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RESEARCH PAPER

New Chiral Monophosphite Ligands Containing BINOL and/or H_8-BINOL Bearing Adamantyl Substituents: Effect of Ligand Scaffold on the Enantioselective 1,4-Conjugate Addition of Diethylzinc to Cyclic Enones

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Abstract: A series of new bulky monophosphite ligands were synthesized from axially chiral BINOL/H_8-BINOL (BINOL: 1-(2-hydroxynaphthalen-1-yl)naphthalen-2-ol) and highly sterically hindered adamantylcarbonyl chloride. The effectiveness of these ligands was evaluated by the Cu-catalyzed asymmetric 1,4-conjugate addition of diethylzinc to cyclic enones with enantioselectivities of up to 79% ee. The results showed that a ligand structure comprising a partially hydrogenated 2,2′-(1,1′-binaphthyl)phosphite scaffold and an adamantyl moiety was effective in improving the enantioselectivity.

Key words: enantioselective 1,4-conjugate addition; phosphite ligand; copper salt; cyclic enone; adamantyl; H_8-binaphtyl

Asymmetric syntheses have been successful in the preparation of chiral motifs for the manipulation of optically active compounds in pharmaceutical and medicinal science. In particular, the enantioselective conjugate addition of organometallic reagents to α,β-unsaturated carbonyl compounds is an attractive method for the stereoselective construction of carbon-carbon bonds in organic synthesis [1–4]. These addition products have been shown to have many applications in the synthesis of natural and biologically active compounds such as (*R*)-Muscone [5–7], Clavularin B [8,9], and Pumiliotoxin C [10]. Cu-catalyzed enantioselective 1,4-conjugate addition using chiral trivalent phosphorous ligands has been investigated extensively since the pioneering report by Alexakis et al. in 1993 [11]. A plethora of chiral phosphorous ligands such as phosphoramidites [1,12–14], phosphite ligands [15–17], and chiral P, N ligands [18–21] have been synthesized and successfully applied in reactions to afford good to excellent enantioselectivities. Nevertheless, the dynamic behavior of the equilibria among several species of organocuprate compounds in solution is problematic. Therefore, if the more reactive cuprates give racemic products a loss of enantioselectivity is unavoidable [22,23]. The design and synthesis of new chiral ligands that can rapidly react with substrates and suppress the formation of unwanted competing products is desirable.

Recently, Reetz et al. [24] reported a helical C_3-symmetric monophosphite ligand with a sterically encumbered adamantyl group (Scheme 1), which gave respectable enantioselectivities (79%–98% ee) in Rh-catalyzed asymmetric hydrogenation. Inspired by this excellent work, we undertook phosphite ligand development and focused on the bulky adamantyl moiety (Scheme 2, R group).

In addition to the chiral element from the binaphthyl skeleton, the partially hydrogenated H_8-binapthyl (5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthyl) scaffold is also of interest.

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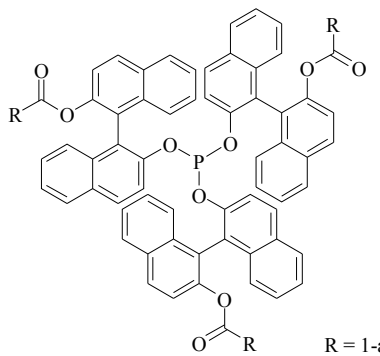
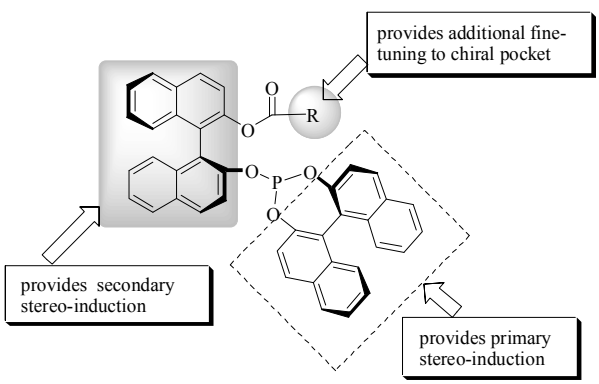


Scheme 1. Reetz's helical C_3-symmetric monophosphite ligand.



Scheme 2. Design of a modulated ligand bearing a bulky R group.

