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Synthesis of a chiral *N*-heterocyclic carbene bearing a *m*-terphenyl-based phosphate moiety as an anionic N-substituent and its application to copper-catalyzed enantioselective boron conjugate additions

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ABSTRACT

A chiral *N*-heterocyclic carbene (NHC) ligand **1a** bearing a *m*-terphenyl-based phosphate moiety as an anionic N-substituent has been developed. A rhodium complex [Rh(**1a**)(cod)]$_2$ was synthesized and its structure was characterized by NMR and ESI-MS spectroscopy. This ligand gave high enantioselectivities in copper-catalyzed enantioselective boron conjugate additions to an α,β-unsaturated ester to give a chiral β-boryl ester.

1. Introduction

N-Heterocyclic carbenes (NHCs) have attracted considerable interest both in organic and organometallic chemistry due to their highly electron-donating and strong coordination abilities in forming transition metal complexes.[1] Therefore, NHC–transition metal complexes exhibit a unique catalytic activity and enantioselectivity in asymmetric catalysis.[2] Recently, multidentate chiral NHC ligands presenting an anionic functional group have become a useful strategy for constructing effective chiral environments in proximity to the metal center. For instance, NHC ligands with hydroxy,[3] sulfonate,[4] or amide[5] moieties in the N-substituent have been introduced (Fig. 1), and these ligands enable highly enantioselective transformations with various transition metals. However

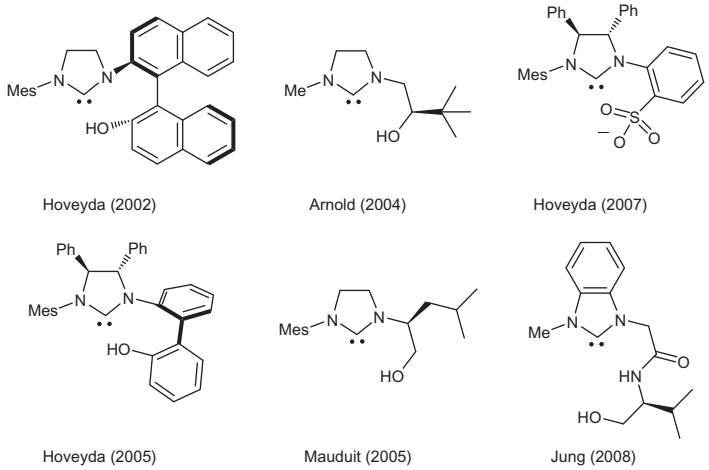

Figure 1. Representative examples of chiral NHC ligands bearing an anionic functional group.

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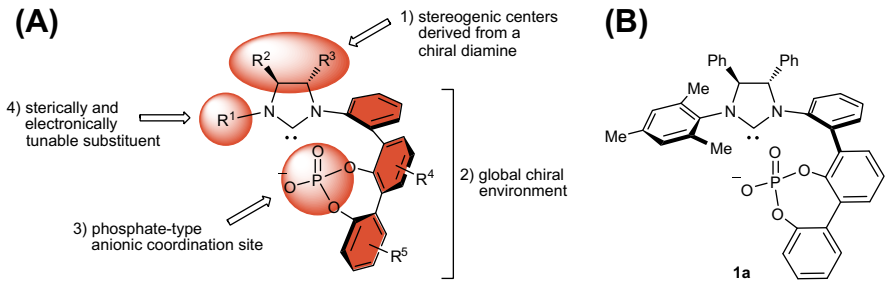
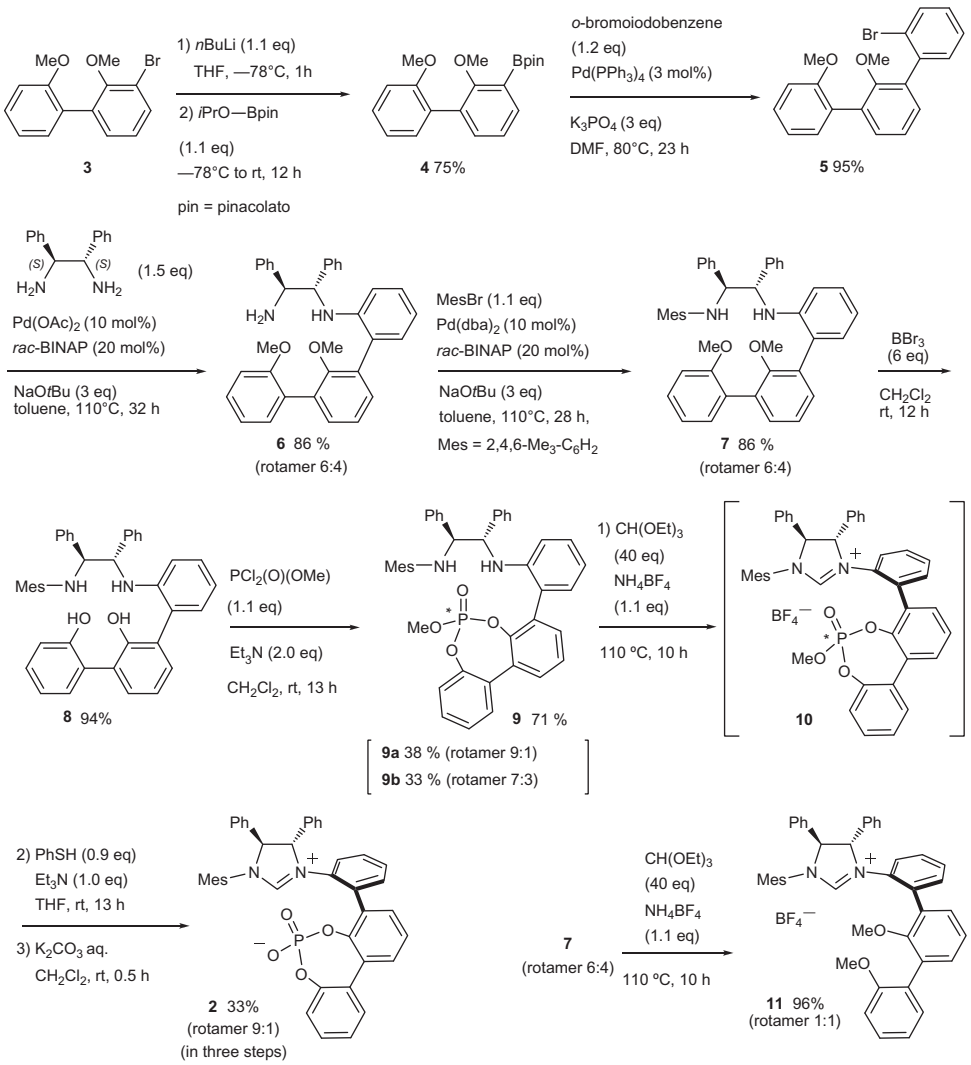


