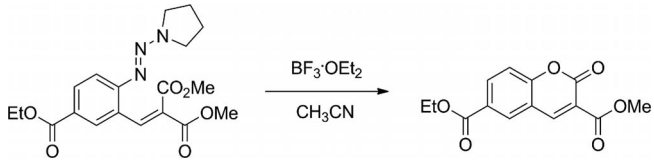
EurJOC European Journal of Organic Chemistry

Intramolecular Nucleophilic Substitution



The synthesis of coumarins through $BF_3{\cdot}OEt_2$-promoted intramolecular nucleophilic substitution has been demonstrated. The efficient synthetic methodology provides good to excellent yields of dibenzopyranones and phenanthridinones.

X. Shang, L. Xu, W. Yang, J. Zhou, M. Miao, H. Ren* **1–11**

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BF_3·OEt_2-Promoted Intramolecular Nucleophilic Substitution; Synthesis of Dibenzopyranones and Coumarins from Biaryltriazenes

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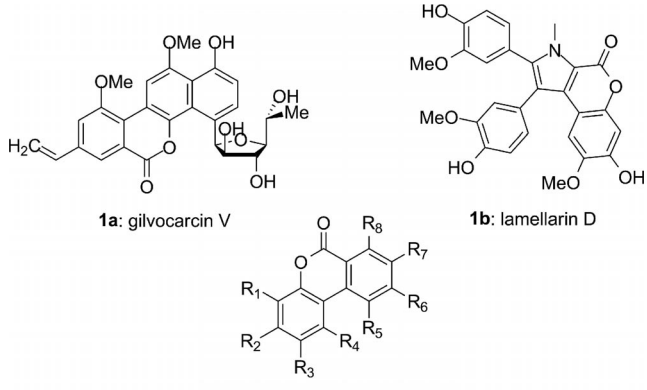
Keywords: Synthetic methods / Nucleophilic substitution / Fused-ring systems / Lactones / Lewis acids

A simple and highly efficient reaction promoted by Lewis acid has been demonstrated for the synthesis of dibenzopyranones. The metal-free annulation can tolerate a series of functional groups and also allows the synthesis of coumarins and phenanthridinones in good to excellent yields.

Introduction

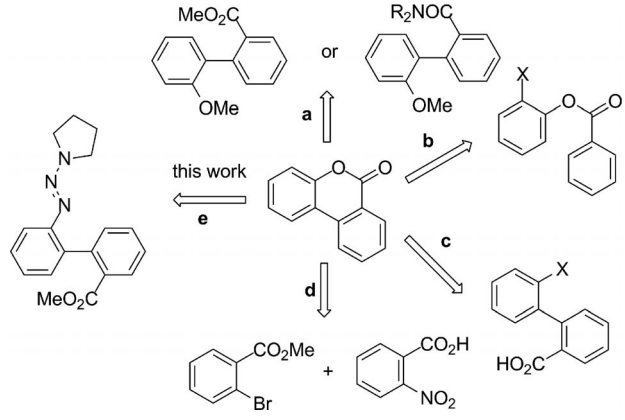
Dibenzopyranone serves as the structural core in many natural products[1] including gilvocarcin V (**1a**; Scheme 1), lamellarin D (**1b**), and other biologically active compounds (**1c**–**g**).[2] Dibenzopyranones also exist naturally in many food sources including citrus fruits, herbs, and vegetables.[3] In addition, they have been used as intermediates in the synthesis of cannabinoids[4] and several pharmaceutically interesting compounds such as androgen, progesterone, glucocorticoid receptor agonists, endothelial proliferation inhibitors, and antidyslipidemic agents.[5]



1c: $R_1 = R_3 = R_4 = R_7 = R_8 = H$, $R_2 = R_5 = R_6 = OH$, fasciculiferol
1d: $R_1 = R_4 = R_5 = R_7 = H$, $R_2 = OMe$, $R_3 = R_6 = R_8 = OH$, altenuisol
1e: $R_1 = R_3 = R_5 = R_7 = H$, $R_2 = R_6 = R_8 = OH$, $R_4 = Me$, alternariol
1f: $R_1 = R_3 = R_5 = R_6 = R_8 = H$, $R_2 = R_7 = OH$, $R_4 = Me$, autumnariol
1g: $R_1 = OMe$, $R_2 = R_8 = OH$, $R_3 = R_5 = R_6 = R_7 = H$, $R_4 = Me$, autumnariniol

Scheme 1. Examples of natural products containing the dibenzopyranone core.

Several synthetic methodologies are available for the synthesis of dibenzopyranone derivatives. The most popular method is BBr_3-mediated lactonization from the corresponding methoxy-biphenylcarboxylates and methoxy-biphenylcarboxamides (Scheme 2, Path a).[6] The Pd-catalyzed intramolecular direct arylation from the halo-substituted phenyl benzoates provides an alternative pathway for the construction of phenyl benzoate derivatives (Path b).[7] Copper-mediated/microwave-assisted C_{aryl}–$O_{carboxylic}$ coupling is another good method with which to synthesize dibenzopyranone cores (Path c).[8] Alternatively, a highly selective palladium bis(acetoacetonate)/copper(I) chloride [$Pd(acac)_2$/CuCl] catalytic system also provides an efficient method with which to synthesize dibenzopyranones through a decarboxylative cross-coupling and lactonization sequence (Path d).[9] More recently, ruthenium-catalyzed cyclotrimerization of aryl diynes,[10] domino reactions of 1,3-bis-silyl enol ethers with benzopyrylium triflates,[11]



Scheme 2. Approaches used for the synthesis of the dibenzopyranone core.

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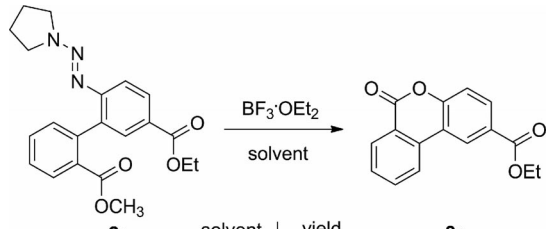
Diels–Alder or inverse electron-demand Diels–Alder reaction,[12] and *o*-phenylbenzoic acid with DIH under irradiation with a tungsten lamp,[13] have been reported.

Theoretically, phenyl cations can be used directly as electrophiles to construct aromatic compounds, but their application is limited owing to their instability.[14] Triazenes are useful and versatile compounds. They have been studied for their anticancer potential[15] and used as protecting groups in combinatorial chemistry[16] and natural product synthesis,[17] and have been incorporated into polymer[18] and oligomer[19] syntheses. Triazenes can also be transferred to various functional groups under appropriate conditions.[20k] Moreover, triazenes have been applied in organic synthesis,[20] organometallic chemistry,[21] as chemodosimeters,[22] and in pharmacology.[23] Triazene functionality (ArN=N–NR_2) can be viewed as a synthetic equivalent of the diazonium salt. This allows the reactive diazonium salt to be replaced by the more stable triazine moiety, thus making reactions easier to handle. In previous work, we reported the Lewis acid promoted synthesis of carbazoles, dibenofurans, dihydrobenzofurans, dibenzothiophenes, and polycyclic aromatic hydrocarbons from biaryl triazenes.[24] Here, we describe the annulation reaction of triazene bearing an methyl ester group, leading to dibenzopyranone derivatives through Lewis acid promoted intramolecular nucleophilic substitution (Scheme 2, Path e).

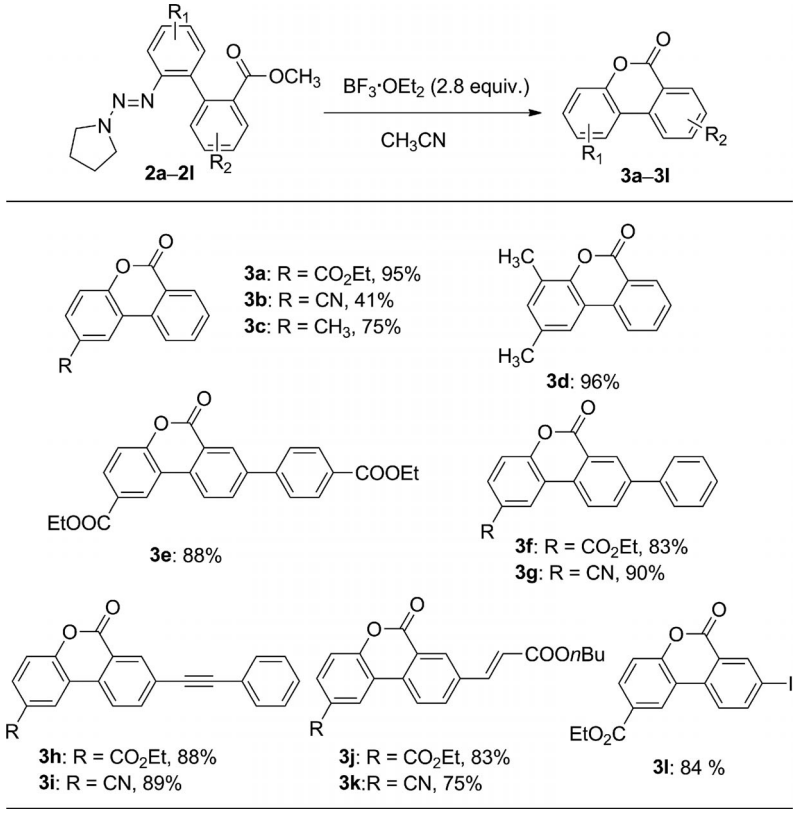
Results and Discussion

Initially, our research started with the model reaction of **2a**, which was treated with $BF_3{\cdot}OEt_2$ (2.8 equiv.) in CH_2Cl_2 at 40 °C; under these conditions, product **3a** was obtained in 70% yield. To improve the yield of the reaction, a range of solvents were screened (Scheme 3). The yield decreased greatly when the reaction was carried out in tetra-



solvent	yield
DCM	70%
THF	< 10%
DMF	< 10%
MeOH	75%
CH_3CN	95%

Scheme 3. Optimization of the reaction conditions. *Reagents and conditions:* triazene ester (0.5 mmol), $BF_3{\cdot}OEt_2$ (2.8 equiv.), solvent (20 mL), 40 °C, 4 h, yields refer to isolated product after flash column chromatography.

