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Palladium-Catalyzed Acetoxylation of Arenes by Novel Sulfinyl N-Heterocyclic Carbene Ligand Complexes

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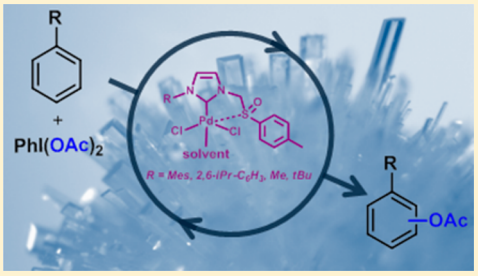
Supporting Information

ABSTRACT: A series of novel ligands based on N-heterocyclic carbene and sulfoxide functionalities have been prepared and characterized. Pd(II) complexes have been synthesized by transmetalation from the corresponding NHC−Ag derivatives, and their behavior as catalysts has been studied in arene C−H bond oxidative activation. Studies conducted toward the elucidation of the reaction mechanism of the acetoxylation suggest a C−H activation step at Pd(IV) rather than Pd(II) intermediates.



INTRODUCTION

The activation of C−H bonds by palladium catalysis in high oxidation states has gained a relevant significance over the last few years, due mainly to the discovery of novel applications and the development of mechanistic studies concerning Pd(IV).[1,2] Although the C−H activation of substrates with directing groups has been widely studied,[3] the functionalization of unactivated C−H bonds remains a significant challenge in organic chemistry and still presents several drawbacks related to reactivity, selectivity, catalytic activity, and scope, among others. Traditionally, the palladium catalysts involved in Pd(II)/Pd(IV) catalytic cycles possess carboxylates or pyridine derivatives as ancillary ligands.[4] However, other types of ligands such as N-heterocyclic carbenes (NHC) have demonstrated a great utility in Pd chemistry[5] (mainly in cross-coupling reactions) due to the high stability of the complexes, resistance to acidic conditions, and a strong σ-donor coordination mode which can both facilitate oxidative addition and stabilize high oxidation states. For these reasons, some examples of NHC−Pd complexes have recently appeared describing the oxidation of both C_{sp^3}−H and C_{sp^2}−H bonds involving Pd(IV) species.[6] On the other hand, sulfoxides are well-known in coordination chemistry and form stable complexes with many metals.[7] Among those, sulfoxides have recently shown to be exceptional ligands in Pd catalysis for the functionalization of allylic C−H bonds, overcoming the regiochemistry troubles inherent to these oxidations.[8] In spite of this, the sulfinyl group has not been previously studied as a part of NHC ligands, and only one example has been reported, to the best of our knowledge.[9] In the present work, we report the synthesis of an adaptable NHC family of ligands containing a sulfinyl group (Figure 1) which could represent a suitable choice for Pd-catalyzed C−H bond activation. Thus, we intend to take advantage of the different properties of both kinds of ligands. Whereas NHC is able to stabilize Pd(IV) species, we expect that the sulfinyl group can act as a hemilabile

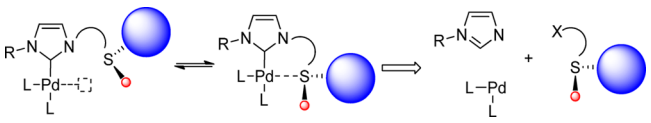


Figure 1. Proposed sulfinyl-NHC ligand and catalyst.

functionality[10] capable of coordinating the reactive metal or creating vacant coordination sites. In order to evaluate these novel Pd catalysts, we have selected the C−H acetoxylation reaction of arenes by hypervalent iodine oxidants.

RESULTS AND DISCUSSION

These new ligand precursors were prepared by nucleophilic substitution of the corresponding N-substituted imidazoles with bromomethyl sulfoxide.[11] The reaction conditions were optimized by the use of microwave irradiation, which improved the yields and shortened the reaction times (Scheme 1). Accordingly, aromatic substituents at the imidazole moiety such as 2,4,6-trimethylphenyl (Mes) and 2,6-diisopropylphenyl groups reacted with the racemic sulfinyl bromide **2** to form the imidazolium salts **3a**,**b** in good yields (76% and 78%, respectively). On the other hand, the alkyl-substituted

Scheme 1. Synthesis of the Imidazolium Bromide Ligand Precursors 3a−d

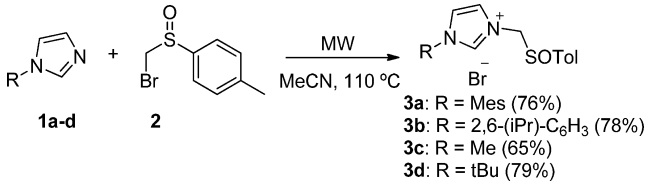


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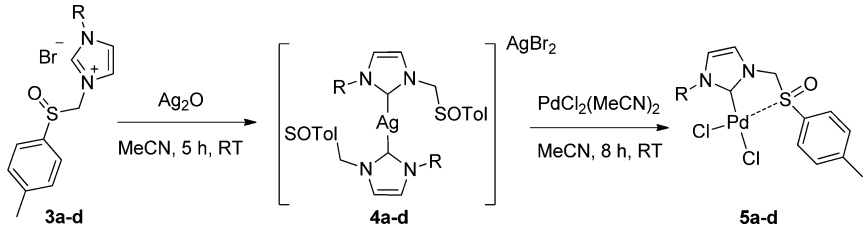
Table 1. Synthesis of the Ag Complexes 4a−d and Sulfinyl-NHC−Pd Complexes 5a−d



		yield, %	
entry[a]	R	$(NHC)_2$−Ag (**4**)	NHC−Pd[b] (**5**)
1	Mes (**3a**)	94 (**4a**)	91 (**5a**)
2	2,6-(iPr)-C_6H_3 (**3b**)	93 (**4b**)	82 (**5b**)
3	Me (**3c**)	95 (**4c**)	95 (**5c**)
4	*t*-Bu (**3d**)	91 (**4d**)	72 (**5d**)

[a]The synthesis of Ag and Pd complexes was carried out in a vial with **3a−d** (0.1 mmol) and Ag_2O (0.1 mmol) in MeCN (1 mL) at room temperature and stirring for 5 h with protection from light. Then, the mixture was filtered through a Celite pad and $Pd(MeCN)_2Cl_2$ (0.1 mmol) was added to the filtrate; the mixture was stirred for 8 h at room temperature. [b]Yield of isolated complex synthesized in a one-pot reaction from the imidazolium bromide.

imidazole rings also gave the corresponding imidazolium salts **3c,d** in 65% and 79% yields for the Me and *t*-Bu derivatives, respectively.

