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# V-Shaped Bis-Coumarins: Synthesis and Optical Properties

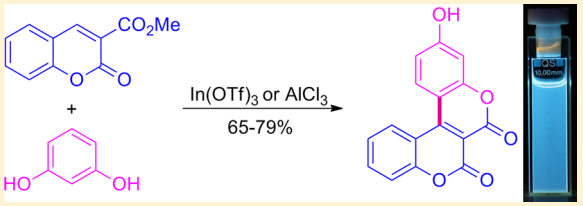
Mariusz Tasior,[†] Yevgen M. Poronik,[†] Olena Vakuliuk,[†,‡] Bartłomiej Sadowski,[†] Maksymilian Karczewski,[†] and Daniel T. Gryko*[,†,‡]

[†]Institute of Organic Chemistry of the Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland

[‡]Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664 Warsaw, Poland

Supporting Information

**ABSTRACT:** A highly efficient procedure for the synthesis of bis-coumarins fused at the pyranone ring has been developed. The electron-rich phenols reacted with esters of coumarin-3-carboxylic acids, leading to substituted chromeno[3,4-*c*]chromene-6,7-diones. The reaction is catalyzed by both Lewis acids and 4-dimethylaminopyridine. The most probable mechanistic pathway involves Lewis acid catalyzed or DMAP catalyzed transesterification, followed by intramolecular conjugate addition of *α*,*β*-unsaturated esters to phenols and subsequent oxidation of the initially formed intermediate. The reaction is compatible with various functionalities such as $NO_2$, Br, and OMe. Not only benzene derivatives but also dihydroxynaphthalenes are reactive in this reaction, and the structure of the product can be controlled by adjusting the reaction conditions. Furthermore, a double addition is possible, leading to a horseshoe-shaped system comprised of seven conjugated rings. Compounds with four structurally unique skeletons have been obtained and have been shown to strongly absorb in the violet, blue, and/or green regions of the visible spectrum. Most of them display strong greenish yellow fluorescence, which can be modulated by both structural changes and the character of the solvents. Again, introduction of an electron-donating group in the chromeno[3,4-*c*]chromene-6,7-diones caused a significant red shift in both the absorption and emission maxima, and the effect became especially noteworthy in the case of amino substituents.




## INTRODUCTION

Since the beginning of the development of the coumarins, *π*-expanded versions of these compounds have been of particular interest.[1] Von Pechmann described the synthesis of benzo[*f*]-coumarin in his second seminal paper,[2] while benzo[*c*]-coumarins have been identified often in plants.[3] These two modes of expansion of the *π* system have dominated coumarin chemistry.[4,5] Recently, Ahn and co-workers developed new methods for the preparation of benzo[*g*]coumarins and employed them in one-photon as well as two-photon fluorescence microscopy.[6,7] Among the more complex *π*-expanded coumarins, many oxapyrenones have been prepared using diverse methods,[8−16] with the first example being published by Dey almost 100 years ago.[17] Interestingly, the oxapyrenone skeleton has been found in the metabolites of various orchids and lichens[18−23] and recently the first total synthesis of santiagonamine, isolated from stems and branches of the South American shrub *Berberis darwinii*, was reported.[24] Regardless of their presence in nature[1,25] and their well-documented biological activity,[26−30] the growing interest in the synthesis of new coumarins has mainly been driven by their applications to photonics.[31−34] As a result of their strong light absorption,[35,36] high fluorescence quantum yield,[37] and large Stokes shift,[38−43] coumarins have been widely investigated as optical brighteners,[44] as fluorescent probes,[45,46] as emitter layers in organic light emitting diodes (OLEDs),[47,48] and as photosensitizers in organic solar cells[49,50] and they have also been successfully incorporated into energy- and electron-transfer arrays.[51−53] An increasing number of possible applications has accelerated recent progress in coumarin synthesis.[54,55]

While working on the design of new *π*-expanded coumarins, we found two short notes describing the synthesis of a rare family of bis-coumarins fused at the pyranone rings, i.e., chromeno[3,4-*c*]chromene-6,7-diones (Figure 1).

In the mid 1980s, Högberg and co-workers discovered that heating of 3-methoxyphenol and diethyl ethoxymethylenemalonate in the presence of zinc chloride led to bis-coumarins fused at C3−C4.[56] A different approach was proposed by Kovtun and co-workers, who heated a mixture of 3-dialkylaminophenols and the ester of coumarin-3-carboxylic acid, obtaining a similar product.[57] Despite the description of intriguing V-shaped structures and branched *π* systems, no reports on the photophysical properties of such coumarins have been published to date. It should also be pointed out that the scope of both aforementioned methods is very limited. Taking into account the importance of *π*-expanded coumarins and the growing number of their applications, we set ourselves the goal to develop a general methodology leading to V-shaped bis-coumarins and to achieve a comprehensive analysis of their optical properties.

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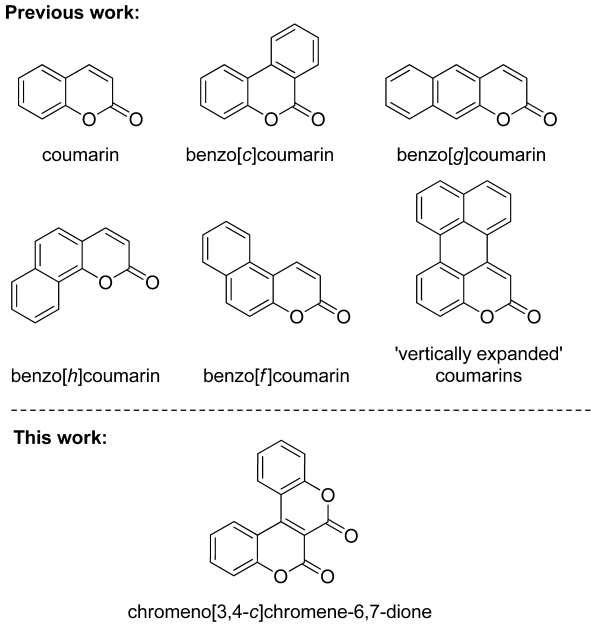
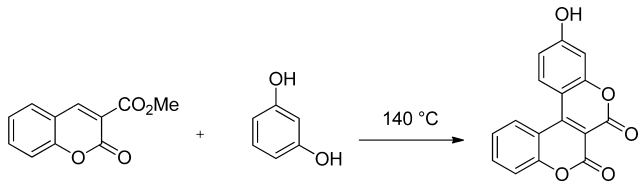



**Figure 1.** Structures of various $\pi$-expanded coumarins.

## RESULTS AND DISCUSSION

The original Kovtun procedure consisted of melting a mixture of 3-carboethoxycoumarin and 3-dialkylaminophenols at elevated temperature (a second equivalent of coumarin is necessary for oxidation of the initially formed Michael adduct). When they were applied to the less electron rich resorcinol, these conditions led to only a 3% yield of the expected product **3** after 24 h of heating at 140 °C (Table 1, entry 1).

**Table 1. Optimization of Reaction Conditions**[a]




| entry | catalyst | amt of catalyst (equiv) | time (h) | oxidant | yield (%)[b] |
|---|---|---|---|---|---|
| 1 | | | 24 | **1** | 3 |
| 2 | $AlCl_3$ | 0.33 | 2 | **1** | 79 |
| 3 | $Sc(OTf)_3$ | 0.01 | 24 | **1** | 51 |
| 4 | $In(OTf)_3$ | 0.01 | 16 | **1** | 65 |
| 5 | K-10 | | 16 | **1** | traces |
| 6 | $ZnCl_2$ | 1.0 | 16 | **1** | traces |
| 7 | $MgBr_2$ | 1.0 | 16 | **1** | traces |
| 7 | $Zn(OTf)_2$ | 0.1 | 16 | **1** | 26 |
| 8 | $Yb(OTf)_3$ | 0.01 | 24 | **1** | 6 |
| 9 | pyridine | 1.0 | 2 | **1** | 52 |
| 10 | DMAP | 0.1 | 2 | **1** | 63 |
| 11 | $Sc(OTf)_3$ | 0.01 | 16 | $O_2$ | 27 |
| 12 | $FeCl_3$ | 2.0 | 2.5 | $FeCl_3$ | 24 |
| 13 | $Sc(OTf)_3$ | 0.01 | 16 | nitrobenzene | 33 |
| 14 | $Sc(OTf)_3$ | 0.01 | 2 | oxone | 0 |
| 15 | | | 16 | PIFA | 0 |

[a]General conditions: substrate ratio **1**:**2** = 2:1; 140 °C, no solvent. [b]Isolated yields calculated on the basis of the phenol.

