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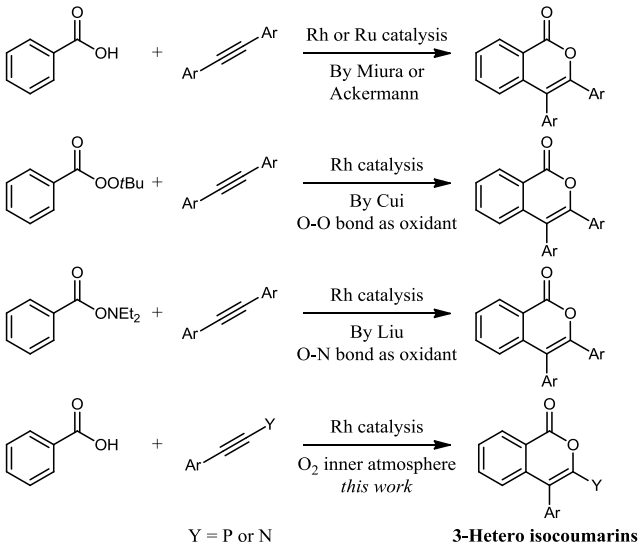
Rh(III)-Catalyzed Regioselective Preparation of 3-Hetero Isocoumarins from Aryl Carboxylic Acids and Alkynes

Lijuan Song, Jing Xiao, Wanrong Dong*, Zhihong Peng* and Delie An*

Abstract: An oxygen-mediated annulation reaction was herein demonstrated. Various unreported 3-hetero substituted isocoumarins were successfully prepared with high efficiency (up to 88% yields) and good functional groups tolerance (35 examples) in the presence of a rhodium catalyst. Moreover, a plausible mechanism was proposed that the high regio-selectivity probably originated from the difference of the electron-density on the alkynyl carbons.

Introduction

Different pharmacophores bearing isocoumarin structural subunit have aroused extensive research interests due to the exhibition of a broad range of clinical and biological properties such as antifungal,[1] antiulcer,[2] anti-inflamatory,[3] antibacterial,[4] herbicidal,[5] cytotoxic,[6] and antiangiogenic activities,[7] etc., as well for being significant synthetic intermediates towards some heterocyclic or carbocyclic compounds like isoquinolines, isochromenes and isocarbostyrils.[8] Thus great efforts have been contributed and plenty of documentation has been delivered towards the versatile molecules. Conventionally, pre-activated substrates including haloed molecules were coupled with unsaturated partners like acetylenes[9], allenes[10] and etc.[11] Subsequently, decarbonylative[12] or decarboxylative[13] addition/annulation reactions were discovered which were realized in the presence of Rh or Ni catalysts. However, the requirement of multiple steps or usage of stoichiometric amount of external metallic oxidants led to low efficiency and poor atom/step economy, which restricted the traditional synthetic methodologies for general applications. Thus, novel strategies involving C-H bond activation and successive functionalization, which have been well-developed for the formations of carbon-carbon bonds[14] and carbon-hetero bonds,[15] were turned to for the construction of isocoumarin derivatives.[16] Pioneered by Miura[17] and Ackermann,[18] reactions between benzoic acids and intermediate acetylenes were demonstrated in the presence of rhodium, ruthenium catalysts with Cu(II) or Ag(I) salts used as external oxidant.[19,20] However, phthalides and naphthalenes[19] were also obtained as side-products due to low regio-selectivity or catalytic efficiency. Recently, the emergence of various reports using N-O bonds,[21] O-O bonds[22] as internal oxidants or other external oxidants have enriched the diversity of the transformations towards the pivotal molecules. Based on the knowledge that alkynyl phosphonates have been successfully applied for the construction of some hetero- or carbo- cyclic compounds,[23] there are still rare literal demonstrations on the synthesis of P or N substituted isocoumarins from alkynyl phosphonates through the direct C-H bond activation pathway using oxygen as a clean oxidant. Within this context, we wish to report an annulation reaction towards the novel products under O_2 atmosphere based on the successful formation of hetero-alkynyl bonds from our group.[24]



Scheme 1. Strategies for the synthesis of isocoumarins

Results and Discussion

Firstly, reactions between benzoic acid (**1a**) and *P*-(2-phenylethynyl) diethyl phosphonate (**2a**) were carried out for the optimal conditions as summarized in Table 1. In the presence of $(Cp^*RhCl_2)_2$ as the catalyst and $Cu(OAc)_2{\cdot}H_2O$ as the oxidant, the reaction took place smoothly in DMF (*N*,*N*-dimethyl formamide) at 120 °C, and 48% of the desired annulated product (**3aa**) was isolated after 24 hours (entry 1). Further optimization was embarked and it was found that CH_3OH offered the best performance for the annulation reaction and 78% yield of **3aa** was obtained (entry 2). Other solvents such as DCE (1,2-dichloromethane), acetonitrile and dioxane produced **3aa** in poor to medium yields, ranging from 18% to 55% (entries 3 – 5). While DMSO (dimethyl sulfoxide) and toluene showed no effect for the transformation for no reaction was detected after 24 hours (entries 6 and 7). Similarly, *tert*-amyl alcohol made the reaction happen and **3aa** was successfully isolated in 72% yield, lower than in MeOH (entry 8). Also, the reaction temperature was significant to the efficiency of the reaction. Decreased temperature led to lower yields (entries 9 and 10) or even no reaction was observed when the reaction was conducted at 60

State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering
Hunan University
Changsha, 410082, P. R. of China.
Tel. (Fax):+86 731 88821380
E-mail: wanrongdong@hnu.edu.cn; pzh7251@hnu.edu.cn; deliean@hnu.edu.cn

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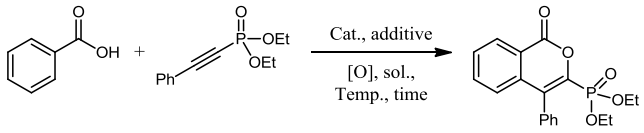
^{o}C (entry 11). On the other hand, it was noticed that organic or inorganic oxidants like TBHP (*tert*-butyl hydroperoxide, 70% in water), DTBP (di-*tert*-butyl peroxide), $K_2S_2O_8$ and $Fe(OAc)_2$ failed to prompt the reaction for no reaction was detected (entries 12 – 15). But usage of the silver salts $AgSbF_6$ led to the formation of **3aa** in 46% yield (entry 16), inferior to entry 1. To our delight, when the reaction was performed with assistance of 50 mol% NaOAc under dioxygen atmosphere, the yield of the expected product **3aa** was dramatically elevated up to 81% after fully consumption of **1a** within 16 hours (entry 17). Disappointingly, other rhodium catalyst or palladium catalysts acted worse in the system (entries 18 – 20). No product was detected without either the catalyst or the additive (entry 21).

Table 1. Optimization of the reaction conditions[a]



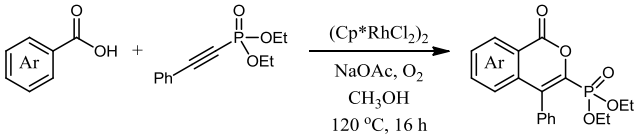
1a **2a** **3aa**

Entry	Cat.	Add./[O]	Sol.	Yield [b]
1	$(Cp^*RhCl_2)_2$	$Cu(OAc)_2{\cdot}H_2O$	DMF	48%
2	$(Cp^*RhCl_2)_2$	$Cu(OAc)_2{\cdot}H_2O$	CH_3OH	78%
3	$(Cp^*RhCl_2)_2$	$Cu(OAc)_2{\cdot}H_2O$	DCE	18%
4	$(Cp^*RhCl_2)_2$	$Cu(OAc)_2{\cdot}H_2O$	MeCN	55%
5	$(Cp^*RhCl_2)_2$	$Cu(OAc)_2{\cdot}H_2O$	dioxane	38%
6	$(Cp^*RhCl_2)_2$	$Cu(OAc)_2{\cdot}H_2O$	DMSO	n.r.[c]
7	$(Cp^*RhCl_2)_2$	$Cu(OAc)_2{\cdot}H_2O$	toluene	trace
8	$(Cp^*RhCl_2)_2$	$Cu(OAc)_2{\cdot}H_2O$	*t*-AmylOH	72%
9[d]	$(Cp^*RhCl_2)_2$	$Cu(OAc)_2{\cdot}H_2O$	CH_3OH	58%
10[e]	$(Cp^*RhCl_2)_2$	$Cu(OAc)_2{\cdot}H_2O$	CH_3OH	30%
11[f]	$(Cp^*RhCl_2)_2$	$Cu(OAc)_2{\cdot}H_2O$	CH_3OH	n.r.
12	$(Cp^*RhCl_2)_2$	TBHP	CH_3OH	trace
13	$(Cp^*RhCl_2)_2$	DTBP	CH_3OH	trace
14	$(Cp^*RhCl_2)_2$	$K_2S_2O_8$	CH_3OH	n.r.
15	$(Cp^*RhCl_2)_2$	$Fe(OAc)_2$	CH_3OH	trace
16	$(Cp^*RhCl_2)_2$	$AgSbF_6$	CH_3OH	46%
17[g]	**$(Cp^*RhCl_2)_2$**	**$NaOAc/O_2$**	**CH_3OH**	**81%**
18	$Cp^*Rh(MeCN)_3(SbF_6)_2$	$NaOAc/O_2$	CH_3OH	42%
19	$Pd(OAc)_2$	$NaOAc/O_2$	CH_3OH	n.r.
20	$Pd(PPh_3)_2Cl_2$	$NaOAc/O_2$	CH_3OH	n.r.
21[h]	--	--	CH_3OH	n.r.

