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# IMPROVED SYNTHESIS OF CYCLOHEXANE-BACKBONE IRIDIUM-COMPLEXES OF QUINOLINE-PHOSPHINE AND THEIR APPLICATIONS IN ASYMMETRIC HYDROGENATION

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**Abstract** – The iridium-complexes **3** and **4** with cyclohexane-backbone derived from quinoline were easily synthesized. The key step is *cis*/*trans* stereoselective reduction of 2-(quinolin-2-yl)cyclohexanone **5** to *trans*-2-(quinolin-2-yl)cyclohexanol **6** using Al(O*i*-Pr)$_3$/*i*-PrOH and the following diastereomeric optical resolution of racemic **6** using 0.50 equiv (*S*)-mandelic acid in EtOAc. These complexes were used in the asymmetric hydrogenation of (*E*)-1,2-diphenylpropene with up to 13% ee/48% conv. using **3** and 35% ee/9% conv. using **4**. For the hydrogenation of (2*H*-chromen-3-yl)methanol, up to 80% ee/95% yield and 72% ee/96% yield were achieved. The same configuration of the products by using **3** and **4** suggested that the absolute configuration was controlled by the configuration of the stereogenic quinolinyl-bearing carbon of the complexes.

In transition-metal catalysis, the development of phosphorus- and nitrogen-based chiral ligands has been extensively investigated.[1-6] Though many chiral *N,P*-ligands successfully applied in the asymmetric hydrogenation, the *N,P*-ligands derived from quinoline were reported in only a few cases.[7,8] In 2007, Zhou reported *N,P*-ligands *trans*-**1** and *cis*-**2** with a cyclohexane backbone derived from pyridine and their applications in asymmetric hydrogenation of arylalkenes with up to 90% ee using *trans*-**1** and 93% ee using *cis*-**2** (Figure 1).[9] However, when R substitute of pyridine ring was not H, Ir-complexes **1** and **2** exhibited no activities. In 2011, Shen reported similar *N,P*-ligands with a cyclohexane backbone derived from quinoline.[10] The synthesis route of the ligands was very similar to Zhou's report, and the overall yield was very low. For asymmetric allylic alkylations, *trans* and *cis N,P*-ligands gave 78% ee and 84% ee, respectively.[10] Herein, this paper presents the improved synthesis of iridium-complexes of

cyclohexane-backbone *N,P*-ligands derived from quinoline and their applications in asymmetric hydrogenation.

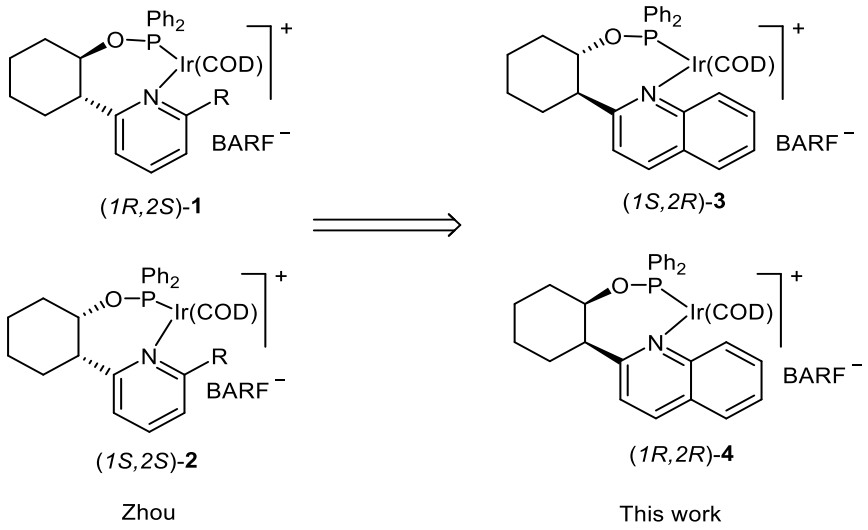
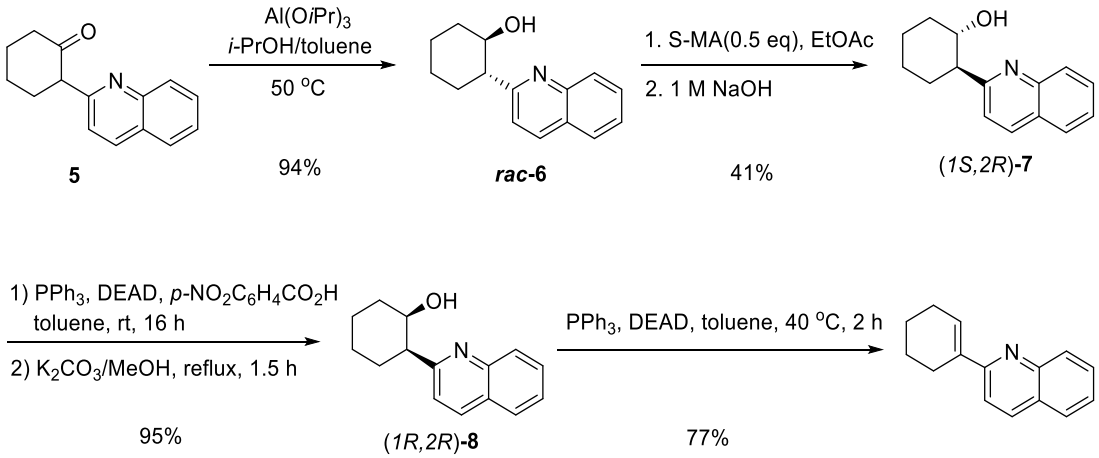



