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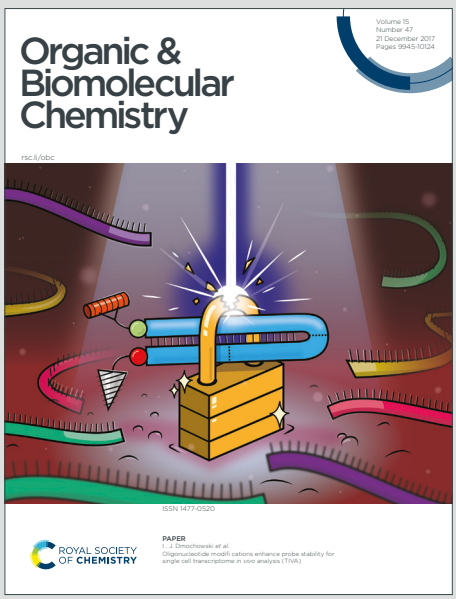

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ARTICLE

BPO promoted direct oxidative C–H functionalization of unactivated alkanes into 6-alkyl 6*H*-benzo[*c*]chromenes under transition-metal-free conditions†

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A simple and efficient BPO-promoted free radical-based cascade reaction of biaryl vinyl ethers with easily available unactivated alkanes has been developed. A series of 6-alkyl 6*H*-benzo[*c*]chromenes have been successfully obtained in moderate to high yields under transition-metal-free conditions. This method can also be utilized to synthesize 6-alkyl 6*H*-benzo[*c*]thiochromenes from the corresponding biaryl vinyl thioethers.

Introduction

The development of effective methods for C–H bond activation and functionalization is particularly important in organic synthesis.[1] Compared with the traditional organic reactions, the direct C–H functionalization can achieve the transformation of simple hydrocarbons to complex organic molecules and reduce the waste emission.[2] Relative to the C(sp^2)–H or C(sp)–H bond, the direct C(sp^3)–H bond functionalization of alkenes is inherently difficult, probably due to its much higher bond dissociation energies.[3] Transition-metal catalyzed C(sp^3)–H bond activation and functionalization to construct carbon–carbon bonds and carbon–heteroatom bonds has aroused much attention in past decade.[4] Despite this, most of the transition-metal catalysts are expensive and toxic, and are difficult to completely remove from the products.[5] Sometimes, in order to enhance catalytic activity, using expensive supporting ligands is unavoidable. Therefore, it is necessary to develop efficient methods for the direct functionalization of C(sp^3)–H bond under transition-metal-free conditions.[6]

Benzo[*c*]chromene is a fundamental building block of some drugs and biologically active natural products (Fig. 1).[7] For example, Cannabinol, an important type of cannabinoids, has antimicrobial activity and sedative effects.[8] Pulchrol (**III**) and pulchral (**IV**), isolated from the metabolites of plant *Bourreria pulchra*, show antiviral and antipyretic activities.[9] The common feature of the above three drug molecules is that there are two methyl groups linked to the C6-position of 6*H*-benzo[*c*]chromene. In addition, the polymer, stemmed from the polymerization of 6-alkyl substituted 6*H*-benzo[*c*]chromene with dithienyl benzothiadiazole or diketopyrrolopyrrole, can also be applied to solar cells.[10] Thus, the rapid and efficient construction of alkyl-substituted 6*H*-benzo[*c*]chromene derivatives is of great significance in the fields of medicinal chemistry and materials.

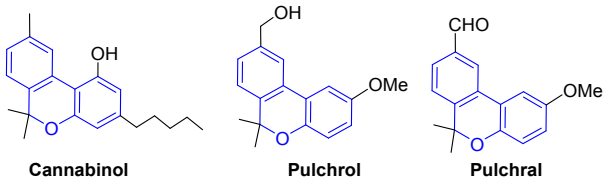

Fig. 1 Examples of bioactive compounds based on benzo[*c*]chromene skeleton.

Many efforts have been devoted to the construction of 6*H*-benzo[*c*]chromene via C–H functionalization strategy. In 2004, Fagnou et al. developed a palladium-catalyzed intramolecular C–H arylation of *ortho*-Bromo-substituted aryl benzyl ethers to synthesize benzo[*c*]chromenes (Scheme 1a).[11a] The same group subsequently extended the substrates to aryl chlorides and iodine compounds.[11b-c] Following a similar inspiration, McGlacken et al. described the C–H arylation with PdO impregnated Fe_3O_4 catalyst in the absence of ligands.[11d] In 2011, Lei and co-workers reported Co-catalyzed intermolecular coupling of non-activated arenes with aryl halides, and found that intramolecular C–H arylation could also proceed smoothly to obtain 6*H*-benzo[*c*]chromene.[12] Interestingly, Shi et al. demonstrated an entirely different intramolecular radical substitution of *ortho*-halogen-substituted aryl benzyl ethers in the presence of ^{t}BuOK and neocuproine to construct 6*H*-benzo[*c*]chromenes.[13] An alternative method involved the intramolecular C–H arylation was described by Du et al., who employed phenyl diazonium tetrafluoroborate with $Pd(OAc)_2$ (Scheme 1b).[14] Besides the direct C–H arylation, Pd-catalyzed intramolecular decarboxylative coupling of aryl carboxylic acids with aryl bromides,[15] Pd-catalyzed and/or KO^{t}Bu mediated intramolecular *O*-arylation of 2'-bromobiphenyl-2-methanol via

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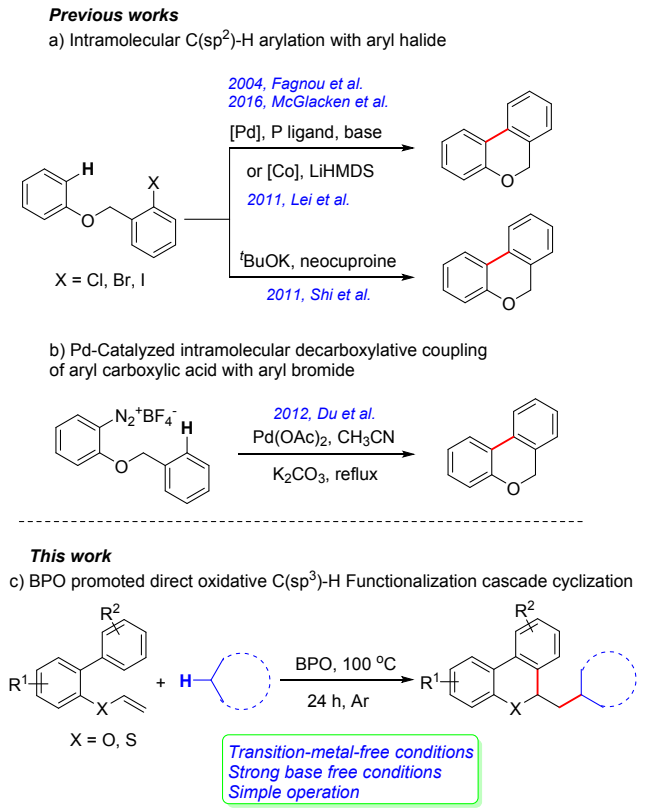
S_NAr pathway,[16] were also successfully applied to the synthesis of 6*H*-benzo[*c*]chromene derivatives. Recently, we used biaryl vinyl ethers as the precursor to obtain 6-fluoroalkyl 6*H*-benzo[*c*]chromenes via a visible-light-promoted radical addition/cyclization reaction.[17]



