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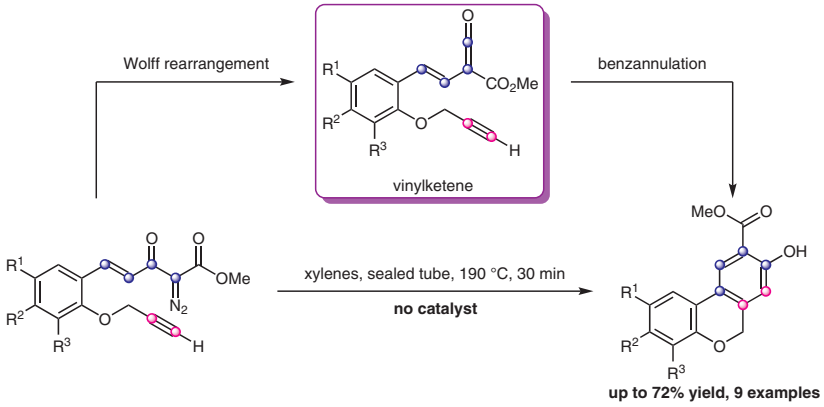
Thermally Induced Intramolecular Benzannulation of Diazoacetoacetate Enones Tethered with Unactivated Alkynes: Synthesis of Substituted 6*H*-Benzo[*c*]chromenes

Yangfan Chen
Di Wu
Jiawen Zhou
Yun Wang
Jing Huang
Xichen Xu*

School of Chemistry and Environmental Engineering, Wuhan Institute of Technology, Wuhan, 430205, P. R. of China
XichenXu@wit.edu.cn



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Abstract A facile and efficient intramolecular benzannulation strategy for the synthesis of substituted 6*H*-benzo[*c*]chromenes from diazoacetoacetate enones tethered with unactivated alkynes has been developed. The reaction proceeds in moderate to good yields under operationally simple conditions with thermally induced [4+2]-annulation of intermediate vinyl ketenes as the key step.

Key words vinyl ketene, Wolff rearrangement, benzannulation, 6*H*-benzo[*c*]chromene, diazoacetoacetate enone

6*H*-Benzo[*c*]chromene has recently emerged as one of the privileged scaffolds in modern drug discovery because of the broad range of significant biological activities and pharmacological properties that its derivatives exhibit.[1] Indeed, 6*H*-benzo[*c*]chromene represents a key structural motif that is found in many natural products (Figure 1).[2] Moreover, 6*H*-benzo[*c*]chromene derived polymers have been integrated into photovoltaic devices as functional materials.[3] Therefore, the application of 6*H*-benzo[c]chromene derivatives in pharmaceutical chemistry and material science have spurred intense research endeavors to discover efficient and high-yielding preparative methods. Towards this end, intramolecular arylations of *ortho*-halo substituted aryl benzyl ethers either under transition-metal catalysis[4] or under transition-metal-free[5] conditions have been reported. The intramolecular Au-catalyzed biaryl coupling of electron-rich arenes by aryltrimethylsilanes represents an alternative approach.[6] The palladium-catalyzed intramolecular decarboxylative[7] or dehydrogenative[8] cross-coupling, and, more recently, the visible-light-driven intermolecular radical cyclization of 2-(vinyloxy)-1,1′-biphenyls with 2-bromo-2,2-difluoroamides/esters have also been devised.[9]

Diazoacetate enones, which are readily prepared in a one-pot protocol,[10] belong to the class of acceptor/acceptor-substituted diazo compounds. Diazoacetoacetate enones, as demonstrated by Doyle et al.,[11] are prone to Wolff rearrangement under catalysis of $Rh_2(OAc)_4$ to afford intermediate vinyl ketenes, which react further with imines to provide lactams (Scheme 1, pathway a). Following the general trend, ketenes have a strong propensity to participate in [2+2]-cycloaddition. Consequently, vinyl ketenes rarely engage in cycloadditions as [4+2] enophiles.[12] Notable exceptions include (trialkylsilyl)vinyl ketenes devised by Danheiser et al.,[13] which react as electron-rich dienes in Diels–Alder and hetero-Diels–Alder reactions, and [4+1]-annulations, due to the stabilization effect of trialkylsilyl

