Supporting Information

Radical Phosphination of Organic Halides and Alkyl Imidazole-1-carbothioates

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Instrumentation and Chemicals

^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra were taken on a Varian UNITY INOVA 500 spectrometer and were obtained in CDCl_3 with tetramethylsilane as an internal standard. DEPT, H-H COSY and H-C COSY analyses allowed for the assignments of the signals of each compounds. ^{31}P NMR (121.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer and were obtained in CDCl_3 with 85% H_3PO_4 solution as an external standard. Yields were in most case determined by fine ^{31}P NMR spectra with $(\text{MeO})_3\text{P}=\text{O}$ as an internal

standard. The first delay of ^{31}P NMR measurements was set for 15 s to make integrals for signals accurate. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL Mstation 700 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Wakogel 200 mesh) was used for column chromatography. Gel permeation chromatography (GPC) was performed by LC-908 (Japan Analytical Industry Ltd., two in-line JAIGEL-2H, toluene, 7.8 mL/min, UV and RI detectors). Elemental analyses were carried out at the Elemental Analysis Center of Kyoto University.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Chlorodiphenylphosphine and tris(trimethylsilyl)silane were purchased from TCI and were stored under argon. Chlorodicyclohexylphosphine and chlorodi(*tert*-butyl)phosphine were gifts from Hokko Chemical Industry Co., Ltd. V-40 was obtained from Wako Pure Chemical. Benzene was dried over slices of sodium. Triethylamine and pyridine were dried over KOH. All the organic halides were commercially available or readily prepared by conventional methods. Alkyl imidazole-1-carbothioates were synthesized from the corresponding alcohols and 1,1'-thiocarbonyldiimidazole (*vide infra*).

Experimental Procedure

Phosphination Reaction of Aryl Iodide (Table 1): Under an atmosphere of argon, 0.24 mL of pyridine (3.0 mmol), 0.45 mL of chlorodiphenylphosphine (2.5 mmol), 0.46 mL of tris(trimethylsilyl)silane (1.5 mmol), and aryl iodide (0.50 mmol) were added to a solution of 24 mg of 1,1'-azobis(cyclohexane-1-carbonitrile) (V-40, 0.10 mmol) in benzene (3.0 mL). The mixture was stirred for 20 h at reflux. The resulting mixture was then cooled to room temperature. Sulfur crystal (0.16 g, 5.0 mmol) was added to the reaction flask. The resulting suspension was stirred for 1 h at ambient temperature. The mixture was poured into water (20 mL). The product was extracted with ethyl acetate three times (15 mL each). The combined organic layer was washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. ^{31}P NMR analysis of the crude oil with $(\text{MeO})_3\text{P}=\text{O}$ as an internal standard showed the yield of the corresponding phosphine sulfide. Silica gel column chromatography followed by GPC purification afforded analytically pure phosphine sulfide (vide infra).

Preparation of Alkyl Imidazole-1-carbothioates: The preparation of **1t** is representative (Table 2, entry 4). Under an atmosphere of argon, 1.1 g of 1,1'-thiocarbonyldiimidazole (6.0 mmol) and 0.35 g of 3-oxacyclopentanol (4.0 mmol) were added to THF (15 mL). The mixture was stirred for 3 days at ambient temperature. The solution was dried over sodium sulfate, filtered, concentrated in vacuo. Silica gel column chromatography (hexane/ethyl acetate = 2:1) afforded the desired 3-oxacyclopentyl imidazole-1-carbothioate (**1t**, 0.55 g, 2.8 mmol) in 70% yield.

Phosphination Reaction of Alkyl Imidazole-1-carbothioates (Table 2): The phosphination of **1t** is representative. Under an atmosphere of argon, 0.21 mL of triethylamine (1.5 mmol), 0.31 mL of chlorodiphenylphosphine (1.75 mmol), 0.23 mL of tris(trimethylsilyl)silane (0.75 mmol), and 99 mg of 3-oxacyclopentyl imidazole-1-carbothioate (**1t**, 0.50 mmol) were added to a solution of 0.15 g of V-40 (0.60 mmol) in benzene (3.0 mL). The mixture was stirred for 18 h at

reflux. The resulting mixture was then cooled down to room temperature. Sulfur crystal (0.13 g, 4.0 mmol) was added to the reaction flask. The resulting suspension was stirred for 1 h at ambient temperature. The mixture was poured into water (20 mL). The product was extracted with ethyl acetate three times (15 mL each). The combined organic layer was washed with brine, dried over sodium sulfate, filtered, and concentrated in vacuo. ^{31}P NMR analysis of the crude oil showed an 87% yield of 3-oxacyclopentylidiphenylphosphine sulfide (**3t**). Silica gel column chromatography (hexane/ethyl acetate = 2:1) afforded analytically pure **3t** as a white solid in 76% yield (111 mg, 0.38 mmol).

Procedure for Purification: We have to use an excess of chlorodiorganophosphine, which rendered the purification of the desired products difficult. As shown in Figure S1, most of the desired products **3** (except for **3t**) were contaminated by other phosphine residues such as tetraphenylbiphosphine disulfide. It was impossible to isolate the desired products by using conventional silica gel column in reasonably pure forms. We thus purified the products **3** in the following manner. A crude reaction mixture was roughly purified on silica gel to obtain **3** of 30–60% purity. The impure product **3** was then subjected to gel permeation chromatography under the conditions described above. The separation with GPC took 3–70 h and 6–50 cycles.

