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Copper-Mediated Oxidative Coupling of Benzamides with Maleimides via Directed C−H Cleavage

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Supporting Information

ABSTRACT: A $Cu(OAc)_2/Cy_2NMe$-mediated oxidative direct coupling of benzamides with maleimides has been developed. The aromatic C−H alkenylation with the aid of an 8-aminoquinoline-based bidentate directing group is followed by an intramolecular aza-Michael-type addition to form the isoindolone-incorporated spirosuccinimides, which are of potent interest in medicinal chemistry.

Over the past two decades, transition-metal-promoted aromatic C−H functionalization has received much attention and grown rapidly because of its capacity to transform ubiquitous C−H bonds into versatile C−C and C−X bonds without prefunctionalization steps, such as halogenation and stoichiometric metalation, which are inevitable in the conventional cross-coupling strategy.[1] To date, numerous transition metal salts and complexes have been employed for this type of transformation. Among them, copper is one of the less expensive, less toxic, and abundant promoters in aromatic C−H activation and enables some unique and challenging transformations, which are frequently difficult to achieve even in the presence of noble metals, including palladium, rhodium, and ruthenium.[2] Particularly, copper-mediated oxidative coupling reactions have been widely studied by many synthetic chemists, and now a variety of carbon- and heteroatom-based nucleophiles are accessible as the coupling partners. However, despite significant advances in this research field, the use of alkenes still remains a challenge. Given the ready availability and robustness of alkenes, further development of copper-promoted direct oxidative coupling with alkenes is greatly appealing.

Recently, our group[3] and others[4] focused on a bidentate coordination strategy[5] and succeeded in otherwise challenging copper-mediated oxidative C−C and C−X formations via a directed C−H cleavage. The above seminal works prompted us to develop the copper-mediated direct coupling with alkenes by using the double coordination strategy. Herein, we report an 8-aminoquinoline-directed, $Cu(OAc)_2/Cy_2NMe$-mediated oxidative coupling of benzamide C−H bonds with maleimides. The reaction proceeds through an oxidative alkenylation of aromatic C−H bonds followed by an intramolecular Michael addition to afford the corresponding isoindolone-incorporated spirosuccinimides,[6] which are of potent interest in medicinal chemistry.[7] To the best of our knowledge, this is the first successful example of the copper-mediated oxidative coupling of aromatic C−H bonds with alkenes.[8]

Our optimization studies commenced with benzamide **1a** bearing an 8-aminoquinoline auxiliary, which was originally introduced by Daugulis,[9] and *N*-methylmaleimide (**2a**; Table 1). In an early experiment, treatment of **1a** with 2.0 equiv of **2a** in the presence of 2.0 equiv of $Cu(OAc)_2$ and 1.0 equiv of PivOH in DMF at 150 °C for 3 h afforded the desired oxidative coupling product, **3aa**, in 49% NMR yield. Concurrently, we also observed a 66:34 diastereomixture of the 1:2 coupling product **4aa** (33% combined NMR yield; entry 1). The structures of **3aa** as well as the major diastereomer of **4aa** were unambiguously confirmed by NMR, HRMS, and X-ray analysis.[10] To improve the chemoselectivity of the reaction, we then tested various additives. To our delight, some organic bases were found to effectively suppress the formation of **4aa** (entries 2−7). Particularly, Cy_2NMe proved to be optimal, and **3aa** was formed in 43% NMR yield with only a trace amount of **4aa** (entry 5). On the other hand, inorganic bases such as Na_2CO_3 completely shut down the reaction (entry 8). Subsequent investigation of the reaction stoichiometry revealed that an increase in the amount of both **2a** and $Cu(OAc)_2$ to 4.0 equiv gave **3aa** in 78% NMR yield (entry 9). Notably, while a longer reaction period (24 h) was required, the oxidative coupling reaction also proceeded well even at 80 °C to furnish **3aa** in a quantitative NMR yield (entry 10). At lower temperature, the effect of Cy_2NMe was more remarkable: in the absence of Cy_2NMe, **3aa** was observed in only 30% NMR yield (entry 11). Thus, Cy_2NMe not only improved the chemoselectivity but also accelerated the reaction itself. In contrast, the addition of PivOH gave a relatively minor effect on the yield (entry 12). Additionally, benzamides that bear monodentate (**A**) and other bidentate coordinating groups (**B** and **C**) gave no coupling product even at 150 °C (see Table 1), indicating that the aminoquinoline-based N,N-chelating nature and relatively acidic NH of **1a**[11] are essential for the successful conversion.[12]

With the optimized conditions in hand (entry 10 in Table 1), we investigated the scope and limitations of the oxidative