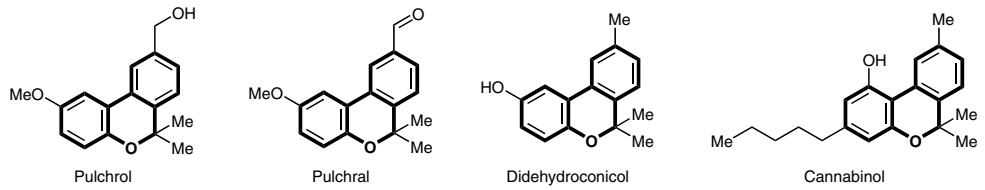

Figure 1 Representative examples of natural products that contain the 6*H*-benzo[*c*]chromene motif

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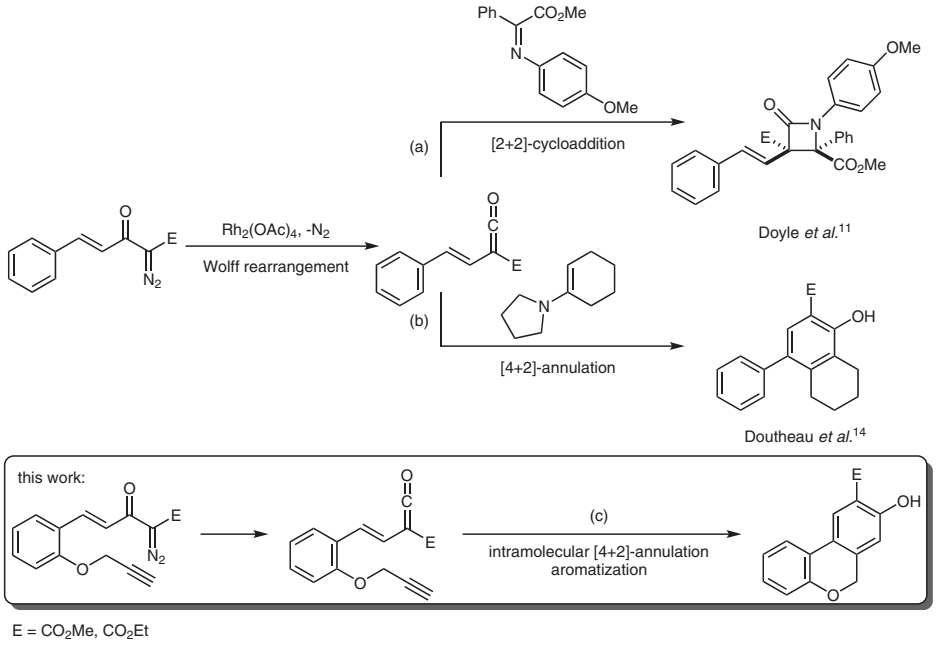
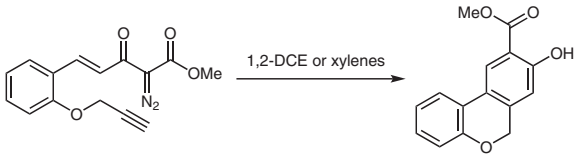


Scheme 1 (a) The intermolecular [2+2]-cycloaddition of vinyl ketene with imines. (b) The intermolecular [4+2]-annulation of vinyl ketene with enamine. (c) Reaction hypothesis for the intramolecular [4+2]-benzannulation of the vinyl ketene with an unactivated alkyne functionality.

substituents.[13] We are particularly interested in expanding the synthetic utility of diazoacetoacetate enones because of their diverse reactivity profiles. Inspired by an intermolecular vinyl ketene-enamine cyclocondensation (pathway b),[14] we hypothesize that the judicious placement of a pendant alkyne functionality on the aryl fragment of the diazoacetoacetate enone would render the intramolecular [4+2]-benzannulation and the subsequent aromatization feasible (pathway c). In principle, this benzannulation strategy would provide a convergent route to densely functionalized 6*H*-benzo[*c*]chromenes that complements the Danheiser benzannulation[15] by offering orthogonally substituted products.

