Synthesis K. Deng et al. Paper

Efficient Synthesis of Functionalized 4*H*-Chromenes via an $Fe(OTf)_3$-Catalyzed Cyclization Reaction of Phenols and Ketones

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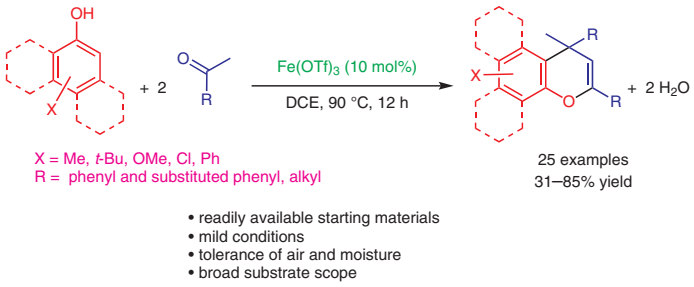

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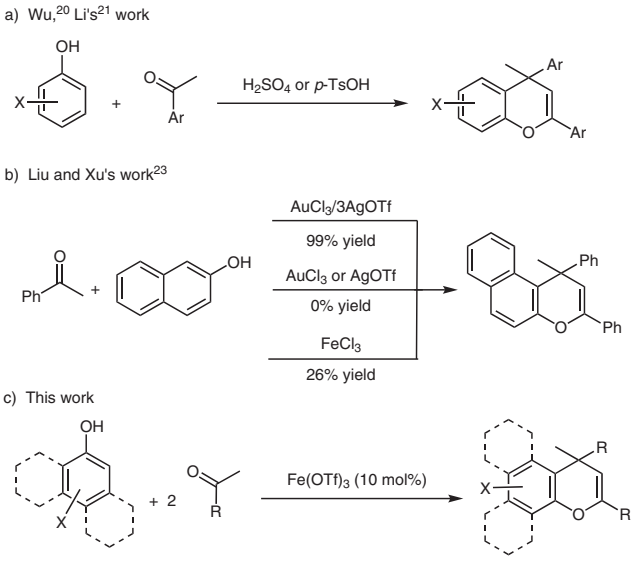
Abstract The iron(III) triflate catalyzed cyclization reaction of phenols and ketones is described; the reaction provides a direct approach to 4*H*-chromene derivatives. 4*H*-Chromene is an important structural fragment of many pharmaceuticals, natural products, and functional materials. The 4*H*-chromene synthetic protocol possesses many advantages, such as using readily available and inexpensive starting materials and a non-toxic catalyst, high selectivity, and operational simplicity, which offer attractive industrial prospects from the point of view of green and sustainable chemistry.

Key words iron catalyst, 4*H*-chromene, cyclization reaction, synthesis, 4*H*-1-benzopyran

4*H*-Chromenes have been a subject of consistent interest due to the presence of their structural motifs in many pharmaceuticals, functional materials, and natural products.[1] It is well-known that 4*H*-chromenes display a broad range of important biological activities, such as antiproliferative,[2] antifungal,[3] antiviral,[4] antimicrobial,[5] antitubercular,[6] antileishmanial,[7] antioxidative,[8] and anticancer[9] properties. Certain examples of 4*H*-chromenes as the pivotal fragment in the construction of natural products and medicinal molecules have been reported;[10,11] these compounds were applied in medicine,[12] health care products,[13] and some functional materials.[14] Hence, various methods for the synthesis of 4*H*-chromenes have been developed: (1) format reagent method;[15] (2) microwave-assisted alkenylation reaction;[16] (3) $FeCl_3$-catalyzed tandem benzylation and cyclization reaction;[17] (4) deep eutectic solvent method;[18] and (5) sodium bisulfate promoted approach.[19] However, these 4*H*-chromene synthetic strategies usually require a heavy metal catalyst, an organocatalyst, or unavailable starting materials. In this context, Wu and co-workers reported an elegant 4*H*-chromene synthesis by the tandem reaction of active polyphenols and ketones in the presence of *p*-toluenesulfonic acid in *n*-hexane under reflux (100 °C, sealed tube).[20] We developed an H_2SO_4-promoted 4*H*-chromene synthesis via the tandem reaction of readily available phenols and acetophenones at 50 °C under solvent-free conditions.[21] These two 4*H*-chromene synthetic protocols (Scheme 1, a) are limited in their application by the need for harsh conditions (*p*-TsOH or H_2SO_4). To overcome this inherent problem, the use of a suitable Lewis acid is required.[22] Indeed, Liu, Xu, and co-workers developed an efficient 4*H*-chromene synthesis via the $AuCl_3$/3AgOTf-catalyzed tandem reaction of phenols and ketones (Scheme 1, b).[23] As this reaction did not occur under the action of either $AuCl_3$ or AgOTf alone,[23] $Au(OTf)_3$ is actually the effective promoter. In contrast to $AuCl_3$, $FeCl_3$ was a relatively effective promoter for this reaction (i.e., 0% versus 26%, Scheme 1, b).[23] Based on these results, we envisioned $Fe(OTf)_3$ as a potentialexcellent promoter for the tandem reaction of phenols and ketones.

Compared with other Lewis acids, iron salts are undoubtedly the most appealing Lewis acids because iron is abundant, inexpensive, and nonhazardous.[24,25] As a consequence, a huge amount of effort has been dedicated to the application of iron salts in the construction of organic compounds.[24] On the other hand, iron salts also have the following properties: stability, nontoxicity, and metabolizability. Thus iron compounds play a significant role in the physiological activity of human beings and show a powerful catalytic ability to promote many bioactivities.[25] Accordingly, iron-catalyzed reactions have been especially taken advantage of in the cosmetic, food, and medicinal industries. It is not an exaggeration to declare that using a suitable iron salt as the Lewis acid would be a significant breakthrough in 4*H*-chromene synthesis in terms of economic efficiency, safety, and low waste disposal. Associate with our previous work on the practical synthesis of various functional com-

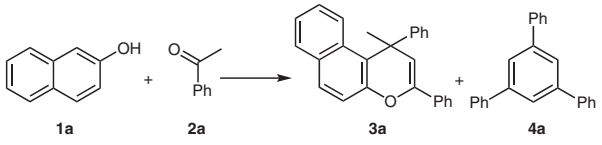


Scheme 1 Synthesis of 4*H*-chromenes

pounds,[26] herein we report an economic synthesis of 4*H*-chromenes via an iron(III)-catalyzed tandem reaction of phenols and ketones (Scheme 1, c). Initially, the reaction conditions were evaluated by using 2-naphthol (**1a**) and acetophenone (**2a**) as a probe, and the valuable results are listed in Table 1.

