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Rhodium-Catalyzed Oxidative C–H Activation/Cyclization for the Synthesis of Phosphaisocoumarins and Phosphorous 2-Pyrones

Youngchul Park, Jungmin Seo, Sangjune Park, Eun Jeong Yoo, and Phil Ho Lee*[a]

Dedicated to Professor Han-Young Kang on the occasion of his 60th birthday

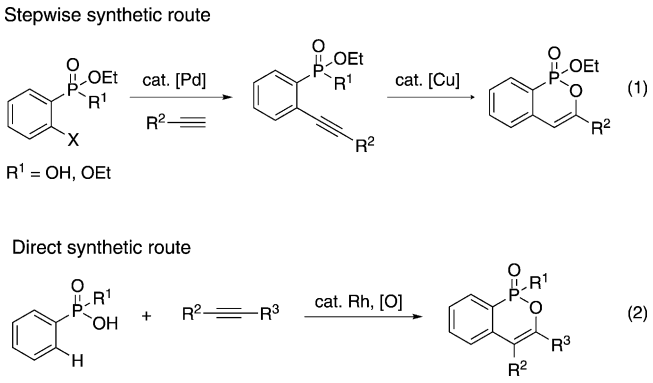
Abstract: Rhodium-catalyzed cyclization of phosphinic acids and phosphonic monoesters with alkynes has been developed. The oxidative annulation proceeds with complete conversion of phosphinic acid derivatives and allowed the atom-economic preparation of useful phosphaisocoumarins with high yield and selectivity. The reaction is tolerant of extensive substitution on the phosphinic acid, phosphonic monoester and alkyne, including halides, ketone, and hydroxyl groups as substituents. Furthermore, we found that alkenylphosphonic monoesters proceed to give a wide range of phosphorus 2-pyrones through oxidative annulation with alkynes. Mechanistic studies revealed that C–H bond metalation was the rate-limiting step.

Keywords: alkynes · annulation · C–H activation · cyclization · phosphorous heterocycles · rhodium

Introduction

Organophosphorus compounds continue to receive widespread attention because of their ubiquity in biological systems[1] and because of their vital role as bioisosteres of carboxylate moieties.[2] Given the prevalence of phosphorus compounds in medicinal chemistry and pharmaceutical industries,[3] both the design of new structures of phosphorus compounds and their applications have been explored. Recently, Kim and our group disclosed various transition-metal-catalyzed C–H functionalizations by using phosphoryl-related compounds as a directing group[4] in an effort to pioneer a new direct synthetic method for introducing structural variation into phosphorous compounds.[5] Moreover, by understanding the unique properties of phosphorous functional groups based on several references to the *ortho*-metalation of aryl-phosphoryl moieties,[6] a novel protocol for the C–H alkenylation of monophosphoric acid and benzylic phosphonic monoesters was developed.[4c,g]

Although less studied, the preparation of phosphaisocoumarins, which are isocoumarin phosphorus analogues, has also continued to be in strong demand because of their interesting biological properties.[3a,7] Ding and Peng have prepared phosphaisocoumarins through intramolecular nucleophilic attack by the oxygen of the phosphonyl group on the activated alkyne after Sonogashira coupling reaction of arylphosphate[8] or arylphosphinic acid[9] [Scheme 1, Eq. (1)].



Scheme 1. Previous synthetic routes to phosphaisocoumarins.

In contrast to usual multistep syntheses [such as Scheme 1, Eq. (1)], economically more attractive routes that proceed through cleavage of C–H bonds, allows the organic syntheses to be streamlined and minimizes byproduct formation.[10] In a continuation of our studies of C–H bond activation reactions,[11] we recently developed a rhodium-catalyzed C–H cyclization of phosphonic acid monoester for the preparation of phosphaisocoumarins [Scheme 1, Eq. (2)].[4d,12]

Although the reactions appear to represent a highly efficient and selective process, this approach is still in its infancy from the synthetic point of view, in that substrate scope is limited. At the present time, for instance, C–H annulation of phosphinic acid with dialkyl-substituted alkynes or electron-deficient diaryl-substituted alkynes remain largely uninvestigated. We therefore became interested in exploring the

[a] Y. Park, J. Seo, S. Park, Prof. Dr. E. J. Yoo, Prof. Dr. P. H. Lee
Department of Chemistry
Kangwon National University
Chuncheon 200-701 (Republic of Korea)
Fax: (+82) 33-253-7582
E-mail: phlee@kangwon.ac.kr

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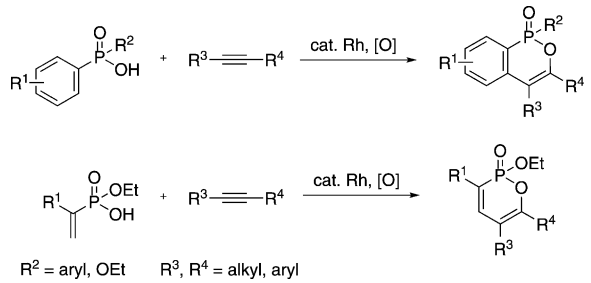
effective C–H activation/cyclization of phosphinic acid derivatives with broadly expanded alkyne reagents. We wish to report the results of these investigations herein.

Encouraged by the our previous results,[4b] the most efficient catalysis was achieved with alkenylphosphonic monoesters, which also allowed the synthesis of phosphorus 2-pyrones (Scheme 2).



Scheme 2. New synthetic routes to phosphaisocoumarins and phosphorus 2-pyrones through rhodium-catalyzed C–H activation/cyclization.

