JOC The Journal of Organic Chemistry

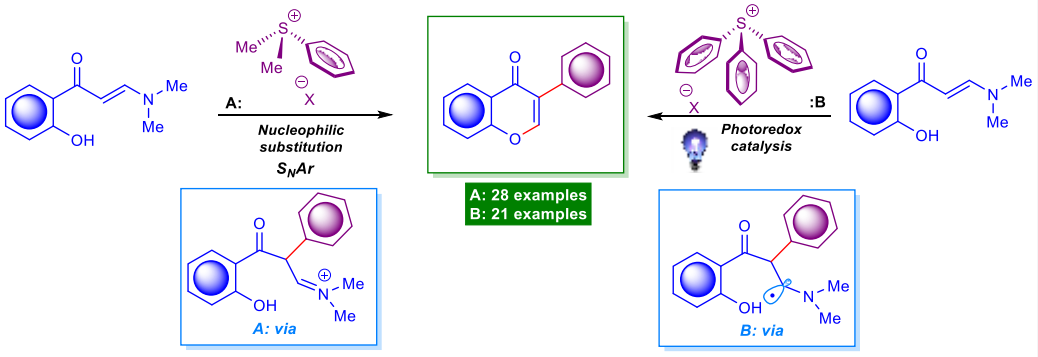
pubs.acs.org/joc Article

Arylation of *ortho*-Hydroxyarylenaminones by Sulfonium Salts and Arenesulfonyl Chlorides: An Access to Isoflavones

Satenik Mkrtchyan* and Viktor O. Iaroshenko*

Cite This: *J. Org. Chem.* 2021, 86, 4896–4916 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information



ABSTRACT: Herein we disclose three new methods for the straightforward and efficient synthesis of 3-arylchromones following the arylation of *ortho*-hydroxyarylenaminones by vast diversities of bench-stable and easy-to-use sulfonium salts and arenesulfonyl chlorides. Both developed methods, namely the light-mediated photoredox and electrophilic arylation, showed good efficiency, and are feasible for the preparation of 3-arylchromones in good-to-excellent yields. This work showcases the first described attempt where the sulfonium salts and arenesulfonyl chlorides were successfully utilized for the construction of the chromone heterocycle system.

INTRODUCTION

It is rather difficult to overestimate the importance and the role of isoflavones, a class of naturally occurring compounds which are often referred to in the contemporary literature as 3-arylchromones. Besides application in various aspects of human life, these compounds have gained a pivotal position in medicine and life science.[1] The application of 3-arylchromones and their functionalized derivatives as a part of herbal extracts can be traced back to ancient times. In addition, nowadays, the 3-arylchromone scaffold is a well-known pharmacophore of utmost importance with a broad spectrum of biological properties, among which one should highlight the following activities: antimicrobial, antiestrogenic, cardiovascular, anti-inflammatory, chemopreventative activities, and antioxidant action.[1]

The importance of this heterocyclic system and its broad application justifies the development of more efficient and low-cost preparative methods as well as strategies for late-stage diversification of chromones and 3-arylchromones. Presently known synthetic routes for construction of 3-arylchromone framework by their virtue can be divided into six main tactics (Figure 1), namely the following: (i) The installation of aryl substituents at the position 3 of the chromone skeleton is very often bolstered on the set of well-developed C−C-couplings using 3-functionalized chromones as a starting point. This includes the C−C couplings between 3-halogen-chromones with arylboronic acids,[2] arylstanyls, triarylbismuths,[3] as well as arylzincbromide reagents[4] used as coupling counterparts, while decarboxylative Suzuki−Miyaura coupling of (hetero)aromatic carboxylic acids was also utilized;[5] palladium-catalyzed oxidative cross-coupling reaction of arylboronic acids with 3-diazo-2,3-dihydro-4*H*-1-benzopyran-4-one is another way to reach 3-arylchromones.[6] (ii) The second disconnection is based upon the arylation of *ortho*-hydroxyarylenaminones which leads via domino cyclization to the construction of the chromone core. Among these are direct arylation of *ortho*-hydroxyarylenaminones following either visible-light-mediated protocol using aryldiazonium and diaryliodonium salts,[7] or oxidative C−H activation route utilizing arylboronic acids[8] along with Pd-catalysis. (iii) Construction of 3-arylchromones can also be achieved by [4 + 2] cyclization reactions of salicylaldehyde with the set of 1,2-CC-building blocks.[9] At the same time, other

Received: September 26, 2020
Published: March 15, 2021

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896–4916

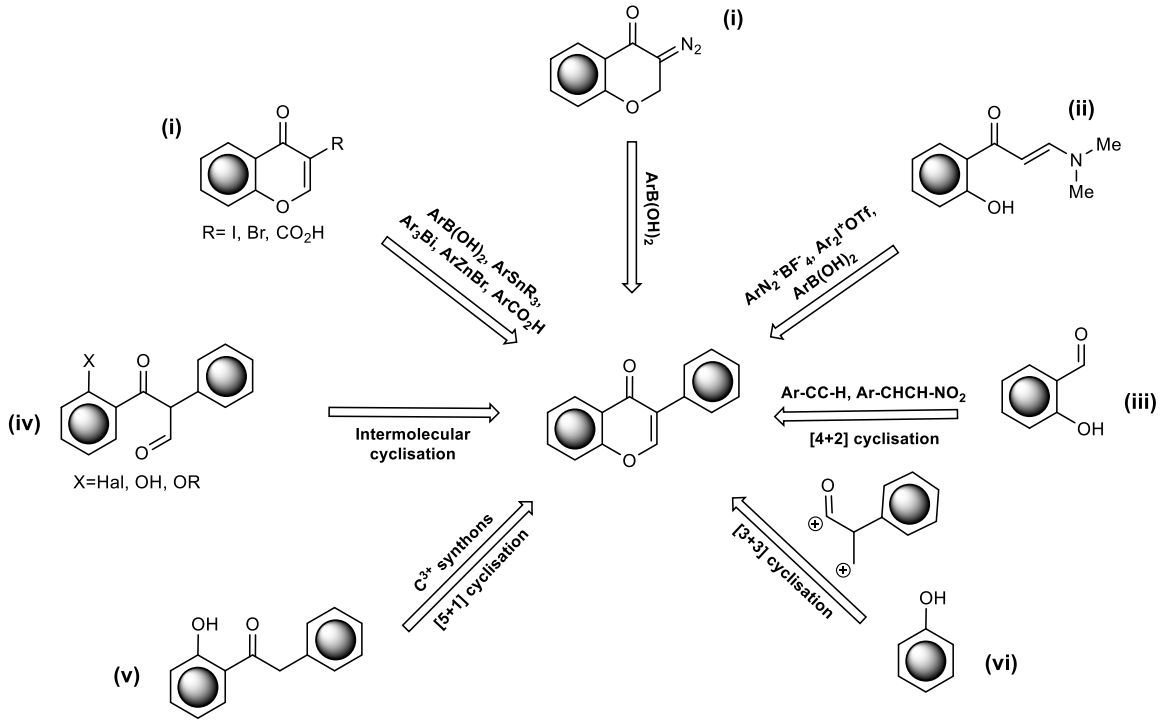


Figure 1. Synthetic tactics for construction of isoflavone framework.

strategies like (iv) [3 + 3]-cyclizations,[10] (v) [5 + 1]-cyclizations,[11] and (vi) intermolecular cyclizations of appropriate linear precursors[12] constitute a vast set of reaction used for preparation of the title heterocycles. On the other hand, more obsolete strategies which have no practical applications nowadays were also utilized.[13,14] Many of the presented tactics are tedious multistep routes which involve cumbersome procedures, in some cases with poor functional group tolerance and insufficient efficiency. Thus, there is a growing need of new synthetic tactics which can address the current challenges in concise preparation of 3-arylchromones. A recent tendency in contemporary organic chemistry literally implies search for new, green, low-cost, and more efficient methods which would allow for generation of vast diversities of privileged complex organic molecules. The preparation of 3-substituted chromones is very often based upon the functionalization of *ortho*-hydroxyarylenaminones featuring either electrophilic[15] or radical reagents.[16] The latest tactics involving carbon-centered radicals are still at a nascent stage of development and scarcely presented in the modern literature by seven examples only.[7,17,18]

Owing to the great potential the light-mediated synthetic strategies have, very recently we expanded the pool of known concise methodologies for 3-arylchromone preparation by two methods, which are based upon the arylation of *ortho*-hydroxyarylenaminones by aryl diazonium and diaryliodonium salts catalyzed by Eosin Y and $Ru(bpy)_3Cl_2$, respectively.[7] Both synthetic methodologies exerted high yields and excellent functional group tolerance. As we continue our quest for new strategies aimed at an efficient preparation of chromones,[7,16,19] and in a view of our recently developed methods which utilize aryldiazonium tetrafluoroborates and the diaryliodonium hexafluorophosphates,[7] we considered other onium salts, namely the sulfonium salts, which are often described as synthetic equivalents of aryl halides in photoredox and transition metal-catalyzed cross-coupling reactions, as reagents fit for the application for the highlighted arylation scenario. Given the recent literature data on the chemical properties and behavior of sulfonium reagents, we also assumed that the aryl sulfonium moiety can undergo photocatalytic reduction by numerous photoredox catalysts enabling the generation of the elusive aryl radical intermediates.[20]

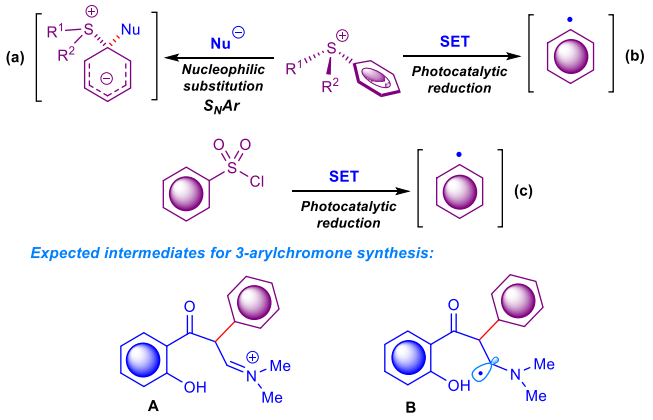
On the other hand, dialkyl aryl sulfonium salts showed propensity to react with numerous soft and hard nucleophiles, thus being used as efficient arylation agents in reaction with various heteroatom nucleophiles, providing a facile route for N−C, O−C, B−C, S−C, Se−C, Si−C, and Sn−C bond formation.[21] Recent studies show that mechanistically these reactions represent a classical aromatic nucleophilic substitution (S_NAr). Moreover, sulfonyl chlorides are widely used precursor for photo generation of aryl radicals using transition-metal and organic dye photocatalysts; further, these processes were coupled with numerous arylation scenarios.[20e,22] Thus, taking into account at least two different reaction mechanisms known for the reactivity of aryl sulfonium salts and the propensity of sulfonyl chlorides to be utilized as precursors for generation of aryl radicals, we set three synthetic scenarios, meant for aryl functionalization of *ortho*-hydroxyarylenaminones based on (a) the direct transition-metal free electrophilic arylation and (b, c) photoredox arylation protocols, respectively (Schemes 1, 2). In turn, we presumed that these transformations might have to proceed via the formation of the intermediates **A** and **B**, respectively (Scheme 1).

RESULTS AND DISCUSSION

Initial studies were aimed at the design of efficient reaction conditions for the three title model reactions. First, we assumed that for the direct arylation of *ortho*-hydroxyarylenaminones optimal reagent, due to the sterical encumbrance caused by bulkier Ar_2S residue, should be the dimethyl(aryl)sulfoniums and the reaction should take place in polar aprotic solvents in the presence of a base. This was the starting point in the reaction

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

Scheme 1. Mechanism-Based Reactivity of Aryl Sulfonium Salts and Aryl Sulfonyl Chloride with *ortho*-Hydroxyarylenaminones



conditions optimization for the model reaction of the Scheme 2a between the corresponding *ortho*-hydroxyarylenaminone **1b** and the (4-fluorophenyl)dimethylsulfonium trifluoromethanesulfonate **2i** illustrated in the Table S1 in the Supporting Information. Thus, the best outcome was observed when we took DMF as a solvent and Cs_2CO_3 as a base; these conditions allowed for the preparation of the model compound **5e** in 89% yield (Table S1, Entries 8−12). Other variations, for instance K_2CO_3 as a base (Entries 4, 5, 7, 13) and solvents such as CH_3CN and DMSO (Entries 1−6), appeared to be less operational and delivered the desired product in lower yields. Overall, we formulated the best reaction conditions which consisted of using of Cs_2CO_3 as a base and dry DMF as a solvent. It requires 1.3 excess of dimethyl(aryl)sulfonium salt; with this composition the reaction reached its completion within 5 h at 90 °C (Table S1, Entry 9).

Noteworthy, relatively low reduction potential of sulfonium salts conditions the use of stronger reductants for the photoredox-promoted generation of free aryl radicals. In particular, the iridium and ruthenium complexes such as *fac*-$Ir(ppy)_3$ **I**, $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ **II** and $Ru(bpy)_3Cl_2 \cdot 6H_2O$ **III** are often used for the photoreductive generation of aryl radicals via a reductive cleavage of C−S bound in sulfonium salts.[23] We commenced by testing the complexes **I**−**III** as potential photocatalysts to the model reaction depicted in the Scheme 2b, where we aimed to exploit the reactivity of the dimethyl(aryl)sulfoniums **2** under the photoredox conditions. Unfortunately, the initial screening of reaction conditions showcased that salts **2** were actually prone to reacting with the *ortho*-hydroxyarylenaminone generating the expected chromones, albeit with low efficiency—the best hit within the Ir catalyst **II** based conditions yielded the chromone molecule in 47% yield (not mentioned in the Supporting Information). Thus, as the second option, corresponding triarylsulfonium salts **3** were put into consideration. To our great delight first setups with these salts using iridium complexes **I** and **II** in combination with either sodium carbonate or acetate led to the successful formation of the compound **5e** (Table S2, Entries 1−10). The best reaction conditions for iridium photocatalysts **I** and **II** were the utilization of 1.5 equiv of sulfonium salt, NaOAc (1.8 equiv) as a base with DMSO as solvent; in both cases the corresponding chromone was isolated in 84% and 89% yield, respectively (Entries 6, 10). We witnessed that the elimination of the base resulted in a drastic drop of the yields of the model compound **5e** for these two reactions (Table S2, Entries 7, 8). Next, we switched our attention to the more readily available ruthenium photocatalysts **III**−**V**. It is of note that all three catalytic species were prone to promote the title model reaction and enabled the formation of chromone derivative **5e** in different yields (Table S2, Entries 11−16, 20, 21). After changing such variables like solvent, base, and the reaction duration, we came onto the formulation of the optimal reaction conditions, which we further used for deployment of this synthetic protocol, preceding the range of experiments where we used different Ru-based photocatalysts from Scheme 2 and tested numerous solvents and additives (for more details see Table S2). Finally, after optimization the chromone **5e** was prepared in 92% yield utilizing the nonsophisticated reaction conditions by using sulfonium salt **3d** (1.4 equiv), photocatalyst $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (2 mol %), NaOAc (1.8 equiv), reaction took place in CH_3CN, reached completions within 3 h at room temperature under intensive blue LED irradiation (Table S2, Entry 14). Notably, to prove that this synthetic scenario takes a radical arylation pathway, we conducted a classical TEMPO quenching experiment under the best reaction conditions, which completely suppressed the radical domino cyclization and did not yield the expected chromone product (Table S2, Entry 17). The reactions conducted in the dark without photocatalysts also experienced a failure (Table S2, Entries 18, 19). Despite the fact that the best reaction conditions were successfully identified, we screened the photocatalysts **VI**−**VIII**, which showed lower efficiency to our great disappointment (Table S2, Entries 22−27).

