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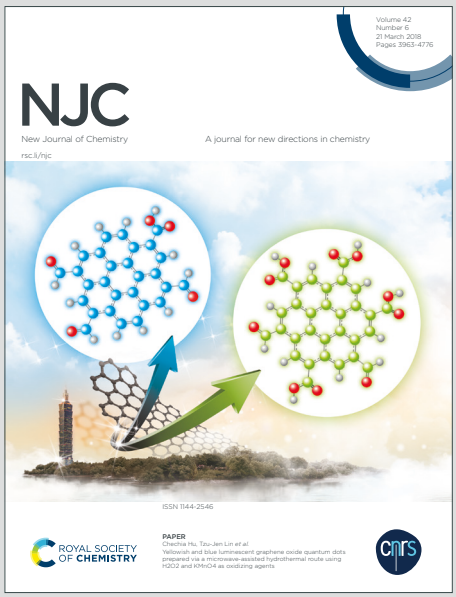

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ARTICLE

Synthesis of 3-halochromones with simple KX halogen sources enabled by in situ halide oxidation

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On the basis of a designated in situ oxidation tactic, the synthesis of 3-halochromones has been realized for the first time by using simple KX (X= Br, I) salts as halogen source. Instead of free radical process, the control experiments indicate that the reported reactions proceed through halogenium intermediate. Comparing with the known synthetic methods relying on molecular halogen, haloid acid or *N*-halosuccinimide as halogen source, the present method is attractive for the higher atom economy, and more friendly to operator, thus providing a practical complimentary approach in the preparation of useful halochromone compounds.

Introduction

Chromone is biologically relevant *O*-containing heterocycle, it is well-known as the central structure of flavone and isoflavonoid natural products.[1] In addition, as privileged skeleton, chromone also plays pivotal roles in drug discovery and organic synthesis.[2] A variety of chromone derivatives have been identified with attractive antibacterial activity,[3] antitumor activity[4] anti-oxidation activity[5] *etc*. The valuable application and unexplored functions of chromone has accordingly triggered significant interests in the research of chromone synthesis. Over the past decades, splendid advances have been witnessed in the synthetic research of chromone synthesis via either direct elaboration on readily available chromone heterocycle or tandem transformations involving chromone ring construction and C-C/C-heteroatom bond formation.[6]

On the other hand, owing to the versatile and indispensable application of C-halogen bond in both organic synthesis and designation of pharmaceuticals, the synthetic works toward C-X bond formation have also received tremendous attention.[7] As a class of featured halogenated molecules, the 3-halochromones have been identified as indispensable structures in the synthesis of isoflavonoids and analogous chromone derivatives.[8] Despite the fact that significant advances have taken place in the synthesis of C3 functionalized chromones, the methods toward the synthesis of 3-halochromones are still underdeveloped. In 1979, Gammill[9] reported the synthesis of 3-halogenated chromones using molecular halogen as halo-source. Larrosa *et al* developed the synthesis of 3-iodochromones via the reactions of 3-carbonxylated chromones and molecular iodine.[10] Kim and co-workers disclosed the synthesis of 3-bromo- and 3-chlorochormones via the C3-H halogenation of chromone using HX acid as halogen source.[11] In addition, Knochel and co-workers reported the switchable synthesis of C2- and C3-iodinated chromones in the presence of zinc agent.[12] Although the synthesis of 3-halogchromones are now accessible by different approaches, one or more of the restrictions remain to prevent these methods from satisfactory application: a) using operator unfriendly and toxic molecular halogen such as Cl_2 and Br_2 as halogen source; b) transition metal catalysis or harsh reaction conditions; c) limited availability of the chromone starting materials. In this context, developing new methods featuring operator friendly and simple halogen source, atom economy and step efficiency is yet highly desirable for the synthesis of 3-halochormones.

Due to the easy availability and good shelf stability, enaminones have in recent years displayed amazingly broad application in the synthesis of diverse organic molecules by acting as key substrates.[13] On the basis of our experience in such type of synthesis and the fact that halogen anion can be in situ oxidized to molecular halogen as disclosed by us and others,[14] we envisaged that it is possible to develop step economical and operator friendly method for 3-halochormones synthesis by employing simple and nontoxic halide salt to react with readily available 2-hydroxylphenyl enaminones. Herein, we report our results on the reactions of 2-hydroxylphenyl enaminones and potassium halides (I and Br) in the presence of $PhI(OAc)_2$ as a practical method for the synthesis of 3-halochromones by employing biomass-based available ethyl lactate (EL)[15] as green medium.