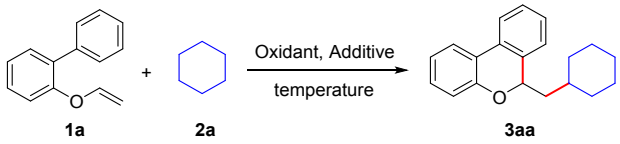
Scheme 1 C-H functionalization strategy to access benzo[*c*]chromene derivatives.

The above methods are efficient for the preparation of 6*H*-benzo[*c*]chromenes. However, some drawbacks such as the use of transition-metal and/or strong base still exist. In the previous works, we described a tunable decarboxylative alkylation of cinnamic acids in which the unactivated alkanes were used as the alkyl sources in the presence of organic peroxides.[18] To extend the application of this radical reaction strategy in the synthesis of heterocyclic derivatives, herein we describe a preparation of 6-alkyl 6*H*-benzo[*c*]chromenes through the radical addition/cyclization of biaryl vinyl ethers under transition-metal-free conditions (Scheme 1c).

Results and discussion

The 2-(vinyloxy)-1,1'-biphenyl (**1a**) was chosen as the model substrate to test the feasibility. Cyclohexane was used as the alkyl source and solvent (Table 1). Without the oxidant, the reaction could not take place at all (entry 1). Using *tert*-butyl benzoate (TBPB, 3 equiv.) as the oxidant, at 100 °C and in Ar atmosphere, the reaction provided the desired product 6-(cyclohexylmethyl)-6*H*-benzo[*c*]chromene (**3aa**) in 15% yield after 12 h (entry 2). The oxidants seemed affect the reaction obviously. The organic or inorganic oxidants, such as di-*tert*-butyl peroxide (DTBP), *tert*-butyl hydroperoxide (TBHP), dicumyl peroxide (DCP), di-lauroyl peroxide (LPO), benzoyl peroxide (BPO), $(NH_4)S_2O_8$, $K_2S_2O_8$ or $Na_2S_2O_8$ were tested (entries 3–10), in which BPO was proved to be most effective and the reaction gave the product **3aa** in 65% yield (entry 7). Adjustment of the amount of BPO to 4 equiv. or 2 equiv. did not effectively increase the yield of **3aa** (entries 11 and 12). Prolonging the reaction time to 24 h, the yield of **3aa** increased to 70% (entry 13). Additionally, inferior results were obtained at lower or higher temperature than 100 °C (entries 14–16). It should be noted that the reaction did not occur under air atmosphere (entry 17). Furthermore, The presence of transition-metal compounds (10 mol%) such as CuBr or $FeCl_2$ could not improve the yield (entries 18 and 19). Finally, equivalent (3 or 5 equiv.) amount of cyclohexane in solvent 1,2-dichloroethane (DCE) resulted in lower yields of **3aa** (entry 20).

Table 1 Optimization of reaction conditions[a]



1a **2a** **3aa**

Entry	Additive	Oxidant (equiv.)	Temp. (°C)	Time	Yield (%)[b]
1	–	–	100	12	0
2	–	TBPB (3)	100	12	15
3	–	DTBP (3)	100	12	<10
4	–	TBHP (3)	100	12	<10
5	–	DCP (3)	100	12	15
6	–	LPO (3)	100	12	40
7	–	BPO (3)	100	12	65
8	–	$(NH_4)S_2O_8$ (3)	100	12	0
9	–	$K_2S_2O_8$ (3)	100	12	0
10	–	$Na_2S_2O_8$ (3)	100	12	0
11	–	BPO (4)	100	12	66
12	–	BPO (2)	100	12	55
13	**–**	**BPO (3)**	**100**	**24**	**70**
14	–	BPO (3)	90	24	53
15	–	BPO (3)	110	24	68
16	–	BPO (3)	120	24	65
17[c]	–	BPO (3)	100	24	trace
18	CuBr[d]	BPO (3)	100	24	55
19	$FeCl_2$[d]	BPO (3)	100	24	25
20	–	BPO (3)	100	24	12[e], 20[f]

[a] Reaction conditions: **1a** (0.2 mmol), oxidant (3 equiv.) and solvent (2 mL) were carried out in a sealed tube under Ar atmosphere at 100 °C for 12 h. [b] Isolated yield, based on **1a**. [c] Under air. [d] 10 mol%. [e] **2a** (3 equiv.) in DCE (2 mL). [f] **2a** (5 equiv.) in DCE (2 mL).

With the optimized conditions in hand, we investigated a wide range of diaryl vinyl ethers (**1**) with cyclohexane (**2a**) (Scheme 2).

