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Note

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# Giving a Second Chance to Ir/sulfoximine-based Catalysts for the Asymmetric Hydrogenation of Olefins Containing Poorly Coordinative Groups

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**KEYWORDS:** *Asymmetric hydrogenation, olefins, iridium, P-N ligands, sulfoximine-based ligand, phosphite.*

**ABSTRACT:** This work identifies a family of Ir/phosphite-sulfoximines catalysts that has been successfully used in the asymmetric hydrogenation of olefins with poorly coordinative or non-coordinative groups. In comparison with analogue Ir/phosphine-sulfoximines catalysts previously reported, the presence of a phosphite group extended the range of olefins than can be efficiently hydrogenated. High enantioselectivities, comparable to the best ones reported, have been achieved for a wide range of olefins containing relevant poorly coordinative groups such as α,β-unsaturated enones, esters, lactones and lactams as well as alkenylboronic esters.

Asymmetric hydrogenation (AH) is one of the most popular and straightforward catalyzed transformations for the preparation of chiral compounds. It has a perfect atom economy and a high functional group tolerance, which makes it very attractive for preparing complex chiral molecules (i.e. drugs, crop-protecting products … ).[1] The development of chiral analogues of Crabtree catalysts opened the possibility of hydrogenating olefins with poorly coordinative groups or non-coordinative groups,[2] which is not feasible with classical Rh and Ru diphosphine catalysts.[3] Since then, many efforts have been devoted to extend the substrate scope by developing new catalyst types.[4] Bolm's group early found that Ir-catalysts with phosphine-sulfoximine ligands (Figure 1a) can efficiently hydrogenate α,β-unsaturated ketones[5] and non-olefinic substrates such as quinolines[6] and imines[7]. This important finding opened a direct, atom efficient path for preparing valuable optically pure ketones, whose synthesis up to then mainly relied on non-catalyzed methods with a limited substrate scope.[8] Nevertheless, the efficiency of those Ir/phosphine-sulfoximine catalysts depended highly on the substitution pattern of the enone and the steric constrains of the olefin substituents.[5a,b] Excellent enantioselectivities were only obtained for β,β'-disubstituted enones containing two large substituents (Figure 1b). This may be a reason why researchers have overlooked the use of sulfoximines-based ligands for the AH of olefins containing poorly or non-coordinative groups despite the high enantioselectivities achieved in other asymmetric transformations[9].

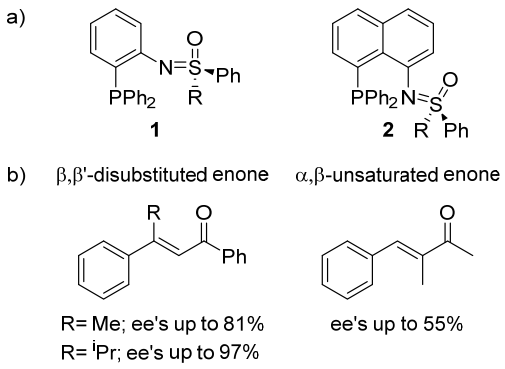



**Figure 1.** (a) Representative phosphine-sulfoximine ligands developed by Bolm's group. (b) Summary of the enantioselectivities achieved in the asymmetric hydrogenation of representative enones (data from refs. 5a,b).

Our group has contributed to the Ir-hydrogenation of olefins containing poorly or non-coordinative groups with new types of efficient P-N ligands. We have shown that biaryl phosphite groups improve the ligand's efficiency and substrate scope.[10] Here, we disclose whether the replacement of the phosphine moiety by a more adaptive biaryl phosphite group[11] can overcome the substrate scope limitation of Ir/phosphine-sulfoximines. For this purpose we report the synthesis of phosphite-sulfoximines ligands **L1**–**L3a**–**c** (Figure 2) with different biaryl phosphite groups (**a**–**c**). These new ligands are based on already reported phosphine-sulfoximines **1** and **2**.[5-7] Thus, ligands **L1** differ from **1** by having biaryl phosphite groups instead of a diphenylphosphine moiety. Ligands **L2** differ from **L1** by having bulky tBu groups in the Ph backbone ring. Ligands **L3** are a more rigid version of **L1** and **L2**.

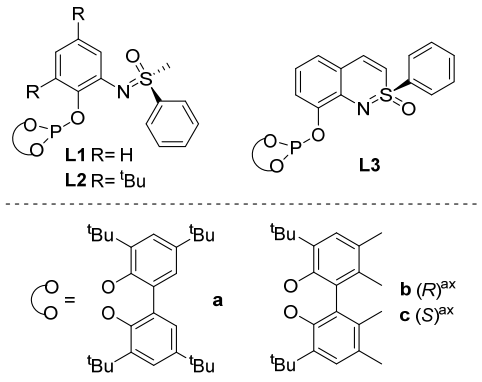



**Figure 2.** Phosphite-sulfoximine ligands **L1**–**L3a**–**c**.

Ir-catalyst precursors [Ir(cod)(**L1**–**L3a**–**c**)]$BAr_F$ were synthesized in a few steps from the corresponding commercially available 1-bromo-phenols **3**–**5** (Scheme 1). Protection of the hydroxyl group with methoxymethyl chloride (MOMCl; step i), subsequent coupling with the enantiopure sulfoximine **9** (using either Cu/DMEDA[12] for **6** and **7** or Pd/BINAP[13] for **8**; steps ii and iii, respectively) and deprotection with HCl (step iv) provided hydroxyl-sulfoximines **13**–**15**. Compounds **13**–**15** were then converted into the corresponding phosphite-sulfoximines by treatment with the desired phosphorochloridite ($ClP(OR)_2$; $(OR)_2$= **a**–**c**; step v) under basic conditions.[14] Finally, treatment of the appropriate phosphite-sulfoximine ligand (**L1**–**L3a**–**c**) with $[Ir(\mu\text{-}Cl)(cod)]_2$ in dichloromethane at 40 °C for 1 h, followed by insitu $Cl^-/BAr_F^-$ counterion exchange with sodium tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate ($NaBAr_F$; 1 equiv) in water gave access to the desired [Ir(cod)(**L1**–**L3a**–**c**)]$BAr_F$ catalyst precursors (step vi). They were obtained as air-stable orange solids. The HRMS-ESI spectra show the heaviest ions at m/z which correspond to the loss of the $BAr_F$ anion from the parent molecular species. The spectral $^1H$, $^{13}C$ and $^{31}P$ assignments, made using $^1H$–$^1H$ and $^{13}C$–$^1H$ correlation measurements, were as expected for these $C_1$-symmetric iridium complexes. It should be noted, that for complexes containing ligands **L1** and **L2**, two species in solution were detected. The $^2D$ DOSY $^{31}P\{^1H\}$ NMR experiments showed that these two species have the same diffusion coefficient, which indicates that they must be isomers. This is likely due to the presence of two different stable conformations for the 6-membered chelate ring, since only a single isomer is formed for complexes containing ligands **L3** which has a more rigid backbone.

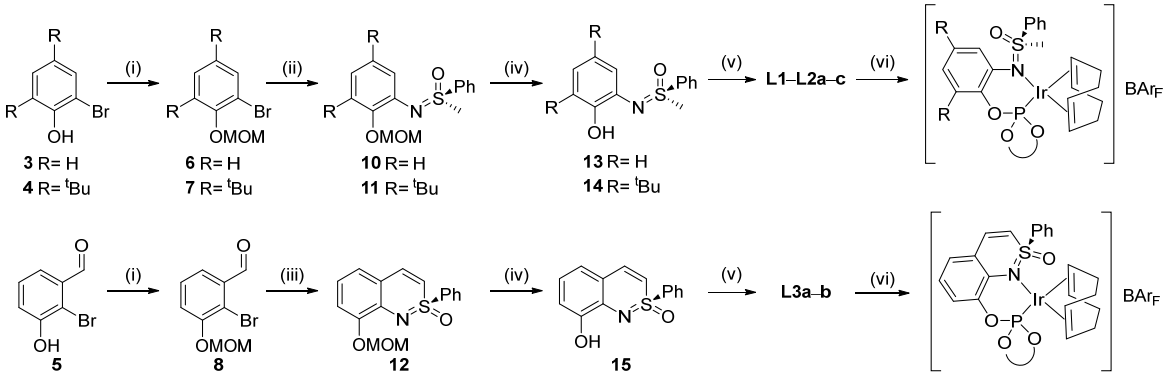
In a first set of experiments we tested [Ir(cod)(**L1**–**L3a**–**c**)]$BAr_F$ catalyst precursors in the asymmetric hydrogenation of two benchmark α,β-unsaturated ketones with different substitution patterns, β,β'-disubstitued substrate 1,3-diphenylbut-2-en-1-one **S1** and α,β substituted 3-methyl-4-phenylbut-3-en-2-one **S2**. These substrates were selected because the previous Ir/sulfoximine-based catalysts **1**–**2** provided suboptimal enantioselectivities (Figure 1b).[5a,b] Improving those results we obtained higher enantioselectivities (>91% ee) for both substrates using the new Ir/phosphite-sulfoximine catalysts (Table 1; entries 2 and 6 vs. 7).

