Synthesis of *P*,*P*′-Heterotopic Binaphthyldiphosphanes (BINAPP′) Devoid of C_2 Symmetry from 2,2′-Binaphthol

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The introduction of two nonequivalent diarylphosphanyl substituents into the 2- and 2′-positions of 1,1′-binaphthalene has been successfully accomplished in four steps from 1,1′-binaphthalene-2,2′-diol (BINOL) through conversion into the ditriflate followed by sequential substitution of triflate groups mediated by palladium or nickel catalysts. The selective monosubstitution of the triflate has been achieved by introducing the first phosphorated substituent in the form of phosphane oxide through a Pd-catalyzed reaction. The *o*-tolyl-substituted diphosphane **4c** is a chiral inducer that is more efficient than BINAP both in the Rh-catalyzed asymmetric hydrogenation of acetamido acrylic acid derivatives and in the Pd-catalyzed allylic alkylation of 1,3-diphenylprop-2-enyl acetate (85% *ee*).

Introduction

Atropisomeric diaryl-core diphosphanes like BINAP are attracting continued interest in view of their exceptional ability to induce asymmetry in transition metal-catalyzed reactions.[1] Recently the variety of axial templates has been expanded with the synthesis of the first diheteroaryl-core chiral diphosphanes.[2] Due to the presence of homotopic phosphorus centres, these ligands associate the axial chirality to C_2 symmetry. This fulfils an old criterion established since the early days of asymmetric catalysis.[3]

A modern trend in the design of chiral diphosphane ligands is related to the differentiation of the electronic and/or the steric properties of the phosphorus donors.[4] This follows from the observation that the presence of nonequivalent phosphorus centres can sometimes result in chiral controllers of higher efficiency.[5] The case of the chiral ferrocenyldiphosphane JOSIPHOS is quite illustrative of this behaviour.[6]

We were interested in expanding the library of BINAP-related diphosphanes to include ligands having two nonequivalent phosphorus donors appended onto the 2- and 2′-positions of the binaphthyl backbone. Atropisomeric ligands of this design, while reported in the biphenyl family,[7] have no precedent in the binaphthyl case.[8]

In principle, unsymmetrically disubstituted binaphthyl derivatives can be prepared either by heterocoupling of the appropriate 2-substituted naphthalenes, or by asymmetrization of a suitable C_2-symmetric 2,2′-homodisubstituted binaphthalene. The second route seemed to us more practicable in this case and we addressed our efforts to find a viable procedure for the sequential substitution of the hydroxyl groups of BINOL (**1**) with two different diarylphosphanyl groups in a stepwise fashion.

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Results and Discussion

Basically there are two ways to connect a low-valent phosphorus centre to an aryl nucleus: the reaction of a metallated arene with a phosphanyl or a phosphinic acid chloride [R_2PCl or $R_2P(O)Cl$, respectively] and the substitution of a triflate group with a secondary phosphane, R_2PH, or phosphane oxide, $R_2P(O)H$, mediated by Ni[9] or Pd[10] catalysts, respectively.

The first methodology we explored relied on the sequential monometallation previously exploited in the biphenyl case.[7] The introduction of a single diphenylphosphanyl substituent was successfully accomplished according to the literature[11] by treatment of 2,2′-dibromobinaphthalene (**2**) with one equivalent of BuLi followed by quenching of the monolithiated species with diphenylchlorophosphane (Scheme 1). This led to the 2-bromo-2′-diphenylphosphanyl derivative **3a** in 75% isolated yield. Unfortunately, repetition of the metallation/quenching sequence on **3a** produced the expected BINAP **4a** only in trace amounts, probably due to the instability of the putative intermediate, the lithio phosphanyl derivative **3b**.

In the search for a different procedure for appending a phosphorated substituent onto an aryl ring, we reasoned that the synthesis of BINAP from BINOL ditriflate (**5**) reported few years ago could be turned to our advantage.[9] This novel methodology is far more expedient than the original preparation of BINAP since it avoids the critical step of bromination of BINOL and provides a much better yield. It provides for the introduction of two diphenylphosphanyl groups in a single step through the Ni-catalyzed substitution of the triflate substituents by diphenylphosphane.

