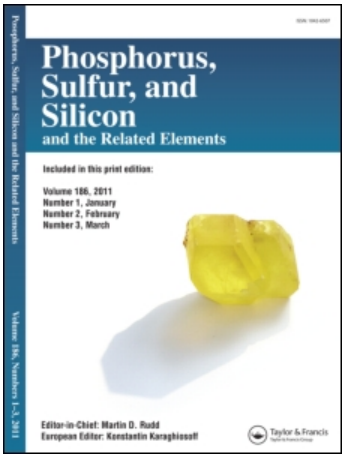

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CHIRAL DIPHOSPHOLES 4. SYNTHESIS AND NMR STUDY OF PHOSPHOLYL-BASED OPTICALLY ACTIVE DIPHOSPHINES

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CHIRAL DIPHOSPHOLES 4.† SYNTHESIS AND NMR STUDY OF PHOSPHOLYL-BASED OPTICALLY ACTIVE DIPHOSPHINES

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Chiral 1,4-diphospholes bearing 2,5-diphenylphosphol-1-yl and 3,4-dimethylphosphol-1-yl moieties are prepared and fully characterized by multinuclear NMR spectroscopy.

Key words: 1,4-Diphosphines; phospholes; diphospholes; synthesis; chirality; NMR.

INTRODUCTION

Enantioselective organometallic catalysis is making a handsome contribution to the synthesis of scalemic products of high enantiomeric purity. Considerable success and impressive results have been obtained in an increasing number of enantioselective catalytic reactions,[1] historically from the first developed hydrogenation of dehydroaminoacids[2] up to the recently reported cyclopolymerization of α,ω-diolefins.[3]

C2-symmetric chiral diphosphines have emerged as valuable and practical ligands for transition metal precursors leading to, in several cases, ideal catalytic systems, i.e. that produce a single enantiomer among two or more possible stereoisomers.[4] Most of these diphosphines contain two PPh_2 groups connected by a chiral carbon backbone, the prototype being Kagan's DIOP.[5]

The diversity of these diphosphines has expanded rapidly through variations of the chiral carbon backbone, among which are the very efficient Bosnich's CHIRAPHOS[6] or Noyori's BINAP[7] to cite a few.

A less well-studied approach, in the design of chiral diphosphines, is to keep the same chiral carbon backbone and to modify the other phosphorus substituents.[8] The replacement of one or both of the traditional PPh_2 groups by PAr_2,[9–13] dibenzophosphol-1-yl[9,14–18] or PR_2[19–22] groups has led to significant improvements of catalyst efficiency.

In this context, following our earlier work on the use of phospholes in homogeneous catalysis,[23] we recently reported the synthesis[24] and coordination chemistry[25]

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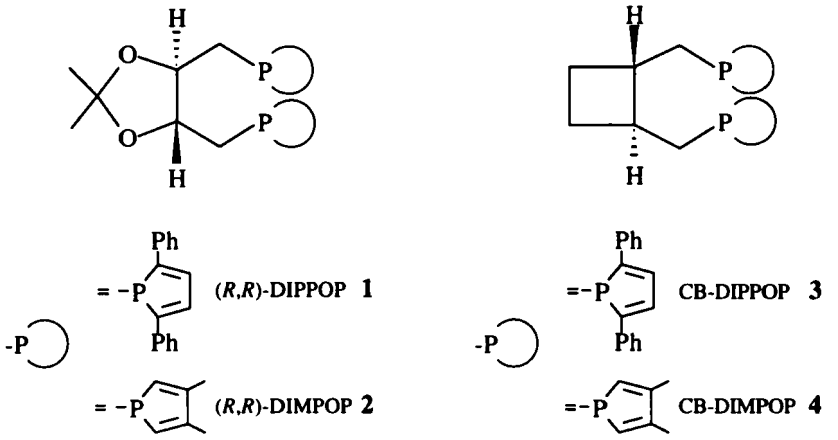


FIGURE 1 Chiral diphospholes synthesized with their acronym.

of (*R*,*R*)-DIPPOP **1** (Figure 1), the 2,5-diphenylphosphol-1-yl analog of (*R*,*R*)-DIOP and demonstrated its potential for the rhodium-catalyzed enantioselective hydrogenation of (Z)-α-acetamidocinnamic acid.[26] We now wish to describe three new chiral diphospholes, namely (*R*,*R*)-DIMPOP **2** [the 3,4-dimethylphosphol-1-yl analog of (*R*,*R*)-DIOP], (*S*,*S*)-CB-DIPPOP **3** and (*S*,*S*)-CB-DIMPOP **4** [the 2,5-diphenylphosphol-1-yl and 3,4-dimethylphosphol-1-yl analogs of (*S*,*S*)-1,2-bis(diphenylphosphinomethyl)cyclobutane (BDCB or CB-DIOP),[27] respectively] (Figure 1).

