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Palladium-Catalyzed Tandem Carbene Migratory Insertion and Intramolecular Cyclization: Synthesis of Chromeno[4,3-*b*]chromene Compounds

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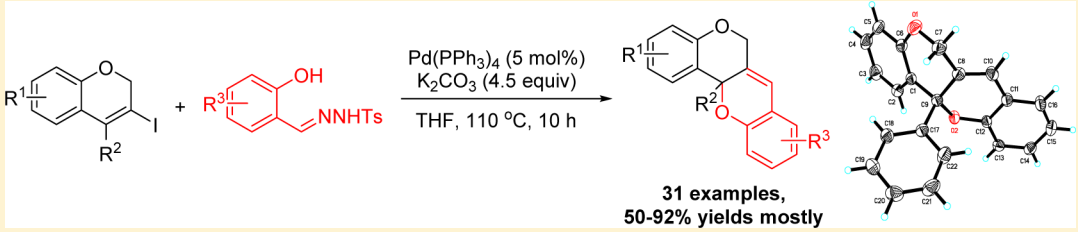
Supporting Information



ABSTRACT: Chromeno[4,3-*b*]chromene is a ubiquitous structural motif found in various pharmaceuticals and biologically active compounds. A concise palladium-catalyzed reaction of vinyl iodides and salicyl *N*-tosylhydrazones has been achieved to afford a series of compounds containing the chromeno[4,3-*b*]chromene scaffold in moderate to high yield. This tandem reaction involves palladium(II) carbene migratory insertion and intramolecular cyclization assisted by an O nucleophile and tolerates various functional groups.

The pyranobenzopyran skeleton is an important structural motif in many pharmaceuticals, biologically active compounds, and natural products.[1] For instance, the related isoflavonoid pterocarpan analogue 6a,12a-dihydro-6*H*,7*H*-[1]-benzopyran-[4,3-*b*]-benzopyran (homopterocarpane) and its derivatives show antitumor, antiestrogen, and perhaps anti-HIV activity.[2] Blepharocalyxin D **I**, isolated from the seeds of *Alpinia blepharocalyx*, acts as an antiproliferative agent against murine colon 26-L5 carcinoma cells;[3] dependensin **II**, present as a racemate in crude extracts from *Uvaria dependens*, shows potent antimalarial activity;[4] and (+)-peltogynol **III**, isolated from the purpleheart tree *Peltogyne porphyrocardia*, is a type of leuko-anthocyanin (Figure 1).[5]

The significant biological and pharmaceutical activities of fused pyranobenzopyrans have led researchers to construct related novel and useful skeletons. They have used several synthetic methods, including intramolecular [4 + 2] cyclo-addition promoted by ionic liquids,[6] *p*-toluenesulfonic acid,[7] or iodine;[8] radical cyclization;[9] Lewis acid-catalyzed Prins cyclization;[10] and hetero Diels−Alder reaction.[11] Despite all of this progress, the only description of the construction of a chromeno[4,3-*b*]chromene skeleton was reported by Schneider and his co-worker.[12] In their work, the conjugate addition of 2-(hydroxymethyl)phenol derivatives to heterocyclic enamides was achieved in the presence of chiral BINOL-based phosphoric acid catalyst, although only a few examples of products with the chromeno[4,3-*b*]chromene skeleton were presented. Therefore, a more concise synthetic approach to the chromeno[4,3-*b*]chromene skeleton remains desirable for facilitating the synthesis of an even broader range of bioactive compounds.

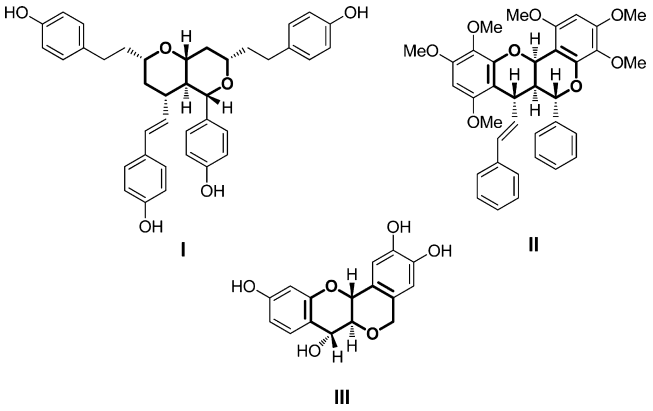


Figure 1. Natural products containing the pyrano[4,3-*b*]pyran or pyrano[3,2-*b*]pyran moiety.

Palladium-catalyzed cross-coupling of diazo compounds with aryl or vinyl halides has recently attracted significant attention because of its versatility in constructing polycyclic aromatic hydrocarbons and their heterocyclic analogues. Wang,[13] Liang,[14] and Valdés[15] et al. have reported many such carbene migratory insertion reactions involving alkyl, vinyl, aryl, alkynyl, and acyl group migration. Most of these reactions use the

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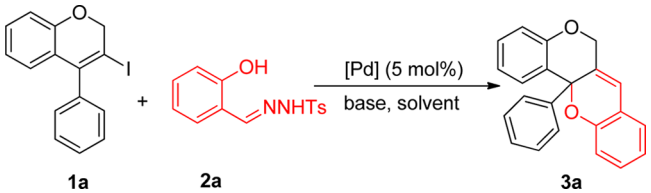
versatile synthon *N*-tosylhydrazone as the diazo precursor. When these reactions involve vinyl group migration, η^3-allylpalladium intermediates are generated that can be trapped with various nucleophiles, either inter- or intramolecularly,[16] which have been used to yield various heterocyclic compounds.[17]

Continued with our ongoing studies in heterocycle construction,[18] here we report a new protocol to generate the chromeno[4,3-*b*]chromene skeleton by using the reaction of vinyl iodides and salicyl *N*-tosylhydrazones, which involves tandem carbene migratory insertion and intramolecular cyclization. The reaction occurs efficiently in the presence of $Pd(PPh_3)_4$ catalyst without external ligands, yielding a series of compounds in moderate to high yield with good tolerance for various functional groups.

We began to investigate the tandem reaction using palladium catalysts and the model substrates 3-iodo-4-phenyl-2*H*-chromene **1a** and *N*′-(2-hydroxybenzylidene)-4-methylbenzenesulfonohydrazide **2a** (Table 1). Screening several bases in the catalytic reaction of **1a** and **2a** in THF showed that K_2CO_3 led to product **3a** in 36% yield at 80 °C in the presence of 5 mol % $PdCl_2(PPh_3)_2$ (entry 1). Under the same conditions, other bases such as KOH and Cs_2CO_3 afforded product **3a** in substantially lower yields (entries 2−3). Only trace amounts of **3a** were obtained when Na_2CO_3 was used (entry 4). The structure of **3a** was confirmed by single-crystal X-ray diffraction analysis (Figure 2). Screening various solvents showed that

