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Pd-catalyzed chemo-selective mono-arylations and bis-arylations of functionalized 4-chlorocoumarins with triarylbismuths as threefold arylating reagents

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ABSTRACT

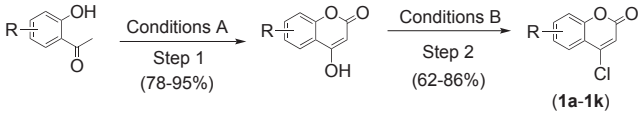
Cross-coupling reactions of differently substituted 4-chlorocoumarins were studied under palladium catalysis using triarylbismuths as threefold arylating reagents. The high reactivity of 4-chlorocoumarins was demonstrated delivering mono- and bis-arylation products in a chemo-selective manner. The reaction conditions employed are simple, robust and the threefold coupling reactivity of triarylbismuth reagents was witnessed with good to high yields in 2–4 h conditions. The utility of the methodology was explored in the synthesis of a few natural occurring neoflavones (**3.27**–**3.30**). In addition, the 4-arylcoumarin **3.1** product is a useful precursor for the preparation of (*R*)-tolterodine.

1. Introduction

Neoflavone or 4-arylcoumarin scaffolds are of considerable medicinal interest as they exhibit a variety of biological activities including anti-inflammatory, anti-tumor, anti-tuberculosis, anti-HCV, and anti-HIV properties.[1,2] This motif is useful for the preparation of (*R*)-tolterodine[3], which is known for antimuscarinic property. Functionalized 4-arylcoumarins have been studied as fluorescence probes for gold(III) ion[4] and in biological systems.[5] Synthesis of neoflavone skeletons was earlier explored under transition-metal catalyzed coupling reactions.[6] Organometallic nucleophiles such as arylboronic acids,[6a–c] aryltin,[6d] arylindium,[6e] and arylzinc[6c,f] were coupled with coumaryl derivatives such as bromo,[6c,7a] carbamate,[7b] phosphonate,[7c] triflate,[7a,d] and tosylate[6a,c,7e] as organic electrophiles. However, the coupling study of 4-chlorocoumarins was scarcely addressed.[6c,7d] More so, a few reactions reported with 4-chlorocoumarin and arylboronic acids require longer reaction time using Pd-catalyzed conditions.[6c,7d] This prompted us to investigate the coupling study of 4-chlorocoumarin with triarylbismuths as we have earlier initiated the studies with bromo and triflate derivatives of coumarins.[7a] This was to exploit the faster reactivity and threefold arylating ability of triarybismuth reagents[8] in 4-chlorocoumarin couplings. Herein, we report the arylation study of 4-chlorocoumarin derivatives using triarylbismuth reagents in palladium coupling conditions.

2. Results and discussion

Our investigation started with the cross-coupling reaction of 4-chlorocoumarin (**1a**) and triphenylbismuth under palladium coupling conditions. 4-Chlorocoumarins required for this study have been prepared according to Scheme 1 following the literature procedures.[9] Triarylbismuth reagents have been prepared by adopting the known methods of preparations either by using aryl Grignard or lithium reagent and $BiCl_3$.[10]



(**1a**-**1k**)

1a, R = H; **1b**, R = 6-methyl; **1c**, R = 5,7-dimethyl; **1d**, R = 6-methoxy; **1e**, R = 6-phenyl; **1f**, R = 7,8-benzofused; **1g**, R = 6-methyl-5-nitro; **1h**, R = 5,7-dimethoxy; **1i**, R = 6-Cl; **1j**, R = 6-bromo; **1k**, R = 6,8-dibromo

Conditions A: (a) Et_2CO_3 (1.5 equiv) NaH (60% w/w, 5 equiv), toluene, reflux, 5 h; (b) HCl (2N); Conditions B: Et_3N (1.5 equiv), $POCl_3$, reflux, 1-3 h

Scheme 1. Synthesis of 4-chlorocoumarins.

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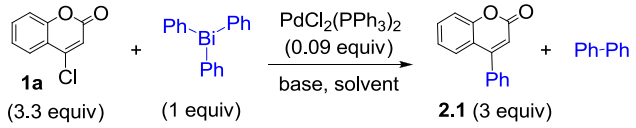
0040-4020/

It was of interest to explore the desired study under the coupling conditions of bromo and triflate derivatives of coumarins.[7a] Under these conditions using $PdCl_2(PPh_3)_2$ (0.09 equiv) in anhydrous *N*,*N*-dimethylacetamide (DMA) at 90 °C and 2 h conditions with K_3PO_4 in different amounts (1 and 4 equiv), the reaction of **1a** and $BiPh_3$ furnished 4-phenylcoumarin (**2.1**) in 59% and 70% yields along with a minor amount of biphenyl (Table 1, entries 1 and 2). Under similar conditions but with KOAc (4 equiv) the desired yield was improved to 86% (Table 1, entry 3). Further runs using KOAc in *N*,*N*-dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone provided 81% and 61% yields (Table 1, entries 4 and 5). This coupling reaction was low yielding in 1 h condition (Table 1, entry 6). Lowering of the base amount furnished 61% yield (Table 1, entry 7). Different reaction temperatures delivered 61–82% yield (Table 1, entries 8–11) and the best yield was obtained under 90 °C condition (Table 1, entry 3). The desired coupling was moderate in the case of lower amount of catalyst (Table 1, entry 12), in the presence of air (Table 1, entry 13) or in analytical grade DMA solvent (Table 1, entry 14). In these cases, formation of the more amount of biphenyl was observed. The coupling reaction was found to be ineffective without either base or the catalytic system (Table 1, entries 15 and 16). Overall, this investigation revealed the conditions with $PdCl_2(PPh_3)_2$ (0.09 equiv) and KOAc (4 equiv) in *N*,*N*-dimethylacetamide (DMA) at 90 °C and 2 h as optimized for the efficient threefold coupling of $BiPh_3$ with 4-chlorocoumarin (Table 1, entry 3).

Table 1
Screening conditions[a,b,c]

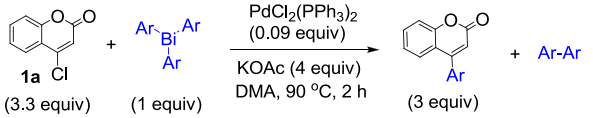


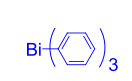
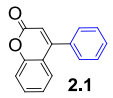
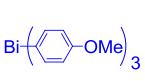
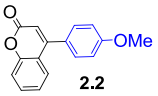
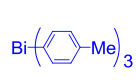
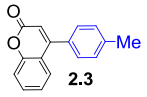
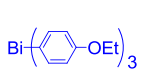
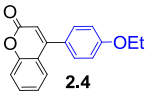
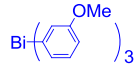
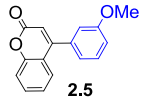
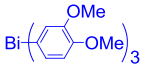
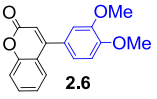
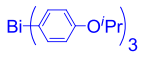
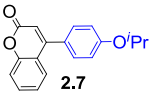
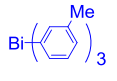
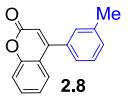
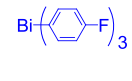
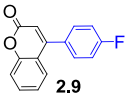
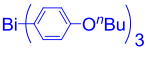
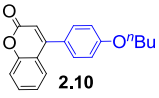
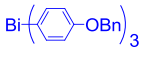
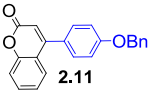
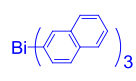
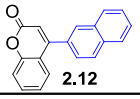
Entry	Base (equiv)	Solvent	Temp (°C)	Yield (%)
1	K_3PO_4 (1)	DMA	90	59 (*12*)
2	K_3PO_4 (4)	DMA	90	70 (*12*)
3	KOAc (4)	DMA	90	86 (*5*)
4	KOAc (4)	DMF	90	81 (*8*)
5	KOAc (4)	NMP	90	61 (*14*)
6	KOAc (4)	DMA	90	75[d] (*12*)
7	KOAc (3.3)	DMA	90	61 (*16*)
8	KOAc (4)	DMA	100	61 (*18*)
9	KOAc (4)	DMA	80	82 (*11*)
10	KOAc (4)	DMA	70	76 (*11*)
11	KOAc (4)	DMA	60	72 (*14*)
12	KOAc (4)	DMA	90	58[e] (*20*)
13	KOAc (4)	DMA	90	56[f] (*40*)
14	KOAc (4)	DMA	90	62[g] (*24*)
15	—	DMA	90	10[h] (*19*)
16	KOAc (4)	DMA	90	—

[a] Reaction conditions: **1a** (0.825 mmol, 3.3 equiv), $BiPh_3$ (0.25 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (0.022 mmol, 0.09 equiv), base (1.0 mmol, 4.0 equiv), DMA (3 mL), and 2 h under heating conditions.
[b] Isolated yields based on three aryl couplings from $BiPh_3$ reagents.
[c] Biaryl yields in parenthesis.
[d] With 1 h condition.
[e] With 0.05 equiv catalyst.
[f] In air.
[g] Analytical grade DMA.
[h] GC conversion.

The threefold cross-coupling reactivity of various $BiAr_3$ reagents was further tested with **1a** under the above-optimized conditions (Table 2). For instance, triarylbismuth reagent containing phenyl (as shown above) or electronically deficient 4-fluorophenyl furnished products **2.1** and **2.9** in 86% and 80% high yields. Whereas, $BiAr_3$ reagents with electronically rich aryls containing 4-methyl, 4-methoxy, 4-ethoxy, 3-methoxy, 3,4-dimethoxy, 4-isopropoxy, 3-methyl, 4-*n*-butoxy, 4-benzyloxy groups provided **2.2**–**2.8**, **2.10**, and **2.11** in 75–91% yield. The reaction of 2-naphthyl substituted bismuth reagent gave **2.12** in 65% yield. A reaction carried out with *p*-cyano substituted $BiPh_3$ did not yield cross-coupling product.

Table 2
Threefold coupling of different $BiAr_3$ reagents with 4-chlorocoumarin[a,b]

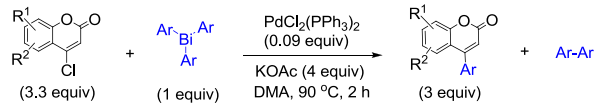


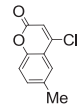
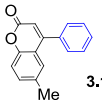
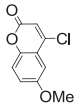
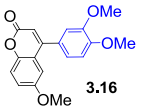
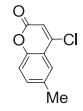
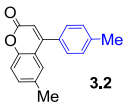
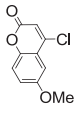
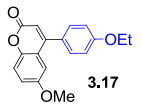
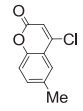
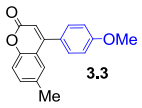
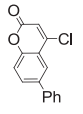
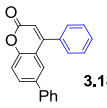
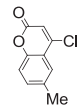
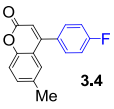
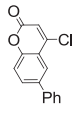
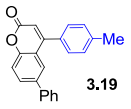
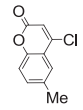
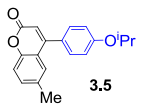
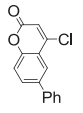
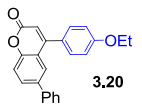
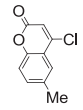
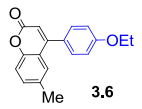
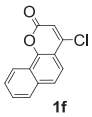
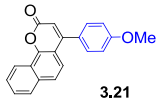
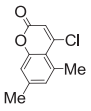
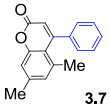
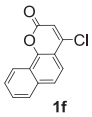
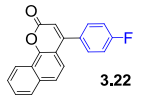
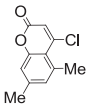
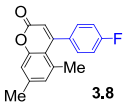
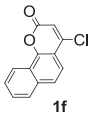
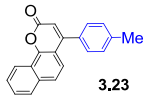
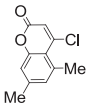
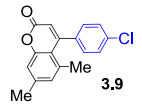
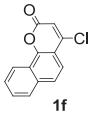
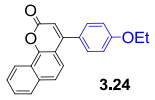
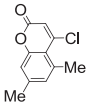
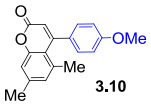
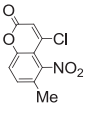
Entry	$BiAr_3$	Product	Yield (%)
1		 **2.1**	86 (*5*)
2		 **2.2**	84 (*6*)
3		 **2.3**	87 (*6*)
4		 **2.4**	91 (*4*)
5		 **2.5**	78 (*11*)
6		 **2.6**	87 (*6*)
7		 **2.7**	90 (*4*)
8		 **2.8**	82 (*6*)
9		 **2.9**	80 (*10*)
10		 **2.10**	75 (*11*)
11		 **2.11**	78 (*12*)
12		 **2.12**	65 (*14*)

[a] Reaction conditions: **1a** (0.825 mmol, 3.3 equiv), $BiAr_3$ (0.25 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (0.022 mmol, 0.09 equiv), KOAc (1 mmol, 4 equiv), and DMA (3 mL), 90 °C, 2 h.
[b] Isolated product yields based on three aryl couplings along with biaryl yields in parenthesis.

