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Novel MOP-type H_8-binaphthyl monodentate phosphite ligands and their applications in transition metal-catalyzed asymmetric 1,4-conjugate additions and hydroformylations

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ABSTRACT

A new series of monodentate phosphites based on the rigid, axially chiral monoesterified H_8-BINOL, which are easy to prepare from the readily accessible phosphorylating reagents (S_a)- or (R_a)-1,1′-binaphthyl-2,2′-diylchlorophosphite and (S_a)- or (R_a)-1,1′-H_8-binaphthyl-2,2′-diylchlorophosphite, have been synthesized. All ligands were purified on a silica gel column under a nitrogen atmosphere with moderate yields, and were white solids and air-stable at room temperature. These ligands afforded good to excellent enantioselectivities in the Cu-catalyzed 1,4-conjugate addition of 2-cyclohexenone with nucleophiles Et_2Zn (96% ee) and with Ph_2Zn (65% ee), 2-cyclopentenone with Et_2Zn (95% ee), 2-cycloheptenone with Et_2Zn (76% ee), and 5,6-dihydro-2*H*-pyran-2-one with Et_2Zn (90% ee). In the Rh-catalyzed asymmetric hydroformylation of styrene, these ligands showed a chemoselectivity of >99% in aldehydes, and a satisfactory branched over linear ratio (96/4). Moreover, the sense of the enantiodiscrimination of the products was mainly determined by the configuration of the BINOL-based or H_8-BINOL-based phosphocycle.

1. Introduction

The synthesis of chiral compounds plays a vital role in important areas such as pharmaceuticals, fine chemicals, agrochemicals, and natural product chemistry.[1] Asymmetric catalysis using transition-metal/ligand complexes has emerged as the basis for a vast array of stereoselective reactions and has become a powerful tool for producing enantiopure compounds in modern synthetic chemistry.[2] In this respect, the Cu-catalyzed asymmetric 1,4-conjugate addition and the Rh-catalyzed asymmetric hydroformylation are two types of powerful reactions for the construction of enantioriched synthons for both biologically active and natural compounds.[3]

Key to these reactions has been the design of simple and highly efficient chiral ligands to achieve maximum chiral multiplication. To date, many chiral trivalent phosphorus compounds, such as phosphines, phosphites and phosphoromidites, have been synthesized. Among the above mentioned ligands, phosphites are extremely attractive because they can be simply synthesized from readily accessible precursors, exhibit high resistance to oxidative destruction, and are inexpensive.[4] Five types of monodentate phosphite ligands $\mathbf{L_a}$–$\mathbf{L_e}$ (Fig. 1) have been applied in the Cu-catalyzed asymmetric 1,4-conjugate addition of 2-cyclohexenone with Et_2Zn, and afforded 30% ee,[5] 96% ee,[6] 19% ee,[6,7] 83% ee,[8] 57% ee,[9] respectively. However, the enantioselectivities in analogous Cu-catalyzed asymmetric 1,4-conjugate additions of organozinc to 2-cyclopentenone and 2-cycloheptenone were disappointingly low. Thus, it is desirable to search for simple and efficient phosphite ligands, which overcome the limitations of substrate specificity. In the Rh-catalyzed asymmetric hydroformylation, there are only a few reports concerning monodentate phosphite so far, because the use of monodentate phosphorus donor usually provides only poor to moderate enantioselectivities.[7] For instance, ligand $\mathbf{L_f}$ (Fig. 1) gave 38% ee, 43% ee and 8% ee in the Rh-catalyzed asymmetric hydroformylation of styrene, allyl cyanide and vinyl acetate respectively.[10] The search for efficient chiral monodentate phosphite ligands in terms of high enantioselectivity remains one of the most important goals in the Rh-catalyzed asymmetric hydroformylation.

In 2007, Lyubimov et al. used readily accessible *O*-methyl-BINOL as starting materials, and synthesized MOP-type binaphthyl monodentate phosphite $\mathbf{L_g}$ (Fig. 2). This ligand was employed in the Pd-catalyzed allylic substitution of (*E*)-1,3-diphenylallyl acetate

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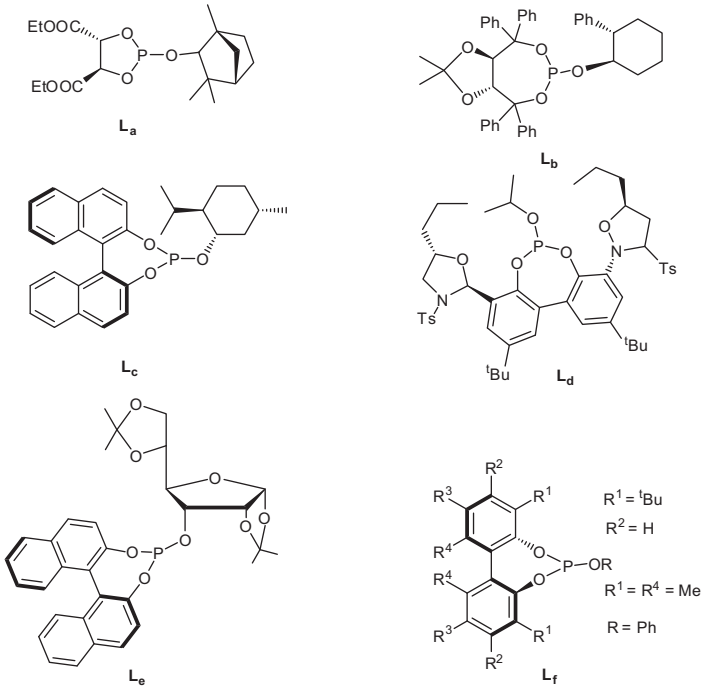


Figure 1. Monodentate phosphite ligands for the Cu-catalyzed asymmetric 1,4-conjugate addition and the Rh-catalyzed asymmetric hydroformylation.

