Tf₂O/DMSO-mediated dual activation of aryl phosphinate to access various aryl phosphonates

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1. General information

$^1$H, $^{13}$C NMR, $^{31}$P NMR and $^{19}$F NMR spectra were recorded on a 500M Bruker AVANCE NEO spectrometer and a 400M JEOL ECZ400s in CDCl$_3$ with TMS as internal standard. High resolution mass spectroscopic (HRMS) and mass spectra were measured using Thermo Scientific DS II mass spectrometer, Thermo Q Exactive Focus and Bruker micro TOF-Q mass spectrometer. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification. Solvents were dried and purified according to the procedure from “Purification of Laboratory Chemicals book”. Column chromatography was carried out on silica gel (particle size 200-400 mesh ASTM). Substrates of 2$_t$,$^{[1]}$ 2$_t$,$^{[2]}$ were prepared according to literature procedure. $^{[1, 2]}$ The P(O)-H reagents of 1b-1e, $^{[3]}$ 1aa-1ag, $^{[4a]}$ 1ah $^{[4b]}$ were prepared according to literature procedure. $^{[3, 4]}

2. Full Optimization Table S1$^a$

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Conditions: $^a$ 1a (0.2 mmol), 2a (4.0 eq.), solvent (2.0 mL), N$_2$, stirred at 90 $^\circ$C for 11 h, isolated yield; $^b$ 2a (3.0 eq.); $^c$ 2a (5.0 eq.); $^d$ MeCN (1.0 mL); $^e$ MeCN (3.0 mL); $^f$ MeCN (4.0 mL); $^g$ Under air.
3. General Procedure

3.1 Phenols and alcohols as substrates

To a Schlenk tube were added 2 (0.8 mmol, 4.0 eq.), (for 2d-2h, 2j-2p and 1ab-1ad, 0.15 eq. TBAB was added), and charged with nitrogen for three times. Then, anhydrous MeCN (3.0 mL), 1 (0.2 mmol, 1.0 eq.), Tf₂O (0.7 mmol, 3.5 eq.) and DMSO (0.2 mmol, 1.0 eq.) were added via syringe in turn. The mixture was allowed to stir at 110 °C in oil bath for 11h. At the completion of the reaction, the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 9: 1) to afford the products 3 or 5a-5c.

3.2 Thiophenols (4f-4h) as substrates

To a Schlenk tube were added 4f-4h (0.6 mmol, 3.0 eq.) and charged with nitrogen for three times. Then, anhydrous MeCN (3.0 mL), 1a (0.2 mmol, 1.0 eq.), Tf₂O (0.3 mmol, 1.5 eq.) and DMSO (0.2 mmol, 1.0 eq.) were added via syringe in turn. The mixture was allowed to stir at RT for 11h. At the completion of the reaction, the solvent was removed by rotary evaporation. The resulting residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 9: 1) to afford the products 5f-5h.
4. Thermal analysis of DOPO and selected samples.

![Thermal analysis graph]

**Figure S1** Thermal analysis of DOPO and selected samples.

**Table S2.** TG data of DOPO, 3q, 3r, 3s and 3t under nitrogen atmosphere.

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<th>T_{50wt%} (°C)</th>
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5. Control Experiments

![Control experiments diagram]

**3a,** 65% 
**M+1: M+3= 25:1**
6. Characterization of the Products

**diphenyl phenylphosphonate.** Performed according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3a as colorless oil (47.2 mg, 76%): $^1$H NMR (400 MHz, CDCl$_3$): δ 7.99-7.93 (m, 2H), 7.58-7.54 (m, 1H), 7.49-7.44 (m, 2H), 7.29-7.25 (m, 4H), 7.20-7.17 (m, 4H), 7.14-7.10 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 150.3 (d, $J_{C,P}$ = 7.0 Hz), 133.1 (d, $J_{C,P}$ = 3.0 Hz), 132.1 (d, $J_{C,P}$ = 10.0 Hz), 129.6, 128.5 (d, $J_{C,P}$ = 16.0 Hz), 126.8 (d, $J_{C,P}$ = 192.0 Hz), 125.0, 120.5 (d, $J_{C,P}$ = 5.0 Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): δ 11.72. MS (ESI): 311.5 (M+1)$^+$. The analytical data matched those reported in the literature.$^5$

**bis(4-fluorophenyl) phenylphosphonate.** Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3b as colorless oil (56.8 mg, 82%): $^1$H NMR (400 MHz, CDCl$_3$): δ 7.97-7.91 (m, 2H), 7.65-7.60 (m, 1H), 7.54-7.49 (m, 2H), 7.16-7.12 (m, 4H), 7.00-6.95 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 159.8 (d, $J_{C,P}$ = 243.0 Hz), 146.0 (dd, $J_1$ = 3.0 Hz, $J_2$ = 8.0 Hz), 133.5 (d, $J_{C,P}$ = 3.0 Hz), 132.2 (d, $J_{C,P}$ = 11.0 Hz), 128.7 (d, $J_{C,P}$ = 16.0 Hz), 126.2 (d, $J_{C,P}$ = 192.0 Hz), 122.0 (dd, $J_1$ = 4.0 Hz, $J_2$ = 8.0 Hz), 116.3 (d, $J_{C,P}$ = 24.0 Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): δ 1.26. $^{19}$F NMR (376 MHz, CDCl$_3$): δ -117.4. MS (ESI): 347.1 (M+1)$^+$. The analytical data matched those reported in the literature.$^5$

**bis(4-chlorophenyl) phenylphosphonate.** Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3c as colorless oil (61.7 mg, 81%): $^1$H NMR (400 MHz, CDCl$_3$): δ 7.96-7.90 (m, 2H), 7.65-7.60 (m, 1H), 7.54-7.49 (m, 2H), 7.28-7.24 (m, 4H), 7.13-7.11 (m, 4H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 148.7 (d, $J_{C,P}$ = 7.0 Hz), 133.6 (d, $J_{C,P}$ = 4.0 Hz), 132.2 (d, $J_{C,P}$ = 10.0 Hz), 130.7, 129.8, 128.8 (d, $J_{C,P}$ = 16.0 Hz), 126.0 (d, $J_{C,P}$ = 191.0 Hz), 121.9 (d, $J_{C,P}$ = 4.0 Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): δ 12.42. HRMS calc. for C$_{18}$H$_{14}$ClO$_3$P (M+H)$^+$ = 379.0052, found 379.0055.

