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Synthesis of Enantiopure 1-*r*-Alkyl-2-*c*,5-*t*-Diphenylphospholanes and Phospholanium Salts through Direct Alkylation of Phospholane

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Chiral enantiopure 1-alkyl-2,5-diphenylphospholanium salts were obtained in one step through alkylation of phospholane with alkyl triflates. The resulting air-stable phosphonium salts are electron-rich trialkylphosphane precursor ligands for transition metals, and they offer a convenient route toward chiral quaternary phosphonium salts as phase-transfer agents.

Introduction

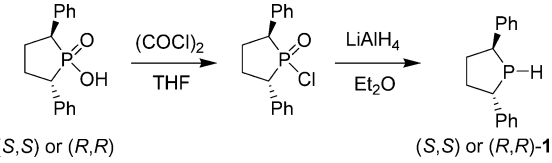
Interest in monophosphanes as ligands for transition metals but also as organic catalysts has grown recently.[1] Because organic catalysis mediated by phosphanes involves their nucleophilic properties, it appears of interest to build up new dialkylaryl- and trialkylphosphanes. The dialkyl or trialkyl substitution of the phosphorus atom provides an electron-rich and basic ligand that differs from the usual asymmetric phosphanes, which often possess two or three aryl substituents on the phosphorus atom.[2] In a previous paper, we described the preparation of enantiopure dialkylarylphosphorus compounds derived from 2,5-diphenylphospholane by catalyzed C–P cross coupling.[3] Moreover, a convenient use of air-stable phosphonium salt as ligand precursors has been described.[4] With this in mind, we attempted to find a convenient way to obtain basic and nucleophilic chiral phospholanes. Then, electron-rich 1-alkyl-2,5-diphenylphospholanes became a target of choice. However these trialkylphosphanes suffer from easy oxidation when handled in air. It was then desirable to find a convenient method for the synthesis, protection, storage, and deprotection of these air-sensitive phosphanes. So, we report here the synthesis of chiral enantiopure 1-alkyl-2,5-diphenylphospholanes via phospholanium salt derivatives through alkylation reactions by using alkyl triflate reagents.

The alkylation of a phosphorus atom to introduce an alkyl chain is one of the principal processes used to generate 1-alkylphosphanes. This process was used with success from phosphide,[5] secondary phosphane oxide,[6] secondary phosphane borane complex,[7] tris(cyanoethyl)phosphane,[8] and free secondary phosphane.[9] In the case of 2,5-*trans*-diphenylphospholane, the formation of a catalytic amount of anion could be responsible for epimerization at the benzylic position as a result of the presence of a rather acidic hydrogen atom.[10] So, the most convenient method is the alkylation of phosphane without the use of a base. Beller et al. described the direct alkylation of bis(adamantyl)phosphane with an excess amount of alkyl halides.[11] The treatment of the resulting salt with triethylamine gave the phosphane. The authors report that no alkylation occurred with mesylate or more sterically hindered electrophiles.

Results and Discussion

Although perfluoroalkylsulfonate esters are considered to be strong alkylating agents,[12] alkyl halides are the usual alkylating reagents for phosphorus atoms. To the best of our knowledge, there are only a few examples of addition reactions of alkyl triflates on phosphane.[13]

In this context, we thought enantiopure *trans*-2,5-diphenylphospholane (**1**) could be alkylated with simple electrophiles. This compound is obtained in two steps from 1-oxo-1-hydroxy-2,5-diphenylphospholanic acid (Scheme 1).[14]



Scheme 1.

In a first way, we tried to alkylate phospholane **1** in enantiopure form with methyl iodide (1 equiv.) in toluene to obtain the resulting phospholanium salt (Scheme 2). The

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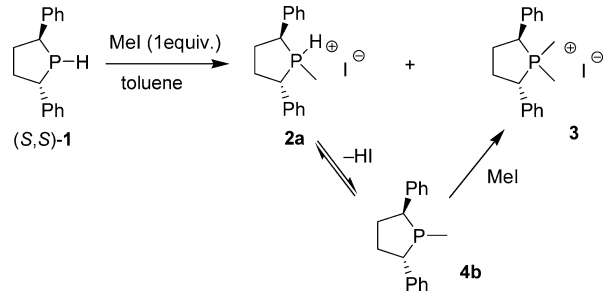
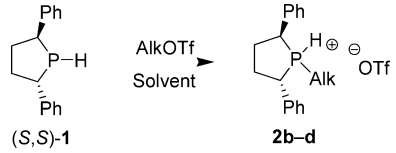
expected phospholanium salt **2a** was obtained as the major product, but it was contaminated by **1** and quaternary dimethylphospholanium salt **3**. Formation of **3** could be the result of the weak stability of **2a** under the reaction conditions. We suppose this salt presumably released free phospholane **4b** through dissociation, which could then subsequently react with methyl iodide to give the corresponding quaternary dimethylphospholanium salt **3**.



Scheme 2.

Attempts to obtain selective formation of **2a** failed. Contrary, alkylation of phospholane **1** with alkyl triflate gave a cleaner and more efficient reaction (Table 1).

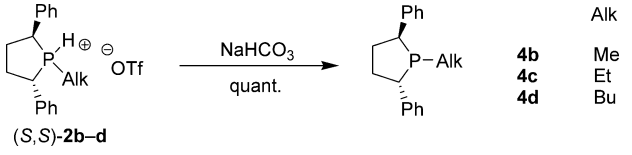
Table 1. Alkylation of phospholane **1** with alkyl triflates.



Entry	Alk	Product	Yields[a] [%]	Reaction conditions
1	Me	**2b**	84	Et_2O/25 °C
2	Et	**2c**	80	Tol./50 °C/12 h
3	Bu	**2d**	92	Tol./50 °C/72 h

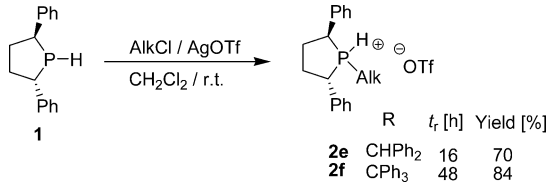
[a] Isolated yields.

Thus, the mixture of phospholane **1** and methyl triflate in ether resulted in the formation of a white precipitate corresponding to the enantiomerically pure 1-methyl-(2*S*,5*S*)-diphenylphospholanium trifluoromethanesulfonate salt (**2b**) in excellent yield (Table 1, Entry 1). Addition of ethyl and butyl triflates was more difficult and required both a higher temperature and a longer reaction time for completion (Table 1, Entries 2 and 3). Treatment of the corresponding phospholanium salt with saturated hydrogen carbonate solution gave the free 1-alkyl-2,5-diphenylphospholanes **4b**–**d** quantitatively (Scheme 3).