The treatment of **1a** (1.0 equiv) and **2a** (2.5 equiv) in the presence of $Fe(OTf)_3$ (0.05 equiv) in 1,2-dichloroethane (DCE) at 50 °C for 12 hours gave 4*H*-chromene **3a** in 8% yield (entry 1). The yield of 4*H*-chromene **3a** increased from 8% to 31% when the reaction was conducted at 70 °C under otherwise the same conditions (entries 1 and 2). A series of catalysts were tested for this reaction, in which $Fe(OTf)_3$ was found to be a relatively effective catalyst (entries 2–17). The most effective reaction temperature was found to be 90 °C (entries 2 and 18–21). The yield of byproduct **4a** increased dramatically when the reaction was performed at temperatures higher than 90 °C (entries 19–21). The solvent played an important role in this reaction. With the use of tetrahydrofuran, *N*,*N*-dimethylformamide, or ethanol as the solvent, no reaction took place and the starting materials were recovered (entries 22–24). With the use of *n*-hexane, toluene, or xylene as the solvent, or under solvent-free conditions, lower yields were observed in comparison to that with DCE as solvent (entries 19 and 25–28). Byproduct **4a** became the major product when the reaction was performed in nitromethane or 1,4-dioxane (entries 29 and 30). Further parameter optimization identified the most effective catalyst loading as 5 mol% (entries 19 and 31–32). The reaction went smoothly under an atmosphere of air or argon (entries 19 and 33). Furthermore, the excellent yield was maintained on scaling up the reaction using 1.44 g of **1a** (10.0 mmol) (entry 34).

Table 1 Survey of Conditions for the Reaction of 2-Naphthol with Acetophenone[a]



Entry	Catalyst	Conditions	Yield (%)	
			3a	**4a**
1	$Fe(OTf)_3$	DCE, 50 °C	8	0
2	$Fe(OTf)_3$	DCE, 70 °C	31	trace
3	$Fe(OTf)_2$	DCE, 70 °C	0	0
4	$Fe(Cp)_2$	DCE, 70 °C	0	0
5	$Fe(NO_3)_3$	DCE, 70 °C	0	0
6	$Fe_2(SO_4)_3$	DCE, 70 °C	0	0
7	$FeCl_3$	DCE, 70 °C	trace	0
8	$Cu(OTf)_2$	DCE, 70 °C	0	0
9	AgOTf	DCE, 70 °C	0	0
10	$Mg(OTf)_2$	DCE, 70 °C	0	0
11	$Al(OTf)_3$	DCE, 70 °C	0	0
12	$Ga(OTf)_3$	DCE, 70 °C	0	0
13	$Zn(OTf)_2$	DCE, 70 °C	0	0
14	$Bi(OTf)_3$	DCE, 70 °C	16	trace
15	$Hf(OTf)_4$	DCE, 70 °C	5	0
16	$Sn(OTf)_2$	DCE, 70 °C	<5	0
17	TfOH	DCE, 70 °C	0	trace
18	$Fe(OTf)_3$	DCE, 80 °C	53	5

Table 1 (continued)

Entry	Catalyst	Conditions	Yield (%)	
			3a	4a
19	$Fe(OTf)_3$	DCE, 90 °C	84	11
20	$Fe(OTf)_3$	DCE, 100 °C	73	23
21	$Fe(OTf)_3$	DCE, 110 °C	46	52
22	$Fe(OTf)_3$	THF, 90 °C	0	0
23	$Fe(OTf)_3$	DMF, 90 °C	0	0
24	$Fe(OTf)_3$	EtOH, 90 °C	0	0
25	$Fe(OTf)_3$	*n*-hexane, 90 °C	72	12
26	$Fe(OTf)_3$	toluene, 90 °C	50	12
27	$Fe(OTf)_3$	xylene, 90 °C	52	14
28	$Fe(OTf)_3$	solvent-free, 90 °C	33	32
29	$Fe(OTf)_3$	CH_3NO_2, 90 °C	17	25
30	$Fe(OTf)_3$	1,4-dioxane, 90 °C	trace	30
31[b]	$Fe(OTf)_3$	DCE, 90 °C	42	trace
32[c]	$Fe(OTf)_3$	DCE, 90 °C	61	36
33[d]	$Fe(OTf)_3$	DCE, 90 °C	83	11
34[e]	$Fe(OTf)_3$	DCE, 90 °C	84	12

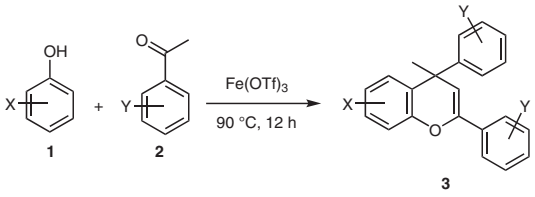
[a] General conditions: **1a** (1.0 mmol), **2a** (2.5 mmol), catalyst (0.05 mmol), solvent (1.0 mL), 12 h (sealed tube).
[b] $Fe(OTf)_3$ (0.01 mmol) was used.
[c] $Fe(OTf)_3$ (0.10 mmol) was used.
[d] Under an argon atmosphere.
[e] Scale of reaction: **1a** (1.44 g, 10.0 mmol).

Next we investigated the scope of the reaction using the optimized reaction conditions (Table 2). Acetophenones **2a–e** reacted effectively with 2-naphthol (**1a**) in the presence of $Fe(OTf)_3$ (0.05 equiv) for 12 hours in 1,2-dichloroethane at 90 °C in an atmosphere of air (1 atm) to give 4*H*-chromenes **3a–e** in 67–85% yields (entries 1–5). This reactivity of the acetophenones was observed in all cases, in absence of a substituting group and as well when a weak electron-withdrawing group (entries 2–4) or a weak electron-donating group (entry 5) was present in *para* position. Inert acetophenones, such as 4′-nitroacetophenone (**2f**) and 4′-(trifluoromethyl)acetophenone (**2g**) reacted with **1a** to afford products **3f**,**g** in 33% and 68% yields, respectively, under the standard conditions, albeit with a longer reaction time (i.e., 12 hours vs 36 hours, entries 6 and 7). As the deactivated acetophenones **2f**,**g** prevented the cyclization reaction using the reported procedure in the literature,[20] the method expanded the substrate scope of the acetophenones. Moreover, the cyclization reaction of **1a** with sterically hindered acetophenone **2h** went favorably under the same conditions to give product **3h** in 55% yield (entry 8); this reaction did not take place using the $AuCl_3$/3AgOTf procedure.[23] Aliphatic ketones **2i–k** reacted uneventfully with **1a** to afford the corresponding products **3i–k** in 43–62% yields (entries 9–11). 7-Bromo-2-naphthol (**1b**) and 6-bromo-2-naphthol were also investigated and they reacted smoothly with **2a** and **2b**, respectively, to give 4*H*-chromenes **3l** and **3m** in 79% and 71% yields (entries 12 and 13). As in the case of 2-naphthol (**1a**), 1-naphthol (**1d**) reacted equally well with acetophenones **2e**,**f**,**h**,**l** to afford 4*H*-chromenes **3n–q** in moderate to good yields (entries 14–17), irrespective of whether the acetophenone substrate bears a weak electron-donating group (entry 14), a strong electron-donating group (entry 15), or a strong electron-withdrawing group (entry 16). On the other hand, various phenols such as 4-substituted phenols **1e–h**, 2,4-disubstituted phenol **1i**, 3,4-disubstituted phenol **1j**, and 3,4,5-disubstituted phenol **1k** were also investigated and these reacted successfully with acetophenone **2c** under the standard conditions to obtain 4*H*-chromenes **3r–x** in 53–80% yields (entries 18–24). By treatment of naphthalene-2,6-diol (**1l**) with acetophenone (**2a**) in the presence of $Fe(OTf)_3$ (5 mol%) in 1,2-dichloroethane at 110 °C for 12 hours, tetracyclic product **3y** was isolated in 65% yield (entry 25). These reactions are easy to perform without the need for an inert atmosphere, and displayed a wide substrate scope.