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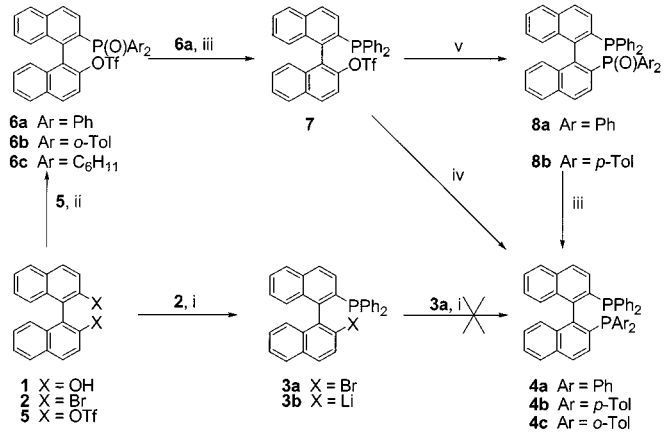


Scheme 1. Synthesis of diphosphanes:
(i) 1 equiv. BuLi in THF, then 1 equiv. PPh_2Cl; (ii) $Ar_2P(O)H$, $Pd(AcO)_2$/dppb, Et_3N, DMSO, 100 °C; (iii) $HSiCl_3$, Et_3N, xylene, 130 °C; (iv) Ar_2PH, $NiCl_2$ /dppe, DMF, 70 °C; (v) $Ar_2P(O)H$, $Pd(AcO)_2$/dppb, Et_3N, DMF, 100 °C

Apparently, however, this procedure is suitable only for the introduction of two identical phosphorus substituents and its scope seems restricted to derivatives of C_2 symmetry because the second triflate group is displaced much faster than the first one.[9]

We were well aware, however, that dissymetrization of BINOL ditriflate (**5**) can be efficiently achieved by reaction with diphenylphosphane oxide in the presence of Pd catalysts. This reaction affords selectively the monosubstituted product **6a** in good yield and this can be converted into the monophosphanyl derivative **7** by deoxygenation with trichlorosilane.[12]

We have recently exploited this procedure in the preparation of the phosphanyl-phosphinyl-binaphthalene (BINAPO) **8a**.[13] This compound is an immediate precursor of BINAP **4a**, which can be readily prepared by removing the oxygen from the phosphinyl substituent. According to this synthetic procedure, BINAP can be prepared in 35% overall yield from BINOL in five steps.

This reaction sequence is of modest value for the preparation of BINAP as compared with the most recent one,[9] but it does demonstrate that the stepwise substitution of the homotopic triflate groups of **5** by two phosphanyl groups is a feasible process and opens the way to the preparation of binaphthyldiphosphanes with different substituents at the phosphorus centres.

Thus, by using di-*p*-tolylphosphane oxide in place of the diphenyl derivative in the Ni-catalyzed reaction of (*S*)-**7**, we were able to introduce a group with a different substitution pattern at the phosphorus centre and to obtain the phosphanylphosphane (*S*)-**8b**. Upon deoxygenation with trichlorosilane, (*S*)-**8b** gave the C_1-symmetrical diphosphane (*S*)-**4b**, the first representative of this new class of atropisomeric ligands with nonequivalent phosphorus donors (BINAPP′).

The diphosphane (*S*)-**4b** was obtained in 24% overall yield from BINOL, with most of the product being lost in the final, low-yielding (45−50%) reduction step. This critical deoxygenation can be avoided by using a diarylphosphane instead of a diarylphosphane oxide in the substitution of the second triflate group. For this reason we thought it better in the following procedure to postpone the introduction of the diphenylphosphanyl substituent until the last step of the synthesis, given that diphenylphosphane is a commercially available reagent.

The Pd-catalyzed reaction of the ditriflate (*S*)-**5** with either di-*o*-tolylphosphane oxide or dicyclohexylphosphane oxide gave the expected monophosphinyl derivatives (*S*)-**6** in remarkably different yields. Much to our surprise, the phosphinyl groups of both of these products turned out to be extremely resistant to deoxygenation with silane reagents and could not be reduced even under forcing conditions (48 h at 160 °C). To obviate this difficulty, we had to reverse the order of introduction of the phosphorated substituents.

