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Asymmetric hydrogenation and allylic substitution reaction with novel chiral pinene-derived N,P-ligands

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ABSTRACT

A series of new chiral tetrahydroquinoline ligands, derived from chiral α-pinene, were successfully synthesized. Iridium and palladium complexes of these ligands were proven to be efficient catalysts for enantioselective hydrogenation and allylic substitution reactions with moderate to excellent enantioselectivities (90–95% ee) and high yields.

1. Introduction

Transition-metal-catalyzed asymmetric transformations in the presence of chiral ligands have proven to be one of the most efficient methods for the construction of enantioenriched compounds.[1] Therefore, the design and synthesis of novel chiral ligands have been of a great interest in organic and organometallic chemistries over the past few decades. Among these, phosphorus- and nitrogen-based chiral ligands have been the most extensively investigated.[2] Crabtree reported the first homogenous achiral iridium hydrogenation catalysts in 1977,[3] while in 1997, Pfaltz et al. developed the first chiral iridium catalysts with chiral oxazolidine–phosphine ligands.[4] Since then, several highly efficient chiral N,P-ligands have been developed and used for iridium-catalyzed asymmetric hydrogenation and allylic substitution reactions.[5] Although chiral phosphine–oxazolidines have been extensively researched, the aza-heterocycle-phosphine ligands have scarcely been developed. Typical efficient iridium complexes based on thiazole **1**[6] and pyridines **2**[7] and **3**[8] were developed by several research groups (Fig. 1). The derivatives of α-pinene, bearing a pyridine ring, have been used in asymmetric additions,[9] cyclopropanations[10], and allylic oxidation and substitution reactions.[11] Recently, Andersson et al. reported the iridium complexes of **4**, bearing a chiral pinene moiety, in asymmetric hydrogenations with moderate to good enantioselectivities and conversions (Fig. 1).[12] Taking into consideration that the formation of a six-membered ring when ligands **4** complexes with iridium may reduce the enantiocontrol of the chiral environment, we developed a series of new N,P-ligands that form five-membered rings in the metal complex and applied them to the Ir-catalyzed hydrogenation of olefins and Pd-catalyzed allylic alkylations.

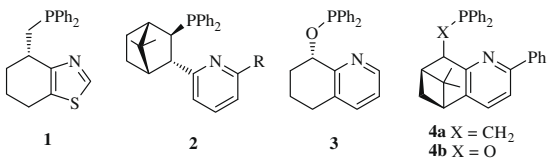

Figure 1.

2. Results and discussion

2.1. Preparation of chiral Ir complexes 8

After deprotonation of **5** with *n*-BuLi at −78 °C, the reactions were quenched with either chlorodiarylphosphine or chlorodicyclohexylphosphine and borane–dimethylsulfide to afford only one isomer of phosphine–borane **6** in 80–92% yields. The crystal structure of compound **6a** was determined by X-ray analysis (Fig. 2).[13] After removal of the BH_3 with diethylamine, the resulting pyridine–phosphines **7** reacted with an iridium complex and NaBArF (NaBArF: sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) to provide chiral iridium complex catalysts **8** in high yields (Scheme 1).

2.2. Ir-catalyzed asymmetric hydrogenation

2-Methyl-3-phenylallyl acetate **9a** was chosen as a model substrate to test the efficiency of catalysts **8a**–**8g**. The hydrogenation was carried out with a pressure of 50 bar of H_2 in CH_2Cl_2 at room temperature for 4 h. As shown in Table 1, all catalysts **8a**–**8g** were effective for the reaction as high conversions and moderate enantioselectivities were obtained (Table 1, entries 1–7). The results show that the electronic nature of the aromatic ring of the Ar_2P moiety has an important influence on the enantioselectivities of the reaction. For example, the aryl ring of the Ar_2P moiety with an electron-withdrawing substituent reduced enantioselectivities

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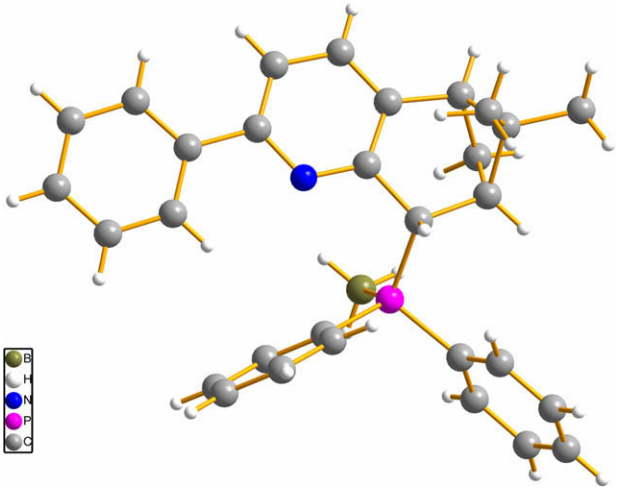
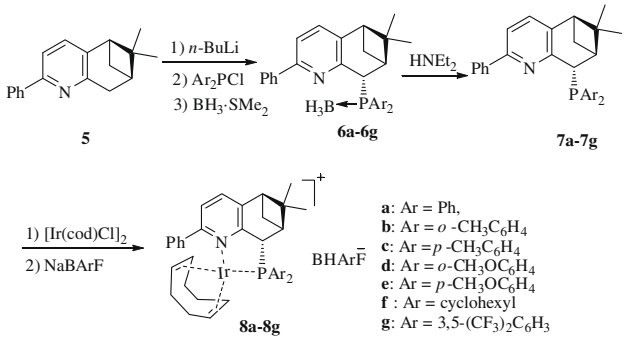


Figure 2. Molecular structure of **6a**.

