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Palladium-Catalyzed Synthesis of Dibenzophosphole Oxides via Intramolecular Dehydrogenative Cyclization

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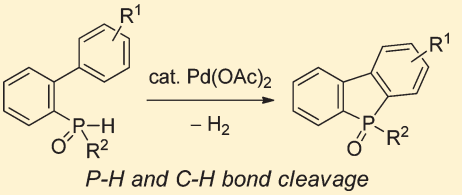
Supporting Information

ABSTRACT: Dibenzophosphole oxides were obtained from secondary hydrophosphine oxides with a biphenyl group by dehydrogenation via phosphine−hydrogen and carbon−hydrogen bond cleavage in the presence of a catalytic amount of palladium(II) acetate, $Pd(OAc)_2$. By using this reaction, a ladder-type dibenzophosphole oxide could also be synthesized by double intramolecular dehydrogenative cyclization.



INTRODUCTION

Organic π-conjugated oligomers and polymers are useful compounds as organic materials, such as organic light-emitting diodes (OLEDs), organic field-effect transisters (OFETs), nonlinear optical (NLO) devices, and organic solar cells. Heteroatom(s) are often contained in the π-conjugated systems, and these heteroatom(s) play an important role in the properties of the materials. Dibenzophosphole oxides are among the most useful compounds for organic materials[1] and therefore have received much attention. There are several methods to synthesize dibenzophospholes.[2,3] The most frequently used method is the reaction between 2,2′-dilithiated biaryls and $PhPCl_2$ followed by oxidation of the formed dibenzophospholes by air or H_2O_2.[4] The following methods have also been reported: cyclization of 2-biphenylphenylphosphinic acids by intramolecular Friedel−Crafts reaction,[5] treatment of triphenylphosphine oxide with 2 equiv of PhLi and successive oxidation of the formed dibenzophospholes,[6] treatment of tetraphenylphosphonium bromide with lithium diethylamide followed by oxidation,[7] thermolysis of *m*-terphenyldichlorophosphines,[8] and Et_3B- and O_2-mediated radical cyclization of secondary phosphine oxides with a biphenyl group.[9] Our new strategy for the synthesis of dibenzophosphole oxides is shown in Figure 1. In this reaction, dibenzophosphole oxides will be synthesized from hydrophosphine oxides bearing a biphenyl group in the presence of a transition-metal catalyst via the elimination of H_2.[10−12] This transformation should contain successive P−H and C−H bond cleavage steps.

RESULTS AND DISCUSSION

By heating a secondary hydrophosphine oxide having a biphenyl group (**1a**, phosphine oxide) in the presence of a catalytic amount of palladium(II) acetate in THF at 65 °C for 3 h, dibenzophosphole oxide **2a** was obtained in 94% yield (Scheme 1).[13−17] Since **1a** and **2a** are both air stable, they are easily handled.

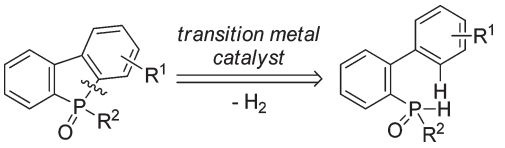
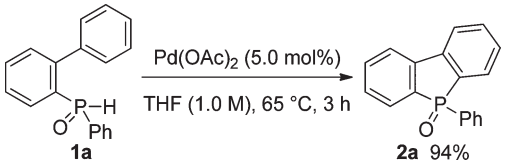


Figure 1. Retrosynthesis for the formation of dibenzophospholes.

Scheme 1. Synthesis of Dibenzophosphole Oxide 2a from Phosphine Oxide 1a



We investigated several phosphine oxides with a functional group, **1** (Table 1). A phosphine oxide with an electron-donating group, **1b**, gave dibenzophosphole oxide **2b** in 93% yield (entry 1). A higher temperature and longer reaction time were necessary when employing a phosphine oxide with an electron-withdrawing group, **1c** (entry 2).[18] In the case of a phosphine oxide bearing a chlorine atom, **1d**, the corresponding dibenzophosphole oxide **2d** was provided without loss of the chlorine atom (entry 3).[17] When a phosphine oxide with a substituent at the 3-position, **1e**, was employed as a substrate, a mixture of two regioisomers, **2e** and **2e′**, was formed (entry 4). The cyclization reaction was not inhibited by a substituent at the 2-position, and the corresponding dibenzophosphole oxide **2f** was isolated in 93% yield (entry 5). The corresponding dibenzophosphole oxide **2g** was afforded when a phosphine oxide with a phenyl group, **1g**, was employed as a substrate (entry 6). The C−P bond formation

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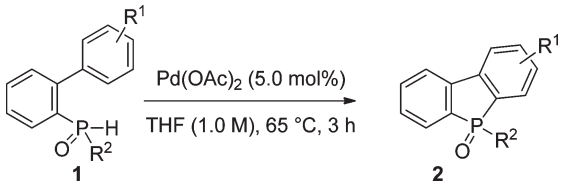
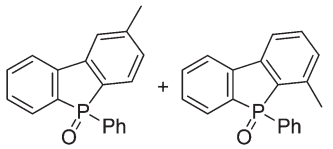
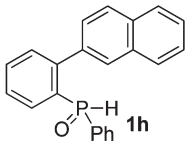
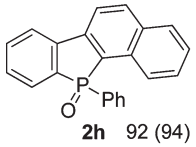
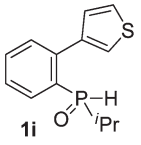
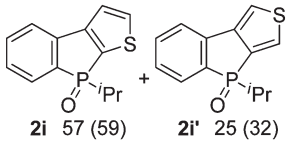
Table 1. Synthesis of Dibenzophosphole Oxides 2 from Several Phosphine Oxides 1



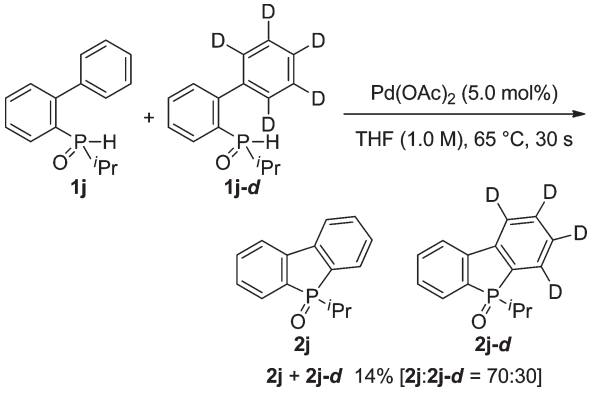
entry	R^1	R^2		yield / %[a]
1[b]	4-MeO	Ph	**1b**	**2b** 93 (95)
2[c]	4-CF_3	Ph	**1c**	**2c** 86 (90)
3[c]	4-Cl	Ph	**1d**	**2d** 90 (92)
4	3-Me	Ph	**1e**	 **2e** + **2e'** 90 (93)[d] [**2e** : **2e'** = 88 : 12]
5	2-MeO	Ph	**1f**	**2f** 93 (95)
6[e]	4-Ph	Ph	**1g**	**2g** 61 (–)
7[b]	 **1h**			 **2h** 92 (94)
8[c]	 **1i**			 **2i** 57 (59) + **2i'** 25 (32)
9[f]	H	^{i}Pr	**1j**	**2j** 94 (95)
10[g]	H	^{t}Bu	**1k**	**2k** 85 (93)

[a] The yield determined by ^{1}H NMR is reported in parentheses. [b] 6 h. [c] 1,4-Dioxane, 115 °C, 24 h. [d] Total yield of **2e** and **2e'**. [e] 115 °C, 24 h. [f] 30 min. [g] $Pd(OAc)_2$ (10 mol %), 24 h.

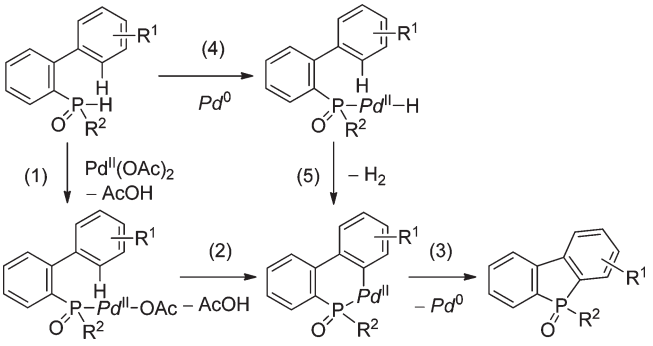
occurred regioselectively only at the 1-position of the naphthyl group of **1h**, and dibenzophosphole oxide **2h** was isolated in 92% yield (entry 7). The reaction also proceeded at the thiophene ring of phenyl[2-(thiophene-3-yl)phenyl]phosphine oxide **1i** and provided a mixture of two regioisomers, **2i** and **2i'** (entry 8). The reaction also proceeded when phosphine oxides with aliphatic substituents on the phosphorus atom, **1j** and **1k**, were employed as substrates, and the corresponding dibenzophosphole oxides **2j** and **2k** were obtained in excellent yields (entries 9 and 10). However, the desired reaction did not proceed using phenyl-(2-vinylphenyl)phosphine oxide (substrate with an alkene partner) as a substrate because of the polymerization of the substrate.