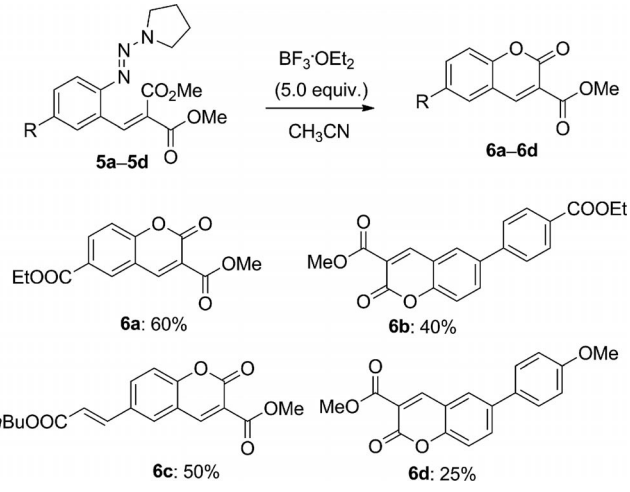


Scheme 4. Lactonization of triazene esters promoted by $BF_3{\cdot}OEt_2$. *Reagents and conditions:* triazene ester (0.5 mmol), $BF_3{\cdot}OEt_2$ (2.8 equiv.), CH_3CN (20 mL), 40 °C, 4 h, yields refer to isolated products after flash column chromatography.

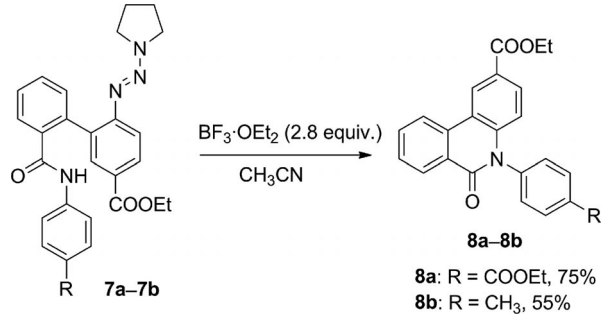
hydrofuran (THF) or *N*,*N*-dimethylformamide (DMF), whereas the use of MeOH enhanced the yield of the product to 75%. When the reaction was carried out in CH_3CN at 40 °C, the yield improved to 95%.

To examine the general applicability of this methodology in the synthesis of dibenzopyranones, lactonization of various diaryltriazene esters with $BF_3{\cdot}OEt_2$ were conducted; the results are summarized in Scheme 4. The annulation of triazene esters with a range of functional groups gave the corresponding dibenzopyranones in good to excellent yields (**3a**–**l**; Scheme 4). Functional groups such as ester, cyano, alkenyl and alkynyl all tolerated the reaction conditions (**3a**, **3b**, and **3h**–**k**), even the iodo group was not affected in the $BF_3{\cdot}OEt_2$ promoted process (**3l**). Furthermore, steric bulk near the reaction center had no influence on the yield of the product (**3d**).

We then extended the reaction to synthesize coumarins from a range of triazene dimethyl malonates. Under the optimized conditions, **5a** was partially transformed into coumarin **6a**. When the amount of $BF_3{\cdot}OEt_2$ was increased to 5.0 equivalents and the reaction time was extended to overnight, the reaction went to completion. However, if only one methyl ester group was substituted on the alkene skeleton of **5a**, the coumarin was not formed because of the *trans* conformation of the alkene. Biphenyl (**6b** and **6d**) and alkenyl (**6c**) conjugated coumarins could also be formed under the new conditions (Scheme 5). This method was also expanded to the synthesis of phenanthridinones. When substrates **7a** and **7b** were treated with 2.8 equivalents of $BF_3{\cdot}OEt_2$, 75 and 55% yield of the corresponding phenanthridinones **8a** and **8b** were obtained, respectively (Scheme 6).

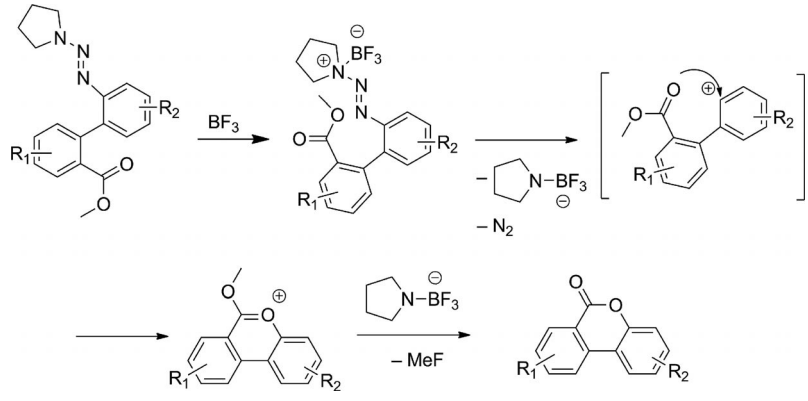


Scheme 5. Application of the annulation for the synthesis of coumarins. *Reagents and conditions:* triazene dimethyl ester (0.5 mmol), $BF_3{\cdot}OEt_2$ (5.0 equiv.), CH_3CN (20 mL), 40 °C, overnight, yields refer to isolated products after flash column chromatography.

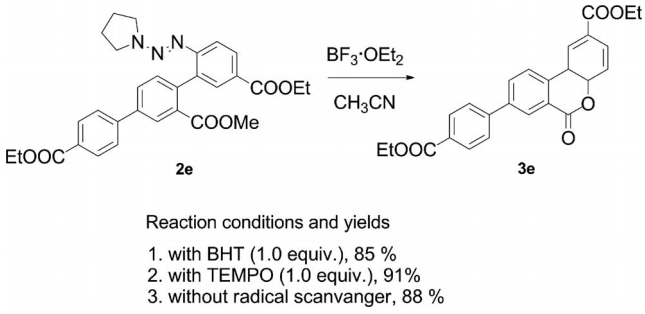


Scheme 6. Application of the annulation for the synthesis of phenanthridinones. *Reagents and conditions:* triazene amide (0.5 mmol), $BF_3{\cdot}OEt_2$ (2.8 equiv.), CH_3CN (20 mL), 40 °C, overnight, yields refer to isolated products after flash column chromatography.

With respect to the mechanism, the terminal nitrogen atom and Lewis acid probably form a complex that is essential to enhance the cleavage of the sp^2 C–N bond and subsequent reactions through either aryl cations or aryl radicals (Scheme 7).[25] The methyl ester group serves as an nucleophile to attack the aryl group on the unsaturated nitrogen atom and forms the target product dibenzopyranone. To investigate the mechanism of the reaction, radical scavengers such as BHT (butylated hydroxytoluene) and TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) (Scheme 8) were added to the standard reaction systems, but the yield of the reaction was not affected. We therefore conclude that the formation of an aryl cation intermediate is favored in this reaction.



Scheme 7. Proposed mechanism for the annulation reaction.



Scheme 8. The presence of radical scavengers has no effect on the reaction.

Conclusions

We have developed an efficient method for the lactonization of triazene esters promoted by $BF_3{\cdot}OEt_2$. This approach works well to form various dibenzopyranones with moderate to excellent yield under mild and transition-metal-free conditions. Moreover, the approach has been successfully applied to form coumarins and phenanthridinones. Further extensions of this methodology are being investigated in our laboratory.

Experimental Section

General: THF was dried by sodium and freshly distilled. CH_2Cl_2 was dried with CaH_2 and freshly distilled. DMF was dried with CaH_2 and distilled under reduced pressure. The other materials and solvents were purchased from commercial suppliers and used without additional purification. NMR spectra were recorded with Bruker Avance spectrometers operating at 400 or 500 MHz for ^1H, and at 100 or 125 MHz for ^{13}C using TMS as internal standard. Chemical shifts are given relative to $CDCl_3$ (δ = 7.26 ppm for ^1H NMR, 77.0 ppm for ^{13}C NMR). Mass spectroscopy data of the products were collected with an HRMS-TOF instrument or a low-resolution MS instrument using EI ionization. IR spectra were recorded with a Bruker ATR-FTIR spectrometer. Melting points were measured with an WRS-1A digital point apparatus.

General Procedure for the Synthesis of Aryltriazenes 2a–k: Synthesized from the corresponding substituted phenyl halide (3 mmol) and substituted boronic acid (1.2 equiv.) in the presence of $[Pd(PPh_3)_4]$ (0.05 equiv.) and Cs_2CO_3 (2.0 equiv.) in 1,4-dioxane (6 mL) and water (1.5 mL). The mixture was stirred at 100 °C overnight under a nitrogen atmosphere in a screw-cap vial. Upon completion of the reaction (determined by TLC analysis), the reaction was diluted with ethyl acetate and washed with water. The organic fractions were dried with anhydrous Na_2SO_4 and concentrated under vacuo. Purification was carried out by flash chromatography to afford the desired product.