The reaction mechanism of this 4*H*-chromene synthetic method was next studied, and the representative results are given in Scheme 2. A small amount of 1,3,5-triphenylbenzene (**4a**) was also generated when the reaction was performed under the standard conditions (Table 1, entry 19). The yield of byproduct **4a** increased to 36% when the reaction was performed in the absence of **1a** under otherwise identical conditions, in which a trace of dypnone (**5a**) was also detected (Scheme 2, a). The reaction temperature played an important role in the formation of **4a** (Table 1, entries 19–21). Cyclotrimerization of **2a** in the presence of $Fe(OTf)_3$ (5 mol%) in DCE at 110 °C for 12 hours gave 1,3,5-triphenylbenzene (**4a**) in 67% yield (Scheme 2, b). This is also the case when the cyclotrimerization of **2a** was performed in the presence of *p*-toluenesulfonic acid.[27] As mentioned by Jia and co-workers, only a trace of **4a** was detected when the cyclotrimerization of **2a** was performed in the presence of *p*-toluenesulfonic acid (5 mol%) at 80 °C for 12 hours.[27] In contrast, the yield of **4a** increased to 85% when the reaction was performed at 130 °C for 10 hours under otherwise identical conditions.[27] We had previously observed that the rearrangement of dypnones to 1,3,5-triarylbenzenes goes smoothly under obviously milder conditions in comparison to the cyclotrimerization of acetophenones to 1,3,5-triarylbenzenes [*p*-TsOH (10 mol%), 80 °C vs 130–148 °C].[28] We found that rearrangement of dypnone (**5a**) occurs smoothly in the presence of $Fe(OTf)_3$ (5 mol%) at 90 °C to give 1,3,5-triphenylbenzene (**4a**) in 65% yield (Scheme 2, c). The reaction of dypnone (**5a**) with acetophenone (**2a**) goes equally well under the standard conditions (Scheme 2, d) to give **4a** in 69% yield. The results indicated that the formation of byproduct **4a** is not favored in the reaction with 2-naphthol (**1a**, 1 equiv) under the action of $Fe(OTf)_3$ (0.05 equiv) in DCE at 90 °C for 12 hours and this

reaction instead affords 4*H*-chromene **3a**. Indeed, treatment of dypnone (**5a**, 1 equiv) with **1a** under the standard conditions gave **3a** and 1,3,5-triphenylbenzene (**4a**) in 53% and 42% yields, respectively (Scheme 2, e), reflecting the limited contribution of dypnones **5** to this iron(III)-catalyzed cyclization reaction of phenols **1** and acetophenones **2**.

Table 2 $Fe(OTf)_3$-Catalyzed Tandem Reaction of Phenols with Ketones[a]



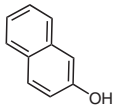
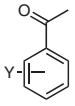
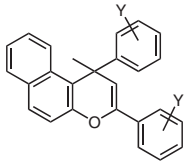
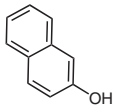
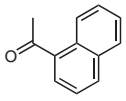
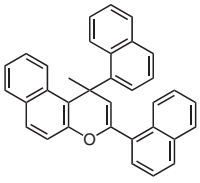
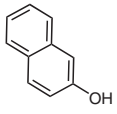
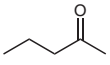
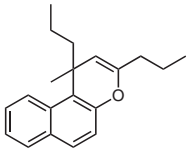
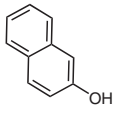
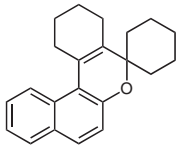
Entry	**1** (X)	**2** (Y)	Product: Yield
			
1	**1a**	**2a** (H)	**3a**: 84%
2	**1a**	**2b** (4-F)	**3b**: 73%
3	**1a**	**2c** (4-Cl)	**3c**: 85%
4	**1a**	**2d** (4-Br)	**3d**: 77%
5	**1a**	**2e** (4-Me)	**3e**: 67%
6[b]	**1a**	**2f** (4-NO_2)	**3f**: 33%
7[b]	**1a**	**2g** (4-CF_3)	**3g**: 68%
			
8	**1a**	**2h**	**3h**: 55%
9			
	1a	**2i**	**3i**: 62%
			
10[b]	**1a**	**2j**	**3j**: 43%

Table 2 (continued)

