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Graphical Abstract

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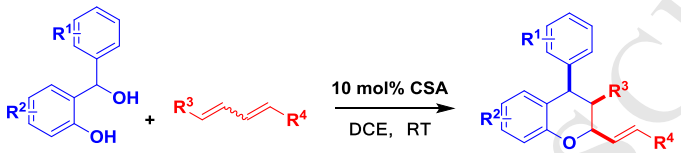

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ABSTRACT

The synthetically important 2-alkenylchromane derivatives were constructed in good yields under metal-free condition via inverse electron demand Hetero-Diels-Alder reaction of o-quinone methides with unactivated dienes. This strategy features mild condition, good diastereoselectivity and wide substrate scope.

1. Introduction

Chromanes are privileged structural motifs, which are present in a large number of natural products and bioactive agents with a wide range of biological activities (Figure 1).[1] For examples, sideroxylonal B exhibited antibacterial activities against Gram-positive bacteria and inhibition of aldose reductase;[1a,1b] Rhododaurichromanic acid A showed potent *anti*-HIV activity;[1c] Guajadial had long been used to treat diabetes and hypertension;[1d] Myristinins A displayed dual biochemical activities both as potent DNA damaging agents and DNA polymerase β inhibitors;[1f,1e,1g] Rubicordifolin was found to possess cytotoxic and antitumor activities;[1h,1i] Cytosporolides A showed modest antibiotic activity against the Gram-positive bacteria, staphylococcus aureus and streptococcus pneumonia.[1j]

Among miscellaneous chromane derivatives, 2-alkenylchromanes have distinguished themselves as key intermediates in total synthesis.[2] Despite their importance, the approaches available to access 2-alkenylchromanes in a straightforward fashion are still rare and only few strategies were reported, such as Pd/Au-catalyzed Tsuji-Trost cyclization,[3] Au-catalyzed cyclization[4], Wacker-type cyclization[5] and Pd-catalyzed allylic C-H oxidation.[6] However, these methods suffered from the employment of noble metal catalysts, the laborious preparation of starting materials, high catalyst loading as well as generation of only one stereogenic centre. Given the synthetic difficulties associated with the lack of efficient and straightforward strategies to access 2-alkenylchromanes, it is highly desirable to develop a general and highly efficient methodology to prepare 2-alkenylchromanes, which can be employed to construct biologically molecules containing this motif and their analogues with potential pharmacological activities.

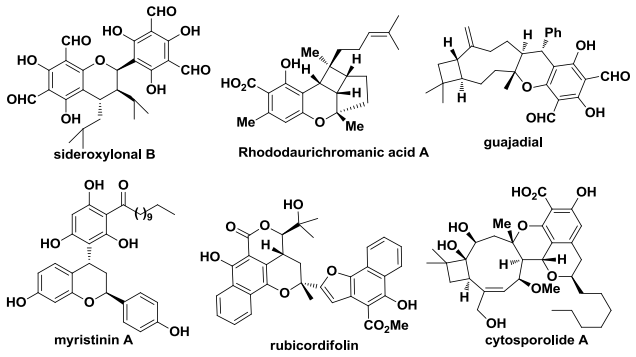


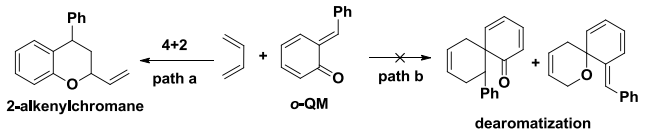
Figure 1. Natural products containing chromane motifs.

Catalytic inverse-electron-demand (IED) Hetero-Diels–Alder (HDA) reactions are versatile and powerful synthetic tools to construct 6-membered heterocyclic systems. [7] For instance, the pharmaceutically valuable 6-membered nitrogenous heterocycles such as tetrahydropyridines[7e,7d,7c] and tetrahydroquinolines[7f] can be established readily via IED-HDA reactions. In contrast, the oxygen-containing IED-HDA reactions are far less investigated [7h-j] although oxygen-containing 6-membered heterocyclic frameworks are also pharmaceutically important. *Ortho*-quinone methides (*o*-QMs) are highly reactive and transient intermediates,[8] which can be considered as unusual α,β-unsaturated ketones and have been employed as versatile electron-deficient species such as Michael acceptors[9] and

heterodienes of IED-HDA reactions.[10] All of the IED-HDA reactions involving o-QMs with monoalkenes has been well documented, whereas this elegant strategy has rarely been exploited to access 2-alkenylchromanes.[11] Among various precursors to generate *o*-QMs, *ortho*-hydroxybenzyl alcohols have shown attractive advantages over other counterparts such as atomic economy, generation of water as the only side product and easy preparation.

2. Results and discussions

To the best of our knowledge, conjugated dienes are rarely exploited as dienophiles, which can be rationalized that both normal electron-demand and inverse-electron-demand Diels–Alder reactions would compete to mess up the reactions. Only few reactions using conjugated dienes as dienophiles have been reported.[12a,7f,12b,11,12c] Reaction of *o*-QM intermediate with diene would produce IED-[4+2] cycloaddition products (path a) or normal electron-demand [4+2] cycloaddition products (path b). As far as we know, this fascinating chemistry has never been investigated, which encouraged us to investigate this process. The results demonstrated that path b are highly disfavoured, which might be ascribed to the dearomatization of phenyl group. The synthetically significant 2-alkenyl-chromanes can be constructed conveniently via path a.

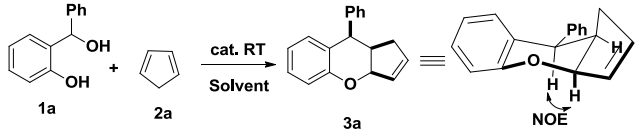


Scheme 1. Synthesis of 2-alkenyl-chromanes via IED-HDA reaction.

As continuous work to develop green and efficient methods for construction of pharmaceutically significant heterocycles,[13] herein we disclose an IED-HDA reaction of *o*-QM intermediate with alkenes, including conjugated dienes and non-conjutated dienes, affording multi-substituted 2-alkenylchromane derivatives in moderate to high yields. This strategy features metal-free and mild condition, good diastereoselectivity and wide substrate scope. The most fascinating characteristic of this reaction is that the conjugated dienes could be chemospecifically exploited as dienophiles to afford 2-alkenylchromane derivatives, which could be further elaborated in miscellaneous manners.

Subsequently, the stronger acids were investigated and (+)-10-camphorsulfonic acid (CSA) was identified as the best catalyst which furnished the cycloaddition product 3a in 92% yield and 13:1 diastereoselectivity (Table 1, entrie 4-8). However, further increasing the acidity of catalyst only resulted in inferior results (Table 1, entry 9). In addition to Brønsted acids, strong Lewis acids like $InBr_3$ and $In(OTf)_3$ were also examined, whereas only poor diastereoselectivity were observed although high yield could be achieved (Table 1, entries 10-11). Afterwards, a variety of solvents were evaluated, which had dramatic effect on the diastereoselectivities (Table 1, entries 12-16). DCE was shown to be the solvent of choice, in which 3a could be afforded in both highest yield (97%) and highest diastereoselectivity (20:1) (Table 1, entry 12). Notably, no product could be yielded in THF (Table 1, entry 14).

