JOC Article

Biphenol-Based Phosphoramidite Ligands for the Enantioselective Copper-Catalyzed Conjugate Addition of Diethylzinc

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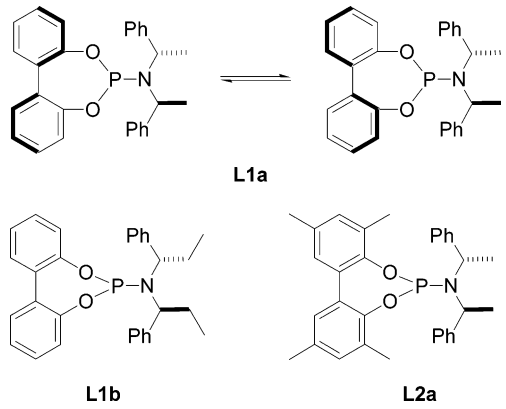
Phosphoramidite ligands, based on *ortho*-substituted biphenols and a chiral amine, induce high enantioselectivities (ee's up to 99%) in the copper-catalyzed conjugate addition of dialkylzinc reagents to a variety of Michael acceptors. Particularly, the best reported ee's were obtained for acyclic nitroolefins.

The asymmetric copper-catalyzed conjugate addition is, nowadays, a well-developed methodology to create chiral C−C bonds.[1] Many efforts have been made in designing efficient systems and identifying new ligands to improve enantioselectivities with specific classes of substrates.[2] Among the most efficient ligands, the ones based on the atropoisomerism of a binaphthol or a biphenol moiety play a prominent role.[3,4] We have recently demonstrated that phophoramidite ligands based on the atropoisomerically flexible biphenol unit are also excellent ligands.[5] Thus, the induced atropoisomerism of ligand **L1a**, and its analogues **L1b** and **L2a** (Scheme 1), allows high enantioselectivity in the asymmetric conjugate addition of dialkylzincs to a variety of Michael acceptors. Furthermore, improved ee's were obtained using diethyl ether as solvent and copper thiophenecarboxylate as copper salt.[6]

The modularity of these phosphoramidite ligands allows for easy variation of the amino part[7] as well as the biphenol part. We describe herein the modification of the biphenol scaffold of **L1a** and the consequence in the enantioselectivity on each substrate under these new

SCHEME 1. Conformational Atropoisomerism and Derivatives of L1a



experimental conditions. Using the same amines as in **L1a** or **L1b**, we modified the biphenol core by introducing different functional groups in *ortho* and *ortho*′ positions (R^2, Scheme 2). For some biphenols, it was easier to introduce an additional substitution on the R^1 position, although not playing an indispensable role. All ligands **L1**−**L11** were synthesized by reaction of the chiral amine (**a** or **b**) with PCl_3 and then addition of the biphenol **B2**−**B11**. They are isolated as white powders or colorless oils in 12−76% yield.

The corresponding biphenols **B2**−**B11** were synthesized by known, or improved, methods. Thus, **B3** and **B4** were obtained by halogenation of biphenol, with SO_2Cl_2[8] or Br_2,[9] respectively. The complete tetrachlorination or -bromination was easier to carry out than the selective *ortho* halogenation. The tetraphenylbiphenol, **B5**, was obtained by Suzuki-type coupling of phenyl boronic acid and MOM-protected **B4** (Scheme 3).[10] **B2**, **B6**, and **B7** were synthesized by coupling of the corresponding phenols, with $FeSO_4$ and $Na_2S_2O_8$ for **B2**[11] or catalytic CuBr(OH)·TMEDA for **B6** and **B7**.[12] The *ortho*,*ortho*′ disily-

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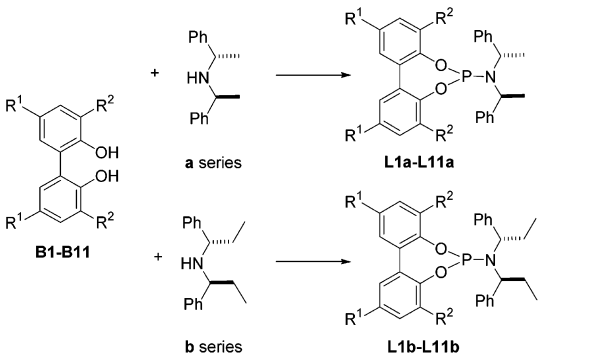
SCHEME 2. Ligands Used in This Study



	R^1	R^2	Yield (%)		R^1	R^2	Yield (%)
L1	H	H	54	**L7**	*t*-Bu	*t*-Bu	61
L2	Me	Me	76	**L8**	H	$Si(Me)_3$	12
L3	Cl	Cl	45	**L9**	H	allyl	64
L4	Br	Br	55	**L10**	H	methallyl	53
L5	Ph	Ph	71	**L11**	H	*n*-Pr	53
L6	Me	OMe	31				

lated biphenol, **B8**, could be obtained by a sequence starting with the selective dibromination of biphenol.[13] This selectivity was rather low, and the pure dibrominated biphenol could be isolated in only 25% yield. The next steps were original and involved an O-disilylation with trimethylchlorosilane, followed by an *ortho*,*ortho*′ dimetalation, with *t*-BuLi, and a retro-Brook rearrangement, in 59% overall yield (Scheme 4). Finally, **B9** and **B10** were prepared by a double Claisen rearrangement of the corresponding bis(allyl) (**4**) or methallyl (**5**) ethers. Instead of heating **4** in Decalin,[14] we found a simple thermic treatment in the Kugelrohr (190 °C) was sufficient to provide **B9** in good yield. Under the same conditions, the Claisen rearrangement of **5** did not take place. We found, however, that basic conditions were necessary to obtain **B10** in 89% isolated yield (Scheme 5). A simple classical hydrogenation of **B9** led, quantitatively, to **B11**.

To have a general picture of the influence of the *ortho* subsituent, ligands **L1a**−**L11a** were all tested with representative enones: a typical cyclic enone, cyclohexenone **S1**, and a typical acyclic one, 5-methyl-3-hexen-2-one, **S2**. The results are shown in Table 1.

The first striking results show that too sterically hindered substituents (R^1 = *t*-Bu or $SiMe_3$, entries 7 and 8) were unfavorable for catalytic activity. Both conversion and enantioselectivity fell down using these ligands particularly with the less reactive acyclic substrate **S2**. The presence of electron-withdrawing groups, such as the chloro and bromo derivatives, **L3a** and **L4a**, did not improve enantioselectivity and even shows a deleterious effect with the acyclic substrate **S2**. In contrast, the presence of an *ortho* methoxy group in **L6a**, designed to see any additional coordinating effect, shows a similar reactivity pattern as the two previous ligands **L1a** and **L2a**, and the conjugate adduct has the same absolute configuration. The allyl **L9a**, and the slightly more hindered methallyl **L10a** derivatives, showed complementary results compared to the methyl derivative **L1a**. Interestingly, these two ligands were very efficient on the acyclic substrate **S2**, maintaining excellent efficiency on the cyclic substrate **S1**. **L11a**, with a propyl substituents, gave similar results to **L10a**, although needing one more step to be synthesized. We therefore chose **L9a** and **L10a** to be tested on a large number of Michael acceptors (Scheme 6). We also tested the ligands with the **b** series of amine moiety and the same biphenol part. The results are shown in Table 2.

