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Homoenolate Annulation

Synthesis of Cyclopentachromans by *N*-Heterocyclic Carbene-Mediated Homoenolate Annulation of Chroman-3-ene-4-ones

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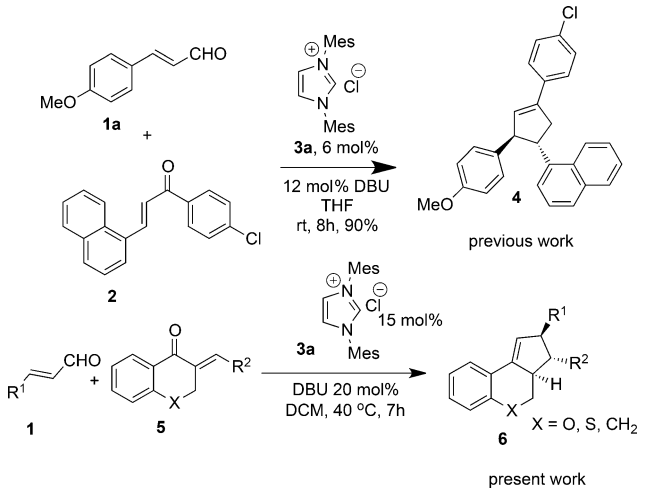
Dedicated with best wishes to Professor S. Chandrasekaran on the occasion of his 70th birthday

Abstract: An *N*-heterocyclic carbene (NHC)-mediated homoenolate reaction strategy for the efficient synthesis of a wide variety of tricyclic pentenes with potential biological activity is reported.

Introduction

The discovery of *N*-heterocyclic carbene (NHC)[1] catalyzed annulation of enals to aldehydes leading to γ-lactones,[2] in 2004, heralded a new era in homoenolate chemistry. A plethora of homoenolate reactions leading to the formation of a wide variety of compounds, such as, δ-lactones,[3] lactams,[4] cyclopentanones and spirocyclopentanones,[5] cyclopentenes,[6,7] pyranones,[8] pyrazolones,[9] GABA (gamma-aminobutyric acid) analogs,[10] cyclopentanoids,[11] etc., have been reported by several groups, including our own. Of special interest to us has been the diastereoselective formation of tri-substituted cyclopentenes by the annulation of homoenolates to chalcones (Scheme 1).[6a,c]

The novelty and efficiency of the cyclopentene synthesis warranted further exploration in this area.[6] Thus, we became interested in studying the reactivity of NHC-bound homoenolates towards arylidene chroman-4-ones, arylidene-1-thiochroman-4-ones, and arylidene tetralones, with a view to obtaining tricyclic chroman and thiochroman derivatives and analogous compounds. Additional impetus for this study was provided by the fact that chromanones and related ring systems have important biological activities. Chroman-4-one derivatives have been reported to have antibacterial and antifungal properties. They are also known to have good phosphodiesterase IV inhibition activity, anti-inflammatory and anti-ulcer activity.[12] Homoenolate annulation of arylidene derivatives of chroman-4-ones and thiochroman-4-ones offered a potential route for the synthesis of complex molecules integrating chromanone and thiochromanone units. Current interest in this area is underscored by the recent synthesis of an impressive estrogen receptor β-agonist, a cyclopentachroman.[13]



Scheme 1. NHC-catalyzed annulation reactions.

Results and Discussion

Our studies were initiated by exposing 4-methoxycinnamaldehyde with 3-(4-methylbenzylidene)chroman-4-one in the presence of a catalytic amount of 1,3-dimesityl imidazole-2-ylidene chloride (IMes·HCl) and 1,8-diazabicyclo[5.4.0]undec-7-ene

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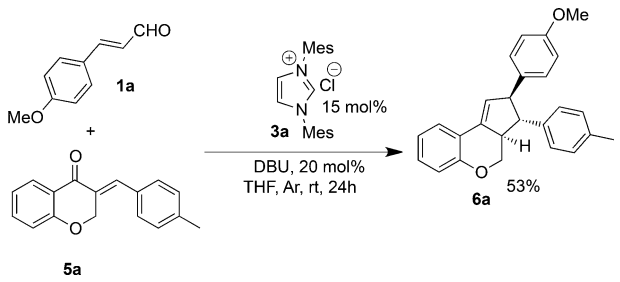
(DBU) at room temperature for 24 h under an argon atmosphere. The reaction afforded a white solid in 53% yield and it was characterized as the substituted cyclopentachromene **6a** (Scheme 2).



Scheme 2. Reaction of enal with chroman-3-ene-4-one.

The structure of compound **6a** was elucidated by the usual spectroscopic analysis. The proton NMR spectrum contained a singlet at $\delta = 3.76$ corresponding to the methoxy group, a singlet at $\delta = 2.33$ corresponding to the methyl group, and one down-field proton at $\delta = 6.05$ corresponding to the olefinic proton of the pentene. This was supported by the ^{13}C NMR spectrum, which contained a peak at $\delta = 157.2$ indicating the aromatic carbon bearing the -OCH_3 group. It also displayed a peak at $\delta = 53.9$ for the methoxy carbon. A signal at $\delta = 20.0$ was attributed to the methyl carbon. Final confirmation of the structure and relative stereochemistry of the cyclopentachromene was obtained from single-crystal X-ray determination of **6k** (Figure 1).

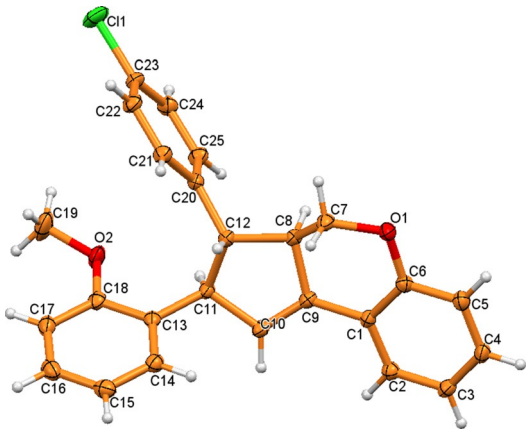
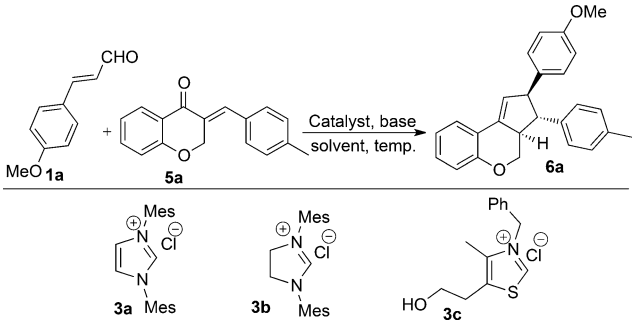


Figure 1. ORTEP diagram of compound **6k**.

In view of the success of the above reaction, we examined the usefulness of other commonly available NHC catalysts in this reaction. A number of experiments were conducted, and the results are summarized in Table 1. Among the catalysts investigated, imidazolium catalyst **3a** gave the best results. Subsequently, we investigated the effect of other parameters such as solvent, base, and temperature on the reaction. As shown in Table 1, it was clear that the cyclopentannulation was facilitated by the combination of imidazolium carbene precursor **3a** and DBU in CH_2Cl_2 as solvent under reflux.

