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# Rhodium-Catalyzed Oxidative Synthesis of Quinoline-Fused Sydnones via 2-fold C−H Bond Activation

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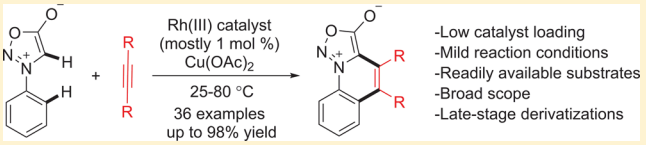
Supporting Information

**ABSTRACT:** Rh(III)-catalyzed synthesis of mesoionic heterocycles has been achieved via C−H activation of sydnones and oxidative coupling with internal alkynes. This reaction occurred under mild conditions with high efficiency, broad substrate scope, and low catalyst loading. Moreover, synthetic applications of a coupled product have been demonstrated in the late-stage derivatization into a variety of highly functionalized scaffolds.



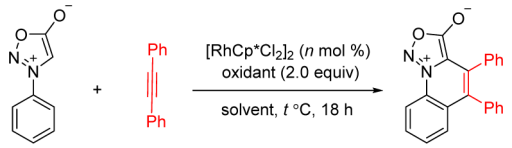



Heterocyclic frameworks are embedded in a large number of conjugated π-systems that exhibit important electrochemical and photochemical properties with potential applications as organic semiconductors and luminescence materials.[1] Owing to their broad applications, numerous traditional and metal-mediated methods have been developed for synthesis of fused (hetero)aromatics.[2] Sydnones[3] are a useful class of mesoionic heterocycles that have received considerable attention with intriguing structural, chemical, and biological properties.[3a] The most common functionalizations of sydnones include electrophilic aromatic substitution, metalation, Pd-catalyzed C−H arylation, and alkenylation[4] at the most acidic C4−H position.[3a] In particular, sydnones have been widely employed in cycloaddition reactions with various dipolarophiles.[3a] Despite the significance, very limited examples have been reported for the functionalization of sydnones leading to synthesis of fused, π-extended systems,[5] which required highly functionalized starting materials and multistep synthesis. In this regard, the development of efficient strategies for the mild synthesis of fused sydnones is highly desirable.

Transition metal catalyzed C(aryl)−H bond activation and functionalization has proved to be a powerful tool for the construction of complex structures.[6] In particular, Cp*Rh(III) catalysts have been extensively employed as catalysts in the functionalization of a large array of arenes owing to high efficiency, broad scope, and high functional group tolerance.[7] Recently, Miura and Satoh reported the synthesis of π-conjugated molecules via Rh(III)-catalyzed double/multiple C−H activation−oxidative annulation between arenes/heteroarenes and alkynes.[8] Afterward, the groups of Li,[9] Wang,[10] Chen,[11] Choudhury,[12] and others[13] made progress in the synthesis of various π-conjugated molecules. Very recently, Cheng, You, and others independently reported Rh(III)-catalyzed C−H activation of arenes for the synthesis of ionic heterocycles such as isoquinolinium, cinnolinium, quinolizinium, pyridinium, and related salts.[14] Despite the progress, such annulation reactions typically required high temperature, and only very limited examples have been reported for heterocycle synthesis under mild conditions.[12d,15] In addition, the synthesis of fused sydnones via the transition metal catalyzed C−H activation remains unexplored. In order to solve the limitation of sydnone functionalization, we now report a Rh(III)-catalyzed efficient oxidative synthesis of quinoline-fused sydnones via 2-fold C−H bond activation under mild conditions.

We initiated our investigation by utilizing the coupling of *N*-phenylsydnone (**1a**) with diphenylacetylene (**2a**) as the model reaction (Table 1). Using $[RhCp^*Cl_2]_2$ (4 mol %) as a catalyst,

**Table 1. Optimization of the Reaction Conditions**[a]




1a 2a 3aa

| entry | *n* | oxidant | *t* (°C) | solvent | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | 4 | $Cu(OAc)_2$ | 80 | $CH_3CN$ | 81 |
| 2 | 4 | $Cu(OAc)_2$ | 60 | $CH_3CN$ | 91 |
| 3 | 4 | $Cu(OAc)_2$ | 40 | $CH_3CN$ | 96 |
| 4 | 4 | $Cu(OAc)_2$ | 25 | $CH_3CN$ | 97 |
| 5 | 1 | $Cu(OAc)_2$ | 25 | $CH_3CN$ | 97 (22[c]) |
| 6 | 1 | $Cu(OAc)_2$ | 25 | MeOH | 10 |
| 7 | 1 | $Cu(OAc)_2$ | 25 | DCM | nd |
| 8 | 1 | $Cu(OAc)_2$ | 25 | 1,4-dioxane | 15 |
| 9 | 1 | $Cu(OAc)_2$ | 25 | toluene | <5 |
| 10 | 1 | AgOAc | 25 | $CH_3CN$ | nd |
| 11 | 1 | $Ag_2CO_3$ | 25 | $CH_3CN$ | 12 |
| 12 | 1 | | 25 | $CH_3CN$ | nd |
| 13 | 0 | $Cu(OAc)_2$ | 25 | $CH_3CN$ | nd |

[a]The reaction was carried out using sydnone (0.2 mmol), alkyne (0.3 mmol), $[RhCp^*Cl_2]_2$ (1 mol %), and $Cu(OAc)_2$ (0.4 mmol) in a solvent (3 mL) under nitrogen at 25 °C for 18 h. [b]Isolated yield after column chromatography. [c]Reaction was performed under air.

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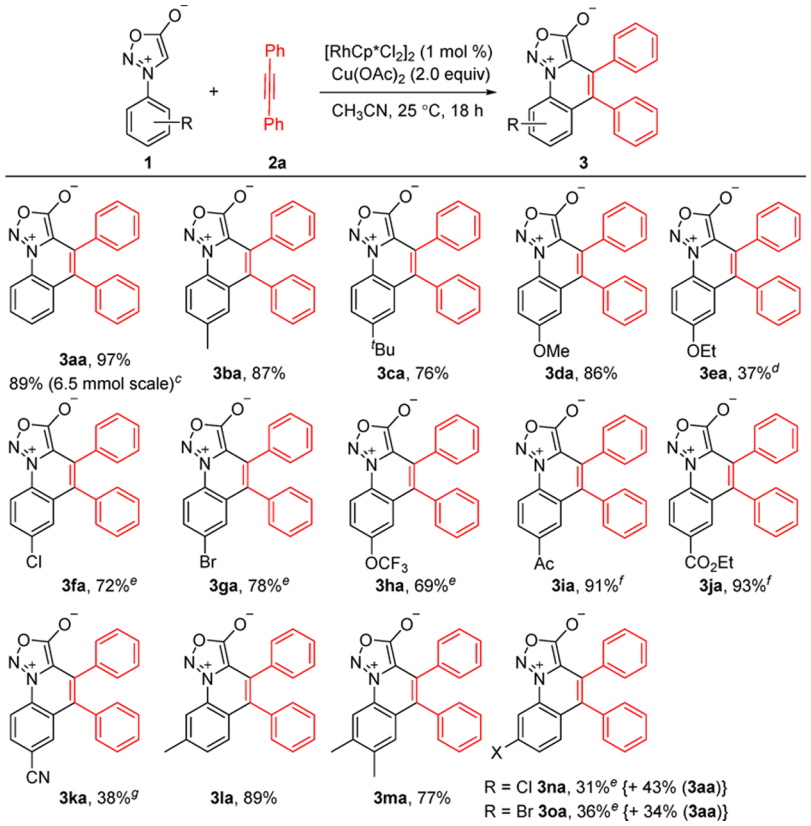
**Scheme 1. Scope of Sydnones**[a,b]