**Table 1. Asymmetric hydrogenation of S1 and S2 using [Ir(cod)(L1–L3a–c)]$BAr_F$ catalyst precursors[a]**

| | | S1 | | S2 | |
|---|---|---|---|---|---|
| Entry | L | % Conv[b] | % ee[c] | % Conv[b] | % ee[c] |
| 1 | **L1a** | 100 | 70 (*R*) | 85 | 13 (*S*) |
| 2 | **L1b** | 100 (96) | 91 (*R*) | 90 (85) | 76 (*S*) |
| 3 | **L1c** | 100 | 7 (*S*) | 80 | 57 (*R*) |
| 4 | **L2a** | 70 | 61 (*R*) | 24 | 11 (*S*) |
| 5 | **L3a** | 89 | 17 (*S*) | 100 | 73 (*R*) |
| 6 | **L3b** | 100 (94) | 30 (*S*) | 100 (97) | 96 (*R*) |
| 7 | **2**[d] | 100 | 81 (*S*)[e] | 100 | 55 (*S*)[f] |

[a] Reactions conditions: 1 mol% Ir-catalyst precursor, substrate (0.5 mmol), DCM, rt for 18 h, $H_2$ (50 bar). [b] Conversions measured by $^1H$-NMR. Isolated yields in parenthesis. [c] Enantioselectivies measured by chiral HPLC. [d] R=$^i$Bu. [e] Data from ref 5a. [f] Data from ref 5b.

**Scheme 1. Synthesis of [Ir(cod)(L1–L3a–c)]$BAr_F$ catalyst precursors.**




(i) MOMCl, $NEt_3$, THF, rt, 2-16 h; (ii) (*S*)-S-methyl-S-phenylsulfoximine (**9**), CuI, DMEDA, NaI, $Cs_2CO_3$, toluene, 110 °C, 40-80 h; (iii) **9**, $Pd(OAc)_2$, *rac*-BINAP, $Cs_2CO_3$, toluene, reflux, 48 h; (iv) $^i$PrOH/HCl/THF (2:1:1), rt, 3 h; (v) $ClP(OR)_2$; $(OR)_2$= **a**–**c**, Py, toluene, rt, 18 h. (vi) $[Ir(\mu\text{-}Cl)(cod)]_2$, DCM, reflux, 1 h then $NaBAr_F$, $H_2O$, rt, 30 min.

Results also indicated that, as expected, each substrate requires a different ligand to maximize the enantioselectivity. Thus, while for the β,β'-disubstitued substrate **S1** enantioselectivities were best with the more flexible Ir-**L1b** catalyst, the more rigid Ir-**L3b** catalyst was better for substrate **S2**. Interestingly, for both substrate types the presence of a chiral *R*-biaryl phosphite moiety (**b**) in the ligand is needed to maximize enantioselectivities (e.g. entries 2 vs 3). This suggests a cooperative effect between the configurations of the sulfoximine and the phosphite groups.

We next studied the potential of the Ir-**L1b** and Ir-**L3b** catalytic systems to hydrogenate other enones (Figure 3). We found out that Ir-**L1b** is also able to hydrogenate β,β'-disubstituted enones containing two large substituents such as the 4-methyl-1,3-diphenylpent-2-en-1-one **S3** in high enantioselectivities. This overcome the previously observed dependence of the steric constrains of the β-substituents on enantioselectivity using catalysts **1** and **2** (Figure 1b). Interestingly, Ir-**L3b** was also able to hydrogenate other α,β-unsaturated enones (**S4**–**S9**) in high ee's regardless the different decorations at the phenyl group and the different substituents at the ketonic group.

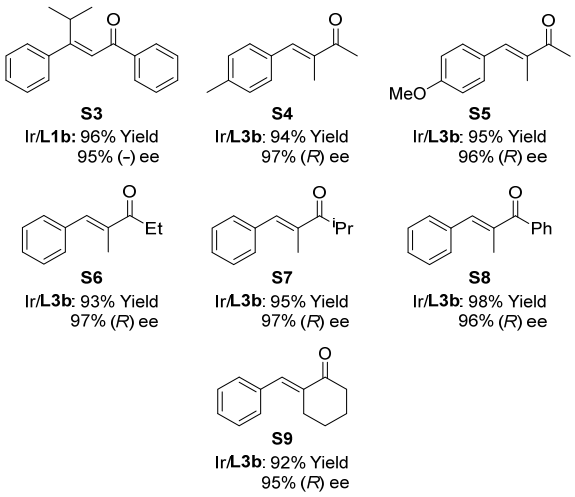



**Figure 3.** Asymmetric hydrogenation of α,β-unsaturated enones **S3**–**S9**. Typical reaction conditions: 1 mol% Ir-catalyst precursor, substrate (0.5 mmol), DCM, rt for 18 h, $H_2$ (50 bar). Full conversions were achieved in all cases.

Finally, we tested whether the high enantioselectivities can be maintained for olefins containing other relevant poorly coordinative groups than a ketone (Figure 4). We found that high enantioselectivities can also be achieved for a range of β,β'-disubstituted unsaturated esters (substrates **S10**–**S17**), α,β-unsaturated lactones (**S18**–**S19**) and lactams (**S20**–**S21**) and alkenylboronic ester **S22**. The efficient hydrogenation of olefins containing such a variety of functional groups is interesting because they are highly versatile building blocks for the synthesis of complex chiral molecules such as fragrances, natural products and pharmaceuticals. Interestingly, we also found that Ir-**L1b** is able to hydrogenate tri- and disubstituted olefins without an extra functional group (substrates **S23** and **S24**) in ee's as high as 93%.

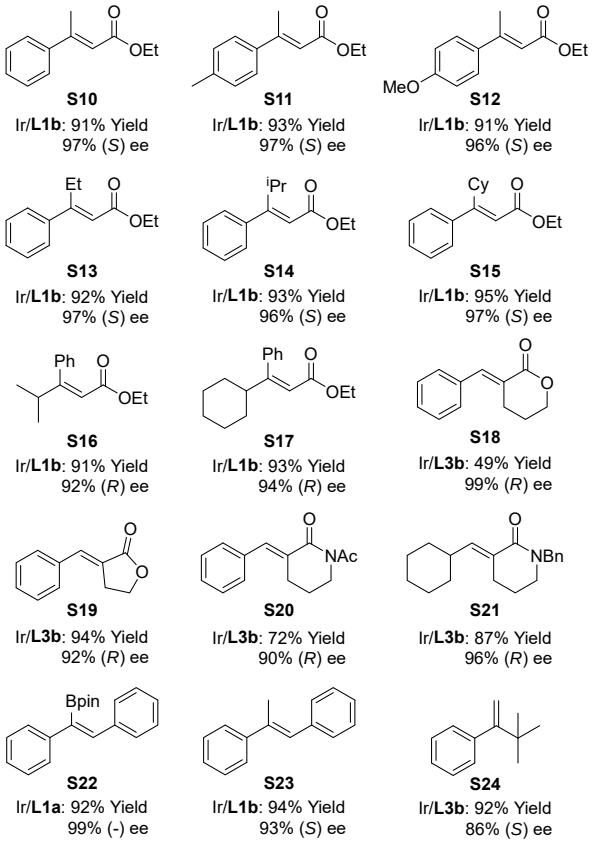



**Figure 4.** Asymmetric hydrogenation of α,β-unsaturated esters, lactones and lactams, alkenylboronic ester and unfunctionalized olefins **S10**–**S24**. Typical reaction conditions: 1 mol% Ir-catalyst precursor, substrate (0.5 mmol), DCM, rt for 18 h, $H_2$ (50 bar for **S10**–**S23** and 1 bar for **S24**). Full conversions were obtained in all cases (except for **S18** and **S20** with 56% conv and 81% conv, respectively)

In summary, we have demonstrated that sulfoximines, which are useful in other asymmetric transformations and in others areas such as medicinal and crop protecting chemistry,[15] can also be useful when combined with a biaryl phosphite group as ligands for the AH of the so-called minimally functionalized olefins. High enantioselectivities, comparable to the best ones reported,[16] have been therefore achieved in the hydrogenation of a wide range of olefins containing relevant poorly coordinative groups such as α,β-unsaturated enones, esters, lactones and lactams as well as alkenylboronic esters.

## EXPERIMENTAL SECTION

**General Methods.** All reactions were carried out using standard Schlenk techniques under an argon atmosphere. Solvents were purified and dried by standard procedures. Hydroxyl-sulfoximine **15**[13] and sulfoximine **9**[12] were prepared as previously described. Phosphorochloridites are easily prepared in one step from the corresponding biaryls.[17] $^1$H, $^{13}$C, and $^{31}$P NMR spectra were recorded using a 400 MHz spectrometer. Chemical shifts are relative to that of $SiMe_4$ ($^1$H and $^{13}$C) as internal standard or $H_3PO_4$ ($^{31}$P) as external standard. $^1$H, $^{13}$C, and $^{31}$P assignments were made on the basis of $^1$H-$^1$H gCOSY, $^1$H-$^{13}$C gHSQC and $^1$H-$^{31}$P gHMBC experiments. Substrates **S2**,[18] **S3**,[5a] **S4**–**S8**,[5b] **S9**,[19] **S10**–**S12**,[20] **S13**–**S17**,[21] **S18**–**S21**[22] and **S24**[23] were prepared following the reported procedures, while

substrates **S1**, **S22** and **S23** were commercially available and used as received.

**Preparation of compounds 6–7.** A flame dried Schlenk flushed with argon was charged with compounds **3** or **4** (10 mmol, 1 eq.) which was dissolved in dry THF (25 mL) along with dry triethylamine (49.6 mmol, 6.8 mL, 5 eq.), and a stir bar. MOMCl (20 mmol, 1.5 mL, 2 eq.) was added dropwise resulting in the formation of a white precipitate. The reaction was allowed to stir during 4 h for compound **3**, and 16 h for compound **4**. The reaction was taken up in water (20 mL) and extracted with ethyl acetate (3 x 20 mL). The combined organic layers were washed with brine, dried with $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (94% (petroleum ether): 6% (ethyl acetate) for **6** and 100% (petroleum ether) for **7**).