Table 1. Optimization of Reaction Conditions for Palladium-Catalyzed Tandem Reaction of Vinyl Iodide (1a) and Salicyl *N*-tosylhydrazone (2a)[a]



entry	[Pd]	base	solvent	temp (°C)	yield (**3a**, %)[b]
1	$PdCl_2(PPh_3)_2$	K_2CO_3	THF	80	36
2	$PdCl_2(PPh_3)_2$	KOH	THF	80	6
3	$PdCl_2(PPh_3)_2$	Cs_2CO_3	THF	80	8
4	$PdCl_2(PPh_3)_2$	Na_2CO_3	THF	80	trace
5	$PdCl_2(PPh_3)_2$	K_2CO_3	toluene	80	trace
6	$PdCl_2(PPh_3)_2$	K_2CO_3	MeCN	80	10
7	$PdCl_2(PPh_3)_2$	K_2CO_3	1,2-DCE	80	ND
8	$PdCl_2(PPh_3)_2$	K_2CO_3	dioxane	80	12
9	$PdCl_2(PPh_3)_2$	K_2CO_3	DMF	80	ND
10	$PdCl_2(PPh_3)_2$	K_2CO_3	THF	60	trace
11	$PdCl_2(PPh_3)_2$	K_2CO_3	THF	110	38
12	$PdCl_2(PPh_3)_2$	none	THF	110	ND
13	none	K_2CO_3	THF	110	ND
14[c]	$PdCl_2(PPh_3)_2$	K_2CO_3	THF	110	40
15[c]	$Pd(MeCN)_2Cl_2$	K_2CO_3	THF	110	ND
16[c]	$Pd(PhCN)_2Cl_2$	K_2CO_3	THF	110	ND
17[c,d]	$Pd_2(\eta^3\text{-}C_3H_5)_2Cl_2$	K_2CO_3	THF	110	ND
18[c,d,e]	$Pd_2(dba)_3$	K_2CO_3	THF	110	46
19[c]	$Pd(dppf)Cl_2$	K_2CO_3	THF	110	62
20[c]	**$Pd(PPh_3)_4$**	**K_2CO_3**	**THF**	**110**	**80**
21[f]	$Pd(PPh_3)_4$	K_2CO_3	THF	110	75
22[c,g]	$Pd(PPh_3)_4$	K_2CO_3	THF	110	39

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), [Pd] (0.01 mmol, 5 mol %), base (0.70 mmol, 3.5 equiv), solvent (1.5 mL), 10 h, under N_2, unless otherwise noted. [b]Determined by ^1H NMR using $PhSiMe_3$ as the internal standard. [c]**2a** (0.40 mmol) and K_2CO_3 (0.90 mmol, 4.5 equiv) were used. [d][Pd] (0.005 mmol, 2.5 mol %). [e]PPh_3 (0.03 mmol, 15 mol %) was added. [f]K_2CO_3 (0.90 mmol, 4.5 equiv) was used. [g]$Pd(PPh_3)_4$ (0.004 mmol, 2 mol %). ND = not detected.

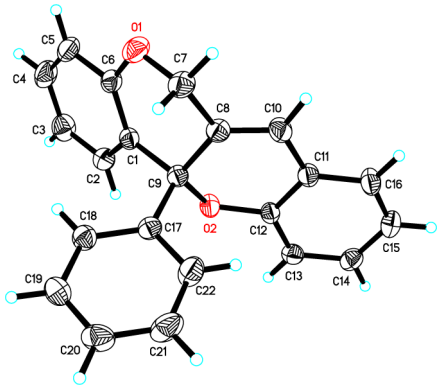


Figure 2. ORTEP diagram of **3a** with ellipsoids shown at the 30% probability level.

THF gave the best results (entries 5−9). Lowering the reaction temperature to 60 °C gave only trace amounts of **3a** (entry 10). Increasing the reaction temperature from 80 to 110 °C slightly increased the yield of product **3a** (entry 11). Performing the reaction in the absence of either palladium catalyst or base led to no detectable product (entries 12−13). Changing the ratio of **1a**:**2a** from 1:1.5 to 1:2 and increasing the number of K_2CO_3 equivalents from 3.5 to 4.5 gave **3a** in only 40% yield (entry 14). The observed low activity of $PdCl_2(PPh_3)_2$ led us to screen several palladium catalysts, and $Pd(PPh_3)_4$ gave the best results, affording **3a** in 80% yield (entry 20). $Pd(MeCN)_2Cl_2$, $Pd(PhCN)_2Cl_2$, and $Pd_2(\eta^3\text{-}C_3H_5)_2Cl_2$ were ineffective (entries 15−17), while $Pd_2(dba)_3$ and $Pd(dppf)Cl_2$ gave product **3a** in respective yields of 46% and 62% (entries 18−19). The amount of **2a** was also decreased to 1.5 equiv, and a slightly reduced yield of **3a** was obtained (entry 21). Reducing the amount of catalyst decreased the yield of **3a** (entry 22).

These screening experiments led to the optimized tandem reaction conditions of **1**:**2**=1:2, 5 mol % $Pd(PPh_3)_4$, 1.5 mL THF, 110 °C, and 10 h. Using these conditions, we explored the reaction scope and limitations (Table 2). First, we tested a variety of salicyl *N*-tosylhydrazones **2** for their ability to react with 3-iodo-4-phenyl-2*H*-chromene **1a** and thereby generate different chromeno[4,3-*b*]chromene derivatives. Salicyl *N*-tosylhydrazones with an electron-donating OMe or Me group at the *para* position of the hydroxyl group reacted well with **1a** to give the corresponding products **3b** and **3c** in respective isolated yields of 85% and 79%, higher than the 75% isolated yield of **3a**. The results illustrate that the electron-donating substitution is beneficial for the reaction. Salicyl *N*-tosylhydrazone substituted with F gave substantially lower yield of **3d,** even in the presence of 7.5 mol % $Pd(PPh_3)_4$. Reactions of salicyl *N*-tosylhydrazones substituted with Cl, Br, or NO_2 groups gave complex product mixtures and low yields, which demonstrated the negative effect of the electron-withdrawing substituents. Salicyl *N*-tosylhydrazones containing electron-donating OMe or NEt_2 at the *para* position of the imine group gave the products **3e** and **3f** in respective yields of 80% and

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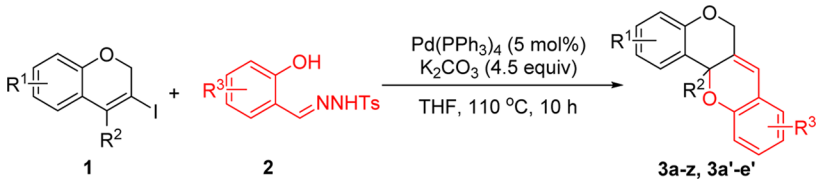
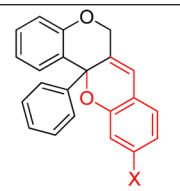
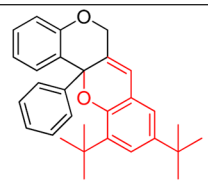
Table 2. Reaction of Vinyl Iodides (1a–x) with Various Salicyl *N*-tosylhydrazones (2a–h) in the Presence of $Pd(PPh_3)_4$[a,b]



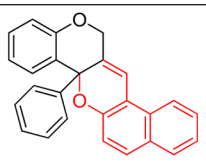
X = H, **3a**, 75%
X = OMe, **3b**, 85%
X = Me, **3c**, 79%
[c]X = F, **3d**, 50%



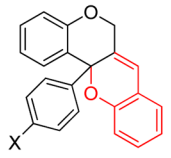
X = OMe, **3e**, 80%
X = NEt_2, **3f**, 70%



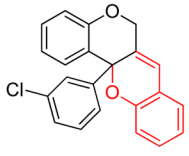
3g, 92%



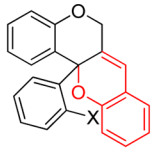
3h, 69%



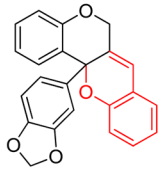
X = OMe, **3i**, 74%
X = Me, **3j**, 67%
X = F, **3k**, 70%
X = Cl, **3l**, 66%
X = CF_3, **3m**, 55%



