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Enantioselective synthesis of chiral 1,2-diamines by the catalytic ring opening of azabenzonorbornadienes: application in the preparation of new chiral ligands

Yong-Hwan Cho, Aude Fayol and Mark Lautens*

Davenport Laboratories, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5H 3H6

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Abstract—In the presence of a rhodium catalyst (5 mol %) generated in situ from $[Rh(cod)Cl]_2$ and (*S*,*S*′)-(*R*,*R*′)-C_2-ferriphos-tolyl, the asymmetric ring-opening reaction of *N*-Boc-azabenzonorbornadienes with dibenzylamine proceeded with excellent enantioselectivity (up to >99% ee) to give the corresponding 1,2-diamine scaffolds in high yields. The sequential deprotection of the ring-opened products and treatment with tartaric acid gave the enantiomerically pure 1,2-diamine tartrate salts. These salts were used for the preparation of new chiral ligands such as the salen-type ligands and Trost-type ligands.

1. Introduction

Chiral vicinal 1,2-diamines have been found to be an important subunit in a large number of bioactive natural products, such as biotin[1] (vitamin H) and several peptidic antibiotics.[2] This functionality can also be found in important medicinal compounds such as 1,2-diaminoplatinum(II) complexes.[3]

In addition, 1,2-diamines have found extensive use as chiral auxiliaries for a variety of asymmetric reactions and scaffolds for the synthesis of chiral ligands,[4] such as the salen-type[5] and Trost-type ligands.[6] These applications are brought about considerable attention for their preparation and the development of synthetic methods which can realize high diastereoselectivity and enantioselectivity in the synthesis of vicinal 1,2-diamines.[7] There are many methods for the synthesis of chiral 1,2-diamines using stoichiometric amounts of chiral auxiliaries, however, a catalytic process giving enantiomerically enriched 1,2-diamines from achiral substrates using transition metal catalysts still remains to be developed.

Herein we report the asymmetric synthesis of enantiomerically pure 1,2-diamine scaffolds by using rhodium-catalyzed ring-opening reactions of azabenzonorbornadienes with dibenzylamine. Also described is the preparation of new chiral ligands from the 1,2-diamine scaffolds thus obtained.

2. Results and discussion

For the catalytic asymmetric synthesis of 1,2-diamine scaffolds starting from *N*-Boc protected azabenzonorbornadienes, four azabenzonorbornadienes **1a–d** were prepared and reacted (Scheme 1). Since the deprotection of the Boc group is easier than others and high-yielding, *N*-Boc-azabenzonorbornadienes **1** are more versatile substrates to find efficient conditions for ring-opening than others. *N*-Boc-azabenzonorbornadiene **1a** and 5,8-dimethyl product **1b** were prepared by Diels–Alder reaction of *N*-Boc-pyrrole with arynes generated in situ by diazotization of the corresponding anthranilic acids[8] with isoamyl nitrite followed by heating in 55% yield and 30% yield, respectively. Also, the Diels–Alder reaction of *N*-Boc-pyrrole with arynes generated by treatment of 1,2-dibromotetramethylbenzene[9] and 1,2-dibromo-4,5-di-methylbenzene[10] with *n*-butyllithium[11] gave 5,6,7,8-tetramethyl product **1c** and 6,7-dimethyl product **1d** in 36% yield and 33% yield, respectively.

With a range of azabenzonorbornadiene starting materials in hand, we proceeded to study the synthesis of chiral

* Corresponding author. Tel.: +1 416 978 6083; fax: +1 416 946 8185; e-mail: mlautens@chem.utoronto.ca

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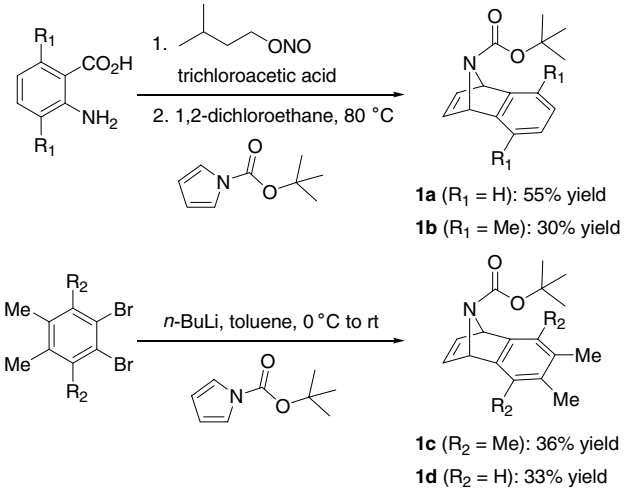


Scheme 1. Synthesis of *N*-Boc-azabenzonorbornadienes **1a**–**d**.

1,2-diamine scaffolds using the catalytic asymmetric ring-opening with several primary and secondary amines. Amines with removable functional groups were selected to enable the synthesis of free primary diamines as the final products. For these studies, we started by using conditions previously reported by our group utilizing rhodium catalysts and ferrocenyl phosphine ligands for the ring opening of azabicyclic alkenes with amine nucleophiles.[12] Among those amines, *N*,*N*-dibenzylamine was found to be effective for the present reaction. The reaction of **1a** with primary amines, such as benzylamine and 4-methoxy-benzylamine, used successfully for the asymmetric ring-opening reaction of oxabenzonorbornadiene, did not give the desired ring-opening product under the same conditions.[13] However, in the presence of 2.5 mol % of $[Rh(cod)Cl]_2$ and 10 mol % of (*S*,*S*′)-(*R*,*R*′)-C_2-ferriphos **3a**,[14] the reaction of **1a** with *N*,*N*-dibenzylamine (5.0 equiv) at 110 °C for 24 h gave the corresponding ring-opening product **2a** in 80% yield. The enantiomeric purity of **2a** was determined to be 89% ee by HPLC analysis with a chiral stationary phase column (Chiralcel OD). The absolute configuration was determined to be 1*S*,2*S* by X-ray analysis of 1,2,3,4-tetrahydronaphthyl-1,2-diamine tartrate salt prepared from **2a** (see Fig. 1).

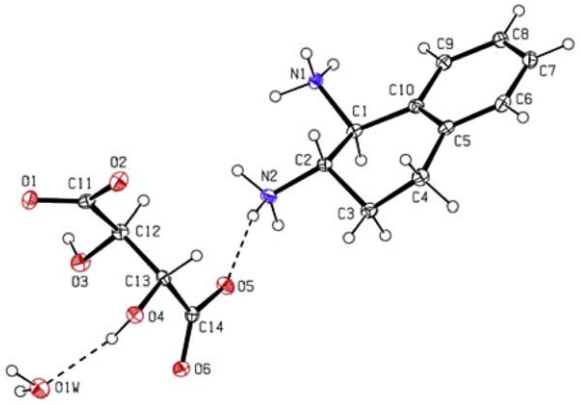
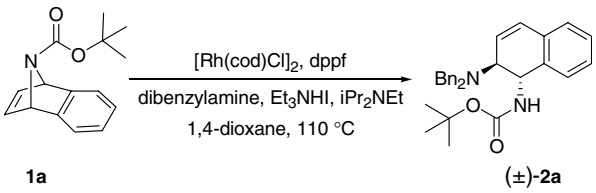


Figure 1. Crystal structure of **5a**.

However, this reaction requires relatively high catalytic loading and excess amount of amine nucleophile. Therefore, it was necessary to develop new conditions for a large scale synthesis. We were fortunate to find that the use of a catalytic amount (20 mol %) of triethylammonium hydroiodide (Et_3NHI) and *N*,*N*-diisopropylethylamine (*i*-Pr_2NEt) as a base showed a dramatic improvement in reducing the catalyst loading and amount of nucleophile in the present reaction (Scheme 2, Table 1). It was found that the combined use of protic and halide additives effectively alleviate the poisoning of a catalyst by amines which are known to bind strongly to the metal center.[15] Whereas the reaction of **1a** with dibenzylamine gave 58% yield of **2a** in the presence of 2.5 mol % of $[Rh(cod)Cl]_2$ (Table 1, entry 1), the reaction using Et_3NHI and *i*-Pr_2NEt proceeded with a lower catalytic loading (1.0 mol % of $[Rh(cod)Cl]_2$) to give 86% yield of **2a** (entry 3).



Scheme 2. Catalytic ring opening of *N*-Boc-azabenzonorbornadiene **1a** with dibenzylamine in the presence of Et_3NHI.

Table 1. Catalytic ring opening of **1a** with dibenzylamine in the presence of triethylammonium iodide[a]

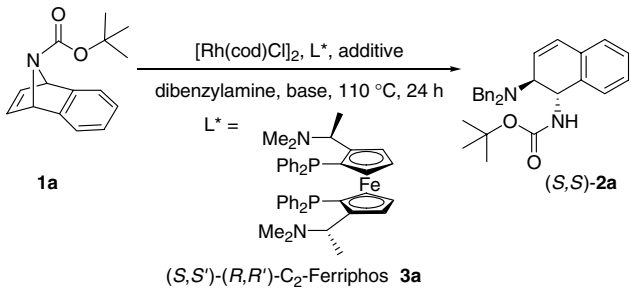
Entry	$[Rh(cod)Cl]_2$ (mol %)	Et_3NHI (mol %)	Concd. (M)	Base	Time (h)	Yield[b] (%)
1[c]	2.5	—	Neat	—	48	58
2	1.0	20	0.2	—	48	n.d.
3	1.0	20	0.2	*i*-Pr_2NEt	48	86
4	1.0	20	0.4	*i*-Pr_2NEt	24	90
5	0.5	10	0.4	*i*-Pr_2NEt	24	84
6	0.1	2	0.4	*i*-Pr_2NEt	60	38[d]
7	0.1	2	2.0	*i*-Pr_2NEt	60	25[e]

[a] The reaction was carried out with **1a** (0.25 mmol), dibenzylamine (1.1 equiv), Et_3NHI, and *i*-Pr_2NEt (1.1 equiv) in 1,4-dioxane at 110 °C in the presence of $[Rh(cod)Cl]_2$ and dppf (1.5 equiv to Rh).
[b] Isolated yield after silica gel column chromatography.
[c] The reaction was carried out with 5.0 equiv of dibenzylamine without additive and solvent.
[d] 55% of **1a** was recovered.
[e] 70% of **1a** was recovered.