RESULTS AND DISCUSSION

The synthesis of (*R*,*R*)-DIMPOP **2** is traced from the first synthesis of (*R*,*R*)-DIOP[5] and is similar to that of (*R*,*R*)-DIPPOP **1**.[24,25] It relies on the reaction of 3,4-dimethylphospholyllithium **5** with the (*S*,*S*)-ditosylate **6** (Figure 2).

Generation of **5** was achieved, as usual, by cleavage of the exocyclic phosphorus-carbon bond of the readily available 1-phenyl-3,4-dimethylphosphole **7**[28] with lithium in THF,[29] followed by selective destruction of the concomitantly generated phenyllithium by *tert*-butyl chloride.[30] Following the reaction by $^{31}P\{^1H\}$ NMR spectroscopy, the resonance of **5** (THF solution, δ = 57.2 ppm) decreased and disappeared with the appearance of the resonance of **2** (δ = −14.7 ppm). After purification, the dextrorotatory (*R*,*R*)-DIMPOP **2** was isolated in 71% yield.

The diphospholes **3** and **4** were prepared accordingly by the reaction of the (*S*,*S*)-ditosylate **8** with 2,5-diphenylphospholyllithium **9** and 3,4-dimethylphospholyllithium **5** in situ generated from 1,2,5-triphenylphosphole **10** and from 1-phenyl-3,4-dimethylphosphole **7**, respectively (Figure 3).

The reactions were followed by $^{31}P\{^1H\}$ NMR spectroscopy: the disappearance of the resonance of the phospholyllithium **9** (δ = 86.3 ppm) or **5** (δ = 57.2 ppm) was followed by the growth of the resonance of **3** (δ = 1.4 ppm) or **4** (δ = −10.9 ppm). Dextrorotatory (*S*,*S*)-CB-DIPPOP **3** and levorotatory (*S*,*S*)-CB-DIMPOP **4** were isolated in 81 and 75% yield, respectively.

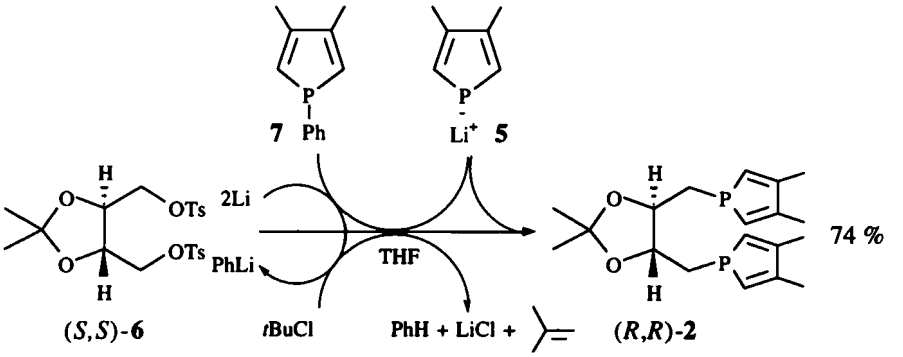


FIGURE 2 Synthesis of (*R*,*R*)-DIMPOP **2**.

