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Catalytic Regioselective C−H Acetoxylation of Arenes Using 4,6-Dimethoxy-1,3,5-triazin-2-yloxy as a Removable/Modifiable Directing Group

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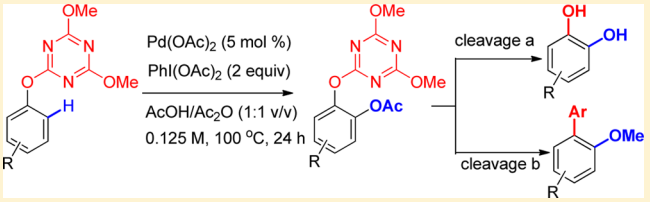
Supporting Information

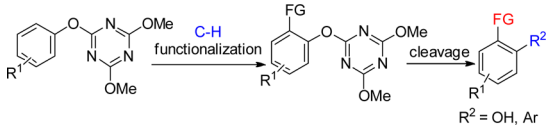
ABSTRACT: One of the major current challenges in the field of C−H functionalization is the development of new removable/modifiable directing groups (DGs). We report here the 4,6-dimethoxy-1,3,5-triazin-2-yloxy group as a new readily removable/modifiable DG for the regioselective acetoxylation of 2-(aryloxy)-4,6-dimethoxy-1,3,5-triazine. This developed phenol-derived DG can be easily removed to offer synthetically versatile pyrocatechols or converted into a useful biphenyl skeleton. In addition, the acetoxylation of 2-(aryloxy)-4,6-dimethoxy-1,3,5-triazine offers a new avenue to synthesize polysubstituted *s*-triazine derivatives.



INTRODUCTION

The coordinating directing group (DG) strategy has been extensively utilized to achieve the regioselective functionalization of C−H bonds in metal-catalyzed reactions.[1] Accordingly, a wide range of DGs have been developed for the selective construction of new C−C and C−X bonds through C−H activation.[2] However, the removal or further transformation of the DGs from C−H functionalized products often represents a challenging synthetic task, thus limiting the diverse utilities of the products. One approach for improving the structural diversity of the products entails the use of removable/modifiable or traceless DGs which can be conveniently removed from the products or undergo further versatile transformations after C−H functionalization.[3] In recent years, the disclosed functional groups involving carboxylic acid,[4] picolinamide,[5] 2-pyridinyloxy,[6] 8-aminoquinoline,[7] 2-pyridylmethyl ether,[8] 2,6-dimethoxylbenzaldoxime,[9] (2-pyridyl)-sulfonyl group,[10] and triazolyldimethylmethyl (TAM) group[11] could serve as DGs for various C−H bond functionalization reactions and then could be easily removed from C−H functionalized products. Despite the outstanding advances that have been made in this still-growing field, to date, very few DGs can be applied to a broad range of further transformations. An elegant manifestation from Gevorgyan and colleagues illustrated that a silicon-tethered pyridyldiisopylsilyl group as a modifiable DG in Pd-catalyzed C−H ortho acryloxylation and ortho halogenation of arenes could undergo diverse transformations such as protonation, halogenation, and hydroxylation, as well as Hiyama−Denmark cross-coupling reactions.[12] In addition, Chatani and co-workers performed a one-pot, catalytic borylative cleavage of the 2-pyridyloxy (OPy) group, which is an extremely effective DG for a number of selective C−H functionalization reactions and is normally removed by the cleavage of the C(pyridinium)−O to give the corresponding phenol, installing the synthetically useful boryl functional group.[13] However, for arenes bearing an oxygen-tethered DG, it is nontrivial to form a new carbon−carbon bond by the cleavage of the C_{Ar}-O bond. Given the prevalence of hydroxyl groups in organic molecules, it is highly desirable to develop novel removable/modifiable phenol-derived DGs for the selective functionalization of C−H bonds. Herein, we report that the 4,6-dimethoxy-1,3,5-triazin-2-yloxy group serving as a new easily removable and modifiable directing group allows for a Pd-catalyzed C−H acetoxylation reaction of arenes. Importantly, this phenol-derived DG can be cleaved by Suzuki−Miyaura coupling reaction to construct a new carbon−carbon bond (Scheme 1).

Scheme 1. 4,6-Dimethoxy-1,3,5-triazin-2-yloxy Group as a Removable/Modifiable DG for C−H Functionalization and Its Subsequent Transformations



Metal-catalyzed C−H acetoxylation reactions of aryl 2,4-dimethoxy-1,3,5-triazin-6-yl ethers are among the most attractive transformations because (1) they allow the direct formation of *s*-triazine derivatives, which are of potential biological importance, and (2) the oxygen-tethered DG can be easily attached to the starting materials and also undergo further versatile transformations after the C−H bond

