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FULL PAPER

The C-H Bond Functionalization of *1,4*-Benzoquinone by Silver-mediated Regioselective Phosphination and Amination Reactions

Yu-Chang Chang,[a] Pin-Ting Yuan,[a] and Fung-E Hong*[a]

Abstract: The one-pot synthesis of 2,5-bis(diarylphosphoryl)-3,6-bis(arylamino)cyclohexa-2,5-diene-1,4-dione has been achieved from Ag(I)-mediated fully C-H functionalization of 1,4-benzoquinone (BQ) *via* regioselectively dual phosphination and amination reactions. The BQ, diarylphosphine oxide (SPO, $Ar_2PH(=O)$), and imine were reacted under mild conditions. The 1,4-naphthoquinone (NQ) could also be used to replace BQ. When aniline was used instead of its corresponding imine, lower yield of the desired product was obtained. Without the presence of Ag_2CO_3, hydrophosphinylation of imine by SPO occurs as the competitive side reaction. Ag(I) plays versatile roles here, such as a mediator for facilitating the consecutive additions of $Ar_2P(=O)^-$ and aniline on the related β-carbon atoms of BQ, oxidant for hydroquinone (HQ) intermediates to form the substituted BQ counterparts, and inhibitor of the hydrophosphinylation of imine by SPO as side reaction. X-ray crystal structures of several new products were determined. A reaction mechanism is also proposed based on the experimental results.

Introduction

Quinones are remarkable building blocks which could be found in molecules of natural products,[1] antitumor drugs,[2] reactants for flame retardation materials,[3] electroactive ligands for valence-tautomeric metal-ligand systems,[4] π-spacer for electronic interactions between redox-active metal terminus,[5] and catalysts of various oxidation reactions.[6] For example, the 1,4-benzoquinone (BQ), one of the redox-active simple quinones,[7] can be employed to synthesize new phosphate, halogen-free flame retardant of DOPO-HQ where a C_{HQ}-P bond is formed (Figure 1a, HQ: hydroquinone).[3] While the C_{BQ}-N bond containing 2-amino-1,4-napthoquinone derivatives are natural product antibiotics (Figure 1b),[8] the 2,5-bis(amino)benzo-1,4-quinone is a bis-O_{BQ},N-bi-dentate π-conjugated bridging ligand capable of linking two redox-active metal fragments to exhibit interesting electrochemical, magnetic and optical properties (Figure 1c).[9] Among quinones, BQ is also a multi-functional additive in palladium-catalyzed reactions.[10] Namely, BQ stabilizes coordinatively unsaturated active species, promotes the rate of reductive elimination, and oxidizes reduced transition-metal center in a catalytic cycle. Interestingly, the concentration, steric and electronic properties of substituted BQ co-ligands have been shown to have direct influence on the site-selectivity in palladium-catalyzed oxidative C-H activations.[11]

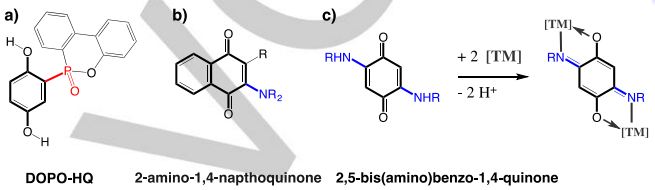

Figure 1. BQ derivatives equipped with C_{BQ}-P or C_{BQ}-N bonds.

Over the past few decades significant development on the subject of C-P bond formation employing transition-metal catalyzed and silver-mediated oxidative reactions has attracted much attention.[12] *H*-phosphinates, and *H*-phosphonates are of the two frequently used substrates for constructing C-P bonds in palladium-catalyzed reactions.[13] Compared with transition-metal free Michaelis-Becker (1897, $(RO)_2P(O)$-H as substrate)[14] and Michaelis-Arbuzov (1900s, $P(OR)_3$)[15] reactions, Hirao reaction is regarded as the seminar work, which employed Pd(0)-catalyzed cross-coupling reaction (1980, $(RO)_2P(O)$-H) for making C-P bonds.[16] While recent studies focused on the coupling between unsaturated (C=C or C≡C) or aromatic C-H and -P(O)H unit,[13] the use of BQ as C-H source has long been on the focus.[17] On the other hand, C-N bond formation employing BQ or NQ as reactant through Michael-type nucleophilic addition has also been reported.[8,18] However, to the best of our knowledge, there is no example that addresses the formations of C-P and C-N bonds on BQ or NQ in one-pot reaction as demonstrated in this work.

Secondary phosphine oxides (SPOs: $R_2P(O)$-H) have been proven to be effective pre-ligands in palladium-catalyzed cross-coupling reactions.[19] It might act as an authentic phosphine ligand through tautomerization to phosphinus acid (PA: R_2P-OH) in the presence of TM salts. Inspired by the enthralling Pd(II)-catalyzed oxidative cross-coupling reactions as shown in Scheme 1a[11,20] and 1b,[21] we initially sought nitrogen-directing imine as a potential alternative of 2-phenylpyridine for constructing C-P bonds with SPO (Scheme 1c). Unexpectedly, the anticipated formation of $C_{imine\text{-}Ar}$-P_{SPO} bond *via* $C_{imine\text{-}Ar}$-H bond activation was not observed (Scheme 1d) despite the analogous Pd(II)-catalyzed C-P bond formation using N-directing (*E*)-azoarenes has been recently reported.[22]

Several elegant synthetic protocols for C-H functionalization of BQ that giving rise to C_{BQ}-halogen[23] or C_{BQ}-C_{Ar}[24] bonds have been nicely established. To our knowledge, we report for the first time an intriguing fully substituted *2,5*-phosphinated and *3,6*-

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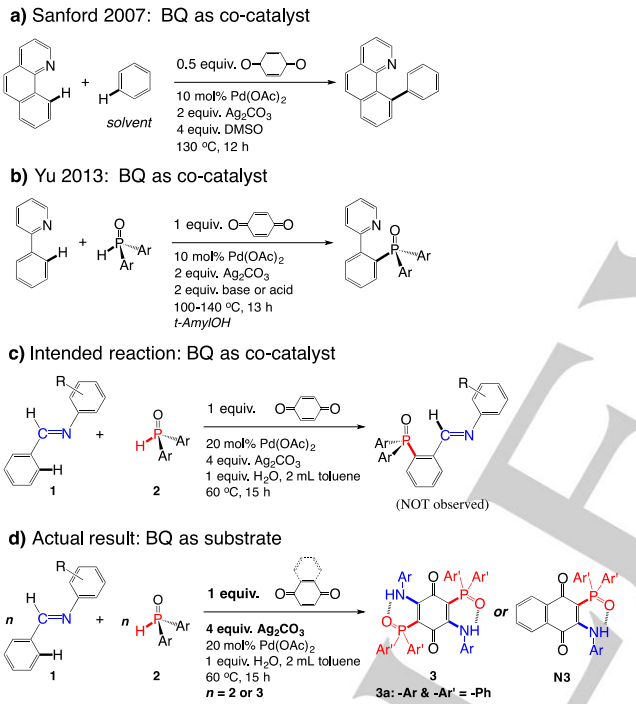
aminated BQ (**3aa**) that could be obtained in a regioselective manner without pre-functionalization of the starting materials using similar reaction conditions to the Pd(II)-catalyzed reactions (Scheme 1a-1b). As demonstrated, the cross-dehydrogenative coupling (CDC)[13e] and dual C_{BQ}-H/P_{SPO}-H and C_{BQ}-H/$N_{aniline}$-H functionalizations of BQ can be carried out in one-pot cascade reaction with good yields under optimized mild conditions. Three major components, Pd(II), Ag(I), and BQ, were typically regarded as *catalyst*, *oxidant*, and *additive* in Pd(II)-catalyzed oxidative reactions for C-H activations;[10b] nevertheless, they turned out to act as *additive*, *mediator/oxidant*, and *reactant* as demonstrated in this study (Scheme 1d). Moreover, one of the specific functions of Ag_2CO_3 has been proven to effectively inhibit the hydrophosphinylation of imine by SPO (**2**).[25] Several crystal structures related to the fully substituted products **3** or **N3** have been well resolved by X-ray diffraction methods.



Scheme 1. Pd(II)-catalyzed C-C or C-P bond formation with 1,4-benzoquinone employed as co-catalyst (**1a**,[11a] **1b**[21]) or substrate in this work (**1d**).

