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tert-Butyl Nitrite-Mediated Synthesis of *N*-Nitrosoamides, Carboxylic Acids, Benzocoumarins, and Isocoumarins from Amides

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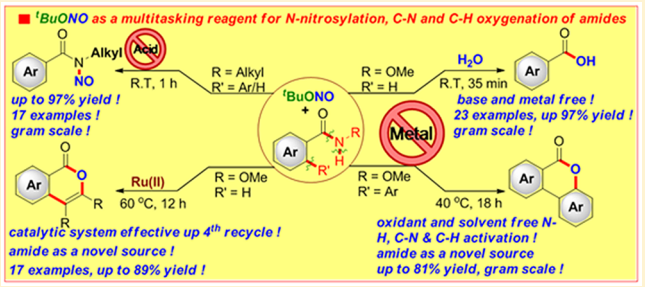
Supporting Information

ABSTRACT: This work reports *tert*-butyl nitrite (TBN) as a multitask reagent for (1) the controlled synthesis of *N*-nitrosoamide from *N*-alkyl amides, (2) hydrolysis of *N*-methoxyamides to carboxylic acids, (3) metal- and oxidant-free benzocoumarin synthesis from *ortho*-aryl-*N*-methoxyamides via N−H, C−N, and C−H bond activation, and (4) isocoumarin synthesis using Ru(II)/PEG as a recyclable catalytic system via *ortho*-C−H activation and TBN as an oxygen source. The sequential functional group interconversion of amide to acid has also been examined using IR spectroscopic analysis. Additionally, this methodology is highly advantageous due to short reaction time, gram scale synthesis, and broad substrate scope.



INTRODUCTION

Amide is an ubiquitous and key backbone in natural peptides and biologically active molecules.[1] Its prevalence in nature is due to its stability, which in turn is due to the presence of the stable C−N bond.[2] This is attributed to the fact that there is an overlap between the lone pair of electrons on nitrogen with the carbonyl π orbital (barrier to N−C resonance of 15−20 kcal/mol).[3] As a result, the partial double bond character $^{+}N{=}C{-}O^{-}$ arises in the amide bond due to resonance, which decreases the electrophilicity of the amide carbonyl group.[4] Classically, in acidic media, the protonation of carbonyl amide is followed by nucleophilic addition to the carbonyl carbon, thus resulting in its hydrolysis.[5] A similar sequence of events take place in transamidation[6] and the Friedel−Crafts acylation reaction.[7] While in basic media or in the presence of organometallic reagents, the direct nucleophilic addition to carbonyl amide results in the synthesis of an acid/ketone.[8] Moreover, an enzyme/DNA catalytic system is also useful for hydrolysis of amide but requires a longer reaction time.[9] To explore the chemistry of amides, contemporary research involves metal-catalyzed functionalization of the amide C−N bond.[10] Independently, Garg,[11] Zou,[12] Szostak,[13] and Zeng[14] have contributed in metal-catalyzed cleavage of sterically hindered tertiary amide C−N bonds for various organic transformations [Scheme 1, A(a)]. However, a few reports are available on metal-catalyzed cleavage of secondary amides (transamidation)[15] due to the formation of thermodynamically stable metallacycle which makes the cleavage of the C−N bond difficult [Scheme 1, A(b)].[16] Importantly, in the absence of a metal catalyst, secondary amides undergo N-nitrosylation followed by rearrangement via cleavage of the C−N bond.[17] The nitrosylation of secondary amides using different nitrosyl sources such as sodium or potassium nitrite in acid,[18] silver nitrate,[19] nitrosyl chloride,[17] and nitrogen oxides (e.g., N_2O_3, N_2O_4, etc.)[20] have been well-documented. However, difficulty in handling, the presence of acidic medium, the formation of side products, utilization of multiple reagents, and a lack of step economy are some of the limitations of the protocols making use of these existing nitrosyl sources.

Recently, TBN has been used in nitrosylation of amines and urea,[21] diazotization,[22] and C-nitration reactions.[23] Moreover, TBN is inexpensive and commercially available, possesses good solvent solubility, and is also easy to handle. Advantageously, when used in organic reactions, it provides only *t*-BuOH as the nontoxic side product.[21−23]

In this perspective, we herein report the first important application of TBN for the *N*-nitrosylation of *N*-alkylamides, synthesis of carboxylic acids, benzocoumarins, and isocoumarins from *N*-alkoxyamides (Scheme 1B). These reactions proceed through one pot cleavage of N−H, C−N, and C−H bonds of amides.

RESULTS AND DISCUSSION

a. *N*-Nitrosoamide Synthesis from Alkyl Amides. *N*-Nitrosoamide is an important intermediate useful in various organic transformations.[24] Synthesis of *N*-nitrosoamides has been well-established and requires tedious reaction processes (Scheme 1, a).[17−20] However, the transformation of this intermediate has limitations due to the use of acidic medium and the generation of hazardous side products. Notably, use of organonitrites provide nitrosyl radical in neutral reaction conditions with only alcohol as the side product.[21−23] In view of the characteristic feature of organonitrites, we have initiated

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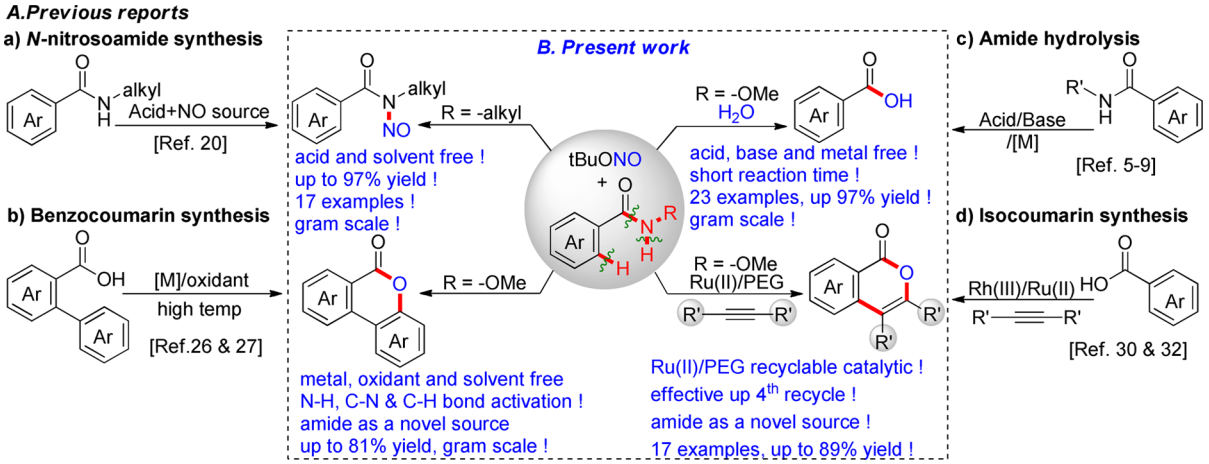
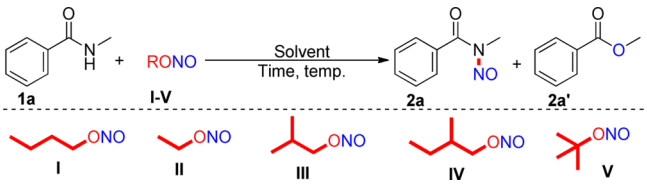
Scheme 1. Comparison of (A) Previous Approaches with (B) Present Work



the optimization of reaction conditions for *N*-nitrosylation of *N*-methyl benzamide **1a**, using *n*-butyl nitrite (**I**) as the nitrosyl source at 60 °C for 3 h.

A mixture of a trace amount of *N*-nitrosoamide **2a** and 96% methylbezoate **2a′** were observed (Table 1, entry 1). On minimizing the temperature, the yield of product **2a** increases while that of **2a′** decreases (Table 1, entries 2−3). Importantly, by decreasing the reaction time, the selectively toward *N*-nitrosoamide **2a** was increased and good yield of **2a** was observed within 1 h (Table 1, entries 4−5). Moreover, the reactivity of other alkyl nitrite isomers was also checked. The yield of **2a** produced on using ethyl nitrite (**II**), isobutyl nitrite (**III**), isopentyl nitrite (**IV**), and *t*-butyl nitrite (**V**) were 74%, 89%, 89%, and 93%, respectively (Table 1, entries 6−9). From the above observations, it was found that the reactivity of nitrites toward the *N*-nitrosylation of **1a** follows the order *tert*-butyl nitrite > isopentyl nitrite = isobutyl nitrite > *n*-butyl nitrite > ethyl nitrite. Subsequently, solvent studies revealed that nonpolar solvents were more effective than polar solvents (Table 1, entries 10−12). Delightfully, the reaction resulted in a 97% yield of **2a** when performed under a neat condition (Table 1, entry 13). Notably, under neat conditions, the solid amide converts into yellow-colored liquid *N*-nitrosoamide, which can be easily observed by the naked eye. With the optimized parameters in hand, we focused our attention on substrate scope for *N*-nitrosoamide synthesis (Table 2). *N*-Methylamides containing electron-donating groups at the -para and -meta positions provided the respective *N*-nitrosoamides (**2b−2g**) in 83% to 96% yields. Ortho-substituted amides regioselectively provided **2h** and **2i** in 84% and 82% yields after 1.25 h. Amides containing electron-withdrawing groups such as −Cl and −Br at the -meta and -para position afforded **2j−2l** in 85% to 89% yields. Significantly, a strong electron-withdrawing group like 4-nitroamide also provided a good yield of **2m** after 1.25 h. Next, *N*-benzylbenzamide provided 62% of *N*-nirosoamide product **2n**. However, aliphatic *N*-methylamide **1o**, benzamide **1p**, phenylbenzamide **1q**, and *N*-*tert*-butylbenzamide **1r** were inactve for nitrosylation. Interestingly, the external double bond containing *N*-methylcinnamamide **1s** provided yellow-colored crystalline *N*-methyl-*N*-nitrosocinnamamide **2s**, which was unambiguously confirmed by an X-ray crystallographic analysis (CCDC 1514778). Furthermore, the alkynyl and heteroaromatic groups containing *N*-methylamides reacted smoothly with TBN and provided 91% and 86% yields of *N*-nitrosoamides **2t** and **2u**, respectively. Additionally, the present reaction was scaled up to gram-scale yielding 83% (1.36 g) of **2a** and 89% (1.6 g) of **2s**.