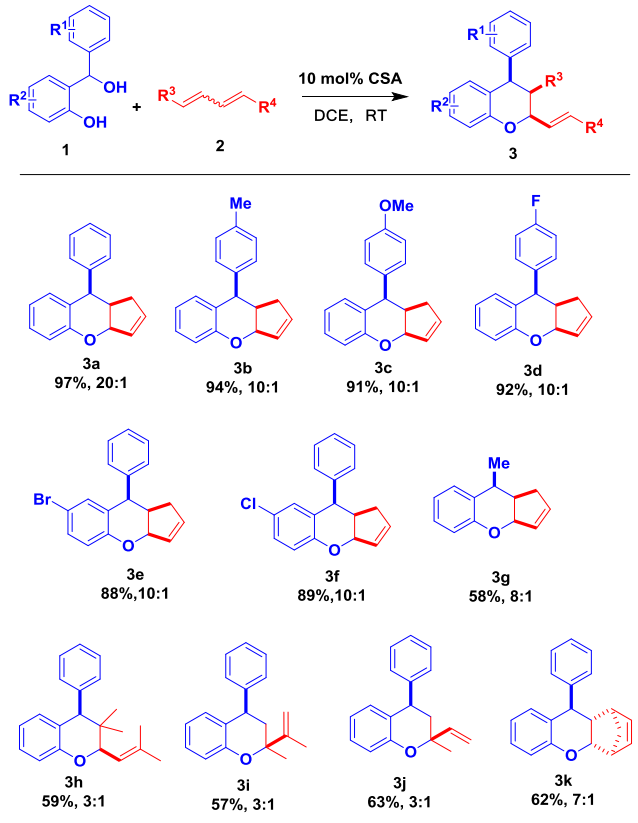
Table 1. Optimization of reaction conditions[a]



Entry	Acids	Solvent	Yield (%)[b]	*d.r* [c]
1	AcOH	DCM	NR	-
2	Benzoic acid	DCM	NR	-
3	2,4-Dinitrobenzoic acid	DCM	54	11:1
4	CCl_3CO_2H	DCM	89	9:1
5	TFA	DCM	97	8:1
6	CSA	DCM	92	13:1
7	CH_3SO_3H	DCM	56	7:1
8	$TsOH{\cdot}H_2O$	DCM	54	11:1
9	TfOH	DCM	trace	-
10	$InBr_3$	DCM	93	4:1
11	$In(OTf)_3$	DCM	68	5:1
12	CSA	DCE	97	20:1
13	CSA	toluene	96	9:1
14	CSA	THF	NR	-
15	CSA	$CHCl_3$	97	13:1
16	CSA	CH_3CN	88	5:1

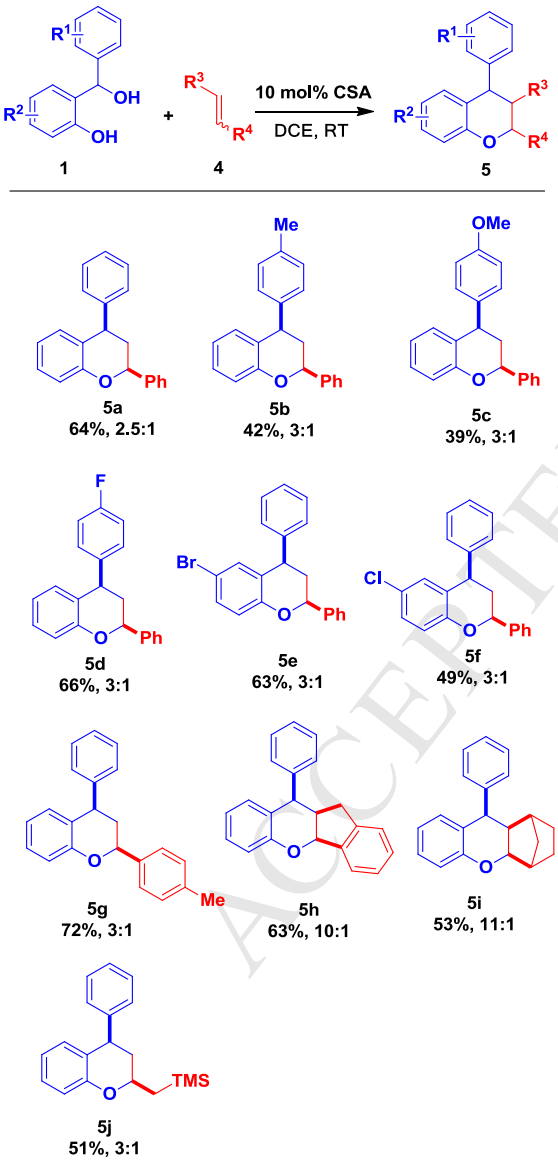
[a] Reaction conditions: 0.1 mmol of **1a**, 0.3 mmol of **2a** and 0.01 mmol catalyst in 1.5 mL of solvent at room temperature.
[b] Isolated yield after column chromatography.
[c] The diastereoselectivities of *endo* products **3a** were measured by crude ^1H NMR.

Under the optimal condition, a variety of electronically and sterically diverse *o*-hydroxybenzyl alcohols and conjugated dienes were examined to investigate the substrate scope (Scheme 2). The electronic characteristics of the substituents on o-



Scheme 2. Substrate scope of 1 and dienes 2.

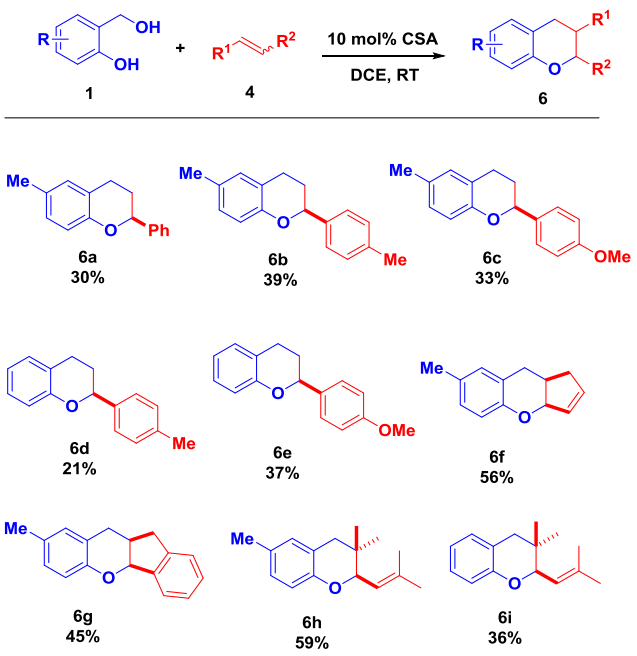
hydroxybenzyl alcohols had trivial influence on the reaction, i.e., both electron-withdrawing and electron-donating groups on the phenyl ring were well tolerated, affording the desired products 3a-3f in good to excellent yields and good diastereoselectivities. However, when phenyl group was replaced with methyl group, the yield of **3g** was decreased significantly. In addition to cyclopentadiene, several other conjugated dienes, including symmetric dienes and unsymmetric diene also furnished the desired products (**3h-3j**) in moderate yields and diastereoselectivities. Even though the yields of the reactions were low, the reactions were clean and no other side product could be observed. As to the products derived from uncyclized dienophiles(**3h-3j**), the relative configurations could also be unambiguously determined by NOE spectra. Notably, when the unconjugated bicyclo[2.2.1]-hepta-2,5-diene was exploited as the dienophile, the *exo* product **3k** was found to be the major diastereomer in good yields, which might be rationalized that bicyclo[2.2.1]hepta-2,5-diene is comparatively rigid and bulky due to double unconjugated alkene moieties, therefore the *exo* transition state of 3k is comparatively favored, resulting in the generation of *exo* products of 3k.