[a]The reaction was carried out using sydnone (0.2 mmol), alkynes (0.3 mmol), $[RhCp^*Cl_2]_2$ (1 mol %), and $Cu(OAc)_2$ (0.4 mmol) in $CH_3CN$ (3 mL) under nitrogen at 25 °C for 18 h. [b]Isolated yield after column chromatography. [c]Reaction was performed using $[RhCp^*Cl_2]_2$ (0.5 mol %) in a gram scale. [d]$[RhCp^*Cl_2]_2$ (4 mol %) at 80 °C. [e]$[RhCp^*Cl_2]_2$ (2 mol %) at 60 °C in MeOH. [f]$[RhCp^*Cl_2]_2$ (2 mol %) at 60 °C. [g]$[RhCp^*Cl_2]_2$ (2 mol %) at 40 °C in MeOH.

the desired mesoionic product **3aa** was indeed isolated in 81% yield in $CH_3CN$ at 80 °C (entry 1). Screening of the reaction temperature revealed that the yield of **3aa** was significantly improved at 25 °C (entry 4 versus entries 2, 3). To our delight, the product **3aa** was isolated in 97% yield when the catalyst loading was lowered to 1 mol % (entry 5). However, a sluggish reaction was observed when the reaction was performed under air (entry 5). Investigation of the solvents showed that $CH_3CN$ is superior to MeOH, DCM, 1,4-dioxane, and toluene (entries 6−9). Further examination of the oxidant revealed that AgOAc or $Ag_2CO_3$ all proved disadvantageous (entries 10, 11). Our control experiments confirmed that no desired product was observed when either the Rh(III) catalyst or $Cu(OAc)_2$ was omitted (entries 12, 13).

With the establishment of the optimal conditions, we next explored the scope and generality of this coupling system (Scheme 1). It was found that sydnones with electron-donating groups such as Me, $^t$Bu, OMe, or OEt at the *para* position of phenyl ring all coupled smoothly with **2a** to afford the products (**3ba**−**3ea**) in moderate to high yields. Introduction of *para* halogen groups (**3fa**, **3ga**) and electron-withdrawing groups (**3ha**−**3ka**) is tolerated, but a higher catalyst loading (2 mol %) and higher temperature are necessary with MeOH being a solvent. Introduction of *meta* alkyl substituents was also tolerated, delivering the products in high yields (**3la**, **3ma**). In contrast, while sydnones bearing *meta* Cl and Br reacted with **2a** to afford the corresponding products **3na** and **3oa**, the hydrodehalogenated product **3aa** was surprisingly isolated in a comparable yield.[16] We speculated that in these cases the C−H activation might competitively occur at the more hindered *ortho* site, followed by dehalogenation at the *ortho* position of the metal. Moreover, product **3aa** was isolated in 89% yield in a gram-scale (6.5 mmol) synthesis from **1a** and **2a** under a reduced loading (0.5 mol %) of the catalyst, indicative of the synthetic practicality of this system.

We next examined the scope with respect to internal alkynes (Scheme 2). Symmetric diarylacetylenes bearing both electron-donating and -withdrawing groups at the *para* or *meta* position all coupled in good to excellent yields (**3ab**−**3ak**). Notably, the diarylactylene substrate has been smoothly extended to bis(2-thienyl)acetylene in good yield (**3al**). The alkyne is not limited to a diarylacetylene; aliphatic internal alkynes (**3am**, **3an**) and diethyl but-2-ynedioate (**3ao**) all reacted smoothly to afford the corresponding products in 77−87% yields under a higher catalyst loading at 80 °C. Unsymmetrical alkynes such as 1-phenyl-1-propyne, 1-phenyl-1-butyne, 1-phenyl-1-pentyne, and ethyl 3-phenylpropiolate were also applicable, but with moderate to low regioselectivity (**3ap**−**3as**). Nevertheless, the overall yields of the isomeric products are generally high and the regioisomers can be chromatographically separated. The identity of the regiosiomer has been established by NOESY analyses (see Supporting Information). In addition, several alkynes were also allowed to couple with sydnone **1b** to further evaluate the generality of the reaction, and the corresponding products were isolated in good to high yields (**3bc**, **3bj**, and **3bm**).



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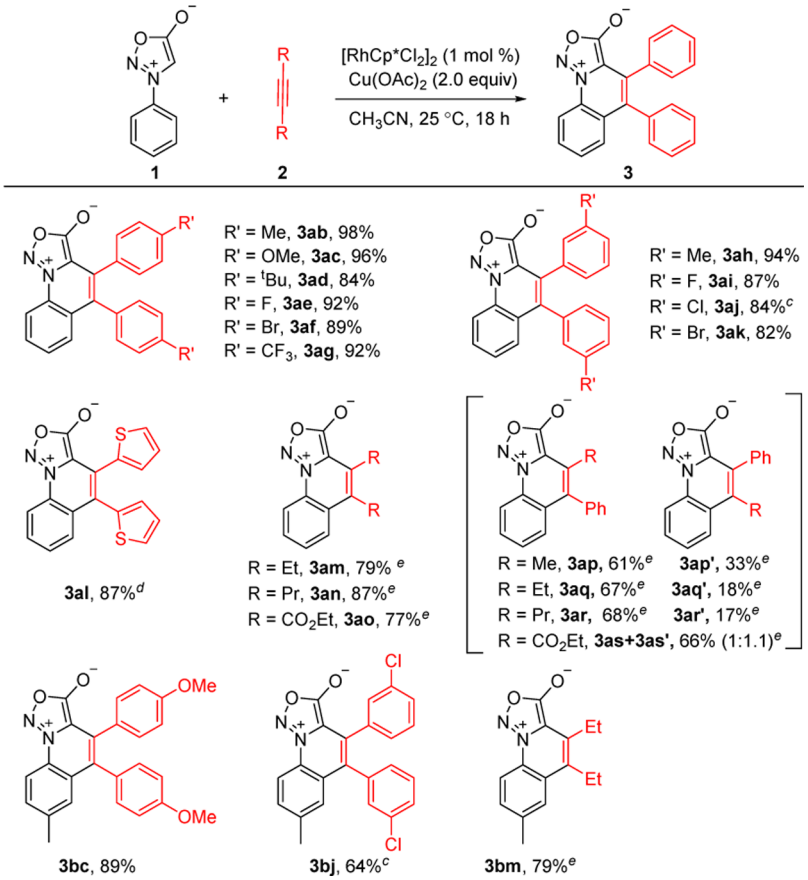
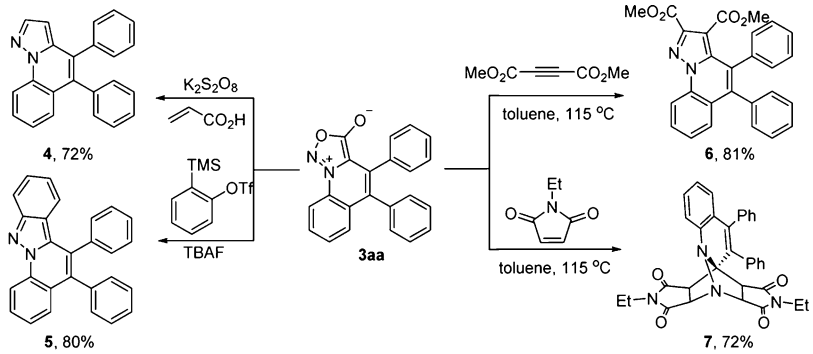
**Scheme 2. Scope of Alkynes in Fused Sydnone Synthesis**[a,b]




[a]The reaction was carried out using sydnone (0.2 mmol), alkyne (0.3 mmol), $[RhCp^*Cl_2]_2$ (1 mol %), and $Cu(OAc)_2$ (0.4 mmol) in MeCN (3 mL) under nitrogen at 25 °C for 18 h. [b]Isolated yield after column chromatography. [c]$[RhCp^*Cl_2]_2$ (2 mol %) at 40 °C. [d]$[RhCp^*Cl_2]_2$ (4 mol %) at 60 °C. [e]I$[RhCp^*Cl_2]_2$ (4 mol %) at 80 °C.