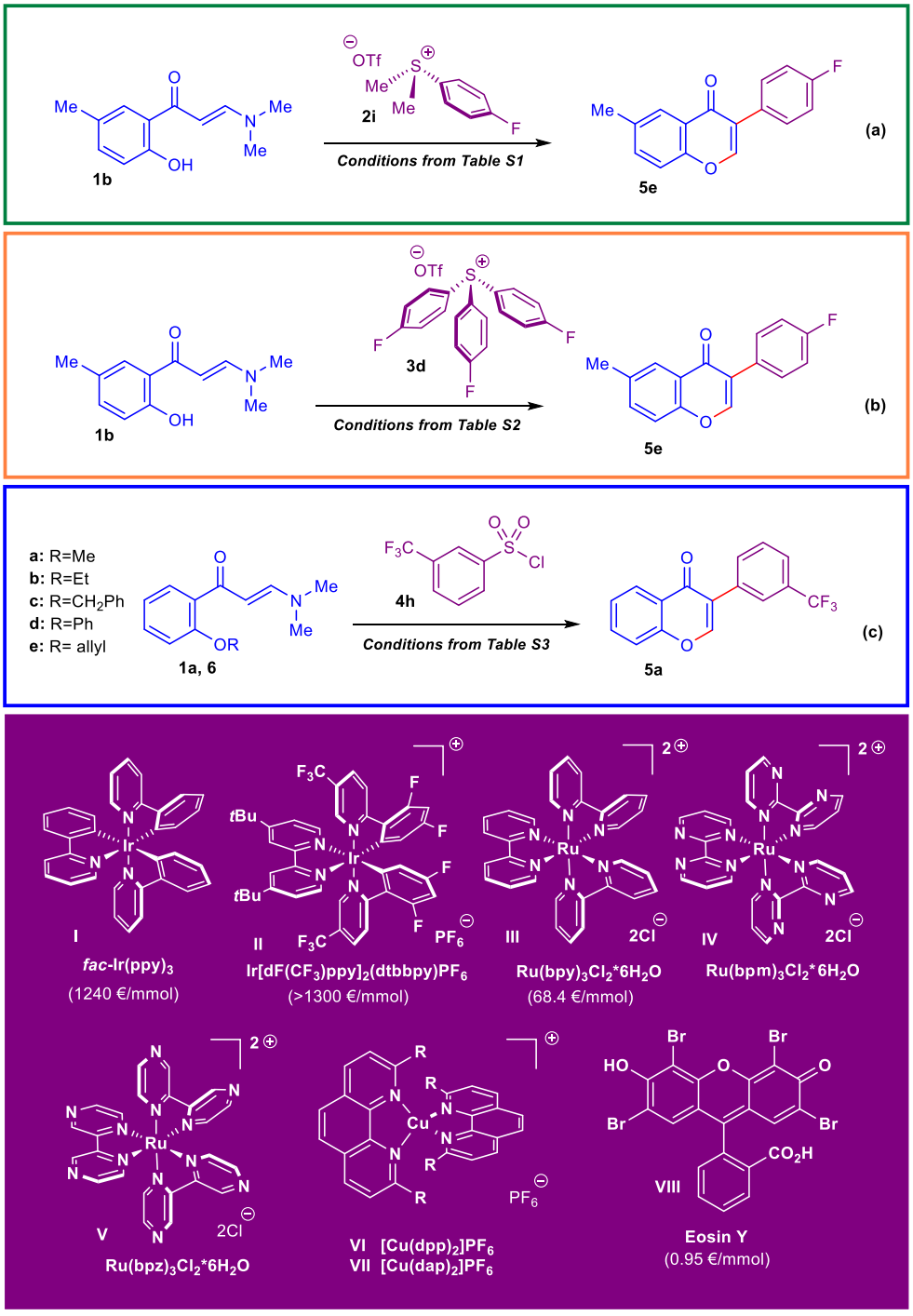
Having in hand optimized reaction conditions for all two synthetic scenarios, next we focused on the evaluation of the scope and limitations of these newly developed protocols. For the synthesis of 3-arylchromones by electrophilic arylation of *ortho*-hydroxyarylenaminones we selected 13 dimethyl(aryl)-sulfonium salts **2** with TfO^-, BF_4^- and $MeSO_3^-$ contra anions and reacted them with eight *ortho*-hydroxyarylenaminones. This resulted in the synthesis of 28 title chromone representatives in good-to-excellent yields (Scheme 3a). This protocol was competent with a variety of electron-deficient and electron-rich substituents on both coupling substrates; even the dimethyl(aryl)sulfoniums bearing substituents in the ortho position showed good outcomes (Scheme 3, Compounds **5d**, **5u**, **5w**, **5y**, **5aa**). This synthetic method not only demonstrated broad functional group tolerance, but also is scalable on 10 and 20 mmol quantities.

Next, we focused on the evaluation of the practical utility of photocatalytic arylation protocol (Scheme 3b): following, the scope was demonstrated on the instance of eight *ortho*-hydroxyarylenaminones and ten triarylsulfoniums possessing TfO^-, PF_6^-, CI^-, Br^- as contra anions, thus allowing for the preparation of 21 3-arylchromones **5**. This methodology demonstrated the same profound degree of tolerance for the diverse substitution patterns. Some discrepancy in yields was observed only for the aryl sulfoniums bearing ortho substituents, for instance, for compounds **5d**, **5w**, **5aa**; this might be addressed by considering the sterical impact of the corresponding aryl substituents. The two protocols described above possess potent synthetic leeway limited only by the accessibility of the corresponding sulfonium reagents.

After successfully developing the optimal reaction conditions for two above presented protocols utilizing sulfonium salts and accurately studying the scope of these methods, next we shifted our focus to the exploration of the reaction between *ortho*-hydroxyarylenaminones and sulfonyl chlorides (Scheme 2c). Here we probed diverse reaction conditions employing the

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

Scheme 2. Model Reactions and Photocatalysts for Reaction Conditions Optimization

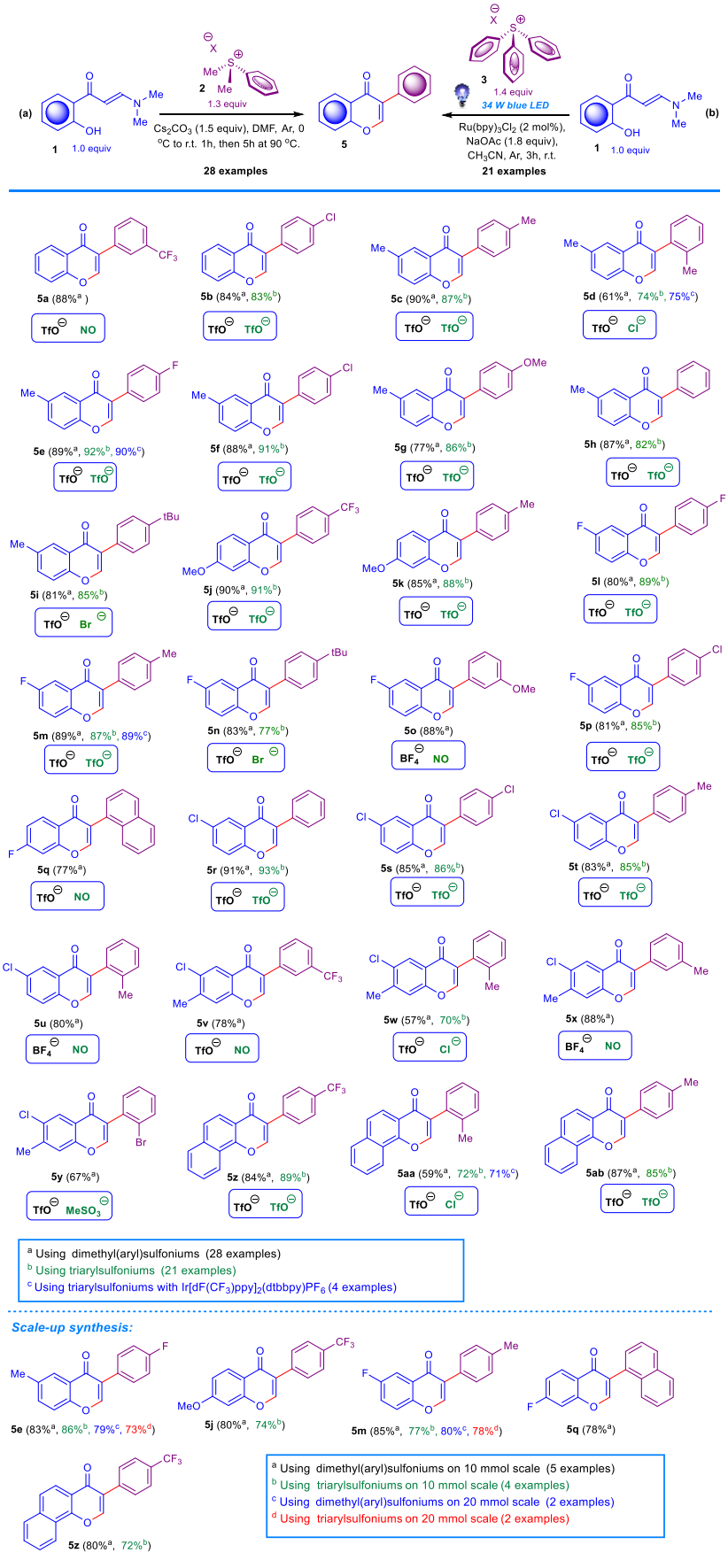


photocatalysts **I**–**VI** and **VIII**. We foreknew that *ortho*-hydroxyarylenaminones might not react efficiently with the sulfonyl chlorides due to the presence of the free OH function, and the OH group can quench the sulfonyl chloride, thus hampering the reaction overall. Indeed, this hypothesis was supported by a range of experiments with poor performance (Table S3, Entries 1–13). Namely, the best outcome overall for all used transition metal catalysts was observed in the case of Ir photocatalyst **II** under intensive blue light irradiation enabling the synthesis of the title chromone **5a** in 44% yield (Table S3, Entry 6). Furthermore, organic dye Eosin Y, with blue LED irradiation source, exerted promising catalytic capacity (Table S3, Entries 9–13), under these conditions the formation of the model chromone was observed in 28% yield (Table S3, Entry 11).

In contrary, the OH-protected enaminone substrates **6**, in particularly OMe derivative **6a**, were prone to undergo efficiently the radical triggered domino arylation catalyzed by numerous transition-metal photocatalysts. As a result, within the frames of these studies we developed several optimal reaction conditions which allowed for the effective preparation of the model chromone compound **5a** (Table S3, Entries 14–17, 21–25, 32, 33). Namely, iridium complexes **I** and **II** as well as ruthenium complexes **III**, **IV**, and **V** showed sufficient catalytic

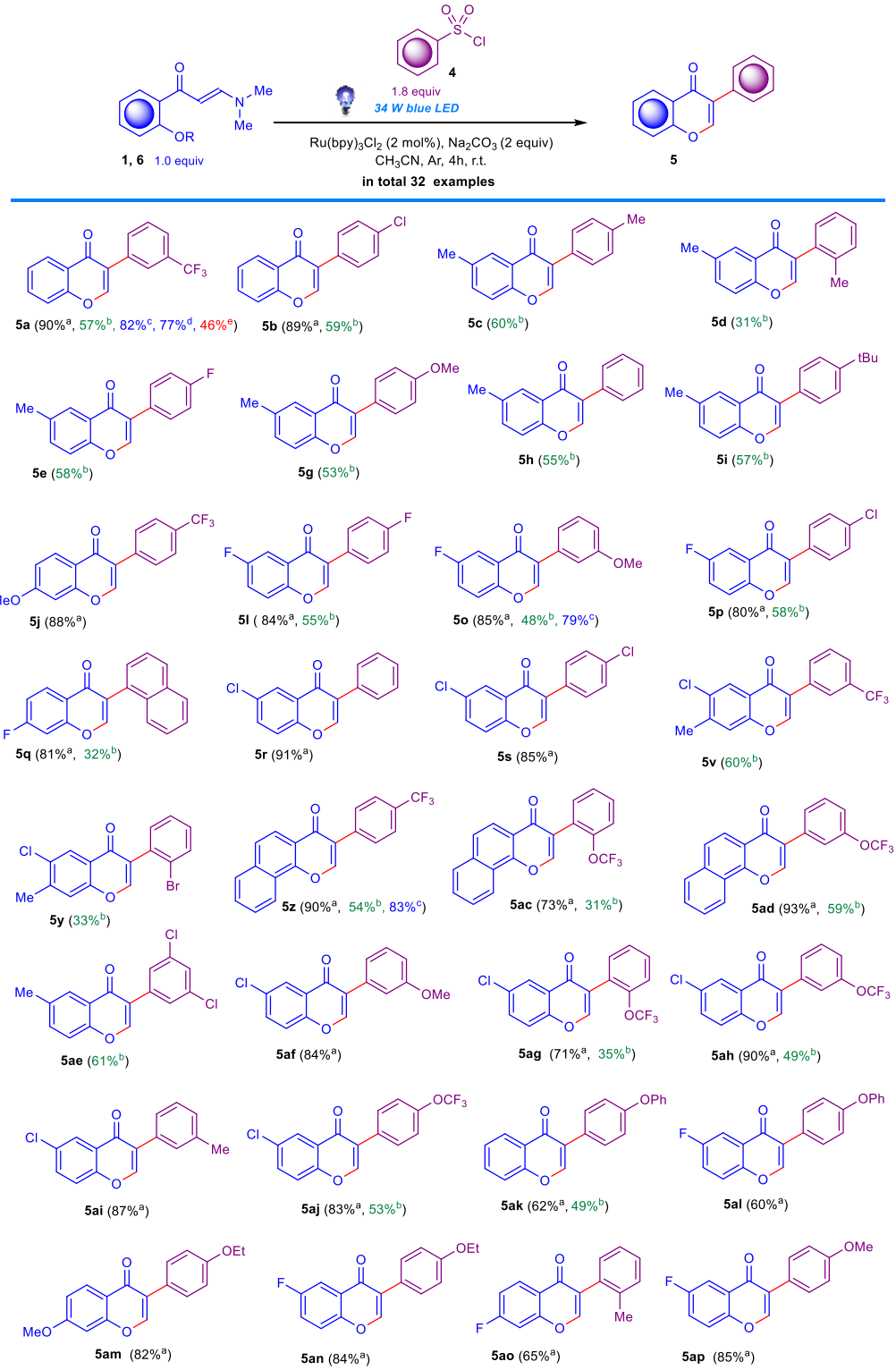
https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896–4916

Scheme 3. Product Scope of 3-Arylchromones Using Sulfonium Salts



https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

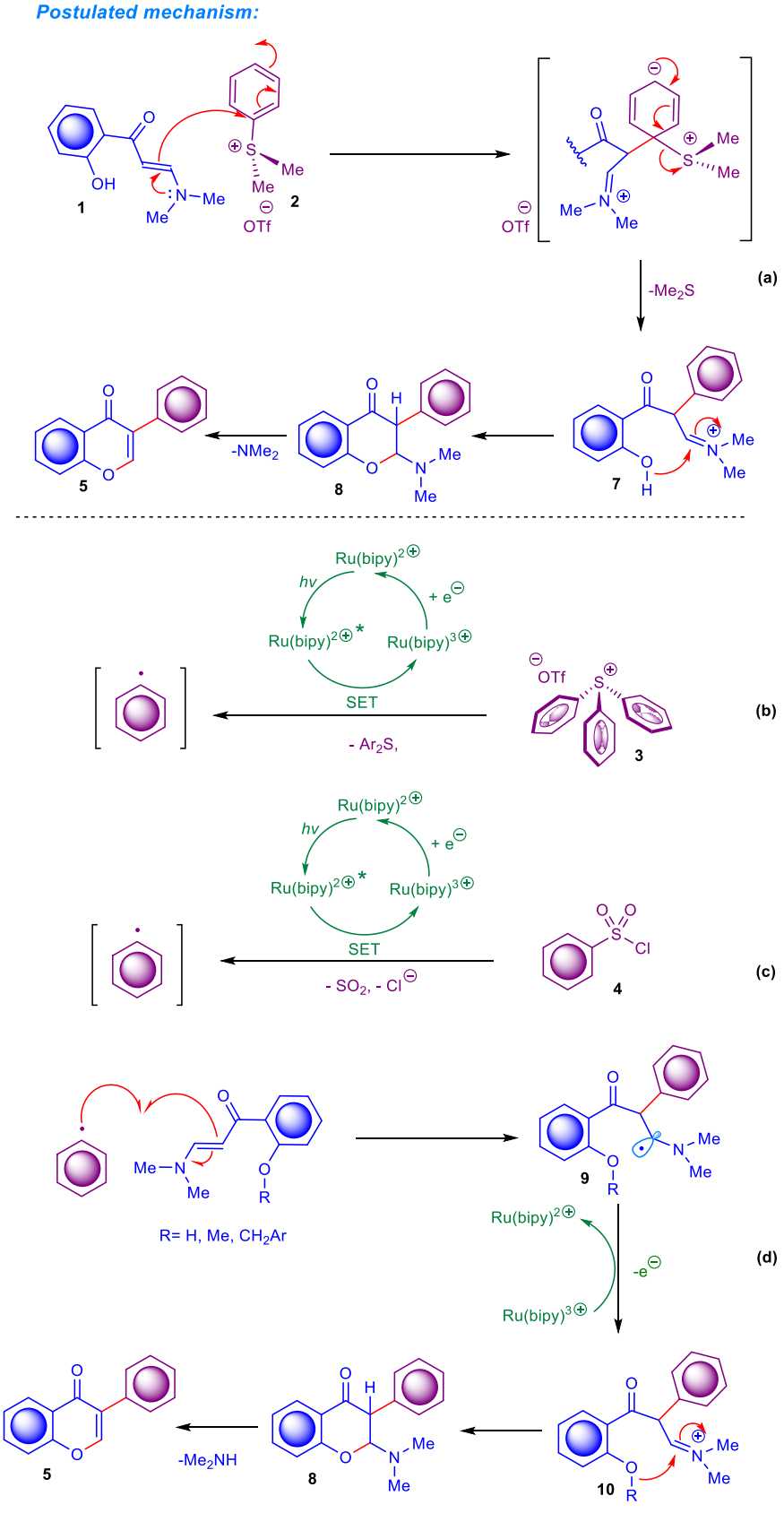
Scheme 4. Product Scope of 3-Arylchromones Using Sulfonyl Chlorides



activity toward the title model reaction. We also ascertained that both, the solvent and the base, make a profound impact on the efficiency of this synthetic protocol. In particular, optimized reaction condition for the catalyst **II** by using the combination of arenesulfonyl chloride (2.2 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)$-$PF_6$ (1 mol %), Na_2CO_3 (2 equiv), conducting reaction in

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

Scheme 5. Proposed Reaction Mechanisms for the Synthesis of 3-Arylchromones



CH_3CN for 12 h enabled the preparation of the model chromone compound in 83%. At the same time the best reaction conditions were prone to transform the OEt, OCH_2Ph, and OPh containing *ortho*-hydroxyarylenaminones **6b**, **6c**, and **6d** into the corresponding chromone **5a** obtained in 80%, 85%, and 68% yields respectively (Table S3, Entries 18−20).

