Asymmetric allylation of aryl aldehydes: studies on the scope and mechanism of the palladium catalysed diethylzinc mediated umpolung using phosphoramidite ligands†

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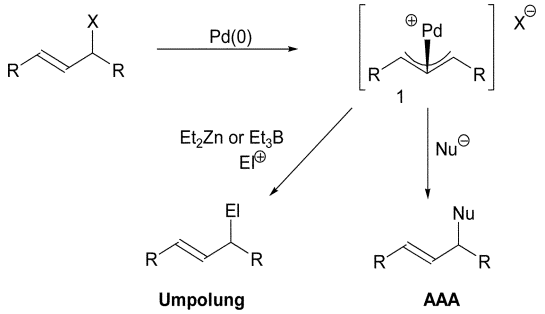
Using modular, monodentate phosphoramidite ligands, enantioselective palladium catalysed diethylzinc mediated allylation of aldehydes was achieved. The scope of the asymmetric C–C bond formation was investigated with respect to nucleophilic and electrophilic components and an alternative reaction mechanism is proposed based on our findings.

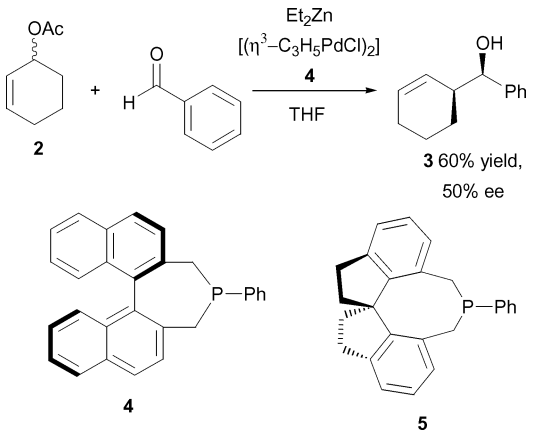
Introduction

The asymmetric allylic alkylation (AAA, Scheme 1) protocol pioneered by Trost and Tsuji represents one of the most studied and highly developed tools in current asymmetric catalysis.[1] High levels of stereocontrol have been demonstrated for an impressive range of allyl (and analogous) systems in conjunction with C, O, N and S nucleophiles, resulting in a large number of target molecule syntheses.[2] Since an initial publication concerning umpolung allylation by H. C. Brown in 1987,[3] Tamaru *et al.* have effectively demonstrated that the latent reactivity of the palladium allyl complex **1** can be reversed from electrophilic to nucleophilic in the presence of dialkylzinc or trialkylboron species.[4] The resulting umpolung reaction represents a complementary reaction to the existing AAA methodology.



Scheme 1

To date, there has been one enantioselective example of this dialkylzinc mediated umpolung allylation reported in the literature. Zanoni *et al.* described the coupling of 2-cyclohexenyl acetate **2** and benzaldehyde (Scheme 2) to yield the *syn*-homoallylic alcohol **3** in modest yield (60%) and ee (50%).[5] The authors found that monodentate phosphorous ligands were well suited to this particular procedure and an impressive range of ligands was screened, with phospholane **4** providing the best results. In recent



Scheme 2

months, Zhou *et al.* (Scheme 2) described the first enantioselective example of the presumably analogous, trialkylboron mediated version of this umpolung reaction, coupling simple allyl and cinnamyl alcohols with aldehydes in good yield and with increased levels of enantioselectivity (58–83% ee); the spiro phospholane ligand **5** was utilised throughout.[6]

We believe that this umpolung protocol is of significant interest as the homoallylic alcohol products, and particularly the functionalised cyclohexyl systems **3** described by Zanoni, represent valuable building blocks for synthesis.[7] Moreover, the opportunity to gain further mechanistic insight into the origins of stereocontrol in this interesting and little-studied reaction would be a worthy exercise. Accordingly, we report the highest enantioselectivities for the diethylzinc mediated, umpolung allylation of aldehydes yet disclosed in the literature, using monodentate phosphoramidite ligands. The results described are comparable to those of Zhou *et al.* concerning the analogous trialkylboron umpolung of allylic alcohols. We also discuss the mechanistic implications of our results and propose a simple reaction pathway involving σ-allylpalladium intermediates.