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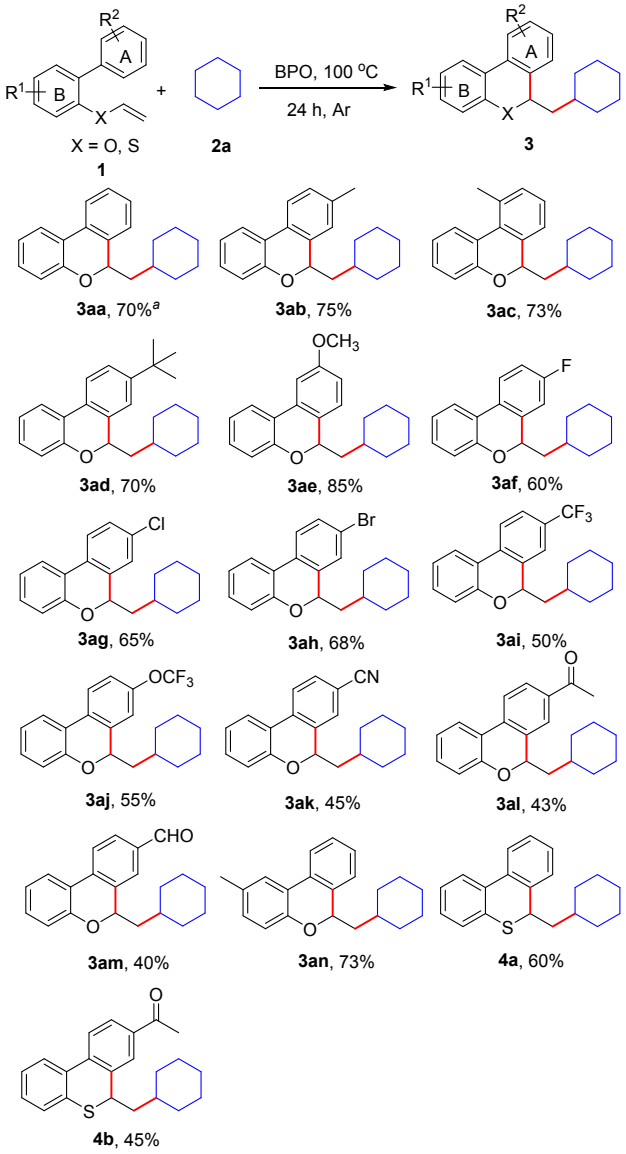
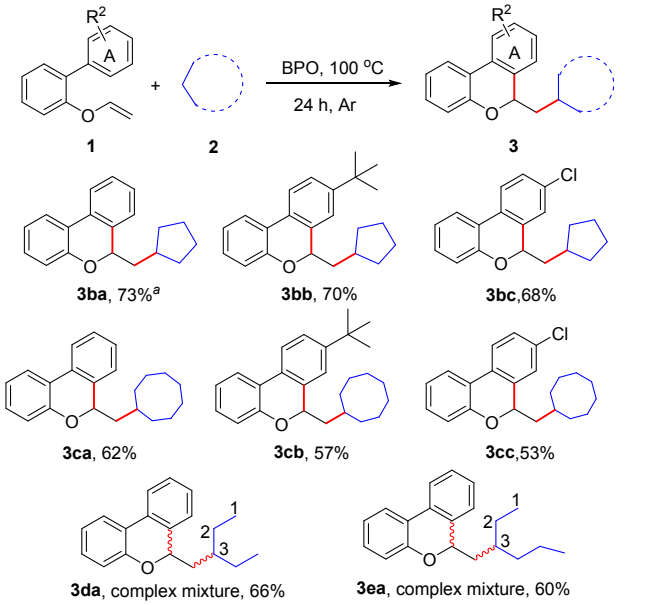
When the substrates **1** bearing an electron-donating group (Me, ^{t}Bu, MeO) at ortho-, meta- or para- position of the benzene ring A, the desired products **3ab**–**3ae** were obtained in 70% to 85% yield. Halogen atom on the para-position of the benzene ring A, such as F, Cl or Br, provided the addition/cyclization products **3af**–**3ah** in satisfactory yields (60%–68%). However, strong electron-withdrawing substituents (CF_3, CF_3O, CN or acetyl group) exhibited lower reactivity at the same position and produced **3ai**–**3al** in moderate yields (43%–55%). To our delight, even readily oxidized formyl group was tolerated, providing the cyclization product **3am** in 40% yield without formation of the aryl acid. Furthermore, when a methyl was linked to the benzene ring B, the reaction proceeded smoothly and afforded **3an** in 73% yield. This strategy is also suitable for thioether. When vinyl thioethers were treated with cyclohexane under the same reaction conditions, the corresponding 6*H*-benzo[*c*]thiochromene derivatives **4a** and **4b** were obtained in 60% and 45% yield, respectively. If a substrate with internal alkenyl, *e.g.*, 2-(prop-1-en-1-yloxy)-1,1'-biphenyl was used, however, no desired product was obtained.



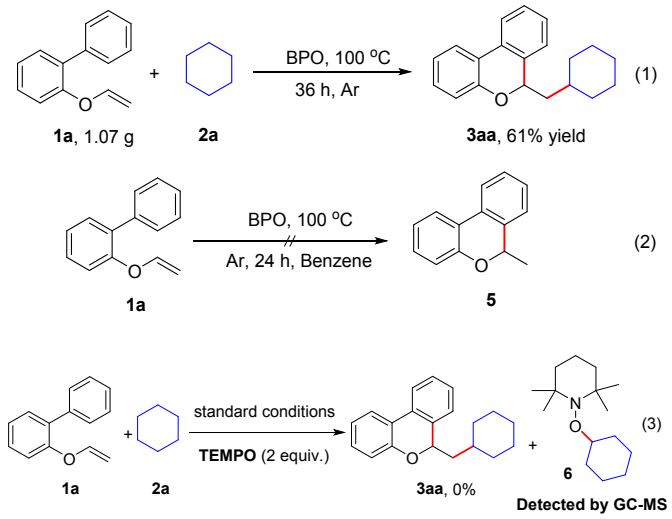
Scheme 2 Addition/cyclization of biaryl vinyl ethers with cyclohexane. Reaction conditions: **1a** (0.2 mmol), BPO (3 equiv.) and cyclohexane (2 mL) were carried out in a sealed tube under Ar atmosphere at 100 °C for 24 h. [a] Isolated yield, based on **1**.

Subsequently, we explored the substrate scope of unactivated alkanes (Scheme 3). When cyclopentane and cyclooctane were used as the alkyl sources at the same reaction conditions, the C(sp^3)–H bond functionalization cascade cyclization proceeded smoothly and produced a series of alkylated 6*H*-benzo[*c*]chromenes. For several substrates **1**, the reaction gave the similar results compared with the reaction of cyclohexane (**3ba–3cc**). Linear saturated alkanes such as pentane and hexane worked well with diaryl vinyl ether **1a**, and the cyclic products **3da**, **3ea** were formed in 66% and 60% yield, respectively. But the inseparable isomers were obtained. From toluene, however, the oxidation product benzaldehyde was detected instead of the addition/cyclization product.



