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One-Pot Synthesis of *O*-Heterocycles or Aryl Ketones Using an $InCl_3/Et_3SiH$ System by Switching the Solvent

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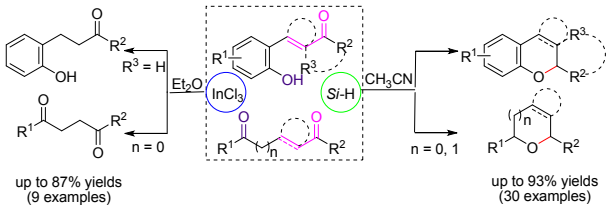
Supporting Information



ABSTRACT: An efficient one-pot synthesis of *O*-heterocycles or aryl ketones has been achieved using Et_3SiH in the presence of $InCl_3$ *via* a sequential ionic hydrogenation reaction by switching the solvent. This methodology can be used to construct C-O bonds and to prepare conjugate reduction products, including chromans, tetrahydrofurans, tetrahydropyrans, dihydroisobenzofurans, dihydrochalcones and 1,4-diones in a facile manner. In addition, a novel plausible mechanism involving a conjugate reduction and a tandem reductive cyclization was verified by experimental investigations.

INTRODUCTION

Chroman and tetrahydrofuran derivatives constitute the core of many natural products and pharmaceutical compounds with extensive biological and pharmacological activities (Fig. 1).[1] The most well-known chroman is α-tocopherol, which is an important member of the vitamin E family that serves as a natural lipophilic antioxidant and radical scavenger.[2] Dihydrochalcones have been reported to exhibit antibacterial and anticancer properties.[3] Moreover, veraguensin, isolated from Virola surinamensis, has been identified as a potent inhibitor of the trypomastigote Y strain of *T. cruzi*.[4]

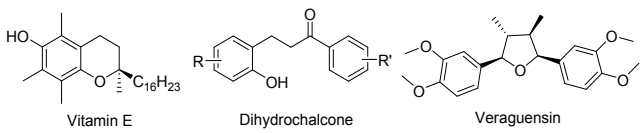


Figure 1. Various *O*-containing bioactive compounds.

Given the importance of the chroman and tetrahydrofuran motifs, in the last decade, many strategies for accessing these structures have been developed.[5] However, most of these strategies demand multiple steps that are conducted under different reaction conditions. To date, there has been only one example for a one-pot synthesis of 2-phenylchroman, and this was achieved in 43% yield *via* a tosylhydrazine-mediated reductive cyclization from 2-hydroxychalcone, which is readily available and easy to handle.[6] Thus, an efficient methodology for the preparation of chroman and tetrahydrofuran in a small number of steps and in high yield is of great interest.

Ionic hydrogenation has become an efficient tool for the reduction of certain functional groups.[7] Recently, we disclosed a facile $Al(OTf)_3$-mediated cascade cyclization and ionic hydrogenation to afford various *N*-heterocyclic skeletons.[8] In this context, we envisioned that it might be possible to synthesize various *O*-heterocycles under the same reaction conditions. Such a method has the potential to be an extremely powerful synthetic tool, as it would offer efficiency with both high atom and step economy. To the best of our knowledge, no Lewis acid-promoted sequential ionic hydrogenation for the synthesis of *O*-heterocycles has been reported to date.

Scheme 1. Synthesis of *O*-heterocycles and aryl ketones using the same Lewis acid and hydrosilane and different solvents

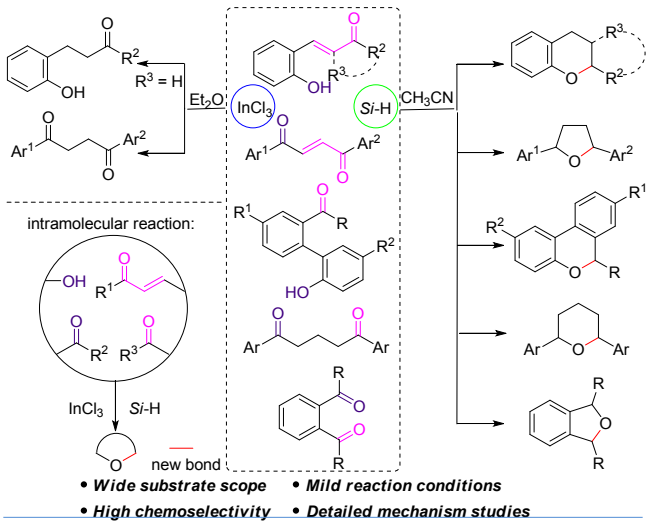
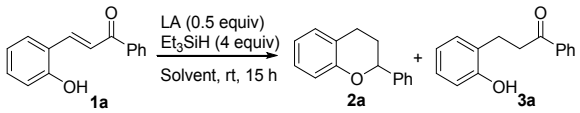


Table 1. Examination of the reaction conditions [a]



Entry	Lewis acid	Solvent	Yield (%)[b]	
			2a	**3a**
1	$Al(OTf)_3$	DCM	52	-
2	$Al(OTf)_3$	MeOH	-	-
3	$Al(OTf)_3$	Toluene	-	-
4	$Al(OTf)_3$	CH_3CN	55	-
5	$InCl_3$	CH_3CN	80	-
6	BF_3 Et_2O	CH_3CN	48	-
7	$Bi(OTf)_3$	CH_3CN	45	-
8	$Cu(OTf)_2$	CH_3CN	53	-
9	$In(OAc)_3$	CH_3CN	-	-
10[c]	$InCl_3$	CH_3CN	73	-
11[d]	$InCl_3$	CH_3CN	70	-
12[e]	-	CH_3CN	-	-
13[f]	$InCl_3$	CH_3CN	-	-
14	$InCl_3$	Et_2O	-	80

[a] Reaction conditions: **1a** (0.25 mmol, 1 equiv), Et_3SiH (4 equiv), Lewis acid (0.5 equiv), solvent (1.25 mL). [b] Yield of isolated product. [c] 0.3 equiv of Lewis acid was used. [d] 3 equiv of Et_3SiH was used. [e] No Lewis acid was used. [f] No Et_3SiH was used.

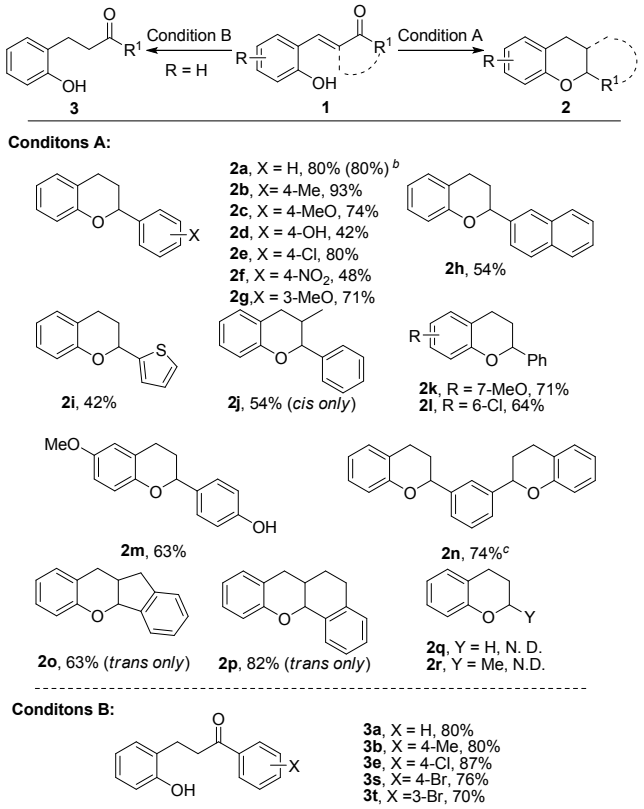
Herein, we report an $InCl_3$-promoted, one-pot ionic hydrogenation cascade cyclization comprising a two-step or four-step sequence to construct a C-O bond to generate chromans, tetrahydrofurans, tetrahydropyrans and dihyroisbenzofurans. Additionally, we disclose a divergent synthesis for accessing conjugate reduction products, such as dihydrochalcones and 1,4-diaryl-1,4-diones, from the same reaction in Et_2O as the solvent, and the two reactions exhibited excellent chemoselectivity (Scheme 1). Notably, this intramolecular reaction can be carried out between a hydroxyl or carbonyl moiety and an α,β-unsaturated keto carbonyl or carbonyl moiety, giving a variety of *O*-heterocycles under mild reaction conditions.

