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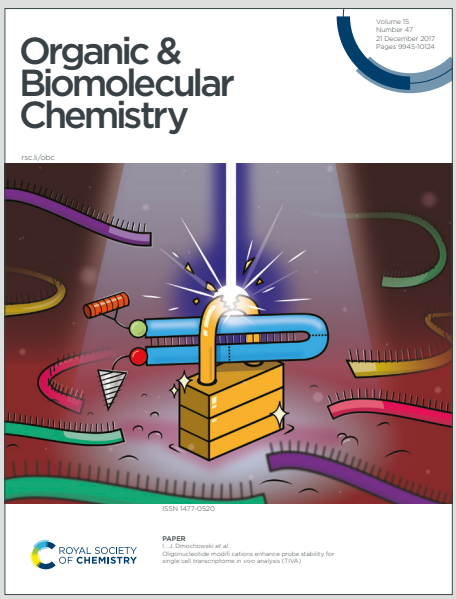

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An efficient tandem synthesis of chromones from *o*-bromoaryl ynones and benzaldehyde oxime

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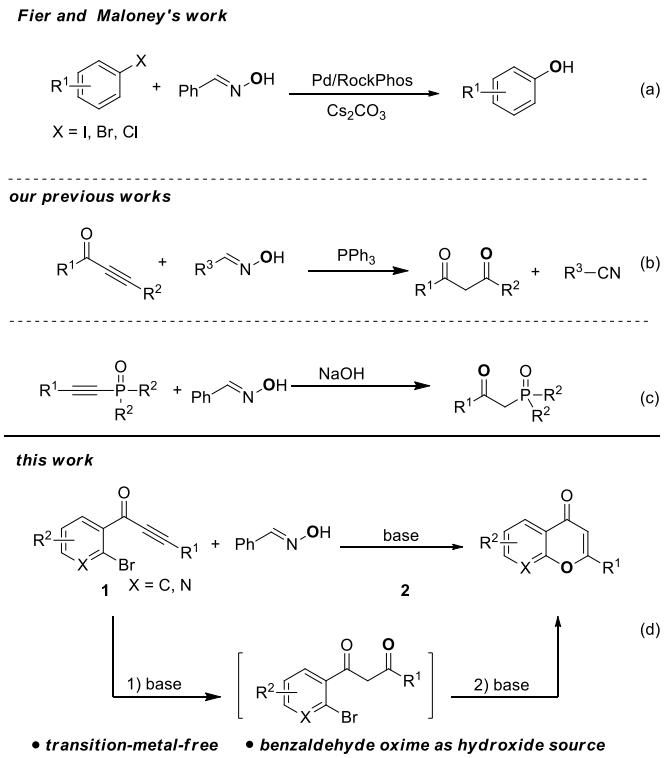
An effective transition-metal-free strategy was developed for the preparation of chromones from *o*-bromoaryl ynones and benzaldehyde oxime through the sequential C-O bond forming. This cyclization reaction could well tolerate a wide range of functional groups, and the corresponding chromones were given in moderate to excellent yields. Mechanistically, benzaldehyde oxime as hydroxide source and 1,3-diketone derivatives as reaction intermediates were involved in this transformation.

Introduction

Chromones as important six-membered oxygen heterocycle compounds, have attracted much attention due to their broad application in natural products and biological activities.[1] The significance of their structures greatly promoted the development of diversified routes for the construction of chromones. Usually, chromones can be prepared by Baker–Venkatamaran rearrangement,[2] Claisen condensation,[3] Kostanecki–Robinson reaction,[4] Vilsmeier–Haack reaction [5] or benzopyrylium salts[6] using 2-hydroxyarylalkyl ketones as starting materials. Alternatively, the Simonis [7] or Ruhemann [8] reactions can be used to synthesize chromones from phenols. Recently, other methods involving intermolecular annulation[9] and intramolecular annulation[10] via C-O bond formations have also been reported. Although those accesses to chromone derivatives have been developed, they often suffer from one or more limitations, such as use of the transition-metal as catalysts, poor substituent tolerance or harsh reaction conditions. Therefore, the exploration of convenient and efficient transition-metal-free synthesis of chromones under mild conditions is highly desirable.

