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Intermolecular electrochemical C(sp^3)-H/N-H cross-coupling of xanthenes with *N*-alkoxyamides: radical pathway mediated by ferrocene as a redox catalyst

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Abstract. Efficient intermolecular dehydrogenative cross-coupling of *N*-alkyloxyamides with xanthenes is reported. The protocol is carried out in an undivided cell under constant current conditions employing simple, cheap and readily available ferrocene (Fc) as a redox catalyst. Cyclic voltammetry and control experiments disclosed that the dehydrogenative cross-coupling reaction may proceed via an amidyl radical.

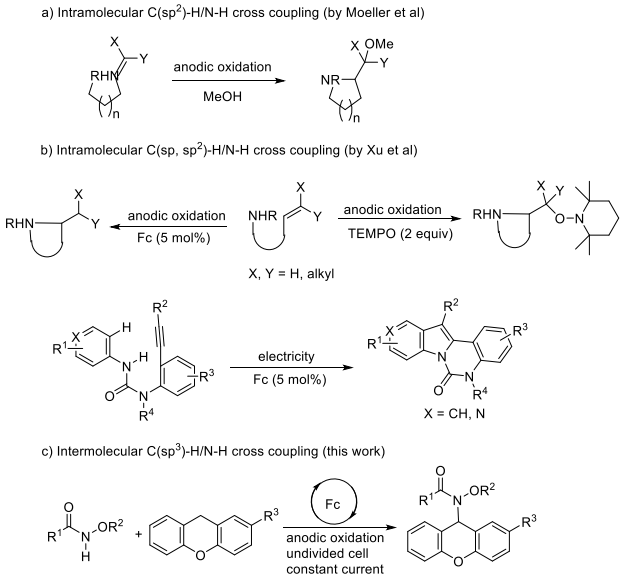
Keywords: Electrochemical oxidative amination; C-N formation; Ferrocene; Redox mediator

Introduction

The cross dehydrogenative coupling to form new C-heteroatom bonds has emerged as a profound method in organic synthesis due to its step- and atom economy characteristics as well as avoiding the prefunctionlization of substrates.[1] Among various C-heteroatom bonds, the C-N bond has been in the central position since C-N bonds are important structural moieties (such as amines, amides, and peptides) in natural products, pharmaceuticals, agrochemicals and material sciences.[2] As a result, efficient and selective construction of a new C-N bond has always been paid much attention in the industrial and academic setting. Although it is taught in a college textbook that the C-N bond could be formed from a nucleophilic substitution reaction of an alkyl halide with a nitrogen-nucleophile, the transition-metal catalyzed *ionic type* cross couplings for forming C-N bonds are more popular and have been widely employed in the synthesis of natural products, polymers, and pharmaceutical compounds.[3] Alternatively, oxidative *radical processes* have also been developed for the formation of C(sp^2)-N[4] and C(sp^3)-N bonds.[5] Despite these advances, most of these strategies mentioned above require either prefunctionalized substrates, such as alkyl halides or sulfonates as nucleophilic partners, or a combination of a transition metal catalyst and an excess amount of chemical oxidant. Moreover, the toxicity of residual traces of transition metal in products, from the employed catalysts or oxidants, is highly concerned. Consequently, mild, metal-free and atom economic oxidative C-N bonds formation is highly desirable.

Electrochemistry provides an alternative, environmentally benign method to generate nitrogen-centred radical for the formation of C-N bonds, either through direct electrolysis or via a redox catalyst playing the role of the electron transfer agent (indirect electrolysis). For example, a direct intramolecular anodic oxidation of olefins tethering a nitrogen trapping group was proceeded to synthesize nitrogen-containing heterocycles by Moeller et al. (Scheme 1a).[6] Xu and co-workers achieved the electrocatalytic hydroamidation and aminooxygenation of unactivated alkenes using Fc or TEMPO as redox catalysts (Scheme 1b).[7] Mechanistically, these processes reported above involves the electrochemical generation of a nitrogen-centred radical and its subsequent intramolecular addition to unsaturated C-C bonds, thus constructing C(sp^2, sp^3)-N bonds. Herein, we describe an intermolecular radical substitution between C(sp^3)-H and N-H bond via electrochemical cross dehydrogenative coupling of *N*-methoxyamides[8] and xanthenes[9] using cheap Fc as the redox catalyst (Scheme 1c). The process is conveniently carried out in an undivided cell under constant current conditions. To the best of our knowledge, this work represents the first example of intermolecular electrochemical C(sp^3)-H/N-H

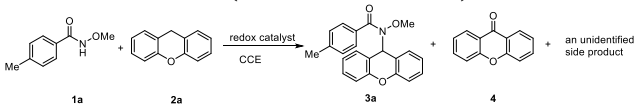
dehydrogenative cross-coupling using a redox mediator.[10]



Scheme 1. Electrochemically oxidative cross-coupling for the formation of C-N bonds.