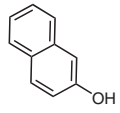
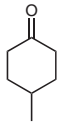
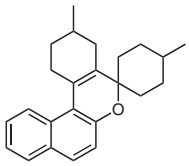
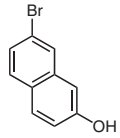
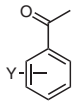
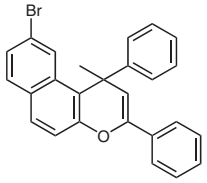
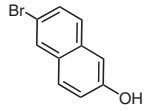
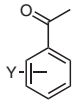
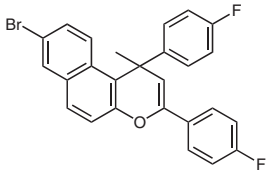
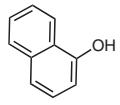
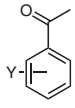
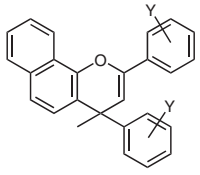
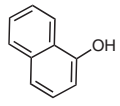
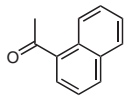
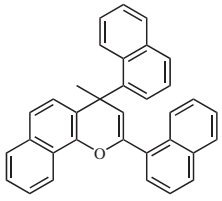
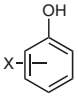
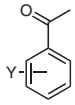
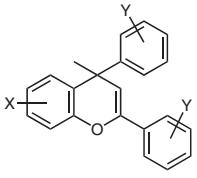
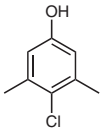
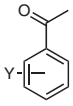
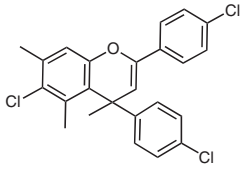
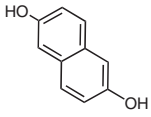
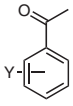
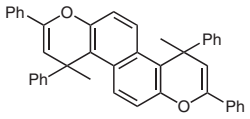
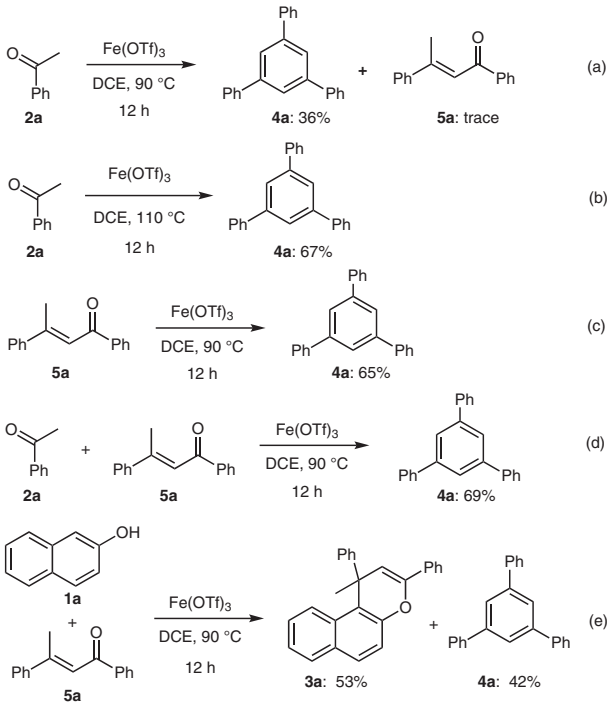
Entry	**1** (X)	**2** (Y)	Product: Yield
			
11[b]	**1a**	**2k**	**3k**: 46%
			
12	**1b**	**2a** (H)	**3l**: 79%
			
13	**1c**	**2b** (4-F)	**3m**: 71%
			
14	**1d**	**2e** (4-Me)	**3n**: 69%
15[b]	**1d**	**2f** (4-NO_2)	**3o**: 31%
16	**1d**	**2l** (4-OMe)	**3p**: 76%
			
17	**1d**	**2h**	**3q**: 53%
			
18	**1e** (4-Me)	**2c** (4-Cl)	**3r**: 66%
19	**1f** (4-*t*-Bu)	**2c** (4-Cl)	**3s**: 74%

Table 2 (continued)

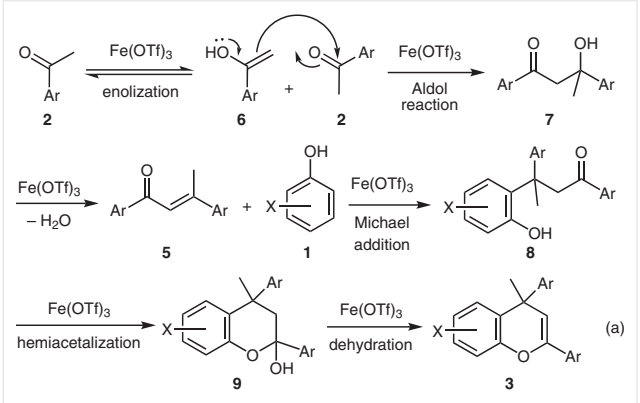
Entry	1 (X)	2 (Y)	Product: Yield
20	**1g** (4-Ph)	**2c** (4-Cl)	**3t**: 58%
21	**1h** (4-OMe)	**2c** (H)	**3u**: 80%
22	**1i** (2,4-Me_2)	**2c** (4-Cl)	**3v**: 61%
23	**1j** (3,4-Me_2)	**2c** (4-Cl)	**3w**: 74%
			
24	**1k**	**2c** (4-Cl)	**3x**: 53%
			
25[c]	**1l**	**2a** (H)	**3y**: 65%

[a] General conditions: **1** (1.0 mmol), **2** (2.5 mmol), $Fe(OTf)_3$ (0.05 mmol), DCE (1 mL), 90 °C, 12 h (sealed tube).
[b] The reaction was performed for 36 h.
[c] Using **2a** (5 equiv) at 110 °C.



Scheme 2 Verification experiments

Based on the above results and related reports in the literature, a possible reaction mechanism is illustrated in Scheme 3. The aldol-type condensation reaction of acetophenones **2** followed by dehydration gives dypnones **5**, which are next converted into compounds **8** by intermolecular Michael addition with phenols **1**. Intramolecular hemiacetalization of **8** followed by dehydration affords 4*H*-chromenes **3** (Scheme 3).



Scheme 3 Proposed mechanism

In summary, we have developed a practical cyclization reaction of phenols and ketones that provides a facile synthesis of 4*H*-chromenes from readily available and inexpensive starting materials. Sterically hindered or inert acetophenones, such as 1-acetonaphthone, 4′-(trifluoromethyl)-acetophenone, and 4′-nitroacetophenone, which prevented the cyclization reaction using procedures reported in the

literature, are suitable substrates in the present 4*H*-chromene synthetic protocol. The use of an iron salt as the Lewis acid is desirable in terms of economic efficiency, safety, and low waste disposal, which offers attractive industrial prospects from the point of view of green and sustainable chemistry. Further mechanistic investigations as well as applications of this method are in progress.

Common reagents and materials were purchased from commercial sources and purified by recrystallization or distillation. Where necessary, organic solvents were routinely dried and/or distilled prior to use and stored over molecular sieves under argon. Organic extracts were, in general, dried over anhyd Na_2SO_4. TLC plates were visualized by exposure to UV light. NMR spectra were referenced to the NMR solvents (^{1}H, $CDCl_3$: δ = 7.26; ^{13}C, $CDCl_3$: δ = 77.0; DMSO-d_6: δ = 39.43).

1-Methyl-1,3-diphenyl-1*H*-benzo[*f*]chromene (3a); Typical Procedure

The mixture of 2-naphthol (**1a**, 99%, 145.6 mg, 1.0 mmol), acetophenone (**2a**, 98%, 303.4 mg, 2.5 mmol), and $Fe(OTf)_3$ (98%, 25.1 mg, 0.05 mmol) in 1,2-dichloroethane (1 mL) was stirred at 90 °C (sealed tube) for 12 h, cooled to r.t., quenched with sat. $NaHCO_3$ solution (20 mL), and extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine, dried (anhyd Na_2SO_4), filtered, and concentrated. The residue was purified by column chromatography (silica gel) to afford **3a** as a pale yellow oil; yield: 292.7 mg (84%).