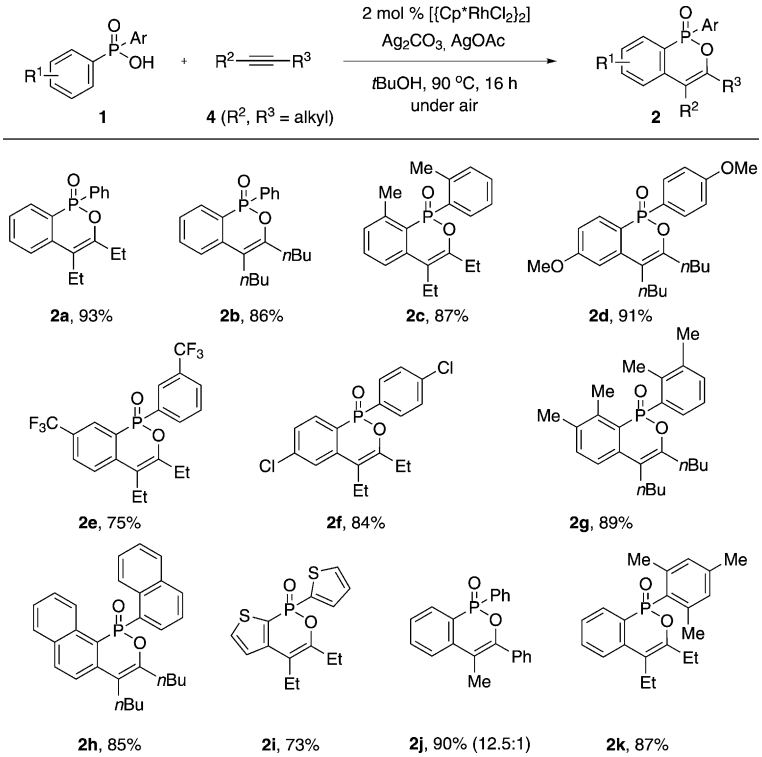
Results and Discussion

C–H cyclization of phosphinic acid with dialkyl-substituted alkynes: Almost all known C–H activated annulations of phosphinic acids proceed with diaryl-substituted alkynes. Thus, the preparation of 3,4-dialkyl-substituted phosphaisocoumarin **2** through C–H activation has been accomplished by employing phosphinic acid **1** and dialkyl-substituted alkynes (Scheme 3). This highly attractive C–H annulation of phosphinic acid **1** with dialkyl-substituted alkynes was realized even more successfully, when commercially available $[\{Cp^*RhCl_2\}_2]$ (2 mol%) was applied as the catalyst. The use of Ag_2CO_3 and AgOAc as co-oxidant with phosphinic acid **1** in *t*BuOH proved viable.

The developed annulation reaction with dialkyl-substituted alkynes tolerated a wide variety of phosphinic acids with a range of functional groups. Diphenylphosphinic acid (**1a**) reacted with each counterpart alkyne smoothly, producing the desired phosphaisocoumarins **2a** and **2b** in 93 and 86% yield, respectively. When substrate **1c**, having an *ortho*-methyl group on the phenyl ring, was annulated with hex-3-yne, **2c** was obtained in 87% yield. An advantage of the present reactions was demonstrated by the direct cyclization of both electron-rich and electron-deficient substrates **1**, giving the corresponding products **2d–f**. Reaction of sterically bulky substrate, bis(2,3-dimethylphenyl)phosphinic acid, with dec-5-yne also produced the cyclized product **2g** in 89% yield. The phosphinic acid derivative bearing a 1-naphthalenyl group also worked well, resulting in the formation of **2h** in 85% yield. Moreover, annulation of di(thiophen-2-yl)phosphinic acid in *t*BuOH afforded the desired product **2i** in 73% yield. Unsymmetrical internal alkyne promoted the C–H activation followed by cyclization, thus producing **2j** with high regioselectivity. We were also pleased to obtain a single product **2k** in 87% yield when mesityl(phenyl)phosphinic acid reacted with hex-3-yne under the reaction conditions.

Use of Ag_2CO_3 and AgOAc as the co-oxidant system was found to be crucial for efficient annulation of arylphosphinic acid derivatives with electron-deficient diaryl-substituted ethynes such as bis(3-chlorophenyl)ethyne or bis(3-bromophenyl)ethyne, although the terminal alkyne did not react with phophinic acid under the optimized reaction conditions.

Annulation of phosphonic monoesters with alkynes: We became interested in the use of phosphonic monoester directing groups for a single-step phosphaisocoumarin synthesis through C–H bond functionalization. In contrast to pioneering works, a protocol for cyclization of phosphonic

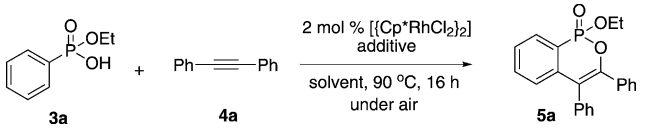


Scheme 3. Rh-catalyzed annulation reactions of phosphinic acids with dialkyl-substituted alkynes. Reagents and conditions: **1** (0.15 mmol), **4** (0.23 mmol), $[\{Cp^*RhCl_2\}_2]$ (2 mol%), Ag_2CO_3 (0.15 mmol), AgOAc (0.15 mmol), *t*BuOH (1 mL), 90°C, 16 h. Numbers in parentheses indicate isomeric ratio.

monoesters gave the phosphaisocoumarins with an alkoxy group on phosphorus; such compounds are readily transformed into useful functional groups including the hydroxyl group.

We initiated our studies by exploring the use of additives and solvents for the catalytic annulation of 1,2-diphenylethyne (**4a**) by ethyl phenylphosphonic monoester (**3a**). Similar tendencies were observed under the optimum reaction conditions to that of annulation of phosphinic acid, which are summarized in Table 1. The use of $AgSbF_6$ and $AgBF_4$, which are known to positively influence Rh-catalyzed C–H functionalization reactions, was tested; however, these systems proved to be incompatible with the cyclization of **3a** with alkyne **4a** (Table 1, entries 2 and 3). Interestingly, the use of AgOAc (0.5 equiv) or Ag_2CO_3 (0.5 equiv) was found to be efficient, provided that reactions were conducted under air, whereas copper salts showed low reactivity (Table 1, entries 4–6). Further screening of the oxidant revealed that the addition of Ag_2CO_3/AgOAc (0.5 equiv each) as a co-oxidant dramatically improved the conversion to over 80% in *t*BuOH (Table 1, entry 8). Surprisingly, the best yield (90%) was obtained under identical reaction conditions of annulation of phosphinic acid with alkyne by using a stoichiometric amount of Ag_2CO_3 and AgOAc together (Table 1, entry 9). The attempted synthesis of phosphaisocoumarins in *t*AmOH or 1,4-dioxane occurred less efficiently (Table 1, entries 10 and 11).

Table 1. Optimization of C–H annulation.[a]