3′-Ethyl 2-Methyl (*E*)-6′-(Pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-2,3′-dicarboxylate (2a): Yield 1.05 g (92%); yellow solid; m.p. 105–107 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.03 (s, 1 H, ArH), 8.00 (d, J = 6.8 Hz, 1 H, ArH), 7.86 (d, J = 6.4 Hz, 1 H, ArH), 7.54 (t, J = 6.0 Hz, 1 H, ArH), 7.45 (d, J = 6.8 Hz, 1 H, ArH), 7.39 (d, J = 4.8 Hz, 2 H, ArH), 4.37 (q, J = 5.6 Hz, 2 H, CH_3CH_2O), 3.79–3.91 (m, 2 H, CH_2N), 3.48 (s, 3 H, CH_3O), 3.18–3.48 (m, 2 H, CH_2N), 1.85–2.02 (m, 4 H, 2 × CH_2CH_2N), 1.39 (t, J = 6.0 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 166.7, 151.7, 139.8, 135.9, 132.4, 131.4, 131.3, 131.0, 129.6, 129.0, 126.9, 126.5, 115.8, 60.7, 51.7, 51.1, 46.5, 23.9, 23.4, 14.4 ppm. IR (thin film): $\tilde{\nu}$ = 3077, 2976, 2877, 1703, 1289, 1239, 1113 cm^{-1}. MS (EI): m/z (%) = 381 (15) $[M]^+$, 336 (7), 311 (12), 283 (100), 255 (80), 240 (26). HRMS (EI-TOF): m/z calcd. for $C_{21}H_{23}N_3O_4$ $[M]^+$ 381.1690; found 381.1690.

Methyl (*E*)-5′-Cyano-2′-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-2-carboxylate (2b): Yield 952 mg (95%); yellow solid; m.p. 88–90 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, J = 6.0 Hz, 1 H, ArH), 7.59 (d, J = 1.6 Hz,1 H, ArH), 7.52–7.58 (m, 2 H, ArH), 7.49 (d, J = 6.4 Hz, 1 H, ArH), 7.37–7.44 (m, 1 H, ArH), 7.29 (d, J = 6.4 Hz, 1 H, ArH), 3.82–3.92 (m, 2 H, CH_2N), 3.47 (s, 3 H, CH_3O), 3.20–3.44 (m, 2 H, CH_2N), 1.83–2.02 (m, 4 H, $2CH_2CH_2N$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 151.5, 138.6, 136.9, 133.3, 132.2, 131.9, 131.6, 131.0, 129.2, 127.4, 119.6, 116.6, 107.5, 51.8, 51.2, 46.7, 23.8, 23.3 ppm. IR (thin film): $\tilde{\nu}$ = 3068, 2948, 2875, 2220, 1718, 1596, 1382, 1265, 1120 cm^{-1}. MS (EI): m/z (%) = 334 (11) $[M]^+$, 277 (4), 264 (17), 236 (100), 221 (64), 193 (32). HRMS (EI-TOF): m/z calcd. for $C_{19}H_{18}N_4O_2$ $[M]^+$ 334.1430; found 334.1432.

Methyl (*E*)-5′-Methyl-2′-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-2-carboxylate (2c): Yield 368 mg (38%); brown oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.85 (dd, J = 8.0, 1.2 Hz, 1 H, ArH), 7.50–7.55 (m, 1 H, ArH), 7.36–7.41 (m, 2 H, ArH), 7.31 (d, J = 8.4 Hz, 1 H, ArH), 7.17 (s, 1 H, ArH), 7.11–7.15 (m, 1 H, ArH), 3.54 (s, 3 H, CH_3O), 3.00–4.00 (m, 4 H, 2 × CH_2N), 2.41 (s, 3 H, CH_3), 1.83–1.97 (m, 4 H, 2 × CH_2CH_2N) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.8, 145.8, 140.6, 135.7, 134.5, 132.5, 131.3, 131.1, 130.0, 128.8, 128.7, 126.4, 116.0, 51.7, 31.5, 23.7, 22.6, 21.0, 14.1 ppm. IR (thin film): $\tilde{\nu}$ = 3057, 2947, 2870, 1715, 1419, 1318, 1289, 1212, 1123, 1085 cm^{-1}. MS (EI): m/z (%) = 323 (15) $[M]^+$, 253 (11), 225 (100), 210 (96), 181 (30), 152 (14). HRMS (EI-TOF): m/z calcd. for $C_{19}H_{21}N_3O_2$ $[M]^+$ 323.1634; found 323.1637.

Methyl (*E*)-3′,5′-Dimethyl-2′-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-2-carboxylate (2d): Yield 597 mg (59%); brown oil. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.76 (dd, J = 6.4, 1.2 Hz, 1 H, ArH), 7.42–7.45 (m, 1 H, ArH), 7.27–7.31 (m, 2 H, ArH), 6.99 (s, 1 H, ArH), 6.93 (s, 1 H, ArH), 3.59 (s, 3 H, CH_3O), 3.30–3.50 (m, 4 H, 2 × CH_2N), 2.34 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 1.80–1.97 (m, 4 H, 2 × CH_2CH_2N) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 145.3, 142.2, 134.6, 133.6, 131.8, 131.6, 131.0, 130.9, 129.6, 128.9, 128.0, 126.0, 51.7, 31.6, 23.7, 22.6, 20.9, 18.8, 14.1 ppm. IR (thin film): $\tilde{\nu}$ = 3062, 2948, 2869, 1714, 1424, 1322, 1290, 1251, 1121 cm^{-1}. MS (EI): m/z (%) = 337 (14) $[M]^+$, 267 (6), 239 (100), 224 (93), 209 (28), 181 (18). HRMS (EI-TOF): m/z calcd. for $C_{20}H_{23}N_3O_2$ $[M]^+$ 337.1790; found 337.1790.

3,4′′-Diethyl 2′-Methyl (*E*)-6-(Pyrrolidin-1-yldiazenyl)-[1,1′:4′,1′′-terphenyl]-2′,3,4′′-tricarboxylate (2e): Yield 1.45 g (91%); yellow solid; m.p. 106–108 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.11–8.16 (m, 3 H, ArH), 8.07 (s, 1 H, ArH), 8.01 (d, J = 8.4 Hz, 1 H, ArH), 7.82 (dd, J = 8.4, 1.6 Hz, 1 H, ArH), 7.75 (d, J = 8.4 Hz, 2 H, ArH), 7.49 (t, J = 8.4 Hz, 2 H, ArH), 4.32–4.45 (m, 4 H, 2 × CH_3CH_2O), 3.82–3.95 (m, 2 H, CH_2N), 3.51 (s, 3 H, CH_3O), 3.20–3.50 (m, 2 H, CH_2N), 1.85–2.02 (m, 4 H, 2 × CH_2CH_2N), 1.34–1.46 (m, 6 H, 2 × CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.5, 166.6, 166.3, 151.8, 144.0, 139.6, 138.5, 135.3, 133.1, 132.0, 131.0, 130.1, 129.8, 129.8, 129.5, 127.7, 126.8, 126.6, 115.9, 61.0, 60.7, 51.8, 51.1, 46.6, 23.8, 23.4, 14.3, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3062, 2978, 2874, 1709, 1603, 1232, 1103 cm^{-1}. MS (EI): m/z (%) = 529 (16) $[M]^+$, 484 (13), 431 (100), 403 (36), 385 (26), 343 (29). HRMS (EI-TOF): m/z calcd. for $C_{30}H_{31}N_3O_6$ $[M]^+$ 529.2213; found 529.2219.

3-Ethyl 2′-Methyl (*E*)-6-(Pyrrolidin-1-yldiazenyl)-[1,1′:4′,1′′-terphenyl]-2′,3-dicarboxylate (2f): Yield 1.262 g (92%); yellow solid; m.p. 70–72 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.13 (d, J = 1.6 Hz, 1 H, ArH), 8.09 (d, J = 2.4 Hz, 1 H, ArH), 8.01 (dd, J = 8.4, 2.0 Hz, 1 H, ArH), 7.80 (dd, J = 8.0, 2.0 Hz, 1 H, ArH), 7.69 (d, J = 7.2 Hz, 2 H, ArH), 7.43–7.51 (m, 4 H, ArH), 7.36–7.41 (m, 1 H, ArH), 4.39 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 3.80–3.95 (m, 2 H, CH_2N), 3.52 (s, 3 H, CH_3O), 3.20–3.50 (m, 2 H, CH_2N), 1.86–2.02 (m, 4 H, 2 × CH_2CH_2N), 1.41 (t, J = 7.2 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.6, 166.6, 151.8, 139.8, 139.7, 138.7, 135.6, 132.9, 131.9, 131.0, 129.7, 129.6, 128.8, 127.7, 127.6, 127.0, 126.6, 115.9, 60.7, 51.7, 51.1, 46.6, 23.8, 23.4, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3057, 2977, 2879, 1708, 1306, 1231, 1104 cm^{-1}. MS (EI): m/z (%) = 457 (11) [M]$^+$, 359 (100), 331 (28), 316 (26), 299 (19), 215 (16). HRMS (EI-TOF): m/z calcd. for $C_{27}H_{27}N_3O_4$ [M]$^+$ 457.2002; found 457.2001.

