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Palladium-Catalyzed One-pot Highly Regioselective 6-*Endo* Cyclization and Alkylation of Enynoates: Synthesis of 2-Alkanone Pyrones

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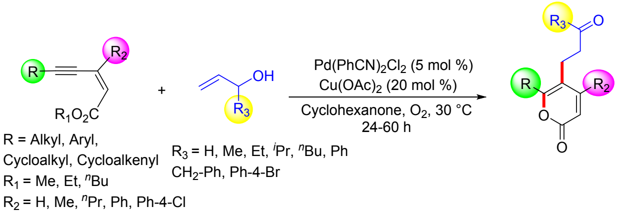
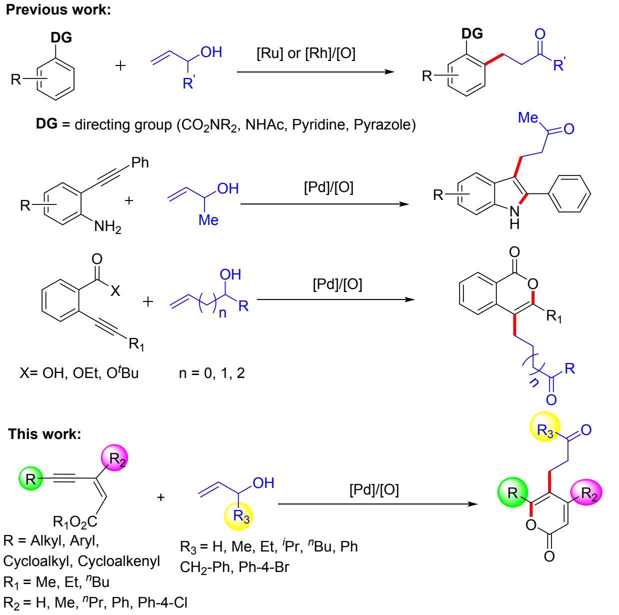
Supporting Information



ABSTRACT:Pd(II)-catalyzed one-pot tandem cyclization/alkylation reactions of enyanoates with allylic alcohols has been demonstrated. In this reaction, an innovative protocol proceeded well through Pd-catalyzed intramolecular selective *6-endo* cyclization, insertion of allylic alcohols into the Pd-C bond of vinylpalladium species generated *in situ*, and β-hydrogen elimination processes. This conversion provides a convenient and efficient methodology for the synthesis of 2-alkanone pyronesin moderate to good yields.

INTRODUCTION

Pyrones are fundamental structural motifs in numerous natural products [1]and also versatile building blocks for the synthesis of various biologically active heterocyclic compounds.[2] As a result, considerable attention has been devoted to preparing diverse pyrone compounds by employing differentmethods.[3] Owing to the limitation of traditional methods, thegroupsof Rossi,[4] Larock,[5] and Burton, *et al*.[6] have developed more convenient approaches[4b, 7]by using different electrophiles such as I_2, NIS, ICl, PhSeCletcfor the cyclization of enynoates to form pyrone derivatives. Recently, Loh,[8]Pardasani, *et al*.[9] studied the palladium-catalyzed difunctionalization reaction of internal alkynes of enynoates*via6-endo* cyclization and using different coupling partners such as electron-deficient olefins to capture the vinylpalladium species generated *in situ*.[10]Despite the fact these methods made processes more facile and efficient, there still need to develop a new methodology to broaden the diversity of the pyrone compounds.[11]Therefore, we selected allylic alcohol as an alkylating agent in order to develop a convenient and dominant protocol for the synthesis of multisubstitutedpyrones through the Heck-type C-C bond formation.[12]Allylic alcohols exhibiting several advantages like abundant in nature, easy preparation, inexpensive and as a simple starting material offer synthetic applications.[13] It has been extensively utilized in transition metal catalyzed reactions in three different ways such as nucleophilic substitution of –OH groups,[14]formations of C=C bonds[15] and as a carbonyl alkylating agent.[16] To the best of our knowledge, rare examples of the palladium-catalyzed oxidative cross coupling reactions between internal alkynes and allylic alcohols have been developed (Scheme 1).[17,13a,18]Inspired by the previous work, we became interested to discover the application of vinyl-Pd species produced *in situ* during cross coupling reaction[19] for the synthesis of 2-alkanonepyrone compounds using enynoate.

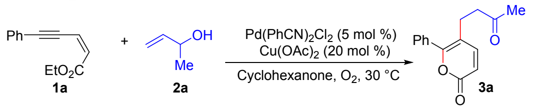


Scheme 1.Reported Methods forAlkylationwith Allylic Alcohols.

RESULTS AND DISCUSSION

The *Z*-enynoate**1a** and allylic alcohol **2a** were employed as model substrates. Recently, we found that the combination of Pd(II) catalyst with an oxidant favored such cyclization/coupling reactions. So our investigation began with 5 mol % of $PdCl_2$, 10 mol % $Cu(OAc)_2$ and O_2 in DMSO at 30°C (Chart 1). Pleasingly, the desired 5-(3-oxobutyl)-6-phenyl-2*H*-pyran-2-one **3a** could be obtained but in a low yield (25%).For the optimization of the reaction condition, an extensive screening of solvents, to our delight, the desired product **3a** was obtained in 62% yield in 2-butanone (Chart 1, entry 7). Cyclohexanone was also an effective solvent as compared to the other tested solvents, and the product **3a** was obtained in 68 % yield (entry 8). The reaction was also run with various Pd(II) catalysts, except for $Pd(OAc)_2$ and $Pd(dba)_2$ (entries 13, 14), other Pd(II) catalysts gave comparable results. Next screening the combined oxidant system such as $Cu(OAc)_2$ with oxygen, $CuCl_2$ with oxygen and $Cu(OAc)_2$ in the air could afford the desired product in acceptable yield, while the silver salt, BQ, and $K_2S_2O_8$ with oxygen were not effective.After screening the reaction conditions it was revealed that chlorine anion, oxidant acetate anion, O_2 (atm) and solvent as well had a significant influence on the yield and efficiency of the reaction. Especially, a good yield of the desired product was obtained when $Pd(PhCN)_2Cl_2$ and $Cu(OAc)_2$ as an oxidant with O_2 (atm) were applied in this reaction. Moreover, it was found that higher temperature decreased the product yield (entries 21).Finally, it was found that increasing the oxidant loading to 20 mol% could afford the desired product **3a** in 76% yield (entry 9).

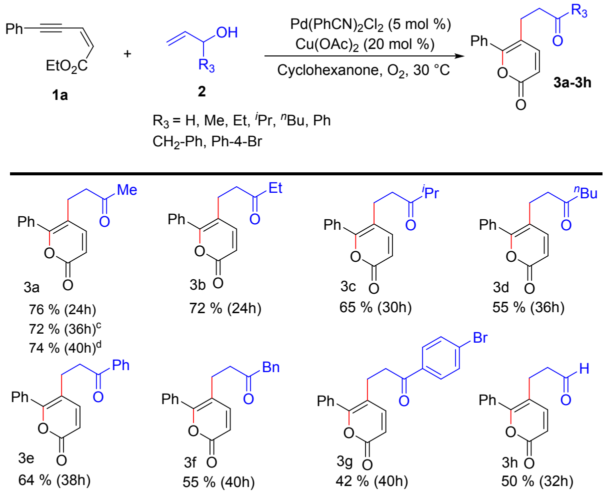
Chart 1. Optimization of Reaction Conditions.[a,b]



entry	catalyst (05 mol %)	oxidant (20 mol %)	solvent	temp (°C)	time (h)	yield (%)
1	$PdCl_2$	$Cu(OAc)_2$ (10) + O_2 (1 atm)	DMSO	30	24	25
2	$Pd(PhCN)_2Cl_2$	$Cu(OAc)_2$ (10) + O_2 (1 atm)	DMSO	30	30	40
3	$Pd(PhCN)_2Cl_2$	$Cu(OAc)_2$ (10) + O_2 (1 atm)	CH_3CN	30	32	<5
4	$Pd(PhCN)_2Cl_2$	$Cu(OAc)_2$ (10) + O_2 (1 atm)	1,4-Dioxane	30	30	28
5	$Pd(PhCN)_2Cl_2$	$Cu(OAc)_2$ (10) + O_2 (1 atm)	DCE	30	36	34
6	$Pd(PhCN)_2Cl_2$	$Cu(OAc)_2$ (10) + O_2 (1 atm)	Acetone	30	24	58
7	$Pd(PhCN)_2Cl_2$	$Cu(OAc)_2$ (10) + O_2 (1 atm)	2-Butanone	30	32	62
8	$Pd(PhCN)_2Cl_2$	$Cu(OAc)_2$ (10) + O_2 (1 atm)	Cyclohexanone	30	36	68
9	$Pd(PhCN)_2Cl_2$	$Cu(OAc)_2$ (20) + O_2 (1 atm)	Cyclohexanone	30	24	76
10	$Pd(PhCN)_2Cl_2$	$Cu(OAc)_2$ (30) + O_2 (1 atm)	Cyclohexanone	30	26	71
11	$PdCl_2$	$Cu(OAc)_2$ (20) + O_2 (1 atm)	Cyclohexanone	30	36	72
12	$Pd(MeCN)_2Cl_2$	$Cu(OAc)_2$ (20) + O_2 (1 atm)	Cyclohexanone	30	32	60
13	$Pd(OAc)_2$	$Cu(OAc)_2$ (20) + O_2 (1 atm)	Cyclohexanone	30	36	N.R
14	$Pd(dba)_2$	$Cu(OAc)_2$ (20) + O_2 (1 atm)	Cyclohexanone	30	36	N.R
15	$Pd(PhCN)_2Cl_2$	BQ (20) + O_2 (1 atm)	Cyclohexanone	30	36	17
16	$Pd(PhCN)_2Cl_2$	$K_2S_2O_8$ (20) + O_2 (1 atm)	Cyclohexanone	30	30	10
17	$Pd(PhCN)_2Cl_2$	$CuCl_2$ (20) + O_2 (1 atm)	Cyclohexanone	30	30	53
18	$Pd(PhCN)_2Cl_2$	Ag_2O(20) + O_2 (1 atm)	Cyclohexanone	30	30	N.R
19	$Pd(PhCN)_2Cl_2$	AgOAc(20) + O_2 (1 atm)	Cyclohexanone	30	24	N.R
20	$Pd(PhCN)_2Cl_2$	$Cu(OAc)_2$ (20) + Air (1 atm)	Cyclohexanone	30	24	49
21	$Pd(PhCN)_2Cl_2$	$Cu(OAc)_2$ (20) + O_2 (1 atm)	Cyclohexanone	50	24	64