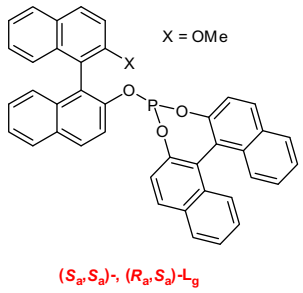


Figure 2. Structure of MOP-type binaphthyl monodentate phosphite.

with sodium *p*-toluenesulfinate (99% ee), pyrrolidine (97% ee), dipropylamine (95% ee), dimethyl malonate (99% ee), in the Pd-catalyzed deracemization of ethyl (*E*)-1,3-diphenylallyl carbonate with 96% ee, and in the Rh-catalyzed hydrogenation of dimethyl itaconate with 90% ee.[11] Inspired by this excellent work, we undertook phosphite ligand development and focused on MOP-type binaphthyl monodentate phosphite. The partially hydrogenated H_8-binaphthyl scaffold is also of interest in addition to the chiral element from the binaphthyl skeleton. Chiral phosphorus donors based on the H_8-binaphthyl moiety have recently received considerable attention.[12] The improved stereo-communication in H_8-BINOL compared to BINOL in enantioselective transformations has been explicitly highlighted.[13] Herein, we describe that the synthesis of novel monodentate phosphites (Scheme 1) using monoesterified H_8-BINOL as well as their catalytic performance in the Cu-catalyzed asymmetric 1,4-conjugate addition and the Rh-catalyzed asymmetric hydroformylation. The results indicated that these ligands gave 95% ee and 96% ee in the Cu-catalyzed asymmetric 1,4-conjugate addition of organozincs to 2-cyclopentenone and 2-cyclohexenone respectively, and provided high chemoselectivity (>99%) and regioselectivity (96/4, b/n) in the Rh-catalyzed asymmetric hydroformylation of styrene.

2. Results and discussion

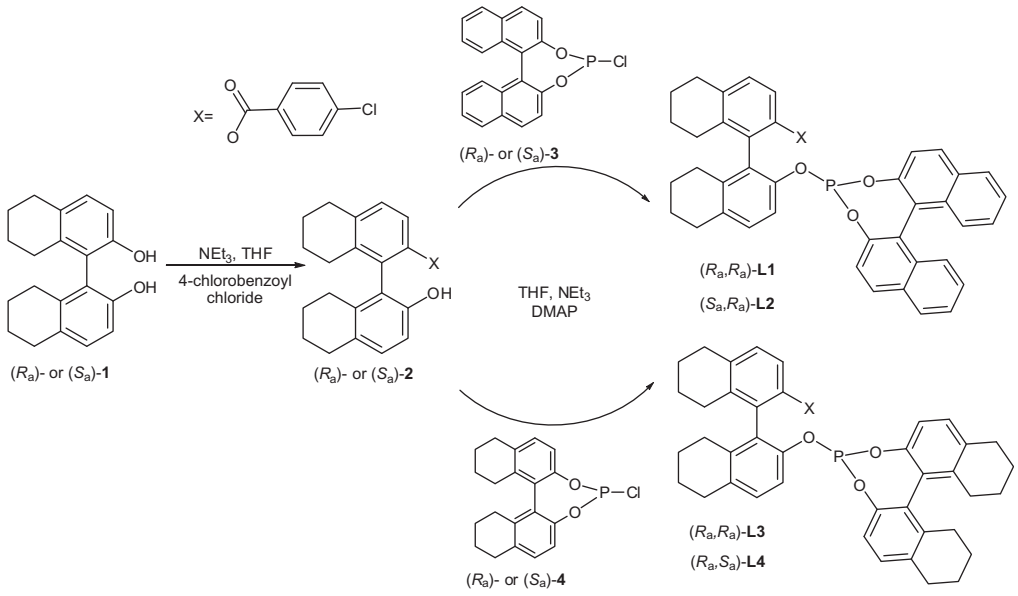
2.1. Synthesis of monodentate phosphate ligands

The novel MOP-type monodentate phosphites were easily obtained by direct phosphorylation of (R_a)- or (S_a)-2′-hydroxy-5,5′,6,6′,7,7′,8,8′-octahydro-[1,1′-binaphthalen]-2-yl 4-chlorobenzoate **2** in the presence of NEt_3 in THF (Scheme 1). All of the ligands were purified on a silica gel column under a nitrogen atmosphere with moderate yields, and were white solids and air-stable at room temperature. The ^{31}P, ^{1}H and ^{13}C NMR spectra were consistent with the expectation for these ligands.

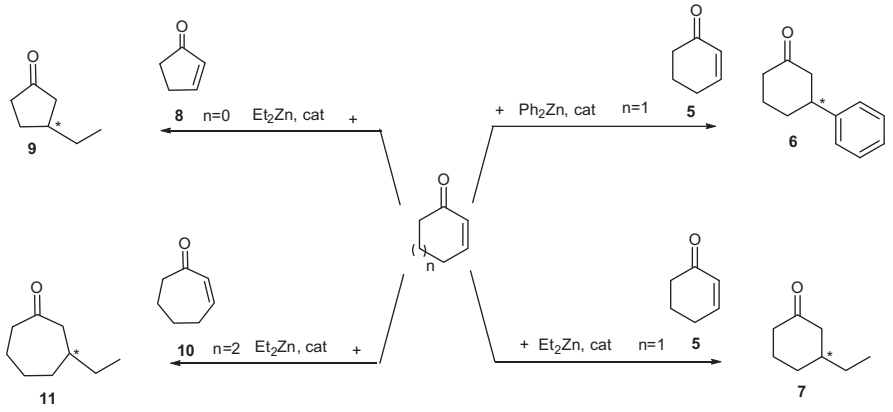
2.2. Cu-catalyzed asymmetric 1,4-conjugate addition

For the Cu-catalyzed asymmetric 1,4-conjugate addition (Scheme 2), we choose 2-cyclohexenone **5** as the substrate, which has been performed with ligands **L_a**–**L_e**. In the Cu-catalyzed asymmetric 1,4-conjugate addition of 2-cyclohexenone with Ph_2Zn, ligand (S_a,R_a)-**L2** shown good activity and enantioselectivity (68% yield, 65% ee, Table 1, entries 3 and 4). Its diastereoisomer (R_a, R_a)-**L1** afforded product **6** with low enantioselectivity (43% ee, Table 1, entries 1–2). Compounds(R_a,R_a)-**L3** and (R_a,S_a)-**L4** gave 30% and 35% ee, respectively, and afforded product **6** with the opposite absolute configuration (Table 1, entries 5–8). The ligands with *O*-methyl-BINOL (S_a,S_a)-L_g and (R_a,S_a)-L_g demonstrated moderate enantioselectivity up to 45% ee and 55% ee, respectively (Table 1, entries 9–12). Moreover, it was found that the absolute configuration of product **6** depended on the configuration of the BINOL-based and H_8-BINOL-based phosphocycle (Table 1, entries 1–12). Rather unexpectedly, these ligands gave no conversion in the Cu-catalyzed asymmetric 1,4-conjugate addition of 2-cyclopentenone **8** and 2-cycloheptenone **10** with Ph_2Zn as nucleophiles. When Me_2Zn was used in the reaction instead of Ph_2Zn, these ligands showed very low activity under the same conditions.

