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Chiral 2-(2-diphenylphosphinophenyl)-5,6,7,8-tetrahydroquinolines: new P–N ligands for asymmetric catalysis

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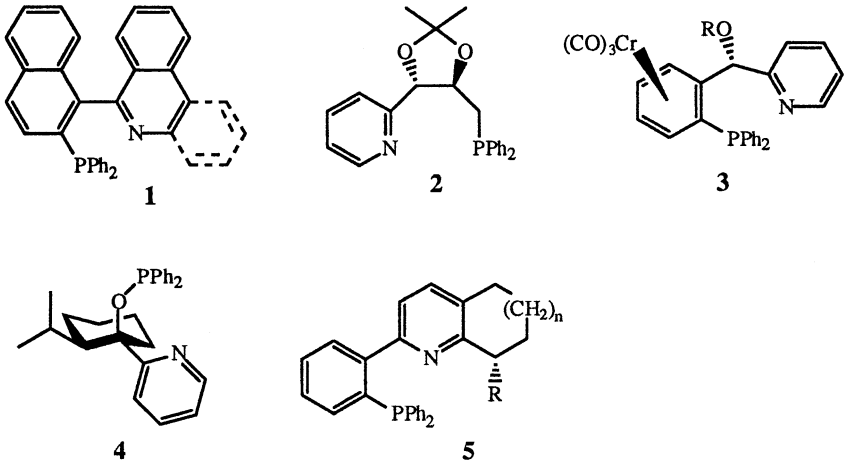
Abstract—New chiral phosphorus–nitrogen ligands, specifically, 2-(2-diphenylphosphinophenyl)-5,6,7,8-tetrahydroquinolines were prepared and assessed in the enantioselective palladium catalyzed allylic substitution of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate. Enantioselectivity up to 71% was obtained. © 2001 Published by Elsevier Science Ltd.

1. Introduction

Enantioselective reactions using metal complexes with ligands having hetero-donor atoms are an actively pursued research area. The interest toward this type of ligand comes from the fact that a control element for optimizing a particular catalytic system is the modulation of the electron density on the metal both by changing the nature of the heteroatoms and by modifying the electron donating or accepting properties of the ligand by a proper choice of the substituents bonded to it.[1] The easier way to obtain this goal is the use of ligands with different donating atoms. This is the case of phosphorus–nitrogen (P–N) ligands which are very successful in asymmetric catalysis.[2] In this context, relatively few examples of bidentate P–N ligands where the nitrogen atom is included in a pyridine framework have been reported so far.[3] Representative examples of phosphinopyridines (**1**–**5**)[4] are reported in Scheme 1.

Recently, Katsuki et al. reported the application of (phosphinoaryl)pyridine ligands **5** to palladium-catalyzed asymmetric allylic alkylation.[4f–l] Although these ligands afforded very good results in this process, their use is limited because only small amount of these ligands are available. In fact, their preparation requires a rather elaborate synthesis or the separation of a racemic mixture by preparative chiral HPLC.[5] With the aim of obtaining similar ligands more easily, we have prepared a series of (phosphinoaryl)pyridines derived from naturally occurring compounds.

In this paper, we report the synthesis of the chiral 2-(2-diphenylphosphinophenyl)-5,6,7,8-tetrahydroquinoline ligands **9**, **20**, **25**, **30** (Schemes 3 and 4) and the results



Scheme 1.

Keywords: phosphinopyridine ligands; palladium catalysts; enantioselective allylic substitution reactions.
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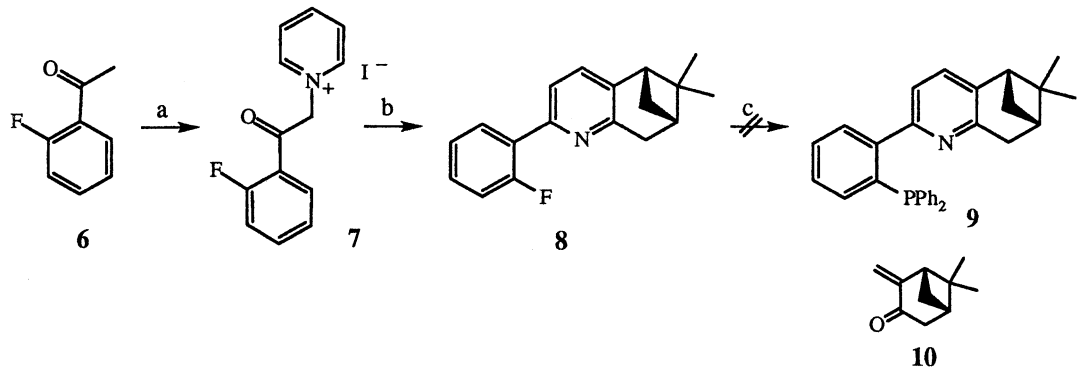


Scheme 2. (a) I_2, pyridine; (b) **10**, AcOH, $AcONH_4$, 120°C, 4 h, 46%; (c) $KPPh_2$, THF.

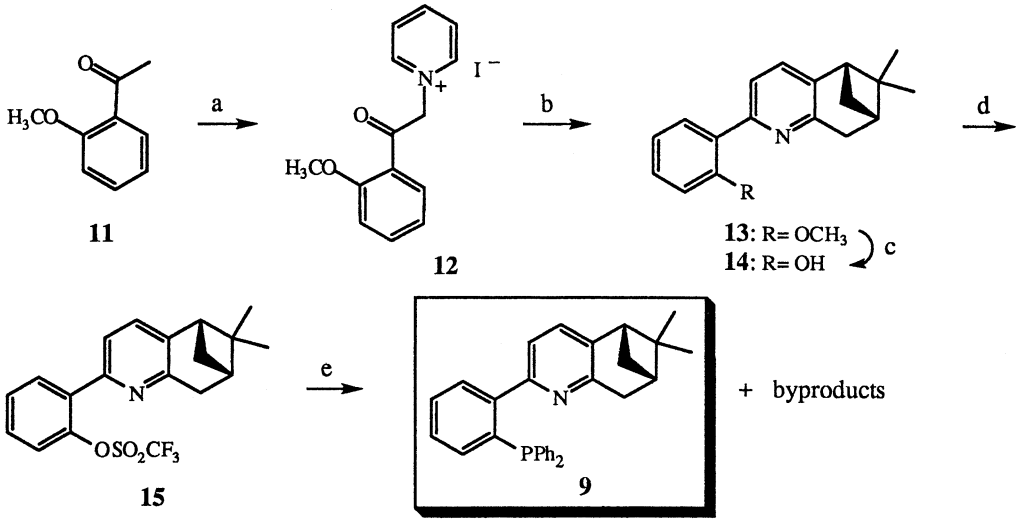
obtained with these ligands in the enantioselective palladium catalyzed allylic substitution of 1,3-diphenyl-prop-2-enyl acetate with dimethyl malonate.