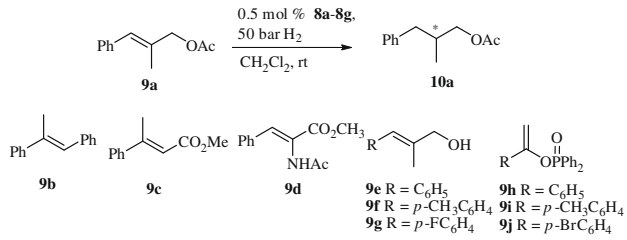


Scheme 1. Preparation of Ir complexes.

(Table 1, entry 7). The activities and enantioselectivities of catalysts **8c** and **8e** with $(p\text{-Tol})_2P$ and $(p\text{-anisole})_2P$ group were slightly superior to those of the other corresponding catalysts (Table 1, entries 3 and 5). This indicated that the position of the substituent of the aromatic ring of the Ar_2P moiety can also strongly influence the enantioselectivities of the catalysts. Electron-donating groups at the *para*-positions of the aryl ring led to higher activities and enantioselectivities (Table 1, entries 3 and 5), while substituents on the *ortho*-positions gave lower enantioselectivities (Table 1, entries 2 and 4).

Other substrates, including diphenylpropene, methyl 3-phenylbut-2-enoate, dehydrogen amino acid ester, phenylallyl alcohols, and vinyl phosphinates, were also hydrogenated in the presence of catalyst **8c** (0.5 mol % cat.; 50 bar H_2), and the desired reduced products were obtained in high yields and with moderate to good enantioselectivities (Table 1, entries 8–16). Vinyl phosphinates, terminal olefins with a small steric hindrance, gave much better enantioselectivities than other substrates. Substrates **9e–9j**, regardless of whether they contained electron-withdrawing or electron-donating groups at the *para*-position of phenyl ring, were observed to give reduced enantioselectivities (Table 1, entries 11–15). These results show that these bulkier ligands are both less active and selective than those of ligands **3**. While catalyst **8** gave higher activities than **4**, the enantioselectivities of **8c** lies between **4a** and **4b**. Repulsion between the pinene moiety and a phosphorus phenyl group may result in a conformational change that produces a more crowded active site which may reduce the enantioselectivity of hydrogenation. This phenomenon was supported by the results of hydrogenation.

Table 1
The results of asymmetric hydrogenation with 0.5 mol % **8** as a catalyst



Entry	Sub.	Cat.	Con.[a] (%)	ee[b] (%)
1	**9a**	**8a**	99	28 (*S*)
2	**9a**	**8b**	77	14 (*S*)
3	**9a**	**8c**	99	51 (*S*)
4	**9a**	**8d**	99	20 (*S*)
5	**9a**	**8e**	99	47 (*S*)
6	**9a**	**8f**	75	29 (*S*)
7	**9a**	**8g**	65	16 (*S*)
8	**9b**	**8c**	93	37 (*S*)[c]
9	**9c**	**8c**	99	42 (*S*)[c]
10	**9d**	**8c**	99	52 (*R*)[d]
11	**9e**	**8c**	99	59 (*S*)
12	**9f**	**8c**	99	47[e]
13	**9g**	**8c**	99	42[e]
14	**9h**	**8c**	99	90 (*S*)[f]
15	**9i**	**8c**	92	86 (*S*)[f]
16	**9j**	**8c**	99	70 (*S*)[f]

[a] Determined by GC.
[b] Determined by GC using a chiral CP-Chirasil-Dex CB column.[6b] The absolute configurations of the products were determined by comparison of the retention times with literature data.
[c] Determined by HPLC using a chiral Chiracel OJ-H column.[6b,14]
[d] Determined by GC using a chiral Chiralsil-L-Val column.[7]
[e] Compounds **10f** and **10g** were converted to corresponding acetic esters and compared with literature data.[15]
[f] Determined by HPLC using a chiral Chiracel AD-H column.[16]

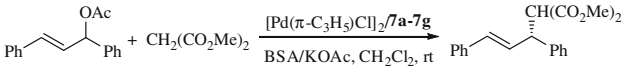
2.3. Pd-catalyzed asymmetric allylic alkylation of 1,3-diphenylallyl acetate

With the new ligands in hand, the asymmetric allylic alkylation of racemic 1,3-diphenylallyl acetate with dimethyl malonate was tested in the presence of the catalyst formed in situ from 2.5 mol % of $[Pd(\pi\text{-}C_3H_5)Cl]_2$ and 6 mol % of ligands **7** at room temperature. The results are listed in Table 2. All ligands **7a–7g** provided the substituted products in high yields (Table 2, entries 1–7). Ligand **7d**, which afforded the product with quantitative yield (>99%) and good enantiomeric excess (84% ee), was found to be the ligand of choice (Table 2, entry 4).