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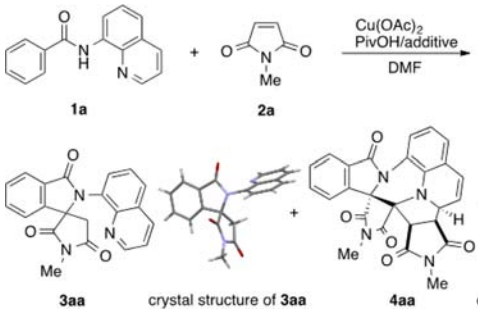
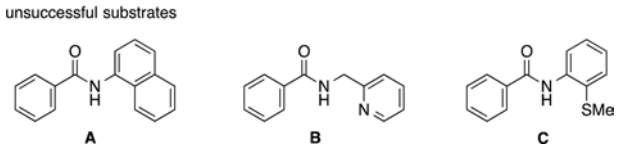
Table 1. Optimization Studies for Copper-Mediated Oxidative Coupling of Benzamide 1a with *N*-Methylmaleimide (2a)[a]



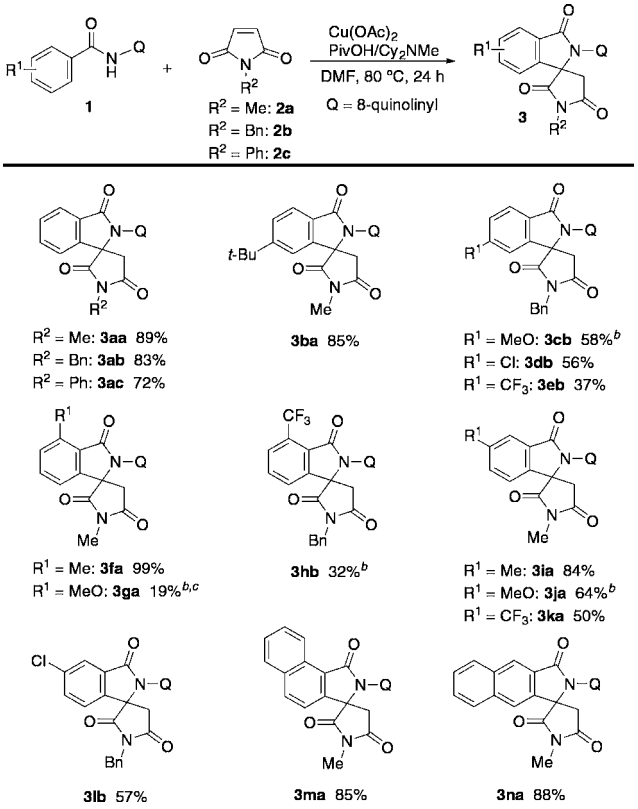
			NMR yield (%)[b]	
entry	additive	conditions	3aa	4aa
1	none	150 °C, 3 h	49	33 (66:34)[c]
2	pyridine	150 °C, 3 h	32	trace
3	Et_3N	150 °C, 3 h	46	5
4	*i*-PrNEt$_2$	150 °C, 3 h	41	5
5	Cy_2NMe	150 °C, 3 h	43	trace
6	DABCO	150 °C, 3 h	28	trace
7	DBU	150 °C, 3 h	0	0
8	Na_2CO_3	150 °C, 3 h	0	0
9[d]	Cy_2NMe	150 °C, 3 h	78	trace
10[d]	Cy_2NMe	80 °C, 24 h	quant (89)	0
11[d]	none	80 °C, 24 h	30	0
12[d,e]	Cy_2NMe	80 °C, 24 h	95	0

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.50 mmol), $Cu(OAc)_2$ (0.50 mmol), PivOH (0.25 mmol), additive (1.0 mmol), DMF (1.5 mL), N_2. [b]^{1}H NMR yield. Yield is given in parentheses. [c]Diastereomeric ratio. [d]With **2a** (1.0 mmol) and $Cu(OAc)_2$ (1.0 mmol). [e]Without PivOH.