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), cat. (5.0 mol%), additive or oxidant (0.6 mmol otherwise noted) under air atmosphere or noted, at 120 ^{o}C for 24 h. [b] Isolated yields. [c] n.r. stands for no reaction. [d] The reaction was performed at 100 ^{o}C. [e] The reaction was performed at 80 ^{o}C. [f] The reaction was performed at 60 ^{o}C. g) NaOAc (0.15 mmol) under O_2 atmosphere for 16 h was used instead of $Cu(OAc)_2$ (0.6 mmol) under air atmosphere for 24 h. [h] The reaction was conducted in the abesence of either the catalyst or the additive.

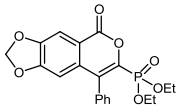
With the optimal conditions in hand, the scope and limitations of the substrate were evaluated. Under the optimal conditions, 4-methyl benzoic acid (**1b**) reacted with *P*-(2-phenylethynyl)-diethyl phosphonate **2a** readily, furnishing the desired 3-(diethyl phosphoryl)-4-phenyl-6-methyl-*1H*-2-benzopyran-1-one **3ba** as the product in 79% yield (entry 1). However, *ortho*-substituted aryl carboxylic acid exhibited negative effect to the annulation reaction. For example, only medium yields were obtained when 2-methyl benzoic acid (**1c**) and 2,3-dimethyl benzoic acid (**1d**) were employed for coupling with **2a**, 62% and 64% for **3ca** and **3ba**, respectively (entries 2 and 3). Methoxy group decorated carboxylic acids on the *para*-position provided the corresponding 3-phosphoryl substituted isocoumarin **3ea** in 83% yield (entry 4). The occupation on the *meta*-position did not affect the efficiency of the transformation severely for 3-(diethyl phosphoryl)-4-phenyl-6,7-dioxolo-*1H*-2-benzopyran-1-one (**3fa**) was successfully furnished in 80% yield, close to that of entry 4 (entry 5). Additionally, the compatibilities of the halogen groups on the aryl carboxylic acid were also tested in the rhodium-catalyzed protocol. Pleasingly, 4-fluoro benzoic acid (**1g**) coupled smoothly with **2a**, and fluorinated isocoumarin **3ga** was offered in 82% yield (entry 6). However, installation of other halo groups showed slightly lower efficiency for the formation of the corresponding isocoumarin derivatives, and yields ranging from 75% to 78% were recorded for **3ha** – **3ja** (entries 7 – 9). Polyaryl and heteroaryl carboxylic acids were also well-tolerated in the system. For instance, 2-naphthoic acid (**1k**) and 2-thenoic acid (**1l**) underwent the annulation reaction smoothly, and the desired molecules **3ka** and **3la** were successfully provided in 79% and 70% yields, separately (entries 10 and 11).

Table 2. Substrates scope of the aryl carboxylic acids[a]



1b - 1l **2a** **3ba - 3la**

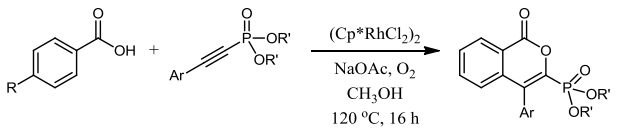
Entry	**1**	**3**	Ar	Yield [b]
1	**1b**	**3ba**	4-$CH_3C_6H_4$	79%
2	**1c**	**3ca**	2-$CH_3C_6H_4$	62%
3	**1d**	**3da**	2,3-$(CH_3)_2C_6H_3$	64%
4	**1e**	**3ea**	4-$CH_3OC_6H_4$	83%

5	**1f**	**3fa**		80%
6	**1g**	**3ga**	4-FC_6H_4	82%
7	**1h**	**3ha**	4-ClC_6H_4	78%
8	**1i**	**3ia**	4-BrC_6H_4	75%
9	**1j**	**3ja**	4-IC_6H_4	77%
10	**1k**	**3ka**	2-Naphthyl	79%
11	**1l**	**3la**	2-Thiophenyl	70%

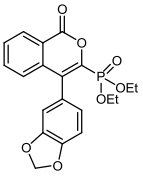
[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.75 mmol), $(Cp^*RhCl_2)_2$ (5.0 mol%), NaOAc (0.25 mmol) under O_2 atmosphere at 120 °C for 16 h. [b] Isolated yields.

Then, the tolerance of the functional groups on alkynyl phosphonates was also tested in the system as shown in Table 3. To our satisfaction, *P*-[2-(4-methylphenyl)-ethynyl] diethyl phosphonate (2b) reacted with benzoic acid (1a) readily, furnishing the corresponding 3-phosphoryl isocoumarin 3ab in 81% yield (entry 1). By comparison, variation of the methyl group on the phenyl group did not affect the efficiency of the protocol for *P*-[2-(3-methylphenyl)-ethynyl] diethyl phosphonate (2c) afforded the relevant product in the same manner, but in 78% yield (entry 2). Meanwhile, methoxy or dimethoxy substituted phenyl groups were also compatible in the system, which were well exemplified by *P*-[2-(4-methoxyphenyl)-ethynyl] phosphonic diethyl ester (2d), [2-(2,5-dimethoxyphenyl)-ethynyl] phosphonic diethyl ester (2e) and P-[2-(1,3-benzodioxol-5-yl) ethynyl]- phosphonic diethyl ester (2f) (entries 3 – 5). Reactions between 2e – 2g and 1a or 1i took place smoothly, approaching the desired isocoumarin derivatives 3ad, 3ie and 3af in yields from 79% - 81%. Haloed phosphonate like *P*-[(4-chlorophenyl) ethynyl] diethyl phosphonate (2g) coupled with 1a successfully in the presence of the rhodium catalyst, providing the isocoumarin derivative 3ag in 85% yield (entry 6). Polyaryl and heteroaryl like 2-naphthyl and 2-thiophenyl decorated alkynyl diethyl phosphonates 2h and 2i produced the corresponding phosphoryl fused isocoumarins in 75% and 72% yields (entries 7 and 8). Except for diethyl phosphonates, dimethyl (entry 9), di-isopropyl (entry10) and di-*n*-butyl (entry 11) phosphonates 2j – 2l were well-tolerated in the system and gave the adducts 3aj – 3al in yields ranging from 72% to 80%.

Table 3. Substrates scope on alkynyl phosphonates[a]



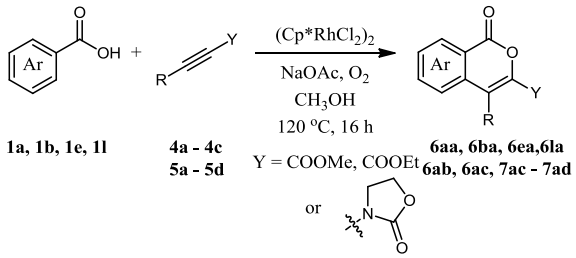
1a, R = H
1i, R = Br **2a** **3ba - 3la**

Entry	1/2	3	Ar	R'	Yield[b]
1	**1a/2b**	**3ab**	4-CH_3Ph	Et	81%
2	**1a/2c**	**3ac**	3-CH_3Ph	Et	78%
3	**1a/2d**	**3ad**	4-CH_3OPh	Et	79%
4	**1i/2e**	**3ie**	2,5-$(CH_3O)_2Ph$	Et	81%
5	**1a/2f**	**3af**			80%
6	**1a/2g**	**3ag**	4-ClPh	Et	85%
7	**1a/2h**	**3ah**	2-Naphthyl	Et	75%
8	**1a/2i**	**3ai**	2-Thiophenyl	Et	72%
9	**1a/2j**	**3aj**	Ph	Me	72%
10	**1a/2k**	**3ak**	Ph	*i*Pr	80%
11	**1a/2l**	**3al**	Ph	*n*Bu	79%

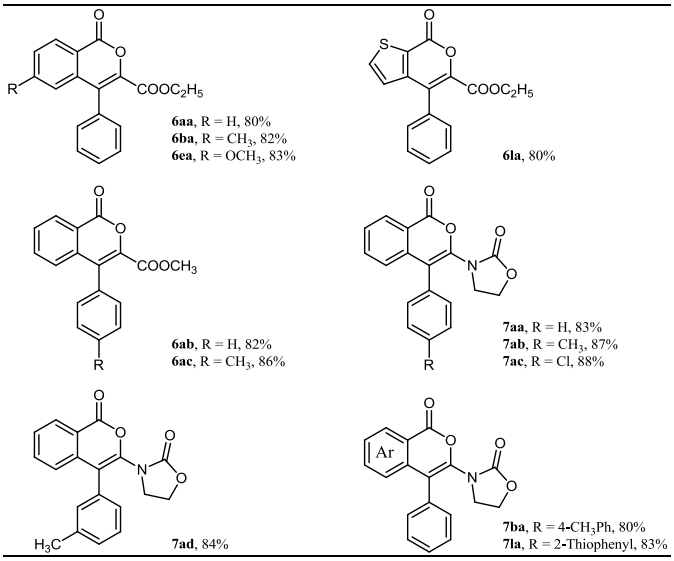
[a] Reaction conditions: **1a** or **1i** (0.5 mmol), **2** (0.75 mmol), $(Cp^*RhCl_2)_2$ (5.0 mol%), NaOAc (0.25 mmol) under O_2 atmosphere at 120 °C for 16 h. [b] Isolated yields.

