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Cite this: DOI: 10.1039/c9ob02670c

Rh-Catalyzed aldehydic C–H alkynylation and annulation†

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Received 16th December 2019,
Accepted 23rd January 2020

DOI: 10.1039/c9ob02670c

rsc.li/obc

Novel Rh-catalyzed aldehydic C–H bond alkynylation and annulation for the *in situ* synthesis of chromones and aurones are described. It involves the sequential aldehyde C–H bond alkynylation of salicylaldehyde with *in situ* generated 1-bromoalkyne from 1,1-dibromoalkene followed by annulation. This protocol shows good functional group tolerance including aryl, alkenyl, alkyl and heteroaryl-1,1-dibromoalkenes. The steric/electronic effect was demonstrated during the base-mediated *in situ* cyclization of *o*-hydroxyynones to generate aurones.

Introduction

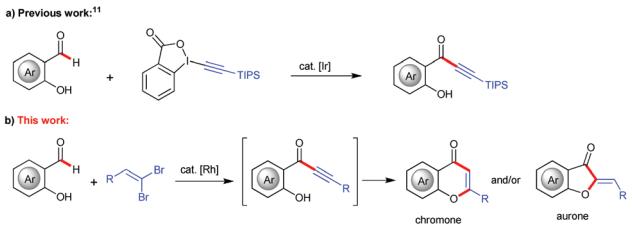
Metal-catalyzed C–H bond functionalizations have attracted much attention in the construction of complex molecular skeletons and scaffolds.[1] Alkynes are ubiquitous functionalities and their synthesis through C–H bond alkynylations is one of the most appealing ways to append alkyne in the synthesis of internal alkynes.[2] The regio-selectivity in C–H bond alkynylations is usually controlled by directing groups[3–5] and these groups also facilitate the C–H bond alkynylations under mild reaction conditions.[5] Of note, the directing groups used in C–H bond functionalizations are highly limited and require an additional removal step as part of the synthetic maneuvering. In particular, utilization of phenolic –OH as a nucleophilic directing group is highly advantageous in the preparation of multifunctional molecular scaffolds.[6] Given this, salicylaldehydes are often used to construct heterocycles[7] by taking advantage of the *o*-hydroxy group in the well-established aldehyde C–H bond functionalization[8] by arylation, olefin hydroacylation, and dehydrogenative coupling reactions.[9,10]

Directed C–H bond alkynylations of aryl C–H bonds are well known in the literature using electrophilic alkynylating reagents.[3,4] However, aldehyde C–H bond alkynylation reactions are limited due to their sensitivity and poor reactivity.[11] For example, Li[11a] and Zhou[11b] independently reported Ir(III)-catalyzed synthesis of *o*-hydroxyynones from salicylaldehydes and a hypervalent iodine-alkynylating reagent (TIPS-EBX) (Scheme 1a). The scope of this approach is limited to alkynylsilanes as part of the EBX reagent. Importantly, the use of haloalkynes as alkynylating reagents is more useful as they can be *in situ* prepared directly from 1,1-dibromoalkenes.[12] Surprisingly this useful approach has not been reported to date (Scheme 1b) and hence we focused our efforts in this direction under Rh-catalyzed conditions in continuation of our earlier studies.[8]

Utilization of 1,1-dichloroalkenes[13] or 1-bromoalkynes[14] in combination with salicylaldehyde was earlier reported in the synthesis of chromones under palladium catalysis. These reactions involve the nucleophilic addition of a phenolic group as a first step either to 1,1-dichloroalkenes[13] or 1-bromoalkynes.[14] This nucleophilic addition is a competitive pathway in our proposed study of directed C–H bond alkynylations of salicylaldehydes using 1,1-dibromoalkenes (Scheme 1b). Hence, it is challenging and requires viable catalytic protocol conditions to overcome the competitive pathways. This is to bring out the desired reactivity of aldehydic C–H bond alkynylation for the *in situ* preparation of *o*-hydroxyynones towards the synthesis of chromones and/or aurones.[15] Herein, we describe the Rh-catalyzed *in situ* aldehydic C–H bond alkynylation and annulation towards the synthesis of chromones and aurones.

Results and discussion

The reaction screening commenced with salicylaldehyde (**1a**) and 1-(2,2-dibromovinyl)-4-methylbenzene (**2a**) as the reaction



Scheme 1 Directed aldehyde C–H bond alkynylation.

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†Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ob02670c

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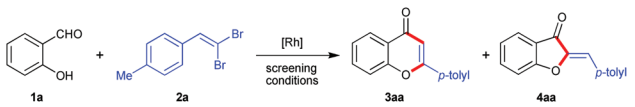
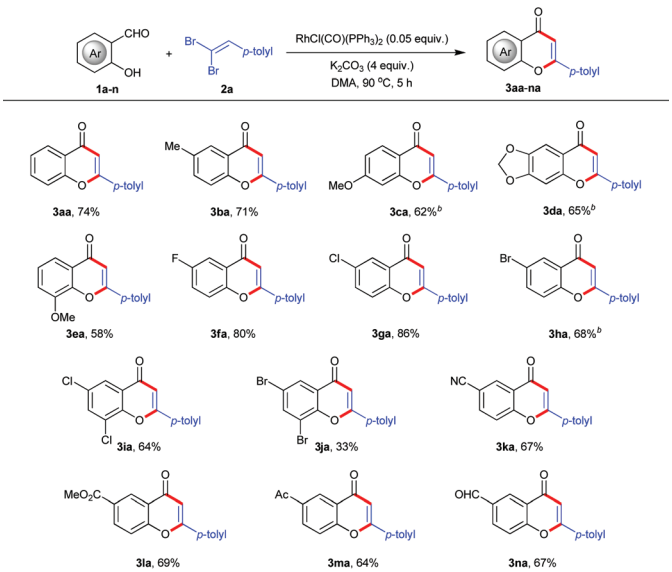
Table 1 Optimization studies[a,b]



Entry	Catalyst	Base (equiv.)	Solvent	Yield[b] **3aa**/**4aa** (%)
1	$RhCl(CO)(PPh_3)_2$	$NaHCO_3$ (3)	DMF	55/13
2	$RhCl(CO)(PPh_3)_2$	Na_2CO_3 (3)	DMF	48/13
3	$RhCl(CO)(PPh_3)_2$	K_3PO_4 (3)	DMF	59/17
4	$RhCl(CO)(PPh_3)_2$	KOAc (3)	DMF	46/18
5	$RhCl(CO)(PPh_3)_2$	Cs_2CO_3 (3)	DMF	24/19
6	$RhCl(CO)(PPh_3)_2$	K_2CO_3 (3)	DMF	63/10
7	$RhCl(CO)(PPh_3)_2$	K_2CO_3 (3)	DMSO	26/15
8	$RhCl(CO)(PPh_3)_2$	K_2CO_3 (3)	NMP	62/12
9	$RhCl(CO)(PPh_3)_2$	K_2CO_3 (3)	DMA	70/10
10	$RhCl(CO)(PPh_3)_2$	K_2CO_3 (3)	Toluene	9/0
11	$RhCl(CO)(PPh_3)_2$	K_2CO_3 (3)	1,4-Dioxane	20/24
12	$RhCl(CO)(PPh_3)_2$	K_2CO_3 (2)	DMA	59/14
13	$RhCl(CO)(PPh_3)_2$	K_2CO_3 (4)	DMA	74/7
14	$RhCl_3/2PPh_3$	K_2CO_3 (4)	DMA	49/19
15	$RhCl(PPh_3)_3$	K_2CO_3 (4)	DMA	41/13
16	$Rh(CO)_2(acac)$	K_2CO_3 (4)	DMA	18/20

[a] Reaction conditions: **1a** (0.75 mmol), **2a** (0.5 mmol), catalyst (0.025 mmol), base, solvent (2 mL), 90 °C, 5 h. [b] Isolated yields.

Table 2 Scope of functionalized salicylaldehydes[a,b]



[a] Reaction conditions: **1a–1n** (0.75 mmol), **2a** (0.5 mmol), $RhCl(CO)(PPh_3)_2$ (0.025 mmol), K_2CO_3 (2 mmol), DMA (2 mL), 90 °C, 5 h. [b] A minor aurone product was formed.

partners under rhodium catalysis (Table 1). The initial use of $RhCl(CO)(PPh_3)_2$ as the catalyst yielded chromone **3aa** and its structural isomer aurone **4aa** in 55% and 13% yields, respectively (entry 1). The screening of different bases revealed the effectiveness of K_2CO_3 (3 equiv.) to give **3aa** in 63% yield and **4aa** in 10% yield (entry 6). At the same time, other bases gave an inferior ratio of the distribution of the products (entries 2–5). Different solvents such as DMSO, NMP, DMA, toluene and 1,4-dioxane were further screened, and it was found that DMA was an effective solvent that furnished **3aa** in 70% yield along with **4aa** in 10% yield (entry 9). Delightfully, excess base (4 equiv.) delivered the product **3aa** in 74% yield (entry 13). Employing other Rh-catalysts did not improve the yield of the reaction (entries 14–16). Thus, the combination of catalytic $RhCl(CO)(PPh_3)_2$ and K_2CO_3 (4 equiv.) in DMA at 90 °C for 5 h was found to be the optimized conditions for the synthesis of chromone **3aa** in a high yield (entry 13).