2. Results and discussion

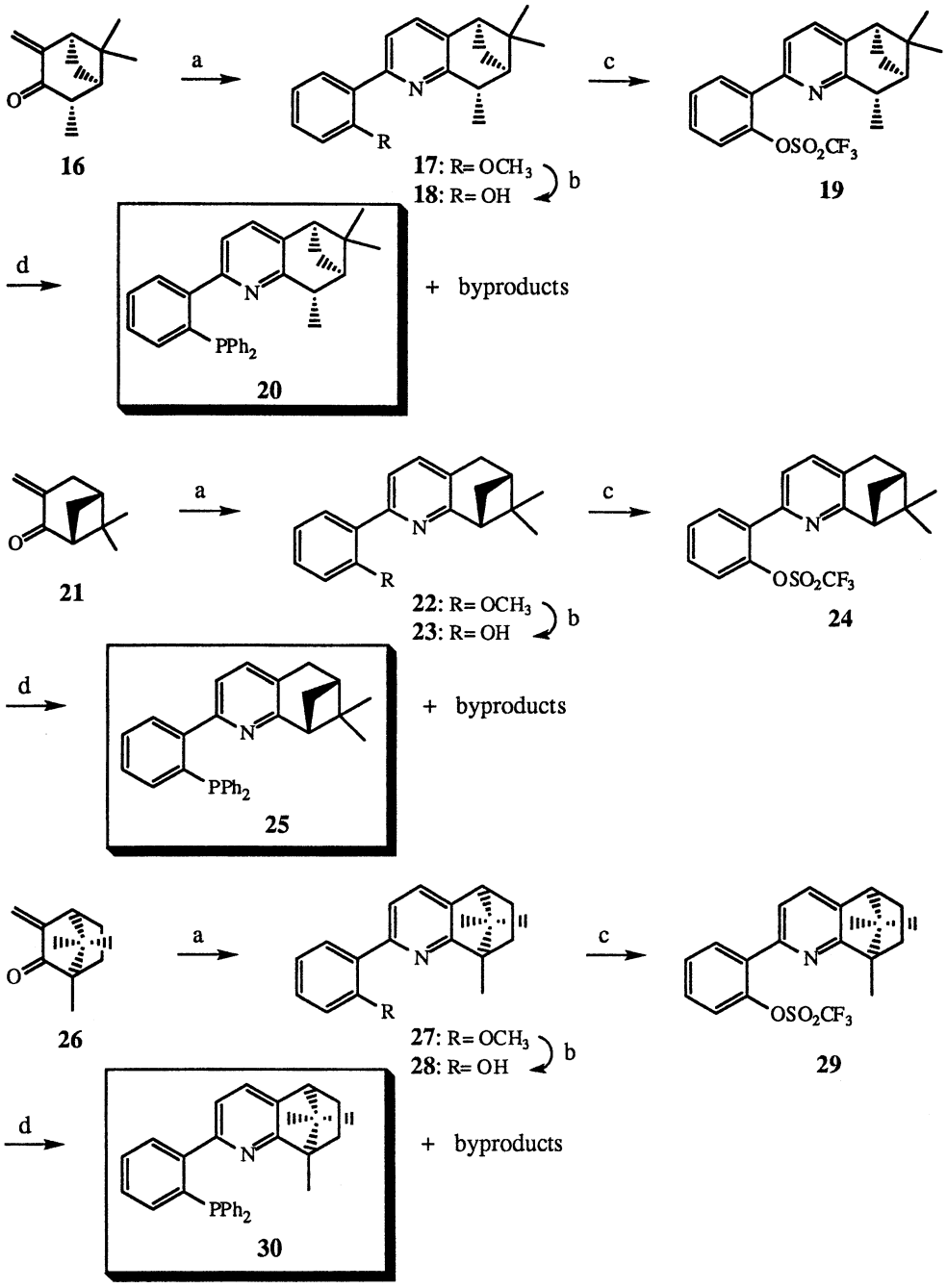
For the synthesis of this class of ligand, we considered that a convenient approach could involve the nucleophilic substitution of an electrophilic aryl fluoride with potassium diphenylphosphide.[6] Thus, as a substrate to test the feasibility of this idea, the fluoro derivative **8** was prepared (Scheme 2) following the Kröhnke methodology which demands the reaction of an α,β-unsaturated ketone with a pyridinium salt.[7] Thus, (−)-pinocarvone **10**[8] underwent annelation with the pyridinium iodide **7**, prepared in turn by reaction of 2-fluoroacetophenone **6** with iodine in pyridine, to give the fluoropyridine **8** in moderate yield. Unfortunately, several attempts to convert **8** into the desired phosphinoquinoline **9** failed.

Therefore, we examined the possibility of introducing the diphenylphosphino group by nickel(0)-catalyzed cross-coupling of aryl sulfonates with chlorodiphenylphosphine.[9] For this purpose, the methoxyquinoline **13** was prepared by reaction of (−)-pinocarvone **10** with 1-phenacylpyridinium iodide **12**, in turn prepared by reaction of 2-methoxyacetophenone **11** with iodine in pyridine (Scheme 3).[10] Demethylation of the methyl ether **13** with boron tribromide occurred in good yield (79%) to give the phenol **14** which was converted into the trifluoromethansulphonate **15** with $(CF_3CO_2)_2O$ in pyridine (88%). Finally, treatment of triflate **15** with diphenylphosphine in the presence of 10 mol% of $NiCl_2$(dppe) and 2 equiv. of 1,4-diazabicyclo[2.2.2]octane (DABCO) in DMF at 100°C gave the corresponding phosphinoquinoline ligands **9** (20%) with the corresponding N-oxide (20%) and the phenyl derivative (16%). The last one results from the reduction of the trifluoromethansulphonate group.

Having obtained the desired phosphinoquinoline **9**, this protocol was extended to other α,β-methylene ketones (Scheme 4). Thus, the ketones **16**, **21**, **26** obtained from (−)-isopinocampheol,[11] (−)-β-pinene[12] and (+)-camphor,[12] respectively, yielded the methoxyquinolines **17**, **22**, **27** (46, 24, 24% yields, respectively). Cleavage of the methyl ether afforded the phenols **18**, **23**, **28** (80, 86, 85% yields, respectively) which were converted into the trifluoromethansulphonates **19**, **24**, **29** (82, 82, 79% yields, respectively). Finally cross-coupling of **19**, **24**, **29** with



Scheme 3. (a) I_2, pyridine; (b) **10**, AcOH, $AcONH_4$, 120–140°C, 4–20 h; (c) BBr_3, CH_2Cl_2; (d) $(CF_3SO_2)_2O$, pyridine, CH_2Cl_2; (e) $HPPh_2$, 10 mol% $NiCl_2$(dppe), DABCO, DMF, 100°C.



