Supporting Information

Synthesis of Bulky Phosphines by Rhodium-Catalyzed Formal [2+2+2] Cycloaddition Reactions of Tethered Diynes with 1-Alkynylphosphine Sulfides

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Preparation of Alkynylphosphine Sulfide

Alkynylphosphines were prepared according to the literature.¹ The sulfides were prepared quantitatively by treatment of alkynylphosphines with 3 equiv of crystalline sulfur in THF or DMF with monitoring TLC.

Typical Procedure for the Rhodium-Catalyzed Reaction

Synthesis of **3ca** is representative. [RhCl(cod)]₂ (3.7 mg, 0.0075 mmol), AgBF₄ (2.9 mg, 0.015 mmol), and BINAP (9.3 mg, 0.015 mmol) were placed in a 20-mL reaction flask under argon. Dichloromethane (4.0 mL), 1-octynyldiphenylphosphine sulfide (**2a**, 0.16 g, 0.50 mmol), and 4,4-di(methoxycarbonyl)-1,6-heptadiyne (**1c**, 0.13 g, 0.60 mmol) were sequentially added. The resulting solution was stirred for 4 h at 25 °C. Water (10 mL) was added, and the product was extracted with ethyl acetate (10 mL × 3). The combined organic layer was dried over sodium sulfate and concentrated under reduced pressure. Chromatographic purification on silica gel yielded **3ca** (0.26 g, 0.49 mmol, 97%) as a white solid.

Typical Procedure for the (Me₃Si)₃SiH-Mediated Radical Desulfidation Reaction

Synthesis of **3gb–S** is representative. AIBN (1.6 mg, 0.010 mmol) and **3gb** (0.068 g, 0.10 mmol) were placed in a 20-mL reaction flask under argon. Benzene (2.0 mL) and tris(trimethylsilyl)silane (0.037 g, 0.15 mmol) were sequentially added. The resulting solution was stirred for 12 h at reflux. After being cooled to room temperature, the mixture was concentrated in vacuo. Silica gel column purification provided **3gb–S** (0.054 g, 0.084 mmol, 84%) as a white solid.

¹ Kondoh, A.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2007**, *129*, 4099–4104.

Scheme for the Synthesis of Diphenyl(2,6-diphenylphenyl)phosphine (Reference 9 in the main text)

Characterization Data

6,6-Di(methoxycarbonyl)-2,10-dimethyl-3,8-undecadiyne (1h): IR (neat) 2970, 2873, 1744, 1436, 1326, 1293, 1210, 1181, 1062, 950, 902, 854 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.09 (d, J = 7.0 Hz, 12H), 2.46 (sep, J = 7.0 Hz, 2H), 2.88 (s, 4H), 3.72 (s, 6H); ^{13}C NMR (CDCl_3) δ 20.41, 22.86, 23.16, 52.71, 57.55, 73.42, 89.34, 169.65. Found: C, 68.58; H, 8.23%. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_4$: C, 69.84; H, 8.27%.

1-Octynyldiphenylphosphine sulfide (2a): IR (neat) 2930, 2857, 2193, 1437, 1103, 1027, 999, 747, 720, 619, 666 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.87 (t, J = 7.0 Hz, 3H), 1.22–1.34 (m, 4H), 1.36–1.46 (m, 2H), 1.62 (tt, J = 7.5, 7.5 Hz, 2H), 2.46 (dt, J = 3.5, 7.5 Hz, 2H), 7.39–7.49 (m, 6H), 7.89–7.97 (m, 4H); ^{13}C NMR (CDCl_3) δ 13.80, 19.87 (d, J = 2.9 Hz), 22.27, 27.38 (d, J = 1.9 Hz), 28.35, 30.94, 73.80 (d, J = 157.0 Hz), 110.16 (d, J = 26.3 Hz), 128.35 (d, J = 13.9 Hz), 130.56 (d, J = 12.4 Hz), 131.43 (d, J = 3.4 Hz), 134.00 (d, J = 97.9 Hz); ^{31}P NMR (CDCl_3) δ 17.55. Found: C, 73.81; H, 7.18%. Calcd for $\text{C}_{20}\text{H}_{23}\text{PS}$: C, 73.59; H, 7.10%.

Diphenyl(phenylethynyl)phosphine sulfide (2b): IR (nujol) 2923, 2854, 2171, 1684, 1653, 1558, 1457, 1436, 1100, 849, 720, 688 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.34–7.64 (m, 11H), 7.96–8.06 (m, 4H); ^{13}C NMR (CDCl_3) δ 81.96 (d, J = 151.3 Hz), 105.77 (d, J = 25.9 Hz), 120.12 (d, J = 4.3 Hz), 128.48, 128.60 (d, J = 13.9 Hz), 130.57, 130.80 (d, J = 12.4 Hz), 131.74 (d, J = 2.9 Hz), 132.37 (d, J = 2.4 Hz), 133.76 (d, J = 98.4 Hz); ^{31}P NMR (CDCl_3) δ 18.39. Found: C, 75.58; H, 4.65%. Calcd for $\text{C}_{20}\text{H}_{15}\text{PS}$: C, 75.45; H, 4.75%. m.p.: 108.0–109.5 $^{\circ}\text{C}$.

(3-Methyl-1-butynyl)diphenylphosphine sulfide (2c): IR (nujol) 2924, 2854, 2187, 1478, 1436, 1311, 1111, 978, 835, 720, 662 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.30 (d, J = 7.0 Hz, 6H), 2.84 (dsep, J = 3.5, 7.0 Hz, 1H), 7.42–7.52 (m, 6H), 7.88–7.96 (m, 4H); ^{13}C NMR (CDCl_3)

δ 21.72 (d, J = 3.4 Hz), 21.79 (d, J = 1.9 Hz), 72.94 (d, J = 33.5 Hz), 114.68 (d, J = 25.3 Hz), 128.52 (d, J = 13.9 Hz), 130.73 (d, J = 12.4 Hz), 131.56 (d, J = 2.9 Hz), 134.19 (d, J = 99.3 Hz); ^{31}P NMR (CDCl_3) δ 17.40. Found: C, 71.58; H, 6.03%. Calcd for $\text{C}_{17}\text{H}_{17}\text{PS}$: C, 71.80; H, 6.03%. m.p.: 80.5–82.0 °C.

(3,3-Dimethyl-1-butynyl)diphenylphosphine sulfide (2d): IR (nujol) 2922, 2853, 2158, 1684, 1653, 1558, 1506, 1457, 1437, 1250, 1096, 752, 710 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.35 (s, 9H), 7.41–7.51 (m, 6H), 7.88–7.96 (m, 4H); ^{13}C NMR (CDCl_3) δ 28.69 (d, J = 2.9 Hz), 29.98 (d, J = 1.9 Hz), 72.31 (d, J = 157.0 Hz), 117.02 (d, J = 24.9 Hz), 128.51 (d, J = 13.9 Hz), 130.69 (d, J = 11.9 Hz), 131.50 (d, J = 3.3 Hz), 134.43 (d, J = 97.9 Hz); ^{31}P NMR (CDCl_3) δ 17.28. m.p.: 136.0–137.5 °C.

