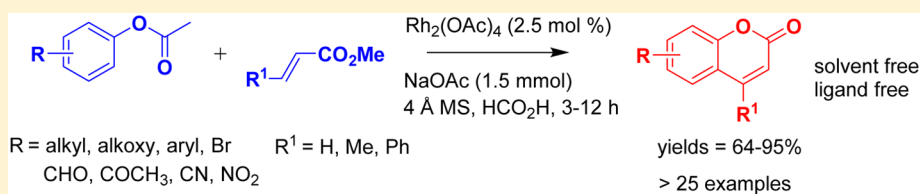# Rh-Catalyzed Synthesis of Coumarin Derivatives from Phenolic Acetates and Acrylates *via* C−H Bond Activation

Sunita K. Gadakh, Soumen Dey, and Arumugam Sudalai*

Chemical Engineering & Process Development Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra, India-411008

S *Supporting Information*

ABSTRACT: An efficient annulation strategy involving the reaction of phenolic acetates with acrylates in the presence of [Rh$_2$(OAc)$_4$] as catalyst and formic acid as reducing agent, leading to the high yield synthesis of coumarin derivatives, has been developed. The addition of NaOAc as a base increased the yield of the products. The reaction is quite successful for both electron-rich as well as electron-deficient phenolic acetates, affording coumarins with excellent regioselectivity, and proceeds *via* C−H bond activation proven by deuterium incorporation studies.

The activation of C−H bonds of aromatic hydrocarbons is one of the most challenging processes since these C−H bonds are relatively strong for chemical transformations. It is also an environmentally friendly process as it does not require toxic halogens for activation.[1] Thus, directed metalation of aromatic substrates has emerged as one of the most versatile methods to functionalize the C−H bonds of aromatic hydrocarbons.[2] Coumarin derivatives[3] are useful natural products widely found in plants and exhibit excellent biological and pharmacological activity including antitumor,[4a] anti-HIV,[4b,c] anticoagulation, antibacterial,[4d] antiinflammatory,[4e,f] and antioxidant.[4g] In addition, they are also widely used as food additives, as optical brightening agents, light-emitting diodes, as fluorescent probes, and laser dyes[5] (Figure 1).

Traditionally, the most common approach to their synthesis is undoubtedly the Pechmann condensation[6] and its related reactions.[7] Unfortunately, these classical methods employ

stoichiometric quantities of strong Lewis or Brønsted acids, often leading to mixtures of regioisomers. To a certain extent, some of these difficulties have been overcome by transition-metal-catalyzed coupling reactions.[8] However, starting materials (halides and organometallic reagents) for such processes need to be prefunctionalized, making these reactions unfavorable environmentally. Recently, Trost and others have reported a Pd-catalyzed atom economical method for the synthesis of coumarins *via* C−H bond activation, leading to many applications.[9] However, these reactions are applicable to only electron-rich phenols, probably following a Friedel−Crafts pathway. Alkenylation of phenols with acrylates using Pd/Cu as catalysts and employing expensive ligands provides another strategy for the synthesis of coumarins[10] (eqs i−ii, Scheme 1).

As part of our ongoing research on new catalytic synthesis of heterocyclic scaffolds, we have recently reported an elegant Rh(II)/HCO$_2$H catalytic system for the synthesis of quinoline carboxylates proceeding through rhodacycle as an intermediate.[11] In this communication, we wish to report, a Rh-catalyzed *ortho* C−H bond activation of phenolic acetates with acrylates in the presence of NaOAc as base and HCO$_2$H as reducing agent that produces synthetically useful coumarin derivatives **3a−ω** (eq iii, Scheme 1).

Our initial efforts toward the synthesis of coumarin structural units *via* annulation of phenyl acetate (**1** mmol) with methyl acrylate (1.2 mmol) focused on the catalytic system comprising Rh(II) acetate (5 mol %) in excess formic acid (1 mL) and heating at 70 °C (Table 1). However, under these conditions, only 18% of the desired coumarin **3a** was obtained.
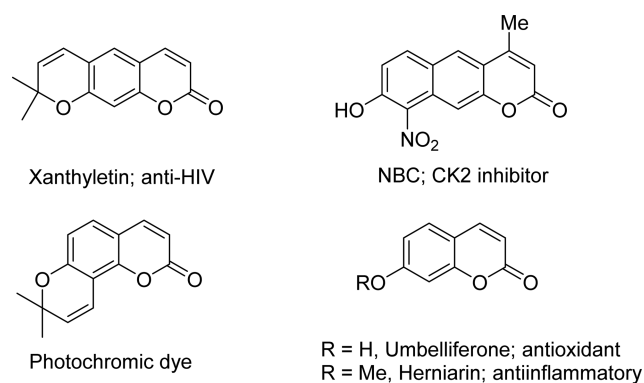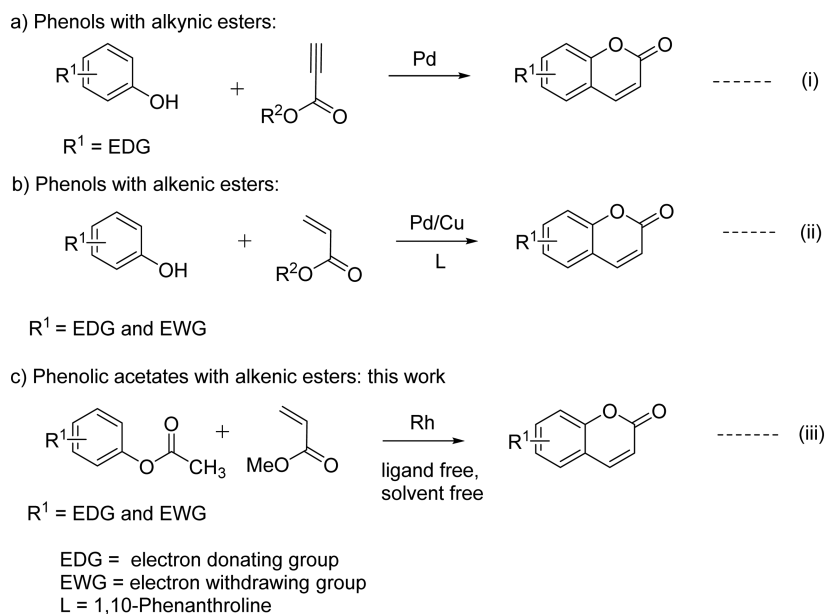

Figure 1. Some of the bioactive coumarin derivatives.

Scheme 1. Synthesis of Coumarins *via* C−H Activation Strategy

a) Phenols with alkynic esters:

R[1] = EDG

b) Phenols with alkenic esters:

R[1] = EDG and EWG

c) Phenolic acetates with alkenic esters: this work

R[1] = EDG and EWG

EDG = electron donating group
EWG = electron withdrawing group
L = 1,10-Phenanthroline

Table 1. Rhodium-Catalyzed Reaction of Phenyl Acetate with Methyl Acrylate: Optimization Studies[a]

entry	catalyst	catalyst (mol %)	solvent (2 mL)	additive	t (°C)	3a[b] (%)
1	Rh$_2$(OAc)$_4$	5			70	18
2		5		NaOAc	70	50
3		5		NaOAc	80	68
4		5		NaOAc	100	71
5		2.5		NaOAc	100	71
6		1		NaOAc	100	41
7		2.5		Na$_2$CO$_3$	100	19
8		2.5		K$_2$CO$_3$	100	20
9		2.5		Cs$_2$CO$_3$	100	19
10		2.5	PhCH$_3$	NaOAc	100	30
11		2.5	PhH	NaOAc	100	21
12		2.5	DMF	NaOAc	100	20
13		2.5	[c]EDC	NaOAc	100	25
14		2.5		NaOAc	80	62
15	Rh/Al$_2$O$_3$	2.5		NaOAc	100	11
16	[RhCOCl$_2$]$_2$	2.5		NaOAc	100	30
17	Pd(OAc)$_2$	2.5		NaOAc	100	31
18	no catalyst			NaOAc	100	

[a]Phenyl acetate (1 mmol), methyl acrylate (1.2 mmol), 98% HCO$_2$H (1 mL, 26 mmol), additive (1.5 mmol), 4 Å molecular sieves, 12 h. [b]Isolated yield of **3a** after chromatographic purification. [c]1,2-Dichloroethane.

