Tetrahedron 69 (2013) 5152–5159

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Palladium(II)-catalyzed *ortho*-arylation via phosphate-group-directed C–H activation

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ARTICLE INFO

Article history:
Received 8 March 2013
Received in revised form 12 April 2013
Accepted 15 April 2013
Available online 18 April 2013

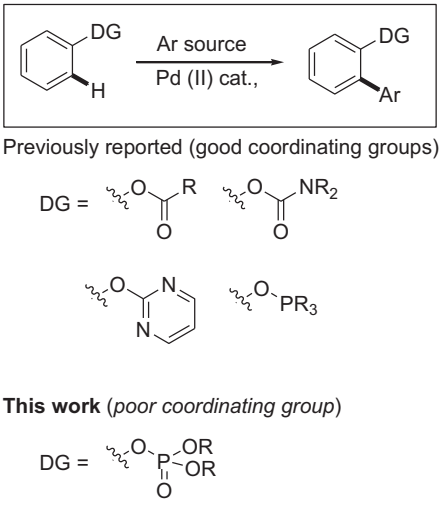
Keywords:
Phosphate
Palladium catalyst
C–H activation
Diaryliodonium salt
Directing group

ABSTRACT

Aryl dialkyl phosphate, which is readily available from phenol, was a good substrate for the Pd(II) catalyzed aryl–aryl coupling reaction through *ortho*-C–H activation. Although a phosphate group is regarded as a poor coordinating group, highly regioselective *ortho*-arylation could be achieved by employing $Pd(OTf)_2 \cdot 2H_2O$ and Ar_2IOTf as a catalyst and an aryl group source, respectively. The phosphate group of the resulting coupled product can be transformed into an aryl anion via reductive cleavage and used for further C–C bond formation.

1. Introduction

Transition-metal-catalyzed C–H activation is a very attractive approach to aryl–aryl coupling reactions because it bypasses the need for a pre-activated aryl group, such as an aryl halide or aryl triflate. However, a directing group is typically required to dictate the regioselectivity of such coupling reactions.[1] Good coordinating groups, such as aldehyde, ketone, imine, ester, amide, and triazene are known to be efficient in assisting *ortho*-C–H bond activation with high regioselectivity.[2] In the case of phenol, since a phenolic group alone does not induce high *ortho*-specific regioselectivity, temporary transformation of the phenol into a good directing group followed by removal of the temporary group after the coupling reaction was performed. Some examples of temporary directing groups include phenol ester, phenoxypyrimidine, phenol carbamate, and phenylphosphinite.[3] A common feature of these directing groups is that they are highly polarizable and exhibit strong coordinating ability. While a convenient and efficient transformation method for phenol masking is phosphorylation, the utility of the phosphate group as an *ortho*-directing group in C–H activated aryl–aryl coupling reactions has not yet been reported, likely due to its poor coordinating characteristics (Scheme 1). In this paper, we report the first successful example of a palladium-catalyzed *ortho*-arylation via phosphate-group-directed C–H activation.



Scheme 1. Various directing groups developed for palladium catalyzed aryl–aryl coupling reaction via *ortho*-C–H activation. DG=directing group. Ar=aryl group.

2. Results and discussion

Initially, we explored many different aryl C–H bond activation reaction conditions[4] and learned that employment of more electrophilic transition metal complexes along with a pre-oxidized coupling partner was desirable for phosphate-directed C–H bond

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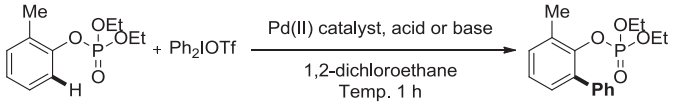
http://dx.doi.org/10.1016/j.tet.2013.04.067

activation. To optimize the reaction conditions, we chose *o*-tolyl diethyl phosphate (**1a**) as a test substrate and screened various Pd catalysts for the coupling reaction using diphenyliodonium triflate as the coupling partner.[5,6] The results of this study are summarized in Table 1. Aryl phosphate **1a** was prepared from diethyl phosphite following the literature procedure.[7] Yields of the coupling reactions were determined by ^{1}H NMR spectroscopy using *n*-decane as an internal reference.

4 Å molecular sieves in the reaction mixture did not improve the yields.

We also investigated the effect of the base on the reaction. The use of mild organic bases, such as pyridine (entry 14) and 2,6-lutidine (entry 15) completely inhibited the reaction. This is probably because these stronger coordinating bases competitively inhibit coordination of the palladium species with the neighboring phosphate group. In contrast, when a non-coordinating, sterically

Table 1
Optimization of the *ortho*-C–H activated arylation reaction conditions with diethyl *o*-tolyl phosphate (**1a**)[a]



1a **2a** **3a**

Entry	Pd(II) cat.(10 mol %)	Acid (mol %)	*T* (°C)	Yield[b] (%)	Entry	Pd(II) cat. (10 mol %)	Acid (mol %)	Base (1.0 equiv)	*T* (°C)	Yield[b] (%)
1[c]	$Pd(OAc)_2$	TfOH (10)	40	23	14	$Pd(OTf)_2\cdot 2H_2O$	—	Pyridine	60	NR[e]
2	$Pd(OAc)_2$	TfOH (20)	40	30	15	$Pd(OTf)_2\cdot 2H_2O$	—	2,6-Lutidine	60	NR[e]
3	$Pd(OAc)_2$	TfOH (50)	40	52	16	$Pd(OTf)_2\cdot 2H_2O$	—	2,6-Di-*tert*-butyl-4-methylpyridine	60	47
4	$Pd(OAc)_2$	TfOH (100)	40	20	17[f]	$Pd(OTf)_2\cdot 2H_2O$	—	$CaCO_3$	60	32
5	$Pd(OAc)_2$ (5)[d]	TfOH (50)	40	11	18[f]	$Pd(OTf)_2\cdot 2H_2O$	—	Cs_2CO_3	60	41
6	$Pd(OAc)_2$ (20)[d]	TfOH (50)	40	76	19[f]	$Pd(OTf)_2\cdot 2H_2O$	—	K_3PO_4	60	44
7	$Pd(OAc)_2$	TfOH (50)	60	60	20[f]	$Pd(OTf)_2\cdot 2H_2O$	—	K_2CO_3	60	55
8	$Pd(OAc)_2$	TfOH (50)	80	65	21[f]	$Pd(OTf)_2\cdot 2H_2O$	—	$KHCO_3$	60	56
9	$Pd(OAc)_2$	TFA (50)	60	40	22[f]	$Pd(OTf)_2\cdot 2H_2O$	—	$NaHCO_3$	60	44
10	$Pd(OAc)_2$	TsOH (50)	60	Trace	23[f]	$Pd(OTf)_2\cdot 2H_2O$	—	**Na_2CO_3**	**60**	**67**
11	$Pd(OAc)_2$	PivOH (50)	60	NR[e]	24	—	—	Na_2CO_3	60	NR[e]
12	$Pd(OTf)_2\cdot 2H_2O$	—	60	37	25	—	TfOH		60	NR[e]
13	$Pd(OTf)_2\cdot 2H_2O$	TfOH (30)	60	45						

[a] *o*-Tolyl diethyl phosphate (**1a**, 0.25 mmol), diphenyliodonium triflate (**2a**, 0.5 mmol), Pd(II) catalyst (0.025 mmol), and acid or base were reacted in 1,2-dichloroethane (0.5 mL) at the designated temperature under Ar for 1 h.
[b] Determined by ^{1}H NMR spectroscopy with *n*-decane as an internal standard.
[c] Liu conditions except pivaloyl anhydride. Ref. 3e.
[d] Loading amounts of Pd catalyst were varied to 5 mol % and 20 mol % for entries 5 and 6, respectively.
[e] No reaction. Starting material was recovered.
[f] The amount of 1,2-dichloroethane was increased to 1.0 mL.

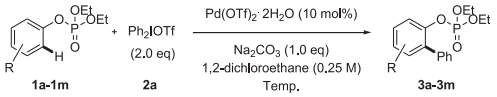
The first attempt employing Liu's reaction conditions [$Pd(OAc)_2$, TfOH in 1,2-dichloroethane] provided the desired coupling product **3a** at a 23% yield (Table 1, entry 1).[3e,8] Yields were improved when the amount of TfOH was increased up to 0.5 equiv (52%) (entries 2 and 3). However, the use of more than 0.5 equiv of TfOH was detrimental to the reaction. For example, the yield diminished to 20% when 1.0 equiv of TfOH was used (entry 4).

The yield of the coupling reaction was significantly improved as the amount of $Pd(OAc)_2$ catalyst was increased (entries 5 and 6). However, the amount of catalyst was fixed at 10 mol % for subsequent reactions. Since the temperature effect was minimal for the reactions (entries 7 and 8), subsequent reactions were performed at 60 °C.

