Supporting Information

for

Copper-Mediated Reaction of Oxazirconacyclopentenes with Dichlorophenylphosphine: A New Pathway for the Formation of 1,2-Oxaphosphole Derivatives

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Table of Contents

General Considerations .................................................................S2
Experimental Procedures .............................................................S2
Copies of $^1$H $^{13}$C NMR and $^{31}$P Spectra .............................................S11
General Considerations

All reactions were carried out with standard Schlenk techniques under nitrogen atmosphere. THF, toluene was distilled and stored over sodium. All materials were commercially available and were used without further purification. Thin-layer chromatography (TLC) was carried out on silica gel or aluminium oxide purchased from commercial sources, and components were located by observation under UV light. $^1$H NMR $^{13}$C and $^{31}$P NMR spectra were recorded on NMR spectrometer at ambient temperature with CDCl$_3$ as the solvent and TMS as internal standard. GC-MS spectra were recorded on Hewlett Packard GC-MS system. The reaction progress was monitored by GC.

Experimental Procedures

Typical procedure for the synthesis of 2,5-dihydro-1,2-oxaphosphole

To a solution of Cp$_2$ZrCl$_2$ (176 mg, 0.6 mmol) in THF (3 mL) was added EtMgCl (2.0 M THF solution, 0.6 mL, 1.2 mmol) at -78 °C, and the mixture was stirred for 1 h at -78 °C. Then 4-octyne (77 μL, 0.5 mmol) was added and the mixture was stirred for 1 h at 0 °C. 3-pentone (60 μL, 0.5 mmol) was added and the mixture was kept at 50 °C for 3 h. When the solution was cooled to 0 °C, CuCl (49 mg, 0.5 mmol) was added and the mixture was kept at 0 °C for 10 min. Dichlorophenylphosphine (82 μL, 0.6 mmol) was added and the mixture was kept at 50 °C overnight. HCl (1 M) (1 mL) was added to quench the reaction. Then sulfide powder (32 mg, 1 mmol) was added and mixture was stirred for 1 h. Finally, ethyl acetate was used to extract and evaporated in vacuo and the residue was purified by column chromatography on Al$_2$O$_3$ (PE : EA =50 : 1) to afford product 3a.

![Chemical Structure](image)

5,5-Diethyl-2-phenyl-3,4-dipropyl-5H-1,2-oxaphosphole 2-sulfide (3a)

The crude product was purified by column chromatography on Al$_2$O$_3$ with petroleum: ethyl acetate = 50 : 1 to give the desired product as yellow oil 139.4 mg, isolated yield was 84%. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.97 – 7.82 (m, 2H), 7.52 –
7.40 (m, 3H), 2.47 – 2.29 (m, 1H), 2.29 – 2.10 (m, 2H), 2.11 – 1.95 (m, 2H), 1.89 (td, 
\(J = 14.4, 7.3\) Hz, 1H), 1.79 – 1.63 (m, 2H), 1.63 – 1.47 (m, 2H), 1.48 – 1.32 (m, 2H), 
1.08 – 0.96 (m, 6H), 0.91 (t, \(J = 7.3\) Hz, 3H), 0.82 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR 
(CDCl\(_3\), 100 MHz) 157.0 (d, \(J = 17.8\) Hz), 135.2 (d, \(J = 102.1\) Hz), 131.8, 131.4 (d, \(J = 12.5\) Hz), 130.7 (d, \(J = 88.5\) Hz), 128.2 (d, \(J = 13.4\) Hz), 98.6, 32.1, 30.0 (d, \(J = 16.2\) Hz), 29.7, 28.1 (d, \(J = 14.5\) Hz), 22.4, 15.1, 14.5, 9.0, 8.4. \(^{31}\)P NMR (80 MHz, CDCl\(_3\), 85\% H\(_3\)PO\(_4\)) \(\delta\) 103.5; GC-MS (EI, m/z): 336; HRMS calcd for C\(_{19}\)H\(_{30}\)OPS\(^+\) 337.1755, 
found 337.1753.