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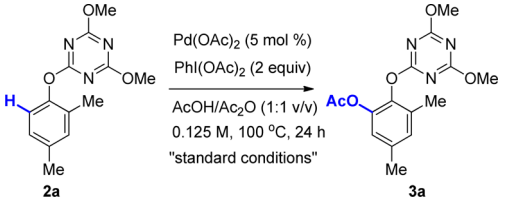
functionalization. Despite the fact that the *s*-triazine core is a prevalent structure in a vast array of bioactive organic compounds, C−H functionalization reactions using the 4,6-dimethoxy-1,3,5-triazin-2-yloxy group as a DG have not yet been exploited. We hypothesized that the use of 4,6-dimethoxy-1,3,5-triazin-2-yloxy as a DG should be viable for arene C−H oxidation, as the selective C−H activation of the aryl 2,4-dimethoxy-1,3,5-triazin-6-yl ethers could be realized through a six-membered metallacycle.[14]

RESULTS AND DISCUSSION

Next, we tested our hypothesis. Initially, 2-(2,4-dimethylphenoxy)-4,6-dimethoxy-1,3,5-triazine (**2a**), readily prepared from 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT) and 2,4-dimethylphenol,[15] was used as the model substrate to investigate Pd-catalyzed C−H acetoxylation of arenes. Pleasingly, in the presence of 5 mol % $Pd(OAc)_2$ and 2.0 equiv of $PhI(OAc)_2$, the expected ortho-acetoxylated product **3a** was obtained in $AcOH/Ac_2O$ (1/1) at 100 °C within 24 h in 68% isolated yield (Table 1). In the absence of either the Pd catalyst or the oxidant $PhI(OAc)_2$, an ortho-acetoxylated product was not detected (Table 1, entries 2 and 3). The use of other oxidants instead of PhI(OAc), such as $K_2S_2O_8$, $(NH_4)_2S_2O_8$, and benzoxyl peroxide, gave only a trace of the desired product **3a** (Table 1, entries 4−6). Moreover, by using other hypervalent iodine compounds such as [bis(trifluoroacetoxy)-iodo]benzene and bis(*tert*-butylcarbonyloxy)iodobenzene, the isolated yield of **3a** can reach 33−63% (Table 1, entries 7 and 8). When the reaction proceeded in air or at 150 °C, the yields of **3a** decreased to 32% and 65%, respectively (Table 1, entries 9 and 10). When 2.5 mol % of $RuCl_2(p\text{-cymene})_2$ was used as a metal catalyst, traces of product were formed in the presence of 20 mol % of $AgSbF_6$ and $PhI(OAc)_2$ (2 equiv) (Table 1, entry 11).

Table 1. Optimization of Reaction Conditions[a]

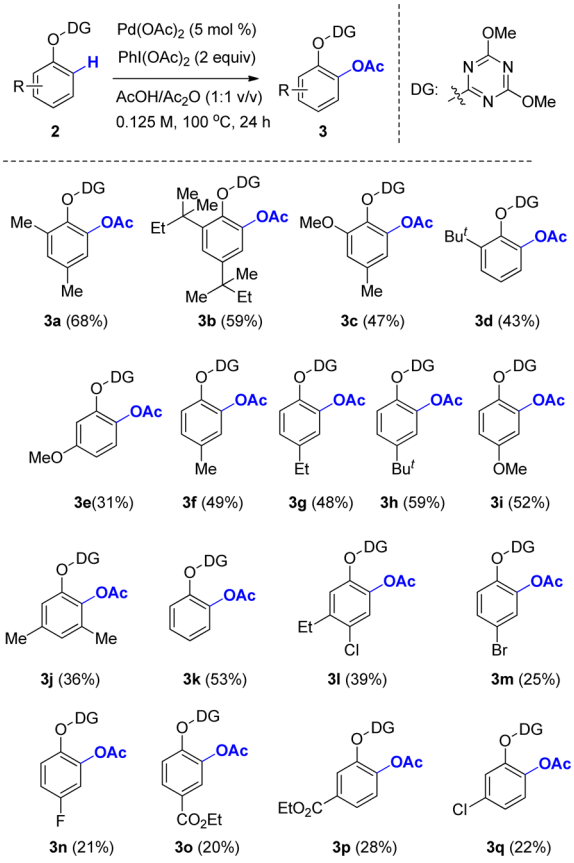


entry	change from the "standard conditions"	yield (%)[b]
1	none	68
2	without $Pd(OAc)_2$	0
3	no $PhI(OAc)_2$	0
4	$K_2S_2O_8$ (2 equiv) instead of $PhI(OAc)_2$	trace
5	$(NH_4)_2S_2O_8$ (2 equiv) instead of $PhI(OAc)_2$	trace
6	benzoxyl peroxide (2 equiv) instead of $PhI(OAc)_2$	trace
7	PIFA (2 equiv) instead of $PhI(OAc)_2$	33
8	$PhI(OPiv)_2$ (2 equiv) instead of $PhI(OAc)_2$	62
9	in air	32
10	150 °C instead of 100 °C	65
11	$RuCl_2(p\text{-cymene})_2$ (2.5 mol %), $AgSbF_6$ (20 mol %), DCE/AcOH (3/1 v/v), $PhI(OAc)_2$ (2 equiv), 100 °C, 24 h	trace

[a]Reaction conditions: all the reactions were run on a 0.5 mmol scale with 4 mL of solvents. [b]Isolated yield.

