Title	One-Step Synthesis of Benzophosphole Derivatives from Arylalkynes by Phosphenium-Dication-Mediated Sequential C-P/C-C Bond Forming Reaction
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One-Step Synthesis of Benzophosphole Derivatives from Arylalkynes by Phosphenium-Dication-Mediated Sequential C–P/C–C Bond Forming Reaction

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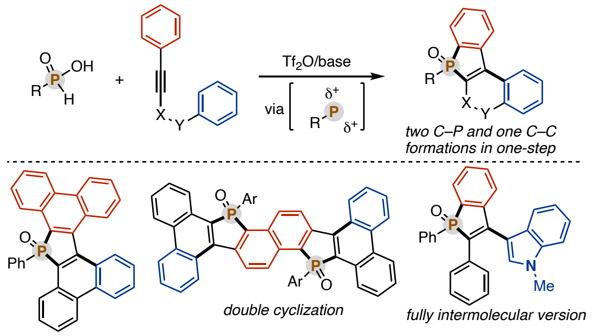
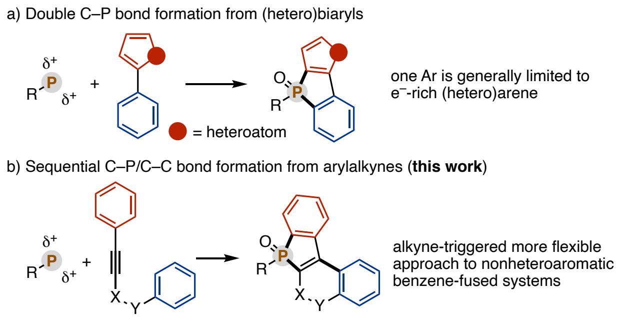
Supporting Information Placeholder



ABSTRACT: A metal-free, phosphenium-dication-mediated sequential C–P and C–C bond forming reaction has been developed. This protocol can provide concise access to the (di)benzophosphole derivatives in one synthetic operation from the readily available and simple arylalkynes and phosphinic acids. Application to the multiple cyclization reaction and the fully intermolecular three-component-coupling-type reaction are also described.

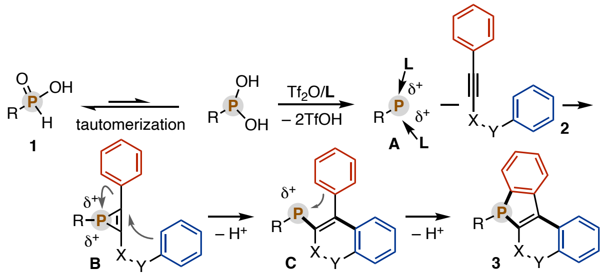
Phosphole derivatives have recently received significant attention in fields of phosphorus-based organic functional materials because of their unique optoelectronic and physical properties.[1] Accordingly, numerous strategies for the preparation and decoration of phosphole nuclei have been developed so far. While most traditional protocols largely relied on the transition-metal-mediated multistep sequence with some toxic and sensitive reagents,[1,2] P-radical,[3] -cation,[4] and -dication[5]-promoted methods recently appeared to streamline the synthesis of targeted phosphole cores via efficient C–P bond formation. In particular, our previous work using the phosphenium dication equivalent[5a] enabled the rapid construction of the dibenzophospholes from the corresponding simple biaryls and phosphinic acids (Scheme 1a). However, electron-rich (hetero)aromatics such as indole, thiophene, and phenoxy moieties were generally essential to trigger the reaction, which apparently limited the versatility of the phosphole product. Herein, we repot a more flexible approach to the benzophospholes from the arylalkynes and phosphinic acids: the phosphenium-dication-mediated sequential C–P/C–C bond forming reaction is developed (Scheme 1b). By using the alkyne moiety as the reaction trigger, this strategy easily accesses the non-heteroaromatic benzene-fused phosphole derivatives with high efficiency. The starting arylalkynes are also readily available by the Sonogashira coupling, same as in the preparation of biaryls via the Suzuki-Miyaura coupling. Thus, this protocol significantly expands the applicability of the P-cation-based strategy in the phosphole synthesis. Additionally, the multiple phosphole-constructing cyclization and application to the fully intermolecular three-component-coupling reaction of alkynes, phosphinic acids, and external nucleophiles are achieved. We note that during the course of this study, Huang and Xiao reported the related reaction of *ortho*-MeO- and MeS-substituted diarylalkynes,[5b] but the products were restricted to the furan- and thiophene-fused dibenzophospholes, which are more readily synthesized by our previous double C–P bond forming reaction of heterobiaryls.[5a] In addition, the intermolecular process was not mentioned at all.

