Chiral Wide Bite Angle Diphosphine Ligands: Synthesis, Coordination Chemistry and Application in Pd-catalyzed Allylic Alkylation

*Christine F. Czauderna,[a] Amanda G. Jarvis,[a] Frank J. L. Heutz,[a] David B. Cordes,[a] Alexandra M. Z. Slawin,[a] Jarl Ivar van der Vlugt,[b] Paul C. J. Kamer[a,]**

[a] *EASTCHEM, School of Chemistry University of St. Andrews, North Haugh, St. Andrews, Fife, KY16 9ST, United Kingdom. E-mail: pcjk@st-andrews.ac.uk*

[b] *van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Science Park 904, 1098 XH Amsterdam, the Netherlands.*

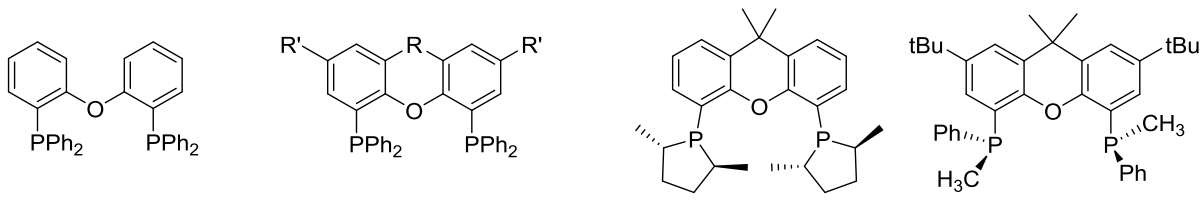
Abstract

A series of diphosphine ligands bearing ester- and ether-modified diphenylether backbones have been prepared. The introduction of carboxylic acid or ether auxiliaries in the *ortho*-positions relative to the diphenylphosphine groups was achieved *via* straightforward four-step synthetic protocols, prior to introduction of the phosphines. The electronic properties of these backbone-modified DPEPhos ligands were evaluated by probing the relevant carbonyl stretching frequencies (ν_{CO}) of $Ni(CO)_2$(**PP**) species (**PP** = diphosphine) using IR spectroscopy and by determining the phosphorus-selenium coupling constant $J_{Se\text{-}P}$ of phosphine selenide derivatives using $^{31}P\{^1H\}$ NMR spectroscopy. Also the X-ray structure for the bis(carbonyl)nickel(0) species with one of the ligands is reported. The [Pd(η^3-allyl)(**PP**)]-complexes were characterized by multinuclear NMR spectroscopy and applied in the asymmetric allylic alkylation of l,3-diphenyl-2-propenyl acetate and cyclohex-2-enyl

acetate with dimethyl malonate in order to benchmark their catalytic potential. The enantioselectivity (ranging from 3 to 70 %) was found to depend on the size of the chiral auxiliary introduced within the diphenyl ether backbone and its proximity to the phosphorus donor groups and hence to the active metal centre. These studies revealed that substituents on the backbone have only a minor effect on the electronic character of the diphenylphosphine groups.

Introduction

Achiral diphosphorus ligands with a natural bite angle between 100 and 110° (*i.e.* wide bite angle ligands) have been found to have a significant impact on the reactivity of various transition metal catalysed reactions, including Rh-catalyzed hydroformylation and Pd-catalyzed allylic substitution.[1] The correlation between bite angle and selectivity has been studied systematically using a specific series of the Xantphos ligand family (**1**-**4**, Figure 1).[2]



DPEPhos **1**

Xantphos (R = $C(CH_3)_2$; R' = H) **2**
Sixantphos (R = $S(CH_3)_2$; R' = H) **3**
Thixantphos (R = Si; R' = CH_3) **4**

(S,S)-Duxantphos **5**

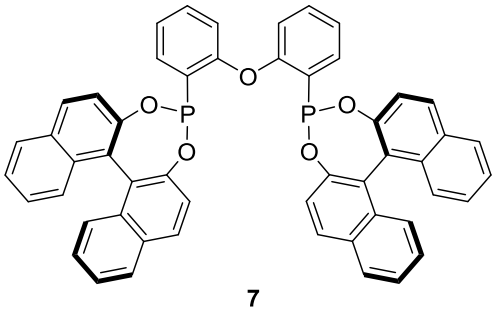
P-stereogenic Xantphos **6**

Fig. 1 *Examples of wide bite angle diphosphine ligands*

Also in asymmetric catalysis, wide bite angle ligands such as Duxantphos **5** have shown encouraging results with respect to chemo-, regio- and enantioselectivity.[3,4] Chirality has been introduced in wide bite angle diphosphine ligands mainly through the use of chiral substituents on the phosphorus donors (**5**) and *via* the introduction of P-stereogenic centres

(**6**).[5] We herein discuss an unexplored approach to develop new chiral wide bite angle diphosphine ligands, using chiral backbones, with the aim to disclose potential new ligand classes for asymmetric catalysis.

Concerning the choice of wide bite angle backbone, it can be anticipated that chiral substituents have a higher impact towards the active centre of the catalyst when they are located at a flexible backbone instead of a rigid backbone. Diphenyl ether was selected as a promising candidate to assess this approach of chiral auxiliary modification, as the backbone is more easily subjected to alterations by organic transformations and displays more flexibility compared to 9,9-dimethylxanthene. DPEPhos, with a calculated natural bite angle of 102.9°, has displayed high selectivity in a variety of reactions, including rhodium catalyzed hydroformylation,[6] palladium catalyzed cross-couplings,[7] and allylic alkylation.[2] The only chiral diphosphorus ligands based on diphenylether as backbone carry either chiral auxiliaries at phosphorus[8,9] (**7**-**9** in Figure 2) or possess stereogenic phosphorus atoms (**10**).[10] The former systems have been successfully applied in a number of asymmetric catalytic transformations, including conjugate addition of arylboronic acids, hydrogenation, allylic alkylation, hydrocyanation and hydroformylation.[9,11-13]



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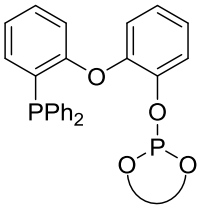

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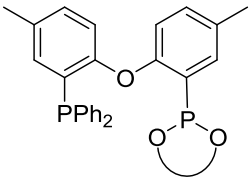

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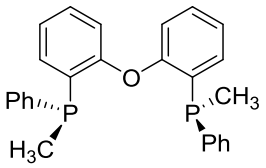

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Fig. 2 *Chiral DPEPhos ligand* ***7****, hybrid analogues* ***8*** *and* ***9*** *and P-stereogenic derivative* ***10***

Recent years have shown a growing interest in combining the reactivity of transition metal complexes with the unrivalled selectivity of enzymes.[14] So far, focus has mainly been on anchoring strategies and genetic optimization, whereas rational ligand design could also contribute to novel unnatural enzymes. Lu et al. have shown that dual anchoring of artificial cofactors could be very beneficial to the induced selectivity of a catalytic reaction.[15] Flexible wide bite angle ligands such as DPEphos are promising candidates for such an approach. Therefore, we wanted to explore the effect and impact of dual chiral entities in close proximity to wide bite angle bidentate phosphorus donor centers in model structures.

Altogether the above considerations have resulted in a modular design concept that is depicted in Figure 3. For the modification of the diphenyl ether with chiral auxiliaries, alkoxy- as well as ester functionalities have been considered as chiral entities. These groups have the advantage that they are easily accessible from the chiral pool, starting from commercial chiral carboxylic acids and alcohols. The novel wide bite angle diphosphorus ligands have been evaluated in several homogeneously catalysed reactions. The influence of the chiral auxiliaries on various transition metal complexes was studied.

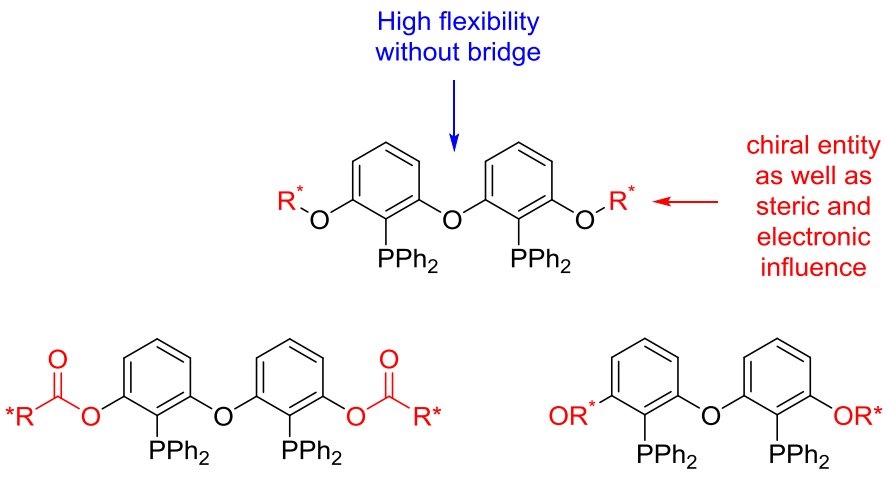
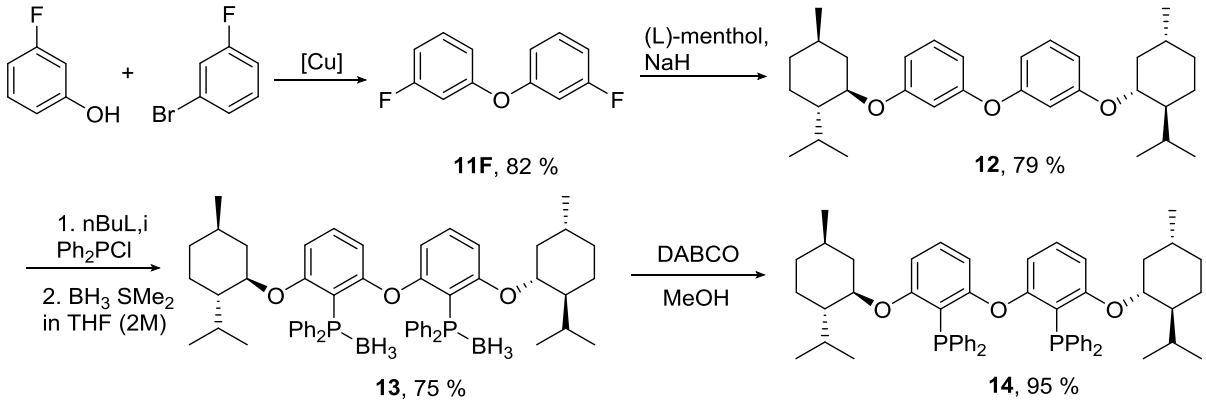


Fig. 3 *(top) Schematic representation of the potentially modular approach with modified chiral DPEPhos backbone through the introduction of chiral carboxylic acid or alcohol auxiliaries in the backbone.*

Synthesis of DPEPhos Derivatives Bearing Chiral Ether Side-Groups

To install a chiral ether entity in the backbone of DPEPhos, thereby generating novel chiral diphosphines, the diphenyl ether skeleton could be coupled with a chiral alcohol. Menthol was used as an example as it is a cheap and commercially available reagent. 3,3'-Difluorodiphenyl ether **11F**, obtained by Cu-catalyzed coupling of 3–fluorophenol and 3-bromofluorobenzene as a colourless oil, was reacted with (*L*)-menthol in the presence of NaH in DMF at 120 °C to yield product **12** as an oil (see Scheme 1).



