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Synthesis of Pyridyl-dihydrobenzooxaphosphole Ligands and Their Application in Asymmetric Hydrogenation of Unfunctionalized Alkenes

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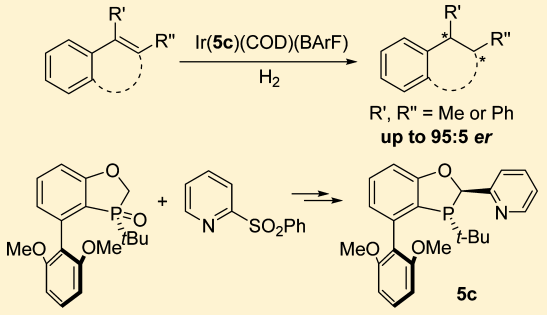
Supporting Information

ABSTRACT: Synthesis of the electron-rich 2-substituted-6-(phenylsulfonyl)pyridines is presented. A series of air-stable, tunable, *P*-chiral pyridyl-dihydrobenzooxaphosphole ligands were designed and synthesized by a diastereoselective S_NAr substitution of the corresponding sulfonyl pyridines. The ligands were successfully applied in the Ir-catalyzed asymmetric hydrogenation of unfunctionalized alkenes with good enantioselectivities.

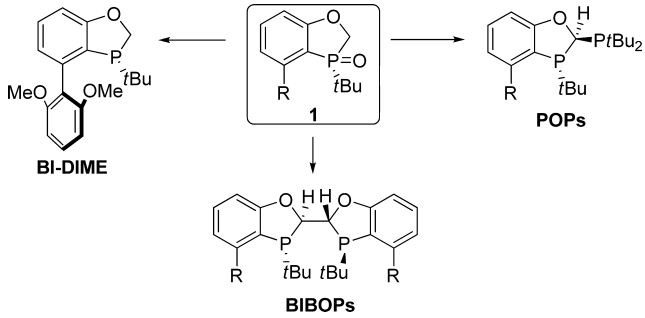


INTRODUCTION

Chiral phosphine ligands have played a central role in the field of asymmetric catalysis toward the rapid synthesis of enantiomerically pure pharmaceuticals and fine chemicals.[1] Development of structurally novel, sterically or electronically tunable, and operationally convenient chiral phosphorus ligands continues to be of great interest in further broadening the scope of asymmetric hydrogenation as well as in the discovery of new efficient transition-metal-catalyzed asymmetric reactions.[2] Even though an impressive number of chiral phosphine ligands have been developed since the pioneering work of Kagan, Noyori, Knowles, and others,[3] only a limited set of these has been applied in large-scale chemical processes presumably due to their lengthy synthesis as well as the challenges associated with the fine-tuning of the electronic and steric properties.[4]

Recently, we have developed a rigid modular *P*-chiral dihydrobenzooxaphosphole core structure **1** (Scheme 1). A series of ligands, such as BIBOP and POP, were derived from this chiral intermediate to enable high enantioselectivities in the rhodium-catalyzed asymmetric hydrogenation of functionalized alkenes, such as enamides and unsaturated amino acid derivatives.[5] BI-DIME has been demonstrated as a highly efficient ligand for the palladium-catalyzed Suzuki−Miyuara and Buchwald−Hartwig couplings of sterically demanding substrates.[6] Herein, we report the synthesis of a new series of air-stable chiral pyridyl-phosphine ligands (BoQPhos) and the application of these ligands in the iridium-catalyzed asymmetric hydrogenation of *unfunctionalized* tri- and tetrasubstituted alkenes.

Scheme 1. Chiral Ligands Developed from the *P*-Chiral Dihydrobenzooxaphosphole 1



Despite the success of many chiral ligands applied for rhodium- and ruthenium-catalyzed hydrogenations, particularly for alkenes bearing a coordinating group next to the C=C bond,[7] unfunctionalized alkenes have remained a challenging class of substrates, as there are no functional groups in position to guide the catalyst in differentiating between the enantiofaces of the alkenes.[8] Pfaltz and others have shown that P,N ligands, such as phosphinooxazoline (PHOX) ligands, are particularly effective for the Ir-catalyzed asymmetric hydrogenation of unfunctionalized alkenes and furnishing high enantioselectivities.[9] Inspired by these results, we aimed to develop a new class of pyridyl-phosphine P,N ligands based on the dihydroben-

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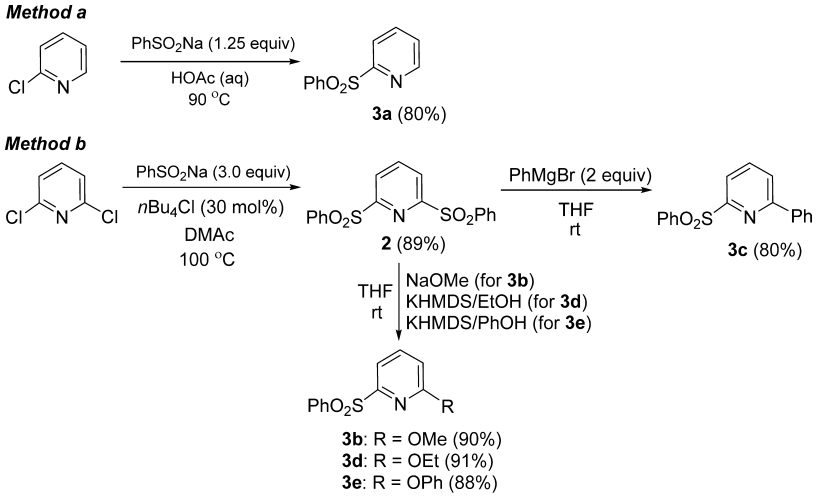
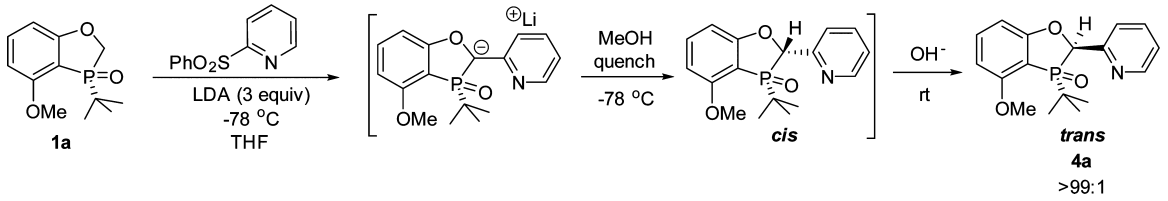
Scheme 2. Synthesis of Phenylsulfonylpyridines



Scheme 3. Mechanism of the *trans*-Diastereomer Formation



zooxaphosphole core **1**. The notable features of these new P,N ligands are their tunability by variation of the substitution on both the phenyl and the pyridyl rings. We anticipated that the steric and electronic variation of the substituents would have a great impact on the efficiency of their iridium complexes when applied to the asymmetric hydrogenation of unfunctionalized alkenes.

RESULTS AND DISCUSSION

To construct the pyridyl-phosphines in a concise manner, S_NAr coupling of 2-sulfonylpyridines with the derivatives of **1** was explored due to the necessary acidity of the α-proton to the phosphorus atom in the dihydrobenzooxaphosphole core. The sulfonylpyridines are valuable building blocks, which can be easily displaced under nucleophilic substitution conditions to incorporate pyridine moieties into complex molecules.[10] Unsubstituted sulfonylated pyridine **3a** was readily obtained from a direct S_NAr displacement of 2-chloropyridine with benzene sulfinic acid sodium salt in 80% yield in the presence of acetic acid (Scheme 2, Method a). However, no product formation was observed with 2-chloro-6-phenylpyridine or electron-rich 2-chloro-6-alkoxypyridines. Aryl sulfones are generally prepared by oxidation of the sulfides,[11] metal-catalyzed cross-coupling of aryl halides with arenesulfinic acid salts,[12] or the corresponding electrophilic aromatic substitution reactions.[13] Most of these methods are only applicable to the electron-deficient aryl halides. Indeed, an alternative approach applying Cu(I)-catalyzed coupling of 2-bromo-6-methoxypyridine with phenyl sulfinic acid salts provided a low yield for **3b** (<20%). Gratifyingly, **3b** was obtained in 90% yield from S_NAr displacement of the 2,6-disulfonylated pyridine **2** (Method b). Even though not previously reported, pyridine disulfone **2** was readily synthesized in 89% yield by treatment of the 2,6-dichloropyridine with phenyl sulfinic acid salt at 100 °C in DMAc.[13] Similarly, 2-phenyl-6-(phenylsulfonyl)pyridine **3c** was obtained in 80% yield from the reaction with PhMgBr. 2-Ethoxy-6-(phenylsulfonyl)pyridine **3d** and 2-phenoxy-6-(phenylsulfonyl)pyridine **3e** were also isolated in high yields, 91% and 88% respectively, by treatment with the corresponding alcohols in the presence of KHMDS. Electron-rich 2-substituted 6-(phenylsulfonyl)pyridines could be readily prepared through Method b.