Next a deuterium-labeling experiment was carried out to gain insight into the reaction mechanism (Scheme 2). If the C–H

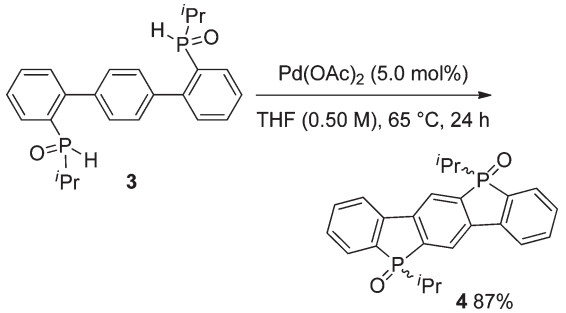
Scheme 2. Deuterium-Labeling Experiment



Scheme 3. Proposed Mechanism for the Formation of Dibenzophosphole Oxides 2



Scheme 4. Synthesis of Ladder-Type Dibenzophosphole Oxide



bond activation is the rate-determining step, a kinetic isotope effect (KIE) should be observed using a mixture of phosphine oxide **1j** and its pentadeuterated substrate **1j-*d***. By the reaction of a 1:1 mixture of **1j** and **1j-*d*** with a catalytic amount of $Pd(OAc)_2$ in THF at 65 °C for 30 s, dibenzophosphole oxides **2j** and **2j-*d*** were formed in 14% yield (**2j**:**2j-*d*** = 70:30, KIE = 2.3) (Scheme 2). This result shows that the rate-determining step is C–H bond activation of the aromatic ring.

The proposed mechanism for the formation of dibenzophosphole oxides is as follows (Scheme 3): (1) P–H bond activation via the elimination of acetic acid;[19] (2) sequential C–H bond activation via the elimination of another acetic acid unit;[20,21] (3)

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reductive elimination to give dibenzophosphole oxide **2** and Pd(0) species. After step 3, or in the case of using Pd(0) catalysts, the reaction will proceed via the following pathway: (4) P−H bond activation by oxidative addition; (5) sequential C−H bond activation by σ-bond metathesis; (3) reductive elimination leading to dibenzophosphole oxide **2**. In steps 2 and 5, one of the most important factors in promoting C−H bond activation is that the phosphoryl moiety of the formed phosphorylpalladium species works as a directing group, and thus, the palladium center is brought close to the C−H bond. In this mechanism, the catalytic cycle proceeds between Pd(0) and Pd(II) species.[22,23]

This method could be applied to the synthesis of ladder-type dibenzophosphole oxide **4** (Scheme 4). By heating a mixture of **3**, $Pd(OAc)_2$, and THF, ladder-type 5,11-diphenyl-5,11-dihydrobenzo[1,2-*b*:4,5-*b*′]bis(phosphindole) 5,11-dioxide (**4**) was obtained in 87% yield.[24−26] In this reaction, a mixture of two diastereomers, which are attributable to the orientation of the two P═O double bonds (or two P−^{i}Pr bonds), was formed. This is the first example of the synthesis of this ladder-type dibenzophosphole oxide.

In conclusion, we have succeeded in the synthesis of dibenzophosphole oxides from hydrophosphine oxides using palladium acetate, $Pd(OAc)_2$, as a catalyst. This reaction proceeds by P−H and C−H bond cleavage via dehydrogenation. By using this method, ladder-type dibenzophosphole oxides were also synthesized. We hope that this reaction will become a useful method to synthesize dibenzophosphole oxides.

EXPERIMENTAL SECTION

General Procedures. All reactions were carried out in a dry solvent under an argon atmosphere. THF and 1,4-dioxane were purchased and dried and degassed before use. $Pd(OAc)_2$ was purchased. 2-Bromobiaryls were prepared by Suzuki−Miyaura cross-coupling reaction between aryl iodides (or aryl bromides) and arylboronic acids.[27,28] Proton chemical shifts are reported relative to Me_4Si ($CDCl_3$) at δ 0.00 ppm or residual solvent peak ($CDCl_3$ at δ 7.26 ppm). Carbon chemical shifts are reported relative to $CDCl_3$ at δ 77.00 ppm. Phosphorus chemical shifts are reported relative to external 85% H_3PO_4 at δ 0.00 ppm.

Typical Procedure for the Synthesis of Biphenylphenylphosphine Oxide (1a). Magnesium turnings (0.267 g, 11.0 mmol) were suspended in THF (20 mL). A bead of iodine was added to the above mixture, and the mixture was stirred at room temperature until the color of iodine faded. To this mixture was added dropwise a solution of bromobiphenyl (2.33 g, 10.0 mmol) in THF (10 mL) over 5 min. The reaction mixture was stirred at 80 °C for 1 h and was then cooled to room temperature. To this Grignard reagent was added dropwise a solution of dichlorophenylphosphine (2.69 g, 15.0 mmol) in THF (7.5 mL) over 5 min. After the addition was completed, the mixture was stirred at 80 °C for 3 h and then cooled to 0 °C. To this solution was added ca. 2 mL of water, and the mixture was stirred at 0 °C for 10 min. To this solution was added ca. 4 mL of triethylamine, and the mixture was stirred at 0 °C for 10 min. The mixture was extracted with ethyl acetate (15 mL × 3), and the organic layer was dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The product was isolated by column chromatography on silica gel (ethyl acetate) to give **1a** (2.03 g, 73% yield).

Typical Procedure for the Synthesis of Dibenzophosphole Oxide (2a). A mixture of a secondary hydrophosphine oxide with a biphenyl group (**1a**; 41.7 mg, 0.150 mmol), THF (0.15 mL), and $Pd(OAc)_2$ (1.7 mg, 7.5 μmol) was stirred at 65 °C for 3 h in a sealed tube. The solvent was removed in vacuo, and the product was isolated by column chromatography on silica gel (ethyl acetate) to give **2a** (39.0 mg, 94% yield).

Data for biphenylphenylphosphine oxide (1a): 73%; colorless oil; purification, silica gel column chromatography (AcOEt); TLC (AcOEt) R_f = 0.38; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22−7.25 (m, 2H), 7.28−7.37 (m, 8H), 7.39−7.45 (m, 1H), 7.52 (tt, J = 7.6, 1.6 Hz, 1H), 7.61 (tt, J = 7.6, 1.6 Hz, 1H), 7.88 (d, J = 492.8 Hz, 1H), 7.96 (ddd, J = 13.9, 7.6, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.4 (d, J = 12.8 Hz), 127.8, 128.1, 128.3 (d, J = 12.8 Hz), 129.3, 130.3 (d, J = 127.7 Hz), 130.4 (d, J = 12.9 Hz), 130.6 (d, J = 9.1 Hz), 131.4 (d, J = 102.2 Hz), 131.8, 132.2, 132.7 (d, J = 9.1 Hz), 139.1 (d, J = 5.4 Hz), 145.9, (d, J = 9.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.1; IR (neat, ν/cm^{-1}) 3507, 3448, 3055, 2343, 1589, 1468, 1439, 1196, 1133, 1115, 945, 778, 750, 703, 694, 668; HRMS (EI$^+$) m/z calcd for $C_{18}H_{15}OP$ (M^+) 278.0861, found 278.0852.

Data for (4′-chlorobiphenyl)phenylphosphine oxide (1b): 64%; colorless oil; purification, silica gel column chromatography (AcOEt); TLC (AcOEt) R_f = 0.55; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 7.2 Hz, 2H), 7.29−7.35 (m, 5H), 7.42−7.48 (m, 1H), 7.54 (tt, J = 7.6, 1.6 Hz, 1H), 7.62 (tt, J = 7.6, 1.6 Hz, 1H), 7.88 (d, J = 419.2 Hz, 1H), 7.94 (ddd, J = 14.8, 7.6, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 127.8 (d, J = 12.8 Hz), 128.2, 128.4 (d, J = 12.8 Hz), 130.3 (d, J = 12.8 Hz), 130.4 (d, J = 100.4 Hz), 130.6 (d, J = 9.1 Hz), 130.7, 130.9 (d, J = 102.2 Hz), 132.0, 132.4, 132.9 (d, J = 12.8 Hz), 134.2, 137.6 (d, J = 3.6 Hz), 144.7, (d, J = 9.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.1; IR (neat, ν/cm^{-1}) 3509, 3455, 3055, 3015, 2336, 1591, 1570, 1558, 1495, 1464, 1437, 1396, 1198, 1134, 1115, 1088, 1018, 1005, 945, 831, 775, 741, 692; HRMS (EI$^+$) m/z calcd for $C_{18}H_{14}ClOP$ (M^+) 312.0471, found 312.0473.

