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Aryl Pyrazoles from Photocatalytic Cycloadditions of Arenediazonium

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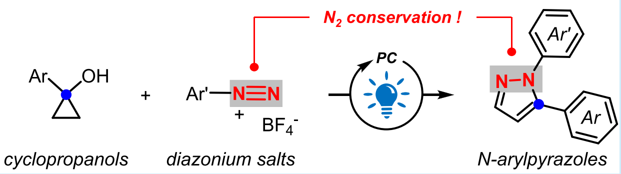
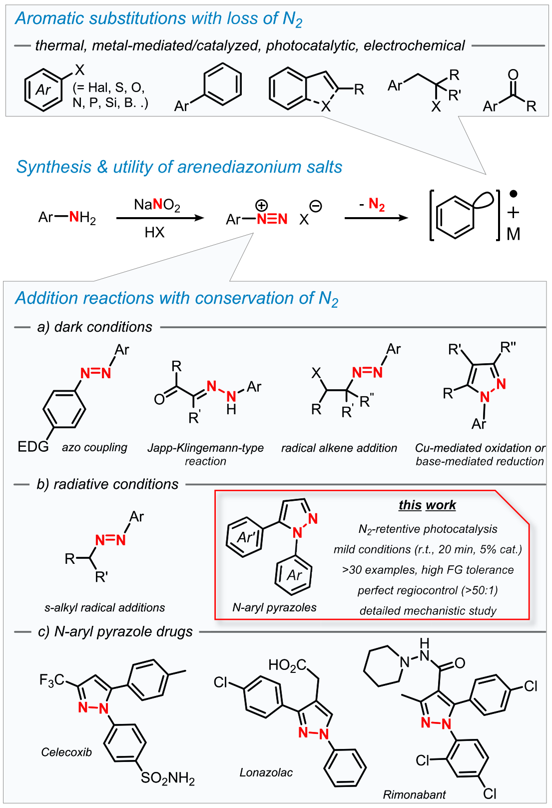
ABSTRACT: A photocatalytic synthesis of 1,5-diaryl pyrazoles from arenediazoniums and arylcyclopropanols is reported. The reaction proceeded under mild conditions (rt, 20 min) with catalytic $[Ru(bpy)_3]^{2+}$ under blue-light irradiation and exhibited compatibility with several functional groups (e.g., I, SF_5, SO_2NH_2, N_3, CN) and perfect levels of regiocontrol. Mechanistic studies (luminescence spectroscopy, CV, DFT, radical trapping, quantum yield determination) documented an initial oxidative quenching of the excited photocatalyst and the operation of a radical-chain mechanism.



Arenediazonium salts constitute synthetically versatile building blocks for aromatic substitutions by virtue of their easy availability as stable crystalline solids, the high thermodynamic driving force to form reactive aryl radical, aryl cation, or arylmetal species by loss of N_2 (Scheme 1, middle), and the wide variety of onward reactions with many reagents.[1] Numerous protocols involving thermal, metal-catalyzed, electrochemical, and photoredox conditions were reported that enable facile formations of C−C and C−Het bonds (X = Hal, S, O, N, P, Si, B, and many more, see Scheme 1, top).[2] On the other hand, the arsenal of addition reaction mechanisms that conserve the N_2 function into the product structure is much less diverse. Examples include azo-couplings with electron-rich benzenes,[3] cycloadditions,[4] radical trappings,[5] and Japp−Klingemann-type reactions.[6] These protocols proceed through thermal, oxidative, or metal-catalyzed reaction mechanisms (Scheme 1, b). Photocatalytic reaction pathways of arenediazonium salts that operate with retention of N_2 are very rare due to the facile reductive mesolysis of arenediazonium salts at very low redox potentials of ∼0 V (vs SCE).[7] There are only three literature reports of photocatalytic arenediazonium reactions which all include the trapping of alkyl radicals to give acyclic azo-compounds.[8] Minimal mechanistic insight has been provided, especially with regard to the inertness of arenediazonium to 1e-reduction in the presence of sufficiently strong photoreductants. This work reports an unprecedented photocatalytic cycloaddition of arenediazonium with cyclopropanol to form 1,5-diaryl pyrazoles with perfect regiocontrol. A detailed analysis of the underlying mechanism by preparative, spectroscopic, and theoretical methods is given. This method provides a straightforward access to *N*-aryl pyrazoles,[9] which constitute key motifs of pharmaceutical blockbusters such as celecoxib, lonazolac, and rimonabant (Scheme 1, c), agrochemicals, and ligands of metal-catalyzed cross-coupling reactions.[10]