We carried out further investigations using functionalized 4-chlorocoumarins (**1b**–**1h**) and triarylbismuth reagents (Table 3).

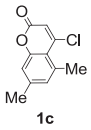
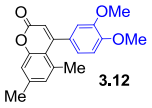
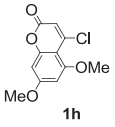
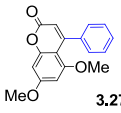
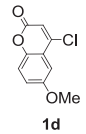
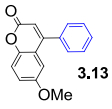
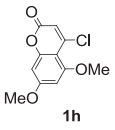
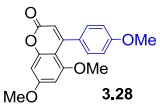
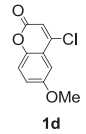
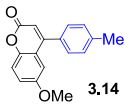
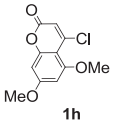
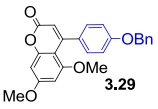
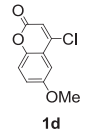
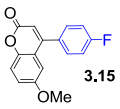
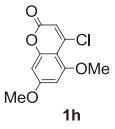
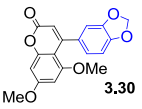
Table 3
Threefold coupling of triarylbismuths with different 4-chlorocoumarins[a,b]



Entry	4-Chlorocoumarin	4-Arylcoumarin	Yield (%)	Entry	4-Chlorocoumarin	4-Arylcoumarin	Yield (%)
1	 **1b**	 **3.1**	76 (*11*)	16	 **1d**	 **3.16**	76 (*12*)
2	 **1b**	 **3.2**	84 (*6*)	17	 **1d**	 **3.17**	84 (*8*)
3	 **1b**	 **3.3**	85 (*8*)	18	 **1e**	 **3.18**	80 (*10*)
4	 **1b**	 **3.4**	78 (*12*)	19	 **1e**	 **3.19**	87 (*6*)
5	 **1b**	 **3.5**	90 (*4*)	20	 **1e**	 **3.20**	81 (*11*)
6	 **1b**	 **3.6**	87 (*6*)	21	 **1f**	 **3.21**	81 (*13*)
7	 **1c**	 **3.7**	81 (*8*)	22	 **1f**	 **3.22**	62 (*14*)
8	 **1c**	 **3.8**	86 (*6*)	23	 **1f**	 **3.23**	79 (*12*)
9	 **1c**	 **3.9**	68 (*12*)	24	 **1f**	 **3.24**	78 (*11*)
10	 **1c**	 **3.10**	82 (*10*)	25	 **1g**	**3.25**	75 (*10*)
11	**1c**	**3.11**	83 (*8*)	26	**1g**	**3.26**	73 (*12*)

(*continued on next page*)

Table 3 (*continued*)

Entry	4-Chlorocoumarin	4-Arylcoumarin	Yield (%)	Entry	4-Chlorocoumarin	4-Arylcoumarin	Yield (%)
12	 **1c**	 **3.12**	81 (*10*)	27	 **1h**	 **3.27**	71 (*12*)
13	 **1d**	 **3.13**	81 (*8*)	28	 **1h**	 **3.28**	82 (*7*)
14	 **1d**	 **3.14**	78 (*12*)	29	 **1h**	 **3.29**	74 (*10*)
15	 **1d**	 **3.15**	79 (*11*)	30	 **1h**	 **3.30**	80 (*11*)

[a] Reaction conditions: 4-chlorocoumarin (0.825 mmol, 3.3 equiv), $BiAr_3$ (0.25 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (0.022 mmol, 0.09 equiv), KOAc (1 mmol, 4 equiv), and DMA (3 mL), 90 °C, 2 h.

[b] Isolated product yields based on three aryl couplings along with biaryl yields in parenthesis.

In this study, the cross-couplings of 4-chloro-6-methylcoumarin (**1b**) and 4-chloro-6-methoxycoumarin (**1d**) with different $BiAr_3$ reagents gave the corresponding 6-methyl-4- arylcoumarins (**3.1**–**3.6**) and 6-methoxy-4-arylcoumarins (**3.13**–**3.17**) in 76–90% yield. Similar couplings with 4-chloro-5,7-dimethylcoumarin (**1c**) furnished 5,7-dimethyl-4-arylcoumarins (**3.7**–**3.12**) in 68–86% yield. The reactivity of 4-chloro-6-phenylcoumarin (**1e**) and 4-chloro-benzocoumarin (**1f**) was also found to be good with arylated products **3.18**–**3.24** in 62–87% yield. The reaction of 4-chloro-6-methyl-5-nitrocoumarin (**1g**) delivered **3.25** and **3.26** in 73–75% yield. Our methodology was further applied in the synthesis of a few naturally occurring polyoxygenated 4-arylcoumarins using 5,7-dimethoxy-4-chlorocoumarin (**1h**) and functionalized triarylbismuth reagents. These reactions furnished polyoxygenated coumarins **3.27**–**3.30** (**3.29**, benzyl protected) in 71–82% yield. Compounds **3.27** and **3.28** are reported to be effective for anti-tumor reactivity with minimal side effects[2b] along with anti-fungal, anti-inflammatory, and antiallergenic properties.[11] These compounds were earlier isolated from *Streptomyces aureofaciens*.[2b] Similarly, natural occurring neoflavone **3.30** was isolated from *Coutarea hexandra*.[12] Further product **3.27** is an important intermediate for the synthesis of (+)-Inophyllum B, which is active against HIV-1.[2e] Notably, these medicinally important skeletons have been prepared in high yields by applying our method and this demonstrates the general and broad applicability of this method. In addition, it is to be mentioned that **3.1** is a useful precursor for the synthesis of (*R*)-tolterodine (Fig 1).[3b]

The possibility of carrying out chemo- or regio-selective couplings using halogenated 4-chlorocoumarins (**1i**–**1k**) was further explored (Table 4). Recently, 6-chloro-4-phenylcoumarin (**4.1**) was isolated from polypore mushroom *Fomitopsis officinalis*.[13] This skeleton and its derivatives are active against *Mycobacterium tuberculosis*. The interest was to test our method in the synthesis of naturally occurring halogenated coumarins and their analogs. This was accomplished with

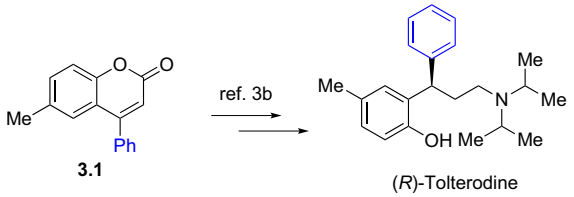
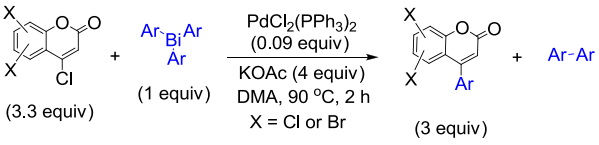


Fig. 1. Use of **3.1** as a precursor for (*R*)-tolterodine.

Table 4
Chemo- and regio-selective couplings[a,b,c]



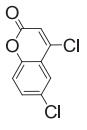
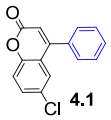
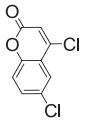
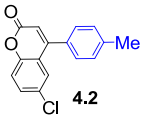
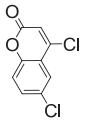
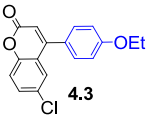
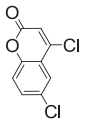
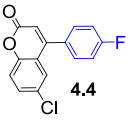
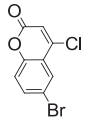
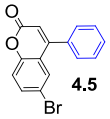
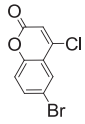
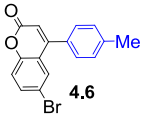
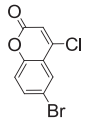
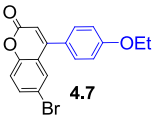
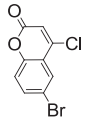
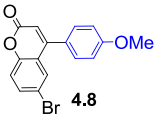
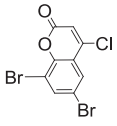
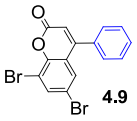
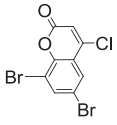
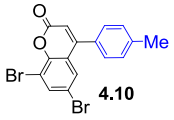
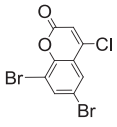
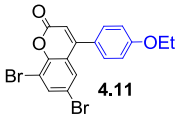
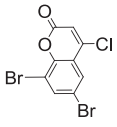
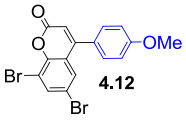
Entry	4-Chlorocoumarin	4-Arylcoumarin	Yield (%)
1	 **1i**	 **4.1**	77 (*12*)
2	 **1i**	 **4.2**	85 (*6*)
3	 **1i**	 **4.3**	75 (*10*)
4	 **1i**	 **4.4**	81 (*8*)

Table 4 (*continued*)

Entry	4-Chlorocoumarin	4-Arylcoumarin	Yield (%)
5	 **1j**	 **4.5**	61 (*14*)
6	 **1j**	 **4.6**	75 (*9*)
7	 **1j**	 **4.7**	71 (*11*)
8	 **1j**	 **4.8**	70 (*8*)
9	 **1k**	 **4.9**	53 (*14*)
10	 **1k**	 **4.10**	65 (*12*)
11	 **1k**	 **4.11**	71 (*10*)
12	 **1k**	 **4.12**	75 (*9*)

[a] Reaction conditions: 4-chlorocoumarin (0.825 mmol, 3.3 equiv), $BiAr_3$ (0.25 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (0.022 mmol, 0.09 equiv), KOAc (1 mmol, 4 equiv), and DMA (3 mL), 90 °C, 2 h.

[b] Isolated product yields based on three aryl couplings along with biaryl yields in parenthesis.