Thus, di-*o*-tolylphosphane was prepared by $LiAlH_4$ reduction of the relevant phosphane oxide[14] and the product was coupled with the phosphane triflate (*S*)-**7** in the presence of a Ni-catalyst, affording the unsymmetrical diphosphane (*S*)-**4c** in 42% yield. The success of this preparation is illustrative of the degree of flexibility inherent with the synthetic methodology reported here.

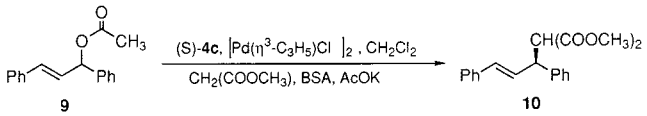
Our subsequent attempts aimed at the preparation of a dicyclohexylphosphanyl derivative were frustrated due to the poor stability of the cyclohexyl-substituted phosphorus reagents under the reaction conditions.

The two diphosphanes (*S*)-**4b** and (*S*)-**4c** show in their ^1H NMR spectra two separate peaks for the diastereotopic methyl groups, the chemical shift difference being more significant (0.5 ppm) in the case of the *o*-tolyl derivative **4c**. Notably, the more deshielded methyl resonance of (*S*)-**4c** is split into two lines (separation 1.5 Hz at room temperature) that coalesce to a broad singlet at 323 K.

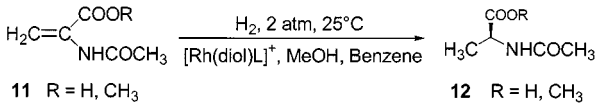
The ^{31}P NMR spectrum of the *p*-tolyl derivative **4b** shows two sharp singlets at $\delta = -16.52$ and $\delta = -15.05$, which is consistent with the presence of two nonequivalent diarylphosphanyl substituents. In contrast, the ^{31}P NMR spectrum of the *o*-tolyldiphosphane **4c** is more complicated and shows one broad singlet at $\delta = -30.27$, attributed to the tolyl-substituted phosphorus, while the diphenylphosphanyl group gives a two-line signal centred at $\delta = -14.12$ (separation 15.2 Hz). While the latter resonance

maintains its shape between 293 and 223 K, in this range of temperatures the first peak displays a dynamic behaviour giving rise to a sharp two-line system below 250 K. We can confidently exclude the possibility that this is due to a $^5J_{P,P'}$ because such a coupling is not observed in the case of the diphosphane **4b** and has no precedent in the literature.[15] Therefore, it can be concluded that the fluxional behaviour of **4c** in solution is due to the presence of two diastereomeric conformers arising from the hindered rotation of the *o*-tolyl groups around the P−C bond.

Both the ligands (*S*)-**4b** and (*S*)-**4c** have been compared with (*S*)-BINAP in the Pd-catalyzed allylic alkylation of 1,3-diphenylpropenyl acetate (**9**) (Scheme 2) and in the Rh-catalyzed hydrogenation of acetamido acrylic acid derivatives **11** (Scheme 3).



Scheme 2. Asymmetric allylic alkylation of 1,3-diphenyl-2-propenyl acetate



Scheme 3. Asymmetric hydrogenation of 2-acetamidoacrylic acid derivatives

In the first screening, the catalysts were prepared in situ by adding the required amount of ligand to a solution of a suitable Rh- or Pd-complex. While, not surprisingly, the *p*-tolyl-substituted diphosphane (*S*)-**4b** gave practically the same results as (*S*)-BINAP, the *o*-tolyl derivative **4c** was more efficient than its C_2 counterpart in both processes.

The improvement was particularly pronounced in the allylic alkylation with dimethyl malonate where the alkylated malonate (*R*)-**10** was obtained in 85% *ee* with (*S*)-**4c** as compared to 32% *ee* for the (*R*)-enantiomer obtained with (*S*)-BINAP (34% *ee* using THF as solvent).[16]

In the hydrogenation of **11**, the in situ Rh catalysts obtained from **4c** were also more efficient, but the *ee* improvement over BINAP was less significant and the catalytic activity was definitely lower than expected. This prompted us to prepare the relevant rhodium(I) complexes with (*S*)-**4c** in order to gain a more detailed insight into this process.

