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Design and Synthesis of Donor–Acceptor Stenhouse Adducts: A Visible Light Photoswitch Derived from Furfural

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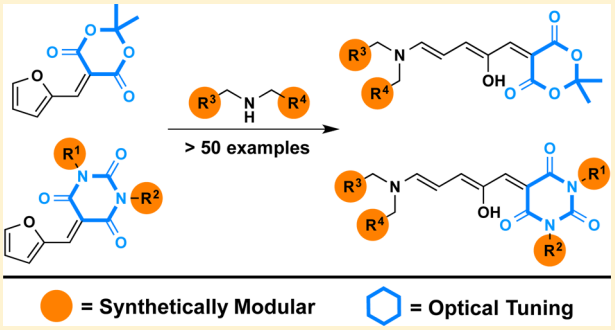
Supporting Information

ABSTRACT: The development of an easily synthesized, modular, and tunable organic photoswitch that responds to visible light has been a long-standing pursuit. Herein we provide a detailed account of the design and synthesis of a new class of photochromes based on furfural, termed donor–acceptor Stenhouse adducts (DASAs). A wide variety of these derivatives are easily prepared from commercially available starting materials, and their photophysical properties are shown to be dependent on the substituents of the push–pull system. Analysis of the switching behavior provides conditions to access the two structural isomers of the DASAs, reversibly switch between them, and use their unique solubility behavior to provide dynamic phase-transfer materials. Overall, these negative photochromes respond to visible light and heat and display an unprecedented level of structural modularity and tunabilty.



INTRODUCTION

In recent decades, significant effort has been devoted to the chemistry of organic photochromic systems. Their ability to undergo reversible spectral and physical property changes has led to applications ranging from energy production,[1] chemical sensing,[2] and molecular actuators[3] to biological systems.[4,5] The driving force for this focus is the abundant and versatile nature of light as a stimulus which enables both temporal and spatial resolution.

Recently, we reported a new class of T-type organic photochromic molecules (Scheme 1) that operate using visible light,[6] termed donor–acceptor Stenhouse adducts (DASAs).[7] The synthesis of these organic photoswitches can be conducted on large scale under simple reaction conditions starting from furfural, a commodity chemical derived from nonedible biomass. In our initial communication, we focused on the properties and application of this new class of organic photochromic molecules. Herein we provide a detailed report on our synthetic efforts in this area and describe a range of additional properties for these compounds.

During the initial design stage, we established three criteria for an ideal new class of organic photochromic material that helped guide our discovery efforts: (1) intrinsic activation by visible light, (2) significant change in spectral absorption, solubility, and volume, and (3) facile synthetic access, modularity and tunability (Scheme 1).

A number of important contributions helped us establish the basis for the discovery of DASAs as a photoswitching platform. In 1870, Stenhouse discovered that in the presence of 2 equiv of a primary or secondary aniline and 1 equiv of protic acid furfural undergoes ring opening to give stable, intensely colored salts whose structure, five-carbon cyanine dyes with an OH group at the second carbon atom, was established by Schiff in 1887 (Figure 1A).[8] Initial imine/iminium formation between furfural and the aniline activates the furan nucleus to nucleophilic attack, which then leads to ring opening of furan and formation of the Stenhouse salt. Nearly a century later, in 1982, Honda disclosed the visible light mediated negative photochromism of Stenhouse salts (Figure 1B).[9] Although the mechanism and product of the photochromic reaction was not reported, the enolic OH group was determined to be critical for the photobleaching–thermal recoloration process since the parent cyanine dyes with no OH group (obtained by the Zincke ring opening of pyridinium salts) do not display these properties.[10] In Honda's report, the photobleaching-thermal recoloration process was strongly dependent on the concentration of added acid, and in the presence of 100 equiv of HCl photobleaching did not occur. This result is consistent with related studies on Stenhouse salts by Lewis and Mulquiney, even though they did not study the photochromic properties of these systems.[11] In the Lewis study, treatment of the Stenhouse salts with base only gave the corresponding colorless cyclopentenone adducts (Figure 1C).[11a] Further, in 2000, Safar and co-workers reported a preliminary study on the rearrangement of 5-(furan-2-ylmethylene-)-2,2-dimethyl-1,3-dioxane-4,6-dione **6** with cyclic secondary aliphatic amines (Figure 1D).[12] In contrast to Stenhouse's work, this system