Data for [4′-(trifluoromethyl)biphenyl]phenylphosphine oxide (1c): 68%; colorless oil; purification, silica gel column chromatography (AcOEt); TLC (AcOEt) R_f = 0.50; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21−7.35 (m, 7H), 7.39−7.45 (m, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.58 (tt, J = 7.6, 1.2 Hz, 1H), 7.65 (tt, J = 7.6, 1.6 Hz, 1H), 7.88 (d, J = 500.8 Hz, 1H), 7.98 (ddd, J = 14.8, 7.6, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 123.8 (q, J = 271 Hz), 124.8 (q, J = 3.6 Hz), 128.0 (d, J = 12.7 Hz), 128.2 (d, J = 12.8 Hz), 129.5 (q, J = 29.2 Hz), 129.7, 130.0 (d, J = 3.6 Hz), 130.1 (d, J = 10.9 Hz), 130.4 (d, J = 9.1 Hz), 131.0 (d, J = 10.9 Hz), 131.8 (d, J = 3.7 Hz), 132.4 (d, J = 3.7 Hz), 133.0 (d, J = 10.9 Hz), 142.7 (d, J = 3.6 Hz), 144.3 (d, J = 9.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.3; IR (neat, ν/cm^{-1}) 3519, 3449, 3059, 3016, 2994, 2339, 1618, 1590, 1563, 1484, 1471, 1439, 1404, 1322, 1256, 1206, 1106, 1067, 1045, 1021, 1007, 950, 844, 770, 744, 710, 693, 638, 611; HRMS (EI$^+$) m/z calcd for $C_{19}H_{14}F_3OP$ (M^+) 346.0734, found 346.0729.

Data for (4′-methoxybiphenyl)phenylphosphine oxide (1d): 70%; colorless oil; purification, silica gel column chromatography (AcOEt); TLC (AcOEt) R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.84 (d, J = 8.8 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.30−7.37 (m, 5H), 7.35−7.45 (m, 1H), 7.49 (td, J = 7.6, 1.6 Hz, 1H), 7.59 (tt, J = 7.4, 1.4 Hz, 1H), 7.91 (ddd, J = 14.0, 7.6, 0.8 Hz, 1H), 7.94 (d, J = 451.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.1, 113.4, 127.0, 128.1 (d, J = 12.8 Hz), 130.15, 130.19 (d, J = 107.7 Hz), 130.3 (d, J = 12.8 Hz), 130.6, (d, J = 9.1 Hz), 131.2 (d, J = 102.2 Hz), 131.4 (d, J = 5.4 Hz), 131.6, 132.1, 132.5, 145.6 (d, J = 10.9 Hz), 159.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.0; IR (neat, ν/cm^{-1}) 3523, 3459, 3055, 3013, 2961, 2937, 2837, 2349, 1609, 1590, 1576, 1516, 1464, 1456, 1436, 1302, 1248, 1934, 1182, 1133, 1115, 1035, 1017, 1000, 944, 835, 805, 768, 748, 707, 694; HRMS (EI$^+$) m/z calcd for $C_{19}H_{17}O_2P$ (M^+) 308.0966, found 308.0976.

Data for (3′-methylbiphenyl)phenylphosphine oxide (1e): 70%; colorless oil; purification, silica gel column chromatography (AcOEt); TLC (AcOEt) R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 6.92 (s, 1H), 7.05 (d, J = 7.6 Hz, 1H), 7.14, (d, J = 7.2 Hz, 1H), 7.21, (t, J = 7.6 Hz, 1H), 7.29−7.36 (m, 5H), 7.41−7.46 (m, 1H), 7.52 (td, J = 7.4, 1.6 Hz, 1H), 7.59 (td, J = 7.4, 1.4 Hz, 1H), 7.87 (d, J = 494.4 Hz, 1H),

7.89 (ddd, J = 13.6, 7.6, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 126.4, 127.4 (d, J = 12.8 Hz), 128.1, 128.3 (d, J = 12.9 Hz), 128.9, 129.9 (d, J = 104.0 Hz), 130.1, 130.46 (d, J = 10.9 Hz), 130.52, 130.6 (d, J = 104.0 Hz), 131.8 (d, J = 3.6 Hz), 132.2 (d, J = 3.6 Hz), 132.6 (d, J = 10.9 Hz), 137.9, 139.0 (d, J = 3.6 Hz), 146.0 (d, J = 10.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.4; IR (neat, ν/cm^{-1}) 3506, 3455, 3055, 2918, 2860, 2344, 1606, 1560, 1589, 1465, 1438, 1375, 1330, 1255, 1195, 1133, 1115, 1049, 943, 887, 860, 793, 764, 750, 707, 693; HRMS (EI$^+$) m/z calcd for $C_{19}H_{17}OP$ (M^+) 292.1017, found 292.1018.

Data for (2′-methoxybiphenyl)phenylphosphine oxide (1f, a mixture of two stereoisomers): 70%; colorless oil; purification, silica gel column chromatography (AcOEt); TLC (AcOEt) R_f = 0.28; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33 (s, 3H), 3.68 (s, 3H), 6.69 (d, J = 8.0 Hz, 1H), 6.82 (d, J = 4.4 Hz, 2H + 1H), 7.00 (t, J = 7.0 Hz, 1H), 7.11−7.40 (m, 7H + 7H), 7.41−7.47 (m, 1H), 7.50−7.56 (m, 1H + 1H), 7.59 (t, J = 7.4 Hz, 1H + 1H), 7.88 (d, J = 494.4 Hz, 1H), 7.90 (d, J = 494.4 Hz, 1H), 8.02 (dd, J = 12.0, 7.6 Hz, 1H), 8.11 (dd, J = 13.4, 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 54.7, 55.2, 110.4 (d, J = 18.2 Hz), 120.4 (d, J = 23.6 Hz), 127.6 (d, J = 12.7 Hz), 128.2 (d, J = 12.7 Hz), 129.8 (d, J = 12.7 Hz), 129.96 (d, J = 101.8 Hz), 130.04 (d, J = 10.9 Hz), 130.7 (d, J = 10.9 Hz), 131.1 (d, J = 9.0 Hz), 131.2 (d, J = 11.0 Hz), 131.6, 131.7 (d, J = 12.7 Hz), 131.9, 132.0 (d, J = 9.1 Hz), 132.2, 132.3 (d, J = 9.1 Hz), 132.8, 141.4 (d, J = 10.9 Hz), 141.9 (d, J = 9.1 Hz), 156.0 (d, J = 49.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.4, 20.2; IR (neat, ν/cm^{-1}) 3503, 3447, 3055, 3011, 2961, 2938, 2835, 2357, 1734, 1601, 1580, 1562, 1497, 1456, 1435, 1296, 1277, 1257, 1180, 1115, 1051, 1024, 1003, 939, 802, 768, 710, 692, 678, 617; HRMS (EI$^+$) m/z calcd for $C_{19}H_{17}O_2P$ (M^+) 308.0966, found 308.0976.

Data for [1,1′:4′,1″-terphenyl]-2-ylphenylphosphine oxide (1g): 92%; colorless oil; purification, silica gel column chromatography (hexane/AcOEt = 1/1); TLC (hexane/AcOEt = 1/1) R_f = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.45 (m, 9H), 7.46−7.56 (m, 5H), 7.58−7.66 (m, 3H), 8.00 (ddd, J = 14.4, 7.6, 1.2 Hz, 1H), 7.95 (d, J = 494.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.9, 127.1, 127.5, 127.57, 127.63, 128.3 (d, J = 12.7 Hz), 129.4 (d, J = 96.4 Hz, 2C), 130.5 (d, J = 12.8 Hz), 130.6 (d, J = 9.1 Hz), 131.9, 132.4, 132.9 (d, J = 10.9 Hz), 138.17, 138.23, 140.5, 140.8, 145.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.1; IR (neat, ν/cm^{-1}) 1762, 1718, 1670, 1589, 1439, 1190, 1132, 1115, 1076, 1045, 1007, 947, 843, 760, 750, 727, 694, 665; HRMS (EI$^+$) m/z calcd for $C_{24}H_{19}OP$ (M^+) 354.1174, found 354.1177.

