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Comparison of 2-Arylnaphtho[2,3-*b*]phospholes and 2-Arylbenzo[*b*]phospholes: Effects of 2-Aryl Groups and Fused Arene Moieties on Their Optical and Photophysical Properties

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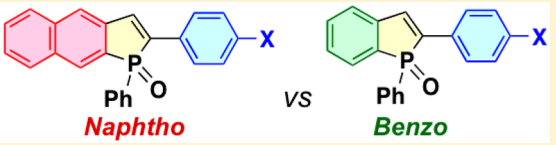
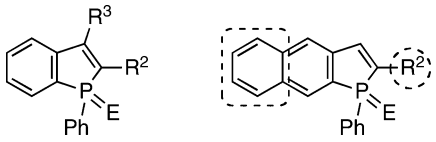
Supporting Information

ABSTRACT: Suzuki–Miyaura cross-coupling reactions were used in the divergent synthesis of a series of 2-arylnaphtho[2,3-*b*]phosphole *P*-oxides and their benzo[*b*]phosphole counterparts. We elucidated the electronic and steric effects of the 2-aryl groups and fused arene moieties on the optical and photophysical properties of these two types of phosphole-based π-systems.



Pi-conjugated phosphole derivatives are receiving attention as new phosphorus-containing materials for use in organic electronics.[1] 2-Aryl- and 2,3-diaryl-benzo[*b*]phospholes (Chart 1) have been extensively investigated because of their light-emitting and electron-transporting properties.[2−11] These intrinsic features of π-conjugated benzo[*b*]phospholes originate from rigid and coplanar π-frameworks bridged by a phosphorus atom. Furthermore, the fundamental properties of benzo[*b*]-phospholes can be finely tuned, like other phosphole-based π-systems, by chemical functionalizations at the phosphole ring carbons and phosphorus center. Several research groups have independently developed efficient methods for the introduction of aryl substituents at the 2- and 3-positions of a phosphole ring, using intramolecular cyclizations of 2-(arylethynyl)-phenylphosphine derivatives,[2−7] intermolecular cycloadditions of disubstituted acetylenes with phosphine derivatives,[8−10] and cross-coupling reactions of 2- or 3-bromobenzo[*b*]phosphole *P*-oxides.[7,11] Yoshikai et al. also established a highly modular approach that allowed for the regioselective functionalization of the fused benzene ring (benzo moiety) of the benzo[*b*]-phosphole skeleton.[10] However, to the best of our knowledge, little attention has been paid to replacing the benzo moiety by a polycyclic aromatic hydrocarbon (PAH).[12−14] Recently, Marinetti and co-workers reported photochemical and nickel-catalyzed annulation reactions of 5,6-substituted benzo[*b*]-phosphole derivatives for the synthesis of phosphorus-embedded [6]helicene structures.[14] We envisioned that naphtho[2,3-*b*]phosphole (Chart 1) would be a promising π-extended framework for the development of new phosphole-based fluorophores and semiconductors. Here, we report the first divergent synthesis of a series of 2-arylnaphtho[2,3-*b*]phosphole *P*-oxides and their benzo[*b*]phosphole counterparts using Suzuki–Miyaura cross-coupling reactions of the corresponding 2-bromoareno[*b*]phosphole *P*-oxides with arylboronic acids. The electronic and steric effects of the 2-aryl groups and fused-arene moieties on the optical and photophysical properties of these two types of π-systems will be compared.[15]

Chart 1. Benzo[*b*]phospholes (Left) and Naphtho[2,3-*b*]phospholes (Right)[a]



[a]R^2 = aryl; R^3 = H or aryl; E = O, S, lone pair, etc.

We have recently reported the syntheses of 2-heteroaryl-, 2-alkenyl-, and 2-alkynyl-benzo[*b*]phosphole π-systems,[11] using Stille, Heck, and Sonogashira reactions, respectively, of 2-bromobenzo[*b*]phosphole *P*-oxide.[16] 2-Bromonaphtho[2,3-*b*]-phosphole *P*-oxide **4** was chosen as a common precursor to use the same cross-coupling strategy for the synthesis of 2-arylnaphtho[2,3-*b*]phosphole derivatives. The precursor was prepared from 2-bromo-3-(trimethylsilylethynyl)naphthalene **1**[17] (Scheme 1). Treatment of **1** with diisobutylaluminum hydride (DIBAL-H) in THF followed by addition of *N*-bromosuccinimide (NBS) gave 2-bromo-3-[2-bromo-2-(trimethylsilyl)vinyl]naphthalene **2** as an inseparable mixture with 2-bromo-3-[2-(trimethylsilyl)vinyl]naphthalene. Lithiation of crude **2** with ca. 2 equiv of *n*BuLi, followed by sequential treatments with dichloro(phenyl)phosphine and hydrogen peroxide, afforded 2-(trimethylsilyl)naphtho[2,3-*b*]phosphole *P*-oxide **3**. Bromolysis of the C(sp^2)–Si bond of **3** with NBS produced bromide **4** as a colorless solid.

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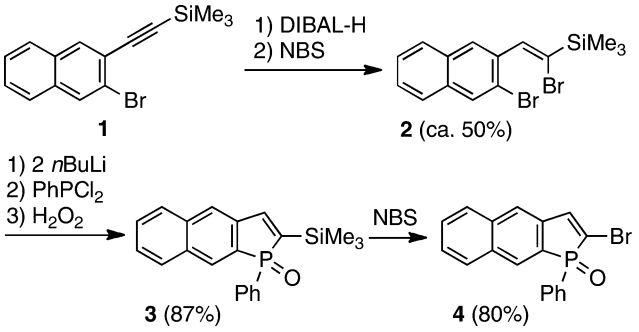
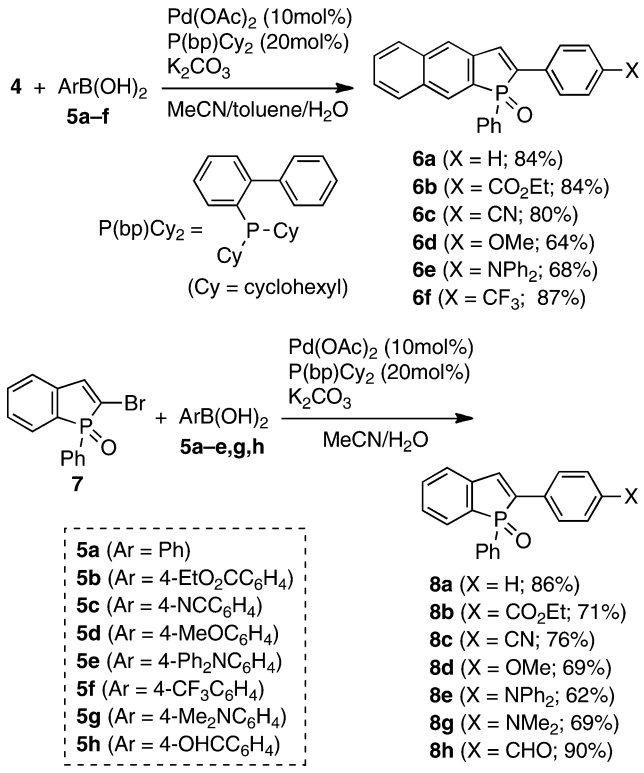
Scheme 1. Synthesis of Bromide 4



We first screened the reaction conditions for Suzuki–Miyaura cross-coupling of **4** with phenylboronic acid **5a** and found that the use of $Pd(OAc)_2$, 2-(dicyclohexylphosphino)-biphenyl [CyJohnPhos, denoted here by $P(bp)Cy_2$], and a mixed solvent system was effective for the desired C–C bond formation. The reaction of **4** with **5a** in the presence of catalytic amounts of $Pd(OAc)_2$ (10 mol %) and $P(bp)Cy_2$ (20 mol %) in acetonitrile–toluene–water (2:2:1 v/v/v) at 90 °C (bath temperature) for 1 h gave 2-phenylnaphtho[2,3-*b*]phosphole *P*-oxide **6a** in 84% isolated yield after silica-gel column chromatography (Scheme 2). Other bulky phosphine ligands

Scheme 2. Synthesis of 2-Arylnaphtho[2,3-*b*]phosphole *P*-Oxides 6 and 2-Arylbenzo[*b*]phosphole *P*-Oxides 8



such as DavePhos and XPhos (see Experimental Section for definitions) showed similar efficiencies in terms of the reaction time (1 h) and product yield (86–87%). When PPh_3 was used instead of $P(bp)Cy_2$, however, the reaction rate was slower, and **6a** was obtained in ca. 65% NMR yield after heating for 3 h.