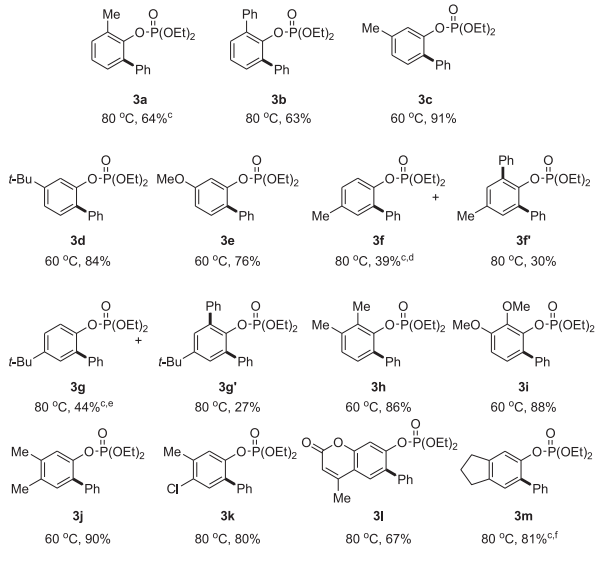
We also screened weaker organic acids, such as trifluoroacetic acid (TFA), *p*-toluenesulfonic acid (TsOH), and pivalic acid (PivOH) instead of trifluorosulfonic acid (TfOH) (entries 9–11). However, the use of weaker organic acids was not beneficial for the reaction. Employment of the strong, non-nucleophilic acid, TfOH, was essential for the coupling reaction. Since it was presumed that co-addition of $Pd(OAc)_2$ and TfOH formed $Pd(OTf)_2$ as an intermediate in situ, we determined whether the reaction could be catalyzed by pre-formed $Pd(OTf)_2$. $Pd(OTf)_2\cdot 2H_2O$ was prepared following the literature procedure.[9] When 10 mol % of $Pd(OTf)_2\cdot 2H_2O$ was used as the catalyst, the reaction proceeded readily as expected, and the product was obtained at a 37% yield (entry 12), which was analogous to the reaction conditions of entry 2 (10 mol % of $Pd(OAc)_2$, 20 mol % of TfOH, 30% yield). When TfOH (30 mol %) was added to this system, the yield was slightly improved, which is consistent with the results given in entry 7. An attempt to trap the water molecules from $Pd(OTf)_2\cdot 2H_2O$ by adding bulky pyridine, 2,6-di-*tert*-butyl-4-methylpyridine,[4i] was employed, the desired coupling product was obtained in reasonable yield (47%, entry 16). To our delight, the reaction also proceeded successfully in the presence of various inorganic bases, such as $CaCO_3$, Cs_2CO_3, K_3PO_4, K_2CO_3, $KHCO_3$, $NaHCO_3$, and Na_2CO_3 (entries 17–23). Among these, Na_2CO_3 gave the highest yield (67%) under similar reaction conditions. As control experiments, reactions were attempted with either Na_2CO_3 or TfOH as the sole reagent, but no desired product was obtained under these conditions (entries 24 and 25). Therefore, we concluded that the reactions were truly catalyzed by palladium species, and not by Brønsted acids or bases. From this investigation, we learned that the phosphate-directed C–H activation–arylation reaction could be promoted by $Pd(OTf)_2$ in conjunction with diphenyliodonium salt as an aryl group source and that higher yields could be obtained either with strong acids or non-coordinating, mild bases.

Once the reaction conditions were optimized, the scope and limitations of the reaction were explored with various aryl diethyl phosphates, as shown in Table 2. Aryl diethyl phosphates were prepared from diethyl phosphite and commercially available phenols following the literature procedure.[7] The amounts of $Pd(OTf)_2\cdot 2H_2O$ and Ph_2IOTf were fixed at 10 mol % and 2.0 equiv, respectively. In general, phosphates with an electron-rich aryl group provided the desired *ortho*-arylated products in good yields. In particular, introduction of an electron-donating substituent at the *meta*-position of the phenyl ring greatly improved the yields (**3c**–**e**, **3h**–**m** in Table 2). This result implies that the *ortho*-C–H bond activation step is significantly influenced by the *meta*-substituent, which is analogous to the conventional electrophilic aromatic substitution reaction. While *meta*-tolyl phosphate **1c**

Table 2
Pd(II)-catalyzed *ortho*-arylation of various phosphates (**1**) with diphenyliodonium triflate (**2a**) via C–H activation[a,b]



1a-1m 2a 3a-3m



[a] General conditions: phosphate (**1**, 0.25 mmol), diphenyliodonium triflate (**2a**, 0.5 mmol), $Pd(OTf)_2{\cdot}2H_2O$ (0.025 mmol), and Na_2CO_3 (0.25 mmol) in 1,2-dichloroethane (1.0 mL, 0.25 M) at the designated temperature under argon for 1 h. [b] Isolated yields after column chromatography, if not stated otherwise. [c] Estimated yield by ^1H NMR analysis. The mixture of starting material and product could not be separated. (**1a**: **3a** = 1: 2.3). [d] **1f**: **3f** = 1: 1.3. [e] **1g**: **3g** = 1: 1.4. [f] **1m**: **3m**: bisphenylated product = 0.12: 4.0: 0.33.

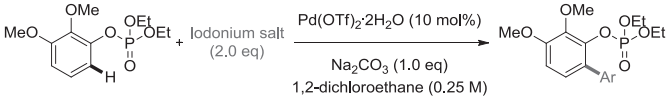
provided the mono-*ortho*-phenylated product **3c** in the highest yield (91%), the reaction with *ortho*-tolyl phosphate **1a** did not go to completion under the same conditions, and the desired product **3a** was obtained in moderate yield (64%). In the case of *para*-tolyl phosphate **1f**, the desired mono-*ortho*-phenylated product **3f** was obtained in 39% yield along with the bis-*ortho*-phenylated product **3f′** in 30% yield. Yields of the mono-phenylated products **3a** and **3f** were estimated by ^1H NMR spectral analyses of the reaction mixtures because these products were not separable from the starting materials **1a** and **1f** by conventional flash chromatography.

The reaction with pre-*ortho*-phenylated phenyl phosphate **1b** also afforded the coupled product **3b** in 63% yield, and the product was readily separable from the reaction mixture by conventional column chromatography. While the reaction with 3-*tert*-butylphenyl diethyl phosphate (**1d**) provided the *mono*-*ortho*-arylation product **3d** in 84% yield, the analogous reaction with 4-*tert*-butylphenyl diethyl phosphate (**1g**) provided not only *mono*-arylation product **3g** in 44% yield but also bis-arylation product **3g′** in 27% yield. Bis-arylation product **3g′** could be separated from the reaction mixture, but *mono*-arylation product **3g** was inseparable from the starting material **1g**, and its yield was estimated by ^1H NMR spectral analysis of the mixture.

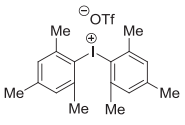
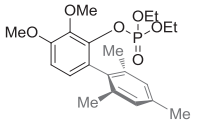
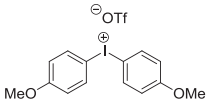
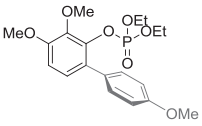
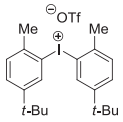
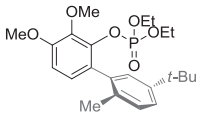
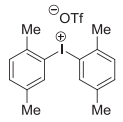
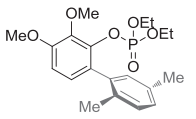
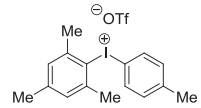
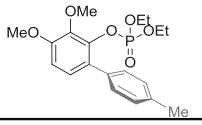
Introduction of an electron-donating group, such as a methoxy group to the *meta*-position of the aryl phosphate delivered high yields of the coupled products (**3e** and **3i**). Similarly, reactions with dimethylphenyl diethyl phosphates provided the desired products **3h** and **3j** in good yields. The presence of a halide at the *para*-position to the phosphate group was not deleterious to the *ortho*-arylation reaction, and the desired product **3k** was obtained in high yield (80%). The *ortho*-arylation reaction was also applicable to more complicated bicyclic aromatic compounds. For example, *ortho*-arylation products, **3l** and **3m**, were obtained in reasonable yields (67% and 81%, respectively) starting from the corresponding 7-hydroxy-4-methylcoumarin and 5-indanol derived phosphates.

The scope of the reaction was also investigated by varying the diaryliodonium triflate, and the results are summarized in Table 3. For this study, the phosphate substrate was fixed as 2,3-dimethoxyphenyl diethyl phosphate (**1b**). Various diaryliodonium salts were prepared from the corresponding aryl iodide or arene with iodine using *m*-CPBA as an oxidant.[5] To our surprise, even the sterically demanding dimesityliodonium triflate (**2b**) provided the *ortho*-arylation product **4b** in moderate yield (61%, entry 1 in Table 3). This reaction did not go to completion under the reaction conditions, and a small amount of starting material was recovered, which is probably due to the high steric bulkiness of the mesityl group. On the other hand, use of less sterically demanding diaryliodonium triflates, **4c**–**f**, provided the desired *ortho*-arylation products in higher yields with complete conversion, even at a lower reaction temperature (60 °C) (entries 2–5, Table 3).

