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Ring-opening of tertiary cyclopropanols derived from β-diketones

Le-Zhen Li, Bin Xiao, Qing-Xiang Guo and Song Xue*

Department of Chemistry, University of Science and Technology of China, Hefei 230026, PR China

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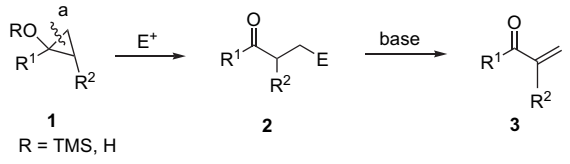
Dedicated to Professor Yaozhong Jiang on the occasion of his 70th birthday

Abstract—The ring-opening reaction of 1,2-disubstituted cyclopropanols, prepared from β-diketones, mediated by $Cu(NO_3)_2$, *p*-TsOH, and NaOH is reported. The Cu(II)-mediated ring-opening of cyclopropanols gave α-methylene-γ-diketones in good yields. The reaction took place at the less substituted carbon of the cyclopropanols, involving mild conditions and a simple procedure. The reaction induced by *p*-TsOH in CH_2Cl_2 afforded α-methyl-γ-diketones as the major product with minor amounts of δ-diketones. The 2,3,5-trisubstituted furans were obtained in high yields when the ring-opening reaction was mediated by *p*-TsOH in methanol under reflux conditions. In the presence of sodium hydroxide the reaction proceeded smoothly in preference to the formation of δ-diketones, particularly for substrates with an aromatic group on the cyclopropane.

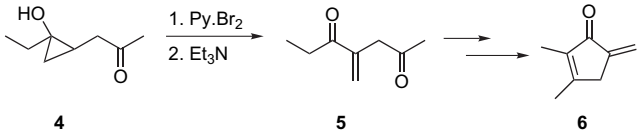
1. Introduction

The unique reactivity of cyclopropanes due to their high level of strain offers considerable utility in organic synthesis. Many applications of cyclopropanes as useful building blocks have been described but not for regio- and stereo-controlled ring-opening reactions of substituted cyclopropanes.[1] However, heteroatom-substituted cyclopropanes exhibit enhanced reactivity and also undergo regio- and stereo-controlled ring cleavage.[2] Among those heteroatom-substituted cyclopropanes, the ring-opening of cyclopropanols and its derivatives, which are important intermediates in organic synthesis, have been reported in the literature.[3] Typically, tertiary cyclopropyl silyl ethers **1** (R=TMS) are easily prepared from the cyclopropanation of enol silyl ethers and can be converted into the corresponding carbonyl compounds via ring-opening reactions.[4] Several methods have been developed to achieve α-methylene ketones **3** by the specific cleavage at bond 'a' of compound **1** (Scheme 1).[5] Reactions of cyclopropyl silyl ethers **1** with $SnCl_4$,[5a] $TeCl_4$,[5b] and Br_2 gave β-trichlorostannyl, β-trichlorotelluro, and β-bromo ketones **2**, respectively, followed by treatment with DMSO or Et_3N to furnish α-methylene ketones **3** in good yields. Recently, the use of cyclopropanols as synthetic intermediates has increased since the advent of the Kulinkovich reaction.[6] Also, the cyclopropanols can be converted into α-methylene ketones **3** in the presence of $Py\cdot Br_2$ or NBS, followed by addition of Et_3N.



Scheme 1.

Among those α-methylene ketones, α-methylene-γ-diketones are important precursors for the synthesis of substituted cyclopentenones, five-membered heterocyclic compounds, and natural products. In 2000, Chevtchouk reported an operationally simple approach to synthesize the cyclopentenoid antibiotic methylenomycin B **6**. The key intermediate **5** of this reaction was prepared in a reasonable yield via ring-opening of 1,2-disubstituted cyclopropanol **4** in the presence of $Py\cdot Br_2$, followed by addition of Et_3N (Scheme 2).[7] Though these elegant ring-opening reactions to synthesize α-methylene ketones are simple to perform, the main disadvantage of the above procedures is the requirement of long reaction times and the utility of toxic reagents.



Scheme 2.

Keywords: 1,2-Disubstituted cyclopropanol; $Cu(NO_3)_2$; α-Methyl-γ-diketone; 2,3,5-Trisubstituted furans.
* Corresponding author. Tel.: +86 551 3607794; fax: +86 551 3607864; e-mail: xuesong@ustc.edu.cn

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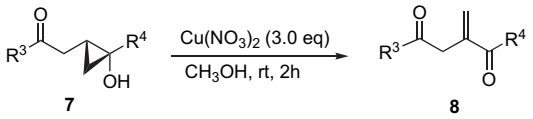
The bond 'a' in the tertiary cyclopropyl silyl ethers **1** can be specially cleaved with silver(I) tetrafluoroborate and copper(II) tetrafluoroborate.[8] Surprisingly, Cu(II)-mediated ring-opening of unprotected hydroxyl-cyclopropanes has not been reported. Herein, we develop a mild and efficient procedure to synthesize α-methylene-γ-diketones from cyclopropanols, prepared from β-diketones, in a one-pot reaction mediated by $Cu(NO_3)_2$. To the best of our knowledge, this is the first report on the use of $Cu(NO_3)_2$ for the synthesis of α-methylene-γ-diketones from 1,2-disubstituted cyclopropanols. At the same time, the procedure for cyclopropanol conversion to γ- and δ-diketones under basic or acidic conditions is described.

2. Results and discussion

2.1. Copper(II)-mediated ring-opening reaction

Very recently, we have developed a new procedure for the synthesis of 1,2-disubstituted cyclopropanols from β-diketones.[9] Treatment of 1-phenyl-butane-1,3-diketone with 4.0 equiv of Et_2Zn, 2.0 equiv of CF_3CO_2H, and 4.0 equiv of CH_2I_2 resulted in the formation of the *trans*-1,2-disubstituted cyclopropanol **7a**, an analog of compound **4**, in 93% yield. It was found that Cu(II)-induced ring-opening reaction of various cyclopropanols **7** in methanol worked efficiently and gave rise to α-methylene-γ-diketones **8** in good yields. To begin our study, we chose cyclopropanol **7a** as the standard substrate to search for suitable reaction conditions. The results are shown in Table 1. The amount of $Cu(NO_3)_2$ and solvent were crucial for efficient ring-opening reaction. Treatment of **7a** with 1.0 equiv of $Cu(NO_3)_2$ in CH_3OH gave 3-methylene-1-phenyl-pentane-1,4-dione **8a** in 37% yield at room temperature over 5 h (entry 1, Table 1). When the amount of $Cu(NO_3)_2$ was increased to 3.0 equiv, clean reaction took place to give the desired compound **8a** in 90% isolated yield at room temperature over 2 h (entry 3, Table 1). The reaction performed in toluene and CH_2Cl_2 afforded trace amount of the product **8a** under the same reaction conditions. These poor results may be due to the insolvable $Cu(NO_3)_2$ in a non-polar solvent. The desired product **8a** was obtained in 62% yield when the reaction was carried out in THF. $Cu(OAc)_2$ and $Cu(SO_4)_2$ were also acceptable as a mediated resource, which afforded **8a** in 74 and 70% yields, respectively (entries 7 and 8, Table 1). However, treatment of **7a** with $CuCl_2$ in CH_3OH gave a complex reaction mixture.

Table 2. $Cu(NO_3)_2$-mediated ring-opening of tertiary cyclopropanols



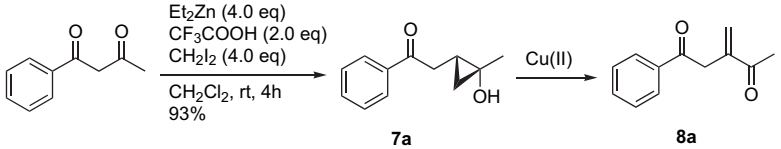
7 8

Entry	R^3	R^4	Product	Yield[a] (%)
1	C_6H_5	Me	**8a**	90
2	*p*-MeC_6H_4	Me	**8b**	80
3	*p*-$MeOC_6H_4$	Me	**8c**	93
4	*p*-ClC_6H_4	Me	**8d**	85
5	*p*-FC_6H_4	Me	**8e**	80
6	*m,p*-$(MeO)_2C_6H_3$	Me	**8f**	75
7	*p*-$MeOC_6H_4$	*n*-Pr	**8g**	77
8	*p*-$MeOC_6H_4$	C_6H_5	**8h**	67
9	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	**8i**	76
10	C_6H_5	C_6H_5	**8j**	73
11	C_6H_5	*p*-ClC_6H_4	**8k**	89
12	*p*-ClC_6H_4	C_6H_5	**8l**	75
13	2-Thienyl	Me	**8m**	75
14	Me	*o*-$MeOC_6H_4$	**8n**	76
15	CH_3CH_2	CH_3CH_2	**8o**	64
16	But	Me	**8p**	70

[a] Isolated yields.