**bis(4-bromophenyl) phenylphosphonate.** Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3d as colorless oil (67.9 mg, 73%): $^1$H NMR (500 MHz, CDCl$_3$): δ 7.95-7.91 (m, 2H), 7.64-7.61 (m, 1H), 7.53-7.49 (m, 2H), 7.41 (d, $J$=8.9 Hz, 4H), 7.07 (d, $J$=8.9 Hz, 4H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 149.2 (d, $J_{C,P}$ = 7.5 Hz), 133.6...
(d, \( J_{CP} = 3.0 \) Hz), 132.8, 132.2 (d, \( J_{CP} = 10.3 \) Hz), 128.8 (d, \( J_{CP} = 15.7 \) Hz), 125.9 (d, \( J_{CP} = 191.3 \) Hz), 122.3 (d, \( J_{CP} = 4.5 \) Hz), 118.3 (d, \( J_{CP} = 1.4 \) Hz). \(^{31}\)P NMR (203 MHz, CDCl\(_3\)): \( \delta \) 12.27. HRMS calc. for C\(_{15}\)H\(_{14}\)Br\(_2\)O\(_3\)P (M+H)\(^+\) = 468.9021, found 468.9025.

\[ \text{di-}p\text{-tolyl phenylphosphonate.} \]

Performed according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3e as colorless oil (48.0 mg, 71%): \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.96-7.92 (m, 2H), 7.59-7.56 (m, 1H), 7.49-7.45 (m, 2H), 7.06 (s, 8H), 2.27 (s, 6H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 148.1 (d, \( J_{CP} = 7.4 \) Hz), 134.6, 133.0 (d, \( J_{CP} = 3.0 \) Hz), 132.2 (d, \( J_{CP} = 10.3 \) Hz), 130.1, 128.5 (d, \( J_{CP} = 15.6 \) Hz), 127.0 (d, \( J_{CP} = 191.0 \) Hz), 120.3 (d, \( J_{CP} = 4.5 \) Hz), 20.6. \(^{31}\)P NMR (203 MHz, CDCl\(_3\)): \( \delta \) 11.87. MS (ESI): 339.2 (M+1)\(^+\).

The analytical data matched those reported in the literature.\(^5\)

\[ \text{bis(4-} \text{-(tert-butyl)phenyl) phenylphosphonato.} \]

Performed according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3f as colorless oil (57.4 mg, 68%): \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.81-7.76 (m, 2H), 7.51-7.46 (m, 1H), 7.41-7.35 (m, 6H), 7.27 (d, \( J=8.0 \) Hz, 4H), 1.27 (s, 18H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 152.7 (d, \( J_{CP} = 3.0 \) Hz), 135.4 (d, \( J_{CP} = 5.0 \) Hz), 133.5 (d, \( J_{CP} = 107 \) Hz), 132.5 (d, \( J_{CP} = 4 \) Hz), 121.6 (d, \( J_{CP} = 11.0 \) Hz), 128.3 (d, \( J_{CP} = 14.0 \) Hz), 126.4 (d, \( J_{CP} = 2.0 \) Hz), 122.7 (d, \( J_{CP} = 6.0 \) Hz), 34.7, 31.1. \(^{31}\)P NMR (203 MHz, CDCl\(_3\)): \( \delta \) 11.84. HRMS calc. for C\(_{20}\)H\(_{12}\)O\(_3\)P (M+H)\(^+\) = 423.2084, found 423.2081.

\[ \text{di(1,1'-biphenyl)-4-yl) phenylphosphonate.} \]

Performed according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3g as white solid (63.8 mg, 69%): \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 8.05-7.99 (m, 2H), 7.66-7.61 (m, 1H), 7.55-7.50 (m, 10H), 7.42 (t, \( J=5 \) Hz, 4H), 7.35-7.26 (m, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 149.8 (d, \( J_{CP} = 8 \) Hz), 140.2, 138.3, 133.3 (d, \( J_{CP} = 3 \) Hz), 132.3 (d, \( J_{CP} = 11 \) Hz), 128.8, 128.6, 128.4, 126.8 (d, \( J_{CP} = 192 \) Hz), 127.3, 127.0, 120.9 (d, \( J_{CP} = 5 \) Hz). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \( \delta \) 12.74. HRMS calc. for C\(_{30}\)H\(_{26}\)O\(_3\)P (M+H)\(^+\) = 463.1458, found 463.1458.

\[ \text{bis(3,4-dimethylphenyl) phenylphosphonate.} \]

Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3h as colorless oil (62.3 mg, 85%): \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.98-7.92 (m, 2H), 7.60-7.55 (m, 1H), 7.50-7.45 (m, 2H), 7.02-7.69 (m, 4H), 6.90-7.87 (m, 2H), 2.18 (s, 6H), 2.18 (s, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \)
148.3 (d, $J_{CP} = 7.0$ Hz), 138.1, 133.2, 132.9 (d, $J_{CP} = 3.0$ Hz), 132.3 (d, $J_{CP} = 10.0$ Hz), 130.4, 128.5 (d, $J_{CP} = 15.0$ Hz), 127.3 (d, $J_{CP} = 192.0$ Hz), 121.6 (d, $J_{CP} = 4.0$ Hz), 117.6 (d, $J_{CP} = 4.0$ Hz), 19.8, 19.0. $^{31}$P NMR (203 MHz, CDCl$_3$): $\delta$ 11.67. HRMS calc. for C$_{25}$H$_{25}$O$_3$P (M+H)$^+$ = 367.1458, found 367.1457.