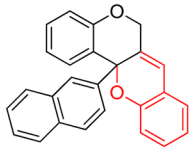
3n, 65%



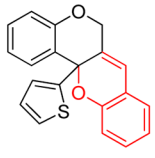
X = Me, **3o**, 59%
X = Cl, **3p**, 52%



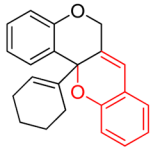
3q, 69%



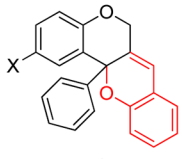
3r, 69%



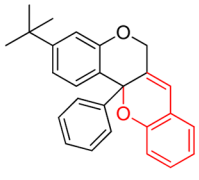
3s, 56%



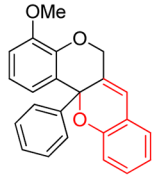
3t, 26%



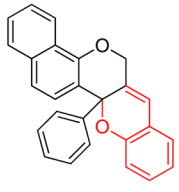
X = Me, **3u**, 78%
X = *t*-Bu, **3v**, 67%
X = F, **3w**, 71%
X = Cl, **3x**, 72%
X = CF_3, **3y**, 54%



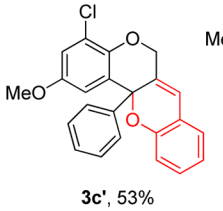
3z, 83%



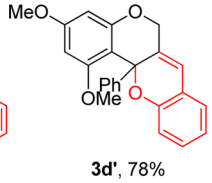
3a', 72%



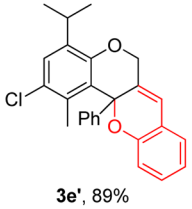
3b', 78%



3c', 53%



3d', 78%



3e', 89%

[a]Reaction conditions: **1a–x** (0.20 mmol), **2a–h** (0.40 mmol), $Pd(PPh_3)_4$ (0.01 mmol), K_2CO_3 (0.90 mmol), THF (1.5 mL), 110 °C, 10 h, under N_2, unless otherwise noted. [b]Isolated yield. [c]$Pd(PPh_3)_4$ (0.015 mmol).

70%. Intriguingly, salicyl *N*-tosylhydrazone substituted with 3,5-di-*tert*-butyl was efficient in this catalytic reaction, giving product **3g** in 92% yield. Further examination with *N*-tosylhydrazones showed that a naphthalene-based substrate generated the product **3h** in moderate yield.

Next we tested the ability of 3-iodo-2*H*-chromenes **1** with various substituents at the R^2 position to react with **2a**. Derivatives of 3-iodo-2*H*-chromenes substituted at the *para* position of the benzene ring (4-OMe, 4-Me, 4-F, 4-Cl, 4-CF_3) reacted with **2a** to give the products **3i–m** in yields of 55–74%, which indicated that the electron-donating property of substituents only promoted the reaction slightly. The corresponding derivatives **1** with substituents at the *meta* or *ortho* positions on the benzene ring generated the products **3n–3p** in yields of 52–65%. Moreover, 3-iodo-2*H*-chromene **1** with a cyclic $-OCH_2O-$ substituent reacted smoothly with **2a** to produce **3q** in 69% yield. The reaction also tolerated other substituents, including naphthyl and thienyl moieties, which

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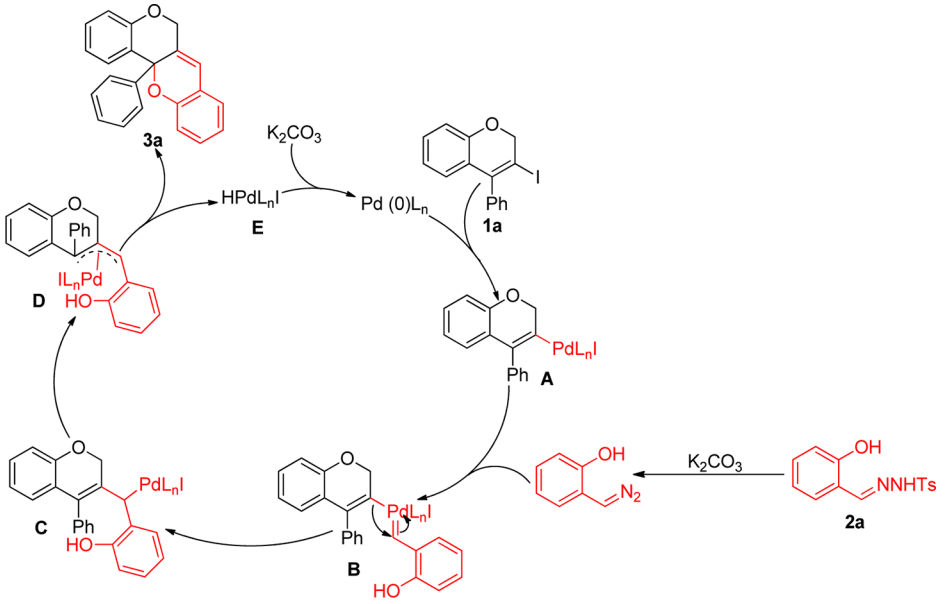
Scheme 1. Proposed Mechanism of the Palladium-Catalyzed Tandem Reaction of Vinyl Iodide (1a) with Salicyl *N*-tosylhydrazone (2a)



gave the respective products **3r** and **3s** in yields of 69% and 56%. The substrate with 1-cyclohexenyl at R^2 position was used in the reaction with **2a** to give product **3t** in a much lower 26% yield, indicating that an aromatic R^2-group may be required for the process, in line with the π-allyl-Pd-intermediate proposed in the mechanism.

To further explore the flexibility of this tandem reaction, we tested the ability of 3-iodo-4-phenyl-2*H*-chromenes **1** carrying different substituents at the R^1 position to react with **2a**. Chromenes bearing Me, *t*-Bu, F, Cl, or CF_3 groups at the *para* position of O proved suitable for this catalytic reaction, giving products **3u**-**3y** in yields of 54−78%, which indicates that the electronic properties of the substituents exert little influence on the reaction. Chromenes substituted with *t*-Bu on the *meta* position of O or OMe on the *ortho* position of O reacted with **2a** to afford, respectively, **3z** and **3a′** in 83% and 72% yields. A naphthalene-based chromene was also effective, forming the product **3b′** in 78% yield. Chromene containing two substituents on the benzene ring reacted with **2a** to afford **3c′** in 53% yield and **3d′** in 78% yield. Even a triple-substituted chromene worked well, delivering the product **3e′** in good yield.

Based on our results and earlier studies of palladium-catalyzed carbene migratory insertion reactions, we propose the tentative mechanism shown in Scheme 1. First, oxidative addition of Pd(0) to 3-iodo-4-phenyl-2*H*-chromene **1a** affords Pd(II) intermediate **A**. The diazo compound, previously generated in situ from salicyl *N*-tosylhydrazone **2a**, reacts with **A** to give palladium carbene complex **B**, which undergoes migratory insertion of the vinyl group to deliver the intermediate **C**. The η^1-allylpalladium complex **C** isomerizes to a more stable η^3-allylpalladium species **D**, which serves as a key intermediate in intramolecular nucleophilic substitution that forms the final product **3a** and simultaneously releases the Pd(II) species **E**. Finally, the initial Pd(0) catalyst is regenerated after reductive elimination with the aid of K_2CO_3. In summary, we have developed a concise catalytic reaction of vinyl iodides and salicyl *N*-tosylhydrazones to access the chromeno[4,3-*b*]chromene skeleton. The reaction involves tandem carbene migratory insertion and intramolecular cyclization in the presence of 5 mol % $Pd(PPh_3)_4$ catalyst. This new approach generates various compounds carrying a broad array of functional groups in moderate to high yields. This protocol may prove useful in future studies of drug development and natural product synthesis.