**Figure 1**

According to the known literatures, reduction of 2-(quinolin-2-yl)cyclohexanone **5** with 1.0 equiv $NaBH_4$ in ethanol refluxing for several hours gave *trans* products.[11] After color of the reaction solution changed from red to light yellow, the material **5** had been completely consumed in 10 min at room temperature. However, the mixtures of *trans* and *cis* isomer with 3/1 ratio was obtained, and pure *trans* isomer was only obtained after column separation. It was found that the reduction reagent was changed from $NaBH_4$ to Al(O*i*-Pr)$_3$/*i*-PrOH, pure *trans*-2-(quinolin-2-yl)cyclohexanol **6** with *cis* isomer of less than 1% could be afforded in 94% yield at 50 $^oC$ overnight (**Scheme 1**) .

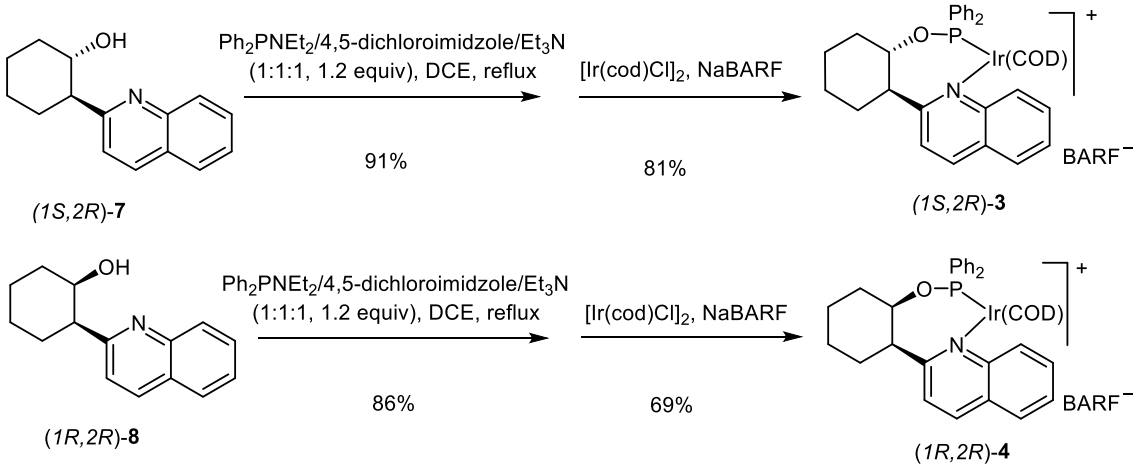
Shen reported optical resolution of *trans* isomers was conducted by using the di-benzyltartaric acid (DBTA) as an efficient resolving agent.[10] The optically pure (*1S,2R*)-**7** could be obtained using the mixed solvents of ethanol/petroleum ether and crystallization three times in 11% yield (based on *rac*-**6**). Compared with different resolution agent such as tartaric acid (TA), camphorsulfonic acid (CSA), DBTA, di-toluoyltartaric acid (DTTA), mandelic acid (MA), it was found the optimal resolution agent was mandelic acid in EtOAc. When 0.50 equiv (*S*)-mandelic acid was added, the dissociation product of the diastereomer salts was up to 92% ee, and more than 99.5% ee and 41% yield based on *rac*-**6** was achieved in only one crystallization. The *cis* optically pure (*1R,2R*)-**8** was easily obtained in 95% yield with perfect inversion of alcohol stereochemistry after modified Mitsunobu reaction using *p*-nitrobenzoic acid and deprotection with potassium carbonate in methanol. Interestingly, the same reaction conditions were adopted to (*1R,2R*)-**8** to get optically pure *trans* isomer (*1S,2R*)-**7**. Only the elimination product was obtained which again proved that there was a distinct intramolecular hydrogen bond in the *cis* isomer. To further confirm the results, triphenylphosphine ($PPh_3$) and diethyl azodicarboxylate (DEAD) only were