Chiral phosphorus donor ligands based on the H_8-binaphtyl moiety have received considerable attention recently [25–29]. The improved stereo-communication in H_8-BINOL compared to BINOL in asymmetric reactions has been explicitly highlighted [30–33]. Herein, we report the synthesis of a new series of bulky monophosphite ligands **L1**–**L9** based on the (*S*)-BINOL and the (*S*)-H_8-BINOL skeleton. The effectiveness of these ligands was examined in the copper-catalyzed enantioselective 1,4-conjugate addition of diethylzinc to cyclic enones.

1 Experimental

1.1 General

All experiments were carried out under nitrogen using standard Schlenk techniques. Reactions were monitored by thin layer chromatography (TLC). Column chromatography was carried out using silica gel. Toluene, ether, and tetrahydrofuran (THF) were distilled from sodium. Dichloromethane was distilled over calcium hydride. The other commercially available reagents were used as received without further purification. NMR (nuclear magnetic resonance) spectroscopy was recorded on a Bruker 400 MHz spectrometer. ^{1}H NMR and ^{13}C NMR spectra are reported in parts per million and TMS (δ = 0.00) was used as an internal standard. ^{31}P NMR spectra are reported in parts per million and 85% H_3PO_4 was used as an external reference. Proton chemical shifts (δ) and coupling constants (J) are given in ppm and in Hz, respectively. Spin multiplicities are reported as s (singlet), d (doublet), t (triplet), and m (multiplet) as well as b (broad). All the melting points were determined on an X-4 melting point apparatus and were uncorrected.

1.2 Synthesis of chiral monophosphite ligands

1.2.1 General protocol for the preparation of carboxylic acid esters of BINOL

A flame-dried flask was charged with BINOL (2.5 mmol), 4-dimethylaminopyridine (DMAP, 25 mg), 10 ml of THF, and Et_3N (3.25 mmol), and cooled to –10 °C. Acyl chloride or acetic anhydride (2.5 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 24 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 $NaHCO_3$, brine, and then dried over anhydrous sodium sulfate, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (EtOAc/ hexanes) to provide the title compound (*S*)-**2a**, (*S*)-**2b**, or (*S*)-**2c** as a solid with > 95% yield (Scheme 3).

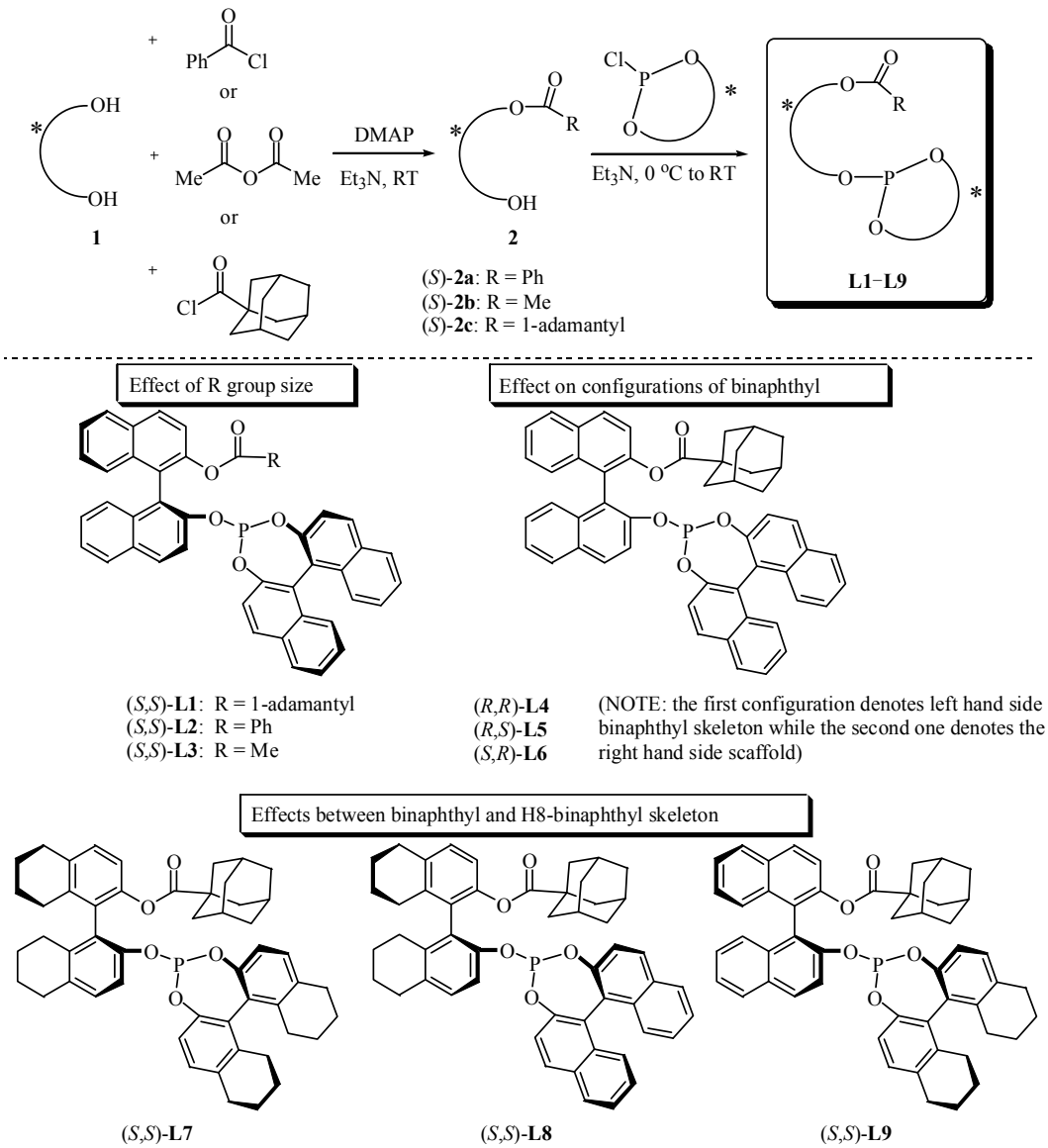
(*S*)-**2a**: White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.30 (s, 1H), 7.14−7.15 (m, 1H),7.16−7.45 (m, 8H), 7.54−7.56 (m, 2H), 7.65−7.67 (m, 2H), 7.78−7.80 (m, 2H), 8.00 (d, J = 8.4, 1H), 8.12 (d, J = 8.8, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 113.9, 118.2, 121.9, 123.2, 123.4, 124.6, 125.8, 126.3, 126.7, 127.5, 128.0, 128.3, 128.4, 128.7, 129.0, 130.0, 130.4, 130.8, 132.3, 133.5, 133.6, 133.7, 148.3, 151.8, 165.9.