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

Finally, ruthenium bipyridyl complex **III**, which due to its low price was often preferred by us over iridium 2-phenylpyrdine complexes as a suitable photocatalyst of choice, was successfully introduced into this study (Table S3, Entries 21−25). As a result, the optimized reaction conditions employed the use of arenesulfonyl chloride (1.8 equiv), $Ru(bpy)_3Cl_2$ (2 mol %), Na_2CO_3 (2 equiv), reaction conducted in CH_3CN were developed allowing for the preparation of the model 3-arylchromone in 90% yield (Table S3, Entry 25). Moreover, we studied the role of R substituent for the Ru-based reaction conditions: not only the Me-group-containing *ortho*-hydroxyarylenaminones **6a**, but also derivatives furnished with other functionalities like Et, CH_2Ph, Ph, and allyl were tested within the frames of this synthetic protocol. It appeared that (a) The presence of Me, Et, and CH_2Ph substituents enables the facile chromone ring formation, and all these functionalities are efficient leaving groups within the current protocol; (b) On the other hand, the Ph group, placed onto the OH, had also showcased visible propensity to be cleaved within this synthetic protocol leading to the formation of the title chromone, albeit in lower yield (Table S3, Entries 26−29). In the case of allyl derivative, the reaction did not experience a failure delivering the model compound in 10% yield.

Unexpectedly and to our great delight the optimized reaction conditions can also be transferred onto the *ortho*-hydroxyarylenaminones **1a**, thus synthesis of chromone **5a** was achieved in 42% yield when the reaction was run 4 h, increasing the reaction time to 10 h enabled synthesis of corresponding compound in 57% yield (Table S3, Entries 30, 31). The substitution of the 2,2′-bipyridine ligand versus 2,2′-bipyrimidine (Photocatalyst **IV**) and versus 2,2′-bipyrazine (Photocatalyst **V**) caused an inferior efficiency (Table S3, Entries 32, 33). Notably, the Cu-based complexes **VI** and **VII** were not prone at all to catalyze the title transformation (Table S3, Entries 34−37).

With these results in hand and aiming at elaborating more efficient and low-cost methodologies, we decided to use readily available $Ru(bpy)_3Cl_2{\cdot}6H_2O$ **III** instead of high-priced Ir-based photocatalysts **I** and **II**. Following, the optimized reaction conditions for further deployment of this synthetic protocol were employed as follows: sulfonium salt (1.8 equiv), $Ru(bpy)_3Cl_2$ (2 mol %), Na_2CO_3 (2 equiv), as solvent CH_3CN was used, reaction was conducted under Ar atmosphere, at room temperature. Our observation shows that the maximum duration of reaction to be completed was 4 h (Table S3, Entry 25). Noteworthy, in order to find an evidence that the described radical-triggered domino cyclization involves the formation of the aryl radicals, several control experiments were performed for the arylation of enaminones **1a**, **6a**, **6c** by arenesulfonyl chloride, such as addition of TEMPO (2 equiv) under the optimal reaction conditions as well as reactions conducted with no light irradiation and without photocatalyst experienced failure (Table S3, Entries 38−46).

To the scope for arylation of the O-substituted *ortho*-hydroxyarylenaminones **6**: here ten corresponding enaminone precursors **6** and 20 sulfonyl chlorides **4** were reacted, and this led to the preparation of the chromone library of 25 compounds. Noteworthy, this protocol demonstrated high tolerance toward multiple functional groups, with two synthetic scenarios discussed earlier, it even was efficient in case of *ortho*-substituted sulfonyl chlorides (Scheme 4). For instance, compounds **5ac**, **5ag**, and **5ao** were prepared in 73%, 71% and 65% yields, respectively. Here we also compared the efficiency of two arylation protocols, namely the one starting from the *ortho*-hydroxyarylenaminones **1** with the one which utilizes corresponding O-alkylated derivatives **6** (Scheme 4, the yields for the case using *ortho*-hydroxyarylenaminones **1** are highlighted in green).

To further demonstrate the synthetic utility of these two protocols, the gram-scale reactions were performed using 10 and 20 mmol of corresponding *ortho*-hydroxyarylenaminones and O-alkylated derivatives, which successfully yielded the corresponding chromones with negligible discrepancy in yields (Scheme 3, 4).

On the basis of the described vide supra results and the presently known literature on the chemical properties of sulfonium salts, their reactions with nucleophiles via an S_NAr pathway,[21a,24] and light-mediated photoredox radical arylation reactions, we postulated plausible reaction mechanisms which are presented schematically in the Scheme 5. The arylation of *ortho*-hydroxyarylenaminones by dimethyl(aryl)sulfonium salts perhaps commences with the initial electrophilic attack following the S_NAr nucleophilic substitution, which undergoes via the corresponding transition state followed by the mentioned vide supra intermediary cation structure **7** (Scheme 5). Subsequently, the latest in turn cyclizes to form 2-(dimethylamino)chromanone **8** which then, after elimination of dimethylamine, gives rise to the final 3-arylchromone **5**. Noteworthy, in order to deliver an evidence that the arylation reaction does not proceed via radical mechanism, we conducted an experiment with the widely used radical scavenger—the TEMPO; this resulted in the slight decrease of the yield to 81% (Entry 14). We repeated this experiment several times and always observed insignificant yields depression. This result can be accepted as indisputable evidence, which allows us to rule out the involvement of radical intermediates.

Regarding the visible-light photocatalyzed synthesis of 3-arylchromones **5** by using triarylsulfonium and arenesulfonyl chlorides catalyzed by $Ru(bpy)_3Cl_2{\cdot}6H_2O$ **III**, the pathways commence by a SET oxidation of the excited photocatalyst in triplet state leading to the C−S bond fragmentation and subsequent generation of the reactive aryl radical (Ar·); the latest in turn then attacks the enaminone moiety to afford the carbon-centered radical intermediate **9**. This type of radical intermediate species was previously described in several visible-light driven syntheses of chromones, in particular 3-thiocyanato, 3-polyfluoroalkyl, and 3-aryl chromones.[7,17,18] The latest undergoes prompt oxidation to carbocation **10**, which subsequently follows the sequence described in the Scheme 5a to yield the target chromone **5**.

Summing up, for the first time sulfonium salts and arenesulfonyl chlorides were successfully utilized for the direct C−H functionalization of *ortho*-hydroxyarylenaminones and corresponding O-substituted derivatives. Three novel strategies which enable an efficient and concise access to vast diversities of 3-arylchromones, build upon the electrophilic arylation using dimethyl(aryl)sulfonium salts, and upon photoredox arylation by triarylsulfonium and arenesulfonyl chlorides, respectively, with $Ru(bpy)_3Cl_2{\cdot}6H_2O$ as a photocatalyst, were ascertained within this study. The scope of the developed tactics is thoroughly studied and covers vast substitution patterns on both the chromone and the aryl parts. We also compared these three methodologies in terms of their efficiencies and scalability. Noteworthy, the large structural diversities of arenesulfonyl chlorides available commercially, even despite the required prefunctionalization of *ortho*-hydroxyarylenaminones, highlights the overall value of this synthetic protocol. The

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

mechanistic studies revealed the involvement of free-radical pathways in the case of visible-light-mediated photoredox arylation routes.

EXPERIMENTAL SECTION

Commercially available starting materials, reagents, catalysts, anhydrous and degassed solvents were used without further purification. Flash column chromatography was performed with Merck Silica gel 60 (230−400 mesh). The solvents for column chromatography were distilled before use. Thin layer chromatography was carried out using Merck TLC Silica gel 60 F_{254} and visualized by short-wavelength ultraviolet light or by treatment with potassium permanganate ($KMnO_4$) stain. ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker 250 and 500 MHz at 20 °C. All ^1H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for $CHCl_3$ (7.26 ppm) and DMSO (2.50 ppm). All ^{13}C NMR spectra were reported in ppm relative to residual $CHCl_3$ (77.00 ppm) or DMSO (39.70 ppm) and were obtained with ^1H decoupling. Coupling constants, *J*, are reported in Hertz (Hz). Gas chromatographic analyses was performed on a gas chromatograph mass spectrometer GCMS-QP2010 Ultra instrument.

The optimal reaction conditions were identified by microscale high-throughput experimentation screening. Parallel synthesis was accomplished in an MBraun glovebox operating with a constant Ar-purge (oxygen and water <5 ppm). As a light source a standard commercially available Kessil KSH150B Blue LED Grow Light was used. Screening reactions were carried out in 10 mL vials using suitable heating blocks. Liquid chemicals were dosed using gastight microsyringes. Isolation of obtained compounds was achieved by column chromatography on Silica gel.

All used reagents **1**, **2**, **3**, **4**, and **6** are literature known compounds and were prepared according to the known literature; the spectral data is identical with the corresponding literature sources. Namely, *ortho*-hydroxyarylenaminones **1**,[25] which we used several times in our previous research, corresponding O-substituted derivatives **6**,[26] and sulfonium salts **2**[27] and **3**[28] are literature described substances. All arenesulfonyl chlorides **4** used here are commercially available and were purchased from appropriate vendors.

General Procedure for the Synthesis of 3-Arylchromones 5 by the Reaction of *ortho*-Hydroxyarylenaminones 1 with Dimethyl(aryl)sulfonium Salts 2. Under inert atmosphere (glovebox operating with a constant Ar-purge) to an 10 mL flask equipped with a stir bar was placed appropriate *ortho*-hydroxyarylenaminone (1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt (1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv), then the reaction vial was properly capped by rubber septum. Finally, the reaction vessel was removed from the glovebox, connected to a pressure compensator (balloon partially filled with Argon equipped with a needle), and installed on the stirring plate equipped with an ice bath; subsequently the dry DMF (0.3 mmol/mL) was added using a syringe and the reaction mixture left by at 0 °C for 30 min. Subsequently, the reaction mixture was kept 1 h at room temperate and then subjected to heating at 90 °C for 5 h. The reaction was controlled by both GC MS and TLC. After completion the reaction mixture was evaporated until dryness using rotary evaporator, the crude was generously treated with distilled water, dried once more, and afterward was directly subjected to gradient flash chromatography on silica gel using appropriate mixture of hexane/ethyl acetate as eluent to isolate the desired chromone derivative.

The gram scale synthesis was performed on 10 and 20 mmol of the starting *ortho*-hydroxyarylenaminone.

General Procedure for the Synthesis of 3-Arylchromones 5 by the Reaction of *ortho*-Hydroxyarylenaminones 1 with Triarylsulfonium Salts 3 Using Ru Catalyst. Under inert atmosphere (glovebox operating with a constant Ar-purge) to a 20 mL vial equipped with a stir bar was placed photocatalyst $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone (1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt (1.4 mmol, 1.4 equiv); then the dry CH_3CN (0.12 mmol/mL) was added and the reaction vial was properly capped by Teflon Mininert Valve. Finally, the reaction vial was removed from the glovebox and subjected to irradiation under vigorous stirring using 34 W blue LED lamps (Kessil KSH150B Blue LED Grow Light; 5−6 cm away, with cooling fan on top to keep the reaction mixture at room temperature) for 3 h. The reaction was controlled by both GC MS and TLC. After completion the reaction mixture was evaporated until dryness using rotary evaporator, the content of the flask was generously treated with distilled water, filtrated, and finally properly dried in a vacuum. The resulting crude was directly subjected to gradient flash chromatography on silica gel using appropriate mixture of hexane/ethyl acetate as eluent to isolate the desired chromone derivative.

The gram scale synthesis was performed on 10 and 20 mmol of the starting *ortho*-hydroxyarylenaminone.

General Procedure for the Synthesis of 3-Arylchromones 5 by the Reaction of *ortho*-Hydroxyarylenaminones 1 with Triarylsulfonium Salts 3 Using Ir Catalyst. Under inert atmosphere (glovebox operating with a constant Ar-purge) to a 20 mL vial equipped with a stir bar was placed photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11 mg, 0.01 mmol, 0.01 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone (1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt (1.5 mmol, 1.5 equiv); then the dry DMSO (0.2 mmol/mL) was added and the reaction vial was properly capped by Teflon Mininert Valve. Finally, the reaction vial was removed from the glovebox and subjected to irradiation under vigorous stirring using 34 W blue LED lamps (Kessil KSH150B Blue LED Grow Light; 5−6 cm away, with cooling fan on top to keep the reaction mixture at room temperature) for 4 h. The reaction was controlled by both GC MS and TLC. After completion the reaction mixture was evaporated until dryness using rotary evaporator, the content of the flask was generously treated with distilled water, filtrated, and finally properly dried in a vacuum. The resulting crude was directly subjected to gradient flash chromatography on silica gel using appropriate mixture of hexane/ethyl acetate as eluent to isolate the desired chromone derivative.

General Procedure for the Synthesis of 3-Arylchromones 5 by the Reaction of O-Alkylated *ortho*-Hydroxyarylenaminones 6 and *ortho*-Hydroxyarylenaminones 1 with Arenesulfonyl Chlorides 4 Using Ru Catalyst. Under inert atmosphere (glovebox operating with a constant Ar-purge) to an 25 mL vial equipped with a stir bar was placed photocatalyst $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv) appropriate O-alkylated *ortho*-hydroxyarylenaminone or *ortho*-hydroxyarylenaminone (1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride (1.8 mmol, 1.8 equiv); then the dry CH_3CN (0.10 mmol/mL) was added and the reaction vial was properly capped by Teflon Mininert Valve. Finally, the reaction vial was removed from the glovebox and subjected to irradiation under vigorous stirring using 34 W blue LED lamps (Kessil KSH150B Blue LED Grow Light; 5−6 cm away, with cooling fan on top to keep the reaction mixture at room temperature) for 4 h. The reaction was controlled by both GC MS and TLC. After completion the reaction mixture was evaporated until dryness using rotary evaporator, the content of the flask was generously treated with distilled water, filtrated, and finally properly dried in a vacuum. The resulting crude was directly subjected to gradient flash chromatography on silica gel using appropriate mixture of hexane/ethyl acetate as eluent to isolate the desired chromone derivative.

The gram scale synthesis was performed on 10 and 20 mmol of the starting *ortho*-hydroxyarylenaminone.

3-(3-(Trifluoromethyl)phenyl)-4*H*-chromen-4-one (5a). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1a** (191 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)-sulfonium salt **2e** (463 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5a** (255 mg, 0.88 mmol, 88%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2 \cdot 6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6a** (205 mg, 1.0 mmol, 1.0 equiv) and

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

appropriate arenesulfonyl chloride **4h** (440 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5a** (261 mg, 0.90 mmol, 90%). The gram scale synthesis was performed on 10 and 20 mmol of the starting O-alkylated *ortho*-hydroxyarylenaminone and desired **5a** was prepared in 82% (2.38 g, 8.2 mmol) and 77% (4.47 g, 15.4 mmol) yields, respectively.