Scheme 3. Deprotection of phospholanium salts **2b**–**d**.

Secondary alkyl triflates are known to be unstable at moderate temperatures[15] and tertiary electrophiles could be isolated only if no elimination of triflic acid can occur[16] So, alkylation of phospholane with secondary or tertiary alkyl triflates appears to be difficult. We proposed a protocol to generate more sterically hindered triflates in situ,[17] which could react with the phosphorus center. Alkylation of (*S*,*S*)-**1** in the presence of benzhydryl or trityl chloride and silver triflate in dichloromethane gave 1-alkyl-(2*S*,5*S*)-diphenylphospholanes **2e** and **2f** in good yields (Scheme 4).

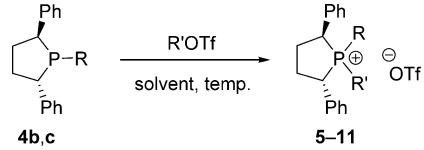


Scheme 4. Alkylation of phospholane **1** with alkyl chlorides.

The presence of small amount of dimethylphospholanium salt **3** (Scheme 1) suggests the possibility to produce quaternary chiral phospholanium salts by direct alkylation of 1-alkyl-2,5-diphenylphospholane compounds. These salts could be used as chiral phosphorus transfer agents. If chiral quaternary ammonium salts are well known as phase transfer agents,[18] the use of phosphonium salts has not been well investigated, and in all cases, the chiral part of the transfer agent is far from the cationic site.[19] With this in mind, we developed the synthesis of 1-dialkyl-2,5-diphenylphospholanium salts to be used as chiral transfer agents. The phospholane structure suggests that the cationic phosphorus atom would be near the active site and could improve the results in term of reactivity and enantioselectivity in heterogeneous catalysis.

Simple treatment of enantiopure phospholanes **4b**,**c** with appropriate alkyl triflates gave the expected quaternary phospholanium salts **5**–**11** in good yield (Table 2).

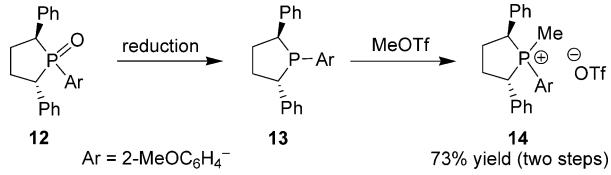
Table 2. Synthesis of chiral quaternary phospholanium salts **5**–**11**.



Entry	Product	R	R′	Solvent/ temp. [°C]	Reaction time [h]	Yield[a] [%]
1	**5**	Me	Me	Et_2O/r.t.	0.25	87
2	**6**		Et	tol./50	24	76
3	**7**		Bu	tol./60	48	86
4	**8**		Oct	tol./60	72	84
5	**6**	Et	Me	Et_2O/r.t.	0.25	88
6	**9**		Et	tol./50	24	86
7	**10**		Bu	tol./50	24	61
8	**11**		Oct	tol./50	24	45

[a] Isolated yields.

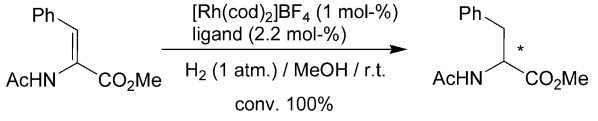
For best results, free phospholanes **4b–d** must necessarily be generated from tertiary phospholanium salts **2b–d**, as described in Scheme 3, before the alkylation step. In most cases, the alkylation proceeded smoothly in toluene at 50–60 °C, except for methyl triflate, which proceeded at room temperature in diethyl ether (Table 2, Entries 1 and 5). Also, we developed a synthesis of enantiopure 1-aryl-1-alkylphospholanium salt from phospholane **12** (Scheme 5). Phospholane **12**[3] was reduced by using the Imamoto procedure[20] to give free phosphane **13**, which was not isolated but treated with methyl triflate to give chiral quaternary phospholanium salt **14** in good yield (Scheme 5). Preliminary experiments with tertiary and quaternary phospholanium salts were conducted.



Scheme 5. Synthesis of 1-aryl-1-alkylphospholanium salt **14**.

The newly prepared chiral tertiary phosphonium salts **2b–d** were used in the asymmetric hydrogenation of methyl-(*Z*)-2-acetamidocinnamate. The catalyst was generated by mixing the rhodium precursor (1 mol-%) with phosphonium salt **2** (2.2 mol-%) without a base. Because the 2,5-diarylphospholanes proved to form very active catalytic species, most of the first tests were performed under an atmosphere of hydrogen and at room temperature (Table 3).

Table 3. Rh-catalyzed enantioselective hydrogenation of methyl (*Z*)-2-acetamidocinnamate by using (*S*,*S*)-phospholanium salt **2b–d**[a] and $[Rh(cod)_2]BF_4$ as rhodium source.

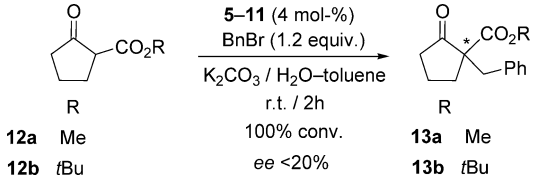


Ligand	Reaction time [h]	% *ee* (configuration)[b]
2b	0.5	34 (*S*)
2c	1	47 (*R*)
2d	1	62 (*R*)

[a] All reactions were carried out under a hydrogen atmosphere (1 atm.) at room temperature. [b] Determined by chiral HPLC analysis on a Chiralcel OD-H column, with hexane/2-propanol (9:1) as eluent.

1-Alkylphospholanium salts **2b–d** were excellent ligands in term of activity. A total conversion was obtained in all cases in less than 1 h reaction time under atmospheric pressure of hydrogen at room temperature, but with modest enantiomeric excess values. We observed an increase in enantioselectivity with the length of the alkyl chain group on the phosphorus atom. Surprisingly, there is a clear inversion of configuration of the product for small alkyl groups (Alk = Me) in comparison to larger alkyl groups (Alk = Et, Bu).

Chiral quaternary phospholanium salts **5–11** and **14** were used in asymmetric phase-transfer benzylation of alkyl-2-oxo-cyclopentanecarboxylates (Scheme 6).



