Supporting Information for

A Convenient Method for the Synthesis of 2,5-Difunctionalized Phospholes Bearing Ester Groups

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General

All melting points are uncorrected. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded using CDCl_3 as the solvent unless otherwise noted. Chemical shifts are reported as the relative value vs. tetramethylsilane (^1H and ^{13}C) and phosphonic acid (^{31}P). The ^1H and ^{13}C NMR charts of the key compounds (**4b**, **4e**, **4f**, **4g**, **7–10**) are provided in Figures S1–S15. MALDI-TOF mass spectra were measured using CHCA as a matrix. IR spectra were observed as KBr pellets. All solvents were distilled from sodium benzophenone ketyl (ether, THF), sodium (hexane), or calcium hydride (CH_2Cl_2 , toluene) before use. All the reactions were performed under an argon or nitrogen atmosphere. Column chromatography was performed on silica gel or on a fast flow liquid chromatography system fitted with a silica gel column. Dienes **1a–h** were prepared starting from 1,7-octadiyne (for **1a**), 1,6-heptadiyne (for **1b,c,e–h**), and dipropargyl ether (for **1d**) according to Scheme S1. Other chemicals were of reagent grade quality, purchased commercially and used without further purification unless otherwise noted.

Synthesis and Characterization of **1**, **4b–g**, **6–10**

Diethyl deca-2,8-diynedioate (1a**¹):** ^1H NMR δ 1.31 (t, 6H, $J = 7.2$ Hz), 1.72 (m, 4H), 2.39 (m, 4H), 4.22 (q, 4H, $J = 7.2$ Hz).

Diethyl nona-2,7-diynedioate (1b**¹):** ^1H NMR δ 1.31 (t, 6H, $J = 7.1$ Hz), 1.86 (quin, 2H, $J = 7.1$ Hz), 2.49 (t, 4H, $J = 7.1$ Hz), 4.22 (q, 4H, $J = 7.1$ Hz).

Dimethyl nona-2,7-diynedioate (1c**²):** ^1H NMR δ 1.86 (quin, 2H, $J = 7.0$ Hz), 2.50 (t, 4H,

¹ Jones, G. B.; Wright, J. M.; Plourde, G. W. II; Hynd, G.; Huber, R. S.; Mathews, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 1937.

² Scheffer, J. R.; Wostradowski, R. A. *J. Org. Chem.* **1972**, *37*, 4317.

$J = 7.0$ Hz), 3.77 (s, 4H).

Bis[3-(ethoxycarbonyl)propargyl] ether (1d³): ^1H NMR δ 1.32 (t, 6H, $J = 7.2$ Hz), 4.25 (q, 4H, $J = 7.2$ Hz), 4.41 (s, 4H).

1-Ethoxycarbonyl-7-phenyl-1,6-heptadiyne (1e): ^1H NMR δ 1.31 (t, 3H, $J = 7.1$ Hz), 1.89 (tt, 2H, $J = 7.1, 7.1$ Hz), 2.54 (t, 2H, $J = 7.1$ Hz), 2.56 (t, 2H, $J = 7.1$ Hz), 4.22 (q, 4H, $J = 7.1$ Hz), 7.28 (m, 3H, m), 7.39 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 14.0, 17.8, 18.6, 26.7, 61.9, 73.7, 81.7, 88.2, 88.3, 123.6, 127.8, 128.2, 131.6, 153.7; IR (KBr) ν_{max} 1712 (C=O) cm^{-1} ; MS (MALDI-TOF) m/z 241 (M^+). Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{O}_2$: C, 79.97; H, 6.71. Found: C, 79.72; H, 6.68.

1-Ethoxycarbonyl-7-(2-pyridyl)-1,6-heptadiyne (1f): ^1H NMR δ 1.31 (t, 3H, $J = 7.2$ Hz), 1.92 (tt, 2H, $J = 7.0, 7.0$ Hz), 2.55 (t, 2H, $J = 7.0$ Hz), 2.60 (t, 2H, $J = 7.0$ Hz), 4.22 (q, 4H, $J = 7.2$ Hz), 7.20 (ddd, 1H, $J = 7.6, 4.9, 1.6$ Hz), 7.38 (dd, 1H, $J = 7.6, 1.6$ Hz), 7.63 (ddd, 1H, $J = 7.6, 7.6, 1.8$ Hz), 8.55 (dd, 1H, $J = 4.9, 1.8$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 14.1, 18.0, 18.6, 26.4, 61.9, 73.8, 81.4, 87.9, 88.8, 122.4, 126.8, 136.0, 143.4, 149.8, 153.6; IR (KBr) ν_{max} 1709 (C=O) cm^{-1} ; MS (MALDI-TOF) m/z 242 (M^+). Anal. Calcd for $\text{C}_{15}\text{H}_{15}\text{NO}_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.68; H, 6.22; N, 5.63.