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Scheme 1. Organic Photochromic Materials: Design, Synthesis, and Properties

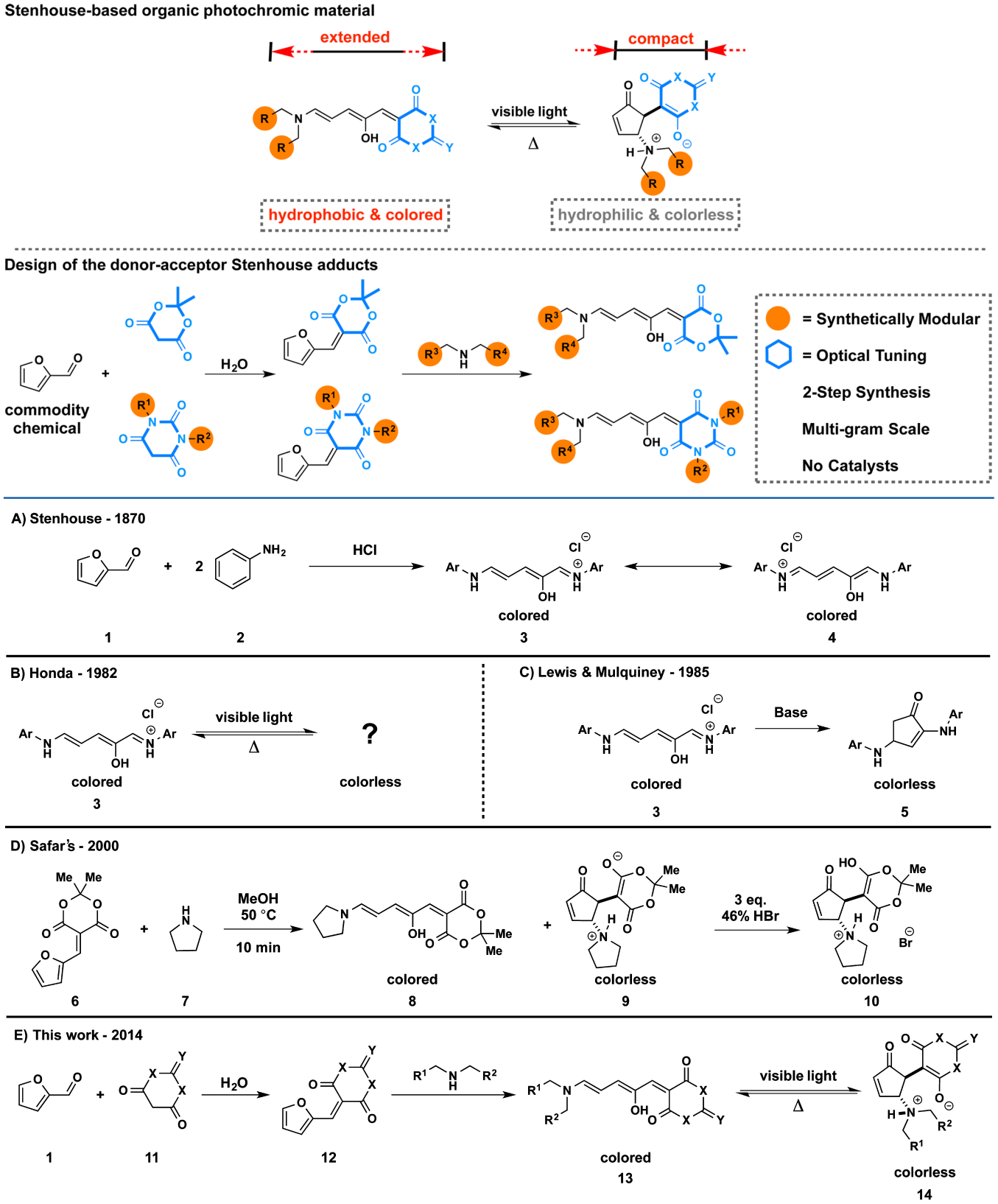

Figure 1. (A) Stenhouse's ring opening of furfural by aniline and protic acid, (B) photochromism of Stenhouse salts examined by Honda, (C) Lewis and Mulquiney's base-mediated cyclization of Stenhouse salts, (D) Safar's secondary amine ring opening and rearrangement of activated furans, (E) this work: photochromic donor–acceptor Stenhouse adducts.

