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# α-Allenyl Ethers as Starting Materials for Palladium Catalyzed Suzuki–Miyaura Couplings of Allenylphosphine Oxides with Arylboronic Acids

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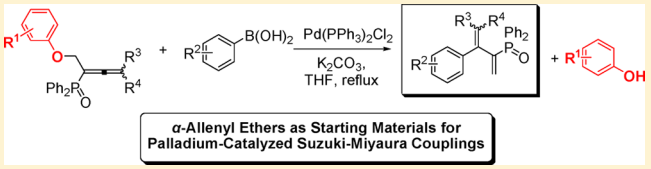
Supporting Information

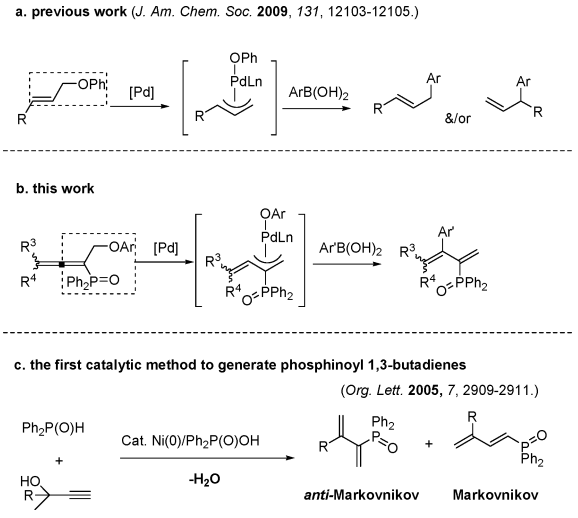
**ABSTRACT:** We disclose here the first palladium-catalyzed Suzuki–Miyaura couplings of aryl ethers functionalized allenylphosphine oxides with arylboronic acids. This new methodology with α-allenyl ethers as starting materials provides a novel approach to generate phosphinoyl 1,3-butadienes and derivatives with medium to excellent yields. The reaction tolerates a variety of functional groups to afford ranges of structurally diverse substituted phosphionyl 1,3-butadienes. For unsymmetrical allene substrates, high stereospecific additions to give *E*-isomers are usually observed. On the basis of the known palladium and allene chemistry, a mechanism is proposed.




The unique reactivity of allenes or 1,2-dienes due to the existence of two orthogonal π-bonds makes them versatile precursors for a variety of significant industrial and bioactive compounds.[1] In the past two decades, the organic transformation of allenes, particularly in the presence of transition metal catalysts, has received extensive attention.[2] Transition metal catalysts, containing palladium,[3] silver, platinum,[4] rhodium,[5] gold,[6] ruthenium,[7] or lanthanides,[8] etc., were applied to build functional blocks with electrophiles and/or nucleophiles. Various examples of palladium-catalyzed hydroalkenylation,[9] carbopalladation,[10] carbonylation,[11] dimerization,[12] oxidative carbocyclization,[13] hydropalladation,[14] and Heck coupling[15] involving allenes have been documented. Among these developments, mechanistically, π-allylpalladium species is the most commonly generated intermediates.[16]

Meanwhile, a broad range of allylic/allenyl fragments with electron-deficient substituents, such as acetates, carbonates, halides, and pseudohalides as π-allylmetal precursors are well established to undergo cross-couplings with organoboronic derivatives or other nucleophiles.[17,18a−c] However, the oxidative addition of Pd(0) to electron-rich bonds is particularly challenging, which results in scattered reports limited to allylic substrates bearing electron-rich functionality (C-OAr).[18d,19] For a leading research, Lipshutz et al.[19a] described the first general Suzuki–Miyaura coupling of allylic aryl ethers with boronic acids catalyzed by palladium bidentate–phosphine complex in water at room temperature (Scheme 1a). Interestingly, to the best of our knowledge, the coupling reaction of allenes bearing aryl ether functionality (α-position) with boronic acids has never been previously reported until date,[18e−l] let alone aryl ethers functionalized allenylphosphine oxides (Scheme 1b).[20]

**Scheme 1. (a) First General Suzuki–Miyaura Couplings of Allylic Aryl Ethers with Boronic Acids Catalyzed by Palladium Complex in Water; (b) This Work; (c) Han's First Catalytic Method to Generate Phosphinoyl 1,3-Butadienes**




Organophosphorus compounds play key roles in organic synthesis, biochemistry, materials chemistry, and catalysis,

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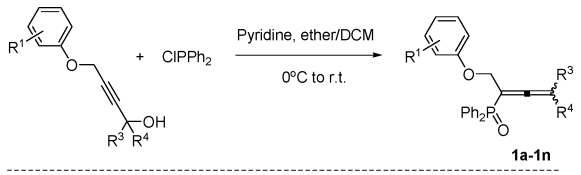
which shows their significance of preparation.[21] Phosphinoyl 1,3-dienes and derivatives as representative functionalized phosphorus compounds are readily transformed to other valuable compounds. They undergo Michael addition with nucleophiles to form allylic phosphonates,[22] Diels–Alder reaction with dienophiles to give cycloadducts,[23] cycloaddition with enamines to afford cyclohexadienylphosphonates,[24] addition with aldehydes to yield vinyl allenes,[25] etc. However, the conventional methods for synthesizing phosphinoyl 1,3-dienes are mostly focused on simplest 1,3-butadienylphosphonates, remaining complicated and trivial substrate preparations. Multisubstituted phosphinoyl 1,3-dienes are generally more challengeable. Until recently, Han et al. reported the first nickel-catalyzed generation of phosphinoyl 1,3-butadienes (Scheme 1c), consisting of the metal catalyzed addition of diphenylphosphine oxide and related P(O)H compounds to propargyl alcohols followed by an acid-catalyzed dehydration.[26] Although this method provided a quite convenient catalytic approach to phosphinoyl 1,3-butadienes, the substrates were limited with terminal propargyl alcohols; moreover, the products suffered from mixtures of Markovnikov and *anti*-Markovnikov adducts, especially for aliphatic substrates. Thus, the potential development in such chemical synthesis with easily accessible substrates, higher diversity, and higher selectivity/efficiency is in a great demand. As our continuing research on synthesis and application of organophosphorus chemistry,[27] we report here, for the first time, a palladium-catalyzed Suzuki–Miyaura coupling of aromatic ether-based allenylphosphine oxides with arylboronic acids to generate phosphinoyl 1,3-butadienes and derivatives (Scheme 1b).

The allenylphosphine oxides (**1a–1n**) used in this study were easily accessible from the reactions of substituted acetylenic alcohols with diphenylphosphine chloride,[28] as shown in Scheme 2. With these substrates in hand, the

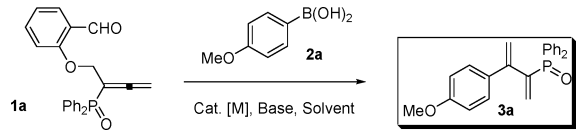
**Scheme 2. Preparation of Aryl Ethers Functionalized Allenylphosphine Oxides and the Substrates (1a–1n) Used in This Study**




**1a:** $R^1$ = *o*-CHO; $R^3$, $R^4$ = H, H;
**1b:** $R^1$ = *o*-Br; $R^3$, $R^4$ = H, H;
**1c:** $R^1$ = *p*-OMe; $R^3$, $R^4$ = H, H;
**1d:** $R^1$ = *m*-OMe; $R^3$, $R^4$ = H, H;
**1e:** $R^1$ = *p*-Me; $R^3$, $R^4$ = H, H;
**1f:** $R^1$ = 2,6-dimethyl; $R^3$, $R^4$ = H, H;
**1g:** $R^1$ = H; $R^3$, $R^4$ = H, H;
**1h:** $R^1$ = 2,4-difluoro; $R^3$, $R^4$ = H, H;
**1i:** $R^1$ = 2,6-dimethyl; $R^3$, $R^4$ = $CH_3$, $CH_3$;
**1j:** $R^1$ = 2,6-dimethyl; $R^3$, $R^4$ = $-C_5H_{10}-$;
**1k:** $R^1$ = 2,6-dimethyl; $R^3$, $R^4$ = *p*-$MeOC_6H_4$, H;
**1l:** $R^1$ = 2,6-dimethyl; $R^3$, $R^4$ = *p*-$CF_3C_6H_4$,$CH_3$;
**1m:** $R^1$ = 2,6-dimethyl; $R^3$, $R^4$ = Et, H;
**1n:** $R^1$ = 2,6-dimethyl; $R^3$, $R^4$ = Ph,Ph;

additions of *p*-methoxyphenylboronic acid (**2a**) to allenylphosphine oxide (**1a**) in the presence of transition metal catalysts were initially conducted to find optimal reaction conditions (Table 1). The reactions in the presence of 5 mol % of nickel or rhodium catalyst[29] and potassium carbonate at 66 °C for 2 h proceeded smoothly to give moderate yields of phosphinoyl 1,3-butadiene (**3a**) (52% and 57%, respectively). Although a palladium-catalyzed three component coupling of arylboronic

**Table 1. Screening of Conditions**[a]




| entry | catalyst | solvent/base | yield of **3a**[b] |
|---|---|---|---|
| 1 | $Ni(PPh_3)_2Cl_2$ | $THF/K_2CO_3$ | 52 |
| 2 | $(Ph_3P)_3RhCl$ | $THF/K_2CO_3$ | 57 |
| 3 | $Pd(TFA)_2/PCy_3$ | $THF/K_2CO_3$ | 78 |
| 4 | $Pd(OAc)_2/PCy_3$ | $THF/K_2CO_3$ | 65 |
| 5 | $Pd(TFA)_2$/XPhos | $THF/K_2CO_3$ | 70 |
| 6 | $Pd(OAc)_2$/DPPF | $THF/K_2CO_3$ | 75 |
| 7 | $Pd(PPh_3)_4$ | $THF/K_2CO_3$ | 60 |
| **8** | **$Pd(PPh_3)_2Cl_2$** | **$THF/K_2CO_3$** | **86** |
| 9 | $Pd(PPh_3)_2Cl_2$ | toluene/$K_2CO_3$ | 45 |
| 10 | $Pd(PPh_3)_2Cl_2$ | 1,4-dioxane/$K_2CO_3$ | 62 |
| 11 | $Pd(PPh_3)_2Cl_2$ | DMF/$K_2CO_3$ | 73 |

[a]1 mmol allenylphosphine oxides, 2 mmol *p*-methoxyphenyl- boronic acid, 3 mmol base, 5 mL of solvent, 5 mol % catalyst, refluxed for 2 h. [b]Isolated yield based on allenes.

acid with allenes and aldehydes has been reported to form homoallylic alcohols,[19d] formyl group survived under current conditions. Gratifyingly, palladium complexes such as $Pd(OAc)_2/PCy_3$, $Pd(TFA)_2$/XPhos, $Pd(OAc)_2$/DPPF, $Pd(PPh_3)_4$, and $Pd(PPh_3)_2Cl_2$ showed superior activities to nickel and rhodium catalysts (entries 1–8). After we tested this model reaction in several solvents, the highest yields of the product phosphinoyl 1,3-butadiene (**3a**) (86%) and its counterpart, salicaldehyde (82%), were obtained in refluxing THF (entry 8). Reactions in other bases including $Et_3N$, KOH, and *t*-BuOK led to lower conversion even after longer reaction time.