FTIR (film): 3055, 2960, 2925, 2853, 1678, 1671, 1599, 1572, 1506, 1490, 1465, 1396, 1372, 1313, 1288, 1261, 1227, 1204, 1094, 1077, 1014, 962, 893, 858, 814, 748 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.65 (m, 4 H), 7.53 (d, *J* = 8.7 Hz, 1 H), 7.43 (d, *J* = 7.5 Hz, 2 H), 7.33–7.04 (m, 9 H), 5.27 (s, 1 H), 2.14 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.1, 148.9, 142.9, 133.8, 131.9, 131.4, 129.3, 128.8, 128.5, 128.3, 128.2, 127.0, 126.3, 125.8, 125.6, 124.5, 123.5, 118.8, 118.3, 109.1, 40.8, 29.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{21}O$: 349.1587; found: 349.1585.

1,3-Bis(4-fluorophenyl)-1-methyl-1*H*-benzo[*f*]chromene (3b)

White solid; yield: 280.3 mg (73%); mp 159–160 °C.

FTIR (film): 1640, 1599, 1494, 1437, 1381, 1089, 1008, 813 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.62 (m, 4 H), 7.54–7.31 (m, 4 H), 7.25–7.11 (m, 2 H), 7.06–6.93 (m, 4 H), 5.18 (s, 1 H), 2.15 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.5 (d, $^1J_{C-F}$ = 188 Hz, 1 C), 160.3 (d, $^1J_{C-F}$ = 185 Hz, 1 C), 148.7, 145.9 (d, $^4J_{C-F}$ = 4 Hz, 1 C), 142.3, 131.9, 131.2, 129.8 (d, $^4J_{C-F}$ = 4 Hz, 1 C), 129.5, 128.9, 128.5 (d, $^3J_{C-F}$ = 10 Hz, 1 C), 126.4 (d, $^3J_{C-F}$ = 11 Hz, 1 C), 126.1, 125.7, 123.7, 118.5, 118.2, 115.3 (d, $^2J_{C-F}$ = 28 Hz, 1 C), 115.2 (d, $^2J_{C-F}$ = 29 Hz, 1 C), 108.6, 40.3, 29.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{19}F_2O$: 385.1399; found: 385.1401.

1,3-Bis(4-chlorophenyl)-1-methyl-1*H*-benzo[*f*]chromene (3c)

White solid; yield: 354.4 mg (85%); mp 172–173 °C.

FTIR (film): 3056, 2966, 2926, 2853, 1713, 1673, 1598, 1575, 1490, 1468, 1397, 1381, 1369, 1319, 1289, 1202, 1094, 1074, 1012, 830, 812, 748 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.4 Hz, 2 H), 7.60 (d, *J* = 7.5 Hz, 2 H), 7.49 (d, *J* = 8.7 Hz, 1 H), 7.38–7.12 (m, 9 H), 5.21 (s, 1 H), 2.14 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.6, 148.5, 142.4, 134.3, 132.1, 131.9, 131.8, 131.1, 129.6, 128.9, 128.7, 128.6, 128.5, 128.4, 126.0, 125.8 (d), 123.7, 118.1, 108.9, 40.5, 29.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{19}Cl_2O$: 417.0808; found: 417.0792.

1,3-Bis(4-bromophenyl)-1-methyl-1*H*-benzo[*f*]chromene (3d)

White solid; yield: 389.6 mg (77%); mp 181–182 °C.

FTIR (film): 3025, 2966, 2924, 2855, 1667, 1621, 1491, 1453, 1401, 1324, 1289, 1262, 1093, 1014, 828 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.7 Hz, 2 H), 7.56–7.23 (m, 11 H), 7.15 (t, *J* = 8.4 Hz, 1 H), 5.22 (s, 1 H), 2.14 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.0, 148.6, 142.5, 132.5, 131.9, 131.7, 131.4, 131.1, 129.6, 129.0, 128.8, 126.1, 126.0, 125.9, 123.8, 122.5, 120.0, 118.1, 118.0, 108.9, 40.6, 28.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{19}Br_2O$: 504.9797; found: 504.9790.

1-Methyl-1,3-di(4-tolyl)-1*H*-benzo[*f*]chromene (3e)

White solid; yield: 251.9 mg (67%); mp 165–166 °C.

FTIR (film): 2920, 2849, 1647, 1513, 1322, 1232, 812 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.56 (m, 5 H), 7.32–7.08 (m, 9 H), 5.21 (s, 1 H), 2.34 (s, 3 H), 2.28 (s, 3 H), 2.13 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.9, 147.4, 142.8, 138.1, 135.2, 131.8, 131.5, 131.0, 129.2, 129.1, 128.9, 128.7, 126.9, 126.3, 125.5, 124.4, 123.4, 119.0, 118.3, 108.5, 40.4, 29.1, 21.2, 20.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{25}O$: 377.1900; found: 377.1910.

1-Methyl-1,3-bis(4-nitrophenyl)-1*H*-benzo[*f*]chromene (3f)

Yellow foam; yield: 144.5 mg (33%).

FTIR (film): 1622, 1514, 1347, 854 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.25–8.10 (m, 5 H), 7.84–7.62 (m, 6 H), 7.36–7.25 (m, 3 H), 5.42 (s, 1 H), 2.26 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.4, 148.4, 147.8, 147.4, 146.3, 142.5, 139.3, 130.3, 129.3, 127.9, 126.33, 126.28, 125.6, 125.3, 124.2, 124.1, 123.7, 123.4, 118.0, 110.7, 41.4, 29.0.

Anal. Calcd for $C_{26}H_{18}N_2O_5$: C, 71.23; H, 4.14; N, 6.39. Found: C, 71.45; H, 4.01; N, 6.58.

1-Methyl-1,3-bis[4-(trifluoromethyl)phenyl]-1*H*-benzo-[*f*]chromene (3g)

White solid; yield: 329.1 mg (68%); mp 132–134 °C.

FTIR (film): 2934, 2360, 1618, 1411, 1323, 1232, 1166, 1122, 1072, 1015, 908, 814, 734 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.76 (m, 4 H), 7.65–7.58 (m, 6 H), 7.44–7.42 (d, *J* = 8.5 Hz, 1 H), 7.38–7.35 (d, *J* = 8.8 Hz, 1 H), 7.30–7.28 (d, *J* = 8.8 Hz, 1 H), 7.19–7.15 (t, *J* = 7.3 Hz, 1 H), 5.34 (s, 1 H), 2.23 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.5, 148.6, 142.5, 136.9, 132.1, 131.0, 130.4 (q, J_{C-F} = 32 Hz, 1 C), 129.9, 129.1, 128.3 (q, J_{C-F} = 32.3 Hz, 1 C), 127.3, 126.1, 125.9, 125.7 (q, J_{C-F} = 3.6 Hz, 1 C), 125.3 (q, J_{C-F} = 3.7 Hz, 1 C), 124.8, 123.9, 122.8, 122.7, 118.1, 117.7, 109.9, 41.0, 28.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{19}F_6O$: 485.1262; found: 485.1260.