Methyl (*E*)-5-Cyano-2-(pyrrolidin-1-yldiazenyl)-[1,1′:4′,1′′-terphenyl]-2′-carboxylate (2g): Yield 1.182 g (96%); yellow solid; m.p 85–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (d, J = 2.0 Hz, 1 H, ArH), 7.79 (dd, J = 8.0, 2.0 Hz, 1 H, ArH), 7.69 (d, J = 7.6 Hz, 2 H, ArH), 7.64 (d, J = 2.0 Hz, 1 H, ArH), 7.58 (dd, J = 8.4, 1.6 Hz, 1 H, ArH), 7.45–7.53 (m, 3 H, ArH), 7.35–7.43 (m, 2 H, ArH), 3.82–3.94 (m, 2 H, CH_2N), 3.54 (s, 3 H, CH_3O), 3.22–3.53 (m, 2 H, CH_2N), 1.85–2.04 (m, 4 H, 2 × CH_2CH_2N) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.3, 151.7, 140.2, 139.5, 137.4, 136.6, 133.3, 132.8, 131.9, 131.5, 129.8, 128.8, 127.8, 127.8, 127.0, 119.6, 116.7, 107.5, 51.8, 51.3, 46.8, 23.8, 23.3 ppm. IR (thin film): $\tilde{\nu}$ = 3067, 2948, 2875, 2221, 1719, 1410, 1309, 1238, 1088 cm^{-1}. MS (EI): m/z (%) = 410 (14) [M]$^+$, 340 (18), 312 (100), 297 (66), 269 (19), 240 (18). HRMS (EI-TOF): m/z calcd. for $C_{25}H_{22}N_4O_2$ [M]$^+$ 410.1743; found 410.1740.

3′-Ethyl (*E*)-2-Methyl-4-(phenylethynyl)-6′-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-2,3′-dicarboxylate (2h): Yield 1.083 g (75%); yellow solid; m.p. 126–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03–8.05 (m, 2 H, ArH), 8.00 (dd, J = 8.4, 2.4 Hz, 1 H, ArH), 7.70 (dd, J = 7.6, 2.0 Hz, 1 H, ArH), 7.52–7.58 (m, 2 H, ArH), 7.47 (d, J = 8.4 Hz, 1 H, ArH), 7.33–7.41 (m, 4 H, ArH), 4.38 (q, J = 6.8 Hz, 2 H, CH_3CH_2O), 3.82–3.93 (m, 2 H, CH_2N), 3.51 (s, 3 H, CH_3O), 3.21–3.49 (m, 2 H, CH_2N), 1.85–2.04 (m, 4 H, 2 × CH_2CH_2N), 1.40 (t, J = 7.2 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.9, 166.6, 151.7, 139.7, 135.2, 134.0, 132.7, 132.2, 131.6, 131.4, 130.9, 129.9, 128.4, 128.3, 126.5, 122.9, 122.0, 115.8, 90.3, 88.5, 60.7, 51.8, 51.1, 46.6, 23.8, 23.4, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3072, 2969, 2259, 1709, 1392, 1230, 1103 cm^{-1}. MS (EI): m/z (%) = 481 (16) [M]$^+$, 383 (100), 355 (28), 340 (41). HRMS (EI-TOF): m/z calcd. for $C_{29}H_{27}N_3O_4$ [M]$^+$ 481.2002; found 481.2009.

Methyl (*E*)-5′-Cyano-4-(phenylethynyl)-2′-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-2-carboxylate (2i): Yield 1.082 g (83%); yellow solid; m.p. 161–164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.05 (d, J = 1.2 Hz, 1 H, ArH), 7.69 (dd, J = 8.0, 1.6 Hz, 1 H, ArH), 7.48–7.61 (m, 5 H, ArH), 7.33–7.39 (m, 3 H, ArH), 7.29 (d, J = 7.2 Hz, 1 H, ArH), 3.82–3.94 (m, 2 H, CH_2N), 3.54 (s, 3 H, CH_3O), 3.20–3.50 (m, 2 H, CH_2N), 1.86–2.04 (m, 4 H, 2 × CH_2CH_2N) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 151.5, 138.4, 136.3, 134.2, 133.1, 132.5, 132.3, 132.1, 131.6, 131.1, 131.0, 128.5, 128.4, 122.8, 122.6, 119.5, 116.6, 107.5, 90.7, 88.2, 51.9, 51.3, 46.8, 23.8, 23.3 ppm. IR (thin film): $\tilde{\nu}$ = 3043, 2947, 2884, 2218, 1710, 1596, 1383, 1306, 1266 cm^{-1}. MS (EI): m/z (%) = 434 (21) [M]$^+$, 336 (100), 321 (98), 293 (28), 264 (29). HRMS (EI-TOF): m/z calcd. for $C_{27}H_{22}N_4O_2$ [M]$^+$ 434.1743; found 434.1743.

3′-Ethyl 2-Methyl 4-[(*E*)-3-Butoxy-3-oxoprop-1-en-1-yl]-6′-[(*E*)-pyrrolidin-1-yldiazenyl]-1,1′-biphenyl-2,3′-dicarboxylate (2j): Yield 472 mg (31%); brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (s, 2 H, ArH), 7.99 (dd, J = 8.4, 2.0 Hz, 1 H, ArH), 7.66–7.76 (m, 2 H, ArH), 7.46 (d, J = 8.4 Hz, 1 H, ArH), 7.42 (d, J = 7.6 Hz, 1 H, ArH), 6.54 (d, J = 16.0 Hz, 1 H, C=C*H*), 4.37 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 4.22 (t, J = 6.8 Hz, 2 H, CH_2CH_2O), 3.80–3.95 (m, 2 H, CH_2N), 3.49 (s, 3 H, CH_3O), 3.13–3.50 (m, 2 H, CH_2N), 1.85–2.02 (m, 4 H, 2 × CH_2CH_2N), 1.65–1.72 (m, 2 H, $CH_2CH_2CH_2O$), 1.38–1.50 (m, 5 H, $CH_3CH_2CH_2CH_2O$), 0.96 (t, J = 7.2 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.1, 166.8, 166.5, 151.7, 143.2, 141.6, 135.1, 133.1, 133.1, 131.9, 130.8, 130.5, 129.9, 128.6, 126.5, 119.0, 115.8, 64.4, 60.7, 51.8, 51.1, 46.6, 30.7, 23.8, 23.4, 19.1, 14.3, 13.7 ppm. IR (thin film): $\tilde{\nu}$ = 3068, 2960, 2874, 1710, 1638, 1394, 1309, 1234, 1171, 1105 cm^{-1}. MS (EI): m/z (%) = 507 (8) [M]$^+$, 409 (100), 262 (50), 183 (35). HRMS (EI-TOF): m/z calcd. for $C_{28}H_{33}N_3O_2$ [M]$^+$ 507.2369; found 507.2372.

Methyl 4-[(*E*)-3-butoxy-3-oxoprop-1-en-1-yl]-5′-cyano-2′-[(*E*)-pyrrolidin-1-yldiazenyl]-1,1′-biphenyl-2-carboxylate (2k): Yield 1.091 g (79%); yellow solid; m.p. 123–124 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 1.6 Hz, 1 H, ArH), 7.65–7.75 (m, 2 H, ArH), 7.53–7.61 (m, 2 H, ArH), 7.49 (d, J = 8.4 Hz, 1 H, ArH), 7.33 (d, J = 8.0 Hz, 1 H, ArH), 6.54 (d, J = 16.0 Hz, 1 H, C*H*=C), 4.22 (t, J = 6.8 Hz, 2 H, CH_3CH_2O), 3.81–3.92 (m, 2 H, CH_2N), 3.52 (s, 3 H, CH_3O), 3.18–3.48 (m, 2 H, CH_2N), 1.86–2.02 (m, 4 H, 2 × CH_2CH_2N), 1.63–1.71 (m, 2 H, $CH_2CH_2CH_2O$), 1.38–1.49 (m, 2 H, $CH_2CH_2CH_2O$), 0.96 (t, J = 7.2 Hz, 3 H, $CH_3CH_2CH_2CH_2O$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7, 166.7, 151.5, 142.9, 140.3, 136.1, 133.7, 133.1, 133.0, 132.2, 131.6, 130.7, 128.7, 119.5, 119.4, 116.6, 107.6, 64.5, 51.9, 51.3, 46.8, 30.7, 23.8, 23.3, 19.1, 13.7 ppm. IR (thin film): $\tilde{\nu}$ = 3087, 2950, 2221, 1729, 1702, 1411, 1309, 1259, 1193, 1085 cm^{-1}. MS (EI): m/z (%) = 460 (26) [M]$^+$, 390 (14), 362 (100), 306 (76), 291 (15), 274 (26). HRMS (EI-TOF): m/z calcd. for $C_{26}H_{28}N_4O_4$ [M]$^+$ 460.2111; found 460.2108.

3′-Ethyl 2-Methyl (*E*)-4-Iodo-6′-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-2,3′-dicarboxylate (2l): The substituted aniline (10 mmol, 1.0 equiv.) was dissolved in CH_3CN (10 mL) at room temperature, then concentrated hydrochloric acid (4 mL, 50 mmol, 5.0 equiv.) was added to the mixture. The solution was stirred and cooled to –10 °C. After 15 min, a solution of $NaNO_2$ (10.5 mmol, 1.05 equiv.) in cold water (10 mL) was added dropwise. The resulting solution of the diazonium salt was stirred for 2 h and then potassium iodide solution (1.2 equiv.) in water (12.4 mL) was slowly added to the mixture, which was then warmed to room temperature and stirred for 2 h. After completion (reaction monitored by TLC), the reaction mixture was extracted with ethyl acetate. The organic layer was dried with anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by silica gel chromatography to give pure product **2l** (1.014 g, 20%) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, J = 1.6 Hz, 1 H, ArH), 7.95–8.01 (m, 2 H, ArH), 7.86 (dd, J = 8.4, 1.6 Hz, 1 H, ArH), 7.44 (d, J = 8.4 Hz, 1 H, ArH), 7.11 (d, J = 8.0 Hz, 1 H, ArH), 4.37 (q, J = 6.8 Hz, 2 H, CH_3CH_2O), 3.81–3.93 (m, 2 H, CH_2N), 3.48 (s, 3 H, CH_3O), 3.18–3.45 (m, 2 H, CH_2N), 1.85–2.02 (m, 4 H, 2 × CH_2CH_2N), 1.39 (t, J = 6.8 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 166.5, 151.6, 140.2, 139.4, 137.6, 134.8, 134.1, 133.0, 130.8, 129.9, 126.5, 115.9, 91.8, 60.7, 51.9, 51.1, 46.6, 23.8, 23.4, 14.3 ppm. IR (thin film):$\tilde{\nu}$ = 3057, 2918, 2850, 1704, 1435, 1259, 1230, 1101, 1031 cm^{-1}. MS (EI): m/z (%) = 507 (8) [M]$^+$, 409 (100), 381 (54), 366 (26), 349 (23). HRMS (EI-TOF): m/z calcd. for $C_{21}H_{22}IN_3O_4$ [M]$^+$ 507.0655; found 507.0655.