Scheme 1. Phosphenium-Dication-Mediated Approaches to (Di)Benzophospholes



Our reaction design is shown in Scheme 2. The active phosphenium dication equivalent **A** is initially generated from the phosphinic acid **1** by the action of 2 equiv of dehydrating reagent Tf_2O and Lewis base (**L**) via P(V)/P(III) tautomerization.[6] Subsequent [1+2] cycloaddition with the alkyne moiety of **2** generates the corresponding three-membered phosphirenium species **B**.[7] The ring-opening process is induced by the intramolecular attack of the tethered Ar group to form **C**. The intermediate **C** has still one positive charge on the phosphorus and thus undergoes the intramolecular phospha-Friedel-Crafts-type reaction[8] to furnish the benzophosphole derivative **3**. Overall, two C–P bonds and one C–C bond are constructed in one synthetic operation.

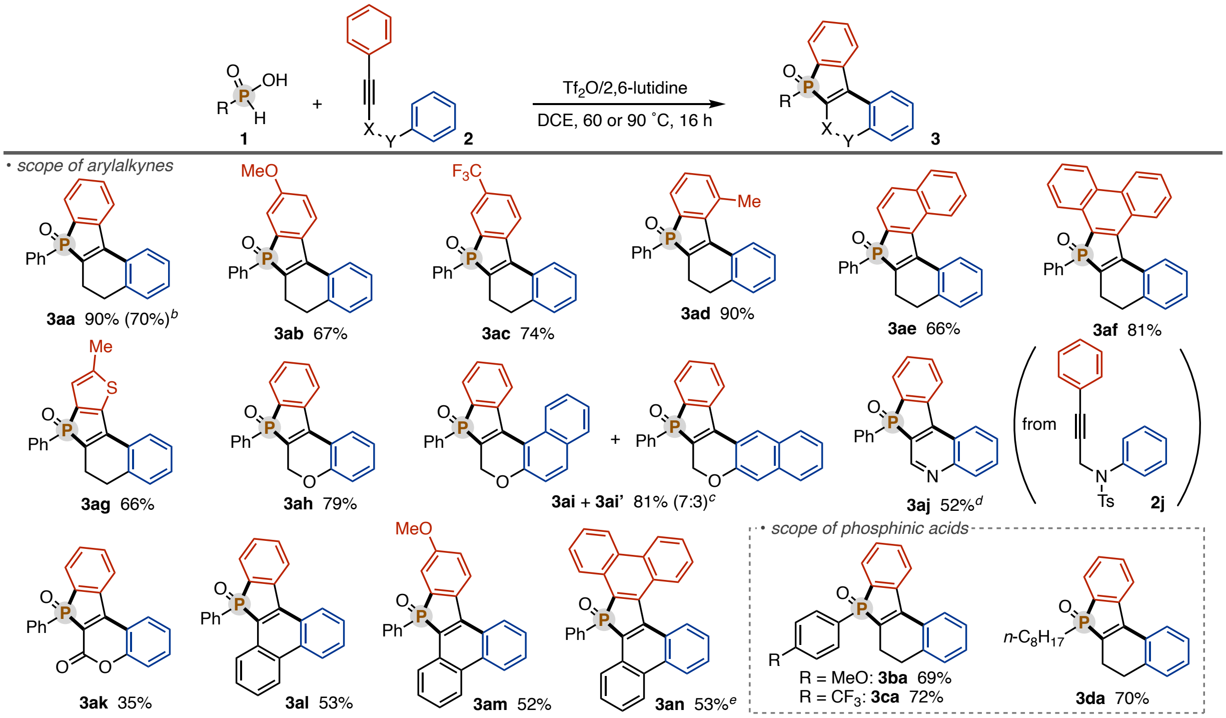
Scheme 2. Working Hypothesis



We selected phenylphosphinic acid (**1a**) and the arylalkyne **2a** as model substrates and started optimization studies to identify the suitable conditions including the dehydrating reagent, Lewis base, and solvent. After extensive screening, the targeted benzophosphole oxide derivative **3aa** was found to be isolated in 90% yield by using the combination of Tf_2O and 2,6-lutidine in heated DCE (Scheme 3). Some observations are to be noted: the corresponding P(III) phosphole derivative was not detected at all, and **3aa** was only formed even without any additional oxidative treatment.[9] Tf_2O was the critical dehydrating reagent as far as we tested. No reaction occurred under Lewis-base-free conditions. Some other pyridine-type Lewis bases also promoted the reaction, whereas sluggish conversion of **1a** was observed in the presence of alkylamines and inorganic bases (see the Supporting Information for details).