Results and Discussion

To prove the concept described above, *N*-methoxyamide **1a** and xanthene **2a** were chosen as model substrates to optimize the reaction conditions (Scheme 2 and Table 1). The electrochemical cross-coupling reaction of **1a** with **2a** was performed in an undivided cell equipped with a carbon anode and a carbon cathode. When NaBr was used as a mediator, initial screening of supporting electrolyte/solvent system indicates that $LiClO_4$ in CH_3CN/CH_2Cl_2 (v: v = 2: 1) was the best (entries 1-7). Based on our experience in the halide mediated electrochemical formation of chemical bonds,[11] various halide-containing salts as a redox catalyst in the optimal solution were then screened (entries 8-11). After some attempts, NH_4Br was proved to be the best halide-based catalyst (entry 8); the electrochemical cross-coupling led to the formation of product **3a** in 40% yield, along with the generation of xanthone, **4**, and another side-product. Based on the spectroscopic analysis, the side product should derive from **1a**, but its structure could not be identified at this stage. The yield of **3a** increased to 51% in the presence of Na_2CO_3 as an additive (entry 12). By switching the catalyst to Fc, the yield of product **3a** increased to 46% and 62% before and after the addition of Na_2CO_3 (entries 13 and 14). These results indicate that additive plays an important role, as a result, different additives were examined in the next. However, other commonly used bases such as NaOH, pyridine, DBU, and Et_3N, failed to give better yields (entries 15-18). Control experiment revealed that Fc is essential for this electrochemical cross-coupling reaction, while only 23% yield of product **3a** was obtained in the absence of Fc along with the formation of the unidentified side product (entry 19). Lowering the catalyst loading to 25 mol % decreased the yield of product **3a** to 38% (entry 20). Notably, the redox catalyst Fc could be recovered in almost quantitatively after column chromatography. Finally, other anodes and cathodes were also examined, however, the results showed that none of the ones tested gave better yield than that of with carbon as the anode and cathode (entries 21-22 *vs* 14).



Scheme 2. Electrochemical dehydrogenative cross-coupling of **1a** and **2a**.

Table 1. Optimization of the reaction conditions[a].

Entry	Catalyst	Additive	Anode /Cathode	Supporting electrolyte	Yield (%) [b]
1	NaBr	-	C/C	MeOH	20
2	NaBr	-	C/C	$LiClO_4/CH_3CN$	14
3	NaBr	-	C/C	$LiClO_4$/EtOH	18
4	NaBr	-	C/C	$LiClO_4$/THF:MeOH (5:1)	trace
5	NaBr	-	C/C	MeOH:CH_2Cl_2 (2:1)	22
6	NaBr	-	C/C	$LiClO_4/CH_3CN:H_2O$ (4:1)	12
7	NaBr	-	C/C	$LiClO_4/CH_3CN:CH_2Cl_2$ (2:1)	34
8	NaBr	-	C/C	$LiClO_4/CH_3CN:CH_2Cl_2$ (2:1)	40
9	Et_4NBr	-	C/C	$LiClO_4/CH_3CN:CH_2Cl_2$ (2:1)	23
10	n-Bu_4NI	-	C/C	$LiClO_4/CH_3CN:CH_2Cl_2$ (2:1)	trace
11	NH_4I	-	C/C	$LiClO_4/CH_3CN:CH_2Cl_2$ (2:1)	12
12	NH_4Br	Na_2CO_3	C/C	$LiClO_4/CH_3CN:CH_2Cl_2$ (2:1)	51
13	Fc	-	C/C	$LiClO_4/CH_3CN:CH_2Cl_2$ (2:1)	46
14	Fc	Na_2CO_3	C/C	$LiClO_4/CH_3CN:CH_2Cl_2$ (2:1)	62
15	Fc	NaOH	C/C	$LiClO_4/CH_3CN:CH_2Cl_2$ (2:1)	58
16	Fc	Pyridine	C/C	$LiClO_4/CH_3CN:CH_2Cl_2$ (2:1)	trace
17	Fc	DBU	C/C	$LiClO_4/CH_3CN:CH_2Cl_2$ (2:1)	46
18	Fc	Et_3N	C/C	$LiClO_4/CH_3CN:CH_2Cl_2$ (2:1)	42
19	---	Na_2CO_3	C/C	$LiClO_4/CH_3CN:CH_2Cl_2$ (2:1)	23
20	Fc	Na_2CO_3	C/C	$LiClO_4/CH_3CN:CH_2Cl_2$ (2:1)	38
21	Fc	Na_2CO_3	Pt/C	$LiClO_4/CH_3CN:CH_2Cl_2$ (2:1)	60
22	Fc	Na_2CO_3	C/Fe	$LiClO_4/CH_3CN:CH_2Cl_2$ (2:1)	55

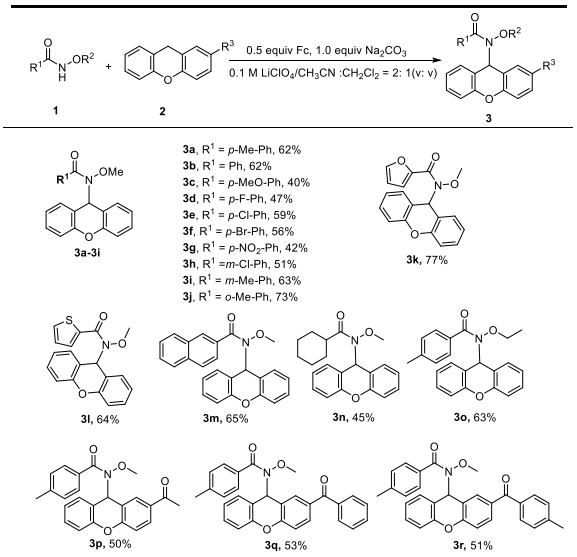
[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.2 mmol), catalyst (0.5 mmol) and additive (1.0 mmol) in an undivided cell, J = 5 mA/cm^2, room temperature. Xanthone and an

unidentified material were also formed in different amounts. [b] Isolated yields. [c] Along with xanthone in 15% yield. [d] Fc (0.25 mmol).