On the other hand, oximes were easily synthesized by the reaction of aldehydes or ketones with hydroxylamine[11] and they as basic building units have been widely used to construct functionalized compounds.[12] More recently, it is noteworthy that Fier and Maloney's group (Scheme 1a) [13] and us[14] (Scheme 1b and 1c) have successfully utilized oximes as hydroxide source. Based on these works, we postulated that the 1-(2-bromoaryl)-propane-1,3-diones, which may be obtained from *o*-bromoaryl ynones and oximes by choosing suitable base, could be transformed into chromones via the intramolecular Ullmann-type O-arylation reaction.[9h, 10d] In continuation of our recent efforts on transition-metal-free catalytic transformation of alkyne,[14, 15] herein, we wish to report a convenient, efficient and transition-metal-free approach for the construction of various chromones from *o*-bromoaryl ynones with benzaldehyde oxime as hydroxide source under mild condition. This system showed broad substrate scope and a series of chromones were successfully afforded in moderate to excellent yields (Scheme 1d).



Scheme 1 Reaction of aryl halides or alkynes with oximes using as a hydroxide surrogate

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† Electronic Supplementary Information (ESI) available: Mechanism study and copies of ^{1}H NMR and ^{13}C NMR spectra for products **2** and **4**; See DOI: 10.1039/x0xx00000x

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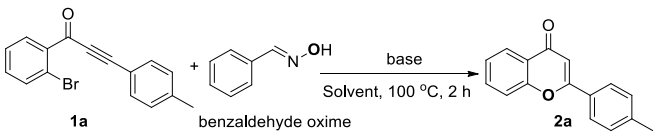
Results and discussion

Table 1. Optimization of reaction conditions for this cyclization reaction [a]