Once the synthesis of ligands **3a−d** was complete, we directed our efforts to the preparation of novel potentially active metal complexes. Sulfinyl-NHC−Pd complexes were synthesized according to the Ag(I)−NHC transfer protocol. Thus, imidazolium precursors **3a−d** were treated with Ag_2O in MeCN at room temperature and subjected to subsequent transmetalation to a Pd source. This route involves the formation of $[(NHC)_2Ag]\cdot[AgBr_2]$ complexes **4a−d**, as shown by mass spectrometry. In a further step, these silver carbene complexes were reacted with $Pd(MeCN)_2Cl_2$, affording the Pd complexes **5a−d** in good yields (95−72%) as yellow crystalline products starting from the corresponding imidazolium bromides **3a−d** (Table 1).

Although the reaction was performed in one pot, the intermediate NHC−Ag complexes were isolable and relatively stable. The ^{1}H NMR of complexes **5a−d** in noncoordinating solvents (CD_2Cl_2, $CDCl_3$, toluene-d_8) only showed broad signals, probably due to dynamic equilibration between monomeric and dimeric species (Figure 2). However, coordinating solvents such as MeCN-d_3, CD_3OD, and THF-d_8 allowed the observation of well-defined signals in the ^{1}H NMR spectra. Complete shifting of the dynamic equilibrium to the solvent-coordinated complex **5** may be the reason for this behavior (Figure 2). Coordination of solvent was confirmed by X-ray diffraction of a single crystal obtained by slow evaporation of a MeCN solution of **5a**.[12]

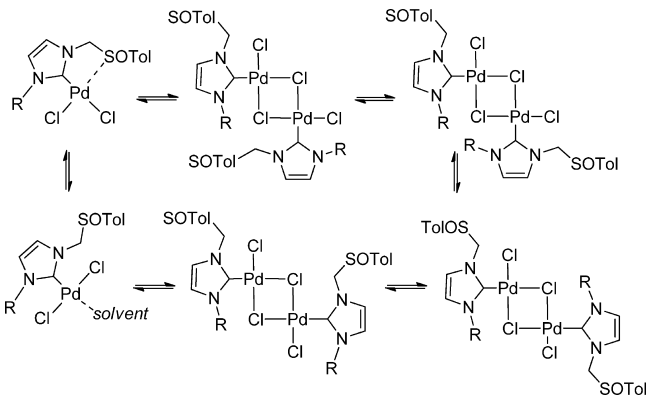


Figure 2. Putative species involved in the dynamic equilibrium of complex **5** derivatives.

The molecular structure of complex **5a** exhibits the usual square-planar geometry for a Pd(II) complex with nearly no distortion. As expected from ^{1}H NMR experiments, a MeCN molecule completes the coordination sphere in a position *trans* to the NHC, while the sulfinyl function is orientated in an axial position with regard to Pd. This makes the torsion angle between the NHC unit and the coordination main plane reach 121.9°. In fact, the Pd···S distance is 3.34(2) Å, which is slightly lower than the sum of the van der Waals radii and suggests a weak interaction between sulfur and Pd (Figure 3, left). Unexpectedly, heating complex **5d** in a $AcOH/Ac_2O$ (9/1) mixture allowed us to isolate **5d′**, which exhibits a dimeric square-planar geometry (Figure 3, right). It is important to note that the sulfoxide remains uncoordinated even in this case, suggesting that the coordinating ability of this ligand is not strong enough to open up the dimer.[12]

We were interested in the reactivity of these novel complexes in the activation of aromatic C−H bonds and how the combined properties conferred by the presence of both sulfoxide and NHC ligands could influence the reactivity. The initial report by Crabtree on the acetoxylation of arenes revealed an interesting process involving oxidation of initially formed Ph−Pd derivatives, although the reaction was not regioselective.[13] From then on, studies on arene acetoxylation have mainly centered on substituted systems, in which the presence of coordinating groups determines the regioselectivity.[3] Thus, ortho acetoxylation of arylpyridines and other substituted arenes has enabled elegant mechanistic studies (mainly by the group of Sanford) based on the isolation of intermediate complexes and the separate study of the different reaction steps: C−H activation, oxidation of Pd(II) palladacycles, and reductive elimination. Alternatively, acetoxylation of activated substrates such as indoles[14] and quinaxolines[15] proceeds with high regioselectivity due to the special features of the C−H bonds. Recently, more reactive catalytic systems based on pyridine ligands have been reported for the

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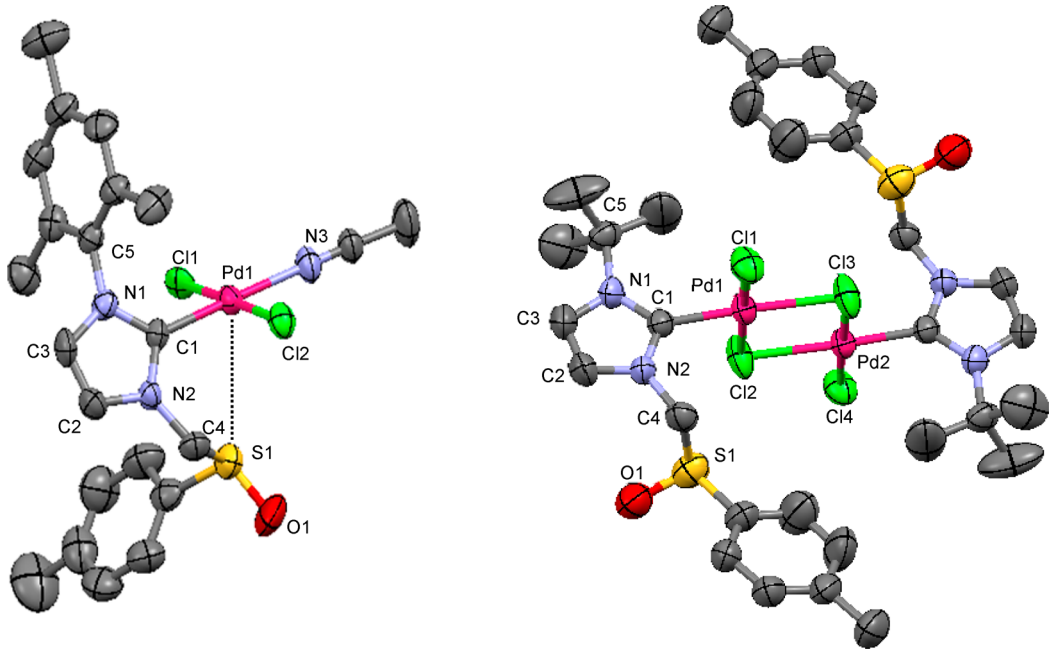