Having established the optimized reaction conditions, we set out to investigate the scope of this reaction. As shown in Scheme 2, in the presence of $Pd(OAc)_2$ (5 mol %), a broad range of 2-(aryloxy)-4,6-dimethoxy-1,3,5-triazines smoothly underwent C−H acetoxylation using $PhI(OAc)_2$ (2 equiv) as an oxidant in $AcOH/Ac_2O$ (1/1 v/v) at 100 °C within 24 h, providing the expected ortho-acetoxylated products in moderate to good yields. The efficiency of this transformation was related to the electron density and the position of substituents on the phenyl ring. Substrates bearing an electron-donating group afforded relatively good yields in comparison to those substrates with an electron-withdrawing group. For substrates bearing two electron-donating groups such as methyl, neopentyl, and methoxy at the ortho and para positions of the phenyl ring, the reactions gave the desired products **3a−c** in 47−68% yield. The substrate bearing one electron-donating group at the ortho position of phenyl groups smoothly underwent Pd-catalyzed C−H acetoxylation, providing the desired product **3d** in 43% yield. The yield decreased slightly in comparison to those substrates activated by two electron-donating groups. Steric hindrance influence was observed for meta-substituted phenoxytriazine which even bore electron-donating groups such as a methoxy group, and the reaction occurred at the less sterically hindered site, affording the product **3e** in a yield of 31%. Under similar conditions, Pd-catalyzed C−H acetoxylation of substrates bearing two ortho C−H bonds such as 2-(4-methylphenoxy)-4,6-dimethoxy-1,3,5-triazine, 2-(4-ethylphenoxy)-4,6-dimethoxy-1,3,5-triazine, 2-(4-

Scheme 2. Substrate Scope of Pd-Catalyzed C−H Acetoxylation of Arenes[a]



[a]Reaction conditions: 1.0 mmol of **2**, $Pd(OAc)_2$ (5 mol %), and 2.0 mmol of $PhI(OAc)_2$ in $AcOH/Ac_2O$ (8 mL) at 100 °C for 24 h. Isolated yields are given.

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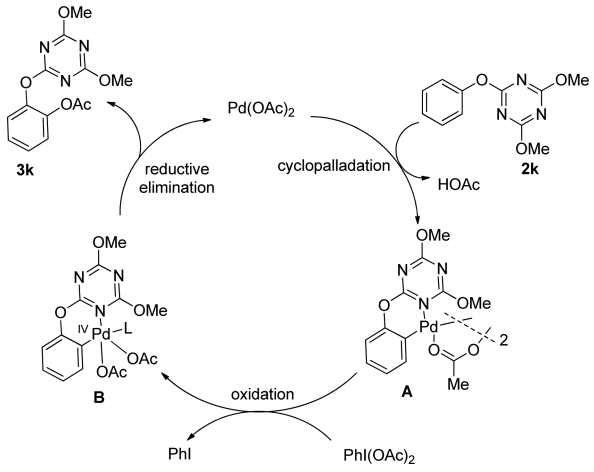
tert-butylphenoxy)-4,6-dimethoxy-1,3,5-triazine, and 2-(4-methoxyphenoxy)-4,6-dimethoxy-1,3,5-triazine gave the monoacetoxylated products **3f–i** in 48–59% yield. The acetoxylation of 2-(3,5-dimethylphenoxy)-4,6-dimethoxy-1,3,5-triazine gave the product **3j** in a yield of 36% due to the steric hindrance influence. Pd-catalyzed C–H acetoxylation of 2-(phenoxy)-4,6-dimethoxy-1,3,5-triazine without any substitute led to the expected product **3k** in a moderate yield. Under similar conditions, substrates bearing electron-withdrawing groups such as halogen and carboxylate could also undergo Pd-catalyzed C–H acetoxylation reactions, providing the desired products **3l–q** in 20–39% yields. In contrast to those substrates bearing electron-donating groups, the yields were comparatively low, probably due to the low electron density on the phenyl ring which would reduce the tendency of C–H oxidative addition. Additionally, it is worth mentioning that a variety of functional groups such as OMe (**3c**,**e**,**i**), Cl (**3l**,**q**), Br (**3m**), F (**3n**), and ester (**3o**,**p**) were tolerated well under the reaction conditions.

According to previous reports,[16] a plausible mechanism for the DMT-directed acyloxylation of C–H bonds is proposed. Initially, the reaction of palladium acetate with **2k** affords the six-membered palladacycle intermediate **A**. The subsequent oxidation of palladacycle intermediate **A** with $PhI(OAc)_2$ generates the intermediate **B**. Finally, the intermediate **B** undergoes reductive elimination, providing the product **3k** and regenerating the Pd(II) catalyst (Scheme 3).