Scheme 1 *Synthetic route to ligand **14** bearing chiral ether auxiliaries in the DPE backbone.*

Subsequent selective lithiation of both phenyl rings followed by phosphorylation and *in situ* protection with BH_3 gave the air-stable diphosphine-borane **13** after recrystallisation from an acetone/methanol mixture in high yield. Slow diffusion of hexane into a concentrated diethyl ether solution of **13** resulted in single crystals suitable for X-ray crystallographic analysis. The molecular structure is shown in Figure 4, including relevant bond distances and angles and the absolute configuration of the ligand was confirmed (Flack parameter 0.05(17)). As

expected from the free rotation of the C-O-C bond the two phenyl rings are not in one plane. The phosphorus atoms are close to ideal tetrahedral geometry. The P-C bond lengths are similar to those of other wide bite angle ligands such as Xantphos.[6] The two BH_3-groups are positioned inward, resulting in a large intramolecular distance between the two phosphorus atoms (5.34 Å), which is larger than P····P distance of 4.876 Å[16] in unprotected DPEphos where the P····P distance in Xantphos is only 4.080 Å.[6] The average intramolecular P·····O distance of 3.089 Å suggests that the menthol substituents are too far away to show direct interaction with the diphenylphosphine group, although this situation may change upon coordination to a transition metal. Free diphosphine **14** was obtained as a white solid on removal of the BH_3-protecting group by treatment of **13** with DABCO.

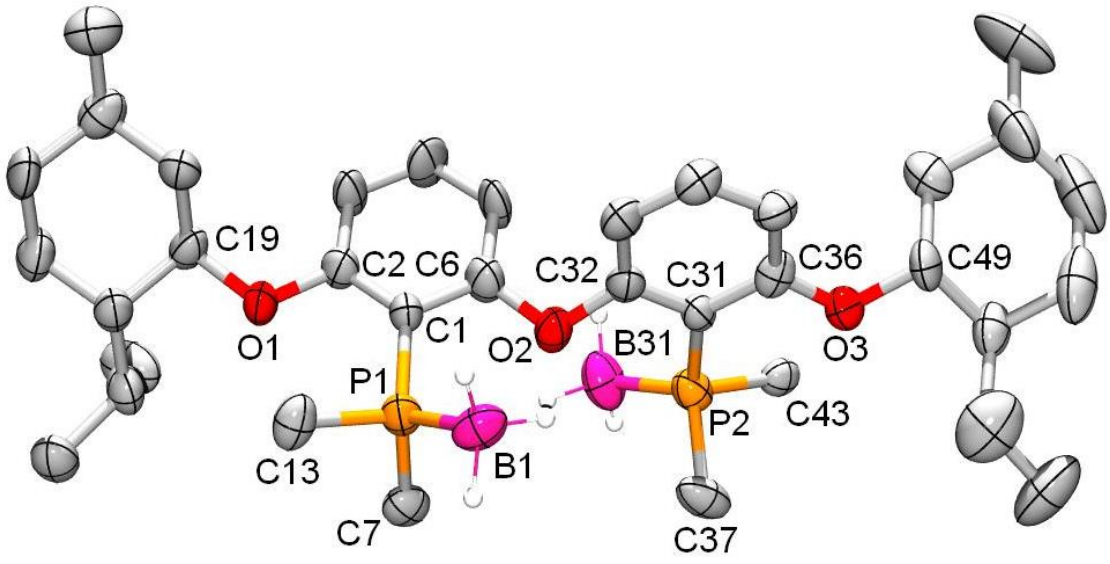
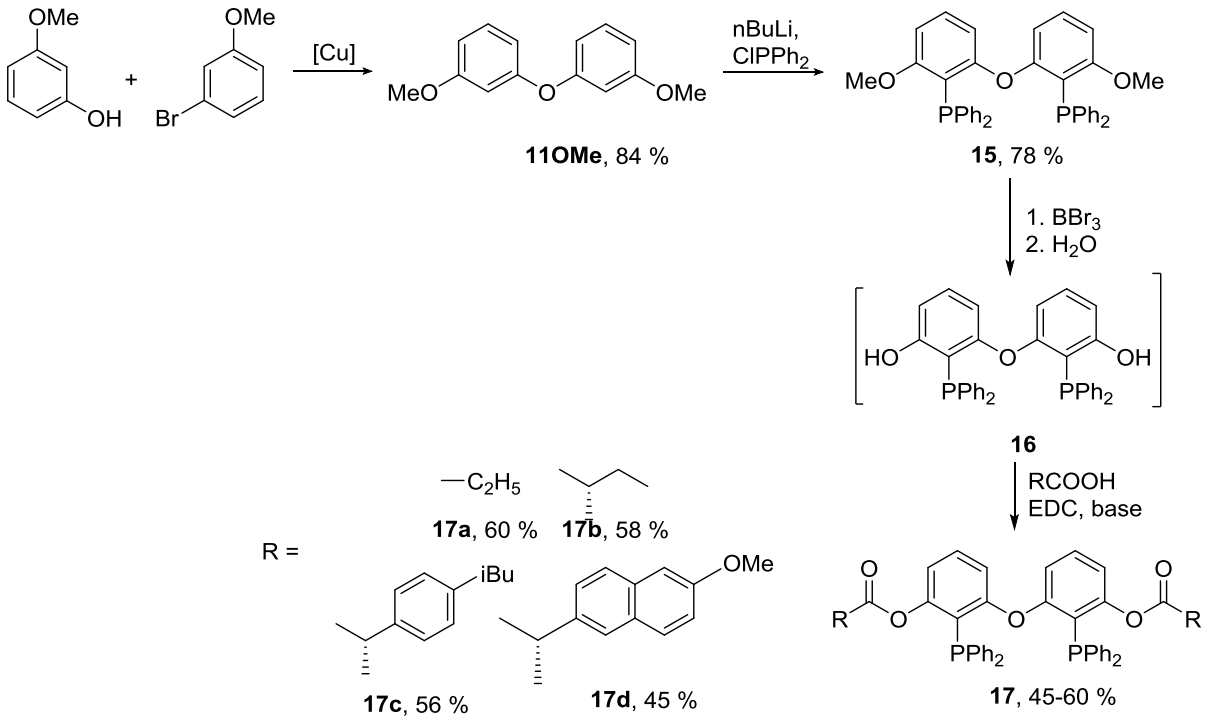


Fig. 4 *ORTEP representation of compound **13**. Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms and carbon atoms of the phenyl rings at the phosphorus atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): P_1-C_1 1.829(10); P_2-C_{31} 1.812(10); P_1-B_1 1.940(18); P_2-B_{31} 1.917(19); P_1---P_2 5.34; P_1---O_1 3.132(8); P_2---O_3*

3.045(8); C_{13}-P_1-B_1 105.0(6); C_{43}-P_2-B_{31} 103.6(6); C_1-P_1-C_7 106.4(5); C_{31}-P_2-C_{37} 107.1(5); C_6-O_2-C_{32} 117.4(7).

Synthesis of DPEPhos Derivatives Bearing Chiral Ester Auxiliaries

As an alternative to the ether functionalization, a chiral *ester* entity can also be introduced in the backbone of DPEPhos. Cheap and commercially available carboxylic acids give access to a series of different new chiral ligands. As the starting point, the same diphenyl ether backbone bearing two methoxy groups (**11OMe**) (*vide supra*) was employed (Scheme 2). Subsequent selective lithiation of both phenyl rings (*ortho* of the two oxygen substituents) followed by phosphorylation by chlorodiphenylphosphine resulted in compound **15** in 78% yield.



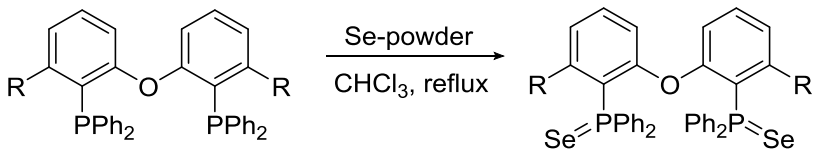
Scheme 2 *Synthetic route to members of new chiral DPEPhos ligand family (**17a-d**).*

After slow addition of an excess of BBr_3 to a solution of species **15** in CH_2Cl_2 and subsequent hydrolysis, the $^{31}P\{^1H\}$ NMR spectrum indicated full conversion of the starting material after six hours of reaction. However, isolation of this species, presumably structure **16**, in pure form proved to be very difficult and as a consequence, this compound was used without further purification for the introduction of chiral ester fragments. After careful optimization of the reaction conditions, and by using different commercially available carboxylic acids, a prototypical achiral (**17a**) as well as three chiral ligands (**17b**-**17d**) were accessible. The products were obtained in good yields after crystallization from methanol or by flash filtration over silica-gel.

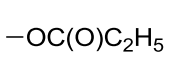
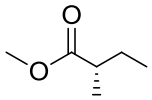
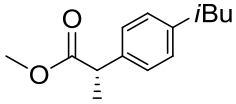
Electronic properties of the ligands

The *σ*-donation can be assessed by measuring the coupling constant of the corresponding phosphine selenide species, observable by $^{31}P\{^1H\}$ NMR spectroscopy.[17,18] To estimate the *σ*-donation abilities of the new ligands, the corresponding diselenides were synthesised by treating the diphosphines with elemental selenium in refluxing chloroform. For the chiral ether modified backbones, the phosphorus-selenium coupling constant $^1J_{P\text{-}Se}$ was 740 Hz, whilst for the ester derivatives a value of 750 Hz was found (Table 1). These values are slightly higher than for the parent DPEPhos system ($^1J_{P\text{-}Se}$ 734 Hz).[19] Therefore, comparable *σ*-donation abilities of the modified ligands can be expected compared to DPEPhos.

Table 1 *Corresponding diselenides of the modified DPEPhos ligands and parent DPEPhos.*



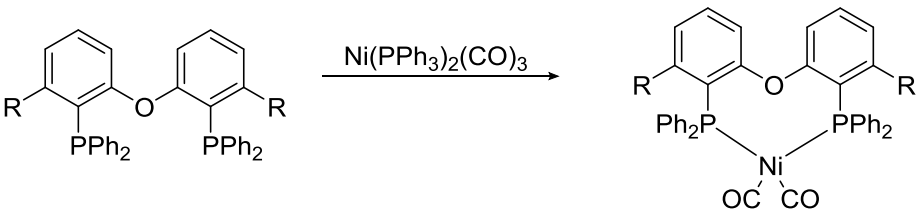
Ligand	R	$^{31}P\{^1H\}$ NMR (ppm)	$^1J_{P\text{-}Se}$ (Hz)
15	$-OCH_3$	23.4	740

17a		23.6	749
17b		23.90, 23.67	750
17c		24.61, 23.48	749
DPEPhos	H	29.4	734

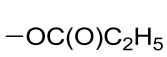
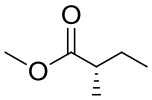
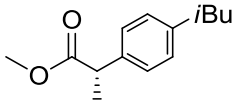
Note: $^{31}P\{^{1}H\}$ NMR: 161 MHz, $CDCl_3$, 297 K

The degree of ligand π-acceptor character can be probed by measuring the carbonyl stretching frequencies of Ni($\mathbf{L_x}$)$(CO)_{4-x}$ complexes with IR spectroscopy.[20] This methodology has primarily been utilized to assess the electronic properties of monodentate phosphorus ligands,[21] although also some Ni(**L**)$(CO)_2$ complexes with diphosphine systems have been reported.[20] The nickel-carbonyl complexes are easily prepared by reaction of the respective ligand with $[Ni(CO)_2(PPh_3)_2]$. The corresponding DPEPhos-derived Ni-complex was also investigated for comparison as no literature data for this compound was available. The carbonyl frequencies (ν_{CO}) are summarized in Table 2. It is evident that chiral modification of the ligand skeleton infers significant electronic differences (of up to 25 cm^{-1}) in the frameworks compared to DPEPhos.[21]

Table 2 *IR and $^{31}P\{^{1}H\}$ NMR data of [Ni(**L**)$(CO)_2$] of selected modified DPEPhos ligands and parent DPEPhos.*



Ligands	R	$^{31}P\{^{1}H\}$ NMR (ppm)	ν_{CO} (Ni(**L**)$(CO)_2$)
15	$-OCH_3$	16.7	1986, 1920

17a		17.6	1992, 1932
17b		17.6	1999,1936
17c		17.3	2004, 1945
DPEPhos	H	25.9	1999, 1940

Note: $^{31}P\{^{1}H\}$ NMR: 161 MHz, $CDCl_3$, 297 K

Besides the information gathered from the IR spectroscopic study on these nickel-carbonyl complexes, an X-ray crystallographic analysis of single crystals of complex **21**, Ni(**15**)$(CO)_2$, obtained by slow diffusion of diethylether into a CH_2Cl_2-solution, provided the molecular structure depicted in Figure 5. The Ni^0 centre has a tetrahedral geometry, as expected, with a P_1-Ni_1-P_2 bite angle of 109.32(8)°.

