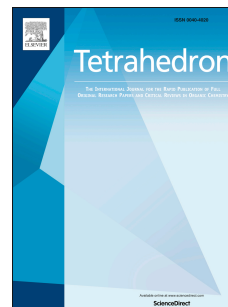# Accepted Manuscript

Rose Bengal-photosensitized oxidation of tertiary amines for the synthesis of bis-1,3-dicarbonyl compounds

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# Graphical Abstract



$R^3$ = H, Me
$R^4$ = Me, Et, $(CH_3)_2CH$
$R^5$ = Ph, Et, $(CH_3)_2CH$

21 examples, yields: 33-80%

# Rose Bengal-photosensitized oxidation of tertiary amines for the

# synthesis of bis-1,3-dicarbonyl compounds

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**Abstract:** We report an example of Rose Bengal-photosensitized oxidation of tertiary amines for the synthesis of bis-1,3-dicarbonyl compounds. This protocol employs Rose Bengal as a visible-light absorbing photocatalyst without the need of a transition metal, and air as a green oxidant. Various functional groups were well tolerated to afford products with yields of up to 80% under mild reaction conditions.

**Key words:** visible light; Rose Bengal; bis-1,3-dicarbonyl compounds; photocatalysis; tertiary amines

## 1. Introduction

Sunlight is an abundant and renewable energy source that can meet the needs of the earth in the future. Scientific community long ago recognized the potential of photochemistry which plays a crucial role in the conversion of solar energy into chemical transformations.[1] However, most organic molecules don't tend to absorb photons in the visible light region that greatly limited the

potential application of photochemical reactions. In order to overcome this drawback, various photosensitizers have been widely employed in visible light photoredox catalysis.[2] Costly complexes of transition-metal catalysis have been successfully applied in organic synthesis, such as inorganic ruthenium[3] and iridium[4] based polypyridyl complexes, or copper-containing photocatalysts.[5] However, the potential toxicity of the metal catalysts may cause pollution to the environment when deal with it at the end of the reaction. Recently, cheap metal-free organic dyes have been applied as effective visible light photosensitizers[6] such as eosin Y,[7] methylene blue,[8] Rose Bengal (RB), etc. The application of Rose Bengal in organic synthesis has attracted the attention of chemists. It has been successfully used as a photosensitizer to oxidize amines to generate highly reactive iminium ion intermediates under visible light irradiation, which can be attacked by a variety of nucleophiles. Many new visible-light promoted chemical reactions have been developed utilizing Rose Bengal as a photosensitizer.[9]

Bis-1,3-dicarbonyl compounds are valuable intermediates or precursors for organic synthesis and transition metal complexes.[10] Recently, using amine as carbon source to construct C-C bond for the synthesis of bis-1,3-dicarbonyl compounds has received considerable attention. However, among these reactions, metals,[11] peroxides,[12] or inorganic oxidants[13] are necessary for promoting the oxidation. These classic methods are often harmful to our environment. In order to avoid the use of those toxic reagents, new synthetic methods for this type of reaction under mild conditions are highly desirable. Currently, visible light-mediated oxidation of amines to iminium ions and the subsequent addition of nucleophiles are extensively studied as an efficient method for C-H functionalization,[3d, 14] which can provide new reaction protocols for the synthesis of bis-1,3-dicarbonyl compounds. But, to the best of our knowledge, up to date only two reports have

been available for the visible-light photocatalyzed reactions of this type (**Scheme 1**).[15] In these two works, the range of substrates is relatively limited, and only methylene-bridged bis-1,3-dicarbonyl compounds have been obtained via oxidation of N-methyl amines under the condition of visible light. Visible-light-induced oxidation of N-ethyl amines for the synthesis of ethylidene-bridged bis-1,3-dicarbonyl compounds has never been reported. Therefore, it is still necessary to develop the application of photosensitized oxidation of tertiary amines for synthesis of bis-1,3-dicarbonyl compounds. Moreover, as far as we know, there are no precedent methods for the application of Rose Bengal-photosensitized oxidation of tertiary amines with 1,3-dicarbonyl compounds for synthesis of bis-1,3-dicarbonyl compounds. We herein wish to report our results about this work.

Previous works: [15a, 15b]
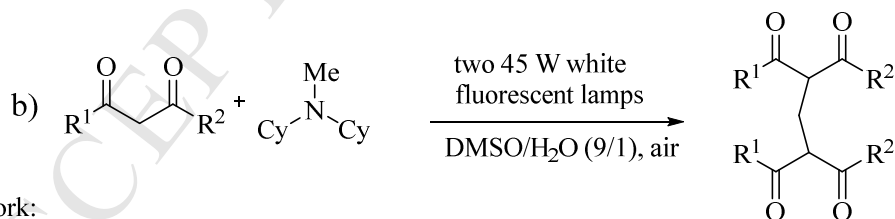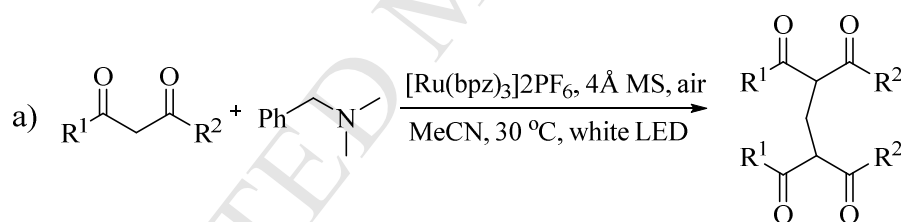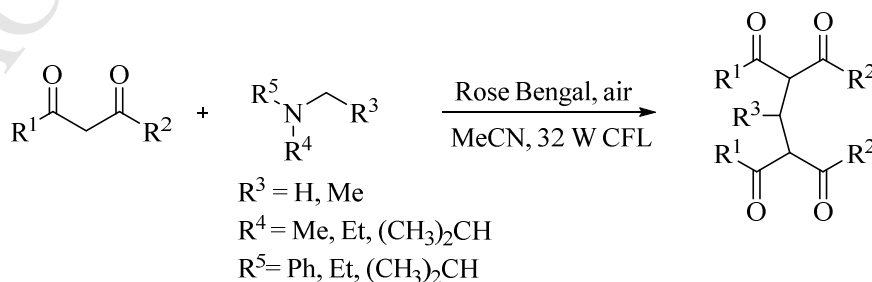


**Scheme 1.** Visible-light photocatalyzed synthesis of bis-1,3-dicarbonyl compounds.

## 2. Results and Discussion

Our initial study was conducted by investigating the reaction of ethyl 3-oxo-3-phenylpropanoate (**1a**) with N,N-dimethyl aniline (**2a**) in the presence of 2 mol% of Rose Bengal in MeCN at room temperature under air atmosphere. After 24 h of irradiation with a 15 W compact fluorescent light (CFL) bulb ($\lambda$ = 405-577 nm), we were delight to find that the reaction indeed proceeded and the desired methylene-bridged bis-1,3-dicarbonyl compound (**3a**) was obtained with 72% yield (**Table 1**, entry 1). To verify if visible light and Rose Bengal were necessary in this catalytic process, some control experiments were conducted (**Table 1**). In the absence of visible-light irradiation, no desired product was observed (**Table 1**, entry 2), indicating that visible light was necessary for the reaction. When the reaction was conducted without Rose Bengal, a low yield of 22% was obtained (**Table 1**, entry 3), suggesting that Rose Bengal could promote the reaction. Additionally, to confirm if air played a role in this process, the reaction was performed under $N_2$ instead of air, which only gave a very low yield of 8% (**Table 1**, entry 4). The result indicated that air was essential for the reaction.