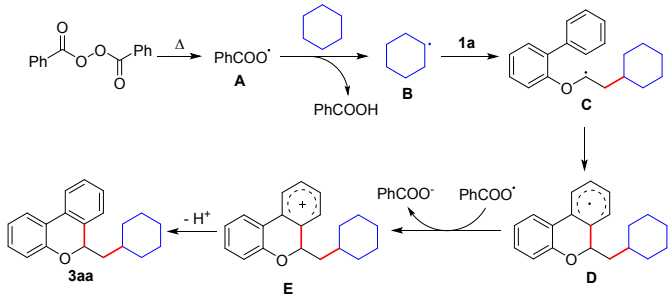
Scheme 3 Addition/cyclization of biaryl vinyl ethers with other alkanes. Reaction conditions: **1** (0.2 mmol), BPO (3 equiv.) and alkanes (2 mL) were carried out in a sealed tube under Ar atmosphere at 100 °C for 24 h. [a] Isolated yield, based on **1**.

The scalability of this synthetic method was evaluated by performing the reaction with 5.45 mmol of diaryl vinyl ether **1a** under the optimal conditions. Extending the reaction time to 36 h, the desire product **3aa** was obtained in 61% yield (3.32 mmol, 0.93 g) (Scheme 4, eq (1)). In order to elucidate the mechanism of this reaction, two control experiments were designed and carried out. The intramolecular cyclization of **1a** did not occur without **2a** under the standard reaction conditions (Scheme 4, eq (2)). Meanwhile, the template reaction was completely inhibited and the adduct **6** was detected by GC-MS when the radical trapping agent 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 2 equiv.) was added. The product **3aa** was not detected and the substrate **1a** was almost quantitatively recovered (Scheme 4, eq (3)). Thus, the reaction might involve a radical addition to the carbon-carbon double bond of **1a** prior to the cyclization to construct 6*H*-benzo[*c*]chromene skeleton.



Scheme 4 Gram scale reaction and control experiments.

Based on the above results and previous studies,[18,19] a proposed mechanism for the addition cascade cyclization of diaryl vinyl ether **1a** with cyclohexane was presented in Scheme 5. Firstly, thermal decomposition of BPO produced benzoyloxy radical **A**, [19b,c] which underwent hydrogen atom transfer with cyclohexane to generate cyclohexyl radical **B**. Subsequently, the addition of radical **B** to the C=C double bond of **1a** formed radical intermediate **C**, followed by the intramolecular cyclization on benzene ring to produce radical intermediate **D**. The oxidation of **D** by benzoyloxy radical **A** gave the carbocation **E**. Finally, the product **3aa** was produced *via* deprotonation of intermediate **E**.



Scheme 5 Proposed mechanism.

Experimental section

General remarks

All reactions were run in a sealed tube with a Teflon lined cap under ambient Ar atmosphere. All commercially available reagent grade chemicals were used as received without further purification.^{1}H NMR (400 MHz) spectra were recorded on a Bruker Avance 400 spectrometer in $CDCl_3$ [using $(CH_3)_4Si$ (for ^{1}H, δ = 0.00) as internal standard]. ^{13}C NMR (100 MHz) spectra on a Bruker Avance 400 spectrometer in $CDCl_3$ [using $CDCl_3$ (for ^{13}C, δ = 77.00) as internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, dt = doublet of triplet, td = triplet of doublet, q = quartet, m = multiplet, ddd = doublet of doublet of doublet. High-resolution mass spectra were obtained with an AB Triple 5600 mass spectrometer by ESI on a TOF mass analyzer. Melting points are uncorrected. Column chromatography was performed on silica gel (300-400 mesh). Substrates **1** was prepared by reference to our previous procedures and related literature methods.[17, 20]

General procedure for the synthesis of products 3 or 4

An oven-dried Schlenk tube (25 mL) was charged with 2-(vinyloxy)-1,1'-biphenyl (**1a,** 0.2 mmol), BPO (3 equiv.) and cyclohexane (**2a**, 2 mL). The reaction mixture was stirred under Ar atmosphere at 100 ℃ for 24 h. After the reaction was completed, the resulting solution was diluted with water (10 mL), extracted with CH_2Cl_2 (15 mL × 3). The combined organic layers were washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel chromatography using hexane/ethyl acetate (100:1) as eluent to give the desired product **3aa**.

6-(Cyclohexylmethyl)-6*H*-benzo[*c*]chromene (**3aa**). Yellow oil (38.9 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80–7.71 (m, 2H), 7.39 (td, *J* = 7.6, 1.3 Hz, 1H), 7.31 (td, *J* = 7.5, 1.3 Hz, 1H), 7.27 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.07 (td, *J* = 7.6, 1.2 Hz, 1H), 7.03 (dd, *J* = 8.0, 1.0 Hz, 1H), 5.31 (dd, *J* = 10.2, 4.1 Hz, 1H), 2.00–1.88 (m, 2H), 1.82–1.60 (m, 5H), 1.52–1.41 (m, 1H), 1.39–1.14 (m, 3H), 1.05–0.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.7, 135.5, 129.4, 129.0, 127.9, 127.6, 124.6, 122.9, 122.6, 122.1, 121.7, 118.1, 75.2, 42.2, 33.94, 33.92, 32.6, 26.6, 26.3, 26.2; HRMS (ESI) m/z calcd for $C_{20}H_{22}O$ $(M+H)^+$ 279.1743, found 279.1744.

6-(Cyclohexylmethyl)-8-methyl-6*H*-benzo[*c*]chromene (**3ab**). Yellow oil (43.9 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.24 (td, *J* = 8.0, 1.5 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.05 (td, *J* = 7.6, 1.1 Hz, 1H), 7.03–6.98 (m, 1H), 6.95 (s, 1H), 5.27 (dd, *J* = 10.4, 3.8 Hz, 1H), 2.41 (s, 3H), 2.03–1.86 (m, 2H), 1.82–1.60 (m, 5H), 1.45–1.32 (m, 4H), 1.21–0.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.5, 137.5, 135.6, 128.9, 128.7, 126.2, 125.2, 122.8, 122.7, 122.1, 121.6, 118.0, 75.3, 42.4, 33.9, 32.56, 26.6, 26.4, 26.2, 21.4; HRMS (ESI) m/z calcd for $C_{21}H_{24}O$ $(M+H)^+$ 293.1900, found 293.1895.

6-(Cyclohexylmethyl)-10-methyl-6*H*-benzo[*c*]chromene (**3ac**). Pale yellow oil (42.7 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.82 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.31–7.22 (m, 3H), 7.10 (t, *J* = 7.3 Hz, 2H), 7.04 (dd, *J* = 5.9, 2.8 Hz, 1H), 5.19 (dd, *J* = 10.1, 4.3 Hz, 1H), 2.70 (s, 3H), 1.95 (d, *J* = 11.5 Hz, 1H), 1.89–1.70 (m, 6H), 1.63–1.47(m, 1H), 1.35–1.31 (m, 3H), 1.05–0.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.1, 138.3, 134.3, 131.7, 128.6, 128.3, 127.6, 127.1, 124.2, 122.5, 121.0, 118.2, 76.1, 40.8, 34.0, 33.9, 32.6, 26.6, 26.3, 26.2, 23.4; HRMS (ESI) m/z calcd for $C_{21}H_{24}O$ $(M+H)^+$ 293.1900, found 293.1894.