General Procedure for the Synthesis of Dibenzopyranones 3a–l: Boron trifluoride–diethyl ether (2.8 equiv.) was added dropwise to

a stirred solution of **2** (0.5 mmol) in the anhydrous CH_3CN (20 mL) at 40 °C. The mixture was stirred for 4 h. Upon completion of the reaction (determined by TLC analysis), the mixture was washed with $NaHCO_3$ and extracted with ethyl acetate. The combined organic extracts were dried with anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The product was purified by column chromatography.

Ethyl 6-Oxo-6*H*-benzo[*c*]chromene-2-carboxylate (3a): Yield 128 mg (95%); white solid; m.p. 134–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.76 (d, J = 1.2 Hz, 1 H, ArH), 8.40 (d, J = 6.4 Hz, 1 H, ArH), 8.21 (d, J = 6.4 Hz, 1 H, ArH), 8.13 (dd, J = 6.8, 1.2 Hz, 1 H, ArH), 7.87 (t, J = 7.0 Hz, 1 H, ArH), 7.63 (t, J = 7.0 Hz, 1 H, ArH), 7.39 (d, J = 6.8 Hz, 1 H, ArH), 4.44 (q, J = 5.6 Hz, 2 H, CH_3CH_2O), 1.44 (t, J = 5.2 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5, 160.5, 154.1, 135.1, 134.1, 131.4, 130.6, 129.4, 126.8, 124.9, 122.0, 121.1, 117.9, 117.9, 61.4, 14.4 ppm. IR (thin film): $\tilde{\nu}$ = 3062, 2973, 2876, 1719, 1410, 1309, 1239 cm^{-1}. MS (EI): m/z (%) = 268 (83) $[M]^+$, 253 (10), 240 (47), 223 (100), 195 (10), 167 (34), 139 (60). HRMS (EI-TOF): m/z calcd. for $C_{16}H_{12}O_4$ $[M]^+$ 268.0736; found 268.0738.

6-Oxo-6*H*-benzo[*c*]chromene-2-carbonitrile (3b): Yield 46 mg (41%); white solid; m.p. 256–257 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (d, J = 6.0 Hz, 1 H, ArH), 8.40 (s, 1 H, ArH), 8.13 (d, J = 6.4 Hz, 1 H, ArH), 7.93 (t, J = 7.0 Hz, 1 H, ArH), 7.76 (d, J = 6.8 Hz, 1 H, ArH), 7.71 (t, J = 6.4 Hz, 1 H), 7.48 (d, J = 6.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 153.7, 135.5, 133.4, 132.8, 130.9, 130.3, 127.7, 121.9, 121.3, 119.2, 119.2, 118.0, 108.7 ppm. IR (thin film): $\tilde{\nu}$ = 3087, 2923, 2859, 2225, 1731, 1606, 1292, 1265, 1242, 1067, 1031 cm^{-1}. MS (EI): m/z (%) = 221 (100) $[M]^+$, 193 (42), 164 (26), 138 (9). HRMS (EI-TOF): m/z calcd. for $C_{14}H_7NO_2$ $[M]^+$ 221.0477; found 221.0476.

2-Methyl-6*H*-benzo[*c*]chromen-6-one (3c): Yield 79 mg (75%); white solid; m.p. 123–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (dd, J = 6.0, 0.8 Hz, 1 H, ArH), 8.09 (d, J = 6.4 Hz, 1 H, ArH), 7.78–7.85 (m, 2 H, ArH), 7.54–7.60 (m, 1 H, ArH), 7.21–7.28 (m, 2 H, ArH), 2.45 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.3, 149.3, 134.8, 134.7, 134.1, 131.3, 130.5, 128.7, 122.7, 121.6, 121.2, 117.6, 117.4, 21.1 ppm. IR (thin film): $\tilde{\nu}$ = 3057, 2920, 2869, 1717, 1267, 1211, 1073, 1037 cm^{-1}. MS (EI): m/z (%) = 210 (100) $[M]^+$, 181 (43), 152 (22). HRMS (EI-TOF): m/z calcd. for $C_{14}H_{10}O_2$ $[M]^+$ 210.0681; found 210.0682.

2,4-Dimethyl-6*H*-benzo[*c*]chromen-6-one (3d): Yield 108 mg (96%); white solid; m.p. 173–175 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.36 (dd, J = 8.0, 0.8 Hz, 1 H, ArH), 8.05 (d, J = 8.4 Hz, 1 H, ArH), 7.73–7.79 (m, 1 H, ArH), 7.62 (s, 1 H, ArH), 7.53 (t, J = 7.6 Hz, 1 H, ArH), 7.11 (s, 1 H, ArH), 2.42 (s, 3 H, CH_3), 2.40 (s, 3 H, CH_3) ppm. ^{13}C NMR (100 Hz, $CDCl_3$): δ = 161.3, 147.6, 135.1, 134.5, 133.3, 132.7, 130.4, 128.4, 126.5, 121.7, 121.0, 120.2, 117.2, 21.0, 15.8 ppm. IR (thin film): $\tilde{\nu}$ = 3082, 2920, 2859, 1714, 1316, 1123, 1072 cm^{-1}. MS (EI): m/z (%) = 224 (100) $[M]^+$, 209 (30), 181 (21), 165 (17). HRMS (EI-TOF): m/z calcd. for $C_{15}H_{12}O_2$ $[M]^+$ 224.0837; found 224.0834.

Ethyl 8-(4-Ethoxycarbonylphenyl)-6-oxo-6*H*-benzo[*c*]chromene-2-carboxylate (3e): Yield 183.1 mg (88%); white solid; m.p. 171–174 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70 (d, J = 2.0 Hz, 1 H, ArH), 8.54 (d, J = 1.6 Hz, 1 H, ArH), 8.22 (d, J = 8.4 Hz, 1 H, ArH), 8.04–8.12 (m, 4 H, ArH), 7.70 (d, J = 8.0 Hz, 2 H, ArH), 7.34 (d, J = 8.4 Hz, 1 H, ArH), 4.37–4.45 (m, 4 H, 2 × CH_3CH_2O), 1.40–1.46 (m, 6 H, 2 × CH_3CH_2O) ppm. ^{13}C NMR (100 Hz, $CDCl_3$): δ = 166.0, 165.3, 160.2, 153.9, 142.6, 140.9, 133.5, 133.3, 131.4, 130.2, 128.7, 126.9, 126.8, 124.9, 122.7, 121.4, 117.8, 117.5, 61.4, 61.1, 14.3, 14.2 ppm. IR (thin film): $\tilde{\nu}$ = 3082, 2985, 2903, 1735, 1708, 1610, 1271, 1238, 1114, 1032 cm^{-1}. MS (EI): m/z (%) = 416 (100) $[M]^+$, 371 (68), 343 (23), 315 (10), 287 (8), 259 (8), 213 (18). HRMS (EI-TOF): m/z calcd. for $C_{25}H_{20}O_6$ $[M]^+$ 416.1260; found 416.1259.

Ethyl 6-Oxo-8-phenyl-6*H*-benzo[*c*]chromene-2-carboxylate (3f): Yield 143 mg (83%); white solid; m.p. 212–214 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, J = 2.0 Hz, 1 H, ArH), 8.57 (d, J = 2.0 Hz, 1 H, ArH), 8.23 (d, J = 8.4 Hz, 1 H, ArH), 8.11 (dd, J = 8.8, 2.0 Hz, 1 H, ArH), 8.07 (dd, J = 8.4, 1.6 Hz, 1 H, ArH), 7.67 (d, J = 7.2 Hz, 2 H, ArH), 7.49 (t, J = 7.6 Hz, 2 H, ArH), 7.42 (d, J = 7.2 Hz, 1 H, ArH), 7.38 (d, J = 8.8 Hz, 1 H, ArH), 4.44 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 1.45 (t, J = 7.2 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4, 160.5, 153.9, 142.2, 138.5, 133.6, 132.6, 131.2, 129.0, 128.4, 128.4, 126.9, 126.8, 124.8, 122.6, 121.4, 117.7, 61.4, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3062, 2985, 2928, 1716, 1610, 1256, 1199, 1107, 1035 cm^{-1}. MS (EI): m/z (%) = 344 (100) $[M]^+$, 316 (28), 299 (63), 271 (6), 243 (23), 215 (29). HRMS (EI-TOF): m/z calcd. for $C_{22}H_{16}O_4$ $[M]^+$ 344.1049; found 344.1046.