RESULTS AND DISCUSSION

Initially, the sequential ionic hydrogenation reaction of 2-hydroxychalcone (**1a**) with Et_3SiH in the presence of 0.5 equiv of $Al(OTf)_3$ was studied as a model reaction (Table 1). We were encouraged to find that the reaction in dichloromethane gave the desired cyclized product, 2-phenylchroman (**2a**), in 52% yield (entry 1). However, when the reaction was conducted in methanol or toluene, desired product **2a** was not obtained (entries 2 and 3). Gratifyingly, the reaction in acetonitrile gave a higher yield (entry 5). On the other hand, a screening of Lewis acid revealed that $InCl_3$ performed best and afforded **2a** in 80% yield (entries 5 *vs* 6-9). Then, running the reaction with a lower loading of $InCl_3$ (entry 10) or with Et_3SiH (entry 11) led to a dramatic decrease in the yield. Notably, in the absence of a Lewis acid or Et_3SiH, no product **2a** was observed (entries 12 and 13). Surprisingly, conjugate reduction product **3a** was isolated from the reaction conducted in ether (entry 14). Consequently, the combination of 0.5 equiv of $InCl_3$ and 4 equiv of Et_3SiH in acetonitrile was found to give the best result for this reaction.

To generalize this reaction, various 2-hydroxychalcones were subjected to the optimized reaction conditions (Scheme 2, conditions A). It was found that both electron-donating (X = 4-Me, 4-MeO, and 4-OH) and electron-withdrawing groups (X = 4-Cl and 4-NO_2) were well tolerated and gave the desired 2-arylchromans (**2b**–**2f**) in moderate to good yields. Notably, functional groups such as a nitro and hydroxyl, which are sensitive to conventional reductive conditions, were unaffected by our standard reaction conditions. Meta substitution (X = 3-MeO) was also tolerated in the reaction, and corresponding product **2g** was obtained in good yield. Replacement of the phenyl substituent with a 2-naphthyl (**2h**) or 2-thienyl (**2i**) unit had little effect on the reaction results but resulted in slightly decreased yields. Substrate **1j**, which was derived from propiophenone, was tolerated and gave disubstituted chroman **2j** (C2-C3 *cis*) in a low yield, but only the C2-C3 isomer was observed.[9] Furthermore, substrates derived from salicylaldehydes with various substitution patterns proceeded efficiently, giving the desire products (**2k-2m**) in good yields. Remarkably, a special chroman (**2n**) was also obtained in good yield. In addition, tetracyclic chromans (**2o** and **2p**) were prepared in 63% and 82% yields with complete *trans* selectivity.[10] Unfortunately, attempts to use a hydrogen atom (**2q**) or methyl group (**2r**) in place of the phenyl ring failed under the optimized conditions. However, the reaction could be scaled up without loss of yield. For example, the desired chroman **2a** could be obtained in high yield (1.17 g, 80%) when the reaction was scaled up with 7 mmol of chalcone **1a** using

Scheme 2. Preparations of a variety of chromans and dihydrochalcones [a]

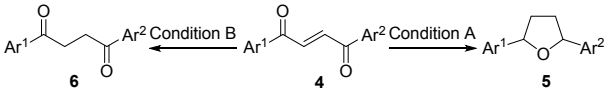


[a] Reaction conditions A: **1** (0.5 mmol, 1 equiv), Et_3SiH (4 equiv) and $InCl_3$ (0.5 equiv) in CH_3CN (2.5 mL) at rt. Reaction conditions B: **1** (1 equiv), Et_3SiH (4 equiv) and $InCl_3$ (0.5 equiv) in Et_2O (2.5 mL) at rt. The yields shown are of isolated products. [b] Gram-scale reaction: **2a** (1.17 g, 80%) was obtained. [c] 2 equiv of $InCl_3$ and 16 equiv of Et_3SiH were used at reflux.

the standard condition. These results proved that the $InCl_3/Et_3SiH$ system worked as a relatively mild reducing system. This sequential reductive cyclization resulted in bond formation between the hydroxyl moiety of a substituted phenol and an α,β-unsaturated keto carbonyl, and all cases showed total diastereoselectivity (>99:1).

During the optimization of the sequential ionic hydrogenation reaction, 1,4-reduction product **3a** was generated in 80% yield when ether was used as the solvent, which may have poor solubility than acetonitrile(Table 1, entry 14). Compared with other reduction systems, such as $H_2/Pd/C$ or $NaBH_4$, our system exhibited excellent chemoselectivity, and no over-reduction products were observed. Substrates **1b** and **1e** were suitable for this reation (Scheme 2, conditions B), giving the conjugate reduction products (**3b** and **3e**) in good yields. In addition, substrates with either para-bromo or meta-bromo groups were compatible and were converted into the 1,4-reduction products (**3s** and **3t**) in 76% and 70% yields, respectively.

Table 2. Substrates scope for tetrahydrofurans and 1,4-diones[a]



Entry	Ar^1	Ar^2	Product	Yield (%) (trans:cis)[b,c]
1	Ph	Ph	**5a**	85% (1:0.70)
2	4-MePh	4-MePh	**5b**	66% (1:0.95)
3	4-EtPh	4-EtPh	**5c**	63% (1:1.00)
4	4-FPh	4-FPh	**5d**	72% (1:0.98)
5	Ph	4-MePh	**5e**	72% (1:0.75)
6[d]	Mes	Mes	**6f**	69%
7	Ph	Ph	**6a**	61%
8	4-MeOPh	4-MeOPh	**6g**	68%
9	4-BrPh	4-BrPh	**6h**	85%

[a] Reaction conditions A: **4** (0.5 mmol, 1 equiv), Et_3SiH (6 equiv) and $InCl_3$ (0.5 equiv) in CH_3CN (2.5 mL) at rt. Reaction conditions B: **4** (0.5 mmol, 1 equiv), Et_3SiH (6 equiv) and $InCl_3$ (0.5 equiv) in Et_2O (2.5 mL) at reflux. [b] Yield of isolated product. [c] Product ratios were judged by ^1H NMR spectroscopic analysis of the crude reaction mixture. [d] The reaction condition is the same as condition A. Mes = mesityl.