Scheme 4. (a) **12**, AcOH, $AcONH_4$, 120–140°C, 4–20 h; (b) BBr_3, CH_2Cl_2; (c) $(CF_3SO_2)_2O$, pyridine, CH_2Cl_2; (d) $HPPh_2$, 10 mol% $NiCl_2$(dppe), DABCO, DMF, 100°C.

diphenylphosphine gave the corresponding phosphinoquinoline ligands **20**, **25**, **30** in 32, 43, 19% yields, respectively, with a variable quantity of the corresponding N-oxides (16–20%) and the phenyl derivatives (16–39%).

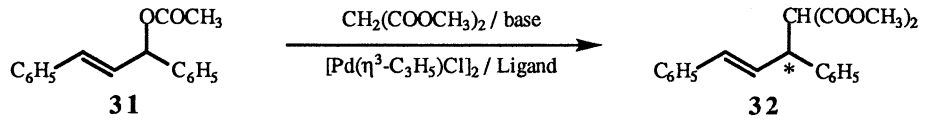
As a model for the evaluation of the ability of the new P–N ligands to provide asymmetric induction in catalytic processes we selected the palladium-catalyzed allylic substitutions and in particular, the alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate, which serves as a representative substrate to compare the outcome of different ligands.[13]

Allylic substitutions were carried out employing $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ as procatalyst and a mixture of dimethyl malonate, *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and potassium acetate in methylene chloride.[14] The results of the catalytic reactions are reported in Table 1.

Ligands **9**, **20**, **25**, **30** were able to provide effective palladium catalysts and to give the dimethyl 1,3-diphenylprop-2-enyl malonate **32** in good yield and in low to moderate enantiomeric excess. Both the reaction rate and enantioselectivity were increased when the stereocenter is closer to the tetrahydroquinoline nitrogen.

Thus, ligand **25**, differing from **9** by the position of the dimethylmethylene bridge, which in the former ligand is

Table 1. Allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethyl malonate



31 **32**

Entry	Method[a]	Ligand	Reaction time (h)	Yield (%)[b]	ee (%)[c]	Configuration[d]
1	A	**9**	96	87	37	*S*
2	A	**20**	15	95	68	*S*
3	A	**25**	70	92	70	*S*
4	B	**25**	0.3	96	71	*S*
5	C	**25**	90	88	66	*S*
6	A	**30**	12	96	50	*S*

[a] *Method A*: reaction of the ligand (10 mol%) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.5 mol%) with 1,3-diphenylprop-2-enyl acetate (0.4 mmol), $CH_2(COOMe)_2$ (1.2 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (BSA) (1.2 mmol) and KOAc (3.5 mol%) in CH_2Cl_2 (2 mL) at room temperature. *Method B*: reaction of the ligand (10 mol%) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (2.5 mol%) with 1,3-diphenylprop-2-enyl acetate (0.8 mmol), $NaCH(COOMe)_2$ (1.2 mmol), 15-crown-5 (1.2 mmol) in CH_3CN (2.5 mL) at room temperature. *Method C*: reaction of the ligand (10 mol%) and $[\{Pd(\eta^3\text{-}C_3H_5)Cl\}_2]$ (2.5 mol%) in CH_2Cl_2 (1 mL) for 30 min, followed by a solution of 1,3-diphenylprop-2-enyl acetate (0.8 mmol) in CH_2Cl_2 (0.5 mL). Then, a solution of dimethyl malonate (2.4 mmol), BSA (2.4 mmol) and tetrabutylammonium fluoride trihydrate (2.4 mmol) in CH_2Cl_2 (3.5 mL) was added over 1 h.

[b] Isolated yields.

[c] Determined by ^1H NMR spectroscopy using $Eu(hfc)_3$ as chiral shift reagent.

[d] The assignment is based on the sign of the optical rotation, see Ref. 18.

in close proximity to the nitrogen donor center, increased both the reaction rate and the stereoselectivity of the reaction. A similar improvement in the results were obtained passing from ligand **9** to ligand **20** which are different due to the presence of a methyl group on the 8-position of the tetrahydroquinoline ring.

Surprisingly, both ligands **9** and **20**, gave the reaction product **32** with the same sense of chirality, even though they have opposite configurations to the stereogenic centers on the 5,7-positions of the tetrahydroquinoline ring indicating that the course of the reaction reasonably depends on the stereogenic center bonded to the 8-position.

It has been reasoned that one of the critical factors in controlling the selective addition of nucleophiles to π-allyl palladium intermediates is the nature of the ion pair of the attacking nucleophile.[13,15] Thus, the complexation of the cation with crown ether[4f–l,16] or the use of tetraalkylammonium as a bulky counterion[17] can have a dramatic effect on the enantioselectivity of the process.

Therefore, in an effort to increase the enantioselectivity of the reaction, we chose the best performing ligand **25** to test other two methods for the generation of the malonate anion. When the reaction was carried out in acetonitrile with sodium malonate, generated using sodium hydride, in the presence of 15-crown-5,[16] a rapid reaction was observed (the reaction was complete in less than 20 min), but the enantioselectivity remained unchanged (Table 1, entry 4). In contrast, the reaction in methylene chloride of tetrabutylammonium malonate, generated from dimethyl malonate and using the BSA/tetrabutylammonium fluoride system as the base,[17] depressed both reaction rate and enantioselecivity (Table 1, entry 5).

In summary, we have prepared new chelating ligands of the type P–N and demonstrated that they are worthy of attention for their applications in the field of asymmetric catalysis.[20] The preliminary results obtained in enantioselective palladium catalyzed allylic substitutions indicate that the stereoselectivity of the reaction could be increased both by the introduction of encumbering substituents on the 8-position of the tetrahydroquinoline ring and/or by modifying the substituents on the phosphorus. Further studies aimed at modifying the ligand design and application to other catalytic asymmetric reactions are in progress.

3. Experimental

3.1. General methods

Melting points were determined on a Büchi 510 capillary apparatus and are uncorrected. The NMR spectra were obtained with a Varian VXR-300 spectrometer at 300 MHz for ^1H and 101.4 MHz for ^{31}P. Chemical shifts are reported in ppm downfield from internal Me_4Si in $CDCl_3$. Optical rotations were measured with a Perkin–Elmer 241 polarimeter in a 1 dm tube. Elemental analyses were performed on a Perkin–Elmer 240 B analyzer.