Instead of sulfidation with crystal sulfur, oxidation with aqueous hydrogen peroxide yielded the corresponding phosphine oxides. The phosphine oxides are generally easy to isolate, although reduction of the oxides to trivalent phosphines requires rather harsh reaction conditions. Attempted purification of the product after addition of borane to the reaction mixture resulted in failure.

Figure S1. TLC analysis of the crude product. Hexane/ethyl acetate = 3:1, Merck silica gel 60F₂₅₄, visualized under UV irradiation.

Characterization Data

O-cyclohexyl 1*H*-imidazole-1-carbothioate (**1r**):

IR (neat) 657, 972, 1003, 1094, 1230, 1284, 1387, 1464, 1529, 2860, 2938, 3123 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.35–1.44 (m, 1H), 1.44–1.55 (m, 2H), 1.55–1.65 (m, 1H), 1.65–1.75 (m, 2H), 1.75–1.82 (m, 2H), 2.00–2.09 (m, 2H), 5.47–5.55 (m, 1H), 7.03 (s, 1H), 7.64 (s, 1H), 8.35 (s, 1H); ^{13}C NMR (CDCl_3) δ 23.35, 25.00, 30.55, 82.44, 117.74, 130.48, 136.65, 183.25. Found: C, 56.83; H, 6.80%. Calcd for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{OS}$: C, 57.11; H, 6.71%.

O-(3-ethoxy-1-methyl-3-oxopropyl) 1*H*-imidazole-1-carbothioate (**1s**):

IR (neat) 656, 969, 1032, 1101, 1232, 1286, 1387, 1467, 1733, 1739, 2983, 3130 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.24 (t, $J = 7.0$ Hz, 3H), 1.54 (d, $J = 6.5$ Hz, 3H), 2.75 (dd, $J = 16.0, 5.5$ Hz, 1H), 2.92 (dd, $J = 16.0, 7.5$ Hz, 1H), 4.11–4.20 (m, 2H), 5.93–6.00 (m, 1H), 7.02–7.04 (m, 1H), 7.61–7.63 (m, 1H), 8.31–8.33 (m, 1H); ^{13}C NMR (CDCl_3) δ 14.04, 18.90, 40.15, 60.97, 76.95, 117.82, 130.64, 136.65, 169.34, 182.94. Found: C, 49.68; H, 5.92%. Calcd for $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_3\text{S}$: C, 49.57; H, 5.82%.

O-(3-oxacyclopentyl) 1*H*-imidazole-1-carbothioate (**1t**):

IR (neat) 657, 746, 970, 1077, 1115, 1231, 1286, 1387, 1464, 1532, 2867, 3125 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.25–2.32 (m, 1H), 2.39 (dtd, $J = 14.3, 8.2, 6.2$ Hz, 1H), 3.94 (td, $J = 8.5, 4.5$

Hz, 1H), 4.00–4.07 (m, 2H), 4.09–4.14 (m, 1H), 5.93–5.97 (m, 1H), 7.04–7.05 (m, 1H), 7.62–7.64 (m, 1H), 8.35 (s, 1H); ^{13}C NMR (CDCl_3) δ 32.53, 67.07, 72.50, 84.11, 117.71, 130.75, 136.69, 183.24. Found: C, 48.47; H, 5.11%. Calcd for $\text{C}_8\text{H}_{10}\text{N}_2\text{O}_2\text{S}$: C, 48.47; H, 5.08%.

***O*-hexyl 1*H*-imidazole-1-carbothioate (1u):**

IR (neat) 657, 744, 990, 1095, 1232, 1286, 1329, 1387, 1464, 1530, 2931, 2956, 3123 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.87–0.96 (m, 3H), 1.30–1.40 (m, 4H), 1.42–1.50 (m, 2H), 1.84–1.91 (m, 2H), 4.66 (t, $J = 6.8$ Hz, 2H), 7.03–7.05 (m, 1H), 7.63–7.65 (m, 1H), 8.34–8.36 (m, 1H); ^{13}C NMR (CDCl_3) δ 13.91, 22.43, 25.51, 27.91, 31.24, 73.87, 117.76, 130.63, 136.64, 184.28. Found: C, 56.96; H, 7.57%. Calcd for $\text{C}_{10}\text{H}_{16}\text{N}_2\text{OS}$: C, 56.57; H, 7.60%.

***O*-{(1*S*,2*R*)-1-(1,1-dimethylethoxycarbonyl)amino-2-indanyl} 1*H*-imidazole-1-carbothioate (1w) (86:14 mixture of two rotamers):**

IR (nujol) 1019, 1109, 1232, 1244, 1293, 1389, 1525, 1681, 3342 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.44 (s, 9H), 3.25 (dd, $J = 17.1, 2.2$ Hz, 1H), 3.41 (dd, $J = 17.1, 5.3$ Hz, 1H), 4.86–5.00 (br, 0.14 $\times$ H), 5.05–5.18 (br, 0.86 $\times$ 1H), 5.28–5.39 (br, 0.14 $\times$ 1H), 5.50 (dd, $J = 8.5, 5.3$ Hz, 0.86 $\times$ 1H), 6.25 (ddd, $J = 5.3, 5.3, 2.2$ Hz, 1H), 6.94 (s, 1H), 7.25–7.40 (m, 4H), 7.51 (s, 1H), 8.16 (s, 1H); ^{13}C NMR (CDCl_3) δ 28.24, 36.57, 57.28, 80.30, 84.31, 117.96, 124.00, 125.09, 127.63, 128.81,

130.65, 136.53, 138.57, 139.57, 155.42, 183.14. Found: C, 60.14; H, 5.94%. Calcd for $C_{18}H_{21}N_3O_3S$: C, 60.15; H, 5.89%.