Inspired by the promising result, different solvents, molar ratios of substrates and catalyst loading were examined to improve the reaction efficiency (**Table 1**, entries 5-15). The data confirmed that solvent played an important role in this reaction. The reaction in MeCN gave the best yield of 72% after 24 h (**Table 1**, entry 1). No better results were obtained in other tested solvents such as MeOH, $H_2O$, 1,2-dichloroethane, DMF, DMSO and cyclohexane. A slightly improved yield of product **3a** was achieved when molar ratio ranged from 1:0.5 to 1:2 (**1a**:**2a**) (**Table 1**, entries 1, 10-12). Next, the catalyst loading was screened. When increasing the loading of Rose Bengal from 0.5 mol% to 3 mol%, the yield increased slightly (**Table 1**, entries 1, 13-15).

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Taking into consideration of the yield and the cost of the reaction, MeCN, **1a**:**2a** = 1:1 and catalyst

dosage of 1 mol% were chosen as the suitable conditions for the reaction.

**Table 1.** Control experiments and optimization studies for the reaction of **1a** and **2a**[a].
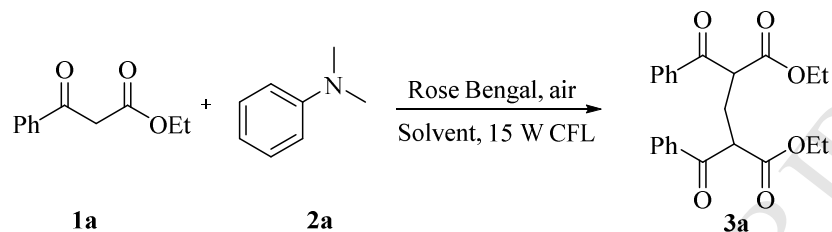
| | 1a | 2a | | 3a |
|---|---|---|---|---|

| Entry | Rose Bengal (mol%) | Solvent | Molar ratio (**1a**:**2a**) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | 2 | MeCN | 1:1 | 72 |
| 2 | 2 (dark) | MeCN | 1:1 | -- |
| 3 | none | MeCN | 1:1 | 22 |
| 4 | 2 ($N_2$ instead of air) | MeCN | 1:1 | 8 |
| 5 | 2 | EtOH | 1:1 | 49 |
| 6 | 2 | $H_2O$ | 1:1 | 10 |
| 7 | 2 | EtOAc | 1:1 | 45 |
| 8 | 2 | $CH_2Cl_2$ | 1:1 | 49 |
| 9 | 2 | $ClCH_2CH_2Cl$ | 1:1 | 5 |
| 10 | 2 | MeCN | 1:0.5 | 67 |
| 11 | 2 | MeCN | 1:1.5 | 74 |
| 12 | 2 | MeCN | 1:2 | 76 |
| 13 | 0.5 | MeCN | 1:1 | 68 |
| **14** | **1** | **MeCN** | **1:1** | **71** |
| 15 | 3 | MeCN | 1:1 | 72 |

[a] Reaction conditions: A mixture of **1a** (0.3 mmol), **2a** (0.15-0.6 mmol), Rose Bengal (0.5-3 mol %) in solvent (1.0

mL) was irradiated with a 15 W CFL bulb in air for 24 h.

[b] Yield of the isolated product after silica gel chromatography.

Next, the effect of different solvent volume and sources of light on the reaction was

investigated (For details, please see the Supporting Information **Table S1**). Based on the

experiment results, 1.0 mL of MeCN and 32 W CFL bulb were chosen as the optimum conditions

for the reaction (0.3 mmol of **1a** and 0.3 of mmol **2a**). Moreover, time course of the reaction was

also investigated, extending the reaction time led to an increase of the yield (**Tables S1**, entries

10-13), but yield did not improve obviously after 24 h.

With the optimized conditions established, the substrate scope of the reaction was explored using N,N-dimethylaniline (**2a**) as a model substrate to react with various $\beta$-ketoesters, 1,3-diketones and 2-benzoylacetanilide (**Table 2**). It can be seen that substituted ethyl benzoylacetate could be proceeded smoothly to give the corresponding products in moderate yields (**Table 2**, entries 2-5). Other $\beta$-ketoesters such as benzyl benzoylacetate and cyclohexyl benzoylacetate also performed well (**Table 2,** entries 6 and 7), and several kinds of 1,3-diketones were applicable to the reaction (**Table 2,** entries 8-10). In addition, heteroaromatic $\beta$-ketoesters were also successfully applied in this transformation (**Table 2,** entries 12 and 13). This is an efficient method for the synthesis of methylene-bridged bis-1,3-dicarbonyl compounds through oxidation of N, N-dimethylaniline.

**Table 2.** Reaction of **1** with N, N-dimethylaniline (**2a**)[a].



| Entry | $R^1$ | $R^2$ | Product | Time (h) | Yield (%)[b] |
|-------|-------|-------|---------|----------|-----------|
| 1 | Ph | OEt | **3a** | 24 | 76 |
| 2 | 4-F-C$_6$H$_4$ | OEt | **3b** | 29 | 65 |
| 3 | 4-Br-C$_6$H$_4$ | OEt | **3c** | 26 | 72 |
| 4 | 4-NO$_2$-C$_6$H$_4$ | OEt | **3d** | 24 | 63 |
| 5 | 3-NO$_2$-C$_6$H$_4$ | OEt | **3e** | 24 | 63 |
| 6 | Ph | OCH$_2$-C$_6$H$_5$ | **3f** | 24 | 77 |
| 7 | Ph | (cyclohexyloxy) | **3g** | 29 | 56 |
| 8 | Ph | Me | **3h** | 24 | 62 |
| 9 | Ph | Ph | **3i** | 24 | 45 |
| 10 | Ph | 2-OH-C$_6$H$_4$ | **3j** | 24 | 52 |
| 11 | Ph | NH-C$_6$H$_5$ | **3k** | 24 | 60 |

| 12 |  | OEt | **3l** | 24 | 52 |
| 13 |  | OEt | **3m** | 24 | 39 |

[a] Reaction conditions: A mixture of **1** (0.3 mmol), **2a** (0.3 mmol), Rose Bengal (1 mol %) in MeCN (1.0 mL) was irradiated with a 32 W CFL bulb in air.

[b] Yield of the isolated product after silica gel chromatography.

The above data show that, Rose Bengal can oxidize N-methyl amines give methylene-bridged bis-1,3-dicarbonyl compounds under the irradiation of visible light. We were curious to know whether Rose Bengal can catalyze N-ethyl amines to give the same type of products. It was nice to see that the results were consistent with what we expected. 1.5 mmol of $Et_3N$ (**2b**) with 0.3 mmol of **1a** led to a 40% yield of the desired product ethylidene-bridged bis-1,3-dicarbonyl compound (**4a**) after 8 h (For details, please see the Supporting Information **Table S2**). In order to study the applicability of the substrate, $Et_3N$ (**2b**) as a substrate was used to react with **1** (**Table 3**). The reaction with various $\beta$-ketoesters could be proceeded smoothly to give the corresponding products.