(*S*) **2b**: White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.86 (s, 3H), 5.20 (s, 1H), 7.03 (d, 1H, J = 8.4 Hz), 7.23−7.49 (m, 7H), 7.85 (d, 1H, J = 8.0 Hz), 7.90 (d, 1H, J = 9.2 Hz), 7.96 (m, 1H), 8.06 (d, 1H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 114.0, 118.2, 121.8, 123.1, 123.5, 124.5, 125.7, 126.3, 126.7, 127.5, 128.0, 128.3, 129.0, 130.4, 130.8, 132.2, 133.4, 133.5, 148.0, 151.7, 170.4.

(*S*)-**2c**: White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39−1.45 (m, 9H), 1.54−1.57 (d, J = 12.4, 3H), 1.77 (s, 3H), 5.14 (s, 1H), 7.05 (d, J = 8.4, 1H), 7.25−7.38 (m, 6H), 7.50 (m, 1H), 7.82 (d, J = 8.0, 1H), 7.88 (d, J = 9.2, 1H), 8.00 (d, J = 8.4, 1H), 8.06 (d, J = 8.8, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.6, 36.2, 38.0, 40.7, 114.3, 118.3, 121.9, 123.0, 123.5, 124.6, 125.6, 126.1, 126.6, 127.4, 127.9, 128.3, 129.0, 130.2, 130.7, 132.2, 133.5, 133.6, 148.4, 151.8, 177.0.

1.2.2 Synthesis of chiral monophosphite ligands

In a typical procedure for ligand synthesis, to a stirred solution of compound **2** (1.0 mmol) in THF (10 ml) was added Et_3N



Scheme 3. Synthesis of the bulky monophosphite ligands.

(1.0 mmol) under nitrogen. The mixture was then cooled to 0 °C and BINOL or H_8-BINOL-derived chlorophosphite (1.1 mmol) was slowly added. The reaction mixture was allowed to warm to room temperature and stirred overnight. The $Et_3N{\cdot}HCl$ salt precipitate was then removed by filtration. The solvent was removed in vacuo and the residue was purified by flash chromatography using toluene as the eluent to yield a white foamy solid in 50%–60% yield.