EXPERIMENTAL SECTION

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. The solvents were distilled under nitrogen from sodium-benzophenone (THF, toluene, dioxane) or calcium hydride (DMF, MeCN, 1,2-DCE) before used. The vinyl iodides[19] and salicyl *N*-tosylhydrazones[20] were prepared according to the literature methods. $Pd(PPh_3)_4$ and other palladium catalysts were purchased from various chemical suppliers. Other chemicals were obtained from commercial sources, and were used without further purification. Chemical shifs (δ, ppm) in the ^{1}H NMR spectra were recorded using TMS as internal standard. Chemical shifs in $^{13}C\{^1H\}$ NMR spectra were internally referenced to $CHCl_3$ (δ = 77.16 ppm).

General Procedure for Palladium-Catalyzed Tandem Reaction of Vinyl Iodides (1) and Salicyl *N*-tosylhydrazones (2). A mixture of vinyl iodides **1** (0.20 mmol), salicyl *N*-tosylhydrazones **2** (0.40 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol), and K_2CO_3 (124.4 mg, 0.90 mmol) in THF (1.5 mL) was stirred at 110 °C (oil bath temperature) in a sealed tube under nitrogen atmosphere for 10 h. Then, the resulting mixture was cooled down to room temperature and diluted with CH_2Cl_2. The solvent was evaporated under reduced press, and the residue was passed through column chromatography on silica gel to afford the target products **3**.

*12a-Phenyl-6,12a-dihydrochromeno[4,3-b]chromene (**3a**).* The product **3a** was obtained in 75% yield (46.9 mg) as a white solid after column chromatography (eluent = petroleum ether). Mp: 163.5−165.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.62 (dd, J_1 = 1.60 Hz, J_2 = 7.84 Hz, 1H), 7.34−7.38 (m, 2H), 7.22−7.28 (m, 4H), 7.13−7.18 (m, 1H), 7.01−7.07 (m, 2H), 6.84−6.91 (m, 3H), 6.53 (s, 1H), 4.62−4.71 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 154.00, 153.41, 144.90, 130.22, 129.69, 129.51, 128.45, 128.23, 128.16, 127.13, 126.53, 126.29, 121.51, 121.33, 120.86, 120.26, 116.97, 116.07, 78.61, 67.82; HRMS (ESI, TOF) calcd for $C_{22}H_{17}O_2^+$ $[M + H]^+$: 313.1223, found: 313.1224.

*9-Methoxy-12a-phenyl-6,12a-dihydrochromeno[4,3-b]chromene (**3b**).* The product **3b** was obtained in 85% yield (57.9 mg) as a white

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solid after column chromatography (eluent = petroleum ether/ethyl acetate 200:1 v/v). Mp: 136.0−138.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.62 (dd, J_1 = 1.60 Hz, J_2 = 7.84 Hz, 1H), 7.35−7.39 (m, 2H), 7.24−7.28 (m, 2H), 7.23 (d, J = 1.72 Hz, 2H), 7.01−7.06 (m, 1H), 6.89 (dd, J_1 = 0.96 Hz, J_2 = 8.24 Hz, 1H), 6.83−6.86 (m, 1H), 6.71 (dd, J_1 = 3.00 Hz, J_2 = 8.76 Hz, 1H), 6.59 (d, J = 2.96 Hz, 1H), 6.51 (s, 1H), 4.65−4.75 (m, 2H), 3.76 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 154.09, 153.97, 147.35, 144.66, 130.69, 129.63, 128.41, 128.24, 128.15, 126.52, 126.37, 121.60, 121.00, 120.98, 117.01, 116.72, 115.24, 112.15, 78.15, 67.91, 55.82; HRMS (ESI, TOF) calcd for $C_{23}H_{19}O_3^+$ $[M + H]^+$: 343.1329, found: 343.1329.

*9-Methyl-12a-phenyl-6,12a-dihydrochromeno[4,3-b]chromene (**3c**).* The product **3c** was obtained in 79% yield (57.9 mg) as a white vesiculose solid (eluent = petroleum ether). Mp: 46.5−49.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.61 (dd, J_1 = 1.64 Hz, J_2 = 7.88 Hz, 1H), 7.35−7.38 (m, 2H), 7.24−7.28 (m, 2H), 7.23 (d, J = 1.72 Hz, 2H), 7.01−7.06 (m, 1H), 6.95 (dd, J_1 = 1.92 Hz, J_2 = 8.28 Hz, 1H), 6.88 (J_1 = 1.00 Hz, J_2 = 8.28 Hz, 1H), 6.79−6.84 (m, 2H), 6.49 (s, 1H), 4.62−4.73 (m, 2H), 2.25 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 154.01, 151.27, 144.95, 130.66, 130.49, 129.61, 129.58, 128.40, 128.22, 128.13, 127.55, 126.51, 126.40, 121.52, 121.02, 120.07, 116.96, 115.81, 78.34, 67.91, 20.66; HRMS (ESI, TOF) calcd for $C_{23}H_{19}O_2^+$ $[M + H]^+$: 327.1380, found: 327.1383.

*9-Fluoro-12a-phenyl-6,12a-dihydrochromeno[4,3-b]chromene (**3d**).* The product **3d** was obtained in 50% yield (33.3 mg) as a white solid after column chromatography (eluent = petroleum ether). Mp: 168.0−170.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.61 (dd, J_1 = 1.48 Hz, J_2 = 7.88 Hz, 1H), 7.34−7.37 (m, 2H), 7.24−7.29 (m, 4H), 7.03−7.07 (m, 1H), 6.90 (d, J = 8.44 Hz, 1H), 6.84−6.86 (m, 2H), 6.76 (d, J = 8.00 Hz, 1H), 6.49 (s, 1H), 4.64−4.74 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 158.59, 156.22, 153.90, 149.23 (d, J_{C-F} = 2.08 Hz), 144.28, 131.33, 129.79, 128.50, 128.35, 128.10, 126.49, 126.04, 121.66, 121.31 (d, J_{C-F} = 8.25 Hz), 120.17 (d, J_{C-F} = 1.99 Hz), 117.06, 116.99 (d, J_{C-F} = 8.09 Hz), 116.24 (d, J_{C-F} = 23.39 Hz), 113.21 (d, J_{C-F} = 24.00 Hz), 78.54, 67.71; HRMS (EI, TOF) calcd for $C_{22}H_{15}FO_2$ $[M]^+$: 330.1056, found: 330.1052.

*10-Methoxy-12a-phenyl-6,12a-dihydrochromeno[4,3-b]-chromene (**3e**).* The product **3e** was obtained in 80% yield (54.8 mg) as a white solid after column chromatography (eluent = petroleum ether/ethyl acetate 200:1 v/v). Mp: 98.5−100.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.59 (dd, J_1 = 1.60 Hz, J_2 = 7.84 Hz, 1H), 7.34−7.37 (m, 2H), 7.23−7.29 (m, 4H), 7.01−7.06 (m, 1H), 6.94 (d, J = 8.28 Hz, 1H), 6.88 (dd, J_1 = 1.00 Hz, J_2 = 8.28 Hz, 1H), 6.48−6.50 (m, 2H), 6.43 (dd, J_1 = 2.44 Hz, J_2 = 8.28 Hz, 1H), 4.59−4.69 (m, 2H), 3.78 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 161.51, 154.74, 154.14, 145.07, 129.68, 128.44, 128.21, 128.19, 127.85, 126.52, 126.43, 126.18, 121.40, 120.59, 116.99, 113.46, 107.26, 101.74, 78.79, 67.88, 55.51; HRMS (ESI, TOF) calcd for $C_{23}H_{19}O_3^+$ $[M + H]^+$: 343.1329, found: 343.1328.