(2-Methoxyphenylethynyl)diphenylphosphine sulfide (2e): IR (nujol) 2920, 2851, 1773, 1718, 1684, 1653, 1559, 1507, 1457, 1420, 1263, 1024, 665 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.91 (s, 3H), 6.90–6.97 (m, 2H), 7.38–7.55 (m, 8H), 8.02–8.10 (m, 4H); ^{13}C NMR (CDCl_3) δ 55.84, 85.47 (d, J = 155.1 Hz), 103.04 (d, J = 27.3 Hz), 109.63 (d, J = 4.4 Hz), 110.80, 120.48, 128.52 (d, J = 13.4 Hz), 130.93 (d, J = 12.4 Hz), 131.58 (d, J = 2.9 Hz), 132.17, 134.04 (d, J = 2.0 Hz), 134.20 (d, J = 98.4 Hz), 161.54; ^{31}P NMR (CDCl_3) δ 18.42. Found: C, 72.47; H, 4.97%. Calcd for $\text{C}_{21}\text{H}_{17}\text{OPS}$: C, 72.40; H, 4.92%. m.p.: 77.0–78.5 °C.

(Trimethylsilylethynyl)diphenylphosphine sulfide (2f): IR (nujol) 2920, 2851, 2401, 1735, 1685, 1560, 1540, 1438, 1252, 1097, 713 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.28 (s, 9H), 7.43–7.53 (m, 6H), 7.88–7.96 (m, 4H); ^{13}C NMR (CDCl_3) δ –0.77, 97.60 (d, J = 133.6 Hz), 116.01 (d, J = 14.8 Hz), 128.60 (d, J = 13.8 Hz), 130.81 (d, J = 12.0 Hz), 131.73 (d, J = 3.4 Hz), 133.58 (d, J = 97.4 Hz); ^{31}P NMR (CDCl_3) δ 17.12. Found: C, 64.75; H, 6.25%. Calcd for $\text{C}_{17}\text{H}_{19}\text{PSSi}$: C, 64.93; H, 6.09%. m.p.: 158.0–159.5 °C.

(2-Methoxy-1-naphthylethynyl)diphenylphosphine sulfide (2g): IR (nujol) 2923, 2854, 2333, 2164, 1587, 1460, 1438, 1378, 1277, 1095, 812, 718, 660 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.01 (s, 3H), 7.22 (d, J = 9.0 Hz, 1H), 7.34–7.40 (m, 1H), 7.46–7.55 (m, 7H), 7.76 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 9.0 Hz, 1H), 8.10–8.20 (m, 5H); ^{13}C NMR (CDCl_3) δ 56.49, 90.56 (d, J = 155.0 Hz), 102.12 (d, J = 27.3 Hz), 102.98, 112.16, 124.51, 124.69, 128.05, 128.19, 128.22, 128.51 (d, J = 13.9 Hz), 130.90 (d, J = 12.0 Hz), 131.57 (d, J = 3.3 Hz), 132.83, 134.33 (d, J = 97.9 Hz), 134.44, 161.39 (d, J = 1.9 Hz); ^{31}P NMR (CDCl_3) δ 18.59. Found: C, 75.10; H, 4.72%. Calcd for $\text{C}_{25}\text{H}_{19}\text{OPS}$: C, 75.36; H, 4.81%. m.p.: 117.5–119.0 °C.

(6-Hexyl-*N*-tosyl-5-isoindolinyl)diphenylphosphine sulfide (3aa): IR (nujol) 2923, 2854, 1597, 1459, 1437, 1378, 1350, 1166, 1099, 695, 665 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.79 (t, J = 7.5 Hz, 3H), 0.98–1.07 (m, 4H), 1.10–1.20 (m, 2H), 1.28–1.38 (m, 2H), 2.41 (s, 3H), 2.66–2.74 (m, 2H), 4.43 (s, 2H), 4.60 (s, 2H), 6.76 (d, J = 14.5 Hz, 1H), 7.17 (d, J = 4.0 Hz,

1H), 7.31 (d, $J = 7.5$ Hz, 2H), 7.41–7.55 (m, 6H), 7.70–7.81 (m, 6H); ^{13}C NMR (CDCl_3) δ 13.97, 21.47, 22.40, 29.14, 30.81, 31.43, 34.19 (d, $J = 5.8$ Hz), 53.40, 53.58, 125.15 (d, $J = 11.0$ Hz), 126.82 (d, $J = 13.4$ Hz), 127.55, 128.54 (d, $J = 12.4$ Hz), 129.83, 131.58 (d, $J = 2.9$ Hz), 131.66 (d, $J = 84.9$ Hz), 132.20 (d, $J = 10.0$ Hz), 132.66 (d, $J = 83.5$ Hz), 133.38 (d, $J = 13.9$ Hz), 133.55, 140.15 (d, $J = 2.4$ Hz), 143.80, 147.48 (d, $J = 10.0$ Hz); ^{31}P NMR (CDCl_3) δ 40.52. Found: C, 68.90; H, 6.29%. Calcd for $\text{C}_{33}\text{H}_{36}\text{NO}_2\text{PS}$: C, 69.08; H, 6.32%. m.p.: 189.0–191.0 °C.

(6-Hexyl-1,3-dihydro-5-isobenzofuranyl)diphenylphosphine sulfide (3ba): IR (nujol) 2925, 2853, 1684, 1653, 1558, 1437, 1097, 1049, 904, 759 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.80 (t, $J = 7.5$ Hz, 3H), 1.02–1.10 (m, 4H), 1.11–1.21 (m, 2H), 1.35–1.44 (m, 2H), 2.75–2.82 (m, 2H), 4.94 (s, 2H), 5.09 (s, 2H), 6.86 (d, $J = 14.5$ Hz, 1H), 7.25 (d, $J = 4.5$ Hz, 1H), 7.43–7.55 (m, 6H), 7.78–7.86 (m, 4H); ^{13}C NMR (CDCl_3) δ 13.97, 22.40, 29.17, 30.88, 31.45, 34.25 (d, $J = 6.1$ Hz), 73.24, 73.28, 123.55 (d, $J = 11.4$ Hz), 125.25 (d, $J = 13.3$ Hz), 128.46 (d, $J = 12.4$ Hz), 132.24 (d, $J = 85.9$ Hz), 131.43 (d, $J = 2.9$ Hz), 132.23 (d, $J = 10.5$ Hz), 132.98 (d, $J = 83.5$ Hz), 136.36 (d, $J = 13.4$ Hz), 143.33 (d, $J = 2.9$ Hz), 147.03 (d, $J = 10.5$ Hz); ^{31}P NMR (CDCl_3) δ 40.87. Found: C, 74.00; H, 6.97%. Calcd for $\text{C}_{26}\text{H}_{29}\text{OPS}$: C, 74.26; H, 6.95%. m.p.: 117.5–119.0 °C.