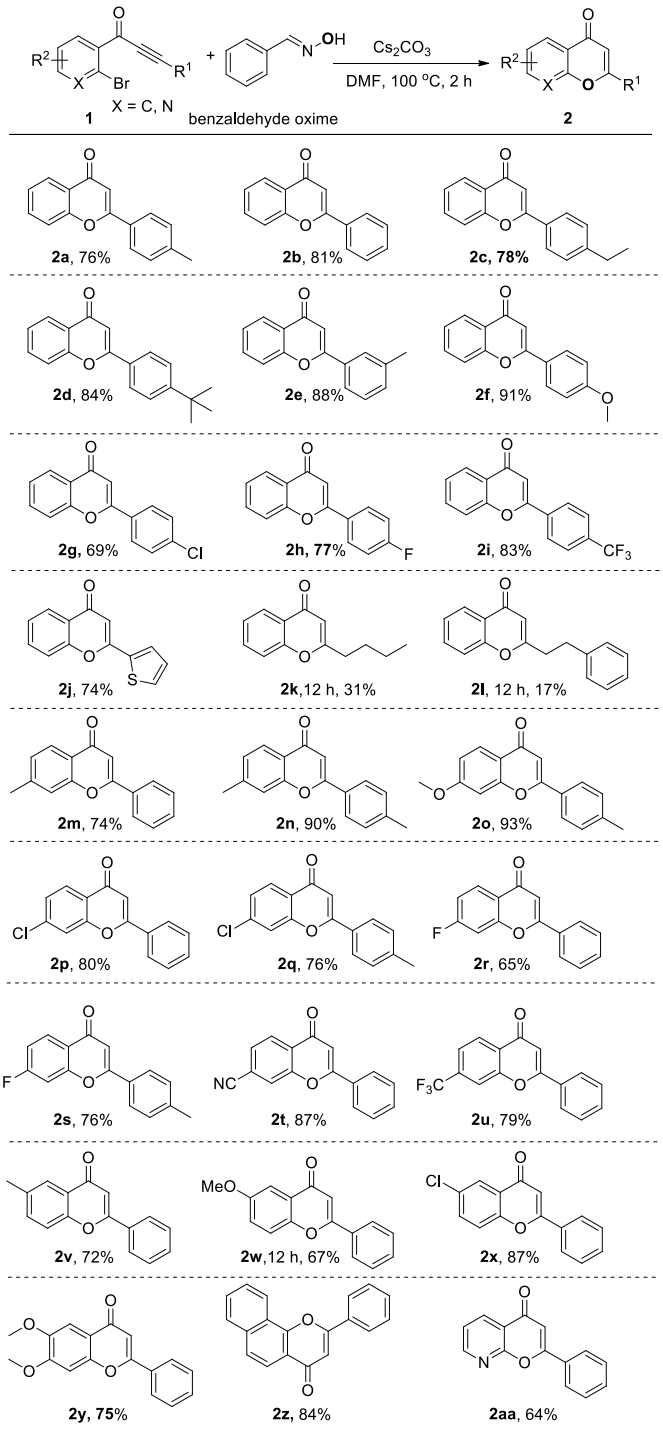


Entry	base (X equiv.)	Solvent	Yield [b] (%)
1	K_2CO_3 (1.5)	DMF	46
2	Cs_2CO_3(1.5)	DMF	69
3	NaOH (1.5)	DMF	30
4	KOH (1.5)	DMF	54
5	NaO^{t}Bu (1.5)	DMF	31
6	KO^{t}Bu (1.5)	DMF	55
7	DBU (1.5)	DMF	50
8	PPh_3 (1.5)	DMF	-
9	-	DMF	-
10	Cs_2CO_3 (1.5)	DMSO	63
11	Cs_2CO_3 (1.5)	NMP	66
12	Cs_2CO_3 (1.5)	CH_3CN	58
13	Cs_2CO_3 (1.5)	Toluene	trace
14	Cs_2CO_3 (1.5)	1,4-dioxane	18
15	Cs_2CO_3 (1.5)	DCE	trace
16	Cs_2CO_3 (2)	DMF	76
17 [c]	Cs_2CO_3 (2)	DMF	61
18 [d]	Cs_2CO_3 (2)	DMF	73

[a]Reaction conditions: **1a** (0.30 mmol, 1.0 equiv), benzaldehyde oxime (0.3 mmol), solvent (1.5 mL), base, 100 °C, 2 h, N_2. [b]Isolated yield. [c]110 °C. [d]90 °C.

Initially, we choose the reaction of o-bromoaryl ynone **1a** with benzaldehyde oxime to determine the optimal conditions and the results are summarized in Table 1. To our delight, when the reaction of o-bromoaryl ynone **1a** with benzaldehyde oxime using 1.5 equiv. amount of K_2CO_3 as base in DMF was attempted, the desired product **2a** was delivered in 46% yield (Table 1, entry 1). Encouraged by the above result, we screened other inorganic or organic base and Cs_2CO_3 shown higher yield (Table 1, entries 2-8). Product **2a** was failed to afford in the absence of base (Table 1, entry 9). Next, other solvents were further examined. DMSO, NMP or CH_3CN proved to be better solvents (Table 1, entries 10-12). Toluene, 1,4-dioxane or DCE were found to be inferior solvents (Table 1, entries 13-15). Gratifyingly, improved yield was achieved when the loading of Cs_2CO_3 was increased (Table 1, entry 16). However, lowering or increasing the temperature failed to improve the yield (Table 1, entries 17-18). Thus, the optimal reaction conditions were obtained as follows: 0.3 mmol **1a**, 0.3 mmol benzaldehyde oxime, 2 equiv. Cs_2CO_3 in 1.5 mL DMF at 100 °C.

Table 2. Scope of substrates [a]



[a]Reaction conditions: 0.3 mmol ynones **1**, 0.3 mmol benzaldehyde oxime, 0.6 mmol Cs_2CO_3, 1.5 mL DMF, 100 °C, 2 h, N_2.

Under the optimized conditions, various o-bromoaryl ynones with benzaldehyde oxime were studied and the experimental results were shown in Table 2. A variety of chromones were synthesized in moderate to excellent yields. When the R^1 substituent was an aromatic group, substrates **1b-1i** having common groups (such as alkyl, ether, halo, and CF_3 group) at *para* or *meta* positions of the