To further verify the generality of this novel Suzuki–Miyaura coupling reaction to generate phosphinoyl 1,3-butadienes,[30] we explored the substrate scopes, and the coupling results of terminal allenylphosphine oxides **1a–1h** with various arylboronic acids under optimized conditions were summarized in Table 2. The catalytic efficiency was not significantly altered by changing the substituents on the aryl ether part of allenes. Both electron-rich and electron-deficient groups were effective to afford adducts with modest to good yields. To be noted, similar to the formyl group, bromo groups also survived without producing classical Suzuki–Miyaura coupling products (entries 2, 17), which further demonstrate the mild and high chemoselectivity of this reaction. Substrate having high steric hindrance as **1h** did not impair the catalytic efficiency, as coupling yields were comparable with those resulted from less steric ones (entry 6 vs entry 1). In sharp contrast, substituents on arylboronic acids, dramatically undermined the efficiency of couplings. Electron-deficient groups, including Br–, F–, and $NO_2$–, led to decrease of coupling yields from good to medium (entries 14–18).

As shown in Table 3, the allenylphosphine oxides with terminal substituents were then studied. Substrates with groups ranged from alkyl to aromatic, electron-rich to electron-deficient were proven to be viable for couplings. Good to excellent yields were obtained except for diphenyl substitution (entries 11, 12), which could be attributed to high steric effect in the vicinity of catalytic active sites. For unsymmetrical phosphinoylallenes **1k**, **1l**, and **1m**, the couplings gave exclusively *E*-isomers of **3o**, **3p**, **3q**, **3r**, and **3s**, respectively.


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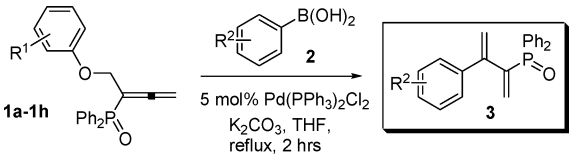
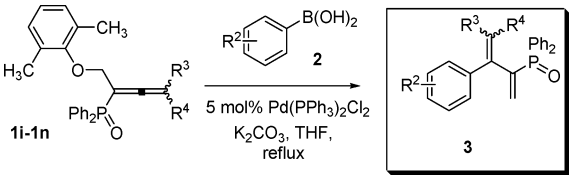
**Table 2. Palladium-Catalyzed Couplings of Allenylphosphine Oxides (Substitution on Aromatic Ether Moiety) with Various Arylboronic Acids**[a]




| entry | $R^1$ | $R^2$ | yield of 3[b] |
|---|---|---|---|
| 1 | *o*-CHO (**1a**) | *p*-MeO | 86(**3a**) |
| 2 | *o*-Br (**1b**) | *p*-MeO | 62(**3a**) |
| 3 | *p*-MeO (**1c**) | *p*-MeO | 81(**3a**) |
| 4 | *m*-MeO (**1d**) | *p*-MeO | 72(**3a**) |
| 5 | *p*-Me (**1e**) | *p*-MeO | 83(**3a**) |
| 6 | 2,6-dimethyl (**1f**) | *p*-MeO | 87(**3a**) |
| 7 | *o*-CHO (**1a**) | H | 85(**3b**) |
| 8 | H (**1g**) | H | 76(**3b**) |
| 9 | *p*-MeO (**1c**) | H | 73(**3b**) |
| 10 | 2,6-dimethyl (**1f**) | H | 68(**3b**) |
| 11 | 2,4-difluoro (**1h**) | *o*-Me | 64(**3c**) |
| 12 | 2,6-dimethyl (**1f**) | *p*-$CH_3$ | 57(**3d**) |
| 13 | 2,6-dimethyl (**1f**) | 2,4,6-trimethyl− | 68(**3e**) |
| 14 | 2,6-dimethyl (**1f**) | *p*-Br | 54(**3f**) |
| 15 | *m*-MeO (**1d**) | *p*-F | 37(**3g**) |
| 16 | *p*-Me (**1e**) | *p*-F | 57(**3g**) |
| 17 | *o*-Br (**1b**) | *m*-$NO_2$ | 56(**3h**) |
| 18 | 2,6-dimethyl (**1f**) | *m*-$NO_2$ | 45(**3h**) |
| 19 | 2,4-difluoro (**1h**) | *p*-acetyl | 78(**3i**) |
| 20 | 2,6-dimethyl (**1f**) | *p*-acetyl | 52(**3i**) |

[a]1 mmol allenylphosphine oxides, 2 mmol arylboronic acid, 5 mol % $Pd(PPh_3)_2Cl_2$, 3 mmol $K_2CO_3$, 5 mL THF, reflux; [b]Isolated yield based on allenes

**Table 3. Palladium-Catalyzed Couplings of Allenylphosphine Oxides (Substitution on Allenes Moiety) with Various Arylboronic Acids**[a]



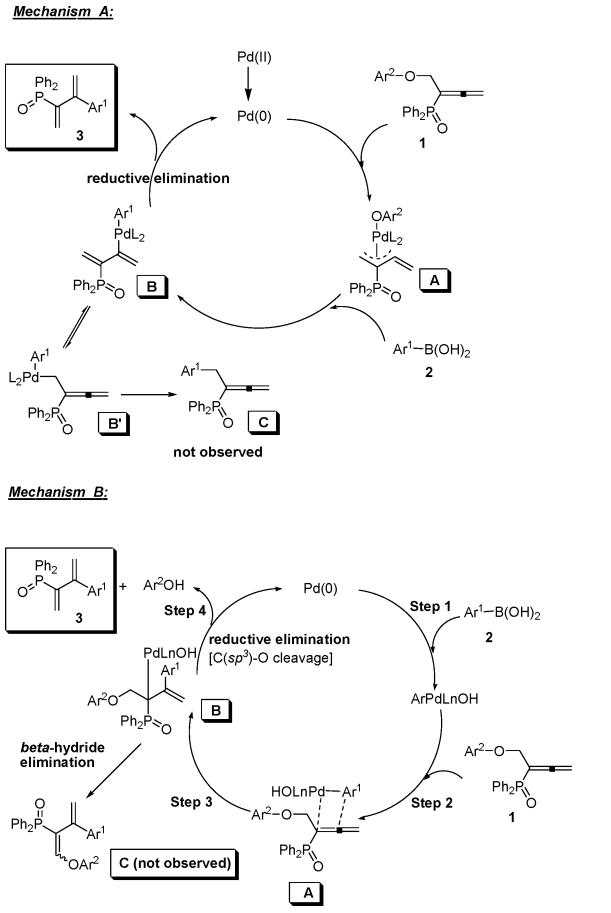

| entry | $R^3$ | $R^4$ | $R^2$ | yield of 3[b] |
|---|---|---|---|---|
| 1 | $CH_3$ | $CH_3$ (**1i**) | *p*-MeO | 94(**3j**) |
| 2 | $CH_3$ | $CH_3$ (**1i**) | H | 95(**3k**) |
| 3 | $-C_5H_{10}$-(**1j**) | | *p*-MeO | 98(**3l**) |
| 4 | $-C_5H_{10}$-(**1j**) | | H | 89(**3m**) |
| 5 | *p*-$MeOC_6H_4$ | H (**1k**) | H | 88(**3n**) (2.5:1)[c] |
| 6 | *p*-$MeOC_6H_4$ | H (**1k**) | *p*-Br | 88(**3o**) (only *E*)[c] |
| 7 | *p*-$CF_3C_6H_4$ | $CH_3$ (**1l**) | H | 80(**3p**) (only *E*)[c] |
| 8 | *p*-$CF_3C_6H_4$ | $CH_3$ (**1l**) | *p*-F | 80(**3q**) (only *E*)[c] |
| 9 | $CH_3CH_2$ | H (**1m**) | H | 85(**3r**) (only *E*)[c] |
| 10 | $CH_3CH_2$ | H (**1m**) | *p*-acetyl | 64(**3s**) (only *E*)[c] |
| 11 | Ph | Ph (**1n**) | *p*-MeO | 47(**3t**) |
| 12 | Ph | Ph (**1n**) | H | 65(**3u**) |

[a]1 mmol allenylphosphine oxides, 2 mmol arylboronic acid, 5 mol % $Pd(PPh_3)_2Cl_2$, 3 mmol $K_2CO_3$, 5 mL THF, reflux. [b]Isolated yield based on allenes; [c]*E*:*Z* ratios and relative stereochemistries were determined by $^{31}P$ NMR and NOESY experiments, respectively.

This improved selectivity might be rationalized by relative differences in the stability and reactivity of intermediates affected by the substitution groups on allenes. It is worth mentioning that all of these substrates afforded higher yields on average than terminal phosphinoylallenes even in the case of coupling with electron-deficient arylboronic acids (entries 6, 8, 10).

Although the mechanism of this reaction is still under exploration, a plausible pathway is proposed based on the known palladium and allenes chemistry (Scheme 3, mechanism

**Scheme 3. Plausible Mechanism for Palladium-Catalyzed Suzuki−Miyaura Coupling of Allenylphosphine Oxides with Arylboronic Acids**




A).[18a,31] At first, cleavage of C($sp^3$)-O(Ar) bond leads to the formation of $\pi$-allylpalladium species **A**. Subsequently, transmetalation between **A** and arylboronic acid produces intermediates **B** and **B′**; simultaneously, no observation of product **C** evidence the priority of forming intermediate **B** in the step (as mentioned in ref 30, the analogue of phosphorus-free allenes led to low yields of mixtures, thus, this priority might be attributed to the existence of phosphinoyl group to achieve larger conjugated system in final product). Finally, reductive elimination of **B** generates the final coupling products **3**, along with the recycle of the palladium(0) catalyst. Another mechanism B via palladium-catalyzed hydroarylation of diphenylphosphinylallenes with arylboronic acids[19j,29] described as below was excluded where the C($sp^3$)-O(Ar) cleavage at step four is unlikely to occur. Furthermore, adverse effect of high steric substituents on allenes should be observed at step second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and third, which is in conflict with experimental data in Table 2 and 3.

In summary, a novel palladium-catalyzed Suzuki−Miyaura coupling with $\alpha$-allenyl ethers as educts has been established. This coupling of allenylphosphine oxides with arylboronic acids provides a facile catalytic method of generating phosphinoyl 1,3-butadienes and their derivatives with modest to excellent yields. This work stands for a new transformation of allenes to multisubstituted conjugated phosphinoyldienes, which inspires the ongoing application of this method in tandem reactions to build bioactive compounds.[32]

## EXPERIMENTAL SECTION

**General Methods.** Solvents and reagents were reagent grade and used without purification unless otherwise noted. Anhydrous solvents were obtained as follows: THF, 1,4-dioxane, and toluene were dried by distillation from sodium and benzophenone; DMF was redistilled over $CaH_2$. All reactions were carried out in oven-dried glassware under nitrogen unless otherwise specified. Column chromatography was performed using silica gel (300−400 mesh). $^1$H NMR, $^{13}$C NMR, and $^{31}$P NMR spectra were recorded in $CDCl_3$ operating at 400, 100, and 162 MHz in the presence of tetramethylsilane (TMS) as an internal standard and are reported in ppm ($\delta$). Coupling constants are reported in hertz (Hz). Spectral splitting patterns are designated as: s, singlet; d, doublet; t, triplet; q, quartet; p, pentet; m, multiplet; and br, broad. High resolution MS measurements were made with a FT-ICR mass spectrometer.