*1-Bromo-2-(methoxymethoxy)benzene (**6**).* Yield: 1.73 g (80%). $^1$H NMR (400 MHz, $CDCl_3$): δ= 3.52 (s, 3H, $CH_3$), 5.24 (s, 2H, $CH_2$), 6.88 (ddd, 1H, CH=, $^3J_{H\text{-}H}$= 7.9 Hz, $^3J_{H\text{-}H}$= 7.4 Hz, $^4J_{H\text{-}H}$= 1.5 Hz), 7.15 (dd, 1H, CH=, $^3J_{H\text{-}H}$= 8.3 Hz, $^4J_{H\text{-}H}$= 1.5 Hz), 7.24 (ddd, 1H, CH=, $^3J_{H\text{-}H}$= 8.3 Hz, $^3J_{H\text{-}H}$= 7.4 Hz, $^4J_{H\text{-}H}$= 1.6 Hz), 7.55 (dd, 1H, CH=, $^3J_{H\text{-}H}$= 7.9 Hz, $^4J_{H\text{-}H}$= 1.6 Hz). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): δ = 56.4 ($CH_3$), 95.0 ($CH_2$), 112.9 (C), 116.2 (CH=), 123.1 (CH=), 128.5 (CH=), 133.4 (CH=), 153.8 (C).

*1-Bromo-3,5-di-tert-butyl-2-(methoxymethoxy)benzene (**7**).* Yield: 1.97 g (60%). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 9H, $CH_3$, $^t$Bu), 1.43 (s, 9H, $CH_3$, $^t$Bu), 3.69 (s, 3H, $CH_3$), 5.21 (s, 2H, $CH_2$), 7.30 (d, 1H, CH=, $^4J_{H\text{-}H}$= 2.4 Hz), 7.39 (d, 1H, CH=, $^4J_{H\text{-}H}$= 2.4 Hz). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): δ = 30.8 ($CH_3$, $^t$Bu), 31.3 ($CH_3$, $^t$Bu), 34.6 (C, $^t$Bu), 35.9 (C, $^t$Bu), 57.7 ($CH_3$), 99.3 ($CH_2$), 117.5 (C), 123.9 (CH=), 128.7 (CH=), 144.4 (CH=), 147.5 (CH=), 150.5 (C).

**Preparation of compounds 10–11.** Under an argon atmosphere a dry flamed Schlenk flask was charged with the MOM-protected hydroxyl-aryl bromide **6** or **7** (2.0 equiv, 5.0 mmol), CuI (0.1 equiv, 0.25 mmol, 47.5 mg), DMEDA (0.2 equiv, 0.5 mmol, 44.1 mg) and NaI (4.0 equiv, 10 mmol, 1.5 g). Then, degassed toluene (50 mL) was added, and the resulting heterogeneous mixture was heated to 110 °C for 20 h for **6** and 40 h for **7**. Then, sulfoximine **9** (1.0 equiv, 2.5 mmol, 0.4 g) and $Cs_2CO_3$ (2.5 equiv, 12.5 mmol, 4.0 g) were added and the mixture was kept at 110 °C for additional 20 h for **6**, and 40 h for **7**. Subsequently, the mixture was cooled to room temperature, and extracted with dichloromethane and an aqueous ammonia solution. The combined organic extracts were dried with $MgSO_4$, filtered and concentrated under reduced pressure. Purification by column chromatography on silica gel with 100% ethyl acetate afforded compounds **10**–**11**.

*(S)-((2-(Methoxymethoxy)phenyl)imino)(methyl)(phenyl)-λ$^6$-sulfanone (**10**).* Yield: 619.1 mg (85%). $^1$H NMR (400 MHz, $CDCl_3$): δ = 3.21 (s, 3H, $CH_3$), 3.48 (s, 3H, $CH_3$), 5.16 (d, 2H, $CH_2$, $^2J_{H\text{-}H}$= 6.6 Hz), 5.21 (d, 2H, $CH_2$, $^2J_{H\text{-}H}$= 6.6 Hz), 6.75 (td, 1H, CH=, $^3J_{H\text{-}H}$= 7.6 Hz, $^4J_{H\text{-}H}$= 1.5 Hz), 6.82 (td, 1H, CH=, $^3J_{H\text{-}H}$= 7.6 Hz, $^4J_{H\text{-}H}$= 1.7 Hz), 7.03 (dd, 1H, CH=, $^3J_{H\text{-}H}$= 8.0 Hz, $^4J_{H\text{-}H}$= 1.5 Hz), 7.08 (dd, 1H, CH=, $^3J_{H\text{-}H}$= 7.8 Hz, $^4J_{H\text{-}H}$= 1.7 Hz), 7.45-7.68 (m, 3H, CH=), 8.00 (dd, 2H, CH=, $^3J_{H\text{-}H}$= 8.4 Hz, $^4J_{H\text{-}H}$= 1.2 Hz). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): δ = 46.2 ($CH_3$), 56.1 ($CH_3$), 95.5 ($CH_2$), 116.9 (CH=), 122.5 (CH=), 122.7 (CH=), 124.6 (CH=), 128.4 (CH=), 129.4 (CH=), 133.1 (CH=), 135.0 (C), 140.1 (C), 150.7 (C).

*(S)-((2,3-Di-tert-butyl-6-(methoxymethoxy)phenyl)imino)(methyl)-(phenyl)-λ$^6$-sulfanone (**11**).* Yield: 585.2 mg (58%). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.11 (s, 9H, $CH_3$, $^t$Bu), 1.41 (s, 9H, $CH_3$, $^t$Bu), 3.24 ($CH_3$), 3.69 ($CH_3$), 5.31 (d, 1H, $CH_2$, $^2J_{H\text{-}H}$= 4.5 Hz), 5.44 (d, 1H, $CH_2$, $^2J_{H\text{-}H}$= 4.5 Hz), 6.87 (dd, 2H, CH=, $^3J_{H\text{-}H}$= 8.2 Hz, $^4J_{H\text{-}H}$= 2.4 Hz), 7.48-7.56 (m, 3H, CH=), 8.01-8.05 (m, 2H, CH=). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): δ = 30.7 ($CH_3$, $^t$Bu), 31.3 ($CH_3$, $^t$Bu), 34.3 (C, $^t$Bu), 35.2 (C, $^t$Bu), 45.6 ($CH_3$), 57.5 ($CH_3$), 98.4 ($CH_2$), 117.5 (CH=), 119.4 (CH=), 128.5 (CH=), 129.4 (CH=), 133.1 (CH=), 137.0 (C), 139.6 (C), 141.8 (C), 145.2 (C), 147.1 (C).

**Preparation of compounds 13–14.** The corresponding compound **10** or **11** (1 equiv, 2.0 mmol) was added to a solution of 2-propanol (50 equiv, 7.7 mL, 100 mmol), HCl (25 equiv, 12.1 N, 4.1 mL, 50 mmol) and THF (25 equiv, 4.1 mL, 50 mmol). The mixture was stirred at room temperature for 3 h. The mixture was diluted with water (10 mL) and extracted with ether (3 × 10 mL). The combined organic layers were washed with 5% (w/w) $NaHCO_3$ and brine, dried ($MgSO_4$) and concentrated *in vacuo* affording pure hydroxy-sulfoximine **13**–**14**.

*(S)-((2-Hydroxyphenyl)imino)(methyl)(phenyl)-λ$^6$-sulfanone (**13**).* Yield: 474.8 mg (96%). $^1$H NMR (400 MHz, $CDCl_3$): δ = 3.32 (s, 3H, $CH_3$), 6.57 (td, 1H, CH=, $^3J_{H\text{-}H}$= 7.6 Hz, $^4J_{H\text{-}H}$= 1.6 Hz), 6.79-6.89 (m, 3H, CH=), 7.53-7.63 (m, 3H, CH=), 7.91-7.93 (m, 2H, CH=). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): δ = 46.0 ($CH_3$), 113.9 (CH=), 119.9 (CH=), 120.9 (CH=), 122.8 (CH=), 128.4 (CH=), 129.8 (CH=), 131.8 (C), 133.7 (CH=), 138.2 (C), 149.9 (C). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{13}H_{13}NO_2SNa$ 270.3012; Found: 270.3116.

*(S)-((2,3-Di-tert-butyl-6-hydroxyphenyl)imino)(methyl)(phenyl)-λ$^6$-sulfanone (**14**).* Yield: 675.9 mg (94%). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.14 (s, 9H, $CH_3$, $^t$Bu), 1.26 (s, 9H, $CH_3$, $^t$Bu), 4.11 (s, 3H, $CH_3$), 6.96 (d, 1H, CH=, $^4J_{H\text{-}H}$= 2.4 Hz), 7.06 (d, 1H, CH=, $^4J_{H\text{-}H}$= 2.4 Hz), 7.59 (t, 2H, CH=, $^3J_{H\text{-}H}$= 7.7Hz), 7.71 (t, 1H, CH=, $^3J_{H\text{-}H}$= 7.4 Hz), 8.16 (d, 2H, CH=, $^3J_{H\text{-}H}$= 7.9 Hz). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): δ = 29.3 ($CH_3$, $^t$Bu), 31.3 ($CH_3$, $^t$Bu), 34.1 (C, $^t$Bu), 35.2 (C, $^t$Bu), 42.5 ($CH_3$), 121.1 (CH=), 123.4 (CH=), 129.0 (CH=), 130.1 (CH=), 131.7 (C), 136.1 (CH=), 138.3 (C), 142.2 (C), 148.1 (C). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{29}NO_2SNa$ 382.5172; Found: 382.5177.

