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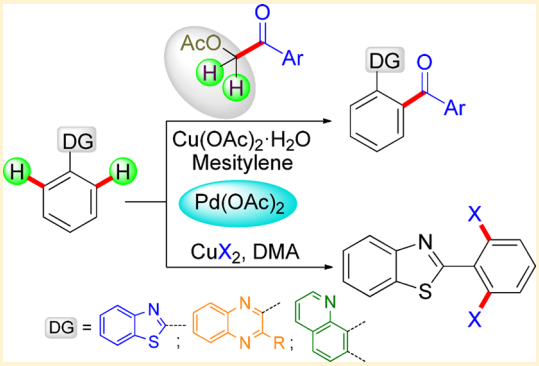
Peroxide-Free Pd(II)-Catalyzed Ortho Aroylation and Ortho Halogenation of Directing Arenes

Sourav Kumar Santra, Arghya Banerjee, Prakash Ranjan Mohanta, and Bhisma K. Patel*

Department of Chemistry, Indian Institute of Technology, Guwahati 781 039, Assam, India

Supporting Information

ABSTRACT: A Pd(II)-catalyzed peroxide-free ortho aroylation of directing arenes has been developed via cross dehydrogenative coupling (CDC) in the presence of the terminal oxidant $Cu(OAc)_2·H_2O$. Ortho aroylation of directing arenes proceeds via decarbonylation of the in situ generated phenyl glyoxal, which is obtained from 2-acetoxyacetophenone in the presence of the oxidant $Cu(OAc)_2·H_2O$. However, changing the oxidant to CuX_2 (X = Cl, Br) provided exclusive di-ortho-halogenated 2-arylbenzothiazoles. During the halogenation, CuX_2 served the dual role of a halogen source as well as a co-oxidant.



INTRODUCTION

Selective functionalization of ubiquitous C−H bonds has been a longstanding goal of the synthetic organic community, as it avoids prefunctionalization of substrates and hence minimizes the steps and maximizes atom economy.[1] Functionalization of sp^3 C−H bonds is trickier in comparison to that of sp^2 C−H bonds, as it involves higher bond dissociation energy. A combination of transition metals/oxidants facilitates the functionalization of sp^3 C−H bonds, which afford C−C,[2] C−X,[3] C−O,[4] and C−N[5] bonds. However, among these transformations, C−C bond formation, especially installation of a carbonyl functionality into the aryl systems via C−H bond cleavage, is very attractive. Currently, ortho aroylation (ketone synthesis) is achieved via two most elegant approaches: viz., directing group assisted C−H functionalization and cross dehydrogenative coupling (CDC). A combination of both these approaches directly installs an aroyl functionality at the ortho site of a directing arene. To date various aroyl surrogates, viz. aldehyde,[6] alkene,[7] alkyne,[7] benzil,[8] α-keto acid,[9] benzyl alcohol,[10] benzylamine,[11] and alkylbenzene,[12] have been employed for ortho aroylation. However, few of these processes involve the cleavage of an inert sp^3 C−H bond and hence require a stronger peroxide oxidant for the bond cleavage.[10−12] Peroxides are highly reactive, explosive, flammable, and toxic and are also an exceptionally corrosive chemical to skin and mucous membranes and cause respiratory distress. A peroxide-free Pd(II)-catalyzed ortho aroylation of directing arenes has been reported only once from aldehydes via direct sp^2 C−H bond cleavage using air as the oxidant (Scheme 1).[13]

Depending upon the quantity of $Pd(OAc)_2$ used, phenylglyoxal can undergo either monodecarbonylation to benzaldehyde or double decarbonylation to benzene (Scheme 1).[14] A careful retrosynthetic analysis of phenylglyoxal shows that it can also be obtained from 1-hydroxy-2-oxo-2-phenylethyl acetate (**A**). Further, **A** can be obtained from 2-acetoxyacetophenone (**a**) via hydroxylation at the sp^3 C−H bond adjacent to both acetate oxygen atom and the keto group. Now a query arises whether the in situ generated phenylglyoxal obtained from 2-acetoxyacetophenone (**a**) would generate an aroyl (ArCO−) moiety via single decarbonylation[14] or to a aryl (Ar−) unit via double decarbonylation.[14] Thus, a substrate directed ortho aroylation[13] or an ortho arylation in the presence of a Pd(II)/Cu(II) catalytic combination could be achieved (Scheme 1).

Scheme 1. Pd(II)-Catalyzed *o*-Aroylation and Decarbonylation Strategy

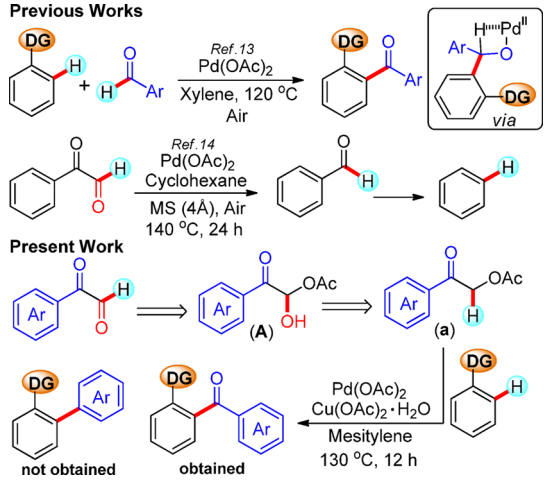


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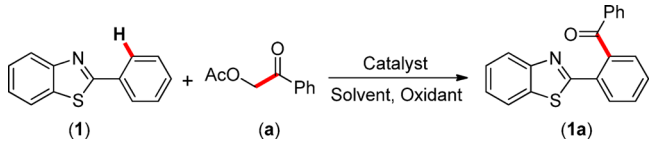
Table 1. Optimization of the Reaction Conditions for Ortho Aroylation[a]



(1) (a) (1a)

entry	catalyst (amt (mol %))	solvent	oxidant	additive	yield (%)[b]
1	$Pd(OAc)_2$ (5.0)	*p*-xylene	$Cu(OAc)_2{\cdot}H_2O$		21
2	$Pd(OAc)_2$ (5.0)	DMF	$Cu(OAc)_2{\cdot}H_2O$		trace
3	$Pd(OAc)_2$ (5.0)	DMSO	$Cu(OAc)_2{\cdot}H_2O$		0
4	$Pd(OAc)_2$ (5.0)	DCE	$Cu(OAc)_2{\cdot}H_2O$		0
5	$Pd(OAc)_2$ (5.0)	cyclohexane	$Cu(OAc)_2{\cdot}H_2O$		0
6	$Pd(OAc)_2$ (5.0)	toluene	$Cu(OAc)_2{\cdot}H_2O$		0
7	$Pd(OAc)_2$ (5.0)	mesitylene	$Cu(OAc)_2{\cdot}H_2O$		32
8	$Pd(OAc)_2$ (10.0)	mesitylene	$Cu(OAc)_2{\cdot}H_2O$		47
9	$Pd(OAc)_2$ (15.0)	mesitylene	$Cu(OAc)_2{\cdot}H_2O$		51
10	$Pd(OAc)_2$ (10.0)	mesitylene	$CuCl_2$		0
11	$Pd(OAc)_2$ (10.0)	mesitylene	$CuBr_2$		0
12	$Pd(OAc)_2$ (10.0)	mesitylene	$Cu(OAc)_2$		00
13	$Pd(OAc)_2$ (10.0)	mesitylene	$Cu(OAc)_2{\cdot}xH_2O$		40
14	$Pd(TFA)_2$ (10.0)	mesitylene	$Cu(OAc)_2{\cdot}H_2O$		42
15	$PdCl_2$ (10.0)	mesitylene	$Cu(OAc)_2{\cdot}H_2O$		34
16	$Pd(PPh_3)_2Cl_2$ (10.0)	mesitylene	$Cu(OAc)_2{\cdot}H_2O$		trace
17	$Pd(MeCN)_2Cl_2$ (10.0)	mesitylene	$Cu(OAc)_2{\cdot}H_2O$		trace
18	$Pd(OAc)_2$ (10.0)	mesitylene	$Cu(OAc)_2{\cdot}H_2O$	PTSA	49[c]
19	$Pd(OAc)_2$ (10.0)	mesitylene	$Cu(OAc)_2{\cdot}H_2O$	AcOH	52[c]
20	$Pd(OAc)_2$ (10.0)	mesitylene	$Cu(OAc)_2{\cdot}H_2O$	PivOH	31[c]
21	**$Pd(OAc)_2$ (10.0)**	**mesitylene**	**$Cu(OAc)_2{\cdot}H_2O$**	**AcOH**	**58[d]**
22	$Pd(OAc)_2$ (10.0)	mesitylene	$Cu(OAc)_2{\cdot}H_2O$	AcOH	31[d,e]
23	$Pd(OAc)_2$ (10.0)	mesitylene	$Cu(OAc)_2{\cdot}H_2O$	AcOH	28[d,f]

[a]Reaction conditions: 2-phenylbenzothiazole (**1**; 0.25 mmol), **a** (0.33 mmol), Cu salt (1.5 equiv), mesitylene (1 mL), 130 °C. [b]Isolated yield after 12 h. [c]Acid additives (0.5 mmol). [d]$Cu(OAc)_2{\cdot}H_2O$ (2.0 equiv). [e]Oxone (1.0 equiv). [f]$K_2S_2O_8$ (1.0 equiv).