Table 1. Optimization of the reaction conditions.[a]



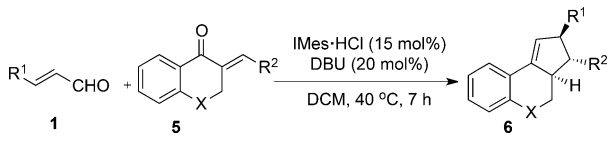
Entry	Catalyst	Base, solvent, T [°C]	t [h][b]	Yield [%][c]
1	**3a**	DBU, THF, rt	24	53
2	**3b**	DBU, THF, rt	24	–
3	**3c**	DBU, THF, rt	24	–
4	**3a**	DBU, CH_2Cl_2, rt	24	50
5	**3a**	DBU, toluene, 110	6	81
6	**3a**	DBU, CH_3CN, 82	24	13
7	**3a**	DBU, CH_2Cl_2, 40	7	95
8	**3a**	DBU, THF, 66	6	85
9	**3a**	KO*t*Bu, CH_2Cl_2, 40	24	70
10	**3a**	K_2CO_3, CH_2Cl_2, 40	24	56
11	**3a**	NEt_3, CH_2Cl_2, 40	24	86

[a] Reaction conditions: **1a** (0.75 mmol), **5a** (0.5 mmol), carbene precursor (15 mol%), base (20 mol%) in 4 mL of solvent. [b] The time shown is that required for the complete consumption of the enone. [c] Isolated yield.

Further, the generality of this promising reaction was investigated by using a number of arylidene chroman-4-ones, 1-thiochroman-4-ones, and arylidene-3,4-dihydronaphthalen-1-ones with various α,β-unsaturated aldehydes.

Initially, we examined the annulation of enones with enals that have electron-donating as well as electron-withdrawing substituents (Table 2). Also, three types of enones (X = O, S, and CH_2) were subjected to the homoenolate annulation reaction. In all three cases, the reactivity of enones towards various enals was similar (Table 2, entries 1, 2, 5, 6, and 7). It appears that the substituents on the enal have only marginal influence

Table 2. Scope of enals.[a]



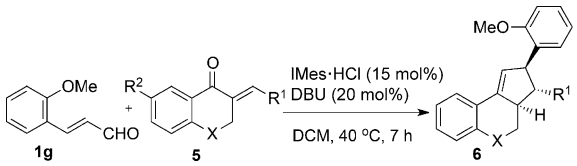
Entry	X	R^1	R^2	Product	Yield [%][b]
1	O	4-MeO-Ph	4-Me-Ph	**6a**	95
2	O	4-Br-Ph	4-Me-Ph	**6b**	85
3	O	furyl	4-Me-Ph	**6c**	75
4	S	furyl	Ph	**6d**	87
5	S	4-F-Ph	Ph	**6e**	86
6	S	4-Me-Ph	Ph	**6f**	91
7	CH_2	4-MeO-Ph	Ph	**6g**	73
8	CH_2	Ph	Ph	**6h**	71

[a] Reactions were carried out with **1** (0.75 mmol), **5** (0.5 mmol), carbene precursor (15 mol%), DBU (20 mol%) in 4 mL of anhydrous CH_2Cl_2 (at reflux for 7 h). [b] Isolated yield.

on the annulation reaction; the products are formed in generally high yields. Delightfully, hetero aryl substituted enals also participated in the annulation reaction to afford the tricyclopentenes in comparable yields (Table 2, entries 3 and 4).

Investigation of the scope of enones was carried out by using 2-methoxy cinnamaldehyde **1g** as the enal under the optimized reaction conditions. In this case also, we have utilized three types of enones (X = O, S, and CH_2) with different substituents on the alkene part. As shown in Table 3, it was found that arylidene chomanone and thiochromanones gave the corresponding annulation products in excellent yields (Table 3, entries 1–7). It was noticed that the yield decreased to 70–73% when arylidene tetralones were used as the substrate (Table 3, entries 8–10). We decided to explore the effect of substituents on the aromatic ring of the arylidene chomanone. It is worth mentioning that 8-fluoro-substituted arylidene chomanone was found to be a good reaction partner for this homoenolate annulation and gave the expected product in 86% yield (Table 3, entry 11).

Table 3. Scope of enones.[a]



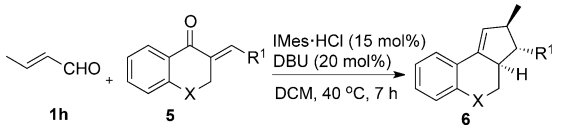
Entry	X	R^1	R^2	Product	Yield [%][b]
1	O	furyl	H	**6i**	89
2	O	4-F-Ph	H	**6j**	97
3	O	4-Cl-Ph	H	**6k**	92
4	O	thienyl	H	**6l**	94
5	S	4-F-Ph	H	**6m**	91
6	S	thienyl	H	**6n**	93
7	S	4-Me-Ph	H	**6o**	92
8[c]	CH_2	thienyl	H	**6p**	72
9	CH_2	Ph	H	**6q**	73
10	CH_2	4-Me-Ph	H	**6r**	70
11	O	4-Me-Ph	F	**6s**	86

[a] Reactions were carried out with **1** (0.75 mmol), **5** (0.5 mmol), carbene precursor (15 mol%), DBU (20 mol%) in 4 mL of anhydrous CH_2Cl_2 (at reflux for 7 h). [b] Isolated yield. [c] An isolated example of an analogous compound of **6p** was reported in ref. [6a].

In view of the interesting results obtained by the reaction of arylidene chroman-4-ones, 1-thiochroman-4-ones, and tetralones with various aromatic enals, it was irresistible to extend our studies to β-alkyl substituted enal. (*E*)-But-2-enal was our choice and the above homoenolate reaction strategy was applied to various arylidene chroman-4-ones and 1-thiochroman-4-ones. Gratifyingly, all the reactions afforded the products in good yields (Table 4).

In view of the success of the above reactions, we decided to extend the investigation to cinnamylidene chromanones and thiochromanones. In all cases, tricyclic pentenes endowed with an alkenyl side chain were obtained in good yields (Table 5).

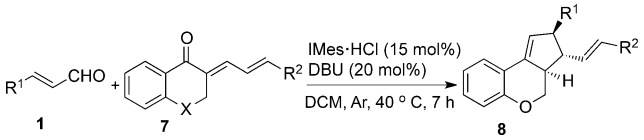
Table 4. Scope of the reaction of β-alkenyl substituted enals with enones.[a]



Entry	X	R^1	Product	Yield [%][b]
1	O	4-MeO-Ph	**6t**	73
2	O	4-F-Ph	**6u**	71
3	O	furyl	**6v**	68
4	O	Br-Ph	**6w**	71
5	S	thienyl	**6x**	70
6	S	furyl	**6y**	71
7	S	Ph	**6z**	67

[a] Reactions were carried out with **1** (0.75 mmol), **5** (0.5 mmol), carbene precursor (15 mol%), DBU (20 mol%) in 4 mL of anhydrous CH_2Cl_2 (at reflux for 7 h). [b] Isolated yield.

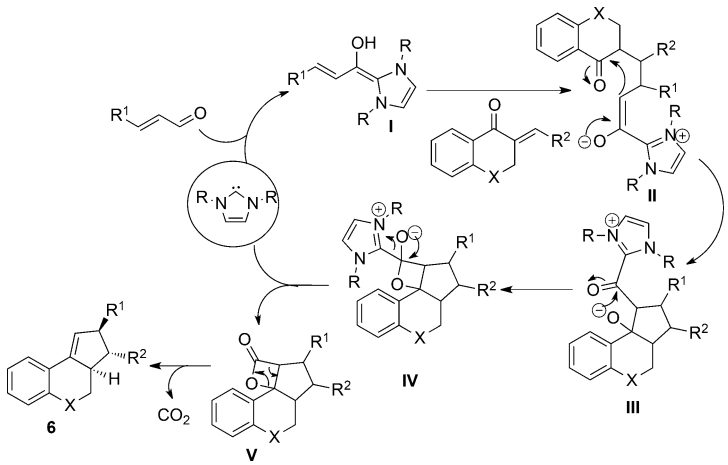
Table 5. Reaction of enals with cinnamylidene chromanones and thiochromanones.