Figure 3. ORTEP view of complexes **5a** (left) and **5d′** (right). Ellipsoids are represented at the 50% probability level. Hydrogen atoms and acetic acid (**5d′**) have been omitted for clarity. The Pd···S interaction in complex **5a** has been represented as a dashed line.

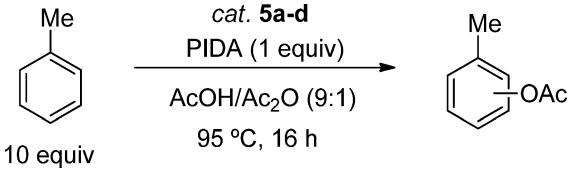
nondirected acetoxylation of arenes.[4c] Previously, the simple $Pd(OAc)_2$ has been used as the catalyst for these processes.

In our work, we intended to study the catalytic activity of NHC-sulfoxide derivatives. The high electron richness of the NHC ligand seems to promote a different pathway, which starts with oxidation prior to C−H activation, in contrast to the reported mechanisms, as will be shown below.

Complexes **5a−d** were evaluated in the Pd-catalyzed acetoxylation of arenes, involving C−H bond oxidative activation. Toluene was used as the model substrate, and PIDA was the oxidant of choice. The results are shown in Table 2.

Initially, the use of AcOH as solvent afforded low yields of acetoxylation products for catalysts **5a−d**. Slightly higher yields were obtained for the non-N-aromatic catalysts **5c,d** (Table 2, entries 2−5). Nevertheless, enhanced yields of acetoxy derivatives, up to 69% with **5d**, could be obtained when a $AcOH/Ac_2O$ (9/1) mixture was employed as solvent (Table 2, entries 6−9). Trace amounts of benzaldehyde were detected in all assays, which came from the oxidation of the more activated benzylic position. When the reaction was performed in the absence of Pd catalyst, we found that the aldehyde was formed in 35% yield (Table 2, entry 1). On the other hand, PIDA was observed to decompose in the reaction medium; however, the decomposition rate decreased with dilution and therefore the yield of acetoxy derivatives increased up to 79% when the concentration was lowered (Table 2, entry 10). Catalytic loading of **5d** could be reduced to 0.25 mol % without a significant loss of yield (Table 2, entries 11 and 12). As expected, in all cases the process is not regioselective and *ca.* 1/1/1 mixtures of acetoxylation at *ortho*/*meta*/*para* positions were collected for each reaction. Additionally, PIFA was tested in this reaction, affording similar results in both yield and regioselectivity (Table 2, entry 13). Moreover, this reaction can be carried out under microwave irradiation and, although no improvement concerning the yield was detected, the reaction time was reduced to 1 h (Table 2, entry 14). We intended to obtain mechanistic information concerning the reaction mechanism, since not many examples of strong donating ligands involved in Pd-catalyzed oxidation reactions have been reported. Exceptionally, the use of NHC ligands in Pd-catalyzed C−H activation has been previously described by Sanford et al. for the chlorination of arenes possessing a directing group.[6d]

Table 2. Evaluation of Novel Pd Complexes 5a−d in Acetoxylation of Toluene



entry[a]	cat. (mol%)	solvent	yield, %[b]
1	none	AcOH	*c*
2	**5a** (1)	AcOH	38
3	**5b** (1)	AcOH	34
4	**5c** (1)	AcOH	42
5	**5d** (1)	AcOH	45
6	**5a** (1)	$AcOH/Ac_2O$ (9/1)	63
7	**5b** (1)	$AcOH/Ac_2O$ (9/1)	56
8	**5c** (1)	$AcOH/Ac_2O$ (9/1)	67
9	**5d** (1)	$AcOH/Ac_2O$ (9/1)	69
10[d]	**5d** (1)	$AcOH/Ac_2O$ (9/1)	79
11[d]	**5d** (0.5)	$AcOH/Ac_2O$ (9/1)	76
12[d]	**5d** (0.25)	$AcOH/Ac_2O$ (9/1)	74
13[d,e]	**5d** (1)	$AcOH/Ac_2O$ (9/1)	78
14[f]	**5d** (0.25)	$AcOH/Ac_2O$ (9/1)	73

[a]Unless otherwise noted, a sealed tube was charged with toluene (10 equiv), PIDA (0.167 mmol, 1 equiv), Pd complex (**5a−d**), and solvent (0.4 M). Then, the reaction mixture was heated to 95 °C for 16 h. [b]Yield based on GC using chlorobenzene as internal standard. [c]35% yield of benzaldehyde based on GC. [d]Reaction conducted at 0.2 M in $AcOH/Ac_2O$ (9/1). [e]PIFA was used as oxidant. [f]Reaction was carried out under microwave irradiation for 1 h.