1-Ethoxycarbonyl-7-(2-thienyl)-1,6-heptadiyne (1g): ^1H NMR δ 1.31 (t, 3H, $J = 7.1$ Hz), 1.88 (tt, 2H, $J = 7.1, 7.1$ Hz), 2.52 (t, 2H, $J = 7.1$ Hz), 2.55 (t, 2H, $J = 7.1$ Hz), 4.22 (q, 4H, $J = 7.1$ Hz), 6.94 (dd, 1H, $J = 5.2, 3.7$ Hz), 7.13 (dd, 1H, $J = 3.7, 1.1$ Hz), 7.19 (dd, 1H, $J = 5.2, 1.1$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 14.2, 17.9, 18.9, 26.6, 61.8, 73.7, 74.8, 87.9, 92.2, 123.5, 126.1, 126.7, 131.2, 153.5; IR (KBr) ν_{max} 1710 (C=O) cm^{-1} ; MS (MALDI-TOF) m/z 246 (M^+). Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{S}$: C, 68.26; H, 5.73. Found: C, 68.23; H, 5.52.

1-(9-Anthryl)-7-ethoxycarbonyl-1,6-heptadiyne (1h): Mp 42–43 $^{\circ}\text{C}$; ^1H NMR δ 1.31 (t,

³ Yamamoto, Y.; Nagata, A.; Nagata, H.; Ando, Y.; Arikawa, Y.; Tatsumi, K.; Itoh, K. *Chem. Eur. J.* **2003**, 9, 2469.

3H, $J = 7.1$ Hz), 2.10 (tt, 2H, $J = 7.0, 7.0$ Hz), 2.70 and 2.91 (each t, 2H, $J = 7.0$ Hz), 4.23 (q, 4H, $J = 7.1$ Hz), 7.46–7.58 (m, 4H), 7.99 (d, 2H, $J = 8.4$ Hz), 8.39 (s, 1H), 8.51 (d, 2H, $J = 8.4$ Hz); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 14.0, 18.1, 19.4, 27.0, 61.8, 73.8, 78.2, 87.9, 99.6, 117.6, 125.4, 126.2, 126.5, 126.9, 128.5, 131.0, 132.5, 153.5; IR (neat) ν_{max} 1708 (C=O) cm^{-1} ; MS (MALDI-TOF) m/z 340 (M^+). Although spectroscopic data clearly supported a high state of purity of **1h**, we were not successful in obtaining satisfactory analytical data of an accuracy within $\pm 0.4\%$.

SCHEME S1. Synthesis of **1a-h**.

Phosphole 4b: Mp 75–76 °C; ^1H NMR δ 1.17 (t, 6H, $^1J = 6.4$ Hz), 2.33 (br, 2H), 2.80 (br, 2H), 3.13 (br, 2H), 4.15 (br, 4H), 7.27–7.42 (m, 5H); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 14.1, 28.3, 30.1, 60.5, 128.4 (d, $^3J_{\text{P-C}} = 8.7$ Hz), 129.8 (d, $^4J_{\text{P-C}} = 1.9$ Hz), 132.9, 133.7 (d, $^2J_{\text{P-C}} = 19.9$ Hz), 164.7 (d, $^2J_{\text{P-C}} = 20.4$ Hz), 167.3 (d, $^2J_{\text{P-C}} = 10.6$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ + 32.7; IR (KBr) ν_{max} 1703, 1689 (C=O) cm^{-1} ; MS (MALDI-TOF) m/z 345 ($[\text{M}+\text{H}]^+$). Anal. Calcd for $\text{C}_{11}\text{H}_{21}\text{O}_4\text{P}$: C, 66.27; H, 6.15; P, 9.00. Found: C, 66.13; H, 6.36; P, 8.75. The *ipso* carbon of the phenyl

group could not be detected clearly in the ^{13}C NMR.