[6-Hexyl-2,2-di(methoxycarbonyl)-5-indanyl]diphenylphosphine sulfide (3ca): IR (nujol) 2923, 2853, 1731, 1654, 1560, 1457, 1430, 1250, 1120, 1162, 1075, 1059, 701, 665 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.80 (t, $J = 7.5$ Hz, 3H), 1.00–1.10 (m, 4H), 1.11–1.21 (m, 2H), 1.30–1.41 (m, 2H), 2.67–2.73 (m, 2H), 3.44 (s, 2H), 3.59 (s, 2H), 3.74 (s, 6H), 6.79 (d, $J = 14.5$ Hz, 1H), 7.19 (d, $J = 4.5$ Hz, 1H), 7.42–7.54 (m, 6H), 7.76–7.84 (m, 4H); ^{13}C NMR (CDCl_3) δ 14.02, 22.46, 29.27, 30.89, 31.53, 34.26 (d, $J = 5.8$ Hz), 40.30, 40.60, 53.02, 60.07, 126.83 (d, $J = 11.4$ Hz), 128.44 (d, $J = 12.0$ Hz), 128.47 (d, $J = 12.9$ Hz), 130.11 (d, $J = 85.9$ Hz), 131.36 (d, $J = 2.9$ Hz), 132.33 (d, $J = 10.5$ Hz), 133.19 (d, $J = 83.5$ Hz), 137.04 (d, $J = 13.8$ Hz), 144.20 (d, $J = 2.9$ Hz), 146.57 (d, $J = 10.0$ Hz), 171.83; ^{31}P NMR (CDCl_3) δ 40.69. Found: C, 69.44; H, 6.33%. Calcd for $\text{C}_{31}\text{H}_{35}\text{O}_4\text{PS}$: C, 69.64; H, 6.60%. m.p.: 159.0–160.5 °C.

(6-Hexyl-5-indanyl)diphenylphosphine sulfide (3da): IR (neat) 3054, 2848, 1963, 1898, 1817, 1775, 1675, 1607, 1557, 1436, 1391, 1309, 1097, 998 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.81 (t, $J = 7.5$ Hz, 3H), 1.00–1.10 (m, 4H), 1.12–1.22 (m, 2H), 1.34–1.44 (m, 2H), 2.03 (tt, $J = 7.5$, 7.5 Hz, 2H), 2.71 (t, $J = 7.5$ Hz, 2H), 2.73 (t, $J = 7.5$ Hz, 2H), 2.90 (t, $J = 7.5$ Hz, 2H), 6.83 (d, $J = 15.0$ Hz, 1H), 7.22 (d, $J = 4.5$ Hz, 1H), 7.41–7.53 (m, 6H), 7.79–7.86 (m, 4H); ^{13}C NMR (CDCl_3) δ 14.03, 22.47, 25.25, 29.30, 31.05, 31.56, 32.47, 32.90, 34.27 (d, $J = 6.1$ Hz), 127.06 (d, $J = 11.5$ Hz), 128.36 (d, $J = 12.0$ Hz), 128.62 (d, $J = 12.9$ Hz), 128.65 (d, $J = 84.5$ Hz), 131.21 (d, $J = 2.9$ Hz), 132.33 (d, $J = 10.5$ Hz), 133.58 (d, $J = 83.1$ Hz), 141.25 (d, $J =$

13.4 Hz), 145.48 (d, $J = 10.0$ Hz), 148.64 (d, $J = 2.9$ Hz); ^{31}P NMR (CDCl_3) δ 40.83. Found: C, 77.62; H, 7.29%. Calcd for $\text{C}_{27}\text{H}_{31}\text{PS}$: C, 77.47; H, 7.46%.

(7-Hexyl-1,2,3,4-tetrahydro-6-naphthyl)diphenylphosphine sulfide (3ea): IR (neat) 3055, 2848, 2218, 1962, 1896, 1817, 1602, 1554, 1436, 1309, 1097, 1028, 912 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.81 (t, $J = 7.5$ Hz, 3H), 1.00–1.10 (m, 4H), 1.12–1.22 (m, 2H), 1.33–1.42 (m, 2H), 1.68–1.80 (m, 4H), 2.52 (t, $J = 6.0$ Hz, 2H), 2.64–2.68 (m, 2H), 2.75 (t, $J = 6.0$ Hz, 2H), 6.69 (d, $J = 15.5$ Hz, 1H), 7.04 (d, $J = 5.0$ Hz, 1H), 7.41–7.53 (m, 6H), 7.78–7.87 (m, 4H); ^{13}C NMR (CDCl_3) δ 14.01, 22.46, 22.84, 22.97, 28.90, 29.25, 29.26, 30.91, 31.54, 33.85 (d, $J = 5.8$ Hz), 128.02 (d, $J = 84.5$ Hz), 128.31 (d, $J = 12.4$ Hz), 131.19 (d, $J = 2.9$ Hz), 131.67 (d, $J = 11.0$ Hz), 132.28 (d, $J = 10.5$ Hz), 133.47 (d, $J = 83.5$ Hz), 133.77 (d, $J = 12.4$ Hz), 134.17 (d, $J = 12.9$ Hz), 141.27 (d, $J = 2.9$ Hz), 143.84 (d, $J = 9.6$ Hz); ^{31}P NMR (CDCl_3) δ 39.86. Found: C, 77.56; H, 7.65%. Calcd for $\text{C}_{28}\text{H}_{33}\text{PS}$: C, 77.74; H, 7.69%.

[2,2-Di(methoxycarbonyl)-6-phenyl-5-indanyl]diphenylphosphine sulfide (3cb): IR (nujol) 2923, 2853, 1738, 1436, 1286, 1243, 1199, 1098, 1069 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.58 (s, 2H), 3.64 (s, 2H), 3.76 (s, 6H), 6.92–7.03 (m, 3H), 7.06–7.14 (m, 3H), 7.25–7.40 (m, 7H), 7.69–7.77 (m, 4H); ^{13}C NMR (CDCl_3) δ 40.36, 40.54, 53.07, 60.04, 126.91, 126.96, 128.00 (d, $J = 12.5$ Hz), 128.58 (d, $J = 11.0$ Hz), 129.31 (d, $J = 12.9$ Hz), 130.19, 130.86 (d, $J = 2.9$ Hz), 130.93 (d, $J = 84.5$ Hz), 132.20 (d, $J = 10.0$ Hz), 132.56 (d, $J = 84.5$ Hz), 138.85 (d, $J = 13.9$ Hz), 140.15 (d, $J = 3.9$ Hz), 143.79 (d, $J = 2.9$ Hz), 145.81 (d, $J = 9.5$ Hz), 171.73; ^{31}P NMR (CDCl_3) δ 40.69. Found: C, 70.48; H, 5.07%. Calcd for $\text{C}_{31}\text{H}_{27}\text{O}_4\text{PS}$: C, 70.71; H, 5.17%. m.p.: 165.0–167.0 $^\circ\text{C}$.

[2,2-Di(methoxycarbonyl)-6-(1-methylethyl)-5-indanyl]diphenylphosphine sulfide (3cc): IR (nujol) 2923, 2854, 1734, 1479, 1436, 1271, 1243, 1198, 1098, 1066, 712 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.99 (d, $J = 7.0$ Hz, 6H), 3.43 (s, 2H), 3.57 (dsep, $J = 1.5, 7.0$ Hz, 1H), 3.61 (s, 2H), 3.74 (s, 6H), 6.67 (d, $J = 14.5$ Hz, 1H), 7.27 (d, $J = 5.5$ Hz, 1H), 7.43–7.55 (m, 6H), 7.76–7.84 (m, 4H); ^{13}C NMR (CDCl_3) δ 23.66, 31.31 (d, $J = 6.6$ Hz), 40.31, 40.68, 53.02, 59.98, 124.20 (d, $J = 11.5$ Hz), 128.02 (d, $J = 13.4$ Hz), 128.40 (d, $J = 12.0$ Hz), 129.73 (d, $J = 86.4$ Hz), 131.39 (d, $J = 2.9$ Hz), 132.36 (d, $J = 10.5$ Hz), 133.18 (d, $J = 83.5$ Hz), 137.14 (d, $J = 13.8$ Hz), 144.50 (d, $J = 2.9$ Hz), 152.80 (d, $J = 10.5$ Hz), 171.84; ^{31}P NMR (CDCl_3) δ 40.82. Found: C, 68.08; H, 5.75%. Calcd for $\text{C}_{28}\text{H}_{29}\text{O}_4\text{PS}$: C, 68.27; H, 5.93%. m.p.: 216.0–217.5 $^\circ\text{C}$.