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exploited the electron-withdrawing nature of the cyclic dicarbonyl to impart the same result as imine/iminium activation. Interestingly, reaction of furan **6** with morpholine or piperidine in a 2:1 or 1:1 molar ratio resulted in a mixture of two compounds, the Stenhouse-based adduct **8** and the corresponding cyclopentenone **9**. All attempts to separate this mixture were unsuccessful; however, treatment of this mixture with excess HBr gave exclusively the cyclopentenone hydrobromide **10**, and presumably the equilibrium was driven to the product by precipitation of the salt.

Based on these reports and our interest in the cascade rearrangements of furylcarbinols,[13] we hypothesized that the photochromic behavior observed by Honda was due to a reversible interconversion between the open Stenhouse salt and the closed 4,5-aminocyclopentenone. Combined, these studies also suggest that the ability to tune and control the process by which the open Stenhouse adduct and the closed cyclopentenone adduct interconvert is dependent on the substituents of the push−pull system derived from the amine ring opening of furfural or its derivatives. With these considerations in mind, the Stenhouse-based adducts with a general structure of **13** were selected for initial studies (Figure 1E).

RESULTS AND DISCUSSION

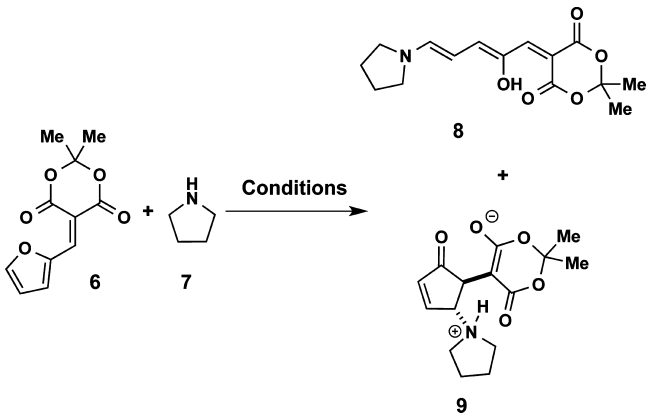
Synthesis. At the outset, we sought to develop optimal conditions, compatible with a diverse range of secondary aliphatic amines, for the selective formation of the colored triene Stenhouse adduct **8** without concomitant generation of the cyclopentenone **9**. The optimal conditions were initially identified using pyrrolidine (Table 1). Reacting an equimolar ratio of furylidene−Meldrum's acid **6** and pyrrolidine in tetrahydrofuran provided the desired Stenhouse adduct **8** in 95% yield with filtration as the only purification necessary (entry 7). In direct contrast, the use of other solvents required heating to 50 °C and resulted in lower yields (entries 5 and 6) or inseparable mixtures of Stenhouse adduct **8** and cyclopentenone **9** (entries 1−4). While the addition of Lewis acids or bases such as dysprosium triflate or DABCO increased yields, these conditions also produced mixtures of **8** and **9** (entries 2 and 3).

With optimized conditions for the selective formation and isolation of the Stenhouse-based adduct **8**, we next proceeded to evaluate the generality of this process with a range of amines (Figure 2). We found that a broad array of secondary aliphatic amines were competent reaction partners, including both cyclic and acyclic amines, while secondary aniline derivatives also led to ring opened triene products, albeit in diminished yield (22%). Unfortunately, reaction of **6** with primary anilines and primary aliphatic amines resulted in decomposition.

With these results in hand, we then sought to determine if other active methylene compounds could effectively activate the furan ring toward ring opening.[14] To this end, the substrates outlined in Scheme 2 were prepared by Knoevenagel condensation with furfural, followed by treatment with diethylamine. To our gratification, the reactions provided the anticipated highly colored crystalline trienes **34** and **36** in 85% and 87% yield, respectively. Interestingly, the use of 1,1-dicyanomethylene-3-indanone and 1,3-bis(dicyanomethylene)-indan did not produce the desired triene, instead giving the expanded ring dihydroindenopyridine carbonitrile derivatives **38** and **40**, which upon standing oxidize to the pyridine adduct.[15]