**Scheme 3. Chemical Transformations of Product 3aa**




We next examined the synthetic utility of a fused sydnone product (Scheme 3). The 1,3-dipolar cycloaddition of **3aa** with acrylic acid in the presence of $K_2S_2O_8$ afforded a pyrazole-fused quinoline (**4**) in good yield.[17] Next, a dipolar addition−decarboxylation reaction between **3aa** and a benzyne precursor gave heteroarene **5** in high efficiency via an addition−elimination pathway.[18] When the aryne was replaced by dimethyl acetylenedicarboxylate, an analogous product **6** was isolated in 81% yield.[19] Moreover, the addition of **3aa** to *N*-ethylmaleimide afforded exclusively a bis-adduct (**7**) in 72% yield.[20] These important derivatization reactions for synthesis of functionalized scaffolds suggested the synthetic utility of the coupled products.

Several experiments have been performed to explore the reaction mechanism. An intermolecular competition between two different alkynes showed that the electron-rich one reacted preferentially (eq 1). H/D exchange reactions have been carried out for sydnone **1a** in the presence of alkyne **2a**, but no deteurium was incorporated into the product (eq 2). On the other hand, H/D exchange of **1a** was observed at the 4-position in the absence of any diphenylacetyene (see Supporting Information), indicating that the C(4)−H cleavage is reversible. The kinetic isotope effect (KIE) was thus measured. Two



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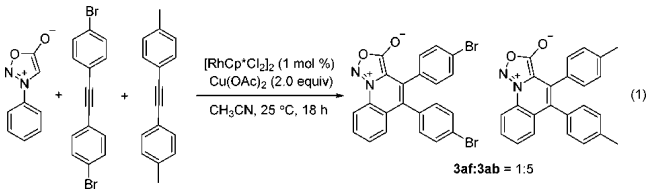
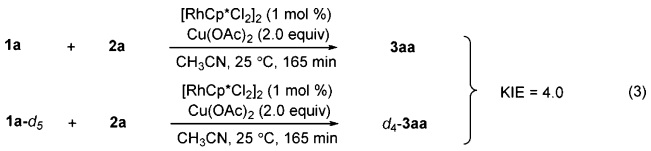
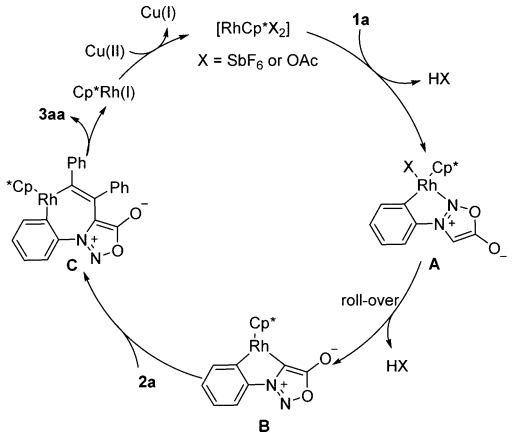



parallel reactions have been performed at a low conversion (eq 3), and a value of $k_H/k_D$ = 4.0 was obtained on the basis of $^1$H NMR analysis, suggesting that C−H bond cleavage is likely involved in the turnover-limiting step.




On the basis of these preliminary results and our previous studies,[9a] a plausible catalytic cycle has been proposed starting from an active [RhCp*$X_2$] (X = $SbF_6$ or OAc) species (Scheme 4, see Supporting Information for alternative mechanisms). The

**Scheme 4. Proposed Mechanism**




reaction is initiated by cyclometalation of the sydnone to deliver a rhodacyclic intermediate **A**, which is proposed to undergo nitrogen decoordination and rollover C−H activation to give a Rh(III) diaryl intermediate **B**. Subsequent insertion of an incoming alkyne furnishes a seven-membered rhodacycle **C**. Reductive elimination of **C** then affords the product **3aa** together with a Rh(I) species, which is reoxidized by $Cu(OAc)_2$ to regenerate the rhodium(III) active catalyst for the next catalytic cycle. We noted that in another alternative pathway the Rh−C(aryl) bond of **A** may undergo migratory insertion into the alkyne, followed by nitrogen decoordination and rollover C−H activation to reach the same intermediate **C**. Besides this proposed mechanism, two other related pathways that involve different seven-membered rhodacyclic species as a result of the migratory insertion of alkyne are given in the Supporting Information.

In summary, we have achieved an efficient Rh(III)-catalyzed synthesis of quinoline-fused sydnones via C−H activation of simple *N*-arylsydnones. This catalytic system features mild conditions and tolerates a broad scope of both sydnones and internal alkynes under low catalyst loading. Preliminary mechanistic studies have been performed, and a plausible catalytic cycle has been proposed. Furthermore, the synthetic applications of coupled products have been demonstrated in their diverse dipolar addition reactions to afford highly functionalized scaffolds.

## EXPERIMENTAL SECTION

**General Information.** All chemicals were obtained from commercial sources and were used as received unless otherwise noted. *N*-Arylsydnones[21] and alkynes[22] were prepared by following literature reports. All Rh(III)-catalyzed reactions were carried out in a nitrogen-filled drybox. $^1$H and $^{13}$C NMR spectra were recorded using $CDCl_3$ or DMSO as a solvent on a 400 MHz spectrometer at 298 K. The chemical shift is given in dimensionless $\delta$ values and is frequency referenced relative to TMS in $^1$H and $^{13}$C NMR spectroscopy. HRMS data were obtained via ESI mode with a TOF mass analyzer. All solvents were obtained from commercial sources and were used as received. Column chromatography was performed on silica gel (300−400 mesh) using ethyl acetate (EA)/petroleum ether (PE).

**General Procedure for Synthesis of 3.** *N*-Arylsydnone (0.20 mmol), alkyne (0.3 mmol), $[Cp^*RhCl_2]_2$ (1.2 mg, 1 mol %), $Cu(OAc)_2$ (72.6 mg, 0.4 mmol), and $CH_3CN$ (2.0 mL) were charged into a reaction tube. The reaction mixture was stirred under nitrogen at rt for 18 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA (20:1−4:1) to afford the desired product **3**.

*4,5-Diphenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3aa**):* yellow solid (97%, 65.5 mg); mp 244−245 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.50 (d, $J$ = 8.3 Hz, 1H), 7.72 (t, $J$ = 7.7 Hz, 1H), 7.65 (t, $J$ = 7.6 Hz, 1H), 7.58 (d, $J$ = 8.1 Hz, 1H), 7.30−7.29 (m, 3H), 7.24−7.22 (m, 3H), 7.16−7.11 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.4, 134.9, 132.1, 131.8, 131.4, 131.2, 130.9, 130.34, 129.4, 129.2, 128.4, 128.3, 128.2, 127.9, 127.6, 127.3, 116.2, 106.2; HRMS (ESI) calcd for $[C_{22}H_{14}N_2O_2 + H]^+$ 339.1128, found 339.1127.

*7-Methyl-4,5-diphenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ba**):* yellow solid (87%, 61.0 mg); mp 231−232 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.37 (d, $J$ = 8.6 Hz, 1H), 7.53 (d, $J$ = 8.6 Hz, 1H), 7.33−7.29 (m, 4H), 7.24−7.21 (m, 3H), 7.14−7.10 (m, 4H), 2.43 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.4, 141.7, 135.0, 131.9, 131.9, 131.4, 131.2, 131.0, 130.4, 129.2, 128.3, 128.1, 127.8, 127.7, 127.6, 125.4, 116.0, 105.9, 22.0; HRMS (ESI) calcd for $[C_{23}H_{16}N_2O_2 + H]^+$ 353.1285, found 353.1282.

*7-(tert-Butyl)-4,5-diphenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ca**):* yellow solid (76%, 59.9 mg); mp 229−230 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.44 (d, $J$ = 8.9 Hz, 1H), 7.80 (dd, $J$ = 8.9, 1.8 Hz, 1H), 7.56 (s, 1H), 7.31−7.28 (m, 3H), 7.25−7.22 (m, 3H), 7.16−7.12 (m, 4H), 1.28 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.5, 154.6, 135.0, 132.3, 132.0, 131.2, 131.1, 130.4, 129.0, 128.2, 128.1, 127.8, 127.7, 127.6, 125.3, 124.2, 115.9, 106.0, 35.4, 31.0; HRMS (ESI) calcd for $[C_{26}H_{22}N_2O_2 + H]^+$ 395.1754, found 395.1755.