Scheme 3. Cycloaddition using styrenes and aliphatic monoenes as dienophiles.

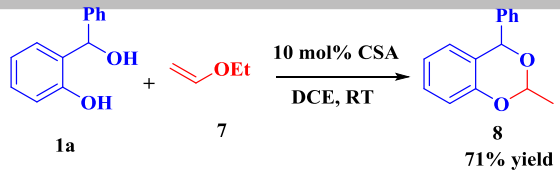
To further elaborate the application of this strategy, styrene, indene and aliphatic mono-enes were exploited as dienophiles (Scheme 3). To our delight, the desired 2-aryl- or 2-alkylchromanes could be furnished in moderate to good yields, albeit with moderate diasteroselectivities. In this case, the substituents on both of the substrates had significant impact on the yields. The electron-withdrawing group on *o*-hydroxybenzyl alcohols like fluoro had positive influence on the yield (**5d-5f**) whereas the electron-donating groups like methyl and methoxy were detrimental to the yields (**5a-5c**). As to the dienophile, the yield was significantly increased when styrene was substituted with electron-donating group (**5g**). The aforementioned phenomena might be explained by that the LUMO energy of *o*-QMs intermediate could be increased by electron-donating group, thus increasing the LUMO-HOMO energy gap between the two substrates and disfavoring the cycloaddition. In contrast, the LUMO energy of *o*-QM intermediate would be lowered by electron-withdrawing group, despite its destabilization of *o*-QM. Notably, when indene was subjected to the cycloaddition, high diastereoselectivity was observed (**5h**). Aliphatic monoene such as bicyclo[2.2.1]-hept-2-ene and allyltrimethylsilane could be well tolerated to furnish the desired products in moderate to good yields (**5i-5j**). Remarkably, the silyl group could be potentially mannipulated for a versatile synthetic utility.

A number of natural products like Vitamin E have no substituent on C4 of the chromane motif. This type of chromane derivatives had rarely been accessed via *o*-QM intermediate, which might be ascribed to the destabilization of corresponding *o*-QMs without aromatic substituent on C4 position. Normally, this labile intermediate could be generated with hydroxyl protected 2-hydroxylbenzol as precursor.[14] To the best of our knowledge, unprotected *o*-hydroxylbenzol has never been exploited for this purpose. Subsequently 2-hydroxybenzol was examined for the preparation of the non-C4-substituted chromane derivatives. Gratifyingly, the desired products **6** could be obtained readily, albeit in low to moderate yields (Scheme 4, **6a-6i**).



Scheme 4. 2-(hydroxymethyl)phenols without C4 substituents serving as the precursors of *o*-QMs for IED DA reaction.

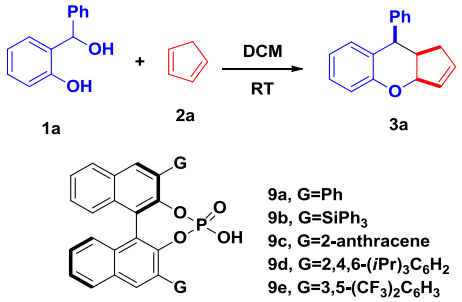
In addition to normal alkenes, ethyl vinyl ether **7** was also examined as dienophile under the optimal condition. However, only the acetal product **8** was observed, whereas no desired cycloaddition product was observed (Scheme 5).



Scheme 5. Ethyl vinyl ether was exploited as dienophile.

Finally, the asymmetric version of this reaction was investigated using chiral phosphoric acids as the catalyst (Table 2). Disappointedly, chiral catalyst **9a-9b** does not catalyze this reaction at all and the excellent yields could be obtained for **9c-9e**, but no asymmetric induction was observed, which might be attributed to the absence of heteroatom linkage in cyclopentadiene for chelation with chiral phosphoric acid.

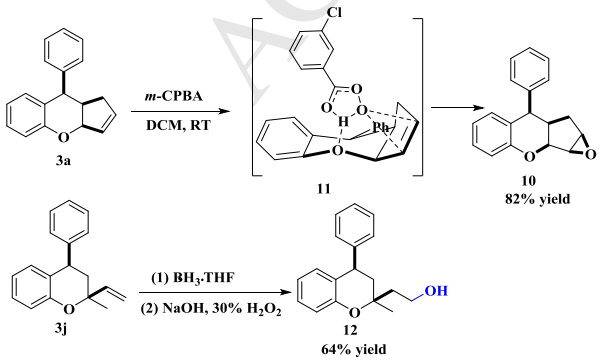
Table 2. Investigation of the asymmetric cycloaddition.[a]



Entry	Catalyst	Time	Yield (%)[b]	*d.r* [c]	*e.e.* (%)[d]
1	**9a**	4d	NR	12:1	-
2	**9b**	4d	NR	15:1	-
3	**9c**	1d	97	17:1	2
4	**9d**	1d	86	20:1	5
5	**9e**	2h	92	19:1	1

[a] Reaction conditions: 0.1 mmol of **1a**, 0.3 mmol of **2a**, 0.01 mmol catalyst in 1.5 ml of DCM at room temperature.
[b] Isolated yield after column chromatography.
[c] The diastereoselectivities of *endo* products **3a** were measured by crude ^{1}H NMR.
[d] The enatioselectivity of product **3a** was determined by chiral HPLC.

To demonstrate the synthetic utilities of 2-alkenylchromanes, epoxidation and hydroboration were selected for further elaboration of alkenyl group of the cycloaddition product 3 (Scheme 6). Satisfyingly, the desired products **10** and **12** could be afforded in good yields. Moreover, the stereoselectivity of epoxidation of **3a** was thoroughly under substrate control, providing the desired product 10 as the only diastereomer. The diastereospecificity might be rationalized by the transition state 11.[15]



Scheme 6. Epoxidation and hydroboration of **3a** and **3j**.