It is worth mentioning that the expected product wasn't achieved when using 1-(2-hydroxyphenyl)-3-phenyl-1,3-propanedione (**1j**) as a substrate, but 3-benzoyl-2-methylchroman-4-one (**5a**) and 3-benzoyl-2-methyl-4*H*-chromen-4-one (**5b**) were obtained instead (**Scheme 2**). And we further found that **5a** could be converted into the **5b** by an oxidation process under the standard conditions (**Scheme 3**).
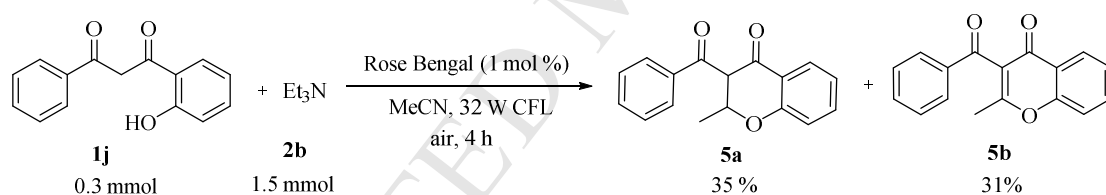
**Table 3.** Reaction of **1** with $Et_3N$ (**2b**)[a]
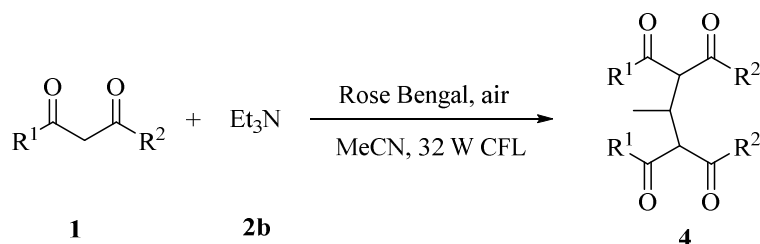
| Entry | R[1] | R[2] | Product | Time (h) | Yield (%)[b] |
|-------|------|------|---------|----------|-----------|
| 1 | Ph | OEt | **4a** | 8 | 40 |
| 2 | 4-F-C$_6$H$_4$ | OEt | **4b** | 4 | 60 |
| 3 | 4-Br-C$_6$H$_4$ | OEt | **4c** | 5 | 80 |
| 4 | 4-NO$_2$-C$_6$H$_4$ | OEt | **4d** | 8 | 40 |
| 5 | 3-NO$_2$-C$_6$H$_4$ | OEt | **4e** | 8 | 33 |
| 6 | (thiophene) | OEt | **4f** | 8 | 55 |
| 7 | (pyridine) | OEt | **4g** | 4 | 65 |

[a] Reaction conditions: A mixture of **1** (0.3 mmol), **2b** (1.5 mmol), Rose Bengal (1 mol %) in MeCN (1.0 mL) was irradiated with a 32 W CFL bulb in air.

[b] Yield of the isolated product after silica gel chromatography.



**Scheme 2**. Reaction of **1j** with Et$_3$N (**2b**).
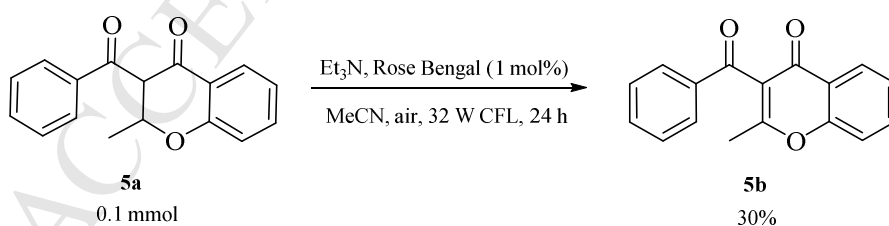


**Scheme 3**. Conversion of **5a** to **5b**.

Encouraged by the above experimental results, other tertiary amines were also investigated. In the case of N-ethyl-N-methylethanamine (**2c**), methylene-bridged bis-1,3-dicarbonyl product **3a** was obtained as a major product in a yield of 45%, along with a 12% yield of **4a** after 11 h

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(**Scheme 4**). The N-ethyl-N-isopropylpropan-2-amine (**2d**) reacted with **1a** only led to a 25% yield

of **4a** after 24 h, but no reaction was observed when using tripropylamine as a substrate.

In total, 21 bis-1,3-dicarbonyl compounds were prepared, and 11 of them are new compounds

and their structures were confirmed by HRMS, ^{1}HNMR and ^{13}CNMR.
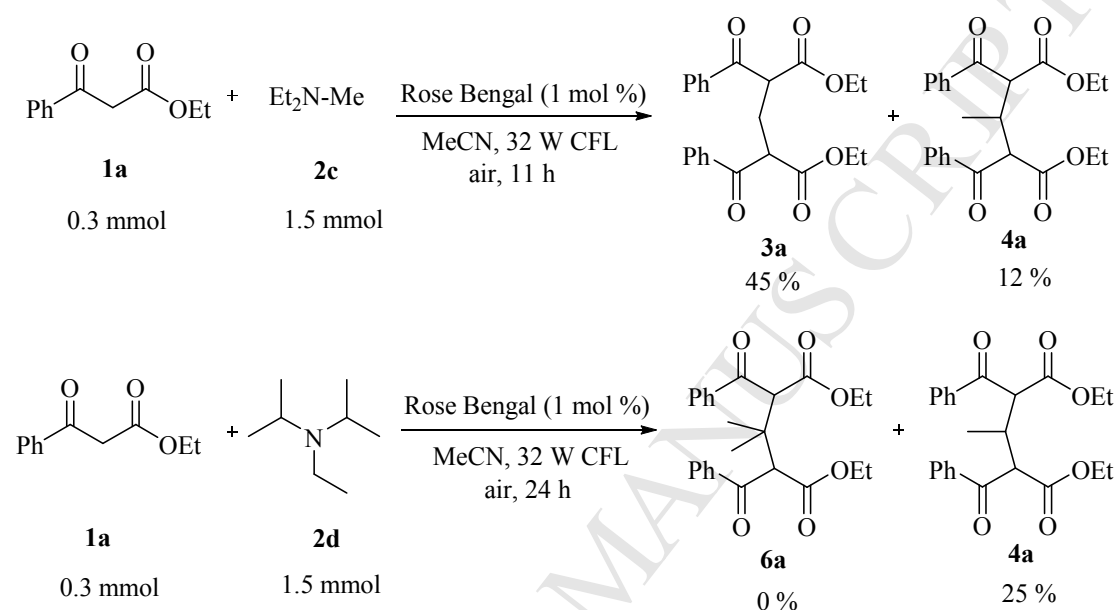


**Scheme 4**. Reaction of **1a** with tertiary amines **2c** and **2d**.

Finally, in order to understand the mechanism of the Rose Bengal-photosensitized oxidation of

tertiary amines, a number of control experiments were conducted. The UV-visible absorption

spectra of Rose Bengal was performed (the spectrum was shown in the Supporting information).