However, conducting the reaction in the presence of NaOAc (1.5 equiv) as a base moderately increased the yield of **3a** (50%), which could be gradually improved to 71% by increasing the temperature from 80 to 100 °C. Screening of other bases was attempted and found to be less effective to promote *ortho* C−H bond activation (entries 7−9), so also with other catalysts (entries 15−17). Interestingly, by lowering the catalyst loading to 2.5 mol %, the product yield (71%) was not affected, although further lowering to 1 mol % led to a significant reduction in the yield of the product (41%). Thus, the proper choice of catalyst and base is critical in order to realize high yields of **3a**. Also, by lowering the concentration of

HCO$_2$H (5 mmol), a decrease in yield of **3a** was observed. Use of other solvents such as toluene, benzene, 1,2-dichloroethane, or DMF was found to be less suitable for the reaction (only 20−30% yield). Control experiment has, however, proven that, in the absence of catalyst, no reaction took place. Also, with use of AcOH or TFA as reaction medium instead of HCO$_2$H, only deprotection of phenyl acetate took place, forming phenol exclusively, thus proving that HCO$_2$H acts as a better reducing agent in addition to being used as solvent.

We have then applied the optimized procedure of the Rh-catalyzed annulation process to a variety of phenolic acetates (**1b−r**) to determine the scope of the process, and the results

Table 2. Substrate Scope for Rh-Catalyzed Annulation[a,b]
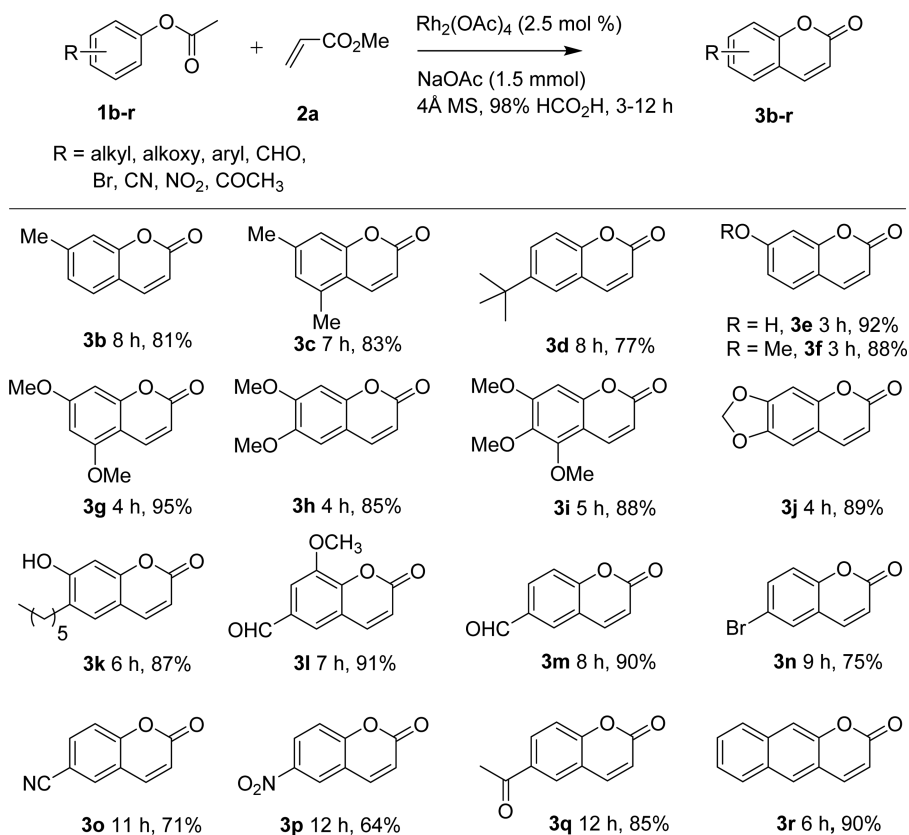
^{a}Phenolic acetates (1 mmol), methyl acrylate (1.5 mmol), Rh$_2$(OAc)$_4$ (2.5 mol %), NaOAc (1.5 mmol), 4 Å molecular sieves, 98% HCO$_2$H (1 mL), 100 °C, 3−12 h. ^{b}Isolated yield after column purification.

Table 3. Olefin Variation in the Annulation Process[a,b]
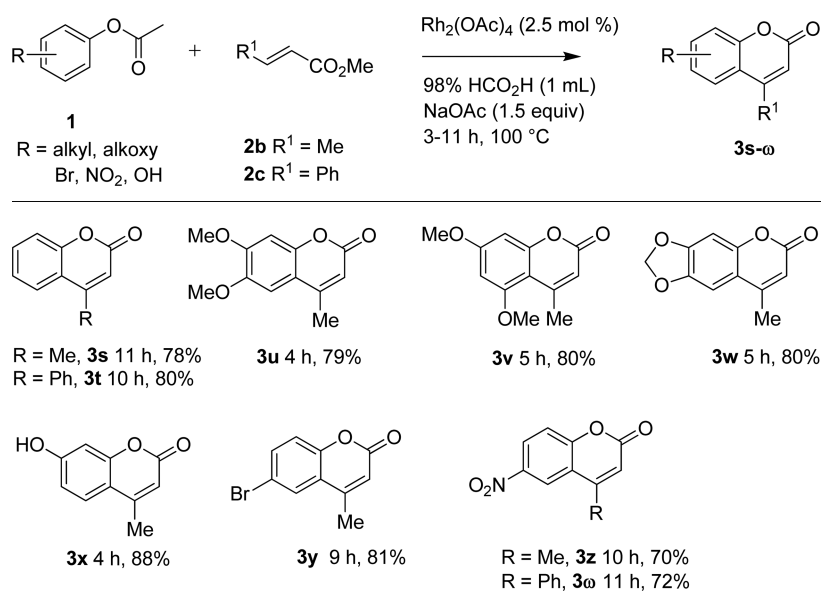
^{a}For reaction conditions, refer to the footnote of Table 1, and methyl crotonate or cinnamate (1.2 mmol) was used. ^{b}Isolated yield after column chromatographic purification.

are presented in Table 2. Thus, several phenolic acetates with electron-donating and electron-withdrawing groups underwent this annulation process successfully and produced the corresponding coumarin derivatives (**3b−r**) in excellent yields. Remarkably, substrates having −CHO, −Br, −CN, −NO$_2$, and −COCH$_3$ groups (**3l−q**) were well-tolerated under the reaction conditions. In the case of unsymmetrical phenolic acetates, complete regiocontrolled products were obtained as C−H activation has occurred at the less sterically hindered position exclusively (**3b, 3e−f, 3h, 3j−k**). 2-Naphthyl acetate was also annulated regiospecifically with methyl acrylate to afford the corresponding coumarin **3r** in 90% yield.