3. Conclusions

The synthetically important 2-alkenylchromane derivatives was efficiently constructed via inverse electron demand hetero-Diels-Alder reaction of *o*-quinone methides with dienes, which features mild and metal-free reaction condition, good diastereoselectivity and wide substrate scope. Additionally, styrenes and aliphatic monoenes could also be exploited as dienophiles to prepare the multi-substituted chromane derivatives in moderate yields and diastereoselectivities.

4. Experimental Section

4.1. General methods

All the chemical reagents were purchased from commercial companies. All reactions were performed in flask and monitored by TLC (0.2 mm silica gel-coated HSGF 254 plate). The reaction mixtures were purified by flash column chromatography (200-300 mesh silica gel) eluted with the gradient of petroleum ether and ethyl acetate. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on a Bruker AMX 500 spectrophotometer ($CDCl_3$ as solvent). Chemical shifts were reported in ppm using tetramethylsilane (TMS, δ (ppm) = 0.00 ppm) as the internal standard, and relative to the signal of chloroform-d (δ 7.26, singlet). The number of protons for a given resonance was indicated by nH. Coupling constants were reported as a *J* value in Hz. The following abbreviations were used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), and multiplet (m). Carbon nuclear magnetic resonance spectra (^{13}C NMR) were reported in ppm using solvent $CDCl_3$ (δ (ppm) =77.17 ppm) as an internal standard. HRMS analyses were performed on a Waters XEVO QTOF mass spectrometer. X-ray structure for compounds was determined on X-ray single crystal diffractmeter (Model Specifications: D8 QUEST).

4.2. General Procedure for Diels Alder reaction:

Cyclopentadiene **2a** (3.0 equiv, 0.3mmol) was added to a solution of hydroxybenzyl alcohol **1a** (1.0 equiv, 0.1 mmol) and CSA (0.01 mmol) in DCE (1.5 mL). The reaction mixture was stirred at room temperature for 3h until alcohol 1a was completely consumed (monitored with TLC). The solution was then concentrated *in vacuo* and the residue was directly loaded on a silica column which was eluted with the gradient of ethylacetate/petroleum ether to furnish the [4+2] cycloaddition products.

4.2.1. 9-phenyl-1,3a,9,9a-tetrahydrocyclopenta[b]chromene (**3a**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.31 (m, 5H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 2H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.06-5.96 (m, 2H), 5.42-5.36 (m,1H), 4.50 (d, *J* = 5.0 Hz, 1H), 3.20-3.13 (m, 1H), 2.36-2.28 (m, 1H), 2.27-2.19 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.00, 140.89, 137.74, 130.62, 129.63, 128.65, 128.18, 127.98, 127.34, 126.97, 121.08, 117.83, 84.73, 43.62, 43.52, 34.91; HRMS (ESI) calcd. for $C_{18}H_{16}ONa$, $[M+Na]^+$: 271.1099; found: 271.1096. IR v/cm^{-1}: 3085, 1613, 1495, 1472, 1288, 1013, 775, 712.

4.2.2. 9-(p-tolyl)-1,3a,9,9a-tetrahydrocyclopenta[b]-chromene(**3b**) Physical Appearance: white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.21 (m, 2H), 7.20-7.15 (m, 2H), 7.11-7.06 (m, 1H), 6.90-6.84 (m, 2H), 6.83-6.78 (m, 1H), 5.99-5.95 (m, 1H), 5.95-5.90 (m, 1H), 5.33 (dt, *J* = 7.3, 2.1 Hz, 1H), 4.42 (d, J = 5.0 Hz, 1H), 3.10 (qd, *J* = 7.4, 5.2 Hz, 1H), 2.37 (s, 3H), 2.31-2.24 (m, 1H), 2.23-2.15 (m, 1H); ^{13}C NMR (125 MHz, CDCl3) δ 153.90, 144.84, 143.51, 140.69, 129.92, 129.00, 128.72, 127.95,

126.81, 124.70, 120.20, 117.60, 112.92, 42.08, 39.81, 29.00, 23.00; HRMS (ESI) calcd. for $C_{19}H_{18}ONa$, $[M+Na]^+$: 285.1255; found: 285.1247. IR v/cm^{-1}: 3085, 1613, 1480, 1457, 1221, 1012, 760, 735.

4.2.3. 9-(4-fluorophenyl)-1,3a,9,9a-tetrahydrocyclopenta-[b]chromene (**3c**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 8.3, 5.5 Hz, 2H), 7.13-7.08 (m, 1H), 7.05 (t, *J* = 8.6 Hz, 2H), 6.91-6.78 (m, 3H), 5.95 (dd, *J* = 12.4, 5.8 Hz, 2H), 5.32 (d, *J* = 7.2 Hz, 1H), 4.44 (d, *J* = 5.1 Hz, 1H), 3.13-3.04 (m, 1H), 2.28-2.13 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.23, 151.78, 143.19, 137.53, 134.68, 128.65, 126.55, 125.20, 124.27, 122.56, 120.09, 110.47, 108.86, 53.34, 45.04, 14.35; HRMS (ESI) calcd. for $C_{18}H_{15}FONa$, $[M+Na]^+$: 289.1005; found: 289.1004. IR v/cm^{-1}: 3079, 1618, 1516, 1481, 1250, 1044, 851, 762.

4.2.4. 7-chloro-9-phenyl-1,3a,9,9a-tetrahydrocyclopenta[b]-chromene (**3d**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.36 (m, 2H), 7.34-7.29 (m, 3H), 7.07-7.02 (m, 1H), 6.85-6.82 (m, 1H), 6.79 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.01-5.94 (m, 1H), 5.94-5.88 (m, 1H), 5.36-5.32 (m, 1H), 4.40 (d, *J* = 4.8 Hz, 1H), 3.16-3.09 (m, 1H), 2.30-2.17 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.56, 152.48, 142.94, 135.98, 132.58, 128.87, 127.45, 126.57, 124.20, 122.30, 119.85, 110.36, 108.36, 53.73, 44.26, 21.31; HRMS (ESI) calcd. for $C_{18}H_{15}ClONa$, $[M+Na]^+$: 282.0811; found: 282.0807. IR v/cm^{-1}: 3058, 1620, 1509, 1486, 1224, 1016, 854, 758.

4.2.5. 7-bromo-9-phenyl-1,3a,9,9a-tetrahydrocyclopenta-[b]chromene (**3e**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.34 (m, 2H), 7.34-7.28 (m, 3H), 7.21-7.17 (m, 1H), 6.97 (dd, *J* = 2.4, 1.1 Hz, 1H), 6.75 (d, *J* = 8.5 Hz, 1H), 5.98-5.95 (m, 1H), 5.93-5.89 (m, 1H), 5.33 (dt, *J* = 7.3, 2.1 Hz, 1H), 4.40 (d, *J* = 4.9 Hz, 1H), 3.15-3.08 (m, 1H), 2.30-2.17 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.14, 139.89, 137.82, 130.62, 130.55, 130.35, 130.23, 129.45, 128.88, 127.28, 119.65, 113.51, 85.08, 43.50, 43.34, 34.91; HRMS (ESI) calcd. for $C_{18}H_{15}BrONa$, $[M+Na]^+$: 326.0306; found: 326.0300. IR v/cm^{-1}: 3078, 1637, 1498, 1479, 1228, 1013, 850, 762.