Results and discussion

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Electronic Supplementary Information (ESI) available: [General experimental information, procedure for the chromone product synthesis, ^1H and ^{13}C NMR spectra of all products]. See DOI: 10.1039/x0xx00000x

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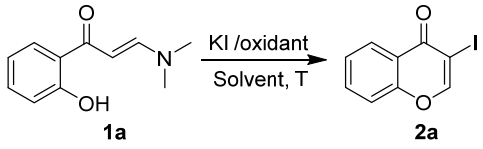
To start the work, the reaction of enaminone **1a** and KI was first examined by heating at 80 °C (reflux) in EtOH in the presence of benzoyl peroxide (BPO), which afforded the target product **2a** with 67% yield (entry 1, Table 1). Successive experiments in lowering the reaction temperature proved that room temperature was more proper for this reaction (entries 2-3, Table 1). Subsequently, a series of different oxidants, including $PhI(OAc)_2$, $K_2S_2O_8$, TBHP and DTBP were screened whereby $PhI(OAc)_2$ exhibited the best effect (entries 4-7, Table 1). Furthermore, different solvents were independently used as the medium of this reaction, and the bio-based green solvent EL was found as amongst the best candidate (entries 8-16, Table 1). On the other hand, reducing the amount of $PhI(OAc)_2$ was accompanied with decrease in the yield of **2a** (entry 17, Table 1).

Table 1 Optimization on reaction conditions[a]