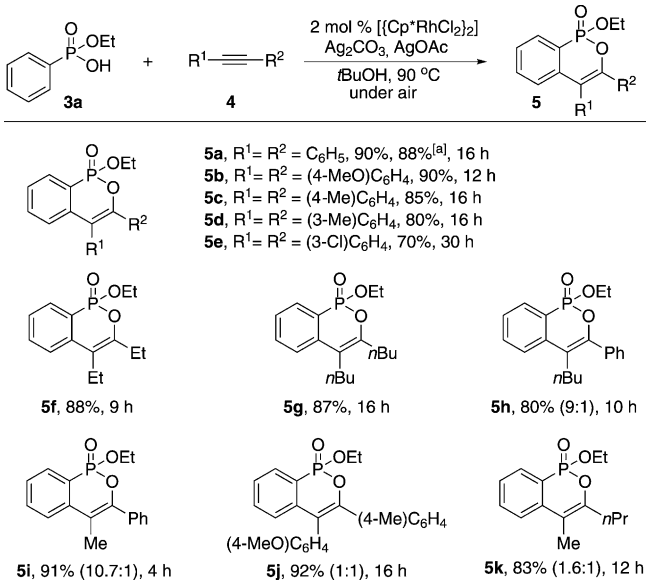


3a 4a 5a

Entry	Additive (equiv)	Solvent	Yield [%][b]
1	none	*t*BuOH	0
2	$AgSbF_6$ (0.5)	*t*BuOH	0
3	$AgBF_4$ (0.5)	*t*BuOH	0
4	$Cu(OAc)_2{\cdot}H_2O$ (0.5)	*t*BuOH	23
5	AgOAc (0.5)	*t*BuOH	45
6	Ag_2CO_3 (0.5)	*t*BuOH	57
7	Ag_2CO_3 (0.5)/$Cu(OAc)_2{\cdot}H_2O$ (0.5)	*t*BuOH	49
8	Ag_2CO_3 (0.5)/AgOAc (0.5)	*t*BuOH	81
9	Ag_2CO_3 (1)/AgOAc (1)	*t*BuOH	90
10	Ag_2CO_3 (1)/AgOAc (1)	*t*AmOH	68
11	Ag_2CO_3 (1)/AgOAc (1)	1,4-dioxane	49

[a] Reaction conditions: **3a** (0.15 mmol), **4a** (0.23 mmol), [{Cp*RhCl$_2$}$_2$] (2 mol%), additive, solvent (1 mL), 90°C, 16 h. [b] Yield of isolated product.

We next explored the scope of the Rh-catalyzed C–H annulation with internal alkynes, including unsymmetrical disubstituted alkynes **4**, by using the optimized catalytic conditions (Scheme 4). Reaction of ethyl phenylphosphonic monoester (**3a**) with various diaryl-substituted alkynes proceeded smoothly to provide the desired products **5a–d** in good to excellent yields. Synthesis of phosphaisocoumarin



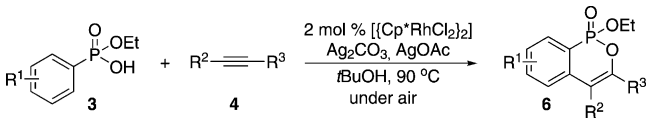
Scheme 4. Rh-catalyzed C–H annulation of ethyl phenylphosphonic monoester with various alkynes. Reagents and conditions: **3a** (0.15 mmol), **4** (0.23 mmol), [{Cp*RhCl$_2$}$_2$] (2 mol%), Ag_2CO_3 (0.15 mmol), AgOAc (0.15 mmol), *t*BuOH (1 mL), 90°C. Numbers in parentheses indicate isomeric ratio. [a] **3a** (1.0 mmol), **4** (1.5 mmol), [{Cp*RhCl$_2$}$_2$] (2 mol%), Ag_2CO_3 (1.0 mmol), AgOAc (1.0 mmol), *t*BuOH (6.7 mL), 90°C, 16 h.

was performed on 1.0 mmol scale without encountering problems, thereby delivering **5a** in excellent yield.

Notably, electron-deficient (thus deactivated for an oxidative coupling) bis(3-chlorophenyl)ethyne was effectively converted, generating **5e** in 70% yield, although longer reaction time was required. Dialkyl-substituted alkynes were converted with high yields, furnishing the desired phosphaisocoumarins **5f** and **5g**, as did diaryl-substituted alkynes. The unsymmetrical disubstituted alkynes could be employed, giving a unique reactivity, thereby illustrating the practicalities of the developed reaction. Various unsymmetrical alkyne substrates provided the desired product **5h–k** in high yields, and **5h** and **5i** were predominantly produced with high regioselectivity. However, unfortunately, only low site selectivity of products **5j** and **5k** was observed.

To establish the synthetic versatility, we probed the scope of the reaction with arylphosphonic monoesters containing useful functional groups with internal alkynes (Table 2). Substrates with a halogen atom gave the corresponding products in high yields (Table 2, entries 1–3). Indeed, *para*-fluoro substituted substrate reacted with unsymmetrically substituted alkyne with high regioselectivity, providing phosphaisocoumarin **6b**. The substrate scope of this reaction was found to be remarkably broad in terms of tolerance towards a strongly electron-withdrawing acetyl group on the aryl ring (Table 2, entry 4). Annulation of electron-rich substrates afforded phosphaisocoumarins **6e–j** in 85–95% isolated yields (Table 2, entries 5–10). It should be mentioned that valuable functional groups such as a free hydroxyl group was completely tolerated under the present reaction conditions (Table 2, entry 11). Ethyl naphthalen-1-ylphos-

Table 2. Substrate scope for C–H annulation of arylphosphonic monoesters with alkynes.[a,b]



3 4 6

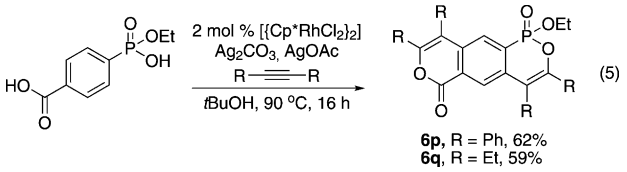
Entry	R^1	R^2	R^3	Time [h]	6	Yield [%]
1	4-F	Ph	Ph	16	**6a**	82
2	4-F	Me	Ph	5	**6b**	84 (10:1)
3	4-I	(4-MeO)C_6H_4	(4-MeO)C_6H_4	16	**6c**	86
4	4-Ac	Ph	Ph	16	**6d**	78
5	2-Me	(4-Me)C_6H_4	(4-Me)C_6H_4	16	**6e**	92
6	2-Me	Me	Ph	6	**6f**	95 (10:1)
7	3-Me	(4-MeO)C_6H_4	(4-MeO)C_6H_4	16	**6g**	86
8	3-Me	Me	Ph	6	**6h**	85 (8.8:1)
9	4-MeO	Ph	Ph	16	**6i**	93
10	4-MeO	Me	Ph	6	**6j**	90 (6.7:1)
11	4-OH	(4-Me)C_6H_4	(4-Me)C_6H_4	16	**6k**	76
12	[c]	(3-Me)C_6H_4	(3-Me)C_6H_4	16	**6l**	89
13	[c]	Me	Ph	8	**6m**	82 (10:1)

[a] Reaction conditions: **3** (0.15 mmol), **4** (0.23 mmol), [{Cp*RhCl$_2$}$_2$] (2 mol%), Ag_2CO_3 (0.15 mmol), AgOAc (0.15 mmol), *t*BuOH (1 mL), 90°C. [b] Numbers in parentheses indicate isomeric ratio. [c] Ethyl naphthalen-1-ylphosphonic monoester was used as substrate **3**.

phonic monoester gave the cyclic compounds **6l** and **6m** with high yields and selectivities (Table 2, entries 12 and 13).