4.2.6. 9-(4-methoxyphenyl)-1,3a,9,9a-tetrahydrocyclopenta[b]-chromene (**3f**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.22 (m, 2H), 7.11-7.06 (m, 1H), 6.93-6.85 (m, 4H), 6.83-6.78 (m,1H), 5.97-5.90 (m, 2H), 5.33 (dt, *J* = 7.3, 2.1 Hz, 1H), 4.40 (d, *J* = 5.0 Hz, 1H), 3.81 (s, 3H), 3.12-3.06 (m, 1H), 2.29-2.22 (m, 1H), 2..22-2.15 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.58, 155.98, 137.62, 132.83, 130.62, 130.54, 128.60, 127.89, 127.23, 121.04, 117.76, 114.01, 84.79, 55.35, 43.77, 42.69, 34.88; HRMS (ESI) calcd. for $C_{19}H_{19}O_2$, $[M+H]^+$: 279.1385; found: 279.1382. IR v/cm^{-1}: 3067, 1639, 1489, 1477, 1223, 1009, 854, 771.

4.2.7. 9-methyl-1,3a,9,9a-tetrahydrocyclopenta[b]chromene (**3g**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12-7.06 (m, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 7.9 Hz, 1H), 5.84 – 5.79 (m, 1H), 5.78-5.74 (m, 1H), 5.35 (dt, *J* = 8.3, 2.1 Hz, 1H), 3.18 – 3.09 (m, 1H), 3.01-2.93 (m, 1H), 2.22 – 2.11 (m, 1H), 1.86 – 1.79 (m, 1H), 1.34 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.67, 136.95, 131.07, 130.69, 126.83, 125.49, 121.45, 118.00, 85.71, 43.13, 33.58, 30.08, 15.11; HRMS (ESI) calcd. for $C_{13}H_{14}ONa$, $[M+Na]^+$: 186.1045; found: 186.1040. IR v/cm^{-1}: 3092, 1602, 1484, 1459, 1216, 1127, 805, 756.

4.2.8. (2R,4S)-3,3-dimethyl-2-(2-methylprop-1-en-1-yl)-4-phenylchroman (**3h**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.23 (m, 4H), 7.12 – 7.09 (m, 2H), 6.93 – 6.86 (m, 1H), 6.79 – 6.72 (m, 2H), 5.47 (d, J = 9.0 Hz, 1H), 4.66 (d, J = 9.1 Hz, 1H), 4.04 (s, 1H), 1.84 (s, 3H), 1.76 (s, 3H), 0.83 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.36, 140.45, 138.94, 131.12, 130.51, 127.66, 127.47, 126.83, 125.36, 121.20, 120.34, 116.46, 81.05, 55.77, 35.61, 26.37, 24.15, 18.98, 15.36; HRMS (ESI) calcd. for $C_{21}H_{24}ONa$, $[M+Na]^+$: 315.1725; found: 315.1721. IR v/cm^{-1}: 3072, 1628, 1487, 1456, 1243, 1022, 750, 705.

4.2.9. (2S,4R)-2-methyl-4-phenyl-2-(prop-1-en-2-yl)chroman (**3i**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.27 – 7.24 (m, 1H), 7.22 – 7.18 (m, 2H), 7.13 (dd, *J* = 8.4, 4.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 4.2 Hz, 2H), 5.18 (s, 1H), 4.88 (s, 1H), 4.12 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.19 (dd, *J* = 13.6, 6.0 Hz, 1H), 2.09 – 2.01 (m, 1H), 1.83 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.06, 149.28, 144.86, 129.79, 129.00, 128.68, 127.91, 126.78, 124.65, 120.03, 117.56, 110.18, 78.36, 41.20, 39.87, 22.71, 18.88; HRMS (ESI) calcd. for $C_{19}H_{21}O$, $[M+H]^+$: 265.1592; found: 265.1594. IR v/cm^{-1}: 3059, 1628, 1488, 1449, 1241, 1203, 755, 700.

4.2.10. (2S,4R)-2-methyl-4-phenyl-2-vinylchroman (**3j**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.3 Hz, 3H), 7.20 (d, *J* = 7.2 Hz, 3H), 7.14 – 7.09 (m, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.78 – 6.73 (m, 2H), 6.03 (dd, *J* = 17.3, 10.9 Hz, 1H), 5.38 (d, *J* = 17.4 Hz, 1H), 5.13 (d, *J* = 10.7 Hz, 1H), 4.13 (dd, *J* = 11.7, 6.3 Hz, 1H), 2.10 – 2.00 (m, 2H), 1.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.99, 137.73, 136.50, 130.60, 129.50, 129.34, 128.43, 127.95, 127.24, 121.04, 117.78, 84.79, 43.72, 43.11, 34.93, 21.20; HRMS (ESI) calcd. for $C_{18}H_{19}O$, $[M+H]^+$: 251.1436; found: 265.1428. IR v/cm^{-1}: 3071, 1619, 1486, 1455, 1245, 1114, 755, 701.

4.2.11. (1R,4S,4aS,9R,9aS)-9-phenyl-4,4a,9,9a-tetrahydro-1H-1,4-methanoxanthene (**3k**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.36 – 7.30 (m, 3H), 7.15 – 7.10 (m, 1H), 6.96 (dd, *J* = 7.9, 1.0 Hz, 1H), 6.84 – 6.80 (m, 1H), 6.60 – 6.57 (m, 1H), 6.17 (dd, *J* = 5.7, 3.0 Hz, 1H), 6.04 (dd, *J* = 5.7, 3.2 Hz, 1H), 4.07 (d, *J* = 6.7 Hz, 1H), 3.58 (d, *J* = 10.8 Hz, 1H), 3.16 (s, 1H), 2.59 (s, 1H), 2.38 (d, *J* = 9.0 Hz, 1H), 2.22 (ddd, *J* = 10.8, 6.7, 1.5 Hz, 1H), 1.73 – 1.69 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.93, 141.24, 133.86, 133.47, 129.83, 128.85, 127.47, 127.16, 126.95, 122.08, 117.22, 82.43, 50.62, 48.98, 46.95, 45.15, 43.80; HRMS (ESI) calcd. for $C_{20}H_{19}O$, $[M+H]^+$: 275.1436; found: 275.1429. IR v/cm^{-1}: 3089, 1633, 1480, 1461, 1231, 1056, 745, 762.