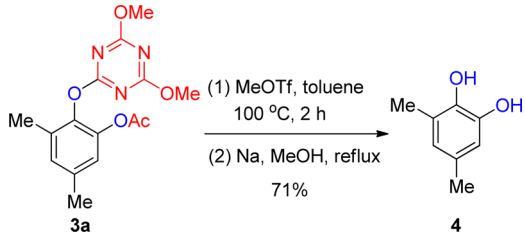
Scheme 3. Proposed Mechanism for the Pd-Catalyzed Acyloxylation



Next, we explored the further conversion of the 4,6-dimethoxy-1,3,5-triazin-2-yloxy group from the products after the development of the directed C–H acyloxylation of 2-(aryloxy)-4,6-dimethoxy-1,3,5-triazine. The 4,6-dimethoxy-1,3,5-triazin-2-yloxy group could be readily removed by the cleavage of the C(DMT)–O bond. Herein, the acyloxylated product **3a** was converted into substituted pyrocatechols **4** in 71% yield in two steps by the treatment of **3a** with MeOTf in dry toluene and subsequent addition to a refluxing Na/MeOH solution[6a] (Scheme 4).

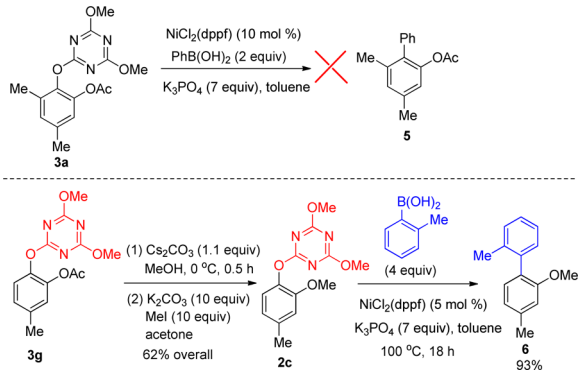
Another synthetic utility of the 4,6-dimethoxy-1,3,5-triazin-2-yloxy group as a removable/modifiable DG lies in the cleavage of the DG through C_{Ar}–O activation. The cleavage of the DG in **3a** using a direct nickel-catalyzed Suzuki–Miyaura coupling reaction with phenylboronic acid was tested first.[15b] However,

Scheme 4. Cleavage of the Directing Group



substituted pyrocatechol **4** instead of the expected coupling product **5** was afforded, suggesting that the hydrolysis of the acetoxy group and protection of the furnished phenol are required prior to the coupling step. The selective hydrolysis of the acetoxy group in **3g** with Cs_2CO_3 in methanol, followed by the protection of the generated 2-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)-5-methylphenol with MeI under basic conditions, gave the intermediate **2c** in 62% yield in two steps. It was found that compound **2c** underwent an efficient Suzuki–Miyaura cross-coupling with *o*-tolylboronic acid,[15b] providing the C_{Ar}–O bond cleavage product **6** in 93% yield (Scheme 5).

Scheme 5. Cleavage of Directing Group via C_{Ar}–O Activation



CONCLUSION

In conclusion, we have developed a new readily removable/modifiable directing group for regioselective acetoxylation of 2-(aryloxy)-4,6-dimethoxy-1,3,5-triazine. Using the developed method, a variety of *s*-triazine derivatives can be synthesized in moderate to good yields. In addition, the 4,6-dimethoxy-1,3,5-triazin-2-yloxy group proved to be a highly efficient DG, which can be removed to offer synthetically versatile pyrocatechols or act in a modifiable fashion to give the corresponding Suzuki–Miyaura coupling product.

EXPERIMENTAL SECTION

All reactions were carried out under a nitrogen atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with nitrogen prior to use. Yields refer to isolated yields of compounds estimated to be >95% pure as determined by ^{1}H NMR (25 °C). NMR spectra were recorded on solutions in deuterated chloroform ($CDCl_3$) with residual chloroform (δ 7.25 ppm for ^{1}H NMR and δ 77.0 ppm for ^{13}C NMR). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, br, broad. Column chromatographic purifications were performed using SiO_2 (200–300 mesh ASTM) from Branch of Qingdao Haiyang Chemical Co., Ltd., if not indicated otherwise.

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TP: Typical Procedure for the Direct Ortho Acetoxylation of Ar-O-DMT Ethers. A solution of Ar-−O-DMT ether (1 mmol), $Pd(OAc)_2$ (11 mg, 0.05 mmol), and $PhI(OAc)_2$ (644 mg, 2 mmol) in AcOH (4.0 mL) and Ac_2O (4.0 mL) was stirred in a 25 mL Schlenk tube at 100 °C for 24 h. The solvent was evaporated to dryness in vacuo. The residue was purified by column chromatography (petroleum ether/ethyl acetate) to give the desired product.