All the ligands, and particularly **L10b**, show a broad spectrum of applicability, despite the variety of substrates. In most cases, with the exception of chalcone **S5**, these new ligands show among the best reported enantioselectivities for many substrates. For example **S2** afforded 95% ee, the highest reported. **S4**, the precursor of the valuable fragrance (*R*)-muscone also shows a very high enantioselectivity. Of particular importance are the results with the five nitroalkenes **S8**−**S12**. With the exception of nitrocyclohexene (although 86% ee is among the best), the other nitroalkenes provide adducts with 91−96% ee, an unprecedented result for these Michael acceptors.

In summary, we have disclosed a series of simpler new phosphorus ligands, based on the induced atropoisomerism of the biphenol moiety. In many cases these new ligands afforded much better results than the parent ligand based on chiral binaphthol and sometimes the best reported in the literature. Although no ligand showed general enantioselectivity on every substrates, these results serve as a "fine-tuning" study, allowing to improve the efficiency of 1,4-addition using an optimal ligand for a definite substrate. Theoretical studies are under way to get deeper insight on the atropoisomerism of biphenol systems under the influence of a proximal chiral moiety.

Experimental Section

Materials. Unless otherwise stated, all the reagents were obtained commercially and were used without further purification.

3,3′,5,5′-Tetramethylbiphenyl-2,2′-diol (B2).[11] To a mechanically stirred aqueous solution of $FeSO_4$ heptahydrate (1.39 g, 5 mmol) in 150 mL of water was suspended 12 mL (100 mmol) of 2,4-dimethylphenol. A solution of $Na_2S_2O_8$ (23.9 g, 100 mmol) in 100 mL of water was added dropwise over 4 h. The mixture was then stirred overnight at room temperature. The resulting suspension was extracted with ethyl acetate, dried over Na_2CO_3, and filtered on silica gel. The solvent was evaporated in vacuo affording 10.3 g of a red-brown powder, which was purified by a Kugelrohr distillation (0.4 mmHg, 170 °C) followed by a recrystallization in cyclohexane to obtain 6.66 g (55%) of colorless crystals, mp 139 °C (lit. mp 137−138 °C).[15] ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.06 (dd, 2H, J = 1.5, 0.8 Hz), 6.92 (dd, 2H, J = 2.0, 0.5 Hz), 5.16 (brs, 2H), 2.33 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 149.2, 132.1, 120.1, 128.6, 125.3, 122.3, 20.5, 16.2. IR ($CHCl_3$): ν 3547, 3295, 2923, 1480, 1323, 1282, 1225, 1216, 1209, 1186, 1118, 1016, 865 cm^{-1}. HRMS (EI) (*m*/*z*): calcd for $C_{16}H_{18}O_2$ ($M^{+\bullet}$), 242.1307; found, 242.1288.

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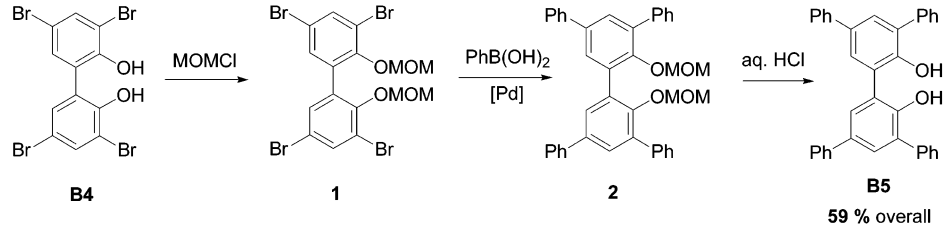
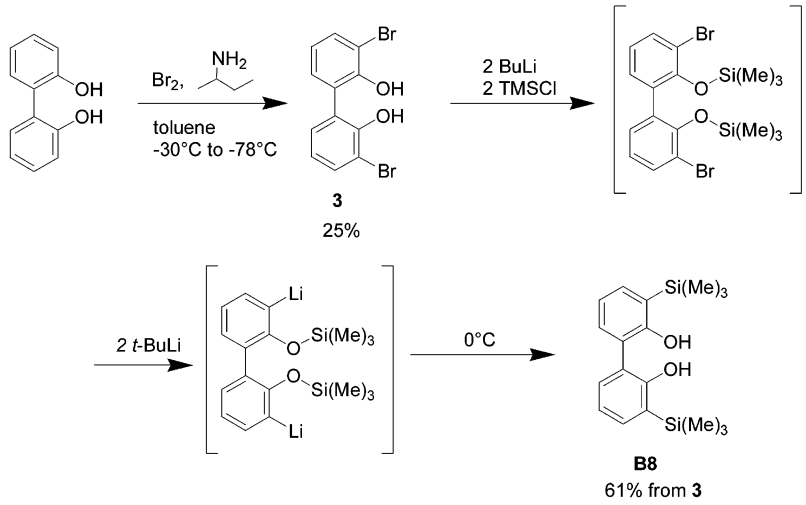
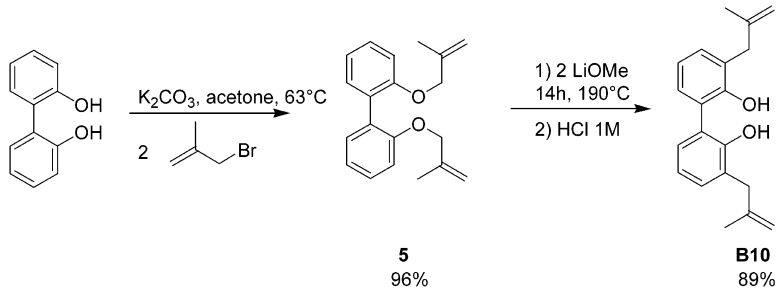
SCHEME 3. Synthesis of Biphenol B5



SCHEME 4. Synthesis of B8 by a Retro-Brook Rearrangement



SCHEME 5. Synthesis of B10 by Claisen Rearrangement



SCHEME 6. Enones and Nitroalkenes Tested in This Study

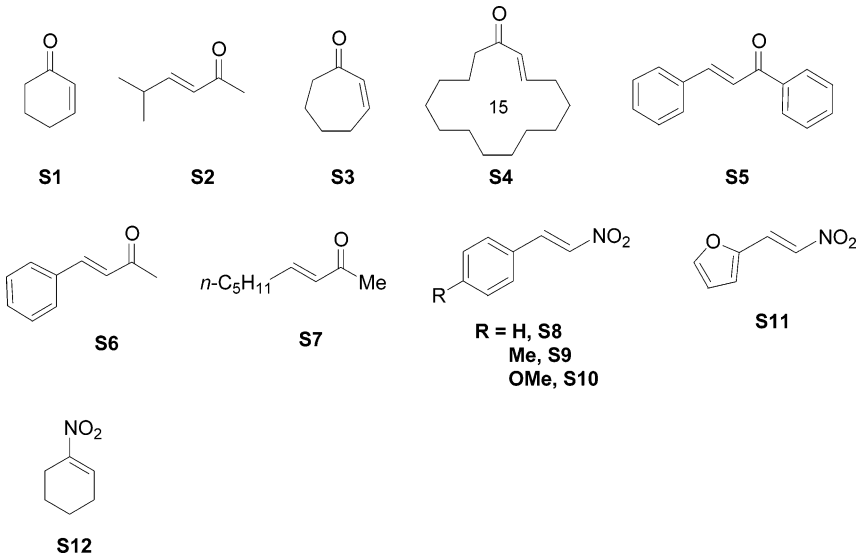
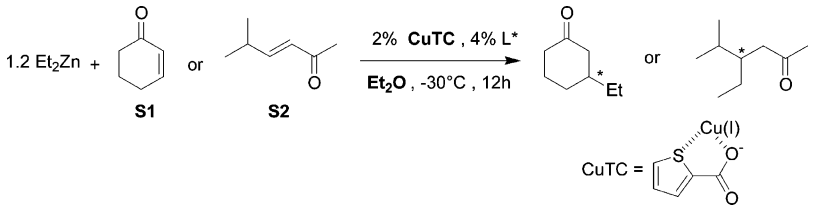