Among the many mechanistic hypotheses to be considered the most probable one starts with transesterification as the first step, followed by an entropically driven C−C bond forming step. Such transesterification can be catalyzed by both bases and Lewis acids. Another option is that the conjugate C−C addition is the first step followed by transesterification and oxidation of the intermediate. Regardless, the needed oxidation step most probably is a spontaneous aromatization, driven enthalpically. Since both Lewis acids and some types of organic bases are known to catalyze transesterification, and at the same time they can activate one of the reactants (either the resorcinol or the $\alpha,\beta$-unsaturated lactone ring of coumarin), we reasoned that they should accelerate this transformation. Consequently, we decided to investigate the influence of a Lewis acid on the reaction outcome. To our delight, the addition of 0.33 equiv of $AlCl_3$ significantly increased the yield and reduced the reaction time (entry 2). Subsequently, we found that 1 mol % addition of scandium(III) trifluoromethanesulfonate ($Sc(OTf)_3$) or indium(III) trifluoromethanesulfonate ($In(OTf)_3$) also gave good yields of bis-coumarin **3**; however, longer reaction times were required (Table 1, entries 3 and 4). Addition of zinc-, magnesium-, and ytterbium-based Lewis acids or K-10 clay had little or no effect on the reaction outcome (Table 1, entries 5−8).

Encouraged by these results, we decided to study another possibility—addition of base. Inorganic bases, such as sodium ethanolate, did not catalyze the reaction of ester **1** with resorcinol (**2**), probably because of the ring opening of coumarin, while high-boiling amines showed notable catalytic efficiency in this transformation. Initially we found that carbomethoxycoumarins underwent double nucleophilic addition with both DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) and DBN (1,5-diazabicyclo[4.3.0]non-5-ene). These bases acted as reagents, and novel, pentacyclic, fused coumarins were formed: i.e., 3*H*-chromeno[3,4-*c*]pyridine-4,5-diones.[58] Among the many amines investigated (pyridine, 1,4-diazabicyclo[2.2.2]-octane, 2,6-dimethylpyridine, etc.), DMAP (4-dimethylamino-pyridine) showed the strongest catalytic effect (Table 1, entries 9 and 10). We attributed this remarkable effect on the reaction rate to more efficient transesterification under basic conditions. The addition of high-boiling solvents caused notable decreases in reaction yields in all cases.

The necessity to oxidize the conjugated adduct by a second equivalent of 3-carboethoxycoumarin can be a problem in the case of more expensive salicylaldehydes. In an attempt to overcome this obstacle, we performed a series of experiments where coumarin and resorcinol were reacted in a 1:1 ratio and various oxidants were added in a stoichiometric amount. We found that neither pure oxygen nor air was a suitable oxidant for this transformation, because the yield was reduced to ca. 50% of the initial value (Table 1, entry 11). The addition of anhydrous iron(III) chloride, which could in principle act as both catalyst and oxidant, led to a decrease in yield of dye **3** (Table 1, entry 12). We have also tried to apply nitrobenzene and 3-nitrotoluene, as in the classical Skraup reaction,[59] as well as potassium monopersulfate, PIFA (iodosobenzene bis-(trifluoroacetate)), *p*-chloranil (2,3,5,6-tetrachlorobenzoquinone), and $Ph_3C^+BF_4^-$, but none of them were effective in this transformation (Table 1, entries 13−15). This may suggest that the needed oxidation step is a spontaneous aromatization, driven enthalpically.

Having the optimized conditions in hand, we studied the scope of this methodology choosing $In(OTf)_3$ as the catalyst


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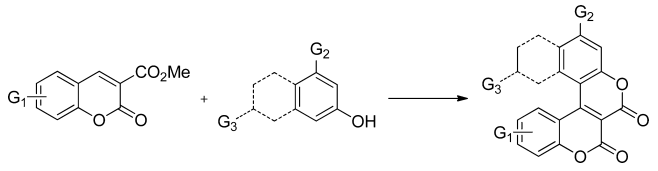
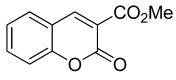
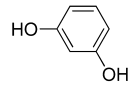
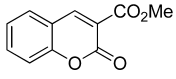
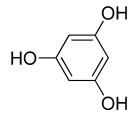
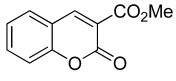
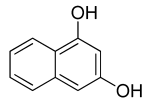
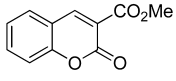
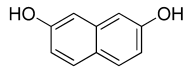
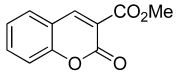
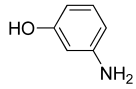
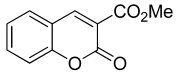
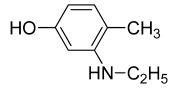
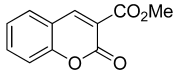
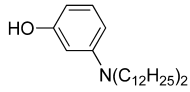
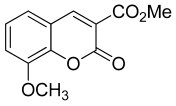
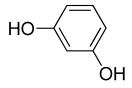
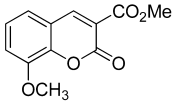
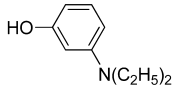
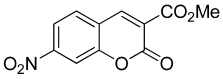
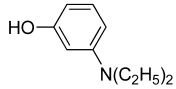
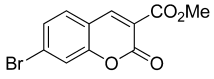
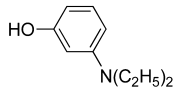
**Table 2. Scope of the Preparation of Chromeno[3,4-*c*]chromene-6,7-diones in the Presence of $In(OTf)_3$[d]**




| Entry | Coumarin | | Phenol | | Product | Yield[a] |
|---|---|---|---|---|---|---|
| 1 | **1** |  | **2** |  | **3** | 28% |
| 2 | **1** |  | **7** |  | **14** | 35% |
| 3 | **1** |  | **8** |  | **15 + 16**[b] | 64% |
| 4 | **1** |  | **9** |  | **17** | 8% |
| 5 | **1** |  | **10** |  | **18** | 37%(2%)[c] |
| 6 | **1** |  | **11** |  | **19** | 33% |
| 7 | **1** |  | **12** |  | **20** | 38% |
| 8 | **4** |  | **2** |  | **21** | 77% |
| 9 | **4** |  | **13** |  | **22** | 79% |
| 10 | **5** |  | **13** |  | **23** | 65% |
| 11 | **6** |  | **13** |  | **24** | 87% |

[a]Isolated yields calculated on the basis of the phenol. [b]In the absence of $In(OTf)_3$, the different product **16** was formed in 21% yield (see Scheme 1). [c]Yield of reaction performed without catalyst (i.e., under Kovtun conditions). [d]General reaction conditions: coumarin (5 mmol), phenol (2.5 mmol), 1 mol % of $In(OTf)_3$, 140 °C.

(Table 1, entry 4). It should be pointed out that electron density on the phenolic substrate had a crucial effect on the reaction outcome. Electron-rich phenols such as resorcinol and phloroglucinol reacted smoothly in the presence of indium(III) triflate (Table 2, entries 1 and 2). Most probably, the decrease in yield in the second entry can be explained by the numerous side reactions observed.

Additionally, series of 3-aminophenols proved to be efficient substrates in these types of transformations, showing no additional N reactivity. In all cases, selective formation of the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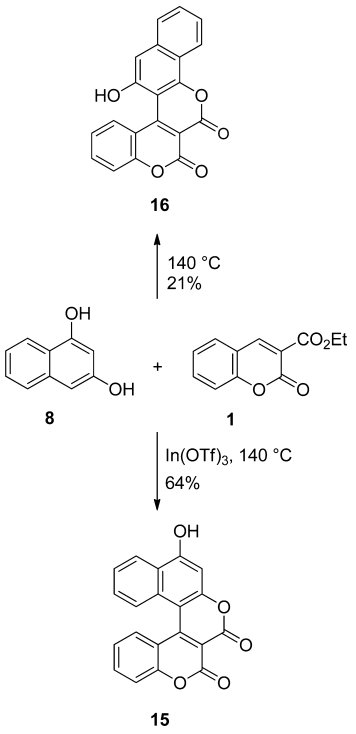
O-fused products in moderate yields was observed (Table 2, entries 5−7). In contrast to our expectations, addition of the catalyst, which can form complexes with amino groups thereby deactivating the ring, improved the reaction outcome remarkably (37% versus 2% in the reaction carried out without any catalyst, Table 2, entry 5). It is worth noting that the reaction of *N*-ethyl-3-amino-4-methylphenol (**11**) with coumarin **1** gave the fused coumarin derivative **19** in an acceptable 35% yield, whereas under the original Kovtun conditions the reaction was rather sluggish (4% yield). In general, phenols lacking a second activating group did not react with 3-carbomethoxycoumarins under either acidic or basic conditions.