Data for [2-(2-naphthalenyl)phenyl]phenylphosphine oxide (1h): 55%; white solid; purification, silica gel column chromatography (AcOEt); TLC (AcOEt) R_f = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28−7.30 (m, 4H), 7.36 (t, J = 7.8 Hz, 2H), 7.44 (t, J = 6.2 Hz, 1H), 7.52 (t, J = 4.0 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.67 (s, 1H), 7.73 (d, J = 8.4 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 6.8 Hz, 1H), 7.89 (d, J = 480.8 Hz, 1H), 8.02 (dd, J = 14.0, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 126.3 (d, J = 3.6 Hz), 126.8, 127.3 (d, J = 9.1 Hz), 127.7, 128.0, 128.1 (d, J = 12.8 Hz), 128.5 (2C), 130.1 (d, J = 12.8 Hz), 130.2 (d, J = 102.2 Hz), 130.5 (d, J = 3.6 Hz), 130.61, 130.62 (d, J = 12.8 Hz), 131.3 (d, J = 102.2 Hz), 131.6 (d, J = 3.6 Hz), 132.0 (d, J = 3.6 Hz), 132.4, 132.5 (d, J = 10.9 Hz), 136.3 (d, J = 5.4 Hz), 145.5 (d, J = 10.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.1; IR (neat, ν/cm^{-1}) 3501, 3445, 3053, 3015, 2959, 2926, 2851, 2351, 2335, 1964, 1823, 1587, 1562, 1557, 1504, 1479, 1435, 1362, 1230, 1188, 1130, 1115, 1086, 974, 858, 820, 729, 706, 692; HRMS (EI$^+$) m/z calcd for $C_{22}H_{17}OP$ (M^+) 328.1017, found 328.1020.

Data for isopropyl[2-(thiophene-3-yl)phenyl]phosphine oxide (1i): 51%; colorless oil; purification, silica gel column chromatography (AcOEt/methanol = 95/5); TLC (AcOEt/methanol = 95/5) R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (dd, J = 20.8, 7.2 Hz, 3H), 1.09 (dd, J = 17.2, 7.2 Hz, 3H), 1.61−1.72 (m, 1H), 7.11 (dd, J = 468.0, 4.4 Hz, 1H), 7.23 (dd, J = 4.8, 0.8 Hz, 1H), 7.41−7.46 (m, 2H), 7.48−7.54 (m, 2H), 7.57−7.62 (m, 1H), 7.86−7.93 (dd, J = 13.2, 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 15.6, 26.5 (d, J = 67.2 Hz), 124.6 (d, J = 3.7 Hz), 126.2 (d, J = 3.6 Hz), 127.5 (d, J = 10.9 Hz), 128.7, 129.0 (d, J = 91.3 Hz), 130.5 (d, J = 9.1 Hz), 132.0, 132.7 (d, J = 9.1 Hz), 134.3 (d, J = 5.5 Hz), 139.9 (d, J = 5.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.4; IR (neat, ν/cm^{-1}) 3499, 3445, 3061, 2963, 2930, 2868, 1589, 1564, 1531, 1464, 1435, 1387, 1364, 1260, 1182, 1128, 1096, 1061, 966, 934, 916, 880, 858, 820, 799, 762, 721, 683, 654; HRMS (EI$^+$) m/z calcd for $C_{13}H_{15}OPS$ (M^+) 250.0581, found 250.0591.

Data for biphenylisopropylphosphine oxide (1j): 81%; white solid; purification, silica gel column chromatography (AcOEt/methanol = 95/5); TLC (AcOEt) R_f = 0.10; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (dd, J = 20.2, 7.2 Hz, 3H), 1.02 (dd, J = 17.6, 7.2 Hz, 3H), 1.53−1.66 (m, 1H), 7.10 (dd, J = 469.6, 3.6 Hz, 1H), 7.35−7.48 (m, 6H), 7.54 (tt, J = 7.6, 1.6 Hz, 1H), 7.61 (tt, J = 7.6, 1.2 Hz, 1H), 7.97 (ddd, J = 12.8, 8.0, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 15.4, 26.8 (d, J = 69.4 Hz), 127.4 (d, J = 10.9 Hz), 128.0, 128.3, 128.5 (d, J = 89.5 Hz), 129.1, 130.4 (d, J = 9.1 Hz), 131.8, 132.4 (d, J = 9.1 Hz), 139.5 (d, J = 3.7 Hz), 145.0 (d, J = 10.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.1; IR (neat, ν/cm^{-1}) 3046, 2955, 2922, 2855, 1964, 1881, 1859, 1813, 1755, 1672, 1589, 1562, 1501, 1447, 1433, 1385, 1379, 1366, 1254, 1180, 1128, 1098, 1059, 1018, 976, 966, 935, 912, 893, 870, 783, 754, 745, 702; HRMS (EI$^+$) m/z calcd for $C_{15}H_{17}OP$ (M^+) 244.1017, found 244.1019.

Data for biphenyl-*tert*-butylphosphine oxide (1k): 11%; white solid; purification, silica gel column chromatography (AcOEt/methanol = 95/5); TLC (AcOEt) R_f = 0.09; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (d, J = 16.8 Hz, 9H), 7.00 (d, J = 471.6 Hz, 1H), 7.25−7.39 (m, 6H), 7.46 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.92 (dd, J = 11.0 Hz, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.6, 32.6 (d, J = 69.4 Hz), 127.2 (d, J = 10.9 Hz), 127.9, 128.2, 129.8, 130.8 (d, J = 9.1 Hz), 131.3 (d, J = 91.3 Hz), 131.8, 132.4 (d, J = 7.3 Hz), 139.8 (d, J = 3.6 Hz), 145.7 (d, J = 9.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.1; IR (neat, ν/cm^{-1}) 3055, 2953, 2924, 2853, 1587, 1558, 1462, 1427, 1377, 1366, 1261, 1207, 1165, 1121, 1096, 1047, 1030, 997, 955, 943, 918, 852, 814, 783, 766, 752, 741; HRMS (EI$^+$) m/z calcd for $C_{16}H_{19}OP$ (M^+) 258.1174, found 258.1183.

Data for biphenylisopropylphosphine oxide-d_5 (1j-*d*): 41%; white solid; purification, silica gel column chromatography (AcOEt/methanol = 95/5); TLC (AcOEt/methanol = 95/5) R_f = 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (dd, J = 20.2, 7.2 Hz, 3H), 1.02 (dd, J = 17.6, 7.2 Hz, 3H), 1.53−1.65 (m, 1H), 7.10 (dd, J = 470.2, 3.4 Hz, 1H), 7.38 (ddd, J = 7.4, 4.6, 0.8 Hz, 1H), 7.54 (tt, J = 7.4, 1.6 Hz, 1H), 7.61 (tt, J = 7.4, 1.4 Hz, 1H), 7.97 (ddd, J = 12.7, 7.5, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 15.5, 26.9 (d, J = 69.0 Hz), 127.5 (d, J = 10.9 Hz), 127.9 (t, J = 25.5 Hz), 128.0 (t, J = 25.0 Hz), 128.7 (t, J = 23.6 Hz), 130.5 (d, J = 9.1 Hz), 131.9, 132.5 (d, J = 9.1 Hz), 139.4 (d, J = 3.6 Hz), 145.1 (d, J = 10.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.8; IR (neat, ν/cm^{-1}) 3046, 2955, 2924, 2855, 1589, 1562, 1321, 1254, 1171, 1128, 1092, 1059, 1016, 976, 934, 872, 835, 781, 760, 692, 650, 606; HRMS (EI$^+$) m/z calcd for $C_{15}H_{12}D_5OP$ (M^+) 249.1326, found 249.1328.

Data for 2,2″-bis(phenylphosphine oxide)-*p*-terphenyl (3, a mixture of two stereoisomers): 52%; white solid; purification, silica gel column chromatography (AcOEt/methanol = 5/1); TLC (AcOEt/methanol = 5/1) R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (d, J = 7.2 Hz, 3H), 0.93 (d, J = 7.2 Hz, 3H), 1.07 (dd, J = 7.2, 3.2 Hz, 3H), 1.12 (dd, J = 7.2, 2.8 Hz, 3H), 1.67−1.82 (m, 2H), 7.01 (dd, J = 466.0, 1.6 Hz, 1H), 7.09 (dd, J = 466.0, 1.6 Hz, 1H), 7.43 (dd, J = 7.6, 4.8 Hz, 2H), 7.55 (s, 4H), 7.57 (t, J = 8.0 Hz, 2H), 7.64 (d, J = 7.2 Hz, 2H), 7.96 (dd, J = 13.2, 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.9, 15.6, 27.2 (d, J = 69.4 Hz), 127.8 (d, J = 10.9 Hz), 128.6 (d, J = 91.3 Hz), 129.5, 130.8 (d, J = 9.1 Hz), 132.1 (d, J = 3.6 Hz), 132.6, (d, J = 9.1 Hz), 139.6 (d, J = 3.6 Hz), 144.4 (d, J = 9.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.3, 39.5; IR (Nujol, ν/cm^{-1}) 3428, 2727, 2669, 2320, 1589, 1564, 1258, 1186, 1157, 1059, 920, 876, 847, 764, 746, 721, 681, 638;

HRMS (EI$^+$) m/z calcd for $C_{24}H_{28}O_2P_2$ (M^+) 410.1565, found 410.1555.