With the sulfonylated pyridines in hand, S_NAr reaction of 2-(phenylsulfonyl)pyridine with chiral precursor **1a** was first evaluated. Subjecting the mixture to 1 equiv of LDA at −78 °C provided only a 35% conversion. However, complete conversion was obtained by increasing the LDA stoichiometry to 3 equiv (Scheme 3). Two diastereomers were observed from the coupling. The *cis*-diastereomer was the initial major isomer right after MeOH quench at −78 °C. After warming up to rt, the *cis*-isomer gradually converted to the thermodynamically more stable *trans*-isomer with the bulky *tert*-butyl group positioned *trans* to the pyridyl functionality. A high *trans*:*cis* ratio of >99:1 could be obtained after treating with additional aqueous NaOH. The trace amount of the *cis*-diastereomer was removed easily by silica gel purification or by recrystallization. Pure **4a** was isolated in 85% yield. The absolute configuration of the *trans*-isomer was confirmed by the X-ray single crystal structure of phosphine oxide **4a** (Figure 1).[14] Reduction of the P,N oxide **4a** with polymethylhydrosiloxane (PMHS) and $Ti(OiPr)_4$ conditions provided phosphine ligand **5a** as a white solid in 86% yield.

Under the same reaction conditions, a series of pyridyl-dihydrobenzooxaphosphole ligands **5b**−**5f** were synthesized in good yields starting from **1** in two steps (Scheme 4). Both the S_NAr coupling and the reduction reactions are stereoselective. Phosphine oxides and free phosphines are all >99% ee.[20] The isolated free phosphines proved to be air-stable. Compound **5a**

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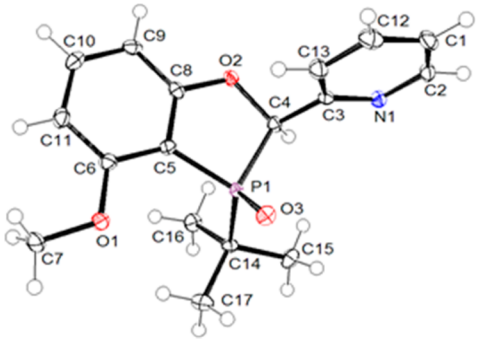
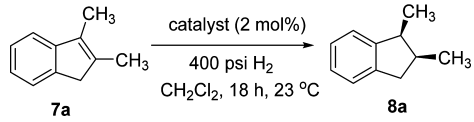


Figure 1. X-ray single crystal structure of **4a**, ellipsoids at 50% probability.

was exposed to air at ambient temperature for 1 month with no detectable amount of oxidation product as determined by ^{31}P NMR analysis. The corresponding cationic iridium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BArF) complexes were then prepared according to known procedures and purified by silica gel chromatography.[15] The iridium complexes of **6a**–**6d** from the unsubstituted pyridyl phosphine ligands were obtained as red-orange solids. However, the iridium complexes **6e** and **6f** from the *ortho*-substituted pyridyl phosphine ligands were obtained as light yellow solids. More importantly, the ^{1}H NMR spectroscopy of catalyst **6e** from the bis-methoxy ligand **5e** showed only one methoxy signal at 3.96 ppm. The detailed NMR analyses indicated that complex **6e** is a five-membered chelate hydridoiridium derivative that resulted by an intramolecular C–H activation of the methoxy group on pyridine.[21] The cyclometalated methylene group was identified by two unequal ^{1}H signals at 6.72 and 7.32 ppm and one methylene group ^{13}C NMR signal at 61.62 ppm from the DEPT ^{13}C NMR spectroscopy. Additionally, a metal hydride was located at −13.34 ppm as a doublet from coupling with the phosphorus atom. Similarly, hydridoiridium complex **6f** was formed by C–H bond oxidative addition of the phenyl substituent that is in close proximity to the metal center. The resulting hydridoiridium complexes **6e** and **6f** are stable in solution for at least 1 week ($CDCl_3$, 293 K).

With the new pyridyl-phosphorus iridium complexes in hand, asymmetric hydrogenation of tetrasubstituted 2,3-dimethylindene **7a** was examined using the complexes **6a**–**6f** as catalysts (Table 1). Screening of solvents has identified methylene

Table 1. Asymmetric Hydrogenation of Dimethylindene 7a



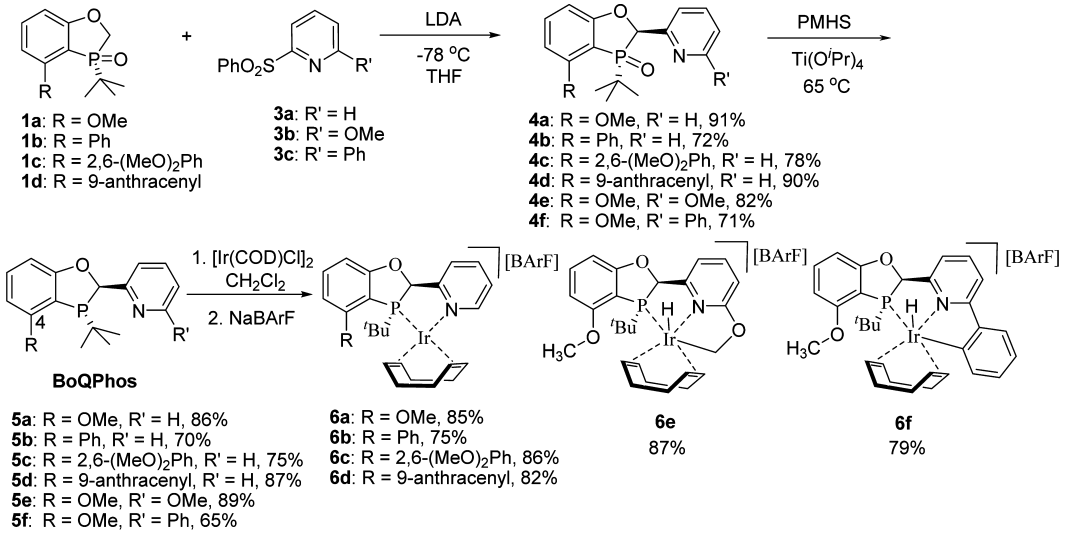
7a **8a**

entry	catalyst	conv %	*er* of **8a**
1	**6a**	100%	86:14
2	**6b**	40%	72:28
3	**6c**	**90%**	**88:12**
4	**6d**	6%	77:23
5	**6e**	15%	52:48
6	**6f**	10%	55:45

chloride as the best hydrogenation solvent. Complete conversion and a good enantioselectivity of 86:14 *er* were obtained at 400 psi H_2 and 23 °C with Ir-complex **6a** derived from the unsubstituted pyridyl ligand **5a** (Table 1, entry 1). However the hydridoiridium complexes **6e** and **6f** impeded both the reactivity and the selectivity (entries 5 and 6). Aryl groups were also incorporated at the 4-position of compound **1**; low reactivity and selectivity were observed with 4-phenyl substituted catalyst **6b** (entry 2) and 9-anthracenyl substituted **6d** (entry 4). To our delight, the catalyst **6c** obtained from incorporation of the 2,6-dimethoxyphenyl functionality produced **8a** with the optimal results of up to 88:12 *er* (entry 3).

Catalyst **6c** was further evaluated on asymmetric hydrogenation of additional tri- and tetrasubstituted alkenes (Scheme 5). Treatment of *trans*-α-methylstilbene **7b** in the presence of complex **6c** produced the adduct **8b** in a 95:5 *er*. Reduction of phenyldihydronaphthalene **7c** with catalyst **6c** generated the adduct **8c** in an 88:12 *er*. Dihydronaphthalene **7d** is generally more difficult to hydrogenate enantioselectively; a good enantiomeric ratio of 90:10 was obtained for **8d** with an 80% conversion at 400 psi H_2 in the presence of catalyst **6c**. In comparison, the optimized PHOX ligand produced **8d** in an

Scheme 4. Synthesis of the Iridium Pyridyl-Dihydrobenzooxaphosphole Complexes



1a: R = OMe
1b: R = Ph
1c: R = 2,6-$(MeO)_2$Ph
1d: R = 9-anthracenyl

3a: R' = H
3b: R' = OMe
3c: R' = Ph

4a: R = OMe, R' = H, 91%
4b: R = Ph, R' = H, 72%
4c: R = 2,6-$(MeO)_2$Ph, R' = H, 78%
4d: R = 9-anthracenyl, R' = H, 90%
4e: R = OMe, R' = OMe, 82%
4f: R = OMe, R' = Ph, 71%

5a: R = OMe, R' = H, 86%
5b: R = Ph, R' = H, 70%
5c: R = 2,6-$(MeO)_2$Ph, R' = H, 75%
5d: R = 9-anthracenyl, R' = H, 87%
5e: R = OMe, R' = OMe, 89%
5f: R = OMe, R' = Ph, 65%