Scheme 2. Control Experiments To Probe Mechanism
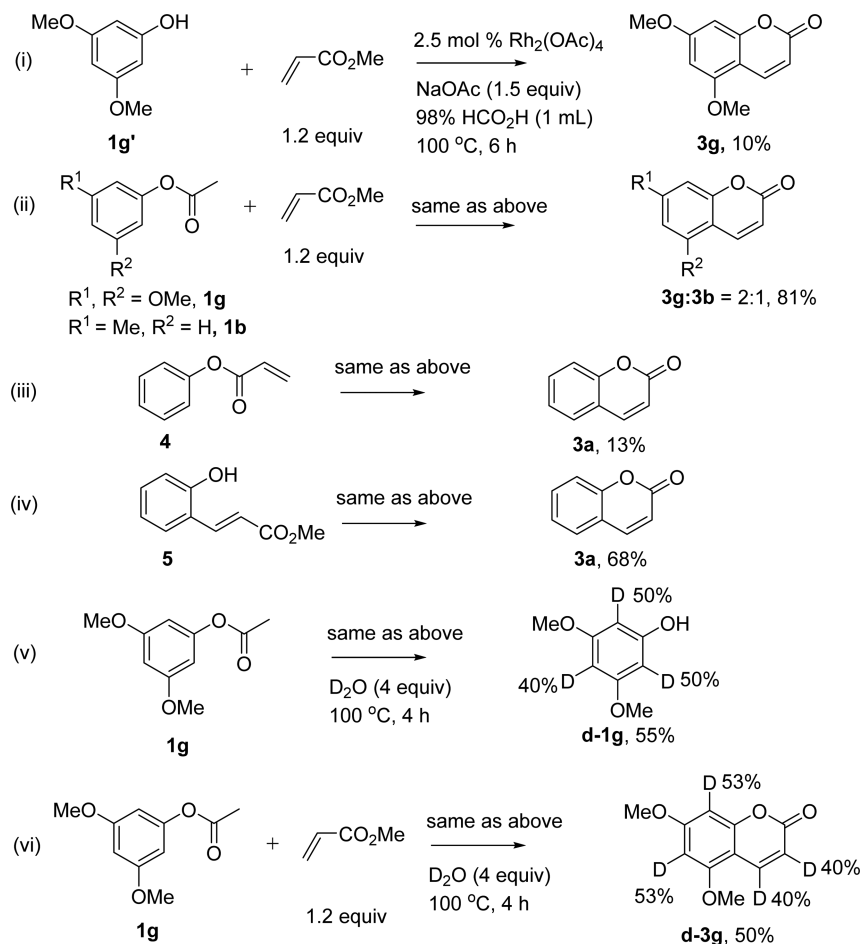
Next, we turned our attention to examine the substituent's effect on acrylates, and the results are given in Table 3. As can be seen, sterically hindered acrylate **2c** (R^2 = Ph) showed comparable activity for the annulation process as that of acrylate **2b** (R^2 = Me). Here again, substrates with electron-donating and electron-withdrawing groups have reacted smoothly with β-substituted acrylates to afford coumarin derivatives **3s−ω** in excellent yields.

Scheme 2 shows results of several control experiments that were carried out in order to obtain some insights into the mechanistic course of the reaction: (i) When 3,5-dimethoxyphenol **1g′** was subjected to oxidative coupling with methyl acrylate under the reaction conditions, only 10% of the desired product **3g** was obtained, indicating that directing acetate group is required for forming rhodacycle **II**. (ii) Competitive experiments (**1g** and **1b**) have shown that electron-rich phenolic acetates have generally reacted faster for the annulation process *via* C−H bond activation, giving **3g:3b** (2:1) in 81% combined yield. (iii−iv) We have conducted the following two experiments to establish whether this reaction proceeds by alkenylation or esterification. Thus, when phenyl acrylate (**4**) or (*E*)-methyl(2-hydroxy phenyl acrylate (**5**) is reacted under the same reaction conditions (Rh/HCO₂H/NaOAc), product **3a** was isolated in 13% and 68% yields, respectively; indicating that the reaction undergoes alkenylation first *via* C−H activation, followed by lactonization. (v) When **1g** was reacted with D₂O in the *absence of methyl acrylate* under the same reaction conditions, product **d-1g** was isolated in 55%

yield, in which 40% of deuterium was incorporated at the C-4 and 50% each at C-2 and C-6 positions of **d-1g**. (vi) When **1g** was reacted with methyl acrylate in the presence D₂O under the reaction conditions, product **d-3g** was isolated in 50% yield, in which 40% of deuterium was incorporated at the C-3 and C-4 positions of the coumarin derivative, along with 53% deuterium incorporation each at C-6 and C-8 of **d-3g**. This result clearly supports that the *ortho* C−H bond cleavage in phenolic acetate occurs in a reversible manner.[12]

A probable catalytic cycle based on the control experiments for the formation of coumarin derivatives **3a−ω** is shown in Scheme 3. Coordination of the carbonyl group of phenyl acetate to Rh species **I**, obtained from [Rh₂(OAc)₄] on reduction with formic acid, followed by *ortho*-metalation, provides a 6-membered rhodacycle intermediate **II**. Coordinative regioselective insertion of alkene ester **2** into the Rh−C bond of intermediate **II** gives the intermediate **III**, followed by the β-hydride elimination, releasing the alkenated product **IV** *in situ*. Acetate deprotection under acidic condition, followed by intramolecular cyclization, produced coumarins **3**. Finally, Rh(L)H species on reduction with formic acid liberates reactive Rh(I) species for the next catalytic cycle.

In conclusion, we have disclosed a simple annulation strategy that affords a variety of substituted coumarin derivatives **3a−ω** in excellent yields from the corresponding phenolic acetates and acrylates *via* rhodium-catalyzed C−H bond activation in a single step. This protocol is quite useful in the case of phenolic substrates with electron-deficient groups and is complementary

Scheme 3. Proposed Catalytic Cycle for Coumarin Derivatives 3
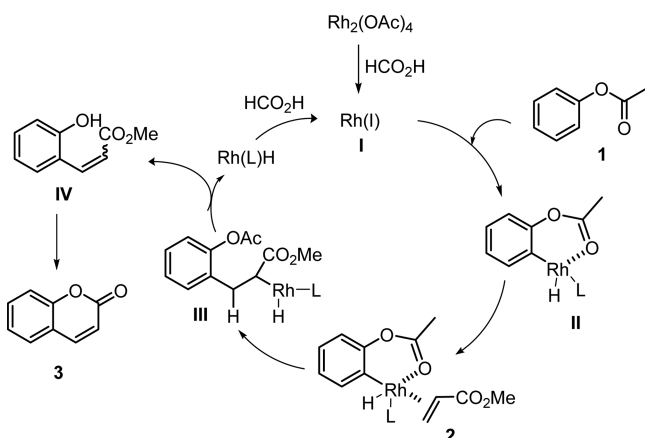
to the reported methods generally applicable for electron-donating substrates only, thus providing for the diversity-oriented synthesis of bioactive coumarin derivatives in high yields. This cyclization strategy proceeds through a rhodacycle as the intermediate formed by the *ortho* C−H bond activation of phenolic acetates and is well supported by deuterium incorporation studies. We believe that this method may find applications in the synthesis of various bioactive coumarin derivatives as it is convenient to carry out under mild conditions, displaying a wide range of substrate scope.