TABLE 1. Copper-Catalyzed Conjugate Addition of Diethylzinc onto S1 and S2



entry	ligand	config of the amine	conv,[a] ee,[b] absolute config S1	S2
1	**L1a**[c]	(*S*,*S*)	>99, 96, *R*[c]	>99, 65, *R*[c]
2	**L2a**[c]	(*S*,*S*)	>99, 99, *R*[c]	>99, 58, *R*[c]
3	**L3a**	(*S*,*S*)	>99, 84, *R*	16, 31, *R*
4	**L4a**	(*S*,*S*)	>99, 91, *R*	22, 25, *R*
5	**L5a**	(*R*,*R*)	>99, 90, *S*	40, 54, *S*
6	**L6a**	(*R*,*R*)	>99, 91, *S*	>99, 36, *S*
7	**L7a**	(*R*,*R*)	>99, 0	24, 0
8	**L8a**	(*R*,*R*)	84, 0	
9	**L9a**	(*R*,*R*)	>99, 96, *S*	>99, 88, *S*
10	**L10a**	(*R*,*R*)	>99, 89, *S*	>99, 95, *S*
11	**L11a**	(*R*,*R*)	>99, 89, *S*	>99, 94, *S*

[a] Determined by GC-MS. [b] Ee determined by chiral GC. [c] Taken from ref 6.

TABLE 2. Copper-Catalyzed Conjugate Addition of Diethylzinc onto Various Michael Acceptors

substrate	conv,[a] ee,[b] config L9a	L9b	L10a	L10b
S1	>99, 96, *S*	>99, 96, *S*	>99, 89, *S*	>99, 87, *S*
S2	>99, 88, *S*	80, 84, *S*	>99, 95, *S*	>99, 92, *S*
S3	97, 73, *S*	>99, 81, *S*	>99, 63, *S*	>99, 42, *S*
S4	>99, 60, (+)	>99, 30, (+)	>99, 80, (+)	76, 83, (+)
S5	90, 11, *S*	95, 40, *R*	>99, 37, *S*	57, 18, *R*
S6	>99, 93, *R*	30, 80, *R*	71, 89, *R*	16, 51, *R*
S7	>99, 35, (−)	>99, 30, (−)	>99, 75, (−)	>99, 88, (−)
S8	>99, 92, *R*	>99, 95, *R*	>99, 90, *R*	>99, 95, *R*
S9	>99, 95, *R*	>99, 95, *R*	>99, 91, *R*	>99, 94, *R*
S10		>99, 96, *R*	>99, 91, *R*	>99, 94, *R*
S11	>99, 91, (−)			
S12	>99, 86[c]			

[a] Determined by GC-MS. [b] Ee determined by chiral GC. [c] Trans major diastereomer obtained with a de of 89%.

3,3′,5,5′-Tetrachlorobiphenyl-2,2′-diol (B3).[8] 2,2′-Dihydroxybiphenyl (**B1**, 10.0 g, 54 mmol) was dissolved portionwise in 80 mL of SO_2Cl_2 (966 mmol) under nitrogen atmosphere. The solution was then stirred at room temperature. The reaction was followed by TLC (c-hexane/ethyl acetate, 8:2; R_f product = 0.43). After disappearance of the starting material, water was carefully added to quench the reaction. The mixture was extracted with ethyl acetate, and the organic layer was rinsed twice with water, dried over $MgSO_4$, and evaporated in vacuo. An orange solid was obtained, and recrystallization of the latter in hexane afforded 9.3 g of **B3** as a white powder (55%), mp 178−179 °C (lit. mp 174−175 °C).[8] ^{1}H NMR (400 MHz, DMSO-d_6), δ (ppm): 9.54 (s, 2H), 7.51 (d, 2H, J = 2.2 Hz), 7.16 (d, 2H, J = 2.2 Hz). ^{13}C NMR (100 MHz, DMSO-d_6), δ (ppm): 150.1, 129.9, 129.0, 128.0, 123.2, 122.5. IR ($CHCl_3$): ν 3533, 3254, 1566, 1461, 1398, 1324, 1286, 1222, 1167, 1074, 967, 866 cm^{-1}. HRMS (EI) (*m*/*z*): calcd for $C_{12}H_6{}^{35}Cl_4O_2$ ($M^{+\bullet}$), 321.9122; found, 321.9106. HRMS (EI) (*m*/*z*): calcd for $C_{12}H_6{}^{35}Cl_3{}^{37}ClO_2$, 323.9092; found, 323.9091.

3,3′,5,5′-Tetrabromo-2,2′-dihydroxybiphenyl (B4).[9] Bromine (13.8 mL, 268.6 mmol) was rapidly added to a solution of **B1** (10.08 g, 54.1 mmol) in 400 mL of methanol. After 1 h of stirring, the resulting precipitate was filtered through a sintered-glass funnel and washed sequentially with aqueous solutions of $NaHCO_3$, Na_2SO_3, and water. The resulting white powder was dissolved in acetone and dried over Na_2SO_4. Pure **B4** (20.5 g, 76%) was obtained by recrystallization in acetone, mp 300 °C (dec). ^{1}H NMR (500 MHz, DMSO-d_6), δ (ppm): 7.65 (d, 2H, J = 2.0 Hz), 7.33 (d, 2H, J = 2.0 Hz) 3.39 (brs, 2H). ^{13}C NMR (500 MHz, DMSO-d_6), δ (ppm): 155.9, 134.1, 133.0, 130.2, 118.8, 108.5. IR (film): ν 1613, 1541, 1441, 1385, 1255, 1220, 1182, 1154, 1090, 1055 cm^{-1}. MS (electrospray in acetone) did not give any rational signals.

3,3′,5,5′-Tetrabromo-2,2′-bis(methoxymethyloxy)biphenyl (1). A solution of **B4** (5.0 g, 10 mmol) in 40 mL of dry THF was slowly added, under nitrogen, to a suspension of NaH (0.717 g, 30 mmol) in 150 mL of dry THF. After 2 h, a solution of methoxymethyl chloride (2.3 mL, 2.41 g, 30 mmol) in 20 mL of dry THF was added to the mixture. The resulting suspension was stirred overnight under nitrogen, and water was then added to quench the reaction. The organic layer was washed with an aqueous solution of saturated $NaHCO_3$ and dried over Na_2SO_4. After removal of the solvent in vacuo and recrystallization in ethyl acetate, **1** was obtained as colorless crystals (4.31 g, 73%), mp 110 °C. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.75 (d, 2H, J = 2.2 Hz), 7.48 (d, 2H, J = 2.2 Hz), 4.87 (s, 4H), 3.07 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 151.7, 135.7, 134.3, 133.7, 118.8, 117.1, 99.7, 57.2. IR (film): ν 2940, 2833, 1541, 1475, 1450, 1434, 1409, 1385, 1277, 1240, 1201, 1150, 1104, 1080, 1053, 920 cm^{-1}. HRMS (EI) (*m*/*z*): calcd for $C_{16}H_{14}{}^{79}Br_2{}^{81}Br_2O_4$ ($M^{+\bullet}$), 589.7625; found, 589.7585.