Scheme 1. Dark and Photocatalytic Reactions of Arenediazonium Salts



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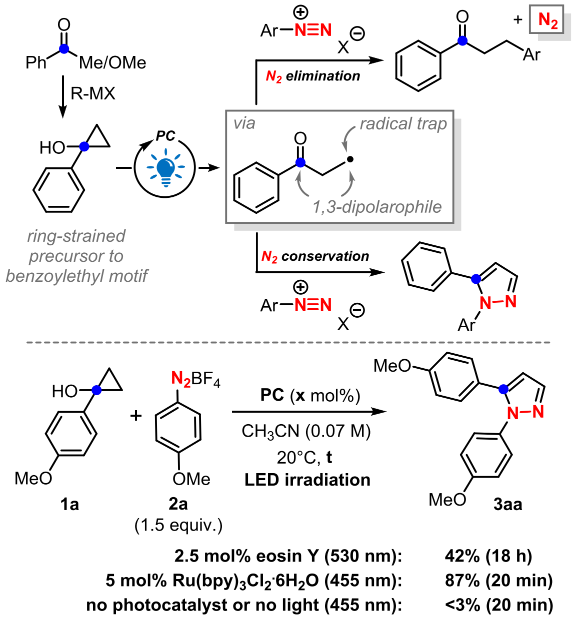
We envisioned utilizing 1-aryl-1-cyclopropanols as C_3-building blocks that can easily be prepared by organometallic addition to benzoyl derivatives in a Simmons–Smith[11] or Kulinkovich reaction.[12] 1-Aryl-1-cyclopropanols could engage in photocatalytic ring-opening to provide a benzoylethyl motif exhibiting 1,3-dipolarophilic reactivity.[13] In the presence of arenediazonium, radical trapping would result in the formation of *β*-aryl propiophenones via N_2-elimination[14] or diaryl pyrazoles via N_2-retentive formal cycloaddition (Scheme 2).

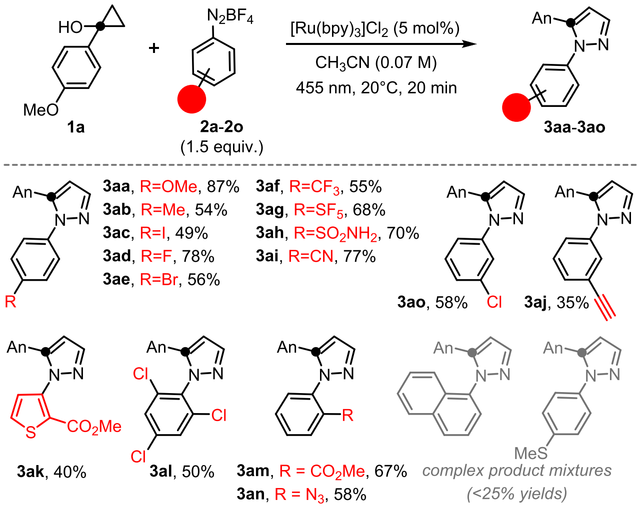
Scheme 2. (Top) Postulated Reactions of Arylcyclopropanol with Arenediazonium to Give *β*-Aryl Phenones (via N_2-Elimination) or 1,5-Diaryl Pyrazoles (via N_2-Conservation). (Bottom) Key Discoveries of Photocatalytic Aryl Pyrazole Synthesis