Table 1. Optimization of Reaction Conditions[a]



entry	−NO reagent (equiv)	solvent	time (h)	temp (°C)	yield (%)[b] 2a	2a′
1	I	DCE	3	60	–	96
2	I	DCE	3	40	46	51
3	I	DCE	3	rt	83	trace
4	I	DCE	1	rt	87	–
5	I	DCE	0.5	rt	63	–
6	II	DCE	1	rt	74	–
7	III	DCE	1	rt	89	–
8	IV	DCE	1	rt	89	–
9	V	DCE	1	rt	93	–
10	V	DMF	1	rt	48	–
11	V	CH_2Cl_2	1	rt	93	–
12	V	*n*-hexane	1	rt	93	–
13	V	–	1	rt	97	–

[a]Reaction conditions: *N*-methylbenzamide **1a** (1 mmol), alkyl nitrite **I−V** (1.5 mmol), and solvent (3 mL). Isolated yield; rt = room temperature (29 °C).

b. Carboxylic Acid Synthesis from *N*-Alkoxyamides. After the successful synthesis of *N*-nitrosoamide using organo-nitrite, this protocol was further extended for the synthesis of carboxylic acids by the hydrolysis of *N*-alkoxyamides. Generally, the classical hydrolysis of amides using stoichiometric amount of acid/base as well as catalytic amount of enzyme/DNA has been documented (Scheme 1, b).[5,8a,b,9] However, the aforementioned protocols require harsh reaction conditions and long reaction times, which suggests the use of TBN for the reaction. To overcome this drawback and extend the scope of TBN, we selected alkoxyamide as a model substrate and water as a solvent. Interestingly, 97% yield of benzoic acid **4a** was

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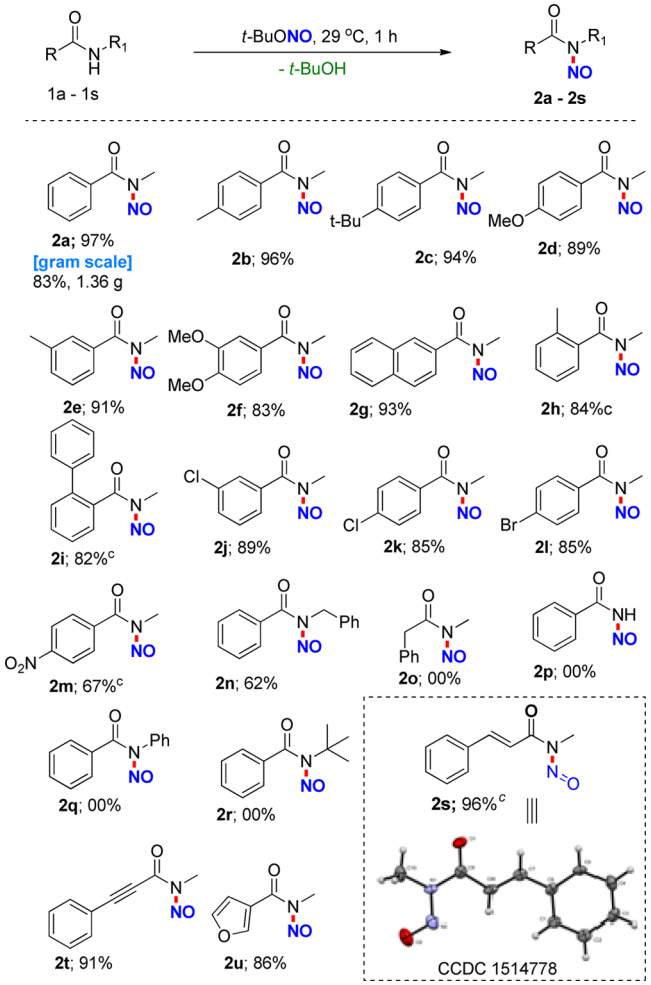
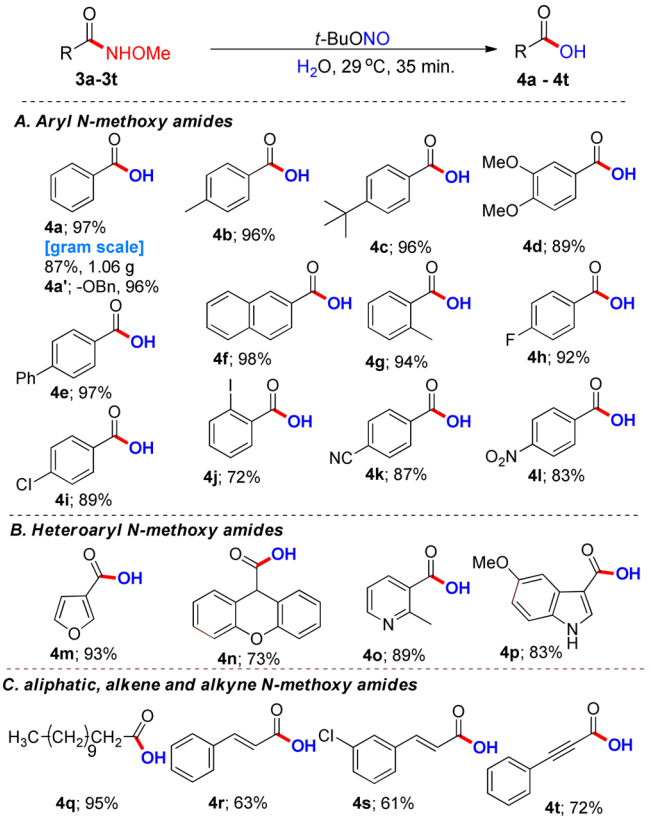
Table 2. Substrate Scope of *N*-Nitrosoamide Synthesis[a]



[a]Reaction conditions: amide **1a**−**1u** (1 mmol) and *t*-BuONO (1.5 mmol) were stirred at room temperature. Within the graphic: isolated yields. [b]1.25 h. [c]20 min.

Table 3. Substrate Scope of Carboxylic Acid Synthesis via Cleavage of Amide C−N Bond[a]



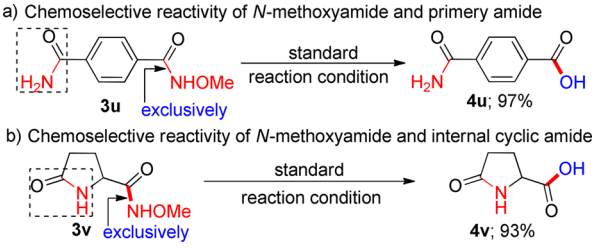
[a]Reaction conditions: amide **3a**−**3t** (1 mmol), *t*-BuONO (1.5 mmol), H_2O (3 mL), room temperature (29 °C), 35 min. Isolated yield.

observed within 35 min. The acid formation from amide was easily observed by the formation of a white-colored solid on the surface of water with the simultaneous liberation of nitrogen. With optimal reaction conditions in hand, we explored the substrate scope for acid synthesis from respective *N*-alkoxyamides (Table 3). Various *N*-methoxyamides such as aromatic, heteroaromatic, as well as aliphatic amides were well-tolerated and provided the respective carboxylic acids in excellent yields. The *N*-benzyloxyamide reacted smoothly affording 96% yield of **4a′**. Notably, **3a** could be transformed into **4a** even at the gram scale, resulting in 87% yield of the corresponding benzoic acid. The effect of electron-donating and -withdrawing groups on the aromatic ring was studied using *N*-methoxy aromatic amide. The amides containing electron-donating groups such as −Me, −OMe, *tert*-butyl, and −Ph on the phenyl ring also provided the carboxylic acids **4b**−**4g** in 89% to 98% yields.

Significantly, the present protocol is easily tolerated with an electron-withdrawing substituent like −F, −Cl, −I, −CN, and $-NO_2$ on *N*-methoxybenzamide, and the carboxylic acids **4h**−**4l** were obtained in 72% to 92% yields, respectively. This method is also useful for the conversion of heteroaromatic *N*-methoxyamides to the respective acids **4m**−**4p**. Moreover, hydrolysis of aliphatic, alkenyl, and alkynyl *N*-methoxyamides, **3q3t**, could also be satisfactorily carried out.

To investigate the chemoselectivity of amides with TBN, we employed the substrate **3u** containing a primary as well as *N*-methoxyamide and substrate **3v** containing both an internal secondary amide and *N*-methoxyamide. In both cases, the selective hydrolysis of *N*-methoxyamide was observed, while the primary and internal secondary amides were stable toward hydrolysis (Scheme 2).

Scheme 2. TBN for Chemoselective Hydrolysis of Amides



For better understanding, the selective reactivity of amides with TBN at room temperature for the synthesis of *N*-nitrosoamide/acid has been classified into three groups (Scheme 3). The amides in group 1 containing electron-rich *N*-substituents show low reactivity. Group 2 contains moderately reactive amides in which *N*-methylamides exclusively undergo nitrosylation and *N*-benzylamides undergo nitrosylation and were further transformed into carboxylic

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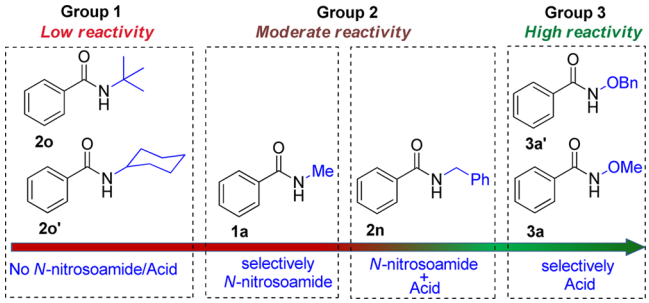
Scheme 3. Classification of Amides Based on Reactivity with *t*-BuONO for the Nitrosylation and Hydrolysis Reactions



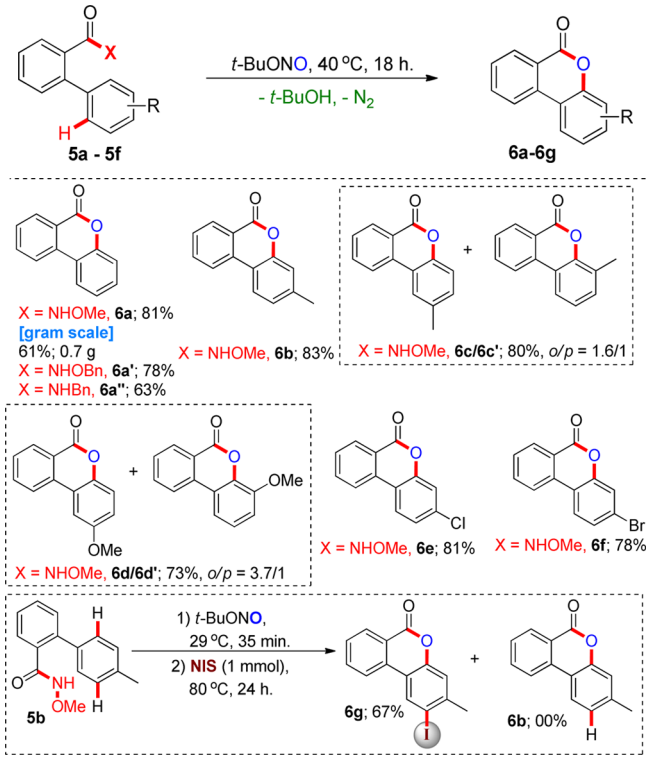
acids. The amides present in group 3 show high reactivity toward the hydrolysis reaction as compared to other groups.

From these observations, we concluded that the TBN reactivity increases with decreasing electron deficiency on the nitrogen of the amides.

C. Benzocoumarin Synthesis from *ortho*-Aryl-*N*-methoxybenzamide. Inspired by the results obtained with TBN in the case of nitrosylation and hydrolysis of amides, we further extended this protocol for the synthesis of benzocoumarin. Benzocoumarin and their derivatives are important scaffolds found in natural products and pharmaceuticals due to their remarkable biological activity.[25] Consequently, extensive efforts have been developed for their synthesis. Benzocoumarin can be synthesized from *ortho*-aryl benzoic acid using metal catalyst[26] or under metal-free conditions[27] using a stoichiometric amount of oxidizing agents (Scheme 1, c). On the basis of the above one-pot conversion of *N*-methoxyamide to a carboxylic acid, we tested *ortho*-aryl-*N*-methoxybenzamide **5a** as a new substrate for the benzocoumarin synthesis. Guided by prior reports,[26,27] $(NH_4)_2S_2O_8$, Ag_2O, $Cu(OAc)_2$, benzo quinone, and *N*-iodosuccinimide (NIS) oxidants were screened in DCE at 60 °C for 18 h. Remarkably, even in the absence of oxidant and solvent, 76% yield of **6a** was observed. Assuming the radical reaction pathway, on decreasing the reaction temperature, 81% (GC yield) yield of product **6a** was observed at 40 °C. However, decreasing the reaction temperature below 40 °C and time less than 18 h, the yield of product decreased.

