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Efficient Synthesis of 4-Halo-2,5-dihydro-1,2-oxaphosphole 2-Oxides from 1,2-Allenylphosphonates and CuX_2 and Subsequent Suzuki Cross-Coupling of the C–Cl Bonds

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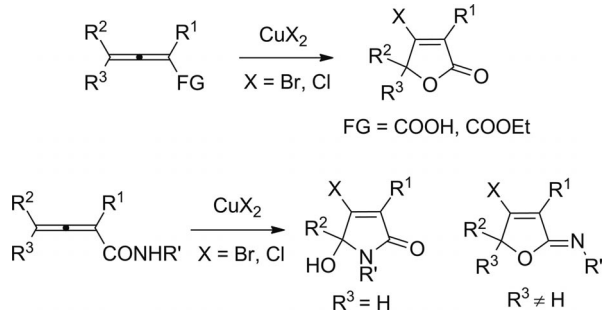
Keywords: Synthetic methods / Cyclization / Cross-coupling / Chirality / Allenes / Phosphorous heterocycles

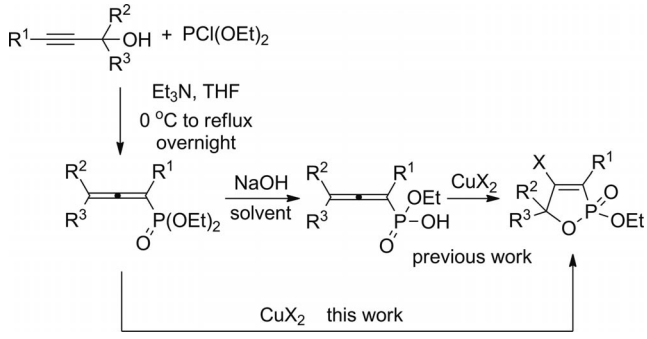
A convenient and efficient synthesis of 4-halo-2,5-dihydro-1,2-oxaphosphole 2-oxides through CuX_2-mediated direct halocyclization of diethyl 1,2-allenylphosphonates was developed. The yields range from moderate to excellent. The efficiency of axial-to-central chirality transfer has also been studied. Further Suzuki cross-coupling of the resulting vinylic chlorides with dicyclohexyl(2,4,6-trimethoxyphenyl)-phosphane (LB-Phos) as the ligand, was established.

Introduction

Many phosphorus-containing compounds may be considered as potential insecticides, bactericides, fungicides, and antibiotic reagents, because of their biological activities,[1] and such compounds exist widely in nature.[2] In recent decades, a number of groups have studied the synthesis and transformations of allenylphosphonates,[3–6] such as palladium-catalyzed coupling reactions with 2-iodophenols, 2-iodobenzoic acids and 2-iodobenzyl alcohols,[3] cycloaddition reactions,[4] selenochlorination with PhSeCl,[5] and halocyclizations.[6] Several observations have already been disclosed on the halocyclization of allenylphosphonates with relatively active electrophiles such as bromine, sulfenyl- and selenenylbromides, and mercuric acetate.[7] In the bromolactonization reactions, bromine was predominantly used to produce bromine-containing oxaphospholene structures. Previously, we have observed that the nontoxic and mild CuX_2 could serve as an efficient halogenation reagent with easier manipulation and better functional group tolerance in the cyclization of functionalized allenes, such as 2,3-allenoic acids,[8] 2,3-allenamides,[9] and 2,3-allenoates[10] (Scheme 1). Recently, we have developed the halocyclization of monoesters of 1,2-allenylphosphonic acids giving 4-halo-2,5-dihydro-1,2-oxaphosphole 2-oxides in good yields, in which the monoesters were prepared in an extra step involving hydrolysis from diethers with excess NaOH in H_2O.[11] Herein, we present our recent results on direct chloro/bromo-lactonization of 1,2-allenylphosphonates with CuX_2 (Scheme 2) and Suzuki coupling of the corresponding cyclic chlorides with dicyclohexyl(2,4,6-trimethoxyphenyl)phosphane (LB-Phos), which was developed in our group, as the ligand.[12]



Scheme 1. Halocyclization of functionalized allenes with CuX_2.



Scheme 2. Halolactonization of monoesters of 1,2-allenylphosphonic acids and 1,2-allenylphosphonates.

Results and Discussion

1,2-Allenylphosphonates were prepared through intermolecular Claisen rearrangement of propargylic alcohols

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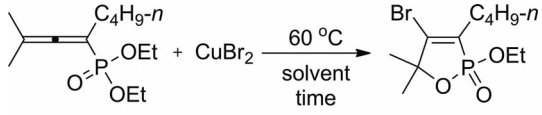
and $P(OEt)_2Cl$.[13] We used diethyl (2-methylocta-2,3-dien-4-yl)phosphonate (**1a**) as the substrate to screen a series of different reaction conditions for the bromocyclization reaction. The desired product was afforded in 82% yield when **1a** was treated with 4.0 equiv. $CuBr_2$ at 60 °C in *N*,*N*-dimethylformamide (DMF), which was observed to be the best conditions for the halocyclization of monoesters of 1,2-allenylphosphonic acids[11] (Table 1, entry 1). A variety of solvents such as toluene, acetonitrile, dichloromethane, ethanol, and tetrahydrofuran (THF) were tested: ethanol gave the best result, whereas THF gave the product **2a** with some inseparable impurities (Table 1, entries 2–8). Increasing or reducing the amount of $CuBr_2$ only slightly changed the yields (Table 1, entries 9–11). Finally, it was observed that the best result was obtained when the reaction was conducted with 2.2 equiv. $CuBr_2$ in EtOH at 60 °C (Table 1, entry 10).

Table 1. $CuBr_2$-mediated bromocyclization reaction of **1a**.[a]



1a **2a**

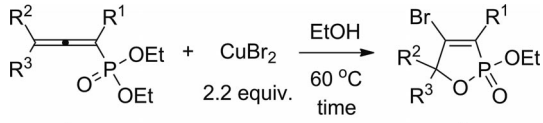
Entry	$CuBr_2$ [equiv.]	Solvent	Time [h]	Yield of **2a** [%][b]
1	4.0	DMF	1	82
2	4.0	*i*PrOH	2	76
3	4.0	PrOH	2	60
4	4.0	EtOH	2	86
5	4.0	CH_2Cl_2	1	76
6	4.0	THF	1	94[c]
7	4.0	MeCN	2	64
8	4.0	toluene	1	55
9	1.5	EtOH	13	89
10	2.2	EtOH	1	91
11	3.0	EtOH	1	86

[a] The substrate **1a** (0.3 mmol) and $CuBr_2$ were dissolved in solvent (2 mL) and the resulting mixture was heated at 60 °C. [b] Isolated yield. [c] The product was contaminated with some inseparable impurities with a purity of ca. 90%.

With the optimized reaction conditions in hand, a range of substituted substrates were examined and the reaction was found to proceed smoothly to give 4-bromo-2,5-dihydro-1,2-oxaphosphole 2-oxides **2** in moderate to good yields, indicating a broad substrate scope; R^1 could be allyl, alkyl, or phenyl groups whereas R^2 and R^3 could be alkyl groups (Table 2, entries 1–11).

Chlorides are a better potential halide source with respect to atom economy and safety. With the commercially available $CuCl_2{\cdot}2H_2O$, the results of chlorocyclization under different reaction conditions are summarized in Table 3. In contrast to the results obtained in the former case, the reaction in toluene with 3.0 equiv. $CuCl_2{\cdot}2H_2O$ led to the best result, considering the loading of each reagent (Table 3, entry 6). The use of higher or lower temperatures gave inferior results (Table 3, entries 8 and 9). It should be noted that electrophilic cyclization reactions with other typical cyclization reagents (e.g., Cl_2 or NCS), are not very convenient.[14]

Table 2. $CuBr_2$-mediated bromocyclization reaction of 1,2-allenylphosphonates.[a]

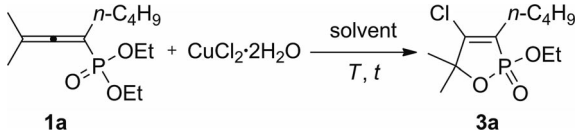


1 **2**

Entry	R^1	R^2	R^3	Time [h]	Yield of **2** [%][b]
1	*n*Bu	Me	Me (**1a**)	1	91 (**2a**)
2	Ph	Me	Me (**1b**)	3	69 (**2b**)
3	allyl	Me	Me (**1c**)	1	75 (**2c**)
4	2-methylallyl	Me	Me (**1d**)	1	77 (**2d**)
5	2-chloroallyl	Me	Me (**1e**)	1	79 (**2e**)
6	*n*Bu	–$(CH_2)_5$– (**1f**)		1	88 (**2f**)
7	*n*Bu	–$(CH_2)_4$– (**1g**)		1	91 (**2g**)
8	Ph	–$(CH_2)_5$– (**1h**)		3	85 (**2h**)
9	Ph	–$(CH_2)_4$– (**1i**)		3	72 (**2i**)
10	Ph	Et	Et (**1j**)	3	81 (**2j**)
11	*n*Bu	*n*Pr	*n*Pr (**1k**)	5	85 (**2k**)

[a] Reagents and conditions: **1** (0.3 mmol), $CuBr_2$ (0.66 mmol), EtOH (2 mL), 60 °C. [b] Isolated yield.

Table 3. $CuCl_2{\cdot}2H_2O$-mediated chlorocyclization reaction of **1a**.[a]



1a **3a**

Entry	$CuCl_2{\cdot}2H_2O$ [equiv.]	Solvent	Time [h]	*T* [°C]	Yield of **3a** [%][b]
1	4.0	CH_2Cl_2	4	70	83
2	4.0	EtOH	8	70	84
3	4.0	toluene	2	70	86
4	4.0	MeCN	1	70	76
5	4.0	THF	4	70	81
6	3.0	toluene	5	70	87
7	2.2	toluene	5	70	84
8	3.0	toluene	4	80	78
9	3.0	toluene	7	60	84

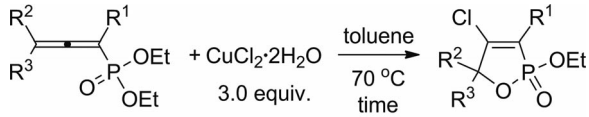
[a] Reagents and conditions: **1a** (0.3 mmol), $CuCl_2{\cdot}2H_2O$, solvent (2 mL). [b] Isolated yield.

Moderate to excellent yields were observed in the $CuCl_2{\cdot}2H_2O$-mediated chlorocyclization reaction, although longer reaction times were necessary (Table 4, entries 1–8).

When R^2 and R^3 were not the same, as expected, a mixture of diastereoisomers were obtained in the presence of 4.0 equiv. $CuCl_2{\cdot}2H_2O$ under otherwise identical conditions (Scheme 3). The relative configuration of the two isomers was unambiguously confirmed by an X-ray diffraction study of *cis*-**3k** (Figure 1).[15]

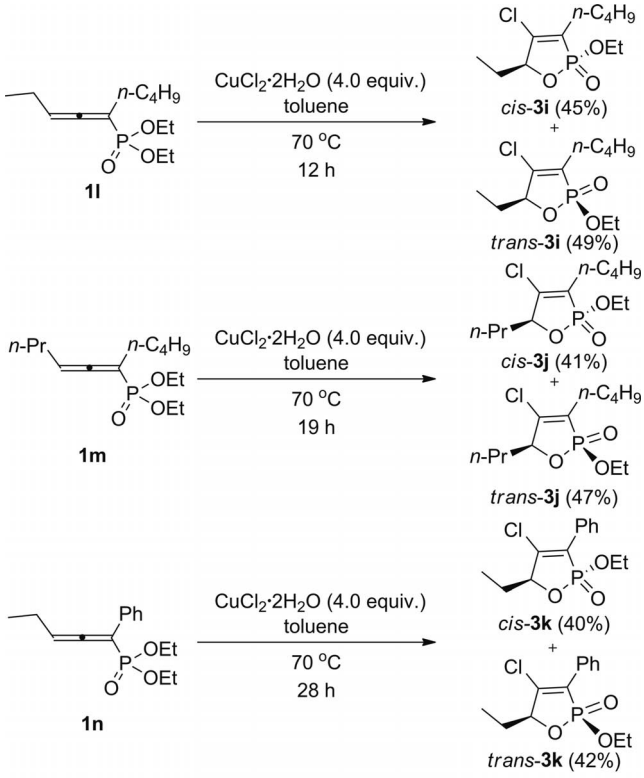
Furthermore, optically active substrate (S_a)-(–)-**1n** was synthesized from optically active (*S*)-1-phenylpenta-1-yn-3-ol according to a known procedure.[16] Under the standard conditions, the reaction afforded a mixture of (*S*,*S*)-**3k** and (*S*,*R*)-**3k** (Scheme 4) and the absolute configurations in (*S*,*S*)-**3k** were unambiguously established by an X-ray diffraction analysis,[17] indicating the efficient transformation

Table 4. $CuCl_2·2H_2O$-mediated chlorocyclization reaction of 1,2-allenylphosphonates.[a]



Entry	R^1	R^2	R^3	Time [h]	Yield [%][b]
1	*n*Bu	Me	Me (**1a**)	5	85 (**3a**)
2	Ph	Me	Me (**1b**)	24	97 (**3b**)
3	allyl	Me	Me (**1c**)	22.5	68 (**3c**)
4	2-methyl-allyl	Me	Me (**1d**)	22.5	87 (**3d**)
5	*n*Bu	–$(CH_2)_5$– (**1f**)		5	82 (**3e**)
6	*n*Bu	–$(CH_2)_4$– (**1g**)		5	72 (**3f**)
7	Ph	–$(CH_2)_5$– (**1h**)		7	90 (**3g**)
8	Ph	–$(CH_2)_4$– (**1i**)		7	83 (**3h**)

[a] Reagents and conditions: **1** (0.3 mmol), $CuCl_2·2H_2O$ (0.9 mmol), toluene (2 mL), 70 °C. [b] Isolated yield.



Scheme 3. Chlorocyclization reaction of 1,2-allenylphosphonates.

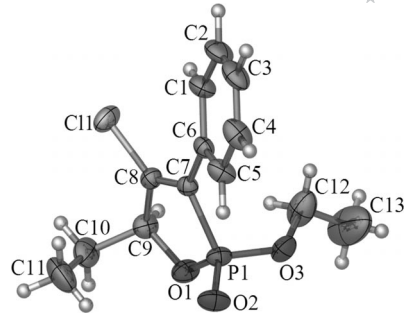
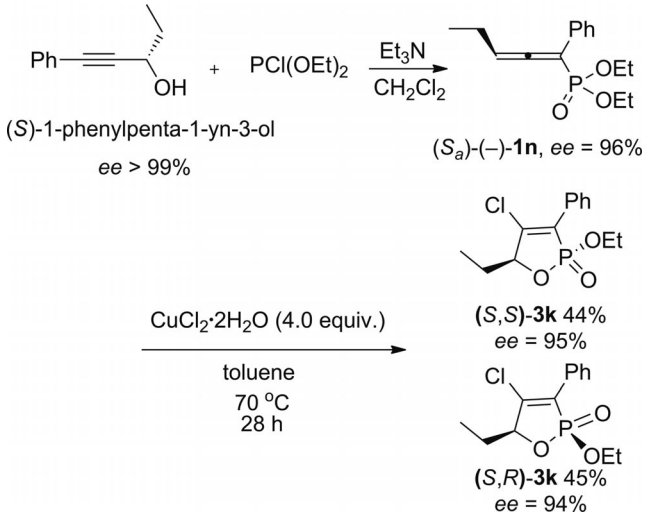


Figure 1. ORTEP representation of *cis*-**3k**.