6-Oxo-8-phenyl-6*H*-benzo[*c*]chromene-2-carbonitrile (3g): Yield 134 mg (90%); white solid; m.p. 268–270 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.66 (d, J = 1.6 Hz, 1 H, ArH), 8.41 (d, J = 2.0 Hz, 1 H, ArH), 8.12–8.22 (m, 2 H, ArH), 7.76 (dd, J = 8.8, 2.0 Hz, 1 H, ArH), 7.71 (d, J = 7.6 Hz, 2 H, ArH), 7.42–7.55 (m, 4 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 153.6, 143.3, 138. 4, 134.0, 133.3, 131.4, 129.2, 128.8, 128.7, 127.6, 127.1, 122.6, 121.7, 119.2, 119.1, 118.0, 108.8 ppm. IR (thin film): $\tilde{\nu}$ = 3072, 2921, 2854, 2229, 1748, 1483, 1278, 1249, 1202, 1067 cm^{-1}. MS (EI): m/z (%) = 297 (100) $[M]^+$, 269 (13), 240 (15), 214 (4). HRMS (EI-TOF): m/z calcd. for $C_{20}H_{11}NO_2$ $[M]^+$ 297.0790; found 297.0789.

Ethyl 6-Oxo-8-(phenylethynyl)-6*H*-benzo[*c*]chromene-2-carboxylate (3h): Yield 162 mg (88%); white solid; m.p. 171–173 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.70–8.75 (m, 1 H, ArH), 8.45–8.53 (m, 1 H, ArH), 8.08–8.21 (m, 2 H, ArH), 7.90–7.96 (m, 1 H, ArH), 7.54 (d, J = 3.6 Hz, 2 H, ArH), 7.35–7.45 (m, 4 H, ArH), 4.43 (q, J = 6.8 Hz, 2 H, CH_3CH_2O), 1.45 (t, J = 6.8 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4, 159.7, 154.0, 137.5, 133.5, 133.2, 131.8, 131.6, 128.9, 128.5, 127.0, 125.1, 124.9, 122.4, 122.2, 121.2, 117.9, 117.5, 92.4, 87.6, 61.5, 14.4 ppm. IR (thin film): $\tilde{\nu}$ = 3052, 2923, 2859, 1733, 1712, 1612, 1248, 1112, 1030 cm^{-1}. MS (EI): m/z (%) = 368 (100) $[M]^+$, 340 (23), 323 (35), 267 (16), 239 (24). HRMS (EI-TOF): m/z calcd. for $C_{24}H_{16}O_4$ $[M]^+$ 368.1049; found 368.1048.

6-Oxo-8-(phenylethynyl)-6*H*-benzo[*c*]chromene-2-carbonitrile (3i): Yield 143 mg (89%); white solid; m.p. 214–216 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.56 (s, 1 H, ArH), 8.37 (s, 1 H, ArH), 8.10 (d, J = 8.4 Hz, 1 H, ArH), 8.01 (dd, J = 8.8, 1.6 Hz, 1 H, ArH), 7.76 (dd, J = 8.4, 1.6 Hz, 1 H, ArH), 7.56–7.62 (m, 2 H, ArH), 7.48 (d, J = 8.4 Hz, 1 H, ArH), 7.35–7.43 (m, 3 H, ArH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.1, 153.7, 137.9, 133.7, 133.6, 131.9, 131.8, 129.1, 128.5, 127.8, 125.9, 122.2, 122.1, 121.5, 119.2, 118.9, 117.9, 108.9, 93.2, 87.3 ppm. IR (thin film): $\tilde{\nu}$ = 3063, 2923, 2859, 2229, 1739, 1611, 1483, 1245, 1112, 1067 cm^{-1}. MS (EI): m/z (%) = 321 (100) $[M]^+$, 293 (10), 264 (16), 238 (4). HRMS (EI-TOF): m/z calcd. for $C_{22}H_{11}NO_2$ $[M]^+$ 321.0790; found 321.0793.

Ethyl (*E*)-8-(3-Butoxy-3-oxoprop-1-en-1-yl)-6-oxo-6*H*-benzo[*c*]-chromene-2-carboxylate (3j): Yield 164 mg (83%); white solid; m.p. 144–145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.72 (d, J = 1.2 Hz, 1 H, ArH), 8.48 (s, 1 H, ArH), 8.20 (d, J = 8.4 Hz, 1 H, ArH), 8.14 (dd, J = 8.4, 1.6 Hz, 1 H, ArH), 7.96 (d, J = 8.0 Hz, 1 H,

ArH), 7.72 (d, J = 16.0 Hz, 1 H, C=C*H*), 7.38 (d, J = 8.0 Hz, 1 H, ArH), 6.59 (d, J = 16.0 Hz, 1 H, C*H*=C), 4.43 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 4.23 (t, J = 6.8 Hz, 2 H, CH_2CH_2O), 1.66–1.74 (m, 2 H, CH_2CH_2O), 1.39–1.48 (m, 5 H, $CH_3CH_2CH_2CH_2O$), 0.97 (t, J = 7.2 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 165.3, 160.0, 154.1, 141.8, 135.7, 135.0, 133.8, 131.9, 130.0, 127.1, 125.1, 122.8, 121.5, 120.9, 117.9, 117.5, 64.7, 61.5, 30.7, 19.1, 14.3, 13.7 ppm. IR (thin film): $\tilde{\nu}$ = 3062, 2956, 2864, 1749, 1706, 1612, 1255, 1169, 1028 cm^{-1}. MS (EI): *m*/*z* (%) = 394 (57) $[M]^+$, 349 (17), 338 (100), 321 (43), 293 (61), 265 (11). HRMS (EI-TOF): *m*/*z* calcd. for $C_{23}H_{22}O_6$ $[M]^+$ 394.1416; found 394.1413.

Butyl (*E*)-3-(2-Cyano-6-oxo-6*H*-benzo[*c*]chromen-8-yl)acrylate (3k): Yield 131 mg (75%); white solid; m.p. 238–240 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (s, 1 H, ArH), 8.39 (s, 1 H, ArH), 8.14 (d, J = 8.0 Hz, 1 H, ArH), 8.03 (d, J = 8.8 Hz, 1 H, ArH), 7.73–7.78 (m, 2 H, ArH), 7.48 (d, J = 8.4 Hz, 1 H, ArH), 6.63 (d, J = 16.0 Hz, 1 H, C=C*H*), 4.24 (t, J = 6.4 Hz, 2 H, CH_2CH_2O), 1.68–1.75 (m, 2 H, CH_2CH_2O), 1.42–1.49 (m, 2 H, $CH_2CH_2CH_2O$), 0.98 (t, J = 7.2 Hz, 3 H, $CH_3CH_2CH_2CH_2O$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.3, 159.3, 153.8, 141.5, 136.7, 134.2, 133.9, 133.6, 130.2, 127.9, 122.7, 121.8, 121.6, 119.3, 118.8, 117.8, 109.0, 64.9, 30.7, 19.2, 13.7 ppm. IR (thin film): $\tilde{\nu}$ = 3062, 2958, 2879, 2228, 1752, 1713, 1638, 1166, 1060 cm^{-1}. MS (EI): *m*/*z* (%) = 347 (24) $[M]^+$, 291 (100), 274 (58), 247 (40). HRMS (EI-TOF): *m*/*z* calcd. for $C_{21}H_{17}NO_4$ $[M]^+$ 347.1158; found 347.1155.

Ethyl 8-Iodo-6-oxo-6*H*-benzo[*c*]chromene-2-carboxylate (3l): Yield 166 mg (84%); white solid; m.p. 181–191 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.73 (d, J = 0.9 Hz, 2 H, ArH), 8.16 (t, J = 2.0 Hz, 1 H, ArH), 8.14 (t, J = 2.0 Hz, 1 H, ArH), 7.94 (d, J = 9.2 Hz, 1 H, ArH), 7.39 (d, J = 8.4 Hz, 1 H, ArH), 4.44 (q, J = 6.8 Hz, 2 H, CH_3CH_2O), 1.44 (t, J = 7.2 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.4, 159.0, 154.0, 143.9, 139.3, 133.4, 131.8, 127.1, 124.8, 123.6, 122.5, 118.0, 117.4, 94.5, 61.5, 14.4 ppm. IR (thin film): $\tilde{\nu}$ = 3072, 2922, 2859, 1712, 1249, 1103 cm^{-1}. MS (EI): *m*/*z* (%) = 394 (40) $[M]^+$, 349 (39), 86 (77), 58 (53), 43 (100). HRMS (EI-TOF): *m*/*z* calcd. for $C_{16}H_{11}IO_4$ $[M]^+$ 393.9702; found 393.9706.

General Procedure for the Synthesis of Aryltriazenes 5a–d: A mixture of substituted 2-(pyrrolidin-1-ylazo)benzaldehyde (10 mmol), dimethyl malonate (1.2 equiv.), piperidine (0.2 mL) and benzoic acid (0.14 g) in benzene (10 mL) was heated to reflux overnight in a 25 mL flask using a Dean–Stark trap. Upon completion of the reaction (TLC), the residue was extracted with ethyl acetate. The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was purified by flash column chromatography and recrystallization using hexane and ethyl acetate.