Scheme 6. Phase-transfer alkylation.

In the presence of potassium carbonate as base and **5–11**, **14** (4 mol-%), benzylation of **12a** and **12b** was complete in 2 h. Unfortunately, the enantiomeric excess values did not exceed 20 %*ee* in all cases. We verified that the presence of potassium carbonate did not modify the phospholane structure. In particular, possible epimerization at the benzylic position did not occur. The nature of base is crucial for activity, as the use of potassium or sodium hydroxide instead of potassium carbonate led to decomposition of the catalyst.

Conclusions

We described an efficient and simple alkylation of *trans*-2,5-diphenylphospholane (**1**) with alkyl triflate to form directly some enantiopure tertiary phospholanium salts as a protected form of electron-rich chiral ligands. A second alkylation step of tertiary phospholanes gives a convenient route to enantiopure quaternary phospholanium salts. Studies involving chiral 1-alkyl-2,5-diphenylphospholanes bearing different alkyl groups on the phosphorus atom are in progress. We are currently exploring the use of these electron-rich chiral phosphanes as organic catalysts. The aspect of chiral quaternary phospholanium salt as a viscous paste suggests that a change in the counterion may potentially result in ionic liquids; this work is underway.

Experimental Section

General: Proton NMR spectra were recorded with Bruker 250, 360 or 400 MHz spectrometers. ^1H and ^{13}C NMR analysis of free phospholane **1** and **4b–d** were realized under argon atmosphere. Proton chemical shifts are reported in ppm relative to tetramethylsilane as internal reference (TMS, δ = 0.0 ppm). Carbon NMR spectra were recorded with Bruker 250 MHz (62.9 MHz) or 300 MHz (75.45 MHz) spectrometers with complete proton decoupling. Phosphorus NMR spectra were recorded with a 101.2 MHz spectrometer with complete proton decoupling. The corresponding chemical shifts are reported in ppm relative to the residual deuterated solvent or external phosphoric acid (H_3PO_4, δ = 0.0 ppm). Flash column chromatography was performed by using silica gel Merck (0.04–0.063 μm). Optical rotations were recorded at the sodium D line with a Perkin–Elmer 341 polarimeter. The specific rotation [*a*] is always given without the units (understood to be $cm^2\,g^{-1}$). High-resolution mass spectra were obtained with a MAT95 Thermo-Finnigan spectrometer by using electrospray or GC analysis. All reactions were carried out in Schlenk tubes under

an argon atmosphere. All solvents were distilled from appropriate drying agents prior to use. Ethyl and butyl triflates were prepared from the corresponding alcohol and triflic anhydride. All other reagents are available commercially and were used without further purification. *tert*-Butyl chloride, benhydryl chloride, silver trifluoromethanesulfonate were purchased from Acros, and methyl triflate was purchased from Fluka. The synthesis and experimental data of (2*S*,5*S*)-diphenylphospholane (**1**) were reported in our previous papers.[3,14]

(2*S*,5*S*)-(–)-1-Methyl-2,5-diphenylphospholanium Trifluoromethanesulfonate (2b): MeOTf (0.12 mL, 1.1 equiv.) was added dropwise to a solution of phospholane **1** (0.36 g, 1.5 mmol) in diethyl ether (10 mL). After 10 min at ambient temperature, the white precipitate was filtered and washed with diethyl ether. The phospholanium salt was obtained as a white powder. M.p. 110–111 °C. $[\alpha]_D^{20}$ = –6 (*c* = 0.5, THF). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.04 (dd, $^2J_{P,H}$ = 15.1, $^3J_{H,H}$ = 5.4 Hz, 3 H, PC*H*$_3$), 2.39–2.90 (m, 4 H, PCHPhC*H*$_2$), 4.14–4.31 (m, 1 H, PC*H*Ph), 4.73–4.90 (m, 1 H, PC*H*Ph), 6.68 (dm, $^1J_{P,H}$ = 499 Hz, 1 H), 7.30–7.55 (m, 10 H, C$_6$*H*$_5$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 0.88 (d, $^1J_{P,C}$ = 46 Hz, P*C*H$_3$), 32.67 [d, $^2J_{P,C}$ = 6 Hz, PCH(Ph)*C*H$_2$], 33.33 [d, $^2J_{P,C}$ = 9.2 Hz, PCH(Ph)*C*H$_2$], 39.32 (d, $^1J_{P,C}$ = 44.6 Hz, P*C*HPh), 42.98 (d, $^1J_{P,C}$ = 45.5 Hz, P*C*HPh), 121 (q, $^1J_{C,F}$ nd, OSO$_2$*C*F$_3$), 127.93 (s), 128.06 (s), 128.98 (s), 129.09 (s), 129.12 (d, $J_{P,C}$ = 2.5 Hz) 129.18 (d, $J_{P,C}$ = 2.8 Hz), 129.83 (d, $J_{P,C}$ = 2.8 Hz), 130.02 (d, $J_{P,C}$ = 2.8 Hz), 131.84 (d, $J_{P,C}$ = 5.5 Hz), 133.24 (d, $J_{P,C}$ = 4.6 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 32.3 (d, $J_{P,H}$ = 500 Hz) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –19.54 (s) ppm. LRMS (ES): *m*/*z* (%) = 269.2 [M + NH$_4$]$^+$, 255.1 (100) [M]$^+$, 121.1. HRMS (ES): calcd. for C$_{17}$H$_{20}$P$^+$ 255.1297; found 255.1301.

General Procedure for the Synthesis of 2c,d: A mixture of phospholane **1** (240 mg, 1 mmol) and alkyl triflate (1.1 mmol) was stirred at 50 °C in toluene for the appropriate time under an argon atmosphere. After removal of the solvent, diethyl ether was added. The residue was filtered and washed with diethyl ether to give salts **2c**,**d** as white solids.