[2,2-Di(methoxycarbonyl)-6-(1,1-dimethylethyl)-5-indanyl]diphenylphosphine sulfide (3cd): IR (nujol) 2924, 2854, 1743, 1734, 1456, 1436, 1259, 1198, 1156, 1098, 901, 754, 707 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.47 (s, 9H), 3.37 (s, 2H), 3.63 (s, 2H), 3.74 (s, 6H), 6.86 (d, $J = 18.0$ Hz, 1H), 7.36–7.51 (m, 6H), 7.57 (d, $J = 5.5$ Hz, 1H), 7.60–7.70 (m, 4H); ^{13}C NMR

(CDCl₃) δ 33.51, 38.74 (d, J = 2.1 Hz), 40.27, 40.83, 53.03, 59.90, 126.23 (d, J = 12.9 Hz), 128.35 (d, J = 12.5 Hz), 129.18 (d, J = 75.9 Hz), 131.02 (d, J = 2.9 Hz), 132.15 (d, J = 13.8 Hz), 132.22 (d, J = 10.0 Hz), 136.51 (d, J = 13.9 Hz), 136.37 (d, J = 85.4 Hz), 144.00 (d, J = 2.9 Hz), 155.35 (d, J = 9.0 Hz), 171.86; ³¹P NMR (CDCl₃) 50.66. Found: C, 68.55; H, 6.05%. Calcd for C₂₉H₃₁O₄PS: C, 68.76; H, 6.17%. m.p.: 165.0–166.5 °C.

[2,2-Di(methoxycarbonyl)-6-(2-methoxyphenyl)-5-indanyl]diphenylphosphine sulfide (3ce): IR (nujol) 2922, 2853, 1734, 1684, 1653, 1559, 1507, 1457, 1437, 1276, 1198, 1095, 895 cm⁻¹; ¹H NMR (CDCl₃) δ 3.46 (s, 3H), 3.59 (s, 1H), 3.61 (s, 1H), 3.65 (s, 2H), 3.75 (s, 3H), 3.77 (s, 3H), 6.31 (d, J = 8.0 Hz, 1H), 6.65 (dd, J = 7.5, 7.5 Hz, 1H), 6.95–7.02 (m, 1H), 7.04 (d, J = 4.5 Hz, 1H), 7.14–7.47 (m, 8H), 7.58–7.68 (m, 2H), 7.80–7.88 (m, 2H); ¹³C NMR (CDCl₃) δ 40.43, 40.56, 53.05, 53.09, 54.39, 59.99, 109.31, 119.00, 127.43 (d, J = 12.4 Hz), 127.90 (d, J = 12.5 Hz), 128.46 (d, J = 4.3 Hz), 128.99 (d, J = 11.9 Hz), 129.04, 129.49 (d, J = 12.9 Hz), 130.38 (d, J = 2.9 Hz), 130.83 (d, J = 2.9 Hz), 131.28 (d, J = 85.4 Hz), 131.67 (d, J = 10.5 Hz), 132.36, 132.47 (d, J = 84.5 Hz), 132.53 (d, J = 10.5 Hz), 133.65 (d, J = 84.0 Hz), 138.91 (d, J = 13.9 Hz), 141.78 (d, J = 9.6 Hz), 143.42 (d, J = 2.9 Hz), 155.69, 171.81, 171.91; ³¹P NMR (CDCl₃) δ 40.56. Found: C, 68.80; H, 5.38%. Calcd for C₃₂H₂₉O₅PS: C, 69.05; H, 5.25%. m.p.: 89.5–92.0 °C.

[2,2-Di(methoxycarbonyl)-6-trimethylsilyl-5-indanyl]diphenylphosphine sulfide (3cf): IR (nujol) 2925, 2855, 1740, 1457, 1436, 1377, 1304, 1247, 1198, 1099, 848, 710 cm⁻¹; ¹H NMR (CDCl₃) δ 0.18 (s, 9H), 3.43 (s, 2H), 3.64 (s, 2H), 3.74 (s, 6H), 6.73 (d, J = 15.0 Hz, 1H), 7.40–7.53 (m, 6H), 7.62–7.69 (m, 4H), 7.72 (d, J = 3.0 Hz, 1H); ¹³C NMR (CDCl₃) δ 2.73, 40.59, 40.68, 53.04, 59.70, 128.37 (d, J = 12.4 Hz), 129.20 (d, J = 15.3 Hz), 131.32 (d, J = 2.9 Hz), 132.58 (d, J = 10.5 Hz), 133.84 (d, J = 17.1 Hz), 134.34 (d, J = 82.6 Hz), 137.95 (d, J = 87.8 Hz), 139.70 (d, J = 13.8 Hz), 142.33 (d, J = 2.9 Hz), 144.88 (d, J = 19.5 Hz), 171.81; ³¹P NMR (CDCl₃) δ 44.97. HRMS (EI) Observed, 522.1431 (Δ = -3.6 ppm). Exact, 522.1450. m.p.: 178.0–180.0 °C.

[6-Hexyl-2,2-di(methoxycarbonyl)-4,7-dimethyl-5-indanyl]diphenylphosphine sulfide (3fa): IR (nujol) 2924, 2854, 1734, 1653, 1558, 1457, 1437, 1260, 1165, 749, 701, 651 cm⁻¹; ¹H NMR (CDCl₃) δ 0.82 (t, J = 7.5 Hz, 3H), 0.93–1.01 (m, 2H), 1.04–1.12 (m, 2H), 1.16–1.30 (m, 4H), 1.80 (s, 3H), 2.16 (s, 3H), 2.34–2.41 (m, 2H), 3.45 (s, 2H), 3.61 (s, 2H), 3.77 (s, 6H), 7.31–7.41 (m, 6H), 7.84–7.93 (m, 4H); ¹³C NMR (CDCl₃) δ 14.01, 15.97 (d, J = 0.9 Hz), 21.06 (d, J = 7.3 Hz), 25.51, 29.51, 30.53, 31.40, 33.04 (d, J = 7.3 Hz), 40.39 (d, J = 1.9 Hz), 40.80, 53.04, 58.67, 128.35 (d, J = 11.9 Hz), 129.73 (d, J = 88.9 Hz), 130.37 (d, J = 2.9 Hz), 130.69 (d, J = 10.5 Hz), 131.26 (d, J = 11.9 Hz), 135.63 (d, J = 11.0 Hz), 137.59 (d, J = 81.1 Hz), 138.24 (d, J = 12.9 Hz), 142.92 (d, J = 2.9 Hz), 145.76 (d, J = 10.5 Hz), 172.16; ³¹P

NMR (CDCl₃) δ 35.01. m.p.: 59.5–61.0 °C.