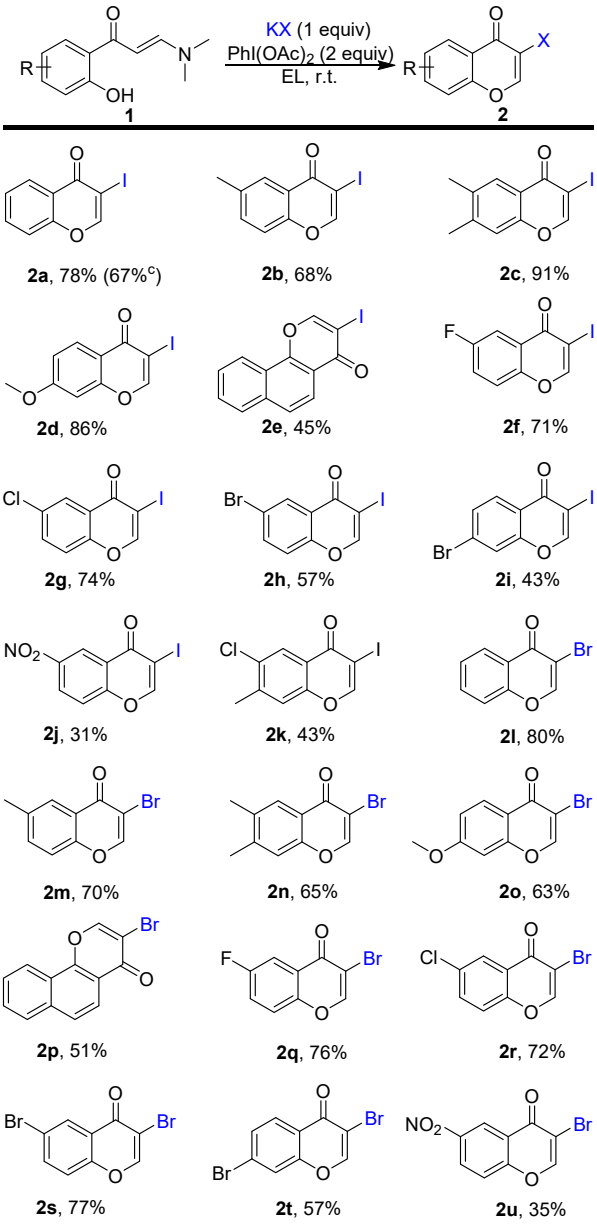


entry	oxidant	*t* (°C)	solvent	Yield (%)[b]
1	BPO	80	EtOH	67
2	BPO	60	EtOH	73
3	BPO	rt	EtOH	75
4	$PhI(OAc)_2$	rt	EtOH	77
5	$K_2S_2O_8$	rt	EtOH	trace
6	TBHP	rt	EtOH	45
7	DTBP	rt	EtOH	trace
8	$PhI(OAc)_2$	rt	EL	78
9	$PhI(OAc)_2$	rt	MeCN	37
10	$PhI(OAc)_2$	rt	p-xylene	43
11	$PhI(OAc)_2$	rt	DMSO	34
12	$PhI(OAc)_2$	rt	water	0
13	$PhI(OAc)_2$	rt	DCM	41
14	$PhI(OAc)_2$	rt	glycol	58
15	$PhI(OAc)_2$	rt	THF	trace
16	$PhI(OAc)_2$	rt	dioxane	32
17[c]	$PhI(OAc)_2$	rt	EL	56

[a]General conditions: **1a** (0.2 mmol), KI (0.2 mmol), oxidant (0.4 mmol) in solvent (2 mL), stirred under air for 12 h. [b]Yield of isolated product based on **1a**. [c]With 0.2 mmol $PhI(OAc)_2$.

With the satisfactory results from the optimization experiments, the application scope of this method was examined by employing different enaminone substrates and potassium halides. As outlined in Table 2, the present method displayed general tolerance to the synthesis of 3-iodochromones (**2a**-**2k**, Table 2) and 3-bromochromones (**2l**-**2u**, Table 2). Generally, the enaminones containing alkyl(s) (**2b**-**2c** and **2m**-**2n**, Table 2), halogen (**2f**-**2i**, **2k** and **2q**-**2t**, Table 1), nitro (**2j** and **2u**, Table 2) in phenyl ring, the enaminones functionalized with fused aryl ring (**2e** and **2p**, Table 2) were all applicable substrates. The majority of products were afforded with good to excellent yield. However, the yields of the products resulting from strong electron withdrawing group (**2j** and **2u**, Table 2) and naphthyl functionalized (**2e** and **2p**, Table 2) enaminones were evidently lower, suggesting the electron withdrawing effect from induction and conjugation were both negative to the titled synthesis. Furthermore, KCl was also employed to reaction with **1a** under the standard reaction conditions, but the 3-chlorochromone product was not formed in the reaction. Notably, conducting the reactions synthesizing **2a** in 5 mmol scale provided good result by affording the product with good yield.

Table 2 Scope on the synthesis of 3-halochromones[a,b]



Conditions: **1** (0.2 mmol), KX (0.2 mmol), $PhI(OAc)_2$ (0.4 mmol) in EL (2 mL), stirred under air for 12 h. [b]Yield of isolated product. [c]The yield from 5 mmol scale.

In order to explore the reaction mechanism, some control experiments were conducted. At first, the model reaction was performed in the presence free radical trapper BHT and TEMPO, respectively (Eqs 1-2), and the formation of product