bis(3,4-difluorophenyl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3i as colorless oil (59.5 mg, 78%): $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.95-7.91 (m, 2H), 7.68-7.65 (m, 1H), 7.51-7.53 (m, 2H), 7.12-7.05 (m, 4H), 6.96-6.93 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 149.1 (dd, $J_1 = 13.8$ Hz, $J_2 = 59.6$ Hz), 149.0 (t, $J_{CF} = 14.3$ Hz), 145.6-145.5 (m), 133.9 (d, $J_{CP} = 3.3$ Hz), 132.2 (d, $J_{CP} = 10.6$ Hz), 128.9 (d, $J_{CP} = 15.7$ Hz), 125.3 (d, $J_{CP} = 191.6$ Hz), 117.6 (d, $J_{CP} = 18.6$ Hz), 116.6-116.5 (m), 110.7 (dd, $J_1 = 4.5$ Hz, $J_2 = 20.3$ Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): $\delta$ 13.01. $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -133.5 (d, $J_{CP} = 21.7$ Hz), -141.2 (d, $J_{CP} = 23.2$ Hz). HRMS calc. for C$_{31}$H$_{21}$F$_4$O$_3$P (M+H)$^+$ = 383.0455, found 383.0455.

di(naphthalen-2-yl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3j as yellow oil (53.3 mg, 65%): $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.06-8.02 (m, 2H), 7.80-7.77 (m, 4H), 7.73 (d, $J = 8.0$ Hz, 2H), 7.69 (s, 2H), 7.62-7.59 (m, 1H), 7.53-7.49 (m, 2H), 7.47-7.41 (m, 4H), 7.36-7.34 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 148.0 (d, $J_{CP} = 7.8$ Hz), 133.8, 133.3 (d, $J_{CP} = 3.2$ Hz), 132.3 (d, $J_{CP} = 10.2$ Hz), 131.0, 129.9, 128.8, 128.7, 127.6 (d, $J_{CP} = 14.5$ Hz), 126.7 (d, $J_{CP} = 191.0$ Hz), 126.6, 125.5, 120.5 (d, $J_{CP} = 4.5$ Hz), 117.2 (d, $J_{CP} = 4.8$ Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): $\delta$ 12.10. HRMS calc. for C$_{26}$H$_{25}$O$_3$P (M+H)$^+$ = 411.1145, found 411.1144.

bis(5,6,7,8-tetrahydronaphthalen-2-yl) phenylphosphonate. Performed according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3k as colorless oil (64.4 mg, 77%): $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.98-7.93 (m, 2H), 7.60-7.56 (m, 1H), 7.50-7.46 (m, 2H), 6.95-6.87 (m, 6H), 2.68 (s, 8H), 1.74-1.71 (m, 8H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 147.9 (d, $J_{CP} = 7.5$ Hz), 138.6, 133.8, 132.9 (d, $J_{CP} = 3.2$ Hz), 132.3 (d, $J_{CP} = 10.2$ Hz), 130.0, 128.5 (d, $J_{CP} = 15.6$ Hz), 127.3 (d, $J_{CP} = 191.3$ Hz), 120.7 (d, $J_{CP} = 4.1$ Hz), 117.7 (d, $J_{CP} = 4.1$ Hz) , 29.4, 28.7, 23.1, 22.8. $^{31}$P NMR (203 MHz, CDCl$_3$): $\delta$ 11.67. HRMS calc. for C$_{26}$H$_{25}$O$_3$P (M+H)$^+$ = 419.1771, found 419.1772.
**di-o-tolyl phenylphosphonate.** Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3l as colorless oil (42.6 mg, 63%): $^1$H NMR (500 MHz, CDCl$_3$): δ 8.03-7.99 (m, 2H), 7.64-7.60 (m, 1H), 7.54-7.50 (m, 2H), 7.22 (d, $J$ = 8.1 Hz, 2H), 7.16 (d, $J$ = 7.3 Hz, 2H), 7.11-7.08 (m, 2H), 7.04 (t, $J$ = 7.3 Hz, 2H), 2.20 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 149.1 (d, $J_{C,P}$ = 8.2 Hz), 133.1 (d, $J_{C,P}$ = 3.3 Hz), 132.1 (d, $J_{C,P}$ = 10.3 Hz), 131.3, 129.5 (d, $J_{C,P}$ = 5.6 Hz), 128.6 (d, $J_{C,P}$ = 15.6 Hz), 128.5, 126.9, 125.0, 120.5 (d, $J_{C,P}$ = 2.6 Hz), 165. $^{31}$P NMR (203 MHz, CDCl$_3$): δ 11.34. HRMS calc. for C$_{20}$H$_{20}$O$_3$P (M+H)$^+$: = 339.1145, found 339.1140.

**bis(2-methoxyphenyl) phenylphosphonate.** Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3m as colorless oil (30.4 mg, 41%): $^1$H NMR (400 MHz, CDCl$_3$): δ 8.09-8.03 (m, 2H), 7.60-7.55 (m, 1H), 7.51-7.45 (m, 2H), 7.26-7.22 (m, 2H), 7.12-7.07 (m, 2H), 6.90-6.83 (m, 4H), 3.71 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ 150.9 (d, $J_{C,P}$ = 4 Hz), 139.7 (d, $J_{C,P}$ = 8 Hz), 132.7 (d, $J_{C,P}$ = 4 Hz), 132.3 (d, $J_{C,P}$ = 10 Hz), 127.7 (d, $J_{C,P}$ = 195 Hz), 128.1 (d, $J_{C,P}$ = 16 Hz), 125.8, 122.1 (d, $J_{C,P}$ = 4 Hz), 112.7, 120.5, 52.7. $^{31}$P NMR (162 MHz, CDCl$_3$): δ 13.31. HRMS calc. for C$_{20}$H$_{20}$O$_3$P (M+H)$^+$: = 371.1043, found 371.1042.

