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Regioselective Synthesis of Benzo[*b*]phosphole Derivatives via Direct *ortho*-Alkenylation and Cyclization of Arylthiophosphinamides

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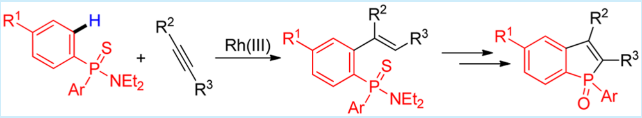
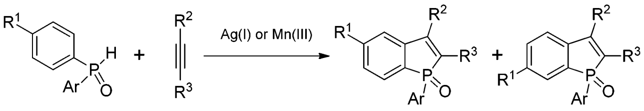
Ⓢ *Supporting Information*

ABSTRACT: A new regioselective synthetic methodology for benzo[*b*]phosphole derivatives has been developed. Thus, a range of functionalized benzo[*b*]phosphole oxides could be synthesized via Rh(III)-catalyzed C−H alkenylation of arylthiophosphinamides with alkynes followed by formal phospha-Friedel−Crafts cyclization.



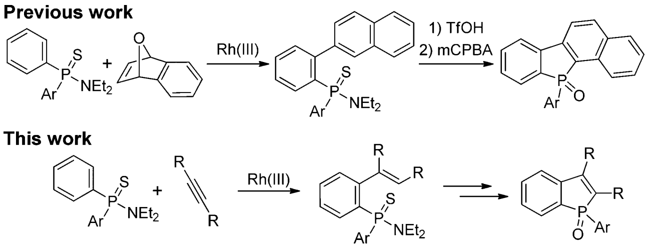
Benzo[*b*]phospholes are unique and attractive building blocks among a series of benzoheterole scaffolds, which show intriguing electronic and optical properties caused by distinctive orbital interaction between butadiene π^* and σ^*(P-R).[1] While they have attracted considerable interest in the area of materials chemistry, their synthetic methods have been less explored than those of the isosteric indoles.[2] Conventionally, benzo[*b*]phosphole scaffolds have been constructed through the cyclization of *ortho*-alkynylarylphosphines,[3a−c] *H*-phosphine oxides,[3d] and aminophosphines.[3e,f] These methods often require tedious multistep preparations of the corresponding cyclization precursors, involving air- and moisture-sensitive intermediates. In 2013, we[4a] and the Duan group[4b] independently reported the Ag(I)- or Mn(III)-mediated synthesis of benzo[*b*]phosphole derivatives via the direct annulation reaction of secondary phosphine oxides with internal alkynes (Scheme 1).[4] While this protocol provides a short access to benzo[*b*]phosphole derivatives, a regioselectivity problem arises when substituted phenylphosphine oxides are employed due to the radical intermediate involving the rearrangement of a phosphorus moiety. After these reports, several improved methods based on a similar radical mechanism under metal-catalyzed,[5a] photocatalyzed,[5b] and metal-free conditions[5c,d] have also been disclosed. However, the regioselectivity issue has not been overcome. Recently, Yoshikai and co-workers reported an elegant multicomponent coupling for the synthesis of benzo[*b*]phosphole derivatives via carbometalation of alkynes with arylzinc and magnesium reagents.[6] Yet, development of more efficient synthetic routes to benzo[*b*]phospholes is desired.

Scheme 1. Synthesis of Benzo[*b*]phosphole Derivatives by Radical Cyclization



Meanwhile, transition-metal-catalyzed directed C−H bond functionalization reactions have been regarded as powerful synthetic tools from atom- and step-economical points of view.[7,8] In the context of our studies on the C−H bond functionalization of aromatic phosphorus compounds,[9,10] we recently developed the Cp*Rh(III)-catalyzed *ortho*-naphthylation reaction of arylthiophosphinamides with oxabicyclic alkenes (Scheme 2).[9d]

Scheme 2. Rh(III)-Catalyzed C−H Bond Functionalization Approaches to Benzo[*b*]phosphole Scaffolds



The naphthylated products were readily converted to fused dibenzo[*b*]phosphole derivatives by intramolecular phospha-Friedel−Crafts reaction[11] in a one-pot procedure. Subsequently, we envisioned that a regioselective synthesis of benzo[*b*]phospholes could be achieved through the *ortho*-alkenylation of arylthiophosphinamides and subsequent intramolecular phospha-Friedel−Crafts reaction. Herein, we report a new method for constructing benzo[*b*]phosphole oxides by the C−H alkenylation/cyclization protocol.