Figure 2. (a) Features of chiral NHC ligands **1** bearing a *m*-terphenyl-based phosphate moiety as an N-substituent. (b) Structure of **1a**.

to date, a chiral NHC ligand bearing a diorganophosphate moiety [$(RO)_2P(O)O^-$] as an anionic N-substituent has not been reported in the literature despite the ubiquitous utilities of biarylphosphates in transition metal catalysis as counter anions of the metal[6] or in organocatalysis as Brønsted acid–base components.[7]

We envisioned that the synthesis of chiral NHC ligands **1** bearing a *m*-terphenyl-based phosphate moiety as an anionic N-substituent would be a useful strategy for developing efficient chiral catalysts (Fig. 2a). The structural features of these chiral NHC ligands are as follows: (1) the NHC backbone has stereogenic centers derived from easily-available chiral diamines; (2) the *m*-terphenyl moiety as an N-substituent can provide global chiral environment in proximity to the metal center; (3) the *m*-terphenyl-based diorganophosphate moiety works as an anionic coordination site resulting in C,O-bidentate coordination; and (4) the steric and electronic nature of the catalyst is tunable by the other N-substituent (R^1). Based on these considerations, we selected chiral NHC ligand **1a**, which has a non-substituted *m*-terphenyl-based phosphate moiety ($R^4 = R^5 = H$), an *N*-mesityl group (R^1 = 2,4,6-Me_3-C_6H_2), and a 1,2-diphenylethylenediamine-derived NHC core ($R^2 = R^3$ = Ph) as the initial synthetic target (Fig. 2b). Details of the ligand synthesis, the coordination behavior toward a Rh(I) complex, and application to the Cu(I)-catalyzed enantioselective boron conjugate addition are described below.



Scheme 1. Synthesis of chiral imidazolinium salt **2** and **11** as a precursor to NHC. One of the possible rotamers is shown for **2**, **10,** and **11**.

2. Results and discussion

The synthesis of imidazolinium zwitterion **2**, which is a precursor to the NHC ligand **1a**, is outlined in Scheme 1. Halogen/lithium exchange of **3**[8] followed by treatment with isopropoxyboronic acid pinacol ester gave **4** in 75% yield. The Pd-catalyzed Suzuki–Miyaura cross-coupling of 1-bromo-2-iodobenzene with **4** afforded *m*-terphenyl bromide **5** in excellent yield. For the preparation of the unsymmetrical diamine and imidazolinium salt, Hoveyda's procedures for the synthesis of chiral bidentate NHCs were followed with a slight modification.[3g] Thus, commercially available (1*S*,2*S*)-1,2-diphenylethylenediamine was coupled with **5** to give monoarylated diamine **6** through Pd-catalyzed C–N coupling. The ^{1}H and ^{13}C NMR spectra of **6** at room temperature showed the existence of rotamers in a 6:4 ratio. The second C–N coupling of **6** with mesityl bromide catalyzed by the $Pd(dba)_2$/BINAP complex afforded unsymmetrical diaryldiamine **7** in 86% yield. Next, demethylation of **7** with BBr_3 gave the corresponding biphenol **8** in a quantitative yield. The ^{1}H and ^{13}C NMR spectra of **8** did not show the existence of rotamers.

Next, the reaction of **8** with dichlorophosphoric acid methyl ester in the presence of Et_3N gave organophosphate **9**. The ^{31}P NMR spectrum of the crude product **9** showed four peaks (Fig. 3a), which were assigned to signals of a pair of diastereomers, each consisting of rotamers (**9a** with 9:1 rotamer ratios and **9b** with 7:3 rotamer ratios): the appearance of the diastereomers is due to the existence of the P stereogenic center. The diastereomers **9a** and **9b** could be separated by silica gel column chromatography for characterization by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy (Fig. 3b). Construction of the imidazolinium ring was performed by treatment of the diastereomer mixtures of **9** (**9a** and **9b**) with $CH(OEt)_3/NH_4BF_4$ to give imidazolinium salt **10**. Finally, deprotection of the phosphate methyl ester followed by anion exchange with K_2CO_3 afforded the desired chiral imidazolinium zwitterion **2** bearing a diorganophosphate moiety in a useful yield. The two rotamers of **2** were observable in a 9:1 ratio by ^{1}H NMR spectroscopy in $CDCl_3$ at room temperature. Although definitive structure determination for the major rotamer has yet to be successful, an analogy from Hoveyda's X-ray structures for *N*-biaryl-substituted NHC–metal complexes[3g] suggests that the rotameric isomerization is due to rotation around the C–C bond connecting the *N*-phenyl group and the biphenyl phosphate unit and that the major rotamer is the one in which the biphenyl phosphate unit is *anti* to the phenyl group at the nearby stereogenic center of the imidazolinium ring as depicted in Scheme 1. We also synthesized di-MeO-substituted imidazolinium salt **11**, which existed as a 1:1 rotamer mixture, as a reference compound in order to evaluate an effect of the phosphate moiety of **2** by treating **7** with $CH(OEt)_3/NH_4BF_4$.