**bis(2-bromophenyl) phenylphosphonate.** Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3n as colorless oil (32.6 mg, 35%): $^1$H NMR (500 MHz, CDCl$_3$): δ 8.17-8.12 (m, 2H), 7.66-7.63 (m, 1H), 7.55-7.51 (m, 4H), 7.46 (d, $J$ = 8.2 Hz, 2H), 7.26-7.21 (m, 2H), 7.02 (t, $J$ = 7.6 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 147.7 (d, $J_{C,P}$ = 7.3 Hz), 133.7, 133.6 (d, $J_{C,P}$ = 3.0 Hz), 132.6 (d, $J_{C,P}$ = 10.9 Hz), 128.7, 128.5, 126.1 (d, $J_{C,P}$ = 194.3 Hz), 126.3, 121.9 (d, $J_{C,P}$ = 2.7 Hz), 114.9 (d, $J_{C,P}$ = 7.2 Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): δ 12.40. HRMS calc. for C$_{13}$H$_{14}$Br$_2$O$_3$P (M+H)$^+$: = 468.9021, found 468.9026.

**bis(2,5-dimethylphenyl) phenylphosphonate.** Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3o as colorless oil (31.5 mg, 43%): $^1$H NMR (500 MHz, CDCl$_3$): δ 8.02-7.97 (m, 2H), 7.63-7.60 (m, 1H), 7.53-7.49 (m, 2H), 7.03 (t, $J$ = 8.0 Hz, 4H), 6.85 (d, $J$ = 7.6 Hz, 2H), 2.24 (s, 6H), 2.15 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 145.4 (d, $J_{C,P}$ = 7.5 Hz), 136.3, 133.9, 133.5 (d, $J_{C,P}$ = 2.8 Hz), 132.6 (d, $J_{C,P}$ = 10.6 Hz), 129.1, 128.5 (d, $J_{C,P}$ = 16.3 Hz), 126.3 (d, $J_{C,P}$ = 193.3 Hz), 121.5 (d, $J_{C,P}$ = 2.6 Hz), 114.3 (d, $J_{C,P}$ = 6.8 Hz).
bis(2-bromo-4-methyphenyl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3p as colorless oil (35.5 mg, 36%): $^1$H NMR (500 MHz, CDCl$_3$): δ 8.14-8.09 (m, 2H), 7.63-7.60 (m, 1H), 7.53-7.49 (m, 2H), 7.33 (t, J = 10.5 Hz, 4H), 7.01 (d, J = 8.3 Hz, 2H), 2.27 (s, 6H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 145.4 (d, $J_{CP}$ = 7.5 Hz), 136.3, 133.9, 133.5 (d, $J_{CP}$ = 2.8 Hz), 132.6 (d, $J_{CP}$ = 10.6 Hz), 129.1, 128.5 (d, $J_{CP}$ = 16.3 Hz), 126.3 (d, $J_{CP}$ = 193.3 Hz), 121.5 (d, $J_{CP}$ = 2.6 Hz), 114.3 (d, $J_{CP}$ = 6.8 Hz), 204. $^{31}$P NMR (203 MHz, CDCl$_3$): δ 12.48. HRMS calc. for C$_{20}$H$_{18}$Br$_2$O$_5$P (M+H)$^+$ = 496.9334, found 496.9338.

4-phenyldinaphtho[2,1-d:1’,2’-f][1,3,2]dioxaphosphepine 4-oxide. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 3q as white solid (71.0 mg, 87%): $^1$H NMR (500 MHz, CDCl$_3$): δ 8.07 (d, J = 8.9 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.84 (d, J = 8.9 Hz, 1H), 7.68-7.56 (m, 4H), 7.51-7.45 (m, 3H), 7.38-7.28 (m, 5H), 7.00 (d, J = 8.8 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 147.5 (d, $J_{CP}$ = 10.4 Hz), 145.7 (d, $J_{CP}$ = 9.8 Hz), 133.5 (d, $J_{CP}$ = 3.1 Hz), 132.4 (d, $J_{CP}$ = 9.8 Hz), 132.1 (d, $J_{CP}$ = 66.6 Hz), 131.5, 131.3, 130.7, 128.5 (d, $J_{CP}$ = 7.5 Hz), 128.4 (d, $J_{CP}$ = 12.1 Hz), 127.1 (d, $J_{CP}$ = 36.9 Hz), 126.7, 125.7 (d, $J_{CP}$ = 1.8 Hz), 124.7 (d, $J_{CP}$ = 185.7 Hz), 121.8 (d, $J_{CP}$ = 2.4 Hz), 121.7 (d, $J_{CP}$ = 1.7 Hz), 121.2 (d, $J_{CP}$ = 1.7 Hz), 120.8 (d, $J_{CP}$ = 3.1 Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): δ 27.19. HRMS calc. for C$_{20}$H$_{18}$O$_5$P (M+H)$^+$ = 409.0988, found 409.0989.

9,14-dibromo-4-phenyldinaphtho[2,1-d:1’,2’-f][1,3,2]dioxaphosphepine 4-oxide. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 3r as white solid (78.9 mg, 70%): $^1$H NMR (500 MHz, CDCl$_3$): δ 8.15 (d, J = 2.0 Hz, 1H), 8.10 (d, J = 2.0 Hz, 1H), 8.00 (d, J = 8.9 Hz, 1H), 7.77 (d, J = 8.9 Hz, 1H), 7.68 (d, J = 9.4 Hz, 1H), 7.62-7.58 (m, 3H), 7.44-7.37 (m, 4H), 7.28 (s, 1H), 7.19 (d, J = 9.1 Hz, 1H), 7.03 (d, J = 8.9 Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 147.8 (d, $J_{CP}$ = 10.3 Hz), 146.1 (d, $J_{CP}$ = 9.9 Hz), 133.8 (d, $J_{CP}$ = 2.8 Hz), 133.0, 132.7, 132.4 (d, $J_{CP}$ = 10.0 Hz), 130.8 (d, $J_{CP}$ = 5.5 Hz), 130.6, 130.5, 130.3 (d, $J_{CP}$ = 3.8 Hz), 130.0, 128.6 (d, $J_{CP}$ = 5.0 Hz), 128.4 (d, $J_{CP}$ = 18.4 Hz), 124.3 (d, $J_{CP}$ = 185.8 Hz), 122.5 (d, $J_{CP}$ = 1.7 Hz), 122.1 (d, $J_{CP}$ = 2.9 Hz), 121.7 (d, $J_{CP}$ = 2.6 Hz), 121.5 (d, $J_{CP}$ = 1.7 Hz), 120.1 (d, $J_{CP}$ = 7.2 Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): δ 27.27. HRMS calc. for C$_{20}$H$_{18}$Br$_2$O$_5$P (M+H)$^+$ = 566.9178, found 566.9178.
6-phenylbenzendo[d,f][1,3,2]dioxaphosphepine 6-oxide. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 3s as white solid (54.3 mg, 88%): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.76-7.70 (m, 2H), 7.62-7.56 (m, 3H), 7.45-7.34 (m, 6H), 7.12-7.10 (m, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 147.8 (d, $J_{CP} = 10.0$ Hz), 133.5 (d, $J_{CP} = 3.0$ Hz), 132.3 (d, $J_{CP} = 10.0$ Hz), 130.0 (d, $J_{CP} = 14.0$ Hz), 128.7, 128.5, 128.3, 126.3, 124.7 (d, $J_{CP} = 188.0$ Hz), 121.8 (d, $J_{CP} = 3.0$ Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): $\delta$ 26.00. HRMS calc. for C$_{18}$H$_4$O$_3$P (M+H): 309.0675, found 309.0671.