directly used to obtain the same elimination product in 77% yield.




**Scheme 1**

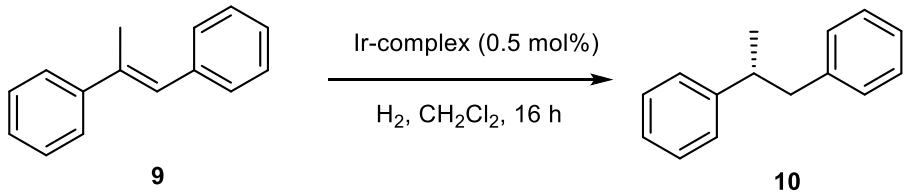
Iridium complexes of (*1S,2R*)-**3** and (*1R,2R*)-**4** were successfully obtained after *trans* isomer (*1S,2R*)-**7** and *cis* isomer (*1R,2R*)-**8** reacted with $Ph_2PNEt_2$/$Et_3N$/4,5-dichloroimidazole/DCE/reflux and then complexed with $[Ir(cod)Cl]_2$/NaBARF in 74% and 59% yields of two steps, respectively.[11,12] The resulting complexes are air stable foaming red solids, which can be conveniently purified by simple chromatography (**Scheme 2**). The synthesized two complexes showed slight difference of 86.1 ppm and 89.4 ppm in $^{31}P$ NMR spectra, possibly because of the *trans* and *cis* configuration of $OPPh_2$ (1 position) with quinoline ring (2 position) which the later had more planar steric hindrance.




**Scheme 2**

Hydrogenation of (*E*)-1,2-diphenylpropene **9** was chosen as a model reaction using the standard condition to test iridium-complex catalysts.[12,13] The hydrogenations were carried out at room temperature under 50

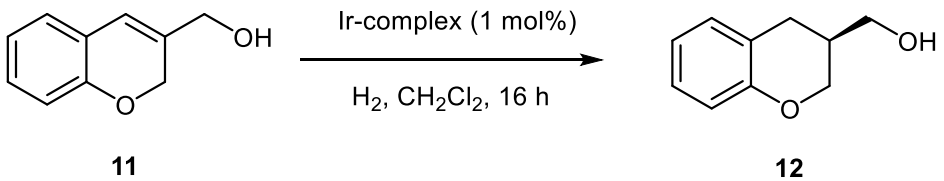
bar of hydrogen pressure using dichloromethane as the solvent. Unfortunately, neither iridium-complex catalyst of (*1S,2R*)-**3** or (*1R,2R*)-**4** was active under the above standard conditions. Under increased pressure and reaction temperature conditions (85 bar /50 $^{o}$C), 48% conv. /13% ee and 9% conv. /35% ee were obtained using (*1S,2R*)-**3** and (*1R,2R*)-**4**, respectively (**Scheme 3**). In previous report, R substitution of pyridine ring in Ir-complexes **1** and **2** exhibited no activities except for R = H.[9] The result was consistent with previous report, which shown that the planar steric hindrance of quinoline ring had a significant effect on hydrogenation.