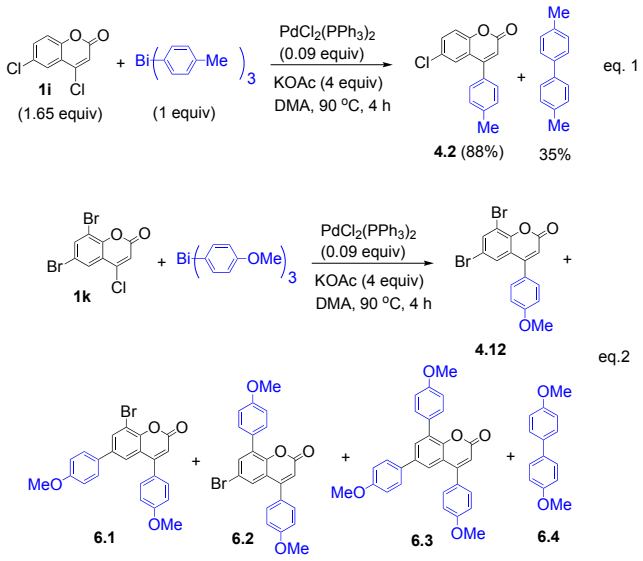
[c] For entry5, 20% bis-coupled product was formed, in other cases it was <10%.

chloro- and bromo-substituted 4-chlorocoumarins (**1i**–**1k**). The initial investigation was carried out with **1i** using $BiAr_3$ reagents using established conditions. The couplings occurred selectively at 4-chloro position leading to the formation of regio-selective 6-chloro-4-arylcoumarins (**4.1**–**4.4**) in 75–85% yield. The reactions of 6-bromo-4-chlorocoumarin (**1j**) and 6,8-dibromo-4-chlorocoumarin (**1k**) were further tested in the presence of more reactive 6-bromo and 6,8-bromo aryl terminus. Appreciably these reactions delivered chemo-selective couplings at 4-chloro position under mono-arylation conditions leaving the aryl bromide position(s) largely unreacted with the formation of bis-coupled product in minor amounts. This led to the formation of 6-bromo-4-arylcoumarins (**4.5**–**4.8**) and 6,8-dibromo-4-arylcoumarins (**4.9**–**4.12**) in 53–75% yield.

The formation of minor amount bis-coupled product prompted us to study the one-pot bis-coupling with appropriate stoichiometric amount of bismuth reagent. The desired bis-coupling was studied with 6-bromo-4-chlorocoumarin (**1j**, 1.65 equiv) and triarylbismuth reagents (1 equiv) in 4 h conditions. This endeavor has afforded bis arylated 4,6-diarylcoumarins (**5.1**–**5.4**) in 55–64% yield. The formation of bis-coupled product was expected to involve the initial 4-chloro coupling prior to the coupling at aryl bromide position.

Additional reactivity study of 4,6-dichlorocoumarin (**1i**, 1.65 equiv) using bis-coupling conditions gave mono arylated 6-chloro-4-arylcoumarin (**4.2**) in high yield (Fig 2, Eq. 1). In this case, we have not observed any cross-coupling at 6-chloro position as was seen in the case of 6-bromo-4-chlorocoumarin (Table 5). Similar bis-couplings using 6,8-dibromo-4-chlorocoumarin (**1k**, 1.65 equiv) furnished a mixture of products comprising 6,8-dibromo-4-arylcoumarin (**4.12**), an inseparable regio isomeric mixture of 8-bromo-4,6-diaryl-coumarin and 6-bromo-4,8-diarylcoumarin (**6.1** and **6.2**), 4,6,8-triarylproduct (**6.3**), and biaryl (**6.4**) (Fig 2, Eq. 2). The reaction explored for tris-couplings with 6,8-dibromo-4-chlorocoumarin (1 equiv) and $BiAr_3$ (1 equiv) also furnished a mixture of products but with increase in the amount of tris-coupling product **6.3** only up to 22% (Fig 2, Eq. 2).

The formation of 4-arylcoumarins from 4-chlorocoumarins involving triarylbismuth reagents may involve the similar catalytic

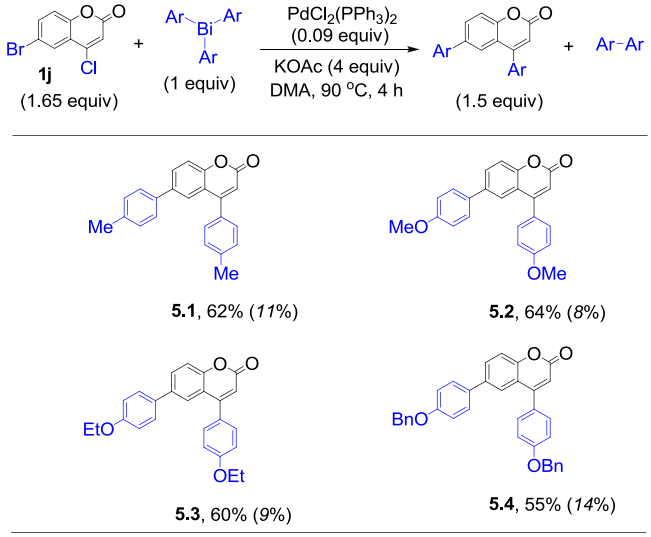


Coupling	Equiv		Yield (%)			
	Compound **1k**	$BiAr_3$	**4.12**	**6.1 and 6.2**	**6.3**	**6.4**
bis	1.65	1	14	58	5	15
tris	1	1	0	42	22	14

Fig. 2. Couplings of 4,6-dichloro- and 6,8-dibromo-4-chlorocoumains.

cycle[7a] usually known in such reactions (Fig 3). This comprises the steps of oxidative addition and transmetallation to give **3a** and **3b**, respectively, followed by reductive elimination to deliver the cross-coupling product. The repetitive involvement arylbismuth species during the catalytic cycle was expected to transfer all three aryl groups from bismuth reagent for coupling purpose.

Table 5
Bis-couplings toward 4,6-diarylcoumarins[a]



[a] Isolated product yields based on three aryl couplings along with biaryl yields in parenthesis.

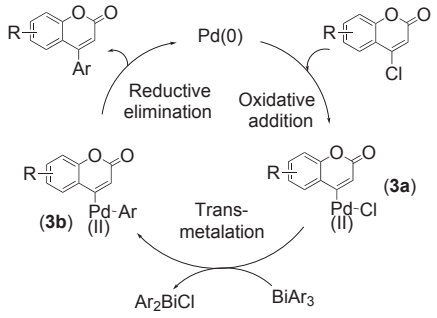


Fig. 3. Proposed catalytic cycle.[7a]

3. Conclusion

We have disclosed an unprecedented palladium-catalyzed arylations of substituted 4-chlorocoumarins using triarylbismuth reagents. In this study, we have demonstrated various couplings of mono-arylations, regio- and chemo-selective mono-arylations, and diarylations in high yields. Synthesis of medicinally important natural products (**3.27**–**3.30**) was demonstrated with good yields by using the developed method. The product **3.1** obtained is useful for the preparation of (*R*)-tolterodine. Given the fact that 4-chlorocoumarin couplings are less studied in comparison to other derivatives of coumarin, the present methodology thus enriches the scope of 4-chlorocoumarin couplings in the synthesis of polyoxygenated 4-arylcoumarins under palladium coupling conditions.

4. Experimental section

4.1. General remarks

Reaction products were analyzed using Perkin Elmer (Clarus 500) Gas Chromatograph. Pure products were isolated using silica gel column chromatography. GF-254 silica gel (Merck) was used for TLC purpose.

4.2. Representative procedure for the preparation of 1a–1k

Preparation of 4-hydroxycoumarin (step 1)[9a]

A solution of 2-hydroxy-5-methoxyacetophenone (9 mmol, 1.5 g) in toluene (15 mL) was added dropwise to a dry three-neck round-bottom flask containing sodium hydride (60% w/w suspension, 45 mmol, 1.8 g) in toluene (10 mL). This was done under N_2 atmosphere at ice bath temperature. The mixture was stirred at the same temperature for 15 min and followed by the dropwise addition of diethylcarbonate (13.5 mmol, 1.6 g) in toluene (10 mL). After complete addition, the reaction mixture was stirred at rt for 30 min and refluxed for five more hours. The reaction mixture was quenched at ice bath temperature by slow addition of water (20 mL) and acidified with 2 N HCl. The product obtained as a solid precipitate was filtered, washed with water, and dried under vacuum to get 4-hydroxy-6-methoxy-2*H*-chromen-2-one as a white solid (1.4 g, 82%). This product was directly used in step 2.

*Preparation of **1d** (step 2)*[9b]

To an oven-dried two-neck round-bottom flask, 4-hydroxy-6-methoxycoumarin (8 mmol, 1.53 g) was charged in phosphorus oxychloride (20 mL). To this mixture, triethylamine (12 mmol, 1.6 mL) was added slowly in a period of 5–10 min and the mixture was refluxed for 2 h. After the reaction time, it was cooled to rt and quenched slowly by pouring into ice-cold water and extracted with dichloromethane. The organic extract was washed with water, brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude was purified by silica gel column chromatography (5% EtOAc/petroleum ether) to obtain 4-chloro-6-methoxy-2*H*-chromen-2-one (**1d**) as gray solid (1.15 g, 70% yield) and it was identified by spectroscopic analysis and in comparison with the literature data.

*4.2.1. Compound **1a**.* White solid (86%);[14a] mp 84–86 °C, R_f (20% ethyl acetate in hexane) 0.72; IR (neat, cm^{-1}): 1724, 1562, 1309, 1176, 934, 852, 824; δ_H NMR (400 MHz, $CDCl_3$): 7.87 (dd, J=1.58, 8.28 Hz, 1H, Ar–H), 7.63–7.59 (m, 1H, Ar–H), 7.38–7.35 (m, 2H, Ar–H), 6.61 (s, 1H); δ_C NMR (125 MHz, $CDCl_3$): 159.00, 152.91, 149.62, 133.23, 125.47, 124.78, 117.92, 116.98, 115.42; ESI (HRMS) (*m*/*z*) calcd for $C_9H_6ClO_2$ $[M+H]^+$ 181.0056, found: 181.0058.

*4.2.2. Compound **1b**.* White solid (82%);[9b] mp 102–104 °C, R_f (20% ethyl acetate in hexane) 0.72; IR (neat, cm^{-1}): 1722, 1566, 1348, 1179, 936, 858, 824, 611; δ_H NMR (400 MHz, $CDCl_3$): 7.62 (s, 1H, Ar–H), 7.39 (dd, J=1.96, 8.28 Hz, 1H, Ar–H), 7.24 (d, J=8.28 Hz, 1H, Ar–H), 6.56 (s, 1H), 2.43 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 159.36, 151.19, 149.71, 134.80, 134.36, 125.27, 117.70, 116.86, 115.40, 21.02; ESI (HRMS) (*m*/*z*) calcd for $C_{10}H_8ClO_2$ $[M+H]^+$ 195.0213, found: 195.0217.

*4.2.3. Compound **1c**.* Light yellow solid (72%); mp 138–140 °C, R_f (20% ethyl acetate in hexane) 0.60; IR (neat, cm^{-1}): 3066, 2975, 2922, 1755, 1729, 1618, 1591, 1449, 1207, 944, 876; δ_H NMR (400 MHz, $CDCl_3$): 7.03 (s, 1H, Ar–H), 6.93 (s, 1H, Ar–H), 6.48 (s, 1H, Ar–H), 2.80 (s, 3H), 2.38 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 158.96, 154.62, 150.43, 143.51, 137.03, 130.30, 116.12, 115.68, 114.09, 24.10, 21.31; ESI (HRMS) (*m*/*z*) calcd for $C_{11}H_{10}ClO_2$ $[M+H]^+$ 209.0369, found: 209.0363.

*4.2.4. Compound **1d**.* Gray solid (70%);[14a] mp 156–158 °C, R_f (20% ethyl acetate in hexane) 0.42; IR (neat, cm^{-1}): 1713, 1568, 1467, 1239, 1182, 934, 842, 615; δ_H NMR (400 MHz, $CDCl_3$): 7.23–7.21 (m, 2H, Ar–H), 7.13 (dd, J=2.92, 9.04 Hz, 1H, Ar–H), 6.56 (s, 1H), 3.84 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 159.20, 156.36, 149.27, 147.34, 121.10, 118.36, 118.16, 115.68, 107.42, 55.91; ESI (HRMS) (*m*/*z*) calcd for $C_{10}H_8ClO_3$ $[M+H]^+$ 211.0162, found: 211.0164.