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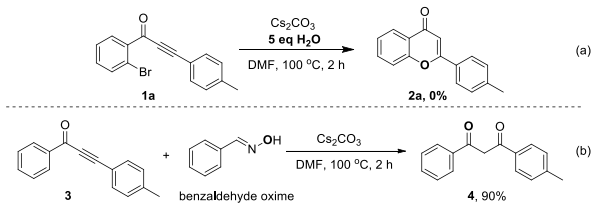
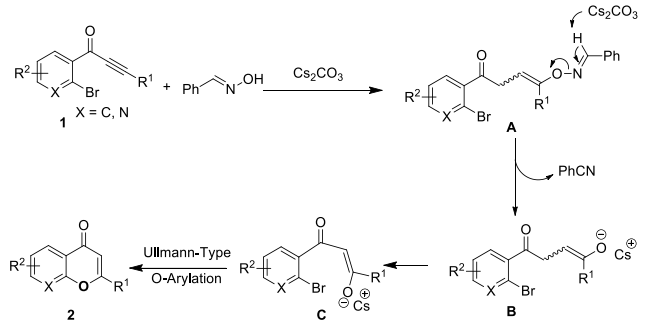
aryl groups could smoothly transform into the corresponding products in high reactivity. The heteroaromatic substrate **1j** could also be suitable to this reaction. Conversely, when the R^1 substituent was an aliphatic group, the substrates **1k-1l** showed lower reactivity. Additionally, when the R^2 substituent was alkyl, ether, halo, cyano, CF_3 or phenyl group at the different position of aromatic ring, the products **2m-2z** were given in good to excellent yields. Furthermore, it was noteworthy that the intramolecular cyclization of 1-(2-bromo-pyridin-3-yl) ynone **1aa** was also tolerated, affording the product **2aa** in 64% yield.

To insight this reaction mechanism, the following control experiments were performed (Scheme 2). When 1-(2-bromophenyl) ynone **1a** reacted with 5 equiv. H_2O under the standard conditions, product **2a** failed to be obtained (Scheme 2a). This could exclude the possible interference of trace water as a hydroxide surrogate in the reaction system. To further prove the 1,3-diketone or its corresponding salt as reaction intermediate, ynone **3** reacted with benzaldehyde oxime under the standard conditions, 1,3-diketone **4** was expectedly obtained in 90% yield (Scheme 2b).



Scheme 2 Control experiments.

Base on the above results and previous literatures,[13-14] a plausible mechanism was proposed and shown in Scheme 3. When substrates **1** reacted with benzaldehyde oxime in the presence of Cs_2CO_3, intermediates **A** were afforded by an O-aza Michael addition. Subsequently, the intermediates **B** were obtained by elimination of benzonitrile and benzonitrile was detected by MS (see Fig. S1 in the ESI† for details). Finally, intermediates **B** tautomerize to give the intermediates **C**, which was suitable to the intramolecular Ullmann-type O-arylation reaction to give products **2**. 9h, 10d



Scheme 3 Plausible mechanism for this cyclization reaction of o-bromoaryl ynones with benzaldehyde oxime.

Conclusions

In summary, we have developed a simple and efficient transition-metal-free method for the preparation of chromones from *o*-bromoaryl ynones and benzaldehyde oxime as hydroxide source under mild conditions. Various functionalized chromones could be afforded in moderate to excellent yields. This protocol sequentially underwent the Michael addition and Ullmann-type *O*-arylation reaction for constructing two C-O bonds to deliver chromones. On the other hand, further utility of oximes as hydroxide surrogate in the preparation of other useful organic chemicals continue to be the focus of efforts in our laboratory.

Experimental

Unless otherwise statement, all manipulations were performed using standard Schlenk techniques under a dry nitrogen atmosphere. NMR spectra were recorded with tet-ramethylsilane as the internal standard. NMR spectra were recorded on a BrukerAvanceII400M type (^{1}H NMR, 400 MHz; ^{13}C NMR, 100 MHz) spectrometer. 1,4-Dioxane was distilled from sodium/ benzophenone under N_2 atmosphere. Acetonitrile was distilled from phosphorus pentoxide under N_2 atmosphere. DCE, DMSO, DMF and NMP were distilled from calcium hydride under N_2 atmosphere. Substrates **1** were prepared according to the corresponding literatures.[16]

*General Procedure for the Synthesis of Products **2***

General Procedure: A 10 mL oven-dried Schlenck tube was successively charged with 0.30 mmol ynones **1**, 0.30 mmol benzaldehyde oxime, 0.6 mmol Cs_2CO_3 and 1.5 mL DMF. The tube was sealed and the reaction mixture was stirred at 100 °C for 2-12 h. After completion of this reaction and cooling to room temperature, the mixture was diluted with ethyl acetate (10 mL) and washed with brine (10 mL). The aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in-vacuo. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give products **2**.