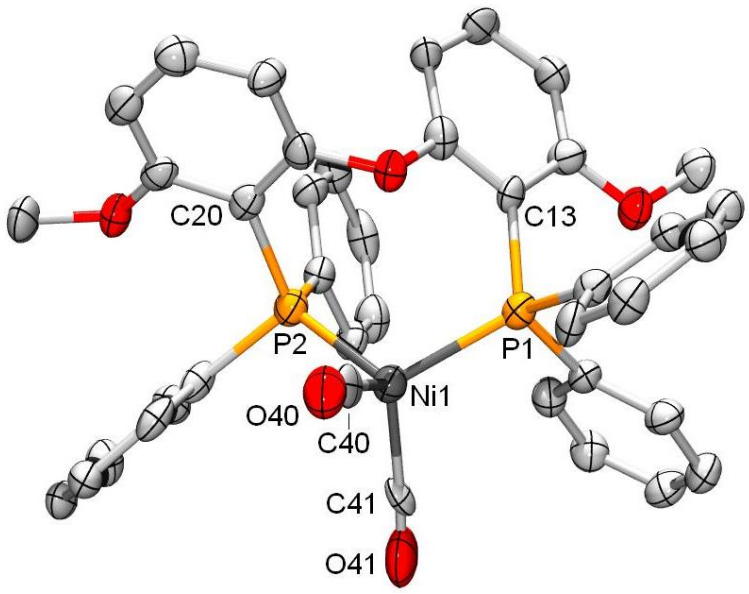


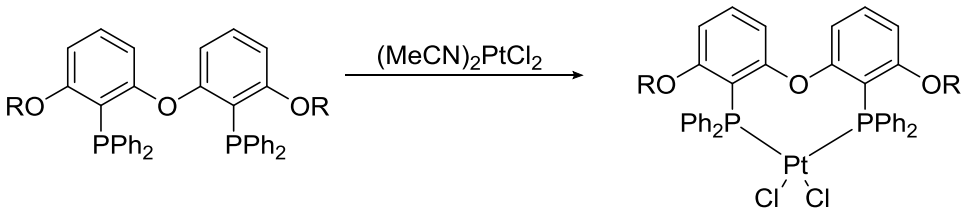
Fig. 5 *ORTEP representation of complex **21**, Ni(**15**)$(CO)_2$. Displacement ellipsoids are drawn at the 50% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni_1-P_1 2.253(2); Ni_1-P_2 2.254(2); P_1-C_{13} 1.848(6); P_2-C_{20}*

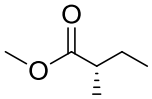
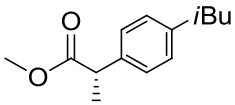
1.844(7); Ni_1-C_{41} 1.856(8); Ni_1-C_{40} 1.819(9); P_1---P_2 3.67; P_1-Ni_1-P_2 109.32(8); P_1-Ni_1-C_{41} 107.3(2); P_2-Ni_1-C_{40} 105.06(3); Ni_1-C_{40}-O_{40} 176.0(8); Ni_1-C_{41}-O_{41} 173.9(8).

Coordination behaviour to Pt and Pd

The natural bite angle of $PdCl_2$(DPEPhos) was calculated to be 102.9°[6] and the platinum-phosphorus coupling constant $^1J_{Pt\text{-}P}$ of 3795 Hz, observable by $^{31}P\{^1H\}$ NMR spectroscopy, for the related square-planar species $PtCl_2$(DPEPhos) indicates *cis*-coordination of the diphosphine ligand.[7] To assess the structural similarity with the modified diphenyl ether ligands, the corresponding [$PtCl_2$(**L**)]-complexes were synthesized by reaction of $PtCl_2(MeCN)_2$ with the chiral diphosphines. All complexes showed similar large coupling constants $^1J_{Pt\text{-}P}$ (between 3858 and 3877 Hz), comparable with DPEPhos (Table 3). These coupling constants indicate *cis*-coordination of the ligands in the square-planar Pt-complex. In the case of **15** the *trans*-compound was also observed.

Table 3 *$^{31}P\{^1H\}$ NMR data of $PtCl_2$(**L**)-complexes using selected DPEPhos-analogues.*



Ligand	R	$^{31}P\{^1H\}$ NMR (ppm)	$^1J_{Pt\text{-}P}$ (Hz)
15	$-OCH_3$	–3.74	3858
17a	$-OC(O)C_2H_5$	–3.49	3863
17b		–3.63	3862
17c		–3.12	3877
DPEPhos	H	2.0[9]	3795[9]

Note: reactions performed at room temperature in dichloromethane/MeCN overnight. *$^{31}P\{^{1}H\}$ NMR: 161 MHz, $CDCl_3$, 297 K.*

The cationic Pd allyl complex of **15** (**22**) was prepared by reaction with $[Pd(\eta^3\text{-allyl})(Cl)]_2$ using two molar equiv. of **15**, followed by chloride abstraction using NH_4PF_6. Single crystals of complex **22** ($[Pd(\eta^3\text{-allyl})(\mathbf{15})]PF_6$) were obtained by slow diffusion of hexane into a saturated dichloromethane solution (see Figure 6 for molecular structure). Both intra- and intermolecular π-π interactions between the phenyl rings (both from the backbone and PPh_2 fragments) are observed in the unit cell. The bite angle P_1-Pd-P_2 (β of 106.62(9)°) is slightly larger than in the complex [(DPEPhos)Pd(1,1-$(CH_3)_2$-η^3-allyl)] (β = 103.93°).[22] The Pd-P bond lengths are in the same range as found previously for [(DPEPhos)Pd(1,1-$(CH_3)_2$-η^3-allyl)][23] and [(tcne)Pd(DPEPhos)].[24] The allyl moiety is coordinated in almost symmetric fashion to the Pd center, as reflected by the Pd-C bond lengths (Pd_1-C_{39} 2.191(16); Pd_1-C_{40} 2.09(2); Pd_1-C_{41} 2.206(14) Å, similar to e.g. the Pd-C distances reported for $[Pd(\eta^3\text{-allyl})(\mu\text{-Cl})]_2$.[25] There are two independent molecules in the monoclinic asymmetric unit cell (space group $P1_n/1$).

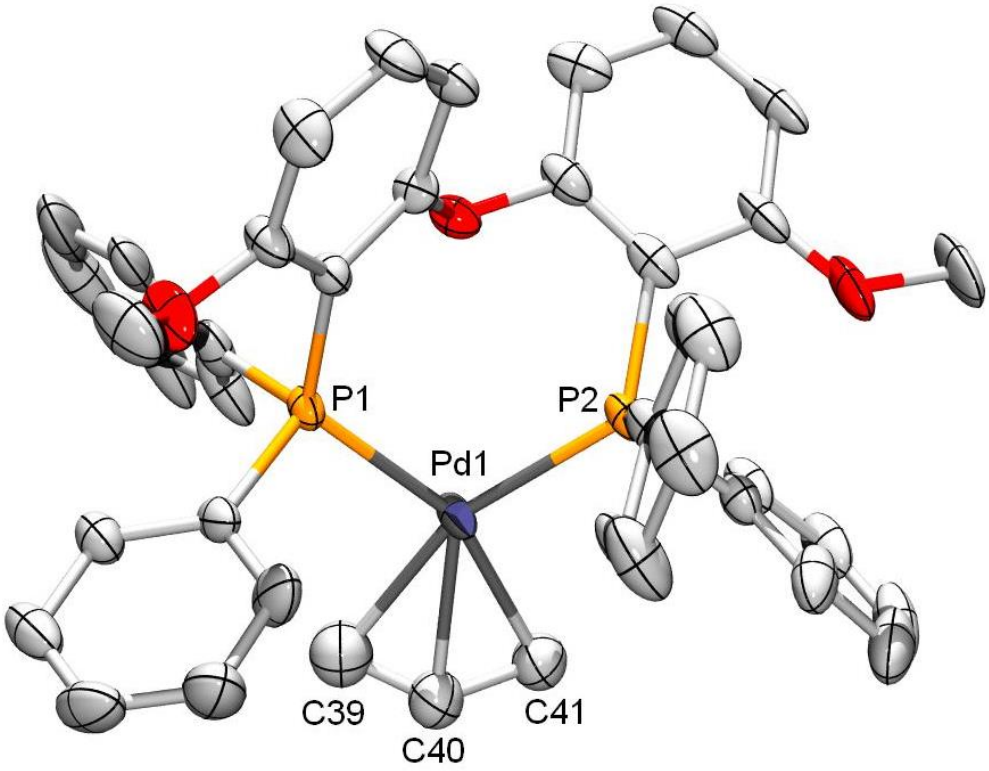
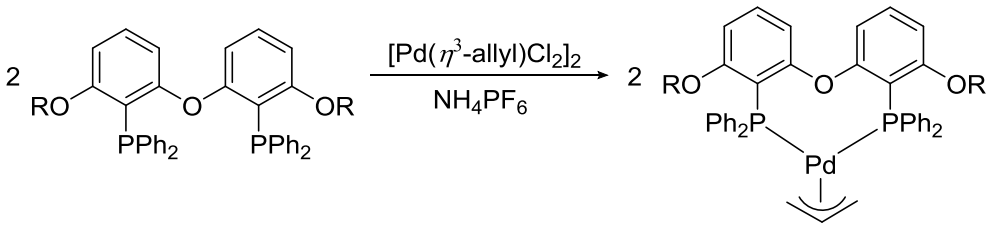
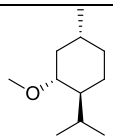
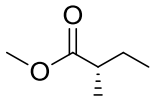
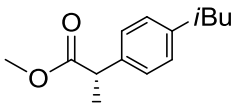
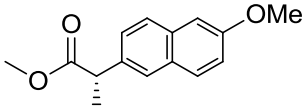


Fig. 6 *ORTEP representation for one of the two molecules in the asymmetric unit cell of complex* ***22****, [Pd(η^3-allyl)(**15**)]PF_6. Displacement ellipsoids are drawn at the 50% probability level. The PF_6 anion is omitted for clarity. Selected approximate bond lengths (Å) and angles (°): Pd_1-P_1 2.321(3); Pd_1-P_2 2.349(3); Pd_1-C_{39} 2.191(16); Pd_1-C_{40} 2.09(2); Pd_1-C_{41} 2.206(14); P_1-Pd_1-P_2 106.62(9); C_{39}-Pd_1-C_{41} 67.4(6); P_1-Pd_1-C_{39} 90.6(5); P_2-Pd_1-C_{39} 161.8(5).*

The coordination behaviour of the related ligands to Pd were also probed *via* the corresponding cationic [Pd(η^3-allyl)(**L**)]$^+$ species. The reactions were followed by ^{1}H NMR and ^{31}P{^{1}H} NMR spectroscopy and the results are summarized in Table 4.