Results and Discussion

Our efforts towards optimizing the reaction conditions were shown in Table 1-3. The distinct reactivity of BQ is achieved using (*E*)-N,1-diphenylmethanimine (**1a**) as substrate. As known, imine is a common *N*-directing substrate used in transition-metal catalyzed C-H activation.[26] However, in the presence of diphenylphosphine oxide (**2a**), no *ortho*-C-H on phenyl groups of **2a** was activated but the formation of **3aa** (Table 1). The yield of **3aa** was improved with the increase of temperature, reaching maximum of 62% at 60 °C (entries 1-5). Addition of trace amount of water (1 equiv.) also helps promoting the yield of **3aa** to 76% (entry 6). This could be attributed to the increase of hydrolysis rate of imine (**1a** in this case) to aniline. Besides, the proton released from **2a** could also play a role in acid-catalyzed imine hydrolysis. However, the yield of **3aa** is reduced when H_2O was added more than one molar equivalent,[27] which suggests that too fast hydrolysis rate of imine will negatively affect the formation of the target compound. Moreover, the formation of excess aniline can be coordinated to Ag(I) cation, and eventually leads to inactive Ag(I) complex(es). Entries 6-9 show that the optimal reaction time is 15 hours, and entries 6 and 10-13 illustrate that toluene is the best solvent among DCM, THF, DMF, and H_2O. Degassed toluene was found crucial to the reaction yield since SPO can be oxidized to $R_2P(O)$-OH in the presence of dissolved oxygen.

The fact that the yield of **3aa** appears to be stoichiometrically proportional to the amounts of added $Pd(OAc)_2$ (entries 6 and 14-16 in Table 1) is noteworthy. The yields of **3aa** were 76%, 66%, 61%, and 57% for the addition of 20 mol-%, 10 mol-%, 5 mol-% and null of $Pd(OAc)_2$, respectively. Initially, this observation seemingly contradicts to the idea that large excess amount of $R_2P(O)$-H substrates would hinder the formation of C-P coupling product in the Pd(II)-catalyzed reaction (Scheme 1b).[21] As known, a relatively stable SPO-coordinated Pd(II)-complex could be easily obtained from the reaction of $R_2P(O)$-H with $Pd(OAc)_2$.[28] However, in this reaction, $Pd(OAc)_2$ is regarded as a beneficial additive rather than the major catalytic agent (entries 6 and 14-16). When 10 mol-% of SPO-coordinating [μ_2-ClPd(PPh_2-OH)(PPh_2O)]$_2$ (**Pd-I**) was employed as additive, the yield of **3b** is similar to the case without the addition of $Pd(OAc)_2$ (entry 17 vs. 16). This observation demonstrates that SPO-coordinated **Pd-I** is ineffective for the reaction, which is indeed consistent with the results of Yu et al. (i.e. Pd-SPO complex is an inactive catalyst for C-P bond formation).[21] In addition, 10 mol-% of two palladacycles, [μ_2-(OAc)(η^2-C,N-**1a**)Pd]$_2$ (**Pd-II**) and [μ_2-Cl(η^2-C,N-**1a**)Pd]$_2$ (**Pd-III**), were employed as additives (entries 18-19), respectively. However, no discernible difference in yield of **3aa** was obtained (entries 17-19). Moreover, using 20 mol-% of $Pd(cod)Cl_2$ yielded **3aa** in matching yield to that without the presence of $Pd(OAc)_2$ (c.f. entries 20 and 16). Although $Pd(TFA)_2$ has been reported as an excellent catalyst for C_{Ar}-C_{BQ} coupling reactions,[25] it is, obviously, not a competitive Pd(II) additive here in this type of reaction. The X-ray structure of **3aa** confirms the formation of fully substituted product through 2,5-phosphinations and 3,6-aminations (Figure 2a). There are two intramolecular hydrogen bonds between $O_3\cdots H_1A$ (1.925 Å) and $O_4\cdots H_2A$ (1.772 Å).

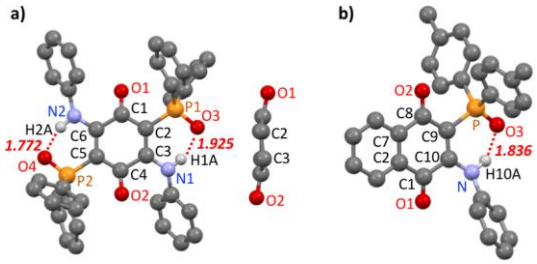
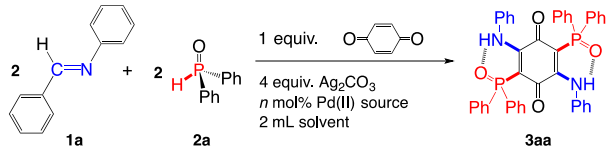


Figure 2. Crystal structures of (a) product **3aa** and (b) **N3ab**. Hydrogen atoms except the N-H protons are omitted for clarity.

Table 1. Optimizing the reaction conditions for the formation of **3aa**.[a]



Entry	Additives (mol-%)	Temp. (°C)	H_2O (equiv.)	Time (h)	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$ (20)	100	0	15	Toluene	32
2	$Pd(OAc)_2$ (20)	80	0	15	Toluene	56
3	$Pd(OAc)_2$ (20)	60	0	15	Toluene	62
4	$Pd(OAc)_2$ (20)	40	0	15	Toluene	38
5	$Pd(OAc)_2$ (20)	r.t.	0	15	Toluene	21
6	$Pd(OAc)_2$ (20)	60	1	15	Toluene	76
7	$Pd(OAc)_2$ (20)	60	1	6	Toluene	48
8	$Pd(OAc)_2$ (20)	60	1	12	Toluene	64
9	$Pd(OAc)_2$ (20)	60	1	24	Toluene	70
10	$Pd(OAc)_2$ (20)	60	1	15	DCM	51
11	$Pd(OAc)_2$ (20)	60	1	15	THF	55
12	$Pd(OAc)_2$ (20)	60	1	15	DMF	33
13	$Pd(OAc)_2$ (20)	60	-	15	H_2O	36
14	$Pd(OAc)_2$ (10)	60	1	15	Toluene	66
15	$Pd(OAc)_2$ (5)	60	1	15	Toluene	61
16	$Pd(OAc)_2$ (0)	60	1	15	Toluene	57
17	**Pd-I** (10)	60	1	15	Toluene	50
18	**Pd-II** (10)	60	1	15	Toluene	51
19	**Pd-III** (10)	60	1	15	Toluene	47
20	$Pd(cod)Cl_2$ (20)	60	1	15	Toluene	53
21	$Pd(TFA)_2$ (20)	60	1	15	Toluene	39

[a] Reaction conditions: 2 equiv. of **1a**, 2 equiv. of **2a**, 1 equiv. of BQ, 4 equiv. of Ag_2CO_3, 2mL of degassed solvent. [b] Isolated yields.

The results from the variations of the amount of Ag_2CO_3 and the usages of different Ag(I) sources and $Cu(OAc)_2$ as oxidants in the reaction are compiled in Table 2. Clearly, Ag_2CO_3 is indispensable for the synthesis of **3aa** despite 20 mol-% of $Pd(OAc)_2$ additive was employed (entry 1, Table 2). The yield of **3aa** decreased to 34% when 5 equiv. of Ag_2CO_3 was used (entry 2). The employments of 4 equiv. of Ag_2O and 8 equiv. of Ag(OAc) gave rise to the comparable yields of **3aa** (entries 3-4). In the presence of Ag(OAc), 7% of acetanilide was isolated, indicating the existence of aniline in the reaction system. Oxidants such as AgF, $AgBF_4$ and $Cu(OAc)_2$ are ineffective here (entries 6-8). Recently, Larrosa[29] and Sanford[30] had independently come to the same conclusion that Ag(I) is capable of activating electron-deficient arene C-H bond through a concerted metalation-deprotonation (CMD) mechanism[31] when appropriate base such as CO_3^{2-}, OAc^-, or $OPiv^-$ is the counterion in silver salt. Although the capacity of Ag(I) to oxidize HQ intermediates to the corresponding BQ derivatives is known, other roles played by it have not yet revealed in this reaction.

Table 2. Exploring the optimal oxidant for the synthesis of **3aa**.[a]

Entry	**Oxidant** (equiv.)	**Isolated Yield** (%)
1[b]	Ag_2CO_3 (0)	-[c]
2	Ag_2CO_3 (5)	34
3	Ag_2O (4)	35
4	Ag(OAc) (8)	37
5	AgF (8)	9
6	$AgBF_4$ (8)	-[c]
7	$Cu(OAc)_2$ (8)	-[c]

[a] Reaction conditions: 2 equiv. of **1a**, 2 equiv. of **2a**, 1 equiv. of BQ, oxidant (*n* equiv.), 1 equiv. of H_2O, 2mL of degassed solvent, reacted at 60 °C for 15 hours. [b] 20 mol-% of $Pd(OAc)_2$ was loaded. [c] Not detected.