2-(*p*-Tolyl)-4*H*-chromen-4-one (2a):[9f] white solid (76% yield); mp 112.6-114.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.21 (d, *J* = 8.0 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 2.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.5, 163.6, 156.3, 142.3, 133.7, 129.8, 128.9, 126.2, 125.7, 125.2, 124.0, 118.1, 107.0, 21.6.

2-Phenyl-4*H*-chromen-4-one (2b):[9f] white solid (81% yield); mp 100.3-102.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.23 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.93–7.91 (m, 2H), 7.71–7.67 (m, 1H), 7.57–7.49 (m, 4H), 7.41 (t, *J* = 7.6 Hz, 1H), 6.82 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.5, 163.5, 156.4, 133.9, 131.9, 131.7, 129.1, 126.4, 125.8, 125.3, 124.1, 118.2, 107.7.

2-(4-Ethylphenyl)-4*H*-chromen-4-one (2c):[9e] slight yellow solid (78% yield); mp 106.8-108.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.68 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.43–7.39 (m, 1H), 7.34 (d, *J*

= 8.4 Hz, 2H), 6.80 (s, 1H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.5, 163.7, 156.3, 148.6, 133.7, 129.2, 128.7, 126.4, 125.7, 125.2, 124.1, 118.1, 107.1, 28.9, 15.3.

2-(4-(Tert-butyl)phenyl)-4*H*-chromen-4-one (2d):[9l] white solid (84% yield); mp 97.2-98.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.21 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.86–7.83 (m, 2H), 7.66 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.55–7.51 (m, 3H), 7.40–7.37 (m, 1H), 6.79 (s, 1H), 1.35 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.5, 163.6, 156.3, 155.4, 133.7, 129.0, 126.2, 126.1, 125.7, 125.2, 124.1, 118.1, 107.1, 35.1, 31.2.

2-(m-Tolyl)-4*H*-chromen-4-one (2e):[9l] white solid (88% yield); mp 107.1-108.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.72–7.66 (m, 3H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.40 (ddd, *J* = 8.0, 4.4, 2.0 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 1H), 6.80 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.6, 163.7, 156.4, 139.0, 133.8, 132.5, 131.9, 129.1, 127.0, 125.8, 125.3, 124.1, 123.6, 118.2, 107.7, 21.6.

2-(4-Methoxyphenyl)-4*H*-chromen-4-one (2f):[10c] white solid (91% yield); mp 150.3-152.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.89–7.86 (m, 2H), 7.68 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.54 (d, *J* = 8.4 Hz, 1H), 7.42–7.38 (m, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.74 (s, 1H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.4, 163.4, 162.4, 156.2, 133.6, 128.0, 125.7, 125.1, 124.0, 123.9, 118.0, 114.5, 106.2, 55.5.

2-(4-Chlorophenyl)-4*H*-chromen-4-one (2g):[10c] light yellow solid (69% yield); mp 177.8-179.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.87–7.84 (m, 2H), 7.70 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.51–7.48 (m, 2H), 7.42 (dd, *J* = 11.2, 4.0 Hz, 1H), 6.78 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.3, 162.3, 156.2, 138.0, 134.0, 130.3, 129.5, 127.6, 125.8, 125.5, 124.0, 118.1, 107.7.

2-(4-Fluorophenyl)-4*H*-chromen-4-one (2h):[9j] slight yellow solid (77% yield); mp 134.6-136.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.20 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.93–7.88 (m, 2H), 7.68 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.42–7.38 (m, 1H), 7.23–7.17 (m, 2H), 6.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.3, 164.8 (d, $J_{C\text{-}F}$ = 251.7 Hz), 162.4, 156.2, 133.9, 128.6 (d, $J_{C\text{-}F}$ = 8.8 Hz), 128.0 (d, $J_{C\text{-}F}$ = 3.2 Hz), 125.8, 125.4, 123.9, 118.1, 116.4 (d, $J_{C\text{-}F}$ = 22 Hz), 107.4.

2-(4-(Trifluoromethyl)phenyl)-4*H*-chromen-4-one (2i):[9k] light brown oil (83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.24 (dd, *J* = 8.0, 1.6 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 7.73 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.48–7.42 (m, 1H), 6.87 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.1, 161.6, 156.2, 135.1 (q, $J_{C\text{-}F}$ = 1.5 Hz), 134.1, 133.1 (q, $J_{C\text{-}F}$ = 32.8 Hz), 126.6, 126.0 (q, $J_{C\text{-}F}$ =3.8 Hz), 125.8, 125.5, 123.9, 123.5 (q, $J_{C\text{-}F}$ = 272.8 Hz), 118.1, 108.7.