With the optimized conditions in hand, the scope of functionalized salicylaldehyde (**1a–1n**) with 1,1-dibromoalkene **2a** was investigated. The results are summarized in Table 2. Salicylaldehyde substituted with electron-donating groups such as methyl and alkoxy groups delivered the corresponding chromones **3aa–3ea** in 58–74% yields. Halogen containing salicylaldehydes furnished the halogenated chromones **3fa–3ja** in 33–86% yields.

Interestingly, the electron-deficient salicylaldehydes bearing cyano, ester and acetyl groups also reacted efficiently and delivered the corresponding chromones **3ka–3ma** in 64–69% yields. Selective reactivity was demonstrated by isophthalaldehyde as it furnished only the formyl chromone **3na** in 67% yield. Overall, the substitution of both electron-rich and electron-deficient groups on salicylaldehyde was tolerated during the C–H bond functionalization reaction to furnish the chromone products **3aa–3na** in good to excellent yields.

Encouraged by the reactivity of functionalized salicylaldehydes, the scope of functionalized 1,1-dibromoalkenes was explored next. As shown in Table 3, salicylaldehyde (**1a**) reacted with 2-aryl-1,1-dibromoalkenes (**2b–2j**) having methyl, methoxy and halogen groups as substituents under the optimized conditions and gave the corresponding chromones **3ab–3aj** in 53–72% yields. The 1,3-dienyldibromides (**2k–2m**) also reacted smoothly to furnish 2-styrylchromones **3ak–3am** in 56–65% yields.

It is worth noting that the reaction of alkyl substituted 1,1-dibromoalkenes **2n** and **2o** was facile with salicylaldehyde and gave the corresponding chromones **3an** and **3ao** in 63% and 76% yields, respectively. It is important to note that chromones **3ac** and **3ah** were found to exhibit anti-microbial activity.[16] The flindersiachromone **3ao** and its derivatives isolated from plant species are known to possess anti-inflammatory and antitumor activities.[17]

Of note, we have successfully prepared efloxate (**3ob**) in one step from salicylaldehyde **1o** and 2-phenyl-1,1-dibromoalkene (**2b**) in 61% yield (Scheme 2) and this is useful in the treatment of cardiac-related diseases.[18]

Since a mixture of chromone and aurone products was formed from salicylaldehyde and 1,1-dibromoalkene (Table 4), we hypothesize that they arise most probably from the regioselective cyclization of a single *o*-hydroxyynone intermediate.[15] Thus, different *ortho*-substituted 2-aryl-1,1-dibromoalkenes **2p–2t** having the substitution of methyl, alkoxy and chloro groups were investigated under the optimized protocol con-

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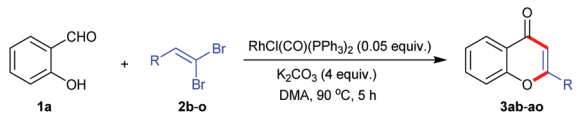
Table 3 Scope of functionalized 1,1-dibromoalkenes[a,b]

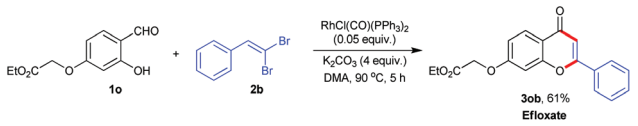


Entry	1,1-Dibromoalkene	Product	Yield (%)
1	**2b**, R = H	**3ab**, R = H	70
2	**2c**, R = OMe	**3ac**, R = OMe	66
3	**2d**, R = F	**3ad**, R = F	65
4	**2e**, R = Cl	**3ae**, R = Cl	57
5	**2f**, R = OMe	**3af**, R = OMe	64
6	**2g**, R = Cl	**3ag**, R = Cl	53
7	**2h**, R = H	**3ah**, R = H	61
8	**2i**, R = OMe	**3ai**, R = OMe	72
9	**2j**	**3aj**	62
10	**2k**, R = H	**3ak**, R = H	60
11	**2l**, R = OMe	**3al**, R = OMe	65
12	**2m**, R = Cl	**3am**, R = Cl	56
13	**2n**	**3an**	63
14	**2o**	**3ao**	76

[a] Reaction conditions: **1a** (0.75 mmol), **2b–2o** (0.5 mmol), RhCl(CO)$(PPh_3)_2$ (0.025 mmol), K_2CO_3 (2 mmol), DMA (2 mL), 90 °C, 5 h. [b] Aurone was formed in a minor amount.

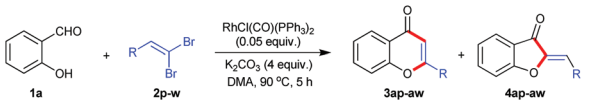
ditions. These reactions gave mixtures of the corresponding chromone **3ap–3at** and aurone **4ap–4at** products.

Furthermore, 2-heteroaryl-1,1-dibromoalkenes **2u–2w** also reacted with salicylaldehyde under the optimized reaction conditions and furnished a mixture of chromone **3au** and aurones **4au–4aw**. Overall, in the case of *ortho*-substitution and also the heterocyclic 1,1-dibromides, the formation of aurone products in major amounts highlights the steric/electronic effects in the course of *o*-hydroxyynone cyclization.



Scheme 2 Synthesis of efloxate.

Table 4 Scope of sterically hindered aryl and heteroaryl 1,1-dibromoalkenes[a]



Entry	1,1-Dibromoalkene	Product and yield	
1	**2p**, R = Me	**3ap**, R = Me, 44%	**4ap**, R = Me, 22%
2	**2q**, R = Cl	**3aq**, R = Cl, 17%	**4aq**, R = Cl, 51%
3	**2r**, R = OMe	**3ar**, R = OMe, 36%	**4ar**, R = OMe, 43%
4	**2s**, R = OBn	**3as**, R = OBn, 36%	**4as**, R = OBb, 39%
5	**2t**, R = OPh	**3at**, R = OPh, 18%	**4at**, R = OPh, 39%
6	**2u**	**3au**, 19%	**4au**, 42%
7	**2v**	**3av**, 0%	**4av**, 53%
8	**2w**	**3aw**, 0%	**4aw**, 43%

[a] Reaction conditions: **1a** (0.75 mmol), **2p–2w** (0.5 mmol), RhCl(CO)$(PPh_3)_2$ (0.025 mmol), K_2CO_3 (2 mmol), DMA (2 mL), 90 °C, 5 h.

To elucidate the reaction pathway, the following experiments were performed. The role of the hydroxyl group was first investigated by performing reactions with benzaldehyde and 2-methoxybenzaldehyde under the optimized conditions. In these reactions, the expected products were not formed (Scheme 3a) and the aldehydes were recovered. This shows that the phenolic –OH acts as a directing group for the observed reactivity. Next, 1-bromoalkyne **2i′** was used in place of 1,1-dibromoalkene **2i** when chromone **3ai** was formed in 52% yield (Scheme 3b). This shows that the reaction proceeds through the 1-bromoalkyne **2i′** intermediate. The steric effect in salicylaldehyde was also investigated with the use of **1p** and it furnished only the aurone product **4pa** in 12% yield (Scheme 3c). This is by the literature,[15] which highlights the significance of steric effects in *o*-hydroxyynone cyclization. Furthermore, salicylaldehyde was treated with 1,1-dibromoalkene **2a** in the presence of a base and this reaction afforded (*Z*)-alkenyl bromide **3aa′** in 46% yield along with unreacted 1-bromoalkyne **2a′** in 15% yield (Scheme 3d). This control reac-