When aniline instead of **1a** was used as substrate in the reaction carried out at the optimized conditions, the yield of **3aa** dropped significantly from 76% to 36% (entry 1, Table 3). This could be associated with the formation of inactive Ag(I)-aniline complex(es) under excess amount of aniline. The yield of **3aa** could also be drastically attenuated to 18% when the reaction was carried out in air (entry 2). By contrast, it has been reported elsewhere for a related reaction that phosphinyl radical ($R_2P(O)\cdot$) was presumably generated while it was carried out with SPO in air and thereby enhanced the yields of products.[32]

Table 3. Refining the optimized reaction conditions for synthesizing **3aa**.[a]

Entry	**Reaction Conditions** (equiv.)	**Isolated Yield** (%)
1	NH_2Ph (2)	36
2	in air	18
3	TEMPO (2)	52
4	TEMPO (4)	56
5	TEMPO (4)[b]	57
6	**1a** (3), **2a** (3)[c]	91

[a] Reaction conditions: 2 equiv. of **1a**, 2 equiv. of **2a**, 1 equiv. of BQ, *n* equiv. of oxidant, 20 mol-% of $Pd(OAc)_2$ as additive, 1 equiv. of H_2O, 2mL of degassed toluene, reacted at 60 °C for 15 hours. [b] No $Pd(OAc)_2$ additive was employed.

At the first glance, the yield of **3aa** is seemingly to be influenced negatively by the addition of 2 to 4 equiv. of TEMPO (entry 6 in Table 1 vs. entries 3-4 in Table 3). However, it was found that the yields of **3aa** were not much in difference in the absence of $Pd(OAc)_2$ with 4 equiv. of TEMPO (57%, entry 5 in Table 3) or in the presence of $Pd(OAc)_2$ with 2 or 4 equiv. of TEMPO (52% or 56%, entries 3-4 in Table 3). Here, TMEPO appears to diminish the positive effect brought by $Pd(OAc)_2$ in terms of the yield of **3aa**. Based on these observations, a previously speculated free radical mechanism is unlikely for this type of reactions.[33] To our delight, the yield of **3aa** could be increased up to 91% when 3 equiv. of **1a** and **1b** were employed (entry 6 in Table 3).

After carefully screening the relevant variables, the optimized conditions for the synthesis of **3aa** are listed as follows: 3 equiv. **1a**, 3 equiv. **2a**, 1 equiv. BQ, 4 equiv. Ag_2CO_3, 20 mol-% $Pd(OAc)_2$, 2 mL degassed toluene, 1 equiv. H_2O, under nitrogen atmosphere and reacted at 60 °C for 15 hours. With the optimized conditions, the influences on the yields of **3** caused by the steric and electronic effects of various SPOs and imines were further evaluated (Figure 3). Note that the abbreviations for products **3**s are given based on the uses of imines and SPOs: **3**(amino group)(phosphine oxide). For example, the product **3ab** stands for the employments of (*E*)-N,1-diphenylmethanimine (**1a**) and di-*p*-tolylphosphine oxide (**2b**). The yield of **3ab** (77%) is moderately reduced, compared to that of **3aa** (91%), by using di-*p*-tolylphosphine oxide (**2b**), equipped with electron-donating methyl group on the *para*-position of phenyl substituent, as SPO source. Neither bulky di-*tert*-butylphosphine oxide (**2c**) nor diphenyl *H*-phosphonate (**2d**) gave the anticipated product of **3ac** or **3ad**. The ineffectiveness of substrates of **2c** and **2d** may be attributed to much slower tautomerization rates, from SPO to PA, than that of **2a** (i.e. the order of initial tautomerization rates of SPOs: $Ph_2P(O)H$ > $(PhO)_2P(O)H$ >> $tBu_2P(O)H$).[34]

Several imine derivatives Ph-CH=N-Ar (Ar: 4-tert-butylphenyl (**1b**), 4-methoxyphenyl (**1c**), 2-fluorophenyl (**1e**), 3-fluorophenyl (**1f**), 4-fluorophenyl (**1g**), 4-(trifluoromethyl)phenyl (**1h**); and (E)-N-tert-butyl-1-phenylmethanimine (**1d**)) were employed as substrates as well. The presence of electron-donating group (EDG) on the *para*-position of -Ar or electron-withdrawing group (EWG) on the *meta*-position of -Ar has less impact on the yields of **3** (**3ba**, **3ca** and **3fa** in Figure 3b). However, the functionalization of EWG on the *ortho*- or *para*-position of -Ph on imine resulted in slightly reduction in yields (**3ea**, **3ga**, **3ha** in Figure 3b and **3cb** in Figure 3c). The production of **3** is not very sensitive to the electronic effect caused by imine, but it could be drastically influenced by the steric effect of imine in the production of **3da**. Notably, the fully C-H functionalization of BQ is also applicable to NQ, giving rise to the 2-phosphination and 3-amination products with moderate yields (**N3aa**: 44% and **N3ab**: 44% in Figure 3c). The crystal structure of **N3ab** is shown in Figure 2b. The well-resolved crystal structures for **3ba**, **3ca**, **3fa** and **3ga** are shown in the Supporting Information.

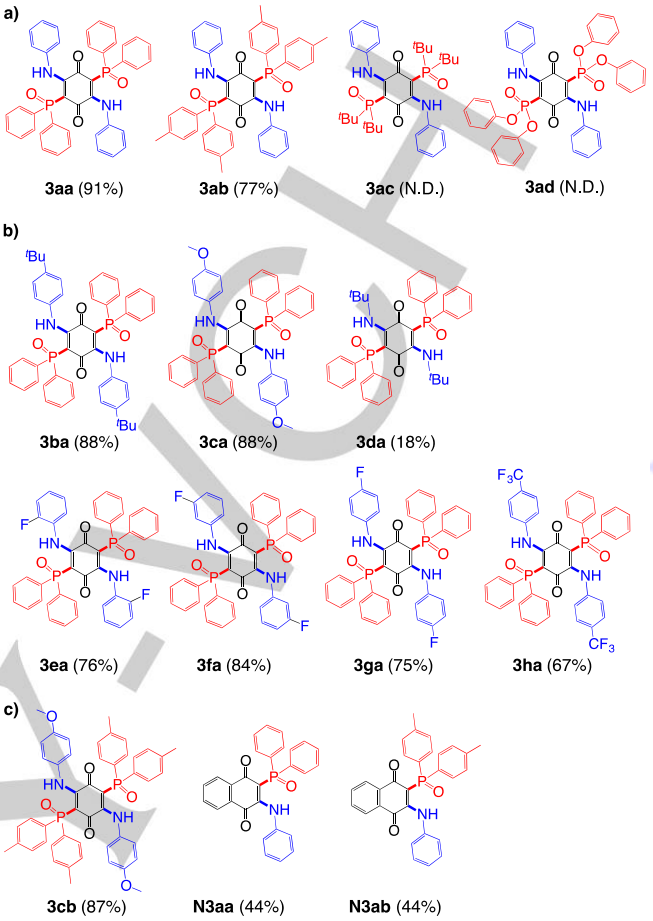
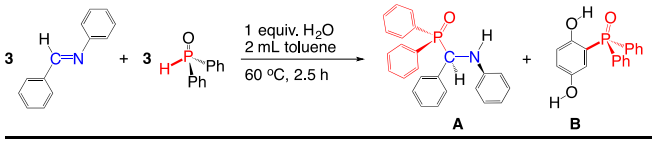


Figure 3. Fully functionalization of BQ with various SPO and imine derivatives. The 2 equiv. of imine and SPO were used when NQ was employed. Note that the abbreviations for the products are given based on the rules: the first alphabet stands for the employed imine, the second for the SPO, while N for NQ.

Preliminary mechanistic studies concerning the water-assisted reactivity between SPO and imine w/wo the presence of BQ or Ag_2CO_3 were carried out under the optimized reaction conditions (Scheme 2). The hydrophosphinylation product **A** *via* 1,2-addition of the C=N bond of imine **1a** by $R_2P(O)$-H **2a** was obtained from the control reaction in 2 mL toluene reacted at 60 °C for 2.5 hours. The isolated yield of **A** was 88% (entry 1 in Scheme 2). While BQ was loaded into the previous control reaction, 79% yield of **A** was isolated (entry 2). Moreover, the byproduct of 2-phosphoryl hydroquinone (HQ) **B** was also detected through 1,4-addition of BQ by SPO **2a** (^{31}P NMR yield in DMSO-d^6: c.a. 20%),[33b] implying that $P(O)R_2^-$ is the first nucleophile that attaching BQ. Compared to the control reaction, the yield of **A** (22%) was greatly reduced at the presence of 4 equiv. of Ag_2CO_3 (entry 3, Scheme 2). It is presumed that Ag(I) is of crucial importance in the reaction not only acting as an indispensable oxidant but also as a handy reagent to avoid hydrophosphinylation of C=N bond of imine by SPO.

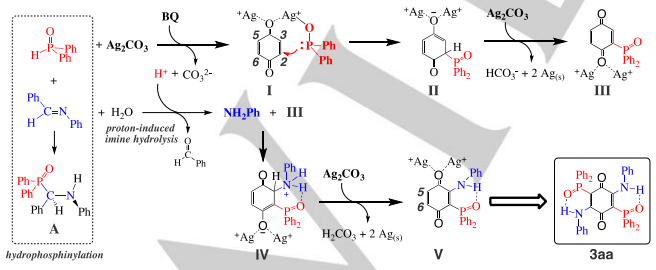


1) Control	88%[a]	—
2) 1 equiv. BQ	79%[a]	20% (by NMR)
3) 4 equiv. Ag_2CO_3	22%[a]	—

Scheme 2. Preliminary mechanistic studies for fully functionalization of BQ. [a] Yields were estimated based on the amount of imine.