*2-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-3,5-dimethylphenyl Acetate (**3a**).* According to TP, 2-(2,4-dimethylphenoxy)-4,6-dimethoxy-1,3,5-triazine (261 mg, 1 mmol) gave the desired product **3a** (217 mg, 68%) as a white solid (mp 78.2−79.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.91 (s, 1 H), 6.83 (s, 1 H), 3.96 (s, 6 H), 2.30 (s, 3 H), 2.15 (s, 3 H), 2.12 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.9, 172.8, 168.5, 141.9, 139.6, 136.2, 131.5, 128.9, 121.4, 55.5, 20.9, 20.7, 16.1. IR (KBr): 3129, 1766, 1568, 1400, 1357, 1216, 1122, 816, 693 cm^{-1}. HRMS ($C_{15}H_{17}N_3O_5$ + H): calcd, 320.1246; found, 320.1246 (M^+ + H).

*2-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-3,5-dineopentylphenyl Acetate (**3b**).* According to TP, 2-(2,4-dineopentylphenoxy)-4,6-dimethoxy-1,3,5-triazine (373 mg, 1 mmol) gave the desired product **3b** (256 mg, 59%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.12 (d, J = 2.2 Hz, 1 H), 6.98 (d, J = 2.2 Hz, 1 H), 3.90 (s, 6 H), 1.97 (s, 3 H), 1.59 (dt, J = 14.6 Hz, 7.3 Hz, 4 H), 1.28 (s, 6 H), 1.25 (s, 6 H), 1.59 (ddd, J = 16.0 Hz, 7.5 Hz, 7.3 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.8, 173.0, 167.9, 146.6, 142.2, 139.8, 139.6, 123.1, 118.9, 55.4, 38.8, 37.9, 36.9, 34.6, 28.3, 28.2, 20.6, 9.3, 8.9. IR (KBr): 3129, 1768, 1596, 1558, 1400, 1367, 1230, 1200, 1137, 977, 816 cm^{-1}. HRMS ($C_{23}H_{33}N_3O_5$ + H): calcd, 432.2498; found, 432.2502 (M^+ + H).

*2-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-3-methoxy-5-methylphenyl Acetate (**3c**).* According to TP, 2,4-dimethoxy-6-(2-methoxy-4-methylphenoxy)-1,3,5-triazine (275 mg, 1 mmol) gave the desired product **3c** (158 mg, 47%) as a pale yellow solid (mp 124.5−125.7 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.63 (d, J = 1.2 Hz, 1 H), 6.58 (d, J = 1.2 Hz, 1 H), 3.93 (s, 6 H), 3.73 (s, 3 H), 2.31 (s, 3 H), 2.14 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.7, 172.8, 168.3, 151.8, 142.8, 136.4, 130.5, 115.6, 110.7, 56.1, 55.3, 21.5, 20.6. IR (KBr): 3130, 1766, 1585, 1400, 1369, 1216, 1192, 1101, 819 cm^{-1}. HRMS ($C_{15}H_{17}N_3O_6$ + H): calcd, 336.1196; found, 336.1192 (M^+ + H).

*3-(tert-Butyl)-2-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)phenyl Acetate (**3d**).* According to TP, 2-(2-(*tert*-butyl)phenoxy)-4,6-dimethoxy-1,3,5-triazine (289 mg, 1 mmol) gave the desired product **3d** (149 mg, 43%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.32−7.28 (m, 1 H), 7.21 (t, J = 8.1 Hz, 1 H), 7.10 (dd, J = 7.9 Hz, 1.6 Hz, 1 H), 3.96 (s, 6 H), 2.03 (s, 3 H), 1.34 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.7, 172.9, 167.9, 142.9, 142.7, 142.0, 125.6, 124.2, 121.2, 55.4, 34.8, 30.2, 20.5. IR (KBr): 3457, 1775, 1587, 1560, 1469, 1357, 1203, 1122, 820 cm^{-1}. HRMS ($C_{17}H_{21}N_3O_5$ + H): calcd, 348.1559; found, 348.1559 (M^+ + H).

*2-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-4-methoxyphenyl Acetate (**3e**).* According to TP, 2,4-dimethoxy-6-(3-methoxyphenoxy)-1,3,5-triazine (526 mg, 2 mmol) gave the desired product **3e** (199 mg, 31%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.12−7.07 (m, 1 H), 6.80−6.75 (m, 2 H), 3.96 (s, 6 H), 3.76 (s, 3 H), 2.11 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.8, 172.8, 168.5, 157.7, 143.5, 135.8, 123.8, 111.9, 108.8, 55.7, 55.5, 20.5. IR (KBr): 2952, 1768, 1588, 1568, 1505, 1471, 1362, 1202, 1124, 1031, 819 cm^{-1}. HRMS ($C_{14}H_{15}N_3O_6$ + H): calcd, 322.1039; found, 322.1037 (M^+ + H).

*2-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-5-methylphenyl Acetate (**3f**).* According to TP, 2,4-dimethoxy-6-(p-tolyloxy)-1,3,5-triazine (247 mg, 1 mmol) gave the desired product **3f** (151 mg, 49%) as a white solid (mp 81.5−82.3 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.14−7.10 (m, 1 H), 7.07−7.00 (m, 2 H), 3.96 (s, 6 H), 2.35 (s, 3 H), 2.15 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.8, 172.9, 168.4, 141.7, 140.7, 136.9, 127.2, 124.1, 122.7, 55.5, 20.9, 20.7. IR (KBr): 3129, 1767, 1586, 1552, 1400, 1216, 1136, 1022, 820 cm^{-1}. HRMS ($C_{14}H_{15}N_3O_5$ + H): calcd, 306.1090; found, 306.1092 (M^+ + H).