With the $Pd(OAc)_2/P(bp)Cy_2$ catalyst in hand, we performed Suzuki–Miyaura cross-coupling reactions of **4** with *para*-substituted phenylboronic acids **5b–f** (Scheme 2). In all cases, C–C bond formation was complete within 1–2 h, affording the corresponding 2-arylnaphtho[2,3-*b*]phosphole *P*-oxides **6b–f** in 64–87% yields. The same catalyst also promoted Suzuki–Miyaura cross-coupling reactions of 2-bromobenzo[*b*]phosphole *P*-oxide **7** with arylboronic acids **5a–e,g,h**, affording 2-arylbenzo[*b*]phosphole *P*-oxides **8a–e,g,h** in 62–90% yields (Scheme 2).[18] A synthetic advantage of the present cross-coupling protocol is its high functional group tolerance; ethoxycarbonyl, cyano, and formyl groups were delivered from **5b,c,h** to final products **6b,c** and **8b,c,h**. Compounds **6** and **8** were characterized using conventional spectroscopic techniques. The ^{31}P NMR peaks of **6** and **8** appeared at δ_P 37.4–37.8 and 38.7–39.6 ppm, respectively. In the IR spectra of **6** and **8** in KBr pellets, the P=O stretching vibration bands were observed at 1192–1197 and 1182–1201 cm^{-1}, respectively. The structures of **6d** and **8c** were unambiguously elucidated by X-ray crystallography. As shown in Figure 1, the naphtho[2,3-*b*]phosphole and *p*-anisyl rings in

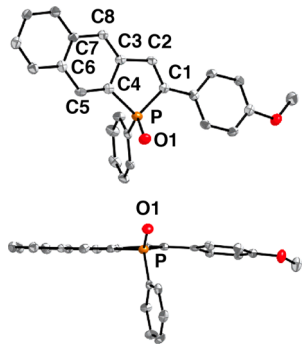


Figure 1. Crystal structure of **6d** (50% ellipsoids). Top view (left) and front view (right). Selected bond lengths (Å): P–C1, 1.814(3); P–C4, 1.819(2); P–O1, 1.487(2); C1–C2, 1.341(3); C2–C3, 1.466(3); C3–C4, 1.429(4); C3–C8, 1.370(3); C4–C5, 1.356(4); C5–C6, 1.439(3); C6–C7, 1.436(4); C7–C8, 1.426(3).

6d are almost coplanar (dihedral angle between the two mean planes = 10.0°), indicating that they are effectively π-conjugated. Benzo[*b*]phosphole **8c** also has a highly flat structure (Figure S1, Supporting Information) with a narrow dihedral angle of 7.4°. There are clear differences among the C–C bond lengths of the fused benzene ring of **6d**. The C3–C4/C5–C6/C6–C7/C7–C8 bond lengths [1.426(3)–1.439(3) Å] are appreciably longer than the C4–C5/C3–C8 bond lengths [1.356(4)–1.370(3) Å]. The average difference between the six contiguous C–C bond lengths of **6d** (0.05 Å) is greater than that of **8c** (0.02 Å), implying that the fused-arene moieties of **6** and **8** keep the intrinsic nature of the naphthalene and benzene rings, respectively.

We obtained UV/vis absorption and fluorescence spectra of **6** and **8** in CH_2Cl_2 to compare the electronic effects of the 2-aryl substituents on the optical properties of the naphtho[2,3-*b*]phosphole and benzo[*b*]phosphole *P*-oxides. Selected spectra are shown in Figure 2, and the absorption/emission maxima ($\lambda_{abs}/\lambda_{em}$) and fluorescence quantum yields (Φ_F) are summarized in Table 1.

As shown in Figure 2a, the absorption and fluorescence spectra of **6a–c** showed vibrational progressions derived from their rigid π-frameworks. In each series of **6** and **8**, electron-withdrawing substituents (CO_2Et, CN, CF_3, CHO) had small or negligible impacts on the spectral features, whereas electron-

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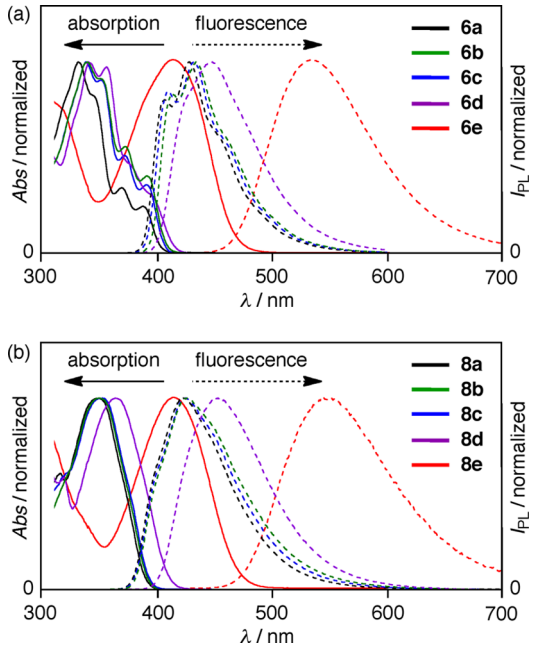

Figure 2. UV/vis absorption (solid line) and fluorescence spectra (dotted line, excited at the absorption maxima) of (a) **6a**–**e** and (b) **8a**–**e** in CH_2Cl_2.