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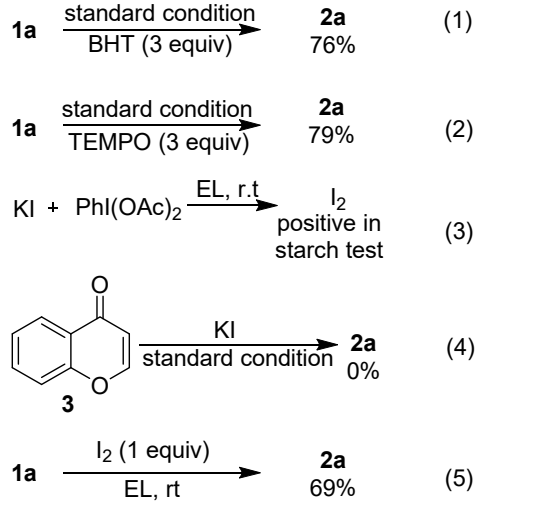
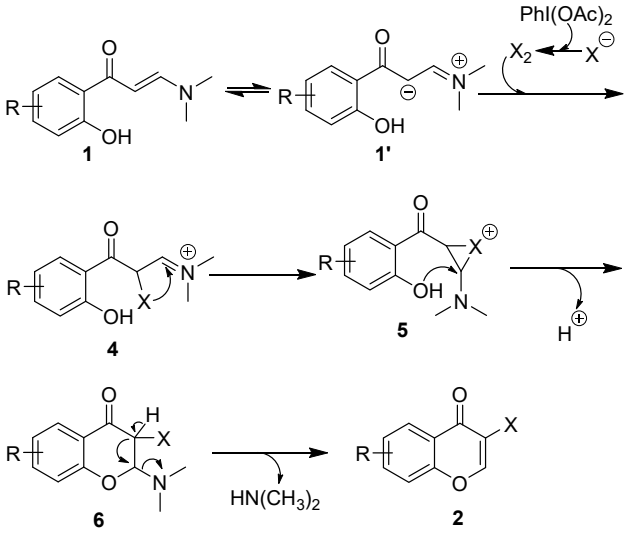
2a was not inhibited. On the other hand, stirring KI and $PhI(OAc)_2$ was proved to generate molecular iodine as observed by the starch test (Eq 3). At last, subjecting chromone **3** and KI to the standard condition did not give product **2a** (Eq 4), indicating that the C-H halogenation takes place before the chromone annulation. Furthermore, using only molecular iodine to react with enaminone **1a** in EL provided product **2a** with high yield (Eq 5), proving that molecular iodine was the effective iodo-source for the production of 3-iodochromone.



With the inspiration of the control experiment results, the reaction mechanism is proposed. As shown in Scheme 1, the oxidation of KX by oxidant provides molecular halgen, which couples to enaminone **1** via its isomeric form **1'** to yield halogenated species **4** by means of electrophilic halogenation. The halogenium ion **5** was generated from **4** and undergoes intramolecular attack by the hydroxyl leads to the formation of intermediate **6**, which gives rise to 3-halochromones **2** via the elimination of dimethylamine.



Scheme 1 The plausible reaction mechanism

Conclusions

In summary, we have developed a facile method for 3-halochromone synthesis by using easily available 2-hydroxylphenyl enaminones and potassium halides as starting materials. The key point enabling such synthesis is the successful in situ oxidation of halogen anion to molecular halogen in the presence of $PhI(OAc)_2$ oxidant. In addition to the facile operation and simple materials, the present synthetic approach possessing individual advantages of biomass-based green medium as well as ambient reaction conditions. The work thus provides a practical access to important 3-halochromones as complementary option to those known methods.

Experimental section

General procedure for the synthesis of products 2

To a 25 mL round bottom flask were charged with enaminone **1** (0.2 mmol), KX (X = Br or I, 0.2 mmol), $PhI(OAc)_2$ (0.4 mmol), and EL (2 mL). The mixture was then stirred at room temperature for 12 h. Upon completion, 5 mL of water and 5 mL ethyl acetate was added to the flask, and the resulting mixture was extracted with ethyl acetate (3 × 8 mL). The organic phases were collected and dried with anhydrous Na_2SO_4. After filtration, the resulting solution was employed to reduced pressure to remove the solvent. The acquired residue was subjected to flash silica gel column chromatography to provide pure products by elution with mixed petroleum ether/ethyl acetate (v/v = 50:1).

Procedure for the scale-up synthesis of 2a

To a 50 mL round bottom flask were added enaminone **1a** (5 mmol), KI (5 mmol), $PhI(OAc)_2$ (10 mmol), and EL (8 mL). The mixture was then stirred at room temperature for 12 h. Upon completion, 15 mL of water and 15 mL ethyl acetate was added to the flask, and the resulting mixture was extracted with ethyl acetate (3 × 20 mL). The organic phases were collected and dried with anhydrous Na_2SO_4. After filtration, the resulting solution was employed to reduced pressure to remove the solvent. The resulting residue was purified by silica gel flash column chromatography by using mixed petroleum ether and ethyl acetate (v/v = 50/1) as eluent to provide pure product.

3-Iodo-4*H*-chromen-4-one (**2a**).[7f] Yield 78% (42.4 mg); white solid; mp 88-89 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1 H), 8.23 (d, *J* = 8.0 Hz, 1 H), 7.71 (t, *J* = 7.8 Hz, 1 H), 7.48-7.42 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 173.3, 157.7, 156.1, 134.1, 126.6, 125.9, 121.8, 118.0, 86.8.