**Synthetic Procedures.** *General Procedure for the Synthesis of Aromatic Ether-Based Allenylphosphine Oxides (**1**). 2-(2-(Diphenylphosphine oxide)buta-2,3-dienyloxy)benzaldehyde (**1a**).* To a stirred and cooled (0 °C) solution of the 2-(4-hydroxybut-2-ynyloxy)benzaldehyde (3.80 g, 20 mmol) in anhydrous ether (50 mL) and pyridine (1.94 mL, 24 mmol) under nitrogen was dropwisely added diphenylphosphine chloride (4.41 g, 20 mmol) in $CH_2Cl_2$ (50 mL). The stirring was maintained 1 h at 0 °C and at room temperature overnight. The reaction was then quenched with ice-cold water and extracted with $CH_2Cl_2$ (10 mL × 3), and the organic layer was dried with anhydrous $Na_2SO_4$. Concentration in vacuo gave the crude product, which was further subjected to flash chromatography on silica gel to afford product **1a** as pale-yellow solids (6.46 g, 85% yield, mp 101.5−102.6 °C). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 4.92−4.96 (m, 2H), 5.01−5.04 (m, 2H), 7.01−7.05 (m, 2H), 7.47−7.61 (m, 7H), 7.76−7.81 (m, 5H), 9.96 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 64.6 (d, $J_{C-P}$ = 8.7 Hz), 78.5 (d, $J_{C-P}$ = 11.8 Hz), 94.8 (d, $J_{C-P}$ = 100.7 Hz), 112.7, 121.2, 125.1, 128.2, 128.5 (d, $J_{C-P}$ = 12.5 Hz), 131.3 (d, $J_{C-P}$ = 106.4 Hz), 131.7 (d, $J_{C-P}$ = 9.8 Hz), 132.3, 132.4, 135.7, 160.1, 189.6, 212.4 (d, $J_{C-P}$ = 5.9 Hz). HR-MS (ESI): calcd for $C_{23}H_{19}NaO_3P$ $[M + Na]^+$, 397.0970; found, 397.0973.

*(1-(2-Bromophenoxy)buta-2,3-dien-2-yl)diphenylphosphine oxide (**1b**).* A white solid, mp 108.5−109.7 °C (3.10 g, 48% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 4.72−4.76 (m, 4H), 6.87−6.97 (m, 2H), 7.23−7.27 (m, 1H), 7.42−7.57 (m, 7H), 7.78−7.84 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 52.7 (d, $J_{C-P}$ = 4.2 Hz), 56.9, 82.1, 82.5 (d, $J_{C-P}$ = 9.0 Hz), 112.4, 114.2, 122.9, 128.4, 128.6 (d, $J_{C-P}$ = 13.0 Hz), 131.8 (d, $J_{C-P}$ = 10.1 Hz), 132.6, 133.6, 154.0 (d, $J_{C-P}$ = 4.3 Hz), 212.6 (d, $J_{C-P}$ = 5.7 Hz). HR-MS (ESI): calcd for $C_{22}H_{18}BrNaO_2P$ $[M + Na]^+$, 447.0125; found, 447.0129.

*(1-(4-Methoxyphenoxy)buta-2,3-dien-2-yl)diphenylphosphine Oxide (**1c**).* A white solid, mp 98.5−100.7 °C (2.70 g, 38% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 4.10 (s, 3H), 5.11−5.14 (m, 2H), 5.21−5.25 (m, 2H), 7.04−7.14 (m, 4H), 7.79−7.91 (m, 6H), 8.10−8.15 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 55.7, 65.2 (d, $J_{C-P}$ = 9.3 Hz), 78.4 (d, $J_{C-P}$ = 12.1 Hz), 95.4 (d, $J_{C-P}$ = 100.3 Hz), 114.5, 116.1, 128.4 (d, $J_{C-P}$ = 12.4 Hz), 131.7 (d, $J_{C-P}$ = 106.0 Hz), 131.8 (d, $J_{C-P}$ = 9.8 Hz), 132.0, 132.1, 152.0, 154.2, 212.4 (d, $J_{C-P}$ = 5.6 Hz). HR-MS (ESI): calcd for $C_{23}H_{21}NaO_3P$ $[M + Na]^+$, 399.1126; found, 399.1130.

*(1-(3-Methoxyphenoxy)buta-2,3-dien-2-yl)diphenylphosphine Oxide (**1d**).* A pale-yellow viscous liquid (3.70 g, 52% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.73 (s, 3H), 4.79−4.83 (m, 2H), 4.86−4.90 (m, 2H), 6.30 (t, $J$ = 2.4 Hz, 1H), 6.38 (dd, $J_1$ = 2.4 Hz, $J_2$ = 8.4 Hz, 1H), 6.48 (dd, $J_1$ = 2.4 Hz, $J_2$ = 8.4 Hz, 1H), 7.10 (t, $J$ = 8.4 Hz, 1H), 7.42−7.55 (m, 6H), 7.73−7.79 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 55.4, 60.6, 64.5 (d, $J_{C-P}$ = 9.3 Hz), 78.6 (d, $J_{C-P}$ = 12.0 Hz), 95.3 (d, $J_{C-P}$ = 100.6 Hz), 101.4, 107.1 (d, $J_{C-P}$ = 12.8 Hz), 128.5 (d, $J_{C-P}$ = 12.5 Hz), 129.9, 131.6 (d, $J_{C-P}$ = 106.2 Hz), 132.0 (d, $J_{C-P}$ = 9.9 Hz), 132.2, 132.3, 159.2, 160.8, 212.5 (d, $J_{C-P}$ = 5.6 Hz). HR-MS (ESI): calcd for $C_{23}H_{21}NaO_3P$ $[M + Na]^+$, 399.1126; found, 399.1129.

*(1-(p-Tolyloxy)buta-2,3-dien-2-yl)diphenylphosphine Oxide (**1e**).* A pale-yellow solid, mp 91.2−92.7 °C (2.80 g, 68% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.25 (s, 3H), 4.76−4.80 (m, 2H), 4.84−4.87 (m, 2H), 6.66 (d, $J$ = 8.8 Hz, 2H), 6.99 (d, $J$ = 8.8 Hz, 2H), 7.41−7.54 (m, 6H), 7.74−7.79 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 20.6, 64.5 (d, $J_{C-P}$ = 9.5 Hz), 78.5 (d, $J_{C-P}$ = 12.0 Hz), 95.3 (d, $J_{C-P}$ = 100.4 Hz), 114.8, 128.4 (d, $J_{C-P}$ = 12.5 Hz), 129.8, 130.4, 131.0, 131.8 (d, $J_{C-P}$ = 9.9 Hz), 132.1, 132.2, 155.8, 212.3 (d, $J_{C-P}$ = 5.5 Hz). HR-MS (ESI): calcd for $C_{23}H_{21}NaO_2P$ $[M + Na]^+$, 383.1177; found, 383.1180.

*(1-(2,6-Dimethylphenoxy)buta-2,3-dien-2-yl)diphenylphosphine Oxide (**1f**).* A colorless crystal, mp 93.5−96.4 °C (3.30 g, 61% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.15 (s, 6H), 4.48−4.51 (m, 2H), 4.92−4.96 (m, 2H), 6.86−6.95 (m, 3H), 7.45−7.56 (m, 6H), 7.80−7.85 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 16.3, 67.5 (d, $J_{C-P}$ = 9.8 Hz), 78.3 (d, $J_{C-P}$ = 11.7 Hz), 96.0 (d, $J_{C-P}$ = 101.5 Hz), 124.3, 128.4 (d, $J_{C-P}$ = 12.3 Hz), 128.8, 131.6 (d, $J_{C-P}$ = 109.4 Hz), 131.9 (d, $J_{C-P}$ = 9.7 Hz), 155.3, 213.0 (d, $J_{C-P}$ = 5.1 Hz). HR-MS (ESI): calcd for $C_{24}H_{23}NaO_2P$ $[M + Na]^+$, 397.1333; found, 397.1337.

*(1-Phenoxybuta-2,3-dien-2-yl)diphenylphosphine Oxide (**1g**).* A colorless viscous liquid (1.10 g, 45% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 4.80−4.88 (m, 4H), 6.76 (d, $J$ = 8 Hz, 2H), 6.90 (t, $J$ = 7.2 Hz, 1H), 7.17−7.21 (m, 2H), 7.41−7.54 (m, 6H), 7.74−7.79 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 64.3 (d, $J_{C-P}$ = 9.3 Hz), 78.5 (d, $J_{C-P}$ = 12.0 Hz), 95.1 (d, $J_{C-P}$ = 100.6 Hz), 114.9, 121.2, 128.4 (d, $J_{C-P}$ = 12.4 Hz), 129.4, 131.4 (d, $J_{C-P}$ = 106.2 Hz), 131.8 (d, $J_{C-P}$ = 9.8 Hz), 132.1, 132.2, 157.8, 212.4 (d, $J_{C-P}$ = 5.6 Hz). HR-MS (ESI): calcd for $C_{22}H_{19}NaO_2P$ $[M + Na]^+$, 369.1020; found, 369.1018.

*(1-(2,4-Difluorophenoxy)buta-2,3-dien-2-yl)diphenylphosphine Oxide (**1h**).* A pale-yellow solid, mp 111.3−112.7 °C (2.10 g, 76% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 4.82−4.90 (m, 4H), 6.67−6.89 (m, 3H), 7.44−7.56 (m, 6H), 7.74−7.79 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 66.4 (d, $J_{C-P}$ = 9.4 Hz), 78.6 (d, $J_{C-P}$ = 11.9 Hz), 94.9 (d, $J_{C-P}$ = 100.4 Hz), 104.8 (dd, $J_{C-F}$ = 26.6, 4.6 Hz), 110.3 (dd, $J_{C-F}$ = 22.4, 4.0 Hz), 116.7 (dd, $J_{C-F}$ = 9.4, 6.8 Hz), 128.4 (d, $J_{C-P}$ = 12.5 Hz), 128.5 (d, $J_{C-P}$ = 12.3 Hz), 131.3 (d, $J_{C-P}$ = 106.4 Hz), 131.8 (d, $J_{C-F}$ = 9.9 Hz), 132.1 (d, $J_{C-F}$ = 9.8 Hz), 132.2, 132.3, 142.3 (dd, $J_{C-F}$ = 10.7, 7.2 Hz), 151.4 (d, $J_{C-F}$ = 11.9 Hz), 153.9 (d, $J_{C-F}$ = 11.9 Hz), 155.7 (d, $J_{C-F}$ = 10.2 Hz), 158.1 (d, $J_{C-F}$ = 10.2 Hz), 212.6 (d, $J_{C-P}$ = 5.7 Hz). HR-MS (ESI): calcd for $C_{22}H_{17}F_2NaO_2P$ $[M + Na]^+$, 405.0832; found, 405.0835.

*(1-(2,6-Dimethylphenoxy)-4-methylpenta-2,3-dien-2-yl)-diphenylphosphine Oxide (**1i**).* A white solid, mp 97.6−99.6 °C (1.20 g, 40% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.45 (s, 3H), 1.46 (s, 3H), 4.42 (d, $J$ = 8.8 Hz, 2H), 6.78−6.88 (m, 3H), 7.38−7.48 (m, 6H), 7.71−7.76 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 16.3, 19.1, 19.2, 68.0 (d, $J_{C-P}$ = 12.9 Hz), 94.5 (d, $J_{C-P}$ = 104.2 Hz), 99.7 (d, $J_{C-P}$ = 13.3 Hz), 124.0, 128.2 (d, $J_{C-P}$ = 12.2 Hz), 128.7, 131.2, 131.7, 131.75 (d, $J_{C-P}$ = 9.6 Hz), 131.77, 132.5 (d, $J_{C-P}$ = 104.7 Hz), 155.6, 209.6 (d, $J_{C-P}$ = 5.4 Hz). HR-MS (ESI): calcd for $C_{26}H_{27}NaO_2P$ $[M + Na]^+$, 425.1646; found, 425.1650.