Of these activating groups, we chose to further evaluate the scope of the furan ring opening with 1,3-dimethylbarbituric acid activated furan (**33**) and a range of secondary amines. We were particularly attracted to 1,3-disubstituted barbituric acids, as these moieties are readily prepared and the nitrogen

Table 1. Optimization of Reaction Conditions for the Selective Formation of Stenhouse-Based Adducts (DASAs)[a]



entry	solvent	temp (°C)	time (min)	product	yield[b] (%)
1	MeCN	50	60	8 + 9	60[c]
2[d]	MeCN	50	60	8 + 9	70[c]
3[e]	MeCN	50	60	8 + 9	80[c]
4	MeOH	50	30	8 + 9	80[c]
5	CH_2Cl_2	23	60	8	50
6	PhMe	50	30	8	50
7	**THF**	**23**	**10**	**8**	**95**

[a]Activated furan **6** (1 equiv) and pyrrolidine **7** (1 equiv) were sequentially added to the solvent and stirred at the temperature indicated. [b]Isolated yields. [c]Inseparable mixture of **8** and **9**. [d]10 mol % of dysprosium triflate added. [e]10 mol % of DABCO added.

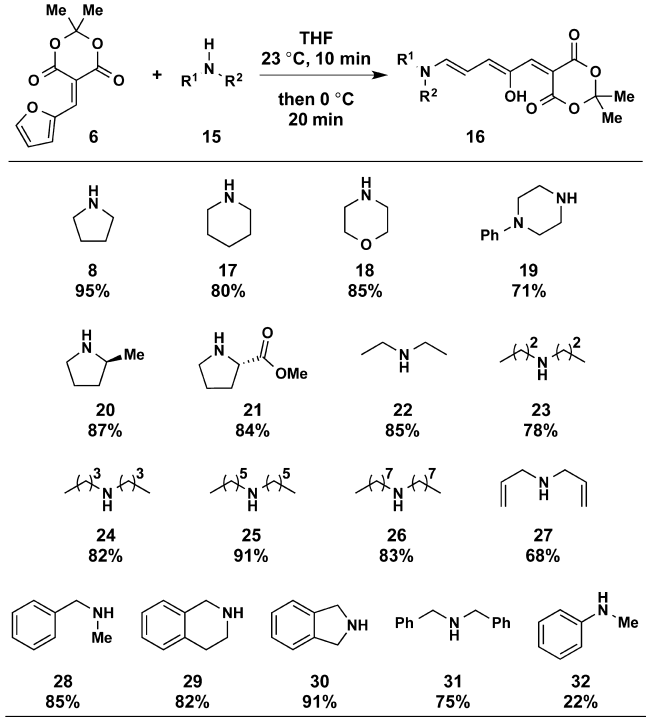


Figure 2. Synthesis of Meldrum's acid derived DASAs. [a]Isolated yields.

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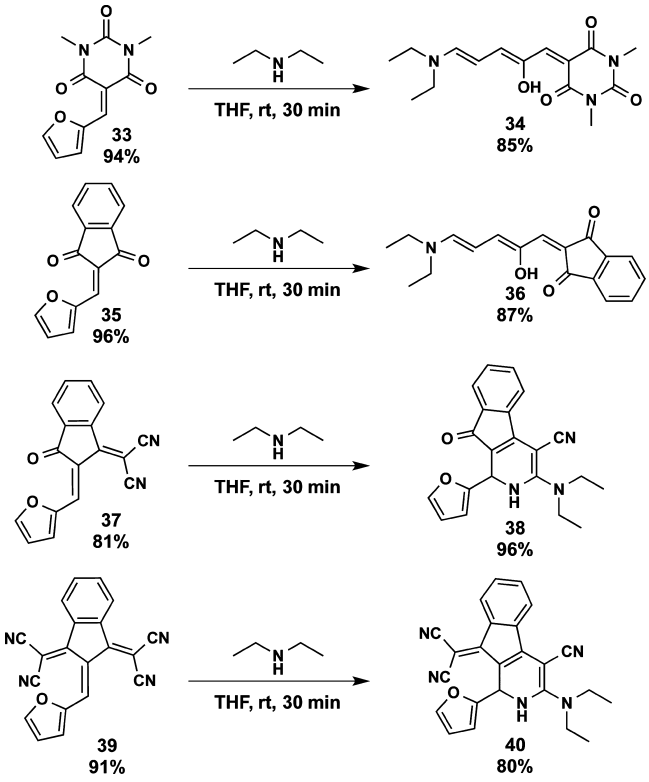
Scheme 2. Investigation of Furan Activating Groups for the Synthesis of DASAs