The coordination behavior of **1a** toward a Rh(I) complex was investigated through the reaction between **2** and $[RhCl(cod)]_2$ in the presence of KO*t*Bu in THF (Scheme 2). Air- and moisture-stable dimeric Rh(I) complex $[Rh(\mathbf{1a})(cod)]_2$ was obtained in 64% yield after silica gel chromatography. The ESI mass spectrum showed the dimeric nature of this Rh(I) complex (Fig. 4a). The ^{1}H, ^{13}C, and ^{31}P NMR spectroscopic analyses indicated that the two rotamers of **2** converged with a single stereoisomer. A doublet signal due to a P-Rh coupling in the ^{31}P NMR spectrum (δ 5.8, $^{2}J_{Rh\text{-}P}$ = 8.9 Hz in Fig. 4b) indicates that the diorganophosphate moiety on **1a** has a direct interaction with the rhodium center. Thus, a C,O-bidentate coordination of **1a** was confirmed. Similar dimeric NHC–metal complexes with an anionic N-substituent have been reported by Hoveyda[3g,4a] and Jung.[5a]

In order to evaluate the utility of the chiral NHC ligand **1a** bearing a phosphate moiety, we examined the copper-catalyzed enantioselective boron conjugate addition to an α,β-unsaturated carbonyl compound.[9] Although this enantioselective catalysis has

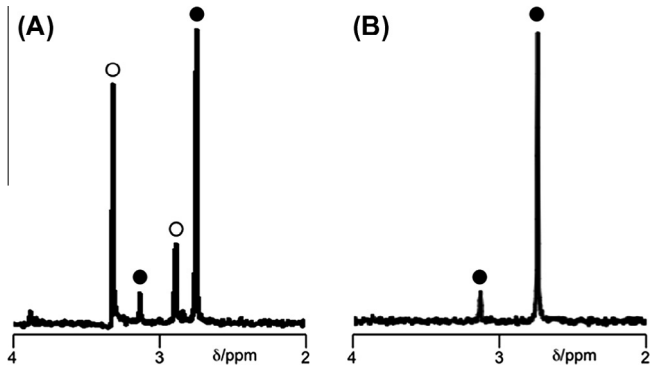


Figure 3. ^{31}P NMR spectra of (a) crude product **9** and (b) **9a** purified by silica gel chromatography. Filled (●) and open circles (○) indicate **9a** and **9b**, each having two rotamers, respectively.

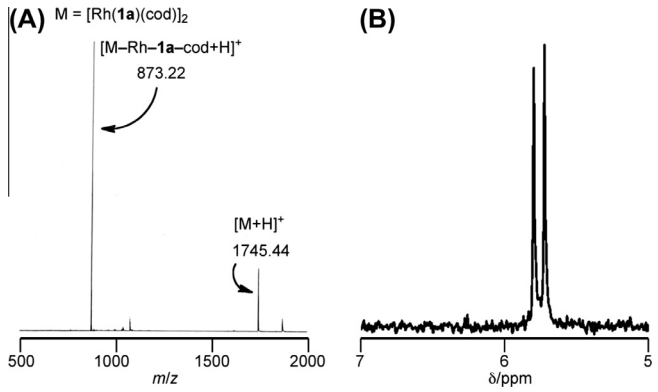
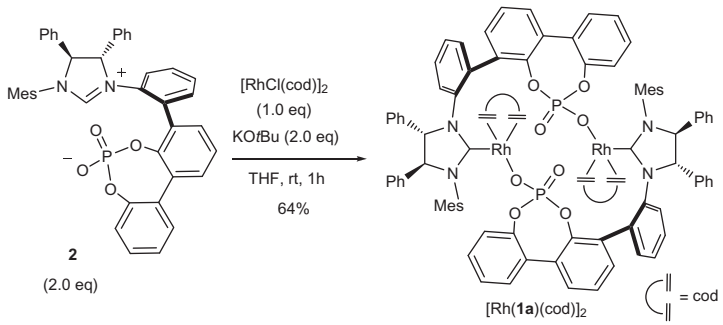
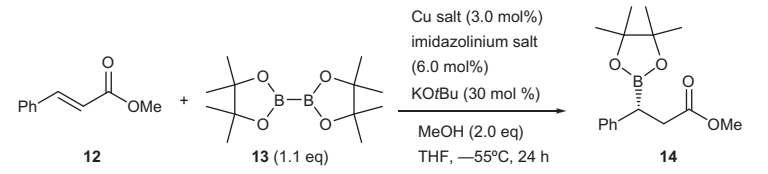


Figure 4. (a) ESI-Mass and (b) ^{31}P NMR ($CDCl_3$) spectra of $[Rh(\mathbf{1a})(cod)]_2$.

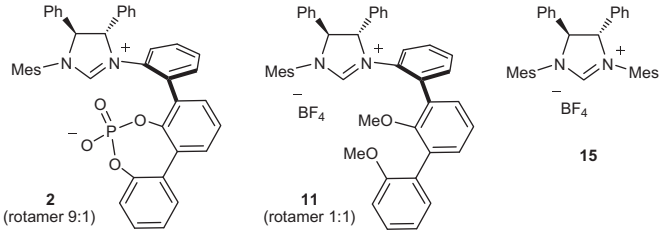


Scheme 2. Synthesis of $[Rh(\mathbf{1a})(cod)]_2$.



imidazolinium salt

Cu salt, enantioselectivity and isolated yield of **14**



CuO*t*Bu	89% ee 86% yield	96% ee 94% yield	32% ee 83% yield
CuI	77% ee 88% yield	87% ee 73% yield	31% ee 82% yield
$CuCl_2$•$2H_2O$	79% ee 83% yield	95% ee 72% yield	10% ee 83% yield

Scheme 3. Ligand effects of copper-catalyzed enantioselective boron conjugate addition to **12**. Reaction conditions: **12** (0.20 mmol), **13** (0.22 mmol), Cu salt (0.0060 mmol, 3.0 mol %), imidazolinium salt (0.012 mmol, 6.0 mol %), KO*t*Bu (0.060 mmol, 30 mol %), MeOH (0.40 mmol), THF (1.0 mL), −55 °C, 24 h.

mainly been developed by studies with phosphine-based chiral ligands,[10] recent work by McQuade and Hoveyda has shown that some chiral NHC ligands are useful for obtaining high catalyst turnover efficiencies or a broad substrate scope.[11] Accordingly, we expected that **1a** may show favorable effects for these reactions.