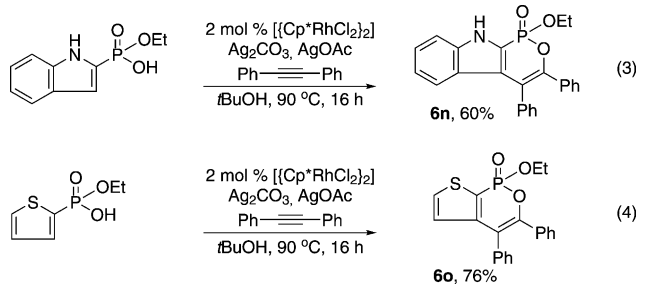
This method was also effective for the direct annulation of substrates containing heterocyclic moieties, such as ethyl 1*H*-indol-2-ylphosphonic monoester and ethyl thiophen-2-ylphosphonic monoester (Scheme 5).

Surprisingly, the *para*-carboxylic acid substituted phenylphosphonic monoester smoothly cyclized with internal alkynes to give **6p** and **6q** in 62 and 59% yield, respectively [Eq. (5)].

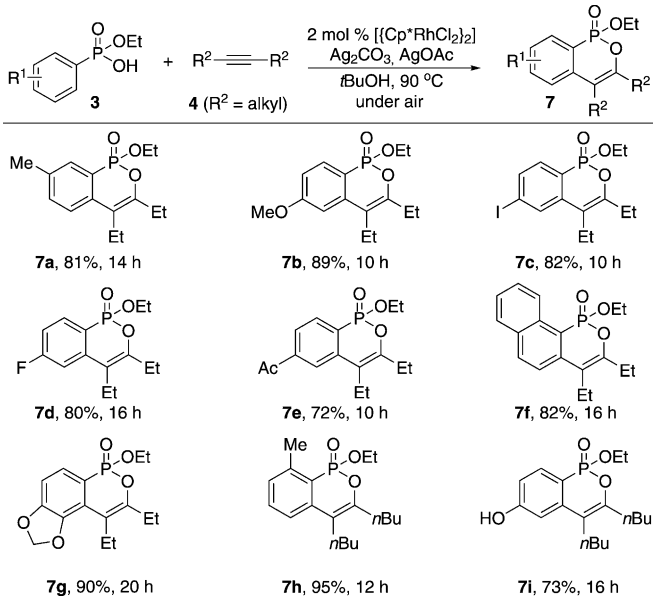


There was little difference in reactivity between diaryl and dialkyl substituted alkynes (Scheme 6). A variety of arylphosphonic monoesters, with *meta*- or *para*-substituents, furnished the desired products **7a** and **7b**, respectively, with excellent yields. The catalytic system proved to be broadly applicable and was found to be tolerant of electron-withdrawing functional groups such as iodo, fluoro and ketone substituents (**7c**–**e**). Exposure of naphthalen-1-ylphosphonic monoester with hex-3-yne in the presence of [{Cp*RhCl$_2$}$_2$] catalyst led to the formation of phosphaisocoumarin **7f** in 82% yield.

Unexpectedly, C–H activation of 3,4-(methylenedioxy)-phenylphosphonic monoester occurred at C2 instead of the sterically less hindered C6 position to afford product **7g** in



Scheme 5. Rhodium-catalyzed oxidative cyclization of phosphonic monoesters with alkyne.

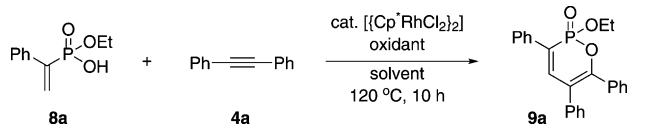


Scheme 6. Rh-catalyzed C–H annulation of arylphosphonic monoesters with dialkyl-substituted alkynes. Reagents and conditions: **3** (0.15 mmol), **4** (0.23 mmol), [{Cp*RhCl$_2$}$_2$] (2 mol%), Ag_2CO_3 (0.15 mmol), AgOAc (0.15 mmol), *t*BuOH (1 mL), 90°C.

90% yield, whereas most substrates underwent rhodium-catalyzed cyclization regioselectively at the sterically less hindered reaction site. Although the the reasons behind the observed selectivity remain unclear at this stage, one plausible explanation is that coordination of the 3-oxy could participate in C–H activation of the C2 reaction site.

As a consequence of the application of our novel step-economical strategy for annulation, we wished to develop a direct synthetic method to generate phosphorus 2-pyrones by using the cyclization reaction of alkenylphosphonic monoesters with alkynes. Gratifyingly, the envisioned direct reaction for the formation of phosphorus 2-pyrones occurred readily with alkenylphosphonic monoester to give the corresponding phosphorus 2-pyrones (Table 3). When the established reaction conditions (Ag_2CO_3 and AgOAc as co-oxidant in *t*BuOH at 120°C) were applied to cyclization of **8a**, product **9a** was obtained in 21% yield (Table 3, entry 1). Employing Ag_2CO_3 as the sole oxidant with 2 mol% [{Cp*RhCl$_2$}$_2$] gave desired product in 19% yield, which re-

Table 3. Optimization studies for the formation of phosphorus 2-pyrones through C–H functionalization.[a]



8a 4a 9a

Entry	Oxidant (equiv)	Solvent	Yield [%][b]
1	Ag_2CO_3 (1)/AgOAc (1)	*t*BuOH	21
2	Ag_2CO_3 (1)	*t*BuOH	19
3	Ag_2CO_3 (1)	toluene	30
4	Ag_2CO_3 (1)	C_6H_5Cl	68
5	Ag_2CO_3 (1)	*t*AmOH	65
6	Ag_2CO_3 (1)	DMF	75
7	Ag_2O (1)	DMF	0
8	$Cu(OAc)_2$. H_2O (1)	DMF	25
9	Ag_2CO_3 (2)	DMF	82

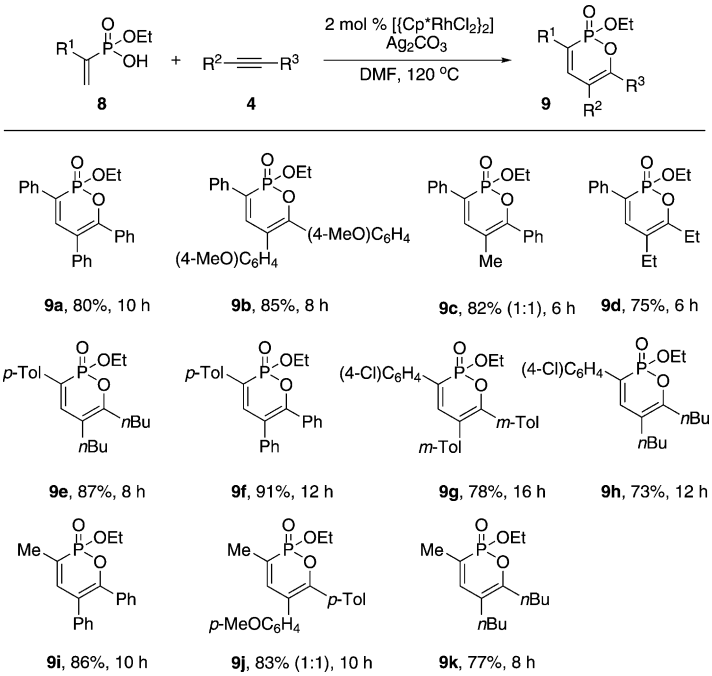
[a] Reaction conditions: **8a** (0.15 mmol), **4a** (0.23 mmol), [{Cp*RhCl$_2$}$_2$] (2 mol%), oxidant, solvent (1 mL), 120°C, 10 h under N_2. [b] Determined by ^{1}H NMR spectroscopic analysis of the crude products using CH_2Br_2 as internal standard.