Under the optimized conditions, the substrate scope of this electrochemical cross-coupling reaction with various *N*-methoxyamides **1** was investigated. As shown in Table 2, reactions with all of the *N*-methoxyamides bearing electron-donating or electron-withdrawing substituents gave the corresponding products in good to moderate yields. For *para*-substituted *N*-methoxyamides, strong electron-donating group (such as methoxyl) and the electron-withdrawing nitro-group were not compatible with the optimized conditions, leading to the formation of **3c** and **3g** in much lower yields. *N-M*ethoxyamides with *meta*-substituents were also good substrates for theses electrochemical cross-coupling reactions, giving corresponding products **3h** and **3i** in 51% and 63% yields, respectively. In addition, *ortho*-methyl substituted substrate **1j** gave corresponding cross-coupling product **3j** in up to 73%. It is noteworthy that heteroarene amides and 2-naphthamide also tolerated well to give cross-coupling products **3k-3m** in 64-77% yields. In addition to aromatic amides, aliphatic amides, such as **2n**, also worked well to give the corresponding **3n** in 45% yield. For the R^2 group, when the methyl group was replaced by an ethyl group, the corresponding product **3o** was obtained in 63% yield.

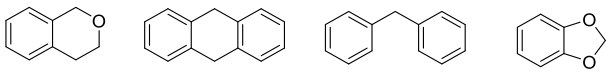
Next, some substituted xanthenes were tested under the optimized conditions. As shown in Table 2, acyl-substituted xanthenes **1p**-**1r** were well tolerated to give corresponding products **3p**-**3r** in 50-53% yields.

Table 2. Substrate scope of amides and xanthenes[a].



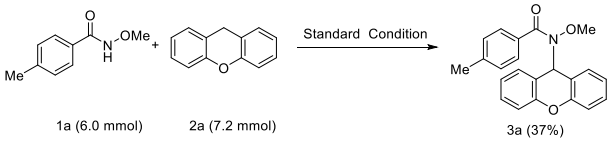
[a] Reaction conditions: *N*-alkyloxy amides **1** (1.0 mmol), xanthenes **2** (1.2 mmol), Fc (0.5 mmol) and Na_2CO_3 (1.0 mmol) in a mixed solvent CH_3CN/CH_2CH_2 (2: 1 = v: v), undivided cell, J = 5 mA/cm^2, room temperature.

To further examine the limitation of this reaction, other substrates were also investigated. As shown in Scheme 3, when isochromane, 9,10-dihydroanthracene, diphenylmethane and 1,2-methylenedioxybenzene were subjected to react with **1a** under the standard conditions, the desired corresponding products were not detected and most of the starting **1a** was decomposed, although the exact reason was not clear yet.



Scheme 3. Molecular structures of C(sp^3)-H–containing reagents that failed to react under the optimized reaction conditions.

The large-scale preparation of product **3a** highlights the utility of this procedure (Scheme 4). Upon scaling up the electrochemical reaction to 6.0 mmol, the product **3a** was obtained in 37% yield.



Scheme 4. Gram-scale synthesis.

As mentioned above, apart from the most effective ferrocene, NH_4Br also mediated the cross-coupling of **1a** with **2a**, although in a slightly lower yield (See Table 1, entry 12 vs entry 14). Therefore, the electrochemical cross-coupling of *N*-alkyloxy amides and xanthenes was also investigated to demonstrate the generality of NH_4Br as the redox catalyst. As shown in Table 3, when xanthene **2a** was subjected to electrolysis with **1f** under the standard conditions but using NH_4Br as the mediator, the adduct **3f** was generated in 32% yield, less than with ferrocene (56% yield). A similar trend was also observed for other substrates. For example, NH_4Br-mediated cross coupling gave **3i**, **3j**, **3m,** and **3o** in 51%, 59%, 29% and 48% yields, respectively, whereas slightly higher yields were obtained using ferrocene as the mediator.