Encouraged by the good compatibilities of the rhodium-catalyzed protocol, the broader scope of the substrates was then investigated on other alkynyl derivatives as shown in Table 4. For example, the reactivity of yamines and alkynyl esters also was evaluated in the practical methodology. Under the optimal conditions, benzoic acid (**1a**), 4-methyl benzoic acid (**1b**) and 4-methoxy benzoic acid (**1e**) reacted with 3-phenyl-2-propynoic ethyl ester (**4a**) readily, furnishing the corresponding aryl-1-oxo-*1H*-2-benzopyran-3-carboxylic ethyl ester **6aa** – **6ca** in yields from 80% to 83%. Heteroaryl carboxylic acid such as 2-thenoic acid (**1l**) offered 4-phenyl-1-oxo-*1H*-thienopyran-3-carboxylic ethyl ester (**6la**) in 80% yield. In the same way, 4-phenyl-1-oxo-*1H*-2-benzopyran-3-carboxylic methyl ester (**6ab**) and 4-(4-methylphenyl-1-oxo-*1H*-2-benzopyran-3-carboxylic methyl ester (**6ac**) were synthesized in 82% and 86% yields, separately. When the representative yamines such as 3-alkynyl-2-oxazolidinones were used as the coupling partner in the system with aryl carboxylic acids, the protocol exhibited good efficiency. As shown in Table 4, diverse 3-(2-Oxo-3-oxazolidinyl) *1H*-2-benzopyran-1-ones **7aa** – **7ad** and **7ba**, **7la** were provided from the Rh(III)-catalyzed strategy in yields from 80% - 88%.

Table 4. Substrates scope on alkynyl esters and yamines[a]



1a, 1b, 1e, 1l **4a - 4c** **5a - 5d** **6aa, 6ba, 6ea,6la** **6ab, 6ac, 7ac - 7ad**



[a] Reaction conditions: **1a** (0.5 mmol), **4** or **5** (0.75 mmol), $(Cp^*RhCl_2)_2$ (5.0 mol%), NaOAc (0.25 mmol) under O_2 atmosphere at 120 °C for 16 h.

Additionally, the structure of **3ja** was unequivocally determined by single crystal X-ray diffraction, which was obtained from methanol (Figure 1).[25]

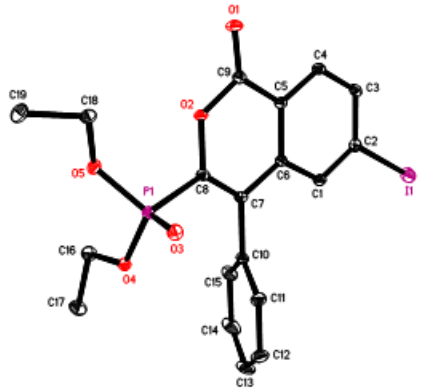
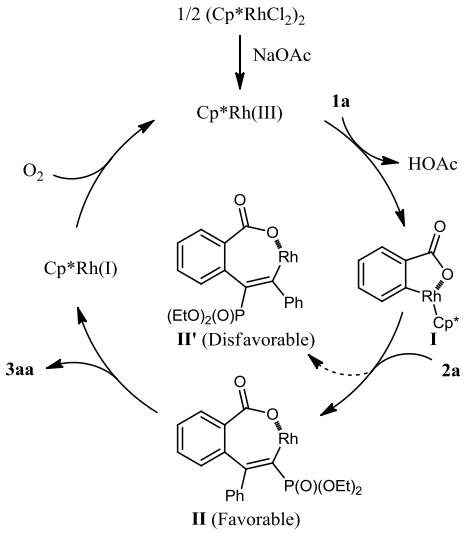


Figure 1. ORTEP diagram of the X-ray crystal structure of **3ja** (Thermal ellipsoids are drawn at 30% probability)

Based on the disclosed precedents, the mechanism of the annulation protocol was proposed (Scheme 2). Initially, the dimer $(Cp^*RhCl_2)_2$ was transformed into singlet rhodium species Cp*Rh(III) of higher activity. Then, oxidative insertion of the Rh(III) on the *ortha*-C-H bond took place, leading to a five-membered rhodacycle **I** with assistance of the carboxylic group. Successive coupling of the alkynyl substrate **2a** with **I** gave two optional accesses to novel seven-member rhodacyclic intermediate **II** and **II'**. But the formation of **II** was favourable while **II'** was disfavoured due to the difference of the electronic density on the two alkynyl carbon atoms, which made a good illustration for the high regio-selectivity. Finally, the product **3aa** was afforded by a reductive elimination step with a release of Cp*Rh(I), which was then re-oxided into Cp*Rh(III) by the molecular oxygen for the completion of the catalytic cycle.



Scheme 2. Proposed mechanism

Conclusions

In conclusion, a rhodium catalysed annulation reaction was developed for the formation of novel hetero substituted isocoumarins. The methodology was featured for the high atom/step efficiency and high regio-selectivity and broad substrate scope. In addition, oxygen played an important role in the protocol as clean oxidant. Further systemic investigations on the isocoumarin derivatives are still in progress in our laboratory.

Experimental Section

General Remarks: All carboxylic reagents were purchased from commercial companies and used without further purification, alkynyl phosphonates and yamines were prepared by the methods described in reported literatures[24b,26]. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA-400 spectrometer in deuterated chloroform at 25 °C with residue solvent peaks as internal standards (δ = 7.26 ppm for ^1H-NMR and δ = 77.16 ppm for ^{13}C-NMR). Chemical shifts (δ) are reported in ppm, and spin-spin coupling constants (*J*) are given in Hz, while multiplicities are abbreviated by s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Mass spectra were recorded on a ThermoFinnigan MAT95XP microspectrometer and High resolution mass spectra (HRMS) were recorded on an Agilent Technologies Accurate Mass Q-TOF 6530 microspectrometer. Infrared (IR) spectra were reported in reciprocal centimeter (cm^{-1}). Melting points were recorded on a national standard melting point apparatus (Model: Taike XT-4) and were uncorrected.

General Procedure: A sealed tube (35 mL) equipped with a stirring bar was charged with oxygen for three times and then was loaded with aryl carboxylic acid (0.5 mmol), alkynyl (0.75 mmol), NaOAc (0.25 mmol) and $(Cp^*RhCl_2)_2$ (5 mol%) and the reaction mixture was allowed to stir at 120 °C for 16 h. After cooling to room temperature, the mixture was filtered through a short celite pad and washed with dichloromethane (15 mL × 3). The filtrate was concentrated and the oily crude product was purified by column chromatography using silica gel (200-300 mesh) as

stationary phase and a mixture of petroleum and ethyl acetate as eluent to give the desired product **3**, **6** and **7** in noted yields.

3-(Diethyl phosphoryl)-4-phenyl-*1H*-2-benzopyran-1-one (3aa): colorless oil (150.0 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 (d, *J* = 7.6 Hz, 1H), 7.62 (m, 2H), 7.48 (d, *J* = 6.7 Hz, 3H), 7.36 (dd, *J* = 7.3, 2.0 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 1H), 4.13 – 4.02 (m, 2H), 3.99 – 3.88 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.7 ($J_{C\text{-}P}$ = 9.0 Hz), 145.6, 143.2, 137.2 ($J_{C\text{-}P}$ = 14.5 Hz), 134.9, 132.2 ($J_{C\text{-}P}$ = 2.6 Hz), 130.6 ($J_{C\text{-}P}$ = 1.5 Hz), 130.2, 129.7, 128.8, 128.5, 127.8 ($J_{C\text{-}P}$ = 20.2 Hz), 126.6 ($J_{C\text{-}P}$ = 1.4 Hz), 122.0, 63.5, 63.4, 16.3, 16.2 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 4.07 (ppm). IR (in KBr) *v* = 3464, 2983, 2933, 2910, 2872, 1739, 1600, 1481, 1448, 1392, 1371, 1263, 1203, 1166, 1128, 1101, 1026, 975, 800, 752, 700 (cm^{-1}). MS (EI): *m/z*(%) = 121.1 (100), 139.1 (10), 165.1 (78), 193.1 (24), 221.1 (50), 358.1 (52, M^+). HRMS (EI) (m/z) $[C_{19}H_{19}O_5P]^+$: Calcd. 358.0970, Found 358.0975.

3-(Diethyl phosphoryl)-4-phenyl-6-methyl-*1H*-2-benzopyran-1-one (3ba): white solid (146.9 mg, 79% yield). m.p.:102 – 104 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 8.1 Hz, 1H), 7.49 (d, *J* = 6.7 Hz, 3H), 7.38 (dd, *J* = 19.6, 7.3 Hz, 3H), 6.81 (s, 1H), 4.12 – 4.01 (m, 2H), 4.00 – 3.88 (m, 2H), 2.35 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.8 ($J_{C\text{-}P}$ = 9.0 Hz), 146.2, 145.7, 143.3, 137.3, 132.3, 131.4, 130.7, 129.8, 128.8, 128.5, 127.8 ($J_{C\text{-}P}$ = 20.1 Hz), 127.7, 127.5, 126.6, 119.6, 63.5, 63.4, 22.2, 16.3, 16.2 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 4.21 (ppm). IR (in KBr) *v* = 3479, 2983, 2929, 2908, 1741, 1701, 1610, 1489, 1444, 1392, 1340, 1307, 1255, 1224, 1174, 1132, 1116, 1099, 1026, 1026, 975, 958, 810, 783, 763, 750, 702 (cm^{-1}). MS (EI): *m/z*(%) = 121.2 (69), 179.2 (68), 207.2 (30), 235.2 (84), 372.3 (100, M^+). HRMS (EI) (m/z) $[C_{20}H_{21}O_5P]^+$: Calcd. 372.1127, Found. 372.1116.