4.2.12. (2S,4R)-2,4-diphenylchroman (**5a**).[16] Physical Appearance: white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.46 (m,2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.30 (m, 4H), 7.26-7.20 (m, 3H), 6.95 (d, *J* = 8.1 Hz, 1H), 6.82-6.75 (m, 2H), 5.21 (d, *J* = 12.6 Hz, 1H), 4.35 (dd, *J* = 12.2, 5.8 Hz, 1H), 2.44 – 2.37 (m, 1H), 2.29 – 2.22 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.62, 144.63, 141.31, 129.92, 128.78, 128.69, 128.59, 128.18, 127.90, 126.90, 126.21, 125.82, 120.70, 117.12, 78.21, 43.62, 40.76; IR v/cm^{-1}: 3091, 1609, 1493, 1455, 1241, 1020, 750, 702.

4.2.13. (2S,4R)-6-chloro-2,4-diphenylchroman (**5b**).[16] Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 - 7.45 (m, 2H), 7.41 - 7.37 (m, 2H), 7.36 – 7.30 (m, 5H), 7.22 – 7.19 (m, 2H), 6.88 (d, *J* = 8.7 Hz, 1H), 6.74 (dd, *J* = 2.5, 1.0 Hz, 1H), 5.18 (dd, *J* = 11.5, 1.5 Hz, 1H), 4.31 (dd, *J* = 12.2, 5.8 Hz, 1H), 2.46 – 2.37 (m, 1H), 2.29 – 2.20 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.30, 143.72, 140.91, 129.43, 129.02, 128.75, 128.62, 128.34, 127.98, 127.25, 126.18, 125.52, 118.56, 78.44, 73.63, 43.60, 40.33; IR v/cm^{-1}: 3069, 1628, 1489, 1455, 1272, 1233, 824, 754.

4.2.14. (2S,4R)-4-(4-fluorophenyl)-2-phenylchroman (**5c**).[16] Physical Appearance: white solid, ^{1}H NMR (500 MHz, CDCl3) δ 7.48 (d, J = 7.3 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.21 – 7.12 (m, 3H), 7.04 – 6.93 (m, 4H), 6.83 – 6.77 (m, 1H), 6.74 (d, J = 7.7 Hz, 1H), 5.23 – 5.17 (m, 1H), 4.36 (dd, J = 12.2, 5.8 Hz, 1H), 2.49 – 2.35 (m, 1H), 2.27 – 2.17 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.85, 160.90, 155.62, 141.24, 130.14, 130.08, 129.76, 128.73, 128.24, 128.06, 126.18, 120.79, 117.24, 115.71, 115.54, 78.18, 42.90, 40.94; IR v/cm^{-1}: 3067, 1620, 1518, 1486, 1253, 1034, 834, 755.

4.2.15. (2S,4R)-6-bromo-2,4-diphenylchroman (**5d**).[16] Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.28 (m, 5H), 7.20 – 7.16 (m, 3H), 7.12 – 7.08 (m, 1H), 6.91 – 6.85 (m, 1H), 6.82 (d, *J* = 8.7 Hz, 1H), 5.15 (dd, *J* = 11.4, 1.2 Hz, 1H), 4.28 (dd, *J* = 12.2, 5.8 Hz, 1H), 2.43 – 2.33 (m, 1H), 2.27 – 2.18 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.78, 143.64, 140.82, 132.31, 130.85, 128.99, 128.71, 128.57, 128.30, 127.22, 126.14, 119.02, 112.86, 78.36, 43.49, 40.27; IR v/cm^{-1}: 3058, 1629, 1509, 1483, 1237, 1011, 834, 754.

4.2.16. (2S,4R)-2-phenyl-4-(p-tolyl)chroman (**5e**).[16] Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.34 – 7.31 (m, 2H), 7.12 (d, *J* = 1.4 Hz, 4H), 7.02 (d, *J* = 8.0 Hz, 1H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.78 (d, *J* = 4.1 Hz, 2H), 5.20 (d, *J* = 10.9 Hz, 1H), 4.32 (dd, *J* = 12.1, 5.8 Hz, 1H), 2.42 – 2.35 (m, 1H), 2.33 (s, 3H), 2.30 – 2.21 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.63, 141.58, 141.41, 136.46, 129.90, 129.48, 128.69, 128.58, 128.15, 127.83, 126.23, 120.67, 117.09, 78.28, 43.23, 40.76, 21.19; IR v/cm^{-1}: 3065, 1633, 1505, 1481, 1266, 1234, 753, 701.

4.2.17. (2S,4R)-4-(4-methoxyphenyl)-2-phenylchroman (**5f**).[16] Physical Appearance: white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.3 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.34 – 7.31 (m, 2H), 7.16 – 7.10 (m, 3H), 6.94 (d, *J* = 8.1 Hz, 1H), 6.87 – 6.84 (m, 2H), 6.80 – 6.76 (m, 2H), 5.21 (dd, *J* = 11.4, 1.4 Hz, 1H), 4.31 (dd, *J* = 12.2, 5.8 Hz, 1H), 3.79 (s, 3H), 2.41 – 2.34 (m, 1H), 2.29 – 2.18 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.59, 155.60, 141.42, 136.63, 129.86, 129.64, 128.69, 128.15, 127.83, 126.21, 120.67, 117.08, 114.20, 78.31, 55.41, 42.81, 40.83; IR v/cm^{-1}: 3080, 1642, 1659, 1481, 1263, 1235, 748, 696.

4.2.18. (2S,4R)-4-phenyl-2-(p-tolyl)chroman (**5g**).[16] Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.0 Hz, 2H), 7.32 – 7.29 (m, 2H), 7.24 – 7.19 (m, 5H), 7.16 – 7.11 (m, 2H), 6.96 – 6.92 (m, 1H), 6.79 – 6.74 (m, 1H), 5.17 (dd, *J* = 11.4, 1.5 Hz, 1H), 4.34 (dd, *J* = 12.1, 5.9 Hz, 1H), 2.41 – 2.36 (m, 1H), 2.35 (s, 3H), 2.32 – 2.26 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.77, 144.74, 138.37, 137.92, 129.91, 129.36, 128.78, 128.73, 127.86, 126.88, 126.24, 120.63, 117.15, 78.15, 43.70, 40.62, 21.31; IR v/cm^{-1}: 3075, 1645, 1493, 1458, 1273, 1235, 756, 705.

4.2.19. (4bS,10R,10aR)-10-phenyl-4b,10,10a,11-tetrahydroindeno[1,2-b]chromene (**5h**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 9.6, 8.2 Hz, 1H), 7.35 (dd, *J* = 9.9, 4.4 Hz, 2H), 7.27 – 7.19 (m, 4H), 7.14 – 7.03 (m, 3H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.83 – 6.75 (m, 2H), 5.46 (d, *J* = 4.7 Hz, 1H), 4.64 (d, *J* = 6.0 Hz, 1H), 3.06 – 2.99 (m, 1H), 2.96 – 2.89 (m, 1H), 2.45 (dd, *J* = 15.1, 7.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.21, 144.42, 142.46, 142.12, 129.53, 129.25, 128.58, 127.58, 126.93, 125.32, 125.13, 120.58, 117.02, 81.24, 45.82, 43.22, 33.58; HRMS (ESI) calcd. for $C_{22}H_{18}ONa$, $[M+Na]^+$: 321.1255; found: 321.1256. IR v/cm^{-1}: 3078, 1629, 1486, 1458, 1251, 1224, 943, 752.