(2*S*,5*S*)-(+)-1-Ethyl-2,5-diphenylphospholanium Trifluoromethanesulfonate (2c): $[\alpha]_D^{20}$ = +5.24 (*c* = 0.53, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = +0.85 (dt, $^3J_{P,H}$ = 20.7 Hz, $^2J_{H,H}$ = 7.6 Hz, 3 H, PCH$_2$C*H*$_3$), 2.04 (dm, $^2J_{P,H}$ = 66.2 Hz, $^2J_{H,H}$ = 7.6 Hz, 2 H, PC*H*$_2$CH$_3$), 2,44–2.82 (m, 4 H, PCHPhC*H*$_2$), 4.23–4.40 (m, 1 H, PC*H*Ph), 4.70–4.87 (m, 1 H, PC*H*Ph), 6.44 (dm, $^1J_{P,H}$ = 490 Hz, 1 H), 7.16–7.50 (m, 10 H, C$_6$*H*$_5$) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 6.97 (d, $^2J_{P,C}$ = 5.9 Hz, PCH$_2$*C*H$_3$), 11.09 (d, $^1J_{P,C}$ = 41.2 Hz, P*C*H$_2$CH$_3$), 32.96 [d, $^2J_{P,C}$ = 5.9 Hz, PCH(Ph)*C*H$_2$], 34.33 [d, $^2J_{P,C}$ = 8 Hz, PCH(Ph)*C*H$_2$], 39.6 (d, $^1J_{P,C}$ = 42.4 Hz, P*C*HPh), 42.2 (d, $^1J_{P,C}$ = 44.1 Hz, P*C*HPh), 120.8 (q, $^1J_{C,F}$ = 320 Hz, OSO$_2$*C*F$_3$), 127.54 (d, $J_{P,C}$ = 6.8 Hz), 128.2 (d, $J_{P,C}$ = 6.8 Hz), 128.89 (d, $J_{P,C}$ = 4.2 Hz), 129.69 (d, $J_{P,C}$ = 2.2 Hz), 129.88 (d, $J_{P,C}$ = 1.7 Hz), 130.17 (d, $J_{P,C}$ = 2.6 Hz), 131.69 (d, $J_{P,C}$ = 5.1 Hz), 133.23 (d, $J_{P,C}$ = 4.7 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 40.6 (d, $^1J_{P,H}$ = 487 Hz) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –79.53 (s) ppm. HRMS (ES): calcd. for C$_{18}$H$_{22}$P$^+$ 269.1454; found 269.1442.

(2*S*,5*S*)-(–)-1-(*n*-Butyl)-2,5-diphenylphospholanium Trifluoromethanesulfonate (2d): M.p. 132–135 °C. $[\alpha]_D^{20}$ = –8 (*c* = 1.2, CH_2Cl_2). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.59 (t, *J* = 7 Hz, 3 H), 1.0–1.26 (m, 4 H), 1.91 (m, 1 H), 2.17 (m, 1 H), 2.42–2.85 (m, 4 H), 4.38 (m, 1 H, PC*H*Ph), 4.90 (m, 1 H, PC*H*Ph), 6.55 (dm, $^1J_{P,H}$ = 488 Hz, 1 H), 7.33–7.53 (m, 10 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.93 (s), 16.59 (d, $J_{P,C}$ = 39 Hz), 23.25 (d, $J_{P,C}$ = 14 Hz), 24.62 (d, $J_{P,C}$ = 6 Hz), 33.09 (d, $J_{P,C}$ = 6 Hz), 34.43 (d, $J_{P,C}$ = 8 Hz), 39.64 (d, $^1J_{P,C}$ = 42 Hz, P*C*HPh), 42.98 (d, $^1J_{P,C}$ = 42 Hz, P*C*HPh), 121 (q, $^1J_{C,F}$ = 318 Hz, OSO$_2$*C*F$_3$), 128.27 (d, $J_{P,C}$ = 7 Hz), 128.78 (d, $J_{P,C}$ = 1 Hz), 128.81 (d, $J_{P,C}$ = 1 Hz), 128.99 (d, $J_{P,C}$ = 5 Hz), 129.62 (d, $J_{P,C}$ = 3 Hz), 129.82 (s), 131.9 (d, $J_{P,C}$ = 5 Hz), 133.35 (d, $J_{P,C}$ = 5 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 36.00 (d, $^1J_{P,H}$ = 486 Hz) ppm. HRMS (IE): calcd. for C$_{20}$H$_{26}$P$^+$ 297.1767; found 297.1724.

General Procedure for the Synthesis of 2e,f: To a Schlenk tube containing silver trifuoromethanesulfonate (250 mg, 1.05 mmol) and phospholane **1** (240 mg, 1 mmol) was added under an argon atmosphere a solution of the appropriate alkyl chloride (1.1 mmol) in dichloromethane (5 mL). The mixture was stirred for the appropriate time and filtered under an argon atmosphere. The solvent was evaporated, and the residue was washed with ether/pentane (1: 1) to give a white powder.

(2*S*,5*S*)-(+)-1-(Benzhydryl)-2,5-diphenylphospholanium Trifluoromethanesulfonate (2e): M.p. 58–60 °C. $[\alpha]_D^{20}$ = +72.5 (*c* = 1.05, CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.49–2.9 (m, 4 H), 3.89 (m, 1 H, PC*H*Ph), 4.65 (m, 1 H, PC*H*Ph), 4.97 (m, 1 H, PC*H*Ph), 6.55 (dm, $^1J_{P,H}$ = 488 Hz, 1 H), 6.91–7.44 (m, 20 H, C$_6$*H*$_5$) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 33.22 (d, $J_{P,C}$ = 6 Hz, *C*H$_2$), 34.84 (d, $J_{P,C}$ = 10 Hz, *C*H$_2$), 40.48 (d, $^1J_{P,C}$ = 37 Hz, P*C*HPh$_2$), 42.84 (d, $^1J_{P,C}$ = 5 Hz, P*C*HPh), 43.63 (d, $^1J_{P,C}$ = 11 Hz, P*C*HPh), 127.79–128.25 (m, 5 C), 128.61–129.29 (m, 9 C), 129.64 (s, 2 C), 131.51 (d, $J_{P,C}$ = 6 Hz), 132.82 (d, $J_{P,C}$ = 5 Hz), 133.11 (d, $J_{P,C}$ = 4 Hz), 133.6 (d, $J_{P,C}$ = 6 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 34.81 (d, $^1J_{P,H}$ = 468 Hz) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –78.03 (s) ppm. MS (ES): *m*/*z* (%) = 407.2 (24) [M$_{cat}$]$^+$, 320.1 (8), 295.0 (5), 279.1 (15), 257.1 (16), 215.1 (13), 168 (15), 167 (100). HRMS (IE): calcd. for C$_{29}$H$_{28}$P$^+$ 407.1929; found 407.1935.