Table 1. Optical and Photophysical Data of 6 and 8–10 in CH_2Cl_2

6/8	λ_{abs}/nm (log ε)	λ_{em}/nm[a] (Φ_F[b])	τ_F/ns[c]	k_r/s^{-1}	k_{nr}/s^{-1}
6a	331 (4.44), 387[d]	428 (0.37)	3.5	1.1×10^8	1.8×10^8
6b	338 (4.48), 390[d]	432 (0.54)	2.8	1.9×10^8	1.6×10^8
6c	339 (4.49), 391[d]	434 (0.54)	2.5	1.8×10^8	1.8×10^8
6d	340 (4.46), 395[d]	448 (0.46)	3.8	1.2×10^8	1.4×10^8
6e	414 (4.49)	533 (0.85)	4.7	1.8×10^8	3.2×10^7
6f	332 (4.45), 387[d]	425 (0.42)	3.0	1.4×10^8	1.9×10^8
8a[e]	350 (4.04)	423 (0.85)	7.2	1.2×10^8	2.1×10^7
8b	353 (4.12)	425 (0.82)	5.1	1.6×10^8	3.6×10^7
8c	350 (4.19)	426 (0.87)	4.8	1.8×10^8	2.7×10^7
8d[e]	365 (4.09)	454 (0.82)	6.4	1.3×10^8	2.8×10^7
8e	415 (4.29)	544 (0.81)	6.0	1.3×10^8	3.2×10^7
8g	413 (4.29)	536 (0.81)	6.1	1.3×10^8	3.1×10^7
8h	357 (4.21)	427 (0.056)			
9	344 (4.53), 378[d]	429 (0.035)			
10	323 (4.52), 387[d]	425 (<0.01)			

[a]Excited at λ_{abs}. [b]Absolute fluorescence quantum yields. [c]Excitation wavelengths are given in the Experimental Section. [d]Absorption maxima at the longest wavelength. [e]The optical data for **8a** and **8d** in THF were independently reported by Sanji et al. and Yamaguchi et al. in refs 6 and 7a, respectively.

donating substituents (OMe, NPh_2, NMe_2) caused moderate or large bathochromic shifts of the λ_{abs} and λ_{em} values relative to those of the *para*-unsubstituted references **6a** and **8a**. It is worth noting that the Ph_2N- and Me_2N-substituted derivatives **6e** and **8e**,**g** showed considerably broadened, structureless absorption and emission bands in the visible region. These spectral features suggest that **6e** and **8e**,**g** have large intramolecular charge transfer (CT) from the donor (Ph_2N or Me_2N) to the acceptor (arene-fused phosphole *P*-oxide) units.[19]

To compare the CT properties of these π-systems quantitatively, we measured the solvatochromism of **6e** and **8e** (Figure S2, Supporting Information) and analyzed the results using the Lippert–Mataga plots.[20] The $\lambda_{abs}/\lambda_{em}$ values of **6e** varied from 412/478 nm (in toluene) to 404/561 nm (in acetonitrile), and the Stokes shifts ($\Delta\nu = \nu_{abs} - \nu_{em}$) of **6e** greatly increased with increasing orientation polarizability (Δf) of the solvent. The same trend was observed for **8e**. As shown in Figure S3 in the Supporting Information, the Lippert–Mataga analyses gave linear solvation energy relationships (LSERs) versus the Δf values (R = 0.97 in each case). The LSERs of **6e** ($\Delta\nu/\Delta f = 1.15 \times 10^4$ cm^{-1}) and **8e** ($\Delta\nu/\Delta f = 1.20 \times 10^4$ cm^{-1}) are comparable, indicating that the highly electron-donating *para* substituent enhances the CT properties of the 2-arylnaphtho[2,3-*b*]phosphole and 2-arylbenzo[*b*]-phosphole π-systems to the same degree.

The first oxidation potentials of **6a** and **6e** in CH_2Cl_2 (with Bu_4NPF_6 as the supporting electrolyte) were determined to be E_{pa} = +1.34 and +0.49 V (vs ferrocene/ferrocenium), respectively (Figure S4, Supporting Information). The *para* substitution with the NPh_2 group induced a large cathodic shift of E_{pa}, reflecting its high electron-donating ability. To gain further insight into the electronic effects of the *para* substituents on the HOMO and LUMO characteristics of the 2-arylnaphtho[2,3-*b*]phosphole π-system, we performed density functional theory (DFT) calculations for **6a**,**e** at the B3LYP/6-31G* level. As shown in Figure S5 in the Supporting Information, the HOMO of **6a** is delocalized over the conjugated π-system, whereas that of **6e** is localized on the triphenylamine unit. The HOMO of **6e** is higher than that of **6a**, which qualitatively supports the observed result. In contrast, the LUMOs of **6a** and **6e** reside mainly on the naphtho[2,3-*b*]phosphole ring. These orbital characteristics imply that the HOMO-to-LUMO transition of **6e** has an intrinsic CT character.

Most of the naphtho[2,3-*b*]phosphole derivatives (**6a**–**d**,**f**) are moderately fluorescent, whereas **6e** and most of the benzo[*b*]phosphole derivatives (**8a**–**e**,**g**) are highly fluorescent. To compare the photophysical properties of these two fused π-systems, we measured the fluorescence lifetimes (τ_F) of **6a**–**f** and **8a**–**e**,**g** in CH_2Cl_2 at room temperature. The τ_F values of **6a**–**f** (2.5–4.7 ns) are appreciably shorter than those of **8a**–**e**,**g** (4.8–7.2 ns). The radiative and nonradiative decay rate constants (k_r and k_{nr}) calculated from the observed τ_F and Φ_F values are summarized in Table 1. In a series of the naphtho[2,3-*b*]phosphole π-systems, the k_{nr} value of **6e** is significantly smaller than those of the other derivatives, indicating that the exceptionally high Φ_F value (0.85) of **6e** stems from the relatively small k_{nr} value. It is apparent that the nonradiative dynamics of the excited CT state of **6e** is essentially different from that of the locally excited state of **6a**. The effects of the fused-arene moieties are also worth noting. The k_r values of **6a**–**d** ($1.1–1.9 \times 10^8$ s^{-1}) and **8a**–**d** ($1.2–1.8 \times 10^8$ s^{-1}) are comparable, whereas the k_{nr} values of **6a**–**d** ($1.4–1.8 \times 10^8$ s^{-1}) are considerably larger than those of **8a**–**d** ($2.1–3.6 \times 10^7$ s^{-1}). Furthermore, we tried to measure phosphorescence spectra of **6a** and **8a** in toluene at 77 K. Under these conditions, **6a** showed phosphorescence peaks at λ_{max} = 618 and 682 nm (Figure S6, Supporting Information), but **8a** did not. In these less or slightly polarized rigid π-systems, internal conversion from the excited singlet state to the ground state is probably slower than intersystem crossing (ISC) to the triplet state, i.e., the relatively large k_{nr} values of

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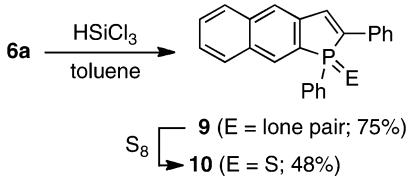
6a–**d** may indicate high efficiencies of the ISC processes of **6a**–**d** compared with those of **8a**–**d**.

Finally, we examined chemical functionalizations at the phosphorus center of **6a** (Scheme 3). Treatment of **6a** with an excess of $HSiCl_3$ in refluxing toluene gave the σ^3-phosphorus derivative **9**, which further reacted with S_8 in toluene to give *P*-sulfide **10**. Deoxygenation at the phosphorus center (from **6a** to **9**) shifts the longest λ_{abs} value hypsochromically, whereas replacement with a thioxo function (from **6a** to **10**) does not affect this value (Table 1). These chemical modifications significantly reduce the Φ_F values, although the reason for this is not clearly understood.

Scheme 3. Chemical Functionalizations of 6a



In summary, we have established a convenient method for the divergent synthesis of 2-arylnaphtho[2,3-*b*]phosphole *P*-oxides and their benzo[*b*]phosphole counterparts using Suzuki–Miyaura cross-coupling reactions of the corresponding 2-bromoareno[*b*]phosphole *P*-oxides. We have also shown that the optical and photophysical properties of the naphtho[2,3-*b*]- and benzo[*b*]phosphole π-systems can be finely tuned by changing the 2-aryl groups. It is worth noting that the *para*-R_2N-substituted derivatives (R = Ph, Me) behave as polarity-sensitive fluorophores because of the intrinsic CT character of their excited states. The large solvatochromism and high fluorescence quantum yields observed for these derivatives show that donor–acceptor naphtho[2,3-*b*]phospholes and benzo[*b*]phospholes would be promising π-frameworks for constructing medium-sensitivity fluorescent probes and sensors.[19] The construction of different types of PAH-fused phosphole derivatives for developing new phosphole-based optical and semiconducting materials is now in progress.