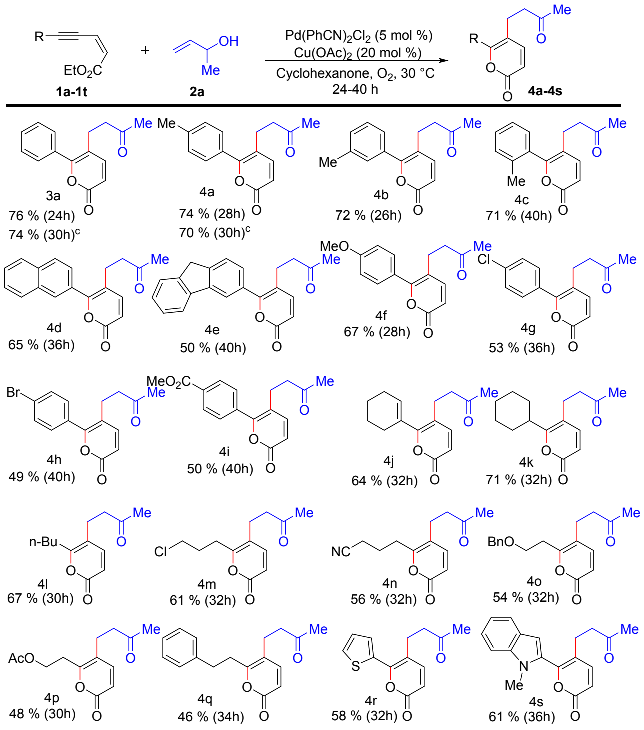
[a]Reaction conditions: A mixture of**1a** (0.2 mmol), **2a** (0.6 mmol, 3 equiv), $Pd(PhCN)_2Cl_2$ (0.01 mmol, 0.05 equiv), $Cu(OAc)_2$ (0.04 mmol, 0.2 equiv), and oxidant in solvent (1mL) were stirred at 30 °C for 24 h. [b]Isolated yields.

Chart 2. Scope of Allylic Alcohol



[a]Reaction conditions: Unlessotherwise specified, the reactions were performed with**1a** (0.2 mmol), **2** (0.6 mmol, 3 equiv), $Pd(PhCN)_2Cl_2$ (0.01 mmol, 0.05 equiv), $Cu(OAc)_2$ (0.04 mmol, 0.2 equiv), and O_2 (1 atm) in cyclohexanone(1 mL) were stirred at 30 °C for 24-40 h. [b]Isolated yields. [c]With use ofmethyl (Z)-5-phenylpent-2-en-4-ynoate(**1a'**). [d]With use of*n*-butyl (Z)-5-phenylpent-2-en-4-ynoate (**1a″**).

Chart 3. Substrate Scope of Enynoate.[a,b]

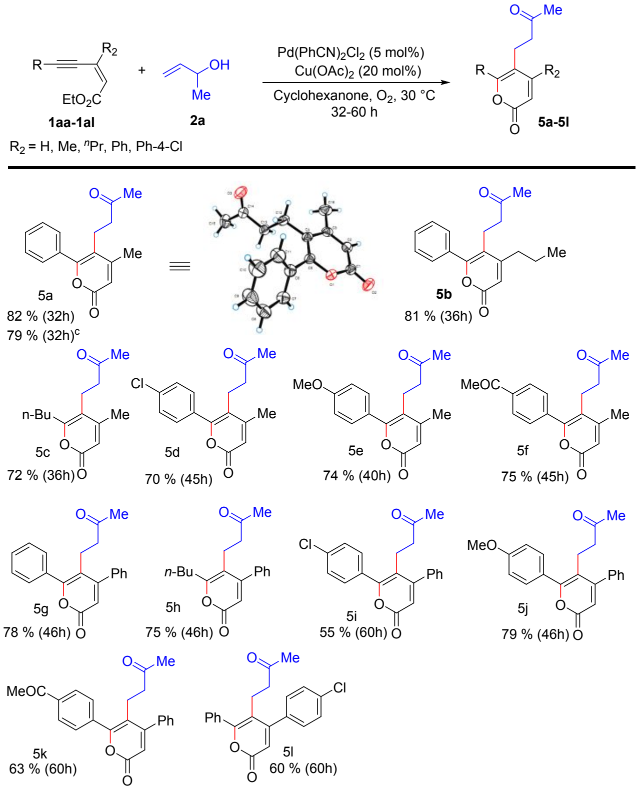


[a]Reaction conditions: Unless otherwise specified, all the reactions were carried out with **1** (0.2 mmol), **2a** (0.6 mmol, 3 equiv),$Pd(PhCN)_2Cl_2$ (0.01 mmol, 0.05 equiv), $Cu(OAc)_2$ (0.04 mmol, 0.2 equiv), and O_2 (1 atm) in cyclohexanone(1 mL) were stirred at 30 °C for 24-40 h. [b]Isolated yields.[c]The reaction was run on 0.5 mmol scale.

After concluding optimization of the reaction conditions, we next probed the generality of different allylic alcohols as coupling partner and the results are summarized in Chart 2. The but-3-en-2-ol (**2a**) was first investigated with differentenynoates(**1a, 1a' and 1a″**).Among them, the enynoate**1a**gave the corresponding product (**3a**) in good yield with short reaction time.Then the enynoate**1a**was selected as substrate for the synthesis of products(**3b-3h**).When an alkyl chain was increased and/or branched on allylic alcohols,the corresponding products were obtained (**3b-3d**) in moderate to good yield. Additionally, the phenyl and benzyl group were well tolerated to afford the desired products**3e** and **3f** in good yields, respectively. Furthermore, the bromo substituted phenyl group was transformed into the product (**3g**) in 42% yield. It shows that the steric effect is very significant as it prolongs the reaction time to obtain the desired products (Chart 2, **3e-3f, 3g**). Finally, the simplest allyl alcohols were successfully converted into an active aldehyde (**3h**) in 50 % yield.

We next tested the substrate scope of this highly regioselective *6-endo* cyclization and alkylation (Chart 3). In general, the phenyl ring bearing methyl group at *meta* and *para*-position could afford the desired product in moderate to good yield (**4a-4b**). However, the presence of a methyl group at the *ortho*-position of the aryl ring prolonged the reaction time due to steric effect (**4c**). The electron-donating group substituted phenyl ring and bulky substituents such as naphthyl and fluorenyl all favored this transformation under the standard conditions (Chart 3, **4d-4f**). The substrates with the electron-withdrawing group or halides on the phenyl ring were also compatible with the reaction system by prolonging the reaction time (**4g-4i**). Additionally, the cyclohexyl, cyclohexenyl, and aliphatic substituted enynoates were all well tolerated. The corresponding products obtained in moderate to good yields (**4j-4q**). Moreover, thioenyl and indole-substituted enynoate were utilized with the allylic alcohols, the desired products **4r** and **4s** could be obtained in 58% and 61% yield, respectively.

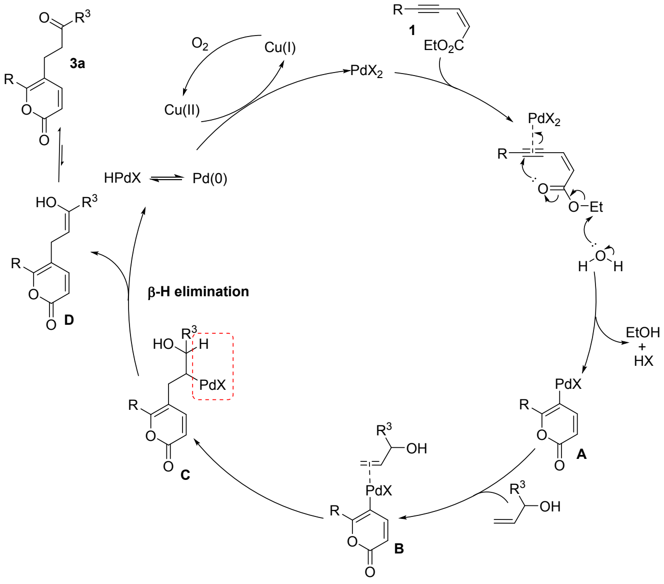
Chart 4. Scope of β-substituted Enynoate.[a,b]



[a]Reaction conditions: Unless otherwise specified, the reacions were performed with**1**(0.2 mmol), **2a** (0.6 mmol, 3 equiv), Pd(PhCN)$_2$Cl$_2$ (0.01 mmol, 0.05 equiv), Cu(OAc)$_2$ (0.04 mmol, 0.2 equiv), and O$_2$ (1 atm) in cyclohexanone(1mL) were stirred at 30 °C for 32-60 h. [b]Isolated yields. [c]The reaction was run on 0.5 mmol scale.

Finally, we proceeded to examine the substrates with β-substituent of enynoates achieving good to excellent yield (Chart 4). It was observed that the substrates with methyl or propyl at β-position led to the corresponding product in highyield (70%-82%, **5a-5f**).The structure **5a** was clearly confirmed by the X-ray crystallography (CCDC: 1836656, Chart 4). In addition, a series of substrates with a phenyl group at β-position were also converted to the desired products in moderate to good yields (**5g-5l**). In this case, due to the bulkiness of the phenyl group at theβ-position, prolonging the reaction time is necessary.

The proposed reaction mechanism for the Pd(II)-catalyzed regioselective 6-*endo* cyclization and alkylation of enynoate is illustrated in Scheme 2.[20] First, the carbonyl oxygen of ester moiety attacks the Pd(II) activated alkyne of enyanoate to afford the vinylpalladium intermediate **A**, *via6-endo* cyclization. Subsequently, an allylic alcohol will insert into the C-Pd bond of vinylpalladium species to form thealkylpalladium species **C**, which is followed by β-hydrogen elimination to form the enol product **D** and then produces the final product **3a**. The released Pd(0) species will be oxidized into Pd(II) in the presence of the oxidants Cu(OAc)$_2$, O$_2$ and utilized in the next catalytic cycle.



Scheme 2. Proposed Mechanism

CONCLUSION

In conclusion, we have reportedthepalladium catalyzed highly regioselective *6-endo* cyclization and alkylation. The corresponding products were obtained in good yields. This work provides a simple and general approach for the synthesis of highly substituted pyronealkanones from readily available nonbiased allylic alcoholsunder mild and efficient reaction condition.