■ EXPERIMENTAL SECTION

Solvents were distilled and dried by standard procedures before use; petroleum ether with a boiling range of 60−80 °C was used. Melting points were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on 200, 400, and 500 MHz NMR spectrometers. Infrared spectra were recorded on an FTIR system, and absorption is expressed in cm^{-1}. HRMS data for new compounds were recorded using an Orbitrap mass analyzer associated with an Accela 1250 pump. Rhodium diacetate was purchased from Sigma-Aldrich. Purification was done using column chromatography (230−400 mesh).

General Experimental Procedure for the Synthesis of Phenolic Acetates. Phenolic acetates (**1a**−**r**) were readily prepared from the corresponding phenols as follows: Phenols (1 mmol) were dissolved in 5 mL of dry pyridine, and the resulting mixture was cooled to 0 °C. Acetic anhydride (1.5 mmol) was added dropwise to it. The reaction mixture was allowed to rise to room temperature and stirred for 0.5−1 h. Then, pyridine was removed under high *vacuo*, and the remaining reaction mass dissolved in ethyl acetate. The organic layer was washed with water/aq HCl/water, dried over anhydrous Na$_2$SO$_4$, and concentrated to give the pure phenolic acetates (**1a**−**r**), which were used further for studies without purification.

General Experimental Procedure for the Preparation of Coumarin Derivatives (3a−ω). To a mixture of substituted phenolic acetates (**1a**−**r**) (1 mmol), Rh$_2$(OAc)$_4$ (2.5 mol %), commercially available 98% formic acid (1 mL), NaOAc (1.5 mmol), and 4 Å MS under a nitrogen atmosphere was added methyl acrylate **2a** or methyl crotonate **2b** or cinnamate **2c** (1.2 mmol) as the case may be. The resulting brown solution was stirred at 100 °C for 3−12 h. After completion of reaction (monitored by TLC), it was diluted with ethyl acetate (10 mL), and washed with water (10 mL), 5% aqueous sodium bicarbonate (15 mL), and brine (10 mL). The organic layer was dried over anhydrousNa$_2$SO$_4$ and concentrated in *vacuo* to give brown solids. On purification with flash chromatography using pet ether and ethyl acetate (7:3), coumarin derivatives (**3a**−**ω**) were obtained as solids.

2H-Chromen-2-one (3a). Yield: 71%; 0.110 g; colorless solid, **mp**: 71 °C (lit.[7] mp 70−72 °C); **IR** (CHCl$_3$, cm^{-1}): v_{max} 3060, 2958, 1715,

1605, 1453, 1106; ^{1}**H NMR** (200 MHz, CDCl$_3$): δ 7.70 (d, *J* = 9.6 Hz, 1H), 7.45−7.60 (m, 2H), 7.24−7.39 (m, 2H), 6.42 (d, *J* = 9.5 Hz, 1H); ^{13}**C NMR** (50 MHz, CDCl$_3$): δ 160.4, 154.2, 143.2, 131.8, 127.8, 124.4, 118.9, 117.0, 116.9; **HRMS** (ESI): calc. for [(C$_9$H$_6$O$_2$)H] (M + H) 147.0446, found 147.0440.

7-Methyl-2H-chromen-2-one (3b). Yield: 81%; 0.120 g; colorless solid, **mp**: 165−167 °C; **IR** (CHCl$_3$, cm^{-1}): v_{max} 3079, 2930, 1716, 1620, 1573, 1530; ^{1}**H NMR** (200 MHz, CDCl$_3$): δ 7.67 (d, *J* = 9.5 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.06−7.14 (m, 2H), 6.35 (d, *J* = 9.5 Hz, 1H), 2.45 (s, 3H); ^{13}**C NMR** (50 MHz, CDCl$_3$): δ 161.1, 154.1, 143.4, 143.1, 127.5, 125.6, 117.0, 116.4, 115.4, 21.8; **HRMS** (ESI): calc. for [(C$_{10}$H$_8$O$_2$)H] (M + H) 161.0603, found 161.0605.

5,7-Dimethyl-2H-chromen-2-one (3c). Yield: 83%; 0.118 g; colorless solid, **mp**: 104−105 °C; **IR** (CHCl$_3$, cm^{-1}): v_{max} 1710, 1623, 1437; ^{1}**H NMR** (200 MHz, CDCl$_3$): δ 7.87 (d, *J* = 9.8 Hz, 1H), 6.97 (s, 1H), 6.93 (s, 1H), 6.35 (d, *J* = 9.8 Hz, 1H), 2.48 (s, 3H), 2.40 (s, 3H); ^{13}**C NMR** (50 MHz, CDCl$_3$): δ 161.1, 154.7, 142.7, 140.4, 135.6, 126.9, 115.3, 115.0, 114.6, 21.6, 18.1; **HRMS** (ESI): calc. for [(C$_{11}$H$_{10}$O$_2$)H] (M + H) 175.0759, found 175.0765.

6-(tert-Butyl)-4-phenyl-2H-chromen-2-one (3d). Yield: 77%; 0.081 g; liquid; **IR** (CHCl$_3$, cm^{-1}): v_{max} 2936, 1728, 1610, 1556, 1507, 1282; ^{1}**H NMR** (200 MHz, CDCl$_3$): δ 7.71 (d, *J* = 9.5 Hz, 1H), 7.58 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.45 (d, *J* = 2.2 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 6.41 (d, *J* = 9.5 Hz, 1H), 1.36 (s, 9H); ^{13}**C NMR** (50 MHz, CDCl$_3$): δ 161.1, 152.0, 147.5, 143.9, 129.5, 124.1, 118.2, 116.4, 116.4, 31.3; **HRMS** (ESI): calc. for [(C$_{13}$H$_{14}$O$_2$)H] (M + H) 203.1072, found 203.1077.

7-Hydroxy-2H-chromen-2-one (3e). Yield: 92%; 0.120 g; colorless solid, **mp**: 235 °C (lit.[8g] mp 234−237 °C); **IR** (CHCl$_3$, cm^{-1}): v_{max} 3220, 1705, 1670, 1380, 1237, 1077, 986, 570; ^{1}**H NMR** (200 MHz, CDCl$_3$): δ 7.86 (d, *J* = 9.8 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 1H), 6.83 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.75 (s, 1H), 6.16 (d, *J* = 9.5 Hz, 1H); ^{13}**C NMR** (50 MHz, CDCl$_3$): δ 162.3, 161.2, 157.1, 144.8, 130.5, 113.9, 112.9, 112.8, 103.4; **HRMS** (ESI): calc. for [(C$_9$H$_6$O$_3$)H] (M + H) 163.0395, found 163.0398.

7-Methoxy-2H-chromen-2-one (3f). Yield: 88%; 0.124 g; colorless solid, **mp**: 122−123 °C; **IR** (CHCl$_3$, cm^{-1}): v_{max} 2936, 1728, 1610, 1556, 1507, 1282; ^{1}**H NMR** (200 MHz, CDCl$_3$): δ 7.62 (d, *J* = 9.3 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 6.78−6.87 (m, 2H), 6.24 (d, *J* = 9.5 Hz, 1H), 3.88 (s, 3H); ^{13}**C NMR** (50 MHz, CDCl$_3$): δ 162.8, 160.8, 156.0, 143.1, 128.6, 113.2, 112.6, 112.5, 100.8, 55.6; **HRMS** (ESI): calc. for [(C$_{10}$H$_8$O$_3$)H] (M + H) 177.0552, found 177.0558.