(−)-Pinocarvone **10** was obtained by oxydation of (1*R*)-(+)-α-pinene (90% ee by GLC, Aldrich).[8] (1*R*,4*S*,5*R*)-4,6,6-Trimethyl-2-methylenebicyclo[3.1.1]heptan-3-one **16**, (1*R*,5*R*)-6,6-dimethyl-3-methylene bicyclo[3.1.1] heptan-2-one **21** and (1*R*,4*S*)-1,7,7-trimethyl-3-methylenebicyclo-[2.2.1]heptan-2-one **26** were prepared from (−)-isopinocampheol,[11] (−)-β-pinene[12] and (+)-camphor,[12] respectively. 1-[2-(2-Methoxy phenyl)-2-oxoethyl]pyridinium iodide **12** was prepared according to a reported procedure.[19]

3.1.1. 1-[2-(2-Fluorophenyl)-2-oxoethyl]pyridinium iodide 7. 2-Fluoroacetophenone (25 g, 166.5 mmol) was added dropwise to a mixture of iodine (46 g, 0.181 mol) in pyridine (90 mL). Then the mixture was heated to 100°C for 45 min. After this period, the solution was cooled in ice and the formed solid filtered off. Recrystallization from methanol gave yellow crystals of **7**: 23.4 g (38%); mp 183–184°C; ^1H NMR (DMSO-d_6) δ 8.99 (d, 2H, J= 6.0 Hz), 8.76 (t, 1H, J=7.8 Hz), 8.29 (t, 2H, J=7.2 Hz), 8.04 (m, 1H), 7.85 (m, 1H), 7.52 (m, 2H), 6.32 (d, 2H,

J=3.0 Hz). Anal. calcd for $C_{13}H_{11}FINO$: C, 45.48; H, 3.23; N, 4.08. Found: C, 45.59; H, 3.34; N, 4.15.

3.1.2. (5*S*,7*S*)-(+)-5,6,7,8-Tetrahydro-6,6-dimethyl-2-(2-fluorophenyl)-5,7-methanoquinoline 8. A mixture of 1-[2-(2-fluorophenyl)-2-oxoethyl]pyridinium iodide **7** (23.4 g, 68 mmol), ammonium acetate (75 g) and glacial acetic acid (260 mL) was heated at 100°C for 10 min. Then a solution of (−)-pinocarvone (10.15 g, 68 mmol) in glacial acetic acid (10 mL) was added dropwise and the resulting solution was heated at 120°C for 4 h. After cooling, the mixture was taken up in H_2O (1 L) and extracted with ethyl ether (3×200 mL). The combined organic phases were dried over anhydrous Na_2SO_4, the solvent was evaporated and the residue was purified by flash chromatography (eluent: petroleum ether/ethyl acetate=9:1) to give pure **8** as a pale yellow oil: 8.32 g (46%); $[\alpha]_D^{25}$=+71.3 (*c* 1.8, $CHCl_3$); ^{1}H NMR δ 7.96 (dt, 1H, J=7.8, 1.8 Hz), 7.51–7.44 (m, 1H), 7.36–7.09 (m, 4H), 3.19 (d, 2H, J=2.7 Hz), 2.80 (t, 1H, J=5.7 Hz), 2.70 (m, 1H), 2.40 (m, 1H), 1.42 (s, 3H), 1.32 (d, 1H, J=9.3 Hz), 0.70 (s, 3H). Anal. calcd for $C_{18}H_{18}FN$: C, 80.86; H, 6.79; N, 5.24. Found: C, 80.99; H, 6.55; N, 5.11.

3.2. General procedure for the preparation of quinolines 13, 17, 22, 27

A mixture of 1-[2-(2-methoxyphenyl)-2-oxoethyl]pyridinium iodide **12** (12 g, 33.8 mmol), ammonium acetate (20 g) and glacial acetic acid (46 mL) was heated at 100°C for 10 min. Then a solution of the α,β-methylene ketone (33.8 mmol) in glacial acetic acid (5 mL) was added dropwise and the resulting solution was heated at 120–140°C for 4–20 h. After cooling, the mixture was taken up in H_2O (1 L) and extracted with ethyl ether (3×100 mL). The combined organic phases were dried over anhydrous Na_2SO_4, the solvent was evaporated and the residue was purified by flash chromatography.

3.2.1. (5*S*,7*S*)-(+)-5,6,7,8-Tetrahydro-6,6-dimethyl-2-(2-methoxyphenyl)-5,7-methanoquinoline 13. The reaction was carried out at 120°C for 4 h using the α,β-methylene ketone **10**. Chromatographic eluent: petroleum ether/ethyl acetate=7:3; 4.15 g (44%); colorless powder of mp 103–104°C; $[\alpha]_D^{25}$=+63.7 (*c* 1.8, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 7.77 (dd, 1H, J=7.8, 1.8 Hz), 7.50 (d, 1H, J=7.8 Hz), 7.33 (dt, 1H, J=8.1, 1.8 Hz), 7.22 (d, 1H, J=8.1 Hz), 7.06 (dt, 1H, J=7.8, 0.9 Hz), 6.98 (d, 1H, J=8.1 Hz), 3.85 (s, 3H), 3.18 (d, 2H, J=3.0 Hz), 2.78 (t, 1H, J=5.7 Hz), 2.69 (m, 1H), 2.38 (m, 1H), 1.42 (s, 3H), 1.33 (d, 1H, J=9.6 Hz), 0.7 (s, 3H). Anal. calcd for $C_{19}H_{21}NO$: C, 81.67; H, 7.58; N, 5.02. Found: C, 81.76; H, 7.81; N, 5.11.