(*S*,*S*)-**L1**: White solid; mp 232–233 °C; $[\alpha]_D^{20}$ = +92 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24–1.36 (m, 9H), 1.46–1.49 (m, 3H), 1.66 (s, 3H), 6.59 (d, J = 8.8, 1H), 7.18–7.53 (m, 15H), 7.70 (d, J = 8.8, 1H), 7.87–7.96 (m, 6H), 8.03 (d, J = 8.8, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.5, 35.1, 36.8, 39.4, 119.6, 119.7, 120.7, 120.8, 121.1, 121.4, 121.4, 121.5, 121.5, 122.8, 123.2, 123.3, 123.7, 124.0, 124.1, 124.6, 124.9, 125.2, 125.3, 125.7, 125.8, 125.8, 125.9, 127.1, 128.5, 128.8, 129.1, 129.8, 130.1, 130.4, 130.5, 131.3, 131.7, 132.7, 132.7, 145.9, 146.0, 146.5, 146.6, 174.3; ^{31}P NMR (161 MHz, $CDCl_3$) δ 145.2.

(*S*,*S*)-**L2**: White solid; mp 128–130 °C; $[\alpha]_D^{20}$ = +110.5 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.58 (d, J = 8.8, 1H), 7.04–7.27 (m, 15H), 7.40 (m, 2H), 7.49 (d, J = 7.2, 2H), 7.62 (d, J = 8.8, 2H), 7.75–7.80 (m, 5H) 7.91 (d, J = 8.0, 1H), 8.01 (d, J = 9.2, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 119.8, 120.7, 120.8, 122.9, 123.8, 124.1, 124.3, 124.8, 124.9, 125.1, 125.2, 125.3, 126.0, 127.1, 127.3, 128.0, 128.6, 128.8, 129.1, 129.2, 129.8, 130.2, 130.5, 130.7, 132.0, 146.0, 146.5, 163.4; ^{31}P NMR (161 MHz, $CDCl_3$) δ 145.0.

(*S*,*S*)-**L3**: White solid; mp 78–80 °C; $[\alpha]_D^{20}$ = +59 (c 0.16, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.64 (s, 3H), 6.41 (d, J = 8.8, 1H), 7.19–7.37 (m, 13H), 7.44 (m, 2H), 7.61 (d, J = 8.8, 1H), 7.78–7.88 (m, 6H); 7.99 (d, J = 8.8, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.7, 120.7, 120.9, 123.8, 124.1, 124.2, 124.8, 124.9, 125.1, 125.2, 125.9, 125.9, 126.0 126.9, 127.0, 127.1,

127.2, 127.3, 128.0, 128.5, 128.6, 129.0, 129.2, 129.8, 130.1, 130.5, 130.7, 131.3, 131.7, 131.8, 132.6, 132.7, 145.9, 146.0, 146.3, 168.0; ^{31}P NMR (161 MHz, $CDCl_3$) δ 144.5.

(*S*,*S*)-**L7**: White solid; mp 132–134 °C; $[\alpha]_D^{20}$ = +36.5 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54–1.84 (m, 31H), 2.10–2.35 (m, 6H), 2.61–2.80 (m, 10H) , 6.25 (d, *J* = 8.0, 1H), 6.90 (m, 3H), 7.02 (m, 3H), 7.15 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 21.5, 21.6, 21.7, 21.8, 21.9, 22.0, 26.2, 26.7, 26.8, 26.9, 28.1, 28.2, 28.5, 28.6, 28.7, 35.4, 37.2, 39.7, 118.4, 128.0, 132.4, 132.6, 133.6, 136.0, 136.3, 136.7, 137.3, 137.3, 145.5, 174.6; ^{31}P NMR (161 MHz, $CDCl_3$) δ 137.89.

(*S*,*S*)-**L8**: White solid; mp 126–128 °C; $[\alpha]_D^{20}$ = +130.8 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.51–1.80(m, 23H), 2.14–2.42 (m, 4H), 2.80 (m, 4H), 6.85 (d, *J* = 8.8, 1H), 7.04 (m, 3H), 7.24 (m, 3H), 7.31–7.44 (m, 5H), 7.77 (d, *J* = 8.8, 1H), 7.90 (m, 3H); ^{13}C NMR (100 MHz, CDCl3) δ 22.8, 22.9, 23.0, 27.2, 27.8, 29.6, 36.4, 38.2, 40.7, 119.6, 121.9, 122.3, 124.7, 125.0, 125.3, 125.9, 126.2, 126.9, 127.1, 128.3, 129.1, 129.5, 130.2, 131.2, 131.5, 132.4, 132.8, 133.8, 134.8, 137.4, 137.9, 146.5, 175.6; ^{31}P NMR (161 MHz, $CDCl_3$) δ 146.0.