Thus, the optimized reaction conditions for benzocoumarin synthesis was **5a** (1 mmol), *t*-BuONO (1.5 mmol), at 40 °C for 18 h. The optimized reaction conditions were subsequently applied for the synthesis of a variety of benzocoumarin from 2-phenyl-*N*-methoxybenzamide derivatives (Table 4). It was found that a variety of 2-phenyl-*N*-methoxybenzamides could be converted to the desired product in good yields. The model reaction having *N*-methoxy, *N*-benzyloxy, and *N*-benzyl shows 81%, 78%, and 63% isolated yield of product **6a**, **6a**′, and **6a**″, respectively. The present reaction could also tolerate electron-donating groups. *Para*-CH_3 containing amide **5b** provided the 83% yield of **6b**. However, the meta-substituted amides **5c** and **5d** gave a good yield with two regioisomers in ratios of **6c**/**6c**′ 1.6:1 and **6d**/**6d**′ 3.7:1, respectively. Furthermore, the reaction tolerates electron-withdrawing groups like −Cl and −Br, resulting in the synthesis of **6e** and **6f** in 81% and 78% yields, respectively. To check the reactivity, amide **5b** was stirred with the addition of 1 mmol of *N*-iodosuccinimide at 80 °C for 24 h. Surprisingly, 2-iodo-3-methyl benzocoumarin **6g** was observed instead of 3-methyl benzocoumarin **6b**. Notably, **6g** is an important iodo derivative useful for coupling reactions.

Table 4. Substrate Scope of Benzocoumarin Synthesis[a]



[a]Reaction conditions: amide (**5a**−**5f**, 1 mmol), *t*-BuONO (1.5 mmol), 40 °C, 18 h. Isolated yield.

d. Isocoumarin Synthesis from *N*-Methoxybezoamide. Isocoumarin as a structural motif has attracted attention of synthetic and medicinal chemists due to numerous biological activities.[28] Traditionally, multistep synthesis of isocoumarin has been well-reported.[29] Importantly, one pot synthesis of isocoumarin has been developed using a Rh(III)/Ru(II) catalytic system via ortho C−H activation of benzoic acid (Scheme 1, d).[30] Of late, PEG was used as a biodegradable solvent in organic transformations due to the recyclability of homogeneous transition metal catalytic system.[31] We have earlier reported the Ru(II)/PEG-400 catalytic system for the isocoumarin synthesis from benzoic acid.[32] Considering the importance of isocoumarins, herein we report *N*-methoxyamide as a novel surrogate for the isocoumarin synthesis using TBN as an oxygen source for the rapid cleavage of the amide C−N bond and the Ru(II)/PEG catalytic system for ortho-C−H bond activation. The model reaction of *N*-methoxybenzamide **3a**, TBN, and diphenylacetylene **7a** was chosen for lactonization in the presence of $[RuCl_2(p\text{-cymene})]_2$ (5 mol %), $Cu(OAc)_2$ (0.25 mmol), and $AgSbF_6$ (5 mol %).

The reaction proceeded with an 89% yield of **8aa** in DCE as the solvent. The catalyst loading plays a crucial role, whereby, decreasing the catalyst amount to less than 3 mol % resulted in a lower yield of **8aa**. Next, PEG-400 as a recyclable and green solvent was tested and up to 81% yield of **8aa** was observed. However, as compared to PEG-400, in the presence of PEG-600, the yield of **8aa** decreases. This might be due to the low solubility of the starting material in the latter. In the temperature study, it was observed that by increasing or decreasing the temperature above or below 60 °C, the yield of **8aa** also decreased. Whenever, the reaction time is less than 12 h, the yield of the product decreases. Thus, the final optimized

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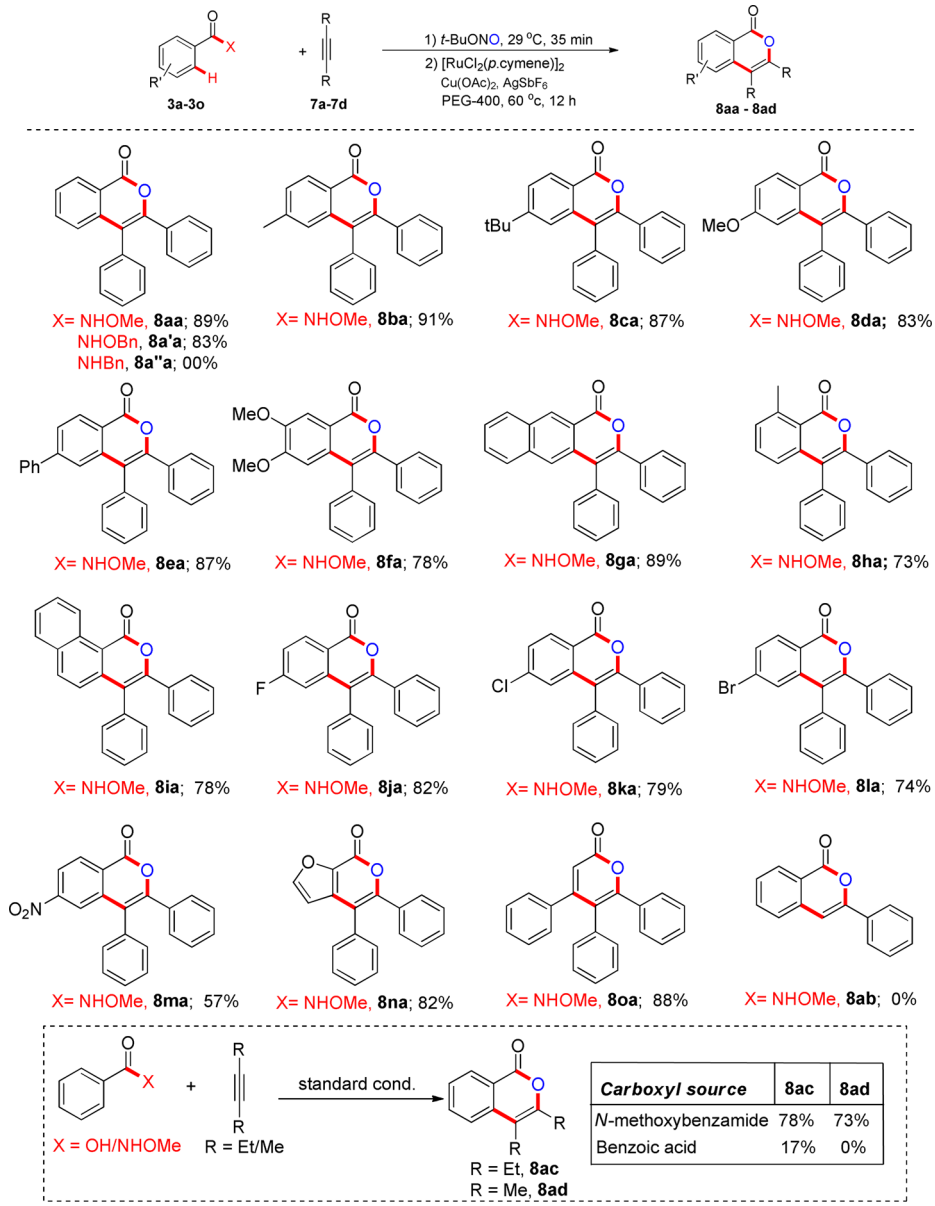
Table 5. Substrate Scope of the Ruthenium-Catalyzed Isocoumarin Synthesis[a]



Carboxyl source	8ac	8ad
N-methoxybenzamide	78%	73%
Benzoic acid	17%	0%

[a]Reaction conditions: *N*-methoxybenzamide **3a**−**3o** (0.5 mmol), *t*-BuONO (0.75 mmol), alkyne **7a**−**7d** (1 mmol), [{$RuCl_2$(*p*-cymene)}$_2$] (3 mol %), $Cu(OAc)_2$ (0.25 mmol), $AgSbF_6$ (5 mol %), PEG-400 (4 mL). Isolated yield.

reaction conditions for isocoumarin synthesis are **3a** (0.5 mmol), diphenylacetylene **7a** (1 mmol), *t*-BuONO (0.7 mmol) [{$RuCl_2$(*p*-cymene)}$_2$] (3 mol %), $Cu(OAc)_2$ (0.25 mmol), $AgSbF_6$ (10 mol %), and PEG-400 (4 mL) at 60 °C for 12 h and showed a 92% (GC yield) yield of **8aa**. With the optimal reaction conditions in hand, we further explored the detailed substrate scope for isocoumarin synthesis from *N*-methoxyaromatic amides with alkyne (Table 5). The model reaction having *N*-methoxy and *N*-benzyloxy shows 89% and 83% isolated yield of product **8aa** and **8a′a**, respectively. However, *N*-benzyl-containing amide was inactive for isocoumarin synthesis. The reaction tolerates a broad range of *N*-methoxybenzamide containing various electron-donating and -withdrawing groups. The electron-donating groups like −Me, −*tert*-butyl, −OMe, and −Ph at the para position of *N*-methoxybenzamide afforded the corresponding products, **8ba**−**8ea**, in 83% to 91% yields. The reaction proceeded regioselectively resulting in products **8fa**−**8ga** with exclusive coupling at the less hindered side. In addition, ortho-substituted aromatic amides such as *N*-methoxy-2-naphthamide and 2-methyl-*N*-methoxybenzamide were also tolerated, and the corresponding isocoumarins **8ha** and **8ia** were observed in 73% and 78% yield, respectively. Next, the halide-containing amides at the para position also provided good yields of **8ja**−**8la**. Notably, the strong electron-withdrawing group like $-NO_2$ could be tolerated and **8ma** was obtained in 57% yield. Moreover, the reactivity study of heteroarene was carried out, and *N*-methoxyfuran-2-carboxamide led to product **8na** in 82% yield. Next, the substrate containing the external double bond (methoxycinnamamide) was studied, and **8oa** was obtained in 88% yield. Unfortunately, terminal alkyne (phenylacetylene) was not effective for the present reaction, and **8ab** was not observed. After the substrate scope of *N*-methoxybenzamides, the comparative reactivity of benzoic acid and *N*-methox-

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ybenzamide was checked. The aliphatic internal alkynes, 3-hexyne and 2-butyne, reacted effectively in the case of *N*-methoxybenzamide and provided **8ac** and **8ad** in 78% and 73% yield, respectively. However, they reacted ineffectively when benzoic acid was used as the substrate. After the successful substrate study for isocoumarin synthesis, the recyclability study of Ru(II) homogeneous catalyst was carried out. It was observed that the catalytic system was effective up to the fourth recycle [92, 90, 89, and 89% (GC yield)].

To gain insight into the reaction mechanism, we analyzed the TBN-mediated functional group interconversion of amide to acid, using IR spectroscopy (Figure 1). The spectrum (a) and (b) denotes only TBN and *N*-methoxybenzamide, respectively. The spectrum (c) is the reaction mixture after 5 min and shows the disappearance of ~3216 cm^{-1} (amide N−H) and ~1646 cm^{-1} (amide C═O) of the amide. At the same time, a new band at ~1726 cm^{-1} was observed, which represents the formation of a *N*-nitrosoamide intermediate. After 15 min, the band at ~1726 cm^{-1} disappears and a new band at ~1761 cm^{-1} was observed, which represents the formation of a 1-(benzoyloxy)-2-methoxydiazene intermediate (spectrum d). After 25 min, the band ~1761 cm^{-1} disappears with the liberation of N_2 and a new band at ~1702 cm^{-1} was observed which corresponds to C═O of benzoic acid (spectrum e). Finally, after 35 min, the band at ~1761 cm^{-1} completely disappears and we observed an intense band at ~1702 cm^{-1} that confirmed the complete conversion into benzoic acid (spectrum f).