In an effort to validate our hypothesis, we evaluated the dinitrogen extrusion and subsequent benzannulation of diazoacetoacetate enone **1a**; the results are summarized in Table 1. First, we surveyed a series of transition-metal catalysts that have been conventionally used to catalyze the dinitrogen extrusion of diazo compounds to afford metal carbenes (entries 1–6). Although $Rh_2(OAc)_4$ (entry 1) and $Pd(OAc)_2$ (entry 2) actively catalyzed the decomposition of **1a**, the formation of complex mixtures were indicated by TLC analysis. Unexpectedly, $Cu(hfacac)_2$, $Cu(OTf)_2$, AgOTf, and $AgSbF_6$ failed to promote the denitrogenation of diazoacetoacetate enone **1a** (entries 3–6). The reaction outcomes implied that diazoacetoacetate enone **1a** might coordinate to the copper and silver catalysts, leading to catalyst deactivation. At this stage, we reasoned that the [4+2]-benzannulation of **1a** may require a higher temperature to initiate. Accordingly, we decided to substitute 1,2-dichloroethane with xylenes, which could provide a broader temperature range for probing the optimal reaction conditions. In addition, we speculated that the slow addition of **1a** to the reaction system may not be required because free carbenes generated from acceptor/acceptor-substituted diazo compounds under thermal induction tend to be resistant to dimerization. To our delight, when the xylenes solution of **1a** was heated without a metal catalyst in a sealed Schlenk tube at 100 °C for 12 hours, the formation of a product, which was highly fluorescent under UV irradiation by TLC analysis, was observed (entry 7). Elevation in the reaction temperature to 140 °C effectively improved the reaction yield to 41% (entry 8). The identity of the product **2a** was assigned according to the ^1H and ^{13}C NMR spectra and the *ortho* positions for the phenolic hydroxy and the carbomethoxy were consolidated by the phenolic proton signal resonating at 10.86 ppm, which supported the [4+2]-annulation pathway in preference to the Danheiser benzannulation. After a thorough search for the combinations of temperature and reaction time, we discovered that heating the reaction mixture at 190 °C for 30 minutes enhanced the reaction yield to 66% (entry 9). Finally, a decrease in the reactant concentration resulted in the formation of the 6*H*-benzo[*c*]chromene **2a** in 72% yield under otherwise identical conditions (entry 10).

Table 1 Optimization of the Reaction Conditions[a]



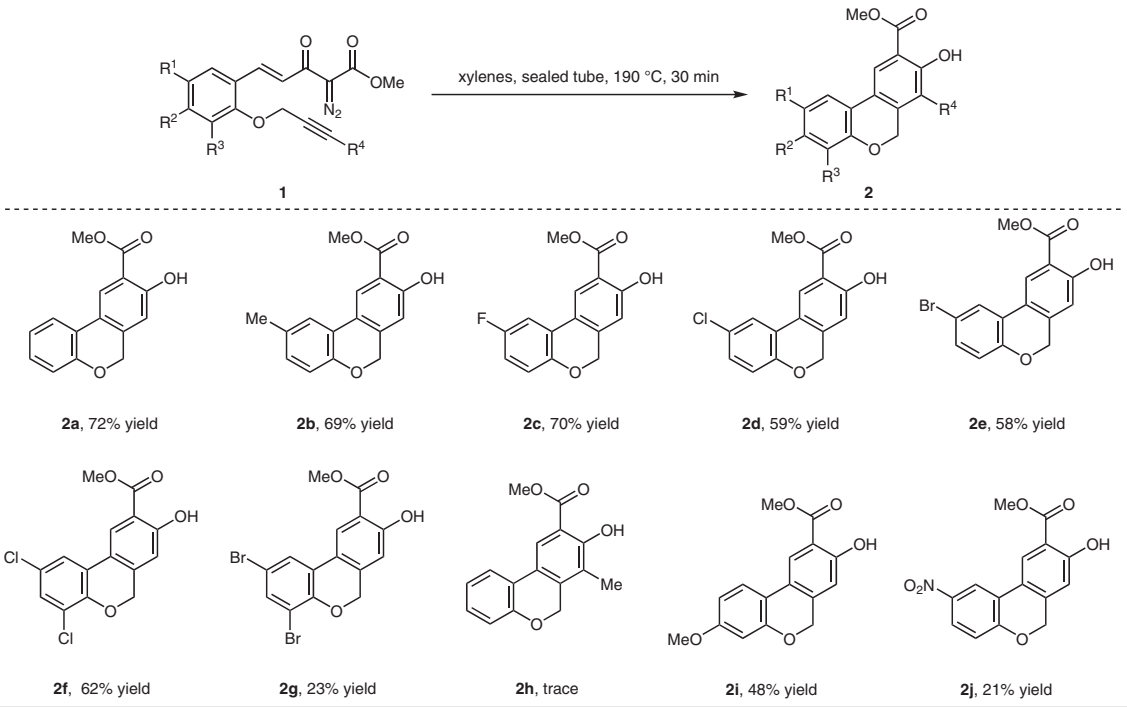
diazoacetoacetate enone **1a** — 6*H*-benzo[*c*]chromene **2a**