6a: R = OMe, 85%
6b: R = Ph, 75%
6c: R = 2,6-$(MeO)_2$Ph, 86%
6d: R = 9-anthracenyl, 82%

6e 87%

6f 79%

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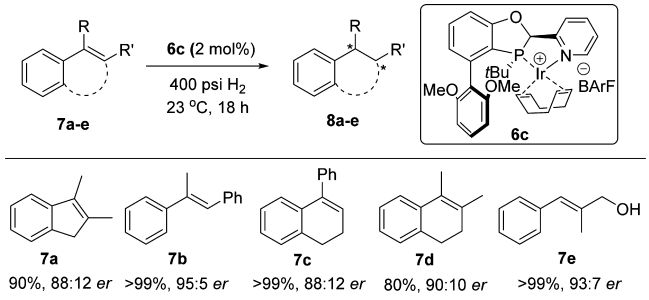
Scheme 5. Asymmetric Hydrogenation of Alkenes with Catalyst 6c



89:11 *er* and 46% conversion.[16] Recently, we have reported a higher *er* of 95:5 for **8d** using the phosphine imidazoline-based iridium BIPI 238 complex.[17] Reduction of (*E*)-2-methyl-3-phenylpropenol (**7e**) containing an allylic hydroxyl group with catalyst **6c** provided the adduct **8e** in a 93:7 *er* and complete conversion.

CONCLUSIONS

A new method for the synthesis of electron-rich 2-substituted 6-(phenylsulfonyl)pyridines was reported starting from 2,6-disulfonylated pyridine. A series of new air-stable chiral pyridyldihydrobenzooxaphosphole ligands (BoQPhos) were conveniently synthesized by a diastereoselective S_NAr displacement of the key intermediate **1** with the sulfonylated pyridine derivatives. Initial application of these ligands to the asymmetric hydrogenation of challenging unfunctionalized alkenes yielded good enantioselectivities. The electronic and steric properties of the ligand system can be readily tuned by the judicious choice of substituents on the chiral core structure and on the pyridine ring, thereby providing a facile approach to ligand optimization toward a diverse number of transition-metal-catalyzed asymmetric transformations.

EXPERIMENTAL SECTION

General Methods. All starting materials and reagents were purchased from the commercial sources and used without further purification. All ^1H and ^{13}C NMR data were referenced to the internal deuterated solvent relative to TMS at 0 ppm. High-resolution mass spectroscopy was performed on a TOF instrument with ESI and positive and negative ionization modes. Flash chromatography was performed on an automated system with silica columns. Compounds **1a**,[5a] **1b**,[5a] **1c**,[6a] and **1d**[18] have been previously described. Sulfonyl pyridines **3a**[11]and **3c**[19] are known compounds; alternative syntheses are described herein.

Synthesis of the Sulfonyl Pyridines. *2,6-Bis(phenylsulfonyl)-pyridine (**2**).* To a N_2-purged reactor was charged 10.0 g (67.57 mmol) of 2,6-dichloropyridine, 16.64 g (101.4 mmol) of sodium benzenesulfinate, 5.6 g (20.73 mmol) of tetrabutylammonium chloride, and 100 mL of *N*,*N*-dimethylacetamide. The mixture was heated to 100 °C and stirred for 4 h. Then another portion of 16.64 g (101.4 mmol) of sodium benzenesulfinate was charged, and the mixture was stirred at 100 °C for 14 h until more than 95% conversion was obtained. The mixture was cooled down to rt, and 300 mL of water was added to observe formation of white precipitates. The slurry was stirred at rt for 1 h. The solid was filtered and washed with 20 mL of isopropanol. **2** (21.6 g) was obtained as a white solid after drying under vacuum at 50 °C: 89% yield; mp 178.1−180.4 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 7.6 Hz, 2H), 8.18−8.16 (m, 1H), 7.94−7.91 (m, 4H), 7.66 (tt, J = 7.5, 1.2 Hz, 2H), 7.51 (t, J = 7.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 140.6, 137.4, 134.2, 129.4, 129.1, 124.2; HRMS (ESI) m/z 360.0358 (M + H^+), calcd for $C_{17}H_{14}NO_4S_2$ 360.0359.

*2-(Phenylsulfonyl)pyridine (**3a**).* To a 500 mL reactor was charged 113.6 g (1.0 mol) of 2-chloropyridine, the first portion of $PhSO_2Na$ (82 g, 0.5 mol, 0.5 equiv), 226 mL of acetic acid, and 72 mL of water. The mixture was heated to 90 °C and stirred for 2 h. Then 0.75 equiv of $PhSO_2Na$ was added in three portions (41 g, 0.25 equiv each) in 15 h. HPLC analysis showed >97% conversion. The mixture was cooled down to rt, and 150 mL of water was added. Stirring was continued for 30 min. The slurry was filtered. The crude solid was recharged to a reactor, and 250 mL of isopropanol was added. The slurry was stirred at 60 °C for 30 min and then cooled down to rt. The resultant white solid was filtered and dried in the oven to give 175 g of **3a** in 80% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 4.8 Hz, 1H), 8.21 (d, J = 7.9 Hz, 1H), 8.08 (m, 2H), 7.95 (dt, J = 7.8, 1.7 Hz, 1H), 7.60 (m, 1H), 7.55 (m, 2H), 7.48 (ddd, J = 7.6, 4.7, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 150.5, 138.9, 138.1, 133.8, 129.1, 128.9, 126.9, 122.2.

*2-Methoxy-6-(phenylsulfonyl)pyridine (**3b**).* To a N_2-purged reactor was charged 5.0 g (13.9 mmol) of **2a** and 50 mL of anhydrous THF to obtain a slurry. MeONa (25 wt % in MeOH) (1.1 equiv) was added dropwise to the stirring reaction mixture. The resulting slurry was stirred for 1 h at room temperature. A complete conversion was observed by LC-MS. The slurry was filtered and washed with IPA and dried in oven overnight at 50 °C to give 1.94 g **3b** as a white solid. The mother liquor was concentrated, and 15 mL of IPA was added and warmed until complete dissolution. The mixture was cooled down to 10 °C and held for 1 h. The second crop of solid was filtered and dried to yield another 1.17 g of white solid: total 90% yield; mp 74.6−75.8 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.12−8.09 (m, 2H), 7.78−7.73 (m, 2H), 7.64 (tt, J = 7.4, 1.3 Hz, 1H), 7.58−7.53 (m, 2H), 6.88 (dd, J = 7.7, 1.4 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 155.7, 139.7, 138.9, 133.6, 129.1, 128.9, 115.5, 114.9, 54.0; HRMS (ESI) m/z 250.0528 (M + H^+), calcd for $C_{12}H_{12}NO_3S$ 250.0532.

*2-Phenyl-6-(phenylsulfonyl)pyridine (**3c**).* To a stirring solution of bis(phenylsulfonyl)pyridine **2a** (1.0 g, 2.78 mmol) in 10 mL of THF at room temperature was charged 1.0 M PhMgBr (5.56 mL, 2.0 equiv) slowly over a period of 10 min. The progress of the reaction was monitored by LC-MS. Upon complete consumption of the starting material after 2 h, the mixture was quenched with MeOH (2 mL). The crude mixture was then evaporated to dryness, and **3c** was isolated by flash column chromatography (silica gel, 15% ethyl acetate in hexanes) to yield 656 mg of a white solid after dryness: 80% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.14−8.08 (m, 3H), 7.95−7.91 (m, 3H), 7.83−7.86 (m, 1H), 7.62−7.51 (m, 3H), 7.46−7.40 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 158.0, 138.9, 138.7, 137.1, 133.7, 130.0, 129.2, 128.9, 128.8, 127.0, 123.1, 119.8.

*2-Ethoxy-6-(phenylsulfonyl)pyridine (**3d**).* To a N_2-purged reactor was charged 1.08 g (3.0 mmol) of 2,6-bis(phenylsulfonyl)pyridine **2**, 7 mL of anhydrous THF, and 0.18 mL of EtOH (3.06 mmol, 1.02 equiv). A 3.0 mL portion of 1.0 M KHMDS in THF (3.0 mmol, 1.0 equiv) was added dropwise to the stirring reaction at rt. The resulting mixture was stirred for 1 h at rt. A complete conversion was observed by LC-MS. Upon completion, 5 mL of water was added. The mixture was then concentrated, and 10 mL of EtOAc was added. The layers were separated, and the aqueous layer was further extracted. The combined organic layer was dried and purified on silica to yield 723 mg of **3d** as a white solid after dryness: 91% yield; mp 95.1−96.1 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.6 Hz, 2H), 7.74 (m, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 6.84 (dd, J = 7.3, 1.7 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 155.6, 139.7, 139.0, 133.5, 129.0, 128.8, 115.6, 114.6, 62.6, 14.1; HRMS (ESI) m/z 264.0684 (M + H^+), calcd for $C_{13}H_{14}NO_3S$ 264.0694.