3,3′,5,5′-Tetraphenyl-2,2′-bis(methoxymethyloxy)biphenyl (2). Freshly made $Pd[P(Ph)_3]_4$ (1.65 g, 1.43 mmol) was added under argon to a solution of **1** (4.21 g, 7.14 mmol) in

200 mL of 1,2-dimethoxyethane. This mixture was stirred at room temperature until all the palladium complex was dissolved, and then 50 mL of an aqueous 1 M solution of $NaHCO_3$ was added. After 30 min of stirring, phenylboronic acid (6.97 g, 57.1 mmol) in solution in a minimum of EtOH was added. This mixture was stirred over 70 h under argon at room temperature and was then heated to 100 °C over 24 h. The resulting brown mixture was allowed to cool to RT (room temperature) and was then filtered through a Celite pad. The solvent was evaporated in vacuo, and the product was dissolved in ethyl acetate. The organic layer was washed respectively with water, aqueous 5% NaOH, 2 N HCl, saturated $NaHCO_3$, and brine and was then dried over anhydrous $MgSO_4$. Evaporation of the solvent in vacuo followed by purification by chromatography (cyclohexane/ethyl acetate, 98:2) yielded 3.41 g (82%) of pure **2** as a white foam. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.84 (d, 2H, J = 2.6 Hz), 7.77−7.73 (m, 8H), 7.69 (d, 2H, J = 2.2 Hz), 7.54−7.49 (m, 8H), 7.44−7.39 (m, 4H), 4.62 (s, 4H), 2.81 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 152.0, 140.3, 139.9, 137.0, 136.1, 133.9, 130.0, 129.6, 129.2, 128.8, 128.3, 127.2, 127.0, 99.0, 56.3. IR (film): ν 3032, 2928, 2849, 1600, 1576, 1496, 1471, 1424, 1392, 1313, 1228, 1183, 1153, 1064, 954 cm^{-1}. HRMS (EI) (*m*/*z*): calcd for $C_{40}H_{34}O_4$ ($M^{+\bullet}$), 578.2457; found, 578.2474.

3,3′,5,5′-Tetraphenyl-2,2′-dihydroxybiphenyl (B5). A suspension of **2** (2.88 g, 4.98 mmol) in 300 mL of methanol was heated to 65 °C under nitrogen atmosphere. A 2 mL volume of fuming hydrochloric acid (37%) was then added. After 2 h of stirring under these conditions, the mixture was cooled to RT and an aqueous solution of saturated $NaHCO_3$ was added until no more CO_2 was evolved. The methanol was evaporated in vacuo, and the residue was dissolved in ethyl acetate, washed with an aqueous solution of saturated $NaHCO_3$, and dried over $MgSO_4$. Evaporation of the solvent gave **B5** as an orange foam (2.41 g, 99%), mp 194−197 °C. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.68 (d, 2H, J = 2.5 Hz), 7.65 (m, 10H), 7.53 (t, 4H, J = 7.9 Hz), 7.45 (m, 6H), 7.35 (t, 2H, J = 7.3 Hz), 5.95 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 149.3, 140.2, 137.3, 134.6, 130.0, 129.7, 129.4, 128.9, 128.8, 127.9, 127.0, 126.8, 125.5. IR (film): ν 3512, 3030, 1600, 1497, 1465, 1431, 1308, 1220, 1154, 1074 cm^{-1}. HRMS (EI) (*m*/*z*): calcd for $C_{36}H_{26}O_2$ ($M^{+\bullet}$), 490.1933; found, 490.1948.

3,3′-Dimethoxy-5,5′-dimethylbiphenyl-2,2′-diol (B6).[16] 2-Methoxy-4-methylphenol (0.3 mL, 2.4 mmol) was dissolved in 4 mL of freshly distilled dichloromethane. A catalytic amount of CuBrOH·TMEDA[12] (0.007 g, 0.0024 mmol) was added to this solution. The mixture was then stirred under pure oxygen atmosphere at room temperature over 4 days. An aqueous solution of 10% HCl was then added. The two layers were separated, and the organic layer was dried over $MgSO_4$. The solvent was removed in vacuo, affording an oil which was chromatographed on silica gel (cyclohexane/ethyl acetate, 8:2) affording 0.17 g of **B6** as a white powder (52%), mp 133−135 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 6.75 (s, 2H), 6.74 (s, 2H), 5.99 (s, 2H), 3.94 (s, 6H), 2.35 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 147.1, 140.3, 129.6, 124.3, 123.4, 111.3, 56.1, 21.2. IR ($CHCl_3$): ν 3536, 3027, 3019, 2967, 2949, 2861, 2401, 1602, 1492, 1464, 1416, 1361, 1329, 1282, 1256, 1230, 1210, 1190, 1143, 1089, 1053 cm^{-1}. HRMS (EI) (*m*/*z*): calcd for $C_{16}H_{18}O_4$ ($M^{+\bullet}$), 274.1205; found, 274.1210.

3,3′,5,5′-Tetra-*tert*-butylbiphenyl-2,2′-diol (B7).[17] 2,4-Di-*tert*-butylphenol (10 g, 48.5 mmol) was dissolved in 75 mL of freshly distilled dichloromethane. The resulting solution was cooled to 0 °C, and a catalytic amount of CuBrOH·TMEDA[12] (0.14 g, 0.49 mmol) was added in the solution. The air-opened mixture was stirred at this temperature over 3 days. An aqueous solution of 5% H_2SO_4 was then added at room temperature to quench the reaction. The two layers were separated, and the organic layer was dried over $MgSO_4$. The solvent was removed in vacuo, affording 9.77 g (93%) of **B7** as yellow crystals, mp 200−203 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.42 (d, 2H, J = 2.5 Hz), 7.14 (d, 2H, J = 2.5 Hz), 5.24 (s, 2H, OH), 1.48 (s, 18H), 1.35 (s, 18H). ^{13}C NMR (400 MHz, $CDCl_3$), δ (ppm): 149.8, 143.0, 136.2, 125.3, 124.9, 122.3, 35.2, 34.5, 31.7, 29.7. IR ($CHCl_3$): ν 3531, 2965, 2909, 2871, 1477, 1437, 1364, 1332, 1282, 1236, 1200, 1168, 1096 cm^{-1}. HRMS (EI) (*m*/*z*): calcd for $C_{28}H_{42}O_2$ ($M^{+\bullet}$), 410.3185; found, 410.3222.

3,3′-Dibromobiphenyl-2,2′-diol (3).[18] To a solution of 12.2 mL of *sec*-butylamine (120 mmol) in 300 mL of dry toluene in a mechanically stirred 500 mL flask at −30 °C was added dropwise bromine (3.2 mL, 62 mmol). The resulting orange suspension was cooled to an internal temperature of −78 °C. A solution of **B1** (5.6 g, 30 mmol) in 10 mL of dry THF was added dropwise. The resulting mixture was stirred for 6 h at −78 °C and quenched with 1 M HCl. The layers were separated, and the aqueous layer was extracted 3 times with diethyl ether. The combined organic layers were sequentially washed with an aqueous solution of 10% Na_2SO_3 and brine, dried over $MgSO_4$, and evaporated in vacuo. A purification by silica gel chromatography (pentane/diethyl ether, 7:3) afforded 2.625 g (25%) of **3** as a white powder, mp 127−130 °C (lit. mp 124−125 °C).[18] ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.58 (dd, 2H, J = 8.1, 1.5 Hz), 7.26 (dd, 2H, J = 7.6 Hz, 1.5 Hz), 6.96 (t, 2H, J = 8.1 Hz), 5.94 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 149.5, 132.4, 131.1, 125.6, 122.0, 111.4. IR ($CHCl_3$): ν 3512, 3018, 1439, 1328, 1215 cm^{-1}. HRMS (EI) (*m*/*z*): calcd for $C_{12}H_8{}^{79}Br^{81}BrO_2$ ($M^{+\bullet}$), 343.8871; found, 343.8862.[13]

