.

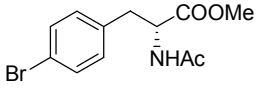
(*R*)-*N*-acetyl-*p*-fluorophenylalanine methyl ester (9m)[15]



^{1}H NMR (400 MHz, $CDCl_3$): δ 6.95–7.10 (m, 2H), 6.42 (s, 1H), 4.83 (q, J = 6.5 Hz, 1H), 3.71 (s, 3H), 3.00–3.14 (m, 2H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.07, 169.93, 163.16, 160.72, 131.76, 131.74, 130.75, 130.67, 115.46, 115.25, 53.27, 52.30, 37.02, 29.65, 22.92. IR (thin film): ν_{max} (cm^{-1}) = 3246, 3002, 2954, 1723, 1668, 1437, 1373, 1311, 1230, 1203, 835, 799.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 165 °C, isothermal; t_R (**8m**) = 27.24 min; t_R (*S*) = 9.04 min; t_R (*R*) = 9.96 min.

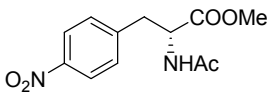
(*R*)-*N*-acetyl-*p*-bromophenylalanine methyl ester (9n)[19]



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 8.4 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 6.35 (d, J = 7.2 Hz, 1H), 4.84 (q, J = 6.5 Hz, 1H), 3.71 (s, 3H), 2.98–3.13 (m, 2H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.92, 169.82, 135.06, 131.61, 130.95, 121.06, 53.02, 52.39, 37.23, 23.99. IR (thin film): ν_{max} (cm^{-1}) = 3242, 3000, 2952, 1724, 1668, 1486, 1436, 1402, 1371, 1311, 1284, 1252, 1204, 894, 819.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 170 °C, isothermal; t_R (**8n**) = 46.41 min; t_R (*S*) = 16.85 min; t_R (*R*) = 18.39 min.

(*R*)-*N*-acetyl-*p*-nitrophenylalanine methyl ester (9o)[15]

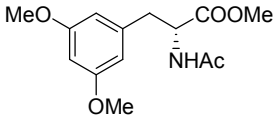


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.13 (d, J = 6.8 Hz, 1H), 4.93 (q, J = 6.4 Hz, 1H), 3.75 (s, 3H), 3.16–3.32 (m, 2H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$):

δ 171.52, 169.76, 147.16, 143.89, 130.19, 130.09, 123.69, 52.91, 52.65, 37.82, 23.11. IR (thin film): ν_{max} (cm^{-1}) = 3237, 3003, 2953, 1724, 1666, 1517, 1435, 1374, 1342, 1310, 866, 762.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 180 °C, isothermal; t_R (**8o**) = 92.98 min; t_R (*S*) = 54.79 min; t_R (*R*) = 60.34 min.

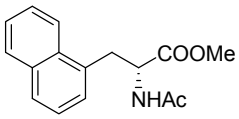
(*R*)-*N*-acetyl-3,5-bis(methoxyl)phenylalanine methyl ester (9p)[20]



^{1}H NMR (400 MHz, $CDCl_3$): δ 6.33 (s, 1H), 6.23 (d, *J* = 2.4 Hz, 2H), 6.05 (d, *J* = 6.0 Hz, 1H), 4.86 (q, *J* = 6.5 Hz, 1H), 3.76 (s, 6H), 3.74 (s, 3H), 2.98–3.08 (m, 2H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.07, 169.67, 160.85, 138.07, 107.27, 98.94, 55.26, 52.99, 52.35, 37.99, 23.14. IR (thin film): ν_{max} (cm^{-1}) = 3152, 2953, 2838, 1724, 1643, 1455, 1429, 1373, 1292, 1273, 1238, 1206, 1156, 1122, 851, 840.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 175 °C, isothermal; t_R (**8p**) = 92.51 min; t_R (*S*) = 28.62 min; t_R (*R*) = 31.00 min.

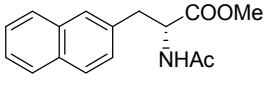
(*R*)-*N*-acetyl-1-Naphthylalanine methyl ester (9q)[15]



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–8.09 (m, 7H), 6.01 (d, *J* = 7.2 Hz, 1H), 5.01 (q, *J* = 6.8 Hz, 1H), 3.62 (s, 3H), 3.54–3.59 (m, 2H), 1.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.35, 169.76, 133.89, 132.37, 132.31, 128.85, 128.01, 127.37, 126.32, 125.82, 125.26, 123.66, 53.27, 52.26, 35.08, 29.71, 23.12. IR (thin film): ν_{max} (cm^{-1}) = 3231, 1720, 1657, 1431, 1375, 1341, 1250, 1124, 787, 770, 751.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 180 °C, isothermal; t_R (**8q**) = 56.20 min; t_R (*S*) = 31.17 min; t_R (*R*) = 33.72 min.