*2-Phenoxy-6-(phenylsulfonyl)pyridine (**3e**).* The same procedures as above with 288 mg of phenol (3.06 mmol, 1.02 equiv). **3e** (820 mg) was isolated as a white solid: 88% yield; mp 108.1−109.6 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88−7.83 (m, 4H), 7.58 (t, J = 7.5 Hz, 1H), 7.40 (t, J = 7.8 Hz, 2H), 7.36 (t, J = 7.9 Hz, 2H), 7.26 (m, 1H), 7.05 (m, 1H), 6.99 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 156.3, 152.9, 140.8, 138.3, 133.5, 129.5, 129.3, 128.7, 125.2,

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121.5, 115.7, 115.3; HRMS (ESI) m/z (M + H^+) 312.0678, calcd for $C_{17}H_{14}NO_3S$ 312.0689.

Synthesis of the Phosphine Oxides. *(2R,3S)-3-(tert-Butyl)-4-methoxy-2-(pyridin-2-yl)-2H-benzo[d][1,3]oxaphosphole 3-oxide (**4a**).* Intermediate **1a** (1.0 g, 4.163 mmol) and pyridine sulfone **3a** (0.913 g, 4.163 mmol) were dissolved in 10 mL of anhydrous THF under argon. The mixture was cooled to −78 °C with a dry ice/acetone bath. To the stirred solution was added 2.64 mL (12.5 mmol) of LDA (2.0 M in THF/ethylbenzene) dropwise. The internal temperature was maintained under −70 °C for an additional hour. Upon completion, the reaction was quenched with MeOH at −78 °C. The mixture was warmed to rt, and stirring continued for 2 h. The reaction mixture should be basic at pH ≥ 12. Aqueous NaOH (30 wt %) was added if necessary. The mixture was then concentrated to dryness. The organic layer was extracted with CH_2Cl_2 and dried with anhydrous Na_2SO_4, and compound **4a** was purified on silica with 5% MeOH in CH_2Cl_2 to yield 1.2 g of white solid after dryness: 91% yield; mp 186.1−188.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 4.7 Hz, 1H), 7.68 (dt, J = 7.7, 1.7 Hz, 1H), 7.45 (t, J = 8.3 Hz, 1H), 7.40 (dd, J = 8.0, 0.5 Hz, 1H), 7.21 (t, J = 6.2 Hz, 1H), 6.68 (dd, J = 8.3, 3.0 Hz, 1H), 6.53 (dd, J = 8.3, 4.2 Hz, 1H), 5.67 (d, J_{H-P} = 2.9 Hz, 1H), 3.88 (s, 3H), 1.39 (d, J_{H-P} = 16.6 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6 (d, J_{C-P} = 15.0 Hz), 161.5 (d, J_{C-P} = 1.9 Hz), 154.4 (d, J_{C-P} = 3.4 Hz), 149.2, 136.7, 136.6, 123.0 (d, J_{C-P} = 1.8 Hz), 122.3 (d, J_{C-P} = 2.2 Hz), 106.1 (d, J_{C-P} = 5.1 Hz), 103.6 (d, J_{C-P} = 5.5 Hz), 103.2 (d, J_{C-P} = 89.2 Hz), 79.1 (d, J_{C-P} = 53.9 Hz), 55.6, 34.3 (d, J_{C-P} = 73.9 Hz), 25.0; ^{31}P NMR (160 MHz, $CDCl_3$) δ 61.65; HRMS (ESI) m/z 318.1237 (M + H^+), calc. for $C_{17}H_{21}NO_3P$ 318.1254.

*(2R,3S)-3-(tert-Butyl)-4-phenyl-2-(pyridin-2-yl)-2H-benzo[d][1,3]-oxaphosphole 3-Oxide (**4b**).* A white solid (1.09 g) was isolated after purification with 0−2% MeOH in CH_2Cl_2: 72% yield; mp 99.2−101.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 5.0 Hz, 1H), 7.76−7.73 (m, 3H), 7.57 (dt, J = 7.9, 0.9 Hz, 1H), 7.48 (dd, J = 8.0, 0.9 Hz, 1H), 7.18−7.34 (m, 3H), 7.26−7.22 (m, 1H), 7.13−7.07 (m, 2H), 5.71 (d, J = 1.0 Hz, 1H), 0.91 (d, J_{H-P} = 16.5 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6 (d, J_{C-P} = 17.6 Hz), 154.8 (d, J_{C-P} = 3.7 Hz), 149.3 (d, J_{C-P} = 1.2 Hz), 147.0 (d, J_{C-P} = 5.6 Hz), 140.6 (d, J_{C-P} = 1.8 Hz), 136.7 (d, J_{C-P} = 1.8 Hz), 134.9 (d, J_{C-P} = 1.9 Hz), 129.9, 128.5, 128.4, 123.9 (d, J_{C-P} = 7.8 Hz), 122.9 (d, J_{C-P} = 1.8 Hz), 121.6 (d, J_{C-P} = 2.2 Hz), 112.8 (d, J_{C-P} = 85.9 Hz), 112.4 (d, J_{C-P} = 5.3 Hz), 77.8 (d, J_{C-P} = 55.6 Hz), 34.6 (d, J_{C-P} = 71.3 Hz), 24.4; ^{31}P NMR (160 MHz, $CDCl_3$) δ 62.19; HRMS (ESI) m/z 364.1459 (M + H^+), calc. for $C_{22}H_{23}NO_2P$ 364.1461.

*(2R,3S)-3-(tert-Butyl)-4-(2,6-dimethoxyphenyl)-2-(pyridin-2-yl)-2H-benzo[d][1,3]oxaphosphole 3-Oxide (**4c**).* A white solid (1.37 g) was obtained after purification with 100% EtOAc: 78% yield; mp 186.0−188.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, J = 4.7 Hz, 1H), 7.68 (dt, J = 7.8, 1.6 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.47 (d, J = 7.8 Hz, 1H), 7.27 (t, J = 8.3 Hz, 1H), 7.21 (t, J = 6.2 Hz, 1H), 7.05 (dd, J = 8.2, 3.2 Hz, 1H), 6.98 (dd, J = 7.4, 3.2 Hz, 1H), 6.58 (dd, J = 8.2, 5.0 Hz, 2H), 5.60 (d, J = 1.6 Hz, 1H), 3.74 (s, 3H), 3.58 (s, 3H), 0.95 (d, J_{H-P} = 16.2 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.2 (d, J_{C-P} = 17.7 Hz), 158.8, 157.3, 154.9 (d, J_{C-P} = 3.1 Hz), 149.1 (d, J_{C-P} = 0.9 Hz), 138.8 (d, J_{C-P} = 5.3 Hz), 136.4, 134.3, 129.9, 125.6 (d, J_{C-P} = 8.4 Hz), 122.9 (d, J_{C-P} = 1.4 Hz), 122.4 (d, J_{C-P} = 2.3 Hz), 117.4 (d, J_{C-P} = 2.0 Hz), 114.7 (d, J_{C-P} = 89.5 Hz), 112.3 (d, J_{C-P} = 5.4 Hz), 104.6, 103.0, 78.2 (d, J_{C-P} = 55.3 Hz), 56.1, 55.4, 34.2 (d, J_{C-P} = 71.8 Hz), 23.9 (d, J_{C-P} = 0.7 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 60.11; HRMS (ESI) m/z 424.1654 (M + H^+), calcd for $C_{24}H_{27}NO_4P$ 424.1672.

*(2R,3S)-4-(Anthracen-9-yl)-3-(tert-butyl)-2-(pyridin-2-yl)-2H-benzo[d][1,3]oxaphosphole 3-Oxide (**4d**).* A white solid (1.73 g) was obtained after purification with 0−2% MeOH in CH_2Cl_2: 90% yield; mp 243−246 °C (decomp). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 5.0 Hz, 1H), 8.51 (s, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.4 Hz, 1H), 7.76−7.69 (m, 3H), 7.62 (t, J = 8.6 Hz, 2H), 7.47−7.36 (m, 4H), 7.30 (dd, J = 8.4, 2.6 Hz, 1H), 7.22 (d, J = 6.0 Hz, 1H), 7.16 (dd, J = 7.2, 3.2 Hz, 1H), 5.60 (d, J = 4.4 Hz, 1H), 0.45 (d, J_{H-P} = 16.5 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9 (d, J_{C-P} = 16.2 Hz), 154.3 (d, J_{C-P} = 3.2 Hz), 148.9, 142.1 (d, J_{C-P} = 5.6 Hz), 136.6 (d, J_{C-P} = 1.4 Hz), 134.5 (d, J_{C-P} = 1.5 Hz), 134.4 (d, J_{C-P} = 1.9 Hz), 131.3, 131.1, 130.3 (d, J_{C-P} = 4.5 Hz), 128.7, 128.4, 127.8, 127.2, 126.5 (d, J_{C-P} = 8.1 Hz), 126.2, 125.9, 125.7, 125.4, 124.8, 123.3 (d, J_{C-P} = 2.2 Hz), 123.1 (d, J_{C-P} = 1.5 Hz), 117.2 (d, J_{C-P} = 85.5 Hz), 113.4 (d, J_{C-P} = 4.9 Hz), 78.9 (d, J_{C-P} = 55.7 Hz), 33.8 (d, J_{C-P} = 71.3 Hz), 24.0; ^{31}P NMR (160 MHz, $CDCl_3$) δ 58.55; HRMS (ESI) m/z 464.1770 (M + H^+), calcd for $C_{30}H_{27}NO_2P$ 464.1774.