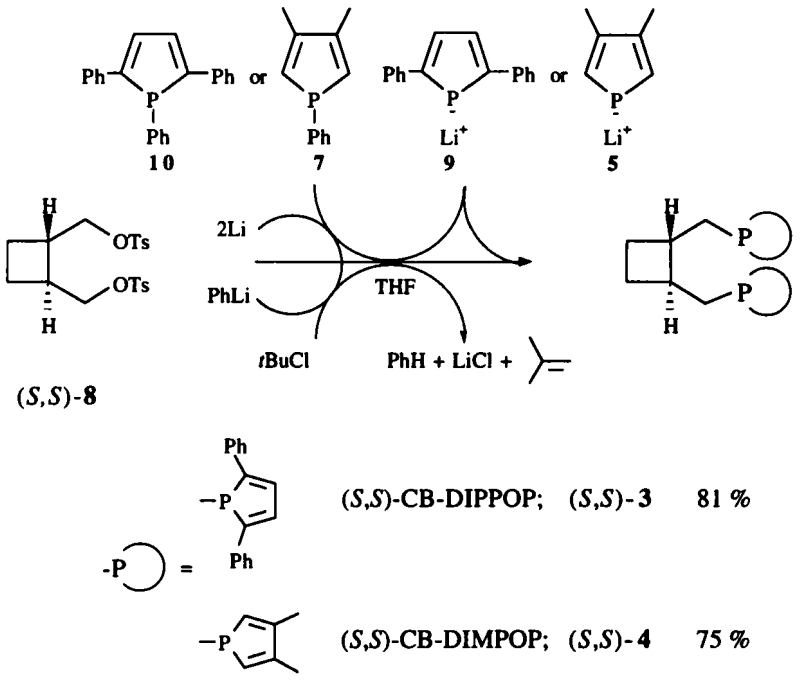


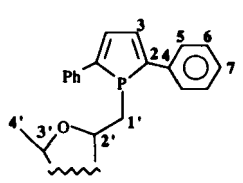
FIGURE 3 Synthesis of (*S*,*S*)-CB-DIPPOP **3** and of (*S*,*S*)-CB-DIMPOP **4**.

The synthesized diphospholes have been characterized by mass spectrometry and thoroughly studied by multinuclear NMR spectroscopy. The NMR spectra are temperature dependent, indicating that conformational changes occur in solution for **2**, **3** and **4**. A similar behaviour has been observed for **1**.

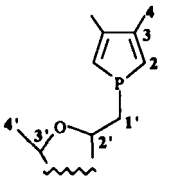
$^{31}P\{^{1}H\}$ NMR data (Table I) indicate that the chemical shifts for **1** and **3** are between those of 1,2,5-triphenylphosphole **10** (δ ^{31}P = +3.0 ppm)[31] and of 1-methyl-2,5-diphenylphosphole (δ ^{31}P = −15.5 ppm).[32] The same observation holds for the ^{31}P chemical shifts of **2** and **4** in comparison with those of **7** (δ ^{31}P = −2.5 ppm) and of 1,3,4-trimethylphosphole (δ ^{31}P = −20.2 ppm).[31] If it is possible to correlate the ^{31}P chemical shift with the ligating ability of a phosphorus compound,

TABLE I

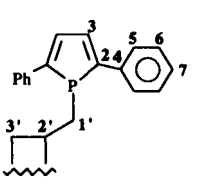
^1H and ^{31}P NMR data for **1–4**[a]



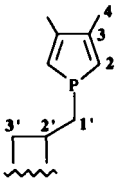
(*R,R*)-**1**



(*R,R*)-**2**



(*S,S*)-**3**



(*S,S*)-**4**

Compound	NMR $^{31}P\{^1H\}$[a]	NMR ^1H [δ (ppm) ; *J* (Hz)][a]							
	δ (ppm)	$H^{1'}$	$H^{2'}$	$H^{3'}$	$H^{4'}$	H^2	H^3	H^4	H^5-H^7
(*R,R*)-**1**	- 8.3	1.71 (m)	3.39 (m)		1.09 (s)		7.11 (d) ^3J(H-P) = 10 Hz		7.3-7.5 (m)
(*R,R*)-**2**	- 13.3	1.86 (m)	3.92 (m)		1.39 (s)	6.39 (d) ^2J(H-P) = 38 Hz		2.07 (s) 2.08 (s)	
(*S,S*)-**3**	- 0.8	0.7-2.0					n. a.[b]		6.5-8.0 (m)
(*S,S*)-**4**	- 9.0	1.3-2.0				6.33 (d) ^2J(H-P) = 38 Hz		2.05 (s) 2.06 (s)	

[a] $CDCl_3$ or CD_2Cl_2 solutions at 297 to 303 K; Bruker WM 250, at 250.13 and 101.26 MHz for ^1H and ^{31}P NMR, respectively.

[b] n.a. = not assigned, superimposed resonances.

then the diphospholes **1–4** have a donor ability between those of the corresponding phenyl- and alkyl monophospholes.

The ^1H NMR spectra are intricate and do not give information of major importance as a result of superimposed H—H and H—P couplings. It is, however, easy to recognize the 3,4-dimethylphospholyl moiety in compounds **2** and **4** since it gives rise to a characteristic doublet for the H^2 hydrogen atoms [δ = 6.30–6.40 ppm; ^2J(H—H) = 38 Hz] (Table I). In the case of **1**, decoupling the ^{31}P nucleus with simultaneous decoupling of the $H^{2'}$ hydrogen atoms allows the observation of an AB-type system for the diastereotopic $H^{1'}$ hydrogen atoms. Each $H^{1'}$ hydrogen atom couples with the $H^{2'}$ hydrogen atom with a different coupling constant [^3J(H—H) = 3 and 8 Hz]. In contrast, the corresponding $H^{1'}$ hydrogen atoms of **2** remain magnetically equivalent under the same NMR conditions.