**(1*S*,2*R*)-3:** <5% conv. at 50 bar/rt
**(1*S*,2*R*)-3:** 48% conv. 13% ee at 85 bar/50 $^{o}$C
**(1*R*,2*R*)-4:** <5% conv. at 50 bar/rt
**(1*R*,2*R*)-4:** 9% conv. 35% ee at 85 bar/50 $^{o}$C

**Scheme 3**

To further evaluate the effectiveness of iridium-complex catalysts, (2*H*-chromen-3-yl)methanol **11** was used as a new substrate (**Scheme 4**). The hydrogenation was carried out using 1 mol% catalyst under a hydrogen pressure of 50 bar in dichloromethane. As shown, (*1S,2R*)-**3** and (*1R,2R*)-**4** gave 77% conv./82% ee and 68% conv./73% ee at room temperature after 16 h, respectively. Full conversion and similar enantioselectivities were achieved after the pressure and temperature (85 bar/50 $^{o}$C) was raised. The absolute configuration of the product was determined by comparing the specific rotation value with the reference.[14]




**(1*S*,2*R*)-3:** 77% conv. 82% ee at 50 bar/rt
**(1*S*,2*R*)-3:** >99% conv.(95% yield), 80% ee at 85 bar/50 $^{o}$C
**(1*R*,2*R*)-4:** 68% conv. 73% ee at 50 bar/rt
**(1*R*,2*R*)-4:** >99% conv.(96% yield). 72% ee at 85 bar/50 $^{o}$C

**Scheme 4**

In the above experiments, *trans* and *cis* iridium-complexes **3** and **4** all gave the product with the same configuration. It was suggested that the absolute configuration of the product was controlled by the configuration of the stereogenic quinolinyl-bearing carbon of the complexes. At the same time, upon the changing from (*E*)-1,2-diphenylpropene **9** to (2*H*-chromen-3-yl)methanol **11**, the selectivity and reactivity of catalyst improved significantly.

In conclusion, the author has developed improved synthesis of iridium-complexes with cyclohexane-backbone chiral *N*,*P*-ligands derived from quinoline especially in regioselective reduction and diastereomeric optical resolution. Poor to good reactivities and enantioselectivities were obtained in the asymmetric hydrogenation of (*E*)-1,2-diphenylpropene and (2*H*-chromen-3-yl)methanol. *Trans* and *cis* iridium-complexes **3** and **4** all gave the product with the same configuration. Further studies on application to other asymmetric reactions are underway.

## EXPERIMENTAL

2-(Quinolin-2-yl)cyclohexanone **5**[15] and NaBARF (tetrakis[3,5-bis(trifluoromethyl)phenyl]boron sodium)[16] were essentially prepared according to the literature method in 74% and 87% yields, respectively. Other reagents were purchased from common commercial suppliers (AccelaChem and Aladdin) and were used without further purification. NMR spectra were recorded on Brucker Advance DMX 400 MHz spectrometer using $CDCl_3$ or DMSO-$d_6$ as solvent, and tetramethylsilane (TMS) as internal standard. High resolution mass spectra were recorded on Applied Biosystems Mariner System 5303. Optical rotations were measured with JASCO P-1010 polarimeter. Flash column chromatography was performed on silica gel (200–300 mesh). All reactions were monitored by TLC analysis. Enantiomeric excess was determined by HPLC analysis, using chiral column described below in detail.

**(±)-*trans*-2-(Quinolin-2-yl)cyclohexanol (6)**

To a solution of 2-(quinolin-2-yl)cyclohexanone **5** (22.5 g, 100 mmol) dissolved in the mixed solution of *i*-PrOH (45 mL) and toluene (135 mL) was added Al(O*i*-Pr)$_3$ (10.2 g, 50 mmol) at room temperature, and the mixture was heated to 50 $^oC$ overnight under inert atmosphere of nitrogen. The mixture was evaporated under reduced pressure. 1M HCl was added to crude mixture and the water layer was extracted with DCE. The solution was dried and evaporated under reduced pressure to give **(±)-*trans*-2-(quinolin-2-yl)cyclohexanol (6)** [11]**:** White solid; mp 129-131 $^oC$ (lit.[11] 129-130 $^oC$); 94% yield. $^1H$ NMR (400 MHz, $CDCl_3$): δ 8.09 (d, *J* = 8.3 Hz, 1 H), 7.98 (d, *J* = 8.3 Hz, 1 H), 7.77 (d, *J* = 7.9 Hz, 1 H), 7.61 (t, *J* = 8.3 Hz, 1 H), 7.45 (t, *J* = 8.0 Hz, 1 H), 7.29 (d, *J* = 8.3 Hz, 1 H), 4.65 (*br* s, 1 H), 3.92 (m, 1 H), 2.70-2.72 (m, 1 H), 2.03-2.09 (m, 2 H), 1.84-1.86 (m, 2 H), 1.61-1.72 (m, 2 H), 1.44-1.53 (m, 2 H).