*2-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-5-ethylphenyl Acetate (**3g**).* According to TP, 2-(4-ethylphenoxy)-4,6-dimethoxy-1,3,5-triazine (261 mg, 1 mmol) gave the desired product **3g** (152 mg, 48%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.14−7.10 (m, 1 H), 7.06−6.99 (m, 2 H), 3.93 (s, 6 H), 2.62 (q, J = 7.6 Hz, 2 H), 2.12 (s, 3 H), 1.210 (t, J = 7.6 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.8, 172.9, 168.3, 143.0, 141.8, 140.8, 125.9, 122.8, 122.7, 55.5, 28.2, 20.7, 15.0. IR (KBr): 3248, 2965, 1775, 1567, 1506, 1470, 1362, 1266, 1212, 1189, 1129, 935, 820 cm^{-1}. HRMS ($C_{15}H_{17}N_3O_5$ + H): calcd, 320.1246; found, 320.1248 (M^+ + H).

*5-(tert-Butyl)-2-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)phenyl Acetate (**3h**).* According to TP, 2-(4-(*tert*-butyl)phenoxy)-4,6-dimethoxy-1,3,5-triazine (289 mg, 1 mmol) gave the desired product **3h** (205 mg, 59%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.30−7.26 (m, 1 H), 7.21−7.17 (m, 2 H), 3.99 (s, 6 H), 2.18 (s, 3 H), 1.32 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.7, 172.8, 168.2, 149.9, 141.4, 140.5, 123.4, 122.3, 120.5, 55.4, 34.5, 31.2, 20.6. IR (KBr): 3129, 1775, 1562, 1400, 1208, 1180, 817 cm^{-1}. HRMS ($C_{17}H_{21}N_3O_5$ + H): calcd, 348.1559; found, 348.1562 (M^+ + H).

*2-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-5-methoxyphenyl Acetate (**3i**).* According to TP, 2,4-dimethoxy-6-(4-methoxyphenoxy)-1,3,5-triazine (263 mg, 1 mmol) gave the desired product **3i** (158 mg, 52%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.16 (d, J = 8.8 Hz, 1 H), 6.82−6.75 (m, 2 H), 3.98 (s, 6 H), 3.80 (s, 3 H), 2.17 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.8, 173.2, 168.1, 157.7, 142.6, 136.7, 123.4, 111.8, 109.2, 55.7, 55.5, 20.7. IR (KBr): 3373, 2952, 1774, 1571, 1505, 1470, 1364, 1210, 1124, 819 cm^{-1}. HRMS ($C_{14}H_{15}N_3O_6$ + H): calcd, 322.1039; found, 322.1037 (M^+ + H).

*2-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-4,6-dimethylphenyl Acetate (**3j**).* According to TP, 2-(3,5-dimethylphenoxy)-4,6-dimethoxy-1,3,5-triazine (261 mg, 1 mmol) gave the desired product **3j** (114 mg, 36%) as a white solid (mp 101.5−102.3 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.93 (s, 1 H), 6.88 (s, 1 H), 3.98 (s, 6 H), 2.30 (s, 3 H), 2.18 (s, 3 H), 2.15 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.8, 173.0, 168.2, 143.1, 138.7, 136.2, 131.9, 129.2, 121.0, 55.5, 20.9, 20.3, 16.2. IR (KBr): 3130, 1759, 1571, 1400, 1360, 1315, 1189, 1145, 901, 853, 819 cm^{-1}. HRMS ($C_{15}H_{17}N_3O_5$ + H): calcd, 320.1246; found, 320.1248 (M^+ + H).

*2-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)phenyl Acetate (**3k**).* According to TP, 2,4-dimethoxy-6-phenoxy-1,3,5-triazine (233 mg, 1 mmol) gave the desired product **3k** (154 mg, 53%) as a white solid (mp 49.7−51.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.31−7.21 (m, 4 H), 3.98 (s, 6 H), 2.18 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.8, 172.8, 168.2, 143.1, 142.2, 126.7, 126.5, 123.6, 123.2, 55.5, 20.6. IR (KBr): 3129, 1772, 1573, 1400, 1247, 1208, 1120, 938, 911, 820 cm^{-1}. HRMS ($C_{13}H_{13}N_3O_5$ + H): calcd, 292.0933; found, 292.0934 (M^+ + H).