Carbon 13 NMR spectra were less problematic. All the resonances have been assigned for the four diphospholes (Table II) on the basis of the ^{13}C, $^{13}C\{^1H\}$, $^{13}C\{^{31}P\}$ and $^{13}C\{^1H,^{31}P\}$ NMR spectra. The carbon atoms which do not belong to the chiral carbon backbone are magnetically equivalent (by pairs or by fours) and give rise to two resonances in the low temperature $^{13}C\{^1H,^{31}P\}$ NMR spectra (Table II). This observation clearly shows that the diphospholes assume a preferred conformation which allows the diastereotopic carbon atoms to be distinguished. This phenomenon is shown for diphosphole **1** in Figure 4. Interestingly, the $^{13}C\{^1H\}$ NMR spectrum at the same temperature (Figure 4) shows that the C^2 carbon atoms

TABLE II

Variable temperature ^{13}C NMR data for **1–4**[a]

	(*R,R*)-1					(*R,R*)-2					(*S,S*)-3					(*S,S*)-4				
	303 K			193 K		302 K			233 K		297 K			233 K		303 K			233 K	
	δ	|J(C-P)|	^{1}J(C-H)	δ	|J(C-P)|	δ	|J(C-P)|	^{1}J(C-H)	δ	|J(C-P)|	δ	|J(C-P)|	^{1}J(C-H)	δ	|J(C-P)|	δ	|J(C-P)|	^{1}J(C-H)	δ	|J(C-P)|
$C^{1'}$	28.7	17(d)	132(t)	26.6	17(d)	27.8	17(d)	130(t)	27.0	17(d)	31.2	17(d)	129(t)	30.7	17(d)	30.9	15(d)	131(t)	30.5	15(d)
$C^{2'}$	78.8	~0	130(d)	77.2	6(d)	80.4	8(t)	146(d)	79.6	7(t)	42.0	6(d)	136(d)	42.0	6(d)	42.5	9+5(dd)	137(d)	42.1	9+5(dd)
$C^{3'}$	109.6	~0	-	107.9	0	109.0	~0	-	108.5	0	26.8	4(d)	136(t)	26.8	4(d)	26.3	7(d)	135(t)	26.3	7(d)
$C^{4'}$	26.9	~0	126(q)	26.4	0	27.5	~0	126(q)	27.0	0										
C^2	152.0(b) 152.3(b)	~0 ~0	- -	150.6 150.7	5(d) 0	129.8 130.1	~0 ~0	167(d) 167(d)	129.1 129.4	3(d) 3(d)	151(b) 152(b)	~0 ~0	- -	149.9 151.3	0 0	129.1	3(d)	167(d)	128.4 128.6	3(d) 3(d)
C^3	132.0	~0	162(d)	130.9 132.5	7(d) 7(d)	149.0	~0	-	148.6 148.8	8(d) 8(d)	131.7(b)	~0	n.d.[b]	131.2 131.9	8(d) 8(d)	148.0	8(d)	-	147.9 148.4	7(d) 7(d)
C^4	136.7(b) 137.1(b)	17(d) 17(d)	- -	135.2 136.3	17(d) 17(d)	17.6	4(d)	126(q)	17.8	4(d)	137.1(b)	17(d)	-	136.5 136.8	17(d) 17(d)	17.6	4(d)	126(q)	17.8 17.9	4(d) 4(d)
C^5	126.6	9(d)	159(d)	125.8 125.9	9(d) 9(d)						126.3	10(d)	159(d)	126.0 126.1	10(d) 10(d)					
C^6	128.7	~0	161(d)	128.1 128.4	0 0						128.7	0	161(d)	128.6 128.7	0 0					
C^7	127.1	~0	160(d)	126.7 126.8	0 0						126.9	~0	160(d)	126.7 126.9	0 0					

[a] Bruker WM 250 at 62.89 MHz in $CDCl_3$ or CD_2Cl_2. δ, |J(C-P)|, ^{1}J(C-H) measured from the $^{13}C\{^1H,^{31}P\}$, $^{13}C\{^1H\}$ and $^{13}C\{^{31}P\}$ spectra respectively ; b = broad. [b] n.d. = not determined.