3-(Diethyl phosphoryl)-4-phenyl-8-methyl-*1H*-2-benzopyran-1-one (3ca): yellow solid (115.3 mg, 62% yield). m.p.: 82 – 84 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 – 7.43 (m, 4H), 7.37 (dd, *J* = 15.0, 6.9 Hz, 3H), 6.88 (d, *J* = 7.9 Hz, 1H), 4.15 – 4.02 (m, 2H), 4.02 – 3.87 (m, 2H), 2.87 (s, 3H), 1.22 (t, *J* = 7.0 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.1 ($J_{C\text{-}P}$ = 9.0 Hz),145.4, 143.9, 138.9, 138.8, 134.1, 133.2, 132.9 ($J_{C\text{-}P}$ = 2.6 Hz), 130.8, 128.8, 128.5, 128.0, 127.8, 125.0, 120.5, 63.52, 63.46, 23.6, 16.32, 16.25 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 4.16 (ppm). IR (in KBr) *v* = 3059, 2981, 2926, 2858, 1735, 1586, 1467, 1388, 1263, 1228, 1159, 1097, 1049, 1020, 972, 810, 754, 702 (cm^{-1}). MS (EI): m/z(%) = 93.0 (44), 121.1 (100), 179.0 (70), 236.1 (38), 372.0 (66, M^+). HRMS (ESI) (m/z) $[C_{20}H_{21}O_5P+H^+]$: Calcd. 373.1199, Found.373.1201.

3-(Diethyl phosphoryl)-4-phenyl-7,8-dimethyl-*1H*-2-benzopyran-1-one (3da): yellow solid (123.8 mg, 64% yield). m.p.: 58 – 60 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (d, *J* = 6.6 Hz, 3H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.36 – 7.29 (m, 2H), 6.77 (d, *J* = 8.2 Hz, 1H), 4.12 – 4.01(m, 2H), 3.99 – 3.89 (m, 2H), 2.81 (s, 3H), 2.40 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.5 ($J_{C\text{-}P}$ = 9.0 Hz), 144.4, 142.0 ($J_{C\text{-}P}$ = 3.9 Hz), 140.1, 136.8 ($J_{C\text{-}P}$ = 14.2 Hz), 136.1, 132.9 ($J_{C\text{-}P}$ = 2.6 Hz), 130.8 ($J_{C\text{-}P}$ = 1.4 Hz), 128.6, 128.4, 128.2, 124.2 ,120.5, 63.4, 63.3, 21.3, 18.0, 16.3, 16.2 (ppm). ^{31}P NMR (160MHz, $CDCl_3$) δ = 4.37 (ppm). IR (in KBr) *v* = 3479, 2981, 2927, 2868, 1732, 1712, 1556, 1475, 1444, 1392, 1259, 1165, 1111, 1049, 1024, 1001, 977, 750 (cm^{-1}). MS (EI): m/z(%) = 121.1 (98), 193.1 (56), 221.1 (44), 249.1 (47), 386.0 (100, M^+). HRMS (ESI) (m/z) $[C_{21}H_{23}O_5P+H^+]$: Calcd. 387.1356, Found.387.1354.

3-(Diethyl phosphoryl)-4-phenyl-6-methoxyl-*1H*-2-benzopyran-1-one (3ea): white solid (161.0 mg, 83% yield). m.p.: 114 – 116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.30 (d, *J* = 8.8 Hz, 1H), 7.47 (t, *J* = 6.3 Hz, 3H), 7.41 – 7.34 (m, 2H), 7.11 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.42 (d, *J* = 2.3 Hz, 1H), 4.12 – 4.01 (m, 2H), 3.99 – 3.89 (m, 2H), 3.72 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.8 ($J_{C\text{-}P}$ = 1.2 Hz), 160.6 ($J_{C\text{-}P}$ = 9.0 Hz), 140.0 ($J_{C\text{-}P}$ = 14.7 Hz), 132.4, 132.2, 130.6 ($J_{C\text{-}P}$ = 1.4 Hz), 128.9, 128.5, 127.8 ($J_{C\text{-}P}$ = 15.5 Hz), 127.5, 117.4, 115.1, 110.0, 63.53, 63.47, 55.7, 16.30, 16.23 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 4.12 (ppm). IR (in KBr) *v* = 3456, 2983, 2929, 2933, 2862, 1734, 1602, 1563, 1487, 1446, 1359, 1313, 1263, 1224, 1163, 1132, 1105, 1022, 972, 808, 756, 707 (cm^{-1}). MS (EI): m/z(%) = 121.2 (62), 152.2 (56), 195.2 (54), 251.2 (100), 388.2 (100, M^+). HRMS (EI) (m/z) $[C_{20}H_{21}O_6P]$+: Calcd. 388.1076, Found.388.1061.

3-(Diethyl phosphoryl)-4-phenyl-6,7-dioxolo-*1H*-2-benzopyran-1-one (3fa): yellow solid (160.8 mg, 80% yield). m.p.: 170 – 172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 2.0 Hz, 5H), 7.06 (d, *J* = 8.3 Hz, 1H), 5.79 (s, 2H), 4.08 – 4.02 (m, 2H), 3.95 – 3.88 (m, 2H), 1.20 (d, *J* = 7.0 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.7 ($J_{C\text{-}P}$ = 6.7 Hz), 160.2, 153.6, 145.7, 143.8, 133.1, 130.6, 130.4, 128.9, 128.6, 127.8, 126.4, 124.6, 124.4, 120.0 ($J_{C\text{-}P}$ = 15.8 Hz), 111.1, 102.6, 63.6, 63.5, 16.32, 16.26 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 4.31 (ppm). IR (in KBr) *v* = 3446, 2981, 2926, 2864, 1760, 1618, 1570, 1496, 1479, 1454, 1167, 1274, 1201, 1155, 1130, 1082, 1026, 987, 935, 800, 752, 723, 700 (cm^{-1}). MS (EI): m/z(%) = 121.1 (100), 151.1 (28), 237.0 (26), 265.0 (68), 402.0 (85, M^+). HRMS (ESI) (m/z) $[C_{20}H_{19}O_7P+H^+]$: Calcd. 403.0941, Found.403.0940.

3-(Diethyl phosphoryl)-4-phenyl-6-fluoro-*1H*-2-benzopyran-1-one (3ga): white solid (154.1 mg, 82% yield). m.p.: 112 – 114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (dd, *J* = 8.8, 5.6 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.34 (dd, *J* = 7.1, 2.2 Hz, 2H), 7.24 (s, 1H), 6.68 (dd, *J* = 9.6, 2.4 Hz, 1H), 4.10 – 4.02 (m, 2H), 3.97 – 3.89 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 168.1 ($J_{C\text{-}P}$ = 1.0 Hz), 159.9 ($J_{C\text{-}P}$ = 7.0 Hz), 147.1, 144.8 ($J_{C\text{-}P}$ = 2.0 Hz), 133.2, 133.1, 131.8, 131.7, 130.6 ($J_{C\text{-}P}$ = 2.0 Hz), 129.2, 128.8, 128.0, 118.5, 118.5 ($J_{C\text{-}P}$ = 3.0 Hz), 113.0 ($J_{C\text{-}P}$ = 1.0 Hz), 112.8 ($J_{C\text{-}P}$ = 1.0 Hz), 63.73, 63.67, 16.33, 16.26 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 3.59 (ppm). ^{19}F NMR (375 MHz, $CDCl_3$) δ = -100.07 (ppm). IR (in KBr) *v* = 2983, 2931, 1739, 1608, 1560, 1483, 1442, 1255, 1120, 1099, 1029, 974, 756, 700 (cm^{-1}). MS (EI): m/z(%) = 93.0 (52), 121.1 (94), 183.0 (100), 211.0 (31), 239.0 (86), 376.0 (60, M^+). HRMS (EI) (m/z) $[C_{19}H_{18}FO_5P]^+$: Calcd. 376.0876, Found.376.0867.

3-(Diethyl phosphoryl)-4-phenyl-6-chloro-*1H*-2-benzopyran-1-one (3ha) : yellow solid (152.8 mg, 78% yield). m.p.: 158 – 160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.31 (d, *J* = 8.5 Hz, 1H), 7.61 – 7.47 (m, 4H), 7.36 (dd, *J* = 7.0, 2.2 Hz, 2H), 7.02 (d, *J* = 1.9 Hz, 1H), 4.13 – 4.05 (m, 2H), 4.00 – 3.89 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.1 ($J_{C\text{-}P}$ = 13.0 Hz), 160.0, 147.2, 144.9, 142.1, 138.9, 138.8, 131.6 ($J_{C\text{-}P}$ = 2.0 Hz), 130.7($J_{C\text{-}P}$ = 1.2 Hz), 129.2, 128.8, 126.8, 126.6, 126.3, 120.3 ($J_{C\text{-}P}$ = 2.0 Hz), 63.74, 63.68, 16.33, 16.27 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 3.56 (ppm). IR (in KBr) *v* = 3730, 2924, 2862, 1739, 1546, 1514, 1336, 1265, 1259, 1193, 1029, 958, 752, 698, 669 (cm^{-1}). MS (EI): m/z(%) = 93.0 (45), 121.1 (100), 199.0 (48), 255.0 (35), 392.0 (7, M^+). HRMS (ESI) (m/z) $[C_{19}H_{18}ClO_5P+H^+]$: Calcd. 393.0653, Found.393.0657.