Table 4 *NMR spectroscopic data for selected [$PdCl_2$(**L**)]$^+$-complexes of the modified DPEPhos ligands.*



Ligand	-OR	$^{31}P\{^{1}H\}$ NMR (ppm)	$^{1}H\ \{^{31}P\}$ NMR (η^3-allyl, ppm)		
			H_1	H_3	H_2
14		5.7 (AB, J_{PP} = 38 Hz) 4.1 (AB, J_{PP} = 38 Hz)	3.60 3.48	3.26 3.06	5.71 (sep)
15	$-OCH_3$	7.4 (s)	3.53, 3.17		5.72 (sep)
17a	$-OC(O)C_2H_5$	7.5 (s)	3.55, 3.2		5.75 (sep)
17b		7.08 (AB, J_{PP} = 30 Hz) 7.02 (AB, J_{PP} = 30 Hz)	3.55, 3.2		5.75 (sep)
17c		7.8 (AB, J_{PP} = 37 Hz) 7.0 (AB, J_{PP} = 37 Hz)	3.64 3.14	3.55 3.28	5.75 (sep)
17d		7.4 (AB, J_{PP} = 38 Hz) 7.1 (AB, J_{PP} = 38 Hz)	3.59 3.25	3.47 3.05	5.70 (sep)

Note: Reactions were carried out at room temperature in CH_2Cl_2/MeCN overnight. ^{1}H NMR: 400 MHz, $CDCl_3$, 297 K; $^{31}P\{^{1}H\}$ NMR: 161 MHz, $CDCl_3$, 297 K

In case of achiral ligands **15** and **17a** the NMR analysis of the Pd complexes is as expected, showing singlets in the $^{31}P\{^{1}H\}$ NMR and one signal for each of the allyl-related protons (H_1, H_2 and H_3). The Pd allyl complexes of the chiral ligands **14, 17b, 17c** and **17d** display an AB system in the $^{31}P\{^{1}H\}$ NMR, indicating magnetic inequivalence of the two phosphorus atoms, due to the C_2-symmetry of the phosphine. The inequivalence of the phosphorous atoms leads to the observation of two sets of signals for the terminal (H_1 and H_3) allylic protons in the ^{1}H

NMR spectrum giving 5 signals overall for all the chiral ligands except ligand **17b**. In this case the H_1 and H_3 protons appear as a single signal each, which can be attributed to flipping of the allyl fragment, which can adopt two orientations. The resulting isomers (species **I** and **II** in Figure 7) interconvert via either a formal π-rotation or via a π-σ isomerisation involving a η^3-η^1-η^3 process.[22] Alternatively, the chemical shifts of the anti and syn protons may overlap. Ligand **17b** only bears a small stereogenic group, *i.e.* the (*S*)-methylpropyl-moiety, compared to the larger groups on the other chiral ligands which may account for the difference if an isomerisation process is expected.

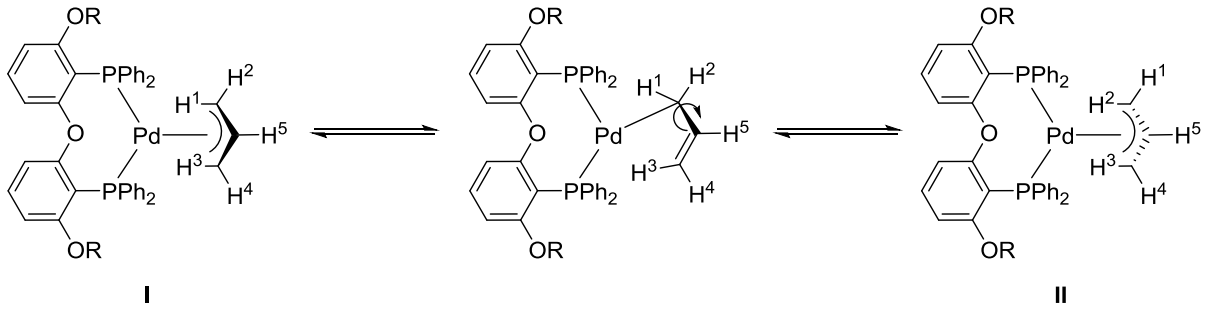


Fig. 7 *Interconversion of the [Pd(η^3-allyl)(**L**)]X- isomers **I** and **II***

Catalysis

The palladium catalysed asymmetric allylic substitution is a widely studied benchmark reaction,[26] which provides a good indication for ligand performance with respect to chiral induction. The novel chiral ligands were studied in the asymmetric allylic alkylation of l,3-diphenyl-2-propenyl acetate and cyclohexyl-2-enyl acetate with dimethyl malonate as nucleophile. The catalysis was carried out in CH_2Cl_2 at room temperature for 20 h (full conversion) under argon atmosphere and in the presence of bis(trimethylsilyl)acetamide (BSA) as base.[27] The results are summarized in Figure 8.

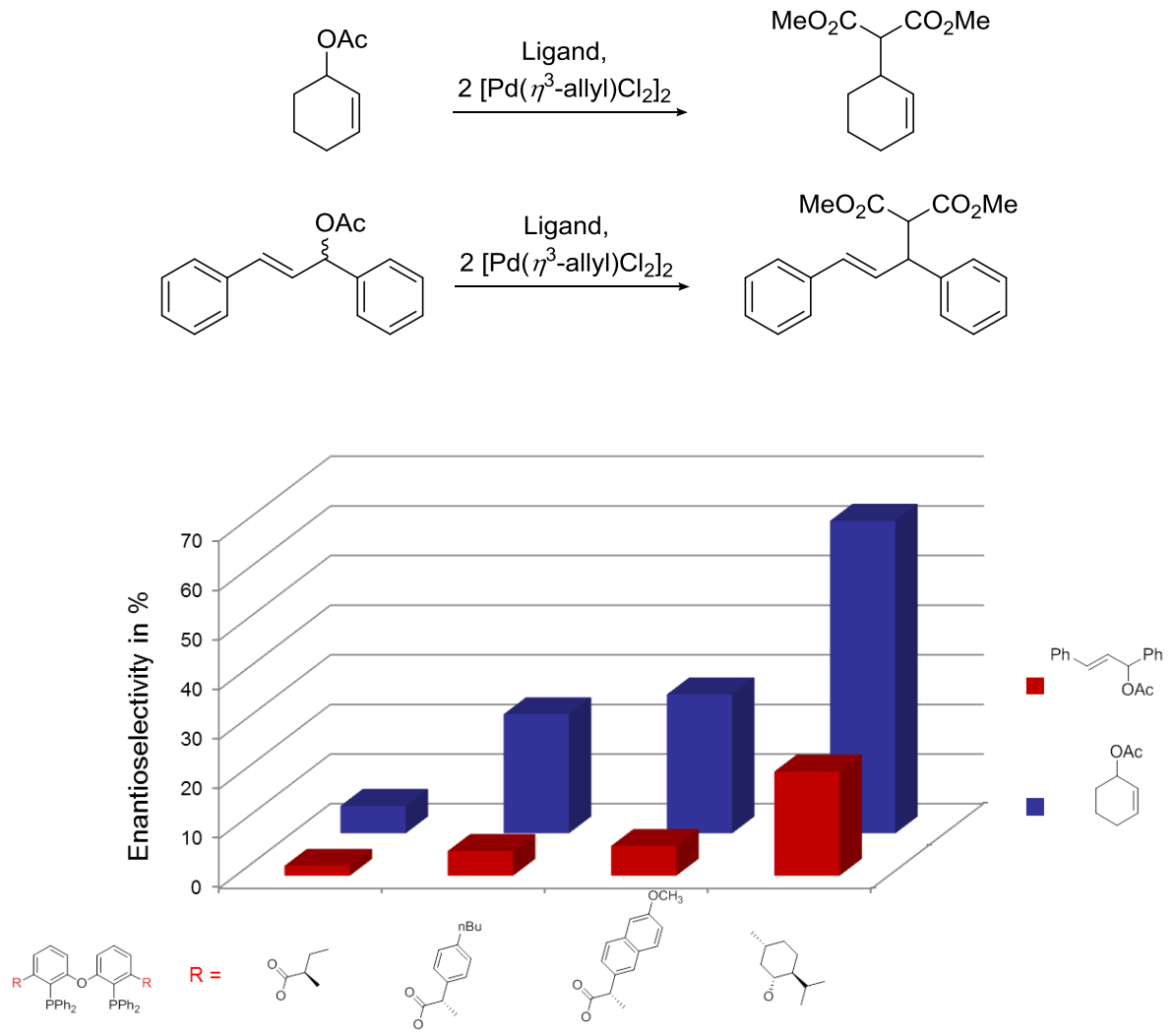


Fig. 8 *Palladium-catalyzed allylic alkylation of rac-l,3-diphenyl-2-propenyl acetate and cyclohexyl-2-enyl acetate in CH_2C1_2. Reaction conditions:* L:Pd(η^3-allyl)$Cl_2]_2$ = 2:1, [S]:[C] = 100, 0.1 mmol substrate (*rac*-l,3-diphenyl-2-propenyl acetate and cyclohexyl-2-enyl acetate), 1 mL CH_2C1_2, 20 °C, 0.3 mmol of dimethyl malonate, 0.3 mmol of *N,O-bis*(trimethylsilyl)acetamide (BSA) and a catalytic amount of KOAc.

In case of the chiral ester-modified DPEPhos, the enantioselectivity for both substrates increased with increasing steric bulk of the chiral auxiliary. Ligand **17d** - with naproxen as chiral moiety - showed the highest enantioselectivity of the ester modified DPEPhos class of ligands. Small chiral groups, such as found in **17b**, induced only low levels of

enantioselectivity. When comparing the ester- and ether-modified DPEPhos systems, the menthol-derived ether derivative (**14**) led to the highest enantioselectivity for both substrates. This is likely due to closer proximity of the chiral auxiliary group to the phosphorus atoms, hence giving more chiral induction onto the catalytic metal centre. Although state-of-the-art asymmetric induction for this reaction provides enantioselectivities over 95%,[28] the levels of enantioselectivity achieved under standard conditions with the novel ligand systems were promising. Further optimisation of the catalytic efficiency was undertaken and lowering the reaction temperature to 10 °C led to 68% ee, whilst performing the reaction at 4 °C even resulted in 70% ee, albeit at the expense of a lower conversion (33% after 20 hours). The choice of reaction medium had little effect on the enantioselectivity, as polar solvents like MeCN, THF, DMF or 1,4-dioxane gave comparable results to DCM (64-68% ee) at 20 °C.

Summary and Conclusion

By introduction of chiral ether or ester substituents in the 3,3'-positions of diphenylether and subsequent phosphorylation at the 2,2'-positions using tailor-made synthetic procedures, a small series of new wide bite-angle ligands related to DPEPhos has been realized. The chiral ether needed to be installed before phosphorylation, in contrast to the ester groups, which could be introduced in the final step, which might prove more powerful for the construction of larger ligand libraries, using commercially available chiral carboxylic acids. NMR and IR spectroscopic investigations on Ni-carbonyl and selenide derivatives of these compounds showed little influence on the electronic character of the P-donor atoms compared to non-substituted (parent) DPEPhos. Coordination to Pt(II) occurred in a *cis*-fashion , according to the large coupling constants of $PtCl_2$**L** complexes (between 3858 and 3877 Hz). In Pd-allyl complexes, larger substituents on the ligand backbone result in larger chemical shift differences for the allyl protons in [Pd(η^3-allyl)(**L**)]X-complexes. The molecular structures of complex **21**, Ni(**15**)$(CO)_2$, revealed no interaction of the substituents with the metal centre.