First, we carried out optimization studies on the C−H alkenylation using *N*,*N*-diethyl-*P*,*P*-diphenylthiophosphinamide (**1a**) and diphenylacetylene (**2a**) as model substrates (Table S1). Pleasingly, we found that the desired coupling reaction proceeded smoothly in the presence of [Cp*Rh(MeCN)$_3$(SbF$_6$)$_2$] (4 mol %) and AcOH (4 equiv) in PhCl at

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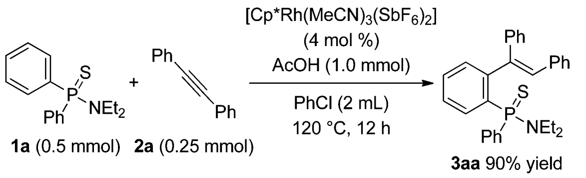
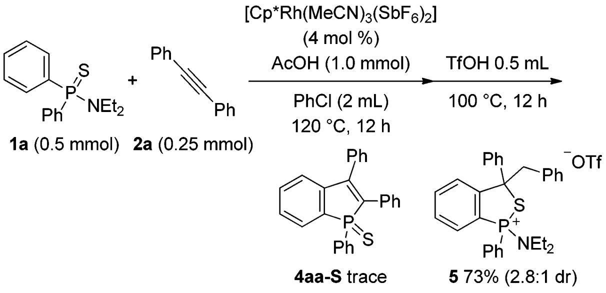
120 °C to give alkenylated product **3aa** in 90% isolated yield (Scheme 3). The geometry of the alkenyl moiety was determined to be *E* by X-ray crystal structure analysis (see the Supporting Information for details).

Scheme 3. Rh(III)-Catalyzed Regioselective C−H Alkenylation of 1a with 2a



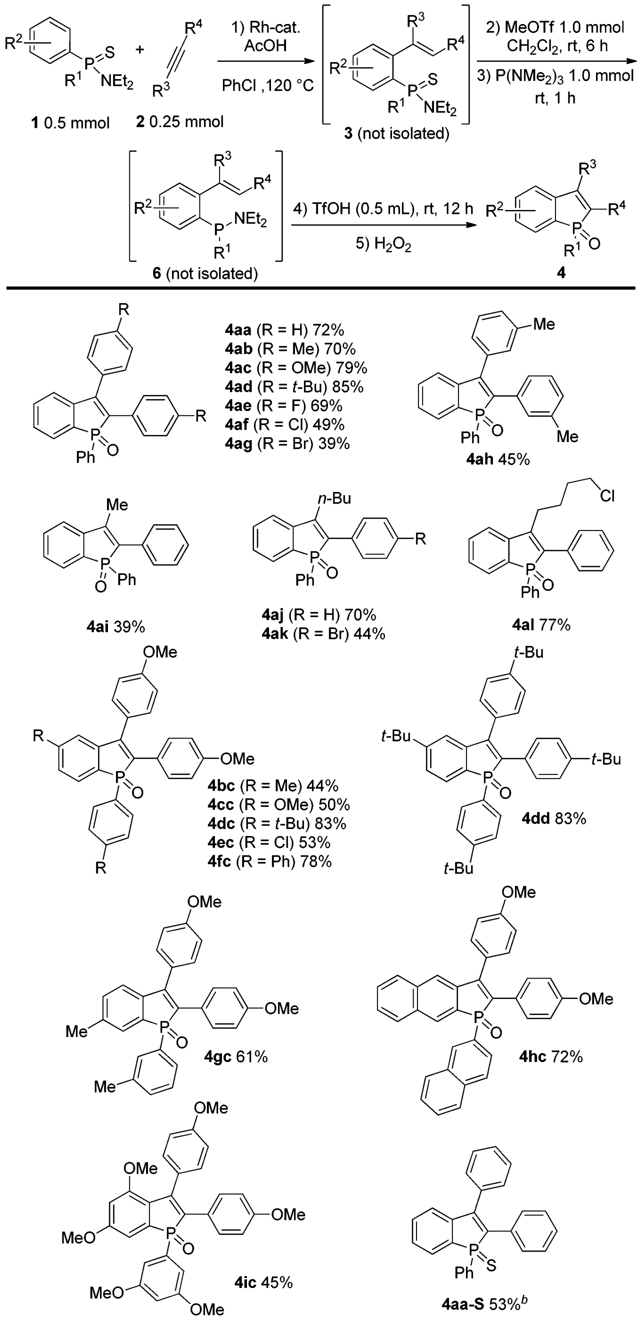
We next examined the second step, that is, cyclization. In our previous report for the intramolecular phospha-Friedel−Crafts reaction of arylthiophosphinamides, an excess amount of TfOH was used.[9d] Thus, the crude product formed by the Rh-catalyzed alkenylation in Scheme 3 was treated with TfOH under similar conditions (Scheme 4). Unfortunately, the desired benzo[*b*]phosphole **4aa-S** was observed only in a trace amount, and instead, phosphonium salt **5** was formed in 73% yield as a diastereomeric mixture. Obviously, **5** seems to be formed via protonation of the alkenyl moiety of **3aa** with TfOH and electrophilic attack of a resulting carbocation to the P=S bond. We also examined other activating reagents including HCl, $AlCl_3$, $BF_3{\cdot}OEt_2$, AgOTf, and Me_3OBF_4, but the attempts were unsuccessful (Table S2).