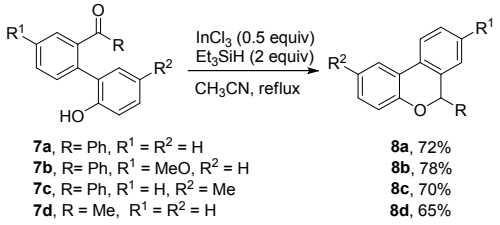
The extension of the sequential reductive cyclization system to keto carbonyls with an α,β-unsaturation was investigated starting with the reaction of trans-1,2-dibenzoylethylene (**4a**) with 0.5 equiv of $InCl_3$ and 6 equiv of Et_3SiH (Table 2, conditions A). To our delight, cyclized product **5a**[11] and 1,4-reduction product **6a** were generated in good yields from the reactions in different solvents (Table 2, entries 1 and 7). Aryl rings with either electron-donating groups (4-Me and 4-Et) or with an electron-withdrawing group (4-F) were all well tolerated and gave the desired cyclized products (Table 2, entries 2-4) in good yields (63-72%). Asymmetrical substrate **4e** also reacted under the optimized conditions and afforded cyclized product **5e** (Table 2, entry 5). However, potentially due to steric hindrance, the mesityl substituted α,β-unsaturated dicarbonyl substrate (**4f**) failed to afford the cyclized product under the current reaction conditions, but conjugate reduction product **6f** was observed in 69% yield.

At the same time, when the solvent was changed from acetonitrile to ether, as expected, the 1,4-reduction products were generated in good yields (Table 2, conditions B). A range of α,β-unsaturated 1,4-dicarbonyl substrates with electron-donating (4-MeO) and electron-withdrawing groups (4-Br) on their aryl rings reacted smoothly under conditions B to give the conjugate reduction products (**6g** and **6h**) in 68% and 85% yields.

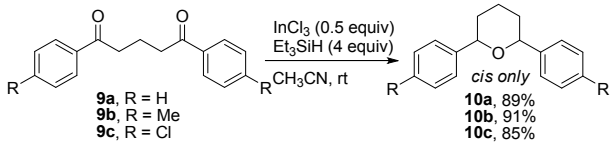
To assess whether the protocol was applicable across a range of keto phenols, the conversion of substrates **7** into

substituted 6*H*-benzo[*c*]chromenes **8** was studied (Scheme 3). The reaction scope was further examined, and both

Scheme 3. Extension to various keto phenols



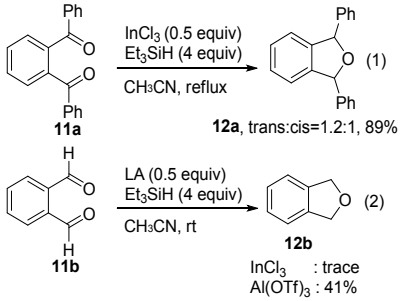
Scheme 4. Synthesis of tetrahydropyrans



methyl- and methoxy-substituted aryl rings were tolerated (**7b**-**7c**). Moreover, substituted methyl aryl ketone **7d** also performed well, delivering corresponding product **8d** in 65% yield.

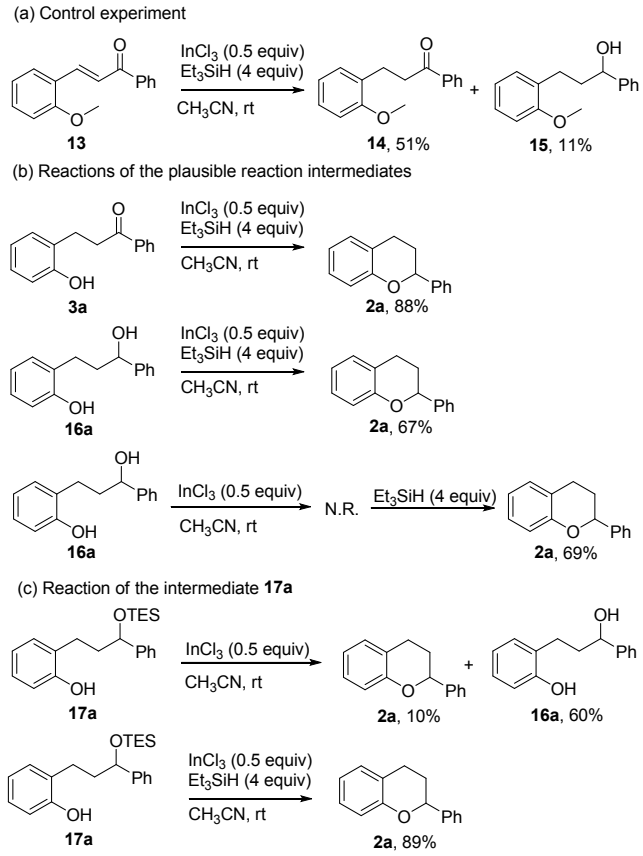
Moreover, this system was extended to the conversion of 1,5-dicarbonyl substrates (**9**) into 2,6-disubstituted tetrahydropyrans (**10**) (Scheme 4).[12] Substrates bearing electron-donating and electron-withdrawing aryl substituents (**9b** and **9c**) gave similarly excellent yields with complete *cis* selectivity.

To access products with a variety of skeletons, 1,2-dibenzoylbenzene (**11a**) and 1,2-diformylbenzene (**11b**) were investigated to give the corresponding 1,3-dihydroisobenzofurans (**12a** and **12b**).[13] Under similar reaction conditions, the reaction of **11a** worked well (89% yield) and gave *trans*:*cis* = 1.2:1 [eq. (1)]. The reaction of **11b** afforded trace product using $InCl_3$ as the Lewis acid. Changing the Lewis acid to $Al(OTf)_3$ led to a dramatic improvement in both the reactivity and yield [eq. (2)].

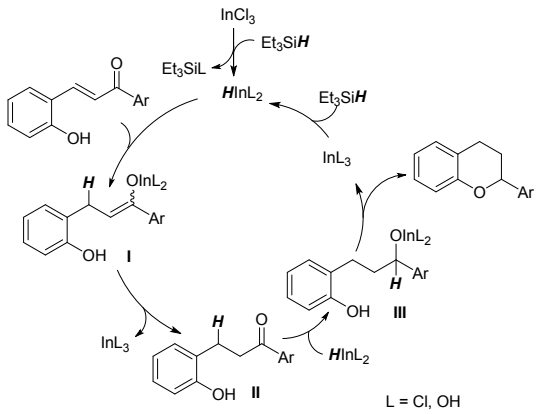


To elucidate the mechanism of this sequential ionic hydrogenation, several preliminary studies were carried out. First, 2-methoxy chalcone **13** was prepared and subjected to the previously described reaction conditions (Scheme 5a). In the reaction, conjugate reduction product **14** and corresponding over-reduction product **15** were observed, supporting a mechanism involving sequential reductions. Second, cyclization product **2a** was obtained under the standard reaction conditions when both conjugate reduction product **3a** and over-reduction product **16a** were used as

Scheme 5. Mechanistic studies



Scheme 6. A tentative reaction pathway



starting materials. These results indicated that a conjugate sequential reduction may be involved in this ionic hydrogenation. Furthermore, substrate **16a** did not undergo the cyclization in the presence of 0.5 equiv of $InCl_3$. Surprisingly, when 4 equiv of Et_3SiH was added to the above reaction system, cyclization product **2a** was isolated in 69% yield. This experiment confirmed that Et_3SiH not only served as the reductant but also played a vital role in the

cyclization (Scheme 5b). Finally, the transformation of **17a** into **2a** and **16a** was observed in the presence of 0.5 equiv of $InCl_3$ only. Meanwhile, treatment of **17a** under the standard conditons could afford the cyclization product **2a** in 89% yield. These experiments could verify that the silyl reagent was important for the cyclization (Scheme 5c).