RESULTS AND DISCUSSION

To see which of the above possibilities (aroylation or arylation) works initially, 2-phenylbenzothiazole (**1**), a pharmacophorically privileged motif, was treated with 2-acetoxyacetophenone (**a**; 1.3 equiv) in the presence of $Pd(OAc)_2$ (5 mol %) and $Cu(OAc)_2{\cdot}H_2O$ (1.5 equiv) in *p*-xylene at 130 °C. From this reaction the ortho-aroylated product **1a** was obtained but only in a minor quantity (21%) without any trace of ortho-arylated product (Table 1, entry 1). We looked forward to improving this ortho-aroylation process by changing other reaction parameters such as solvent, catalyst, oxidants, and their quantities. Polar aprotic solvents such as DMF and DMSO and nonpolar solvents such as DCE, cyclohexane, and toluene all failed to give the desired ortho-aroylated product **1a** (Table 1, entries 2−6). However, mesitylene as solvent provided a 32% yield of the ortho-aroylated product **1a** under otherwise identical reaction conditions (Table 1, entry 7). Significant improvement in the yield (47%) was observed when the catalyst loading was increased to 10 mol % (Table 1, entry 8). However, a further increase in the catalyst loading to 15 mol % did not affect the product yield (51%) significantly (Table 1, entry 9). Changing the oxidant from $Cu(OAc)_2{\cdot}H_2O$ to $CuCl_2$, $CuBr_2$, and anhydrous $Cu(OAc)_2$ gave no desired ortho-aroylated product (Table 1, entries 10−12), whereas $Cu(OAc)_2{\cdot}xH_2O$ provided 40% of ortho-aroylated product **1a** (Table 1, entry 13). Other Pd catalysts such as $Pd(TFA)_2$ and $PdCl_2$ gave lower yields, while $Pd(PPh_3)_2Cl_2$ and $Pd(MeCN)_2Cl_2$ afforded only a trace amount of the desired ortho-aroylated product **1a** in the presence of $Cu(OAc)_2{\cdot}H_2O$ oxidant (Table 1, entries 14−17). To check the effect, if any, of acid additives in the reaction, acids such as *p*-toluenesulfonic acid (PTSA), acetic acid (AcOH), and pivalic acid (PivOH) were tested during the reaction (Table 1, entries 18−20). After the reaction was screened with these additives, it was found that the application of 2.0 equiv of AcOH under otherwise identical conditions enhanced the yield of the desired ortho-aroylated product **1a** up to 52% (Table 1, entry 19). Further, increasing the oxidant $Cu(OAc)_2{\cdot}H_2O$ quantity from 1.5 to 2.0 equiv provided the ortho-aroylated product **1a** in an improved yield of 58% (Table 1, entry 21). In order to further increase the yield of the product **1a**, other co-oxidants such as oxone and $K_2S_2O_8$ were tested with $Cu(OAc)_2{\cdot}H_2O$, but both were found to be inferior (Table 1, entries 22 and 23).

It may be noted that most of the ortho-aroylation processes proceed in the presence of peroxide oxidants such as TBHP[6−8,10−12] and persulfate.[9] Thus, this peroxide-free ortho-aroylation strategy was further pursued using 2-phenylbenzothiazole (**1**) and a variety of 2-acetoxyacetophenones. 2-Acetoxyacetophenones having activated and deactivated phenyl rings efficiently coupled with 2-phenylbenzothiazole (**1**) to give the desired ortho-aroylated products **1a−g** in yields ranging from 46 to 66%. 2-Oxo-2-phenylethyl acetate containing moderately electron withdrawing groups such as *p*-Cl (**b**), *m*-Cl (**c**) and *p*-F (**d**) afforded ortho-aroylated products **1b** (60%), **1c** (59%), and **1d** (61%), respectively, in moderate yields. However, this peroxide-free strategy was less effective for electron rich 2-oxo-2-arylethyl acetate possesing *p*-Me (**e**), *m*-Me (**f**), and *p*-OMe (**g**), giving the products **1e** (53%), **1f**

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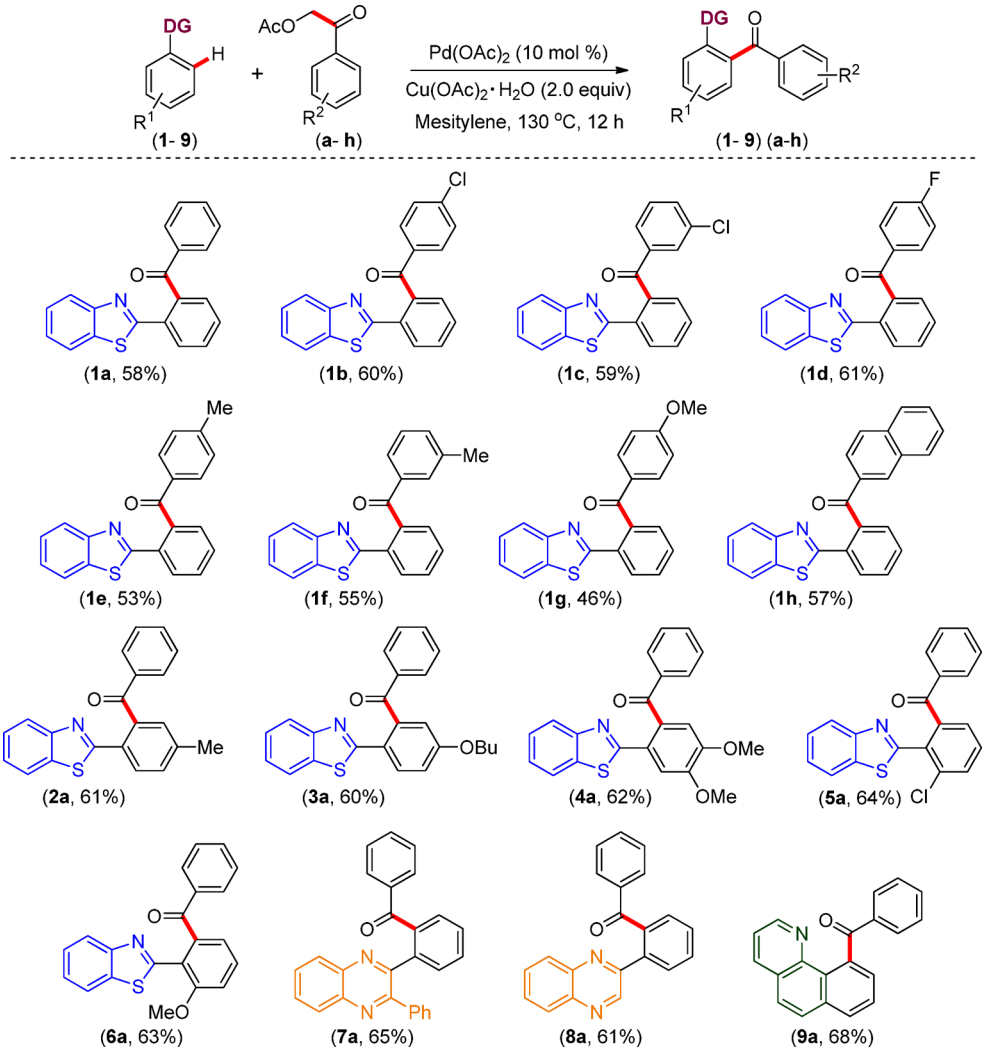
Scheme 2. Pd-Catalyzed Ortho Aroylation of Directing Arenes[a,b]



[a]Reaction conditions: **1**–**9** (0.25 mmol), **a** (0.33 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.5 mmol), and acetic acid (0.5 mmol) at 130 °C for 12 h. [b]Isolated yield.

(55%), and **1g** (46%), respectively (Scheme 2). Then this selective ortho-aroylation strategy was further extended to other substituted 2-phenylbenzothiazoles with 2-oxo-2-phenylethyl acetate (**a**) as the aroyl source. Substituted 2-phenylbenzothiazoles containing electron-donating groups such as *p*-Me (**2**), *p*-OBu (**3**), and 3,4-di-OMe (**4**) in their aryl rings gave decent yields of their desired aroylated products **2a** (61%), **3a** (60%), and **4a** (62%) when reacted with 2-oxo-2-phenylethyl acetate (**a**) under the optimized reaction conditions. Ortho-substituted 2-phenylbenzothiazoles such as *o*-Cl (**5**) and *o*-OMe (**6**) provided better yields of their desired ortho-aroylated products **5a** (64%) and **6a** (63%), respectively (Scheme 2).

To verify whether this sp^3 C–H functionalization strategy for ortho aroylation could be equally applicable to other directing arenes, 2,3-diphenylquinoxaline (**7**), 2-phenylquinoxaline (**8**), and benzo[*h*]quinoline (**9**) were treated with 2-oxo-2-phenylethyl acetate (**a**) under the above optimized conditions. All three directing arenes **7**–**9** efficiently coupled with **a**, affording their ortho-aroylated products **7a**–**9a** in 65%, 61%, and 68% yields, respectively (Scheme 2).