3,4,5,5-Tetraethyl-2-phenyl-5H-1,2-oxaphosphole 2-sulfide (3b)

The crude product was purified by column chromatography on Al\(_2\)O\(_3\) with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 110.5 mg, 
isolated yield was 72%. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.95 – 7.89 (m, 2H), 7.54 – 
7.40 (m, 3H), 2.55 – 2.38 (m, 1H), 2.38 – 2.22 (m, 2H), 2.23 – 2.06 (m, 1H), 2.13 – 
1.96 (m, 1H), 1.96 – 1.89 (m, 1H), 1.81 – 1.63 (m, 2H), 1.19 (t, \(J = 7.6\) Hz, 3H), 1.02 
(t, \(J = 6.4\) Hz, 3H), 1.00 (t, \(J = 6.4\) Hz, 3H), 0.94 (t, \(J = 7.4\) Hz, 3H); \(^{13}\)C NMR 
(CDCl\(_3\), 100 MHz) 157.9 (d, \(J = 17.1\) Hz), 135.3 (d, \(J = 101.8\) Hz), 131.9, 131.7 (d, \(J = 89.1\) Hz), 131.5 (d, \(J = 12.5\) Hz), 128.3 (d, \(J = 13.5\) Hz), 98.7, 32.1, 29.8, 20.6 (d, \(J = 16.8\) Hz), 18.9 (d, \(J = 14.7\) Hz), 14.1, 13.5, 9.0, 8.5; \(^{31}\)P NMR (80 MHz, CDCl\(_3\), 85\% H\(_3\)PO\(_4\)) \(\delta\) 100.8; GC-MS (EI, m/z): 308. HRMS calcd for C\(_{17}\)H\(_{26}\)OPS\(^+\) 309.1442, 
found 309.1446.

3,4-Dibutyl-5,5-diethyl-2-phenyl-5H-1,2-oxaphosphole 2-sulfide (3c)

The crude product was purified by column chromatography on Al\(_2\)O\(_3\) with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 133.1 mg, 
isolated yield was 73%. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.90 – 7.63 (m, 2H), 7.48 –
7.27 (m, 3H), 2.44 – 2.27 (m, 1H), 2.25 – 2.03 (m, 2H), 2.05 – 1.89 (m, 2H), 1.84 (td, \( J = 14.5, 7.3 \) Hz, 1H), 1.72 – 1.52 (m, 2H), 1.52 – 1.09 (m, 8H), 0.98 – 0.82 (m, 9H), 0.70 (t, \( J = 7.2 \) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) 157.1 (d, \( J = 18.0 \) Hz), 135.2 (d, \( J = 102.1 \) Hz), 131.8, 131.5 (d, \( J = 12.5 \) Hz), 130.7 (d, \( J = 88.8 \) Hz), 128.2 (d, \( J = 13.4 \) Hz), 98.6, 32.2, 31.1, 29.7, 27.5 (d, \( J = 16.2 \) Hz), 25.6 (d, \( J = 14.5 \) Hz), 23.6, 23.0, 13.9, 13.7, 9.0, 8.4; \(^{31}\)P NMR (80 MHz, CDCl\(_3\), 85% H\(_3\)PO\(_4\)) \( \delta 101.5 \); GC-MS (EI, m/z): 364. HRMS calcd for C\(_{21}\)H\(_{34}\)OPS\(^+\) 365.2068, found 365.2065.

**5,5-Diethyl-2,3,4-triphenyl-5H-1,2-oxaphosphole 2-sulfide (3d)**

The crude product was purified by column chromatography on Al\(_2\)O\(_3\) with petroleum : ethyl acetate = 25 : 1 to give the desired product as yellow oil 109.0 mg, isolated yield was 54%. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta 7.94 – 7.78 \) (m, 2H), 7.47 – 7.30 (m, 3H), 7.28 – 7.17 (m, 5H), 7.15 – 7.08 (m, 2H), 7.06 – 6.94 (m, 3H), 2.01 – 1.86 (m, 3H), 1.75 – 1.63 (m, 1H), 1.16 (t, \( J = 7.4 \) Hz, 3H), 0.92 (t, \( J = 7.4 \) Hz, 3H); \(^{13}\)C NMR (CDCl\(_3\), 100 MHz) 157.3 (d, \( J = 19.5 \) Hz), 135.1 (d, \( J = 91.9 \) Hz), 134.5 (d, \( J = 4.3 \) Hz), 133.5 (d, \( J = 88.4 \) Hz), 132.1, 131.8 (d, \( J = 16.8 \) Hz), 131.3 (d, \( J = 12.4 \) Hz), 129.4, 129.4, 128.8, 128.6 (d, \( J = 12.1 \) Hz), 128.4 (d, \( J = 13.7 \) Hz), 128.2, 127.9, 98.7, 31.9, 30.1, 9.3, 8.8; \(^{31}\)P NMR (80 MHz, CDCl\(_3\), 85% H\(_3\)PO\(_4\)) \( \delta 95.6 \); GC-MS (EI, m/z): 404. HRMS calcd for C\(_{25}\)H\(_{26}\)POS\(^+\) 405.1442, found 405.1440.