EXPERIMENTAL SECTION

General Remarks. All melting points were recorded on a micro melting point apparatus and are uncorrected. The identity and purity of prepared compounds were established by ^1H (400 or 700 MHz), ^{13}C (100 or 175 MHz), and ^{31}P (162 MHz) NMR spectroscopy and high-resolution mass (HRMS) spectrometry (electron spray–quadrupole). The chemical shifts are reported in ppm as relative values vs tetramethylsilane (^1H, ^{13}C) or H_3PO_4 (^{31}P). IR spectra were obtained using KBr pellets or neat films. UV/vis absorption, fluorescence, and phosphorescence spectra and absolute fluorescence quantum yields were obtained on the respective spectrometers. Electrochemical measurements were performed using a glassy carbon working electrode, a platinum wire counter electrode, and an Ag/Ag^+ [0.01 M $AgNO_3$, 0.1 M Bu_4NPF_6 (MeCN)] reference electrode. The potentials were calibrated with ferrocene/ferrocenium (Fc/Fc^+). Compounds **1**[17b] and **7**[11a] were prepared according to reported procedures. Other chemicals and solvents were of reagent grade and used without further purification unless otherwise noted. Thin-layer chromatography was performed with Kieselgel 60 F254, and preparative column chromatography was performed using Silica Gel 60 (spherical, neutrality). All reactions were performed under an argon atmosphere.

Synthesis of 2. To a solution of 2-bromo-3-(trimethylsilylethynyl)naphthalene **1** (2.2 g, 7.3 mmol) in THF (12 mL) was added diisobutylalminum hydride (DIBAL-H) (1 M, 9 mL, 9 mmol) at 0 °C, and the mixture was stirred for 18 h at room temperature. *N*-Bromosuccinimide (NBS) (2.0 g, 11 mmol) was then added at 0 °C, and the resulting mixture was stirred for 1 h at room temperature. After quenching with water at 0 °C, the mixture was passed through a Celite bed and the filtrate was separated. The aqueous layer was extracted with hexane, and the combined organic extracts were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure to leave an oily residue, which was subjected to silica-gel column chromatography (hexane/CH_2Cl_2 = 100:1). The fraction of R_f = 0.76 (hexane/CH_2Cl_2 = 100:1) was collected and evaporated to give an inseparable mixture of 2-bromo-3-[2-bromo-2-(trimethylsilyl)vinyl]naphthalene (**2**) (ca. 1.4 g, ca. 3.6 mmol, ca. 50% based on ^1H NMR) and (2-(3-bromonaphthalen-2-yl)vinyl)-trimethylsilane (ca. 1.4 mmol, ca. 19%). Compound **2** was characterized by only ^1H NMR spectroscopy. ^1H NMR (400 MHz, CD_2Cl_2) δ 0.34 (s, 9H), 7.44 (s, 1H), 7.48–7.52 (m, 2H), 7.72–7.86 (m, 2H), 8.10 (s, 1H), 8.23 (s, 1H).

Synthesis of 3. To a solution of crude **2** (ca. 1.4 g, ca. 3.6 mmol) in Et_2O (30 mL) was added *n*-BuLi (1.65 M, 7.25 mL, 12 mmol) at 0 °C, and the mixture was stirred for 2 h at room temperature, followed by addition of $PhPCl_2$ (0.80 mL, 5.9 mmol) at 0 °C. The resulting mixture was stirred for 14 h at room temperature, and an excess of aqueous H_2O_2 solution was then added to the mixture. After stirring for 30 min, a saturated aq. $NaHCO_3$ solution was added, and the separated aqueous layer was extracted with EtOAc, and the combined organic extracts were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was subjected to silica gel column chromatography (CH_2Cl_2/acetone/Et_3N = 100:10:1). The violet fluorescent fraction of R_f = 0.54 (CH_2Cl_2/acetone = 10:1) was collected, evaporated, and reprecipitated from hexane to give 2-(trimethylsilyl)-1-phenylnaphtho[2,3-*b*]phosphole 1-oxide (**3**) as a pale yellow solid (1.1 g, 3.2 mmol, 87%). mp 177–179 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 0.13 (s, 9H), 7.38–7.41 (m, 2H), 7.47–7.51 (m, 2H), 7.54–7.57 (m, 1H), 7.68 (d, 1H, J_{HP} = 44.1 Hz), 7.67–7.70 (m, 2H), 7.73 (d, 1H, J_{HP} = 2.8 Hz), 7.79 (d, 1H, J = 7.7 Hz), 7.86 (d, 1H, J = 8.4 Hz) 8.07 (d, 1H, J_{HP} = 9.8 Hz); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ −1.1 (d, J_{CP} = 1.5 Hz), 123.4 (d, J_{CP} = 9.7 Hz), 127.3, 128.3, 128.5 (d, J_{CP} = 11.9 Hz), 128.8, 129.3, 130.5 (d, J_{CP} = 9.7 Hz), 130.9 (d, J_{CP} = 11.1 Hz), 131.1 (d, J_{CP} = 98.2 Hz), 131.8 (d, J_{CP} = 2.9 Hz), 132.6 (d, J_{CP} = 102.7 Hz), 133.5 (d, J_{CP} = 11.1 Hz), 135.4 (d, J_{CP} = 2.2 Hz), 139.5 (d, J_{CP} = 37.9 Hz), 142.4 (d, J_{CP} = 59.5 Hz), 152.2 (d, J_{CP} = 6.7 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 47.2; IR (neat) ν 1191 (P═O) cm^{-1}; HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{21}H_{22}OPSi$, 349.1172; found, 349.1168.

Synthesis of 4. To a solution of **3** (1.1 g, 3.2 mmol) in MeCN (30 mL) was added NBS (1.1 g, 6.1 mmol) at 0 °C, and the mixture was stirred for 15 h at room temperature. Water was then added to the mixture, the separated aqueous layer was extracted with CH_2Cl_2, and the combined organic extracts were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was reprecipitated from acetone to give 2-bromo-1-phenylnaphtho[2,3-*b*]phosphole 1-oxide **4** as a colorless solid (0.89 g, 2.5 mmol, 80%). mp 284–286 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 7.44–7.49 (m, 2H), 7.52–7.62 (m, 3H), 7.64 (d, 1H, J_{HP} = 28.7 Hz), 7.71 (d, 1H, J_{HP} = 3.5 Hz), 7.73–7.78 (m, 2H), 7.82 (d, 1H, J = 7.7 Hz), 7.87 (d, 1H, J = 7.7 Hz), 8.12 (d, 1H, J_{HP} = 11.9 Hz); $^{13}C\{^1H\}$ NMR (175 MHz, $CDCl_3$) δ 122.4 (d, J_{CP} = 99.9 Hz), 123.3 (d, J_{CP} = 9.3 Hz), 127.6, 127.7 (d, J_{CP} = 108.0 Hz), 128.4 (d, J_{CP} = 107.8 Hz), 128.7, 128.9 (d, J_{CP} = 13.0 Hz), 129.1, 129.4, 131.4 (d, J_{CP} = 11.0 Hz), 132.0 (d, J_{CP} = 10.0 Hz), 132.88 (d, J_{CP} = 12.4 Hz), 132.94 (d, J_{CP} = 2.6 Hz), 135.4 (d, J_{CP} = 1.2 Hz), 137.5 (d, J_{CP} = 24.8 Hz), 144.1 (d, J_{CP} = 21.5 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 33.2; IR (neat) ν 1207 (P═O) cm^{-1}; HRMS (ESI) *m*/*z*: $[M + H]^+$ calcd for $C_{18}H_{13}BrOP$, 354.9882; found, 354.9868.