Entry	X	R^1	R^2	Product	Yield [%][b]
1	O	4-MeO-Ph	Ph	**8a**	67
2	O	2-MeO-Ph	Ph	**8b**	75
3	O	4-MeO-Ph	4-OMe-Ph	**8c**	66
4	O	2-MeO-Ph	4-OMe-Ph	**8d**	71
5	O	Ph	4-OMe-Ph	**8e**	69
6	S	4-MeO-Ph	4-OMe-Ph	**8f**	72
7	S	4-Cl-Ph	4-OMe-Ph	**8g**	71

[a] Reactions were carried out with **1** (0.75 mmol), **7** (0.5 mmol), carbene precursor (15 mol%), DBU (20 mol%) in 4 mL of anhydrous CH_2Cl_2 (at reflux for 7 h). [b] Isolated yield.

A mechanistic rationale for the reaction may be advanced along the following lines (Scheme 3). Conceivably, the homo-



Scheme 3. Mechanism of the reaction.

enolate **I** formed by the reaction of IMes with enal undergoes conjugate addition to the arylidene chroman-4-one and, consequent to a proton transfer, generates the enolate **II**, which participates in an intramolecular aldol reaction to deliver the cyclopentane carbinolate **III**. The latter undergoes β-lactonization to eject IMes, allowing the catalytic cycle to continue. The β-lactone **V** thus formed is unstable and undergoes a retro [2+2] process to yield the substituted cyclopentene **6** with the loss of carbon dioxide.

Conclusion

We have developed an NHC-mediated homoenolate annulation of enals to arylidene chroman-4-ones, arylidene 1-thiochroman-4-ones, and tetralones leading to an efficient synthesis of substituted tetrahydrocyclopentachromenes, tetrahydrocyclopentathiochromenes, and tetrahydrocyclopentanaphthalenes, respectively.

Experimental Section

Melting points were recorded with a MEL-TEMP® melting point apparatus and are uncorrected. NMR spectra were recorded at 500 (^{1}H) and 126 (^{13}C) MHz on a Bruker DPX-500 MHz NMR spectrometer. Chemical shifts (δ) are reported relative to TMS (^{1}H) and $CDCl_3$ (^{13}C) as the internal standards. Coupling constants (J) are reported in Hertz (Hz). Mass spectra were recorded with a Thermo Scientific Orbitrap spectrophotometer.

Preparation of arylidene chroman-4-ones, thiochroman-4-ones, and tetralone

Chroman-4-one/thichroman-4-one/tetralone (4.00 mmol) and the corresponding aryl aldehydes (4.40 mmol) were added to a round-bottom flask and ethanol (7 mL) was added; this reaction mixture was kept in an ice bath. An aqueous solution of sodium hydroxide (10%, 10 mL) was added dropwise into this reaction mixture with vigorous stirring. The precipitate formed was filtered, and washed with cold water and hexane. It was dried and used for the further reactions.

General procedure for the synthesis of tricyclic pentenes

The substituted arylidene tetralone/chroman/thiochroman-4-one (0.5 mmol) was treated with α,β-unsaturated aldehyde (0.75 mmol) in presence of IMes·HCl (15 mol%) and DBU (20 mol%) in anhydrous CH_2Cl_2 (4 mL) under an inert atmosphere of argon and the mixture was heated at reflux for about 7 h. The reaction mixture was purified by column chromatography by using 100–200 mesh silica gel with ethyl acetate/hexane (1:99) as eluent to afford the corresponding tricyclic cyclopentenes.

2-(4-Methoxyphenyl)-3-(*p*-tolyl)-2,3,3 a,4-tetrahydrocyclopenta[*c*]chromene (6 a)

Chemical formula: $C_{26}H_{24}O_2$, white solid, m.p.: 110–112 °C, yield: 95%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.5 Hz, 1 H), 7.15 (t, J = 7.5 Hz, 1 H), 7.07 (d, J = 8.0 Hz, 2 H), 7.04 (d, J = 8.0 Hz, 2 H), 6.95 (d, J = 8.5 Hz, 2 H), 6.91 (d, J = 7.5 Hz, 1 H), 6.89–6.86 (m, 1 H), 6.75 (d, J = 8.5 Hz, 2 H), 6.05 (s, 1 H), 4.41 (dd, J = 10.0, 5.0 Hz, 1 H), 4.07 (d, J = 9.0 Hz, 1 H), 3.84–3.78 (m, 1 H), 3.76 (s, 3 H), 3.41–3.34 (m, 1 H), 2.80 (t, J = 9.5 Hz, 1 H), 2.33 ppm (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.22, 153.29, 136.98, 135.11, 135.03, 134.92, 128.11, 127.37, 126.67, 124.13, 121.86, 119.75, 116.32, 112.65, 70.19, 59.19, 57.64, 53.95, 47.74, 20.00 ppm. HRMS (ESI) m/z calcd. for $C_{26}H_{24}O_2$ $[M-H]^+$: 367.1776; found: 367.1779.

2-(4-Bromophenyl)-3-(*p*-tolyl)-2,3,3 a,4-tetrahydrocyclopenta[*c*]chromene (6 b)

Chemical formula: $C_{25}H_{21}BrO$, white solid, m.p.: 95–97 °C, yield: 85%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57 (d, J = 7.5 Hz, 1 H), 7.36 (d, J = 8.0 Hz, 2 H), 7.20 (t, J = 7.5 Hz, 1 H), 7.10 (d, J = 7.0 Hz, 2 H), 7.04 (d, J = 7.5 Hz, 2 H), 6.96–6.90 (m, 4 H), 6.05 (s, 1 H), 4.42 (dd, J = 9.9, 5.1 Hz, 1 H), 4.11 (d, J = 9.1 Hz, 1 H), 3.82 (t, J = 11.0 Hz, 1 H), 3.40 (s, 1 H), 2.80 (t, J = 9.5 Hz, 1 H), 2.33 ppm (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 154.38, 142.99, 137.49, 136.93, 136.58, 131.45, 129.58, 129.31, 127.74, 125.28, 122.03, 120.99, 120.37, 119.01, 117.43, 71.27, 60.19, 58.87, 48.91, 21.06 ppm. HRMS (ESI) m/z calcd. for $C_{25}H_{21}BrO$ $[M+H]^+$: 417.0776; found: 417.0771.

2-(Furan-2-yl)-3-(*p*-tolyl)-2,3,3 a,4-tetrahydrocyclopenta[*c*]-chromene (6 c)

Chemical formula: $C_{23}H_{20}O_2$, colorless viscous liquid, yield: 75%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.54 (dd, J = 7.5, 1.5 Hz, 1 H), 7.31 (dd, J = 2.0, 1.0 Hz, 1 H), 7.19–7.12 (m, 5 H), 6.94–6.88 (m, 2 H), 6.27 (dd, J = 3.0, 1.5 Hz, 1 H), 6.08 (t, J = 2.0 Hz, 1 H), 6.00 (d, J = 3.0 Hz, 1 H), 4.46 (dd, J = 10.0, 5.0 Hz, 1 H), 4.25 (dt, J = 9.5, 2.0 Hz, 1 H), 3.85 (dd, J = 12.0, 10.0 Hz, 1 H), 3.37 (ttd, J = 10.5, 5.2, 2.7 Hz, 1 H), 3.17 (t, J = 9.7 Hz, 1 H), 2.33 ppm (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.43, 154.37, 141.51, 137.99, 136.52, 136.30, 129.51, 129.33, 127.58, 125.34, 120.95, 120.43, 119.03, 117.33, 110.18, 105.31, 71.16, 55.64, 52.45, 48.56, 21.06 ppm. HRMS (ESI) m/z calcd. for $C_{23}H_{20}O_2$ $[M+H]^+$: 329.1463; found: 329.1469.