With the optimized reaction conditions established, various substrates were subjected to the ring-opening reactions. These cyclopropanols reacted smoothly using 3.0 equiv of $Cu(NO_3)_2$ at room temperature in CH_3OH. Representative results are given in Table 2. R^3 group with an electron-donating or electron-withdrawing substituent on the benzene ring has little effect on the reaction yield. However, the reaction is sensitive to R^4 group substitution of the substrates. When the R^4 was varied from a methyl to a propyl group, the yield of the corresponding product decreased (entries 3 and 7, Table 2). A lower yield was obtained when R^4 was a phenyl group (entry 8, Table 2). Similarly, a bulky group resulted in the loss of yield apparently due to steric effect. It is notable that when R^4 was 4-chlorophenyl group, the substrate could afford the product **8k** in 89% yield. On the basis of these

Table 1. Copper(II)-mediated ring-opening of compound **7a**



7a 8a

Entry	Solvent	Copper salts	Time (h)	Yield[a] (%)
1	CH_3OH	$Cu(NO_3)_2$, 1 equiv	5	37
2	CH_3OH	$Cu(NO_3)_2$, 2 equiv	2	72
3	CH_3OH	$Cu(NO_3)_2$, 3 equiv	2	90
4	Toluene	$Cu(NO_3)_2$, 3 equiv	2	Trace
5	CH_2Cl_2	$Cu(NO_3)_2$, 3 equiv	2	Trace
6	THF	$Cu(NO_3)_2$, 3 equiv	2	62
7	CH_3OH	$Cu(OAc)_2$, 3 equiv	2	74
8	CH_3OH	$Cu(SO_4)_2$, 3 equiv	2	70
9	CH_3OH	$CuCl_2$, 3 equiv	1	Complex mixture

[a] Isolated yields.

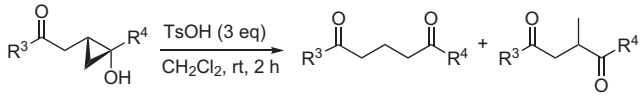
results, a new procedure for the synthesis of α-methylene-γ-diketones, the analog of compound **5**, was developed. The ring-opening reaction mediated by $Cu(NO_3)_2$ was remarkably clean and efficient, involving mild reaction conditions and a simple procedure.

2.2. Acid-catalyzed ring-opening reaction

We have reported a new procedure for the synthesis of γ-diketones from β-diketones.[9] Practical application of this methodology appeared limited to the use of α-substituted β-diketones, since substitution at the α-position resulted in no reaction. Now, we report a variation on the ring-opening reaction that provides a partial solution to this problem. The cyclopropanols **7** will be converted into α-methyl-γ-diketones via ring-opening reaction under acidic conditions. For example, treatment of **7a** with 3.0 equiv of *p*-TsOH in CH_2Cl_2 for 2 h at room temperature afforded α-methyl γ-diketone **10a** in 72% yield, along with a 16% yield of the isomer δ-diketone **9a** (entry 1, Table 3). Various 1,2-disubstituted cyclopropanols could be efficiently converted into the corresponding diketones in good yields. The reaction is also sensitive to the R^4 group of the substrates. When the R^4 varied from a methyl to a propyl group, the yield of isomer **9e** increased to 24%, but that of compound **10e** decreased to 66% (entry 5, Table 3). When both R^3 and R^4 were phenyl groups, the ring-opening reaction did not occur after stirring at room temperature for 6 h, even at reflux. The reason may be the steric hindrance of the aromatic ring under the reaction conditions.

In the process of optimizing reaction conditions, it was found that the ring-opening reaction in methanol solvent worked inefficiently. For example, treatment of **7a** with 3.0 equiv of *p*-TsOH in methanol for 5 h at room temperature afforded trace amount of the diketone, even after prolonging the reaction time. When the reaction was carried out at reflux, a new compound was obtained in a 91% isolated yield. This compound was determined to be 2,3,5-trisubstituted furan **11a** by NMR and HRMS spectra. It was notable that the isomer **9a** was not observed under the reaction conditions. However, the reaction performed in CH_2Cl_2 under reflux for 6 h could afford trisubstituted furan **11a** in 65% yield along with a 13% yield of the isomer **9a** and trace amount of **10a**. The furan moieties are common structures in numerous natural products, such as kallolides and

Table 3. Acid-catalyzed ring-opening of tertiary cyclopropanols

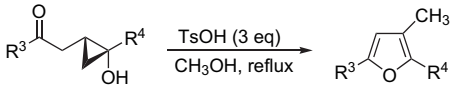


7 9 10

Entry	R^3	R^4	**9**, yield[a] (%)	**10**, yield[a] (%)
1	C_6H_5	Me	**9a**, 16	**10a**, 72
2	*p*-MeC_6H_4	Me	**9b**, 23	**10b**, 75
3	*p*-$MeOC_6H_4$	Me	**9c**, 18	**10c**, 72
4	2-Thienyl	Me	**9d**, 20	**10d**, 78
5	*p*-$MeOC_6H_4$	*n*-Pr	**9e**, 24	**10e**, 66
6	C_6H_5	C_6H_5	NR[b]	

[a] Isolated yields.
[b] NR=no reaction.

Table 4. Synthesis of 2,3,5-trisubstituted furans from 1,2-disubstituted cyclopropanols



7 11

Entry	R^3	R^4	Time (h)	Product	Yield[a] (%)
1	C_6H_5	Me	5	**11a**	91
2	*p*-MeC_6H_4	Me	6	**11b**	90
3	*p*-$MeOC_6H_4$	Me	3	**11c**	92
4	*p*-ClC_6H_4	Me	8	**11d**	87
5	*p*-FC_6H_4	Me	6	**11e**	89
6	*p*-$MeOC_6H_4$	*n*-Pr	3	**11f**	69
7	*p*-$MeOC_6H_4$	$C_6H_5CH_2CH_2$	10	**11g**	66
8	*m*,*p*-$(MeO)_2C_6H_3$	CH_3CH_2	6	**11h**	80
9	2-Thienyl	Me	8	**11i**	75
10	Me	*o*-$MeOC_6H_4$	6	**11j**	41
11[b]	C_6H_5	C_6H_5	24	**11k**	50

[a] Isolated yields.
[b] Performed in THF at reflux.

cembranolides.[10] Highly substituted furans play an important role in organic chemistry, not only as key structural units in many natural products, but also as useful building blocks in synthetic chemistry.[11] Many strategies have been developed for the preparation of furans.[12] Typically, the most widely used approach to furan synthesis is the Paal–Knorr reaction in which 1,4-dicarbonyl compounds are converted to furan derivatives induced by acid, such as HCl, H_2SO_4, P_2O_5, *p*-TsOH.[13] Recently, radical cyclization of divinyl ethers, gold(III) porphyrin-catalyzed cycloisomerization of allenones, palladium-catalyzed reaction of 2-propynyl-1, 3-dicarbonyls, and microwave-mediated Paal–Knorr cyclization reaction to give the corresponding 2,3,5-trisubstituted furans were reported.[14] Herein, we report a new procedure to synthesize 2,3,5-trisubstituted furans by the *p*-TsOH induced ring-opening of 1,2-disubstituted cyclopropanols. The reactions were completed in methanol at reflux for 3–8 h, and the products were easily purified by silica gel chromatography. Various 1,2-disubstituted cyclopropanols underwent smooth cyclization to give the corresponding trisubstituted furans in high yields under the reaction conditions. These results are summarized in Table 4. The R^4 group on the three-membered ring has an obvious influence on the reaction yield. When the R^4 varied from a methyl to a propyl group, the yield of **11f** decreased to 69%. A bulky phenethyl group resulted in a dramatic loss of yield under the same conditions, thus prolonging reaction time was required (entry 7, Table 2). When R^4 was *o*-methoxy-phenyl group, the yield of the desired product **11j** was dramatically decreased to 41% (entry 10, Table 4). However, when both R^3 and R^4 were phenyl groups, no reaction was noticed in methanol under reflux for 6 h. The reaction performed in THF, in place of methanol, under reflux for 24 h could give the desired compound **11k** in 50% isolated yield.