*4.2.5. Compound **1e**.* White solid (78%); mp 136–138 °C, R_f (20% ethyl acetate in hexane) 0.54; IR (neat, cm^{-1}): 1724, 1615, 1567, 1473,

1251, 1190, 932, 840, 762, 691, 525; δ_H NMR (400 MHz, $CDCl_3$): 8.03 (d, J=2.2 Hz, 1H, Ar–H), 7.82 (dd, J=2.2, 8.8 Hz, 1H, Ar–H), 7.60 (d, J=7.6 Hz, 2H, Ar–H), 7.51–7.39 (m, 4H, Ar–H), 6.65 (s, 1H); δ_C NMR (125 MHz, $CDCl_3$): 158.94, 152.26, 149.68, 139.09, 138.25, 132.13, 129.07, 128.03, 127.12, 123.64, 118.11, 117.43, 115.71; ESI (HRMS) (m/z) calcd for $C_{15}H_{10}ClO_2$ $[M+H]^+$ 257.0369, found: 257.0363.

4.2.6. Compound ***1f****.* White solid (74%);[14b] mp 160–162 °C, R_f (20% ethyl acetate in hexane) 0.52; IR (neat, cm^{-1}): 1720, 1594, 1334, 1046, 811, 750; δ_H NMR (400 MHz, $CDCl_3$): 8.55–8.52 (m, 1H, Ar–H), 7.89–7.64 (m, 5H, Ar–H), 6.67 (s, 1H); δ_C NMR (125 MHz, $CDCl_3$): 159.11, 150.64, 150.60, 135.36, 129.46, 127.81, 127.58, 124.75, 122.78, 122.62, 120.38, 114.43, 113.40; ESI (HRMS) (m/z) calcd for $C_{13}H_8ClO_2$ $[M+H]^+$ 231.0213, found: 231.0215.

4.2.7. Compound ***1g****.* Pale yellow solid (62%); mp 138–140 °C, R_f (20% ethyl acetate in hexane) 0.48; IR (neat, cm^{-1}): 1742, 1537, 1373, 1186, 1003, 817; δ_H NMR (500 MHz, $CDCl_3$): 7.55 (d, J=8.6 Hz, 1H, Ar–H), 7.43 (d, J=8.6 Hz, 1H, Ar–H), 6.68 (s, 1H), 2.34 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 156.91, 151.57, 144.40, 135.26, 127.01, 119.08, 119.01, 109.45, 16.87; ESI (HRMS) (m/z) calcd for $C_{10}H_7ClNO_4$ $[M+H]^+$ 240.0064, found: 240.0064.

4.2.8. Compound ***1h****.* Pale yellow solid (64%); mp 122–124 °C, R_f (20% ethyl acetate in hexane) 0.34; IR (neat, cm^{-1}): 1736, 1718, 1613, 1586, 1345, 1306, 1205, 1162, 1063, 832; δ_H NMR (400 MHz, $CDCl_3$): 6.43 (d, J=2.2 Hz, 1H, Ar–H), 6.30 (d, J=2.44 Hz, 1H, Ar–H), 6.25 (s, 1H), 3.86(s, 3H), 3.80 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 163.78, 159.27, 158.41, 156.66, 148.85, 112.21, 102.52, 96.21, 93.38, 56.07, 55.82; ESI (HRMS) (m/z) calcd for $C_{11}H_{10}ClO_4$ $[M+H]^+$ 241.0268, found: 241.0269.

4.2.9. Compound ***1i****.* White solid (73%); mp 162–164 °C, R_f (20% ethyl acetate in hexane) 0.74; IR (neat, cm^{-1}): 1745, 1729, 1557, 1470, 1299, 1272, 1165, 1088, 834, 739, 703; δ_H NMR (400 MHz, $CDCl_3$): 7.84 (d, J=2.44 Hz, 1H, Ar–H), 7.56 (dd, J=2.56, 9.04 Hz, 1H, Ar–H), 7.31 (d, J=9.04 Hz, 1H, Ar–H), 6.65 (s, 1H); δ_C NMR (125 MHz, $CDCl_3$): 158.31, 151.31, 148.35, 133.22, 130.41, 124.97, 119.05, 118.51, 116.39; ESI (HRMS) (m/z) calcd for $C_9H_5Cl_2O_2$ $[M+H]^+$ 214.9667, found: 214.9668.

4.2.10. Compound ***1j****.* Pale yellow solid (66%);[14a] mp 134–136 °C, R_f (20% ethyl acetate in hexane) 0.78; IR (neat, cm^{-1}): 1740, 1606, 1555, 1467, 1334, 1297, 1183, 926, 840, 823, 666; δ_H NMR (400 MHz, $CDCl_3$): 7.92(s, 1H, Ar–H), 7.64 (d, J=9.04 Hz, 1H, Ar–H), 7.19 (d, J=8.8 Hz, 1H, Ar–H), 6.57 (s, 1H); δ_C NMR (125 MHz, $CDCl_3$): 158.22, 151.81, 148.23, 136.07, 127.98, 119.46, 118.75, 117.64, 116.38; ESI (HRMS) (m/z) calcd for $C_9H_5BrClO_2$ $[M+H]^+$ 258.9161, found: 258.9168.

4.2.11. Compound ***1k****.* White solid (75%); mp 140–142 °C, R_f (20% ethyl acetate in hexane) 0.78; IR (neat, cm^{-1}): 1764, 1744, 1540, 1435, 1322, 1161, 926, 873, 826, 608; δ_H NMR (400 MHz, $CDCl_3$): 7.96–7.95 (m, 2H, Ar–H), 6.67 (s, 1H); δ_C NMR (125 MHz, $CDCl_3$): 157.05, 148.90, 147.92, 138.86, 127.34, 120.23, 117.47, 116.88, 111.73; ESI (HRMS) (m/z) calcd for $C_9H_4Br_2ClO_2$ $[M+H]^+$ 338.8246, found: 338.8250.

4.3. Representative cross-coupling procedures

Mono-arylation (for Tables 2–4). To a mixture of **1a** (0.825 mmol, 0.148 g) and $BiPh_3$ (0.25 mmol, 0.11 g) in a dry Schlenk tube were added KOAc (1.0 mmol, 0.098 g), $PdCl_2(PPh_3)_2$ (0.022 mmol, 0.015 g), and dry DMA (3 mL) under N_2 atmosphere. The reaction mixture was stirred in an oil bath at 90 °C for 2 h and was brought to rt after completion of the reaction time. It was quenched with water and extracted with ethyl acetate. The combined organic extract was washed with water, brine and dried over anhydrous $MgSO_4$, and filtered and concentrated under reduced pressure. The crude residue was purified on silica gel column chromatography using 3% EtOAc/petroleum ether to afford 4-phenyl-2*H*-chromen-2-one (**2.1**) as white solid (0.144 g, 86% yield). The product yield was calculated considering threefold coupling from bismuth reagent leading to 0.75 mmol of the mono arylated product as 100% yield.

Bis-couplings (for Table 5). To a mixture of **1j** (0.412 mmol, 0.106 g) and trianisylbismuth (0.25 mmol, 0.132 g) in a dry Schlenk tube were added KOAc (1.0 mmol, 0.098 g), $PdCl_2(PPh_3)_2$ (0.022 mmol, 0.015 g), and dry DMA (3 mL) under N_2 atmosphere. The reaction mixture was stirred in an oil bath at 90 °C for 4 h and was brought to rt after completion of the reaction time. It was quenched with water and extracted with ethyl acetate. The combined organic extract was washed with water, brine and dried over anhydrous $MgSO_4$ and filtered and concentrated under reduced pressure. The crude residue was purified on silica gel column chromatography using 10% EtOAc/petroleum ether to afford 4,6-bis(4-methoxyphenyl)-2*H*-chromen-2-one (**5.2**) as white solid (0.086 g, 64% yield). The product yield was calculated considering threefold coupling from bismuth reagent leading to 0.37 mmol of bis-coupled product as 100% yield.

The characterization data for the new compounds are given below. For other compounds the data is same as given in Ref. 7a. The ^1H and ^{13}C NMR spectra for compounds **2.1**–**2.12**, **3.1**–**3.30**, **4.1**–**4.12**, and **5.1**–**5.4** are available in Supplementary data.

4.3.1. 4-(3,4-Dimethoxyphenyl)-2H-chromen-2-one[2f] *(**2.6**).* White solid (0.184 g, 87%); mp 144–146 °C, R_f (20% ethyl acetate in hexane) 0.26; IR (neat, cm^{-1}): 3067, 2835, 1729, 1603, 1516, 1416, 1253, 1185, 1138, 1025, 938, 853, 747, 604; δ_H NMR (500 MHz, $CDCl_3$): 7.59–7.53 (m, 2H, Ar–H), 7.40 (d, J=8.3 Hz, 1H, Ar–H), 7.23 (d, J=8.0 Hz, 1H, Ar–H), 7.05–6.96 (m, 3H, Ar–H), 6.36 (s, 1H), 3.95 (s, 3H), 3.91 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.86, 155.37, 154.17, 150.23, 149.10, 131.80, 127.61, 126.95, 124.09, 121.32, 119.05, 117.32, 114.65, 111.49, 111.17, 56.04, 56.00; ESI (HRMS) (m/z) calcd for $C_{17}H_{15}O_4$ $[M+H]^+$ 283.0970, found: 283.0974.

*4.3.2. 4-(4-(Benzyloxy)phenyl)-2H-chromen-2-one (**2.11**).* White solid (0.192 g, 78%); mp 120–122 °C, R_f (20% ethyl acetate in hexane) 0.34; IR (neat, cm^{-1}): 3062.69, 2904.21, 2862.16, 1709.69, 1602.30, 1509.32, 1368.61, 1244.45, 1178.94, 1018.89, 943.83, 835.97, 751.69; δ_H NMR (500 MHz, $CDCl_3$): 7.57–7.53 (m, 2H, Ar–H), 7.47 (d, J=7.45 Hz, 2H, Ar–H), 7.44–7.35 (m, 6H, Ar–H), 7.23 (d, J=6.9 Hz, 1H, Ar–H), 7.12 (d, J=8.55 Hz, 2H, Ar–H), 6.35 (s, 1H), 5.15 (s, 2H); δ_C NMR (125 MHz, $CDCl_3$): 160.91, 159.99, 155.25, 154.20, 136.40, 131.79, 129.96, 128.69, 128.19, 127.67, 127.47, 126.99, 124.06, 119.07, 117.33, 115.17, 114.62, 70.15; ESI (HRMS) (m/z) calcd for $C_{22}H_{17}O_3$ $[M+H]^+$ 329.1178, found: 329.1176.

4.3.3. 4-(Naphthalen-2-yl)-2H-chromen-2-one[15] *(**2.12**).* White solid (0.133 g, 65%); mp 172–174 °C, R_f (20% ethyl acetate in hexane) 0.42; IR (neat, cm^{-1}): 3058.67, 2923.91, 1735.89, 1605.16, 1321.47, 1254.19, 1184.13, 939.20, 890.57, 864.97, 750.69, 480.17; δ_H NMR (500 MHz, $CDCl_3$): 7.99 (d, J=8.55 Hz, 1H, Ar–H), 7.96–7.92 (m, 3H, Ar–H), 7.62–7.54 (m, 5H, Ar–H), 7.44 (d, J=8.25 Hz, 1H, Ar–H), 7.24–7.22 (m, 1H, Ar–H), 6.49 (s, 1H); δ_C NMR (125 MHz, $CDCl_3$): 160.75, 155.69, 154.21, 133.54, 133.01, 132.62, 131.95, 128.61, 128.35, 128.11, 127.85, 127.30, 127.11, 127.01, 125.66, 124.21, 119.11, 117.37, 115.46; ESI (HRMS) (m/z) calcd for $C_{19}H_{13}O_2$ $[M+H]^+$ 273.0916, found: 273.0913.