The effect of the base, solvent, and palladium precursor on the catalytic activity and enantioselectivity was investigated in the presence of **7d** as the ligand. The representative results are summarized in Table 3. The results showed that these factors strongly affect the activities and enantioselectivities of the allylic alkylation. The best result (up to 99% yield and 92% ee) was obtained with Cs_2CO_3 as a base in CH_2Cl_2 (Table 3, entry 3). Stronger bases, such as NaH and *n*-BuLi, and weaker BSA led to reduced ee values (Table 3, entries 2, 4, and 1). Other solvents, including toluene and THF, gave slightly lower enantioselectivities (Table 3, entries 5 and 6). Furthermore, $Pd(PhCN)_2Cl_2$, $Pd(CH_3CN)_2Cl_2$, and $Pd_2(bda)_3$ were examined as palladium precursors and enantioselectivities were obtained that were lower than $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (Table 3, entries 7–9).

To extend the scope of nucleophiles of the allylic substitution catalyzed by the $[Pd(\pi\text{-}C_3H_5)Cl]_2$ complex of ligand **7d,** some other

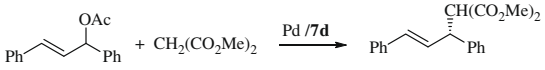
Table 2
Enantioselective allylic alkylation of 1,3-diphenylallyl acetate with dimethyl malonate[a]



Entry	Ligand	Time (h)	Yield[b] (%)	ee[c] (%)
1	**7a**	2	95	66 (*R*)
2	**7b**	2	90	56 (*R*)
3	**7c**	2	88	62 (*R*)
4	**7d**	2	>99	84 (*R*)
5	**7e**	2	76	65 (*R*)
6	**7f**	2	75	56 (*R*)
7	**7g**	2	69	30 (*R*)

[a] All reactions were conducted with ligand (6% equiv), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (2.5% equiv), BSA-AcOK (3 equiv) in CH_2Cl_2 at room temperature.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis with a Chiralcel AD-H column. The absolute configurations were determined by comparison of the retention times with literature data.[17]

Table 3
The effect of various base, solvents, and Pd precursors in allylic alkylation with **7d** as a ligand[a]



Entry	Pd precursor	Base	Solvent	Time	Yield[b] (%)	ee[c] (%)
1	$[Pd(\pi\text{-}C_3H_5)Cl]_2$	BSA	CH_2Cl_2	2	>99	84 (*R*)
2	$[Pd(\pi\text{-}C_3H_5)Cl]_2$	NaH	CH_2Cl_2	8	77	77 (*R*)
3	$[Pd(\pi\text{-}C_3H_5)Cl]_2$	Cs_2CO_3	CH_2Cl_2	8	>99	92 (*R*)
4	$[Pd(\pi\text{-}C_3H_5)Cl]_2$	*n*-BuLi	CH_2Cl_2	0.5	98	65 (*R*)
5	$[Pd(\pi\text{-}C_3H_5)Cl]_2$	Cs_2CO_3	Toluene	8	95	85 (*R*)
6	$[Pd(\pi\text{-}C_3H_5)Cl]_2$	Cs_2CO_3	THF	8	92	85 (*R*)
7	$Pd(PhCN)_2Cl_2$	Cs_2CO_3	CH_2Cl_2	8	85	50 (*R*)
8	$Pd(CH_3CN)_2Cl_2$	Cs_2CO_3	CH_2Cl_2	8	88	73 (*R*)
9	$Pd_2(bda)_3$	Cs_2CO_3	CH_2Cl_2	8	95	78 (*R*)

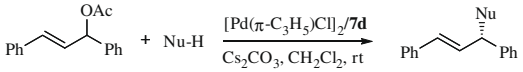
[a] All reactions were conducted with ligand **7d** (6% equiv), Pd complexes (2.5% equiv), base (3 equiv) at room temperature.
[b] Isolated yield.
[c] Determined by chiral HPLC analysis with a Chiralcel AD-H column. The absolute configurations were determined by comparison of the retention times with literature data.[17]

nucleophiles were applied in the catalytic system. The results of the allylic substitution under the optimum conditions are listed in Table 4. The results showed that all nucleophiles could offer the desired products with high yields and enantiomeric excesses (Table 4, entries 2–5). When $CH_2(CO_2Et)_2$ was used as a nucleophile, the enantiomeric excess of the product was slightly reduced to 90% ee (Table 4, entry 2). A bulky substituent of nucleophiles such as $CH_3CH(COOMe)_2$ or $CH_3CH(COOEt)_2$, could increase the enantioselectivities to 95% ee and 94% ee, respectively (Table 4, entries 3 and 4). Moderate enantiomeric excess was obtained with $CNCH_2CN$ as the nucleophile (Table 4, entry 5).