*N,N-Diethyl-12a-phenyl-6,12a-dihydrochromeno[4,3-b]-chromen-10-amine (**3f**).* The product **3f** was obtained in 70% yield (53.5 mg) as a light-brown solid after column chromatography (eluent = petroleum ether/ethyl acetate 200:1 v/v). Mp: 131.4−132.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.58 (dd, J_1 = 1.60 Hz, J_2 = 7.84 Hz, 1H), 7.37−7.40 (m, 2H), 7.21−7.28 (m, 4H), 6.98−7.03 (m, 1H), 6.84−6.88 (m, 2H), 6.43 (s, 1H), 6.25 (d, J = 2.36 Hz, 1H), 6.17 (dd, J_1 = 2.48 Hz, J_2 = 8.40 Hz, 1H), 4.56−4.69 (m, 2H), 3.33 (q, J = 7.08 Hz, 4H), 1.16 (t, J = 7.08 Hz, 6H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 155.05, 154.33, 149.89, 145.83, 129.45, 128.33, 128.31,128.00, 127.90, 126.68, 126.61, 123.39, 121.19, 121.07, 116.92, 108.49, 104.49, 98.77, 78.67, 68.18, 44.53, 12.85; HRMS (EI, TOF) calcd for $C_{26}H_{25}NO_2$ $[M]^+$: 383.1885, found: 383.1887.

*9,11-Ditert-butyl-12a-phenyl-6,12a-dihydrochromeno[4,3-b]-chromene (**3g**).* The product **3g** was obtained in 92% yield (78.1 mg) as a white vesiculose solid after column chromatography (eluent = petroleum ether). Mp: 49.2−52.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.68 (dd, J_1 = 1.32 Hz, J_2 = 7.84 Hz, 1H), 7.25−7.31 (m, 3H), 7.20−7.23 (m, 4H), 7.07 (t, J = 7.40 Hz, 1H), 6.92 (d, J = 2.24 Hz, 1H), 6.88 (d, J = 8.24 Hz, 1H), 6.52 (s, 1H), 4.51−4.60 (m, 2H), 1.30 (s, 9H), 1.29 (s, 9H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 154.13, 149.28, 144.07, 143.00, 135.71, 129.55, 128.96, 128.31, 128.27, 127.94, 126.84, 125.95, 124.96, 122.56, 121.83, 121.13, 119.66, 116.87, 79.28, 67.03, 34.81, 34.38, 31.67, 29.94; HRMS (EI, TOF) calcd for $C_{30}H_{32}O_2$ $[M]^+$: 424.2402, found: 424.2401.

*14a-Phenyl-6,14a-dihydrobenzo[f]chromeno[4,3-b]chromene (**3h**).* The product **3h** was obtained in 69% yield (50.2 mg) as a light yellow solid after column chromatography (eluent = petroleum ether). Mp: 187.6−189.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.94 (d, J = 8.48 Hz, 1H), 7.75 (d, J = 8.12 Hz, 1H), 7.71 (d, J = 8.84 Hz, 1H), 7.63 (dd, J_1 = 1.64 Hz, J_2 = 7.88 Hz, 1H), 7.42−7.51 (m, 3H), 7.32−7.37 (m, 1H), 7.26−7.30 (m, 1H), 7.20−7.26 (m, 5H), 7.03−7.08 (m, 1H), 6.93 (dd, J_1 = 0.92 Hz, J_2 = 8.24 Hz, 1H), 4.82−4.92 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 154.22, 151.88, 144.73, 130.46, 130.06, 129.78, 129.47, 128.78, 128.49, 128.40, 128.16, 126.96, 126.43, 126.35, 123.85, 121.74, 121.34, 118.04, 117.23, 117.04, 113.06, 78.23, 68.38; HRMS (EI, TOF) calcd for $C_{26}H_{18}O_2$ $[M]^+$: 362.1307, found: 362.1309.

*12a-(4-Methoxyphenyl)-6,12a-dihydrochromeno[4,3-b]-chromene (**3i**).* The product **3i** was obtained in 74% yield (50.8 mg) as a white vesiculose solid after column chromatography (eluent = petroleum ether/ethyl acetate 200:1 v/v). Mp: 39.2−42.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.63 (dd, J_1 = 1.64 Hz, J_2 = 7.84 Hz, 1H), 7.22−7.28 (m, 3H), 7.11−7.16 (m, 1H), 7.01−7.07 (m, 2H), 6.83−6.89 (m, 3H), 6.74−6.78 (m, 2H), 6.52 (s, 1H), 4.59−4.67 (m, 2H), 3.73 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 159.42, 153.87, 153.28, 137.07, 130.13, 129.76, 129.59, 128.09, 127.93, 127.03, 126.38, 121.40, 121.24, 120.54, 120.27, 116.92, 116.10, 113.68, 78.30, 67.74, 55.32; HRMS (EI, TOF) calcd for $C_{23}H_{18}O_3$ $[M]^+$: 342.1256, found: 342.1255.

*12a-(p-Tolyl)-6,12a-dihydrochromeno[4,3-b]chromene (**3j**).* The product **3j** was obtained in 67% yield (43.8 mg) as a colorless viscous oil after column chromatography (eluent = petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.62 (dd, J_1 = 1.48 Hz, J_2 = 7.84 Hz, 1H), 7.20−7.26 (m, 3H), 7.10−7.15 (m, 1H), 6.98−7.05 (m, 4H), 6.81−6.89 (m, 3H), 6.48 (s, 1H), 4.58−4.69 (m, 2H), 2.25 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 153.96, 153.41, 142.03, 138.03, 130.13, 129.69, 129.59, 129.11, 128.15, 127.06, 126.47, 126.42, 121.45, 121.25, 120.68, 120.33, 116.92, 116.07, 78.46, 67.80, 21.14; HRMS (EI, TOF) calcd for $C_{23}H_{18}O_2$ $[M]^+$: 326.1307, found: 326.1308.

*12a-(4-Fluorophenyl)-6,12a-dihydrochromeno[4,3-b]chromene (**3k**).* The product **3k** was obtained in 70% yield (46.2 mg) as a white solid after column chromatography (eluent = petroleum ether). Mp: 130.0−132.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.61 (dd, J_1 = 1.60 Hz, J_2 = 7.84 Hz, 1H), 7.31−7.35 (m, 2H), 7.24−7.29 (m, 1H), 7.14−7.19 (m, 1H), 7.02−7.08 (m, 2H), 6.85−6.95 (m, 5H), 6.55 (s, 1H), 4.65 (d, J = 0.92 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 163.74, 161.28, 153.91, 153.06, 140.68 (d, J_{C-F} = 3.36 Hz), 130.32, 129.82, 129.46, 128.46 (d, J_{C-F} = 8.18 Hz), 127.94, 127.16, 126.12, 121.55 (d, J_{C-F} = 10.22 Hz), 120.91, 120.16, 117.09, 116.12, 115.28 (d, J_{C-F} = 21.36 Hz), 78.01, 67.71; HRMS (EI, TOF) calcd for $C_{22}H_{15}FO_2$ $[M]^+$: 330.1056, found: 330.1054.