(2-methylphenyl)diphenylphosphine sulfide (3b):

IR (nujol) 511, 525, 637, 692, 716, 756, 1097, 1435 cm^{-1} ; 1H NMR ($CDCl_3$) δ 2.40 (s, 3H, Hk), 6.94 (ddd, $J = 14.8, 7.8, 1.0$ Hz, 1H, Hf), 7.09–7.14 (m, 1H, Hg), 7.25–7.29 (m, 1H, Hi), 7.37–7.41 (m, 1H, Hh), 7.45–7.50 (m, 4H, Hc), 7.51–7.56 (m, 2H, Hd), 7.79–7.85 (m, 4H, Hb); ^{13}C NMR ($CDCl_3$) δ 22.09 (d, $J = 5.6$ Hz, Ck), 125.49 (d, $J = 12.4$ Hz, Cg), 128.55 (d, $J = 12.4$ Hz, Cc), 131.45 (d, $J = 84.9$ Hz, Ce), 131.50 (d, $J = 2.9$ Hz, Cd), 131.66 (d, $J = 2.9$ Hz, Ch), 132.24 (d, $J = 10.5$ Hz, Cb), 132.32 (d, $J = 84.0$ Hz, Ca), 132.54 (d, $J = 10.5$ Hz, Ci), 132.77 (d, $J = 11.9$ Hz, Cf), 142.52 (d, $J = 9.5$ Hz, Cj); ^{31}P NMR ($CDCl_3$) δ 40.17. Found: C, 73.70; H, 5.60%. Calcd for $C_{19}H_{17}PS$: C, 74.00; H, 5.56%. Isolated yield: 86 mg, 0.28 mmol, 52% starting from 0.54 mmol of 2-iodotoluene.

(4-butylphenyl)diphenylphosphine sulfide (3c):

IR ($CHCl_3$) 511, 627, 692, 716, 748, 1103, 1437, 1599, 2930, 2957 cm^{-1} ; 1H NMR ($CDCl_3$) δ 0.92 (t, $J = 7.4$ Hz, 3H, Hl), 1.35 (tq, $J = 7.4, 7.4$ Hz, 2H, Hk), 1.60 (tt, $J = 8.0, 7.4$ Hz, 2H, Hj), 2.65 (t, $J = 8.0$ Hz, 2H, Hi), 7.25 (dd, $J = 8.5, 2.5$ Hz, 2H, Hg), 7.42–7.46 (m, 4H, Hc), 7.48–7.52 (m, 2H, Hd), 7.59–7.64 (m, 2H, Hf), 7.69–7.75 (m, 4H, Hb); ^{13}C NMR ($CDCl_3$) δ 13.86 (Cl),

22.28 (Ck), 33.20 (Cj), 35.51 (d, $J = 1.4$ Hz, Ci), 128.42 (d, $J = 12.4$ Hz, Cc), 128.61 (d, $J = 12.9$ Hz, Cg), 129.51 (d, $J = 86.9$ Hz, Ce), 131.40 (d, $J = 2.9$ Hz, Cd), 132.19 (d, $J = 10.5$ Hz, Cb), 132.24 (d, $J = 11.0$ Hz, Cf), 133.11 (d, $J = 85.0$ Hz, Ca), 146.97 (d, $J = 2.9$ Hz, Ch); ^{31}P NMR (CDCl_3) δ 41.02. HRMS Found: 351.1333. Calcd for $\text{C}_{22}\text{H}_{24}\text{PS}$: 351.1336 $[\text{MH}]^+$.

diphenyl(2,4,6-trimethylphenyl)phosphine sulfide (3d):

IR (nujol) 426, 517, 604, 665, 704, 721, 760, 862, 1092, 1437, 1605 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.93 (s, 6H, Hi), 2.29 (s, 3H, Hj), 6.85 (d, $J = 4.0$ Hz, 2H, Hg), 7.37–7.44 (m, 6H, Hc, Hd), 7.94–8.00 (m, 4H, Hb); ^{13}C NMR (CDCl_3) δ 20.93 (d, $J = 1.0$ Hz, Cj), 23.96 (d, $J = 6.3$ Hz, Ci), 127.63 (d, $J = 88.4$ Hz, Ce), 128.51 (d, $J = 12.4$ Hz, Cc), 130.79 (d, $J = 2.9$ Hz, Cd), 131.10 (d, $J = 10.5$ Hz, Cb), 131.31 (d, $J = 11.5$ Hz, Cg), 136.19 (d, $J = 81.6$ Hz, Ca), 141.06 (d, $J = 2.9$ Hz, Ch), 142.43 (d, $J = 10.0$ Hz, Cf); ^{31}P NMR (CDCl_3) δ 34.32. Found: C, 74.87; H, 6.31%. Calcd for $\text{C}_{21}\text{H}_{21}\text{PS}$: C, 74.97; H, 6.291%.