Dimethyl (*E*)-2-[5-(Ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)benzylidene]malonate (5a): Yield 2.53 g (65%); white solid; m.p. 117–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.51 (s, 1 H, ArH), 8.06 (d, J = 1.6 Hz, 1 H, ArH), 7.97 (dd, J = 6.8, 1.6 Hz, 1 H, ArH), 7.50 (d, J = 6.8 Hz, 1 H), 4.34 (q, J = 5.6 Hz, 2 H, CH_3CH_2O), 3.96 (t, J = 4.8 Hz, 2 H, CH_2N), 3.84 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 3.71 (t, J = 5.2 Hz, 2 H, CH_2N), 2.01–2.08 (m, 4 H, 2 × CH_2CH_2N), 1.38 (t, J = 5.6 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 Hz, $CDCl_3$): δ = 167.1, 166.0, 164.7, 153.3, 141.0, 132.1, 129.9, 126.6, 126.3, 125.2, 116.7, 60.8, 52.5, 52.4, 51.4, 47.1, 23.9, 23.4, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3048, 2954, 2884, 1727, 1699, 1388, 1243, 1210, 1164, 1122 cm^{-1}. MS (EI): *m*/*z* (%) = 389 (12) $[M]^+$, 358 (2), 344 (7), 291 (84), 263 (100). HRMS (EI-TOF): *m*/*z* calcd. for $C_{19}H_{23}N_3O_6$ $[M]^+$ 389.1587; found 389.1589.

Dimethyl (*E*)-2-{[4′-(Ethoxycarbonyl)-4-(pyrrolidin-1-yldiazenyl)-(1,1′-biphenyl)-3-yl]methylene}malonate (5b): Yield 3.40 g (73%); white solid; m.p. 129–131 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.57 (s, 1 H, ArH), 8.09 (d, J = 6.8 Hz, 2 H, ArH), 7.66 (s, 1 H, ArH), 7.61 (d, J = 6.8 Hz, 3 H, ArH), 7.55 (d, J = 6.8 Hz, 1 H, ArH), 4.40 (q, J = 5.6 Hz, 2 H, CH_3CH_2O), 3.90–4.01 (m, 2 H, CH_2N), 3.85 (s, 3 H, CH_3O), 3.75 (s, 3 H, CH_3O), 3.67–3.75 (m, 3 H, CH_3O), 2.00–2.10 (m, 4 H, $2CH_2CH_2N$), 1.41 (t, J = 5.6 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3, 166.4, 164.8, 149.9, 144.4, 141.8, 136.0, 130.1, 129.7, 129.0, 127.5, 126.8, 126.3, 124.9, 117.6, 60.9, 52.4, 52.4, 51.2, 46.8, 23.9, 23.5, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3048, 2955, 2874, 1714, 1603, 1254, 1166, 1108 cm^{-1}. MS (EI): *m*/*z* (%) = 465 (28) $[M]^+$, 396 (24), 367 (100), 339 (36), 325 (13). HRMS (EI-TOF): *m*/*z* calcd. for $C_{25}H_{27}N_3O_6$ $[M]^+$ 465.1900; found 465.1900.

Dimethyl 2-{5-[(*E*)-3-Butoxy-3-oxoprop-1-en-1-yl]-2-[(*E*)-pyrrolidin-1-yldiazenyl]benzylidene}malonate (5c): Yield 2.57 g (58%); white solid; m.p. 69–71 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.47 (s, 1 H, ArH), 7.59 (d, J = 16.0 Hz, 1 H, C=C*H*), 7.43–7.51 (m, 3 H, ArH), 6.34 (d, J = 16.0 Hz, 1 H, C*H*=C), 4.19 (t, J = 6.4 Hz, 2 H, CH_3CH_2O), 3.90–4.00 (m, 2 H, CH_2N), 3.84 (s, 3 H, CH_3O), 3.75 (s, 3 H, CH_3O), 3.66–3.74 (m, 2 H, CH_2N), 1.98–2.10 (m, 4 H, 2 × CH_2CH_2N), 1.63–1.73 (m, 2 H, CH_2CH_2O), 1.37–1.47 (m, 2 H, $CH_2CH_2CH_2O$), 0.96 (t, J = 7.2 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1, 164.7, 151.4, 143.7, 141.6, 130.8, 130.3, 128.3, 127.6, 125.3, 117.4, 117.2, 64.4, 52.5, 52.5, 51.4, 47.0, 30.7, 23.9, 23.4, 19.2, 13.7 ppm. IR (thin film): $\tilde{\nu}$ = 3033, 2954, 2874, 1726, 1702, 1625, 1396, 1255, 1220, 1159 cm^{-1}. MS (EI): *m*/*z* (%) = 443 (13) $[M]^+$, 373 (7), 345 (100), 289 (57). HRMS (EI-TOF): *m*/*z* calcd. for $C_{23}H_{29}N_3O_6$ $[M]^+$ 443.2056; found 443.2057.

Dimethyl (*E*)-2-{[4′-Methoxy-4-(pyrrolidin-1-yldiazenyl)-(1,1′-biphenyl)-3-yl]methylene}malonate (5d): Yield 2.29 g (54%); yellow solid; m.p. 111–113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.59 (s, 1 H, ArH), 7.58 (d, J = 1.6 Hz, 1 H, ArH), 7.46–7.55 (m, 4 H, ArH), 6.96 (d, J = 8.4 Hz, 2 H, ArH), 3.88–4.04 (m, 2 H, CH_2N), 3.85 (s, 3 H, CH_3O), 3.84 (s, 3 H, CH_3O), 3.76 (s, 3 H, CH_3O), 3.66–3.74 (m, 2 H, CH_2N), 1.95–2.12 (m, 4 H, $2CH_2CH_2N$) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 165.0, 159.1, 148.8, 142.3, 137.1, 132.7, 129.4, 127.6, 127.4, 126.0, 124.5, 117.4, 114.3, 55.3, 52.4, 51.1, 46.8, 23.8, 23.6 ppm. IR (thin film): $\tilde{\nu}$ = 3033, 2951, 2874, 1726, 1610, 1435, 1245, 1214, 1168, 1070 cm^{-1}. MS (EI): *m*/*z* (%) = 423 (5) $[M]^+$, 231 (100), 203 (12), 121 (69). HRMS (EI-TOF): *m*/*z* calcd. for $C_{23}H_{25}N_3O_5$ $[M]^+$ 423.1794; found 423.1792.

General Procedure for the Synthesis of Coumarins 6a–d: Boron trifluoride–diethyl ether (5.0 equiv.) was added dropwise to a stirred solution of **5** (0.5 mmol) in anhydrous CH_3CN (20 mL) at 40 °C. The mixture was stirred overnight. Upon completion of the reaction (TLC), the mixture was washed with satd. aq $NaHCO_3$ and extracted with ethyl acetate. The combined organic extracts were dried with anhydrous $MgSO_4$ and removed under reduced pressure. The product was purified by column chromatography.

6-Ethyl 3-Methyl 2-Oxo-2*H*-chromene-3,6-dicarboxylate (6a): Yield 83 mg (60%); white solid; m.p. 169–172 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.60 (s, 1 H, ArH), 8.33 (d, J = 2.0 Hz, 1 H, ArH), 8.30 (dd, J = 8.4, 2.0 Hz, 1 H, ArH), 7.40 (d, J = 8.8 Hz, 1 H, ArH), 4.41 (q, J = 7.2 Hz, 2 H, CH_3CH_2O), 3.96 (s, 3 H, CH_3O), 1.41 (t, J = 7.2 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7, 163.2, 157.7, 155.9, 148.7, 135.1, 131.5, 127.4, 118.7, 117.5, 117.0, 61.6, 53.0, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3062, 2999, 2953, 1751, 1719, 1702, 1572, 1302, 1242, 1208, 1022 cm^{-1}. MS (EI): *m*/*z* (%) = 276 (51) $[M]^+$, 261 (6), 245 (33), 231 (100), 217

(30). HRMS (EI-TOF): *m/z* calcd. for $C_{14}H_{12}O_6$ $[M]^+$ 276.0634; found 276.0630.

Methyl 6-(4-Ethoxycarbonylphenyl)-2-oxo-2*H*-chromene-3-carboxylate (6b): Yield 71 mg (40%); yellow solid; m.p. 205–207 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (s, 1 H, ArH), 8.14 (d, J = 11.2 Hz, 2 H, ArH), 7.89 (dd, J = 11.2, 3.2 Hz, 1 H, ArH), 7.83 (d, J = 2.4 Hz, 1 H, ArH), 7.64 (d, J = 11.2 Hz, 2 H, ArH), 7.45 (d, J = 11.6 Hz, 1 H, ArH), 4.40 (q, J = 9.6 Hz, 2 H, CH_3CH_2O), 3.96 (s, 3 H,CH_3O), 1.41 (t, J = 9.6 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.1, 163.5, 156.4, 154.9, 148.9, 143.0, 137.1, 133.3, 130.3, 130.0, 127.8, 126.9, 118.5, 118.1, 117.4, 61.1, 52.9, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3052, 2956, 2929, 1758, 1705, 1266, 1204, 1214, 1106 cm^{-1}. MS (EI): *m/z* (%) = 352 (100) $[M]^+$, 321 (14), 307 (62), 293 (10). HRMS (EI-TOF): *m/z* calcd. for $C_{20}H_{16}O_6$ $[M]^+$ 352.0947; found 352.0949.

Methyl (*E*)-6-(3-Butoxy-3-oxoprop-1-en-1-yl)-2-oxo-2*H*-chromene-3-carboxylate (6c): Yield 83 mg (50%); yellow solid; m.p. 140–142 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.55 (s, 1 H, ArH), 7.81 (dd, J = 8.8, 1.6 Hz, 1 H, ArH), 7.72 (d, J = 1.6 Hz, 1 H, ArH), 7.68 (d, J = 16.0 Hz, 1 H, C=C*H*), 7.38 (d, J = 8.8 Hz, 1 H, ArH), 6.46 (d, J = 16.0 Hz, 1 H, C*H*=C), 4.23 (t, J = 6.4 Hz, 2 H, CH_3CH_2O), 3.97 (s, 3 H, CH_3O), 1.65–1.75 (m, 2 H, CH_2CH_2O), 1.38–1.48 (m, 2 H, $CH_2CH_2CH_2O$), 0.97 (t, J = 7.2 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 163.4, 155.9, 148.5, 141.8, 133.1, 131.6, 129.1, 119.9, 118.7, 118.1, 117.6, 64.7, 53.0, 30.7, 19.2, 13.7 ppm. IR (thin film): $\tilde{\nu}$ = 3048, 2961, 2879, 1768, 1747, 1700, 1612, 1568, 1248, 1170, 1007 cm^{-1}. MS (EI): *m/z* (%) = 330 (25) $[M]^+$, 299 (9), 274 (100), 257 (58), 243 (26), 229 (13). HRMS (EI-TOF): *m/z* calcd. for $C_{18}H_{18}O_6$ $[M]^+$ 330.1103; found 330.1106.