Our initial investigations of the model reaction between 1-anisyl-1-cyclopropanol (**1a**) and 4-methoxybenzenediazonium tetrafluoroborate (**2a**) with the organic photocatalyst eosin Y indeed afforded the pyrazole **3aa** in 42% yield as the sole product (Table S1). The product yield could be increased to 87% after 20 min reaction time when using $[Ru(bpy)_3]Cl_2\cdot 6H_2O$ as photocatalyst and the appropriate irradiation wavelength. Further decrease of the catalyst loading (<5 mol %) or reaction time gave inferior yields. The observed reactivity is noteworthy as the photocatalytic conditions with virtually all common molecular photocatalysts (including eosin Y, $Ru(bpy)_3Cl_2\cdot 6H_2O$, $Ir(ppy)_3$) provide sufficient reduction ability to mesolyze arenediazonium salts irreversibly via an SET.[15] Control experiments in the absence of photocatalyst and light, respectively, did not afford any products.[17,18] The optimal conditions involved reaction of the arene-diazonium salt **1a** (1.5 equiv) with the arylcyclopropanol **2a** in acetonitrile at room temperature for 20 min under blue light irradiation (455 nm) in the presence of catalytic $Ru(bpy)_3Cl_2\cdot 6H_2O$. The resultant 1,5-diaryl pyrazole is a common structural motif of fine chemicals and pharmaceuticals that is conventionally assembled from aryl 1,3-dicarbonyl derivatives and aryl hydrazines, with the latter substrates being prepared by Cu-catalyzed aminations of aryl halides.[16] A related Cu-mediated oxidative cyclization to *N*-aryl pyrazoles was reported, and a dark proton-coupled electron transfer mechanism in the presence of stoichiometric Cu(II) salt was postulated.[9i]

The substrate scope was explored upon variation of both starting materials. Arenediazonium salts bearing electron-withdrawing and electron-donating substituents in the *ortho*-, *meta*-, and *para*-positions were equally reactive (Scheme 3).

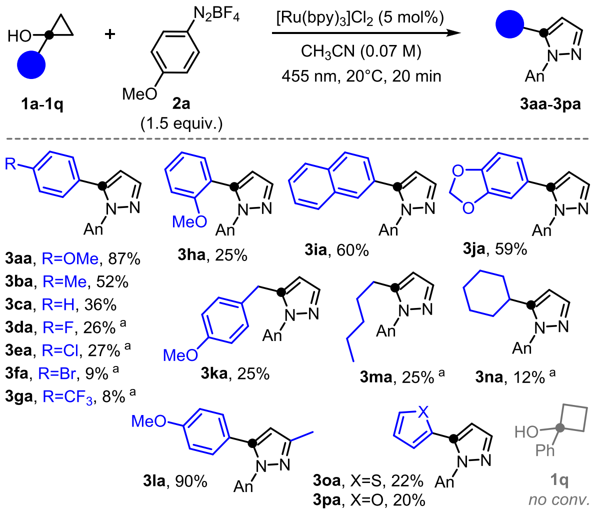
Scheme 3. Substrate Scope of Arenediazonium Salts[a]



[a] An = 4-anisyl; isolated yields are given.

Generally, no significant electronic effect on the reactivity of the diazonium salts was observed (**3aa**–**3ao**). However, naphthalenediazonium tetrafluoroborate and 4-(methylthio)-benzenediazonium tetrafluoroborate gave complex product mixtures and only low yields of the corresponding pyrazoles (<25%), possibly by unwanted radical attack on the naphthalene and thioether moieties.[19] Variations of the cyclopropanol derivative revealed a significant influence of their individual electronic properties (Scheme 4): electron-donating substituents enabled high yields of the diaryl pyrazoles (**3aa**–**3ca**, **3ha**–**3ja**); electron-withdrawing substituents showed poor conversions under the reaction conditions

Scheme 4. Substrate Scope of Cyclopropanols[a]



[a] An = 4-anisyl; isolated yields are given; 24 h.