vealed that there was no significant difference between co-oxidant Ag_2CO_3/AgOAc and single Ag_2CO_3 (Table 3, entry 2). After surveying a wide array of organic solvents, we observed that the use of *N*,*N*-dimethylformamide (DMF) gave the best reactivity (Table 3, entries 2–6). Attempted rhodium-catalyzed annulation with other oxidants such as AgO and $Cu(OAc)_2{\cdot}H_2O$ turned out to be unsuitable for efficient annulation of **8a** with diphenylethyne (Table 3, entries 7 and 8). Further screening of reaction conditions revealed that the use of 2.0 equiv Ag_2CO_3 increased the yield to 82% (Table 3, entry 9).

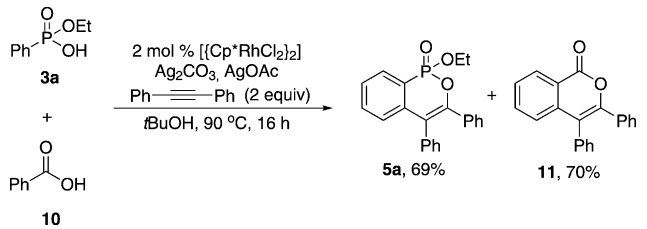
With the optimized conditions in hand, we examined the scope of this C–H annulation protocol (Scheme 7). Ethyl (1-phenylvinyl)phosphonic monoester **8a** reacted with diaryl-substituted alkynes to give **9a** and **9b** in high yields. Unsymmetrical internal alkynes and dialkyl-substituted alkynes also worked well (**9c**–**e**).

Electron-deficient alkenylphosphonic monoesters underwent efficient cyclization with alkynes, affording the desired product **9g** and **9h** in 78 and 73% yields, respectively. We were pleased to obtain annulated products **9i**, **9j**, and **9k** from the reaction of ethyl prop-1-en-2-ylphosphonic monoester. Considering the potential bioactivities of phosphorous 2-pyrones, this approach for the syntheses of phosphorous 2-pyrones is valuable for future applications.

Mechanistic studies: We conducted a series of experiments to establish the C–H annulation reaction mechanism. First, competition experiments with **3a** were conducted to gain insight into the innate ability of phosphonic monoester as a directing group for C–H bond activation (Scheme 8). Treatment of equimolar amounts of phenylphosphonic monoester (**3a**) and benzoic acid (**10**) with 2 equiv diphenylethyne under the optimized reaction conditions gave **5a** and **11** in 69 and 70% yields, respectively; thereby, the phosphonic monoester turned out to be a directing group as effective as



Scheme 7. Rh-catalyzed annulations of alkenylphosphonic esters with alkynes. Reagents and conditions: **8** (0.15 mmol), **4** (0.23 mmol), [{Cp*RhCl$_2$}$_2$] (2 mol%), Ag_2CO_3 (1 equiv), DMF (1 mL), 120°C, 10 h under N_2. Numbers in parentheses indicate isomeric ratio.

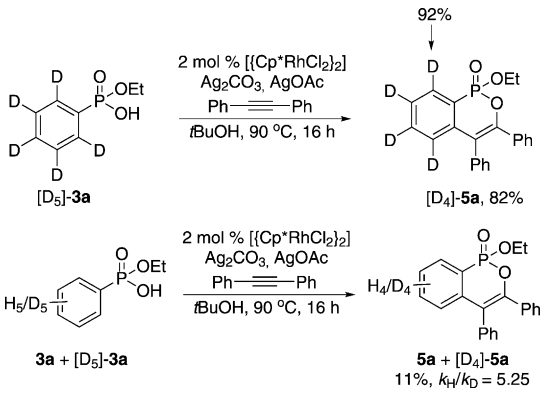


Scheme 8. Competition experiments of C–H annulation by using phosphonic monoester **3a**.

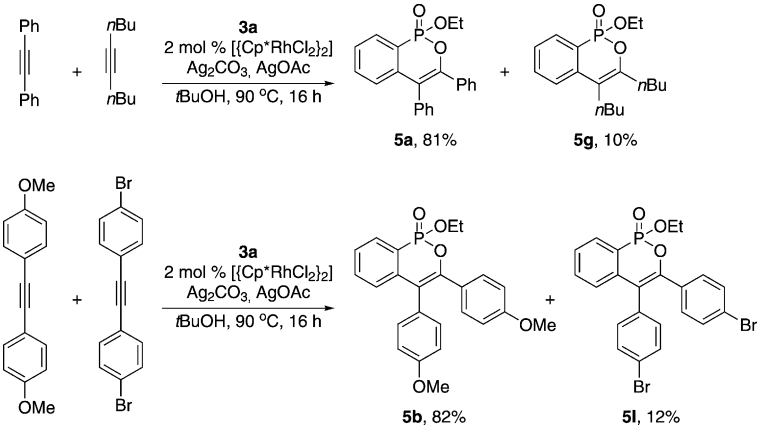
a carboxylic acid functional group for C–H functionalization.

Next, mechanistic studies with isotopically labeled substrate [D_5]-**3a** revealed the C–H bond metalation to be irreversible in nature (Scheme 9). A significant KIE was observed ($k_H/k_D = 5.3$),[13] implying that C–H bond cleavage at the 2-position of phosphonic monoester is most likely involved in the rate-determining step.