3. Conclusion

In conclusion, a series of new chiral tetrahydroquinoline ligands, derived from the chiral α-pinene, were successfully synthesized and evaluated in the Ir-catalyzed asymmetric hydrogenation and Pd-catalyzed asymmetric allylic substitution reactions, which afforded the hydrogenated products with moderate enantioselectivities (up to 90% ee) and the substituted products with high enantioselectivities (up to 95% ee). Further studies on the modifications of ligands and their applications to other asymmetric reactions are currently in progress in our laboratory.

Table 4
Enantioselective allylic alkylation of 1,3-diphenylallyl acetate in CH_2Cl_2[a]



Entry	Nu-H	Time	Yield[b] (%)	ee[c] (%)
1	$CH_2(CO_2Me)_2$	8	>99	92 (*R*)
2	$CH_2(CO_2Et)_2$	8	98	90 (*R*)
3	$CH_3CH(CO_2Me)_2$	8	85	95 (*R*)
4	$CH_3CH(CO_2Et)_2$	8	72	94 (*R*)
5	$CNCH_2CN$	8	85	64 (*R*)

[a] All reactions were conducted with ligand **7d** (6% equiv), $[Pd(\pi\text{-}C_3H_5)Cl]_2$ (2.5% equiv), Cs_2CO_3 (3 equiv) in CH_2Cl_2 at room temperature.
[b] Isolated yield.
[c] Determined by chiral HPLC using Chiralcel AD-H column or OJ-H column. The absolute configurations were determined by comparison of the retention times with literature data.[17]

4. Experimental

4.1. General methods

Melting points were measured on a Yanagimoto micro apparatus and are uncorrected. Optical rotations were measured with WZZ-2B digital polarimeter. The ee value was determined by HPLC using Chiralcel™ AD-H, OD-H, OB-H, and OJ-H column with 2-propanol–hexane as the eluent. The conversion was determined on an Agilent 6820 or a Bruker AV-400 MHz spectrometer. NMR spectra were recorded on a Bruker AV-400 MHz instrument using TMS as internal standard for ^1H NMR and ^{13}C NMR and 85% H_3PO_4 as external referencing for ^{31}P NMR in $CDCl_3$. Elemental analyses were performed on Elementar Vario EL III CHNS Foss-instrument. All reactions were carried out in dry glassware under nitrogen.

4.2. Synthesis of phosphine–borane ligand 6

A colorless stirred solution of **5** (0.30 g, 1.20 mmol) in Et_2O (6 mL) under nitrogen was cooled to −78 °C. To this mixture was added *n*-BuLi (0.58 mL, 1.44 mmol). After stirring at −78 °C for 0.5 h, the orange reaction mixture was transferred to an ice bath and stirred for a further 0.5 h. The resulting solution was cooled to −78 °C again and PAr_2C1 (0.28 mL, 1.56 mmol) was added. The reaction mixture was allowed to warm to room temperature slowly for 3 h. Borane–dimethylsulfide (2 M in THF, 0.78 mL, 1.56 mmol) was added to the mixture. The solution was stirred under nitrogen for a further 2 h and quenched with water. After extraction of the mixture with ethyl acetate, the combined organic layers were washed with brine, and dried over sodium sulfate, filtered, and the solvent was removed under reduced pressure. The crude phosphine–borane was purified by flash chromatography to yield **6** as a colorless solid.

Compound **6a**: Yield 90%, mp 215–217 °C. [$\alpha_D^{20} = +118$ (*c* 0.72, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.52–1.18 (br m, 3H, BH_3), 0.73 (s, 3H), 1.21 (d, J = 10 Hz, 1H),1.40 (s, 3H), 2.43–2.46 (m, 1H), 2.65 (t, J = 4.8 Hz, 1H), 2.76–2.77 (m, 1H), 4.42 (d, J = 13.6 Hz, 1H), 7.19–7.28 (m, 6H), 7.35–7.46 (m, 3H), 7.48–7.49 (m, 4H), 7.71–7.75 (m, 2H), 7.83–7.85 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.9, 26.0, 28.4, 42.4, 42.5, 42.8, 45.7, 117.1, 126.2, 128.2, 128.3, 128.4, 128.5, 130.2, 131.0, 131.4, 132.5, 132.6, 134.3, 134.4, 134.5, 138.5, 140.8, 153.1, 153.4; ^{31}P NMR ($CDCl_3$) δ 27.2. Anal. Calcd for

$C_{30}H_{31}BNP$: C, 80.54; H, 6.98; N, 3.13. Found: C, 80.51; H, 6.97; N, 3.12.