The addition of an iodide source led to an increase in reactivity, which follows the halide effect trends (i.e., iodide more reactive than chloride) which have been observed in the rhodium-catalyzed asymmetric ring opening of oxabicyclic alkenes.[15,16] While the use of Et_3NHI in the catalytic ring opening gave the best result, the use of triethylamine hydrochloride (Et_3NHCl), which has been found to be an effective additive in the ring-opening reactions of oxabenzonorbornadiene and azabenzonorbornadiene, gave only 30% yield under the same conditions.

It is most likely that the halide exchange between $[Rh(cod)Cl]_2$ and Et_3NHI generates the more stable rhodium iodide bridged dimer. The proposed catalytic pathway for the ring opening of azabenzonorbornadienes closely follows that put forward regarding oxabicyclic alkenes[17] and dimeric catalyst precursors are implicated in the reaction pathway. Since it is believed that the amine-induced cleavage of the dimeric rhodium complex leads to catalyst poisoning,[18] increasing the stability of the dimeric complex toward the catalyst poisoning could improve the catalyst activity.[19] Also, the use of *i*-Pr_2NEt is required to ensure high conversion. Without *i*-Pr_2NEt, the reaction did not proceed with Et_3NHI only (entry 2). Increasing the concentration from 0.2 to 0.4 M reduced the reaction time, with the reaction for 24 h giving 90% yield (entries 3 and 4). The reaction with only 0.5 mol % of $[Rh(cod)Cl]_2$ gave good results (entry 5), but the use of 0.1 mol % of $[Rh(cod)Cl]_2$ gave an incomplete reaction (entry 6), even when using higher concentration (2.0 M) (entry 7).

The optimized conditions found for the catalytic ring opening of **1a** with dibenzylamine (1.1 equiv) (Table 1, entry 4) were applied to the catalytic asymmetric ring opening of **1a** in the presence of $[Rh(cod)Cl]_2$ and (*S*,*S*′)-(*R*,*R*′)-C_2-ferriphos **3a** with the results are summarized in Table 2 (Scheme 3). Using a rhodium catalyst generated from 1.0 mol % of $[Rh(cod)Cl]_2$ and 3.0 mol % of ligand **3a**, the reaction with Et_3NHI and *i*-Pr_2NEt in 1,4-dioxane gave 25% yield of **2a** with 22% ee (entry 1). Considering that the reaction conditions using Et_3NHI and *i*-Pr_2NEt gave 90% yield of **2a** in the reaction of **1a** using dppf as a ligand, this low reactivity is rather surprising.



Scheme 3. Catalytic asymmetric ring opening of **1a** with dibenzylamine.

Our experiments indicate that the trends of the halide effect in the asymmetric ring opening of **1a** are strongly dependent on the nature of phosphine ligands; in fact, both reactivity and enantioselectivity show different trends in different systems with respect to the halide. For example, while the halide effect observed in the asymmetric ring-opening reaction of oxabenzonorbornadiene using PPF-P(*t*-Bu)$_2$ as a chiral ligand showed that the reactivity and the enantioselectivity increased (Cl < Br < I) in the presence of Bu_4NX, the reaction using BPPFA resulted in an inverse trend of the halide effect with respect to the enantioselectivity.[15] These results show that the halide and phosphine ligand work at the rhodium metal together to influence the reactivity and enantioselectivity. The use of Et_3NHCl, instead of Et_3NHI, was also tested and gave 83% ee, but the yield was still very low (entry 2). The increase of the catalytic loading from 1.0 mol % of $[Rh(cod)Cl]_2$ to 2.5 mol % gave reasonable yield and higher enantioselectivity (entry 5). Also, it was found that there are no positive effects of Et_3NHCl (entry 3 vs entry 4) and *i*- Pr_2NEt (entry 5 vs entry 6) on the asymmetric reaction. The use of 5.0 equiv of dibenzylamine is required to shorten the reaction time for complete conversion. In the case of the reaction using 10 equiv of amine, a slightly lower enantioselectivity was observed (83% ee) under the same conditions. It was found that the enantiomeric purity of **2a** is dependent on the amount of **3a** in the reaction (Table 3). The use of 1.5 equiv of **3a** to rhodium (7.5 mol %) in the ring-opening reaction gave 78% ee (Table 3, entry 1), whereas the use of 2.0 equiv

Table 2. Catalytic asymmetric ring opening of *N*-Boc-azabenzonorbornadiene **1a** with dibenzylamine[a]

Entry	Additive (mol %)	Dibenzylamine (equiv)	Base (equiv)	Yield[b] (%)	% ee[c]
1[d]	Et_3NHI (20)	1.2	*i*-Pr_2NEt (1.2)	25	22[f]
2[d]	Et_3NHCl (20)	1.2	*i*-Pr_2NEt (1.2)	30	83
3	Et_3NHCl (20)	2.5	*i*-Pr_2NEt (2.5)	52	77
4	—	2.5	*i*-Pr_2NEt (2.5)	61	78
5[e]	—	5.0	*i*-Pr_2NEt (5.0)	81	82
6[e]	—	5.0	—	83	89

[a] The reaction was carried out with **1a** (0.25 mmol), dibenzylamine, additive, and base at 110 °C for 24 h in the presence of 1.0 mol % of $[Rh(cod)Cl]_2$ and 4.0 mol % of ligand **3a** (2.0 equiv to Rh).
[b] Isolated yield after silica gel column chromatography.
[c] Determined by HPLC analysis of the ring-opened product **2a** with chiral stationary column (Chiralcel OD).
[d] The reaction was performed with 1,4-dioxane (1.0 M).
[e] The reaction was carried out in the presence of 2.5 mol % of $[Rh(cod)Cl]_2$ and 10.0 mol % of ligand **3a**.
[f] 22% ee of (*R*,*R*)-**2a** was obtained.

Table 3. Study of chiral ligands and temperature on the asymmetric ring opening of **1a** with dibenzylamine[a]

Entry	Ligand (equiv to Rh)	Temperature (°C)	Time (h)	Yield[b] (%)	% ee[c]
1	**3a** (1.5)	110	24	84	78
2	**3a** (2.0)	110	24	83	89
3	**3a** (2.2)	110	24	85	92
4	**3a** (3.0)	110	24	80	92
5	**3b** (2.2)	110	24	97	95
6	**3c** (2.2)	110	24	81	81
7	**3b** (2.2)	80	48	98	97
8	**3b** (2.2)	60	72	38[d]	97

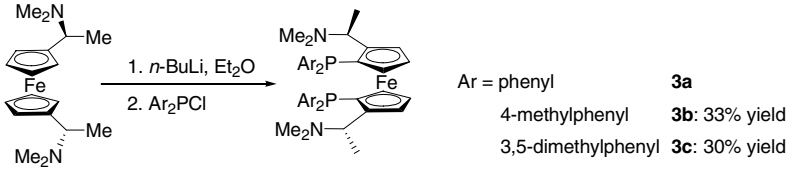
[a] The reaction was carried out with **1a** (0.25 mmol) and 5.0 equiv of dibenzylamine (1.25 mmol) in the presence of 2.5 mol % of $[Rh(cod)Cl]_2$ and chiral ligand.
[b] Isolated yield after silica gel column chromatography.
[c] Determined by HPLC analysis of the ring-opened product **2a** with chiral stationary column (Chiralcel OD).
[d] 61% of **1a** was recovered.

(10 mol %) gave 89% ee (entry 2). Higher enantioselectivity was observed in the reaction using 3.0 equiv of **3a** (15 mol %) which gave 92% ee (entry 4). Finally, the use of 2.2 equiv of **3a** (11 mol %) was found to be most effective (92% ee) for the present asymmetric reaction (entry 3).

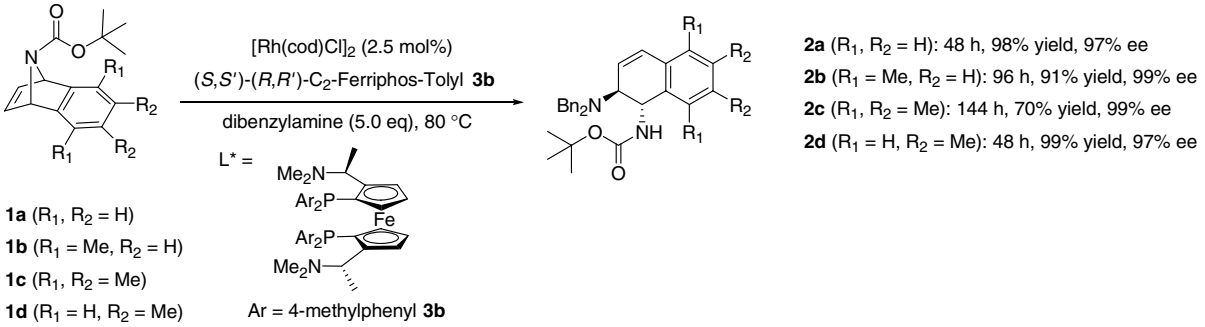
Chiral ligands **3b** and **3c** were obtained by lithiation of (*S*,*S*)-1,1′-bis(α-*N*,*N*-dimethylaminoethyl)ferrocene, whose preparation has been reported by Knochel,[14b] followed by the substitution of dilithium salts with the corresponding diarylchlorophosphines[20] (Scheme 4). Among those chiral ligands prepared here, (*S*,*S*′)-(*R*,*R*′)-C_2-ferriphos-tolyl **3b** showed the best result (entry 5). In the presence of 2.5 mol % of $[Rh(cod)Cl]_2$ and 11 mol % of (*S*,*S*′)-(*R*,*R*′)-**3b**, the reaction at 110 °C for 24 h gave 98% yield of **2a** in 95% ee, whereas the use of C_2-ferriphos-xylyl **3c** gave only 81% ee (entry 6). The best results were obtained by decreasing the reaction temperature. The ring-opening reaction proceeded at 80 °C for 48 h to give 98% yield of **2a** in 97% ee (entry 7). At 60 °C, the reaction gave 38% yield of **2a** with 97% ee while 61% of the starting material **1a** was recovered (entry 8).