**Preparation of ligands L1–L3a–c.** To a solution of *in situ* generated phosphorochloridite (0.55 mmol) in dry toluene (3 mL), pyridine (0.08 mL, 1.0 mmol) was added. Then, this solution was placed in a -78 °C bath and a solution of the hydroxyl-sulfoximine (0.50 mmol) and pyridine (0.08 mL, 1.0 mmol) in toluene (3 mL) was added dropwise. The mixture was left to warm to room temperature and stirred overnight at this temperature. The precipitate formed was filtered under argon, and the solvent was evaporated under vacuum. The residue was purified by flash chromatography (under argon, using neutral alumina and dry toluene (1% $NEt_3$) as eluent system) to afford the corresponding phosphite-sulfoximine as white solids for **L1–L2a–c** or as yellow solids for **L3a–b**.

**L1a.** Yield: 174.9 mg (51%). $^{31}$P NMR (161.9 MHz, $C_6D_6$): δ = 137.8 (s). $^1$H NMR (400 MHz, $C_6D_6$): δ = 1.28 (s, 18H, $CH_3$, $^t$Bu), 1.62 (s, 9H, $CH_3$, $^t$Bu), 1.64 (s, 9H, $CH_3$, $^t$Bu), 2.72 (s, 3H, $CH_3$), 6.52-6.58 (m, 2H, CH=), 6.79-6.91 (m, 4H, CH=), 6.91-7.01 (m, 3H, CH=), 7.63 (s, 2H, CH=), 7.98 (s, 2H, CH=). $^{13}$C{$^1$H} NMR

(100.6 MHz, $C_6D_6$): δ = 31.1 ($CH_3$, $^t$Bu), 31.2 (d, $CH_3$, $^t$Bu, $J_{C\text{-}P}$= 2.6 Hz), 31.3 ($CH_3$, $^t$Bu), 34.4 (d, C, $^t$Bu, $J_{C\text{-}P}$= 3.0 Hz), 35.4 (C, $^t$Bu), 45.0 ($CH_3$), 121.9-146.7 (aromatic carbons). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{41}H_{52}NO_4PSNa$ 708.3250; Found 708.3247.

**L1b.** Yield: 120.3 mg (40%). $^{31}$P NMR (161.9 MHz, $C_6D_6$): δ = 133.0 (s). $^1$H NMR (400 MHz, $C_6D_6$): δ = 1.54 (s, 9H, $CH_3$, $^t$Bu), 1.72 (s, 9H, $CH_3$, $^t$Bu), 1.75 (s, 3H, $CH_3$), 1.76 (s, 3H, $CH_3$), 2.07 (s, 6H, $CH_3$), 2.66 (s, 3H, $CH_3$), 6.49-6.53 (m, 1H, CH=), 6.57-6.60 (m, 1H, CH=), 6.82-6.84 (m, 1H, CH=), 6.89-6.91 (m, 3H, CH=), 7.02-7.31 (m, 1H, CH=), 7.32 (s, 1H, CH=), 7.41-7.43 (m, 1H, CH=), 7.92-7.94 (m, 2H, CH=). $^{13}$C{$^1$H} NMR (100.6 MHz, $C_6D_6$): δ = 16.3 ($CH_3$), 16.5 ($CH_3$), 20.1 ($CH_3$), 31.1 ($CH_3$, $^t$Bu, $J_{C\text{-}P}$= 5.1 Hz), 31.8 ($CH_3$, $^t$Bu), 34.6 (C, $^t$Bu), 34.9 (C, $^t$Bu), 44.7 ($CH_3$), 122.0-146.1 (aromatic carbons). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{37}H_{44}NO_4PSNa$ 652.2624; Found 652.2621.

**L1c.** Yield: 66.2 mg (22%). $^{31}$P NMR (161.9 MHz, $C_6D_6$): δ = 131.0 (s). $^1$H NMR (400 MHz, $C_6D_6$): δ = 1.55 (s, 9H, $CH_3$, $^t$Bu), 1.75 (s, 9H, $CH_3$, $^t$Bu), 1.78 (s, 3H, $CH_3$), 1.80 (s, 3H, $CH_3$), 2.08 (s, 6H, $CH_3$), 2.68 (s, 3H, $CH_3$), 6.49-6.51 (m, 1H, CH=), 6.53-6.56 (m, 1H, CH=), 6.95-7.04 (m, 5H, CH=), 7.11-7.16 (m, 1H, CH=), 7.27 (s, 1H, CH=), 7.34 (s, 1H, CH=), 7.35-7.37 (m, 1H, CH=), 8.02-8.03 (m, 2H, CH=). $^{13}$C{$^1$H} NMR (100.6 MHz, $C_6D_6$): δ = 16.4 ($CH_3$), 16.6 ($CH_3$), 20.0 ($CH_3$), 20.1 ($CH_3$), 31.2 (d, $CH_3$, $^t$Bu, $J_{C\text{-}P}$= 5.5 Hz), 31.7 (s, $CH_3$, $^t$Bu), 34.6 (C, $^t$Bu), 35.0 (C, $^t$Bu), 45.1 ($CH_3$), 121.9-145.7 (aromatic carbons). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{37}H_{44}NO_4PSNa$ 652.2621; Found 652.2623.

**L2a.** Yield: 39.9 mg (10%). $^{31}$P NMR (161.9 MHz, $C_6D_6$): δ = 131.1 (s). $^1$H NMR (400 MHz, $C_6D_6$): δ = 1.08 (s, 9H, $CH_3$, $^t$Bu), 1.26 (s, 9H, $CH_3$, $^t$Bu), 1.29 (s, 9H, $CH_3$, $^t$Bu), 1.52 (s, 9H, $CH_3$, $^t$Bu), 1.71 (s, 18H, $CH_3$, $^t$Bu), 2.65 (s, 3H, $CH_3$), 6.90-7.04 (m, 4H, CH=), 7.26 (d, 1H, CH=, $^4J_{H\text{-}H}$= 2.2 Hz), 7.43 (d, 1H, $^4J_{H\text{-}H}$= 2.4 Hz), 7.57 (d, 1H, CH=, $^4J_{H\text{-}H}$= 2.4 Hz), 7.67 (d, 1H, CH=, $^4J_{H\text{-}H}$= 2.5 Hz), 7.71 (d, 1H, CH=, $^4J_{H\text{-}H}$= 2.4 Hz), 7.94-7.97 (m, 2H, CH=). $^{13}$C{$^1$H} NMR (100.6 MHz, $C_6D_6$): δ = 30.4 ($CH_3$, $^t$Bu), 31.0 ($CH_3$, $^t$Bu), 31.2 ($CH_3$, $^t$Bu), 31.3 ($CH_3$, $^t$Bu), 31.4 ($CH_3$, $^t$Bu), 34.1 (C, $^t$Bu), 34.3 (C, $^t$Bu), 34.5 (C, $^t$Bu), 35.2 (C, $^t$Bu), 35.5 (C, $^t$Bu), 35.6 (C, $^t$Bu), 44.3 ($CH_3$), 116.8-150.3 (aromatic carbons). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{49}H_{68}NO_4PSNa$ 820.4499; Found 820.4501.

**L3a.** Yield: 160.0 mg (46%). $^{31}$P NMR (161.9 MHz, $C_6D_6$): δ = 138.2 (s). $^1$H NMR (400 MHz, $C_6D_6$): δ = 1.22 (s, 9H, $CH_3$, $^t$Bu), 1.25 (s, 9H, $CH_3$, $^t$Bu), 1.51 (s, 9H, $CH_3$, $^t$Bu), 1.58 (s, 9H, $CH_3$, $^t$Bu), 5.64 (d, 1H, CH=, $^3J_{H\text{-}H}$= 9.5 Hz), 6.60-6.69 (m, 2H, CH=), 6.75 (d, 1H, CH=, $^3J_{H\text{-}H}$= 9.5 Hz), 6.87-6.91 (m, 3H, CH=), 7.07-7.12 (m, 1H, CH=), 7.32 (dd, 2H, CH=, $^3J_{H\text{-}H}$= 6.5 Hz, $^4J_{H\text{-}H}$= 2.1 Hz), 7.56 (dd, 2H, CH=, $^3J_{H\text{-}H}$= 12.1 Hz, $^4J_{H\text{-}H}$= 2.1 Hz), 7.72 (dd, 2H, CH=, $^3J_{H\text{-}H}$= 7.3 Hz, $^4J_{H\text{-}H}$= 1.1 Hz). $^{13}$C{$^1$H} NMR (100.6 MHz, $C_6D_6$): δ = 31.1 ($CH_3$, $^t$Bu), 31.2 (d, $CH_3$, $^t$Bu, $J_{C\text{-}P}$= 2.3 Hz), 34.3 (d, C, $^t$Bu, $J_{C\text{-}P}$= 4.2 Hz), 35.4 (C, $^t$Bu), 35.5 (C, $^t$Bu), 110.8 (CH=), 117.7-146.5 (aromatic carbons). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{42}H_{50}NO_4PSNa$ 718.3090; Found718.3092.