Scheme 4. Attempt at Phospha-Friedel−Crafts Reaction via Intermediate 3aa



Next, we examined another cyclization route via a P(III) intermediate. Thus, **3aa** was reduced to aminophosphine by treatment with MeOTf and $P(NMe_2)_3$.[12] The resulting P(III) compound **6** was treated with TfOH. After workup with H_2O_2, benzo[*b*]phosphole oxide **4aa** was successfully obtained in 72% yield (Scheme 5).

Scheme 5. Synthesis of Benzo[*b*]phosphole Oxides 4 by Semi-One-Pot Protocol[a]

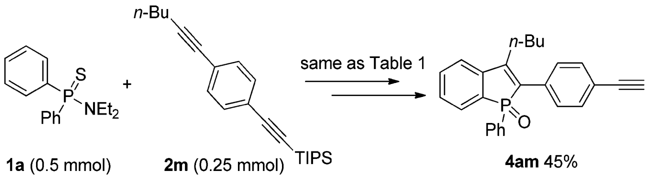


[a] Reaction conditions: (1) **1** (0.5 mmol), **2** (0.25 mmol), [Cp*Rh(MeCN)$_3$][SbF$_6$]$_2$ (0.01 mmol), AcOH (1.0 mmol) in PhCl (2 mL) at 120 °C under N_2 for 12 h; (2) MeOTf (1.0 mmol) in CH_2Cl_2 (3 mL), rt, 6 h; (3) $P(NMe_2)_3$ (1.0 mmol), rt, 1 h; (4) TfOH (0.5 mL), rt, 12 h; (5) H_2O_2 workup. See the Supporting Information for details. Isolated yields are shown based on the amount of **2**. [b] Workup was carried out using S_8 powder instead of H_2O_2.

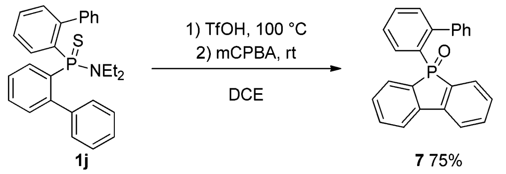
The results for the synthesis of a series of benzo[*b*]phosphole oxides by the semi-one-pot protocol are summarized in Scheme 5. A variety of diarylacetylenes **2a−2h** smoothly coupled with **1a** to afford the corresponding benzo[*b*]phosphole oxides **4aa−4ah** in moderate to good yields. The reaction of a more electron-deficient alkyne, bis(4-ethoxycarbonylphenyl)acetylene, did not give any expected product at all. In the cases with asymmetrical alkylarylacetylenes, the Rh-catalyzed hydroarylation reaction proceeded regioselectively to lead to 2-aryl-3-alkylbenzo[*b*]phosphole derivatives **4ai−4aj** exclusively. It is worth noting that this regioselectivity is complementary to that of Ag(I)- or Mn(III)-mediated annulation reaction reported previously.[4,5] A dialkylacetylene, 4-octyne, did not couple with **1a** at all. Next, the reactions of substituted diarylthiophosphinamides were carried out. The *para*-substituted **1b−1f** reacted with **2c** or **2d** regioselectively to give **4bc−4fc** and **4dd** in good yields. 3-Methylphenyl and 2-naphtylthiophosphinamides, **1g** and **1h**, coupled with **2c** at the less hindered positions to form **4gc** and **4hc**. By post-treatment using sulfur powder in place of H_2O_2 in the reaction of **1a** with **2a**, benzo[*b*]phosphole sulfide **4aa-S** was selectively obtained in 53% yield.

Under our new conditions, silyl acetylenes did not undergo the Rh-catalyzed hydroarylation with **1**. Utilizing the different reactivity of alkynes, we attempted the chemoselective coupling reaction of **1a** with diyne **2m** (Scheme 6). Under standard conditions, the alkyl acetylene unit of **2m** over the silyl acetylene moiety selectively coupled with **1a** to form **4am** in 45% yield. The TIPS group was removed upon treatment with TfOH.