8-(*tert*-Butyl)-6-(cyclohexylmethyl)-6*H*-benzo[*c*]chromene (**3ad**). Pale yellow oil (46.8. mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75 (d, *J* = 7.7 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.43 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.28–7.22 (m, 1H), 7.14 (d, *J* = 1.5 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 5.33 (dd, *J* = 10.0, 4.4 Hz, 1H), 2.00–1.87 (m, 2H), 1.83–1.60 (m, 5H), 1.49–1.43 (m, 1H), 1.40 (s, 9H), 1.34–1.16 (m, 3H), 1.01–0.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.5, 150.7, 135.1, 129.0, 126.2, 124.9, 122.7, 122.6, 121.9, 121.6, 118.0, 75.6, 42.3, 34.7, 34.0, 33.9, 32.7,

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31.3, 26.6, 26.4, 26.2; HRMS (ESI) m/z calcd for $C_{24}H_{30}O$ $(M+H)^+$ 335.2369, found 335.2365.

6-(Cyclohexylmethyl)-9-methoxy-6*H*-benzo[*c*]chromene (**3ae**). Yellow solid (52.4 mg, 85% yield) ; mp 55–56 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.39–7.31 (m, 2H), 7.27 (td, *J* = 7.8, 1.5 Hz, 1H), 7.08–7.01 (m, 2H), 6.85 (dd, *J* = 7.7, 1.2 Hz, 1H), 5.77 (dd, *J* = 10.4, 3.3 Hz, 1H), 3.89 (s, 3H), 2.08–2.00 (m, 1H), 1.83–1.72 (m, 2H), 1.69 (m, 4H), 1.37–1.29 (m, 3H), 1.26–1.23 (m, 1H), 1.08–0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 154.6, 152.4, 129. 9, 129.5, 128.3, 124.3, 123.3, 122.4, 121.4, 118.3, 114.5, 109.4, 70.3, 55.5, 40.7, 34.2, 33.9, 32.4, 26.7, 26.4, 26.2; HRMS (ESI) m/z calcd for $C_{21}H_{24}O_2$ $(M+H)^+$ 309.1849, found 309.1852.

6-(Cyclohexylmethyl)-8-fluoro-6*H*-benzo[*c*]chromene (**3af**). Yellow oil (35.6 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.72–7.66 (m, 2H), 7.26 (td, *J* = 8.3, 1.9 Hz, 1H), 7.10–7.04 (m, 2H), 7.02 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.86 (dd, *J* = 8.8, 2.6 Hz, 1H), 5.25 (dd, *J* = 10.2, 4.0 Hz, 1H), 1.91 (dt, *J* = 14.2, 5.1 Hz, 2H), 1.77–1.68 (m, 4H), 1.44 (ddd, *J* = 14.1, 8.4, 4.0 Hz, 1H), 1.38–1.17 (m, 4H), 1.02–0.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 162.4 (d, *J* = 247.2 Hz), 152.3, 137.8 (d, *J* = 6.9 Hz), 129.4, 125.4 (d, *J* = 3.1 Hz), 124.0 (d, *J* = 8.2 Hz), 122.7, 122.0, 121.9, 118.1, 114.9 (d, *J* = 21.7 Hz), 111.6 (d, *J* = 22.3 Hz), 74.8 (d, *J* = 1.9 Hz), 41.8, 33.9, 33.8, 32.5, 26.6, 26.3, 26.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) -114.1; HRMS (ESI) m/z calcd for $C_{20}H_{21}FO$ $(M+H)^+$ 297.1649, found 297.1648.

8-Chloro-6-(cyclohexylmethyl)-6*H*-benzo[*c*]chromene (**3ag**). Yellow oil (40.7 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.34 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.28 (ddd, *J* = 8.9, 7.2, 1.5 Hz, 1H), 7.12 (d, *J* = 2.0 Hz, 1H), 7.06 (td, *J* = 7.6, 1.1 Hz, 1H), 7.04–6.97 (m, 1H), 5.24 (dd, *J* = 10.5, 3.8 Hz, 1H), 1.97–1.90 (m, 2H), 1.72 (d, *J* = 9.8 Hz, 4H), 1.46–1.40 (m, 1H), 1.36–1.17 (m, 4H), 0.99 (td, *J* = 12.3, 2.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.5, 137.2, 133.3, 129.8, 128.0, 127.7, 124.7, 123.6, 122.9, 121.9, 121.7, 118.1, 74.7, 41.9, 34.0, 33.9, 32.5, 26.6, 26.3, 26.1; HRMS (ESI) m/z calcd for $C_{20}H_{21}ClO$ $(M+H)^+$ 313.1354, found 313.1357.

8-Bromo-6-(cyclohexylmethyl)-6*H*-benzo[*c*]chromene (**3ah**). Pale yellow oil (48.6 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.49 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.31–7.26 (m, 2H), 7.06 (td, *J* = 7.6, 1.2 Hz, 1H), 7.01 (dd, *J* = 8.1, 1.1 Hz, 1H), 5.24 (dd, *J* = 10.5, 3.8 Hz, 1H), 1.97–1.89 (m, 2H), 1.72 (d, *J* = 9.7 Hz, 4H), 1.45–1.39 (m, 1H), 1.37–1.17 (m, 4H), 1.03–0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.6, 137.5, 131.0, 129.9, 128.2, 127.6, 123.9, 122.9, 121.9, 121.8, 121.4, 118.2, 74.6, 41.9, 33.9, 33.8, 32.5, 26.6, 26.3, 26.2; HRMS (ESI) m/z calcd for $C_{20}H_{21}BrO$ $(M+H)^+$ 357.0849, found 357.0843.