3.2.2. (5*R*,7*R*,8*S*)-5,6,7,8-Tetrahydro-6,6,8-trimethyl-2-(2-methoxyphenyl)-5,7-methanoquinoline 17. The reaction was carried out at 120°C for 20 h using the α,β-methylene ketone **16**. Chromatographic eluent: petroleum ether/ethyl acetate=7:3; 4.55 g (46%); this compound was obtained as a distereomeric mixture of **17** (77%) and its epimer at the C_8-carbon (23%). ^{1}H NMR (major isomer) δ 7.87 (dd, 1H, J=7.5, 1.8 Hz), 7.55 (d, 1H, J=7.5 Hz), 7.33 (dt, 1H, J=7.5, 1.8 Hz), 7.19 (d, 1H, J=7.5 Hz), 7.07 (dt, 1H, J=7.5, 0.9 Hz), 6.95 (d, 1H, J=7.5 Hz), 3.85 (s, 3H), 3.26 (dq, 1H, J=6.9, 2.4 Hz), 2.77 (t, 1H, J=5.7 Hz), 2.59–2.52 (m, 1H), 2.18–2.13 (m, 1H), 1.44 (d, 3H, J=7.5 Hz), 1.42 (s, 3H), 1.35 (d, 1H, J=9.9 Hz), 0.69 (s, 3H). ^{1}H NMR (minor isomer) δ 7.87 (dd, 1H, J=7.5, 1.8 Hz), 7.55 (d, 1H, J=7.5 Hz), 7.33 (dt, 1H, J=7.5, 1.8 Hz), 7.19 (d, 1H, J=7.5 Hz), 7.07 (dt, 1H, J=7.5, 0.9 Hz), 6.95 (d, 1H, J=7.5 Hz), 3.85 (s, 3H), 3.26 (dq, 1H, J=6.9, 2.4 Hz), 2.77 (t, 1H, J=5.7 Hz), 2.59–2.52 (m, 1H), 2.18–2.13 (m, 1H), 1.55 (d, 3H, J=7.5 Hz), 1.42 (s, 3H), 1.35 (d, 1H, J=9.9 Hz), 0.74 (s, 3H). Anal. calcd for $C_{20}H_{23}NO$: C, 81.86; H, 7.91; N, 4.78. Found: C, 81.78; H, 7.686; N, 4.65.

3.2.3. (6*R*,8*R*)-(+)-5,6,7,8-Tetrahydro-7,7-dimethyl-2-(2-methoxyphenyl)-6,8-methanoquinoline 22. The reaction was carried out at 120°C for 20 h using the α,β-methylene ketone **21**. Chromatographic eluent: petroleum ether/ethyl acetate=7:3; 2.26 g (24%); colorless powder of mp 103°C; $[\alpha]_D^{25}$=+9.89 (*c* 2.1, $CHCl_3$); ^{1}H NMR δ 7.79 (dd, 1H, J=7.8, 1.8 Hz), 7.54 (d, 1H, J=7.8 Hz), 7.36 (dt, 1H, J=8.1, 1.8 Hz), 7.23 (d, 1H, J=8.1 Hz), 7.06 (dt, 1H, J=7.8, 0.9 Hz), 6.98 (d, 1H, J=8.1 Hz), 3.85 (s, 3H), 3.01 (t, 1H, J=5.4 Hz), 2.98–2.90 (m, 2H), 2.78–2.72 (m, 1H), 2.42–2.32 (m, 1H), 1.44 (s, 3H), 1.34 (d, 1H, J=9.9 Hz), 0.69 (s, 3H). Anal. calcd for $C_{19}H_{21}NO$: C, 81.67; H, 7.58; N, 5.02. Found C, 81.55; H, 7.45; N, 5.13.

3.2.4. (5*S*,8*R*)-(−)-5,6,7,8-Tetrahydro-8,9,9-trimethyl-2-(2-methoxyphenyl)-5,8-methanoquinoline 27. The reaction was carried out at 140°C for 20 h using the α,β-methylene ketone **26**. Chromatographic eluent: petroleum ether/ethyl acetate=20:1; 2.38 g (24%); colorless powder of mp 106–108°C; $[\alpha]_D^{25}$=−30.6 (*c* 1.0, $CHCl_3$); ^{1}H NMR δ 7.92 (dd, 1H, J=7.5, 1.5 Hz), 7.58 (d, 1H, J=7.5 Hz), 7.34 (d, 1H, J=7.5 Hz), 7.28 (dt, 1H, J=7.5, 1.5 Hz), 7.06 (t, 1H, J=7.5 Hz), 6.95 (d, 1H, J=7.5 Hz), 3.82 (s, 3H), 2.84 (d, 1H, J=3.9 Hz), 2.16–2.06 (m, 1H), 1.85 (dt, 1H, J=3.3 Hz), 1.37 (s, 3H), 1.31–1.12 (m, 2H), 0.99 (s, 3H), 0.59 (s, 3H). Anal. calcd for $C_{20}H_{23}NO$: C, 81.86; H, 7.91; N, 4.78. Found: C, 81.78; H, 7.68; N, 4.65.

3.3. General procedure for preparation of 2-(2-hydroxyphenyl)-5,6,7,8-tetrahydroquinolines 14, 18, 23, 28

Boron tribromide (2.0 g, 8.0 mmol) was added dropwise by a syringe to a cooled (0°C) solution of 2-(2-methoxyphenyl)-5,6,7,8-tetrahydroquinolines **13**, **17**, **22**, **27** (4.0 mmol) in anhydrous CH_2Cl_2 (20 mL) under nitrogen. After stirring overnight to room temperature, water was added cautiously at 0°C. The resulting mixture was treated with 5% sodium hydroxide then neutralized with glacial acetic acid and finally extracted with CH_2Cl_2 (2×50 mL). The organic phase was dried on anhydrous Na_2SO_4 and the solvent was evaporated. The residue was purified by flash chromatography to give pure phenol derivatives **14**, **18**, **23**, **28**.

3.3.1. (5*S*,7*S*)-(+)-5,6,7,8-Tetrahydro-6,6-dimethyl-2-(2-hydroxyphenyl)-5,7-methanoquinoline 14. Chromatographic eluent: petroleum ether/ethyl acetate=40:1; 0.98 g (92%); white solid of mp 122–124°C; $[\alpha]_D^{25}$=+98.5 (*c* 0.7, $CHCl_3$); ^{1}H NMR δ 7.77 (d, 1H, J=6.9 Hz), 7.62 (d, 1H, J=8.1 Hz), 7.37 (d, 1H, J=8.1 Hz), 7.26 (m, 1H), 7.00 (d,

1H, *J*=7.8 Hz), 6.89 (t, 1H, *J*=7.8 Hz), 3.14 (d, 2H, *J*=2.7 Hz), 2.84–2.68 (m, 2H), 2.40 (m, 1H), 1.43 (s, 3H), 1.31 (d, 1H, *J*=9.6 Hz), 0.68 (s, 3H). Anal. calcd for $C_{18}H_{19}NO$: C, 81.48; H, 7.22; N, 5.28. Found: C, 81.65; H, 7.39; N, 5.15.