(*R*)-*N*-acetyl-2-Naphthylalanine methyl ester (9r)[15]

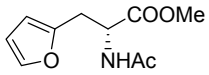


^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20–7.81 (m, 7H), 6.01 (d, *J* =

7.2 Hz, 1H), 4.96 (q, J = 6.4 Hz, 1H), 3.72 (s, 3H), 3.22–3.33 (m, 2H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.17, 169.71, 133.44, 133.42, 132.52, 128.30, 128.04, 127.70, 127.57, 127.25, 126.24, 125.83, 53.20, 52.38, 38.04, 23.14. IR (thin film): ν_{max} (cm^{-1}) = 3251, 3004, 2955, 2850, 1729, 1667, 1645, 1455, 1439, 1374, 1305, 1263, 1235, 1187, 1130, 1101, 809, 758.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 180 °C, isothermal; t_R (**8r**) = 110.2 min; t_R (*S*) = 37.07 min; t_R (*R*) = 40.46 min.

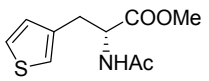
(*R*)-*N*-acetyl-2-furanylalanine methyl ester (9s)[21]



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (s, 1H), 6.28 (s, 1H), 6.24 (br, 1H), 6.07 (d, J = 3.2 Hz, 1H), 4.85 (q, J = 4.4 Hz, 1H), 3.75 (s, 3H), 3.18 (d, J = 5.2 Hz, 2H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.74, 169.78, 150.37, 142.20, 110.36, 107.91, 52.54, 51.48, 30.53, 23.10. IR (thin film): ν_{max} (cm^{-1}) = 3261, 3004, 2954, 1720, 1670, 1660, 1473, 1437, 1368, 1286, 1213, 1150, 1119, 798, 751.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 160 °C, isothermal; t_R (**8s**) = 15.01 min; t_R (*S*) = 4.99 min; t_R (*R*) = 5.30 min.

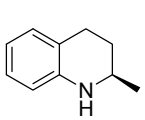
(*R*)-*N*-acetyl-3-thiophenylalanine methyl ester (9t)[20]



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (t, J = 3.6 Hz, 1H), 6.98 (s, 1H), 6.84 (d, J = 4.8 Hz, 1H), 6.02 (d, J = 6.0 Hz, 1H), 4.86 (q, J = 7.6 Hz, 1H), 3.74 (s, 3H), 3.15–3.19 (m, 2H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.10, 169.69, 136.00, 128.25, 126.06, 122.72, 52.66, 52.45, 32.38, 23.18. IR (thin film): ν_{max} (cm^{-1}) = 3254, 2952, 1720, 1666, 1436, 1353, 1261, 1207, 1165, 1119, 788.

The conversion and ee value were determined by Capillary GC with a Chrompack Chirasil-L-Val column (25 m × 0.25 mm, carrier gas, N_2), 170 °C, isothermal; t_R (**8t**) = 27.59 min; t_R (*S*) = 8.04 min; t_R (*R*) = 8.69 min.

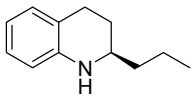
(*R*)-2-Methyl-1,2,3,4-tetrahydroquinoline (11a)[13b,c]



^{1}H NMR (500 MHz, $CDCl_3$): δ 6.96–6.99 (m, 2H), 6.62 (t, J = 7.8 Hz, 1H), 6.49 (d, J = 9.0 Hz, 1H), 3.69 (br, 1H), 3.39–3.45 (m, 1H), 2.72–2.89 (m, 2H), 1.92–1.97 (m, 1H), 1.65–1.57 (m, 1H), 1.23 (d, J = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.81, 129.28, 126.71, 121.13, 117.01, 114.03, 47.20, 30.19, 26.62, 22.63; MS-EI Calculated for $C_{10}H_{13}N$ [M^+]: 147.1; found: 147.0.

The ee value was determined by chiral HPLC analysis with a 25 cm × 4.6 mm Daicel Chiralcel OJ-H column (eluent, hexanes/*i*-PrOH = 95/5, flow rate: 0.5 mL•min^{-1}; detection: 254 nm light), t_R (*S*) =29.61 min, t_R (*R*) = 33.33 min.