Application of these novel ligands in Pd-catalyzed asymmetric allylic substitution reactions showed a dependency of the enantioselectivity on the size of the stereogenic centre and its proximity to the phosphorus moiety. For future applications, we envision the use of these functionalized ligand backbone structures in enantioselective catalysis *via* non-covalent secondary interactions of ligands and substrates, mimicking the behaviour of enzymes.[14] Although the enantioselectivity displayed by these novel ligands is still modest, the effect of small changes in sterics is such that the combination of ligand design and protein interactions seems really promising.

Experimental Section

General methods

All reactions were carried out using standard Schlenk techniques under an atmosphere of purified argon. Toluene was distilled from sodium, THF and Et_2O from sodium/benzophenone, hexane from sodium/benzophenone/triglyme, methanol and ethanol from magnesium and DCM from CaH_2 under argon atmosphere. *N*-methyl-2-pyrrolidone (NMP) over molecular sieves was purchased from Fluka. Chemicals were purchased from Acros Organics, Sigma-Aldrich and Alfa Aesar. For the phosphine synthesis the washing solutions (water, brine) were degassed by three freeze-pump-thaw cycles. TLC analysis was performed using Silica F254 TLC plates from VWR. Silica gel 60 (0.063-0.2 mm; Fluka) was used for flash chromatography. Melting points were determined on a Gallenkamp MF-370 melting point apparatus in open capillaries. ^{1}H, ^{13}C, and ^{31}P spectra were measured on a Bruker Advance II 400, a Bruker Advance 300 or a Bruker Ascend 500 NMR spectrometer. $CDCl_3$ was distilled over CaH_2 and stored over K_2CO_3 under argon. Other deuterated solvents were degassed by three freeze-pump-thaw cycles. Mass spectra were collected using a Micromass GC mass spectrometer or a Thermo Scientific DSQ II Single Quadrupole GC/MS spectrometer. IR spectra were taken on an AVATAR E.S.P. 360 FTIR spectrometer. Propionyl chloride was prepared according to a literature procedure.[29] The esterification was carried out under similar conditions as described in literature.[30]

General procedure for copper catalysed C-O-coupling to form diphenylethers 11X (X = OMe, F)

Cs_2CO_3 (2 equiv.) was added to a solution of phenol (1 equiv.) in NMP in a Schlenk flask that was subsequently evacuated and backfilled with argon three times. Aryl halide (one equiv.), ligand (5 mol %) and metal precursor (2.5 mol%) were added successively. The flask was evacuated and backfilled with argon three times again. Then the reaction mixture was heated to 120 °C under argon. The reaction was monitored by GC/MS and TLC. After complete conversion of aryl halide the reaction mixture was allowed to cool down to RT and diluted with methyl-*tert*butyl ether (MTBE). The solution was filtered (glass frit, Por. 3) and the filter cake was washed with MTBE. The combined organic phases were washed with 2 M HCl, 0.6 M HCl, 2 M NaOH and brine. After drying of the organic phase over $MgSO_4$ and evaporation under reduce pressure (rotary evaporator) the crude product was purified by crystallisation, distillation or column chromatography.

di(3-methoxyphenyl)ether 11OMe

Modified literature procedure[31]: 3-iodoanisole (1.78 mL, 15 mmol), 3-methoxyphenol (3.29 mL, 30 mmol), Cs_2CO_3 (9.77 g, 30 mmol), 2,2,6,6,-*tetra*methyl-*hepta*-3,5-dione (0.276 g, 1.5 mmol) and CuCl (0.074 g, 0.75 mmol) in NMP (50 mL) were used. The crude product was purified by column chromatography (silica gel, eluent from 100 % PE to 97.5 % PE + 2.5 % AcOEt). **11OMe** was obtained as colourless oil (2.934 g, 85 %). ^{1}H NMR (400 MHz, CD_2Cl_2, 295 K): δ (ppm) 7.22-7.20 (m, 2H), 6.68-6.65 (m, 2H), 6.60-6.58 (m, 4H), 3.76 (s, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, 297 K): δ (ppm) 161.49, 158.67, 130.52, 111.38, 109.36, 105.38, 55.71. GC-MS (*m/z* (EI), rel.intensity): 230. Mass (TOF MS ESI+) *m/z* calculated for $[C_{14}H_{14}O+H]^+$ 231.1021 $[M+H]^+$, obs.: 231.1023 $[M+H]^+$.

di(3-fluorophenyl)ether 11F

Modified literature procedure[32]: 1-Bromo-3-fluorobenzene (30.8 mL, 0.276 mol), 3-fluorophenol (50 mL, 0.552 mol), Cs_2CO_3 (180 g, 0.552 mol), 2,2,6,6,-*tetra*methyl-*hepta*-3,5-dione (5.75 mL, 27 mmol) and CuCl (1.36 g, 13.8 mmol) in NMP (200 mL) were used. The crude product was purified by column chromatography (silica gel, eluent from 100 % PE to 97.5 % PE + 2.5 % AcOEt). **11F** was obtained as a colourless oil (36.56 g, 64 %) that was used without further purification. ^{1}H NMR (500 MHz, CD_2Cl_2, 296 K): δ (ppm) 7.35-7.27 (m, 2H), 6.89-6.74 (m, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 295 K): δ (ppm) 163.9 (d, $^1J_{CF}$ = 246 Hz), 158.3 (d, $^3J_{CF}$ = 10.5 Hz), 131.2 (d, $^2J_{CF}$ = 9.9 Hz), 115.1 (d, $^3J_{CF}$ = 3.1 Hz), 111.0 (d, $^1J_{CF}$ = 21.3 Hz), 107.1 (d, $^1J_{CF}$ = 24.4 Hz). $^{19}F\{^1H\}$ NMR (282 MHz, CD_2Cl_2, 295

K): δ (ppm) 111.2 (s). Mass (TOF MS CI+) *m/z* calculated for $[C_{12}H_8F_2O+H]^+$ 207.0621 $(M+H)^+$, obs.: 207.0624 $(M+H)^+$.

(*S*,*S*,*R*)-3,3'-oxy-bis(((1*S*,2*R*,5*S*)-2-*iso*propyl-5-methylcyclohexyl)-oxy)benzene) 12

A suspension of NaH (3.2 g, 133.3 mmol) in DMF (30 mL, dry) was added slowly at 0 °C to a solution of menthol (16.68 g, 106.8 mmol) in DMF (70 mL, dry) (strong effervescence). The reaction mixture was slowly warmed up to RT and stirred for 30 min. The conversion was checked by a deuterium exchange in the GC/MS. After full deprotonation, **11F** (5.5 g, 26.69 mmol) in DMF (20 mL) was slowly added to the reaction via a cannula. The reaction mixture was stirred at 120 °C for 48 h. The reaction mixture was cooled to r.t., diluted with dichloromethane (100 mL) and washed with water and brine. The organic phase was dried with $MgSO_4$ and the solvent was evaporated at reduced pressure. Compound **12** was purified by column chromatography (silica gel, hexane: ethyl acetate (2%) and obtained as highly viscous clear oil (8.71 g, 68 %). ^{1}H NMR (400 MHz, CD_2Cl_2, 296 K): δ (ppm) 7.19 (t, 2H; $^3J_{HH}$ = 8.1 Hz), 6.66-6.53 (6H, m), 4.02 (m, 2H), 2.20-2.13 (m, 4H), 1.73-1.68 (m, 4H), 1.53-1.43 (m, 4H), 1.17-1.04 (m, 18H), 0.76 (d, 6H, $^3J_{HH}$ = 6.96 Hz). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 295 K): δ (ppm) 160.2, 158.6, 130.4, 110.98, 110.91, 106.89, 77.91, 48.46, 40.60, 34.83, 31.70, 26.51, 24.05, 22.26, 20.8, 16.73. Mass (TOF-MS ESI+) m/z calculated for $[C_{32}H_{46}O_3+Na]^+$ 501.3345 $(M+Na)^+$, obs.: 501.3329 $(M+Na)^+$. GC/MS: *m/z* calculated for $[C_{32}H_{46}O_3]$ 478.7 $(M)^+$, obs.: 478.2 (9.38 min, 50 – 320 °C, flow = 20, helium).

bis(2-diphenylphosphino-3-menthoxy)phenyl)ether 13

TMEDA (0.83 g, 1.1 mL, 7.18 mmol) was added to a solution of **12** (1.560 g, 3.26 mmol) in diethyl ether (50 mL), via syringe. The solution was stirred for 15 min at RT and cooled to −78 °C. A 1.6 M ^{n}BuLi hexane solution (2.9 mL, 7.2 mmol) was added slowly whilst maintaining the temperature at −78 °C. The reaction mixture was allowed to warm up to RT over 8 h. The reaction was followed by GC/MS of a sample quenched by D_2O in THF. Chlorodiphenylphosphine (1.17 mL, 6.52 mmol) was added dropwise to the reaction mixture at −78 °C and the reaction mixture was allowed to warm slowly up to RT over 20 h. A white precipitate was formed. The reaction mixture was quenched with 5 mL of methanol and evaporated to dryness. The precipitate was azeotropically dried with toluene (2 × 3 mL) and suspended in 50 mL of THF. $BH_3{\cdot}SMe_2$ in THF (2.5 M, 2.5 mL, 5 mmol) was added to the suspension. The reaction mixture was stirred overnight before the solvent was removed under

high vacuum. The resulting precipitate was solved in dichloromethane (50 mL) and washed with water (50 mL). The aqueous layer was extracted three times with dichloromethane. The combined organic layer was washed with brine, dried over $MgSO_4$ and the solvent was evaporated under vacuum. The resulting white precipitate was purified either by column chromatography (silica gel, diethyl ether:hexane (1:20 to 1:10, crude product was impregnated on silica gel, diameter: 5 cm, length: 25 cm). Yield of **13**: 1.74 g = 61 %. Alternatively, the crude reaction mixture was purified by or precipitation from methanol/acetone in good yields. ^{1}H NMR (400 MHz, CD_2Cl_2, 296 K): δ (ppm) 7.56-7.23 (m, 18H), 7.12-7.08 (m, 4H), 6.63-6.69 (m, 2H), 6.43-6.40 (m, 2H), 3.98-3.89 (m, 2H), 1.82-1.79 (m, 2H), 1.55-0.47 (m, 38H), 0.18 (q, 2H; $^{3}J_{HH}$ = 11.24 Hz). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 296 K): δ (ppm) 162.21, 160.64, 133.91-128.07, 113.47, 107.39, 77.07, 46.48, 37.84, 34.53, 31.55, 24.64, 22.82, 22.06, 20.96, 15.29. ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2, 296 K):: 12.28 ppm (s). Mass (TOF-MS ESI+) *m/z* calculated for $[C_{56}H_{70}{}^{10}B_2O_3P_2+NH_4]^+$ 890.5402 $(M+NH_4)^+$, obs.: 890.5397 $(M+NH_4)^+$. M.p. 153 °C (dec.). Anal. Calcd. For $C_{56}H_{70}B_2O_3P_2$: C, 76.89; H, 8.07. Found: C, 76.84; H, 8.14.