3.3.2. (5*R*,7*R*,8*S*)-5,6,7,8-Tetrahydro-6,6,8-trimethyl-2-(2-hydroxyphenyl)-5,7-methanoquinoline 18. Chromatographic eluent: petroleum ether/ethyl acetate=8:2; 0.95 g (85%); this compound was obtained as a distereomeric mixture of **18** (85%) and its epimer at the C_8-carbon (15%). ^{1}H NMR (major isomer) δ 7.76 (dd, 1H, *J*=9.1, 1.5 Hz), 7.60 (d, 1H, *J*=9.1 Hz), 7.34 (d, 1H, *J*=9.1 Hz), 7.29–7.23 (m, 1H), 7.01 (dd, 1H, *J*=9.1, 1.2 Hz), 6.88 (dt, 1H, *J*=9.1, 1.2 Hz), 3.23 (dq, 1H, *J*=6.9, 2.4 Hz), 2.79 (t, 1H, *J*=6.0 Hz), 2.63–2.56 (m, 1H), 2.16 (dt, 1H, *J*=6.0, 2.4 Hz), 1.43 (s, 3H), 1.41 (d, 3H, *J*=6.9 Hz), 1.32 (d, 1H, *J*=9.6 Hz), 0.66 (s, 3H). ^{1}H NMR (minor isomer) δ 7.78 (dd, 1H, *J*=9.1, 1.5 Hz), 7.62 (d, 1H, *J*=9.1 Hz), 7.36 (d, 1H, *J*=9.1 Hz), 7.29–7.23 (m, 1H), 7.01 (dd, 1H, *J*=9.1, 1.2 Hz), 6.88 (dt, 1H, *J*=9.1, 1.2 Hz), 3.23 (dq, 1H, *J*=6.9, 2.4 Hz), 2.79 (t, 1H, *J*=6.0 Hz), 2.63–2.56 (m, 1H), 2.31 (dt, 1H, *J*=6.0, 2.4 Hz), 1.53 (d, 3H, *J*=6.9 Hz), 1.43 (s, 3H), 1.32 (d, 1H, *J*=9.6 Hz), 0.71 (s, 3H). Anal. calcd for $C_{19}H_{21}NO$: C, 81.67; H, 7.58; N, 5.02. Found: C, 81.58; H, 7.66; N, 5.15.

3.3.3. (6*R*,8*R*)-(+)-5,6,7,8-Tetrahydro-7,7-dimethyl-2-(2-hydroxyphenyl)-6,8-methanoquinoline 23. Chromatographic eluent: petroleum ether/ethyl acetate=9:1; 1.0 g (95%); white solid of mp 153–154°C; $[\alpha]_D^{25}$=+48.5 (*c* 1.6, $CHCl_3$); ^{1}H NMR δ 7.77 (d, 1H, *J*=8.1 Hz), 7.70 (d, 1H, *J*=8.1 Hz), 7.36 (d, 1H, *J*=8.1 Hz), 7.26 (t, 1H, *J*=6.9 Hz), 7.00 (d, 1H, *J*=8.1 Hz), 6.88 (t, 1H, *J*=8.1 Hz), 3.01 (t, 1H, *J*=5.4 Hz), 2.98–2.90 (m, 2H), 2.78–2.72 (m, 1H), 2.42–2.32 (m, 1H), 1.44 (s, 3H), 1.34 (d, 1H, *J*=9.9 Hz), 0.69 (s, 3H). Anal. calcd for $C_{18}H_{19}NO$: C, 81.48; H, 7.22; N, 5.28. Found C, 81.56; H, 7.35; N, 5.19.

3.3.4. (5*S*,8*R*)-(−)-5,6,7,8-Tetrahydro-8,9,9-trimethyl-2-(2-hydroxyphenyl)-5,8-methanoquinoline 28. Chromatographic eluent: petroleum ether/ethyl acetate=8:2; 0.95 g (85%); white solid of mp 106–107°C; $[\alpha]_D^{25}$=−58.5 (*c* 0.8, $CHCl_3$); ^{1}H NMR δ 7.50 (d, 1H, *J*=7.8 Hz); 7.60 (d, 1H, *J*=7.8 Hz); 7.51(d, 1H, *J*=7.8 Hz); 7.25 (t, 1H, *J*=7.8 Hz); 7.00 (d, 1H, *J*=7.8 Hz); 6.87 (t, 1H, *J*=7.2 Hz); 2.87 (d, 1H, *J*=3.9 Hz); 2.20–2.09 (m, 1H); 1.95–1.87 (m, 1H); 1.36 (1, 3H); 1.26–1.14 (m, 3H); 1.00 (s, 3H); 0.58 (s, 3H). Anal. calcd for $C_{19}H_{21}NO$: C, 81.67; H, 7.58; N, 5.02. Found: C, 81.58; H, 7.66; N, 5.15.

3.4. General procedure for the preparation of 2-(2-trifluoromethanesulfonyloxy)-5,6,7,8-tetrahydro-quinolines 15, 19, 24, 29

Triflic anhydride (1.6 mL, 8.1 mmol) was added dropwise to a cooled (0°C) solution of 2-(2-hydroxyphenyl)-5,6,7,8-tetrahydroquinolines **14**, **18**, **23**, **28** (6.3 mmol) and pyridine (0.56 mL, 7.0 mmol) in anhydrous CH_2Cl_2 (8 mL) under nitrogen. The resulting solution was allowed to warm to room temperature and stirred overnight. The mixture was treated with a saturated aqueous NH_4Cl solution and extracted with CH_2Cl_2. The organic phase was washed with brine, dried on anhydrous Na_2SO_4 and the solvent was evaporated. The residue was purified by flash chromatography to give pure aryl sulfonates **15**, **19**, **24**, **29**.

3.4.1. (5*S*,7*S*)-5,6,7,8-Tetrahydro-6,6-dimethyl-2-(2-trifluoromethanesulfonyloxy)-5,7-methanoquinoline 15. Chromatographic eluent: petroleum ether/ethyl acetate=8:2; 2.45 g (98%); pale yellow oil; ^{1}H NMR δ 7.74–7.71 (m, 1H), 7.49–7.40 (m, 2H), 7.38–7.34 (m, 1H), 7.31 (d, 1H, *J*=7.8 Hz), 7.31 (d, 1H, *J*=7.8 Hz), 7.25 (d, 1H, *J*=7.8 Hz), 3.20 (d, 2H, *J*=2.7 Hz), 2.82 (t, 1H, *J*=5.7 Hz), 2.72 (dt, 1H, *J*=9.6, 5.7 Hz), 2.41–2.36 (m, 1H), 1.43 (s, 3H), 1.32 (d, 1H, *J*=9.6 Hz), 0.69 (s, 3H). Anal. calcd for $C_{19}H_{18}F_3NO_3S$: C, 57.42; H, 4.57; N, 3.53. Found: C, 57.55; H, 4.66; N, 3.44.