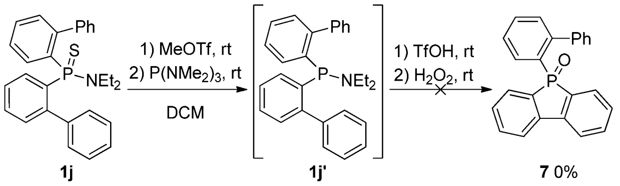
Scheme 6. Chemoselective Coupling Reaction of 1a with Diyne 2m



To gain some mechanistic information about the C−P bond-forming ring-closure step, we investigated the difference of reactivities between P(III) and P(V) intermediates using an aryl model substrate **1j**. Under our previous conditions (TfOH, 100 °C),[9d] **1j** was smoothly converted to dibenzophosphole **7** in 75% yield (eq 1). In sharp contrast, the present ring-closing procedure involving P(III) species did not give **7** at all (eq 2). These results indicate that phospha-Friedel−Crafts-type aromatic electrophilic substitution in P(III) intermediate **1j**′ does not occur on its benzene ring under the present conditions. The lack of such a reactivity was also observed in related Lewis-acid-promoted phospha-Friedel−Crafts reactions.[11a,c,e]



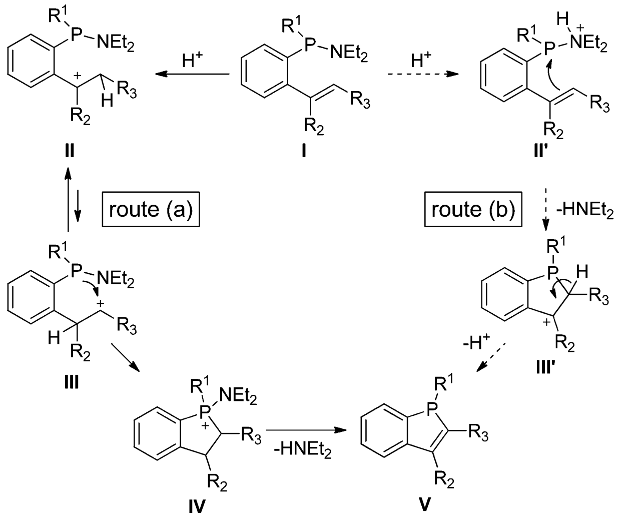
(1)



(2)

Based on the experimental results, plausible reaction pathways are depicted in Scheme 7. In route (a), TfOH protonates the alkenyl moiety of amino phosphine **I** (= **6**) to generate carbocations **II** and **III**, which may exist in equilibrium with the major contribution of tertiary carbocation **II**. The phosphonium salt **5** in Scheme 4 may be generated from **3aa** via a similar tertiary carbocation. In the case of aminophosphine **I**, five-membered phosphonium salt **IV** selectively formed from the secondary carbocation **III** with "nucleophilic P center", after which diethylamine is eliminated to generate benzo[*b*]-phosphole **V**.[3e] Although the other general phospha-Friedel−Crafts route from "electrophilic P center" in route (b)[6] cannot be completely excluded at this stage, route (a) seems to be the major route based on the control experiment shown in eq 2.

Scheme 7. Plausible Reaction Mechanism of C−P Bond-Forming Step



As expected, most of benzo[*b*]phosphole oxides obtained in this study showed remarkable fluorescence in their solid state.[13] Optical properties including absolute fluorescent quantum yields determined by using an integrating sphere system are summarized in Table S4. 2,3-Diaryl products **4aa**−**4ie** exhibit relatively strong fluorescence in a range of 446 to 519 nm. Remarkably, 3-methyl **4ai** showed a blue-shifted emission in a high quantum yield (420 nm, $\Phi_F = 0.9$).

In summary, we have developed a new regioselective synthetic sequence leading to benzo[*b*]phosphole derivatives via rhodium(III)-catalyzed C−H alkenylation followed by intramolecular cyclization in a semi-one-pot manner. Thus, a range of functionalized benzo[*b*]phosphole oxides can be synthesized from readily available arylthiophosphinamides. This new methodology may contribute to expand the utility of benzophospholes in materials chemistry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b02868.

Experimental procedures, additional results, and characterization data of products (PDF)
Crystallographic data for **3aa** (CIF)
Crystallographic data for **5** (CIF)

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Notes

The authors declare no competing financial interest.

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