**L3b.** Yield: 165.2 mg (54%). $^{31}$P NMR (161.9 MHz, $C_6D_6$): δ = 133.3 (s). $^1$H NMR (400 MHz, $C_6D_6$): δ = 1.48 (s, 9H, $CH_3$, $^t$Bu), 1.66 (s, 3H, $CH_3$), 1.68 (s, 9H, $CH_3$, $^t$Bu), 1.70 (s, 3H, $CH_3$), 1.98 (s, 3H, $CH_3$), 2.00 (s, 3H, $CH_3$), 5.74 (d, 1H, CH=, $^3J_{H\text{-}H}$= 9.8 Hz), 6.62 (t, 1H, CH=, $^3J_{H\text{-}H}$= 7.1 Hz), 6.72 (d, 1H, CH=, $^3J_{H\text{-}H}$= 7.8 Hz), 6.83 (d, 1H, CH=, $^3J_{H\text{-}H}$= 9.8 Hz), 6.86-6.98 (m, 3H, CH=), 7.14 (s, 1H, CH=), 7.21 (s, 1H, CH=), 7.27 (d, 1H, CH=, $^3J_{H\text{-}H}$= 7.7 Hz), 7.78-7.80 (m, 2H, CH=). $^{13}$C{$^1$H} NMR (100.6 MHz, $C_6D_6$): δ = 16.3 ($CH_3$), 16.5 ($CH_3$), 20.1 ($CH_3$), 31.2 (d, $CH_3$, $^t$Bu, $J_{C\text{-}P}$= 5.2 Hz), 31.8 ($CH_3$, $^t$Bu), 34.6 (C, $^t$Bu), 35.2 (C, $^t$Bu), 111.1 (CH=), 118.0-145.6 (aromatic carbons). HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{38}H_{42}NO_4PSNa$ 662.2464; Found662.2467.

**Preparation of [Ir(cod)(L1–L3a–c)]$BAr_F$ catalyst precursors.** The corresponding ligand (0.074 mmol) was dissolved in $CH_2Cl_2$ (5 mL) and $[Ir(\mu\text{–}Cl)(cod)]_2$ (25.0 mg, 0.037 mmol) was added. The reaction mixture was heated to reflux at 40 °C for 1 h. After 5 min at rt, $NaBAr_F$ (77.2 mg, 0.080 mmol) and water (5 mL) were added and the reaction mixture was stirred vigorously for 30 min at rt. The phases were separated and the aqueous phase was extracted twice with $CH_2Cl_2$. The combined organic phases were dried with $MgSO_4$ filtered through a plug of Celite and the solvent was evaporated to give the corresponding products as orange solids.

**[Ir(cod)(L1a)]$BAr_F$.** Yield: 124 mg (91%). Major isomer (57%): $^{31}$P NMR (161.9 MHz, $CDCl_3$): δ = 122.4 (s). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.27 (s, 9H, $CH_3$, $^t$Bu), 1.40 (s, 9H, $CH_3$, $^t$Bu), 1.44 (s, 9H, $CH_3$, $^t$Bu), 1.68 (s, 9H, $CH_3$, $^t$Bu), 1.57-1.67 (m, 2H, $CH_2$, cod), 1.95-2.16 (m, 2H, $CH_2$, cod), 2.28-2.35 (m, 3H, $CH_2$, cod), 2.49-2.52 (m, 1H, $CH_2$, cod), 3.91 (m, 1H, CH=, cod), 3.95 (s, 3H, $CH_3$), 4.57 (m, 1H, CH=, cod), 5.42 (m, 1H, CH=, cod), 6.15 (m, 1H, CH=, cod), 6.39-8.45 (m, 25H, CH=). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): δ = 25.9 ($CH_2$, cod), 29.8 ($CH_2$, cod), 31.1 ($CH_3$, $^t$Bu), 31.2 ($CH_3$, $^t$Bu), 31.5 ($CH_3$, $^t$Bu), 32.3 ($CH_2$, cod), 34.9-35.8 (C, $^t$Bu), 36.9 ($CH_2$, cod), 44.1 ($CH_3$), 65.3 (CH=, cod), 66.7 (CH=, cod), 99.8 (d, CH=, cod, $J_{C\text{-}P}$= 20.1 Hz), 109.2 (d, CH=, cod, $J_{C\text{-}P}$= 12.9 Hz), 117.8-150.2 (aromatic carbons), 162.1 (q, C-B, $BAr_F$, $^1J_{C\text{-}B}$= 49.8 Hz). Minor isomer (43%): $^{31}$P NMR (161.9 MHz, $CDCl_3$): δ = 120.8 (s). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.05-1.07 (m, 2H, $CH_2$, cod), 1.14 (s, 9H, $CH_3$, $^t$Bu), 1.34 (s, 9H, $CH_3$, $^t$Bu), 1.57 (s, 9H, $CH_3$, $^t$Bu), 1.73 (s, 9H, $CH_3$, $^t$Bu), 1.87-1.91 (m, 3H, $CH_2$, cod), 1.91 (m, CH=, cod), 2.08-2.24 (m, 2H, $CH_2$, cod), 2.50 (m, 1H, $CH_2$, cod), 3.12 ($CH_3$), 3.89 (m, 1H, CH=, cod), 4.41 (m, 1H, CH=, cod), 6.08 (m, 1H, CH=, cod), 7.11-8.02 (m, 25H, CH=). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): δ = 24.6 ($CH_2$, cod), 29.0 ($CH_2$, cod), 30.1 ($CH_2$, cod), 30.9 ($CH_3$, $^t$Bu), 31.1 ($CH_3$, $^t$Bu), 31.5 ($CH_3$, $^t$Bu), 33.2 ($CH_2$, cod), 34.9-35.8 (C, $^t$Bu), 50.0 ($CH_3$), 54.5 (CH=, cod), 66.3 (CH=, cod), 99.7 (d, CH=, cod, $J_{C\text{-}P}$= 22.5 Hz), 108.1 (d, CH=, cod, $J_{C\text{-}P}$= 13.8 Hz), 117.8-150.2 (aromatic carbons), 162.1 (q, C-B, $BAr_F$, $^1J_{C\text{-}B}$= 49.8 Hz). HRMS (ESI-TOF) m/z: $[M\text{-}BAr_F]^+$ Calcd for $C_{49}H_{64}IrNO_4PS$ 986.3923; Found 986.3919.

**[Ir(cod)(L1b)]$BAr_F$.** Yield: 122 mg (92%). Major isomer (80%): $^{31}$P NMR (161.9 MHz, $CDCl_3$): δ = 121.4 (s). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.15 (s, 9H, $CH_3$, $^t$Bu), 1.43-1.46 (m, 1H, $CH_2$, cod), 1.62 (s, 9H, $CH_3$, $^t$Bu), 1.70-1.82 (m, 1H, $CH_2$, cod), 1.72 (s, 3H, $CH_3$), 1.90 (s, 3H, $CH_3$), 2.05-2.08 (m, 1H, $CH_2$, cod), 2.25-2.33 (m, 3H, $CH_2$, cod), 2.28 (s, 3H, $CH_3$), 2.33 (s, 3H, $CH_3$), 2.50-2.54 (m, 1H, $CH_2$, cod), 2.33 (m, 1H, CH=, cod), 4.01 (s, 3H, $CH_3$), 4.32 (m, 1H, CH=, cod), 5.46 (m, 1H, CH=, cod), 6.58 (m, 1H, CH=, cod), 6.71-7.89 (m, 23H, CH=). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): δ = 16.9 ($CH_3$), 17.0 ($CH_3$), 20.0 ($CH_3$), 20.6 ($CH_3$), 25.8 ($CH_2$, cod), 29.8 ($CH_2$, cod), 31.5 ($CH_3$, $^t$Bu), 31.6 ($CH_3$, $^t$Bu), 32.6 ($CH_2$, cod), 35.2 (C, $^t$Bu), 35.3 (C, $^t$Bu), 37.5 ($CH_2$, cod), 49.6 ($CH_3$), 54.9 (CH=, cod), 68.8 (CH=, cod), 100.0 (d, CH=, cod, $J_{C\text{-}}$

$_P$= 21.3 Hz), 108.6 (d, CH=, cod, $J_{C\text{-}P}$= 14.1 Hz), 117.8-145.3 (aromatic carbons), 162.1 (q, C-B, $BAr_F$, $^1J_{C\text{-}B}$= 49.9 Hz). Minor isomer (20%): $^{31}$P NMR (161.9 MHz, $CDCl_3$): δ = 119.3 (s). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.28 (s, 9H, $CH_3$, $^t$Bu), 1.57 (s, 9H, $CH_3$, $^t$Bu), 1.70 (s, 3H, $CH_3$), 1.73-1.93 (m, 4H, $CH_2$, cod), 1.96 (s, 3H, $CH_3$), 2.00-2.30 (m, 4H, $CH_2$, cod), 2.30 (s, 3H, $CH_3$), 2.34 (s, 3H, $CH_3$), 3.54 (s, 3H, $CH_3$), 4.10 (m, 1H, CH=, cod), 4.14 (m, 1H, CH=, cod), 4.74 (m, 1H, CH=, cod), 5.89 (m, 1H, CH=, cod), 6.46-7.80 (m, 23H, CH=). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): δ = 16.8 ($CH_3$), 16.9 ($CH_3$), 20.7 ($CH_3$), 20.9 ($CH_3$), 25.8 ($CH_2$, cod), 30.4 ($CH_2$, cod), 31.4 ($CH_3$, $^t$Bu), 31.5 ($CH_3$, $^t$Bu), 31.9 ($CH_2$, cod), 32.3 ($CH_2$, cod), 35.8 (C, $^t$Bu), 44.6 ($CH_3$), 53.8 (CH=, cod), 63.1 (CH=, cod), 100.0 (CH=, cod), 109.0 (d, CH=, cod, $J_{C\text{-}P}$= 14.4 Hz), 121.8-147.3 (aromatic carbons), 162.1 (q, C-B, $BAr_F$, $^1J_{C\text{-}B}$= 49.9 Hz). HRMS (ESI-TOF) m/z: [M- $BAr_F$]$^+$ Calcd for $C_{45}H_{61}IrNO_4PS$ 930.3297; Found 930.3293.