Data for 5-phenyl-5*H*-dibenzophosphole 5-oxide (2a): 94%; white solid; purification, silica gel column chromatography (AcOEt); TLC (AcOEt) R_f = 0.35; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.43 (m, 4H), 7.49 (td, J = 7.5, 1.6 Hz, 1H), 7.59 (td, J = 7.6, 1.2 Hz, 2H), 7.65 (dd, J = 12.8, 1.6 Hz, 1H), 7.67 (dd, J = 12.8, 1.2 Hz, 1H), 7.69−7.75 (m, 2H), 7.83 (dd, J = 7.6, 2.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.2 (d, J = 10.9 Hz), 128.7 (d, J = 12.8 Hz), 129.4 (d, J = 10.9 Hz), 129.9 (d, J = 9.0 Hz), 130.7 (d, J = 104.0 Hz), 131.0 (d, J = 10.9 Hz), 132.2, 132.7 (d, J = 105.8 Hz), 133.4, 141.7 (d, J = 21.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.0; IR (Nujol, ν/cm^{-1}) 1589, 1204, 1130, 764, 750, 725, 718, 698; HRMS (EI$^+$) m/z calcd for $C_{18}H_{13}OP$ (M^+) 276.0704, found 276.0712.

Data for 3-chloro-5-phenyl-5*H*-dibenzophosphole 5-oxide (2b): 90%; white solid; purification, silica gel column chromatography (AcOEt); TLC (AcOEt) R_f = 0.48; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.46 (m, 3H), 7.50−7.58 (m, 2H), 7.58−7.68 (m, 4H), 7.68−7.73 (m, 1H), 7.76 (dd, J = 8.2, 3.4 Hz, 1H), 7.80 (dd, 7.8, 3.0 Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.1 (d, J = 9.1 Hz), 122.3 (d, J = 10.9 Hz), 128.6 (d, J = 12.8 Hz), 129.4 (d, J = 10.9, 3.6 Hz), 129.6 (d, J = 9.1 Hz), 129.7 (d, J = 104.1 Hz), 130.7 (d, J = 10.9 Hz, 2C), 132.1 (d, J = 107.7 Hz), 132.2 (d, J = 3.6 Hz), 133.1, 133.4, 134.7 (d, J = 105.8 Hz), 135.1 (d, J = 14.6 Hz), 139.7 (d, J = 20.1 Hz), 140.5 (d, J = 21.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.5; IR (Nujol, ν/cm^{-1}) 1202, 1134, 1098, 885, 829, 772, 762, 727, 696; HRMS (EI$^+$) m/z calcd for $C_{18}H_{12}ClOP$ (M^+) 310.0314, found 310.0304.

Data for 3-(trifluoromethyl)-5-phenyl-5*H*-dibenzophosphole 5-oxide (2c): 86%; white solid; purification, silica gel column chromatography (AcOEt); TLC (AcOEt) R_f = 0.48; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (td, J = 7.6, 3.2 Hz, 2H), 7.48 (td, J = 7.4, 3.6 Hz, 1H), 7.54 (td, J = 7.6, 1.6 Hz, 1H), 7.62−7.70 (m, 3H), 7.76 (dd, J = 9.6, 7.6 Hz, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.90 (dd, J = 7.8, 3.0 Hz, 1H), 7.92−7.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.5 (d, J = 9.1 Hz), 121.9 (d, J = 10.9 Hz), 123.5 (q, J = 270.9 Hz), 126.6 (q, J = 3.7 Hz), 126.8 (q, J = 3.7 Hz), 128.9 (d, J = 12.7 Hz), 130.0, 130.1 (d, J = 9.1 Hz), 130.4 (d, J = 3.6 Hz), 130.5 (d, J = 10.9 Hz), 130.9 (d, J = 10.9 Hz, 2C), 131.3 (q, J = 32.8 Hz), 131.4 (d, J = 32.8 Hz), 133.2 (d, J = 114.5 Hz), 134.0 (d, J = 103.7 Hz), 140.3 (d, J = 21.8 Hz), 144.9 (d, J = 21.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.5; IR (Nujol, ν/cm^{-1}) 1568, 1335, 1261, 1194, 1132, 1086, 880, 851, 779, 721; HRMS (EI$^+$) m/z calcd for $C_{19}H_{12}F_3OP$ (M^+) 344.0578, found 344.0581.

Data for 3-methoxy-5-phenyl-5*H*-dibenzophosphole 5-oxide (2d): 93%; white solid; purification, silica gel column chromatography (AcOEt); TLC (AcOEt) R_f = 0.19; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (s, 3H), 7.10 (ddd, J = 8.4, 2.4, 0.8 Hz, 1H), 7.22 (dd, J = 11.0, 2.6 Hz, 1H), 7.31 (tdd, J = 7.6, 3.6, 0.8 Hz, 1H), 7.40 (td, J = 7.4, 3.2 Hz, 2H), 7.50 (td, J = 7.5, 1.6 Hz, 1H), 7.55 (tt, J = 7.6, 1.4 Hz, 1H), 7.63−7.70 (m, 3H), 7.72 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 8.4, 3.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.4, 119.7, 120.3 (d, J = 9.1 Hz), 113.8 (dd, J = 10.9, 3.7 Hz), 122.4 (d, J = 12.8 Hz), 128.1 (d, J = 10.9 Hz), 128.6 (d, J = 12.8 Hz), 129.6 (dd, J = 10.9, 3.6 Hz), 130.7 (d, J = 104.0 Hz), 130.8 (d, J = 10.9 Hz), 132.0 (d, J = 3.7 Hz), 132.1 (d, J = 107.7 Hz), 133.8, 134.2 (d, J = 21.9 Hz), 134.3 (d, J = 105.8 Hz), 141.8 (d, J = 20.1 Hz), 160.6 (d, J = 14.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.6; IR (Nujol, ν/cm^{-1}) 1591, 1576, 1569, 1333, 1298, 1275, 1257, 1198, 1132, 1109, 1057, 1036, 1026, 853, 837, 770, 729, 716; HRMS (EI$^+$) m/z calcd for $C_{19}H_{15}O_2P$ (M^+) 306.0810, found 306.0820.

Data for 2-methyl-5-phenyl-5*H*-dibenzophosphole 5-oxide (2e) and 4-methyl-5-phenyl-5*H*-dibenzophosphole 5-oxide (2e′): 93%; white solid; purification, silica gel column chromatography (AcOEt); TLC (AcOEt) R_f = 0.19; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H, **2e′**), 2.47 (s, 3H, **2e**), 7.20 (dd, J = 7.6, 2.8 Hz, 1H), 7.38 (td, J = 7.4, 3.2 Hz, 3H), 7.48 (t, J = 7.2 Hz, 1H), 7.55−7.73 (m, 6H), 7.81 (dd, J = 7.6, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 22.0, 118.5 (d, J = 10.9 Hz), 121.0 (d, J = 10.9 Hz), 121.1 (d, J = 10.9 Hz), 121.9 (d, J = 10.9 Hz), 127.8, 128.0, 128.7 (d, J = 12.7 Hz, mixture of regioisomers), 129.3 (d, J = 10.9 Hz), 129.7 (d, J = 9.1 Hz), 129.8 (d, J = 9.1 Hz), 129.94 (d, J = 9.1 Hz), 129.95 (d, J = 109.0 Hz), 130.1 (d, J = 127.2 Hz), 130.2 (d, J = 10.9 Hz), 130.3 (d, J = 10.9 Hz), 130.9 (d, J = 10.9 Hz), 131.0 (d, J = 10.9 Hz), 131.1, 131.2, 132.0 (d, J = 120.0 Hz), 132.6 (d, J = 120.0 Hz), 133.4, 133.5, 133.6, 133.7, 141.8 (d, J = 21.8 Hz), 141.9 (d, J = 21.8 Hz), 142.0 (d, J = 21.8 Hz), 142.1 (d, J = 21.8 Hz), 144.1 (mixture of regioisomers); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.6, 34.1; IR (Nujol, ν/cm^{-1}) 1603, 1203, 1186, 1136, 1111, 1090, 1065, 1022, 995, 959, 924, 885, 870, 853, 820, 775, 770, 752, 731, 721; HRMS (EI$^+$) m/z calcd for $C_{19}H_{15}OP$ (M^+) 290.0861, found 290.0847.

Data for 2-methyl-5-phenyl-5*H*-dibenzophosphole 5-oxide (2e): purification, recrystallization of a mixture of **2e** and **2e′** from 1,2-dichloromethane/hexane; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (s, 3H), 7.20 (dd, J = 7.6, 2.8 Hz, 1H), 7.38 (td, J = 7.4, 3.2 Hz, 3H), 7.48 (t, J = 7.2 Hz, 1H), 7.55−7.73 (m, 6H), 7.81 (dd, J = 7.6, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.0, 121.0 (d, J = 10.9 Hz), 121.9 (d, J = 9.1 Hz), 128.7 (d, J = 10.9 Hz), 129.3 (d, J = 12.8 Hz), 129.8 (d, J = 10.9 Hz), 129.9 (d, J = 10.9 Hz), 130.2 (d, J = 120.0 Hz), 130.3 (d, J = 10.9 Hz), 130.8 (d, J = 9.1 Hz), 131.9 (d, J = 10.9 Hz), 132.1 (d, J = 120.0 Hz), 132.6 (d, J = 120.0 Hz), 133.7 (d, J = 21.8 Hz), 141.8 (d, J = 21.8 Hz), 142.1 (d, J = 21.8 Hz), 144.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.1; IR (Nujol, ν/cm^{-1}) 1603, 1589, 1568, 1204, 1184, 1109, 1062, 818, 731, 696, 642; HRMS (EI$^+$) m/z calcd for $C_{19}H_{15}OP$ (M^+) 290.0861, found 290.0847.