(2*S*,5*S*)-(+)-1-Triphenylmethyl-2,5-diphenylphospholanium Trifluoromethanesulfonate (2f): M.p. 92–95 °C. $[\alpha]_D^{20}$ = +35.4 (*c* = 0.74, CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.26–2.82 (m, 4 H), 4.0 (m, 1 H, PC*H*Ph), 5.4 (m, 1 H, PC*H*Ph), 6.91–7.44 (m, 20 H), 6.79–6.88 (m, 7 H), 6.95–7.02 (m, 2 H), 7.07–7.29 (m, 16 H), 8.02 (d, $^1J_{P,H}$ = 500 Hz, 1 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 33.89 (d, $J_{P,C}$ = 6 Hz, *C*H$_2$), 34.77 (d, $J_{P,C}$ = 8 Hz, *C*H$_2$), 44.96 (d, $J_{P,C}$ = 29 Hz, P*C*HPh), 46.04 (d, $J_{P,C}$ = 38 Hz, P*C*HPh), 61.1 (d, $J_{P,C}$ = 30 Hz, P*C*HPh), 127.34 (s), 127.99 (s), 128.15 (d, $J_{P,C}$ = 3 Hz), 128.29 (d, $J_{P,C}$ = 2 Hz), 128.46 (s), 128.57–128.61 (m), 129.07 (m), 129.22 (s), 129.55 (d, $J_{P,C}$ = 5 Hz), 129.58 (s), 129.92–130.03 (m), 130.79 (d, $J_{P,C}$ = 6 Hz), 134.79 (d, $J_{P,C}$ = 5 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 41.58 (d, $^1J_{P,H}$ = 495 Hz) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –77.99 (s) ppm. MS (ES): *m*/*z* (%) = 521.2 (4), 259.1 (8), 244.1 (13), 243.1 (63.4), 229.1 (4), 228.1 (21), 216.1 (3), 215.1 (10), 166.0 (15), 165.0 (100). HRMS (IE): calcd. for C$_{35}$H$_{32}$P$^+$ 483.2242; found 483.2246.

General Procedure for the Deprotection of Phospholanium Salts 2b–d: In a Schlenk tube placed under an argon atmosphere a solution of phospholanium salts **2b**–**d** (1 mmol) in dichloromethane (10 mL) was treated with a saturated solution of $NaHCO_3$. When the effervescence stopped, the mixture was stirred vigorously under an argon atmosphere for 20 min and decanted. The organic phase was dried with sodium sulfate under an argon atmosphere, and the solvents were evaporated. Free phospholanes **4b**–**d** were obtained and stored in a glove box without purification.

(2*S*,5*S*)-(+)-1-Methyl-2,5-diphenylphospholane (4b): $[\alpha]_D^{20}$ = +142.6 (*c* = 0.70, CH_2Cl_2). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.77 (d, $^2J_{P,H}$ = 4 Hz, 3 H, PC*H*$_3$), 1.86–2.03 (m, 1 H, PCHPhC*H*$_2$), 2.22–2.45 (m, 2 H, PCHPhC*H*$_2$), 2.52–2.67 (m, 1 H, PCHPhC*H*$_2$), 3.15 (dt, *J* = 11 Hz, *J* = 7 Hz, 1 H, PC*H*Ph), 3.71 (td, *J* = 13 Hz, *J* = 6 Hz, 1 H, PC*H*Ph), 7.18–7.42 (m, 10 H) ppm. ^{13}C NMR (62.9 MHz,

$CDCl_3$): δ = 9.45 (d, $^1J_{P,C}$ = 25 Hz, PCH_3), 31.48 [d, $^2J_{P,C}$ = 5 Hz, PCH(Ph)CH_2], 37.46 [s, PCH(Ph)CH_2], 45.83 (d, $^1J_{P,C}$ = 14 Hz, PCHPh), 52.22 (d, $^1J_{P,C}$ = 14.7 Hz, PCHPh), 125.76 (d, $J_{P,C}$ = 2 Hz) 125.92 (d, $J_{P,C}$ = 2 Hz), 127.66 (d, $J_{P,C}$ = 4 Hz), 127.77 (s), 128.36 (s), 128.57 (s), 139.19 (s, C_q), 144.78 (d, $J_{P,C}$ = 16 Hz, C_q) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 0.59 ppm. LRMS (ES): *m*/*z* (%) = 255.1 (100) $[M + H]^+$, 223.1 (3), 215 (16), 207.1 (3), 155 (11), 151 (7), 131 (4), 129 (17). HRMS (IE): calcd. for $C_{17}H_{19}P$ 254.1219; found 254.1206.

(2*S*,5*S*)-1-Ethyl-2,5-diphenylphospholane (4c): ^{1}H NMR (200 MHz, CD_6D_6): δ = 0.65 (dt, $^3J_{P,H}$ = 16 Hz, $J_{H,H}$ = 8 Hz, 3 H, PCH_2CH_3), 0.92–1.05 (m, 2 H, PCH_2CH$_3$), 1.52–1.62 (m, 1 H, PCHPhCH_2), 1.74–1.86 (m, 2 H, PCHPhCH_2), 2.09–2.33 (m, 1 H, PCHPhCH_2), 2.76–2.89 (m, 1 H, PC*H*Ph), 3.38–3.54 (m, 1 H, PC*H*Ph), 7.05–7.33 (m, 10 H) ppm. ^{13}C NMR (50 MHz, CD_6D_6): δ = 10.17 (d, $^2J_{P,C}$ = 18.5 Hz, PCH$_2$CH_3), 18.62 (d, $^1J_{P,C}$ = 22.5 Hz, PCH$_2$CH$_3$), 32.16 (d, $^2J_{P,C}$ = 4 Hz, PCHPhCH$_2$), 38.19 (s, PCHPhCH$_2$), 46.64 (d, $^1J_{P,C}$ = 16.3 Hz, PCHPh), 51.16 (d, $^1J_{P,C}$ = 17.8 Hz, PCHPh), 125.96 (d, $J_{P,C}$ = 2 Hz), 126.09 (d, $J_{P,C}$ = 2 Hz), 127.89 (d, $J_{P,C}$ = 3.3 Hz), 128.49 (s), 128.6 (d, $J_{P,C}$ = 1 Hz), 128.8 (s), 139.66 (d, $J_{P,C}$ = 1.5 Hz), 145.69 (d, $J_{P,C}$ = 16.6 Hz) ppm. ^{31}P NMR (101.2 MHz, CD_6D_6): δ = 1.2 ppm. HRMS (IE): calcd. for $C_{18}H_{21}P$ 268.1375; found 268.1360.