*5-Chloro-2-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)-4-ethylphenyl Acetate (**3l**).* According to TP, 2-(4-chloro-3-ethylphenoxy)-4,6-dimethoxy-1,3,5-triazine (296 mg, 1 mmol) gave the desired product **3l** (138 mg, 39%) as a pale yellow solid (mp 49.1−50.4 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.22 (s, 1 H), 7.11 (s, 1 H), 3.96 (s, 6 H), 2.71 (q, J = 7.5 Hz, 2 H), 2.13 (s, 3 H), 1.21 (t, J = 7.5 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.8, 172.7, 167.9, 141.7, 140.3, 140.2, 130.9, 124.4, 123.3, 55.6, 26.3, 20.6, 13.6. IR (KBr): 3129, 1777, 1591, 1400, 1200, 1153, 1020, 901, 813 cm^{-1}. HRMS ($C_{15}H_{16}ClN_3O_5$ + H): calcd, 354.0857; found, 354.0855 (M^+ + H).

*5-Bromo-2-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)phenyl Acetate (**3m**).* According to TP, 2-(4-bromophenoxy)-4,6-dimethoxy-1,3,5-triazine (312 mg, 1 mmol) gave the desired product **3m** (94 mg, 25%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.40−7.36 (m, 2 H), 7.15−7.09 (m, 1 H), 3.97 (s, 6 H), 2.15 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.8, 172.6, 167.7, 142.8, 142.4, 129.6, 127.0, 124.5, 118.9, 55.6, 20.6. IR (KBr): 3105, 2952, 1780, 1594, 1575, 1471, 1362, 1265, 1201, 1123, 1011, 921, 819 cm^{-1}. HRMS ($C_{13}H_{12}BrN_3O_5$ + H): calcd, 370.0039; found, 370.0040 (M^+ + H).

*2-((4,6-Dimethoxy-1,3,5-triazin-2-yl)oxy)-5-fluorophenyl Acetate (**3n**).* According to TP, 2-(4-fluorophenoxy)-4,6-dimethoxy-1,3,5-triazine (251 mg, 1 mmol) gave the desired product **3n** (65 mg,

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21%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.24−7.17 (m, 1 H), 7.05−6.95 (m, 2 H), 3.97 (s, 6 H), 2.16 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.8, 172.8, 167.8, 159.9 (d, J = 247 Hz), 142.8 (d, J = 11 Hz), 139.3 (d, J = 4 Hz), 123.8 (d, J = 10 Hz), 113.3 (d, J = 23 Hz), 111.5 (d, J = 26 Hz), 55.6, 20.7. IR (KBr): 3467, 2922, 1776, 1590, 1561, 1501, 1469, 1358, 1250, 1205, 1013, 890, 818 cm^{-1}. HRMS ($C_{13}H_{12}FN_3O_5$ + H): calcd, 310.0839; found, 310.0838 (M^+ + H).

*Ethyl 3-Acetoxy-4-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)-benzoate (**3o**).* According to TP, ethyl 4-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)benzoate (305 mg, 1 mmol) gave the desired product **3o** (74 mg, 20%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.97 (dd, J = 8.6 Hz, 1.9 Hz, 1 H), 7.89 (d, J = 1.9 Hz, 1 H), 7.32 (d, J = 8.6 Hz, 1 H), 4.36 (q, J = 7.3 Hz, 2 H), 3.96 (s, 6 H), 2.18 (s, 3 H), 1.37 (t, J = 7.3 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.8, 172.4, 168.0, 165.0, 146.7, 142.1, 129.2, 128.1, 125.2, 123.3, 61.4, 55.6, 20.6, 14.3. IR (KBr): 3347, 3148, 1775, 1728, 1590, 1369, 1224, 820 cm^{-1}. HRMS ($C_{16}H_{17}N_3O_7$ + H): calcd, 364.1145; found, 364.1141 (M^+ + H).

*Ethyl 4-Acetoxy-3-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)-benzoate (**3p**).* According to TP, ethyl 3-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)benzoate (305 mg, 1 mmol) gave the desired product **3p** (101 mg, 28%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.99−7.93 (m, 2 H), 7.31 (d, J = 8.6 Hz, 1 H), 4.36 (q, J = 7.1 Hz, 2 H), 3.97 (s, 6 H), 2.18 (s, 3 H), 1.37 (t, J = 7.1 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.9, 172.7, 167.7, 165.0, 146.0, 142.9, 129.1, 128.1, 124.8, 123.6, 61.4, 55.6, 20.7, 14.3. IR (KBr): 3540, 2957, 1774, 1721, 1589, 1562, 1472, 1364, 1287, 1205, 1173, 1123, 1017, 903, 820 cm^{-1}. HRMS ($C_{16}H_{17}N_3O_7$ + H): calcd, 364.1145; found, 364.1144 (M^+ + H).

*4-Chloro-2-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)phenyl Acetate (**3q**).* According to TP, 2-(3-chlorophenoxy)-4,6-dimethoxy-1,3,5-triazine (268 mg, 1 mmol gave the desired product **3q** (72 mg, 22%) as a white solid (mp 93.7−95.0 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.31−7.24 (m, 2 H), 7.20−7.16 (m, 1 H), 4.00 (s, 6 H), 2.17 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.8, 172.5, 167.9, 143.4, 141.0, 131.3, 126.8, 124.5, 123.7, 55.6, 20.6. IR (KBr): 3129, 1756, 1401, 1368, 1216, 1178, 1015, 892, 818 cm^{-1}. HRMS ($C_{13}H_{12}ClN_3O_5$ + H): calcd, 326.0544; found, 326.0539 (M^+ + H).