5,7-Dimethoxy-2H-chromen-2-one (3g). Yield: 95%; 0.127 g; colorless solid, **mp**: 148−150 °C (lit.[8g] mp 147−148 °C); **IR** (CHCl$_3$, cm^{-1}): v_{max} 2936, 1725, 1615, 1552, 1509, 1382, 1130; ^{1}**H NMR** (200 MHz, CDCl$_3$): δ 7.95 (d, *J* = 9.6 Hz, 1H), 6.41 (d, *J* = 2.2 Hz, 1H), 6.26 (d, *J* = 2.2 Hz, 1H), 6.15 (d, *J* = 9.7 Hz, 1H), 3.86 (s, 3 H), 3.90 (s, 3H); ^{13}**C NMR** (50 MHz, CDCl$_3$): δ 163.7, 161.2, 156.9, 138.5, 111.1, 104.0, 94.8, 92.8, 55.9, 55.7; **HRMS** (ESI): calc. for [(C$_{11}$H$_{10}$O$_4$)H] (M + H) 207.0657, found 207.0654.

6,7-Dimethoxy-2H-chromen-2-one (3h). Yield: 85%; 0.113 g; colorless solid, **mp**: 140−142 °C; **IR** (CHCl$_3$, cm^{-1}): v_{max} 2970, 1725, 1615, 1552, 1509; ^{1}**H NMR** (200 MHz, CDCl$_3$): δ 7.60 (d, *J* = 9.5 Hz, 1H), 6.84 (s, 2H), 6.28 (d, *J* = 9.5 Hz, 1H), 3.92 (s, 3H), 3.95 (s, 3H); ^{13}**C NMR** (50 MHz, CDCl$_3$): δ 161.0, 152.8, 150.1, 146.3, 143.0, 108.0, 100.0, 56.2; **HRMS** (ESI): calc. for [(C$_{11}$H$_{10}$O$_4$)H] (M + H) 207.0657, found 207.0659.

5,6,7-Trimethoxy-2H-chromen-2-one (3i). Yield: 88%; 0.113 g; colorless solid, **mp**: 147−149 °C; **IR** (CHCl$_3$, cm^{-1}): v_{max} 2933, 1722, 1617, 1558, 1509, 1382, 1130; ^{1}**H NMR** (200 MHz, CDCl$_3$): δ 7.91 (d, *J* = 9.5 Hz, 1H), 6.60 (s, 1H), 6.22 (d, *J* = 9.5 Hz, 1H), 4.03 (s, 3H), 3.93 (s, 3H), 3.85 (s, 3H); ^{13}**C NMR** (50 MHz, CDCl$_3$): δ 160.9, 157.1, 151.5, 149.2, 138.6, 138.0, 112.5, 107.1, 95.4, 61.7, 61.1, 56.2; **HRMS** (ESI): calc. for [(C$_{12}$H$_{12}$O$_5$)H] (M + H) 237.0763, found 237.0757.

6H-[1,3]Dioxolo[4,5-g]chromen-6-one (3j). Yield: 89%; 0.122 g; colorless solid, **mp**: 218−220 °C (lit.[8g] mp 223 °C); **IR** (CHCl$_3$, cm^{-1}): v_{max} 3087, 1721, 1640, 1500, 1455, 1146, 1130; ^{1}**H NMR** (200 MHz, CDCl$_3$): δ 7.57 (d, *J* = 9.1 Hz, 1H), 6.82 (s, 2H), 6.27 (d, *J* = 9.3 Hz, 1H), 6.07 (s, 2H); ^{13}**C NMR** (50 MHz, CDCl$_3$): δ 161.0, 151.3,

144.9, 143.3, 113.5, 112.7, 105.0, 102.3, 98.5; **HRMS** (ESI): calc. for [(C$_{10}$H$_6$O$_4$)H] (M + H) 191.0344, found 191.0349.

6-Hexanoyl-7-hydroxy-2H-chromen-2-one (3k). **Yield**: 87%; 0.110 g; colorless solid, **mp**: 202−203 °C; **IR** (CHCl$_3$, cm^{-1}): v_{max} 3220, 1710, 1670, 1380, 1224, 1056, 967, 580; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 7.66 (d, J = 9.4 Hz, 1H), 7.17 (s, 1H), 7.18 (s, 1H), 6.22 (d, J = 9.5 Hz, 1H), 2.64 (d, J = 7.3 Hz, 2H), 1.51−1.72 (m, 2H), 1.27−1.42 (m, 6H), 0.81−0.95 (m, 3H); **^{13}C NMR** (50 MHz, CDCl$_3$): δ 163.2, 159.3, 153.9, 144.8, 128.4, 128.1, 111.8, 111.4, 102.8, 31.8, 29.7, 29.5, 29.2, 22.7, 14.2; **HRMS** (ESI): calc. for [(C$_{15}$H$_{18}$O$_3$)H] (M + H) 247.1334, found 247.1331.

8-Methoxy-2-oxo-2H-chromene-6-carbaldehyde (3l). **Yield**: 91%; 0.122 g; colorless solid, **mp**: 182−183 °C; **IR** (CHCl$_3$, cm^{-1}): v_{max} 3085, 1729, 1717, 1615, 1506, 1440, 1136, 1125; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 9.99 (s, 1H), 7.79 (d, J = 9.5 Hz, 1H), 7.60 (d, J = 3.1 Hz, 2H), 6.54 (d, J = 9.5 Hz, 1H), 4.04 (s, 4H); **^{13}C NMR** (50 MHz, CDCl$_3$): δ 190.1, 159.0, 148.3, 147.9, 142.9, 132.8, 123.5, 119.3, 118.0, 111.1, 56.4; **HRMS** (ESI): calc. for [(C$_{11}$H$_8$O$_4$)H] (M + H) 205.0501, found 205.0505.

2-Oxo-2H-chromene-6-carbaldehyde (3m). **Yield**: 90%; 0.128 g; colorless solid, **mp**: 192−194 °C; **IR** (CHCl$_3$, cm^{-1}): v_{max} 3085, 1727, 1714, 1630; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 10.05 (s, 1H), 7.99−8.16 (m, 2H), 7.81 (d, J = 9.6 Hz, 1H), 7.49 (d, J = 8.8 Hz, 1H), 6.54 (d, J = 9.6 Hz, 1H); **^{13}C NMR** (50 MHz, CDCl$_3$): δ 190.0, 159.5, 157.7, 142.8, 132.8, 132.4, 130.0, 119.1, 117.9, 117.9; **HRMS** (ESI): calc. for [(C$_{10}$H$_6$O$_3$)H] (M + H) 175.0395, found 175.0390.

6-Bromo-2H-chromen-2-one (3n). **Yield**: 75%; 0.078 g; colorless solid, **mp**: 156−158 °C (lit.[7g] mp 156−159 °C); **IR** (CHCl$_3$, cm^{-1}): v_{max} 3085, 1727, 1615, 1556, 1470, 1126, 1130; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 7.51−7.77 (m, 4H), 7.22 (d, J = 9.4 Hz, 1H), 6.45 (d, J = 9.6 Hz, 1H); **^{13}C NMR** (50 MHz, CDCl$_3$): δ 159.5, 153.0, 141.9, 134.6, 130.1, 120.3, 118.7, 118.0, 117.0; **HRMS** (ESI): calc. for [(C$_9$H$_5$BrO$_2$)H] (M + H) 224.9551, found 224.9555.