Two cationic rhodium complexes of general formula [(**4c**)Rh(diol)]$^+X^-$ ("diol" = 1,5-cyclooctadiene, X = BF_4, **13a**; "diol" = norbornadiene, X = PF_6, **13b**) have been prepared from $[Rh(diol)Cl]_2$ and (*S*)-**4c** following established procedures.[17] Complex **13a** is highly fluxional at room temperature and its NMR resonances are hardly separable from the ground noise. This is not the case for complex **13b**, which could be readily characterized by multinuclear NMR spectroscopy. In this complex the chelate binding of the diphosphane is readily apparent from the significant downfield shift of the phosphorus resonances (δ = 22.14 and δ = 26.75, respectively) and from the presence of two sets of doublet of doublets with a P,P′ coupling constant of 33 Hz, consistent with two phosphane donors *cis*-coordinated to a rhodium centre. Some attempts have been made to convert complexes **13** into the corresponding *bis*-solvato species through displacement of the diolefin by methanol under hydrogen.[18] As these attempts were inconclusive, complexes **13** were used as such in the catalytic experiments.

The hydrogenations were run at room temperature in 1:1 methanol/benzene under a pressure of 2 bar of hydrogen, because at lower pressure the reaction was too sluggish. In spite of the NMR differences, both complexes **13a** and **13b** showed the same catalytic activity and produced almost the same *ee* values in the hydrogenation of acetamido acrylic acid derivatives **9**. Modest differences with the catalyst prepared in situ were observed.

Under our reaction conditions, the methyl ester **11** was hydrogenated in 40% *ee* by complex **13b**, whereas we obtained only 21% *ee* with the corresponding BINAP/Rh catalyst. The improvement was more pronounced in the case of the free acid **11** where the 46% *ee* obtained with complex **13a** compares favourably with the 13% obtained with BINAP.[19] In all these experiments the prevailing enantiomer of **12** showed the (*R*) configuration. Although the *ee* values recorded in the asymmetric hydrogenation and allylic alkylation with the new ligand **4c** are modest or moderate, and are far from the best values quoted in the literature for the reactions of **9** and **11**, they prove that, at least in some cases, the double *o*-methyl substitution in BINAP can exert a beneficial effect on the enantioselection ability of the ligand.

Conclusions

A synthetic methodology that is useful for generating ligand diversity in the series of binaphthalene-core diphosphanes has been established and preliminary evidence shows that differentiation of the donor centres in binaphthalene-template chelating diphosphane can result in chiral inducers of higher efficiency.

Experimental Section

General: Nuclear magnetic resonance spectra were obtained on a Varian VXR-300 spectrometer at 300 MHz for ^1H, 75 MHz for ^{13}C and 121.4 for ^{31}P. Chemical shifts are reported in ppm downfield from internal Me_4Si or external H_3PO_4. − Gas chromatographic analyses were performed using a Hewlett Packard 5890/A gas chromatograph equipped with an HP 3396 integrator. − Optical rotations were measured on a Perkin−Elmer Model 241 polarimeter. − Melting points were obtained with a Leitz Laborlux S melting

point apparatus and are not corrected. − Elemental analyses were performed with a Perkin−Elmer Analyzer 240B by Mr. A. Canu (Dipartimento di Chimica, Università di Sassari). Solvents were dried and distilled under nitrogen before use. Commercial reagents (Aldrich) were used as received. Compounds **5**, **6a**, **7** and **8a** [(*S*)-configuration] were prepared from (*S*)-BINOL as reported in ref.[12] Compound **2** was prepared from racemic BINOL as reported in ref.[18]

Preparation of Monophosphinyl Monotriflates 6: These compounds were prepared from (*S*)-BINOL ditriflate **5** according to the procedure reported in ref. [12]

(*S*)-6b: 73% yield. − ^{1}H NMR ($CDCl_3$): δ = 2.12 (s, 3 H, CH_3), 2.44 (s, 3 H, CH_3), 6.86−7.09 (series of m, 6 H, Ar), 7.21−7.42 (series of m, 9 H, Ar), 7.58 (t, *J* = 7.2 Hz, 1 H, Ar), 7.85 (d, *J* = 8.1 Hz, 2 H, Ar), 7.96 (dd, *J* = 5.4, 9.3 Hz, 2 H, Ar). − ^{31}P NMR ($CDCl_3$): δ = 35.00. − $C_{35}H_{26}F_3O_4PS$ (630.62): calcd. C 66.66, H 4.16; found C 66.38, H 4.24.