Results and discussion

Our primary goal was to investigate the use of modular, chiral, monodentate phosphoramidite ligands **6** (Scheme 3) in this

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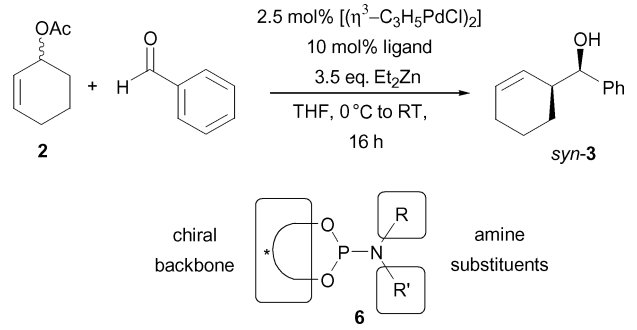


Scheme 3

umpolung protocol. We have previously found this ligand family to be effective in a range of copper and rhodium catalysed procedures.[8] The modular properties of the phosphoramidite skeleton allow for facile synthesis of structural variants and, as such, we hoped to find a readily attainable and high-performing ligand structure.

Ligand screening

As a test reaction, we studied the combination of cyclohexenyl acetate **2** with benzaldehyde (Scheme 3) using Et_2Zn and [(η^3-$C_3H_5PdCl)_2$] as catalyst. A wide range of phosphoramidite ligands was screened (Fig. 1), and the crude reaction mixtures were analysed by chiral HPLC to allow determination of the enantioselectivity of reaction. The results of the stereoselectivity obtained *via* this initial screen can be seen in Fig. 2.

To summarise our findings, simple *N*,*N*-dialkyl substituted phosphoramidites (**A1**–**A10**, **B5**–**B8**) gave low levels of