General Procedure for the Synthesis of 6. A mixture of **4** (41 mg, 0.12 mmol), phenylboronic acid **5** (0.28 mmol), (2-biphenyl)-dicyclohexylphosphine [CyJohnPhos] (8.6 mg, 24 μmol), $Pd(OAc)_2$ (2.7 mg, 12 μmol), K_2CO_3 (52 mg, 0.38 mmol), MeCN (2 mL), toluene (2 mL), and H_2O (1 mL) was heated at 90 °C (bath

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temperature) for 2 h. The mixture was diluted with water, and the aqueous layer was separated and then extracted with CH_2Cl_2. The combined organic extracts were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was subjected to silica-gel column chromatography (CH_2Cl_2/acetone/Et_3N = 100:10:1). The fluorescent fraction was collected and reprecipitated from hexane to give **6** as a solid. Other bulky phosphine ligands such as DavePhos (2-dimethylamino-2′-dicyclohexylphosphinobiphenyl) and XPhos (2-dicyclohexylphosphino-2′,4′,6′-triisopropylbiphenyl) were also effective for the present Suzuki−Miyaura cross-coupling reactions.

*1,2-Diphenylnaphtho[2,3-b]phosphole 1-Oxide (**6a**).* R_f = 0.74 (CH_2Cl_2/acetone = 10:1); mp 267−268 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.29 (t, 1H, J = 7.7 Hz), 7.34 (t, 2H, J = 7.7 Hz), 7.38−7.40 (m, 2H), 7.46−7.51 (m, 2H), 7.56−7.59 (m, 1H), 7.75 (d, 2H, J = 7.7 Hz), 7.78−7.80 (m, 2H), 7.78 (d, 1H, J_{HP} = 35.0 Hz), 7.81 (d, 2H, J = 7.0 Hz), 7.86 (d, 1H, J = 7.7 Hz), 8.11 (d, 1H, J_{HP} = 11.2 Hz); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 123.7 (d, J_{CP} = 9.3 Hz), 126.6 (d, J_{CP} = 6.5 Hz), 127.2, 128.6 (d, J_{CP} = 1.9 Hz), 128.86 (d, J_{CP} = 12.4 Hz), 128.87, 128.94, 129.3, 130.6 (d, J_{CP} = 99.4 Hz), 130.86 (d, J_{CP} = 109.2 Hz), 130.87, 130.93, 131.1 (d, J_{CP} = 10.3 Hz), 132.2 (d, J_{CP} = 2.6 Hz), 132.7 (d, J_{CP} = 9.8 Hz), 133.2 (d, J_{CP} = 11.9 Hz), 135.7 (d, J_{CP} = 1.2 Hz), 137.5 (d, J_{CP} = 18.4 Hz), 137.7 (d, J_{CP} = 28.2 Hz), 139.4 (d, J_{CP} = 94.3 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.7; IR (KBr) ν 1195 (P═O) cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{24}H_{18}OP$, 353.1090; found, 353.1079.

*2-(4-Ethoxycarbonylphenyl)-1-phenylnaphtho[2,3-b]phosphole 1-Oxide (**6b**).* R_f = 0.64 (CH_2Cl_2/acetone = 10:1); mp 248−250 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 1.37 (t, 3H, J = 7.7 Hz), 4.33−4.37 (m, 2H), 7.38−7.41 (m, 2H), 7.47−7.50 (m, 1H), 7.52 (t, 1H, J = 7.7 Hz), 7.59 (t, 1H, J = 7.7 Hz), 7.76−7.80 (m, 2H), 7.82 (d, 1H, J = 8.4 Hz), 7.83−7.85 (m, 2H), 7.84 (d, 1H, J = 3.5 Hz), 7.86 (d, 1H, J_{HP} = 35.0 Hz), 7.89 (d, 1H, J = 8.4 Hz), 8.00 (d, 2H, J = 8.4 Hz), 8.13 (d, 1H, J_{HP} = 11.2 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.3, 61.1, 124.4 (d, J_{CP} = 8.4 Hz), 126.4 (d, J_{CP} = 5.8 Hz), 127.5, 128.7 (d, J_{CP} = 3.3 Hz), 128.9 (d, J_{CP} = 13.5 Hz), 129.4, 130.11 (d, J_{CP} = 100.1 Hz), 130.12, 130.4, 130.6 (d, J_{CP} = 109.2 Hz), 130.8, 130.9, 131.2 (d, J_{CP} = 10.5 Hz), 132.4 (d, J_{CP} = 2.6 Hz), 133.4 (d, J_{CP} = 11.7 Hz), 135.6 (d, J_{CP} = 1.2 Hz), 137.0 (d, J_{CP} = 9.8 Hz), 137.3 (d, J_{CP} = 28.0 Hz), 138.6 (d, J_{CP} = 94.9 Hz), 139.3 (d, J_{CP} = 17.8 Hz), 166.1; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.5; IR (KBr) ν 1709 (C═O), 1194 (P═O) cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{27}H_{22}O_3P$, 425.1301; found, 425.1293.

*2-(4-Cyanophenyl)-1-phenylnaphtho[2,3-b]phosphole 1-Oxide (**6c**).* R_f = 0.58 (CH_2Cl_2/acetone = 10:1); mp > 300 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.39−7.42 (m, 2H), 7.49−7.52 (m, 1H), 7.53−7.56 (m, 1H), 7.59−7.62 (m, 2H), 7.62 (d, 1H, J = 8.4 Hz), 7.74−7.78 (m, 2H), 7.83−7.86 (m, 3H), 7.87 (d, 1H, J_{HP} = 2.8 Hz), 7.87 (d, 1H, J_{HP} = 32.9 Hz), 7.90 (d, 1H, J = 8.4 Hz), 8.14 (d, 1H, J_{H-P} = 11.2 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 111.9, 118.9, 124.9 (d, J_{CP} = 8.9 Hz), 127.0 (d, J_{CP} = 6.7 Hz), 127.8, 128.8, 128.9, 129.0 (d, J_{CP} = 12.6 Hz), 129.4, 129.7 (d, J_{CP} = 101.2 Hz), 130.3 (d, J_{CP} = 110.1 Hz), 130.8 (d, J_{CP} = 11.1 Hz), 131.4 (d, J_{CP} = 10.4 Hz), 132.6 (d, J_{CP} = 3.0 Hz), 132.7, 133.5 (d, J_{CP} = 11.9 Hz), 135.6, 136.9 (d, J_{CP} = 28.3 Hz), 137.2 (d, J_{CP} = 10.4 Hz), 137.7 (d, J_{CP} = 94.5 Hz), 140.3 (d, J_{CP} = 17.9 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.3; IR (KBr) ν 2227 (CN), 1193 (P═O) cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{25}H_{17}NOP$, 378.1042; found, 378.1031.