Scheme 4. Synthesis and cyclization of optically active 1,2-allenylphosphonate (S_a)-(–)-**1n**.

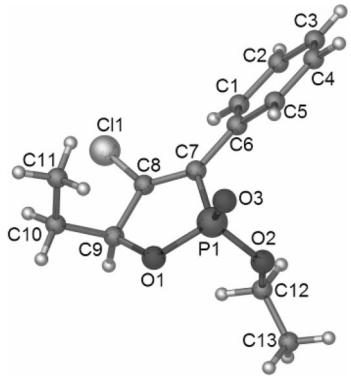
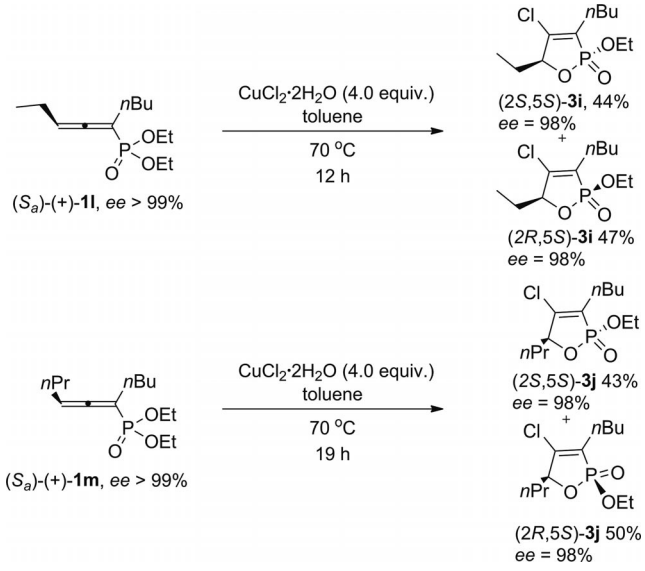


Figure 2. ORTEP representation of (*S*,*S*)-**3k**.

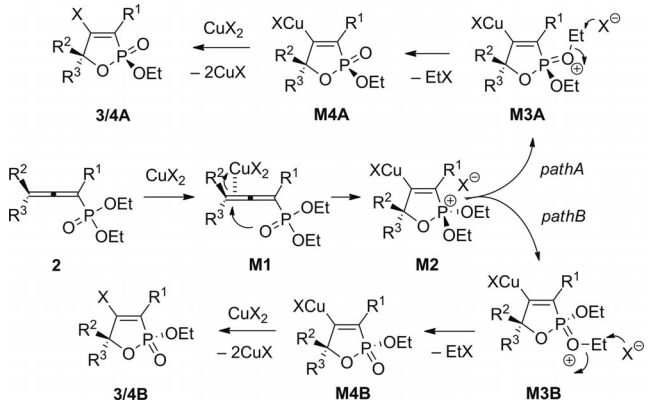
of axial chirality from the easily available optically active propargylic alcohol into the central chirality of the final products (Figure 2). Optically active diethyl 1,2-allenylphosphonate was also tested in the chlorocyclization; the results are summarized in Scheme 5.

Based on these results and on previous reports,[10] we propose a possible mechanism (Scheme 6). Firstly, coordination of the copper salt to the relatively electron-rich C=C bond forms intermediate **M1**. Then, anti-oxy-metalation affords the five-membered intermediate **M2**. Arbuzov type dealkylation of the ethoxy groups mediated by a chloride anion leads to the formation of intermediates **M4A** and **M4B**. Subsequently, C–X bond formation in the presence of a second molecule of CuX_2 generates the final product **3** together with two molecules of CuX.[8–10]

We then studied the Suzuki cross-coupling reaction of the C–Cl bonds in **3**.[18] We have previously developed an



Scheme 5. Chorocyclization of optically active 1,2-allenylphosphonates.



Scheme 6. Proposed mechanism for the halocyclization.

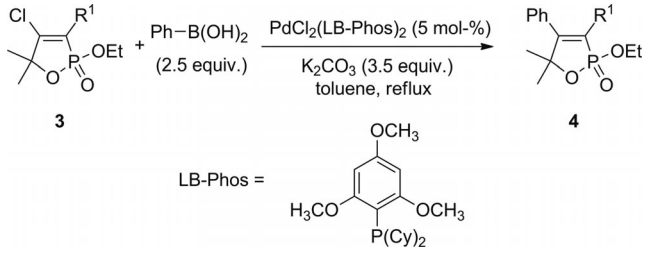
electron-rich, sterically bulky phosphane ligand, dicyclohexyl(2,4,6-trimethoxyphenyl)phosphane (LB-Phos),[12] that can be used to selectively activate the relatively inert C–Cl bond over the more reactive lactonic allylic C–O bond.[12b] We used the prepared [$PdCl_2$(LB-Phos)$_2$] complex as the catalyst and 3.5 equiv. K_2CO_3 as the base. The reaction with phenylboronic acid in toluene at reflux proceeded smoothly to afford the corresponding coupling products in moderate to good yields (Table 5).

When R^2 and R^3 were not the same, Suzuki coupling of both diastereoisomers could be conducted under standard conditions to afford the corresponding products with similar yields (Scheme 7).When optically active substrates were used, coupling products were obtained in good yields without apparent racemization (Scheme 8).

Conclusions

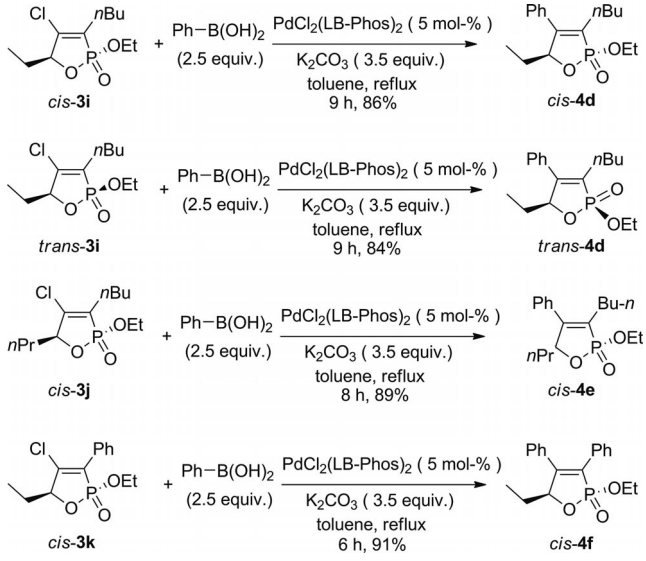
We have demonstrated a CuX_2-mediated direct halocyclization of diethyl 1,2-allenylphosphonates for the convenient and efficient synthesis of 4-halo-2,5-dihydro-1,2-oxaphosphole 2-oxides in satisfactory yields and the subsequent Suzuki cross-coupling of the resulting vinylic chlorides. Compared with the results described in the previous report,[11] this transformation shows better functional

Table 5. The Suzuki cross-coupling reaction of 4-chloro-2,5-dihydro-1,2-oxaphosphole 2-oxides **3** with phenylboronic acid.[a]

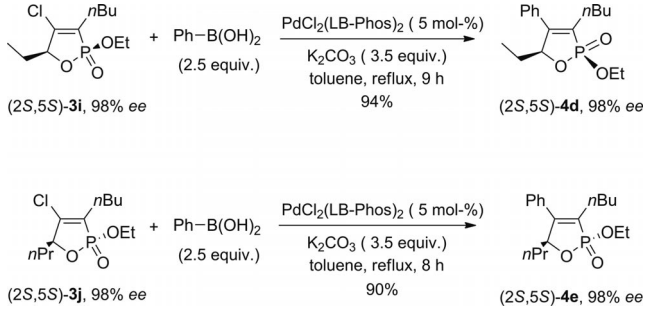


Entry	R^1	Time [h]	Yield of **4** [%][b]
1	*n*Bu (**3a**)	5	75 (**4a**)
2	Ph (**3b**)	17	78 (**4b**)
3	allyl (**3c**)	10.5	55 (**4c**)

[a] Reagents and conditions: **3** (0.3 mmol), phenylboronic acid (0.75 mmol), [$PdCl_2$(LB-Phos)$_2$] (0.015 mmol), K_2CO_3 (1.05 mmol), toluene (2 mL), reflux. [b] Isolated yield.



Scheme 7. Suzuki coupling reaction of diastereoisomers of **3**.



Scheme 8. Suzuki coupling reaction of optically active phosphonates.

group tolerance, requires fewer steps, and is simpler to perform. Furthermore, the axial chirality of substrate was transferred efficiently to the central carbon atom in the final, optically active 4-chloro-2,5-dihydro-1,2-oxaphosphole 2-oxides. Considering the high loading of functionalities, ready availability of the optically active starting materials, and potential application of phosphorus-containing compounds, this reaction should be useful in organic synthesis. Further studies in this area are in progress in our laboratory.

Experimental Section

General: Racemic starting materials **1a**–**n** and optically active starting materials (*S*)-(+)-**1l**, (*S*)-(+)-**1m**, and (*S*)-(–)-**1n** were prepared according to known procedures.[11] The *ee* values were determined by HPLC analysis using chiral columns under the conditions noted in the procedures. For details of all analytical instruments used, see ref.[12]

Synthesis of Starting Materials

Diethyl (6-Chloro-2-methylhepta-2,3,6-trien-4-yl)phosphonate (1e). Typical Procedure: To a solution of 6-chloro-2-methylhepta-6-en-3-yn-2-ol (1.2645 g, 8 mmol) and Et_3N (1295.2 mg, 12.8 mmol) in CH_2Cl_2 (15 mL), was added a solution of $P(OEt)_2Cl$ (2003.8 mg, 12.8 mmol) in CH_2Cl_2 (9 mL) dropwise at –78 °C. After the addition, the resulting mixture was warmed to room temp. and then stirred at room temperature overnight. After complete conversion of the corresponding propargylic alcohol (reaction monitored by TLC; petroleum ether/ethyl acetate, 3:1) the solvent was evaporated, then H_2O (80 mL) and ethyl acetate (80 mL) were added. The organic layer was separated and the organic layer was washed with brine (80 mL) and dried with anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 5:1) to afford **1e** (1.1147 g, 50%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.24 (s, 1 H, =C*H*H), 5.21 (s, 1 H, =CH*H*), 4.14–3.94 (m, 4 H, 2× OCH_2), 3.12 (d, J = 11.4 Hz, 2 H, CH_2), 1.77 (s, 3 H), 1.75 (s, 3 H), 1.29 (t, J = 7.1 Hz, 6 H, OCH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 208.7 (d, $J_{P,C}$ = 6.0 Hz), 139.3 (d, $J_{P,C}$ = 7.5 Hz), 114.3, 98.9 (d, $J_{P,C}$ = 15.8 Hz), 87.8 (d, $J_{P,C}$ = 193.8 Hz), 62.1 (d, $J_{P,C}$ = 6.0 Hz), 39.2 (d, $J_{P,C}$ = 10.6 Hz), 19.2 (d, $J_{P,C}$ = 6.8 Hz), 16.2 (d, $J_{P,C}$ = 6.8 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 17.6 ppm. IR (neat): $\tilde{\nu}$ = 2984, 2940, 2909, 1962, 1635, 1444, 1378, 1244, 1163, 1022 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 280 (7.25) [M(^{37}Cl)]$^+$, 278 (19.76) [M(^{35}Cl)]$^+$, 243 (100) (M – Cl)$^+$. HRMS (EI): calcd. for $C_{12}H_{20}O_3P^{35}Cl$ [M]$^+$ 278.0839; found 278.0831.

Diethyl (3,3-Pentamethylene-1-phenylpropa-1,2-dien-1-yl)phosphonate (1h): The reaction of 1,1-pentamethylene-3-phenylprop-2-yn-1-ol (1001.5 mg, 5 mmol), $P(OEt)_2Cl$ (1174.2 mg, 7.5 mmol), and Et_3N (758.9 mg, 7.5 mmol) afforded **1h** (1369.6 mg, 85%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, J = 8.1 Hz, 2 H, 2 × Ph-H), 7.38–7.18 (m, 3 H, 3 × Ph-H), 4.24–4.00 (m, 4 H, 2× OCH_2), 2.40–2.20 (m, 4 H), 1.82–1.48 (m, 6 H), 1.30 (t, J = 6.9 Hz, 6 H, 2× OCH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 205.8 (d, $J_{P,C}$ = 3.8 Hz), 133.3 (d, $J_{P,C}$ = 10.6 Hz), 128.4, 127.5 (d, $J_{P,C}$ = 5.3 Hz), 127.0, 105.9 (d, $J_{P,C}$ = 15.1 Hz), 94.6 (d, $J_{P,C}$ = 190.8 Hz), 62.3 (d, $J_{P,C}$ = 6.0 Hz), 30.2 (d, $J_{P,C}$ = 6.0 Hz), 27.0 (d, $J_{P,C}$ = 3.0 Hz), 25.7, 16.2 (d, $J_{P,C}$ = 6.0 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 16.4 ppm. IR (neat): $\tilde{\nu}$ = 2982, 2932, 2855, 1945, 1597, 1493, 1445, 1391, 1340, 1316, 1256, 1163, 1053, 1029 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 320 (84.04) [M]$^+$, 182 (100). HRMS (EI): calcd. for $C_{18}H_{25}O_3P$ [M]$^+$ 320.1541; found 320.1542.

Diethyl (3,3-Tetramethylene-1-phenylpropa-1,2-dien-1-yl)phosphonate (1i): The reaction of 1,1-tetramethylene-3-phenylprop-2-yn-1-ol (931.3 mg, 5 mmol), $P(OEt)_2Cl$ (1174.1 mg, 7.5 mmol), and Et_3N (708.3 mg, 7 mmol) afforded **1i** (714.4 mg, 47%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55 (d, J = 8.1 Hz, 2 H, 2 × Ph-H), 7.37–7.18 (m, 3 H, 3 × Ph-H), 4.22–4.00 (m, 4 H, 2× OCH_2), 2.70–2.48 (m, 4 H), 1.86–1.70 (m, 4 H), 1.30 (t, J = 7.2 Hz, 6 H, OCH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 204.9 (d, $J_{P,C}$ = 4.5 Hz), 133.4 (d, $J_{P,C}$ = 10.6 Hz), 128.4, 127.6 (d, $J_{P,C}$ = 6.0 Hz), 127.1, 107.3 (d, $J_{P,C}$ = 15.8 Hz), 97.0 (d, $J_{P,C}$ = 191.5 Hz), 62.4 (d, $J_{P,C}$ = 6.0 Hz), 31.1 (d, $J_{P,C}$ = 6.0 Hz), 27.3, 16.3 (d, $J_{P,C}$ = 6.0 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 17.0 ppm. IR (neat): $\tilde{\nu}$ = 3537, 3479, 3058, 2959, 1943, 1598, 1491, 1442, 1388, 1250, 1025 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 306 (33.02) [M]$^+$, 168 (100). HRMS (EI): calcd. for $C_{17}H_{23}O_3P$ [M]$^+$ 306.1385; found 306.1388.