2-(Thiophen-2-yl)-4*H*-chromen-4-one (2j):[9e] light yellow solid (74% yield); mp 124.6-126.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.21 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.73 (d, *J* = 3.6 Hz, 1H), 7.71–7.64 (m, 1H), 7.58 (d, *J* = 4.9 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.23–7.15 (m, 1H), 6.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.9, 159.1, 156.0, 135.3, 133.8, 130.3, 128.6, 128.5, 125.8, 125.4, 124.1, 118.0, 106.3.

2-Butyl-4*H*-chromen-4-one (2k):[9e] light yellow oil (31% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.17 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.63 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.38–7.34 (m, 1H), 6.16 (s, 1H), 2.61 (t, *J* = 8.0 Hz, 2H), 1.72 (dt, *J* = 15.2, 7.6 Hz, 2H), 1.42 (dd, *J* = 15.2, 7.6 Hz, 2H), 0.95 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.5, 170.0, 156.6, 133.5, 125.8, 125.0, 123.9, 118.0, 109.9, 34.2, 29.0, 22.2, 13.9.

2-Phenethyl-4*H*-chromen-4-one (2l):[2e] light yellow oil (17% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.18 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.65 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 7.44– 7.36 (m, 2H), 7.29 (dd, *J* = 10.0, 4.8 Hz, 2H), 7.22 (dd, *J* = 10.4, 4.4 Hz, 3H), 6.15 (s, 1H), 3.07 (t, *J* = 7.6 Hz, 2H), 2.93 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.4, 168.5, 156.6, 139.8, 133.6, 128.8, 128.4, 126.7, 125.8, 125.1, 123.9, 117.9, 110.4, 36.2, 33.1.

7-Methyl-2-phenyl-4*H*-chromen-4-one (2m):[9p] yellow solid (74% yield); mp 124.8-126.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.09 (d, *J* = 8.0 Hz, 1H), 7.90 (dd, *J* = 7.2, 2.4 Hz, 2H), 7.52–7.49 (m, 3H), 7.36 (s, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 6.79 (s, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.5, 163.2, 156.5, 145.2, 132.0, 131.6, 129.1, 126.8, 126.3, 125.6, 121.8, 118.0, 107.7, 22.0.

7-Methyl-2-(p-tolyl)-4*H*-chromen-4-one (2n): [9p] yellow solid (90% yield); mp 186.6-188.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.08 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.33 (s, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.20 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.74 (s, 1H), 2.48 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.5, 163.4, 156.4, 145.0, 142.2, 129.8, 129.1, 126.7, 126.2, 125.5, 121.8, 117.9, 106.9, 21.9, 21.6.

7-Methoxy-2-(p-tolyl)-4*H*-chromen-4-one (2o):[10d] yellow solid (93% yield); mp 140.6-142.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.13 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.00–6.96 (m, 2H), 6.73 (s, 1H), 3.93 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.9, 164.2, 163.2, 158.0, 142.1, 129.8, 129.0, 127.0, 126.1, 117.9, 114.3, 106.9, 100.5, 55.9, 21.6.

7-Chloro-2-phenyl-4*H*-chromen-4-one (2p):[9i] yellow solid (80% yield); mp 156.2-157.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.15 (d, *J* = 8.4 Hz, 1H), 7.88 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.55–7.49 (m, 3H), 7.37 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.79 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.6, 163.6, 156.4, 139.8, 131.9, 131.4, 129.2, 127.2, 126.4, 126.2, 122.6, 118.3, 107.8.

7-Chloro-2-(p-tolyl)-4*H*-chromen-4-one (2q):[9i] yellow solid (76% yield); mp 201.3-202.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.15 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.59 (s, 1H), 7.35 (dd, *J* = 15.5, 8.3 Hz, 3H), 6.78 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.7, 163.9, 156.5, 142.7, 139.8, 130.0, 128.7, 127.2, 126.4, 126.1, 122.7, 118.3, 107.3, 21.7.