[6-Hexyl-2,2-di(methoxycarbonyl)-4,7-diphenyl-5-indanyl]diphenylphosphine sulfide (3ga): IR (nujol) 2924, 2854, 1741, 1724, 1456, 1437, 1377, 1267, 1201, 1091, 714, 697 cm⁻¹; ¹H NMR (CDCl₃) δ 0.69 (t, J = 7.0 Hz, 3H), 0.72–0.86 (m, 4H), 0.95–1.05 (m, 2H), 1.16–1.27 (m, 2H), 2.46–2.54 (m, 2H), 3.26 (s, 2H), 3.37 (s, 2H), 3.66 (s, 6H), 6.90–7.04 (m, 5H), 7.10–7.23 (m, 6H), 7.24–7.46 (m, 5H), 7.56–7.66 (m, 4H); ¹³C NMR (CDCl₃) δ 13.93, 22.21, 29.17, 30.89, 30.98, 34.57 (d, J = 7.6 Hz), 40.82 (d, J = 1.3 Hz), 41.10, 52.91, 59.09, 126.71, 127.19, 127.52, 127.72 (d, J = 12.4 Hz), 128.50, 129.24, 129.73 (d, J = 2.9 Hz), 130.03 (d, J = 89.3 Hz), 130.45, 130.99 (d, J = 10.0 Hz), 136.69 (d, J = 83.1 Hz), 137.61 (d, J = 11.9 Hz), 138.91 (d, J = 4.8 Hz), 139.22 (d, J = 10.5 Hz), 139.26, 142.69 (d, J = 2.9 Hz), 143.01 (d, J = 11.0 Hz), 147.43 (d, J = 10.5 Hz), 171.90; ³¹P NMR (CDCl₃) δ 36.66. Found: C, 75.23; H, 6.37%. Calcd for C₄₃H₄₃O₄PS: C, 75.19; H, 6.31%. m.p.: 122.0–124.0 °C.

[2,2-Di(methoxycarbonyl)-4,6,7-triphenyl-5-indanyl]diphenylphosphine sulfide (3gb): IR (nujol) 2924, 2854, 2364, 1735, 1701, 1654, 1559, 1457, 1420, 1267, 696, 668 cm⁻¹; ¹H NMR (CDCl₃) δ 3.34 (s, 2H), 3.43 (s, 2H), 3.66 (s, 6H), 6.57–6.74 (m, 3H), 6.80–7.30 (m, 18H), 7.54–7.68 (m, 4H); ¹³C NMR (CDCl₃) δ 41.27, 41.63, 52.95, 59.00, 125.85, 126.09, 126.32, 126.72, 127.03, 127.28 (d, J = 12.4 Hz), 127.57, 129.39 (2C), 131.06, 131.11 (d, J = 85.4 Hz), 131.22 (d, J = 10.0 Hz), 133.02, 134.79 (d, J = 83.6 Hz), 137.40 (d, J = 5.1 Hz), 138.52 (d, J = 4.8 Hz), 138.86, 139.03 (d, J = 11.0 Hz), 139.92 (d, J = 11.3 Hz), 142.73 (d, J = 2.9 Hz), 143.63 (d, J = 10.5 Hz), 146.43 (d, J = 10.5 Hz), 171.81; ³¹P NMR (CDCl₃) δ 36.49. Found: C, 76.06; H, 5.58%. Calcd for C₄₃H₃₅O₄PS: C, 76.09; H, 5.20%. m.p.: 140.0–142.0 °C.

[2,2-di(methoxycarbonyl)-4,6,7-tri(1-methylethyl)-5-indanyl]diphenylphosphine sulfide (3hc): IR (neat) 2924, 2854, 1735, 1462, 1438, 1377, 1261, 1167, 1046, 665 cm⁻¹; ¹H NMR (CDCl₃) δ 0.75 (t, J = 7.0 Hz, 12H), 1.28 (d, J = 7.5 Hz, 6H), 3.44 (sep, J = 7.0 Hz, 1H), 3.47 (dsep, J = 2.0, 7.0 Hz, 1H), 3.54 (s, 2H), 3.68 (dsep, J = 2.5, 7.5 Hz, 1H), 3.69 (s, 2H), 3.76 (s, 6H), 7.26–7.36 (m, 6H), 7.82–7.93 (m, 4H); ¹³C NMR (CDCl₃) δ 20.72, 20.92, 22.37, 28.22, 34.22 (d, J = 9.1 Hz), 34.55 (d, J = 10.5 Hz), 39.28, 40.05, 52.92, 60.72, 128.06 (d, J = 11.9 Hz), 130.02 (d, J = 2.9 Hz), 130.57 (d, J = 10.0 Hz), 131.22 (d, J = 94.5 Hz), 137.91 (d, J = 12.4 Hz), 138.66 (d, J = 82.0 Hz), 141.96 (d, J = 10.5 Hz), 144.58 (d, J = 2.8 Hz), 147.07 (d, J = 11.0 Hz), 149.84 (d, J = 10.0 Hz), 171.86; ³¹P NMR (CDCl₃) δ 35.79. Found: C, 70.55; H, 7.07%. Calcd for C₃₄H₄₁O₄PS: C, 70.81; H, 7.17%.

[2,2-Di(methoxycarbonyl)-6-(2-methoxy-1-naphthyl)-4,7-di(1-methylethyl)-5-indanyl]diphenylphosphine sulfide (3hg): IR (nujol) 2923, 2854, 1737, 1457, 1437, 1263,

1172, 1071, 750 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.72 (d, $J = 7.0$ Hz, 3H), 0.75 (d, $J = 7.0$ Hz, 3H), 1.01 (d, $J = 7.0$ Hz, 3H), 1.21 (d, $J = 7.0$ Hz, 3H), 2.14 (qq, $J = 7.0, 7.0$ Hz, 1H), 3.62–3.68 (m, 2H), 3.69 (s, 3H), 3.77 (s, 3H), 3.80 (s, 3H), 3.80–3.87 (m, 2H), 4.12 (dq, $J = 2.5, 7.0, 7.0$ Hz, 1H), 6.47 (d, $J = 9.0$ Hz, 1H), 6.72–6.81 (m, 2H), 6.87–6.90 (m, 3H), 7.14–7.40 (m, 7H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.59–7.72 (m, 2H); ^{13}C NMR (CDCl_3) δ 18.93, 20.42, 20.51, 20.68, 29.72, 32.46 (d, $J = 8.6$ Hz), 40.12, 40.39, 52.97 (2C), 54.61, 60.81, 110.93, 121.68, 121.73, 123.46, 126.18 (d, $J = 10.0$ Hz), 126.28 (d, $J = 16.8$ Hz), 127.13, 127.44 (d, $J = 10.5$ Hz), 128.39, 129.06 (d, $J = 2.9$ Hz), 129.93, 130.49, 131.10 (d, $J = 10.0$ Hz), 132.02, 132.10 (d, $J = 86.9$ Hz), 134.22, 135.95 (d, $J = 84.5$ Hz), 136.92 (d, $J = 83.0$ Hz), 137.29 (d, $J = 10.0$ Hz), 140.90 (d, $J = 12.0$ Hz), 141.36 (d, $J = 10.5$ Hz), 143.15, 146.31 (d, $J = 11.5$ Hz), 153.62, 171.88, 172.04; ^{31}P NMR (CDCl_3) δ 40.13. m.p.: 247.5–249.0 $^\circ\text{C}$.