Diethyl (3-Ethyl-1-phenylpenta-1,2-dien-1-yl)phosphonate (1j): The reaction of 3-ethyl-1-phenylpenta-1-yn-3-ol (941.0 mg, 5 mmol), $P(OEt)_2Cl$ (1174.1 mg, 7.5 mmol), and Et_3N (708.3 mg, 7 mmol) afforded **1j** (854.1 mg, 55%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, J = 8.1 Hz, 2 H, 2 × Ph-H), 7.37–7.18 (m, 3 H, 3 × Ph-H), 4.22–4.00 (m, 4 H, 2× OCH_2), 2.28–2.10 (m, 4 H), 1.29 (t, J = 7.0 Hz, 6 H), 1.11 (t, J = 7.4 Hz, 6 H, 2× CH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 208.3 (d, $J_{P,C}$ = 4.3 Hz), 133.4 (d, $J_{P,C}$ = 10.2 Hz), 128.4, 127.2 (d, $J_{P,C}$ = 5.9 Hz), 127.1, 112.3 (d, $J_{P,C}$ = 14.6 Hz), 98.9 (d, $J_{P,C}$ = 190.9 Hz), 62.2 (d, $J_{P,C}$ = 6.2 Hz), 25.4 (d, $J_{P,C}$ = 6.0 Hz), 16.2 (d, $J_{P,C}$ = 6.7 Hz), 12.1 (d, $J_{P,C}$ = 2.0 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 16.9 ppm. IR (neat): $\tilde{\nu}$ = 3059, 3026, 2959, 2904, 2869, 1943, 1598, 1493, 1477, 1447, 1390, 1284, 1254, 1162, 1097, 1053, 1026 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 308 (25.20) [M]$^+$, 170 (100). HRMS (EI): calcd. for $C_{17}H_{25}O_3P$ [M]$^+$ 308.1541; found 308.1541.

Diethyl (7-Propyldeca-5,6-dien-5-yl)phosphonate (1k): The reaction of 4-propyldeca-5-yn-4-ol (1980.0 mg, 10 mmol), $P(OEt)_2Cl$ (2348.2 mg, 15 mmol), and Et_3N (1416.8 mg, 14 mmol) afforded **1k** (1610.9 mg, 51%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.15–3.92 (m, 4 H, 2× OCH_2), 2.18–1.89 (m, 6 H), 1.50–1.20 (m, 14 H), 0.96–0.80 (m, 9 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 205.6 (d, $J_{P,C}$ = 4.2 Hz), 106.0 (d, $J_{P,C}$ = 17.0 Hz), 93.6 (d, $J_{P,C}$ = 189.2 Hz), 60.9 (d, $J_{P,C}$ = 2.9 Hz), 33.5 (d, $J_{P,C}$ = 5.4 Hz), 29.9 (d, $J_{P,C}$ = 6.6 Hz), 27.9 (d, $J_{P,C}$ = 8.3 Hz), 21.6, 20.0, 15.6 (d, $J_{P,C}$ = 5.7 Hz), 13.1 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 19.8 ppm. IR (neat): $\tilde{\nu}$ = 2959, 2932, 2872, 1951, 1725, 1462, 1392, 1253, 1163, 1098, 1055, 1029 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 316 (30.17) [M]$^+$, 245 (100). HRMS (EI): calcd. for $C_{17}H_{33}O_3P$ [M]$^+$ 316.2167; found 316.2169.

Diethyl (Nona-3,4-dien-5-yl)phosphonate (1l): The reaction of non-4-yn-3-ol (1822.9 mg, 13 mmol), $P(OEt)_2Cl$ (3256.2 mg, 20.8 mmol), and Et_3N (2104.8 mg, 20.8 mmol) afforded **1l** (1176.6 mg, 55%) as a liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.50–5.35 (m, 1 H, CH=), 4.20–3.96 (m, 4 H, 2× OCH_2), 2.21–1.97 (m, 4 H), 1.54–1.19 (m, 10 H), 1.04 (t, J = 7.4 Hz, 3 H), 0.89 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 208.0 (d, $J_{P,C}$ = 6.0 Hz), 95.0 (d, $J_{P,C}$ = 16.6 Hz), 94.7 (d, $J_{P,C}$ = 187.7 Hz), 62.0 (d, $J_{P,C}$ = 6.0 Hz), 30.2 (d, $J_{P,C}$ = 6.8 Hz), 28.1 (d, $J_{P,C}$ = 7.5 Hz), 22.1, 21.2 (d, $J_{P,C}$ = 6.8 Hz), 16.3 (d, $J_{P,C}$ = 6.8 Hz), 13.8, 13.3 (d, $J_{P,C}$ = 3.8 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 18.9 ppm. IR (neat): $\tilde{\nu}$ = 2964, 2933, 2873, 2734, 2232, 1952, 1636, 1460, 1392, 1301, 1244, 1164, 1098, 1052, 1023 cm^{-1}. MS (70 eV,

EI): *m*/*z* (%) = 260 (5.66) $[M]^+$, 79 (100). HRMS (EI): calcd. for $C_{13}H_{25}O_3P$ $[M]^+$ 260.1541; found 260.1542.

Diethyl (Deca-5,6-dien-5-yl)phosphonate (1m): The reaction of dec-5-yn-4-ol (2743.0 mg, 10 mmol), $P(OEt)_2Cl$ (2348.2 mg, 15 mmol), and Et_3N (1416.7 mg, 14 mmol) afforded **1m** (1690.5 mg, 62%) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.45–5.28 (m, 1 H, CH=), 4.18–3.95 (m, 4 H, 2× OCH_2), 2.20–1.95 (m, 4 H), 1.52–1.26 (m, 12 H), 0.99–0.82 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 208.1 (d, $J_{P,C}$ = 6.0 Hz), 93.6 (d, $J_{P,C}$ = 188.2 Hz), 92.9 (d, $J_{P,C}$ = 15.8 Hz), 61.8 (d, $J_{P,C}$ = 5.9 Hz), 30.1, 30.0, 29.9 (d, $J_{P,C}$ = 6.3 Hz), 28.0 (d, $J_{P,C}$ = 6.9 Hz), 22.2 (d, $J_{P,C}$ = 4.2 Hz), 21.9, 16.1 (d, $J_{P,C}$ = 6.4 Hz), 13.5 (d, $J_{P,C}$ = 13.3 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 19.0 ppm. IR (neat): $\tilde{\nu}$ = 2959, 2932, 2873, 1952, 1464, 1443, 1392, 1246, 1164, 1098, 1052, 1024 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 274 (1.81) $[M]^+$, 81 (100). HRMS (EI): calcd. for $C_{14}H_{27}O_3P$ $[M]^+$ 274.1698; found 274.1700.

Diethyl (1-Phenylpenta-1,2-dien-1-yl)phosphonate (1n): The reaction of 1-phenylpenta-1-yn-3-ol (1602.3 mg, 10 mmol), $P(OEt)_2Cl$ (2348.2 mg, 15 mmol), and Et_3N (1416.7 mg, 14 mmol) afforded **1n** (1910.9 mg, 68%) as a liquid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.57 (d, *J* = 7.5 Hz, 2 H, 2 × Ph-H), 7.40–7.19 (m, 3 H, 3 × Ph-H), 5.87–5.72 (m, 1 H, CH=), 4.26–4.01 (m, 4 H, 2× OCH_2), 2.32–2.15 (m, 2 H, CH_2), 1.30 (t, *J* = 7.2 Hz, 6 H, 2× CH_2CH_3), 1.14 (t, *J* = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 210.4 (d, $J_{P,C}$ = 4.5 Hz), 132.4 (d, $J_{P,C}$ = 8.3 Hz), 128.5, 127.5 (d, $J_{P,C}$ = 6.0 Hz), 127.4, 98.0 (d, $J_{P,C}$ = 189.2 Hz), 96.3 (d, $J_{P,C}$ = 15.1 Hz), 62.5 (d, $J_{P,C}$ = 6.0 Hz), 21.2 (d, $J_{P,C}$ = 6.0 Hz), 16.2 (d, $J_{P,C}$ = 6.8 Hz), 13.2 (d, $J_{P,C}$ = 3.0 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 16.0 ppm. IR (neat): $\tilde{\nu}$ = 3062, 2978, 2934, 2905, 1943, 1597, 1579, 1494, 1448, 1391, 1369, 1245, 1163, 1097, 1051, 1021 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 280 (11.07) $[M]^+$, 128 (100). HRMS (EI): calcd. for $C_{15}H_{21}O_3P$ $[M]^+$ 280.1228; found 280.1226.

Diethyl (Nona-3,4-dien-5-yl)phosphonate [(S_a)-(+)-1l]: The reaction of (*S*)-non-4-yn-3-ol (1402.5 mg, 10 mmol), $P(OEt)_2Cl$ (2348.2 mg, 15 mmol), and Et_3N (1517.8 mg, 15 mmol) afforded (S_a)-(+)-**1l** (1133.1 mg, 44%) as a liquid; *ee* > 99% [HPLC conditions: Chiralcel IC-H column; hexane/*i*PrOH = 95:5; 0.5 mL/min; λ = 214 nm; t_R = 33.4 (major), 35.1 (minor) min]; $[\alpha]_D^{20}$ = +35.2 (*c* = 1.04, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 5.48–5.31 (m, 1 H, CH=), 4.12–3.92 (m, 4 H, 2× OCH_2), 2.16–1.96 (m, 4 H), 1.50–1.21 (m, 10 H), 1.00 (t, *J* = 7.4 Hz, 3 H), 0.85 (t, *J* = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 207.9 (d, $J_{P,C}$ = 6.0 Hz), 94.9 (d, $J_{P,C}$ = 15.8 Hz), 94.5 (d, $J_{P,C}$ = 187.7 Hz), 61.9 (d, $J_{P,C}$ = 6.0 Hz), 30.1 (d, $J_{P,C}$ = 6.8 Hz), 28.0 (d, $J_{P,C}$ = 6.8 Hz), 22.0, 21.1 (d, $J_{P,C}$ = 6.8 Hz), 16.2 (d, $J_{P,C}$ = 6.8 Hz), 13.7, 13.2 (d, $J_{P,C}$ = 3.0 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 18.9 ppm. IR (neat): $\tilde{\nu}$ = 2981, 2958, 2933, 2909, 2861, 2714, 1959, 1639, 1445, 1379, 1294, 1243, 1164, 1097, 1052, 1023 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 260 (16.04) $[M]^+$, 79 (100). HRMS (EI): calcd. for $C_{13}H_{25}O_3P$ $[M]^+$ 260.1541; found 260.1542.

Diethyl (Deca-5,6-dien-5-yl)phosphonate [(S_a)-(+)-1m]: The reaction of (*S*)-dec-5-yn-4-ol (925.5 mg, 6 mmol), $P(OEt)_2Cl$ (1408.9 mg, 9 mmol), and Et_3N (911.0 mg, 9 mmol) afforded (S_a)-(+)-**1m** (1028.3 mg, 62%) as a liquid; *ee* > 99% [HPLC conditions: Chiralcel IC-H column; hexane/*i*PrOH = 95:5; 0.5 mL/min; λ = 214 nm; t_R = 30.7 (major), 32.8 (minor) min]; $[\alpha]_D^{20}$ = +42.0 (*c* = 1.04, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 5.42–5.28 (m, 1 H, CH=), 4.18–3.90 (m, 4 H, 2× OCH_2), 2.20–1.92 (m, 4 H), 1.50–1.20 (m, 12 H), 1.00–0.81 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 208.2 (d, $J_{P,C}$ = 6.0 Hz), 93.8 (d, $J_{P,C}$ = 188.4 Hz), 93.1 (d, $J_{P,C}$ = 16.0 Hz), 62.0 (d, $J_{P,C}$ = 6.0 Hz), 30.10 (d, $J_{P,C}$ = 7.8 Hz), 30.06 (d, $J_{P,C}$ = 8.1 Hz), 28.1 (d, $J_{P,C}$ = 7.5 Hz), 22.3 (d, $J_{P,C}$ = 3.8 Hz), 22.0, 16.3, 16.2, 13.7 (d, $J_{P,C}$ = 13.6 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 19.0 ppm. IR (neat): $\tilde{\nu}$ = 2959, 2932, 2873, 1952, 1464, 1443, 1392, 1246, 1164, 1098, 1052, 1024 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 274 (20.19) $[M]^+$, 203 (100). HRMS (EI): calcd. for $C_{14}H_{27}O_3P$ $[M]^+$ 274.1698; found 274.1697.

Diethyl (1-Phenylpenta-1,2-dien-1-yl)phosphonate [(S_a)-(–)-1n]: The reaction of (*S*)-1-phenylpenta-1-yn-3-ol (801.1 mg, 5 mmol), $P(OEt)_2Cl$ (1174.2 mg, 7.5 mmol), and Et_3N (758.9 mg, 7.5 mmol) afforded (S_a)-(–)-**1n** (580.6 mg, 41%) as a liquid; *ee* = 97% [HPLC conditions: Chiralcel IC-H column; hexane/*i*PrOH = 95:5; 0.5 mL/min; λ = 214 nm; t_R = 53.9 (major), 57.8 (minor) min]; $[\alpha]_D^{20}$ = –52.5 (*c* = 1.06, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, *J* = 8.4 Hz, 2 H, 2 × Ph-H), 7.40–7.19 (m, 3 H, 3 × Ph-H), 5.86–5.73 (m, 1 H, CH=), 4.25–4.02 (m, 4 H, 2× OCH_2), 2.31–2.17 (m, 2 H, CH_2), 1.30 (t, *J* = 7.1 Hz, 6 H, 2× OCH_2CH_3), 1.14 (t, *J* = 7.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 210.2 (d, $J_{P,C}$ = 2.9 Hz), 132.2 (d, $J_{P,C}$ = 8.9 Hz), 128.2, 127.3, 127.2, 97.8 (d, $J_{P,C}$ = 189.6 Hz), 96.1 (d, $J_{P,C}$ = 14.6 Hz), 62.3 (d, $J_{P,C}$ = 5.9 Hz), 21.0 (d, $J_{P,C}$ = 6.6 Hz), 16.0 (d, $J_{P,C}$ = 6.7 Hz), 13.0 (d, $J_{P,C}$ = 2.3 Hz) ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 16.0 ppm. IR (neat): $\tilde{\nu}$ = 3062, 2978, 2934, 2905, 1943, 1597, 1579, 1494, 1448, 1391, 1369, 1245, 1163, 1097, 1051, 1021 cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 280 (11.07) $[M]^+$, 128 (100). HRMS (EI): calcd. for $C_{15}H_{21}O_3P$ $[M]^+$ 280.1228; found 280.1226.

$CuBr_2$-Mediated Bromocyclization Reaction of 1,2-Allenylphosphonates Affording 4-Bromo-2,5-dihydro-1,2-oxaphosphole 2-Oxides 2

4-Bromo-3-butyl-5,5-dimethyl-2-ethoxy-2,5-dihydro-1,2-oxaphosphole 2-Oxide (2a). Typical Procedure: A mixture of **1a** (78.1 mg, 0.30 mmol) and $CuBr_2$ (147.4 mg, 0.66 mmol) was stirred at 60 °C in EtOH (2 mL). After 1 h, the reaction was complete (reaction monitored by TLC; petroleum ether/ethyl acetate, 3:1). The solvent was evaporated and the residue was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate, 5:1) to afford **2a** (84.9 mg, 91%) as an oil.[11] ^1H NMR (300 MHz, $CDCl_3$): δ = 4.22–3.90 (m, 2 H, OCH_2), 2.42–2.00 (m, 2 H, CH_2 from C_4H_9), 1.60–1.45 (m, 8 H, CH_2 and 2 × CH_3), 1.45–1.15 (m, 5 H), 0.82 (t, *J* = 6.9 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 143.2 (d, $J_{P,C}$ = 52.8 Hz), 128.3 (d, $J_{P,C}$ = 150.8 Hz), 86.0 (d, $J_{P,C}$ = 4.0 Hz), 62.8 (d, $J_{P,C}$ = 6.8 Hz), 29.1 (d, $J_{P,C}$ = 1.6 Hz), 27.3, 27.2 (d, $J_{P,C}$ = 3.2 Hz), 26.5, 22.2, 16.3 (d, $J_{P,C}$ = 6.1 Hz), 13.5 ppm. MS (70 eV, EI): *m*/*z* (%) = 312 (1.16) $[M(^{81}Br)]^+$, 310 (1.31) $[M(^{79}Br)]^+$, 41 (100).