Table 3. Cross-coupling of *N*-alkyloxy amides and xanthenes mediated by NH_4Br. [a,b]

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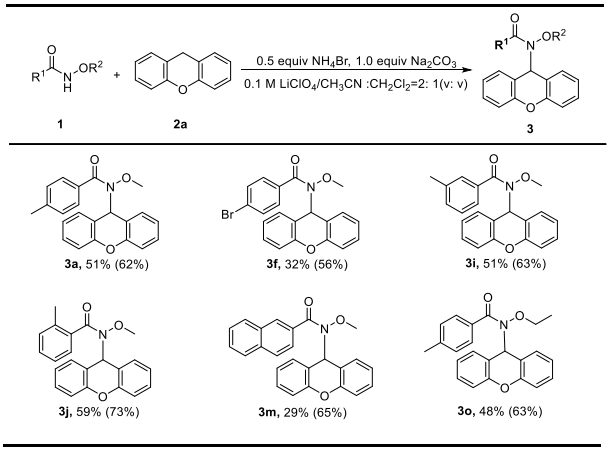


[a] Reaction conditions: *N*-alkyloxy amides **1** (1.0 mmol), xanthenes **2** (1.2 mmol), NH_4Br (0.5 mmol) and Na_2CO_3 (1.0 mmol) in a mixed solvent CH_3CN/CH_2CH_2 (2: 1 = v: v), undivided cell, J = 5 mA/cm^2, room temperature. [b] The yields using ferrocene as mediator are shown in parentheses for a comparison

To better understand the mechanism for the electrochemical dehydrogenative cross-coupling of *N*-alkoxyamides and xanthenes, cyclic voltammetry was initially employed. As shown in Figure 1, *N*-alkoxyamide **1a** was redox inactive in the range of 0.0 V – 2.0 V vs $Ag/AgNO_3$ (0.1 M in CH_3CN) (curve a), whereas it afforded an irreversible oxidation wave at 0.73 V vs $Ag/AgNO_3$ (0.1 M in CH_3CN) when stoichiometric amount of *t*-BuOK was added to prepare its corresponding anion (curve b). This result indicates that **1a** is easily oxidized in the presence of a base. In a contrast, xanthene **2a** give an obvious oxidation wave at 1.61 V vs $Ag/AgNO_3$ (0.1 M in CH_3CN) in the absence and presence of *t*-BuOK (curves c and d). Curve e was CV of Fc, giving a reversible oxidation peak at 0.48 V and reduction peak at 0.40 V vs. $Ag/AgNO_3$ (0.1 M in CH_3CN). The CV of Fc did not change when either **1a** (curve f) or *t*-BuOK was added (curve g). However, an obvious catalytic current was observed in the presence of **1a** and *t*-BuOK, along with complete disappear of reduction current (curve h), or decrease of intensity of cathodic peak current at 100 mV/s scan rate (see Figure S1 in Supporting Information for details). These results drop a hint that a homogeneous electron transfer occurs between Fc at its oxidized form and **1a** with the assistance of *t*-BuOK. This observation is reasonable when one takes note of only 0.25 V of peak potential gap between Fc and **1a** in the presence of a base (0.73 for **1a** in the presence of *t*-BuOK vs. 0.48 V for Fc). Notably, the homogeneous electron transfer did not occur between Fc and **2a** in the absence and presence of *t*-BuOK, due to a large potential gap (1.61 V for **2a** vs. 0.48 V for Fc).

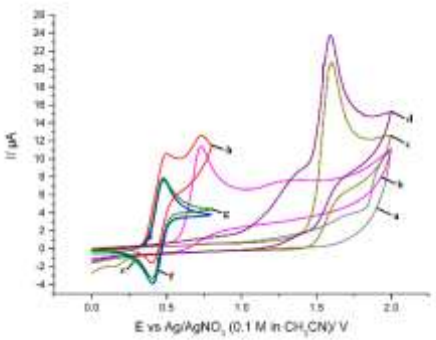
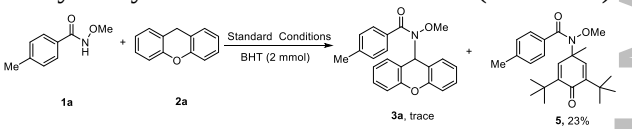


Figure 1. Cyclic voltammograms of Fc and related compounds in 0.1 M $LiClO_4/CH_3CN$: CH_2Cl_2 (2: 1 = v/ v)), using Pt working electrode, Pt wire and $Ag/AgNO_3$ (0.1 M in CH_3CN) as counter and reference electrode at 20 mV/s scan rate. a: **1a** (1.0 mmol/L), b: **1a** (1.0 mmol/L) and *t*-BuOK (20.0 mmol/L), c: **2a** (1 mmol/L); d: **2a** (1.0 mmol/L) and *t*-BuOK (20.0 mmol/L), e: Fc (1 mmol/L), f: Fc (1 mmol/L) and **1a** (2.0 mmol/L), g: Fc (1 mmol/L) and *t*-BuOK (20.0 mmol/L), h: Fc (1 mmol/L) and **1a** (2.0 mmol/L) in the presence of *t*-BuOK (40.0 mmol/L).

In addition, when the electrolysis was repeated under the standard conditions in the presence of 2 equiv of butylated hydroxytoluene (BHT), a trapping adduct **5** was isolated in 23% yield, along with trace amount of product **3a**. This result indicates that the cross-coupling may involve a radical process via an alkoxyamidyl radical as the intermediate (Scheme 5).



Scheme 5. Control experiment.