Although Ag(I)-P(O)Ph_2 might be formed in reaction,[35] the adduct was speculated to be readily fragmented to $R_2P(O)$· and zero-valent Ag(0). Herein, the formation of BQ-Ag(I)-O-PPh_2 (**I**) adduct is thereby proposed in the presence of a redox-active moiety such as BQ (Scheme 3). In addition, the attenuation of the hydrophosphinylation in production allows the generation of some more amount of aniline through proton-assisted hydrolysis of imine.[36] When **A** was employed as reagent to replace both SPO and imine in the title reaction (Scheme 1d), no targeted product of fully substituted BQ (**3aa**) was observed by judging from both ^{1}H and ^{31}P NMR spectra of the reaction mixture.

A proposed mechanism is thereby shown and illustrated as follows (Scheme 3). Firstly, the two lone-pair electrons of oxygen atom(s) in BQ could coordinate to two Ag(I) ions,[37] and grants BQ a better electrophile for P(O)Ph_2^- which is presumably released from the adduct BQ-Ag(I)-O-PPh_2 (**I**). After the formation of intermediate **II**, the deprotonation process takes place by the assistance of CO_3^{2-} and then two electrons transfer from the intermediate to two Ag(I) ions, giving rise to the P-monosubstituted BQ **III** along with two equivalents of Ag(0) species. Based on the quantum-mechanical calculations pursued by Houk,[38] the subsequent nucleophilic addition of aniline presumably prefers to take place at the 3-position of **III** because an electron-withdrawing group such as -P(O)Ph_2 has been functionalized on the 2-position of BQ. In addition, the ^{31}P NMR peak at 34 ppm is always observed in the quenched reaction mixtures, indicating the formation of **A** through hydrophosphinylation between SPO and imine.



Scheme 3. Preliminary mechanistic studies for fully functionalization of BQ.

Recently, Han *et al.* demonstrated that the reaction of BQ and diphenylphosphine oxide yielded 98% of P-monosubstituted HQ (**B**) with no mention of the potential production of *2,5*-disubstituted HQ.[33b] Although the formation of higher substituted HQ was not mentioned, Han's work indeed implies a stepwise-substitution mechanism on BQ in the title reaction. Therefore, the nucleophilic attack of aniline on the *3*-position of **III** to form intermediate **IV** could be expected albeit P(O)Ph_2^- could be a better nucleophile than aniline. The aniline derivatives are believed to be formed from the acid-catalyzed hydrolysis of their corresponding imines. The regioselectivity of *2*-phosphination and *3*-amination on BQ (**III**) could be originated from large steric repulsion between two neighboring -P(O)Ph_2 substituents when functionalized on the *2*- and *3*-positions of BQ.

Subsequently, *2,3*-substituted intermediate **V** could be obtained from **IV** through deprotonation by the assistance of CO_3^{2-} and further oxidation by two Ag(I) cations which are coordinated by one of the oxygen atoms of **IV**. Based on our DFT calculations, the C6 contributes more π-type 2p atomic orbital than C5 to the LUMO of **V**,[39] which is again consistent with the previously reported computational predictions for donor- or acceptor-functionalized BQ substituent.[38] Thus, the succeeding C-H functionalization through nucleophilic attack of aniline on the C6-position of **V** might be anticipated. Eventually, the fully substituted product could be obtained from repeating the previous elementary steps. Although the role played by $Pd(OAc)_2$ is not clear, it might act as a mild Lewis acid towards the coordination of N- or P-substituted intermediates. Thereby, the electrophility of those moderate substituted BQ intermediates is increased. As reported in entries 6, 14-16 in Table 1, the yield of **3aa** is proportional to the amounts of Pd species loaded into the reaction flasks.

Conclusions

In conclusion, a new reactivity of BQ has been revealed when N-directing imines (**1**) and SPOs (**2**) are employed as substrates and 20 mol-% $Pd(OAc)_2$ as additive in the Ag(I)-mediated reaction. The reaction is proposed to undergo a series of 1,4-addition and oxidation reactions that eventually giving rise to fully C-H functionalized BQ products. When compared with the previously reported Pd(II)-catalyzed oxidative C-P bond formation analogue, the reagents of Pd(II), Ag(I) and BQ are acting as catalyst, oxidant and additive (as promoter) as demonstrated in this work (c.f. Scheme 1b & 1d). Under similar reaction conditions, the role played by BQ is no longer an additive but a reactant for 2,5-phosphinations and 3,6-aminations. This newly found one-pot reactivity is originated from the replacement of 2-phenylpyridine (Scheme 1b) with N-directing imine (Scheme 1d). The employments of imine and SPO in Ag(I)-mediated reactions leads to the hydrolysis of imine to a well-suited nucleophile, aniline. Several substituted imines, SPOs, and even NQ were also successfully employed and yielded similar reactivities. A mechanism for this Ag(I)-mediated CDC-type (dual C-H/P-H and C-H/N-H) and multi-components reaction is tentatively proposed. Most importantly, these results serve as a reminder that BQ can be an active reactant, besides oxidant, when suitable nucleophiles can be generated in a potentially Pd(II)-catalyzed oxidative reaction where Ag(I) is an oxidant. In view of the various applications of BQ (or HQ) derivatives containing the $C_{BQ/HQ}$-P or

C_{BQ}-N bonds shown in Figure 1, the newly synthesized and highly substituted BQ and NQ products might have versitle applications.

Experimental Section

General: Routine ^{1}H NMR spectra were recorded at 399.756 MHz. The chemical shifts are reported in ppm relative to internal standards TMS (δ = 0.0 ppm). ^{31}P and ^{13}C NMR spectra were recorded at 161.835 and 100.529 MHz, respectively. The chemical shifts for the former and the latter are reported in ppm relative to external standards H_3PO_4 (δ = 0.0 ppm) and $CHCl_3$ (δ = 77 ppm), respectively. Mass spectra were recorded on GC-MS-MS or LC-MS spectrometer. Electron ionization-high resolution mass spectra (EI-HRMS) were recorded on a mass spectrometer with magnetic sector analyzers. Electrospray ionization-high resolution mass spectra (ESI-HRMS) were recorded on a mass spectrometer with LTQ-Orbitrap mass analyzers. All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques or in a nitrogen-flushed glove box. Freshly distilled and degassed solvents were used. All processes of separations of the tetra-substituted BQ products were performed by column chromatography. For palladium complexes **I**, **II**, and **III**, purifications were done by recrystallization. All chemicals purchased from venders were directly used without further purification unless otherwise stated.

X-ray Crystallographic Studies: Suitable crystals for X-ray analysis for respective **3aa, 3ba, 3ca, 3fa, 3ga, N3ab, Pd-III** (red crystals**) and Pd-III** (yellow crystals), were obtained through the liquid-liquid diffusion method in binary solvent system of *n*-hexane and DCM. Suitable crystals were immersed with FOMBLIN®Y under a N_2 atmosphere and mounted on a diffractometer employing graphitemonochromated Mo Kα radiation (λ = 0.710 73 Å). Intensity data were collected with ω□scans. Data collection and reduction were performed with the CrysAlisPro software,[40] and the absorptions were corrected by the SCALE3 ABSPACK multiscan method.[41] The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package.[42] All non-H atoms were located from successive Fourier maps and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms.[43] Crystallographic data with the CCDC numbers of 1497618, 1497619, 1497620, 1497621, 1497622, 1497623, 1497624 and 1497625 for **3aa**, **3ba**, **3ca**, **3fa**, **3ga**, **N3ab**, **Pd-III** (red crystals) and **Pd-III** (yellow crystals), respectively. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Preparation of palladium complexes Pd-III: Note that the [μ_2-ClPd(PPh$_2$-OH)(PPh$_2$O)]$_2$ (**Pd-I**),[44] [μ_2-(OAc)(η^2-C,N-**1a**)Pd]$_2$ (**Pd-II**),[45] and [μ_2-Cl(η^2-C,N-**1a**)Pd]$_2$ (**Pd-III**)[46] were all synthesized based on their respective literature. The synthesis of **Pd-III** is presented because two crystal structures belonging to different space groups were obtained, and their structures were determined by X-ray diffraction methods. Into a 100 mL round-bottomed flask with stir bar was placed Pd(MeCN)$_2$Cl$_2$ (0.100 g, 0.386 mmol), **1a** (0.069 g, 0.386 mmol), and NaOAc (0.063 g, 0.772 mmol). Then, 10 mL of freshly distilled CH_2Cl_2 was added into the mixtures. The solution was stirred at room temperature for 18 hours. Subsequently, brine was added to the crude mixture, and the mixture was extracted with ethyl acetate from a separatory funnel for three times. The combined organic layer was dried with anhydrous $MgSO_4$ then filtered with celite. The solution was concentrated under vacuum, and yellow solids were obtained. The solids were dissolved in CH_2Cl_2 and *n*-hexane, and two layers will form. The yellow crystals of **Pd-III** were obtained as the major product from the recrystallization process while a small amount of red crystals of **Pd-III** were also attained. The yield of **Pd-III** was 86% (0.106 g, 0.166 mmol).