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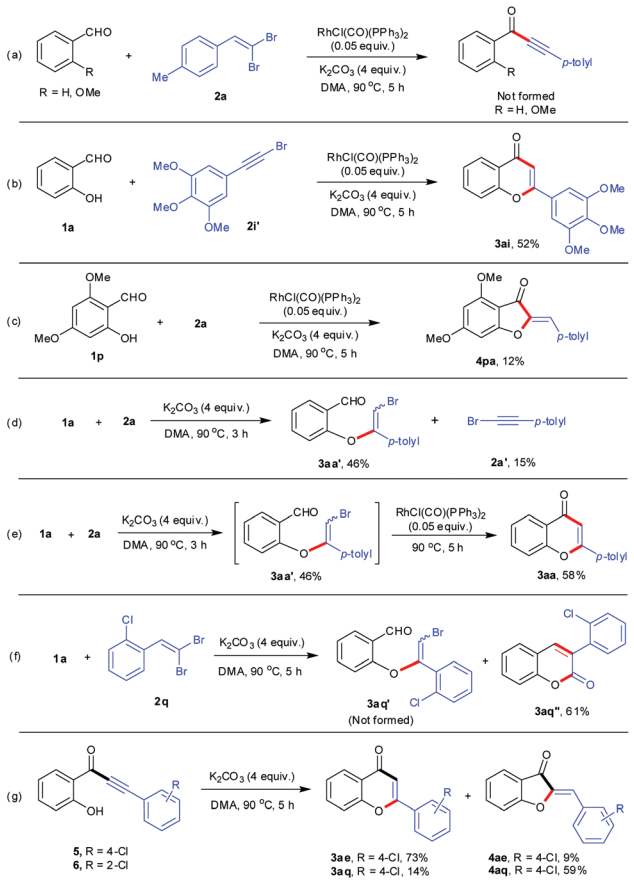
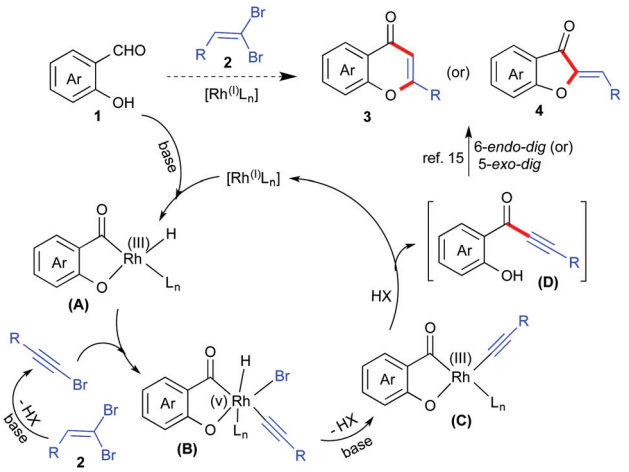


Scheme 3 Mechanistic studies.

tion highlights the *in situ* generation of 1-bromoalkyne from 1,1-dibromoalkene and also the competitive formation of (*Z*)-alkenyl bromide as an addition product, a possible intermediate for the formation of chromone under metal-catalyzed conditions.[14] A one-pot two-step reaction was also performed using salicylaldehyde (**1a**) and 1,1-dibromoalkene **2a** under the established conditions (Scheme 3e). This reaction gave chromone **3aa** in 58% yield and thus established the alternate possibility for the nucleophilic addition pathway and its subsequent intramolecular coupling for the generation of the chromone product. However, when salicylaldehyde **1a** was treated with 1-chloro-2-(2,2-dibromovinyl)benzene **2q** in the presence of a base, the expected ether-tethered alkenyl bromide **3aq′** as the nucleophilic addition product was not formed (Scheme 3f). This reaction but afforded the base mediated 3-arylcoumarin product.[7] This finding thus suggests suppression of the nucleophilic addition pathway[14] due to *ortho* steric effects in the case of *o*-substituted 1,1-dibromoalkenes. Again, the formation of aurone as a major isomer product in the case of *o*-substituted 1,1-dibromoalkenes thus indicates the C–H alkynylation of salicylaldehyde as the preferred pathway leading to the formation of *o*-hydroxyynone and its cyclization to give either aurone or chromone.

To further check the regio-selectivity in the product formation, we reacted chloro-substituted *o*-hydroxyynones **5** and **6**



Scheme 4 Proposed catalytic cycle.

with *para* and *ortho* chloro substitutions, respectively, under base-mediated conditions (Scheme 3g). These two control experiments furnished a mixture of the corresponding chromones and aurones (**3ae**, **3aq** and **4ae**, **4aq**) as *o*-hydroxyynone cyclization products. From this, we conclude that the steric/electronic effect in *o*-hydroxyynones thus plays an important role in the observed selectivity under our established Rh-catalyzed conditions.

From the above mechanistic findings, we propose the catalytic cycle as given in Scheme 4 for the formation of both chromone and aurone products. The Rh-catalyst oxidatively inserts initially at the aldehyde C–H bond of salicylaldehyde to form rhodacycle **A**. The alkynyl bromide *in situ* generated from 1,1-dibromoalkene in the reaction with a base[12a] undergoes oxidative addition[11] to give the intermediate **B**. This undergoes elimination of HBr to form the alkynylrhodium(III) species **C**. Finally, reductive elimination of the Rh-species from **C** forms ynone **D** along with the regeneration of the catalyst. Base-mediated *in situ* cyclizations of ynone **D** through the 6-*endo-dig* or 5-*exo-dig* process gives the chromone **3** or aurone **4** products, respectively.[15] However, the alternate mechanism for the formation of chromone *via* (*Z*)-alkenyl bromide as reported in the literature[14] cannot be ruled out in the case of *meta* and *para*-substituted 1,1-dibromoalkenes based on our control experiments (Schemes 3d and e).

Conclusions

In summary, we have developed an efficient protocol for the Rh-catalyzed *in situ* aldehydic C–H bond alkynylation and annulation from salicylaldehydes and 1,1-dibromoalkenes for the synthesis of chromones and aurones. The aldehyde C–H bond alkynylation by 1,1-dibromoalkenes is directed by the neighboring *o*-hydroxy group. Our reactions showed good functional group tolerance with 2-aryl-, 2-alkenyl-, 2-alkyl- and 2-heteroaryl-1,1-dibromoalkenes. We have also demonstrated the steric effects of the substituted ynone during the base-

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mediated cyclization in the formation of chromone and aurone products.

Experimental

General

The coupling reactions were performed in dry Schlenk tubes under nitrogen atmosphere conditions. All the NMR (^{1}H and ^{13}C) spectra were recorded on a JEOL ECS-400/ECX-500 spectrometer in $CDCl_3$ solvent. Infrared (IR) spectra were obtained using a PerkinElmer FT/IR spectrometer and absorptions are reported in reciprocal centimeters. High-resolution mass spectra (HRMS) were obtained using Waters GCT Premier-CAB155 and Waters-Q-Tof Premier-HAB213 instruments with electron ionization and electrospray ionization techniques. Melting points were determined using a Yamato melting point apparatus. Standard procedures were followed to dry various solvents used in coupling reactions. The functionalized salicylaldehyde derivatives (**1a–1p**),[19] 1,1-dibromoalkenes (**2a–2w**)[12a,d,20] and 1-bromoalkyne (**2i′**)[20c] were prepared by the literature known methods. All the commercially available chemicals are used without further purifications.

Representative procedure for coupling reactions

The coupling reaction was performed by charging a dry Schlenk tube with salicylaldehyde (**1a**) (91.6 mg, 1.5 mmol), 1-(2,2-dibromovinyl)-4-methylbenzene (**2a**) (138 mg, 0.5 mmol), $RhCl(CO)(PPh_3)_2$ (17.3 mg, 0.025 mmol), K_2CO_3 (276.4 mg, 2 mmol) and DMA (2 mL) solvent. This mixture was stirred in a pre-heated oil bath at 90 °C for 5 hours. The reaction mixture was brought to rt, quenched with dilute HCl and extracted with ethyl acetate (30 mL). The organic content was washed with water (15 mL) and brine (15 mL), dried with anhydrous $MgSO_4$ and concentrated. The crude product was purified by silica gel column chromatography using ethyl acetate/hexane as an eluent. The product chromone **3aa** was obtained as a colorless solid (88 mg, 74%) along with aurone **4aa** as a yellow solid (9 mg, 7%).

The characterization data for all the products (**3** and **4**) are given below.

2-*p*-Tolyl-4*H*-chromen-4-one (3aa).[14] Colourless solid (88 mg, 74%); mp 95–97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (dd, J = 8.0, 1.6 Hz, 1H), 7.82 (d, J = 8.3 Hz, 2H), 7.69 (ddd, J = 8.6, 7.1, 1.6 Hz, 1H), 7.56 (d, J = 8.3 Hz, 1H), 7.43–7.39 (m, 1H), 7.32 (d, J = 8.1 Hz, 2H), 6.80 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.6, 163.7, 156.4, 142.4, 133.8, 129.9, 129.1, 126.4, 125.8, 125.3, 124.1, 118.2, 107.1, 21.7. IR (KBr, cm^{-1}): 3060, 2920, 1644, 1568, 1466, 1374, 1042, 855, 819, 756. HRMS (ESI): calcd for $C_{16}H_{13}O_2$ $[M + H]^+$ 237.0916; found 237.0910.

6-Methyl-2-*p*-tolyl-4*H*-chromen-4-one (3ba).[13] Yellow solid (89 mg, 71%); mp 145–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.01–8.00 (m, 1H), 7.81 (d, J = 8.3 Hz, 2H), 7.50–7.44 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 6.77 (s, 1H), 2.46 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.7, 163.6, 154.6, 142.2, 135.2, 135.0, 129.9, 129.2, 126.3, 125.1, 123.7, 117.9, 106.9, 21.7, 21.1. IR (KBr, cm^{-1}): 3039, 2921, 1645, 1615, 1510, 1366, 818. HRMS (ESI): calcd for $C_{17}H_{15}O_2$ $[M + H]^+$ 251.1072; found 251.1073.