2.3. Base-catalyzed ring-opening reaction

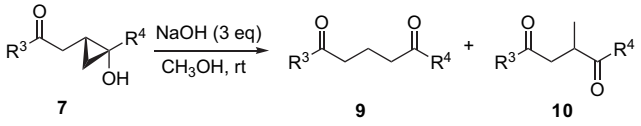
It has been reported that cyclopropanols are converted into 2-methyl ketones in the presence of sodium hydroxide.[15] Acidic treatment of the compound **7a** afforded a 4.5:1 mixture of the two regioisomers **10a** and **9a** in combined 88% yield (entry 1, Table 3). However, treatment of **7a** with

Table 5. Base-catalyzed ring-opening of tertiary cyclopropanols

Entry	R^3	R^4	Time (h)	**9**, yield[a] (%)	**10**, yield[a] (%)
1	*p*-$MeOC_6H_4$	*n*-Pr	24	**9e**, 14	**10e**, 24
2[b]	*p*-$MeOC_6H_4$	*n*-Pr	2	**9e**, 35	**10e**, 62
3	C_6H_5	C_6H_5	1	**9f**, 81	**10f**, 13
4	*p*-$MeOC_6H_4$	C_6H_5	2	**9g**, 80	**10g**, 14
5	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	3	**9h**, 80	**10h**, 15
6	*m,p*-$(MeO)_2C_6H_3$	C_6H_5	2	**9i**, 66	**10i**, 14

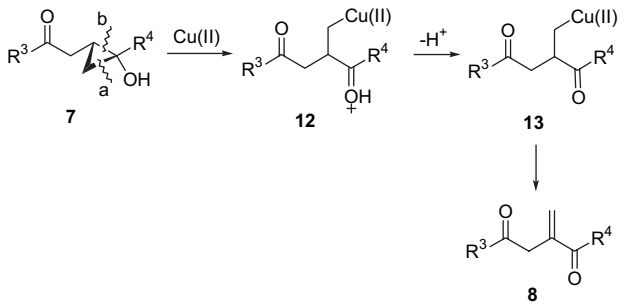
[a] Isolated yields.
[b] Performed at reflux.

sodium hydroxide resulted in a complex mixture, probably due to the formation of the diketone, which easily carried out condensation reaction under strong basic conditions. So we turned our attention to the ring-opening of cyclopropanols with a bulky R^4 substitution. When R^4 was propyl group, the ring-opening reaction performed at room temperature for 24 h afforded **9e** and **10e** in 14 and 24% yields, respectively. It was found that the reaction worked efficiently under reflux conditions. The cyclopropanol was consumed completely within 2 h affording the major product **10e** in 62% yield along with a 35% yield of **9e**. Interestingly, when both R^3 and R^4 were aromatic group, the ring-opening reaction of cyclopropanols with 3.0 equiv of sodium hydroxide in methanol at room temperature worked smoothly and afforded the δ-diketones **9f–i** in good yields. For example, 81% yield of **9f** was obtained under the standard conditions, along with a 13% yield of **10f** (Table 5). Whereas no reaction was observed when the ring-opening reaction of this type of cyclopropanols was induced by *p*-TsOH (Table 5).



2.4. Plausible mechanism of the ring-opening reaction

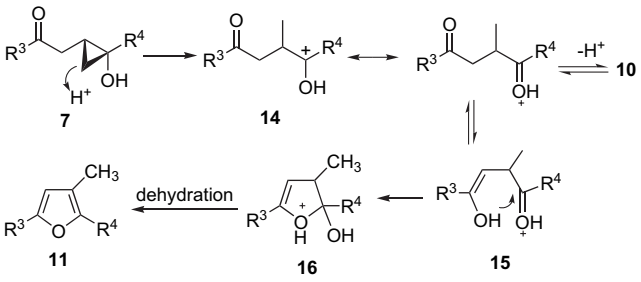
The Cu(II)-mediated ring-opening of cyclopropanols **7** to α-methylene-γ-diketones **8** occurred with site-selective cleavage of the cyclopropane ring at the bond 'a', and no product arising from bond 'b' scission was obtained. This high regioselectivity may be explained by attack of Cu(II) at the least hindered site.[16] A possible ring-opening reaction pathway is shown in Scheme 3. The electrophilic attack of Cu(II) at the least sterically crowded site of **7** followed by



Scheme 3.

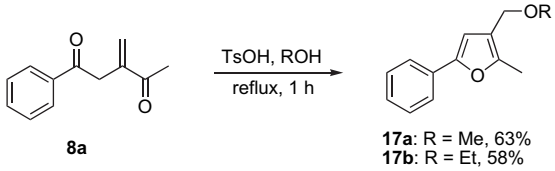
elimination of H^+ via **12** would give the β-copper(II) diketone **13**. Subsequently, the intermediate **13** would undergo elimination to form the desired α-methylene-γ-diketone **8**.[8]

The acid-catalyzed ring-opening reaction of cyclopropanols to form carbonyl compounds was assigned an S_E2 mechanism.[4] Therefore, a proposed mechanism for the acid-promoted ring-opening and cyclization reaction of 1,2-disubstituted cyclopropanols **7** to synthesize trisubstituted furans **11** is given in Scheme 4. The first step is the acid-catalyzed ring-opening reaction of **7** to furnish species **14**. The species **14** undergoes enolization to generate intermediate **15**. The trisubstituted furans **11** are formed via intramolecular nucleophilic attack of the enol oxygen upon the electrophilic carbon of the protonated carbonyl group, followed by dehydration of **16**. The species **14** gave compound **10** via deprotonation when the reaction conditions were mild at room temperature. When the reaction was carried out in methanol at reflux, the species **14** were easily converted into trisubstituted furans **11**. These results demonstrated that the conversion of **15** to **16** was the rate-controlling step in the reaction.[17,14a]



Scheme 4.

To corroborate the proposed mechanism, in which the species **14** is the key intermediate, exposure of 3-methyl-1-phenyl-pentane-1,4-dione **10a** to 1.0 equiv of *p*-TsOH in methanol at reflux for 1 h provided the furan **11a** in 91% yield. Furthermore, α-methylene-γ-diketones **8** afforded 2,3,5-trisubstituted furans under the similar reaction conditions. For example, treatment of the compound **8a** with 1.0 equiv of *p*-TsOH in methanol and ethanol at reflux for 1 h afforded compounds **17a** and **17b** in 63 and 58% yields, respectively (Scheme 5). The reaction may occur through Michael addition of alcohol to unsaturated diketone and subsequent cyclization under acidic conditions.



Scheme 5.

We have also investigated the direct conversion of cyclopropanol **7a** to **17a** in one-pot reaction. Treatment of **7a** with 3.0 equiv of $Cu(NO_3)_2$ in methanol at room temperature for 2 h, then followed by addition of 1.0 equiv of *p*-TsOH,

afforded the corresponding compound **17a** in 49% isolated yield under reflux for additional 1 h.

3. Conclusion

In conclusion, we have reported the first examples of the use of $Cu(NO_3)_2$ induced ring-opening reaction of 1,2-disubstituted cyclopropanols to synthesize α-methylene-γ-diketones in good yields. The reaction is easy and simple to perform under mild conditions. In addition, the cyclopropanols can be converted into diketones under acidic or basic solutions. When R^4 is a bulky alkyl group, both *p*-TsOH and NaOH can induce the ring-opening reaction in preference to formation of α-methyl-γ-diketones. When R^4 is aromatic group, the ring-opening of cyclopropanols takes place in preference to formation of δ-diketones under basic conditions. Furthermore, treatment of cyclopropanols with *p*-TsOH in methanol at reflux affords the corresponding 2,3,5-trisubstituted furans in high yields.