3-(Diethyl phosphoryl)-4-phenyl-6-bromo -1H-2-benzopyran-1-one (3ia) : yellow solid (163.5 mg, 75% yield). m.p.: 170 – 172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.23 (d, *J* = 8.4 Hz, 1H), 7.72 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.52 (dd, *J* = 7.9, 2.8 Hz, 3H), 7.41 – 7.33 (m, 2H), 7.19 (d, *J* = 1.4 Hz, 1H), 4.15 – 4.03 (m, 2H), 4.01 – 3.89 (m, 2H) , 1.21 (t, *J* = 7.1 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.2 ($J_{C\text{-}P}$ = 9.0 Hz), 147.1, 144.8, 138.9, 138.8, 133.6, 131.5 ($J_{C\text{-}P}$ = 2.0 Hz), 131.4, 130.7 ($J_{C\text{-}P}$ = 2.0 Hz), 129.4 ($J_{C\text{-}P}$ = 2.0 Hz), 129.3, 128.8, 126.7,127.1, 120.7 ($J_{C\text{-}P}$ = 1.0 Hz), 63.8, 63.7, 16.33, 16.27 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ =

3.53 (ppm). IR (in KBr) *v* = 2980, 2924, 2860, 1737, 1544, 1263, 1031, 754, 696, 667 (cm^{-1}). MS (EI): m/z(%) = 93.0 (39), 121.1 (100), 163.1 (35), 243.0 (20), 300 (39), 437.9 (31, M^+). HRMS (EI) (m/z) $[C_{19}H_{18}BrO_5P]^+$: Calcd. 436.0075, Found.436.0063.

3-(Diethyl phosphoryl)-4-phenyl-6-iodo-*1H*-2-benzopyran-1-one (3ja): white solid (186.3mg, 77% yield). m.p.: 188 – 190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 5.6 Hz, 3H), 7.39 (s, 1H), 7.35 (d, *J* = 7.6 Hz, 2H), 4.10 – 4.03 (m, 2H), 4.02 – 3.83 (m, 2H), 1.22 (t, *J* = 7.1 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.5 ($J_{C\text{-}P}$ =9.0 Hz), 144.6, 139.4, 138.6, 138.4, 135.5 ($J_{C\text{-}P}$ =2.0 Hz), 131.5 ($J_{C\text{-}P}$ = 3.0 Hz), 130.6 ($J_{C\text{-}P}$ = 2.0 Hz), 129.2, 128.8, 126.5, 126.3, 121.2 ($J_{C\text{-}P}$ = 1.0 Hz), 103.7 ($J_{C\text{-}P}$ =2.0 Hz), 63.72, 63.66, 16.32, 16.25 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 3.56 (ppm). IR (in KBr) *v* = 2981, 2926, 2858, 1737, 1583, 1394, 1259, 1193, 1031, 752, 700 (cm^{-1}). MS (EI): m/z(%) = 93.0 (55), 121.1 (100), 163.1 (40), 346.9 (38), 483.9 (36, M^+). HRMS (ESI) (m/z) $[C_{19}H_{18}IO_5P+H^+]$: Calcd. 485.0009, Found.485.0008.

3-(Diethyl phosphoryl)-4-phenyl-*1H*-naphtho[2, 3-c]pyran -1-one (3ka): colorless oil (161.2 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (d, *J* = 8.6 Hz, 1H), 8.04 (s, 1H), 7.86 (s, 1H), 7.49 (dd, *J* = 21.1, 7.1 Hz, 6H), 7.13 (dd, *J* = 20.6, 7.9 Hz, 2H), 4.14 – 4.04 (m, 2H), 4.03 – 3.93 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.4 ($J_{C\text{-}P}$ = 9.0 Hz), 144.9, 137.4, 132.2, 131.2 ($J_{C\text{-}P}$ = 1.0 Hz), 130.8 ($J_{C\text{-}P}$ = 2.0 Hz), 129.7, 129.6, 129.3, 129.2, 128.9, 128.8, 128.7, 128.6, 128.0, 127.9, 127.6, 126.7 ($J_{C\text{-}P}$ = 3.0 Hz), 124.3, 63.64, 63.58, 16.4, 16.3 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 4.71 (ppm). IR (in KBr) *v* = 3443, 2956, 2924, 1730, 1640, 1606, 1446, 1376, 1248, 1023, 797, 762, 579, 528 (cm^{-1}). MS (EI): m/z(%) = 93.0 (42), 121.1 (100), 215.1 (75), 270.1 (45), 408.1 (83, M^+). HRMS (EI) (m/z) $[C_{23}H_{21}O_5P]^+$: Calcd. 408.1127, Found.408.1124.

3-(Diethyl phosphoryl)-4-phenyl-*1H*-thieno[2, 3-c]pyran-1-one (3la): colorless oil (127.4mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79 (d, *J* = 5.1 Hz, 1H), 7.44 (dd, *J* = 18.4, 7.1 Hz, 5H), 6.85 (d, *J* = 5.1 Hz, 1H), 4.13 – 4.04 (m, 2H), 4.02 – 3.92 (m, 2H), 1.19 (t, *J* = 7.0 Hz, 6H) (ppm).^{13}C NMR (100 MHz, $CDCl_3$) δ = 156.9 ($J_{C\text{-}P}$ = 4.0 Hz), 147.7, 147.5, 147.4, 145.1, 136.6, 132.8, 129.9, 129.0, 128.6, 126.3, 126.1, 125.9 ($J_{C\text{-}P}$ = 8.0 Hz), 125.8, 63.7, 63.6, 16.24, 16.18 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 3.89 (ppm). IR (in KBr) *v* = 3456, 3061, 2983, 2929, 2868, 1732, 1714, 1492, 1444, 1425, 1392, 1259, 1224, 1168, 1147, 1093, 1045, 1024, 989, 968, 794, 750, 702 (cm^{-1}). MS (EI): m/z(%) = 93.0 (64), 121.1 (100), 171.0 (45), 199.0 (38), 227.0 (63), 364.0 (34, M^+). HRMS (ESI) (m/z) $[C_{17}H_{17}O_5PS+H^+]$: Calcd. 365.0607, Found.365.0608.

3-(Diethyl phosphoryl)-4-(4-methylphenyl)-*1H*-2-benzopyran-1-one (3ab): colorless oil (150.5mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.32 (d, *J* = 7.5 Hz, 1H), 7.58 (m , 2H), 7.30 – 7.18 (m, 4H), 7.06 (d, *J* = 7.9 Hz, 1H), 4.10 – 4.00 (m, 2H), 3.99 – 3.89 (m, 2H), 2.38 (s, 3H), 1.18 (t, *J* = 7.0 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.8 ($J_{C\text{-}P}$ = 9.0 Hz), 138.7, 137.4 ($J_{C\text{-}P}$ = 14.7 Hz), 134.84, 130.5 ($J_{C\text{-}P}$ = 1.3 Hz), 130.1, 129.6, 129.2, 129.1, 128.1, 127.9, 126.7, 122.0, 63.5, 63.4, 21.4, 16.3,16.2 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 4.09 (ppm). IR (in KBr) *v* = 3558, 3462, 3448, 2983, 2929, 2870, 1739, 1645, 1514, 1454, 1394, 1259, 1166, 1128, 1045, 1022, 975, 752 (cm^{-1}). MS (EI): m/z(%) = 93.1 (46), 121.1 (100), 179.1 (41), 235.2 (35), 372.2 (47, M^+). HRMS (EI) (m/z) $[C_{20}H_{21}O_5P]^+$: Calcd. 372.1127, Found.372.1126.

3-(Diethyl phosphoryl)-4-(3-methyphenyl)-*1H*-2-benzopyran-1-one (3ac): colorless oil (145.1mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35 (d, *J* = 7.7 Hz, 1H), 7.60 (dd, *J* = 15.5, 7.6 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.24 (s, 1H), 7.15 (d, *J* = 7.4 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 1H), 4.11 – 4.01 (m, 2H), 3.99 – 3.89 (m, 2H) , 2.39 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.9 ($J_{C\text{-}P}$ = 9.0 Hz), 145.6, 143.2, 138.2, 137.9, 137.5, 137.4, 137.3, 134.9, 132.1, 132.0, 131.3, 130.2, 129.7 ($J_{C\text{-}P}$ = 13.3 Hz), 128.4, 127.8, 126.8, 122.1, 63.6, 63.5, 21.6, 16.31, 16.26 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 4.19 (ppm). IR (in KBr) *v* = 3448, 2966, 2929, 2864, 1939, 1639, 1327, 1265, 1165, 1024, 975, 798, 756, 702 (cm^{-1}). MS (EI): m/z(%) = 93.1 (62), 121.1 (100), 235.1 (60), 372.1 (37, M^+). HRMS (ESI) (m/z) $[C_{20}H_{21}O_5P+H^+]$: Calcd. 373.1199, Found. 373.1203.

3-(Diethyl phosphoryl)-4-(4-methoxyphenyl)-*1H*-2-benzopyran-1-one (3ad): colorless oil (153.3 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.37 (d, *J* = 7.7 Hz, 1H), 7.63 (dd, *J* = 17.7, 7.6 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 2H), 4.15 – 4.05 (m, 2H), 4.02– 3.94 (m, 2H), 3.87 (s, 3H), 1.25 (d, *J* = 6.9 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.9 ($J_{C\text{-}P}$ = 9.0 Hz), 160.8, 160.1, 137.7, 137.5, 134.9, 131.9, 130.1, 129.7, 127.6, 126.7 ($J_{C\text{-}P}$ = 1.2 Hz), 124.1, 122.1, 114.0, 63.6, 63.5, 55.4, 16.4, 16.3 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 4.22 (ppm). IR (in KBr) *v* = 3396, 2962, 2923, 1741, 1604, 1512, 1259, 1098, 1023, 799, 698, 567 (cm^{-1}). MS (EI): m/z(%) = 93.1 (45), 121.1 (100), 152.1 (37), 388.0 (49, M^+). HRMS (EI) (m/z) $[C_{20}H_{21}O_6P]^+$: Calcd. 388.1076, Found.388.1064.