Further insightful data were acquired by intermolecular competition experiments between a range of alkynes with ethyl phenylphosphonic monoester (**3a**) (Scheme 10). Substrate **3a** was treated with diphenylethyne and dec-5-yne (1.5 equiv each) to produce the corresponding phosphaisocoumarin **5a** predominantly. A competition experiment between electron-rich and electron-deficient diaryl-substituted alkyne afforded mainly phosphaisocoumarin **5b** derived from the electron-rich alkyne. These results revealed that electron-rich alkynes were preferentially converted into the



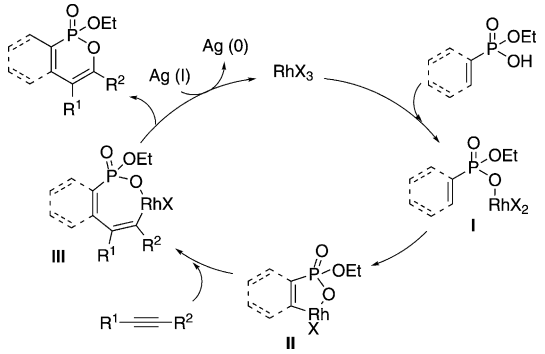
Scheme 9. Experiments with isotopically labeled compound.



Scheme 10. Alkyne competition experiments.

desired product, which is similar to Rh-catalyzed oxidative annulation of carboxylic acids.

In light of these experiments, a plausible mechanism for the reaction of phosphonic monoester with alkyne was developed (Scheme 11). The proposed catalytic cycle is initiated by coordination of the phosphonic monoester to Rh^{III} to afford rhodium(III) phosphonate **I**. Subsequent *o*-metalation to furnish rhodacycle intermediate **II**, alkyne insertion, and reductive elimination gives the corresponding cyclized products, phosphaisocoumarins or phosphorous 2-pyrones.



Scheme 11. A proposed mechanism.

Conclusion

We have described a rhodium-catalyzed oxidative phosphaisocoumarin synthesis by using cyclization of phosphonic acid derivatives with alkynes. A range of both diarylphosphinic acids and arylphosphonic monoesters were selectively cyclized in high yield with excellent functional group tolerance. Additionally, we found that the reaction with alkenylphosphonic monoesters proceeded smoothly to afford the corresponding phosphorus 2-pyrones through oxidative annulations with alkynes. Mechanistic studies indicate that C–H bond metalation is irreversible and a rate-determining key step.

Experimental Section

General procedure for Rh-catalyzed oxidative cyclization of arylphosphinic acid 1a with dialkyl substituted alkynes: To a screw-top V-Vial were added diphenylphosphinic acid (**1a**; 32.7 mg, 0.15 mmol), hex-3-yne (18.5 mg, 0.23 mmol), $[\{Cp^*RhCl_2\}_2]$ (1.9 mg, 0.003 mmol), Ag_2CO_3 (41.0 mg, 0.15 mmol), and AgOAc (26.0 mg, 0.15 mmol) in *t*BuOH (1.0 mL). The resulting mixture was stirred under air at 90 °C (bath temperature) for 16 h. After filtration through Celite and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1:2) to give **2a** (42.0 mg, 93%) as a colorless oil. R_f = 0.3 (EtOAc/hexane = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.77 (m, 2H), 7.59–7.51 (m, 2H), 7.50–7.44 (m, 3H), 7.30–7.26 (m, 1H), 2.60–2.34 (m, 4H), 1.23–1.16 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.8 (d, J = 11.5 Hz), 137.4 (d, J = 5.3 Hz), 132.7 (d, J = 2.8 Hz), 132.6 (d, J = 2.3 Hz), 132.2 (d, J = 10.9 Hz), 130.6 (d, J = 12.4 Hz), 130.3 (d, J = 144.2 Hz), 128.4 (d, J = 13.8 Hz), 126.7 (d, J = 14.5 Hz), 123.6 (d, J = 129.8 Hz), 123.5 (d, J = 10.0 Hz), 114.4 (d, J = 11.2 Hz), 25.5 (d, J = 4.8 Hz), 20.9, 14.2, 11.6 ppm; ^{31}P NMR (121 MHz, $CDCl_3$): δ = 10.34 ppm; IR (film): 3059, 1633, 1469, 1240, 1130, 1046 cm^{-1}; HRMS (EI): m/z calcd for $C_{26}H_{19}O_2P$: 298.1123; found: 298.1123.

General procedure for Rh-catalyzed oxidative cyclization of phenylphosphonic monoester 3a with alkynes: To a screw-top V-Vial were added ethyl phenylphosphonic monoester (**3a**; 28.0 mg, 0.15 mmol), diphenylethyne (**4a**; 40.0 mg, 0.23 mmol), $[\{Cp^*RhCl_2\}_2]$ (1.9 mg, 0.003 mmol), Ag_2CO_3 (41.0 mg, 0.15 mmol), and AgOAc (26.0 mg, 0.15 mmol) in *t*BuOH (1 mL). The resulting mixture was stirred under air at 120 °C (bath temperature) for 16 h. After filtration through Celite and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1:3) to give **5a** (49.0 mg, 90%) as a white solid. R_f = 0.3 (EtOAc/hexane = 1:3); m.p. 123–126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94–7.92 (m, 1H), 7.50–7.40 (m, 2H), 7.39–7.33 (m, 3H), 7.25–7.11 (m, 7H), 6.98–6.93 (m, 1H), 4.33–4.19 (m, 2H), 1.32 ppm (t, J = 7.08 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8 (d, J = 10.66 Hz), 140.2 (d, J = 6.95 Hz), 136.0, 134.5 (d, J = 5.85), 132.8 (d, J = 3.50 Hz), 131.5, 129.3 (d, J = 9.11 Hz), 128.89, 128.85, 128.5, 127.8, 127.66, 127.64 (d, J = 15.33 Hz), 127.1 (d, J = 11.91 Hz), 120.9 (d, J = 181.70 Hz), 119.8 (d, J = 12.02 Hz), 63.0 (d, J = 7.21 Hz), 16.4 ppm (d, J = 5.86 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 10.58 ppm; IR (film): 2982,

1591, 1469, 1443, 1275, 1023, 953, 757 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{22}H_{19}O_3P$: 362.1072; found: 362.1072.