‡ *Spectroscopic data for* ***Pd-III:***

^{1}H NMR (400 MHz, $CDCl_3$, δ/ppm): δ = 9.17-9.15 (d, *J* = 7.6 Hz, 2H), 8.02-7.97 (d, *J* = 19.6 Hz, 2H), 7.97-7.78 (d, *J* = 7.6 Hz, 2H), 7.61-7.48 (m, 4H), 7.46-7.30 (m, 8H), 7.06 (s, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$, δ/ppm): δ = 171.1 (s, NCH), 151.3 (s, NAr), 133.8 (s, CAr), 131.8 (s, Ar), 131.7 (s, Ar), 129.3 (s, Ar), 128.8 (s, Ar), 128.2 (s, Ar), 123.9 (s, Ar); **Element Anal.** Calcd. for $C_{26}H_{20}Cl_2N_2Pd_2$: N, 4.35 %; C, 48.48 %; H, 3.13 %. Found: N, 4.50 %; C, 48.50 %; H, 3.07 %; **HR-MS (EI, M$^+$, m/z):** Calcd. for $C_{26}H_{20}Cl_2N_2Pd_2^+$ [M$^+$]: 641.9073. Found: 641.9063.

Preparation of imine derivatives of 1a-1c and 1e-1h: Into a 100 mL round-bottomed flask with a magnetic stir bar were placed benzaldehyde (1.02 mL, 10 mmol), aniline (0.91 mL, 10 mmol), and then 10 mL of deionized water. The solution was stirred at room temperature for 12 hours Subsequently, brine was added to the crude mixture, and it was extracted with ethyl acetate for three times. The combined organic layer was then dried with anhydrous $MgSO_4$. Lastly, the concentrated organic layer was purified by flash column chromatography to yield the desired pale-yellow product **1a** (1.75 g, 9.69 mmol, 97%).

Similar procedures were applied to the preparations of **1b**, **1c**, and **1e-1h**. The corresponding starting materials, 4-*tert*-butylaniline (1.59 mL, 10 mmol), 4-methoxyaniline (1.23 g, 10 mmol), 2-fluoroaniline (0.96 mL, 10 mmol), 3-fluoroaniline (0.96 mL, 10 mmol), 4-fluoroaniline (0.96 mL, 10 mmol), and 4-(trifluoromethyl)aniline (1.25 mL, 10 mmol) were used. The corresponding yields of purified **1b** (pale-yellow solids), **1c** (brown solids), **1e** (pale-yellow solids), **1f** (yellow liquid), **1g** (pale-green solids), and **1h** (white solids) are 95% (2.37g, 9.51 mmol), 92% (1.94g, 9.17 mmol), 71% (1.42g, 7.11 mmol), 99% (1.97g, 9.90 mmol), 94% (1.87g, 9.40 mmol), and 95% (2.37g, 9.51 mmol), respectively. (*E*)-N-tert-butyl-1-phenylmethanimine (1d) was purchased from Sigma-Aldich.

‡ *Spectroscopic data for compound* ***1a****:* **^{1}H NMR** (400 MHz, $CDCl_3$, δ/ppm): δ = 8.47 (s, 1H), 7.92-7.90 (d, *J* = 7.2 Hz, 2H), 7.49-7.48 (t, *J* = 4 Hz, 3H), 7.42-7.39 (d, *J* = 15.2 Hz, 2H), 7.24-7.21 (t, *J* = 12.4 Hz, 3H).

‡ *Spectroscopic data for compound* ***1b****:* **^{1}H NMR** (400 MHz, $CDCl_3$, δ/ppm): δ = 8.45 (s, 1H), 7.89-7.86 (d, *J* = 9.6 Hz, 2H), 7.43-7.39 (m, 5H), 7.18-7.16 (d, *J* = 8.8 Hz, 2H), 1.33 (s, 9H).

‡ *Spectroscopic data for compound* ***1c****:* **^{1}H NMR** (400 MHz, $CDCl_3$, δ/ppm): δ = 8.49 (s, 1H), 7.90-7.88 (d, *J* = 9.2 Hz, 2H), 7.47-7.45 (t, *J* = 8.0 Hz, 3H), 7.25-7.23 (d, *J* = 8.8 Hz, 2H), 6.95-6.93 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H).

‡ *Spectroscopic data for compound* ***1e****:* **^{1}H NMR** (400 MHz, $CDCl_3$, δ/ppm): δ = 8.53 (s, 1H), 7.95-7.92 (d, *J* = 9.6 Hz, 2H), 7.50-7.48 (t, *J* = 7.2 Hz, 3H), 7.17-7.14 (m, 4H).

‡ *Spectroscopic data for compound* ***1f****:* **^{1}H NMR** (400 MHz, $CDCl_3$, δ/ppm): δ = 8.42 (s, 1H), 7.96-7.94 (d, *J* = 9.2 Hz, 2H), 7.53-7.49 (t, *J* = 16.8 Hz, 3H), 7.37-7.35 (t, *J* = 8.4 Hz, 1H), 7.05-6.96 (m, 3H).

‡ *Spectroscopic data for compound* ***1g****:* **^{1}H NMR** (400 MHz, $CDCl_3$, δ/ppm): δ = 8.45 (s, 1H), 7.91-7.89 (d, *J* = 9.6 Hz, 2H), 7.50-7.47 (t, *J* = 14.0 Hz, 3H), 7.23-7.19 (d, *J* = 14.0 Hz, 2H), 7.11-7.07 (d, *J* = 17.2 Hz, 2H).

‡ *Spectroscopic data for compound **1h**:* **^{1}H NMR** (400 MHz, $CDCl_3$, *δ*/ppm): *δ* = 8.18 (s, 1H), 7.67-7.65 (d, *J* = 9.2 Hz, 2H), 7.41-7.38 (d, *J* = 8.4 Hz, 2H) , 7.28-7.23 (m, 3H), 7.01-6.99 (t, *J* = 8.4 Hz, 2H).

Preparation of diphenylphosphine oxide 2a: Into a 100 mL round-bottomed flask with stir bar was placed chlorodiphenylphosphine (0.61 mL, 3.0 mmol) and then 12 mL of freshly distilled THF. Next, 1 mL of deionized water was slowly added into the flask. The solution was stirred at room temperature for 30 minutes, aiming at the hydrolysis of chlorodiphenylphosphine. The triethylamine (7.0 mL, 15 mmol) in 5 mL THF was then slowly added into the reaction mixture. The solution was reacted for another 1 hour, and white precipitates of $HCl{\cdot}NEt_3$ were observed. Subsequently, brine was added to the crude mixture, and it was extracted with ethyl acetate from a separatory funnel for three times. The combined organic layer was then dried with anhydrous $MgSO_4$. Lastly, the concentrated organic layer was purified by column chromatography to yield the desired white solids of diphenylphosphine oxide **2a** (0.44g, 2.17 mmol, 72%). Note that the di-*p*-tolylphosphine oxide **2b** and diphenyl *H*-phosphonate **2d** were purchased from Alfa Aesar and TCI, respectively.

‡ *Spectroscopic data for **2a**:* **^{1}H NMR** (400 MHz, $CDCl_3$, *δ*/ppm): *δ* = 8.56 (d, $J_{P\text{-}H}$ = 483.7 Hz, 1H), 7.72-7.66 (dd, *J* = 8.0, 8.0 Hz, 4H), 7.57-7.54 (t, *J* = 14.8 Hz, 2H), 7.50-7.46 (m, 4H); **^{31}P NMR** (162 MHz, $CDCl_3$, *δ*/ppm): *δ* = 22.02 (d, $J_{P\text{-}H}$ = 483.7 Hz).

General procedure for fully C-H functionalization of *1,4*-benzoquinone or *1,4*-Napphthoquinone by dual regioselective phosphination and amination reactions:

BQ as reactant:

Into a 20 mL Schlenk tube with a magnetic stir bar was placed diphenylphosphine oxide (130.41 mg, 0.65 mmol, 3 equiv), N-Benzylideneaniline (116.89 mg, 0.65 mmol, 3 equiv), $Pd(OAc)_2$ (9.6 mg, 0.048 mmol, 20 mol-%), benzoquinone (23.7 mg, 0.22 mmol, 1 equiv), Ag_2CO_3 (237.2 mg, 0.86 mmol, 4 equiv). The Schlenk tube was then evacuated and backfilled with nitrogen three times. Next, 2 mL of degassed toluene was slowly added into the flask, and 4 *μ*L of deionized water (1 equiv.) was added with micropipette under the nitrogen atmosphere. The solution was stirred at 60 °C for 15 hours. After the solution was cooled to room temperature, 5 mL CH_2Cl_2 was added into the flask. The solution was filtered over celite, dried with anhydrous $MgSO_4$, and concentrated under vacuum. Subsequently, the reaction mixture was purified by column chromatography on silica gel using hexane/EtOAc = 4/1 to yield the dark-red solids of **3aa** (134.4 mg, 0.19 mmol, 91%).