3.4.2. (5*R*,7*R*,8*S*)-5,6,7,8-Tetrahydro-6,6,8-trimethyl-2-(2-trifluoromethanesulfonyloxy)-5,7-methanoquinoline 19. Chromatographic eluent: petroleum ether/ethyl acetate=8:2; 2.20 g (85%); pale yellow oil; this compound was obtained as a distereomeric mixture of **19** (85%) and its epimer to the C_8-carbon (15%). ^{1}H NMR (major isomer) δ 7.80–7.50 (m, 1H), 7.49–7.41 (m, 2H), 7.38–7.35 (m, 1H), 7.30–7.24 (m, 2H), 3.29 (dq, 1H, *J*=7.2, 2.4 Hz), 2.81 (t, 1H, *J*=5.7 Hz), 2.59 (dt, 1H, *J*=9.6, 5.7 Hz), 2.18 (dt, 1H, *J*=6.0, 2.4 Hz), 1.42 (d, 3H, *J*=6.0 Hz), 1.35 (d, 1H, *J*=9.6 Hz), 0.67 (s, 3H). ^{1}H NMR (minor isomer) δ 7.80–7.50 (m, 1H), 7.49–7.41 (m, 2H), 7.38–7.35 (m, 1H), 7.30–7.24 (m, 2H), 3.29 (dq, 1H, *J*=7.2, 2.4 Hz), 2.81 (t, 1H, *J*=5.7 Hz), 2.59 (dt, 1H, *J*=9.6, 5.7 Hz), 2.18 (dt, 1H, *J*=6.0, 2.4 Hz), 1.54 (d, 3H, *J*=7.5 Hz), 1.35 (d, 1H, *J*=9.6 Hz), 0.74 (s, 3H). Anal. calcd for $C_{20}H_{20}F_3NO_3S$: C, 58.38; H, 4.90; N, 3.41. Found: C, 58.48; H, 4.67; N, 3.33.

3.4.3. (6*R*,8*R*)-5,6,7,8-Tetrahydro-7,7-dimethyl-2-(2-trifluoromethanesulfonyloxy)-6,8-methanoquinoline 24. Chromatographic eluent: petroleum ether/ethyl acetate=95:5 and then 8:2; 2.04 g (82%); pale yellow oil; ^{1}H NMR δ 7.76–7.73 (m, 1H), 7.51 (d, 1H, *J*=7.8 Hz), 7.46–7.42 (m, 2H), 7.37–7.34 (m, 2H), 3.10 (t, 1H, *J*=5.1 Hz), 3.00 (d, 2H, *J*=2.7 Hz), 2.75 (dt, 1H, *J*=9.6, 6.0 Hz), 2.37–2.33 (m, 1H), 1.43 (s, 3H), 1.34 (d, 1H, *J*=9.6 Hz), 0.70 (s, 3H). Anal. calcd for $C_{19}H_{18}F_3NO_3S$: C, 57.42; H, 4.57; N, 3.53. Found: C, 57.66; H, 4.55; N, 3.65.

3.4.4. (5*S*,8*R*)-5,6,7,8-Tetrahydro-8,9,9-trimethyl-2-(2-trifluoromethanesulfonyloxy)-5,8-methanoquinoline 29. Chromatographic eluent: petroleum ether/ethyl acetate=8:2; 2.30 g (89%); pale yellow oil; ^{1}H NMR δ 7.82–7.77 (m, 1H), 7.57 (d, 1H, *J*=7.8 Hz), 7.55–7.47 (m, 2H), 7.37–7.34 (m, 2H), 3.05 (d, 1H, *J*=3.9 Hz), 2.20–2.09 (m, 1H), 1.95–1.87 (m, 1H), 1.36 (s, 3H), 1.26–1.14 (m, 3H), 1.00 (s, 3H), 0.58 (s, 3H). Anal. calcd for $C_{20}H_{20}F_3NO_3S$: C, 58.38; H, 4.90; N, 3.41. Found: C, 58.66; H, 4.62; N, 3.56.

3.5. General procedure for the preparation of 2-(2-diphenylphosphinophenyl)-5,6,7,8-tetrahydroquinolines 9, 20, 25, 30

A mixture of $NiCl_2$(dppe) (115 mg, 0.2 mmol) and diphenylphosphine (0.103 mL, 0.596 mmol) in degassed DMF (2.5 mL) was heated at 100°C for 30 min under

argon. Then a solution of trifluoromethansulphonates **15**, **19**, **24**, **29** (2.0 mmol) and 1,4-diazabicyclo[2.2.2]octane (4.0 mmol) in degassed DMF (2.5 mL) was added by a syringe. Additional diphenylphosphine (0.311 mL, 1.74 mmol) was added and the resulting mixture was heated at 100°C until conversion was complete (about 24 h) as shown by TLC analysis [light petroleum/ethyl acetate=8:2]. After cooling the reaction mixture to room temperature, most of the DMF was removed by vacuum distillation. The residue was diluted with dichloromethane and washed successively with 5% aqueous $Na_2S_2O_3$, 10% aqueous citric acid and finally with brine. The organic phase was dried over anhydrous Na_2SO_4 and the solvent was evaporated. The residue was purified by flash chromatography to give pure 2-(2-diphenylphosphinophenyl)-5,6,7,8-tetrahydroquinolines **9**, **20**, **25**, **30**.

3.5.1. (5*S*,7*S*)-(+)-5,6,7,8-Tetrahydro-6,6-dimethyl-2-(2-diphenylphosphinophenyl)-5,7-methanoquinoline 9. Chromatographic eluent: petroleum ether/ethyl acetate=13:1; 0.173 g (20%); white solid of mp 136–138°C; $[\alpha]_D^{25}$=+59.7 (*c* 0.9, $CHCl_3$); ^{1}H NMR δ 7.60 (m, 1H), 7.40 (t, 1H, *J*=6.6 Hz), 7.32–7.22 (m, 11H), 7.18 (d, 1H, *J*=7.8 Hz), 7.11 (d, 1H, *J*=7.8 Hz), 6.70 (m, 1H), 2.84 (d, 2H, *J*=2.4 Hz), 2.69 (t, 1H, *J*=5.4 Hz), 2.62 (m, 1H), 2.28 (m, 1H), 1.36 (s, 3H), 1.23 (d, 1H, *J*=7.5 Hz), 0.55 (s, 3H). ^{31}P NMR δ −8.35. Anal. calcd for $C_{30}H_{28}NP$: C, 83.10; H, 6.31; N, 3.23. Found: C, 83.17; H, 6.25; N, 3.33.