**5,5-Diethyl-2-phenyl-3,4-di-p-tolyl-5H-1,2-oxaphosphole 2-sulfide (3e)**

The crude product was purified by column chromatography on Al\(_2\)O\(_3\) with petroleum : ethyl acetate = 25 : 1 to give the desired product as yellow oil 103.7 mg, isolated yield was 48%. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \( \delta 8.00 – 7.88 \) (m, 2H), 7.51 – 7.38 (m, 3H), 7.16 (d, \( J = 7.7 \) Hz, 2H), 7.14 – 7.06 (m, 4H), 6.88 (d, \( J = 7.8 \) Hz, 2H), 2.32 (s, 3H), 2.17 (s, 3H), 2.04 – 1.94 (m, 2H), 1.89 – 1.62 (m, 2H), 1.22 (t, \( J = 7.3 \)
Hz, 3H), 0.97 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 156.7 (d, $J = 19.7$ Hz), 138.4, 137.7, 135.2 (d, $J = 104.1$ Hz), 132.8 (d, $J = 89.0$ Hz), 131.9, 131.7 (d, $J = 17.7$ Hz), 131.3 (d, $J = 12.2$ Hz), 129.8 (d, $J = 18.1$ Hz), 129.5, 129.3, 129.2, 129.0, 128.8 (d, $J = 6.5$ Hz), 128.6, 128.4 (d, $J = 13.6$ Hz), 98.8, 77.5, 76.8, 31.9, 30.2, 21.4, 21.3, 9.3, 8.8; $^{31}$P NMR (80 MHz, CDCl$_3$, 85% H$_3$PO$_4$) $\delta$ 98.5; GC-MS (EI, m/z): 432. HRMS calcd for C$_{27}$H$_{30}$OPS$^+$ 433.1755, found 433.1756.

3,4-Bis(4-bromophenyl)-5,5-diethyl-2-phenyl-5H-1,2-oxaphosphole 2-sulfide (3f)

The crude product was purified by column chromatography on Al$_2$O$_3$ with petroleum : ethyl acetate = 25 : 1 to give the desired product as white solid 126.5 mg, isolated yield was 45%. M.P. 71-73 °C. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.95 – 7.85 (m, 2H), 7.52 – 7.39 (m, 5H), 7.22 (d, $J = 8.5$ Hz, 2H), 7.13 (d, $J = 7.9$ Hz, 1H), 7.05 (d, $J = 8.4$ Hz, 2H), 2.09 – 1.88 (m, 3H), 1.72 (dq, $J = 14.4$, 7.2 Hz, 1H), 1.19 (t, $J = 7.4$ Hz, 3H), 1.00 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 156.4 (d, $J = 19.5$ Hz), 134.4 (d, $J = 95.4$ Hz), 133.4 (d, $J = 83.7$ Hz), 133.1 (d, $J = 11.8$ Hz), 132.4 (d, $J = 2.6$ Hz), 132.2, 131.7, 131.3 (d, $J = 12.4$ Hz), 130.9 (d, $J = 5.2$ Hz), 130.6 (d, $J = 13.9$ Hz), 130.3, 128.7, 128.5, 123.2, 122.7, 98.6, 31.8, 30.1, 9.3, 8.8; $^{31}$P NMR (80 MHz, CDCl$_3$, 85% H$_3$PO$_4$) $\delta$ 99.2; GC-MS (EI, m/z): 562. HRMS calcd for C$_{25}$H$_{24}$Br$_2$OPS$^+$ 560.9652, found 560.9658.