2-(3-Phenyl-2,3,3 a,4-tetrahydrocyclopenta[*c*]thiochromen-2-yl)furan (6 d)

Chemical formula: $C_{22}H_{18}OS$, colorless viscous liquid, yield: 87%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69 (dd, J = 7.5, 1.5 Hz, 1 H), 7.35–7.23 (m, 5 H), 7.19–7.16 (m, 1 H), 7.14–7.05 (m, 3 H), 6.29 (t, J = 2.0 Hz, 1 H), 6.27 (dd, J = 3.0, 1.5 Hz, 1 H), 5.99 (d, J = 3.0 Hz, 1 H), 4.24 (dt, J = 9.0, 2.5 Hz, 1 H), 3.42–3.36 (m, 1 H), 3.20 (t, J = 9.4 Hz, 1 H), 3.01 (t, J = 12.1 Hz, 1 H), 2.90 ppm (dd, J = 6.8, 5.3 Hz, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.39, 141.53, 141.39, 138.79, 133.02, 128.67, 127.91, 127.21, 126.99, 126.23, 124.64, 123.73, 110.18, 105.15, 59.76, 51.65, 51.62, 31.56 ppm. HRMS (ESI) m/z calcd. for $C_{22}H_{18}OS$ $[M+H]^+$: 331.1078; found: 331.1083.

2-(4-Fluorophenyl)-3-phenyl-2,3,3 a,4-tetrahydrocyclopenta[*c*]thiochromene (6 e)

Chemical formula: $C_{24}H_{19}FS$, colorless viscous liquid, yield: 86%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (dd, J = 7.5, 1.5 Hz, 1 H), 7.33–7.30 (m, 2 H), 7.27–7.24 (m, 1 H), 7.21–7.18 (m, 3 H), 7.15–7.07 (m, 2 H), 7.02–6.99 (m, 2 H), 6.95–6.90 (m, 2 H), 6.28 (t, J = 2.0 Hz, 1 H), 4.13–4.11 (m, 1 H), 3.45–3.39 (m, 1 H), 2.97 (t, J = 12.0 Hz, 1 H), 2.89–2.83 ppm (m, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.69, 160.75, 141.02, 139.62, 139.04, 133.05, 129.06, 128.89, 128.82, 128.64, 128.11, 127.98, 127.31, 127.21, 126.99, 126.16, 125.80, 124.69, 115.30, 115.13, 64.55, 57.76, 51.85, 31.65 ppm. HRMS (ESI) m/z calcd. for $C_{24}H_{19}FS$ $[M+H]^+$: 359.1192; found: 359.1196.

3-Phenyl-2-(*p*-tolyl)-2,3,3 a,4-tetrahydrocyclopenta[*c*]thiochromene (6 f)

Chemical formula: $C_{25}H_{22}S$, colorless viscous liquid, yield: 91%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71 (dd, J = 7.5, 1.5 Hz, 1H), 7.32–7.28 (m, 2H), 7.25–7.18 (m, 4H), 7.13–7.04 (m, 4H), 6.95 (d, J = 8.0 Hz, 2H), 6.29 (t, J = 2.0 Hz, 1H), 4.13–4.10 (m, 1H), 3.44–3.38 (m, 1H), 2.97 (t, J = 12 Hz, 1H), 2.91–2.85 (m, 2H), 2.30 ppm (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 140.48, 139.92, 137.55, 135.08, 131.91, 128.23, 128.09, 127.52, 127.11, 126.79, 126.33, 126.22, 125.78, 125.47, 125.11, 123.61, 63.20, 57.03, 50.95, 30.69, 20.01 ppm. HRMS (ESI) *m/z* calcd. for $C_{25}H_{22}S$ $[M+H]^+$: 355.1442; found: 355.1443.

2-(4-Methoxyphenyl)-3-phenyl-3,3 a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene (6 g)

Chemical formula: $C_{26}H_{24}O$, colorless viscous liquid, yield: 73%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69–7.67 (m, 1H), 7.30–7.27 (m, 2H), 7.23–7.14 (m, 6H), 7.02–6.99 (m, 2H), 6.79–6.76 (m, 2H), 6.15 (t, J = 2.0 Hz, 1H), 4.15 (d, J = 9.5 Hz, 1H), 3.76 (s, 3H), 3.10–3.06 (m, 1H), 2.91–2.86 (m, 3H), 2.08–2.04 (m, 1H), 1.60–1.58 ppm (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.13, 141.40, 140.53, 139.99, 136.16, 135.74, 130.42, 128.21, 127.46, 127.29, 127.17, 126.50, 125.36, 125.08, 123.62, 122.81, 122.76, 112.65, 63.34, 57.23, 54.19, 51.30, 29.43, 28.02 ppm. HRMS (ESI) *m/z* calcd. for $C_{26}H_{24}O$ $[M-H]^+$: 351.1827; found: 351.1828.

2,3-Diphenyl-3,3 a,4,5-tetrahydro-2*H*-cyclopenta[*a*]naphthalene (6 h)

Chemical formula: $C_{25}H_{22}$, colorless viscous liquid, yield: 71%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.70–7.68 (m, 1H), 7.31–7.28 (m, 2H), 7.25–7.21 (m, 5H), 7.20–7.15 (m, 4H), 7.11–7.09 (m, 2H), 6.17 (t, J = 2.0 Hz, 1H), 4.22–4.20 (m, 1H), 3.13–3.07 (m, 1H), 2.93 (t, J = 9.5 Hz, 1H), 2.90–2.87 (m, 2H), 2.09–2.04 (m, 1H), 1.64–1.58 ppm (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.64, 142.34, 141.83, 137.20, 131.40, 129.24, 128.33, 128.28, 128.20, 127.58, 126.44, 126.34, 126.12, 124.67, 123.46, 64.22, 59.02, 52.48, 30.46, 29.04 ppm. HRMS (ESI) *m/z* calcd. for $C_{25}H_{22}$ $[M-H]^+$: 321.1722; found: 321.1717.

3-(Furan-2-yl)-2-(2-methoxyphenyl)-2,3,3 a,4-tetrahydrocyclopenta[*c*]chromene (6 i)

Chemical formula: $C_{23}H_{20}O_3$, colorless viscous liquid, yield: 89%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.44 (dd, J = 8.0, 1.5 Hz, 1H), 7.25 (d, J = 1.0 Hz, 1H), 7.16–7.07 (m, 3H), 6.86–6.82 (m, 3H), 6.76 (d, J = 8.5 Hz, 1H), 6.17 (dd, J = 3.0, 1.5 Hz, 1H), 6.01 (d, J = 3.0 Hz, 1H), 5.94 (t, J = 2.0 Hz, 1H), 4.70–4.68 (m, 1H), 4.57 (dd, J = 10.0, 5.0 Hz, 1H), 3.81 (dd, J = 11.5, 10.0 Hz, 1H), 3.61 (s, 3H), 3.33–3.27 (m, 1H), 3.06 ppm (t, J = 9.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.29, 154.47, 153.16, 140.29, 134.31, 130.74, 128.14, 127.18, 126.70, 124.15, 122.84, 119.86, 119.76, 118.30, 116.28, 109.65, 108.97, 104.18, 70.39, 54.40, 50.09, 47.45, 45.92 ppm. HRMS (ESI) *m/z* calcd. for $C_{23}H_{20}O_3$ $[M-H]^+$: 343.1412; found: 343.1419

3-(4-Fluorophenyl)-2-(2-methoxyphenyl)-2,3,3 a,4-tetrahydrocyclopenta[*c*]chromene (6 j)

Chemical formula: $C_{25}H_{21}FO_2$, white solid, m.p.: 101–103 °C, yield: 97%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.57–7.56 (m, 1H), 7.23–7.17 (m, 5H), 6.97–6.90 (m, 5H), 6.76 (d, J = 15.0 Hz, 1H), 6.05 (s, 1H), 4.69 (d, J = 9.0 Hz, 1H), 4.43 (dd, J = 10.0, 5.0 Hz, 1H), 3.87–3.82 (m, 1H), 3.44 (s, 3H), 3.38–3.30 (m, 1H), 2.97–2.93 ppm (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.62, 160.68, 157.24, 154.19, 137.45, 136.90, 135.55, 132.07, 129.23, 129.19, 129.13, 128.04, 127.62, 125.26, 123.49, 120.97, 120.84, 119.40, 117.36, 115.01, 114.84, 110.71, 71.21, 58.67, 55.11, 51.66, 49.16 ppm. HRMS (ESI) *m/z* calcd. for $C_{22}H_{18}OS$ $[M+H]^+$: 373.1526; found: 373.1531.