Table 3
Pd(II)-catalyzed arylation of phosphate **1b** with various diaryliodonium triflates (**2**)[a]

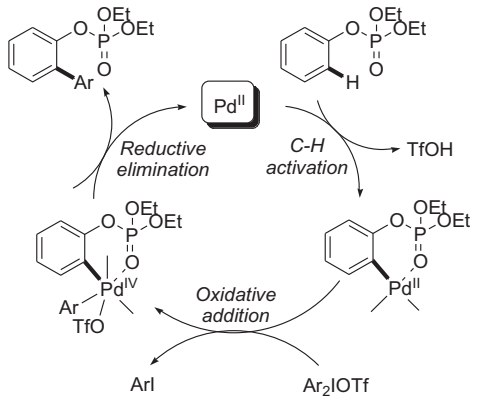


1b 2b-f 4b-f

Entry	Iodonium salt	T (°C)	Product	Yield[b] (%)
1		80		61
2		60		91
3		60		73
4		60		72
5		60		72

[a] General conditions: Phosphate (**1b**, 0.25 mmol), diaryliodonium triflate (**2b**–**f**, 0.5 mmol), $Pd(OTf)_2{\cdot}2H_2O$ (0.025 mmol), and Na_2CO_3 (0.25 mmol) in 1,2-dichloroethane (1.0 mL, 0.25 M) at the designated temperature under Ar for 1 h.
[b] Isolated yields after column chromatography.

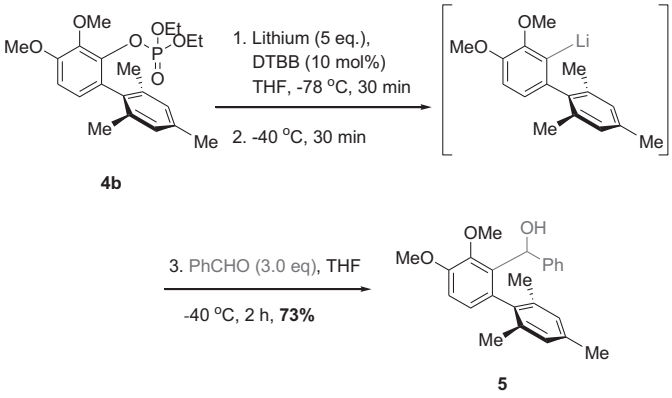
A plausible mechanism for the phosphate-group-directed *ortho*-C–H-activated aryl–aryl coupling reaction is shown in Scheme 2. It appears that Pd(II)/Pd(IV) catalytic species are engaged in the reaction, as has been proposed by other research groups.[10] In a typical C–H activation reaction, Pd(II)/Pd(IV) species are involved in various bond-forming reductive elimination steps. Likewise, the mechanism of our reaction is consistent with the coordination of an electron-deficient Pd(II) species and the directing phosphate group as the initial step. The formation of a palladacycle occurs after the electrophilic aromatic substitution at the Pd(II) site. It seems that the



Scheme 2. A proposed mechanism for phosphate-directed *ortho*-C–H bond activated aryl–aryl coupling reactions.

ortho-C–H bond activation step is the rate determining step since we have observed a significant kinetic isotope effect (KIE) (k_H/k_D=8.4) for the coupling reaction. The detailed scheme and data for the KIE experiment are described in the Supplementary data. Oxidative addition of diaryliodonium salts to the palladacycle would generate the Pd(IV) complex. Subsequent release of aryl iodide and reductive elimination of the complex should provide the desired product. At this stage, the Pd(II) catalyst is restored and can re-enter the catalytic cycle. Therefore, our reaction did not require any additional oxidant.

To further demonstrate the utility of our reaction, we treated **4b** with lithium metal in the presence of DTBB (4,4′-di-*tert*-butylbiphenyl) in THF at −78 °C,[11] and the resulting aryl lithium was successfully trapped with benzaldehyde to afford **5** at a 73% yield (Scheme 3). This reaction demonstrates that the phosphate group can be used not only as a phenol-masking group for directed C–H activation, but also as the precursor of a phenyl anion in which the *ortho*-C–H bond is activated. Further investigation of this reaction is currently underway in our lab.



Scheme 3. Direct transformation of phosphates.

3. Conclusion

We have developed a $Pd(OTf)_2 \cdot 2H_2O$-catalyzed *ortho*-arylation reaction via C–H bond functionalization using a phosphate group as a directing group. This is the first example involving phosphate as a directing group in this class of reaction. Various diaryliodonium salts could be used as the aryl group coupling partner for these reactions. The reactions were particularly favorable for electron-rich aryl phosphates. Substitution at the *meta*-position of the aryl phosphate greatly enhanced the reaction yields and reaction rates. The mechanism of the reaction appears to involve Pd(II)/Pd(IV) species. Additional study of the reaction mechanism is under investigation, and the results will be disclosed in due course.

4. Experimental section

4.1. General

All reactions were carried out with dry, freshly distilled solvent under anhydrous conditions. 1,2-Dichloroethane was freshly distilled from calcium hydride under nitrogen atmosphere *prior* to use. All reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. All experiments involving moisture- and/or air-sensitive compounds were performed in oven- and/or flame-dried glassware with rubber septa under positive pressure of argon using glove box. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck silica gel plate ($60F_{254}$) using UV light and *p*-anisaldehyde solution, phosphomolybdic acid solution (PMA) and/or ninhydrin solution, as a visualizing agent. NMR spectra were taken using a Varian 400 (400 MHz for ^{1}H) or Varian Inova-500 (500 MHz for ^{1}H) NMR spectrometer. Flash chromatography was performed using Merck 230–400 mesh silica gel. Melting points were determined using an Electrothermal capillary melting point apparatus and are uncorrected. Infrared spectra were obtained on a Nicolet avatar FT-IR spectrometer. NMR spectra were obtained either on Varian Inova-500 (500 MHz for ^{1}H, 125 MHz for ^{13}C, 202 MHz for ^{31}P, and 470 MHz for ^{19}F) or Varian 400 (400 MHz for ^{1}H, 100 MHz for ^{13}C, 162 MHz for ^{31}P, and 376 MHz for ^{19}F) NMR spectrometers. ^{1}H NMR spectra were referenced to tetramethylsilane (δ 0.00 ppm) as an internal standard and are reported as follows: (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet). ^{13}C NMR spectra were referenced to the residual $CDCl_3$ (δ 77.16 ppm). Elemental analyses were performed by the Organic Chemistry Research Center at Sogang University using a Carlo Erba EA 1180 elemental analyzer.

4.2. Characterization data for aryl diethyl phosphate (1a–m)

*4.2.1. Diethyl o-tolyl phosphate (**1a**).* Yellow oil (83%). Bp: (100–106 °C (2 mmHg)). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28 (d, J=8 Hz, 1H), 7.19 (d, J=7.5 Hz, 1H), 7.15 (t, J=7.5 Hz, 1H), 7.06 (t, J=7.5 Hz, 1H), 4.19–4.24 (m, 4H), 2.31 (s, 3H), 1.34 (t, J=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.42, 131.38, 129.32, 127.08, 124.98, 119.84, 64.64, 64.59, 16.42, 16.23, 16.17; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.55. IR (neat, cm^{-1}): 2983, 1588, 1496, 1270, 1018, 956, 759. Anal. Calcd for $C_{11}H_{17}O_4P$: C, 54.10; H, 7.02. Found: C, 54.11, H, 7.10.

*4.2.2. [1,1′-Biphenyl]-2-yl diethyl phosphate (**1b**).* Yellow oil (52%). Bp: (154–160 °C (2 mmHg)). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.49 (d, J=8 Hz, 2H), 7.45 (d, J=8.5 Hz, 1H), 7.41 (t, J=7.5 Hz, 2H), 7.30–7.37 (m, 3H), 7.23 (t, J=7.5 Hz, 1H), 3.87–4.98 (m, 4H), 1.19 (t, J=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz, all 2C unless indicated) δ 147.88, 137.65, 133.76, 131.27, 129.64, 128.80, 128.18, 127.47, 125.25, 120.62, 64.52, 64.46, 16.10, 16.04; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −6.37. IR (neat, cm^{-1}): 2983, 1582, 1479, 1274, 1024, 931, 759. Anal. Calcd for $C_{16}H_{19}O_4P$: C, 62.74; H, 6.25. Found: C, 62.77, H, 6.28.

*4.2.3. Diethyl m-tolyl phosphate (**1c**).* Yellow oil (77%). Bp: (116–120 °C (2 mmHg)). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.19 (t, J=8 Hz, 1H), 7.03 (s, 1H), 7.01 (d, J=7 Hz, 1H), 6.97 (d, J=7.5 Hz, 1H), 4.17–4.23 (m, 4H), 2.33 (s, 3H), 1.34 (t, J=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150.85, 140.04, 129.41, 125.80, 120.62, 116.97, 64.66, 64.61, 21.44, 16.24, 16.18; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.79. IR (neat, cm^{-1}): 2984, 1610, 1488, 1272, 1023, 959, 782. Anal. Calcd for $C_{11}H_{17}O_4P$: C, 54.10; H, 7.02. Found: C, 54.07, H, 7.17.