As is well known, compared with Ph_2Zn and Me_2Zn, Et_2Zn is a more effective organozinc reagent in the Cu-catalyzed asymmetric



Scheme 1. The synthesis of the novel MOP-type monodentate phosphites.



Scheme 2. The Cu-catalyzed asymmetric conjugate addition.

Table 1
The Cu-catalyzed enantioselective conjugate addition of diphenylzinc to 2-cyclohexenone[a]

Entry	Catalyst	L/Cu	Conversion (%)[b]	Yield.[b]	ee (%)[b]
1	$(CuOTf)_2{\cdot}C_6H_6/(R_a,R_a)$-**L1**	1	55	30	33 (*R*)
2	$(CuOTf)_2{\cdot}C_6H_6/(R_a,R_a)$-**L1**	2	60	41	43 (*R*)
3	$(CuOTf)_2{\cdot}C_6H_6/(S_a,R_a)$-**L2**	1	87	60	46 (*R*)
4	$(CuOTf)_2{\cdot}C_6H_6/(S_a,R_a)$-**L2**	**2**	**89**	**68**	**65 (*R*)**
5	$(CuOTf)_2{\cdot}C_6H_6/(R_a,R_a)$-**L3**	1	44	33	26 (*R*)
6	$(CuOTf)_2{\cdot}C_6H_6/(R_a,R_a)$-**L3**	2	48	38	30 (*R*)
7	$(CuOTf)_2{\cdot}C_6H_6/(R_a,S_a)$-**L4**	1	50	40	18 (*S*)
8	$(CuOTf)_2{\cdot}C_6H_6/(R_a,S_a)$-**L4**	2	56	45	35 (*S*)
9	$(CuOTf)_2{\cdot}C_6H_6/(S_a,S_a)$-$\mathbf{L_g}$	1	46	35	38 (*S*)
10	$(CuOTf)_2{\cdot}C_6H_6/(S_a,S_a)$-$\mathbf{L_g}$	2	58	50	45 (*S*)
11	$(CuOTf)_2{\cdot}C_6H_6/(R_a,S_a)$-$\mathbf{L_g}$	1	54	38	40 (*S*)
12	$(CuOTf)_2{\cdot}C_6H_6/(R_a,S_a)$-$\mathbf{L_g}$	2	62	49	55 (*S*)

[a] Reaction conditions: $(CuOTf)_2{\cdot}C_6H_6$ (0.005 mmol), ligand (0.005–0.010 mmol), Ph_2Zn (1.2 mol/L in toluene, 0.6 mmol), solvent: THF (2.5 mL), temperature: 0 °C, 24 h.
[b] Isolated yield, conversion, the ee of **6** was determined by HPLC (Daicel Chiralcel AD-H, hexane/*i*-PrOH = 99/1, 0.5, mL/min at 20 °C, detected at 209 nm.

1,4-conjugate addition. We turned our attention to the applications of these ligands in the Cu-catalyzed asymmetric 1,4-conjugate addition with Et_2Zn as nucleophiles. In the Cu-catalyzed asymmetric 1,4-conjugate addition of 2-cyclohexenone with Et_2Zn, (R_a,R_a)-**L1** gave 3-ethylcyclohexanone **7** in 30% yield and with 73% ee (Table 2, entry 1). (R_a,R_a)-**L3** gave 38% yield and with 60% ee (Table 2, entry 3). 48% yield and 69% ee were gained when using (R_a,S_a)-**L4** as the ligand (Table 2, entry 4). The use of (S_a,R_a)-**L2** showed 88% yield and with 83% ee (Table 2, entry 2). (S_a,S_a)-L_g and (R_a,S_a)-L_g showed moderate yield and enantioselectivity (46%

Table 2
The Cu-catalyzed enantioselective conjugate addition of diethylzinc to cyclic enones[a]

