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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b03266 • Publication Date (Web): 29 Jan 2020

Rhodium(III)-Catalyzed C-H Activation: A Cascade Approach for the Regioselective Synthesis of Fused Heterocyclic Lactone Scaffolds

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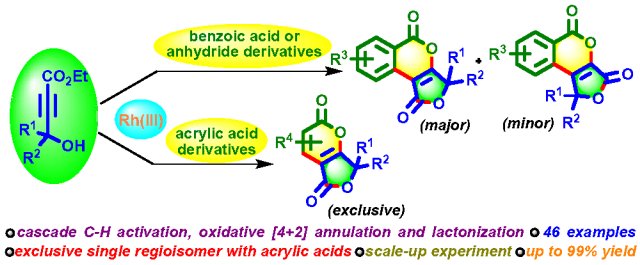
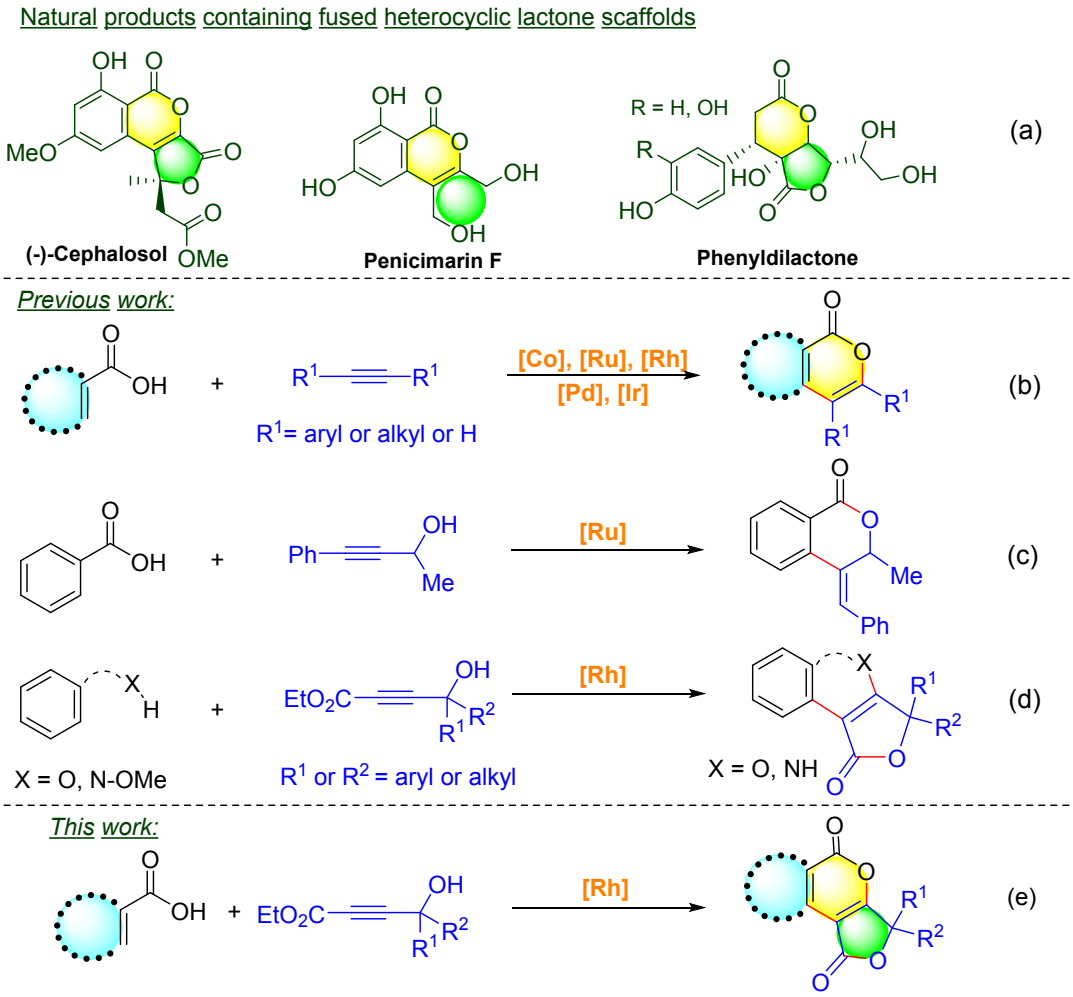


Abstract: A Rh(III)-catalyzed cascade C–H activation, regioselective [4+2] oxidative annulation, and lactonization of aromatic acids, anhydrides and acrylic acid derivatives with 4-hydroxy-2-alkynoates have been disclosed. This strategy leads to fused heterocyclic lactone scaffolds in a single step with moderate functional group tolerance, excellent site selectivity. Besides, in one step, an antipode of Cephalosol intermediate natural product that contains a tricyclic isocoumarin framework has been synthesized.

Introduction

α-Pyrone and isocoumarin, are privileged heterocycles found in many natural products and are key intermediates in synthesizing a few natural products and drug molecules (Scheme 1a).[1-3] Cephalosol is potent naturally occurring antimicrobial metabolites,[4] and there have been continued efforts for synthesizing these molecules.[5,6a,b] However, many of these methods require either prefunctionalized starting materials or multistep sequence.[5b,6] Thus, continued efforts are going on for avoiding multistep sequence to achieve the synthesis of these heterocyclic unsaturated lactones. Transition metal-catalyzed C-H bond activation has become a powerful tool in designing atom- and step-economical strategies.[7] In this context, Miura's group reported Rh(III)-catalyzed oxidative [4+2] annulation of benzoic acid[8] and acrylic acids[9] with internal alkynes. Later, several groups employed carboxylic acid directed strategies, using alkynes as coupling partners to synthesize isocoumarin and α-pyrone heterocycles (Scheme 1b).[10,11] In recent years, substantial advancement has been made using functionalized coupling partners to obtain desired functionalized molecules.[12] In this direction, Gooßen's group reported a carboxylate directed hydroarylation of alkynes followed by lactonization to obtain γ-alkylidene-δ-lactones (Scheme 1c).[13] Shi's and Fan's groups, independently, utilized functionalized alkyne as a coupling partner for synthesizing fused polycyclic quinolines[14a] and furanone heterocyclic compound,[14b] respectively (Scheme 1d). Recently, we reported a regioselective synthesis of furanone-fused naphthol derivatives using sulfoxonium ylide as a directing group with a functionalized alkyne.[16a] There are several reports on C-H functionalization reactions using a functionalized alkenes and alkynes for synthesizing polycyclic compounds in cascade fashion since they are efficient and step-economical.[15] As part of our efforts on C-H functionalization reactions,[16] an attempt was made for a one pot synthesis of fused heterocyclic lactone scaffolds using carboxylic acid with 4-hydroxyl-2-alkynoates (Scheme 1d). The key challenges associated with the reaction are, achieving the regioselectivity in the alkyne insertion, and compatibility of both the reactants at harsh conditions wherein acid, ester, and alcohol functionalities are involved. Despite the above challenges, this reaction led to the formation of a variety of tricyclic isocoumarin and bicyclic α-pyrone heterocyclic lactone derivatives with moderate functional group tolerance, and good to excellent regioselectivity.

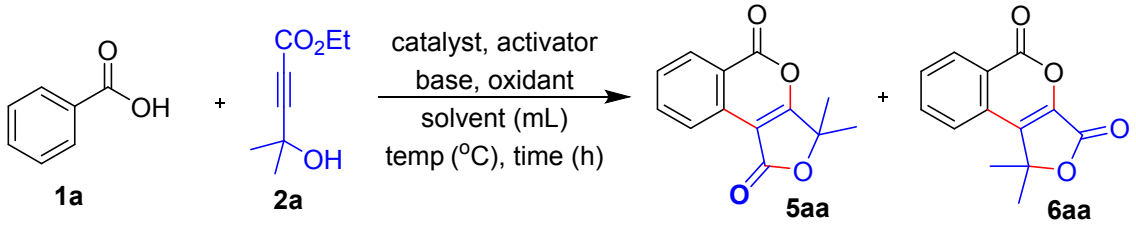
Scheme 1. Natural Products Containing Fused Heterocyclic Lactone Scaffolds and Comparison of Previous Works



The reaction of benzoic acid **1a** with ethyl 4-hydroxy-4-methylpent-2-ynoate **2a**, catalyst $[Cp^*RhCl_2]_2$, activator $AgSbF_6$, base NaOAc, oxidant $Cu(OAc)_2 \cdot H_2O$ in dioxane at 100 °C for 16 h furnished the corresponding benzo-fused heterocyclic lactones **5aa** and **6aa** as a separable regioisomers in a yield of 51 and 5%, respectively (entry 1, Table 1). Optimization of solvents suggested that ethyl acetate is an efficient solvent for this transformation (entries 2-6, Table 1). Screening of bases revealed the suitability of LiOAc (entries 7-11, Table 1). Changing $Cu(OAc)_2 \cdot H_2O$ to Ag_2CO_3 oxidant brought a significant improvement in the formation of regioisomers **5aa** in 76% and **6aa** in 21% (entry 12, Table 1). Lowering the oxidant loading to 0.5 equiv. resulted in decreasing the yields of **5aa** and **6aa** to 63 and 7% yields, respectively (entry 13, Table 1). Increasing or decreasing the reaction temperature did not help in improving

the selectivity of regioisomers (entries 14-15, Table 1). Reactions in the absence of catalysts were not successful (entries 16, Table 1). Replacing [Rh]-catalyst with other transition metal catalysts such as [Co], [Ru], [Ir], or [Pd] catalysts did not helpful (entries 17-20, Table 1). Further screening for improvisation of the selectivity was not successful (for detailed optimization studies see the Supporting Information, Table SI-1, and SI-2).

Table 1. Optimization Studies[a]



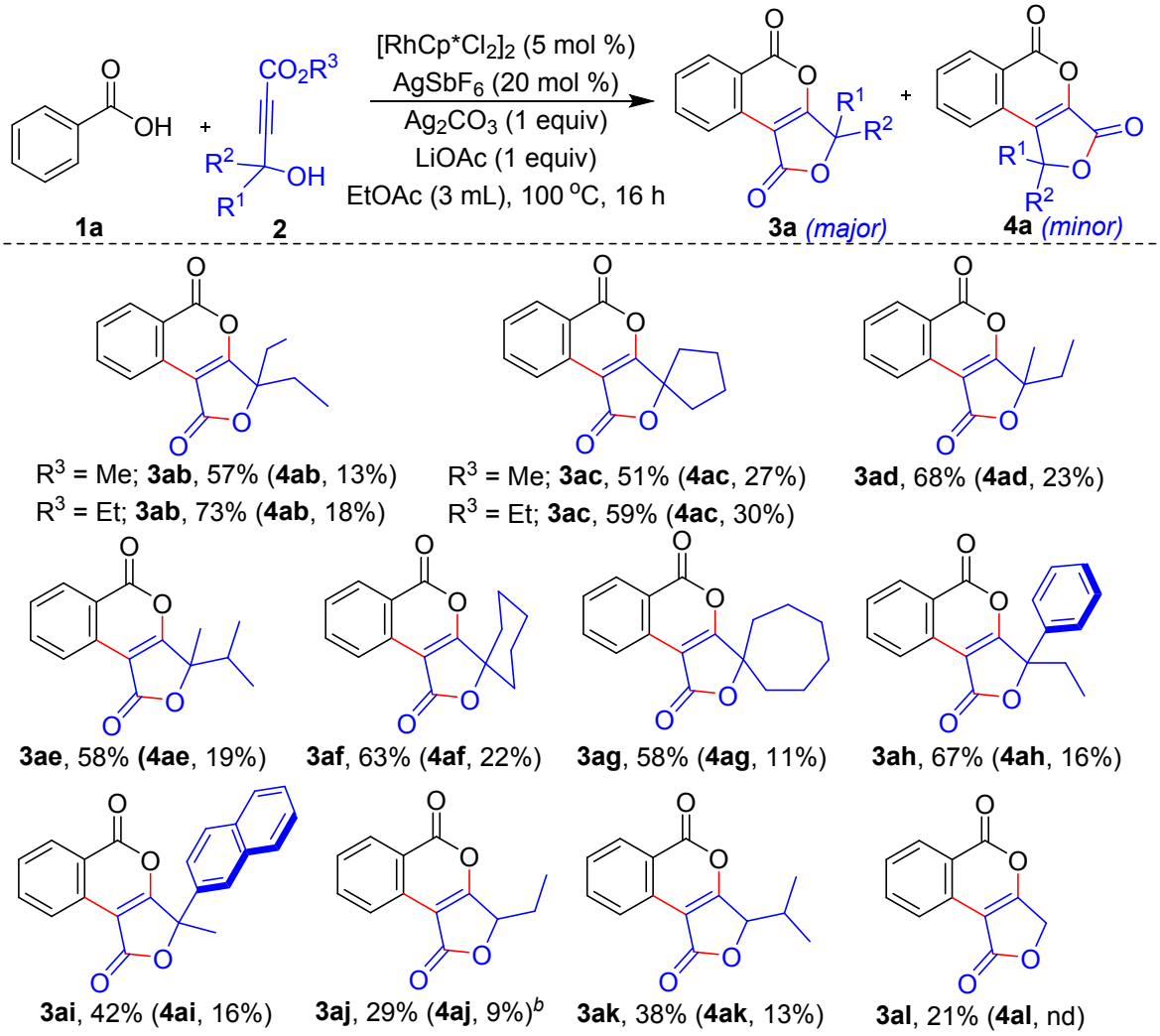
entry	base (1 equiv)	oxidant	solvent (2 mL)	NMR yield (%)[b] 5aa	6aa
1	NaOAc	$Cu(OAc)_2.H_2O$	dioxane	51	**5**
2	NaOAc	$Cu(OAc)_2.H_2O$	^{t}AmOH	nd	nd
4	NaOAc	$Cu(OAc)_2.H_2O$	DCE	50	traces
4	NaOAc	$Cu(OAc)_2.H_2O$	toluene	35	nd
5	NaOAc	$Cu(OAc)_2.H_2O$	THF	52	traces
6	NaOAc	$Cu(OAc)_2.H_2O$	EtOAc	56	traces
7	Cs_2CO_3	$Cu(OAc)_2.H_2O$	EtOAc	nd	nd
8	$AdCO_2H$	$Cu(OAc)_2.H_2O$	EtOAc	23	traces
9	AgOAc	$Cu(OAc)_2.H_2O$	EtOAc	41	7
10	CsOAc	$Cu(OAc)_2.H_2O$	EtOAc	18	nd
11	LiOAc	$Cu(OAc)_2.H_2O$	EtOAc	63	5
12	**LiOAc**	**Ag_2CO_3**	**EtOAc**	**76 (73)**[c]	**21 (19)**[c]
13[d]	LiOAc	Ag_2CO_3	EtOAc	63	7
14[e]	LiOAc	Ag_2CO_3	EtOAc	67	9
15[f]	LiOAc	Ag_2CO_3	EtOAc	65	25
16[g]	LiOAc	Ag_2CO_3	EtOAc	nd	nd
17[h]	LiOAc	Ag_2CO_3	EtOAc	nd	nd
18[i]	LiOAc	Ag_2CO_3	EtOAc	trace	nd
19[j]	LiOAc	Ag_2CO_3	EtOAc	10	trace
20[k]	LiOAc	Ag_2CO_3	EtOAc	nd	nd