*4.3.4. 4-(4-Ethoxyphenyl)-6-methyl-2H-chromen-2-one (**3.6**).* White solid (0.183 g, 87%); mp 116–118 °C, R_f (20% ethyl acetate in hexane) 0.40; IR (neat, cm^{-1}): 3049, 2972, 1723, 1610, 1515, 1256, 1183, 1047, 835, 819; δ_H NMR (500 MHz, $CDCl_3$): 7.39 (d, J=8.6 Hz, 2H, Ar–H), 7.34–7.28 (m, 3H, Ar–H), 7.03 (d, J=8.6 Hz, 2H, Ar–H), 6.31 (s, 1H), 4.12 (q, J=7.0 Hz, 2H), 2.34 (s, 3H), 1.47 (t, J=7.0 Hz, 3H); δ_C NMR (125 MHz, $CDCl_3$): 161.13, 160.14, 155.32, 152.35, 133.70, 132.73,

129.88, 127.41, 126.74, 118.84, 117.04, 114.76, 114.56, 63.66, 20.93, 14.77; ESI (HRMS) (*m*/*z*) calcd for $C_{18}H_{17}O_3$ $[M+H]^+$ 281.1178, found: 281.1174.

*4.3.5. 4-(4-Chlorophenyl)-5,7-dimethyl-2H-chromen-2-one (**3.9**).* White solid (0.146 g, 68%); mp 134–136 °C, R_f (20% ethyl acetate in hexane) 0.40; IR (neat, cm^{-1}): 3053, 2965, 1738, 1617, 1600, 1442, 1356, 1202, 1161, 1089, 900, 850, 730, 513; δ_H NMR (500 MHz, $CDCl_3$): 7.43 (d, *J*=8.55 Hz, 2H, Ar–H), 7.23 (d, *J*=8.55 Hz, 2H, Ar–H), 7.08 (s, 1H, Ar–H), 6.84 (s, 1H), 6.15 (s, 1H), 2.38 (s, 3H), 1.81 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.25, 155.48, 155.18, 142.64, 137.99, 136.70, 134.92, 129.59, 128.87, 128.77, 116.38, 115.92, 115.21, 23.63, 21.33; ESI (HRMS) (*m*/*z*) calcd for $C_{17}H_{14}ClO_2$ $[M+H]^+$ 285.0682, found: 285.0681.

*4.3.6. 4-(4-Ethoxyphenyl)-5,7-dimethyl-2H-chromen-2-one (**3.11**).* White solid (0.184 g, 83%); mp 146–148 °C, R_f (20% ethyl acetate in hexane) 0.42; IR (neat, cm^{-1}): 3071, 2924, 1722, 1611, 1508, 1240, 1181, 921, 884, 866; δ_H NMR (500 MHz, $CDCl_3$): 7.17 (d, *J*=8.85 Hz, 2H, Ar–H), 7.06 (s, 1H, Ar–H), 6.94 (d, *J*=8.85 Hz, 2H, Ar–H), 6.82 (s, 1H, Ar–H), 6.16 (s, 1H), 4.08 (q, *J*=7.05 Hz, 2H), 2.38 (s, 3H), 1.83 (s, 3H), 1.45 (t, *J*=7.05 Hz, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.71, 159.38, 156.73, 155.19, 142.16, 137.11, 131.66, 129.46, 128.64, 116.07, 115.83, 115.73, 114.41, 63.56, 23.45, 21.29, 14.78; ESI (HRMS) (*m*/*z*) calcd for $C_{19}H_{19}O_3$ $[M+H]^+$ 295.1334, found: 295.1336.

*4.3.7. 4-(3,4-Dimethoxyphenyl)-5,7-dimethyl-2H-chromen-2-one (**3.12**).* White solid (0.189 g, 81%); mp 158–160 °C, R_f (20% ethyl acetate in hexane) 0.30; IR (neat, cm^{-1}): 3069, 2930, 1712, 1617, 1513, 1460, 1407, 1242, 1139, 1025; δ_H NMR (500 MHz, $CDCl_3$): 7.06 (s, 1H, Ar–H), 6.92 (d, *J*=8.3 Hz, 1H, Ar–H), 6.84–6.82 (m, 2H, Ar–H), 6.76 (d, *J*=2.0 Hz, 1H, Ar–H), 6.17 (s, 1H), 3.93(s, 3H), 3.86 (s, 3H), 2.37 (s, 3H), 1.86 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.59, 156.52, 155.18, 149.40, 148.92, 142.22, 137.07, 132.01, 129.46, 119.87, 116.08, 115.72, 111.05, 110.71, 55.99, 55.92, 23.07, 21.26; ESI (HRMS) (*m*/*z*) calcd for for $C_{19}H_{19}O_4$ $[M+H]^+$ 311.1283, found: 311.1288.

*4.3.8. 6-Methoxy-4-phenyl-2H-chromen-2-one[16] (**3.13**).* White solid (0.153 g, 81%); mp 148–150 °C, R_f (20% ethyl acetate in hexane) 0.41; IR (neat, cm^{-1}): 3077, 2934, 2831, 1718, 1565, 1420, 1366, 1272, 1237, 1180, 1033, 943, 823, 780; δ_H NMR (500 MHz, $CDCl_3$): 7.53–7.52 (m, 3H, Ar–H), 7.47–7.45 (m, 2H, Ar–H), 7.35 (d, *J*=9.15 Hz, 1H, Ar–H), 7.13 (dd, *J*=3.00, 9.15 Hz, 1H, Ar–H), 6.93 (d, *J*=2.9 Hz, 1H, Ar–H), 6.38 (s, 1H), 3.73 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.62, 155.85, 155.33, 148.56, 135.26, 129.68, 128.91, 128.32, 119.42, 118.96, 118.23, 115.63, 109.96, 55.77; ESI (HRMS) (*m*/*z*) calcd for $C_{16}H_{13}O_3$ $[M+H]^+$ 253.0865, found: 253.0866.

*4.3.9. 6-Methoxy-4-p-tolyl-2H-chromen-2-one (**3.14**).* White solid (0.156 g, 78%); mp 112–114 °C, R_f (20% ethyl acetate in hexane) 0.36; IR (neat, cm^{-1}): 3078, 2940, 1715, 1561, 1442, 1235, 1185, 1024, 936, 824; δ_H NMR (500 MHz, $CDCl_3$): 7.36–7.32 (m, 5H, Ar–H), 7.13–7.10 (m, 1H, Ar–H), 6.97 (d, *J*=2.85 Hz, 1H, Ar–H), 6.35 (s, 1H), 3.74 (s, 3H), 2.45 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 161.06, 155.80, 155.40, 148.56, 139.88, 132.35, 129.58, 128.26, 119.50, 118.96, 118.18, 115.31, 109.91, 55.76, 21.35; ESI (HRMS) (*m*/*z*) calcd for $C_{17}H_{15}O_3$ $[M+H]^+$ 267.1021, found: 267.1022.

*4.3.10. 4-(4-Fluorophenyl)-6-methoxy-2H-chromen-2-one (**3.15**).* White solid (0.160 g, 79%); mp 140–142 °C, R_f (20% ethyl acetate in hexane) 0.38; IR (neat, cm^{-1}): 3074, 2959, 1727, 1602, 1563, 2934, 2831, 1718, 1565, 1420, 1366, 1272, 1237, 1180, 1033, 943, 823, 780; δ_H NMR (500 MHz, $CDCl_3$): 7.46–7.44 (m, 2H, Ar–H), 7.34 (d, *J*=8.85 Hz, 1H, Ar–H), 7.24–7.21 (m, 2H, Ar–H), 7.14–7.12 (m, 1H, Ar–H), 6.87 (d, *J*=2.75 Hz, 1H, Ar–H), 6.35 (s, 1H), 3.74 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 163.47 (d, J_{C-F}=248.36 Hz), 160.75, 155.88, 154.25, 148.47, 131.18, 130.25 (d, J_{C-F}=8.4 Hz), 119.27, 119.01, 118.30, 116.13 (d, J_{C-F}=21.6 Hz), 115.75, 109.71, 55.76; ESI (HRMS) (*m*/*z*) calcd for $C_{16}H_{12}FO_3$ $[M+H]^+$ 271.0770, found: 271.0776.

*4.3.11. 4-(3,4-Dimethoxyphenyl)-6-methoxy-2H-chromen-2-one[2f] (**3.16**).* Pale yellow solid (0.178 g, 76%); mp 152–154 °C, R_f (20% ethyl acetate in hexane) 0.20; IR (neat, cm^{-1}): 3075, 2945, 2831, 1714, 1624, 1352, 1227, 1107, 839; δ_H NMR (500 MHz, $CDCl_3$): 7.34 (d, *J*=8.85 Hz, 1H, Ar–H), 7.12 (dd, *J*=2.9, 9.0 Hz, 1H, Ar–H), 7.06–6.96 (m, 4H, Ar–H), 6.37 (s, 1H) 3.96 (s, 3H), 3.91(s, 3H), 3.75 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 161.09, 155.80, 155.05, 150.22, 149.13, 148.56, 127.70, 121.21, 119.48, 119.06, 118.27, 115.09, 111.38, 111.23, 109.73, 56.06, 56.01, 55.75; ESI (HRMS) (*m*/*z*) calcd for $C_{18}H_{17}O_5$ $[M+H]^+$ 313.1076, found: 313.1078.

*4.3.12. 4-(4-Ethoxyphenyl)-6-methoxy-2H-chromen-2-one (**3.17**).* Pale yellow solid (0.186 g, 84%); mp 178–180 °C, R_f (20% ethyl acetate in hexane) 0.34; IR (neat, cm^{-1}): 3080, 2990, 2937, 1712, 1610, 1561, 1438, 1297, 1261, 1181, 1035, 848, 821; δ_H NMR (500 MHz, $CDCl_3$): 7.4 (d, *J*=8.6 Hz, 2H, Ar–H), 7.33 (d, *J*=8.85 Hz, 1H, Ar–H), 7.13–7.10 (m, 1H, Ar–H), 7.03–7.00 (m, 3H, Ar–H), 6.34 (s, 1H), 4.11 (q, *J*=6.45 Hz, 2H), 3.74 (s, 3H), 1.46 (t, *J*=6.45 Hz, 3H); δ_C NMR (125 MHz, $CDCl_3$): 161.15, 160.20, 155.79, 155.07, 148.60, 129.81, 127.31, 119.58, 118.90, 118.22, 115.00, 114.81, 109.94, 63.67, 55.77, 14.78; ESI (HRMS) (*m*/*z*) calcd for $C_{18}H_{17}O_4$ $[M+H]^+$ 297.1127, found: 297.1126.

*4.3.13. 4,6-Diphenyl-2H-chromen-2-one[16] (**3.18**).* White solid (0.179 g, 80%); mp 120–122 °C, R_f (20% ethyl acetate in hexane) 0.40; IR (neat, cm^{-1}): 3061, 1722, 1612, 1561, 1251, 1186, 935, 900, 761, 696; δ_H NMR (500 MHz, $CDCl_3$): 7.77 (d, *J*=8.3 Hz, 1H, Ar–H), 7.67 (s, 1H, Ar–H), 7.54–7.35 (m, 11H, Ar–H), 6.42 (s, 1H); δ_C NMR (125 MHz, $CDCl_3$): 160.67, 155.69, 153.58, 139.65, 137.57, 135.13, 130.87, 129.76, 128.96, 128.93, 128.42, 127.67, 127.06, 125.22, 119.16, 117.71, 115.53; ESI (HRMS) (*m*/*z*) calcd for $C_{21}H_{15}O_2$ $[M+H]^+$ 299.1072, found: 299.1079.