*4.2.4. 3-(tert-Butyl)phenyl diethyl phosphate (**1d**).* Yellow oil (86%). Bp: (134–138 °C (2 mmHg)). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.24

(t, *J*=8 Hz, 1H), 7.20 (s, 1H), 7.18 (d, *J*=8 Hz, 1H), 7.04 (d, *J*=8 Hz, 1H), 4.19–4.24 (m, 4H), 1.35 (t, *J*=7 Hz, 6H), 1.30 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.50, 150.80, 129.22, 122.06, 117.38, 116.98, 64.63, 64.58, 34.91, 31.35, 16.26, 16.21; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.77. IR (neat, cm^{-1}): 2964, 1583, 1487, 1268, 1024, 963, 796. Anal. Calcd for $C_{14}H_{23}O_4P$: C, 58.73; H, 8.10. Found: C, 58.63, H, 8.16.

*4.2.5. Diethyl (3-methoxyphenyl) phosphate (**1e**).* Yellow oil (66%). Bp: (126–130 °C (2 mmHg)). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.21 (t, *J*=8 Hz, 1H), 6.81 (d, *J*=8 Hz, 1H), 6.77 (s, 1H), 6.71 (dd, *J*=8, 2.5 Hz, 1H), 4.15–4.24 (m, 4H), 3.78 (s, 3H), 1.34 (t, *J*=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.83, 151.83, 130.13, 112.26, 110.95, 106.29, 64.73, 64.68, 55.56, 16.24, 16.19; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.93. IR (neat, cm^{-1}): 2984, 1606, 1491, 1268, 1024, 966, 771. Anal. Calcd for $C_{11}H_{17}O_5P$: C, 50.77; H, 6.58. Found: C, 50.63, H, 6.62.

*4.2.6. Diethyl p-tolyl phosphate (**1f**).* Yellow oil (79%). Bp: (120–122 °C (2 mmHg)). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.07–7.12 (m, 4H), 4.16–4.22 (m, 4H), 2.30 (s, 3H), 1.33 (t, *J*=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz, all 2C unless indicated) δ 148.72, 134.62, 130.21, 119.81, 64.62, 64.57, 20.80, 16.22, 16.17; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.59. IR (neat, cm^{-1}): 2985, 1608, 1507, 1272, 1030, 956, 757. Anal. Calcd for $C_{11}H_{17}O_4P$: C, 54.10; H, 7.02. Found: C, 54.18, H, 7.16.

*4.2.7. 4-(tert-Butyl)phenyl diethyl phosphate (**1g**).* Yellow oil (67%). Bp: (134–136 °C (2 mmHg)). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32 (d, *J*=8 Hz, 2H), 7.12 (d, *J*=8 Hz, 2H), 4.18–4.22 (m, 4H), 1.35 (t, *J*=7 Hz, 6H), 1.29 (s, 9H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.58, 147.91, 126.65, 126.60, 119.43, 64.62, 64.57, 34.48, 31.51, 16.24, 16.18; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.56. IR (neat, cm^{-1}): 2963, 1604, 1510, 1269, 1034, 957, 785. Anal. Calcd for $C_{14}H_{23}O_4P$: C, 58.73; H, 8.10. Found: C, 58.82, H, 8.15.

*4.2.8. 2,3-Dimethylphenyl diethyl phosphate (**1h**).* Yellow oil (73%). Bp: (106–110 °C (2 mmHg)). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.13 (d, *J*=8 Hz, 1H), 7.03 (t, *J*=8 Hz, 1H), 6.95 (d, *J*=7.5 Hz, 1H), 4.17–4.25 (m, 4H), 2.27 (s, 3H), 2.20 (s, 3H), 1.34 (t, *J*=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.06, 138.58, 127.75, 126.33, 125.95, 117.29, 64.40, 64.35, 20.03, 16.07, 16.02, 12.29; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.49. IR (neat, cm^{-1}): 2984, 1581, 1469, 1271, 1030, 959, 779. Anal. Calcd for $C_{12}H_{19}O_4P$: C, 55.81; H, 7.42. Found: C, 55.86, H, 7.44.

*4.2.9. 2,3-Dimethoxyphenyl diethyl phosphate (**1i**).* Yellow oil (55%). Bp: (148–152 °C (2 mmHg)). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.88–6.92 (m, 2H), 6.68 (d, *J*=8 Hz, 1H), 4.17–4.21 (m, 4H), 3.82 (s, 3H), 3.79 (s, 3H), 1.29 (t, *J*=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.91, 144.41, 140.38, 123.48, 113.54, 108.94, 64.55, 64.50, 60.99, 56.03, 16.04, 15.99; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.75. IR (neat, cm^{-1}): 2984, 1597, 1473, 1277, 1020, 975, 736. Anal. Calcd for $C_{12}H_{19}O_6P$: C, 49.66; H, 6.60. Found: C, 49.62; H, 6.62.

*4.2.10. 3,4-Dimethylphenyl diethyl phosphate (**1j**).* Yellow oil (77%). Bp: (140–144 °C (2 mmHg)). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.05 (d, *J*=8 Hz, 1H), 6.99 (s, 1H), 6.93 (d, *J*=8.5 Hz, 1H), 4.16–4.23 (m, 4H), 2.23 (s, 3H), 2.20 (s, 3H), 1.34 (t, *J*=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.79, 138.25, 133.28, 130.53, 121.08, 117.09, 64.60, 64.55, 20.00, 19.16, 16.24, 16.19; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.55. IR (neat, cm^{-1}): 2982, 1609, 1498, 1272, 1009, 965, 757. Anal. Calcd for $C_{12}H_{19}O_4P$: C, 55.81; H, 7.42. Found: C, 55.77, H, 7.45.

*4.2.11. 4-Chloro-3-methylphenyl diethyl phosphate (**1k**).* Yellow oil (79%). Bp: (138–140 °C (2 mmHg)). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.28 (d, *J*=9 Hz, 1H), 7.11 (s, 1H), 7.00 (d, *J*=8.5 Hz, 1H), 4.17–4.24 (m, 4H), 2.35 (s, 3H), 1.35 (t, *J*=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.23, 137.75, 130.53, 130.01, 122.49, 118.74, 64.81, 64.76, 20.30, 16.21, 16.16; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.82. IR (neat, cm^{-1}): 2984, 1601, 1477, 1270, 1023, 967, 756. Anal. Calcd for $C_{11}H_{16}ClO_4P$: C, 47.41; H, 5.79. Found: C, 47.38, H, 5.78.

*4.2.12. Diethyl (4-methyl-2-oxo-2H-chromen-7-yl) phosphate (**1l**).* Colorless oil (75%). Bp: (220–224 °C (2 mmHg)). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.55 (d, *J*=8.5 Hz, 1H), 7.18 (d, *J*=8.5 Hz, 1H), 7.17 (s, 1H), 4.19–4.25 (m, 4H), 2.39 (s, 3H), 1.35 (t, *J*=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.52, 154.51, 153.33, 151.95, 125.88, 117.23, 116.53, 114.24, 108.69, 65.11, 65.06, 18.74, 16.19, 16.14; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −6.34. IR (neat, cm^{-1}): 2985, 1735, 1612, 1566, 1388, 1267, 1010, 985, 748. Anal. Calcd for $C_{14}H_{17}O_6P$: C, 58.85; H, 5.49. Found: C, 58.86, H, 5.50.

*4.2.13. 2,3-Dihydro-1H-inden-5-yl diethyl phosphate (**1m**).* Yellow oil (80%). Bp: (150–154 °C (2 mmHg)). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.11 (d, *J*=8.5 Hz, 1H), 7.05 (s, 1H), 6.93 (d, *J*=9.5 Hz, 1H), 4.15–4.22 (m, 4H), 2.86 (t, *J*=7.5 Hz, 2H), 2.83 (t, *J*=7.5 Hz, 2H), 2.02–2.08 (m, 2H), 1.33 (t, *J*=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 149.15, 146.04, 140.76, 124.93, 117.69, 116.12, 64.52, 64.47, 33.07, 32.23, 25.83, 16.18, 16.13; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.49. IR (neat, cm^{-1}): 2981, 1609, 1484, 1272, 1024, 980, 763. Anal. Calcd for $C_{13}H_{19}O_4P$: C, 57.77; H, 7.09. Found: C, 57.66, H, 7.01.