The same protocol and was applied to other imines and SPOs substrates. The isolated yields for fully substituted BQ products were dark-red solids of **3ab** (124.0 mg, 0.17 mmol, 77%), dark-red solids of **3ba** (151.8 mg, 0.19 mmol, 88%), dark-red solids of **3ca** (141.7 mg, 0.19 mmol, 88%), orange solids of **3da** (25.1 mg, 0.04 mmol, 18%), dark-red solids of **3ea** (118.9 mg, 0.16 mmol, 76%), dark-red solids of **3fa** (131.4 mg, 0.18 mmol, 84%), dark-red solids of **3ga** (116.4 mg, 0.16 mmol, 75%), dark-red solids of **3ha** (118.9 mg, 0.14 mmol, 67%), and dark-red solids of **3cb** (151.4 mg, 0.19 mmol, 87%). All the products were purified by column chromatography on silica gel using hexane/EtOAc = 4/1 solvent system.

‡ *Spectroscopic data for **3aa**:* **^{1}H NMR** (400 MHz, $CDCl_3$, *δ*/ppm): *δ* = 12.54(s, 2H), 7.86-7.81 (dd, *J* = 13.2, 12. 8Hz, 8H), 7.60-7.58 (t, *J* = 7.6 Hz, 4H), 7.57-7.45 (m, 8H), 7.07-7.03 (t, *J* = 14.4 Hz, 2H), 7.01-6.97 (t, *J* = 14.8 Hz, 4H), 6.64-6.62 (d, *J* = 7.6 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$, δ/ppm): *δ* = 177.4 (s, CO), 159.8 (s, CN), 138.9(s, Ar), 132.8 (d, *J* = 109.4 Hz, Ar), 132.2 (d, *J* = 11.5 Hz, Ar), 128.6 (s, Ar), 128.3 (d, *J* = 13.0 Hz, Ar), 125.6 (s, Ar), 123.6 (s, Ar), 97.8 (d, *J* = 101.9 Hz, CP); **^{31}P NMR** (162 MHz, $CDCl_3$, *δ*/ppm): *δ* = 38.9; **Element Anal.** Calcd for $C_{42}H_{32}N_2O_4P_2$: N, 4.06 %; C, 73.04%; H, 4.67%; O, 9.27%. Found: N, 4.00%; C, 72.89%; H, 5.02 %; O, 9.48%; **HR-MS (EI)** *m/z* Calcd for $C_{42}H_{32}N_2O_4P_2^+$ $[M]^+$: 690.1837. Found: 690.1841.

‡ *Spectroscopic data for **3ab**:* **^{1}H NMR** (400 MHz, $CDCl_3$, *δ*/ppm): *δ* = 12.51(s, 2H), 7.73-7.68(dd, *J* = 12.8, 12.8 Hz, 8H), 7.26-7.24(d, *J* = 8.0 Hz, 8H), 7.04-7.02(t, *J* = 7.6 Hz, 2H), 6.98-6.94(d, *J* = 15.2 Hz, 4H), 6.50-6.48(d, *J* = 8.0 Hz, 4H), 2.43(s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$, δ/ppm): *δ* = 177.4 (s, CO), 159.6 (s, CN), 142.4 (d, *J* = 2.6 Hz, Ar), 139.0(s, Ar), 132.1 (d, *J* = 11.5 Hz, Ar), 129.7 (d, *J* = 111.4 Hz, Ar), 128.9 (d, *J* = 13.4 Hz, Ar), 128.4 (s, Ar), 125.4 (s, Ar), 123.5 (s, Ar), 98.2 (d, *J* = 101.4 Hz, CP), 21.6 (s, CH_3); **^{31}P NMR** (162 MHz, $CDCl_3$, *δ*/ppm): *δ* = 38.8; **Element Anal.** Calcd for $C_{46}H_{40}N_2O_4P_2$: N, 3.75%; C, 73.98%; H, 5.40%. Found: N, 3.73%; C, 71.90%; H, 5.40%; **HR-MS (EI)** *m/z* Calcd for $C_{46}H_{40}N_2O_4P_2^+$ $[M]^+$: 746.2463. Found: 746.2466.

‡ *Spectroscopic data for **3ba**:* **^{1}H NMR** (400 MHz, $CDCl_3$, *δ*/ppm): *δ* = 12.44(s, 2H), 7.86-7.81(dd, *J* = 12.8, 12.8 Hz, 8H), 7.60-7.57(t, *J* = 14.8 Hz, 4H), 7.48-7.44(m, 8H), 6.97-6.95(d, *J* = 8.8 Hz, 4H), 6.52-6.50(d, *J* = 8.4 Hz, 4H), 1.27(s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$, δ/ppm): *δ* = 177.4 (s, CO), 160.2 (s, CN), 148.4 (s, Ar), 136.2 (s, Ar), 133.0 (s, Ar), 132.3 (d, *J* = 11.1 Hz, Ar), 131.9 (s, Ar), 128.3 (d, *J* = 12.6 Hz, Ar), 125.6 (s, Ar), 123.0 (s, Ar), 118.9 (s, Ar), 97.6 (d, *J* = 101.9 Hz, CP), 34.4 (s, *t*Bu), 31.2 (s, *t*Bu); **^{31}P NMR** (162 MHz, $CDCl_3$, *δ*/ppm): *δ* = 38.9; **Element Anal.** Calcd for $C_{50}H_{48}N_2O_4P_2$: N, 3.49 %; C, 74.80 %; H, 6.03 %. Found: N, 3.52 %; C, 74.69 %; H, 5.78 %; **HR-MS (ESI)** *m/z* Calcd for $[C_{50}H_{48}N_2O_4P_2 + H]^+$ $[M + H]^+$: 803.3162. Found: 803.3143.

‡ *Spectroscopic data for **3ca**:* **^{1}H NMR** (400 MHz, $CDCl_3$, *δ*/ppm): *δ* = 12.49(s, 2H), 7.87-7.82(dd, *J* = 12.8, 12.8 Hz, 8H), 7.60-7.56(t, *J* = 14.4 Hz, 4H), 7.49-7.45(m, 8H), 6.55-6.53(d, *J* = 8.8 Hz, 4H), 6.50-6.48(d, *J* = 9.2 Hz, 4H), 3.75(s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$, δ/ppm): *δ* = 177.2 (s, CO), 159.6 (s, CN), 157.3 (s, Ar), 132.9 (d, *J* = 124.1 Hz, Ar), 132.2 (d, *J* = 11.1 Hz, Ar), 131.9 (s, Ar), 128.3 (d, *J* = 13.0 Hz, Ar), 124.6 (s, Ar), 113.8 (s, Ar), 96.8 (d, *J* = 102.5 Hz, CP), 55.3 (s, OCH_3); **^{31}P NMR** (162 MHz, $CDCl_3$, *δ*/ppm): *δ* = 39.2; **Element Anal.** Calcd. for $C_{44}H_{36}N_2O_6P_2$: N, 3.73 %; C, 70.40 %; H, 4.83 %. Found: N, 3.55 %; C, 70.06 %; H, 4.72 %; **HR-MS (ESI)** *m/z* Calcd for $[C_{44}H_{36}N_2O_6P_2 + H]^+$ $[M + H]^+$: 751.2121. Found: 751.2101.

‡ *Spectroscopic data for **3da**:* **^{1}H NMR** (400 MHz, $CDCl_3$, *δ*/ppm): *δ* = 11.32(s, 2H), 7.87-7.82(dd, *J* = 132, 12.8 Hz, 8H), 7.52-7.49(m, 4H), 7.49-7.42(m, 8H), 1.12(s, 18H); **^{13}C NMR** (100 MHz, $CDCl_3$, δ/ppm): *δ* = 177.9 (s, CO), 163.8 (s, CN), 133.5 (d, *J* = 108.8 Hz, Ar), 132.2 (d, *J* = 11.1 Hz, Ar), 131.6 (d, *J* = 3.1 Hz, Ar), 128.0 (d, *J* = 13.0 Hz, Ar), 93.4 (d, *J* = 107.6 Hz, CP), 56.5 (s, *t*Bu), 29.9 (s, *t*Bu); **^{31}P NMR** (162 MHz, $CDCl_3$, *δ*/ppm): *δ* = 40.0; **Element Anal.** Calcd. for $C_{38}H_{40}N_2O_4P_2$: N, 4.31 %; C, 70.14 %; H, 6.20 %. Found: N, 4.19 %; C, 69.13 %; H, 6.27 %; **HR-MS (EI)** *m/z* Calcd for $C_{38}H_{40}N_2O_4P_2^+$ $[M]^+$: 650.2463. Found: 650.2470.