3-Iodo-6-methyl-4*H*-chromen-4-one (**2b**).[8a] Yield 68% (38.8 mg); white solid; mp 130-131 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1 H), 7.99 (s, 1 H), 7.50 (dd, *J* = 8.6, 2.0 Hz, 1 H), 7.35 (d, *J* = 8.6 Hz, 1 H), 2.45 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 173.3, 157.6, 154.4, 136.0, 135.3, 125.8, 121.5, 117.7, 86.6, 21.

3-Iodo-6,7-dimethyl-4*H*-chromen-4-one (**2c**).[9] Yield 91% (54.6 mg); white solid; mp 156-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1 H), 7.92 (s, 1 H), 7.20 (s, 1 H), 2.36 (s, 3 H), 2.34 (s, 3

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H); ^{13}C NMR (100 MHz, $CDCl_3$): 173.2, 157.4, 154.7, 144.7, 135.4, 126.0, 119.6, 118.0, 86.7, 20.5, 19.4.

3-Iodo-7-methoxy-4*H*-chromen-4-one (**2d**).[8c] Yield 86% (51.9 mg); white solid; mp 157-158 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1 H), 8.13 (d, *J* = 9.0 Hz, 1 H), 6.99 (dd, *J* = 8.8, 2.4 Hz, 1 H), 6.83 (d, *J* = 2.4 Hz, 1 H), 3.91 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 172.6, 164.3, 157.9, 157.2, 128.1, 115.7, 115.3, 100.1, 87.2, 55.9.

3-Iodo-4*H*-benzo[h]chromen-4-one (**2e**). Yield 45% (29.2 mg); white solid; mp 166-167 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (s, 1 H), 8.38 (d, *J* = 8.2 Hz, 1 H), 8.11 (d, *J* = 8.8 Hz, 1 H), 7.90 (d, *J* = 8.0 Hz, 1 H), 7.77-7.64 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 173.0, 156.8, 153.6, 135.8, 129.7, 128.2, 127.4, 126.1, 123.5, 122.2, 121.2, 118.0, 88.9; ESI-HRMS Calcd for $C_{13}H_8IO_2$ $[M + H]^+$ 322.9563, found 322.9558.

6-Fluoro-3-iodo-4*H*-chromen-4-one (**2f**).[2a] Yield 71% (41.2 mg); white solid; mp 123-124 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1 H), 7.92-7.81 (m, 1 H), 7.53-7.39 (m, 2 H); ^{13}C NMR (100MHz, $CDCl_3$): 172.8, 159.8 (d, $^1J_{C-F}$ = 247 Hz), 157.9, 152.4, 122.8 (d, $^3J_{C-F}$ = 8 Hz), 122.5 (d, $^2J_{C-F}$ = 25 Hz), 120.3 (d, $^3J_{C-F}$ = 8 Hz), 111.4 (d, $^2J_{C-F}$ = 24 Hz), 86.0.

6-Chloro-3-iodo-4*H*-chromen-4-one (**2g**). Yield 74% (45.3 mg); white solid; mp 145-146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1 H), 8.18 (d, *J* = 2.4 Hz, 1 H), 7.65 (dd, *J* = 8.8, 2.4 Hz, 1 H), 7.44 (d, *J* = 8.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 172.3, 157.8, 154.5, 134.4, 131.8, 125.9, 122.5, 119.8, 86.6; ESI-HRMS Calcd for $C_9H_5ClIO_2$ $[M + H]^+$ 306.9017, found 306.9013.

6-Bromo-3-iodo-4*H*-chromen-4-one (**2h**). Yield 57% (40.1 mg); white solid; mp 163-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1 H), 8.09 (d, *J* = 8.4 Hz, 1 H), 7.66 (d, *J* = 1.6 Hz, 1 H), 7.56 (dd, *J* = 8.4, 1.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 172.6, 157.6, 156.1, 129.6, 128.5, 128.0, 121.1, 120.5, 87.1; ESI-HRMS Calcd for $C_9H_5BrIO_2$ $[M + H]^+$ 350.8512, found 350.8507.