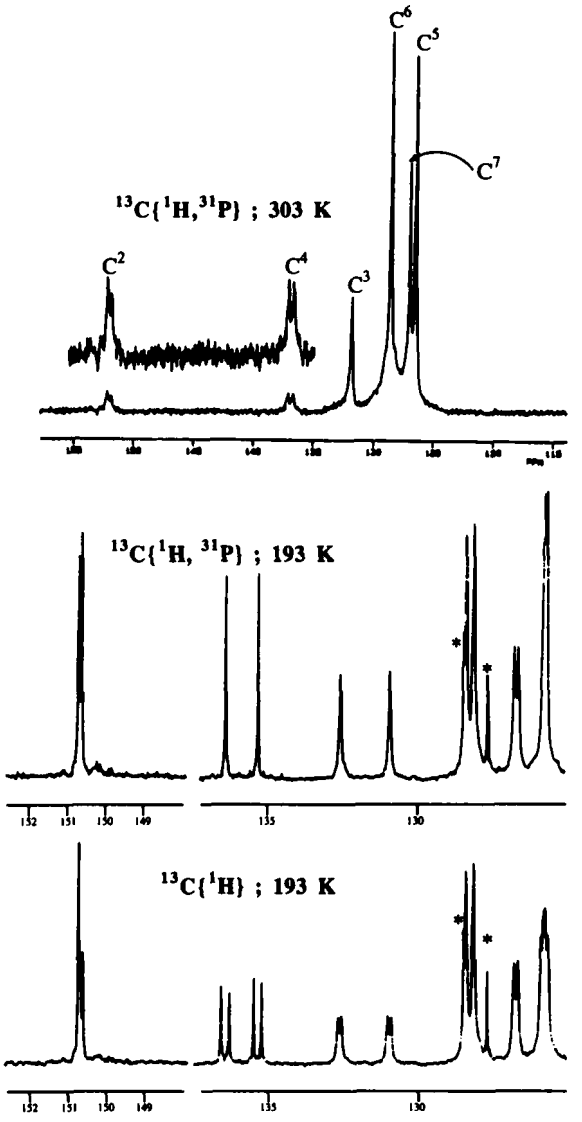


FIGURE 4 Low field portion of the carbon 13 NMR spectra of diphosphole **1** at 303 and 193 K (* denotes carbon atoms of residual toluene).

couple differently with the phosphorus nucleus (0 and 5 Hz) which means that, in each phospholyl cycle, the carbon atoms C^2 are magnetically nonequivalent. Similar observations have been made for the other diphospholes with the exception of diphosphole **2** for which C^4 carbon atoms are not distinguishable in the low temperature NMR spectrum. The dynamic behavior of **2** has also been followed by ^1H NMR spectroscopy. At 193 K, the $^1H\{^{31}P\}$ NMR spectrum with selective decoupling of the H^4 methyl hydrogen atoms exhibits an AB-type spectrum for the resonances of the H^2 hydrogen atoms (Figure 5). This result corroborates those

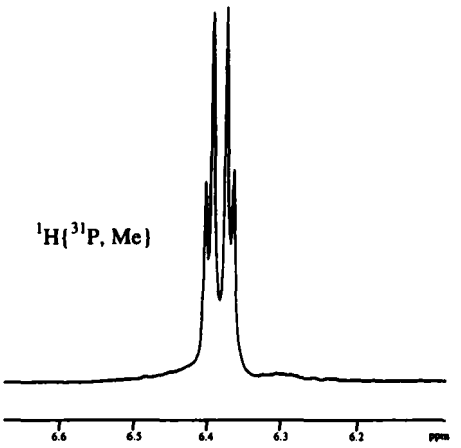


FIGURE 5 Low field portion of the proton NMR spectrum of diphosphole **2** at 193 K.

obtained by ^{13}C NMR spectroscopy and leads to the conclusion that in each phospholyl cycle, the diastereotopic H^2 hydrogen atoms couple together.

CONCLUSION

The results described here show that chiral diphospholes bearing 2,5-diphenylphosphol-1-yl or 3,4-dimethylphosphol-1-yl moieties can be prepared in good yield by a simple experimental procedure.

As 1-phenylphospholes are now widely available with various ring substitutions,[31] the present work should allow to prepare chiral diphospholes with the stereoelectronic properties required for applications in enantioselective catalysis. We are actively investigating this fascinating field.