4.2.20. (1S,4R,4aR,9R,9aR)-9-phenyl-2,3,4,4a,9,9a-hexahydro-1H-1,4-methanoxanthene (**5i**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (t, *J* = 7.4 Hz, 2H), 7.35 – 7.29 (m, 3H), 7.15 – 7.10 (m, 1H), 6.94 (dd, *J* = 7.8, 0.7 Hz, 1H), 6.84 – 6.80 (m, 1H), 6.58 – 6.54 (m, 1H), 3.95 (d, *J* = 6.8 Hz, 1H), 3.49 (d, *J* = 10.8 Hz, 1H), 2.60 (d, *J* = 4.8 Hz, 1H), 2.20 – 2.12 (m, 2H), 2.07 (d, *J* = 2.7 Hz, 1H), 1.66 – 1.57 (m, 1H), 1.49 – 1.40 (m, 1H), 1.27 – 1.23 (m, 1H), 1.21 – 1.14 (m, 1H), 1.12 – 1.03 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.19, 141.40, 133.28, 129.89, 128.79, 127.37, 127.03, 126.81, 122.06, 117.12, 84.96, 55.17, 44.85, 43.41, 40.53, 33.52, 29.08, 24.86; HRMS (ESI) calcd. for $C_{20}H_{21}O$, $[M+H]^+$: 277.1592; found: 277.1588. IR v/cm^{-1}: 3091, 1628, 1478, 1459, 1230, 1034, 745, 701.

4.2.21. trimethyl(((2S,4R)-4-phenylchroman-2-yl)methyl)silane (**5j**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.22 – 7.16 (m, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.85 – 6.81 (m, 2H), 6.75 – 6.70 (m, 1H), 4.23 – 4.15 (m, 2H), 2.08 – 1.93 (m, 2H), 1.16 – 1.10 (m, 1H), 1.01 – 0.95 (m, 1H), 0.13 (s, 4H), 0.01 (s, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.50, 145.93, 131.56, 129.39, 129.07, 128.28, 127.37, 126.97, 123.89, 120.90, 117.73, 70.65, 44.22, 41.07, 24.57, 0.00; HRMS (ESI) calcd. for $C_{19}H_{25}OSi$, $[M+H]^+$: 297.1675; found: 297.1671. IR v/cm^{-1}: 3062, 1638, 1496, 1458, 1231, 1065, 841, 751.

4.2.22. 6-methyl-2-phenylchroman (**6a**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 4H), 7.33 – 7.29 (m, 1H), 6.95 – 6.88 (m, 2H), 6.81 (d, *J* = 8.2 Hz, 1H), 5.03 (dd, *J* = 10.1, 2.3 Hz, 1H), 3.00-2.91 (m, 1H), 2.78 – 2.72 (m, 1H), 2.27 (s, 3H), 2.22 – 2.16 (m, 1H), 2.12 – 2.03 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.06, 142.02, 129.99, 129.60, 128.63, 128.09, 127.90, 126.13, 121.60, 116.80, 77.83, 30.19, 25.19, 20.63; HRMS (ESI) calcd. for $C_{16}H_{16}ONa$, $[M+Na]^+$: 247.1099; found: 247.1094. IR v/cm^{-1}: 3065, 1623, 1500, 1251, 1214, 945, 817, 749.

4.2.23. 2-(4-methoxyphenyl)chroman (**6b**); Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.6 Hz, 2H), 7.10 (dd, *J* = 17.6, 8.3 Hz, 2H), 6.94 – 6.84 (m, 4H), 5.01 (dd, *J* = 10.2, 2.2 Hz, 1H), 3.82 (s, 3H), 3.05 – 2.95 (m, 1H), 2.84 – 2.77 (m, 1H), 2.21 – 2.15 (m, 1H), 2.14 – 2.05 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.46, 155.40, 134.04, 129.65, 127.51, 121.96, 120.39, 117.08, 114.08, 77.65, 55.47, 29.96, 25.38; HRMS (ESI) calcd. for $C_{16}H_{16}O_2Na$, $[M+Na]^+$: 263.1048; found: 263.1042. IR v/cm^{-1}: 3072, 1601, 1522, 1499, 1254, 1230, 836, 815.

4.2.24. 7-methyl-1,3a,9,9a-tetrahydrocyclopenta[b]chromene (**6c**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.86-6.76 (m, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.88 – 5.85 (m, 1H), 5.75 – 5.72 (m, 1H), 5.13 (dd, *J* = 6.1, 3.9 Hz, 1H), 2.87 – 2.74 (m, 2H), 2.53 – 2.46 (m, 1H), 2.40 (dd, *J* = 14.2, 6.0 Hz, 1H), 2.19 (s, 3H), 2.09-2.01 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.97, 135.84, 130.87, 130.71, 129.14, 127.77, 127.29, 117.42, 85.33, 38.94, 37.02, 29.86, 20.84; HRMS (ESI) calcd. for $C_{13}H_{15}O$, $[M+H]^+$: 187.1123; found: 187.1120. IR v/cm^{-1}: 3089, 1630, 1619, 1513, 1248, 1043, 832, 813.

4.2.25. 3,3-dimethyl-2-(2-methylprop-1-en-1-yl)chroman (**6d**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (t, *J* = 7.6 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.86 – 6.78 (m, 2H), 5.33 (d, *J* = 9.3 Hz, 1H), 4.46 (d, *J* = 9.3 Hz, 1H), 2.66 (d, *J* = 16.2 Hz, 1H), 2.51 (d, *J* = 16.2 Hz, 1H), 1.81 (s, 3H), 1.74 (s, 3H), 0.97 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.00, 138.66, 129.89, 127.22, 121.78, 121.13, 120.27, 116.58, 79.76, 40.16, 31.93, 26.46, 26.32, 21.04, 18.88; HRMS (ESI)

calcd. for $C_{15}H_{20}ONa$, $[M+Na]^+$: 239.1412; found: 239.1403. IR v/cm^{-1}: 3089, 1618, 1532, 1439, 1287, 1290, 876, 785.

4.2.26. 2-(4-methoxyphenyl)-6-methylchroman (**6e**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.6 Hz, 2H), 6.94 – 6.88 (m, 4H), 6.79 (d, *J* = 8.2 Hz, 1H), 4.97 (dd, *J* = 10.2, 2.4 Hz, 1H), 3.81 (s, 3H), 3.00 - 2.90 (m, 1H), 2.79 – 2.72 (m, 1H), 2.26 (s, 3H), 2.19 – 2.02 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.41, 153.19, 134.17, 129.98, 129.52, 128.04, 127.50, 121.59, 116.80, 114.05, 77.58, 55.45, 30.05, 25.34, 20.63; HRMS (ESI) calcd. for $C_{17}H_{18}O_2Na$, $[M+Na]^+$: 277.1204; found: 277.1201. IR v/cm^{-1}: 3075, 1619, 1609, 1483, 1248, 1049, 835, 783.