These optimized reaction conditions gave excellent yields and enantioselectivities in the reactions with azabenzonorbornadienes **1a**–**d** (Scheme 5). In the presence of 2.5 mol % of $[Rh(cod)Cl]_2$ and 11 mol % of **3b**, the ring-opening reaction of **1a** with 5.0 equiv of dibenzylamine proceeded at 80 °C for 48 h to give 98% yield of the corresponding product **2a** with 97% ee. The asymmetric ring-opening reactions of **1b** and **1c** showed the highest enantioselectivity but lower reactivity while its completion needed a longer reaction time. The reaction of **1b** for 96 h gave 91% yield of **2b** with 99% ee. In the case of more bulky **1c**, the reaction needed 144 h until completion to give 70% yield of **2c** in 99% ee. The reaction of **1d** was completed within 48 h and gave 99% yield of **2d** in 97% ee.

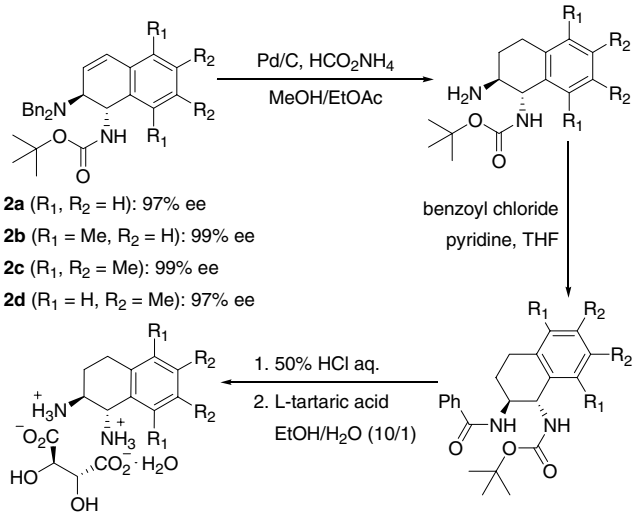
The optically active ring-opening products obtained here were used for the synthesis of the enantiomerically pure free 1,2-diamine scaffolds. The reactions starting



Scheme 4. Preparation of C_2-ferriphos-Ar ligands.



Scheme 5. Asymmetric ring opening of *N*-Boc-azabenzonorbornadienes **1a**–**d** with dibenzylamine under the optimized reaction conditions.

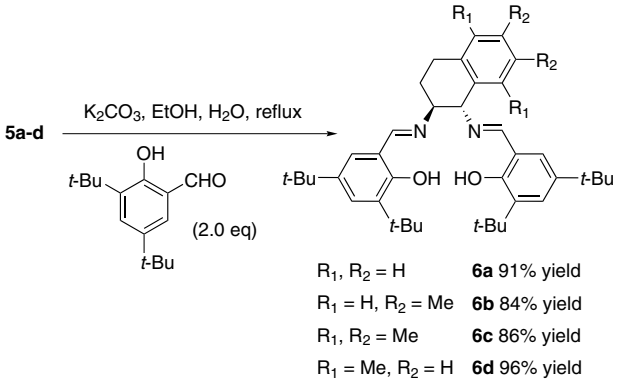


Scheme 6. Synthesis of 1,2-diamine scaffolds **5a**–**d**.

from (1*S*,2*S*)-**2a**–**d** are summarized in Scheme 6. The reduction of the double bond and debenzylation of the dibenzylamino group were carried out at the same time by catalytic hydrogenation of **2a**–**d** with ammonium formate in the presence of 30 mol % of Pd/C at 60 °C in methanol/ethyl acetate.[21] In order to facilitate the purification of these polar substrates, the resulting debenzylated products were converted into the corresponding benzoylamides **4a**–**d** by acylation with benzoyl chloride.

Recrystallization of **4a**–**d** from ethanol or 2-propanol gave the enantiomerically pure (>99% ee) products in 65–70% yield. Treatment of **4a**–**d** with 50% aq HCl at 100 °C for 48 h gave unstable free 1,2-diamines with the resulting 1,2-diamines immediately converted into the storable tartrate salts **5a**–**d**. The reaction of 1,2-diamino-1,2,3,4-tetrahydronaphthalenes with L-tartaric acid gave (*S*,*S*)-**5a**–**d**. The absolute configuration was determined to be 1*S*,2*S* by X-ray analysis of **5a** (Fig. 1).[22]

These bench-stable salts were used as synthetic intermediates for the preparation of new chiral ligands. The resulting tartrates **5a**–**d** were easily converted into



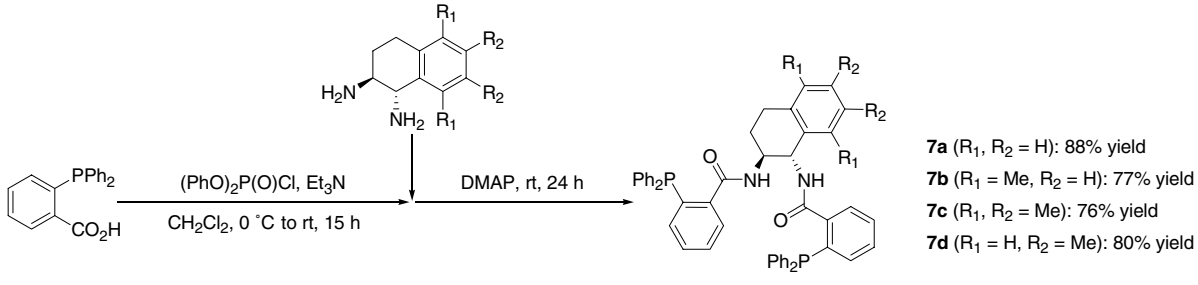
Scheme 7. Synthesis of salen-type ligands **5a**–**d**.

Jacobsen-type salen ligands **6a**–**d**.[23] In the presence of K_2CO_3, treatment of the (*S*,*S*)-diamine (*R*,*R*)-tartrates with 3,5-di-*tert*-butylsalicylaldehyde in ethanol/H_2O at 80 °C gave the corresponding salen products **6a**–**d** in 84–96% yield (Scheme 7).

The preparation of new Trost-type ligands from the 1,2-diamine derivatives obtained here was also attempted. For the successful amide bond formation, diphenylchlorophosphate was employed as the coupling reagent to activate the carboxylic acid.[6c] The method of amide bond formation promoted by DCC[6b] was examined for this reaction but did not give the desired product. After the reaction of 2-(diphenylphosphino)benzoic acid with triethylamine and diphenylchlorophosphate in CH_2Cl_2 at room temperature for 15 h, (1*S*,2*S*)-1,2-diaminotetrahydro-naphthalenes, obtained by treatment of (*S*,*S*)-diamine (*R*,*R*)-tartrates **5** with 4 M NaOH aq, were added in the mixture. The amide-forming reactions proceeded in the presence of DMAP for 24 h to give bisphosphine ligands **7a**–**d** (Scheme 8). An X-ray structure of the ligand **7a** is shown in Figure 2.[24]

3. Conclusion

In conclusion, we have developed new reaction conditions for the catalytic asymmetric ring-opening reaction of azabenzonorbornadienes **1a**–**d** with dibenzylamine, giving the optically active 1,2-diamine derivatives **2a**–**d** in high yields and excellent enantioselectivity (up to >99% ee). (*S*,*S*′)-(*R*,*R*′)-C_2-ferriphos-tolyl **3b** was found



Scheme 8. Synthesis of Trost-type ligands **7a**–**d**.

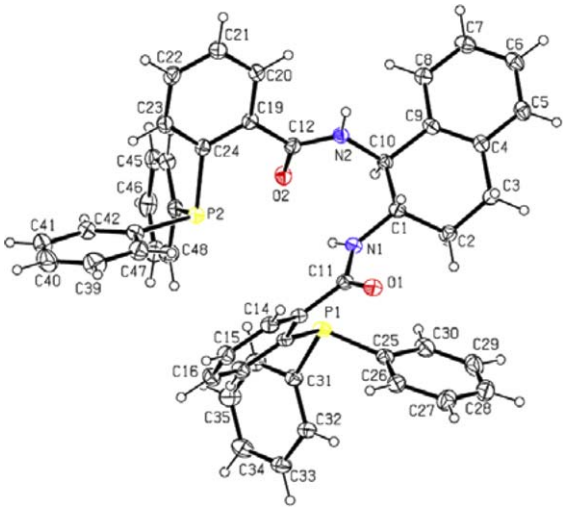


Figure 2. Crystal structure of **7a**. Solvent (CH_2Cl_2) is omitted for clarity.

to be the best enantioselective ligand. The sequential deprotection of the ring-opening products **2** and treatment with tartaric acid gave the enantiomerically pure 1,2-diamine salts **5** that are stable and easy to handle. These 1,2-amine derivatives were used for the preparation of new chiral ligands, such as the salen-type ligands **6** and Trost-type ligands **7**. Applications of these ligands in catalytic asymmetric synthesis are currently being investigated.