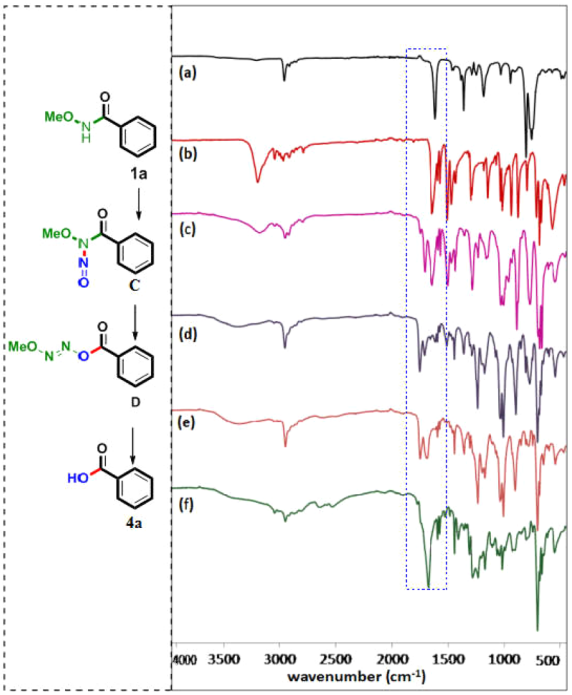
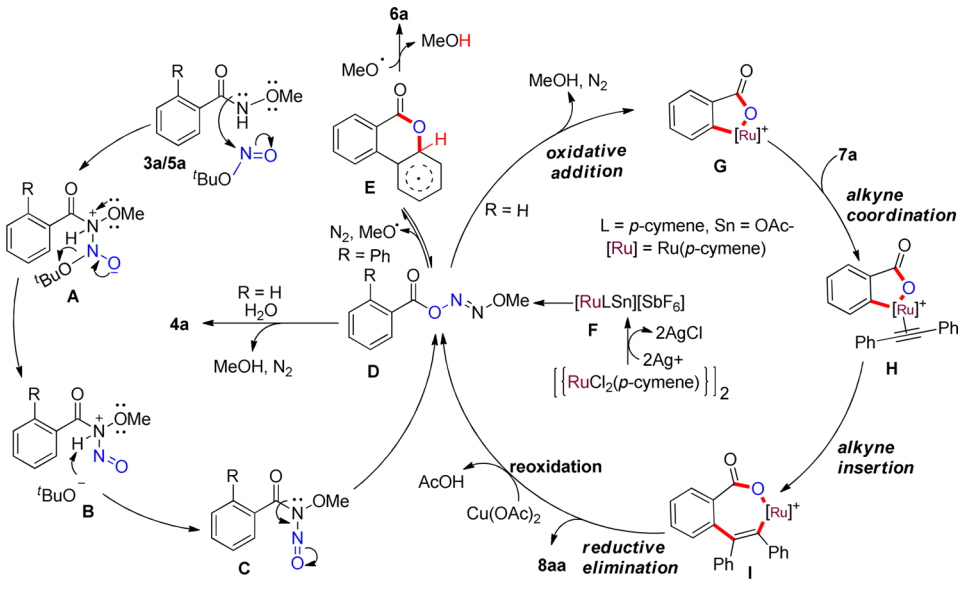


Figure 1. IR spectroscopic observations of TBN for sequential interconversions of amide to acid via the N-nitrosoamide intermediate.

A tentative reaction mechanism based on existing literature[23c,33] and control experiments has been proposed (Scheme 4). Initially, the nucleophilic addition of the amide N−H to electron-deficient nitrogen of TBN takes place to generate intermediate **A**. From the intermediate **A**, release of the $^tBuO^-$ ion results in the formation of intermediate **B**, which absorbs the proton form intermediate **C** and undergoes rearrangement to **D**.[17] **D** is highly air- and moisture-sensitive and undergoes rapid hydrolysis to furnish carboxylic acid **4a**. In the case of the presence of ortho-aryl functionality in **D**, it subsequently forms intermediate **E** through the expulsion of the N_2 radical and the OMe radical.[26a] The generated OMe radical thus abstracts H radical from intermediate **E** to affords **6a**.

In isocoumarin synthesis, the removal of the chloride ligand from the $[RuCl_2(p\text{-cymene})]_2$ complex by $AgSbF_6$ salt gives active ruthenium species **F**.[32] Then Ru(II) forms a complex with hexafluoroantimonate, which transforms into the five-membered ruthenacycle **G** by ortho-C−H bond activation of **D** with the release of MeOH and N_2 (oxidative addition). This is followed by coordination of the ruthenium with diphenylacetylene **7a** to form **H** and subsequent alkyne insertion, which generates the seven-membered intermediate **I**. The reductive elimination of **I** gives the annulated product **8aa**. The Ru^0

Scheme 4. Plausible Reaction Mechanism



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species at the final step is oxidized by Cu(II) to regenerate the active Ru(II) species for the next catalytic cycle.[32]

In conclusion, we have applied TBN as a multitask reagent for sequential nitrosylation reactions for (i) the synthesis of *N*-nitrosoamide from *N*-alkyl amide under solvent-free conditions at room temperature, (ii) the synthesis of carboxylic acids from amides under acid/base/metal/oxidant free condition with short reaction time and water as a green solvent, (iii) the synthesis of benzocoumarin from *ortho*-aryl-*N*-methoxybenzamide under metal/oxidant/solvent-free conditions, and (iv) one-pot synthesis of isocoumarin from the *N*-methoxyaromatic amide using Ru(II)/PEG-400 as a recyclable catalytic system. Significantly, the protocols described herein could tolerate a wide substrate scope and could be carried out at the gram scale. Importantly, the developed protocol is environmentally benign due to the formation of *t*-BuOH, MeOH, and N_2 as nonhazardous side products.

EXPERIMENTAL SECTION

All the nitrite sources, solvents, oxidants, $[RuCl_2(p\text{-cymene})]_2$, $Cu(OAc)_2$, and $AgSbF_6$ were purchased from commercial sources. All reactions were carried out in oven-dried glassware. All amide derivatives were prepared by literature procedures.[1] Analytical TLC was performed with silica gel plates (0.25 mm thickness). Column chromatography was performed with silica gel (40−200 mesh). NMR spectra were recorded with 400 or 300 MHz ^{1}H NMR and 126 or 101 or 76 MHz ^{13}C NMR spectrometer. The chemical shifts are reported in parts per million relative to tetramethylsilane as an internal standard and the coupling constant *J* in hertz. The reaction was monitored by GC and TLC. The products were analyzed by GC-MS and IR. HRMS was recorded on a micromass ESI TOF (time-of-flight) mass spectrometer.

Experimental Procedure for *N*-Nitrosoamide Synthesis. In an oven-dried 10 mL reaction tube equipped with a magnetic stir-bar, *N*-methylbenzamide **1a** (1 mmol, 135 mg) and *tert*-butyl nitrite (1.5 mmol, 155 mg) were added by syringe. The reaction mixture was stirred at 29 °C (room temperature) for 1 h. After completion of the reaction, all volatiles were removed under vacuum. The yellow oil *N*-nitrosoamide product **2a** was purified by column chromatography (silica gel, 40−200 mesh) and confirmed by NMR. In gram scale synthesis, the *N*-methylbenzamide **1a** (10 mmol, 1.35 g) and *tert*-butyl nitrite (1.5 mmol, 1.55 g) were added by syringe in oven-dried 100 mL round-bottom flask. The reaction mixture was stirred at 29 °C (room temperature) for 1.25 h. After completion of the reaction, all volatiles were removed under vacuum. The 1.36 g (83%) of the yellow, oily *N*-nitrosoamide product **2a** was observed.

Experimental Procedure for Acid Synthesis. In an oven-dried 10 mL reaction tube equipped with a magnetic stir-bar, *N*-methoxybenzamide **3a** (1 mmol, 151 mg) and *tert*-butyl nitrite (1.5 mmol, 155 mg) were added by syringe in 3 mL of water. The reaction mixture was stirred at 29 °C (room temperature) for 35 min. The colorless solid benzoic acid product **4a** was purified by column chromatography (silica gel, 40−200 mesh). In gram scale carboxylic acid synthesis, the *N*-methoxybenzamide **3a** (10 mmol, 1.35 g) and *tert*-butyl nitrite (1.5 mmol, 1.55 g) were added dropwise into a 100 mL round-bottom flask at the cool condition. The reaction mixture was stirred at 29 °C (room temperature) for 45 min. After completion of the reaction, all volatiles were removed under vacuum. The 1.06 g (87%) of benzoic acid product **4a** was observed.

Experimental Procedure for Benzocoumarin Synthesis. In an oven-dried 10 mL reaction tube equipped with a magnetic stir-bar, 2-phenyl, *N*-methoxybenzamide **5a** (1 mmol, 227 mg), and *tert*-butyl nitrite (1.5 mmol, 155 mg) was added by syringe. The reaction mixture was stirred at 40 °C for 18 h. After completion of the reaction, all the volatiles were removed under vacuum. The colorless solid benzocoumarin product **6a** was purified by column chromatography (silica gel, 40−200 mesh). In gram scale benzocoumarin synthesis, the 2-phenyl-*N*-methoxybenzamide **5a** (6 mmol, 1.36 g) and *tert*-butyl nitrite (9 mmol, 0.93 g) were added dropwise in a 100 mL round-bottom flask at the cool condition for 1 h. Next, reaction was stirred to 29 °C (room temperature) for 18 h. After completion of the reaction, all the volatiles were removed under vacuum. The 0.7 g (61%) of benzocoumarin product **6a** was observed.

Experimental Procedure for Ru(II)/PEG-400-Catalyzed Isocoumarin Synthesis and Catalyst Recyclability. In a 15 mL Schlenk tube, *N*-methoxybenzamide **3a** (0.50 mmol, 76 mg) and *tert*-butyl nitrite (0.8 mmol, 78 mg) were added by syringe. The reaction mixture was stirred at 29 °C (room temperature) for 35 min, followed by addition of diphenylacetylene **7a** (1 mmol, 178 mg), $[RuCl_2(p\text{-cymene})]_2$ (3 mol %, 18 mg), $Cu(OAc)_2$ (0.25 mmol, 45 mg), and $AgSbF_6$ (5 mmol, 17 mg). To the same mixture, 4 mL PEG-400 was added and the reaction mixture was stirred at 60 °C for 12 h. After completion of the reaction, the reaction mixture was cooled to room temperature. Next, 7−8 mL of diethyl ether was added in the same Schlenk tube and was shaken for 2−3 min. The upper layer containing product mixture was transferred to 150 mL round-bottom flask and the process was repeated for 3−4 times. All volatiles were removed from the product mixture under vacuum. The colorless solid isocoumarin product **8aa** was purified by column chromatography (silica gel, 40−200 mesh). In the recyclability study, the lower layer of PEG-400-containing catalytic system was heated at 40−50 °C for 10 min to remove the miscible diethyl ether and transferred back to the Schlenk tube containing a stirred mixture of *N*-methoxybenzamideand *tert*-butyl nitrite for the next cycle.

*N-Methyl-N-nitrosobenzamide (**2a**).*[20a] Yellow oil. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 97% (159 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 3.25 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 172.8, 132.7, 132.5, 130.7, 128.1, 26.8. **IR (ATR)** ν (cm^{-1}): 1704, 1495, 1342, 961.

***N*,4-Dimethyl-*N*-nitrosobenzamide (2b).**[19] Yellow oil. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 96% (167 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 3.24 (s, 3H), 2.38 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 172.5, 143.4, 130.9, 129.8, 128.8, 26.8, 21.5. **IR (ATR)** ν (cm^{-1}): 1698, 1497, 1339, 1160, 959.

*4-(tert-Butyl)-N-methyl-N-nitrosobenzamide (**2c**).* Yellow oil. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 94% (206 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 3.25 (s, 3H), 1.32 (s, 9H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$) δ 172.4, 156.2, 130.9, 129.8, 125.1, 35.0, 31.0, 26.8. **IR (ATR)** ν (cm^{-1}): 1701, 1497, 1335, 1167, 960, 804. **HRMS** (ESITOF) *m*/*z*: $[M + Na]^+$ calcd for $C_{12}H_{16}N_2O_2Na$, 243.1103; found, 243.1104.