Entry	Catalyst (mol%)	Temp (°C)	Time (h)	Yield (%)[b]
1[c]	$Rh_2(OAc)_4$ (2.5)	60	12	complex mixture
2[c]	$Pd(OAc)_2$ (5.0)	60	12	complex mixture
3[c]	$Cu(hfacac)_2$ (5.0)	60	12	no conversion
4[c]	$Cu(OTf)_2$ (5.0)	60	12	no conversion
5[c]	AgOTf (5.0)	60	12	no conversion
6[c]	$AgSbF_6$ (5.0)	60	12	no conversion
7[d]	none	100	12	trace
8[d]	none	140	12	41
9[d]	none	190	0.5	66
10[d,e]	none	190	0.5	72

[a] The reactions were carried out with **1a** (0.50 mmol) in a pressure-resistant Schlenk tube under a nitrogen atmosphere at a concentration of 0.20 M unless otherwise noted.
[b] Isolated reaction yield.
[c] Compound **1a** (0.50 mmol) was dissolved in 1,2-DCE (1.5 mL) and the solution was added via a syringe pump over 30 min to the Schlenk tube heated at 60 °C, where the corresponding catalysts were either dissolved or suspended in 1,2-DCE (1.0 mL).
[d] Xylenes (a mixture of isomers) was used as the solvent.
[e] The reaction was performed at a concentration of 0.10 M.

Having accomplished the optimization of the reaction conditions, we sought to investigate the scope and generality of this novel [4+2]-benzannulation. As illustrated in Scheme 2, good compatibility with methyl, fluoro, chloro and bromo substituents on the aromatic rings of diazoacetoacetate enones was evident. Although the 3,5-dichloro-substituted substrate **1f** performed reasonably well, the 3,5-dibromo analogue **1g** afforded **2g** in a lower yield. We only observed the formation of **2h** in a trace amount, which may be attributed to the geometric alternation of the corresponding intermediate vinyl ketene by introducing the internal alkyne functionality. Diazoacetate enones incorporating strong electron-donating (**1i**) or electron-withdrawing (**1j**) substituents were tolerated, affording the corresponding 6*H*-benzo[*c*]chromene **2i** and **2j**, respectively, in moderate to low yields. Nonetheless, the synthetic methodology exemplified a practical synthesis of substituted 6*H*-benzo[*c*]chromenes since the reaction was highly operable and dinitrogen was released as the only byproduct.

To conclude, the development of the intramolecular benzannulation of diazoacetoacetate enones with pendant alkynes to produce 6*H*-benzo[*c*]chromenes under thermal induction has been achieved. Noteworthy features include the relative ease of operation, good functional group tolerance, and the circumvention of using a catalyst. Further applications of this methodology towards the total synthesis of related natural products and mechanistic studies are under way.



Scheme 2 Synthesis of functionalized 6*H*-benzo[c]chromenes

All chemicals and catalysts were purchased from commercial sources and were used as received unless otherwise noted. 1,2-Dichloroethane (1,2-DCE) was distilled over calcium hydride under a nitrogen atmosphere. Xylenes (a mixture of isomers) and toluene were purified by distillation from metallic sodium under a nitrogen atmosphere. Tetrahydrofuran was distilled under a nitrogen atmosphere from sodium in the presence of benzophenone. All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques. Analytical thin-layer chromatography (TLC) was conducted with silica gel 60F254 precoated plates (0.25 mm) and visualized by exposure to UV light (254 or 365 nm) or stained with anisaldehyde, ceric ammonium molybdate, or potassium permanganate followed by heating. Column chromatography was performed on silica gel (500–800 mesh) eluting with a mixture of petroleum ether (PE) and ethyl acetate (EtOAc). Nuclear magnetic resonance spectra were recorded in $CDCl_3$ with a 400 MHz spectrometer. Data for ^1H NMR spectra are reported as: chemical shift (δ, ppm), multiplicity, coupling constant (Hz), and integration. The ^1H chemical shift was referenced to the residual solvent signal (δ_H = 7.26 ppm for $CDCl_3$). Multiplicity was reported as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), m (multiplet), brs (broad singlet), etc. ^{13}C NMR spectra were recorded at 100 MHz. Data for ^{13}C NMR spectra are reported in terms of chemical shift. The ^{13}C chemical shift was referenced to the solvent signal (δ_C = 77.0 ppm for $CDCl_3$). High-resolution mass spectra were obtained with a conventional instrument equipped a TOF analyzer.