*2-(4-Methoxyphenyl)-1-phenylnaphtho[2,3-b]phosphole 1-Oxide (**6d**).* R_f = 0.58 (CH_2Cl_2/acetone = 10:1); mp 288−289 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 6.86 (d, 2H, J = 8.4 Hz), 7.36−7.41 (m, 2H), 7.45−7.50 (m, 2H), 7.53−7.58 (m, 1H), 7.65 (d, 1H, J_{HP} = 35.6 Hz), 7.69−7.71 (m, 2H), 7.74 (d, 1H, J_{HP} = 3.2 Hz), 7.76−7.82 (m, 3H), 7.84 (d, 1H, J = 8.4 Hz), 8.08 (d, 1H, J_{HP} = 10.8 Hz); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 55.3, 114.4, 123.0 (d, J_{CP} = 8.4 Hz), 125.3 (d, J_{CP} = 10.5 Hz), 126.9, 128.1 (d, J_{CP} = 6.5 Hz), 128.4 (d, J_{CP} = 9.8 Hz), 128.8 (d, J_{CP} = 12.4 Hz), 129.3, 130.75 (d, J_{CP} = 99.4 Hz), 130.77 (d, J_{CP} = 109.2 Hz), 130.8, 130.89 (d, J_{CP} = 9.8 Hz), 130.90, 132.1 (d, J_{CP} = 2.6 Hz), 133.0 (d, J_{CP} = 11.7 Hz), 135.2 (d, J_{CP} = 19.1 Hz), 135.8 (d, J_{CP} = 1.9 Hz), 138.0 (d, J_{CP} = 28.7 Hz), 138.9 (d, J_{CP} = 94.1 Hz), 160.1; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.8; IR (KBr) ν 1195 (P═O) cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{25}H_{20}O_2P$, 383.1195; found, 383.1188.

*2-(4-(Diphenylamino)phenyl)-1-phenylnaphtho[2,3-b]phosphole 1-Oxide (**6e**).* R_f = 0.65 (CH_2Cl_2/acetone = 10:1); mp 147 °C (dec.); ^{1}H NMR (700 MHz, $CDCl_3$) δ 6.97 (d, 2H, J = 8.4 Hz), 7.05 (t, 2H, J = 7.7 Hz), 7.07−7.09 (m, 4H), 7.24−7.26 (m, 4H), 7.39−7.42 (m, 2H), 7.45−7.51 (m, 2H), 7.53−7.57 (m, 3H), 7.65 (d, 1H, J_{HP} = 35.7 Hz), 7.73 (d, 1H, J_{HP} = 3.5 Hz), 7.79 (d, 1H, J = 11.2 Hz), 7.80−7.83 (m, 2H), 7.84 (d, 1H, J = 7.7 Hz), 8.06 (d, 1H, J_{HP} = 11.2 Hz); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 122.5, 123.0 (d, J_{CP} = 8.6 Hz), 123.6, 125.0, 125.8 (d, J_{CP} = 10.5 Hz), 126.9, 127.6 (d, J_{CP} = 6.5 Hz), 128.4 (d, J_{CP} = 14.3 Hz), 128.9 (d, J_{CP} = 12.4 Hz), 129.30, 129.33, 130.86 (d, J_{CP} = 109.2 Hz), 130.88 (d, J_{CP} = 9.8 Hz), 130.90 (d, J_{CP} = 99.4 Hz), 130.90, 131.0, 132.1 (d, J_{CP} = 2.6 Hz), 133.0 (d, J_{CP} = 11.7 Hz), 134.9 (d, J_{CP} = 18.2 Hz), 135.8 (d, J_{CP} = 1.2 Hz), 138.1 (d, J_{CP} = 28.7 Hz), 139.0 (d, J_{CP} = 94.1 Hz), 147.1, 148.4; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.6; IR (KBr) ν 1194 (P═O) cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{36}H_{27}NOP$, 520.1825; found, 520.1805.

*2-(4-(Trifluoro)phenyl)-1-phenylnaphtho[2,3-b]phosphole 1-Oxide (**6f**).* R_f = 0.72 (CH_2Cl_2/acetone = 10:1); mp 255−257 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.39−7.42 (m, 2H), 7.49−7.54 (m, 2H), 7.58−7.61 (m, 3H), 7.76−7.79 (m, 2H), 7.83 (d, 1H, J = 7.7 Hz), 7.85 (d, 1H, J_{HP} = 35.0 Hz), 7.85−7.87 (m, 3H), 7.89 (d, 1H, J = 9.1 Hz), 8.14 (d, 1H, J_{HP} = 11.2 Hz); ^{13}C{^{1}H} NMR (175 MHz, $CDCl_3$) δ 123.9 (quart, J_{CF} = 270.7 Hz), 124.5 (d, J_{CP} = 9.3 Hz), 125.9 (quart, J_{CF} = 3.9 Hz), 126.8 (d, J_{CP} = 6.0 Hz), 127.6, 128.7, 128.8, 129.0 (d, J_{CP} = 12.4 Hz), 129.4, 129.9 (d, J_{CP} = 85.7 Hz), 130.4 (quart, J_{CF} = 32.0 Hz), 130.5 (d, J_{CP} = 94.8 Hz), 130.9 (d, J_{CP} = 11.0 Hz), 131.3 (d, J_{CP} = 10.3 Hz), 132.5 (d, J_{CP} = 2.1 Hz), 133.5 (d, J_{CP} = 12.4 Hz), 135.6 (d, J_{CP} = 1.4 Hz), 136.2 (d, J_{CP} = 9.3 Hz), 137.2 (d, J_{CP} = 28.0 Hz), 138.1 (d, J_{CP} = 95.5 Hz), 139.6 (d, J_{CP} = 17.7 Hz); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 37.4; IR (KBr) ν 1192 (P═O) cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{25}H_{17}F_3OP$, 421.0964; found, 421.0941.

General Procedure for the Synthesis of 8. A mixture of 7 (0.11 g, 0.36 mmol), phenylboronic acid **5a** (92 mg, 0.59 mmol), (2-biphenyl)dicyclohexylphosphine (26 mg, 75 μmol), $Pd(OAc)_2$ (8.1 mg, 36 μmol), K_2CO_3 (0.21 g, 1.5 mmol), MeCN (3 mL), and H_2O (3 mL) was heated at 90 °C (bath temperature) for 1−3 h. The mixture was diluted with water, and the aqueous layer was separated and then extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was subjected to silica-gel column chromatography (CH_2Cl_2/acetone = 20:1). The fluorescent fraction was collected and reprecipitated from hexane to give **8** as a solid.

*1,2-Diphenylbenzo[b]phosphole 1-oxide (**8a**).*[6,7a,10] R_f = 0.42 (CH_2Cl_2/acetone =20:1); mp 173−175 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27−7.44 (m, 7H), 7.45−7.54 (m, 2H), 7.60 (d, 1H, J_{HP} = 35.6 Hz), 7.60−7.65 (m, 1H), 7.68−7.71 (m, 2H), 7.73−7.79 (m, 2H); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 39.1; IR (neat) ν 1201 (P═O) cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{20}H_{16}OP$, 303.0933; found, 303.0919.