EXPERIMENTAL SECTION

General Information

$Pd(PhCN)_2Cl_2$, $Cu(OAc)_2$ and some of allylic alcohols were purchased from commercial suppliers used as received unless otherwise noted. All Commercial solvents and reagents were employed without further purification. Reactions were monitored through analytical thin layer chromatography (SiO_2 60 F-254 plates). The spots visualization were performed under UV radiation (254 nm), further visualization was possible using a basic solution of potassium permanganate. Flash chromatography was carried out using 200-300 mesh silica gel (SiO_2 60) with distilled solvents. Proton nuclear magnetic resonance (^{1}H NMR) and Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 25 ºC on Bruker Advance 400M NMR spectrometers. Chloroform-*d* was used as the solvent and $Si(CH_3)_4$(TMS) as an internal standard. Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from TMS (δ 0.00 ppm) and relative to the signal of chloroform-*d* (δ 7.260 ppm, singlet). Multiplicities are recorded as: *s* (singlet); *d* (doublet); *t* (triplet); *q* (quartet); *dd*(doublets of doublet); *m* (multiplets). Coupling constants are expressed as a *J* value in Hz. ^{13}C NMR are reported as δ in units of parts per million (ppm) downfield from TMS (δ 0.00 ppm) and relative to the signal of chloroform-*d* (δ 77.03 ppm, triplet). Notable, splitting signals of the ^{13}C nucleus was difficult to differentiate and ^{13}C NMR signals were reported as a singlet. High resolution mass spectral analysis (HRMS) spectra were recorded on Water XEVO-G2 Q-TOF (Waters Corporation). IR spectra were recorded on a FTIR spectrophotometer.

Preparation of (*Z*)-Enynoates:

(*Z*)-Enynoates**1a-1t** were prepared according to the reported literature .[2, 4a, 8, 21]

MethodA: In an oven dried 50 mL round bottom flask with a mixture of (*Z*)-ethyl 3-iodoacrylate(**P$_1$**)(1.13 g, 5 mmol, 1.0 eq.), $Pd(PPh_3)_2Cl_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%), and Et_3N (20 mL) was added the corresponding alkyne (5.5 mmol, 1.1 equiv.). The mixture was stirred at 50 °C under an inert argon atmosphere until the starting material was completely disappeared (monitored by TLC). Then the reaction mixture was cooled to room temperature and diluted with diethyl ether (Et_2O, 10 mL). Then the solution was washed with saturated ammonium chloride (NH_4Cl, 10 mL) twice. The aqueous phase was extracted with Et_2O (10 mL). The combined organic phase was dried over anhydrous sodium sulfate (Na_2SO_4) and concentrated under reduced pressure to give the crude product, which was purifiedby flash column chromatography using petroleum ether/ethyl acetate (97:3) as eluent afforded the desired products (**1a-1t**).

The Enynoate**1a'** and **1a″**were prepared by using (*Z*)-methyl 3-iodoacrylate (**P$_2$**) and(*Z*)-*n*-butyl 3-iodoacrylate (**P$_3$**) respectivelyaccording to theMethod A.The **P$_1$**, **P$_2$**and**P$_3$** were also prepared according to the reported literatures.[2]

Preparation of *β*-substituted(*Z*)-Enynoates:

The*β*-substituted(*Z*) enynoates(**1aa-1al**) were prepared according tothe reported literatures.[2, 4a, 8, 21]

Method B: In an oven dried 50 mL round bottom flask with a mixture of ethyl (Z)-3-iodobut-2-enoate (**P$_4$**),(1.13 g, 5 mmol, 1.0 eq.), $Pd(PPh_3)_2Cl_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%), and Et_3N (20 mL) was added the corresponding alkyne (5.5 mmol, 1.1 equiv.). The mixture was stirred at 50 °C under an inert argon atmosphere until the starting material was completely disappeared (monitored by TLC). Then the reaction mixture was cooled to room temperature and diluted with Et_2O(10 mL). Then the solution was washed with saturated NH_4Cl (10 mL) twice. The aqueous phase was extracted with Et_2O (10 mL). The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give the crude product which was purified by flash column chromatography using petroleum ether/ethyl acetate (97:3 - 95:5) as eluent afforded the desired products (**1aa** and **1ac-1af).**The ethyl (*Z*)-3-iodohex-2-enoate (**P$_5$**) was used to synthesis the **1ab**.The **1ag-1ak** were synthesized by using ethyl (Z)-3-iodo-3-phenylacrylate(**P$_6$**) while the ethyl (Z)-3-(4-chlorophenyl)-3-iodoacrylate (**P$_7$**)was used to prepare the **1al**.

The ^{1}H NMR, ^{13}C NMR, HRMS and FTIRcharacterization dataof newly synthesized *β*-substituted(*Z*) enynoates (**1ad, 1ae, 1af, 1ai, 1aj, 1ak, 1al**) are given below (for spectral data see supporting information), while the *β*-substituted(*Z*) enynoates (**1aa-1ac**, **1ag**and**1ah**) are previously reported in literatures. The **P$_4$**, **P$_5$**, **P$_6$** and **P$_7$** were prepared according to the reported literature.All the Allylic alcohols wereprepared according to the reported literatures.[22](**2c-2h**).

Ethyl(*Z*)-5-(4-chlorophenyl)-3-methylpent-2-en-4-ynoate (**1ad).** To a mixture of ethyl (Z)-3-iodobut-2-enoate (P_4) (1.2 g, 5 mmol, 1.0 eq.), $Pd(PPh_3)_2Cl_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%), and Et_3N (20 mL) was added the 1-chloro-4-ethynylbenzene (0.75 g, 5.5 mmol, 1.1 equiv.). The mixture was stirred for 18 h at 50 °C under an inert argon atmosphere and dealt with according to the similar Method B to give the product **1ad** (0.87 g, 3.5 mmol, 70 % yield) as light green oil;R_f= 0.45 (petroleum ether/ethyl acetate = 95:5);FTIR (KBr neat) υ_{max}2204, 1722, 1620, 1489,1188 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.05 (s, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 2.13 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm;^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$):δ165.0, 135.1, 134.3, 133.2, 128.7, 124.7, 121.2, 98.8, 89.2, 60.1, 25.1, 14.3 ppm;HRMS (EI): m/z Calcd. for $C_{14}H_{13}ClO_2Na$ $[M+Na]^+$: 271.0502, found: 271.0499.

Ethyl(*Z*)-5-(4-methoxyphenyl)-3-methylpent-2-en-4-ynoate (**1ae**).To a mixture of ethyl (Z)-3-iodobut-2-enoate (P_4) (1.2 g, 5 mmol, 1.0 eq.), $Pd(PPh_3)_2Cl_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%), and Et_3N (20 mL) was added the 1-ethynyl-4-methoxybenzene (0.73 g, 5.5 mmol, 1.1 equiv.). The mixture was stirred for 18 h at 50 °C under an inert argon atmosphere and dealt with according to the similar Method B to give the product (**1ae)**(0.91 g, 3.7 mmol, 74% yield) as light brown oil;R_f= 0.44(petroleum ether/ethyl acetate = 95:5);FTIR (KBr neat) υ_{max}2197, 1719, 1616, 1511, 1194, 825 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 5.99 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 2.13 (s, 3H), 1.31 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$): δ 165.3, 160.3, 135.0, 133.5, 123.5, 114.9, 114.0, 100.8, 87.6, 60.0, 55.3, 25.3, 14.4 ppm; HRMS (EI): m/z Calcd. for $C_{15}H_{17}O_3$ $[M+H]^+$: 245.1178, found: 245.1182.

Ethyl(*Z*)-5-(4-acetylphenyl)-3-methylpent-2-en-4-ynoate (**1af**).To a mixture of ethyl (Z)-3-iodobut-2-enoate (P_4) (1.2 g, 5 mmol, 1.0 eq.), $Pd(PPh_3)_2Cl_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%), and Et_3N (20 mL) was added the 1-(4-ethynylphenyl)ethan-1-one (0.79 g, 5.5 mmol, 1.1 equiv.). The mixture was stirred for 18 h at 50 °C under an inert argon atmosphere and dealt with according to the similar Method B to give the product

(**1af**)(0.92 g, 3.6mmol, 72 %yield) as light yellow solid;R_f= 0.40 (petroleum ether/ethyl acetate = 95:5); FTIR (KBr neat) υ_{max}2204, 1720, 1684, 1616, 1556, cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 6.08 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.61 (s, 3H), 2.15 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$): δ 197.3, 164.9, 136.7, 134.0, 132.1, 128.2, 127.6, 125.5, 98.7, 91.1, 60.2, 26.7, 25.0, 14.3 ppm;HRMS (EI): m/z Calcd. for $C_{16}H_{16}O_3Na$ [M+Na]$^+$: 279.0997, found: 279.1001.

Ethyl(*Z*)-5-(4-chlorophenyl)-3-phenylpent-2-en-4-ynoate (**1ai**).To a mixture of ethyl (Z)-3-iodo-3-phenylacrylate(P_6) (1.5 g, 5 mmol, 1.0 eq.), $Pd(PPh_3)_2Cl_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%), and Et_3N (20 mL) was added the 1-chloro-4-ethynylbenzene (0.75 g, 5.5 mmol, 1.1 equiv.). The mixture was stirred for 24 h at 50 °C under an inert argon atmosphere and dealt with according to the similar Method Bto give the product (**1ai**) (0.93 g, 2.96 mmol, 62 % yield) as brown solid;R_f=0.39(petroleum ether/ethyl acetate = 95:5);FTIR (KBr neat) υ_{max}2192, 1720, 1609,1559, 1497, 1101 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79-7.74 (m, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.44-7.41 (m, 3H), 7.35 (d, *J* = 8.4 Hz, 2H), 6.60 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$): δ 165.3, 137.0, 136.1, 135.4, 133.3, 130.0, 128.8, 128.7, 127.2, 123.1, 121.2, 100.7, 87.8, 60.5, 14.4 ppm; HRMS (EI): m/z Calcd. for $C_{19}H_{15}ClO_2$ [M+H]$^+$: 311.0839, found: 311.0840.