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1a** (191 mg, 1.0 mmol, 1.0 equiv), and appropriate arenesulfonyl chloride **4h** (440 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5a** (165 mg, 0.57 mmol, 57%). The gram scale synthesis was performed on 10 mmol of the starting *ortho*-hydroxyarylenaminone and desired **5a** was prepared in 46% (1.33 g, 4.6 mmol) yield.

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 8:1 as eluent to provide corresponding chromone. R_f = 0.3 (Hex:EtAc 5:1).

White solid, mp 97−98 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (dd, 1H, ^3J = 7.9 Hz, ^4J = 1.6 Hz), 8.07 (s, 1H), 7.84 (s, 1H), 7.78 (d, 1H, ^3J = 7.8 Hz), 7.70−7.73 (m, 1H), 7.64 (d, 1H, ^3J = 7.9 Hz), 7.56 (t, 1H, ^3J = 7.7 Hz), 7.51 (d, 1H, ^3J = 8.5 Hz), 7.46 (t, 1H, ^3J = 7.9 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.9, 156.2, 153.4, 134.0, 132.6, 131.0 (q, $^2J_{CF}$ = 33.0 Hz), 128.9, 126.3, 125.6 (m), 125.5, 124.9 (m), 124.3 (d, J_{CF} = 23.5 Hz), 124.0 (q, $^1J_{CF}$ = 272.6 Hz), 118.1. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{16}H_{10}O_2F_3$ 291.0640, found 291.0633.

3-(4-Chlorophenyl)-4*H*-chromen-4-one (5b). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1a** (191 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2j** (419 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5b** (190 mg, 0.84 mmol, 84%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1a** (191 mg, 1.0 mmol, 1.0 equiv), and appropriate triarylsulfonium salt **3e** (722 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5b** (213 mg, 0.83 mmol, 83%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6a** (205 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4o** (381 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5b** (203 mg, 0.79 mmol, 79%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1a** (191 mg, 1.0 mmol, 1.0 equiv), and appropriate arenesulfonyl chloride **4o** (381 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5b** (133 mg, 0.50 mmol, 50%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 10:1 as eluent to provide corresponding chromone. R_f = 0.5 (Hex:EtAc 6:1).

White solid, mp 186−187 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40−7.46 (m, 3H), 7.48−7.52 (m, 3H), 7.68−7.72 (m, 1H), 8.02 (s, 1H), 8.30 (dd, 1H, ^3J = 8.0 Hz, ^4J = 1.6 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 176.0, 156.2, 153.0, 134.2, 133.8, 130.3, 130.2, 128.7, 126.4, 125.4, 124.4, 124.3, 118.1. MS (GC, 70 eV) m/z (%) = 256 (M^+, 100), 136 (16), 120 (66), 110 (16), 92 (65). Anal. Calcd for $C_{15}H_9ClO_2$: C, 70.19; H, 3.53. Found: C, 70.23; H, 3.49.

6-Methyl-3-(*p*-tolyl)-4*H*-chromen-4-one (5c). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2b** (393 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5c** (225 mg, 0.90 mmol, 90%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3b** (636 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5c** (218 mg, 0.87 mmol, 87%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv), and appropriate arenesulfonyl chloride **4b** (343 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5c** (150 mg, 0.60 mmol, 60%).

In all previous cases gradient flash column chromatography was performed using a mixture of hexane/ethyl acetate 7:1 to 5:1 as eluent to provide corresponding chromone. R_f = 0.7 (Hex:EtAc 3:1).

White solid, mp 138−139 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.99 (s, 1H), 7.47−7.51 (m, 3H), 7.36 (d, 1H, ^3J = 8.1 Hz), 7.26 (d, 2H, ^3J = 7.3 Hz), 2.48 (s, 3H), 2.41 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 176.4, 154.5, 152.7, 137.9, 135.1, 134.8, 129.2, 129.0, 128.8, 125.6, 125.1, 124.2, 117.7, 21.2, 21.0. MS (GC, 70 eV) m/z (%) = 250 (M^+, 100), 134 (32), 115 (24). Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.62; H, 5.70.

6-Methyl-3-(*o*-tolyl)-4*H*-chromen-4-one (5d). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2c** (393 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5d** (152 mg, 0.61 mmol, 61%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3c** (636 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5d** (185 mg, 0.74 mmol, 74%).

Alternatively the title compound was prepared starting from $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11 mg, 0.01 mmol, 0.01 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv), and appropriate triarylsulfonium salt **3c** (681 mg, 1.5 mmol, 1.5 equiv) and dry DMSO (0.2 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5d** (188 mg, 0.75 mmol, 75%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv), and appropriate arenesulfonyl chloride **4m** (483 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5d** (77 mg, 0.31 mmol, 31%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 8:1 as eluent to provide corresponding chromone. R_f = 0.6 (Hex:EtAc 3:1).

Light brown solid, mp 221−222 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (br. s, 1H), 7.82 (s, 1H), 7.45 (dd, 1H, ^3J = 8.7 Hz, ^4J = 1.8 Hz), 7.35 (d, 1H, ^3J = 8.7 Hz), 7.25−7.28 (m, 2H), 7.20−7.21 (m, 1H), 7.14

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

(d, 1H, ^3J = 7.3 Hz), 2.43 (s, 3H), 2.22 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 176.0, 154.6, 153.4, 135.1, 138.0, 134.8, 131.7, 130.4, 130.1, 128.5, 126.2, 125.7, 125.6, 123.9, 117.8, 20.9, 20.0. MS (GC, 70 eV) m/z (%) = 250 (M^+, 49), 135 (100), 115 (32), 77 (20). Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64. Found: C, 81.53; H, 5.73.

3-(4-Fluorophenyl)-6-methyl-4*H*-chromen-4-one (5e). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)-sulfonium salt **2i** (398 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5e** (226 mg, 0.89 mmol, 89%). The gram scale synthesis was performed on 10 and 20 mmol of the starting *ortho*-hydroxyarylenaminone and desired **5e** was prepared in 83% (2.11 g, 8.3 mmol) and 79% (4.01 g, 15.8 mmol) yields, respectively.

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3d** (652 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5e** (233 mg, 0.92 mmol, 92%). The gram scale synthesis was performed on 10 and 20 mmol of the starting *ortho*-hydroxyarylenaminone and desired **5e** was prepared in 86% (2.18 g, 8.6 mmol) and 73% (3.76 g, 14.8 mmol) yields, respectively.

Alternatively the title compound was prepared starting from $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11 mg, 0.01 mmol, 0.01 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv), and appropriate triarylsulfonium salt **3d** (699 mg, 1.5 mmol, 1.5 equiv) and dry DMSO (0.2 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5e** (229 mg, 0.90 mmol, 90%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv), and appropriate arenesulfonyl chloride **4n** (350 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5e** (147 mg, 0.58 mmol, 58%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 10:1 as eluent to provide corresponding chromone. R_f = 0.6 (Hex:EtAc 5:1).

White solid, mp 202−203 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (br. s, 1H), 7.99 (s, 1H), 7.53−7.56 (m, 2H), 7.50 (dd, 1H, ^3J = 8.5 Hz, ^4J = 2.0 Hz), 7.38 (d, 1H, ^3J = 9.1 Hz), 7.13 (t, 2H, ^3J = 8.8 Hz), 2.48 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 176.2, 162.7 (d, $^1J_{CF}$ = 242.0 Hz),21.0, 154.5, 152.8, 135.3, 135.0, 130.6 (d, J_{CF} = 8.1 Hz), 127.9, 125.6, 124.2 (d, J_{CF} = 22.9 Hz), 117.8, 115.4 (d, J_{CF} = 21.6 Hz). HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{16}H_{12}O_2F$ 255.0831, found 255.0821.

3-(4-Chlorophenyl)-6-methyl-4*H*-chromen-4-one (5f). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)-sulfonium salt **2j** (419 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5f** (238 mg, 0.88 mmol, 88%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3e** (722 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5f** (246 mg, 0.91 mmol, 91%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 12:1 as eluent to provide corresponding chromone. R_f = 0.5 (Hex:EtAc 5:1).

Light brown solid, mp 208−209 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.08 (br. s, 1H), 8.00 (s, 1H), 7.50−7.53 (m, 3H), 7.42 (s, 1H), 7.38−7.41 (m, 2H), 2.48 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ due to bad solubility it was not possible to measure. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{16}H_{12}O_2Cl$ 271.0529, found 271.0526.

3-(4-Methoxyphenyl)-6-methyl-4*H*-chromen-4-one (5g). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl-(aryl)sulfonium salt **2h** (330 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5g** (205 mg, 0.77 mmol, 77%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3f** (703 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5g** (229 mg, 0.86 mmol, 86%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv), and appropriate arenesulfonyl chloride **4e** (440 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5g** (141 mg, 0.53 mmol, 53%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 5:1 as eluent to provide corresponding chromone. R_f = 0.5 (Hex:EtAc 3:1).

Yellow solid, mp 119−120 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 (br. s, 1H), 7.97 (s, 1H), 7.48 (dd, 1H, ^3J = 8.5 Hz, ^4J = 2.1 Hz), 7.30−7.33 (m, 2H), 7.36 (d, 1H, ^3J = 8.5 Hz), 6.97 (dd, 2H, ^3J = 8.7 Hz, ^4J = 1.9 Hz), 3.48 (s, 3H), 2.47 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 176.5, 159.5, 154.4, 152.4, 135.0, 134.8, 130.1, 125.6, 124.7, 124.3, 124.1, 117.7, 114.0, 55.3, 21.0. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{17}H_{15}O_3$ 267.1033, found 267.1021.

6-Methyl-3-phenyl-4*H*-chromen-4-one (5h). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2a** (374 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5h** (205 mg, 0.87 mmol, 87%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3a** (577 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5h** (193 mg, 0.82 mmol, 82%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv), and appropriate arenesulfonyl chloride **4a** (318 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5h** (130 mg, 0.55 mmol, 55%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 7:1−5:1 as eluent to provide corresponding chromone. R_f = 0.6 (Hex:EtAc 3:1).

Yellow solid, mp 104−105 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.09 (br s, 1H), 7.99 (s, 1H), 7.56−7.58 (m, 2H, CH_{Ar}), 7.43−7.49 (m, 3H), 7.36−7.40 (m, 2H), 2.46 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

176.1, 20.9, 154.4, 152.9, 135.1, 117.7, 134.8, 131.9, 128.8, 128.4, 128.1, 125.6, 125.0, 124.1. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{16}H_{13}O_2$ 237.0925, found 237.0916.

3-(4-(*tert*-Butyl)phenyl)-6-methyl-4*H*-chromen-4-one (5i). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2m** (447 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5i** (236 mg, 0.81 mmol, 81%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3h** (715 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5i** (248 mg, 0.85 mmol, 85%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv), and appropriate arenesulfonyl chloride **4r** (419 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5i** (166 mg, 0.57 mmol, 57%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 5:1−3:1 as eluent to provide corresponding chromone. R_f = 0.7 (Hex:EtAc 3:1).

Light yellow solid, mp 133−134 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (br s, 1H), 8.00 (s, 1H), 7.52−7.53 (m, 2H), 7.47−7.48 (m, 3H), 7.37 (d, 1H, ^3J = 9.1 Hz), 2.47 (s, 3H), 1.37 (s, 9H, *t*Bu). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 176.3, 154.4, 152.8, 151.0, 135.0, 134.7, 129.0, 128.5, 125.6, 125.4, 124.9, 124.1, 117.7, 34.6, 31.2, 20.9. MS (GC, 70 eV) m/z (%) = 292 (M^+, 38), 277 (100), 115 (13). Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 82.23; H, 6.83.

7-Methoxy-3-(4-(trifluoromethyl)phenyl)-4*H*-chromen-4-one (5j). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1c** (221 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2f** (462 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5j** (288 mg, 0.90 mmol, 90%). The gram scale synthesis was performed on 10 mmol of the starting *ortho*-hydroxyarylenaminone and desired **5k** was prepared in 91% (2.56 g, 8.0 mmol) yield.

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1c** (221 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3g** (862 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5j** (291 mg, 0.91 mmol, 91%). The gram scale synthesis was performed on 10 mmol of the starting *ortho*-hydroxyarylenaminone and desired **5j** was prepared in 74% (2.37 g, 7.4 mmol) yield.

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6f** (235 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4d** (440 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5j** (282 mg, 0.88 mmol, 88%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 5:1 as eluent to provide corresponding chromone. R_f = 0.4 (Hex:EtAc 3:1).

Yellow solid, mp 195−196 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, 1H, ^3J = 8.9 Hz), 7.99 (s, 1H), 7.69 (s, 4H), 7.01 (dd, 1H, ^3J = 8.7 Hz, ^4J = 2.5 Hz), 6.87 (d, 1H, ^4J = 2.5 Hz), 3.92 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.2, 164.3, 158.0, 153.0, 135.7, 130.1 (q, $^2J_{CF}$ = 31.8 Hz), 129.2, 127.8, 123.3 (m), 124.2, 124.2 (q, $^1J_{CF}$ = 273.3 Hz), 118.3, 114.9, 55.9. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{17}H_{12}O_3F_3$ 321.0744, found 321.0739.

7-Methoxy-3-(*p*-tolyl)-4*H*-chromen-4-one (5k). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1c** (221 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2b** (393 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5k** (226 mg, 0.85 mmol, 85%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1c** (221 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3g** (862 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5k** (234 mg, 0.88 mmol, 88%).

In all previous cases gradient flash column chromatography was performed using a mixture of hexane/ethyl acetate 5:1 to 1:1 as eluent to provide corresponding chromone. R_f = 0.45 (Hex:EtAc 3:1).

Light yellow solid, mp 135−136 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, 1H, ^3J = 9.0 Hz), 7.92 (s, 1H), 7.44 (d, 2H, ^3J = 8.6 Hz), 7.23 (d, 2H, ^3J = 8.3 Hz), 6.98 (dd, 1H, ^3J = 8.8 Hz, ^4J = 2.2 Hz), 6.83 (d, 1H, ^4J = 2.4 Hz), 3.90 (s, 3H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.7, 164.0, 157.9, 152.3, 137.9, 129.1, 128.9, 128.8, 127.7, 125.1, 118.4, 114.5, 100.0, 55.7, 21.2. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{17}H_{15}O_3$ 267.1024, found 267.1021.

6-Fluoro-3-(4-fluorophenyl)-4*H*-chromen-4-one (5l). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1c** (221 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2i** (398 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5l** (206 mg, 0.80 mmol, 80%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1c** (221 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3d** (862 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5l** (230 mg, 0.89 mmol, 89%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6g** (223 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4n** (350 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5l** (217 mg, 0.84 mmol, 84%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1d** (209 mg, 1.0 mmol, 1.0 equiv), and appropriate arenesulfonyl chloride **4n** (350 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5l** (142 mg, 0.50 mmol, 55%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 5:1−1:1 as eluent to provide corresponding chromone. R_f = 0.4 (Hex:EtAc 3:1).

White solid, mp 190−191 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 8.70 (s, 1H), 7.82−7.89 (m, 1H), 7.77 (dt, 1H, ^3J = 8.9 Hz, ^4J = 3.0 Hz), 7.47−7.53 (m, 3H), 7.23−7.27 (m, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): Due to bed solubility it was not possible to measure. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{15}H_9O_2F_2$ 259.0578, found 259.0571.

6-Fluoro-3-(*p*-tolyl)-4*H*-chromen-4-one (5m). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1d**

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

(209 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2b** (393 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5m** (226 mg, 0.89 mmol, 89%). The gram scale synthesis was performed on 10 and 20 mmol of the starting *ortho*-hydroxyarylenaminone and desired **5n** was prepared in 85% (2.16 g, 8.5 mmol) and 80% (4.06 g, 16 mmol) yields, respectively.

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1d** (209 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3b** (636 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5m** (221 mg, 0.87 mmol, 87%). The gram scale synthesis was performed on 10 and 20 mmol of the starting *ortho*-hydroxyarylenaminone and desired **5n** was prepared in 77% (1.96 g, 7.7 mmol) and 78% (3.96 g, 15.6 mmol) yields, respectively.

Alternatively the title compound was prepared starting from $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11 mg, 0.01 mmol, 0.01 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1d** (209 mg, 1.0 mmol, 1.0 equiv), and appropriate triarylsulfonium salt **3d** (699 mg, 1.5 mmol, 1.5 equiv) and dry DMSO (0.2 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5m** (226 mg, 0.89 mmol, 89%).