*(3-(2,6-Dimethylphenoxy)-1-cyclohexylideneprop-1-en-2-yl)-diphenylphosphine Oxide (**1j**).* A white solid, mp 98.7−100.5 °C (1.50 g, 82% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.92−0.98 (m, 2H), 1.23−1.28 (m, 2H), 1.37−1.45 (m, 2H), 1.83−1.90 (m, 2H), 1.94−2.02 (m, 2H), 2.07 (s, 6H), 4.42 (d, $J$ = 9.6 Hz, 2H), 6.77−6.87 (m, 3H), 7.37−7.47 (m, 6H), 7.72−7.76 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 16.5, 25.6, 26.5 (d, $J_{C-P}$ = 3.0 Hz), 30.1 (d, $J_{C-P}$ = 5.1 Hz), 68.3 (d, $J_{C-P}$ = 12.8 Hz), 94.5 (d, $J_{C-P}$ = 105.6 Hz), 105.8 (d, $J_{C-P}$ = 13.1 Hz), 124.2, 128.5 (d, $J_{C-P}$ = 12.2 Hz), 128.9, 131.4, 131.9, 132.0, 132.1 (d, $J_{C-P}$ = 9.6 Hz), 132.7 (d, $J_{C-P}$ = 104.6 Hz), 155.8, 206.8 (d, $J_{C-P}$ = 6.3 Hz). HR-MS (ESI): calcd for $C_{29}H_{31}NaO_2P$ $[M + Na]^+$, 465.1959; found, 465.1963.


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*(1-(2,6-Dimethylphenoxy)-4-(4-methoxyphenyl)buta-2,3-dien-2-yl)diphenylphosphine Oxide (**1k**).* A pale-yellow liquid (0.77g, 46% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.14 (s, 6H), 3.79 (s, 3H), 4.58−4.68 (m, 2H), 6.30−6.33 (m, 1H), 6.81 (d, $J$ = 8.8 Hz, 2H), 6.85−6.94 (m, 3H), 7.09 (d, $J$ = 8.0 Hz, 2H), 7.37−7.51 (m, 6H), 7.80−7.86 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 16.5, 55.5, 68.1 (d, $J_{C-P}$ = 11.2 Hz), 97.9 (d, $J_{C-P}$ = 13.0 Hz), 100.9 (d, $J_{C-P}$ = 101.1 Hz), 114.4, 123.95 (d, $J_{C-P}$ = 6.6 Hz), 124.4, 128.5 (d, $J_{C-P}$ = 8.6 Hz), 128.6, 129.0, 131.3, 132.0 (dd, $J_{C-P}$ = 10.9 Hz), 132.2 (d, $J_{C-P}$ = 105.3 Hz), 132.3 (dd, $J_{C-P}$ = 6.1 Hz), 132.4, 155.5, 159.6, 212.2 (d, $J_{C-P}$ = 4.9 Hz). HR-MS (ESI): calcd for $C_{31}H_{29}NaO_3P$ [M + Na]$^+$, 503.1752; found, 503.1755.

*(1-(2,6-Dimethylphenoxy)-4-(4-(trifluoromethyl)phenyl)penta-2,3-dien-2-yl)diphenylphosphine Oxide (**1l**).* A pale-yellow oil (1.68 g, 88% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.92 (d, $J$ = 5.6 Hz, 3H), 2.15 (s, 3H), 4.58−4.69 (m, 2H), 6.87−6.96 (m, 3H), 7.32−7.55 (m, 10H), 7.73−7.81 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 16.0 (d, $J_{C-P}$ = 5.4 Hz), 16.3, 67.7 (d, $J_{C-P}$ = 11.7 Hz), 99.7 (d, $J_{C-P}$ = 99.6 Hz), 104.5 (d, $J_{C-P}$ = 13.3 Hz), 124.4, 125.5, 125.6, 126.2, 126.7 (q, $J_{CF3}$ = 249.6 Hz), 127.8, 128.5 (d, $J_{C-P}$ = 6.1 Hz), 129.0, 129.4, 129.8, 131.1, 131.2, 131.5, 131.59 (d, $J_{C-P}$ = 105.2 Hz), 131.6, 131.7 (d, $J_{C-P}$ = 8.2 Hz), 132.3, 139.0 (d, $J_{C-P}$ = 5.9 Hz), 155.4, 211.7 (d, $J_{C-P}$ = 4.3 Hz). HR-MS (ESI): calcd for $C_{32}H_{28}F_3NaO_2P$ [M + Na]$^+$, 555.1677; found, 555.1680.

*(1-(2,6-Dimethylphenoxy)hexa-2,3-dien-2-yl)diphenylphosphine Oxide (**1m**).* A pale-yellow liquid (0.90 g, 26% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.81 (t, $J$ = 7.6 Hz, 3H), 1.86−1.95 (m, 2H), 2.15 (s, 6H), 4.49 (dd, $J_1$ = 2.4 Hz, $J_2$ = 9.2 Hz, 2H), 5.34−5.41 (m, 1H), 6.86−6.95 (m, 3H), 7.44−7.54 (m, 6H), 7.78−7.87 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 13.1 (d, $J_{C-P}$ = 2.7 Hz), 16.2, 21.0 (d, $J_{C-P}$ = 5.2 Hz), 67.9 (d, $J_{C-P}$ = 11.5 Hz), 96.4 (d, $J_{C-P}$ = 12.7 Hz), 97.1 (d, $J_{C-P}$ = 103.5 Hz), 124.1, 128.28 (d, $J_{C-P}$ = 12.3 Hz), 128.3 (d, $J_{C-P}$ = 12.3 Hz), 128.8, 131.1, 131.6 (d, $J_{C-P}$ = 7.3 Hz), 131.8 (d, $J_{C-P}$ = 4.8 Hz), 131.9, 131.95, 131.98, 132.6 (d, $J_{C-P}$ = 7.6 Hz), 155.4, 210.3 (d, $J_{C-P}$ = 6.0 Hz). HR-MS (ESI): calcd for $C_{26}H_{27}NaO_2P$ [M + Na]$^+$, 425.1646; found, 425.1651.

*(1-(2,6-Dimethylphenoxy)-4,4-diphenylbuta-2,3-dien-2-yl)-diphenylphosphine Oxide (**1n**).* A pale-yellow solid, mp 121.5−122.5 °C (2.10 g, 67% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.05 (s, 6H), 4.60 (d, $J$ = 8 Hz, 2H), 6.79−6.87 (m, 3H), 6.99−7.02 (m, 4H), 7.23−7.32 (m, 10H), 7.39−7.43 (m, 2H), 7.64−7.69 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 16.3, 67.6 (d, $J_{C-P}$ = 11.9 Hz), 99.5 (d, $J_{C-P}$ = 101.1 Hz), 113.8 (d, $J_{C-P}$ = 13.4 Hz), 124.3, 128.2 (d, $J_{C-P}$ = 20.5 Hz), 128.49, 128.5 (d, $J_{C-P}$ = 7.4 Hz), 128.9, 131.2, 131.6 (d, $J_{C-P}$ = 105.1 Hz), 131.7 (d, $J_{C-P}$ = 9.9 Hz), 132.1, 132.2, 134.6 (d, $J_{C-P}$ = 6.0 Hz), 155.4, 211.5 (d, $J_{C-P}$ = 4.7 Hz). HR-MS (ESI): calcd for $C_{36}H_{31}NaO_2P$ [M + Na]$^+$, 549.1959; found, 549.1962.

*General Procedure for the Palladium-Catalyzed Couplings of Allenylphosphine Oxides with Arylboronic Acids to Access Phosphinoyl 1,3-Butadienes and Derivatives (**3**). (3-(4-Methoxyphenyl)buta-1,3-dien-2-yl) diphenylphosphine Oxide (**3a**).* To a 25 mL two-necked flask equipped with condenser under nitrogen was added allenylphosphine oxide (**1a**, 374.4 mg, 1 mmol), *p*-methoxyphenyl boronic acid (304.0 mg, 2 mmol), $Pd(PPh_3)_2Cl_2$ (35 mg, 5 mol %), $K_2CO_3$ (415 mg, 3 mmol), and 5 mL of degassed THF. The reaction mixture was then heated to reflux for 2 h until the complete consuming of starting materials monitored by TLC. After all of the volatiles were removed under reduced pressure, the crude product was purified on flash chromatography (eluent: 1:1 ethyl acetate/petroleum ether) to afford product **3a** as pale-yellow viscous liquid (309.9 mg, 86% for entry 1; 223.4 mg, 62% for entry 2; 291.9 mg, 81% for entry 3; 259.5 mg, 72% for entry 4; 299.1 mg, 83% for entry 5; 313.5 mg, 87% for entry 6 in Table 2, respectively). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.74 (s, 3H), 5.31 (s, 1H), 5.55 (s, 1H), 5.87 (d, $J_{P-H}$ = 19.6 Hz, 1H), 6.03 (d, $J_{P-H}$ = 40 Hz, 1H), 6.76 (d, $J$ = 8.8 Hz, 2H), 7.16 (d, $J$ = 8.8 Hz, 2H), 7.39−7.42 (m, 4H), 7.46−7.49 (m, 2H), 7.73−7.78 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 55.3, 113.5, 118.1 (d, $J_{C-P}$ = 5.0 Hz), 128.4 (d, $J_{C-P}$ = 12.1 Hz), 129.1, 131.7 (d, $J_{C-P}$ = 102.8 Hz), 131.85 (d, $J_{C-P}$ = 9.4 Hz), 131.9, 132.7 (d, $J_{C-P}$ = 5.2 Hz), 134.0 (d, $J_{C-P}$ = 9.2 Hz), 144.3 (d, $J_{C-P}$ = 91.0 Hz), 145.4 (d, $J_{C-P}$ = 9.8 Hz), 159.3. $^{31}$P NMR (126 MHz, $CDCl_3$): $\delta$ 29.4. HR-MS (ESI): calcd for $C_{23}H_{21}NaO_2P$ [M + Na]$^+$, 383.1177; found, 383.1171. IR (film) $\nu$ 3054, 2917, 2832, 1606, 1509, 1436, 1246, 1178, 1117, 1028, 909, 836 cm$^{-1}$.

*(3-Phenylbuta-1,3-dien-2-yl)diphenylphosphine Oxide (**3b**).* A pale-yellow viscous liquid (280.8 mg, 85% for entry 7; 251.1 mg, 76% for entry 8; 241.2 mg, 73% for entry 9; 224.6 mg, 68% for entry 10 in Table 2, respectively). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.38 (s, 1H), 5.68 (d, $J$ = 1.6 Hz, 1H), 5.85 (d, $J_{P-H}$ = 19.6 Hz, 1H), 5.99 (d, $J_{P-H}$ = 40.0 Hz, 1H), 7.24−7.26 (m, 4H), 7.42−7.53 (m, 6H), 7.74−7.79 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 119.7 (d, $J_{C-P}$ = 4.9 Hz), 127.8, 128.1 (d, $J_{C-P}$ = 18.6 Hz), 128.5 (d, $J_{C-P}$ = 12.0 Hz), 131.7 (d, $J_{C-P}$ = 103.0 Hz), 131.85, 131.9, 131.94, 134.1 (d, $J_{C-P}$ = 9.3 Hz), 140.4 (d, $J_{C-P}$ = 5.5 Hz), 144.0 (d, $J_{C-P}$ = 91.4 Hz), 145.8 (d, $J_{C-P}$ = 9.8 Hz). $^{31}$P NMR (126 MHz, $CDCl_3$): $\delta$ 30.1. HR-MS (ESI): calcd for $C_{22}H_{19}NaOP$ [M + Na]$^+$, 353.1071; found, 353.1066. IR (film) $\nu$ 3057, 2982, 2923, 2851, 1733, 1591, 1486, 1437, 1373, 1241, 1159, 1116, 1044, 846 cm$^{-1}$.