Ethyl(*Z*)-5-(4-methoxyphenyl)-3-phenylpent-2-en-4-ynoate (**1aj**). To a mixture of ethyl (*Z*)-3-iodo-3-phenylacrylate(P_6) (1.5 g, 5 mmol, 1.0 eq.), $Pd(PPh_3)_2Cl_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%), and Et_3N (20 mL) was added the 1-ethynyl-4-methoxybenzene (0.73 g, 5.5 mmol, 1.1 equiv.). The mixture was stirred for 24 h at 50 °C under an inert argon atmosphere and dealt with according to the similar Method B to give the product(**1aj**) (1.03 g, 3.36mmol, 7% yield) as light brown solid;R_f = 0.39(petroleum ether/ethyl acetate = 95:5);FTIR (KBr neat) υ_{max}2191, 1715, 1608, 1561, 1511, 1160, 771 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81-7.77 (m, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.43-7.40 (m, 3H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.54 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 165.6, 160.5, 137.4, 136.7, 133.8, 129.8, 128.6, 127.2, 121.8, 114.8, 114.1, 102.8, 86.2, 60.3, 55.4, 14.4 ppm; HRMS (EI): m/z Calcd. for $C_{20}H_{19}O_3$ [M+H]$^+$: 307.1334, found: 307.1337.

Ethyl(*Z*)-5-(4-acetylphenyl)-3-phenylpent-2-en-4-ynoate (**1ak**). To a mixture of ethyl (Z)-3-iodo-3-phenylacrylate(P_6) (1.5 g, 5 mmol, 1.0 eq.), $Pd(PPh_3)_2Cl_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%), and Et_3N (20 mL) was added the 1-(4-ethynylphenyl)ethan-1-one (0.79 g, 5.5 mmol, 1.1 equiv.). The mixture was stirred for 24 h at 50 °C under an inert argon atmosphere and dealt with according to the similar Method B to give the product (**1ak**) (1.0 g, 3.14mmol, 63 % yield) as light yellow solid;R_f= value 0.36(petroleum ether/ethyl acetate = 95:5);FTIR (KBr neat) υ_{max}2192, 1715, 1687,1605, 1510, 1462, 771 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.9 Hz, 2H), 7.80-7.76 (m, 2H), 7.71 (d, *J* = 8.1 Hz, 2H), 7.46-7.42 (m, 3H), 6.64 (s, 1H), 4.31 (q, *J* = 7.2 Hz, 2H), 2.63 (s, 3H), 1.36 (t, *J* = 7.0 Hz, 3H) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$): δ 197.3, 165.2, 136.9, 136.8, 135.9, 132.2, 130.1, 128.8, 128.3, 127.5, 127.2, 123.8, 100.6, 89.6, 60.6, 26.7, 14.4 ppm; HRMS (EI): m/z Calcd. for $C_{21}H_{19}O_3$ [M+H]$^+$: 319.1334, found: 319.1335.

Ethyl(*Z*)-3-(4-chlorophenyl)-5-phenylpent-2-en-4-ynoate (**1al**).To a mixture of ethyl (Z)-3-(4-chlorophenyl)-3-iodoacrylate (P_7) (1.7 g, 5 mmol, 1.0 eq.), $Pd(PPh_3)_2Cl_2$ (35.6 mg, 0.05 mmol, 1.0 mol%), CuI (4.9 mg, 0.025 mmol, 0.5 mol%), and Et_3N (20 mL) was added the ethynylbenzene (0.56 g, 5.5 mmol, 1.1 equiv.). The mixture was stirred for 24 h at 50 °C under an inert argon atmosphere and dealt with according to theMethod B to give the product**1al**(0.90 g, 2.90 mmol, 58 % yield) as brown solid;R_f= 0.39(petroleum ether/ethyl acetate = 95:5);FTIR (KBr neat) υ_{max}2202, 1719, 1601, 1563, 1490, 1093 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.71 (m, 2H), 7.64-7.60 (m, 2H), 7.41-7.37 (m, 5H), 6.56 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 165.2, 136.0, 135.6, 135.1, 132.1, 131.5, 130.5, 129.4, 129.1, 128.9, 128.5, 128.3, 127.9, 122.9,122.5, 102.4,86.5, 60.5, 14.4 ppm; HRMS (EI): m/z Calcd. for $C_{19}H_{16}ClO_2$ [M+H]$^+$: 311.0839, found: 311.0836.

Procedure forthe synthesis of2-alkanone pyrones(3a-3h), (4a-4s), (5a-5l). An oven dried 10 mL schlenk tube charged with a stir bar, cyclohexanone (1.0 mL) was added to a mixture of $Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) under O_2 atmosphere. The mixture was stirred for 5 minutes and then enynoate**1**(0.2 mmol, 1.0 equiv.) and corresponding allylic alcohols**2** (0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The reaction mixture was stirred at 30 °C until the starting material **1** was completely disappeared (Monitored by TLC). The reaction mixture was diluted with ethyl acetate and washed with water (10 mL × 2) and brine (5 mL). The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to afford the corresponding 2-alkanones pyrone.

5-(3-oxobutyl)-6-phenyl-2*H*-pyran-2-one(**3a**) $Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) andPd$(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) wereadded in cyclohexanone (1.0 mL) under O_2 atmosphere.Afterstirring for5 minutes,**1a** (40 mg, 0.2 mmol, 1.0 equiv.) and 3-buten-2-ol**2a** (43 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The system was stirring at 30 °Cfor 24 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2- 7:3) to afford the pure product(**3a**)as a light green oil (37 mg, 0.15 mmol, Yield: 76%);R_f= 0.44(petroleum ether/ethyl acetate = 7:3);FTIR (KBr neat) υ_{max}1725, 1706,1631, 1540cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.50 (m, 2H), 7.44-7.48 (m, 3H), 7.35 (d, *J* = 9.5 Hz, 1H), 6.30 (d, *J* = 9.5 Hz, 1H), 2.74 (t, *J* = 7.3 Hz, 2H), 2.63 (t, *J* = 7.3 Hz, 2H), 2.12 (s, 3H) ppm, $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$): δ 206.7, 161.9, 158.6, 146.8, 132.2, 130.1, 128.6, 114.9, 114.8, 43.4, 29.9, 23.4 ppm; HRMS (EI): m/z Calcd. for $C_{15}H_{14}O_3Na$ [M+Na]$^+$: 265.0841, found: 265.0858.

5-(3-oxopentyl)-6-phenyl-2*H*-pyran-2-one (**3b**)$Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes,**1a** (40 mg, 0.2 mmol, 1.0 equiv.) and pent-1-en-3-ol **2b** (52 mg, 0.6 mmol, 3.0 equiv.)were subsequently added to the mixture. The system was stirring at 30 °C for 24 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2- 7:3) to afford the pure product(**3b**)as a light green oil (37 mg, 0.14 mmol, Yield: 72%); R_f= 0.44(petroleum ether/ethyl acetate = 7:3); FTIR (KBr neat) υ_{max} 1735, 1713,1633, 1545cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.54 (m, 2H), 7.44-7.49 (m, 3H), 7.36 (d, *J* = 9.5 Hz, 1H), 6.30 (d, *J* = 9.5 Hz, 1H), 2.75 (t, *J* = 7.3 Hz, 2H), 2.60 (t, *J* = 7.4 Hz, 2H), 2.39 (q, *J* = 7.2 Hz, 2H), 1.03 (t, *J* = 7.3 Hz, 3H) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$): δ 209.5, 162.0, 158.5, 146.9, 132.2, 130.1, 128.6, 115.0, 114.9, 42.1, 36.0, 23.5, 7.7 ppm; HRMS (EI): m/z Calcd. for $C_{16}H_{16}O_3Na$ [M+Na]$^+$: 279.0997, found: 279.0999.

5-(4-methyl-3-oxopentyl)-6-phenyl-2*H*-pyran-2-one (**3c**).$Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere.After stirringfor 5 minutes**1a** (40 mg, 0.2 mmol, 1.0 equiv.) and 4-methylpent-1-en-3-ol**2c** (60 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture.The system was stirring at 30 °Cfor 30 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to afford the pure product(**3c**) as a light green oil (35 mg, 0.13 mmol, Yield: 65%);R_f= 0.45(petroleum ether/ethyl acetate = 7:3); FTIR (KBr neat) υ_{max} 1730, 1709,1628, 1545 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.55 (m, 2H), 7.43-7.48 (m, 3H), 7.36 (d, *J* = 9.5 Hz, 1H), 6.30 (d, *J* = 9.5 Hz, 1H), 2.75 (t, *J* = 7.3 Hz, 2H), 2.63 (t, *J* = 7.3 Hz, 2H), 2.57-2.50 (m, 1H), 1.06 (d, *J* = 6.9 Hz, 6H) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$): δ 212.8, 162.0, 158.5, 147.0, 132.2, 130.1, 128.6, 115.1, 114.8, 41.0, 40.0, 23.5, 18.1 ppm; HRMS (EI): m/z Calcd. for $C_{17}H_{19}O_3$ [M+H]$^+$: 271.1334, found: 271.1321.

5-(3-oxoheptyl)-6-phenyl-2*H*-pyran-2-one (**3d**).$Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes**1a** (40 mg, 0.2 mmol, 1.0 equiv.) and hept-1-en-3-ol **2d** (68 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The system was stirring at 30 °Cfor 36 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 -7:3) to afford the pure product(**3d**)as a light brown oil (31.5 mg, 0.11 mmol, Yield: 55%);R_f= 0.46(petroleum ether/ethyl acetate = 7:3); FTIR (KBr neat) υ_{max} 1732, 1709, 1630, 1541 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.44 (m, 5H), 7.35 (d, *J* = 9.5 Hz, 1H), 6.30 (d, *J* = 9.5 Hz, 1H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.59 (t, *J* = 7.4 Hz, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.56-1.47 (m, 2H), 1.32-1.22 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 209.2, 162.0, 158.5, 146.9, 132.2, 130.1, 128.6, 115.0, 114.8, 42.6, 42.4, 25.9, 23.4, 22.3, 13.8ppm;HRMS (EI): m/z Calcd. for $C_{18}H_{20}O_3$ [M+H]$^+$: 285.1491, found: 285.1488.

5-(3-oxo-3-phenylpropyl)-6-phenyl-2*H*-pyran-2-one (**3e**). $Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes**1a** (40 mg, 0.2 mmol, 1.0 equiv.) and 1-phenylprop-2-en-1-ol **2e** (80 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The system was stirring at 30 °Cfor 38 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to afford the pure product (**3e**) as a brown solid (39 mg, 0.13 mmol, Yield: 64%);R_f= 0.42(petroleum ether/ethyl acetate = 7:3);mp 60-61°C; FTIR (KBr neat) υ_{max}1731, 1685, 1636,1590, 1548 cm^{-1};1H NMR (400 MHz, $CDCl_3$): δ 7.88 (d, *J* = 7.9 Hz, 2H), 7.59-7.53 (m, 3H), 7.48 – 7.40 (m, 6H), 6.32 (d, *J* = 9.5 Hz, 1H), 3.16 (t, *J* = 7.5 Hz, 2H), 2.93 (t, *J* = 7.5 Hz, 2H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 198.2, 162.0, 158.7, 147.0, 136.3, 133.45, 132.2, 130.1, 128.7, 128.6, 128.0, 115.0, 114.9, 38.6, 24.0 ppm; HRMS (EI): m/z Calcd. for $C_{20}H_{17}O_3$ [M+H]$^+$: 305.1178, found: 305.1184.