In all previous cases gradient flash column chromatography was performed using a mixture of hexane/ethyl acetate 7:1 to 5:1 as eluent to provide corresponding chromone. R_f = 0.65 (Hex:EtAc 3:1).

White solid, mp 160−161 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.93 (dd, 1H, ^3J = 8.2 Hz, ^4J = 3.2 Hz), 7.47−7.50 (m, 1H), 7.45 (d, 2H, ^3J = 8.2 Hz), 7.37−7.41 (m, 1H), 7.25 (d, 2H, ^3J = 8.0 Hz), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.5, 159.5 (d, $^1J_{CF}$ = 248.6 Hz), 152.9, 152.3, 138.1, 129.2, 128.7, 128.4, 125.6 (d, J_{CF} = 7.1 Hz), 124.5, 121.7 (d, J_{CF} = 25.7 Hz), 120.0 (d, J_{CF} = 7.1 Hz), 111.0 (d, J_{CF} = 22.1 Hz), 21.2. MS (GC, 70 eV) *m*/*z* (%) = 254 (M^+, 85), 253 (100), 126 (19), 115 (42), 110 (14). Anal. Calcd for $C_{16}H_{11}FO_2$: C, 75.58; H, 4.36. Found: C, 75.63; H, 4.41.

3-(4-(*tert*-Butyl)phenyl)-6-fluoro-4*H*-chromen-4-one (5n). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1d** (209 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2m** (447 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5n** (246 mg, 0.83 mmol, 83%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1d** (209 mg, 1.0 mmol, 1.0 equiv), and appropriate triarylsulfonium salt **3h** (714 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5n** (228 mg, 0.77 mmol, 77%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 7:1−5:1 as eluent to provide corresponding chromone. R_f = 0.6 (Hex:EtAc 5:1).

White solid, mp 160−162 °C. ^{1}H NMR (500 MHz, $CDCl_3$): 8.03 (s, 1H), 7.95 (dd, 1H, ^3J = 8.2 Hz, ^4J = 2.9 Hz), 7.47−7.52 (m, 5H), 7.39−7.43 (m, 1H), 1.14 (s, 9H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.6, 159.6 (d, $^1J_{CF}$ = 247.2 Hz), 153.0, 152.4, 151.4, 128.6, 128.5, 125.6 (d, J_{CF} = 8.3 Hz), 125.6, 124.6, 121.8 (d, $^1J_{CF}$ = 25.6 Hz), 120.1 (d, J_{CF} = 8.5 Hz), 111.2 (d, J_{CF} = 22.6 Hz), 34.7, 31.2. HRMS (TOF MS ES+) *m*/*z* $[M + H]^+$ calcd for $C_{19}H_{18}O_2F$ 297.1292, found 297.1291.

6-Fluoro-3-(3-methoxyphenyl)-4*H*-chromen-4-one (5o). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1d** (209 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2g** (333 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5o** (238 mg, 0.88 mmol, 88%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6g** (223 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4j** (372 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5o** (230 mg, 0.85 mmol, 85%). The gram scale synthesis was performed on 10 mmol of the starting O-alkylated *ortho*-hydroxyarylenaminone and desired **5o** was prepared in 79% (2.13 g, 7.9 mmol) yields.

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1d** (209 mg, 1.0 mmol, 1.0 equiv), and appropriate arenesulfonyl chloride **4j** (372 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5o** (130 mg, 0.48 mmol, 48%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 3:1 as eluent to provide corresponding chromone. R_f = 0.45 (Hex:EtAc 3:1).

White solid, mp 133−134 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.92 (dd, 1H, ^3J = 8.5 Hz, ^4J = 3.0 Hz), 7.47−7.50 (m, 1H), 7.38−7.41 (m, 1H), 7.34 (t, 1H, ^3J = 8.1 Hz), 7.13−7.14 (m, 1H), 7.10 (d, 1H, ^3J = 7.5 Hz), 6.92 (dd, 1H, ^3J = 8.0 Hz, ^4J = 2.3 Hz), 3.83 (s 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.3, 159.54 (d, $^1J_{CF}$ = 249.7 Hz), 159.5, 153.3, 152.3, 132.7, 129.5, 125.6 (d, J_{CF} = 7.3 Hz), 124.4, 121.8 (d, J_{CF} = 25.9 Hz), 121.1, 120.1 (d, J_{CF} = 7.6 Hz), 114.2 (d, J_{CF} = 48.0 Hz), 111.0 (d, J_{CF} = 24.0 Hz), 55.2. MS (GC, 70 eV) *m*/*z* (%) = 270 (M^+, 100), 239 (24), 170 (11), 132 (12), 89 (15). Anal. Calcd for $C_{16}H_{11}FO_3$: C, 71.11; H, 4.10. Found: C, 71.03; H, 4.19.

3-(4-Chlorophenyl)-6-fluoro-4*H*-chromen-4-one (5p). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1d** (209 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2g** (333 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5p** (222 mg, 0.81 mmol, 81%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1d** (209 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3e** (722 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5p** (233 mg, 0.85 mmol, 85%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6g** (223 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4o** (380 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5p** (220 mg, 0.80 mmol, 80%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1d** (209 mg, 1.0 mmol, 1.0 equiv), and appropriate arenesulfonyl chloride **4o** (380 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5p** (159 mg, 0.58 mmol, 58%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 5:1 as eluent to provide corresponding chromone. R_f = 0.5 (Hex:EtAc 3:1).

White solid, mp 191−192 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.93 (dd, 1H, ^3J = 8.2 Hz, ^4J = 2.8 Hz), 7.50−7.52 (m, 3H),

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

7.41−7.45 (m, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.3, 160.7, 153.4 (d, $^1J_{CF}$ = 253.0 Hz), 153.2, 134.4, 130.2, 129.9, 128.8, 125.5 (d, J_{CF} = 7.9 Hz), 123.7, 122.2 (d, J_{CF} = 25.9 Hz), 120.2 (d, J_{CF} = 7.9 Hz), 111.1 (d, J_{CF} = 28.0 Hz), 109.0, 104.1. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{15}H_9O_2FCl$ 275.0275, found 275.0275.

7-Fluoro-3-(naphthalen-1-yl)-4*H*-chromen-4-one (5q). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1e** (209 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)-sulfonium salt **2d** (439 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5q** (223 mg, 0.77 mmol, 77%). The gram scale synthesis was performed on 10 mmol of the starting *ortho*-hydroxyarylenaminone and desired **5q** was prepared in 78% (2.26 g, 7.8 mmol) yields.

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6h** (223 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4c** (408 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5q** (235 mg, 0.81 mmol, 81%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1e** (209 mg, 1.0 mmol, 1.0 equiv), and appropriate arenesulfonyl chloride **4c** (408 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5q** (93 mg, 0.32 mmol, 32%).

In all previous cases gradient flash column chromatography was performed using a mixture of hexane/ethyl acetate 7:1 to 3:1 as eluent to provide corresponding chromone. R_f = 0.6 (Hex:EtAc 3:1).

Yellow solid, mp 134−135 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.35−8.37 (m, 1H), 8.00 (s, 1H), 7.90−7.94 (m, 2H), 7.74 (d, 1H, ^3J = 8.3 Hz), 7.42−7.55 (m, 4H), 7.19−7.24 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.6, 165.6 (d, $^1J_{CF}$ = 256.1 Hz), 157.3 (d, J_{CF} = 13.2 Hz), 154.2, 133.6, 132.3, 129.3, 129.0 (d, J_{CF} = 9.9 Hz), 128.2 (d, J_{CF} = 22.6 Hz), 126.3, 126.0, 125.5, 125.3 (d, $^1J_{CF}$ = 24.4 Hz), 121.2, 114.1 (d, J_{CF} = 23.1 Hz), 104.6 (d, J_{CF} = 26.0 Hz). HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{19}H_{12}O_2F$ 291.0826, found 291.0821.

6-Chloro-3-phenyl-4*H*-chromen-4-one (5r). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1f** (226 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2a** (374 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5r** (233 mg, 0.91 mmol, 91%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1f** (226 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3a** (577 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5r** (238 mg, 0.93 mmol, 93%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6i** (240 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4a** (318 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5r** (233 mg, 0.91 mmol, 91%).

In all previous cases gradient flash column chromatography was performed using a mixture of hexane/ethyl acetate 8:1 to 7:1 as eluent to provide corresponding chromone. R_f = 0.6 (Hex:EtAc 3:1).

White solid, mp 179−180 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, 1H, ^4J = 2.6 Hz), 8.02 (s, 1H), 7.63 (dd, 1H, ^3J = 8.9 Hz, ^4J = 2.6 Hz), 7.55 (d, 2H, ^3J = 7.1 Hz), 7.44−7.47 (m, 3H), 7.39−7.42 (m, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.1, 154.5, 153.2, 133.9, 131.4, 131.2, 128.9, 128.6, 128.4, 125.8, 125.5, 125.4, 119.8. MS (GC, 70 eV) m/z (%) = 256 (M^+, 75), 255 (100), 154 (26), 126 (31), 102 (20). Anal. Calcd for $C_{15}H_9ClO_2$: C, 70.19; H, 3.53. Found: C, 70.03; H, 3.59.

6-Chloro-3-(4-chlorophenyl)-4*H*-chromen-4-one (5s). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1f** (226 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)-sulfonium salt **2j** (419 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5s** (247 mg, 0.85 mmol, 85%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1f** (226 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3e** (722 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5s** (250 mg, 0.86 mmol, 86%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6i** (240 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4o** (381 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5s** (247 mg, 0.85 mmol, 85%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 10:1 as eluent to provide corresponding chromone. R_f = 0.45 (Hex:EtAc 5:1).

Yellow solid, mp 179−180 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, 1H, ^4J = 2.6 Hz), 8.02 (s, 1H), 7.63 (dd, 1H, ^3J = 8.9 Hz, ^4J = 2.6 Hz), 7.50 (d, 2H, ^3J = 8.5 Hz), 7.46 (d, 1H, ^3J = 9.0 Hz), 7.42 (d, 2H, ^3J = 8.5 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 174.9, 154.5, 153.1, 134.5, 134.1, 131.4, 130.2, 129.8, 128.8, 125.8, 125.4, 124.4, 119.9. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{15}H_9O_2Cl_2$ 290.9983, found 290.9980.

6-Chloro-3-(*p*-tolyl)-4*H*-chromen-4-one (5t). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1f** (226 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2b** (393 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5t** (225 mg, 0.83 mmol, 83%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1f** (226 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3b** (636 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5t** (230 mg, 0.85 mmol, 85%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 10:1 as eluent to provide corresponding chromone. R_f = 0.6 (Hex:EtAc 5:1).

White solid, mp 175−176 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, 1H, ^4J = 2.5 Hz), 8.00 (s, 1H), 7.61 (dd, 1H, ^3J = 8.9 Hz, ^4J = 2.6 Hz), 7.43−7.45 (m, 3H), 7.25 (d, 2H, ^3J = 8.1 Hz), 2.40 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.2, 154.5, 152.9, 138.3, 131.1, 129.3, 128.7, 128.4, 125.7, 125.4, 125.3, 119.8, 21.2. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{16}H_{12}O_2Cl$ 271.0526, found 271.0526.

6-Chloro-3-(*o*-tolyl)-4*H*-chromen-4-one (5u). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1f** (226 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2c** (393 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5u** (216 mg, 0.80 mmol, 80%).

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

The flash column chromatography was performed using a mixture of hexane/ethyl acetate 7:1−5:1 as eluent to provide corresponding chromone. R_f = 0.7 (Hex:EtAc 3:1).

White solid, mp 131−132 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, 1H, ^4J = 2.5 Hz), 7.89 (s, 1H), 7.63 (d, 1H, ^3J = 8.9 Hz, ^4J = 2.6 Hz), 7.47 (d, 1H, ^3J = 8.9 Hz), 7.29−7.34 (m, 2H), 7.43 (d, 1H, ^3J = 8.5 Hz), 7.23−7.35 (m, 1H), 7.17 (d, 1H, ^3J = 7.1 Hz), 2.25 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.8, 154.7, 153.7, 138.0, 133.9, 131.2, 131.1, 130.4, 130.3, 128.8, 126.5, 125.8, 125.7, 125.3, 119.9, 20.0. HRMS (TOF MS ES+) m/z [M + H]$^+$: $C_{16}H_{12}O_2Cl$ 271.0533, found 271.0526.

6-Chloro-7-methyl-3-(3-(trifluoromethyl)phenyl)-4*H*-chromen-4-one (5v). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1f** (226 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2e** (463 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5v** (264 mg, 0.78 mmol, 78%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1g** (240 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4h** (440 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5v** (203 mg, 0.60 mmol, 60%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 5:1 as eluent to provide corresponding chromone. R_f = 0.5 (Hex:EtAc 3:1).

Yellow solid, mp 162−163 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.03 (s, 1H), 7.80 (s, 1H), 7.76 (m, 1H, ^3J = 7.9 Hz), 7.64 (d, 1H, ^3J = 7.9 Hz), 7.56 (t, 1H, ^3J = 7.9 Hz), 7.39 (s, 1H), 2.52 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.7, 154.4, 153.4, 143.4, 132.3 (m), 130.9 (q, $^2J_{CF}$ = 32.0 Hz), 128.9, 125.9, 125.6 (m), 125.0 (m), 124.1, 124.5 (q, $^1J_{CF}$ = 267.9 Hz), 119.9, 20.9. HRMS (TOF MS ES+) m/z [M + H]$^+$ calcd for $C_{17}H_{11}O_2F_3Cl$ 339.0409, found 339.0400.

6-Chloro-7-methyl-3-(*o*-tolyl)-4*H*-chromen-4-one (5w). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1g** (240 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)-sulfonium salt **2c** (393 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5w** (162 mg, 0.57 mmol, 57%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1g** (240 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3c** (636 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5w** (199 mg, 0.70 mmol, 70%).

In all previous cases gradient flash column chromatography was performed using a mixture of hexane/ethyl acetate 10:1 to 7:1 as eluent to provide corresponding chromone. R_f = 0.7 (Hex:EtAc 3:1).

Yellow solid, mp 160−161 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (br. s, 1H), 7.84 (s, 1H), 7.39 (s, 1H), 7.28−7.32 (m, 2H), 7.23 (dt, 1H, ^3J = 7.2 Hz, ^4J = 1.2 Hz), 7.17 (dd, 1H, ^3J = 7.5 Hz, ^4J = 1.0 Hz), 2.51 (s, 3H), 2.25 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.7, 154.6, 153.4, 142.8, 137.9, 131.8, 131.2, 130.3, 130.1, 128.6, 126.2, 125.8, 125.7, 123.4, 119.8, 20.7, 19.9. HRMS (TOF MS ES+) m/z [M + H]$^+$ calcd for $C_{17}H_{14}O_2Cl$ 285.0688, found 285.0682.

6-Chloro-7-methyl-3-(*m*-tolyl)-4*H*-chromen-4-one (5x). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1g** (240 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)-sulfonium salt **2l** (393 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5x** (250 mg, 0.88 mmol, 88%).

In all previous cases gradient flash column chromatography was performed using a mixture of hexane/ethyl acetate 7:1 to 5:1 as eluent to provide corresponding chromone. R_f = 0.75 (Hex:EtAc 3:1).

Yellow solid, mp 107−109 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.96 (s, 1H), 7.32−7.36 (m, 4H), 7.21 (br. s, 1H), 2.51 (s, 3H), 2.40 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 175.1, 154.4, 152.9, 142.8, 138.1, 131.9, 131.4, 129.6, 129.1, 128.4, 126.0, 125.9, 125.3, 123.6, 119.8, 21.5, 20.8. HRMS (TOF MS ES+) m/z [M + H]$^+$ calcd for $C_{17}H_{14}O_2Cl$ 285.0685, found 285.0682.

3-(2-Bromophenyl)-6-chloro-7-methyl-4*H*-chromen-4-one (5y). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1g** (240 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2k** (407 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5y** (167 mg, 0.67 mmol, 67%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1g** (240 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3j** (833 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5y** (182 mg, 0.73 mmol, 73%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1g** (240 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4f** (461 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5y** (82 mg, 0.33 mmol, 33%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 10:1 as eluent to provide corresponding chromone. R_f = 0.65 (Hex:EtAc 5:1).