Recently, we have reported a Pd(II)/$CuBr_2$ catalyzed keto α-C_{sp^3}–H benzoxylation of *N*,*N*-dialkylamides directed by an *o*-hydroxy group; a simultaneous ring bromination took place at the ortho or para position with respect to the –OH group of salicylaldehyde and 2-hydroxyacetophenones.[15] Since Pd(II)/$CuBr_2$ combinations provided ring bromination of activated aromatic rings, this strategy may be applied to substrate-directed ortho bromination. Aryl halides are important synthetic intermediates for nucleophilic substitution reactions as well as synthetic precursors for the synthesis of various organometallic reagents.[16] In addition to these applications, aryl halides have been widely used in transition-metal-catalyzed cross-coupling reactions such as Suzuki, Heck, and Negishi.[17] Along with *N*-halosuccinimides, other halogen sources such as LiX, CuX_2, CaX_2, and DDQ have also been used in metal-catalyzed halogenation reactions.[18]

To verify whether this Pd(II)/$CuBr_2$ combination could provide ortho bromination or not, 2-phenylbenzothiazole (**1**; 1 equiv) was treated with $CuBr_2$ (1.2 equiv) in the presence of $Pd(OAc)_2$ (5 mol %) in DMA (1.0 mL) at 120 °C. Surprisingly, the exclusive ortho-dibrominated product **1a′** was obtained in 57% yield instead of the ortho-monobrominated product along with the unreacted starting material. This observation is consistent with our previous report on ortho halogenation of benzothiazoles using *N*-halosuccinamides.[19] From the energy calculations[19] and literature reports[20] it is

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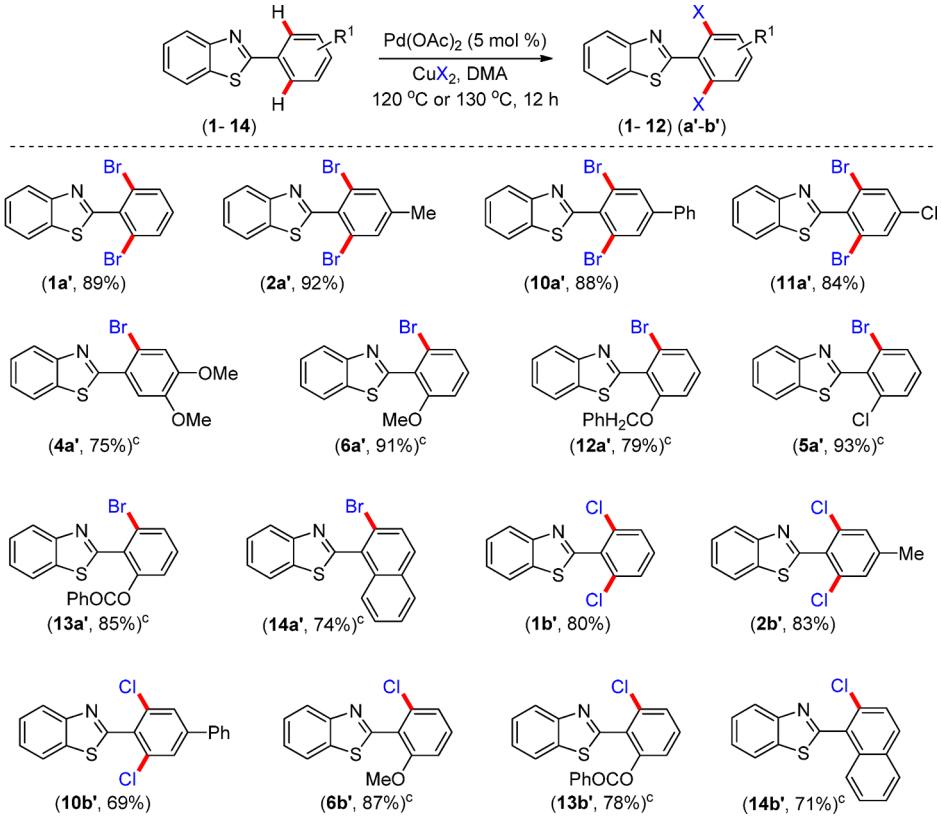
Scheme 3. Pd-Catalyzed Ortho Halogenation of 2-Arylbenzothiazoles[a,b]



[a]Reaction conditions: **1**−**14** (0.25 mmol), and Cu salts (0.5 mmol) at 120−130 °C for 16 h. [b]Isolated yield. [c]Cu salts (0.3 mmol).

revealed that, due to the sulfur (S)···X (X = Br, Cl) interaction, the initially formed ortho-monohalogenated 2-arylbenzothiazole adopts a periplanar orientation there by facilitating further ortho palladation for subsequent halogenation. The yield of the *o*-dibromo product **1a′** increased up to 89% by enhancing the quantity of $CuBr_2$ to 2.0 equiv. 2-Arylbenzothiazoles having moderately electron donating groups such as *p*-Me (**2**) and *p*-Ph (**10**) in its 2-aryl ring gave 92% and 88% yields of ortho-dibrominated products **2a′** and **10a′**, respectively. The benzothiazole **11**, substituted with the moderately electron withdrawing group *p*-Cl, provided an 84% yield of the desired ortho-dibrominated product **11a′** under the reaction conditions. An exception to this observation is 3,4-di-OMe-substituted benzothiazole **4**, which gave only the ortho-monobrominated product **4a′** in 75% yield, where bromination took place at the less sterically hindered site of the 2-aryl ring. When the reaction was carried out with ortho-monosubstituted benzothiazoles such as *o*-Cl (**5**), *o*-OMe (**6**), *o*-OCH_2Ph (**12**), and *o*-OCOPh (**13**), all substrates provided the ortho-monobrominated products **5a′** (93%), **6a′** (91%), **12a′** (79%), and **13a′** (85%) in excellent yields as shown in Scheme 3. When the ortho-bromination strategy was applied to 2-(naphthalen-1-yl)benzo[*d*]thiazole (**14**), interestingly bromination occurred selectively at the ortho site, giving product **14a′** in 74% yield. To check whether $CuCl_2$ would provide ortho chlorination similar to ortho bromination, 2-phenylbenzothiazole (**1**) was treated with $CuCl_2$ in lieu of $CuBr_2$ under otherwise identical conditions, but no trace of ortho-chlorinated product was obtained. However, efficient ortho chlorination was observed when the reaction temperature was increased from 120 to 130 °C, affording 80% of *o*-dichloro product **1b**. The success of this chlorination strategy was then applied to other substituted 2-arylbenzothiazoles such as *p*-Me (**2**) and *p*-Ph (**10**), providing *o*-dichloro products **2b′** (83%) and **10b′** (69%) in good yields. Ortho-monoubstituted benzothiazoles such as *o*-OMe (**6**) and *o*-OCOPh (**13**) gave excellent yields of ortho-chlorinated products **6b′** (87%) and **13b′** (78%), respectively, at the other available ortho site (Scheme 3). With substrate **14** possessing both ortho and peri C−H bonds, chlorination occurred regioselectively at the ortho site, giving product **14b′** in 71% yield.

The mechanism is expected to be similar to ortho aroylation of 2-arylpyridine as reported by Cheng et al. via direct sp^2 C−H bond cleavage of aromatic aldehydes or via decarboxylation as proposed by various groups.[9] To ascertain the actual intermediate involved in this reaction, three independent experiments were performed using benzaldehyde, phenylglyoxal, and phenylglyoxalic acid. Both phenylglyoxal and phenylglyoxalic acid provided the desired ortho-aroylated product **1a** in 56% and 61% yields, respectively, whereas benzaldehyde gave only a trace of the product **1a** (Scheme 4).

Thus, the reaction may be going via either decarbonylation of the in situ generated phenylglyoxal or decarboxylation of phenylglyoxalic acid obtained from the oxidation of 2-acetoxyacetophenone (**a**). A spot test of the reaction mixture using a $PdCl_2$-phosphomolybdic acid (PMA) strip confirmed the evolution of CO, there by supporting the decarbonylation path (see the Supporting Information).[21] Cyclopalladation of 2-phenylbenzothiazole (**1**) leads to the formation of intermediate **I** followed by the insertion of an aroyl moiety obtained via decarbonylation of phenylglyoxal to form intermediate **II**. In the final stage reductive elimination gave an ortho-aroylated

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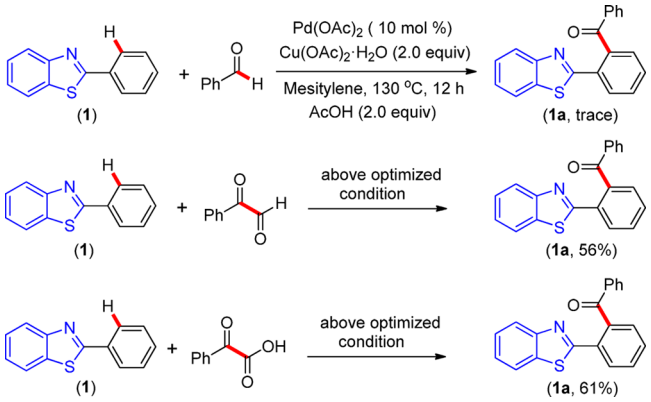
Scheme 4. Control Experiments Performed



product releasing Pd(0), which was oxidized to Pd(II) by air/$Cu(OAc)_2$ for the next catalytic cycle. Since phenylglyoxalic acid also provided the ortho-aroylated product **1a**, a decarboxylation path cannot be completely ruled out.[9] For ortho halogenation, initial cyclopalladation of substrate **1** provided intermediate **I**. This intermediate then underwent a ligand exchange with halides (Br^- or Cl^-), forming the Pd(II) intermediate **III**. Finally, reductive elimination of the intermediate **III** led to the formation of *o*-monohalo product **1A′** with the extrusion of Pd(0), which was oxidized to Pd(II) by air/$CuBr_2$ for the next catalytic cycle as shown in Scheme 5. The *o*-monohalo product so formed adopts a syn-periplanar orientation due to an S···X interaction, which facilitated ortho palladation for the second halogenations.[19]

CONCLUSION

In conclusion, we have developed peroxide-free Cu(II)-mediated ortho-aroylation and -halogenation protocols for various directing arenes in the presence of Pd(II) catalyst. For halogenation CuX_2 (X = Cl, Br) played the dual role of halogen source as well as co-oxidant, while for ortho aroylation $Cu(OAc)_2·H_2O$ facilitated the oxidation of 2-acetoxyacetophenone via the cleavage of an sp^3 C−H bond along with the regeneration of Pd(II) catalyst. This is the first report on Pd(II)-catalyzed decarbonylative ortho aroylation using 2-acetoxyacetophenone as the aroyl source in the absence of any peroxide.