Removal of BH_3 from 3 with DABCO to yield 14

DABCO (1.00 g, 8.9 mmol) in toluene was added to a solution of **13** (1.560 g, 3.26 mmol) in toluene (50 mL) via cannula at RT. The solution was stirred at 50 °C overnight. The reaction mixture was followed by phosphorus NMR for completion. After complete reaction the solvent was evaporated under vacuum. The white precipitate was purified by a short filtration over silica gel (100 % DCM) to give a crude product that was used directly in subsequent steps without further purification. ^{1}H NMR (400 MHz, CD_2Cl_2, 296 K): δ (ppm) 7.34-7.13 (m, 22H), 6.59 (d, 2H; $^{3}J_{HH}$ = 8.4 Hz), 6.19 (dd, 2H; $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{HP}$ = 3.1 Hz), 3.92 (td,2H, $^{3}J_{HH}$ = 10.4, 4.0 Hz), 1.83-1.76 (m, 2H), 1.64-1.40 (m, 6H), 1.34-1.21 (m, 2H), 1.03-0.82 (m, 4H), 0.76 (d, 6H, $^{3}J_{HH}$ = 6.5 Hz), 0.72-0.62 (m, 2H), 0.60 (d, 6H, $^{3}J_{HH}$ = 7.0 Hz), 0.56 (d, 6H, $^{3}J_{HH}$ =6.9 Hz), 0.17-0.05 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 296 K): δ (ppm) 162.64 (d, $^{3}J_{CP}$ = 16.70 Hz), 161.75, 139.19 (d, $^{3}J_{CP}$ = 13.6 Hz), 136.63 (d, $^{3}J_{CP}$ = 11.6 Hz), 133.26 (d, $^{3}J_{CP}$ =10.3 Hz), 132.7 (d, $^{3}J_{CP}$ =10.6 Hz), 128.07, 127.57 (d, $^{3}J_{CP}$ =26.1 Hz), 115.63 (d, $^{3}J_{CP}$ = 26.2 Hz), 110.99, 107.70, 76.92, 46.87, 46.58, 38.76, 34.68, 31.55, 24.822, 23.03, 22.09, 20.89, 15.56. ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2, 296 K): -23.66 ppm (s). Mass (TOF-MS ESI+) *m/z* calculated for $[C_{56}H_{64}O_3P_2+H]^+$ 847.4384 $(M+H)^+$, obs.: 847.4403 $(M+H)^+$. M.p. 94 °C. FT-IR (ATR mode, solid, selected peaks) ν (cm^{-1}) 3064 (C-H), 2998

(C-H), 2960 (C-H), 2933 (C-H), 2833 (C-H), 1582, 1561, 1481, 1457, 1424, 1264, 1235, 1179, 1087 (C-O-C), 1067, 1052, 1026, 798, 776, 737, 721, 692.

bis(2-diphenylphosphino(3-methoxy)phenyl)ether 15

TMEDA (1.201 g, 1.54 mL, 10.34 mmol) was added to a solution of **8** (1.081 g, 4.7 mmol) in THF (5 mL), via syringe. The solution was stirred for 15 min at RT and cooled to –78 °C. A 2.5 M ^{n}BuLi hexane solution (4.14 mL, 10.34 mmol) was added slowly whilst maintaining the temperature at -78 °C. The reaction mixture was slowly warmed up to RT. After 20 h the deprotonation was checked by GC/MS after quenching a sample with D_2O in THF. The reaction mixture was diluted with THF (20 mL) and chlorodiphenylphosphine (1.856 mL, 10.34 mmol) dissolved in hexane (3 mL) was added dropwise to the reaction mixture at –78 °C. The reaction mixture was allowed to warm up to RT and stirred for 20 h at RT. A white precipitate was formed. The precipitate was dissolved in DCM (100 mL) and washed with degassed water (2× 50 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed under high vacuum. The remaining sticky solid was purified by crystallisation from DCM and hexane (1.913 g, 67 %). ^{1}H NMR (400 MHz, CD_2Cl_2, 297 K): δ (ppm) 7.36-7.7.18 (m, 22H), 6.59 (d, 2H; $^{3}J_{HH}$ = 8.2 Hz), 6.17 (dd, 2H; $^{3}J_{HH}$ = 8.2 Hz, $^{3}J_{HP}$ = 2.8 Hz), 3.45 (s, 6H, CH_3). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2, 297 K): δ (ppm) 163.66, 162.10 (d, J_{CP} = 15.3 Hz), 137.84 (d, J_{CP} = 12.3 Hz), 133.15 (d, J_{CP} = 20.7 Hz), 132.51, 128.14 (d, J_{CP} = 6.7 Hz), 127.82, 115.59 (d, J_{CP} = 24.5 Hz), 112,12 107.10, 55.78. ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2, 296 K): δ (ppm) -23.82. M.p.: 177 °C (decomp.). Mass (FD MS+) *m*/*z* calculated for $[C_{38}H_{32}O_3P_2+H]^+$ 599.1894 $[M+H]^+$, obs.: 599.1899 $[M+H]^+$. FT-IR (ATR mode, solid, selected peaks) ν (cm^{-1}) 3064 - 2933 (C-H), 1582, 1561, 1481, 1457, 1424, 1264, 1235, 1179, 1087 (C-O-C), 1067, 1052, 1026, 798, 776, 737, 721, 692. Anal. Calcd. For $C_{38}H_{32}O_3P_2$: C, 76.25; H, 5.39. Found: C, 76.10; H, 5.47.

Bis(2-diphenylphosphino-3-hydroxy)phenyl)ether 16

A solution of BBr_3 (1.927 mL, 20 mmol) in dry DCM (8 mL) was added dropwise to a solution of **15** (962 mg, 2 mmol) in dry DCM (25 mL) at –78 °C. The reaction mixture was allowed to warm up to RT and was stirred for 20 h. After full conversion of the starting material the excess of BBr_3 and DCM was evaporated and the solid dried azeotropically with toluene (3 × 2 mL). The mixture was quenched with ice-cold water (20 mL), and after phase-

separation, the aqueous phase was extracted with DCM (3 × 20 mL). The combined organic phases were subsequently washed with water (30 mL) and brine (30 mL), and dried over $MgSO_4$. Compound **16** was obtained in quantitative yield and was used without further purification. $^{31}P\{^1H\}$ NMR (400 MHz, $CDCl_3$, 294.8 K): δ (ppm) –34.79 (s).

Bis(2-diphenylphosphino-3-propionyl)phenyl)ether 17a

A solution of **16** (3.06 g, 5.3 mmol), propionic acid (0.830 mL, 11.13 mmol) and DMAP (0.123 g, 1.0 mmol) in DCM (3 mL) was added to a solution of EDC·HCl (2.84 g, 14.8 mmol) and *N*,*N*-diisopropylethylamine (0.2.59 mL, 14.8 mmol) in DCM (150 mL) at 0 °C. The reaction was allowed to warm up to r.t., stirred for 20 h. and monitored by $^{31}P\{^1H\}$ NMR spectroscopy. After complete reaction, the reaction mixture was diluted with DCM and extracted with 10% aqueous HCl and water. The organic layer was dried over Na_2SO_4, concentrated and purified by crystallisation from methanol (1.88 g, 56%). ^1H NMR (400 MHz, CD_2Cl_2, 297 K): δ (ppm) 7.28-7.15 (m, 22H), 6.76 (ddd, 2H; $^3J_{HH}$ = 8.1, $^4J_{HP}$ = 1.75 $^4J_{HH}$ = 1.05 Hz), 6.16 (ddd, 2H; $^3J_{HH}$ = 8.1, $^4J_{HP}$ = 2.5, $^4J_{HH}$ = 0.9 Hz), 2.09 (q, 4H; $^3J_{HH}$ 7.4 Hz), 0.98 (t, 6 H, $^3J_{HH}$ 7.4 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 297 K): δ (ppm) 171.77, 161.51 (d, $^3J_{CP}$ = 11.1 Hz), 155.07 (d, $^3J_{CP}$ = 8.79 Hz), 136.31 (d, $^3J_{CP}$ = 11.66 Hz), 133.16 (d, $^3J_{CP}$ = 20.48 Hz), 131.81, 128.57 (d, $^3J_{CP}$ 7.0 Hz), 128.3, 120.80 (d, $^3J_{CP}$ = 26.9 Hz), 118.92, 116.88, 27.27, 8.79. $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2, 296 K): δ (ppm) –22.28. M.p.: 93 °C. FT-IR (ATR mode, solid, selected peaks) ν (cm^{-1}) 3051 (CH), 2982 (CH), 2940 (CH), 1758 (C=O), 1587, 1569, 1479, 1433, 1383, 1359, 1252, 1214, 1182, 1124, 1076, 1060, 1026, 863, 807, 779, 741, 726, 692. Anal. Calcd. For $C_{42}H_{36}O_5P_2$: C, 73.89; H, 5.32. Found: C, 73.74; H, 5.38.

(*S*,*S*)-bis(2-diphenylphosphino(3-(2-methylbutyroyl))phenyl)ether 17b

A solution of **16** (2.57 g, 4.5 mmol), (*S*)-2-methylbutyric acid (1.03 mL, 9.45 mmol) and DMAP (0.123 g, 1.0 mmol) in DCM (3 mL) was added to a solution of EDC·HCl (2.68 g, 14 mmol) and *N*,*N*-diisopropylethylamine (2.43 mL, 14 mmol) in DCM (10 mL) at 0 °C. The reaction was allowed to warm up to RT and stirred for 20 h. The reaction mixture was worked up as for **17a** and purified by filtration over silica gel, using CH_2Cl_2 as eluent (Yield: 1.92 g, 58 %). ^1H NMR (400 MHz, CD_2Cl_2, 297 K): δ (ppm) 7.29-7.08 (br. m, 22H), 6.77 (br. d, 2H; $^3J_{HH}$ 8.2 = Hz), 6.13 (br. d, 2H; $^3J_{HH}$ = 8.2 Hz), 2.03 (m, 2H), 1.63 (m, 2H), 1.42 (m, 2H), 1.04 (d, 6H; $^3J_{HH}$ =7.00 Hz, (CH_3)), 0.87 (t, 6H; $^3J_{HH}$ = 7.41 Hz, (CH_3)). $^{13}C\{^1H\}$

NMR (100 MHz, CD_2Cl_2, 297 K): δ (ppm) 175.14, 161.67 (d, $^3J_{CP}$ = 9.60 Hz), 155.40 (d, $^3J_{CP}$ = 10.32 Hz), 136.28, 133.28-132.83 (m), 131.86, 128.53-128.23 (m), 120.77 (d, $^3J_{CP}$ = 26.5 Hz), 118.61, 116.90, 40.50, 26.59. $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2, 297 K): δ (ppm) –22.85. M.p.: 121 °C. Mass (FD MS+) *m*/*z* calculated for $[C_{46}H_{44}O_5P_2+H]^+$ 739.2737 $[M+H]^+$, obs.: 739.2728 $[M+H]^+$. FT-IR (ATR mode, solid, selected peaks): ν (cm^{-1}) 3071 (CH), 3039 (CH), 2968 (CH), 2931 (CH), 2874 (CH), 1758 (C=O), 1592, 1560, 1480, 1435, 1382, 1370, 1356, 1253, 1214, 1165, 1094, 1084, 1053, 1023 771, 741, 731, 720, 694. Anal. Calcd. For $C_{46}H_{44}O_5P_2$: C, 74.78; H, 6.00. Found: C, 74.64; H, 5.93.