Phosphole 4c : Mp 107–108 °C; ^1H NMR δ 2.33 (br, 2H), 2.81 (br, 2H), 3.13 (br, 2H), 3.69 (s, 6H), 7.28–7.40 (m, 5H); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 28.3, 30.1, 51.7, 128.6 (d, $^3J_{\text{P-C}} = 8.7$ Hz), 129.8, 129.9 (d, $^1J_{\text{P-C}} = 8.7$ Hz), 132.5 (d, $^1J_{\text{P-C}} = 3.1$ Hz), 133.6 (d, $^2J_{\text{P-C}} = 19.9$ Hz), 165.1 (d, $^2J_{\text{P-C}} = 20.5$ Hz), 167.6 (d, $^2J_{\text{P-C}} = 9.9$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ + 32.6; IR (KBr) ν_{max} 1699 (C=O) cm^{-1} ; MS (MALDI-TOF) m/z 317 (M^+). Anal. Calcd for $\text{C}_9\text{H}_{17}\text{O}_4\text{P}$: C, 64.56; H, 5.42; P, 9.79. Found: C, 64.44; H, 5.57; P, 9.65.

Phosphole 4d: Mp 89–90 °C; ^1H NMR δ 1.19 (t, 6H, $J = 7.1$ Hz), 4.17 (q, 4H, $J = 7.1$ Hz), 4.97 (m, 4H), 7.31–7.45 (m, 5H); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 14.1, 61.0, 69.6, 128.7 (d, $^3J_{\text{P-C}} = 9.3$ Hz), 130.3, 132.1, 133.9 (d, $^2J_{\text{P-C}} = 20.5$ Hz), 161.6 (d, $^1J_{\text{P-C}} = 10.6$ Hz), 163.8 (d, $^2J_{\text{P-C}} = 15.6$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ + 40.5; IR (KBr) ν_{max} 1690 (C=O) cm^{-1} ; MS (MALDI-TOF) m/z 347 ($[\text{M}+\text{H}]^+$). Anal. Calcd for $\text{C}_{10}\text{H}_{19}\text{O}_5\text{P}$: C, 62.43; H, 5.53; P, 8.94. Found: C, 62.16; H, 5.73; P, 8.66. The *ipso* carbon of the phenyl group could not be detected clearly in the ^{13}C NMR.

Phosphole 4e: Mp 135–136 °C; ^1H NMR δ 1.20 (t, 3H, $J = 7.3$ Hz), 2.35 (m, 2H), 2.65–3.15 (m, 4H), 4.14 (m, 2H), 7.17–7.24 (m, 4H), 7.27–7.31 (m, 2H), 7.39 (m, 2H), 7.49 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 14.3, 29.1, 29.2, 30.0, 60.0, 126.1, 127.4, 128.0 (d, $^3J_{\text{P-C}} = 10.6$ Hz), 128.5 (d, $^3J_{\text{P-C}} = 8.8$ Hz), 128.6, 129.3, 131.7 (d, $^1J_{\text{P-C}} = 12.3$ Hz), 133.6 (d, $^2J_{\text{P-C}} = 19.3$ Hz), 136.2 (d, $^2J_{\text{P-C}} = 17.4$ Hz), 144.6, 153.1 (d, $^2J_{\text{P-C}} = 8.1$ Hz), 165.1 (d, $^2J_{\text{P-C}} = 21.7$ Hz), 170.1 (d, $^2J_{\text{P-C}} = 11.8$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ + 32.0; IR (KBr) ν_{max} 1690 (C=O) cm^{-1} ; MS (MALDI-TOF) m/z 348 (M^+). Anal. Calcd for $\text{C}_{22}\text{H}_{21}\text{O}_2\text{P}$: C, 75.85; H, 6.08; P, 8.89. Found: C, 75.55; H, 6.25; P, 8.86.

Phosphole 4f: Mp 135–136 °C; ^1H NMR δ 1.19 (t, 3H, $J = 7.2$ Hz), 2.37 (m, 2H), 2.75–3.25 (m, 4H), 4.15 (m, 2H), 7.06 (m, 1H), 7.19–7.28 (m, 3H), 7.41–7.46 (m, 2H), 7.47 (m, 1H), 7.56 (m, 1H), 8.53 (m, 1H); ^{13}C NMR δ 14.3, 28.9, 29.8, 30.0, 60.1, 121.4, 122.1 (d, $^3J_{\text{P-C}} =$