substituents provide a functional group handle to further tailor the acceptor group to specific applications. We were pleased to find that the desired Stenhouse adducts were formed in good yield and had nearly equal scope as the Meldrum's acid derivatives with respect to the compatibility of the amine nucleophile with few exceptions. In the case of morpholine (**44**) and phenylpiperazine (**45**) decomposition of **33** is observed, whereas for isoindoline (**55**), dibenzylamine (**56**), and *N*-methylaniline (**57**) the starting material is recovered (Figure 3).

To probe the potential diversity of substituents on the barbituric acid group and to provide evidence that the *N*-group could serve as a functional handle for the incorporation of these molecules into materials, we prepared six 1,3-disubstituted barbituric acids with various alkyl and aryl substituents. After condensation with furfural, reaction with diethylamine resulted in ring opening to give the anticipated colored trienes in high yield (Figure 4).

In terms of synthetic ease, it is worth noting that the two-step synthesis of the organic photochromic molecules can be achieved in a one-pot fashion "on water" without affecting yield. As shown in Scheme 3, on-water Knoevenagel condensation between furfural and either Meldrum's acid or 1,3-dimethylbarbituric acid is complete within 2 h.[16] Direct addition of the amine nucleophile results in formation of the Stenhouse adduct, which then can be isolated by extraction with dichloromethane (see the Supporting Information for full experimental details). The facile nature of this process further highlights the practicality and user-friendly protocol to access these novel organic photochromic materials. Of greater importance for the widespread use of these materials is the observation that these highly colored Stenhouse adducts are benchtop-stable, crystalline solids that can be stored without

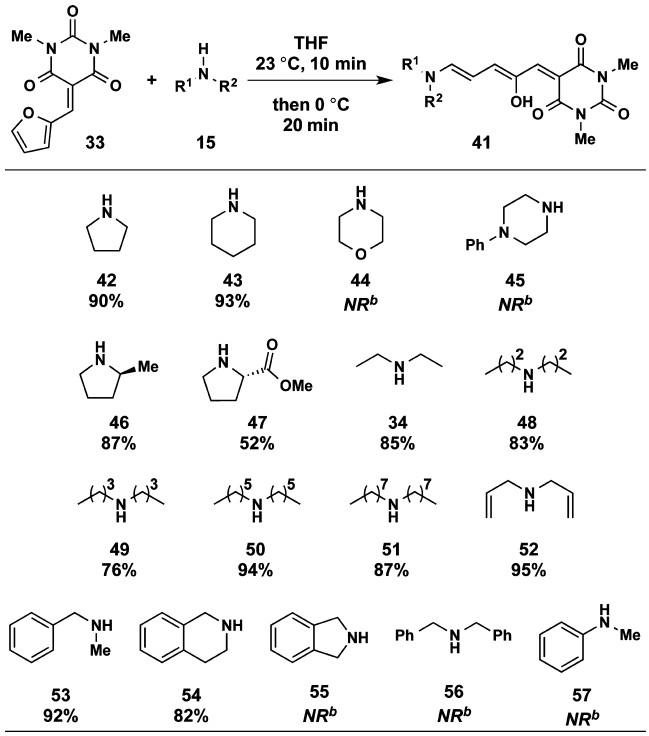


Figure 3. Synthesis of 1,3-dimethylbarbituric acid derived DASAs. [a]Isolated yields. [b]NR: no reaction.