4.3. Characterization data for bis(5-(*tert*-butyl)-2-methylphenyl)iodonium triflate (2d)

Off-white solid (54%). Mp: 186–188 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.86 (s, 2H), 7.51 (d, *J*=8 Hz, 2H), 7.36 (d, *J*=8 Hz, 2H), 2.56 (s, 6H), 1.26 (s, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.90, 138.13, 133.65, 131.94, 130.45, 120.54 (q, J = 318.25 Hz, $CF_3SO_3^-$), 117.98, 35.14, 31.10, 24.91; ^{19}F NMR ($CDCl_3$, 470 MHz) δ −78.70. IR (neat, cm^{-1}): 2963, 1249, 1156, 1027. Anal. Calcd for $C_{23}H_{30}F_3IO_3S$: C, 48.43; H, 5.30; S, 5.62. Found: C, 48.47; H, 5.38; S, 5.68.

4.4. General procedure for the synthesis of 3a–m and characterization data

Iodonium salt **2** (0.5 mmol), $Pd(OTf)_2 \cdot 2H_2O$ (0.025 mmol), 1,2-dichloroethane (1 mL, 0.25 M), phosphate **1** (0.25 mmol), and dried Na_2CO_3 (0.25 mmol) were added sequentially to a flame-dried reaction flask equipped with a magnetic stir bar under an argon atmosphere. The reaction mixture was subsequently stirred at the designated temperature for 1 h. The reaction mixture was cooled to room temperature, diluted with EtOAc (10 mL), and filtered through a short pad of silica gel using EtOAc (10 mL) as eluent to remove the remaining iodonium salts. The filtrate was concentrated under vacuum, and the resulting crude product was further purified by column chromatography to afford product **3**.

*4.4.1. Diethyl (3-methyl-[1,1′-biphenyl]-2-yl) phosphate (**3a**).* (Inseparable mixture) Reaction temperature: 83 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. Yellow oil (64%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.49 (d, *J*=7.5 Hz, 2H), 7.40 (t, *J*=7.5 Hz, 2H), 7.32 (d, *J*=7.5 Hz, 1H), 7.28 (d, *J*=8 Hz, starting material), 7.19 (d, *J*=7.5 Hz, starting material), 7.18 (t, *J*=7.5 Hz, 2H), 7.15 (t, *J*=7.5 Hz, starting material), 7.14 (d, *J*=7 Hz, 1H), 7.06 (t, *J*=7.5 Hz, starting material), 4.19–4.24 (m, 1.75H, starting material), 3.78–3.83 (m, 2H), 3.62–3.67 (m, 2H), 2.46 (s, 3H), 2.32 (s, 1.3H, starting material), 1.35 (t, *J*=7 Hz, 2.6H, starting material), 1.11 (t, *J*=7 Hz, 6H).

*4.4.2. [1,1′:3′,1″-Terphenyl]-2′-yl diethyl phosphate (**3b**).* Reaction temperature: 83 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. Off-white solid (63%). Mp: 65–68 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.59 (d, *J*=7.5 Hz, 4H), 7.44 (t, *J*=8 Hz, 4H), 7.28–7.35 (m, 5H), 3.41–3.46 (m, 2H), 3.11–3.16 (m, 2H), 0.86 (t, *J*=7 Hz, 6H); ^{13}C NMR ($CDCl_3$,

125 MHz) δ 145.22, 145.15, 138.61, 136.01, 135.97, 130.81, 130.79, 130.05, 128.24, 127.42, 125.72, 125.70, 63.45, 63.40, 15.94, 15.88; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −6.30. IR (neat, cm^{-1}): 2982, 1596, 1419, 1267, 1029, 908, 710. Anal. Calcd for $C_{22}H_{23}O_4P$: C, 69.10; H, 6.06. Found: C, 69.13; H, 6.07.

*4.4.3. Diethyl (4-methyl-[1,1′-biphenyl]-2-yl) phosphate (**3c**).* Reaction temperature: 60 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. Yellow oil (91%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 (d, J=7.5 Hz, 2H), 7.31 (t, J=7.5 Hz, 2H), 7.24 (t, J=8 Hz, 1H), 7.20 (s, 1H), 7.17 (d, J=8 Hz, 1H), 6.96 (d, J=8 Hz, 1H), 3.78–3.91 (m, 4H), 2.31 (s, 3H), 1.11 (t, J=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 147.60, 147.53, 139.11, 137.67, 130.91, 130.71, 129.60, 128.12, 127.22, 126.07, 121.10, 121.06, 64.45, 64.38, 21.28, 16.10, 16.03; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −6.28. IR (neat, cm^{-1}): 2983, 1618, 1485, 1267, 1026, 968, 767. Anal. Calcd for $C_{17}H_{21}O_4P$: C, 63.74; H, 6.61. Found: C, 63.75; H, 6.60.

*4.4.4. 4-(tert-Butyl)-[1,1′-biphenyl]-2-yl diethyl phosphate (**3d**).* Reaction temperature: 60 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. Yellow oil (84%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.50 (d, J=8 Hz, 2H), 7.46 (s, 1H), 7.39 (t, J=8 Hz, 2H), 7.26–7.31 (m, 3H), 3.87–3.97 (m, 4H), 1.35 (s, 9H), 1.18 (t, J=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.47, 152.45, 147.54, 137.67, 130.69, 130.64, 129.68, 128.15, 127.26, 122.30, 117.90, 117.88, 64.42, 64.37, 34.87, 31.37, 16.17, 16.11; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −6.24. IR (neat, cm^{-1}): 2965, 1616, 1485, 1271, 1029, 970, 720. Anal. Calcd for $C_{20}H_{27}O_4P$: C, 66.28; H, 7.51. Found: C, 66.26; H, 7.50.

*4.4.5. Diethyl (4-methoxy-[1,1′-biphenyl]-2-yl) phosphate (**3e**).* Reaction temperature: 60 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. Yellow oil (76%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.46 (d, J=7.5 Hz, 2H), 7.40 (t, J=7.5 Hz, 2H), 7.31 (t, J=7.5 Hz, 1H), 7.27 (dd, J=7.5, 1.0 Hz, 1H), 7.04 (dd, J=2.5, 1.0 Hz, 1H), 6.79 (ddd, J=7.5, 2.5, 1.0 Hz, 1H), 3.87–4.00 (m, 4H), 3.83 (s, 3H), 1.19 (t, J=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.91, 148.43, 148.37, 137.54, 131.62, 129.62, 128.16, 127.06, 126.16, 126.10, 111.23, 106.51, 64.55, 64.50, 55.70, 16.14, 16.08; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −6.35. IR (neat, cm^{-1}): 2983, 1614, 1484, 1274, 1158, 1020, 970, 765. Anal. Calcd for $C_{17}H_{21}O_5P$: C, 60.71; H, 6.29. Found: C, 60.65; H, 6.31.

*4.4.6. Diethyl (5′-methyl-[1,1′:3′,1″-terphenyl]-2′-yl) phosphate (**3f**′).* Reaction temperature: 83 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. Off-white solid (27%). Mp: 76–79 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.58 (d, J=8 Hz, 4H), 7.42 (t, J=8 Hz, 4H), 7.33 (t, J=7 Hz, 2H), 7.14 (s, 2H), 3.40–3.46 (m, 2H), 3.10–3.16 (m, 2H), 2.38 (s, 3H), 0.86 (t, J=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 142.95, 142.88, 138.67, 135.52, 135.49, 135.20, 135.18, 131.37, 131.35, 129.96, 128.20, 127.32, 63.36, 63.32, 20.91, 15.94, 15.88; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.97. IR (neat, cm^{-1}): 2925, 1596, 1424, 1271, 1026, 928, 781. Anal. Calcd for $C_{23}H_{25}O_4P$: C, 69.69; H, 6.36. Found: C, 69.72; H, 6.25.

*4.4.7. Diethyl (5-methyl-[1,1′-biphenyl]-2-yl) phosphate (**3f**).* (Inseparable mixture) Reaction temperature: 83 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.48 (d, J=7 Hz, 2H), 7.39 (t, J=7 Hz, 2H), 7.32 (t, J=7.5 Hz, 2H), 7.16 (s, 1H), 7.08–7.12 (m, starting material, contained the one proton of product), 4.18–4.22 (m, 3.07H, starting material), 3.85–3.96 (m, 4H), 2.35 (s, 3H), 2.31 (s, 2.3H, starting material), 1.34 (t, J=7 Hz, 4.56H, starting material), 1.17 (t, J=7 Hz, 6H).

*4.4.8. 5′-(tert-Butyl)-[1,1′:3′,1″-terphenyl]-2′-yl diethyl phosphate (**3g**′).* Reaction temperature: 83 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. Off-white solid (27%). Mp: 80–83 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.61 (d, J=8.5 Hz, 4H), 7.44 (t, J=8 Hz, 4H), 7.36 (t, J=4 Hz, 2H), 7.34 (s, 2H), 3.42–3.48 (m, 2H), 3.13–3.19 (m, 2H), 1.36 (s, 9H), 0.88 (t, J=7.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 148.26, 148.24, 142.79, 142.73, 139.08, 135.01, 134.98, 130.03, 128.16, 127.95, 127.93, 127.25, 63.33, 63.28, 34.64, 31.53, 15.91, 15.85; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −6.06. IR (neat, cm^{-1}): 2963, 1593, 1426, 1268, 1030, 924, 728. Anal. Calcd for $C_{26}H_{31}O_4P$: C, 71.22; H, 7.13. Found: C, 71.26; H, 7.10.