7.2 Hz), 128.2 (d, $^3J_{\text{P-C}} = 8.4$ Hz), 129.2 (d, $^4J_{\text{P-C}} = 1.7$ Hz), 131.8 (d, $^1J_{\text{P-C}} = 12.8$ Hz), 133.6 (d, $^2J_{\text{P-C}} = 19.5$ Hz), 136.2 (d, $^4J_{\text{P-C}} = 1.1$ Hz), 143.7, 149.6, 154.5 (d, $^2J_{\text{P-C}} = 17.8$ Hz), 156.3 (d, $^2J_{\text{P-C}} = 8.4$ Hz), 165.0 (d, $^2J_{\text{P-C}} = 21.2$ Hz), 169.2 (d, $^2J_{\text{P-C}} = 11.7$ Hz); ^{31}P NMR $\delta + 32.6$; IR (KBr) ν_{max} 1695 (C=O) cm^{-1} ; MS (MALDI-TOF) m/z 350 (M^+). Anal. Calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_2\text{P}$: C, 72.20; H, 5.77; N, 4.01; P, 8.89. Found: C, 72.10; H, 5.79; N, 3.97; P, 8.76. One of the α carbons could not be detected clearly in the ^{13}C NMR.

Phosphole 4g: Mp 131–132 °C; ^1H NMR δ 1.18 (t, 3H, $J = 7.1$ Hz), 2.39 (m, 2H), 2.65–3.20 (m, 4H), 4.12 (m, 2H), 6.93 (m, 1H), 7.04 (m, 1H), 7.27 (m, 1H), 7.29 (m, 3H), 7.45 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 14.2, 28.7, 29.1, 30.2, 60.0, 125.1, 126.2 (d, $^5J_{\text{P-C}} = 1.9$ Hz), 126.4 (d, $^3J_{\text{P-C}} = 8.0$ Hz), 127.7, 128.6 (d, $^3J_{\text{P-C}} = 8.8$ Hz), 129.7, 132.0 (d, $^1J_{\text{P-C}} = 13.7$ Hz), 133.8 (d, $^2J_{\text{P-C}} = 19.9$ Hz), 137.9 (d, $^1J_{\text{P-C}} = 3.7$ Hz), 139.5 (d, $^2J_{\text{P-C}} = 21.2$ Hz), 152.1 (d, $^2J_{\text{P-C}} = 8.1$ Hz), 165.0 (d, $^2J_{\text{P-C}} = 21.7$ Hz), 170.3 (d, $^2J_{\text{P-C}} = 10.6$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR $\delta + 33.4$; IR ν_{max} 1690 (C=O) cm^{-1} ; MS (MALDI-TOF) m/z 354 (M^+). Anal. Calcd for $\text{C}_{22}\text{H}_{19}\text{O}_2\text{PS}$: C, 67.78; H, 5.40; P, 8.74. Found: C, 67.63; H, 5.46; P, 8.45.

Phospholes 6 and 7: To a solution of **4b** (300 mg, 0.87 mmol) in 10 mL of hexane was added a hexane solution of DIBAL (1.0 M, 3.5 mL, 3.5 mmol) at -78°C . After stirring for 1 h at -50°C , elemental sulfur (40 mg, 1.3 mmol) was added, and the resulting mixture was allowed to warm slowly to room temperature. A saturated NH_4Cl solution (5 mL) was then added, and the mixture was filtered through a Celite bed. The organic phase was separated from the filtrate, and the aqueous phase was extracted with Et_2O (5 mL $\times$ 3). The combined organic extracts were washed with brine (20 mL), dried over Na_2SO_4 , and evaporated to give a crude product, which was recrystallized from EtOAc /hexane to give **7** (160 mg, 0.55 mmol, 63%) as a pale yellow solid. When the reaction was quenched without adding elemental sulfur, the $\square^3$ -phosphine **6** was obtained as a rather air-sensitive substance. The

structure of **6** was characterized on the basis of ^1H NMR and MS.

Phosphole 6: ^1H NMR δ 1.77 (br, 2H), 2.14 (m, 1H), 2.28 (m, 1H), 2.45 (m, 2H), 2.64 (m, 2H), 4.38 (m, 2H), 4.52 (m, 2H), 7.28–7.40 (m, 5H); MS (MALDI-TOF) m/z 503 ($[\text{2M-OH}]^+$).