Based on CV results and control experiment, as well as previous reports, a possible reaction mechanism for the electrochemical dehydrogenative cross-coupling of *N*-methoxyamides with xanthenes is proposed and depicted in Scheme 6. The anodic oxidation of Fc (II) affords Fc (III), which undergoes homogeneous electron transfer with *N*-alkoxyamide anion **6**, generated from the reaction of *N*-alkoxyamide with a base, to give alkoxyamidyl radical, **7**. Alkoxyamidyl radical abstracts a benzylic hydrogen atom from xanthene to afford xanthene radical **8**. Then, the xanthene radical **8** loses an electron to generate cation **9**. Trapping cation **9** with *N*-alkoxyamide anion **6** gives product **3**. On the other hand, the cathodic reduction of a proton gives hydrogen. It is reported that pK_a for xanthene in DMSO is 30.0[12] and $CH_3CONHOMe$ is 17.1,[13] which indicates that the acidity of hydroxamic acid is much stronger than that of xanthene. Consequently, we believe that the homogeneous electron transfer occurs between Fc (III) and *N*-alkoxyamide anion **6**, instead of the conjugated base of xanthene.

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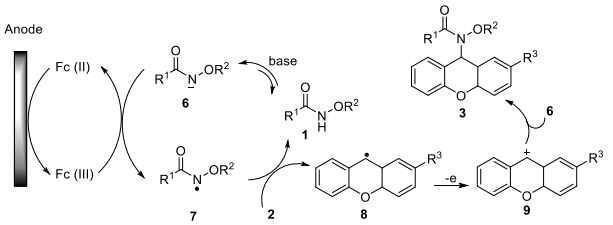
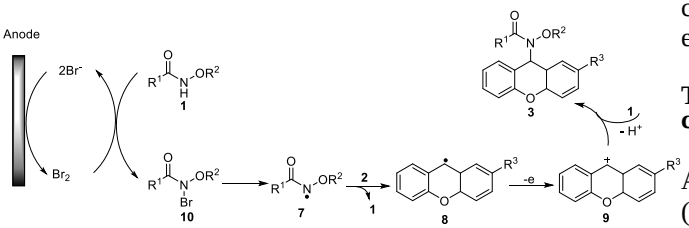


Scheme 6. A plausible mechanism for the electrochemical dehydrogenative cross-coupling of *N*-methoxyamides with xanthenes.

A plausible mechanism mediated by NH_4Br is illustrated in the Scheme 7. The reaction sequence begins with the anodic oxidation of bromide to form bromine and its subsequent reaction with *N*-alkoxyamide **1** to afford **10**. Then, a homolytic cleavage of intermediate **10** affords alkoxyamidyl radical **7**. Radical **7** abstracts a benzylic hydrogen atom from xanthene **2** to afford xanthene radical **8**. Then, the xanthene radical **8** loses an electron to generate cation **9**. Trapping cation **9** with *N*-alkoxyamide **1** gives product **3**.



Scheme 7. The plausible mechanism mediated by NH_4Br

Conclusion

In conclusion, we have developed a novel electrochemical protocol to generate *N*-alkoxyamidyl radical from *N*-methoxyamides using Fc as the mediator. By virtue of this strategy, the first example of intermolecular dehydrogenative cross-coupling of $C(sp^3)$-H and N-H was realized via mediated electrolysis. The protocol proceeds in an undivided cell under constant current conditions employs simple, cheap and readily available Fc as the redox catalyst, rather than the combination of transition metals and excess amounts of external oxidant, thereby providing an environmentally benign method to generate amidyl radical. Further application in organic synthesis of this electrochemical generation of amidy radical from *N*-alkoxyamides is underway in our laboratory

Experimental Section

Instruments and reagents

All melting points were measured with an electrothermal melting point apparatus and are uncorrected. NMR spectra were recorded using a 400 MHz spectrometer (400 MHz ^1H frequency, 100 MHz ^{13}C frequency). Chemical shifts are given as δ values (internal standard: TMS). Coupling constants are reported in Hz. Amides were synthesized according to known procedure.[14] Various xanthene derivatives 1-(9*H*-xanthen-2-yl)ethan-1-one, phenyl(9*H*-xanthen-2-yl)methanone, and *p*-tolyl(9*H*-xanthen-2-yl)methanone) were prepared according to literature procedures.[15] Other starting materials and solvents were obtained from commercial sources and used without further purification. Products were purified by chromatography on silica gel (petroleum ether/EtOAc).

Cyclic voltammetry

Cyclic voltammograms were measured using a Princeton Applied Research 273A Potentiostat/Galvanostat equipped with electrochemical analysis software, using a conventional three-electrode cell. The working electrode was a platinum disk electrode (ca. φ= 3 mm). The auxiliary and reference electrodes consisted of a Pt wire and $Ag/AgNO_3$ (0.1 M in CH_3CN), respectively. Platinum was polished with a polishing cloth before each measurement. All electrodes for CV experiments were obtained from CH Instruments, Inc. USA. The concentration of all tested compounds was 1 mmol/L, while that of the supporting electrolyte was 0.1 mol/L.

Typical procedure for the electrochemical cross-coupling of *N*-alkoxyamides and xanthenes

An undivided cell was equipped with a carbon anode (2.5×2.0 cm^2) and a carbon cathode (2.5×2.0 cm^2) and connected to a DC regulated power supply. To the cell was added amide (1 mmol), xanthene (1.2 mmol) , Fc (0.5 mmol) , Na_2CO_3 (1.0 mmol) and 15 mL of 0.1 M $LiClO_4/CH_3CN$:CH_2Cl_2 (2: 1 = v/ v). The mixture was electrolyzed using constant current conditions (~5 mA/cm^2) at room temperature under magnetic stirring. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of the amide), the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc (v: v = 8: 1) as eluent to afford the desired pure product.