1-Methyl-1,3-di(1-naphthyl)-1*H*-benzo[*f*]chromene (3h)

Green foam; yield: 246.4 mg (55%).

FTIR (film): 3054, 2959, 2923, 2851, 1626, 1595, 1511, 1454, 1396, 1373, 1259, 1210, 1163, 1015, 862, 815, 798, 778, 747 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21–6.92 (m, 20 H), 5.28 (s, 1 H), 2.01 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.9, 143.5, 140.8, 136.6, 135.0, 134.0, 133.5, 131.9, 130.2, 129.1, 128.9, 128.8, 128.3, 127.7, 127.4, 126.7, 126.3, 126.1, 126.0, 125.9, 125.8, 125.5, 125.4, 125.1, 124.3, 120.3, 115.1, 104.2, 102.5, 102.0, 38.4, 29.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{34}H_{25}O$: 449.1900; found: 449.1903.

1-Methyl-1,3-dipropyl-1*H*-benzo[*f*]chromene (3i)

Yellow oil; yield: 173.6 mg (62%).

FTIR (film): 2958, 2931, 2871, 1740, 1463, 1372, 1345, 1235, 1046, 813, 748 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (d, *J* = 8.7 Hz, 1 H), 7.75–7.73 (m, 1 H), 7.60 (d, *J* = 8.8 Hz, 1 H), 7.41 (t, *J* = 8.8 Hz, 1 H), 7.32 (t, *J* = 8.8 Hz, 1 H), 7.04 (d, *J* = 8.8 Hz, 1 H), 4.30 (s, 1 H), 2.61–2.53 (m, 2 H), 2.18 (t, *J* = 7.4 Hz, 2 H), 1.75 (s, 3 H), 1.64 (qd, J_1 = 7.4 Hz, J_2 = 14.7 Hz, 3 H), 1.40–1.34 (m, 2 H), 1.26 (s, 2 H), 0.99 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.6, 147.5, 132.5, 131.4, 129.2, 128.5, 125.4, 125.4, 123.2, 118.4, 118.3, 108.0, 45.7, 37.0, 34.7, 32.0, 19.9, 19.6, 14.4, 13.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{25}O$: 281.1900; found: 281.1902.

1′,2′,3′,4′-Tetrahydrospiro[cyclohexane-1,5′-dibenzo[*c*,*f*]chromene] (3j)

Yellow oil; yield: 130.7 mg (43%).

FTIR (film): 2929, 2853, 1737, 1593, 1447, 1371, 1236, 1044, 998, 806, 745 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 8.6 Hz, 1 H), 7.76 (d, *J* = 7.9 Hz, 1 H), 7.64 (d, *J* = 8.7 Hz, 1 H), 7.41–7.37 (m, 1 H), 7.30 (t, *J* = 7.4 Hz, 1 H), 7.19 (d, *J* = 8.7 Hz, 1 H), 2.75 (t, *J* = 5.6 Hz, 2 H), 2.23 (t, *J* = 6.3 Hz, 2 H), 1.98 (d, *J* = 13.3 Hz, 2 H), 1.84–1.64 (m, 8 H), 1.49–1.44 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1, 135.1, 130.3, 130.0, 128.8, 128.7, 125.8, 125.6, 125.1, 122.6, 120.3, 118.4, 77.2, 31.3, 31.1, 25.5, 25.2, 23.4, 22.9, 21.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{25}O$: 305.1900; found: 305.1901.

3′,4-Dimethyl-1′,2′,3′,4′-tetrahydrospiro[cyclohexane-1,5′-dibenzo[*c*,*f*]chromene] (3k)

Yellow solid; yield: 152.7 mg (46%); mp 135–136 °C.

FTIR (film): 2949, 2921, 2853, 1738, 1456, 1371, 1234, 1045, 989, 810, 745 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.16 (d, *J* = 8.6 Hz, 1 H), 7.76 (d, *J* = 8.1 Hz, 1 H), 7.64 (d, *J* = 8.7 Hz, 1 H), 7.40 (t, *J* = 7.6 Hz, 1 H), 7.29 (t, *J* = 7.4 Hz, 1 H), 7.18 (d, *J* = 8.7 Hz, 1 H), 3.04–2.97 (m, 1 H), 2.60 (d, *J* = 8.7 Hz, 1 H), 2.28 (dd, J_1 = 9.1 Hz, J_2 = 21.1 Hz, 2 H), 2.00–1.56 (m, 8 H), 1.27–1.21 (m, 4 H), 1.09 (d, *J* = 5.7 Hz, 3 H), 0.95 (d, *J* = 6.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.1, 134.7, 130.3, 130.1, 128.8, 128.7, 125.6, 125.5, 125.1, 122.6, 120.1, 118.5, 76.7, 34.1, 32.8, 32.0, 31.7, 31.2, 30.2, 30.1, 29.7, 29.6, 29.0, 22.5, 22.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{29}O$: 333.2213; found: 333.2212.

9-Bromo-1-methyl-1,3-diphenyl-1*H*-benzo[*f*]chromene (3l)

White solid; yield: 337 mg (79%); mp 187–188 °C.

FTIR (film): 2979, 2359, 1737, 1614, 1498, 1445, 1373, 1320, 1044, 835, 762, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 1.3 Hz, 1 H), 7.73–7.70 (m, 3 H), 7.61 (d, *J* = 8.6 Hz, 1 H), 7.51–7.49 (m, 2 H), 7.39–7.29 (m, 7 H), 7.25 (t, *J* = 7.3 Hz, 1 H), 5.32 (s, 1 H), 2.16 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.4, 142.9, 133.5, 132.7, 130.2, 130.1, 129.0, 128.6, 128.5, 128.4, 128.2, 127.3, 127.0, 126.8, 126.1, 124.4, 120.0, 118.7, 118.3, 108.8, 40.6, 28.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{20}BrO$: 427.0692; found: 427.0695.

8-Bromo-1,3-bis(4-fluorophenyl)-1-methyl-1*H*-benzo[*f*]chromene (3m)

White solid; yield: 328.7 mg (71%); mp 199–200 °C.