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The oxidation to Pd(IV) with $PhICl_2$ occurs at the preformed cyclometalated benzoquinoline palladacycle with subsequent reductive elimination. On the other hand, (NHC)Pd-catalyzed alkane C−H activation has been proposed at Pd(II) followed by an oxidation step.[6e−h] However, we suspected that the presence of strong σ-donor NHC ligands could play an additional role in the mechanism. We hypothesized that the electron-rich Pd(II) catalyst could result in oxidation to Pd(IV) prior to C−H activation (Figure 4, path A). Although reductive elimination at Pd(IV) should occur rapidly, C−H activation at Pd(IV) has been also described.[16]

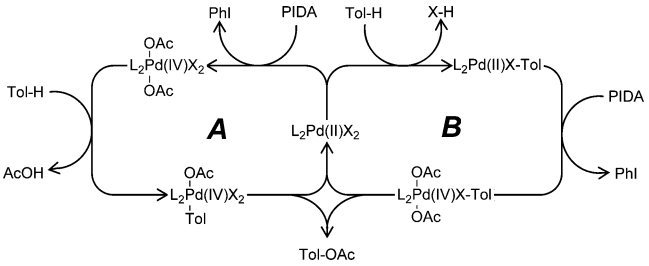
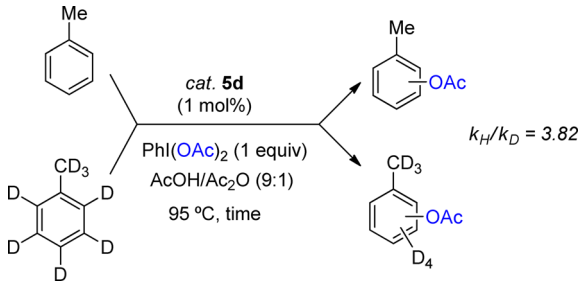


Figure 4. Plausible catalytic cycles for C−H activation an acetoxylation of toluene.

In order to get an insight into the reaction mechanism and the actual behavior of these electron-rich NHC−Pd(II) catalysts, different experiments were performed, which gave the following information. (1) The catalyst stability was studied under the reaction conditions. Thus, **5d** was stirred for 3 h in $AcOH/Ac_2O$ (9/1) at 95 °C and no decomposition was observed by ^1H NMR. (2) The sulfinyl-NHC−Pd catalysts afforded the highest conversion of the acetoxylation in 5 h; after this point, solutions became greenish, indicating the presence of Pd(0), and finally Pd black starts to appear in the crude reaction mixture, indicating the complete consumption of the oxidant. (3) The intermolecular kinetic isotopic effect obtained by comparing the acetoxylation reaction rate of toluene and toluene-d_8 reveals k_H/k_D = 3.82, which suggests that the C−H bond cleavage is involved in the rate-determining step (Scheme 2).[17] (4) Additionally, when the catalytic reaction was carried

Scheme 2. Intermolecular Kinetic Isotopic Effect



out in CD_3CO_2D as solvent, the acetoxytoluene derivatives did not show any deuterium incorporation in either the acetyl group or in the arene (Scheme 3, eq 1). Therefore, the whole acetoxy group incorporated into the product comes from PIDA, and no exchange with the solvent is taking place at the Pd complex. On the other hand, when the reaction was carried out with toluene-d_8 as substrate in AcOH, only the acetoxylated d_7-arene was produced, which implies the occurrence of an irreversible C−H activation step (Scheme 3, eq 2). (5) On the other hand, the reaction between the Pd complex and PIDA was studied by ^1H NMR and GC. While the oxidant slightly decomposed in the presence of a $AcOH/Ac_2O$ (9/1) mixture after heating at 95 °C, as had been previously described,[18] the presence of stoichiometric Pd complex **5d** totally consumed the PIDA in 2.5 h. ^1H NMR spectra of this reaction mixture only showed PhI (coming from the oxidant) and broad signals which could indicate Pd complexes. Additionally, catalyst **5d** and toluene were heated at 95 °C in $AcOH/Ac_2O$ (9/1) for 3 h without oxidant, and the residue was analyzed by NMR and GC. The fact that complex **5d** did not afford aryl homocoupling products, along with the absence of deuterium exchange, suggests that the C−H activation step does not occur at Pd(II), in contrast to what has been proposed for $Pd(OAc)_2$. (6) Moreover, the reaction of Pd complex **5d**, PIDA or PIFA, and toluene afforded 64% and 88% yields of chlorotoluene (with respect to complex **5d**), respectively. The presence of this product suggests the existence of a transient Pd(IV) intermediate which afforded chlorotoluene by C−Cl reductive elimination (Scheme 4).

All these data suggest that the reaction mechanism could involve a Pd(II)/Pd(IV) cycle in which oxidation of Pd(II) with PIDA takes place prior to C−H activation. Additionally, C−H activation is relatively slow, in accord with the observed KIE, but fast in comparison to the acetate scrambling with solvent. The intimate mechanism of the C−H activation cannot be elucidated from these data. It could take place in a single step, with or without acetate assistance, or follow the formation of an intermediate reminiscent of the Wheland intermediate for S_EAr reactions. In any case, formation of the C−O bond by reductive elimination must be fast enough to explain the absence of H/D exchange.

Furthermore, other substrates were subjected to this reaction conditions using catalyst **5d** in other to recover additional information about the mechanism. For this purpose, different substitutions on the aromatic ring were evaluated, taking into account the electronic and the steric effects.

First of all, it is important to note that, in most of the reactions of Scheme 5, traces of the corresponding chloroarenes were detected by GC/MS, supporting the formation of Pd(IV) intermediates, as mentioned above. Substitution of the methyl group of toluene by propyl provoked a decrease of the acetoxylation rate at the *ortho* and *meta* positions, probably due to steric and electronic influences, respectively. For the naphathalene derivative a *ca.* 1/1 mixture was obtained. However, electron-rich methoxy-substituted substrates showed a clear preference for the usual S_EAr substitution pattern, and a single regisomer was obtained from 1,2-dimethoxybenzene. A competitive substrate such as *p*-iodoanisole revealed the prevalence of the influence of strongly activating groups, yielding mostly acetoxylation at the *ortho* position. An electron-withdrawing group such as a methyl ester also gave the reaction mainly in the *meta* position, as expected, but in lower yield (28%). Finally, a substrate carrying an *ortho*-directing azo group exclusively afforded the activation at the *ortho* position. All these data suggest an electrophilic aromatic substitution for the Pd-catalyzed C−H activation.