On the basis of these mechanistic studies, we proposed a tentative reaction pathway as shown in Scheme 6: (1) transmetalation between Et_3SiH and $InCl_3$ forms an indium hydride species ($HInL_2$),[14] (2) the Michael addition of the hydride to a 2-hydroxychalcone affords the corresponding indium enolate **I**,[14b] (3) isomerization of intermediate **I** would lead to dihydrochalcone **II**, (4) 1,2-addition of the hydride to a dihydrochalcone **II** leads to the intermediate **III**, (5) intramolecular cyclization of intermediate **III** lead to the expected chroman, (6) transmetalation between InL_3 and Et_3SiH regenerates $HInL_2$.

CONCLUSION

In conclusion, we have developed an $InCl_3$-promoted, one-pot synthesis of *O*-heterocycles and aryl ketones *via* sequential ionic hydrogenation by switching the solvent. This reaction was compatible with a diverse range of functions groups, including nitro, hydroxyl and bromo groups, that are typically sensitive to reductive conditions. A variety of chroman, tetrahydrofuran, tetrahydropyran and dihydroisobenzofuran derivatives were obtained in moderate to excellent yields. When the reaction was conducted in Et_2O as the solvent, the conjugate reduction reaction occurred to generate the dihydrochalcone or 1,4-dione as the sole product. This sequential ionic hydrogenation was achieved by the reaction between a hydroxyl or carbonyl moiety and an α,β-unsaturated keto carbonyl or a carbonyl and afforded various *O*-heterocycles. In addition, detailed mechanistic studies involving conjugate reduction, over-reduction and intramolecular cyclization pathways were verified by control experiments. The synthesis of other heterocycles *via* the sequential ionic hydrogenation reaction is under way in our laboratory.

EXPERIMENTAL SECTION

General. Unless otherwise indicated, all reactions were carried out under anhydrous, air-free conditions. All solvents and chemicals were obtained from commercial sources and used without further purification. Flash column chromatography was performed with silica gel 300 - 400 mesh on Biotage Isolera one. NMR spectra were recorded on a Mercury-400 or Mercury-500 spectrometer, with tetramethylsilane as an internal standard and reported in ppm (δ). ESI-HRMS data were measured on Thermo Exactive Orbitrap plus spectrometer. Melting points were determined on Yanaco MP-J3 microscope melting point apparatus. 2-hydroxychalcones (**1**)[5b], (*E*)-1,4-enediones (**4**)[15], 1,5-dicarbonyl compounds (**9**)[16], 1,2-Dibenzoylbenzene (**11a**)[17], **13**[5b], **15**[18] and **16a**[5b] were prepared according to the literatures.

Typical procedure for sequential ionic hydrogenation using 2-hydroxychalcone (1), $InCl_3$ and Et_3SiH: To a stirred solution of **1** (0.5 mmol, 1 equiv) and $InCl_3$ (0.5 equiv) in dry acetonitrile (2.5 mL) was added Et_3SiH (4 equiv). The reaction mixture was stirred at room temperature for 15 h. After completion of the reaction, water was added to the reaction mixture, which was extracted with dichloromethane. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, concentrated in vacuo and purified by column chromatography on silica gel (PE : EA = 50:1) to afford the desired products (**2**).

*2-phenylchroman (**2a**)*.[6] Yield: 80% (86.1 mg), light yellow oil. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 - 7.41 (m, 4H), 7.39 - 7.37 (m, 1H), 7.20 - 7.13 (m, 2H), 6.99 - 6.91 (m, 2H), 5.11 (d, *J* = 10.0 Hz, 1H), 3.08 - 3.00 (m, 1H), 2.86 - 2.81 (m, 1H), 2.28 - 2.22 (m, 1H), 2.19 - 2.11 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.2, 141.8, 129.6, 128.6, 127.9, 127.4, 126.1, 121.9, 120.4, 117.0, 77.8, 30.0, 25.1. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{15}H_{14}O$, 210.1045, Found 210.1042.

*2-p-tolylchroman (**2b**)*.[6] Yield: 93% (104.1 mg), white solid, mp: 79-81 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). ^1H NMR (400 MHz,) δ 7.31 (d, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.13 - 7.07 (m, 2H), 6.90 - 6.84 (m, 2H), 5.03 (dd, *J* = 9.9, 2.5 Hz, 1H), 3.03 - 2.95 (m, 1H), 2.82 - 2.76 (m, 1H), 2.36 (s, 3H), 2.22 - 2.16 (m, 1H), 2.11 - 2.04 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.3, 138.9, 137.6, 129.6, 129.3, 127.4, 126.1, 121.9, 120.3, 117.0, 77.8, 30.0, 25.3, 21.3. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{16}H_{17}O$, 225.1274, Found 225.1270.

*2-(4-methoxyphenyl)chroman (**2c**)*.[6] Yield: 74% (88.8 mg), white solid, mp: 70-72 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). 1H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.14 - 7.08 (m, 2H), 6.94 - 6.85 (m, 4H), 5.01 (dd, *J* = 10.1, 2.4 Hz, 1H), 3.82 (s, 3H), 3.04 - 2.96 (m, 1H), 2.84 - 2.78 (m, 1H), 2.21 - 2.14 (m, 1H), 2.12 - 2.05 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.4, 155.3, 134.0, 129.6, 127.5, 127.4, 121.9, 120.3, 117.0, 114.0, 77.6, 55.4, 29.9, 25.3. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{16}H_{17}O_2$, 241.1223, Found 241.1220.

*4-(chroman-2-yl)phenol (**2d**)*. Yield: 42% (47.4 mg), white solid, mp: 85-87 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 - 7.29 (m, 2H), 7.11 - 7.07 (m, 2H), 6.89 - 6.82 (m, 4H), 4.99 (dd, *J* = 10.1, 2.5 Hz, 1H), 3.01 - 2.94 (m, 1H), 2.82 - 2.76 (m, 1H), 2.19 - 2.13 (m, 1H), 2.12 - 2.02 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.3, 155.3, 134.1, 129.6, 127.7, 127.4, 121.9, 120.4, 117.0, 115.4, 77.6, 29.9, 25.3. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{15}H_{15}O_2$, 227.1067, Found 227.1062.

*2-(4-chlorophenyl)chroman (**2e**)*.[6] Yield: 80% (97.6 mg), white solid, mp: 73-75 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 4H), 7.14 - 7.07 (m, 2H), 6.90 - 6.85 (m, 2H), 5.04 (dd, *J* = 10.0, 2.6 Hz, 1H), 3.02 - 2.94 (m, 1H), 2.81 - 2.75 (m, 1H), 2.22 - 2.16 (m, 1H), 2.09 - 1.98 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.9, 140.3, 133.6, 129.6, 128.8, 127.5, 127.5, 121.7, 120.6, 117.0, 77.1, 30.0, 25.0. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{15}H_{13}ClO$, 244.0655, Found 244.0659.