4. Experimental

All moisture and air-sensitive manipulations were carried out under a dried nitrogen atmosphere. NMR spectra were recorded on a Varian Mercury NMR spectrometer (300 MHz for ^{1}H, 75 MHz for ^{13}C, and 121 MHz for ^{31}P). Chemical shifts are reported in δ ppm referenced to $SiMe_4$ or DMSO-d_6 (2.50 ppm) as the internal standard for ^{1}H NMR, chloroform-*d* (δ 77.0) or DMSO-d_6 (39.52 ppm) for ^{13}C NMR, and an external 85% H_3PO_4 standard for ^{31}P NMR. IR spectra were obtained using a Perkin–Elmer Spectrum 1000 FT-IR spectrometer as a neat film on a NaCl plate. High resolution mass spectra were obtained from a Micromass 70S-250 mass spectrometer (EI) or an ABI/Sciex Qstar mass spectrometer (ESI). Optical rotations were measured on a Perkin–Elmer Model 243 Polarimeter and melting points were taken on a Fisher–Johns melting point apparatus. HPLC analysis was performed on an Agilent 1100 Series HPLC with Chiralcel OD or AD columns.

4.1. Preparation of azabenzonorbornadienes

4.1.1. *N*-Boc-Azabenzonorbornadienes, 1a. To a stirred solution of anthranilic acid (8.0 g, 58.3 mmol) and trichloroacetic acid (67 mg, 0.4 mmol) in dry THF (120 mL) was slowly added isoamyl nitrite (13 mL, 93.3 mmol) at 0 °C for 30 min and the mixture was stirred at room temperature for 1.5 h. The dark yellow precipitate of benzenediazonium-2-carboxylate was collected by filtration and washed with cold THF using minimal suction for draining so as to prevent complete drying. The salt was immediately transferred to a flask and 1,2-dichloroethane (100 mL) and *N*-*tert*-butyl pyrrole 1-carboxylate (7.8 mL, 46.7 mmol) were added. The mixture was heated at 60 °C for 45 min and the black mixture was cooled to room temperature. After concentration under reduced pressure, the residue was purified by flash column chromatography (hexane/ethyl acetate = 95/5) and recrystallization with hexane to give 7.8 g of *N*-Boc-azabicycle **1a** (55% yield). Mp 70–72 °C (lit.[25] mp 72–73 °C for **1a**); IR (NaCl, cm^{-1}) 2976, 2931, 1708, 1455, 1367, 1332, 1252, 1167, 1074, 857, 830, 782, 748, 694, 643. ^{1}H NMR ($CDCl_3$): δ 1.37 (s, 9H), 5.48 (br s, 2H), 6.94–6.98 (m, 4H), 7.22–7.29 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 155.3, 148.5, 143.1 (d, $J = 85.0$ Hz), 125.1, 121.0 (d, $J = 31.5$ Hz), 80.7, 66.7 (d, $J = 47.3$ Hz), 28.3.

4.1.2. 5,8-Dimethyl-*N*-Boc-azabenzonorbornadienes, 1b. To a stirred solution of 3,6-dimethylanthranilic acid[8] (14.0 g, 84.7 mmol) and trichloroacetic acid (0.2 g, 0.9 mmol) in dry THF (100 mL) was slowly added isoamyl nitrite (14 mL, 101.7 mmol) at −20 °C for 40 min by syringe pump under nitrogen atmosphere. The mixture was allowed to stir at −20 °C for another 2 h. Then, *N*-*tert*-butyl pyrrole 1-carboxylate (11 mL, 67.8 mmol) and 1,2-dichloroethane (100 mL) were added and the mixture heated immediately at 80 °C for 30 min. The resulting mixture was then cooled to room temperature and all volatile substrates removed under reduced pressure. The residue was purified by flash column chromatography (hexane/ethyl acetate = 95/5) and recrystallization with hexane to give 6.9 g (30% yield) of **1b**. Mp 95–97 °C; IR (NaCl, cm^{-1}) 2974, 1709, 1490, 1455, 1366, 1329, 1253, 1167, 1073. ^{1}H NMR ($CDCl_3$): δ 1.38 (s, 9H), 2.29 (s, 6H), 5.53–5.57 (m, 2H), 6.67 (s, 2H), 6.95–6.99 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 155.5, 146.3, 142.9 (d, $J = 97.9$ Hz), 127.9 (d, $J = 38.5$ Hz), 126.6, 80.6, 65.2 (d, $J = 42.9$ Hz), 28.3, 17.9. Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16. Found: C, 75.19; H, 7.71; N, 5.19.

4.1.3. 5,6,7,8-Tetramethyl-*N*-Boc-azabenzonorbornadienes, 1c. To a solution of 1,2-dibromotetramethylbenzene[9] (20.0 g, 68.5 mmol) prepared from commercially available 1,2,3,4-tetramethylbenzene according to previously reported procedure[10] in dry toluene (200 mL) was slowly added *n*-butyllithium solution in hexane (95 mL, 150.7 mmol) diluted with dry toluene (24 mL) and *N*-*tert*-butyl pyrrole 1-carboxylate solution in dry toluene (14 mL, 82.2 mmol in 110 mL of toluene) at 0 °C by syringe pump for 3 h under a nitrogen atmosphere. The mixture was allowed to stir at room temperature for 48 h and quenched with water. The resulting mixture was extracted with ethyl acetate and the organic phase dried over anhydrous $MgSO_4$. After removal of all volatile solvents under reduced pressure, flash column chromatography on silica gel (hexane/ethyl acetate = 95/5) and recrystallization with hexane gave 7.0 g (34% yield) of **1c**. Mp 125–127 °C; IR (NaCl, cm^{-1}) 2973, 1708, 1366, 1330, 1257, 1167, 1073. ^{1}H NMR ($CDCl_3$): δ

1.39 (s, 9H), 2.11 (s, 6H), 2.24 (s, 6H), 5.56–5.60 (m, 2H), 6.94–6.98 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 155.3, 143.5, 143.1 (d, $J = 101.6$ Hz), 131.6, 127.2 (d, $J = 40.1$ Hz), 80.5, 65.8 (d, $J = 46.1$ Hz), 28.4, 16.5, 16.0. Anal. Calcd for $C_{19}H_{25}NO_2$: C, 76.32; H, 8.42; N, 4.68. Found: C, 76.71; H, 8.59; N, 4.65.

4.1.4. 6,7-Dimethyl-*N*-Boc-azabenzonorbornadienes, 1d. Prepared from 1,2-dibromo-4,5-dimethylbenzene[10] in a similar manner to **1a** in 35% yield. Mp 93–95 °C; IR (NaCl, cm^{-1}) 2974, 1706, 1593, 1455, 1366, 1328, 1251, 1167, 1071. ^{1}H NMR ($CDCl_3$): δ 1.38 (s, 9H), 2.17 (s, 6H), 5.42 (m, 2H), 6.95 (m, 2H), 7.05 (s, 2H); ^{13}C NMR ($CDCl_3$): δ 155.2, 146.0, 143.3 (d, $J = 81.2$ Hz), 132.6, 122.9 (d, $J = 27.1$ Hz), 80.6, 66.4 (d, $J = 47.5$ Hz), 28.4, 19.9. Anal. Calcd for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N, 5.16. Found: C, 75.10; H, 7.89; N, 5.07.

4.2. Rhodium-catalyzed asymmetric ring opening of 1a–d with dibenzylamine

A typical procedure is given for the reaction of **1a** with 5.0 equiv of *N*,*N*-dibenzylamine in the presence of 2.5 mol % of $[Rh(cod)Cl]_2$ and 11.0 mol % of **3b** (Table 3, entry 7).

To a 10 mL round bottom flask were added *N*-Boc-azabenzonorbornadiene **1a** (80 mg, 0.33 mmol), $[Rh(cod)Cl]_2$ (4 mg, 8 μmol), and (*S*,*S*)-(*R*,*R*)-C_2-ferriphos-tolyl **3b** (27 mg, 36 μmol) under a nitrogen atmosphere. Then, dibenzylamine (0.3 mL, 1.6 mmol) was added and the mixture allowed to stir at 80 °C for 48 h. The resulting mixture was cooled to room temperature and diluted in CH_2Cl_2. The black solution was filtered through Celite and the filtrate concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane/ethyl acetate = 95/5) to give 142 mg (98% yield) of **2a** as a semisolid.

4.2.1. (1*S*,2*S*)-(2-*N*,*N*-Dibenzylamino-1,2-dihydro-naphthalen-1-yl)-carbamic acid *tert*-butyl ester, 2a. Ee (97%) by HPLC analysis with a chiral column (Chiralcel OD, hexane/2-propanol = 99/1, 0.5 mL/min), t_R (*S*)-(+), 15.4 min (major); (*R*)-(−), 17.0 min (minor). $[\alpha]_D^{25} = +150.4$ (*c* 1.00, $CHCl_3$) for **2a** of 97% ee. (lit.[12] $[\alpha]_D^{25} = +96.1$ (*c* 1.06, CCl_4) for **2a** of 89% ee); ^{1}H NMR ($CDCl_3$): δ 1.53 (s, 9H), 3.43–3.50 (m, 1H), 3.55 (d, $J = 13.5$ Hz, 2H), 3.74 (d, $J = 13.5$ Hz, 2H), 4.48 (d, $J = 9.0$ Hz, 1H), 5.24 (t, $J = 9.0$ Hz, 1H), 6.05 (dd, $J = 9.9$, 3.3 Hz, 1H), 6.59 (dd, $J = 9.9$, 1.8 Hz, 1H), 7.02–7.05 (m, 1H), 7.18–7.33 (m, 9H), 7.37 (d, $J = 6.9$ Hz, 4H); ^{13}C NMR ($CDCl_3$): δ 155.7, 140.0, 135.8, 132.6, 129.5, 129.2, 129.1, 128.3, 128.1, 127.9, 127.4, 127.0, 126.9, 126.7, 79.5, 59.5, 54.0, 49.4, 28.6, 28.5.