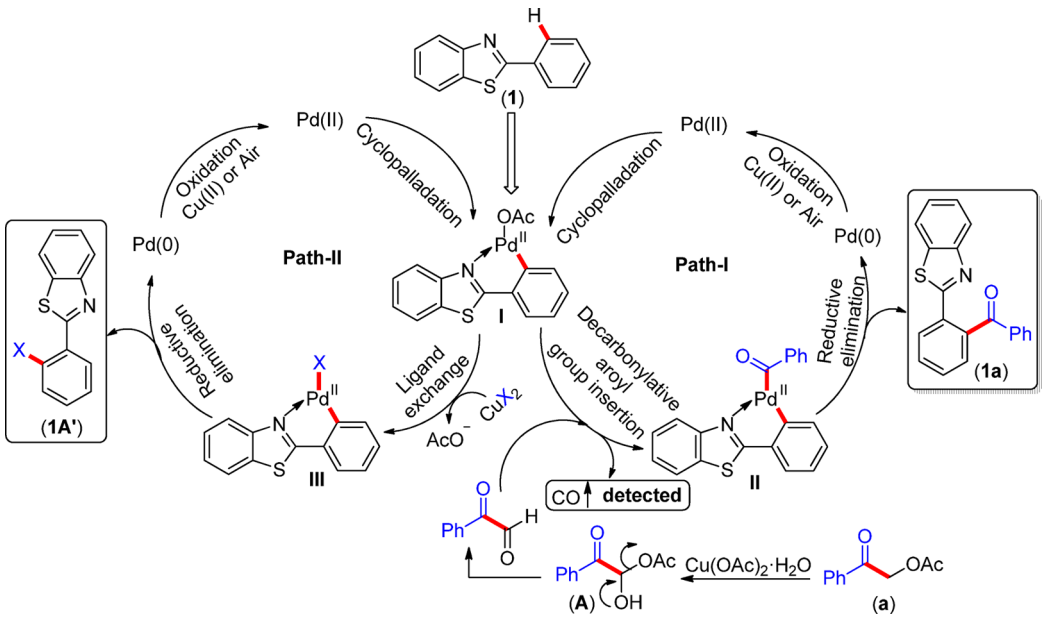
EXPERIMENTAL SECTION

General Information. All reagents were commercial grade and were purified according to the established procedures. Organic extracts were dried over anhydrous sodium sulfate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (60−120 mesh size) was used for column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254} (0.25 mm). NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for ^1H NMR (400 and 600 MHz) and $CDCl_3$ solvent as the internal standard for ^{13}C NMR (100 and 150 MHz). MS spectra were recorded using ESI mode. IR spectra were recorded in KBr.

Experimental Procedures. *A. Synthesis of (2-(Benzo[d]thiazol-2-yl)phenyl)(phenyl)methanone (**1a**) from 2-Phenylbenzo[d]-thiazole (**1**).* 2-Phenylbenzo[*d*]thiazole (**1**; 53 mg, 0.25 mmol), 2-oxo-2-phenylethyl acetate (**a**; 59 mg, 0.33 mmol), $Pd(OAc)_2$ (6 mg, 0.025 mmol), acetic acid (30 mg, 0.13 mmol), and mesitylene (1.5 mL) were placed in an oven-dried 25 mL round-bottom flask. The reaction mixture was then placed in an oil bath preheated at 130 °C. After completion of the reaction (12 h) the reaction mixture was cooled to room temperature and the crude product was admixed with ethyl acetate (30 mL). The combined organic layer was washed with saturated sodium bicarbonate solution (2 × 5 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product so obtained was purified by silica gel column chromatography (hexane/ethyl acetate, 9.4/0.6) to give pure colorless gummy (2-(benzo[*d*]thiazol-2-yl)phenyl)(phenyl)methanone (**1a**; 46 mg, yield 58%). The identity and purity of the product were confirmed by spectroscopic analysis.

*B. Synthesis of 2-(2,6-Dibromophenyl)benzo[d]thiazole (**1a′**) from 2-Phenylbenzo[d]thiazole (**1**).* 2-Phenylbenzo[*d*]thiazole (**1**; 53 mg, 0.25 mmol), $CuBr_2$ (112 mg, 0.5 mmol), $Pd(OAc)_2$ (3 mg, 0.013 mmol), and *N*,*N*-dimethylacetamide (DMA; 1.0 mL) were placed in an oven-dried 25 mL round-bottom flask. The reaction mixture was then heated in an oil bath preheated at 120 °C. After completion (12 h) the reaction mixture was cooled to room temperature and the crude product was admixed with ethyl acetate

Scheme 5. Plausible Mechanistic Cycles for Ortho Aroylation and Halogenation



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(30 mL). The organic layer was washed with saturated sodium bicarbonate solution (2 × 5 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product so obtained was purified by silica gel column chromatography (hexane/ethyl acetate, 9.8/0.2) to give pure yellow gummy 2-(2,6-dibromophenyl)-benzo[*d*]thiazole (**1a′**; 82 mg, yield 89%). The identity and purity of the product were confirmed by spectroscopic analysis.

*(2-(Benzo[d]thiazol-2-yl)phenyl)(phenyl)methanone (**1a**):*[6b] colorless gummy material; yield 46 mg, 58%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (d, 1H, J = 7.2 Hz), 7.79−7.75 (m, 4H), 7.65−7.58 (m, 2H), 7.54 (d, 1H, J = 6.8 Hz), 7.40−7.33 (m, 2H), 7.31−7.27 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.8, 165.4, 153.6, 139.9, 137.9, 135.5, 132.8, 132.3, 130.5, 130.4, 129.8, 129.4, 129.0, 128.4, 126.3, 125.5, 123.6, 121.6; IR (KBr, cm^{-1}) 3055, 3024, 2921, 2853, 1665, 1594, 1579, 1501, 1450, 1426, 1311, 1268, 1243, 1227, 1146, 970, 924, 752, 726; HRMS (ESI) calcd for $C_{20}H_{13}NOS$ (M + H$^+$) 316.0797, found 316.0806.

*(2-(Benzo[d]thiazol-2-yl)phenyl)(4-chlorophenyl)methanone (**1b**):*[6b] white solid; yield 52 mg, 60%; mp 134.5−137 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, 1H, J = 7.6 Hz), 7.78−7.75 (m, 2H), 7.69 (d, 2H, J = 8.4 Hz), 7.64−7.57 (m, 2H), 7.50 (d, 1H, J = 6.8 Hz), 7.36 (t, 1H, J = 7.6 Hz), 7.31 (t, 1H, J = 7.8 Hz), 7.25 (d, 2H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.5, 165.2, 153.5, 139.3, 139.1, 136.4, 135.3, 132.0, 130.6, 130.5, 129.8, 128.9, 128.7, 126.4, 125.6, 123.5, 121.6; IR (KBr, cm^{-1}) 3087, 3051, 2916, 2846, 1670, 1585, 1570, 1489, 1429, 1402, 1315, 1304, 1288, 1264, 1241, 1183, 1152, 1091, 1013, 968, 935, 924, 854, 844, 760, 752, 742, 726; HRMS (ESI) calcd for $C_{20}H_{12}ClNOS$ (M + H$^+$) 350.0408, found 350.0417.

*(2-(Benzo[d]thiazol-2-yl)phenyl)(3-chlorophenyl)methanone (**1c**):*[6b] yellow gummy material; yield 51 mg, 59%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91 (d, 1H, J = 6.8 Hz), 7.79−7.74 (m, 3H), 7.64−7.57 (m, 3H), 7.53 (d, 1H, J = 6.8 Hz), 7.36 (t, 1H, J = 7.6 Hz), 7.32−7.28 (m, 2H), 7.19 (t, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.4, 165.2, 153.5, 139.7, 139.0, 135.3, 134.6, 132.6, 132.1, 130.7, 130.6, 129.8, 129.7, 129.1, 129.0, 127.3, 126.4, 125.7, 123.5, 121.6; IR (KBr, cm^{-1}) 3052, 2921, 2844, 1669, 1569, 1432, 1290, 1281, 1256, 1242, 1158, 1074, 971, 967, 775, 766, 753, 732, 725; HRMS (ESI) calcd for $C_{20}H_{12}ClNOS$ (M + H$^+$) 350.0408, found 350.0413.

*(2-(Benzo[d]thiazol-2-yl)phenyl)(4-fluorophenyl)methanone (**1d**):* pale yellow gummy material; yield 51 mg, 61%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (d, 1H, J = 8.0 Hz), 7.81−7.76 (m, 4H), 7.66−7.59 (m, 2H), 7.53 (d, 1H, J = 7.6 Hz), 7.37 (t, 1H, J = 7.2 Hz), 7.31 (t, 1H, J = 7.8 Hz), 6.96 (t, 2H, J = 8.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 196.3, 165.5 (d, $^1J_{C-F}$ = 253 Hz), 165.3, 153.6, 139.6, 135.4, 134.49, 134.47, 132.2, 131.9 (d, $^3J_{C-F}$ = 9.5 Hz), 130.6, 130.5, 129.9, 128.9, 126.4, 125.6, 123.6, 121.6, 115.6 (d, $^2J_{C-F}$ = 21.9 Hz); IR (KBr, cm^{-1}) 3058, 2959, 2927, 2850, 1661, 1597, 1502, 1455, 1429, 1411, 1294, 1255, 1239, 1226, 1145, 968, 929, 858, 767, 761, 727; HRMS (ESI) calcd for $C_{20}H_{12}FNOS$ (M + H$^+$) 334.0703, found 334.0709.

*(2-(Benzo[d]thiazol-2-yl)phenyl)(p-tolyl)methanone (**1e**):*[6b] pale yellow gummy material; yield 44 mg, 53%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, 1H, J = 8.0 Hz), 7.81 (d, 1H, J = 8.0 Hz), 7.78 (d, 1H, J = 8.4 Hz), 7.67 (d, 2H, J = 8.4 Hz), 7.63−7.56 (m, 2H), 7.49 (d, 1H, J = 7.6 Hz), 7.36 (t, 1H, J = 7.2 Hz), 7.29 (t, 1H, J = 7.6 Hz), 7.10 (d, 2H, J = 8.0 Hz), 2.29 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.5, 165.6, 153.7, 143.8, 140.1, 135.6, 135.4, 132.2, 130.4, 130.2, 129.9, 129.7, 129.2, 128.9, 126.3, 125.4, 123.7, 121.6, 21.9; IR (KBr, cm^{-1}) 3060, 3025, 2921, 2852, 1660, 1603, 1518, 1453, 1431, 1308, 1300, 1269, 1227, 1179, 1151, 969, 957, 928, 855, 785, 770, 761, 742, 731; HRMS (ESI) calcd for $C_{21}H_{15}NOS$ (M + H$^+$) 330.0954, found 330.0961.