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.36 mmol), catalyst $[Cp^*RhCl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), oxidant $Cu(OAc)_2.H_2O$ (2.2 equiv) was used, and Ag_2CO_3 (1 equiv) was used, base (1 equiv), solvent (3 mL), at 100 °C for 16 h. [b] ^{1}H NMR yield using terephthaldehyde as an

internal standard. [c] Isolated yield. [d] Ag_2CO_3 (0.5 equiv) was used. [e] Reaction at 120 °C. [f] Reaction at 80 °C. [g] Absence of [Rh] catalyst. [h] [Cp*Co(CO)I_2] was used. [i] [Ru(*p*-cymene)Cl_2]$_2$ was used. [j] [Cp*IrCl_2]$_2$ was used. [k] $Pd(OAc)_2$ was used. nd = not detected.

Based on these screening experiments, we employed the optimal conditions presented in entry 12 for examining the scope of the reaction (Scheme 2). We studied the scope of the lactonization reaction using various 4-hydroxy-2-alkynoates. First, we evaluated the influence of the alkyl group of alkynoate derivatives on the reaction. The reaction of methyl 4-ethyl-4-hydroxyhex-2-ynoate with benzoic acid **1a** was furnishing the products **3ab** in 52% yield along with **4ab** in 13% yield. However, the reaction of benzoic acid with ethyl 4-ethyl-4-hydroxyhex-2-ynoate resulted in a substantial increase in the yield of **3ab** to 73% along with the minor isomer **4ab** in 18% yield. A similar observation was made with cyclopentyl-substituted alkynoate derivatives. These experiments suggest that ethyl esters of 4-hydroxy-2-alkynoates are slightly more reactive than the corresponding methyl esters. Therefore, we continued further investigation using ethyl 4-hydroxy-2-alkynoaloates. As can be seen in Scheme 2, the reactions of symmetrical as well as unsymmetrical alkyl substituted alkynoate with **1a** proceeded smoothly, forming major isomers **3ad-3ag** in 58-73% along with the minor isomers **4ad-4ag** in 11-23% yields, respectively. Aryl alkyl substituted alkynoate reacted well with **1a** under the reaction optimal conditions furnishing **3ah-3ai** and **4ah-4ai** in good yields as a separable mixture. Further, the reactions of alkynoates derivatives having secondary alcohols with benzoic acid (**1a**) under the optimal reaction conditions furnished a mixture of **3aj** and **4aj** (29 and 9% yields, respectively) as well as **3ak** and **4ak** (38 and 13% yields, respectively). Similarly, the reaction of alkynoate derivative having primary alcohol with benzoic acid furnished the cyclized product **3al** in a low yield of 21%, and then the corresponding uncyclized product was not observed.

Scheme 2. Substrate Scope for 4-Hydroxy-2-alkynoate Derivatives[a]



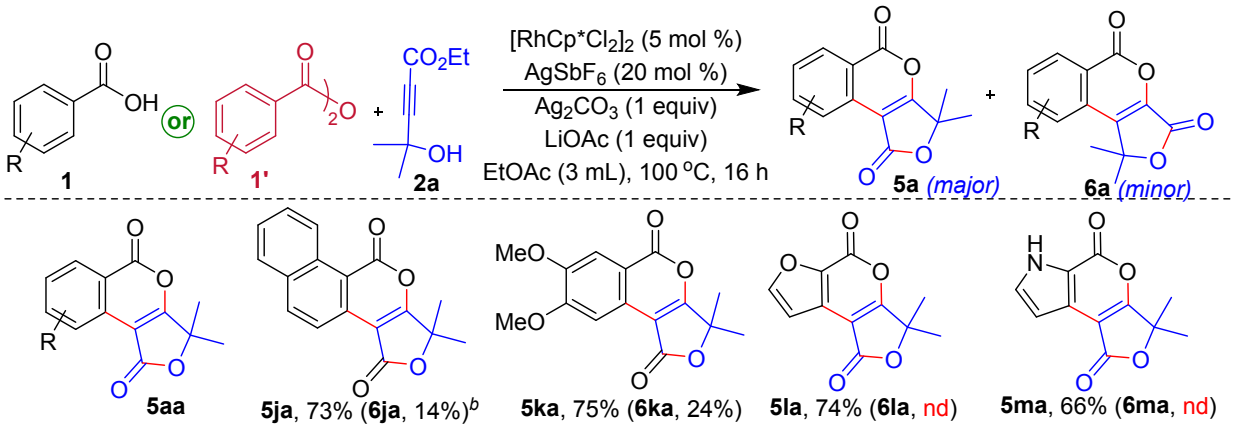
[a] Unless otherwise indicated all products were obtained from ethyl 4-hydroxy-2-alkynoates (R^3 = Et). [b] Values inside parentheses represent NMR yields of minor regioisomers.

Further, we investigated the reactions of a variety of aromatic acids with alkynoate **2a** (Scheme 3). Thus, *para*-methoxy benzoic acid and halo-substituted benzoic acids reacted well with **2a** furnishing the corresponding lactones **5ba-5ea** in major amounts and **6ba-6ea** in minor amounts. This result suggests that the yields drop significantly while installing an electron-withdrawing group on benzoic acid. Further, the reactions of **2a** with benzoic acid derivatives substituted with strong electron-withdrawing groups such as nitro, cyano, keto, aldehyde, and trifluoromethyl groups at *para*-position were unsuccessful under optimal reaction condition. This

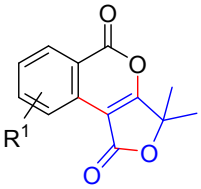
observation agrees with the observation made by Li's group in their reaction of styrene with benzoic acid derivatives.[17] However, the reaction of **2a** with benzoic acid derivatives with electron-donating methoxy and methyl groups at the *meta*-position exhibited a site-selectivity at C6-position of acid derivatives furnishing the regioisomers **5fa** and **5ga** in 60 and 76% yields, respectively along with minor isomers **6fa** and **6ga** in 19 and 21% yield, respectively. The single-crystal X-ray analysis confirmed the structure of **5ga**. The reactions of 2-methoxy benzoic acid and 2-methyl benzoic acid with **2a** furnished the corresponding lactones **5ha** and **5ia** exclusively in 73 and 62% yields, respectively and corresponding minor regioisomers **6ha** and **6ia** were not observed. 1-Napthoic acid and 3,4-dimethoxy benzoic acid underwent smooth reaction with **2a** under the reaction conditions rendering the regioisomers **5ja** and **5ka** in 73 and 75% yields, respectively along with minor isomers **6ja** and **6ka** in 14 and 24% yields, respectively. The reactions of furan-2-carboxylic acid and pyrrole-2-carboxylic acid with **2a** were facile furnishing the corresponding exclusively single regioisomers **5la** and **5ma** in 74 and 66% yields, respectively**.** A scale-up reaction of **1a** with **2a** on a 4 mmol scale furnished the major product **5aa** in 71% yield along with the minor isomer **6aa** in 19% yield.

The reaction was also applicable to anhydrides derivatives (see brown color graphics, Scheme 3). Thus, the reaction of benzoic anhydride **1'** with **2a** furnished the corresponding lactone **5aa** as a major product in 71% along with the minor product **6aa** in 22% yields. Similarly, 4-methoxybenzoic anhydride in a reaction with **2a** furnished a separable mixture of lactones **5ba** and **6ba** in 64 and 27% yields, respectively. These results suggest that benzoic acids and anhydrides behave similarly under the reaction conditions.

Scheme 3. Scope for Carboxylic Acid/Anhydride Derivatives

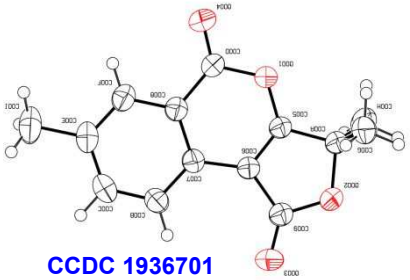


R = H **5aa**, 73% (4 mmol scale, 71%)[a]
6aa, 19% (4 mmol scale, 20%)[a]
R = 4-OMe **5ba**, 66% + **6ba**, 27%
R = 4-Br **5ca**, 54% + **6ca**, 16%
R = 4-Cl **5da**, 20% + **6da**, 23%
R = 4-F **5ea**, 18% + **6ea**, (13%)[b]
R = 3-OMe **5fa**, 60% + **6fa**,19%
R = 3-Me **5ga**, 76% + **6ga**, 21%
R = 2-OMe **5ha**, 73% + **6ha**, nd
R = 2-Me **5ia**, 62% + **6ia**, nd



R^1 = 4-CN
R^1 = 4-NO_2
R^1 = 4-$COCH_3$
R^1 = 4-CHO
R^1 = 4-CF_3

product(s) not detected



CCDC 1936701
5ga, X-ray crystal structure

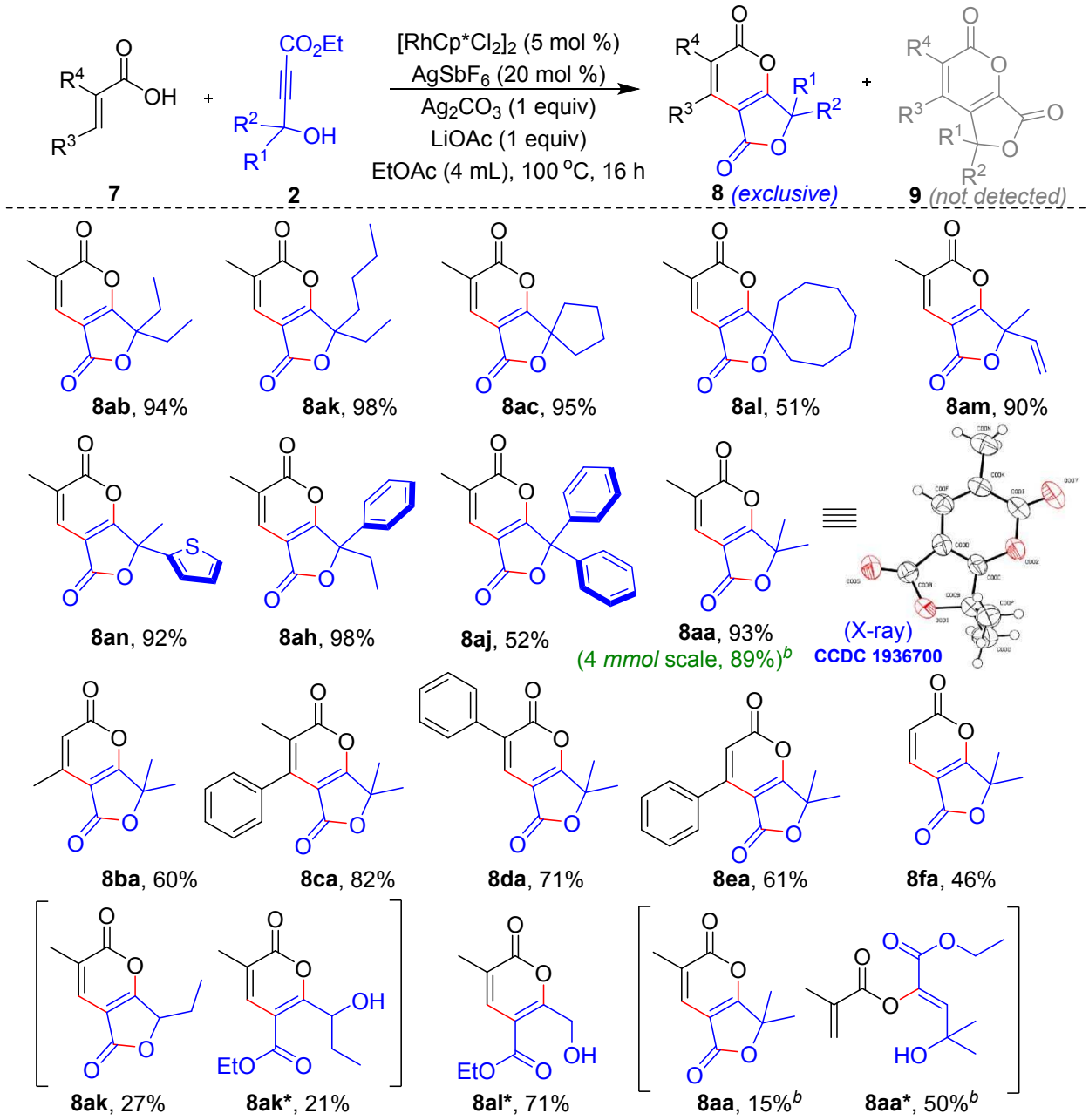
R = H **5aa**, 71% + **6aa**, 22%
R = 4-OMe **5ba**, 64% + **6ba**, 27%

← Products are obtained from benzoic anhydride (derivatives)

[a] Scale-up experiment on 4 mmol scale. [b] Values inside parentheses represent NMR yields of minor regioisomers.