Phosphole 7: Mp 131–132 °C; ^1H NMR δ 2.03 (t, 2H, $J = 6.0$ Hz), 2.10–2.27 (m, 2H), 2.58–2.73 (m, 4H), 4.38–4.52 (m, 4H), 7.43–7.55 (m, 3H), 7.82–7.88 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 27.0 (d, $^4J_{\text{P-C}} = 1.8$ Hz), 27.4 (d, $^3J_{\text{P-C}} = 11.2$ Hz), 57.6 (d, $^2J_{\text{P-C}} = 15.6$ Hz), 127.6 (d, $^1J_{\text{P-C}} = 70.3$ Hz), 128.9 (d, $^2J_{\text{P-C}} = 12.4$ Hz), 130.0, 130.3 (d, $^3J_{\text{P-C}} = 11.9$ Hz), 132.2 (d, $^4J_{\text{P-C}} = 2.4$ Hz), 157.3 (d, $^2J_{\text{P-C}} = 23.0$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ +67.5; IR (KBr) ν_{max} 3390 (OH) cm^{-1} ; MS (MALDI-TOF) m/z 292 (M^+). HRMS: Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2\text{PS}$ ($[\text{M}+\text{H}]^+$), 293.0765; Found, 293.0766.

Phosphole 8: To a solution of **4b** (1.17 g, 3.40 mmol) in 7 mL of THF was added MeMgBr (15 mL, 0.96 M in THF, 14 mmol) at -78 °C. The mixture was gradually warmed to room temperature during 30 min, and stirred for an additional 30 min at 50 °C. The mixture was then acidified by sat. NH_4Cl aq (3 mL) at 0 °C, and elemental sulfur (160 mg, 5.0 mmol) was added at the same temperature. After stirring for 30 min, an aqueous phase was extracted with ether. The organic extracts were combined, washed with brine, dried over Na_2SO_4 , and evaporated to give an oily residue, which was subjected on silica gel column chromatography (hexane/EtOAc = 2/1: R_f = 0.2) to afford **8** as a pale yellow solid (475 mg, 1.36 mmol, 40%). Mp 133–134 °C; ^1H NMR δ 1.28 (s, 6H), 1.43 (s, 6H), 2.12–2.18 (m, 2H), 2.64–2.69 (m, 4H), 3.03 (s, 2H), 7.26–7.49 (m, 3H), 7.85–7.91 (m, 2H); ^{13}C NMR δ 27.1 (d, $^4J_{\text{P-C}} = 1.7$ Hz), 28.5 (d, $^3J_{\text{P-C}} = 12.3$ Hz), 29.8 (d, $^3J_{\text{P-C}} = 1.6$ Hz), 31.3 (d, $^3J_{\text{P-C}} = 2.5$ Hz), 72.9 (d, $^2J_{\text{P-C}} = 11.5$ Hz), 128.6 (d, $^1J_{\text{P-C}} = 71.8$ Hz), 128.6 (d, $^2J_{\text{P-C}} = 12.3$ Hz), 130.0 (d, $^3J_{\text{P-C}} = 11.5$ Hz), 131.5 (d, $^4J_{\text{P-C}} = 3.3$ Hz), 136.8 (d, $^1J_{\text{P-C}} = 75.9$ Hz), 157.3 (d, $^2J_{\text{P-C}} = 23.0$

Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ + 68.9; IR (KBr) ν_{max} 3390 (OH) cm^{-1} ; MS (MALDI-TOF) m/z 314 ($[\text{M}-2(\text{OH})]^+$). HRMS: Calcd for $\text{C}_{19}\text{H}_{25}\text{O}_2\text{PS}$ (M^+), 348.1313; Found, 348.1317.

Phosphole 9: A mixture of **4g** (53 mg, 0.15 mmol), elemental sulfur (24 mg, 0.75 mmol), and CH_2Cl_2 (2 mL) was stirred for 5 days at room temperature. The solvent was then evaporated, and the crude product was purified on a silica gel column using CH_2Cl_2 as an eluent (R_f = 0.2) to give **9** (20 mg, 35%) as a yellow solid. Mp 111–112 °C; ^1H NMR δ 1.16 (t, 3H, J = 7.1 Hz), 2.35 (m, 2H), 2.91 (m, 2H), 3.10 (m, 2H), 4.14 (m, 2H), 7.00 (m, 1H), 7.38 (m, 1H), 7.42 (m, 1H), 7.42 (m, 2H), 7.50 (m, 1H), 7.86 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 14.0, 27.0 (d, $^4J_{\text{P-C}}$ = 1.7 Hz), 29.4 (d, $^3J_{\text{P-C}}$ = 9.9 Hz), 30.9 (d, $^3J_{\text{P-C}}$ = 9.1 Hz), 60.5, 120.4 (d, $^1J_{\text{P-C}}$ = 81.3 Hz), 128.0, 128.4, 128.6 (d, $^2J_{\text{P-C}}$ = 13.2 Hz), 129.1 (d, $^3J_{\text{P-C}}$ = 4.1 Hz), 129.2 (d, $^1J_{\text{P-C}}$ = 82.5 Hz), 130.5, 130.5 (d, $^3J_{\text{P-C}}$ = 12.4 Hz), 132.1 (d, $^4J_{\text{P-C}}$ = 2.8 Hz), 135.1 (d, $^2J_{\text{P-C}}$ = 18.2 Hz), 149.7 (d, $^2J_{\text{P-C}}$ = 19.8 Hz), 162.0 (d, $^2J_{\text{P-C}}$ = 17.4 Hz), 173.6 (d, $^2J_{\text{P-C}}$ = 19.8 Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ + 66.2; IR ν_{max} 1692 (C=O) cm^{-1} ; MS (MALDI-TOF) m/z 387 (M^+). HRMS: Calcd for $\text{C}_{20}\text{H}_{19}\text{O}_2\text{PS}_2$, 386.0564 (M^+); Found, 386.0566.