*(2-(Benzo[d]thiazol-2-yl)phenyl)(m-tolyl)methanone (**1f**):*[22] pale yellow gummy material; yield 45 mg, 55%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.93 (d, 1H, J = 8.0 Hz), 7.82−7.77 (m, 2H), 7.65−7.57 (m, 3H), 7.53−7.51 (m, 2H), 7.36 (t, 1H, J = 7.2 Hz), 7.29 (t, 1H, J = 7.2 Hz), 7.21−7.14 (m, 2H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 197.9, 165.6, 153.7, 140.1, 138.2, 137.9, 135.6, 133.7, 132.3, 130.4, 130.3, 129.91, 129.87, 129.0, 128.3, 126.9, 126.3, 125.5, 123.6, 121.6, 21.4; IR (KBr, cm^{-1}) 3095, 3059, 2920, 2856, 1668, 1558, 1455, 1432, 1278, 1228, 1207, 1082, 967, 761, 728; HRMS (ESI) calcd for $C_{21}H_{15}NOS$ (M + H$^+$) 330.0954, found 330.0966.

*(2-(Benzo[d]thiazol-2-yl)phenyl)(4-methoxyphenyl)methanone (**1g**):*[6b] pale yellow gummy material; yield 40 mg, 46%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (d, 1H, J = 7.2 Hz), 7.83 (d, 1H, J = 8.0 Hz), 7.78−7.74 (m, 3H), 7.62−7.54 (m, 2H), 7.48 (d, 1H, J = 7.2 Hz), 7.36 (t, 1H, J = 7.8 Hz), 7.29 (d, 1H, J = 7.6 Hz), 6.78 (d, 2H, J = 8.8 Hz), 3.75 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.4, 165.6, 163.5, 153.7, 140.2, 135.6, 132.9, 132.1, 131.9, 130.8, 130.3, 129.9, 128.7, 126.3, 125.4, 123.6, 121.5, 113.7, 55.5; IR (KBr, cm^{-1}) 3078, 3057, 2963, 2928, 2831, 1652, 1600, 1575, 1509, 1418, 1302, 1261, 1226, 1175, 1150, 1029, 970, 928, 850, 772, 764, 750; HRMS (ESI) calcd for $C_{21}H_{15}NO_2S$ (M + H$^+$) 346.0903, found 346.0910.

*(2-(Benzo[d]thiazol-2-yl)phenyl)(naphthalen-2-yl)methanone (**1h**):*[6b] yellow gummy material; yield 52 mg, 57%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08 (s, 1H), 8.05 (d, 1H, J = 8.8 Hz), 7.97 (d, 1H, J = 7.2 Hz), 7.79 (d, 1H, J = 8.8 Hz), 7.76−7.74 (m, 3H), 7.69 (d, 1H, J = 7.6 Hz), 7.66−7.61 (m, 2H), 7.59−7.56 (m, 1H), 7.48 (t, 1H, J = 7.4 Hz), 7.41 (t, 1H, J = 7.6 Hz), 7.28 (t, 1H, J = 7.6 Hz), 7.21 (t, 1H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.8, 165.4, 153.6, 139.9, 135.54, 135.49, 135.4, 132.4, 132.2, 131.5, 130.5, 130.3, 129.9, 129.7, 128.9, 128.5, 127.9, 126.7, 126.3, 125.4, 124.9, 123.6, 121.5; IR (KBr, cm^{-1}) 3056, 2924, 2852, 1663, 1626, 1593, 1505, 1465, 1431, 1352, 1298, 1285, 1232, 1198, 1149, 1121, 967, 919, 871, 826, 789, 763, 753, 729; HRMS (ESI) calcd for $C_{24}H_{15}NOS$ (M + H$^+$) 366.0954, found 366.0955.

*(2-(Benzo[d]thiazol-2-yl)-5-methylphenyl)(phenyl)methanone (**2a**):*[6b] yellow gummy material; yield 50 mg, 61%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, 1H, J = 8.0 Hz), 7.69−7.66 (m, 4H), 7.33 (d, 1H, J = 8.0 Hz), 7.29−7.25 (m, 2H), 7.23−7.18 (m, 4H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.1, 165.6, 153.5, 141.1, 139.7, 137.9, 135.3, 132.8, 131.0, 129.7, 129.5, 129.4, 129.3, 128.6, 126.2, 125.3, 123.4, 121.5, 21.6; IR (KBr, cm^{-1}) 3059, 3020, 2916, 2846, 1669, 1597, 1472, 1449, 1431, 1315, 1288, 1256, 1256, 1209, 1075, 975, 957, 826, 757, 730; HRMS (ESI) calcd for $C_{21}H_{15}NOS$ (M + H$^+$) 330.0954, found 330.0963.

*(2-(Benzo[d]thiazol-2-yl)-5-butoxyphenyl)(phenyl)methanone (**3a**):*[6b] white solid; yield 58 mg, 60%; mp 128.7−132.3 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.86 (d, 1H, J = 8.8 Hz), 7.79−7.77 (m, 2H), 7.73 (t, 2H, J = 8.8 Hz), 7.38 (t, 1H, J = 7.4 Hz), 7.34−7.23 (m, 4H), 7.11 (dd, 1H, J_1 = 2.6 Hz, J_2 = 6.0 Hz), 7.01 (d, 1H, J = 2.8 Hz), 4.05 (t, 2H, J = 6.6 Hz), 1.84−1.77 (m, 2H), 1.56−1.46 (m, 2H), 0.99 (t, 3H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.6, 165.3, 160.9, 153.7, 141.4, 137.8, 135.2, 132.9, 131.3, 129.4, 128.4, 126.2, 125.1, 124.4, 123.2, 121.4, 116.5, 114.5, 68.4, 31.3, 19.4, 14.0; IR (KBr, cm^{-1}) 2963, 2944, 2927, 2870, 1672, 1605, 1595, 1567, 1516, 1482, 1472, 1451, 1437, 1414, 1311, 1294, 1224, 1180, 1112, 1074, 1043, 972, 953, 856, 841, 824, 810, 762, 730; HRMS (ESI) calcd for $C_{24}H_{21}NO_2S$ (M + H$^+$) 388.1372, found 388.1379.

*(2-(Benzo[d]thiazol-2-yl)-4,5-dimethoxyphenyl)(phenyl)-methanone (**4a**):* white solid; yield 58 mg, 62%; mp 186−188.4 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.80 (d, 1H, J = 8.0 Hz), 7.75−7.71 (m, 3H), 7.39 (s, 1H), 7.36−7.30 (m, 2H), 7.27−7.22 (m, 3H), 7.07 (s, 1H), 4.04 (s, 3H), 3.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.3, 165.4, 153.5, 150.6, 150.3, 138.1, 135.5, 132.8, 132.7, 129.3, 128.3, 126.2, 125.7, 125.2, 123.2, 121.4, 111.9, 56.5, 56.4; IR (KBr, cm^{-1}) 3048, 2999, 2955, 2924, 2846, 1653, 1597, 1573, 1521, 1501, 1458, 1430, 1381, 1353, 1290, 1274, 1240, 1174, 1119, 1008, 969, 897, 865, 832, 784, 762, 722; HRMS (ESI) calcd for $C_{22}H_{17}NO_3S$ (M + H$^+$) 376.1009, found 376.1003.

*(2-(Benzo[d]thiazol-2-yl)-3-chlorophenyl)(phenyl)methanone (**5a**):*[6b] colorless gummy material; yield 56 mg, 64%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (d, 1H, J = 8.0 Hz), 7.78 (d, 1H, J = 8.0 Hz), 7.69−7.64 (m, 3H), 7.54−7.47 (m, 2H), 7.39−7.29 (m, 3H), 7.24 (t, 2H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 195.9, 162.2, 152.3, 143.0, 137.1, 136.4, 134.3, 132.9, 132.1, 131.9, 130.7, 129.5, 128.3, 127.6, 126.2, 125.7, 123.7, 121.4; IR (KBr, cm^{-1}) 3057, 2925, 2847, 1670, 1595, 1559, 1416, 1317, 1281, 1236, 1196, 1141, 968, 953, 798, 769, 758, 749, 729; HRMS (ESI) calcd for $C_{20}H_{12}ClNOS$ (M + H$^+$) 350.0408, found 350.0415.

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(2-(Benzo[d]thiazol-2-yl)-3-methoxyphenyl)(phenyl)methanone (**6a**): white solid; yield 54 mg, 63%; mp 145.4−147.6 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.77−7.68 (m, 4H), 7.53 (t, 1H, J = 8.0 Hz), 7.32−7.27 (m, 2H), 7.24−7.21 (m, 3H), 7.16 (d, 1H, J = 8.4 Hz), 7.12 (d, 1H, J = 8.4 Hz), 4.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.3, 160.5, 157.2, 151.5, 142.4, 138.3, 136.0, 132.2, 131.4, 128.8, 128.2, 125.8, 125.0, 123.0, 121.2, 121.1, 120.9, 112.8, 56.2; IR (KBr, cm^{-1}) 3049, 3025, 2984, 2944, 2842, 1669, 1575, 1576, 1449, 1425, 1316, 1303, 1288, 1267, 1161, 974, 956, 834, 782, 760, 744, 734, 724; HRMS (ESI) calcd for $C_{21}H_{15}NO_2S$ (M + H$^+$) 346.0903, found 346.0914.