*(3-o-Tolylbuta-1,3-dien-2-yl)diphenylphosphine Oxide (**3c**).* A pale-yellow viscous liquid (220.4 mg, 64%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.23 (s, 3H), 5.256 (s, 1H), 5.46−5.62 (m, 2H), 6.08 (s, 1H), 7.10−7.24 (m, 5H), 7.49−7.59 (m, 6H), 7.80−7.85 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 19.7, 122.5 (d, $J_{C-P}$ = 4.1 Hz), 125.7, 127.6, 128.6 (d, $J_{C-P}$ = 12.0 Hz), 129.5, 130.0, 131.8 (d, $J_{C-P}$ = 9.6 Hz), 131.97, 132.0, 132.1 (d, $J_{C-P}$ = 102.8 Hz), 133.1 (d, $J_{C-P}$ = 10.5 Hz), 135.9, 140.5 (d, $J_{C-P}$ = 7.3 Hz), 142.6 (d, $J_{C-P}$ = 91.0 Hz), 144.7 (d, $J_{C-P}$ = 10.3 Hz). $^{31}$P NMR (126 MHz, $CDCl_3$): $\delta$ 33.6. HR-MS (ESI): calcd for $C_{23}H_{21}NaOP$ [M + Na]$^+$, 367.1228; found, 367.1222. IR (film) $\nu$ 3059, 2983, 2924, 1735, 1591, 1437, 1372, 1239, 1182, 1161, 1116, 1099, 1044, 847 cm$^{-1}$.

*(3-p-Tolylbuta-1,3-dien-2-yl)diphenylphosphine Oxide (**3d**).* A pale-yellow viscous liquid (196.3 mg, 57%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.31 (s, 3H), 5.35 (s, 1H), 5.63 (d, $J$ = 1.6 Hz, 1H), 5.84 (d, $J_{P-H}$ = 20.0 Hz, 1H), 6.00 (d, $J_{P-H}$ = 40.4 Hz, 1H), 7.05 (d, $J$ = 8.0 Hz, 2H), 7.13 (d, $J$ = 8.0 Hz, 2H), 7.41−7.53 (m, 6H), 7.74−7.79 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 21.1, 119.0 (d, $J_{C-P}$ = 4.9 Hz), 127.8, 128.4 (d, $J_{C-P}$ = 12.1 Hz), 128.8, 131.7 (d, $J_{C-P}$ = 102.8 Hz), 131.8, 131.81 (d, $J_{C-P}$ = 9.4 Hz), 133.9 (d, $J_{C-P}$ = 9.3 Hz), 137.4, 137.5 (d, $J_{C-P}$ = 5.6 Hz), 144.5 (d, $J_{C-P}$ = 91.2 Hz), 145.6 (d, $J_{C-P}$ = 9.7 Hz). $^{31}$P NMR (126 MHz, $CDCl_3$): $\delta$ 30.2. HR-MS (ESI): calcd for $C_{23}H_{21}NaOP$ [M + Na]$^+$, 367.1228; found, 367.1222. IR (film) $\nu$ 3055, 2954, 2920, 1737, 1647, 1608, 1589, 1510, 1437, 1387, 1315, 1185, 1157, 1118, 1100, 826 cm$^{-1}$.

*(3-Mesitylbuta-1,3-dien-2-yl)diphenylphosphine Oxide (**3e**).* A pale-yellow viscous liquid (253.3 mg, 68%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.18 (s, 6H), 2.32 (s, 3H), 5.23 (s, 1H), 5.41−5.58 (m, 2H), 6.11 (s, 1H), 6.91 (s, 2H), 7.52−7.62 (m, 6H), 7.83−7.89 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 19.9, 21.1, 123.1 (d, $J_{C-P}$ = 3.9 Hz), 128.2, 128.4 (d, $J_{C-P}$ = 12.2 Hz), 128.6 (d, $J_{C-P}$ = 12.0 Hz), 131.8, 131.9, 132.0, 132.4 (d, $J_{C-P}$ = 102.8 Hz), 136.1, 136.8, 136.9 (d, $J_{C-P}$ = 7.6 Hz), 141.8 (d, $J_{C-P}$ = 90.1 Hz), 143.0 (d, $J_{C-P}$ = 10.3 Hz). $^{31}$P NMR (126 MHz, $CDCl_3$): $\delta$ 31.5. HR-MS (ESI): calcd for $C_{25}H_{25}NaOP$ [M + Na]$^+$, 395.1541; found, 395.1535. IR (film) $\nu$ 3056, 2920, 2859, 1735, 1612, 1587, 1437, 1193, 1178, 1117, 852 cm$^{-1}$.

*(3-(4-Bromophenyl)buta-1,3-dien-2-yl)diphenylphosphine Oxide (**3f**).* A pale-yellow viscous liquid (221.0 mg, 54%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.39 (s, 1H), 5.67 (d, $J$ = 1.6 Hz, 1H), 5.88 (d, $J_{P-H}$ = 19.6 Hz, 1H), 6.01 (d, $J_{P-H}$ = 40 Hz, 1H), 7.10 (d, $J$ = 8.4 Hz, 2H), 7.38 (d, $J$ = 8.4 Hz, 2H), 7.45−7.59 (m, 6H), 7.73−7.78 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 119.9 (d, $J_{C-P}$ = 4.9 Hz), 121.9, 126.7, 128.6 (d, $J_{C-P}$ = 12.1 Hz), 129.6, 130.8, 131.3, 131.5 (d, $J_{C-P}$ = 97.4 Hz), 131.8 (d, $J_{C-P}$ = 10.2 Hz), 131.9 (d, $J_{C-P}$ = 9.6 Hz), 132.1 (d, $J_{C-P}$ = 2.6 Hz), 134.3 (d, $J_{C-P}$ = 9.0 Hz), 139.2 (d, $J_{C-P}$ = 5.3 Hz), 144.3 (d, $J_{C-P}$ = 88.0 Hz), 144.9 (d, $J_{C-P}$ = 9.9 Hz). $^{31}$P NMR (126 MHz, $CDCl_3$): $\delta$ 29.5. HR-MS (ESI): calcd for $C_{22}H_{18}BrNaOP$ [M + Na]$^+$, 431.0176; found, 431.0171. IR (film) $\nu$ 3059, 2923, 2853, 1738, 1590, 1483, 1437, 1168, 1116, 818 cm$^{-1}$.

*(3-(4-Fluorophenyl)buta-1,3-dien-2-yl)diphenylphosphine Oxide (**3g**).* A pale-yellow viscous liquid (128.9 mg, 37% for entry 15;


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198.6 mg, 57% for entry 16). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.34 (s, 1H), 5.62 (d, $J$ = 2.0 Hz, 1H), 5.86 (d, $J_{P-H}$ = 19.6 Hz, 1H), 6.00 (d, $J_{P-H}$ = 39.6 Hz, 1H), 6.92 (t, $J$ = 8.8 Hz, 2H), 6.89−7.19 (m, 2H), 7.42−7.54 (m, 6H), 7.72−7.77 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 115.1 (d, $J_{C-F}$ = 21.3 Hz), 119.4 (d, $J_{C-P}$ = 5.1 Hz), 128.5 (d, $J_{C-P}$ = 12.1 Hz), 128.6 (d, $J_{C-P}$ = 12.1 Hz), 129.6 (d, $J_{C-F}$ = 8.1 Hz), 131.4 (d, $J_{C-P}$ = 103.1 Hz), 131.9 (d, $J_{C-P}$ = 9.6 Hz), 132.0, 132.04, 132.1, 132.2, 134.1 (d, $J_{C-P}$ = 9.1 Hz), 136.2 (dd, $J_{C-F}$ = 5.1, 1.7 Hz), 144.2 (d, $J_{C-P}$ = 91.3 Hz), 145.0 (d, $J_{C-P}$ = 10.0 Hz), 162.4 (d, $J_{C-F}$ = 245.5 Hz). $^{31}$P NMR (126 MHz, $CDCl_3$): $\delta$ 29.6. HR-MS (ESI): calcd for $C_{22}H_{18}FNaOP$ $[M + Na]^+$, 371.0977; found, 371.0972. IR (film) $\nu$ 3057, 2924, 2841, 1761, 1601, 1506, 1437, 1223, 1158, 1117, 839 cm$^{-1}$.

*(3-(4-Nitrophenyl)buta-1,3-dien-2-yl)diphenylphosphine Oxide (**3h**).* A pale-yellow viscous liquid (210.2 mg, 56% for entry 17; 168.9 mg, 45% for entry 18 in Table 2, respectively). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 5.49 (s, 1H), 5.74 (d, $J$ = 2.0 Hz), 5.91 (d, $J_{P-H}$ = 21.6 Hz, 1H), 6.03 (d, $J_{P-H}$ = 39.2 Hz, 1H), 7.42−7.52 (m, 8H), 7.72−7.77 (m, 4H), 7.97−8.09 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 121.2 (d, $J_{C-P}$ = 5.3 Hz), 122.7 (d, $J_{C-P}$ = 6.8 Hz), 128.4, 128.56 (d, $J_{C-P}$ = 12.1 Hz), 128.61 (d, $J_{C-P}$ = 12.1 Hz), 129.2, 131.2 (d, $J_{C-P}$ = 116.1 Hz), 131.7 (d, $J_{C-P}$ = 3.2 Hz), 131.9 (d, $J_{C-P}$ = 9.6 Hz), 132.1, 132.2, 134.0, 134.2 (d, $J_{C-P}$ = 8.9 Hz), 135.7, 141.7 (d, $J_{C-P}$ = 4.6 Hz), 144.0 (d, $J_{C-P}$ = 91.0 Hz), 144.3 (d, $J_{C-P}$ = 9.9 Hz), 148.0. $^{31}$P NMR (126 MHz, $CDCl_3$): $\delta$ 28.7. HR-MS (ESI): calcd for $C_{22}H_{18}NNaO_3P$ $[M + Na]^+$, 398.0922; found, 398.0917. IR (film) $\nu$ 3057, 2921, 2841, 1733, 1625, 1525, 1437, 1348, 1187, 1117, 1097, 878 cm$^{-1}$.

*(3-(4-Acetylphenyl)buta-1,3-dien-2-yl)diphenylphosphine Oxide (**3i**).* A pale-yellow viscous liquid (290.5 mg, 78% for entry 19; 193.6 mg, 52% for entry 20 in Table 2, respectively). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 2.58 (s, 3H), 5.46 (s, 1H), 5.70 (d, $J$ = 1.6 Hz, 1H), 5.88 (d, $J_{P-H}$ = 19.6 Hz, 1H), 6.00 (d, $J_{P-H}$ = 40 Hz, 1H), 7.32 (d, $J$ = 8.4 Hz, 2H), 7.43−7.55 (m, 6H), 7.72−7.84 (m, 6H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 26.7, 128.5, 128.58 (d, $J_{C-P}$ = 12.0 Hz), 128.61 (d, $J_{C-P}$ = 12.1 Hz), 129.9, 131.9 (d, $J_{C-P}$ = 9.5 Hz), 131.98 (d, $J_{C-P}$ = 4.3 Hz), 132.04 (d, $J_{C-P}$ = 102.9 Hz), 132.06, 132.1, 132.2 (d, $J_{C-P}$ = 9.9 Hz), 133.0, 136.0, 136.6 (d, $J_{C-P}$ = 10.0 Hz), 139.3 (d, $J_{C-P}$ = 4.8 Hz), 143.9, 144.3 (d, $J_{C-P}$ = 91.4 Hz), 197.9. $^{31}$P NMR (126 MHz, $CDCl_3$): $\delta$ 29.8. HR-MS (ESI): calcd for $C_{24}H_{21}NaO_2P$ $[M + Na]^+$, 395.1177; found, 395.1171. IR (film) $\nu$ 3058, 2923, 2851, 1736, 1683, 1605, 1438, 1373, 1267, 1243, 1183, 1118, 847 cm$^{-1}$.