*12a-(4-Chlorophenyl)-6,12a-dihydrochromeno[4,3-b]chromene (**3l**).* The product **3l** was obtained in 66% yield (45.9 mg) as a white solid after column chromatography (eluent = petroleum ether). Mp: 131.6−133.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.60 (dd, J_1 = 1.52 Hz, J_2 = 7.84 Hz, 1H), 7.24−7.32 (m, 3H), 7.14−7.22 (m, 3H), 7.02−7.07 (m, 2H), 6.86−6.91 (m, 3H), 6.55 (s, 1H), 4.67 (d, J = 0.60 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 153.97, 153.06, 143.28, 134.19, 130.36, 129.88, 129.26, 128.60, 127.98, 127.94, 127.20, 125.91, 121.68, 121.59, 121.10, 120.22, 117.16, 116.14, 77.92, 67.73; HRMS (EI, TOF) calcd for $C_{22}H_{15}ClO_2$ $[M]^+$: 346.0761, found: 346.0758.

*12a-(4-(Trifluoromethyl)phenyl)-6,12a-dihydrochromeno[4,3-b]-chromene (**3m**).* The product **3m** was obtained in 55% yield (42.1 mg) as a colorless viscous oil after column chromatography (eluent = petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.59 (dd, J_1 = 1.60 Hz, J_2 = 7.84 Hz, 1H), 7.47−7.53 (m, 4H), 7.24−7.29 (m, 1H), 7.14−7.20 (m, 1H), 7.01−7.07 (m, 2H), 6.85−6.94 (m, 3H), 6.55 (s, 1H), 4.69 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 154.07,

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153.05, 148.54, 148.53, 130.48, 130.04, 128.97, 127.94, 127.32, 126.86, 125.71, 125.45 (q, J_{C-F} = 3.65 Hz), 122.69, 121.84, 121.77, 121.43, 120.22, 117.29, 116.13, 77.88, 67.73; HRMS (EI, TOF) calcd for $C_{23}H_{15}F_3O_2$ $[M]^+$: 380.1024, found: 380.1025.

*12a-(3-Chlorophenyl)-6,12a-dihydrochromeno[4,3-b]chromene (**3n**).* The product **3n** was obtained in 65% yield (44.8 mg) as a white solid after column chromatography (eluent = petroleum ether). Mp: 115.2−117.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.61 (dd, J_1 = 1.64 Hz, J_2 = 7.88 Hz, 1H), 7.32−7.34 (m, 1H), 7.25−7.31 (m, 2H), 7.15−7.24 (m, 3H), 7.02−7.08 (m, 2H), 6.86−6.93 (m, 3H), 6.57 (s, 1H), 4.65−4.73 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 153.97, 152.97, 146.66, 134.42, 130.41, 129.95, 129.76, 128.98, 128.38, 127.93, 127.25, 126.81, 125.77, 124.77, 121.74, 121.65, 121.39, 120.14, 117.21, 116.15, 77.86, 67.82; HRMS (EI, TOF) calcd for $C_{22}H_{15}ClO_2$ $[M]^+$: 346.0761, found: 346.0762.

*12a-(o-Tolyl)-6,12a-dihydrochromeno[4,3-b]chromene (**3o**).* The product **3o** was obtained in 59% yield (38.2 mg) as a white solid after column chromatography (eluent = petroleum ether). Mp: 132.5−135.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.54 (dd, J_1 = 1.60 Hz, J_2 = 7.76 Hz, 1H), 7.13−7.24 (m, 4H), 6.94−7.07 (m, 3H), 6.80−6.86 (m, 3H), 6.64 (d, J = 7.68 Hz, 1H), 6.47 (s, 1H), 4.41−4.50 (m, 2H), 2.50 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 153.55, 152.53, 141.04, 138.59, 132.75, 130.67, 130.15, 129.59, 129.48, 129.28, 128.75, 127.29, 125.67, 125.64, 122.32, 121.19, 121.02, 118.92, 116.79, 115.42, 82.08, 68.85, 20.91; HRMS (EI, TOF) calcd for $C_{23}H_{18}O_2$ $[M]^+$: 326.1307, found: 326.1306.

*12a-(2-Chlorophenyl)-6,12a-dihydrochromeno[4,3-b]chromene (**3p**).* The product **3p** was obtained in 52% yield (35.7 mg) as a white solid after column chromatography (eluent = petroleum ether). Mp: 142.2−144.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.58 (dd, J_1 = 1.64 Hz, J_2 = 7.76 Hz, 1H), 7.45 (dd, J_1 = 1.24 Hz, J_2 = 7.88 Hz, 1H), 7.26−7.30 (m, 1H), 7.22−7.26 (m, 1H), 7.08−7.18 (m, 2H), 7.01−7.06 (m, 1H), 6.96 (dd, J_1 = 1.56 Hz, J_2 = 7.36 Hz, 1H), 6.80−6.86 (m, 3H), 6.77 (dd, J_1 = 1.60 Hz, J_2 = 7.88 Hz, 1H), 6.49 (s, 1H), 4.42−4.55 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 153.58, 152.83, 139.91, 135.02, 132.05, 131.11, 130.50, 129.92, 129.90, 129.08, 127.37, 127.22, 126.38, 125.87, 123.13, 121.18, 121.04, 119.17, 116.98, 115.15, 80.86, 68.78; HRMS (EI, TOF) calcd for $C_{22}H_{15}ClO_2$ $[M]^+$: 346.0761, found: 346.0760.

*12a-(Benzo[d][1,3]dioxol-5-yl)-6,12a-dihydrochromeno[4,3-b]-chromene (**3q**).* The product **3q** was obtained in 69% yield (49.0 mg) as a white solid after column chromatography (eluent = petroleum ether/ethyl acetate 180:1 v/v). Mp: 113.6−116.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.64 (dd, J_1 = 1.64 Hz, J_2 = 7.88 Hz, 1H), 7.22−7.28 (m, 1H), 7.12−7.17 (m, 1H), 7.01−7.07 (m, 2H), 6.91 (d, J = 1.84 Hz, 1H), 6.83−6.88 (m, 3H), 6.75 (dd, J_1 = 1.92 Hz, J_2 = 8.20 Hz, 1H), 6.64−6.67 (m, 1H), 6.52 (s, 1H), 5.89 (s, 2H), 4.60−4.69 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 153.82, 153.05, 147.87, 147.52, 138.81, 130.24, 129.70, 129.61, 127.89, 127.10, 126.34, 121.44, 121.36, 120.72, 120.61, 120.10, 116.99, 116.12, 107.85, 107.36, 101.33, 78.40, 67.77; HRMS (EI, TOF) calcd for $C_{23}H_{16}O_4$ $[M]^+$: 356.1049, found: 356.1050.

*12a-(naphthalen-2-yl)-6,12a-dihydrochromeno[4,3-b]chromene (**3r**).* The product **3r** was obtained in 69% yield (49.8 mg) as a white solid after column chromatography (eluent = petroleum ether). Mp: 110.4−112.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.63−7.76 (m, 5H), 7.60 (s, 1H), 7.37−7.45 (m, 2H), 7.26−7.31 (m, 1H), 7.12−7.18 (m, 1H), 7.01−7.09 (m, 2H), 6.92 (d, J = 8.28 Hz, 2H), 6.83−6.88 (m, 1H), 6.55 (s, 1H), 4.62−4.74 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 154.09, 153.37, 142.02, 132.99, 132.73, 130.29, 129.78, 129.41, 128.72, 128.57, 128.19, 127.52, 127.18, 126.54, 126.36, 126.27, 125.86, 124.34, 121.57, 121.38, 121.14, 120.25, 117.04, 116.07, 78.74, 67.89; HRMS (EI, TOF) calcd for $C_{26}H_{18}O_2$ $[M]^+$: 362.1307, found: 362.1306.