3,3′-Bis(trimethylsilanyl)biphenyl-2,2′-diol (B8). 3,3′-Dibromobiphenyl-2,2′-diol (**3**) (2.26 g, 6.57 mmol) was dissolved in 26 mL of dry THF under argon atmosphere. The latter solution was cooled to −78 °C, and 7.6 mL (14.45 mmol, 2.2 equiv) of a *n*-BuLi solution (1.9 M in hexane) was added over 5 min followed by trimethylsilyl chloride (1.85 mL, 14.45 mmol). The temperature was slowly raised to 0 °C, and 9.65 mL (14.45 mmol, 2.2 equiv) of a solution of *t*-BuLi (1.5 M in hexane) was slowly added over 10 min. The temperature was then allowed to raise to RT, and the solution was stirred for about 1 h. An aqueous solution of saturated NH_4Cl was added to the reaction mixture. The resulting layers were separated, and the aqueous layer was extracted once using methylene chloride. The combined organic layers were dried over $MgSO_4$ and evaporated in vacuo. Purification on silica gel (c-Hex/AcOEt, 8:2) afforded 1.33 g (61%) of **B8** as a white powder, mp 93−96 °C (lit. mp 94−95 °C).[18] ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.49 (dd, 2H, J = 7.2, 1.5 Hz), 7.29 (dd, 2H, J = 7.2, 1.7 Hz), 7.08 (t, 2H, J = 7.3 Hz), 5.32 (s, 2H), 0.37 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 158.0, 136.0, 132.1, 126.9, 121.2, 121.1, −0.9. IR ($CHCl_3$): ν 3546, 3262, 2957, 2901, 1589, 1567, 1418, 1322, 1246, 1215, 1179, 1140, 1079, 968 cm^{-1}. HRMS (EI) (*m*/*z*): calcd for $C_{18}H_{26}O_2Si_2$ ($M^{+\bullet}$), 330.1471; found, 330.1476.

2,2′-Bis(allyloxy)biphenyl (4).[14] To a well-stirred refluxing (63 °C) solution of **B1** (5 g, 26.9 mmol) and allyl bromide (5.2 mL, 59.18 mmol) in acetone (100 mL) was added potassium carbonate (12 g, 86.08 mmol) slowly over 15 min. The reaction was followed by TLC. After 9 h of stirring, 10 g of K_2CO_3 (72.35 mmol) was added. After a total of 24 h of stirring, the reaction mixture was allowed to cool to RT and the suspension was filtered on Celite. The filtrate was concentrated in vacuo, and the resulting brown oil was dissolved in 100 mL of DCM, washed with an aqueous solution of 1 M NaOH, rinsed with water, dried on $MgSO_4$, concentrated in vacuo, and purified by silica gel chromatography (eluant: DCM) affording **4** (4.8 g) as a viscous oil (99%). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.32 (d, 2H, J = 7.1), 7.05 (td, 2H, J = 7.3, 1.0 Hz), 6.98 (d, 2H, J = 7.8 Hz), 6.0−5.9 (m, 2H), 5.20 (m, 4H), 3.53 (d, 4H, J

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= 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 156.0, 133.6, 131.5, 128.4, 120.4, 116.3, 112.3, 68.9. IR ($CHCl_3$): ν 3072, 3017, 2919, 2866, 1704, 1649, 1594, 1503, 1481, 1443, 1382, 1362, 1284, 1265, 1231, 1162, 1123, 1051, 1022 cm^{-1}. HRMS (EI) (*m*/*z*): calcd for $C_{18}H_{18}O_2$ ($M^{+\bullet}$), 266.1307; found, 266.1294.

3,3′-Diallylbiphenyl-2,2′-diol (B9).[14] 2,2′-Bis(allyloxy)-biphenyl **(4)** (1 g, 3.8 mmol) was heated (Kugelrohr 190 °C, ambient pressure) over 24 h under nitrogen atmosphere. The resulting brown oil was distilled in the same apparatus (200 °C 0.4 mmHg), and **B9** was obtained pure as a colorless oil (0.80 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.11 (dd, 2H J = 7.4, 1.5 Hz), 7.05 (dd, 2H, J = 7.6, 1.5 Hz), 6.90 (t, 2H, J = 7.3 Hz), 5.96 (ddt, 2H, J = 16.9, 10.1, 6.6 Hz), 5.36 (s, 2H), 5.05 (m, 4H), 3.39 (d, 4H, J = 6.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 151.2, 136.5, 130.6, 129.3, 127.3, 123.4, 121.3, 116.3, 35.0. IR ($CHCl_3$): ν 3545, 3082, 3013, 2914, 1360, 1639, 1587, 1447, 1326, 1231, 1215, 1195, 1167, 1115, 1074 cm^{-1}. HRMS (EI) (*m*/*z*): calcd for $C_{18}H_{18}O_2$ ($M^{+\bullet}$), 266.1307; found, 266.1299.

2,2′-Bis((2-methylallyl)oxy)biphenyl (5). To a well-stirred refluxing (63 °C) suspension of **B1** (2.79 g, 15 mmol), methallyl chloride (6.25 mL, 63.5 mmol), and NaI (0.2 g, 1.32 mmol) in acetone (30 mL) was added potassium carbonate (6.7 g, 48 mmol) slowly over 30 min. The reaction was followed by TLC (DCM, R_f product = 0.90, R_f of starting material = 0.28). After 99 h of stirring, the reaction mixture was allowed to cool to RT and the suspension was filtered on Celite. The filtrate was concentrated in vacuo, and the resulting brown oil was dissolved in 100 mL of DCM, washed with an aqueous solution of 1 M NaOH, rinsed with water, dried on $MgSO_4$, concentrated in vacuo, and purified by silica gel chromatography (eluant: DCM) affording **5** (3.55 g, 80%) as a viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.37−7.34 (m, 4H), 7.07 (t, 2H, J = 6.3 Hz), 6.98 (d, 2H, J = 1.0 Hz), 4.96 (s, 2H), 4.89 (s, 2H), 4.42 (s, 4H), 1.73 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 156.2, 141.1, 131.6, 128.4, 120.4, 112.2, 111.6, 71.8, 19.3. IR ($CHCl_3$): ν 3078, 3020, 3978, 2916, 2856, 1659, 1594, 1583, 1504, 1481, 1443, 1377, 1301, 1265, 1231, 1162, 1125, 1061, 1020 cm^{-1}. HRMS (EI) (*m*/*z*): calcd for $C_{20}H_{22}O_2$ ($M^{+\bullet}$), 294.1620; found, 294.1623.