With optimal conditions in hand, we first investigated the scope of the arylalkynes **2**. In addition to the model substrate **2a**, electron-donating and -withdrawing substituents both were well compatible under the reaction conditions (**3ab** and **3ac**). The sterically congested *ortho*-Me group (**3ad**) and more condensed naphthalene (**3ae**) and phenanthrene (**3af**) substitutions were also accommodated. The alkyne containing the heteroaromatic thiophene moiety underwent the reaction without any difficulty (**3ag**). The ethylene tether could also be replaced with the oxygen-, nitrogen-, and ester-based linkers, and the corresponding heteroatom-incorporated benzophosphole derivatives **3ah**–**ak** were isolated in synthetically acceptable yields. In the case of **3ai**, the regioisomeric **3ai'** was also formed probably because of the competitive steric and electronic effects. Notably, in the reaction of the NTs-type substrate **2j**, the additional treatment with KOH in MeOH promoted the elimination of TsH to selectively form the aromatized pyridine-fused phosphole **3aj**. The benzene ring also worked well as the two-carbon tether, and the targeted highly condensed **3al**, **3am**, and **3an** were obtained in good yields. The electronically diverse arylphosphinic acids **1b** and **1c** could also be coupled with **2a** to deliver the corresponding **3ba** and **3ca** in 69% and 72% yields, respectively. Moreover, the aliphatic phosphinic acid was employed with good efficiency (**3da**). On the other hand, the alkene substrate instead of the alkyne did not provide the targeted cyclization product (see the Supporting Information for details).

Scheme 3. Phosphenium-Dication-Mediated Sequential C–C/C–P Bond Formation of Arylalkynes 2 with Phosphinic Acids 1[a]