‡ *Spectroscopic data for **3ea**:* **^{1}H NMR** (400 MHz, $CDCl_3$, *δ*/ppm): *δ* = 12.33(s, 2H), 7.84-7.78(dd, *J* = 12.8, 12.8 Hz, 8H), 7.58-7.55(t, *J* = 14.8 Hz, 4H), 7.48-7.43(m, 8H), 7.05-7.03(m, 2H), 6.89-6.88(m, 4H), 6.72-6.67(m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$, δ/ppm): *δ* = 177.7 (s, CO), 159.4 (s, CN), 156.5 (d, *J* = 248.4 Hz, FAr), 132.3 (d, *J* = 109.1 Hz, Ar), 132.1 (d, *J* = 11.4 Hz, Ar), 132.0 (d, *J* = 2.6 Hz, Ar), 131.8 (d, *J* = 10.4 Hz, Ar), 128.5 (d, *J* = 13.8 Hz, Ar), 128.2 (d, *J* = 13.4 Hz, Ar), 127.8 (d, *J* = 12.3 Hz, Ar), 127.0 (d, *J* = 7.6 Hz, Ar), 125.1 (s, Ar), 124.1 (d, *J* = 3.8 Hz, Ar), 121.3 (d, *J* = 4.5 Hz, Ar), 116.1 (s, Ar), 115.6 (d, *J* = 19.8 Hz, Ar), 97.8 (d, *J* = 101.8 Hz, CP); **^{31}P NMR** (162 MHz, $CDCl_3$, *δ*/ppm): *δ* = 39.6; **Element Anal.** Calcd. for $C_{42}H_{30}F_2N_2O_4P_2$: N, 3.86 %; C, 69.42 %; H, 4.16 %. Found: N, 3.96 %;

C, 69.69 %; H, 4.23 %. **HR-MS (EI)** *m/z* Calcd for $C_{42}H_{30}F_2N_2O_4P_2^+$ $[M]^+$: 726.1649. Found: 726.1640.

‡ *Spectroscopic data for **3fa**:* **^{1}H NMR** (400 MHz, $CDCl_3$, *δ*/ppm): *δ* = 12.60(s, 2H), 7.86-7.81(dd, *J* = 12.8, 12.8 Hz, 8H), 7.61-7.57(t, *J* = 14.4 Hz, 4H), 7.51-7.46(m, 8H), 6.70-6.94(m, 2H), 6.81-6.77(m, 2H), 6.48-6.43(t, *J* = 20.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$, δ/ppm): *δ* = 177.3 (s, CO), 163.6 (d, *J* = 246.9 Hz, FAr), 159.2 (s, CN), 140.5 (d, *J* = 10.3 Hz, Ar), 132.3 (d, *J* = 109.1 Hz, Ar), 132.2 (d, *J* = 1.9 Hz, Ar), 132.0 (d, *J* = 11.1 Hz, Ar), 129.8 (d, *J* = 9.1 Hz, Ar), 128.4 (d, *J* = 13.0 Hz, Ar), 119.6 (d, *J* = 3.0 Hz, Ar), 112.9 (d, *J* = 21.4 Hz, Ar), 111.3 (d, *J* = 23.6 Hz, Ar), 98.8 (d, *J* = 101.0 Hz, CP); **^{31}P NMR** (162 MHz, $CDCl_3$, *δ*/ppm): *δ* = 38.9; **Element Anal.** Calcd. for $C_{42}H_{30}F_2N_2O_4P_2$: N, 3.86 %; C, 69.42 %; H, 4.16 %. Found: N, 3.88 %; C, 69.36 %; H, 4.22 %; **HR-MS (EI)** *m/z* Calcd for $C_{42}H_{30}F_2N_2O_4P_2^+$ $[M]^+$: 726.1649. Found: 726.1642.

‡ *Spectroscopic data for **3ga**:* **^{1}H NMR** (400 MHz, $CDCl_3$, *δ*/ppm): *δ* = 12.48(s, 2H), 7.85-7.80(dd, *J* = 8.4, 12.0 Hz, 8H), 7.62-7.58(t, *J* = 16.0 Hz, 4H), 7.51-7.44(m, 8H), 6.70-6.65(t, *J* = 16.8 Hz, 4H), 6.60-6.57(m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$, δ/ppm): *δ* = 177.3 (s, CO), 161.6 (d, *J* = 246.1 Hz, FAr), 159.7 (s, CN), 134.8 (d, *J* = 3.1 Hz, Ar), 132.6 (d, *J* = 109.1 Hz, Ar), 132.1 (d, *J* = 11.5 Hz, Ar), 128.3 (d, *J* = 13.0 Hz, Ar), 125.2 (d, *J* = 8.3 Hz, Ar), 115.6 (d, *J* = 22.8 Hz, Ar), 97.6 (d, *J* = 101.9 Hz, CP); **^{31}P NMR** (162 MHz, $CDCl_3$, *δ*/ppm): *δ* = 39.2; **Element Anal.** Calcd. for $C_{42}H_{30}F_2N_2O_4P_2$: N, 3.86 %; C, 69.42 %; H, 4.16 %. Found: N, 3.76 %; C, 64.70 %; H, 4.53 %; **HR-MS (EI)** *m/z* Calcd for $C_{42}H_{30}F_2N_2O_4P_2^+$ $[M]^+$: 726.1649. Found: 726.1642.

‡ *Spectroscopic data for **3ha**:* **^{1}H NMR** (400 MHz, $CDCl_3$, *δ*/ppm): *δ* = 12.57(s, 2H), 7.86-7.81(dd, *J* = 12.8, 12.8 Hz, 8H), 7.65-7.61(t, *J* = 15.2 Hz, 4H), 7.52-7.48(m, 8H), 7.24-7.22(d, *J* = 8.0 Hz, 4H), 6.71-6.69(d, *J* = 8.0 Hz, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$, δ/ppm): *δ* = 177.5 (s, CO), 159.7 (s, CN), 142.0 (s, Ar), 132.4 (d, *J* = 2.7 Hz, Ar), 132.3 (d, *J* = 109.2 Hz, Ar), 132.2 (d, *J* = 11.1 Hz, Ar), 128.5 (d, *J* = 13.0 Hz, Ar), 127.6 (d, *J* = 32.9 Hz, Ar), 125.9 (d, *J* = 3.4 Hz, Ar), 125.2 (d, *J* = 272.0 Hz, Ar), 123.8 (s, Ar), 99.5 (d, *J* = 99.5 Hz, CP); **^{31}P NMR** (162 MHz, $CDCl_3$, *δ*/ppm): *δ* = 38.6; **Element Anal.** Calcd. for $C_{44}H_{30}F_6N_2O_4P_2$: N, 3.39 %; C, 63.93 %; H, 3.66 %. Found: N, 3.41 %; C, 64.08 %; H, 3.82 %; **HR-MS (ESI)** *m/z* Calcd for $[C_{44}H_{30}F_6N_2O_4P_2 + H]^+$ $[M + H]^+$: 827.1658. Found: 827.1632.

‡ *Spectroscopic data for **3cb**:* **^{1}H NMR** (400 MHz, $CDCl_3$, *δ*/ppm): *δ* = 12.46(s, 2H), 7.74-7.69(dd, *J* = 12.4, 12.8 Hz, 8H), 7.27-7.26(d, *J* = 4.8 Hz, 8H), 6.55-6.53(d, *J* = 8.4 Hz, 4H), 6.48-6.46(d, *J* = 8.8 Hz, 4H), 3.75(s, 6H) , 2.44(s, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$, δ/ppm): *δ* = 177.4 (s, CO), 159.5 (s, CN), 157.2 (s, Ar), 142.3 (s, Ar), 132.2 (d, *J* = 11.5 Hz, Ar), 131.9 (s, Ar), 129.9 (s, Ar), 128.9 (d, *J* = 13.4 Hz, Ar), 124.6 (s, Ar), 113.7 (s, Ar), 97.8 (d, *J* = 101.4 Hz, CP), 55.2 (s, OCH_3), 21.7 (s, CH_3); **^{31}P NMR** (162 MHz, $CDCl_3$, *δ*/ppm): *δ* = 39.1; **Element Anal.** Calcd. for $C_{48}H_{44}N_2O_6P_2$: N, 3.47 %; C, 71.46 %; H, 5.50 %. Found: N, 3.40 %; C, 69.63 %; H, 5.52 %; **HR-MS (ESI)** *m/z* Calcd for $[C_{48}H_{44}N_2O_6P_2 + H]^+$ $[M + H]^+$: 807.2747. Found: 807.2724.