*4.3.14. 6-Phenyl-4-p-tolyl-2H-chromen-2-one (**3.19**).* White solid (0.204 g, 87%); mp 96–98 °C, R_f (20% ethyl acetate in hexane) 0.40; IR (neat, cm^{-1}): 3057, 2919, 1729, 1612, 1254, 1178, 953, 846, 763; δ_H NMR (500 MHz, $CDCl_3$): 7.77 (dd, *J*=2.3, 8.6 Hz, 1H, Ar–H), 7.72 (d, *J*=2.0 Hz, 1H, Ar–H), 7.48 (d, *J*=8.0 Hz, 3H, Ar–H), 7.43–7.39 (m, 4H, Ar–H), 7.36–7.34 (m, 3H, Ar–H), 6.40 (s, 1H), 2.46 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.79, 155.76, 153.61, 139.98, 139.71, 137.50, 132.25, 130.78, 129.65, 128.92, 128.38, 127.64, 127.08, 125.30, 119.26, 117.68, 115.23, 21.37; ESI (HRMS) (*m*/*z*) calcd for $C_{22}H_{17}O_2$ $[M+H]^+$ 313.1229, found: 313.1223.

*4.3.15. 4-(4-Ethoxyphenyl)-6-phenyl-2H-chromen-2-one (**3.20**).* White solid (0.208 g, 81%); mp 118–120 °C, R_f (20% ethyl acetate in hexane) 0.36; IR (neat, cm^{-1}): 3059, 2982, 1735, 1607, 1511, 1252, 1183, 931; δ_H NMR (500 MHz, $CDCl_3$): 7.77–7.75 (m, 2H, Ar–H), 7.49–7.40 (m, 7H, Ar–H), 7.36–7.33 (m, 1H, Ar–H), 7.04 (d, *J*=8.85 Hz, 2H, Ar–H), 6.38 (s, 1H), 4.12 (q, *J*=6.85 Hz, 2H), 1.47 (t, *J*=7.05 Hz, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.89, 160.25, 155.42, 153.62, 139.69, 137.41, 130.70, 129.91, 128.93, 127.63, 127.15, 127.05, 125.29, 119.31, 117.70, 114.84, 63.66, 14.77; ESI (HRMS) (*m*/*z*) calcd for $C_{23}H_{19}O_3$ $[M+H]^+$ 343.1334, found: 343.1338.

*4.3.16. 4-(4-Methoxyphenyl)-2H-benzo[h]chromen-2-one (**3.21**).* White solid (0.184 g, 81%); mp 158–160 °C, R_f (20% ethyl acetate in hexane) 0.38; IR (neat, cm^{-1}): 3047, 2946, 2843, 1720, 1604, 1513, 1466, 1370, 1256, 1024, 822, 753; δ_H NMR (500 MHz, $CDCl_3$): 8.63–8.61 (m, 1H, Ar–H), 7.87–7.85 (m, 1H, Ar–H), 7.67–7.61 (m, 3H, Ar–H), 7.55 (d, *J*=8.85 Hz, 1H, Ar–H), 7.46 (dd, *J*=2.1, 6.7 Hz, 2H, Ar–H), 7.07 (dd, *J*=2.1, 6.7 Hz, 2H, Ar–H), 6.44 (s, 1H), 3.90 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$):

161.02, 160.78, 156.30, 151.47, 134.77, 130.03, 128.79, 127.85, 127.61, 127.13, 123.83, 123.40, 122.76, 122.44, 114.32, 114.00, 55.45; ESI (HRMS) (m/z) calcd for $C_{20}H_{15}O_3$ $[M+H]^+$ 303.1021, found: 303.1025.

*4.3.17. 4-(4-Fluorophenyl)-2H-benzo[h]chromen-2-one (**3.22**).* White solid (0.135 g, 62%); mp 168–170 °C, R_f (20% ethyl acetate in hexane) 0.48; IR (neat, cm^{-1}): 3064, 1720, 1508, 1465, 1231, 1154, 1094, 845, 816; δ_H NMR (500 MHz, $CDCl_3$): 8.63–8.61 (m, 1H, Ar–H), 7.88–7.86 (m, 1H, Ar–H), 7.68–7.62 (m, 3H, Ar–H), 7.50–7.48 (m, 2H, Ar–H), 7.43 (d, J=8.9 Hz, 1H, Ar–H), 7.27–7.24 (m, 2H, Ar–H), 6.44 (s, 1H); δ_C NMR (125 MHz, $CDCl_3$): 163.46 (d, J_{C-F}=248.36 Hz), 160.66, 155.54, 151.45, 134.80, 131.54, 130.44 (d, J_{C-F}=8.4 Hz), 128.95, 127.65, 127.26, 124.07, 123.28, 122.71, 122.00, 116.08 (d, J_{C-F}=21.6 Hz), 114.61, 114.01; ESI (HRMS) (m/z) calcd for $C_{19}H_{12}FO_2$ $[M+H]^+$ 291.0821, found: 291.0823.

*4.3.18. 4-p-Tolyl-2H-benzo[h]chromen-2-one (**3.23**).* White solid (0.170 g, 79%); mp 138–140 °C, R_f (20% ethyl acetate in hexane) 0.51; IR (neat, cm^{-1}): 3048, 1722, 1366, 824, 755; δ_H NMR (500 MHz, $CDCl_3$): 8.63–8.61 (m, 1H, Ar–H), 7.86–7.84 (m, 1H, Ar–H), 7.67–7.64 (m, 2H, Ar–H), 7.61 (d, J=9.0 Hz, 1H, Ar–H), 7.51 (d, J=9.0 Hz, 1H, Ar–H), 7.40 (d, J=8.0 Hz, 2H, Ar–H), 7.35 (d, J=8.05 Hz, 2H, Ar–H), 6.45 (s, 1H), 2.47 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.96, 156.67, 151.39, 139.81, 134.74, 132.66, 129.53, 128.78, 128.44, 127.60, 127.10, 123.84, 123.31, 122.70, 122.43, 114.27, 114.22, 21.36; ESI (HRMS) (m/z) calcd for $C_{20}H_{15}O_2$ $[M+H]^+$ 287.1072, found: 287.1076.

*4.3.19. 4-(4-Ethoxyphenyl)-2H-benzo[h]chromen-2-one (**3.24**).* Pale yellow solid (0.185 g, 78%); mp 128–130 °C, R_f (20% ethyl acetate in hexane) 0.46; IR (neat, cm^{-1}): 3045, 2980, 1733, 1611, 1514, 1369, 1259, 1175, 1044, 815, 748; δ_H NMR (500 MHz, $CDCl_3$): 8.64–8.62 (m, 1H, Ar–H), 7.87–7.85 (m, 1H, Ar–H), 7.66–7.62 (m, 3H, Ar–H), 7.56 (d, J=8.6 Hz, 1H, Ar–H), 7.44 (d, J=8.6 Hz, 2H, Ar–H), 7.05 (d, J=8.9 Hz, 2H, Ar–H), 6.44 (s, 1H), 4.13 (q, J=6.87 Hz, 2H), 1.48 (t, J=7.0 Hz, 3H); δ_C NMR (125 MHz, $CDCl_3$): 161.06, 160.16, 156.35, 151.39, 134.73, 130.02, 128.77, 127.60, 127.10, 123.81, 123.36, 122.74, 122.46, 114.76, 114.33, 113.90, 63.67, 14.78; EI (HRMS) (m/z) calcd for $C_{21}H_{16}O_3$ $[M]^+$ 316.1099, found: 316.1094.

*4.3.20. 6-Methyl-5-nitro-4-p-tolyl-2H-chromen-2-one (**3.25**).* Yellow solid (0.166 g, 75%); mp 148–150 °C, R_f (20% ethyl acetate in hexane) 0.42; IR (neat, cm^{-1}): 3035, 2921, 1734, 1536, 1348, 818; δ_H NMR (500 MHz, $CDCl_3$): 7.49–7.46 (m, 2H, Ar–H), 7.20 (d, J=7.7 Hz, 2H, Ar–H), 7.16 (d, J=8.3 Hz, 2H, Ar–H), 6.36 (s, 1H), 2.41 (s, 3H), 2.28 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 158.75, 152.67, 152.55, 147.78, 139.98, 134.11, 131.54, 128.89, 127.13, 126.94, 119.72, 119.47, 111.46, 21.42, 17.60; ESI (HRMS) (m/z) calcd for $C_{17}H_{14}NO_4$ $[M+H]^+$ 296.0923, found: 296.0927.

*4.3.21. 4-(4-Ethoxyphenyl)-6-methyl-5-nitro-2H-chromen-2-one (**3.26**).* Yellow solid (0.178 g, 73%); mp 120–122 °C, R_f (20% ethyl acetate in hexane) 0.34; IR (neat, cm^{-1}): 3061, 2976, 1735, 1607, 1532, 1509, 1245, 1182, 1044, 817; δ_H NMR (500 MHz, $CDCl_3$): 7.49–7.45 (m, 2H, Ar–H), 7.18 (d, J=8.85 Hz, 2H, Ar–H), 6.88 (d, J=8.55 Hz, 2H, Ar–H), 6.35 (s, 1H), 4.08 (q, J=7.02 Hz, 2H), 2.28 (s, 3H), 1.44 (t, J=7.02 Hz, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.17, 158.83, 152.69, 152.35, 147.91, 134.06, 128.64, 126.91, 126.59, 119.48, 119.42, 114.10, 111.67, 63.53, 17.60, 14.71; ESI (HRMS) (m/z) calcd for $C_{18}H_{16}NO_5$ $[M+H]^+$ 326.1028, found: 326.1021.

*4.3.22. 5,7-Dimethoxy-4-phenyl-2H-chromen-2-one[17] (**3.27**).* White solid (0.154 g, 71%); mp 160–162 °C, R_f (30% ethyl acetate in hexane) 0.51; IR (neat, cm^{-1}): 3055, 2938, 1711, 1610, 1595, 1353, 1227, 1160, 1111, 821, 781; δ_H NMR (500 MHz, $CDCl_3$): 7.37–7.36 (m, 3H, Ar–H), 7.26–7.24 (m, 2H, Ar–H), 6.52 (d, J=2.4 Hz, 1H, Ar–H), 6.22 (d, J=2.45 Hz, 1H, Ar–H), 6.00 (s, 1H), 3.86 (s, 3H), 3.41 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 163.34, 160.84, 158.21, 157.16, 155.65, 139.76, 127.86, 127.33, 127.09, 112.68, 103.55, 95.76, 93.55, 55.75, 55.37; ESI (HRMS) (m/z) calcd for $C_{17}H_{15}O_4$ $[M+H]^+$ 283.0970, found: 283.0972.

*4.3.23. 5,7-Dimethoxy-4-(4-methoxyphenyl)-2H-chromen-2-one[11] (**3.28**).* White solid (0.192 g, 82%); mp 152–154 °C, R_f (30% ethyl acetate in hexane) 0.37; IR (neat, cm^{-1}): 3075, 2945, 2831, 1714, 1624, 1590, 1509, 1462, 1352, 1227, 1161, 1107, 1027, 839; δ_H NMR (500 MHz, $CDCl_3$): 7.21 (d, J=8.85 Hz, 2H, Ar–H), 6.90 (d, J=8.85 Hz, 2H, Ar–H), 6.52 (d, J=2.4 Hz, 1H, Ar–H), 6.24 (d, J=2.45 Hz, 1H, Ar–H), 5.99 (s, 1H), 3.867 (s, 3H), 3.863 (s, 3H), 3.47 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 163.22, 160.95, 159.53, 158.27, 157.24, 155.43, 132.07, 128.68, 112.70, 112.60, 103.63, 95.78, 93.55, 55.73, 55.44, 55.28; ESI (HRMS) (m/z) calcd for $C_{18}H_{17}O_5$ $[M+H]^+$ 313.1076, found: 313.1075.