(*S*,*S*)-**L9**: White solid; mp 146–148 °C; $[\alpha]_D^{20}$ = +10 (c 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28–1.52(m, 15H), 1.72 (m, 8H), 2.14–2.19 (m, 2H), 2.57 (m, 2H), 2.74 (m, 4H), 6.06 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 7.23–7.30 (m, 4H), 7.38–7.49 (m, 4H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.93 (m, 2H), 8.05 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4, 22.5, 22.6, 22.7, 27.6, 27.7, 29.1, 29.2, 36.2, 37.8, 40.5, 118.8, 122.1, 123.9, 124.9, 125.3, 125.5, 126.7,127.6, 128.0, 128.2, 128.9, 129.3, 129.6, 130.8, 131.6, 133.7, 134.7, 137.1, 138.4 , 145.6, 145.9, 147.5, 147.8, 147.9, 175.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 137.1.

1.3 Typical procedure for asymmetric conjugate addition

In a typical procedure for asymmetric conjugate addition, to a solution of the copper salt (0.01 mmol) and the ligand (0.02 mmol) in anhydrous diethyl ether (4.0 ml) that was stirred at room temperature for 1 h under N_2, 2-cyclohexenone (0.5 mmol) and diethylzinc (1.2 mmol) were added sequentially after the complex was cooled to 0 °C. The solution was stirred for 4 h at this temperature and then quenched with water (~2 ml) and hydrochloric acid solution (2.0 mol/L, ~2 ml). The mixture was extracted with ethyl acetate (5 ml × 3). The combined organic layers were washed with a saturated $NaHCO_3$ solution, brine, and then dried with anhydrous Na_2SO_4. The crude organic phase was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the desired products **L1**–**L9**.

2 Results and discussion

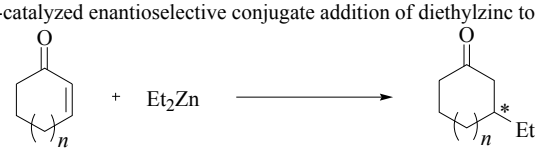
A new series of modulated monophosphite ligands **L1**–**L9** were prepared in high yield from the carboxylic acid esters of BINOL or H_8-BINOL by their reaction with phosphorochloridite in the presence of triethylamine (Scheme 3). The desired ligands were found to be stable on silica gel during the purification procedure and fairly air-stable at room temperature. Indeed, the precursors **2** (carboxylic acid esters of BINOL or H_8-BINOL) were easily accessible from axially chiral H_8-BINOL/BINOL and acyl chloride/acetic anhydride according to a previous reported procedure [24].

Since the modulated ligands consist of two chiral elements (i.e. from two binaphthyl moieties), we were interested in a match/mis-match study with different configurations of the binaphthyl scaffolds. Our previous study [34] was concerned with the application of ligands **L1** and **L4**–**L6** to the Cu-catalyzed enantioselective 1,4-conjugate additions of diethylzinc to 2-cyclohexenone. We found that two BINOL-derived moieties with the (*S*)-configuration in ligand **L1** were matched to give moderate to good enantioselectivities. The absolute configuration of the 2,2′-*o*,*o*-(1,1′-binaphthyl)-dioxophosphite moiety (non-ester containing binaphthyl group) of the ligand was found to be of primary importance in determining the sense of asymmetric induction. Diethyl ether proved to be more effective than other solvents (such as toluene, dichloromethane, and THF).

The influence of R group bulkiness on the carboxylic esters was initially studied. The copper-catalyzed conjugated addition of 2-cyclohexenone to diethylzinc was used as a model reaction for our prototypical investigation (Table 1). **L2** and **L3** bearing R = Ph and R = Me, respectively, gave poor enantioselectivity of the addition product (Table 1, entries 2 and 3). To our delight, the bulkier adamantyl ester **L1** afforded a significant increase in enantioselectivity (entry 1). These results suggest that the highly sterically encumbered adamantly moiety is beneficial for stereo-communication between the binaphthyl moieties and the substrate.