*(2R,3S)-3-(tert-Butyl)-4-methoxy-2-(6-methoxypyridin-2-yl)-2H-benzo[d][1,3]oxaphosphole 3-Oxide (**4e**).* A white solid (1.18 g) was obtained after purification with 80% EtOAc in hexanes: 82% yield; mp 164.9−167.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (t, J = 7.7 Hz, 1H), 7.44 (t, J = 8.2 Hz, 1H), 6.98 (d, J = 7.4 Hz, 1H), 6.69 (dd, J = 8.4, 2.6 Hz, 1H), 6.64 (d, J = 8.4 Hz, 1H), 6.51 (dd, J = 8.0, 4.0 Hz, 1H), 5.55 (d, J = 1.8 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 1.41 (d, J_{H-P} = 16.6 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6 (d, J_{C-P} = 15.1 Hz), 163.4 (d, J_{C-P} = 1.6 Hz), 161.6 (d, J_{C-P} = 1.9 Hz), 151.8 (d, J_{C-P} = 4.3 Hz), 139.1 (d, J_{C-P} = 1.9 Hz), 136.5, 114.0 (d, J_{C-P} = 3.0 Hz), 110.0 (d, J_{C-P} = 2.2 Hz), 106.1 (d, J_{C-P} = 5.2 Hz), 103.5 (d, J_{C-P} = 5.6 Hz), 102.4 (d, J_{C-P} = 89.2 Hz), 78.6 (d, J_{C-P} = 53.9 Hz), 55.6, 53.4, 34.3 (d, J_{C-P} = 74.3 Hz), 25.1; ^{31}P NMR (160 MHz, $CDCl_3$) δ 61.51; HRMS (ESI) m/z 348.1350 (M + H^+), calcd for $C_{18}H_{23}NO_4P$ 348.1359.

*(2R,3S)-3-(tert-Butyl)-4-methoxy-2-(6-phenylpyridin-2-yl)-2H-benzo[d][1,3]oxaphosphole 3-Oxide (**4f**).* A white solid (1.16 g) was obtained after purification with 50% EtOAc in hexanes: 71% yield; mp 172.2−174.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 7.9 Hz, 2H), 7.75 (t, J = 7.8 Hz, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.48−7.35 (m, 5H), 6.71 (dd, J = 8.2, 2.9 Hz, 1H), 6.54 (dd, J = 8.1, 4.1 Hz, 1H) 5.77 (d, J = 3.3 Hz, 1H), 3.88 (s, 3H), 1.45 (d, J = 16.5 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7 (d, J_{C-P} = 15.0 Hz), 161.5 (d, J_{C-P} = 1.9 Hz), 156.6 (d, J_{C-P} = 1.2 Hz), 154.2 (d, J_{C-P} = 3.6 Hz), 139.2, 137.5 (d, J_{C-P} = 1.7 Hz), 136.6, 128.9, 128.6, 127.0, 120.6 (d, J_{C-P} = 2.4 Hz), 119.7 (d, J_{C-P} = 1.9 Hz), 106.2 (d, J_{C-P} = 5.1 Hz), 103.5 (d, J_{C-P} = 5.6 Hz), 102.7 (d, J_{C-P} = 89.0 Hz), 79.5 (d, J_{C-P} = 53.2 Hz), 55.6, 34.3 (d, J_{C-P} = 73.8 Hz), 25.2; ^{31}P NMR (160 MHz, $CDCl_3$) δ 61.24; HRMS (ESI) m/z 394.1572 (M + H^+), calcd for $C_{23}H_{25}NO_3P$ 394.1567.

General Procedure for the Reduction of Phosphine Oxides. *2-((2R,3R)-3-(tert-Butyl)-4-methoxy-2,3-dihydrobenzo[d][1,3]oxaphosphol-2-yl)pyridine (**5a**).* To a Schlenk flask under argon was added **4a** (500 mg, 1.576 mmol), THF (10 mL), PMHS (1.2 mL), and $Ti(OiPr)_4$ (0.93 mL, 3.15 mmol). The mixture was stirred at 65 °C for 14 h. Upon complete conversion by ^{31}P NMR analysis, the mixture was concentrated under vacuum. Then the flask was cooled to 0 °C, and 20 mL of degassed 30% aqueous NaOH was added slowly with caution. Extreme H_2 gas evolution was observed in the beginning. After complete addition, the mixture was heated to 65 °C and stirred for 1 h. The mixture was cooled down to rt, and the product was extracted with degassed MTBE (3 × 30 mL) under argon. The combined organic layer was filtered through a plug of neutral alumina with anhydrous $MgSO_4$ on the top. **5a** (410 mg) was obtained as a white solid after dryness: 86% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, J = 4.7 Hz, 1H), 7.51 (td, J = 7.7, 1.6 Hz, 1H), 7.28 (t, J = 8.1 Hz, 1H), 7.10 (d, J = 7.8 Hz, 1H), 7.06 (t, J = 6.2 Hz, 1H), 6.72 (d, J = 8.2 Hz, 1H), 6.47 (dd, J = 8.1, 3.6 Hz, 1H), 6.02 (s, 1H), 3.78 (s, 3H), 1.11 (d, J_{H-P} = 12.4 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6 (d, J_{C-P} = 15.2 Hz), 161.5 (d, J_{C-P} = 1.8 Hz), 154.4 (d, J_{C-P} = 3.6 Hz), 149.2 (d, J_{C-P} = 0.8 Hz), 136.7, 136.6, 123.0 (d, J_{C-P} = 1.7 Hz), 122.2 (d, J_{C-P} = 2.4 Hz), 106.1 (d, J_{C-P} = 5.2 Hz), 103.6 (d, J_{C-P} = 5.6 Hz), 103.2 (d, J_{C-P} = 89.2 Hz), 79.1 (d, J_{C-P} = 53.8 Hz), 55.6, 34.2 (d, J_{C-P} = 73.7 Hz), 25.0; ^{31}P NMR (160 MHz, $CDCl_3$) δ 12.85; HRMS (ESI) m/z 302.1319 (M + H^+), calcd for $C_{17}H_{21}NO_2P$ 302.1304.

*2-((2R,3R)-3-(tert-Butyl)-4-phenyl-2,3-dihydrobenzo[d][1,3]oxaphosphol-2-yl)pyridine (**5b**).* A white solid (383 mg): 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, J = 4.5 Hz, 1H), 7.59−7.62 (m, 3H), 7.42 (t, J = 7.8 Hz, 1H), 7.25−7.35 (m, 4H), 7.14 (t, J = 6.7 Hz, 1H), 7.08 (d, J = 8.0 Hz, 1H), 7.05 (dd, J = 7.4 Hz, 3.4 Hz, 1H), 6.03 (s, 1H), 0.79 (d, J = 12.2 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 161.3 (d, J_{C-P} = 14.3 Hz), 149.6 (d, J_{C-P} = 1.7 Hz), 146.5 (d, J_{C-P} = 12.9 Hz), 142.1, 136.7 (d, J_{C-P} = 1.2 Hz), 131.6, 129.3, 129.1, 128.4, 127.4, 122.6 (d, J_{C-P} = 2.8 Hz), 121.9 (d, J_{C-P} = 2.5 Hz), 120.6

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(d, J_{C-P} = 22.3 Hz), 119.2 (d, J_{C-P} = 3.5 Hz), 109.9, 85.3 (d, J_{C-P} = 27.4 Hz), 32.8 (d, J_{C-P} = 22.6 Hz), 26.8 (d, J_{C-P} = 13.8 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 15.38; HRMS (ESI) m/z 348.1512 (M + H^+), calc. for $C_{22}H_{23}NOP$ 348.1512.