This methodology was further extended for acrylic acid and its derivatives with various 4-hydroxy-2-alkynoates (Scheme 4). The reaction of methacrylate with a variety of ethyl 4-hydroxy-2-alkynoate derivatives was facile furnishing the corresponding α-pyrones derivatives **8ab**, **8ak**, **8ac**, **8al**, **8am**, **8an**, **8ah,** and **8aj** in good to excellent yields. Similarly, reactions of various alkyl and aryl-substituted acrylic acid derivatives such as α-methylacrylic acid, crotonic acid, α-methylcinnamic acid, (E)-2-phenylbut-2-enoic acid, and cinnamic acid with **2a** proceeded well furnishing the corresponding lactone derivatives **8aa**, **8ba**, **8ca**, **8da,** and **8ea** in good yields as single regioisomers. We believe that the steric factor may be responsible for this regioselectivity,[16b] which is substantiated in examples **5ha, 5ia, 5la,** and **5ma**, which were obtained as single regioisomers (Scheme 3).

Scheme 4. Scope for Acrylic Acid Derivatives and 4-Hydroxy-2-Alkynoates[a]



[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.48 mmol), $[RhCp^*Cl_2]_2$ (5 mol %), $AgSbF_6$ (20 mol %), Ag_2CO_3 (1 equiv), LiOAc (1 equiv), EtOAc (4 mL) at 100 °C for 16 h. [b] Scale-up experiment on 4 mmol scale. [b] Reaction using $[IrCp^*Cl_2]_2$] (5 mol %].

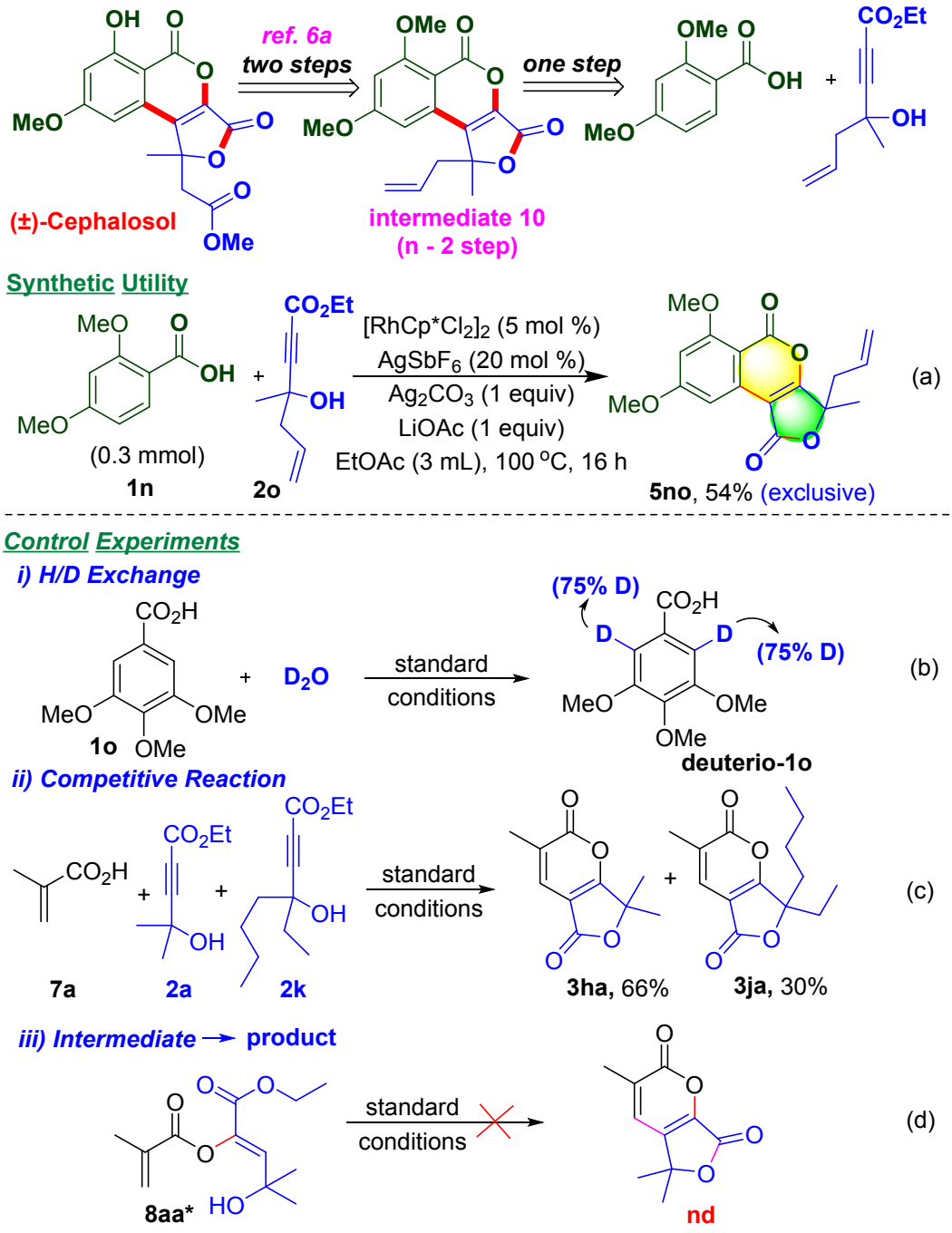
Acrylic acid, which is prone to polymerize, has reacted well with **2a** furnishing the corresponding lactone **8fa** in 46% yield. The reactions of alkynoates derivatives having secondary alcohols with 2-methyacrylic acid under the optimal reaction conditions furnished

both cyclized product **8ak** as well as uncyclized product **8ak*** in 27% and 21% yields respectively. The reaction of alkynoate derivative having primary alcohol with 2-methylacrylic acid furnished the corresponding uncyclized product **8al*** exclusively in 71% yield. However, reaction of 2-methylacrylic acid with the alkynoate **2a** in the presence of $[Cp^*Co(CO)I_2]$ the desired product was not observed. Nevertheless, the reaction of alkynoate **2a** with $[Ru(p\text{-cymene})Cl_2]_2$ catalyst furnished the corresponding cyclized product **8aa** in 44% yield. Similarly, the reaction of alkynoate **2a** with $Cp^*IrCl_2]_2$ catalyst furnishes 15% of **8aa** along with 50% of **8aa*** (See Scheme 4). To show the utility of the reaction, a scale-up reaction of **8aa** on a 4 mmol scale was performed, which furnished the desired cyclic product in an 89% yield indicating the usefulness of the reaction in the preparative method. The single-crystal X-ray analysis confirmed the structure of **8aa.**

As the methodology is useful to obtain tricyclic core, we attempted a synthesis of (±)-Cephalosol (see Scheme 5). Tricyclic lactone **10** is an intermediate for synthesizing cephalosol.[6a] Therefore, we attempted synthesizing the intermediate **10** using the present methodology. However, the reaction of 2,4-dimethoxybenzoic acid **1n** with alkynoate **2o** under the optimal reaction conditions furnished a tricyclic lactone core **5no** (54%)**,** which is an antipode of lactone **10** (Scheme 5a).

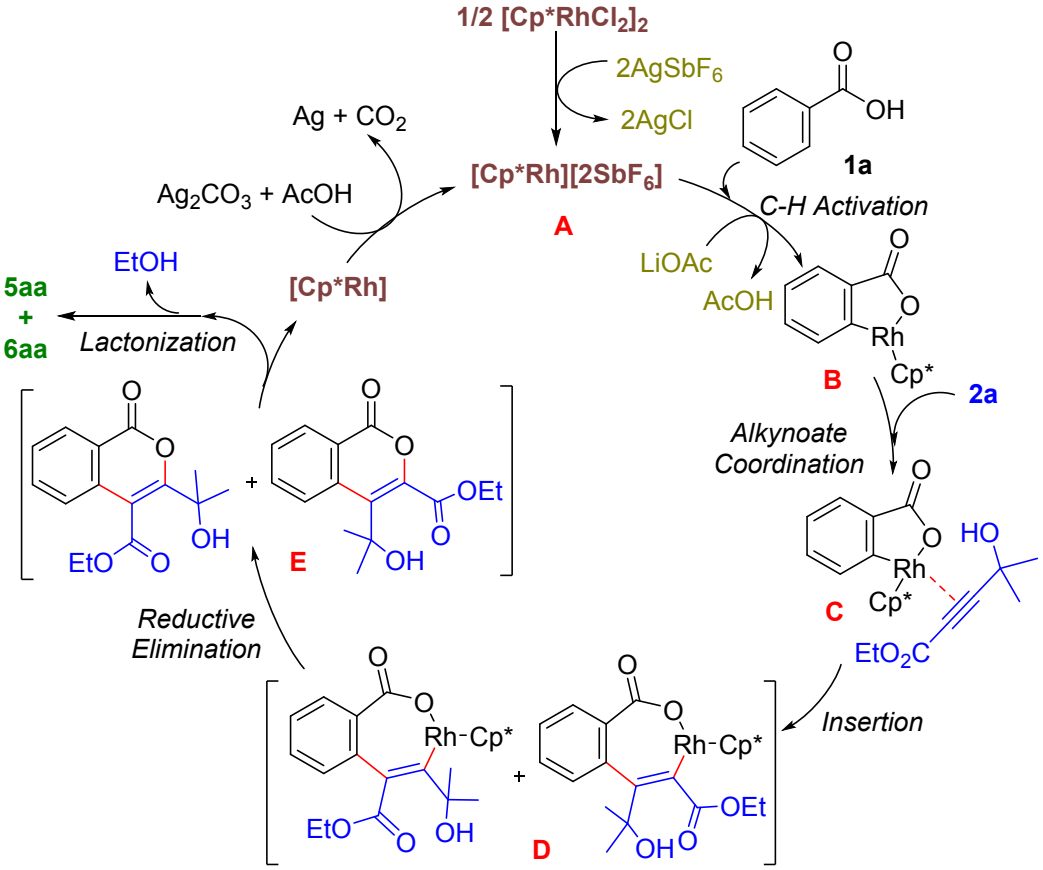
Further, to gain insight into the reaction mechanism, we performed a D_2O labeling experiment. The reaction of 3,4,5-trimethoxy benzoic acid **1o** with D_2O under optimal reaction conditions furnished **deuterio-1o** with 75% deuteration at the *ortho*-positions (Scheme 5b) indicating that the C-H activation step may be reversible. Further, competitive experiment of alkynoates (**2a** and **2k**) having substituent at the C4-position of alkynoates with methacrylic acid **7a** under optimal reaction conditions furnished the corresponding lactones **3ha** and **3ja** in 66 and 30% yields, respectively, indicating that less bulky substituents at the C4-position of the alkynoate dominates over the more bulky substituent (Scheme 5c). **8aa*** and **11** (see the Supporting Information) were subjected to optimal reaction conditions, which did not transform to the corresponding cyclic product indicating that **8aa*** and **11** are not the intermediates in the reaction.

Scheme 5. Synthetic Utility and Control Experiments



Based on the preliminary experiments and the literature precedence,[11,12a,14] a plausible mechanism has been proposed (Scheme 6). The active intermediate **A** generated from $[RhCp^*Cl_2]_2$ undergoes C-H metalation with aromatic acid forming a five-membered rhodacycle **B**. Next, coordination of alkynoate **2a** with **B** leads to the formation of metal complex **C**. A regioselective insertion of 4-hydroxy-2-alkynolate to complex **C** leads to a seven-membered intermediate **D**. The intermediate **D** in the presence of acetic acid, undergoes protodemetallation forming the annulated product **E**, which upon concomitant intramolecular lactonization under the reaction conditions forms lactone **3aa** and **4aa** and the resulting Rh(I)-species is reoxidized into Rh(III)-species by silver carbonate to complete the catalytic cycle.

Scheme 6. Plausible Mechanism



In conclusion, we successfully developed a Rh(III)-catalyzed, efficient one pot synthetic strategy for fused heterocyclic lactone scaffolds. This cascade reaction involves C-H activation, regioselective [4+2] oxidative annulation, and concomitant lactonization. Remarkably, this protocol employs commercially available benzoic acid and acrylic acid derivatives as starting

materials, providing a straightforward and economic strategy for accessing a variety of tricyclic isocoumarin and bicyclic α-pyrone heterocyclic derivatives. In addition, the method is more general, scalable, and provides good regioselectivity and high efficiency. With all these merits, we expect that this protocol will be widely useful in synthesizing useful heterocyclic frameworks.