2,10-dibromo-6-phenylbenzendo[d,f][1,3,2]dioxaphosphepine 6-oxide. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 3t as white solid (73.2 mg, 79%): $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.75-7.70 (m, 4H), 7.66-7.62 (m, 1H), 7.52 (dd, $J_1 = 2.3$ Hz, $J_2 = 8.7$ Hz, 2H), 7.49-7.45 (m, 2H), 7.00 (d, $J = 8.6$ Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 146.9 (d, $J_{CP} = 9.9$ Hz), 133.9 (d, $J_{CP} = 2.8$ Hz), 133.4, 132.6, 132.3 (d, $J_{CP} = 10.0$ Hz), 129.5, 128.7 (d, $J_{CP} = 15.6$ Hz), 124.0 (d, $J_{CP} = 187.4$ Hz), 123.7 (d, $J_{CP} = 3.8$ Hz), 119.5 (d, $J_{CP} = 1.9$ Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): $\delta$ 26.09. HRMS calc. for C$_{18}$H$_2$Br$_2$O$_3$P (M+H): 466.8865, found 466.8867.

12-phenyl-4,5,6,7-tetrahydrodiindenophenophine[7,1-de:1’,7’-fg][1,3,2]dioxaphosphocine 12-oxide. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 4/1) to afford 3u as white solid (37.5 mg, 50%): $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.53 (t, $J = 7.4$ Hz, 1H), 7.47-7.43 (m, 2H), 7.36-7.31 (m, 2H), 7.27 (d, $J = 7.8$ Hz, 1H), 7.18 (d, $J = 7.4$ Hz, 1H), 7.14 (d, $J = 7.9$ Hz, 1H), 7.05 (d, $J = 7.4$ Hz, 1H), 6.82 (t, $J = 7.8$ Hz, 1H), 6.11 (d, $J = 8.1$ Hz, 1H), 3.16-3.09 (m, 2H), 2.93-2.85 (m, 2H), 2.37-2.34 (m, 1H), 2.29-2.26 (m, 1H), 2.14-2.04 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 146.4 (dd, $J_1 = 1.9$ Hz, $J_2 = 12.9$ Hz), 145.7 (d, $J_{CP} = 8.5$ Hz), 143.3 (d, $J_{CP} = 9.3$ Hz), 139.7 (dd, $J_1 = 3.2$ Hz, $J_2 = 22.7$ Hz), 133.1 (d, $J_{CP} = 3.2$ Hz), 132.4 (d, $J_{CP} = 9.2$ Hz), 128.8, 128.0, 127.9, 124.3 (d, $J_{CP} = 186.6$ Hz), 123.0 (d, $J_{CP} = 1.7$ Hz), 122.3 (d, $J_{CP} = 2.4$ Hz), 122.0 (d, $J_{CP} = 2.9$ Hz), 121.8 (d, $J_{CP} = 3.7$ Hz), 59.3, 38.3 (d, $J_{CP} = 18.2$ Hz), 30.6 (d, $J_{CP} = 9.1$ Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): $\delta$ 13.46. HRMS calc. for C$_{23}$H$_{20}$O$_3$P (M+H): 375.1145, found 375.1143.
**diphenyl \( p \)-tolylyphosphonate.** Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3aa as colorless oil (47.4 mg, 73%): \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.87-7.82 (m, 2H), 7.31-7.26 (m, 6H), 7.18 (d, \( J = 8.0 \) Hz, 4H), 7.13 (t, \( J = 7.4 \) Hz, 2H), 2.41 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 150.4 (d, \( J_{CP} = 7.4 \) Hz), 143.9 (d, \( J_{CP} = 3.3 \) Hz), 132.3 (d, \( J_{CP} = 10.9 \) Hz), 129.7, 129.4 (d, \( J_{CP} = 16.3 \) Hz), 125.0, 123.5 (d, \( J_{CP} = 194.0 \) Hz), 120.6 (d, \( J_{CP} = 4.4 \) Hz), 21.7. \(^{31}\)P NMR (203 MHz, CDCl\(_3\)): \( \delta \) 12.50. HRMS calc. for C\(_{19}\)H\(_{12}\)O\(_3\)P (M+H): \(^{11}\): 325.0988, found 325.0985.

![diphenyl \( p \)-tolylyphosphonate](image)

**diphenyl (4-(tert-butyl)phenyl)phosphonate.** Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3ab as colorless oil (47.6 mg, 65%): \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 8.00-7.96 (m,2H), 7.62-7.59 (m, 1H), 7.52-7.48 (m, 2H), 7.28 (d, \( J = 8.8 \) Hz, 4H), 7.10 (d, \( J = 8.7 \) Hz, 4H), 1.27 (s, 18H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 156.8 (d, \( J_{CP} = 3 \) Hz), 150.5 (d, \( J_{CP} = 7.6 \) Hz), 132.1 (d, \( J_{CP} = 10.9 \) Hz), 129.6, 125.7 (d, \( J_{CP} = 16.2 \) Hz), 125.0, 123.6 (d, \( J_{CP} = 194.7 \) Hz), 120.6 (d, \( J_{CP} = 4.5 \) Hz), 35.1, 31.0. \(^{31}\)P NMR (203 MHz, CDCl\(_3\)): \( \delta \) 12.35. HRMS calc. for C\(_{32}\)H\(_{31}\)O\(_3\)P (M+H): \(^{11}\): 367.1458, found 367.1455.