*2-((2R,3R)-3-(tert-Butyl)-4-(2,6-dimethoxyphenyl)-2,3-dihydrobenzo[d][1,3]oxaphosphol-2-yl)pyridine (**5c**).* A white solid (407 mg): 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 4.7 Hz, 1H), 7.58 (dt, J = 8.0, 1.5 Hz, 1H), 7.42 (t, J = 7.8 Hz, 1H), 7.26−7.21 (m, 2H), 7.12 (t, J = 6.0 Hz, 1H), 7.05 (d, J = 8.0 Hz, 1H), 6.93 (dd, J = 7.6, 3.2 Hz, 1H), 6.57 (d, J = 8.4 Hz, 1H), 6.51 (d, J = 8.4 Hz, 1H), 5.99 (s, 1H), 3.73 (s, 3H), 3.26 (s, 3H), 0.88 (d, J_{H-P} = 12.2 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 161.7 (d, J_{C-P} = 14.2 Hz), 157.6, 156.9, 149.2 (d, J_{C-P} = 1.5 Hz), 139.1 (d, J_{C-P} = 17.0 Hz), 136.5, 130.9, 129.1, 124.4 (d, J_{C-P} = 4.1 Hz), 123.9 (d, J_{C-P} = 17.1 Hz), 121.6 (d, J_{C-P} = 2.4 Hz), 119.5 (d, J_{C-P} = 3.7 Hz), 119.3 (d, J_{C-P} = 21.5 Hz), 109.3, 104.4, 103.5, 86.0 (d, J_{C-P} = 28.1 Hz), 55.43, 55.41, 31.9 (d, J_{C-P} = 21.1 Hz), 26.7 (d, J_{C-P} = 14.7 Hz); ^{31}P NMR (160 MHz, $CDCl_3$) δ 17.71; HRMS (ESI) m/z 408.1700 (M + H^+), calcd for $C_{24}H_{27}NO_3P$ 408.1723.

*2-((2R,3R)-4-(Anthracen-9-yl)-3-(tert-butyl)-2,3-dihydrobenzo[d][1,3]oxaphosphol-2-yl)pyridine (**5d**).* A white solid (613 mg): 87% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.4−8.2 (m, 2H), 7.80−7.76 (m, 3H), 7.48−6.79 (m, 11H), 5.88 (s, 1H), 0.45 (d, J_{H-P} = 11.5 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6, 161.2 (d, J_{C-P} = 14.5 Hz), 149.7, 142.8 (d, J_{C-P} = 16.6 Hz), 136.6, 136.0, 131.5, 131.3, 130.6, 128.9, 128.6, 128.3, 127.2, 127.0, 126.9, 125.8 (d, J_{C-P} = 3.6 Hz), 125.6, 125.4, 125.3, 124.9, 124.8 (d, J_{C-P} = 21.3 Hz), 121.9 (d, J_{C-P} = 2.0 Hz), 119.3 (d, J_{C-P} = 3.8 Hz), 110.4, 86.2 (d, J_{C-P} = 27.6 Hz), 31.6 (d, J_{C-P} = 22.4 Hz), 27.1 (d, J_{C-P} = 14.6 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 15.46; HRMS (ESI) m/z 448.1823 (M + H^+), calcd for $C_{30}H_{27}NOP$ 448.1825.

*2-((2R,3R)-3-(tert-Butyl)-4-methoxy-2,3-dihydrobenzo[d][1,3]oxaphosphol-2-yl)-6-methoxypyridine (**5e**).* The same procedure as above with addition of 2.1 mL of PMHS; 465 mg of white solid was obtained in 89% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (t, J_{H-P} = 7.8 Hz, 1H), 7.29 (t, J_{H-P} = 8.2 Hz, 1H), 6.74 (d, J_{H-P} = 7.5 Hz, 1H), 6.70 (d, J_{H-P} = 8.2 Hz, 1H), 6.52 (d, J_{H-P} = 8.2 Hz, 1H), 6.48 (dd, J_{H-P} = 8.2, 3.7 Hz, 1H), 5.92 (s, 1H), 3.88 (s, 3H), 3.79 (s, 3H), 1.13 (d, J_{H-P} = 12.4 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 163.5 (d, J_{C-P} = 1.9 Hz), 162.2 (d, J_{C-P} = 11.8 Hz), 158.7 (d, J_{C-P} = 14.6 Hz), 138.9 (d, J_{C-P} = 1.2 Hz), 132.3, 111.1 (d, J_{C-P} = 3.8 Hz), 109.6 (d, J_{C-P} = 17.5 Hz), 108.7 (d, J_{C-P} = 2.6 Hz), 104.2, 103.1 (d, J_{C-P} = 1.9 Hz), 85.8 (d, J_{C-P} = 27.0 Hz), 55.4, 53.1, 33.3 (d, J_{C-P} = 22.4 Hz), 27.2 (d, J_{C-P} = 14.3 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 14.24; HRMS (ESI) m/z (M + H^+) 332.1401, calcd for $C_{18}H_{23}NO_3P$ 332.1410.

*2-((2R,3R)-3-(tert-Butyl)-4-methoxy-2,3-dihydrobenzo[d][1,3]oxaphosphol-2-yl)-6-phenylpyridine (**5f**).* A white solid (386 mg): 65% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02−8.04 (m, 2H), 7.60 (t, J = 7.8 Hz, 1H), 7.55−7.52 (m, 1H), 7.46−7.43 (m, 2H), 7.40−7.37 (m, 1H), 7.31 (t, J = 8.1 Hz, 1H), 7.09 (d, J = 7.7 Hz, 1H), 6.76 (d, J = 8.1 Hz, 1H), 6.50 (dd, J = 8.2, 3.6 Hz, 1H), 6.14 (s, 1H), 3.80 (s, 3H), 1.17 (d, J = 12.4 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 162.2 (d, J_{C-P} = 11.7 Hz), 161.2 (d, J_{C-P} = 14.8 Hz), 156.5 (d, J_{C-P} = 1.9 Hz), 139.2, 137.3 (d, J_{C-P} = 1.2 Hz), 132.4, 128.9, 128.6, 126.9, 118.2 (d, J_{C-P} = 2.6 Hz), 117.2 (d, J_{C-P} = 3.5 Hz), 109.6 (d, J_{C-P} = 17.7 Hz), 104.2, 103.2 (d, J_{C-P} = 2.0 Hz), 86.3 (d, J_{C-P} = 27.3 Hz), 55.4, 32.5 (d, J_{C-P} = 22.4 Hz), 27.3 (d, J_{C-P} = 14.2 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 14.52; HRMS (ESI) m/z (M + H^+) 378.1600, calcd for $C_{23}H_{25}NO_2P$ 378.1617.

General Procedure for the Synthesis of Iridium Complexes. *{2-((2R,3R)-3-(tert-Butyl)-4-methoxy-2,3-dihydrobenzo[d][1,3]oxaphosphol-2-yl)pyridine}(η^4-1,5-cyclooctadiene)iridium(I) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (**6a**).* A solution of **5a** (100 mg, 0.332 mmol) and $[IrCl(COD)]_2$ (115.0 mg, 0.166 mmol) in degassed CH_2Cl_2 (6 mL) was heated for 1 h at 45 °C under argon. After cooling to rt, $NaBAr_F$ (318 mg, 0.348 mmol) was added, followed immediately by 10 mL of degassed water. The two layers were stirred vigorously for 30 min. After separation of the layers, the aqueous layer was extracted twice with CH_2Cl_2 (2 mL). The combined organic layer was dried over Na_2SO_4 and concentrated to 1 mL. The mixture was then passed through a short plug of silica under argon using CH_2Cl_2 as eluent. The center of the first orange fraction was collected and dried to give 413 mg of **6a** as a red-orange solid: 85% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.09 (d, J = 6.0 Hz, 1H), 8.05 (t, J = 7.6 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.63 (s, BArF), 7.47 (s, BArF), 7.42 (t, J = 6.8 Hz, 1H), 7.32 (t, J = 8.3 Hz, 1H), 6.52−6.55 (m, 2H), 5.96 (s, 1H), 5.25−5.28 (m, 1H), 5.05 (m, 1H), 4.83−4.88 (m, 1H), 4.41−4.43 (m, 1H), 3.84 (s, 3H), 2.61−2.65 (m, 1H), 2.30−2.42 (m, 2H), 2.22−2.28 (m, 2H), 2.01−2.07 (m, 1H), 1.72−1.86 (m, 2H), 1.15 (d, J_{H-P} = 16.2 Hz, 9H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 164.7 (d, J_{C-P} = 10.0 Hz), 162.7 (d, J_{C-P} = 4.1 Hz), 161.5 (q, $^1J_{C-B}$ = 50.2 Hz), 160.4 (d, J_{C-P} = 5.5 Hz), 147.8, 140.6 (d, J_{C-P} = 0.9 Hz), 135.3 (d, J_{C-P} = 1.4 Hz), 134.0 (br), 128.2 (qq, $^2J_{C-F}$ = 31.4 Hz, $^4J_{C-F}$ = 2.8 Hz), 127.0, 126.4 (d, J_{C-P} = 7.4 Hz), 125.7, 124.9 (q, $^1J_{C-F}$ = 272.3 Hz), 116.7 (sept, $^3J_{C-F}$ = 4.0 Hz), 105.2 (d, J_{C-P} = 4.0 Hz), 104.4 (d, J_{C-P} = 5.2 Hz), 94.6 (d, J_{C-P} = 9.7 Hz), 93.4 (d, J_{C-P} = 13.7 Hz), 84.8 (d, J_{C-P} = 24.2 Hz), 63.9 (d, J_{C-P} = 19.8 Hz), 55.1, 34.7 (d, J_{C-P} = 4.5 Hz), 34.5 (d, J_{C-P} = 22.1 Hz), 29.9 (d, J_{C-P} = 1.9 Hz), 29.8 (d, J_{C-P} = 1.9 Hz), 25.5 (d, J_{C-P} = 2.4 Hz), 25.4 (d, J_{C-P} = 4.5 Hz); ^{31}P NMR (200 MHz, CD_2Cl_2) δ 47.33 (s); HRMS (ESI) m/z 602.1853 (M^+), calcd for $[IrC_{25}H_{32}NO_2P]^+$ 602.1795; 863.0658 ($BArF^-$), calcd for $[C_{32}H_{12}BF_{24}]^-$ 863.0654.