(2*S*,5*S*)-1-Butyl-2,5-diphenylphospholane (4d): ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.69 (t, *J* = 7 Hz, 3 H), 0.78–0.88 (m, 1 H), 1.04–1.19 (m, 4 H), 1.21–1.27 (m, 1 H), 1.79–1.97 (m, 1 H), 2.17–2.4 (m, 4 H), 2.46–2.62 (m, 1 H), 3.12 (dt, *J* = 12 Hz, *J* = 7 Hz, 1 H, PC*H*Ph), 3.68 (td, *J* = 12 Hz, *J* = 6 Hz, 1 H, PC*H*Ph), 7.15–7.35 (m, 10 H) ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 13.77 (s), 24.38 (d, $J_{P,C}$ = 12 Hz), 25.32 (d, $J_{P,C}$ = 22 Hz), 28.22 (d, $J_{P,C}$ = 17 Hz), 32.15 (d, $J_{P,C}$ = 4 Hz), 37.9 (s), 46.33 (d, $^1J_{P,C}$ = 15 Hz, PCHPh), 51.1 (d, $^1J_{P,C}$ = 16 Hz, PCHPh), 125.79 (d, $J_{P,C}$ = 2 Hz), 125.86 (d, $J_{P,C}$ = 2 Hz), 127.64 (d, $J_{P,C}$ = 3 Hz), 127.95 (d, $J_{P,C}$ = 5 Hz), 128.36 (s), 128.59 (s), 139.15 (s), 145.15 (d, $J_{P,C}$ = 16.5 Hz) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 10.83 (s) ppm. MS (ES): *m*/*z* (%) = 297.1 (100) $[M + H]^+$, 241.1 (2), 215.1 (4), 155 (3), 141 (3), 137 (4), 131 (10), 129 (28). HRMS (IE): calcd. for $C_{20}H_{25}P$ 296.1688; found 296.1684.

(2*R*,5*R*)-(–)-1,1-Dimethyl-2,5-diphenylphospholanium Trifuoromethanesulfonate (5): phospholanium salt **2b** (0.8 mmol) was treated with a saturated solution of $NaHCO_3$, extracted with freshly distilled methylene chloride and dried with Na_2SO_4 under an argon atmosphere. The solvent was removed under reduced pressure. A Schlenk tube was charged with the tertiary phosphane obtained in freshly distilled diethyl ether, and then methyl triflate (90 μL, 0.8 mmol) was added at room temperature. The mixture was stirred for 15 min, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (CH_2Cl_2/MeOH, 97:3) to give the product as a viscous paste. $[\alpha]_D^{20}$ = –3.9 (*c* = 0.595, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.59 (d, $J_{P,H}$ = 14 Hz, 6 H, P-CH_3), 2.56–2.74 (m, 4 H, P-CHPh-CH_2), 4.31–4.45 (m, 2 H, P-C*H*Ph), 7.33–7.40 (m, 10 H) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 47.58 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 6.48 (d, $J_{P,C}$ = 49 Hz, PCH_3), 30.58 (d, $J_{P,C}$ = 7 Hz, PCHPhCH_2), 43.43 (d, $J_{P,C}$ = 46.5 Hz, PCHPh), 128.44 (d, $J_{P,C}$ = 18.4 Hz), 128.78 (d, $J_{P,C}$ = 61.6 Hz), 132.20 (d, $J_{P,C}$ = 5 Hz) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = 78.23 (s) ppm. HRMS (ES): calcd. for $C_{18}H_{22}P$ 269.1454; found 269.1464.

(2*R*,5*R*)-1,1-Methyl,alkyl-2,5-diphenylphospholanium Trifuoromethanesulfonate (5–8): Phospholanium salt **2b** (0.8 mmol) was treated with a saturated solution of $NaHCO_3$, extracted with freshly distilled methylene chloride, and dried with Na_2SO_4 under an atmosphere of argon. The solvent was removed under reduced pressure. A Schlenk tube was charged with the tertiary phosphane obtained in freshly distilled toluene, and alkyl triflate (0.8 mmol) was then added at room temperature. The mixture was stirred at 60 °C for the appropriate time, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (CH_2Cl_2/MeOH, 97:3) to give the product as a viscous paste.

(2*R*,5*R*)-(–)1-Methyl-1-ethyl-2,5-diphenylphospholanium Trifuoromethanesulfonate (6): $[\alpha]_D^{20}$ = –5.3 (*c* = 0.515, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.95 (dt, 3 H, *J* = 7.5 Hz, $J_{P,H}$ = 18 Hz, PCH$_2$CH_3), 1.78 (d, $J_{P,H}$ = 13 Hz, 3 H, PCH_3), 1.91–2.06 (m, 1 H), 2.30–2.47 (m, 1 H), 2.72–2.82 (m, 4 H, PCHPhCH_2), 4.51–4.67 (m, 2 H, PC*H*Ph), 7.43–7.63 (m, 10 H) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 49.17 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 3.26 (d, $J_{P,C}$ = 47 Hz, CH_3), 5.07 (d, $J_{P,C}$ = 6 Hz, CH_3), 14.73 (d, $J_{P,C}$ = 44.5 Hz, CH$_2$), 30.49 (d, $J_{P,C}$ = 6.5 Hz, CH$_2$), 31.44 (d, $J_{P,C}$ = 6.5 Hz, CH$_2$), 42.80 (d, $J_{P,C}$ = 45 Hz, PCHPh), 43.64 (d, $J_{P,C}$ = 45 Hz, PCHPh), 128.22 (d, $J_{P,C}$ = 5 Hz), 128.64 (d, $J_{P,C}$ = 3 Hz), 128.71 (d, $J_{P,C}$ = 5 Hz), 129.64 (d, $J_{P,C}$ = 3 Hz), 129.68 (d, $J_{P,C}$ = 3 Hz), 131.74 (d, $J_{P,C}$ = 5.5 Hz, C_q), 132.39 (d, $J_{P,C}$ = 7 Hz, C_q) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –78.23 ppm. (s). HRMS (ES): calcd. for $C_{19}H_{24}P$ 283.1610; found 283.1619.