![diphenyl (4-(tert-butyl)phenyl)phosphonate](image)

**diphenyl (4-methoxyphenyl)phosphonate.** Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3ac as colorless oil (42.9 mg, 63%): \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 7.91-7.86 (m, 2H), 7.30-7.26 (m, 4H), 7.19-7.17 (m, 4H), 7.15-7.12 (m, 2H), 6.99-6.97 (m, 2H), 3.85 (s, 3H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 163.4 (d, \( J_{CP} = 3.6 \) Hz), 150.4 (d, \( J_{CP} = 7.3 \) Hz), 134.3 (d, \( J_{CP} = 11.9 \) Hz), 129.7, 125.0, 120.6 (d, \( J_{CP} = 4.5 \) Hz), 117.8 (d, \( J_{CP} = 199.4 \) Hz), 114.2 (d, \( J_{CP} = 17.1 \) Hz), 55.4. \(^{31}\)P NMR (203 MHz, CDCl\(_3\)): \( \delta \) 12.71. HRMS calc. for C\(_{19}\)H\(_{18}\)O\(_3\)P (M+H): \(^{11}\): 341.0937, found 341.0939.

![diphenyl (4-methoxyphenyl)phosphonate](image)

**diphenyl [1,1'-biphenyl]-4-ylphosphonate.** Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3ad as colorless oil (49.5 mg, 64%): \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 8.05-8.00 (m, 2H), 7.73-7.70 (m, 2H), 7.61 (d, \( J = 8.5 \) Hz, 2H), 7.48-7.45 (m, 2H), 7.42-7.39 (m, 1H), 7.30 (t, \( J = 8.3 \) Hz, 4H), 7.23-7.21 (m, 4H), 7.17-7.13 (m, 2H). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta \) 150.4 (d, \( J_{CP} = 7.8 \) Hz), 145.9 (d, \( J_{CP} = 3 \) Hz), 139.6, 132.8 (d, \( J_{CP} = 10.9 \) Hz), 129.7, 129.0, 128.4, 127.3 (d, \( J_{CP} = 16.3 \) Hz), 127.3, 125.2 (d, \( J_{CP} = 193.9 \) Hz), 125.1, 120.6 (d, \( J_{CP} = 4.4 \) Hz). \(^{31}\)P NMR (203 MHz, CDCl\(_3\)): \( \delta \) 11.92. HRMS calc. for C\(_{23}\)H\(_{20}\)O\(_3\)P (M+H): \(^{11}\): 387.1145, found 387.1146.

![diphenyl [1,1'-biphenyl]-4-ylphosphonate](image)

**diphenyl naphthalalen-2-ylphosphonate.** Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3ae as colorless oil (50.4 mg, 70%): \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta \) 8.57 (d, \( J = 16.4 \) Hz, 2H), 7.96-7.87 (m, 4H), 7.63-7.55 (m, 2H),
7.29-7.21 (m, 8H), 7.14-7.11 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 150.3 (d, $J_{CP} = 7.4$ Hz), 135.3 (d, $J_{CP} = 2.8$ Hz), 135.1 (d, $J_{CP} = 10.9$ Hz), 132.2 (d, $J_{CP} = 17.7$ Hz), 129.7, 129.1, 128.7, 128.6 (d, $J_{CP} = 14.8$ Hz), 127.8, 127.1, 126.3 (d, $J_{CP} = 10.1$ Hz), 125.1, 123.7 (d, $J_{CP} = 192.0$ Hz), 120.6 (d, $J_{CP} = 4.5$ Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): δ 12.13. HRMS calc. for C$_{22}$H$_{18}$O$_3$P (M+H)$^+$ = 361.0988, found 361.0988.

![DiPhPO_phosphonate](image)

diphenyl (4-fluorophenyl)phosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3af as colorless oil (41.4 mg, 63%): $^1$H NMR (500 MHz, CDCl$_3$): δ 8.00-7.95 (m, 2H), 7.30 (t, $J = 8.0$ Hz, 4H), 7.20-7.14 (m, 8H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 165.8 (dd, $J_1 = 4.2$ Hz, $J_2 = 253.7$ Hz), 150.2 (d, $J_{CP} = 7.4$ Hz), 135.0 (dd, $J_1 = 9.1$ Hz, $J_2 = 11.8$ Hz), 129.7, 125.2, 122.8 (dd, $J_1 = 3.0$ Hz, $J_2 = 196.6$ Hz), 120.5 (d, $J_{CP} = 4.5$ Hz), 116.1 (dd, $J_1 = 17.1$ Hz, $J_2 = 21.6$ Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): δ 10.66. $^{19}$F NMR (470 MHz, CDCl$_3$): δ -104.1. HRMS calc. for C$_{19}$H$_{15}$FO$_3$P (M+H)$^+$ = 329.0737, found 329.0738.

![Diphenyl-o-tolylphosphonate](image)
diphenyl o-tolylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 3ag as colorless oil (27.9 mg, 43%): $^1$H NMR (500 MHz, CDCl$_3$): δ 8.10-8.05 (m, 1H), 7.51-7.48 (m, 1H), 7.35-7.27 (m, 6H), 7.19-7.12 (m, 6H), 2.76 (d, $J = 1.5$ Hz, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 165.8 (dd, $J_1 = 4.2$ Hz, $J_2 = 253.7$ Hz), 150.2 (d, $J_{CP} = 7.4$ Hz), 142.1 (d, $J_{CP} = 10.3$ Hz), 134.5 (d, $J_{CP} = 11.0$ Hz), 133.3 (d, $J_{CP} = 2.8$ Hz), 131.5 (d, $J_{CP} = 15.6$ Hz), 129.7, 125.7 (d, $J_{CP} = 166.6$ Hz), 125.7 (d, $J_{CP} = 15.8$ Hz), 125.0, 120.4 (d, $J_{CP} = 4.6$ Hz), 21.5 (d, $J_{CP} = 3.5$ Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): δ 12.52. HRMS calc. for C$_{19}$H$_{15}$O$_3$P (M+H)$^+$ = 325.0988, found 325.0987.