General procedure for Rh-catalyzed oxidative cyclization of arylphosphonic monoester 3 with alkynes: To a screw-top V-Vial were added ethyl *o*-tolylphosphonic monoester (30.0 mg, 0.15 mmol), 1,2-di-*p*-tolylethyne (46.4 mg, 0.23 mmol), [{Cp*$RhCl_2$}$_2$] (1.9 mg, 0.003 mmol), Ag_2CO_3 (41.0 mg, 0.15 mmol), and AgOAc (26.0 mg, 0.15 mmol) in *t*BuOH (1 mL). The resulting mixture was stirred under air at 90 °C (bath temperature) for 16 h. After filtration through Celite and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1:3) to give **6e** (55.8 mg, 92 %) as a pale-yellow solid. R_f = 0.3 (EtOAc/hexane = 1:3); m.p. 72–75 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.26 (m, 1H), 7.18–7.11 (m, 5H), 7.07–7.05 (m, 2H), 6.95 (d, *J* = 8.04 Hz, 2H), 6.79–6.76 (m, 1H), 4.31–4.14 (m, 2H), 2.75 (d, *J* = 1.04 Hz, 3H), 2.37 (s, 3H), 2.25 (s, 3H), 1.33 ppm (t, *J* = 7.08 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.1 (d, *J* = 10.98 Hz), 141.4 (d, *J* = 7.33 Hz), 141,1 (d, *J* = 9.10 Hz), 138.3, 137.4, 133.6, 132.3 (d, *J* = 2.19 Hz), 131.7 (d, *J* = 6.60 Hz), 131.4, 129.8, 129.6 (d, *J* = 5.28 Hz), 128.7, 128.3, 125.1 (d, *J* = 12.00 Hz), 119.4 (d, *J* = 177.17 Hz), 118.8 (d, *J* = 11.74 Hz), 62.6 (d, *J* = 7.20 Hz), 21.5 (d, *J* = 4.92 Hz), 21.2 (d, *J* = 7.32 Hz), 16.4 ppm (d, *J* = 6.38 Hz); ^{31}P NMR (161 MHz, $CDCl_3$): δ = 10.04 ppm; IR (film): 2981, 2238, 1609, 1508, 1260, 1027, 973, 794 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{25}H_{25}O_3P$: 404.1541; found: 404.1544.

General procedure for Rh-catalyzed oxidative cyclization of arylphosphonic monoester 3 with dialkyl-substituted alkynes: To a screw-top V-Vial were added ethyl 4-methoxyphenylphosphonic monoester (32.4 mg, 0.15 mmol), hex-3-yne (18.6 mg, 0.23 mmol), [{Cp*$RhCl_2$}$_2$] (1.9 mg, 0.003 mmol), Ag_2CO_3 (41.0 mg, 0.15 mmol), and AgOAc (26.0 mg, 0.15 mmol) in *t*BuOH (1 mL). The resulting mixture was stirred under air at 90 °C (bath temperature) for 16 h. After filtration through Celite and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1:1) to give **7b** (39.6 mg, 89 %) as a pale-yellow oil. R_f = 0.3 (EtOAc/hexane = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79 (dd, *J* = 14.56, 8.48 Hz, 1H), 6.94–6.90 (m, 2H), 4.20–4.05 (m, 2H), 3.87 (s, 3H), 2.57–2.42 (m, 4H), 1.30 (t, *J* = 7.06 Hz, 3H), 1.22 (t, *J* = 7.38 Hz, 3H), 1.16 ppm (t, *J* = 7.52 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.3 (d, *J* = 2.99 Hz), 152.3 (d, *J* = 10.60 Hz), 140.9 (d, *J* = 8.17 Hz), 131.6 (d, *J* = 10.29 Hz), 114.5 (d, *J* = 11.73 Hz), 113.2 (d, *J* = 186.63 Hz), 111.8 (d, *J* = 16.42 Hz), 109.9 (d, *J* = 13.40 Hz), 62.3 (d, *J* = 6.41 Hz), 55.3, 25.4 (d, *J* = 5.86 Hz), 20.9, 16.3 (d, *J* = 6.34 Hz), 14.1, 11.7 ppm; ^{31}P NMR (161 MHz, $CDCl_3$): δ = 12.01 ppm; IR (film): 2970, 1630, 1598, 1475, 1268, 1165, 1031, 956, 822 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{15}H_{21}O_4P$: 296.1177; found: 296.1179.

Synthesis of compound 6o: To a screw-top V-Vial were added ethyl thiophen-2-ylphosphonic monoester (28.8 mg, 0.15 mmol), diphenylethyne (**4a**; 40.0 mg, 0.23 mmol), [{Cp*$RhCl_2$}$_2$] (1.9 mg, 0.003 mmol), Ag_2CO_3 (41.0 mg, 0.15 mmol), and AgOAc (26.0 mg, 0.15 mmol) in *t*BuOH (1.0 mL). The resulting mixture was stirred under air at 90 °C (bath temperature) for 16 h. After filtration through Celite and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1:2) to give **6o** (42.0 mg, 76 %) as a yellow oil. R_f = 0.3 (EtOAc/hexane = 1:2); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (q, *J* = 3.89 Hz, 1H), 7.36–7.32 (m, 3H), 7.26–7.12 (m, 7H), 6.73 (q, *J* = 2.80, 1H), 4.34–4.20 (m, 2H), 1.38 ppm (t, *J* = 7.08 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.7 (d, *J* = 9.14 Hz), 148.4 (d, *J* = 11.90 Hz), 136.3, 133.6 (d, *J* = 7.18 Hz), 132.8 (d, *J* = 10.12 Hz), 130.7, 128.9, 128.6, 127.9, 127.7, 127.4, 127.2, 116.2 (d, *J* = 8.99 Hz), 116.1 (d, *J* = 200.43 Hz), 63.9 (d, *J* = 6.60 Hz), 16.4 ppm (d, *J* = 6.09 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 5.82 ppm; IR (film): 2982, 2241, 1595, 1490, 1268, 1200, 1116, 1005, 966, 741 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{20}H_{17}O_3PS$: 368.0636; found: 368.0633.

Synthesis of compound 6p: To a screw-top V-Vial were added 4-(ethoxy(hydroxy)phosphoryl)benzoic acid (34.5 mg, 0.15 mmol), diphenylethyne (**4a**; 67.0 mg, 0.33 mmol), [{Cp*$RhCl_2$}$_2$] (1.9 mg, 0.003 mmol), Ag_2CO_3 (41.0 mg, 0.15 mmol), and AgOAc (26.0 mg, 0.15 mmol) in *t*BuOH (1.0 mL). The resulting mixture was stirred under air at 90 °C (bath temperature) for 16 h. After filtration through Celite and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1:2) to give **6p** (54.0 mg, 62 %) as a pale-green solid. R_f = 0.3 (EtOAc/hexane = 1:5); m.p. 225–228 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02–8.00 (m, 1H), 7.80–7.76 (m, 1H), 7.44–7.40 (m, 6H), 7.35–7.13 (m, 14H), 4.26–4.15 (m, 2H), 1.24 ppm (t, *J* = 7.06 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1, 151.8, 148.5 (d, *J* = 10.47 Hz), 139.1 (d, *J* = 6.79 Hz), 137.3 (d, *J* = 16.69 Hz), 135.1, 134.0 (d, *J* = 5.37 Hz), 133.6, 132.4, 131.3, 130.2 (d, *J* = 117.00 Hz), 129.36, 129.31, 129.26, 129.21, 128.9, 128.8, 128.6, 128.5, 128.0 (d, *J* = 11.93 Hz), 127.8 (d, *J* = 17.43 Hz), 126.9 (d, *J* = 10.49 Hz), 126.7, 123.3 (d, *J* = 2.43 Hz), 119.9 (d, *J* = 11.00 Hz), 116.4, 63.5 (d, *J* = 6.66 Hz), 16.3 ppm (d, *J* = 5.82 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 7.92 ppm; IR (film): 3058, 2981, 2245, 1736, 1595, 1468, 1281, 1071, 1025, 952, 701 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{37}H_{27}O_5P$: 582.1596; found: 582.1594.