4.2.2. (1*S*,2*S*)-(2-*N*,*N*-Dibenzylamino-1,2-dihydro-5,8-dimethylnaphthalen-1-yl)-carbamic acid *tert*-butyl ester, 2b. Ee (99%) by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 99/1, 0.5 mL/min), t_R (*S*)-(+), 13.3 min (major); (*R*)-(−), 15.3 min (minor). $[\alpha]_D^{25} = +175.8$ (*c* 1.00, $CHCl_3$) for **2b** of 99% ee; IR (NaCl, cm^{-1}) 3408, 2974, 1707, 1493, 1365, 1228, 1163. ^{1}H NMR ($CDCl_3$): δ 1.40 (s, 9H), 2.29 (s, 3H), 2.38 (s, 3H), 3.39 (br s, 1H), 3.43 (d, $J = 13.8$ Hz, 2H), 3.53 (d, $J = 13.5$ Hz, 2H), 4.43 (d, $J = 9.0$ Hz, 1H), 5.32 (d, $J = 9.9$ Hz, 1H), 5.87 (dd, $J = 10.2$, 6.0 Hz, 1H), 6.88 (d, $J = 10.2$ Hz, 1H), 6.95–7.01 (m, 2H), 7.15–7.27 (m, 6H), 7.35 (d, $J = 6.9$ Hz, 4H); ^{13}C NMR ($CDCl_3$): δ 154.5, 140.4, 134.2, 132.3, 131.7, 130.1, 129.6, 129.0, 127.9, 126.6, 126.2, 125.8, 79.2, 58.5, 53.5, 43.9, 28.3, 18.9, 18.6. HRMS (ESI) calcd for $C_{31}H_{37}N_2O_2$ ($[MH]^+$): 469.2849. Found: 469.2833.

4.2.3. (1*S*,2*S*)-(2-*N*,*N*-Dibenzylamino-1,2-dihydro-5,6,7,8-tetramethylnaphthalen-1-yl)-carbamic acid *tert*-butyl ester, 2c. Ee (99%) by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 99/1, 0.5 mL/min), t_R (*S*)-(+), 9.6 min (major); (*R*)-(−), 12.0 min (minor). $[\alpha]_D^{25} = +265.8$ (*c* 1.00, $CHCl_3$) for **2c** of 99% ee; IR (NaCl, cm^{-1}) 3418, 2925, 2358, 1705, 1489, 1365, 1165, 1047. ^{1}H NMR ($CDCl_3$): δ 1.39 (s, 9H), 2.21 (s, 3H), 2.25 (s, 6H), 2.33 (s, 3H), 3.38 (d, $J = 5.4$ Hz, 1H), 3.44 (d, $J = 13.5$ Hz, 2H), 3.52 (d, $J = 13.8$ Hz, 2H), 4.42 (d, $J = 9.0$ Hz, 1H), 5.38 (d, $J = 9.6$ Hz, 1H), 5.83 (dd, $J = 9.3$, 5.1 Hz, 1H), 7.01 (d, $J = 10.2$ Hz, 1H), 7.14–7.25 (m, 6H), 7.35 (d, $J = 7.2$ Hz, 4H); ^{13}C NMR ($CDCl_3$): δ 154.7, 140.7, 135.8, 135.0, 132.5, 130.4, 130.2, 129.2, 128.1, 127.9, 127.3, 126.7, 124.8, 79.2, 58.6, 53.7, 44.9, 28.5, 17.2, 17.0, 15.4, 15.2. HRMS (ESI) calcd for $C_{33}H_{41}N_2O_2$ ($[MH]^+$): 497.3162. Found: 497.3174.

4.2.4. (1*S*,2*S*)-(2-*N*,*N*-Dibenzylamino-1,2-dihydro-6,7-dimethylnaphthalen-1-yl)-carbamic acid *tert*-butyl ester, 2d. Ee (97%) by HPLC analysis with a chiral column (Chiralcel OD, hexane/2-propanol = 99/1, 0.5 mL/min), t_R (*S*)-(+), 14.2 min (major); (*R*)-(−), 18.7 min (minor). $[\alpha]_D^{25} = +135.8$ (*c* 1.00, $CHCl_3$) for **2d** of 97% ee; IR (NaCl, cm^{-1}) 3415, 2973, 1713, 1494, 1364, 1245, 1166. ^{1}H NMR ($CDCl_3$): δ 1.51 (s, 9H), 2.19 (s, 3H), 2.23 (s, 3H), 3.41 (br s, 1H), 3.53 (d, $J = 13.5$ Hz, 2H), 3.70 (d, $J = 13.8$ Hz, 2H), 4.43–4.46 (m, 1H), 5.18 (m, 1H), 5.93–5.96 (m, 1H), 6,54 (dd, $J = 9.9$, 1.8 Hz, 1H), 6.82 (s, 1H), 7.08 (s, 1H), 7.15–7.28 (m, 6H), 7.37 (d, $J = 6.9$ Hz, 4H); ^{13}C NMR ($CDCl_3$): δ 155.6, 140.3, 136.6, 136.1, 133.1, 130.3, 129.4, 129.3, 128.9, 128.3, 128.1, 127.0, 125.8, 79.5, 59.5, 54.0, 48.9, 28.7, 19.9, 19.5. HRMS (ESI) calcd for $C_{31}H_{37}N_2O_2$ ($[MH]^+$): 469.2849. Found: 469.2849.

4.3. Preparation of chiral ferrocenyl phosphine ligands 3b and 3c

4.3.1. C_2-Ferriphos-tolyl, 3b. To a solution of (*S*,*S*)-1,1′-bis(α-*N*,*N*-dimethylaminoethyl)ferrocene (1.2 g, 3.6 mmol) prepared according to the reported procedure by Knochel[14b] in dry ether was slowly added *n*-butyllithium solution in hexane (6.9 mL, 10.9 mmol) by syringe pump at room temperature for 45 min under a nitrogen atmosphere. The reaction mixture was allowed to stir at room temperature for 2.5 h and di(4-methylphenyl)chlorophosphine[20] (2.9 g, 11.7 mmol) was slowly added at room temperature. The mixture was refluxed for another 15 h. The resulting mixture was quenched with saturated $NaHCO_3$ solution and extracted with

benzene. The separated organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 50/50) to give 0.9 g (33% yield) of ferrocenyl bisphosphine **3b**. $[\alpha]_D^{25} = +460.2$ (*c* 1.00, $CHCl_3$). Mp 174–176 °C; IR (NaCl, cm^{-1}) 2966, 2929, 2812, 2796, 1596, 1496, 1447, 1271, 1242, 1184, 1093, 1019, 929, 804, 756, 623. ^1H NMR ($CDCl_3$): δ 1.27 (d, $J = 6.3$ Hz, 6H), 1.73 (s, 12 H), 2.25 (s, 6H), 2.34 (s, 6H), 3.03 (s, 2H), 4.00–4.09 (m, 2H), 4.13 (s, 2H), 4.34 (s, 2H), 6.93–6.97 (m, 12H), 7.19 (t, $J = 7.7$ Hz, 4H); ^{31}P NMR ($CDCl_3$): δ −25.5. Anal. Calcd for $C_{46}H_{54}FeN_2P_2$: C, 73.40; H, 7.23; N, 3.72. Found: C, 73.53; H, 7.31; N, 3.72.

4.3.2. C_2-Ferriphos-xylyl, 3c. Prepared from **3c** in a similar manner to **3b** in 30% yield. $[\alpha]_D^{25} = +366.2$ (*c* 1.00, $CHCl_3$). Mp 248–250 °C (decomp); IR (NaCl, cm^{-1}) 2965, 2927, 2852, 2812, 2769, 1598, 1582, 1453, 1362, 1272, 1242, 1167, 1125, 1095, 1065, 1038, 929, 846, 824, 756, 693. ^1H NMR ($CDCl_3$): δ 1.27 (d, $J = 6.3$ Hz, 6H), 1.69 (s, 12H), 2.17 (s, 12H), 2.23 (s, 12H), 3.03 (s, 2H), 3.95–4.09 (m, 2H), 4.16 (s, 2H), 4.31 (s, 2H), 6.72 (d, $J = 8.4$ Hz, 4H), 6.77 (s, 2H), 6.83 (s, 2H), 6.95 (d, $J = 8.1$ Hz, 4H); ^{31}P NMR ($CDCl_3$): δ −23.1. Anal. Calcd for $C_{50}H_{62}FeN_2P_2$: C, 74.25; H, 7.73; N, 3.64. Found: C, 74.93; H, 7.87; N, 3.41.

4.4. Synthesis of benzoylamides 4a–d

4.4.1. (1*S*,2*S*)-(2-Benzoylamino-1,2,3,4-tetrahydro-naphthalen-1-yl)-carbamic acid *tert*-butyl ester, 4a. To a stirred solution of **2a** (8.3 g, 18.8 mmol) in ethyl acetate (80 mL) and methanol (160 mL) was added ammonium formate (11.9 g, 188.3 mmol) and 30 mol % of Pd/C (10 wt %, 6.0 g, 5.6 mmol). The mixture was refluxed for 25 min and cooled to room temperature. The resulting black suspension was filtered through Celite and the Celite cake washed with triethylamine/methanol (1/1 = v/v) several times. The filtrate was concentrated under reduced pressure. The residue was dissolved with dry THF (100 mL) and pyridine (4.6 mL, 56.5 mmol) was added. Then, benzoyl chloride (2.7 mL, 22.6 mmol) was slowly added at 0 °C and the mixture stirred at room temperature for 15 h under a nitrogen atmosphere. The resulting mixture was quenched with 1 N NaOH solution and was extracted with ether. The separated organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. Flash column chromatography on silica gel (hexane/ethyl acetate = 70/30) and recrystallization with 2-propanol gave 5.0 g (72% yield) of **4a**. Ee (>99%) by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 90/10, 1.0 mL/min), t_R (*R*)-(−), 9.4 min (minor); (*S*)-(+), 11.5 min (major). $[\alpha]_D^{25} = +58.2$ (*c* 1.00, $CHCl_3$) for **4a** of >99% ee. Mp 185–187 °C; IR (NaCl, cm^{-1}) 3320, 2977, 1682, 1638, 1537, 1489, 1365, 1318, 1250, 1173, 1018, 691. ^1H NMR ($CDCl_3$): δ 1.38 (s, 9H), 1.80 (dq, $J = 12.3$, 5.1 Hz, 1H), 2.43–2.49 (m, 1H), 2.87 (dd, $J = 17.3$, 3.2 Hz, 1H), 3.07 (ddd, $J = 17.3$, 12.3, 5.1 Hz, 1H), 4.11–4.22 (m, 1H), 4.97–5.02 (m, 2H), 7.10–7.13 (m, 1H), 7.18–7.25 (m, 3H), 7.38–7.50 (m, 4H), 7.88 (d, $J = 6.9$ Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 28.5, 28.7, 29.0, 54.3, 55.0, 80.5, 126.5, 127.1, 127.3, 127.7, 128.6, 129.1, 131.6, 134.3, 135.4, 136.9, 158.0, 167.5. Anal. Calcd for $C_{22}H_{26}N_2O_3$: C, 72.11; H, 7.15; N, 7.64. Found: C, 72.32; H, 7.26; N, 7.67.