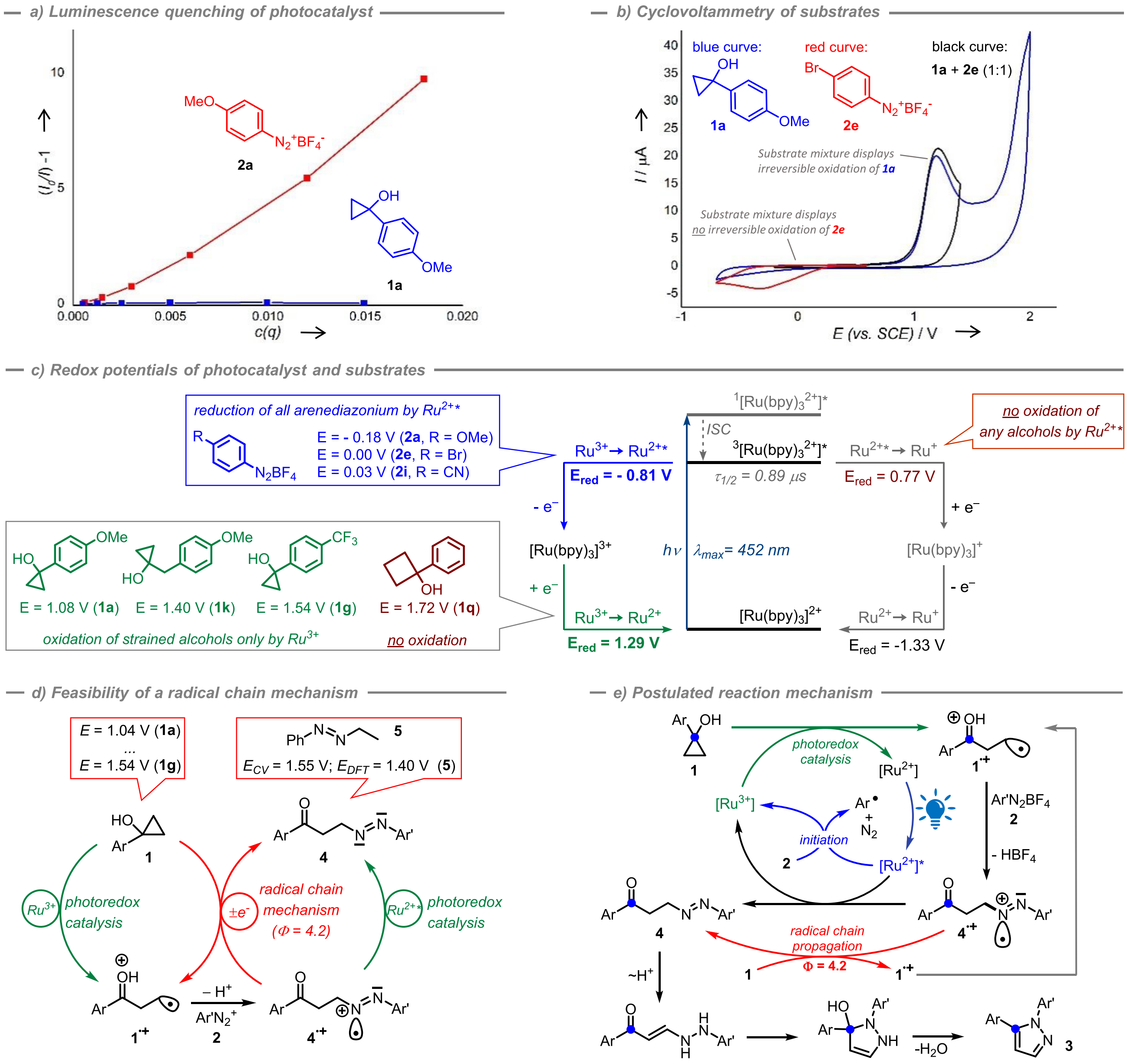


Figure 1. (a) Luminescence quenching of $[Ru(bpy)_3]Cl_2$ with the substrates **1a** and **2a**. c(q) = quencher concentration (mol/L). (b) Cyclic voltammetry spectra of **1a**, **2e**, and an equimolar mixture. (c) Reduction potentials E_{red} of substrates and photocatalyst (vs SCE). (d) Postulated trapping of intermediate $\mathbf{1}^{\bullet+}$ and the feasibility of radical chain propagation. (e) Proposed mechanism based on preparative, spectroscopic, and theoretical studies.