■ CONCLUSIONS

In conclusion, we have developed a novel series of sulfinyl-NHC−Pd catalysts with different substitutions at the imidazolyl nitrogen. Their activity in the C−H activation of arenes has been studied, affording good yields for the acetoxylation of

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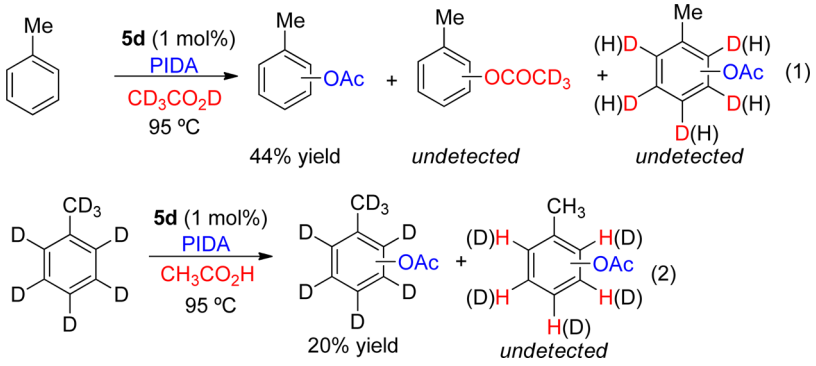
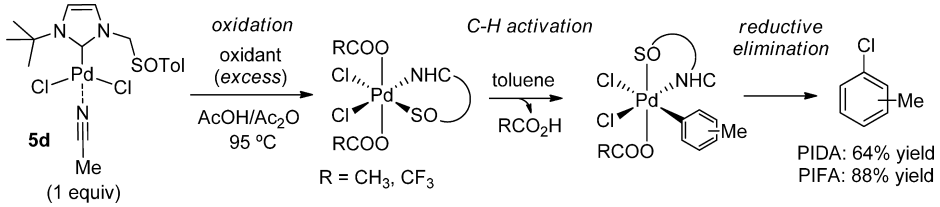
Scheme 3. H/D Exchange Experiments[a]

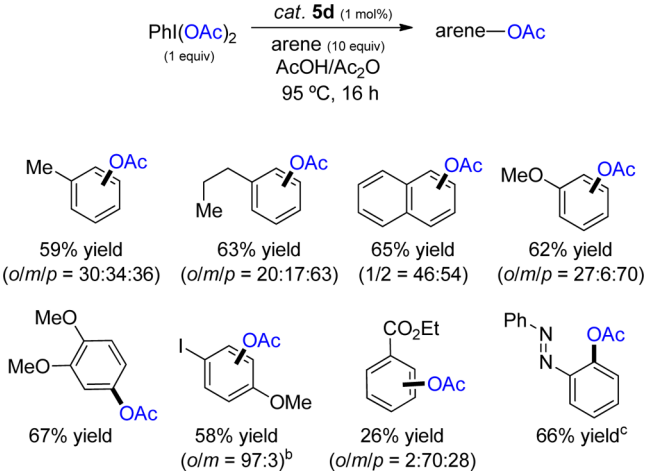


[a]Yields were calculated by GC using chlorobenzene as internal standard.

Scheme 4. Reductive Elimination at Pd(IV) To Afford Chlorotoluene



Scheme 5. Sulfinyl-NHC–Pd-Catalyzed C–H Acetoxylation[a]



[a]Unless otherwise noted, the reaction was carried out as described in Table 2 at a concentration of 0.2 M and the regioisomeric ratio was determined by GC. [b]Regioisomeric ratio with respect to OMe group. [c]Reaction was carried out with 1 equiv of azobenzene and 2 equiv of PIDA in MeCN at 80 °C for 72 h.

arenes. A low catalysis loading (0.25 mol %) allows this transformation, and according to the collected data, the reaction follows a different mechanism in comparison with similar oxidations performed in the absence of strongly donating ligands. Thus, previous oxidation of the catalyst followed by C–H activation at Pd(IV) species seems to be involved in this case.

EXPERIMENTAL DECTION

General Considerations. All of the reactions were run in a sealed tube with a Teflon-lined cap under an air atmosphere. Solvents for synthesis were of reagent grade or better. Additionally, THF, dichloromethane, toluene, and acetonitrile were dried by passage through activated alumina on a commercial solvent purification system if necessary. Thin-layer chromatography was carried out using TLC-aluminum sheets with 0.2 mm of silica gel and visualized by UV or by staining with phosphomolybdic acid or $KMnO_4$ solution. Chromatographic purifications were carried out using flash grade silica gel (40–60 μm). ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded at 23 °C. Proton and carbon chemical shifts were referenced internally to residual solvent resonances, and coupling constants are expressed in Hz. High-resolution mass spectra (HRMS) were recorded using electrospray ionization (ESI) or fast atom bombardment (FAB) (70 eV) and a BR-5 ms column (15 m × 0.25 mm i.d., 0.25 μm thick). Compounds **1a,b,d** and **2** were prepared according to the procedure described in the literature.[19] Other chemicals such as **1c**, PIDA, PIFA, $PdCl_2(MeCN)_2$, arenes, and chlorobenzene as well as deuterated solvents were purchased from standard suppliers and used as received.

General Procedure for the Synthesis of Sulfinylimidazolium Bromides 3a–d. In a microwave vial were added 1-[(bromomethyl)-sulfinyl]-4-methylbenzene (**2**; 140 mg, 0.6 mmol, 1.0 equiv), N-substituted imidazoles **1a–d** (0.6 mmol, 1 equiv), and MeCN (2 mL). The vial was capped, and the reaction mixture was irradiated under microwave conditions (110 °C, 100 W). After consumption or no evolution of starting materials (TLC eluted in CH_2Cl_2/EtOAc 50/50), the solvent was removed under vacuum and the residue was washed by sonication in EtOAc until the complete purification of the products. Finally, sulfinyl imidazolium bromides **3a–d** were dried under vacuum. Additionally, imidazolium bromides can be purified by a chromatography column using DCM/MeOH 95/5 → 90/10 as eluent.

1-Mesityl-3-[(*p*-tolylsulfinyl)methyl]-1*H*-imidazol-3-ium Bromide (3a). 1-Mesitylimidazole (**1a**; 112 mg, 0.6 mmol) was used as the starting material, and the reaction mixture was irradiated for 6 h, affording **3a** (191 mg) in 76% yield as a hygroscopic off-white solid. Mp 161–163 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.83 (t, J = 1.5 Hz, 1H), 7.66 (AA′BB′ system, 2H), 7.34 (AA′BB′ system, 2H), 7.03–6.92 (m, 2H), 7.01 (t, J = 1.5 Hz, 1H), 6.78 (d, J = 13.1 Hz, 1H), 6.02 (d, J = 13.1 Hz, 1H), 2.37 (s, 3H), 2.32 (s, 3H), 2.06 (br s, 3H), 1.79 (br s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 141.5, 137.7, 134.5, 134.3, 134.0, 130.4 (2C), 130.3, 129.9, 129.8, 124.9 (2C), 124.1, 122.2, 66.8, 21.4, 21.1, 17.6, 17.4 ppm; HRMS (FAB+) m/z [M − Br]$^+$ calcd for $C_{20}H_{23}N_2OS$ 339.1530, found 339.1531.