N-Methoxy-4-methyl-*N*-(9*H*-xanthen-9-yl)benzamide (**3a**) Yield: 213 mg, 62%; Yellow oil; Reaction time: 7 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^1H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 3H), 2.94 (s, 3H), 7.08 (s, 1H), 7.12-7.19 (m, 6H), 7.33-7.37 (m, 2H), 7.56 (dd, *J* = 7.7 Hz, 1.3 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 52.7, 64.5, 116.8, 118.8, 123.5, 128.5, 128.8, 129.5, 129.6, 131.2, 141.2, 152.8, 169.9; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{19}NNaO_3$ $(M+Na)^+$: 368.1251, found: 368.1257.

N-Methoxy-*N*-(9*H*-xanthen-9-yl)benzamide (**3b**) Yield: 205 mg, 62%; Yellow solid; mp: 86-89 °C; Reaction time: 6 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^1H NMR (400 MHz, $CDCl_3$) δ 2.92 (s, 3H), 7.08 (s, 1H), 7.12-7.19 (m, 4H), 7.33-7.42 (m, 5H), 7.57 (dd, *J* = 7.7 Hz, 1.2 Hz, 2H), 7.65-7.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

52.7, 64.5, 116.8, 118.8, 123.5, 128.1, 128.2, 129.5, 129.7, 130.7, 134.2, 152.8, 170.0; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{17}NNaO_3$ $(M+Na)^+$: 354.1101, found: 354.1109.

N,4-Dimethoxy-*N*-(9*H*-xanthen-9-yl)benzamide (**3c**) Yield: 145 mg, 40%; Yellow oil; Reaction time: 7.5 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96 (s, 3H), 3.83 (s, 3H), 6.88 (d, *J* = 8.8 Hz, 2H), 7.11 (s, 1H), 7.12-7.20 (m, 4H), 7.34-7.38 (m, 2H), 7.56 (dd, *J* = 7.7 Hz, 1.2 Hz, 2H), 7.73 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.7, 55.3, 64.4, 113.4, 116.7, 118.9, 123.4, 126.1, 129.5, 129.5, 130.6, 152.8, 161.7, 169.2; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{19}NNaO_4$ $(M+Na)^+$: 384.1206, found: 384.1209.

4-Fluoro-*N*-methoxy-N-(9*H*-xanthen-9-yl)benzamide (**3d**) Yield: 163 mg, 47%; Yellow oil; Reaction time: 7 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.91 (s, 3H), 7.03-7.07 (m, 2H), 7.13-7.21 (m, 5H), 7.35-7.39 (m, 2H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.70-7.73 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.5, 64.6, 115.2 (d, *J* = 21.8 Hz), 116.8, 118.7, 123.6, 129.5, 129.7, 130.0 (d, *J* = 3.8 Hz), 130.9 (d, *J* = 8.3 Hz), 152.8, 164.1 (d, *J* = 249.8 Hz), 168.6; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{16}FNNaO_3$ $(M+Na)^+$: 372.1006, found: 372.1007.

4-Chloro-*N*-methoxy-N-(9*H*-xanthen-9-yl)benzamide (**3e**) Yield: 214 mg, 59%; Yellow oil; Reaction time: 6 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90 (s, 3H), 7.10 (s, 1H), 7.12-7.19 (m, 4H), 7.31-7.38 (m, 4H), 7.55 (dd, *J* = 7.6 Hz, 1.2 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.6, 64.7, 116.9, 118.6, 123.6, 128.4, 129.5, 129.8, 129.9, 132.4, 137.0, 152.8, 168.7; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{16}ClNNaO_3$ $(M+Na)^+$: 388.0711, found: 388.0710.

4-Bromo-*N*-methoxy-*N*-(9*H*-xanthen-9-yl)benzamide (**3f**) Yield: 229 mg, 56%; Yellow oil; Reaction time: 6 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.90 (s, 3H), 7.10 (s, 1H), 7.12-7.19 (m, 4H), 7.33-7.37 (m, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.6, 64.8, 116.9, 118.6, 123.6, 125.4, 129.5, 129.8, 130.1, 131.4, 132.9, 152.8, 168.8; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{16}BrNNaO_3$ $(M+Na)^+$: 432.0206, found: 432.0210.

N-Methoxy-4-nitro-*N*-(9*H*-xanthen-9-yl)benzamide (**3g**) Yield: 158 mg, 42%; Yellow oil; Reaction time: 6 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, CDCl3) δ 2.91 (s, 3H), 7.16 (s, 1H), 7.18-7.25 (m, 4H), 7.40-7.44 (m, 2H), 7.59 (d, *J* = 7.2 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 8.24 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.8, 65.0, 117.0, 118.3, 123.3, 123.7, 129.2, 129.4, 130.0, 140.1, 148.9, 152.9, 168.0; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{16}N_2NaO_5$ $(M+Na)^+$: 399.0951, found: 399.0950.