3-(4-Chlorophenyl)-2-(2-methoxyphenyl)-2,3,3 a,4-tetrahydrocyclopenta[*c*]chromene (6 k)

Chemical formula: $C_{25}H_{21}ClO_2$, white solid, m.p.: 150–152 °C, yield: 92%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, J = 7.5 Hz, 1H), 7.23–7.18 (m, 3H), 7.16–7.12 (m, 4H), 6.91–6.85 (m, 3H), 6.71 (d, J = 8.0 Hz, 1H), 6.01 (s, 1H), 4.65 (d, J = 9.0 Hz, 1H), 4.40 (dd, J = 10.0, 5.0 Hz, 1H), 3.81 (t, J = 11.5 Hz, 1H), 3.43 (s, 3H), 3.36–3.32 (m, 1H), 2.89 ppm (t, J = 9.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.07, 154.20, 140.38, 135.72, 132.25, 131.88, 129.19, 129.03, 128.28, 127.95, 127.60, 125.17, 123.12, 120.90, 117.40, 110.48, 70.97, 58.87, 54.88, 51.61, 49.07 ppm. HRMS (ESI) *m/z* calcd. for $C_{25}H_{21}ClO_2$ $[M+H]^+$: 389.1230; found: 389.1234.

2-(2-Methoxyphenyl)-3-(thiophen-2-yl)-2,3,3 a,4-tetrahydrocyclopenta[*c*]chromene (6 l)

Chemical formula: $C_{23}H_{20}O_2S$, colorless viscous liquid, yield: 94%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48 (d, J = 8.0 Hz, 1H), 7.21–7.08 (m, 4H), 6.91–6.84 (m, 4H), 6.78 (d, J = 8.0 Hz, 1H), 6.73 (d, J = 3.0 Hz, 1H), 6.00 (s, 1H), 4.66 (d, J = 9.5 Hz, 1H), 4.59 (dd, J = 10.0, 5.0 Hz, 1H), 3.85 (t, J = 10.5 Hz, 1H), 3.60 (s, 3H), 3.40–3.31 ppm (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.52, 154.25, 145.29, 135.31, 131.43, 129.19, 128.34, 127.77, 126.54, 125.17, 124.09, 123.75, 123.20, 120.91, 120.85, 119.23, 117.41, 110.75, 71.09, 55.26, 53.43, 52.46, 49.71 ppm. HRMS (ESI) *m/z* calcd. for $C_{23}H_{20}O_2S$ $[M+H]^+$: 361.1184; found: 361.1189.

3-(4-Fluorophenyl)-2-(2-methoxyphenyl)-2,3,3 a,4-tetrahydrocyclopenta[*c*]thiochromene (6 m)

Chemical formula: $C_{25}H_{21}FOS$, colorless viscous liquid, yield: 91%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69 (dd, J = 8.0, 1.5 Hz, 1H), 7.22–7.15 (m, 5H), 7.12–7.04 (m, 2H), 6.98–6.90 (m, 3H), 6.75 (d, J = 8.0 Hz, 1H), 6.25 (t, J = 2.0 Hz, 1H), 4.61 (dt, J = 9.5, 2.0 Hz, 1H), 3.43 (s, 3H), 3.39–3.30 (m, 1H), 2.94 (dt, J = 13.3, 10.7 Hz, 2H), 2.85 ppm (dd, J = 12.1, 4.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.66, 160.72, 157.19, 138.16, 137.82, 137.79, 132.72, 132.22, 129.42, 129.35, 127.98, 127.72, 127.62, 127.25, 126.87, 126.11, 124.67, 120.84, 115.03, 114.86, 110.72, 62.45, 55.12, 52.14, 50.93, 31.57 ppm. HRMS (ESI) *m/z* calcd. for $C_{25}H_{21}FOS$ $[M-H]^+$: 387.1297; found: 387.1296.

2-(2-Methoxyphenyl)-3-(thiophen-2-yl)-2,3,3 a,4-tetrahydrocyclopenta[*c*]thiochromene (6 n)

Chemical formula: $C_{23}H_{20}OS_2$, white solid, –m.p.: 110–112 °C, yield: 93%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (dd, J = 8.0, 1.5 Hz, 1H), 7.23–7.17 (m, 3H), 7.13 (dd, J = 5.5, 1.0 Hz, 1H), 7.11–7.08 (td, J = 7.0, 1.5 Hz, 1H), 7.04 (td, J = 7.5, 1.5 Hz, 1H), 6.92 (td, J = 7.0, 1.0 Hz, 1H), 6.89 (dd, J = 5.0, 3.5 Hz, 1H), 6.82–6.80 (m, 2H), 6.24 (t, J = 2.0 Hz, 1H), 4.68–4.57 (m, 1H), 3.60 (s, 3H), 3.43–3.31 (m, 2H), 3.08–2.95 ppm (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.53, 145.46, 137.70, 132.72, 131.51, 129.35, 128.27, 127.79, 127.69, 127.28, 127.22, 126.60, 126.00, 124.69, 124.43, 123.33, 120.82, 110.88, 57.12, 55.39, 52.66, 51.76, 31.55 ppm. HRMS (ESI) *m/z* calcd. for $C_{23}H_{20}OS_2$ $[M-H]^+$: 375.0956; found: 375.0951.

2-(2-Methoxyphenyl)-3-(*p*-tolyl)-2,3,3 a,4-tetrahydrocyclopenta[*c*]thiochromene (6 o)

Chemical formula: $C_{26}H_{24}OS$, white solid, m.p.: 143–145 °C, yield: 92 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, J = 7.8 Hz, 1 H), 7.18 (d, J = 7.5 Hz, 1 H), 7.16–7.09 (m, 4 H), 7.08–6.99 (m, 4 H), 6.87 (t, J = 7.4 Hz, 1 H), 6.71 (d, J = 8.2, 1 H), 6.22 (s, 1 H), 4.61 (d, J = 9.4 Hz, 1 H), 3.44 (s, 3 H), 3.34 (dd, J = 14.8, 5.6 Hz, 1 H), 2.98–2.91 (m, 2 H), 2.87 (dd, J = 12.1, 4.2 Hz, 1 H), 2.31 ppm (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.23, 139.04, 138.10, 135.72, 132.87, 132.43, 129.49, 128.86, 128.01, 127.86, 127.48, 127.38, 127.18, 126.96, 126.01, 124.43, 120.79, 110.70, 62.54, 55.08, 52.06, 50.74, 31.59, 21.08 ppm. HRMS (ESI) m/z calcd. for $C_{26}H_{24}OS$ $[M+H]^+$: 385.1548; found: 385.1545.