*12a-(Thiophen-2-yl)-6,12a-dihydrochromeno[4,3-b]chromene (**3s**).* The product **3s** was obtained in 56% yield (35.7 mg) as a white solid after column chromatography (eluent = petroleum ether). Mp: 131.2−133.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.82 (dd, J_1 = 1.64 Hz, J_2 = 7.88 Hz, 1H), 7.26−7.31 (m, 1H), 7.14−7.20 (m, 2H), 7.05−7.10 (m, 2H), 6.87−6.94 (m, 3H), 6.82−6.85 (m, 2H), 6.59 (s, 1H), 4.68−4.78 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 153.72, 152.55, 147.54, 130.17, 130.09, 129.43, 128.41, 126.98, 126.48, 126.33, 125.62, 121.89, 121.47, 121.18, 121.01, 117.07, 116.99, 75.26, 67.14; HRMS (EI, TOF) calcd for $C_{20}H_{14}O_2S$ $[M]^+$: 318.0715, found: 318.0716.

*12a-(Cyclohex-1-en-1-yl)-6,12a-dihydrochromeno[4,3-b]-chromene (**3t**).* The product **3t** was obtained in 26% yield (16.2 mg) as a colorless oil after column chromatography (eluent = petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.53 (dd, J_1 = 1.64 Hz, J_2 = 7.80 Hz, 1H), 7.17−7.23 (m, 1H), 7.07−7.13 (m, 1H), 6.96−7.01 (m, 1H), 6.94 (dd, J_1 = 1.56 Hz, J_2 = 7.40 Hz, 1H), 6.77−6.84 (m, 3H), 6.48 (s, 1H), 5.32−5.35 (m, 1H), 4.77 (dd, J_1 = 1.44 Hz, J_2 = 12.32 Hz, 1H), 4.53−4.57 (m, 1H), 2.14−2.16 (m, 2H), 1.98−2.00 (m, 2H), 1.59−1.68 (m, 1H), 1.45−1.52 (m, 3H); ^{13}C NMR (100.6 MHz, CDCl3, 25 °C) δ 153.93, 153.89, 140.05, 129.82, 129.17, 127.87, 127.76, 126.94, 126.78, 126.25, 121.54, 120.79, 120.67, 120.00, 116.35, 115.35, 80.51, 67.61, 25.25, 23.67, 22.78, 21.91; HRMS (EI, TOF) calcd for $C_{22}H_{20}O_2$ $[M]^+$: 316.1463, found: 316.1466.

*2-Methyl-12a-phenyl-6,12a-dihydrochromeno[4,3-b]chromene (**3u**).* The product **3u** was obtained in 78% yield (50.6 mg) as a white solid after column chromatography (eluent = petroleum ether). Mp: 113.6−115.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.35−7.40 (m, 3H), 7.23−7.27 (m, 3H), 7.13−7.19 (m, 1H), 7.01−7.07 (m, 2H), 6.92 (d, J = 8.08 Hz, 1H), 6.84−6.89 (m, 1H), 6.79 (d, J = 8.36 Hz, 1H), 6.51 (s, 1H), 4.59−4.71 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 153.46, 151.88, 145.03, 130.84, 130.52, 130.14, 129.86, 128.41, 128.16, 128.10, 127.10, 126.49, 125.84, 121.32, 120.70, 120.37, 116.72, 116.07, 78.62, 67.79, 20.92; HRMS (EI, TOF) calcd for $C_{23}H_{18}O_2$ $[M]^+$: 326.1307, found: 326.1306.

*2-(tert-Butyl)-12a-phenyl-6,12a-dihydrochromeno[4,3-b]-chromene (**3v**).* The product **3v** was obtained in 67% yield (49.1 mg) as a white solid after column chromatography (eluent = petroleum ether). Mp: 170.4−173.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.62 (d, J = 2.44 Hz, 1H), 7.34−7.37 (m, 2H), 7.29 (dd, J_1 = 2.44 Hz, J_2 = 8.60 Hz, 1H), 7.22−7.27 (m, 3H), 7.13−7.18 (m, 1H), 7.03 (dd, J_1 = 1.60 Hz, J_2 = 7.44 Hz, 1H), 6.91 (d, J = 8.08 Hz, 1H), 6.83−6.88 (m, 1H), 6.82 (d, J = 8.64 Hz, 1H), 6.52 (s, 1H), 4.57−4.65 (m, 2H), 1.31 (s, 9H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 153.38, 151.77, 145.00, 144.19, 130.12, 130.03, 128.43, 128.20, 127.06, 126.88, 126.58, 125.25, 124.49, 121.26, 120.61, 120.31, 116.33, 116.10, 78.91, 67.75, 34.51, 31.66; HRMS (EI, TOF) calcd for $C_{26}H_{24}O_2$ $[M]^+$: 368.1776, found: 368.1778.

*2-Fluoro-12a-phenyl-6,12a-dihydrochromeno[4,3-b]chromene (**3w**).* The product **3w** was obtained in 71% yield (46.7 mg) as a colorless oil after column chromatography (eluent = petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.31−7.36 (m, 3H), 7.22−7.28 (m, 3H), 7.13−7.18 (m, 1H), 7.02 (dd, J_1 = 1.56 Hz, J_2 = 7.44 Hz, 1H), 6.81−6.98 (m, 4H), 6.51 (s, 1H), 4.59−4.70 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 158.73, 156.35, 153.05, 150.08 (d, J_{C-F} = 1.99 Hz), 144.30, 130.34, 129.04, 128.54, 128.41, 127.38 (d, J_{C-F} = 6.84 Hz), 127.19, 126.35, 121.55, 120.98, 120.16, 118.13 (d, J_{C-F} = 7.71 Hz), 116.76 (d, J_{C-F} = 23.58 Hz), 116.08, 114.01 (d, J_{C-F} = 24.20 Hz), 78.32, 67.90; HRMS (EI, TOF) calcd for $C_{22}H_{15}FO_2$ $[M]^+$: 330.1056, found: 330.1055.

*2-Chloro-12a-phenyl-6,12a-dihydrochromeno[4,3-b]chromene (**3x**).* The product **3x** was obtained in 72% yield (49.9 mg) as a colorless oil after column chromatography (eluent = petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.59 (d, J = 2.56 Hz, 1H), 7.30−7.35 (m, 2H), 7.23−7.29 (m, 3H), 7.14−7.22 (m, 2H), 7.02 (dd, J_1 = 1.56 Hz, J_2 = 7.44 Hz, 1H), 6.84−6.93 (m, 2H), 6.82 (d, J = 8.80 Hz, 1H), 6.52 (s, 1H), 4.60−4.69 (m, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 153.06, 152.59, 144.28, 130.44, 129.75, 128.58, 128.46, 127.73, 127.67, 127.21, 126.38, 126.32, 121.55, 121.18, 119.97, 118.45, 116.08, 78.34, 67.87; HRMS (EI, TOF) calcd for $C_{22}H_{15}ClO_2$ $[M]^+$: 346.0761, found: 346.0759.

*12a-Phenyl-2-(trifluoromethyl)-6,12a-dihydrochromeno[4,3-b]-chromene (**3y**).* The product **3y** was obtained in 54% yield (41.4 mg) as a white solid after column chromatography (eluent = petroleum ether). Mp: 140.6−142.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.91 (d, J = 1.80 Hz, 1H), 7.51 (dd, J_1 = 1.88 Hz, J_2 = 8.72 Hz, 1H),

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7.26−7.31 (m, 5H), 7.16−7.22 (m, 1H), 7.05 (dd, J_1 = 1.60 Hz, J_2 = 7.44 Hz, 1H), 6.87−6.98 (m, 3H), 6.56 (s, 1H), 4.69 (s, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 156.43, 153.00, 144.15, 130.61, 128.70, 128.62, 127.98, 127.28, 126.77 (q, J_{C-F} = 3.60 Hz), 126.50, 126.39, 125.81, 125.76, 125.73, 125.69, 123.79, 123.46, 123.11, 121.62, 121.40, 119.74, 117.57, 116.12, 78.38, 67.98; HRMS (EI, TOF) calcd for $C_{23}H_{15}F_3O_2$ $[M]^+$: 380.1024, found: 380.1026.