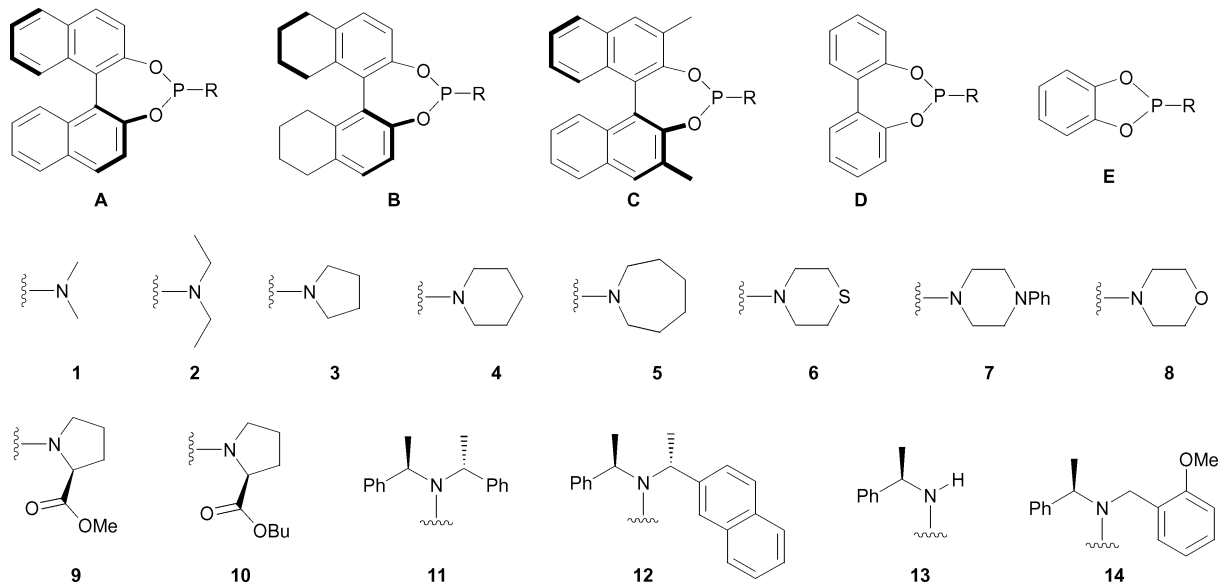


Fig. 1

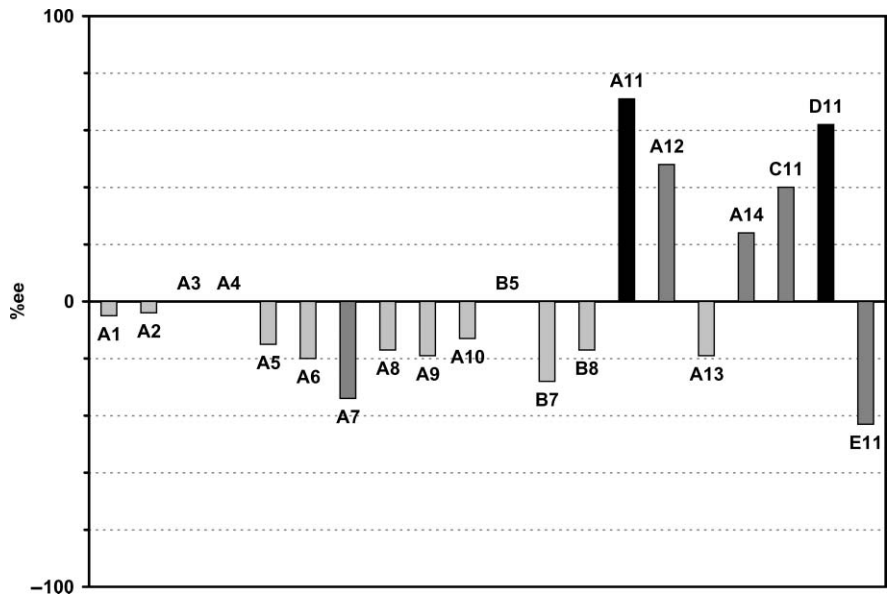


Fig. 2

Table 1 Variation of reaction parameters

Entry	Solvent	Pd Source[a]	Zn Source[b]	Conversion (%)[c]	Ee (%)[d]
1	THF	$[(\eta^3\text{-}C_3H_5PdCl)_2]$	Et_2Zn	>95	70
2	THF	$Pd(OAc)_2$	Et_2Zn	>95	75
3	THF	$Pd(CF_3CO_2)_2$	Et_2Zn	>95	72
4	THF	$Pd(MeCN)_2Cl_2$	Et_2Zn	>95	60
5	THF	$Pd(PhCN)_2Cl_2$	Et_2Zn	>95	81
6	THF	$Pd(acac)_2$	Et_2Zn	>95	66
7	DCM	$Pd(PhCN)_2Cl_2$	Et_2Zn	>95	(−)15
8	Toluene	$Pd(PhCN)_2Cl_2$	Et_2Zn	>95	42
9	Et_2O	$Pd(PhCN)_2Cl_2$	Et_2Zn	>95	35
10	TBME	$Pd(PhCN)_2Cl_2$	Et_2Zn	>95	28
11	THF	$Pd(PhCN)_2Cl_2$	*n*-Bu_2Zn	>95	30
12	THF	$Pd(PhCN)_2Cl_2$	*i*-Pr_2Zn	60	69
13	THF	$Pd(PhCN)_2Cl_2$	Me_2Zn	>95	(−)25

[a] 5.0 mol% Pd used throughout with 10.0 mol% ligand **A11**. [b] 3.5 eq. used throughout. [c] Determined by ^{1}H-NMR. [d] Determined by HPLC.

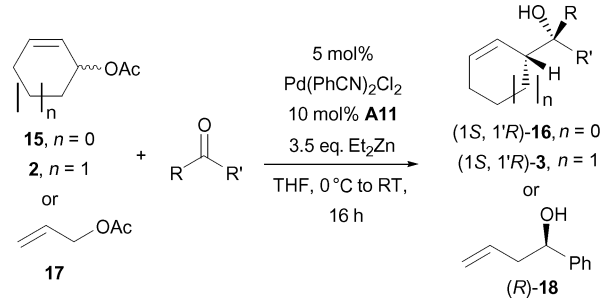
enantiocontrol, although the sense of induction was the same in all cases. The introduction of α-branched *N*-substituents to the phosphoramidite structure resulted in a marked increase in the magnitude of enantioselectivity. As in previous studies by this group[8] and others[9] concerning phosphoramidite based asymmetric transformations, *N*,*N*-bis-α-methylaryl ligands of the type **A11**–**A14** and **C/D/E11** were found to be particularly effective, with 70% ee being obtained for the product **3** when using ligand **A11** (*S*,*R*,*R*, as shown in Fig. 1, indicating *S* configuration for **A** and *R*,*R* configuration for **11**). Interestingly, the *R*,*R*,*R*-diastereomer of **A11** gave the same sense of induction with reduced (21%) *ee*.

Using ligand **A11**, we investigated the effects of varying the Pd and Zn source on the reaction (Table 1). Of the Pd(II) complexes tested, bis-benzonitrile palladium dichloride (entry 5) gave the highest degree of enantiocontrol (81% ee). Exchange of the reaction solvent from THF to toluene, DCM, Et_2O or TBME resulted in attenuation of enantioselectivity. The identity of the Zn source used was found to have a pronounced effect on the reactivity and enantioselectivity of the reaction, with Et_2Zn proving optimal. The use of Et_3B as an umpolung reagent was ineffective in this reaction with little or no conversion to product **3** being observed. In conjunction with the observations made by Zhou *et al.*,[6] this may suggest that Et_2Zn is a superior umpolung reagent to Et_3B when applied to allylic acetates, whilst Et_3B is better suited to allylic alcohols. Attempts to vary the stoichiometries of the various reagents had no beneficial effect, and lowering of the reaction temperature below 0 °C resulted in a severely retarded reaction requiring excessive reaction times.