(*S*)-6c: 14% yield; m.p. 210−212 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.5−2.15 (series of m, 22 H), 7.13 (d, *J* = 8.4 Hz, 1 H, Ar), 7.22−7.80 (series of m, 9 H, Ar), 7.96 (d, *J* = 8.1 Hz, 1 H, Ar), 8.04 (t, *J* = 9.0 Hz, 1 H, Ar). − ^{31}P NMR ($CDCl_3$): δ = 46.90. − $C_{33}H_{34}F_3O_4PS$ (614.66): calcd. C 64.48, H 5.57; found C 64.35, H 5.44.

Preparation of Phosphanyl−Phosphanes 8: A solution of the appropriate diarylphosphane oxide (5.0 mmol) and (dppe)$NiCl_2$ [dppe = 1,2-bis(diphenylphosphanyl)ethane] (0.22 g, 0.43 mmol) in DMF (10 mL) was stirred at 100 °C for 10 min. A solution of 2-diphenylphosphanyl-1,1′-binaphthalene-2′-yl triflate (**7**) (2.5 g, 4.26 mmol) and Et_3N (3 mL) in DMF (15 mL) was added and the mixture was stirred at 100 °C for 10−14 h. After cooling, the mixture was diluted with aqueous NH_4Cl and extracted with CH_2Cl_2 (100 mL). The organic phase was washed with H_2O, dried and evaporated to give a brown solid, which was purified by flash chromatography on silica gel using EtOAc as eluent. Slightly lower yields were obtained using $Pd(OAc)_2$/dppe as the catalyst.

8a: 1.90 g (70%); m.p. 172−173 °C. − IR (KBr): $\tilde{\nu}$ = 1208 cm^{-1}. − ^{1}H NMR ($CDCl_3$): δ = 6.63 (d, *J* = 8.1 Hz, 1 H, Ar), 6.72 (dt, *J* = 1.2, 6.6 Hz, 1 H, Ar) 6.81−7.43 (series of m, 23 H, Ar), 7.60 (m, 3 H, Ar), 7.79 (d, *J* = 8.1 Hz, 1 H, Ar), 7.81 (d, *J* = 8.4 Hz, 1 H, Ar), 7.82 (d, *J* = 7.8 Hz, 1 H, Ar), 7.93 (dd, *J* = 2.4, 8.4 Hz, 1 H, Ar). − ^{31}P NMR ($CDCl_3$): δ = −14.70, 27.69. − $C_{44}H_{32}OP_2$ (638.67): calcd. C 82.74, H 5.05; found C 82.68, H 5.16.

8b: 1.47 g (52%); m.p. 156−158 °C. − ^{1}H NMR ($CDCl_3$): δ = 2.23 (s, 3 H, CH_3), 2.29 (s, 3 H, CH_3), 6.60 (m, 2 H, Ar), 6.70 (m, 2 H, Ar), 6.80−7.91 (series of m, 26 H, Ar). − ^{31}P NMR ($CDCl_3$): δ = −14.79, 27.91. − $C_{46}H_{36}OP_2$ (666.73): calcd. C 82.87, H 5.44; found C 83.13, H 5.31.

Preparation of Diphosphanes 4. − Method A: Reduction of Phosphinyl-phosphanes 8: To a mixture of 2-(diphenylphosphanyl)-2′-(di-*p*-tolylphosphinyl)-1,1′-binaphthalene (**8b**) (1.0 g, 1.5 mmol) and Et_3N (5 mL) in xylene (35 mL) was added $HSiCl_3$ (0.74 mL) at 0 °C. The mixture was stirred at 120 °C for 12 h. After cooling, the mixture was diluted with Et_2O and quenched with saturated $NaHCO_3$. The organic phase was separated, dried over Na_2SO_4 and evaporated. The product was purified by flash chromatography using CH_2Cl_2/petroleum ether (1:1) as eluent.