*4.4.9. 5-(tert-Butyl)-[1,1′-biphenyl]-2-yl diethyl phosphate (**3g**).* (Inseparable mixture) Reaction temperature: 83 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.51 (d, J=7.5 Hz, 2H), 7.41 (t, J=7.5 Hz, 2H), 7.33 (m, 4H), 7.32 (d, J=8 Hz, starting material), 7.12 (d, J=8 Hz, 1.2H, starting material), 4.21–4.23 (m, 2.83H, starting material), 3.88–3.96 (m, 4H), 1.35 (t, J=8 Hz, starting material), 1.32 (s, 9H), 1.29 (s, starting material), 1.19 (t, J=7 Hz, 6H).

*4.4.10. 3,4-Dimethyl-[1,1′-biphenyl]-2-yl diethyl phosphate (**3h**).* Reaction temperature: 60 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. Yellow oil (86%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.49 (d, J=1 Hz, 7.5H), 7.39 (t, J=8 Hz, 2H), 7.30 (t, J=8 Hz, 1H), 7.03–7.08 (m, 2H), 3.77–3.82 (m, 2H), 3.62–3.66 (m, 2H), 2.34 (s, 3H), 2.31 (s, 3H), 1.10 (t, J=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.40, 146.34, 139.01, 138.14, 132.55, 132.52, 129.95, 129.93, 129.79, 128.12, 127.03, 126.93, 63.97, 63.92, 20.42, 16.13, 16.07, 13.86; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.83. IR (neat, cm^{-1}): 2982, 1612, 1477, 1270, 1026, 956, 780. Anal. Calcd for $C_{18}H_{23}O_4P$: C, 64.66; H, 6.93. Found: C, 64.66; H, 6.97.

*4.4.11. 3,4-Dimethoxy-[1,1′-biphenyl]-2-yl diethyl phosphate (**3i**).* Reaction temperature: 60 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. Yellow oil (88%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.46 (d, J=7.5 Hz, 2H), 7.38 (t, J=7.5 Hz, 2H), 7.30 (t, J=8 Hz, 1H), 6.99 (d, J=9 Hz, 1H), 6.80 (d, J=8.5 Hz, 1H), 3.98 (s, 3H), 3.90 (s, 3H), 3.85–3.93 (m, 2H), 3.70–3.78 (m, 2H), 1.14 (t, J=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.16, 142.17, 142.11, 141.33, 137.82, 129.83, 128.29, 128.26, 128.18, 127.15, 124.95, 109.18, 64.03, 63.98, 61.14, 56.24, 16.13, 16.06; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.89. IR (neat, cm^{-1}): 2952, 1607, 1485, 1276, 1026, 973, 758. Anal. Calcd for $C_{18}H_{23}O_6P$: C, 59.01; H, 6.33. Found: C, 59.03; H, 6.24.

*4.4.12. 4,5-Dimethyl-[1,1′-biphenyl]-2-yl diethyl phosphate (**3j**).* Reaction temperature: 60 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. Yellow oil (90%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.48 (d, J=7.5 Hz, 2H), 7.38 (t, J=8 Hz, 2H), 7.30 (t, J=7 Hz, 1H), 7.22 (s, 1H), 7.12 (s, 1H), 3.86–3.98 (m, 4H), 2.28 (s, 3H), 2.25 (s, 3H), 1.18 (t, J=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 145.57, 145.52, 137.77, 137.42, 133.53, 132.12, 130.79, 129.60, 128.10, 127.16, 121.58, 121.56, 64.38, 64.33, 19.78, 19.22, 16.13, 16.07; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −6.04. IR (neat, cm^{-1}): 2983, 1618, 1485, 1272, 1015, 976, 907, 727. Anal. Calcd for $C_{18}H_{23}O_4P$: C, 64.66; H, 6.93. Found: C, 64.67; H, 6.92.

*4.4.13. 5-Chloro-4-methyl-[1,1′-biphenyl]-2-yl diethyl phosphate (**3k**).* Reaction temperature: 83 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. Yellow oil (80%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.46 (d, J=8 Hz, 2H), 7.40 (t, J=8 Hz, 2H), 7.30–7.35 (m, 3H, contained singlet of two protons), 3.87–3.96 (m, 4H), 2.39 (s, 3H), 1.19 (t, J=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 146.16, 146.10, 136.70, 136.48, 132.76, 131.16, 129.52, 128.30, 127.79, 122.92, 122.90, 64.63, 64.58, 20.08, 16.12, 16.07; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −6.26. IR (neat, cm^{-1}): 2982, 1611, 1477, 1277, 1159, 1040, 981, 887, 770. Anal. Calcd for $C_{17}H_{20}ClO_4P$: C, 57.55; H, 5.68. Found: C, 57.57; H, 5.75.

*4.4.14. Diethyl (4-methyl-2-oxo-6-phenyl-2H-chromen-7-yl) phosphate (**3l**).* Reaction temperature: 83 °C. Eluent: 40% EtOAc/1% TEA in Hexane. Off-white solid (67%). Mp: 100–102 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.56 (s, 1H), 7.39–7.50 (m, 6H), 6.28 (s, 1H), 3.95–4.03 (m, 4H), 2.43 (s, 3H), 1.23 (t, J=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 160.44, 153.44, 151.91, 150.21, 150.16, 136.28, 130.68, 130.63,

129.58, 128.37, 127.96, 126.82, 117.28, 114.51, 108.98, 64.87, 64.82, 18.72, 16.04, 15.98; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −6.50. IR (neat, cm^{-1}): 3042, 2985, 1728, 1624, 1485, 1281, 1144, 1031, 870, 774. Anal. Calcd for $C_{20}H_{21}O_6P$: C, 61.85; H, 5.45. Found: C, 61.85; H, 5.49.

*4.4.15. Diethyl (6-phenyl-2,3-dihydro-1H-inden-5-yl) phosphate (**3m**).* Reaction temperature: 83 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. Yellow oil (81%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.47 (d, J=8.5 Hz, 2H), 7.38 (t, J=8 Hz, 2H), 7.32 (t, J=8.5 Hz, 1H), 7.30 (s, 1H), 7.18 (s, 1H), 4.21 (m, 0.12H, starting material), 3.85–3.97 (m, 4H), 3.34 (m, 0.17H, diphenylated product), 3.11 (m, 0.17H, diphenylated product), 2.88–2.95 (m, 4H), 2.08–2.14 (m, 2H), 1.18 (t, J=9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz, all 2C unless indicated) δ 145.23, 141.07, 138.42, 131.50, 129.74, 128.08, 127.12, 126.60, 116.53, 116.51, 64.38, 64.33, 33.09, 32.44, 25.94, 16.13, 16.07. ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.98. IR (neat, cm^{-1}): 2983, 1712, 1615, 1478, 1268, 1027, 969, 727.

4.5. General procedure for the synthesis of 4b–f and characterization data

Iodonium salt **2** (0.5 mmol), $Pd(OTf)_2 \cdot 2H_2O$ (0.025 mmol), 1,2-dichloroethane (1 mL, 0.25 M), phosphate **1** (0.25 mmol), and dried Na_2CO_3 (0.25 mmol) were added sequentially to a flame-dried reaction flask equipped with a magnetic stir bar under an argon atmosphere. The reaction mixture was subsequently stirred at the designated temperature for 1 h. The reaction mixture was cooled to room temperature, diluted with EtOAc (10 mL), and filtered through a short pad of silica gel using EtOAc (10 mL) as eluent to remove the remaining iodonium salts. The filtrate was concentrated under vacuum, and the resulting crude product was further purified by column chromatography to afford product **4**.

*4.5.1. 3,4-Dimethoxy-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-yl diethyl phosphate (**4b**).* Reaction temperature: 83 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. Off-white solid (61%). Mp: 90–92 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.90 (s, 2H), 6.81 (d, J=8.5 Hz, 1H), 6.76 (d, J=8.5 Hz, 1H), 3.96 (s, 3H), 3.91 (s, 3H), 3.70–3.76 (m, 2H), 3.61–3.66 (m, 2H), 2.29 (s, 3H), 2.04 (s, 6H), 1.12 (t, J=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 152.92, 142.66, 142.60, 141.57, 137.74, 137.03, 134.10, 127.95, 126.80, 126.76, 124.89, 109.30, 63.77, 63.72, 61.09, 61.08, 56.21, 21.07, 20.59, 16.07, 16.01; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −6.32. IR (neat, cm^{-1}): 2975, 1603, 1453, 1291, 1031, 970, 808. Anal. Calcd for $C_{21}H_{29}O_6P$: C, 61.76; H, 7.16. Found: C, 61.77; H, 7.11.