4-Bromo-2-ethoxy-2,5-dihydro-5,5-dimethyl-3-phenyl-1,2-oxaphosphole 2-Oxide (2b): The reaction of **1b** (84.1 mg, 0.30 mmol) and $CuBr_2$ (147.9 mg, 0.66 mmol) in EtOH (2 mL) afforded **2b** (68.8 mg, 69%) as an oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, *J* = 6.6 Hz, 2 H, 2 × Ph-H), 7.48–7.32 (m, 3 H, 3 × Ph-H), 4.18–3.96 (m, 2 H, OCH_2), 1.65 (s, 3 H, CH_3), 1.61 (s, 3 H, CH_3), 1.17 (t, *J* = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 142.0 (d, $J_{P,C}$ = 45.5 Hz), 129.9 (d, $J_{P,C}$ = 10.0 Hz), 129.0 (d, $J_{P,C}$ = 1.2 Hz), 128.5, 128.0 (d, $J_{P,C}$ = 6.2 Hz), 127.7 (d, $J_{P,C}$ = 153.9 Hz), 86.4 (d, $J_{P,C}$ = 3.5 Hz), 63.6 (d, $J_{P,C}$ = 7.5 Hz), 27.2 (d, $J_{P,C}$ = 3.8 Hz), 26.9 (d, $J_{P,C}$ = 1.4 Hz), 16.2 (d, $J_{P,C}$ = 5.6 Hz) ppm. MS (70 eV, EI): *m*/*z* (%) = 333 (4.66) $[M(^{81}Br) + 1]^+$, 332 (32.15) $[M(^{81}Br)]^+$, 331 (5.90) $[M(^{79}Br) + 1]^+$, 330 (32.72) $[M(^{79}Br)]^+$, 317 (40.53) $[M(^{81}Br) - CH_3]^+$, 315 (41.20) $[M(^{79}Br) - CH_3]^+$, 251 (50.35) $[M - Br]^+$, 223 (100). HRMS (EI): calcd. for $C_{13}H_{16}O_3P^{79}Br$ $[M]^+$ 330.0020; found 330.0023.

3-Allyl-4-bromo-2-ethoxy-2,5-dihydro-5,5-dimethyl-1,2-oxaphosphole 2-Oxide (2c): The reaction of **1c** (73.3 mg, 0.30 mmol) and $CuBr_2$ (147.5 mg, 0.66 mmol) in EtOH (2 mL) afforded **2c** (66.5 mg, 75%) as an oil.[11] ^1H NMR (300 MHz, $CDCl_3$): δ =

5.92–5.62 (m, 1 H, =CH), 5.24–4.92 (m, 2 H, $=CH_2$), 4.17–3.88 (m, 2 H, OCH_2), 3.17–2.82 (m, 2 H, $=CCH_2$), 1.49 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 1.24 (t, J = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 144.2 (d, $J_{P,C}$ = 47.4 Hz), 131.6 (d, $J_{P,C}$ = 2.5 Hz), 126.6 (d, $J_{P,C}$ = 154.1 Hz), 117.8, 86.3 (d, $J_{P,C}$ = 3.6 Hz), 63.4 (d, $J_{P,C}$ = 6.4 Hz), 31.8 (d, $J_{P,C}$ = 10.1 Hz), 27.3 (d, $J_{P,C}$ = 2.6 Hz), 26.7 (d, $J_{P,C}$ = 1.6 Hz), 16.4 (d, $J_{P,C}$ = 6.3 Hz) ppm. MS (70 eV, EI): m/z (%) = 297 (2.63) $[M(^{81}Br) + 1]^+$, 296 (22.97) $[M(^{81}Br)]^+$, 295 (3.84) $[M(^{79}Br) + 1]^+$, 294 (22.14) $[M(^{79}Br)]^+$, 268 (54.15) $[M(^{81}Br) - C_2H_4]^+$, 266 (53.45) $[M(^{79}Br) - C_2H_4]^+$, 215 (10.08) $[M - Br]^+$, 105 (100).

4-Bromo-2-ethoxy-2,5-dihydro-5,5-dimethyl-3-(2′-methylallyl)-1,2-oxaphosphole 2-Oxide (2d): The reaction of **1d** (77.5 mg, 0.30 mmol) and $CuBr_2$ (147.4 mg, 0.66 mmol) in EtOH (2 mL) afforded **2d** (70.9 mg, 77%) as an oil.[11] ^1H NMR (300 MHz, $CDCl_3$): δ = 4.83 (s, 2 H, $=CH_2$), 4.20–3.97 (m, 2 H, OCH_2), 3.15–2.90 (m, 2 H, $=CCH_2$), 1.72 (s, 3 H, CH_3), 1.54 (s, 3 H, CH_3), 1.51 (s, 3 H, CH_3), 1.25 (td, J = 6.3, 1.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 145.2 (d, $J_{P,C}$ = 47.6 Hz), 139.8 (d, $J_{P,C}$ = 1.6 Hz), 126.9 (d, $J_{P,C}$ = 154.3 Hz), 113.4, 86.2 (d, $J_{P,C}$ = 3.9 Hz), 63.4 (d, $J_{P,C}$ = 6.6 Hz), 35.7 (d, $J_{P,C}$ = 9.4 Hz), 27.3 (d, $J_{P,C}$ = 2.8 Hz), 26.9 (d, $J_{P,C}$ = 1.0 Hz), 22.1, 16.4 (d, $J_{P,C}$ = 5.9 Hz) ppm. MS (70 eV, EI): m/z (%) = 311 (0.97) $[M(^{81}Br) + 1]^+$, 310 (6.74) $[M(^{81}Br)]^+$, 309 (1.08) $[M(^{79}Br) + 1]^+$, 308 (6.87) $[M(^{79}Br)]^+$, 229 (6.48) $[M - Br]^+$, 119 (100).

4-Bromo-3-(2′-chloroallyl)-2-ethoxy-2,5-dihydro-5,5-dimethyl-1,2-oxaphosphole 2-Oxide (2e): The reaction of **1e** (83.4 mg, 0.30 mmol) and $CuBr_2$ (147.3 mg, 0.66 mmol) in EtOH (2 mL) afforded **2e** (78.2 mg, 79%) as an oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.30 (s, 1 H, =C*H*H), 5.26 (s, 1 H, =CH*H*), 4.20–3.92 (m, 2 H, OCH_2), 3.42–3.21 (m, 2 H, $=CCH_2$), 1.53 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 1.26 (t, J = 7.1 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 147.3 (d, $J_{P,C}$ = 45.8 Hz), 136.2 (d, $J_{P,C}$ = 2.6 Hz), 124.6 (d, $J_{P,C}$ = 157.2 Hz), 115.1, 86.6 (d, $J_{P,C}$ = 3.2 Hz), 63.7 (d, $J_{P,C}$ = 6.9 Hz), 37.1 (d, $J_{P,C}$ = 10.9 Hz), 27.3 (d, $J_{P,C}$ = 3.2 Hz), 26.7 (d, $J_{P,C}$ = 1.9 Hz), 16.4 (d, $J_{P,C}$ = 6.4 Hz) ppm. MS (70 eV, EI): m/z (%) = 330 (1.76) $[M(^{81}Br^{35}Cl)]^+$, 328 (1.30) $[M(^{79}Br^{35}Cl)]^+$, 43 (100). HRMS (EI): calcd. for $C_{10}H_{15}O_3P^{35}Cl^{79}Br$ $[M]^+$ 327.9631; found 327.9630.

4-Bromo-3-butyl-2-ethoxy-1-oxa-2-phosphaspiro[4.5]dec-3-ene 2-Oxide (2f): The reaction of **1f** (90.2 mg, 0.30 mmol) and $CuBr_2$ (147.2 mg, 0.66 mmol) in EtOH (2 mL) afforded **2f** (93.0 mg, 88%) as an oil.[11] ^1H NMR (300 MHz, $CDCl_3$): δ = 4.16–3.96 (m, 2 H, OCH_2), 2.41–2.11 (m, 2 H, CH_2 from C_4H_9), 1.92–1.75 (m, 2 H), 1.75–1.40 (m, 9 H), 1.39–1.21 (m, 5 H), 1.16–1.00 (m, 1 H, cyclohexyl), 0.85 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 143.8 (d, $J_{P,C}$ = 48.6 Hz), 128.3 (d, $J_{P,C}$ = 153.0 Hz), 87.8 (d, $J_{P,C}$ = 3.2 Hz), 62.9 (d, $J_{P,C}$ = 6.8 Hz), 35.0 (d, $J_{P,C}$ = 2.3 Hz), 34.3 (d, $J_{P,C}$ = 1.1 Hz), 29.3 (d, $J_{P,C}$ = 2.0 Hz), 27.4 (d, $J_{P,C}$ = 10.3 Hz), 24.2, 22.3, 21.3, 21.2, 16.4 (d, $J_{P,C}$ = 5.4 Hz), 13.6 ppm. MS (70 eV, EI): m/z (%) = 353 (2.54) $[M(^{81}Br) + 1]^+$, 352 (14.33) $[M(^{81}Br)]^+$, 351 (3.82) $[M(^{79}Br) + 1]^+$, 350 (14.15) $[M(^{79}Br)]^+$, 310 (96.82) $[M(^{81}Br) - C_3H_6]^+$, 308 (100) $[M(^{79}Br) - C_3H_6]^+$, 271 (37.19) $[M - Br]^+$.

4-Bromo-3-butyl-2-ethoxy-1-oxa-2-phosphaspiro[4.4]non-3-ene 2-Oxide (2g): The reaction of **1g** (85.8 mg, 0.30 mmol) and $CuBr_2$ (148.0 mg, 0.66 mmol) in EtOH (2 mL) afforded **2g** (92.1 mg, 91%) as an oil.[11] ^1H NMR (300 MHz, $CDCl_3$): δ = 4.14–3.92 (m, 2 H, OCH_2), 2.42–2.16 (m, 2 H, CH_2 from C_4H_9), 2.18–1.96 (m, 2 H), 1.96–1.62 (m, 6 H), 1.59–1.42 (m, 2 H), 1.38–1.20 (m, 5 H), 0.86 (t, J = 7.2 Hz, 3 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 141.2 (d, $J_{P,C}$ = 47.6 Hz), 129.6 (d, $J_{P,C}$ = 151.9 Hz), 96.0 (d, $J_{P,C}$ = 3.6 Hz), 62.9 (d, $J_{P,C}$ = 6.9 Hz), 38.4 (d, $J_{P,C}$ = 3.2 Hz), 37.8 (d, $J_{P,C}$ = 1.8 Hz), 29.3 (d, $J_{P,C}$ = 1.7 Hz), 27.6 (d, $J_{P,C}$ = 10.1 Hz), 24.4 (d, $J_{P,C}$ = 3.8 Hz), 22.3, 16.4 (d, $J_{P,C}$ = 6.2 Hz), 13.6 ppm. MS (70 eV, EI): m/z (%) = 338 (10.74) $[M(^{81}Br)]^+$, 336 (10.82) $[M(^{79}Br)]^+$, 296 (98.70) $[M(^{81}Br) - C_3H_6]^+$, 294 (100) $[M(^{79}Br) - C_3H_6]^+$, 257 (93.32) $[M - Br]^+$.

4-Bromo-2-ethoxy-3-phenyl-1-oxa-2-phosphaspiro[4.5]dec-3-ene-2-oxide (2h): The reaction of **1h** (96.1 mg, 0.30 mmol) and $CuBr_2$ (147.4 mg, 0.66 mmol) in EtOH (2 mL) afforded **2h** (94.4 mg, 85%) as a white solid; m.p. 126–127 °C (petroleum ether/ethyl acetate). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, J = 7.2 Hz, 2 H, 2 × Ph-H), 7.51–7.30 (m, 3 H, 3 × Ph-H), 4.20–3.98 (m, 2 H, OCH_2), 2.18–1.90 (m, 2 H, cyclohexyl), 1.90–1.60 (m, 7 H, cyclohexyl), 1.32–1.12 (m, 4 H, OCH_2CH_3 and cyclohexyl) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 142.5 (d, $J_{P,C}$ = 45.8 Hz), 130.1 (d, $J_{P,C}$ = 10.0 Hz), 129.0, 128.5, 128.2 (d, $J_{P,C}$ = 6.2 Hz), 127.7 (d, $J_{P,C}$ = 154.6 Hz), 88.1 (d, $J_{P,C}$ = 3.4 Hz), 63.5 (d, $J_{P,C}$ = 6.2 Hz), 34.8 (d, $J_{P,C}$ = 2.7 Hz), 34.6, 24.2, 21.3 (d, $J_{P,C}$ = 12.2 Hz), 16.3 (d, $J_{P,C}$ = 5.6 Hz) ppm. MS (70 eV, EI): m/z (%) = 373 (2.44) $[M(^{81}Br) + 1]^+$, 372 (12.05) $[M(^{81}Br)]^+$, 371 (3.40) $[M(^{79}Br) + 1]^+$, 370 (13.23) $[M(^{79}Br)]^+$, 291 (100) $[M - Br]^+$. $C_{16}H_{20}BrO_3P$ (371.21): calcd. C 51.77, H 5.43; found C 51.79, H 5.49.

4-Bromol-2-ethoxy-3-phenyl-1-oxa-2-phosphaspiro[4.4]non-3-ene 2-oxide (2i): The reaction of **1i** (91.5 mg, 0.30 mmol) and $CuBr_2$ (147.6 mg, 0.66 mmol) in EtOH (2 mL) afforded **2i** (76.9 mg, 72%) as an oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.76–7.64 (m, 2 H, 2 × Ph-H), 7.46–7.33 (m, 3 H, 3 × Ph-H), 4.20–3.95 (m, 2 H, OCH_2), 2.36–2.14 (m, 2 H, cyclopentyl), 2.07–1.75 (m, 6 H, cyclopentyl), 1.18 (t, J = 7.0 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.1 (d, $J_{P,C}$ = 45.8 Hz), 130.2 (d, $J_{P,C}$ = 9.7 Hz), 129.1, 128.9 (d, $J_{P,C}$ = 154.1 Hz), 128.6, 128.2 (d, $J_{P,C}$ = 6.3 Hz), 96.3 (d, $J_{P,C}$ = 3.5 Hz), 63.7 (d, $J_{P,C}$ = 7.3 Hz), 38.6 (d, $J_{P,C}$ = 2.9 Hz), 38.5 (d, $J_{P,C}$ = 2.0 Hz), 24.7 (d, $J_{P,C}$ = 1.4 Hz), 16.3 (d, $J_{P,C}$ = 5.2 Hz) ppm. MS (70 eV, EI): m/z (%) = 358 (5.60) $[M(^{81}Br)]^+$, 356 (5.73) $[M(^{79}Br)]^+$, 277 (100) $[M - Br]^+$. HRMS (EI): calcd. for $C_{15}H_{18}O_3P$ ^{79}Br $[M]^+$ 356.0177; found 356.0177.