(*S*,*S*)-bis(2-diphenylphosphino(3-(2-(4-isobutylphenyl)-propionyl))-phenyl)ether 17c

A solution of **16** (3.06 g, 5.37 mmol), (*S*)-(+)-ibuprofen ((*S*)-(+)-2-(4-Isobutylphenyl)propionic acid, 2.21 g, 10.74 mmol) and DMAP (0.13 g, 1.09 mmol) in DCM (50 mL) was added to a solution of EDC·HCl (2.95 g, 15.39 mmol) and *N*,*N*-diisopropylethylamine (2.66 mL, 15.39 mmol) in DCM (150 mL) at 0 °C. The reaction was allowed to warm up to RT and stirred for 20 h. The reaction mixture was worked up as for **17a** and purified by crystallisation from acetone and water (Yield: 3.234 g, 62 %). ^1H NMR (400 MHz, CD_2Cl_2, 297 K): δ (ppm) 7.28-7.07 (br. m, 30H), 6.59 (br. d, 2H, $^3J_{HH}$ = 8.2 Hz), 6.15 (br. d, 2H; $^3J_{HH}$ = 8.3 Hz), 3.63 (q, 2H; $^3J_{HH}$ = 7.1 Hz), 2.45 (d, 4H; $^3J_{HH}$ = 7.2 Hz), 1.84 (m, 2H), 1.30 (d, 6H; $^3J_{HH}$ = 7.12 Hz), 0.89 (d, 12H; $^3J_{HH}$ 6.56 Hz). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 297 K): δ (ppm) 173.12, 161.50 (d, $^3J_{CP}$ = 9.6 Hz), 155.10 (d, $^3J_{CP}$ = 10.3 Hz), 141.11, 137.11-127.69 (m), 120.75 (d, $^3J_{CP}$ = 26.3 Hz), 118.36, 116.87, 45.31, 44.75, 30.60, 22.50, 18.41. $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2, 297 K): δ (ppm) –22.60. M.p. 103 °C. Mass (FD MS+) *m*/*z* calculated for $[C_{62}H_{60}O_5P_2+H]^+$ 947.3989 $[M+H]^+$, obs.: 947.3974 $[M+H]^+$. FT-IR (ATR mode, solid, selected peaks): ν (cm^{-1}) 3052 (CH), 2952 (CH), 2928 (CH), 2866 (CH), 1754 (C=O), 1589, 1561, 1434, 1212, 1130, 117, 1087, 1067, 1020, 999, 741, 692. Anal. Calcd. For $C_{62}H_{60}O_5P_2$: C, 78.63; H, 6.39. Found: C, 78.61; H, 6.28.

(*S*,*S*)-bis(2-diphenylphosphino(3-(2-(6-methoxy-2-naphthyl)-propionyl))-phenyl)ether 17d

A solution of **16** (1.43 g, 2.5 mmol), (*S*)-naproxen ((*S*)-(+)-2-(6-methoxy-2-naphthyl)propionic acid (1.21 g, 5.25 mmol) and DMAP (7.48 mg, 0.061 mmol) in DCM (30 mL) was added to a solution of EDC·HCl (1.34 g, 7 mmol) and *N*,*N*-diisopropylethylamine (1.20 mL, 7 mmol) in DCM (70 mL) at 0 °C. The reaction was allowed to warm up to RT and

stirred for 20 h. The reaction mixture was worked up as described above and purified by quick filtration over silica-gel under an argon atmosphere and with dichloromethane as eluent (Yield: 50%). ^{1}H NMR (400 MHz, CD_2Cl_2, 297 K): δ (ppm) 7.69-7.66 (br. m, 4H), 7.55 (s, 2H), 7.30-7.25 (m, 30 H, 6.57 (br. d, 2H; $^{3}J_{HH}$ = 8.2 Hz), 6.13 (br. d, 2H; $^{3}J_{HH}$ = 8.3 Hz), 3.88 (s, 6H), 3.33 (q, 2H; $^{3}J_{HH}$ = 7.0 Hz), 1.38 (d, 6H; $^{3}J_{HH}$ = 7.0 Hz) ppm. ^{13}C{^{1}H} NMR (100 MHz, C_2Cl_2, 297 K): δ (ppm) 173.02, 161.53 (d, $^{3}J_{CP}$ = 9.6 Hz), 158.14, 155.11 (d, $^{3}J_{CP}$ = 10.3 Hz), 136.98-126.60 (m), 120.75 (d, $^{3}J_{CP}$ = 27.2 Hz), 119.31, 118.35, 116.86, 105.91, 55.65, 45.95, 18.27. ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2, 297 K): δ (ppm) –22.69. Mass (FD MS+) *m*/*z* calculated for $[C_{64}H_{52}O_7P_2+H]^+$ 995.3261 $[M+H]^+$, obs.: 995.3265 $[M+H]^+$. FT-IR (ATR mode, solid, selected peaks): ν (cm^{-1}) 3052 (CH), 2952 (CH), 2928 (CH), 2866 (CH), 1754 (C=O), 1699, 1668, 1589, 1561, 1511, 1480, 1434, 1375, 1330, 1251, 1212, 1130, 117, 1087, 1067, 1020, 999, 741, 692. Anal. Calcd. For $C_{64}H_{52}O_5P_2$: C, 77.25; H, 5.27. Found: C, 77.14; H, 5.39.

Synthesis of phosphine selenide of L

In a typical experiment, the appropriate ligand (0.05 mmol) and an excess of selenium were suspended in toluene and stirred overnight at 60 degrees. After cooling to r.t., the solution was filtered, the solvent was removed *in vacuo* and the ^{31}P{^{1}H} NMR spectrum of the crude solid (obtained in near-quantitative yields) was recorded.

L = **15**: ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2, 297 K): δ (ppm) 23.4 ($^{1}J_{P\text{-}Se}$ = 740 Hz).

L = **17a**: ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2, 297 K): δ (ppm) 23.6 ($^{1}J_{P\text{-}Se}$ = 749 Hz).

L = **17b**: ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2, 297 K): δ (ppm) 23.90, 23.67 ($^{1}J_{P\text{-}Se}$ = 750 Hz).

L = **17c**: ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2, 297 K): δ (ppm) 24.61, 23.48 ($^{1}J_{P\text{-}Se}$ = 749 Hz).

L = DPEPhos: ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2, 297 K): δ (ppm) 29.4 ($^{1}J_{P\text{-}Se}$ = 734 Hz).

Synthesis of $Ni(CO)_2L$

In a typical experiment, an equimolar amount of $Ni(CO)_2(PPh_3)_2$ and ligand (0.10 mmol) were place in a Schlenk tube, flushed with argon and dissolved in 1 mL of deuterated THF. The reaction mixture was stirred for 48 to 72 hours at room temperature. Addition of pentane resulted in precipitation of a green solid. After removal of the mother liquor, the solid was analysed by ^{31}P{^{1}H} NMR and IR spectroscopy.

L = **15**: ^{31}P{^{1}H} NMR (161 MHz, CD_2Cl_2, 297 K): δ (ppm) 16.4. IR (KBr): ν_{CO} 1986, 1920 cm^{-1}.

L = **17a**: $^{31}P\{^{1}H\}$ NMR (161 MHz, CD_2Cl_2, 297 K): δ (ppm) 17.6. IR (KBr): ν_{CO} 1992, 1932 cm^{-1}.

L = **17b**: $^{31}P\{^{1}H\}$ NMR (161 MHz, CD_2Cl_2, 297 K): δ (ppm) 17.6. IR (KBr): ν_{CO} 1999, 1936 cm^{-1}.

L = **17c**: $^{31}P\{^{1}H\}$ NMR (161 MHz, CD_2Cl_2, 297 K): δ (ppm) 17.3. IR (KBr): ν_{CO} 2004, 1945 cm^{-1}.

L = DPEPhos: $^{31}P\{^{1}H\}$ NMR (161 MHz, CD_2Cl_2, 297 K): δ (ppm) 25.9. IR (KBr): ν_{CO} 1999, 1940 cm^{-1}.

Synthesis of $PtCl_2L$.

In a typical experiment, ligand (1 eq.) and *cis*-$PtCl_2(MeCN)_2$ (1 eq.) were placed in a Schlenk flask, and flushed with argon. CH_2Cl_2 (~ 0.05 M) and an equal amount of acetonitrile were added and the reaction mixture was stirred overnight at room temp. The solvent was removed *in vacuo*, the resulting yellow powder was washed three times with diethyl ether, then dried *in vacuo*. The precipitate was analysed by $^{31}P\{^{1}H\}$ NMR spectroscopy.

L = **15**: The product precipitated directly from the $MeCN/CH_2Cl_2$ mixture to give a sparingly soluble white solid (starting from 0.171 mmol of ligand, 110 mg, 74%, *cis*:*trans* 2:1). *Cis*-compound: ^{1}H NMR (500 MHz, $CDCl_3$, 297 K): δ 7.96-7.81 (br m, 2H), 7.72-7.55 (br m, 6H), 7.37-7.16 (m, 14H), 6.31 (dd, 4H, $^{3}J_{HH}$ = 8.0, 2.8 Hz), 2.92 (s, 6H). $^{31}P\{^{1}H\}$ NMR (202 MHz, $CDCl_3$, 297 K): δ (ppm) −3.26 ($^{1}J_{P\text{-}Pt}$ = 3858 Hz, *cis*), -9.85 ($^{1}J_{P\text{-}Pt}$ = 2283 Hz, *trans*). Mass (ESI MS+) *m*/*z* calculated for $[C_{38}H_{32}ClO_3P_2Pt]^+$ 828.1157 $[M\text{-}Cl]^+$, obs.: 828.1149 $[M\text{-}Cl]^+$. Anal. Calcd. For $C_{38}H_{32}Cl_2O_5P_2Pt$: C, 52.79; H, 3.73. Found: C, 52.88; H, 3.63.

L = **17a**: Recrystallisation from CH_2Cl_2 layered with Et_2O gave an off-white crystalline solid (starting from 0.073 mmol, 15 mg, 22%). ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ 7.80-7.60 (m, 8H), 7.40-7.27 (m, 14H), 6.69-6.55 (m, 4H), 1.34 (q, 4H, $^{3}J_{HH}$ = 7.5 Hz), 0.74 (t, 6H, $^{3}J_{HH}$ =7.5 Hz). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 297 K): δ (ppm) −3.49 ($^{1}J_{P\text{-}Pt}$ = 3863 Hz). Mass (ESI MS+) *m*/*z* calculated for $[C_{42}H_{36}ClO_5P_2Pt]^+$ 912.1369 $[M\text{-}Cl]^+$, obs.: 912.1358 $[M\text{-}Cl]^+$. Anal. Calcd. For $C_{42}H_{36}Cl_2O_5P_2Pt$: C, 53.18; H, 3.83. Found: C, 52.92; H, 3.65.

L = **17b**: Recrystallisation from CH_2Cl_2 layered with Et_2O gave a white solid (starting from 0.12 mmol, 75 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ 7.82-7.62 (m, 8H), 7.41-7.21 (m, 14H), 6.65 (br. d, 2H; $^{3}J_{HH}$ 6.7 = Hz), 6.59 (br. d, 2H; $^{3}J_{HH}$ = 6.7 Hz), 1.36-1.24 (m, 2H), 1.23-1.10 (m, 2H), 1.09-0.99 (m, 2H), 0.77-0.67 (m, 12H). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, 297 K): δ (ppm) −3.63 ($^{1}J_{P\text{-}Pt}$ = 3862 Hz). Mass (ESI MS+) *m*/*z* calculated for

$[C_{46}H_{44}ClO_5P_2Pt]^+$ 968.1995 $[M\text{-}Cl]^+$, obs.: 968.1976 $[M\text{-}Cl]^+$. Anal. Calcd. For $C_{46}H_{44}Cl_2O_5P_2Pt$: C, 54.99; H, 4.41. Found: C, 54.87; H, 4.48.