7-Fluoro-2-phenyl-4*H*-chromen-4-one (2r):[10j] white solid (65%

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yield); mp 100.2-101.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.25 (dd, *J* = 8.8, 6.4 Hz, 1H), 7.92–7.89 (m, 2H), 7.56– 7.52 (m, 3H), 7.26 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.15 (td, *J* = 8.8, 2.4 Hz, 1H), 6.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.6, 165.8 (d, J_{C-F} = 253.4 Hz), 163.8, 157.4 (d, J_{C-F} = 13.3 Hz), 131.9, 131.5, 129.2, 128.4 (d, J_{C-F} = 10.6 Hz), 126.4, 120.94 (d, J_{C-F} = 2.3 Hz), 114.1 (d, J_{C-F} = 22.6 Hz), 107.8, 104.9 (d, J_{C-F} = 25.2 Hz).

7-Fluoro-2-(p-tolyl)-4*H*-chromen-4-one (2s): [10c] light yellow solid (76% yield); mp 156.3-158.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.24 (dd, *J* = 8.8, 6.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.26–7.24 (m, 1H), 7.15 (td, *J* = 8.4, 2.4 Hz, 1H), 6.77 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.6, 165.8 (d, J_{C-F} = 253.1 Hz), 164.0, 157.3 (d, J_{C-F} = 13.2 Hz), 142.6, 129.9, 128.7, 128.3 (d, J_{C-F} = 10.5 Hz), 126.3, 121.0 (d, J_{C-F} = 2.3 Hz), 114.0 (d, J_{C-F} = 22.5 Hz), 107.1, 104.9 (d, J_{C-F} = 25.1 Hz), 21.7.

4-Oxo-2-phenyl-4*H*-chromene-7-carbonitrile (2t): white solid (87% yield); mp 184.6–186.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.34 (d, *J* = 8.2 Hz, 1H), 8.02–7.84 (m, 3H), 7.67 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.63–7.49 (m, 3H), 6.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 176.9, 164.3, 155.5, 132.4, 131.0, 129.3, 127.9, 127.3, 126.8, 126.5, 122.9, 117.3, 117.0, 108.3; IR (KBr, cm^{-1}): 3444, 3070, 2924, 2858, 2230, 1646, 1563, 1495, 1425; HRMS (ESI-TOF) calcd for $C_{16}H_{10}NO_2^+$ ([M+H]$^+$): 248.0706, found: 248.0708.

2-Phenyl-7-(trifluoromethyl)-4*H*-chromen-4-one (2u): white solid (79% yield); mp 154.4–156.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.36 (d, *J* = 8.3 Hz, 1H), 7.94 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.89 (s, 1H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.63–7.47 (m, 3H), 6.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.3, 164.1, 155.7, 135.4 (q, *J* = 33.4 Hz), 132.1, 131.2, 129.2, 127.1, 126.4, 126.1, 123.1 (q, *J* = 271.4 Hz), 121.6 (q, *J* = 3.4 Hz), 116.04 (q, *J* = 4.1 Hz), 108.0; IR (KBr, cm^{-1}): 3448, 3069, 2921, 2858, 1645, 1571, 1499, 1443; HRMS (ESI-TOF) calcd for $C_{16}H_{10}F_3O_2^+$ ([M+H]$^+$): 291.0627, found: 291.0628.

6-Methyl-2-phenyl-4*H*-chromen-4-one (2v): [10d] white solid (72% yield); mp 122.1–123.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.02 (s, 1H), 7.93 (dd, *J* = 6.5, 3.1 Hz, 2H), 7.54 (ddd, *J* = 18.5, 9.1, 5.2 Hz, 5H), 6.82 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.7, 163.4, 154.6, 135.3, 135.1, 132.0, 131.6, 129.1, 126.4, 125.1, 123.7, 117.9, 107.5, 21.0.

6-Methoxy-2-phenyl-4*H*-chromen-4-one (2w): [9p] white solid (67% yield); mp 162.7–164.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.02–7.86 (m, 2H), 7.61 (d, *J* = 3.1 Hz, 1H), 7.57–7.46 (m, 4H), 7.30 (dd, *J* = 9.1, 3.1 Hz, 1H), 6.83 (s, 1H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.5, 163.3, 157.1, 151.2, 132.0, 131.6, 129.1, 126.4, 124.7, 123.9, 119.6, 107.0, 105.0, 56.1.