Rose Bengal exhibited a strong absorption in the visible light region at $\lambda_{max} = 563$ nm ($\varepsilon = 33290$

L mol$^{-1}$ cm$^{-1}$). On the other hand, under $N_2$ instead of air conditions, the reaction only gave a low

yield of 8% (**Table 1**, entry 4), indicating that $O_2$ is involved in the reaction. It has been revealed

that in polar aprotic solvents, molecular oxygen could form singlet oxygen $^1O_2$ through energy

transfer from the RB* to ground-state $^3O_2$ under visible light irradiation,[16] and $^1O_2$ is able to

oxidize tertiary amines. [17] In order to understand the role of molecular oxygen in the reaction, we

determined the rate of product formation in the absence and presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) which is known as a quencher of singlet oxygen[18] (**Table 4**). The data showed that DABCO (1 equiv) indeed has inhibitive effect on the reaction, especially at the early stage of the reaction, indicating that singlet oxygen may be involved in the reaction process. However after 24 h, nearly the same yield could be obtained as the reaction under standard conditions suggesting that even in the presence of DABCO the reaction still can proceed. Recently, we reported a chlorophyll-catalyzed visible-light-mediated synthesis of tetrahydroquinolines from N,N‐dimethylanilines and maleimides.[19] Like Rose Bengal, chlorophyll is also a well-known singlet oxygen photosensitizer. In that chlorophyll-mediated photocatalysis, the addition of 1 equiv of DABCO almost completely suppressed the reaction which ruled out the possibility that N,N-dimethyl aniline might be more reactive to singlet oxygen than DABCO, Thus, in consideration of the fact that the present reaction still can proceed at a lower rate with the presence of 1 equiv of DABCO, we speculate that besides singlet oxygen (energy transfer), a photoredox catalysis mechanism may also be involved in the reaction. Furthermore, a test experiment with the presence of (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO), a free radical scavenger,[20] was performed. No desired product **3a** was obtained (**Scheme 5**) but some complicated by-products were observed, and starting materials did not consumed completely. This result suggested that a radical process must be involved in this reaction. The reduction potential of excited state of Rose Bengal [$E^{*}_{red}$ ($RB^{*}$/ $RB^{\bullet-}$) = 0.99 V *vs*. SCE in MeCN][6c, 21] is sufficient enough for the oxidation of N,N-dimethyl aniline (**2a**) [Half-peak oxidation potential ($E_{1/2}^{(ox)}$) = 0.71 V *vs*. SCE in MeCN][22] and $Et_3N$ (**2b**) [Half-peak oxidation potential ($E_{1/2}^{(ox)}$) = 0.96 V *vs*. SCE in MeCN].[22]

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**Table 4** The rate of product formation in the absence and presence of DABCO[a]
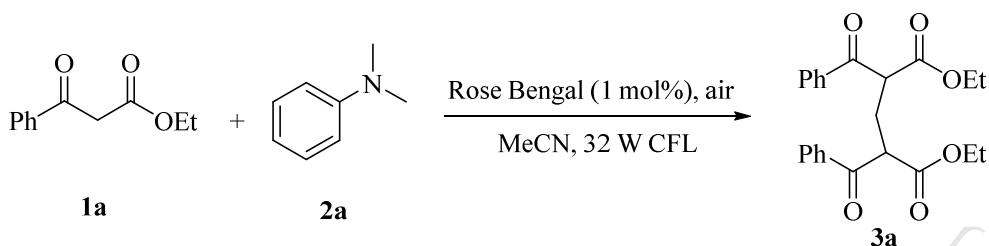


| Entry | Time (h) | Yield (%)[b] | |
|:---:|:---:|:---:|:---:|
| | | With DABCO (0.3 mmol) | Standard conditions |
| 1 | 6 | 27 | 43 |
| 2 | 12 | 51 | 51 |
| 3 | 18 | 55 | 70 |
| 4 | 24 | 75 | 76 |

[a] Standard conditions: A mixture of **1a** (0.3 mmol), **2a** (0.3 mmol), and Rose Bengal (1 mol %) in MeCN (1.0 mL)

was irradiated with a 32 W CFL bulb in air.

[b] Yield of the isolated product after silica gel chromatography.
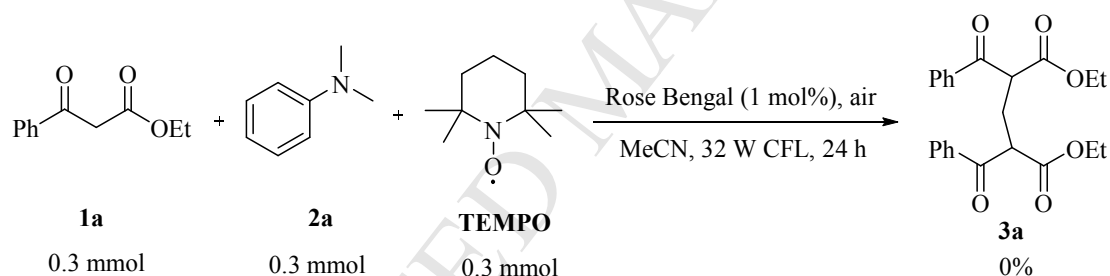


**Scheme 5.** Control experiment.

On the basis of our results and the commonly accepted mechanism from the literature, [11a, 15a] a

plausible mechanism was depicted (**Scheme 6**). On absorption of visible light, the ground state of

RB is induced to its excited state RB*. In path A (energy transfer), RB* transfers its energy to the

ground-state oxygen ($^3O_2$) forming the singlet oxygen ($^1O_2$). A single-electron transfer (SET) from

the tertiary amine **2** to $^1O_2$ leads to the amine cation radical **2'**. At the same time, $^1O_2$ accepts an

electron to form superoxide anion radical ($O_2^{\bullet-}$). Meanwhile, in path B (photoredox catalysis), a

single electron transfer (SET) from the tertiary amine **2** to RB* leads to the amine cation radical

**2'**, [9c, 14b, 14e, 14h, 23] and at the same time, RB* is reduced to the RB$^{\bullet-}$. Upon transfer of an electron to