*2-(4-Ethoxycarbonylphenyl)-1-phenylbenzo[b]phosphole 1-Oxide (**8b**).* R_f = 0.30 (CH_2Cl_2/acetone = 20:1); mp 161−163 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (t, 3H, J = 7.2 Hz), 4.34 (q, 2H, J = 7.2 Hz), 7.35−7.56 (m, 6H), 7.62−7.67 (m, 1H), 7.70 (d, 1H, J_{HP} = 36.0 Hz), 7.70−7.78 (m, 4H), 7.98 (d, 2H, J = 8.0 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 14.3, 61.0, 125.0 (d, J_{CP} = 8.9 Hz), 126.4 (d, J_{CP} = 6.0 Hz), 129.0 (d, J_{CP} = 12.6 Hz), 129.2 (d, J_{CP} = 10.4 Hz), 129.6 (d, J_{CP} = 10.4 Hz), 130.1, 130.31 (d, J_{CP} = 83.3 Hz), 130.33, 130.6, 132.4 (d, J_{CP} = 3.0 Hz), 132.7 (d, J_{CP} = 108.6 Hz), 133.3 (d, J_{CP} = 2.2 Hz), 136.7 (d, J_{CP} = 10.4 Hz), 138.3 (d, J_{CP} = 94.5 Hz), 138.4 (d, J_{CP} = 19.3 Hz), 141.2 (d, J_{CP} = 27.6 Hz), 166.0; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 38.9; IR (neat) ν 1713 (C═O), 1203 (P═O) cm^{-1}; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{23}H_{20}O_3P$, 375.1145; found, 375.1128.

*2-(4-Cyanophenyl)-1-phenylbenzo[b]phosphole 1-Oxide (**8c**).* R_f = 0.58 (CH_2Cl_2/acetone = 10:1); mp 231−232 °C; ^{1}H NMR (700 MHz, $CDCl_3$) δ 7.40−7.43 (m, 3H), 7.47 (dd, 1H, J = 3.5, 7.7 Hz),

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7.51 (dd, 1H, J = 1.4 Hz, 7.7 Hz), 7.56 (t, 1H, J = 7.7 Hz), 7.61 (d, 2H, J = 8.4 Hz), 7.64−7.67 (m, 1H), 7.70 (d, 1H, J_{HP} = 34.3 Hz), 7.70−7.74 (m, 2H), 7.80 (d, 2H, J = 8.4 Hz); $^{13}C\{^1H\}$ NMR (175 MHz, $CDCl_3$) δ 112.0, 118.5, 125.3 (d, J_{CP} = 9.8 Hz), 126.9 (d, J_{CP} = 6.0 Hz), 129.0 (d, J_{CP} = 98.7 Hz), 129.07, 129.14, 129.3 (d, J_{CP} = 10.5 Hz), 130.0 (d, J_{CP} = 10.5 Hz), 130.7 (d, J_{CP} = 11.0 Hz), 132.6 (d, J_{CP} = 2.5 Hz), 132.7 (d, J_{CP} = 108.5 Hz), 133.5 (d, J_{CP} = 1.9 Hz), 137.0 (d, J_{CP} = 3.1 Hz), 137.3 (d, J_{CP} = 87.0 Hz), 139.4 (d, J_{CP} = 19.6 Hz), 140.9 (d, J_{CP} = 27.5 Hz); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 38.7; IR (neat) ν 2226 (CN), 1196 (P═O) cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{15}NOP$, 328.0886; found, 328.0876.

*2-(4-Methoxyphenyl)-1-phenylbenzo[b]phosphole 1-Oxide (**8d**).*[6] R_f = 0.36 (CH_2Cl_2/acetone = 20:1); mp 155−157 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 3.78 (s, 3H), 6.85 (d, 2H, J = 8.4 Hz), 7.28−7.31 (m, 1H), 7.36−7.41 (m, 3H), 7.46−7.50 (m, 2H), 7.47 (d, 1H, J_{HP} = 36.4 Hz), 7.59−7.62 (m, 1H), 7.66 (d, 2H, J = 8.4 Hz), 7.74−7.77 (m, 2H); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 39.3; IR (neat) ν 1182 (P═O) cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{18}O_2P$, 333.1039; found, 333.1025.

*2-(4-(Diphenylamino)phenyl)-1-phenylbenzo[b]phosphole 1-Oxide (**8e**).* R_f = 0.66 (CH_2Cl_2/acetone = 10:1); mp 107−109 °C (dec.); ^1H NMR (700 MHz, $CDCl_3$) δ 6.96 (d, 2H, J = 9.1 Hz), 7.03−7.05 (m, 2H), 7.06−7.08 (m, 4H), 7.23−7.26 (m, 4H), 7.27−7.30 (m, 1H), 7.35−7.37 (m, 1H), 7.39−7.42 (m, 2H), 7.46 (d, 1H, J_{HP} = 36.4 Hz), 7.48−7.51 (m, 4H), 7.57−7.60 (m, 1H), 7.76−7.79 (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 122.4, 123,6, 124.1 (d, J_{CP} = 17.0 Hz), 125.0, 125.7 (d, J_{CP} = 13.4 Hz), 127.5 (d, J_{CP} = 6.7 Hz), 128.5 (d, J_{CP} = 10.5 Hz), 128.89 (d, J_{CP} = 12.6 Hz), 128.95 (d, J_{CP} = 10.4 Hz), 129.3, 130.3 (d, J_{CP} = 97.4 Hz), 130.7, 130.8, 132.1 (d, J_{CP} = 3.0 Hz), 132.5 (d, J_{CP} = 108.6 Hz), 133.1 (d, J_{CP} = 1.5 Hz), 133.9 (d, J_{CP} = 20.1 Hz), 138.3 (d, J_{CP} = 93.7 Hz), 147.0, 148.4; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 39.1; IR (neat) ν 1197 (P═O) cm^{-1}; HRMS (ESI) m/z: $[M]^+$ calcd for $C_{32}H_{24}NOP$, 469.1590; found, 469.1580.

*2-(4-(Dimethylamino)phenyl)-1-phenylbenzo[b]phosphole 1-Oxide (**8g**).* R_f = 0.34 (CH_2Cl_2/acetone = 20:1); mp 180−181 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 2.95 (s, 6H), 6.63 (d, 2H, J = 8.8 Hz), 7.21−7.25 (m, 1H), 7.30−7.33 (m, 1H), 7.35−7.48 (m, 4H), 7.37 (d, 1H, J_{HP} = 37.6 Hz), 7.55−7.62 (m, 3H), 7.74−7.80 (m, 2H); $^{13}C\{^1H\}$ NMR (175 MHz, $CDCl_3$) δ 40.1, 112.1, 120.4 (d, J_{CP} = 10.5 Hz), 123.7 (d, J_{CP} = 9.1 Hz), 127.81 (d, J_{CP} = 7.2 Hz), 127.83 (d, J_{CP} = 10.5 Hz), 128.77 (d, J_{CP} = 11.7 Hz), 128.82 (d, J_{CP} = 10.5 Hz), 130.70 (d, J_{CP} = 96.8 Hz), 130.72 (d, J_{CP} = 10.5 Hz), 131.2 (d, J_{CP} = 20.3 Hz), 131.9 (d, J_{CP} = 2.6 Hz), 132.3 (d, J_{CP} = 108.0 Hz), 133.0 (d, J_{CP} = 1.9 Hz), 138.6 (d, J_{CP} = 93.4 Hz), 142.6 (d, J_{CP} = 28.9 Hz), 150.5; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 39.6; IR (neat) ν 1189 (P═O) cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{22}H_{21}NOP$, 346.1355; found, 346.1343.