(**3da**−**3ga**). Increased steric hindrance on the cyclopropane did not lead to decreased yields (**3la**). Alkyl- and benzyl-substituted cyclopropanols gave low yields (**3ka**, **3ma**, and **3na**). The higher homologue 1-phenyl-1-cyclobutanol (**1q**) gave no ring-opening or heterocycle formation.

In an effort to elucidate the mechanism of this photocatalytic pyrazole synthesis, we conducted a series of preparative, spectroscopic, and theoretical studies. The preservation of the N_2 moiety within the product structure is a very rare feature of reactions with arenediazonium salts.[5a,8,9d] Under photocatalytic conditions, this is even less likely due to the very facile 1e-reduction of arenediazonium salts (at ~0 V vs SCE) followed by irreversible mesolysis and N_2 evolution.[5] Consequently, we probed whether the photocatalytic mechanism involved any reduction event of the arenediazonium at all or rather oxidation of the cyclopropanol by the photocatalyst. A Stern−Volmer study, however, documented that efficient luminescence quenching of excited-state $[Ru(bpy)_3]Cl_2$ ($[Ru^{2+}]^*$) was indeed operative with the diazonium salt **2a** (see the Supporting Information for details). Consistently, no quenching was observed with the electron-poor and electron-rich cyclopropanols **1g** and **1a**, respectively (Figure 1a).