3,3′-Bis(2-methylallyl)biphenyl-2,2′-diol (B10). 2,2′-Bis-((2-methylallyl)oxy)biphenyl **(5)** (2.65 g, 8.99 mmol) was mixed with lithium methoxide (0.725 g, 18 mmol) and heated in a Kugelrohr (190 °C, 1 atm) during 14 h under nitrogen atmosphere. The resulting salt is then hydrolyzed with aqueous 1 M HCl, extracted twice with diethyl ether, rinsed with water, and dried over sodium sulfate. The solvent is removed in vacuo to afford 2.35 g (89%) of **B10** as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.24 (dd, 2H, J = 7.8, 1.5 Hz), 7.21 (dd, 2H, J = 7.7, 1.5 Hz), 7.05 (t, 2H, J = 7.4 Hz), 5.77 (s, 2H), 4.95 (s, 2H), 4.87 (s, 2H), 3.51 (s, 4H), 1.84 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 154.6, 144.8, 131.0, 129.7, 126.7, 124.7, 121.2, 112.2, 39.2, 22.4. IR ($CHCl_3$): ν 3545, 3438, 3078, 3012, 2975, 2917, 1649, 1587, 1445, 1376, 1326, 1230, 1202, 1168, 1106, 1076 cm^{-1}. HRMS (EI) (*m*/*z*): calcd for $C_{20}H_{22}O_2$ ($M^{+\bullet}$), 294.1620; found, 294.1612.

3,3′-Dipropylbiphenyl-2,2′-diol (B11). B9 (1.548 g, 5.81 mmol) was dissolved in 20 mL of methanol, followed by an addition of palladium on charcoal (10%, 75 mg, 0.07 mmol). The system was purged five times with nitrogen and then five times with hydrogen. The reaction mixture was stirred over 2 h under 1 atm of hydrogen and then filtered on Celite. Solvent was evaporated in vacuo. Purification by flash chromatography on silica gel (c-hexane/ethyl acetate, 8:2) afforded 1.193 g (81%) of **B11** as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.22 (dd, 2H, J = 7.3, 1.5 Hz), 7.10 (dd, 2H, J = 7.6, 1.8 Hz), 6.98 (t, 2H, J = 7.6 Hz), 5.18 (s, 2H), 2.69 (t, 4H, J = 7.6 Hz), 1.70 (sext, 4H, J = 7.3 Hz), 1.02 (t, 6H, J = 7.3 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 151.3, 130.8, 130.1, 128.4, 122.3, 120.9, 32.4, 23.0, 14.2. IR ($CHCl_3$): ν 3545, 3295, 2963, 2934, 2873, 2361, 1587, 1448, 1326, 1218, 1168, 1118 cm^{-1}. HRMS (EI) (*m*/*z*): calcd for $C_{18}H_{22}O_2$ ($M^{+\bullet}$), 270.1620; found, 270.1619.

(*S*,*S*)-(5,7-Diox-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl)bis(1-phenylethyl)amine (L1a). Ligand **L1a** was prepared according to the literature.[5]

(*S*,*S*)-Bis(1-phenylethyl)(2,4,8,10-tetramethyl-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl)amine (L2a). Ligand **L1a** was prepared according to the literature.[5]

(*S*,*S*)-Bis(1-phenylethyl)(2,4,8,10-tetrachloro-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl)amine (L3a). Ligand **L3a** was prepared according to the general procedure (see Supporting Information) using bis[(*S*)-phenylethyl]amine (0.135 g, 0.60 mmol) and **B3** (0.192 g, 0.60 mmol). Purification by flash chromatography on neutral alumina using toluene as eluent gave **L3a** as a white foam in 45% yield (0.156 g). $[\alpha]_D$ = −493.0 (c = 0.8 in toluene). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.53 (d, 1H, J = 2.5 Hz), 7.48 (d, 1H, J = 2.5 Hz), 7.33 (d, 1H, J = 2.5 Hz), 7.29 (d, 1H, J = 2.5 Hz), 7.10−7.40 (m, 10H), 4.66 (m, 2H), 1.77 (d, 6H, J = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 147.0 (d), 145.8, 142.4, 132.3 (d), 130.9, 130.8, 130.3, 130.0, 129.8, 128.9, 128.7, 128.5, 128.2, 128.1, 127.9 (d), 126.9, 53.1, 53.0, 21.9. ^{31}P NMR (162 MHz, $CDCl_3$), δ (ppm): 148.6.

(*S*,*S*)-Bis(1-phenylethyl)(2,4,8,10-tetrabromo-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl)amine (L4a). Ligand **L4a** was prepared according to the general procedure usingbis-[(*S*)-phenylethyl]amine (0.104 g, 0.462 mmol) and **B4** (0.232 g, 0.462 mmol). Purification by flash chromatography on neutral alumina using toluene as eluent gave **L4a** as a white solid in 55% yield (0.192 g). $[\alpha]_D$ = −241.0 (c = 2.6 in toluene). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.84 (d, 1H, J = 2.5 Hz), 7.79 (d, 1H, J = 2.5 Hz), 7.51 (d, 1H, J = 2.2 Hz), 7.46 (d, 1H, J = 2.0 Hz), 7.18−7.13 (m, 10H), 4.66 (m, 2H), 1.80 (d, 6H, J = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 148.5, 147.4, 135.9, 135.6, 132.6 (d), 131.8, 131.0, 127.9, 126.9, 118.6, 117.6, 117.4, 116.2, 53.1, 53.0, 27.0. ^{31}P NMR (162 MHz, $CDCl_3$), δ (ppm): 147.8.

1,1′-(4,4′,6,6′-Tetraphenyl)biphenylposphinite-(*R*,*R*)-bis(phenylethyl)amidite (L5a). Ligand **L5a** was prepared according to the general procedure using bis[(*R*)-phenylethyl]-amine (0.14 g, 0.62 mmol) and **B5** (0.232 g, 0.462 mmol). Purification by flash chromatography on neutral alumina using toluene as eluent gave **L5a** as a white foam in 71% yield (0.323 g). $[\alpha]_D$ = +327° (c = 0.23 in toluene). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.80 (m, 4H), 7.69 (m, 4H), 7.48 (m, 7H), 7.38 (m, 4H), 7.29 (m, 5H), 7.18 (m, 2H), 7.02 (t, 2H, J = 7.3 Hz), 6.93 (t, 3H, J = 7.3 Hz), 6.74 (d, 3H, J = 7.0 Hz), 4.42 (s, 2H), 1.11 (d, 6H, J = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 147.7, 140.3, 140.3, 138.3, 137.8, 137.6, 136.8, 135.8, 134.2, 132.7, 131.8, 130.3, 129.7, 129.5, 129.3, 129.0, 128.8-(d), 128.5, 128.2, 128.1, 128.0, 127.6, 127.4, 127.3, 127.1, 127.0, 126.1, 125.2, 52.0, 29.7, 21.4. ^{31}P NMR (162 MHz, $CDCl_3$), δ (ppm): 145.9.

(*R*,*R*)-(4,8-Dimethoxy-2,10-dimethyl-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl)bis(1-phenylethyl)-amine (L6a). Ligand **L6a** was prepared according to the general procedure using bis[(*R*)-phenylethyl]amine (0.14 g, 0.62 mmol) and **B6** (0.17 g, 0.62 mmol). Purification by flash chromatography on neutral alumina using pure toluene as eluent gave **L6a** as a white foam in 31% yield (0.10 g). $[\alpha]_D$ = +201.3 (c = 1.17 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.22−7.24 (m, 4H), 7.13−7.05 (m, 6H), 6.87 (d, 2H, J = 7.3 Hz), 6.75 (d, 2H, J = 5.8 Hz), 4.62 (m, 2H), 3.93 (s, 3H), 3.75 (s, 3H), 2.38 (s, 6H), 1.75 (d, 6H, J = 7.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 151.8, 151.3, 143.4, 139.1, 139.0, 138.3, 133.8, 133.0, 131.9, 130.6, 128.9, 128.0, 127.5, 126.3, 121.9, 121.8, 113.1, 112.3, 56.4, 55.7, 53.0, 52.9, 21.9, 22.0, 21.5, 21.4. ^{31}P NMR (162 MHz, $CDCl_3$), δ (ppm): 145.9.