*7-Methoxy-4,5-diphenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3da**):* yellow solid (86%, 63.4 mg); mp 238−239 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.40 (d, $J$ = 9.2 Hz, 1H), 7.30−7.28 (m, 4H), 7.25−7.22 (m, 3H), 7.14−7.11 (m, 4H), 6.89 (d, $J$ = 1.9 Hz, 1H), 3.74 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.4, 161.2, 135.0, 131.9, 131.9, 131.5, 131.1, 131.1, 130.3, 128.3, 128.2, 127.9, 127.6, 121.7, 118.8, 117.8, 109.1, 105.4, 55.9; HRMS (ESI) calcd for $[C_{23}H_{16}N_2O_3 + H]^+$ 369.1234, found 369.1233.

*7-Ethoxy-4,5-diphenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ea**):* yellow solid (37%, 28.4 mg); mp 248−249 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.42 (d, $J$ = 9.3 Hz, 1H), 7.31−7.28 (m, 4H), 7.23−7.22 (m, 3H), 7.15−7.10 (m, 4H), 6.88 (d, $J$ = 2.4 Hz, 1H), 3.95 (q, $J$ = 6.9 Hz, 2H), 1.38 (t, $J$ = 7.0 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.4, 160.6, 135.1, 131.9, 131.8, 131.5, 131.1, 131.1,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130.3, 128.3, 128.1, 127.8, 127.6, 121.6, 119.0, 117.8, 109.7, 105.4, 64.1, 14.5; HRMS (ESI) calcd for $[C_{24}H_{18}N_2O_3 + H]^+$ 383.1390, found 383.1391.

*7-Chloro-4,5-diphenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3fa**):* yellow solid (72%, 53.8 mg); mp 206−207 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.47 (d, $J$ = 8.9 Hz, 1H), 7.68 (d, $J$ = 8.6 Hz, 1H), 7.54 (s, 1H), 7.32−7.31 (m, 3H), 7.24−7.23 (m, 3H), 7.14−7.09 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.1, 137.4, 134.2, 132.9, 131.3, 131.1, 131.1, 130.6, 130.2, 129.9, 128.5, 128.4, 128.2, 127.7, 127.5, 125.7, 117.8, 106.2; HRMS (ESI) calcd for $[C_{22}H_{13}ClN_2O_2 + H]^+$ 373.0738, found 373.0739.

*7-Bromo-4,5-diphenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ga**):* yellow solid (78%, 64.6 mg); mp 217−218 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.41 (d, $J$ = 8.9 Hz, 1H), 7.83 (dd, $J$ = 8.9, 1.9 Hz, 1H), 7.71 (d, $J$ = 1.9 Hz, 1H), 7.33−7.31 (m, 3H), 7.26−7.22 (m, 3H), 7.14−7.08 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.1, 134.2, 132.9, 132.6, 131.3, 131.1, 131.0, 130.8, 130.7, 130.2, 128.5, 128.4, 128.2, 127.7, 126.0, 125.6, 117.9, 106.2; HRMS (ESI) calcd for $[C_{22}H_{13}BrN_2O_2 + H]^+$ 417.0233, found 417.0238.

*4,5-Diphenyl-7-(trifluoromethoxy)-[1,2,3]oxadiazolo[3,4-a]-quinolin-10-ium-3-olate (**3ha**):* yellow solid (69%, 57.9 mg) mp 163−164 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.60 (d, $J$ = 9.2 Hz, 1H), 7.59 (d, $J$ = 9.2 Hz, 1H), 7.39 (s, 1H), 7.33−7.32 (m, 3H), 7.24−7.22 (m, 1H), 7.15−7.13 (m, 2H), 7.11−7.09 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.0, 150.5, 134.1, 133.1, 131.4, 131.3, 131.0, 130.9, 130.2, 128.6, 128.5, 128.3, 127.7, 125.4, 122.1, 120.2 (q, $J$ = 257.9 Hz), 119.4, 118.6, 106.3; HRMS (ESI) calcd for $[C_{23}H_{13}F_3N_2O_3 + H]^+$ 423.0951, found 423.0956.

*7-Acetyl-4,5-diphenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ia**):* yellow solid (91%, 69.4 mg) mp 222−223 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.58 (d, $J$ = 8.6 Hz, 1H), 8.26 (d, $J$ = 8.5 Hz, 1H), 8.16 (s, 1H), 7.33−7.34 (m, 3H), 7.24−7.25 (m, 3H), 7.14−7.15 (m, 4H), 2.55 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 196.4, 164.0, 138.5, 134.2, 132.5, 132.3, 131.3, 131.1, 130.3, 129.3, 129.2, 129.1, 128.5, 128.5, 128.3, 128.2, 127.7, 116.9, 106.8, 26.7; HRMS (ESI) calcd for $[C_{24}H_{16}N_2O_3 + H]^+$ 381.1234, found 381.1230.

*7-(Ethoxycarbonyl)-4,5-diphenyl-[1,2,3]oxadiazolo[3,4-a]-quinolin-10-ium-3-olate (**3ja**):* yellow solid (93%, 76.1 mg) mp 234−235 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.59 (d, $J$ = 8.7 Hz, 1H), 8.34 (d, $J$ = 9.0 Hz, 1H), 8.31 (s, 1H), 7.33−7.31 (m, 3H), 7.26−7.24 (m, 3H), 7.16−7.10 (m, 4H), 4.38 (q, $J$ = 7.1 Hz, 2H), 1.37 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.9, 164.1, 134.2, 132.7, 132.4, 132.3, 131.4, 131.1, 130.4, 130.3, 129.5, 129.4, 129.1, 128.5, 128.4, 128.2, 127.7, 116.6, 106.8, 62.0, 14.2; HRMS (ESI) calcd for $[C_{25}H_{18}N_2O_4 + H]^+$ 411.1339, found 411.1335.

*7-Cyano-4,5-diphenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ka**):* yellow solid (38%, 27.5 mg) mp 255−256 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.64 (d, $J$ = 8.7 Hz, 1H), 7.93−7.91 (m, 2H), 7.36−7.34 (m, 3H), 7.28−7.22 (m, 3H), 7.14−7.08 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.7, 133.8, 133.5, 133.4, 131.1, 131.0, 130.9, 130.1, 129.6, 128.9, 128.8, 128.7, 128.6, 127.8, 117.8, 117.3, 115.0, 107.0. One carbon signal is not visible due to overlapping; HRMS (ESI) calcd for $[C_{23}H_{13}N_3O_2 + H]^+$ 364.1081, found 364.1087.

*8-Methyl-4,5-diphenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3la**):* yellow solid (89%, 62.7 mg) mp 216−217 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.29 (s, 1H), 7.47−7.46 (m, 2H), 7.30−7.27 (m, 3H), 7.24−7.19 (m, 3H), 7.15−7.10 (m, 4H), 2.58 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.4, 140.7, 135.0, 132.6, 132.1, 131.9, 131.2, 130.5, 130.4, 128.2, 128.2, 128.1, 127.8, 127.6, 127.2, 126.9, 115.7, 106.3, 21.8; HRMS (ESI) calcd for $[C_{23}H_{16}N_2O_2 + H]^+$ 353.1285, found 353.1284.

*7,8-Dimethyl-4,5-diphenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ma**):* yellow solid (77%, 56.6 mg); mp 249−250 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.29 (s, 1H), 7.29−7.28 (m, 4H), 7.23−7.21 (m, 3H), 7.14−7.09 (m, 4H), 2.51 (s, 3H), 2.34 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.5, 141.1, 140.0, 135.2, 132.0, 131.8, 131.2, 130.5, 130.4, 128.2, 128.0, 127.7, 127.5, 127.3, 125.6, 116.1, 106.0, 20.4, 20.4. One carbon signal is not visible due to overlapping; HRMS (ESI) calcd for $[C_{24}H_{18}N_2O_2 + H]^+$ 367.1441, found 367.1445.