![Bis(2,2,2-trifluoroethyl)phenylphosphonate](image)

bis(2,2,2-trifluoroethyl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 5a as colorless oil (47.7 mg, 74%): $^1$H NMR (500 MHz, CDCl$_3$): δ 7.85-7.81 (m, 2H), 7.68-7.64 (m, 1H), 7.56-7.52 (m, 2H), 4.51-4.34 (m, 4H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 133.9 (d, $J_{CP} = 3.3$ Hz), 131.8 (d, $J_{CP} = 10.9$ Hz), 128.9 (d, $J_{CP} = 16.2$ Hz), 124.6 (d, $J_{CP} = 194.9$ Hz), 122.5 (dd, $J_1 = 9.1$ Hz, $J_2 = 275.9$ Hz), 62.3 (qd, $J_1 = 4.8$ Hz, $J_2 = 37.8$ Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): δ 21.33. $^{19}$F NMR (470 MHz, CDCl$_3$): δ -75.2. HRMS calc. for C$_{10}$H$_{10}$F$_6$O$_3$P (M+H)$^+$ = 323.0266, found 323.0266.

![Bis(2,2,2-trichloroethyl) phenylphosphonate](image)
bis(2,2,2-trichloroethyl) phenylphosphonate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 5b as colorless oil (66.8 mg, 80%): $^1$H NMR (500 MHz, CDCl$_3$): δ 7.96-7.91 (m, 2H), 7.67-7.64 (m, 1H), 7.56-7.52 (m, 2H), 4.74-4.70 (m, 2H), 4.67-4.63 (m, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): δ 133.6 (d, $J_{CP} = 2.9$ Hz),
The analytical data matched those reported in the literature. HRMS calc. for C_{10}H_{16}Cl_{2}O_{3}P (M+H)^{+}: = 418.8494, found 418.8499.

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\text{C}_2\text{F}_5\text{O}-\text{P}-\text{O}-\text{C}_2\text{F}_5
\]

**bis(2,2,3,3,3-pentafluoropropyl) phenylphosphonate.** Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 5c as colorless oil (63.3 mg, 75%): ^1H NMR (500 MHz, CDCl3): δ 7.84-7.80 (m, 2H), 7.68-7.64 (m, 1H), 7.56-7.52 (m, 2H), 4.60-4.40 (m, 4H); ^13C NMR (125 MHz, CDCl3): δ 133.9 (d, J_{C-P} = 3.3 Hz), 131.8 (d, J_{C-P} = 10.8 Hz), 128.9 (d, J_{C-P} = 16.3 Hz), 124.5 (d, J_{C-P} = 194.5 Hz), 118.3 (d, J_{C-P} = 19.4 Hz), 124.5 (d, J_{C-P} = 194.5 Hz), 118.3 (d, J_{C-P} = 19.4 Hz), 113.9-109.5 (m), 61.3 (d, J_{C-P} = 4.7 Hz, J_{P-C} = 28.5 Hz). ^31P NMR (203 MHz, CDCl3): δ 21.45. ^19F NMR (470 MHz, CDCl3): δ -83.52, -124.44. HRMS calc. for C_{12}H_{18}F_{10}O_{3}P (M+H)^{+}: = 423.0202, found 423.0201.

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\text{S,S-di-p-tolyl phenylphosphonodithioate.} \text{ Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 5f as colorless oil (48.2 mg, 65%): } ^1H \text{ NMR (400 MHz, CDCl3): } \delta 7.81-7.75 (m, 2H), 7.47-7.42 (m, 1H), 7.38-7.30 (m, 6H), 7.03 (dd, J = 8.0 Hz, 4H), 2.25 (s, 6H); ^13C NMR (100 MHz, CDCl3): \delta 139.4 (d, J_{C-P} = 3.0 Hz), 135.4 (d, J_{C-P} = 4.0 Hz), 133.1 (d, J_{C-P} = 107.0 Hz), 132.4 (d, J_{C-P} = 4.0 Hz), 131.4 (d, J_{C-P} = 11.0 Hz), 129.9 (d, J_{C-P} = 2.0 Hz), 128.1 (d, J_{C-P} = 14.0 Hz), 122.3 (d, J_{C-P} = 6.0 Hz), 21.0. ^31P NMR (203 MHz, CDCl3): δ 49.92. MS (ESI): 315.1 (M+Na)^{+}. \text{ The analytical data matched those reported in the literature.}^{[6]}
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\text{S,S-bis(2,5-dimethylphenyl) phenylphosphonodithioate.} \text{ Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 5g as colorless oil (24.7 mg, 31%): } ^1H \text{ NMR (400 MHz, CDCl3): } \delta 7.82-7.77 (m, 2H), 7.52-7.47 (m, 1H), 7.42-7.37 (m, 2H), 7.25 (s, 2H), 7.07-7.00 (m, 4H), 2.28 (s, 6H), 2.20 (s, 6H); ^13C NMR (100 MHz, CDCl3): \delta 139.8 (d, J_{C-P} = 4 Hz), 137.5 (d, J_{C-P} = 4 Hz), 136.1 (d, J_{C-P} = 3 Hz), 134.5 (d, J_{C-P} = 107 Hz), 132.4 (d, J_{C-P} = 4 Hz), 131.4 (d, J_{C-P} = 11 Hz), 130.5 (d, J_{C-P} = 3 Hz), 128.2 (d, J_{C-P} = 14 Hz), 125.5 (d, J_{C-P} = 6 Hz), 20.9, 20.6. ^31P NMR (165 MHz, CDCl3): \delta 49.81. \text{ HRMS calc. for C}_{22}\text{H}_{26}\text{OPS}_{2} (M+H)^{+}: = 399.1001, \text{ found 399.1002.}
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\text{S,S-bis(4-fluorophenyl) phenylphosphonodithioate.} \text{ Performed according to the general procedure,}
\]