Entry	Catalyst	L/Cu	*T* (°C)	Solvent	Conversion (%)[b]	Yield[b]	ee (%)[c]
2-Cyclohexenone							
1	$(CuOTf)_2{\cdot}C_6H_6/(R_a,R_a)$-**L1**	2	0	Et_2O	42	30	73 (*R*)
2	$(CuOTf)_2{\cdot}C_6H_6/(S_a,R_a)$-**L2**	2	0	Et_2O	94	88	83 (*R*)
3	$(CuOTf)_2{\cdot}C_6H_6/(R_a,R_a)$-**L3**	2	0	Et_2O	49	38	60 (*R*)
4	$(CuOTf)_2{\cdot}C_6H_6/(R_a,S_a)$-**L4**	2	0	Et_2O	57	48	69 (*S*)
5	$(CuOTf)_2{\cdot}C_6H_6/(S_a,S_a)$-**L$_g$**	2	0	Et_2O	52	46	59 (*S*)
6	$(CuOTf)_2{\cdot}C_6H_6/(R_a,S_a)$-**L$_g$**	2	0	Et_2O	61	58	66 (*S*)
7	$CuTc/(S_a,R_a)$-**L2**	2	0	Et_2O	42	25	37 (*R*)
8	$Cu(acac)_2/(S_a,R_a)$-**L2**	2	0	Et_2O	70	56	50 (*R*)
9	$Cu(OTf)_2/(S_a,R_a)$-**L2**	2	0	Et_2O	71	63	54 (*R*)
10	$CuCl/(S_a,R_a)$-**L2**	2	0	Et_2O	16.	9	35 (*R*)
11	$CuBr/(S_a,R_a)$-**L2**	2	0	Et_2O	21	4	29 (*R*)
12	$CuF_2/(S_a,R_a)$-**L2**	2	0	Et_2O	18	5	28 (*R*)
13	$(CuOTf)_2{\cdot}C_6H_6/(S_a,R_a)$-**L2**	2	0	Toluene	56	47	55 (*R*)
14	$(CuOTf)_2{\cdot}C_6H_6/(S_a,R_a)$-**L2**	2	0	CH_2Cl_2	22	17	15 (*R*)
15	$(CuOTf)_2{\cdot}C_6H_6/(S_a,R_a)$-**L2**	1	0	Et_2O	98	93	78 (*R*)
16	$(CuOTf)_2{\cdot}C_6H_6/(S_a,R_a)$-**L2**	0.5	0	Et_2O	92	84	75 (*R*)
17[d]	**$(CuOTf)_2{\cdot}C_6H_6/(S_a,R_a)$-L2**	**2**	**−20**	**Et_2O**	**>99**	**95**	**96 (*R*)**
18	$(CuOTf)_2{\cdot}C_6H_6/(S_a,R_a)$-**L2**	2	20	Et_2O	>99	92	90 (*R*)
2-Cyclopentenone							
19[d]	$(CuOTf)_2{\cdot}C_6H_6/(R_a,R_a)$-**L1**	2	−20	Et_2O	48	37	73 (*R*)
20[d]	**$(CuOTf)_2{\cdot}C_6H_6/(S_a,R_a)$-L2**	**2**	**−20**	**Et_2O**	**30**	**27**	**95 (*R*)**
21[d]	$(CuOTf)_2{\cdot}C_6H_6/(R_a,R_a)$-**L3**	2	−20	Et_2O	46	36	57 (*R*)
22[d]	$(CuOTf)_2{\cdot}C_6H_6/(R_a,S_a)$-**L4**	2	−20	Et_2O	58	49	64 (*S*)
23[d]	$(CuOTf)_2{\cdot}C_6H_6/(S_a,S_a)$-**L$_g$**	2	−20	Et_2O	51	40	58 (*S*)
24[d]	$(CuOTf)_2{\cdot}C_6H_6/(R_a,S_a)$-**L$_g$**	2	−20	Et_2O	56	47	62 (*S*)
2-Cycloheptenone							
25[d]	$(CuOTf)_2{\cdot}C_6H_6/(R_a,R_a)$-**L1**	2	−20	Et_2O	35	26	57 (*R*)
26[d]	**$(CuOTf)_2{\cdot}C_6H_6/(S_a,R_a)$-L2**	**2**	**−20**	**Et_2O**	**50**	**45**	**76 (*R*)**
27[d]	$(CuOTf)_2{\cdot}C_6H_6/(R_a,R_a)$-**L3**	2	−20	Et_2O	40	31	40 (*R*)
28[d]	$(CuOTf)_2{\cdot}C_6H_6/(R_a,S_a)$-**L4**	2	−20	Et_2O	47	38	44 (*S*)
29[d]	$(CuOTf)_2{\cdot}C_6H_6/(S_a,S_a)$-**L$_g$**	2	−20	Et_2O	51	42	54 (*S*)
30[d]	$(CuOTf)_2{\cdot}C_6H_6/(R_a,S_a)$-**L$_g$**	2	−20	Et_2O	58	56	68 (*S*)

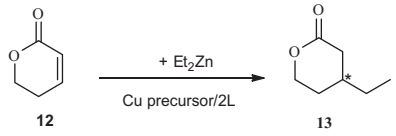
[a] Reaction conditions: Cu precursor (0.005 mmol), ligand (0.0025–0.01 mmol), Et_2Zn (1.0 mol/L in hexane, 0.6 mmol), substrate (0.25 mmol), solvent (4 mL), 0 °C, 4 h.
[b] The data on conversion and yield were determined by GC using dodecane as internal standard with a SE-30 column (30 m × 0.32 mm I.D.).
[c] The enantiomeric excess of **7** and **9** was determined by GC equipped with a Chiraldex A-TA column (50 m × 0.25 mm I.D.). The ee of **11** was determined by GC equipped with a CP-ChirasilDex CB (25 m × 0.25 mm I.D.). The absolute configuration of yjr product was determined by comparison with yjr authentic sample.
[d] Reaction time: 12 h.

yield and 59% ee, 58% yield and 66% ee, respectively, Table 2, entries 5 and 6). It is interesting to note that the sense of enantioselectivity was also determined by the configuration of the BINOL-based and H_8-BINOL-based phosphocycle .

The enantiomeric excess depends significantly on the copper salt and solvent. In all cases, $(CuOTf)_2{\cdot}C_6H_6$ was the optimal copper salt. In comparison to $(CuOTf)_2{\cdot}C_6H_6$, the reaction using CuTc as a catalytic precursor significantly decreased the enantioselectivity with 37% ee (Table 2, entry 7). The use of a Cu(II) salt, such as $Cu(acac)_2$ or $Cu(OTf)_2$ resulted in almost the same enantioselectivity with a slightly lower yield (Table 2, entry 8–9). The Cu precatalysts such as CuCl, CuBr and CuF_2 did not work efficiently (only 9%, 4% and 5% yield respectively, Table 2, entries 10–12). The reaction proceeded with significantly higher enantioselectivity in the coordinating solvent Et_2O (Table 2, entry 2) compared with non-coordinating solvents toluene and CH_2Cl_2 (Table 2, entries 13 and 14). On the contrary, the L/Cu molar ratio has basically no effect on enantioselectivity. The reaction with a L/Cu ratio of 0.5:1, 1:1, and 2:1 occurred in a similar manner to afford the corresponding adduct in 75% ee, 78% ee, and 83% ee, respectively (Table 2, entries 2, 15, and 16). One can conclude that the same catalytic active species were probably formed under these reaction conditions. In the Cu-catalyzed asymmetric 1,4-conjugate addition, it is known that the reaction temperature has an important impact on the enantioselectivity. Therefore, by employing (S_a,R_a)-**L2**, this parameter was investigated. We observed that −20 °C was the optimal temperature for the enantioselectivity; (S_a,R_a)-**L2** showed up to 99% conversion and 96% ee (Table 2, entry 17).

In order to examine the substrate scope and limitations of the reaction, other cyclic enones were investigated regarding the effect of the structural differences of the substrates on the yield and enantioselectivity (Table 2, entries 19–30). The reactions were carried out under the optimized reaction conditions: Et_2O as the solvent, 4 mol % of the ligand, 2 mol % of $(CuOTf)_2{\cdot}C_6H_6$ at −20 °C for 12 h. In the Cu-catalyzed asymmetric 1,4-conjugate addition of 2-cyclopentenone **8** and 2-cycloheptenone **10** with Et_2Zn; (S_a,R_a)-**L2** was more effective than that from either ligand (up to 95% and 76% ee respectively) (Table 2, entries 19–30). The excellent enantioselectivity (95%) achieved in this reaction of 2-cyclopentenone **8** is the best result for all known chiral monodentate phosphite ligands, since it exceeds the previously reported enantiomeric excess shown by the monodentate phosphites $\mathbf{L_a}$–$\mathbf{L_e}$.