L = **17c**: Precipitation from CH_2Cl_2 using hexane and Et_2O gave a white solid (starting from 0.054 mmol, 25 mg, 38%). ^{1}H NMR (400 MHz, CD_2Cl_2, 297 K): δ (ppm) 8.00-6.77 (br. m, 30H), 6.75-6.44 (m, 2H), 6.38-6.06 (m, 2H), 2.48 (d, 4H; $^3J_{HH}$ = 7.0 Hz), 2.21 (q, 2H; $^3J_{HH}$ = 6.9 Hz), 1.97-1.79 (m, 2H), 1.01 (d, 6H; $^3J_{HH}$ = 5.9 Hz), 0.93 (d, 12H; $^3J_{HH}$ 6.6 Hz). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 297 K): δ (ppm) –3.12 ($^1J_{P\text{-}Pt}$ = 3877 Hz). Mass (ESI MS+) *m*/*z* calculated for $[C_{62}H_{60}ClO_5P_2Pt]^+$ 1176.3247 $[M\text{-}Cl]^+$, obs.: 1176.3229 $[M\text{-}Cl]^+$. Attempts to recrystallize the material for elemental analysis failed to give a stable complex.

Synthesis of [Pd($^3\eta$-allyl)L]X

In a typical small-scale experiment, ligand (0.05 mmol), [Pd($^3\eta$-allyl)Cl]$_2$ (0.025 mmol) and NH_4PF_6 (0.05-0.15 mmol) were placed in a Schlenk flask, flushed with argon and dissolved in DCM (5 mL). The reaction mixture was stirred overnight at room temperature before water was added (5 mL). Extraction with CH_2Cl_2 (3 × 5 mL) was followed by drying the organic layer over $MgSO_4$ and removal of volatiles *in vacuo*. The crude precipitate was analysed by ^{31}P{^{1}H} NMR and ^{1}H NMR spectroscopy (see Table 4).

In case of ligand **15**, 299.33 mg (0.5 mmol) of ligand and 87.0 mg of Pd-dimer (0.23 mmol) were reacted together with 224.94 mg (1.38 mmol) NH_4PF_6. An analytical sample was obtained *via* recrystallization of the precipitate from CH_2Cl_2 layered with hexane to give a crystalline orange solid. ^{1}H NMR (500 MHz, CD_2Cl_2, 297 K): δ (ppm) 7.49-7.32 (m, 14H), 7.32-7.21 (m, 8H), 6.61 (d, 2H, $^3J_{HH}$ = 8.4 Hz), 6.53 (br d, 2H, $^3J_{HH}$ = 8.0 Hz), 5.59 (tt, 1H, $^3J_{HH}$ = 13.7, 7.3 Hz), 3.70-3.63 (m, 2H), 3.11 (s, 6H), 3.10-3.02 (m, 2H). ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 297 K): δ (ppm) 5.6 (s). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 297 K): 162.1, 161.0, 134.2, 132.5, 131.6, 130.3, 128.6, 122.1, 111.1, 108.7, 55.4. Mass (ESI MS+) *m*/*z* calculated for $[C_{41}H_{37}O_3P_2Pd]^+$ 747.1409 $[M]^+$, obs.: 747.1239 $[M]^+$. Anal. Calcd. For $C_{41}H_{37}F_6O_3P_3Pd$: C, 55.26; H, 4.19. Found: C, 55.10; H, 4.28.

The Pd allyl complexes of **17a-d** were prepared *in-situ* as described above.

L = **14**: ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ (ppm) 7.59, 7.36-6.98, 6.46-6.12, 5.70 (1H), 3.85, 3.60 (1H), 3.48 (1H), 3.41, 3.26 (1H), 3.06 (1H), 2.28, 2.10, 1.53-1.43, 1.25-0.87, 0.78; ^{31}P{^{1}H} NMR (161 MHz, $CDCl_3$, 297 K): δ (ppm) 5.7 and 4.1 (AB $^2J_{PP}$ = 38 Hz).

L = **17a**: ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ (ppm) 7.48-7.26 (22H), 6.80 (2H), 6.55 (2H), 5.75 (1H), 3.52 (2H), 3.18 (2H), 1.43, (4H), 0.77 (6H); $^{31}P\{^{1}H\}$ NMR (161 MHz, $CDCl_3$, 297 K): δ (ppm) 7.5 (s).

L = **17b**: ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ (ppm) 7.49-7.36 (22H), 6.83 (2H), 6.62 (2H), 5.63 (1H), 3.58 (2H), 3.08 (4H), 1.35 (2H), 1.25 (2H), 0.78 (6H), 0.75 (6H); $^{31}P\{^{1}H\}$ NMR (161 MHz, $CDCl_3$, 297 K): δ (ppm) 7.08 and 7.02 (AB, $^{2}J_{PP}$ = 30 Hz).

L = **17c**: ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ (ppm) 7.70-7.30, 7.20, 7.03, 6.85, 6.53, 6.48, 5.78 (1H), 3.64 (1H), 3.55 (1H), 3.48 (2H), 3.28 (1H), 3.14 (1H), 2.40, 2.20 (2H), 1.81, 1,18, 1.06; $^{31}P\{^{1}H\}$ NMR (161 MHz, $CDCl_3$, 297 K): δ (ppm) 7.8 and 7.0 (AB, $^{2}J_{PP}$ = 37 Hz).

L = **17d**: ^{1}H NMR (400 MHz, $CDCl_3$, 297 K): δ (ppm) 7.58, 7.60-7.20, 7.18-6.98, 6.48-6.32, 5.70 (1H), 4.02-3.84 (8H), 3.59 (1H), 3.47 (1H), 3.25 (1H), 3.05 (1H), 1.51 (6H); $^{31}P\{^{1}H\}$ NMR (161 MHz, $CDCl_3$, 297 K): δ (ppm) 7.4 and 7.1 (AB, $^{2}J_{PP}$ = 38 Hz).

General catalytic procedure for asymmetric allylic alkylation reactions

In a Schlenk tube, $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.005 mmol) and the respective ligand (0.01 mmol) were dissolved in 1 ml of CH_2Cl_2 and degassed. (E)-1,3-diphenylprop-2-ene-1-yl acetate or cyclohex-2-ene-1-yl acetate (1 mmol) was added as the substrate and after 20 min of stirring at room temperature, dimethyl malonate (3mmol), BSA (N,O-bis(trimethylsilyl) acetamide, 3 mmol) and a catalytic amount of KOAc (0.024 mmol) were added consecutively. The reaction mixture was degassed again and stirred at the given temperature.

Analytical methods:

(*E)-1,3-diphenylprop-2-ene-1-yl acetate:* Conversion by GC (Column: Rtx-1 (fused silica), Restek, 30 m x 0.25 mm x 0.1 μm; Carrier gas: Helium; GC settings: 90 kPa, inlet injector 220 °C, oven (50 °C; 20 °C/min; 300 °C; 10 min), FID detector 220 °C). Retention times: (*R*/*S*)-(*E*)-dimethyl 2-(1,3-diphenylallyl)malonate 12.2 min; (*E*)-1,3-diphenylallyl acetate: 10.7 min; Dodecane 5.5 min. Enantioselectivity by HPLC (Column: Chiralcel OD-H; HPLC settings: hexane: 99 %, isopropanol: 1 %; 0.5 ml flow). Retention times: (*R*)-(*E*)-dimethyl 2-(1,3-diphenylallyl)malonate: 21.73 min; (*S*)-(*E*)-dimethyl 2-(1,3-diphenylallyl)malonate: 23.60 min.

Cyclohex-2-ene-1-yl acetate: Conversion by GC (Column: Rtx-1 (fused silica), Restek, 30 m x 0.25 mm x 0.1 μm; Carrier gas: Helium; GC settings: 90 kPa, inlet injector 220°C, oven (50°C; 20 °C/min; 300°C; 10 min), FID detector 220 °C). Retention times: dimethyl 2-

(cyclohex-2-en-1-yl)malonate: 12.5 min; cyclohex-2-en-1-yl acetate: 4.3 min; Dodecane 5.5 min. Enantioselectivity (Column: Varian Chirasil DEX-CB, 25 m x 0.25 mm x 0.25 μm; Carrier gas: Helium; GC settings: 120 kPa, inlet injector 200°C, oven (120°C; 30 min, 5°C/min; 180°C; 0 min), FID detector 200 °C). Retention times: dimethyl 2-(cyclohex-2-en-1-yl)malonate (S): 23.95 min; dimethyl 2-(cyclohex-2-en-1-yl)malonate (R): 24.55 min; cyclohex-2-en-1-yl acetate: 5.21 min.

X-ray crystal structure determinations. X-ray crystal data were collected at 93 K by using a Rigaku MM007 High brilliance RA generator/confocal optics with Mercury CCD diffractometer system. Intensity data were collected using both ω- and φ-steps, accumulating area detector images spanning at least a hemisphere of reciprocal space. All the data were corrected for Lorentz polarization effects. A multi-scan absorption correction was applied using CrystalClear.[33] Structures were solved by direct methods[34] and refined by full-matrix least-squares against F^2 using the programme SHELXTL.[35] Hydrogen atoms bound to carbon were assigned riding isotropic displacement parameters and constrained to idealized geometries. Hydrogen atoms bound to boron had the position of the lead hydrogen atom determined from the difference fourier map, after which the positions of the other two were generated using a riding model. They were refined isotropically subject to distance restraints, with thermal parameters free to refine.

Details for compound 13: $C_{56}H_{70}FB_2O_3P_2$, Fw = 874.43, 0.15×0.05×0.02 mm^3, triclinic, *P*1 (no 1), a = 9.115(3), b = 9.309(4), c = 17.363(8) Å, α = 83.17(5), β = 76.35(4), γ = 70.69(4)º, V = 1349.9(10) $Å^3$, Z = 1, D_x = 1.076 g/cm^3, μ = 0.12 mm^{-1}, T = 93 K. R1/wR2 [I > 2σ(I)]: 0.0816/0.1751. Residual electron density between -0.304 and 0.399 e/$Å^3$.

Details for complex 21: $C_{40}H_{32}NiO_5P_2$, Fw = 713.34, 0.03×0.03×0.03 mm^3, green prism, monoclinic, $P2_1$/n (no 14), a = 12.371(4), b = 20.311(7), c = 13.564(5) Å, β = 92.283(10)º, V = 3406(2) $Å^3$, *Z* = 4, D_x = 1.391 g/cm^3, μ = 0.709 mm^{-1}, T = 93 K. R1/wR2 [I > 2σ(I)]: 0.07777/ 0.0997. Residual electron density between -0.42 and 0.41 e/$Å^3$.

Details for complex 22: $C_{41}H_{37}F_6O_3P_3Pd$, Fw = 891.05, 0.15×0.10×0.03 mm^3, orange platelet, monoclinic, $P1_n$/1 (no 7), a = 14.976(7), b = 14.669(6), c = 18.633(8) Å, β = 108.245(8)º, V = 3888(3) $Å^3$, *Z* = 4, D_x = 1.553 g/cm^3, μ = 0.668 mm^{-1}, T = 93 K. R1/wR2 [I > 2σ(I)]: 0.0638/ 0.1652. Residual electron density between -1.33 and 1.67 e/$Å^3$.

CCDC-1059267, CCDC-1059268 and CCDC-1059269 contain the supplementary crystallographic data for this paper of **13**, **21** and **22** respectively. These data can be obtained

free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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Supporting Information available: NMR spectra of compounds, *cif*-files for **13**, **21** and **22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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