*4.5.2. Diethyl (3,4,4′-trimethoxy-[1,1′-biphenyl]-2-yl) phosphate (**4c**).* Reaction temperature: 60 °C. Eluent: 30% EtOAc/1% TEA in Hexane. Red oil (91%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.38 (d, J=8.5 Hz, 2H), 6.97 (d, J=8.5 Hz, 1H), 6.92 (d, J=8.5 Hz, 2H), 6.78 (d, J=8.5 Hz, 1H), 3.97 (s, 3H), 3.88 (s, 3H), 3.87–3.96 (m, 2H), 3.82 (s, 3H), 3.76–3.85 (m, 2H), 1.16 (t, J=8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 159.00, 152.92, 142.26, 142.2, 141.44, 130.88, 130.31, 128.02, 127.98, 124.85, 113.66, 109.28, 64.03, 63.98, 61.10, 56.28, 55.46, 16.13, 16.07; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.97. IR (neat, cm^{-1}): 2939, 1604, 1491, 1245, 1050, 973, 802. Anal. Calcd for $C_{19}H_{25}O_7P$: C, 57.57; H, 6.36. Found: C, 57.54; H, 6.30.

*4.5.3. 5′-(tert-Butyl)-3,4-dimethoxy-2′-methyl-[1,1′-biphenyl]-2-yl diethyl phosphate (**4d**).* Reaction temperature: 60 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. Off-white solid (73%). Mp: 80–83 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27 (d, J=8.5 Hz, 1H), 7.26 (s, 1H), 7.16 (d, J=8.5 Hz, 1H), 6.89 (d, J=8.5 Hz, 1H), 6.81 (d, J=8.5 Hz, 1H), 3.99 (s, 3H), 3.92 (s, 3H), 3.79–3.87 (m, 2H), 3.60–3.64 (m, 1H), 3.34–3.38 (m, 1H), 2.14 (s, 3H), 1.31 (s, 9H), 1.19 (t, J=7 Hz, 3H), 1.05 (t, J=7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.04, 148.40, 142.52, 142.46, 141.22, 137.06, 134.48, 129.40, 128.54, 127.88, 124.99, 124.59, 109.02, 63.96, 63.92, 63.47, 63.43, 61.12, 56.26, 34.50, 31.58, 19.56, 16.14, 16.07; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −6.11. IR (neat, cm^{-1}): 2962, 1607, 1491, 1290, 1032, 978, 858, 800. Anal. Calcd for $C_{23}H_{33}O_6P$: C, 63.29; H, 7.62. Found: C, 63.24; H, 7.72.

*4.5.4. 3,4-Dimethoxy-2′,5′-dimethyl-[1,1′-biphenyl]-2-yl diethyl phosphate (**4e**).* Reaction temperature: 60 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. Yellow oil (72%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.10 (d, J=7.5 Hz, 1H), 7.06 (s, 1H), 7.03 (d, J=8 Hz, 1H), 6.85 (d, J=8.5 Hz, 1H), 6.78 (d, J=7.5 Hz, 1H), 3.97 (s, 3H), 3.90 (s, 3H), 3.88–3.90 (m, 1H), 3.76–3.80 (m, 1H), 3.63–3.67 (m, 1H), 3.47–3.52 (m, 1H), 2.30 (s, 3H), 2.11 (s, 3H), 1.18 (t, J=7 Hz, 3H), 1.07 (t, J=7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.00, 142.36, 141.23, 137.39, 134.79, 134.28, 131.48, 129.64, 128.29, 128.19, 124.91, 109.00, 63.94, 63.65, 61.10, 56.23, 20.90, 19.62, 16.08, 16.02; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −6.32. IR (neat, cm^{-1}): 2929, 1606, 1456, 1275, 1031, 981, 728. Anal. Calcd for $C_{20}H_{27}O_6P$: C, 60.91; H, 6.90. Found: C, 60.88; H, 7.01.

*4.5.5. 3,4-Dimethoxy-4′-methyl-[1,1′-biphenyl]-2-yl diethyl phosphate (**4f**).* Reaction temperature: 60 °C. Eluent: 20% $CHCl_3$/1% TEA in Hexane. Yellow oil (72%). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.35 (d, J=8 Hz, 2H), 7.19 (d, J=7.5 Hz, 2H), 6.98 (d, J=7.5 Hz, 1H), 6.79 (d, J=9 Hz, 1H), 3.97 (s, 3H), 3.88 (s, 3H), 3.86–3.96 (m, 2H), 3.72–3.82 (m, 2H), 2.36 (s, 3H), 1.44 (t, J=7 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 153.01, 142.22, 142.16, 141.38, 136.80, 134.89, 129.67, 128.83, 128.33, 128.30, 124.86, 109.26, 64.00, 63.95, 61.09, 56.26, 21.22, 16.06, 15.99; ^{31}P NMR ($CDCl_3$, 202 MHz) δ −5.89. IR (neat, cm^{-1}): 2986, 1606, 1492, 1274, 1029, 976, 727. Anal. Calcd for $C_{19}H_{25}O_6P$: C, 59.99; H, 6.62. Found: C, 59.98; H, 6.55.

4.6. LiDTBB-catalyzed reduction of phosphate 4b and reaction with benzaldehyde. (3,4-dimethoxy-2′,4′,6′-trimethyl-[1,1′-biphenyl]-2-yl)(phenyl)methanol (5)

To a flame-dried Schlenk flask equipped with a magnetic stir bar were added DTBB (0.025 mmol) and lithium powder (25% dispersion in oil, 1.25 mmol) in dry THF (1.0 mL) at 0 °C under Ar. After stirring for 30 min, the deep blue suspension was cooled to −78 °C. A solution of phosphate (**4b**) (0.25 mmol) in dry THF (1.0 mL) was slowly added to the mixture for 30 min via dropping funnel. The reaction mixture was then stirred at −78 °C for 30 min, and warmed up to −40 °C. After 30 min of stirring at the same temperature, a solution of benzaldehyde (0.75 mmol) in dry THF (0.5 mL) was added via dropping funnel for 10 min. The brown suspension was stirred at −40 °C for 2 h. The reaction was quenched by pouring the reaction mixture into water (10 mL). The mixture was acidified by adding 2 N HCl. The mixture was extracted with dichloromethane (2×20 mL). The combined organic layers were washed with brine, dried over Na_2CO_3, and concentrated in vacuo. The residue was subjected to flash column chromatograph on silica gel to yield the desired product **5**: Eluent: 5% CH_2Cl_2/5% ether/1% TEA in Hexane. Off-white solid (73%). Mp: 88–91 °C. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.21–7.24 (m, 4H), 7.15–7.17 (m, 1H), 6.97 (d, J=8 Hz, 1H), 6.92 (s, 1H), 6.86 (s, 1H), 6.83 (d, J=8 Hz, 1H), 5.32 (d, J=12 Hz, 1H), 3.90 (s, 3H), 3.85 (d, J=12 Hz, 1H), 3.66 (s, 3H), 2.28 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz, all 2C unless indicated) δ 151.94, 147.55, 145.57, 137.47, 136.87, 136.51, 136.50, 136.16, 133.22, 128.46, 128.29, 127.94, 126.66, 125.87, 125.41, 112.48, 72.85, 60.28., 55.85, 21.42, 20.89, 20.87. IR (neat, cm^{-1}): 3538, 2960, 1601, 1261, 1032, 815. Anal. Calcd for $C_{24}H_{26}O_3$: C, 79.53; H, 7.23. Found: C, 79.50; H, 7.25.

Acknowledgements

This work was supported by the Sogang University Research Grant of 2010 (201010032.01).

Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.04.067.