Methyl 6-(4-Methoxyphenyl)-2-oxo-2*H*-chromene-3-carboxylate (6d): Yield 39 mg (25%); yellow solid; m.p. 145–149 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.62 (s, 1 H, ArH), 7.82 (dd, J = 8.5, 2.0 Hz, 1 H, ArH), 7.73 (d, J = 2.0 Hz, 1 H, ArH), 7.51 (d, J = 8.5 Hz, 2 H, ArH), 7.41 (d, J = 8.5 Hz, 1 H, ArH), 7.01 (d, J = 9.0 Hz, 1 H, ArH), 3.97 (s, 3 H,CH_3O), 3.87 (s, 3 H, CH_3O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 163.8, 159.8, 156.8, 154.2, 149.3, 138.1, 133.1, 131.4, 128.1, 126.9, 118.2, 118.1, 117.1, 114.6, 55.4, 53.0 ppm. IR (thin film): $\tilde{\nu}$ = 3048, 2963, 2922, 2859, 1748, 1696, 1271, 1009 cm^{-1}. MS (EI): *m/z* (%) = 310 (100) $[M]^+$, 295 (35), 279 (19), 267 (14). HRMS (EI-TOF): *m/z* calcd. for $C_{18}H_{14}O_5$ $[M]^+$ 310.0841; found 310.0843.

General Procedure for Synthesis of 7a and 7b: Substituted phenyl halide (3 mmol), substituted boronic acid (1.2 equiv.), tetrakis(triphenylphosphane) palladium(0) (0.05 equiv.) and Cs_2CO_3 (2.0 equiv.) were dissolved in a solution of 1,4-dioxane (6 mL) and water (1.5 mL). The mixture was stirred at 100 °C overnight under a nitrogen atmosphere in a screw-cap vial. Upon completion of the reaction (TLC), the mixture was diluted with ethyl acetate and washed with water. The organic fractions were dried with anhydrous Na_2SO_4, and concentrated under vacuo. Purification was carried out by flash chromatography to afford the corresponding product.

Ethyl (*E*)-2′-[(4-Ethoxycarbonylphenyl)carbamoyl]-6-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carboxylate (7a): Yield 386 mg (25%); brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.26 (br., 1 H, CON*H*), 7.98–8.03 (m, 2 H, ArH), 7.85–7.90 (m, 3 H, ArH), 7.42–7.54 (m, 3 H, ArH), 7.28 (dd, J = 7.2, 0.8 Hz, 1 H, ArH), 7.19 (d, J = 8.4 Hz, 2 H, ArH), 4.25–4.38 (m, 4 H, 2 × CH_3CH_2O), 3.72–3.85 (m, 2 H, CH_2N), 3.22–3.48 (m, 2 H, CH_2N), 1.85–2.00 (m, 4 H, 2 × CH_2CH_2N), 1.32–1.40 (m, 6 H, 2 × CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0, 166.1, 166.0, 152.2, 142.3, 137.0, 135.8, 133.9, 131.8, 131.1, 130.6, 130.6, 130.5, 128.9, 127.7, 126.8, 125.4, 118.2, 117.2, 60.9, 60.7, 51.3, 46.9, 23.7, 23.3, 23.1, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3315, 2976, 2856, 1708, 1596, 1520, 1270, 1235, 1172, 1103 cm^{-1}. MS (EI): *m/z* (%) = 310 (100) $[M]^+$, 514 (11), 441 (8), 416 (100), 388 (29), 360 (46). HRMS (EI-TOF): *m/z* calcd. for $C_{29}H_{30}N_4O_5$ $[M]^+$ 514.2216; found 514.2214.

Ethyl (*E*)-2′-(4-methylphenyl)carbamoyl-6-(pyrrolidin-1-yldiazenyl)-[1,1′-biphenyl]-3-carboxylate (7b): Yield 630 mg (46%); brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98–8.05 (m, 3 H, ArH), 7.88–7.92 (m, 1 H, ArH), 7.42–7.51 (m, 3 H, ArH), 7.23–7.28 (m, 1 H, ArH), 6.98–7.02 (m, 4 H, ArH), 4.35 (q, J = 5.6 Hz, 2 H, CH_3CH_2O), 3.75–3.85 (m, 2 H, CH_2N), 3.23–3.50 (m, 2 H, CH_2N), 2.24 (s, 3 H, CH_3), 1.88–1.98 (m, 4 H, 2 × CH_2CH_2N), 1.37 (t, J = 5.6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.7, 166.3, 152.3, 137.0, 136.5, 135.6, 134.4, 133.4, 131.9, 131.0, 130.5, 130.1, 129.2, 128.8, 127.6, 126.8, 119.6, 117.2, 60.9, 51.3, 46.9, 23.8, 23.4, 20.8, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3306, 3058, 2976, 2875, 1708, 1665, 1598, 1306, 1234, 1106 cm^{-1}. MS (EI): *m/z* (%) = 456 (15) $[M]^+$, 411 (8), 358 (92), 330 (100), 285 (45), 253 (24). HRMS (EI-TOF): *m/z* calcd. for $C_{27}H_{28}N_4O_3$ $[M]^+$ 456.2161; found 456.2166.

General Procedure for Synthesis of 8a and 8b: Boron trifluoride–diethyl ether (2.8 equiv.) was added dropwise to a stirred solution of **7** (0.5 mmol) in anhydrous CH_3CN (20 mL) at 40 °C, and the mixture was stirred for 4 h. Upon completion of the reaction (TLC), the mixture was washed with $NaHCO_3$ and extracted with ethyl acetate. The combined organic extracts were dried with anhydrous Na_2SO_4 and removed under reduced pressure. The product was purified by column chromatography.

Ethyl 5-[4-(Ethoxycarbonyl)phenyl]-6-oxo-5,6-dihydrophenanthridine-2-carboxylate (8a): Yield 156 mg (75%); white solid; m.p. 133–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (s, 1 H, ArH), 8.46 (d, J = 7.6 Hz, 1 H, ArH), 8.02–8.10 (m, 3 H, ArH), 7.97 (d, J = 8.8 Hz, 1 H, ArH), 7.69 (t, J = 8.0 Hz, 1 H, ArH), 7.52 (t, J = 8.0 Hz, 1 H, ArH), 7.22 (d, J = 8.0 Hz, 2 H, ArH), 7.03 (d, J = 8.4 Hz, 1 H, ArH), 4.35–4.45 (m, 4 H, 2 × CH_3CH_2O), 1.38–1.45 (m, 6 H, 2 × CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.5, 165.5, 153.6, 150.6, 148.1, 132.8, 131.0, 130.7, 130.4, 129.3, 128.6, 126.2, 125.8, 124.6, 123.8, 122.3, 121.6, 118.3, 116.8, 61.2, 60.6, 14.3, 14.3 ppm. IR (thin film): $\tilde{\nu}$ = 3072, 2977, 2850, 1706, 1674, 1596, 1279, 1252, 1106, 1032 cm^{-1}. MS (EI): *m/z* (%) = 415 (100) $[M]^+$, 387 (7), 370 (30), 342 (12), 314 (8). HRMS (EI-TOF): *m/z* calcd. for $C_{25}H_{21}NO_5$ $[M]^+$ 415.1420; found 415.1422.

Ethyl 6-Oxo-5-(*p*-tolyl)-5,6-dihydrophenanthridine-2-carboxylate (8b): Yield 99 mg (55%); yellow solid; m.p. 116–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.65 (s, 1 H, ArH), 8.50 (d, J = 8.0 Hz, 1 H, ArH), 8.07 (d, J = 8.0 Hz, 1 H, ArH), 7.99 (dd, J = 8.8, 1.2 Hz, 1 H, ArH), 7.67 (t, J = 8.0 Hz, 1 H, ArH), 7.52 (t, J = 8.0 Hz, 1 H, ArH), 7.20 (s, 4 H, ArH), 7.11 (d, J = 8.0 Hz, 1 H, ArH), 4.42 (q, J = 7.6 Hz, 2 H, CH_3CH_2O), 2.39 (s, 3 H, CH_3), 1.44 (t, J = 7.2 Hz, 3 H, CH_3CH_2O) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.8, 154.1, 147.1, 143.1, 133.6, 132.4, 130.9, 130.5, 129.3, 128.5, 125.9, 124.7, 122.9, 121.6, 118.6, 116.9, 61.2, 21.0, 14.4 ppm. IR (thin film): $\tilde{\nu}$ = 3037, 2904, 2864, 1705, 1663, 1606, 1249, 1106, 1028 cm^{-1}. MS (EI): *m/z* (%) = 357 (100) $[M]^+$, 328 (28), 284 (5), 252 (5). HRMS (EI-TOF): *m/z* calcd. for $C_{23}H_{19}NO_3$ $[M]^+$ 357.1365; found 357.1364.

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization data, copies of ^{1}H and ^{13}C NMR spectra for all products.

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