**[Ir(cod)(L1c)]BAr$_F$.** Yield: 126 mg (95%). Major isomer (80%): $^{31}$P NMR (161.9 MHz, $CDCl_3$): δ = 121.4 (s). $^1$H NMR (400 MHz, $CDCl_3$): δ =1.17-1.28 (m, 2H, $CH_2$, cod), 1.26 (s, 9H, $CH_3$, $^t$Bu), 1.54 (m, 1H, CH=, cod), 1.69 (s, 9H, $CH_3$, $^t$Bu), 1.74 (s, 3H, $CH_3$), 1.90-2.13 (m, 2H, $CH_2$, cod), 2.21-2.29 (m, 2H, $CH_2$, cod), 2.40-2.44 (m, 2H, $CH_2$, cod), 1.98 (s, 3H, $CH_3$), 2.31 (s, 3H, $CH_3$), 2.36 (s, 3H, $CH_3$), 3.87 (s, 3H, $CH_3$), 4.06 (m, 1H, CH=, cod), 5.31 (m, 1H, CH=, cod), 6.11 (m, 1H, CH=, cod), 6.53-8.50 (m, 23H, CH=). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): δ =16.4 ($CH_3$), 16.5 ($CH_3$), 20.2 ($CH_3$), 20.5 ($CH_3$), 25.2 ($CH_2$, cod), 29.6 ($CH_2$, cod), 31.0 ($CH_3$, $^t$Bu), 31.1 ($CH_3$, $^t$Bu), 32.1 ($CH_2$, cod), 34.7 (C, $^t$Bu), 34.8 (C, $^t$Bu), 36.8 ($CH_2$, cod), 49.5 ($CH_3$), 55.1 (CH=, cod), 68.8 (CH=, cod), 99.6 (d, CH=, cod, $J_{C\text{-}P}$= 21.3 Hz), 108.0 (d, CH=, cod, $J_{C\text{-}P}$= 14.1 Hz), 117.4-144.9 (aromatic carbons), 161.6 (q, C-B, $BAr_F$, $^1J_{C\text{-}B}$= 49.9 Hz). Minor isomer (20%): $^{31}$P NMR (161.9 MHz, $CDCl_3$): δ = 119.1 (s). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.00-1.11 (m, 2H, $CH_2$, cod), 1.11 (s, 9H, $CH_3$, $^t$Bu), 1.22-1.25 (m, 2H, $CH_2$, cod), 1.56 (s, 9H, $CH_3$, $^t$Bu), 1.68-1.72 (m, 1H, $CH_2$, cod), 1.85 (s, 3H, $CH_3$), 2.10-2.21 (m, 3H, $CH_2$, cod), 2.24 (s, 3H, $CH_3$), 2.32 (s, 6H, $CH_3$), 3.08 (s, 3H, $CH_3$), 3.89 (m, 1H, CH=, cod), 4.26 (m, 1H, CH=, cod), 4.43 (m, 1H, CH=, cod), 6.05 (m, 1H, CH=, cod), 6.96-7.93 (m, 23H, CH=). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): δ = 16.4 ($CH_3$), 20.2 ($CH_3$), 20.4 ($CH_3$), 25.5 ($CH_2$, cod), 28.2 ($CH_2$, cod), 29.3 ($CH_2$, cod), 30.9 ($CH_3$, $^t$Bu), 31.7 ($CH_2$, cod), 34.9 (C, $^t$Bu), 35.3 (C, $^t$Bu), 36.8 ($CH_2$, cod), 44.1 ($CH_3$), 54.4 (CH=, cod), 68.4 (CH=, cod), 99.6 (CH=, cod), 108.3 (d, CH=, cod, $J_{C\text{-}P}$= 21.5 Hz), 121.2-146.8 (aromatic carbons), 161.6 (q, C-B, $BAr_F$, $^1J_{C\text{-}B}$= 49.9 Hz). HRMS (ESI-TOF) m/z: [M- $BAr_F$]$^+$ Calcd for $C_{45}H_{56}IrNO_4PS$ 930.3297; Found 930.3294.

**[Ir(cod)(L2a)]BAr$_F$.** Yield: 138 mg (95%). Major isomer (78%): $^{31}$P NMR (161.9 MHz, $CDCl_3$): δ = 117.4 (s). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.15 (s, 9H, $CH_3$, $^t$Bu), 1.17 (s, 9H, $CH_3$, $^t$Bu), 1.31 (s, 9H, $CH_3$, $^t$Bu), 1.37 (s, 9H, $CH_3$, $^t$Bu), 1.40 (s, 9H, $CH_3$, $^t$Bu), 1.70 (m, 1H, $CH_2$, cod), 1.74 (s, 9H, $CH_3$, $^t$Bu), 1.92-2.00 (m, 3H, $CH_2$, cod), 2.03 (m, 1H, CH=, cod), 2.30-2.34 (m, 2H, $CH_2$, cod), 2.40-2.58 (m, 2H, $CH_2$, cod), 2.90 (s, 3H, $CH_3$), 3.97 (m, 1H, CH=, cod), 4.63 (m, 1H, CH=, cod), 6.20 (m, 1H, CH=, cod), 7.02-8.43 (m, 23H, CH=). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): δ = 22.7 ($CH_2$, cod), 24.7 ($CH_2$, cod), 30.0 ($CH_2$, cod), 30.6 ($CH_3$, $^t$Bu), 31.0 ($CH_3$, $^t$Bu), 31.3 ($CH_3$, $^t$Bu), 31.9 ($CH_3$, $^t$Bu), 34.4 (C, $^t$Bu), 34.8 (C, $^t$Bu), 34.9 (C, $^t$Bu), 35.1 (C, $^t$Bu), 35.5 (C, $^t$Bu), 35.9 ($CH_2$, cod), 43.3 ($CH_3$), 52.7 (CH=, cod), 66.4 (CH=, cod), 101.3 (d, CH=, cod, $J_{C\text{-}P}$= 20.5 Hz), 107.9 (d, CH=, cod, $J_{C\text{-}P}$= 14.3 Hz), 117.4-149.7 (aromatic carbons), 161.6 (q, C-B, $BAr_F$, $^1J_{C\text{-}B}$= 49.7 Hz). Minor isomer (22%): $^{31}$P NMR (161.9 MHz, $CDCl_3$): δ = 118.6 (s). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.01 (s, 9H, $CH_3$, $^t$Bu), 1.14-1.25 (m, 3H, $CH_2$, cod), 1.28 (s, 9H, $CH_3$, $^t$Bu), 1.33 (s, 9H, $CH_3$, $^t$Bu), 1.38 (s, 9H, $CH_3$, $^t$Bu), 1.46 (s, 9H, $CH_3$, $^t$Bu), 1.59 (s, 9H, $CH_3$, $^t$Bu), 2.08-2.15 (m, 3H, $CH_2$, cod), 2.32-2.45 (m, 2H, $CH_2$, cod), 2.60 (m, 1H, CH=, cod), 3.97 (s, 3H, $CH_3$), 4.49 (m, 1H, CH=, cod), 5.72 (m, 1H, CH=, cod), 6.36 (m, 1H, CH=, cod), 6.39-7.81 (m, 23H, CH=). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): δ = 22.6 ($CH_2$, cod), 25.7 ($CH_2$, cod), 29.5 ($CH_2$, cod), 29.7 ($CH_3$, $^t$Bu), 30.8 ($CH_3$, $^t$Bu), 31.4 ($CH_3$, $^t$Bu), 31.6 ($CH_3$, $^t$Bu), 34.4 (C, $^t$Bu), 34.9 (C, $^t$Bu), 35.2 (C, $^t$Bu), 35.5 (C, $^t$Bu), 35.6 (C, $^t$Bu), 36.5 ($CH_2$, cod), 49.5 ($CH_3$), 55.4 (CH=, cod), 68.1 (CH=, cod), 103.3 (CH=, cod), 109.0 (CH=, cod), 1204-149.7 (aromatic carbons), 161.6 (q, C-B, $BAr_F$, $^1J_{C\text{-}B}$= 49.7 Hz). HRMS (ESI-TOF) m/z: [M- $BAr_F$]$^+$ Calcd for $C_{57}H_{80}IrNO_4PS$ 1098.5175; Found 1098.5170 .