Phenyl[di(phenylethynyl)]phosphine sulfide (5a): IR (nujol) 2919, 2850, 2173, 1685, 1486, 1457, 1364, 1106, 1023, 855, 766 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.34–7.47 (m, 6H), 7.54–7.63 (m, 7H), 8.18–8.26 (m, 2H); ^{13}C NMR (CDCl_3) δ 82.41 (d, $J = 176.0$ Hz), 103.79 (d, $J = 33.0$ Hz), 119.93 (d, $J = 4.8$ Hz), 128.45, 128.78 (d, $J = 15.3$ Hz), 130.46 (d, $J = 13.4$ Hz), 130.67, 132.35 (d, $J = 3.4$ Hz), 132.48 (d, $J = 2.4$ Hz), 133.15 (d, $J = 114.5$ Hz); ^{31}P NMR (CDCl_3) δ -10.56. Found: C, 77.12; H, 4.51%. Calcd for $\text{C}_{22}\text{H}_{15}\text{PS}$: C, 77.17; H, 4.41%. m.p.: 122.0–124.0 $^\circ\text{C}$.

Tri(phenylethynyl)phosphine sulfide (5b): IR (nujol) 2923, 2854, 2181, 1684, 1558, 1489, 1457, 1374, 1231, 1070, 923, 852, 759 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.37–7.43 (m, 6H), 7.45–7.50 (m, 3H), 7.63–7.68 (m, 6H); ^{13}C NMR (CDCl_3) δ 82.19 (d, $J = 205.6$ Hz), 102.46 (d, $J = 40.6$ Hz), 119.78 (d, $J = 4.8$ Hz), 128.53, 130.90, 132.69 (d, $J = 2.4$ Hz); ^{31}P NMR (CDCl_3) δ -43.59. Found: C, 78.57; H, 4.35%. Calcd for $\text{C}_{24}\text{H}_{15}\text{PS}$: C, 78.67; H, 4.13%. m.p.: 129.5–130.5 $^\circ\text{C}$.

Bis[2,2-di(methoxycarbonyl)-6-phenyl-5-indanyl]phenylphosphine sulfide (6a): IR (nujol) 2924, 2853, 1734, 1559, 1507, 1457, 1420, 1240, 1157, 697 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.52 (s, 2H), 3.54 (s, 2H), 3.61 (s, 4H), 3.79 (s, 6H), 3.81 (s, 6H), 6.85–6.91 (m, 4H), 6.92–7.01 (m, 6H), 7.08–7.14 (m, 2H), 7.20–7.26 (m, 2H), 7.31–7.46 (m, 5H); ^{13}C NMR (CDCl_3) δ 40.28, 40.47, 53.05, 53.06, 60.00, 126.85, 126.92, 127.75 (d, $J = 12.5$ Hz), 128.28 (d, $J = 10.9$ Hz), 129.60 (d, $J = 12.9$ Hz), 129.79, 130.39 (d, $J = 82.5$ Hz), 130.49 (d, $J = 2.4$ Hz), 132.52 (d, $J = 10.9$ Hz), 134.47 (d, $J = 85.4$ Hz), 138.53 (d, $J = 13.9$ Hz), 140.95 (d, $J = 3.9$ Hz), 143.24 (d, $J = 2.4$ Hz), 144.79 (d, $J = 9.5$ Hz), 171.76, 171.84; ^{31}P NMR (CDCl_3) δ 42.93. Found: C, 69.77; H, 5.47%. Calcd for $\text{C}_{44}\text{H}_{39}\text{O}_8\text{PS}$: C, 69.64; H, 5.18%. m.p.: 124.0–126.5 $^\circ\text{C}$.

Tris[2,2-di(methoxycarbonyl)-6-phenyl-5-indanyl]phosphine sulfide (6b): IR (nujol) 2923, 2853, 1734, 1653, 1559, 1457, 1420, 1240, 1151, 1051, 768, 698 cm^{-1} ; ^1H NMR (CDCl_3) δ

3.45 (s, 6H), 3.57 (s, 6H), 3.81 (s, 18H), 6.80–7.26 (m, 21H); ^{13}C NMR (CDCl_3) δ 40.17, 40.41, 53.02, 59.97, 126.73, 126.82, 128.17 (d, $J = 11.0$ Hz), 129.89, 130.55 (d, $J = 81.3$ Hz), 130.76 (d, $J = 13.4$ Hz), 137.82 (d, $J = 13.9$ Hz), 141.52 (d, $J = 2.9$ Hz), 142.83 (d, $J = 2.4$ Hz), 144.34 (d, $J = 9.5$ Hz), 171.84; ^{31}P NMR (CDCl_3) δ 44.79. Found: C, 68.75; H, 5.31%. Calcd for $\text{C}_{57}\text{H}_{51}\text{O}_{12}\text{PS}$: C, 69.08; H, 5.19%. m.p.: 157.0–160.0 °C

Dicyclohexyl(1-octynyl)phosphine sulfide (7a): IR (neat) 2930, 2854, 2192, 1448, 1268, 1179, 1115, 1002, 887, 758, 648 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.84 (t, $J = 7.0$ Hz, 3H), 1.12–2.02 (m, 30H), 2.31 (dt, $J = 4.0, 7.0$ Hz, 2H); ^{13}C NMR (CDCl_3) δ 13.82, 19.60 (d, $J = 2.9$ Hz), 22.34, 24.83, 25.62 (d, $J = 1.5$ Hz), 26.01 (d, $J = 15.8$ Hz), 26.13 (d, $J = 14.8$ Hz), 26.20 (d, $J = 3.4$ Hz), 27.55 (d, $J = 1.9$ Hz), 28.31, 30.98, 38.49 (d, $J = 59.3$ Hz), 71.41 (d, $J = 126.5$ Hz), 107.63 (d, $J = 18.6$ Hz); ^{31}P NMR (CDCl_3) δ 41.71. Found: C, 70.71; H, 10.71%. Calcd for $\text{C}_{20}\text{H}_{35}\text{PS}$: C, 70.96; H, 10.42%.

Dicyclohexyl(phenylethynyl)phosphine sulfide (7b): IR (nujol) 2921, 2852, 2177, 1734, 1685, 1489, 1443, 1117, 1048, 885, 757, 665 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.20–2.12 (m, 22H), 7.33–7.38 (m, 2H), 7.39–7.44 (m, 1H), 7.50–7.55 (m, 2H); ^{13}C NMR (CDCl_3) δ 25.05, 25.73 (d, $J = 1.5$ Hz), 26.15 (d, $J = 14.9$ Hz), 26.29 (d, $J = 14.3$ Hz), 26.47 (d, $J = 3.9$ Hz), 38.82 (d, $J = 58.8$ Hz), 80.03 (d, $J = 120.3$ Hz), 103.94 (d, $J = 17.6$ Hz), 120.52 (d, $J = 3.3$ Hz), 128.43, 130.16, 132.34 (d, $J = 2.0$ Hz); ^{31}P NMR (CDCl_3) δ 42.96. Found: C, 72.40; H, 8.38%. Calcd for $\text{C}_{20}\text{H}_{27}\text{PS}$: C, 72.69; H, 8.23%. m.p.: 150.0–151.5 °C.