Phenyl(2-(3-phenylquinoxalin-2-yl)phenyl)methanone (**7a**):[6c] yellow gummy material; yield 63 mg, 65%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (d, 1H, J = 9.2 Hz), 8.01 (d, 1H, J = 8.0 Hz), 7.75−7.69 (m, 2H), 7.66 (d, 1H, J = 7.6 Hz), 7.61−7.57 (m, 1H), 7.45−7.39 (m, 7H), 7.28 (t, 2H, J = 9.0 Hz), 7.23 (d, 1H, J = 7.2 Hz), 7.16 (t, 2H, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 196.6, 153.9, 153.5, 141.4, 141.1, 140.9, 138.8, 138.5, 137.1, 132.7, 131.7, 131.4, 130.4, 130.3, 130.1, 130.0, 129.9, 129.4, 129.2, 128.9, 128.3, 128.0; IR (KBr, cm^{-1}) 3057, 3022, 2925, 2847, 1659, 1596, 1473, 1442, 1389, 1343, 1312, 1269, 1054, 1025, 977, 926, 770, 729, 710; HRMS (ESI) calcd for $C_{27}H_{18}N_2O$ (M + H$^+$) 387.1499, found 387.1509.

Phenyl(2-(quinoxalin-2-yl)phenyl)methanone (**8a**): yellow gummy material; yield 47 mg, 61%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.11 (s, 1H), 7.99 (d, 1H, J = 8.4 Hz), 7.98 (d, 1H, J = 7.8 Hz), 7.78−7.75 (m, 3H), 7.71 (t, 1H, J = 6.6 Hz), 7.68−7.62 (m, 4H), 7.36 (t, 1H, J = 7.6 Hz), 7.26 (t, 2H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 197.9, 151.6, 144.3, 141.6, 141.1, 140.5, 138.0, 136.9, 132.8, 130.7, 130.4, 130.1, 129.8, 129.7, 129.6, 129.4, 129.3, 129.1, 128.4; IR (KBr, cm^{-1}) 3060, 2921, 2849, 1660, 1594, 1579, 1449, 1312, 1286, 1250, 1125, 1037, 957, 937, 923, 769, 753, 706; HRMS (ESI) calcd for $C_{21}H_{14}N_2O$ (M + H$^+$) 311.1186, found 311.1192.

Benzo[h]quinolin-10-yl(phenyl)methanone (**9a**):[7] gray gummy material; yield 48 mg, 68%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.50 (d, 1H, J = 3.6 Hz), 8.10 (d, 1H, J = 8.4 Hz), 8.05 (d, 1H, J = 7.8 Hz), 7.90 (d, 1H, J = 9.0 Hz), 7.79 (t, 1H, J = 7.6 Hz), 7.75−7.74 (m, 3H), 7.63 (d, 1H, J = 7.2 Hz), 7.41 (t, 1H, J = 7.2 Hz), 7.34−7.32 (m, 1H), 7.29 (t, 2H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.9, 147.3, 144.8, 139.4, 139.1, 135.5, 133.9, 131.9, 129.3, 129.2, 128.9, 128.3, 127.98, 127.92, 127.2, 126.6, 126.3, 121.9; IR (KBr, cm^{-1}) 3055, 3028, 2919, 2847, 1673, 1578, 1510, 1450, 1421, 1405, 1315, 1296, 1274, 1212, 1198, 1175, 1138, 1005, 927, 891, 840, 793, 775, 759, 732; HRMS (ESI) calcd for $C_{20}H_{13}NO$ (M + H$^+$) 284.1077, found 284.1074.

2-(2,6-Dibromophenyl)benzo[d]thiazole (**1a′**):[19] yellow gummy material; yield 82 mg, 89%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (d, 1H, J = 8.0 Hz), 7.96 (d, 1H, J = 8.4 Hz), 7.65 (d, 2H, J = 8.0 Hz), 7.55 (t, 1H, J = 7.6 Hz), 7.46 (t, 1H, J = 7.6 Hz), 7.19 (t, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.5, 152.8, 136.4, 135.9, 132.3, 132.0, 126.4, 125.9, 124.6, 124.2, 121.9; IR (KBr, cm^{-1}) 3072, 2959, 2917, 2848, 1575, 1594, 1549, 1514, 1546, 1420, 1316, 1243, 1228, 1195, 1185, 1147, 1123, 1081, 1067, 1015, 962, 941, 900, 852, 776, 765, 741, 730; HRMS (ESI) calcd for $C_{13}H_7Br_2NS$ (M + H$^+$) 369.8725, found 369.8733.

2-(2,6-Dibromo-4-methylphenyl)benzo[d]thiazole (**2a′**):[19] pale yellow solid; yield 88 mg, 92%; mp 84.5−87.1 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.17 (d, 1H, J = 8.0 Hz), 7.96 (d, 1H, J = 8.0 Hz), 7.55 (t, 1H, J = 7.8 Hz), 7.49−7.45 (m, 3H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 165.7, 152.9, 143.2, 136.6, 132.9, 132.7, 126.4, 125.9, 124.18, 124.17, 121.9, 21.0; IR (KBr, cm^{-1}) 3058, 2954, 2921, 2850, 1597, 1526, 1485, 1431, 1379, 1311, 1228, 1195, 1084, 1065, 964, 850, 817, 759, 743, 728, 707; HRMS (ESI) calcd for $C_{14}H_9Br_2NS$ (M + H$^+$) 383.8881, found 383.8875.

2-(3,5-Dibromo-1,1′-biphenyl-4-yl)benzo[d]thiazole (**10a′**): white solid; yield 97 mg, 88%; mp 160.2−163 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.21 (d, 1H, J = 8.0 Hz), 7.99 (d, 1H, J = 8.0 Hz), 7.89 (s, 2H), 7.60−7.56 (m, 3H), 7.51−7.42 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.5, 152.9, 145.7, 137.7, 136.5, 134.3, 130.6, 129.3, 129.1, 127.4, 126.5, 126.0, 124.9, 124.3, 121.9; IR (KBr, cm^{-1}) 3054, 3018, 2923, 2845, 1593, 1520, 1428, 1367, 1230, 1204, 1086, 1064, 1013, 961, 876, 762, 742, 731; HRMS (ESI) calcd for $C_{19}H_{11}Br_2NS$ (M + H$^+$) 445.9038, found 445.9047.

2-(2,6-Dibromo-4-chlorophenyl)benzo[d]thiazole (**11a′**): white solid; yield 84 mg, 84%; mp 127−129.3 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.18 (d, 1H, J = 8.4 Hz), 7.97 (d, 1H, J = 7.8 Hz), 7.69 (s, 2H), 7.57 (t, 1H, J = 7.2 Hz), 7.49 (t, 1H, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 164.6, 152.9, 137.3, 136.5, 134.7, 131.9, 126.6, 126.2, 124.9, 124.3, 121.9; IR (KBr, cm^{-1}) 3071, 2958, 2919, 2855, 1573, 1539, 1527, 1505, 1423, 1406, 1372, 1358, 1233, 1123, 1083, 1064, 965, 860, 789, 758, 742, 736, 729; HRMS (ESI) calcd for C13H6Br$_2$ClNS (M + H$^+$) 403.8335, found 403.8341.

2-(2-Bromo-4,5-dimethoxyphenyl)benzo[d]thiazole (**4a′**): white solid; yield 65 mg, 75%; mp 124.1−126.8 °C; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.11 (d, 1H, J = 7.8 Hz), 7.93 (d, 1H, J = 7.8 Hz), 7.72 (s, 1H), 7.52 (t, 1H, J = 7.2 Hz), 7.42 (t, 1H, J = 7.2 Hz), 7.16 (s, 1H), 3.98 (s, 3H), 3.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 165.7, 152.6, 151.1, 148.6, 136.2, 126.8, 126.4, 125.4, 123.4, 121.5, 116.6, 114.3, 113.2, 56.5, 56.4; IR (KBr, cm^{-1}) 2956, 2923, 2838, 1599, 1515, 1458, 1423, 1379, 1338, 1257, 1208, 1159, 1028, 1019, 869, 829, 776, 754, 749, 724; HRMS (ESI) calcd for $C_{15}H_{12}BrNO_2S$ (M + H$^+$) 349.9852, found 349.9844.

2-(2-Bromo-6-methoxyphenyl)benzo[d]thiazole (**6a′**):[19] colorless gummy material; yield 73 mg, 91%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.16 (d, 1H, J = 8.0 Hz), 7.95 (d, 1H, J = 8.0 Hz), 7.53 (t, 1H, J = 7.6 Hz), 7.44 (t, 1H, J = 7.6 Hz), 7.32−7.31 (m, 2H), 6.97−6.94 (m, 1H), 3.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.8, 159.2, 153.2, 136.7, 132.1, 126.1, 125.5, 125.1, 124.7, 124.5, 123.9, 121.7, 110.2, 56.4; IR (KBr, cm^{-1}) 3061, 2967, 2938, 2835, 1587, 1567, 1518, 1460, 1429, 1312, 1267, 1240, 1221, 1184, 1148, 1125, 1083, 1033, 959, 852, 777, 760, 741, 729; HRMS (ESI) calcd for $C_{14}H_{10}BrNOS$ (M + H$^+$) 319.9746, found 319.9750.

2-(2-(Benzyloxy)-6-bromophenyl)benzo[d]thiazole (**12a′**):[19] yellow gummy material; yield 78 mg, 79%; ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.16 (d, 1H, J = 7.8 Hz), 7.95 (d, 1H, J = 7.8 Hz), 7.52 (t, 1H, J = 7.2 Hz), 7.44 (t, 1H, J = 7.2 Hz), 7.30 (d, 1H, J = 7.8 Hz), 7.25−7.23 (m, 3H), 7.23−7.21 (m, 3H), 6.95 (d, 1H, J = 8.4 Hz), 5.09 (s, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 163.7, 158.2, 153.3, 136.8, 136.3, 132.0, 128.7, 128.0, 126.9, 126.1, 125.51, 125.49, 125.2, 124.7, 123.9, 121.8, 112.1, 70.9; IR (KBr, cm^{-1}) 3064, 3031, 2934, 2870, 1587, 1567, 1518, 1496, 1440, 1380, 1311, 1267, 1238, 1222, 1147, 1125, 1080, 1023, 960, 868, 834, 775, 759, 730; HRMS (ESI) calcd for $C_{20}H_{14}BrNOS$ (M + H$^+$) 396.0059, found 396.0071.