*4.3.24. 4-(4-(Benzyloxy)phenyl)-5,7-dimethoxy-2H-chromen-2-one (**3.29**).* White solid (0.216 g, 74%); mp 164–166 °C, R_f (30% ethyl acetate in hexane) 0.48; IR (neat, cm^{-1}): 3056, 3029, 2980, 1733, 1608, 1595, 1510, 1351, 1239, 1154, 1110, 1046, 1010, 946, 824, 751; δ_H NMR (500 MHz, $CDCl_3$): 7.46 (d, J=7.05 Hz, 2H, Ar–H), 7.42–7.39 (m, 2H, Ar–H), 7.36–7.34 (m, 1H, Ar–H), 7.21 (d, J=8.85 Hz, 2H, Ar–H), 6.97 (d, J=8.85 Hz, 2H, Ar–H), 6.52 (d, J=2.40 Hz, 1H, Ar–H), 6.24 (d, J=2.40 Hz, 1H, Ar–H), 5.99 (s, 1H), 5.12 (s, 2H), 3.86 (s, 3H), 3.46 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 163.21, 160.96, 158.68, 158.23, 157.22, 155.38, 136.73, 132.31, 128.69, 128.61, 128.05, 127.52, 113.67, 112.57, 103.60, 95.77, 93.52, 70.03, 55.73, 55.40; ESI (HRMS) (m/z) calcd for $C_{24}H_{21}O_5$ $[M+H]^+$ 389.1389, found: 389.1384.

*4.3.25. 4-(Benzo[d][1,3]dioxol-5-yl)-5,7-dimethoxy-2H-chromen-2-one[12b] (**3.30**).* Pale yellow solid (0.196 g, 80%); mp 192–194 °C, R_f (30% ethyl acetate in hexane) 0.42; IR (neat, cm^{-1}): 3089, 2923, 2854, 1709, 1609, 1592, 1502, 1380, 1351, 1220, 1159, 1112, 1034, 907, 850, 819; δ_H NMR (500 MHz, $CDCl_3$): 6.81 (d, J=8.55 Hz, 1H, Ar–H), 6.75–6.74 (m, 2H, Ar–H), 6.51 (d, J=2.45 Hz, 1H, Ar–H), 6.24 (d, J=2.45 Hz, 1H, Ar–H), 6.01 (s, 2H), 5.98 (s, 1H), 3.86 (s, 3H), 3.51 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 163.29, 160.86, 158.15, 157.17, 155.19, 147.41, 146.77, 133.54, 120.82, 112.68, 108.25, 107.47, 103.52, 101.16, 95.80, 93.52, 55.74, 55.58; ESI (HRMS) (m/z) calcd for $C_{18}H_{15}O_6$ $[M+H]^+$ 327.0863, found: 327.0869.

*4.3.26. 6-Chloro-4-phenyl-2H-chromen-2-one[6e] (**4.1**).* White solid (0.149 g, 77%); mp 150–152 °C, R_f (20% ethyl acetate in hexane) 0.60; IR (neat, cm^{-1}): 3049, 1722, 1555, 1409, 1353, 1178, 950, 939, 700; δ_H NMR (500 MHz, $CDCl_3$): 7.56–7.54 (m, 3H, Ar–H), 7.50 (dd, J=2.42, 8.55 Hz, 1H, Ar–H), 7.45–7.42 (m, 3H, Ar–H), 7.36 (d, J=8.55 Hz, 1H, Ar–H), 6.41 (s, 1H); δ_C NMR (125 MHz, $CDCl_3$): 160.04, 154.60, 152.54, 134.46, 131.87, 129.98, 129.62, 129.08, 128.27, 126.31, 120.12, 118.73, 116.08; ESI (HRMS) (m/z) calcd for $C_{15}H_{10}ClO_2$ $[M+H]^+$ 257.0369, found: 257.0368.

*4.3.27. 6-Chloro-4-p-tolyl-2H-chromen-2-one[6a] (**4.2**).* White solid (0.173 g, 85%); mp 188–190 °C, R_f (20% ethyl acetate in hexane) 0.60; IR (neat, cm^{-1}): 3068, 2919, 1733, 1610, 1552, 1415, 1353, 1247, 1183, 1122, 935, 816, 536; δ_H NMR (500 MHz, $CDCl_3$): 7.50–7.48 (m, 2H, Ar–H), 7.36–7.32 (m, 5H, Ar–H), 6.39 (s, 1H), 2.46 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.21, 154.70, 152.56, 140.28, 131.77, 131.58, 129.76, 129.57, 128.24, 126.39, 120.24, 118.71, 115.75, 21.37; ESI (HRMS) (m/z) calcd for $C_{16}H_{12}ClO_2$ $[M+H]^+$ 271.0526, found: 271.0529.

*4.3.28. 6-Chloro-4-(4-ethoxyphenyl)-2H-chromen-2-one (**4.3**).* White solid (0.169 g, 75%); mp 168–170 °C, R_f (20% ethyl acetate in hexane) 0.50; IR (neat, cm^{-1}): 3047, 2977, 1731, 1609, 1515, 1308, 1292, 1183, 1153, 951, 820; δ_H NMR (500 MHz, $CDCl_3$): 7.52 (d, J=2.45 Hz, 1H, Ar–H), 7.49 (dd, J=2.45, 8.85 Hz, 1H, Ar–H), 7.38–7.33 (m, 3H, Ar–H), 7.04 (d, J=8.55 Hz, 2H, Ar–H), 6.37 (s, 1H), 4.12 (q, J=6.85 Hz, 2H), 1.47 (t, J=6.87 Hz, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.45, 160.26, 154.35,

152.62, 131.71, 129.81, 129.53, 126.52, 126.40, 120.35, 118.73, 115.42, 115.01, 63.72, 14.75; ESI (HRMS) (*m*/*z*) calcd for $C_{17}H_{14}ClO_3$ $[M+H]^+$ 301.0631, found: 301.0633.

4.3.29. 6-Chloro-4-(4-fluorophenyl)-2H-chromen-2-one[6e] (***4.4***). White solid (0.167 g, 81%); mp 192–194 °C, R_f (20% ethyl acetate in hexane) 0.58; IR (neat, cm^{-1}): 3077, 2920, 1739, 1602, 1507, 1415, 1351, 1231, 1181, 822, 535; δ_H NMR (500 MHz, $CDCl_3$): 7.51 (dd, *J*=2.3, 8.85 Hz, 1H, Ar–H), 7.45–7.42 (m, 2H, Ar–H), 7.40 (d, *J*=2.25 Hz, 1H, Ar–H), 7.36 (d, *J*=8.6 Hz, 1H, Ar–H), 7.27–7.23 (m, 2H, Ar–H), 6.39 (s, 1H); δ_C NMR (125 MHz, $CDCl_3$): 163.64 (d, J_{C-F}=249.57 Hz), 159.87, 153.54, 152.51, 132.02, 130.46, 130.28 (d, J_{C-F}=8.38 Hz), 129.74, 126.09, 120.01, 118.84, 116.36 (d, J_{C-F}=22.78 Hz); ESI (HRMS) (*m*/*z*) calcd for $C_{15}H_9ClFO_2$ $[M+H]^+$ 275.0275, found: 275.0273.

4.3.30. 6-Bromo-4-phenyl-2H-chromen-2-one[16] (***4.5***). White solid (0.138 g, 61%); mp 164–166 °C, R_f (20% ethyl acetate in hexane) 0.66; IR (neat, cm^{-1}): 3074, 1722, 1350, 1183, 880, 825; δ_H NMR (500 MHz, $CDCl_3$): 7.64 (dd, *J*=2.42, 8.6 Hz, 1H, Ar–H), 7.59 (d, *J*=2.3 Hz, 1H, Ar–H), 7.56–7.54 (m, 3H, Ar–H), 7.44–7.42 (m, 2H, Ar–H), 7.30 (d, *J*=8.6 Hz, 1H, Ar–H), 6.40 (s, 1H); δ_C NMR (125 MHz, $CDCl_3$): 159.99, 154.54, 153.03, 134.72, 134.45, 130.00, 129.33, 129.10, 128.28, 120.61, 119.06, 117.00, 116.08; ESI (HRMS) (*m*/*z*) calcd for $C_{15}H_{10}BrO_2$ $[M+H]^+$ 300.9864, found: 300.9869.

4.3.31. 6-Bromo-4-p-tolyl-2H-chromen-2-one (***4.6***). White solid (0.177 g, 75%); mp 180–182 °C, R_f (20% ethyl acetate in hexane) 0.66; IR (neat, cm^{-1}): 3101, 2918, 1733, 1550, 1412, 1351, 1249, 1183, 1122, 934, 816; δ_H NMR (500 MHz, $CDCl_3$): 7.63–7.62 (m, 2H, Ar–H), 7.36–7.28 (m, 5H, Ar–H), 6.38 (s, 1H), 2.46 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.10, 154.62, 153.06, 140.29, 134.63, 131.59, 129.78, 129.39, 128.25, 120.76, 119.03, 116.94, 115.78, 21.37; ESI (HRMS) (*m*/*z*) calcd for $C_{16}H_{12}BrO_2$ $[M+H]^+$ 315.0021, found: 315.0024.

4.3.32. 6-Bromo-4-(4-ethoxyphenyl)-2H-chromen-2-one (***4.7***). White solid (0.185 g, 71%); mp 170–172 °C, R_f (20% ethyl acetate in hexane) 0.62; IR (neat, cm^{-1}): 3045, 2976, 1729, 1608, 1513, 1353, 1308, 1255, 1181, 1044, 819; δ_H NMR (500 MHz, $CDCl_3$): 7.66 (d, *J*=2.3 Hz, 1H, Ar–H), 7.62 (dd, *J*=2.3, 8.9 Hz, 1H, Ar–H), 7.37 (d, *J*=8.9 Hz, 2H, Ar–H), 7.28 (d, *J*=8.9 Hz, 1H, Ar–H), 7.04 (d, *J*=8.6 Hz, 2H, Ar–H), 6.36 (s, 1H), 4.12 (q, *J*=7.0 Hz, 2H), 1.47 (t, *J*=7.0 Hz, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.43, 160.20, 154.28, 153.06, 134.55, 129.81, 129.39, 126.45, 120.79, 119.05, 116.90, 115.37, 114.99, 63.70, 14.75; ESI (HRMS) (*m*/*z*) calcd for $C_{17}H_{14}BrO_3$ $[M+H]^+$ 345.0126, found: 345.0124.

4.3.33. 6-Bromo-4-(4-methoxyphenyl)-2H-chromen-2-one (***4.8***). White solid (0.174 g, 70%); mp 168–170 °C, R_f (20% ethyl acetate in hexane) 0.52; IR (neat, cm^{-1}): 3073, 2926, 2832, 1731, 1600, 1508, 1353, 1249, 1180, 816; δ_H NMR (500 MHz, $CDCl_3$): 7.66–7.62 (m, 2H, Ar–H), 7.39 (d, *J*=7.95 Hz, 2H, Ar–H), 7.28 (d, *J*=8.85 Hz, 1H, Ar–H), 7.06 (d, *J*=8.85 Hz, 2H, Ar–H), 6.36 (s, 1H), 3.90 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 161.04, 160.15, 154.23, 153.09, 134.59, 129.83, 129.38, 126.69, 120.81, 119.07, 116.92, 115.48, 114.56, 55.46; ESI (HRMS) (*m*/*z*) calcd for $C_{16}H_{12}BrO_3$ $[M+H]^+$ 330.9970, found: 330.9971.

4.3.34. 6,8-Dibromo-4-phenyl-2H-chromen-2-one (***4.9***). White solid (0.152 g, 53%); mp 180–182 °C, R_f (20% ethyl acetate in hexane) 0.68; IR (neat, cm^{-1}): 3069, 1735, 1538, 1433, 1221, 1150, 751, 701; δ_H NMR (500 MHz, $CDCl_3$): 7.91 (d, *J*=2.45 Hz, 1H, Ar–H), 7.56–7.55 (m, 3H, Ar–H), 7.52 (d, *J*=2.15 Hz, 1H, Ar–H), 7.42–7.40 (m, 2H, Ar–H), 6.41 (s, 1H); δ_C NMR (125 MHz, $CDCl_3$): 158.85, 154.40, 150.01, 137.53, 134.13, 130.18, 129.19, 128.72, 128.27, 121.57, 116.80, 116.65, 111.95; ESI (HRMS) (*m*/*z*) calcd for $C_{15}H_9Br_2O_2$ $[M+H]^+$ 380.8949, found: 380.8954.