2-Oxo-2H-chromene-6-carbonitrile (3o). **Yield**: 71%; 0.075 g; colorless solid, **mp**: 150−152 °C; **IR** (CHCl$_3$, cm^{-1}): v_{max} 3096, 2990, 2219, 1727; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 7.76−7.88 (m, 2H), 7.72 (d, J = 9.6 Hz, 1H), 7.44 (d, J = 8.5 Hz, 1H), 6.56 (d, J = 9.6 Hz, 1H); **^{13}C NMR** (50 MHz, CDCl$_3$): δ 158.9, 156.3, 141.8, 134.7, 132.3, 119.4, 118.7, 118.3, 117.4, 108.6; **HRMS** (ESI): calc. for [(C$_{10}$H$_5$NO$_2$)H] (M + H) 172.0399, found 172.0398.

6-Nitro-2H-chromen-2-one (3p). **Yield**: 64%; 0.088 g; colorless solid, **mp**: 181−183 °C (lit.[7] 180−182 °C); **IR** (CHCl$_3$, cm^{-1}): v_{max} 3070, 1735, 1610, 1518, 1340; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 8.45 (d, J = 2.4 Hz, 1H), 8.41 (dd, J = 9.2, 2.8 Hz, 1H), 7.82 (d, J = 9.8 Hz, 1H), 7.48 (d, J = 9.2 Hz, 1H), 6.60 (d, J = 9.8 Hz, 1H); **^{13}C NMR** (50 MHz, CDCl$_3$): δ 158.8, 157.5, 144.0, 142.2, 126.6, 123.7, 118.8, 118.1; **HRMS** (ESI): calc. for [(C$_9$H$_5$NO$_4$)H] (M + H) 192.0297, found 192.0295.

6-Acetyl-4-phenyl-2H-chromen-2-one (3q). **Yield**: 85%; 0.089 g; colorless solid, **mp**: 122−123 °C; **IR** (CHCl$_3$, cm^{-1}): v_{max} 3070, 1730, 17122, 1610, 1515, 1344; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 8.11−8.24 (m, 2H), 7.79 (d, J = 9.5 Hz, 1H), 7.41 (d, J = 9.3 Hz, 1H), 6.51 (d, J = 9.5 Hz, 1H), 2.66 (s, 3H); **^{13}C NMR** (50 MHz, CDCl$_3$): δ 196.0, 159.8, 156.9, 143.2, 133.5, 131.7, 128.6, 118.6, 117.6, 117.3, 26.6; **HRMS** (ESI): calc. for [(C$_{11}$H$_8$O$_3$)H] (M + H) 189.0552, found 189.0558.

2H-Benzo[g]chromen-2-one (3r). **Yield**: 90%; 0.122 g; colorless solid, **mp**: 119−121 °C; **IR** (CHCl$_3$, cm^{-1}): v_{max} 3077, 2929, 1717, 1630, 1563, 1514, 1175; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 8.48 (d, J = 9.6 Hz, 1H), 8.22 (d, J = 8.2 Hz, 1H), 7.98 (d, J = 9.2 Hz, 1H), 7.91 (d, J = 8.2 Hz, 1H), 7.68 (td, J = 7.7, 1.1 Hz, 1H), 7.53−7.61 (m, 1H), 7.47 (d, J = 9.2 Hz, 1H), 6.57 (d, J = 10.1 Hz, 1H); **^{13}C NMR** (50 MHz, CDCl$_3$): δ 160.7, 154.0, 139.0, 133.1, 130.4, 129.1, 128.3, 126.1, 121.4, 117.2, 115.8, 113.0; **HRMS** (ESI): calc. for [(C$_{13}$H$_8$O$_2$)H] (M + H) 197.0603, found 197.0609.

4-Methyl-2H-chromen-2-one (3s). **Yield**: 78%; 0.132 g; colorless solid, **mp**: 83 °C (lit.[5b] mp 83−84 °C); **IR** (CHCl$_3$, cm^{-1}): v_{max} 3075, 2988, 1725, 1605, 1453; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 7.45−7.65 (m, 2H), 7.26−7.39 (m, 2H), 6.29 (d, J = 1.1 Hz, 1H), 2.46 (d, J = 1.3 Hz, 3H); **^{13}C NMR** (50 MHz, CDCl$_3$): δ 160.4, 153.7, 151.9, 131.7,

124.5, 124.1, 120.0, 117.2, 115.4, 18.7; **HRMS** (ESI): calc. for [(C$_{10}$H$_8$O$_2$)H] (M + H) 161.0603, found 161.0610.

4-Phenyl-2H-chromen-2-one (3t). **Yield**: 80%; 0.188 g; viscous liquid; **IR** (CHCl$_3$, cm^{-1}): v_{max} 3050, 2930, 1715, 1675, 1353; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 7.49−7.60 (m, 5H), 7.15−7.32 (m, 2H), 6.78−6.97 (m, 2H), 6.38 (s, 1H); **^{13}C NMR** (50 MHz, CDCl$_3$): δ 160.6, 155.6, 154.3, 135.3, 131.9, 129.7, 129.6, 128.9, 128.5, 127.0, 124.2, 120.5, 119.1, 117.4, 115.3; **HRMS** (ESI): calc. for [(C$_{15}$H$_{10}$O$_2$)H] (M + H) 223.0759, found 223.0760.

6,7-Dimethoxy-4-methyl-2H-chromen-2-one (3u). **Yield**: 79%; 0.088 g; colorless solid, **mp**: 128−129 °C; **IR** (CHCl$_3$, cm^{-1}): v_{max} 3060, 2958, 1715, 1605, 1453, 1106, 1018, 956; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 6.92 (s, 1H), 6.82 (s, 1H), 6.15 (s, 1H), 3.93 (s, 3H), 3.94 (s, 3H), 2.41 (s, 3H); **^{13}C NMR** (50 MHz, CDCl$_3$): δ 161.2, 152.7, 152.1, 149.4, 146.1, 112.4, 112.3, 105.1, 100.0, 56.3, 56.2, 18.8; **HRMS** (ESI): calc. for [(C$_{12}$H$_{12}$O$_4$)H] (M + H) 221.0814, found 221.0810.

5,7-Dimethoxy-4-methyl-2H-chromen-2-one (3v). **Yield**: 80%; 0.114 g; colorless solid, **mp**: 171−173 °C (lit.[8h] mp 174 °C); **IR** (CHCl$_3$, cm^{-1}): v_{max} 3110, 2999, 1722, 1625, 1453, 1230, 1051, 986; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 6.41 (d, J = 2.3 Hz, 1H), 6.26 (d, J = 2.3 Hz, 1H), 5.88−5.99 (m, 1H), 3.85 (s, 3H), 3.86 (s, 3H), 2.52 (s, 3H); **^{13}C NMR** (50 MHz, CDCl$_3$): δ 162.8, 160.8, 159.1, 157.1, 154.2, 111.5, 104.9, 95.5, 93.4, 55.7, 55.6, 24.2; **HRMS** (ESI): calc. for [(C$_{12}$H$_{12}$O$_4$)H] (M + H) 221.0814, found 221.0810.