4b: 0.44 g (45%); m.p. 188−189 °C. − $[a]_D^{25}$ = −220 (*c* = 0.4, benzene). − ^{1}H NMR ($CDCl_3$): δ = 2.24 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 6.81−7.48 (series of m, 28 H, Ar), 7.81−7.91 (series of m, Ar, 2 H, Ar). − ^{31}P NMR ($CDCl_3$): δ = −16.52, −15.05. − $C_{46}H_{36}P_2$ (650.73): calcd. C 84.9, H 5.58; found C 85.18; H 5.36. − **Method B: Direct Coupling of 7 with Disubstituted Phosphanes:** A solution of (dppe)$NiCl_2$ (0.1 g, 0.2 mmol) in DMF (5 mL) containing di-*o*-tolylphosphane (0.5 g, 2.33 mmol) was stirred at 100 °C for 10 min. To this mixture was added a solution of 2-diphenylphosphanyl-1,1′-binaphthalene-2′-yl triflate (**7**) (1.17 g, 2.0 mmol) and Et_3N (1.5 mL) in DMF (8 mL) and the mixture was heated at 100 °C for 4 h. After being cooled to room temperature, the mixture was poured into H_2O and the resulting brown solid was filtered off, dissolved in CH_2Cl_2 and dried (Na_2SO_4). Evaporation of the solvent under reduced pressure gave a brown solid, which was purified by flash chromatography on silica gel using CH_2Cl_2 as eluent.

4c: 0.55 g (42%); m.p. 230−236 °C. − $[a]_D^{25}$ = −57.3 (*c* = 1, $CHCl_3$). − ^{1}H NMR ($CDCl_3$): δ = 1.73 (s, 3 H, CH_3), 2.23 (d, *J* = 1.5 Hz, 3 H, CH_3), 6.46 (d, *J* = 7.8 Hz, 1 H, Ar), 6.6−7.9 (series of m, 29 H, Ar). − ^{31}P NMR ($CDCl_3$): δ = −14.12 (d, *J* = 15.2 Hz, 1 P), −30.27 (s, broad, 1 P). − ^{13}C NMR ($CDCl_3$) aliphatic only: δ = 18.16 (d, *J* = 25.1 Hz, 1 C, CH_3), 18.9 (dd, *J* = 18.9, *J* = 7.7 Hz, 1 C, CH_3). − $C_{46}H_{36}P_2$ (650.73): calcd. C 84.9, H 5.58; found C 84.72, H 5.82.

Preparation of Diphosphane Rhodium(I) Diolefin Complexes 13. − Method A, [(4c)Rh(cod)]$^+BF_4^-$ (13a): $AgBF_4$ (56 mg, 0.15 mmol) was added to a solution of $[Rh(cod)Cl]_2$ (37 mg, 0.075 mmol) in THF (10 mL) with vigorous stirring for 30 min. The suspension was filtered through Celite to remove the silver salts and ligand **4c** (100 mg, 0.15 mmol) was added to the yellow solution. After stirring 10 min at room temperature, the solution was concentrated and ether was added causing the precipitation of **13a** as a dark-yellow solid, which was filtered off and washed several times with anhydrous ether; 100 mg (70%). − M.p. decomposition at 120 °C. − ^{1}H NMR: Very broad signals in both the aromatic and the aliphatic regions. − ^{31}P NMR: no detectable signal. − $C_{54}H_{48}P_2RhBF_4$ (948.64)