Substrate screening

Using the conditions outlined in entry 5 (Table 1), we tested the scope of this procedure with a range of aromatic and aliphatic aldehydes and ketones in conjunction with three allylic-substrates (Scheme 4, Table 2). The absolute stereochemistry of products **3**, **16** and **18** was assigned using comparison of $[a]_D$ measurements with literature values. The absolute configuration 1*S*, 1′*R* of compounds **3b**–**f** was assigned by analogy with compounds **3** and **16**.

This protocol worked efficiently for a range of aromatic aldehydes (entries 1–5), with good yields and enantioselectivities being obtained along with very high *syn*-selectivity. The presence of electron withdrawing groups in the aldehyde appeared beneficial (entry 3) compared to electron releasing groups. The heteroaromatic aldehyde (entry 6) did not perform as well with lower enantioselectivity being recorded. As suggested by Tamaru *et al.*,[4] this Et_2Zn mediated protocol is not applicable to aliphatic aldehydes (entries 7 & 8). We found that the allyl-moiety was consumed with no observed homoallylic alcohol formation and we were unable to isolate or identify the products of reaction. Ketones (entries 9 & 10) proved unreactive in this system with the allylic acetate **2** being recovered, even after prolonged reaction times (60 h). We also conclude that this catalyst system is sensitive to the identity of the allyl-fragment, with cyclopentyl and allyl acetate giving lower enantioselectivities (entries 11 & 12).



Scheme 4

Mechanistic discussion

Based on a series of experimental observations concerning the racemic version of this umpolung reaction, Tamaru *et al.* proposed a mechanism involving the generation of a stereochemically defined allylzinc intermediate (**20**, Scheme 5),[4] and subsequent combination with the aldehyde electrophile through a closed, chair transition state (**21a/b**). Whilst the proposed mechanism gives a satisfactory explanation for the racemic reaction, it is more difficult to reconcile with the results gained from the recent, enantioselective versions of this reaction.

If we consider the proposed mechanism as applied to the umpolung of cyclohexenyl acetate **2** with benzaldehyde, two diastereomeric chair-structures are possible (**21a/b**), each satisfying the observed *syn*-selectivity. As the phosphoramidite ligands are the only source of chirality in this catalytic umpolung reaction,

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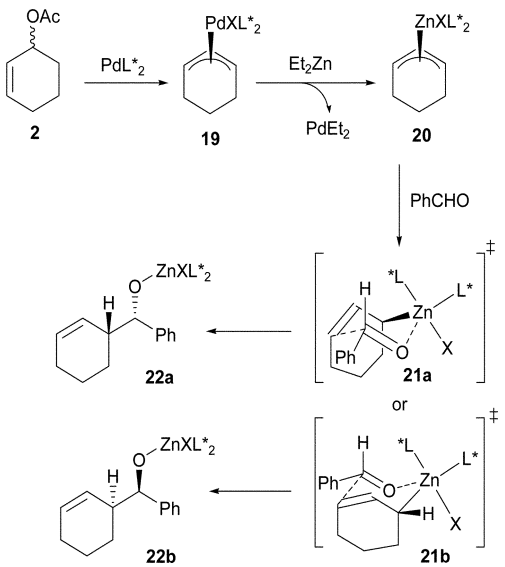
Table 2 Examining the scope of the reaction

Entry	Acetate	Carbonyl	Product	Yield (%)[a]	*syn* : *anti*[b]	Ee (%)[c]
1	**2**	R=H, R′=C_6H_5	**3**	77	>20 : 1	81
2	**2**	R=H, R′=MeO-4-C_6H_4	**3b**	73	>20 : 1	71
3	**2**	R=H, R′=MeO_2C-4-C_6H_4	**3c**	73	>20 : 1	80
4	**2**	R=H, R′=Me-4-C_6H_4	**3d**	82	>20 : 1	72
5	**2**	R=H, R′=Me-2-C_6H_4	**3e**	79	>20 : 1	68
6	**2**	R=H, R′=2-furyl	**3f**	80	>20 : 1	60
7	**2**	R=H, R′=Et	—	<5	—	—
8	**2**	R=H, R′ = *i*-Pr	—	<5	—	—
9	**2**	R=R′=Me	—	<5	—	—
10	**2**	R=Ph, R′=Me	—	<5	—	—
11	**15**	R=H, R′=Ph	**16**	66	>20 : 1	45
12	**17**	R=H, R′=Ph	**18**	73	—	37