Two dihydroxynaphthalenes were also chosen as substrates (Table 2, entries 3−4). 2,7-Dihydroxynaphthalene (**9**) displayed much lower reactivity, most probably because the two hydroxyl groups activate different positions of the aromatic core. Surprisingly, we found that reactions of 1,3-dihydroxynaphthalene (**8**) with ester **1**, with and without addition of the $In(OTf)_3$, led to the two different regioisomeric products **15** and **16** (Scheme 1). The assignment of signals and the

**Scheme 1. Regioselective Formation of Dyes 15 and 16 under Various Reaction Conditions**

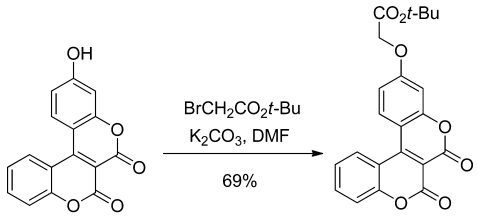



identification of structures of the obtained products were accomplished by NMR techniques (see the Supporting Information). The von Pechmann reaction is known to proceed more efficiently with 1-hydroxynaphthalenes than with 2-hydroxynaphthalenes,[60] while for 1,3-dihydroxynaphthalene (**8**) it occurs exclusively to form the bent product 5-hydroxy-2*H*-benzo[*h*]chromen-2-one.[2,61] Taking this outcome into consideration, it is plausible that the reaction in the absence of Lewis acid occurs with the keto form of 1,3-dihydroxynaphthalene (**8**), with a Michael donor (i.e., **1**) attacking the most reactive 2-position, leading to product **16**. In the presence of indium(III) triflate, the phenolic form predominated, leading to "Pechmann product" **15** (Scheme 1).

Subsequently, we studied variously substituted 3-carbomethoxycoumarins, which are easily accessible from substituted salicylaldehydes. Methoxy, nitro, and bromo substituents did not interfere with the catalysts, and broadly varying biscoumarins were synthesized in moderate yields (Table 2). Only 3-ethoxycarbonyl-7-hydroxycoumarin and 3-ethoxycarbonylbenzo[*h*]coumarin failed to give the expected products. It is noteworthy that the vast majority of prepared chromeno[3,4-*c*]chromene-6,7-diones were isolated and purified by simple crystallization without need for chromatography.

The reactive functional groups present at some chromeno[3,4-*c*]chromene-6,7-diones prompted us to attempt further modifications. The directions of these functionalizations were governed by the desire to obtain compounds with preprogrammed optical properties. It is well-known that 7-alkoxycoumarins[62] and their $\pi$-expanded analogues[63] display particularly high fluorescence quantum yields in polar rather than in nonpolar media. In keeping with this observation, compound **3** was O-alkylated with *tert*-butyl bromoacetate (Scheme 2).

**Scheme 2. Williamson Alkylation of Chromeno[3,4-*c*]chromene-6,7-dione 3**




We also attempted to tune the optical properties of chromeno[3,4-*c*]chromene-6,7-diones by expanding the chromophore. Compound **24**, which contained a bromine atom, was subjected to the Sonogashira reaction conditions with the two exemplary arylacetylenes **26** and **27**. To understand how this structural modification influenced the optical properties of the dye, we chose arylacetylenes **28** and **29** with electron-donating and electron-withdrawing groups (Scheme 3).

It was intriguing to investigate the reaction of coumarin **30**, possessing two pyranone units, with the selected electron-rich phenol. Coumarin **30** was synthesized according to a known method with some modifications (see the Supporting Information).[64−66] We found that the condensation of compound **30** with 3-diethylaminophenol (**13**) indeed led to the double-addition product **31** (Scheme 4). Compound **31** was purified by recrystallization from DMF without the need to use chromatographic methods.

Only a few compounds possessing the chromeno[3,4-*c*]chromene-6,7-dione core have been described before,[56,57] and there have been no analyses of their optical properties; therefore, we decided to study the absorption and emission characteristics of dyes **3**, **14**−**25**, **28**, **29**, and **31** in DCM and DMSO (Table 3). With the addition of appropriate substituents known to enhance intramolecular charge transfer (ICT), coumarin derivatives emitted strong fluorescence in the blue-green region (400−550 nm). As a consequence of the nature of the reaction employed by us, the dyes **3**, **14**−**25**, **28**, **29**, and **31** all possessed electron-donating groups at the site corresponding to position 7 of the newly formed coumarin moiety (Table 1). Among the hydroxy-substituted and amino-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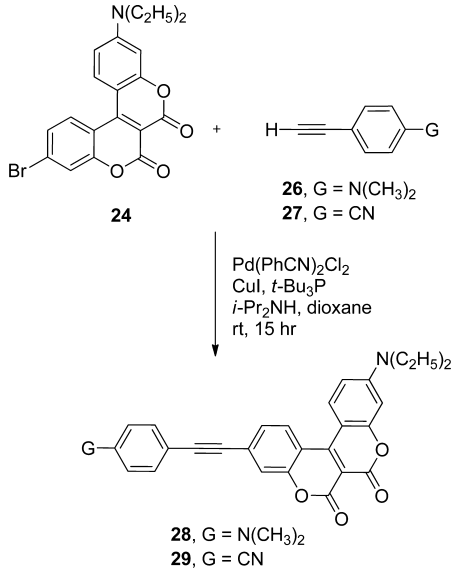
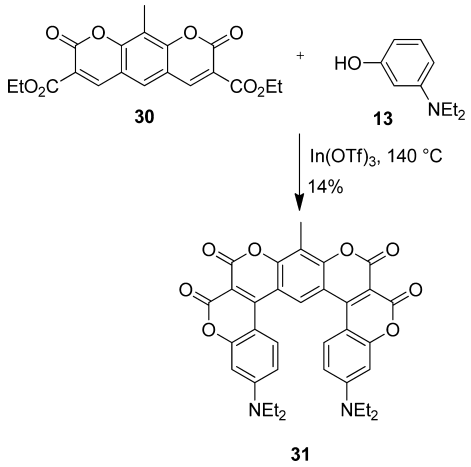
**Scheme 3. Sonogashira Coupling Leading to Compounds 28 and 29**




**Scheme 4. Synthesis of Dye 31**




substituted families, the latter would be expected to emit stronger fluorescence with a larger red shift in comparison to the former, considering the larger dipole moment expected in the case of the stronger electron donor.[50,62] Indeed, bis-coumarins **18**–**20** and **22**–**24** possessing amino groups displayed bathochromically shifted absorption vs dyes **3**, **14**, and **21** possessing hydroxyl groups. The same trend can be observed for fluorescence, although the emission maximum of compound **14** possessing two hydroxyl groups is in the same region as for amines (i.e., 511 nm), leading to the highest Stokes shift in this library (6400 $cm^{-1}$). Clearly, dialkylamino-substituted chromeno[3,4-*c*]chromene-6,7-diones (**20**, **22**–**24**) displayed intense absorption bands in the spectral range 400–500 nm and $\lambda_{max}$ values were almost independent of the solvent polarity. The absorption bands of these dyes were somewhat broadened (the bandwidth at half-maximum (fwhm) is 2800–3200 $cm^{-1}$), and consequently these compounds were characterized by large Stokes shifts (Table 3). Moreover, all of these dyes showed strong fluorescence response ($\Phi_{fl} \approx 0.9$ in DCM) that along with large Stokes shifts make them promising fluorescent materials.

**Table 3. Optical Properties of Synthesized Compounds**

| compd | solvent | $\lambda_{abs}$ (nm) | $\varepsilon_{max}$ ($10^{-3}$ $M^{-1}$ $cm^{-1}$) | $\Delta S$ ($cm^{-1}$) | $\lambda_{em}$ (nm) | $\Phi_{fl}$ |
|---|---|---|---|---|---|---|
| **3** | DCM | 374 | 16.9 | 4760 | 455 | 0.18[a] |
| | DMSO | 376 | 6.0 | | | *b* |
| **14** | DCM | 385 | 11.7 | 6400 | 511 | 0.10[a] |
| | DMSO | 388 | 11.8 | | | *b* |
| | | 512 | 1.0 | | | |
| **15** | DCM | 442 | 11.4 | 3700 | 529 | 0.16[c] |
| | DMSO | 441 | 11.3 | | | |
| **16** | DCM | 447 | 11.3 | 3600 | 533 | 0.29[c] |
| | DMSO | 480 | 10.8 | | | |
| **17** | DCM | 428 | 7.9 | 4000 | 517 | 0.22[c] |
| | DMSO | 428 | 7.0 | 3600 | 506 | 0.02[c] |
| | | 397 | 6.1 | | | |
| **18** | DCM | 411 | 20.0 | 4200 | 498 | 0.96[c] |
| | DMSO | 438 | 17.2 | 4100 | 534 | 0.68[c] |
| **19** | DCM | 441 | 27.2 | 3000 | 509 | 0.84 |
| | DMSO | 454 | 27.4 | 3900 | 552 | 0.27 |
| **20** | DCM | 463 | 30.3 | 2700 | 528 | 0.94[c] |
| | DMSO | 464 | 31.2 | 3800 | 562 | 0.02[c] |
| **21** | DCM | 365 | 6.0 | 4600 | 438 | 0.004[a] |
| | DCM + $(CH_3)_4NOH$ | 479 | 12.7 | 4100 | 597 | 0.34[c] |
| | DMSO | 378 | 12.6 | | | *b* |
| | | 489 | 4.4 | | | |
| **22** | DCM | 458 | 32.3 | 3000 | 530 | 0.91[c] |
| | DMSO | 462 | 29.4 | 4200 | 572 | 0.27[c] |
| **23** | DCM | 494 | 22.2 | | | *b* |
| | DMSO | 498 | 19.0 | | | *b* |
| **24** | DCM | 466 | 31.1 | 2900 | 540 | 0.90[c] |
| | DMSO | 469 | 28.9 | 3800 | 572 | 0.25[c] |
| **25** | DCM | 365 | 17.9 | 4700 | 440 | 0.008[a] |
| | DMSO | 366 | 17.7 | 5000 | 449 | 0.31 |
| **28** | DCM | 459 | 50.2 | 7300 | 691 | 0.04 |
| | DMSO | 468 | 44.3 | | | *b* |
| **29** | DCM | 476 | 26.0 | 3500 | 572 | 0.69 |
| | DMSO | 481 | 24.2 | 4800 | 625 | 0.10 |
| **31** | DCM | 458 | 57.8 | 3400 | 542 | 0.67[c] |
| | DMSO | 463 | 54.2 | 4100 | 558 | 0.002[c] |

[a]Determined with 9,10-diphenylanthracene in cyclohexane as a standard. [b]Fluorescence was not measured due to low *S*/*N* ratio. [c]Determined with fluorescein in NaOH (0.1 M) as a standard.