Method B, [(4c)Rh(nbd)]$^+PF_6^-$ (13b): To a solution of ligand **4c** (100 mg, 0.15 mmol) in benzene (4 mL) and THF (1 mL) was added $[Rh(nbd)Cl]_2$ (35.5 mg, 0.075 mmol). The colour of the solution immediately turned to deep red. After 5 min, KPF_6 (28 mg, 0.15 mmol) in acetone (2 mL) was added, followed by diethyl ether (5 mL). The reaction mixture was stirred for 3 h, during which time an orange solid separated. The solid was filtered off, washed with benzene and diethyl ether and air-dried. The orange crystalline powder was dissolved in the minimal amount of dichloromethane and crystallized by addition of ethanol and diethyl ether; 104 mg (70%); m.p. decomposition at 230 °C − ^{1}H NMR ($CDCl_3$): δ = 1.47 (d, *J* = 9 Hz, 1 H, CH_2), 1.56 (s, 3 H, CH_3), 1.65 (d, *J* = 9 Hz, 1 H, CH_2), 3.26 (s, broad, 3 H, CH_3), 3.65 (s, broad, 1 H, allylic), 4.00 (s, broad, allylic), 4.18 (s, broad, 1 H, vinylic), 4.69 (s, broad, 1 H, vinylic), 5.01 (s, broad, 1 H, vinylic), 5.43 (s, broad, 1 H, vinylic), 6.20−8.48 (series of m, 30 H, Ar). − ^{13}C NMR: δ = 22.8 (d, $^3J_{C,P}$ = 3.5 Hz, 1 C, CH_3), 26.2 (d, $^3J_{C,P}$ = 10.1 Hz, 1 C, CH_3), 52.6 (s, 1 C, CH, allylic), 53.6 (s, 1 C, CH, allylic), 69.6 (s, 1 C, CH_2), 77.2 (m, 1 C, CH, vinylic), 85.0 (m, 1 C, CH, vinylic), 86.0 (m, 1 C, CH, vinylic), 89.0 (m, 1 C, CH, vinylic), 124.4−141.7 (series of m, 44 C, Ar). − ^{31}P NMR ($CDCl_3$): δ = −144.9 (m, PF_6^-), 22.14 (dd, $^1J_{P,Rh}$ = 154.4, $^2J_{P,P'}$ = 33 Hz, 1 P), 26.75 (dd, $^1J_{P,Rh}$ = 156.3, $^2J_{P,P'}$ = 33 Hz, 1 P). − $C_{53}H_{44}P_2RhPF_6$ (990.76): calcd. C 64.25, H 4.48; found C 64.42, H 4.62.

Asymmetric Hydrogenation of Methyl Acetamidoacrylate: Methyl acetamidoacrylate **11** (143 mg, 1 mmol) and complex **13b** (9.5 mg,

0.01 mmol) were placed in a pressure bottle. The flask was purged with nitrogen, the solvent (benzene/methanol, 1:1; 10 mL) was added by syringe through a serum cap and the bottle was connected to the hydrogen reservoir of a Parr mid-pressure apparatus. The nitrogen was evacuated and purged twice with hydrogen. Then hydrogen (2 bar) was admitted into the bottle and the reaction mixture was shaken for 16 h at room temperature.

Conversion and *ee* of methyl alaninate (**12**) were determined by GC analysis on a 25 m × 0.25 mm capillary column coated with diethyl-*tert*-butylsilyl-β-cyclodextrin operated at 95 °C using He (60 Kpa) as the carrier. Retention times: substrate, 13.7 min; (*S*)-**12**, 14.8 min; (*R*)-**12**, 19.1 min.

Asymmetric Allylic Alkylation of 1,3-Diphenylallyl Acetate with Dimethyl Malonate: A solution of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.2 mg, 0.006 mmol) and the ligand **4c** (13 mg, 0.02 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature under nitrogen. After 30 min a solution of 1,3-diphenylprop-2-enyl acetate (**9**) (50 mg, 0.2 mmol) in CH_2Cl_2 (0.5 mL) was added. A solution of dimethyl malonate (80 mg, 0.6 mmol), *N,O*-bis(trimethylsilyl)acetamide (BSA) (122 mg, 0.6 mmol) and potassium acetate (6 mg, 0.6 mmol) in CH_2Cl_2 (3.5 mL) was then added and stirring was continued at room temperature until complete conversion was attained (1.5 h). The reaction mixture was diluted with ether (25 mL) and washed with saturated NH_4Cl. The organic phase was dried (Na_2SO_4), concentrated under reduced pressure and the residue purified by flash chromatography (light petroleum/ether, 3:1) to give dimethyl [(*R*)-1,3-diphenylprop-2-enyl]malonate (**10**) in 85% *ee*.

The *ee* was determined from the integrals of the methoxy groups of (1,3-diphenylprop-2-enyl)malonate, as split by the chiral shift reagent europium tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorate].

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