The ligand effects of several chiral NHCs in the reaction of α,β-unsaturated ester **12** and bis(pinacolato)diboron **13** in the presence of MeOH as a proton source and a catalytic amount of CuO*t*Bu are summarized in Scheme 3. The boron conjugate addition reaction with the chiral imidazolinium zwitterion **2** bearing the diorganophosphate afforded the desired product **14** with 89% ee (*R*) in 86% yield. The di-MeO-substituted imidazolinium salt **11** was then used as a precursor of the NHC ligand in order to evaluate the effect of the phosphate functionality in **1a**. Against our expectation, however, this reaction occurred in excellent enantioselectivity, giving (*R*)-**14** with 96% ee. On the other hand, conventional C_2-symmetrical chiral imidazolinium salt **15**[11a,12] afforded **14** with poor enantioselectivity [32% ee (*R*)]. The use of air- and moisture-stable CuI and $CuCl_2$·$2H_2O$ instead of CuO*t*Bu as a copper source resulted in similar trends in their catalytic activities and enantioselectivities. These results indicate that the heteroatom-functionalized *m*-terphenyl structures in **2** and **11** are effective scaffolds for introducing the N atom of NHC systems, producing effective chiral environments in proximity to the metal center. However, the effect of the diorganophosphate as an anionic functional group in this enantioselective catalysis is unclear.

3. Conclusion

We have developed a novel imidazolinium zwitterion **2** bearing a diorganophosphate anionic functional group, as a precursor to a chiral NHC ligand **1a**. The ^{31}P NMR spectrum of [Rh(**1a**)(cod)]$_2$ indicated that the phosphate moiety is capable of coordinating to the metal center through a negatively charged O atom to form a C,O-chelate complex. In preliminary studies for the copper-catalyzed enantioselective boron conjugate addition to an α,β-unsaturated ester, the *m*-terphenyl-based phosphate moiety caused a favorable ligand effect in comparison with a simple *N*-aryl substituent such as a mesityl group. Further investigation into the development of phosphate-based chiral NHC systems useful for enantioselective catalysis is currently ongoing.

4. Experimental

4.1. General

NMR spectra were recorded on a Varian Gemini 2000 spectrometer, operating at 300 MHz for ^{1}H NMR, 75.4 MHz for ^{13}C NMR, and 121.4 MHz for ^{31}P NMR. Chemical shift values for ^{1}H, ^{13}C, and ^{31}P NMR spectra are referenced to Me_4Si, the residual solvent, and 85% phosphoric acid, respectively. High-resolution mass spectra were recorded on a Thermo Fisher Scientific Exactive, JEOL JMS-T100LP mass spectrometer or JEOL JMS-T100 GC mass spectrometer at the Instrumental Analysis Division, Equipment Management Center, Creative Research Institution, Hokkaido University. HPLC analyses were conducted on a HITACHI ELITE LaChrom system with a HITACHI L-2455 diode array detector. Melting points were determined on a micro melting point apparatus (Yanaco: MP-500D) using micro cover glass. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F_{254}. Silica gel (Kanto Chemical Co., Silica gel 60N, spherical, neutral) was used for column chromatography.

All reactions were carried out under an argon or nitrogen atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted.

4.2. Preparation of imidazolinium zwitterion 2

4.2.1. Boronate 4

At first, *n*BuLi in hexane (1.6 M, 11.8 mL, 18.8 mmol, 1.1 equiv) was added dropwise to a 200-mL two-necked flask of 3-bromo-2,2′-dimethoxy-1,1′-biphenyl[8] **3** (5.01 g, 17.1 mmol, 1.0 equiv) in

THF (50 mL) at −78 °C and the mixture was stirred for 1 h at this temperature. 2-Isopropoxyboronic acid pinacol ester (3.8 mL, 18.8 mmol, 1.1 equiv) was then added at −78 °C and the mixture was allowed to warm to room temperature and stirred for 12 h. After quenching with aq NH_4Cl, the mixture was extracted with Et_2O. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel chromatography (30:1 to 10:1 hexane/EtOAc) to give **4** as a white solid (4.36 g, 75% yield). Mp: 119–121 °C. ^{1}H NMR ($CDCl_3$): δ 1.38 (s, 12H), 3.52 (s, 3H), 3.77 (s, 3H), 6.94–7.00 (m, 2H), 7.17 (t, J = 7.4 Hz, 1H), 7.33 (d, J = 7.4 Hz, 2H), 7.40 (dd, J = 7.7, 1.9 Hz, 1H), 7.76 (d, J = 7.5 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 24.76 (4C), 55.52, 61.86, 83.53 (2C), 110.83, 120.23, 123.09, 127.72, 128.67, 131.85, 131.98, 135.23, 136.20, 156.97, 163.46. A signal for the carbon directly attached to the boron atom was not observed. HRMS-ESI (*m/z*): $[M+Na]^+$ calcd for $C_{20}H_{25}Na^{10}BO_4$, 362.17744; found, 362.17737.