3-Chloro-*N*-methoxy-*N*-(9*H*-xanthen-9-yl)benzamide (**3h**) Yield: 185 mg, 51%; Yellow oil; Reaction time: 5.5 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.92 (s, 3H), 7.10 (s, 1H), 7.14-7.20 (m, 4H), 7.28-7.32 (m, 1H), 7.34-7.41 (m, 3H), 7.52-7.56 (m, 3H), 7.64-7.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.6, 64.8, 116.9, 118.5, 123.7, 126.4, 128.4, 129.5, 129.8, 130.8, 134.1, 135.8, 152.8, 168.4; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{16}ClNNaO_3$ $(M+Na)^+$: 388.0711, found: 388.0715.

N-Methoxy-3-methyl-*N*-(9*H*-xanthen-9-yl)benzamide (**3i**) Yield: 218 mg, 63%; Yellow solid; mp: 64-66 °C; Reaction time: 5.5 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.98 (s, 3H), 7.11 (s, 1H), 7.17-7.23 (m, 4H), 7.29-7.31 (m, 2H), 7.37-7.41 (m, 2H), 7.48 (d, *J* = 6.4 Hz, 1H), 7.52 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 52.6, 64.5, 116.8, 118.8, 123.5, 125.2, 128.0, 128.7, 129.5, 129.6, 131.5, 134.2, 137.9, 152.8, 170.2; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{19}NNaO_3$ $(M+Na)^+$: 368.1257, found: 368.1257.

N-Methoxy-2-methyl-*N*-(9*H*-xanthen-9-yl)benzamide (**3j**) Yield: 253 mg, 73%; Yellow oil; Reaction time: 7 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.20 (s, 3H), 2.78 (s, 3H), 7.12 (s, 1H), 7.14-7.19 (m, 6H), 7.24-7.25 (m, 2H), 7.33-7.38 (m, 2H), 7.61 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 52.0, 64.4, 116.8, 118.8, 123.5, 125.2, 126.4, 129.2, 129.7, 130.1, 134.9, 135.2, 153.1, 171.7; HRMS (ESI-TOF) m/z calcd for $C_{22}H_{19}NNaO_3$ $(M+Na)^+$: 368.1257, found: 368.1257.

N-Methoxy-*N*-(9*H*-xanthen-9-yl)furan-2-carboxamide (**3k**) Yield: 248 mg, 77%; White solid; mp: 108-109 °C; Reaction time: 5.5 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.23 (s, 3H), 6.50 (d, *J* = 2.0 Hz, 1H), 7.09 (d, J = 2.8 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 8.8 Hz, 3H), 7.37 (t, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 2H), 7.64 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.5, 65.0, 111.8, 116.7, 118.3, 118.6, 123.6, 129.7, 129.8, 145.8, 152,9, 159.7; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{15}NNaO_4$ $(M+Na)^+$: 344.0893, found: 344.0895.

N-Methoxy-*N*-(9*H*-xanthen-9-yl)thiophene-2-carboxamide (**3l**) Yield: 216 mg, 64%; Yellow solid; mp: 109-111 °C; Reaction time: 7 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.25 (s, 3H), 7.09-7.14 (m, 3H), 7.18 (d, *J* = 1.2 Hz, 1H), 7.20 (d, *J* = 1.2 Hz, 1H), 7.22 (s, 1H), 7.33-7.38 (m, 2H), 7.51-7.54 (m, 2H), 7.56 (dd, *J* = 5.2 Hz, 1.2 Hz, 1H), 7.99 (dd, *J* = 4.0 Hz, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 50.2, 62.9, 114.3, 116.2, 121.2, 124.6, 127.3, 127.3, 130.6, 131.2, 132.6 150.3, 160.8; HRMS (ESI-TOF) m/z calcd for $C_{19}H_{15}NNaO_3S$ $(M+Na)^+$: 360.0665, found: 360.0666.

N-Methoxy-*N*-(9*H*-xanthen-9-yl)-2-naphthamide (**3m**) Yield: 248 mg, 65%; Yellow solid; mp: 173-175 °C; Reaction time: 7 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.97 (s, 3H), 7.19-7.25 (m, 5H), 7.39-7.43(m, 2H), 7.52-7.59 (m, 2H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.75-7.78 (m, 1H), 7.85-7.91 (m, 3H), 8.27 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.7, 64.7, 116.8, 118.8, 123.6, 125.0, 126.5, 127.5, 127.7, 127.8, 128.8, 128.9, 129.6, 129.7, 131.4, 132.5, 134.3, 152.9,

169.8; HRMS (ESI-TOF) m/z calcd for $C_{25}H_{19}NNaO_3$ $(M+Na)^+$: 404.1257, found: 404.1255.

N-Methoxy-*N*-(9*H*-xanthen-9-yl)cyclohexanecarboxamide (**3n**) Yield: 151 mg, 45%; Yellow oil; Reaction time: 6.5 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16-1.31 (m, 3H), 1.46-1.55 (m, 2H), 1.65-1.83 (m, 5H), 2.48-2.55 (m, 1H), 3.15 (s, 3H), 6.99 (s, 1H),7.07-7.11 (m, 2H), 7.14-7.16 (m, 2H), 7.30-7.34 (m, 2H), 7.42 (dd, *J* = 7.7 Hz, 1.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.7, 25.8, 28.7, 40.7, 51.4, 65.1, 116.6, 119.3, 123.3, 129.4, 129.6, 152.8, 178.9; HRMS (ESI-TOF) m/z calcd for $C_{21}H_{23}NNaO_3$ $(M+Na)^+$: 360.1570, found: 360.1569.