These ligands were also screened in the Cu-catalyzed asymmetric 1,4-conjugate addition of Et_2Zn to 5,6-dihydro-2*H*-pyran-2-one **12** (Scheme 3). The results are summarized in Table 3. It should be noted that the Cu-catalyzed asymmetric 1,4-conjugate addition to



Scheme 3. The Cu-catalyzed asymmetric conjugate addition of 5,6-dihydro-2*H*-pyran-2-one.

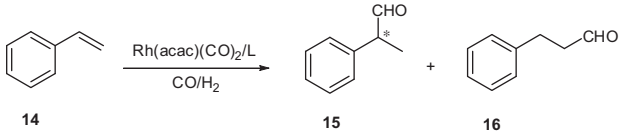
Table 3
The Cu-catalyzed enantioselective conjugate addition of diethylzinc to 5,6-dihydro-2*H*-pyran-2-one[a]

Entry	Catalyst	Solvent	Conversion (%)[b]	Yield[b]	ee (%)[b]
1	$(CuOTf)_2{\cdot}C_6H_6/(R_a,R_a)$-**L1**	THF	10	5	–
2	$(CuOTf)_2{\cdot}C_6H_6/(R_a,R_a)$-**L1**	Et_2O	30	11	6 (*R*)
3	$(CuOTf)_2{\cdot}C_6H_6/(S_a,R_a)$-**L2**	THF	55	44	69 (*R*)
4	**$(CuOTf)_2{\cdot}C_6H_6/(S_a,R_a)$-L2**	**Et_2O**	**60**	**46**	**90 (*R*)**
5	$(CuOTf)_2{\cdot}C_6H_6/(R_a,R_a)$-**L3**	THF	28	20	34 (*R*)
6	$(CuOTf)_2{\cdot}C_6H_6/(R_a,R_a)$-**L3**	Et_2O	34	30	42 (*R*)
7	$(CuOTf)_2{\cdot}C_6H_6/(R_a,S_a)$-**L4**	THF	36	28	38 (*S*)
8	$(CuOTf)_2{\cdot}C_6H_6/(R_a,S_a)$-**L4**	Et_2O	49	37	44 (*S*)
9	$(CuOTf)_2{\cdot}C_6H_6/(S_a,S_a)$-**L$_g$**	THF	23	18	36 (*S*)
10	$(CuOTf)_2{\cdot}C_6H_6/(S_a,S_a)$-**L$_g$**	Et_2O	38	25	54 (*S*)
11	$(CuOTf)_2{\cdot}C_6H_6/(R_a,S_a)$-**L$_g$**	THF	40	36	30 (*S*)
12	$(CuOTf)_2{\cdot}C_6H_6/(R_a,S_a)$-**L$_g$**	Et_2O	51	41	64 (*S*)
13	CuTc/(S_a,R_a)-**L2**	Et_2O	48	40	46 (*R*)
14	$Cu(acac)_2/(S_a,R_a)$-**L2**	Et_2O	51	36	65 (*R*)
15	$Cu(OTf)_2/(S_a,R_a)$-**L2**	Et_2O	42	35	41 (*R*)

The absolute configuration of **13** was determined by comparison with an authentic sample.
[a] Reaction conditions: Cu precursor (0.005 mmol), ligand (0.01 mmol), Et_2Zn (1.0 mol/L in hexane, 0.6 mmol), **12** (0.25 mmol), solvent (4 mL), 0 °C, 6 h.
[b] The data on conversion, yield and the enantiomeric excess were determined by GC equipped with a Chiraldex A-TA column (50 m × 0.25 mm I.D.).

α, β-unsaturated lactones is a transformation of high interest because the chiral lactone products constitute important subunits in many natural products such as α-methylene lactones and macrolides.[14]

Ligands (R_a,R_a)-**L3** and (R_a,S_a)-**L4** afforded products **13** in 30% yield, 42% ee (*R*) and 37% yield, 44% ee (*S*), respectively (Table 3, entries 5 and 8). Ligand (S_a,R_a)-**L2** showed significantly higher yield and asymmetric induction (44% and 90% ee respectively, Table 3, entry 4), while the asymmetric induction and the activity of its diastereoisomer (R_a,R_a)-**L1** were rather low (11% yield and 6% ee, Table 3, entry 2). This is probably due to the mismatched combination of (R_a)-BINOL with (R_a)-monoesterification H_8-BINOL fragment. Ligands (S_a,S_a)-L_g and (R_a,S_a)-L_g in this reaction exhibited 25% yield, 54% ee (*S*) and 41% yield, 64% ee (*S*), respectively (Table 3, entries 9–12). Focusing on ligand (S_a,R_a)-**L2**, the enantioselectivities increased when the reactions were carried out in Et_2O (90% ee) instead of THF (69% ee) (Table 3, entries 3 and 4). The influence of the copper precursor on the catalytic performance was also examined, the yield and enantioselectivity showed $(CuOTf)_2{\cdot}C_6H_6$ to be the optimal copper salts (Table 3, entries 13–15).



Scheme 4. The Rh-catalyzed asymmetric hydroformylation of styrene.

2.3. The Rh-catalyzed hydroformylation of styrene

The efficacy of the ligands was evaluated in the Rh-catalyzed asymmetric hydroformylation of styrene **14** (Scheme 4). The catalytic systems were formed in situ by the addition of 1–3 equiv of the ligand to a solution of $[Rh(acac)(CO)_2]$, followed by addition of the substrate, and pressurization of the autoclave at 40 bar with a 1:1 mixture of syngas at the working temperature. The results are shown in Table 4. All ligands show a chemoselectivity of >99% in the aldehydes. Other products resulting from the hydrogenation or polymerization of styrene were not observed. A satisfactory branched over linear ratio (from 85% to 96%) was achieved.