*2-(4-nitrophenyl)chroman (**2f**)*. Yield: 48% (61.2 mg), yellow solid, mp: 115-117 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.7

Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.16 - 7.13 (m, 1H), 7.09 (d, J = 7.3 Hz, 1H),6.93 - 6.88 (m, 2H), 5.17 (dd, *J* = 9.9, 2.6 Hz, 1H), 3.05 - 2.97 (m, 1H), 2.82 - 2.76 (m, 1H), 2.29 - 2.22 (m, 1H), 2.09 - 1.98 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.4, 149.2, 129.7, 127.7, 126.8, 123.9, 121.6, 121.0, 117.0, 76.6, 30.1, 24.8. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{15}H_{13}NO_3$, 255.0895, Found 255.0894.

*2-(3-methoxyphenyl)chroman (**2g**).*[6] Yield: 71% (85.2 mg), transparent oil. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 8.2 Hz, 1H), 7.16 - 7.12 (m, 1H), 7.10 (d, *J* = 7.3 Hz, 1H), 7.03 - 7.01 (m, 2H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.91 - 6.86 (m, 2H), 5.06 (dd, *J* = 10.1, 2.4 Hz, 1H), 3.83 (s, 3H), 3.05 - 2.96 (m, 1H), 2.84 - 2.78 (m, 1H), 2.28 - 2.20 (m, 1H), 2.15 -2.05 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.8, 155.1, 143.4, 129.6, 127.4, 121.9, 120.4, 118.4, 117.0, 113.3, 111.7, 77.7, 55.3, 30.0, 25.1. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{16}H_{17}O_2$, 241.1223, Found 241.1219.

*2-(naphthalen-2-yl)chroman (**2h**).* Yield: 54% (70.2 mg), transparent oil. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 - 7.96 (m, 1H), 7.94 - 7.92 (m, 3H), 7.62 (d, *J* = 8.3 Hz, 1H), 7.57 (d, *J* = 3.4 Hz, 2H), 7.24 - 7.23 (m, 1H), 7.19 (d, *J* = 7.0 Hz, 1H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.99 (t, *J* = 6.8 Hz, 1H), 5.31 (d, *J* = 7.9 Hz, 1H), 3.14 - 2.89 (m, 1H), 2.92 - 2.89 (m, 1H),2.38 - 2.35 (m, 1H),2.27-2.25 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.2, 133.4, 133.1, 129.6, 128.4, 128.1, 127.8, 127.5, 126.2, 126.0, 124.9, 124.1, 121.9, 120.5, 117.0, 77.9, 30.0, 25.2. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{19}H_{16}O$, 260.1201, Found 260.1204.

*2-(thiophen-2-yl)chroman (**2i**).* Yield: 42% (45.3 mg), transparent oil. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.28 (m, 1H), 7.13 - 7.07 (m, 3H), 7.01 - 6.99 (m, 1H), 6.90 - 6.85 (m, 2H), 5.34 - 5.31 (m, 1H), 3.03 - 2.94 (m, 1H), 2.87 - 2.81 (m, 1H), 2.37 - 2.30 (m, 1H), 2.26 - 2.18 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.7, 144.8, 129.6, 127.5, 126.7, 125.1, 124.5, 121.6, 120.7, 117.1, 73.7, 30.0, 24.8. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{13}H_{12}OS$, 216.0609, Found 216.0610.

*3-methyl-2-phenylchroman (**2j**).* Yield: 54% (60.4 mg), transparent oil. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 - 7.36 (m, 4H), 7.31 - 7.29 (m, 1H), 7.16 - 7.12 (m, 1H), 7.09 (d, *J* =7.3 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.92 - 6.88 (m, 1H), 5.19 (d, *J* = 2.2 Hz, 1H), 3.22 (dd, *J* = 16.2, 5.8 Hz, 1H), 2.59 (dd, *J* = 16.3, 3.3 Hz, 1H), 2.41 - 2.36 (m, 1H), 0.80 (d, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 154.6, 140.4, 130.2, 128.2, 127.3, 127.3, 126.0, 120.9, 120.6, 116.7, 79.7, 33.0, 31.8, 12.6. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{16}H_{16}O$, 224.1201, Found 224.1200.

*7-methoxy-2-phenylchroman (**2k**).*[6] Yield: 71% (85.2 mg), transparent oil. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 - 7.39 (m, 4H), 7.37 - 7.33 (m, 1H), 7.02 - 6.99 (m, 1H), 6.53 - 6.50 (m, 2H), 5.07 (dt, *J* = 10.1, 2.5 Hz, 1H), 3.79 - 3.78 (m, 3H), 2.99 - 2.90 (m, 1H), 2.79 - 2.72 (m, 1H), 2.25 - 2.18 (m, 1H), 2.15 - 2.05 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.1, 155.8, 141.7, 130.0, 128.6, 127.9, 126.1, 114.0, 107.5, 101.6, 78.0, 55.4, 30.2, 24.4. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{16}H_{17}O_2$, 241.1223, Found 241.1219.

*6-chloro-2-phenylchroman (**2l**).* Yield: 64% (78.1 mg), white solid, mp: 58-60 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 - 7.36 (m, 4H), 7.34 - 7.30 (m, 1H), 7.08 - 7.05 (m, 2H), 6.87 - 6.76 (m, 1H), 5.04 (dd, *J* = 10.0, 2.5 Hz, 1H), 2.99 - 2.91 (m, 1H), 2.79 - 2.72 (m, 1H), 2.23 - 2.17 (m, 1H), 2.11 - 2.01 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.8, 141.3, 129.1, 128.7, 128.1, 127.4, 126.0, 125.1, 123.5, 118.3, 78.0, 29.6, 25.0. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{15}H_{13}ClO$, 244.0655, Found 244.0652.

*4-(6-methoxychroman-2-yl)phenol (**2m**).* Yield: 63% (80.6 mg), yellow solid, mp: 150-152 °C, R_f = 0.3 (petroleum ether/ethyl acetate, 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.27 (m, 2H), 6.84 - 6.80 (m, 3H), 6.69 (dd, *J* = 8.9, 3.1 Hz, 1H), 6.62 (d, *J* = 3.0 Hz, 1H), 4.92 (dd, *J* = 10.1, 2.6 Hz, 1H), 3.75 (s, 3H), 2.98 - 2.93 (m, 1H), 2.80 – 2.73 (m, 1H), 2.17 - 2.11 (m, 1H), 2.10 - 2.00 (m, 1H). ^{13}Cc NMR (101 MHz, $CDCl_3$) δ 155.4, 153.4, 149.4, 134.2, 127.7, 122.4, 117.6, 115.4, 114.1, 113.4, 77.5, 55.9, 29.9, 25.6. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{16}H_{16}O_3$, 256.1099, Found 256.1098.

*1,3-di(chroman-2-yl)benzene (**2n**).* Yield: 74% (126.5 mg), yellow solid, mp: 91-93 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 10:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.50 (s, 3H), 7.25 - 7.18 (m, 4H), 7.03 - 6.96 (m, 4H), 5.17 (d, *J* = 10.2 Hz, 2H), 3.14 - 3.06 (m, 2H), 2.90 (d, *J* = 16.3 Hz, 2H), 2.34 - 2.30 (m, 2H), 2.24 - 2.14 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.1, 142.1, 129.6, 128.85, 128.84, 127.4, 125.6, 125.5, 123.8, 123.7, 121.9, 120.4, 117.03, 117.02, 77.87, 77.81, 30.16, 30.13, 25.2. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{24}H_{23}O_2$, 343.1693, Found 343.1700.