4.4.2. (1*S*,2*S*)-(2-Benzoylamino-1,2,3,4-tetrahydro-5,8-dimethylnaphthalen-1-yl)-carbamic acid *tert*-butyl ester, 4b. Prepared from **2b** in a similar manner to **4a** in 68% yield. Ee (>99%) by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 90/10, 1.0 mL/min), t_R (*R*)-(−), 7.3 min (minor); (*S*)-(+), 8.4 min (major). $[\alpha]_D^{25} = +129.6$ (*c* 1.00, $CHCl_3$) for **4b** of >99% ee. Mp 132–134 °C; IR (NaCl, cm^{-1}) 3313, 2974, 1688, 1639, 1532, 1315, 1247, 1166, 1046. ^1H NMR ($CDCl_3$): δ 1.42 (s, 9H), 1.75–2.07 (m, 1H), 2.17–2.30 (m, 7H), 2.60–2.83 (m, 2H), 4.40 (m, 1H), 4.65 (d, $J = 8.1$ Hz, 1H), 4.89 (t, $J = 7.2$ Hz, 1H), 6.50 (m, 1H), 6.99 (d, $J = 7.5$ Hz, 1H), 7.04 (d, $J = 7.5$ Hz, 1H), 7.35–7.49 (m, 3H), 7.75 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 167.7, 155.9, 136.3, 134.7, 134.4, 132.2, 131.5, 130.2, 129.4, 128.9, 128.6, 128.5, 127.2, 80.1, 52.6, 51.4, 28.5, 24.3, 19.7, 19.4. HRMS (ESI) calcd for $C_{24}H_{30}N_2O_3Na$ ($[MNa]^+$): 417.2148. Found: 417.2138.

4.4.3. (1*S*,2*S*)-(2-Benzoylamino-1,2,3,4-tetrahydro-5,6,7,8-tetramethylnaphthalen-1-yl)-carbamic acid *tert*-butyl ester, 4c. Prepared from **2c** in a similar manner to **4a** in 56% yield. Ee (>99%) by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 90/10, 1.0 mL/min), t_R (*R*)-(−), 6.9 min (minor); (*S*)-(+), 11.2 min (major). $[\alpha]_D^{25} = +137.2$ (*c* 1.00, $CHCl_3$) for **4c** of >99% ee. Mp 174–175 °C; IR (NaCl, cm^{-1}) 3307, 2928, 1695, 1653, 1528, 1314, 1245, 1168, 1017, 753. ^1H NMR ($CDCl_3$): δ 1.42 (s, 9H), 1.92–2.04 (m, 1H), 2.18–2.26 (m, 8H), 2.65–2.87 (m, 2H), 4.34 (m, 1H), 4.63 (d, $J = 7.8$ Hz, 1H), 4.92 (t, $J = 7.4$ Hz, 1H), 6.56 (d, $J = 7.5$ Hz, 1H), 7.35–7.48 (m, 3H), 7.76 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR ($CDCl_3$): δ 167.7, 156.0, 135.0, 134.8, 134.3, 134.2, 133.3, 132.4, 131.4, 129.8, 128.5, 127.2, 80.0, 52.9, 51.9, 28.5, 25.3, 24.5, 16.9, 16.8, 16.4, 15.9. Anal. Calcd for $C_{26}H_{34}N_2O_3$: C, 73.90; H, 8.11; N, 6.63. Found: C, 73.85; H, 8.10; N, 6.48.

4.4.4. (1*S*,2*S*)-(2-Benzoylamino-1,2,3,4-tetrahydro-6,7-dimethylnaphthalen-1-yl)-carbamic acid *tert*-butyl ester, 4d. Prepared from **2d** in a similar manner to **4a** in 70% yield. Ee (>99%) by HPLC analysis with a chiral column (Chiralcel AD, hexane/2-propanol = 90/10, 1.0 mL/min), t_R (*R*)-(−), 10.8 min (minor); (*S*)-(+), 15.1 min (major). $[\alpha]_D^{25} = +57.0$ (*c* 1.00, $CHCl_3$) for **4d** of >99% ee. Mp 191–194 °C; IR (NaCl, cm^{-1}) 3325, 2927, 1683, 1639, 1540, 1315, 1248, 1169, 1023. ^1H NMR ($CDCl_3$): δ 1.39 (s, 9H), 1.67–1.82 (m, 1H), 2.22 (s, 3H), 2.25 (s, 3H), 2.41–2.48 (m, 1H), 2.76–2.83 (m, 1H), 2.95–3.07 (m, 1H), 4.06–4.17 (m, 1H), 4.83–4.96 (m, 2H), 6.90 (s, 1H), 7.13 (s, 1H), 7.38–7.50 (m, 3H), 7.87 (d, $J = 7.3$ Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 167.4, 158.0, 136.2, 134.8, 134.3, 134.2, 132.5, 131.5, 130.2, 128.5, 128.0, 127.3, 80.4, 55.5, 53.9, 29.1, 28.5, 28.1, 19.6, 19.4. HRMS (ESI) calcd for $C_{24}H_{30}N_2O_3Na$ ($[MNa]^+$): 417.2148. Found: 417.2149.

4.5. Preparation of the tartrates 5a–d

4.5.1. (1*S*,2*S*)-Diamine (*R*,*R*)-tartrate, 5a. To 50% hydrochloric acid (120 mL) was added **4a** (3.0 g, 8.2 mmol) and the mixture was refluxed for 48 h. The reaction mixture was cooled to room temperature and the acidic solution was washed with ether several times. Then, to the separated aqueous solution was slowly added 4 N NaOH solution at 0 °C for 30 min and its pH was adjusted around pH 11. The resulting basic solution was extracted with CH_2Cl_2 and dried over anhydrous $MgSO_4$. After removal of all volatile solvents under reduced pressure, the crude solid was dissolved with ethanol (80 mL) and H_2O (10 mL) and L-(+)-tartaric acid (1.1 g, 7.4 mmol) solution in ethanol (20 mL) was slowly added. The resulting suspension was refluxed for 18 h and was slowly cooled to room temperature. The precipitate was collected by filtration and the collected solid was washed with cold methanol. After drying under vacuum, 2.1 g (82% yield) of (*S*,*S*)-diamine (*R*,*R*)-tartrate **5a** was obtained. $[\alpha]_D^{25} = +27.2$ (*c* 1.00, H_2O) for **5a** of >99% ee. Mp 238–240 °C (decomp); ^{1}H NMR (DMSO-d_6): δ 1.71–1.85 (m, 1H), 2.08–2.16 (m, 1H), 2.80–2.84 (m, 2H), 3.02–3.10 (m, 1H), 3.80 (d, $J = 9.0$ Hz, 1H), 5.18 (br s, 10H), 7.09 (d, $J = 7.2$ Hz, 1H), 7.15–7.24 (m, 2H), 7.60 (d, $J = 6.9$ Hz, 1H); ^{13}C NMR (DMSO-d_6): δ 174.5, 138.1, 135.3, 128.1, 127.6, 126.8, 126.1, 71.4, 53.5, 53.4, 27.0, 26.4. Anal. Calcd for $C_{14}H_{22}N_2O_7$: C, 50.90; H, 6.71; N, 8.48. Found: C, 51.13; H, 6.70; N, 8.44.

4.5.2. (1*S*,2*S*)-Diamine (*R*,*R*)-tartrate, 5b. Prepared from **4b** in a similar manner to **5a** in 86% yield. $[\alpha]_D^{25} = +7.6$ (*c* 1.00, DMSO) for **5b** of >99% ee. Mp 198–201 °C (decomp); ^{1}H NMR (DMSO-d_6): δ 1.81–1.91 (m, 1H), 2.14 (s, 3H), 2.23–2.32 (m, 1H), 2.35 (s, 3H), 2.51–2.69 (m, 2H), 3.42 (m, 1H), 3.86 (s, 2H), 4.07 (m, 1H), 5.16 (br s, 10H), 6.96 (d, $J = 7.8$ Hz, 1H), 7.01 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR (DMSO-d_6): δ 174.6, 135.2, 133.7, 133.4, 133.2, 128.3, 127.8, 71.5, 71.3, 50.8, 48.4, 20.9, 19.8, 19.1, 18.4. Anal. Calcd for $C_{16}H_{26}N_2O_7$: C, 53.62; H, 7.31; N, 7.82. Found: C, 53.60; H, 7.06; N, 7.66.