4.2.2. Bromide 5

Boronate **4** (4.01 g, 11.8 mmol, 1.0 equiv), $Pd(PPh_3)_4$ (409 mg, 0.354 mmol, 0.03 equiv), and K_3PO_4 (7.51 g, 35.4 mmol, 3.0 equiv) were placed in a 100-mL Schlenk flask and were dissolved in DMF (52 mL) at room temperature. 2-Bromo-iodobenzene (1.8 mL, 14.0 mmol, 1.2 equiv) was then added and the solution was stirred at 80 °C for 23 h. After cooling to room temperature, the reaction mixture was diluted with Et_2O and the organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel chromatography (50:1 to 10:1 hexane/EtOAc) to give **5** as a white solid (4.14 g, 95% yield). Mp: 104–105 °C. ^{1}H NMR ($CDCl_3$): δ 3.16 (s, 3H), 3.81 (s, 3H), 6.97–7.04 (m, 2H), 7.17–7.25 (m, 3H), 7.32–7.42 (m, 5H), 7.68 (d, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 55.56, 60.46, 110.96, 120.40, 122.87, 123.94, 126.98, 127.74, 128.77, 128.81, 130.52, 131.39, 131.67, 131.75, 132.18, 132.64, 134.54, 140.08, 155.61, 156.93. ESI-MS (*m/z*): $[M+H]^+$ 369.05. Anal. calcd for $C_{20}H_{17}BrO_2$, C 65.05, H 4.64; found: C 65.17, H 4.62.

4.2.3. Monoaryl diamine 6

At first, NaO*t*Bu (1.56 g, 16.4 mmol, 3.0 equiv) was placed in a 100-mL Schlenk flask and was dried under vacuum at 110 °C for 10 min. After cooling to room temperature, *rac*-BINAP (718 mg, 1.15 mmol, 0.2 equiv), $Pd(OAc)_2$ (122 mg, 0.54 mmol, 0.1 equiv), and toluene (47 mL) were added and the resulting dark red solution was stirred for 0.5 h at room temperature. Bromide **5** (2.00 g, 5.42 mmol, 1.0 equiv) and (1*S*,2*S*)-(−)-diphenylethylenediamine (1.73 g, 8.15 mmol, 1.5 equiv) were added to the solution and the mixture was stirred at 110 °C for 32 h. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 and the organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel chromatography (3:1 to 2:1 hexane/EtOAc) to give **6** as a light yellow solid (2.33 g, 86% yield). Title compound **6** exists as a mixture of atropisomers and the ratio (6:4) was determined by ^{1}H NMR analysis. Mp: 73–75 °C. ^{1}H NMR ($CDCl_3$): δ 1.32 (br s, 2H), 2.99 (s 1.2H), 3.31 (s, 1.8H), 3.82 (s, 3H), 4.20 (d, J = 4.7 Hz, 0.4H), 4.25 (d, J = 3.6 Hz, 0.6H), 4.43 (br s, 0.6H), 4.50 (br s, 0.4H), 5.13 (d, J = 5.8 Hz, 0.4H), 5.35 (d, J = 6.6 Hz, 0.6H), 6.19 (d, J = 8.0 Hz, 0.6 H), 6.30 (d, J = 8.3 Hz, 0.4 H), 6.61 (q, J = 7.2 Hz, 1H), 6.93–7.46 (m, 19H). ^{13}C NMR ($CDCl_3$): Due to the complexity of the spectra, signal assignment based on the atropisomerism is difficult and not shown here. δ 55.52, 60.31, 60.76, 61.19, 63.29, 63.82, 110.90, 111.08, 111.49, 115.95, 116.36, 120.32, 120.34, 123.57, 123.61, 124.73, 125.30, 126.92, 127.02, 127.09, 127.14, 128.02–128.74 (m), 130.26 130.54, 131.28, 131.32, 131.53, 131.78, 132.04, 132.22, 132.48, 132.55, 132.97, 141.37, 141.90, 142.59, 142.82, 144.40, 144.47, 156.15, 157.00. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{34}H_{33}N_2O_2$, 501.25365; found: 501.25302. $[\alpha]_D^{21} = -41.85$ (*c* 1.07, $CHCl_3$).

4.2.4. Diaryl diamine 7

At first, NaO*t*Bu (548 mg, 5.70 mmol, 3.0 equiv) was placed in a 100-mL Schlenk flask and then dried under vacuum at 110 °C for 10 min. After cooling to room temperature, *rac*-BINAP (238 mg, 0.382 mmol, 0.2 equiv), $Pd(dba)_2$ (110 mg, 0.191 mmol, 0.1 equiv), and toluene (12 mL) were added and the resulting dark red solution was stirred for 0.5 h at room temperature. The monoaryl diamine **6** (950 mg, 1.90 mmol, 1.0 equiv) and mesityl bromide (0.31 mL, 2.05 mmol, 1.1 equiv) were added to the solution and the mixture was stirred at 110 °C for 28 h. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 and the organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel chromatography (50:1 to 10:1 hexane/EtOAc) to give **7** as a light yellow solid (1.01 g, 86% yield). The title compound **7** existed as a mixture of atropisomers and the ratio (6:4) was determined by ^{1}H NMR analysis. Mp: 81–83 °C. ^{1}H NMR ($CDCl_3$): δ 1.78 (s, 3.6H), 1.79 (s, 2.4H), 2.10 (s, 1.2H), 2.11 (s, 1.8H), 3.15 (s, 1.2H), 3.25 (s, 1.8H), 3.50 (br, 1H), 3.65 (s, 1.8H), 3.79 (s, 1.2 H), 4.25 (br, 1H), 4.74–4.80 (m, 1H), 5.54 (d, J = 5.0 Hz, 0.4H), 5.64 (br s, 0.6H), 6.38–6.46 (m, 1H), 6.58 (s, 2H), 6.69–6.90 (m, 4H), 6.98–7.38 (m, 16H). ^{13}C NMR ($CDCl_3$): Due to the complexity of the spectra, signal assignment based on the atropisomerism is difficult and not shown here. δ 19.14, 20.73, 55.58, 55.78, 60.92, 61.01, 63.12, 63.33, 67.67, 67.75, 110.81, 111.13, 112.25, 112.35, 117.29, 117.38, 120.63, 124.02, 124.23, 126.47, 126.57, 127.47–129.55 (m), 130.76, 131.02, 131.93, 132.13, 132.79, 133.16, 133.24, 141.29, 141.42, 141.56, 141.63, 141.87, 142.10, 145.34, 145.77, 156.46, 156.66, 157.13, 157.38. ESI-MS (*m/z*): $[M+H]^+$ 619.33. Anal. calcd for $C_{43}H_{42}N_2O_2$, C 83.46, H 6.84, N 4.53; found, C 83.56, H 6.96, N 4.40. $[\alpha]_D^{24} = -89.2$ (*c* 1.01, $CHCl_3$).