7-Methoxy-2-*p*-tolyl-4*H*-chromen-4-one (3ca).[13] Colourless solid (83 mg, 62%); mp 130–132 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.12 (d, J = 8.7 Hz, 1H), 7.79 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 6.98–6.95 (m, 2H), 6.73 (s, 1H), 3.92 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 178.0, 164.3, 163.5, 158.1, 142.2, 129.9, 129.1, 127.1, 126.2, 117.9, 114.5, 106.9, 100.5, 56.0, 21.7. IR (KBr, cm^{-1}): 3470, 2947, 2840, 1638, 1627, 1604, 1439, 1374, 1355, 1162, 818. HRMS (ESI): calcd for $C_{17}H_{15}O_3$ $[M + H]^+$ 267.1021; found 267.1028.

6-*p*-Tolyl-8*H*-[1,3]dioxolo[4,5-*g*]chromen-8-one (3da). Colourless solid (92 mg, 65%); mp 168–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.3 Hz, 2H), 7.53 (s, 1H), 7.30 (d, J = 8.1 Hz, 2H), 6.96 (s, 1H), 6.77 (s, 1H), 6.10 (s, 2H), 2.43 (s, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.6, 163.2, 153.6, 152.9, 146.3, 142.2, 129.9, 129.0, 126.2, 119.0, 106.4, 102.6, 102.4, 98.2, 21.7. IR (KBr, cm^{-1}): 2921, 1639, 1461, 1362, 1029, 821. HRMS (ESI): calcd for $C_{17}H_{13}O_4$ $[M + H]^+$ 281.0814; found 281.0811.

8-Methoxy-2-*p*-tolyl-4*H*-chromen-4-one (3ea). Colourless solid (78 mg, 58%); mp 208 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.3 Hz, 2H), 7.77 (dd, J = 8.1, 1.3 Hz, 1H), 7.34–7.30 (m, 3H), 7.18 (dd, J = 7.9, 1.2 Hz, 1H), 6.84 (s, 1H), 4.02 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.7, 163.5, 149.2, 146.8, 142.4, 129.9, 129.1, 126.5, 125.0, 124.9, 116.6, 114.5, 106.8, 56.5, 21.7. IR (KBr, cm^{-1}): 3053, 2944, 2844, 1636, 1601, 1579, 1376, 1280, 1061, 802, 748. HRMS (ESI): calcd for $C_{17}H_{15}O_3$ $[M + H]^+$ 267.1021; found 267.1022.

6-Fluoro-2-*p*-tolyl-4*H*-chromen-4-one (3fa). Colourless solid (102 mg, 80%); mp 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (dd, J = 8.2, 3.1 Hz, 1H), 7.81 (d, J = 8.3 Hz, 2H), 7.57 (dd, J = 9.1, 4.1 Hz, 1H), 7.41 (ddd, J = 9.1, 7.6, 3.1 Hz, 1H), 7.33 (d, J = 8.1 Hz, 2H), 6.80 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.8, 164.2, 159.7 (d, J_{C-F} = 245 Hz), 152.6, 142.7, 130.0, 128.8, 126.4, 125.3 (d, J_{C-F} = 7.2 Hz), 122.0 (d, J_{C-F} = 25.5 Hz), 120.3 (d, J_{C-F} = 7.7 Hz), 110.8 (d, J_{C-F} = 23.4 Hz), 106.4, 21.7. IR (KBr, cm^{-1}): 3069, 1639, 1625, 1583, 1481, 1180, 908, 817. HRMS (ESI): calcd for $C_{16}H_{12}FO_2$ $[M + H]^+$ 255.0821; found 255.0820.

6-Chloro-2-*p*-tolyl-4*H*-chromen-4-one (3ga).[13] Colourless solid (117 mg, 86%); mp 172–174 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, J = 2.5 Hz, 1H), 7.79 (d, J = 8.3 Hz, 2H), 7.62 (dd, J = 8.9, 2.5 Hz, 1H), 7.51 (d, J = 8.9 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 6.78 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.3, 164.0, 154.7, 142.8, 134.0, 131.2, 130.0, 128.6, 126.4, 125.3, 125.0, 119.9, 107.0, 21.7. IR (KBr, cm^{-1}): 3072, 1638, 1614, 1568, 1439, 1035, 909, 864, 816. HRMS (ESI): calcd for $C_{16}H_{12}ClO_2$ $[M + H]^+$ 271.0526; found 271.0521.

6-Bromo-2-*p*-tolyl-4*H*-chromen-4-one (3ha). Colourless solid (108 mg, 68%); mp 191–192 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (d, J = 2.5 Hz, 1H), 7.81–7.75 (m, 3H), 7.46 (d, J = 8.9 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 6.80 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.2, 164.1, 155.2, 142.8, 136.8, 130.0,

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128.7, 128.5, 126.4, 125.4, 120.2, 118.7, 107.1, 21.7. IR (KBr, cm^{-1}): 3072, 1639, 1602, 1566, 1436, 1264, 1034, 908, 816. HRMS (ESI): calcd for $C_{16}H_{12}BrO_2$ $[M + H]^+$ 315.0021; found 315.0026.

6,8-Dichloro-2-*p*-tolyl-4*H*-chromen-4-one (3ia). Colourless solid (98 mg, 64%); mp 160–162 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.08 (d, J = 2.5 Hz, 1H), 7.85 (d, J = 8.3 Hz, 2H), 7.71 (d, J = 2.5 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 6.81 (s, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.6, 163.8, 150.6, 143.2, 133.8, 130.9, 130.1, 128.2, 126.5, 125.9, 124.6, 124.0, 106.7, 21.8. IR (KBr, cm^{-1}): 3072, 1651, 1612, 1595, 1563, 1455, 1347, 921, 877, 867, 823. HRMS (ESI): calcd for $C_{16}H_{11}Cl_2O_2$ $[M + H]^+$ 305.0136; found 305.0138.

6,8-Dibromo-2-*p*-tolyl-4*H*-chromen-4-one (3ja). Colourless solid (66 mg, 33%); mp 172–174 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.28 (d, J = 2.4 Hz, 1H), 8.02 (d, J = 2.4 Hz, 1H), 7.88 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 6.82 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.6, 164.0, 151.9, 143.2, 139.4, 130.1, 128.2, 127.9, 126.6, 126.2, 118.6, 113.2, 106.7, 21.8. IR (KBr, cm^{-1}): 3069, 1649, 1613, 1553, 1449, 1423, 1346, 1290, 872, 822. HRMS (ESI): calcd for $C_{16}H_{11}Br_2O_2$ $[M + H]^+$ 392.9126; found 392.9120.

4-Oxo-2-*p*-tolyl-4*H*-chromene-6-carbonitrile (3ka). Yellow solid (88 mg, 67%); mp 212 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.55 (d, J = 2.1 Hz, 1H), 7.91 (dd, J = 8.7, 2.1 Hz, 1H), 7.81 (d, J = 8.3 Hz, 2H), 7.67 (d, J = 8.7 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 6.83 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 176.5, 164.4, 158.1, 143.3, 136.1, 131.5, 130.1, 128.2, 126.5, 124.6, 119.9, 117.7, 109.5, 107.6, 21.8. IR (KBr, cm^{-1}): 3036, 2226, 1649, 1609, 1480, 1441, 1361, 1194, 1033, 904, 819. HRMS (ESI): calcd for $C_{17}H_{12}NO_2$ $[M + H]^+$ 262.0868; found 262.0864.

Methyl 4-oxo-2-*p*-tolyl-4*H*-chromene-6-carboxylate (3la).[21a] Colourless solid (102 mg, 69%); mp 206 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.90 (d, J = 2.1 Hz, 1H), 8.34 (dd, J = 8.7, 2.2 Hz, 1H), 7.81 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.8 Hz, 1H), 7.33 (d, J = 8.1 Hz, 2H), 6.82 (s, 1H), 3.96 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 177.9, 165.9, 164.0, 158.8, 142.8, 134.5, 130.0, 128.6, 128.3, 127.4, 126.4, 123.8, 118.6, 107.4, 52.6, 21.7. IR (KBr, cm^{-1}): 3433, 3093, 2956, 1729, 1654, 1616, 1433, 1348, 1272, 1284, 1126, 1017, 821, 761. HRMS (ESI): calcd for $C_{18}H_{15}O_4$ $[M + H]^+$ 295.0970; found 295.0970.

6-Acetyl-2-*p*-tolyl-4*H*-chromen-4-one (3ma). Colourless solid (89 mg, 64%); mp 162–164 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.76–8.75 (m, 1H), 8.34–8.31 (m, 1H), 7.82 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 8.8 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 6.83 (s, 1H), 2.70 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 196.7, 178.0, 164.1, 158.9, 142.9, 134.0, 132.9, 130.0, 128.5, 127.3, 126.4, 123.6, 119.0, 107.3, 26.8, 21.7. IR (KBr, cm^{-1}): 3033, 1682, 1644, 1614, 1356, 1261, 829, 818. HRMS (ESI): calcd for $C_{18}H_{15}O_3$ $[M + H]^+$ 279.1021; found 279.1022.