EXPERIMENTAL SECTION

General Information. All chemicals were purchased from commercial suppliers and used as delivered unless otherwise specified. Reactions were carried out using distilled solvents. NMR spectra were recorded on a BRUKER-AV400 spectrometer in $CDCl_3$ and DMSO-d_6 (400 MHz, ^1H and 100 MHz, ^{13}C). Tetramethylsilane (TMS; δ = 0 ppm) or residual non-deuterated $CDCl_3$ signal (δ = 7.27 ppm); and residual non-deuterated DMSO signal (δ = 2.5 ppm) served as internal standards for 1H NMR. The corresponding residual non-deuterated solvent signals ($CDCl_3$: δ = 77.16 ppm; DMSO: δ = 39.50 ppm) were used as internal standards for ^{13}C NMR. Chemical shifts (δ) are reported in parts per million downfield from the internal reference and coupling constants in Hertz (Hz). IR spectra were measured using a Perkin-Elmer FT-IR Spectrometer. Mass spectra were measured with Micromass Q-TOF (ESI-HRMS). The melting points of the products were determined using a Buchi melting point apparatus. Flash column chromatography was carried out using commercially obtained silica gel, and thin-layer chromatography was carried out using Merck silica gel 60 F_{254} TLC plates. All 4-hydroxy-2-alkynoates derivatives[1] were prepared according to the reported literature procedure.

(a) Experimental procedure for the synthesis of tricyclic fused lactone derivatives

A 8-mL screw-cap reaction vial, equipped with a magnetic stir bar was charged with benzoic acid or anhydride derivatives (0.3 mmol), 4-hydroxy-2-alkynoate derivatives (0.36 mmol, 1.2 equiv), catalyst $[Cp^*RhCl_2]_2$ (9.2 mg, 5 mol %, 0.05 equiv), activator $AgSbF_6$ (20.1 mg, 20 mol %, 0.2 equiv), base LiOAc (19.8 mg, 0.3 mmol, 1.0 equiv), oxidant Ag_2CO_3 (84 mg, 0.3 mmol, 1.0 equiv), and ethyl acetate solvent (3 mL, 1M). The vial was sealed with a screw cap and placed in a pre-heated metal block at 100 °C and the reaction mixture was stirred at the same temperature for 16 h. After completion of the reaction, the reaction mixture was cooled to the room temperature, filtered through a silica (230-400 mess size) pad using a mixture of EtOAc and petroleum ether (1:1, 100 mL), and concentrated under vacuo. In the optimization Table, the

crude products were submitted directly for ^{1}H-NMR analysis for calculating the yields wherein terephthaldehyde (20.1 mg, 0.15 mmol) has been used as an internal standard. For the substrate scope (Scheme - 2, 3, 4, and 5) the crude product was purified on a silica gel (230-400 mess size) flash column chromatography using EtOAc/ petroleum ether as eluent to obtain the desired product as mixture of regioisomers.

(b) Experimental procedure for the synthesis of bicyclic fused lactone derivatives

A 8-mL screw-cap reaction vial, equipped with a magnetic stir bar was charged with acrylic acid derivatives (0.4 mmol), 4-hydroxy-2-alkynoate derivatives (0.48 mmol, 1.2 equiv), catalyst $[Cp^*RhCl_2]_2$ (12.3 mg, 5 mol %, 0.05 equiv), activator $AgSbF_6$ (26.8 mg, 20 mol %, 0.2 equiv), base LiOAc (26.4 mg, 0.4 mmol, 1.0 equiv), oxidant Ag_2CO_3 (112 mg, 0.4 mmol, 1.0 equiv), and ethyl acetate (4 mL, 1M). The vial was sealed with a screw cap and placed in a pre-heated metal block at 100 °C and the reaction mixture was stirred at the same temperature for 16 h. After completion of the reaction, the reaction mixture was cooled to room temperature and concentrated under vacuo. The crude product was purified on a silica gel (230-400 mess size) using flash column chromatography using EtOAc/petroleum ether as eluent to afford the desired product as an exclusive one regioisomer.

(c) Experimental procedure for the scale-up reaction of benzoic acid

In a 50-mL screw-cap reaction vial, equipped with magnetic stir bar was charged with benzoic acid (488.5 mg, 4.0 mmol), ethyl 4-hydroxy-4-methylpent-2-ynoate (749.7 mg, 4.8 mmol, 1.2 equiv), catalyst $[Cp^*RhCl_2]_2$ (122.5 mg, 5 mol %, 0.05 equiv), $AgSbF_6$ (268 mg, 20 mol %, 0.2 equiv), LiOAc (264 mg, 4.0 mmol, 1.0 equiv), Ag_2CO_3 (1.12 g, 4.0 mmol, 1.0 equiv), and ethyl acetate solvent (40 mL, 1M) were taken. The vial was sealed with a screw cap and placed in a pre-heated oil bath at 100 °C and the reaction mixture was stirred at same temperature for 16 h. After completion of the reaction the reaction mixture was cooled to room temperature and concentrated under vacuo. The crude product was purified on a silica gel (230-400 mess size) using flash column chromatography using EtOAc/petroleum ether as eluent to afford the desired products **5aa**, 654 mg in 71% yield (major isomer) and **6aa**, 183 mg in 20% yield (minor isomer).

(d) Experimental procedure for scale-up reaction of 2-methylacrylic acid

In a 50-mL screw-cap reaction vial, equipped with magnetic stir bar was charged with benzoic acid (344.4 mg, 4.0 mmol), ethyl 4-hydroxy-4-methylpent-2-ynoate (749.7 mg, 4.8 mmol, 1.2 equiv), catalyst $[Cp^*RhCl_2]_2$ (122.5 mg, 5 mol %, 0.05 equiv), $AgSbF_6$ (268 mg, 20 mol %, 0.2 equiv), LiOAc (264 mg, 4.0 mmol, 1.0 equiv), Ag_2CO_3 (1.12 g, 4.0 mmol, 1.0 equiv), and ethyl acetate solvent (40 mL, 1M) were taken. The vial was sealed with a screw cap and placed in a pre-heated oil bath at 100 °C and the reaction mixture was stirred at same temperature for 16 h. After completion of the reaction the reaction mixture was cooled to room temperature and concentrated under vacuo. The crude product was purified on a silica gel (230-400 mess size) using flash column chromatography using EtOAc/petroleum ether as eluent to afford the desired product **8aa**, 691.2 mg in 89% yield as an exclusive one regioisomer.

3,3-Diethyl-1H-furo[3,4-c]isochromene-1,5-dione (3ab). Prepared as shown in general experimental procedure (a). White solid; Yield - (56.6 mg, 73%); ***mp***: 121-123 °C; R_f (30% EtOAc/Petroleum Ether) 0.70; **IR** (KBr, cm^{-1}): 3025, 2980, 2927, 2883, 2850, 1780, 1720, 1604, 1498, 1458, 1402, 1224, 1187, 949; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7.48 Hz, 6 H) 1.95 - 2.13 (m, 4 H) 7.60 - 7.64 (m, 1 H) 7.85 - 7.89 (m, 1 H) 8.30 - 8.32 (m, 2 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 7.4, 28.8, 87.3, 103.4, 118.8, 123.1, 129.5, 130.7, 130.9, 136.2, 160.3, 166.9, 173.7; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{15}H_{14}O_4H$ 259.0970; found 259.0973.

1,1-Diethyl-1H-furo[3,4-c]isochromene-3,5(3H)-dione (4ab). Prepared as shown in general experimental procedure (a). White solid; Yield - (13.9 mg, 18%); ***mp***: 144-146 °C; R_f (30% EtOAc/Petroleum Ether) 0.30; **IR** (KBr, cm^{-1}): 2969, 2922, 2850, 1781, 1714, 1671, 1596, 1460, 1382, 1180, 1097; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.79 (t, *J* = 7.48 Hz, 6 H) 2.09 (dq, *J* = 14.69, 7.41 Hz, 2 H) 2.32 (dq, *J* = 14.65, 7.32 Hz, 2 H) 7.56 (d, *J* = 7.93 Hz, 1 H) 7.75 - 7.78 (m, 1 H) 7.87 - 7.92 (m, 1 H) 8.50 (d, *J* = 7.93 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 7.5, 30.8, 88.8, 122.4, 123.3, 130.1, 131.6, 132.3, 132.6, 135.8, 139.9, 160.3, 162.9; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{15}H_{14}O_4H$ 259.0970; found 259.0970.

1'H,5'H-Spiro[cyclopentane-1,3'-furo[3,4-c]isochromene]-1',5'-dione (3ac). Prepared as shown in general experimental procedure (a). White solid; Yield - (45.4 mg, 59%); ***mp***: 195-197 °C; R_f (30% EtOAc/Petroleum Ether) 0.70; **IR** (KBr, cm^{-1}): 2969, 2927, 2853, 1755, 1721, 1678, 1604, 1495, 1397, 1314, 967; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.93 - 1.99 (m, 2 H) 2.01 - 2.10

(m, 4 H) 2.25 - 2.34 (m, 2 H) 7.60 - 7.64 (m, 1 H) 7.85 - 7.89 (m, 1 H) 8.29 (d, *J* = 7.93 Hz, 1 H) 8.32 (d, *J* = 8.24 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 25.1, 36.5, 91.2, 101.9, 119.0, 123.0, 129.4, 130.9, 131.0, 136.1, 160.5, 166.5, 173.5; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{15}H_{12}O_4H$ 257.0814; found 257.0806.

Spiro[cyclopentane-1,1'-furo[3,4-c]isochromene]-3',5'-dione (4ac) Prepared as shown in general experimental procedure (a). White solid; Yield - (23.1 mg, 30%); ***mp***: 243-245 °C; R_f (30% EtOAc/Petroleum Ether) 0.25; **IR** (KBr, cm^{-1}): 2962, 2922, 2851, 1775, 1757, 1632, 1458, 1115, 978; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.02 - 2.25 (m, 6 H) 2.33 - 2.40 (m, 2 H) 7.51 (d, *J* = 7.93 Hz, 1 H) 7.75 - 7.79 (m, 1 H) 7.91 (td, *J* = 7.71, 1.07 Hz, 1 H) 8.48 - 8.51 (m, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 25.1, 38.0, 92.9, 122.8, 123.3, 130.1, 131.4, 132.3, 132.9, 15.6, 138.8, 160.3, 162.3; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{15}H_{12}O_4H$ 257.0814; found 257.0805.

3-Ethyl-3-methyl-1H-furo[3,4-c]isochromene-1,5(3H)-dione (3ad). Prepared as shown in general experimental procedure (a). White solid; Yield - (49.8 mg, 68%); ***mp***: 153-155 °C; R_f (30% EtOAc/Petroleum Ether) 0.70; **IR** (KBr, cm^{-1}): 2979, 2931, 1753, 1680, 1497, 1397, 1189; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.93 (t, *J* = 7.45 Hz, 3 H) 1.70 (s, 3 H) 2.05 (qq, *J* = 14.84, 7.39 Hz, 2 H) 7.62 - 7.66 (m, 1 H) 7.87 - 7.91 (m, 1 H) 8.29 - 8.33 (m, 2 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 7.6, 22.8, 30.1, 84.3, 102.1, 118.9, 123.1, 129.5, 130.9, 136.2, 160.6, 166.6, 174.9; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{14}H_{12}O_4H$ 245.0814; found 245.0812.

1-Ethyl-1-methyl-1H-furo[3,4-c]isochromene-3,5-dione (4ad). Prepared as shown in general experimental procedure (a). White solid; Yield - (16.8 mg, 23%); ***mp***: 172-174 °C; R_f (30% EtOAc/Petroleum Ether) 0.30; **IR** (KBr, cm^{-1}): 2976, 2937, 1774, 1742, 1671, 1599, 1387, 1315, 1187, 1096; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.83 (t, *J* = 7.39 Hz, 3 H) 1.82 (s, 3 H) 2.11 (dq, *J* = 14.78, 7.37 Hz, 1 H) 2.30 (dq, *J* = 14.76, 7.37 Hz, 1 H) 7.57 - 7.59 (m, 1 H) 7.77 - 7.81 (m, 1 H) 7.93 (td, *J* = 7.71, 1.39 Hz, 1 H) 8.50 (dt, *J* = 7.99, 0.68 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 7.7, 25.3, 31.8, 85.8, 122.6, 123.5, 130.0, 131.6, 132.3, 134.6, 135.7, 139.2, 160.3, 162.5; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{14}H_{12}O_4H$ 245.0814; found 245.0813.

3-Isopropyl-3-methyl-1H-furo[3,4-c]isochromene-1,5(3H)-dione (3ae). Prepared as shown in general experimental procedure (a). White solid; Yield - (44.9 mg, 58%); ***mp***: 151-153 °C; R_f (30% EtOAc/Petroleum Ether) 0.65; **IR** (KBr, cm^{-1}): 2974, 2929, 2884, 1752, 1678, 1604, 1498,

1395, 1185; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.98 (d, *J* = 6.95 Hz, 3 H) 1.11 (d, *J* = 6.95 Hz, 3 H) 1.68 (s, 3 H) 2.24 (spt, *J* = 6.86 Hz, 1 H) 7.61 - 7.65 (m, 1 H) 7.86 - 7.90 (m, 1 H) 8.31 (dddd, *J* = 8.01, 5.29, 1.23, 0.63 Hz, 2 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 16.7, 17.0, 21.2, 34.5, 86.5, 102.1, 118.9, 123.1, 129.5, 130.8, 131.0, 136.2, 160.3, 166.8, 175.4; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{15}H_{14}O_4H$ 259.0970; found 259.0969.