3-(Diethyl phosphoryl)-4-(2,5-dimethoxyphenyl)-6-bromo-*1H*-2-benzopyran-1-one (3ie): yellow solid (200.8 mg, 81% yield). m.p.: 118 – 120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.20 (d, *J* = 8.4 Hz, 1H), 7.69 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.14 (d, *J* = 1.3 Hz, 1H), 6.97 (dd, *J* = 17.7, 5.9 Hz, 2H), 6.85 (d, *J* = 2.9 Hz, 1H), 4.21 – 4.13 (m, 2H), 4.03 – 3.86 (m, 2H), 3.80 (s, 3H), 3.69 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.1 Hz, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.4 ($J_{C\text{-}P}$ = 9.0 Hz), 153.6, 151.8, 147.1, 144.8, 138.5, 138.3, 133.4, 131.2, 130.6 ($J_{C\text{-}P}$ = 1.4 Hz), 129.1 ($J_{C\text{-}P}$ = 1.5 Hz), 121.1($J_{C\text{-}P}$ = 2.5 Hz), 120.7 ($J_{C\text{-}P}$ = 1.3 Hz), 118.0, 115.8, 112.1 , 63.9, 63.8, 63.34, 63.28, 56.2, 55.9, 16.42, 16.36, 16.3, 16.2 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 3.31 (ppm). IR (in KBr) *v* = 3560, 3458, 2929, 2837, 1739, 1589, 1498, 1465, 1398, 1269, 1226, 1166, 1130, 1024, 972, 752 (cm^{-1}). MS (EI): m/z(%) = 93.1 (43),121.1 (48), 358.0 (100), 498.0 (77, M^+). HRMS (EI) (m/z) $[C_{21}H_{22}BrO_7P]^+$: Calcd. 496.0287, Found.496.0278.

3-(Diethyl phosphoryl)-4-(3, 4-dioxolophenyl)-*1H*-2-benzopyran-1-one (3af): bright-yellow oil (160.8 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 (d, *J* = 7.7 Hz, 1H), 7.64 (dd, *J* = 22.5, 7.7 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 6.88 – 6.69 (m, 2H), 6.03 (d, *J* = 9.5 Hz, 2H), 4.18 – 3.97 (m, 4H), 1.27 (m, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.8 ($J_{C\text{-}P}$ = 9.0 Hz), 148.2, 147.8, 145.7, 143.4, 137.5, 137.3, 135.0, 130.2, 129.8, 127.8, 127.6, 126.7, 125.5 ($J_{C\text{-}P}$ = 2.7 Hz), 124.5, 122.0, 111.0, 108.5, 101.5 , 63.7, 63.6, 63.53, 63.46, 16.4, 16.34, 16.27 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 3.95 (ppm). IR(in KBr) *v* = 2983, 2906, 2929, 1739, 1602, 1489, 1438, 1394, 1236, 1166, 1128, 1022, 979, 881, 752 (cm^{-1}). MS (EI): m/z(%) = 93.1 (56), 121.1 (100), 151.1 (49), 237.1 (30), 264.1 (72),402.1 (42, M^+). HRMS (EI) (m/z) $[C_{20}H_{19}O_7P]^+$: Calcd. 402.0868, Found.402.0877.

3-(Diethyl phosphoryl)-4-(4-chlorophenyl)-*1H*-2-benzopyran-1-one (3ag): colorless oil (166.6 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.37 (d, *J* = 7.6 Hz, 1H), 7.69 – 7.59 (m, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 7.04 (d, *J* = 7.9 Hz, 1H), 4.16 – 4.08 (m, 2H), 4.06 – 3.97 (m, 2H), 1.24 (t, *J* = 7.1 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.5 ($J_{C\text{-}P}$ = 9.0 Hz), 145.8, 137.0 ($J_{C\text{-}P}$ = 14.5 Hz), 135.0, 132.1 ($J_{C\text{-}P}$ = 1.4 Hz), 130.4, 129.9, 128.8, 126.8 ($J_{C\text{-}P}$ = 20.0 Hz), 126.4 ($J_{C\text{-}P}$ = 1.3Hz) , 122.0, 63.7, 63.6, 16.30, 16.24 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 6.61 (ppm). IR(in KBr) *v* = 2983, 2906, 2868, 1743, 1597, 1489, 1452, 1394, 1263, 1166, 1130, 1091, 1047, 1020, 975, 873,

752, 696 (cm^{-1}). MS (EI): m/z(%) = 93.1 (43), 121.1 (100), 163.1 (34), 199.1 (32), 392.2 (24, M^+). HRMS (EI) (m/z) $[C_{19}H_{18}ClO_5P]^+$: Calcd. 392.0580, Found.392.0571.

3-(Diethyl phosphoryl)-4-naphthyl-*1H*-2-benzopyran-1-one (3ah): bright-yellow oil (150.8mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.44 – 8.38 (m, 1H), 8.08 (d, *J* = 7.7 Hz, 1H), 7.99 – 7.85 (m, 4H), 7.64 – 7.62 (m, 1H), 7.56 – 7.53 (m, 1H), 7.49 – 7.39 (m, 2H), 7.08 (dd, *J* = 5.8, 3.3 Hz, 1H), 4.13 – 3.78 (m, 4H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.8 (J_{C-P} = 9.0 Hz), 145.9, 143.6, 137.4, 137.3, 135.0, 133.4, 133.3, 133.2, 130.2 (J_{C-P} = 2.0 Hz), 129.8, 129.6 (J_{C-P} = 2.0 Hz), 128.5, 128.3, 128.2, 128.1, 128.0, 127.8, 126.9, 126.8 (J_{C-P} = 8.0 Hz), 122.1 (J_{C-P} = 1.0 Hz) , 63.8, 63.7, 63.54, 63.47, 16.3, 16.21, 16.18, 16.1 (ppm). 31P NMR (160 MHz, $CDCl_3$) δ = 4.17 (ppm). IR (in KBr) *v* = 3739, 2981, 2931, 2866, 1739, 1512, 1458, 1265, 1170, 1126, 1022, 972, 806, 754 (cm^{-1}). MS (EI): m/z(%) = 93.1 (46), 121.1 (100), 215.1 (96), 270.1 (73), 408.1 (95, M^+). HRMS (EI) (m/z) $[C_{23}H_{21}O_5P]^+$: Calcd. 408.1127, Found.408.1111.

3-(Diethyl phosphoryl)-4-thiophenyl-*1H*-2-benzopyran-1-one (3ai): bright-yellow oil (108.5 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 (d, *J* = 7.9 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 5.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.19 (dd, *J* = 12.2, 3.9 Hz, 2H), 4.25 – 4.05 (m, 4H), 1.29 (t, *J* = 7.0 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.4 (J_{C-P} = 9.0 Hz), 137.5, 135.2, 131.8, 130.9 (J_{C-P} = 1.2 Hz), 130.4, 129.7, 128.2, 127.3, 126.5 (J_{C-P} = 1.4 Hz) ,121.6 (J_{C-P} = 1.2 Hz), 121.3, 63.83, 63.77, 16.4, 16.3 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 3.49 (ppm). IR (in KBr) *v* = 2955, 2924, 2852, 1743, 1461, 1377, 1261, 1020, 800 (cm^{-1}). MS (EI): m/z(%) = 93.1 (58), 121.1 (100), 171.1 (38), 199.1 (39), 227.0 (43), 364.0 (52, M^+). HRMS (EI) (m/z) $[C_{17}H_{17}O_5PS]^+$: Calcd.364.0534, Found. 364.0538.

3-(Dimethyl phosphoryl)-4-phenyl-*1H*-2-benzopyran-1-one (3aj): white solid (118.8mg, 72% yield). m.p.: 104 – 106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.39 (d, *J* = 7.5 Hz, 1H), 7.70 – 7.59 (m, 2H), 7.51 (d, *J* = 7.4 Hz, 3H), 7.41 – 7.35 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 1H), 3.63 (d, *J* = 11.3 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.7 (J_{C-P} = 8.0 Hz), 145.2, 142.9, 137.2, 137.1, 135.0, 132.1 (J_{C-P} = 2.7 Hz), 130.6 (J_{C-P} = 1.5 Hz), 130.4, 129.8, 129.0, 128.6, 128.4, 128.2, 126.8 (J_{C-P} = 1.5 Hz), 122.1 (J_{C-P} = 1.3 Hz) , 53.9, 53.8 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 6.61 (ppm). IR (in KBr) *v* = 2960, 1739, 1286, 1247, 1133, 1052, 1025, 891, 766, 565, 519 (cm^{-1}). MS (EI): m/z(%) = 84.0 (80), 93.1 (100), 165.1 (57), 330.1 (40, M^+). HRMS (EI) (m/z) $[C_{17}H_{15}O_5P]^+$: Calcd.330.0657, Found.330.0641.