3.5.2. (5*R*,7*R*,8*S*)-(−)-5,6,7,8-Tetrahydro-6,6,8-trimethyl-2-(2-diphenylphosphinophenyl)-5,7-methanoquino line 20. Chromatographic eluent: petroleum ether/ethyl ether=9:1; 0.286 g (32%); white solid of mp 93–95°C; $[\alpha]_D^{25}$=−6.0 (*c* 0.4, $CHCl_3$); ^{1}H NMR δ 7.62 (dq, 1H, *J*=5.2, 1.2 Hz), 7.41 (dt, 1H, *J*=8.0, 1.2 Hz), 7.32–7.22 (m, 12H), 7.20–7.12 (m, 1H), 7.04 (dq, 1H, *J*=5.2, 1.2 Hz), 2.98 (dq, 1H, *J*=5.2, 2.4 Hz), 2.70 (t, 1H, *J*=5.7 Hz), 2.52–2.45 (m, 1H), 2.05 (dt, 1H, *J*=6.0, 2.4 Hz), 1.38 (s, 3H), 1.26–1.23 (m, 1H), 0.98 (d, 3H, *J*=7.2 Hz), 0.58 (s, 3H). ^{31}P NMR δ −9.56. Anal. calcd for $C_{31}H_{30}NP$: C, 83.18; H, 6.76; N, 3.13. Found: C, 83.29; H, 6.86; N, 3.07.

3.5.3. (6*R*,8*R*)-(+)-5,6,7,8-Tetrahydro-7,7-dimethyl-2-(2-diphenylphosphinophenyl)-6,8-methanoquinoline 25. Chromatographic eluent: petroleum ether/ethyl acetate=13:1; 0.372 g (43%); white solid of mp 138–140°C; $[\alpha]_D^{25}$=+28.6 (*c* 0.9, $CHCl_3$); ^{1}H NMR δ 7.59 (dq, 1H, *J*=5.2, 1.2 Hz), 7.38 (dt, 1H, *J*=7.5, 1.2 Hz), 7.31–7.20 (m, 13H), 7.05–7.02 (m, 1H), 2.87 (d, 2H, *J*=2.4 Hz), 2.62–2.55 (m, 2H), 2.28–2.23 (m, 1H), 1.33 (s, 3H), 1.22–1.19 (m, 1H), 0.60 (s, 3H). ^{31}P NMR δ −9.74. Anal. calcd for $C_{30}H_{28}NP$: C, 83.10; H, 6.31; N, 3.23. Found C, 83.22; H, 6.42; N, 3.15.

3.5.4. (5*S*,8*R*)-(−)-5,6,7,8-Tetrahydro-8,9,9-trimethyl-2-(2-diphenylphosphinophenyl)-7,8-methanoquinoline 8. Chromatographic eluent: petroleum ether/ethyl ether=9:1; 0.170 g (19%); white solid of mp 132–136°C; $[\alpha]_D^{25}$=−22.7 (*c* 0.5, $CHCl_3$); ^{1}H NMR δ 7.60–7.57 (m, 1H), 7.39 (t, 1H, *J*=7.5 Hz), 7.31 (d, 1H, *J*=7.5 Hz), 7.26 (m, 11H), 7.16 (d, 1H, *J*=7.5 Hz), 7.02–6.98 (m, 1H), 2.78 (d, 1H, *J*=3.9 Hz), 2.09–2.02 (m, 1H), 1.77–1.69 (m, 1H), 1.22–1.04 (m, 2H), 0.91 (s, 3H), 0.87 (s, 3H), 0.45 (s, 3H). ^{31}P NMR δ −9.60. Anal. calcd for $C_{31}H_{30}NP$: C, 83.18; H, 6.76; N, 3.13. Found: C, 83.25; H, 6.65; N, 3.09.

3.6. Allylic alkylation of 1,3-diphenyl-2-propenyl acetate with dimethyl malonate: general procedure

Method A. A solution of ligand (0.04 mmol, 10 mol%) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (4 mg, 2.5 mol%) in dry CH_2Cl_2 (2 mL) was stirred at room temperature for 1 h. This solution was treated successively with a solution of *rac*-(*E*)-1,3-diphenyl-2-propenyl acetate (0.4 mmol) in CH_2Cl_2 (1 mL), dimethyl malonate (1.2 mmol), *N*,*O*-bis(trimethylsilyl)acetamide (1.2 mmol) and anhydrous potassium acetate (3.5 mol%). The reaction mixture was stirred until conversion was complete as shown by TLC analysis [light petroleum/ether=3:1]. The reaction mixture was diluted with ether (25 mL) and washed with ice-cold saturated aqueous ammonium chloride. The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash chromatography [light petroleum/ether=3:1] to afford dimethyl 1,3-diphenyl-prop-2-enyl malonate. The enantiomeric excess was determined from the ^{1}H NMR spectrum in the presence of enantiomerically pure shift reagent Eu(hfc)$_3$; splitting of the signals for one of the two methoxy groups was observed. If the right-hand peak of these two is larger, then this is typical of the (*S*)-enantiomer in excess, which was confirmed by comparing the specific rotation obtained with literature values.[18]

Method B. *Rac*-(*E*)-1,3-diphenyl-2-propenyl acetate (0.8 mmol) was added by a syringe to a solution of sodium dimethylmalonate (1.2 mmol) and 15-crown-5 (1.2 mmol) in dry acetonitrile (1.2 mL). To this solution was added a solution prepared by stirring the ligand (0.08 mmol, 10 mol%) and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (8 mg, 2.5 mol%) in dry acetonitrile (2.5 mL) at room temperature for 1 h. The reaction mixture was stirred until conversion was complete. Acid acetic was added and then the solvent removed in vacuo. The residue was diluted with ether and worked up as described in the BSA procedure.

Method C. A solution of ligand (0.08 mmol, 10 mol%) and $[\{Pd(\eta 3\text{-}C_3H_5)Cl\}_2]$ (8 mg, 2.5 mol%) in dry CH_2Cl_2 (1 mL) was stirred at room temperature for 30 min. and then a solution of *rac*-(*E*)-1,3-diphenyl-2-propenyl acetate (0.8 mmol) in CH_2Cl_2 (0.5 mL). After 5 min, a solution of dimethyl malonate (2.4 mmol), BSA (2.4 mmol) and tetrabutylammonium fluoride trihydrate (2.4 mmol) in CH_2Cl_2 (3.5 mL) was added over 1 h and stirring continued at room temperature until conversion was complete and then worked up as described in the BSA procedure.

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