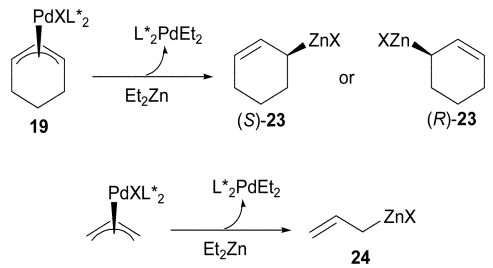
[a] Isolated yield after column chromatography. [b] Determined by ^{1}H-NMR. [c] Determined by HPLC.



Scheme 5

we must assume that they are involved in the enantio-determining step (**20** → **21**). Thus, the chiral ligands (L*) are required to be bound to the zinc centre in **20** and will ultimately reside on the zinc centre in the alcoholate product **22a/b**. Since zinc is not catalytic (3.5 eq.), the source of chirality (L*) would be removed from any catalytic cycle after a single turnover, *unless* the ligands (L*) were capable of continually switching between allyl-Pd, allyl-Zn (**20**) and alkoxide-Zn (**22**) centres. We have studied reaction systems utilising phosphoramidite ligands in the presence of dialkylzinc species and have never observed zinc–phosphoramidite interactions, moreover, we were unable to find any examples of zinc–phosphoramidite complexes in the literature. Based on this, and the known stability of palladium/phosphoramidite systems,[10] we believe that continual migration of the chiral ligands (L*) between various zinc and palladium centres is, at best, unlikely.

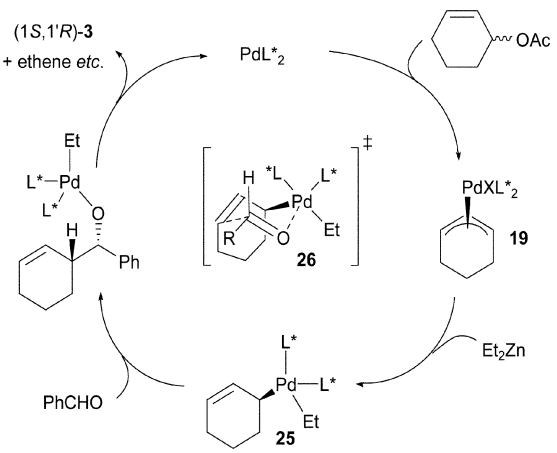
This problem of ligand migration might be avoided by proposing that treatment of the π-allylpalladium species **19** with diethylzinc proceeds directly, and in *enantioselective* fashion to a configurationally stable, σ-allylzinc species **23** (Scheme 6). However, the analogous reaction with allyl acetate (**17**, Table 2, entry 12, and reference 6) would generate a σ-allylzinc species **24** that contains *no*



Scheme 6

chiral information and would be incapable of generating product **18** with any enantioselectivity. This is in direct conflict with the observed experimental data in this study.

Based on experimental observations and computational calculations,[11] Szabó *et al.* have shown that η^1-allylpalladium species can undergo electrophilic allylation with aldehydes; this requires the presence of electron-releasing substituents on palladium to promote the change from η^1 to η^3. By analogy, we propose that the role of Et_2Zn in this umpolung reaction is to alkylate the η^3-allylpalladium species **19** (Scheme 7) and promote the formation of the corresponding η^1-allylpalladium species **25**. This could proceed in enantioselective fashion and allow formation of the observed product **3** *via* a transition state such as **26**. Although suggested to be of low nucleophilicity, allyl-alkyl-palladium species have



Scheme 7

previously been shown to allylate electrophiles[12] and have also been considered as possible intermediates in this reaction pathway by Tamaru *et al.*[4] We would suggest that a pathway such as that shown in Scheme 7 provides a more satisfactory explanation of our results, and the recently reported results of Zanoni[5] and Zhou.[6] The possibility that this umpolung reaction proceeds *via* a more complex, zinc-palladium aggregated species should also be considered; detailed studies are required to investigate this further.

Conclusions

In summary, we have shown that phosphoramidites are versatile ligands in the palladium catalysed diethylzinc mediated umpolung allylation of aldehydes, and provide the highest levels of enantioselectivity yet reported. We have investigated the scope of this methodology with regards to both the nucleophilic and electrophilic reagents and proposed an alternative mechanism that accounts for the formation of enantio-enriched products.