3,5-Dimethylbenzene-1,2-diol (4). To a solution of 2-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)-3,5-dimethylphenyl acetate (**3a**; 160 mg, 0.50 mmol) in PhMe (20 mL) under N_2 was added MeOTf (100 μL, 0.88 mmol). The reaction mixture was stirred under N_2 at 100 °C for 2 h. The reaction mixture was cooled to ambient temperature. Evaporation of the solvent in vacuo yielded a solid. The solid was dissolved in dry methanol (5.0 mL) and was added under N_2 to a solution of Na (294 mg, 12 mmol) in dry methanol (15 mL). The reaction mixture was heated at 80 °C for 15 min. The reaction mixture was cooled to ambient temperature, and the solvent was evaporated in vacuo. H_2O (75 mL) was added, and the resulting mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over $MgSO_4$. After filtration and evaporation of the solvents in vacuo, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to yield **4** (49 mg, 71%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.53 (s, 1 H), 6.51 (s, 1 H), 4.85 (br s, 2 H), 2.21 (s, 3 H), 2.20 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 142.9, 139.6, 129.9, 124.2, 123.3, 113.7, 20.6, 15.5. IR (KBr): 3508, 2935, 1622, 1503, 1308, 1039, 848 cm^{-1}. HRMS ($C_8H_{10}O_2$ + H): calcd, 139.0759; found, 139.0753 (M^+ + H).

2,4-Dimethoxy-6-(2-methoxy-4-methylphenoxy)-1,3,5-triazine (2c). To a solution of 2-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)-5-dimethylphenyl acetate (**3f**; 610 mg, 2 mmol) in MeOH (30 mL) was added Cs_2CO_3 (717 mg, 2.2 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 0.5 h. Water (20 mL) was added, and the resulting mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over $MgSO_4$. Filtration and evaporation of the solvents *in vacuo* gave 2-((4,6-dimethoxy-1,3,5-triazin-2-yl)oxy)-5-methylphenol (419 mg), which was used directly in the next step without further purification. To a solution of this crude intermediate (419 mg, 1.6 mmol) in acetone (25 mL) was added K_2CO_3 (2.2 g, 16 mmol) and MeI (2.3 g, 16 mmol) at room temperature. The reaction mixture was stirred at room temperature for 20 h. Water (20 mL) was added, and the resulting mixture was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over $MgSO_4$. After filtration and evaporation of the solvents in vacuo, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to yield **2c** (343 mg, 62%) as a white solid (mp 130.2−131.5 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.01−6.95 (m, 1 H), 6.79−6.70 (m, 2 H), 3.95 (s, 6 H), 3.74 (s, 3 H), 2.33 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 173.8, 173.4, 150.7, 138.6, 136.9, 121.9, 121.2, 113.5, 55.8, 55.3, 21.4. IR (KBr): 3130, 1571, 1510, 1468, 1400, 1376, 1210, 1154, 1124, 1029, 932, 817 cm^{-1}. HRMS ($C_{13}H_{15}N_3O_4$ + H): calcd, 278.1141; found, 278.1138 (M^+ + H).

2-Methoxy-2′,4-dimethyl-1,1′-biphenyl (6). In a Schlenk tube were placed in turn 2,4-dimethoxy-6-(2-methoxy-4-methylphenoxy)-1,3,5-triazine (**2c**; 277 mg, 1.0 mmol), 2-methylboronic acid (540 mg, 4.0 mmol), $NiCl_2$(dppf) (35 mg, 0.05 mmol), and K_3PO_4 (1,5 g, 7.0 mmol) under an N_2 atmosphere. Toluene (7 mL) was injected by syringe. The mixture was stirred in a preheated oil bath (110 °C) for 24 h. The reaction mixture was cooled to room temperature. Water (20 mL) was added, and the resulting mixture was extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over $MgSO_4$. After filtration and evaporation of the solvents in vacuo, the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to yield **6** (198 mg, 93%) as a colorless viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49−7.39 (m, 4 H), 7.27 (d, J = 7.6 Hz, 1 H), 7.05 (d, J = 7.6 Hz, 1 H), 7.00 (s, 1 H), 3.94 (s, 3 H), 2.64 (s, 3 H), 2.39 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 156.4, 138.6, 138.4, 136.8, 130.7, 130.1, 129.5, 127.9, 127.0, 125.3, 121.0, 111.6, 55.2, 21.5, 19.9. IR (KBr): 3129, 1613, 1463, 1402, 1283, 1271, 1165, 1134, 1041, 923, 873, 816, 764, 726 cm^{-1}. HRMS ($C_{15}H_{16}O$ + H): calcd, 213.1279; found, 213.1275 (M^+ + H).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00314.

NMR spectra and HRMS data of compounds (PDF)

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Notes

The authors declare no competing financial interest.

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