5-(3-oxo-4-phenylbutyl)-6-phenyl-2*H*-pyran-2-one (**3f**). $Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirringfor 5 minutes**1a** (40 mg, 0.2 mmol, 1.0 equiv.) and 1-phenylbut-3-en-2-ol **2f** (88 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture.The system was stirring at 30 °Cfor 40 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to afford the pure product(**3f**) as a white solid (35 mg, 0.11 mmol, Yield: 55%);R_f = 0.41(petroleum ether/ethyl acetate = 7:3);mp 63-64°C; FTIR (KBr neat) υ_{max} 1735, 1709, 1636,1560, 1540 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (s, 5H), 7.35-7.27 (m, 3H), 7.25 (d, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 7.0 Hz, 2H), 6.23 (d, *J* = 9.5 Hz, 1H), 3.64 (s, 2H), 2.70 (t, *J* = 7.1 Hz, 2H), 2.62 (t, *J* = 7.0 Hz, 2H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 206.4, 161.9, 158.5, 146.8, 133.6, 132.1, 130.1, 129.3, 128.9, 128.6, 128.6, 127.3, 114.7, 50.3, 41.4, 23.5 ppm; HRMS (EI): m/z Calcd. for $C_{21}H_{19}O_3$ [M+H]$^+$: 319.1334, found: 319.1336.

5-(3-(4-bromophenyl)-3-oxopropyl)-6-phenyl-2*H*-pyran-2-one (**3g**).$Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes**1a** (40 mg, 0.2 mmol, 1.0 equiv.) and 1-(4-bromophenyl)prop-2-en-1-ol **2g** (127 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The system was stirring at 30 °Cfor 40 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to afford the pure product (**3g**) as a light green solid (32 mg, 0.08 mmol, Yield: 42%);R$_f$= 0.40(petroleum ether/ethyl acetate = 7:3);mp77-78°C; FTIR (KBr neat) υ_{max}1729, 1681, 1635, 1582, 1550 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.55-7.51 (m, 2H), 7.46 (d, *J* = 5.0 Hz, 3H), 7.41 (d, *J* = 9.5 Hz, 1H), 6.33 (d, *J* = 9.5 Hz, 1H), 3.11 (t, *J* = 7.4 Hz, 2H), 2.92 (t, *J* = 7.4 Hz, 2H) ppm; ^{13}C{^{1}H}NMR (101 MHz, CDCl$_3$): δ 197.1, 161.9, 158.8, 146.8, 135.0, 132.2, 132.1, 130.2, 129.5, 128.7, 128.6, 115.0, 114.8, 38.6, 23.9 ppm; HRMS (EI): m/z Calcd. for $C_{20}H_{16}BrO_3$ [M+H]$^+$: 383.0283, found: 383.0294.

5-(3-oxopropyl)-6-phenyl-2*H*-pyran-2-one (**3h**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O$_2$ atmosphere. After stirring for 5 minutes**1a** (35 mg, 0.2 mmol, 1.0 equiv.) and prop-2-en-1-ol **2h** (43 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture.The system was stirring at 30 °Cfor 32 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na$_2$SO$_4$, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleumether/ethyl acetate (8:2) to afford the pure product **3h** as a light brown oil (23 mg, 0.10 mmol, Yield: 50%);R$_f$= 0.36(petroleum ether/ethyl acetate = 8:2);FTIR (KBr neat) υ_{max}1738, 1730, 1627, 1544 cm^{-1};^{1}H NMR (400 MHz,CDCl$_3$**):** δ 9.75 (s, 1H), 7.52-7.45 (m, 5H), 7.35 (d, *J* = 9.5 Hz, 1H), 6.32 (d, *J* = 9.5 Hz, 1H), 2.80 (t, *J* = 7.3 Hz, 2H), 2.68 (t, *J* = 7.4 Hz, 2H) ppm; ^{13}C{^{1}H}NMR (101 MHz, CDCl$_3$):δ 200.0, 161.8, 158.8, 146.5, 132.1, 130.2, 128.7, 128.6, 115.1, 114.3, 43.8, 21.9 ppm; HRMS (EI): m/z Calcd. for $C_{14}H_{12}O_3Na$ [M+Na]$^+$: 251.0684, found: 251.0688.

5-(3-oxobutyl)-6-(p-tolyl)-2*H*-pyran-2-one (**4a**)Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O$_2$ atmosphere. After stirring for 5 minutes followed by the addition of **1b** (43 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol**2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 28 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na$_2$SO$_4$, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolate the pure product (**4a**) as a light brown oil (38 mg, 0.15 mmol, Yield: 74%);R$_f$=0.44 (petroleum ether/ethyl acetate = 7:3);FTIR (KBr neat) υ_{max} 1728, 1713, 1632, 1550, cm^{-1};^{1}H NMR (400 MHz, CDCl$_3$): δ 7.41 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 9.5 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.27 (d, *J* = 9.4 Hz, 1H), 2.74 (t, *J* = 7.3 Hz, 2H), 2.62 (t, *J* = 7.4 Hz, 2H), 2.41 (s, 3H), 2.12 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 206.8, 162.1, 158.8, 146.9, 140.4, 129.4, 129.3, 128.5, 114.5, 114.5, 43.5, 30.1, 23.5, 21.4 ppm; HRMS (EI): m/z Calcd. for $C_{16}H_{17}O_3$ [M+H]$^+$: 257.1178, found: 257.1183.

5-(3-oxobutyl)-6-(m-tolyl)-2*H*-pyran-2-one (**4b**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O$_2$ atmosphere. After stirring for 5 minutes followed by the addition of **1c** (43 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 26 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na$_2$SO$_4$, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolate the pure product(**4b**) as a light brown oil (37 mg, 0.14 mmol, Yield: 72%);R$_f$= 0.44 (petroleum ether/ethyl acetate = 7:3);FTIR (KBr neat) υ_{max} 1733, 1712, 1636, 1553 cm^{-1};^{1}H NMR (400 MHz, CDCl$_3$): δ 7.36-7.25 (m, 5H), 6.29 (d, *J* = 9.4 Hz, 1H), 2.74 (t, *J* = 7.2 Hz, 2H), 2.62 (t, *J* = 7.4 Hz, 2H), 2.40 (s, 3H), 2.12 (s, 3H) ppm; ^{13}C{^{1}H}(101 MHz, CDCl$_3$): δ 207.2, 162.5, 159.3, 147.4, 139.0, 132.6, 131.4, 129.8, 128.9, 126.1, 115.2, 44.0, 30.5, 23.9, 21.9 ppm; HRMS (EI): m/z Calcd. for $C_{16}H_{17}O_3$ [M+H]$^+$: 257.1178, found: 257.1174.

5-(3-oxobutyl)-6-(o-tolyl)-2*H*-pyran-2-one (**4c**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O$_2$ atmosphere. After stirring for 5 minutes followed by the addition of **1d** (43 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 40 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na$_2$SO$_4$, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to obtaine the pure product(**4c**)as a light brown oil (36.5 mg, 0.14 mmol, Yield: 71%);R$_f$=0.44 (petroleum ether/ethyl acetate = 7:3);FTIR (KBr neat) υ_{max} 1734, 1711, 1634, 1551 cm^{-1};^{1}H NMR (400 MHz, CDCl$_3$): δ 7.38-7.33 (m, 2H), 7.31-7.18 (m, 3H), 6.30 (d, *J* = 9.5 Hz, 1H), 2.53-2.43 (m, 4H), 2.27 (s, 3H), 2.07 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 206.8, 162.2, 159.4, 146.5, 137.2, 131.7, 130.8, 130.2, 129.4, 125.9, 115.7, 115.2, 43.2, 30.0, 23.3, 19.6 ppm; HRMS (EI): m/z Calcd. for $C_{16}H_{17}O_3$ [M+H]$^+$: 257.1178, found: 257.1183.

6-(naphthalen-2-yl)-5-(3-oxobutyl)-2*H*-pyran-2-one (**4d**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes followed by the addition of **1e** (50 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 36 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolate the pure product(**4d**) as a brown solid (38 mg, 0.13 mmol, Yield: 65%);R_f=0.40 (petroleum ether/ethyl acetate = 7:3);mp 70-71°C; FTIR (KBr neat) υ_{max}1727, 1710, 1628, 1535, 1169,828 cm^{-1};^{1}H NMR (**400** MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.89 (m, 3H), 7.57 (m, 3H), 7.39 (d, *J* = 9.5 Hz, 1H), 6.33 (d, *J* = 9.5 Hz, 1H), 2.82 (t, *J* = 7.4 Hz, 2H), 2.65 (t, *J* = 7.4 Hz, 2H), 2.10 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 206.7, 162.0, 158.5, 147.0, 133.7, 132.7, 129.5, 128.9, 128.6, 128.4, 127.8, 127.6, 126.9, 125.2, 115.2, 114.9, 43.4, 30.0, 23.5 ppm; HRMS (EI): m/z Calcd. for $C_{19}H_{17}O_3$ $[M+H]^+$: 293.1178, found: 293.1180.

6-(9*H*-fluoren-2-yl)-5-(3-oxobutyl)-2*H*-pyran-2-one (**4e**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes followed by the addition of **1f** (57 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 40 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolate the pure product(**4e**) as a light yellow solid (33 mg, 0.10 mmol, Yield: 50%);R_f= 0.36 (petroleum ether/ethyl acetate = 7:3);mp 128-129°C; FTIR (KBr neat) υ_{max}1730, 1701, 1633, 1549, 1056 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83-7.81 (m, 2H), 7.73 (s, 1H), 7.58 (d, *J* = 7.1 Hz, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.43-7.34 (m, 3H), 6.30 (d, *J* = 9.4 Hz, 1H), 3.95 (s, 2H), 2.82 (t, *J* = 7.3 Hz, 2H), 2.65 (t, *J* = 7.3 Hz, 2H), 2.12 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 206.7, 162.1, 159.0, 147.0, 143.8, 143.6, 143.5, 140.6, 130.3, 127.7, 127.4, 127.0, 125.4, 125.2, 120.5, 119.8, 114.7, 114.5, 43.4, 37.0, 30.0, 23.6 ppm; HRMS (EI): m/z Calcd. for $C_{22}H_{19}O_3$ $[M+H]^+$: 331.1334, found: 331.1335.