*8-Chloro-4,5-diphenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3na**):* yellow solid (31%, 22.9 mg); mp 225−226 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.53 (s, 1H), 7.60 (d, $J$ = 8.0 Hz, 1H), 7.53 (d, $J$ = 8.9 Hz, 1H), 7.31−7.30 (m, 3H), 7.25−7.23 (m, 3H), 7.14−7.12 (m, 2H), 7.10−7.08 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.0, 135.6, 134.4, 131.9, 131.6, 131.5, 131.4, 131.1, 130.3, 129.8, 128.4, 128.4, 128.1, 127.7, 127.6, 116.1, 106.6. One carbon signal is not visible due to overlapping; HRMS (ESI) calcd for $[C_{22}H_{13}ClN_2O_2 + H]^+$ 373.0738, found 373.0739.

*8-Bromo-4,5-diphenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3oa**):* yellow solid (36%, 29.8 mg); mp 228−229 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.69 (s, 1H), 7.73 (dd, $J$ = 8.9, 1.9 Hz, 1H), 7.45 (d, $J$ = 8.9 Hz, 1H), 7.31−7.29 (m, 3H), 7.27−7.20 (m, 3H), 7.14−7.12 (m, 2H), 7.10−7.08 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.0, 134.4, 134.3, 132.0, 131.7, 131.4, 131.1, 130.2, 129.8, 128.4, 128.4, 128.1, 128.0, 127.7, 127.6, 123.4, 119.2, 106.6; HRMS (ESI) calcd for $[C_{22}H_{13}BrN_2O_2 + H]^+$ 417.0233, found 417.0236.

*4,5-Di-p-tolyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ab**):* yellow solid (98%, 71.5 mg); mp 235−236 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.48 (d, $J$ = 8.1 Hz, 1H), 7.69 (t, $J$ = 7.4 Hz, 1H), 7.64−7.56 (m, 2H), 7.11 (d, $J$ = 7.4 Hz, 2H), 7.03 (s, 4H), 6.99 (d, $J$ = 7.4 Hz, 2H), 2.34 (s, 3H), 2.29 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.4, 137.8, 137.5, 132.1, 131.9, 131.5, 131.0, 130.7, 130.3, 129.4, 129.2, 129.0, 128.8, 128.4, 128.4, 127.2, 116.1, 106.4, 21.4, 21.3; HRMS (ESI) calcd for $[C_{24}H_{18}N_2O_2 + H]^+$ 367.1441, found 367.1446.

*4,5-Bis(4-methoxyphenyl)-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ac**):* yellow solid (96%, 76.7 mg); mp 239−240 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.47 (d, $J$ = 8.1 Hz, 1H), 7.71−7.60 (m, 3H), 7.07 (d, $J$ = 8.4 Hz, 2H), 7.02 (d, $J$ = 8.3 Hz, 2H), 6.85 (d, $J$ = 8.3 Hz, 2H), 6.77 (d, $J$ = 8.4 Hz, 2H), 3.80 (s, 3H), 3.76 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.5, 159.2, 159.0, 132.3, 131.8, 131.8, 131.3, 130.8, 129.5, 129.1, 128.4, 127.2, 127.1, 124.0, 116.1, 113.8, 113.2, 106.4, 55.3, 55.1; HRMS (ESI) calcd for $[C_{24}H_{18}N_2O_4 + H]^+$ 399.1339, found 399.1338.

*4,5-Bis(4-(tert-butyl)phenyl)-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ad**):* yellow solid (84%, 75.9 mg); mp 286−287 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.49 (d, $J$ = 8.1 Hz, 1H), 7.70−7.63 (m, 3H), 7.27 (d, $J$ = 8.1 Hz, 2H), 7.19 (d, $J$ = 8.2 Hz, 2H), 7.02 (d, $J$ = 8.2 Hz, 2H), 6.99 (d, $J$ = 8.1 Hz, 2H), 1.29 (s, 9H), 1.25 (s, 9H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.5, 150.8, 150.7, 132.5, 131.9, 131.7, 130.9, 130.7, 130.2, 129.2, 129.2, 128.9, 128.5, 127.2, 124.9, 124.3, 116.1, 106.4, 34.6, 34.5, 31.3, 31.2; HRMS (ESI) calcd for $[C_{30}H_{30}N_2O_2 + H]^+$ 451.2380, found 451.2387.

*4,5-Bis(4-fluorophenyl)-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ae**):* yellow solid (92%, 69.1 mg); mp 237−238 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.52 (d, $J$ = 8.2 Hz, 1H), 7.76 (t, $J$ = 7.7 Hz, 1H), 7.70 (t, $J$ = 7.6 Hz, 1H), 7.56 (d, $J$ = 8.3 Hz, 1H), 7.13−7.08 (m, 4H), 7.03 (t, $J$ = 8.6 Hz, 2H), 6.94 (t, $J$ = 8.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.3, 162.5 (d, $J$ = 246.9 Hz), 162.3 (d, $J$ = 247.0 Hz), 132.8 (d, $J$ = 8.1 Hz), 132.1 (d, $J$ = 8.4 Hz), 131.1, 130.7, 130.6 (d, $J$ = 3.5 Hz), 129.7, 129.0, 128.2, 127.5 (d, $J$ = 3.5 Hz), 127.3, 116.3, 115.7 (d, $J$ = 21.5 Hz), 115.0 (d, $J$ = 21.7 Hz), 106.0. One carbon signal is not visible due to overlapping; HRMS (ESI) calcd for $[C_{22}H_{12}F_2N_2O_2 + H]^+$ 375.0940, found 375.0944.

*4,5-Bis(4-bromophenyl)-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3af**):* yellow solid (89%, 88.3 mg); mp 279−280 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.54 (d, $J$ = 8.3 Hz, 1H), 7.77 (ddd, $J$ = 8.4, 7.2, 1.2 Hz, 1H), 7.69 (ddd, $J$ = 8.3, 7.2, 1.2 Hz, 1H), 7.54 (d, $J$ = 8.2 Hz, 1H), 7.48 (d, $J$ = 8.4 Hz, 2H), 7.40 (d, $J$ = 8.4 Hz, 2H), 7.02-6.98 (m, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.3, 133.7, 132.8, 132.1, 132.0, 131.3 (two overlapping signals), 130.8, 130.6, 130.5, 130.0, 128.9, 128.2, 127.6, 123.2, 122.7, 116.6, 105.8; HRMS (ESI) calcd for $[C_{22}H_{12}Br_2N_2O_2 + H]^+$ 494.9338, found 494.9338.

*4,5-Bis(4-(trifluoromethyl)phenyl)-[1,2,3]oxadiazolo[3,4-a]-quinolin-10-ium-3-olate (**3ag**):* yellow solid (92%, 86.8 mg); mp 269−270 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.56 (d, $J$ = 8.3 Hz, 1H), 7.81 (ddd, $J$ = 8.4, 7.2, 1.1 Hz, 1H), 7.73 (ddd, $J$ = 8.2, 7.2, 1.2 Hz, 1H), 7.61 (d, $J$ = 8.0 Hz, 2H), 7.51 (t, $J$ = 8.2 Hz, 3H), 7.27 (d, $J$ = 8.2 Hz, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.0, 138.3, 135.0, 131.5, 131.4, 130.8, 130.7, 130.6, 130.3 (q, $J$ = 6.3 Hz), 130.2, 128.5, 128.0, 127.5, 125.6 (q, $J$ = 3.6 Hz), 125.1 (q, $J$ = 3.5 Hz), 124.9 (q, $J$ = 3.6 Hz), 123.8 (q, $J$ = 266.4 Hz), 123.7 (q, $J$ = 270.8 Hz), 116.5, 105.5;


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HRMS (ESI) calcd for $[C_{24}H_{12}F_6N_2O_2 + H]^+$ 475.0876, found 475.0879.