*4-Methoxy-N-methyl-N-nitrosobenzamide (**2d**).*[19] Yellow oil. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 89% (172 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.74 (d, *J* = 8.3 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 3.80 (s, 3H), 3.22 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 171.5, 163.2, 133.4, 124.6, 113.5, 55.4, 27.0. **IR (ATR)** ν (cm^{-1}): 1688, 1497, 1255, 1159, 1020, 958.

*N,3-Dimethyl-N-nitrosobenzamide (**2e**).* Yellow oil. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 91% (161 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.56−7.51 (m, 2H), 7.37−7.30 (m, 2H), 3.26 (s, 3H), 2.38 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 173.0, 138.0, 133.3, 132.7, 131.1, 128, 127.9, 26.8, 21.2. **IR (ATR)** ν (cm^{-1}): 1700, 1503, 1342, 1163, 970, 727. **HRMS** (ESITOF) *m*/*z*: $[M + Na]^+$ calcd for $C_9H_{10}N_2O_2Na$, 201.0634; found, 201.0634.

*3,4-Dimethoxy-N-methyl-N-nitrosobenzamide (**2f**).* Yellow oil. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: 83% (185 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.37−7.34 (m, 2H), 6.86 (d, *J* = 8.3 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 3H), 3.27−3.15 (m, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 171.5, 152.9, 148.5, 125.8, 124.6, 113.5, 109.9, 55.98, 55.9, 27.1. **IR (ATR)** ν (cm^{-1}): 1695, 1597, 1493, 1341, 1243, 1132,

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988, 746. **HRMS** (ESITOF) m/z: [M + Na]$^+$ calcd for $C_{10}H_{12}N_2O_4Na$, 247.0690; found, 247.0689.

*N-Methyl-N-nitroso-2-naphthamide (**2g**).* Yellow oil. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 93% (199 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.31 (s, 1H), 7.85 (dt, J = 19.1, 7.6 Hz, 4H), 7.54 (dt, J = 14.8, 7.2 Hz, 2H), 3.34 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 172.8, 135.0, 132.5, 132.1, 129.9, 129.3, 128.5, 127.9, 127.7, 126.9, 126.3, 27.0. **IR (ATR)**ν (cm^{-1}): 1704, 1479, 1335, 1155, 1002, 921, 781, 754. **HRMS** (ESITOF) m/z: [M + Na]$^+$ calcd for $C_{12}H_{10}N_2O_2Na$, 237.0654; found, 237.0634.

*N,2-Dimethyl-N-nitrosobenzamide (**2h**).* Yellow oil. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 84% (149 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.35 (d, J = 8.2 Hz, 2H), 7.29−7.18 (m, 2H), 3.25 (s, 3H), 2.29 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 174.5, 136.1, 133.9, 130.6, 130.6, 128.4, 125.4, 26.0, 19.7. **IR (ATR)**ν (cm^{-1}): 1707, 1502, 1340, 1167, 956, 735. **HRMS** (ESITOF) m/z: [M + Na]$^+$ calcd for $C_9H_{10}N_2O_2Na$, 201.0632; found, 201.0634.

*N-Methyl-N-nitroso-[1,1′-biphenyl]-2-carboxamide (**2i**).* Yellow oil. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 82% (196 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.64 (d, J = 7.5 Hz, 1H), 7.59−7.52 (m, 1H), 7.45 (dd, J = 13.1, 7.5 Hz, 2H), 7.36−7.20 (m, 5H), 2.91 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 175.1, 141.3, 140.1, 133.8, 131.0, 129.6, 128.7, 128.5, 128.2, 127.7, 127.3, 25.7. **IR (ATR)**ν (cm^{-1}): 1707, 1504, 1344, 1167, 962, 742. **HRMS** (ESITOF) m/z: [M + Na]$^+$ calcd for $C_{14}H_{12}N_2O_2Na$, 263.0792; found, 263.0791.

*N,4-Dimethyl-N-nitrosobenzamide (**2j**).* Yellow oil. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 85% (168 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.51 (dd, J = 8.0, 1.0 Hz, 1H), 7.38 (t, J = 7.9 Hz, 1H), 3.26 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 171.6, 134.3, 134.2, 132.4, 130.5, 129.4, 128.7, 26.8. **IR (ATR)**ν (cm^{-1}): 1701, 1496, 1340, 1144, 971, 777, 734. **HRMS** (ESITOF) m/z: [M + Na]$^+$ calcd for $C_8H_7ClN_2O_2Na$, 221.0091; found, 221.0088.

*4-Chloro-N-methyl-N-nitrosobenzamide (**2k**).*[19] Yellow oil. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 89% (176 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.78−7.57 (m, 2H), 7.54−7.22 (m, 2H), 3.24 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 171.7, 138.9, 132.2, 130.9, 128.5, 26.8. **IR (ATR)**ν (cm^{-1}): 1708, 1588, 1488, 1397, 1342, 1164, 963, 804.

*4-Bromo-N-methyl-N-nitrosobenzamide (**2l**).* Yellow solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 85% (206 mg). Mp: 86−88 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.65−7.58 (m, 2H), 7.58−7.47 (m, 2H), 3.23 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 171.8, 132.2, 131.4, 131.1, 127.5, 26.8. **IR (ATR)**ν (cm^{-1}): 1708, 1582, 1497, 1394, 1160, 1069, 946. **HRMS** (ESITOF) m/z: [M + Na]$^+$ calcd for $C_8H_7BrN_2O_2Na$, 264.9579; found, 264.9583.

*N-Methyl-4-nitro-N-nitrosobenzamide (**2m**).*[19] Yellow solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: 67% (140 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.40−8.20 (m, 2H), 7.89 (d, J = 8.4 Hz, 2H), 3.34−3.25 (m, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 171.4, 149.7, 138.4, 131.4, 123.3, 26.7. **IR (ATR)**ν (cm^{-1}): 1711, 1514, 1488, 1346, 1167, 960.

*N-Benzyl-N-nitrosobenzamide (**2n**).*[19] Yellow oil. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 62% (148 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.82−7.75 (m, 2H), 7.57 (dd, J = 10.7, 4.1 Hz, 1H), 7.47 (t, J = 7.5 Hz, 2H), 7.36−7.24 (m, 5H), 5.13 (s, 2H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 172.9, 134.6, 132.9, 132.6, 130.7, 128.7, 128.5, 128.2, 127.9, 42.9. **IR (ATR)**ν (cm^{-1}): 1698, 1497, 1346, 1159, 951, 800.

*N-Methyl-N-nitrosocinnamamide (**2s**).* Yellow solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 96% (182 mg). Mp = 100−102 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97 (d, J = 15.8 Hz, 1H), 7.80 (d, J = 15.8 Hz, 1H), 7.63−7.55 (m, 2H), 7.38 (d, J = 4.7 Hz, 3H), 3.17 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 168.5, 147.2, 134.3, 130.9, 128.9, 128.6, 115.5, 25.8. **IR (ATR)**ν (cm^{-1}): 1695, 1624, 1475, 1206, 1023, 956. **HRMS** (ESITOF) m/z: [M + H]$^+$ calcd for $C_{10}H_{12}N_2O_2$, 191.0742; found, 191.0813.

*N-Methyl-N-nitroso-3-phenylpropiolamide (**2t**).* Yellow oil. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 91% (171 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.73−7.67 (m, 2H), 7.42−7.31 (m, 3H), 3.13 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 166.0, 147.8, 136.9, 133.1, 131.1, 128.7, 127.4, 118.3, 114.5, 25.6. **IR (ATR)**ν (cm^{-1}): 1702, 1490, 1027. **HRMS** (ESITOF) m/z: [M + Na]$^+$ calcd for $C_{10}H_8N_2NaO_2$, 211.0477; found, 211.0478.

*N-Methyl-N-nitrosofuran-3-carboxamide (**2u**).* Yellow oil. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 86% (132 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.46 (t, J = 1.5 Hz, 1H), 7.02−6.94 (m, 1H), 3.24 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 165.38, 149.76, 143.12, 119.49, 111.70, 26.39. **IR (ATR)**ν (cm^{-1}): 1704, 1408, 1163, 956, 802. **HRMS** (ESITOF) m/z: [M + H]$^+$ calcd for $C_6H_7N_2O_3$, 155.0448; found, 155.0451.

*Benzoic Acid (**4a**).*[34a] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 97% (118 mg). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 13.09 (s, 1H), 8.19 (d, J = 7.7 Hz, 2H), 7.66 (t, J = 7.3 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H). **^{13}C{^{1}H}NMR** (75 MHz, $CDCl_3$): δ 172.8, 133.9, 130.3, 129.4, 128.5. **GC-MS** (EI, 70 eV) m/z (%): 122.00 (99.86), 105.00 (100), 77.00 (59.51), 51.00 (21.23). **IR (ATR)**ν (cm^{-1}): 1680, 1449, 1323, 1288, 704.

*4-Methylbenzoic Acid (**4b**).*[34a] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 96% (130 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 12.42 (s, 1H), 8.05 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 2.46 (s, 3H). **^{13}C{^{1}H}NMR** (75 MHz, $CDCl_3$): δ 172.5, 144.7, 130.3, 129.2, 126.6, 21.7. **GC-MS** (EI, 70 eV) m/z (%): 136.00 (92.22), 118.00 (100), 91.05 (69.44), 65.00 (19.18). **IR (ATR)**ν (cm^{-1}): 1672, 1404, 1269, 904, 733.

*4-(tert-Butyl)benzoic Acid (**4c**).*[34b] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 96% (170 mg). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 12.27 (s, 1H), 8.10 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 8.6 Hz, 2H), 1.39 (s, 9H). **^{13}C{^{1}H}NMR** (75 MHz, $CDCl_3$): δ 172.6, 157.6, 130.2, 126.6, 125.4, 35.2, 31.1. **GC-MS** (EI, 70 eV) m/z (%): 177.95 (20.42), 163.00 (100), 135.00 (35.34), 115.00 (5.89), 91.00 (24.55), 77.00 (7.42). **IR (ATR)**ν (cm^{-1}): 1679, 1419, 1285, 933, 706.

*3,4-Dimethoxybenzoic Acid (**4d**).*[34a] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: 89% (161 mg). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 11.50 (s, 1H), 7.80 (dd, J = 8.4, 2.0 Hz, 1H), 7.61 (d, J = 1.9 Hz, 1H), 6.93 (d, J = 8.5 Hz, 1H), 3.97 (d, J = 1.9 Hz, 6H). **^{13}C{^{1}H}NMR** (75 MHz, $CDCl_3$): δ 172.1, 153.8, 148.9, 124.6, 121.7, 112.3, 110.3, 56.1, 56.0. **GC-MS** (EI, 70 eV) m/z (%): 182.00 (100), 166.95 (35.87), 111.00 (20.02), 95.00 (16.19), 77.00 (19.14). **IR (ATR)**ν (cm^{-1}): 1669, 1586, 1420, 1234, 758.

*[1,1′-Biphenyl]-4-carboxylic Acid (**4e**).*[34b] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 97% (192 mg). **^{1}H NMR** (300 MHz, DMSO): δ 8.08−7.96 (m, 2H), 7.63−7.51 (m, 4H), 7.44−7.26 (m, 3H). **^{13}C{^{1}H}NMR** (75 MHz, DMSO): δ 168.1, 145.1, 139.9, 130.3, 129.8, 128.9, 128.1, 127.2, 126.9. **GC-MS** (EI, 70 eV) m/z (%): 197.90 (98.48), 181.95 (43.54), 166.90 (56.18), 153.00 (46.96), 121.00 (43.57), 65.00 (100). **IR (ATR)**ν (cm^{-1}): 1672, 1420, 1286, 932, 746.