Data for 1-methoxy-5-phenyl-5*H*-dibenzophosphole 5-oxide (2f): 93%; white solid; purification, silica gel column chromatography (AcOEt); TLC (AcOEt) R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (s, 3H), 7.13 (d, J = 8.0 Hz, 1H), 7.30−7.42 (m, 5H), 7.48 (td, J = 7.2, 1.6 Hz, 1H), 7.57 (tt, J = 7.8, 1.2 Hz, 1H), 7.64−7.74 (m, 3H), 8.41 (dd, J = 7.8, 3.0 Hz, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.3, 115.7, 121.3 (d, J = 9.1 Hz), 126.3 (d, J = 9.1 Hz), 128.1 (d, J = 12.9 Hz), 128.4 (d, J = 12.9 Hz), 128.9 (d, J = 25.5 Hz), 129.1 (d, J = 10.9 Hz), 130.5 (d, J = 12.8 Hz), 130.7 (d, J = 10.9 Hz), 130.8 (d, J = 102.2 Hz), 131.8, 132.0 (d, J = 105.8 Hz), 133.2, 134.6 (d, J = 104.0 Hz), 141.1 (d, J = 21.9 Hz), 156.6 (d, J = 12.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.5; IR (Nujol, ν/cm^{-1}) 1582, 1265, 1184, 1132, 1109, 1070, 1040, 997, 866, 789, 762, 748, 723, 708, 665; HRMS (EI$^+$) m/z calcd for $C_{19}H_{15}O_2P$ (M^+) 306.0810, found 306.0824.

Data for 3,5-diphenyl-5*H*-benzo[b]phosphindole 5-oxide (2g): 61%; white solid; purification, silica gel column chromatography (hexane/AcOEt = 1/2); TLC (hexane/AcOEt = 1/2) R_f = 0.40; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.55 (m, 7H), 7.58−7.66 (m, 3H), 7.68−7.76 (m, 3H), 7.81−7.96 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 121.2 (d, J = 10.9 Hz), 121.6 (d, J = 10.9 Hz), 126.9, 128.0, 128.5 (d, J = 9.1 Hz), 128.8 (d, J = 12.7 Hz, 2C), 128.9 (d, J = 95 Hz), 129.0, 129.4 (d, J = 10.9 Hz), 130.0 (d, J = 10.9 Hz), 131.1 (d, J = 11.0 Hz, 2C), 131.6 (d, J = 109 Hz), 131.7 (d, J = 109 Hz), 132.2 (d, J = 10.9 Hz, 2C), 133.5, 139.6, 142.5 (d, J = 10.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 34.4; IR (Nujol, ν/cm^{-1}) 1560, 1508, 1198, 1134, 1113, 908, 760, 733, 692, 665; HRMS (EI$^+$) m/z calcd for $C_{24}H_{17}OP$ (M^+) 352.1017, found 352.1019.

Data for 11-phenyl-11*H*-benzo[*a*]phosphafluorene 11-oxide (2h): 92%; white solid; purification, silica gel column chromatography (AcOEt); TLC (AcOEt) R_f = 0.35; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36−7.44 (m, 3H), 7.46−7.53 (m, 2H), 7.58 (td, J = 7.4, 1.2 Hz, 1H), 7.63−7.72 (m, 3H), 7.73−7.79 (m, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 8.01 (dd, J = 7.8, 3.0 Hz, 1H), 8.22−8.28 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 119.8 (d, J = 10.9 Hz), 121.3 (d, J = 9.1 Hz), 126.7, 128.2, 128.3, 128.4, 128.7 (d, J = 3.7 Hz), 129.1 (d, J = 10.9 Hz), 129.3 (d, J = 9.1 Hz), 129.4 (d, J = 9.1 Hz), 130.5 (d, J = 107.3 Hz), 130.7 (d, J = 10.9 Hz), 131.3, 131.7, 131.79 (d, J = 3.6 Hz), 131.80 (d, J = 118.2 Hz), 131.9 (d, J = 118.1 Hz), 135.4, 136.8 (d, J = 20.0 Hz),

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141.6 (d, J = 20.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.3; IR (Nujol, ν/cm^{-1}) 1589, 1566, 1223, 1196, 1132, 1111, 1055, 968, 889, 771, 723, 691, 635, 604; HRMS (EI$^+$) m/z calcd for $C_{22}H_{15}OP$ (M$^+$) 326.0861, found 326.0871.

Data for 8-isopropyl-8*H*-phosphindolo[2,3-*b*]thiophene 8-oxide (2i): 57%; white solid; purification, silica gel column chromatography (AcOEt/methanol = 95/5); TLC (AcOEt/methanol = 95/5) R_f = 0.25; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (dd, J = 18.4, 7.2 Hz, 3H), 1.24 (dd, J = 18.0, 7.2 Hz, 3H), 2.35 (dqq, J = 13.6, 7.2, 7.2 Hz, 1H), 7.30−7.36 (m, 1H), 7.37 (dd, J = 4.4, 1.2 Hz, 1H), 7.48−7.52 (m, 2H), 7.70−7.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 15.6, 28.8 (d, J = 74.6 Hz), 120.6 (d, J = 12.7 Hz), 121.3 (d, J = 9.1 Hz), 127.9 (d, J = 10.9 Hz), 129.4 (d, J = 101.8 Hz), 129.9 (d, J = 10.9 Hz), 132.9, 134.5 (d, J = 101.8 Hz), 137.7 (d, J = 3.7 Hz), 138.6 (d, J = 14.5 Hz), 153.6 (d, J = 21.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 46.6; IR (Nujol, ν/cm^{-1}) 3061, 1595, 1497, 1281, 1190, 1157, 1094, 1072, 1032, 881, 812, 745, 719, 677, 652, 638; HRMS (EI$^+$) m/z calcd for $C_{13}H_{13}OPS$ (M$^+$) 248.0425, found 248.0434.

Data for 4-isopropyl-4*H*-phosphindolo[2,3-*c*]thiophene 4-oxide (2i′): 25%; white solid; purification, silica gel column chromatography (AcOEt/methanol = 95/5); TLC (AcOEt/methanol = 95/5) R_f = 0.13; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (dd, J = 18.0, 7.2 Hz, 3H), 1.24 (dd, J = 18.0, 7.2 Hz, 3H), 2.33 (dqq, J = 14.0, 7.2, 7.2 Hz, 1H), 7.36 (dddd, J = 7.2, 7.2, 3.6, 0.8 Hz, 1H), 7.45 (dd, J = 2.0, 2.0 Hz, 1H), 7.54 (dddd, J = 7.6, 7.6, 1.2, 1.2 Hz, 1H), 7.62 (dd, J = 8.0, 3.2 Hz, 1H), 7.77 (dd, J = 8.4, 8.4 Hz, 1H), 7.83 (dd, J = 4.8, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.3, 15.5, 29.2 (d, J = 72.7 Hz), 116.5 (d, J = 12.7 Hz), 121.9 (d, J = 9.1 Hz), 128.2 (d, J = 10.9 Hz), 130.2 (d, J = 9.1 Hz), 130.8 (d, J = 11.0 Hz), 132.9, 133.7 (d, J = 99.9 Hz), 135.8 (d, J = 98.1 Hz), 138.6 (d, J = 12.7 Hz), 146.3 (d, J = 25.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.2; IR (Nujol, ν/cm^{-1}) 3049, 1595, 1344, 1263, 1258, 1121, 1182, 1126, 1086, 1063, 1032, 939, 885, 841, 777, 748, 718, 681, 662; HRMS (EI$^+$) m/z calcd for $C_{13}H_{13}OPS$ (M$^+$) 248.0425, found 248.0429.

Data for 5-isopropyl-5*H*-dibenzophosphole 5-oxide (2j): 94%; white solid; purification, silica gel column chromatography (AcOEt/methanol = 95/5); TLC (AcOEt) R_f = 0.09; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (d, J = 7.2 Hz, 3H), 1.16 (d, J = 7.2 Hz, 3H), 2.35 (sep, J = 7.2 Hz, 1H), 7.43 (td, J = 7.2, 3.6 Hz, 2H), 7.59 (t, J = 7.6 Hz, 2H), 7.79 (dd, J = 7.6, 2.0 Hz, 2H), 7.83 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 28.7 (d, J = 71.2 Hz), 121.0 (d, J = 9.1 Hz), 128.8 (d, J = 10.9 Hz), 129.5 (d, J = 7.3 Hz), 130.4 (d, J = 98.6 Hz), 133.0, 141.6 (d, J = 20.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 51.4; IR (Nujol, ν/cm^{-1}) 1597, 1258, 1182, 1080, 1030, 883, 758, 727, 709, 656, 619; HRMS (EI$^+$) m/z calcd for $C_{15}H_{15}OP$ (M$^+$) 242.0861, found 242.0871.