Caution: Although we have not experienced any problems handling the diazo compounds prepared and used in this publication, appropriate care should be exercised.

Preparation of 6*H*-Benzo[*c*]chromene 2; General Procedure

In a 25 mL pressure-resistant Schlenk tube charged with a magnetic stirring bar, diazoacetoacetate enone **1** (0.50 mmol) was dissolved in xylenes (5.0 mL) under a nitrogen atmosphere to provide a colorless solution. The Schlenk tube was sealed and then heated in an oil bath at 190 °C for 30 min. The evolution of nitrogen was observed and the reaction mixture became light-yellow. The reaction mixture was cooled to r.t. and concentrated under reduced pressure to afford a residue, which was purified by silica gel column chromatography to afford 6*H*-benzo[*c*]chromenes **2**.

Methyl 8-Hydroxy-6*H*-benzo[*c*]chromene-9-carboxylate (2a)

Yield: 91.7 mg (72%); white solid.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.86 (s, 1 H), 8.15 (s, 1 H), 7.69 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.21 (td, *J* = 7.8, 1.6 Hz, 1 H), 7.05 (td, *J* = 7.5, 1.3 Hz, 1 H), 6.98 (dd, *J* = 8.1, 1.3 Hz, 1 H), 6.77 (s, 1 H), 5.06 (s, 2 H), 3.99 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.22, 161.14, 153.83, 139.62, 128.78, 123.23, 122.66, 122.25, 121.94, 121.64, 117.34, 113.40, 112.12, 67.86, 52.36.

HRMS (ESI–): *m*/*z* [M – H]$^-$ calcd for $C_{15}H_{11}O_4$: 255.0657; found: 255.0659.

Methyl 8-Hydroxy-2-methyl-6*H*-benzo[*c*]chromene-9-carboxylate (2b)

Yield: 93.0 mg (69%); white solid.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.85 (s, 1 H), 8.13 (s, 1 H), 7.48 (d, *J* = 2.0 Hz, 1 H), 7.01 (dd, *J* = 8.2, 2.0 Hz, 1 H), 6.88 (d, *J* = 8.2 Hz, 1 H), 6.77 (s, 1 H), 5.02 (s, 2 H), 4.00 (s, 3 H), 2.36 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.31, 161.11, 151.73, 139.91, 131.56, 129.45, 123.18, 123.00, 121.94, 121.67, 117.06, 113.49, 112.13, 67.99, 52.40, 20.89.

HRMS (ESI–): *m*/*z* [M – H]$^-$ calcd for $C_{16}H_{13}O_4$: 269.0814; found: 269.0817.

Methyl 2-Fluoro-8-hydroxy-6*H*-benzo[*c*]chromene-9-carboxylate (2c)

Yield: 96.5 mg (70%); white solid.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.92 (s, 1 H), 8.09 (s, 1 H), 7.36 (dd, *J* = 9.2, 2.8 Hz, 1 H), 6.97–6.85 (m, 2 H), 6.79 (s, 1 H), 5.04 (s, 2 H), 4.01 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.11, 161.62, 158.22 (d, *J* = 239.2 Hz), 149.80 (d, *J* = 2.0 Hz), 139.66, 123.63, 123.16 (d, *J* = 8.3 Hz), 121.03 (d, *J* = 2.2 Hz), 118.41 (d, *J* = 8.3 Hz), 115.14 (d, *J* = 23.5 Hz), 113.57, 112.24, 108.97 (d, *J* = 24.4 Hz), 68.01, 52.50.

HRMS (ESI–): *m*/*z* [M – H]$^-$ calcd for $C_{15}H_{10}FO_4$: 273.0563; found: 273.0567.

Methyl 2-Chloro-8-hydroxy-6*H*-benzo[*c*]chromene-9-carboxylate (2d)

Yield: 86.2 mg (59%); white solid.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.92 (s, 1 H), 8.11 (s, 1 H), 7.63 (d, *J* = 2.5 Hz, 1 H), 7.14 (dd, *J* = 8.6, 2.5 Hz, 1 H), 6.91 (d, *J* = 8.6 Hz, 1 H), 6.78 (s, 1 H), 5.05 (s, 2 H), 4.01 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.08, 161.61, 152.30, 139.37, 128.40, 127.27, 123.53, 123.38, 122.42, 120.59, 118.72, 113.59, 112.30, 67.94, 52.52.