7-Bromo-3-iodo-4*H*-chromen-4-one (**2i**). Yield 43% (30.2 mg); white solid; mp 163-164 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1 H), 8.09 (d, *J* = 8.6 Hz, 1 H), 7.66 (d, *J* = 1.8 Hz, 1 H), 7.56 (dd, *J* = 8.6, 1.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 172.6, 157.6, 156.1, 129.6, 128.5, 128.0, 121.1, 120.6, 87.1; ESI-HRMS Calcd for $C_9H_5BrIO_2$ $[M + H]^+$ 350.8512, found 350.8507.

3-Iodo-6-nitro-4*H*-chromen-4-one (**2j**). Yield 31% (19.7 mg); white solid; mp 93-94 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.93 (s, 1 H), 8.73 (d, *J* = 2.8 Hz, 1 H), 8.58 (dd, *J* = 9.2, 2.8 Hz, 1 H), 7.94 (d, *J* = 9.2 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6): 172.8, 160.2, 159.1, 145.1, 129.1, 122.1, 121.4, 121.2, 87.6; APCI-HRMS Calcd for $C_9H_5INO_4$ $[M + H]^+$ 317.9258, found 317.9253.

6-Chloro-3-iodo-7-methyl-4*H*-chromen-4-one (**2k**).[8a] Yield 43% (27.5 mg); white solid; mp 167-168 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1 H), 8.16 (s, 1 H), 7.34 (s, 1 H), 2.50 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 172.1, 157.6, 154.4, 143.6, 132.6, 126.1, 120.7, 119.7, 86.5, 20.9.

3-Bromo-4*H*-chromen-4-one (**2l**).[7f] Yield 80% (35.8 mg); white solid; mp 94-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (dd, *J* = 8.0, 1.6 Hz, 1 H), 8.24 (s, 1 H), 7.74-7.70 (m, 1 H), 7.50-7.44 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): 172.2, 156.1, 153.8, 134.1, 126.4, 125.9, 123.1, 118.1, 110.7.

3-Bromo-6-methyl-4*H*-chromen-4-one (**2m**). Yield 70% (33.3 mg); white solid; mp 98-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1 H), 8.02 (s, 1 H), 7.51 (dd, *J* = 8.6, 2.2 Hz, 1 H), 7.37 (d, *J* = 8.6 Hz, 1 H), 2.46 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 172.2, 154.3, 153.7, 136.0, 135.4, 125.6, 122.8, 117.9, 110.4, 20.9; ESI-HRMS Calcd for $C_{10}H_8BrO_2$ $[M + H]^+$ 238.9702, found 238.9699.

3-Bromo-6,7-dimethyl-4*H*-chromen-4-one (**2n**). Yield 65% (32.8 mg); white solid; mp 141-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (s, 1 H), 7.96 (s, 1 H), 7.22 (s, 1 H), 2.38 (s, 3 H), 2.35 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 172.1, 154.6, 153.4, 144.8, 135.3, 125.8, 121.0, 118.1, 110.4, 20.4, 19.3; ESI-HRMS Calcd for $C_{11}H_{10}BrO_2$ $[M + H]^+$ 252.9859, found 252.9855.

3-Bromo-7-methoxy-4*H*-chromen-4-one (**2o**). Yield 63% (32.2 mg); white solid; mp 184-185 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 7.4 Hz, 2 H), 7.03-6.98 (m, 1 H), 6.84 (d, *J* = 2.2 Hz, 1 H), 3.91 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.5, 164.4, 157.9, 153.2, 127.8, 117.0, 115.3, 110.8, 100.2, 55.9; ESI-HRMS Calcd for $C_{10}H_8BrO_3$ $[M + H]^+$ 254.9651, found 254.9647.

3-Bromo-4*H*-benzo[h]chromen-4-one (**2p**). Yield 51% (27.9 mg); yellow solid; mp 133-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, *J* = 8.2 Hz, 1 H), 8.38 (s, 1 H), 8.15 (d, *J* = 8.8 Hz, 1 H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.78 (d, *J* = 8.8 Hz, 1 H), 7.73 (t, *J* = 7.2 Hz, 1 H), 7.68 (t, *J* = 7.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 172.0, 153.6, 152.9, 135.8, 129.7, 128.2, 127.5, 126.1, 123.6, 122.2, 121.0, 119.4, 112.4; ESI-HRMS Calcd for $C_{13}H_8BrO_2$ $[M + H]^+$ 274.9702, found 274.9697.