4,5,5-Triethyl-2,3-diphenyl-5H-1,2-oxaphosphole 2-sulfide (3g)

The crude product was purified by column chromatography on Al$_2$O$_3$ with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 112.1 mg, isolated yield was 63%. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.99 – 7.81 (m, 2H), 7.47 – 7.38 (m, 3H), 7.38 – 7.28 (m, 3H), 7.13 (d, $J = 7.6$ Hz, 2H), 2.27 – 2.11 (m, 1H), 2.02 – 1.91 (m, 2H), 1.79 – 1.72 (m, 2H), 1.61 (dt, $J = 21.8$, 7.2 Hz, 1H), 1.13 (t, $J = 7.3$ Hz, 3H).
Hz, 3H), 0.87 (t, J = 7.3 Hz, 3H), 0.75 (t, J = 7.6 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 156.4 (d, J = 20.0 Hz), 135.1 (d, J = 85.5 Hz), 135.0 (d, J = 103.1 Hz), 134.5 (d, J = 18.4 Hz), 132.08 (s), 131.7 (d, J = 12.6 Hz), 128.8, 128.5, 128.4 (d, J = 14.6 Hz), 128.0, 98.4, 31.9, 29.0, 19.5 (d, J = 14.2 Hz), 14.2, 9.5, 8.5; $^{31}$P NMR (80 MHz, CDCl$_3$, 85% H$_3$PO$_4$) δ 101.2; GC-MS (EI, m/z): 356. HRMS calcd for C$_{21}$H$_{26}$OPS$^+$ 357.1442, found 357.1443.

5,5-Diethyl-4-methyl-2-phenyl-3-(trimethylsilyl)-5H-1,2-oxaphosphole 2-sulfide (3h)

The crude product was purified by column chromatography on Al$_2$O$_3$ with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 121.3 mg, isolated yield was 72%. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.88 – 7.70 (m, 2H), 7.45 – 7.30 (m, 3H), 1.94 (d, J = 2.6 Hz, 3H), 1.92 – 1.83 (m, 1H), 1.77 (dt, J = 14.8, 7.3 Hz, 1H), 1.68 – 1.54 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H), 0.76 (t, J = 7.4 Hz, 3H), 0.09 (s, 9H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 169.0 (d, J = 5.4 Hz), 135.8 (d, J = 101.5 Hz), 131.7, 131.4 (d, J = 12.6 Hz), 129.7 (d, J = 50.3 Hz), 128.1 (d, J = 13.3 Hz), 100.4, 31.4, 29.9, 16.4 (d, J = 23.5 Hz), 8.7, 8.5, -0.3; $^{31}$P NMR (80 MHz, CDCl$_3$, 85% H$_3$PO$_4$) δ 109.1; GC-MS (EI, m/z): 338. HRMS calcd for C$_{17}$H$_{28}$OPSSi$^+$ 339.1368, found 339.1365.

3,4-Diethyl-2-phenyl-1-oxa-2-phosphaspiro[4.4]non-3-ene 2-sulfide (3j)

The crude product was purified by column chromatography on Al$_2$O$_3$ with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 93.4 mg, isolated yield was 61%. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.95 – 7.80 (m, 2H), 7.59 – 7.39 (m, 3H), 2.50 – 2.07 (m, 5H), 2.05 – 1.86 (m, 5H), 1.83 – 1.72 (m, 2H), 1.20 (t, J = 7.6 Hz, 3H), 0.85 (t, J = 7.7 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 156.2 (d, J =
17.2 Hz), 134.7 (d, J = 102.3 Hz), 132.0 (d, J = 2.7 Hz), 132.0 (d, J = 88.7 Hz), 131.8 (d, J = 12.7 Hz), 128.3 (d, J = 13.5 Hz), 102.6, 39.1, 38.1, 38.0, 24.8, 24.4, 20.3 (d, J = 15.9 Hz), 18.9 (d, J = 14.8 Hz), 14.4, 13.7; 31P NMR (80 MHz, CDCl3, 85% H3PO4) δ 98.5; GC-MS (EI, m/z): 306. HRMS calcd for C17H24OPS+ 307.1285, found 307.1280.