Experimental

General

^{1}H-NMR spectra were recorded at 200, 300 or 400 MHz with $CDCl_3$ (referenced to 7.27 ppm) as solvent. ^{13}C-NMR spectra were recorded at 200 or 300 MHz with $CDCl_3$ (referenced to 77.1 ppm) as solvent. Coupling constants (*J*) are given in Hz. Varian Gemini 200, VXR300 and AMX400 spectrometers were used throughout. HRMS data was obtained using a Jeol JMS-600H spectrometer. Infra-red spectra were recorded using an Avatar-series spectrometer. A Shimadzu 10A system was used for HPLC and Hewlett-Packard HP6890 for GC analysis. Optical rotations were measured using a Schmidt & Haendsch polarimeter (Polartronic MH8) with a 10 cm cell (*c* given in g per 100 mL and measurements are given in 10^{-1} deg cm^2 g^{-1}). Thin layer chromatography was performed on commercial Kieselgel $60F_{254}$ silica gel plates; $KMnO_4$ and $H_3[P(Mo_3O_{10})_4].H_2O$ were used for visualisation. Flash chromatography was performed using silica gel.

Synthesis of allylic acetates

Allylic acetate **17** was purchased from Aldrich and used without further purification. Racemic 2-cyclohexenyl acetate **2**[13] and 2-cyclopentenyl acetate **15**[14] are known compounds and were synthesised *via* a 2-step procedure comprising 'Luche' reduction[15] of the corresponding cyclic enone and acylation of the resulting allylic alcohol.[13]

Synthesis of phosphoramidite ligands

Ligand **A1** was kindly donated by DSM. Ligands **A2**, **A4**, **A8**, **A6**, **A11**;[16] **A3**, **A5**, **A7**, **A9**, **A10**, **B8**, **B7**, **B5**;[17] **A13**;[18] **C11**;[19] **D11**[20] and **E11**[21] have been reported previously in the literature.

***O*,*O*′-(*S*)-(1,1′-Dinaphthyl-2,2′-diyl)-*N*-2-methoxy-benzyl-*N*′-(*R*)-1-phenylethylphosphoramidite (A14).** To a flame-dried, round-bottomed flask fitted with a reflux condenser was added (*S*)–BINOL (1.76 mmol, 490 mg). The system was placed under nitrogen and PCl_3 (2.50 mL) was added. The mixture was heated to reflux for 16 h, then allowed to cool to room temperature. The excess PCl_3 was removed *in vacuo* and 3 cycles of toluene addition/evaporation were completed to give the crude BINOL-PCl product as a white semi-solid which was dissolved in toluene (20.0 mL). To a separate flame-dried flask was added (*R*)-(2-methoxy-benzyl)-(1-phenylethyl)-amine (1.95 mmol 471 mg). The flask was placed under nitrogen and dry THF (15.0 mL) was added. The mixture was cooled to 0 °C with stirring and *n*-BuLi (2.10 mmol) was added to give a bright red solution. This mixture was added to the BINOL-PCl–toluene solution at 0 °C and the resulting mixture was stirred for 3 h. The mixture was warmed to room temperature and Et_2O (25.0 mL) was added. The mixture was filtered (celite) and the solvent was removed *in vacuo* to give a pale yellow oil. Flash column chromatography (20 : 1 hexane–EtOAc) gave phosphoramidite **A14** as an off-white solid (340 mg, 35%); $[a]_D^{22}$ +216.4 (*c* 1.0 in $CHCl_3$); ν_{max}/cm^{-1} (solid) 3061, 1589, 1462, 1230, 949, 821 and 750; δ_H (400 MHz; $CDCl_3$) 1.51 (3H, d, *J* 6.8, CH*Me*), 3.65 (3H, s, O*Me*), 3.84, (1H, dd, *J* 16.6, 6.4, NC*H*H′), 3.94 (1H, dd, *J* 16.6, 8.4, NCH*H*′), 4.62, (1H, m, C*H*Me), 6.76 (1H, d, *J* 8.3, Ar–*H*), 7.00 (1H, t, *J* 7.3, Ar–*H*), 7.10 (1H, d, *J* 8.8, Ar–*H*), 7.20–7.50 (12H, m, Ar–*H*), 7.60 (2H, m, Ar–*H*), 7.71 (1H, d, *J* 8.8, Ar–*H*), 7.84 (1H, d, *J* 8.3, Ar–*H*), 7.94 (1H, d, *J* 7.8, Ar–*H*), 8.00 (1H, d, *J* 8.8, Ar–*H*); δ_C (400 MHz; $CDCl_3$) 18.2, 38.7, 52.5, 53.2, 107.6, 116.8, 117.8, 119.4, 119.6, 119.9, 121.9, 122.3, 123.4, 123.5, 124.6, 125.3, 125.4, 125.6, 125.8, 126.1, 126.9, 127.1, 127.7, 128.0, 128.9, 130.1, 130.3, 140.0, 147.0, 147.4, 147.5; δ_P (400 MHz; $CDCl_3$) 146.1; *m*/*z* (EI+) 555 (7%, M$^+$), 524 (50%), 450 (15%), 434 (100%), 433 (59%), 268 (20%), 121 (17%), 91 (20%), HRMS $C_{36}H_{30}NO_3P$ 555.1946 (requires 555.1963).