NQ as reactant:

Into a 20 mL Schlenk tube with a magnetic stir bar was placed diphenylphosphine oxide (173.88 mg, 0.86 mmol, 2 equiv),N-Benzylideneaniline (155.86 mg, 0.86 mmol, 2 equiv),$Pd(OAc)_2$ (19.2 mg, 0.086 mmol, 20 mol-%)), Naphthoquinone (68.0 mg, 0.43 mmol, 1 equiv), Ag_2CO_3 (237.2 mg, 0.86 mmol, 2 equiv). The Schlenk tube was then evacuated and backfilled with nitrogen three times. Next, 2 mL of degassed toluene was slowly added into the flask, and 4 *μ*L of deionized water (1 equiv.) was added with micropipette under the nitrogen atmosphere. The solution was stirred at 60 °C for 15 hours. After the solution was cooled to room temperature, 5 mL CH_2Cl_2 was added into the flask. The solution was filtered over celite, dried with anhydrous $MgSO_4$, and concentrated under vacuum. Subsequently, the reaction mixture was purified by column chromatography on silica gel using hexane/EtOAc = 3/1 to yield the dark-red solids of **N3aa** (85.6 mg, 0.19 mmol, 44%).

The same protocol was applied to the reaction by using imine **1a** and SPO **2b** as substrates. The isolated yields for fully substituted product **N3ab** was in dark-red solids of (90.2 mg, 0.19 mmol, 44%, hexane/EtOAc = 3/1).

‡ *Spectroscopic data for **N3aa**:* **^{1}H NMR** (400 MHz, $CDCl_3$, *δ*/ppm): *δ* = 12.66 (s, 1H), 7.98-7.92 (dd, *J* = 13.6, 13.2 Hz, 5H), 7.89-7.87 (d, *J* = 7.6 Hz, 1H), 7.69-7.66 (t, *J* = 14.8 Hz, 1H), 7.62-7.54 (m, 3H), 7.52-7.49 (m, 4H), 7.38-7.34 (t, *J* = 15.6 Hz, 2H), 7.27-7.23 (t, *J* = 14.4 Hz, 1H), 7.14-7.12 (d, *J* = 8.0 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$, δ/ppm): *δ* = 181.9 (d, *J* = 5.7 Hz, CO), 181.3 (d, *J* = 10.4 Hz, CO), 157.3 (s, CN), 140.1 (s, Ar), 134.6 (s, Ar), 133.2 (d, *J* = 109.5 Hz, Ar), 132.6 (s, Ar), 132.2 (s, Ar), 132.0 (d, *J* = 11.1 Hz, Ar), 131.9 (s, Ar), 129.0 (s, Ar), 128.4 (d, *J* = 13.0 Hz, Ar), 126.5 (s, Ar), 126.0 (s, Ar), 125.9 (d, *J* = 1.9 Hz, Ar), 124.2 (s, Ar), 102.7 (d, *J* = 101.1 Hz, CP); **^{31}P NMR** (162 MHz, $CDCl_3$, *δ*/ppm): *δ* = 40.4; **Element Anal.** Calcd. for $C_{28}H_{20}NO_3P$: N, 3.12 %; C, 74.83 %; H, 4.49 %. Found: N, 3.02 %; C, 75.56 %; H, 5.16 %; **HR-MS (EI)** *m/z* Calcd for $C_{28}H_{20}NO_3P^+$ $[M]^+$: 449.1181. Found: 449.1172.

‡ *Spectroscopic data for **N3ab**:* **^{1}H NMR** (400 MHz, $CDCl_3$, *δ*/ppm): *δ* = 12.69 (s, 1H), 7.96-7.94 (d, *J* = 8.0 Hz, 1H), 7.89-7.80 (m, 5H), 7.69-7.65 (t, *J* = 15.2 Hz, 1H), 7.62-7.58 (t, *J* = 14.8 Hz, 1H), 7.37-7.33 (t, *J* = 16.0 Hz, 2H), 7.31-7.29 (m, 4H), 7.26-7.23 (t, *J* = 14.4 Hz, 1H), 7.13-7.11 (d, *J* = 8.0 Hz, 1H), 2.41 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$, δ/ppm): *δ* = 181.9 (d, *J* = 5.7 Hz, CO), 181.3 (d, *J* = 9.8 Hz, CO), 157.1 (s, CN), 142.4 (s, Ar), 140.3 (s, Ar), 134.5 (s, Ar), 132.7 (d, *J* = 6.9 Hz, Ar), 132.5 (s, Ar), 132.3 (s, Ar), 132.0 (d, *J* = 11.3 Hz, Ar), 130.0 (d, *J* = 111.9 Hz, Ar), 129.1 (s, Ar), 129.0 (d, *J* = 8.3 Hz, Ar), 126.4 (s, Ar), 126.0 (s, Ar), 124.2 (s, Ar), 103.2 (d, *J* = 100.9 Hz, CP); **^{31}P NMR** (162 MHz, $CDCl_3$, *δ*/ppm): *δ* = 40.3; **Element Anal.** Calcd. for $C_{30}H_{24}NO_3P$: N, 2.93 %; C, 75.46 %; H, 5.07 %. Found: N, 3.02 %; C, 75.56 %; H, 5.16 %; **HR-MS (EI)** *m/z* Calcd for $C_{30}H_{24}NO_3P^+$ $[M]^+$: 477.1494. Found: 477.1485.

General procedure for preliminary mechanistic studies: A mixture of N-Benzylideneaniline (117 mg, 0.645 mmol), diphenylphosphine oxide (130 mg, 0.645 mmol), deionized water (4 μL, 0.215 mmol) in degased toluene (2 mL) with *1,4*-benzoquinone (23 mg, 0.215 mmol) (optional), and Ag_2CO_3 (237 mg, 0.86 mmol) (optional) under nitrogen in a Teflon-sealed tube was stirred at 60℃ for 2.5 h. The mixture was filtered over celite and concentrated under vacuum. The residue was purified by silica gel chromatography with dichloromethane/ethyl acetate = 8/1 to afford the product as a white solid. The formation of **B** was confirmed by comparison with the ^{1}H and ^{31}P NMR spectra reported by Han *et al.*[33b]

‡ *Spectroscopic data for compound **A**:* **^{1}H NMR** (400 MHz, $CDCl_3$, *δ*/ppm): *δ* = 7.85-7.90 (m, 2H; P(O)-Ph), 7.50-7.60 (m, 1H; P(O)-Ph), 7.47-7.50 (m, 2H; P(O)-Ph), 7.37-7.41 (m, 3H; P(O)-Ph), 7.25-7.30 (m, 2H; P(O)-Ph), 7.1-7.25 (m, 8H; Ar), 6.67 (t, J = 14 Hz ,1H; CH), 6.59-6.62 (m, 2H; Ar), 5.18 (d, J = 12 Hz,1H; NH); **^{13}C NMR** (150 MHz, $CDCl_3$, *δ*/ppm): *δ* = 146.098, 146.020, 135.018 (d, J=2.0 Hz), 132.288 (d, J=2.6 Hz), 131.931 (d, J=2.6 Hz), 131.669 , 131.612, 130.433, 129.173, 128.820 , 128.744, 128.347 (d, J=4,5 Hz), 128.157, 128.136, 128.056, 127.623 (d, J=2.9 Hz), 118.361, 113,912, 57.329(d, J=75.1 Hz); **^{31}P NMR** (162 MHz, $CDCl_3$, *δ*/ppm): *δ* = 33.9; **Element Anal.** Calcd for $C_{25}H_{22}NOP$: C, 78.31; H, 5.78; N, 3.65. Found: C, 78.25; H, 5.78; N, 3.79; **HR-MS (EI)** *m/z* Calcd for $C_{25}H_{22}NOP^+$ $[M^+]$: 383.1439. Found: 383.1434.

Computational Methods: All calculations were done with Gaussian 09.[47] Incorporated in the process of geometry optimizations. Geometry optimization for 2-(diphenylphosphoryl)-3-(phenylamino)- cyclohexa-2,5-diene-1,4-dione (intermediate V in Scheme 3) was performed with the hybrid functional B3LYP in conjugation with the 6-31+G(d) basis set. Vibrational frequencies were calculated to confirm whether the optimized structure is a local minimum (N_{imag} = 0) or transition state (N_{imag} = 1). In addition, the orbital analysis was done to identify the atomic orbital contributions to LUMO of intermediate **V** (*Gaussian* keyword: pop=(orbitals, threshorbitals=3)).

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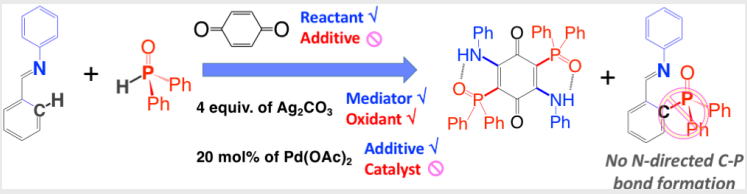

"Like reactions, unlike reactivities" - Imine, a nitrogen-directing substrate in TM-catalyzed C-H activations, turns out to be the precursor of aniline in the presence of $Ar_2P(O)$-H and Ag_2CO_3. Thus, fully functionalized 1,4-benzoquinones *via* unprecedented dual and regioselective C-P and C-N bond formations are obtained in the Ag(I)-mediated one-pot reactions.

Quinone Functionalization

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The C-H Bond Functionalization of *1,4*-Benzoquinone by Silver-mediated Regioselective Phosphination and Amination Reactions