(2-methoxyphenyl)diphenylphosphine sulfide (3e):

IR (nujol) 496, 511, 633, 694, 710, 760, 1011, 1097, 1275, 1433, 1474, 1587 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.50 (s, 3H, Hk), 6.90 (dd, $J = 8.3, 5.3$ Hz, 1H, Hi), 7.09 (dddd, $J = 7.7, 7.6, 2.0, 1.0$ Hz, 1H, Hg), 7.38–7.43 (m, 4H, Hc), 7.44–7.48 (m, 2H, Hd), 7.51–7.55 (m, 1H, Hh), 7.74–7.80 (m, 4H, Hb), 7.94 (ddd, $J = 16.3, 7.7, 1.8$ Hz, 1H, Hf); ^{13}C NMR (CDCl_3) δ 55.19 (Ck),

111.70 (d, $J = 5.6$ Hz, Ci), 120.70 (d, $J = 84.0$ Hz, Ce), 121.03 (d, $J = 12.4$ Hz, Cg), 128.05 (d, $J = 12.9$ Hz, Cc), 130.94 (d, $J = 2.9$ Hz, Cd), 131.77 (d, $J = 11.0$ Hz, Cb), 133.44 (d, $J = 88.4$ Hz, Ca), 134.20 (d, $J = 2.4$ Hz, Ch), 135.71 (d, $J = 10.0$ Hz, Cf), 160.34 (d, $J = 1.9$ Hz, Cj); ^{31}P NMR (CDCl_3) δ 39.23. Found: C, 70.09; H, 5.33%. Calcd for $\text{C}_{19}\text{H}_{17}\text{OPS}$: C, 70.35; H, 5.28%. Isolated yield: 70 mg, 0.22 mmol, 44% starting from 0.49 mmol of 2-iodoanisole.

(3-methoxyphenyl)diphenylphosphine sulfide (3f):

IR (nujol) 509, 638, 691, 714, 1042, 1107, 1240, 1288, 1464, 1572, 1593 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.78 (s, 3H, Hk), 7.01–7.05 (m, 1H, Hh), 7.15–7.21 (m, 1H, Hf), 7.31–7.36 (m, 1H, Hg), 7.33–7.38 (m, 1H, Hj), 7.41–7.46 (m, 4H, Hc), 7.48–7.52 (m, 2H, Hd), 7.69–7.75 (m, 4H, Hb); ^{13}C NMR (CDCl_3) δ 55.34 (Ck), 117.29 (d, $J = 12.4$ Hz, Cj), 117.49 (d, $J = 2.9$ Hz, Ch), 124.38 (d, $J = 10.5$ Hz, Cf), 128.43 (d, $J = 12.4$ Hz, Cc), 129.51 (d, $J = 14.8$ Hz, Cg), 131.52 (d, $J = 2.9$ Hz, Cd), 132.15 (d, $J = 10.5$ Hz, Cb), 132.70 (d, $J = 84.5$ Hz, Ca), 134.14 (d, $J = 84.0$ Hz, Ce), 159.47 (d, $J = 15.8$ Hz, Ci); ^{31}P NMR (CDCl_3) δ 41.69. Found: C, 70.06; H, 5.33%. Calcd for $\text{C}_{19}\text{H}_{17}\text{OPS}$: C, 70.35; H, 5.28%.

(4-methoxyphenyl)diphenylphosphine sulfide (3g):

IR (nujol) 519, 675, 714, 1026, 1105, 1259, 1593 cm^{-1} ; ^1H NMR (CDCl_3) δ 3.83 (s, 3H, Hi), 6.93–6.97 (m, 2H, Hg), 7.41–7.46 (m, 4H, Hc), 7.47–7.51 (m, 2H, Hd), 7.62–7.68 (m, 2H, Hf),

7.68–7.74 (m, 4H, Hb); ^{13}C NMR (CDCl_3) δ 55.35 (Ci), 114.00 (d, $J = 13.4$ Hz, Cg), 123.47 (d, $J = 90.8$ Hz, Ce), 128.40 (d, $J = 12.4$ Hz, Cc), 131.37 (d, $J = 3.4$ Hz, Cd), 132.08 (d, $J = 10.5$ Hz, Cb), 133.33 (d, $J = 85.0$ Hz, Ca), 134.08 (d, $J = 12.5$ Hz, Cf), 162.18 (d, $J = 2.9$ Hz, Ch); ^{31}P NMR (CDCl_3) δ 40.53. Found: C, 70.34; H, 5.47%. Calcd for $\text{C}_{19}\text{H}_{17}\text{OPS}$: C, 70.35; H, 5.28%. Isolated yield: 73 mg, 0.23 mmol, 46% starting from 0.49 mmol of 4-iodoanisole.

diphenyl(4-trifluoromethylphenyl)phosphine sulfide (3h):

IR (CHCl_3) 532, 648, 708, 1016, 1063, 1105, 1130, 1325, 1396, 1437, 3057 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.45–7.50 (m, 4H, Hc), 7.52–7.57 (m, 2H, Hd), 7.68–7.71 (m, 2H, Hg), 7.70–7.75 (m, 4H, Hb), 7.83–7.88 (m, 2H, Hf); ^{13}C NMR (CDCl_3) δ 123.48 (qd, $J = 271.4, 1.1$ Hz, Ci), 125.27 (dq, $J = 12.4, 3.8$ Hz, Cg), 128.67 (d, $J = 12.9$ Hz, Cc), 131.88 (d, $J = 85.5$ Hz, Ca), 131.89 (d, $J = 2.9$ Hz, Cd), 132.13 (d, $J = 11.0$ Hz, Cb), 132.61 (d, $J = 11.0$ Hz, Cf), 133.18 (qd, $J = 32.7, 3.1$ Hz, Ch), 137.76 (d, $J = 82.1$ Hz, Ce); ^{31}P NMR (CDCl_3) δ 40.83. HRMS Found: 363.0583. Calcd for $\text{C}_{19}\text{H}_{15}\text{F}_3\text{PS}$: 363.0584 $[\text{MH}]^+$. Found: C, 62.90; H, 4.09%. Calcd for $\text{C}_{19}\text{H}_{14}\text{F}_3\text{PS}$: C, 62.98; H, 3.89%.