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$O_2$ to form the superoxide radical anion $O_2^{\bullet-}$ with the concurrent regeneration of RB, the photocycle completes. Next, the radical cation **2'** generated from the both paths gave up a hydrogen atom, presumably to the superoxide radical anion to afford hydrogen peroxide anion (HOO⁻) and iminium ion **2''**. Subsequently, the nucleophilic addition of iminium ion **2''** with deprotonated nucleophile **1'** (HOO⁻ abstracts the proton of **1** to form $H_2O_2$ and **1'**) affords the intermediate **a**. The product **3** or **4** can be formed through an elimination/Michael addition pathway via an intermediate **b** in the presence of **1**.[24] Additionally, the generation of $H_2O_2$ was indirectly proved by the evidence that $Ph_3P$ could be oxidized to $Ph_3PO$[25] by the reaction mixture of **1a** and **2a** (After completion of the model reaction, $Ph_3P$ was added to the reaction mixture and stirred in the dark for 12 h. The formation of $Ph_3PO$ could be detected by both HPLC and TLC through comparison with the authentic sample).
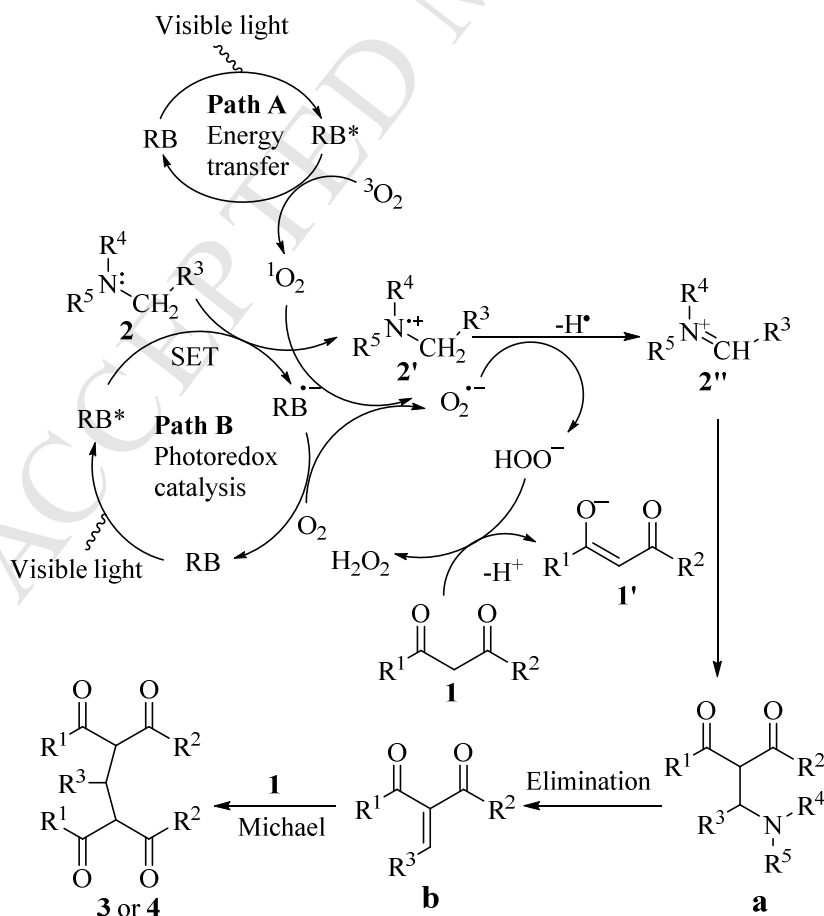
**Scheme 6.** Proposed reaction mechanism for the formation of **3** and **4**.

From the proposed mechanism as shown in **Scheme 6**, it can be seen that when **1j** reacts with N,N-dimethylaniline, $R^3$ in the intermediate **b** is H. While **1j** reacts with Et$_3$N, $R^3$ is Me. The latter is more sterically hindered, which is not easy to react with bulky diketone **1j** to form the normal bis-1,3-dicarbonyl compound, but instead to form **5a** by intramolecular Michael addition. Thus, we also tried to propose the possible reaction mechanism for the formation of **5a** and **5b** (**Scheme 7**). By the same process as described in **Scheme 6,** intermediate **a'** can be obtained. Product **5a** could be formed through elimination/intramolecular Michael addition of **a'**. And product **5b** could be formed by oxidation of **5a** under the standard conditions.
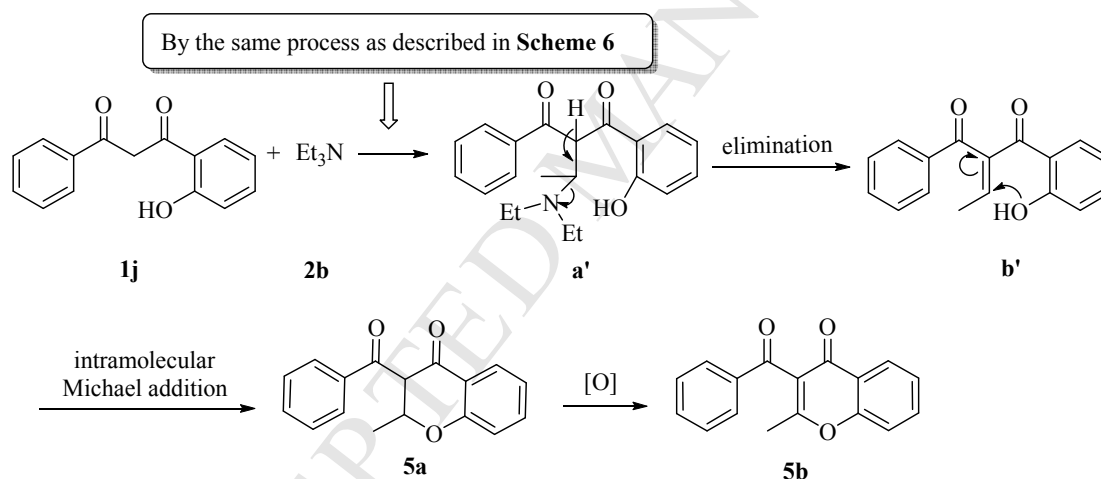


**Scheme 7.** Proposed reaction mechanism for the formation of **5**.

## 3. Conclusion

In conclusion, cheap and readily available Rose Bengal was used as a photosensitizer to oxidize tertiary amines for the synthesis of bis-1,3-dicarbonyl compounds under the irradiation of visible light. This work avoids the use of metal catalyst and peroxides as terminal oxidant, and instead air was used as a clean oxidant. The applicability of the substrate is good. Various

methylene- and ethylidene- bridged bis-1,3-dicarbonyl compounds were obtained with yields of up to 80%. Meanwhile, the 3-benzoyl-2-methylchroman-4-one and 3-benzoyl-2-methyl-4*H*-chromen-4-one were obtained under the standard conditions.

# 4. Experimental Section

## 4.1. *General experimental details*

Rose bengal was purchased from aladdin industrial corporation Shanghai, China. R104993-1g, 95%. Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) with Haiyang GF 254 silica gel plates (Qingdao Haiyang chemical industry Co Ltd, Qingdao, China) using UV light and vanillic aldehyde as visualizing agents. Flash column chromatography was performed using 200-300 mesh silica gel at increased pressure. $^1$H NMR spectra and $^{13}$C NMR spectra were respectively recorded on 600 MHz and 150 MHz NMR spectrometers. Chemical shifts ($\delta$) were expressed in ppm with TMS as the internal standard, and coupling constants ($J$) were reported in Hz. High-resolution mass spectra were obtained by using ESI ionization sources (Varian 7.0 T FTICR-MS). Melting points were taken on a WPX-4 apparatus and were uncorrected (Yice instrument equipment Co Ltd, Shanghai).

## 4.2. *General procedure for the synthesis of products*

A mixture of **1** (0.3 mmol), **2a** (0.3 mmol) or **2b-d** (1.5 mmol) and Rose Bengal (1.0 mol%) in MeCN (1.0 mL) was stirred under irradiation of a 32 W compact fluorescent light bulb (The parallel distance between the bulb and the reaction flask was about 2 cm) for the specified reaction

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time, and monitored by thin layer chromatography (TLC). The MeCN was removed under reduced

pressure. The crude products were purified by column chromatography on silica gel (petroleum

ether/EtOAc: 20/1~4/1) to give the desired products.