Data for 5-*tert*-butyl-5*H*-dibenzophosphole 5-oxide (2k): 85%; white solid; purification, silica gel column chromatography (AcOEt/methanol = 95/5); TLC (AcOEt/methanol = 95/5) R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (d, J = 15.6 Hz, 9H), 7.42 (tdd, J = 7.6, 3.6, 0.8 Hz, 2H), 7.58 (tt, J = 7.6, 1.2 Hz, 2H), 7.78 (dd, J = 7.6, 2.8 Hz, 2H), 7.84 (tt, J = 7.6, 0.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.8, 32.8 (d, J = 71.2 Hz), 121.0 (d, J = 9.1 Hz), 128,7 (d, J = 9.1 Hz), 130.1 (d, J = 7.2 Hz), 130.3 (d, J = 96.7 Hz), 133.0, 142.0 (d, J = 18.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 54.8; IR (Nujol, ν/cm^{-1}) 1593, 1572, 1267, 1213, 1180, 1163, 1123, 1082, 1067, 1013, 962, 941, 878, 818, 785, 758, 729, 715, 702; HRMS (EI$^+$) m/z calcd for $C_{16}H_{17}OP$ (M$^+$) 256.1017, found 256.1010.

Data for 5-isopropyl-5*H*-dibenzophosphole 5-oxide-d_5 (2j-*d*): 91%; white solid; purification, silica gel column chromatography (AcOEt/methanol = 95/5); TLC (AcOEt/methanol = 95/5) R_f = 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (d, J = 7.2 Hz, 3H), 1.16 (d, J = 7.2 Hz, 3H), 2.35 (dqq, J = 14.4, 7.2, 7.2 Hz, 1H), 7.42 (ddd, J = 7.2, 7.2, 3.2 Hz, 1H), 7.59 (ddd, J = 7.6, 7.6, 0.4 Hz, 1H), 7.77−7.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 28.7 (d, J = 69.1 Hz), 120.9, 121.1 (d, J = 9.1 Hz), 128.4 (td, J = 23.6, 9.0 Hz), 128.9 (d, J = 10.9 Hz), 129.3 (td, J = 23.6, 9.1 Hz), 129.7 (d, J = 9.1 Hz), 130.4 (d, J = 95.5 Hz), 130.5 (d, J = 96.4 Hz), 132.6 (t, J = 23.6 Hz), 133.1, 141.6 (d, J = 20.0 Hz), 141.7 (d, J = 20.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 51.8; IR (Nujol, ν/cm^{-1}) 1595, 1564, 1539, 1258, 1182, 1130, 1070, 883, 849, 772, 745, 727, 708, 650; HRMS (EI$^+$) m/z calcd for $C_{15}H_{11}D_4OP$ (M$^+$) 246.1108, found 246.1115.

Data for 6,12-diphenyl-6,12-diphosphaindeno[1,2-*b*]fluorine 6,12-dioxide (4, a mixture of two stereoisomers): 87%; white solid; purification, silica gel column chromatography (AcOEt/methanol = 5/1); TLC (AcOEt/methanol = 5/1) R_f = 0.48, 0.23; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06−1.28 (m, 12H), 2.35−2.53 (m, 2H), 7.50 (td, J = 7.6, 3.2 Hz, 2H), 7.60 (td, J = 7.4, 1.2 Hz, 2H), 7.86 (t, J = 7.8 Hz, 4H), 8.20−8.26 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 15.3, 15.4, 28.7 (d, J = 69.1 Hz), 28.8 (d, J = 70.9 Hz), 121.4 (d, J = 9.1 Hz), 121.5 (d, J = 10.9 Hz), 122.0 (d, J = 9.1 Hz), 122.1 (d, J = 10.9 Hz), 129.5 (d, J = 9.1 Hz, two stereoisomers), 129.9 (d, J = 9.1 Hz, two stereoisomers), 133.5 (two stereoisomers), 136.0 (d, J = 92.7 Hz), 136.6 (d, J = 92.7 Hz), 140.5 (d, J = 20.0 Hz), 140.6 (d, J = 20.0 Hz), 142.1 (d, J = 11.0 Hz), 142.28 (d, J = 10.9 Hz), 142.34 (d, J = 9.1 Hz), 142.5 (d, J = 9.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 50.8, 51.3; IR (Nujol, ν/cm^{-1}) 1732, 1593, 1298, 1254, 1184, 1157, 1130, 1092, 1074, 1024, 951, 926, 881, 777, 766, 748, 721, 700, 671, 629; HRMS (EI$^+$) m/z calcd for $C_{24}H_{24}O_2P_2$ (M$^+$) 406.1252, found 406.1245.

Data for 6,12-diphenyl-6,12-diphosphaindeno[1,2-*b*]fluorine 6,12-dioxide (4): purification, silica gel column chromatography (AcOEt/methanol = 5/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.12 (dd, J = 17.6, 7.2 Hz, 6H), 1.21 (dd, J = 17.6, 7.2 Hz, 6H), 2.46 (dqq, J = 14.8, 7.2, 7.2, 2H), 7.50 (ddd, J = 7.6, 7.6, 3.2 Hz, 2H), 7.65 (dd, J = 7.8, 7.8 Hz, 2H), 7.86 (m, 4H), 8.21 (dd, J = 8.8, 2.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.4, 15.5, 28.8 (d, J = 69.0 Hz), 121.6 (d, J = 9.1 Hz), 122.2 (dd, J = 10.9, 9.1 Hz), 129.7 (d, J = 10.9 Hz), 130.1 (d, J = 9.1 Hz), 133.7, 136.1 (d, J = 94.6 Hz), 140.7 (d, J = 20.0 Hz), 142.5 (d, J = 10.9 Hz), 142.7 (d, J = 10.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 51.4; IR (Nujol, ν/cm^{-1}) 1593, 1574, 1294, 1192, 1153, 1132, 1093, 1074, 1024, 953, 924, 880, 766, 748, 702, 671, 629; HRMS (EI$^+$) m/z calcd for $C_{24}H_{24}O_2P_2$ (M$^+$) 406.1252, found 406.1245.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C NMR spectra of biphenylphenylphosphine oxides **1** and dibenzophosphole oxides **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Makioka, Y.; Hayashi, T.; Tanaka, M. *Chem. Lett.* **2004**, *33*, 44–45. (b) Zhang, Z.; Li, J.; Huang, B.; Qin, J. *Chem. Lett.* **2006**, *35*, 958–959. (c) Chen, R.-F.; Zhu, R.; Fan, Q.-L.; Huang, W. *Org. Lett.* **2008**, *10*, 2913–2916.

(2) For reviews, see: Matano, Y.; Imahori, H. *Org. Biomol. Chem.* **2009**, *7*, 1258–1271.

(3) There have been several reports on the synthesis of dibenzophosphole oxides and their related compounds. Dithienophosphole oxides: Dienes, Y.; Eggenstein, M.; Kárpáti, T.; Sutherland, T. C.; Nyulászi, L.; Baumgartner, T. *Chem.—Eur. J.* **2008**, *14*, 9878–9889. Bis-phosphoryl-bridged stilbene:Fukazawa, A.; Hara, M.; Okamoto, T.; Son, E.-C.; Xu, C.; Tamao, K.; Yamaguchi, S. *Org. Lett.* **2008**, *10*, 913–916.

(4) (a) Bedford, A. F.; Heinekey, D. M.; Millar, I. T.; Mortimer, C. T. *J. Chem. Soc.* **1962**, 2982–2986. (b) Gladiali, S.; Dore, A.; Fabbri, D.; De Lucchi, O.; Valle, G. *J. Org. Chem.* **1994**, *59*, 6363–6371. (c) Baumgartner, T.; Newmann, T.; Wirges, B. *Angew. Chem., Int. Ed.* **2004**, *43*, 6197–6201. (d) Chen, R.-F.; Fan, Q.-L.; Zheng, C.; Huang, W. *Org. Lett.* **2006**, *8*, 203–205.

(5) (a) Campbell, I. G. M.; Way, J. K. *J. Chem. Soc.* **1961**, 2133–2141. (b) Durán, E.; Velasco, D.; López-Calahorra, F. *J. Chem. Soc., Perkin Trans. 1* **2000**, 591–594.

(6) Ogawa, S.; Tajiri, Y.; Furukawa, N. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 3182–3184.

(7) Ezzell, B. R.; Freedman, L. D. *J. Org. Chem.* **1969**, *34*, 1777–1780.

(8) Diaz, A. A.; Young, J. D.; Khan, M. A.; Wehmschulte, R. J. *Inorg. Chem.* **2006**, *45*, 5568–5575.