8-Methyl-6H-[1,3]dioxolo[4,5-g]chromen-6-one (3w). **Yield**: 80%; 0.118 g; colorless solid, **mp**: 120−121 °C; **IR** (CHCl$_3$, cm^{-1}): v_{max} 3033, 2984, 1711, 1605, 1453; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 6.93 (s, 1H), 6.81 (s, 1H), 6.15 (s, 1H), 6.07 (s, 2H), 2.37 (s, 3H); **^{13}C NMR** (50 MHz, CDCl$_3$): δ 161.0, 152.2, 151.0, 150.7, 144.9, 113.8, 112.4, 102.3, 102.1, 98.5, 19.2; **HRMS** (ESI): calc. for [(C$_{11}$H$_8$O$_4$)H] (M + H) 205.0501, found 205.0505.

7-Hydroxy-4-methyl-2H-chromen-2-one (3x). **Yield**: 88%; 0.140 g; colorless solid, **mp**: 183−186 °C; **IR** (CHCl$_3$, cm^{-1}): v_{max} 3165, 1675, 1383, 1237, 1067, 985, 856, 758, 572, 525, 426; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 9.63 (s, 1H), 7.59 (d, J = 8.9 Hz, 1H), 6.85 (dd, J = 8.7, 2.3 Hz, 1H), 6.73 (d, J = 2.4 Hz, 1H), 6.07 (s, 1H), 2.38- 2.42 (m, 3H); **^{13}C NMR** (50 MHz, CDCl$_3$): δ 162.0, 161.2, 156.3, 154.0, 127.3, 113.6, 111.8, 103.3, 18.6; **HRMS** (ESI): calc. for [(C$_{10}$H$_8$O$_3$)H] (M + H) 177.0552, found 177.0555.

6-Bromo-4-methyl-2H-chromen-2-one (3y). **Yield**: 81%; 0.112 g; colorless solid, **mp**: 186−187 °C (lit.[7] 187−189 °C); **IR** (CHCl$_3$, cm^{-1}): v_{max} 3092, 2929, 1748, 1590, 1550, 1479, 1413, 1385, 1257; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 7.72 (d, J = 1.7 Hz, 1H), 7.62 (dd, J = 8.7, 1.8 Hz, 1H), 7.22 (d, J = 8.8 Hz, 1H), 6.33 (s, 1H), 2.43 (s, 3H); **^{13}C NMR** (50 MHz, CDCl$_3$): δ 160.0, 152.3, 151.2, 134.5, 127.2, 121.5, 118.7, 116.9, 116.0, 18.6; **HRMS** (ESI): calc. For [(C$_{10}$H$_7$BrO$_2$)H] (M + H) 238.9708, found 238.9710.

4-Methyl-6-nitro-2H-chromen-2-one (3z). **Yield**: 70%; 0.103 g; colorless solid, **mp**: 183−185 °C; **IR** (CHCl$_3$, cm^{-1}): v_{max} 3077, 1736, 1610, 1518, 1344; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 8.54 (d, J = 2.7 Hz, 1H), 8.42 (dd, J = 9.1, 2.7 Hz, 1H), 7.48 (d, J = 9.1 Hz, 1H), 6.46 (s, 1H), 2.55 (s, 3H); **^{13}C NMR** (200 MHz, CDCl$_3$): δ 158.9, 157.1, 151.3, 150.0, 126.6, 120.8, 120.3, 118.2, 116.9, 29.7, 18.7; **HRMS** (ESI): calc. For [(C$_{10}$H$_7$NO$_4$)H] (M + H) 206.0453, found 206.0458.

6-Nitro-4-phenyl-2H-chromen-2-one (3ω). **Yield**: 72%; 0.138 g; colorless solid, **mp**: 209−210 °C; **IR** (CHCl$_3$, cm^{-1}): v_{max} 3077, 1730, 1616, 1555, 1240; **^{1}H NMR** (200 MHz, CDCl$_3$): δ 8.41−8.46 (m, 2H), 7.59−7.64 (m, 3H), 7.55 (d, J = 9.8 Hz, 1H), 7.48 (dd, J = 6.6, 2.9 Hz, 2H), 6.53 (s, 1H); **^{13}C NMR** (50 MHz, CDCl$_3$): δ 159.0, 157.7, 154.7, 144.0, 133.8, 130.5, 129.4, 128.2, 126.7, 123.1, 119.3, 118.5, 116.7; **HRMS** (ESI): calc. for [(C$_{15}$H$_9$NO$_4$)H] (M + H) 268.0610, found 268.0615.

(E)-Methyl 3-(2-Hydroxyphenyl)acrylate (5). Compound **5** was synthesized according to the literature.[8h] The characterization data were as follows: **^{1}H NMR** (200 MHz, CDCl$_3$): δ 7.98 (d, J = 16.2 Hz, 1H), 7.48 (dd, J = 1.6, 7.7 Hz, 1H), 7.38−7.27 (m, 1H), 7.08−6.95 (m, 1H), 6.81 (dd, J = 0.9, 8.1 Hz, 1H), 6.58 (d, J = 16.2 Hz, 1H), 3.82 (s, 3H).

■ ASSOCIATED CONTENT

⑤ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01713.

> Characterization data and ^{1}H and ^{13}C NMR spectra for new compounds (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: a.sudalai@ncl.res.in.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) (a) Marshall, P. G. *J. Physiol.* **1931**, *73*, 215. (b) Gupta, A. K.; Chakraborty, A.; Giri, S.; Subramanian, V.; Chattaraj, P. *Int. J. Chemoinf. Chem. Eng.* **2011**, *1*, 61. (c) Yu, Y.; Nie, Y. *J. Environ. Prot.* **2011**, *2*, 298.

(2) (a) Shilov, A. E.; Shul'pin, G. B. *Chem. Rev.* **1997**, *97*, 2879. (b) Dyker, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1698. (c) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633. (d) Ritleng, V.; Sirlin, C.; Pfeffer, M. *Chem. Rev.* **2002**, *102*, 1731. (e) Kakiuchi, F.; Murai, S. *Acc. Chem. Res.* **2002**, *35*, 826. (f) Miura, M.; Nomura, M. *Top. Curr. Chem.* **2002**, *219*, 211. (g) Kakiuchi, F.; Chatani, N. *Adv. Synth. Catal.* **2003**, *345*, 1077. (h) Ishiyama, T.; Miyaura, N. *J. Organomet. Chem.* **2003**, *680*, 3.