4. Experimental

4.1. General

All melting points were uncorrected. Chromatographic purification was performed on silica gel (100–200 mesh) and analytical thin layer chromatography (TLC) on silica gel 60-F_{254} (Qindao) was detected by fluorescence and then charring with 10% ethanolic solution of sulfuric acid. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured with a Bruker AC 300 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. High-resolution mass spectra (HRMS) were obtained with a Micromass GCT-TOF mass spectrometer. IR spectra were recorded as thin films or as solids in KBr pellets on a Perkin–Elmer FT210 spectrophotometer.

4.2. General procedure for $Cu(NO_3)_2$-mediated ring-opening of 1,2-disubstituted cyclopropanols

To a round-bottomed flask containing a stirring bar were added $Cu(NO_3)_2 \cdot 3H_2O$ (217 mg, 0.9 mmol), 1,2-substituted cyclopropanol **7a** (57 mg, 0.3 mmol), and 2 mL of methanol sequentially. After stirring at room temperature for 2 h, the reaction mixture was concentrated under reduced pressure on a rotary evaporator, and water (4 mL) was added. The mixture was extracted with diethyl ether (3×10 mL). The combined organic layers were washed twice with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography with petroleum ether/EtOAc (25:1–10:1) to afford 51 mg (90%) of **8a**.

4.2.1. 3-Methylene-1-phenyl-pentane-1,4-dione (8a). Light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.90 (d, *J*=7.2 Hz, 2H), 7.49 (t, *J*=7.2 Hz, 1H), 7.40 (t, *J*=7.2 Hz, 2H), 6.16 (s, 1H), 5.86 (s, 1H), 3.89 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 198.8, 197.2, 143.4, 136.6, 133.3, 128.7, 128.4, 128.3, 40.8, 25.4. IR (neat; cm^{-1}): ν 1674, 1636. HRMS (EI): calcd for $C_{12}H_{12}O_2$ (M^+), 188.0837; found, 188.0844.

4.2.2. 3-Methylene-1-*p*-tolyl-pentane-1,4-dione (8b). White solid (48 mg, 80% yield). Mp: 64–65 °C. ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.82 (d, *J*=7.6 Hz, 2H), 7.21 (d, *J*=7.6 Hz, 2H), 6.17 (s, 1H), 5.87 (s, 1H), 3.89 (s, 2H), 2.36 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 198.8, 196.9, 144.1, 143.6, 134.2, 129.4, 128.5, 128.1, 40.6, 25.5, 21.7. IR (KBr; cm^{-1}): ν 1673, 1606. HRMS (EI): calcd for $C_{13}H_{14}O_2$ (M^+), 202.0994; found, 202.0993.

4.2.3. 1-(4-Methoxy-phenyl)-3-methylene-pentane-1,4-dione (8c). Light yellow solid (61 mg, 93% yield). Mp: 51–53 °C. ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.89 (dd, *J*=6.9, 2.0 Hz, 2H), 6.86 (dd, *J*=6.9, 2.0 Hz, 2H), 6.14 (s, 1H), 5.85 (s, 1H), 3.85 (s, 2H), 3.79 (s, 3H), 2.34 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 198.9, 195.8, 163.7, 143.6, 130.7, 130.6, 129.7, 128.1, 113.9, 55.6, 40.4, 25.5. IR (KBr; cm^{-1}): ν 1679, 1603.1. HRMS (EI): calcd for $C_{13}H_{14}O_3$ (M^+), 218.0943; found, 218.0942.

4.2.4. 1-(4-Chloro-phenyl)-3-methylene-pentane-1,4-dione (8d). Oil (57 mg, 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.88 (d, *J*=8.6 Hz, 2H), 7.40 (d, *J*=8.6 Hz, 2H), 6.21 (s, 1H), 5.91 (s, 1H), 3.87 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 198.7, 196.1, 143.2, 139.8, 135.0, 129.8, 129.0, 128.6, 40.7, 25.4. IR (neat; cm^{-1}): ν 1675, 1587. HRMS (EI): calcd for $C_{12}H_{11}O_2Cl$ (M^+), 222.0448; found, 222.0439.

4.2.5. 1-(4-Fluoro-phenyl)-3-methylene-pentane-1,4-dione (8e). Oil (49 mg, 80% yield). ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.95–7.90 (m, 2H), 7.08–7.03 (m, 2H), 6.17 (s, 1H), 5.88 (s, 1H), 3.85 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 198.7, 195.6, 165.9 (d), 143.2, 133.1 (d), 31.1 (d), 128.4, 115.7 (d), 40.6, 25.4. IR (neat; cm^{-1}): ν 1675, 1597. HRMS (EI): calcd for $C_{12}H_{11}O_2F$ (M^+), 206.0743; found, 206.0745.

4.2.6. 1-(3,4-Dimethoxy-phenyl)-3-methylene-pentane-1,4-dione (8f). Light yellow solid (56 mg, 75% yield). Mp: 66–68 °C. ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.56 (dd, *J*=8.4, 2.0 Hz, 1H), 7.45 (d, *J*=2.0 Hz, 1H), 6.80 (d, *J*=8.4 Hz, 1H), 6.15 (s, 1H), 5.86 (s, 1H), 3.88 (s, 3H), 3.86 (s, 2H), 3.85 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 198.9, 195.9, 153.5, 149.1, 143.6, 129.9, 128.1, 123.2, 110.6, 110.2, 56.2, 56.1, 40.3, 25.5. IR (KBr; cm^{-1}): ν 1672, 1587. HRMS (EI): calcd for $C_{14}H_{16}O_4$ (M^+), 248.1049; found, 248.1046.

4.2.7. 1-(4-Methoxy-phenyl)-3-methylene-heptane-1,4-dione (8g). Solid (57 mg, 77% yield). Mp: 41–43 °C. ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.89 (dd, *J*=8.7, 1.5 Hz, 2H), 6.87 (dd, *J*=8.7, 1.5 Hz, 2H), 6.13 (s, 1H), 5.80 (s, 1H), 3.84 (s, 2H), 3.79 (s, 3H), 2.67 (t, *J*=7.2 Hz, 2H), 1.61 (sextet, *J*=7.2 Hz, 2H), 0.88 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 201.2, 196.0, 163.6, 143.4, 130.7, 129.7, 126.9, 113.8, 55.5, 40.7, 39.3, 17.9, 13.9. IR (KBr; cm^{-1}): ν 2932, 1674, 1595, 1263, 1028, 822. HRMS (EI): calcd for $C_{15}H_{18}O_3$ (M^+), 246.1256; found, 246.1264.

4.2.8. 4-(4-Methoxy-phenyl)-2-methylene-1-phenyl-butane-1,4-dione (8h). Light yellow solid (56 mg, 67% yield). Mp: 55–57 °C. ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.92 (d, *J*=7.2 Hz, 2H), 7.81 (d, *J*=7.2 Hz, 2H), 7.48

(t, J=7.2 Hz, 1H), 7.38 (t, J=7.2 Hz, 2H), 6.88 (d, J=7.2 Hz, 2H), 5.88 (s, 1H), 5.72 (s, 1H), 4.11 (s, 2H), 3.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 197.5, 195.8, 163.8, 142.7, 137.4, 132.3, 130.7, 130.0, 129.5, 128.4, 128.2, 113.9, 55.5, 42.4. IR (KBr; cm^{-1}): ν 1654, 1597. HRMS (EI): calcd for $C_{18}H_{16}O_3$ (M^+), 280.1099; found, 280.1106.