Light brown solid, mp 186−187 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (br. s, 1H, CH_{Ar}), 7.90 (s, 1H, CH_{Ar}), 7.67 (dd, 1H, ^3J = 8.0 Hz, ^4J = 0.9 Hz, CH_{Ar}), 7.39 (s, 1H, CH_{Ar}), 7.36 (dd, 1H, ^3J = 7.4 Hz, ^4J = 1.1 Hz, CH_{Ar}), 7.30−7.33 (m, 1H, CH_{Ar}), 7.25−7.26 (m, 1H, CH_{Ar}), 2.51 (s, 3H, Me). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.3, 154.6, 154.3, 143.1, 133.0, 132.6, 132.2, 132.1, 130.1, 127.4, 126.0, 125.7, 124.7, 123.5, 119.9, 20.8. MS (GC, 70 eV) m/z (%) = 347 (M$^+$, 3), 269 (100), 178 (10), 117 (10), 88 (14). Anal. Calcd for $C_{16}H_{10}BrClO_2$: C, 54.97; H, 2.88. Found: C, 55.00; H, 2.96.

3-(4-(Trifluoromethyl)phenyl)-4*H*-benzo[*h*]chromen-4-one (5z). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1h** (241 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2n** (463 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5z** (286 mg, 0.84 mmol, 84%). The gram scale synthesis was performed on 10 mmol of the starting *ortho*-hydroxyarylenaminone and desired **5z** was prepared in 80% (2.72 g, 8.0 mmol) yield.

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1h** (241 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3g** (862 mg, 1.4 mmol, 1.4 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5z** (303 mg, 0.89 mmol, 89%). The gram scale synthesis was performed on 10 mmol of the starting *ortho*-hydroxyarylenaminone and desired **5z** was prepared in 72% (2.45 g, 7.2 mmol) yield.

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6j** (255 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4d** (440 mg, 1.8 mmol, 1.8 equiv)

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5z** (306 mg, 0.90 mmol, 90%). The gram scale synthesis was performed on 10 mmol of the starting O-alkylated *ortho*-hydroxyarylenaminone and desired **5z** was prepared in 83% (2.82 g, 8.3 mmol) yields.

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1h** (241 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4d** (440 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5z** (184 mg, 0.54 mmol, 54%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 10:1 as eluent to provide corresponding chromone. R_f = 0.4 (Hex:EtAc 5:1).

Yellow solid, mp 230−231 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, 1H, ^3J = 7.7 Hz), 8.24−8.27 (m, 2H), 7.96 (d, 1H, ^3J = 6.7 Hz), 7.71−7.83 (m, 7H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ Due to bad solubility it was not possible to measure. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{20}H_{12}O_2F_3$ 341.0795, found 341.0789.

3-(*o*-Tolyl)-4*H*-benzo[*h*]chromen-4-one (5aa). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1h** (241 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2c** (393 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5aa** (169 mg, 0.59 mmol, 59%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1h** (241 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3c** (636 mg, 1.5 mmol, 1.5 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5aa** (206 mg, 0.72 mmol, 72%).

Alternatively the title compound was prepared starting from $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (11 mg, 0.01 mmol, 0.01 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1h** (241 mg, 1.0 mmol, 1.0 equiv), and appropriate triarylsulfonium salt **3c** (681 mg, 1.4 mmol, 1.4 equiv) and dry DMSO (0.2 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5aa** (203 mg, 0.71 mmol, 71%).

In all previous cases gradient flash column chromatography was performed using a mixture of hexane/ethyl acetate 5:1 to 3:1 as eluent to provide corresponding chromone. R_f = 0.6 (Hex:EtAc 3:1).

Yellow solid, mp 141−142 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, 1H, ^3J = 8.0 Hz), 8.25 (d, 1H, ^3J = 8.5 Hz), 8.20 (s, 1H), 7.93 (d, 1H, ^3J = 7.5 Hz), 7.78 (d, 1H, ^3J = 8.8 Hz), 7.68−7.73 (m, 2H), 7.48 (s, 1H), 7.41 (d, 1H, ^3J = 7.9 Hz), 7.37 (t, 1H, ^3J = 7.4 Hz), 7.23 (d, 1H, ^3J = 7.4 Hz), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 176.1, 153.4, 152.2, 138.1, 135.7, 131.6, 129.7, 129.3, 129.1, 128.5, 128.1, 127.1, 126.7, 126.0, 125.3, 124.0, 122.2, 121.3, 120.9, 21.5. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{20}H_{15}O_2$ 287.1084, found 287.1072.

3-(*p*-Tolyl)-4*H*-benzo[*h*]chromen-4-one (5ab). The title compound was prepared starting from *ortho*-hydroxyarylenaminone **1h** (241 mg, 1.0 mmol, 1.0 equiv), appropriate dimethyl(aryl)sulfonium salt **2b** (393 mg, 1.3 mmol, 1.3 equiv), and Cs_2CO_3 (487 mg, 1.5 mmol, 1.5 equiv) and the dry DMF (0.3 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5ab** (249 mg, 0.87 mmol, 87%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), NaOAc (148 mg, 1.8 mmol, 1.8 equiv) appropriate *ortho*-hydroxyarylenaminone **1h** (241 mg, 1.0 mmol, 1.0 equiv) and appropriate triarylsulfonium salt **3b** (636 mg, 1.5 mmol, 1.5 equiv) and the dry CH_3CN (0.12 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5ab** (243 mg, 0.85 mmol, 85%).

In all previous cases gradient flash column chromatography was performed using a mixture of hexane/ethyl acetate 5:1 to 3:1 as eluent to provide corresponding chromone. R_f = 0.6 (Hex:EtAc 3:1).

Yellow solid, mp 189−190 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, 1H, ^3J = 7.9 Hz), 8.24 (d, 1H, ^3J = 8.5 Hz), 8.17 (s, 1H), 7.92 (d, 1H, ^3J = 7.8 Hz), 7.76 (d, 1H, ^3J = 8.5 Hz), 7.65−7.72 (m, 2H), 7.54 (d, 2H, ^3J = 9.4 Hz), 7.28 (d, 2H, ^3J = 7.9 Hz), 2.41 (s, 3H, Me). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 176.1, 153.5, 151.9, 138.2, 135.7, 129.2, 127.8, 128.7, 128.0, 127.1, 126.4, 125.2, 123.9, 122.2, 121.3, 120.8, 21.3. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{20}H_{15}O_2$ 287.1074, found 287.1072.

3-(2-(Trifluoromethoxy)phenyl)-4*H*-benzo[*h*]chromen-4-one (5ac). The title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6j** (255 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4l** (469 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5ac** (260 mg, 0.73 mmol, 73%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1h** (241 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4l** (469 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5ac** (110 mg, 0.31 mmol, 31%).

In all previous cases gradient flash column chromatography was performed using a mixture of hexane/ethyl acetate 7:1 to 5:1 as eluent to provide corresponding chromone. R_f = 0.5 (Hex:EtAc 3:1).

Yellow solid, mp 131−132 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, 1H, ^3J = 7.9 Hz), 8.23 (d, 1H, ^3J = 8.9 Hz), 8.19 (s, 1H), 7.94 (d, 1H, ^3J = 7.8 Hz), 7.79 (d, 1H, ^3J = 8.7 Hz), 7.68−7.74 (m, 2H), 7.52 (dd, 1H, ^3J = 7.5 Hz, ^4J = 1.8 Hz), 7.45−7.49 (m, 1H), 7.38−7.41 (m, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.2, 153.7, 153.5, 147.3, 135.8, 132.5, 130.0, 129.4, 128.1, 126.8, 125.5, 125.2, 123.9, 122.9, 122.2, 121.2, 120.9, 120.4 (d, $^1J_{CF}$ = 258.8 Hz). HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{20}H_{12}O_3F_3$ 357.0748, found 357.0739.

3-(3-(Trifluoromethoxy)phenyl)-4*H*-benzo[*h*]chromen-4-one (5ad). The title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6j** (255 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4k** (469 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5ad** (331 mg, 0.93 mmol, 93%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1h** (241 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4k** (469 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5ad** (210 mg, 0.59 mmol, 59%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 5:1 as eluent to provide corresponding chromone. R_f = 0.5 (Hex:EtAc 3:1).

Yellow solid, mp 117−118 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, 1H, ^3J = 8.1 Hz), 8.20−8.22 (m, 2H), 7.91 (d, 1H, ^3J = 7.6 Hz), 7.76 (d, 1H, ^3J = 8.6 Hz), 7.66−7.73 (m, 2H), 7.56−7.58 (m, 2H), 7.48 (t, 1H, ^3J = 7.9 Hz), 7.26−7.27 (m, 1H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.5, 153.5, 152.5, 149.3, 135.8, 133.7, 129.8, 129.4, 128.1, 127.3, 127.2, 125.6, 125.1, 123.8, 122.1, 121.6, 121.0, 120.7, 120.6, 120.5 (d, $^1J_{CF}$ = 256.5 Hz). HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{20}H_{12}O_3F_3$ 357.0742, found 357.0739.

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

3-(3,5-Dichlorophenyl)-6-methyl-4*H*-chromen-4-one (5ae). The title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1b** (205 mg, 1.0 mmol, 1.0 equiv), and appropriate arenesulfonyl chloride **4q** (442 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5ae** (186 mg, 0.61 mmol, 61%).

The flash column chromatography was performed using a mixture of hexane/ethyl acetate 10:1 as eluent to provide corresponding chromone. R_f = 0.55 (Hex:EtAc 5:1).

Yellow solid, mp 115−116 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (br. s, 1H), 7.99 (s, 1H), 7.48 (dd, 1H, ^3J = 8.6 Hz, ^4J = 1.8 Hz), 7.44 (d, 2H, ^4J = 1.8 Hz), 7.36 (d, 1H, ^3J = 8.6 Hz), 7.31 (t, 1H, ^4J = 1.8 Hz), 3.45 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 175.4, 154.3, 153.5, 135.6, 135.2, 134.8, 128.0, 127.2, 125.5, 123.9, 122.8, 117.8, 20.9. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{16}H_{11}O_2Cl_2$ 305.0140, found 305.0136.

6-Chloro-3-(3-methoxyphenyl)-4*H*-chromen-4-one (5af). The title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6i** (240 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4j** (372 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5af** (242 mg, 0.84 mmol, 84%).

The column chromatography was performed using a mixture of hexane/ethyl acetate 7:1 to 5:1 as eluent to provide corresponding chromone. R_f = 0.5 (Hex:EtAc 5:1).

Light yellow solid, mp 126−127 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, 1H, ^4J = 2.5 Hz), 8.01 (s, 1H), 7.60 (dd, 1H, ^3J = 8.8 Hz, ^4J = 2.6 Hz), 7.43 (d, 1H, ^3J = 8.9 Hz), 7.34 (t, 1H, ^3J = 7.9 Hz), 7.08−7.13 (m, 2H), 6.93 (dd, 1H, ^3J = 8,3 Hz, ^4J = 2.6 Hz), 3.84 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 175.0, 159.6, 154.4, 153.2, 133.8, 132.6, 131.2, 129.5, 125.7, 125.4, 125.2, 121.1, 119.8, 114.4, 114.1, 55.3. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{16}H_{12}O_3Cl$ 287.0478, found 287.0475.

6-Chloro-3-(2-(trifluoromethoxy)phenyl)-4*H*-chromen-4-one (5ag). The title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6i** (240 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4l** (469 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5ag** (242 mg, 0.71 mmol, 71%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1f** (226 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4l** (469 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5ag** (119 mg, 0.35 mmol, 35%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 8:1 as eluent to provide corresponding chromone. R_f = 0.5 (Hex:EtAc 3:1).

Light brown solid, mp 140−141 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, 1H, ^4J = 2.1 Hz), 7.98 (s, 1H), 7.63 (dd, 1H, ^3J = 8.4 Hz, ^4J = 2.1 Hz), 7.43−7.48 (m, 3H), 7.35−7.38 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.3, 154.6, 154.4, 147.3, 134.0, 132.4, 131.4, 130.1, 126.8, 125.7, 125.2, 124.7, 121.5, 120.8, 120.3 (d, $^1J_{CF}$ = 261.4 Hz), 119.9. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{16}H_9O_3F_3Cl$ 341.0197, found 341.0192.

6-Chloro-3-(3-(trifluoromethoxy)phenyl)-4*H*-chromen-4-one (5ah). The title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6i** (240 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4k** (469 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5ah** (306 mg, 0.90 mmol, 90%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1f** (226 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4k** (469 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5ah** (167 mg, 0.49 mmol, 49%).

In all previous cases gradient flash column chromatography was performed using a mixture of hexane/ethyl acetate 7:1 to 5:1 as eluent to provide corresponding chromone. R_f = 0.7 (Hex:EtAc 3:1).

Light yellow solid, mp 94−95 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, 1H, ^4J = 2.5 Hz), 8.05 (s, 1H), 7.64 (dd, 1H, ^3J = 9.2 Hz, ^4J = 2.5 Hz), 7.46−7.51 (m, 4H), 7.25−7.26 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.7, 154.5, 153.5, 149.3, 134.2, 133.3, 131.5, 129.9, 127.2, 125.8, 125.4, 119.9, 124.1, 121.5, 120.8, 120.5 (d, $^1J_{CF}$ = 258.5 Hz). HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{16}H_9O_3F_3Cl$ 341.0203, found 341.0192.

6-Chloro-3-(*m*-tolyl)-4*H*-chromen-4-one (5ai). The title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6i** (240 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4p** (343 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5ai** (235 mg, 0.87 mmol, 87%).

The gradient flash column chromatography was performed using a mixture of hexane/ethyl acetate 5:1 as eluent to provide corresponding chromone. R_f = 0.5 (Hex:EtAc 3:1).

Light yellow solid, mp 94−95 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, 1H, ^4J = 2.6 Hz), 8.00 (s, 1H), 7.60 (dd, 1H, ^3J = 8.9 Hz, ^4J = 2.7 Hz), 7.43 (d, 1H, ^3J = 8.5 Hz), 7.37 (s, 1H), 7.33−7.34 (m, 2H), 7.21−7.22 (m, 1H), 2.41 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 175.1, 154.5, 153.1, 138.2, 133.8, 131.2, 131.1, 129.6, 129.2, 128.5, 125.9, 125.7, 125.5, 125.4, 119.8, 21.5. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{16}H_{12}O_2Cl$ 271.0524, found 271.0526.

6-Chloro-3-(4-(trifluoromethoxy)phenyl)-4*H*-chromen-4-one (5aj). The title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6i** (240 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4s** (469 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5aj** (283 mg, 0.83 mmol, 83%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1f** (226 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4s** (469 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5aj** (180 mg, 0.53 mmol, 53%).

In all previous cases gradient flash column chromatography was performed using a mixture of hexane/ethyl acetate 7:1 to 5:1 as eluent to provide corresponding chromone. R_f = 0.7 (Hex:EtAc 3:1).

Light yellow solid, mp 162−163 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, 1H, ^4J = 2.6 Hz), 8.03 (s, 1H), 7.64 (dd, 1H, ^3J = 9.0 Hz, ^4J = 2.5 Hz), 7.58−7.61 (m, 2H), 7.46 (d, 1H, ^3J = 9.0 Hz), 7.29 (d, 2H, ^3J = 8.2 Hz). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 174.9, 154.5, 153.2, 149.3, 134.1, 131.5, 130.4, 130.0, 125.8, 125.4, 124.3, 121.1, 120.4 (d, $^1J_{CF}$ = 257.7 Hz), 119.9. HRMS (TOF MS ES+) m/z $[M + H]^+$ calcd for $C_{16}H_9O_3F_3Cl$ 341.0197, found 341.0192.

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

3-(4-Phenoxyphenyl)-4*H*-chromen-4-one (5ak). The title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6a** (205 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4i** (550 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5ak** (206 mg, 0.62 mmol, 62%).

Alternatively, the title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate *ortho*-hydroxyarylenaminone **1a** (191 mg, 1.0 mmol, 1.0 equiv), and appropriate arenesulfonyl chloride **4i** (550 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5ak** (163 mg, 0.49 mmol, 49%).

In all previous cases flash column chromatography was performed using a mixture of hexane/ethyl acetate 5:1 as eluent to provide corresponding chromone. R_f = 0.5 (Hex:EtAc 3:1).

White solid, mp 158−159 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (dd, 1H, ^3J = 8.1 Hz, ^4J = 1.3 Hz), 8.03 (s, 1H), 7.67−7.70 (m, 1H), 7.54 (d, 2H, ^3J = 8.5 Hz), 7.48 (d, 1H, ^3J = 8.5 Hz), 7.43 (t, 1H, ^3J = 7.9 Hz), 7.36 (d, 2H, ^3J = 7.6 Hz), 7.13 (t, 1H, ^3J = 7.4 Hz), 7.06−7.08 (m, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 176.3, 157.4, 156.8, 156.1, 152.7, 133.6, 130.3, 129.7, 126.6, 126.3, 125.2, 124.7, 124.4, 123.5, 119.2, 118.6, 118.0. MS (GC, 70 eV) *m*/*z* (%) = 314 (M^+, 100), 194 (25), 165 (21), 77 (12). Anal. Calcd for $C_{21}H_{14}O_3$: C, 80.24; H, 4.49. Found: C, 80.32; H, 4.41.