FTIR (film): 3057, 2967, 2927, 1674, 1602, 1508, 1381, 1370, 1319, 1232, 1160, 1014, 837, 813, 746 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, *J* = 8.4 Hz, 1 H), 7.85–7.77 (m, 3 H), 7.62–7.38 (m, 5 H), 7.17–7.13 (m, 2 H), 7.03–7.00 (m, 2 H), 5.45 (s, 1 H), 1.94 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.3 (d, $^1J_{C-F}$ = 179 Hz, 1 C), 160.9 (d, $^1J_{C-F}$ = 176 Hz, 1 C), 145.7 (d, $^4J_{C-F}$ = 3 Hz, 1 C), 145.1, 144.6, 133.1, 130.4 (d, $^4J_{C-F}$ = 3 Hz, 1 C), 129.2 (d, $^3J_{C-F}$ = 8 Hz, 1 C), 127.6, 126.6 (d, $^3J_{C-F}$ = 8 Hz, 1 C), 126.4, 126.2, 125.6, 124.1, 123.2, 121.8, 121.7, 115.3 (d, $^2J_{C-F}$ =50 Hz, 1 C), 115.1 (d, $^2J_{C-F}$ = 49 Hz, 1 C), 106.8, 39.6, 30.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{18}BrF_2O$: 463.0504; found: 463.0507.

4-Methyl-2,4-di(4-tolyl)-4*H*-benzo[*h*]chromene (3n)

Yellow oil; yield: 259.4 mg (69%).

FTIR (film): 3054, 3025, 2961, 2923, 2854, 1672, 1574, 1511, 1454, 1380, 1319, 1289, 1201, 1100, 1074, 1015, 810, 748 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (d, *J* = 8.7 Hz, 1 H), 7.78–7.49 (m, 5 H), 7.44–7.27 (m, 4 H), 7.25–7.05 (m, 4 H), 5.49 (s, 1 H), 2.41 (s, 3 H), 2.32 (s, 3 H), 1.93 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.2, 145.8, 144.8, 138.3, 135.7, 133.0, 131.7, 129.1, 128.9, 127.6, 127.5, 126.1, 125.9, 125.8, 124.7, 124.3, 122.8, 122.4, 121.9, 106.7, 39.7, 29.7, 21.3, 20.9;

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{25}O$: 377.1900; found: 377.1910.

4-Methyl-2,4-bis(4-nitrophenyl)-4*H*-benzo[*h*]chromene (3o)

Yellow foam; yield: 135.8 mg (31%).

FTIR (film): 2958, 2923, 2852, 1599, 1517, 1395, 1368, 1346, 1261, 1211, 1106, 810, 752 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.71 (d, *J* = 8.4 Hz, 2 H), 8.16 (d, *J* = 8.4 Hz, 2 H), 7.83–7.57 (m, 6 H), 7.47 (d, *J* = 8.0 Hz, 2 H), 6.90 (d, *J* = 8.0 Hz, 2 H), 5.30 (s, 1 H), 2.17 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.7, 147.1, 145.8, 145.2, 144.3, 133.3, 129.7, 127.7, 126.9, 126.5, 125.6, 124.2, 123.42, 123.37, 122.5, 121.9, 121.8, 121.6, 120.7, 105.3, 43.3, 29.7.

Anal. Calcd for $C_{26}H_{18}N_2O_5$: C, 71.23; H, 4.14; N, 6.39. Found: C, 71.32; H, 4.05; N, 6.53.

2,4-Bis(4-methoxyphenyl)-4-methyl-4*H*-benzo[*h*]chromene (3p)

Pale yellow oil; yield: 310 mg (76%).

FTIR (film): 3053, 2957, 2926, 2853, 1609, 1596, 1578, 1511, 1461, 1385, 1277, 1251, 1179, 1083, 1034, 831, 814, 794, 772 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (d, *J* = 7.6 Hz, 2 H), 7.61 (d, *J* = 7.6 Hz, 2 H), 7.59 (d, *J* = 8.3 Hz, 1 H), 7.35–7.11 (m, 5 H), 6.88 (d, *J* = 6.4 Hz, 2 H), 6.70 (d, *J* = 6.4 Hz, 2 H), 5.14 (s, 1 H), 3.79 (s, 3 H), 3.74 (s, 3 H), 2.12 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 157.5, 148.9, 142.8, 142.5, 131.8, 131.6, 129.1, 128.8, 128.0, 126.5, 126.4, 125.9, 125.5, 123.4, 119.0, 118.3, 113.8, 113.6, 107.8, 55.3, 55.1, 40.1, 29.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{25}O_3$: 409.1798; found: 409.1793.

4-Methyl-2,4-di(1-naphthyl)-4*H*-benzo[*h*]chromene (3q)

Green foam; yield: 237.4 mg (53%).

FTIR (film): 2960, 2922, 2851, 1487, 1378, 1260, 1080, 808, 766 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.52 (d, *J* = 8.4 Hz, 1 H), 7.96 (d, *J* = 8.4 Hz, 2 H), 7.79 (d, *J* = 8.0 Hz, 1 H), 7.71–7.30 (m, 15 H), 7.12 (d, *J* = 8.4 Hz, 1 H), 5.63 (s, 1 H), 2.01 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.0, 145.6, 144.8, 141.3, 140.7, 140.6, 139.0, 133.3, 133.1, 128.9, 128.7, 128.1, 127.54, 127.49, 127.2, 127.1, 127.0, 126.4, 126.3, 126.1, 125.9, 125.2, 124.3, 123.0, 122.0, 121.8, 107.3, 39.9, 29.7.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{34}H_{25}O$: 449.1900; found: 449.1902.

2,4-Bis(4-chlorophenyl)-4,6-dimethyl-4*H*-chromene (3r)

Pale yellow oil; yield: 251.4 mg (66%).

FTIR (film): 2968, 2928, 2857, 1664, 1591, 1494, 1397, 1316, 1291, 1234, 1089, 1008, 813, 724 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.60 (m, 4 H), 7.36–7.28 (m, 4 H), 7.03–6.72 (m, 2 H), 6.72 (s, 1 H), 5.35 (s, 1 H), 2.22 (s, 3 H), 1.85 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.4, 148.0, 141.4, 134.3, 133.1, 129.1, 128.8, 128.53, 128.47, 128.4, 128.3, 127.5, 126.0, 125.0, 116.3, 106.7, 39.5, 29.7, 20.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{19}Cl_2O$: 381.0807; found: 381.0810.

6-*tert*-Butyl-2,4-bis(4-chlorophenyl)-4-methyl-4*H*-chromene (3s)

Yellow solid; yield: 313 mg (74%); mp 96–97 °C.

FTIR (film): 2963, 2868, 1737, 1495, 1400, 1322, 1257, 1092, 1035, 819, 743 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67–7.64 (m, 2 H), 7.37–7.33 (m, 4 H), 7.29–7.27 (m, 2 H), 7.25 (dd, J_1 = 2.3 Hz, J_2 = 8.6 Hz, 1 H), 7.08 (d, *J* = 8.6 Hz, 1 H), 6.98 (d, *J* = 2.3 Hz, 1 H), 5.39 (s, 1 H), 1.89 (s, 3 H), 1.24 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.4, 147.9, 146.4, 145.4, 134.2, 132.6, 131.8, 128.6, 128.4, 128.2, 127.0, 125.9, 124.8, 124.7, 115.9, 106.8, 39.6, 34.3, 31.3, 30.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{25}Cl_2O$: 423.1277; found: 423.1280.