Phosphole 10: To a solution of **4g** (200 mg, 0.56 mmol) in 10 mL of hexane was added a hexane solution of DIBAL (1.0 M, 1.12 mL, 1.12 mmol) at –78 °C. After stirring for 1 h at –50 °C, elemental sulfur (27 mg, 0.85 mmol) was added, and the resulting mixture was allowed to warm slowly to room temperature. A saturated NH_4Cl solution (5 mL) was then added, and the mixture was filtered through a Celite bed. The organic phase was separated from the filtrate, and the aqueous phase was extracted with Et_2O (10 mL $\times$ 2). The combined organic extracts were treated with brine (20 mL), dried over MgSO_4 , and evaporated to give a crude product, which was purified on a silica gel column using hexane/ AcOEt (2:1) as eluents (R_f = 0.3) to afford **10** (160 mg, 83%) as a yellow solid.

Mp 170–171 °C; ^1H NMR δ 2.09 (br, 1H), 2.31 (m, 2H), 2.72 (m, 2H), 2.87 (m, 2H), 4.48 (m, 2H), 6.95 (m, 1H), 7.25 (m, 1H), 7.29 (m, 1H), 7.43 (m, 2H), 7.50 (m, 1H), 7.88 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR δ 27.2 (d, $^4J_{\text{P-C}} = 1.7$ Hz), 27.5 (d, $^3J_{\text{P-C}} = 11.7$ Hz), 29.7 (d, $^3J_{\text{P-C}} = 11.1$ Hz), 57.7 (d, $^2J_{\text{P-C}} = 15.0$ Hz), 125.0 (d, $^1J_{\text{P-C}} = 81.3$ Hz), 126.4, 126.7 (d, $^3J_{\text{P-C}} = 4.5$ Hz), 127.6, 127.8, 128.4 (d, $^1J_{\text{P-C}} = 71.4$ Hz), 128.9 (d, $^2J_{\text{P-C}} = 12.8$ Hz), 130.4 (d, $^3J_{\text{P-C}} = 11.7$ Hz), 132.1 (d, $^4J_{\text{P-C}} = 2.8$ Hz), 135.2 (d, $^2J_{\text{P-C}} = 19.5$ Hz), 151.9 (d, $^2J_{\text{P-C}} = 22.8$ Hz), 158.2 (d, $^2J_{\text{P-C}} = 21.7$ Hz); $^{31}\text{P}\{^1\text{H}\}$ NMR δ + 68.0; IR (KBr) ν_{max} 3475 (OH) cm^{-1} ; MS (MALDI-TOF) m/z 344 (M^+). Anal. Calcd for $\text{C}_{18}\text{H}_{17}\text{OPS}_2$: C, 62.77; H, 4.97; P, 8.99. Found: C, 62.58; H, 5.02; P, 8.73.

^1H and ^{13}C NMR charts of 4b, 4e-g, 7-10

Figure S1. ^1H NMR chart of 4b.

Figure S5. ¹H NMR chart of 4f.

Figure S6. ^{13}C NMR chart of 4f.

Figure S7. ¹H NMR chart of 4g.

Figure S8. ¹³C NMR chart of 4g.

Figure S11. ¹H NMR chart of 8.

Figure S12. ¹³C NMR chart of 8.

Figure S13. ¹H NMR chart of 9.

Figure S14. ^{13}C NMR chart of 9.

Figure S15. ^1H NMR chart of 10.