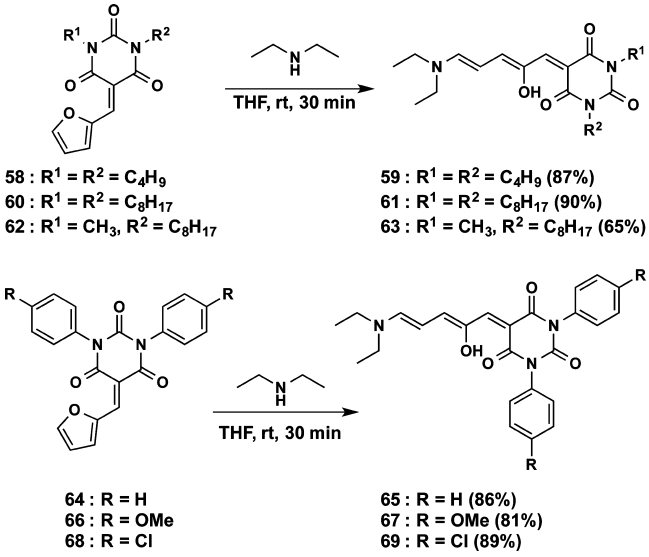
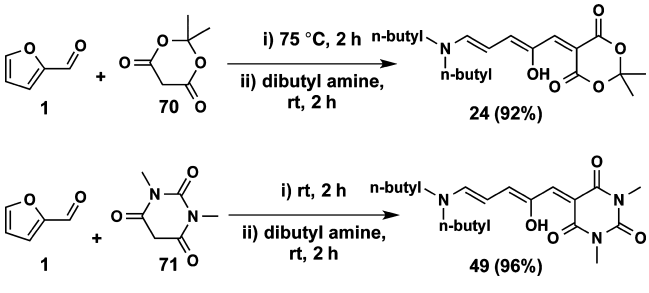


Figure 4. Synthesis of 1,3-disubstituted barbituric acid derived DASAs.

Scheme 3. One-Pot "On Water" Synthesis of DASAs



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precaution over extended periods of time. Significantly, we have observed no solid-state photochromism or decomposition of products stored under ambient conditions for over 2 years.

With straightforward access to the stable, highly colored triene adducts, we sought to develop conditions to isolate and characterize the metastable cyclopentenone adduct. Although the stability of the cyclopentenone adduct is highly dependent on the nature of the secondary amine and the acceptor group, we have found that photoisomerization in polar protic solvents provides access to the closed form for a number of organic photochromic molecules studied. For example, subjecting methanolic suspensions of Stenhouse adducts such as **8** to visible light irradiation results in the formation of the corresponding zwitterionic cyclopentenone. As shown in Figure 5, adducts were converted to their colorless cyclopentenone isomer in excellent yields. Importantly, this mild procedure allows for isolation of these materials without the use of concentrated HBr, previously developed by Safar.[12] It is also important to note that a subset of the triene adducts synthesized do not undergo photoisomerization in methanol or toluene. These include adducts derived from amines bearing two benzylic carbons, isoindoline and dibenzylamine (**30** and **31**), or from amines bearing an electron-withdrawing group, proline methyl ester (**21** and **47**). Further, the Stenhouse adducts derived from acceptors other than Meldrum's acid or 1,3-disubstituted barbituric acids (namely indan-1,3-dione **36**) also fail to exhibit photoisomerization. Future studies to better understand these effects are ongoing in our laboratory.

Negative Photochromism and Related Properties. With efficient access to a range of Stenhouse-based triene derivatives, the properties of these materials were examined with the diethyl amine adducts **22**, **34**, and **36** as model systems.[6] During our initial investigations, we were encouraged by the ability to tune the absorption of the triene by modifying the acceptor group. Of note, the choice of amine donor does not affect the λ_{max} of the Stenhouse-based complexes studied to date. In toluene, all DASAs derived from Meldrum's acid have a λ_{max} centered at 545 nm, from 1,3-disubstituted barbituric acids at 570 nm and from 1,3-indanedione at 600 nm (Figure 6). We have found that these trienes display appreciable solvatochromism similar to other merocyanine-type materials (see the Supporting Information).[17]

The unidirectional conversion of the colored triene **22** to its colorless zwitterionic cyclopentenone isomer **73** can be monitored using NMR spectroscopy (Figure 7A). Irradiating a solution of **22** in deuterated methanol with a standard incandescent bulb or hand-held fluorescent lamp leads to a decrease in the NMR resonances attributable to **22** and an increase in those for **73** over the course of 4 h. This process was further examined by UV−vis spectroscopy for **34** in methanol (Figure 7B). Similarly, visible light irradiation produces a decrease in the absorption of **34** as it cyclizes to **78** over 50 min.[18]