The use of (S_a,R_a)-**L2** was more effective than that from either ligand in toluene, at room temperature for 20 h (Table 4, entries 1–6), but the enantioselectivities were low. Thus, the effect of the solvent and L/Rh ratio on the enantioselectivity was investigated using (S_a,R_a)-**L2** (Table 4, entries 7–13). The ee did not change significantly with the change of L/Rh ratio (Table 4, entries 2, 7 and 8). The solvent has a significant influence on the enantioselectivity of the reaction. The reaction proceeded with significantly higher enantioselectivity in nonpolar solvents such as hexane (Table 4,

Table 4
The Rh-catalyzed asymmetric hydroformylation of styrene[a]

Entry	Ligand	L/Rh	Solvent	Conversion (%)[b]	b/n[b]	ee (%)[b]
1	(R_a,R_a)-**L1**	1	Toluene	98	96/4	5 (*R*)
2	(S_a,R_a)-**L2**	1	Toluene	80	92/8	28 (*R*)
3	(R_a,R_a)-**L3**	1	Toluene	60	85/15	10 (*R*)
4	(R_a,S_a)-**L4**	1	Toluene	85	94/6	8 (*S*)
5	(S_a,S_a)-**Lg**	1	Toluene	67	95/5	10 (*S*)
6	(R_a,S_a)-**Lg**	1	Toluene	90	94/6	18 (*S*)
7	(S_a,R_a)-**L2**	2	Toluene	82	91/9	29 (*R*)
8	(S_a,R_a)-**L2**	3	Toluene	81	91/9	31 (*R*)
9	(S_a,R_a)-**L2**	1	CH_2Cl_2	68	95/5	17 (*R*)
10	(S_a,R_a)-**L2**	1	^tBuOMe	27.5	92/8	10 (*R*)
11	(S_a,R_a)-**L2**	1	Hexane	90	95/5	34 (*R*)
12	(S_a,R_a)-**L2**	1	Ether	55	93/7	19 (*R*)
13	(S_a,R_a)-**L2**	1	THF	36	96/4	9 (*R*)

[a] Reaction conditions: $Rh(acac)(CO)_2$ (1.9×10^{-3} mmol); ligands (1.9×10^{-3}–5.7×10^{-3} mmol), solvent (0.5 mL); styrene (40 μL); CO, 20 bar; H_2, 20 bar; room temperature.
[b] The data on conversion, b/n and the enantiomeric excess were determined by GC equipped with a Beta DEX225 column (30 m × 0.25 mm I.D.). The absolute configuration was determined by comparison with authentic sample.

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entry 11) than in polar solvents (^{t}BuOMe, THF, Table 4, entries 10 and 13).

3. Conclusion

In conclusion, we have shown that novel MOP-type monodentate phosphite ligands are useful for the Cu-catalyzed asymmetric 1,4-conjugate addition and the Rh-catalyzed asymmetric hydroformylation. The stereochemically matched combination of (S_a)-monoesterification H_8-BINOL fragment and (R_a)-BINOL in ligand (S_a)-(2-(4-chlorobenzoic acid)-1,1′-H_8-binaphthalen-2′-yl)-((R_a)-1,1′-binaphthalen-2,2′-yl)phosphite (S_a, R_a)-**L2** was essential to afford 96% ee for 2-cyclohexenone with Et_2Zn and 65% ee with Ph_2Zn, 95% ee for cyclopentenone with Et_2Zn, 76% ee for 2-cycloheptenone with Et_2Zn, and 90% ee for 5,6-dihydro-2*H*-pyran-2-one with Et_2Zn. The sense of enantioselectivity was mainly determined by the configuration of the BINOL-based and H_8-BINOL-based phosphocycle. In the Rh-catalyzed asymmetric hydroformylation of styrene, this MOP-type phosphite ligands show chemoselectivity of >99% in aldehydes, and a satisfactory branched over linear ratio (96/4) were achieved. We think that these benefits will stimulate further applications of the organic synthesis especially in the field of natural product synthesis.

4. Experimental section

4.1. General

All experiments were carried out under nitrogen using standard Schlenk techniques. NMR spectra were recorded on Bruker 300 MHz or 400 MHz spectrometers. ^{1}H and ^{13}C NMR spectra were reported with tetramethylsilane (TMS) as an internal standard. ^{31}P NMR spectra were reported with 85% (volume fraction) H_3PO_4 as an external reference. Coupling constants (J) were reported in Hertz (Hz). Spin multiplicities were given as s (singlet), d (doublet), t (triplet) and m (multiplet). High resolution mass spectra (HRMS) were recorded on a Bruker microTOF-QII mass instrument. Melting points were determined with an X-4 melting point apparatus uncorrected. Optical rotations were measured on a Perkin-Elmer 241 MC polarimeter at 20 °C. Enantiomeric excess determination was carried out using gel chromatography(GC) with a Chiraldex A-TA, Beta-Dex 225 and a Chiralsil-DEX-CB capillary column on an ACME-6100 GC instrument with FID as detector. GC-MS was performed on an Agilent 5975C with Triple-Axis detector. Reaction were monitored by thin layer chromatography (TLC, silica gel GF254 plates). Column chromatography separations were conducted on silica gel (200–300 mesh). NEt_3, tetrahydrofuran (THF), Et_2O and toluene were distilled with Na and benzophenone as an indicator, and CH_2Cl_2 was dried over CaH_2 before use. All the other chemicals were obtained commercially and used without further purification.

4.1.1. Representative procedure of Cu-catalyzed 1,4-conjugate addition of diethylzinc to 2-cyclohexenone

A solution of $Cu(OTf)_2$ (0.005 mmol) and (R_a,R_a)-**L1** (0.005 mmol) in toluene (4 mL) was stirred for 1 h at room temperature under nitrogen. After the solution was cooled to 0 °C, compound **5** (0.25 mmol) was added to it, and the solution was stirred for 10 min at 0 °C, then Et_2Zn (0.6 mmol, 0.6 mL of 1.0 mol/L solution in hexane) was added dropwise using a syringe over 2 min. After 4 h, the reaction was quenched by H_2O (2 mL) and 2 mol/L HCl (2 mL), and the mixture was extracted with ethyl acetate (5 mL × 3). The combined extracts were washed using saturated $NaHCO_3$ solution, brine, and then dried over anhydrous Na_2SO_4, filtered, and concentrated to afford the crude product. The conversion and the yield were determined by GC equipped with an SE-30 column (30 m × 0.32 mm i.d.) using dodecane as an internal standard. The enantiomeric excess was determined by GC analysis with a Chiraldex A-TA column (50 m × 0.25 mm i.d.). The absolute configuration was determined by comparison with authentic samples.