The optical properties of compounds **18** and **19** (bearing primary and secondary amino groups) differed somewhat from those of dialkylamino-substituted coumarino[3,4-*c*]coumarins. The locations of their absorption bands were solvent dependent and were slightly blue shifted in comparison with the bands for dyes **20** and **22**–**24**. The hypsochromic shift of the absorption (**20** (463 nm) → **19** (441 nm) → **18** (411 nm)) is most probably caused by the decreased ability to accept electrons imparted by an amino group, which leads to a weaker intramolecular charge transfer (ICT). In other words, since alkyl groups donate charge to the nitrogen via inductive effects, the higher the number of alkyl chains (and the greater the number of bonds in the alkyl chain), the greater the charge polarization. Similarly to other amino-substituted derivatives, dyes **18** and **19** displayed high fluorescence quantum yields along with large Stokes shifts (Table 3).

Substantially different optoelectronic properties typically originate from attaching the same chemical substituent at different positions in the coumarin framework.[1] The difference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in effect of an electron-donating substituent at position 6 vs 7 was elaborated by Takadate and co-workers.[38] An even more detailed study by Cole and co-workers explained the various effects of electron-withdrawing groups at position 3 vs 4.[43] Needless to say, one can expect similar effects for coumarino-[3,4-*c*]coumarins and their $\pi$-expanded analogues. Indeed, the presence of an additional MeO group in dye **21** (in the place equivalent to position 8 of coumarin) triggers nonradiative deactivation, which results in a significant decrease in fluorescence quantum yield (**3** → **21**, 0.18 vs 0.004). This observation corroborates earlier findings for coumarins.[1,35,38,68]

We found it useful to compare the optical properties of new dyes with those of their simpler donor−acceptor analogues. Direct comparison of dye **3** with 7-hydroxy-3-carboxyethylcoumarin ($\lambda_{abs}$ 344 nm, $\lambda_{em}$ 402 nm, $\Phi_{fl}$ = 0.21)[67] revealed that expansion of the chromophore led to an ∼60 nm bathochromic shift of both absorption and emission, while the fluorescence quantum yield remained comparable (∼0.20). The same held true when the properties of compounds **19** and **20** were compared with those of 7-diethylamino-3-carboxyethylcoumarin ($\lambda_{abs}$ 417 nm, $\lambda_{em}$ 450 nm, $\Phi_{fl}$ = 0.81).[68]

When they were compared with recently described vertically expanded coumarins[69] and bis-coumarins,[70] compounds **3** and **14**−**25** exhibited similarly located $\lambda_{abs}$ (380−500 nm) and $\lambda_{em}$ values (425−529 nm). In comparison with dialkylaminobenzo-[*g*]coumarins ($\lambda_{abs}$ 460 nm, $\lambda_{em}$ 612 nm, and $\Phi_{fl}$ = 0.61)[6,7] dye **20** possesses very similar absorption ($\lambda_{abs}$ 463 nm) but hypsochromically shifted emission ($\lambda_{em}$ 528 nm). At the same time, however, all amino-substituted chromeno[3,4-*c*]-chromene-6,7-diones (**18**−**20**, **22**, and **24**) had higher fluorescence quantum yields in nonpolar solvents ($\Phi_{fl}$ > 0.9) vs all aforementioned analogues.

O-alkylation (**3** → **25**) resulted in a hypsochromic shift of both absorption and emission combined with a sharp decrease in fluorescence quantum yield in nonpolar solvents. In contrast, in polar DMSO the $\Phi_{fl}$ value of ester **25** was much stronger than that for phenol **3** (Table 3). This behavior strongly agreed with previously published results for O-alkylated coumarins.[62,63] This tendency is attributed to the fact that the energies of n−$\pi^*$ and $\pi$−$\pi^*$ transitions are very similar and are affected by the polarity of the solvent. It has been proved for 7-methoxycoumarin that in polar solvents the $\pi$−$\pi^*$ transition becomes the least energetic, which according to the Strickler−Berg equation should lead to a rise in $\Phi_{fl}$.[62]

It is noted that the Stokes shifts of typical coumarins increase by ∼2000 $cm^{-1}$ when a nonpolar solvent, such as toluene, is replaced with the very polar dimethyl sulfoxide.[71,72] For chromeno[3,4-*c*]chromene-6,7-diones the Stokes shift increases even less, typically 1000 $cm^{-1}$ (Table 3). In some cases such as dye **17**, the Stokes shift in DCM is larger than that in DMSO (4000 $cm^{-1}$ vs 3600 $cm^{-1}$).

Solvatochromism displayed by the majority of studied bis-coumarins can be explained by the charge-transfer character of the optical transition.[43,62] Still, in the case of phenol **21** the difference in absorption maxima in DMSO vs DCM is significantly larger. In nonpolar media ($CH_2Cl_2$), the absorption spectra show only a short-wavelength band around 350 nm. However, with an increase in the solvent polarity ($CH_3CN$, $CH_3OH$, DMSO), a second absorption band appeared at around 470−490 nm. Furthermore, the addition of basic reagents to solutions of hydroxyl derivatives shifted the equilibrium to the resonance-stabilized anionic form (Figure 2). The polarity effect of a strong donor group led to bathochromic and hyperchromic effects in the absorption spectrum accompanied by an increase of the fluorescence. The latter reveals the similarity with spectral properties of the dialkylamino-substituted bis-coumarins (Table 3, Figure 3).

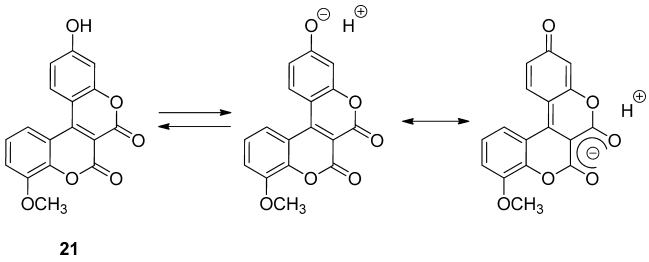


**Figure 2.** Proposed structures of resonance-stabilized anionic form of compound **21**.

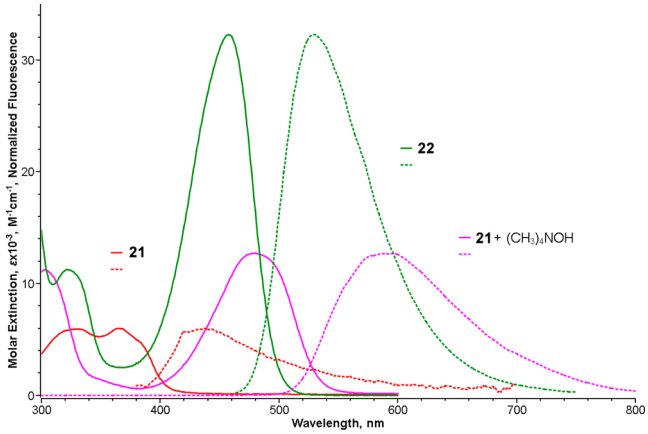


**Figure 3.** Absorption (solid lines) and emission (dashed lines) spectra of compounds **21** (excitation at 400 nm) and **22** (excitation at 480 nm) in DCM.

The signals from the fluorescence measurements for hydroxy derivatives of bis-coumarins were adequate only in a nonpolar aprotic solvent such as DCM. In other solvents, the dependence of the fluorescence curve areas on absorption intensity was not linear, making it impossible to obtain accurate results.

Regardless of the pathway of fusion, the bis-coumarins **15**−**17** derived from dihydroxynaphthalenes displayed strongly (50−80 nm) red shifted absorption vs compounds **3** and **14**. The effect on emission was weaker (Table 3). The details of the spectral behavior of annelated bis-coumarins **15**−**17** differed significantly. For compound **16**, the solvatochromic effect was similar to that observed for dye **21**, probably because of the additional stabilization of the anionic form by the benzene ring. Fluorescence quantum yields determined for dyes **15**−**17** were moderate ($\Phi_{fl}$ = 0.16−0.29), and the Stokes shifts were rather large (3600−4000 $cm^{-1}$). It is reasonable, therefore, to assume that these compounds do not possess entirely flat $\pi$ systems in the ground state (due to steric hindrance by hydrogens at the bay positions) but their geometry may become altered in the excited state.