4.2.9. 1,4-Bis(4-methoxy-phenyl)-2-methylene-butane-1,4-dione (8i). Colorless crystals (71 mg, 76% yield). Mp: 75–77 °C. ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.93–7.84 (m, 4H), 6.89–6.84 (m, 4H), 5.79 (s, 1H), 5.66 (s, 1H), 4.10 (s, 2H), 3.80 (s, 3H), 3.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 196.2, 195.9, 163.7, 163.2, 142.8, 132.4, 130.7, 130.4, 130.0, 129.6, 126.7, 113.9, 113.5, 55.5, 42.8. IR (KBr; cm^{-1}): ν 2938, 1674, 1646, 1603, 1255, 1170. HRMS (EI): calcd for $C_{19}H_{18}O_4$ (M^+), 310.1205; found, 310.1204.

4.2.10. 2-Methylene-1,4-diphenyl-butane-1,4-dione (8j). Colorless solid (55 mg, 73% yield). Mp: 40–42 °C. ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.92 (d, J=8.1 Hz, 2H), 7.81 (d, J=8.1 Hz, 2H), 7.48 (m, 2H), 7.42–7.38 (m, 4H), 5.90 (s, 1H), 5.75 (s, 1H), 4.16 (s, 2H). ^{13}C NMR (300 MHz, $CDCl_3$; δ, ppm): 197.4, 197.3, 142.5, 137.4, 136.5, 133.4, 132.4, 130.0, 128.7, 128.4, 128.3, 42.7. IR (KBr; cm^{-1}): ν 1683, 1658. HRMS (EI): calcd for $C_{17}H_{14}O_2$ (M^+), 250.0994; found, 250.0989.

4.2.11. 1-(4-Chloro-phenyl)-2-methylene-4-phenyl-butane-1,4-dione (8k). Colorless solid (76 mg, 89% yield). Mp: 65–67 °C. ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.90 (d, J=8.4 Hz, 2H), 7.80 (d, J=8.4 Hz, 2H), 7.49 (t, J=8.4 Hz, 1H), 7.40–7.18 (m, 4H), 5.88 (s, 1H), 5.70 (s, 1H), 4.17 (s, 2H). ^{13}C NMR (300 MHz, $CDCl_3$; δ, ppm): 197.2, 196.2, 142.4, 138.9, 136.4, 133.5, 131.4, 130.3, 128.8, 128.6, 128.4, 128.3, 42.6. IR (KBr; cm^{-1}): ν 2967, 2918, 1682, 1660, 1589, 1269, 1091, 1014, 800. HRMS (EI): calcd for $C_{17}H_{13}O_2Cl$ (M^+), 284.0604; found, 284.0608.

4.2.12. 4-(4-Chloro-phenyl)-2-methylene-1-phenyl-butane-1,4-dione (8l). Colorless solid (64 mg, 75% yield). Mp: 67–69 °C. ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.88 (dd, J=6.9, 2.4 Hz, 2H), 7.79 (d, J=7.2 Hz, 2H), 7.48 (t, J=7.2 Hz, 1H), 7.38 (m, 4H), 5.91 (s, 1H), 5.77 (s, 1H), 4.11 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 197.2, 196.1, 142.1, 139.9, 137.3, 134.8, 132.4, 131.4, 129.9, 129.8, 129.1, 128.3, 42.6. IR (KBr; cm^{-1}): ν 2924, 1696, 1600, 1085. HRMS (EI): calcd for $C_{17}H_{13}O_2Cl$ (M^+), 284.0604; found, 284.0599.

4.2.13. 3-Methylene-1-thiophen-2-yl-pentane-1,4-dione (8m). Light yellow oil (44 mg, 75% yield). ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.71 (dd, J=3.8, 1.0 Hz, 1H), 7.57 (dd, J=5.0, 1.0 Hz, 1H), 7.06 (dd, J=5.0, 3.8 Hz, 1H), 6.18 (s, 1H), 5.93 (s, 1H), 3.83 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 198.6, 189.9, 143.8, 142.8, 132.6, 128.6, 128.2, 41.1, 25.4. IR (neat; cm^{-1}): ν 1659, 1605. HRMS (EI): calcd for $C_{10}H_{10}O_2S$ (M^+), 194.0402; found, 194.0397.

4.2.14. 1-(2-Methoxy-phenyl)-2-methylene-pentane-1,4-dione (8n). Oil (50 mg, 76% yield). ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.33 (td, J=7.5, 1.5 Hz, 1H), 7.25 (dd, J=7.5, 1.5 Hz, 1H), 6.91 (q, J=7.5 Hz, 2H), 5.92 (s, 1H), 5.75 (s, 1H), 3.72 (s, 3H), 3.46 (s, 2H), 2.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 205.6, 197.1, 157.2, 143.2, 131.7, 131.6, 129.4, 128.3, 120.3, 111.5, 55.8, 45.5, 29.9. IR (neat; cm^{-1}): ν 1716, 1659. HRMS (EI): calcd for $C_{13}H_{14}O_3$ (M^+), 218.0943; found, 218.0934.

4.2.15. 4-Methylene-octane-3,6-dione (8o). Oil (30 mg, 64% yield). ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 6.09 (s, 1H), 5.76 (s, 1H), 3.29 (s, 2H), 2.69 (q, J=7.2 Hz, 2H), 2.47 (q, J=7.2 Hz, 2H), 1.03 (t, J=7.2 Hz, 3H), 0.98 (t, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 208.8, 202.1, 143.3, 127.4, 45.3, 36.5, 30.9, 8.7, 8.3. IR (neat; cm^{-1}): ν 1718, 1682. HRMS (EI): calcd for $C_9H_{14}O_2$ (M^+), 154.0994; found, 154.0993

4.2.16. 6,6-Dimethyl-3-methylene-heptane-2,5-dione (8p). Oil (32 mg, 63% yield). ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 6.08 (s, 1H), 5.74 (s, 1H), 3.41 (s, 2H), 2.29 (s, 3H), 1.12 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 212.8, 198.9, 143.8, 127.9, 44.4, 39.4, 26.6, 25.4. IR (neat; cm^{-1}): ν 1709, 1680. HRMS (EI): calcd for $C_{10}H_{16}O_2$ (M^+), 168.1150; found, 168.1152.

4.3. General procedure for acid-catalyzed ring-opening of 1,2-disubstituted cyclopropanols

A 25 mL round-bottomed flask was equipped with a stirring bar and charged with methylene chloride (3 mL). p-TsOH·H_2O (171 mg, 0.9 mmol) and 1,2-substituted cyclopropanol **7a** (57 mg, 0.3 mmol) were added. The reaction mixture was stirred at room temperature for 2 h. Water (3 mL) was added and the mixture was extracted with diethyl ether (3×10 mL). The combined organic layers were washed twice with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography with petroleum ether/EtOAc (20:1–10:1) to afford **9a** (9 mg) and **10a** (41 mg) in 16 and 72% yields, respectively.

4.3.1. 1-Phenyl-hexane-1,5-dione (9a). White solid. Mp: 65–67 °C (lit.[18] mp: 66–67 °C). ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.88 (dd, J=7.8 Hz, 2H), 7.47 (t, J=7.8 Hz, 1H), 7.38 (t, J=7.8 Hz, 2H), 2.94 (t, J=7.0 Hz, 2H), 2.50 (t, J=7.0 Hz, 2H), 2.08 (s, 3H), 1.97 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 208.6, 199.9, 136.9, 133.2, 128.7, 128.1, 42.7, 37.5, 30.1, 18.3. IR (KBr; cm^{-1}): ν 1712, 1670. HRMS (EI): calcd for $C_{12}H_{14}O_2$ (M^+), 190.0994; found, 190.1001.

4.3.2. 3-Methyl-1-phenyl-pentane-1,4-dione (10a). Light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.96 (d, J=8.1 Hz, 2H), 7.53 (t, J=8.1 Hz, 1H), 7.44 (t, J=8.1 Hz, 2H), 3.54 (dd, J=18.0, 9.0 Hz, 1H), 3.27–3.20 (m, 1H), 2.95 (dd, J=18.0, 4.5 Hz, 1H), 2.29 (s, 3H), 1.20 (d, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 211.5, 198.6, 136.7, 133.2, 128.6, 128.1, 41.9, 41.8, 28.7, 16.8. IR (neat; cm^{-1}): ν 1712, 1682. HRMS (EI): calcd for $C_{12}H_{14}O_2$ (M^+), 190.0994; found, 190.0987.