4-Bromo-2-ethoxy-5,5-diethyl-2,5-dihydro-3-phenyl-1,2-oxaphosphole 2-Oxide (2j): The reaction of **1j** (92.8 mg, 0.30 mmol) and $CuBr_2$ (147.5 mg, 0.66 mmol) in EtOH (2 mL) afforded **2j** (87.4 mg, 81%) as an oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.60 (m, 2 H, 2 × Ph-H), 7.48–7.32 (m, 3 H, 3 × Ph-H), 4.30–4.01 (m, 2 H, OCH_2), 2.00–1.82 (m, 4 H), 1.19 (t, J = 7.0 Hz, 3 H), 1.01–0.89 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 139.3 (d, $J_{P,C}$ = 47.0 Hz), 131.0 (d, $J_{P,C}$ = 156.5 Hz), 130.4 (d, $J_{P,C}$ = 9.9 Hz), 129.0 (d, $J_{P,C}$ = 1.6 Hz), 128.6, 128.2 (d, $J_{P,C}$ = 6.0 Hz), 92.3 (d, $J_{P,C}$ = 1.9 Hz), 63.8 (d, $J_{P,C}$ = 6.5 Hz), 31.2 (d, $J_{P,C}$ = 2.2 Hz), 30.8 (d, $J_{P,C}$ = 2.9 Hz), 16.5 (d, $J_{P,C}$ = 4.4 Hz), 7.2 (d, $J_{P,C}$ = 2.9 Hz) ppm. MS (70 eV, EI): m/z (%) = 360 (15.82) $[M^+(^{81}Br)]$, 356 (16.30) $[M(^{79}Br)]^+$, 331 (100) $[M(^{81}Br) - C_2H_5]^+$, 331 (100) $[M(^{79}Br) - C_2H_5]^+$, 279 (46.07) $[M - Br]^+$. HRMS (EI): calcd. for $C_{15}H_{20}O_3P^{79}Br$ $[M]^+$ 358.0333; found 358.0336.

4-Bromo-3-butyl-2-ethoxy-2,5-dihydro-5,5-dipropyl-1,2-oxaphosphole 2-Oxide (2k): The reaction of **1k** (95.0 mg, 0.30 mmol) and $CuBr_2$ (147.2 mg, 0.66 mmol) in EtOH (2 mL) afforded **2k** (94.2 mg, 85%) as an oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.25–4.00 (m, 2 H, OCH_2), 2.41–2.10 (m, 2 H, CH_2 from C_4H_9), 1.76–1.55 (m, 4 H), 1.55–1.20 (m, 9 H), 1.15–0.96 (m, 2 H), 0.96–0.70 (m, 9 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 140.8 (d, $J_{P,C}$ = 48.8 Hz), 130.6 (d, $J_{P,C}$ = 154.9 Hz), 91.2 (d, $J_{P,C}$ = 2.0 Hz), 62.9 (d, $J_{P,C}$ = 6.8 Hz), 40.2 (d, $J_{P,C}$ = 1.3 Hz), 40.0 (d, $J_{P,C}$ = 2.3 Hz), 29.4 (d, $J_{P,C}$ = 2.3 Hz), 27.3 (d, $J_{P,C}$ = 10.0 Hz), 22.3, 16.5 (d, $J_{P,C}$ = 5.6 Hz), 15.8 (d, $J_{P,C}$ = 1.4 Hz), 13.8, 13.6 (d, $J_{P,C}$ =

10.4 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 368 (2.54) $[M(^{81}Br)]^+$, 366 (2.58) $[M(^{79}Br)]^+$, 325 (100) $[M(^{81}Br) - C_3H_6]^+$, 323 (100) $[M(^{79}Br) - C_3H_6]^+$, 287 (24.07) $[M - Br]^+$. HRMS (EI): calcd. for $C_{15}H_{28}O_3{}^{79}BrP$ $[M]^+$ 366.0959; found 366.0956.

$CuCl_2 \cdot 2H_2O$-Mediated Chlorocyclization Reaction of 1,2-Allenylphosphonates to Afford 4-Chloro-2,5-Dihydro-1,2-oxaphosphole 2-Oxides 3

3-Butyl-4-chloro-2-ethoxy-2,5-dihydro-5,5-dimethyl-1,2-oxaphosphole 2-Oxide (3a). Typical Procedure I: A mixture of **1a** (78.0 mg, 0.30 mmol) and $CuCl_2 \cdot 2H_2O$ (153.5 mg, 0.9 mmol) was stirred at 70 °C in toluene (2 mL) for 5 h. When the reaction was complete (reaction monitored by TLC; petroleum ether/ethyl acetate, 3:1). The solvent was evaporated, the residue was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate, 4:1) to afford **3a** (68.0 mg, 85%) as an oil.[11] ^1H NMR (300 MHz, $CDCl_3$): δ = 4.18–3.98 (m, 2 H, OCH_2), 2.43–2.09 (m, 2 H, CH_2 from C_4H_9), 1.57–1.42 (m, 8 H), 1.42–1.19 (m, 5 H), 0.84 (t, J = 7.2 Hz, 3 H, CH_3 from C_4H_9) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 150.4 (d, $J_{P,C}$ = 50.0 Hz), 124.6 (d, $J_{P,C}$ = 157.7 Hz), 85.3 (d, $J_{P,C}$ = 2.9 Hz), 62.9 (d, $J_{P,C}$ = 6.9 Hz), 29.3 (d, $J_{P,C}$ = 2.2 Hz), 26.7 (d, $J_{P,C}$ = 2.6 Hz), 26.0 (d, $J_{P,C}$ = 2.6 Hz), 25.3 (d, $J_{P,C}$ = 9.5 Hz), 22.3, 16.4 (d, $J_{P,C}$ = 6.2 Hz), 13.5 ppm. MS (70 eV, EI): *m/z* (%) = 268 (0.50) $[M(^{37}Cl)]^+$, 266 (1.67) $[M(^{35}Cl)]^+$, 240 (1.32) $[M(^{37}Cl) - C_2H_4]^+$, 238 (1.94) $[M(^{35}Cl) - C_2H_4]^+$, 226 (5.49) $[M(^{37}Cl) - C_3H_6]^+$, 224 (12.86) $[M(^{35}Cl) - C_3H_6]^+$, 43 (100).

4-Chloro-2-ethoxy-2,5-dihydro-5,5-dimethyl-3-phenyl-1,2-oxaphosphole 2-Oxide (3b): The reaction of **1b** (84.2 mg, 0.30 mmol) and $CuCl_2 \cdot 2H_2O$ (153.5 mg, 0.9 mmol) in toluene (2 mL) afforded **3b** (83.8 mg, 97%) as an oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.72 (d, $J_{P,C}$ = 6.9 Hz, 2 H, 2 × Ph-H), 7.48–7.28 (m, 3 H, 3 × Ph-H), 4.20–3.94 (m, 2 H, OCH_2), 1.63 (s, 3 H, CH_3), 1.60 (s, 3 H, CH_3), 1.18 (t, J = 7.1 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 148.9 (d, $J_{P,C}$ = 47.7 Hz), 129.0, 128.9 (d, $J_{P,C}$ = 9.2 Hz), 128.4, 128.0 (d, $J_{P,C}$ = 6.8 Hz), 123.4 (d, $J_{P,C}$ = 159.3 Hz), 85.3 (d, $J_{P,C}$ = 3.1 Hz), 63.5 (d, $J_{P,C}$ = 6.5 Hz), 26.6 (d, $J_{P,C}$ = 3.4 Hz), 26.2 (d, $J_{P,C}$ = 1.6 Hz), 16.2 (d, $J_{P,C}$ = 5.8 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 288 (1.56) $[M(^{37}Cl)]^+$, 286 (4.53) $[M(^{35}Cl)]^+$, 43 (100). HRMS (EI): calcd. for $C_{13}H_{16}O_3P^{35}Cl$ $[M]^+$ 286.0526; found 286.0524.

3-Allyl-4-chloro-2-ethoxy-2,5-dihydro-5,5-dimethy-1,2-oxaphosphole 2-Oxide (3c): The reaction of **1c** (73.3 mg, 0.30 mmol) and $CuCl_2 \cdot 2H_2O$ (153.5 mg, 0.9 mmol) in toluene (2 mL) afforded **3c** (51.5 mg, 68%) as an oil.[11] ^1H NMR (300 MHz, $CDCl_3$): δ = 5.88–5.69 (m, =CH), 5.22–5.00 (m, 2 H, $=CH_2$), 4.16–3.98 (m, 2 H, OCH_2), 3.13–2.98 (m, 2 H, $=CCH_2$), 1.52 (s, 3 H), 1.48 (s, 3 H), 1.27 (t, J = 7.1 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 151.2 (d, $J_{P,C}$ = 49.5 Hz), 131.7 (d, $J_{P,C}$ = 7.5 Hz), 122.8 (d, $J_{P,C}$ = 160.6 Hz), 117.7, 85.5 (d, $J_{P,C}$ = 2.9 Hz), 63.2 (d, $J_{P,C}$ = 6.5 Hz), 29.8 (d, $J_{P,C}$ = 9.3 Hz), 26.7 (d, $J_{P,C}$ = 3.0 Hz), 26.1 (d, $J_{P,C}$ = 1.6 Hz), 16.4 (d, $J_{P,C}$ = 6.0 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 252 (3.31) $[M(^{37}Cl)]^+$, 250 (10.15) $[M(^{35}Cl)]^+$, 224 (11.76) $[M(^{37}Cl) - C_2H_4]^+$, 222 (33.72) $[M(^{35}Cl) - C_2H_4]^+$, 43 (100).

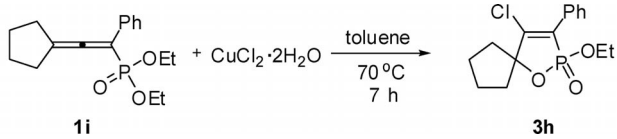
4-Chloro-2-ethoxy-2,5-dihydro-5,5-dimethyl-3-(2′-methylallyl)--1,2-oxaphosphole 2-Oxide (3d): The reaction of **1d** (77.9 mg, 0.30 mmol) and $CuCl_2 \cdot 2H_2O$ (154.0 mg, 0.9 mmol) in toluene (2 mL) afforded **3d** (69.4 mg, 87%) as an oil.[11] ^1H NMR (300 MHz, $CDCl_3$): δ = 4.86 (s, 2 H, $=CH_2$), 4.23–4.01 (m, 2 H, OCH_2), 3.20–3.00 (m, 2 H, $=CCH_2$), 1.76 (s, 3 H), 1.57 (s, 3 H), 1.54 (s, 3 H), 1.30 (t, J = 7.2 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 152.2 (d, $J_{P,C}$ = 50.1 Hz), 140.0 (d, $J_{P,C}$ = 1.9 Hz), 123.0 (d, $J_{P,C}$ = 160.4 Hz), 113.3, 85.4 (d, $J_{P,C}$ = 2.9 Hz), 63.4 (d, $J_{P,C}$ = 6.6 Hz), 33.7 (d, $J_{P,C}$ = 9.9 Hz), 26.7 (d, $J_{P,C}$ = 3.4 Hz), 26.3 (d, $J_{P,C}$ = 2.0 Hz), 22.0, 16.4 (d, $J_{P,C}$ = 6.6 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 266 (8.17) $[M(^{37}Cl)]^+$, 264 (24.74) $[M(^{35}Cl)]^+$, 119 (100).

3-Butyl-4-chloro-2-ethoxy-1-oxa-2-phosphaspiro[4.5]dec-3-ene 2-Oxide (3e): The reaction of **1f** (90.0 mg, 0.30 mmol) and $CuCl_2 \cdot 2H_2O$ (153.6 mg, 0.9 mmol) in toluene (2 mL) afforded **3e** (75.1 mg, 82%) as an oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.18–3.96 (m, 2 H, OCH_2), 2.44–2.16 (m, 2 H), 1.90–1.41 (m, 11 H), 1.41–1.22 (m, 5 H), 1.20–1.05 (m, 1 H), 0.87 (t, J = 7.2 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 150.8 (d, $J_{P,C}$ = 50.5 Hz), 124.7 (d, $J_{P,C}$ = 157.9 Hz), 87.2 (d, $J_{P,C}$ = 3.0 Hz), 62.9 (d, $J_{P,C}$ = 7.0 Hz), 34.5 (d, $J_{P,C}$ = 2.4 Hz), 33.9 (d, $J_{P,C}$ = 1.5 Hz), 29.4 (d, $J_{P,C}$ = 1.6 Hz), 25.6 (d, $J_{P,C}$ = 9.3 Hz), 24.3, 22.4, 21.4, 21.2, 16.4 (d, $J_{P,C}$ = 5.4 Hz), 13.6 ppm. MS (70 eV, EI): *m/z* (%) = 308 (4.19) $[M(^{37}Cl)]^+$, 306 (12.54) $[M(^{35}Cl)]^+$, 271 (37.19) $[M - Cl]^+$, 266 (33.23) $[M(^{37}Cl) - C_3H_6]^+$, 264 (100) $[M(^{35}Cl) - C_3H_6]^+$.

3-Butyl-4-chloro-2-ethoxy-1-oxa-2-phosphaspiro[4.4]non-3-ene 2-Oxide (3f): The reaction of **1g** (85.9 mg, 0.30 mmol) and $CuCl_2 \cdot 2H_2O$ (153.6 mg, 0.9 mmol) in toluene (2 mL) afforded **3f** (63.6 mg, 72%) as an oil.[11] ^1H NMR (300 MHz, $CDCl_3$): δ = 4.16–3.92 (m, 2 H, OCH_2), 2.48–2.17 (m, 2 H), 2.17–1.63 (m, 8 H), 1.63–1.43 (m, 2 H), 1.43–1.23 (m, 5 H), 0.90 (t, J = 7.4 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 148.1 (d, $J_{P,C}$ = 50.0 Hz), 126.0 (d, $J_{P,C}$ = 158.0 Hz), 95.3 (d, $J_{P,C}$ = 2.2 Hz), 63.0 (d, $J_{P,C}$ = 6.8 Hz), 37.9 (d, $J_{P,C}$ = 2.9 Hz), 37.3 (d, $J_{P,C}$ = 1.7 Hz), 29.4 (d, $J_{P,C}$ = 2.2 Hz), 25.6 (d, $J_{P,C}$ = 9.3 Hz), 24.5 (d, $J_{P,C}$ = 2.9 Hz), 22.4, 16.5 (d, $J_{P,C}$ = 6.1 Hz), 13.6 ppm. MS (70 eV, EI): *m/z* (%) = 294 (2.27) $[M(^{37}Cl)]^+$, 292 (6.79) $[M(^{35}Cl)]^+$, 257 (66.67) $[M - Cl]^+$, 252 (32.12) $[M(^{37}Cl) - C_3H_6]^+$, 250 (100) $[M(^{35}Cl) - C_3H_6]^+$.

4-Chloro-2-ethoxy-3-phenyl-1-oxa-2-phosphaspiro[4.5]dec-3-ene 2-Oxide (3g): The reaction of **1h** (96.1 mg, 0.30 mmol) and $CuCl_2 \cdot 2H_2O$ (153.3 mg, 0.9 mmol) in toluene (2 mL) afforded **3g** (87.9 mg, 90%) as a white solid;[11] m.p. 121–122 °C (petroleum ether/ethyl acetate). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.86–7.60 (m, 2 H, Ph-H), 7.50–7.28 (m, 3 H, 3 × Ph-H), 4.21–3.98 (m, 2 H, OCH_2), 2.07–1.90 (m, 2 H), 1.90–1.63 (m, 7 H), 1.40–1.10 (m, 4 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 149.4 (d, $J_{P,C}$ = 48.9 Hz), 129.2 (d, $J_{P,C}$ = 9.4 Hz), 129.0, 128.5, 128.2 (d, $J_{P,C}$ = 6.6 Hz), 123.6 (d, $J_{P,C}$ = 159.8 Hz), 87.3 (d, $J_{P,C}$ = 2.5 Hz), 63.5 (d, $J_{P,C}$ = 6.2 Hz), 34.3 (d, $J_{P,C}$ = 2.9 Hz), 34.1 (d, $J_{P,C}$ = 1.7 Hz), 24.3, 21.3 (d, $J_{P,C}$ = 12.2 Hz), 16.3 (d, $J_{P,C}$ = 6.0 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 328 (6.30) $[M(^{37}Cl)]^+$, 326 (16.78) $[M(^{35}Cl)]^+$, 291 (100) $[M - Cl]^+$. $C_{16}H_{20}ClO_3P$ (326.76): calcd. C 58.81, H 6.17; found C 58.70, H 6.12.