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1-(2,6-Diisopropylphenyl)-3-[(*p*-tolylsulfinyl)methyl]-1*H*-imidazol-3-ium Bromide (3b). 1-(2,6-Diisopropylphenyl)imidazole (**1b**; 137 mg, 0.6 mmol) was used as the starting material, and the reaction mixture was irradiated for 6 h, affording **3b** (216 mg) in 78% yield as a hygroscopic off-white solid: mp 157−159 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.67 (s, 1H), 8.00 (s, 1H), 7.70 (AA′BB′ system, 2H), 7.53 (t, J = 7.8 Hz, 1H), 7.36 (AA′BB′ system, 2H), 7.26 (t, J = 7.8 Hz, 2H), 7.01 (t, J = 1.8 Hz, 1H), 6.89 (d, J = 13.9 Hz, 1H), 6.12 (d, J = 13.9 Hz, 1H), 2.39 (s, 3H), 2.27 (q, J = 6.7 Hz, 1H), 2.04 (q, J = 6.7 Hz, 1H), 1.29 (d, J = 6.8 Hz, 3H), 1.14 (d, J = 6.8 Hz, 3H), 1.12 (d, J = 6.8 Hz, 3H), 1.09 (d, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.5, 145.2, 142.7, 137.8, 134.4, 132.2, 130.5 (2C), 129.8, 125.0, (2C), 124.9, 124.8, 124.3, 123.2, 66.7, 28.7, 28.6, 24.6, 24.4, 24.4, 24.2, 21.6 ppm; HRMS (FAB+) m/z [M − Br]$^+$ calcd for $C_{23}H_{29}N_2OS$ 381.2001, found 381.1998.

1-Methyl-3-[(*p*-tolylsulfinyl)methyl]-1*H*-imidazol-3-ium Bromide (3c). 1-Methylimidazole (**1c**; 49 mg, 0.6 mmol) was used as the starting material, and the reaction mixture was irradiated for 10 h, affording **3c** (123 mg) in 65% yield as a hygroscopic off-white solid: mp 160−162 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.56 (AA′BB′ system, 2H), 7.49 (t, J = 1.4 Hz, 1H), 7.45 (t, J = 1.4 Hz, 1H), 7.31 (AA′BB′ system, 2H), 6.14 (d, J = 13.4 Hz, 1H), 5.84 (d, J = 13.4 Hz, 1H), 4.00 (s, 3H), 2.38 (s, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 137.6, 135.1, 130.5 (2C), 124.7 (2C), 123.6, 122.8, 68.1, 37.1, 21.6 ppm; HRMS (FAB+) m/z [M − Br]$^+$ calcd for $C_{12}H_{15}N_2OS$ 235.0901, found 235.0905.

1-*tert*-Butyl-3-[(*p*-tolylsulfinyl)methyl]-1*H*-imidazol-3-ium Bromide (3d). 1-*tert*-Butylimidazole (**1d**; 75 mg, 0.6 mmol) was used as the starting material, and the reaction mixture was irradiated for 10 h, affording **3d** (169 mg) in 79% yield as an off-white solid: mp 164−166 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.91 (s, 1H), 7.54 (AA′BB′ system, 2H), 7.53−7.50 (m, 1H), 7.41 (t, J = 1.9 Hz, 1H), 7.29 (AA′BB′ system, 2H), 6.09 (d, J = 13.3 Hz, 1H), 5.84 (d, J = 13.3 Hz, 1H), 2.34 (s, 3H), 1.52 (s, 9H) ppm; ^{13}C NMR (76 MHz, $CDCl_3$) δ 142.7, 135.6, 134.8, 130.3 (2C), 124.7 (2C), 123.6, 118.6, 67.6, 60.7, 29.9 (3C), 21.4 ppm; HRMS (FAB+) m/z [M − Br]$^+$ calcd for $C_{15}H_{21}N_2OS$ [M − Br]$^+$ 277.1375, found 277.1379.

General Procedure for the Synthesis of Sulfinyl-NHC−Ag Complexes 4a−d. In a vial were added 1-substituted 3-[(*p*-tolylsulfinyl)methyl]-1*H*-imidazol-3-ium bromides **3** (0.1 mmol, 1.0 equiv), Ag_2O (23 mg, 0.1 mmol, 1.0 equiv), and MeCN (1 mL). The vial was protected from the light, and the reaction mixture was stirred at room temperature for 5 h. Then, the reaction mixture was filtered through a Celite pad and the filtrate was evaporated under reduced pressure, affording the Ag complexes **4a−d**, which were used in the next step without further purification.

Bis{1-mesityl-3-[(*p*-tolylsulfinyl)methyl]imidazol-2-ylidene}-silver(I) Dibromoargentate (4a). 1-Mesityl-3-[(*p*-tolylsulfinyl)-methyl]-1*H*-imidazolium bromide (**3a**; 42 mg, 0.1 mmol) was used as the starting material, and the reaction mixture afforded the silver complex **4a** (53 mg) in a 94% yield as a yellowish solid. ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 7.44 (AA′BB′ system, 2H), 7.32 (AA′BB′ system, 2H), 7.18 (d, J = 1.9 Hz, 1H), 7.00−6.93 (m, 2H), 6.98 (d, J = 1.9 Hz, 1H), 5.55 (d, J = 13.7 Hz, 1H), 5.44 (d, J = 13.7 Hz, 1H), 2.36 (s, 3H), 2.34 (s, 3H), 1.85 (s, 3H), 1.66 (s, 3H) ppm; ^{13}C NMR (76 MHz, acetonitrile-d_3) δ 184.7, 143.4, 140.2, 137.4, 136.4, 135.9, 135.6, 131.3 (2C), 130.0, 129.9, 125.6 (2C), 123.8, 123.6, 71.0, 21.6, 21.2, 17.9, 17.9 ppm; HRMS (ESI+) m/z [M − $AgBr_2$]$^+$ calcd for $C_{40}H_{44}N_4S_2O_2Ag$ [M − $AgBr_2$]$^+$ 785.1951, found 785.1959.