4.2.5. Biphenol 8

Diaryl diamine **7** (1.00 g, 1.62 mmol) and CH_2Cl_2 (70 mL) were added to a 200-mL two-necked flask and the solution was cooled at 0 °C. Next, BBr_3 in CH_2Cl_2 (1.0 M, 9.7 mL, 9.7 mmol, 6 equiv) was added slowly and the solution was allowed to warm to room temperature and stirred for 14 h. After quenching with aq. $NaHCO_3$, the mixture was extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel chromatography (10:1 to 3:1 hexane/EtOAc) to give **8** as a light yellow solid (895 mg, 94% yield). Mp: 89–92 °C. ^{1}H NMR ($CDCl_3$): δ 1.75 (s, 6H), 2.10 (s, 3H), 4.16 (d, J = 9.6 Hz, 1H), 4.73 (d, J = 9.6 Hz, 1H), 6.56 (s, 2H), 6.82–6.89 (m, 2H), 6.90–7.41 (m, 19H). Signals for the four protons (N*H* and O*H*) were not observed. ^{13}C NMR ($CDCl_3$): Due to the complexity of the spectra, the signals are not fully assigned. δ 18.60, 20.28, 63.21, 67.17, 114.40, 118.05, 118.36, 119.08, 120.81, 121.06, 121.79, 122.48, 127.12–129.74 (m), 131.20–132.97 (m), 134.55, 139.87 (br), 143.97 (br), 149.94, 154.38 (br), 162.09, 162.93. ESI-MS (*m/z*): $[M+H]^+$ 591.29. Anal. calcd for $C_{41}H_{38}N_2O_2$, C 83.36, H 6.48, N 4.74; found: C 83.07, H 6.59, N 4.60. $[\alpha]_D^{24} = -1.70$ (*c* 1.01 $CHCl_3$).

4.2.6. Phosphate 9

Biphenol **8** (900 mg, 1.52 mmol) and CH_2Cl_2 (20 mL) were added to a 50-mL two-necked flask and the solution was cooled at 0 °C. Next, methyl phosphorodichloridate (249 mg, 1.67 mmol, 1.1 equiv) was added slowly and the solution was allowed to warm to room temperature and stirred for 13 h. After quenching with aq. $NaHCO_3$, the mixture was extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel chroma-

tography (15:1 to 5:1 hexane/EtOAc) to give diastereomeric phosphates **9a** (eluted first, 385 mg, 38%) and **9b** (eluted later, 335 mg, 33%). Each diastereomer **9** (a light yellow solid) existed as a mixture of atropisomers. The ratios (**9a**, 9:1; **9b**, 7:3) were determined by ^{1}H NMR analysis. **9a**: Mp: 115–118 °C. ^{1}H NMR ($CDCl_3$): δ 1.43 (s, 5.4H), 1.77 (s, 0.6H), 2.11 (s, 0.3H), 2.13 (s, 2.7H), 3.22 (br d, J = 12.1 Hz, 1H), 3.31 (d. J = 11.8 Hz, 0.3H), 3.48 (d, J = 11.8 Hz, 2.7H), 3.75 (t, J = 10.9 Hz, 1H), 4.60 (d, J = 9.6 Hz, 1H), 6.23 (s, 1H), 6.32 (d, J = 8.0 Hz, 1H), 6.43 (s, 2H), 6.56 (t, J = 7.2 Hz, 1H), 6.76 (t, J = 7.4 Hz, 1H), 6.85–6.92 (m, 3H), 6.97–7.60 (m, 15H). ^{13}C NMR ($CDCl_3$): Due to the complexity of the spectra, signal assignment based on the atropisomerism and C–P couplings is difficult and not shown here. δ 18.62, 20.22, 55.08, 55.28, 60.41, 60.50, 62.61, 62.81, 67.15, 67.21, 110.29, 110.62, 111.74, 111.83, 116.77, 116.85, 120.13, 123.50, 123.71, 125.95, 126.05, 126.96–129.03 (m), 129.52, 130.51, 131.28, 131.42, 131.62, 132.27, 132.62, 132.73, 140.77, 140.91, 141.05, 141.12, 141.36, 141.57, 144.83, 145.24, 155.96, 156.62, 156.87. ^{31}P NMR ($CDCl_3$): δ 3.72 (minor), 3.13 (major). ESI-MS (m/z): $[M+H]^+$ 667.27. Anal. $C_{42}H_{39}N_2O_4P$, C 75.66, H 5.90, N 4.20; found, C 75.55, H 6.17, N 4.05. $[\alpha]_D^{25} = -105.8$ (c 1.01, $CHCl_3$). **9b**: Mp: 212–213 °C. ^{1}H NMR ($CDCl_3$): δ 1.65 (s, 3H), 1.72 (s, 3H), 2.10 (s, 3H), 3.14 (d, J = 11.6 Hz, 3H), 3.68 (d, J = 11.6 Hz, 1H), 4.10 (br, 1H), 4.63 (br d, J = 8.2 Hz, 0.3H), 4.70 (dd, J = 8.8, 3.0 Hz, 0.7H), 5.47 (d, J = 2.8 Hz, 0.7H), 5.54 (br s, 0.3H), 6.36–6.42 (m, 1H), 6.49 (s, 0.6H), 6.52 (s, 1.4H), 6.69–6.82 (m, 3H), 6.97–7.63 (m, 17H). ^{13}C NMR ($CDCl_3$): Due to the complexity of the spectra, signal assignment based on the atropisomerism and C–P couplings is difficult and not shown here. δ 18.37, 18.61, 20.27, 20.29, 54.58, 54.64, 55.08, 55.14, 62.30, 63.27, 67.26, 67.31, 112.12, 112.29, 116.54, 117.56, 120.98, 121.03, 122.01, 122.06, 122.71, 123.63, 126.49–132.89 (m), 140.34, 140.37, 140.65, 140.68, 141.01, 141.60, 145.02, 145.38, 145.75, 145.90, 146.04, 146.08, 147.27, 147.37, 147.58. ^{31}P NMR ($CDCl_3$): δ 4.00 (major), 3.35 (minor). ESI-MS (m/z): $[M+H]^+$ 667.27. Anal. calcd for $C_{42}H_{39}N_2O_4P$, C 75.66, H 5.90, N 4.20; found: C 75.22, H 5.82, N 4.19. $[\alpha]_D^{25} = -2.05$ (c 1.01, $CHCl_3$).