*{2-((2R,3R)-3-(tert-Butyl)-4-phenyl-2,3-dihydrobenzo[d][1,3]-oxaphosphol-2-yl)pyridine}(η^4-1,5-cyclooctadiene)iridium(I) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (**6b**).* A red-orange solid (375 mg): 75% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, J = 6.0 Hz, 1H), 7.88−7.92 (m, 2H), 7.63 (s, BArF), 7.39−7.47 (m, 5H), 7.43 (s, BArF), 7.36 (t, J = 7.8 Hz, 1H), 7.29 (dt, J = 6.5, 2.0 Hz, 1H), 6.95 (d, J = 8.3 Hz, 1H), 6.88 (dd, J = 7.5, 4.0 Hz, 1H), 5.86 (s, 1H), 4.90 (m, 1H), 4.75 (m, 1H), 4.26 (m, 1H), 3.69 (m, 1H), 2.36−2.43 (m, 1H), 2.25−2.31 (m, 2H), 2.05−2.16 (m, 2H), 1.85−2.91(m, 2H), 1.77−1.81 (m, 1H), 0.91 (d, J_{H-P} = 15.9 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9 (d, J_{C-P} = 9.7 Hz), 161.5 (d, J_{C-P} = 4.7 Hz), 161.2 (q, $^1J_{C-B}$ = 50.2 Hz), 147.1, 145.4 (d, J_{C-P} = 9.5 Hz), 140.1, 139.8 (d, J_{C-P} = 1.8 Hz), 133.7 (br), 133.4 (d, J_{C-P} = 1.8 Hz), 128.2, 128.0 (qq, $^2J_{C-F}$ = 31.6 Hz, $^4J_{C-F}$ = 3.0 Hz), 127.8, 127.6, 125.7 (d, J_{C-P} = 6.6 Hz), 125.5, 125.3 (d, J_{C-P} = 7.0 Hz), 124.6 (q, $^1J_{C-F}$ = 272.8 Hz), 116.4 (sept, $^3J_{C-F}$ = 4.0 Hz), 113.1 (d, J_{C-P} = 38.2 Hz), 111.5 (d, J_{C-P} = 3.8 Hz), 93.0 (d, J_{C-P} = 14.3 Hz), 92.6 (d, J_{C-P} = 9.1 Hz), 83.0 (d, J_{C-P} = 24.5 Hz), 67.1, 63.1, 34.1 (d, J_{C-P} = 19.9 Hz), 33.4 (d, J_{C-P} = 4.6 Hz), 30.4 (d, J_{C-P} = 2.2 Hz), 28.8 (d, J_{C-P} = 1.7 Hz), 26.3 (d, J_{C-P} = 2.7 Hz), 25.5 (d, J_{C-P} = 4.1 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 47.12 (s); HRMS (ESI) m/z 648.2047 (M^+), calcd for $[IrC_{30}H_{34}NOP]^+$ 648.2002; 863.0632 ($BArF^-$), calcd for $[C_{32}H_{12}BF_{24}]^-$ 863.0654.

*{2-((2R,3R)-3-(tert-Butyl)-4-(2,6-dimethoxyphenyl)-2,3-dihydrobenzo[d][1,3]oxaphosphol-2-yl)pyridine}(η^4-1,5-cyclooctadiene)-iridium(I) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (**6c**).* A red-orange solid (418 mg): 86% yield. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.19 (d, J = 6.0 Hz, 1H), 7.98−8.03 (m, 2H), 7.64 (s, BArF), 7.47 (s, BArF), 7.41 (dt, J = 6.9, 1.8 Hz, 1H), 7.31−7.35 (m, 2H), 6.95 (d, J = 8.0 Hz, 1H), 6.75 (d, J = 8.4 Hz, 1H), 7.72 (dd, J = 7.6, 3.9 Hz, 1H), 6.62 (d, J = 8.4 Hz, 1H), 5.93 (s, 1H), 4.77−4.83 (m, 1H), 4.37−4.40 (m, 1H), 4.19−4.20 (m, 1H), 3.60−3.65 (m, 1H), 3.62 (s, 3H), 3.55 (s, 3H), 2.38−2.45 (m, 2H), 1.89−2.22 (m, 4H), 1.48−1.56 (m, 2H), 1.06 (d, J_{H-P} = 15.8 Hz, 9H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 165.4 (d, J_{C-P} = 9.5 Hz), 162.8 (d, J_{C-P} = 4.5 Hz), 162.3 (q, $^1J_{C-B}$ = 50.4 Hz), 157.8 (d, J_{C-P} = 25.7 Hz), 148.4, 141.4, 139.8 (d, J_{C-P} = 10.3 Hz), 135.1 (br), 134.2 (d, J_{C-P} = 1.8 Hz), 130.7, 129.4 (qq, $^2J_{C-F}$ = 31.6 Hz, $^4J_{C-F}$ = 2.9 Hz), 127.2 (d, J_{C-P} = 1.7 Hz), 127.1, 126.8, 126.0 (q, $^1J_{C-F}$ = 272.7 Hz), 118.2, 117.8 (sept, $^3J_{C-F}$ = 4.2 Hz), 112.1 (d, J_{C-P} = 3.9 Hz), 104.6 (d, J_{C-P} = 17.4 Hz), 93.4 (d, J_{C-P} = 7.7 Hz), 89.6 (d, J_{C-P} = 16.8 Hz), 84.5 (d, J_{C-P} = 24.8 Hz), 67.6, 65.3, 56.3, 55.7, 36.9 (d, J_{C-P} = 5.5 Hz), 34.8 (d, J_{C-P} = 20.6 Hz), 32.9, 29.9, 26.3 (d, J_{C-P} = 4.1 Hz), 25.6 (d, J_{C-P} = 2.9 Hz); ^{31}P NMR (200 MHz, CD_2Cl_2) δ 50.30 (s); HRMS (ESI) m/z 708.2173 (M^+), calcd for $[IrC_{32}H_{38}NO_3P]^+$ 708.2213; 863.0680 ($BArF^-$), calcd for $[C_{32}H_{12}BF_{24}]^-$ 863.0654.

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*{2-((2R,3R)-4-(Anthracen-9-yl)-3-(tert-butyl)-2,3-dihydrobenzo-[d][1,3]oxaphosphol-2-yl)pyridine}(η^4-1,5-cyclooctadiene)iridium(I) Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (**6d**).* A red-orange solid (427 mg): 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.16 (d, J = 8.3 Hz, 1H), 8.12 (d, J = 5.2 Hz, 1H), 8.03 (d, J = 8.2 Hz, 1H), 7.89−7.95 (m, 2H), 7.63 (s, BArF), 7.59 (d, J = 8.7 Hz, 2H), 7.37−7.51 (m, 4H), 7.44 (s, BArF), 7.13 (d, J = 8.2 Hz, 1H), 7.08 (t, J = 7.2 Hz, 1H), 6.88 (d, J = 6.3 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 5.94 (s, 1H), 4.46−4.52 (m, 1H), 3.99−4.05 (m, 1H), 3.68−3.75 (m, 1H), 2.35−2.41 (m, 1H), 1.89−1.95 (m, 1H), 1.68−1.81 (m, 3H), 1.49−1.56 (m, 1H), 1.07−1.17 (m, 2H), 0.88 (d, J = 15.9 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5 (d, J_{C-P} = 9.5 Hz), 161.5 (d, J_{C-P} = 4.5 Hz), 160.1 (q, $^1J_{C-B}$ = 49.8 Hz), 147.2, 141.7 (d, J_{C-P} = 10.2 Hz), 140.1, 133.7 (br), 132.1, 130.6 (d, J_{C-P} = 32.2 Hz), 129.3, 128.9, 128.8, 128.0, 127.9 (qq, $^2J_{C-F}$ = 31.4 Hz, $^4J_{C-F}$ = 3.0 Hz), 127.5, 127.2 (d, J_{C-P} = 7.1 Hz), 126.7, 125.9, 125.7 (d, J_{C-P} = 6.6 Hz), 125.6, 125.2 (d, J_{C-P} = 5.1 Hz), 124.9 (d, J_{C-P} = 11.6 Hz), 124.6 (q, $^1J_{C-F}$ = 273.0 Hz), 124.2, 117.6 (d, J_{C-P} = 37.5 Hz), 116.5 (sept, $^3J_{C-F}$ = 4.0 Hz), 112.0 (d, J_{C-P} = 3.7 Hz), 92.1 (d, J_{C-P} = 7.6 Hz, COD, CH), 89.6 (d, J_{C-P} = 16.2 Hz, COD, CH), 83.6 (d, J_{C-P} = 24.9 Hz), 65.2 (COD, CH), 62.1 (COD, CH), 33.4 (d, J_{C-P} = 5.2 Hz, COD, CH_2), 33.2 (d, J_{C-P} = 20.2 Hz), 31.0 (COD, CH_2), 28.2 (COD, CH_2), 25.5 (d, J_{C-P} = 4.1 Hz), 23.6 (d, J_{C-P} = 3.0 Hz, COD, CH_2); ^{31}P NMR (200 MHz, $CDCl_3$) δ 47.67 (s); HRMS (ESI) m/z 748.2315 (M^+), calcd for $[IrC_{31}H_{36}NO_2P]^+$ 748.2313; 863.0654 ($BArF^-$), calcd for $[C_{32}H_{12}BF_{24}]^-$ 863.0654.