4-Chloro-2-ethoxy-3-phenyl-1-oxa-2-phosphaspiro[4.4]non-3-ene 2-Oxide (3h)



1i **3h**

The reaction of **1i** (91.8 mg, 0.30 mmol) and $CuCl_2 \cdot 2H_2O$ (153.5 mg, 0.9 mmol) in toluene (2 mL) afforded **3h** (77.8 mg, 83%) as an oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.74 (d, J = 7.5 Hz, 2 H, 2 × Ph-H), 7.49–7.25 (m, 3 H, 3 × Ph-H), 4.19–3.98 (m, 2 H, OCH_2), 2.38–2.12 (m, 2 H), 2.12–1.74 (m, 6 H), 1.20 (t, J = 6.6 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 146.8 (d, $J_{P,C}$ = 47.6 Hz), 129.2 (d, $J_{P,C}$ = 10.0 Hz), 129.1, 128.6, 128.2

(d, $J_{P,C}$ = 6.8 Hz), 124.8 (d, $J_{P,C}$ = 158.7 Hz), 95.4 (d, $J_{P,C}$ = 1.5 Hz), 63.6 (d, $J_{P,C}$ = 6.9 Hz), 38.0 (d, $J_{P,C}$ = 3.2 Hz), 37.8 (d, $J_{P,C}$ = 2.1 Hz), 24.7 (d, $J_{P,C}$ = 3.2 Hz), 16.3 (d, $J_{P,C}$ = 5.6 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 314 (1.46) $[M(^{37}Cl)]^+$, 312 (5.01) $[M(^{35}Cl)]^+$, 277 (100) $[M - Br]^+$. HRMS (EI): calcd. for $C_{15}H_{18}O_3P^{35}Cl$ $[M]^+$ 312.0682; found 312.0682.

Syntheses of Optically Active 2,5-Dihydro-1,2-oxaphosphole 2-Oxides

3-Butyl-4-chloro-2-ethoxy-5-ethyl-2,5-dihydro-1,2-oxaphosphole 2-Oxide (*cis*-3i, *trans*-3i). Typical Procedure II: A mixture of **1l** (78.2 mg, 0.30 mmol) and $CuCl_2·2H_2O$ (204.9 mg, 1.2 mmol) were stirred at 70 °C in toluene (2 mL). After 12 h, the reaction was complete (reaction monitored by TLC; petroleum ether/ethyl acetate, 3:1). The reaction mixture was allowed to cool to room temperature, H_2O (20 mL) and ether (20 mL) were then added and the layers were separated. The organic layer was washed with brine (20 mL) and dried with anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane, 10:1:1; 40 cm long column) to afford *cis*-**3i** (36.1 mg, 45%) and *trans*-**3i** (39.4 mg, 49%).

***cis*-3i:** Oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.72–4.61 (m, 1 H, CH), 4.13–3.98 (m, 2 H, OCH_2), 2.46–2.15 (m, 2 H, CH_2 from C_4H_9), 2.05–1.88 (m, 1 H, one proton from CH_2), 1.77–1.59 (m, 1 H, one proton from CH_2), 1.57–1.42 (m, 2 H, CH_2 from C_4H_9), 1.38–1.22 (m, 5 H), 0.96–0.80 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 144.9 (d, $J_{P,C}$ = 52.0 Hz), 126.5 (d, $J_{P,C}$ = 158.5 Hz), 82.2 (d, $J_{P,C}$ = 2.9 Hz), 63.0 (d, $J_{P,C}$ = 6.9 Hz), 29.4 (d, $J_{P,C}$ = 1.8 Hz), 25.8 (d, $J_{P,C}$ = 2.6 Hz), 25.1 (d, $J_{P,C}$ = 8.9 Hz), 22.3, 16.3 (d, $J_{P,C}$ = 6.5 Hz), 13.5, 7.5 ppm. ^{31}P NMR (121.5 MHz, $CDCl_3$): δ = 34.0 ppm. IR (neat): $\tilde{\nu}$ = 2960, 2934, 2874, 1631, 1460, 1388, 1325, 1266, 1182, 1164, 1072, 1034 cm^{-1}. MS(70 eV, EI): *m/z* (%) = 268 (2.34) $[M(^{37}Cl)]^+$, 266 (5.53) $[M(^{35}Cl)]^+$, 231 (29.14) $[M - Cl]^+$, 226 (34.98) $[M(^{37}Cl) - C_3H_6]^+$, 224 (100) $[M(^{35}Cl) - C_3H_6]^+$. HRMS (EI): calcd. for $C_{11}H_{20}O_3P^{35}Cl$ $[M]^+$ 266.0839; found 266.0837.

***trans*-3i:** Oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.75–4.61 (m, 1 H, CH), 4.26–4.01 (m, 2 H, OCH_2), 2.48–2.19 (m, 2 H, CH_2 from C_4H_9), 2.06–1.88 (m, 1 H, one proton from CH_2), 1.72–1.42 (m, 3 H), 1.41–1.25 (m, 5 H), 0.96–0.81 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 145.1 (d, $J_{P,C}$ = 53.1 Hz), 126.4 (d, $J_{P,C}$ = 160.1 Hz), 82.3 (d, $J_{P,C}$ = 3.4 Hz), 63.2 (d, $J_{P,C}$ = 6.9 Hz), 29.4 (d, $J_{P,C}$ = 2.2 Hz), 25.8 (d, $J_{P,C}$ = 1.1 Hz), 25.1 (d, $J_{P,C}$ = 9.6 Hz), 22.3, 16.5 (d, $J_{P,C}$ = 5.3 Hz), 13.6, 7.9 ppm. MS (70 eV, EI): *m/z* (%) = 268 (2.52) $[M(^{37}Cl)]^+$, 266 (6.01) $[M(^{35}Cl)]^+$, 231 (30.50) $[M - Cl]^+$, 226 (34.63) $[M(^{37}Cl) - C_3H_6]^+$, 224 (100) $[M(^{35}Cl) - C_3H_6]^+$. HRMS (EI): calcd. for $C_{11}H_{20}O_3P^{35}Cl$ $[M]^+$ 266.0839; found 266.0841.

3-Butyl-4-chloro-2-ethoxy-5-ethyl-2,5-dihydro-1,2-oxaphosphole 2-Oxide [(*S,S*)-3i and (*S,R*)-3i]: The reaction of (S_a)-(+)-**1l** (78.0 mg, 0.3 mmol, *ee* > 99%) and $CuCl_2·2H_2O$ (204.6 mg, 1.2 mmol) in toluene (2 mL) afforded (*S,S*)-**3i** (34.8 mg, 44%) and (*S,R*)-**3i** (37.9 mg, 47%).

(*S,S*)-3i: 98% *ee* [HPLC conditions: Chiralcel AS-H column; hexane/*i*PrOH, 90:10; 0.5 mL/min; λ = 214 nm; t_R = 6.5 (minor), 6.9 (major) min]; $[\alpha]_D^{20}$ = +8.4 (*c* = 1.50, $CHCl_3$); oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.75–4.62 (m, 1 H, CH), 4.21–4.00 (m, 2 H, CH_2 from C_4H_9), 2.50–2.20 (m, 2 H, one proton from CH_2), 2.09–1.93 (m, 1 H, one proton from CH_2), 1.80–1.64 (m, 1 H, one proton from CH_2), 1.64–1.46 (m, 2 H, CH_2 from C_4H_9), 1.44–1.28 (m, 5 H), 1.02–0.84 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 145.0 (d, $J_{P,C}$ = 52.6 Hz), 126.6 (d, $J_{P,C}$ = 158.4 Hz), 82.3 (d, $J_{P,C}$ = 2.9 Hz), 63.1 (d, $J_{P,C}$ = 6.9 Hz), 29.4 (d, $J_{P,C}$ = 2.5 Hz), 25.9 (d, $J_{P,C}$ = 2.4 Hz), 25.2 (d, $J_{P,C}$ = 9.5 Hz), 22.4, 16.4 (d, $J_{P,C}$ = 6.3 Hz), 13.6, 7.6 ppm. MS (70 eV, EI): *m/z* (%) = 268 (1.67) $[M(^{37}Cl)]^+$, 266 (4.96) $[M(^{35}Cl)]^+$, 231 (23.13) $[M - Cl]^+$, 226 (30.71) $[M(^{37}Cl) - C_3H_6]^+$, 224 (94.79) $[M(^{35}Cl) - C_3H_6]^+$, 43 (100). HRMS (EI): calcd. for $C_{11}H_{20}O_3P^{35}Cl$ $[M]^+$ 266.0839; found 266.0838.

(*S,R*)-3i: oil; 98% *ee* [HPLC conditions: Chiralcel AS-H column; hexane/*i*PrOH, 90:10; 0.5 mL/min; λ = 214 nm; t_R = 13.0 (major), 15.6 (minor) min]; $[\alpha]_D^{20}$ = –23.9 (*c* = 1.60, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.78–4.62 (m, 1 H, CH), 4.30–4.04 (m, 2 H, OCH_2), 2.49–2.21 (m, 2 H, CH_2 from C_4H_9), 2.08–1.92 (m, 1 H, one proton from CH_2), 1.74–1.45 (m, 3 H), 1.42–1.25 (m, 5 H), 0.99–0.85 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 145.2 (d, $J_{P,C}$ = 53.3 Hz), 126.5 (d, $J_{P,C}$ = 160.1 Hz), 82.4 (d, $J_{P,C}$ = 2.9 Hz), 63.3 (d, $J_{P,C}$ = 6.6 Hz), 29.5 (d, $J_{P,C}$ = 2.0 Hz), 25.8 (d, $J_{P,C}$ = 2.1 Hz), 25.2 (d, $J_{P,C}$ = 9.1 Hz), 22.4, 16.6 (d, $J_{P,C}$ = 5.4 Hz), 13.6, 8.0 ppm. MS (70 eV, EI): *m/z* (%) = 268 (1.65) $[M(^{37}Cl)]^+$, 266 (4.72) $[M(^{35}Cl)]^+$, 231 (28.77) $[M - Cl]^+$, 226 (33.28) $[M(^{37}Cl) - C_3H_6]^+$, 224 (100) $[M(^{35}Cl) - C_3H_6]^+$. HRMS (EI): calcd. for $C_{11}H_{20}O_3P^{35}Cl$ $[M]^+$ 266.0839; found 266.0839.

3-Butyl-4-chloro-2-ethoxy-2,5-dihydro-5-propyl-1,2-oxaphosphole 2-Oxide (*cis*-3j, *trans*-3j): The reaction of **1m** (82.2 mg, 0.3 mmol) and $CuCl_2·2H_2O$ (204.8 mg, 1.2 mmol) in toluene (2 mL) afforded *cis*-**3j** (34.6 mg, 41%) and *trans*-**3j** (40.0 mg, 48%).

***cis*-3j:** Oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.75–4.63 (m, 1 H, CH), 4.18–4.02 (m, 2 H, OCH_2), 2.50–2.20 (m, 2 H, CH_2 from C_4H_9), 2.00–1.82 (m, 1 H, one proton from CH_2), 1.74–1.26 (m, 10 H), 1.00–0.83 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 145.5 (d, $J_{P,C}$ = 52.8 Hz), 126.2 (d, $J_{P,C}$ = 158.3 Hz), 81.5 (d, $J_{P,C}$ = 2.8 Hz), 63.2 (d, $J_{P,C}$ = 6.6 Hz), 35.1 (d, $J_{P,C}$ = 2.5 Hz), 29.5 (d, $J_{P,C}$ = 2.5 Hz), 25.2 (d, $J_{P,C}$ = 9.8 Hz), 22.4, 17.1, 16.4 (d, $J_{P,C}$ = 6.7 Hz), 13.6 (d, $J_{P,C}$ = 6.6 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 282 (2.79) $[M(^{35}Cl)]^+$, 280 (8.38) $[M(^{35}Cl)]^+$, 245 (25.70) $[M - Cl]^+$, 240 (29.17) $[M(^{37}Cl) - C_3H_6]^+$, 238 (100) $[M(^{35}Cl) - C_3H_6]^+$. HRMS (EI): calcd. for $C_{12}H_{22}O_3P^{35}Cl$ $[M]^+$ 280.0995; found 280.0992.

***trans*-3j:** Oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.76–4.66 (m, 1 H, CH), 4.24–4.09 (m, 2 H, OCH_2), 2.50–2.20 (m, 2 H, CH_2 from C_4H_9), 2.00–1.85 (m, 1 H, one proton from CH_2), 1.62–1.28 (m, 10 H), 1.00–0.85 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 145.7 (d, $J_{P,C}$ = 53.4 Hz), 126.0 (d, $J_{P,C}$ = 159.6 Hz), 81.4 (d, $J_{P,C}$ = 3.5 Hz), 63.3 (d, $J_{P,C}$ = 6.9 Hz), 35.0 (d, $J_{P,C}$ = 2.0 Hz), 29.5 (d, $J_{P,C}$ = 1.7 Hz), 25.2 (d, $J_{P,C}$ = 9.8 Hz), 22.4, 17.5, 16.6 (d, $J_{P,C}$ = 5.6 Hz), 13.6 (d, $J_{P,C}$ = 4.3 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 282 (2.30) $[M(^{35}Cl)]^+$, 280 (6.02) $[M(^{35}Cl)]^+$, 245 (26.98) $[M^+ - Cl]$, 240 (32.48) $[M(^{37}Cl) - C_3H_6]^+$, 238 (100) $[M(^{35}Cl) - C_3H_6]^+$. HRMS (EI): calcd. for $C_{12}H_{22}O_3P^{35}Cl$ $[M]^+$ 280.0995; found 280.0993.

3-Butyl-4-chloro-2-ethoxy-5-ethyl-2,5-dihydro-1,2-oxaphosphole 2-Oxide [(*S,S*)-3j, (*S,R*)-3j]: The reaction of (*S*)-**1m** (82.3 mg, 0.3 mmol, *ee* > 99%), and $CuCl_2·2H_2O$ (204.9 mg, 1.2 mmol) in toluene (2 mL) afforded (*S,S*)-**3j** (36.2 mg, 43%) and (*S,R*)-**3j** (42.4 mg, 50%).

(*S,S*)-3j: Oil; 98% *ee* [HPLC conditions: Chiralcel AS-H column; hexane/*i*PrOH, 90:10; 0.5 mL/min; λ = 214 nm; t_R = 6.2 (minor), 6.6 (major) min]; $[\alpha]_D^{20}$ = +12.6 (*c* = 0.20, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 4.74–4.63 (m, 1 H, CH), 4.20–3.92 (m, 2 H, OCH_2), 2.50–2.19 (m, 2 H, CH_2 from C_4H_9), 2.00–1.80 (m, 1 H, one proton from CH_2), 1.71–1.20 (m, 10 H), 1.00–0.80 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 145.4 (d, $J_{P,C}$ =

52.8 Hz), 126.0 (d, $J_{P,C}$ = 158.1 Hz), 81.4 (d, $J_{P,C}$ = 2.8 Hz), 63.0 (d, $J_{P,C}$ = 7.2 Hz), 35.0 (d, $J_{P,C}$ = 2.5 Hz), 29.4 (d, $J_{P,C}$ = 1.7 Hz), 25.1 (d, $J_{P,C}$ = 9.3 Hz), 22.3, 17.0, 16.3 (d, $J_{P,C}$ = 6.1 Hz), 13.5 (d, $J_{P,C}$ = 6.2 Hz) ppm. MS (70 eV, EI): *m*/*z* (%) = 282 (1.49) [M(^{37}Cl)]$^+$, 280 (3.96) [M(^{35}Cl)]$^+$, 245 (26.30) [M – Cl]$^+$, 240 (34.35) [M(^{37}Cl) – C_3H_6]$^+$, 238 (100) [M(^{35}Cl) – C_3H_6]$^+$. HRMS (EI): calcd. for $C_{12}H_{22}O_3P^{35}Cl$ [M]$^+$ 280.0995; found 280.0999.