Compound **6b**: Yield 89%, mp 204–206 °C. [$\alpha_D^{20} = -19.1$ (*c* 1.2, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.56–1.20 (br m, 3H, BH_3), 0.77 (s, 3H), 1.32 (s, 3H), 1.76 (d, *J* = 10 Hz, 1H), 1.97–1.99 (m, 1H), 2.18 (s, 3H), 2.46 (s, 3H), 2.52–2.60 (m, 1H), 2.76 (t, *J* = 5.6 Hz, 1H), 4.32 (d, *J* = 13.6 Hz, 1H), 7.10–7.28 (m, 11H), 7.43–7.50 (m, 3H), 8.10–8.12 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.2, 21.5, 26.2, 26.7, 40.8, 42.4, 42.6, 43.0, 46.7, 116.2, 125.3, 126.0, 126.4, 128.1, 128.2, 128.4, 129.8, 133.4, 136.1, 139.0, 140.1, 142.3, 142.6, 143.4, 143.7, 153.7, 157.8; ^{31}P NMR ($CDCl_3$) δ −28.4. Anal. Calcd for $C_{32}H_{35}BNP$: C, 80.84; H, 7.42; N, 2.95. Found: C, 80.82; H, 7.42; N, 2.96.

Compound **6c**: Yield 87%, mp 206–208 °C. [$\alpha_D^{20} = +58.9$ (*c* 0.56, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.53–1.11 (br m, 3H, BH_3), 0.72 (s, 3H), 1.21 (d, *J* = 10 Hz, 1H), 1.40 (s, 3H), 2.31 (s, 3H), 2.41–2.43 (m, 1H), 2.45 (s, 3H), 2.64 (t, *J* = 5.6 Hz, 1H), 2.76–2.78 (m, 1H), 4.36 (d, *J* = 13.6 Hz, 1H), 7.06 (d, *J* = 4.8 Hz, 2H), 7.18–7.25 (m, 6H), 7.28 (d, *J* = 8 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 1H), 7.57 (t, *J* = 4.8 Hz, 2H), 7.71 (t, *J* = 4.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.9, 21.5, 26.0, 28.3, 42.3, 42.4, 42.7, 43.0, 45.8, 117.0, 124.9, 126.3, 128.2, 128.3, 129.0, 129.1, 129.2, 129.3, 132.4, 132.5, 134.2, 134.4, 138.6, 140.3, 140.8, 141.4, 153.4; ^{31}P NMR ($CDCl_3$) δ 25.6. Anal. Calcd for $C_{32}H_{35}BNP$: C, 80.84; H, 7.42; N, 2.95. Found: C, 80.81; H, 7.43; N, 2.94.

Compound **6d**: Yield 85%, mp 178–179 °C. [$\alpha_D^{20} = -23.8$ (*c* 0.55, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.60–1.18 (br m, 3H, BH_3), 0.74 (s, 3H), 1.33 (d, *J* = 10 Hz, 1H),1.37 (s, 3H), 2.24–2.29 (m, 1H), 2.53–2.60 (m, 1H), 2.69 (t, *J* = 5.6 Hz, 1H), 3.10 (s, 3H), 3.73 (s, 3H), 4.97 (d, *J* = 16.8 Hz, 1H), 6.71–6.72 (m, 1H), 6.95–7.49 (m, 13H), 8.20–8.24 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 21.1, 21.9, 27.6, 28.9, 40.3, 41.8, 45.4, 53.9, 55.0, 109.8, 111.2, 119.8, 119.9, 120.0, 125.9, 127.2, 127.4, 131.1, 132.7, 133.4, 136.4, 136.5, 138.7, 139.2, 153.0, 154.7, 160.8, 161.1; ^{31}P NMR ($CDCl_3$) δ 25.7. Anal. Calcd for $C_{32}H_{35}BNO_2P$: C, 75.75; H, 6.95; N, 2.76. Found: C, 77.74; H, 6.93; N, 2.75.

Compound **6e**: Yield 82%, mp 180–181 °C. [$\alpha_D^{20} = +72$ (*c* 0.72, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.62–1.23 (br m, 3H, BH_3), 0.75 (s, 3H), 1.33 (d, *J* = 10 Hz, 1H),1.37 (s, 3H), 2.24–2.29 (m, 1H), 2.53–2.60 (m, 1H), 2.69 (t, *J* = 5.6 Hz, 1H), 3.10 (s, 3H), 3.73 (s, 3H), 4.97 (d, *J* = 16.8 Hz, 1H), 6.72 (dd, *J* = 2.8 Hz, *J* = 5.6 Hz, 2H), 7.14–7.23 (m, 6H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.64 (t, *J* = 4.8 Hz, 2H), 7.79 (t, *J* = 4.8 Hz, 2H), 8.18–8.22 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 20.9, 21.5, 25.4, 28.7, 42.3, 43.8, 45.4, 54.5, 55.2, 108.3, 113.2, 120.8, 120.9, 124.0, 126.9, 129.2, 129.4, 132.1, 133.7, 134.4, 138.4, 138.5, 140.7, 153.2, 162.8, 163.1; ^{31}P NMR ($CDCl_3$) δ 27.4. Anal. Calcd for $C_{32}H_{35}BNO_2P$: C, 75.75; H, 6.95; N, 2.76. Found: C, 77.73; H, 6.94; N, 2.76.