### 4.2.1. Compound 3a[11a]

Yellow solid; 76% yield (45 mg); m.p. 80.4-81.0 $^{o}$C; $R_f$ = 0.30 (PE/EtOAc, 6:1); The ratio of

two diastereomers is 1.4:1. **Two diastereomers**: $^1$H NMR (600 MHz, CDCl$_3$): δ = 8.05-8.03 (m,

4H), 7.61-7.56 (m, 2H), 7.51-7.45 (m, 4H), 4.62 (t, $J$ = 7.3 Hz, 1.17H), 4.55 (t, $J$ = 7.3 Hz, 0.85H),

4.25-4.18 (m, 2.40H), 4.12-4.08 (m, 1.76H), 2.76-56 (m, 2H), 1.21 (t, $J$ = 7.1 Hz, 3.46 H), 1.11 (t,

$J$ = 7.1 Hz, 2.57 H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ = 196.1, 194.8, 169.60, 169.3, 136.1, 135.6,

133.7, 128.9, 128.81, 61.6, 61.5, 51.6, 51.4, 28.2, 27.7, 14.0, 13.8.

### 4.2.2. Compound 3b[12a]

Yellow solid; 65% yield (42 mg); m.p. 61.6-62.1 $^{o}$C; $R_f$ = 0.30 (PE/EtOAc, 5:1); The ratio of

two diastereomers is 1.6:1. **Two diastereomers**: $^1$H NMR (600 MHz, CDCl$_3$): δ = 8.14-8.04 (m,

4H), 7.27-7.14 (m, 4H), 4.59 (t, $J$ = 7.2 Hz, 1.21 H), 4.50 (t, $J$ = 7.2 Hz, 0.78 H), 4.26-4.19 (m,

2.52 H), 4.12-4.10 (m, 1.59 H), 2.73-2.53 (m, 2H), 1.22 (t, $J$ = 7.1 Hz, 3.65 H), 1.13 (t, $J$ = 7.1 Hz,

2.39 H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ193.5, 193.2, 169.5, 169.1,167.0, 165.3, 132.4, 131.9,

131.7, 131.6, 131.6, 131.5, 116.0, 61.7, 61.7, 51.5, 51.3, 28.1, 27.5, 14.0, 13.9.

### 4.2.3. Compound 3c[26]

Yellow oil; 72% yield (60 mg); $R_f$ = 0.30 (PE/EtOAc, 15:1); The ratio of two diastereomers is

1.4:1. **Two diastereomers**: $^1$H NMR (600 MHz, CDCl$_3$): δ = 7.92-7.9(m, 4H), 7.65-7.61 (m, 4H),

4.56 (t, $J$ = 7.2 Hz, 1.20 H), 4.48 (t, $J$ = 7.2 Hz, 0.83 H), 4.25-4.18 (m, 2.50 H), 4.12-4.09 (m, 1.71

H), 2.73-2.51 (m, 4H), 1.22 (t, $J$ = 7.1 Hz, 3.75 H), 1.13 (t, $J$ = 7.1 Hz, 2.66 H); $^{13}$C NMR (150

MHz, CDCl$_3$): δ = 194.1, 193.7, 169.3, 169.0, 134.7, 134.3, 132.1, 130.3, 130.2, 129.2, 129.1,

61.8, 51.4, 51.3, 28.0, 27.4, 14.0, 13.9.

*4.2.4. Compound 3d*[11a]

Yellow oil; 63% yield (46 mg); $R_f$ = 0.30 (PE/EtOAc, 4:1);The ratio of two diastereomers is

1:1. **Two diastereomers**: $^1$H NMR (600 MHz, CDCl$_3$): δ = 8.37-8.34 (m, 4H), 8.24-8.21 (m, 4H),

4.68 (t, $J$ = 7.0 Hz, 1H), 4.58 (t, $J$ = 7.0 Hz, 1H), 4.27-4.20 (m, 2H), 4.16-4.10 (m, 2H), 2.78-2.56

(m, 2H), 1.22 (t, $J$ = 7.1 Hz, 3H), 1.13 (t, $J$ = 7.1 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ = 193.7,

193.4, 168.9, 168.5, 150.7, 150.7, 140.4, 140.0, 129.9, 129.8, 124.0,123.9, 62.17, 51.70, 27.47,

26.9, 13.9, 13.8.

*4.2.5. Compound 3e*

Yellow oil; 63% yield (46 mg); $R_f$ = 0.30 (PE/EtOAc, 6:1); The ratio of two diastereomers is

1:1. **Two diastereomers**: $^1$H NMR (600 MHz, CDCl$_3$): δ = 8.87 (d, $J$ = 5.6 Hz, 2H), 8.47 (t, $J$ =

8.4 Hz, 2H), 8.40 (t, $J$ = 7.5 Hz, 2H), 7.76-7.72 (m, 2H), 4.69 (t, $J$ = 7.0 Hz, 1H), 4.59 (t, $J$ = 7.0

Hz, 1H), 4.28-4.21 (m, 2H), 4.18-4.11 (m, 2H), 2.81-2.61 (m, 2H), 1.22 (t, $J$ = 7.1 Hz, 3H), 1.15 (t,

$J$ = 7.1 Hz, 3H); $^{13}$C NMR (150 MHz, CDCl$_3$): δ = 193.0, 192.7, 168.8, 168.5, 148.7, 137.3, 137.0,

134.3, 130.1, 130.1, 127.9, 123.7, 123.6, 62.2, 62.1, 51.5, 51.4, 27.4, 27.0, 13.9,13.8. HRMS (ESI)

calc. for $C_{31}H_{24}O_6$ (M-H)$^-$: 485.1190, found: 485.1198.

*4.2.6. Compound 3f*

Yellow oil; 77% yield (60 mg); $R_f$ = 0.30 (PE/EtOAc, 10:1); The ratio of two diastereomers is

1.3:1. **Two diastereomers**: $^1$H NMR (600 MHz, CDCl$_3$): δ = 7.95-7.94 (m, 4H), 7.57-7.52 (m,

2H), 7.43-7.38 (m, 4H), 7.28-7.22 (m, 10H), 5.19-5.06 (m, 4H), 4.65 (t, $J$ = 7.3 Hz, 1.10 H), 4.56

(t, $J$ = 7.3 Hz, 0.87 H), 2.82-2.59 (m, 2H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 194.7, 194.5, 169.4, 169.1, 135.9, 135.5, 135.3, 135.2, 133.7, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 67.4, 67.3, 51.63 (s), 51.6, 51.4, 28.2, 27.6, 27.0. HRMS (ESI) calc. for C$_{33}$H$_{28}$O$_6$ (M+Na)[+]: 543.1778, found: 543.1783.

### 4.2.7. Compound *3g*

Yellow oil; 56% yield (42 mg); R$_f$ = 0.25 (PE/EtOAc, 20:1); The ratio of two diastereomers is 1.4:1. **Two diastereomers**: ^{1}H NMR (600 MHz, CDCl$_3$): δ = 8.05-8.01 (m, 4H), 7.59-7.55 (m, 2H), 7.50-7.44 (m, 4H), 4.86 (br, 1.11 H), 4.75 (br, 0.82 H), 4.59-4.50 (m, 2H), 2.78-2.57 (m, 2H), 1.48-1.21 (m, 20H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 195.1, 194.9, 169.0, 168.8, 136.2, 135.8, 133.6, 128.8, 128.7, 128.6, 51.9, 51.7, 31.3, 31.1, 31.0, 27.9, 27.5, 25.2, 25.1, 23.4, 23.3, 23.2. HRMS (ESI) calc. for C$_{31}$H$_{36}$O$_6$ (M+Na)[+]: 527.2404, found: 527.2411.