(4-chlorophenyl)diphenylphosphine sulfide (3i):

IR (nujol) 492, 515, 554, 650, 692, 719, 745, 824, 1084, 1099, 1435 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.40–7.44 (m, 2H, Hg), 7.43–7.48 (m, 4H, Hc), 7.50–7.55 (m, 2H, Hd), 7.63–7.69 (m, 2H, Hf),

7.67–7.73 (m, 4H, Hb); ^{13}C NMR (CDCl_3) δ 128.59 (d, $J = 12.9$ Hz, Cc), 128.76 (d, $J = 13.4$ Hz, Cg), 131.56 (d, $J = 85.4$ Hz, Ce), 131.72 (d, $J = 2.9$ Hz, Cd), 132.12 (d, $J = 11.0$ Hz, Cb), 132.41 (d, $J = 85.4$ Hz, Ca), 133.60 (d, $J = 11.5$ Hz, Cf), 138.20 (d, $J = 3.9$ Hz, Ch); ^{31}P NMR (CDCl_3) δ 40.71. Found: C, 65.91; H, 4.33%. Calcd for $\text{C}_{18}\text{H}_{14}\text{ClPS}$: C, 65.75; H, 4.29%. Isolated yield: 92 mg, 0.28 mmol, 56% starting from 0.50 mmol of 4-chloriodobenzene.

ethyl 3-(diphenylthiophosphinyl)benzoate (3j):

IR (neat) 517, 640, 692, 718, 750, 1101, 1128, 1265, 1437, 1720, 2980, 3055 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.35 (t, $J = 7.0$ Hz, 3H, Hm), 4.35 (q, $J = 7.0$ Hz, 2H, Hl), 7.44–7.49 (m, 4H, Hc), 7.51–7.56 (m, 3H, Hd, Hg), 7.69–7.75 (m, 4H, Hb), 7.95 (dddd, $J = 12.8, 7.6, 1.7, 1.2$ Hz, 1H, Hf), 8.18 (dddd, $J = 7.8, 1.7, 1.7, 1.4$ Hz, 1H, Hh), 8.36 (dddd, $J = 13.4, 1.7, 1.7, 0.6$ Hz, 1H, Hj); ^{13}C NMR (CDCl_3) δ 14.20 (Cm), 61.37 (Cl), 128.63 (d, $J = 12.4$ Hz, Cc), 128.66 (d, $J = 12.4$ Hz, Cg), 130.83 (d, $J = 12.5$ Hz, Ci), 131.76 (d, $J = 2.9$ Hz, Cd), 132.19 (d, $J = 11.0$ Hz, Cb), 132.32 (d, $J = 85.5$ Hz, Ca), 132.47 (d, $J = 2.9$ Hz, Ch), 133.06 (d, $J = 11.5$ Hz, Cj), 133.87 (d, $J = 84.0$ Hz, Ce), 136.32 (d, $J = 11.0$ Hz, Cf), 165.59 (d, $J = 0.9$ Hz, Ck); ^{31}P NMR (CDCl_3) δ 41.04. HRMS Found: 367.0929. Calcd for $\text{C}_{21}\text{H}_{20}\text{O}_2\text{PS}$: 367.0923 $[\text{MH}]^+$. Isolated yield: 88 mg, 0.24 mmol, 47% starting from 0.50 mmol of ethyl 3-iodobenzoate.

(4-bromophenyl)diphenylphosphine sulfide (3k):

IR (nujol) 511, 534, 646, 692, 718, 735, 820, 1011, 1069, 1099, 1385, 1435 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.42–7.47 (m, 4H, Hc), 7.51–7.55 (m, 2H, Hd), 7.55–7.61 (m, 4H, Hf, Hg), 7.67–7.73 (m, 4H, Hb); ^{13}C NMR (CDCl_3) δ 126.80 (d, $J = 3.4$ Hz, Ch), 128.62 (d, $J = 12.5$ Hz, Cc), 131.71 (d, $J = 12.9$ Hz, Cg), 131.74 (d, $J = 2.9$ Hz, Cd), 132.12 (d, $J = 87.9$ Hz, Ce), 132.12 (d, $J = 10.5$ Hz, Cb), 132.35 (d, $J = 85.4$ Hz, Ca), 133.74 (d, $J = 11.5$ Hz, Cf); ^{31}P NMR (CDCl_3) δ 40.88. Found: C, 57.98; H, 3.95%. Calcd for $\text{C}_{18}\text{H}_{14}\text{BrPS}$: C, 57.92; H, 3.78%. Isolated yield: 89 mg, 0.24 mmol, 47% starting from 0.50 mmol of 4-bromiodobenzene.

4-(diphenylthiophosphinyl)benzonitrile (3l):

IR (CHCl_3) 502, 556, 577, 658, 692, 718, 750, 1101, 1389, 1437, 2232, 3055 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.46–7.51 (m, 4H, Hc), 7.54–7.59 (m, 2H, Hd), 7.67–7.74 (m, 4H, Hb), 7.70–7.74 (m, 2H, Hg), 7.80–7.86 (m, 2H, Hf); ^{13}C NMR (CDCl_3) δ 115.13 (d, $J = 2.8$ Hz, Ch), 117.82 (d, $J = 1.4$ Hz, Ci), 128.77 (d, $J = 12.5$ Hz, Cc), 131.48 (d, $J = 86.0$ Hz, Ca), 131.92 (d, $J = 12.4$ Hz, Cg), 132.07 (d, $J = 2.9$ Hz, Cd), 132.14 (d, $J = 10.5$ Hz, Cb), 132.66 (d, $J = 10.5$ Hz, Cf), 139.13 (d, $J = 80.6$ Hz, Ce); ^{31}P NMR (CDCl_3) δ 40.98. HRMS Found: 320.0663. Calcd for $\text{C}_{19}\text{H}_{15}\text{NPS}$: 320.0663 $[\text{MH}]^+$. Isolated yield: 68 mg, 0.21 mmol, 43% starting from 0.49 mmol of 4-iodobenzonitrile.