13.19 (d, J_{C-P} = 10.8 Hz), 128.8 (d, J_{C-P} = 15.9 Hz), 125.6 (d, J_{C-P} = 194.5 Hz), 95.0 (d, J_{C-P} = 10.1 Hz), 75.8 (d, J_{C-P} = 4.6 Hz). ^31P NMR (203 MHz, CDCl3): δ 19.19. HRMS calc. for C_{10}H_{16}Cl_{2}O_{3}P (M+H)^{+}: = 418.8494, found 418.8499.
and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 5h as colorless oil (22.7 mg, 30%): $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.80-7.75 (m, 2H), 7.55-7.51 (m, 1H), 7.45-7.40 (m, 6H), 6.97 (t, $J$ = 8.6 Hz, 4H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 163.7 (dd, $J_1$ = 2.9 Hz, $J_2$ = 249.4), 137.7 (dd, $J_1$ = 3.8 Hz, $J_2$ = 8.4 Hz), 132.9 (d, $J_{CP}$ = 3.5 Hz), 132.7 (d, $J_{CP}$ = 107.5 Hz), 131.6 (d, $J_{CP}$ = 10.9 Hz), 128.6 (d, $J_{CP}$ = 14.2 Hz), 121.0 (dd, $J_1$ = 3.4 Hz, $J_2$ = 6.1 Hz), 116.5 (dd, $J_1$ = 1.9 Hz, $J_2$ = 22.0 Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): $\delta$ 49.52 (d, $J$ = 4.9 Hz). $^{19}$F NMR (470 MHz, CDCl$_3$): $\delta$ -110.75 (d, $J$ = 5.4 Hz). HRMS calc. for C$_{18}$H$_{16}$F$_2$OSeP$_2$ (M+H)$^+$: $\delta$ = 379.0186, found 379.0187.

![O-ethyl Se-phenyl phenylphosphonoselenenate](image)

O-ethyl Se-phenyl phenylphosphonoselenenate. Performed according to the general procedure, and purified by column chromatography (petroleum ether/ethyl acetate = 9/1) to afford 5i as yellow oil (22.8 mg, 35%): $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.63-7.58 (m, 2H), 7.50-7.46 (m, 1H), 7.38-7.26 (m, 5H), 7.20-7.16 (m, 2H), 4.43-4.27 (m, 2H), 1.41 (t, $J$ = 8 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 136.4 (d, $J_{CP}$ = 3 Hz), 132.8 (d, $J_{CP}$ = 138 Hz), 132.4 (d, $J_{CP}$ = 4 Hz), 131.0 (d, $J_{CP}$ = 11 Hz), 129.2 (d, $J_{CP}$ = 2 Hz), 128.7 (d, $J_{CP}$ = 3 Hz), 128.1 (d, $J_{CP}$ = 15Hz), 124.1 (d, $J_{CP}$ = 7 Hz), 62.6 (d, $J_{CP}$ = 7 Hz), 16.2 (d, $J_{CP}$ = 7 Hz). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta$ 39.12. HRMS calc. for C$_{18}$H$_{16}$O$_2$PSe (M+H)$^+$: $\delta$ = 327.0048, found 327.0047.

![ethyl phenyl phenylphosphonate](image)

ethyl phenyl phenylphosphonate. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.89-7.85 (m, 2H), 7.59-7.56 (m, 1H), 7.50-7.46 (m, 2H), 7.27 (t, $J$ = 8.1 Hz, 2H), 7.15-7.11 (m, 3H), 4.29-4.21 (m, 2H), 1.36 (t, $J$ = 7.1 Hz, 2H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 150.5 (d, $J_{CP}$ = 7.15 Hz), 132.8 (d, $J_{CP}$ = 3.2 Hz), 131.9 (d, $J_{CP}$ = 10.1 Hz), 129.6, 128.5 (d, $J_{CP}$ = 3.15 Hz), 127.4 (d, $J_{CP}$ = 190.2 Hz), 124.9, 120.5 (d, $J_{CP}$ = 4.3 Hz), 63.0 (d, $J_{CP}$ = 5.9 Hz), 16.3 (d, $J_{CP}$ = 6.4 Hz). $^{31}$P NMR (203 MHz, CDCl$_3$): $\delta$ 15.46. MS (ESI): 263.1 (M+1)$^+$

The analytical data matched those reported in the literature.$^{(7)}$

7. Reference

8. Charts of compounds

31P NMR (203 MHz, CDCl₃)

$^1$H NMR (400 MHz, CDCl₃)
$^{13}$C NMR (198 MHz, CDCl$_3$)

$^1$H NMR (400 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{31}$P NMR (203 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{31}$P NMR (203 MHz, CDCl$_3$)
$^{31}$P NMR (203 MHz, CDCl$_3$)

$^{19}$F NMR (470 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)

$^1$H NMR (500 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{31}$P NMR (203 MHz, CDCl$_3$)
$^{31}$P NMR (203 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{31}$P NMR (203 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl₃)

$^1$H NMR (500 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{31}$P NMR (203 MHz, CDCl$_3$)
$^{31}$P NMR (203 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{31}$P NMR (203 MHz, CDCl$_3$)
$\text{\textsuperscript{13}C NMR (125 MHz, CDCl}_3\text{)}$

$\text{\textsuperscript{1}H NMR (500 MHz, CDCl}_3\text{)}$
$^{31}$P NMR (203 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)

$^1$H NMR (600 MHz, CDCl$_3$)
$^{31}P$ NMR (203 MHz, CDCl$_3$)

$^{13}C$ NMR (126 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{31}$P NMR (203 MHz, CDCl$_3$)
$^{31}$P NMR (203 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{19}$F NMR (470 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)

$^1$H NMR (500 MHz, CDCl$_3$)
$^{31}$P NMR (203 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)

$^{31}$P NMR (203 MHz, CDCl$_3$)
$^{19}$F NMR (470 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{31}$P NMR (162 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{31}$P NMR (162 MHz, CDCl$_3$)
$^{13}$C NMR (100 MHz, CDCl$_3$)

$^1$H NMR (500 MHz, CDCl$_3$)
$^{31}$P NMR (203 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)