4.1.2. Representative procedure of the Rh-catalyzed asymmetric hydroformylation of styrene

A 50 mL stainless steel autoclave was charged with styrene (40 μL), toluene (0.5 mL), ligand (5.7×10^{-3} mmol), and Rh(acac)$(CO)_2$ (1.9×10^{-3} mmol) under a nitrogen atmosphere. The autoclave was pressurized with CO and H_2. The reaction mixture was stirred with a magnetic stirrer at room temperature. After a prescribed reaction time, the residue gas was released. The data on the conversion, b/n ratio and enantiomeric excess was determined by GC analysis with a Beta-Dex 225 column (30 m × 0.25 mm i.d.). The absolute configuration was determined by comparison with authentic samples.

4.2. Synthesis of monodentate phosphite ligands

4.2.1. General protocol for the preparation of carboxylic acid esters of H_8-BINOL

A flame-dried flask was charged with H_8-BINOL (3 mmol), 10 mL of THF, and Et_3N (3.78 mmol), and cooled to −5 °C. 4-Chlorobenzoyl chloride (3 mmol) was added to the above-mentioned solution dropwise. Once the addition was complete, the reaction mixture was left at room temperature until the near complete disappearance of the starting material. After 20 h, the reaction was quenched with distilled water (2.5 mL) and the mixture was extracted with ethyl acetate (5 mL × 3). The combined organic phases were washed successively with a saturated aqueous solution of $NaHCO_3$, NaCl, and then dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (EtOAc/Petroleum ether) to provide the title compound (R_a)-**2**, (S_a)-**2** as a solid with >85% yield.

(R_a)-**2** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 1.6 Hz, 1H, Ar), 7.75–7.73 (m, 1H, Ar), 7.33 (d, J = 1.8 Hz, 1H, Ar), 7.31 (d, J = 1.8 Hz, 1H, Ar), 7.22 (d, J = 8.4 Hz, 1H, Ar), 7.05 (d, J = 8.0 Hz, 1H, Ar), 6.86 (d, J = 8.4 Hz, 1H, Ar), 6.68 (d, J = 8.4 Hz, 1H, Ar), 4.78 (s, 1H, OH), 2.94–2.37 (m, 8H, CH_2), 1.75–1.61 (m, 8H, CH_2) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.16, 150.47, 147.11, 139.90, 138.57, 136.39, 135.65, 131.22, 130.48, 129.96, 129.42, 128.68, 127.90, 127.62, 121.98, 119.52, 113.68, 29.70, 29.23, 27.39, 26.96, 23.25, 23.17, 22.84, 22.69 ppm. HRMS (ESI^+): calcd for $C_{27}H_{25}NaClO_3$ $[M+Na]^+$ 455.1371; found: 455.1385.

(S_a)-**2** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.68 (m, 2H, Ar), 7.35–7.29 (m, 2H, Ar), 7.22 (d, J = 8.4 Hz, 1H, Ar), 7.05 (d, J = 8.0 Hz, 1H, Ar), 6.86 (d, J = 8.4 Hz, 1H, Ar), 6.68 (d, J = 8.4 Hz, 1H, Ar), 4.57 (s, 1H, OH), 2.92–2.16 (m, 8H, CH_2), 1.81–1.64 (m, 8H, CH_2) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.16, 150.46, 147.11, 139.90, 138.57, 136.39, 135.65, 131.22, 130.49, 129.96, 129.42, 128.68, 127.89, 127.62, 121.99, 119.52, 113.68, 29.70, 29.23, 27.39, 26.96, 23.25, 23.17, 22.84, 22.69 ppm. HRMS (ESI^+): calcd for $C_{27}H_{25}NaClO_3$ $[M+Na]^+$ 455.1371; found: 455.1392.

4.2.2. Synthesis of monodentate phosphite ligands L1–L4

4.2.2.1. (R_a)-(2-(4-Chlorobenzoic acid)-1,1′-H_8-binaphthalen-2′-yl)-((R_a)-1,1′-binaphthalen-2,2′-yl)phosphite [(R_a,R_a)-L1]. To a 100 mL Schlenk flask equipped with a condenser were added 2.0 g of (R_a)-binaphthol, 20 mL of toluene, and 10 mL of PCl_3. The mixture was refluxed under nitrogen atmosphere for 20 h. After the removal of excess PCl_3 and toluene, the residue was dissolved in 20 mL of toluene, then transferred to another Schlenk flask, and toluene was removed in vacuo to obtain compound

(R_a)-1,1′-binaphthyl-2,2′-diylchlorophosphite (R_a)-**3** as a white powder, which was used directly in the following step without further purification. To a stirred solution of compound (R_a)-**2** (345.7 mg, 0.8 mmol), compound (R_a)-**3** (308 mg, 0.88 mmol), and 4-dimethylaminopyridine (DMAP) (12.2 mg, 0.1 mmol) in THF (10 mL) at 0 °C, NEt_3 (0.28 mL, 2.02 mmol) were slowly added using a syringe over 2 min. The mixture was then stirred at room temperature for 1 h. THF was distilled off in vacuo, and then toluene (20 mL) was added. The solid was removed by filtration through a pad of silica gel, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (toluene) to furnish ligand (R_a,R_a)-**L1** as a white foamy solid (286.4 mg, yield 48%). $[\alpha]_D^{20}$ = +45 (*c* 0.1 CH_2Cl_2); Mp 112–114 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–8.32 (m, 6H, Ar), 7.16–7.34 (m, 8H, Ar), 6.62–7.09 (m, 6H, Ar), 2.27–2.79 (m, 8H, CH_2), 1.45–1.76 (m, 8H, CH_2) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.91, 153.13, 152.10, 146.34, 139.53, 137.89, 135.20, 133.74, 131.27, 130.19, 129.44, 129.05, 128.60, 128.29, 128.24, 128.16, 127.07, 126.93, 126.23, 125.31, 124.83, 119.61, 117.40, 117.29, 29.85, 29.71, 29.40, 27.31, 27.25, 22.93, 22.88, 22.81, 22.79, 22.70, 21.47 ppm. ^{31}P NMR (162 MHz, $CDCl_3$) δ 146.03 ppm. HRMS (ESI^+): calcd for $C_{47}H_{36}NaClO_5P$ [M+Na]$^+$ 769.1871; found: 769.1895.

4.2.2.2. (S_a)-(2-(4-Chlorobenzoic acid)-1,1′-H_8-binaphthalen-2′-yl)-((R_a)-1,1′-binaphthalen-2,2′-yl)phosphite [(S_a,R_a)-L2].