4.3.3. 1-*p*-Tolyl-hexane-1,5-dione (9b). White solid (14 mg, 23% yield). Mp: 74–76 °C. ^{1}H NMR (300 MHz,

$CDCl_3$; δ, ppm): 7.79 (d, *J*=8.1 Hz, 2H), 7.16 (d, *J*=8.1 Hz, 2H), 2.91 (t, *J*=7.0 Hz, 2H), 2.49 (d, *J*=7.0 Hz, 2H), 2.33 (s, 3H), 2.07 (s, 3H), 1.93 (quintet, *J*=7.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 208.6, 199.5, 143.9, 134.5, 129.4, 128.3, 42.8, 37.4, 30.0, 21.7, 18.4. IR (neat; cm^{-1}): ν 1710, 1674. HRMS (EI): calcd for $C_{13}H_{16}O_2$ (M^+), 204.1150; found, 204.1159.

4.3.4. 3-Methyl-1-*p*-tolyl-pentane-1,4-dione (10b). Light yellow oil (46 mg, 75% yield). ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.79 (d, *J*=8.1 Hz, 2H), 7.16 (d, *J*=8.1 Hz, 2H), 3.44 (dd, *J*=18.0, 8.7 Hz, 1H), 3.19–3.12 (m, 1H), 2.87 (dd, *J*=18.0, 4.8 Hz, 1H), 2.33 (s, 3H), 2.23 (s, 3H), 1.13 (d, *J*=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 211.6, 198.2, 144.0, 134.2, 129.3, 128.2, 41.85, 41.81, 28.7, 21.6, 16.8. IR (neat; cm^{-1}): ν 1718, 1682. HRMS (EI): calcd for $C_{13}H_{16}O_2$ (M^+), 204.1150; found, 204.1145.

4.3.5. 1-(4-Methoxy-phenyl)-hexane-1,5-dione (9c). White solid (12 mg, 18% yield). Mp: 80–81 °C. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.88 (d, *J*=9.0 Hz, 2H), 6.87 (d, *J*=9.0 Hz, 2H), 3.79 (s, 3H), 2.88 (t, *J*=7.2 Hz, 2H), 2.49 (t, *J*=7.2 Hz, 2H), 2.07 (s, 3H), 1.93 (quintet, *J*=7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 208.6, 198.4, 163.6, 130.4, 130.1, 113.8, 55.6, 42.8, 37.2, 30.0, 18.6. IR (KBr; cm^{-1}): ν 1710, 1668. HRMS (EI): calcd for $C_{13}H_{16}O_3$ (M^+), 220.1099; found, 220.1097.

4.3.6. 1-(4-Methoxy-phenyl)-3-methyl-pentane-1,4-dione (10c). Light yellow crystals (48 mg, 72% yield). Mp: 51–53 °C. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.87 (dd, *J*=6.9, 2.0 Hz, 2H), 6.85 (dd, *J*=6.8, 2.0 Hz, 2H), 3.79 (s, 3H), 3.41 (dd, *J*=18.0, 8.6 Hz, 1H), 3.21–3.17 (m, 1H), 2.28 (dd, *J*=18.0, 4.8 Hz, 1H), 2.22 (s, 3H), 1.13 (d, *J*=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 211.8, 197.2, 163.7, 130.4, 129.9, 113.8, 55.5, 41.9, 41.6, 28.8, 16.8. IR (KBr; cm^{-1}): ν 2924, 1711, 1672, 1599, 1260. HRMS (EI): calcd for $C_{13}H_{16}O_3$ (M^+), 220.1099; found, 220.1097.

4.3.7. 1-Thiophen-2-yl-hexane-1,5-dione (9d). White solid (12 mg, 20% yield). Mp: 30–32 °C. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.66 (dd, *J*=3.9, 0.9 Hz, 1H), 7.56 (dd, *J*=4.8, 0.9 Hz, 1H), 7.05 (dd, *J*=4.8, 3.9 Hz, 1H), 2.88 (t, *J*=7.2 Hz, 2H), 2.50 (t, *J*=7.2 Hz, 2H), 2.07 (s, 3H), 1.94 (quintet, *J*=7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 208.4, 192.8, 144.3, 133.6, 132.0, 128.2, 42.6, 38.2, 30.0, 18.7. IR (KBr; cm^{-1}): ν 1715, 1600. HRMS (EI): calcd for $C_{10}H_{12}O_2S$ (M^+), 196.0588; found, 196.0564.

4.3.8. 3-Methyl-1-thiophen-2-yl-pentane-1,4-dione (10d). Light yellow oil (46 mg, 78% yield). ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.67 (d, *J*=3.9 Hz, 1H), 7.56 (d, *J*=5.1 Hz, 1H), 7.05 (dd, *J*=4.8, 3.9 Hz, 1H), 3.40 (dd, *J*=17.4, 8.4 Hz, 1H), 3.18–3.13 (m, 1H), 2.83 (dd, *J*=17.4, 4.8 Hz, 1H), 2.21 (s, 3H), 1.14 (d, *J*=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 211.3, 191.5, 143.9, 133.7, 132.1, 128.2, 42.2, 41.9, 31.6, 28.7, 16.8. IR (neat; cm^{-1}): ν 1710, 1659. HRMS (EI): calcd for $C_{10}H_{12}O_2S$ (M^+), 196.0558; found, 196.0554.

4.3.9. 1-(4-Methoxy-phenyl)-octane-1,5-dione (9e). White solid (18 mg, 24% yield). Mp: 66–67 °C. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.88 (d, *J*=9.0 Hz, 2H), 6.87 (d, *J*=9.0 Hz, 2H), 3.79 (s, 3H), 2.88 (t, *J*=7.0 Hz, 2H), 2.45 (t, *J*=7.0 Hz, 2H), 2.31 (t, *J*=7.0 Hz, 2H), 1.93 (quintet, *J*=7.2 Hz, 2H), 1.54 (td, *J*=7.0 Hz, 2H), 0.84 (t, *J*=7.0 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 208.8, 198.5, 163.6, 130.4, 130.1, 113.8, 55.5, 44.8, 41.8, 37.3, 18.6, 17.4, 13.8. IR (KBr; cm^{-1}): ν 1710, 1666. HRMS (EI): calcd for $C_{15}H_{20}O_3$ (M^+), 248.1412; found, 248.1417.

4.3.10. 1-(4-Methoxy-phenyl)-3-methyl-heptane-1,4-dione (10e). Light yellow oil (49 mg, 66% yield). ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.87 (dd, *J*=6.9, 2.1 Hz, 2H), 6.85 (dd, *J*=6.9, 2.1 Hz, 2H), 3.79 (s, 3H), 3.43 (dd, *J*=17.6, 9.0 Hz, 1H), 3.19–3.11 (m, 1H), 2.83 (dd, *J*=17.6, 4.5 Hz, 1H), 2.51–2.50 (m, 2H), 1.60–1.53 (m, 2H), 1.10 (d, *J*=7.2 Hz, 3H), 0.86 (t, *J*=7.2 Hz, 3H). ^{13}C NMR (75 MHz, CDCl3; δ, ppm): 213.9, 197.3, 163.6, 130.4, 129.9, 113.8, 55.5, 43.5, 41.6, 41.2, 17.1, 17.0, 13.9. IR (neat; cm^{-1}): ν 2933, 1711, 1675, 1601, 1260. HRMS (EI): calcd for $C_{15}H_{20}O_3$ (M^+), 248.1412; found, 248.1413.

4.4. General procedure for preparation of 2,3,5-trisubstituted furans

A 25 mL round-bottomed flask was equipped with a stirring bar and charged with methanol (3 mL). *p*-$TsOH\cdot H_2O$ (171 mg, 0.9 mmol) and 1,2-disubstituted cyclopropanol **7a** (57 mg, 0.3 mmol) were added under nitrogen. The reaction mixture was stirred for 5 h under nitrogen at reflux. Then the reaction mixture was concentrated under reduced pressure on the rotary evaporator. To the residue was added water (5 mL) and the solution extracted with diethyl ether (3×10 mL). The combined organic layers were washed twice with brine and then dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography with petroleum ether/EtOAc (50:1–25:1), affording **11a** in (47 mg) 91% yield.