2-(2-(2-Methoxyphenyl)-3,3 a,4,5-tetrahydro-2 *H*-cyclopenta[*a*]naphthalen-3-yl)thiophene (6 p)

Chemical formula: $C_{24}H_{22}OS$, colorless viscous liquid, yield: 72 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64–7.62 (m, 1 H), 7.27 (dd, J = 7.5, 1.5 Hz, 1 H), 7.20–7.15 (m, 4 H), 7.12 (dd, J = 5.0, 1.0 Hz, 1 H), 6.93–6.88 (m, 2 H), 6.83–6.80 (m, 2 H), 6.10 (t, J = 2.0 Hz, 1 H), 4.70 (d, J = 9.5 Hz, 1 H), 3.62 (s, 3 H), 3.35 (t, J = 9.5 Hz, 1 H), 3.10–3.02 (m, 1 H), 2.98–2.87 (m, 2 H), 2.29–2.24 (m, 1 H), 1.67–1.58 ppm (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.58, 146.50, 140.78, 132.17, 129.16, 128.17, 127.46, 127.38, 126.43, 126.09, 124.53, 124.04, 122.82, 120.75, 110.80, 57.07, 55.42, 52.94, 51.83, 30.43, 28.90 ppm. HRMS (ESI) m/z calcd. for $C_{24}H_{22}OS$ $[M+H]^+$: 359.1391; found: 359.1392.

2-(2-Methoxyphenyl)-3-phenyl-3,3 a,4,5-tetrahydro-2 *H*-cyclopenta[*a*]naphthalene (6 q)

Chemical formula: $C_{26}H_{24}O$, colorless viscous liquid, yield: 73 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67–7.66 (m, 1 H), 7.30–7.24 (m, 5 H), 7.19–7.12 (m, 5 H), 6.91 (td, J = 7.5, 1.0 Hz, 1 H), 6.74 (dd, J = 8.5, 1.0 Hz, 1 H), 6.12 (t, J = 2.0 Hz, 1 H), 4.77–4.74 (m, 1 H), 3.41 (s, 3 H), 3.08–3.05 (m, 1 H), 2.98 (t, J = 9.5 Hz, 1 H), 2.89–2.84 (m, 2 H), 2.15–1.96 (m, 1 H), 1.65–1.56 ppm (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.34, 141.95, 140.08, 135.99, 132.11, 130.63, 128.15, 127.06, 126.94, 126.27, 126.14, 125.07, 125.02, 123.57, 123.21, 119.72, 109.76, 62.03, 54.21, 51.48, 49.86, 29.47, 27.89 ppm. HRMS (ESI) m/z calcd. for $C_{26}H_{24}O$ $[M-H]^+$: 351.1827; found: 351.1825.

2-(2-Methoxyphenyl)-3-(*p*-tolyl)-3,3 a,4,5-tetrahydro-2 *H*-cyclopenta[*a*]naphthalene (6 r)

Chemical formula: $C_{27}H_{26}O$, colorless viscous liquid, yield: 70 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60–7.58 (m, 1 H), 7.21 (dd, J = 7.5, 2.0 Hz, 1 H), 7.12–7.05 (m, 6 H), 7.01 (d, J = 8.0 Hz, 2 H), 6.84 (td, J = 7.5, 1.0 Hz, 1 H), 6.69 (d, J = 8.0 Hz, 1 H), 6.04 (s, 1 H), 4.68 (d, J = 9.0 Hz, 1 H), 3.40 (s, 3 H), 3.02–2.87 (m, 2 H), 2.83–2.74 (m, 2 H), 2.24 (s, 3 H), 2.06–1.97 (m, 1 H), 1.58–1.50 ppm (m, 1 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 156.37, 139.95, 138.79, 136.01, 134.48, 132.07, 130.67, 128.13, 127.65, 126.97, 126.93, 126.22, 126.09, 124.99, 123.53, 123.41, 119.71, 109.79, 61.31, 54.28, 51.51, 49.64, 29.48, 28.67, 27.86, 20.00 ppm. HRMS (ESI) m/z calcd. for $C_{27}H_{26}O$ $[M-H]^+$: 365.1984; found: 365.1979.

8-Fluoro-2-(2-methoxyphenyl)-3-(*p*-tolyl)-2,3,3 a,4-tetrahydrocyclopenta[*c*]chromene (6 s)

Chemical formula: $C_{26}H_{23}FO_2$, white solid, m.p.: 147–149 °C, yield: 86 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23–7.15 (m, 3 H), 7.09 (dd, J = 21.5, 8.0 Hz, 4 H), 6.91 (td, J = 7.0, 1.0 Hz, 1 H), 6.89–6.82 (m, 2 H), 6.76 (dd, J = 8.0 Hz, 0.5 Hz, 1 H), 6.05 (s, 1 H), 4.70 (dt, J = 10.0, 2.0 Hz, 1 H), 4.43 (dd, J = 10.0, 5.0 Hz, 1 H), 3.82–3.78 (m, 1 H), 3.47 (s, 3 H), 3.37–3.31 (m, 1 H), 3.01 (t, J = 10.0 Hz, 1 H), 2.31 ppm (s, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.11, 156.33, 155.21, 149.31, 137.37, 135.01, 133.88, 130.80, 127.89, 127.03, 126.61, 126.53, 124.32, 119.75, 117.37, 117.30, 115.01, 114.82, 109.84, 109.74, 109.56, 70.30, 57.30, 54.21, 50.49, 47.74, 19.98 ppm. HRMS (ESI) m/z calcd. for $C_{26}H_{23}FO_2$ $[M-H]^+$: 385.1682; found: 385.1678

3-(4-Methoxyphenyl)-2-methyl-2,3,3 a,4-tetrahydrocyclopenta[*c*]chromene (6 t)

Chemical formula: $C_{20}H_{20}O_2$, colorless viscous liquid, yield: 73 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48 (d, J = 8.0 Hz, 1 H), 7.21 (d, J = 8.5 Hz, 2 H), 7.12 (t, J = 7.5 Hz, 1 H), 6.90–6.83 (m, 4 H), 5.93 (s, 1 H), 4.37 (dd, J = 10.0, 5.0 Hz, 1 H), 3.81 (s, 3 H), 3.75–3.70 (m, 1 H), 3.27–3.20 (m, 1 H), 3.02–2.96 (m, 1 H), 2.42 (t, J = 9.6 Hz, 1 H), 1.12 ppm (d, J = 6.8 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ = 158.74, 154.50, 134.92, 134.11, 129.29, 129.08, 125.30, 125.22, 121.06, 119.68, 117.60, 114.26, 71.77, 58.35, 55.44, 49.84, 48.48, 30.01, 19.37 ppm. HRMS (ESI) m/z calcd. for $C_{20}H_{20}O_2$ $[M+H]^+$: 293.1463; found: 293.1462.

3-(4-Fluorophenyl)-2-methyl-2,3,3 a,4-tetrahydrocyclopenta[*c*]chromene (6 u)

Chemical formula: $C_{19}H_{17}FO$, colorless viscous liquid, yield: 71 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.47 (d, J = 8.0 Hz, 1 H), 7.25 (t, J = 6.0 Hz, 2 H), 7.12 (t, J = 7.5 Hz, 1 H), 7.01 (t, J = 9.0 Hz, 2 H), 6.88 (t, J = 7.5 Hz, 1 H), 6.83 (d, J = 8.5 Hz, 1 H), 5.91 (s, 1 H), 4.35 (dd, J = 10.5, 5.5 Hz, 1 H), 3.74–3.70 (m, 1 H), 3.27–3.21 (m, 1 H), 3.02–2.96 (m, 1 H), 2.45 (t, J = 9.5 Hz, 1 H), 1.12 ppm (d, J = 7.5 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 162.74, 154.18, 134.67, 129.24, 129.18, 129.12, 125.03, 124.62, 120.82, 117.35, 115.51, 115.34, 71.25, 58.06, 49.70, 48.32, 29.72, 19.08 ppm. HRMS (ESI) m/z calcd. for $C_{19}H_{17}FO$ $[M+H]^+$: 281.1263; found: 281.1259.