*2-Naphthoic Acid (**4f**).*[34b] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 98% (168 mg). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.76 (s, 1H), 8.16 (dd, J = 8.6, 1.4 Hz, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.94 (dd, J = 8.1, 5.3 Hz, 2H), 7.63 (dt, J = 15.6, 6.8 Hz, 2H). **^{13}C{^{1}H}NMR** (75 MHz, $CDCl_3$): δ 172.2, 135.9, 132.5, 132.2, 129.6, 128.7, 128.3, 127.8, 126.8, 126.6, 125.4. **GCMS** (EI, 70 eV) m/z (%):

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172.00 (77.62), 155.05 (67.47), 127.05 (100), 102.05 (20.71), 63.00 (57.98). **IR (ATR)**ν (cm^{-1}): 1682, 1299, 777, 758.

*2-Methylbenzoic Acid (**4g**)*.[34a] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 94% (127 mg). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.12 (d, J = 7.6 Hz, 1H), 7.54−7.45 (m, 1H), 7.33 (dd, J = 10.6, 3.9 Hz, 2H), 2.71 (s, 3H). **^{13}C{^{1}H}NMR** (75 MHz, $CDCl_3$): δ 173.6, 141.4, 133.0, 131.9, 131.6, 128.4, 125.9, 22.2. **GC-MS** (EI, 70 eV) m/z (%): 136.00 (89.61), 118.05 (100), 91.05 (70.42), 65.00 (19.71). **IR (ATR)**ν (cm^{-1}): 2637, 1673, 1406, 1270, 739.

*4-Fluorobenzoic Acid (**4h**)*.[34b] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 92% (128 mg). **^{1}H NMR** (400 MHz, DMSO): δ 13.00 (s, 1H), 8.09−7.85 (m, 2H), 7.25 (dd, J = 12.0, 5.5 Hz, 2H). **^{13}C{^{1}H}NMR** (101 MHz, DMSO): δ 166.8 (s), 166.6 (s), 164.1 (s), 132.5 (d, J = 9.4 Hz), 127.8 (d, J = 2.7 Hz), 116.1 (s), 115.8 (s). **GC-MS** (EI, 70 eV) m/z (%): 140.00 (82.28), 123.00 (100), 95.00 (57.12), 63.00 (22.77). **IR (ATR)** ν (cm^{-1}): 1676, 1602, 1293, 1156, 885, 767.

*4-Chlorobenzoic Acid (**4i**)*.[34b] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 92% (134 mg). **^{1}H NMR** (400 MHz, DMSO): δ 13.06 (s, 1H), 7.89 (dd, J = 8.4, 3.7 Hz, 2H), 7.61−7.37 (m, 2H). **^{13}C{^{1}H}NMR** (101 MHz, DMSO): δ 166.8, 138.2, 131.5, 131.5, 130.0, 129.1, 129.1. **GC-MS** (EI, 70 eV) m/z (%): 155.95 (46.52), 138.95 (94.28), 110.95 (48.87), 63.00 (100). **IR (ATR)**ν (cm^{-1}): 1679, 1406, 1311, 1265, 904, 741.

*2-Iodobenzoic Acid (**4j**)*.[34c] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 72% (178 mg). **^{1}H NMR** (300 MHz, DMSO): δ 8.78 (s, 1H), 7.86 (dd, J = 7.9, 1.0 Hz, 1H), 7.73 (dd, J = 7.8, 1.7 Hz, 1H), 7.30 (td, J = 7.6, 1.2 Hz, 1H), 7.03 (td, J = 7.7, 1.7 Hz, 1H). **^{13}C{^{1}H}NMR** (75 MHz, DMSO): δ 168.2, 141.0, 135.9, 132.3, 130.8, 128.2, 127.9, 93.9. **GC-MS** (EI, 70 eV) m/z (%): 248.00 (7.51), 207.10 (7.97), 164.10 (57.83), 148.15 (100), 120.15 (31.52), 103.10 (45.23). **IR (ATR)**ν (cm^{-1}): 1672, 1581, 1265, 1014, 735.

*4-Cyanobenzoic Acid (**4k**)*.[34a] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: 87% (128 mg). **^{1}H NMR** (400 MHz, DMSO): δ 13.37 (s, 1H), 7.95 (d, J = 4.5 Hz, 2H), 7.85 (d, J = 6.3 Hz, 2H). **^{13}C{^{1}H}NMR** (101 MHz, DMSO): δ 166.4, 135.2, 133.0, 130.3, 118.6, 115.5. **GC-MS** (EI, 70 eV) m/z (%): 147.00 (41.03), 130.00 (100), 102.00 (52.55), 78.00 (35.53), 63.00 (54.52). **IR (ATR)**ν (cm^{-1}): 1690, 1430, 1287, 932, 768.

*4-Nitrobenzoic Acid (**4l**)*.[34a] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: 83% (138 mg). **^{1}H NMR** (300 MHz, DMSO): δ 8.23−8.15 (m, 2H), 8.15−8.06 (m, 2H). **^{13}C{^{1}H}NMR** (75 MHz, DMSO): δ 166.3, 150.2, 136.8, 130.8, 123.4. **GC-MS** (EI, 70 eV) m/z (%): 166.90 (55.73), 138.95 (29.77), 121.00 (45.63), 95.00 (33.85), 65.00 (100). **IR (ATR)**ν (cm^{-1}): 1685, 1539, 1276, 714.

*Furan-3-carboxylic Acid (**4m**)*.[34a] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 104% (154 mg). **^{1}H NMR** (300 MHz, DMSO): δ 7.93 (dd, J = 1.4, 0.7 Hz, 1H), 7.37 (t, J = 1.7 Hz, 1H), 6.62 (dd, J = 1.9, 0.7 Hz, 1H). **^{13}C{^{1}H}NMR** (75 MHz, DMSO): δ 164.7, 147.6, 143.7, 120.0, 109.9. **GC-MS** (EI, 70 eV) m/z (%): 112.05 (90.39), 95.05 (66.02), 78.05 (91.16), 63.00 (100). **IR (ATR)**ν (cm^{-1}): 1679, 1469, 1293, 1016, 754.

*9H-Xanthene-9-carboxylic Acid (**4n**)*.[35a] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 73% (164 mg). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.36−7.27 (m, 4H), 7.17−7.07 (m, 4H), 4.98 (s, 1H). **^{13}C{^{1}H}NMR** (75 MHz, $CDCl_3$): δ 177.3, 151.4, 129.3, 129.1, 123.4, 117.7, 117.1, 45.0. **GC-MS** (EI, 70 eV) m/z (%): 226.00 (0.01), 181.00 (100), 152.10 (19.77), 127.10 (2.44), 90.85 (5.09), 51.00 (2.37). **IR (ATR)**ν (cm^{-1}): 1685, 1481, 1255, 753.

*2-Methylnicotinic Acid (**4o**)*.[35b] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (60:40 v/v) mixture as eluent. Isolated yield: 89% (121 mg). **^{1}H NMR** (300 MHz, DMSO): δ 8.50 (dd, J = 4.8, 1.6 Hz, 1H), 8.14 (dd, J = 7.8, 1.6 Hz, 1H), 7.17 (dd, J = 7.8, 4.9 Hz, 1H), 2.74 (s, 3H). **^{13}C{^{1}H}NMR** (75 MHz, DMSO): δ 168.3, 159.5, 151.3, 138.6, 126.3, 121.0, 24.7. **GC-MS** (EI, 70 eV) m/z (%): 137.10 (100), 119.10 (38.97), 93.10 (63.63), 63.00 (63.40). **IR (ATR)**ν (cm^{-1}): 1711, 1581, 1581, 1213, 1089, 763.

*5-Methoxy-1H-indole-3-carboxylic Acid (**4p**)*.[35c] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (60:40 v/v) mixture as eluent. Isolated yield: 83% (158 mg). **^{1}H NMR** (300 MHz, DMSO): δ 10.76 (s, 1H), 7.30 (d, J = 8.9 Hz, 1H), 7.03−6.94 (m, 2H), 6.83 (dd, J = 8.9, 2.4 Hz, 1H), 3.75 (s, 3H). **^{13}C{^{1}H}NMR** (75 MHz, DMSO): δ 163.5, 154.2, 132.8, 128.7, 127.5, 116.1, 113.4, 107.5, 102.0, 55.6. **GC-MS** (EI, 70 eV) m/z (%): 191.00 (3.03), 147. 00 (100), 132.10 (76.28), 104.10 (66.97), 78.05 (52.21), 63.00 (52.27). **IR (ATR)**ν (cm^{-1}): 3335, 1690, 1521, 1434, 1188, 834.

*Dodecanoic Acid (**4q**)*.[35d] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 95% (190 mg). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 2.37 (t, J = 7.5 Hz, 2H), 1.72−1.59 (m, 2H), 1.30 (d, J = 11.9 Hz, 16H), 0.90 (t, J = 6.7 Hz, 3H). **^{13}C{^{1}H}NMR** (75 MHz, $CDCl_3$): δ 180.3, 34.1, 31.9, 29.6, 29.4, 29.3, 29.2, 29.0, 24.7, 22.7, 14.1. **GC-MS** (EI, 70 eV) m/z (%): 200 (4.96), 157.05 (27.94), 129.00 (44.13), 85.05 (31.63), 73.00 (100). **IR (ATR)**ν (cm^{-1}): 2914, 2848, 1697, 1302, 935.

*Cinnamic Acid (**4r**)*.[34b] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 63% (93 mg). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.83 (d, J = 16.0 Hz, 1H), 7.59 (dd, J = 6.7, 3.0 Hz, 2H), 7.49−7.40 (m, 3H), 6.49 (d, J = 16.0 Hz, 1H). **^{13}C{^{1}H}NMR** (75 MHz, $CDCl_3$): δ 172.6, 147.1, 134.0, 130.8, 128.9, 128.4, 117.3. **GC-MS** (EI, 70 eV) m/z (%): 148.10 (68.83), 147.10 (100), 120.10 (5.38), 103.10 (57.82), 77.05 (39.89), 51.05 (21.53). **IR (ATR)**ν (cm^{-1}): 1671, 1627, 1282, 1220, 977, 767.

*3-Chlorocinnamic Acid (**4s**)*.[36a] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 61% (90 mg). **^{1}H NMR** (400 MHz, DMSO): δ 12.47 (s, 1H), 7.73 (d, J = 3.6 Hz, 1H), 7.60 (s, 1H), 7.53 (d, J = 16.1 Hz, 1H), 7.43−7.31 (m, 2H), 6.56 (dd, J = 16.0, 1.8 Hz, 1H). **^{13}C{^{1}H}NMR** (101 MHz, DMSO): δ 167.7, 142.7, 136.9, 134.1, 130.9, 130.2, 128.2, 127.1, 121.4. **GC-MS** (EI, 70 eV) m/z (%): 181.00 (100), 165.00 (29.87), 147.05 (68.64), 102.05 (84.33), 75.00 (53.46), 51.00 (33.98). **IR (ATR)**ν (cm^{-1}): 1672, 1634, 1321, 1299, 942.

*3-Phenylpropiolic Acid (**4t**)*.[36b] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 72% (105 mg). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.70−7.59 (m, 2H), 7.56−7.47 (m, 1H), 7.44−7.39 (m, 2H). **^{13}C{^{1}H}NMR** (75 MHz, $CDCl_3$): δ 158.5, 133.3, 131.1, 128.7, 119.1, 89.1, 80.1. **GC-MS** (EI, 70 eV) m/z (%): 147.10 (21.64), 130.10 (4.00), 78.05 (69.13), 63.00 (100). **IR (ATR)**ν (cm^{-1}): 2237, 2202, 1665, 1416, 1300, 1206, 918.

*4-Carbamoylbenzoic Acid (**4u**)*.[37a] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (50:50 v/v) mixture as eluent. Isolated yield: 97% (160 mg). **^{1}H NMR** (400 MHz, DMSO): δ 8.08 (s, 1H), 8.00 (s, 1H), 7.94 (q, J = 8.2 Hz, 4H), 7.50 (s, 1H). **^{13}C{^{1}H}NMR** (101 MHz, DMSO): δ 167.6, 167.2, 138.5, 134.9, 133.4, 129.9, 129.6, 128.1. **GC-MS** (EI, 70 eV) m/z (%): 165.00 (4.71), 148.05 (44.25), 103.05 (32.67), 63.00 (100). **IR (ATR)**ν (cm^{-1}): 3356, 3152, 1658, 1617, 1408, 1387.