coupling. Representative products are shown in Scheme 1. As the alkene partner, *N*-benzyl- and *N*-phenylmaleimides **2b** and **2c** were also suitable, and the corresponding spirosuccinimides **3ab** and **3ac** were obtained in 83% and 72% yields, respectively. The substitution effects in the benzamide were then evaluated. The copper-based system accommodated electron-neutral *tert*-butyl (**3ba**), electron-donating methoxy (**3cb**), and electron-withdrawing chloro (**3db**) and trifluoromethyl (**3eb**) groups at the *para* position, but the latter cases (**3cb**, **3db**, and **3eb**) gave somewhat lower efficiency. Similar trends were observed in the reaction of the *ortho*-substituted benzamides: 2-methylbenzamide resulted in nearly quantitative formation of **3fa**, whereas methoxy (**3ga**) and trifluoromethyl (**3hb**) substituents showed moderate reactivity even at higher temperature (150 °C). When the *meta*-substituted benzamides were applied, the reaction occurred exclusively at the sterically more accessible position, irrespective of electronic nature of the substituent (**3ia**, **3ja**, **3ka**, and **3lb**). The naphthalene ring was also tolerated under the standard conditions (**3ma** and **3na**). In line with the above *meta*-substituted substrates, the naphthalene-2-carboxamide dominantly formed the C3-functionalized product **3na**. Additionally, a more easily removable 5-methoxyquinolinyl group (vide infra) also worked well at 150 °C[13] under

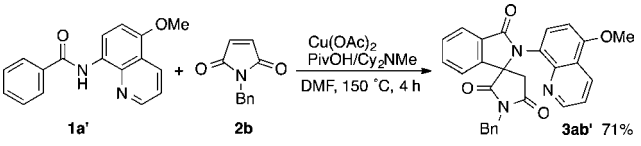
Scheme 1. Copper-Mediated Oxidative Direct Coupling of Various Benzamides 1 and Maleimides 2[a]



[a]Reaction conditions: **1** (0.25 mmol), **2** (1.0 mmol), $Cu(OAc)_2$ (1.0 mmol), PivOH (0.25 mmol), Cy_2NMe (1.0 mmol), DMF (1.5 mL), 80 °C, 24 h, N_2. The yields are given. [b]At 150 °C for 4 h. [c]NMR yield.

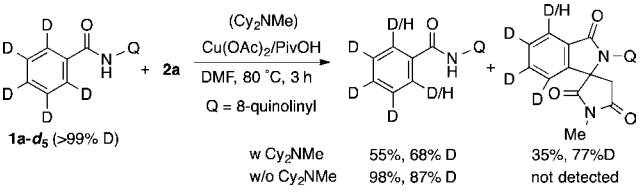
otherwise identical conditions to give **3ab′** in 71% yield (Scheme 2).[14]

Scheme 2. Copper-Mediated Oxidative Direct Coupling of Benzamide 1a′ with *N*-Benzylmaleimide (2b)



To gain some mechanistic insight into the C−H cleavage step, the following deuterium-labeling experiments with **1a-*d*$_5$** were performed (Scheme 3). After 3 h under the standard conditions, both the coupling product and remaining staring material underwent significant H/D scrambling at the *ortho* position. On the other hand, in the absence of Cy_2NMe, the reaction was much slower, and relatively small but significant

Scheme 3. Deuterium-Labeling Experiments



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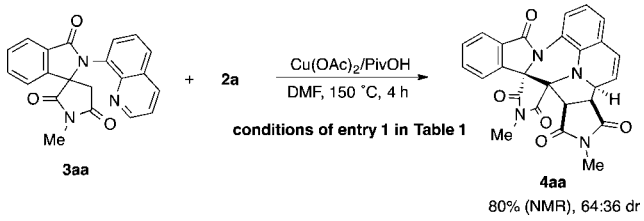
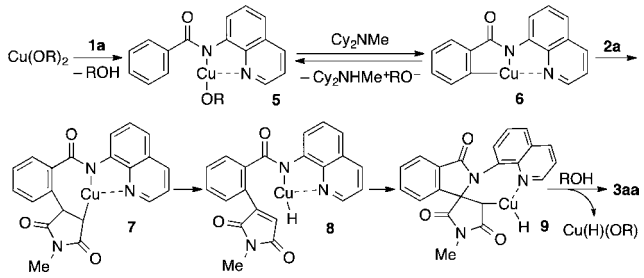
H/D exchange of the recovered benzamide was observed by ^{1}H and ^{2}H NMR analysis. These outcomes suggest that the reversible C−H metalation occurs under the standard conditions and that Cy_2NMe not only facilitates the C−H cleavage of the benzamide **1a** but also accelerates other critical elementary steps. In addition, when the isolated spirosuccinimide **3aa** was resubjected to the conditions of entry 1 in Table 1, a 66:34 diastereomixture of the 1:2 coupling product **4aa** was formed in 80% NMR yield, thus confirming that **3aa** is the intermediate for **4aa** (Scheme 4).