The nonlinearity of the plot for **2a** is a direct consequence of the kinetic salt effect[20] of increased ionic strength of the solution by addition of the diazonium salt. Quencher and catalyst are charged species, so the ionic strength affects the rate of their reaction with each other. According to the Debye−Hückel theory, the Stern−Volmer quenching constants K_3, extrapolated to zero ionic strength, were calculated. K_{SV0} increased with lower electronic density of the arenediazonium: K_{SV0}(**2a**) = 88 dm^3/L; K_{SV0}(**2e**) = 490 dm^3/L; K_{SV0}(**2i**) = 1500 dm^3/L. These data are indicative of an oxidative quenching of the excited photocatalyst [Ru^{2+}]* by the diazonium salt. This is further supported by the observed gas evolution during the reaction. The reductive mesolysis of the arenediazonium salt is also in full accord with the detection of an aryl-TEMPO adduct and the inhibition of product formation by addition of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO, Figure S2). Further insight into the operating redox events was provided by the analysis of the redox potentials (Figure 1c). Cyclic voltammetry (CV) confirmed that facile reduction of arenediazonium salts is thermodynamically feasible with the excited-state photocatalyst: E_{red}(**2a**) = −0.18 V; E_{red}(**2e**) = 0.00 V; E_{red}(**2i**) = +0.03 V; E_{red}([Ru^{2+}]*)= −0.81 V (vs SCE).[21] The difference in redox potentials of this series explains the observed trend in the quenching constants K_{SV0} above where easily reduced compounds quench [Ru^{2+}]* faster. On the other hand, [Ru^{2+}]* (E_{red} = +0.77 V) is not a sufficiently strong oxidant for the 1e-oxidation of any of the cyclopropanols (E_{red} > + 1 V). These data support the notion of an initiating oxidative quenching of [Ru^{2+}]*. The resultant ground-state [Ru^{3+}] is sufficiently oxidizing (E_{red} = +1.29 V) to convert electron-rich cyclopropanols (E_{red}(**1a**) = +1.08 V), while 1e-oxidations of electron-poor cyclopropanols are thermodynamically unfavored and only feasible when coupled with efficient follow-up reactions (E_{red}(**1g**) = +1.40 V; E_{red}(**1k**) = +1.54 V; i.e., <250 mV uphill).[22] Unstrained cycloalkanols have reduction potentials (E_{red} (**1q**) = +1.72 V) that are prohibitive for oxidations with [Ru^{3+}] (Figure 1c). A proton-coupled electron transfer mechanism in combination with a more strongly oxidizing photosensitizers such as acridinium salts could overcome this limitation.[23] The operation of an H atom-abstraction mechanism[9i] was excluded based on the perfect correlation of cycloalkanol reactivities and oxidation potentials. The fate of the oxidized cyclopropanols was another puzzle piece of the operating reaction mechanism. One-electron oxidations of cyclopropanols have been known to result in labile radical cations that undergo rapid ring-opening to β-keto radicals.[14a] The feasibility of trapping of the intermediate benzoylethyl radicals **1**$^{\bullet+}$ with arenediazonium **2** was probed by a CV experiment (Figure 1b): The cyclopropanol **1a** (blue line) displayed an irreversible oxidation wave (E_{red} = +1.08 V), the diazonium salt **2f** (red line) an irreversible reduction wave (E_{red} = +0.00 V). However, subjection of an equimolar mixture of both substrates to such CV electrolysis (black line; increasing potentials from 0.5 V), an unchanged oxidation peak of **1a** was observed while the reduction peak of **2e** disappeared. This is indicating that the oxidized alcohol **1a**$^{\bullet+}$ underwent chemical reaction with the diazonium salt prior to reduction of the latter. The resultant adduct of **1**$^{\bullet+}$ and **2** (i.e., **4**$^{\bullet+}$) engages in 1e-reduction to a neutral compound that cyclizes to a pyrazole. Further insight was derived from the quantum yield of Φ = 4.2 for the formation of **3aa**. This value indicates the presence of an efficient radical chain propagation, which most likely is the oxidation of cyclopropanol **1** with the radical adduct **4**$^{\bullet+}$ (Figure 1d). To probe its feasibility, we utilized the model compound 2-ethyl-1-phenyldiazene (**5**), which should exhibit similar redox properties as **4** but undergo no onward cyclization reaction. CV spectra showed irreversible oxidation of **5** at +1.55 V. This value is likely to include overpotential, so we also obtained a DFT-derived theoretical reduction potential of **5** (+1.40 V, see Supporting Information). In comparison with the reduction potentials of the cyclopropanols (1.08−1.54 V), these support the operation of radical chain propagation by reactions of the cyclopropanols **1** with the radical adduct intermediates **4**$^{\bullet+}$ (Figure 1d). Based on the collected mechanistic data, we propose the reaction mechanism shown in Figure 1e. The reaction is initiated by oxidative quenching of [Ru^{2+}]* with the arenediazonium salt **2**. The resultant [Ru^{3+}] oxidizes the strained alcohol **1** to give **1**$^{\bullet+}$ which undergoes rapid ring-opening and radical trapping with the arenediazonium salt. The radical cation adduct **4**$^{\bullet+}$ can engage in a radical chain process by oxidizing another molecule of **1** or quench the excited catalyst to close the photocatalytic cycle. As the radical chain process is dominant (Φ = 4.2), cocatalytic amounts of the arenediazonium **2** are required to produce the key oxidant [Ru(bpy)$_3$$^{3+}$] salt must be used to activate the catalyst, which is also evident from the optimal reaction conditions involving a slight excess of **2**. The adduct **4** undergoes cyclization and dehydration to give the pyrazole **3**.

In conclusion, this protocol enables a rare photocatalytic reaction of arenediazonium that proceeds with conservation of the diazo function. In the presence of arylcyclopropanols, *N*-arylpyrazoles are obtained within 20 min under blue light irradiation in good yields. The reaction displayed high regiocontrol (only 1,5-diaryl pyrazoles formed) and high functional group tolerance (F, Cl, N_3, CO_2Me, CN, CF_3, SF_5, thiophene, alkyne). Combined synthetic, spectroscopic, and theoretical studies supported the notion of a radical chain mechanism, which involves photocatalytic initiation by oxidative photocatalyst quenching with the arenediazonium, oxidation of the arylcyclopropanol with ground-state [Ru^{3+}]*, and radical chain propagation between the arylcyclopropanol and the radical cationic adduct of both starting materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02514.

Experimental procedures, analytical data, and spectra (PDF)

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Notes

The authors declare no competing financial interest.

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