EXPERIMENTAL

All sample manipulations were carried out under argon using standard Schlenk tube and vacuum techniques. Solvents and reagents were purified according to literature procedures[33] and stored under argon. Argon U (L'Air Liquide) was used after passage through 3-Å molecular sieves. Lithium (wires, Aldrich) was used as received. Purifications by flash chromatography[34] were made on silica gel Merck (40–60 μm). 1,2,5-triphenylphosphole **10**[35] and 1-phenyl-3,4-dimethylphosphole **7**[28] were prepared by the reported procedures. The (*S,S*)-ditosylate **6**, $[\alpha]_D^{22}$ − 12.5 (c = 6.6, $CHCl_3$), was prepared according to a slightly modified literature procedure.[24] The (*S,S*)-ditosylate **8**, $[\alpha]_D^{25}$ + 24.4 (c = 1, C_6H_6), was a generous gift from Professor D. Sinou (Villeurbanne) and from Dr. C. Mercier (Rhône Poulenc, St. Fons).

^1H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 solvents on a Bruker WM 250 spectrometer. ^1H and ^{13}C NMR chemical shifts are referenced to tetramethylsilane assigning the $CDCl_3$ resonances at 7.27 and 77.0 ppm, respectively and the CD_2Cl_2 resonances at 5.35 and 53.6 ppm, respectively. ^{31}P NMR chemical shifts are referenced to external 85% H_3PO_4 in D_2O. Mass spectrometry data were obtained on a Hewlett Packard 5970B instrument (EI, 70 eV). Optical rotations were measured on a Perkin Elmer 241 automatic polarimeter.

(2R,3R)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(3,4-dimethylphosphol-1-yl)butane, (R,R)-DIMPOP **2**. A 100-mL Schlenk flask containing a teflon-coated magnetic stirring bar was charged with 1-phenyl-3,4-dimethylphosphole **7** (940 mg, 5.00 mmol) and submitted to three vacuum-argon cycles.

Dry THF (25 mL) was syringed into the Schlenk flask and the mixture cooled to 0°C. Small cuts of lithium (88 mg, 12.50 mmol) were added and the reaction medium stirred at 10–15°C for 5 h. After filtration through celite into another Schlenk flask to remove unreacted lithium, *tert*-butyl chloride (510 mg, 5.50 mmol) was added and the filtrate stirred for 14 h. The ditosylate **6** (987 mg, 2.10 mmol) was then added and the reaction medium stirred for 30 h. Hydrolysis with a few drops of water and evaporation of THF under reduced pressure led to a residue which was dissolved in diethyl ether (30 mL) and washed with water (3 × 20 mL). Drying on Na_2SO_4 and evaporation of the solvent under reduced pressure afforded a yellow-orange oil. Flash chromatography using CH_2Cl_2 as eluent (R_f = 0.67), yielded (*R,R*)-**2** (520 mg, 71%) as a yellow oil. MS: m/z 350 (M^+). $[\alpha]_D^{20}$ + 16° (*c* = 0.2, $CHCl_3$).

(1S,2S)-1,2-bis(2,5-diphenylphosphol-1-ylmethyl)cyclobutane, (S,S)-CB-DIPPOP **3**. The same procedure was followed by using 1,2,5-triphenylphosphole **10** (780 mg, 2.50 mmol), lithium (44 mg, 6.25 mmol), *tert*-butyl chloride (255 mg, 2.75 mmol) and (*S,S*)-ditosylate **6** (445 mg, 1.10 mmol). Flash chromatography using CH_2Cl_2 as eluent (R_f = 0.60), yielded (*S,S*)-**3** (500 mg, 81%) as a yellow oil. MS: m/z 551 (M^+). $[\alpha]_D^{20}$ + 66° (*c* = 0.5, $CHCl_3$).

(1S,2S)-1,2-bis(3,4-dimethylphosphol-1-ylmethyl)cyclobutane, (S,S)-CB-DIMPOP **4**. The same procedure was followed by using 1-phenyl-3,4-dimethylphosphole **7** (880 mg, 4.70 mmol), lithium (82 mg, 11.70 mmol), *tert*-butyl chloride (515 mg, 5.51 mmol) and (*S,S*)-ditosylate **6** (833 mg, 2.00 mmol). Flash chromatography using EtOAc/*n*-hexane (1/1) as eluent (R_f = 0.60), yielded (*S,S*)-**4** (460 mg, 75%) as a yellow oil. MS: m/z 304 (M^+). $[\alpha]_D^{20}$ – 38° (*c* = 0.5, $CHCl_3$).

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