1-Isopropyl-1-methyl-1H-furo[3,4-c]isochromene-3,5-dione (4ae). Prepared as shown in general experimental procedure (a). White solid; Yield - (14.7 mg, 19%); ***mp***: 227-229 °C; R_f (30% EtOAc/Petroleum Ether) 0.25; **IR** (KBr, cm^{-1}): 2973, 2933, 2878, 1769, 1742, 1667, 1596, 1384, 1308, 1181; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.72 (d, *J* = 6.82 Hz, 3 H) 1.27 (d, *J* = 6.69 Hz, 3 H) 1.81 (s, 3 H) 2.41 (spt, *J* = 6.78 Hz, 1 H) 7.60 (d, *J* = 7.83 Hz, 1 H) 7.76 - 7.80 (m, 1 H) 7.91 (td, *J* = 7.67, 1.33 Hz, 1 H) 8.49 (dd, *J* = 7.96, 1.26 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 16.7, 16.8, 23.8, 35.3, 87.6, 122.6, 123.7, 130.0, 131.6, 132.3, 135.7, 135.7, 138.7, 160.2, 162.9; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{15}H_{14}O_4H$ 259.0970; found 259.0970.

1'H,5'H-Spiro[cyclohexane-1,3'-furo[3,4-c]isochromene]-1',5'-dione (3af). Prepared as shown in general experimental procedure (a). White solid; Yield - (51.0 mg, 63%); ***mp***: 229-231 °C; R_f (30% EtOAc/Petroleum Ether) 0.65; **IR** (KBr, cm^{-1}): 3076, 2931, 2869, 1763, 1677, 1600, 1496, 1396; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.34 - 1.45 (m, 1 H) 1.80 - 1.86 (m, 7 H) 1.98 - 2.05 (m, 2 H) 7.60 - 7.64 (m, 1 H) 7.87 (td, *J* = 7.78, 1.22 Hz, 1 H) 8.29 - 8.32 (m, 2 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 21.6, 24.2, 33.2, 83.3, 101.1, 119.1, 123.1, 129.4, 130.9, 131.1, 136.1, 160.3, 166.6, 176.1; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{16}H_{14}O_4H$ 271.0970; found 271.0971.

Spiro[cyclohexane-1,1'-furo[3,4-c]isochromene]-3',5'-dione (4af). Prepared as shown in general experimental procedure (a). White solid; Yield - (17.8 mg, 22%); ***mp***: 265-247 °C; R_f (30% EtOAc/Petroleum Ether) 0.30; **IR** (KBr, cm^{-1}): 2955, 2923, 2854, 1765, 1662, 1595, 1453, 1387, 1173; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.36 - 1.47 (m, 1 H) 1.83 - 1.97 (m, 7 H) 2.14 - 2.22 (m, 2 H) 7.69 (d, *J* = 7.83 Hz, 1 H) 7.74 - 7.78 (m, 1 H) 7.89 - 7.93 (m, 1 H) 8.49 (dt, *J* = 7.96, 0.63 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 21.8, 24.5, 35.4, 84.8, 122.8, 123.7, 130.1, 131.3, 132.3, 135.4, 136.0, 138.9, 160.2, 162.5; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{16}H_{14}O_4H$ 271.0970; found 271.0972.

1'H,5'H-Spiro[cycloheptane-1,3'-furo[3,4-c]isochromene]-1',5'-dione (3ag). Prepared as shown in general experimental procedure (a). White solid; Yield - (48.6 mg, 58%); ***mp***: 212-214 °C; R_f (30% EtOAc/Petroleum Ether) 0.65; **IR** (KBr, cm^{-1}): 3023, 2951, 2913, 2851, 1776, 1712, 1677, 1608, 1493, 1436, 1350, 1312, 1224; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.67 - 1.71 (m, 2 H) 1.77 - 1.83 (m, 4 H) 1.85 - 1.93 (m, 2 H) 2.03 (dd, *J* = 14.59, 7.64 Hz, 2 H) 2.17 (dd, *J* = 14.91, 10.11 Hz, 2 H) 7.61 (t, *J* = 7.71 Hz, 1 H) 7.86 (t, *J* = 7.64 Hz, 1 H) 8.30 (t, *J* = 8.15 Hz, 2 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 22.6, 29.2, 36.9, 86.7, 100.3, 119.0, 123.1, 129.3, 130.9, 131.1, 136.1, 160.4, 166.7, 177.1; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{17}H_{16}O_4H$ 285.1127; found 285.1122.

Spiro[cycloheptane-1,1'-furo[3,4-c]isochromene]-3',5'-dione (4ag). Prepared as shown in general experimental procedure (a). White solid; Yield - (9.4 mg, 11%); ***mp***: 217-219 °C; R_f (30% EtOAc/Petroleum Ether) 0.30; **IR** (KBr, cm^{-1}): 2927, 2857, 1765, 1596, 1455, 1386, 1312, 1226, 1130; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.66 - 1.72 (m, 2 H) 1.76 - 1.82 (m, 2 H) 1.87 - 1.94 (m, 2 H) 1.96 - 2.10 (m, 4 H) 2.25 - 2.32 (m, 2 H) 7.63 (d, *J* = 7.83 Hz, 1 H) 7.74 - 7.78 (m, 1 H) 7.91 (td, *J* = 7.67, 1.33 Hz, 1 H) 8.49 (dt, *J* = 7.96, 0.63 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 22.6, 27.4, 38.9, 87.9, 122.9, 123.9, 130.0, 131.3, 132.3, 135.4, 137.5, 138.0, 160.2, 162.6; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{17}H_{16}O_4H$ 285.1127; found 285.1125.

3-Ethyl-3-phenyl-1H-furo[3,4-c]isochromene-1,5(3H)-dione (3ah). Prepared as shown in general experimental procedure (a). White solid; Yield - (61.6 mg, 67%); ***mp***: 169-171 °C; R_f (30% EtOAc/Petroleum Ether) 0.60; **IR** (KBr, cm^{-1}): 2975, 2924, 2852, 1762, 1677, 1602, 1497; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.95 (t, *J* = 7.33 Hz, 3 H) 2.31 (dq, *J* = 14.54, 7.28 Hz, 1 H) 2.44 (dq, *J* = 14.64, 7.37 Hz, 1 H) 7.34 - 7.38 (m, 1 H) 7.39 - 7.44 (m, 2 H) 7.58 - 7.65 (m, 3 H) 7.86 (td, *J* = 7.64, 1.39 Hz, 1 H) 8.28 - 8.32 (m, 2 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 7.9, 31.6, 86.8, 101.5, 118.9, 123.2, 124.9, 128.9, 128.9, 129.6, 130.7, 131.0, 136.2, 136.6, 160.2, 166.6, 173.6; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{19}H_{14}O_4H$ 307.0970; found 307.0971.

1-Ethyl-1-phenyl-1H-furo[3,4-c]isochromene-3,5-dione (4ah). Prepared as shown in general experimental procedure (a).White solid; Yield - (14.7 mg, 16%); ***mp***: 217-219 °C; R_f (30% EtOAc/Petroleum Ether) 0.30; **IR** (KBr, cm^{-1}): 2924, 2853, 1774, 1749, 1672, 1599, 1455, 1222; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 7.26 Hz, 3 H) 2.53 (dq, *J* = 14.65, 7.33 Hz, 1 H) 2.88 (dq, *J* = 14.62, 7.25 Hz, 1 H) 7.34 - 7.36 (m, 1 H) 7.38 - 7.41 (m, 3 H) 7.42 - 7.46 (m, 2 H) 7.72

(td, *J* = 7.58, 1.39 Hz, 1 H) 7.77 (td, *J* = 7.52, 1.64 Hz, 1 H) 8.47 - 8.49 (m, 1 H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 7.7, 29.4, 88.0, 122.5, 124.2, 126.3, 129.1, 129.6, 130.3, 131.6, 132.1, 133.4, 135.6, 137.2, 139.9, 160.2, 162.8; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{19}H_{14}O_4H$ 307.0970; found 307.0970.

3-Methyl-3-(naphthalen-2-yl)-1H-furo[3,4-c]isochromene -1,5(3H)-dione (3ai). Prepared as shown in general experimental procedure (a). White solid; Yield - (43.1 mg, 42%); ***mp***: 232-234 °C; R_f (30% EtOAc/Petroleum Ether) 0.60; **IR** (KBr, cm^{-1}): 3056, 2984, 2926, 2854, 1762, 1724, 1675, 1601, 1457, 1317, 1268, 1227, 1082; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.16 (s, 3 H) 7.49 - 7.54 (m, 2 H) 7.60 - 7.68 (m, 2 H) 7.78 - 7.90 (m, 4 H) 8.08 (d, *J* = 1.52 Hz, 1 H) 8.29 - 8.35 (m, 2 H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 25.1, 84.0, 100.8, 118.9, 122.3, 123.3, 124.2, 126.8, 127.0, 127.6, 128.4, 129.0, 129.7, 130.8, 131.1, 133.0, 133.2, 134.3, 136.3, 160.1, 166.5, 174.7; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{22}H_{14}O_4H$ 343.0970; found 343.0973.

1-Methyl-1-(naphthalen-2-yl)-1H-furo[3,4-c]isochromene-3,5-dione (4ai). Prepared as shown in general experimental procedure (a). White solid; Yield - (16.4 mg, 16%); ***mp***: 225-227 °C; R_f (30% EtOAc/Petroleum Ether) 0.20; **IR** (KBr, cm^{-1}): 3056, 2960, 2923, 2852, 1773, 1747, 1673, 1599, 1456, 1220; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.35 (s, 3 H) 7.24 - 7.26 (m, 1 H) 7.40 (dd, *J* = 8.72, 2.02 Hz, 1 H) 7.52 - 7.57 (m, 2 H) 7.66 - 7.71 (m, 2 H) 7.83 - 7.87 (m, 3 H) 7.96 – 7.97 (m, 1 H) 8.45 - 8.49 (m, 1 H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 25.1, 84.0, 100.8, 118.9, 122.3, 123.3, 124.2, 126.8, 127.0, 127.6, 128.4, 129.0, 129.7, 130.8, 131.1, 133.0, 133.2, 134.3, 136.3, 160.1, 166.5, 174.7; **HRMS (ESI-TOF) m/z**: [M + Na]+ Calculated for $C_{22}H_{14}O_4Na$ 3.65.0790; found 365.0793.

3-Ethyl-1H-furo[3,4-c]isochromene-1,5(3H)-dione (3aj). Prepared as shown in general experimental procedure (a). White solid; Yield - (26.7 mg, 29%); ***mp***: 167-169 °C; R_f (30% EtOAc/Petroleum Ether) 0.75; **IR** (KBr, cm^{-1}): 2964, 2924, 2852, 2363, 1781, 1749, 1599, 1461, 1395, 1105; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.02 (t, *J* = 7.4 Hz, 3H) 1.92 (dp, *J* = 14.5, 7.3 Hz, 1H) 2.40 (dqd, *J* = 14.8, 7.4, 3.2 Hz, 1H) 5.55 (dd, *J* = 7.2, 3.2 Hz, 1H) 7.57 (dd, *J* = 7.8, 0.5 Hz, 1H) 7.77 (td, *J* = 7.9, 1.2 Hz, 1H) 7.90 (td, *J* = 7.7, 1.3 Hz, 1H) 8.45 - 8.48 (m, 1H); **$^{13}C\{^{1}H\}$ NMR** (100 MHz, $CDCl_3$): δ 8.4, 26.9, 78.8, 122.4, 123.4, 130.3, 131.7, 132.1, 135.7, 139.8, 160.2, 163.0; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{13}H_{10}O_4H$ 231.0657; found 231.0658.

3-Isopropyl-1H-furo[3,4-c]isochromene-1,5(3H)-dione (3ak). Prepared as shown in general experimental procedure (a). White solid; Yield - (37.1 mg, 38%); ***mp***: 174-176 °C; R_f (30% EtOAc/Petroleum Ether) 0.70; **IR** (KBr, cm^{-1}): 2964, 2924, 2851, 1786, 1743, 1600, 1497, 1459, 1396, 1118, 974; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.70 (d, *J* = 6.8 Hz, 3H) 1.35 (d, *J* = 6.9 Hz, 3H) 2.54 (heptd, *J* = 6.8, 2.4 Hz, 1H) 5.51 (d, *J* = 2.5 Hz, 1H) 7.60 (d, *J* = 7.9 Hz, 1H) 7.74 - 7.78 (m, 1H) 7.90 (td, *J* = 7.7, 1.3 Hz, 1H) 8.46 (d, *J* = 8.0 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 13.7, 19.9, 31.6, 82.1, 122.3, 123.4, 130.3, 131.4, 131.8, 132.1, 135.7, 139.8, 160.2, 163.3; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{14}H_{12}O_4H$ 245.0814; found 245.0812.