6-(4-methoxyphenyl)-5-(3-oxobutyl)-2*H*-pyran-2-one (**4f**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes followed by the addition of **1g** (46 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 28 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolated the pure product(**4f**) was obtained as a brown oil (36 mg, 0.13 mmol, Yield: 67%);R_f= 0.43 (petroleum ether/ethyl acetate = 7:3);FTIR (KBr neat) υ_{max}1726, 1708, 1635, 1545 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 9.5 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 2H), 6.25 (d, *J* = 9.5 Hz, 1H), 3.86 (s, 3H), 2.75 (t, *J* = 7.3 Hz, 2H), 2.63 (t, *J* = 7.3 Hz, 2H), 2.13 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 206.8, 162.2, 160.9, 158.56, 147.0, 130.1, 124.6, 114.2, 114.1, 114.0, 55.4, 43.4, 30.0, 23.5 ppm; HRMS (EI): m/z Calcd. for $C_{16}H_{17}O_4$ $[M+H]^+$: 273.1127, found: 273.1125.

6-(4-chlorophenyl)-5-(3-oxobutyl)-2*H*-pyran-2-one (**4g**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes followed by the addition of **1h** (47 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 36 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolate the pure product (**4g**) as a light brown oil (29.5 mg, 0.11 mmol, Yield: 53%);R_f= 0.43 (petroleum ether/ethyl acetate = 7:3);FTIR (KBr neat) υ_{max}1724, 1700, 1630, 1540, 1090 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 9.5 Hz, 1H), 6.31 (d, *J* = 9.5 Hz, 1H), 2.72 (t, *J* = 7.1 Hz, 2H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.13 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 206.5, 161.6, 157.3, 146.6, 136.3, 130.6, 130.0, 128.9, 115.2, 115.1, 43.2, 30.0, 23.3 ppm; HRMS (EI): m/z Calcd. for $C_{15}H_{14}O_3Cl$ $[M+H]^+$: 277.0631, found: 277.0631.

6-(4-bromophenyl)-5-(3-oxobutyl)-2*H*-pyran-2-one (**4h**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes followed by the addition of **1i** (56 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 40 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over $Na_2SO_{4,}$ filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolate the pure product(**4h**) as a light brown oil (31.5 mg, 0.10 mmol, Yield: 49%);R_f= 0.40 (petroleum ether/ethyl acetate = 7:3); FTIR (KBr neat) υ_{max}1728, 1701, 1628, 1542, 1060 cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 9.5 Hz, 1H), 6.31 (d, *J* = 9.5 Hz, 1H), 2.72 (t, *J* = 7.2 Hz, 2H), 2.63 (t, *J* = 7.3 Hz, 2H), 2.13 (s, 3H) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$): δ 206.5, 161.6, 157.3, 146.6, 131.9, 131.0, 130.2, 124.7, 115.3, 115.1, 43.2, 30.0, 23.3 ppm; HRMS (EI): m/z Calcd. for $C_{15}H_{13}O_3B_rNa$ $[M+Na]^+$: 342.9946, found: 342.9946.

6-(4-methoxycarbonyl)phenyl-5-(3-oxobutyl)-2*H*-pyran-2-one (**4i**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes followed by the addition of **1j** (41 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 40 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over $Na_2SO_{4,}$ filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolate the pure product(**4i)**as a white solid (30 mg, 0.10 mmol, Yield: 50%);R_f= 0.38 (petroleum ether/ethyl acetate = 7:3); mp 68-69°C; FTIR (KBr neat) υ_{max}1738, 1723, 1703, 1634, 1546 cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 9.5 Hz, 1H), 6.34 (d, *J* = 9.5 Hz, 1H), 3.95 (s, 3H), 2.74 (t, *J* = 6.9 Hz, 2H), 2.64 (t, *J* = 7.1 Hz, 2H), 2.13 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 206.3, 166.2, 161.4, 157.2, 146.6, 136.2, 131.5, 129.8, 128.7, 115.7, 115.6, 52.4, 43.2, 30.0, 23.3 ppm; HRMS (EI): m/z Calcd. for $C_{17}H_{17}O_5$ $[M+H]^+$: 301.1076, found: 301.1081.

6-(cyclohex-1-en-1-yl)-5-(3-oxobutyl)-2*H*-pyran-2-one (**4j**). Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes followed by the addition of **1k** (41 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 32 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over $Na_2SO_{4,}$ filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolate the pure product (**4j**) as a light green oil (26 mg, 0.13 mmol, Yield: 64%);R_f= 0.37(petroleum ether/ethyl acetate = 8:2);FTIR (KBr neat) υ_{max}1719, 1706, 1630, 1610, 1531 cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ 7.25-7.23 (d, *J* = 9.5 Hz, 1H), 6.17 (d, *J* = 9.5 Hz, 1H), 5.97 (s, 1H), 2.69-2.61 (m, 4H), 2.68-2.61 (m, 4H), 2.17 (s, 3H), 1.78-1.65 (m, 4H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 206.9, 162.1, 161.4, 146.9, 132.9, 130.8, 114.0, 113.5, 43.9, 30.0, 26.6, 25.3, 23.6, 22.2, 21.5 ppm; HRMS (EI): m/z Calcd. for $C_{15}H_{19}O_3$ $[M+H]^+$: 247.1334, found: 247.1338.

6-cyclohexyl-5-(3-oxobutyl)-2*H*-pyran-2-one (**4k**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes followed by the addition of **1l** (36 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 32 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over $Na_2SO_{4,}$ filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolate the pure product(**4k**) as a light green oil (29 mg, 0.14 mmol, Yield: 71%);R_f= 0.39(petroleum ether/ethyl acetate = 8:2); FTIR (KBr neat) υ_{max}1721, 1703, 1628, 1549, 1463 cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, *J* = 9.5 Hz, 1H), 6.12 (d, *J* = 9.4 Hz, 1H), 2.65 – 2.56 (m, 5H), 2.17 (s, 3H), 1.88-1.81 (m, 2H), 1.75 – 1.64 (m, 5H), 1.36 – 1.24 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 206.8, 165.8, 162.7, 147.1, 113.3, 112.5, 43.9, 39.6, 30.2, 26.0, 25.5, 22.9 ppm; HRMS (EI): m/z Calcd. for $C_{15}H_{21}O_3$ $[M+H]^+$: 249.1491, found: 249.1500.

6-butyl-5-(3-oxobutyl)-2*H*-pyran-2-one (**4l**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes followed by the addition of **1m** (36 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 30 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2)to isolatethe pure product, (**4l**) as a light green oil (30 mg, 0.13 mmol, Yield: 67%);R_f= 0.40 (petroleum ether/ethyl acetate = 8:2); FTIR (KBr neat) υ_{max}1723, 1707, 1630, 1373, 821cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, *J* = 9.3 Hz, 1H), 6.14 (d, *J* = 9.5 Hz, 1H), 2.65-2.56 (m, 4H), 2.51 (t, *J* = 7.7 Hz, 2H), 2.17 (s, 3 H), 1.68-1.60 (m, 2H), 1.42-1.34 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 206.8, 162.6, 162.5, 146.8, 113.8, 113.5, 43.5, 30.6, 30.1, 29.7, 22.9, 22.4, 13.8 ppm; HRMS (EI): m/z Calcd. for $C_{13}H_{19}O_3$ $[M+H]^+$: 223.1334, found: 223.1339.

6-(3-chloropropyl)-5-(3-oxobutyl)-2*H*-pyran-2-one (**4m**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes followed by the addition of **1n** (40 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 32 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolate the pure product(**4m**) was obtained as a light brown oil (29 mg, 0.12 mmol, Yield: 61%);R_f= 0.37(petroleum ether/ethyl acetate = 7:3);FTIR (KBr neat) υ_{max}1725, 1708, 1628, 1173,678 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 9.5 Hz, 1H), 6.17 (d, *J* = 9.4 Hz, 1H), 3.59 (t, *J* = 6.0 Hz, 2H), 2.74 (t, *J* = 7.3 Hz, 2H), 2.69-2.59 (m, 4H), 2.21-2.13 (m, 5H) ppm; ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 206.7, 162.2, 160.3, 146.7, 114.8, 114.1, 44.0, 43.3, 30.1, 29.8, 27.7, 22.9 ppm; HRMS (EI): m/z Calcd. for $C_{12}H_{16}ClO_3$ $[M+H]^+$: 243.0788, found: 243.0793.

6-(3-cyanopropyl)-5-(3-oxobutyl)-2*H*-pyran-2-one (**4n**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes followed by the addition of **1o** (38 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 32 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolate the pure product(**4n**) as a white solid (26 mg, 0.11 mmol, Yield: 56%);mp 54-55°C;R_f= 0.36(petroleum ether/ethyl acetate = 7:3);FTIR (KBr neat) υ_{max}2245, 1724, 1702, 1634cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, *J* = 9.5 Hz, 1H), 6.19 (d, *J* = 9.5 Hz, 1H), 2.75 (t, *J* = 7.5 Hz, 2H), 2.68 (t, *J* = 6.7 Hz, 2H), 2.61 (t, *J* = 6.8 Hz, 2H), 2.46 (t, *J* = 6.9 Hz, 2H), 2.17 (s, 3H), 2.11-2.04 (m, 2H) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$): δ 206.6, 161.9, 159.2, 146.6, 118.9, 115.0, 114.5, 43.0, 30.1, 29.1, 22.8, 22.7, 16.7 ppm; HRMS (EI): m/z Calcd. for $C_{13}H_{15}NO_3Na$ $[M+Na]^+$: 256.0950, found: 256.0953.

6-(2-(benzyloxy)ethyl)-5-(3-oxobutyl)-2*H*-pyran-2-one(**4o**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes followed by the addition of **1p** (52 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 32 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolate the pure product(**4o)**was obtained as a light green oil (34.5 mg, 0.11 mmol, Yield: 54%);R_f= 0.38(petroleum ether/ethyl acetate = 7:3);IR (KBr neat) υ_{max}1726, 1708, 1631, 1540, 1250 cm^{-1};^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 -7.25 (m, 5H), 7.21 (d, *J* = 9.5 Hz, 1H), 6.16 (d, *J* = 9.5 Hz, 1H), 4.48 (s, 2H), 3.79 (t, *J* = 6.1 Hz, 2H), 2.80 (t, *J* = 6.0 Hz, 2H), 2.64-2.52 (m, 4H), 1.96 (s, 3H) ppm; ^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$): δ 207.2, 162.5, 159.2, 147.0, 137.9, 128.4, 127.8, 127.8, 115.7, 113.9, 73.3, 67.1, 43.6, 31.8, 29.9, 23.1 ppm, HRMS (EI): m/z Calcd. for $C_{19}H_{22}O_4Na$ $[M+Na]^+$: 337.1416., found: 337.1411.