The addition of arylethynyl substituents to the bis-coumarin framework did not give rise to significant changes in the absorption spectra of compounds **28** and **29**. This trend probably originates from an increase in the distance between the donor and acceptor (central bis-pyranone unit) as described


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by Meier.[73] Introduction of an electron-rich substituent (compound **28**) led to a significant increase of the molar absorption coefficient; however, this modification caused a negligible spectral shift and a sharp decrease in fluorescence intensity with concomitant increase of the Stokes shift (Table 3, Figure 4). Conversely, the addition of an electron-withdrawing

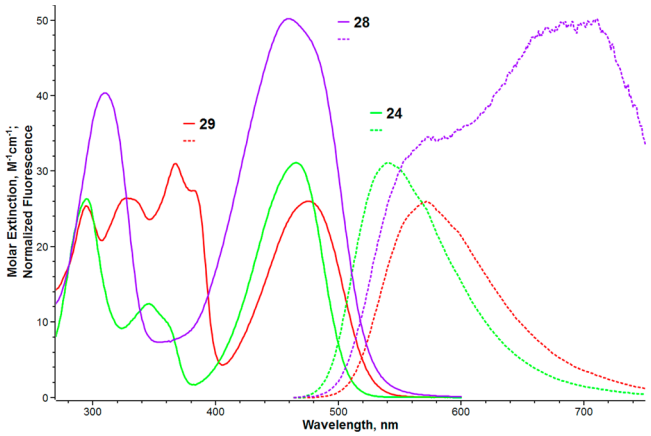


**Figure 4.** Absorption (solid lines) and fluorescence (dashed lines) spectra of compounds **24**, **28**, and **29** in $CH_2Cl_2$. Excitation at 480 nm.

moiety affected the optical properties in a different way. Although the absorption intensity for dye **29** was somewhat reduced, it demonstrated strong fluorescence properties (Table 3).

Fusing two bis-coumarin moieties in compound **31** did not result in significant bathochromic effects in either polar or nonpolar solvents vs the analogous dyes **20** and **22**. At the same time, the molar extinction coefficient was almost 2-fold larger in comparison with those of simple bis-coumarin derivatives. Compound **31** exhibited a strong yellow fluorescence in nonpolar media; however, the fluorescence efficiency in DMSO fell dramatically (Table 3).

## CONCLUSIONS

We found that the scope of the reaction between esters of coumarin-3-carboxylic acids and phenols can be greatly expanded with the use of both Lewis acid[75] and bases (such as DMAP) as catalysts. The use of dihydroxynaphthalenes or compounds bearing two pyranone units allowed us to further expand the scope of this reaction and to synthesize previously unknown architectures. In the case of 1,3-dihydroxynaphthalene, the structure of the product depended on the reaction conditions (hence, the mechanism). Diverse groups on the Michael acceptor unit were tolerated under the optimized reaction conditions. The structural diversity present in the prepared library of 16 V-shaped bis-coumarins (chromeno[3,4-*c*]chromene-6,7-diones) allowed us to control their optical properties. Yellow or orange dyes strongly emitting green-yellow light predominated. Their strongly polarized structures resulted in susceptibility to polarity and, consequently, to marked decreases in fluorescence quantum yield, as often observed in polar media. Given the appreciable bathochromic shift of both absorption and fluorescence versus analogous monocoumarins, typically higher fluorescence quantum yields, acceptable Stokes shifts, and straightforward syntheses, these new dyes hold great potential in photonics-related applications. The modifications to the structures enabled us to have full control over the optical properties. Fluorescence quantum yields can be modulated from a negligible value to 0.9, and fluorescence emission wavelengths can be shifted over 560 nm. In analogy to classical coumarins, the strength of the electron-donating group at the position para to the C−C double bond had a beneficial effect on $\Phi_{fl}$.

## EXPERIMENTAL SECTION

**General Remarks.** All reagents and solvents were purchased from commercial sources and were used as received unless otherwise noted. Reagent grade solvents ($CH_2Cl_2$, hexanes) were distilled prior to use. DMF was dried over magnesium sulfate and then distilled and stored under argon. Transformations with moisture- and oxygen-sensitive compounds were performed under a stream of argon. The reaction progress was monitored by thin-layer chromatography (TLC), which was performed on aluminum foil plates, covered with silica gel 60 $F_{254}$ or aluminum oxide 60 $F_{254}$ (neutral). Product purifications were done by column chromatography with Kieselgel 60 or aluminum oxide. Occasionally, dry column vacuum chromatography (DCVC) was performed for purification of products using silica gel Type D 5F. The identity and purity of prepared compounds were proved by $^1$H NMR and $^{13}$C NMR spectrometry as well as by MS spectrometry (via EI-MS or ESI-MS). HRMS data were acquired using a TOF analyzer. NMR spectra were measured on 400, 500, or 600 MHz instruments with TMS as the internal standard. All chemical shifts are reported in ppm. All melting points for crystalline products were measured with an automated melting point apparatus and are given without correction.

**General Procedures for the Synthesis of Chromeno[3,4-*c*]chromene-6,7-diones.** *Method A.* A mixture of coumarin (5 mmol), phenol (2.5 mmol), and $AlCl_3$ (0.82 mmol) was heated at 140 °C under argon until almost all of the starting material had disappeared (usually 2 h). The resulting mixture was cooled and quenched with diluted HCl. A yellow precipitate was formed, which was filtered off, washed with an excess of water, and recrystallized from EtOH or *i*-PrOH, unless otherwise indicated.

*Method B.* A mixture of coumarin (5 mmol), phenol (2.5 mmol), and $In(OTf)_3$ (0.0025 mmol) was heated at 140 °C under argon until almost all starting material disappeared (usually 16−24 h). The resulting mixture was cooled, and ca. 10 mL of EtOH was added. A yellow precipitate was formed, which was filtered off and recrystallized from EtOH or *i*-PrOH.

*Method C.* A mixture of coumarin (5 mmol), phenol (2.5 mmol), and DMAP (0.25 mmol) was heated at 140 °C under argon for 3 h. The resulting mixture was cooled and washed with EtOH (30 mL). The precipitate was recrystallized from EtOH, *i*-PrOH, or a mixture of pyridine and water (1/1).

*3-Hydroxychromeno[3,4-c]chromene-6,7-dione (**3**).* This compound was prepared according to general procedure B. Recrystallization from EtOH gave 556 mg of **3** (79%) as yellow crystals; mp >300 °C; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$ 11.50 (br s, 1H, OH), 8.36 (d, $J$ = 7.9 Hz, 1H, Ar), 8.28 (d, $J$ = 9.1 Hz, 1H, Ar), 7.84−7.79 (m, 1H, Ar), 7.51−7.46 (m, 2H, Ar), 7.95 (dd, $^3J$ = 9.1, $^4J$ = 2.3 Hz, 1H, Ar), 6.80 (d, $J$ = 2.3 Hz, 1H, Ar); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$ 102.8, 103.0, 107.2, 114.1, 115.2, 117.4, 124.7, 129.3, 131.1, 134.7, 152.3, 154.2, 155.2, 155.3, 156.9, 164.0; HRMS (EI) $m/z$ calculated for $C_{16}H_8O_5$ [$M^{\bullet+}$] 280.0372, found 280.0369; UV−vis ($CH_2Cl_2$) $\lambda_{max}$, nm ($\varepsilon \times 10^{-3}$) 374 (16.9), $\lambda_{em}^{max}$, nm 455; $\Phi_{fl}$ = 0.18.

*1,3-Dihydroxychromeno[3,4-c]chromene-6,7-dione (**14**).* This compound was prepared according to general procedure B. Recrystallization from EtOH gave 228 mg of **14** (39%) as orange crystals: mp >300 °C; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$ 11.22 (s, 1H, OH), 11.01 (s, 1H, OH), 7.97 (dd, $^3J$ = 8.1, $^4J$ = 1.3 Hz, 1H, Ar), 7.72−7.67 (m, 1H, Ar), 7.38 (dd, $^3J$ = 8.3, $^4J$ = 0.8 Hz, 1H, Ar), 7.33−7.29 (m, 1H, Ar), 6.42 (d, $J$ = 2.2 Hz, 1H, Ar), 6.30 (d, $J$ = 2.2 Hz, 1H, Ar); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$ 94.8, 98.1, 100.0, 102.9, 115.7, 116.1, 122.6, 132.0, 134.3, 153.6, 154.2, 155.4, 155.5, 157.1, 158.1, 164.6; HRMS (EI) $m/z$ calculated for $C_{16}H_8O_6$ [$M^{\bullet+}$] 296.0321, found 296.0318; UV−vis ($CH_2Cl_2$) $\lambda_{max}$, nm ($\varepsilon \times 10^{-3}$) 313 (8.3), 385 (11.7), $\lambda_{em}^{max}$, nm 511; $\Phi_{fl}$ = 0.1.