3,4-Diethyl-2-phenyl-1-oxa-2-phosphaspiro[4.5]dec-3-ene 2-sulfide (3k)

The crude product was purified by column chromatography on Al2O3 with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 84.7 mg, isolated yield was 53%. 1H NMR (CDCl3, 400 MHz) δ 7.98 – 7.78 (m, 2H), 7.60 – 7.35 (m, 3H), 2.52 – 2.17 (m, 5H), 1.98 – 1.64 (m, 9H), 1.16 (t, J = 7.6 Hz, 3H), 0.84 (t, J = 7.6 Hz, 3H); 13C NMR (CDCl3, 100 MHz) δ 158.8 (d, J = 17.4 Hz), 134.9 (d, J = 102.7 Hz), 131.9, 131.8 (d, J = 12.7 Hz), 131.1 (d, J = 88.6 Hz), 128.3 (d, J = 13.5 Hz), 94.4, 35.9, 35.2, 24.9, 21.9, 21.7, 20.5 (d, J = 15.9 Hz), 18.6 (d, J = 14.8 Hz), 14.2, 13.8; 31P NMR (80 MHz, CDCl3, 85% H3PO4) δ 98.9; GC-MS (EI, m/z): 320. HRMS calcd for C18H26OPS+ 321.1442, found 321.1447.

3,4-Diethyl-2-phenyl-1-oxa-2-phosphaspiro[4.6]undec-3-ene 2-sulfide (3l)

The crude product was purified by column chromatography on Al2O3 with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 73.6 mg, isolated yield was 44%. 1H NMR (CDCl3, 400 MHz) δ 7.95 – 7.82 (m, 2H), 7.55 – 7.35 (m, 3H), 2.52 – 1.87 (m, 11H), 1.84 – 1.46 (m, 5H), 1.19 (t, J = 7.6 Hz, 3H), 0.84 (t, J = 7.6 Hz, 3H); 13C NMR (CDCl3, 100 MHz) δ 160.0 (d, J = 17.8 Hz), 134.9 (d, J = 102.5 Hz), 132.0, 131.9 (d, J = 12.6 Hz), 129.7 (d, J = 88.8 Hz), 128.3 (d, J = 13.5 Hz), 97.5, 40.2, 39.2, 39.1, 28.7, 28.5, 23.2, 22.9, 20.6 (d, J = 16.0 Hz), 18.5 (d, J =
15.0 Hz), 14.2, 13.8; $^{31}$P NMR (80 MHz, CDCl$_3$, 85% H$_3$PO$_4$) δ 99.2; GC-MS (EI, m/z): 334. HRMS calcd for C$_{19}$H$_{28}$OPS$^+$ 335.1598, found 335.1591.

![5-Ethyl-2-phenyl-3,4-dipropyl-5H-1,2-oxaphosphole 2-sulfide (5a)](image)

5-Ethyl-2-phenyl-3,4-dipropyl-5H-1,2-oxaphosphole 2-sulfide (5a)

The crude product was purified by column chromatography on Al$_2$O$_3$ with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 129.6 mg, isolated yield was 84%. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.97 – 7.84 (m, 2H), 7.54 – 7.38 (m, 3H), 4.19 – 4.08 (m, 1H), 2.97 – 2.87 (m, 1H), 2.41 (d, $J = 15.4$ Hz, 1H), 2.30 (td, $J = 15.0$, 7.7 Hz, 1H), 2.23 – 2.11 (m, 3H), 1.99 – 1.82 (m, 3H), 1.72 – 1.60 (m, 1H), 1.11 (t, $J = 7.5$ Hz, 3H), 0.85 (t, $J = 7.4$ Hz, 3H), 0.76 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 154.4 (d, $J = 5.4$ Hz), 134.4 (d, $J = 106.9$ Hz), 131.7, 131.4 (d, $J = 10.8$ Hz), 130.8 (d, $J = 90.7$ Hz), 128.1 (d, $J = 12.9$ Hz), 82.4 (d, $J = 9.3$ Hz), 33.5, 30.6 (d, $J = 7.4$ Hz), 29.5 (d, $J = 15.3$ Hz), 29.1 (d, $J = 5.3$ Hz), 23.4 (d, $J = 17.6$ Hz), 15.3, 12.6, 10.4; $^{31}$P NMR (80 MHz, CDCl$_3$, 85% H$_3$PO$_4$) δ 89.2; GC-MS (EI, m/z): 308. HRMS calcd for C$_{17}$H$_{26}$OPS$^+$ 309.1442, found 309.1448.