1-Isopropyl-1H-furo[3,4-c]isochromene-3,5-dione (4ak). Prepared as shown in general experimental procedure (a). White solid; Yield - (12.7 mg, 13%); ***mp***: 219-221 °C; R_f (30% EtOAc/Petroleum Ether) 0.35; **IR** (KBr, cm^{-1}): 2985, 2934, 1779, 1752, 148a8, 1374, 1318, 1190; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.99 (d, *J* = 6.9 Hz, 3H) 1.18 (d, *J* = 6.9 Hz, 3H) 2.34 - 2.42 (m, 1H) 5.09 (d, *J* = 4.1 Hz, 1H) 7.64 (dd, *J* = 11.1, 4.4 Hz, 1H) 7.88 (td, *J* = 7.6, 1.0 Hz, 1H) 8.32 (dd, *J* = 13.5, 4.7 Hz, 2H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 15.9, 18.2, 81.8, 103.5, 119.0, 123.1, 129.7, 130.6, 131.0, 136.2, 160.2, 167.3, 171.9; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{14}H_{12}O_4H$ 245.0814; found 245.0814.

1H-Furo[3,4-c]isochromene-1,5(3H)-dione (3al). Prepared as shown in general experimental procedure (a). White solid; Yield - (12.7 mg, 21%); ***mp***: 196-198 °C; R_f (30% EtOAc/Petroleum Ether) 0.70; **IR** (KBr, cm^{-1}): 2985, 2928, 2856, 2364, 1758, 1720, 1601, 1502, 1451, 1407, 1219; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 5.50 (s, 2H) 7.80 - 7.86 (m, 2H) 8.01 (td, *J* = 7.6, 1.1 Hz, 1H) 8.29 (d, *J* = 7.9 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6): δ 67.1, 122.1, 125.0, 130.7, 131.0, 131.6, 132.4, 136.3, 138.6, 160.9, 164.4; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{11}H_6O_4H$ 203.0344; found 203.0345.

3,3-Dimethyl-1H-furo[3,4-c]isochromene-1,5(3H)-dione (5aa). Prepared as shown in general experimental procedure (a). White solid; Yield - (50.4 mg, 73%); ***mp***: 193-195 °C; R_f (30% EtOAc/Petroleum Ether) 0.70; **IR** (KBr, cm^{-1}): 3140, 2997, 2940, 1754, 1676, 1566, 1497, 1194, 979; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.72 (s, 6 H) 7.60 - 7.65 (m, 1 H) 7.88 (td, *J* = 7.78, 1.22 Hz, 1 H) 8.28 - 8.33 (m, 2 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 24.3, 81.5, 101.0, 118.9,

123.1, 129.5, 130.9, 131.0, 136.1, 160.3, 166.2, 175.7; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{13}H_{10}O_4H$ 231.0657; found 231.0661.

1,1-Dimethyl-1H-furo[3,4-c]isochromene-3,5-dione (6aa). Prepared as shown in general experimental procedure (a). White solid; Yield - (13.1 mg, 19%); ***mp***: 245-247 °C; R_f (30% EtOAc/Petroleum Ether) 0.30; **IR** (KBr, cm^{-1}): 3075, 2986, 2936, 1781, 1751, 1458, 1373, 1319, 1193; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.84 (s, 7 H) 7.60 (d, *J* = 7.93 Hz, 1 H) 7.75 - 7.79 (m, 1 H) 7.94 (td, *J* = 7.63, 1.22 Hz, 1 H) 8.47 - 8.49 (m, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 26.5, 83.0, 122.8, 123.6, 129.8, 131.4, 32.3, 135.6, 136.0, 138.7, 160.1, 162.1; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{13}H_{10}O_4H$ 231.0657; found 231.0659.

8-Methoxy-3,3-dimethyl-1H-furo[3,4-c]isochromene-1,5(3H)-dione (5ba). Prepared as shown in general experimental procedure (a). White Solid; Yield - (51.5 mg, 66%); ***mp***: 197-199 °C; R_f (30% EtOAc/Petroleum Ether) 0.50; **IR** (KBr, cm^{-1}): 2980, 2963, 2924, 2851, 1772, 1716, 1677, 1603, 1462, 1373, 1228, 1178; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.70 (s, 6 H) 3.97 (s, 3 H) 7.10 (dd, *J* = 9.00, 2.59 Hz, 1 H) 7.68 (d, *J* = 2.75 Hz, 1 H) 8.20 (d, *J* = 8.85 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 24.3, 56.1, 81.5, 100.7, 105.1, 111.3, 118.1, 133.1, 133.5, 160.1, 165.9, 166.4, 176.6; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{14}H_{12}O_5H$ 261.0763; found 261.0763.

8-Methoxy-1,1-dimethyl-1H-furo[3,4-c]isochromene-3,5-dione (6ba). Prepared as shown in general experimental procedure (a). White Solid; Yield - (21.1 mg, 27%); ***mp***: 261-263 °C; R_f (30% EtOAc/Petroleum Ether) 0.25; **IR** (KBr, cm^{-1}): 2961, 2923, 2852, 1775, 1744, 1599, 1416, 1376, 1237; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.82 (s, 6 H) 4.00 (s, 3 H) 6.93 (d, *J* = 2.44 Hz, 1 H) 7.23 - 7.26 (m, 1 H) 8.43 (d, *J* = 8.85 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 26.4, 56.1, 82.9, 108.4, 115.3, 116.9, 131.8, 134.7, 135.7, 139.4, 160.1, 162.3, 165.0; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{14}H_{12}O_5H$ 261.0763; found 261.0760.

8-Bromo-3,3-dimethyl-1H-furo[3,4-c]isochromene-1,5-dione (5ca). Prepared as shown in general experimental procedure (a). White Solid; Yield - (50.1 mg, 54%); ***mp***: 250-252 °C; R_f (30% EtOAc/Petroleum Ether) 0.60; **IR** (KBr, cm^{-1}): 3102, 3062, 2987, 1745, 1682, 1493, 1418, 1184; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.71 (s, 6 H) 7.73 (dd, *J* = 8.53, 1.96 Hz, 1 H) 8.14 (d, *J* = 8.59 Hz, 1 H) 8.44 (d, *J* = 2.02 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 24.3, 81.8, 100.2,

117.6, 126.2, 132.1, 132.3, 132.4, 133.0, 159.8, 165.7, 176.8; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{13}H_9BrO_4H$ 308.9762; found 308.9759.

8-Bromo-1,1-dimethyl-1H-furo[3,4-c]isochromene-3,5(3H)-dione (6ca). Prepared as shown in general experimental procedure (a). White Solid; Yield - (14.8 mg, 16%); ***mp***: 223-225 °C; R_f (30% EtOAc/Petroleum Ether) 0.25; **IR** (KBr, cm^{-1}): 3098, 2988, 2924, 1776, 1746, 1667, 1587, 1191; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.84 (s, 8 H) 7.68 (d, *J* = 1.89 Hz, 1 H) 7.88 (dd, *J* = 8.53, 1.83 Hz, 1 H) 8.34 (d, *J* = 8.46 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 26.5, 82.9, 121.3, 126.4, 131.3, 133.3, 133.7, 134.7, 139.8, 159.6, 161.7; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{13}H_9BrO_4H$ 308.9762; found 308.9760.

8-Chloro-3,3-dimethyl-1H-furo[3,4-c]isochromene-1,5-dione (5da). Prepared as shown in general experimental procedure (a). White Solid; Yield - (15.9 mg, 20%); ***mp***: 237-239 °C; R_f (30% EtOAc/Petroleum Ether) 0.50; **IR** (KBr, cm^{-1}): 2959, 2924, 2852, 1768, 1730, 1683, 1599, 1460, 1368; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.71 (s, 6 H) 7.58 (dd, *J* = 8.59, 2.15 Hz, 1 H) 8.25 (d, *J* = 8.59 Hz, 1 H) 8.29 (d, *J* = 2.02 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 24.3, 81.8, 100.3, 117.2, 123.1, 130.1, 132.2, 132.5, 143.5, 159.6, 165.8, 176.8; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{13}H_9ClO_4H$ 265.0268; found 265.0268.

8-Chloro-1,1-dimethyl-1H-furo[3,4-c]isochromene-3,5(3H)-dione (6da). Prepared as shown in general experimental procedure (a). White Solid; Yield - (18.3 mg, 23%); ***mp***: 239-241 °C; R_f (30% EtOAc/Petroleum Ether) 0.20; **IR** (KBr, cm^{-1}): 3102, 3069, 2990, 1774, 1745, 1591, 1377, 1193; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.84 (s, 6 H) 7.51 (d, *J* = 1.89 Hz, 1 H) 7.72 (dd, *J* = 8.59, 1.89 Hz, 1 H) 8.43 (d, *J* = 8.59 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 26.5, 82.9, 120.9, 123.4, 131.3, 131.8, 133.8, 134.8, 139.9, 142.6, 159.4, 161.7; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{13}H_9ClO_4H$ 265.0268; found 265.0268.

8-Fluoro-3,3-dimethyl-1H-furo[3,4-c]isochromene-1,5(3H)-dione (5ea). Prepared as shown in general experimental procedure (a). White Solid; Yield - (13.4 mg, 18%); ***mp***: 219-221 °C; R_f (30% EtOAc/Petroleum Ether) 0.50; **IR** (KBr, cm^{-1}): 3074, 2991, 2934, 1744, 1686, 1606, 1572, 1447, 1315, 1209, 1160; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.72 (s, 7 H) 7.31 (td, *J* = 8.53, 2.53 Hz, 1 H) 7.97 (dd, *J* = 8.65, 2.59 Hz, 1 H) 8.36 (dd, *J* = 8.84, 5.31 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 24.3, 81.7, 100.6 ($J_{C\text{-}F}$ = 3.0 Hz), 109.8 ($J_{C\text{-}F}$ = 24.5 Hz), 115.3 ($J_{C\text{-}F}$ = 2.9 Hz),

117.8 ($J_{C\text{-}F}$ = 23.3 Hz), 133.7 ($J_{C\text{-}F}$ = 11.8 Hz), 134.5 ($J_{C\text{-}F}$ = 10.6 Hz), 159.4, 165.8, 167.5 ($J_{C\text{-}F}$ = 259 Hz), 176.8; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{13}H_9FO_4H$ 249.0563; found 249.0566.

7-Methoxy-3,3-dimethyl-1H-furo[3,4-c]isochromene-1,5(3H)-dione (5fa). Prepared as shown in general experimental procedure (a). White Solid; Yield - (46.8 mg, 60%); ***mp***: 231-233 °C; R_f (30% EtOAc/Petroleum Ether) 0.50; **IR** (KBr, cm^{-1}): 3057, 2984, 2922, 2850, 1747, 1680, 1515, 1395; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.69 (s, 6 H) 3.92 (s, 3 H) 7.41 (dd, *J* = 8.72, 2.78 Hz, 1 H) 7.70 (d, *J* = 2.65 Hz, 1 H) 8.18 (d, *J* = 8.72 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 24.4, 55.8, 81.6, 101.1, 112.4, 120.4, 124.2, 124.7, 124.9, 160.3, 160.6, 166.4, 173.5; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{14}H_{12}O_5H$ 261.0763; found 261.0766.

7-Methoxy-1,1-dimethyl-1H-furo[3,4-c]isochromene-3,5-dione (6fa). Prepared as shown in general experimental procedure (a). White Solid; Yield - (14.8 mg, 19%); ***mp***: 178-180 °C; R_f (30% EtOAc/Petroleum Ether) 0.20; **IR** (KBr, cm^{-1}): 3095, 2923, 2851, 1751, 1652, 1480, 1371, 1282, 1188; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.68 (s, 6 H) 4.02 (s, 3 H) 7.34 (d, *J* = 8.34 Hz, 1 H) 7.57 (t, *J* = 8.08 Hz, 1 H) 7.96 (d, *J* = 7.83 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 24.6, 56.5, 79.5, 101.1, 118.3, 120.6, 121.4, 122.8, 130.3, 155.9, 160.1, 163.9, 175.5; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{14}H_{12}O_5H$ 261.0763; found 261.0761.

3,3,7-Trimethyl-1H-furo[3,4-c]isochromene-1,5(3H)-dione (5ga). Prepared as shown in general experimental procedure (a). White Solid; Yield - (55.7 mg, 76%); ***mp***: 226-228 °C; R_f (30% EtOAc/Petroleum Ether) 0.70; **IR** (KBr, cm^{-1}): 2986, 2923, 2852, 1750, 1685, 1510, 1400; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.69 (s, 6 H) 2.49 (s, 3 H) 7.64 - 7.67 (m, 1 H) 8.07 - 8.08 (m, 1 H) 8.14 (d, *J* = 7.96 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 21.6, 24.3, 81.5, 101.0, 118.9, 122.9, 128.3, 130.8, 137.3, 140.0, 160.5, 166.4, 174.9; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{14}H_{12}O_4H$ 245.0814; found 245.0814.

1,1,7-Trimethyl-1H-furo[3,4-c]isochromene-3,5-dione (6ga). Prepared as shown in general experimental procedure (a). White Solid; Yield - (15.4 mg, 21%); ***mp***: 271-273 °C; R_f (30% EtOAc/Petroleum Ether) 0.30; **IR** (KBr, cm^{-1}): 2924, 2853, 1766, 1674, 1462, 1382, 1258; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.82 (s, 6 H) 2.56 (s, 4 H) 7.48 (d, *J* = 8.08 Hz, 1 H) 7.71 - 7.73 (m, 1 H) 8.29 - 8.30 (m, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 21.8, 26.6, 82.9, 122.7, 123.5,

127.3, 132.3, 136.4, 137.9, 142.6, 160.4, 162.3; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{14}H_{12}O_4H$ 245.0814; found 245.0815.