Scheme 4. Formation of 4aa from 3aa and *N*-Methylmaleimide (2a)



On the basis of the above findings and literature information, we are tempted to assume the reaction mechanism of **1a** with **2a** as follows (Scheme 5). Initial neutral and anionic N,N-bidentate coordination of the aminoquinoline moiety in **1a** to the $Cu(OR)_2$ forms chelated species **5**, the coordination mode of which is supported by the unsuccessful conversion of the benzamides bearing other monodentate and bidentate coordinating groups (Table 1). Subsequent Cy_2NMe-assisted C−H cupration (**5** → **6**) is followed by insertion of the maleimide **2a** to the C−Cu bond of **6** to generate the alkylcopper intermediate **7**. The spirosuccinimide **3aa** is then formed by the β-hydride elimination[15]/intramolecular aza-Michael-type addition/protonation sequence (**7** → **8** → **9** → **3aa**). Given the significant acceleration effect of Cy_2NMe observed in Scheme 5, it is believed to work as an ancillary ligand and/or an external base and promote the insertion and/or β-hydride elimination step. The liberated Cu−H species may be unstable and eventually decompose under the standard conditions. An alternative pathway includes a dissociation of the alkenylated product and subsequent off-cycle, spontaneously intramolecular aza-Michael addition.[16] The exact role of PivOH is not clear, but it can provide the pivalate ligand to the Cu center and somewhat accelerate the C−H cleavage step.[17] Additionally, we cannot completely exclude the possibility of Cu(III) intermediacy (see Scheme S1 for another mechanism).[18]

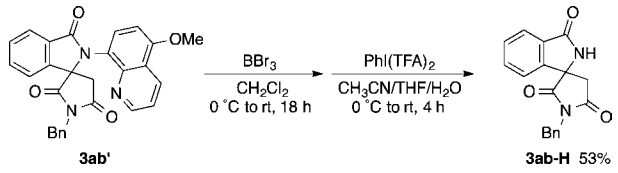
Scheme 5. Plausible Mechanism for Formation of 3aa (R = Ac or Piv)



On the other hand, as shown in Scheme S2, under more harsh conditions (150 °C, without Cy_2NMe), the initially formed **3aa** is remetalated by $Cu(OR)_2$, and successive insertion of the second maleimide **2a** and C−N double bond of the quinoline ring affords the copper amide intermediate **12**. The formation of **4aa** then follows from the cupration at the relatively acidic, proximal C−H α to the carbonyl (**12** → **13**) and reductive elimination (**13** → **4aa**).[19]

We finally attempted the removal of the directing group from the coupling product (Scheme 6). The methoxyquinolinyl group was removed by sequential addition of BBr_3 and $PhI(TFA)_2$,[20] and the corresponding NH-isoindolone-containing spirosuccinimide **3ab-H** was obtained in an acceptable yield. However, the methoxyquinoline-substituted substrate generally showed lower reactivity and required more forcing conditions (**3ab** vs **3ab′**). Thus, overall reaction efficiency is still moderate. Additional optimization studies on both the oxidative coupling and auxiliary removal are essential and currently underway.

Scheme 6. Removal of Directing Group



In summary, we have developed a $Cu(OAc)_2$-mediated oxidative coupling of benzamides with maleimides via an 8-aminoquinoline-directed C−H cleavage to form the corresponding spirosuccinimides, which are of potent interest in medicinal chemistry. The reaction proceeds smoothly even in the presence of a base metal species, $Cu(OAc)_2$, alone. Additionally, significant acceleration effects of the organic base, i.e., Cy_2NMe, are also found. This represents the new, unique example of the Cu-promoted direct oxidative coupling of aromatic C−H bonds with alkenes. Further development of related Cu-based C−H activation/coupling transformations is ongoing in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01940.

^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR spectra for products and ORTEP drawings (PDF)
CIF file of **3aa** (CIF)
CIF file of **4aa** (CIF)

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Notes

The authors declare no competing financial interest.

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(10) Crystallographic data for the structures has been deposited with the Cambridge Crystallographic Data Center (CCDC 1408682 and 1408683). See the Supporting Information for details.

(11) The ^{1}H NMR chemical shifts of NH in **1a**, **A**, **B**, and **C** are 10.76, 8.21, 7.61, and 9.26 ppm, respectively ($CDCl_3$, 25 °C).

(12) Our preliminary attempts to apply catalytic conditions with terminal oxidants such as O_2 and MnO_2 remained unsuccessful. No coupling product was observed, and a large amount of **1a** was recovered intact. See the Supporting Information for more detailed optimization studies.

(13) Under the standard conditions (80 °C, 24 h), **1a′** coupled with **2a** in only 28% yield. The observed lower reactivity of **1a′** can be associated with the lower acidity of NH (^{1}H NMR chemical shift: 10.51 in $CDCl_3$ at 25 °C).

(14) The current major limitation of the present protocol is inaccessibility to alkenes other than the maleimides. Unsuccessful alkenes included maleic anhydride, acrylates, styrenes, and norbornene.

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