4-Oxo-2-*p*-tolyl-4*H*-chromene-6-carbaldehyde (3na). Colourless solid (89 mg, 67%); mp 184–186 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 10.10 (s, 1H), 8.70 (d, J = 2.0 Hz, 1H), 8.24 (dd, J = 8.7, 2.0 Hz, 1H), 7.82 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.7 Hz, 1H), 7.34 (d, J = 8.1 Hz, 2H), 6.84 (s, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.6, 177.6, 164.2, 159.6, 143.1, 133.4, 132.0, 130.8, 130.1, 128.3, 126.5, 124.2, 119.7, 107.5, 21.8. IR (KBr, cm^{-1}): 3038, 2839, 1699, 1642, 1601, 1357, 1180, 826, 815. HRMS (ESI): calcd for $C_{17}H_{13}O_3$ $[M + H]^+$ 265.0865; found 265.0861.

Ethyl 2-(4-oxo-2-phenyl-4*H*-chromen-7-yloxy)acetate (3ob). Colourless solid (99 mg, 61%); mp 116–118 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, J = 8.8 Hz, 1H), 7.91–7.88 (m, 2H), 7.54–7.50 (m, 3H), 7.03 (dd, J = 8.9, 2.4 Hz, 1H), 6.96 (d, J = 2.4 Hz, 1H), 6.78 (s, 1H), 4.75 (s, 2H), 4.31 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 177.9, 168.1, 163.4, 162.3, 157.8, 131.8, 131.7, 129.2, 127.5, 126.3, 118.7, 114.4, 107.7, 101.8, 65.6, 61.9, 14.3. IR (KBr, cm^{-1}): 3490, 3068, 2982, 1756, 1643, 1627, 1607, 1450, 1374, 1209, 1170, 1094, 853, 772. HRMS (ESI): calcd for $C_{19}H_{17}O_5$ $[M + H]^+$ 325.1076; found 325.1070.

2-Phenyl-4*H*-chromen-4-one (3ab).[14] Yellow solid (78 mg, 70%); mp 94–96 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.24 (dd, J = 7.9, 1.6 Hz, 1H), 7.95–7.93 (m, 2H), 7.71 (ddd, J = 8.6, 7.2, 1.7 Hz, 1H), 7.58 (d, J = 8.3 Hz, 1H), 7.55–7.51 (m, 3H), 7.45–7.41 (m, 1H), 6.86 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.6, 163.6, 156.4, 134.0, 131.9, 131.8, 129.2, 126.5, 125.8, 125.4, 124.0, 118.2, 107.7. IR (KBr, cm^{-1}): 3062, 1646, 1569, 1465, 1375, 1128, 768. HRMS (ESI): calcd for $C_{15}H_{11}O_2$ $[M + H]^+$ 223.0759; found 223.0757.

2-(4-Methoxyphenyl)-4*H*-chromen-4-one (3ac).[14] Yellow solid (84 mg, 66%); mp 152–154 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.22 (dd, J = 7.9, 1.6 Hz, 1H), 7.89 (d, J = 9.0 Hz, 2H), 7.69 (ddd, J = 8.7, 7.2, 1.8 Hz, 1H), 7.56–7.54 (m, 1H), 7.43–7.39 (m, 1H), 7.02 (d, J = 8.9 Hz, 2H), 6.78 (s, 1H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.5, 163.7, 162.6, 156.3, 133.8, 128.2, 125.8, 125.3, 124.1, 123.9, 118.1, 114.6, 106.2, 55.6. IR (KBr, cm^{-1}): 3050, 1648, 1608, 1466, 1381, 1268, 827, 768. HRMS (ESI): calcd for $C_{16}H_{13}O_3$ $[M + H]^+$ 253.0865; found 253.0862.

2-(4-Fluorophenyl)-4*H*-chromen-4-one (3ad).[14] Yellow solid (78 mg, 65%); mp 134–136 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.23 (dd, J = 8.0, 1.5 Hz, 1H), 7.94 (dd, J = 8.9, 5.2 Hz, 2H), 7.73–7.69 (m, 1H), 7.56 (d, J = 8.2 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.22 (t, J = 8.6 Hz, 2H), 6.78 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.5, 164.9 (d, J_{C-F} = 252.1 Hz), 162.6, 156.3, 134.0, 128.7 (d, J_{C-F} = 8.8 Hz), 128.1 (d, J_{C-F} = 3.3 Hz), 125.9, 123.5, 124.0, 118.2, 116.5 (d, J_{C-F} = 22.0 Hz), 107.5 (d, J_{C-F} = 1.2 Hz). IR (KBr, cm^{-1}): 3066, 1637, 1511, 1235, 908, 835, 753. HRMS (ESI): calcd for $C_{15}H_{10}FO_2$ $[M + H]^+$ 241.0665; found 241.0663.

2-(4-Chlorophenyl)-4*H*-chromen-4-one (3ae).[14] Colourless solid (73 mg, 57%); mp 178–180 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.22 (dd, J = 7.9, 1.4 Hz, 1H), 7.86 (d, J = 8.8 Hz, 2H), 7.71 (ddd, J = 8.7, 7.1, 1.7 Hz, 1H), 7.57–7.55 (m, 1H), 7.50 (d, J = 8.8 Hz, 2H), 7.43 (ddd, J = 8.1, 7.2, 1.1 Hz, 1H), 6.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.4, 162.4, 156.3, 138.0, 134.1, 130.3, 129.5, 127.7, 125.9, 125.5, 124.0, 118.2, 107.8. IR (KBr, cm^{-1}): 2345, 1667, 1641, 1466, 1408, 1374, 1090, 828, 772, 754. HRMS (ESI): calcd for $C_{15}H_{10}ClO_2$ $[M + H]^+$ 257.0369; found 257.0366.

2-(3-Methoxyphenyl)-4*H*-chromen-4-one (3af).[14] Yellow solid (81 mg, 64%); mp 114–116 °C. ^1H NMR (400 MHz, $CDCl_3$):

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δ = 8.23 (dd, J = 8.0, 1.6 Hz, 1H), 7.70 (ddd, J = 8.6, 7.1, 1.7 Hz, 1H), 7.58–7.56 (m, 1H), 7.52–7.50 (m, 1H), 7.45–7.41 (m, 3H), 7.09–7.07 (m, 1H), 6.83 (s, 1H), 3.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.1, 163.4, 160.1, 156.4, 134.0, 133.3, 130.3, 125.8, 125.4, 118.9, 118.3, 117.3, 111.9, 108.0, 55.6. IR (KBr, cm^{-1}): 3077, 2839, 1650, 1645, 1606, 1466, 1371, 1128, 1035, 756. HRMS (ESI): calcd for $C_{16}H_{13}O_3$ $[M + H]^+$ 253.0865; found 253.0860.

2-(3-Chlorophenyl)-4*H*-chromen-4-one (3ag).[13] Colourless solid (68 mg, 53%); mp 98–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.22 (dd, J = 8.0, 1.7 Hz, 1H), 7.92 (t, J = 1.9 Hz, 1H), 7.80–7.77 (m, 1H), 7.72 (ddd, J = 8.7, 7.1, 1.7 Hz, 1H), 7.58 (dd, J = 8.4, 0.8 Hz, 1H), 7.52–7.41 (m, 3H), 6.81 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.4, 161.9, 156.3, 135.4, 134.2, 133.7, 131.7, 130.5, 126.5, 125.9, 125.6, 124.5, 124.0, 118.2, 108.3. IR (KBr, cm^{-1}): 3069, 2926, 1650, 1606, 1566, 1466, 1371, 1129, 775, 756. HRMS (ESI): calcd for $C_{15}H_{10}ClO_2$ $[M + H]^+$ 257.0369; found 257.0366.

2-(3,4-Dimethoxyphenyl)-4*H*-chromen-4-one (3ah).[21b] Yellow solid (86 mg, 61%); mp 144–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (dd, J = 7.9, 1.6 Hz, 1H), 7.70 (ddd, J = 8.6, 7.3, 1.7 Hz, 1H), 7.57 (d, J = 8.4 Hz, 2H), 7.44–7.39 (m, 2H), 6.99 (d, J = 8.6 Hz, 1H), 6.80 (s, 1H), 3.99 (s, 3H), 3.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.5, 163.6, 156.3, 152.2, 149.4, 133.8, 125.8, 125.3, 124.3, 124.0, 120.2, 118.1, 111.3, 108.9, 106.5, 56.23, 56.21. IR (KBr, cm^{-1}): 3472, 3066, 2936, 2837, 1641, 1602, 1516, 1466, 1374, 1270, 1146, 1023, 772, 756. HRMS (ESI): calcd for $C_{17}H_{15}O_4$ $[M + H]^+$ 283.0970; found 283.0975.

2-(3,4,5-Trimethoxyphenyl)-4*H*-chromen-4-one (3ai).[21b] Colourless solid (112 mg, 72%); mp 154–156 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (dd, J = 8.0, 1.6 Hz, 1H), 7.71 (ddd, J = 8.7, 7.2, 1.7 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.45–7.41 (m, 1H), 7.14 (s, 2H), 6.81 (s, 1H), 3.96 (s, 6H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.5, 163.4, 156.3, 153.7, 141.3, 133.9, 127.1, 125.8, 125.4, 124.0, 118.2, 107.5, 103.8, 61.2, 56.5. IR (KBr, cm^{-1}): 3060, 2989, 2943, 2839, 1651, 1569, 1508, 1338, 1243, 1128, 1001, 750. HRMS (ESI): calcd for $C_{18}H_{17}O_5$ $[M + H]^+$ 313.1076; found 313.1073.