**[Ir(cod)(L3a)]BAr$_F$.** Yield: 125 mg (91%). $^{31}$P NMR (161.9 MHz, $CDCl_3$): δ = 116.2 (s). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.26-1.28 (m, 1H, $CH_2$, cod), 1.38 (s, 18H, $CH_3$, $^t$Bu), 1.42 (s, 9H, $CH_3$, $^t$Bu), 1.49 (s, 9H, $CH_3$, $^t$Bu), 1.66-1.68 (m, 1H, $CH_2$, cod), 1.92-2.10 (m, 3H, $CH_2$, cod), 2.18-2.27 (m, 2H, $CH_2$, cod), 2.43-2.46 (m, 1H, $CH_2$, cod), 3.08 (m, 1H, CH=, cod), 3.54 (m, 1H, CH=, cod), 5.80 (m, 1H, CH=, cod), 6.49 (m, 1H, CH=, cod), 6.68-7.71 (m, 26H, CH=). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): δ = 26.2 ($CH_2$, cod), 28.6 ($CH_2$, cod), 29.7 ($CH_2$, cod), 31.3 ($CH_3$, $^t$Bu), 31.5 ($CH_3$, $^t$Bu), 32.2 ($CH_3$, $^t$Bu), 34.8 (d, C, $^t$Bu, $J_{C\text{-}P}$= 4.2 Hz), 35.6 (d, C, $^t$Bu, $J_{C\text{-}P}$= 7.1 Hz), 36.2 ($CH_2$, cod), 56.7 (CH=, cod), 61.6 (CH=, cod), 107.8 (d, CH=, cod, $J_{C\text{-}P}$= 16.9 Hz), 110.7 (d, CH=, cod, $J_{C\text{-}P}$= 14.1 Hz), 116.1 (CH=), 117.5-149.1 (aromatic carbons), 161.7 (q, C-B, $BAr_F$, $^1J_{C\text{-}B}$= 49.8 Hz). HRMS (ESI-TOF) m/z: [M- $BAr_F$]$^+$ Calcd for $C_{50}H_{62}IrNO_4PS$ 996.3766; Found 996.3762.

**[Ir(cod)(L3b)]BAr$_F$.** Yield: 124 mg (94%). $^{31}$P NMR (161.9 MHz, $CDCl_3$): δ = 113.7 (s). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.28 (m, 1H, $CH_2$, cod), 1.36 (s, 9H, $CH_3$, $^t$Bu), 1.45 (s, 9H, $CH_3$, $^t$Bu), 1.79 (s, 3H, $CH_3$), 1.73-1.95 (m, 2H, $CH_2$, cod), 1.85 (s, 3H, $CH_3$), 2.13-2.22 (m, 3H, $CH_2$, cod), 2.30 (s, 3H, $CH_3$), 2.31 (s, 3H, $CH_3$), 2.42 (m, 1H, $CH_2$, cod), 3.02 (m, 1H, CH=, cod), 3.59 (m, 1H, CH=, cod), 5.76 (m, 1H, CH=, cod), 6.39 (m, 1H, CH=, cod), 6.66-7.73 (m, 26H, CH=). $^{13}$C{$^1$H} NMR (100.6 MHz, $CDCl_3$): δ = 16.5 ($CH_3$), 16.6 ($CH_3$), 20.4 ($CH_3$), 26.1 ($CH_2$, cod), 28.6 ($CH_2$, cod), 31.2 ($CH_2$, cod) 31.6 ($CH_3$, $^t$Bu), 32.4 ($CH_3$, $^t$Bu), 34.9 (C, $^t$Bu), 35.0 (C, $^t$Bu), 36.2 ($CH_2$, cod), 56.8 (CH=, cod), 62.1 (CH=, cod), 107.4 (d, CH=, cod, $J_{C\text{-}P}$= 14.8 Hz), 109.4 (d, CH=, cod, $J_{C\text{-}P}$= 17.8 Hz), 115.8 (CH=), 117.5-144.7 (aromatic carbons), 161.6 (q, C-B, $BAr_F$, $^1J_{C\text{-}B}$= 49.8 Hz). HRMS (ESI-TOF) m/z: [M- $BAr_F$]$^+$ Calcd for $C_{46}H_{54}IrNO_4PS$ 940.3140; Found: 940.3138.

**General procedure for the asymmetric hydrogenation.** The alkene (0.25 mmol) and Ir complex (1 mol%) were dissolved in $CH_2Cl_2$ (1.5 mL) and placed in a high-pressure autoclave. The autoclave was purged 4 times with hydrogen. Then, it was pressurized at the desired pressure. After the desired reaction time, the autoclave was depressurized, and the solvent evaporated off. The residue was dissolved in $Et_2O$ (1.5 ml) and filtered through a short plug of Celite. Conversions were determined by $^1$H NMR and enantiomeric excesses were determined by chiral HPLC or GC.

*(R)-1,3-diphenylbutan-1-one.*[5a] Yield: 54 mg (96%). Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=97/3, 0.5 mL/min, 220 nm). $t_R$ 31.0 min (*R*); $t_R$ 33.8 min (*S*). $^1$H NMR ($CDCl_3$), δ: 1.33 (d, 3H, *J*= 6.7 Hz), 3.17 (m, 1H), 3.28 (m, 1H), 3.50 (m, 1H), 7.1-7.9 (m, 5H).

*(R)-3-Methyl-4-phenylbutan-2-one.*[5b] Yield: 39 mg (97%). Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=97/3, 1 mL/min, 220 nm). $t_R$ 8.6 min (*S*); $t_R$ 9.2 min (*R*). $^1$H NMR ($CDCl_3$), δ: 1.08 (d, 3H, *J*= 6.8 Hz), 2.08 (s, 3H), 2.56 (m, 1H), 2.82 (m, 1H), 2.98 (m, 1H), 7.1-7.3 (m, 5H).

*(-)-4-Methyl-1,3-diphenylpentan-1-one.*[5a] Yield: 60 mg (96%). Enantiomeric excess determined by HPLC using Chiracel AD column (hexane/2-propanol=97/3, 0.5 mL/min, 220 nm). $t_R$ 16.2 min (+); $t_R$ 19.0 min (-). $^1$H NMR ($CDCl_3$), δ: 0.78 (d, 3H, *J*= 6.9 Hz), 0.97 (d, 3H, *J*= 6.6 Hz), 1.93 (m, 1H), 3.15 (m, 1H), 3.35 (m, 1H), 7.1-7.5 (m, 8H), 7,86 (m, 2H).

*(R)-4-(4-Methylphenyl)-3-methylbutan-2-one.*[5b] Yield: 41 mg (94%). Enantiomeric excess determined by HPLC using Chiracel Lux-Amylose-1 column (hexane/2-propanol=97/3, 0.5 mL/min, 220 nm). $t_R$ 11.0 min (*R*); $t_R$ 11.6 min (*S*).$^1$H NMR ($CDCl_3$), δ: 1.04 (d, 3H, *J*= 6.8 Hz), 2.06 (s, 3H), 2.50 (dd, 1H, *J*= 7.4 Hz, *J*= 13.4 Hz), 2.76 (m, 1H), 2.92 (dd, 1H, *J*= 6.8 Hz, *J*= 13.4 Hz), 3.77 (s, 3H), 6.80 (m, 2H), 7.0-7.3 (m, 2H).

*(R)-4-(4-Methoxyphenyl)-3-methylbutan-2-one.*[5b] Yield: 46 mg (95%). Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=95/5, 0.5 mL/min, 220 nm). $t_R$ 25.5 min (*S*); $t_R$ 27.8 min (*R*). $^1$H NMR ($CDCl_3$), δ: 1.07 (d, 3H, *J*= 6.8 Hz), 2.08 (s, 3H), 2.52 (dd, 1H, *J*= 7.4 Hz, *J*= 13.4 Hz), 2.78 (m, 1H), 2.93 (dd, 1H, *J*= 6.8 Hz, *J*= 13.4 Hz), 3.77 (s, 3H), 6.82 (m, 2H), 7.0-7.3 (m, 2H).

*(R)-2-Methyl-1-phenylpentan-3-one.*[5b] Yield: 41 mg (93%). Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=99/1, 0.5 mL/min, 220 nm). $t_R$ 15.2 min (*S*); $t_R$ 16.2 min (*R*). $^1$H NMR ($CDCl_3$), δ: 0.96 (t, 3H, *J*= 7.2 Hz), 1.07 (d, 3H, *J*= 6.8 Hz), 2.21 (m, 1H), 2.43 (m, 1H), 2.57 (dd, 1H, *J*= 7.0 Hz, *J*= 13.4 Hz), 2.83 (m, 1H), 2.92 (dd, 1H, *J*= 6.8 Hz, *J*= 13.4 Hz), 7.1-7.3 (m, 5H).

*(R)-2,4-Dimethyl-1-phenylpentan-3-one.*[5b] Yield: 45 mg (95%).Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=99/1, 0.5 mL/min, 220 nm). $t_R$ 15.2 (*S*); $t_R$ 17.8 min (*R*). $^1$H NMR ($CDCl_3$), δ: 0.80 (d, 3H, *J*= 6.8 Hz), 0.95 (d, 3H, *J*= 6.8 Hz), 1.01 (d, 1H, *J*= 6.8 Hz), 2.49 (m, 2H), 2.95 (m, 2H), 7.0-7.2 (m, 5H).

*(R)-2-Methyl-1,3-diphenylpropan-1-one.*[5b] Yield: 55 mg (98%). Enantiomeric excess determined by HPLC using Chiracel OB column (hexane/2-propanol=98.2, 0.5 mL/min, 220 nm). $t_R$ 12.9 min (*S*); $t_R$ 13.7 min (*R*). $^1$H NMR ($CDCl_3$), δ: 1.13 (d, 3H, *J*= 6.8 Hz), 2.61 (dd, 1H, *J*= 13.2 Hz, *J*= 7.2 Hz), 3.09 (dd, 1H, *J*= 13.2 Hz, *J*= 6.4 Hz), 3.69 (m, 1H), 7.1-7.9 (m, 10H).

*(R)-2-Benzylcyclohexanone.*[5b] Yield: 43 mg (92%). Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=97/3, 1 mL/min, 210 nm). $t_R$ 8.4 min (*S*); $t_R$ 9.1 min (*R*). $^1$H NMR ($CDCl_3$), δ: 1.35 (m, 1H), 1.63 (m, 2H), 1.83 (m, 1H), 2.04 (m, 2H), 2.44 (m, 4H), 3.24 (dd, 1H, *J* = 14.0 Hz, *J*= 4.6 Hz), 7.18 (m, 3H), 7.28 (m, 2H).