4.2.27. 2-(p-tolyl)chroman (**6f**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 7.11 – 7.07 (m, 2H), 6.92 – 6.84 (m, 2H), 5.03 (dd, *J* = 10.2, 2.3 Hz, 1H), 3.05 -2.95 (m, 1H), 2.83 – 2.76 (m, 1H), 2.36 (s, 3H), 2.22 – 2.16 (m, 1H), 2.14 – 2.04 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.41, 153.19, 134.17, 129.98, 129.52, 128.04, 127.50, 121.59, 116.80, 114.05, 77.58, 55.45, 30.05, 25.34, 20.63; HRMS (ESI) calcd. for $C_{16}H_{16}ONa$, $[M+Na]^+$: 247.1099; found: 247.1094. IR v/cm^{-1}: 3081, 1608, 1478, 1432, 1241, 1098, 789, 755.

4.2.28. 3,3,6-trimethyl-2-(2-methylprop-1-en-1-yl)chroman (**6g**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.82 (s, 1H), 6.75 – 6.67 (m, 1H), 5.34 – 5.30 (m, 1H), 4.42 (d, *J* = 9.3 Hz, 1H), 2.61 (d, *J* = 16.2 Hz, 1H), 2.47 (d, *J* = 16.3 Hz, 1H), 2.24 (s, 3H), 1.80 (d, *J* = 1.2 Hz, 3H), 1.73 (d, *J* = 1.3 Hz, 3H), 0.96 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.72, 138.52, 130.22, 129.37, 127.85, 121.41, 121.20, 116.32, 79.66, 40.12, 31.96, 26.46, 26.31, 21.10, 20.64, 18.87; HRMS (ESI) calcd. for $C_{16}H_{22}ONa$, $[M+Na]^+$: 253.1568; found: 253.1569. IR v/cm^{-1}: 3079, 1603, 1473, 1436, 1231, 1156, 903, 785.

4.2.29. 8-methyl-4b,10,10a,11-tetrahydroindeno[1,2-b]chromene (**6h**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 1H), 7.28 – 7.20 (m, 3H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.75 (d, *J* = 7.9 Hz, 1H), 5.49 (d, *J* = 6.5 Hz, 1H), 3.10 (dd, *J* = 15.6, 7.1 Hz, 1H), 3.00 – 2.90 (m, 2H), 2.79 (dd, *J* = 15.6, 5.0 Hz, 1H), 2.58 – 2.51 (m, 1H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.24, 142.75, 142.66, 130.07, 129.48, 128.80, 127.89, 126.98, 125.44, 125.24, 123.74, 116.85, 81.89, 38.03, 37.23, 28.42, 20.72; HRMS (ESI) calcd. for $C_{17}H_{16}ONa$, $[M+Na]^+$: 259.1099; found: 259.1087. IR v/cm^{-1}: 3055, 1623, 1498, 1456, 1258, 1025, 999, 813.

4.2.30. 6-methyl-2-(p-tolyl)chroman (**6i**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 6.94 – 6.87 (m, 2H), 6.80 (d, *J* = 8.2 Hz, 1H), 4.99 (dd, *J* = 10.1, 2.3 Hz, 1H), 2.99 - 2.90 (m, 1H), 2.78 – 2.71 (m, 1H), 2.35 (s, 3H), 2.26 (s, 3H), 2.19 – 2.02 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.16, 139.04, 137.60, 129.98, 129.50, 129.30, 128.04, 126.13, 121.61, 116.81, 77.75, 30.10, 25.26, 21.29, 20.63; HRMS (ESI) calcd. for $C_{17}H_{18}ONa$, $[M+Na]^+$: 261.1255; found: 261.1259. IR v/cm^{-1}: 3078, 1633, 1588, 1491, 1242, 1041, 800, 755.

4.2.31. 2-methyl-4-phenyl-4H-benzo[d][1,3]dioxine (**8**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, CDCl3) δ 7.38 – 7.33 (m, 6H), 7.15 (t, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.80 (t, *J* = 7.8 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 1H), 5.98 (s, 1H), 5.47 (q, *J* = 5.1 Hz, 1H), 1.60 (d, *J* = 5.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.27, 140.51, 128.79, 128.77, 128.75, 128.42, 127.36, 127.12, 121.13, 116.64, 97.33, 79.84, 21.02; HRMS (ESI) calcd. for $C_{15}H_{15}O_2$, $[M+H]^+$: 227.1067; found: 227.1064. IR v/cm^{-1}: 3075, 1589, 1497, 1465, 1273, 1235, 885, 756.

4.2.32. 7-phenyl-1a,1b,7,7a,8,8a-hexahydrooxireno[2',3':4,5]-cyclopenta[1,2-b]chromene (**10**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2H), 7.29 (dt, *J* = 4.9, 2.0 Hz, 1H), 7.20 – 7.12 (m, 3H), 6.92 – 6.84 (m, 2H), 6.83 – 6.78 (m, 1H), 4.76 (d, *J* = 4.6 Hz, 1H), 4.43 (d, *J* = 6.0 Hz, 1H), 3.72 (d, *J* = 2.4 Hz, 1H), 3.49 (d, *J* = 2.1 Hz, 1H), 2.50 – 2.43 (m, 1H), 1.66 (dd, *J* = 13.9, 7.2 Hz, 1H), 1.58 – 1.54 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.84, 141.54, 129.46, 129.40, 128.61, 128.01, 127.06, 123.32, 120.74, 116.55, 57.65, 55.85, 40.71, 37.66, 28.26; HRMS (ESI) calcd. for $C_{18}H_{17}O_2$, $[M+H]^+$: 265.1229; found: 265.1225. IR v/cm^{-1}: 3085, 1593, 1478, 1458, 1228, 1024, 943, 752.

4.2.33. 2-(2-methyl-4-phenylchroman-2-yl)ethanol (**12**). Physical Appearance: white solid, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 3H), 7.22 – 7.19 (m, 2H), 7.12 – 7.08 (m, 1H), 6.82 (dd, *J* = 8.0, 4.5 Hz, 1H), 6.76 (dd, *J* = 6.3, 1.1 Hz, 2H), 4.13 (dd, *J* = 12.5, 6.1 Hz, 1H), 4.01 – 3.86 (m, 2H), 2.49 (s, 1H), 2.15 – 2.08 (m, 1H), 2.02 – 1.97 (m, 3H), 1.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.31, 144.86, 130.01, 128.91, 128.79, 127.96, 126.88, 124.82, 120.55, 117.49, 77.60, 59.09, 44.30, 42.23, 39.60, 22.74; HRMS (ESI) calcd. for $C_{18}H_{20}O_2Na$, $[M+Na]^+$: 291.1361; found: 291.1362. IR v/cm^{-1}: 3327, 3068, 1603, 1458, 1251, 1124, 943, 752.

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