*3-(tert-Butyl)-12a-phenyl-6,12a-dihydrochromeno[4,3-b]-chromene (**3z**).* The product **3z** was obtained in 83% yield (60.8 mg) as a white vesiculose solid after column chromatography (eluent = petroleum ether). Mp: 46.5−49.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.53 (d, J = 8.28 Hz, 1H), 7.37−7.41 (m, 2H), 7.22−7.28 (m, 3H), 7.12−7.17 (m, 1H), 7.08 (dd, J_1 = 1.96 Hz, J_2 = 8.28 Hz, 1H), 7.02 (dd, J_1 = 1.56 Hz, J_2 = 7.40 Hz, 1H), 6.83−6.91 (m, 3H), 6.53 (s, 1H), 4.62−4.71 (m, 2H), 1.31 (s, 9H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 153.67, 153.57, 153.34, 144.93, 130.14, 129.75, 128.40, 128.14, 127.77, 127.09, 126.55, 123.10, 121.27, 120.99, 120.43, 119.05, 116.13, 113.75, 78.45, 67.92, 34.76, 31.35; HRMS (EI, TOF) calcd for $C_{26}H_{24}O_2$ $[M]^+$: 368.1776, found: 368.1774.

*4-Methoxy-12a-phenyl-6,12a-dihydrochromeno[4,3-b]chromene (**3a′**).* The product **3a′** was obtained in 72% yield (49.6 mg) as a white solid after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v). Mp: 111.5−113.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.33−7.38 (m, 2H), 7.21−7.26 (m, 4H), 7.13−7.18 (m, 1H), 6.97−7.05 (m, 2H), 6.82−6.91 (m, 3H), 6.54 (s, 1H), 4.69−4.79 (m, 2H), 3.91 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 153.41, 148.23, 144.87, 143.68, 130.23, 129.17, 128.42, 128.24, 127.15, 126.89, 126.48, 121.33, 121.06, 120.90, 120.17, 119.67, 116.03, 110.94, 78.66, 68.14, 56.14; HRMS (EI, TOF) calcd for $C_{23}H_{18}O_3$ $[M]^+$: 342.1256, found: 342.1254.

*12a-Phenyl-6,12a-dihydrobenzo[h]chromeno[3,2-c]chromene (**3b′**).* The product **3b′** was obtained in 78% yield (56.7 mg) as a light yellow solid after column chromatography (eluent = petroleum ether). Mp: 119.2−122.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.22−8.25 (m, 1H), 7.77−7.81 (m, 1H), 7.64−7.67 (m, 1H), 7.46−7.54 (m, 3H), 7.37−7.41 (m, 2H), 7.21−7.24 (m, 3H), 7.14−7.20 (m, 1H), 7.05 (dd, J_1 = 1.56 Hz, J_2 = 7.44 Hz, 1H), 6.94 (d, J = 8.04 Hz, 1H), 6.85−6.90 (m, 1H), 6.57 (s, 1H), 4.86 (d, J = 0.68 Hz, 2H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 153.84, 149.42, 145.20, 134.34, 130.26, 129.15, 128.44, 128.21, 127.62, 127.19, 127.04, 126.59, 125.76, 125.02, 124.96, 122.38, 121.33, 121.07, 120.95, 120.37, 119.28, 116.08, 78.86, 68.04; HRMS (EI, TOF) calcd for $C_{26}H_{18}O_2$ $[M]^+$: 362.1307, found: 362.1309.

*4-Chloro-2-methoxy-12a-phenyl-6,12a-dihydrochromeno[4,3-b]-chromene (**3c′**).* The product **3c′** was obtained in 53% yield (39.8 mg) as a white solid after column chromatography (eluent = petroleum ether/ethyl acetate 200:1 v/v). Mp: 149.4−151.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.32−7.36 (m, 2H), 7.24−7.28 (m, 3H), 7.14−7.20 (m, 1H), 7.09 (d, J = 3.00 Hz, 1H), 7.04 (dd, J_1 = 1.52 Hz, J_2 = 7.40 Hz, 1H), 6.96 (d, J = 3.04 Hz, 1H), 6.86−6.92 (m, 2H), 6.54 (s, 1H), 4.73 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 153.77, 152.98, 144.32, 144.03, 130.36, 128.94, 128.55, 128.48, 128.39, 127.24, 126.40, 121.96, 121.57, 121.00, 119.99, 116.53, 116.00, 111.16, 78.75, 68.28, 56.06; HRMS (EI, TOF) calcd for $C_{23}H_{17}ClO_3$ $[M]^+$: 376.0866, found: 376.0868.

*1,3-Dimethoxy-12a-phenyl-6,12a-dihydrochromeno[4,3-b]-chromene (**3d′**).* The product **3d′** was obtained in 78% yield (58.1 mg) as a white solid after column chromatography (eluent = petroleum ether/ethyl acetate 100:1 v/v). Mp: 157.8−160.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.35−7.39 (m, 2H), 7.16−7.21 (m, 4H), 6.95−7.02 (m, 2H), 6.83−6.88 (m, 1H), 6.42 (s, 1H), 6.15 (d, J = 2.44 Hz, 1H), 6.10 (d, J = 2.44 Hz, 1H), 4.67 (dd, J_1 = 1.12 Hz, J_2 = 12.00 Hz, 1H), 4.48−4.52 (m, 1H), 3.78 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 161.60, 160.35, 157.04, 155.07, 145.80, 130.17, 129.03, 127.93, 127.44, 127.05, 125.43, 121.09, 120.91, 120.27, 115.92, 108.24, 94.90, 93.77, 79.18, 67.99, 56.32, 55.49; HRMS (EI, TOF) calcd for $C_{24}H_{20}O_4$ $[M]^+$: 372.1362, found: 372.1363.

*2-Chloro-4-isopropyl-1-methyl-12a-phenyl-6,12a-dihydrochromeno[4,3-b]chromene (**3e′**).* The product **3e′** was obtained in 89% yield (71.9 mg) as a colorless viscous oil after column chromatography (eluent = petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 7.31−7.34 (m, 3H), 7.22−7.27 (m, 2H), 7.18−7.22 (m, 2H), 7.04 (dd, J_1 = 1.52 Hz, J_2 = 7.32 Hz, 1H), 6.87−6.93 (m, 2H), 6.40 (s, 1H), 4.49−4.61 (m, 2H), 3.23−3.31 (m, 1H), 2.21 (s, 3H), 1.24 (d, J = 6.88 Hz, 3H), 1.19 (d, J = 6.92 Hz, 3H); ^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C) δ 154.49, 151.32, 145.90, 135.87, 133.92, 130.35, 128.59, 128.53, 128.50, 128.20, 127.23, 127.16, 125.55, 125.30, 121.31, 119.94, 119.74, 115.30, 81.17, 66.63, 26.80, 22.73, 22.71, 19.17; HRMS (EI, TOF) calcd for $C_{26}H_{23}ClO_2$ $[M]^+$: 402.1387, found: 402.1389.

■ ASSOCIATED CONTENT

Supporting Information

The X-ray crystallographic data of **3a**, the copies of ^{1}H NMR and ^{13}C NMR spectra for products **3a**−**z** and **3a′**−**e′**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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