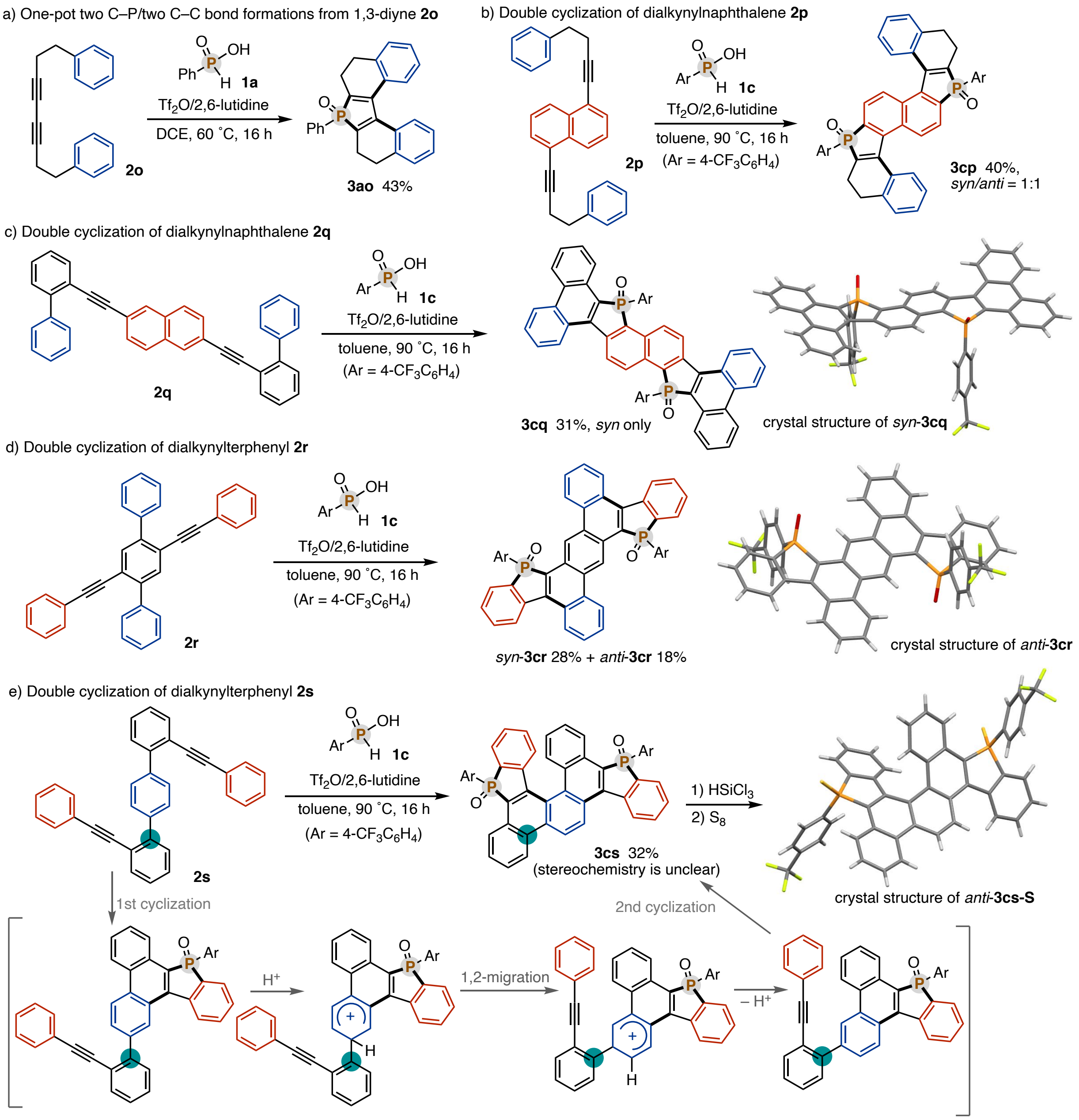


[a] Reaction conditions: **1** (0.20 mmol), **2** (0.10 mmol), Tf_2O (0.48 mmol), 2,6-lutidine (0.48 mmol), DCE (1.5 mL), 60 or 90 ˚C, 16 h. Isolated yields are shown. [b] On a 1.0 mmol scale. [c] Obtained as a 7:3 mixture of regioisomers. [d] With additional treatment with KOH in MeOH. See the Supporting Information for details. [e] On a 0.20 mmol scale in toluene.