(*S*,*R*)-3j: Oil; 98% *ee* [HPLC conditions: Chiralcel AS-H column; hexane/*i*PrOH, 90:10; 0.5 mL/min; λ = 214 nm; t_R = 10.8 (major), 13.7 (minor) min]; $[a]_D^{20}$ = –36.8 (*c* = 0.22, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.78–4.64 (m, 1 H, CH), 4.28–4.04 (m, 2 H, OCH_2), 2.48–2.21 (m, 2 H, CH_2 from C_4H_9), 1.99–1.85 (m, 1 H, one proton from CH_2), 1.63–1.27 (m, 10 H), 1.00–0.85 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 145.6 (d, $J_{P,C}$ = 53.3 Hz), 125.9 (d, $J_{P,C}$ = 160.4 Hz), 81.3 (d, $J_{P,C}$ = 3.6 Hz), 63.2 (d, $J_{P,C}$ = 6.7 Hz), 34.9 (d, $J_{P,C}$ = 0.8 Hz), 29.4 (d, $J_{P,C}$ = 2.6 Hz), 25.1 (d, $J_{P,C}$ = 9.8 Hz), 22.3, 17.4, 16.5 (d, $J_{P,C}$ = 5.4 Hz), 13.5 (d, $J_{P,C}$ = 4.2 Hz) ppm. MS (70 eV, EI): *m*/*z* (%) = 282 (1.97) [M-(^{37}Cl)]$^+$, 280 (5.36) [M(^{35}Cl)]$^+$, 245 (31.09) [M – Cl]$^+$, 240 (34.41) [M(^{37}Cl) – C_3H_6]$^+$, 238 (100) [M$^+$(^{35}Cl) – C_3H_6]. HRMS (EI): calcd. for $C_{12}H_{22}O_3P^{35}Cl$ [M]$^+$ 280.0995; found 280.1001.

4-Chlorol-2-ethoxy-5-ethyl-2,5-dihydro-3-pheny-1,2-oxaphosphole 2-Oxide (*cis*-3k, *trans*-3k): The reaction of **1n** (84.1 mg, 0.3 mmol), and $CuCl_2{\cdot}2H_2O$ (204.5 mg, 1.2 mmol) in toluene (2 mL) afforded *cis*-**3k** (34.2 mg, 40%) and *trans*-**3k** (36.0 mg, 42%).

***cis*-3k:** White solid; m.p. 76–77 °C (petroleum ether/ethyl acetate). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82–7.68 (m, 2 H, 2 × Ph-H), 7.50–7.32 (m, 3 H, 3 × Ph-H), 4.92–4.78 (m, 1 H, CH), 4.20–3.98 (m, 2 H, OCH_2), 2.21–2.04 (m, 1 H, one proton from CH_2), 1.94–1.76 (m, 1 H, one proton from CH_2), 1.22 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3), 1.04 (t, *J* = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 143.6 (d, $J_{P,C}$ = 50.3 Hz), 129.3 (d, $J_{P,C}$ = 10.6 Hz), 128.8 (d, $J_{P,C}$ = 10.2 Hz), 128.7, 128.2 (d, $J_{P,C}$ = 6.9 Hz), 125.2 (d, $J_{P,C}$ = 159.7 Hz), 82.5 (d, $J_{P,C}$ = 2.9 Hz), 63.7 (d, $J_{P,C}$ = 6.9 Hz), 26.0 (d, $J_{P,C}$ = 3.2 Hz), 16.3 (d, $J_{P,C}$ = 6.2 Hz), 7.8 ppm. MS (70 eV, EI): *m*/*z* (%) = 288 [M$^+$(^{37}Cl), 2.88], 286 [M$^+$(^{35}Cl), 8.65], 251 (22.52) [M$^+$ – Cl], 102 (100). $C_{13}H_{16}ClO_3P$ (286.69): calcd. C 54.46, H 5.63; found C 54.46, H 5.58.

***trans*-3k:** Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78–7.66 (m, 2 H, 2 × Ph-H), 7.48–7.32 (m, 3 H, 3 × Ph-H), 4.92–4.79 (m, 1 H, CH), 4.30–4.03 (m, 2 H, OCH_2), 2.22–2.04 (m, 1 H, one proton from CH_2), 1.88–1.70 (m, 1 H, one proton from CH_2), 1.22 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.04 (t, *J* = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 143.8 (d, $J_{P,C}$ = 51.3 Hz), 129.2, 129.0 (d, $J_{P,C}$ = 10.1 Hz), 128.6, 128.2 (d, $J_{P,C}$ = 6.5 Hz), 125.4 (d, $J_{P,C}$ = 161.7 Hz), 82.4 (d, $J_{P,C}$ = 2.6 Hz), 63.9 (d, $J_{P,C}$ = 6.9 Hz), 26.2 (d, $J_{P,C}$ = 1.9 Hz), 16.4 (d, $J_{P,C}$ = 5.2 Hz), 8.2 ppm. MS (70 eV, EI): *m*/*z* (%) = 288 (2.88) [M(^{37}Cl)]$^+$, 286 (10.13) [M(^{35}Cl)]$^+$, 251 (14.84) [M – Cl]$^+$, 43 (100). HRMS (EI): calcd. for $C_{13}H_{16}O_3P^{35}Cl$ [M]$^+$ 286.0526; found 286.0528.

4-Chloro-2-ethoxy-5-ethyl-2,5-dihydro-3-phenyl-1,2-oxaphosphole 2-Oxide [(*S*,*S*)-3k, (*S*,*R*)-3k]: The reaction of (S_a)-(–)-**1n** (84.3 mg, 0.3 mmol, *ee* = 96%), and $CuCl_2{\cdot}2H_2O$ (204.5 mg, 1.2 mmol) in toluene (2 mL) afforded (*S*,*S*)-3**k** (37.7 mg, 44%) and (*S*,*R*)-**3k** (38.9 mg, 45%).

(*S*,*S*)-3k: White solid; m.p. 85–86 °C (petroleum ether/ethyl acetate); 95% *ee* [HPLC conditions: Chiralcel AS-H column; hexane/*i*PrOH, 90:10; 0.5 mL/min; λ = 214 nm; t_R = 9.0 (minor), 11.8 (major) min]; $[a]_D^{20}$ = +12.2 (*c* = 1.70, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.1 Hz, 2 H, 2 × Ph-H), 7.51–7.32 (m, 3 H, 3 × Ph-H), 4.92–4.81 (m, 1 H, CH), 4.21–4.00 (m, 2 H, OCH_2), 2.22–2.05 (m, 1 H, one proton from CH_2), 1.95–1.78 (m, 1 H, one proton from CH_2), 1.23 (t, *J* = 7.1 Hz, 3 H, OCH_2CH_3), 1.05 (t, *J* = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 143.6 (d, $J_{P,C}$ = 50.3 Hz), 129.3 (d, $J_{P,C}$ = 1.0 Hz), 128.8 (d, $J_{P,C}$ = 10.0 Hz), 128.7, 128.2 (d, $J_{P,C}$ = 6.8 Hz), 125.2 (d, $J_{P,C}$ = 159.8 Hz), 82.5 (d, $J_{P,C}$ = 2.9 Hz), 63.7 (d, $J_{P,C}$ = 6.8 Hz), 26.0 (d, $J_{P,C}$ = 2.5 Hz), 16.3 (d, $J_{P,C}$ = 6.1 Hz), 7.8 ppm. MS (70 eV, EI): *m*/*z* (%) = 288 (12.37) [M$^+$(^{37}Cl)], 286 (37.01) [M$^+$(^{35}Cl)], 251 (84.15) [M$^+$ – Cl], 223 (100). $C_{13}H_{16}ClO_3P$ (286.69): calcd. C 54.46, H 5.63; found C 54.46, H 5.58.

(*S*,*R*)-4k: Oil; 94% *ee* [HPLC conditions: Chiralcel AS-H column; hexane/*i*PrOH, 90:10; 0.5 mL/min; λ = 214 nm; t_R = 15.0 (major), 19.8 (minor) min]; $[a]_D^{20}$ = –84.9 (*c* = 1.78, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80–7.60 (m, 2 H, 2 × Ph-H), 7.50–7.30 (m, 3 H, 3 × Ph-H), 4.93–4.78 (m, 1 H, CH), 4.30–4.03 (m, 2 H, OCH_2), 2.22–2.05 (m, 1 H, one proton from CH_2), 1.90–1.70 (m, 1 H, one proton from CH_2), 1.22 (t, *J* = 7.2 Hz, 3 H, OCH_2CH_3), 1.04 (t, *J* = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 143.8 (d, $J_{P,C}$ = 50.7 Hz), 129.2 (d, $J_{P,C}$ = 1.1 Hz), 128.9 (d, $J_{P,C}$ = 10.2 Hz), 128.6, 128.1 (d, $J_{P,C}$ = 6.5 Hz), 125.3 (d, $J_{P,C}$ = 161.6 Hz), 82.4 (d, $J_{P,C}$ = 2.7 Hz), 63.9 (d, $J_{P,C}$ = 6.4 Hz), 26.1 (d, $J_{P,C}$ = 1.6 Hz), 16.4 (d, $J_{P,C}$ = 5.2 Hz), 8.1 ppm. MS (70 eV, EI): *m*/*z* (%) = 288 (10.44) [M$^+$(^{37}Cl)], 286 (32.04) [M(^{35}Cl)]$^+$, 251 (72.15) [M – Cl]$^+$, 223 (100). HRMS (EI): calcd. for $C_{13}H_{16}O_3P^{35}Cl$ [M]$^+$ 286.0526; found 286.0534.

[$PdCl_2$(LB-Phos)$_2$]-Catalyzed Suzuki Cross-Coupling Reaction of 4-Halo-2-ethoxy-2,5-dihydro-1,2-oxaphosphole 2-Oxides with Phenylboronic Acids

3-Butyl-2-ethoxy-2,5-dihydro-5,5-dimethyl-4-phenyl-1,2-oxaphosphole 2-Oxide (4a); Typical Procedure: To a Schlenk tube containing K_2CO_3 (145.1 mg, 1.05 mmol) dried with a heat gun, were charged phenylboronic acid (91.5 mg, 0.75 mmol), [$PdCl_2$(LB-Phos)$_2$] (13.5 mg, 0.015 mmol), **3a** (80.0 mg, 0.3 mmol), and toluene (2 mL) sequentially under an Ar atmosphere. The mixture was stirred under reflux until the reaction was complete (ca. 5 h) (reaction monitored by TLC; petroleum ether/ethyl acetate, 3:1). The reaction mixture was allowed to cool to room temperature, H_2O (10 mL) and diethyl ether (10 mL) were added and the layers were separated. The organic layer was washed with brine (10 mL) and dried with anhydrous Na_2SO_4. After filtration and evaporation, the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane, 8:1:1; 40 cm long column) to afford **4a** (69.3 mg, 75%) as an oil.[11] ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.27 (m, 3 H, 3 × Ph-H), 7.11–6.98 (m, 2 H, 2 × Ph-H), 4.21–4.05 (m, 2 H, OCH_2), 2.18–1.83 (m, 2 H, CH_2 from C_4H_9), 1.50–1.25 (m, 11 H), 1.22–1.06 (m, 2 H, CH_2 from C_4H_9), 0.80–0.65 (m, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 161.1 (d, $J_{P,C}$ = 24.3 Hz), 133.8 (d, $J_{P,C}$ = 22.1 Hz), 128.4, 128.2, 127.8, 126.0 (d, $J_{P,C}$ = 155.7 Hz), 85.9 (d, $J_{P,C}$ = 8.6 Hz), 62.4 (d, $J_{P,C}$ = 6.9 Hz), 30.4 (d, $J_{P,C}$ = 2.3 Hz), 27.3 (d, $J_{P,C}$ = 2.3 Hz), 26.7 (d, $J_{P,C}$ = 1.5 Hz), 25.4 (d, $J_{P,C}$ = 12.4 Hz), 22.3, 16.5 (d, $J_{P,C}$ = 5.8 Hz), 13.5 ppm. MS (70 eV, EI): *m*/*z* (%) = 308 (2.45) [M]$^+$, 266 (15.19) [M – C_3H_6]$^+$, 43 (100).

2-Ethoxy-2,5-dihydro-5,5-dimethyl-3,4-diphenyl-1,2-oxaphosphole 2-Oxide (4b): The reaction of **3b** (80.0 mg, 0.3 mmol), and K_2CO_3 (145.1 mg, 1.05 mmol), $PhB(OH)_2$ (91.5 mg, 0.75 mmol), [$PdCl_2$(LB-Phos)$_2$] (13.5 mg, 0.015 mmol) in toluene (2 mL), afforded **4a** (76.8 mg, 78%) as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.24 (m, 5 H, 5 × Ph-H), 7.22–7.08 (m, 5 H, 5 × Ph-H), 4.28–4.05 (m, 2 H, OCH_2), 1.64 (s, 3 H, CH_3), 1.54 (s, 3 H, CH_3), 1.27 (t, *J* = 7.0 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 160.2 (d, $J_{P,C}$ = 23.0 Hz), 134.2 (d, $J_{P,C}$ = 20.9 Hz),

130.8 (d, $J_{P,C}$ = 13.1 Hz), 128.7, 128.6, 128.5 (d, $J_{P,C}$ = 2.0 Hz), 128.24, 128.21, 128.0 (d, $J_{P,C}$ = 1.0 Hz), 125.4 (d, $J_{P,C}$ = 158.6 Hz), 86.0 (d, $J_{P,C}$ = 7.8 Hz), 63.1 (d, $J_{P,C}$ = 6.4 Hz), 27.5 (d, $J_{P,C}$ = 3.7 Hz), 26.8 (d, $J_{P,C}$ = 2.6 Hz), 16.4 (d, $J_{P,C}$ = 5.8 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 328 (8.92) $[M]^+$, 313 (13.62) $[M - CH_3]^+$, 43 (100). HRMS (EI): calcd. for $C_{19}H_{21}O_3P$ $[M]^+$ 328.1228; found 328.1230.

3-Allyl-2-ethoxy-2,5-dihydro-5,5-dimethyl-4-phenyl-1,2-oxaphosphole 2-Oxide (4c): The reaction of **3c** (75.2 mg, 0.3 mmol), and K_2CO_3 (145.0 mg, 1.05 mmol), $PhB(OH)_2$ (91.6 mg, 0.75 mmol), $[PdCl_2(LB\text{-}Phos)_2]$ (13.6 mg, 0.015 mmol) in toluene (2 mL), afforded **4c** (48.1 mg, 55%) in oil.[11] ^1H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.31 (m, 3 H, 3 × Ph-H), 7.16–7.02 (m, 2 H, 2 × Ph-H), 5.86–5.63 (m, 1 H, CH), 5.10–4.90 (m, 2 H, $=CH_2$), 4.25–4.02 (m, 2 H, OCH_2), 2.99–2.62 (m, 2 H, CH_2), 1.47 (s, 3 H, CH_3), 1.45 (s, 3 H, CH_3), 1.34 (t, J = 7.2 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 161.9 (d, $J_{P,C}$ = 24.8 Hz), 133.8 (d, $J_{P,C}$ = 2.1 Hz), 133.5 (d, $J_{P,C}$ = 21.3 Hz), 128.49, 128.48, 127.8 (d, $J_{P,C}$ = 1.7 Hz), 124.1 (d, $J_{P,C}$ = 158.0 Hz), 116.9, 86.1 (d, $J_{P,C}$ = 8.3 Hz), 62.8 (d, $J_{P,C}$ = 6.6 Hz), 30.1 (d, $J_{P,C}$ = 12.7 Hz), 27.3 (d, $J_{P,C}$ = 2.7 Hz), 26.8 (d, $J_{P,C}$ = 2.0 Hz), 16.5 (d, $J_{P,C}$ = 6.1 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 292 (90.67) $[M]^+$, 277 (11.01) $[M - CH_3]^+$, 141 (100).