*(3-(4-Methoxyphenyl)-4-methylpenta-1,3-dien-2-yl)-diphenylphosphine Oxide (**3j**).* A pale-yellow viscous liquid (365.1 mg, 94%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.31 (s, 3H), 1.32 (s, 3H), 3.49 (d, $J$ = 8.4 Hz, 2H), 3.76 (s, 3H), 6.73 (d, $J$ = 8.8 Hz, 2H), 7.04 (d, $J$ = 8.8 Hz, 2H), 7.40−7.49 (m, 6H), 7.65−7.70 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 18.9 (d, $J_{C-P}$ = 5.9 Hz), 33.3 (d, $J_{C-P}$ = 9.1 Hz), 55.1, 97.0 (d, $J_{C-P}$ = 102.8 Hz), 99.2 (d, $J_{C-P}$ = 14.1 Hz), 113.4, 128.1 (d, $J_{C-P}$ = 11.9 Hz), 128.5 (d, $J_{C-P}$ = 12.1 Hz), 130.0, 131.0 (d, $J_{C-P}$ = 6.6 Hz), 131.5 (d, $J_{C-P}$ = 9.5 Hz), 132.0 (d, $J_{C-P}$ = 9.9 Hz), 132.3 (d, $J_{C-P}$ = 103.3 Hz), 157.9, 208.6 (d, $J_{C-P}$ = 7.2 Hz). $^{31}$P NMR (126 MHz, $CDCl_3$): $\delta$ 31.5. HR-MS (ESI): calcd for $C_{25}H_{25}NaO_2P$ $[M + Na]^+$, 411.1490; found, 411.1484. IR (film) $\nu$ 3059, 2917, 2849, 1736, 1611, 1512, 1464, 1438, 1373, 1245, 1177, 1119, 819 cm$^{-1}$.

*(4-Methyl-3-phenylpenta-1,3-dien-2-yl)diphenylphosphine Oxide (**3k**).* A pale-yellow solid, mp 85.6−86.8 °C. (340.5 mg, 94%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.29 (s, 3H), 1.31 (s, 3H), 3.55 (d, $J$ = 8.4 Hz, 2H), 7.11−7.22 (m, 5H), 7.40−7.51 (m, 6H), 7.66−7.71 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 18.9 (d, $J_{C-P}$ = 5.9 Hz), 34.1 (d, $J_{C-P}$ = 9.2 Hz), 97.0 (d, $J_{C-P}$ = 103.1 Hz), 99.3 (d, $J_{C-P}$ = 14.0 Hz), 126.2, 128.1, 128.2 (d, $J_{C-P}$ = 11.9 Hz), 129.1, 131.6, 131.61 (d, $J_{C-P}$ = 9.4 Hz), 132.4 (d, $J_{C-P}$ = 103.3 Hz), 139.1 (d, $J_{C-P}$ = 6.7 Hz), 208.8 (d, $J_{C-P}$ = 7.1 Hz). $^{31}$P NMR (126 MHz, $CDCl_3$): $\delta$ 31.3. HR-MS (ESI): calcd for $C_{24}H_{23}NaOP$ $[M + Na]^+$, 381.1384; found, 381.1379. IR (KBr) $\nu$ 3057, 3026, 2976, 2918, 2852, 1953, 1717, 1602, 1590, 1495, 1438, 1377, 1177, 1118, 1101, 797 cm$^{-1}$.

*(1-Cyclohexylidene-1-(4-methoxyphenyl)prop-2-en-2-yl)-diphenylphosphine Oxide (**3l**).* A pale-yellow viscous liquid (420.0 mg, 98%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.990−1.058 (m, 2H), 1.18−1.26 (m, 4H), 1.66−1.72 (m, 2H), 1.78−1.84 (m, 2H), 3.50 (d, $J$ = 7.6 Hz, 2H), 3.75 (s, 3H), 6.75 (d, $J$ = 8.8 Hz, 2H), 7.04 (d, $J$ = 8.8 Hz, 2H), 7.40−7.56 (m, 6H), 7.64−7.73 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 25.6, 26.5 (d, $J_{C-P}$ = 3.1 Hz), 30.0 (d, $J_{C-P}$ = 5.4 Hz), 33.6 (d, $J_{C-P}$ = 9.3 Hz), 55.5, 97.5 (d, $J_{C-P}$ = 104.0 Hz), 105.8 (d, $J_{C-P}$ = 13.7 Hz), 113.7, 128.4 (d, $J_{C-P}$ = 12.0 Hz), 128.7 (d, $J_{C-P}$ = 12.0 Hz), 130.3, 131.4 (d, $J_{C-P}$ = 7.2 Hz), 131.68, 131.7, 131.9 (d, $J_{C-P}$ = 9.4 Hz), 132.1, 132.2, 132.3 (d, $J_{C-P}$ = 9.8 Hz), 133.2 (d, $J_{C-P}$ = 4.2 Hz), 158.2, 205.4 (d, $J_{C-P}$ = 8.1 Hz). $^{31}$P NMR (126 MHz, $CDCl_3$): $\delta$ 31.3. HR-MS (ESI): calcd for $C_{28}H_{29}NaO_2P$ $[M + Na]^+$ 451.1803, found: 451.1797. IR (film) $\nu$ 3056, 2930, 2853, 1952, 1610, 1585, 1510, 1437, 1245, 1177, 1118, 1102, 831 cm$^{-1}$.

*(1-Cyclohexylidene-1-phenylprop-2-en-2-yl)diphenylphosphine Oxide (**3m**).* A pale-yellow viscous liquid (354.6 mg, 89%). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 0.98−1.26 (m, 6H), 1.61−1.69 (m, 2H), 1.75−1.82 (m, 2H), 3.56 (d, $J$ = 7.6 Hz, 2H), 7.12−7.21 (m, 5H), 7.38−7.49 (m, 6H), 7.69−7.74 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 25.4, 26.3 (d, $J_{C-P}$ = 3.1 Hz), 29.7 (d, $J_{C-P}$ = 5.3 Hz), 34.2 (d, $J_{C-P}$ = 9.2 Hz), 97.1 (d, $J_{C-P}$ = 104.3 Hz), 105.7 (d, $J_{C-P}$ = 13.6 Hz), 126.1, 128.0, 128.2 (d, $J_{C-P}$ = 12.0 Hz), 129.2, 131.5, 131.6 (d, $J_{C-P}$ = 9.6 Hz), 132.4 (d, $J_{C-P}$ = 103.4 Hz), 139.1 (d, $J_{C-P}$ = 7.3 Hz), 205.3 (d, $J_{C-P}$ = 8.0 Hz). $^{31}$P NMR (126 MHz, $CDCl_3$): $\delta$ 30.8. HR-MS (ESI): calcd for $C_{27}H_{27}NaOP$ $[M + Na]^+$, 421.1697; found, 421.1692. IR (film) $\nu$ 3059, 3029, 2980, 2929, 2851, 1951, 1736, 1602, 1587, 1495, 1437, 1372, 1240, 1179, 1118, 1101, 846 cm$^{-1}$.

*(4-(4-Methoxyphenyl)-3-phenylbuta-1,3-dien-2-yl)-diphenylphosphine Oxide (**3n**).* A pale-yellow viscous liquid (384.1 mg, 88%, *E*:*Z* = 2.6:1). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.70 (s, 3H), 3.81 (s, 1H), 5.51 (d, $J_{P-H}$ = 20.0 Hz, 1H), 5.70 (d, $J_{P-H}$ = 41.6 Hz, 1H), 6.58 (d, $J$ = 8.8 Hz, 2H), 6.69 (d, $J$ = 8.8 Hz, 2H), 7.16−7.22 (m, 4H), 7.35−7.57 (m, 7H), 7.83−7.88 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 55.1, 55.3, 97.5, 97.7, 102.6, 103.6, 113.3, 114.1, 126.5, 127.5, 127.9, 128.0, 128.2, 128.3, 128.4, 128.5, 128.7, 129.0, 129.2, 129.9, 131.2, 131.5, 131.6, 131.7, 131.8, 131.9, 132.4, 132.5, 132.7, 133.7, 136.4, 136.5, 139.0, 139.1, 144.7, 145.6, 158.7, 159.2, 210.8, 210.9. $^{31}$P NMR (126 MHz, $CDCl_3$): $\delta$ 32.2, 29.7. HR-MS (ESI): calcd for $C_{29}H_{25}NaO_2P$ $[M + Na]^+$, 459.1490; found, 459.1484. IR (film) $\nu$ 3061, 2925, 2852, 1735, 1604, 1569, 1510, 1463, 1438, 1252, 1178, 1117, 838 cm$^{-1}$.

*(3-(4-Bromophenyl)-4-(4-methoxyphenyl)buta-1,3-dien-2-yl)-diphenylphosphine Oxide (**3o**).* A pale-yellow viscous liquid (453.5 mg, 88%, only *E*-isomer). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 3.59−3.74 (m, 2H), 3.78 (s, 3H), 5.99−6.03 (m, 1H), 6.75 (d, $J$ = 8.4 Hz, 2H), 6.86 (d, $J$ = 8.4 Hz, 2H), 7.04 (d, $J$ = 8.4 Hz, 2H), 7.26−7.33 (m, 4H), 7.37−7.41 (m, 2H), 7.47−7.52 (m, 2H), 7.64−7.74 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 55.3, 97.7 (d, $J_{C-P}$ = 13.5 Hz), 102.7 (d, $J_{C-P}$ = 99.3 Hz), 114.2, 120.4, 124.0 (d, $J_{C-P}$ = 7.0 Hz), 126.8, 127.97, 128.0, 128.3 (d, $J_{C-P}$ = 12.2 Hz), 128.4 (d, $J_{C-P}$ = 12.2 Hz), 128.6, 131.0, 131.4, 131.5 (d, $J_{C-P}$ = 9.8 Hz), 131.7 (d, $J_{C-P}$ = 9.6 Hz), 131.77 (d, $J_{C-P}$ = 104.8 Hz), 131.8, 131.9, 131.97 (d, $J_{C-P}$ = 10.3 Hz), 132.00 (d, $J_{C-P}$ = 10.3 Hz), 137.6 (d, $J_{C-P}$ = 6.0 Hz), 159.3, 210.6 (d, $J_{C-P}$ = 6.4 Hz). $^{31}$P NMR (126 MHz, $CDCl_3$): $\delta$ 29.5. HR-MS (ESI): calcd for $C_{29}H_{24}BrNaO_2P$ $[M + Na]^+$, 537.0595; found, 537.0590. IR (film) $\nu$ 3055, 3009, 2957, 2926, 2833, 1896, 1712, 1603, 1585, 1509, 1484, 1437, 1251, 1174, 1117, 1098, 827 cm$^{-1}$.

*(4-(4-(Trifluoromethyl)phenyl)-3-phenylpenta-1,3-dien-2-yl) diphenylphosphine Oxide (**3p**).* A pale-yellow viscous liquid (390.8 mg, 80%, only *E*-isomer). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 1.70 (d, $J$ = 6.0 Hz, 3H), 3.71 (d, $J$ = 8.8 Hz, 2H), 6.94 (d, $J$ = 8.4 Hz, 2H), 7.12−7.21 (m, 5H), 7.29−7.34 (m, 2H), 7.38−7.52 (m, 6H), 7.62−7.71 (m, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ 14.7 (d, $J_{C-P}$ = 5.7 Hz), 33.2 (d, $J_{C-P}$ = 7.7 Hz), 101.2 (d, $J_{C-P}$ = 97.8 Hz), 103.1 (d, $J_{C-P}$ = 13.9 Hz), 124.0, 124.1, 124.57, 124.6, 125.5, 125.8 (q, $J_{CF3}$ = 270.3 Hz), 127.2 (d, $J_{C-P}$ = 15.1 Hz), 127.3 (d, $J_{C-P}$ = 12.4 Hz), 128.0, 130.3 (d, $J_{C-P}$ = 12.5 Hz), 130.4 (d, $J_{C-P}$ = 12.5 Hz), 130.5 (d, $J_{C-P}$ = 104.0 Hz), 130.9 (d, $J_{C-P}$ = 5.6 Hz), 137.3 (d, $J_{C-P}$ = 6.7 Hz), 138.2 (d, $J_{C-P}$ = 6.5 Hz), 209.6 (d, $J_{C-P}$ = 6.1 Hz). $^{31}$P NMR (126 MHz, $CDCl_3$): $\delta$ 30.5. HR-MS (ESI): calcd for $C_{30}H_{24}F_3NaOP$ $[M + Na]^+$, 511.1415; found, 511.1409. IR (film) $\nu$ 3079, 3059, 3026, 2989, 2915, 2848, 1936, 1713,


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1615, 1586, 1494, 1454, 1437, 1413, 1324, 1165, 1114, 1074, 840 $cm^{-1}$.