3-Bromo-6-fluoro-4H-chromen-4-one (**2q**). Yield 76% (36.7 mg); white solid; mp 134-135 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (s, 1 H), 7.88 (dd, *J* = 8.2, 3.0 Hz, 1 H), 7.52 (dd, *J* = 9.2, 4.2 Hz, 1 H), 7.48-7.42 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.5, 159.8 (d, $^1J_{C-F}$ = 247 Hz), 153.9, 152.3, 124.2 (d, $^3J_{C-F}$ = 8 Hz), 122.5 (d, $^2J_{C-F}$ = 25 Hz), 120.4 (d, $^3J_{C-F}$ = 8 Hz), 111.2 (d, $^2J_{C-F}$ = 24 Hz), 110.1; ESI-HRMS Calcd for $C_9H_5BrFO_2$ $[M + H]^+$ 242.9451, found 242.9448.

3-Bromo-6-chloro-4*H*-chromen-4-one (**2r**). Yield 72% (37.2 mg); white solid; mp 128-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1 H), 8.22 (d, *J* = 2.6 Hz, 1 H), 7.65 (dd, *J* = 9.0, 2.6 Hz, 1 H), 7.46 (d, *J* = 8.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.1, 154.4, 153.9, 134.4, 131.9, 125.7, 124.0, 119.9, 110.6; ESI-HRMS Calcd for $C_9H_5BrClO_2$ $[M + H]^+$ 258.9156, found 258.9152.

3,6-Dibromo-4*H*-chromen-4-one (**2s**). Yield 77% (46.5 mg); white solid; mp 141-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 2.2 Hz, 1 H), 8.24 (s, 1 H), 7.79 (dd, *J* = 8.8, 2.2 Hz, 1 H), 7.39 (d, *J* = 8.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 170.9, 154.8, 153.9, 137.2, 128.9, 124.3, 120.1, 119.3, 110.7; APCI-HRMS Calcd for $C_9H_5Br_2O_2$ $[M + H]^+$ 302.8651, found 302.8648.

3,7-Dibromo-4*H*-chromen-4-one (**2t**). Yield 57% (34.4 mg); white solid; mp 143-144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1 H), 8.12 (d, *J* = 8.6 Hz, 1 H), 7.68 (d, *J* = 1.6 Hz, 1 H), 7.58 (dd, *J* = 8.6, 1.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): 171.5, 156.0, 153.6, 129.6, 128.5, 127.8, 121.9, 121.2, 111.0; APCI-HRMS Calcd for $C_9H_5Br_2O_2$ $[M + H]^+$ 302.8651, found 302.8647.

3-Bromo-6-nitro-4*H*-chromen-4-one (**2u**). Yield 35% (18.7 mg); white solid; mp 110-111°C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.99 (s, 1 H), 8.74 (d, *J* = 2.8 Hz, 1 H), 8.59 (dd, *J* = 9.2, 2.8 Hz, 1 H), 7.96 (d, *J* = 9.2 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6): 171.2, 159.0, 156.7, 145.1, 129.1, 122.9, 121.9, 121.4, 110.4;

APCI-HRMS Calcd for $C_9H_5BrNO_4$ $[M + H]^+$ 269.9396, found 269.9392.

Conflicts of interest

There are no conflicts to declare.

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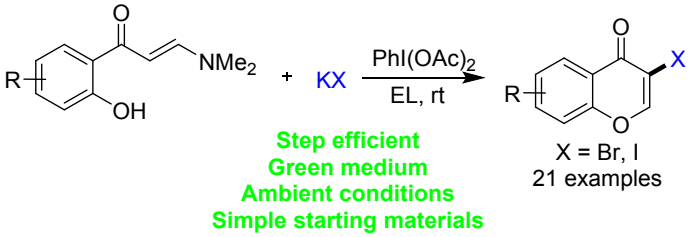

The in situ oxidation generating molecular halogen strategy has been developed for the synthesis of 3-halochromones by employing simple potassium halides as halogen source. The reactions feature advantages of step efficiency, green medium, ambient conditions and simple starting materials.