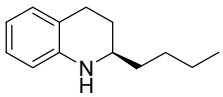
(*R*)-2-Propyl-1,2,3,4-tetrahydroquinoline (11b)[13b,c]



^{1}H NMR (500 MHz, $CDCl_3$): δ 6.97–7.00 (m, 2H), 6.62 (t, J = 7.5 Hz, 1H), 6.49 (d, J = 7.5 Hz, 1H), 3.77 (br, 1H), 3.25–3.30 (m, 1H), 2.73–2.87 (m, 2H), 1.96–2.01 (m, 1H), 1.43–1.66 (m, 5H), 0.99 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.77, 129.28, 126.72, 121.41, 116.90, 114.06, 51.35, 38.95, 28.17, 26.48, 18.94, 14.24. MS-EI Calculated for $C_{12}H_{17}N$ [M^+]: 175.1; found: 175.0.

The ee value was determined by chiral HPLC analysis with a 25 cm × 4.6 mm Daicel Chiralcel OJ-H column (eluent, hexanes/*i*-PrOH = 95/5, flow rate: 0.5 mL•min^{-1}; detection: 254 nm light), t_R (*S*) = 22.37 min, t_R (*R*) = 28.78 min.

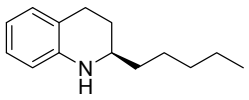
(*R*)-2-Butyl-1,2,3,4-tetrahydroquinoline (11c)[13b,c]



^{1}H NMR (500 MHz, $CDCl_3$): δ 6.95–6.98 (m, 2H), 6.61 (t, J = 7.3 Hz, 1H), 6.48 (d, J = 7.5 Hz, 1H), 3.77 (br, 1H), 3.22–3.27 (m, 1H), 2.71–2.86 (m, 2H), 1.95–2.00 (m, 1H), 1.39–1.65 (m, 7H), 0.95 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.77, 129.26, 126.71, 121.41, 116.89, 114.04, 51.62, 36.46, 28.17, 27.95, 26.47, 22.87, 14.11. MS-EI Calculated for $C_{13}H_{19}N$ [M^+]: 189.2; found: 189.0.

The ee value was determined by chiral HPLC analysis with a 25 cm × 4.6 mm Daicel Chiralcel OJ-H column (eluent, hexanes/*i*-PrOH = 95/5, flow rate: 0.5 mL•min^{-1}; detection: 254 nm light), t_R (*S*) = 19.24 min, t_R (*R*) = 22.73 min.

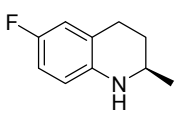
(*R*)-2-Pentyl-1,2,3,4-tetrahydroquinoline (11d)[13b,c]



^{1}H NMR (500 MHz, $CDCl_3$): δ 6.95–6.98 (m, 2H), 6.61 (t, J = 7.8 Hz, 1H), 6.48 (d, J = 8.0 Hz, 1H), 3.77 (br, 1H), 3.22–3.27 (m, 1H), 2.71–2.86 (m, 2H), 1.95–2.00 (m, 1H), 1.56–1.65 (m, 1H), 1.30–1.52 (m, 8H), 0.93 (t, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 144.76, 129.26, 126.71, 121.41, 116.89, 114.04, 51.63, 36.72, 31.99, 28.17, 26.47, 25.43, 22.67, 14.07. MS-EI Calculated for $C_{14}H_{21}N$ [M^+]: 203.2; found: 203.0.

The ee value was determined by chiral HPLC analysis with a 25 cm × 4.6 mm Daicel Chiralcel OJ-H column (eluent, hexanes/*i*-PrOH = 95/5, flow rate: 0.5 mL•min^{-1}; detection: 254 nm light), t_R (*S*) = 17.43 min, t_R (*R*) = 19.22 min.

(*R*)-6-Fluoro-2-methyl-1,2,3,4-tetrahydroquinoline (11e)[13b,c]



^{1}H NMR (400 MHz, $CDCl_3$): δ 6.66–6.71 (m, 2H), 6.39–6.42 (m, 1H), 3.53 (br, 1H), 3.31–3.39 (m, 1H), 2.67–2.87 (m, 2H), 1.89–1.95 (m, 1H), 1.51–1.62 (m, 1H), 1.21 (d, J = 6.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 156.45, 154.59, 140.99, 122.50, 122.45, 115.48, 115.31, 114.73, 114.68, 113.25, 113.08, 47.32, 29.92, 26.73, 22.51. MS-EI Calculated for $C_{10}H_{12}FN$ [M^+]: 165.1; found: 165.1.

The ee value was determined by chiral HPLC analysis with a 25 cm × 4.6 mm Daicel Chiralcel OD-H column (eluent, hexanes/*i*-PrOH = 94/6, flow rate: 1.0 mL•min^{-1}; detection: 254 nm light), t_R (*R*) = 6.37 min, t_R (*S*) = 7.95 min.

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