1-{4-(diphenylthiophosphinyl)phenyl}ethanone (3m):

IR (nujol) 511, 610, 655, 692, 716, 1103, 1263, 1393, 1437, 1595, 1690, 3055 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.62 (s, 3H, Hj), 7.44–7.49 (m, 4H, Hc), 7.52–7.56 (m, 2H, Hd), 7.69–7.75 (m, 4H, Hb), 7.79–7.85 (m, 2H, Hf), 7.97–8.01 (m, 2H, Hg); ^{13}C NMR (CDCl_3) δ 26.83 (Cj), 128.04 (d, $J = 12.5$ Hz, Cg), 128.66 (d, $J = 12.4$ Hz, Cc), 131.84 (d, $J = 2.9$ Hz, Cd), 132.12 (d, $J = 85.4$ Hz, Ca), 132.19 (d, $J = 11.0$ Hz, Cb), 132.52 (d, $J = 10.5$ Hz, Cf), 138.32 (d, $J = 81.6$ Hz, Ce), 139.07 (d, $J = 2.9$ Hz, Ch), 197.43 (d, $J = 0.9$ Hz, Ci); ^{31}P NMR (CDCl_3) δ 40.90. Found: C, 71.17; H, 5.37%. Calcd for $\text{C}_{20}\text{H}_{17}\text{OPS}$: C, 71.41; H, 5.09%.

4-(diphenylthiophosphinyl)phenyl trifluoromethanesulfonate (3n):

IR (neat) 885, 1016, 1103, 1139, 1200–1230 (br), 1251, 1420–1440 (br), 1486, 1585, 3057 cm^{-1} ; ^1H NMR (CDCl_3) δ 7.33–7.37 (m, 2H, Hg), 7.46–7.51 (m, 4H, Hc), 7.53–7.58 (m, 2H, Hd), 7.68–7.74 (m, 4H, Hb), 7.80–7.86 (m, 2H, Hf); ^{13}C NMR (CDCl_3) δ 118.61 (q, $J = 319.1$ Hz, Ci), 121.45 (d, $J = 12.9$ Hz, Cg), 128.74 (d, $J = 12.5$ Hz, Cc), 131.90 (d, $J = 85.5$ Hz, Ca), 131.97 (d, $J = 3.4$ Hz, Cd), 132.14 (d, $J = 10.5$ Hz, Cb), 134.29 (d, $J = 83.5$ Hz, Ce), 134.49 (d, $J = 11.9$ Hz, Cf), 151.52 (d, $J = 3.3$ Hz, Ch); ^{31}P NMR (CDCl_3) δ 40.41. HRMS Found: 443.0149. Calcd for $\text{C}_{19}\text{H}_{15}\text{O}_3\text{F}_3\text{PS}_2$: 443.0152 $[\text{MH}]^+$. Found: C, 51.49; H, 2.94%. Calcd for $\text{C}_{19}\text{H}_{14}\text{O}_3\text{F}_3\text{PS}_2$: C, 51.58; H, 3.19%. Isolated yield: 127 mg, 0.29 mmol, 57% starting from 0.50 mmol of 4-iodophenyl trifluoromethanesulfonate.

allyl (4-diphenylthiophosphinyl)benzoate (3o):

IR (neat) 650, 692, 718, 1094, 1102, 1271 1394, 1436, 1722, 3056 cm^{-1} ; ^1H NMR (CDCl_3) δ 4.82–4.86 (m, 2H, Hj), 5.30 (dm, $J = 17.2$ Hz, 1H, Hl), 5.41 (dm, $J = 10.9$ Hz, 1H, Hl), 6.02 (ddt, $J = 17.2, 10.9, 10.5$ Hz, 1H, Hk), 7.44–7.49 (m, 4H, Hc), 7.51–7.56 (m, 2H, Hd), 7.68–7.75 (m, 4H, Hb), 7.78–7.84 (m, 2H, Hf), 8.10–8.14 (m, 2H, Hg); ^{13}C NMR (CDCl_3) δ 65.91 (Cj), 118.60 (Cl), 128.63 (d, $J = 12.4$ Hz, Cc), 129.43 (d, $J = 13.0$ Hz, Cg), 131.76 (Ck), 131.81 (d, $J = 2.9$ Hz, Cd), 132.11 (d, $J = 86.0$ Hz, Ca), 132.17 (d, $J = 11.0$ Hz, Cb), 132.25 (d, $J = 10.0$ Hz, Cf), 132.76 (d, $J = 2.9$ Hz, Ch), 138.23 (d, $J = 82.0$ Hz, Ce), 165.31 (d, $J = 1.4$ Hz, Ci); ^{31}P NMR (CDCl_3) δ 41.00. HRMS Found: 379.0928. Calcd for $\text{C}_{22}\text{H}_{20}\text{O}_2\text{PS}$: 379.0922 $[\text{MH}]^+$.