**(*1S*,*2R*)-*trans*-2-(Quinolin-2-yl)cyclohexanol (7)**

The flask was charged with the **(±)**-*trans*-**6** (16.2 g, 71.4 mmol) dissolved in EtOAc (160 mL) and a

solution of (*S*)-mandelic acid (5.4 g, 35.7 mmol) in EtOAc (80 mL) was added via the addition funnel over a period of 3 h at room temperature. After addition of one-fourth of the mandelic acid solution, the salt began to precipitate. The reaction mixture was stirred overnight at room temperature, followed by 3 h at 0 $^{o}$C. The precipitated salt was collected by filtration and was subsequently washed with a small amount of EtOAc (5 mL). The white solid was crystallized a second time by adding 80 mL of EtOAc and then heating to reflux. After the solution was cooled to room temperature, filtered and dried in a vacuum for 2 h, the final diastereomeric salt (11.9 g) was obtained as a white solid. The final product (*1S,2R*)-*trans*-2-(quinolin-2-yl)cyclohexanol **7** as white solid of 6.6 g was obtained in 41% yield by adding 1.0 mol/L NaOH to DCE solution of the above diastereomeric salt at room temperature stirring for 30 min. $[\alpha]^{27}_{D}$ -23.8 (*c* 0.48, $CHCl_3$); 99.8% ee. (Chiralcel AS-H column, *i*-PrOH/hexane 10/90, 1.0 mL min$^{-1}$, 254 nm: t (*1S, 2R*) = 7.2 min, t (*1R, 2S*) = 8.9 min). The absolute stereochemistry of (*1S,2R*)-**7** was determined by comparison of the sign of the optical rotation with reported data.[10]

**(*1R,2R*)-*cis*-2-(Quinolin-2-yl)cyclohexanol (8):**

To a stirred solution of optical pure (*1S,2R*)-*trans*-2-(quinolin-2-yl)cyclohexanol **7** (1.0 mmol, dissolved in 15 mL toluene), *p*-$NO_2C_6H_4CO_2H$ (251 mg, 1.5 mmol) and $PPh_3$ (393 mg, 1.5 mmol) under nitrogen atmosphere was slowly added a solution of DEAD (0.15 mmol) in toluene (10 mL) at room temperature. The reaction mixture became clear after stirring for 5-10 min. After the reaction was stirred for 16 h (monitored by TLC), the mixture was concentrated in vacuo to dryness, and directly subjected to flash chromatography to give (*1R,2R*)-*cis*-2-(quinolin-2-yl)cyclohexyl 4-nitrobenzoate. The resulting carboxylic esters in MeOH (10 mL) was added $K_2CO_3$ (0.92 g, 6.65 mmol) and then the solution was stirred at reflux for 1.5 h. The reaction mixture was concentrated *in vacuo* to dryness and then diluted with water (120 mL) and extracts were with DCE (3×10 mL). The combined organic extracts were washed with 1.0 mol/L NaOH solution, $H_2O$ and brine, dried over anhydrous $Na_2SO_4$, and concentrated *in vacuo* to give the white crystalline solid (*1R,2R*)-*cis*-2-(quinolin-2-yl)cyclohexanol **8** of 95% yield. $[\alpha]^{26}_{D}$ +19.3 (*c* 0.78, $CHCl_3$). $^1$H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, *J* = 8.3 Hz, 1 H), 8.01 (d, *J* = 8.3 Hz, 1 H), 7.78 (d, *J* = 7.9 Hz, 1 H), 7.69 (t, *J* = 8.3 Hz, 1 H), 7.51 (t, *J* = 8.0 Hz, 1 H), 7.27 (d, *J* = 8.3 Hz, 1 H), 6.53 (*br* s, 1 H), 4.45 (s, 1 H), 2.88-2.92 (m, 1 H), 2.03-2.09 (m, 2 H), 1.84-1.87 (m, 2 H), 1.63-1.73 (m, 2 H), 1.45-1.55 (m, 2 H).