(*R*,*R*)-Bis(1-phenylethyl)(2,4,8,10-tetra-*tert*-butyl-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl)amine (L7a). Ligand **L7a** was prepared according to the general procedure using bis[(*R*)-phenylethyl]amine (0.25 g, 1.11 mmol) and **B7**

(0.456 g, 1.11 mmol). Purification by flash chromatography on neutral alumina using toluene as eluent gave **L7a** as a white foam in 30% yield (0.22 g). $[\alpha]_D = +171.8$ ($c = 1.08$ in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.50 (d, 1H, $J = 2.3$ Hz), 7.42 (d, 1H, $J = 2.3$ Hz), 7.21 (d, 1H, $J = 2.5$ Hz), 7.20−7.00 (m, 11H), 4.70−4.35 (brs, 2H), 1.65 (s, 9H), 1.38 (s, 18H), 1.14 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 168.2, 165.6, 147.9, 147.8(d), 145.8, 145.2, 140.2, 139.6, 132.9, 132.6 (d), 127.9, 126.9, 126.1, 124.1, 124.0, 35.6, 35.1, 34.6 (d), 31.8, 31.7, 31.6 (d), 30.8, 30.7, 19.9. ^{31}P NMR (162 MHz, $CDCl_3$), δ (ppm): 149.1.

(*R*,*R*)-(4,8-Bis(trimethylsilanyl)-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl)bis(1-phenylethyl)amine (L8a). Ligand **L8a** was prepared according to the general procedure using bis[(*R*)-phenylethyl]amine (0.225 g, 1.0 mmol) and **B8** (0.331 g, 1.0 mmol). Purification by flash chromatography on neutral alumina using toluene as eluent gave **L8a** as a white foam in 12% yield (0.07 g). $[\alpha]^{20}_D = +353.1$ ($c = 1.02$ in $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.54 (dd, 1H, $J = 7.3$, 1.5 Hz), 7.50 (dd, 1H, $J = 7.3$, 1.8 Hz), 7.41 (dd, 1H, $J = 7.6$, 1.5 Hz), 7.31 (dd, 1H, $J = 7.8$, 1.8 Hz), 7.25−7.19 (m, 4H), 7.11 (m, 8H), 4.54 (brs, 2H), 1.72−1.58 (m, 6H), 0.49 (s, 9H); 0.15 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 156.0 (d), 155.7, 155.6, 135.5, 135.1, 133.0, 131.7, 131.6, 131.0, 130.7(d), 128.4, 127.9, 127.8, 126.7, 124.0, 123.8, 53.2, 53.1, 1.1, 0.0, −0.1. ^{31}P NMR (162 MHz, $CDCl_3$), δ (ppm): 149.4.

(*R*,*R*)-(4,8-Diallyl-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl)bis(1-phenylethyl)amine (L9a). Ligand **L9a** was prepared according to the general procedure using bis[(*R*)-phenylethyl]amine (0.266 g, 1.18 mmol) and **B9** (0.315 g, 1.18 mmol). Purification by flash chromatography on neutral alumina using toluene as eluent, gave **L9a** as a white foam in 64% yield (0.39 g). $[\alpha]_D = +248.8$ ($c = 0.98$ in toluene). ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.40−7.00 (m, 16H), 6.10 (ddt, 1H, $J = 17.0$, 10.0, 6.8 Hz), 5.89 (ddt, 1H, $J = 17.1$, 10.0, 6.6 Hz), 5.23 (dq, 1H, $J = 17.1$, 1.7 Hz), 5.17 (dq, 1H, $J = 12.5$, 1.7 Hz), 5.03 (dq, 1H, $J = 13.4$, 1.7 Hz), 4.93 (dq, 1H, $J = 15.3$, 1.7 Hz), 4.71 (m, 2H), 3.92 (dd, 1H, $J = 15.1$, 6.6 Hz), 3.59 (dd, 1H, $J = 16.8$, 6.9 Hz), 3.23 (d, 2H, $J = 6.6$ Hz), 1.76 (d, 6H, $J = 6.4$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 137.1, 137.0, 133.2, 132.3, 130.0, 129.9, 128.9, 128.8, 128.7, 128.4, 128.2, 127.2, 124.8, 124.2, 116.6, 116.1, 53.0, 52.9, 35.9, 34.9. ^{31}P NMR (122 MHz, $CDCl_3$), δ (ppm): 145.5.

(*R*,*R*)-(4,8-Diallyl-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl)bis(1-phenylpropyl)amine (L9b). Ligand **L9b** was prepared according to the general procedure using bis[(*R*)-1-phenylpropyl)]amine (0.253 g, 1.0 mmol) and **B9** (0.266 g, 1.0 mmol). Purification by flash chromatography on neutral alumina using toluene as eluent gave **L9b** as a colorless oil in 19% yield (0.11 g). $[\alpha]_D = +219.1$ ($c = 1.08$ in $CHCl_3$). ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.36−6.95 (m, 16H), 6.07 (ddt, 1H, $J = 16.9$, 10.1, 6.8 Hz), 5.84(ddt, 1H, $J = 13.6$, 10.4, 6.5 Hz), 5.20 (dq, 1H, $J = 17.0$, 1.7 Hz), 5.16 (dq, 1H, $J = 10.0$, 1.8 Hz), 4.99 (dq, 1H, $J = 10.0$, 1.8 Hz), 4.85 (dq, 1H, $J = 17.0$, 1.9 Hz), 4.30 (m, 2H), 3.88 (dd, 1H, $J = 15.2$, 6.7 Hz), 3.59 (dd, 1H, $J = 15.3$, 6.8 Hz), 3.11 (dd, 1H, AB system, $J = 14.7$, 6.3 Hz), 3.07 (dd, 1H, AB system $J = 14.6$, 7.0 Hz), 2.34 (m, 2H), 2.10 (m, 2H), 0.81 (t, 6H, $J = 7.4$ Hz). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 149.4 (d), 148.8 (d), 136.7 (d), 132.8, 131.8, 131.7, 131.6, 130.8 (d), 129.6, 129.5, 129.0, 128.6, 128.5 (d), 128.2, 127.7, 127.6, 126.6, 125.3, 124.2, 123.8, 116.1, 115.6, 60.1, 35.3, 34.4, 29.7, 12.0, 11.8. ^{31}P NMR (203 MHz, $CDCl_3$), δ (ppm): 143.3.

(*R*,*R*)-[4,8-Bis(2-methylallyl)-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl]bis(1-phenylethyl)amine (L10a). Ligand **L10a** was prepared according to the general procedure using bis[(*R*)-phenylethyl]amine (0.225 g, 1.0 mmol) and **B10** (0.294 g, 1.0 mmol). Purification by flash chromatography on neutral alumina using toluene as eluent gave **L10a** as a colorless oil in 53% yield (0.290 g). $[\alpha]_D = +249.1$ ($c = 1.06$ in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.46−7.21 (m, 16H), 4.95 (s, 1H), 4.87 (s, 2H), 4.76 (brs, 2H), 4.55 (s, 1H), 4.05 (d, 1H, $J = 14.5$ Hz), 3.50 (d, 1H, $J = 14.5$ Hz), 3.30 (d, 1H, AB system, $J = 15.6$ Hz), 3.23 (d, 1H, AB system, $J = 15.6$ Hz), 1.91−1.73 (m, 12H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 150.0, 149.9, 149.2(d), 144.8, 144.5, 132.3, 132.2, 132.1, 132.0, 131.5, 130.8(d), 130.3, 130.2, 128.7, 128.6, 128.2, 127.9, 126.8, 124.3, 123.7, 112.0, 111.7, 52.5, 52.4, 39.5, 38.1, 22.9, 22.8, 22.6. ^{31}P NMR (122 MHz, $CDCl_3$), δ (ppm): 145.0.