2-(Naphthalen-2-yl)-4*H*-chromen-4-one (3aj).[13] Yellow solid (84 mg, 62%); mp 152–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.48 (s, 1H), 8.26 (dd, J = 7.9, 1.6 Hz, 1H), 7.99–7.88 (m, 4H), 7.75–7.71 (m, 1H), 7.64 (d, J = 7.9 Hz, 1H), 7.62–7.56 (m, 2H), 7.46–7.42 (m, 1H), 6.98 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.6, 163.5, 156.5, 134.8, 134.0, 133.0, 129.2, 129.1, 129.0, 128.2, 128.0, 127.2, 127.1, 125.9, 125.4, 124.1, 122.6, 118.3, 108.0. IR (KBr, cm^{-1}): 3058, 1640, 1565, 1464, 1382, 1347, 751. HRMS (ESI): calcd for $C_{19}H_{13}O_2$ $[M + H]^+$ 273.0916; found 273.0913.

(*E*)-2-Styryl-4*H*-chromen-4-one (3ak).[21c] Yellow solid (74 mg, 60%); mp 132–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (dd, J = 7.9, 1.6 Hz, 1H), 7.69 (ddd, J = 8.7, 7.3, 1.7 Hz, 1H), 7.64–7.58 (m, 3H), 7.54 (d, J = 8.4 Hz, 1H), 7.44–7.38 (m, 4H), 6.80 (d, J = 16.0 Hz, 1H), 6.36 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.6, 161.9, 156.1, 137.2, 135.1, 133.9, 130.0, 129.1, 127.8, 125.8, 125.2, 124.2, 120.4, 118.0, 110.7. IR (KBr, cm^{-1}): 3474, 3060, 1651, 1644, 1614, 1562, 1383, 1123, 968, 754. HRMS (ESI): calcd for $C_{17}H_{13}O_2$ $[M + H]^+$ 249.0916; found 249.0913.

(*E*)-2-(4-Methoxystyryl)-4*H*-chromen-4-one (3al).[21c] Brown solid (90 mg, 65%); mp 126–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (dd, J = 8.0, 1.4 Hz, 1H), 7.68 (ddd, J = 8.5, 7.3, 1.5 Hz, 1H), 7.60–7.51 (m, 4H), 7.39 (t, J = 7.5 Hz, 1H), 6.94 (d, J = 8.7 Hz, 2H), 6.66 (d, J = 15.9 Hz, 1H), 6.35 (s, 1H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.5, 162.5, 161.3, 156.2, 137.0, 133.8, 129.5, 127.9, 125.8, 125.1, 124.2, 118.0, 117.9, 114.6, 110.0, 55.6. IR (KBr, cm^{-1}): 3473, 3063, 2837, 1633, 1602, 1561, 1511, 1465, 1387, 1255, 1171, 968, 756. HRMS (ESI): calcd for $C_{18}H_{15}O_3$ $[M + H]^+$ 279.1021; found 279.1028.

(*E*)-2-(4-Chlorostyryl)-4*H*-chromen-4-one (3am). Brown solid (79 mg, 56%); mp 180–182 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (dd, J = 7.9, 1.6 Hz, 1H), 7.69 (ddd, J = 8.6, 7.3, 1.7 Hz, 1H), 7.58–7.51 (m, 4H), 7.42–7.38 (m, 3H), 6.76 (d, J = 16.0 Hz, 1H), 6.36 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.6, 161.5, 156.1, 135.9, 135.7, 134.0, 133.6, 129.4, 129.0, 125.9, 125.2, 124.2, 121.0, 118.0, 111.0. IR (KBr, cm^{-1}): 2926, 1635, 1464, 1386, 1091, 969, 756. HRMS (ESI): calcd for $C_{17}H_{12}ClO_2$ $[M + H]^+$ 283.0526; found 283.0524.

2-Pentyl-4*H*-chromen-4-one (3an).[21d] Yellow liquid (68 mg, 63%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (dd, J = 8.0, 1.7 Hz, 1H), 7.64 (ddd, J = 8.6, 7.1, 1.6 Hz, 1H), 7.43 (d, J = 8.3 Hz, 1H), 7.40–7.36 (m, 1H), 6.20 (s, 1H), 2.64–2.60 (m, 2H), 1.74 (p, J = 7.4 Hz, 2H), 1.41–1.35 (m, 4H), 0.93–0.90 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.6, 170.1, 156.7, 133.6, 125.8, 125.1, 123.8, 118.0, 109.9, 34.4, 31.3, 26.6, 22.5, 14.1. IR (KBr, cm^{-1}): 3492, 2957, 2862, 1658, 2932, 1466, 1384, 1221, 759. HRMS (ESI): calcd for $C_{14}H_{17}O_2$ $[M + H]^+$ 217.1229; found 217.1220.

2-Phenethyl-4*H*-chromen-4-one (3ao).[17b] Yellow liquid (96 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (dd, J = 7.9, 1.7 Hz, 1H), 7.65 (ddd, J = 8.7, 7.3, 1.8 Hz, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.40–7.37 (m, 1H), 7.32–7.28 (m, 2H), 7.24–7.20 (m, 3H), 6.15 (s, 1H), 3.09–3.05 (m, 2H), 2.96–2.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.4, 168.6, 156.6, 139.8, 133.7, 128.8, 128.4, 126.7, 125.8, 125.1, 123.8, 118.0, 110.4, 36.2, 33.1. IR (KBr, cm^{-1}): 3026, 2920, 2850, 1654, 1465, 1383, 758. HRMS (ESI): calcd for $C_{17}H_{15}O_2$ $[M + H]^+$ 251.1072; found 251.1071.

2-*o*-Tolyl-4*H*-chromen-4-one (3ap).[13] Liquid (52 mg, 44%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (dd, J = 8.0, 1.7 Hz, 1H), 7.70 (ddd, J = 8.8, 7.2, 1.7 Hz, 1H), 7.54–7.46 (m, 2H), 7.44–7.41 (m, 2H), 7.33 (d, J = 7.2 Hz, 2H), 6.49 (s, 1H), 2.49 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 178.4, 166.2, 156.6, 136.9, 133.9, 132.8, 131.4, 130.9, 129.4, 126.4, 125.9, 125.4, 124.0, 118.2, 112.1, 20.7. IR (KBr, cm^{-1}): 3065, 2926, 1651, 1465, 1370, 1036, 911, 759. HRMS (ESI): calcd for $C_{16}H_{13}O_2$ $[M + H]^+$ 237.0916; found 237.0910.

2-(2-Chlorophenyl)-4*H*-chromen-4-one (3aq).[13] Colourless solid (11 mg, 17%); mp 104–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (dd, J = 7.9, 1.6 Hz, 1H), 7.71 (ddd, J = 8.6, 7.2, 1.7 Hz, 1H), 7.64 (dd, J = 7.4, 1.9 Hz, 1H), 7.56–7.51 (m, 2H), 7.49–7.40 (m, 3H), 6.66 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.3, 162.8, 156.8, 134.1, 133.1, 132.1, 131.9, 131.0, 130.8, 127.2, 125.9, 125.5, 124.0, 118.4, 113.2. IR (KBr, cm^{-1}): 3483,

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3067, 2924, 2853, 1651, 1466, 1372, 1128, 757. HRMS (ESI): calcd for $C_{15}H_{10}ClO_2$ $[M + H]^+$ 257.0369; found 257.0363.

2-(2-Methoxyphenyl)-4*H*-chromen-4-one (3ar).[22a] Brown solid (46 mg, 36%); mp 88–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (dd, J = 7.9, 1.7 Hz, 1H), 7.90 (dd, J = 7.8, 1.8 Hz, 1H), 7.67 (ddd, J = 8.7, 7.2, 1.7 Hz, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.50–7.45 (m, 1H), 7.42–7.38 (m, 1H), 7.15 (s, 1H), 7.10 (td, J = 7.7, 0.9 Hz, 1H), 7.04 (d, J = 8.5 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.1, 161.0, 158.1, 156.6, 133.7, 132.5, 129.4, 125.7, 125.0, 123.9, 120.98, 120.82, 118.1, 112.7, 111.9, 55.8. IR (KBr, cm^{-1}): 3463, 3069, 2938, 2839, 1639, 1466, 1372, 1252, 1122, 1022, 756. HRMS (ESI): calcd for $C_{16}H_{13}O_3$ $[M + H]^+$ 253.0865; found 253.0864.