6-(Cyclohexylmethyl)-8-(trifluoromethyl)-6*H*-benzo[*c*]chromene (**3ai**). Pale yellow solid (34.6 mg, 50% yield); mp 55–56 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.81 (d, *J* = 8.2 Hz, 1H), 7.76 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.65–7.59 (m, 1H), 7.38 (s, 1H), 7.33 (td, *J* = 8.1, 1.6 Hz, 1H), 7.09 (td, *J* = 7.6, 1.2 Hz, 1H), 7.04 (dd, *J* = 8.1, 1.1 Hz, 1H), 5.34 (dd, *J* = 10.5, 3.8 Hz, 1H), 2.01–1.91 (m, 2H), 1.77–1.68 (m, 4H), 1.44 (ddd, *J* = 14.1, 8.6, 3.9 Hz, 1H), 1.39–1.13 (m, 4H), 1.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.2, 135.9, 132.7, 132.7, 130.7, 129.4 (q, *J* = 32.5 Hz), 124.8 (q, *J* = 3.7 Hz), 123.5, 122.5, 122.0, 121.6 (q, *J* = 3.9 Hz), 121.3, 118.3, 74.9, 41.9, 34.0, 33.9, 32.4, 26.5, 26.3, 26.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) -62.4; HRMS (ESI) m/z calcd for $C_{21}H_{21}F_3O$ $(M+H)^+$ 347.1617, found 347.1615.

6-(Cyclohexylmethyl)-8-(trifluoromethoxy)-6*H*-benzo[*c*]chromene (**3aj**). Pale yellow oil (39.9 mg, 55% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77–7.69 (m, 2H), 7.34–7.26 (m, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 7.06–6.99 (m, 2H), 5.28 (dd, *J* = 10.2, 4.2 Hz, 1H), 1.93 (dt, *J* = 8.8, 4.8 Hz, 2H), 1.78–1.69 (m, 4H), 1.49–1.42 (m, 1H), 1.38–1.18 (m, 4H), 1.04–0.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.6, 148.6, 137.3, 129.9, 128.0, 123.7, 123.0, 121.9, 121.6, 120.5, 119.3, 118.2, 117.3, 74.8, 41.8, 33.9, 32.6, 26.6, 26.3, 26.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) -57.8; HRMS (ESI) m/z calcd for $C_{21}H_{21}F_3O_2$ $(M+H)^+$ 363.1566, found 363.1561.

6-(Cyclohexylmethyl)-6*H*-benzo[*c*]chromene-8-carbonitrile (**3ak**). Pale yellow oil (27.3 mg, 45% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.78 (d, *J* = 8.1 Hz, 1H), 7.74 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.64 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.41 (d, *J* = 1.7 Hz, 1H), 7.38–7.32 (m, 1H), 7.13–7.07 (m, 1H), 7.03 (d, *J* = 8.2 Hz, 1H), 5.29 (dd, *J* = 10.3, 4.1 Hz, 1H), 1.92 (dt, *J* = 9.5, 5.5 Hz, 2H), 1.77–1.69 (m, 4H), 1.46–1.40 (m, 1H), 1.37–1.28 (m, 4H), 1.03–0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 153.4, 136.2, 133.8, 131.7, 131.4, 128.3, 123.7, 122.8, 122.2, 120.9, 118.9, 118.5, 110.8, 74.5, 41.8, 33.9, 33.8, 32.5, 26.5, 26.3, 26.1; HRMS (ESI) m/z calcd for $C_{21}H_{21}NO$ $(M+H)^+$ 304.1696, found 304.1695.

1-(6-(Cyclohexylmethyl)-6*H*-benzo[*c*]chromen-8-yl)ethan-1-one (**3al**). Yellow oil (27.6 mg, 43% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.79–7.75 (m, 2H), 7.73 (d, *J* = 1.4 Hz, 1H), 7.32 (td, *J* = 8.1, 1.5 Hz, 1H), 7.07 (td, *J* = 7.6, 1.1 Hz, 1H), 7.02 (dd, *J* = 8.1, 0.9 Hz, 1H), 5.35 (dd, *J* = 10.5, 3.8 Hz, 1H), 2.64 (s, 3H), 1.97–1.88 (m, 2H), 1.75–1.66 (m, 4H), 1.48–1.41 (m, 1H), 1.37–1.13 (m, 4H), 1.04–0.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 197.4, 153.4, 136.0, 135.7, 133.8, 130.9, 128.3, 124.6, 123.7, 122.2, 121.9, 121.5, 118.4, 75.1, 42.1, 34.0, 33.9, 32.5, 26.7, 26.6, 26.3, 26.2; HRMS (ESI) m/z calcd for $C_{22}H_{24}O_2$ $(M+H)^+$ 321.1849, found 321.1849.

6-(Cyclohexylmethyl)-6*H*-benzo[*c*]chromene-8-carbaldehyde (**3am**). Pale yellow oil (24.5 mg, 40% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.02 (s, 1H), 7.86 (d, *J* = 0.8 Hz, 2H), 7.79 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.66 (s, 1H), 7.36–7.31 (m, 1H), 7.09 (td, *J* = 7.6, 1.0 Hz, 1H), 7.04 (dd, *J* = 8.1, 0.9 Hz, 1H), 5.36 (dd, *J* = 10.5, 3.8 Hz, 1H), 1.99–1.92 (m, 2H), 1.76–1.68 (m, 4H), 1.52–1.48 (m, 1H), 1.35–1.25 (m, 4H), 1.04–0.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 191.6, 153.6, 136.1, 135.4, 135.2, 131.2, 130.1, 125.5, 123.9, 122.7, 122.1, 121.5, 118.4, 74.9, 41.9, 34.0, 33.9, 32.5, 26.5, 26.3, 26.2; HRMS (ESI) m/z calcd for $C_{21}H_{22}O_2$ $(M+H)^+$ 307.1692, found 307.1693.

6-(Cyclohexylmethyl)-2-methyl-6*H*-benzo[*c*]chromene (**3an**). Pale yellow oil (42.7 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.73 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.56 (d, *J* = 2.0 Hz, 1H), 7.37 (td, *J* = 7.6, 1.4 Hz, 1H), 7.30 (td, *J* = 7.5, 1.9 Hz, 1H), 7.12 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.08 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 5.27 (dd, *J* = 10.2, 4.2 Hz, 1H), 2.40 (s, 3H), 1.98–1.86 (m, 2H), 1.78–1.68 (m, 4H), 1.46–1.38 (m, 1H), 1.35–1.21 (m, 4H), 1.03–0.91 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.5, 135.7, 130.8, 130.1, 129.2, 127.9, 127.5, 124.7, 123.4, 122.2, 122.1, 117.8, 75.2, 42.1, 34.0, 33.9, 32.6, 26.6, 26.3, 26.2, 21.0; HRMS (ESI) m/z calcd for $C_{21}H_{24}O$ $(M+Na)^+$ 315.1719, found 315.1723.