2-(2-Bromo-6-chlorophenyl)benzo[d]thiazole (**5a′**):[19] colorless gummy material; yield 75 mg, 93%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.17 (d, 1H, J = 8.4 Hz), 7.95 (d, 1H, J = 8.0 Hz), 7.59 (d, 1H, J = 8.0 Hz), 7.53 (t, 1H, J = 7.6 Hz), 7.47−7.43 (m, 2H), 7.25 (t, 1H, J = 8.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.8, 152.9, 136.4, 135.6, 134.2, 131.9, 131.5, 128.9, 126.4, 125.9, 124.8, 124.1, 121.8; IR (KBr, cm^{-1}) 3055, 2918, 2858, 1579, 1553, 1516, 1456, 1428, 1313, 1240, 1225, 1194, 1091, 1072, 962, 776, 762, 741, 728; HRMS (ESI) calcd for $C_{13}H_7BrClNS$ (M + H$^+$) 323.9251, found 323.9254.

2-(Benzo[d]thiazol-2-yl)-3-bromophenyl benzoate (**13a′**):[19] pale yellow gummy material; yield 87 mg, 85%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.06 (d, 1H, J = 8.0 Hz), 7.88−7.85 (m, 3H), 7.66 (d, 1H, J = 7.6 Hz), 7.50−7.42 (m, 3H), 7.40−7.36 (m, 2H), 7.29 (t, 2H, J = 7.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.7, 161.8, 153.0, 150.4, 136.3, 133.9, 131.8, 130.8, 130.3, 129.0, 128.7, 128.6, 126.3, 125.7, 124.3, 123.9, 122.6, 121.7; IR (KBr, cm^{-1}) 3061, 2928, 2868, 1743, 1598, 1555, 1528, 1441, 1428, 1313, 1271, 1221, 1175, 1137, 1077, 1055, 1023, 962, 873, 855, 760, 729; HRMS (ESI) calcd for $C_{20}H_{12}BrNO_2S$ (M + H$^+$) 409.9852, found 409.9861.

2-(2-Bromonaphthalen-1-yl)benzo[d]thiazole (**14a′**):[19] pale yellow gummy material; yield 63 mg, 74%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.16 (d, 1H, J = 8.0 Hz), 8.00 (d, 1H, J = 8.4 Hz), 7.97 (d, 1H, J = 8.0 Hz), 7.90 (d, 1H, J = 8.0 Hz), 7.86 (d, 1H, J = 7.6 Hz), 7.74 (d, 1H, J = 7.2 Hz), 7.58−7.53 (m, 2H), 7.46 (t, 1H, J = 7.6 Hz), 7.35 (t, 1H, J = 7.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 168.2, 153.2, 136.9, 136.1, 134.4, 131.9, 131.8, 131.6, 130.1, 128.9, 126.9, 126.4, 125.4, 125.1, 123.7, 121.6, 119.7; IR (KBr, cm^{-1}) 3052, 2962, 2925, 2856, 1660, 1510, 1488, 1448, 1433, 1358, 1308, 1106, 1067, 946, 875, 825,

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814, 769, 762, 730; HRMS (ESI) calcd for $C_{17}H_{10}BrNS$ (M + H^+) 339.9796, found 339.9802.

*2-(2,6-Dichlorophenyl)benzo[d]thiazole (**1b′**):*[19] colorless gummy material; yield 56 mg, 80%; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.18 (d, 1H, J = 8.0 Hz), 7.98 (d, 1H, J = 8.0 Hz), 7.56 (t, 1H, J = 7.8 Hz), 7.50−7.44 (m, 3H), 7.38 (t, 1H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 162.3, 153.1, 136.5, 135.8, 132.5, 131.7, 128.4, 126.5, 125.9, 124.2, 121.9; IR (KBr, cm^{-1}) 3058, 2924, 2853, 1582, 1558, 1516, 1457, 1431, 1311, 1241, 1224, 1191, 1106, 1076, 1013, 964, 788, 759, 743, 729; HRMS (ESI) calcd for $C_{13}H_7Cl_2NS$ (M + H^+) 279.9756, found 279.9762.

*2-(2,6-Dichloro-4-methylphenyl)benzo[d]thiazole (**2b′**):*[19] colorless gummy material; yield 61 mg, 83%; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.17 (d, 1H, J = 8.0 Hz), 7.96 (d, 1H, J = 8.0 Hz), 7.54 (t, 1H, J = 7.6 Hz), 7.46 (t, 1H, J = 7.4 Hz), 7.26 (s, 2H), 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 162.5, 153.2, 142.6, 136.6, 135.3, 129.5, 129.0, 126.4, 125.9, 124.1, 121.8, 21.2; IR (KBr, cm^{-1}) 3067, 3055, 2954, 2920, 2848, 1603, 1546, 1524, 1451, 1442, 1430, 1388, 1311, 1276, 1244, 1224, 1201, 1096, 1070, 966, 850, 752, 723; HRMS (ESI) calcd for $C_{14}H_9Cl_2NS$ (M + H^+) 293.9912, found 293.9904.

*2-(3,5-Dichloro-1,1′-biphenyl-4-yl)benzo[d]thiazole (**10b′**):* orange solid; yield 61 mg, 69%; mp 142.3−144.7 °C; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.21 (d, 1H, J = 8.0 Hz), 7.99 (d, 1H, J = 8.0 Hz), 7.68 (s, 2H), 7.61−7.55 (m, 3H), 7.51−7.44 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.2, 153.2, 145.1, 137.9, 136.6, 135.9, 130.9, 129.3, 129.1, 127.3, 126.9, 126.4, 125.9, 124.2, 121.9; IR (KBr, cm^{-1}) 3057, 3028, 2923, 2848, 1597, 1533, 1431, 1375, 1311, 1235, 1206, 1098, 1071, 964, 875, 807, 776, 761, 732; HRMS (ESI) calcd for $C_{19}H_{11}Cl_2NS$ (M + H^+) 356.0069, found 356.0058.

*2-(2-Chloro-6-methoxyphenyl)benzo[d]thiazole (**6b′**):* pale yellow gummy material; yield 60 mg, 87%; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.16 (d, 1H, J = 8.0 Hz), 7.94 (d, 1H, J = 8.0 Hz), 7.52 (t, 1H, J = 7.8 Hz), 7.43 (t, 1H, J = 7.6 Hz), 7.37 (t, 1H, J = 8.2 Hz), 7.12 (d, 1H, J = 7.6 Hz), 6.91 (d, 1H, J = 8.4 Hz) 3.76 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.2, 159.1, 153.3, 136.7, 135.2, 131.7, 126.1, 125.4, 123.8, 122.6, 122.0, 121.7, 109.7, 56.4; IR (KBr, cm^{-1}) 3058, 2967, 2935, 2838, 1588, 1572, 1462, 1431, 1310, 1269, 1217, 1041, 961, 856, 780, 760, 742, 730; HRMS (ESI) calcd for $C_{14}H_{10}ClNOS$ (M + H^+) 276.0251, found 276.0246.

*2-(Benzo[d]thiazol-2-yl)-3-chlorophenyl benzoate (**13b′**):*[19] colorless gummy solid; yield 71 mg, 78%; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.00 (d, 1H, J = 8.0 Hz), 7.89 (d, 2H, J = 8.4 Hz), 7.84 (d, 1H, J = 8.0 Hz), 7.51−7.45 (m, 3H), 7.42 (d, 1H, J = 7.2 Hz), 7.36 (d, 1H, J = 8.0 Hz), 7.34−7.28 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.8, 160.2, 152.9, 150.5, 136.3, 135.0, 133.8, 131.4, 130.3, 128.7, 128.6, 127.7, 127.1, 126.2, 125.7, 123.8, 122.1, 121.6; IR (KBr, cm^{-1}) 3061, 2914, 2845, 1741, 1599, 1569, 1518, 1445, 1430, 1313, 1262, 1222, 1176, 1125, 1077, 1056, 1023, 964, 892, 855, 760, 729, 705; HRMS (ESI) calcd for $C_{20}H_{12}ClNO_2S$ (M + H^+) 366.0357, found 366.0364.

*2-(2-Chloronaphthalen-1-yl)benzo[d]thiazole (**14b′**):*[19] colorless gummy material; yield 52 mg, 71%; ^1H NMR ($CDCl_3$, 600 MHz) δ 8.13 (d, 1H, J = 7.8 Hz), 8.03 (d, 1H, J = 7.8 Hz), 7.97 (d, 1H, J = 7.8 Hz), 7.88 (d, 1H, J = 8.4 Hz), 7.71 (d, 1H, J = 7.2 Hz), 7.60 (d, 1H, J = 7.8 Hz), 7.59−7.54 (m, 2H), 7.48−7.44 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 168.8, 153.2, 136.8, 135.9, 131.8, 131.6, 131.0, 130.8, 130.2, 129.0, 128.4, 126.6, 126.5, 125.4, 125.2, 123.7, 121.6; IR (KBr, cm^{-1}) 3055, 2924, 2844, 1516, 1496, 1451, 1362, 1344, 1327, 1312, 1278, 1199, 1110, 1067, 1013, 959, 884, 820, 758, 728; HRMS (ESI) calcd for $C_{17}H_{10}ClNS$ (M + H^+) 296.0302, found 296.0308.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01170.