4.5.3. (1*S*,2*S*)-Diamine (*R*,*R*)-tartrate, 5c. Prepared from **4c** in a similar manner to **5a** in 75% yield. $[\alpha]_D^{25} = +0.8$ (*c* 1.00, DMSO) for **5c** of >99% ee. Mp 198–201 °C (decomp); ^{1}H NMR (DMSO-d_6): δ 1.80–1.85 (m, 1H), 2.09 (s, 3H), 2.16–2.29 (m, 10H), 2.51–2.69 (m, 2H), 3.38 (m, 1H), 3.82 (s, 2H), 4.10 (m, 1H), 4.81 (br s, 10H); ^{13}C NMR (DMSO-d_6): δ 174.5, 133.4, 132.8, 132.7, 131.3, 130.5, 71.3, 54.9, 51.1, 49.2, 21.9, 20.4, 16.4, 15.4, 15.2. Anal. Calcd for $C_{18}H_{30}N_2O_7$: C, 55.94; H, 7.82; N, 7.25. Found: C, 56.13; H, 7.81; N, 7.29.

4.5.4. (1*S*,2*S*)-Diamine (*R*,*R*)-tartrate, 5d. Prepared from **4d** in a similar manner to **5a** in 80% yield. $[\alpha]_D^{25} = -44.2$ (*c* 1.00, DMSO) for **5d** of >99% ee. Mp 235–237 °C (decomp); ^{1}H NMR (DMSO-d_6): δ 1.65–1.79 (m, 1H), 2.06–2.14 (m, 1H), 2.16 (s, 3H), 2.18 (s, 3H), 2.73 (m, 2H), 3.01 (m, 1H), 3.75 (d, $J = 8.7$ Hz, 1H), 3.85 (s, 2H), 5.50 (br s, 10H), 6.84 (s, 1H), 7.34 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 174.5, 134.8, 134.7, 133.7, 132.5, 129.1, 128.5, 71.4, 53.4, 53.3, 26.6, 26.5, 19.1, 18.8. Anal. Calcd for $C_{16}H_{26}N_2O_7$: C, 53.62; H, 7.31; N, 7.82. Found: C, 53.56; H, 7.31; N, 7.74.

4.6. Synthesis of the salen-type ligands 6a–d

4.6.1. Salen-type ligand, 6a. (*S*,*S*)-Diamine (*R*,*R*)-tartrate **5a** (0.9 g, 2.9 mmol, >99% ee) and K_2CO_3 (0.8 g, 5.7 mmol) were dissolved with H_2O (4 mL) and ethanol (10 mL) then a solution of 3,5-di-*tert*-butylsalicylaldehyde (1.3 g, 5.5 mmol) in ethanol (40 mL) was slowly added at 80 °C by syringe pump for 40 min to the suspension. The yellow suspension was refluxed for 2 h, cooled to room temperature, and stirred at room temperature for another 15 h. The resulting mixture was quenched with H_2O and stored in ice bath for 1 h. The yellow solid was collected by filtration and dissolved with CH_2Cl_2. The organic solution was washed with H_2O and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude solid was purified by recrystallization with methanol to give 1.6 g (91% yield) of salen **6a** as a light yellow solid. $[\alpha]_D^{25} = +265.8$ (*c* 1.00, $CHCl_3$) for **6a** of >99% ee. Mp 197–198 °C; IR (NaCl, cm^{-1}) 2935, 1623, 1437, 1361, 1273, 1249, 1173, 749. ^{1}H NMR ($CDCl_3$): δ 1.24 (s, 9H), 1.26 (s, 9H), 1.40 (s, 9H), 1.42 (s, 9H), 2.14–2.32 (m, 2H), 3.00–3.18 (m, 2H), 3.74 (ddd, $J = 10.5$, 6.3, 4.2 Hz, 1H), 4.59 (d, $J = 13.5$ Hz, 1H), 6.99 (d, $J = 2.4$ Hz, 1H), 7.07 (d, $J = 2.4$ Hz, 1H), 7.12–7.23 (m, 4H), 7.34 (dd, $J = 6.6$, 4.2 Hz, 2H), 8.37 (s, 1H), 8.46 (s, 1H), 13.47 (br s, 1H), 13.53 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ 168.55, 166.95, 158.34, 158.13, 140.32, 140.27, 136.75, 136.69, 135.86, 135.61, 128.92, 128.49, 127.50, 127.41, 127.25, 126.61, 126.53, 126.46, 118.05, 117.88, 73.75, 70.42, 35.21, 34.29, 31.64, 30.07, 29.65, 28.34. Anal. Calcd for $C_{40}H_{54}N_2O_2$: C, 80.76; H, 9.15; N, 4.71. Found: C, 81.02; H, 8.96; N, 4.72.

4.6.2. Salen-type ligand, 6b. Prepared from **5b** in a similar manner to **6a** in 86% yield. $[\alpha]_D^{25} = +219.8$ (*c* 1.00, $CHCl_3$) for **6b** of >99% ee. Mp 135–137 °C; IR (NaCl, cm^{-1}) 2955, 1623, 1465, 1439, 1361, 1272, 1249, 1171, 807, 772. ^{1}H NMR ($CDCl_3$): δ 1.26 (s, 9H), 1.29 (s, 9H), 1.39 (s, 9H), 1.43 (s, 9H), 1.92–2.08 (m, 1H), 2.13–2.25 (m, 4H), 2.30 (s, 3H), 2.71–2.94 (m, 2H), 3.88 (m, 1H), 4.87 (d, $J = 8.4$ Hz, 1H), 6.96–6.98 (m, 2H), 7.07–7.09 (m, 2H), 7.36 (t, $J = 2.4$ Hz, 2H), 8.12 (s, 1H), 8.53 (s, 1H), 13.23 (br s, 1H), 13.82 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ 166.43, 158.36, 158.07, 140.31, 140.20, 136.84, 136.21, 135.98, 134.20, 131.22, 129.28, 128.47, 127.34, 127.27, 126.51, 126.35, 118.09, 118.05, 69.41, 68.45, 35.24, 34.34, 31.70, 29.67, 29.62, 25.63, 23.97, 20.06, 19.88. Anal. Calcd for $C_{42}H_{58}N_2O_2$: C, 80.98; H, 9.38; N, 4.50. Found: C, 80.79; H, 9.48; N, 4.45.

4.6.3. Salen-type ligand, 6c. Prepared from **5c** in a similar manner to **6a** in 94% yield. $[\alpha]_D^{25} = +185.0$ (*c* 1.00, $CHCl_3$) for **6c** of >99% ee. Mp 210–212 °C; IR (NaCl, cm^{-1}) 2954, 1625, 1439, 1360, 1273, 1250, 1171, 773. ^{1}H NMR ($CDCl_3$): δ 1.24 (s, 9H), 1.29 (s, 9H), 1.40 (s,

9H), 1.43 (s, 9H), 1,94–2.15 (m, 5H), 2.22 (s, 3H), 2.26 (s, 3H), 2.30 (s, 3H), 2.73–2.96 (m, 2H), 3.84 (m, 1H), 5.01 (d, $J = 8.4$ Hz, 1H), 6.97 (d, $J = 4.0$ Hz, 1H), 7.08 (d, $J = 2.7$ Hz, 1H), 7.36 (d, $J = 2.1$ Hz, 2H), 8.08 (s, 1H), 8.53 (s, 1H), 13.32 (br s, 1H), 13.95 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ 166.41, 166.24, 158.43, 158.06, 140.28, 140.05, 136.82, 136.77, 134.60, 133.89, 133.54, 133.49, 132.13, 128.55, 127.20, 126.49, 126.36, 118.13, 69.63, 68.59, 35.25, 35.23, 34.32, 31.70, 29.68, 29.63, 25.99, 25.00, 17.07, 16.92, 15.99. Anal. Calcd for $C_{44}H_{62}N_2O_2$: C, 81.18; H, 9.60; N, 4.30. Found: C, 81.24; H, 9.53; N, 4.29.

4.6.4. Salen-type ligand, 6d. Prepared from **5d** in a similar manner to **6a** in 84% yield. $[\alpha]_D^{25} = +220.2$ (c 1.00, $CHCl_3$) for **6d** of >99% ee. Mp 132–135 °C; IR (NaCl, cm^{-1}) 2955, 2358, 1626, 1439, 1361, 1250, 1173, 879, 772. ^{1}H NMR ($CDCl_3$): δ 1.24 (s, 9H), 1.26 (s, 9H), 1.40 (s, 9H), 1.42 (s, 9H), 2.13–2.22 (m, 5H), 2.24 (s, 3H), 2.92–3.04 (m, 2H), 3.70 (ddd, $J = 10.5$, 6.9, 4.2 Hz, 1H), 4.53 (d, $J = 8.4$ Hz, 1H), 6.87 (s, 1), 6.98 (m, 2H), 7.08 (d, $J = 2.4$ Hz, 1H), 7.34 (dd, $J = 8.1$, 2.4 Hz, 2H), 8.37 (s, 1H), 8.45 (s, 1H), 13.12 (br s, 1H), 13.56 (br s, 1H); ^{13}C NMR ($CDCl_3$): δ 168.17, 166.85, 158.42, 158.14, 140.28, 140.17, 136.77, 136.66, 135.99, 134.85, 133.11, 132.86, 130.05, 129.41, 127.32, 127.18, 126.59, 126.44, 118.09, 117.93, 73.64, 70.71, 35.22, 35.20, 34.30, 34.28, 31.65, 30.24, 29.65, 27.90, 19.61, 19.56. Anal. Calcd for $C_{42}H_{58}N_2O_2$: C, 80.98; H, 9.38; N, 4.50. Found: C, 80.94; H, 9.50; N, 4.45.