4.4.1. 2,3-Dimethyl-5-phenyl-furan (11a). Light yellow oil. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.52 (dd, *J*=8.4, 1.2 Hz, 2H), 7.25 (t, *J*=8.4 Hz, 1H), 7.11 (td, *J*=8.4, 1.2 Hz, 2H), 6.35 (s, 1H), 2.19 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 151.0, 147.4, 131.4, 128.6, 126.6, 123.4, 116.2, 108.5, 11.6, 10.0. IR (neat; cm^{-1}): ν 1601, 1555, 1260. HRMS (EI): calcd for $C_{12}H_{12}O$ (M^+), 172.0888; found, 172.0891.

4.4.2. 2,3-Dimethyl-5-*p*-tolyl-furan (11b). White solid (50 mg, 90% yield). Mp: 52–54 °C. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.40 (d, *J*=8.1 Hz, 2H), 7.06 (d, *J*=8.1 Hz, 2H), 6.28 (s, 1H), 2.24 (s, 3H), 2.17 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 151.2, 147.0, 136.4, 129.3, 128.7, 123.3, 116.1, 107.7, 21.3, 11.5, 10.0. IR (KBr; cm^{-1}): ν 2924, 1554, 1504, 1055, 808. HRMS (EI): calcd for $C_{13}H_{14}O$ (M^+), 186.1045; found, 186.1053.

4.4.3. 5-(4-Methoxy-phenyl)-2,3-dimethyl-furan (11c). White solid (56 mg, 92% yield). Mp: 54–56 °C. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.45 (dd, *J*=6.9, 2.1 Hz, 2H), 6.80 (dd, *J*=6.9, 2.1 Hz, 2H), 6.22 (s, 1H), 3.74 (s, 3H), 2.18 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 158.6, 151.1, 146.6, 124.7, 124.6, 116.0, 114.1,

106.9, 55.4, 29.8, 11.5, 10.0. IR (KBr; cm^{-1}): ν 2920, 2849, 1612, 1584, 1500, 1248. HRMS (EI): calcd for $C_{13}H_{14}O_2$ (M^+), 202.0994; found, 202.0997.

4.4.4. 5-(4-Chloro-phenyl)-2,3-dimethyl-furan (11d). White solid (54 mg, 87% yield). Mp: 87–89 °C. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.45 (d, J=8.4 Hz, 2H), 7.20 (d, J=8.4 Hz, 2H), 6.35 (s, 1H), 2.19 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 150.0, 147.8, 132.0, 129.9, 128.8, 124.5, 116.4, 109.0, 11.6, 10.0. IR (KBr; cm^{-1}): ν 2963, 2923, 1547, 1418, 1261, 1088, 808. HRMS (EI): calcd for $C_{12}H_{11}OCl$ (M^+), 206.0498; found, 206.0491.

4.4.5. 5-(4-Fluoro-phenyl)-2,3-dimethyl-furan (11e). Oil (51 mg, 89% yield). Mp: 67–69 °C. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.49–7.44 (m, 2H), 6.97–6.92 (m, 2H), 6.28 (s, 1H), 2.18 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 161.8 (d), 150.2, 147.4, 127.8 (d), 125.0, 124.8 (d), 116.2, 115.6 (d), 108.1 (d), 11.5, 10.0. IR (neat; cm^{-1}): ν 2924, 1729, 1598, 1496, 1232, 1096. HRMS (EI): calcd for $C_{12}H_{11}OF$ (M^+), 190.0794; found, 190.0785.

4.4.6. 5-(4-Methoxy-phenyl)-3-methyl-2-propyl-furan (11f). Oil (48 mg, 69% yield). ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.45 (d, J=9.0 Hz, 2H), 6.81 (d, J=9.0 Hz, 2H), 6.22 (s, 1H), 3.73 (s, 3H), 2.49 (t, J=7.2 Hz, 2H), 1.89 (s, 3H), 1.59 (sextet, J=7.2 Hz, 2H), 0.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 158.6, 151.0, 150.7, 124.7, 116.0, 114.1, 106.8, 55.4, 28.1, 22.1, 13.8, 10.0. IR (neat; cm^{-1}): ν 2960, 2925, 2558, 1500, 1248, 1034. HRMS (EI): calcd for $C_{15}H_{18}O_2$ (M^+), 230.1307; found, 230.1315.

4.4.7. 5-(4-Methoxy-phenyl)-3-methyl-2-phenethyl-furan (11g). White solid (58 mg, 66% yield). Mp: 94–96 °C. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.45 (d, J=8.7 Hz, 2H), 7.22–7.08 (m, 2H), 6.84 (d, J=8.7 Hz, 2H), 6.20 (s, 1H), 3.75 (s, 3H), 2.91–2.80 (m, 4H), 1.74 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 158.7, 151.2, 149.5, 141.6, 128.6, 128.4, 126.0, 124.8, 124.6, 116.6, 114.2, 106.9, 55.4, 35.1, 28.3, 9.8. IR (KBr; cm^{-1}): ν 2932, 1504, 1247, 1208, 808. HRMS (EI): calcd for $C_{20}H_{20}O_2$ (M^+), 292.1463; found, 292.155.

4.4.8. 5-(3,4-Dimethoxy-phenyl)-2-ethyl-3-methyl-furan (11h). Colorless oil (59 mg, 80% yield). ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.10 (dd, J=8.4, 1.8 Hz, 1H), 7.05 (d, J=1.8 Hz, 1H), 6.79 (d, J=8.4 Hz, 1H), 6.25 (s, 1H), 3.86 (s, 3H), 3.81 (s, 3H), 2.57 (q, J=7.5 Hz, 2H), 1.91 (s, 3H), 1.17 (t, J=7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 152.0, 150.9, 149.2, 148.2, 124.9, 116.1, 115.2, 111.6, 107.3, 107.0, 56.1, 56.0, 19.6, 13.2, 9.9. IR (neat; cm^{-1}): ν 2932, 1588, 1556, 1506, 1460, 1265, 1027. HRMS (EI): calcd for $C_{15}H_{18}O_3$ (M^+), 246.1256; found, 246.1258.

4.4.9. 2,3-Dimethyl-5-thiophen-2-yl-furan (11i). Light yellow oil (40 mg, 75% yield). ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.06 (m, 2H), 7.91 (dd, J=5.0, 3.8 Hz, 1H), 6.21 (s, 1H), 2.17 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 147.1, 146.6, 134.5, 127.6, 123.2, 121.5, 116.2, 108.6, 11.5, 9.9. IR (neat; cm^{-1}): ν 2922, 1636, 1429, 1261, 1083, 1026. HRMS (EI): calcd for $C_{10}H_{10}OS$ (M^+), 178.0452; found, 178.0459.

4.4.10. 2-(2-Methoxy-phenyl)-3,5-dimethyl-furan (11j). Oil (25 mg, 41% yield). ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.31 (dd, J=7.5, 1.7 Hz, 1H), 7.22 (td, J=7.5, 1.7 Hz, 1H), 6.91 (q, J=7.5 Hz, 2H), 5.86 (s, 1H), 3.76 (s, 3H), 2.23 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 156.7, 151.1, 144.9, 130.6, 129.0, 121.1, 120.5, 118.8, 111.4, 110.3, 55.6, 13.7, 11.3. IR (neat; cm^{-1}): ν 2926, 1730, 1463, 1261, 910. HRMS (EI): calcd for $C_{13}H_{14}O_2$ (M^+), 202.0994; found, 202.0991.

4.4.11. 2-Methyl-2,5-diphenyl-furan (11k). White solid (35 mg, 50% yield). Mp: 30–32 °C. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.65 (d, J=8.4 Hz, 4H), 7.35–7.26 (m, 4H), 7.22–7.15 (m, 2H), 6.51 (s, 1H), 2.23 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 151.8, 148.3, 131.9, 130.9, 128.8, 128.7, 126.8, 125.3, 123.8, 118.7, 110.9, 12.2. IR (neat; cm^{-1}): ν 2921, 1595, 1493, 1261, 763. HRMS (EI): calcd for $C_{17}H_{14}O$ (M^+), 234.1045; found, 234.1037.