(*R*,*R*)-[4,8-Bis(2-methylallyl)-5,7-dioxa-6-phosphadibenzo[*a*,*c*]cyclohepten-6-yl]bis(1-phenylethyl)amine (L10b). Ligand **L10b** was prepared according to the general procedure using bis[(*R*)-1-phenyl-propyl)]amine (0.253 g, 1.0 mmol) and **B10** (0.294 g, 1.0 mmol). Purification by flash chromatography on neutral alumina using toluene as eluent gave **L10b** as a colorless oil in 32% yield (0.326 g). $[\alpha]_D = +215.4$ ($c = 0.81$ in $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.26−6.99 (m, 16H), 4.75 (d, 1H, $J = 0.4$ Hz), 4.66 (d, 1H, $J = 0.6$ Hz), 4.65 (d, 1H, $J = 0.4$ Hz), 4.31 (s, 1H), 4.19 (brs, 2H), 3.84 (d, 1H, $J = 8.7$ Hz), 3.32 (d, 1H, $J = 8.7$ Hz), 3.01 (d, 1H, AB system, $J = 9.3$ Hz), 2.95 (d, 1H, AB system, $J = 9.4$ Hz), 2.25−1.80 (m, 4H), 1.67 (s, 3H), 1.48 (s, 3H), 0.90−0.25 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 149.8, 149.7, 149.1 (d), 144.9, 144.6, 132.2 (d), 131.9 (d), 131.3, 130.8 (d), 130.1, 128.6, 128.5, 127.7, 126.6, 124.1, 123.5, 111.8, 111.6, 50.7, 39.2, 37.8, 29.7, 22.7, 22.4, 11.8. ^{31}P NMR (122 MHz, $CDCl_3$), δ (ppm): 142.6.

(*S*,*S*)-(4,8-Dipropyl-5,7-dioxa-6-phosphadibenzo[*a*,*c*]-cyclohepten-6-yl)bis(1-phenylethyl)amine (L11a). Ligand **L11a** was prepared according to the general procedure using bis[(*S*)-phenylethyl]amine (0.834 g, 3.7 mmol) and **B11** (1.00 g, 3.7 mmol). Purification by flash chromatography on neutral alumina using toluene as eluent gave **L11a** as a colorless oil in 53% yield (1.034 g). $[\alpha]_D = -241.64$ ($c = 1.05$ in toluene). ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.36−7.11 (m, 16H), 4.70 (brs, 2H), 3.26−3.19 (m, 1H), 2.74−2.67 (m, 1H), 2.53 (t, 2H, $J = 7.8$ Hz), 1.83−1.57 (m, 10H), 1.08 (t, 2H, $J = 7.3$ Hz), 0.93 (t, 2H, $J = 7.3$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 150.0, 149.9, 149.2 (d), 144.8, 144.5, 132.3, 132.2, 132.1, 132.0, 131.5, 130.8 (d), 130.3, 130.2, 128.7, 128.6, 128.2, 127.9, 126.8, 124.3, 123.7, 112.0, 111.7, 52.5, 52.4, 39.5, 38.1, 22.9, 22.8, 22.6. ^{31}P NMR (162 MHz, $CDCl_3$), δ (ppm): 145.0.

3-Ethylcyclohexanone. Enantiomer separation by chiral GC: Lipodex E (25 m, H_2, 50 cm·s^{-1}). *T*: 60 °C. $R_t = 24.7$ min for enantiomer (*R*), and $R_t = 28.1$ min for enantiomer (*S*).

3-Ethylcycloheptanone. Enantiomer separation by chiral GC: Lipodex E (25 m, H_2, 50 cm·s^{-1}). *T*: 60 °C. $R_t = 45.6$ min for enantiomer (*S*), and $R_t = 47.2$ min for enantiomer (*R*).

3-Ethylcyclopentadecanone. Enantiomer separation by chiral GC: Hydrodex β-3P, (25 m, H_2, 50 cm·s^{-1}). *T*: 140 °C, 60 min; 1°/min. $R_t = 56.9$ min for enantiomer (−)-(*R*), and $R_t = 58.2$ min for enantiomer (+)-(*S*).

4-Ethylnonan-2-one. Enantiomer separation by chiral GC: Lipodex E (25 m, H_2, 50 cm·s^{-1}). *T*: 60 °C; 1°/min. $R_t = 17.8$ min for enantiomer (*S*), and $R_t = 18.3$ min for enantiomer (*R*).

4-Phenylhexan-2-one. Enantiomer separation by chiral GC: Lipodex E (25 m, H_2, 50 cm·s^{-1}). *T*: 75 °C. $R_t = 39.9$ min for enantiomer (*S*), and $R_t = 41.8$ min for enantiomer (*R*).

1,3-Diphenylpentan-2-one. Enantiomer separation by chiral SFC: Chiralcel OD-H, 0.25 m, 2% MeOH for 6 min, 3% until 15 min, 2 mL·min^{-1}. $R_t = 5.6$ min for enantiomer (+)-(*S*), and $R_t = 6.3$ min for enantiomer (−)-(*R*).

4-Ethyl-5-methylhexanone. Enantiomer separation by chiral GC: Lipodex E (25 m, H_2, 50 cm·s^{-1}). *T*: 60 °C; 1°/min. $R_t = 7.8$ min for enantiomer (*R*), and $R_t = 8.3$ min for enantiomer (*S*).

(1-(Nitromethyl)propyl)benzene. Enantiomer separation: Lipodex E (25 m, H_2, 50 cm·s^{-1}). *T*: 100 °C; 1 °C/min. $R_t = 17.0$ min for enantiomer (*S*), and $R_t = 17.6$ min for enantiomer (*R*).

1-Methyl-4-(1-(nitromethyl)propyl)benzene. Enantiomer separation by chiral GC: Lipodex E (25 m, H_2, 50 cm·s^{-1}). *T*: 100 °C; 1°/min. $R_t = 19.2$ min for enantiomer (*S*), and $R_t = 19.5$ min for enantiomer (*R*).

1-Methoxy-4-(1-(nitromethyl)propyl)benzene. Enantiomer separation by chiral SFC: Chiralcel OD-H, 250 mm, 2% MeOH 6 min, 3% until 15 min, 2 mL·min^{-1}. R_t = 3.6 min for enantiomer (*R*), and R_t = 3.9 min for enantiomer (*S*).

2-(1-(Nitromethyl)propyl)furan. Enantiomer separation by chiral GC: Hydrodex β-3P (25 m, H_2, 50 cm·s^{-1}). *T*: 100 °C. R_t = 11.2 min for enantiomer (−), and R_t = 11.6 min for enantiomer (+).

1-Ethyl-2-nitrocyclohexane. Enantiomer separation by chiral GC: Lipodex E (25 m, H_2, 50 cm·s^{-1}). *T*: 60 °C; 3°/min. R_t = 16.16 (trans), 16.37 (cis), 16.78 (cis), and 17.12 min (trans).

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Supporting Information Available: Spectral data for all compounds and general procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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