6-(2-acetoxyethyl)-5-(3-oxobutyl)-2*H*-pyran-2-one(**4p**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes followed by the addition of **1q** (42 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 30 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolate the pure product(**4p**) as a light brown oil (24 mg, 0.09 mmol, Yield: 48%);R_f= 0.29 (petroleum ether/ethyl acetate = 7:3);FTIR

(KBr neat) υ_{max}1740, 1723, 1703, 1633 cm^{-1};^{1}H NMR (400 MHz, CDCl$_3$): δ 7.22 (d, *J* = 9.5 Hz, 1H), 6.19 (d, *J* = 9.5 Hz, 1H), 4.35 (t, *J* = 6.5 Hz, 2H), 2.88 (t, *J* = 6.6 Hz, 2H), 2.67 (t, *J* = 6.9 Hz, 2H), 2.59 (t, *J* = 7.1 Hz, 2H), 2.17 (s, 3H), 2.05 (s, 3H) ppm; ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ 206.5, 170.7, 162.0, 157.8, 146.5, 115.5, 114.6, 61.2, 43.3, 30.4, 30.1, 22.8, 20.8 ppm; HRMS (EI): m/z Calcd. for $C_{13}H_{16}O_5Na$ $[M+Na]^+$: 275.0895, found: 275.0900.

5-(3-oxobutyl)-6-phenethyl-2*H*-pyran-2-one (**4q**)Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O$_2$ atmosphere. After stirring for 5 minutes followed by the addition of **1r** (45 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 34 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na$_2$SO$_4$, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolate the pure product(**4q**)as a light green oil (25 mg, 0.09 mmol, Yield: 46%);R_f= 0.41(petroleum ether/ethyl acetate = 7:3);FTIR (KBr neat) υ_{max} 1725,1703, 1632, 1549, 1460 cm^{-1};^{1}H NMR (400 MHz, CDCl$_3$): δ 7.30-7.19 (m, 3H), 7.16-7.10 (m, 3H), 6.15 (d, *J* = 9.5 Hz, 1H), 3.00 (t, *J* = 7.3 Hz, 2H), 2.81 (t, *J* = 7.4 Hz, 2H), 2.35 (t, *J* = 7.3 Hz, 2H), 2.15 (t, *J* = 7.3 Hz, 2H), 2.03 (s, 3H) ppm; ^{13}C{^{1}H}NMR (101 MHz, CDCl$_3$): δ206.8, 162.5, 160.6, 146.7, 140.3, 128.6, 126.5, 114.8, 113.8, 43.1, 33.4, 32.9, 29.9, 22.7 ppm; HRMS (EI): m/z Calcd. for $C_{17}H_{19}O_3$ $[M+H]^+$: 271.1334, found: 271.1334.

5-(3-oxobutyl)-6-(thiophen-2-yl)-2*H*-pyran-2-one (**4r**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O$_2$ atmosphere. After stirring for 5 minutes followed by the addition of **1s** (41 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 32 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na$_2$SO$_4$, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolate the pure product(**4r**)as a red oil (29 mg, 0.12 mmol, Yield: 58%);R_f= 0.46(petroleum ether/ethyl acetate = 7:3); FTIR (KBr neat) υ_{max} 3094, 1730, 1701, 1625cm^{-1};^{1}H NMR (400 MHz, CDCl$_3$): δ 7.58 (d, *J* = 3.5 Hz, 1H), 7.52 (d, *J* = 5.0 Hz, 1H), 7.36 (d, *J* = 9.4 Hz, 1H), 7.16-7.14 (dd, *J* = 4.5, 4.3 Hz, 1H), 6.23 (d, *J* = 9.4 Hz, 1H), 2.93 (t, *J* = 7.3 Hz, 2H), 2.77 (t, *J* = 7.3 Hz, 2H), 2.18 (s, 3H) ppm; ^{13}C{^{1}H}NMR (101 MHz, CDCl$_3$): δ 206.7, 161.1, 152.6, 148.1, 133.9, 129.2, 129.1, 127.8, 114.0, 42.7, 30.1, 24.3 ppm; HRMS (EI): m/z Calcd. for $C_{13}H_{12}O_3SNa[M+Na]^+$: 271.0405, found: 271.0408.

6-(1-methyl-1H-indol-2-yl)-5-(3-oxobutyl)-2*H*-pyran-2-one (**4s**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O$_2$ atmosphere. After stirring for 5 minutes followed by the addition of **1t**(51 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.). The system was stirring at 30 °C for 36 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na$_2$SO$_4$, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to isolate the pure product(**4s**)as a red oil (36 mg, 0.12 mmol, Yield: 61%);%);R_f= 0.41(petroleum ether/ethyl acetate = 7:3);FTIR (KBr neat) υ_{max} 1727, 1706, 1627, 1550, 1101 cm^{-1};^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.43-7.37 (m, 2H), 7.36-7.30 (m, 1H), 7.19-7.14 (m, 1H), 6.70 (s, 1H), 6.33 (d, *J* = 9.5 Hz, 1H), 3.81 (s, 3H), 2.80 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.12 (s, 3H) ppm; ^{13}C{^{1}H}NMR (101 MHz, CDCl$_3$) δ 206.6, 161.4, 151.3, 146.4, 138.2, 129.5, 126.8, 123.7, 121.5, 120.4, 118.2, 115.4, 109.9, 105.9, 43.4, 31.5, 30.0, 23.8 ppm; HRMS (EI): m/z Calcd. for $C_{18}H_{18}NO_3$ $[M+H]^+$: 296.1287, found: 296 .1291.

4-methyl-5-(3-oxobutyl)-6-phenyl-2*H*-pyran-2-one (**5a**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O$_2$ atmosphere. After stirring for 5 minutes**1aa** (43 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol**2a** (43 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The system was stirring at 30 °C for 32 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na$_2$SO$_4$, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 -7:3) to afford the pure product(**5a**) as a white solid crystal (42 mg, 0.16 mmol, Yield: 82%);R_f= 0.46(petroleum ether/ethyl acetate = 7:3);mp 47-48°C; FTIR (KBr neat) υ_{max} 1721, 1705, 1628, 1546 cm^{-1};^{1}H NMR (400 MHz, CDCl$_3$): δ 7.45 (s, 5H), 6.18 (s, 1H), 2.70 (t, *J* = 7.8 Hz, 2H), 2.50 (t, *J* = 7.8 Hz, 2H), 2.23 (s, 3H), 2.07 (s, 3H) ppm; ^{13}C{^{1}H}NMR (101 MHz, CDCl$_3$): δ 206.5, 161.8, 158.4, 156.7, 132.7, 130.0, 128.6, 128.6, 115.7, 113.8, 43.4, 29.8, 20.8, 20.2 ppm; HRMS (EI): m/z Calcd. for $C_{16}H_{17}O_3$ $[M+H]^+$: 257.1178, found: 257.1180.

5-(3-oxobutyl)-6-phenyl-4-propyl-2*H*-pyran-2-one (**5b**).Cu(OAc)$_2$ (7.2 mg, 0.04 mmol, 20 mol%) and Pd(PhCN)$_2$Cl$_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O$_2$ atmosphere. After stirring for 5 minutes**1ab** (48 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol**2a** (43 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The system was stirring at 30 °C for 36 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 -7:3) to afford the pure product(**5b**) as a white solid crystal (46 mg, 0.16 mmol, Yield: 81%);R_f= 0.47(petroleum ether/ethyl acetate = 7:3);mp 48-49°C; FTIR (KBr neat) υ_{max}1723, 1706, 1628, 1547, 1370 cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (s, 5H), 6.17 (s, 1H), 2.70 (t, *J* = 7.8 Hz, 2H), 2.50-2.41 (m, 4H), 2.05 (s, 3H), 1.69-1.60 (m, 2H), 1.05 (t, *J* = 7.3 Hz, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 206.6, 162.2, 160.4, 158.5, 132.8, 130.0, 128.7, 128.6, 115.4, 112.4, 43.7, 34.5, 29.8, 21.8, 20.3, 13.9 ppm; HRMS (EI): m/z Calcd. for $C_{18}H_{21}O_3$ $[M+H]^+$: 285.1491, found: 285.1490.

6-butyl-4-methyl-5-(3-oxobutyl)-2*H*-pyran-2-one (**5c**).$Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes**1ac** (39 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol**2a** (43 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The system was stirring at 30 °C for 36 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2) to afford the pure product(**5c)**as a light brown oil (34 mg, 0.14 mmol, Yield: 72%);R_f= 0.41(petroleum ether/ethyl acetate = 8:2);mp 53-54°C; FTIR (KBr neat) υ_{max}1730, 1710, 1631, 1372, cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ 6.01 (s, 1H), 2.64-2.54 (m, 4H), 2.49 (t, *J* = 7.6 Hz, 2H), 2.19 (s, 3H), 2.14 (s, 3H), 1.68-1.60 (m, 2H), 1.42-1.32 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$): δ 206.8, 162.6, 161.7, 156.6, 114.4, 112.3, 43.4, 30.7, 30.0, 29.8, 22.5, 20.2, 20.1, 13.8 ppm; HRMS (EI): m/z Calcd. for $C_{14}H_{21}O_3$ $[M+H]^+$: 237.1491, found: 237.1493.

6-(4-chlorophenyl)-4-methyl-5-(3-oxobutyl)-2*H*-pyran-2-one (**5d**).$Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes**1ad** (50 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol**2a** (43 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The system was stirring at 30 °C for 45 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 -7:3) to afford the pure product(**5d**) as a white solid (40.5 mg, 0.14 mmol, Yield: 70%);R_f= 0.44(petroleum ether/ethyl acetate = 7:3);mp 64-65°C; FTIR (KBr neat) υ_{max} 1725, 1706, 1631, 1540, 1092 cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ 7.45-7.38 (m, 4H), 6.18 (s, 1H), 2.69 (t, *J* = 7.8 Hz, 2H), 2.50 (t, *J* = 7.9 Hz, 2H), 2.23 (s, 3H), 2.10 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 206.2, 161.5, 157.0, 156.6, 136.2, 131.0, 130.0, 129.0, 116.0, 114.1, 43.2, 29.9, 20.8, 20.2 ppm; HRMS (EI): m/z Calcd. for $C_{16}H_{16}ClO_3$ $[M+H]^+$: 291.0788, found: 291.0791.