Compound **6f**: Yield 90%, mp 208–210 °C. [$\alpha_D^{20} = +17.8$ (*c* 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.30–0.70 (br m, 3H, BH_3), 0.63–0.65 (m, 1H), 0.66 (s, 3H), 0.72–0.78 (m, 1H), 1.06–1.08 (m, 2H), 1.20–1.43 (m, 8H), 1.45 (s, 3H),1.54 (d, *J* = 10 Hz, 1H), 1.62–1.72 (m, 2H), 1.74–1.78 (m, 2H), 1.81–1.91 (m, 2H), 2.16–2.27 (m, 3H), 2.62 -2.78 (m, 4H), 3.65 (d, *J* = 13.2 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.46–7.53 (m, 3H), 8.04 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 20.9, 25.9, 26.1, 26.2, 26.6, 26.9, 27.0, 27.1, 27.3, 29.1, 29.5, 31.1, 33.2, 33.4, 37.0, 37.2, 41.2, 43.3, 45.5, 117.2, 126.4, 128.6, 128.7, 134.3, 139.2, 140.5, 153.9, 154.1; ^{31}P NMR ($CDCl_3$) δ 36.6. Anal. Calcd for $C_{30}H_{43}BNP$: C, 78.42; H, 9.43; N, 3.05. Found: C, 78.40; H, 9.40; N, 3.04.

Compound **6g**: Yield 84%, mp 217–219 °C. [$\alpha_D^{20} = -61.3$ (*c* 0.72, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.70–1.32 (br m, 3H, BH_3), 0.71 (s, 3H), 1.21 (d, *J* = 10 Hz, 1H),1.41 (s, 3H), 2.46 (m, 1H), 2.66 (t, *J* = 4.8 Hz, 1H), 2.76 (m, 1H), 4.52 (d, *J* = 13.6 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.48–7.55 (m, 3H), 8.01 (d, *J* = 5.6 Hz, 2H), 8.03–8.05 (m, 2H), 8.27–8.29 (m, 2H), 8.64–8.67 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.9, 26.0, 28.4, 42.4, 42.5, 42.8, 45.7, 117.1, 126.2, 128.2, 128.3, 128.4, 128.5, 130.2, 131.0, 131.4, 132.5, 132.6, 134.3, 134.4, 134.5, 138.5, 140.8, 153.1, 153.4; ^{31}P NMR ($CDCl_3$) δ 20.3. Anal. Calcd for $C_{34}H_{27}BF_{12}NP$: C, 56.77; H, 3.78; N, 1.95. Found: C, 56.76; H, 3.76; N, 1.92.

4.3. General procedure for the preparation of iridium complexes 8

The borane-protected phosphine ligand **6** (0.2 mmol) was treated with neat diethylamine (1 mL), under argon and warmed to 50 °C. The reaction mixture was stirred with monitoring by TLC. After the TLC showed the disappearance of the starting material, the reaction mixture was cooled to RT. Removal of diethylamine and the diethylamine–borane complex under reduced pressure gave ligand **7** as an air-sensitive foam. Ligand **7** (0.2 mmol), $[Ir(cod)Cl]_2$ (67.2 mg, 0.1 mmol), and CH_2Cl_2 (5 mL) were added to a flask under N_2. The solution was stirred at room temperature for about 2 h until TLC indicated that the ligand had been consumed. Next, NaBArF (0.22 g, 0.25 mmol) was added followed by H_2O (5 mL), and the resulting two-phase mixture was stirred vigorously for 30 min. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic phase was washed with H_2O (5 mL) and dried over anhydrous Na_2SO_4. After removing solvent under reduced pressure, the residue was purified by column chromatography to afford yellow or red complexes.

Compound **8a**: Yield 91%, mp 66–68 °C. [$\alpha_D^{20} = +100.8$ (*c* 1.05, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.94 (d, *J* = 17.2 Hz, 3H), 1.21 (d, *J* = 10 Hz, 1H), 1.26–1.27 (m, 1H, COD), 1.40 (d, *J* = 10 Hz, 3H), 1.61–1.70 (m, 2H, COD), 1.90–2.20 (m, 5H, COD), 2.21–2.29 (m, 1H, COD), 2.61 (m, 1H), 2.65 (t, *J* = 4.8 Hz, 1H), 2.75 (m, 1H), 3.38–3.46 (m, 1H, COD), 4.23–4.79 (m, 2H, COD), 5.39 (dd, *J* = 10.4 Hz, *J* = 416 Hz, 1H), 7.28–7.43 (m, 6H), 7.46–7.49 (m, 1H), 7.50 (s, 4H, BArF-H), 7.52–7.68 (m, 7H), 7.70 (sbr, 8H, BArF-H), 7.75–7.91 (m, 2H), 8.10–7.15 (m, 1H); ^{31}P NMR ($CDCl_3$) δ 44.4. Anal. Calcd for $C_{70}H_{52}BF_{24}IrNP$: C, 52.64; H, 3.28; N, 0.88. Found: C, 52.66; H, 3.24; N, 0.84.