Dicyclohexyl[6-hexyl-2,2-di(methoxycarbonyl)-5-indanyl]phosphine sulfide (8a): IR (neat) 2918, 2852, 2214, 1733, 1559, 1436, 1258, 1200, 1162, 1072, 913, 762, 732, 615 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.92 (t, $J = 7.0$ Hz, 3H), 1.10–2.05 (m, 28H), 2.20–2.30 (m, 2H), 2.70–2.80 (m, 2H), 3.59 (s, 2H), 3.61 (s, 2H), 3.74 (s, 6H), 7.10 (d, $J = 4.5$ Hz, 1H), 8.21 (d, $J = 15.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 14.07, 22.61, 25.58 (d, $J = 1.5$ Hz), 26.50 (d, $J = 11.9$ Hz), 26.55 (d, $J = 13.4$ Hz), 26.56, 27.99 (d, $J = 1.1$ Hz), 29.79, 31.85, 32.13, 34.58 (d, $J = 1.5$ Hz), 39.45, 40.23 (d, $J = 23.4$ Hz), 40.47, 53.02, 60.11, 125.05, 125.57, 125.64 (d, $J = 10.5$ Hz), 131.79, 137.69 (d, $J = 12.9$ Hz), 143.53 (d, $J = 2.4$ Hz), 171.97; ^{31}P NMR (CDCl_3) δ 63.80.

Dicyclohexyl[2,2-di(methoxycarbonyl)-4,6,7-triphenyl-5-indanyl]phosphine sulfide (8b): IR (nujol) 2922, 2853, 1735, 1457, 1378, 1262, 1198, 1165, 1071, 771, 665 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.90–1.90 (m, 22H), 3.15 (s, 2H), 3.33 (s, 2H), 3.66 (s, 6H), 6.83–6.89 (m, 2H), 7.00–7.13 (m, 8H), 7.23–7.30 (m, 2H), 7.37–7.44 (m, 3H); ^{13}C NMR (CDCl_3) δ 25.51, 26.20 (d, $J = 13.9$ Hz), 26.52 (d, $J = 13.9$ Hz), 27.06, 28.13 (d, $J = 2.4$ Hz), 40.92 (d, $J = 48.1$ Hz), 41.57, 41.84, 52.93, 58.63, 125.78 (d, $J = 59.3$ Hz), 126.19, 126.39, 127.09, 127.19, 127.55, 127.61, 129.28, 129.68, 132.07, 139.32, 139.41 (d, $J = 2.3$ Hz), 139.77 (d, $J = 9.6$ Hz),

140.69 (d, $J = 3.3$ Hz), 140.91 (d, $J = 10.5$ Hz), 141.16 (d, $J = 2.9$ Hz), 143.70, 144.30, 171.91; ^{31}P NMR (CDCl_3) δ 65.01. Found: C, 74.61; H, 7.15%. Calcd for $\text{C}_{43}\text{H}_{47}\text{O}_4\text{PS}$: C, 74.76; H, 6.86%. m.p.: 118.5–121.0 °C.

[6-Hexyl-2,2-di(methoxycarbonyl)-5-indanyl]diphenylphosphine (3ca-S): IR (neat) 2953, 2928, 2855, 1738, 1434, 1273, 1247, 1200, 1162, 1070, 910, 734, 698 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.84 (t, $J = 7.5$ Hz, 3H), 1.14–1.32 (m, 6H), 1.44–1.53 (m, 2H), 2.76–2.83 (m, 2H), 3.45 (s, 2H), 3.60 (s, 2H), 3.74 (s, 6H), 6.66 (d, $J = 4.0$ Hz, 1H), 7.09 (d, $J = 4.5$ Hz, 1H), 7.22–7.29 (m, 4H), 7.30–7.36 (m, 6H); ^{13}C NMR (CDCl_3) δ 14.05, 22.49, 29.23, 31.46 (d, $J = 2.9$ Hz), 31.59, 34.42 (d, $J = 21.5$ Hz), 40.34, 40.55, 52.92, 59.99, 124.78 (d, $J = 5.8$ Hz), 128.41 (d, $J = 7.1$ Hz), 128.48, 129.02, 133.79 (d, $J = 11.0$ Hz), 133.86 (d, $J = 19.6$ Hz), 137.23 (d, $J = 11.0$ Hz), 137.56, 140.98, 146.48 (d, $J = 25.8$ Hz), 172.16; ^{31}P NMR (CDCl_3) δ –16.30. Found: C, 73.73; H, 7.08%. Calcd for $\text{C}_{31}\text{H}_{35}\text{O}_4\text{P}$: C, 74.09; H, 7.02%.

[2,2-Di(methoxycarbonyl)-6-phenyl-5-indanyl]diphenylphosphine (3cb-S): IR (nujol) 2923, 2854, 1731, 1655, 1462, 1377, 1262, 1027, 665 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.54 (s, 2H), 3.64 (s, 2H), 3.76 (s, 6H), 6.85 (d, $J = 3.5$ Hz, 1H), 7.11–7.32 (m, 16H); ^{13}C NMR (CDCl_3) δ 40.44, 40.53, 53.02, 59.99, 125.95 (d, $J = 4.8$ Hz), 127.06, 127.48, 128.32 (d, $J = 6.8$ Hz), 128.39, 129.47, 129.76 (d, $J = 3.9$ Hz), 133.89 (d, $J = 19.5$ Hz), 134.53 (d, $J = 12.8$ Hz), 137.75 (d, $J = 12.5$ Hz), 139.14, 140.84, 141.73 (d, $J = 6.6$ Hz), 147.30 (d, $J = 29.0$ Hz), 172.10; ^{31}P NMR (CDCl_3) δ –14.84. Found: C, 75.12; H, 5.55%. Calcd for $\text{C}_{31}\text{H}_{27}\text{O}_4\text{P}$: C, 75.29; H, 5.50%. m.p.: 55.5–58.0 °C.

[2,2-Di(methoxycarbonyl)-4,6,7-triphenyl-5-indanyl]diphenylphosphine (3gb-S): IR (nujol) 2924, 2855, 1735, 1462, 1377, 1262, 1159, 1027, 697, 665 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.23 (s, 2H), 3.49 (s, 2H), 3.68 (s, 6H), 6.76–7.17 (m, 25H); ^{13}C NMR (CDCl_3) δ 41.27, 41.38, 52.88, 58.98, 125.93, 126.17 (d, $J = 1.9$ Hz), 126.55, 126.71, 127.49 (2C), 127.58 (d, $J = 10.5$ Hz), 128.68, 129.54, 130.65 (d, $J = 2.4$ Hz), 131.76 (d, $J = 20.5$ Hz), 132.12 (d, $J = 19.6$ Hz), 137.30, 137.41, 138.22 (d, $J = 4.8$ Hz), 139.58, 139.75 (d, $J = 2.9$ Hz), 140.11 (d, $J = 3.4$ Hz), 140.47, 140.56 (d, $J = 7.6$ Hz), 144.65 (d, $J = 10.5$ Hz), 148.15 (d, $J = 25.3$ Hz), 172.07; ^{31}P NMR (CDCl_3) δ –8.31. Found: C, 80.08; H, 5.71%. Calcd for $\text{C}_{43}\text{H}_{35}\text{O}_4\text{P}$: C, 79.86; H, 5.45%. m.p.: 97.5–99.5 °C.