dicyclohexylphenylphosphine sulfide (4a):

IR (nujol) 540, 625, 694, 745, 760, 1435, 1452 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.08–1.18 (m, 2H), 1.20–1.41 (m, 8H), 1.57–1.64 (m, 2H), 1.64–1.71 (m, 2H), 1.72–1.79 (m, 2H), 1.81–1.88 (m, 2H), 2.04–2.11 (m, 2H), 2.18–2.27 (m, 2H), 7.45–7.54 (m, 3H), 7.81–7.87 (m, 2H); ^{13}C NMR (CDCl_3) δ 25.25 (d, $J = 2.4$ Hz), 25.71 (d, $J = 1.4$ Hz), 25.95 (d, $J = 3.4$ Hz), 26.33 (d, $J = 13.9$ Hz), 26.38 (d, $J = 13.4$ Hz), 36.96 (d, $J = 50.0$ Hz), 128.06 (d, $J = 67.3$ Hz), 128.18 (d, $J = 10.5$ Hz), 131.23 (d, $J = 2.8$ Hz), 132.19 (d, $J = 8.6$ Hz); ^{31}P NMR (CDCl_3) δ 56.78. Found: C, 70.34; H, 8.89%. Calcd for $\text{C}_{18}\text{H}_{27}\text{PS}$: C, 70.55; H, 8.88%.

(2,3-dihydro-3-benzofurymethyl)diphenylphosphine sulfide (3p):

IR (neat) 507, 625, 692, 750, 1103, 1232, 1437, 1481, 1597, 2895, 2928, 3053 cm^{-1} ; ^1H NMR (CDCl_3) δ 2.82 (ddd, $J = 14.6, 10.4, 9.5$ Hz, 1H, He), 2.98 (ddd, $J = 14.6, 11.9, 2.9$ Hz, 1H, He), 3.93–4.02 (m, 1H, Hf), 4.08 (dd, $J = 9.3, 6.8$ Hz, 1H, Hg), 4.46 (dd, $J = 9.3, 9.3$ Hz, 1H, Hg), 6.76 (d, $J = 8.5$ Hz, 1H, Hi), 6.83 (ddd, $J = 7.5, 7.5, 1.0$ Hz, 1H, Hk), 7.07–7.14 (m, 2H, Hl, Hj), 7.45–7.56 (m, 6H, Hc, Hd), 7.83–7.92 (m, 4H, Hb); ^{13}C NMR (CDCl_3) δ 36.86 (d, $J = 1.5$ Hz, Cf), 38.38 (d, $J = 53.9$ Hz, Ce), 76.72 (d, $J = 1.9$ Hz, Cg), 109.72 (Ci), 120.59 (Ck), 123.88 (Cl), 128.68 (Cj), 128.78 (d, $J = 12.0$ Hz, 2C of Cc), 128.83 (d, $J = 11.9$ Hz, 2C of Cc), 129.99 (d, $J = 2.4$ Hz, Cm), 131.06 (d, $J = 10.0$ Hz, 2C of Cb), 131.08 (d, $J = 10.5$ Hz, 2C of Cb), 131.75 (d, $J = 2.9$ Hz, 1C of Cd), 131.79 (d, $J = 2.9$ Hz, 1C of Cd), 132.44 (d, $J = 80.6$ Hz, 1C of Ca), 132.74 (d, $J = 79.3$ Hz, 1C of Ca), 159.49 (Ch); ^{31}P NMR (CDCl_3) δ 37.85. Found: C, 72.05; H, 5.37%. Calcd for $\text{C}_{21}\text{H}_{19}\text{OPS}$: C, 71.98; H, 5.47%. Isolated yield: 96 mg, 0.28 mmol, 55%, 90% purity, starting from 0.50 mmol of allyl 2-iodophenyl ether.

ethyl 3-(diphenylthiophosphinyl)butanoate (3s):

IR (neat) 610, 694, 712, 752, 1028, 1100, 1156, 1224, 1436, 1733, 2979, 3055 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.18 (dd, $J = 18.8, 6.8$ Hz, 3H, Hf), 1.22 (t, $J = 7.1$ Hz, 3H, Hj), 2.46–2.55 (m, 2H, Hg), 3.31–3.40 (m, 1H, He), 4.06 (dq, $J = 10.6, 7.1$ Hz, 1H, Hi), 4.11 (dq, $J = 10.6, 7.1$ Hz, 1H, Hi), 7.44–7.52 (m, 6H, Hc, Hd), 7.93–8.00 (m, 4H, Hb); ^{13}C NMR (CDCl_3) δ 13.30 (Cf),

14.10 (Cj), 29.98 (d, $J = 57.8$ Hz, Ce), 35.03 (d, $J = 2.4$ Hz, Cg), 60.83 (Ci), 128.68 (d, $J = 11.9$ Hz, 2C of Cc), 128.69 (d, $J = 12.0$ Hz, 2C of Cc), 130.86 (d, $J = 77.9$ Hz, 1C of Ca), 131.04 (d, $J = 77.3$ Hz, 1C of Ca), 131.35 (d, $J = 9.6$ Hz, Cb), 131.53 (d, $J = 2.9$ Hz, 1C of Cd), 131.58 (d, $J = 2.9$ Hz, 1C of Cd), 171.95 (d, $J = 20.1$ Hz, Ch); ^{31}P NMR (CDCl_3) δ 50.02. HRMS Found: 333.1078. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_2\text{PS}$: 333.1078 $[\text{MH}]^+$. Isolated yield: 112 mg, 0.34 mmol, 67%, starting from 0.51 mmol of **1s**.