(9) (a) Haga, S.; Kobayashi, J.; Kawashima, T. Presented at the 89th Annual Meeting of the Chemical Society of Japan; Funabashi, Japan, March 30, 2009; Paper 4G5-09. (b) Furukawa, S.; Haga, S.; Kobayashi, J.; Kawashima, T. Presented at the 90th Annual Meeting of the Chemical Society of Japan; Higashi-Osaka, Japan, March 26, 2010; Paper 1E7-37.

(10) Palladium-catalyzed synthesis of benzo[*b*]thiophenes from thioenols. See: Inamoto, K.; Arai, Y.; Hiroya, K.; Doi, T. *Chem. Commun.* **2008**, 5529–5531.

(11) Palladium-catalyzed synthesis of carbazoles from 2-phenylacetanilides. See: Tsang, W. C. P.; Zheng, N.; Buchwald, S. L. *J. Am. Chem. Soc.* **2005**, *127*, 14560–14561.

(12) For some recent dehydrogenative reactions, see: (a) Li, Z.; Li, C.-J. *J. Am. Chem. Soc.* **2006**, *128*, 56–57. (b) Zhang, Y.; Li, C.-J. *J. Am. Chem. Soc.* **2006**, *128*, 4242–4243. (c) Zhang, Y.; Li, C.-J. *Angew. Chem., Int. Ed.* **2006**, *45*, 1949–1952. (d) Zweifel, T.; Naubron, J.-V.; Grützmacher, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 559–563. (e) Itazaki, M.; Ueda, K.; Nakazawa, H. *Angew. Chem., Int. Ed.* **2009**, *48*, 3313–3316. (f) Zhang, C.; Jiao, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 6174–6177. (g) Xie, J.; Huang, Z.-Z. *Angew. Chem., Int. Ed.* **2010**, *49*, 10181–10185. For an account and review, see: (h) Li, C.-J. *Acc. Chem. Res.* **2009**, *42*, 335–344. (i) Yeumg, C. S.; Dong, V. M. *Chem. Rev.* **2011**, *111*, 1215–1292.

(13) Investigation of several catalysts (5.0 mol %, dioxane, 150 °C, 24 h): Pd, 21%; Pd/C, 85%; Pd/$CaCO_3$, 12%; $Pd(PPh_3)_4$, 73%; $PdBr_2$, 41%; $PdCl_2$, 64%; $PdCl_2(PPh_3)_2$, 94%; $PdCl_2(PhCN)_2$, 84%; $Ni(OAc)_2 \cdot 4H_2O$, 32%; $Fe(OAc)_2$, 40%; $Cu(OAc)_2 \cdot H_2O$, 50%; $Cu(OAc)_2$, 38%; AgOAc, 7%; $Cr(CO)_6$, 6%; $Mo(CO)_6$, trace; $W(CO)_6$, trace; $Re_2(CO)_{10}$, 9%; $[ReBr(CO)_3(thf)]_2$, 5%; $RhCl(PPh_3)_3$, 17%; $Ru_3(CO)_{12}$, 10%.

(14) Investigation of catalytic amounts (THF, 65 °C, 3 h): 1.0 mol %, 47%; 3.0 mol %, 81%.

(15) Investigation of several solvents (50 °C, 4 h): neat, 6%; hexane, 15%; toluene, 28%; CH_2ClCH_2Cl, 22%; diethyl ether, 20%; THF, 52%; dioxane, 48%; DME, 48%; ethyl acetate, 29%; acetone, 47%; EtOH, 29%; CH_3CN, 40%; DMSO, 24%; DMF, 37%.

(16) At the reviewer's suggestion, we have added a catalytic amount of sodium pivalate or mesityl carboxylate to decrease the catalyst loading. However, the amount of the palladium catalyst could not be decreased by the addition of the pivalate or carboxylate.

(17) A blue-purple fluorescence was observed when 254 and 365 nm UV light was irradiated on a chloroform solution of **2a** or a solid sample of **2a**.

(18) In this reaction, a hydrogen acceptor, such as norbornene or 3,3-dimethyl-1-butene, was added to improve the yield of the dibenzophosphole oxide. However, the yield was not increased.

(19) There have been several reports on palladium-catalyzed transformations via P—H bond cleavage. See: (a) Han, L.-B.; Choi, N.; Tanaka, M. *Organometallics* **1996**, *15*, 3259–3261. (b) Han, L.-B.; Hua, R.; Tanaka, M. *Angew. Chem., Int. Ed.* **1998**, *37*, 94–96. (c) Han, L.-B.; Zhao, C.-Q.; Onozawa, S.-y.; Goto, M.; Tanaka, M. *J. Am. Chem. Soc.* **2002**, *124*, 3842–3843. (d) Butti, P.; Rochat, R.; Sadow, A. D.; Togni, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 4878–4881. For reviews, see: (e) Han, L.-B.; Tanaka, M. *Chem. Commun.* **1999**, 395–402. (f) Alonso, F.; Beletskaya, I. P.; Yus, M. *Chem. Rev.* **2004**, *104*, 3079–3159. (g) Greenberg, S.; Stephan, D. W. *Chem. Soc. Rev.* **2008**, *37*, 1482–1489.

(20) There have been several reports on palladium(II) acetate-catalyzed aromatic C—H bond activations. See: (a) Yoneyama, T.; Crabtree, R. H. *J. Mol. Catal. A* **1996**, *108*, 35–40. (b) Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 2300–2301. (c) Daugulis, O.; Zaitsev, V. G. *Angew. Chem., Int. Ed.* **2005**, *44*, 4046–4048. (d) Chen, X.; Li, J.-J.; Hao, X.-S.; Goodhue, C. E.; Yu, J.-Q. *J. Am. Chem. Soc.* **2006**, *128*, 78–79. (e) Thu, H.-Y.; Yu, W.-Y.; Che, C.-M. *J. Am. Chem. Soc.* **2006**, *128*, 9048–9049. (f) Shi, Z.; Li, B.; Wan, X.; Cheng, J.; Fang, Z.; Cao, B.; Qin, C.; Wang, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 5554–5558. (g) Jia, X.; Zhang, S.; Wang, W.; Luo, F.; Cheng, J. *Org. Lett.* **2009**, *11*, 3120–3123.

(21) The order of steps 1 and 2 could be reversed. In this case, C—H bond activation is promoted by the coordination of the oxygen atom or phosphorus atom of the phosphinous acid, which is formed by tautomerization of the phosphine oxide to the palladium center, and successive P—H bond activation occurs. For examples of metal—phosphinous acid compounds, see: (a) Ghaffar, T.; Parkins, A. W. *Tetrahedron Lett.* **1995**, *36*, 8657–8660. (b) Cobley, C. J.; van den Heuvel, M.; Abbadi, A.; de Vries, J. G. *Tetrahedron Lett.* **2000**, *41*, 2467–2470. (c) Li, G. Y. *Angew. Chem., Int. Ed.* **2001**, *40*, 1513–1516. (d) Bigeault, J.; Giordano, L.; Buono, G. *Angew. Chem., Int. Ed.* **2005**, *44*, 4753–4757.

(22) The second possible mechanism is as follows: (1) oxidative addition of a hydrophosphine oxide to a metal center (P—H bond activation); (2) sequential oxidative addition of the C—H bond of the aromatic ring to a metal center (C—H bond activation); (3) reductive elimination to give dibenzophosphole oxide **2** and dihydrogen and regeneration of the metal catalyst via dehydrogenation. In this mechanism, the catalytic cycle proceeds among Pd(0), Pd(II), and Pd(IV) species.

(23) The third possible pathway is an electrophilic reaction by palladium catalyst, $Pd(OAc)_2$, which functions as a Lewis acid. However, this possibility must be low because the reaction did not proceed well using the following Lewis acids (1,2-dichloroethane, 65 °C, 3 h): $Pd(OAc)_2$, 92%; $Sc(OTf)_3$, 0%; $FeCl_3$, trace; $AlCl_3$, trace; $In(OTf)_3$, trace; $InCl_3$, 7%.

(24) Ladder-type π-conjugated molecules with main group elements are important and useful as organic materials. See: (a) Fukazawa, A.; Yamaguchi, S. *Chem.—Asian J.* **2009**, *4*, 1386–1400. (b) Ren, Y.; Baumgartner, T. *J. Am. Chem. Soc.* **2011**, *133*, 1328–1340.

(25) The diastereomer ratios of **3** (60:40) and **4** (58:42) were almost the same.

(26) A blue-purple fluorescence was observed when 254 and 365 nm UV light was irradiated on a solid sample of **4**. In addition, a stronger blue-purple fluorescence was observed in the case of a chloroform solution of **4**.

(27) Li, C.-W.; Wang, C.-I.; Liao, H.-Y.; Chaudhuri, R.; Liu, R.-S. *J. Org. Chem.* **2007**, *72*, 9203–9207.

(28) Velian, A.; Lin, S.; Miller, A. J. M.; Day, M. W.; Agapie, T. *J. Am. Chem. Soc.* **2010**, *132*, 6296–6297.