Treatment of (S_a)-**2** (259.2 mg, 0.6 mmol), compound (R_a)-**3** (231 mg, 0.66 mmol), DMAP (9.15 mg, 0.075 mmol) and NEt_3 (0.21 mL, 1.51 mmol) as described for the synthesis of ligand (R_a,R_a)-**L1** afforded ligand (S_a,R_a)-**L2**, which was purified by flash chromatography (toluene) to produce a white foamy solid (228.3 mg, yield 51%). $[\alpha]_D^{20}$ = +435 (*c* 0.1 CH_2Cl_2); Mp 142–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–8.13 (m, 6H, Ar), 7.21–7.57 (m, 8H, Ar), 6.45–7.15 (m, 6H, Ar), 2.01–2.88 (m, 8H, Ar), 1.30–1.72 (m, 8H, Ar) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.94, 153.16, 152.13, 146.37, 139.56, 137.92, 135.23, 133.77, 131.30, 130.22, 129.47, 129.08, 128.63, 128.32, 128.27, 128.19, 127.10, 126.96, 126.26, 125.34, 124.86, 119.64, 117.43, 117.32, 29.88, 29.74, 29.43, 27.34, 27.28, 22.96, 22.91, 22.84, 22.82, 22.73, 21.50 ppm. ^{31}P NMR (162 MHz, $CDCl_3$) δ 146.92 ppm. HRMS (ESI^+): calcd for $C_{47}H_{36}NaClO_5P$ [M+Na]$^+$ 769.1871; found: 769.1891.

4.2.2.3. (R_a)-(2-(4-Chlorobenzoic acid)-1,1′-H_8-binaphthalen-2′-yl)-((R_a)-1,1′-H_8-binaphthalen-2,2′-yl)phosphite [(R_a,R_a)-L3].

To a 100 mL Schlenk flask equipped with a condenser were added 2.0 g of (R_a)-H_8-binaphthol, 20 mL of toluene, and 10 mL of PCl_3. The mixture was refluxed under nitrogen atmosphere for 20 h. After the removal of excess PCl_3 and toluene, the residue was dissolved in 20 mL of toluene, then transferred to another Schlenk flask, and toluene was removed in vacuo to obtain compound (R_a)-1,1′-H_8-binaphthyl-2,2′-diylchlorophosphite (R_a)-**4** as a white powder, which was used directly in the following step without further purification. To a stirred solution of compound (R_a)-**2** (259.2 mg, 0.6 mmol), compound (R_a)-**4** (231 mg, 0.66 mmol), and 4-dimethylaminopyridine (DMAP) (9.15 mg, 0.075 mmol) in THF (10 mL) at 0 °C, NEt_3 (0.21 mL, 1.51 mmol) were slowly added using a syringe over 2 min. The mixture was then stirred at room temperature for 1 h. THF was distilled off in vacuo, and then toluene (20 mL) was added. The solid was removed by filtration through a pad of silica gel, and the solvent was removed under reduced pressure. The residue was purified by flash chromatography (toluene) to furnish ligand (R_a,R_a)-**L_3** as a white foamy solid (241.7 mg, yield 54%). $[\alpha]_D^{20}$ = +55 (*c* 0.1 CH_2Cl_2); Mp 101–104 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71–7.51 (m, 2H, Ar), 7.26–7.20 (m, 4H, Ar), 7.19–7.10 (m, 2H, Ar), 7.08–7.02 (m, 1H, Ar), 6.99–6.91 (m, 2H, Ar), 6.85 (d, *J* = 8.2 Hz, 1H, Ar), 3.01–2.53 (m, 8H, CH_2), 2.50–1.92 (m, 8H, CH_2), 1.88–1.47 (m, 16H, CH_2) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.92, 151.45, 147.12, 146.33, 145.60, 139.50, 138.51, 137.38, 137.14, 136.96, 135.13, 134.72, 133.68, 131.32, 131.24, 131.02, 129.41, 129.35, 129.25, 129.18, 128.79, 128.58, 128.09, 29.88, 29.40, 29.28, 29.15, 27.83, 27.70, 27.30, 27.14, 22.99, 22.93, 22.64, 22.44 ppm. ^{31}P NMR (162 MHz, $CDCl_3$) δ 137.95 ppm. HRMS (ESI^+): calcd for $C_{47}H_{44}NaClO_5P$ [M+Na]$^+$ 777.1871; found: 777.1898.

4.2.2.4. (R_a)-(2-(4-Chlorobenzoic acid)-1,1′-H_8-binaphthalen-2′-yl)-((S_a)-1,1′-H_8-binaphthalen-2,2′-yl)phosphite [(R_a,S_a)-L4].

Treatment of (R_a)-**2** (259.2 mg, 0.6 mmol), compound (S_a)-**4** (231 mg, 0.66 mmol), DMAP (9.15 mg, 0.075 mmol) and NEt_3 (0.21 mL, 1.51 mmol) as described for the synthesis of (R_a,R_a)-**L3** afforded (R_a,S_a)-**L4**, which was purified by flash chromatography (toluene) to produce a white foamy solid (196.9 mg, yield 44%). $[\alpha]_D^{20}$ = −395 (*c* 0.1 CH_2Cl_2); Mp 121–124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.58 (m, 2H, Ar), 7.32 (dd, *J* = 24.4, 15.8 Hz, 2H, Ar), 7.21–7.10 (m, 3H, Ar), 7.09–6.77 (m, 5H, Ar), 3.08–2.51 (m, 10H, CH_2), 2.41 (m, 1H, CH_2), 2.32–1.98 (m, 5H, CH_2), 1.88–1.40 (m, 16H, CH_2) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.84, 151.37, 147.04, 146.25, 145.52, 139.42, 138.43, 137.30, 137.06, 136.88, 135.05, 134.64, 133.60, 131.24, 131.16, 130.94, 129.33, 129.27, 129.17, 129.10, 128.71, 128.50, 128.01, 29.80, 29.32, 29.20, 29.07, 27.75, 27.62, 27.22, 27.06, 22.91, 22.85, 22.56, 22.36 ppm. ^{31}P NMR (162 MHz, $CDCl_3$) δ 138.65 ppm. HRMS (ESI^+): calcd for $C_{47}H_{44}NaClO_5P$ [M+Na]$^+$ 777.1871; found: 777.1887.

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A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetasy.2017.01.011.

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