*(S)-Ethyl 3-phenylbutanoate.*[24] Yield: 44 mg (91%). Enantiomeric excess determined by HPLC using Chiracel IB column (hexane/2-propanol=99.5/0.5, 1 mL/min, 254 nm). $t_R$ 10.6 min (*R*); $t_R$ 18.5 min (*S*). $^1$H NMR ($CDCl_3$), δ: 1.16 (t, 3H, *J*= 7.2 Hz), 1.30 (d, 3H, *J*= 6.8 Hz), 2.54 (m, 2H), 3.28 (m, 1H), 4.08 (q, 2H, *J*= 7.2 Hz), 7.2-7.3 (m, 5H).

*(S)-Ethyl 3-(p-tolyl)butanoate.*[25] Yield: 48 mg (93%). Enantiomeric excess determined by HPLC using Chiracel IB column (hexane/2-propanol=99.5/0.5, 0.5 mL/min, 254 nm). $t_R$ 12.3 min (*R*); $t_R$ 13.0 min (*S*). $^1$H NMR ($CDCl_3$), δ: 1.11 (t, 3H, *J*= 7.2 Hz), 1.21 (d, 3H, *J*= 6.0 Hz), 2.24 (s, 3H), 2.49 (m, 2H), 3.17 (m, 1H), 4.00 (q, 2H, *J*= 7.2 Hz), 7.04 (m, 4H).

*(S)-Ethyl 3-(4-methoxyphenyl)butanoate.*[25] Yield: 51 mg (91%). Enantiomeric excess determined by HPLC using Chiracel IB column (hexane/2-propanol=99.5/0.5, 0.5 mL/min, 254 nm). $t_R$ 18.5 min (*R*); $t_R$ 19.5 min (*S*). $^1$H NMR ($CDCl_3$), δ: 1.11 (t, 3H, *J*= 7.2 Hz), 1.26 (d, 3H, *J*= 6.4 Hz), 2.54 (m, 2H), 3.24 (m, 1H), 3.77 (s, 3H), 4.07 (q, 2H, *J*= 7.2 Hz), 6.82 (m, 2H), 7.13 (m, 2H).

*(S)-Ethyl 3-phenylpentanoate.*[25] Yield: 46 mg (92%). Enantiomeric excess determined by HPLC using Chiracel IC column (hexane/2-propanol=99.5/0.5, 0.5 mL/min, 254 nm). $t_R$ 11.6 min (*R*); $t_R$ 12.0 min (*S*). $^1$H NMR ($CDCl_3$), δ: 0.79 (t, 3H, *J*= 7.2 Hz), 1.13 (t, 3H, *J*= 7.2 Hz), 1.62 (m, 2H), 2.60 (m, 2H), 2.99 (m, 1H), 4.03 (q, 2H, *J*= 7.2 Hz), 7.17 (m, 2H), 7.26 (m, 3H).

*(S)-Ethyl 4-methyl-3-phenylpentanoate.*[26] Yield: 52 mg (93%). Enantiomeric excess determined by HPLC using Chiracel OD-H column (hexane/2-propanol=99/1, 0.5 mL/min, 254 nm). $t_R$ 11.0 min (*R*); $t_R$ 18.8 min (*S*). $^1$H NMR ($CDCl_3$), δ: 0.75 (d, 3H, *J*= 6.0 Hz), 0.95 (d, 3H, *J*= 6.0 Hz), 1.06 (t, 3H, *J*= 6.8 Hz), 1.86 (m, 1H), 2.58 (m, 1H), 2.76 (m, 1H), 2.86 (m, 1H), 3.94 (q, 2H, *J*= 6.8 Hz), 7.1-7.3 (m, 5H).

*(S)-Ethyl 3-cyclohexyl-3-phenylpropanoate.*[27] Yield: 61 mg (95%). Enantiomeric excess determined by HPLC using Chiracel OD-H column (hexane/2-propanol=99/1, 0.5 mL/min, 254 nm). $t_R$ 10.3 min (*R*); $t_R$ 17.9 min (*S*). $^1$H NMR ($CDCl_3$), δ: 0.92 (m, 1H), 0.93 (m, 1H), 1.06 (t, 3H, *J*= 7.2 Hz), 1.12 (m, 1H), 1.24 (m, 2H), 1.42 (m, 2H), 1.60 (m, 2H), 1.72 (m, 1H), 1.80 (m, 1H), 2.54 (m, 1H), 2.78 (m, 1H), 2.89 (m, 1H), 3.92 (q, 2H, *J*= 7.2 Hz), 7.1-7.3 (m, 5H).

*(R)-3-Benzyltetrahydro-2H-pyran-2-one.*[16f] Yield: 23 mg (49%). Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=90/10, 1 mL/min, 210 nm). $t_R$ 39.4 min (*R*); $t_R$ 44.4 min (*S*). $^1$H NMR ($CDCl_3$), δ: 1.51 (m, 1H), 1.83 (m, 3H), 2.71 (m, 2H), 3.35 (m, 1H), 4.26 (m, 2H), 7.1-7.3 (m, 5H).

*(R)-3-Benzyldihydrofuran-2(3H)-one.*[16f] Yield: 41 mg (94%). Enantiomeric excess determined by HPLC using Chiracel OD-H column (hexane/2-propanol=90/10, 1 mL/min, 254 nm). $t_R$ 17.3 min (*S*); $t_R$ 18.8 min (*R*). $^1$H NMR ($CDCl_3$), δ: 1.98 (m, 1H), 2.12 (m, 1H), 2.64 (m, 1H), 2.84 (m, 1H), 3.12 (m, 1H), 4.16 (m, 1H), 4.22 (m, 1H), 7.2-7.3 (m, 5H).

*(R)-1-Acetyl-3-benzylpiperidin-2-one.*[10e] Yield: 42 mg (72%). Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=80/20, 0.5 mL/min, 210 nm). $t_R$ 21.5 min (*S*); $t_R$ 23.6 min (*R*). $^1$H NMR ($CDCl_3$), δ: 1.47 (m, 1H), 1.71 (m, 1H), 1.82 (m, 2H), 2.47 (s, 3H), 2.69 (m, 2H), 3.30 (m, 1H), 3.54 (m, 1H), 3.77 (m, 1H), 7.1-7.3 (m, 5H).

*(R)-1-benzyl-3-(cyclohexylmethyl)piperidin-2-one.*[10e] Yield: 62 mg (87%). Enantiomeric excess determined by HPLC using Chiracel IA column (hexane/2-propanol=90/10, 0.5 mL/min, 210 nm). $t_R$ 16.3 min (*S*); $t_R$ 19.1 min (*R*). $^1$H NMR ($CDCl_3$), δ: 0.82 (m, 1H), 0.92 (m, 1H), 1.0-1.4 (m, 5H), 1.43 (m, 1H), 1.64 (m, 5H), 1.81 (m, 1H), 1.92 (m, 2H), 2.41 (m, 1H), 3.18 (m, 1H), 4.42 (m, 2H), 7.1-7.3 (m, 5H).

*(-)-2-(1,2-Diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.*[16g] Yield: 71 mg (92%). Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=99/1, 0.5 mL/min, 254 nm). $t_R$ 9.5 min (-); $t_R$ 12.9 min (+). $^1$H NMR ($CDCl_3$), δ: 1.02 (s, 6H), 1.09 (s, 6H), 2.67 (dd, 1H, *J*= 6.8 Hz, *J*= 10.0 Hz), 2.95 (dd, 1H, *J*= 7.0 Hz, *J*= 13.6 Hz), 3.15 (dd, 1H, *J*= 9.6 Hz, *J*= 13.6 Hz), 7.1-7.2 (m, 10H).

*(S)-Propane-1,2-diyldibenzene.*[24] Yield: 46 mg (94%). Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=99/1, 0.5 mL/min, 254 nm). $t_R$ 12.7 min (*R*); $t_R$ 17.5 min (*S*). $^1$H NMR ($CDCl_3$), δ: 1.26 (d, 3H, *J*= 6.8 Hz), 2.78 (m, 1H), 3.00 (m, 2H), 7.10 (m, 2H), 7.2-7.3 (m, 8H).

*(S)-(3,3-Dimethylbutan-2-yl)benzene.*[24] Yield: 37 mg (92%). Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa $H_2$, 60 °C for 30 min, 3 °C/min until 175 °C). $t_R$ 36.0 min (*S*); $t_R$ 37.1 min (*R*). $^1$H NMR ($CDCl_3$), δ: 0.86 (s, 9H), 1.25 (d, 3H, *J*= 6.8 Hz), 2.54 (q, 1H, *J*= 6.8 Hz), 7.1-7.3 (m, 5H).

## ASSOCIATED CONTENT

Copies of NMR spectra of intermediates (**6**, **7**, **10**, **11**, **13** and **14**), ligands (**L1**–**L3a**–**c**), [[Ir(cod)(**L1**–**L3a**–**c**)]$BAr_F$ complexes. Copies of $^1$H–NMR and GC/HPLC traces for all hydrogenated products. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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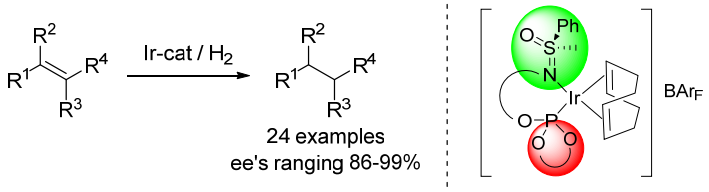
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