Bis{1-(2,6-diisopropylphenyl)-3-[(*p*-tolylsulfinyl)methyl]-imidazol-2-ylidene}silver(I) Dibromoargentate (4b). 1-(2,6-Diisopropylphenyl)-3-[(*p*-tolylsulfinyl)methyl]-1*H*-imidazolium bromide (**3b**; 46 mg, 0.1 mmol) was used as the starting material, and the reaction mixture afforded the silver complex **4b** (57 mg) in 93% yield as a yellowish solid. ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 7.52−7.34 (m, 5 H), 7.32−6.98 (m, 4H), 5.60 (bs, 1H), 5.35 (d, J = 13.4 Hz, 1H), 2.39 (s, 3H), 2.25 (q, J = 6.8 Hz, 1H), 2.21−2.10 (m, 1H), 1.24−0.89 (m, 6H), 1.10 (s, 3H), 1.08 (s, 3H) ppm; ^{13}C NMR (76 MHz, acetonitrile-d_3) δ 146.9, 146.5, 143.5, 137.4, 135.7, 131.3 (2C), 125.4 (3C), 125.0, 125.0, 124.8, 123.8, 70.7, 28.9 (2C), 24.8, 24.6, 24.4, 24.3, 21.6 ppm ($C_{carbene}$ not observed); HRMS (ESI+) m/z [M − $AgBr_2$]$^+$ calcd for $C_{46}H_{56}N_4S_2O_2Ag$ [M − $AgBr_2$]$^+$ 869.2892, found 869.2895.

Bis{1-methyl-3-[(*p*-tolylsulfinyl)methyl]imidazol-2-ylidene}-silver(I) Dibromoargentate (4c). 1-Methyl-3-[(*p*-tolylsulfinyl)-methyl]-1*H*-imidazolium bromide (**3c**; 32 mg, 0.1 mmol) was used as the starting material, and the reaction mixture afforded the silver complex **4c** (42 mg) in 95% yield as a white solid. ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 7.39 (AA′BB′ system, 2H), 7.33 (AA′BB′ system, 2H), 7.10 (d, J = 1.8 Hz, 1H), 7.05 (d, J = 1.8 Hz, 1H), 5.38 (d, J = 13.3 Hz, 1H), 5.15 (d, J = 13.3 Hz, 1H), 3.74 (s, 3H), 2.38 (s, 3H) ppm; ^{13}C NMR (76 MHz, acetonitrile-d_3) δ 184.1, 143.7, 138.0, 131.3 (2C), 125.5 (2C), 123.7, 123.5, 72.2, 39.4, 21.6 ppm; HRMS (ESI+) m/z [M − $AgBr_2$]$^+$ calcd for $C_{24}H_{28}N_4S_2O_2Ag$ 575.0699, found 575.0698; MS (ESI−) calcd for $AgBr_2$ [M] 266.74.

Bis{1-*tert*-butyl-3-[(*p*-tolylsulfinyl)methyl]imidazol-2-ylidene}silver(I) Dibromoargentate (4d). 1-*tert*-Butyl-3-[(*p*-tolylsulfinyl)methyl]-1H-imidazolium bromide (**3d**; 36 mg, 0.1 mmol) was used as the starting material, and the reaction mixture afforded the silver complex **4d** (46 mg) in 91% yield as a yellowish solid. ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 7.31 (br s, 4H), 7.28 (d, J = 2.0 Hz, 1H), 7.08 (d, J = 2.0 Hz, 1H), 5.41 (d, J = 13.4 Hz, 1H), 5.28 (d, J = 13.4 Hz, 1H), 2.36 (s, 3H), 1.60 (s, 9H) ppm; ^{13}C NMR (76 MHz, acetonitrile-d_3) δ 181.3, 143.5, 137.6, 131.4 (2C), 125.3 (2C), 122.2, 120.3, 73.0, 58.9, 31.9 (3C), 21.5 ppm; HRMS (ESI+) m/z [M − $AgBr_2$]$^+$ calcd for $C_{30}H_{40}N_4S_2O_2Ag$ 661.1636, found 661.1628.

General Procedure for the Synthesis of Sulfinyl-NHC−Pd Complexes 5a−d. In a vial were added 1-substituted 3-[(*p*-tolylsulfinyl)methyl]-1*H*-imidazol-3-ium bromides **3a−d** (0.30 mmol, 1.0 equiv), Ag_2O (70 mg, 0.30 mmol, 1.0 equiv), and MeCN (2 mL). The vial was protected from the light, and the reaction mixture was stirred at room temperature for 5 h. Then, the reaction mixture was filtered through a Celite pad, the pad was rinsed with MeCN (1 mL), and $PdCl_2(MeCN)_2$ (78 mg, 0.30 mmol, 1 equiv) was added to the filtrate. The reaction mixture was stirred for 16 h at room temperature and filtered through a Celite pad. The filtrate was evaporated under reduced pressure, and the residue was dissolved in CH_2Cl_2. The suspension was filtered again through a Celite pad, and the solvent was evaporated under vacuum. Finally, the residue was washed with Et_2O and dried under vacuum, affording the pure complexes. If necessary, further purification was performed by recrystallization in CH_2Cl_2/Et_2O.