4.2.7. Imidazolinium zwitterion 2

Phosphate **9** (a mixture of **9a** and **9b**, 300 mg, 0.45 mmol), $CH(OEt)_3$ (3.0 mL, 18 mmol, 40 equiv), and NH_4BF_4 (52.0 mg, 0.50 mmol, 1.1 equiv) were placed in a 10-mL Schlenk flask. The mixture was stirred at 110 °C for 10 h. After cooling to room temperature, the volatiles were removed under vacuum. The residue was passed through a short pad of silica gel to give **10** containing impurities. The mixture was placed in a 10-mL Schlenk flask and dissolved in THF (1.0 mL). Next, PhSH (0.042 mL, 0.41 mmol, 0.90 equiv) and Et_3N (0.069 mL, 0.45 mmol, 1.0 equiv) were added and the resulting mixture was stirred at room temperature for 13 h. After quenching with H_2O, the mixture was extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel chromatography ($CHCl_3$ then 10:1 $CHCl_3$/MeOH). Next, the material was dissolved in CH_2Cl_2 (10 mL) and satd K_2CO_3 aq (10 mL) was added. The resulting mixture was stirred vigorously at room temperature for 0.5 h. The mixture was then extracted with CH_2Cl_2 and the organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated to give **2** as a light yellow solid (106.9 mg, 33% yield in three steps). The title compound **2** existed as a mixture of atropisomers and the ratio (9:1) was determined by ^{1}H NMR analysis. Mp: >250 °C. ^{1}H NMR ($CDCl_3$): δ 1.15 (s, 3H), 2.10 (s, 3H), 2.48 (s, 3H), 5.27 (d, J = 13.5 Hz, 0.2H), 5.52 (q, J = 9.4 Hz, 1.8H), 6.23 (s, 0.1H), 6.50 (s, 0.9H), 6.67 (s, 0.1H), 6.79 (s, 0.9H), 6.81 (d, J = 7.9 Hz, 1H), 6.98 (d, J = 7.1 Hz, 2H), 7.11–7.64 (m, 17H), 7.77 (dd, J = 7.4, 1.6 Hz, 0.9H), 7.94 (d, J = 8.2 Hz, 0.1 H), 10.22 (s, 0.1H), 10.54 (s, 0.9H). ^{13}C NMR ($CDCl_3$): Due to the complexity of the spectra, signal assignment based on the atropisomerism and C–P couplings is difficult and not shown here. δ 16.44, 16.90, 17.07, 18.99, 20.65, 20.71, 70.17, 74.38, 74.97, 75.24, 122.73, 122.78, 123.85, 124.09, 125.06, 128.10–131.35 (m), 132.41–134.03 (m), 134.15, 135.24, 136.09, 136.97, 138.34, 138.78, 139.70, 148.84, 148.96, 149.14, 149.25, 151.36, 151.48, 151.62, 151.74, 161.04, 160.08, 161.50. ^{31}P NMR ($CDCl_3$): δ 5.94 (minor), 5.29 (major). HRMS-ESI (m/z): $[M+Na]^+$ calcd for $C_{42}H_{35}N_2NaO_4P$, 685.22267; found, 685.22205. $[\alpha]_D^{25} = +19.55$ (c 1.00, $CHCl_3$).

4.2.8. Imidazolinium salt 11

Diaryl diamine **7** (50.3 mg, 0.081 mmol), $CH(OEt)_3$ (0.54 mL, 3.23 mmol 40 equiv), and NH_4BF_4 (9.5 mg, 0.090 mmol 1.1 equiv) were placed in a 10-mL Schlenk flask. The mixture was stirred at 110 °C for 10 h. After cooling to room temperature, the volatiles were removed under vacuum. The residue was purified by silica gel chromatography ($CHCl_3$ then 20:1 $CHCl_3$/MeOH) to give **11** as a white solid (52.7 mg, 96% yield). The title compound **11** existed as a mixture of atropisomers and the ratio (55:45) was determined by ^{1}H NMR analysis. Mp: 139–143 °C. ^{1}H NMR ($CDCl_3$): δ 1.54 (s, 1.35H), 1.76 (s, 1.65H), 2.16 (s, 1.35H), 2.19 (s, 1.65H), 2.33 (s, 1.65H), 2.57 (s, 1.35H), 3.17 (s, 1.35H), 3.21 (s, 1.65H), 3.27 (s, 1.35H), 3.74 (s, 1.65H), 5.39–5.48 (m, 1.45H), 6.17 (d, J = 10.2 Hz, 0.55H), 6.60–6.67 (m, 2H), 6.83–7.62 (m, 20H), 7.78 (d, J = 8.1 Hz, 0.55H), 7.93 (d, J = 8.2 Hz, 0.45H), 8.54 (s, 0.55H), 8.59 (s, 0.45H). ^{13}C NMR ($CDCl_3$): Due to the complexity of the spectra, signal assignment based on the atropisomerism is difficult and not shown here. δ 17.81, 18.24, 18.64, 20.73, 54.75, 55.10, 60.97, 61.03, 72.31, 72.62, 75.13, 75.26, 110.72, 110.89, 120.08, 120.53, 124.22, 124.67, 126.63, 126.71, 128.00, 128.57–130.63 (m), 131.08, 131.18, 131.21, 131.53, 131.88, 131.98, 132.07, 132.32, 132.64, 133.27, 133.29, 133.44, 133.65, 134.46, 134.81, 134.91, 134.99, 135.20, 135.79, 135.85, 136.07, 140.04, 140.24, 155.64, 155.73, 156.72, 156.75, 157.14, 157.90. HRMS-ESI (m/z): $[M-BF_4]^+$ calcd for $C_{44}H_{41}N_2O_2$, 629.31626; found: 629.31556. $[\alpha]_D^{25} = -227.0$ (c 1.02, $CHCl_3$).