6-Fluoro-3-(4-phenoxyphenyl)-4*H*-chromen-4-one (5al). The title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6g** (223 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4i** (483 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5al** (262 mg, 0.79 mmol, 79%).

The gradient flash column chromatography was performed using a mixture of hexane/ethyl acetate 7:1 to 5:1 as eluent to provide corresponding chromone. R_f = 0.6 (Hex:EtAc 3:1).

Yellow solid, mp 152−153 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.95 (dd, 1H, ^3J = 8.2 Hz, ^4J = 3.1 Hz), 7.54 (td, 2H, ^3J = 9.0 Hz, ^4J = 2.2 Hz), 7.50−7.52 (m, 1H), 7.40−7.44 (m, 1H), 7.35−7.39 (m, 2H), 7.13−7.16 (m, 1H), 7.06−7.10 (m, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 111.1 (d, J_{CF} = 23.5 Hz), 118.6, 119.2, 120.1 (d, J_{CF} = 8.9 Hz), 121.0 (d, J_{CF} = 26.1 Hz), 123.6, 124.2, 125.5 (d, J_{CF} = 7.7 Hz), 126.1, 129.8, 130.3, 152.4, 152.9, 156.7, 157.6, 159.5 (d, $^1J_{CF}$ = 247.1 Hz), 175.6. HRMS (TOF MS ES+) *m*/*z* $[M + H]^+$ calcd for $C_{21}H_{14}O_3F$ 333.0930, found 333.0927.

3-(4-Ethoxyphenyl)-7-methoxy-4*H*-chromen-4-one (5am). The title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6f** (235 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4t** (397 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5am** (243 mg, 0.82 mmol, 82%).

The flash column chromatography was performed using a mixture of hexane/ethyl acetate 5:1 to 1:1 as eluent to provide corresponding chromone. R_f = 0.3 (Hex:EtAc 3:1).

Yellow solid, mp 130−131 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, 1H, ^3J = 8.8 Hz), 7.92 (s, 1H), 7.48 (d, 2H, ^3J = 8.8 Hz), 6.98 (dd, 1H, ^3J = 8.6 Hz, ^4J = 2.5 Hz), 6.95 (d, 2H, ^3J = 8.6 Hz), 7.84 (d, 1H, ^4J = 2.5 Hz), 4.06 (q, 2H, ^3J = 7.5 Hz), 3.91 (s, 3H), 1.43 (t, 3H, ^3J = 7.5 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 196.3, 190.2, 175.9, 163.9, 158.9, 157.9, 152.0, 130.1, 127.8, 124.9, 124.0, 118.4, 114.4, 105.3, 100.0, 63.5, 55.8, 14.8. HRMS (TOF MS ES+) *m*/*z* $[M + H]^+$ calcd for $C_{18}H_{17}O_4$ 297.1130, found 297.1127.

3-(4-Ethoxyphenyl)-6-fluoro-4*H*-chromen-4-one (5an). The title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6g** (223 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4t** (397 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5an** (239 mg, 0.84 mmol, 84%).

The flash column chromatography was performed using a mixture of hexane/ethyl acetate 5:1 to 3:1 as eluent to provide corresponding chromone. R_f = 0.5 (Hex:EtAc 3:1).

White solid, mp 163−164 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.92 (dd, 1H, ^3J = 8.2 Hz, ^4J = 3.1 Hz), 7.46−7.49 (m, 3H), 7.35−7.41 (m, 1H), 6.95 (d, 2H, ^3J = 8.6 Hz), 4.05 (q, 2H, ^3J = 6.8 Hz),1.43 (t, 3H, ^3J = 6.8 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.6, 159.5 (d, $^1J_{CF}$ = 245.8 Hz), 159.0, 152.7, 152.3, 130.0, 125.5 (d, J_{CF} = 6.3 Hz), 124.3, 123.4, 121.7 (d, J_{CF} = 25.4 Hz), 120.1 (d, J_{CF} = 7.6 Hz), 111.0 (d, J_{CF} = 25.6 Hz), 63.4, 14.8. MS (GC, 70 eV) *m*/*z* (%) = 284 (M^+, 100), 255 (98), 199 (12), 139 (20), 118 (39). Anal. Calcd for $C_{17}H_{13}FO_3$: C, 71.82; H, 4.61. Found: C, 71.77; H, 4.53.

7-Fluoro-3-(*o*-tolyl)-4*H*-chromen-4-one (5ao). The title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6h** (223 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4m** (343 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5ao** (165 mg, 0.65 mmol, 65%).

The flash column chromatography was performed using a mixture of hexane/ethyl acetate 7:1 to 5:1 as eluent to provide corresponding chromone. R_f = 0.7 (Hex:EtAc 3:1).

Light brown solid, mp 163−164 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30−8.33 (m, 1H), 7.86 (s, 1H), 7.29−7.33 (m, 2H), 7.23−7.26 (m, 1H),.7.15−7.20 (m, 3H), 2.26 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.1, 165.5 (d, $^1J_{CF}$ = 258.4 Hz), 157.3 (d, J_{CF} = 13.9 Hz), 153.6, 138.0, 131.1, 130.2 (d, J_{CF} = 25.9 Hz), 128.9 (d, $^1J_{CF}$ = 10.9 Hz), 128.7, 126.6, 125.8, 121.1, 104.6 (d, J_{CF} = 26.1 Hz), 114.0 (d, J_{CF} = 22.1 Hz), 20.0. HRMS (TOF MS ES+) *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{12}O_2F$ 255.0832, found 255.0821.

6-Fluoro-3-(4-methoxyphenyl)-4*H*-chromen-4-one (5ap). The title compound was prepared starting from photocatalyst $Ru(bpy)_3Cl_2·6H_2O$ (15.0 mg, 0.02 mmol, 0.02 equiv), Na_2CO_3 (212 mg, 2 mmol, 2 equiv), appropriate O-alkylated *ortho*-hydroxyarylenaminone **6g** (223 mg, 1.0 mmol, 1.0 equiv) and appropriate arenesulfonyl chloride **4e** (440 mg, 1.8 mmol, 1.8 equiv) and dry CH_3CN (0.10 mmol/mL). The purification of the dry crude performed by column chromatography on silica gel provides the desired chromone **5ap** (230 mg, 0.85 mmol, 85%).

The flash column chromatography was performed using a mixture of hexane/ethyl acetate 7:1 to 3:1 as eluent to provide corresponding chromone. R_f = 0.7 (Hex:EtAc 3:1).

White solid, mp 177−179 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (s, 1H, 3.85 (s, 3H), 7.93 (dd, 1H, ^3J = 8.3 Hz, ^4J = 2.9 Hz), 7.48−7.51 (m, 3H), 7.40−7.42 (m, 1H), 6.98 (d, 2H, ^3J = 8.7 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 175.7, 159.7, 159.6 (d, $^1J_{CF}$ = 252.0 Hz), 152.7, 152.4, 130.1, 125.6, 124.4, 121.8 (d, J_{CF} = 25.6 Hz), 123.7, 120.1 (d, J_{CF} = 9.0 Hz), 114.0, 111.1 (d, J_{CF} = 23.7 Hz), 55.3. HRMS (TOF MS ES+) *m*/*z* $[M + H]^+$ calcd for $C_{16}H_{12}O_3F$ 271.0775, found 271.0770.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02294.

General information, copies of ^{1}H and $^{13}C\{^1H\}$ NMR spectra for all new compounds (PDF)

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

AUTHOR INFORMATION

Corresponding Authors

Satenik Mkrtchyan − *Laboratory of Homogeneous Catalysis and Molecular Design at Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, PL-90-363 Łodź, Poland*; Email: sm19860214@gmail.com

Viktor O. Iaroshenko − *Laboratory of Homogeneous Catalysis and Molecular Design at Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, PL-90-363 Łodź, Poland; Dipartimento di Chimica e Biologia "A. Zambelli", Università di Salerno, 84084 Fisciano, SA, Italy; Department of Chemistry, University of Helsinki, 00014 Helsinki, Finland;* orcid.org/0000-0002-5647-5326; Email: iva108@gmail.com, viktori@cbmm.lodz.pl

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.joc.0c02294

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research is supported by a grant from National Science Centre (NSC) Poland within the framework of European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 665778 (POLONEZ 2 grant, No. 2016/21/P/ST5/00630) obtained by Dr. Satenik Mkrtchyan. This research project is also supported by a grant from National Science Centre (NSC) Poland, the SONATA 10 (No. 2015/19/D/ST5/02774) obtained by Dr. Viktor O. Iaroshenko. Dr. Viktor O. Iaroshenko also appreciates the funding for his Visiting Professorship from the University of Salerno.

REFERENCES

(1) (a) Ellis, G. P., Ed.; Chromenes, Chromanones, and Chromones. In *The Chemistry of Heterocyclic Compounds*; Springer, 2009; Vol. *31*, p 1196. (b) Gaspar, A.; Matos, M. J.; Garrido, J.; Uriarte, E.; Borges, F. Chromone: A Valid Scaffold in Medicinal Chemistry. *Chem. Rev.* **2014**, *114*, 4960−4992. (c) Wetzel, S.; Bon, R. S.; Kumar, K.; Waldmann, H. Biology-Oriented Synthesis. *Angew. Chem., Int. Ed.* **2011**, *50*, 10800−10826. (d) Lampe, J. W. Isoflavonoid and Lignan Phytoestrogens as Dietary Biomarkers. *J. Nutr.* **2003**, *133*, 956−964. (e) Yeung, D. K. Y.; Leung, S. W. S.; Xu, Y. C.; Vanhoutte, P. M.; Man, R. Y. K. Puerarin, an isoflavonoid derived from Radix puerariae, potentiates endothelium-independent relaxation via the cyclic AMP pathway in porcine coronary artery. *Eur. J. Pharmacol.* **2006**, *552*, 105−111. (f) Wagle, A.; Seong, S. H.; Jung, H. A.; Choi, J. S. Identifying an isoflavone from the root of Pueraria lobata as a potent tyrosinase inhibitor. *Food Chem.* **2019**, *276*, 383−389. (g) Kim, Y.-W.; Hackett, J. C.; Brueggemeier, R. W. Synthesis and Aromatase Inhibitory Activity of Novel Pyridine-Containing Isoflavones. *J. Med. Chem.* **2004**, *47*, 4032−4040. (h) Miadoková, E. Isoflavonoids - an overview of their biological activities and potential health benefits. *Interdiscip. Toxicol.* **2009**, *2* (4), 211−218.

(2) (a) Dawood, K. M. Microwave-assisted Suzuki−Miyaura and Heck−Mizoroki cross-coupling reactions of aryl chlorides and bromides in water using stable benzothiazole-based palladium(II) precatalysts. *Tetrahedron* **2007**, *63* (39), 9642−9651. (b) Biegasiewicz, K. F.; Gordon, J. S.; Rodriguez, D. A.; Priefer, R. Development of a general approach to the synthesis of a library of isoflavonoid derivatives. *Tetrahedron Lett.* **2014**, *55* (37), 5210−5212. (c) Eisnor, C. R.; Gossage, R. A.; Yadav, P. N. Oxazoline Chemistry. Part 11: Syntheses of natural and synthetic isoflavones, stilbenes and related species via C−C bond formation promoted by a Pd−oxazoline complex. *Tetrahedron* **2006**, *62* (14), 3395−3401. (d) Mutai, P.; Pavadai, E.; Wiid, I.; Ngwane, A.; Baker, B.; Chibale, K. Synthesis, antimycobacterial evaluation and pharmacophore modeling of analogues of the natural product formononetin. *Bioorg. Med. Chem. Lett.* **2015**, *25* (12), 2510−2513.

(3) Rao, M.; Venkatesh, V.; Jadhav, D. Pd-Catalyzed Efficient Cross-Couplings of 3-Iodochromones with Triarylbismuths as Substoichiometric Multicoupling Organometallic Nucleophiles. *Synlett* **2009**, *2009* (16), 2597−2600.

(4) (a) Zhang, Z.; Han, L.; Wang, D.; Qiao, J.; Du, Z. CN 103275052, 2013, CAN159:486047. (b) Zhang, Z.; Qiao, J.; Wang, D.; Han, L.; Ding, R. Synthesis of isoflavones by room-temperature nickel-catalyzed cross-couplings of 3-iodo(bromo)chromones with arylzincs. *Mol. Diversity* **2014**, *18* (2), 245−251.

(5) Quibell, J. M.; Duan, G.; Perry, G. J. P.; Larrosa, I. Decarboxylative Suzuki−Miyaura coupling of (hetero)aromatic carboxylic acids using iodine as the terminal oxidant. *Chem. Commun.* **2019**, *55* (45), 6445−6448.

(6) Tsoi, Y.-T.; Zhou, Z.; Chan, A. S. C.; Yu, W.-Y. Palladium-Catalyzed Cross Coupling Reaction of Benzyl Bromides with Diazoesters for Stereoselective Synthesis of (E)-α,β-Diarylacrylates. *Org. Lett.* **2010**, *12* (20), 4506−4509.

(7) Mkrtchyan, S.; Iaroshenko, V. O. Visible-light-mediated arylation of ortho-hydroxyarylenaminones: Direct access to isoflavones. *Chem. Commun.* **2020**, *56*, 2606−2609.

(8) Wan, J.-P.; Tu, Z.; Wang, Y. Transient and Recyclable Halogenation Coupling (TRHC) for Isoflavonoid Synthesis with Site-Selective Arylation. *Chem. - Eur. J.* **2019**, *25* (28), 6907−6910.

(9) (a) Jia, H.; Tang, Y.; Shi, Y.; Ma, L.; He, Z.; Lai, W.; Yang, Y.; Wang, Y.; Zang, Y.; Xu, S. Rhodium complexes catalyze oxidative coupling between salicylaldehyde and phenylacetylene via C−H bond activation. *Chemical Papers* **2017**, *71* (9), 1791−1795. (b) Mishra, P.; Singh, S.; Ankit, P.; Fatma, S.; Singh, D.; Singh, J. Synthesis of Dihydropyran Subunit of (+)-Sorangicin A Using RCM Reaction. *Bull. Korean Chem. Soc.* **2013**, *34* (4), 1070−1076. (c) Mitra, R. N.; Show, K.; Barman, D.; Sarkar, S.; Maiti, D. K. NHC-Catalyzed Dual Stetter Reaction: A Mild Cascade Annulation for the Syntheses of Naphthoquinones, Isoflavanones, and Sugar-Based Chiral Analogues. *J. Org. Chem.* **2019**, *84* (1), 42−52. (d) Li, R.; Kobayashi, H.; Tong, J.; Yan, X.; Tang, Y.; Zou, S.; Jin, J.; Yi, W.; Fan, J. Radical-Involved Photosynthesis of AuCN Oligomers from Au Nanoparticles and Acetonitrile. *J. Am. Chem. Soc.* **2012**, *134* (44), 18286−18294.

(10) Kshatriya, R. B.; Shaikh, Y. I.; Nazeruddin, G. M. Microwave assisted synthesis of Isoflavones. *J. Chem. Pharm. Res.* **2015**, *7* (5), 543−548.

(11) (a) Li, W.; Liu, F.; Zhang, P. Synthesis of isoflavones via base catalysed condensation reaction of deoxybenzoin. *J. Chem. Res.* **2008**, *2008* (12), 683−685. (b) Li, Q.-L.; Liu, Q.-L.; Ge, Z.-Y.; Zhu, Y.-M. A Novel Synthesis of Isoflavones via Copper(I)-Catalyzed Intramolecular Cyclization Reaction. *Helv. Chim. Acta* **2011**, *94* (7), 1304−1309. (c) Frasinyuk, M. S.; Zhang, W.; Wyrebek, P.; Yu, T.; Xu, X.; Sviripa, V. M.; Bondarenko, S. P.; Xie, Y.; Ngo, H. X.; Morris, A. J.; Mohler, J. L.; Fiandalo, M. V.; Watt, D. S.; Liu, C. Developing antineoplastic agents that target peroxisomal enzymes: cytisine-linked isoflavonoids as inhibitors of hydroxysteroid 17-beta-dehydrogenase-4 (HSD17B4). *Org. Biomol. Chem.* **2017**, *15*, 7623−7629. (d) Nam, G.; Ji, Y.; Lee, H. J.; Kang, J.; Yi, Y.; Kim, M.; Lin, Y.; Lee, Y.-H.; Lim, M. H. Orobol: An Isoflavone Exhibiting Regulatory Multifunctionality against Four Pathological Features of Alzheimer's Disease. *ACS Chem. Neurosci.* **2019**, *10* (8), 3386−3390.