**Ir-complex (*1S,2R*)-3 and Ir-complex (*1R,2R*)-4**

(*1S,2R*)-*trans*-2-(Quinolin-2-yl)cyclohexanol **7** *or* (*1R,2R*)-*cis*-2-(quinolin-2-yl)cyclohexanol **8** (0.30 mmol), and 4,5-dichloroimidazole (62 mg, 0.45 mmol) were dissolved in DCE (4 mL) to give a white suspension. To the reaction mixture was added triethylamine (63 μL, 0.45 mmol) to give a clear solution. The mixture was cooled to 0 $^{o}$C and *N*-ethyl-*N*-(diphenylphosphino)ethanamine (116 mg, 0.45 mmol) dissolved in DCE (2 mL) was added. The cooling bath was removed and the solution was heated to reflux

for 6 h until the reaction was complete by TLC. The mixture was then concentrated and directly purified by flash chromatography (hexane/EtOAc = 10:1~15:1).

**[(*1S,2R*)-*trans*-2-(Quinolin-2-yl)cyclohexan-1-oxy]diphenylphosphine:** Pale yellow oil; 91% yield; $[\alpha]^{26}_{D}$ +26.1 (*c* 0.10, $CHCl_3$); $^1$H NMR (400 MHz, DMSO-*d*$_6$): δ 8.16 (d, *J* = 8.4 Hz, 1 H), 7.88-7.91 (m, 2 H), 6.70 (m, 1 H), 7.54 (t, *J* = 7.9 Hz, 1 H), 7.47 (d, *J* = 8.4 Hz, 1 H), 7.29-7.31 (m, 5 H), 6.89 (t, *J* = 7.9 Hz, 1 H), 6.66 (t, *J* = 7.7 Hz, 1 H), 6.50 (t, *J* = 7.5 Hz, 1 H), 4.39-4.44 (m, 1 H), 3.10-3.16 (m, 1 H), 2.16-2.19 (m, 1 H), 1.69-1.92 (m, 3 H), 1.35-1.52 (m, 4 H); $^{31}$P NMR (162 MHz, DMSO-*d*$_6$): δ 105.8; HRMS Calcd for $C_{27}H_{26}NOP$(M+1) 412.1752, found 412.1766.

**[(*1R,2R*)-*cis*-2-(Quinolin-2-yl)cyclohexan-1-oxy]diphenylphosphine:** White solid; mp 72-74 ºC; 86% yield; $[\alpha]^{25}_{D}$ -265.5 (*c* 1.34, $CHCl_3$); $^1$H NMR (400 MHz, DMSO-*d*$_6$): δ 8.15 (d, *J* = 8.6 Hz, 1 H), 7.91 (t, *J* = 8.1 Hz, 2 H), 7.71 (m, 1 H), 7.55 (t, *J* = 7.0 Hz, 1 H), 7.48 (d, *J* = 8.6 Hz, 1 H), 7.32-7.40 (m, 5 H), 6.94 (m, 1 H), 6.58-6.68 (m, 4 H), 4.62-4.64 (m, 1 H), 3.20 (m, 1 H), 2.36-2.39 (m, 1 H), 2.04-2.07 (m, 1 H), 1.90-1.98 (m, 2 H), 1.73 (m, 1 H), 1.48-1.53 (m, 3H); $^{31}$P NMR (162 MHz, DMSO-*d*$_6$): δ 104.1; HRMS Calcd for $C_{27}H_{26}NOP$(M+1) 412.1752, found 412.1759.

To a stirred solution of [(*1S,2R*)-*trans*-2-(quinolin-2-yl)cyclohexan-1-oxy]diphenylphosphine *or* [(*1R,2R*)-*cis*-2-(quinolin-2-yl)cyclohexan-1-oxy]diphenylphosphine (0.16 mmol) dissolved in DCE (5 mL) was added $[Ir(COD)Cl]_2$ (54 mg, 0.08 mmol) to give an orange-red solution. The reaction mixture was heated to reflux for 1.5 h. The solution was cooled to room temperature and NaBARF (142 mg, 0.16 mmol) was added in one portion causing the solution to become much darker. The solution was reheated to reflux for an additional 30 min. At the end of this period, the solution was cooled, and water (5 mL) was added. After 10 min, the layers were separated and the aqueous phase extracted three times with DCE (5 mL). The combined organic layer was dried over anhydrous $Na_2SO_4$ and concentrated *in vacuo* to afford the crude product. Flash chromatography with DCE as the eluant afforded pure iridium complex.