4.3. Preparation of [Rh(1a)(cod)]$_2$ (Scheme 2)

At first, $[RhCl(cod)]_2$ (11.2 mg, 0.023 mmol, 1.0 equiv) and KO*t*Bu (5.1 mg, 0.045 mmol, 2.0 equiv) were placed in a 5-mL test tube with a screw cap. Next, THF (0.6 mL) was added to the vessel and the mixture was stirred at room temperature for 1 h. Imidazolium salt **2** (30.0 mg, 0.045 mmol, 2.0 equiv) in THF (0.4 mL) was then added and the mixture was stirred at room temperature for 2 h. The volatiles were removed under vacuum, and the residue was purified by preparative TLC (10:1 $CHCl_3$/MeOH) to give [Rh(**1a**)(cod)]$_2$ as a yellow solid (25.4 mg, 64%). Mp: 210–215 °C (decomp). ^{1}H NMR ($CDCl_3$): δ 1.39–1.62 (m, 7H), 1.71–1.84 (m, 3H), 1.89 (s, 6H), 1.93–2.13 (m, 4H), 2.16 (s, 6H), 2.23 (s, 6H), 2.28–2.63 (m, 2H), 2.63 (br, 2H), 3.49 (br, 2H), 4.61 (d, J = 5.2 Hz, 2H), 4.82 (br, 2H), 4.99 (br, 2H), 5.75 (d, J = 7.1 Hz, 2H), 6.36 (d, J = 7.1 Hz, 4H), 6.70–6.85 (m, 8H), 7.05 (t, J = 7.6 Hz, 2H), 7.17–7.50 (m, 26H), 7.62 (dd, J = 7.4, 1.6 Hz, 2H), 7.74 (dd, J = 7.4, 1.6 Hz, 2H), 8.06 (d, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): Due to the complexity of the spectra, signal assignment based on C–P couplings is difficult and not shown here. δ 19.18, 19.25, 20.75, 27.38, 27.50, 32.18, 32.45, 63.30, 63.53, 66.15, 66.37, 75.19, 98.09, 98.18, 98.76, 98.86, 122.54, 122.59, 123.95, 124.53, 127.07, 127.57, 127.76, 128.50–128.70 (m), 129.27–130.26 (m), 131.82, 132.58, 132.99, 133.02, 134.58, 134.69, 136.32, 137.81, 138.13, 138.96, 139.09, 139.93, 148.81, 148.94, 150.81, 150.92, 211.38, 212.01. ^{31}P NMR ($CDCl_3$): δ 5.74 (d, $^2J_{P\text{-}Rh}$ = 8.9 Hz). ESI-MS (m/z): $[M+H]^+$ 1745.44, [M-Rh-**1a**-cod+H]$^+$ 873.22. $[\alpha]_D^{25} = -50.3$ (c 1.02, $CHCl_3$).

4.4. Typical procedures for the catalytic reactions

Methyl cinnamate **12** (0.20 mmol) and bis(pinacolato)diboron **13** (0.22 mmol) were placed in a vial containing a magnetic stirrer bar, and the vial was sealed with a Teflon®-coated silicon rubber septum. Next, THF (0.80 mL) and MeOH (0.40 mmol) were added to the vial, and the mixture was cooled at −55 °C. A Cu salt (0.0060 mmol), an imidazolinium salt (0.012 mmol), and KO*t*Bu (0.060 mmol) were then placed in another vial with a Teflon®-coated silicon rubber septum. After THF (0.20 mL) was added to the vial, the mixture was stirred at 25 °C for 15 min. Next, the Cu–NHC complex solution was transferred to the vial containing **12** and **13** at −55 °C. After 24 h stirring at −55 °C, the reaction mixture was filtered through silica gel and washed with Et_2O. The filtrate was concentrated under vacuum and the residue was purified by silica gel column chromatography (20:1 hexane/EtOAc) to afford the desired product **14**. ^{1}H NMR ($CDCl_3$): δ 1.17 (s, 6H), 1.22 (s, 6H), 2.63–2.76 (m, 2H), 2.86–2.94 (m, 1H), 3.65 (s, 3H), 7.13–7.29 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 24.34 (2C), 24.43 (2C), 28.20 (br), 37.00, 51.49, 83.54 (2C), 125.76, 128.23 (2C), 128.56 (2C), 141.37, 173.97. $[\alpha]_D^{24} = -17.5$ (*c* 1.01, $CHCl_3$). The ee value was determined by chiral HPLC analysis [CHIRALCEL® OJ-H column, 4.6 mm × 250 mm, Daicel Chemical Industries, hexane/2-propanol = 97:3, 0.50 mL/min, 40 °C, 220 nm UV detector, retention time = 10.60 min for the (*R*)-isomer and 11.86 min for the (*S*)-isomer]. The absolute configuration of **14** was assigned according to the literature.[10h]

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