![5-Ethyl-2,3,4-triphenyl-5H-1,2-oxaphosphole 2-sulfide (5b)](image)

5-Ethyl-2,3,4-triphenyl-5H-1,2-oxaphosphole 2-sulfide (5b)

The crude product was purified by column chromatography on Al$_2$O$_3$ with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 120.1 mg, isolated yield was 64%. $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.09 – 8.01 (m, 0.3H), 7.87 – 7.79 (m, 2H), 7.46 – 7.33 (m, 5H), 7.32 – 7.26 (m, 3H), 7.22 – 7.05 (m, 5H), 5.81 – 5.76 (m, 1H), 5.59-5.60 (m, 0.15H), 1.99 – 1.83 (m, 1.2H), 1.82 – 1.70 (m, 1H), 1.08 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) δ 152.0 (d, $J = 20.5$ Hz), 133.9 (d, $J = 95.0$ Hz), 133.0 (d, $J = 28.0$ Hz), 132.6 (d, $J = 73.2$ Hz), 132.2 (d, $J = 2.5$ Hz), 131.5 (d, $J = 13.7$ Hz), 131.3(d, $J = 12.4$ Hz), 129.2, 129.0 (d, $J = 22.0$ Hz), 128.5, 128.5, 128.4, 128.1, 89.5, 27.4, 9.1. $^{31}$P NMR (80 MHz, CDCl$_3$, 85% H$_3$PO$_4$) δ 102.8, 102.1; GC-MS (EI, m/z): 376. HRMS calcd for C$_{23}$H$_{32}$OPS$^+$ 377.1129, found 377.1127.
5-Pentyl-2,3,4-triphenyl-5H-1,2-oxaphosphole 2-sulfide (5c)

The crude product was purified by column chromatography on Al₂O₃ with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 117.3 mg, isolated yield was 56%. ¹H NMR (CDCl₃, 400 MHz) δ 8.17 – 7.98 (m, 1H), 7.93 – 7.73 (m, 2H), 7.63 – 7.50 (m, 2H), 7.44 – 7.33 (m, 5H), 7.32 – 7.26 (m, 4H), 7.22 – 7.06 (m, 8H), 6.89 (d, J = 7.4 Hz, 1H), 5.84 – 5.69 (m, 1H), 1.89 – 1.72 (m, 3H), 1.73 – 1.48 (m, 4H), 1.36 – 1.17 (m, 7H), 0.93 – 0.72 (m, 5H); ¹³C NMR (CDCl₃, 100 MHz) δ 153.2 (d, J = 20.3 Hz), 152.5 (d, J = 20.5 Hz), 134.4 (d, J = 104.3 Hz), 133.8 (d, J = 118.6 Hz), 133.3 (d, J = 3.5 Hz), 132.7 (d, J = 11.6 Hz), 132.3, 130.2 (d, J = 7.7 Hz), 131.7 (d, J = 28.6 Hz), 131.6 (d, J = 13.7 Hz), 131.3 (d, J = 12.4 Hz), 129.4 (d, J = 5.3 Hz), 129.2 (d, J = 5.8 Hz), 129.2 (d, J = 7.1 Hz), 128.9, 128.7 (d, J = 13.5 Hz), 128.4, 128.2, 128.1, 88.8, 87.7, 34.9, 34.7, 31.4, 31.3, 25.7, 24.6, 22.5, 14.1, 14.0; ³¹P NMR (80 MHz, CDCl₃, 85% H₃PO₄) δ 102.9, 102.1; GC-MS (EI, m/z): 418. HRMS calcd for C₂₆H₂₈OPS⁺ 419.1598, found 419.1563.