*4,5-Di-m-tolyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ah**):* yellow solid (94%, 69.1 mg); mp 221−222 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.49 (d, $J$ = 8.2 Hz, 1H), 7.70 (ddd, $J$ = 8.3, 6.8, 1.2 Hz, 1H), 7.64 (t, $J$ = 7.2 Hz, 1H), 7.59 (d, $J$ = 8.1 Hz, 1H), 7.18 (t, $J$ = 7.5 Hz, 1H), 7.13−7.08 (m, 2H), 7.03 (d, $J$ = 7.5 Hz, 1H), 6.96−6.93 (m, 3.0 Hz, 3H), 6.90 (d, $J$ = 7.5 Hz, 1H), 2.28 (s, 3H), 2.23 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.4, 137.8, 137.0, 134.8, 132.2, 131.8, 131.7, 131.5, 131.1, 130.8, 129.3, 129.3, 128.9, 128.5, 128.2, 128.1, 127.4, 127.2, 116.1, 106.3, 21.4; HRMS (ESI) calcd for $[C_{24}H_{18}N_2O_2 + H]^+$ 367.1441, found 367.1441.

*4,5-Bis(3-fluorophenyl)-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ai**):* yellow solid (87%, 64.8 mg); mp 226−227 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.51 (d, $J$ = 8.3 Hz, 1H), 7.77 (t, $J$ = 7.7 Hz, 1H), 7.71 (t, $J$ = 7.5 Hz, 1H), 7.57 (d, $J$ = 8.2 Hz, 1H), 7.34−7.29 (m, 1H), 7.26−7.21 (m, 1H), 7.03 (td, $J$ = 8.5, 1.8 Hz, 1H), 7.00−6.95 (m, 3H), 6.86 (d, $J$ = 9.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.1, 162.5 (d, $J$ = 246.5), 162.0 (d, $J$ = 245.1), 136.6 (d, $J$ = 7.8), 133.5 (d, $J$ = 8.2), 131.3, 130.7 (d, $J$ = 1.8), 130.2 (d, $J$ = 2.1), 130.1 (d, $J$ = 8.4), 129.9, 129.4 (d, $J$ = 8.3), 128.6, 128.2, 127.4, 126.9 (d, $J$ = 2.9), 126.1 (d, $J$ = 3.0), 118.0 (d, $J$ = 21.7), 117.4 (d, $J$ = 22.5), 116.3, 115.5 (d, $J$ = 20.8), 115.3 (d, $J$ = 20.8), 105.7; HRMS (ESI) calcd for $[C_{22}H_{12}F_2N_2O_2 + H]^+$ 375.0940, found 375.0946.

*4,5-Bis(3-chlorophenyl)-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3aj**):* yellow solid (84%, 68.1 mg); mp 240−241 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.52 (d, $J$ = 8.2 Hz, 1H), 7.78 (t, $J$ = 7.6 Hz, 1H), 7.71 (t, $J$ = 7.5 Hz, 1H), 7.55 (d, $J$ = 8.1 Hz, 1H), 7.32−7.13 (m, 4H), 7.14 (s, 1H), 7.13 (s, 1H), 7.06 (d, $J$ = 7.1 Hz, 1H), 7.02 (d, $J$ = 6.4 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.1, 136.3, 134.4, 133.7, 133.1, 131.3, 130.9, 130.6, 130.3, 130.2, 130.0, 129.8, 129.4, 129.1, 128.7, 128.6, 128.5, 128.5, 128.2, 127.4, 116.4, 105.6; HRMS (ESI) calcd for $[C_{22}H_{12}Cl_2N_2O_2 + H]^+$ 407.0349, found 407.0348.

*4,5-Bis(3-bromophenyl)-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ak**):* yellow solid (82%, 80.7 mg); mp 250−251 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.54 (d, $J$ = 8.3 Hz, 1H), 7.79 (t, $J$ = 7.6 Hz, 1H), 7.72 (t, $J$ = 7.7 Hz, 1H), 7.56 (d, $J$ = 8.1 Hz, 1H), 7.48 (d, $J$ = 8.0 Hz, 1H), 7.41 (d, $J$ = 7.8 Hz, 1H), 7.31 (s, 1H), 7.28 (s, 1H), 7.22 (t, $J$ = 7.7 Hz, 1H), 7.16 (t, $J$ = 7.8 Hz, 1H), 7.11 (d, $J$ = 7.6 Hz, 1H), 7.05 (d, $J$ = 6.4 Hz, 1H).$^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.1, 136.5, 133.8, 133.3, 133.2, 131.6, 131.4, 131.3, 130.5, 130.1, 130.0, 129.9, 129.8, 129.4, 128.9, 128.6, 128.2, 127.4, 122.5, 121.8, 116.4, 105.6; HRMS (ESI) calcd for $[C_{22}H_{12}Br_2N_2O_2 + H]^+$ 494.9338, found 494.9336.

*4,5-Di(thiophen-2-yl)-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3al**):* yellow solid (87%, 61.0 mg); mp 228−229 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.46 (d, $J$ = 7.8 Hz, 1H), 7.77−7.68 (m, 3H), 7.43 (d, $J$ = 4.8 Hz, 1H), 7.36 (d, $J$ = 4.8 Hz, 1H), 7.17 (d, $J$ = 2.4 Hz, 1H), 7.09 (t, $J$ = 4.4 Hz, 1H) 7.03−7.00 (m, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.9, 135.0, 131.3, 131.2, 131.1, 131.0, 129.9, 129.3, 128.5, 128.4, 128.1, 127.2, 127.1, 127.0, 126.5, 125.6, 116.1, 105.8; HRMS (ESI) calcd for $[C_{18}H_{10}N_2O_2S_2 + H]^+$ 351.0256, found 351.02562.

*4,5-Diethyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3am**):* yellow solid (79%, 38.4 mg); mp 164−165 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.39 (d, $J$ = 8.3 Hz, 1H), 7.98 (d, $J$ = 8.4 Hz, 1H), 7.77 (t, $J$ = 7.8 Hz, 1H), 7.66 (t, $J$ = 7.7 Hz, 1H), 3.12 (q, $J$ = 7.2 Hz, 2H), 2.99 (q, $J$ = 7.5 Hz, 2H), 1.32−1.27 (m, 6H).$^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.0, 132.4, 130.7, 130.6, 128.5, 128.3, 127.0, 125.3, 116.6, 107.3, 19.9, 19.8, 15.2, 15.0; HRMS (ESI) calcd for $[C_{14}H_{14}N_2O_2 + H]^+$ 243.1128, found 243.1126.

*4,5-Dipropyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3an**):* yellow solid (87%, 46.8 mg); mp 152−153 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.38 (d, $J$ = 8.3 Hz, 1H), 7.95 (d, $J$ = 8.4 Hz, 1H), 7.76 (t, $J$ = 7.7 Hz, 1H), 7.65 (t, $J$ = 7.7 Hz, 1H), 3.06 (t, $J$ = 8.0 Hz, 2H), 2.91 (t, $J$ = 8.0 Hz, 2H), 1.72−1.60 (m, 4H), 1.13−1.07 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.1, 131.4, 130.7, 129.6, 128.7, 128.3, 127.0, 125.5, 116.5, 107.5, 29.0, 28.3, 24.2, 23.9, 14.4, 14.1; HRMS (ESI) calcd for $[C_{16}H_{18}N_2O_2 + H]^+$ 271.1441, found 271.1444.

*4,5-Bis(ethoxycarbonyl)-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ao**):* yellow solid (77%, 51.0 mg); mp 112−113 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.54−8.51 (m, 1H), 8.44−8.40 (m, 1H), 7.87−7.80 (m, 2H), 4.52 (q, $J$ = 7.2 Hz, 2H), 4.45 (q, $J$ = 7.1 Hz, 2H), 1.45 (t, $J$ = 6.0 Hz, 3H), 1.42 (t, $J$ = 6.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 163.9, 162.9, 162.7, 132.2, 131.2, 128.4, 127.9, 127.2, 125.5, 120.3, 116.5, 104.2, 63.2, 62.7, 14.1, 14.0; HRMS (ESI) calcd for $[C_{16}H_{14}N_2O_6 + H]^+$ 331.0925, found 331.0920.