### 4.2.8. Compound *3h*[11a]

Yellow oil; 62% yield (31 mg); R$_f$ = 0.30 (PE/EtOAc, 6:1); The ratio of two diastereomers is 1:1. **Two diastereomers**: ^{1}H NMR (600 MHz, CDCl$_3$): δ = 8.06-8.02 (m, 4H), 7.64-7.59 (m, 2H), 7.53-7.44 (m, 4H), 4.71 (t, $J$ = 6.9 Hz, 1.08 H), 4.64 (t, $J$ = 6.9 Hz, 0.91 H), 2.60-2.15 (m, 2H), 2.19 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 203.8, 203.3, 196.6, 196.4, 136.0, 135.8, 134.0, 129.0, 128.9, 128.9, 128.8, 59.4, 59.3, 29.3, 29.0, 27.4, 27.1.

### 4.2.9. Compound *3i*[11a]

Yellow oil; 45% yield (31 mg); R$_f$ = 0.25 (PE/EtOAc, 15:1); ^{1}H NMR (600 MHz, CDCl$_3$): δ = 8.13 (d, $J$ = 7.7 Hz, 8H), 7.58 (t, $J$ = 7.2 Hz, 4H), 7.48 (t, $J$ = 7.4 Hz, 8H), 5.74 (t, $J$ = 6.8 Hz, 2H), 2.78-2.75 (m, 2H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 196.6, 135.6, 133.9, 129.0, 128.8, 54.1, 29.0.

*4.2.10. Compound 3j*

Yellow oil; 52% yield (41 mg); $R_f$ = 0.30 (PE/EtOAc, 6:1); ^{1}H NMR (600 MHz, CDCl$_3$): δ = 11.91 (s, 1H), 11.87 (s, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 8.14 (d, *J* = 7.6 Hz, 2H), 8.06 (d, *J* = 7.6 Hz, 2H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.62-7.57 (m, 2H), 7.52-7.46 (m, 7H), 7.02-6.99 (m, 3H), 6.94-6.91 (m, 1H), 5.72-5.70 (m, 2H), 2.80-2.79 (m, 2H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 202.4, 202.3, 195.7, 195.7, 163.5, 163.4, 137.4, 130.4, 130.1, 129.2, 129.2, 128.8, 128.6, 119.9, 119.0, 118.9, 118.4, 118.2, 53.8, 29.2, 29.0. HRMS (ESI) calc. for C$_{31}$H$_{24}$O$_6$ (M+Na)$^+$: 515.1465, found: 515.1472.

*4.2.11. Compound 3k*[11a]

Yellow oil; 60% yield (44 mg); $R_f$ = 0.25 (PE/EtOAc, 5:1); ^{1}H NMR (600 MHz, DMSO-*d$_6$*): δ = 10.41 (s, 1H), 10.36 (s, 1H), 8.14 (m, 4H), 7.68-7.50 (m, 10H), 7.35-7.27 (m, 4H), 7.10-7.04 (m, 2H), 4.74-4.72 (m, 2H), 2.49-2.37 (m, 2H); ^{13}C NMR (150 MHz, DMSO-*d$_6$*): δ = 196.4, 195.6, 167.4, 139.4, 139.1, 136.5, 135.9, 134.1, 129.7, 129.3, 129.2, 129.2, 129.2, 128.9, 124.2, 124.1, 120.1, 120.0, 53.9, 53.7, 29.1, 29.0.

*4.2.12. Compound 3l*[12a]

Yellow oil; 52% yield (32 mg); $R_f$ = 0.30 (PE/EtOAc, 6:1);The ratio of two diastereomers is 1.1:1. **Two diastereomers**: ^{1}H NMR (600 MHz, CDCl$_3$): δ = 7.92 (dd, *J* = 16.0, 3.2 Hz, 2H), 7.71 (dd, *J* = 21.2, 4.9 Hz, 2H), 7.18-7.12 (m, 2H), 4.43 (t, *J* = 7.3 Hz, 1.06 H), 4.38 (t, *J* = 7.3 Hz, 0.94 H), 4.23-4.21 (m, 2.28 H), 4.15-4.13 (m, 1.84 H), 2.74-2.60 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 3.44 H), 1.16 (t, *J* = 7.1 Hz, 2.66 H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 187.5, 187.3, 169.1, 168.8, 143.1, 142.8, 135.2, 135.1, 133.9, 133.7, 128.4, 61.8, 61.7, 52.6, 28.6, 28.0, 14.0, 13.9. HRMS (ESI) calc. for C$_{19}$H$_{20}$O$_6$S$_2$ (M+Na)$^+$: 431.0594, found: 431.0598.

*4.2.13. Compound **3m***

Yellow oil; 39% yield (23 mg); $R_f$ = 0.30 (PE/EtOAc, 4:1); The ratio of two diastereomers is

1:1. **Two diastereomers**: ^{1}H NMR (600 MHz, CDCl$_3$): δ = 8.59 (d, $J$ = 4.4 Hz, 1H), 8.51 (d, $J$ =

4.4 Hz, 1H), 8.06 (d, $J$ = 7.8 Hz, 2H), 7.84-7.81 (m, 2H), 7.45-7.40 (m, 2H), 4.92 (t, $J$ = 7.3 Hz,

1H), 4.85 (t, $J$ = 7.3 Hz, 1H), 4.14-4.08 (m, 4H), 2.76-2.67 (m, 2H), 1.14 (t, $J$ = 7.1 Hz, 3H), 1.10

(t, $J$ = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 196.2, 195.9, 170.2, 170.1, 152.3, 148.8,

136.9, 127.2, 122.4, 61.1, 50.7, 50.5, 26.9, 26.5, 13.9, 13.8. HRMS (ESI) calc. for C$_{21}$H$_{22}$N$_2$O$_6$

(M+Na)[+]: 421.1370, found: 421.1378.

*4.2.14. Compound **4a***[27]

Yellow oil; 40% yield (25 mg); $R_f$ = 0.25 (PE/EtOAc, 10:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ =

8.08-7.98 (m, 4H), 7.62-7.56 (m, 2H), 7.52-7.44 (m, 4H), 4.88-4.71 (m, 2H), 4.21-4.05 (m, 2H),

4.09-4.03 (m, 2H), 3.40-3.29 (m, 1H), 1.26-1.18 (m, 5H), 1.09-1.06 (m, 4H); ^{13}C NMR (150 MHz,

CDCl$_3$): δ = 195.1, 194.9, 169.2, 168.7, 137.1, 136.2, 133.7, 128.8, 128.7, 128.7, 61.6, 61.4, 61.3,

61.2, 56.5, 56.0, 55.7, 33.7, 32.9, 14.0, 13.9, 13.8, 13.7, 13.4.

*4.2.15. Compound **4b***

Yellow oil; 60% yield (40 mg); $R_f$ = 0.3 (PE/EtOAc, 10:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ =

8.13-8.02 (m, 4H), 7.20-7.12 (m, 4H), 4.84-4.66 (m, 1H), 4.67-4.66 (m, 1H), 4.21-4.18 (m, 2H),

4.09-4.07 (m, 4H), 3.37-3.24 (m, 1H), 1.24-1.05 (m, 9H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 193.5,

193.3, 169.1, 168.9, 168.5, 167.0, 165.3, 133.4, 132.5, 132.2, 131.6, 131.5, 131.4, 131.2, 131.1,

116.1, 116.0, 115.9, 115.8, 61.7, 61.6, 61.4, 56.4, 55.8, 55.5, 54.9, 33.6, 32.8, 14.0, 13.9, 13.8,

13.7, 13.4. HRMS (ESI) calc. for C$_{24}$H$_{24}$F$_2$O$_6$ (M+Na)[+]: 469.1433, found: 469.1431.