General procedure for Rh-catalyzed oxidative cyclization of alkenylphosphonic monoester 8 with alkynes: To a test tube were added alkenylphosphonic monoester (**8a**; 32.0 mg, 0.15 mmol), diphenylethyne (**4a**; 40.0 mg, 0.23 mmol), [{Cp*$RhCl_2$}$_2$] (1.9 mg, 0.003 mmol), and Ag_2CO_3 (41.0 mg, 0.15 mmol) in DMF (0.75 mL). The resulting mixture was stirred at 120 °C (bath temperature) for 10 h under N_2. After filtration through Celite and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1:1) to give **9a** (47.0 mg, 80 %) as a colorless oil. R_f = 0.3 (EtOAc/hexane = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.70 (m, 2H), 7.42–7.34 (m, 3H), 7.31–727 (m, 5H), 7.25–7.17 (m, 6H), 4.28–4.18 (m, 2H), 1.29 ppm (t, *J* = 7.08 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.8 (d, *J* = 12.76 Hz), 142.1, 142.0, 138.1 (d, *J* = 1.18 Hz), 134.7 (d, *J* = 10.11 Hz), 133.2 (d, *J* = 6.04 Hz), 129.5, 129.3, 129.1, 128.9 (d, *J* = 4.51 Hz), 128.5, 127.8, 127.6, 127.1 (d, *J* = 7.30 Hz), 124.2 (d, *J* = 168.42 Hz), 117.7 (d, *J* = 16.17 Hz), 63.7 (d, *J* = 6.99 Hz), 16.3 ppm (d, *J* = 6.06 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 9.49 ppm; IR (film): 2982, 2240, 1615, 1536, 1444, 1260, 1159, 1036, 968, 756 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{24}H_{21}O_3P$: 388.1228; found: 388.1227.

Competition experiments of C–H annulation between phosphonic monoester 3a and benzoic acid 10: To a screw-top V-Vial were added ethyl phenylphosphonic monoester (**3a**; 28.0 mg, 0.15 mmol), benzoic acid (**10**; 18.3 mg, 0.15 mmol), diphenylethyne (**4a**; 53.4 mg, 0.3 mmol), [{Cp*$RhCl_2$}$_2$] (1.9 mg, 0.003 mmol), Ag_2CO_3 (41 mg, 0.15 mmol), and AgOAc (26 mg, 0.15 mmol) in *t*BuOH (1.0 mL). The resulting mixture was stirred at 120 °C (bath temperature) for 16 h under air. After filtration through Celite and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1:3) to give **5a** (37.5 mg, 69 %) and **11** (31.3 mg, 70 %).

Experiments with isotopically labeled substrates: To a solution of ethyl 1,2,3,4,5-pentadeuteriophenylphosphonic monoester ([D_5]-**3a**; 38.0 mg, 0.2 mmol) in *t*BuOH (1.3 mL), were added diphenylethyne (**4a**; 53.5 mg, 0.3 mmol), [{Cp*$RhCl_2$}$_2$] (2.5 mg, 2 mol %), Ag_2CO_3 (55.0 mg, 0.2 mmol), and AgOAc (33.0 mg, 0.2 mmol). The resulting mixture was stirred under air at 120 °C (bath temperature) for 16 h. After filtration through Celite and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1:3) to give the desired product (60.0 mg, 82 %) as a white solid. R_f = 0.3 (EtOAc/hexane = 1:3); m.p. 124–127 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98–7.92 (m, 0.08H), 7.49–7.41 (m, 0.16H), 7.35–7.34 (m, 3H), 7.25–7.11 (m, 7H), 6.98–6.94 (m, 0.08H), 4.33–4.19 (m, 2H), 1.32 ppm (t, *J* = 7.06 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.7 (d, *J* = 10.66 Hz), 139.0 (d, *J* = 6.93 Hz), 135.0, 133.4 (d, *J* = 5.60), 131.7 (d, *J* = 2.48 Hz), 130.4, 128.2 (d, *J* = 9.00 Hz), 127.85, 127.80, 127.4, 126.8, 126.62, 127.60 (d, *J* = 15.39 Hz), 126.0 (d, *J* = 12.00 Hz), 119.7 (d, *J* = 167.72 Hz), 118.7 (d, *J* = 11.70 Hz), 61.9 (d, *J* = 6.64 Hz), 15.4 ppm (d, *J* = 6.01 Hz); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 10.64 ppm; IR (film): 2981, 2352, 1598, 1444, 1263, 1159, 1057, 1023, 944, 755 cm^{-1}; HRMS (EI): *m/z* calcd for $C_{22}H_{15}D_4O_3P$: 366.1323; found: 366.1322.

Intermolecular competition experiment between substrates 3a and [D_5]-3a: A mixture of ethyl phenylphosphonic monoester (**3a**; 18.0 mg, 0.1 mmol), ethyl 1,2,3,4,5-pentadeuteriophenylphosphonic monoester ([D_5]-**3a**; 19.0 mg, 0.1 mmol), diphenylethyne (**4a**; 53.5 mg, 0.3 mmol), [{Cp*$RhCl_2$}$_2$] (2.5 mg, 2 mol %), Ag_2CO_3 (55 mg, 0.2 mmol), and AgOAc (33.0 mg, 0.2 mmol) in *t*BuOH (1.3 mL) was stirred under air at 120 °C

(bath temperature) for 1 h. After filtration through Celite and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1:3) to give **5a** and [D_4]-**5a** (8.0 mg, 11%) as a white solid. The ratio of **5a**/[D_4]-**5a** was determined to be 86:14 by ^{1}H NMR spectroscopic analysis.

Competition experiments with alkyne: To a screw-top V-Vial were added ethyl phenylphosphonic monoester (**3a**; 28.0 mg, 0.15 mmol), diphenylethyne (**4a**; 40.0 mg, 0.23 mmol), dec-5-yne (20.7 mg, 0.23), [{Cp*$RhCl_2$}$_2$] (1.9 mg, 0.003 mmol), Ag_2CO_3 (41.0 mg, 0.15 mmol), and AgOAc (26.0 mg, 0.15 mmol) in *t*BuOH (1.0 mL). The resulting mixture was stirred at 90 °C (bath temperature) for 16 h under air. After filtration through Celite and evaporation of the solvents in vacuo, the crude product was purified by column chromatography on silica gel (EtOAc/hexane = 1:3) to give **5a** (44.0 mg, 81%) and **5g** (4.8 mg, 10%).

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