General procedure for the palladium catalysed, diethylzinc-mediated umpolung allylation of aldehydes

To a flame-dried, round-bottom flask was added $Pd(PhCN)_2Cl_2$ (0.05 eq., 10 μmol, 3.80 mg) and ligand **A11** (0.10 eq., 20 μmol, 10.80 mg). The flask was placed under nitrogen, THF (1.50 mL) was added and the mixture was stirred at 0 °C for 15 min. The allyl acetate (1.20 eq., 0.24 mmol) and aldehyde (1.00 eq., 0.20 mmol) were added, followed by Et_2Zn (1.0 M in hexanes, 3.50 eq., 0.70 mmol, 0.70 mL). The mixture was allowed to warm to room temperature over 16 h before quenching with saturated NH_4Cl (aq.). After stirring for 30 min, Et_2O (5 mL) was added and the organic phase was separated, washed with brine (2 × 10 mL), dried ($MgSO_4$) and evaporated to give the crude homo-allylic alcohol product. Purification was achieved *via* flash column chromatography (hexane–EtOAc).

(1*S*, 1′*R*)(Cyclohex-2-enyl)(phenyl)methanol (3). Obtained as a clear oil (29 mg, 77%); absolute stereochemistry assigned by optical rotation $[a]_D^{22}$ +14.8 (*c* 0.85 in C_6H_6) (lit.,[22] +11.1); HPLC (Chiralcel OD-H [300 mm], heptane–propan-2-ol 99 : 1, 0.50 mL min^{-1}, 30.3 min [major], 35.6 min [minor]) shows 81% ee; ^{1}H and ^{13}C-NMR in full agreement with literature.[23]

(1*S*, 1′*R*)(Cyclohex-2-enyl)(4-methoxy-phenyl)methanol (3b). Obtained as a clear oil (32 mg, 73%); absolute stereochemistry assigned by analogy to compounds **3** and **16**; HPLC (Chiralcel OD–H [300 mm], heptane–propan-2-ol 99 : 1, 0.50 mL min^{-1}, 47.8 min [minor], 52.8 min [major]) shows 71% ee; ^{1}H and ^{13}C-NMR in full agreement with literature.[24]

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(1*S*, 1′*R*)-4-(Cyclohex-2-enyl-hydroxy-methyl)-benzoic acid methyl ester (3c). Obtained as a clear oil (36 mg, 73%); absolute stereochemistry assigned by analogy to compounds **3** and **16**; HPLC (Chiralcel OD-H [300 mm], heptane–propan-2-ol 95 : 5, 0.50 mL min^{-1}, 23.5 min [minor], 27.8 min [major]) shows 80% ee; ν_{max}/cm^{-1} (deposited on KBr powder) 3507 (OH), 2928, 1723 (CO), 1436, 1280, 1112; δ_H (400 MHz; $CDCl_3$) 1.42–1.70 (6H, m), 1.93 (2H, m), 2.46 (1H, br-s, O*H*), 3.86 (3H, s, CO*Me*), 4.64 (1H, d, *J* 5.9, C*H*OH), 5.35 (1H, d, *J* 10.2), 5.80 (1H, m), 7.35 (2H, d, *J* 8.0, Ar–H), 7.95 (2H, d, *J* 8.0, Ar–H); δ_C (200 MHz; $CDCl_3$) 18.5, 20.8, 22.6, 40.5, 49.5, 74.2 (CO*Me*), 123.9, 125.0, 126.5, 127.0, 128.6, 145.5, 164.5; *m*/*z* (EI+) 215 (3%, M^+), 166 (14%), 165 (100%); HRMS $C_{15}H_{18}O_3$ 246.1253 (requires 246.1256).