3-(Furan-2-yl)-2-methyl-2,3,3 a,4-tetrahydrocyclopenta[*c*]-chromene (6 v)

Chemical formula: $C_{17}H_{16}O_2$, colorless viscous liquid, yield: 68 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.45 (d, J = 7.5 Hz, 1 H), 7.35 (s, 1 H), 7.12 (t, J = 7.5 Hz, 1 H), 6.87 (dd, J = 14.0, 8.0 Hz, 2 H), 6.31 (d, J = 1.6 Hz, 1 H), 6.11 (d, J = 3.0 Hz, 1 H), 5.91 (s, 1 H), 4.57 (dd, J = 10.0, 5.5 Hz, 1 H), 3.79–3.74 (m, 1 H), 3.32–3.27 (m, 1 H), 3.17–3.09 (m, 1 H), 2.60 (t, J = 9.5 Hz, 1 H), 1.24 ppm (d, J = 7.0 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.87, 154.18, 141.41, 134.70, 129.12, 125.00, 120.82, 119.20, 117.33, 110.08, 104.86, 71.44, 50.65, 47.11, 45.16, 19.65 ppm. HRMS (ESI) m/z calcd. for $C_{17}H_{16}O_2$ $[M-H]^+$: 251.1150; found: 251.1146.

3-(4-Bromophenyl)-2-methyl-2,3,3 a,4-tetrahydrocyclopenta[*c*]chromene (6 w)

Chemical formula: $C_{19}H_{17}BrO$, colorless viscous liquid, yield: 71 %. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.46–7.44 (m, 3 H), 7.17 (d, J = 8.0 Hz, 2 H), 7.12 (t, J = 8.0 Hz, 1 H), 6.89–6.82 (m, 2 H), 5.90 (s, 1 H), 4.34 (dd, J = 10.0, 5.0 Hz, 1 H), 3.71 (t, J = 11.0 Hz, 1 H), 3.27–3.20 (m, 1 H), 3.03–2.97 (m, 1 H), 2.42 (t, J = 9.5 Hz, 1 H), 1.12 ppm (d, J = 6.8 Hz, 3 H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 154.17, 140.89, 134.68, 131.72, 131.37, 129.58, 129.17, 125.04, 124.53, 120.85, 120.60, 119.10, 117.37, 71.17, 58.22, 49.59, 48.27, 19.13 ppm. HRMS (ESI) m/z calcd. for $C_{19}H_{17}BrO$ $[M+H]^+$: 341.0463; found: 341.0468.

2-Methyl-3-(thiophen-2-yl)-2,3,3a,4-tetrahydrocyclopenta[*c*]-thiochromene (6x)

Chemical formula: $C_{17}H_{16}S_2$, colorless viscous liquid, yield: 70%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.64 (d, J = 7.5 Hz, 1H), 7.20 (d, J = 5.0 Hz, 1H), 7.16 (d, J = 7.8 Hz, 1H), 7.09–7.03 (m, 2H), 7.00–6.98 (m, 1H), 6.93 (d, J = 3.0 Hz, 1H), 6.17 (s, 1H), 3.31–3.26 (m, 1H), 3.00–2.97 (m, 2H), 2.89 (t, J = 12 Hz, 1H), 2.81 (t, J = 9.5, 1H), 1.19 ppm (d, J = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 145.49, 137.05, 132.73, 129.23, 128.42, 127.62, 127.31, 126.96, 125.78, 124.64, 124.52, 123.43, 57.07, 53.16, 47.91, 31.57, 19.13 ppm. HRMS (ESI) m/z calcd. for $C_{17}H_{16}S_2$ $[M+H]^+$: 285.0693; found: 285.0697.

2-(2-Methyl-2,3,3a,4-tetrahydrocyclopenta[*c*]thiochromen-3-yl)furan (6y)

Chemical formula: $C_{17}H_{16}OS$, colorless viscous liquid, yield: 71%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59 (d, J = 7.5 Hz, 1H), 7.34 (s, 1H), 7.13 (d, J = 7.5 Hz, 1H), 7.06–6.99 (m, 2H), 6.30 (s, 1H), 6.12 (s, 2H), 3.37–3.26 (m, 1H), 3.04 (dt, J = 7.9, 5.9 Hz, 2H), 2.91 (t, J = 12.2 Hz, 1H), 2.63 (t, J = 9.5 Hz, 1H), 1.22 ppm (d, J = 6.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 155.79, 141.47, 137.27, 132.83, 128.35, 127.53, 127.25, 125.78, 124.47, 110.08, 105.25, 54.60, 49.73, 44.17, 31.94, 19.68 ppm. HRMS (ESI) m/z calcd. for $C_{17}H_{16}OS$ $[M+H]^+$: 269.0922; found: 269.0926.

2-Methyl-3-phenyl-2,3,3a,4-tetrahydrocyclopenta[*c*]thiochromene (6z)

Chemical formula: $C_{19}H_{18}S$, colorless viscous liquid, yield: 67%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.63 (d, J = 7.5 Hz, 1H), 7.34–7.29 (m, 5H), 7.13 (d, J = 7.5 Hz, 1H), 7.08–7.01 (m, 2H), 6.14 (s, 1H), 3.32–3.27 (m, 1H), 3.05–2.95 (m, 1H), 2.90–2.81 (m, 2H), 2.49 (t, J = 9.5 Hz, 1H), 1.12 ppm (d, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 142.08, 137.14, 132.82, 129.41, 128.58, 128.45, 128.40, 128.14, 127.50, 127.25, 126.78, 125.87, 124.49, 62.81, 52.47, 47.24, 31.78, 19.35 ppm. HRMS (ESI) m/z calcd. for $C_{19}H_{18}S$ $[M+H]^+$: 279.1129; found: 279.1133.

2-(4-Methoxyphenyl)-3-styryl-2,3,3a,4-tetrahydrocyclopenta[*c*]chromene (8a)

Chemical formula: $C_{27}H_{24}O_2$, colorless viscous liquid, yield: 67%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, J = 8.0 Hz, 1H), 7.32–7.27 (m, 4H), 7.23–7.15 (m, 2H), 7.13 (d, J = 8.5 Hz, 2H), 6.91 (t, J = 8.0 Hz, 2H), 6.82 (d, J = 8.5 Hz, 2H), 6.37 (dd, J = 15.5, 8.0 Hz, 1H), 6.21 (d, J = 16.0 Hz, 1H), 6.06 (s, 1H), 4.53 (dd, J = 10.0, 5.0 Hz, 1H), 3.89 (d, J = 4.0 Hz, 1H), 3.81–3.77 (m, 4H), 3.18–3.13 (m, 1H), 2.50 ppm (q, J = 9.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 158.40, 154.37, 137.06, 136.61, 135.67, 131.56, 130.02, 129.35, 128.69, 128.52, 127.31, 126.19, 125.21, 123.38, 120.92, 119.17, 117.44, 113.87, 71.07, 58.52, 56.85, 55.13, 47.25 ppm. HRMS (ESI) m/z calcd. for $C_{27}H_{24}O_2$ $[M+H]^+$: 381.1776; found: 381.1771.