3-(Diisopropyl phosphoryl)-4-phenyl- *1H*-2-benzopyran-1-one (3ak): white solid (154.4mg, 80% yield). m.p.: 110 – 112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.38 (d, *J* = 7.7 Hz, 1H), 7.62 (m, 2H), 7.47 (d, *J* = 5.0 Hz, 3H), 7.39 – 7.31 (m, 2H), 7.07 (d, *J* = 7.8 Hz, 1H), 4.71– 4.64 (m, 2H), 1.28 (d, *J* = 6.2 Hz, 6H), 1.21 (d, *J* = 6.2 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.9 (J_{C-P} = 11.0 Hz), 143.9, 137.6, 137.5, 134.9, 132.5 (J_{C-P} = 2.5 Hz), 130.9 (J_{C-P} = 1.4 Hz), 129.7, 128.8, 128.5, 126.7 (J_{C-P} = 1.2 Hz), 122.1 (J_{C-P} = 1.2 Hz), 72.7, 72.6, 24.19, 24.15, 23.7, 23.6 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 2.22 (ppm). IR (in KBr) *v* = 3460, 3442, 2981, 2933, 2981, 2873, 1739, 1643, 1514, 1454, 1381, 1259, 1172, 1105, 999, 891, 754 (cm^{-1}). MS (EI): m/z(%) = 57.1 (57), 71.1 (50) , 165.1 (47), 210.1 (50), 238.0 (100), 386.0 (28, M^+). HRMS (ESI) (m/z) $[C_{21}H_{23}O_5P+H^+]$: Calcd.387.1356, Found.387.1358.

3-(Dibutyl phosphoryl)-4-phenyl-*1H*-2-benzopyran-1-one (3al): colorless oil (129.6 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.37 (d, *J* = 7.7 Hz, 1H), 7.62 (m, 2H), 7.47 (d, *J* = 6.0 Hz, 3H), 7.36 (d, *J* = 5.4 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 1H), 4.05 – 3.98 (m, 2H), 3.92 – 3.80 (m, 2H), 1.60 – 1.46 (m, 4H), 1.34 –1.27 (m, 4H), 0.87 (t, *J* = 7.4 Hz, 6H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.7 (J_{C-P} = 9.0 Hz), 145.8, 143.4, 137.3, 137.2, 134.9, 132.3 (J_{C-P} = 2.7Hz), 130.7 (J_{C-P} =1.3 Hz), 130.1, 129.7, 128.8, 128.5, 127.9, 126.7 (J_{C-P} = 1.3 Hz), 122.0, 67.2, 67.1, 32.4, 32.3, 18.7, 13.6 (ppm). ^{31}P NMR (160 MHz, $CDCl_3$) δ = 4.19 (ppm). IR (in KBr) *v* = 2960, 2933, 2872, 1741, 1600, 1456, 1313, 1261, 1128, 1022, 759, 698, 584, 524 (cm^{-1}). MS (EI): m/z(%) = 121.1 (54), 165.1 (92), 210.1 (53), 221.1 (82), 238.1 (73), 303.0 (46), 414.1 (36, M^+). HRMS (ESI) (m/z) $[C_{23}H_{27}O_5P+H^+]$: Calcd.415.1669, Found. 415.1672.

4-Phenyl-1-oxo-*1H*-2-benzopyran-3-carboxylic ethyl ester (6aa): yellow solid (117.6 mg, 80% yield). m.p.: 100 – 102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 (d, *J* = 7.9 Hz, 1H), 7.77 (m, 2H), 7.65 (d, *J* = 7.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (d, *J* = 6.8 Hz, 3H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.04 (t, *J* = 7.1 Hz, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.5, 161.2, 155.5, 135.4, 134.8, 132.7, 130.7, 130.0, 128.9, 128.6, 128.3, 124.3, 119.9, 111.1, 62.1, 13.7 (ppm). IR (in KBr) *v* = 3062, 2981, 2933, 2902, 1747, 1722, 1624, 1685, 1448, 1371, 1342, 1315, 1241, 1232, 1124, 1091, 1053, 1018, 754, 694 (cm^{-1}). MS (EI): m/z(%) = 77.0 (36), 92.0 (25), 105.0 (100), 238.0 (34), 294.0 (83, M^+). HRMS (ESI) (m/z) $[C_{18}H_{14}O_4+H^+]$: Calcd.295.0965, Found. 295.0973.

4-Phenyl-6-methyl-1-oxo-1H-2-benzopyran-3-carboxylic ethyl ester (6ba): yellow oil (126.3 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.25 (d, *J* = 8.1 Hz, 1H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.52 (s, 1H), 7.46 (d, *J* = 6.8 Hz, 3H), 7.39 (d, *J* = 8.1 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.51 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.6, 161.3, 155.6, 146.7, 134.8, 132.9, 130.6, 130.3, 130.0, 128.6, 128.3, 124.2, 117.5, 111.0, 62.0, 22.4, 13.7 (ppm). IR (in KBr) *v* = 3057, 2962, 2937, 2862, 1726, 1496, 1446, 1375, 1257, 1228, 1211, 1180, 1151, 1074, 1033, 800, 754 (cm^{-1}). MS (EI): m/z(%) = 77.0 (40) , 105.0 (100), 252.0 (37), 308.1 (70, M^+). HRMS (ESI) (m/z) $[C_{19}H_{16}O_4+H^+]$: Calcd.309.1121, Found.309.1128.

4-Phenyl-6-methoxyl-1-oxo-*1H*-2-benzopyran-3-carboxylic ethyl ester (6ea): yellow solid (134.5mg, 83% yield). m.p.: 138 – 140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.27 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 7.0 Hz, 2H), 7.45 (d, *J* = 7.1 Hz, 3H), 7.17 (s, 1H), 7.09 (d, *J* = 8.8 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 1.00 (t, *J* = 7.1 Hz, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.6, 165.2, 161.0, 156.6, 137.1, 132.9, 132.2, 130.6, 128.5, 128.3, 117.0, 112.9, 110.7, 106.9, 61.9, 55.9, 13.6 (ppm). IR (in KBr) *v* = 3059, 2964, 2927, 2850, 1728, 1606, 1568, 1487, 1452, 1369, 1325, 1263, 1215, 1178, 1093, 1039, 800, 758 (cm^{-1}). MS (EI): m/z(%) = 77.0 (39) , 105.0 (100), 268.0 (58), 324.0 (98, M^+). HRMS (ESI) (m/z) $[C_{19}H_{16}O_5+H^+]$: Calcd.325.1071, Found.325.1072.

4-Phenyl-1-oxo-*1H*- thieno[2, 3-*c*]pyran-3-carboxylic ethyl ester (6la): yellow oli (120.1 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (d, *J* = 5.1 Hz, 1H), 7.59 (dd, *J* = 9.8, 6.5 Hz, 3H), 7.47 (dd, *J* = 11.9, 7.0 Hz, 3H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.02 (t, *J* = 7.1 Hz, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 165.8, 160.1, 157.1, 145.5, 137.3, 132.8, 131.8, 130.8, 128.8, 128.4, 125.4, 123.0, 109.1,61.8, 13.6 (ppm). IR (in KBr) *v* = 3086, 2962, 2936, 1737, 1712, 1524, 1416, 1364, 1244, 1223, 1180, 1066, 846, 807, 767, 687 (cm^{-1}). MS (EI): m/z(%) = 77.1 (35) , 105.1 (100), 272.0 (17), 300.1 (46, M^+). HRMS (ESI) (m/z) $[C_{16}H_{12}O_4S+H^+]$: Calcd.301.0529, Found.301.0564.

4-Phenyl-1-oxo-*1H*-2-benzopyran-3-carboxylic methyl ester (6ab): yellow oli (114.8mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 (d, *J* = 7.9 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.47 (d, *J* = 6.2 Hz, 3H), 3.72 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 167.0, 161.2, 155.5, 135.4, 134.7, 132.6, 130.8, 130.0, 129.0, 128.7, 128.1, 124.3, 119.9, 110.7,

52.80 (ppm). IR (in KBr) *v* = 2958, 2924, 2854, 1735, 1602, 1444, 1263, 1132, 1083, 1026, 800, 756 (cm^{-1}). MS (EI): m/z(%) = 165.0 (90), 193 (60), 221.0 (100),280.0 (97, M^+). HRMS (ESI) (m/z) [$C_{17}H_{12}O_4$+H^+]: Calcd.281.0808, Found. 281.0813.

4-(4-Methylphenyl)-1-oxo-*1H*-2-benzopyran-3-carboxylic methyl ester (6ac): white solid (126.5mg, 86% yield). m.p.: 116 – 118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.34 (d, *J* = 7.9 Hz, 1H), 7.77 (t, *J* = 7.7 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.54 (dd, *J* = 13.0, 7.6 Hz, 3H), 7.27 – 7.23 (m, 2H), 3.73 (s, 3H), 2.40 (s, 3H) (ppm). ^{13}C NMR (100MHz, $CDCl_3$) δ = 167.2, 161.3, 155.5, 141.2, 135.4, 134.9, 130.0, 129.7, 129.43, 128.8, 128.0, 124.2, 119.8, 110.28, 52.8, 21.6 (ppm). IR (in KBr) *v* = 2958, 2868, 1726, 1618, 1560, 1483, 1435, 1346, 1315, 1257, 1089, 1020, 754 (cm^{-1}). MS (EI): m/z(%) = 91.0 (35), 119.0 (100), 266.0 (44), 294.0 (78, M^+). HRMS (ESI) (m/z) [$C_{18}H_{14}O_4$+H^+]: Calcd.295.0965, Found. 295.0961.