Chloro{1-mesityl-3-[(*p*-tolylsulfinyl)methyl]imidazol-2-ylidene}palladium(II) (5a). 1-Mesityl-3-[(*p*-tolylsulfinyl)methyl]-1*H*-imidazol-3-ium bromide (**3a**; 126 mg, 0.30 mmol) was used as the starting material, and the reaction afforded the Pd complex **5a** (141 mg) in 91% yield as a crystalline yellow solid: mp 218 °C dec; ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 7.74 (AA′BB′ system, 2H), 7.44 (AA′BB′ system, 2H), 7.11−7.03 (m, 3H), 6.98 (d, J = 1.9 Hz, 1H), 5.62 (d, J = 7.7 Hz, 1H), 2.44 (s, 3H), 2.38 (s, 3H), 2.17 (s, 3H), 2.13 (s, 3H) ppm; ^{13}C NMR (76 MHz, acetonitrile-d_3) δ 150.0, 144.0, 140.6, 139.2, 137.2, 137.1, 135.6, 131.2 (2C), 130.0, 130.0, 125.9, 125.7 (2C), 124.6, 73.7, 21.6, 21.2, 19.1 (2C) ppm; HRMS (ESI+) m/z [M − Cl − MeCN]$^+$ calcd for $C_{20}H_{22}ClN_2OSPd$ 481.0168, found 481.0194. Anal. Calcd for $C_{22}H_{26}Cl_2N_3OPdS$: C, 47.37; H, 4.70; N, 7.53; S, 5.75. Found: C, 47.48; H, 4.49; N, 7.42; S, 6.05.

Chloro{1-(2,6-diisopropylphenyl)-3-[(*p*-tolylsulfinyl)methyl]-imidazol-2-ylidene}palladium(II) (5b). 1-(2,6-Diisopropylphenyl)-3-[(*p*-tolylsulfinyl)methyl]-1*H*-imidazol-3-ium bromide (**3b**; 138 mg, 0.30 mmol) was used as the starting material, and the reaction afforded the Pd complex **5b** (137 mg) in 82% yield as a crystalline yellow solid: mp 175 °C dec; ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 7.74 (AA′BB′ system, 2H), 7.54 (t, J = 8.2 Hz, 1H), 7.43 (AA′BB′ system, 2H), 7.04 (dd, J = 2.1 and 9.7 Hz, 1H), 5.81 (d, J = 13.3 Hz, 1H), 5.58 (d, J = 13.3 Hz, 1H), 2.80 (q, J = 6.7 Hz, 1H), 2.54 (q, J = 6.7 Hz, 1H), 2.44 (s, 3H), 1.38 (d, J = 6.7 Hz, 3H), 1.35 (d, J = 6.7 Hz, 3H), 0.99 (d, J = 6.7 Hz, 3H), 0.97 (d, J = 6.7 Hz, 3H) ppm; ^{13}C NMR (76 MHz, acetonitrile-d_3) δ 147.8, 147.7, 144.1, 139.0, 139.0, 135.2, 131.6, 131.2 (2C), 127.5, 126.0 (2C), 126.0, 125.1, 124.0, 73.3, 29.4, 29.3, 26.3, 26.2, 23.5, 23.3, 21.6 ppm; HRMS (ESI+) m/z [M − Cl − MeCN]$^+$ calcd for $C_{23}H_{28}ClN_2OPdS$ 523.0638, found 523.0628.

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Chloro{1-methyl-3-[(*p*-tolylsulfinyl)methyl]imidazol-2-ylidene}palladium(II) (5c). 1-Methyl-3-[(*p*-tolylsulfinyl)methyl]-1*H*-imidazol-3-ium bromide (**3c**; 95 mg, 0.30 mmol) was used as the starting material, and the reaction afforded the Pd complex **5c** (117 mg) in 95% yield as a crystalline yellow solid: mp 205 °C dec; ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 7.70 (AA′BB′ system, 2H), 7.44 (AA′BB′ system, 2H), 7.07 (d, J = 2.0 Hz, 1H), 6.98 (d, J = 2.0 Hz, 1H), 5.63 (d, J = 12.8 Hz, 1H), 5.24 (d, J = 12.8 Hz, 1H), 4.04 (s, 3H), 2.45 (s, 3H) ppm; ^{13}C NMR (76 MHz, acetonitrile-d_3) δ 148.7, 143.9, 139.3, 131.2 (2C), 125.6 (2C), 125.0, 124.4, 73.7, 38.8, 21.5 ppm; HRMS (ESI+) m/z [M − Cl − MeCN]$^+$ calcd for $C_{12}H_{14}ClN_2OPdS$ 374.9546, found 374.9545.

Chloro{1-*tert*-butyl-3-[(*p*-tolylsulfinyl)methyl]imidazol-2-ylidene}palladium(II) (5d). 1-*tert*-Butyl-3-[(*p*-tolylsulfinyl)methyl]-1*H*-imidazol-3-ium bromide (**3d**; 107 mg, 0.30 mmol) was used as the starting material, and the reaction afforded the Pd complex **5d** (98 mg) in 72% yield as a crystalline yellow solid: mp 191−192 °C; ^{1}H NMR (300 MHz, acetonitrile-d_3) δ 7.76 (AA′BB′ system, 2H), 7.47 (AA′BB′ system, 2H), 7.29 (d, J = 2.0 Hz, 1H), 7.08 (d, J = 2.0 Hz, 1H), 6.07 (d, J = 12.7 Hz, 1H), 5.31 (d, J = 12.7 Hz, 1H), 2.45 (s, 3H), 2.0.1 (s, 9H) ppm; ^{13}C NMR (76 MHz, acetonitrile-d_3) δ 146.4, 143.8, 139.6, 131.3 (2C), 125.4 (2C), 124.0, 122.5, 76.1, 60.9, 32.1 (3C), 21.5 ppm; HRMS (ESI+) m/z [M + Na − MeCN]$^+$ calcd for $C_{15}H_{20}Cl_2N_2OPdSNa$ 476.9591, found 476.9581. Anal. Calcd for $C_{17}H_{24}Cl_2N_3OPdS$: C, 41.18; H, 4.88; N, 8.48; S, 6.47. Found: C, 41.43; H, 4.56; N, 8.31; S, 6.65.

General Procedure for the Acetoxylation Reaction of Arenes. Arene (2.0 mmol, 10 equiv), PIDA (65 mg, 0.2 mmol, 1.0 equiv), and Pd complex **5d** (1 mg, 1 mol %) were place in a sealed tube. Then, 1 mL of an AcOH/Ac_2O (9/1) mixture was added and the reaction mixture was stirred for 16 h at 95 °C. Unless otherwise noted, the solvent was evaporated under vacuum and the residue was purified by a chromatography column in silica gel.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving experimental procedures, intermolecular kinetic isotopic effects, NMR and MS spectra for all new compounds, and X-ray data for compounds **5a** and **5d′**. 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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