*(4-(4-(Trifluoromethyl)phenyl)-3-(4-fluorophenyl)penta-1,3-dien-2-yl)diphenylphosphine Oxide (**3q**).* A pale-yellow viscous liquid (405.2 mg, 80%, only *E*-isomer). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.77 (d, $J$ = 6.0 Hz, 3H), 3.74 (d, $J$ = 8.4 Hz, 2H), 6.91 (t, $J$ = 8.8 Hz, 2H), 7.03 (d, $J$ = 8.4 Hz, 2H), 7.15−7.18 (m, 2H), 7.34−7.38 (m, 2H), 7.43−7.57 (m, 6H), 7.66−7.75 (m, 4H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 15.9 (d, $J_{C-P}$ = 5.6 Hz), 33.7 (d, $J_{C-P}$= 7.7 Hz), 102.4 (d, $J_{C-P}$ = 97.7 Hz), 104.4 (d, $J_{C-P}$ = 13.9 Hz), 115.2 (d, $J_{C-F}$ = 21.2 Hz), 124.2 (q, $J_{CF3}$ = 270.3 Hz), 125.28, 125.3, 125.7, 125.74, 128.4 (d, $J_{C-P}$ = 15.1 Hz), 128.5 (d, $J_{C-P}$ = 15.2 Hz), 129.2, 129.5, 130.7 (d, $J_{C-P}$ = 7.9 Hz), 131.1, 131.46 (d, $J_{C-P}$ = 13.0 Hz), 131.54 (d, $J_{C-P}$ = 104.6 Hz), 131.6 (d, $J_{C-P}$ = 12.9 Hz), 132.1 (d, $J_{C-P}$ = 7.1 Hz), 134.3 (q, $J_{C-F}$ = 3.3 Hz), 139.2 (d, $J_{C-P}$ = 6.5 Hz), 161.8 (d, $J_{C-F}$ = 243.2 Hz), 210.6 (d, $J_{C-P}$ = 6.1 Hz). $^{31}P$ NMR (126 MHz, $CDCl_3$): $\delta$ 30.3. HR-MS (ESI): calcd for $C_{30}H_{23}F_4NaOP$ $[M + Na]^+$, 529.1320; found, 529.1315. IR (film) $\nu$ 3059, 2983, 2918, 1936, 1735, 1615, 1508, 1484, 1437, 1414, 1324, 1221, 1166, 1114, 1074, 839 $cm^{-1}$.

*(3-Phenylhexa-1,3-dien-2-yl)diphenylphosphine Oxide (**3r**).* A pale-yellow viscous liquid (304.7 mg, 85%, only *E*-isomer). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 0.66 (t, $J$ = 7.6 Hz, 3H), 1.74−1.81 (m, 2H), 5.38 (d, $J_{P-H}$ = 20.4 Hz, 1H), 5.52 (d, $J_{P-H}$ = 42.0 Hz, 1H), 6.50 (t, $J$ = 7.6 Hz, 1H), 7.10 (d, $J$ = 6.8 Hz, 2H), 7.22−7.33 (m, 3H), 7.42−7.50 (m, 6H), 7.77−7.82 (m, 4H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 13.6, 23.3, 127.1, 128.3, 128.4 (d, $J_{C-P}$ = 12.0 Hz), 129.4, 131.7, 131.74 (d, $J_{C-P}$ = 9.3 Hz), 131.8, 132.3 (d, $J_{C-P}$ = 92.1 Hz), 137.4 (d, $J_{C-P}$ = 9.9 Hz), 138.5 (d, $J_{C-P}$ = 7.2 Hz), 138.6 (d, $J_{C-P}$ = 4.7 Hz), 144.4 (d, $J_{C-P}$ = 91.3 Hz). $^{31}P$ NMR (126 MHz, $CDCl_3$): $\delta$ 32.2. HR-MS (ESI): calcd for $C_{24}H_{23}NaOP$ $[M + Na]^+$ 381.1384, found: 381.1379. IR (film) $\nu$ 3055, 2960, 2928, 2867, 1722, 1698, 1590, 1438, 1179, 1158, 1118, 1098, 870 $cm^{-1}$.

*(3-(4-Acetylphenyl)hexa-1,3-dien-2-yl)diphenylphosphine Oxide (**3s**).* A pale-yellow viscous liquid (256.3 mg, 64%, only *E*-isomer). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 0.73 (t, $J$ = 7.6 Hz, 3H), 1.77−1.85 (m, 2H), 2.65 (s, 3H), 5.41−5.58 (m, 2H), 6.50−6.54 (m, 1H), 7.22 (d, $J$ = 8.0 Hz, 2H), 7.49−7.59 (m, 6H), 7.68−7.82 (m, 4H), 7.96 (d, $J$ = 8.0 Hz, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 13.5, 23.3, 26.7, 128.4, 128.5 (d, $J_{C-P}$ = 12.0 Hz), 128.6 (d, $J_{C-P}$ = 12.1 Hz), 129.8, 131.8 (d, $J_{C-P}$ = 9.5 Hz), 131.9 (d, $J_{C-P}$ = 4.3 Hz), 132.0 (d, $J_{C-P}$ = 102.9 Hz), 132.0, 132.03, 132.1 (d, $J_{C-P}$ = 9.9 Hz), 133.0, 135.9, 136.6 (d, $J_{C-P}$ = 10.0 Hz), 139.2 (d, $J_{C-P}$ = 4.8 Hz), 143.8, 144.2 (d, $J_{C-P}$ = 91.4 Hz), 197.83. $^{31}P$ NMR (126 MHz, $CDCl_3$): $\delta$ 31.6. HR-MS (ESI): calcd for $C_{26}H_{25}NaO_2P$ $[M + Na]^+$, 423.1490; found, 423.1484. IR (film) $\nu$ 3056, 2962, 2926, 2872, 1735, 1681, 1603, 1483, 1437, 1266, 1186, 1118, 1099, 848 $cm^{-1}$.

*(3-(4-Methoxyphenyl)-4,4-diphenylbuta-1,3-dien-2-yl)-diphenylphosphine Oxide (**3t**).* A pale-yellow viscous liquid (240.9 mg, 47%). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 3.70 (d, $J$ = 7.6 Hz, 2H), 3.72 (s, 3H), 6.68−6.73 (m, 6H), 7.04 (d, $J$ = 8.8 Hz, 2H), 7.18−7.33 (m, 6H), 7.41−7.45 (m, 6H), 7.61−7.66 (m, 4H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 33.9 (d, $J_{C-P}$ = 7.9 Hz), 55.5, 102.8 (d, $J_{C-P}$ = 98.3 Hz), 113.9, 127.9, 128.17, 128.2, 128.4, 128.6, 130.4 (d, $J_{C-P}$ = 7.4 Hz), 130.6, 131.75 (d, $J_{C-P}$ = 9.7 Hz), 131.83 (d, $J_{C-P}$ = 103.8 Hz), 132.1 (d, $J_{C-P}$ = 2.7 Hz), 135.2 (d, $J_{C-P}$ = 6.2 Hz), 158.5, 210.1 (d, $J_{C-P}$ = 6.3 Hz). $^{31}P$ NMR (126 MHz, $CDCl_3$): $\delta$ 29.8. HR-MS (ESI): calcd for $C_{35}H_{29}NaO_2P$ $[M + Na]^+$, 535.1803; found, 535.1800. IR (film) $\nu$ 3068, 2937, 2913, 1934, 1715, 1598, 1511, 1493, 1438, 1207, 1179, 1119, 896 $cm^{-1}$.

*(3,4,4-Triphenylbuta-1,3-dien-2-yl)diphenylphosphine Oxide (**3u**).* A pale-yellow solid, mp 92.5−93.6 °C. (313.7 mg, 65%). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 3.74 (d, $J$ = 7.6 Hz, 2H), 6.64−6.66 (m, 4H), 7.11−7.23 (m, 10H), 7.30−7.35 (m, 4H), 7.43−7.47 (m, 3H), 7.61−7.66 (m, 4H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 34.6 (d, $J_{C-P}$ = 7.8 Hz), 102.3 (d, $J_{C-P}$ = 98.8 Hz), 113.7 (d, $J_{C-P}$ = 14.0 Hz), 126.7, 127.8, 128.0, 128.1, 128.35 (d, $J_{C-P}$ = 7.2 Hz), 128.41 (d, $J_{C-P}$ = 12.2 Hz), 129.5, 131.6 (d, $J_{C-P}$ = 103.9 Hz), 131.7 (d, $J_{C-P}$ = 9.7 Hz), 132.0 (d, $J_{C-P}$ = 2.8 Hz), 135.0 (d, $J_{C-P}$ = 6.1 Hz), 138.2 (d, $J_{C-P}$ = 7.3 Hz), 210.1 (d, $J_{C-P}$ = 6.3 Hz). $^{31}P$ NMR (126 MHz, $CDCl_3$): $\delta$ 29.8. HR-MS (ESI): calcd for $C_{34}H_{27}NaOP$ $[M + Na]^+$, 505.1697; found, 505.1692. IR (KBr) $\nu$ 3060, 3048, 3024, 2959, 2926, 1979, 1928, 1727, 1594, 1490, 1448, 1438, 1202, 1151, 1116, 1101, 894 $cm^{-1}$.

## ■ ASSOCIATED CONTENT

### Supporting Information

Experimental details and procedures, compound characterization data, and copies of $^1H$, $^{13}C$, $^{31}P$ NMR, and HR-MS for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES


(1) Krause, N.; Hashmi, A. S. K. *Modern Allene Chemistry*; Wiley-VCH, Weinheim, 2008.

(2) (a) Ma, S. M. *Chem. Rev.* **2005**, *105*, 2829−2871. (b) Ma, S. M. *Pure Appl. Chem.* **2006**, *78*, 197−208. (c) Bai, T.; Ma, S. M.; Jia, G. C. *Coord. Chem. Rev.* **2009**, *253*, 423−448.

(3) (a) Zimmer, R.; Dinesh, C. U.; Nandanan, E.; Khan, F. A. *Chem. Rev.* **2000**, *100*, 3067−3125. (b) Lechel, T.; Pfrengle, F.; Reissig, H.-U.; Zimmer, R. *ChemCatChem* **2013**, *5*, 2100−2130.

(4) Muñoz, M. P. *Chem. Soc. Rev.* **2014**, *43*, 3164−3183.

(5) (a) Brummond, K. M.; Chen, H.-F.; Sill, P.; You, L.-F. *J. Am. Chem. Soc.* **2002**, *124*, 15186−15187. (b) Li, C.-K.; Breit, B. *J. Am. Chem. Soc.* **2014**, *136*, 862−865.

(6) (a) Bandini, M. *Chem. Soc. Rev.* **2011**, *40*, 1358−1367. (b) Krause, N.; Winter, C. *Chem. Rev.* **2011**, *111*, 1994−2009.

(7) Hill, A. F.; Ho, C. T.; Wilton-Ely, J. D. E. T. *Chem. Commun.* **1997**, 2207−2208.