4.3.35. 6,8-Dibromo-4-p-tolyl-2H-chromen-2-one (***4.10***). White solid (0.192 g, 65%); mp 196–198 °C, R_f (20% ethyl acetate in hexane) 0.68; IR (neat, cm^{-1}): 3069, 1735, 1538, 1433, 1221, 1150, 751, 701; δ_H NMR (500 MHz, $CDCl_3$): 7.90 (d, *J*=2.15 Hz, 1H, Ar–H), 7.56 (d, *J*=2.4 Hz, 1H, Ar–H), 7.35–7.29 (m, 4H, Ar–H), 6.39 (s, 1H), 2.46 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 158.97, 154.49, 150.03, 140.52, 137.44, 131.25, 129.86, 128.80, 128.23, 121.70, 116.73, 116.32, 111.91, 21.39; ESI (HRMS) (*m*/*z*) calcd for $C_{16}H_{11}Br_2O_2$ $[M+H]^+$ 394.9105, found: 394.9103.

4.3.36. 6,8-Dibromo-4-(4-ethoxyphenyl)-2H-chromen-2-one (***4.11***). White solid (0.223 g, 71%); mp 154–156 °C, R_f (20% ethyl acetate in hexane) 0.62; IR (neat, cm^{-1}): 3082, 2977, 2878, 1742, 1605, 1511, 1253, 1174, 1042, 873; δ_H NMR (500 MHz, $CDCl_3$): 7.89 (d, *J*=2.15 Hz, 1H, Ar–H), 7.60 (d, *J*=2.1 Hz, 1H, Ar–H), 7.35 (d, *J*=8.55 Hz, 2H, Ar–H), 7.04 (d, *J*=8.85 Hz, 2H, Ar–H), 6.38 (s, 1H), 4.12 (q, *J*=7.0 Hz, 2H), 1.47 (t, *J*=7.05 Hz, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.57, 159.05, 154.16, 150.06, 137.38, 129.83, 128.82, 126.12, 121.78, 116.68, 115.94, 115.08, 111.93, 63.76, 14.74; ESI (HRMS) (*m*/*z*) calcd for $C_{17}H_{13}Br_2O_3$ $[M+H]^+$ 424.9211, found: 424.9216.

4.3.37. 6,8-Dibromo-4-(4-methoxyphenyl)-2H-chromen-2-one (***4.12***). White solid (0.231 g, 75%); mp 156–158 °C, R_f (20% ethyl acetate in hexane) 0.54; IR (neat, cm^{-1}): 3074, 2932, 2841, 1742, 1605, 1513, 1253, 1179, 843; δ_H NMR (500 MHz, $CDCl_3$): 7.90 (d, *J*=2.15 Hz, 1H, Ar–H), 7.60 (d, *J*=2.15 Hz, 1H, Ar–H), 7.36 (d, *J*=8.55 Hz, 2H, Ar–H), 7.06 (d, *J*=8.85 Hz, 2H, Ar–H), 6.38 (s, 1H), 3.90 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 161.17, 159.01, 154.09, 150.07, 137.40, 129.85, 128.79, 126.32, 121.76, 116.70, 116.02, 114.64, 111.94, 55.48; ESI (HRMS) (*m*/*z*) calcd for $C_{16}H_{11}Br_2O_3$ $[M+H]^+$ 410.9054, found: 410.9063.

4.3.38. 4,6-Bis(-p-tolyl)-2H-chromen-2-one (***5.1***). White solid (0.076 g, 62%); mp 110–112 °C, R_f (30% ethyl acetate in hexane) 0.81; IR (neat, cm^{-1}): 3029, 2921, 1728, 1610, 1557, 1361, 1259, 1179, 931, 825, 805; δ_H NMR (500 MHz, $CDCl_3$): 7.74 (d, *J*=8.55 Hz, 1H, Ar–H), 7.68 (s, 1H, Ar–H), 7.46 (d, *J*=8.55 Hz, 1H, Ar–H), 7.40–7.33 (m, 6H, Ar–H), 7.22 (d, *J*=8.25, 2H, Ar–H), 6.39 (s, 1H), 2.46 (s, 3H), 2.37 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.85, 155.78, 153.41, 139.93, 137.53, 137.44, 136.82, 132.25, 130.61, 129.62, 128.37, 126.91, 125.04, 119.19, 117.61, 115.14, 21.36, 21.05; ESI (HRMS) (*m*/*z*) calcd for $C_{23}H_{19}O_2$ $[M+H]^+$ 327.1385, found: 327.1380 .

4.3.39. 4,6-Bis(4-methoxyphenyl)-2H-chromen-2-one[18] (***5.2***). Pale yellow solid (0.086 g, 64%); mp 148–150 °C, R_f (30% ethyl acetate in hexane) 0.47; IR (neat, cm^{-1}): 2924, 1727, 1610, 1515, 1302, 1247, 1184, 1027, 942, 811; δ_H NMR (500 MHz, $CDCl_3$): 7.71 (dd, *J*=2.45, 8.55 Hz, 1H, Ar–H), 7.68 (d, *J*=2.1 Hz, 1H, Ar–H), 7.46–7.40 (m, 5H, Ar–H), 7.05 (d, *J*=8.55, 2H, Ar–H), 6.95 (d, *J*=8.85 Hz, 2H, Ar–H), 6.37 (s, 1H), 3.89 (s, 3H), 3.83 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.93, 160.80, 159.37, 155.38, 153.22, 137.08, 132.16, 130.35, 129.92, 128.09, 127.42, 124.67, 119.25, 117.63, 114.84, 114.37, 55.42, 55.35; ESI (HRMS) (*m*/*z*) calcd for $C_{23}H_{19}O_4$ $[M+H]^+$ 359.1283, found: 359.1283.

4.3.40. 4,6-Bis(4-ethoxyphenyl)-2H-chromen-2-one (***5.3***). Pale yellow solid (0.087 g, 60%); mp 120–122 °C, R_f (30% ethyl acetate in hexane) 0.70; IR (neat, cm^{-1}): 3064, 2979, 2924, 1736, 1607, 1512, 1477, 1391, 1249, 1182, 1118, 1048, 923, 841, 807; δ_H NMR (500 MHz, $CDCl_3$): 7.72–7.69 (m, 2H, Ar–H), 7.45–7.39 (m, 5H, Ar–H), 7.04 (d, *J*=8.55 Hz, 2H, Ar–H), 6.94 (d, *J*=8.85, 2H, Ar–H), 6.37 (s, 1H), 4.12 (q, *J*=6.9 Hz, 2H), 4.06 (q, *J*=7.0 Hz, 2H), 1.47 (t, *J*=7.0 Hz, 3H), 1.43 (t, *J*=7.0 Hz, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.96, 160.22, 158.75, 155.45, 153.20, 137.11, 131.99, 130.32, 129.92, 128.06, 127.25, 124.65, 119.26, 117.61, 114.89, 114.82, 114.78, 63.66, 63.54, 14.80; ESI (HRMS) (*m*/*z*) calcd for $C_{25}H_{23}O_4$ $[M+H]^+$ 387.1596, found: 387.1599.

4.3.41. 4,6-Bis(4-(benzyloxy)phenyl)-2H-chromen-2-one (***5.4***). Pale yellow solid (0.106 g, 55%); mp 170–172 °C, R_f (30% ethyl acetate in hexane) 0.60; IR (neat, cm^{-1}): 3035, 2926, 2869, 1710, 1606, 1510, 1384, 1365, 1241, 1183, 1012, 823, 749, 702; δ_H NMR (500 MHz, $CDCl_3$):

7.72–7.68 (m, 2H, Ar–H), 7.48–7.33 (m, 15H, Ar–H), 7.13 (d, J=8.55 Hz, 2H, Ar–H), 7.03 (d, J=8.55, 2H, Ar–H), 6.37 (s, 1H), 5.15 (s, 2H), 5.10 (s, 2H); δ_C NMR (125 MHz, $CDCl_3$): 160.92, 160.03, 158.58, 155.34, 153.26, 137.06, 136.75, 136.39, 132.43, 130.39, 129.96, 128.70, 128.64, 128.23, 128.14, 128.06, 127.70, 127.53, 127.41, 124.68, 119.25, 117.66, 115.30, 115.27, 114.92, 70.19, 70.08; ESI (HRMS) (m/z) calcd for $C_{35}H_{27}O_4$ $[M+H]^+$ 511.1909, found: 511.1909.

*4.3.42. 8-Bromo-4,6-bis(4-methoxyphenyl)-2H-chromen-2-one (**6.1**) and 6-bromo-4,8-bis(4-methoxyphenyl)-2H-chromen-2-one (**6.2**).* Pale yellow solid (0.096 g, 58%); R_f (30% ethyl acetate in hexane) 0.85; IR (neat, cm^{-1}): 1731, 1607, 1512, 1451, 1249, 1178, 1033, 825, 782; δ_H NMR (400 MHz, $CDCl_3$): 7.95 (d, J=2.04 Hz, 1H, Ar–H), 7.67 (d, J=2.28 Hz, 1H, Ar–H), 7.61 (d, J=2.04 Hz, 1H, Ar–H), 7.58 (d, J=2.52 Hz, 1H, Ar–H), 7.55–7.53 (m, 2H, Ar–H), 7.43–7.37 (m, 6H, Ar–H), 7.08–7.00 (m, 6H, Ar–H), 6.95–6.93 (m, 2H, Ar–H), 6.38 (s, 1H), 6.37 (s, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 3.87 (s, 3H), 3.83 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.96, 159.89, 159.82, 159.73, 155.19, 154.68, 149.99, 149.76, 137.82, 135.21, 133.65, 132.37, 130.91, 130.73, 129.93, 129.86, 128.10, 127.95, 127.07, 126.91, 124.04, 121.24, 120.60, 116.79, 115.46, 115.42, 114.53, 114.46, 114.08, 111.19, 55.44, 55.37; ESI (HRMS) (m/z) calcd for $C_{23}H_{18}BrO_4$ $[M+H]^+$ 437.0388, found: 437.0382.

*4.3.43. 4,6,8-Tris(4-methoxyphenyl)-2H-chromen-2-one (**6.3**).* Off white solid (0.006 g, 5%); mp 198–200 °C, R_f (30% ethyl acetate in hexane) 0.70; IR (neat, cm^{-1}): 1724, 1608, 1574, 1450, 1376, 1291, 1247, 1178, 1031, 831; δ_H NMR (400 MHz, $CDCl_3$): 7.75 (d, J=2.04 Hz, 1H, Ar–H), 7.63–7.61 (m, 3H, Ar–H), 7.47–7.44 (m, 4H, Ar–H), 7.05 (t, J=9.04 Hz, 4H, Ar–H), 6.95 (d, J=8.92 Hz, 2H, Ar–H), 6.38 (s, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.83 (s, 3H); δ_C NMR (125 MHz, $CDCl_3$): 160.76, 160.60, 159.51, 159.42, 155.78, 150.07, 136.74, 132.21, 131.48, 130.78, 130.65, 129.96, 128.34, 128.13, 127.84, 123.56, 119.82, 114.89, 114.37, 114.01, 55.42, 55.36; ESI (HRMS) (m/z) calcd for $C_{30}H_{25}O_5$ $[M+H]^+$ 465.1702, found: 465.1708.

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Supplementary data

^1H and ^{13}C NMR for all the products (**2.1**–**2.12**, **3.1**–**3.30**, **4.1**–**4.12**, **5.1**–**5.4**, and **6.1**–**6.3**). Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2014.07.059.

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