[2,2-Di(methoxycarbonyl)-4,6,7-tri(1-methylethyl)-5-indanyl]diphenylphosphine (3hc-S): IR (neat) 2958, 2874, 2259, 1733, 1584, 1461, 1436, 1259, 1209, 1171, 1069, 910, 742, 698 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.80–1.10 (m, 12H), 1.31 (d, $J = 7.0$ Hz, 6H), 3.50–3.62 (m, 1H), 3.59 (s, 2H), 3.68 (s, 2H), 3.70–3.85 (m, 1H), 3.76 (s, 6H), 4.00–4.20 (m, 1H), 7.20–7.25 (m, 2H), 7.28–7.34 (m, 4H), 7.36–7.43 (m, 4H); ^{13}C NMR (CDCl_3) δ 20.56, 20.80, 22.36, 28.64, 33.17 (d, $J = 20.0$ Hz), 33.93 (d, $J = 21.6$ Hz), 39.55, 40.19, 52.87, 60.83,

127.08, 128.14 (d, $J = 4.9$ Hz), 128.24 (d, $J = 18.6$ Hz), 131.39 (d, $J = 18.1$ Hz), 132.25 (d, $J = 14.9$ Hz), 137.73 (d, $J = 16.8$ Hz), 141.58, 143.40, 148.47 (d, $J = 12.5$ Hz), 151.59 (d, $J = 10.3$ Hz), 172.09; ^{31}P NMR (CDCl_3) δ -12.58.

[2,2-Di(methoxycarbonyl)-6-(2-methoxy-1-naphthyl)-4,7-di(1-methylethyl)-5-

indanyl]diphenylphosphine (3hg-S): IR (nujol) 2920, 2851, 1734, 1685, 1559, 1507, 1457, 1437, 1260, 1072, 1020, 804 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.52 (d, $J = 7.0$ Hz, 3H), 0.81 (d, $J = 7.0$ Hz, 3H), 1.03 (d, $J = 7.0$ Hz, 3H), 1.10 (d, $J = 7.0$ Hz, 3H), 2.61 (qq, $J = 7.0, 7.0$ Hz, 1H), 3.17 (qq, $J = 7.0, 7.0$ Hz, 1H), 3.54 (s, 3H), 3.70 (s, 1H), 3.72 (s, 1H), 3.78 (s, 1H), 3.79 (s, 3H), 3.80 (s, 1H), 3.81 (s, 3H), 7.05–7.38 (m, 14H), 7.77 (d, $J = 8.0$ Hz, 1H), 7.83 (d, $J = 9.0$ Hz, 1H); ^{13}C NMR (CDCl_3) δ 19.68, 20.18, 20.87, 20.89, 31.53 (d, $J = 3.4$ Hz), 32.22, 39.67, 39.84, 52.93, 52.94, 55.12, 60.72, 112.08, 123.25, 125.84, 126.51 (d, $J = 13.9$ Hz), 126.67 (d, $J = 8.6$ Hz), 127.62 (d, $J = 11.5$ Hz), 127.66 (d, $J = 11.4$ Hz), 127.88, 128.39, 128.48, 131.27 (d, $J = 19.0$ Hz), 131.77 (d, $J = 17.6$ Hz), 134.07 (d, $J = 12.9$ Hz), 134.15, 137.45 (d, $J = 18.6$ Hz), 138.53 (d, $J = 21.0$ Hz), 139.83, 140.94, 141.01, 142.11, 143.79, 144.14, 147.36 (d, $J = 3.9$ Hz), 154.21 (d, $J = 3.8$ Hz), 172.25 (2C); ^{31}P NMR (CDCl_3) δ -9.51. m.p.: 258.0–260.0 $^\circ\text{C}$.

Tris[2,2-di(methoxycarbonyl)-6-phenyl-5-indanyl]phosphine (6b-S): IR (nujol) 2924, 2854, 1731, 1655, 1462, 1377, 1239, 1158, 1049, 893, 768 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.56 (s, 6H), 3.61 (s, 6H), 3.78 (s, 18H), 6.66–6.72 (m, 6H), 6.79 (d, $J = 2.5$ Hz, 3H), 6.92 (d, $J = 4.0$ Hz, 3H), 7.01–7.08 (m, 6H), 7.10–7.15 (m, 3H); ^{13}C NMR (CDCl_3) δ 40.47, 40.48, 52.99, 60.09, 125.43 (d, $J = 4.3$ Hz), 126.31, 127.01, 129.56 (d, $J = 4.3$ Hz), 130.21, 135.12 (d, $J = 19.6$ Hz), 138.75, 140.19, 141.61 (d, $J = 6.8$ Hz), 146.77 (d, $J = 30.5$ Hz), 172.18; ^{31}P NMR (CDCl_3) δ -27.93. m.p.: 250.0–252.0 $^\circ\text{C}$.

Dicyclohexyl[2,2-di(methoxycarbonyl)-4,6,7-triphenyl-5-indanyl]phosphine (8b-S): IR (nujol) 2923, 2853, 2363, 1735, 1654, 1560, 1453, 1365, 1261, 1046, 952, 665 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.83–1.74 (m, 22H), 3.24 (s, 2H), 3.41 (s, 2H), 3.67 (s, 6H), 6.90–7.00 (m, 4H), 7.02–7.15 (m, 6H), 7.20–7.24 (m, 2H), 7.36–7.48 (m, 3H); ^{13}C NMR (CDCl_3) δ 26.21, 26.85 (d, $J = 17.6$ Hz), 26.94 (d, $J = 12.9$ Hz), 31.59 (d, $J = 11.5$ Hz), 32.75 (d, $J = 25.3$ Hz), 35.58 (d, $J = 15.3$ Hz), 41.29, 41.41, 52.84, 59.00, 125.86, 125.93, 126.43, 126.82, 127.39, 127.85, 129.36, 129.56, 131.52, 132.32 (d, $J = 29.1$ Hz), 137.94 (d, $J = 3.3$ Hz), 138.56 (d, $J = 3.4$ Hz), 139.09, 140.06, 141.59 (2C), 144.73, 148.07, 172.17; ^{31}P NMR (CDCl_3) δ 0.83. m.p.: 102.0–105.0 $^\circ\text{C}$.

Figure S1. ^1H NMR spectrum of **3cf**

Figure S2. ^{13}C NMR spectrum of **3cf**

Figure S3. ^1H NMR spectrum of **8a**

Figure S4. ^{13}C NMR spectrum of **8a**

Figure S5. ^1H NMR spectrum of **3fa**

Figure S6. ^{13}C NMR spectrum of **3fa**

Figure S7. ^1H NMR spectrum of **3hg**

Figure S8. ^{13}C NMR spectrum of **3hg**

Figure S9. ^1H NMR spectrum of **8b-S**

Figure S10. ^{13}C NMR spectrum of **8b-S**

Figure S12. ^{13}C NMR spectrum of **3hc-S**

Figure S13. ^1H NMR spectrum of **6b-S**

Figure S14. ^{13}C NMR spectrum of **6b-S**

Figure S15. ^1H NMR spectrum of **3hg-S**

Figure S16. ^{13}C NMR spectrum of **3hg-S**

Figure S17. ^1H NMR spectrum of **2b**

Figure S18. ^{13}C NMR spectrum of **2b**

Figure S19. ^1H NMR spectrum of **2d**

Figure S20. ^{13}C NMR spectrum of **2d**

Figure S21. ^1H NMR spectrum of **2f**

Figure S22. ^{13}C NMR spectrum of **2f**

Figure S23. ^1H NMR spectrum of **1h**

Figure S24. ^{13}C NMR spectrum of **1h**