HRMS (ESI–): *m*/*z* [M – H]$^-$ calcd for $C_{15}H_{10}ClO_4$: 289.0268; found: 298.0273.

Methyl 2-Bromo-8-hydroxy-6*H*-benzo[*c*]chromene-9-carboxylate (2e)

Yield: 97.9 mg (58%); white solid.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.92 (s, 1 H), 8.10 (s, 1 H), 7.78 (d, *J* = 2.4 Hz, 1 H), 7.28 (dd, *J* = 8.6, 2.4 Hz, 1 H), 6.86 (d, *J* = 8.6 Hz, 1 H), 6.78 (s, 1 H), 5.06 (s, 2 H), 4.01 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.07, 161.60, 152.79, 139.31, 131.30, 125.33, 123.90, 123.52, 120.44, 119.15, 114.69, 113.60, 112.31, 67.90, 52.53.

HRMS (ESI–): *m*/*z* [M – H]$^-$ calcd for $C_{15}H_{10}BrO_4$: 332.9762; found: 332.9770.

Methyl 2,4-Dichloro-8-hydroxy-6*H*-benzo[*c*]chromene-9-carboxylate (2f)

Yield: 100.2 mg (62%); white solid.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.96 (s, 1 H), 8.11 (s, 1 H), 7.55 (d, *J* = 2.4 Hz, 1 H), 6.81 (s, 1 H), 5.16 (s, 2 H), 4.02 (s, 3 H) (one aromatic proton signal is missing due to overlapping with the chloroform signal).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.81, 161.89, 148.18, 138.82, 128.43, 126.92, 124.38, 123.98, 123.19, 120.88, 119.82, 113.65, 112.42, 68.26, 52.47.

HRMS (ESI–): *m*/*z* [M – H]$^-$ calcd for $C_{15}H_9Cl_2O_4$: 322.9878; found: 322.9882.

Methyl 2,4-Dibromo-8-hydroxy-6*H*-benzo[*c*]chromene-9-carboxylate (2g)

Yield: 47.0 mg (23%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.96 (s, 1 H), 8.10 (s, 1 H), 7.72 (d, *J* = 2.2 Hz, 1 H), 7.56 (d, *J* = 2.2 Hz, 1 H), 6.80 (s, 1 H), 5.15 (s, 2 H), 4.02 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.99, 162.10, 149.85, 138.98, 134.08, 124.99, 124.65, 124.18, 119.94, 114.63, 113.83, 112.63, 112.44, 68.51, 52.66.

HRMS (ESI–): *m*/*z* [M – H]$^-$ calcd for $C_{15}H_9Br_2O_4$: 412.8847; found: 412.8850.

Methyl 8-Hydroxy-3-methoxy-6*H*-benzo[*c*]chromene-9-carboxylate (2i)

Yield: 68.0 mg (48%); white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.79 (s, 1 H), 8.05 (s, 1 H), 7.59 (d, *J* = 8.6 Hz, 1 H), 6.75 (s, 1 H), 6.63 (dd, *J* = 8.6, 2.6 Hz, 1 H), 6.54 (d, *J* = 2.6 Hz, 1 H), 5.05 (s, 2 H), 3.98 (s, 3 H), 3.81 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.38, 160.56, 160.44, 155.07, 138.64, 123.57, 122.33, 122.03, 114.95, 113.41, 112.21, 109.02, 102.29, 68.23, 55.40, 52.39.

HRMS (ESI+): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{14}NaO_5$: 309.0733; found: 309.0733.

Methyl 8-Hydroxy-2-nitro-6*H*-benzo[*c*]chromene-9-carboxylate (2j)

Yield: 32.2 mg (21%); yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 11.00 (s, 1 H), 8.59 (d, *J* = 2.7 Hz, 1 H), 8.23 (s, 1 H), 8.09 (dd, *J* = 9.0, 2.7 Hz, 1 H), 7.04 (d, *J* = 9.0 Hz, 1 H), 6.80 (s, 1 H), 5.20 (s, 2 H), 4.05 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.01, 162.24, 158.90, 142.85, 138.41, 124.42, 124.26, 122.28, 119.56, 118.65, 118.11, 113.81, 112.91, 68.32, 52.73.

HRMS (ESI+): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{11}NNaO_6$: 324.0479; found: 324.0478.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0039-1690191.

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