4.5. General procedure for base-catalyzed ring-opening of 1,2-disubstituted cyclopropanols

To a magnetically stirred solution of sodium hydroxide (22 mg, 0.9 mmol) in methanol (2 mL) was added the cyclopropanol (**7**, R^3=R^4=Ph) (76 mg, 0.3 mmol). The reaction mixture was stirred at room temperature for 1 h. The methanol solvent was removed on the rotary evaporator. To the residue was added water (3 mL) and the solution extracted with diethyl ether (3×10 mL). The combined organic layers were washed with brine and then dried over anhydrous magnesium sulfate, filtered, and concentrated on the rotary evaporator. The residue was purified by silica gel chromatography with petroleum ether/EtOAc (20:1–10:1), affording **9f** (61 mg) and **10f** (10 mg) in 81 and 13% yields, respectively.

4.5.1. 1,5-Diphenyl-pentane-1,5-dione (9f). White crystals (61 mg, 81% yield). Mp: 64–65 °C (lit.[18] mp: 65–66 °C). ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.89 (d, J=7.2 Hz, 4H), 7.48 (t, J=7.2 Hz, 2H), 7.38 (t, J=7.2 Hz, 4H), 3.05 (t, J=6.9 Hz, 4H), 2.13 (quintet, J=6.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 199.9, 137.0, 133.2, 128.7, 128.2, 37.7, 18.9. IR (KBr; cm^{-1}): ν 1682.

4.5.2. 2-Methyl-1,4-diphenyl-butane-1,4-dione (10f). White solid (10 mg, 13% yield). Mp: 81–83 °C. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.97 (d, J=7.2 Hz, 2H), 7.88 (d, J=7.2 Hz, 2H), 7.48–7.34 (m, 6H), 4.13–4.06 (m, 1H), 3.65 (dd, J=18.0, 8.4 Hz, 1H), 3.05 (dd, J=18.0, 4.8 Hz, 1H), 1.21 (d, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 203.5, 198.6, 136.8, 136.3, 133.3, 133.1, 128.8, 128.7, 128.6, 128.2, 42.5, 36.4, 18.1. IR (KBr; cm^{-1}): ν 1672, 1596. HRMS (EI): calcd for $C_{17}H_{16}O_2$ (M^+), 252.1150; found, 252.1155.

4.5.3. 1-(4-Methoxy-phenyl)-5-phenyl-pentane-1,5-dione (9g). Colorless crystals (68 mg, 80% yield). Mp: 78–79 °C. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.92–7.88 (m, 4H), 7.41 (t, J=7.2 Hz, 1H), 7.38 (t, J=7.2 Hz, 2H), 6.87 (d, J=9.0 Hz, 2H), 3.79 (s, 3H), 3.01 (m, 4H), 2.12 (quintet, J=6.9 Hz, 2H). ^{13}C NMR (75 MHz, CDCl3; δ, ppm): 200.2, 198.5, 163.5, 137.0, 133.1, 130.4, 130.1,

128.6, 128.1, 113.8, 55.5, 37.7, 37.3, 19.0. IR (KBr; cm^{-1}): ν 1683, 1658. HRMS (EI): calcd for $C_{18}H_{18}O_3$ (M^+), 282.1256; found, 282.1261.

4.5.4. 4-(4-Methoxy-phenyl)-2-methyl-1-phenyl-butane-1,4-dione (10g). Colorless crystals (12 mg, 14% yield). Mp: 87–88 °C. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.98 (d, J=7.2 Hz, 2H), 7.90 (d, J=9.0 Hz, 2H), 7.47 (t, J=9.0 Hz, 1H), 7.41 (t, J=9.0 Hz, 2H), 6.86 (d, J=7.2 Hz, 2H), 4.13–4.06 (m, 1H), 3.79 (s, 3H), 3.60 (dd, J=17.7, 8.1 Hz, 1H), 3.02 (dd, J=17.7, 5.1 Hz, 1H), 1.21 (d, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 203.7, 197.1, 163.7, 133.0, 130.5, 128.8, 128.6, 113.8, 55.6, 42.1, 36.5, 18.0. IR (KBr; cm^{-1}): ν 2962, 1729, 1674, 1598, 1260, 1094, 1022, 799. HRMS (EI): calcd for $C_{18}H_{18}O_3$ (M^+), 282.1256; found, 282.1249.

4.5.5. 1,5-Bis(4-methoxy-phenyl)-pentane-1,5-dione (9h). Colorless crystals (75 mg, 80% yield); Mp: 95–96 °C. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.91 (d, J=9.0 Hz, 2H), 6.88 (d, J=9.0 Hz, 2H), 3.80 (s, 3H), 2.99 (t, J=6.9 Hz, 2H), 2.11 (quintet, J=6.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 198.6, 163.6, 130.5, 130.2, 113.8, 55.6, 37.5, 19.4; IR (neat; cm^{-1}): ν 1682. HRMS (EI): calcd for $C_{19}H_{20}O_4$ (M^+), 312.1362; found, 312.1363.

4.5.6. 1,4-Bis(4-methoxy-phenyl)-2-methyl-butane-1,4-dione (10h). White solid (14 mg, 15% yield). Mp: 143–145 °C. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.98 (d, J=9.0 Hz, 2H), 7.90 (d, J=9.0 Hz, 2H), 6.90 (d, J=9.0 Hz, 2H), 6.84 (d, J=9.0 Hz, 2H), 4.08 (m, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.57 (dd, J=17.7, 8.1 Hz, 1H), 2.95 (dd, J=17.7, 5.1 Hz, 1H), 1.20 (d, J=6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 202.2, 197.2, 163.7, 163.6, 130.9, 130.5, 130.1, 129.2, 113.9, 113.8, 55.6, 42.1, 36.1, 29.8, 18.3. IR (KBr; cm^{-1}): ν 1674, 1595. HRMS (EI): calcd for $C_{19}H_{20}O_4$ (M^+), 312.1362; found, 312.1368.

4.5.7. 1-(3,4-Dimethoxy-phenyl)-5-phenyl-pentane-1,5-dione (9i). Colorless crystals (61 mg, 65% yield). Mp: 69–70 °C. ^1H NMR (300 MHz, $CDCl_3$; δ, ppm): 7.92 (d, J=8.4 Hz, 2H), 7.59 (dd, J=8.4, 2.0 Hz, 2H), 7.50 (t, J=8.4 Hz, 1H), 7.41 (t, J=8.4 Hz, 2H), 6.85 (d, J=8.4 Hz, 2H), 3.89 (s, 6H), 3.09–3.00 (m, 4H), 2.15 (quintet, J=7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 200.0, 198.6, 153.3, 149.1, 136.9, 133.1, 130.2, 128.6, 128.1, 122.8, 110.2, 110.1, 56.1, 56.0, 37.7, 37.2, 19.2. IR (KBr; cm^{-1}): ν 2960, 1730, 1676, 1261, 1022. HRMS (EI): calcd for $C_{19}H_{20}O_4$ (M^+), 312.1362; found, 312.1366.

4.5.8. 4-(3,4-Dimethoxy-phenyl)-2-methyl-1-phenyl-butane-1,4-dione (10i). White solid (14 mg, 15% yield). Mp: 65–66 °C. ^1H NMR (75 MHz, $CDCl_3$; δ, ppm): 8.00 (m, 2H), 7.57 (dd, J=8.4, 2.0 Hz, 1H), 7.48–7.42 (m, 4H), 6.83 (d, J=8.4 Hz, 1H), 4.14–4.07 (m, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 3.63 (dd, J=16.8, 8.4 Hz, 1H), 3.05 (dd, J=16.8, 4.8 Hz, 1H), 1.20 (d, J=7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$; δ, ppm): 203.7, 197.2, 153.5, 149.1, 136.3, 133.0, 130.1, 128.8, 128.7, 123.0, 110.3, 110.2, 56.2, 56.1, 42.1, 36.5, 29.8, 18.0. IR (KBr; cm^{-1}): ν 1730, 1670. HRMS (EI): calcd for $C_{19}H_{20}O_4$ (M^+), 312.1362; found, 312.1371.

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