3-Butyl-2-ethoxy-5-ethyl-2,5-dihydro-4-phenyl-1,2-oxaphosphole 2-Oxide (*cis*-4d): The reaction of *cis*-**3i** (80.0 mg, 0.3 mmol), and K_2CO_3 (145.0 mg, 1.05 mmol), $PhB(OH)_2$ (91.5 mg, 0.75 mmol), $[PdCl_2(LB\text{-}Phos)_2]$ (13.6 mg, 0.015 mmol) in toluene (2 mL), afforded *cis*-**4d** (80.0 mg, 86%) as an oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.30 (m, 3 H, 3 × Ph-H), 7.14 (d, J = 7.2 Hz, 2 H, 2 × Ph-H), 5.12–5.00 (m, 1 H, CH), 4.22–4.04 (m, 2 H, OCH_2), 2.46–2.14 (m, 2 H, CH_2 from C_4H_9), 1.78–1.61 (m, 1 H, one proton from CH_2), 1.61–1.48 (m, 2 H), 1.48–1.15 (m, 6 H), 0.93–0.75 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 154.5 (d, $J_{P,C}$ = 26.5 Hz), 133.3 (d, $J_{P,C}$ = 22.2 Hz), 128.7, 128.6, 127.3, 126.2 (d, $J_{P,C}$ = 157.1 Hz), 82.9 (d, $J_{P,C}$ = 9.0 Hz), 62.4 (d, $J_{P,C}$ = 6.7 Hz), 30.5 (d, $J_{P,C}$ = 1.7 Hz), 26.7 (d, $J_{P,C}$ = 1.4 Hz), 25.3 (d, $J_{P,C}$ = 12.1 Hz), 22.5, 16.3 (d, $J_{P,C}$ = 6.2 Hz), 13.5, 8.2 ppm. MS (70 eV, EI): *m/z* (%) = 308 (13.66) $[M]^+$, 266 (100) $[M^+ - C_3H_6]$. HRMS (EI): calcd. for $C_{17}H_{25}O_3P$ $[M]^+$ 308.1541; found 308.1540.

3-Butyl-2-ethoxy-5-ethyl-2,5-dihydro-4-phenyl-1,2-oxaphosphole 2-Oxide (*trans*-4d): The reaction of *trans*-**3i** (80.0 mg, 0.3 mmol), and K_2CO_3 (145.1 mg, 1.05 mmol), $PhB(OH)_2$ (91.6 mg, 0.75 mmol), $[PdCl_2(LB\text{-}Phos)_2]$ (13.7 mg, 0.015 mmol) in toluene (2 mL), afforded *trans*-**4d** (77.8 mg, 84%) as an oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.29 (m, 3 H, 3 × Ph-H), 7.12 (d, J = 7.5 Hz, 2 H, 2 × Ph-H), 5.12–5.00 (m, 1 H, CH), 4.32–4.07 (m, 2 H, OCH_2), 2.43–2.09 (m, 2 H, CH_2 from C_4H_9), 1.75–1.43 (m, 3 H), 1.43–1.19 (m, 6 H), 0.92–0.75 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 154.9 (d, $J_{P,C}$ = 26.7 Hz), 133.5 (d, $J_{P,C}$ = 23.0 Hz), 128.7, 127.4 (d, $J_{P,C}$ = 1.2 Hz), 126.3 (d, $J_{P,C}$ = 159.0 Hz), 83.1 (d, $J_{P,C}$ = 9.1 Hz), 62.6 (d, $J_{P,C}$ = 6.3 Hz), 30.7 (d, $J_{P,C}$ = 2.6 Hz), 26.6 (d, $J_{P,C}$ = 1.1 Hz), 25.3 (d, $J_{P,C}$ = 12.7 Hz), 22.6, 16.6 (d, $J_{P,C}$ = 5.3 Hz), 13.6, 8.3 ppm. MS (70 eV, EI): *m/z* (%) = 308 (30.31) $[M]^+$, 266 (100) $[M - C_3H_6]^+$. HRMS (EI): calcd. for $C_{17}H_{25}O_3P$ $[M]^+$ 308.1541; found 308.1539.

3-Butyl-2-ethoxy-2,5-dihydro-4-phenyl-5-propyl-1,2-oxaphosphole 2-Oxide (*cis*-4e): The reaction of *cis*-**3j** (84.3 mg, 0.3 mmol), and K_2CO_3 (145.0 mg, 1.05 mmol), $PhB(OH)_2$ (91.5 mg, 0.75 mmol), $[PdCl_2(LB\text{-}Phos)_2]$ (13.6 mg, 0.015 mmol) in toluene (2 mL), afforded *cis*-**4e** (86.4 mg, 89%) as an oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.48–7.30 (m, 3 H, 3 × Ph-H), 7.20–7.03 (m, 2 H, 2 × Ph-H), 5.13–4.99 (m, 1 H, CH), 4.21–4.01 (m, 2 H, OCH_2), 2.42–2.12 (m, 2 H, CH_2 from C_4H_9), 1.65–1.13 (m, 11 H), 0.89–0.69 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 155.1 (d, $J_{P,C}$ = 26.8 Hz), 133.5 (d, $J_{P,C}$ = 21.6 Hz), 128.8, 127.5, 125.9 (d, $J_{P,C}$ = 157.2 Hz), 82.1 (d, $J_{P,C}$ = 9.5 Hz), 62.6 (d, $J_{P,C}$ = 6.8 Hz), 36.1 (d, $J_{P,C}$ = 2.6 Hz), 30.6 (d, $J_{P,C}$ = 2.0 Hz), 25.4 (d, $J_{P,C}$ = 13.0 Hz), 22.6, 17.8, 16.5 (d, $J_{P,C}$ = 5.9 Hz), 13.6 (d, $J_{P,C}$ = 6.0 Hz) ppm. MS (70 eV, EI): *m/z* (%) = 322 (13.84) $[M]^+$, 280 (100) $[M - C_3H_6]^+$. HRMS (EI): calcd. for $C_{18}H_{27}O_3P$ $[M]^+$ 322.1698; found 322.1706.

2-Ethoxy-2,5-dihydro-5,5-dimethyl-3,4-diphenyl-1,2-oxaphosphole 2-Oxide (*cis*-4f): The reaction of *cis*-**3k** (86.0 mg, 0.3 mmol), and K_2CO_3 (145.0 mg, 1.05 mmol), $PhB(OH)_2$ (91.5 mg, 0.75 mmol), $[PdCl_2(LB\text{-}Phos)_2]$ (13.6 mg, 0.015 mmol) in toluene (2 mL), afforded *cis*-**4f** (89.6 mg, 91%) as a white solid; m.p. 93–94 °C (petroleum ether/ethyl acetate). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.19 (m, 8 H, 8 × Ph-H), 7.19–7.08 (m, 2 H, 2 × Ph-H), 5.40–5.25 (m, 1 H, CH), 4.20–3.94 (m, 2 H, OCH_2), 1.90–1.69 (m, 1 H, one proton from CH_2), 1.65–1.45 (m, 1 H, one proton from CH_2), 1.15 (t, J = 7.2 Hz, 3 H, CH_3), 0.99 (t, J = 7.2 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 153.8 (d, $J_{P,C}$ = 25.6 Hz), 133.1 (d, $J_{P,C}$ = 21.1 Hz), 130.9 (d, $J_{P,C}$ = 12.7 Hz), 129.1, 128.9, 128.7 (d, $J_{P,C}$ = 6.4 Hz), 128.5, 128.2, 127.9, 125.7 (d, $J_{P,C}$ = 161.7 Hz), 83.0 (d, $J_{P,C}$ = 8.1 Hz), 63.3 (d, $J_{P,C}$ = 6.4 Hz), 26.8 (d, $J_{P,C}$ = 2.3 Hz), 16.3 (d, $J_{P,C}$ = 5.1 Hz), 8.4 ppm. MS (70 eV, EI): *m/z* (%) = 328 (12.29) $[M]^+$, 299 (100) $[M^+ - C_2H_4]$. $C_{19}H_{21}O_3P$ (328.35): calcd. C 69.50, H 6.45; found C 69.33, H 6.43.

3-Butyl-2-ethoxy-5-ethyl-2,5-dihydro-4-phenyl-1,2-oxaphosphole 2-Oxide [(*S*,*S*)-4d]: The reaction of (*S*,*S*)-**3i** (80.1 mg, 0.3 mmol, *ee* = 98%), and K_2CO_3 (145.1 mg, 1.05 mmol), $PhB(OH)_2$ (91.5 mg, 0.75 mmol), $[PdCl_2(LB\text{-}Phos)_2]$ (13.5 mg, 0.015 mmol) in toluene (2 mL), afforded (*S*,*S*)-**4d** (87.2 mg, 94%) as an oil. 98% *ee* [HPLC conditions: Chiralcel AS-H column; hexane/*i*PrOH, 80:20; 0.5 mL/min; λ = 230 nm; t_R = 9.7 (minor), 12.9 (major) min]; $[\alpha]_D^{20}$ = +142.9 (c = 2.64, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.28 (m, 3 H, 3 × Ph-H), 7.18–7.05 (m, 2 H, 2 × Ph-H), 5.10–4.99 (m, 1 H, CH), 4.20–4.00 (m, 2 H, OCH_2), 2.42–2.14 (m, 2 H, CH_2 from C_4H_9), 1.74–1.61 (m, 1 H, one proton from CH_2), 1.61–1.48 (m, 2 H, CH_2 from C_4H_9), 1.48–1.15 (m, 6 H), 0.93–0.75 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 154.6 (d, $J_{P,C}$ = 26.2 Hz), 133.4 (d, $J_{P,C}$ = 21.6 Hz), 128.74, 128.70, 127.4, 126.3 (d, $J_{P,C}$ = 157.3 Hz), 83.0 (d, $J_{P,C}$ = 8.7 Hz), 62.5 (d, $J_{P,C}$ = 6.4 Hz), 30.6 (d, $J_{P,C}$ = 2.3 Hz), 26.8 (d, $J_{P,C}$ = 2.0 Hz), 25.4 (d, $J_{P,C}$ = 13.0 Hz), 22.6, 16.4 (d, $J_{P,C}$ = 5.7 Hz), 13.5, 8.3 ppm. MS (70 eV, EI): *m/z* (%) = 308 (14.94) $[M]^+$, 266 (100) $[M - C_3H_6]^+$. HRMS (EI): calcd. for $C_{17}H_{25}O_3P$ $[M]^+$ 308.1541; found 308.1544.

3-Butyl-2-ethoxy-2,5-dihydro-4-phenyl-5-propyl-1,2-oxaphosphole 2-Oxide [(*S*,*S*)-4e]: The reaction of (*S*,*S*)-**3j** (84.0 mg, 0.3 mmol, *ee* = 98%), and K_2CO_3 (145.1 mg, 1.05 mmol), $PhB(OH)_2$ (91.5 mg, 0.75 mmol), $[PdCl_2(LB\text{-}Phos)_2]$ (13.7 mg, 0.015 mmol) in toluene (2 mL), afforded (*S*,*S*)-**4e** (86.7 mg, 90%) as an oil. 98% *ee* [HPLC conditions: Chiralcel AS-H column; hexane/*i*PrOH, 80:20; 0.5 mL/min; λ = 230 nm; t_R = 12.8 (minor), 14.8 (major) min]; $[\alpha]_D^{20}$ = +136.2 (c = 1.00, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.29 (m, 3 H, 3 × Ph-H), 7.11 (d, J = 6.9 Hz, 2 H, 2 × Ph-H), 5.12–4.98 (m, 1 H, CH), 4.20–4.00 (m, 2 H, OCH_2), 2.42–2.10 (m, 2 H, CH_2 from C_4H_9), 1.61–1.12 (m, 11 H), 0.85–0.69 (m, 6 H) ppm. ^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 155.1 (d, $J_{P,C}$ = 26.6 Hz), 133.5 (d, $J_{P,C}$ = 23.0 Hz), 128.8, 127.5, 126.0 (d, $J_{P,C}$ = 157.2 Hz), 82.1 (d, $J_{P,C}$ = 9.2 Hz), 62.6 (d, $J_{P,C}$ = 7.1 Hz), 36.1 (d, $J_{P,C}$ = 2.2 Hz), 30.6 (d, $J_{P,C}$ = 2.3 Hz), 25.4 (d, $J_{P,C}$ = 12.4 Hz), 22.6, 17.8, 16.5 (d, $J_{P,C}$ = 6.4 Hz), 13.6 (d, $J_{P,C}$ = 5.3 Hz) ppm. MS

(70 eV, EI): *m/z* (%) = 322 (12.77) $[M]^+$, 280 (100) $[M - C_3H_6]^+$. HRMS (EI): calcd. for $C_{18}H_{27}O_3P$ $[M]^+$ 322.1698; found 322.1696.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra of all the products.

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[15] Crystal data for compound *cis*-**3k**: $C_{13}H_{16}ClO_3P$; *MW* = 286.68; orthorhombic; space group *P*2(1)2(1)2(1); final *R* indices $[I>2\sigma(I)]$, *R*1 = 0.0355, *wR*2 = 0.1015, *R* indices (all data) *R*1 = 0.0368, *wR*2 = 0.1032; *a* = 6.0093(2) Å, *b* = 13.5764(5) Å, *c* = 17.8709(7) Å, *α* = 90°, *β* = 90°, *γ* = 90°; *V* = 1457.99(9) $Å^3$; *T* = 296(2) K; *Z* = 4; reflections collected/unique 16841/2567 (R_{int} = 0.0236), number of observations $[I>2\sigma(I)]$ 2178, parameters: 164. Supplementary crystallographic data have been deposited at the Cambridge Crystallographic Data Center. CCDC-862988 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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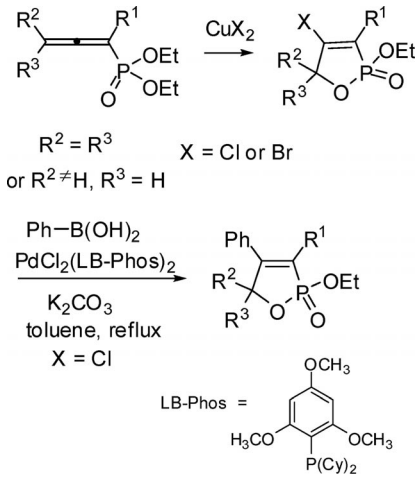
Halocyclization

CuX_2-mediated direct halocyclization of diethyl 1,2-allenylphosphonates was developed to afford 4-halo-2,5-dihydro-1,2-oxaphosphole 2-oxides. The efficiency of axial-to-central chirality transfer and subsequent Suzuki cross-coupling of the resulting vinylic chlorides with dicyclohexyl(2,4,6-trimethoxyphenyl)phosphane (LB-Phos) as the ligand were also investigated.



Keywords: Synthetic methods / Cyclization / Cross-coupling / Chirality / Allenes / Phosphorous heterocycles