*5-Oxopyrrolidine-2-carboxylic Acid (**4v**)*.[37b] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (60:40 v/v) mixture as eluent. Isolated yield: 93% (119 mg). **^{1}H NMR** (400 MHz, DMSO): δ 12.75 (s, 1H), 7.89 (s, 1H), 4.03 (dd, J = 8.9, 4.2 Hz, 1H), 2.28 (dd, J = 20.6, 9.1 Hz, 1H), 2.10 (dd, J = 10.6, 5.9 Hz, 2H), 1.98−1.87 (m, 1H). **^{13}C{^{1}H}NMR** (101 MHz, DMSO): δ 177.5, 174.9, 55.2, 29.5, 25.0. **GC-MS** (EI, 70 eV) m/z (%): 129.15 (3.75), 127.10 (18.22), 84.05 (100), 63.00 (45.82). **IR (ATR)**ν (cm^{-1}): 3299, 1704, 1612, 1232, 696.

*6H-Benzo[c]chromen-6-one (**6a**)*.[26a] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20

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v/v) mixture as eluent. Isolated yield: 81% (158 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.32 (d, J = 7.9 Hz, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.27 (t, J = 8.1 Hz, 2H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 161.1, 151.1, 134.8, 134.6, 130.4, 130.3, 128.8, 124.5, 122.7, 121.6, 121.1, 117.9, 117.6. **GC-MS** (EI, 70 eV) m/z (%): 196.00 (100), 168.05 (58.12), 139.10 (57.06), 69.75 (7.98). **IR (ATR)**ν (cm^{-1}): 1725, 1605, 1455, 1432, 1077.

*3-Methyl-6H-benzo[c]chromen-6-one (**6b**).*[26a] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 83% (174 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.32 (d, J = 7.9 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 7.2 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.09 (s, 2H), 2.40 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 161.4, 151.1, 141.2, 134.9, 134.7, 130.4, 128.3, 125.6, 122.4, 121.4, 120.7, 117.8, 115.3, 21.4. **GC-MS** (EI, 70 eV) m/z (%): 210.05 (100), 181.05 (93.64), 152.05 (78.89), 127.00 (17.83), 76.05 (64.97). **IR (ATR)**ν (cm^{-1}): 1735, 1606, 1252, 1080.

*2-Methyl-6H-benzo[c]chromen-6-one (**6c**) and 4-Methyl-6H-benzo[c]chromen-6-one (**6c′**).*[27b] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 80% (168 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.21 (d, J = 6.0 Hz, 1.68H), 7.86 (d, J = 7.5 Hz, 1.84H), 7.65 (t, J = 7.1 Hz, 2.30H), 7.58 (s, 1.18H), 7.42 (t, J = 7.2 Hz, 1.85H), 7.17 (d, J = 7.0 Hz, 0.75H), 7.11−7.03 (m, 2.74H), 2.35 (s, 1.90H), 2.32 (s, 3.03H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 161.1, 160.9, 149.3, 149.1, 134.8, 134.5, 133.9, 131.6, 131.1, 130.2, 130.1, 128.5, 128.4, 126.7, 123.8, 122.5, 121.7, 121.4, 121, 120.8, 120.2, 117.4, 117.3, 117.2, 21, 15.8. **GC-MS** (EI, 70 eV) m/z (%): 210.05 (100), 181.05 (38.54), 152.10 (19.09), 76.05 (13.87). **IR (ATR)**ν (cm^{-1}): 1718, 1605, 1265, 1074.

*2-Methoxy-6H-benzo[c]chromen-6-one (**6d**) and 4-Methoxy-6H-benzo[c]chromen-6-one (**6d′**).*[27b] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 73% (164 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.29 (t, J = 10.6 Hz, 1H), 7.96 (d, J = 7.6 Hz, 1.08H), 7.75 (t, J = 7.1 Hz, 1.11H), 7.53 (d, J = 6.5 Hz, 1.12H), 7.37 (s, 0.96H), 7.19 (d, J = 8.4 Hz, 1.01H), 6.97 (d, J = 8.7 Hz, 0.85H), 3.93 (s, 0.84H), 3.86 (s, 2.94H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 161.2, 160.5, 156.2, 154.9, 145.4, 145.3, 134.8, 134.7, 134.5, 133.9, 130.6, 130.5, 129.2, 128.9, 128.3, 121.6, 121.4, 121.2, 121.1, 118.5, 118.4, 117.1, 106.2, 102.6, 88.2, 56.9, 55.8. **GC-MS** (EI, 70 eV) m/z (%): 226.10 (100), 211.05 (62.60), 183.05 (39.62), 127.10 (35.34), 101.05 (9.61), 77.05 (8.77). **IR (ATR)**ν (cm^{-1}): 1709, 1497, 1271, 1208, 1034.

*3-Chloro-6H-benzo[c]chromen-6-one (**6e**).*[26b] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 81% (186 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.27 (d, J = 7.7 Hz, 1H), 7.95 (d, J = 7.9 Hz, 1H), 7.86 (d, J = 8.3 Hz, 1H), 7.75 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.3 Hz, 1H), 7.22 (d, J = 9.7 Hz, 2H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 160.4, 151.3, 135.8, 134.9, 133.8, 130.6, 129.1, 124.9, 123.7, 121.6, 120.7, 117.8, 116.6. **GC-MS** (EI, 70 eV) m/z (%): 232.65 (60.43), 230.75 (100), 203.80 (87.36), 167.05 (77.87), 139.85 (77.77), 112.95 (57.59), 96.95 (58.65), 69.05 (93.37). **IR (ATR)**ν (cm^{-1}): 1728, 1595, 1259, 1028, 813.

*3-Bromo-6H-benzo[c]chromen-6-one (**6f**).*[26b] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 78% (214 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.37−8.17 (m, 1H), 7.99−7.92 (m, 1H), 7.78−7.72 (m, 1H), 7.59−7.30 (m, 4H). **^{13}C{^{1}H}NMR** (126 MHz, $CDCl_3$): δ 160.5, 151.4, 135.9, 135.0, 133.9, 130.6, 129.1, 124.9, 123.7, 121.6, 120.8, 117.8, 116.6. **GC-MS** (EI, 70 eV) m/z (%): 276.00 (97.97), 274 (100), 245.65 (27.61), 207.05 (18.94), 167.05 (41.00), 139.10 (92.75), 69.50 (39.66). **IR (ATR)**ν (cm^{-1}): 1732, 1596, 1265, 1065.

*2-Iodo-3-methyl-6H-benzo[c]chromen-6-one (**6g**).* Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 67% (225 mg). Mp = 186−188 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.35 (d, J = 7.9 Hz, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.80 (t, J = 7.7 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.21 (s, 1H), 2.48 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 160.8, 151.2, 144.1, 134.9, 133.4, 132.8, 130.6, 129.0, 121.5, 120.9, 118.4, 117.7, 95.0, 28.2. **GC-MS** (EI, 70 eV) m/z (%): 336 (100), 208.90 (36.31), 180.95 (39.37), 152.00 (71.42), 127.00 (9.59), 76.95 (12.80). **IR (ATR)**ν (cm^{-1}): 1730, 1605, 1374, 1265, 1163. **HRMS** (ESITOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{11}IO_2$, 336.9647; found, 336.9716.

*3,4-Diphenyl-1H-isochromen-1-one (**8aa**).*[32] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 89% (132 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.40 (d, J = 7.8 Hz, 1H), 7.63 (t, J = 7.7 Hz, 1H), 7.51 (t, J = 7.5 Hz, 1H), 7.40 (d, J = 5.4 Hz, 3H), 7.32 (d, J = 8.0 Hz, 2H), 7.21−7.16 (m, 6H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 162.2, 150.9, 138.8, 134.6, 134.3, 132.8, 131.2, 129.5, 129.2, 129.0, 128.9, 128.0, 128.1, 127.8, 125.3, 120.4, 116.9. **GC-MS** (EI, 70 eV) m/z (%): 298.00 (100), 269.90 (27.17), 220.90 (32.10), 164.95 (16.80), 105.00 (48.69), 77.00 (27.54). **IR (ATR)**ν (cm^{-1}): 1725, 1602, 1479, 1311, 1078, 756.

*6-Methyl-3,4-diphenyl-1H-isochromen-1-one (**8ba**).*[32] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 91% (141 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.29 (d, J = 7.9 Hz, 1H), 7.40 (s, 3H), 7.36−7.28 (m, 3H), 7.25−7.17 (m, 5H), 6.96 (s, 1H), 2.36 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 162.3, 150.9, 145.8, 142.5, 138.8, 134.4, 133.0, 131.2, 129.6, 129.5, 129.2, 129.0, 128.8, 128.0, 127.78, 125.26, 118.52, 118.01, 22.20. **GC-MS** (EI, 70 eV) m/z (%): 311.95 (100), 283.95 (26.16), 177.90 (13.82), 105.00 (55.60), 77.00 (24.89). **IR (ATR)**ν (cm^{-1}): 1726, 1605, 1442, 1318, 1073.

*6-(tert-Butyl)-3,4-diphenyl-1H-isochromen-1-one (**8ca**).*[32] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 87% (153 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.34 (d, J = 6.7 Hz, 1H), 7.58 (d, J = 6.3 Hz, 1H), 7.41−7.20 (m, 11H), 1.24 (s, 9H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 162.3, 158.6, 150.8, 138.7, 134.4, 133.1, 131.2, 129.3, 129.2, 128.9, 128.8, 128.1, 127.8, 125.9, 121.7, 117.9, 117.2, 35.5, 30.9. **GC-MS** (EI, 70 eV) m/z (%): 354.00 (27.33), 352.95 (100), 337.95 (40.34), 206.90 (11.73), 164.95 (8.68), 104.00 (8.72), 77.00 (10.99). **IR (ATR)**ν (cm^{-1}): 1725, 1602, 1483, 1442, 1072, 768.

*6-Methoxy-3,4-diphenyl-1H-isochromen-1-one (**8da**).*[32] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 83% (136 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.33 (d, J = 8.7 Hz, 1H), 7.39 (d, J = 6.0 Hz, 3H), 7.31 (d, J = 7.7 Hz, 2H), 7.28−7.13 (m, 6H), 7.05 (d, J = 7.4 Hz, 1H), 6.57 (s, 1H), 3.74 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 164.6, 162.0, 151.5, 141.2, 134.4, 132.9, 131.9, 131.1, 129.2, 129.0, 128.9, 128.1, 127.8, 116.7, 115.6, 113.6, 108.4, 55.5. **GC-MS** (EI, 70 eV) m/z (%): 327.90 (100), 299.95 (25.82), 250.90 (51.56), 194.90 (14.64), 152.00 (28.40), 105.00 (87.85), 77.00 (39.71). **IR (ATR)**ν (cm^{-1}): 1728, 1609, 1483, 1294, 1076, 770.

*3,4,6-Triphenyl-1H-isochromen-1-one (**8ea**).* Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 87% (162 mg). Mp = 202−204 °C. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.46 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.49 (d, J = 7.4 Hz, 2H), 7.39 (dd, J = 9.7, 6.7 Hz, 7H), 7.34 (d, J = 7.5 Hz, 2H), 7.30 (d, J = 6.8 Hz, 2H), 7.25−7.18 (dd, J = 16.2, 8.4 Hz, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 162.2, 151.3, 147.5, 139.7, 139.3, 134.2, 132.9, 131.2, 130.2, 129.2, 129.1, 128.9, 128.9, 128.6, 128.2, 127.9, 127.4, 127.2, 123.6, 119.1, 117.0. **GC-MS** (EI, 70 eV) m/z (%): 373.90 (92.94), 296.90 (40.09), 268.95 (21.53), 238.90 (46.36), 105.00 (100), 77.00 (41.54). **IR (ATR)**ν (cm^{-1}): 1725, 1609, 1472, 1272, 1087. **HRMS** (ESITOF) m/z: $[M + H]^+$ calcd for $C_{27}H_{20}O_2$, 375.1307; found, 375.1376.