6-(4-methoxyphenyl)-4-methyl-5-(3-oxobutyl)-2*H*-pyran-2-one (**5e**).$Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes**1ae** (49 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol**2a** (43 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The system was stirring at 30 °C for 40 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 -7:3) to afford the pure product(**5e)**as a brown solid (42 mg, 0.15 mmol, Yield: 74%);R_f= 0.43(petroleum ether/ethyl acetate = 7:3);mp 68-69°C; FTIR (KBr neat) υ_{max}1727, 1711, 1633, 1565, 1163 cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.14 (s, 1H), 3.85 (s, 3H), 2.72 (t, *J* = 7.8 Hz, 2H), 2.51 (t, *J* = 7.9 Hz, 2H), 2.22 (s, 3H), 2.09 (s, 3H) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$): δ 206.6, 162.0, 160.7, 158.3, 156.8, 130.1, 125.0, 115.2, 114.0, 113.3, 55.4, 43.4, 29.8, 20.9, 20.2 ppm; HRMS (EI): m/z Calcd. for $C_{17}H_{19}O_4$ $[M+H]^+$: 287.1283, found: 287.1289**.**

6-(4-acetylphenyl)-4-methyl-5-(3-oxobutyl)-2*H*-pyran-2-one (**5f**).$Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes**1af** (51 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol**2a** (43 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The system was stirring at 30 °C for 45 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 -7:3) to afford the pure product(**5f)**was obtained as a white solid (45 mg, 0.15 mmol, Yield: 75%); R_f= 0.40(petroleum ether/ethyl acetate = 7:3);mp 77-78°C; FTIR (KBr neat) υ_{max}1730, 1703, 1683, 1629, 1542 cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 6.21 (s, 1H), 2.71 (t, *J* = 7.8 Hz, 2H), 2.65 (s, 3H), 2.52 (t, *J* = 7.8 Hz, 2H), 2.25 (s, 3H), 2.09 (s, 3H) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$): δ 206.1, 197.2, 161.3, 156.9, 156.5, 137.9, 136.8, 129.0, 128.5, 116.5, 114.4, 43.2, 29.8, 26.7, 20.7, 20.1 ppm; HRMS (EI): m/z Calcd. for $C_{18}H_{19}O_4$ $[M+H]^+$: 299.1283, found: 299.1291.

5-(3-oxobutyl)-4,6-diphenyl-2*H*-pyran-2-one (**5g**).$Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes**1ag** (55 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol**2a** (43 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The system was stirring at 30 °C for 46 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 -7:3) to afford the pure product(**5g)**was obtained as a light brown solid (50 mg, 0.16 mmol, Yield: 78%);R_f= 0.43(petroleum ether/ethyl acetate = 7:3);mp 95-96°C; FTIR (KBr neat) υ_{max}1722, 1705, 1613, 1523, 1485 cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ 7.56-7.52 (m, 2H), 7.49-7.44 (m, 6H), 7.37-7.33 (m, 2H), 6.22 (s, 1H),2.74 (t, *J* = 7.9 Hz, 2H), 2.09 (t, *J* = 8.0 Hz, 2H), 1.77 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 206.5, 161.7, 159.5, 159.2, 137.1, 132.7, 130.2, 129.2, 128.9, 128.8, 128.6, 127.4, 114.6, 114.5, 42.8, 29.4, 21.5 ppm; HRMS (EI): m/z Calcd. for $C_{21}H_{19}O_3$ $[M+H]^+$: 319.1334, found: 319.1335**.**

6-butyl-5-(3-oxobutyl)-4-phenyl-2*H*-pyran-2-one (**5h**).$Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and

$Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes**1ah** (51 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol**2a** (43 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The system was stirring at 30 °C for 46 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 -7:3) to afford the pure product(**5h**)was obtained as a white solid (45 mg, 0.15 mmol, Yield: 75%);R_f= 0.39(petroleum ether/ethyl acetate = 7:3);mp 88-89°C; FTIR (KBr neat) υ_{max} 1725, 1707, 1626, 1540, 1363 cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ 7.46-7.42 (m, 3H), 7.26-7.23 (m, 2H), 6.05 (s, 1H), 2.61-2.55 (m, 4H), 2.20 (t, *J* = 7.9 Hz, 2H), 1.92 (s, 3H), 1.74-1.65 (m, 2H), 1.46-1.36 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$): δ 206.7, 162.7, 162.3, 159.5, 137.2, 129.0, 128.7, 127.3, 113.4, 113.2, 43.3, 31.1, 29.9, 29.7, 22.5, 20.7, 13.8 ppm; HRMS (EI): m/z Calcd. for $C_{19}H_{23}O_3$ $[M+H]^+$: 299.1647, found: 299.1647.

6-(4-chlorophenyl)-5-(3-oxobutyl)-4-phenyl-2*H*-pyran-2-one (**5i**).$Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes**1ai** (62 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol**2a** (43 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The system was stirring at 30 °C for 60 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 -7:3) to afford the pure product(**5i)**as a light green solid (39 mg, 0.11 mmol, Yield: 55%);R_f= 0.38(petroleum ether/ethyl acetate = 7:3);mp 110-111°C; FTIR (KBr neat) υ_{max}1721, 1706, 1620, 1540, 1532, 1489, 1100 cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ 7.51-7.44 (m, 7H), 7.36-7.33 (m, 2H), 6.23 (s, 1H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.08 (t, *J* = 8.0 Hz, 2H), 1.79 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 206.2, 161.4, 159.4, 157.9, 136.9, 136.4, 131.1, 130.3, 129.3, 129.0, 128.9, 127.4, 114.9, 114.8, 42.6, 29.5, 21.4 ppm; HRMS (EI): m/z Calcd. for $C_{21}H_{18}ClO_3$ $[M+H]^+$: 353.0944, found: 353.0940.

6-(4-methoxyphenyl)-5-(3-oxobutyl)-4-phenyl-2*H*-pyran-2-one (**5j**).$Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes**1aj** (61 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol**2a** (43 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The system was stirring at 30 °C for 46 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 -7:3) to afford the pure product(**5j**) as a white solid (55 mg, 0.16 mmol, Yield: 79%);R_f= 0.36(petroleum ether/ethyl acetate = 7:3);mp 117-118°C; FTIR (KBr neat) υ_{max}1729, 1706, 1624, 1572 1540, 1165 cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ 7.51-7.44 (m, 5H), 7.35 (d, *J* = 6.8 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.18 (s, 1H), 3.86 (s, 3H), 2.76 (t, *J* = 8.0 Hz, 2H), 2.10 (t, *J* = 8.0 Hz, 2H), 1.78 (s, 3H)ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$): δ 206.6, 161.9, 160.9, 159.7, 159.2, 137.2, 130.5, 129.1, 128.8, 127.4, 125.0, 114.0, 114.0, 55.4, 42.8, 29.4, 21.6 ppm; HRMS (EI): m/z Calcd. for $C_{22}H_{21}O_4$ $[M+H]^+$: 349.1440, found: 349.1441.

6-(4-acetylphenyl)-5-(3-oxobutyl)-4-phenyl-2*H*-pyran-2-one (**5k**).$Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for5 minutes**1ak** (64 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol**2a** (43 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The system was stirring at 30 °C for 60 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 -7:3) to afford the pure product(**5k)**as a white solid (45 mg, 0.13 mmol, Yield: 63%);R_f= 0.31(petroleum ether/ethyl acetate = 7:3);mp 127-128°C; FTIR (KBr neat) υ_{max}1723, 1708, 1684, 1603 1550, 1525 cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.50-7.46 (m, 3H), 7.38-7.33 (m, 2H), 6.26 (s, 1H), 2.78-2.71 (m, 2H), 2.65 (s, 3H), 2.12-2.07 (m, 2H), 1.79 (s, 3H) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$): δ 206.1, 197.2, 161.3, 159.3, 157.7, 138.0, 136.9, 136.8, 129.3, 129.3, 128.9, 128.5, 127.4, 115.3, 115.2, 42.5, 29.5, 26.8, 21.4 ppm; HRMS (EI): m/z Calcd. for $C_{23}H_{21}O_4$ $[M+H]^+$: 361.1440, found: 361.1438.

4-(4-chlorophenyl)-5-(3-oxobutyl)-6-phenyl-2*H*-pyran-2-one (**5l**).$Cu(OAc)_2$ (7.2 mg, 0.04 mmol, 20 mol%) and $Pd(PhCN)_2Cl_2$ (3.8 mg, 0.01 mmol, 5 mol%) were added in cyclohexanone (1.0 mL) under O_2 atmosphere. After stirring for 5 minutes**1al** (62 mg, 0.2 mmol, 1.0 equiv.) and 3-Buten-2-ol **2a** (43 mg, 0.6 mmol, 3.0 equiv.) were subsequently added to the mixture. The system was stirring at 30 °C for 60 h.The reaction mixture was diluted with ethyl acetate washed with water and brine. The organic layer was dried over Na_2SO_4, filtered, concentrated in *vacuo*. The residue was purified by flash column chromatography on silica gel using as eluent petroleum ether/ethyl acetate (8:2 - 7:3) to afford the pure product(**5l**) as a white solid (42.5 mg, 0.12 mmol, Yield: 60%);R_f= 0.38(petroleum ether/ethyl acetate = 7:3);mp 112-113°C; FTIR (KBr neat) υ_{max}1723, 1705, 1622, 1550, 1530, 1085 cm^{-1};^1H NMR (400 MHz, $CDCl_3$): δ 7.54-7.45 (m, 7H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.19 (s, 1H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.10 (t, *J* = 8.0 Hz, 2H), 1.82 (s, 3H) ppm; $^{13}C\{^1H\}$NMR (101 MHz, $CDCl_3$): δ 206.2, 161.4, 159.5, 158.4, 135.5, 132.6, 130.3, 129.3, 128.9, 128.7, 114.7, 114.2, 42.7, 29.5, 21.3 ppm; HRMS (EI): m/z Calcd. for $C_{21}H_{18}ClO_3$ $[M+H]^+$: 353.0944, found: 353.0949.

Supporting Information

Single crystaldata of **5a** andspectral data for all novel compounds (^1H NMR, ^{13}C NMR).

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Notes

The authors declare no competing financial interest.

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