6-Methoxy-3,3-dimethyl-1H-furo[3,4-c]isochromene-1,5(3H)-dione (5ha). Prepared as shown in general experimental procedure (a). White Solid; Yield - (60.0 mg, 73%); ***mp***: 221-223 °C; R_f (30% EtOAc/Petroleum Ether) 0.35; **IR** (KBr, cm^{-1}):2959, 2923, 2852, 1756, 1688, 1571, 1490, 1459, 1276, 1188; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.69 (s, 6 H) 4.04 (s, 3 H) 7.08 (d, *J* = 8.34 Hz, 1 H) 7.79 (t, *J* = 8.15 Hz, 1 H) 7.89 (d, *J* = 7.83 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 24.2, 56.4, 81.2, 100.2, 106.8, 111.6, 114.7, 133.2, 137.6, 156.4, 162.4, 166.4, 176.6; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{14}H_{12}O_5H$ 261.0763; found 261.0763.

3,3,6-Trimethyl-1H-furo[3,4-c]isochromene-1,5(3H)-dione (5ia). Prepared as shown in general experimental procedure (a). White Solid; Yield - (45.4 mg, 62%); ***mp***: 215-217 °C; R_f (30% EtOAc/Petroleum Ether) 0.65; **IR** (KBr, cm^{-1}): 3072, 2988, 2925, 2854, 1761, 1728, 1691, 1594, 1470, 1375, 1276, 1215, 1155; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.69 (s, 6 H) 2.80 (s, 3 H) 7.38 - 7.40 (m, 1 H) 7.70 (t, *J* = 7.71 Hz, 1 H) 8.17 - 8.19 (m, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 23.4, 24.3, 81.2, 100.8, 117.2 121.0, 132.2, 132.6, 135.5, 144.9, 159.4, 166.5, 175.8; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{14}H_{12}O_4H$ 245.0814; found 245.0816.

1,1-Dimethyl-3H-benzo[h]furo[3,4-c]isochromene-3,10(1H)-dione (5ja). Prepared as shown in general experimental procedure (a). White Solid; Yield - (61.4 mg, 73%); ***mp***: 263-265 °C; R_f (30% EtOAc/Petroleum Ether) 0.45; **IR** (KBr, cm^{-1}): 2959, 2923, 2852, 2361, 1768, 1731, 1683, 1599, 1459, 1367, 1221, 1018; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.76 (s, 6 H) 7.64 - 7.67 (m, 1 H) 7.76 - 7.80 (m, 1 H) 7.94 (d, *J* = 8.08 Hz, 1 H) 8.24 (d, *J* = 8.59 Hz, 1 H) 8.40 (dd, *J* = 8.53, 1.96 Hz, 1 H) 9.52 (d, *J* = 8.84 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 24.4, 81.4, 101.0, 112.3, 119.5, 125.9, 127.5, 129.4, 130.2, 131.6, 134.1, 138.2, 159.3, 166.3, 177.0; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{17}H_{12}O_4H$ 281.0814; found 281.0811.

7,8-Dimethoxy-3,3-dimethyl-1H-furo[3,4-c]isochromene-1,5(3H)-dione (5ka). Prepared as shown in general experimental procedure (a). White Solid; Yield - (66.1 mg, 75%); ***mp***: 277-279 °C; R_f (30% EtOAc/Petroleum Ether) 0.25; **IR** (KBr, cm^{-1}): 2983, 2922, 2852, 1763, 1738, 1679, 1598, 1519, 1459, 1416, 1270, 991; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.69 (s, 6 H) 3.97 (s, 3 H) 4.04 (s, 3 H) 7.62 (s, 2 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 24.4, 56.3, 56.7, 81.7, 100.7,

103.9, 110.8, 111.8, 126.7, 150.3, 156.2, 160.3, 166.6, 174.7; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{15}H_{14}O_6H$ 291.0869; found 291.0870.

7,8-Dimethoxy-1,1-dimethyl-1H-furo[3,4-c]isochromene-3,5-dione (6ka). Prepared as shown in general experimental procedure (a). White Solid; Yield - (20.9 mg, 24%); ***mp***: 238-240 °C; R_f (50% EtOAc/Petroleum Ether) 0.40; **IR** (KBr, cm^{-1}): 3021, 2985, 2925, 2852, 1768, 1730, 1668, 1596, 1520, 1464, 1392, 1282, 1152; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.82 (s, 6 H) 4.03 (s, 3 H) 4.06 (s, 3 H) 6.85 (s, 1 H) 7.84 (s, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 26.6, 56.5, 56.6, 82.6, 104.2, 112.3, 116.6, 124.9, 136.2, 137.5, 151.9, 155.3, 160.3, 162.2; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{15}H_{14}O_6H$ 291.0869; found 291.0869.

3,3-Dimethyl-1H-difuro[3,4-b:3',2'-d]pyran-1,5(3H)-dione (5la). Prepared as shown in general experimental procedure (a). White Solid; Yield - (66.0 mg, 74%); ***mp***: 229-231 °C; R_f (30% EtOAc/Petroleum Ether) 0.40; **IR** (KBr, cm^{-1}): 3152, 3122, 2960, 2923, 2850, 1746, 1711, 1648, 1580, 1458, 1376; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.70 (s, 6 H) 7.05 - 7.06 (m, 1 H) 7.96 – 7.97 (m, 1 H); **^{13}C{^{1}H} NMR** (400 MHz, $CDCl_3$) δ 24.5, 82.7, 100.5, 107.0, 129.9, 136.9, 150.9, 152.5, 164.8, 177.1; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{11}H_8O_5H$ 221.0450; found 221.0453.

3,3-Dimethyl-3,6-dihydrofuro[3',4':5,6]pyrano[3,4-b]pyrrole-1,5-dione (5ma). Prepared as shown in general experimental procedure (a). White Solid; Yield - (58.0 mg, 66%); ***mp***: 291-293 °C; R_f (30% EtOAc/Petroleum Ether) 0.30; **IR** (KBr, cm^{-1}): 3062, 2987, 2923, 2851, 1768, 1718, 1557, 1464, 1426, 1218; **^{1}H NMR** (400 MHz, DMSO-d_6): δ 1.58 (s, 6 H) 6.54 - 6.56 (m, 1 H) 7.58 - 7.60 (m, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, DMSO-d_6): δ 24.5, 82.6, 100.8, 103.2, 114.9, 124.6, 132.2, 154.0, 166.6, 174.3; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{11}H_9NO_4H$ 220.0610; found 220.0612.

7,7-Diethyl-3-methyl-2H-furo[3,4-b]pyran-2,5(7H)-dione (8ab). Prepared as shown in general experimental procedure (b). White Solid; Yield - (83.5 mg, 94%); ***mp***: 169-171 °C; R_f (30% EtOAc/Petroleum Ether) 0.60; **IR** (KBr, cm^{-1}): 3031, 2970, 2925, 2851, 1763, 1739, 1662, 1600, 1459, 1237; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.81 (t, J = 7.24 Hz, 6 H) 1.89 - 2.04 (m, 4 H) 2.14 (s, 3 H) 7.37 (s, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 17.6, 21.6, 24.2, 27.6, 32.8, 86.9,

103.4, 124.9, 133.2, 161.2, 165.8, 180.7; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{12}H_{14}O_4H$ 223.0970; found 223.0968.

7-Butyl-7-ethyl-3-methyl-2H-furo[3,4-b]pyran-2,5(7H)-dione (8ak). Prepared as shown in general experimental procedure (b). White Solid; Yield - (98.2 mg, 98%); ***mp***: 94-96 °C; R_f (30% EtOAc/Petroleum Ether) 0.55; **IR** (KBr, cm^{-1}): 3040, 2974, 2926, 2855, 1733, 1708, 1668, 1602, 1412, 1222; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.80 - 0.86 (m, 6 H) 0.99 - 1.01 (m, 1 H) 1.27 (br. s., 3 H) 1.83 - 2.03 (m, 4 H) 2.15 (br. s., 3 H) 7.38 (s, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 7.3, 13.8, 17.6, 22.5, 25.0, 29.2, 35.5, 87.3, 105.8, 124.7, 132.7, 161.3, 166.1, 177.6; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{14}H_{18}O_4H$ 251.1283; found 251.1282.

3'-Methyl-2'H,5'H-spiro[cyclopentane-1,7'-furo[3,4-b]pyran]-2',5'-dione (8ac). Prepared as shown in general experimental procedure (b). White Solid; Yield - (83.7 mg, 95%); ***mp***: 83-85 °C; R_f (30% EtOAc/Petroleum Ether) 0.60; **IR** (KBr, cm^{-1}): 3041, 2956, 2923, 2853, 1759, 1730, 1663, 1602, 1416; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.89 - 1.92 (m, 2 H) 1.98 - 2.00 (m, 4 H) 2.14 (s, 3 H) 2.16 - 2.18 (m, 2 H) 7.37 (s, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 17.6, 25.1, 36.6, 91.4, 104.4, 124.9, 132.7, 161.3, 165.6, 177.2; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{12}H_{12}O_4H$ 221.0814; found 221.0814.

3'-Methyl-2'H,5'H-spiro[cyclooctane-1,7'-furo[3,4-b]pyran]-2',5'-dione (8al). Prepared as shown in general experimental procedure (b). White Solid; Yield - (53.0 mg, 51%); ***mp***: 172-174 °C; R_f (30% EtOAc/Petroleum Ether) 0.60; **IR** (KBr, cm^{-1}): 3039, 2957, 2923, 2851, 1755, 1729, 1662, 1600, 1411; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.56 (br. s., 3 H) 1.70 (br. s., 3 H) 1.82 (br. s., 4 H) 1.97 - 2.10 (m, 4 H) 2.15 (s, 3 H) 7.38 (s, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 17.6, 21.6, 24.2, 27.6, 32.8, 86.8, 103.4, 124.9, 133.2, 161.1, 165.8, 180.7; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{15}H_{18}O_4H$ 263.1283; found 263.1282.

3,7-Dimethyl-7-vinyl-2H-furo[3,4-b]pyran-2,5(7H)-dione (8am). Prepared as shown in general experimental procedure (b). White Solid; Yield - (81.0 mg, 90%); ***mp***: 89-91 °C; R_f (30% EtOAc/Petroleum Ether) 0.70; **IR** (KBr, cm^{-1}): 3066, 2958, 2921, 2852, 1759, 1707, 1664, 1602, 1462, 1446, 1377, 1245, 1123; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.33 Hz, 4 H) 2.15 (d, *J* = 1.39 Hz, 3 H) 2.24 (dq, *J* = 14.53, 7.28 Hz, 1 H) 2.37 (dq, *J* = 14.64, 7.37 Hz, 1 H) 7.34 - 7.44 (m, 4 H) 7.50 - 7.60 (m, 2 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 17.7, 22.8, 83.2, 103.4,

118.3, 125.3, 132.8, 133.6, 160.9, 165.4, 177.4; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{11}H_{10}O_4H$ 207.0657; found 207.0659.

3,7-Dimethyl-7-(thiophen-2-yl)-2H-furo[3,4-b]pyran-2,5(7H)-dione (8an). Prepared as shown in general experimental procedure (b). White Solid; Yield - (97.0 mg, 92%); ***mp***: 128-130 °C; R_f (30% EtOAc/Petroleum Ether) 0.55; **IR** (KBr, cm^{-1}): 3069, 2960, 2924, 2853, 1745, 1710, 1664, 1599, 1458, 1408; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.06 (br. s., 3 H) 2.16 (br. s., 3 H) 6.99 - 7.01 (m, 1 H) 7.12 (br. s., 1 H) 7.31 - 7.33 (m, 1 H) 7.40 (br. s., 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 17.7, 25.1, 82.2, 103.1, 125.7, 125.8, 126.8, 127.5, 132.6, 139.3, 160.7, 164.9, 176.9; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{13}H_{10}O_4SH$ 263.0378; found 263.0380.

7-Ethyl-3-methyl-7-phenyl-2H-furo[3,4-b]pyran-2,5(7H)-dione (8ah). Prepared as shown in general experimental procedure (b). White Solid; Yield - (106.0 mg, 98%); ***mp***: 114-116 °C; R_f (30% EtOAc/Petroleum Ether) 0.70; **IR** (KBr, cm^{-1}): 3064, 2978, 2929, 2849, 1784, 1749, 1661, 1600, 1450, 1409; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 0.90 (t, *J* = 7.33 Hz, 4 H) 2.15 (d, *J* = 1.39 Hz, 3 H) 2.24 (dq, *J* = 14.53, 7.28 Hz, 1 H) 2.37 (dq, *J* = 14.64, 7.37 Hz, 1 H) 7.33 - 7.42 (m, 4 H) 7.54 - 7.67 (m, 2 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 7.8, 17.6, 31.7, 87.1, 104.5, 124.8, 125.1, 128.9, 129.0, 132.7, 136.3, 160.9, 165.7, 177.1; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{16}H_{14}O_4H$ 271.0970; found 271.0971.

3-Methyl-7,7-diphenyl-2H-furo[3,4-b]pyran-2,5(7H)-dione (8aj). Prepared as shown in general experimental procedure (b). White Solid; Yield - (67.0 mg, 52%); ***mp***: 251-253 °C; R_f (30% EtOAc/Petroleum Ether) 0.50; **IR** (KBr, cm^{-1}): 3063, 2959, 2923, 2852, 1746, 1661, 1600, 1451, 1407; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.19 (s, 3 H) 7.40 (br. s., 5 H) 7.42 - 7.44 (m, 6 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 17.7, 87.7, 104.6, 125.6, 126.7, 128.9, 129.4, 132.7, 136.9, 160.8, 165.4, 176.1; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{20}H_{14}O_4H$ 319.0970; found 319.0973.