(3) (a) Venugopala, K. N.; Rashmi, V.; Odhav, B. *BioMed Res. Int.* **2013**, *2013*, 963248. (b) Fedorov, A. Y.; Nyuchev, A. V.; Beletskaya, I. P. *Chem. Heterocycl. Compd.* **2012**, *48*, 166. (c) Jerezano, A.; Jimenez, F.; del Carmen Cruz, M.; Montiel, L. E.; Delgado, F.; Tamariz, J. *Helv. Chim. Acta* **2011**, *94*, 185. (d) Riveiro, M. E.; De Kimpe, N.; Moglioni, A.; Vazquez, R.; Monczor, F.; Shayo, C.; Davio, C. *Curr. Med. Chem.* **2010**, *17*, 1325. (e) Kostova, I. *Curr. Med. Chem.: Anti-Cancer Agents* **2005**, *5*, 29. (f) Garazd, M. M.; Garazd, Y. L.; Khilya, V. P. *Chem. Nat. Compd.* **2005**, *41*, 245. (g) Borges, F.; Roleira, F.; Milhazes, N.; Santana, L.; Uriarte, E. *Curr. Med. Chem.* **2005**, *12*, 887. (h) Lacy, A. *Curr. Pharm. Des.* **2004**, *10*, 3797. (i) Fylaktakidou, K. C.; Hadjipavlou-Litina, D. J.; Litinas, K. E.; Nicolaides, D. N. *Curr. Pharm. Des.* **2004**, *10*, 3813. (j) Sardari, S.; Nishibe, S.; Daneshtalab, M. *Stud. Nat. Prod. Chem.* **2000**, *23*, 335. (k) Malikov, V. M.; Saidkhodzhaev, A. I.; Aripov, Kh. N. *Chem. Nat. Compd.* **1998**, *34*, 202. (l) Estevez-Braun, A.; Gonzalez, A. G. *Nat. Prod. Rep.* **1997**, *14*, 465. (m) Hoult, J. R. S.; Paya, M. *Gen. Pharmacol.* **1996**, *27*, 713. (n) Murray, R. D. H. *Nat. Prod. Rep.* **1995**, *12*, 477. (o) Murray, R. D. H. *Prog. Chem. Org. Nat. Prod.* **1991**, *58*, 83. (p) Sethna, S. M.; Shah, N. M. *Chem. Rev.* **1945**, *36*, 1.

(4) (a) Zhao, H.; Donnelly, A. C.; Kusuma, B. R.; Brandt, G. E. L.; Brown, D.; Rajewski, R. A.; Vielhauer, G.; Holzbeierlein, J.; Cohen, M. S.; Blagg, B. S. J. *J. Med. Chem.* **2011**, *54*, 3839. (b) Dayam, R.; Gundla, R.; Al-Mawsawi, L. Q.; Neamati, N. *Med. Res. Rev.* **2008**, *28*, 118. (c) Xie, L.; Takeuchi, Y.; Cosentino, L. M.; Lee, K.-H. *J. Med. Chem.* **1999**, *42*, 2662. (d) Melliou, E.; Magiatis, P.; Mitaku, S.; Skaltsounis, A.-L.; Chinou, E.; Chinou, I. *J. Nat. Prod.* **2005**, *68*, 78. (e) Gosselin, F.; Britton, R. A.; Davies, I. W.; Dolman, S. J.; Gauvreau, D.; Hoerrner, R. S.; Hughes, G.; Janey, J.; Lau, S.; Molinaro, C.; Nadeau, C.; O'Shea, P. D.; Palucki, M.; Sidler, R. *J. Org. Chem.* **2010**, *75*, 4154. (f) Kontogiorgis, C. A.; Hadjipavlou-Litina, D. J. *J. Med. Chem.* **2005**, *48*, 6400. (g) Symeonidis, T.; Chamilos, M.; Hadjipavlou-Litina, D. J.; Kallitsakis, M.; Litinas, K. E. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 1139.

(5) (a) Sheng, R.; Wang, P.; Gao, Y.; Wu, Y.; Liu, W.; Ma, J.; Li, H.; Wu, S. *Org. Lett.* **2008**, *10*, 5015. (b) Koefod, R. S.; Mann, K. R. *Inorg. Chem.* **1989**, *28*, 2285. (c) Xu, X.; Hu, X.; Wang, J. *Beilstein J. Org. Chem.* **2013**, *9*, 254. (d) Zhou, Y.; Liu, K.; Li, J.-Y.; Fang, Y.; Zhao, T.-C.; Yao, C. *Org. Lett.* **2011**, *13*, 1290.

(6) (a) Joule, J. A.; Mills, K. *Heterocyclic Chemistry*, 4th ed.; Blackwell: Oxford, U.K., 2000. (b) Valizadeh, H.; Shockravi, A. *Tetrahedron Lett.* **2005**, *46*, 3501.

(7) (a) Audisio, D.; Messaoudi, S.; Brion, J.-D.; Alami, M. *Eur. J. Org. Chem.* **2010**, *2010*, 1046. (b) Fillion, E.; Dumas, A. M.; Kuropatwa, B. A.; Malhotra, N. R.; Sitler, T. C. *J. Org. Chem.* **2006**, *71*, 409. (c) Reddy, M. S.; Thirupathi, N.; Haribabu, M. *Beilstein J. Org. Chem.* **2013**, *9*, 180.

(8) (a) Valente, S.; Kirsch, G. *Tetrahedron Lett.* **2011**, *52*, 3429. (b) Giguere, D.; Cloutier, P.; Roy, R. *J. Org. Chem.* **2009**, *74*, 8480. (c) Yamamoto, Y.; Kirai, N. *Org. Lett.* **2008**, *10*, 5513. (d) Catellani, M.; Chiusoli, G. P.; Marzolini, G.; Rossi, E. *J. Organomet. Chem.* **1996**, *525*, 65. (e) Sasano, K.; Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2013**, *135*, 10954. (f) Ferguson, J.; Zeng, F.; Alper, H. *Org. Lett.* **2012**, *14*, 5602. (g) Schmidt, B.; Krehl, S. *Chem. Commun.* **2011**, *47*, 5879. (h) Fernandes, T. A.; Vaz, B. G.; Eberlin, M. N.; da Silva, A. J. M.; Costa, P. R. R. *J. Org. Chem.* **2010**, *75*, 7085−7091.

(9) (a) Jia, C.; Piao, D.; Oyamada, J.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Science* **2000**, *287*, 1992. (b) Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1996**, *118*, 6305. (c) Jia, C.; Lu, W.; Oyamada, J.; Kitamura, T.; Matsuda, K.; Irie, M.; Fujiwara, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7252. (d) Trost, B. M.; Toste, F. D.; Greenman, K. *J. Am. Chem. Soc.* **2003**, *125*, 4518. (e) Shi, Z.; He, C. *J. Org. Chem.* **2004**, *69*, 3669. (f) Wegner, H. A.; Ahles, S.; Neuburger, M. *Chem. - Eur. J.* **2008**, *14*, 11310. (g) Cao, J.-L.; Shen, S.-L.; Yang, P.; Qu, J. *Org. Lett.* **2013**, *15*, 3856. (h) Aoki, S.; Oyamada, J.; Kitamura, T. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 468.

(10) (a) Zhang, X.-S.; Li, Z.-W.; Shi, Z.-J. *Org. Chem. Front.* **2014**, *1*, 44. (b) Sharma, U.; Naveen, T.; Maji, A.; Manna, S.; Maiti, D. *Angew. Chem., Int. Ed.* **2013**, *52*, 12669.

(11) Unpublished results.

(12) (a) Kurita, T.; Hattori, K.; Seki, S.; Mizumoto, T.; Aoki, F.; Yamada, Y.; Ikawa, K.; Maegawa, T.; Monguchi, Y.; Sajiki, H. *Chem. - Eur. J.* **2008**, *14*, 664−673. (b) Sawama, Y.; Yabe, Y.; Iwata, H.; Fujiwara, Y.; Monguchi, Y.; Sajiki, H. *Chem. - Eur. J.* **2012**, *18*, 16436−16442. (c) Fujiwara, Y.; Iwata, H.; Sawama, Y.; Monguchi, Y.; Sajiki, H. *Chem. Commun.* **2010**, *46*, 4977−4979.