**Iridium-complex (*1S,2R*)-3:** Deep-red foaming solid; 81% yield; $[\alpha]^{25}_{D}$ -21.2 (*c* 0.26, $CHCl_3$); $^1$H NMR (400 MHz, DMSO-*d*$_6$): δ 8.54 (d, 1H), 8.16 (d, 1H), 7.36-7.71 (m, 22H), 6.92-6.96 (m, 2H), 6.81-6.83 (m, 2H), 5.22(m, 1H), 5.12 (m, 1H), 4.64 (m, 1H), 4.45 (m, 1H), 4.22-4.24 (m, 1H), 3.65 (m, 1H), 0.86-2.52 (m, 16H); $^{31}$P NMR (162 MHz, $CDCl_3$): δ 86.1; HRMS (cation) Calcd for $C_{35}H_{38}NOPIr$ (M) 712.2320, found 712.2315; HRMS (anion) Calcd for $C_{32}H_{12}BF_{24}$ 863.0649, found 863.0654.

**Iridium-complex (*1R,2R*)-4:** Deep-red foaming solid; 69% yield; $[\alpha]^{25}_{D}$ +30.5 (*c* 0.28, $CHCl_3$); $^1$H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, 1H), 8.21 (d, 1H), 7.00-7.71 (m, 14H), 5.71 (t, 1H), 4.93 (m, 1H), 4.74 (m, 1H), 4.19-4.25 (m, 2H), 3.36 (m, 1H), 2.64(m, 1H), 0.76-2.28 (m, 15H); $^{31}$P NMR (162 MHz, $CDCl_3$): δ 89.4; HRMS (cation) Calcd for $C_{35}H_{38}NOPIr$ (M) 712.2320, found 712.2307; HRMS (anion) Calcd for $C_{32}H_{12}BF_{24}$ 863.0649, found 863.0645.

**Asymmetric hydrogenation procedure:**

A high pressure steel autoclave along with a dry glass bottle were taken into a glove-box. To a stirred solution of the substrate **9** or **11** (0.5 mmol) dissolved in $CH_2Cl_2$ (2 mL) was added the catalyst (0.0025/0.005 mmol). After stirring for additional 5-10 min, the solution was then transferred into an autoclave, taken out of the glove-box and then pressurized to 50 bar with hydrogen. After stirring for 16 h for the specified temperature, the reaction mixture was carefully releasing the hydrogen and concentrated in vacuo to give a crude residue (*R*)-**10** or (*S*)-**12**. Flash chromatography using hexane/EtOAc (10:1~1:1) afforded the samples suitable for direct analysis. The conversion was determined by $^1$H NMR.

(*R*)-**10**[12]**:** Colorless oil. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.20-7.33 (m, 10H), 6.44 (d, $J$ = 15.8 Hz, 1H), 6.29 (dd, $J$ = 8.8 Hz, 15.8 Hz, 1H), 4.22-4.31 (m, 1H), 3.94 (d, $J$ = 10.8 Hz, 1H), 3.70 (s, 3H), 3.52 (s, 3H); The enantiomeric excess of (*R*)-**10** was determined by chiral HPLC (Chiralcel OJ-H column, *i*-PrOH / hexane 3 / 97, 1.0 mL min$^{-1}$ , 30 $^o$C, 254 nm): t (*R*) = 5.7 min, t (*S*) = 8.6 min.

(*S*)-**12**[14]**:** White solid, $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.04-7.11 (m, 2H), 6.79-6.87 (m, 2H), 4.29 (ddd, $J$ = 1.2 Hz, 3.2 Hz, 10.8 Hz, 1H), 4.01 (dd, $J$ = 7.6 Hz, 10.8 Hz, 1H), 3.64-3.75 (m, 2H), 2.88 (dd, $J$ = 5.6 Hz, 16.4 Hz, 1H), 2.59 (dd, $J$ = 7.6 Hz, 16.4 Hz, 1H), 2.24-2.27 (m, 1H), 1.61 (broad s, 1H). The enantiomeric excess of (*S*)-**12** was determined by chiral HPLC (Chiralcel OJ-H column, *i*-PrOH / hexane 5 / 95, 0.8 mL min$^{-1}$, 30 $^o$C, 215 nm): t (*R*) = 21.5 min ,t (*S*) = 22.6 min.

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