2-(2-(Benzyloxy)phenyl)-4*H*-chromen-4-one (3as).[22b] Yellow solid (60 mg, 36%); mp 70–72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.24 (d, J = 7.2 Hz, 1H), 7.86 (d, J = 6.9 Hz, 1H), 7.69–7.66 (m, 1H), 7.52–7.32 (m, 9H), 7.11–7.07 (m, 2H), 5.24 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.9, 161.6, 157.0, 156.6, 136.3, 133.7, 132.5, 129.7, 128.8, 128.2, 127.1, 125.8, 125.1, 123.9, 121.7, 121.2, 118.1, 113.5, 112.8, 70.7. IR (KBr, cm^{-1}): 3065, 3034, 2928, 1642, 1466, 1371, 1248, 1121, 755. HRMS (ESI): calcd for $C_{22}H_{17}O_3$ $[M + H]^+$ 329.1178; found 329.1176.

2-(2-Phenoxyphenyl)-4*H*-chromen-4-one (3at). Yellow solid (28 mg, 18%); mp 108–110 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (dd, J = 8.3, 1.6 Hz, 1H), 7.92 (dd, J = 7.8, 1.7 Hz, 1H), 7.67–7.63 (m, 1H), 7.47–7.33 (m, 5H), 7.29–7.25 (m, 2H), 7.15–7.11 (m, 1H), 7.05 (s, 1H), 7.03–7.00 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 178.8, 161.1, 156.6, 155.7, 133.8, 132.5, 130.1, 129.8, 125.8, 125.2, 124.04, 124.00, 123.95, 123.74, 119.9, 119.2, 118.2, 112.6. IR (KBr, cm^{-1}): 3065, 1645, 1575, 1485, 1466, 1371, 1237, 756. HRMS (ESI): calcd for $C_{21}H_{15}O_3$ $[M + H]^+$ 315.1021; found 315.1021.

2-(Thiophen-2-yl)-4*H*-chromen-4-one (3au).[13] Colourless solid (22 mg, 19%); mp 86–88 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (dd, J = 7.9, 1.7 Hz, 1H), 7.74 (dd, J = 3.7, 1.0 Hz, 1H), 7.69 (ddd, J = 8.6, 7.0, 1.6 Hz, 1H), 7.59 (dd, J = 5.0, 1.0 Hz, 1H), 7.54 (d, J = 8.7 Hz, 1H), 7.44–7.40 (m, 1H), 7.19 (dd, J = 5.0, 3.8 Hz, 1H), 6.74 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.1, 159.2, 156.1, 135.3, 133.9, 130.5, 128.66, 128.65, 125.8, 125.4, 124.1, 118.1, 106.3. IR (KBr, cm^{-1}): 3077, 1651, 1644, 1621, 1569, 1464, 1385, 1127, 835, 755, 712. HRMS (ESI): calcd for $C_{13}H_9O_2S$ $[M + H]^+$ 229.0323; found 229.0323.

(*Z*)-2-(4-Methylbenzylidene)benzofuran-3(2*H*)-one (4aa).[23a] Yellow solid (8 mg, 7%); mp 94–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.80 (m, 3H), 7.67–7.63 (m, 1H), 7.34 (d, J = 8.3 Hz, 1H), 7.27 (d, J = 8.5 Hz, 2H), 7.22 (t, J = 7.5 Hz, 1H), 6.90 (s, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.9, 166.2, 146.7, 140.7, 136.9, 131.7, 129.9, 129.7, 124.8, 123.5, 121.9, 113.5, 113.1, 21.8. IR (KBr, cm^{-1}): 3028, 2922, 2851, 1714, 1610, 1476, 1462, 1300, 756. HRMS (ESI): calcd for $C_{16}H_{13}O_2$ $[M + H]^+$ 237.0916; found 237.0910.

(*Z*)-2-(4-Chlorobenzylidene)benzofuran-3(2*H*)-one (4ae).[23b] Yellow solid (12 mg, 9%); mp 136–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.6 Hz, 2H), 7.82 (dd, J = 7.7, 1.0 Hz, 1H), 7.68 (ddd, J = 8.4, 7.4, 1.4 Hz, 1H), 7.43 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 8.2 Hz, 1H), 7.24–7.22 (m, 1H), 6.84 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.8, 166.3, 147.2, 137.2, 136.0, 132.8, 131.0, 129.4, 124.9, 123.8, 121.7, 113.1, 111.7. IR (KBr, cm^{-1}): 2923, 2953, 1705, 1650, 1601, 1490, 1462, 1299, 1188, 1086, 885, 823, 755. HRMS (ESI): calcd for $C_{15}H_{10}ClO_2$ $[M + H]^+$ 257.0369; found 257.0361.

(*Z*)-2-(2-Methylbenzylidene)benzofuran-3(2*H*)-one (4ap). Yellow solid (26 mg, 22%); mp 92–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (dd, J = 7.2, 2.0 Hz, 1H), 7.84–7.81 (m, 1H), 7.66 (ddd, J = 8.7, 7.3, 1.5 Hz, 1H), 7.34–7.30 (m, 3H), 7.28–7.21 (m, 2H), 7.15 (s, 1H), 2.52 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 184.9, 166.4, 147.2, 139.4, 137.0, 131.3, 131.0, 130.8, 130.0, 126.6, 124.9, 123.6, 121.9, 113.1, 110.1, 20.4. IR (KBr, cm^{-1}): 3060, 2923, 1703, 1649, 1594, 1458, 1299, 1185, 1131, 1095, 886, 749. HRMS (ESI): calcd for $C_{16}H_{13}O_2$ $[M + H]^+$ 237.0916; found 237.0919.

(*Z*)-2-(2-Chlorobenzylidene)benzofuran-3(2*H*)-one (4aq).[23c] Yellow solid (66 mg, 51%); mp 134–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (dd, J = 7.8, 1.6 Hz, 1H), 7.83 (d, J = 7.6 Hz, 1H), 7.67 (ddd, J = 7.9, 7.4, 1.4 Hz, 1H), 7.47 (dd, J = 7.9, 1.3 Hz, 1H), 7.41–7.30 (m, 4H), 7.26–7.22 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.7, 166.3, 147.8, 137.2, 136.1, 132.4, 130.8, 130.6, 130.2, 127.2, 125.0, 123.9, 121.7, 113.1, 108.2. IR (KBr, cm^{-1}): 1709, 1652, 1600, 1459, 1299, 1184, 885, 748. HRMS (ESI): calcd for $C_{15}H_{10}ClO_2$ $[M + H]^+$ 257.0369; found 257.0368.

(*Z*)-2-(2-Methoxybenzylidene)benzofuran-3(2*H*)-one (4ar).[23b] Yellow solid (54 mg, 43%); mp 168–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.31 (dd, J = 7.8, 1.6 Hz, 1H), 7.81 (d, J = 7.0 Hz, 1H), 7.66–7.62 (m, 1H), 7.49 (s, 1H), 7.40–7.35 (m, 1H), 7.32 (d, J = 8.3 Hz, 1H), 7.21 (t, J = 7.5 Hz, 1H), 7.07 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 8.3 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.9, 166.1, 159.0, 147.0, 136.8, 132.1, 131.6, 124.7, 123.4, 122.0, 121.4, 121.0, 113.0, 110.9, 107.4, 55.7. IR (KBr, cm^{-1}): 2929, 2838, 1698, 1592, 1461, 1250, 1186, 1136, 1026, 883, 744. HRMS (ESI): calcd for $C_{16}H_{13}O_3$ $[M + H]^+$ 253.0865; found 253.0860.

(*Z*)-2-(2-(Benzyloxy)benzylidene)benzofuran-3(2*H*)-one (4as). Yellow solid (65 mg, 39%); mp 96–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.34 (dd, J = 7.9, 1.6 Hz, 1H), 7.83–7.80 (m, 1H), 7.64 (ddd, J = 8.5, 7.4, 1.4 Hz, 1H), 7.56 (s, 1H), 7.46 (d, J = 7.2 Hz, 2H), 7.40 (t, J = 7.4 Hz, 2H), 7.35–7.31 (m, 3H), 7.23–7.20 (m, 1H), 7.08 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 5.20 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.8, 166.1, 158.1, 147.2, 136.76, 136.69, 132.3, 131.5, 128.8, 128.2, 127.3, 124.8, 123.4, 122.0, 121.9, 121.3, 113.0, 112.6, 107.4, 70.6. IR (KBr, cm^{-1}): 3064, 2929, 1704, 1645, 1596, 1454, 1300, 1251, 1185, 1132, 1096, 886, 752, 697. HRMS (ESI): calcd for $C_{22}H_{17}O_3$ $[M + H]^+$ 329.1178; found 329.1178.

(*Z*)-2-(2-Phenoxybenzylidene)benzofuran-3(2*H*)-one (4at). Yellow solid (62 mg, 39%); mp 105–106 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (dd, J = 7.9, 1.6 Hz, 1H), 7.82–7.80 (m, 1H), 7.68–7.64 (m, 1H), 7.45 (s, 1H), 7.38–7.30 (m, 4H), 7.22 (t, J = 7.5 Hz, 2H), 7.14 (t, J = 7.4 Hz, 1H), 7.03 (d, J = 7.8 Hz, 2H), 6.90 (d, J = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.8, 166.2, 163.7, 157.0, 137.0, 132.3, 131.4, 130.0, 124.9, 124.0, 123.9, 123.7, 123.6, 119.3, 118.5, 113.1, 106.8, 100.1. IR (KBr,

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cm^{-1}): 3065, 2926, 1708, 1651, 1599, 1482, 1453, 1299, 1243, 1227, 1129, 1090, 886, 753. HRMS (ESI): calcd for $C_{21}H_{15}O_3$ $[M + H]^+$ 315.1021; found 315.1027.