6-(Cyclopentylmethyl)-6*H*-benzo[*c*]chromene (**3ba**). Yellow oil (37.5 mg, 55% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79–7.73 (m, 2H), 7.39 (td, *J* = 7.6, 1.3 Hz, 1H), 7.32 (td, *J* = 7.5, 1.2 Hz, 1H), 7.29–7.25 (m, 1H), 7.18–7.14 (m, 1H), 7.08 (td, *J* = 7.5, 1.1 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 5.23 (dd, *J* = 9.4, 4.7 Hz, 1H), 2.15–2.01 (m, 2H), 1.96–1.86 (m, 2H), 1.68–1.53 (m, 5H), 1.23–1.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.8, 135.3, 129.5, 128.9, 128.01, 127.6, 124.8, 122.9, 122.5, 122.2, 121.7, 118.1, 77.3, 41.0, 36.6, 33.0, 32.5, 25.2, 25.0; HRMS (ESI) m/z calcd for $C_{19}H_{20}O$ $(M+H)^+$ 265.1587, found 265.1584.

8-(*tert*-Butyl)-6-(cyclopentylmethyl)-6*H*-benzo[*c*]chromene (**3bb**). Pale yellow oil (61.8 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.74 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.68 (d, *J* = 8.2 Hz, 1H), 7.42 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.24 (ddd, *J* = 7.9, 7.3, 1.6 Hz, 1H), 7.15 (d, *J* = 2.0 Hz, 1H), 7.08–6.98 (m, 2H), 5.22 (dd, *J* = 9.4, 4.6 Hz, 1H), 2.12–2.00 (m, 2H), 1.97–1.87 (m, 2H), 1.68–1.57 (m, 5H), 1.39 (s, 9H), 1.23–1.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.5, 150.8, 134.9, 128.9, 126.1, 124.9, 122.7, 122.6, 121.9, 121.7, 121.5, 117.9, 77.7, 41.1, 36.7, 34.7, 33.0, 32.5, 31.3, 25.2, 24.9; HRMS (ESI) m/z calcd for $C_{23}H_{28}O$ $(M+H)^+$ 321.2213, found 321.2217.

8-Chloro-6-(cyclopentylmethyl)-6*H*-benzo[*c*]chromene (**3bc**). Yellow oil (43.8 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.34 (dd, *J* = 8.3, 2.2 Hz, 1H), 7.27 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.14 (d, *J* = 2.0 Hz, 1H), 7.07 (td, *J* = 7.5, 1.3 Hz, 1H), 7.02 (dd, *J* = 8.1, 1.3 Hz, 1H), 5.16 (dd, *J* = 9.6, 4.4 Hz, 1H), 2.13–2.00 (m, 2H), 1.94–1.85 (m, 2H), 1.68–1.57 (m, 5H), 1.22–1.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.6, 136.9, 133.3, 129.8, 128.1, 127.6, 124.9, 123.6, 122.9, 121.9, 121.7, 118.2, 76.7, 40.8, 36.5, 33.1, 32.4, 25.2, 25.0; HRMS (ESI) m/z calcd for $C_{19}H_{19}ClO$ $(M+H)^+$ 299.1197, found 299.1195.

6-(Cyclooctylmethyl)-6*H*-benzo[*c*]chromene (**3ca**). Yellow oil (38.0 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77 (t, *J* = 7.2 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.35–7.26 (m, 2H), 7.16 (d, *J* = 7.3 Hz, 1H), 7.11–7.01 (m, 2H), 5.29 (dd, *J* = 9.8, 4.1 Hz, 1H), 1.97–1.83 (m, 4H), 1.70–1.64 (m, 5H), 1.59–1.52 (m, 5H), 1.44–1.31 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.8, 135.6, 129.5, 129.1, 127.9, 127.6, 124.7, 123.0, 122.7, 122.2, 121.7, 118.1, 75.6, 42.7, 33.1, 32.9, 31.1, 27.5, 27.4, 26.4, 25.4, 25.3; HRMS (ESI) m/z calcd for $C_{22}H_{26}O$ $(M+H)^+$ 307.2056, found 307.2054.

8-(*tert*-Butyl)-6-(cyclooctylmethyl)-6*H*-benzo[*c*]chromene (**3cb**). Yellow oil (68.7 mg, 57% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.77–7.67 (m, 2H), 7.43 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.29–7.22 (m, 1H), 7.15 (d, *J* = 2.1 Hz, 1H), 7.09–7.00 (m, 2H), 5.28 (dd, *J* = 9.5, 4.6 Hz, 1H), 1.96–1.80 (m, 4H), 1.70–1.62 (m, 5H), 1.61–1.47 (m, 8H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.6, 150.8, 135.2, 129.1, 126.3, 125.0, 122.8, 122.7, 121.9, 121.7, 121.6, 118.0, 76.0, 43.0, 34.7, 33.1, 32.9, 31.5, 31.4, 27.4, 27.3, 26.4, 25.6, 25.4; HRMS (ESI) m/z calcd for $C_{26}H_{34}O$ $(M+H)^+$ 363.2682, found 363.2678.

8-Chloro-6-(cyclooctylmethyl)-6*H*-benzo[*c*]chromene (**3cc**). Yellow oil (51.2 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.70 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.34 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.28 (td, *J* = 7.8, 1.6 Hz, 1H), 7.15–7.12 (m, 1H), 7.07 (td, *J* = 7.5, 1.3 Hz, 1H), 7.02 (dd, *J* = 8.1, 1.3 Hz, 1H), 5.21 (dd, *J* = 10.3, 3.9 Hz, 1H), 2.01–1.83 (m, 4H), 1.73–1.60 (m, 8H), 1.58–1.51 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.6, 137.3, 133.3, 129.8, 128.1, 127.8, 124.7, 123.6, 122.9, 121.9, 121.8, 118.1, 75.1, 42.4, 33.1, 32.9, 30.9, 27.5, 27.4, 26.3, 25.3, 25.2; HRMS (ESI) m/z calcd for $C_{22}H_{25}ClO$ $(M+H)^+$ 341.1667, found 341.1666.