*4b,10,10a,11-tetrahydroindeno[1,2-b]chromene (**2o**).* Yield: 63% (69.9 mg), white solid, mp: 125-127 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 - 7.53 (m, 1H), 7.29 - 7.27 (m, 3H), 7.16 - 7.13 (m, 2H), 7.01 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.92 (td, *J* = 7.4, 1.3 Hz, 1H), 4.91 (d, *J* = 10.0 Hz, 1H), 3.17 - 3.10 (m, 1H), 3.07 - 2.97 (m, 2H), 2.63 - 2.56 (m, 1H), 2.50 - 2.42 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.6, 141.7, 141.6, 130.6, 127.9, 127.6, 126.8, 125.1, 123.3, 122.7, 120.9, 117.8, 84.1, 44.3, 34.4, 32.1. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{16}H_{14}O$, 222.1045, Found 222.1046.

*6,6a,7,12a-tetrahydro-5H-benzo[c]xanthene (**2p**).* Yield: 82% (96.7 mg), yellow solid, mp: 69-71 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 5.9 Hz, 1H), 7.15 - 7.09 (m, 3H), 6.99 - 6.97 (m, 1H), 6.88 (td, *J* = 7.4, 1.1 Hz, 1H), 4.79 (d, *J* = 9.9 Hz, 1H), 3.04 - 2.96 (m, 1H), 2.88 (dd, *J* = 16.0, 4.9 Hz, 2H), 2.69 (dd, *J* = 16.2, 11.7 Hz, 1H), 2.15 - 2.05 (m, 2H), 1.70 - 1.59 (m, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 155.3, 136.5, 135.8, 129.7, 128.8, 127.5, 127.3, 126.6, 126.2, 122.4, 120.5, 117.2, 78.0, 34.6, 32.8, 28.9, 27.8. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{17}H_{17}O$, 237.1274, Found 237.1271.

*3-(2-hydroxyphenyl)-1-phenylpropan-1-one (**3a**).*[6] Yield: 80% (90.4 mg), white solid, mp: 83-85 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.87 (s, 1H), 7.58 - 7.54 (m, 1H), 7.46 - 7.42 (m, 2H), 7.12 - 7.10 (m, 2H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.84 (td, *J* = 7.4, 1.3 Hz, 1H), 3.46 - 3.43 (m, 2H), 3.05 - 3.02 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 202.1, 154.6, 136.2, 133.9, 130.7, 128.8, 128.4, 128.1, 127.9, 120.8,

117.6, 40.5, 23.4. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{15}H_{15}O_2$, 227.1067, Found 227.1065.

*3-(2-hydroxyphenyl)-1-p-tolylpropan-1-one (**3b**).*[6] Yield: 80% (96.0 mg), white solid, mp: 130-132 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.08 (m, 2H), 6.91 (d, *J* = 7.5 Hz, 1H), 6.86 - 6.82 (m, 1H), 3.43 - 3.40 (m, 2H), 3.03 – 3.01 (m, 2H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 201.7, 154.6, 144.8, 133.6, 130.6, 129.3, 128.4, 127.9, 127.9, 120.6, 117.5, 40.3, 23.4, 21.7. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{16}H_{17}O_2$, 241.1223, Found 241.1215.

*1-(4-chlorophenyl)-3-(2-hydroxyphenyl)propan-1-one (**3e**).*[6] Yield: 87% (113.1 mg), white solid, mp: 145-147 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 - 7.88 (m, 2H), 7.60 (s, 1H), 7.42 - 7.40 (m, 2H), 7.12 - 7.08 (m, 2H), 6.90 - 6.88 (m, 1H), 6.85 (td, *J* = 7.4, 1.0 Hz, 1H), 3.43 - 3.40 (m, 2H), 3.04 - 3.01 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 200.8, 154.5, 140.4, 134.5, 130.7, 129.8, 129.1, 128.1, 127.6, 120.9, 117.4, 40.4, 23.6. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{15}H_{14}ClO_2$, 261.0677, Found 261.0673.

*1-(4-bromophenyl)-3-(2-hydroxyphenyl)propan-1-one (**3s**).*[6] Yield: 76% (115.9 mg), white solid, mp: 135-137 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.83 - 7.81 (m, 2H), 7.59 - 7.56 (m, 2H), 7.55 (s, 1H), 7.12 - 7.08 (m, 2H), 6.88 (dd, *J* = 8.5, 1.2 Hz, 1H), 6.84 (td, *J* = 7.4, 1.2 Hz, 1H), 3.40 - 3.37 (m, 2H), 3.03 – 3.00 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 201.0, 154.5, 134.9, 132.1, 130.7, 129.9, 129.1, 128.1, 127.6, 120.9, 117.4, 40.4, 23.5. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{15}H_{14}BrO_2$, 305.0172, Found 305.0188.

*1-(3-bromophenyl)-3-(2-hydroxyphenyl)propan-1-one (**3t**).*[6] Yield: 70% (106.7 mg), white solid, mp: 80-82 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (t, *J* = 1.8 Hz, 1H), 7.88 - 7.85 (m, 1H), 7.66 (ddd, *J* = 8.0, 2.0, 1.0 Hz, 1H), 7.55 (s, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 7.13 - 7.09 (m, 2H), 6.92 - 6.89 (m, 1H), 6.86 (td, *J* = 7.4, 1.2 Hz, 1H), 3.39 - 3.36 (m, 2H), 3.04 - 3.01 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 200.6, 154.3, 137.9, 136.5, 131.4, 130.6, 130.3, 128.1, 127.5, 126.9, 123.0, 120.9, 117.3, 40.3, 23.7. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{15}H_{14}BrO_2$, 305.0172, Found 305.0167.

*2,5-diphenyltetrahydrofuran (**5a**).*[11] Yield: 80% (89.6 mg) (trans:cis = 1:0.7), yellow waxy. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). Trans: ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, J = 7.3 Hz, 4H), 7.35 (t, *J* = 7.6 Hz, 4H), 7.28 - 7.24 (m, 2H), 5.26 (t, *J* = 6.6 Hz, 2H), 2.52 – 2.44 (m, 2H), 2.03 - 1.97 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.7, 128.5, 127.3, 125.7, 81.4, 35.7. Cis: ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.2 Hz, 4H), 7.38 - 7.34 (m, 4H), 7.30 - 7.25 (m, 2H), 5.06 (t, *J* = 5.3 Hz, 2H), 2.47 - 2.40 (m, 2H), 2.02 - 1.97 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.0, 128.4, 127.4, 126.1, 81.3, 34.5.

*2,5-dip-tolyltetrahydrofuran (**5b**).* Yield: 66% (83.1 mg) (trans:cis = 1:0.95), yellow waxy. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). Trans: ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.0 Hz, 4H), 7.15 (d, *J* = 7.9 Hz, 4H), 5.21 (t, *J* = 6.6 Hz, 2H), 2.45 - 2.40 (m, 2H), 2.34 (s, 6H), 2.00 - 1.94 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.8, 136.8, 129.14, 125.1, 81.26, 35.6, 21.27. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{18}H_{20}O$, 252.1514, Found 252.1510. Cis: two isomers mixture (trans:cis=1.08:1) ^1H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 4H), 7.16 (d, *J* = 7.2 Hz, 4H), 5.00 (t, *J* = 5.2 Hz, 2H), 2.45 - 2.37 (m, 2H), 2.34 (s, 6H), 1.98 - 1.95 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.1, 137.0, 129.12, 126.1, 81.23, 34.5, 21.26. HRMS (ESI) m/z: $[M]^+$ Calc. for: $C_{18}H_{20}O$, 252.1514, Found 252.1516.