Compound **8b**: Yield 89%, mp 86–88 °C. [$\alpha_D^{20} = +148.9$ (*c* 0.68, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.94 (s, 3H), 1.26–1.31 (m, 1H, COD), 1.44 (d, *J* = 10 Hz, 1H), 1.47 (s, 3H), 1.54–1.56 (m, 1H), 1.61–1.70 (m, 2H, COD), 1.80 (s, 3H), 1.81 (s, 3H), 1.90–2.00 (m, 2H, COD), 2.13–2.25 (m, 2H, COD), 2.40–2.58 (m, 2H, COD), 2.70–2.74 (m, 1H), 2.78 (t, *J* = 5.6 Hz, 1H), 3.03–3.05 (m, 1H, COD), 4.66–4.78 (m, 2H, COD), 5.10 (d, *J* = 9.6 Hz, 1H), 6.90–7.12 (m, 5H), 7.27–7.29 (m, 2H), 7.42–7.47 (m, 4H), 7.48 (s, 4H, BArF-H), 7.59–7.68 (m, 3H), 7.70 (sbr, 8H, BArF-H), 8.00–8.05 (m, 1H); ^{31}P NMR ($CDCl_3$) δ 36.1. Anal. Calcd for $C_{72}H_{56}BF_{24}IrNP$: C, 53.21; H, 3.47; N, 0.86. Found: C, 53.27; H, 3.40; N, 0.82.

Compound **8c**: Yield 92%, mp 72–74 °C. [$\alpha_D^{20} = +102.3$ (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.89 (s, 3H), 1.05–1.15 (m, 1H, COD), 1.39 (d, *J* = 10 Hz, 1H), 1.41 (s, 3H), 1.45–1.62 (m, 2H, COD), 1.63–1.82 (m, 2H, COD), 1.97–2.05 (m, 2H, COD), 2.08–2.19 (m, 2H, COD), 2.28–2.30 (m, 1H), 2.35 (s, 3H), 2.49 (s, 3H), 2.62–2.64 (m, 1H), 2.74 (t, *J* = 5.6 Hz, 1H), 3.16–3.23 (m, 1H, COD), 3.34–3.38 (m, 1H, COD), 4.59–4.62 (m, 1H, COD), 5.81 (dd, *J* = 10.4 Hz, *J* = 416 Hz, 1H), 7.07 (d, *J* = 4.8 Hz, 2H), 7.18–7.28 (m, 4H), 7.32–7.40 (m, 2H), 7.46 (s, 4H, BArF-H), 7.50–7.60 (m, 3H), 7.70 (sbr, 8H, BArF-H), 7.72–7.80 (m, 3H), 8.10–8.15 (m, 1H); ^{31}P NMR ($CDCl_3$) δ 44.8. Anal. Calcd for $C_{72}H_{56}BF_{24}IrNP$: C, 53.21; H, 3.47; N, 0.86. Found: C, 53.25; H, 3.39; N, 0.81.

Compound **8d**: Yield 88%, mp 62–64 °C. [$\alpha_D^{20} = +63.0$ (*c* 0.9, $CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.95 (s, 3H), 1.13–1.21 (m, 1H, COD), 1.35 (d, *J* = 10 Hz, 1H), 1.50 (s, 3H), 1.60–1.75 (m, 2H, COD), 1.98–2.13 (m, 3H, COD), 2.20–2.34 (m, 2H, COD), 2.42–2.52 (m, 1H, COD), 2.83–2.84 (m, 1H), 2.98–3.10 (m, 1H, COD), 3.33 (s, 3H), 3.35 (s, 3H), 3.49–3.50 (m, 1H), 3.73–3.83 (m, 1H, COD), 4.03 (t, *J* = 5.6 Hz, 1H), 4.61 (d, *J* = 16.8 Hz, 1H), 4.83–4.94 (m, 1H, COD),

6.84–7.49 (m, 11H), 7.52 (s, 4H, BArF-H),7.60–7.74 (m, 3H), 7.77 (sbr, 8H, BArF-H), 8.20–8.24 (m, 1H); ^{31}P NMR ($CDCl_3$) δ 46.1. Anal. Calcd for $C_{72}H_{56}BF_{24}IrNO_2P$: C, 52.18; H, 3.41; N, 0.85. Found: C, 52.26; H, 3.35; N, 0.87.

Compound **8e**: Yield 85%, mp 68–70 °C. [$\alpha_D^{20} = +94.7$ (*c* 0.35, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.88 (d, *J* = 10 Hz, 1H), 0.92 (s, 3H), 1.08–1.12 (m, 1H, COD), 1.40 (s, 3H), 1.50–1.57 (m, 2H, COD), 1.65–1.72 (m, 2H, COD), 2.01–2.07 (m, 3H, COD), 2.08–2.14 (m, 1H, COD), 2.18–2.21 (m, 1H), 2.58–2.60 (m, 1H), 2.75 (t, *J* = 5.6 Hz, 1H), 3.18–3.24 (m, 1H, COD), 3.35–3.40 (m, 1H, COD), 3.76 (s, 3H), 3.89 (s, 3H), 4.56–4.60 (m, 1H, COD), 5.76 (d, *J* = 16.8 Hz, 1H), 6.90 (dd, *J* = 2.8 Hz, *J* = 5.6 Hz, 2H), 7.16–7.25 (m, 5H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.50 (s, 4H, BArF-H),7.67 (t, *J* = 4.8 Hz, 3H), 7.71 (sbr, 8H, BArF-H), 7.82 (t, *J* = 4.8 Hz, 2H), 8.08–8.12 (m, 1H); ^{31}P NMR ($CDCl_3$) δ 44.2. Anal. Calcd for $C_{72}H_{56}BF_{24}IrNO_2P$: C, 52.18; H, 3.41; N, 0.85. Found: C, 52.23; H, 3.38; N, 0.79.