6-(2-Ethylbutyl)-6*H*-benzo[*c*]chromene (**3da**). Pale yellow oil (41.2 mg, complex mixture, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.78–7.73 (m, 2H), 7.38 (td, *J* = 7.6, 1.4 Hz, 1H), 7.34–7.24 (m, 2H), 7.14 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.07 (td, *J* = 7.6, 1.2 Hz, 1H), 7.01 (dd, *J* = 8.1, 1.3 Hz, 1H), 5.32–5.25 (m, 1H), 2.09–1.76 (m, 2H), 1.50–1.37 (m, 2H), 1.32–1.24 (m, 3H), 1.06 (d, *J* = 6.6 Hz, 1H), 0.98 (d, *J* = 6.5 Hz, 1H), 0.95–0.91 (m, 2H), 0.89–0.85 (m, 1H), 0.81 (t, *J* = 7.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.8, 152.7, 135.7, 135.4, 129.5, 129.1, 129.0, 128.9, 128.0, 127.9, 127.7, 127.6, 127.5, 124.7, 124.6, 124.5, 122.9, 122.7, 122.6, 122.5, 122.2, 122.1, 122.1, 121.8, 121.7, 121.6, 75.9, 75.8, 75.4, 42.1, 41.7, 39.7, 38.5, 38.2, 36.4, 29.7, 29.2, 28.7, 25.6, 24.8, 20.2, 19.9, 19.8, 19.2, 14.3, 14.2, 10.8, 10.4.; HRMS (ESI) m/z calcd for $C_{19}H_{22}O$ $(M+H)^+$ 267.1743, found 267.1749.

6-(2-Ethylpentyl)-6*H*-benzo[*c*]chromene (**3ea**). Pale yellow oil (45.1 mg, complex mixture, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.76 (ddd, *J* = 7.5, 6.1, 1.4 Hz, 2H), 7.39 (td, *J* = 7.6, 1.4 Hz, 1H), 7.32 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.29–7.25 (m, 1H), 7.15 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.07 (tt, *J* = 7.5, 1.2 Hz, 1H), 7.01 (dt, *J* = 7.9, 1.1 Hz, 1H), 5.32–5.25 (m, 1H), 2.09–1.81 (m, 2H), 1.49–1.42 (m, 1H), 1.34–1.22 (m, 5H), 1.07 (d, *J* = 6.6 Hz, 1H), 0.99 (d, *J* = 6.6 Hz, 1H), 0.96–0.92 (m, 2H), 0.91–0.87 (m, 2H), 0.82 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 152.7, 152.6, 135.7, 135.6, 135.4, 129.5, 129.4, 129.2, 129.1, 129.0, 128.0, 127.9, 127.7, 127.6, 127.5, 124.8, 124.7, 124.6, 124.5, 123.0, 122.9, 122.7, 122.6, 122.5, 122.2, 122.1, 121.8, 121.7, 121.6, 118.2, 118.1, 75.9, 75.8, 75.7, 75.4, 42.1, 41.8, 38.7, 38.6, 37.2, 35.9, 35.6, 35.1, 35.0, 34.7, 34.6, 31.8, 29.4, 29.2, 29.1, 29.0, 28.9, 26.3, 25.6, 25.3, 23.0, 22.9, 22.7, 20.2, 19.7, 19.6, 19.3, 14.6, 14.4, 14.2, 14.1, 10.8, 10.4; HRMS (ESI) m/z calcd for $C_{20}H_{24}O$ $(M+H)^+$ 281.1900, found 281.1893.

6-(Cyclohexylmethyl)-6*H*-benzo[*c*]thiochromene (**4a**). Yellow oil (56.8 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.83 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.46–7.43 (m, 1H), 7.39 (td, *J* = 7.5, 1.5 Hz, 1H), 7.36–7.31 (m, 1H), 7.30–7.25 (m, 2H), 7.24–7.19 (m, 1H), 3.92 (dd, *J* = 8.7, 6.6 Hz, 1H), 1.75–1.59 (m, 7H), 1.50–1.44 (m, 1H), 1.30–1.18 (m, 3H), 0.95–0.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 137.9, 134.1, 133.1, 131.4, 129.3, 127.9, 127.8, 127.5, 126.6, 126.4, 126.2, 125.2, 42.0, 41.6, 34.5, 33.5, 32.6, 26.6, 26.2, 26.1; HRMS (ESI) m/z calcd for $C_{20}H_{22}S$ $(M+H)^+$ 295.1515, found 295.1518.

1-(6-(Cyclohexylmethyl)-6*H*-benzo[*c*]thiochromen-8-yl)ethan-1-one (**4b**). Yellow oil (45.1 mg, 45% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.95 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.88–7.84 (m, 1H), 7.82 (dd, *J* = 5.0, 3.1 Hz, 2H), 7.48–7.45 (m, 1H), 7.33–7.30 (m, 2H), 3.99 (dd, *J* = 9.3, 5.8 Hz, 1H), 2.66 (s, 3H), 1.71–1.60 (m, 7H), 1.52–1.47 (m, 1H), 1.30–1.21 (m, 3H), 0.94–0.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 197.6, 138.2, 137.6, 136.1, 133.2, 132.3, 129.5, 128.9, 127.5, 126.6, 126.4, 125.8, 41.6, 34.5, 33.6, 32.5, 26.7, 26.5, 26.2, 26.0; HRMS (ESI) m/z calcd for $C_{22}H_{24}OS$ $(M+H)^+$ 337.1620, found 337.1620.

Conclusions

In summary, we developed a new radical addition cascade intramolecular cyclization/aromatization of diaryl vinyl ethers with

unactivated alkanes for accessing 6-alkyl-6*H*-benzo[*c*]chromenes. The obvious advantage of our method is the simple reaction conditions. It did not employ costly transition-metal catalysts and strong base. Moreover, 6-alkyl-6*H*-benzo[*c*]thiochromenes could also been obtained by using diaryl vinyl thioethers as the substrates. We were optimistic that this work would find use in medicinal chemistry through the construction of oxygen-containing or sulfur-containing fused heterocyclic compounds.

Conflicts of interest

There are no conflicts to declare.

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Graphical Abstract

BPO promoted direct oxidative C–H functionalization of unactivated alkanes into 6-alkyl 6*H*-benzo[*c*]chromenes under transition-metal-free conditions†

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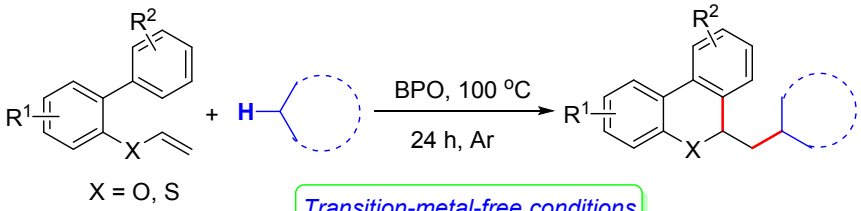

Transition-metal-free conditions
Strong base free conditions
Simple operation