4.7. Synthesis of the Trost ligands 7a–d

4.7.1. Trost-type ligand, 7a. To a stirred solution of 2-(diphenylphosphino)benzoic acid (2.6 g, 8.4 mmol) and triethylamine (3.5 mL, 25.2 mmol) in anhydrous CH_2Cl_2 was slowly added diphenylchlorophosphate (1.9 mL, 9.2 mmol) at 0 °C for 10 min under a nitrogen atmosphere. The mixture was warmed to room temperature and stirred for 15 h. Then a solution of (*S*,*S*)-1,2,3,4-tetrahydronaphthalen-1,2-diamine **5a** (0.6 g, 3.8 mmol) and DMAP (47 mg, 0.4 mmol) in anhydrous CH_2Cl_2 was added by cannula and the mixture was stirred at room temperature for another 24 h. The reaction was quenched with saturated $NaHCO_3$ solution and extracted with CH_2Cl_2. The separated organic layer was washed with brine and dried over anhydrous $MgSO_4$. After concentration under reduced pressure, the residue was purified by flash column chromatography (hexane/ethyl acetate = 70/30) to give 2.6 g of **7a** (93% yield) as a white solid. $[\alpha]_D^{25} = -29.8$ (c 1.00, $CHCl_3$). Mp 129–135 °C (decomp); IR (NaCl, cm^{-1}) 3311, 3051, 2925, 1635, 1583, 1528, 1433, 1325, 1156, 1087, 1026, 743, 695. ^{1}H NMR ($CDCl_3$): δ 1.48–1.62 (m, 1H), 2.01–2.13 (m, 1H), 2.73–2.79 (m, 1H), 2.88–2.97 (m, 1H), 4.09–4.23 (m, 1H), 5.30 (t, $J = 9.3$ Hz, 1H), 6.34 (d, $J = 9.3$ Hz, 1H), 6.63 (d, $J = 7.8$ Hz, 1H), 6.88–6.93 (m, 1H), 6.98–7.02 (m, 1H), 7.04–7.15 (m, 4H), 7.18–7.34 (m, 24H), 7.64–7.68 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 170.41, 169.41, 140.77 (d, $J = 24.5$ Hz), 140.60 (d, $J = 24.5$ Hz), 138.13 (d, $J = 11.5$ Hz), 137.98 (d, $J = 11.5$ Hz), 137.83 (d, $J = 12.2$ Hz), 137.77 (d, $J = 12.2$ Hz), 137.25 (d, $J = 22.5$ Hz), 136.94 (d, $J = 22.5$ Hz), 136.58, 135.18, 134.77, 134.35, 134.09 (d, $J = 20.2$ Hz), 133.99 (d, $J = 20.2$ Hz), 130.63, 130.32, 129.11, 128.94, 128.75, 128.66, 128.59, 128.51, 127.95, 127.73, 127.45, 126.53, 53.55, 53.29, 28.65, 28.50. ^{31}P NMR ($CDCl_3$): δ −10.3, −11.5. Anal. Calcd for $C_{48}H_{40}N_2O_2P_2$: C, 78.03; H, 5.46; N, 3.79. Found: C, 78.23; H, 5.60; N, 3.76.

4.7.2. Trost-type ligand, 7b. Prepared from **5b** in a similar manner to **7a** in 77% yield. $[\alpha]_D^{25} = +94.0$ (c 1.00, $CHCl_3$). Mp 119–123 °C (decomp); IR (NaCl, cm^{-1}) 3398, 3300, 3053, 2931, 1647, 1522, 1433, 1321, 1258, 1217, 1156, 1090, 1026, 745, 696. ^{1}H NMR ($CDCl_3$): δ 1.57–1.68 (m, 1H), 1.91–2.03 (m, 1H), 2.14 (s, 3H), 2.28 (s, 3H), 2.35–2.59 (m, 2H), 4.24–4.32 (m, 1H), 5.21 (dd, $J = 8.4$, 4.2 Hz, 1H), 5.88 (d, $J = 8.4$ Hz, 1H), 6.04 (d, $J = 6.9$ Hz, 1H), 6.87–6.96 (m, 3H), 6.99–7.08 (m, 3H), 7.12–7.38 (m, 22H), 7.56–7.63 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 168.80, 167.76, 141.68 (d, $J = 25.4$ Hz), 141.32 (d, $J = 25.4$ Hz), 137.31 (d, $J = 11.3$ Hz), 137.20 (d, $J = 11.3$ Hz), 137.08 (d, $J = 11.8$ Hz), 136.94 (d, $J = 11.8$ Hz), 136.82, 135.98 (d, $J = 21.5$ Hz), 135.92, 135.81 (d, $J = 21.5$ Hz), 134.60, 134.23, 133.96 (d, $J = 20.6$ Hz), 133.95 (d, $J = 20.6$ Hz), 133.89 (d, $J = 19.7$ Hz), 133.85 (d, $J = 19.7$ Hz), 130.87, 130.50, 130.10, 129.43, 129.09, 128.93, 128.87, 128.84, 128.81, 128.76, 128.71, 128.66, 128.63, 128.57, 128.49, 128.42, 128.35, 50.15, 49.14, 23.04 (d, $J = 2.8$ Hz), 22.51, 19.64, 19.50 (d, $J = 4.5$ Hz); ^{31}P NMR ($CDCl_3$): δ −11.9, −12.3. Anal. Calcd for $C_{50}H_{44}N_2O_2P_2$: C, 78.31; H, 5.78; N, 3.65. Found: C, 78.29; H, 5.91; N, 3.46.

4.7.3. Trost-type ligand, 7c. Prepared from **5c** in a similar manner to **7a** in 76% yield. $[\alpha]_D^{25} = +58.4$ (c 1.00, $CHCl_3$). Mp 116–120 °C (decomp); IR (NaCl, cm^{-1}) 3404, 3314, 3052, 2925, 1643, 1521, 1458, 1433, 1321, 1089, 744, 695. ^{1}H NMR ($CDCl_3$): δ 1.65–1.77 (m, 1H), 1.85–1.95 (m, 1H), 2.11 (s, 3H), 2.17 (s, 3H), 2.20 (s, 3H), 2.24 (s, 3H), 2.42–2.64 (m, 2H), 4.22–4.28 (m, 1H), 5.25 (dd, $J = 8.1$, 5.1 Hz, 1H), 5.89 (d, $J = 8.1$ Hz, 1H), 6.09 (d, $J = 7.8$ Hz, 1H), 6.86–6.95 (m, 2H), 7.07 (t, $J = 7.8$ Hz, 2H), 7.14–7.36 (m, 22H), 7.55–7.59 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 168.94, 167.84, 141.80 (d, $J = 26.5$ Hz), 141.41 (d, $J = 26.5$ Hz), 137.62 (d, $J = 11.5$ Hz), 137.46 (d, $J = 11.7$ Hz), 137.31 (d, $J = 11.5$ Hz), 137.26 (d, $J = 11.7$ Hz), 136.30 (d, $J = 21.3$ Hz), 135.97 (d, $J = 21.3$ Hz), 134.98, 134.69, 134.58, 133.98 (d, $J = 20.1$ Hz), 133.94 (d, $J = 20.1$ Hz), 133.92, 133.17, 132.34, 130.49, 130.05, 129.81 (d, $J = 4.3$ Hz), 129.04, 128.91, 128.81, 128.75, 128.72, 128.66, 128.62, 128.56, 128.31 (d, $J = 4.3$ Hz), 128.19, 128.11, 50.87, 50.09, 24.35, 23.17, 16.94, 16.88, 16.48 (d, $J = 4.1$ Hz), 15.82. ^{31}P NMR ($CDCl_3$): δ −11.7, −12.2. Anal. Calcd for $C_{52}H_{48}N_2O_2P_2$: C, 78.57; H, 6.09; N, 3.52. Found: C, 78.22; H, 6.40; N, 3.47.

4.7.4. Trost-type ligand, 7d. Prepared from **5d** in a similar manner to **7a** in 80% yield. $[\alpha]_D^{25} = -28.9$ (c 1.00, $CHCl_3$). Mp 131–136 °C (decomp); IR (NaCl, cm^{-1}) 3417, 3304, 3052, 2922, 1638, 1522, 1433, 1320, 1187, 1158, 1088, 962, 744, 695. ^{1}H NMR ($CDCl_3$): δ

1.42–1.58 (m, 1H), 2.01–2.11 (m, 1H), 2.18 (s, 3H), 2.20 (s, 3H), 2.65–2.71 (m, 1H), 2.83–2.91 (m, 1H), 4.08–4.17 (m, 1H), 5.27 (t, $J = 9.3$ Hz, 1H), 6.30 (d, $J = 9.3$ Hz, 1H), 6.64 (d, $J = 7.8$ Hz, 1H), 6.85 (s, 1H), 6.88–6.92 (m, 1H), 7.01–7.06 (m, 1H), 7.19–7.39 (m, 25H), 7.63–7.69 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 170.35, 169.39, 141.49 (d, $J = 25.6$ Hz), 140.89 (d, $J = 25.6$ Hz), 138.15 (d, $J = 12.2$ Hz), 138.06 (d, $J = 11.5$ Hz), 138.03 (d, $J = 12.2$ Hz), 137.87 (d, $J = 11.5$ Hz), 137.12 (d, $J = 21.8$ Hz), 136.91 (d, $J = 21.8$ Hz), 136.09, 135.10, 134.87, 134.14 (d, $J = 20.5$ Hz), 134.10 (d, $J = 20.5$ Hz), 133.92 (d, $J = 19.8$ Hz), 133.84 (d, $J = 19.8$ Hz), 132.39, 130.65, 130.31, 129.99, 129.23, 128.94, 128.77, 128.72, 128.67, 128.62, 128.58, 128.52, 128.06 (d, $J = 4.2$ Hz), 127.99 (d, $J = 4.2$ Hz), 53.71, 53.30, 28.57, 28.11, 19.60, 19.47. ^{31}P NMR ($CDCl_3$): δ −10.2, −11.9. Anal. Calcd for $C_{50}H_{44}N_2O_2P_2$: C, 78.31; H, 5.78; N, 3.65. Found: C, 78.46; H, 6.02; N, 3.53.

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