2,4-Bis(4-chlorophenyl)-4-methyl-6-phenyl-4*H*-chromene (3t)

Pale yellow oil; yield: 256.9 mg (58%).

FTIR (film): 2964, 2924, 2854, 1666, 1490, 1276, 1085, 833, 819 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70–7.60 (m, 3 H), 7.47–7.29 (m, 11 H), 7.21–7.15 (m, 2 H), 5.41 (s, 1 H), 1.92 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.6, 148.2, 145.4, 140.8, 135.1, 132.4, 132.2, 129.1, 128.8, 128.7, 128.6, 128.4, 128.2, 127.1, 127.0, 126.8, 126.5, 126.0, 117.0, 106.9, 39.7, 30.5.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{28}H_{21}Cl_2O$: 443.0964; found: 443.0961.

2,4-Bis(4-phenyl)-6-ethoxy-4-methyl-4*H*-chromene (3u)

Yellow solid; yield: 317.6 mg (80%); mp 100–101 °C.

FTIR (film): 3372, 2969, 2357, 1666, 1496, 1445, 1275, 1205, 1049, 759, 735, 699 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.72 (m, 2 H), 7.45–7.30 (m, 8 H), 7.20 (t, *J* = 7.30 Hz, 1 H), 7.09 (d, *J* = 8.9 Hz, 1 H), 6.76 (dd, J_1 = 3.0 Hz, J_2 = 8.9 Hz, 1 H), 5.41 (s, 1 H), 3.69 (s, 3 H), 1.90 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 149.6, 146.1, 144.5, 134.2, 129.3, 128.3, 128.2, 128.1, 127.3, 126.0, 124.6, 117.1, 113.1, 113.0, 106.1, 55.5, 40.1, 30.3.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{21}O_2$: 329.1536; found: 329.1539.

2,4-Bis(4-chlorophenyl)-4,6,8-trimethyl-4*H*-chromene (3v)

Pale yellow solid; yield: 240.9 mg (61%); mp 105–108 °C.

FTIR (film): 2966, 2924, 2852, 1670, 1598, 1492, 1438, 1401, 1375, 1329, 1296, 1278, 1260, 1216, 1147, 1093, 1040, 1012, 919, 859, 833, 808, 744, 716, 678 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.1 Hz, 2 H), 7.28–7.17 (m, 6 H), 6.77 (s, 1 H), 6.47 (s, 1 H), 5.28 (s, 1 H), 2.32 (s, 3 H), 2.09 (s, 3 H), 1.74 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.6, 146.2, 145.3, 134.2, 132.8, 132.3, 131.9, 129.8, 128.8, 128.5, 128.3, 127.2, 126.1, 125.9, 125.4, 106.7, 39.7, 29.7, 20.7, 16.2.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{21}Cl_2O$: 395.0964; found: 395.0963.

2,4-Bis(4-chlorophenyl)-4,6,7-trimethyl-4*H*-chromene (3w)

Pale yellow oil; yield: 292.3 mg (74%).

FTIR (film): 2969, 2921, 1672, 1494, 1397, 1324, 1283, 1089, 1008, 837, 805 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71–7.32 (m, 8 H), 7.01 (s, 1 H), 6.75 (s, 1 H), 5.42 (s, 1 H), 2.30 (s, 3 H), 2.19 (s, 3 H), 1.91 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.5, 148.0, 145.4, 136.2, 134.2, 132.7, 129.0, 128.9, 128.7, 128.5, 128.4, 128.2, 125.9, 125.0, 117.2, 106.8, 39.2, 30.3, 19.4, 19.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{21}Cl_2O$: 395.0964; found: 395.0969.

6-Chloro-2,4-bis(4-chlorophenyl)-4,5,7-trimethyl-4*H*-chromene (3x)

Yellow oil; yield: 227.3 mg (53%).

FTIR (film): 2981, 2928, 2359, 1737, 1492, 1393, 1312, 1238, 1093, 1045, 1012, 830 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.56 (m, 2 H), 7.32–7.18 (m, 6 H), 6.98 (s, 1 H), 5.12 (s, 1 H), 2.39 (s, 3 H), 1.89 (s, 3 H), 1.88 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.8, 148.4, 142.0, 136.1, 135.3, 134.2, 132.0, 131.7, 131.2, 128.6, 128.4, 128.1, 125.7, 123.9, 116.9, 108.2, 40.5, 28.6, 20.8, 19.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{20}Cl_3O$: 429.0574; found: 429.0575.

4,10-Dimethyl-2,4,8,10-tetraphenyl-4,10-dihydrochromeno[6,5-*f*]chromene (3y)

Pale yellow oil; yield: 369.2 mg (65%).

FTIR (film): 3058, 2965, 2360, 2342, 1654, 1599, 1447, 1324, 1261, 906, 762, 731, 699, 668 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.66–7.64 (d, *J* = 7.4 Hz, 4 H), 7.56–7.54 (d, *J* = 9.4 Hz, 2 H), 7.49–7.47 (d, *J* = 7.4 Hz, 4 H), 7.38–7.34 (m, 10 H), 7.24–7.21 (t, *J* = 7.0 Hz, 2 H), 7.01–7.00 (d, *J* = 9.4 Hz, 2 H), 5.25 (s, 2 H), 2.19 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.3, 147.1, 142.7, 133.8, 129.8, 128.5, 128.2, 128.2, 127.1, 127.0, 125.8, 124.4, 119.7, 117.4, 109.0, 40.9, 29.4.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{42}H_{33}O_2$: 569.2479; found: 569.2475.

1,3,5-Triphenylbenzene (4a)

White solid; mp 172–174 °C.

FTIR (film): 1648, 1048, 1026, 997, 827, 766, 633 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (s, 3 H), 7.73–7.71 (m, 6 H), 7.51–7.48 (m, 6 H), 7.42–7.39 (m, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 141.6, 140.0, 128.8, 127.6, 127.1, 124.3.

Anal. Calcd for $C_{24}H_{18}$: C, 94.08; H, 5.92. Found: C, 94.18; H, 5.99.

Dypnone (5a)

Pale yellow oil.

FTIR (film): 3027, 2919, 1658, 1601, 1575, 1493, 1448, 1380, 1356, 1275, 1214, 1179, 1047, 1025, 951, 868, 855, 753, 693 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.04–7.40 (m, 10 H), 7.20 (d, *J* = 0.3 Hz, 1 H), 2.64 (d, *J* = 0.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.3, 154.7, 142.4, 139.1, 132.2, 128.9, 128.3, 128.2, 128.0, 126.2, 121.7, 18.5.

Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.58; H, 6.23.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-00xx-xxxxxxx.

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