(1*S*, 1′*R*)(Cyclohex-2-enyl)(*p*-tolyl)methanol (3d). Obtained as a clear oil (33 mg, 82%); absolute stereochemistry assigned by analogy to compounds **3** and **16**; HPLC (Chiralpak AD [300 mm], heptane–propan-2-ol 99 : 1, 1.00 mL min^{-1}, 19.9 min [major], 21.2 min [minor]) shows 72% ee; ^1H and ^{13}C-NMR in full agreement with literature.[25]

(1*S*, 1′*R*)(Cyclohex-2-enyl)(*o*-tolyl)methanol (3e). Obtained as a clear oil (32 mg, 82%); absolute stereochemistry assigned by analogy to compounds **3** and **16**; HPLC (Chiralcel OD–H [300 mm], heptane–propan-2-ol 99 : 1, 0.50 mL min^{-1}, 27.4 min [major], 32.3 min [minor]) shows 68% ee; ν_{max}/cm^{-1} (deposited on KBr powder) 3403 (O*H*), 2927, 1488, 1448, 1017, 760, 730; δ_H (400 MHz; $CDCl_3$) 1.40–1.80 (4H, m), 1.95 (2H, m), 2.27 (3H, Ar*Me*), 2.42 (1H, m, C*H*CHOH), 4.80 (1H, dd, *J* 6.6, 2.6, C*H*OH), 5.27 (1H, dd, *J* 10.3, 2.2), 5.77 (1H, m), 7.05–7.22 (3H, m, Ar–*H*), 7.44 (1H, d, *J* 7.7, Ar–*H*); δ_C (200 MHz; $CDCl_3$) 17.9, 19.6, 22.6, 23.7, 40.4, 71.8 (*C*HOH), 124.5, 124.6, 125.6, 126.5, 128.7, 128.9, 133.3, 139.6; *m*/*z* (EI+) 202 (1%, M^+), 122 (9%), 121 (100%), 93 (25%), 91 (14%), 77 (11%); HRMS $C_{14}H_{18}O$ 202.1361 (requires 202.1357).

(1*S*, 1′*R*)(Cyclohex-2-enyl)(furan-2-yl)methanol (3f). Obtained as a clear oil (28 mg, 80%); absolute stereochemistry assigned by analogy to compounds **3** and **16**; HPLC (Chiralcel OD–H [300 mm], heptane–propan-2-ol 99 : 1, 0.50 mL min^{-1}, 29.6 min [major], 33.1 min [minor]) shows 60% ee; ν_{max}/cm^{-1} (deposited on KBr powder) 3399 (OH), 2927, 2856, 1448, 1148, 1009, 734; δ_H (400 MHz; $CDCl_3$) 1.42–1.58 (2H, m), 1.64–1.84 (3H, m), 1.88–2.00 (2H, m), 2.60 (1H, m, C*H*CHOH), 4.49 (1H, d, *J* 7.3, C*H*OH), 5.33 (1H, dd, *J* 10.2, 2.2), 5.75 (1H, m), 6.21 (1H, d, *J* 2.9, furyl-*H*), 6.28 (1H, dd, *J* 2.9, 1.9, furyl-*H*), 7.38 (1H, d, *J* 1.9, furyl-*H*); δ_C (200 MHz; $CDCl_3$) 19.4, 22.9, 23.6, 39.2, 69.8, 105.3, 108.6, 125.7, 128.6, 140.3, 157.5; *m*/*z* (EI+) 178 (6%, M^+), 157 (28%), 149 (13%), 132 (34%), 131 (37%), 116 (19%), 103 (13%), 97 (100%), 91 (30%); HRMS $C_{11}H_{14}O_2$ 178.0999 (requires 178.0994).

(1*S*, 1′*R*)(Cyclopent-2-enyl)(phenyl)methanol (16). Obtained as a clear oil (23 mg, 66%); absolute stereochemistry assigned by optical rotation $[\alpha]_D^{22}$ +13.8 (*c* 1.00 in $CHCl_3$) (lit.,[22] +27.2); GC (Chiralsil-L-val, [25.0 m × 0.25 mm], 0.50 mL min^{-1}, initial temp. 120 °C for 15 min, then 5 °C min^{-1} to final temp. 160 °C, 22.7 min [minor], 22.8 min [major]) shows 45% ee; ^1H and ^{13}C-NMR in full agreement with literature.[26]

(*R*)-1-Phenyl-but-3-en-1-ol (18). Obtained as a clear oil (22 mg, 73%); absolute stereochemistry assigned by optical rotation $[\alpha]_D^{22}$ +22.8 (*c* 1.00 in C_6H_6) (lit.,[27] +45.0); HPLC (Chiralcel OD-H [300 mm], heptane–propan-2-ol 99 : 1, 0.50 mL min^{-1}, 35.2 min [major], 39.0 min [minor]) shows 37% ee; ^1H and ^{13}C-NMR in full agreement with literature.[27]

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