*2,5-bis(4-ethylphenyl)tetrahydrofuran (**5c**).* Yield: 63% (88.2 mg) (trans:cis = 1:1.0), yellow waxy. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). Trans: two isomers mixture (trans:cis=1:0.98) ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.9 Hz, 4H), 7.19 (d, *J* = 6.7 Hz, 4H), 5.22 (t, *J* = 6.6 Hz, 2H), 2.68 - 2.62 (m, 4H), 2.46 - 2.38 (m, 2H), 2.02 - 1.97 (m, 2H), 1.26 - 1.22 (m, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.31, 141.0, 127.95, 125.7, 81.25, 35.6, 28.69, 15.79. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{20}H_{25}O$, 281.1900, Found 281.1896. Cis: ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 - 7.35 (m, 4H), 7.20 - 7.18 (m, 4H), 5.04 - 5.01 (m, 2H), 2.66 (q, *J* = 7.2 Hz, 4H), 2.42 – 2.37 (m, 2H), 1.99 - 1.97 (m, 2H), 1.27 - 1.22 (m, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.38, 140.3, 127.91, 126.1, 81.24, 34.5, 28.70, 15.76. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{20}H_{25}O$, 281.1900, Found 281.1895.

*2,5-bis(4-fluorophenyl)tetrahydrofuran (**5d**).* Yield: 72% (93.6 mg) (trans:cis = 1:0.98), yellow waxy. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). Trans: ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.34 (m, 4H), 7.05 - 7.01 (m, 4H), 5.21 (t, *J* = 6.6 Hz, 2H), 2.48 - 2.42 (m, 2H), 1.99 - 1.93 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 243 Hz), 139.2 (d, *J* = 3 Hz), 127.3 (d, *J* = 8 Hz), 115.3 (d, *J* = 21 Hz), 80.9, 35.8. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{16}H_{15}F_2O$, 261.1086, Found 261.1079. Cis: ^1H NMR (400 MHz, $CDCl_3$) δ 7.39 - 7.36 (m, 4H), 7.05 - 7.01 (m, 4H), 5.00 (t, *J* = 5.3 Hz, 2H), 2.45 - 2.37 (m, 2H), 1.97 - 1.88 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 162.3 (d, *J* = 244 Hz), 138.5 (d, *J* = 3 Hz), 127.7 (d, *J* = 8 Hz), 115.3 (d, *J* = 22 Hz), 80.7, 34.4. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{16}H_{14}F_2O$, 260.1013, Found 260.1015.

*2-phenyl-5-p-tolyltetrahydrofuran (**5e**).* Yield: 72% (85.6 mg) (trans:cis = 1:0.75), yellow waxy. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). Trans: ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.41 (m, 3H), 7.37 - 7.34 (m, 3H), 7.31 - 7.26 (m, 2H), 7.16 (d, *J* = 7.9 Hz, 1H), 5.28 - 5.23 (m, 2H), 2.49 - 2.45 (m, 2H), 2.35 (s, 3H), 2.03 - 1.96 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.8, 143.7, 140.7, 136.93, 129.16, 128.49, 127.3, 125.7, 81.47, 81.39, 35.7, 35.6, 21.27. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{17}H_{18}O$, 238.1358, Found 238.1362. Cis: ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 - 7.43 (m, 3H), 7.37 - 7.32 (m, 3H), 7.29 -7.25 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 1H), 5.07 - 5.02 (m, 2H), 2.45 - 2.39 (m, 2H), 2.35 (s, 3H), 1.99 - 1.95 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.1, 143.0, 140.0, 137.05, 129.14, 128.47, 127.4, 126.1, 81.38, 81.31, 34.6, 34.5, 21.29. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{17}H_{19}O$, 239.1430, Found 239.1434.

*1,4-diphenylbutane-1,4-dione (**6a**).* Yield: 61% (72.6 mg), white solid, mp: 151-153 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 5:1). ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.3 Hz, 4H), 7.59 - 7.55 (m, 2H), 7.47 (t, *J* = 7.8 Hz, 4H), 3.46 (s, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.8, 136.9, 133.3, 128.7, 128.2, 32.7. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{16}H_{15}O_2$, 239.1067, Found 239.1066.

*1,4-dimesitylbutane-1,4-dione (**6f**).* Yield: 69% (111.1 mg), white solid, mp: 128-130 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 4H), 3.12 (s, 4H), 2.28 (s, 6H), 2.26 (s, 12H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 208.6, 139.2, 138.5, 132.9, 128.6, 38.1, 21.1, 19.2. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{22}H_{27}O_2$, 323.2006, Found 323.1996.

*1,4-bis(4-methoxyphenyl)butane-1,4-dione (**6g**).* Yield: 68% (101.3 mg), white solid, mp: 151-153 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 4H), 6.94 (d, *J* = 8.8 Hz, 4H), 3.86 (s, 6H), 3.39 (s, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.5, 163.6, 130.5, 130.0, 113.8, 55.6, 32.4. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{18}H_{19}O_4$, 299.1278, Found 299.1277.

*1,4-bis(4-bromophenyl)butane-1,4-dione (**6h**).* Yield: 85% (167.4 mg), white solid, mp: 175-177 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.6 Hz, 4H), 7.63 - 7.60 (m, 4H), 3.40 (s, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.6, 135.5, 132.1, 129.7, 128.5, 32.5. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{16}H_{12}Br_2O_2$, 393.9204, Found 393.9196.

*6-phenyl-6H-benzo[c]chromene (**8a**).* Yield: 72% (92.9 mg), white solid, mp: 73-75 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 - 7.74 (m, 2H), 7.41 - 7.32 (m, 6H), 7.24 - 7.19 (m, 2H), 7.04 (td, *J* = 7.6, 1.3 Hz, 1H), 6.99 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.85 (d, *J* = 7.6 Hz 1H), 6.16 (s, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.7, 139.6, 134.0, 130.1, 129.7, 128.6, 128.6, 128.5, 128.2, 127.7, 126.3, 123.2, 122.9, 122.2, 118.0, 79.7. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{19}H_{14}O$, 258.1045, Found 258.1043.

*8-methoxy-6-phenyl-6H-benzo[c]chromene (**8b**).* Yield: 78% (112.3 mg), white solid, mp: 91-93 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 10:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 - 7.67 (m, 2H), 7.39 - 7.32 (m, 5H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.98 - 6.93 (m, 2H), 6.40 (d, *J* = 2.6 Hz, 1H), 6.12 (s, 1H), 3.75 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 159.4, 152.9, 139.5, 135.6, 128.7, 128.6, 128.5, 128.2, 123.7, 123.1, 122.9, 122.5, 122.2, 117.9, 113.9, 112.1, 79.78, 55.46. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{20}H_{16}O_2$, 288.1150, Found 288.1154.

*2-methyl-6-phenyl-6H-benzo[c]chromene (**8c**).* Yield: 70% (95.2 mg), transparent oil. R_f = 0.3 (petroleum ether/ethyl acetate, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 1H), 7.56 (s, 1H), 7.41 - 7.32 (m, 6H), 7.25 - 7.21 (m, 1H), 7.03 (d, *J* = 8.3 Hz, 1H), 6.91 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.86 (d, *J* = 7.4 Hz, 1H), 6.13 (s, 1H), 2.36 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 151.5, 139.7, 134.2, 131.3, 130.4, 130.3, 128.5, 128.5, 128.4, 128.2, 127.5, 126.3, 123.6, 122.5, 122.1, 117.7, 79.7, 21.0. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{20}H_{16}O$, 272.1201, Found 272.1205.