2,5-Diphenyl-3,4-dipropyl-2,5-dihydro-1,2-oxaphosphole 2-sulfide(5d)

The crude product was purified by column chromatography by column chromatography on Al₂O₃ with petroleum : ethyl acetate = 50 : 1 to give the desired product as yellow oil 53.4 mg, isolated yield was 15%. ¹H NMR (CDCl₃, 400 MHz) δ 7.93 – 7.87 (m, 2H), 7.54 – 7.34 (m, 8H), 6.01 – 5.99 (d, J = 7.8 Hz, 1H), 2.47 – 2.12 (m, 4H), 1.40 – 1.28 (m, 4H), 0.93 – 0.88 (m, 3H), 0.85 -0.78 (m, 3H); ³¹P NMR (80 MHz, CDCl₃, 85% H₃PO₄) δ 106.7, 104.8; GC-MS (EI, m/z): 356.

5,5-Diethyl-2-phenyl-3,4-dipropyl-5H-1,2-oxaphosphole 2-oxide (4a)
The crude product was purified by column chromatography on Al$_2$O$_3$ with petroleum : ethyl acetate = 10 : 1 to give the desired product as yellow oil 86.5 mg, isolated yield was 54%.  $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.82 – 7.72 (m, 2H), 7.46 – 7.30 (m, 3H), 2.49 – 2.25 (m, 1H), 2.17 (dt, $J$ = 13.3, 8.4 Hz, 1H), 2.11 – 1.83 (m, 2H), 1.79 – 1.65 (m, 2H), 1.60 – 1.46 (m, 5H), 0.99 (t, $J$ = 7.3 Hz, 3H), 0.94 – 0.84 (m, 6H), 0.81 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 151.0 (d, $J$ = 11.6 Hz), 137.5 (d, $J$ = 17.6 Hz), 133.1 (d, $J$ = 26.7 Hz), 132.7 (d, $J$ = 18.8 Hz), 131.5, 128.5 (d, $J$ = 10.0 Hz), 102.2 (d, $J$ = 9.4 Hz), 32.8, 30.2 (d, $J$ = 4.5 Hz), 29.9 (d, $J$ = 10.2 Hz), 28.9 (d, $J$ = 16.7 Hz), 22.9 (d, $J$ = 4.0 Hz), 22.7, 15.1, 14.7, 8.7, 8.4; $^{31}$P NMR (80 MHz, CDCl$_3$, 85% H$_3$PO$_4$) $\delta$ 116.4; GC-MS (EI, m/z): 320. HRMS calcd for C$_{19}$H$_{20}$O$_2$P$^+$ 321.1983, found 321.1986.
1H NMR of Compound 3a
$^{13}$C NMR of Compound 3a
$^{31}$P NMR of Compound 3a
$^1$H NMR of Compound 3b
$^{13}$C NMR of Compound 3b
$^{31}$P NMR of Compound 3b
$^1$H NMR of Compound 3c
$^{13}$C NMR of Compound 3c
$^{31}$P NMR of Compound 3c
$^1$H NMR of Compound 3d
$^{13}$C NMR of Compound 3d
$^{31}\text{P NMR of Compound 3d}$
$^1$H NMR of Compound 3e
$^{13}$C NMR of Compound 3e

S24
$^{31}$P NMR of Compound 3e
$^1$H NMR of Compound 3f
$^{13}$C NMR of Compound 3f
$^{31}$P NMR of Compound 3f
$^1$H NMR of Compound 3g
$^{13}$C NMR of Compound 3g
$^{31}$P NMR of Compound 3g
$^1$H NMR of Compound 3h
$^{13}$C NMR of Compound 3h
$^{31}$P NMR of Compound 3h
$^1$H NMR of Compound 3j
$^{13}$C NMR of Compound 3j
$^{31}$P NMR of Compound 3j
$^1$H NMR of Compound 3k
\(^{13}\)C NMR of Compound 3k
$^{31}$P NMR of Compound 3k
$^1$H NMR of Compound 3l
$^{13}$C NMR of Compound 3l
$^{31}$P NMR of Compound 31
$^1$H NMR of Compound 5a
$^{13}$C NMR of Compound 5a
$^{31}$P NMR of Compound 5a
$^1$H NMR of Compound 5b
$^{13}$C NMR of Compound 5b
31P NMR of Compound 5b
$^1$H NMR of Compound 5c
13C NMR of Compound 5c
$^{31}$P NMR of Compound 5c
$^1$H NMR of Compound 5d
$^{31}$P NMR of Compound 5d
$^1$H NMR of Compound 4a
$^{13}$C NMR of Compound 4a
$^{31}$P NMR of Compound 4a