*4-Methyl-5-phenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ap**):* yellow solid (61%, 33.6 mg); mp 226−227 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.42 (d, $J$ = 8.2 Hz, 1H), 7.66 (t, $J$ = 7.6 Hz, 1H), 7.61 (t, $J$ = 7.6 Hz, 1H), 7.57−7.48 (m, 3H), 7.39 (d, $J$ = 8.1 Hz, 1H), 7.26 (d, $J$ = 7.1 Hz, 2H), 2.44 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.7, 135.2, 131.8, 130.7, 130.3, 129.4, 129.0, 128.6, 128.4, 127.7, 127.4, 126.6, 116.0, 107.6, 13.9; HRMS (ESI) calcd for $[C_{17}H_{12}N_2O_2 + H]^+$ 277.0972, found 277.0971.

*5-Methyl-4-phenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ap′**):* yellow solid (33%, 18.0 mg); mp 227−228 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.51 (d, $J$ = 8.3 Hz, 1H), 8.05 (d, $J$ = 8.2 Hz, 1H), 7.84 (t, $J$ = 7.6 Hz, 1H), 7.77 (t, $J$ = 7.7 Hz, 1H), 7.52−7.48 (m, 3H), 7.34 (d, $J$ = 7.3 Hz, 2H), 2.39 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.3, 132.4, 131.2, 131.0, 129.8, 129.2, 129.2, 128.7, 128.3, 127.4, 126.1, 126.0, 116.6, 106.5, 14.9; HRMS (ESI) calcd for $[C_{17}H_{12}N_2O_2 + H]^+$ 277.0972, found 277.0973.

*4-Ethyl-5-phenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3aq**):* yellow solid (67%, 38.9 mg); mp 170−171 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.43 (d, $J$ = 8.3 Hz, 1H), 7.66 (t, $J$ = 7.6 Hz, 1H), 7.59 (t, $J$ = 7.8 Hz, 1H), 7.56−7.49 (m, 3H), 7.32 (d, $J$ = 8.1 Hz, 1H), 7.28 (d, $J$ = 6.7 Hz, 2H), 2.82 (q, $J$ = 7.4 Hz, 2H), 1.16 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.0, 135.1, 133.7, 131.2, 130.6, 130.3, 129.7, 128.9, 128.6, 128.4, 127.9, 126.7, 116.0, 107.2, 21.1, 15.3; HRMS (ESI) calcd for $[C_{18}H_{14}N_2O_2 + H]^+$ 291.1128, found 291.1128.

*5-Ethyl-4-phenyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3aq′**):* yellow solid (18%, 10.6 mg); mp 195−196 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.51 (d, $J$ = 8.3 Hz, 1H), 8.06 (d, $J$ = 8.3 Hz, 1H), 7.83 (t, $J$ = 7.6 Hz, 1H), 7.75 (t, $J$ = 7.7 Hz, 1H), 7.54−7.49 (m, 3H), 7.34−7.32 (m, 2H), 2.81 (q, $J$ = 7.5 Hz, 2H), 1.19 (t, $J$ = 7.5 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.4, 132.6, 132.1, 131.0, 130.9, 129.3, 129.1, 128.7, 128.4, 128.2, 127.8, 126.1, 116.9, 106.5, 21.2, 15.3; HRMS (ESI) calcd for $[C_{18}H_{14}N_2O_2 + H]^+$ 291.1128, found 291.1126.

*5-Phenyl-4-propyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ar**):* yellow solid (68%, 41.2 mg); mp 162−163 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.42 (d, $J$ = 8.2 Hz, 1H), 7.65 (t, $J$ = 7.5 Hz, 1H), 7.61−7.57 (m, 1H), 7.56−7.49 (m, 3H), 7.33 (d, $J$ = 8.2 Hz, 1H), 7.27 (d, $J$ = 6.3 Hz, 2H), 2.79−2.75 (m, 2H), 1.57 (dq, $J$ = 14.9, 7.3 Hz, 2H), 0.86 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.1, 135.2, 132.3, 131.5, 130.6, 130.4, 129.6, 128.8, 128.6, 128.3, 127.9, 126.7, 116.0, 107.4, 29.5, 24.2, 14.1; HRMS (ESI) calcd for $[C_{19}H_{16}N_2O_2 + H]^+$ 305.1285, found 305.1287.

*4-Phenyl-5-propyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3ar′**):* yellow solid (17%, 10.3 mg); mp 184−185 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.51 (d, $J$ = 8.3 Hz, 1H), 8.03 (d, $J$ = 8.3 Hz, 1H), 7.82 (t, $J$ = 7.7 Hz, 1H), 7.75 (t, $J$ = 7.7 Hz, 1H), 7.54−7.48 (m, 3H), 7.33−7.30 (m, 2H), 2.76−2.72 (m, 2H), 1.64−1.55 (m, 2H), 0.89 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.4, 132.6, 131.1, 130.9, 130.8, 129.4, 129.1, 128.7, 128.5, 128.3, 127.7, 126.2, 116.8, 106.5, 30.1, 24.2, 14.3; HRMS (ESI) calcd for $[C_{19}H_{16}N_2O_2 + H]^+$ 305.1285, found 305.1286.

*Mixed products **3as** and **3as′**:* obtained in 1:1.1 ratio as a yellow solid in 66% yield (44.3 mg); mp 143−144 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.48 (d, $J$ = 8.2 Hz, 2H), 8.03 (d, $J$ = 7.8 Hz, 1H), 7.84−7.76 (m, 3H), 7.71 (t, $J$ = 7.3 Hz, 1H), 7.62 (d, $J$ = 8.2 Hz, 1H), 7.51−7.42 (m, 8H), 7.39−7.36 (m, 2H), 4.21 (q, $J$ = 7.1 Hz, 2H), 4.08 (q, $J$ = 7.1 Hz, 2H), 1.07 (t, $J$ = 7.1 Hz, 3H), 0.90 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 166.0, 163.9, 163.5, 163.0, 133.7, 132.8, 131.7, 131.6, 131.4, 131.3, 130.7, 130.0, 129.4, 129.1, 129.0, 128.8, 128.7, 128.3, 128.2, 127.8, 127.1, 126.9, 125.9, 123.9, 123.6, 116.4, 105.0,



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104.8, 62.4, 62.0, 13.7, 13.5; HRMS (ESI) calcd for $[C_{19}H_{14}N_2O_4 + H]^+$ 335.1026, found 335.1026.

*4,5-Bis(4-methoxyphenyl)-7-methyl-[1,2,3]oxadiazolo[3,4-a]-quinolin-10-ium-3-olate (**3bc**):* yellow solid (89%, 73.4 mg); mp 218−219 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.34 (d, $J$ = 8.5 Hz, 1H), 7.50 (d, $J$ = 8.4 Hz, 1H), 7.35 (s, 1H), 7.06−7.00 (m, 4H), 6.85 (d, $J$ = 8.1 Hz, 2H), 6.76 (d, $J$ = 8.2 Hz, 2H), 3.81 (s, 3H), 3.76 (s, 3H), 2.44 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.5, 159.1, 158.9, 141.5, 132.3, 131.8, 131.6, 131.2, 130.7, 129.5, 127.7, 127.2, 125.3, 124.1, 115.9, 113.8, 113.1, 106.1, 55.2, 55.1, 22.0; HRMS (ESI) calcd for $[C_{25}H_{20}N_2O_4 + H]^+$ 413.1496, found 413.1498.

*4,5-Bis(3-chlorophenyl)-7-methyl-[1,2,3]oxadiazolo[3,4-a]-quinolin-10-ium-3-olate (**3bj**):* yellow solid (64%, 54.1 mg); mp 231−232 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.40 (d, $J$ = 7.4 Hz, 1H), 7.59 (d, $J$ = 7.0 Hz, 1H), 7.31−7.20 (m, 5H), 7.12 (s, 2H), 7.05−7.00 (m, 2H), 2.48 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.1, 142.2, 136.4, 134.4, 133.7, 133.2, 131.5, 130.9, 130.4, 130.3, 130.1, 129.8, 129.4, 129.1, 128.6, 128.6, 128.5, 128.4, 127.5, 125.5, 116.2, 105.3, 22.0.HRMS (ESI) calcd for $[C_{23}H_{14}Cl_2N_2O_2 + H]^+$ 421.0505, found 421.0507.