*4.2.16. Compound **4c***

Yellow oil; 80% yield (68 mg); $R_f$ = 0.3 (PE/EtOAc, 10:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ = 7.94-7.83 (m, 4H), 7.66-7.59 (m, 4H), 4.79-4.74 (m, 1H), 4.63-4.62 (d, 1H), 4.22-4.16 (m, 2H), 4.11-4.05 (m, 2H), 3.36-3.22 (m, 1H), 1.23-1.15 (m, 5H), 1.12-1.04 (m, 4H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 194.1, 194.0, 193.8, 168.9, 168.8, 168.4, 135.7, 134.8, 134.6, 132.2, 132.2, 132.1, 130.2, 130.2, 130.2, 129.9, 129.2, 129.1, 61.7, 61.6, 61.5, 61.4, 56.4, 55.8, 55.5, 54.9, 33.5, 32.6, 14.0, 14.0, 13.9, 13.8, 13.5. HRMS (ESI) calc. for C$_{24}$H$_{24}$Br$_2$O$_6$ (M+Na)[+]: 588.9832, found: 588.9831.

### 4.2.17. Compound *4d*

Yellow oil; 40% yield (30 mg); $R_f$ = 0.3 (PE/EtOAc, 5:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ = 8.35-8.15 (m, 8H), 4.90-4.69 (m, 2H), 4.20-4.04 (m, 4H), 3.34-3.30 (m, 1H), 1.26-1.02 (m, 9H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 193.9, 193.5, 193.2, 168.5, 168.3, 167.9, 150.7, 150.7, 150.6, 141.5, 141.2, 140.6, 140.4, 138.3, 130.3, 129.7, 129.4, 128.0, 124.0, 123.8, 62.1, 62.0, 61.9, 61.7, 60.0, 56.5, 55.7, 33.2, 33.2, 14.3, 14.0, 13.9, 13.7. HRMS (ESI) calc. for C$_{24}$H$_{24}$N$_2$O$_{10}$ (M+Na)[+]: 523.1323, found: 523.1320.

### 4.2.18. Compound *4e*

Yellow oil; 33% yield (25 mg); $R_f$ = 0.3 (PE/EtOAc, 5:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ = 8.89-8.81 (m, 2H), 8.48-8.32 (m, 4H), 7.77-7.72 (m, 2H), 4.91-4.86 (m, 1H), 4.70-4.69 (m, 1H), 4.23-4.22 (m, 2H), 4.21-4.12 (m, 2H), 3.42-3.32 (m, 1H), 1.26-1.20 (m, 5H), 1.16-1.12 (m, 4H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 193.2, 193.1, 192.8, 192.5, 168.5, 168.4, 168.3, 168.0, 148.7, 138.1, 137.4, 134.1, 130.2, 130.1, 127.9, 127.9, 127.8, 123.5, 123.4, 123.2, 62.2, 62.0, 62.0, 56.7, 56.3, 55.6, 33.2, 32.2, 14.3, 14.0, 13.9, 13.9, 13.8, 13.7. HRMS (ESI) calc. for C$_{24}$H$_{24}$N$_2$O$_{10}$ (M+Na)[+]: 523.1323, found: 523.1322.

*4.2.19. Compound **4f***

Yellow oil; 55% yield (35 mg); $R_f$ = 0.3 (PE/EtOAc, 6:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ = 7.97-7.67 (m, 4H), 7.21-7.10 (m, 2H), 4.68-4.59 (m, 2H), 4.23-4.17 (m, 2H), 4.13-4.09 (m, 2H), 3.31-3.27 (m, 1H), 1.26-1.20 (m, 5H), 1.19-1.12 (m, 4H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 187.6, 187.4, 187.3, 168.9, 168.6, 168.3, 144.4, 143.3, 143.2, 135.3, 135.2, 134.9, 133.8, 133.6, 128.5, 128.3, 61.7, 61.4, 61.3, 57.4, 57.2, 56.7, 34.3, 33.8, 14.1, 14.0, 13.9, 13.7, 13.2. HRMS (ESI) calc. for $C_{20}H_{22}O_6S_2$ (M+K)$^+$: 461.0489, found: 461.0483.

*4.2.20. Compound **4g***

Yellow oil; 55% yield (34 mg); $R_f$ = 0.3 (PE/EtOAc, 3:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ = 8.62-8.36 (m, 2H), 8.10-8.04 (m, 2H), 7.84-7.80 (m, 2H), 7.46-7.37 (m, 2H), 5.25-5.20 (m, 1H), 5.05 (d, *J* = 6.06 Hz, 0.49H), 4.90 (d, *J* = 6.72 Hz, 0.52H), 4.19-4.00 (m, 4H), 3.52-3.37 (m, 1H), 1.21-1.18 (m, 3H), 1.13-1.02 (m, 6H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 196.7, 196.1, 195.5, 195.3, 169.9, 169.7, 169.3, 169.2, 152.7, 148.8, 148.7, 148.6, 136.8, 136.8, 127.2, 127.1, 127.1, 127.0, 122.2, 122.1, 122.0, 61.0, 60.9, 60.9, 56.0, 55.4, 54.4, 54.3, 33.3, 32.0, 30.2, 15.1, 14.8, 14.5, 14.0, 13.9, 13.8, 13.7. HRMS (ESI) calc. for $C_{22}H_{24}N_2O_6$ (M+Na)$^+$: 435.1527, found: 435.1524.

*4.2.21. Compound **5a***

Yellow solid; 35% yield (14 mg); m.p. 105.6.1-106.0 $^o$C; $R_f$ = 0.3 (PE/EtOAc, 15:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ = 7.98-7.97 (m, 2H), 7.88-7.87 (m, 1H), 7.63-7.60 (m, 1H), 7.53-7.49 (m, 3H), 7.04-7.01 (m, 2H), 5.10-5.07 (m , 1H), 4.64 (d, *J* = 11.5 Hz, 1H), 1.49 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 196.5, 190.0, 161.3, 137.8, 136.4, 133.7, 128.8, 128.7, 127.3, 121.5, 120.6, 117.9, 76.3, 60.0, 19.9. HRMS (ESI) calc. for $C_{17}H_{14}O_3$ (M+Na)$^+$:289.0835, found:

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289.0832.

*4.2.22. Compound **5b**[28]*

Yellow solid; 31% yield (12 mg); m.p. 76.4-76.9 $^{\circ}$C; $R_f$ = 0.3 (PE/EtOAc, 5:1); ^{1}H NMR (600 MHz, CDCl$_3$) δ = 8.18 (d, *J* = 7.9 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.72-7.69 (m, 1H), 7.60-7.57 (m, 1H), 7.49-7.41 (m, 4H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, CDCl$_3$): δ = 193.8, 175.8, 165.4, 156.0, 137.1, 134.0, 133.8, 129.4, 128.7, 126.1, 125.5, 123.5, 123.2, 117.9, 19.1.

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