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*6-Hydroxybenzo[f]chromeno[3,4-c]chromene-2,3-dione* (**15**). This compound was prepared according to general procedure B. Recrystallization from DMSO/$H_2O$ gave 532 mg of **15** (64%) as yellow crystals: mp >300 °C; $R_f$ = 0.52 (silica, MeOH/DCM, 1/9); $^1$H NMR (500 MHz, DMSO) $\delta$ 6.38 (s, 1H, S), 7.02 (dt, 1H, $J$ = 7.5, 1 Hz, A), 7.46−7.49 (m, 2H, B and C), 7.55 (dt, 1H, $J$ = 7.5, 1 Hz, D), 7.68 (d, 1H, $J$ = 8 Hz, E), 7.73 (dt, 1H, $J$ = 8.0, 1.5 Hz, F), 7.96 (d, 1H, $J$ = 8 Hz, G), 8.26 (dd, 1H, $J$ = 7.5, 1 Hz, H), 12.25 (bs, OH); $^{13}$C NMR (125 MHz, DMSO) $\delta$ 97.9, 102.5, 103.1, 116.3, 117.3, 122.7, 123.1, 123.6, 125.6, 126.8, 127.4, 129.7, 130.4, 134.7, 153.4, 153.9, 155.5, 155.52, 157.6, 161.8; HRMS (EI) $m/z$ calculated for $C_{20}H_{10}O_5$,Na $[M + Na]^+$ 353.0426, found 353.0419; UV−vis ($CH_2Cl_2$) $\lambda_{max}$, nm ($\varepsilon \times 10^{-3}$) 442 (11.4). $\lambda_{em}^{max}$, nm 529; $\Phi_{fl}$ = 0.16.

*7-Hydroxybenzo[h]chromeno[3,4-c]chromene-1,14-dione* (**16**). A mixture of coumarin (5 mmol) and 1,3-dihydroxynaphthalene (2.5 mmol) was heated at 140 °C for 2 h. The resulting mixture was cooled, and ca. 10 mL of EtOH was added. A yellow precipitate was formed, which was filtered off and recrystallized from a DMSO/$H_2O$ mixture, giving 173 mg of **16** (21%) as yellow crystals: mp >300 °C; $R_f$ = 0.52 (silica, MeOH/DCM, 1/9); $^1$H NMR (500 MHz, DMSO) $\delta$ 7.27 (s, 1H, S), 7.46 (t, 1H, $J$ = 8 Hz, A), 7.55 (m, 2H, B and C), 7.44 (t, 1H, $J$ = 8 Hz, D), 7.83 (t, 1H, $J$ = 8 Hz, E), 7.91 (d, 1H, $J$ = 8 Hz, F), 8.10 (d, 1H, $J$ = 7.5 Hz, G), 8.33 (d, 1H, $J$ = 7.5 Hz, H), 11.16 (s, OH); $^{13}$C NMR (125 MHz, DMSO) $\delta$ 104.5, 105.9, 106.9, 115.9, 116.1, 117.0, 122.4, 122.9, 124.4, 126.0, 130.4, 131.9, 134.5, 136.5, 151.0, 152.9, 153.6, 153.7, 154.9, 155.2; HRMS (EI) $m/z$ calculated for $C_{20}H_{10}O_5$ $[M^{\bullet+}]$ 330.0528, found 330.0525; UV−vis ($CH_2Cl_2$) $\lambda_{max}$, nm ($\varepsilon \times 10^{-4}$) 447 (11.3), $\lambda_{em}^{max}$, nm 533; $\Phi_{fl}$ = 0.29.

*9-Hydroxybenzo[f]chromeno[3,4-c]chromene-2,3-dione* (**17**). This compound was prepared according to general procedure B. Recrystallization from EtOH gave 68 mg of **17** (8%) as yellow crystals: mp >300 °C; $R_f$ = 0.58 (silica, MeOH/DCM, 5/95); $^1$H NMR (500 MHz, DMSO) $\delta$ 7.12 (dd, 1H, $J_1$ = 8.8 Hz, $J_2$ = 2.3 Hz, Ar), 7.26 (m, 2H, Ar), 7.36 (d, 1H, $J$ = 8.8 Hz, Ar), 7.53 (m, 1H, Ar), 7.77 (m, 2H, Ar), 7.94 (d, 1H, $J$ = 8.8 Hz, Ar) 8.23 (d, 1H, $J$ = 8.8 Hz, Ar), 10.12 (s, OH); $^{13}$C NMR (125 MHz, DMSO) $\delta$ 107.3, 108.8, 110.4, 113.3, 116.4, 117.7, 118.5, 124.0, 125.5, 130.1, 131.1, 131.6, 135.4, 137.0, 154.0, 154.4, 155.66, 155.69, 155.74, 158.0; HRMS (EI) $m/z$ calculated for $C_{20}H_{10}O_5$ $[M^{\bullet+}]$ 330.0528, found 330.0529; UV−vis ($CH_2Cl_2$) $\lambda_{max}$, nm ($\varepsilon \times 10^{-4}$) 428 (7.8), $\lambda_{em}^{max}$, nm 517; $\Phi_{fl}$ = 0.22.

*3-Aminochromeno[3,4-c]chromene-6,7-dione* (**18**). This compound was prepared according to general procedure B. Recrystallization from EtOH gave 260 mg of **18** (37%) as orange crystals, which were recrystallized from a dilute DMF/$H_2O$ mixture to afford analytically pure product: mp 180−181 °C dec; $R_f$ = 0.6 (silica, MeOH/DCM, 5/95); $^1$H NMR (500 MHz, DMSO) $\delta$ 6.48 (d, 1H, $J$ = 2 Hz, Ar), 6.73 (dd, 1H, $J_1$ = 9.5 Hz, $J_2$ = 1 Hz, Ar), 6.99 (s, $NH_2$), 7.45 (m, 2H, Ar), 7.78 (m, 1H, Ar), 8.1 (d, 1H, $J$ = 9 Hz, Ar), 8.32 (d, 1H, $J$ = 7.5 Hz, Ar); $^{13}$C NMR (125 MHz, DMSO) $\delta$ 98.4, 99.1, 103.7, 104.6, 115.5, 117.3, 124.4, 129.3, 130.8, 134.2, 152.0, 154.0, 155.6, 155.9, 156.0, 157.7; HRMS (EI) $m/z$ calculated for $C_{16}H_{10}NO_4$ $[M + H]^+$ 280.0610, found 280.0601; UV−vis ($CH_2Cl_2$) $\lambda_{max}$, nm ($\varepsilon \times 10^{-4}$) 411 (19.9), $\lambda_{em}^{max}$, nm 498; $\Phi_{fl}$ = 0.96.

*3-Ethylamino-2-methylchromeno[3,4-c]chromene-6,7-dione* (**19**). This compound was prepared according to general procedure B. Recrystallization from *i*PrOH gave 283 mg of **19** (35%) as orange crystals: mp 200−201 °C; $^1$H NMR ($CDCl_3$, 500 MHz) $\delta$ 8.22 (d, $J$ = 8.0 Hz, 1H, Ar), 7.87 (s, 1H, Ar), 7.66 (t, $J$ = 7.5 Hz, 1H, Ar), 7.42−7.35 (m, 2H, Ar), 6.44 (s, 1H, Ar), 4.50 (br s, 1H, NH), 3.31 (q, $J$ = 7.0 Hz, 2H, $NCH_2CH_3$), 2.25 (s, 3H, $CH_3$), 1.38 (t, $J$ = 7.0 Hz, 3H, $NCH_2CH_3$); $^{13}$C NMR ($CDCl_3$, 125 MHz) $\delta$ 14.2, 17.2, 38.2, 96.2, 100.8, 104.6, 116.0, 118.1, 119.8, 124.1, 128.8, 129.0, 134.0, 152.4, 154.8, 156.7, 157.0, 157.4. HRMS (EI) $m/z$ calculated for $C_{19}H_{15}NO_4$ $[M^{\bullet+}]$ 321.1001, found 321.1002; UV−vis ($CH_2Cl_2$) $\lambda_{max}$, nm ($\varepsilon \times 10^{-3}$) 345 (7.47), 441 (27.2), $\lambda_{em}^{max}$, nm 509; $\Phi_{fl}$ = 0.84.