(2*R*,5*R*)-(+)-1-Methyl-1-butyl-2,5-diphenylphospholanium Trifuoromethanesulfonate (7): $[\alpha]_D^{20}$ = +12.6 (*c* = 0.975, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.68 (t, *J* = 7 Hz, 3 H), 1.05–1.27 (m, 4 H), 1.62 (d, $J_{P,H}$ = 13 Hz, 3 H, PCH_3), 1.76–1.92 (m, 1 H), 2.06–2.23 (m, 1 H), 2.54–2.70 (m, 4 H, PCHPhCH_2), 4.36–4.54 (m, 2 H, PC*H*Ph), 7.29–7.51 (m, 10 H) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 50.72 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 3.84 (d, $J_{P,C}$ = 47 Hz, PCH_3), 13.05 (s, CH_3), 20.39 (d, $J_{P,C}$ = 43 Hz, CH$_2$), 22.92 (d, $J_{P,C}$ = 6 Hz, CH$_2$), 23.60 (d, $J_{P,C}$ = 15 Hz, CH$_2$), 43.00 (d, $J_{P,C}$ = 45 Hz, PCHPh), 43.76 (d, $J_{P,C}$ = 45 Hz, PCHPh), 128.27–128.74 (m), 129.57 (s), 132.06 (d, $J_{P,C}$ = 5.5 Hz, C_q), 132.44 (d, $J_{P,C}$ = 5.5 Hz, C_q) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –78.17 ppm. (s). HRMS (ES): calcd. for $C_{21}H_{28}P$ 311.1923; found 311.1925.

(2*R*,5*R*)-(+)-1-Methyl-1-octyl-2,5-diphenylphospholanium Trifuoromethanesulfonate (8): $[\alpha]_D^{20}$ = +15.6 (*c* = 1.075, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.84 (t, *J* = 7 Hz, 3 H), 1.11–1.24 (m, 12 H), 1.62 (d, $J_{P,H}$ = 13 Hz, 3 H, PCHPhCH_3), 1.77–1.93 (m, 1 H), 2.06–2.22 (m, 1 H), 2.54–2.69 (m, 4 H, PCHPhCH_2), 4.38–4.53 (m, 2 H, PC*H*Ph), 7.29–7.51 (m, 10 H) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 47.41 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 3.84 (d, $J_{P,C}$ = 47 Hz, PCH_3), 14.00 (s, CH_3), 20.70 (d, $J_{P,C}$ = 40 Hz, CH$_2$), 21.08 (d, $J_{P,C}$ = 3 Hz, CH$_2$), 22.50 (s, CH$_2$), 28.63 (s, CH$_2$), 28.67 (s, CH$_2$), 30.69 (d, $J_{P,C}$ = 7 Hz, PCHPhCH$_2$), 31.33 (d, $J_{P,C}$ = 7 Hz, PCHPhCH$_2$), 31.50 (s, CH$_2$), 43.03 (d, $J_{P,C}$ = 44 Hz, PCHPh), 43.74 (d, $J_{P,C}$ = 44 Hz, PCHPh), 128.34 (d, $J_{P,C}$ = 5 Hz), 128.52 (d, $J_{P,C}$ = 2 Hz), 128.60 (d, $J_{P,C}$ = 3 Hz), 128.72 (d, $J_{P,C}$ = 5.5 Hz), 129.55 (d, $J_{P,C}$ = 2 Hz), 129.59 (d, $J_{P,C}$ = 3 Hz), 132.13 (d, $J_{P,C}$ = 5.5 Hz, C_q), 132.45 (d, $J_{P,C}$ = 5.5 Hz, C_q) ppm. ^{19}FNMR (235 MHz, $CDCl_3$): δ = –78.14 ppm. (s). HRMS (ES): calcd. for $C_{25}H_{36}P$ 367.2549; found 367.2540.

(2*R*,5*R*)-1-Ethyl-1-methyl-2,5-diphenylphospholanium Trifuoromethanesulfonate (6): Phospholanium salt **2c** (0.24 mmol) was treated with a saturated solution of $NaHCO_3$, extracted with freshly distilled methylene chloride, and dried with Na_2SO_4 under an atmosphere of argon. The solvent was removed under reduced pressure. A Schlenk tube was charged with tertiary phosphane **4c** in freshly distilled diethyl ether, and methyl triflate (33 μL, 0.29 mmol) was then added at room temperature. The mixture was stirred at room

temperature for 15 min, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (CH_2Cl_2/MeOH, 97:3) to give the product as a viscous paste.

(2*S*,5*S*)-1-Ethyl-1-alkyl-2,5-diphenylphospholanium Trifuoromethanesulfonate (9–11): Phospholanium salt **2c** (0.24 mmol) was treated with a saturated solution of $NaHCO_3$, extracted with freshly distilled methylene chloride, and dried with Na_2SO_4 under an atmosphere of argon. The solvent was removed under reduced pressure. A Schlenk tube was charged with the tertiary phosphane in freshly distilled toluene, and alkyl triflate (0.29 mmol) was then added at room temperature. The mixture was stirred at 60 °C for the appropriate time, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (CH_2Cl_2/MeOH, 97:3) to give the product as a viscous paste.

(2*S*,5*S*)-(+)-1,1-Diethyl-2,5-diphenylphospholanium Trifuoromethanesulfonate (9): $[a]_D^{20}$ = +17 (*c* = 0.575, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.68–0.81 (dt, $J_{P,C}$ = 17.6 Hz, *J* = 7.5 Hz, 6 H, C*H*$_3$), 1.75–1.90 (m, 2 H), 2.25–2.39 (m, 2 H), 2.48–2.56 (m, 4 H), 4.39–4.54 (m, 2 H, PC*H*Ph), 7.24–7.44 (m, 10 H) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 49.72 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 5.07 (d, $J_{P,C}$ = 6.4 Hz, *C*H$_3$), 12.1 (d, $J_{P,C}$ = 42 Hz, *C*H$_2$), 31.5 (d, $J_{P,C}$ = 6 Hz, *C*H$_2$), 43.04 (d, $J_{P,C}$ = 43 Hz, P*C*HPh), 128.5 (d, $J_{P,C}$ = 2.7 Hz), 128.7 (d, $J_{P,C}$ = 5 Hz), 129.5 (d, $J_{P,C}$ = 2.2 Hz), 132.3 (d, $J_{P,C}$ = 5 Hz, C_q) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –78.23 (s) ppm. HRMS (ES): calcd. for $C_{20}H_{26}P$ 297.1762; found 297.17627.