Spectral data for all compounds reported (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*B.H.K.: e-mail, patel@iitg.ernet.in; fax, +91-3612690762.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Yang, L.; Huang, H. *Chem. Rev.* **2015**, *115*, 3468. (b) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (c) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (d) C−H activation in: *Topics in Current Chemistry*; Eds. Yu, J.-Q.; Shi, Z., Eds.; Springer: Berlin, 2010. (e) Sun, C.-L.; Li, B.-J.; Shi, Z.-J. *Chem. Rev.* **2011**, *111*, 1293. (f) Hussain, I.; Singh, T. *Adv. Synth. Catal.* **2014**, *356*, 1661. (g) Minami, Y.; Hiyama, T. *Acc. Chem. Res.* **2016**, *49*, 67 and review references for C−H functionalization cited therein.

(2) (a) Yoo, E. J.; Wasa, M.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010**, *132*, 17378. (b) Li, Z.; Li, C.-J. *J. Am. Chem. Soc.* **2004**, *126*, 11810. (c) Li, Y.-Z.; Li, B.-J.; Lu, X.-Y.; Lin, S.; Shi, Z.-J. *Angew. Chem., Int. Ed.* **2009**, *48*, 3817. (d) Zhang, Y.; Li, C.-J. *Eur. J. Org. Chem.* **2007**, *2007*, 4654. (e) Wasa, M.; Engle, K. M.; Yu, J.-Q. *J. Am. Chem. Soc.* **2010**, *132*, 3680. (f) He, J.; Li, S.; Deng, Y.; Fu, H.; Laforteza, B. N.; Spangler, J. E.; Homs, A.; Yu, J.-Q. *Science* **2014**, *343*, 1216.

(3) (a) Rit, R. K.; Yadav, M. R.; Ghosh, K.; Shankar, M.; Sahoo, A. K. *Org. Lett.* **2014**, *16*, 5258. (b) Hull, K. L.; Anani, W. Q.; Sanford, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 7134. (c) Giri, R.; Chen, X.; Yu, J. Q. *Angew. Chem., Int. Ed.* **2005**, *44*, 2112.

(4) (a) Zhang, S.-Y.; He, G.; Zhao, Y.; Wright, K.; Nack, W. A.; Chen, G. *J. Am. Chem. Soc.* **2012**, *134*, 7313. (b) Zhao, J.; Fang, H.; Zhou, W.; Han, J.; Pan, Y. *J. Org. Chem.* **2014**, *79*, 3847. (c) Rout, S. K.; Guin, S.; Ali, W.; Gogoi, A.; Patel, B. K. *Org. Lett.* **2014**, *16*, 3086.

(5) (a) Gephart, R. T.; Huang, D. L.; Aguila, M. J. B.; Schmidt, G.; Shahu, A.; Warren, T. H. *Angew. Chem., Int. Ed.* **2012**, *51*, 6488. (b) Wang, Z.; Zhang, Y.; Fu, H.; Jiang, Y.; Zhao, Y. *Org. Lett.* **2008**, *10*, 1863. (c) Cheng, Y.; Dong, W.; Wang, L.; Parthasarathy, K.; Bolm, C. *Org. Lett.* **2014**, *16*, 2000. (d) McNally, A.; Haffemayer, B.; Collins, B. S. L.; Gaunt, M. J. *Nature* **2014**, *510*, 129. (e) Nadres, E. T.; Daugulis, O. *J. Am. Chem. Soc.* **2012**, *134*, 7. (f) Wu, X.; Yang, K.; Zhao, Y.; Sun, H.; Li, G.; Ge, H. *Nat. Commun.* **2015**, *6*, 6462.

(6) (a) Wu, X.-F. *Chem. - Eur. J.* **2015**, *21*, 12252 and references cited therein. (b) Banerjee, A.; Santra, S. K.; Guin, S.; Rout, S. K.; Patel, B. K. *Eur. J. Org. Chem.* **2013**, *2013*, 1367. (c) Santra, S. K.; Banerjee, A.; Patel, B. K. *Tetrahedron* **2014**, *70*, 2422.

(7) Khatun, N.; Banerjee, A.; Santra, S. K.; Behera, A.; Patel, B. K. *RSC Adv.* **2014**, *4*, 54532.

(8) Zhou, W.; Li, H.; Wang, L. *Org. Lett.* **2012**, *14*, 4594.

(9) (a) Li, H.; Li, P.; Zhao, Q.; Wang, L. *Chem. Commun.* **2013**, *49*, 9170 and references for decarboxylative ortho aroylation cited therein. (b) Xu, B.; Liu, W.; Kuang, C. *Eur. J. Org. Chem.* **2014**, *2014*, 2576 and references for decarboxylative ortho aroylation cited therein. (c) Li, H.; Li, P.; Tan, H.; Wang, L. *Chem. - Eur. J.* **2013**, *19*, 14432.

(10) (a) Xiao, F.; Shuai, Q.; Zhao, F.; Basle, O.; Deng, G.; Li, C.-J. *Org. Lett.* **2011**, *13*, 1614. (b) Kim, M.; Sharma, S.; Park, J.; Kim, M.; Choi, Y.; Jeon, Y.; Kwak, J. H.; Kim, I. S. *Tetrahedron* **2013**, *69*, 6552. (c) Sharma, S.; Kim, M.; Park, J.; Kim, M.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *Eur. J. Org. Chem.* **2013**, *2013*, 6656. (d) Yuan, Y.; Chen, D.; Wang, X. *Adv. Synth. Catal.* **2011**, *353*, 3373. (e) Park, J.; Kim, A.; Sharma, S.; Kim, M.; Park, E.; Jeon, Y.; Lee, Y.; Kwak, J. H.; Jung, Y. H.; Kim, I. S. *Org. Biomol. Chem.* **2013**, *11*, 2766.

(11) Zhang, Q.; Yang, F.; Wu, Y. *Chem. Commun.* **2013**, *49*, 6837.

DOI: 10.1021/acs.joc.6b01170
J. Org. Chem. 2016, 81, 6066−6074

(12) Guin, S.; Rout, S. K.; Banerjee, A.; Nandi, S.; Patel, B. K. *Org. Lett.* **2012**, *14*, 5294.
(13) Jia, X.; Zhang, S.; Wang, W.; Luo, F.; Cheng, J. *Org. Lett.* **2009**, *11*, 3120.
(14) Modak, A.; Deb, A.; Patra, T.; Rana, S.; Maity, S.; Maiti, D. *Chem. Commun.* **2012**, *48*, 4253.
(15) Santra, S. K.; Banerjee, A.; Rajamanickam, S.; Khatun, N.; Patel, B. K. *Chem. Commun.* **2016**, *52*, 4501.
(16) (a) Sotomayor, N.; Lete, E. *Curr. Org. Chem.* **2003**, *7*, 275. (b) *Handbook of Grignard Reagents*; Silverman, G. S., Rakita, P. E., Eds.; Dekker: New York, 1996. (c) Crampton, M. R. In *Organic Reaction Mechanism*; Knipe, A. J., Ed.; Wiley: New York, 2007.
(17) (a) de Meijere, A.; Diederich, F. *Metal-Catalyzed Cross-Coupling Reactions*; Wiley-VCH: Weinheim, Germany, 2004. (b) Nicolaou, K. C.; Bulger, P. G.; Sarlah, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 4442. (c) Corbet, J. P.; Mignani, G. *Chem. Rev.* **2006**, *106*, 2651. (d) Campeau, L. C.; Fagnou, K. *Chem. Commun.* **2006**, 1253. (e) Yin, L. X.; Liebscher, J. *Chem. Rev.* **2007**, *107*, 133. (f) McGlacken, G. P.; Fairlamb, I. J. S. *Eur. J. Org. Chem.* **2009**, *2009*, 4011.
(18) (a) Li, B.; Liu, B.; Shi, B.-F. *Chem. Commun.* **2015**, *51*, 5093. (b) Du, B.; Jiang, J.; Sun, P. *J. Org. Chem.* **2013**, *78*, 2786. (c) Dubost, E.; Fossey, C.; Cailly, T.; Rault, S.; Fabis, F. *J. Org. Chem.* **2011**, *76*, 6414. (d) Purohit, V. B.; Karad, S. C.; Patel, K. H.; Raval, D. K. *Catal. Sci. Technol.* **2015**, *5*, 3113. (e) Mo, S.; Zhu, Y.; Shen, Z. *Org. Biomol. Chem.* **2013**, *11*, 2756. (f) Du, Z.; Gao, L.; Lin, Y. *Chem. Res. Chin. Univ.* **2015**, *31*, 167. (g) Wan, X.; Ma, Z.; Li, B.; Zhang, K.; Cao, S.; Zhang, S.; Shi, Z. *J. Am. Chem. Soc.* **2006**, *128*, 7416. (h) Song, B.; Zheng, X.; Mo, J.; Xu, B. *Adv. Synth. Catal.* **2010**, *352*, 329. (i) Zhang, Q.; Yang, F.; Wu, Y. *Org. Chem. Front.* **2014**, *1*, 694.
(19) Santra, S. K.; Banerjee, A.; Khatun, N.; Samanta, A.; Patel, B. K. *RSC Adv.* **2015**, *5*, 11960.
(20) (a) Arman, H. D.; Gieseking, R. L.; Hanks, T. W.; Pennington, W. T. *Chem. Commun.* **2010**, *46*, 1854 and references therein. (b) Sahoo, S. K.; Jena, H. S.; Majji, G.; Patel, B. K. *Synthesis* **2014**, *46*, 1886.
(21) (a) Feigl, F.; Anger, V. *Spot Tests in Inorganic Analysis*, 6th ed.; Elsevier: Amsterdam, 1982; p 169. (b) Wang, L.; Ren, X.; Yu, J.; Jiang, Y.; Cheng, J. *J. Org. Chem.* **2013**, *78*, 12076. (c) Rout, S. K.; Guin, S.; Gogoi, A.; Majji, G.; Patel, B. K. *Org. Lett.* **2014**, *16*, 1614.
(22) Zheng, Y.; Song, W.-B.; Zhang, S.-W.; Xuan, L.-J. *Tetrahedron* **2015**, *71*, 1574.

DOI: 10.1021/acs.joc.6b01170
J. Org. Chem. 2016, 81, 6066−6074