*6,7-Dimethoxy-3,4-diphenyl-1H-isochromen-1-one (**8fa**).*[30g] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 78% (140 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76 (s, 1H), 7.40 (d, J = 5.7 Hz, 3H), 7.28 (dd, J = 16.2, 7.6 Hz, 4H), 7.18 (dd, J = 14.9, 7.6 Hz, 3H), 6.55 (s, 1H), 4.00 (s, 3H), 3.72 (s, 3H). **^{13}C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 162.1, 154.8, 150.0, 149.6, 134.6, 134.5, 133.0, 131.1, 129.1, 129.0, 128.7, 128.1, 127.8, 116.7, 113.7, 109.4, 106.1, 56.4, 55.9. **GC-**

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MS (EI, 70 eV) *m*/*z* (%): 357.90 (100), 280.90 (32.77), 252.90 (30.03), 214.90 (13.77), 139.00 (16.85), 105.00 (83.02), 77.00 (27.24). **IR (ATR)**ν (cm^{-1}): 1713, 1598, 1511, 1388, 1278, 1224, 1070.

3,4-Diphenyl-1H-benzo[g]isochromen-1-one (**8ga**).[32] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 89% (155 mg). ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.03 (s, 1H), 8.04 (d, J = 7.9 Hz, 1H), 7.76 (d, J = 7.9 Hz, 1H), 7.55 (dd, J = 16.2, 8.3 Hz, 3H), 7.45 (d, J = 4.6 Hz, 3H), 7.34 (dd, J = 11.8, 4.9 Hz, 4H), 7.25−7.17 (m, 3H). ^{13}**C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 162.6, 149.3, 136.3, 134.7, 133.9, 133.2, 132.1, 131.8, 131.3, 129.4, 129.2, 129.1, 128.8, 128.2, 128.1, 127.8, 126.9, 124.4, 118.8, 116.9. **GC-MS** (EI, 70 eV) *m*/*z* (%): 347.90 (5.18), 279.00 (5.41), 214.95 (5.02), 166.90 (35.27), 148.95 (100), 113.10 (10.72), 71.05 (21.19). **IR (ATR)**ν (cm^{-1}): 1732, 1619, 1493, 1259, 1174, 1067.

8-Methyl-3,4-diphenyl-1H-isochromen-1-one (**8ha**).[32] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 73% (113 mg). ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.47−7.43 (m, 4H), 7.30 (s, 3H), 7.21 (dd, J = 21.7, 8.8 Hz, 5H), 6.99 (d, J = 8.3 Hz, 1H), 2.90 (s, 3H). ^{13}**C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 161.5, 150.6, 143.5, 140.4, 134.9, 133.7, 132.9, 131.3, 131.0, 129.1, 128.9, 128.8, 127.9, 127.8, 123.6, 118.9, 116.9, 23.6. **GCMS** (EI, 70 eV) *m*/*z* (%): 311.95 (100), 283.95 (28.62), 234.90 (28.33). **IR (ATR)**ν (cm^{-1}): 1723, 1605, 1472, 1440, 1272, 962, 763.

3,4-Diphenyl-1H-benzo[h]isochromen-1-one (**8ia**).[32] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 78% (135 mg). ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 9.86 (d, J = 8.7 Hz, 1H), 7.99 (d, J = 8.6 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.78 (dd, J = 8.4, 7.3 Hz, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 4.5 Hz, 3H), 7.41−7.35 (m, 2H), 7.30 (dd, J = 5.1, 2.1 Hz, 2H), 7.26−7.18 (m, 4H). ^{13}**C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 161.4, 152.5, 141.0, 139.2, 135.9, 134.8, 132.8, 132.6, 131.6, 131.5, 129.5, 129.2, 129.2, 129.1, 128.5, 128.2, 127.9, 127.0, 122.7, 117.4, 114.1, 114. **GC-MS** (EI, 70 eV) *m*/*z* (%): 347.90 (90.51), 319.95 (20.93), 270.90 (34.99), 214.90 (72.15), 105.00 (100), 77.00 (44.38). **IR (ATR)**ν (cm^{-1}): 1735, 1623, 1493, 1262, 1172, 1065, 774.

6-Fluoro-3,4-diphenyl-1H-isochromen-1-one (**8ja**).[30d] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 82% (129 mg). ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.39 (dd, J = 8.1, 6.0 Hz, 1H), 7.41 (d, J = 4.6 Hz, 3H), 7.31 (d, J = 7.4 Hz, 2H), 7.21−6.81 (m, 6H), 6.83 (d, J = 10.1 Hz, 1H). ^{13}**C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 168.0, 165.5, 161.3, 152.1, 141.9, 141.8, 133.7, 132.9, 132.8, 132.5, 131.0, 129.2, 129.2, 129.2, 128.4, 127.9, 116.9, 116.8, 116.4, 116.4, 116.4, 116.2, 111.4, 111.2. **GC-MS** (EI, 70 eV) *m*/*z* (%): 316.05 (100), 288.05 (26.86), 239.00 (39.66), 105.05 (51.75), 77.00 (33.00). **IR (ATR)**ν (cm^{-1}): 1714, 1581, 1469, 1441, 1188, 1069.

6-Chloro-3,4-diphenyl-1H-isochromen-1-one (**8ka**).[32] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 79% (131 mg). ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 4.6 Hz, 3H), 7.31 (dd, J = 7.0, 4.8 Hz, 3H), 7.21−7.16 (m, 5H). ^{13}**C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 161.6, 152.2, 140.4, 133.5, 132.5, 131.4, 131.2, 131.1, 130.5, 129.3, 129.3, 129.2, 128.4, 128.0, 127.9, 119.1, 115.9. **GC-MS** (EI, 70 eV) *m*/*z* (%): 332.10 (100), 304.10 (23.65), 254. (39.66), 105.05 (51.75), 77.00 (35.40). **IR (ATR)**ν (cm^{-1}): 1728, 1584, 1444, 1311, 1072, 771.

6-Bromo-3,4-diphenyl-1H-isochromen-1-one (**8la**).[32] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 74% (137 mg). ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.23 (d, J = 8.3 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.42 (s, 3H), 7.33−7.15 (m, 8H). ^{13}**C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 161.6, 152.2, 140.4, 133.5, 132.5, 131.4, 131.2, 131.1, 130.5, 129.3, 129.3, 129.2, 128.4, 128.01, 127.9, 119.1, 115.9. **GC-MS** (EI, 70 eV) *m*/*z* (%): 377.75 (71.54), 375.80 (85.23), 347.80 (19.54), 298.80 (24.26), 238.90 (35.68), 162.95 (37.15), 105.00 (100), 77.00 (60.86). **IR (ATR)**ν (cm^{-1}): 1725, 1584, 1437, 1195, 107.

6-Nitro-3,4-diphenyl-1H-isochromen-1-one (**8ma**).[30c] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 57% (97 mg). ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.56 (d, J = 8.6 Hz, 1H), 8.26 (d, J = 8.6 Hz, 1H), 8.03 (s, 1H), 7.56−7.41 (m, 3H), 7.38−7.16 (m, 7H). ^{13}**C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 160.5, 153.1, 151.7, 140.3, 132.8, 132.0, 131.6, 131.5, 130.9, 129.7, 129.6, 129.2, 128.9, 128.3, 128.2, 128.0, 124.2, 123.2, 121.9, 120.5, 116.2. **GC-MS** (EI, 70 eV) *m*/*z* (%): 342.90 (96.09), 297.90 (34.71), 239.90 (51.52), 162.95 (31.61), 105.00 (100), 77.00 (92.08). **IR (ATR)**ν (cm^{-1}): 1728, 1612, 1532, 1325, 1072.

4,5-Diphenyl-7H-furo[2,3-c]pyran-7-one (**8na**).[30h] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 82% (118 mg). ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.80 (d, J = 1.9 Hz, 1H), 7.40−7.30 (m, 5H), 7.26−7.19 (m, 5H), 6.52 (d, J = 1.9 Hz, 1H). ^{13}**C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 153.5, 153.2, 150.4, 137.9, 137.4, 134.0, 132.2, 129.8, 129.4, 129.3, 129.0, 128.2, 128.0, 113.9, 108.0. **GC-MS** (EI, 70 eV) *m*/*z* (%): 287.90 (74.62), 259.90 (17.16), 230.90 (38.18), 210.85 (44.98), 201.90 (54.14), 105.00 (85.54), 77.00 (100). **IR (ATR)**ν (cm^{-1}): 1737, 1546, 1485, 1276, 1017, 693.

4,5,6-Triphenyl-2H-pyran-2-one (**8oa**).[30i] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (75:25 v/v) mixture as eluent. Isolated yield: 88% (142 mg). ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 7.27−7.07 (m, 11H), 6.99 (d, J = 8.0 Hz, 2H), 6.87 (d, J = 7.8 Hz, 2H), 6.36 (d, J = 0.9 Hz, 1H). ^{13}**C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 161.9, 159.2, 158.3, 136.9, 134.3, 132.6, 131.3, 129.5, 129.4, 128.8, 128.6, 128.3, 127.9, 127.9, 127.5, 118.5, 113.4. **GC-MS** (EI, 70 eV) *m*/*z* (%): 323.90 (55.51), 295.95 (100), 266.95 (47.52), 188.90 (18.64), 104.95 (32.12), 77.00 (26.36). **IR (ATR)**ν (cm^{-1}): 1707, 1609, 1514, 1479, 1381, 1012, 890.

3,4-Diethyl-1H-isochromen-1-one (**8ac**).[30e] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (90:10 v/v) mixture as eluent. Isolated yield: 78% (78 mg). ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.29 (d, J = 8.0 Hz, 1H), 7.71 (dd, J = 8.1, 7.3 Hz, 1H), 7.52 (d, J = 8.1 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 2.77−2.41 (m, 4H), 1.26 (td, J = 7.5, 1.1 Hz, 3H), 1.18 (td, J = 7.5, 1.0 Hz, 3H). ^{13}**C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 162.9, 154.9, 137.7, 134.6, 129.9, 127.0, 122.4, 120.8, 113.0, 24.1, 19.3, 14.3, 12.6. **GC-MS** (EI, 70 eV) *m*/*z* (%): 201.90 (100), 186.90 (94.45), 158.95 (28.71), 131.05 (100), 115.00 (43.36), 91.00 (24.55), 77.00 (13.03). **IR (ATR)**ν (cm^{-1}): 1721, 1641, 1473, 1286, 1076, 774.

3,4-Dimethyl-1H-isochromen-1-one (**8ad**).[30e] Colorless solid. Isolated through 40−200 mesh silica gel using pet ether: ethyl acetate (90:10 v/v) mixture as eluent. Isolated yield: 73% (63 mg). ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.26 (d, J = 7.9 Hz, 1H), 7.75−7.67 (m, 1H), 7.44 (dd, J = 15.6, 7.8 Hz, 2H), 2.29 (s, 3H), 2.14 (s, 3H). ^{13}**C{^{1}H}NMR** (101 MHz, $CDCl_3$): δ 162.8, 150.0, 138.6, 134.6, 129.6, 127.1, 122.4, 120.3, 107.7, 17.3, 12.1. **GC-MS** (EI, 70 eV) *m*/*z* (%): 174.20 (100), 132.20 (68.81), 103.15 (39.31), 77.10 (20.18). **IR (ATR)**ν (cm^{-1}): 1718, 1651, 1482, 1286, 1192, 1086, 1048.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00570.

Copies of ^{1}H and ^{13}C NMR spectra and crystal structure description of **2s** (PDF)

Crystallographic data of compound **2s** (CIF)

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Notes

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