Compound **8f**: Yield 92%, mp 63–65 °C. [$\alpha_D^{20} = -27.3$ (*c* 1.36, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.65–0.70 (m, 1H), 0.81 (s, 3H), 0.92–0.97 (m, 1H), 1.07–1.11 (m, 2H), 1.19–1.21 (m, 1H, COD),1.32–1.45 (m, 8H), 1.57 (s, 3H),1.51 (d, *J* = 10 Hz, 1H), 1.72–1.80 (m, 4H, COD), 1.61–1.65 (m, 3H), 1.95–2.05 (m, 4H), 2.09–2.17 (m, 3H, COD), 2.20–2.26 (m, 1H, COD), 2.40–2.55 (m, 2H), 2.60 -2.70 (m, 2H), 2.81–2.85 (m, 1H), 2.92 (t, *J* = 5.6 Hz, 1H), 4.10–4.15 (m, 1H, COD), 4.28 (d, *J* = 6.8 Hz, 1H), 4.70–4.80 (m, 2H, COD), 7.48–7.50 (m, 3H), 7.52 (s, 4H, BArF-H), 7.60–7.66 (m, 3H), 7.72 (sbr, 8H, BArF-H), 8.04 (d, *J* = 5.6 Hz, 1H); ^{31}P NMR ($CDCl_3$) δ 68.1. Anal. Calcd for $C_{70}H_{64}BF_{24}IrNP$: C, 52.25; H, 4.01; N, 0.87. Found: C, 52.29; H, 3.96; N, 0.81.

Compound **8g**: Yield 90%, mp 77–79 °C. [$\alpha_D^{20} = -34.1$(*c* 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 0.73 (s, 3H), 1.29–1.31 (m, 1H, COD), 1.33 (d, *J* = 10 Hz, 1H), 1.48 (s, 3H), 1.40–1.44 (m, 2H, COD), 1.82–1.95 (m, 2H, COD), 2.38 (m, 1H), 2.46–2.78 (m, 3H, COD), 2.84–2.88 (m, 1H, COD), 3.03 (t, *J* = 5.2 Hz, 1H), 3.65 (m, 1H), 4.61–4.70 (m, 1H, COD), 4.85–4.88 (m, 1H, COD), 5.01 (d, *J* = 13.6 Hz, 1H), 6.96 (t, *J* = 8.0 Hz, 2H), 7.05–7.09 (m, 1H), 7.22 (d, *J* = 7.2 Hz, 2H), 7.31–7.40 (m, 3H), 7.49 (s, 4H, BArF-H),7.56 (d, *J* = 8.0 Hz, 2H), 7.69 (sbr, 8H, BArF-H), 7.87–7.94 (m, 2H), 8.08–8.10 (m, 1H); ^{31}P NMR ($CDCl_3$) δ 43.7. Anal. Calcd for $C_{74}H_{48}BF_{36}IrNP$: C, 47.55; H, 2.59; N, 0.75. Found: C, 47.59; H, 2.52; N, 0.72.

4.4. General procedure for the hydrogenation of olefins using 0.5 mol % iridium complexes 6a–6g

Enantioselective hydrogenation of olefins: olefin **9** (0.5 mmol) and iridium complexes **8** (0.0025 mmol) in 2 mL dry degassed CH_2Cl_2 were added to the autoclave under inert atmosphere. The autoclave was sealed immediately and pressurized to 50 bar H_2. The mixture was stirred for 5 h. The CH_2Cl_2 was removed and the crude product was passed through a short silica-gel column with 10% ethyl acetate in hexane as eluent. After evaporation of the solvent, **10** was obtained and analyzed for conversion (GC) and ee (HPLC).

4.5. General experimental procedure for the Pd-catalyzed asymmetric allylic alkylation

To a Schlenk tube containing Pd complexes (0.005 mmol) and chiral ligands **7a**–**7g** (0.012 mmol) were added dry solvents (2 mL), and the mixture was stirred at room temperature for 1 h. Then 1,3-diphenylallyl acetate (50 mg, 0.2 mmol) was added and the mixture was stirred for further 10 min, nucleophiles (0.6 mmol) was added to the reaction mixture followed by base (0.6 mmol). The resultant mixture was stirred for an appropriate time. After the reaction was concentrated under vacuum, the crude residue was purified by flash column chromatography with 15% ethyl acetate in hexane.

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