*4,5-Diethyl-7-methyl-[1,2,3]oxadiazolo[3,4-a]quinolin-10-ium-3-olate (**3bm**):* yellow solid (79%, 40.3 mg); mp 153−154 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.25 (d, $J$ = 8.6 Hz, 1H), 7.71 (s, 1H), 7.46 (d, $J$ = 8.5 Hz, 1H), 3.10 (q, $J$ = 7.5 Hz, 2H), 2.96 (q, $J$ = 7.5 Hz, 2H), 2.59 (s, 3H), 1.31−1.26 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 165.0, 141.3, 132.4, 130.3, 129.8, 128.5, 125.1, 124.8, 116.3, 107.0, 22.1, 19.9, 19.7, 15.2, 15.0; HRMS (ESI) calcd for $[C_{15}H_{16}N_2O_2 + H]^+$ 257.1285, found 257.1287.

**Procedure for Synthesis of 4.** A mixture of **3aa** (67.6 mg, 0.2 mmol), acrylic acid (28.8 mg, 0.4 mmol), and $K_2S_2O_8$ (108.0 mg, 0.4 mmol) in 1,2-dichloroethane (3 mL) was placed into a pressure tube. The tube was heated at 120 °C for 16 h. After the reaction was completed (as monitored by thin-layer chromatography), the mixture was cooled to room temperature. The solvent was then evaporated in vacuum. The resulting residue was purified by flash column chromatography using PE/EA (50:1−20:1) to yield **4** as a white solid (72%, 46.1 mg).

*4,5-Diphenylpyrazolo[1,5-a]quinoline (**4**):* mp 214−215 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.41 (d, $J$ = 6.4 Hz, 2H), 7.30 (d, $J$ = 8.0 Hz, 1H), 7.25−7.15 (m, 6H), 7.12−7.10 (m, 2H), 7.05 (t, $J$ = 7.2 Hz, 1H), 6.65 (t, $J$ = 7.6 Hz, 1H), 6.52 (d, $J$ = 7.1 Hz, 1H), 4.07 (d, $J$ = 6.6 Hz, 2H), 3.31 (d, $J$ = 6.6 Hz, 2H), 3.26 (q, $J$ = 7.2 Hz, 4H), 0.71 (t, $J$ = 7.2 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 141.3, 139.2, 137.0, 136.8, 134.2, 134.0, 131.1, 130.1, 129.1, 129.0, 128.0, 127.9, 127.4, 127.3, 124.6, 124.1, 115.4, 101.0 (one carbon is not visible due to overlapping peaks); HRMS (ESI) calcd for $[C_{23}H_{16}N_2 + H]^+$ 321.1386, found 321.1389.

**Procedure for Synthesis of 5.** To an oven-dried 35 mL pressure tube equipped with a stir bar was added 0.24 mmol (71.5 mg) of the aryne precursor, followed by 0.2 mmol of **3aa** (67.6 mg). THF (2 mL if using solid TBAF, 1.7 mL if using a solution of TBAF) was added, and the mixture was stirred until all solid dissolved under nitrogen. To this solution was added 0.3 mmol of solid TBAF (1.6 equiv) in one portion (or 0.3 mL of 1 M TBAF solution in THF dropwise). The reaction mixture was stirred at room temperature overnight. Upon completion, the reaction mixture was poured into saturated aqueous $NaHCO_3$ and extracted three times with EtOAc. The combined extracts were washed once with brine, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography using PE/EA (50:1−20:1) to afford the product **5** (80%, 59.6 mg) as a yellow solid.

*5,6-Diphenylindazolo[2,3-a]quinoline (**5**):* mp 251−252 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.07 (d, $J$ = 8.4 Hz, 1H), 7.93 (d, $J$ = 8.7 Hz, 1H), 7.75 (t, $J$ = 7.5 Hz, 1H), 7.59 (d, $J$ = 8.1 Hz, 1H), 7.47−7.41 (m, 2H), 7.33−7.32 (m, 3H), 7.28−7.24 (m, 5H), 7.21−7.19 (m, 2H), 6.88 (t, $J$ = 7.5 Hz, 1H), 6.66 (d, $J$ = 8.5 Hz, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 149.6, 136.4, 136.4, 133.9, 133.4, 131.6, 131.1, 130.6, 130.2, 129.1, 128.4, 127.9, 127.9, 127.9, 127.7, 127.4, 126.1, 125.5, 121.7, 120.4, 117.5, 117.3, 116.5; HRMS (ESI) calcd for $[C_{27}H_{18}N_2 + H]^+$ 371.1543, found 371.1546.

**Procedure for Synthesis of 6.** A mixture of **3aa** (67.6 mg, 0.2 mmol) and dimethyl acetylenedicarboxylate (34.1 mg, 0.24 mmol) in toluene (2 mL) in a sealed tube was heated at 115 °C overnight. The mixture was cooled to room temperature. The solvent was then evaporated in vacuum. The resulting residue was purified by silica column chromatography using PE/EA (4:1) to afford the product **6** (81%, 70.8 mg) as a white solid.

*Dimethyl 4,5-diphenylpyrazolo[1,5-a]quinoline-2,3-dicarboxylate (**6**):* mp 272−273 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.83 (d, $J$ = 8.4 Hz, 1H), 7.71 (t, $J$ = 7.0 Hz, 1H), 7.47−7.41 (m, 2H), 7.28−7.26 (m, 3H), 7.22−7.20 (m, 3H), 7.16−7.12 (m, 4H), 3.99 (s, 3H), 3.26 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 164.2, 162.1, 141.9, 137.7, 136.8, 135.7, 135.2, 133.3, 130.6, 130.2, 129.8, 128.7, 128.1, 128.0, 127.8, 127.7, 127.6, 126.4, 124.7, 116.5, 111.8, 52.7, 52.3; HRMS (ESI) calcd for $[C_{27}H_{20}N_2O_4 + H]^+$ 437.1496, found 437.1499.

**Procedure for Synthesis of 7.** A mixture of **3aa** (67.6 mg, 0.2 mmol) and *N*-ethylmaleimide (50.0 mg, 0.4 mmol) in toluene (2 mL) in a sealed tube was heated at 115 °C overnight. The mixture was cooled to room temperature. The solvent was then evaporated in vacuum. The resulting residue was purified by silica column chromatography using PE/EA (2:1−1:1) to afford the product **6** (72%, 78.3 mg) as a yellow solid.

*8,14-Diethyl-5,6-diphenyl-6b,9a-dihydro-7H-6a,10-[3,4]-epipyrrolopyrrolo[3′,4′:3,4]pyrazolo[1,5-a]quinoline-7,9,13,15(8H)-tetraone (**7**):* mp 204−205 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.41 (d, $J$ = 6.4 Hz, 2H), 7.30 (d, $J$ = 8.0 Hz, 1H), 7.22−7.15 (m, 6H), 7.12−7.10 (m, 2H), 7.05 (t, $J$ = 7.2 Hz, 1H), 6.65 (t, $J$ = 7.6 Hz, 1H), 6.52 (d, $J$ = 7.1 Hz, 1H), 4.07 (d, $J$ = 6.6 Hz, 2H), 3.31 (d, $J$ = 6.6 Hz, 2H), 3.26 (q, $J$ = 7.2 Hz, 4H), 0.71 (t, $J$ = 7.2 Hz, 6H); $^{13}$C NMR (100 MHz, DMSO) $\delta$ 173.3, 173.2, 139.6, 138.2, 138.2, 137.3, 131.0, 130.1, 129.7, 128.4, 127.4, 127.2, 127.1, 126.8, 122.9, 121.0, 113.1, 76.4, 68.3, 53.9, 33.6, 12.1; HRMS (ESI) calcd for $[C_{33}H_{28}N_4O_4 + H]^+$ 545.2183, found 545.2185.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b02356.

Experimental procedures, characterization data, alternative mechanisms, and $^1$H and $^{13}$C NMR spectra (PDF)

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### Notes

The authors declare no competing financial interest.

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