2-(2-Methoxyphenyl)-3-styryl-2,3,3a,4-tetrahydrocyclopenta[*c*]chromene (8b)

Chemical formula: $C_{27}H_{24}O_2$, colorless viscous liquid, yield: 75%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (d, J = 7.7 Hz, 1H), 7.30 (d, J = 7.5 Hz, 2H), 7.27–7.21 (m, 3H), 7.18–7.12 (m, 3H), 6.93–6.87 (m, 3H), 6.81 (d, J = 9.0 Hz, 1H), 6.43 (dd, J = 16.0, 8.5 Hz, 1H), 6.21 (d, J = 16.0 Hz, 1H), 6.02 (s, 1H), 4.55–4.49 (m, 2H), 3.79 (t, J = 11 Hz, 1H), 3.70 (s, 3H), 3.16–3.12 (m, 1H), 2.58 ppm (q, J = 9.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 157.26, 154.26, 137.41, 136.08, 131.99, 131.12, 130.14, 129.11, 128.46, 128.15, 127.56, 127.05, 126.09, 125.18, 123.83, 120.86, 119.43, 117.40, 110.59, 71.04, 57.72, 55.45, 49.69, 47.22 ppm. HRMS (ESI) m/z calcd. for $C_{27}H_{24}O_2$ $[M+H]^+$: 381.1776; found: 381.1772.

2-(4-Methoxyphenyl)-3-(4-methoxystyryl)-2,3,3a,4-tetrahydrocyclopenta[*c*]chromene (8c)

Chemical formula: $C_{28}H_{26}O_3$, colorless viscous liquid, yield: 66%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.51 (d, J = 7.5 Hz, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.18–7.11 (m, 3H), 6.90 (t, J = 7.5 Hz, 2H), 6.82 (d, J = 7.0 Hz, 4H), 6.22 (dd, J = 15.5, 8.0 Hz, 1H), 6.14 (d, J = 16.0 Hz, 1H), 6.05 (s, 1H), 4.53 (dd, J = 10.0, 5.0 Hz, 1H), 3.87 (d, J = 9.0 Hz, 1H), 3.79–3.76 (m, 7H), 3.13 (s, 1H), 2.47 ppm (q, J = 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.02, 158.35, 154.37, 136.62, 135.77, 130.92, 129.88, 129.30, 128.69, 127.78, 127.29, 125.18, 123.39, 120.88, 119.20, 117.43, 113.93, 113.82, 71.11, 58.58, 56.90, 55.17, 55.11, 47.29 ppm. HRMS (ESI) m/z for $C_{28}H_{26}O_3$ $[M+H]^+$: 411.1882; found: 411.1885.

2-(2-Methoxyphenyl)-3-(4-methoxystyryl)-2,3,3a,4-tetrahydrocyclopenta[*c*]chromene (8d)

Chemical formula: $C_{28}H_{26}O_3$, colorless viscous liquid, yield: 71%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (dd, J = 8.0, 1.5 Hz, 1H), 7.24–7.20 (m, 3H), 7.18–7.12 (m, 2H), 6.93–6.87 (m, 3H), 6.82–6.78 (m, 3H), 6.28 (dd, J = 15.5, 8.5 Hz, 1H), 6.15 (d, J = 16.0 Hz, 1H), 6.02 (s, 1H), 4.54 (dd, J = 10.0, 5.0 Hz, 1H), 4.47 (d, J = 9.5 Hz, 1H), 3.80–3.78 (m, 4H), 3.71 (s, 3H), 3.16–3.10 (m, 1H), 2.56 ppm (q, J = 9.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 158.81, 157.26, 154.26, 136.08, 132.08, 130.22, 129.51, 129.04, 128.86, 128.13, 127.47, 127.14, 125.13, 123.81, 120.84, 120.80, 119.43, 117.38, 113.84, 110.58, 71.05, 57.74, 55.45, 55.09, 49.72, 47.24 ppm. HRMS (ESI) m/z calcd. for $C_{28}H_{26}O_3$ $[M+H]^+$: 411.1882; found: 411.1887.

3-(4-Methoxystyryl)-2-phenyl-2,3,3a,4-tetrahydrocyclopenta[*c*]chromene (8e)

Chemical formula: $C_{27}H_{24}O_2$, colorless viscous liquid, yield: 69%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.52–7.50 (m, 1H), 7.30–7.28 (m, 1H), 7.25–7.19 (m, 6H), 7.18–7.14 (m, 1H), 6.92–6.89 (m, 2H), 6.81 (d, J = 8.5 Hz, 2H), 6.23 (dd, J = 16.0, 8.5 Hz, 1H), 6.14 (d, J = 15.5 Hz, 1H), 6.07 (t, J = 1.5 Hz, 1H), 4.53 (dd, J = 10.0, 5.0 Hz, 1H), 3.93–3.90 (m, 1H), 3.83–3.76 (m, 4H), 3.24–3.05 (m, 1H), 2.52 ppm (dd, J = 17.6, 9.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.04, 154.38, 143.66, 136.92, 131.00, 129.83, 129.35, 128.42, 127.79, 127.63, 127.29, 126.57, 125.19, 123.03, 120.89, 119.14, 117.43, 113.92, 71.08, 58.40, 57.67, 55.15, 47.37 ppm. HRMS (ESI) m/z calcd. for $C_{27}H_{24}O_2$ $[M+H]^+$: 381.1776; found: 381.1759.

2-(4-Methoxyphenyl)-3-(4-methoxystyryl)-2,3,3a,4-tetrahydrocyclopenta[*c*]thiochromene (8f)

Chemical formula: $C_{28}H_{26}O_2S$, colorless viscous liquid, yield: 72%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, J = 7.5 Hz, 1H), 7.25 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.0 Hz, 1H), 7.09 (dd, J = 13.5, 7.5 Hz, 3H), 7.05–7.02 (dd, J = 10.9, 3.9 Hz, 1H), 6.81 (d, J = 7.5 Hz, 4H), 6.25 (s, 1H), 6.23–6.14 (m, 2H), 3.81 (s, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.12 (t, J = 8.5 Hz, 1H), 2.98 (dd, J = 12.0, 4.0 Hz, 1H), 2.89 (t, J = 12.0 Hz, 1H), 2.47 ppm (dd, J = 17.0, 8.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 159.03, 158.33, 139.09, 135.87, 133.07, 131.41, 129.89, 129.26, 128.63, 127.94, 127.73, 127.34, 127.31, 126.80, 126.01, 124.59, 113.93, 113.85, 62.54, 55.96, 55.20, 55.14, 49.96, 31.37 ppm. HRMS (ESI) m/z calcd. for $C_{28}H_{26}O_2S$ $[M+H]^+$: 427.1654; found: 427.1649.

2-(4-Chlorophenyl)-3-(4-methoxystyryl)-2,3,3a,4-tetrahydrocyclopenta[*c*]thiochromene (8g)

Chemical formula: $C_{27}H_{23}ClOS$, colorless viscous liquid, yield: 71%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 4H), 7.19 (d, J = 8.0 Hz, 1H), 7.11 (dd, J = 16.5, 8.0 Hz, 3H), 7.04 (t, J = 7.5 Hz, 1H), 6.82 (d, J = 8.5 Hz, 2H), 6.23 (s, 1H), 6.21–6.13 (m, 2H), 3.83 (d, J = 9.0 Hz, 1H), 3.80 (s, 3H), 3.15–3.12 (m, 1H), 2.99 (dd, J = 12.5, 4.0 Hz, 1H), 2.89 (t, J = 12.0 Hz, 1H), 2.45 ppm (dd, J = 16.5, 9.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ = 158.06, 141.13, 138.84, 132.10, 131.27, 130.78, 128.53, 127.93, 127.91, 127.51, 126.86, 126.29, 126.27, 126.21, 124.95, 124.59, 123.55, 112.88, 61.52, 55.01, 54.12, 48.97, 30.21 ppm. HRMS (ESI) *m/z* calcd. for $C_{27}H_{23}ClOS$ $[M+H]^+$: 431.1158; found: 431.1154.

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