References and notes

1. For recent general reviews on transition metal catalyzed C–H activation, see: (a) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731; (b) Chen, X.; Engle, K. M.; Wang, D.-H.; Yu, J.-Q. *Angew. Chem.* **2009**, *121*, 5196; *Angew. Chem., Int. Ed.* **2009**, *48*, 5094; (c) Colby, D. A.; Gergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624; (d) Ackermann, L. *Chem. Rev.* **2011**, *111*, 1315; (e) Rousseau, G.; Breit, B. *Angew. Chem., Int. Ed.* **2011**, *50*, 2450; (f) Engle, K. M.; Mei, T.-S.; Wasa, M.; Yu, J.-Q. *Acc. Chem. Res.* **2012**, *45*, 788; (g) Dick, A. R.; Sanford, M. S. *Tetrahedron* **2006**, *62*, 2439.
2. (a) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826; (b) Shi, Z.; Li, B.; Wan, X.; Cheng, J.; Fang, Z.; Cao, B.; Qin, C.; Wang, Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 5554; (c) Kitazawa, K.; Kochi, T.; Sato, M.; Kakiuchi, F. *Org. Lett.* **2009**, *11*, 1951; (d) Hurst, T. E.; Macklin, T. K.; Becker, M.; Hartmann, E.; Kügel, W.; Parisienne-La Salle, J.-C.; Batsanov, A. S.; Marder, T. B.; Snieckus, V. *Chem.—Eur. J.* **2010**, *16*, 8155; (e) Park, S. H.; Kim, J. Y.; Chang, S. *Org. Lett.* **2011**, *13*, 2372; (f) Muralirajan, K.; Parthasarathy, K.; Cheng, C.-H. *Angew. Chem., Int. Ed.* **2011**, *50*, 4169; (g) Lee, P.-S.; Fujita, T.; Yoshikai, N. *J. Am. Chem. Soc.* **2011**, *133*, 17283; (h) Hesp, K. D.; Bergman, R. G.; Ellman, J. A. *Org. Lett.* **2012**, *12*, 2304; (i) Wang, C.; Chen, H.; Wang, Z.; Chen, J.; Huang, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 7242; (j) Li, D.-D.; Yuan, T.-T.; Wang, G.-W. *J. Org. Chem.* **2012**, *77*, 3341.
3. Recent papers of directing groups with phenol on C–H activation: for phenol-directed examples, see: (a) Xiao, B.; Gong, T.-J.; Liu, Z.-J.; Luo, D.-F.; Xu, J.; Liu, L. *J. Am. Chem. Soc.* **2011**, *133*, 9250; (b) Ochiai, M.; Fukui, K.; Iwatsuki, S.; Ishihara, K.; Matsumoto, K. *Organometallics* **2005**, *24*, 5528; (c) Hirano, M.; Kurata, N.; Komiya, S. *J. Organomet. Chem.* **2000**, *607*, 18; (d) Kawamura, Y.; Satoh, T.; Miura, M.; Nomura, M. *Chem. Lett.* **1999**, *961* for phenol ester-directed examples, see; (e) Xiao, B.; Fu, Y.; Xu, J.; Gong, T.-J.; Dai, J.-J.; Yi, J.; Liu, L. *J. Am. Chem. Soc.* **2010**, *132*, 468 for phenoxypyrimidine-directed examples, see; (f) Gu, S.; Chen, C.; Chen, W. *J. Org. Chem.* **2009**, *74*, 7203 for phenol carbamates-directed examples, see; (g) Gong, T.-J.; Xiao, B.; Liu, Z.-J.; Wan, J.; Xu, J.; Luo, D.-F.; Fu, Y.; Liu, L. *Org. Lett.* **2011**, *13*, 3235; (h) Zhao, X.; Yeung, C. S.; Dong, V. M. *J. Am. Chem. Soc.* **2010**, *132*, 5837 for phenylphosphinite-directed examples, see; (i) Bedford, R. B.; Haddow, M. F.; Webster, R. L.; Mitchell, C. J. *Org. Biomol. Chem.* **2009**, *7*, 3119; (j) Bedford, R. B.; Webster, R. L.; Mitchell, C. J. *Org. Biomol. Chem.* **2009**, *7*, 4853; (k) Bedford, R. B.; Betham, M.; Caffyn, A. J. M.; Charmant, J. P. H.; Lewis-Alleyne, L. C.; Long, P. D.; Polo-Cerón, D.; Prachar, S. *Chem. Commun.* **2008**, 990; (l) Bedford, R. B.; Limmert, M. E. *J. Org. Chem.* **2003**, *68*, 8669; (m) Bedford, R. B.; Coles, S. J.; Hursthouse, M. B.; Limmert, M. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 112 for miscellaneous examples, see; (n) Boebel, T. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 7534.
4. Recent review and papers on C–H activation under mild conditions: (a) Wencel-Delord, J.; Dröge, T.; Liu, F.; Glorius, F. *Chem. Soc. Rev.* **2011**, *40*, 4740; (b) Kalyani, D.; McMurtrey, K. B.; Neufeldt, S. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2011**, *133*, 18566; (c) Tredwell, M. J.; Gulias, M.; Bremeyer, N. G.; Johansson, C. C. C.; Collins, B. S. L.; Gaunt, M. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 1076; (d) Nishikata, T.; Abela, A. R.; Lipshutz, B. H. *Angew. Chem., Int. Ed.* **2010**, *49*, 781; (e) Nishikata, T.; Abela, A. R.; Huang, S.; Lipshutz, B. H. *J. Am. Chem. Soc.* **2010**, *132*, 4978; (f) Fang, P.; Li, M.; Ge, H. *J. Am. Chem. Soc.* **2010**, *132*, 11898; (g) Nishikata, T.; Lipshutz, B. H. *Org. Lett.* **2010**, *12*, 1972; (h) Houlden, C. E.; Hutchby, M.; Bailey, C. D.; Gair Ford, J.; Tyler, S. N. G.; Gagné, M. R.; Lloyd-Jones, G. C.; Booker-Milburn, K. I. *Angew. Chem., Int. Ed.* **2009**, *48*, 1830; (i) Phipps, R. J.; Grimster, N. P.; Gaunt, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 8172.
5. Preparation of diaryliodonium salts: (a) Bielawski, M.; Zhu, M.; Olofsson, B. *Adv. Synth. Catal.* **2007**, *349*, 2610; (b) Bielawski, M.; Olofsson, B. *Chem. Commun.* **2007**, 2521; (c) Petersen, T. B.; Khan, R.; Olofsson, B. *Org. Lett.* **2011**, *13*, 3462.
6. Recent review and papers about iodonium salts and C–H activation with diaryliodonium salts as a reagent: (a) Zhdankin, V. V. *Chem. Rev.* **2008**, *108*, 5299; (b) Lapointe, D.; Markiewicz, T.; Whipp, C. J.; Toderian, A.; Fagnou, K. *J. Org. Chem.* **2011**, *76*, 749; (c) Jalalian, N.; Ishikawa, E. E.; Silvar, L. F., Jr.; Olofsson, B. *Org. Lett.* **2011**, *13*, 1552; (d) Norrby, P.-O.; Petersen, T. B.; Bielawski, M.; Olofsson, B. *Chem.—Eur. J.* **2010**, *16*, 8251; (e) Aydin, J.; Larsson, J. M.; Selander, N.; Szabó, K. J. *Org. Lett.* **2009**, *11*, 2852; (f) Becht, J.-M.; Drian, C. L. *Org. Lett.* **2008**, *10*, 3161; (g) Carroll, M. A.; Wood, R. A. *Tetrahedron* **2007**, *63*, 11349; (h) Beletskaya, I. P.; Davydov, D. V.; Gorovoy, M. S. *Tetrahedron Lett.* **2002**, 6221.
7. Preparation of phosphates: (a) Purnanand; Batra, B. S.; Pant, B. P. *Tetrahedron Lett.* **1989**, *30*, 1687; (b) Lusch, M. J.; Woller, K. R.; Keller, A. M.; Turk, M. C. *Synthesis* **2005**, 551.
8. Although diethyl *o*-tolyl phosphate (**1a**) was activated for phenylation, a mixture of starting material (**1a**) and mono-phenylated product (**3a**) could not be separated. Thus, we determined the conversion from ^{1}H NMR data of the mixture using the ethoxy protons along with *n*-decane as an internal standard.
9. Preparation of the $Pd(OTf)_2 \cdot 2H_2O$ Murata, S.; Ido, Y. *Bull. Chem. Soc. Jpn.* **1994**, *67*, 1746.
10. Recent reviews and papers on Pd(II)/Pd(IV) chemistry: (a) Canty, A. J. *Acc. Chem. Res.* **1992**, *25*, 83; (b) Canty, A. J.; Patel, J.; Rodemann, T.; Ryan, J. H.; Skelton, B. W.; White, A. H. *Organomatallics* **2004**, *23*, 3466; (c) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527; (d) Kalyani, D.; Deprez, N. R.; Desai, L. V.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 7330; (e) Deprez, N. R.; Kalyani, D.; Krause, A.; Sanford, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 4972; (f) Deprez, N. R.; Sanford, M. S. *Inorg. Chem.* **2007**, *46*, 1924; (g) Whitfield, S. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2007**, *129*, 15142; (h) Jordan-Hore, J. A.; Johansson, C. C. C.; Gulias, M.; Beck, E. M.; Gaunt, M. J. *J. Am. Chem. Soc.* **2008**, *130*, 16184; (i) Deprez, N. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 11234; (j) Xu, L.-M.; Li, B.-J.; Yang, Z.; Shi, Z.-J. *Chem. Soc. Rev.* **2010**, *39*, 712; (k) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147.
11. Papers on reduction of phosphates, sulfonates, sulfates, and aliphatic halides with LiDTBB: (a) Yus, M.; Herrera, R. P.; Guijarro, A. *Tetrahedron Lett.* **2003**, *44*, 5025; (b) Yus, M.; Herrera, R. P.; Guijarro, A. *Tetrahedron Lett.* **2001**, *42*, 3455; (c) Guijarro, D.; Mancheño, B.; Yus, M. *Tetrahedron* **1994**, *50*, 8551; (d) Guijarro, D.; Guillena, G.; Mancheño, B.; Yus, M. *Tetrahedron* **1994**, *50*, 3427; (e) Guijarro, D.; Mancheño, B.; Yus, M. *Tetrahedron* **1992**, *48*, 4593; (f) Guijarro, D.; Mancheño, B.; Yus, M. *Tetrahedron Lett.* **1992**, *33*, 5597.