*Complex **6e**.* After addition of NaBArF, the mixture was stirred at rt for 12 h until ^{31}P NMR indicated complete conversion. A light yellow solid (431 mg) was isolated in 87% yield after the same workup as above. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, BArF), 7.64 (t, J = 8.1 Hz, 1H), 7.49 (s, BArF), 7.45 (t, J = 8.5 Hz, 1H), 7.32 (dd, $^3J_{H-P}$ = 7.1 Hz, J = 5.1 Hz, 1H, OCH_2), 7.23 (d, J = 7.1 Hz, 1H), 6.89 (dd, J = 8.7, 1.0 Hz, 1H), 6.72 (m, 1H, OCH_2), 6.69 (t, J = 4.0 Hz, 1H), 6.66 (dd, J = 8.4, 1.8 Hz, 1H), 6.50 (d, J = 6.3 Hz, 1H), 4.37−4.39 (m, 1H), 4.29−4.31 (m, 2H), 3.96 (s, 3H), 3.87−3.90 (m, 1H), 2.57−2.62 (m, 2H), 2.18−2.32 (m, 2H), 1.95−2.01 (m, 1H), 1.71−1.75 (m, 1H), 1.51−1.53 (m, 1H), 1.21 (d, J = 17.0 Hz, 9H), 0.83−0.93 (m, 1H), −13.34 (dd, $^2J_{H-P}$ = 22.8 Hz, J = 3.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9 (d, J_{C-P} = 9.3 Hz), 162.5 (d, J = 6.3 Hz), 162.3 (q, $^1J_{C-B}$ = 50.2 Hz), 160.3 (d, J_{C-P} = 3.8 Hz), 153.1 (d, J_{C-P} = 7.8 Hz), 141.6 (d, J_{C-P} = 1.4 Hz), 136.5 (d, J_{C-P} = 1.7 Hz), 134.8 (br), 129.0 (qq, $^2J_{C-F}$ = 31.5 Hz, $^4J_{C-F}$ = 2.8 Hz), 125.6 (q, $^1J_{C-F}$ = 272.7 Hz), 117.7 (d, J_{C-P} = 9.5 Hz), 117.4 (sept, $^3J_{C-F}$ = 4.1 Hz), 111.1, 106.7 (d, J_{C-P} = 3.8 Hz), 105.6 (d, J_{C-P} = 5.4 Hz), 104.3 (d, J_{C-P} = 38.2 Hz), 101.2 (t, J_{C-P} = 2.3 Hz), 95.2 (t, J_{C-P} = 1.9 Hz, COD, CH), 93.7 (d, J_{C-P} = 29.0 Hz, COD, CH), 68.0 (d, J_{C-P} = 1.9 Hz, COD, CH), 65.3 (d, J_{C-P} = 3.6 Hz, COD, CH), 61.6 (dd, J = 57.0, 0.8 Hz, CH_2O), 55.7, 34.2 (dd, J_{C-P} = 24.8, 0.8 Hz), 32.8 (d, J_{C-P} = 4.5 Hz, COD, CH_2), 31.7 (COD, CH_2), 26.3 (d, J = 3.6 Hz, COD, CH_2), 25.8 (COD, CH_2), 25.4 (d, J_{C-P} = 3.6 Hz); ^{31}P NMR (200 MHz, $CDCl_3$) δ 46.45 (d, J = 6.5 Hz); HRMS (ESI) m/z 632.1863 (M^+), calcd for $[IrC_{26}H_{34}NO_3P]^+$ 632.1900; 863.0648 ($BArF^-$), calcd for $[C_{32}H_{12}BF_{24}]^-$ 863.0654.

*Complex **6f**.* The mixture was stirred at rt for 30 min after addition of NaBArF. Complete conversion was observed by ^{31}P NMR. A light yellow solid (404 mg) was isolated in 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 7.9, 5.4 Hz, 1H), 7.96 (dd, J = 8.4, 1.3 Hz, 1H), 7.87 (t, J = 7.8 Hz, 1H), 7.79 (td, J = 7.8, 1.7 Hz, 1H), 7.69 (br s, BArF), 7.62 (dd, J = 7.4, 1.4 Hz, 1H), 7.52 (m, 2H), 7.49 (br s, BArF), 7.36 (t, J = 7.8 Hz, 1H), 6.69−6.74 (m, 2H), 6.59 (d, J = 6.3 Hz, 1H), 4.85−4.91 (m, 1H), 4.45−4.49 (m, 2H), 3.99 (s, 3H), 3.19 (br t, J = 8.1 Hz, 1H), 2.74−2.80 (m, 1H), 2.33−2.43 (m, 2H), 1.88−2.06 (m, 2H), 1.61−1.63 (m, 1H), 1.20 (d, J = 17.6 Hz, 9H), 0.82−1.04 (m, 2H), −13.09 (d, $^2J_{H-P}$ = 19.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4 (d, J_{C-P} = 6.3 Hz), 162.6 (d, J_{C-P} = 6.8 Hz), 161.5 (q, $^1J_{C-B}$ = 50.0 Hz), 160.2 (d, J_{C-P} = 3.6 Hz), 156.3 (d, J_{C-P} = 9.3 Hz), 149.6, 148.9, 145.2, 139.7, 137.6, 136.8 (d, J_{C-P} = 1.4 Hz), 134.7 (br), 131.9 (d, J_{C-P} = 5.0 Hz), 129.3 (qq, $^2J_{C-F}$ = 31.2 Hz, $^4J_{C-F}$ = 3.0 Hz), 127.3 (d, J_{C-P} = 2.8 Hz), 125.8 (q, $^1J_{C-F}$ = 272.6 Hz), 124.7, 122.7 (d, J_{C-P} = 9.3 Hz), 121.4, 117.4 (sept, $^3J_{C-F}$ = 3.9 Hz), 106.9 (d, J_{C-P} = 3.7 Hz), 105.9 (d, J_{C-P} = 5.2 Hz), 105.4, 104.8 (d, J_{C-P} = 38.7 Hz), 93.1 (d, J_{C-P} = 29.4 Hz, COD, CH), 92.1 (COD, CH), 73.8 (d, J_{C-P} = 1.5 Hz, COD, CH), 72.0 (d, J_{C-P} = 4.0 Hz, COD, CH), 55.8, 34.6 (d, J_{C-P} = 24.6 Hz), 34.3 (d, J_{C-P} = 5.2 Hz, COD, CH_2), 29.1 (COD, CH), 29.0 (COD, CH), 25.3 (COD, CH), 25.2 (d, J_{C-P} = 3.6 Hz); ^{31}P NMR (160 MHz, $CDCl_3$) δ 49.72 (d, J = 4.0 Hz); HRMS (ESI) m/z 678.2071 (M^+), calcd for $[IrC_{31}H_{36}NO_2P]^+$ 678.2107; 863.0671 ($BArF^-$), calcd for $[C_{32}H_{12}BF_{24}]^-$ 863.0654.

General Procedure for Asymmetric Hydrogenation of Alkenes. A high-pressure steel autoclave (HEL CAT 24) with a glass insert equipped with a magnetic stir bar was taken into a glovebox. The glass insert was loaded with alkene **7a** (20 mg, 0.138 mmol), freshly prepared catalyst **6a** (4.0 mg, 0.0028 mmol), and 0.5 mL of CH_2Cl_2. The vessel was sealed and taken out of the box. The reactor was purged with N_2 and then H_2, and stirred under 400 psi H_2 and rt for 18 h. The reactor was then vented. The reaction conversion and enantiomeric ratio were determined by chiral analysis.[22]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H and ^{13}C NMR spectra of the compounds, crystallographic data of **4a**, and chiral HPLC analyses of **4e** and **5e**. 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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