Additionally notable is that the conjugated 1,3-diyne **2o** was readily converted to the phosphole derivative **3ao** by the sequential two C–P and two C–C bond formations in one synthetic operation (Scheme 4a). The phosphenium-dication-promoted strategy was also applied to the double cyclization reaction of the dialkynylnaphthalenes **2p** and **2q** (Scheme 4b and c). In these cases, four C–P and two C–C bonds were successively formed to deliver the corresponding octa- and decacyclic systems **3cp** and **3cq** with two phosphole rings. The structure of *syn*-**3cq** was confirmed by X-ray analysis (CCDC 2210187). Moreover, the dialkynylterphenyl **2r** also participated in the double cyclization reaction to afford benzophosphole-fused dibenzanthracene **3cr** in an acceptable yield (Schemes 4d). Its crystal structure was also successfully obtained (CCDC 2210186). On the other hand, the regioisomeric dialkynylterphenyl **2s** gave the helical, unexpected double cyclization product **3cs** (Scheme 4e). This is probably because of the acid-mediated aryl ring 1,2-migration after the first cyclization event, a similar process of which is frequently found in the acid-promoted Scholl reaction of the condensed aromatic compounds.[10] The structure was finally determined by the crystallographic analysis after the conversion of P=O to P=S (*anti*-**3cs-S**; CCDC 2231651). Notably, in Schemes 4b–e, the use of CF_3-containing phosphinic acid **1c** was critical to success: with simple phenyl-substituted **1a**, the reaction stopped after the single cyclization. The outcome indicates that the electron-withdrawing group on the phosphorus increases the electrophilicity of the phosphenium dication species and enables the otherwise difficult second cyclization process.

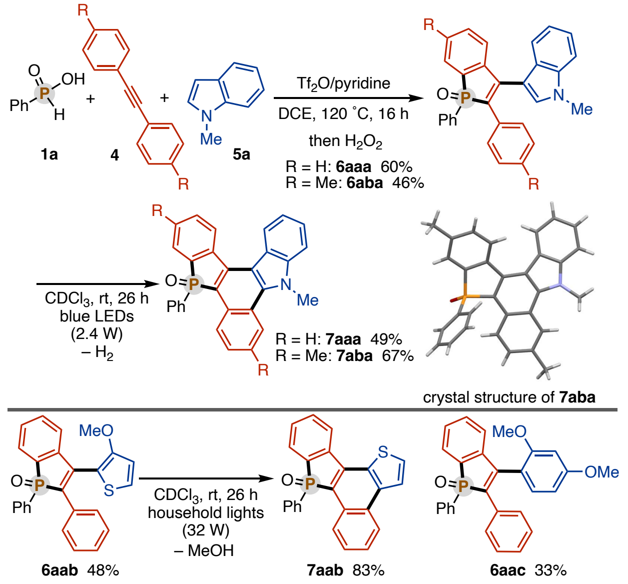
The preliminary optoelectronic properties of highly condensed *syn*-**3cq**, *syn*-**3cr**, *anti*-**3cr**, and **3cs** were investigated.

Scheme 4. Double Cyclizations from 1,3-Diyne and Dialkynylarenes



Their UV/vis absorption, fluorescence spectra, and images in $CHCl_3$ are shown in Figures S6 and S7, and the absorption/emission properties ($\lambda_{abs}/\lambda_{em}$) and fluorescence quantum yields (Φ_F) are summarized in Table S5. All compounds were strongly fluorescent in solution and gave a relatively broad range of their longest wavelength absorption maxima in the visible light region. In particular, the decacyclic system *syn*-**3cq** showed a large bathochromic shift of its λ_{abs} value (470 nm) with a higher molar extinction coefficient (ε) and fluorescence in the green color region (492–522 nm). Whereas the quantum efficiencies of *syn*-**3cq**, *syn*-**3cr**, and *anti*-**3cr** were good (Φ_F = 62–69%), the helical **3cs** showed a relatively poor value of Φ_F = 25%, thus indicating that the planarity is critical for the fluorescence event. The generally observed smaller Stokes shifts reflect their rigid structures associated with the highly condensed acene-type cores. The electrochemical properties of the aforementioned compounds were examined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in MeCN with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as an electrolyte *versus* ferrocene/ferrocenium ion (Fc/Fc^+) (Figures S8-10), and their HOMO and LUMO levels were estimated according to the first oxidation potentials and the optical band gaps (E_g^{opt}). Due to its poor solubility, any clear spectra of *anti*-**3cr** were not obtained, and the HOMO/LUMO levels were thus investigated by density functional theory (DFT) calculations at the PBE0/6-31+G(d) level of theory (Figure S11). The data are summarized in Table S6. The CV of *syn*-**3cq**, *syn*-**3cr**, and **3cs** all showed irreversible oxidation waves, and oxidation potential values $E^{1/2}_{ox}$ are thus determined by the DPV. The HOMO levels were almost identical but an even lower LUMO level was estimated for *syn*-**3cq**, which may suggest the larger intramolecular charge transfer ability.