6-Chloro-2-phenyl-4*H*-chromen-4-one (2x): [10d] white solid (87% yield); mp 183.5–185.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ(ppm): 8.20 (d, *J* = 2.5 Hz, 1H), 7.91 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.64 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.54 (dt, *J* = 9.0, 4.4 Hz, 4H), 6.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.1, 163.7, 154.6, 133.9, 131.9, 131.4, 131.2, 129.1, 126.3, 125.2, 124.9, 119.8, 107.5.

6,7-Dimethoxy-2-phenyl-4*H*-chromen-4-one (2y): [10m] yellow solid (75% yield); mp 189.3-190.8 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.11–7.80 (m, 1H), 7.68–7.40 (m, 2H), 6.98 (s, 1H), 6.77 (s, 1H), 4.01 (s, 1H), 3.97 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 177.6, 162.7, 154.5, 152.3, 147.7, 132.0, 131.3, 129.0, 126.1, 117.4, 107.1, 104.4, 99.8, 56.5, 56.4.

2-phenyl-4*H*-benzo[h]chromen-4-one (2z): [10e] yellow solid (84% yield); mp 155.3-156.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.67–8.57 (m, 1H), 8.19 (d, *J* = 8.7 Hz, 1H), 8.04 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.96 (dd, *J* = 6.7, 2.6 Hz, 1H), 7.80 (d, *J* = 8.7 Hz, 1H), 7.77–7.67 (m, 2H), 7.66–7.53 (m, 3H), 6.98 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.2, 162.5, 153.5, 136.0, 131.9, 131.5, 129.2, 129.2, 128.2, 127.1, 126.2, 125.3, 124.1, 122.3, 120.7, 120.2, 108.7.

2-Phenyl-4*H*-pyrano[2,3-b]pyridin-4-one (2aa): [10d] yellow solid (64% yield); mp 92.3-93.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.74 (dd, *J* = 4.6, 2.0 Hz, 1H), 8.63 (dd, *J* = 7.7, 2.0 Hz, 1H), 8.03 (dd, *J* = 7.7, 1.5 Hz, 2H), 7.64–7.52 (m, 3H), 7.49 (dd, *J* = 7.7, 4.6 Hz, 1H), 6.89 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 178.7, 164.1, 160.8, 153.3, 136.4, 132.1, 131.1, 129.1, 126.6, 122.2, 118.8, 107.7.

*General Procedure for the Synthesis of Product **4***

General Procedure: A 10 mL oven-dried Schlenck tube was successively charged with 0.30 mmol ynone **1**, 0.30 mmol benzaldehyde oxime, 0.6 mmol Cs_2CO_3 and 1.5 mL DMF. The tube was sealed and the reaction mixture was stirred at 100 °C for 2 h. After completion of this reaction, the resulting mixture was neutralized with 1N HCl (1 mL). Then, the mixture was diluted with ethyl acetate (10 mL) and washed with brine (10 mL). The aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated in-vacuo. The crude reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc) to give corresponding product **4**.

1-Phenyl-3-(p-tolyl)propane-1,3-dione (4): [14a] white solid (90% yield); mp 79.5–81.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 16.92 (s, 1H), 8.04–7.95 (m, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.51–7.49 (m, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.84 (s, 1H), 2.43 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 186.2, 185.3, 143.4, 135.7, 133.0, 132.4, 129.5, 128.8, 127.4, 127.2, 93.0, 21.8.

Conflicts of interest

There are no conflicts to declare.

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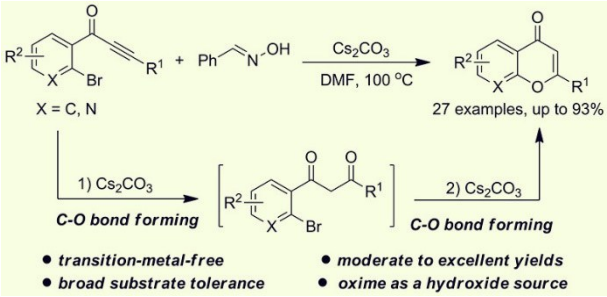

A transition-metal-free approach was developed to synthesize chromones from o-bromoaryl ynones and benzaldehyde oxime by the sequential C-O bond forming.