*3-Didodecylaminochromeno[3,4-c]chromene-6,7-dione* (**20**). This compound was prepared according to general procedure B. Purification by means of column chromatography (DCM/hexanes, 1/2) followed by crystallization from DCM/cyclohexane afforded 584 mg of **20** (38%) as yellow crystals: mp 170−171 °C; $R_f$ = 0.61 (silica, MeOH/DCM, 2/98); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 0.88 (m, 6H, $NR_2$), 1.27−1.35 (m, 33H, $NR_2$), 1.54 (bs, 3H, $NR_2$), 1.65 (m, 4H, $NR_2$), 3.38 (t, 4H, $J$ = 8 Hz, $NR_2$) 6.52 (d, 1H, $J$ = 2.6 Hz, Ar), 6.88 (dd, 1H, $J_1$ = 9.4 Hz, $J_2$ = 2.6 Hz, Ar), 7.36 (m, 1H, Ar), 7.41 (dd, 1H, $J_1$ = 8.3 Hz, $J_2$ = 1 Hz, Ar), 7.66 (m, 1H, Ar), 8.11 (d, 1H, $J$ = 8.3 Hz, Ar), 8.23 (d, 1H, $J$ = 8.1 Hz, Ar); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 14.0, 27.0, 29.27, 29.32, 29.4, 29.55, 29.59, 29.60, 29.61, 31.9, 51.4, 97.9, 100.0, 104.0, 109.9, 116.1, 118.1, 124.1, 128.7, 130.1, 134.0, 152.3, 153.1, 154.8, 156.8, 157.1, 158.0; HRMS (EI) $m/z$ calculated for $C_{40}H_{57}NO_4$ $[M^{\bullet+}]$ 615.4288, found 615.4301; UV−vis ($CH_2Cl_2$) $\lambda_{max}$, nm ($\varepsilon \times 10^{-4}$) 463 (30.3), $\lambda_{em}^{max}$, nm 528; $\Phi_{fl}$ = 0.94.

*3-Hydroxy-9-methoxychromeno[3,4-c]chromene-6,7-dione* (**21**). The product was obtained according to method A. The product was recrystallized from a mixture of pyridine and water (1/1): yield 0.6 g (77%); mp 339 °C dec; $^1$H NMR (500 MHz, pyridine-$d_5$) $\delta$ 8.23 (d, $J$ = 8.5 Hz, 1H), 7.84 (d, $J$ = 8.0 Hz, 1H), 7.32 (t, $J$ = 8.0 Hz, 1H), 7.26 (d, $J$ = 8.0 Hz, 1H), 7.13 (dd, $J$ = 8.5 2.0 Hz, 1H), 7.02 (d, $J$ = 2.5 Hz, 1H), 3.85 (s, 3H); $^{13}$C NMR (125 MHz, pyridine-$d_5$) $\delta$ 165.8, 158.2, 156.2, 155.9, 153.3, 148.3, 145.3, 131.6, 124.3, 120.5, 116.7, 116.2, 114.8, 108.1, 104.1, 103.9, 56.3; HRMS (EI) $m/z$ calculated for $C_{17}H_{10}O_6$ $[M^+]$ 310.0477, found 310.0470; UV−vis ($CH_2Cl_2$) $\lambda_{max}$, nm ($\varepsilon \times 10^{-3}$) 365 (5.97), $\lambda_{em}^{max}$, nm 438; $\Phi_{fl}$ = 0.004.

*3-(Diethylamino)-9-methoxychromeno[3,4-c]chromene-6,7-dione* (**22**). The product was obtained following the general published method.[57] The product was recrystallized from ethanol: yield 0.72 g (79%); mp 185−186 °C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.06 (d, $J$ = 9.0 Hz, 1H), 7.74 (d, $J$ 8.0 Hz, 1H), 7.27 (t, $J$ = 8.0 Hz, 1H), 7.17 (d, $J$ = 8.0 Hz, 1H), 6.70 (dd, $J$ = 9.0, 2.5 Hz, 1H), 6.50 (d, $J$ = 3.0 Hz, 1H), 3.96 (s, 3H), 3.48 (q, $J$ = 7.0 Hz, 4H), 1.27 (t, $J$ = 7.0 Hz, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 158.1, 157.0, 156.1, 152.6, 152.5, 148.1, 144.9, 130.4, 123.7, 119.8, 116.6, 115.3, 109.7, 104.4, 100.4, 97.8, 56.3, 45.2, 12.5; HRMS (EI) $m/z$ calculated for $C_{21}H_{19}NO_5$ $[M^{\bullet+}]$ 365.1263, found 365.1270; UV−vis ($CH_2Cl_2$) $\lambda_{max}$, nm ($\varepsilon \times 10^{-3}$) 322 (11.2), 458 (32.3), $\lambda_{em}^{max}$, nm 530; $\Phi_{fl}$ = 0.91.

*3-(Diethylamino)-10-nitrochromeno[3,4-c]chromene-6,7-dione* (**23**). Coumarin **5** (263 mg, 1 mmol) and 3-diethylaminophenol (165 mg, 1 mmol) were heated at 120 °C for 1.5 h. When it was cooled, the mixture was solidified with $Et_2O$ (5 mL) and the precipitate was filtered off and washed with $Et_2O$ (5 mL). The crude product was recrystallized twice from MeCN to give 123 mg (65%) of the title compound as deep red crystals: mp 230 °C dec; $^1$H NMR (500 MHz, $CF_3COOD$) $\delta$ (ppm) 8.78 (d, $J$ = 9 Hz, 1H), 8.68 (d, $J$ = 9.5 Hz, 1H), 8.43 (m, 2H), 7.90 (s, 1H), 7.88 (d, $J$ = 9 Hz, 1H), 3.92 (q, $J$ = 7 Hz, 4H), 1.34 (t, $J$ = 7 Hz, 6H); $^{13}$C NMR (125 MHz, $CF_3COOD$) $\delta$ (ppm) 157.8, 156.8, 154.9, 153.6, 144.8, 134.0, 132.3, 122.2, 122.1, 121.6, 119.3, 118.0, 116.0, 115.7, 114.9, 114.6, 57.6, 11.2; EI-HRMS $m/z$ calcd for $[C_{20}H_{16}N_2O_6]^{\bullet+}$ 380.1008, found 380.1012; UV−vis ($CH_2Cl_2$) $\lambda_{max}$, nm ($\varepsilon \times 10^{-3}$) 350 (22.1), 494 (22.2). Anal. Calcd for $C_{20}H_{16}N_2O_6$: C, 63.16; H, 4.24; N, 7.37. Found: C, 63.02; H, 4.42; N, 7.38.

*3-Bromo-10-(diethylamino)chromeno[3,4-c]chromene-6,7-dione* (**24**). The product was obtained from ethyl 7-bromocoumarin-3-carboxylate[74] and 3-diethylaminophenol according to the literature method.[57] The product was recrystallized from ethanol: yield 0.90 g (87%); mp 237−238 °C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.06 (d, $J$ = 8.5 Hz, 1H), 7.98 (d, $J$ = 8.0 Hz, 1H), 7.54 (d, $J$ = 2.0 Hz, 1H), 7.48 (dd, $J$ = 9.0, 2.5 Hz, 1H), 6.72 (dd, $J$ = 9.5, 3.0 Hz, 1H), 6.52 (d, $J$ = 3.0 Hz, 1H), 3.49 (q, $J$ = 7.0 Hz, 4H), 1.28 (t, $J$ = 7.0 Hz, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 158.2, 156.8, 156.0, 155.0, 153.0, 151.6, 129.8, 129.6, 128.4, 127.5, 121.2, 115.0, 110.0, 103.9, 99.8, 97.8, 45.2, 12.5; HRMS (EI) $m/z$ calculated for $C_{20}H_{16}BrNO_4$ $[M^{\bullet+}]$ 413.02627, found 413.02579; UV−vis ($CH_2Cl_2$) $\lambda_{max}$, nm ($\varepsilon \times 10^{-3}$) 346 (12.4), 466 (31.1), $\lambda_{em}^{max}$, nm 540; $\Phi_{fl}$ = 0.90. Anal. Calcd for $C_{20}H_{16}BrNO_4$ (414.25): C, 57.99; H, 3.89; N, 3.38. Found: C, 57.69; H, 3.78; N, 3.28.

*3-(2-tert-Butoxy-2-oxoethoxy)chromeno[3,4-c]chromene-6,7-dione* (**25**). A mixture of **3** (560 mg, 2 mmol), *tert*-butyl bromoacetate (443 $\mu$L, 3 mmol), and $K_2CO_3$ (414 mg, 3 mmol) in dry DMF (10 mL) was heated at 60 °C for 16 h. The resulting solution was poured into a mixture of AcOEt and water, and the organic phase was


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separated, washed with water, and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was recrystallized from AcOEt to afford 542 mg of **25** (69%) as a white powder: mp 172−174 °C dec; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$ 8.38−8.34 (m, 2H, Ar), 7.84−7.79 (m, 1H, Ar), 7.51−7.49 (m, 2H, Ar), 7.09−7.05 (m, 2H, Ar), 4.90 (s, 2H, $CH_2$), 1.44 (s, 9H, $CH_3$); $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$ 28.2, 65.9, 82.4, 102.5, 104.7, 109.4, 113.9, 115.7, 117.9, 125.3, 129.7, 131.2, 135.3, 152.6, 154.7, 155.59, 155.64, 157.0, 163.4, 167.5; HRMS (EI) $m/z$ calculated for $C_{22}H_{18}O_7$ [$M^{\bullet+}$] 394.1053, found 394.1052; UV−vis ($CH_2Cl_2$) $\lambda_{max}$, nm ($\varepsilon \times 10^{-3}$) 305 (11.0), 365 (17.9), $\lambda_{em}^{max}$, nm 440; $\Phi_{fl}$ = 0.008.