*6-methyl-6H-benzo[c]chromene (**8d**).* Yield: 65% (63.7 mg), yellow oil. Rf = 0.3 (petroleum ether/ethyl acetate, 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 - 7.71 (m, 2H), 7.38 (td, *J* = 7.6, 1.4 Hz, 1H), 7.31 (td, *J* = 7.4, 1.4 Hz, 1H), 7.28 - 7.23 (m, 1H), 7.19 - 7.16 (m, 1H), 7.06 (td, *J* = 7.5, 1.3 Hz, 1H), 7.01 (dd, *J* = 8.0, 1.3 Hz, 1H), 5.29 (q, *J* = 6.6 Hz, 1H), 1.64 (d, *J* = 6.6 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.5, 135.9, 129.5, 129.4, 128.2, 127.9, 124.1, 123.2, 122.7, 122.2, 121.9, 117.9, 73.7, 20.3. HRMS (ESI) m/z: $[M]^+$ Calc. for: $C_{14}H_{12}O$, 196.0888, Found 196.0887.

*2,6-diphenyltetrahydro-2H-pyran (**10a**).* Yield: 89% (105.9 mg), transparent oil. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). Cis: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.8 Hz, 4H), 7.38 -7.34 (m, 4H), 7.29 - 7.25 (m, 2H), 4.59 (d, *J* = 11.2 Hz, 2H), 2.09 - 2.05 (m, 1H), 1.95 -1.92 (m, 2H), 1.91 - 1.83 (m, 1H), 1.68 - 1.59 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 143.6, 128.3, 127.3, 125.9, 80.3, 34.0, 24.6. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{17}H_{18}O$, 238.1358, Found 238.1355.

*2,6-di-p-tolyltetrahydro-2H-pyran (**10b**).* Yield: 91% (121.0 mg), white solid, mp: 38-40 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 10:1). Cis: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 4H), 7.15 - 7.13 (m, 4H), 4.53 (dd, *J* = 11.3, 1.5 Hz, 2H), 2.33 (s, 6H), 2.05 - 2.00 (m, 1H), 1.90 - 1.79 (m, 3H), 1.64 - 1.55 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 140.7, 136.8, 128.9, 125.9, 80.18, 33.9, 24.6, 21.2. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{19}H_{23}O$, 267.1743, Found 267.1743.

*2,6-bis(4-chlorophenyl)tetrahydro-2H-pyran (**10c**).* Yield: 85% (130.0 mg), white solid, mp: 95-97 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). Cis: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 - 7.33 (m, 4H), 7.32 - 7.29 (m, 4H), 4.55 - 4.51 (m, 2H), 2.06 - 2.02 (m, 1H), 1.90 - 1.79 (m, 3H), 1.59 - 1.50 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 141.8, 133.0, 128.5, 127.3, 79.6, 33.8, 24.3. HRMS (EI) m/z: $[M]^+$ Calc. for: $C_{17}H_{16}Cl_2O$, 306.0578, Found 306.0580.

*1,3-diphenyl-1,3-dihydroisobenzofuran (**12a**).*[13] Yield: 89% (121.0 mg), yellow waxy. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). two isomers mixture (trans:cis=1.2:1) ^{1}H NMR (500 MHz, Acetone) δ 7.54 - 7.50 (m, 4.8H), 7.47 - 7.38 (m, 6.3H), 7.36 -7.35 (m, 1H), 7.32 - 7.31 (m, 2.6H), 7.22 - 7.20 (m, 1.2H, trans isomer), 7.08 - 7.06 (m ,1H, cis isomer), 6.52 (s, 1.2H, trans isomer), 6.20 (s, 1H, cis isomer). $^{13}C\{^1H\}$ NMR (101 MHz, Acetone) δ 144.12, 143.62, 142.91, 142.78, 129.30, 128.91, 128.70, 128.61, 128.58, 128.40, 127.38, 123.06, 122.86, 86.70, 85.85.

*1,3-dihydroisobenzofuran (**12b**).*[19] Yield: 41% (24.0 mg), transparent oil. R_f = 0.3 (petroleum ether/ethyl acetate, 30:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 - 7.22 (m, 4H), 5.11 (s, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 139.1, 127.3, 121.0, 73.7.

*3-(2-methoxyphenyl)-1-phenylpropan-1-one (**14**).* Yield: 51% (61.2 mg), transparent oil. R_f = 0.3 (petroleum ether/ethyl acetate, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 - 7.96 (m, 2H), 7.56 - 7.52 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.21 - 7.18 (m, 2H), 6.91 - 6.84 (m, 2H), 3.82 (s, 3H), 3.28 - 3.24 (m, 2H), 3.06 - 3.04 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 200.1, 157.6, 137.1, 133.0, 130.3, 129.6, 128.6, 128.2, 127.6, 120.6, 110.3, 55.3, 39.0, 25.8. HRMS (ESI) m/z: $[M+H]^+$ Calc. for: $C_{16}H_{17}O_2$, 241.1223, Found 241.1221.

*3-(2-methoxyphenyl)-1-phenylpropan-1-ol (**15**).* Yield: 11% (13.3 mg), transparent oil. R_f = 0.3 (petroleum ether/ethyl acetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 - 7.33 (m, 4H), 7.27 - 7.24 (m, 1H), 7.21 - 7.14 (m, 2H), 6.90 (t, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 4.63 (dd, *J* = 8.3, 4.8 Hz, 1H), 3.83 (s, 3H), 2.78 - 2.73 (m, 2H), 2.08 - 1.97 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.4, 144.7, 130.2, 130.1, 128.5, 127.4, 127.3, 126.0, 120.8, 110.4, 73.6, 55.4, 39.5, 26.5. HRMS (ESI) m/z: $[M-H_2O+H]^+$ Calc. for: $C_{16}H_{17}O$, 225.1274, Found 225.1269.

*2-(3-hydroxy-3-phenylpropyl)phenol (**16a**).* Yield: 60% (68.4 mg), white solid, mp: 85-87 °C. R_f = 0.3 (petroleum ether/ethyl acetate, 2:1). ^{1}H NMR (400 MHz, *d6*-DMSO) δ 9.12 (s, 1H), 7.29 - 7.27 (m, 4H), 7.20 - 7.15 (m, 1H), 6.97 (d, *J* = 7.4 Hz, 1H), 6.93 (td, *J* = 7.7, 1.7 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 6.65 (t, *J* = 7.4 Hz, 1H), 5.15 (s, 1H), 4.48 (t, *J* = 6.5 Hz, 1H), 2.61 - 2.54 (m, 1H), 2.43 - 2.39 (m, 1H), 1.83 - 1.77 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, *d6*-DMSO) δ 155.0, 146.3, 129.5, 128.1, 127.9, 126.6, 126.5, 125.8, 118.8, 114.8, 72.1, 39.2, 26.2. HRMS (EI) m/z: [M]$^+$ Calc. for: $C_{15}H_{16}O_2$, 228.1150, Found 228.1154.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

^{1}H and ^{13}C{^{1}H} NMR spectra for all products (PDF)

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Notes

The authors declare no competing financial interest.

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