(12) (a) Ishiyama, T.; Kizaki, H.; Hayashi, T.; Suzuki, A.; Miyaura, N. Palladium-Catalyzed Carbonylative Cross-Coupling Reaction of Arylboronic Acids with Aryl Electrophiles: Synthesis of Biaryl Ketones. *J. Org. Chem.* **1998**, *63* (14), 4726−4731. (b) Khupse, R. S.; Erhardt, P. W. Practical Synthesis of Lespedezol A1. *J. Nat. Prod.* **2008**, *71* (2), 275−277. (c) Miyake, H.; Nishimura, A.; Yago, M.; Sasaki, M. Direct Syntheses of Benzofuran-2(3H)-ones and Benzofuran-3(2H)-ones from 1-(2-Hydroxyphenyl)alkan-1-ones by $CuBr_2$ or $CuCl_2$. *Chem. Lett.* **2007**, *36* (2), 332−333. (d) Kunyane, P.; Sonopo, M. S.; Selepe, M. A. Synthesis of Isoflavones by Tandem Demethylation and Ring-

Opening/Cyclization of Methoxybenzoylbenzofurans. *J. Nat. Prod.* **2019**, *82* (11), 3074−3082.
(13) (a) Aitmambetov, A.; Khilya, V. P. Synthetic and modified isoflavonoids. XI. Synthesis of analogues of maxima isoflavone A and xanthocercin. *Chem. Nat. Compd.* **1994**, *30* (3), 307−311. (b) Otsalyuk, V. M.; Tkachuk, T. M.; Bondarenko, S. P.; Chkhalo, V. V.; Khilya, V. P. Synthetic analogs of xanthocercin. *Chem. Nat. Compd.* **1998**, *34* (3), 284−288. (c) Khilya, V. P.; Tkachuk, T. M.; Shevchuk, L. I. Thiazole analogs of isoflavolignans. *Chem. Nat. Compd.* **2000**, *36* (6), 574−578.
(14) (a) Semenov, V. V.; Tsyganov, D. V.; Semenova, M. N.; Chuprov-Netochin, R. N.; Raihstat, M. M.; Konyushkin, L. D.; Volynchuk, P. B.; Marusich, E. I.; Nazarenko, V. V.; Leonov, S. V.; Kiselyov, A. S. Efficient Synthesis of Glaziovianin A Isoflavone Series from Dill and Parsley Extracts and Their in Vitro/in Vivo Antimitotic Activity. *J. Nat. Prod.* **2016**, *79* (5), 1429−1438. (b) Lozinskii, O. A.; Shokol, T. V.; Khilya, V. P. Synthesis and biological activity of chromones annelated at the C(7)-C(8) bond with heterocycles. *Chem. Heterocycl. Compd.* **2011**, *47* (9), 1055−1077.
(15) (a) Fu, L.; Wan, J.-P. C3-Functionalized Chromones Synthesis by Tandem C−H Elaboration and Chromone Annulation of Enaminones. *Asian J. Org. Chem.* **2019**, *8*, 767−776. (b) Mrug, G. P.; Myshko, N. V.; Bondarenko, S. P.; Sviripa, V. M.; Frasinyuk, M. S. One-Pot Synthesis of B-Ring Ortho-Hydroxylated Sappanin-Type Homoisoflavonoids. *J. Org. Chem.* **2019**, *84* (11), 7138−7147. (c) Lin, Y.; Wan, J.-P.; Liu, Y. Synthesis of 3-halochromones with simple KX halogen sources enabled by in situ halide oxidation. *New J. Chem.* **2020**, *44*, 8120−8124. (d) Huang, J.; Yu, F. Recent Advances in Organic Synthesis Based on N,N-Dimethyl Enaminones. *Synthesis* **2021**, *53*, 587−610.
(16) (a) Mkrtchyan, S.; Iaroshenko, V. O. New Entries to 3-Acylchromones: TM-Catalysed Decarboxylative Cross-Coupling of α-Keto Acids with ortho-Hydroxyarylenaminones, 2,3-Unsubstituted Chromones and 3-Iodochromones. *Eur. J. Org. Chem.* **2018**, *2018*, 6867−6875. (b) Mkrtchyan, S.; Iaroshenko, V. O.; Dudkin, S.; Gevorgyan, A.; Vilches-Herrera, M.; Ghazaryan, G.; Volochnyuk, D.; Ostrovskyi, D.; Ahmed, Z.; Villinger, A.; Sosnovskikh, V. Ya.; Langer, P. 3-Methoxalylchromone − A Novel Versatile Reagent for the Regioselective Purine Isostere Synthesis. *Org. Biomol. Chem.* **2010**, *8*, 5280−5284.
(17) (a) Xiang, H.; Zhao, Q.; Tang, Z.; Xiao, J.; Xia, P.; Wang, C.; Yang, C.; Chen, X.; Yang, H. Visible-Light-Driven, Radical-Triggered Tandem Cyclization of o-Hydroxyaryl Enaminones: Facile Access to 3-CF_2/CF_3-Containing Chromones. *Org. Lett.* **2017**, *19*, 146−149. (b) Gao, H.; Hu, B.; Dong, W.; Gao, X.; Jiang, L.; Xie, X.; Zhang, Z. Synthesis of 3-CF_2-Containing Chromones via a Visible-Light-Induced Radical Cascade Reaction of o-Hydroxyaryl Enaminones. *ACS Omega* **2017**, *2* (7), 3168−3174. (c) Yu, Q.; Liu, Y.; Wan, J.-P. Transition metal-free synthesis of 3-trifluoromethyl chromones via tandem C−H trifluoromethylation and chromone annulation of enaminones. *Org. Chem. Front.* **2020**, *7*, 2770−2775.
(18) Gao, Y.; Liu, Y.; Wan, J.-P. Visible Light-Induced Thiocyanation of Enaminone C−H Bond to Access Polyfunctionalized Alkenes and Thiocyano Chromones. *J. Org. Chem.* **2019**, *84*, 2243−2251.
(19) Mkrtchyan, S.; Iaroshenko, V. O. Photoredox functionalisation of 3-halogenchromones, 3-formylchromones and chromone-3-carboxilyc acids: Routes to 3-acylchromones. *J. Org. Chem.* **2020**, *85* (11), 7152−7174.
(20) (a) Majek, M.; von Wangelin, A. J. Mechanistic Perspectives on Organic Photoredox Catalysis for Aromatic Substitutions. *Acc. Chem. Res.* **2016**, *49*, 2316−2327. (b) Narayanam, J. M. R.; Stephenson, C. R. J. Visible light photoredox catalysis: applications in organic synthesis. *Chem. Soc. Rev.* **2011**, *40*, 102−113. (c) Romero, N. A.; Nicewicz, D. A. Photoredox Catalysis for Building C−C Bonds from $C(sp^2)$−H Bonds. *Chem. Rev.* **2016**, *116*, 10075−10166. (d) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113*, 5322−5363. (e) Ghosh, I.; Marzo, L.; Das, A.; Shaikh, R.; König, B. Visible Light Mediated Photoredox Catalytic Arylation Reactions. *Acc. Chem. Res.* **2016**, *49*, 1566−1577. (f) Matsui, J. K.; Lang, S. B.; Heitz, D. R.; Molander, G. A. Photoredox-Mediated Routes to Radicals: The Value of Catalytic Radical Generation in Synthetic Methods Development. *ACS Catal.* **2017**, *7*, 2563−2575. (g) Bugaenko, D. I.; Volkov, A. A.; Karchava, A. V.; Yurovskaya, M. A. Generation of aryl radicals by redox processes. Recent progress in the arylation methodology. *Russ. Chem. Rev.* **2021**, *90*, 116−148.
(21) (a) Zhao, J.-N.; Kayumov, M.; Wang, D.-Y.; Zhang, A. Transition-Metal-Free Aryl−Heteroatom Bond Formation via C−S Bond Cleavage. *Org. Lett.* **2019**, *21* (18), 7303−7306. (b) Uno, D.; Minami, H.; Otsuka, S.; Nogi, K.; Yorimitsu, H. Palladium-Catalyzed Mizoroki−Heck-Type Alkenylation of Monoaryldialkylsulfoniums. *Chem. - Asian J.* **2018**, *13*, 2397−2400. (c) Huang, C.; Feng, J.; Ma, R.; Fang, S.; Lu, T.; Tang, W.; Du, D.; Gao, J. Redox-Neutral Borylation of Aryl Sulfonium Salts via C−S Activation Enabled by Light. *Org. Lett.* **2019**, *21* (23), 9688−9692.
(22) (a) Chaudhary, R.; Natarajan, P. Visible Light Photoredox Activation of Sulfonyl Chlorides: Applications in Organic Synthesis. *ChemistrySelect* **2017**, *2*, 6458−6479. (b) Natarajan, P.; Bala, A.; Mehta, S. K.; Bhasin, K. K. Visible-light photocatalyzed synthesis of 2-aryl N-methylpyrroles, furans and thiophenes utilizing arylsulfonyl chlorides as a coupling partner. *Tetrahedron* **2016**, *72*, 2521−2526. (c) Deng, G.-B.; Wang, Z.-Q.; Xia, J.-D.; Qian, P.-C.; Song, R.-J.; Hu, M.; Gong, L.-B.; Li, J.-H. Tandem Cyclizations of 1,6-Enynes with Arylsulfonyl Chlorides by Using Visible-Light Photoredox Catalysis. *Angew. Chem., Int. Ed.* **2013**, *52*, 1535−1538. (d) Gu, L.; Jin, C.; Liu, J.; Ding, H.; Fan, B. Transition-metal-free, visible-light induced cyclization of arylsulfonyl chlorides with 2-isocyanobiphenyls to produce phenanthridines. *Chem. Commun.* **2014**, *50*, 4643−4945.
(23) (a) Fensterbank, L.; Goddard, J.-P.; Malacria, M.; Ollivier, C. Homolytic Reduction of Onium Salts. *Chimia* **2012**, *66*, 425−432. (b) Koike, T.; Akita, M. Fine Design of Photoredox Systems for Catalytic Fluoromethylation of Carbon−Carbon Multiple Bonds. *Acc. Chem. Res.* **2016**, *49*, 1937−1945.
(24) (a) van der Born, D.; Pees, A.; Poot, A. J.; Orru, R. V. A.; Windhorst, A. D.; Vugts, D. Fluorine-18 labelled building blocks for PET tracer synthesis. *Chem. Soc. Rev.* **2017**, *46*, 4709−4773. (b) Maeda, M.; Fukumura, T.; Kojima, M. Dimethylsulfonium salts as substrates in aromatic nucleophilic substitution with fluoride ions. *Chem. Pharm. Bull.* **1985**, *33*, 1301−1304. (c) Gendron, T.; Sander, T.; Cybulska, K.; Benhamou, L.; Sin, P. K. B.; Khan, A.; Wood, M.; Porter, M. J.; Årstad, E. Ring-Closing Synthesis of Dibenzothiophene Sulfonium Salts and Their Use as Leaving Groups for Aromatic ^{18}F-Fluorination. *J. Am. Chem. Soc.* **2018**, *140*, 11125−11132.
(25) (a) Mutai, P.; Pavadai, E.; Wiid, I.; Ngwane, A.; Baker, B.; Chibale, K. Synthesis, antimycobacterial evaluation and pharmacophore modelling of analogues of the natural product formononetin. *Bioorg. Med. Chem. Lett.* **2015**, *25*, 2510−2513. (b) Davies, S. G.; Mobbs, B. E.; Goodwin, C. J. Substituted 4H-1-benzopyran-4-ones (chromones): synthesis via palladium-catalysed coupling of their halogeno derivatives with alkenes. *J. Chem. Soc., Perkin Trans. 1* **1987**, *1*, 2597−2604.
(26) (a) Wang, F.; Sun, W.; Wang, Y.; Jiang, Y.; Loh, T.-P. Highly Site-Selective Metal-Free C−H Acyloxylation of Stable Enamines. *Org. Lett.* **2018**, *20* (4), 1256−1260. (b) Bagle, P. N.; Mane, M. V.; Sancheti, S. P.; Gade, A. B.; Shaikh, S. R.; Baik, M.-H.; Patil, N. T. Gold(I)-Catalyzed Hydroxy Group Assisted C(sp2)−H Alkylation of Enaminones with Diazo Compounds To Access 3-Alkyl Chromones. *Org. Lett.* **2019**, *21* (1), 335−339. (c) Wan, J.-P.; Wang, C.; Liu, Y. Direct synthesis of enaminone functionalized biaryl ethers by CuI-catalyzed O-arylation of enaminone functionalized phenols. *Org. Biomol. Chem.* **2011**, *9*, 6481−6483. (d) Xiang, H.; Zhao, Q.-L.; Xia, P.-J.; Xiao, J.-A.; Ye, Z.-P.; Xie, X.; Sheng, H.; Chen, X.-Q.; Yang, H. Visible-Light-Induced External Radical-Triggered Annulation To Access CF_2-Containing Benzoxepine Derivatives. *Org. Lett.* **2018**, *20* (5), 1363−1366. (e) Bindal, S.; Kumar, D.; Kommi, D. N.; Bhatiya, S.; Chakraborti, A. K. Efficient Organocatalytic Dual Activation Strategy for Preparing the Versatile Synthons (2E)-1-(Het)Aryl/styryl-3-(dimethylamino)prop-2-en-1-ones and α-(E)-[(Dimethylamino)-methylene]cycloalkanones. *Synthesis* **2011**, *12*, 1930−1935. (f) Ku-

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916

nyane, P.; Sonopo, M. S.; Selepe, M. A. Synthesis of Isoflavones by Tandem Demethylation and Ring-Opening/Cyclization of Methoxybenzoylbenzofurans. *J. Nat. Prod.* **2019**, *82* (11), 3074−3082. (g) Borah, A.; Goswami, L.; Neog, K.; Gogoi, P. DMF Dimethyl Acetal as Carbon Source for α-Methylation of Ketones: A Hydrogenation−Hydrogenolysis Strategy of Enaminones. *J. Org. Chem.* **2015**, *80* (9), 4722−4728.

(27) (a) Huang, C.; Feng, J.; Ma, R.; Fang, S.; Lu, T.; Tang, W.; Du, D.; Gao, J. Redox-Neutral Borylation of Aryl Sulfonium Salts via C−S Activation Enabled by Light. *Org. Lett.* **2019**, *21* (23), 9688−9692. (b) Yanagi, T.; Somerville, R. J.; Nogi, K.; Martin, R.; Yorimitsu, H. Ni-Catalyzed Carboxylation of $C(sp^2)$−S Bonds with CO_2: Evidence for the Multifaceted Role of Zn. *ACS Catal.* **2020**, *10* (3), 2117−2123. (c) Uno, D.; Minami, H.; Otsuka, S.; Nogi, K.; Yorimitsu, H. Palladium-Catalyzed Mizoroki−Heck-Type Alkenylation of Monoaryldialkylsulfoniums. *Chem. - Asian J.* **2018**, *13* (17), 2397−2400.

(28) (a) Tian, Z.-Y.; Wang, S.-M.; Jia, S.-J.; Song, H.-X.; Zhang, C.-P. Sonogashira Reaction Using Arylsulfonium Salts as Cross-Coupling Partners. *Org. Lett.* **2017**, *19* (19), 5454−5457. (b) Ming, X.-X.; Tian, Z.-Y.; Zhang, C.-P. Base-Mediated O-Arylation of Alcohols and Phenols by Triarylsulfonium Triflates. *Chem. - Asian J.* **2019**, *14* (19), 3370−3379. (c) Tian, Z.-Y.; Ming, X.-X.; Teng, H.-B.; Hu, Y.-T.; Zhang, C.-P. Transition-Metal-Free N-Arylation of Amines by Triarylsulfonium Triflates. *Chem. - Eur. J.* **2018**, *24* (18), 13744−13748. (d) Imazeki, S.; Sumino, M.; Fukasawa, K.; Ishihara, M.; Akiyama, T. Facile Method for the Preparation of Triarylsulfonium Bromides Using Grignard Reagents and Chlorotrimethylsilane as an Activator. *Synthesis* **2004**, *10*, 1648−1654.

https://dx.doi.org/10.1021/acs.joc.0c02294
J. Org. Chem. 2021, 86, 4896−4916