N-Ethoxy-4-methyl-*N*-(9*H*-xanthen-9-yl)benzamide (**3o**) Yield: 224 mg, 63%; Orange solid; mp: 100-102 °C; Reaction time: 6.5 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.58 (t, J = 7.2 Hz, 3H), 2.34 (s, 3H), 3.06 (q, *J* = 7.2 Hz, 2H), 7.08(s, 1H), 7.11-7.17 (m, 6H), 7.31-7.35 (m, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 21.5, 52.8, 72.9, 116.7, 119.1, 123.5, 128.5, 128.7, 129.5, 129.6, 131.4, 141.0, 153.0, 170.0; HRMS (ESI-TOF) m/z calcd for $C_{23}H_{21}NNaO_3$ $(M+Na)^+$: 382.1414, found: 382.1418.

N-(2-Acetyl-9*H*-xanthen-9-yl)-*N*-methoxy-4-methylbenzamide (**3p**) Yield: 194 mg, 50%; Yellow oil; Reaction time: 7 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ2.36 (s, 3H), 2.58 (s, 3H), 2.97 (s, 3H), 7.04 (s, 1H), 7.17-7.23 (m, 5H), 7.35-7.39 (m, 1H), 7.58-7.61 (m, 3H), 7.98 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 8.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 26.5, 52.6, 64.5, 116.9, 117.1, 118.6, 118.9, 124.2, 128.4, 128.9, 129.4, 129.8, 129.9, 130.7, 131.0, 132.8, 141.4, 152.2, 156.2, 170.1, 196.3; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{21}NNaO_4$ $(M+Na)^+$: 410.1363, found: 410.1367.

N-(2-Benzoyl-9H-xanthen-9-yl)-*N*-methoxy-4-methylbenzamide (**3q**) Yield: 235 mg, 53%; Yellow solid; mp: 118-120 °C ; Reaction time: 9 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 3.03 (s, 3H), 7.03 (s, 1H), 7.18-7.26 (m, 4H), 7.29-7.32 (m, 1H), 7.39-7.50 (m, 3H), 7.56-7.63 (m, 4H), 7.79 (d, *J* = 7.5 Hz, 2H), 7.93 (d, *J* = 8.4 Hz, 1H), 8.00 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 52.9, 64.5, 116.9, 117.1, 118.5, 118.7, 124.2, 128.3, 128.4, 128.9, 129.5, 129.8, 129.9, 131.0, 131.7, 132.4, 132.5, 132.9, 137.7, 141.4, 152.3, 155.9, 170.0, 195.0; HRMS (ESI-TOF) m/z calcd for $C_{29}H_{23}NNaO_4$ $(M+Na)^+$: 472.1519, found: 472.1512.

N-Methoxy-4-methyl-*N*-(2-(4-methylbenzoyl)-9*H*-xanthen-9-yl)benzamide(**3r**) Yield: 236 mg, 51%; Yellow solid; mp: 142-145 °C; Reaction time: 8 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ2.38 (s, 3H), 2.45 (s, 3H), 3.03 (s, 3H), 7.04 (s, 1H), 7.18-7.31 (m, 7H), 7.39 (t, *J* = 9.6 Hz, 1H), 7.58-7.63 (m, 3H),7.71 (d, *J* = 8.1 Hz, 2H), 7.90 (d, *J* = 8.4 Hz, 1H), 8.00(s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 21.7, 52.8, 64.5, 116.9, 117.0, 118.4, 118.7, 124.2, 128.4, 128.9, 129.1, 129.5, 129.9, 130.1, 131.0, 131.6, 132.3, 133.2, 135.0, 141.1, 143.3, 152.3, 155.7, 170.0, 194.8; HRMS (ESI-TOF) m/z calcd for $C_{30}H_{25}NNaO_4$ $(M+Na)^+$: 486.1676, found: 486.1678.

Xanthone (**4**)[14] Yield: 30 mg, 15%; White solid; mp:177-178 °C; Reaction time: 6.5 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.6 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.74-7.78 (m, 2H), 8.37 (dd, *J* = 8.0 Hz, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 118.0, 121.8, 123.9, 126.7, 134.8, 156.2, 177.2.

N-(3,5-di-tert-butyl-1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-*N*-methoxy-4-methylbenzamide (**5**) Yield: 88 mg, 23%; Yellow oil; Reaction time: 7 h; Flash chromatography (Petroleum ether/EtOAc, 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (s, 18H), 1.74 (s, 3H), 2.39 (s, 3H), 3.42 (s, 3H), 6.95 (s, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 26.2, 29.4, 34.7, 62.5, 64.5, 128.3, 128.6, 132.4, 140.7, 141.1, 145.1, 172.1, 186.0; HRMS (ESI-TOF) m/z calcd for $C_{24}H_{33}NNaO_3$ $(M+Na)^+$: 406.2353, found: 406.2358.

Supporting Information Available: Copies of ^{1}H NMR, ^{13}C NMR spectral and HRMS.

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FULL PAPER

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