*3-(Diethylamino)-10-((4-(dimethylamino)phenyl)ethynyl)-chromeno[3,4-c]chromene-6,7-dione (**28**).* Bis(benzonitrile)palladium(II) chloride (6 mg, 15 $\mu$mol), copper(I) iodide (2 mg, 10 $\mu$mol), a 0.25 M solution of tri-*tert*-butylphosphine in toluene (0.13 mL, 32 $\mu$mol), and diisopropylamine (0.09 mL, 60 $\mu$mol) in anhydrous dioxane (1 mL) were stirred under an Ar atmosphere at room temperature for 20 min. Compound **24** (0.21 g, 0.5 mmol) and 4-ethynyl-*N*,*N*-dimethylaniline (**26**; 0.09 g, 0.6 mmol) were placed in the reaction flask, and the mixture was stirred under an Ar atmosphere at room temperature overnight. Dichloromethane (10 mL) was added, and the solution was filtered. The filtrate was evaporated, and the product was eluted with a DCM/$CH_3OH$ mixture (98/2) through a silica gel column. The fraction with the product was evaporated, and the residue was recrystallized from $CHCl_3$ to yield 0.18 g (77%) of the title compound: mp 160 °C; $^1$H NMR (500 MHz, DMSO-$d_6$): $\delta$ 8.25 (d, $J$ = 8.5 Hz, 1H), 8.08 (d, $J$ = 9.5 Hz, 1H), 7.44−7.47 (m, 2H), 7.40 (d, $J$ = 9.0 Hz, 2H), 6.86 (dd, $J$ = 9.5 2.5 Hz, 1H), 6.72 (d, $J$ = 9.0 Hz, 2H), 6.59 (d, $J$ = 2.5 Hz, 1H), 3.52 (q, $J$ = 7.0 Hz, 4H), 2.98 (s, 6H), 1.18 (t, $J$ = 7.0 Hz, 6H); $^{13}$C NMR (125 MHz, DMSO-$d_6$) $\delta$ 158.1, 156.4, 155.9, 154.6, 153.0, 151.4, 151.1, 133.4, 130.8, 129.8, 129.5, 127.1, 119.0, 115.3, 112.2, 110.6, 107.6, 103.8, 99.1, 97.3, 97.0, 87.1, 79.6, 44.8, 12.9; HRMS (EI) $m/z$ calculated for $C_{30}H_{26}N_2O_4$ [$M^{\bullet+}$] 478.1893, found 478.1888 UV−vis ($CH_2Cl_2$) $\lambda_{max}$, nm ($\varepsilon \times 10^{-3}$) 310 (40.3), 459 (50.2), $\lambda_{em}^{max}$, nm 691; $\Phi_{fl}$ = 0.04.

*3-(Diethylamino)-10-((4-cyanophenyl)ethynyl)chromeno[3,4-c]-chromene-6,7-dione (**29**).* The reaction was carried out similarly as for compound **28** using bis-coumarin **24** (0.21 g, 0.5 mmol) and 4-ethynylbenzonitrile (**27**, 0.076 g, 0.6 mmol). The product was eluted with a mixture of DCM-$CH_3OH$ (96:4) through a silica gel column. The fraction with the product was evaporated, and the residue was solidified with $CH_3CN$ (20 mL) to yield 0.19 g (81%) of the title compound: mp 306−307 °C dec; $^1$H NMR (500 MHz, $CF_3COOD$) $\delta$ 8.79 (d, $J$ = 9.0 Hz, 1H), 8.42 (d, $J$ = 8.5 Hz, 1H), 8.82−7.87 (m, 2H), 8.69−7.75 (m, 6H), 3.89 (q, $J$ = 7.5 Hz, 4H), 1.32 (d, $J$ = 7.0 Hz, 6H); $^{13}$C NMR (125 MHz, $CF_3COOD$) $\delta$ 157.9, 157.0, 156.3, 144.6, 134.8, 134.7, 134.6, 134.5, 131.8, 130.7, 130.1, 123.3, 122.0, 116.9, 114.7, 113.1, 108.3, 96.5, 92.1, 78.5, 57.8, 11.4; HRMS (EI) $m/z$ calculated for $C_{29}H_{20}N_2O_4$ [$M^{\bullet+}$] 460.14231, found 460.14422; UV−vis ($CH_2Cl_2$) $\lambda_{max}$, nm ($\varepsilon \times 10^{-3}$) 367 (30.9), 476 (26.0), $\lambda_{em}^{max}$, nm 572; $\Phi_{fl}$ = 0.69.

*Diethyl 10-Methyl-2,8-dioxo-2,8-dihydropyrano[3,2-g]chromene-3,7-dicarboxylate (**30**).* 4,6-Dihydroxy-5-methylisophthalaldehyde[66] (1 g, 5.5 mmol), diethyl malonate (3.52 g, 22 mmol), and a few drops of piperidine were heated at 130 °C for 4 h. When the mixture was cooled, 15 mL of ethyl acetate was added, and the mixture was stirred for an additional 10 min. The precipitate was filtered off and washed twice with ethyl acetate (2 × 5 mL). The crude product was recrystallized twice from MeCN to give 1.45 g (70%) of pure compound **30** as colorless plates: mp 295 °C dec, lit.[65] mp 292.5−294.5 °C; $^1$H NMR (500 MHz, $CF_3COOD$) $\delta$ (ppm) 9.05 (s, 1H), 8.24 (s, 1H), 4.64 (q, $J$ = 7.1 Hz, 4H), 2.67 (s, 3H) 1.57 (t, $J$ = 7.5 Hz, 6H); $^{13}$C NMR (125 MHz, $CF_3COOD$) $\delta$ (ppm) 164.4, 160.0, 156.1, 150.9, 130.1, 116.3, 116.1, 116.0, 64.1, 12.0, 6.0; EI-HRMS $m/z$ calcd for $[C_{19}H_{16}O_8]^{\bullet+}$ 372.0845, found 372.0857; UV−vis ($CH_2Cl_2$) $\lambda_{abs}^{max}$, nm ($\varepsilon \times 10^{-3}$) 363 (21.0), $\lambda_{em}^{max}$, nm 412; $\Phi_{fl}$ = 0.02. Anal. Calcd for $C_{19}H_{16}O_8$: C, 61.29; H, 4.33. Found: C, 61.07; H, 4.28. $^1$H NMR and $^{13}$C NMR spectra were used to establish the identity and purity of compound **30**.

*Synthesis of π-Expanded Coumarin **31**.* Compound **30** (372 mg, 1 mmol) and 3-diethylaminophenol (330 mg, 2 mmol) were heated at 140 °C for 5 h. When the reaction mixture was cooled, *i*-PrOH (20 mL) was added. The precipitate was filtered off and washed twice with *i*-PrOH (2 × 5 mL). The crude product was recrystallized from DMF to give 22 mg (14%) of the title compound as orange needles: mp 351 °C dec; $^1$H NMR (500 MHz, $CF_3COOD$) $\delta$ (ppm) 9.29 (s, 1H), 8.53 (d, $J$ = 6.5 Hz, 2H), 7.92 (s, 2H), 7.81 (d, $J$ = 6.5 Hz, 2H), 3.88 (q, $J$ = 7 Hz, 8H), 2.70 (s, 3H), 1.34 (t, $J$ = 7 Hz, 12H); $^{13}$C NMR (125 MHz, $CF_3COOD$) $\delta$ (ppm) 160.0, 159.0, 158.3, 155.8, 145.7, 145.6, 133.2, 129.8, 122.8, 120.9, 119.6, 115.1, 114.6, 109.5, 57.2, 11.2, 9.1; EI-HRMS $m/z$ calcd for $[C_{35}H_{30}N_2O_8]^{\bullet+}$ 606.2002, found 606.1996; UV−vis ($CH_2Cl_2$) $\lambda_{abs}^{max}$, nm ($\varepsilon \times 10^{-3}$) 380 (28.1), 458 (57.8); $\lambda_{em}^{max}$, nm 542; $\Phi_{fl}$ = 0.67.

**Optical Measurements.** A standard UV/vis spectrophotometer and a spectrofluorimeter were used to acquire the absorption and emission spectra. Spectrophotometric grade solvents were used without further purification. Quartz cells (10 mm) were used. Fluorescence quantum yields were determined using 9,10-diphenylanthracene as standard or fluorescein in NaOH (0.1 M) as a standard. Excitation wavelengths were 400 nm (for dyes **3**, **14**, **21**, and **25**), 440 nm (for dyes **15**−**19**), 480 nm (for dyes **20**, **22**, **24**, **28**, **29**, and **31**) and 510 nm (for compound **23**), respectively.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Figures giving $^1$H NMR and $^{13}$C NMR spectra for compounds **3**, **14**−**25**, and **28**−**31**, as well as detailed analysis of the structures of compounds **15** and **16** on the basis of 2D NMR. This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail for D.T.G.: dtgryko@icho.edu.pl.

### Notes

The authors declare no competing financial interest.

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