3,7,7-trimethyl-2H-furo[3,4-b]pyran-2,5(7H)-dione (8aa). Prepared as shown in general experimental procedure (b). White Solid; Yield - (72.2 mg, 93%); ***mp***: 144-146 °C; R_f (30% EtOAc/Petroleum Ether) 0.55; **IR** (KBr, cm^{-1}): 3054, 2985, 2925, 2852, 1733, 1707, 1664, 1601, 1415, 1365, 1116; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.60 (s, 6 H) 2.12 (d, *J* = 1.26 Hz, 3 H) 7.36 (d, *J* = 1.26 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 24.2, 82.0, 103.3, 114.9, 137.6,

159.1, 164.9, 181.9; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{10}H_{10}O_4H$ 195.0657; found 195.0656.

4,7,7-trimethyl-2H-furo[3,4-b]pyran-2,5(7H)-dione (8ba). Prepared as shown in general experimental procedure (b). White Solid; Yield - (46.6 mg, 60%); ***mp***: 124-126 °C; R_f (30% EtOAc/Petroleum Ether) 0.50; **IR** (KBr, cm^{-1}): 3068, 2958, 2858, 1770, 1737, 1658, 1572, 1432, 1274, 1031, 933; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.63 (s, 6 H) 2.41 (s, 3 H) 6.04 (s, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 17.9, 24.2, 81.5, 103.6, 111.8, 152.9, 159.5, 165.3, 181.2; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{10}H_{10}O_4H$ 195.0657; found 195.0657.

3,7,7-Trimethyl-4-phenyl-2H-furo[3,4-b]pyran-2,5(7H)-dione (8ca). Prepared as shown in general experimental procedure (b). White Solid; Yield - (88.2 mg, 82%); ***mp***: 92-94 °C; R_f (30% EtOAc/Petroleum Ether) 0.45; **IR** (KBr, cm^{-1}): 3060, 2988, 2924, 2853, 1782, 1731, 1660, 1561, 1416, 1361; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.67 (s, 6 H) 2.01 - 2.02 (m, 3 H) 7.29 (d, J = 3.16 Hz, 2 H) 7.46 - 7.48 (m, 3 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 14.4, 24.5, 80.3, 121.4, 128.3, 128.5, 129.5, 131.5, 147.9, 161.6, 164.4, 178.5; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{16}H_{14}O_4H$ 271.0970; found 271.0969.

7,7-Dimethyl-3-phenyl-2H-furo[3,4-b]pyran-2,5(7H)-dione (8da). Prepared as shown in general experimental procedure (b). White Solid; Yield - (72.7 mg, 71%); ***mp***: 157-159 °C; R_f (30% EtOAc/Petroleum Ether) 0.50; **IR** (KBr, cm^{-1}): 3065, 2985, 2934, 2872, 1777, 1748, 1662, 1582, 1413, 1127, 1025; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.70 (s, 6 H) 7.42 - 7.46 (m, 3 H) 7.58 - 7.60 (m, 2 H) 7.67 (s, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 24.4, 82.0, 104.0, 127.2, 128.3, 128.7, 129.5, 133.5, 133.6, 159.6, 165.3, 180.0; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{15}H_{12}O_4H$ 257.0814; found 257.0815.

7,7-Dimethyl-4-phenyl-2H-furo[3,4-b]pyran-2,5(7H)-dione (8ea). Prepared as shown in general experimental procedure (b). White Solid; Yield - (62.5mg, 61%); ***mp***: 191-193 °C; R_f (30% EtOAc/Petroleum Ether) 0.50; **IR** (KBr, cm^{-1}): 3058, 2990, 2937, 2880, 1769, 1743, 1640, 1541, 1449, 1418, 1359, 1256, 1074; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.59 - 1.79 (m, 6 H) 6.28 (d, J = 0.76 Hz, 1 H) 7.46 - 7.56 (m, 3 H) 7.63 (d, J = 7.58 Hz, 2 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 24.4, 80.8, 101.8, 111.6, 128.6, 128.7, 131.2, 131.9, 153.6, 159.5, 164.3, 182.7; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{15}H_{12}O_4H$ 257.0814; found 257.0813.

7,7-Dimethyl-2H-furo[3,4-b]pyran-2,5(7H)-dione (8fa). Prepared as shown in general experimental procedure (b). White Solid; Yield - (49.7 mg, 46%); ***mp***: 140-142 °C; R_f (30% EtOAc/Petroleum Ether) 0.55; **IR** (KBr, cm^{-1}): 3059, 2999, 2935, 2873, 1788, 1753, 1661, 1611, 1575, 1368, 1304, 1123; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.65 (s, 6 H) 6.32 (d, *J* = 9.60 Hz, 1 H) 7.60 (d, *J* = 9.47 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 24.2, 82.0, 103.3, 114.8, 137.6, 159.1, 164.9, 181.9; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_9H_8O_4H$ 181.0501; found 181.0501.

7-Ethyl-3-methyl-2H-furo[3,4-b]pyran-2,5(7H)-dione (8ak). Prepared as shown in general experimental procedure (b). White solid; Yield - (21.0 mg, 27%); ***mp***: 159-161 °C; R_f (30% EtOAc/Petroleum Ether) 0.55; **IR** (KBr, cm^{-1}): 3045, 2977, 2929, 2883, 1786, 1736, 1661, 1601, 1460, 1451, 965; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.04 (t, *J* = 7.4 Hz, 3H) 1.82 - 1.93 (m, 1H) 2.06 - 2.18 (m, 1H) 2.18 (s, 3H) 2.06 - 2.18 (m, 1H) 5.11 - 5.14 (m, 1H) 7.41 (d, *J* = 0.9 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 8.3, 17.6, 25.0, 78.5, 105.4, 125.3, 132.6, 161.0, 166.3, 175.8; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{10}H_{10}O_4H$ 195.0657; found 195.0658.

Ethyl 6-(1-hydroxypropyl)-3-methyl-2-oxo-2H-pyran-5-carboxylate (8ak*). Prepared as shown in general experimental procedure (b). Colorless Oil; Yield - (23.1 mg, 21%); R_f (30% EtOAc/Petroleum Ether) 0.40; **IR** (KBr, cm^{-1}): 3469, 3062, 2986, 2928, 1746, 1693, 1638, 1574, 1444, 1378, 1335, 1271, 1223, 1158, 1031 ; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.03 (t, *J* = 7.4 Hz, 3H) 1.38 (t, *J* = 7.1 Hz, 3H) 1.86 (p, *J* = 7.3 Hz, 2H) 2.13 (d, *J* = 1.1 Hz, 3H) 4.34 (q, *J* = 7.1 Hz, 2H) 5.07 (t, *J* = 6.9 Hz, 1H) 7.60 (d, *J* = 1.2 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 10.0, 14.1, 16.4, 28.2, 61.9, 71.4, 108.6, 123.2, 139.3, 161.3, 164.3, 170.4; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{12}H_{16}O_5Na$ 263.0895; found 263.0895.

Ethyl 6-(hydroxymethyl)-3-methyl-2-oxo-2H-pyran-5-carboxylate (8al*). Prepared as shown in general experimental procedure (b). Colorless Oil; Yield - (60.3 mg, 71%); R_f (30% EtOAc/Petroleum Ether) 0.35; **IR** (KBr, cm^{-1}): 3437, 3064, 2975, 2931, 2740, 1757, 1703, 1573, 1462, 1416, 1378, 1334, 1247, 1159, 1026; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.39 (t, J = 7.1 Hz, 3H) 2.13 (s, 3H) 3.81 (s, br., 1H) 4.36 (q, *J* = 7.1 Hz, 2H) 4.74 (s, 2H) 7.62 (d, *J* = 1.1 Hz, 1H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 14.1, 16.4, 61.3, 62.0, 109.3, 123.6, 138.9, 161.4, 164.4,

168.5; **HRMS (ESI-TOF) m/z**: [M + Na]+ Calculated for $C_{10}H_{12}O_5Na$ 235.0582; found 235.0582.

Ethyl 4-hydroxy-2-(methacryloyloxy)-4-methylpent-2-enoate (8aa*). Prepared as shown in general experimental procedure (b); $[Cp^*IrCl_2]_2$ catalyst (16.0 mg, 5 mol %, 0.05 equiv) was used instead of $[Cp^*RhCl_2]_2$ catalyst. Colorless Oil; Yield - (48.5 mg, 50%); R_f (30% EtOAc/Petroleum Ether) 0.35; **IR** (KBr, cm^{-1}): 3446, 3055, 2985, 2925, 2362, 1745, 1708, 1636, 1568, 1448, 1377, 1335, 1279, 1234, 1120; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.32 (t, *J* = 7.16 Hz, 3 H) 2.08 (s, 3 H) 2.13 (s, 3 H) 4.27 (q, *J* = 7.12 Hz, 2 H) 5.30 (s, 1 H) 5.38 (s, 1 H) 7.52 (d, *J* = 1.0 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 13.8, 16.3, 20.5, 61.5, 109.3, 120.3, 123.2, 137.4, 139.5, 161.8, 164.7, 165.8; **HRMS (ESI-TOF) m/z**: [M + Na]+ Calculated for $C_{12}H_{18}O_5Na$ 265.1052; found 265.1053.

Ethyl 4-hydroxy-4-methylhept-6-en-2-ynoate (2o). Prepared as shown in reference number 1a. Light yellow oil; R_f (30% EtOAc/Petroleum Ether) 0.30; **IR** (KBr, cm^{-1}): 3405, 3080, 2985, 2937, 2234, 1718, 1641, 1447, 1360, 1277; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.28 (t, *J* = 7.14 Hz, 3 H) 1.50 (s, 3 H) 2.41 (dd, *J* = 13.20, 8.40 Hz, 1 H) 2.50 (dd, *J* = 13.58, 6.63 Hz, 1 H) 4.21 (q, *J* = 7.20 Hz, 2 H) 5.16 - 5.23 (m, 2 H) 5.84 - 5.95 (m, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 14.0, 28.3, 47.3, 62.2, 66.9, 75.3, 90.0, 120.4, 132.2, 132.2, 153.6; **HRMS (ESI-TOF) m/z**: [M + H]+ Calculated for $C_{10}H_{14}O_3H$ 183.1021; found 183.1021.

3-Allyl-6,8-dimethoxy-3-methyl-1H-furo[3,4-c]isochromene-1,5(3H)-dione (5no). Prepared as shown in general experimental procedure (a). White Solid; Yield - (39.8 mg, 42%); ***mp***: 140-142 °C; R_f (30% EtOAc/Petroleum Ether) 0.20; **IR** (KBr, cm^{-1}): 3079, 2962, 2922, 2850, 1755, 1686, 1599, 1565, 1460, 1282, 1206, 1158; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.66 (s, 3 H) 2.63 - 2.78 (m, 2 H) 3.97 (s, 3 H) 3.97 (s, 3 H) 5.11 - 5.20 (m, 2 H) 5.65 (ddt, *J* = 17.13, 9.93, 7.31, 7.31 Hz, 1 H) 6.54 (d, *J* = 2.27 Hz, 1 H) 7.37 (d, *J* = 2.27 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 22.7, 41.1, 56.2, 56.4, 83.1, 97.7, 100.1, 100.4, 101.3, 121.1, 129.6, 135.2, 156.4, 164.1, 166.8, 167.1, 176.1; **HRMS (ESI-TOF) m/z**: [M + Na]+ Calculated for $C_{17}H_{16}O_6Na$ 339.0845; found 339.0845.

3-Ethoxy-3-oxoprop-1-en-1-yl benzoate (11)[18]. Prepared as shown in reference number 18. Colorless Oil; R_f (20% EtOAc/Petroleum Ether) 0.65; **IR** (KBr, cm^{-1}): 3093, 2983, 2934, 1753,

1715, 1656, 1601, 1451, 1313, 1289, 1257, 1234, 1138, 1100; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.31 (t, *J* = 7.12 Hz, 3 H) 4.23 (q, *J* = 7.16 Hz, 2 H) 5.9 (d, *J* = 12.52 Hz, 1 H) 7.47 (t, *J* = 7.96 Hz, 2 H) 7.60 - 7.64 (m, 1 H) 2.11 (dd, *J* = 8.24, 1.0 Hz, 2 H) 8.53 (d, *J* = 12.52 Hz, 1 H); **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 14.2, 60.4, 106.3, 127.7, 128.7, 130.3, 134.3, 149.7, 162.4, 166.0; **HRMS (ESI-TOF) m/z**: [M + Na]+ Calculated for $C_{12}H_{12}O_4Na$ 243.0633; found 243.0633.

SUPPORTING INFORMATION:

The optimization data**,** ^{1}H, and ^{13}C NMR spectral data of all compounds and X-ray crystallography data and CIF of compound **5ga** (CCDC1936701) and **8aa** (CCDC1936701) included.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by SERB (EMR/2016/006358), New-Delhi, Indian Institute of Science, R. L. Fine Chem, SYNMR Chemicals Pvt. Ltd. We thank Dr. A. R. Ramesha (R. L. Fine Chem) and Dr. S. Iyer (SYNMR) for useful discussion. Anil thanks UGC, New-Delhi for fellowship.

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