(*Z*)-2-(Thiophen-2-ylmethylene)benzofuran-3(2*H*)-one (4au). Yellow solid (48 mg, 42%); mp 126–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80 (dd, J = 7.8, 1.0 Hz, 1H), 7.67–7.63 (m, 1H), 7.61 (d, J = 5.1 Hz, 1H), 7.55 (d, J = 3.7 Hz, 1H), 7.34 (d, J = 8.3 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.18 (s, 1H), 7.15 (dd, J = 5.0, 3.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.0, 165.8, 145.4, 136.8, 135.7, 133.3, 131.9, 128.2, 124.7, 123.6, 122.4, 113.2, 107.2. IR (KBr, cm^{-1}): 3094, 1699, 1645, 1594, 1456, 1415, 1295, 1184, 1122, 1096, 882, 757, 709. HRMS (ESI): calcd for $C_{13}H_9O_2S$ $[M + H]^+$ 229.0323; found 229.0325.

(*Z*)-2-(Furan-2-ylmethylene)benzofuran-3(2*H*)-one (4av). Yellow solid (56 mg, 53%); mp 118–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.78 (m, 1H), 7.66–7.62 (m, 2H), 7.32 (d, J = 8.3 Hz, 1H), 7.22 (t, J = 7.2 Hz, 1H), 7.14 (d, J = 3.6 Hz, 1H), 6.90 (s, 1H), 6.60 (dd, J = 3.2, 1.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 184.1, 165.9, 148.9, 145.6, 145.2, 136.8, 124.7, 123.6, 122.2, 117.4, 113.3, 113.1, 101.8. IR (KBr, cm^{-1}): 3135, 3066, 1697, 1650, 1598, 1470, 1298, 966, 878, 752. HRMS (ESI): calcd for $C_{13}H_9O_3$ $[M + H]^+$ 213.0552; found 213.0551.

(*Z*)-2-((1*H*-Pyrrol-2-yl)methylene)benzofuran-3(2*H*)-one (4aw). Yellow liquid (46 mg, 43%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.58 (s, 1H), 7.81 (dd, J = 7.7, 0.8 Hz, 1H), 7.63 (ddd, J = 8.6, 7.3, 1.4 Hz, 1H), 7.31 (d, J = 8.3 Hz, 1H), 7.24–7.20 (m, 1H), 7.16–7.14 (m, 1H), 6.97 (s, 1H), 6.73 (ddd, J = 3.7, 2.4, 1.4 Hz, 1H), 6.37 (dt, J = 3.7, 2.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 183.1, 164.7, 143.9, 136.1, 126.3, 124.7, 124.6, 123.5, 122.8, 118.5, 112.7, 111.6, 105.2. IR (KBr, cm^{-1}): 3313, 1689, 1633, 1591, 1424, 1298, 1189, 1112, 1090, 1037, 878, 752. HRMS (ESI): calcd for $C_{13}H_{10}NO_2$ $[M + H]^+$ 212.0712; found 212.0713.

(*Z*)-4,6-Dimethoxy-2-(4-methylbenzylidene)benzofuran-3(2*H*)-one (4pa).[23a] Yellow solid (18 mg, 12%); mp 168–170 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 7.9 Hz, 2H), 6.77 (s, 1H), 6.40 (d, J = 1.8 Hz, 1H), 6.14 (d, J = 1.8 Hz, 1H), 3.96 (s, 3H), 3.92 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 180.9, 169.2, 169.0, 159.6, 147.6, 139.9, 131.3, 130.0, 129.7, 111.2, 94.2, 89.4, 56.4, 56.3, 21.7. IR (KBr, cm^{-1}): 2943, 1697, 1615, 1591, 1503, 1249, 1210, 1155, 1093, 817. HRMS (ESI): calcd for $C_{18}H_{17}O_4$ $[M + H]^+$ 297.1127; found 297.1129.

(*Z*)-2-(2-Bromo-1-*p*-tolylvinyloxy)benzaldehyde (3aa′). Colourless solid (73 mg, 46%); mp 152–154 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.76 (s, 1H), 7.91 (dd, J = 7.7, 1.8 Hz, 1H), 7.41–7.36 (m, 3H), 7.15 (d, J = 8.1 Hz, 2H), 7.08 (t, J = 7.5 Hz, 1H), 6.81 (d, J = 8.4 Hz, 1H), 6.57 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.3, 158.6, 153.0, 140.1, 135.9, 130.4, 129.9, 128.7, 125.7, 125.2, 122.7, 115.2, 95.5, 21.5. IR (KBr, cm^{-1}): 3033, 2923, 2853, 1736, 1683, 1607, 1264, 1180, 820, 753. HRMS (ESI): calcd for $C_{16}H_{14}BrO_2$ $[M + H]^+$ 317.0177; found 317.0182.

3-(2-Chlorophenyl)-2*H*-chromen-2-one (3aq″).[23d] Colourless solid (78 mg, 61%); mp 132–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (s, 1H), 7.60–7.53 (m, 2H), 7.51–7.48 (m, 1H), 7.44–7.38 (m, 2H), 7.37–7.29 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.0, 154.1, 142.8, 133.86, 133.77, 132.0, 131.5, 130.2, 130.1, 128.2, 127.2, 127.0, 124.7, 119.2, 116.9. IR (KBr, cm^{-1}): 3042, 1725, 1606, 1453, 1121, 960, 754, 742. HRMS (ESI): calcd for $C_{15}H_{10}ClO_2$ $[M + H]^+$ 257.0369; found 257.0365.

General procedure for the synthesis of *o*-hydroxyynones (5 and 6)

In an oven-dried 150 mL RB flask, 1,1-dibromoalkene (6 mmol) in THF (30 mL) was taken and cooled to −78 °C. At this temperature, *n*-BuLi (12 mmol) was added dropwise and stirred for 1 hour. To this, salicylaldehyde (3 mmol) in THF (10 mL) was added slowly for 10 minutes. After addition, the mixture was warmed to rt and stirred for 1 h followed by quenching with aq. NH_4Cl. The THF was evaporated and the mixture was extracted with ethyl acetate. The crude product was purified by column chromatography to obtain alcohol. The formed alcohol was dissolved in dry DCM followed by portionwise addition of MnO_2 in an interval of time. The reaction was monitored by TLC, and the product mixture was passed through Celite and evaporated. The crude product was purified by column chromatography to furnish the corresponding *o*-hydroxyynones. The characterization data for *o*-hydroxyynones (**5** and **6**) are as follows.

3-(4-Chlorophenyl)-1-(2-hydroxyphenyl)prop-2-yn-1-one (5). Yellow solid (125 mg, 42%); mp 112–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.69 (s, 1H), 8.09 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 7.1 Hz, 2H), 7.54 (t, J = 7.6 Hz, 1H), 7.43 (d, J = 7.1 Hz, 2H), 7.02–6.98 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.2, 163.0, 137.8, 137.4, 134.4, 133.1, 129.4, 120.9, 119.6, 118.4, 118.3, 94.6, 86.5. IR (KBr, cm^{-1}): 3087, 2410, 2206, 1627, 1592, 1489, 1343, 1257, 1204, 1015, 825, 753. HRMS (ESI): calcd for $C_{15}H_{10}ClO_2$ $[M + H]^+$ 257.0360; found 257.0369.

3-(2-Chlorophenyl)-1-(2-hydroxyphenyl)prop-2-yn-1-one (6). Yellow solid (169 mg, 57%); mp 94–96 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 11.68 (s, 1H), 8.28 (dd, J = 8.2, 1.7 Hz, 1H), 7.73 (dd, J = 7.7, 1.6 Hz, 1H), 7.56–7.50 (m, 2H), 7.44 (td, J = 7.8, 1.6 Hz, 1H), 7.34 (td, J = 7.6, 1.2 Hz, 1H), 7.02–6.99 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 182.2, 163.0, 137.8, 137.5, 135.2, 133.5, 132.3, 129.9, 127.1, 121.0, 120.3, 119.7, 118.2, 92.0, 89.9. IR (KBr, cm^{-1}): 3067, 2211, 1625, 1472, 1250, 1156, 1014, 750, 711. HRMS (ESI): calcd for $C_{15}H_{10}ClO_2$ $[M + H]^+$ 257.0369; found 257.0369.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are happy to acknowledge the financial support provided by the Science and Engineering Research Board (SERB) under the Department of Science and Technology, New Delhi (grant number SR/S1/OC-20/2012). B. S. R acknowledges the CSIR, New Delhi for the award of research fellowship.

Published on 31 January 2020. Downloaded by Universite Paris Descartes on 2/1/2020 6:21:47 AM.

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