3-(2-Oxo-3-oxazolidinyl)-4-phenyl-*1H*-2-benzopyran-1-one (7aa): yellow solid (127.4mg, 83% yield). m.p.: 218 – 220 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35 (d, *J* = 6.6 Hz, 1H), 7.76 (d, *J* = 45.9 Hz, 3H), 7.54 (d, *J* = 37.7 Hz, 5H), 4.54 (d, *J* = 5.8 Hz, 1H), 4.32 (d, *J* = 7.4 Hz, 1H), 3.76 (d, *J* = 7.6 Hz, 1H), 3.38 (d, *J* = 5.8 Hz, 1H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.9, 157.9, 154.7, 135.6, 135.2, 130.9, 130.8, 130.7, 129.2, 129.03, 128.1, 121.7, 120.8, 113.9, 63.1, 45.9 (ppm). IR (in KBr) *v* = 2958, 2920, 2927, 2850, 1743, 1633, 1602, 1481, 1419, 1309, 1257, 1228, 1128, 1072, 1024, 759, 694 (cm^{-1}). MS (EI): m/z(%) = 77.1 (74), 105.1 (100), 130.1 (34), 165.1 (36), 248.1 (65), 263.1 (47), 307.1 (12, M^+). HRMS (EI) (m/z) [$C_{18}H_{13}NO_4$]$^+$: Calcd. 307.0845, Found.307.0836.

3-(2-Oxo-3-oxazolidinyl)-4-(4-methylphenyl)-*1H*-2-benzopyran-1-one (7ab): yellow solid (139.7mg, 87% yield). m.p.: 220 – 222 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35 (d, *J* = 7.9 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.59 (dd, *J* = 15.8, 7.8 Hz, 3H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 4.55 (dd, *J* = 15.4, 8.9 Hz, 1H), 4.34 (dd, *J* = 16.8, 8.5 Hz, 1H), 3.75 (dd, *J* = 16.7, 8.5 Hz, 1H), 3.41 (dd, *J* = 15.3, 8.8 Hz, 1H), 2.42 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.0, 157.9, 154.8, 141.3, 135.5, 135.4, 130.6, 129.7, 129.0, 128.0, 121.6, 120.8, 113.3, 63.1, 45.8, 21.7 (ppm). IR (in KBr) *v* = 2960, 2920, 1743, 1627, 1602, 1481, 1417, 1305, 1253, 1228, 1126, 1068, 1026, 767 (cm^{-1}). MS (EI): m/z(%) = 91.1 (51), 119.1 (95), 234.1 (42), 262.1 (100), 277.1 (71), 321.1 (70, M^+). HRMS (ESI) (m/z) [$C_{19}H_{15}NO_4$+H^+]: Calcd. 322.1074, Found.322.1081.

3-(2-Oxo-3-oxazolidinyl)-4-(3-methylphenyl-*1H*-2-benzopyran-1-one (7ac): white solid (141.3mg, 88% yield). m.p.: 170 – 172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.35 (d, *J* = 7.9 Hz, 1H), 7.82 (t, *J* = 7.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 4.54 (dd, *J* = 15.4, 8.8 Hz, 1H), 4.31 (dd, *J* = 16.9, 8.5 Hz, 1H), 3.75 (dd, *J* = 16.7, 8.4 Hz, 1H), 3.40 (dd, *J* = 15.3, 8.7 Hz, 1H), 2.41 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.0, 157.9, 154.8, 138.9, 135.5, 135.3, 131.7, 130.8, 130.6, 129.1, 128.9, 128.7, 125.1, 121.7, 120.8, 113.7, 63.1, 45.9, 21.6 (ppm). IR (in KBr) *v* = 2960, 2920 , 2856, 1747, 1631, 1602, 1479, 1417, 1259, 1226, 1076, 1026, 758 (cm^{-1}). MS (EI): m/z(%) = 91.1 (27), 119.1 (52), 262.1 (100), 277.1 (56), 321.1 (53, M^+). HRMS (ESI) (m/z) [$C_{19}H_{15}NO_4$+H^+]: Calcd. 322.1074, Found.322.1087.

3-(2-Oxo-3-oxazolidinyl)-4-(4-chlorophenyl)-*1H*-2-benzopyran-1-one (7ad): white solid (143.3mg, 84% yield). m.p.: 256 – 258 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.36 (d, *J* = 7.9 Hz, 1H), 7.83 (t, *J* = 7.6 Hz, 1H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 8.6 Hz, 3H), 4.58 (dd, *J* = 15.3, 9.0 Hz, 1H), 4.38 (dd, *J* = 16.9, 8.7 Hz, 1H), 3.79 (dd, *J* = 16.8, 8.5 Hz, 1H), 3.41 (dd, *J* = 15.2, 8.8 Hz, 1H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.6, 157.9, 153.6, 148.7, 137.2, 136.0, 135.7, 135.0, 132.6, 130.8, 129.5, 129.4, 129.4, 129.3, 125.7, 121.7, 120.9, 118.4, 114.1, 63.1, 46.0 (ppm). IR (in KBr) *v* = 2956, 2920, 2850, 1741, 1483, 1417, 1255, 1228, 1068, 1024, 839, 765 (cm^{-1}). MS (EI): m/z(%) = 111.1 (47), 130.1 (57), 139.0 (100), 282.0 (90) , 297.1 (97), 341.1 (50, M^+). HRMS (ESI) (m/z) [$C_{18}H_{12}NO_4Cl$+H^+]: Calcd. 342.0528, Found.342.0538.

3-(2-Oxo-3-oxazolidinyl)-4-phenyl-6-methyl-*1H*-2-benzopyran-1-one (7ba): white solid (128.4mg, 80% yield). m.p.: 250 – 252 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.24 (d, *J* = 8.1 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.49 (d, *J* = 4.6 Hz, 3H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.22 (s, 1H), 4.55 (dd, *J* = 15.3, 8.9 Hz, 1H), 4.34 – 4.28 (m, 1H), 3.75 (dd, *J* = 16.8, 8.5 Hz, 1H), 3.36 (dd, *J* = 15.3, 8.7 Hz, 1H), 2.52 (s, 3H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.0, 158.0, 154.7, 147.0, 135.3, 130.9, 130.7, 130.6, 129.0, 128.1, 121.6, 118.5, 113.7, 63.1, 45.9, 22.5 (ppm). IR (in KBr) *v* = 2956, 2920, 2854, 1741, 1614, 1485, 1417, 1265, 1228, 1132, 1072, 1033, 765 (cm^{-1}). MS (EI): m/z(%) = 77.1 (44), 105.1 (67), 141.1 (48), 262.1 (100), 277.1 (88), 321.1 (42, M^+). HRMS (ESI) (m/z) [$C_{19}H_{15}NO_4$+H^+]: Calcd. 322.1074, Found.322.1086.

3-(2-Oxo-3-oxazolidinyl)-4-phenyl -*1H*- thieno [2, 3-c] pyran -1-one (7la): yellow solid (129.9mg, 83% yield). m.p.: 206 – 208 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (d, *J* = 5.1 Hz, 1H), 7.77 – 7.68 (m, 2H), 7.49 (d, *J* = 4.8 Hz, 3H), 7.19 (d, *J* = 5.1 Hz, 1H), 4.51 (dd, *J* = 14.6, 8.6 Hz, 1H), 4.32 (q, *J* = 8.4 Hz, 1H), 3.74 (q, *J* = 8.5 Hz, 1H), 3.42 (dd, *J* = 14.6, 8.4 Hz, 1H) (ppm). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.5, 156.9, 155.8, 146.4, 137.9, 131.0, 130.5, 129.1, 128.1, 123.6, 122.6, 113.4, 63.2, 46.0 (ppm). IR (in KBr) *v* = 3084, 2960, 2922, 2856, 1730, 1610, 1487, 1436, 1257, 1083, 1031, 1018, 798, 765, 694 (cm^{-1}). MS (EI): m/z(%) = 77.1 (68), 105.1 (100), 171.1 (48), 254.1 (66), 269.1 (72), 313.1 (97, M^+). HRMS (ESI) (m/z) [$C_{16}H_{11}NO_4S$+H^+]: Calcd. 314.0482, Found.314.0488.

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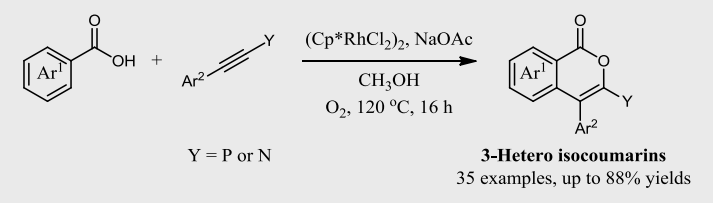

Various novel 3-hetero substituted isocoumarins were successfully prepared under O_2 atmosphere with assistance of a rhodium catalyst in regioselective manner. And the high regioselectivity was propably attributed for the difference of the electron-density on the alkynyl carbons.

Transition metal-catalysis

Lijuan Song, Jing Xiao, Wanrong Dong, Zhihong Peng* and Delie An**

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Rh(III)-Catalyzed Regioselective Preparation of 3-Hetero Isocoumarins from Aryl Carboxylic Acid and Alkynes

State Key Laboratory of Chemo/Biosensing and Chemometrics, Co
Chemistry and Chemical Engineering
Hunan University
Changsha, 410082, P. R. of China.
Tel. (Fax):+86 731 88821380
E-mail: wanrongdong@hnu.edu.cn; pzh7251@hnu.edu.cn;
deliean@hnu.edu.cn

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