*2-(4-Formylphenyl)-1-phenylbenzo[b]phosphole 1-Oxide (**8h**).* R_f = 0.33 (CH_2Cl_2/acetone = 20:1); mp 84−87 °C (dec.); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39−7.79 (m, 10H), 7.82−7.88 (m, 4H), 9.96 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 125.2 (d, J_{CP} = 9.7 Hz), 127.0 (d, J_{CP} = 3.4 Hz), 129.0 (d, J_{CP} = 11.9 Hz), 129.19 (d, J_{CP} = 10.4 Hz), 129.20 (d, J_{CP} = 98.2 Hz), 129.8, 130.2, 130.6 (d, J_{CP} = 11.1 Hz), 132.5 (d, J_{CP} = 3.0 Hz), 132.8 (d, J_{CP} = 108.6 Hz), 133.4 (d, J_{CP} = 1.4 Hz), 135.9, 137.7 (d, J_{CP} = 94.5 Hz), 138.3 (d, J_{CP} = 10.4 Hz), 139.2 (d, J_{CP} = 19.3 Hz), 141.1 (d, J_{CP} = 26.8 Hz), 191.5; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 38.8; IR (neat) ν 1697 (C═O), 1195 (P═O) cm^{-1}; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{21}H_{16}O_2P$, 331.0882; found, 331.0874.

Synthesis of 9. A mixture of **6a** (102 mg, 0.29 mmol), trichlorosilane (60 μL, 0.59 mmol), and toluene (10 mL) was refluxed, and progress of the reaction was monitored by TLC. After 6 h, aqueous NaOH solution (2M) was added, and the organic phase was separated, dried over Na_2SO_4, and evaporated under reduced pressure to give a colorless solid (104 mg). A part of the solid (47 mg) was immediately subjected to silica-gel column chromatography (CH_2Cl_2). The fraction of R_f = 0.18 (hexane) was collected and reprecipitated from MeOH to give 1,2-diphenylnaphtho[2,3-*b*]-phosphole (**9**) (33 mg, 0.99 μmol, 75%) as a colorless solid. mp 250−252 °C (dec.); ^1H NMR (400 MHz, $CDCl_3$) δ 7.18−7.25 (m, 4H), 7.34 (t, 2H, J = 7.6 Hz), 7.39−7.50 (m, 4H), 7.69 (d, 2H, J = 8.4 Hz), 7.73 (d, 1H, J_{HP} = 9.2 Hz), 7.77 (d, 1H, J = 8.4 Hz), 7.87 (d, 1H, J = 8.0 Hz), 8.00 (s, 1H), 8.06 (d, 1H, J_{HP} = 5.6 Hz); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 122.2, 125.7, 126.3, 127.1 (d, J_{CP} = 9.3 Hz), 127.9 (d, J_{CP} = 3.8 Hz), 128.0 (d, J_{CP} = 29.0 Hz), 128.1, 128.70 (d, J_{CP} = 5.8 Hz), 128.71, 128.73, 129.3 (d, J_{CP} = 22.2 Hz), 129.5 (d, J_{CP} = 1.2 Hz), 133.2 (d, J_{CP} = 4.5 Hz), 133.3 (d, J_{CP} = 20.3 Hz), 133.7, 134.5 (d, J_{CP} = 17.7 Hz), 136.3 (d, J_{CP} = 17.0 Hz), 141.4, 144.3 (d, J_{CP} = 3.1 Hz), 149.9 (d, J_{CP} = 7.9 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ −3.5; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{18}P$, 337.1141; found, 337.1131.

Synthesis of 10. Crude **9** (57 mg) was treated with elemental sulfur (116 mg, 3.63 mmol) in refluxing toluene. After **9** was consumed completely, the reaction mixture was evaporated under reduced pressure. The residue was subjected to silica-gel column chromatography (toluene/CH_2Cl_2 = 10:1), and the violet fluorescent fraction of R_f = 0.28 (hexane/EtOAc = 10:1) was collected and reprecipitated from MeOH to give 1,2-diphenylnaphtho[2,3-*b*]-phosphole 1-sulfide (**10**) (30 mg, 0.082 mmol, 48%) as a pale pink solid. mp 209−211 °C; ^1H NMR (700 MHz, $CDCl_3$) δ 7.28−7.30 (m, 1H), 7.33 (t, 2H, J = 7.0 Hz), 7.38−7.41 (m, 2H), 7.45−7.48 (m, 1H), 7.50 (t, 1H, J = 7.7 Hz), 7.57 (t, 1H, J = 7.0 Hz), 7.76 (d, 2H, J = 7.7 Hz), 7.81 (d, 1H, J_{HP} = 35.0 Hz), 7.82 (d, 1H, J = 7.7 Hz), 7.88−7.93 (m, 4H), 8.09 (d, 1H, J_{HP} = 11.9 Hz); $^{13}C\{^1H\}$ NMR (175 MHz, $CDCl_3$) δ 123.9 (d, J_{CP} = 7.9 Hz), 127.0 (d, J_{CP} = 7.2 Hz), 127.1, 128.4 (d, J_{CP} = 28.2 Hz), 128.81, 128.82 (d, J_{CP} = 12.4 Hz), 128.9, 129.1, 130.0 (d, J_{CP} = 77.9 Hz), 130.2 (d, J_{CP} = 11.7 Hz), 130.9 (d, J_{CP} = 12.4 Hz), 132.0 (d, J_{CP} = 3.1 Hz), 132.3 (d, J_{CP} = 11.0 Hz), 133.3 (d, J_{CP} = 12.4 Hz), 134.4, 135.1 (d, J_{CP} = 72.6 Hz), 135.3, 136.4 (d, J_{CP} = 15.7 Hz), 138.2 (d, J_{CP} = 24.9 Hz), 140.4 (d, J_{CP} = 77.9 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 45.18; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{24}H_{18}PS$, 369.0861; found, 369.0863.

X-ray Crystallographic Data. 6d (CCDC 1048750): $C_{25}H_{19}O_2P$, MW = 382.37, 0.36 × 0.094 × 0.090 mm^3, monoclinic, $P2_1/n$, a = 12.2059(5) Å, b = 6.2367(2) Å, c = 13.0601(5) Å, β = 108.2880(10)°, V = 943.98(6) $Å^3$, Z = 2, ρ = 1.345 g cm^{-3}, μ = 1.64 cm^{-1}, collected 6413, independent 3004, parameters 254, R_w = 0.0741, R = 0.0311 ($I > 2\sigma(I)$), GOF = 1.341. **8c** (CCDC 1048751): $C_{21}H_{14}NOP$, MW = 327.30, 0.36 × 0.22 × 0.20 mm^3, monoclinic, $P2_1$, a = 12.0467(6) Å, b = 6.5161(3) Å, c = 12.2531(5) Å, β = 117.784(2)°, V = 850.95(7) $Å^3$, Z = 2, ρ = 1.277 g cm^{-3}, μ = 1.67 cm^{-1}, collected 7077, independent 3681, parameters 218, R_w = 0.0956, R = 0.0446 ($I > 2\sigma(I)$), GOF = 1.197.

Fluorescence Lifetime Measurements. The fluorescence lifetimes of **6** and **8** were measured in CH_2Cl_2 using a streak camera as a fluorescence detector. The excitation wavelengths were chosen depending on the sample absorptions (**6a−d**, 385 nm; **6e,f**, 330 nm; **8a,d**, 360 nm; **8b**, 360 nm; **8c**, 380 nm; **8e**, 420 nm). The excitation pulse was generated by taking the second harmonic pulse (from 330 to 420 nm) of the output of an optical parametric amplifier (from 660 to 840 nm) operated by an amplified Ti:sapphire laser system.

DFT Calculations. The geometry optimization was performed by B3LYP method[21] with basis sets of 6-31G* for all atoms.[22] All calculations were carried out with the Gaussian 09 package.[23]

■ ASSOCIATED CONTENT

Supporting Information

Complete ref 23, crystal structure of **8c**, spectral data for **6e** and **8e**, cyclic voltammograms, results of DFT calculations, NMR spectra for new compounds, and CIFs of **6d** and **8c**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00541.

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Notes

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