(3-oxacyclopentyl)diphenylphosphine sulfide (3t):

IR (nujol) 504, 614, 625, 693, 713, 914, 1095, 1105, 1436 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.97–2.07 (m, 1H, Hh), 2.31–2.43 (m, 1H, Hh), 3.77–3.46 (m, 1H, He), 3.84–3.92 (m, 2H, Hf), 3.92–4.01 (m, 2H, Hg), 7.44–7.53 (m, 6H, Hc, Hd), 7.82–7.89 (m, 4H, Hb); ^{13}C NMR (CDCl_3) δ 27.76 (Ch), 38.73 (d, $J = 59.1$ Hz, Ce), 69.38 (d, $J = 4.8$ Hz, Cg), 68.88 (d, $J = 8.6$ Hz, Cf), 128.68 (d, $J = 11.9$ Hz, 2C of Cc), 128.70 (d, $J = 11.9$ Hz, 2C of Cc), 131.05 (d, $J = 10.1$ Hz, 2C of Cb), 131.09 (d, $J = 10.0$ Hz, 2C of Cb), 131.57 (d, $J = 3.4$ Hz, 1C of Cd), 131.66 (d, $J = 2.9$ Hz, 1C of Cd), 132.32 (d, $J = 79.8$ Hz, 1C of Ca), 132.57 (d, $J = 80.8$ Hz, 1C of Ca); ^{31}P NMR (CDCl_3) δ 45.30. Found: C, 66.72; H, 5.86%. Calcd for $\text{C}_{16}\text{H}_{17}\text{OPS}$: C, 66.65; H, 5.94%. Isolated yield: 111 mg, 0.39 mmol, 76%, starting from 0.50 mmol of **1t**.

***tert*-butyl (1*S*, 2*S*)-2-(diphenylthiophosphinyl)-1-indanecarbamate (3w)** (75:25 mixture of 2 rotamers):

IR (nujol) 691, 711, 744, 1100, 1168, 1437, 1456, 1684, 3338 (br) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.26 (s, $0.25 \times 9\text{H}$), 1.30 (s, $0.75 \times 9\text{H}$), 2.86–3.02 (br, $0.25 \times 1\text{H}$), 2.96–3.07 (m, $0.75 \times 1\text{H}$), 3.28–3.40 (m, 1H), 3.60–3.72 (br, $0.25 \times 1\text{H}$), 3.88–3.98 (m, $0.75 \times 1\text{H}$), 4.30–4.42 (br, $0.25 \times 1\text{H}$), 4.59 (d, $J = 8.0$ Hz, $0.75 \times 1\text{H}$), 5.52–5.68 (m, 1H), 7.08–7.13 (m, 1H), 7.13–7.22 (m, 3H), 7.42–7.54 (m, 6H), 7.90–8.04 (br, 2H), 7.99–8.06 (m, 2H); ^{13}C NMR (CDCl_3) δ 28.23, 32.52, 44.80 (d, $J = 58.8$ Hz), 57.01, 79.23, 123.33, 124.36, 127.06, 127.94, 128.46 (d, $J = 12.0$ Hz), 128.68 (d, $J = 11.9$ Hz), 131.23 (d, $J = 9.5$ Hz), 131.41, 131.50 (d, $J = 2.9$ Hz), 131.66 (d, $J = 10.0$ Hz), 132.37 (d, $J = 80.1$ Hz), 139.43 (d, $J = 10.0$ Hz), 142.56 (d, $J = 10.9$ Hz), 154.20; ^{31}P NMR (CDCl_3) δ 46.74 (br, 0.75P), 47.19 (br, 0.25P). HRMS Found: 450.1657. Calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_2\text{PS}$: 450.1657 $[\text{MH}]^+$.

The inseparable mixture of the rotamers of **3w** was subjected to deprotection of the Boc group to yield the corresponding amine quantitatively.

(1S, 2S)-2-diphenylthiophosphinyl-1-indaneamine:

IR (Et_2O) 638, 749, 1436, 1480, 1589, 3052, 3377 (br) cm^{-1} ; ^1H NMR (CDCl_3) δ 1.40–1.65 (br, 2H), 3.04–3.11 (m, 1H), 3.28–3.39 (m, 2H), 4.94 (dd, $J = 15.8, 7.3$ Hz, 1H), 7.11–7.15 (m, 1H), 7.17–7.24 (m, 2H), 7.26–7.30 (m, 1H), 7.48–7.56 (m, 6H), 7.94–8.00 (m, 2H), 8.01–8.07 (m, 2H); ^{13}C NMR (CDCl_3) δ 33.09 (d, $J = 1.0$ Hz), 50.52 (d, $J = 57.3$ Hz), 58.28 (d, $J = 1.9$ Hz), 123.72, 124.23, 127.07, 127.83, 128.72 (d, $J = 11.4$ Hz), 128.74 (d, $J = 11.9$ Hz), 131.49 (d, $J =$

10.1 Hz), 131.64 (d, $J = 2.9$ Hz), 131.69 (d, $J = 10.0$ Hz), 131.93 (d, $J = 76.9$ Hz), 132.17 (d, $J = 77.8$ Hz), 139.91 (d, $J = 10.0$ Hz), 144.99 (d, $J = 11.4$ Hz); ^{31}P NMR (CDCl_3) δ 46.51. HRMS Found: 350.1136. Calcd for $\text{C}_{21}\text{H}_{21}\text{NPS}$: 350.1132 $[\text{MH}]^+$.