(2*S*,5*S*)-(–)-1-Ethyl-1-butyl-2,5-diphenylphospholanium Trifuoromethanesulfonate (10): $[a]_D^{20}$ = –3.3 (*c* = 0.700, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.61–0.79 (m, 6 H), 1.06–1.23 (m, 4 H), 1.75–1.92 (m, 4 H), 2.13–2.37 (m, 2 H), 2.48–2.56 (m, 4 H, PCHPhC*H*$_2$), 4.33–4.40 (m, 2 H, PC*H*Ph), 7.19–7.44 (m, 10 H) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 48.22 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 5.17 (d, $J_{P,C}$ = 6 Hz, *C*H$_3$), 12.66 (d, $J_{P,C}$ = 43 Hz, P*C*H$_2$), 13.11 (s, *C*H$_3$), 17.9 (d, $J_{P,C}$ = 41 Hz, P,CH$_2$), 22.85 (d, $J_{P,C}$ = 5.5 Hz, *C*H$_2$), 23.7 (d, $J_{P,C}$ = 14.5 Hz, *C*H$_2$), 31.39 (d, $J_{P,C}$ = 5 Hz, *C*H$_2$), 31.56 (d, $J_{P,C}$ = 5.5 Hz, *C*H$_2$), 43.04 (d, $J_{P,C}$ = 43 Hz, P*C*HPh), 128.53 (d, $J_{P,C}$ = 2.7 Hz), 128.67 (d, $J_{P,C}$ = 2.7 Hz), 128.74 (d, $J_{P,C}$ = 2.7 Hz), 129.52 (sl), 132.42 (d, $J_{P,C}$ = 5 Hz, C_q), 132.62 (d, $J_{P,C}$ = 5 Hz, C_q) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –78.17 ppm. (s). HRMS (ES): calcd. for $C_{22}H_{30}P$ 325.2080; found 325.20841.

(2*S*,5*S*)-(–)-1-Ethyl-1-octyl-2,5-diphenylphospholanium Trifuoromethanesulfonate (11): $[a]_D^{20}$ = –4.6 (*c* = 0.735, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.73–0.87 (m, 6 H), 1.10–1.23 (m, 12 H), 1.87–2.01 (m, 2 H), 2.21–2.44 (m, 2 H), 2.55–2.63 (m, 4 H, PCHPhC*H*$_2$), 4.39–4.41 (m, 2 H, PC*H*Ph), 7.30–7.47 (m, 10 H) ppm. ^{31}P NMR (101.2 MHz, $CDCl_3$): δ = 46.23 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 5.19 (d, $J_{P,C}$ = 6.5 Hz, *C*H$_3$), 12.70 (d, $J_{P,C}$ = 43 Hz, P*C*H$_2$), 14.00 (s, *C*H$_2$), 18.31 (d, $J_{P,C}$ = 40 Hz, *C*H$_2$), 20.99 (d, $J_{P,C}$ = 6 Hz, *C*H$_2$), 22.51 (s, *C*H$_2$), 28.69 (d, $J_{P,C}$ = 2.7 Hz, *C*H$_2$), 29.70 (s, *C*H$_2$), 30.53 (s, *C*H$_2$), 31.50 (s, *C*H$_2$), 31.53 (s, *C*H$_2$), 43.30 (d, $J_{P,C}$ = 7.5 Hz, P*C*HPh), 43.30 (d, $J_{P,C}$ = 7.5 Hz, P*C*HPh) 128.55 (d, $J_{P,C}$ = 2.7 Hz), 128.65 (d, $J_{P,C}$ = 2.2 Hz), 128.73 (d, $J_{P,C}$ = 2.2 Hz), 129.58 (s), 132.35 (dd, $J_{P,C}$ = 5 Hz, C_q), 132.60 (dd, $J_{P,C}$ = 5 Hz, C_q) ppm. ^{19}F NMR (235 MHz, $CDCl_3$): δ = –78.17 ppm. (s). HRMS (ES): calcd. for $C_{26}H_{38}P$ 381.2706; found 381.27159.

(2*R*,5*R*)-(+)-1-(*o*-Anisyl)-1-methyl-2,5-diphenylphospholanium Trifluoromethanesulfonate (14): To a solution of (2*R*,5*R*)-1-oxo-1-(*o*-anisyl)-2,5-diphenylphospholane (1 mmol) in DME (10 mL) was added methyl trifluoromethanesulfonate (1.1 mmol) under an atmosphere of argon. After 2 h, the mixture was cooled down to 0 °C and lithium aluminium hydride (1.5 mmol) was added. The mixture was warmed to room temperature and stirred for an additional 15 h. After hydrolysis with a minimum amount of water, the mixture was filtered under an argon atmosphere through Celite by cannula, and the solvent was evaporated. The tertiary phosphane obtained was diluted in dry toluene (5 mL) and methyl trifluoromethanesulfonate (1.2 mmol) was added. The mixture was stirring at room temperature overnight. Evaporation of the solvent gave a residue, which was purified by flash column chromatography (CH_2Cl_2/MeOH, 97:3) to give salt **14** as a viscous paste. $[a]_D^{20}$ = +90.8 (*c* = 1.225, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.98 (d, $J_{P,H}$ = 13.3 Hz, 3 H, PC*H*$_3$), 2.41–2.93 (m, 4 H), 3.45 (s, 3 H, OC*H*$_3$), 4.59–4.83 (m, 2 H), 6.70–7.75 (m, 14 H) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = 45.59 ppm. ^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 6.29 (d, $J_{P,C}$ = 53 Hz, P*C*H$_3$), 29.37 (d, $J_{P,C}$ = 8.75 Hz), 31.74 (d, $J_{P,C}$ = 6.5 Hz), 41.36 (d, $J_{P,C}$ = 47 Hz, P*C*HPh), 45.37 (d, $J_{P,C}$ = 47 Hz, P*C*HPh), 55.72 (s), 104.23 (d, $J_{P,C}$ = 77 Hz), 111.54 (d, $J_{P,C}$ = 6.9 Hz), 122.33 (d, $J_{P,C}$ = 12 Hz), 127.57 (t, $J_{P,C}$ = 6, $J_{P,C}$ = 2.3 Hz), 128.35 (d, $J_{P,C}$ = 2.3 Hz), 128.4 (s), 128.5 (d, $J_{P,C}$ = 3.2 Hz),129.40 (d, $J_{P,C}$ = 3 Hz), 131.61 (d, $J_{P,C}$ = 4.5 Hz), 133.49 (d, $J_{P,C}$ = 5.5 Hz), 133.80 (d, $J_{P,C}$ = 6.5 Hz), 137.54 (d, $J_{P,C}$ = 2 Hz), 161.14 (d, $J_{P,C}$ = 1.8 Hz) ppm. HRMS (ES): calcd. for $C_{24}H_{26}OP$ 361.1716; found 361.1716.

Supporting Information (see footnote on the first page of this article): Spectroscopic data for all compounds.

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