Scheme 5. Fully Intermolecular Three Component Coupling of Phosphinic Acids, Diarylacetylenes, and Electron-Rich (Hetero)aromatics



We finally attempted to apply the phosphenium dication strategy to the fully intermolecular three component coupling reaction with the external nucleophiles. After the optimization studies (see the Supporting Information for details), we were pleased to find that the reaction of phosphinic acid **1a**, diphenylacetylene (**4a**), and *N*-Me indole (**5a**) proceeded in the presence of Tf_2O and pyridine to afford the C3-indolylbenzophosphole **6aaa** in 60% yield after the oxidative workup with aq. H_2O_2 (Scheme 5).[11] The C3-indolyl **6aaa** was isolable but gradually underwent the dehydrogenative cyclization under visible light irradiation to finally deliver the *P,N*-containing heteroacene **7aaa**. The structure of the Me-substituted analogue **7aba** was unambiguously confirmed by X-ray analysis (CCDC 2202706). In addition to the indole **5a**, electron-rich (hetero)aromatics, including 3-methoxythiophene and 1,3-dimethoxybenzne, could also be used as the external nucleophiles, and the corresponding 2,3-diarylbenzophospholes **6aab** and **6aac** were successfully formed. Similar to the indole derivatives **6aaa** and **6aba**, the thiophene-substituted **6aab** could be converted to **7aab** by the visible-light-promoted cyclization with concomitant elimination of MeOH, while the benzene-derived **6aac** was stable and unchanged even under photoirradiation.

In conclusion, we have developed a phosphenium-dication-mediated sequential C–P/C–C bond forming reaction of the relatively simple arylalkynes and phosphinic acids, giving the corresponding benzophosphole derivatives in good to high yields under Tf_2O-promoted, metal-free conditions. The alkyne-triggered reaction enables the construction of arene-fused phosphole rings without any assistance of electron-rich heteroaromatics, which are inevitable in the previous phospha-Friedel-Crafts reaction.[5a] Additionally, the reaction is successfully applicable to the double cyclization of dialkynyl arenes with 2 equiv of phosphinic acids, thus delivering the highly condensed P-containing acene-type molecules of potent interest in material chemistry. Moreover, the fully intermolecular three-component-coupling reaction of arylalkynes, phosphinic acids, and electron-rich arenes is possible to provide potentially modular access to the C2,C3-diarylated benzophospholes. Detailed mechanistic studies and further applications to the design and synthesis of phosphole-based organic functional materials are ongoing in our laboratory.

ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are openly available in the published article and its online Supporting Information.

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.xxxx.

^{1}H, ^{13}C{^{1}H}, ^{19}F{^{1}H}, and ^{31}P{^{1}H} NMR spectra, ORTEP drawing, detailed optimization studies, optoelectronic properties, and DFT calculations (PDF)

Accession Codes

CCDC 2202706, 2210186, 2210187, and 2202706 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

§K.N. and S.X. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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(9) A similar trend was observed in our previous work on the Tf_2O-mediated phosphole synthesis. See refs 4a, 4b, and 5a. The initially formed P(III) phosphole could be spontaneously oxidized with residual Tf_2O and/or its derivatives.

(10) For example, see: Skraba-Joiner, S. L.; McLaughlin, E. C.; Ajaz, A.; Thamatam R.; Johnson, R. P. Scholl Cyclizations of Aryl Naphthalenes: Rearrangement Precedes Cyclization. *J. Org. Chem.* **2015**, *80*, 9578–9583.

(11) In the three component coupling reaction, the phosphole product was somewhat resistant to the in-situ oxidation, and a mixture of P(III) and P=O benzophospholes was detected after

the reaction. Thus, for ease of the purification, additional treatment with aq. H_2O_2 was performed for full conversion into the P=O benzophosphole.