(8) Bates, R. W.; Satcharoen, V. *Chem. Soc. Rev.* **2002**, *31*, 12−21.

(9) Ma, S. M.; Jiao, N.; Ye, L.-W. *Chem.—Eur. J.* **2003**, *9*, 6049−6056.

(10) (a) Huang, X.; Jiang, X. P.; Fu, C. L.; Ma, S. M. *Adv. Synth. Catal.* **2013**, *355*, 3295−3303. (b) Ma, S. M. *Acc. Chem. Res.* **2003**, *36*, 701−712. (c) Negishi, E.; Copéret, C.; Ma, S. M.; Liou, S.-Y.; Liu, F. *Chem. Rev.* **1996**, *96*, 365−393.

(11) (a) Kang, S.-K.; Kim, K.-J. *Org. Lett.* **2001**, *3*, 511−514. (b) Wu, X.-F.; Neumann, H.; Beller, M. *Chem. Rev.* **2013**, *113*, 1−35.

(12) Ma, S. M.; Yu, Z. Q. *Angew. Chem., Int. Ed.* **2002**, *41*, 1775−1778.

(13) Persson, A. K. Å.; Bäckvall, J.-E. *Angew. Chem., Int. Ed.* **2010**, *49*, 4624−4627.

(14) (a) Trost, B. M.; Jäkel, C.; Plietker, B. *J. Am. Chem. Soc.* **2003**, *125*, 4438−4439. (b) Trost, B. M.; Simas, A. B. C.; Plietker, B.; Jäkel, C.; Xie, J. *Chem.—Eur. J.* **2005**, *11*, 7075−7082.

(15) (a) Grigg, R.; Brown, S.; Sridharan, V.; Uttley, M. D. *Tetrahedron Lett.* **1998**, *39*, 3247−3250. (b) Fu, C. L.; Ma, S. M. *Org. Lett.* **2005**, *7*, 1605−1607. (c) Yu, F.; Lian, X. D.; Ma, S. M. *Org. Lett.* **2007**, *9*, 1703−1706. (d) Deagostino, A.; Prandi, C.; Toppino, A.; Venturello, P. *Tetrahedron* **2008**, *64*, 10344−10349. (e) Braun, M.-G.; Katcher, M. H.; Doyle, A. G. *Chem. Sci.* **2013**, *4*, 1216−1220. (f) Reddy, M. N.; Swamy, K. C. K. *Synthesis* **2014**, *46*, 1091−1099.

(16) Tsuji, J. *Palladium Reagents and Catalysis—New Perspectives for the 21st Century*; John Wiley & Sons: New York, 2004.

(17) Selected examples of allylic fragments: (a) Nájera, C.; Gil-Moltó, J.; Karlström, S. *Adv. Synth. Catal.* **2004**, *346*, 1798−1811. (b) Kabalka, G. W.; Al-Masum, M. *Org. Lett.* **2006**, *8*, 11−13. (c) Kabalka, G. W.; Dadush, E.; Al-Masum, M. *Tetrahedron Lett.* **2006**, *47*, 7459−7461. (d) Tsukamoto, H.; Uchiyama, T.; Suzuki, T.; Kondo, Y. *Org. Biomol. Chem.* **2008**, *6*, 3005−3013. (e) Matsubara, R.; Jamison, T. F. *J. Am. Chem. Soc.* **2010**, *132*, 6880−6881. (f) Ohmiya, H.; Yokokawa, N.; Sawamura, M. *Org. Lett.* **2010**, *12*, 2438−2440. (g) Ohmiya, H.; Makida, Y.; Li, D.; Tanabe, M.; Sawamura, M. *J. Am. Chem. Soc.* **2010**, *132*, 879−889. (h) Li, C.-G.; Xing, J.-X.; Zhao, J.-M.; Huynh, P.; Zhang, W.-B.; Jiang, P.-K.; Zhang, Y. J. *Org. Lett.* **2012**, *14*, 390−393.

(18) For employing $\alpha$-allenyl esters or alcohols as $\pi$-allylmetal precursors, see: (a) Djahanbini, D.; Cazes, B.; Gore, J. *Tetrahedron Lett.* **1984**, *25*, 203−206. (b) Nokami, J.; Maihara, A.; Tsuji, J. *Tetrahedron Lett.* **1990**, *31*, 5629−5630. (c) Ni, Z.; Padwa, A. *Synlett* **1992**, *11*, 869−970. (d) Li, W.; Shi, M. *J. Org. Chem.* **2008**, *73*, 6698−6705. For palladium catalyzed addition of arylboronic acids to allenes: (e) Oh, C. H.; Ahn, T. W.; Reddy, R. V. *Chem. Commun.* **2003**, 2622−2623. (f) Yoshida, M.; Gotou, T.; Ihara, M. *Chem. Commun.* **2004**, 1124−1125. (g) Hopkins, C. D.; Malinakova, H. C. *Org. Lett.* **2004**, *6*, 2221−2224. (h) Hopkins, C. D.; Malinakova, H. C. *J. Org. Chem.* **2005**, *70*, 6848−6862. (i) Ma, S. M.; Guo, H.; Yu, F. *J. Org. Chem.* **2006**, *71*, 6634−6636. (j) Yoshida, M.; Matsuda, K.; Shoji, Y.; Gotou, T.; Ihara, M.; Shishido, K. *Org. Lett.* **2008**, *10*, 5183−5186. (k) Liu, Z.; Gu, P.; Shi, M. *Chem.—Eur. J.* **2011**, *17*, 5796−5799. (l) Tatsumi, K.; Fujihara, T.; Terao, J.; Tsuji, Y. *Chem. Commun.* **2014**, *50*, 8476−8479.

(19) Palladium: (a) Nishikata, T.; Lipshutz, B. H. *J. Am. Chem. Soc.* **2009**, *131*, 12103−12105. (b) Mino, T.; Kogure, T.; Abe, T.; Koizumi, T.; Fujita, T.; Sakamoto, M. *Eur. J. Org. Chem.* **2013**, 1501−1505. Copper: (c) Park, J. K.; Lackey, H. H.; Ondrusek, B. A.; McQuade, D. T. *J. Am. Chem. Soc.* **2011**, *133*, 2410−2413. Iron: (d) Asako, S.; Ilies, L.; Nakamura, E. *J. Am. Chem. Soc.* **2013**, *135*, 17755−17757.

(20) For selected papers utilizing allenylphosphonates/allenyl phosphine oxides under catalytic conditions, see: (a) Xin, N.; Ma, S.-M. *Eur. J. Org. Chem.* **2012**, 3806−3817. (b) Sajna, K. V.; Swamy, K. C. K. *J. Org. Chem.* **2012**, *77*, 5345−5356. (c) Suresh, R. R.; Swamy, K. C. K. *J. Org. Chem.* **2012**, *77*, 6959−6969. (d) Pavan, M. P.; Reddy, M. N.; Kumar, N. N. B.; Swamy, K. C. K. *Org. Biomol. Chem.* **2012**, *10*, 8113−8118. (e) de los Santos, J. M.; Ochoa, Z.; Palacios, F. *ARKIVOC* **2012**, *iv*, 54−62. (f) Kumar, N. N. B.; Reddy, M. N.; Swamy, K. C. K. *J. Org. Chem.* **2009**, *74*, 5395−5404. (g) Pavan, M. P.; Chakravarty, M.; Swamy, K. C. K. *Eur. J. Org. Chem.* **2009**, 5927−5940. (h) Guo, H.; Ma, S.-M. *Adv. Synth. Catal.* **2008**, *350*, 1213−1217. (i) Ma, S.-M.; Guo, H.; Yu, F. *J. Org. Chem.* **2006**, *71*, 6634−6636. (j) Chakravarty, M.; Swamy, K. C. K. *J. Org. Chem.* **2006**, *71*, 9128−9138.

(21) (a) Quin, L. D. *A Guide to Organophosphorus Chemistry*; Wiley-Interscience: New York, 2000. (b) Crepy, K. V. L; Imamoto, T. *Top. Curr. Chem.* **2003**, *229*, 111−141. (c) Demmer, C. S.; Krogsgaard-Larsen, N.; Bunch, L. *Chem. Rev.* **2011**, *111*, 7981−8006.

(22) Darling, S. D.; Muralidharan, F. N.; Muralidharan, V. B. *Tetrahedron Lett.* **1979**, 2761−2762.

(23) (a) Griffin, C. E.; Daniewski, W. M. *J. Org. Chem.* **1970**, *35*, 1691−1693. (b) Villemin, E.; Robeyns, K.; Robiette, R.; Herent, M.-F.; Marchand-Brynaert, J. *Tetrahedron* **2013**, *69*, 1138−1147.

(24) Darling, S. D.; Subramanian, N. *J. Org. Chem.* **1975**, *40*, 2851−2852.

(25) Xi, Z.-F.; Zhang, W.-X.; Song, Z.-Y.; Zheng, W.-X.; Kong, F.-Z.; Takahashi, T. *J. Org. Chem.* **2005**, *70*, 8785−8789.

(26) Han, L.-B.; Ono, Y.; Yazawa, H. *Org. Lett.* **2005**, *7*, 2909−2911.

(27) (a) Wu, L.; Li, B.-L.; Huang, Y.-Y.; Zhou, H.-F.; He, Y.-M.; Fan, Q.-H. *Org. Lett.* **2006**, *8*, 3605−3608. (b) Wu, L.; Li, Z.-W.; Zhang, F.; He, Y.-M.; Fan, Q.-H. *Adv. Synth. Catal.* **2008**, *350*, 846−862. (c) Wu, L.; Ling, J.; Wu, Z.-Q. *Adv. Synth. Catal.* **2011**, *353*, 1452−1456. (d) Wu, L.; Zhang, X.; Tao, Z.-M. *Catal. Sci. Technol.* **2012**, *2*, 707−710. (e) Wu, L.; Zhang, X.; Chen, Q.-Q.; Zhou, A.-K. *Org. Biomol. Chem.* **2012**, *10*, 7859−7862. (f) Liu, T.; Dong, J.; Cao, S. J.; Guo, L. C.; Wu, L. *RSC Adv.* **2014**, *4*, 61722−61726.

(28) Santelli-Rouvier, C.; Toupet, L.; Santelli, M. *J. Org. Chem.* **1997**, *62*, 9039−9047.

(29) For rhodium-catalyzed asymmetric hydroarylation of diphenylphosphinylallenes with arylboronic acids, see: (a) Nishimura, T.; Hirabayashi, S.; Yasuhara, Y.; Hayashi, T. *J. Am. Chem. Soc.* **2006**, *128*, 2556−2557. (b) Guo, X.-X.; Sawano, T.; Nishimura, T.; Hayashi, T. *Tetrahedron: Asymmetry* **2010**, *21*, 1730−1736.

(30) The generality of this coupling reaction was also tested by using analogue of phosphorus-free allenes; however, the catalysis was proven to be ineffective, as suffering from mixtures of hydroarylation adducts and 1,3-butadienes (∼1:1) with low yields.

(31) Wan, B. Q.; Ma, S. M. *Angew. Chem., Int. Ed.* **2013**, *52*, 441−445.

(32) For phosphine oxide-related cyclization and *aza*-Diels−Alder reaction to build bioactive heterocycles, please see: (a) Ivanov, I. K.; Ismailov, I. E.; Christov, V. Ch. *ARKIVOC* **2013**, *iv*, 152−163. (b) Rubin, M.; Markov, J.; Chuprakov, S.; Wink, D. J.; Gevorgyan, V. *J. Org. Chem.* **2003**, *68*, 6251−6256. (c) Eschenbrenner-Lux, V.; Kumar, K.; Waldmann, H. *Angew. Chem., Int. Ed.* **2014**, *53*, 11146−11157.