We then examined the asymmetric induction ability of the chiral binaphthyl and H_8-binaphthyl scaffolds of the phosphite ligands in the Cu-catalyzed asymmetric conjugate addition of diethylzinc to cyclic enones. Results for the application of ligands (*S*,*S*)-**L7**, (*S*,*S*)-**L8**, and (*S*,*S*)-**L9** are shown in Table 1 (entries 4–6). A comparison of ligands **L8** and **L9** reveals that the H_8-binaphthyl scaffold (as the non-ester containing ring) was better at driving the asymmetric induction (entries 5–6). **L9** gave a slightly better result than **L1** (entry 6 vs. entry 1). Ligand **L7**, with both the (*S*)-H_8-BINOL moieties, gave similar results to its parent ligand **L1** (entry 4 vs. entry 1). It is known that the copper precursor plays a crucial role in the high catalytic activity and enantioselectivity of these reactions [35,36]. In our study, the copper precursors $Cu(OTf)_2$ and $(CuOTf)_2{\cdot}C_6H_6$ gave similar results (entries 6 and 7). When the temperature was decreased from 0 to –40 °C the ee of the addition product improved significantly from 66% to 79%. The best ee was achieved when the reaction temperature was –40 °C (entries 7–10).

Table 1 Cu-catalyzed enantioselective conjugate addition of diethylzinc to cyclic enones



n = 0,1,2

Entry	n	Ligand	Cu salt	Temperature (°C)	Yield[a] (%)	ee[b] (%) (Config.)
1	1	(*S*,*S*)-**L1**	$Cu(OTf)_2$	0	88	61 (*S*)
2	1	(*S*,*S*)-**L2**	$Cu(OTf)_2$	0	20	33 (*S*)
3	1	(*S*,*S*)-**L3**	$Cu(OTf)_2$	0	98	40 (*S*)
4	1	(*S*,*S*)-**L7**	$Cu(OTf)_2$	0	57	62 (S)
5	1	(*S*,*S*)-**L8**	$Cu(OTf)_2$	0	51	33 (S)
6	1	(*S*,*S*)-**L9**	$Cu(OTf)_2$	0	88	66 (S)
7	1	(*S*,*S*)-**L9**	$(CuOTf)_2{\cdot}C_6H_6$	0	96	66 (*S*)
8	1	(*S*,*S*)-**L9**	$(CuOTf)_2{\cdot}C_6H_6$	– 20	93	73 (*S*)
9	1	(*S*,*S*)-**L9**	$(CuOTf)_2{\cdot}C_6H_6$	– 40	98	79 (*S*)
10	1	(*S*,*S*)-**L9**	$(CuOTf)_2{\cdot}C_6H_6$	– 60	81	69 (*S*)
11	0	(*S*,*S*)-**L9**	$(CuOTf)_2{\cdot}C_6H_6$	– 40	42	23 (*S*)
12	2	(*S*,*S*)-**L9**	$(CuOTf)_2{\cdot}C_6H_6$	– 40	46	34 (*S*)

Reaction conditions: Cu salts 0.01 mmol, L*/Cu salts molar ratio = 2, Et_2Zn 1.2 mmol, cyclic enone 0.5 mmol, solvent ether 4.0 ml, 4 h.

[a]Determined by GC using dodecane as an internal standard with a SE-30 column (50 m × 0.25 mm).

[b]The ee values of 3-ethylcyclohexanone and 3-ethylcyclopentenone were determined using a GC equipped with a Chiraldex A-TA column (50 m × 0.25 mm). The ee values of 3-ethylcycloheptenone were determined using a GC equipped with a Chiralsil-DEX-CB column (25 m × 0.25 mm). The absolute configuration of the product was determined by comparison with authentic samples.

To evaluate the effectiveness of the new catalyst system, we carried out conjugate additions of Et_2Zn to other cyclic enones of different ring size. Low enantioselectivities in the reaction between 2-cyclopentenone and 2-cycloheptenone were obtained (entries 11 and 12).

3 Conclusions

In summary, we prepared a series of new bulky monophosphite ligands derived from axially chiral BINOL and H_8-BINOL with highly sterically encumbered adamantanecarbonyl chloride. The results indicate that the ligand structure comprising a partially hydrogenated 2,2′-(1,1′-binaphthyl) phosphite scaffold and a bulky adamantyl moiety was effective in enhancing the stereo-induction to the substrate and thus the enantioselectivity of the product. Further fine-tuning and application of these ligands in other asymmetric catalytic reactions are currently underway.

Dedicated to Professor Albert S. C. CHAN on the occasion of his 60th birthday.

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