The reversible conversion between the colored triene and the colorless cyclopentenone adduct is most dramatically effected by solvent (Figure 8A). This is similar to spiropyran[19] and diarylethene[20] systems, which have also been shown to be highly solvent dependent. In protic solvents (methanol or water), the colored triene can be triggered by visible light and converted into the colorless zwitterionic cyclopentenone form; however, thermal reversion to the triene does not occur. In contrast, thermal reversion to the colored triene form is facile in halogenated solvents (dichloromethane, chloroform, or chlorobenzene), but photoisomerization to the cyclopentenone does not occur. For reversible photocyclization of the triene to cyclopentenone with thermal reversion of the cyclopentenone back to the triene, aromatic solvents (toluene, benzene, or xylenes) are ideal. While the difference in the rate of photocyclization for **22** vs **34** is negligible, it should be noted that adducts derived from 1,3-dimethylbarbituric acid undergo thermal reversion nearly twice as fast as those derived from Meldrum's acid (Figure 8B).[21]

Intrigued by the solution-state behavior of our DASA materials, we reasoned that these compounds could engage in dynamic phase transfer. If true, this enables applications of these compounds as visible light activated phase-transfer tags.[22]

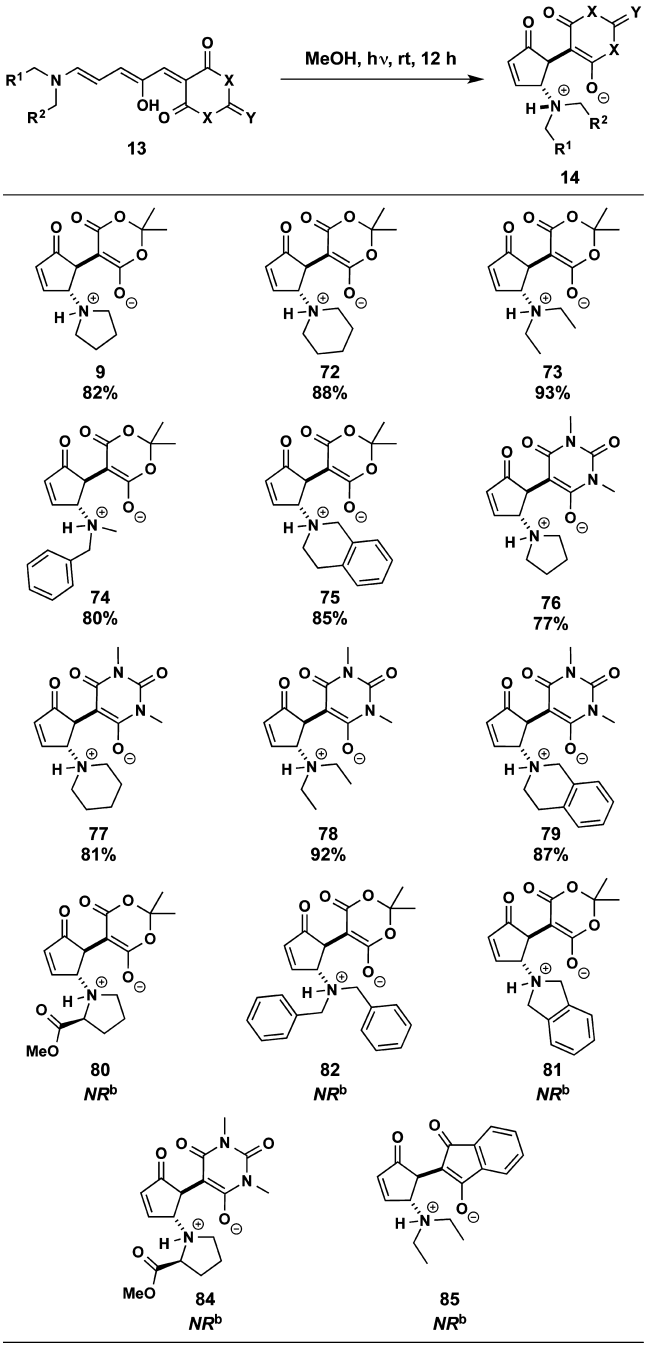

Figure 5. Photoisomerization of select DASAs. [a]Isolated yields. [b]NR: no reaction.

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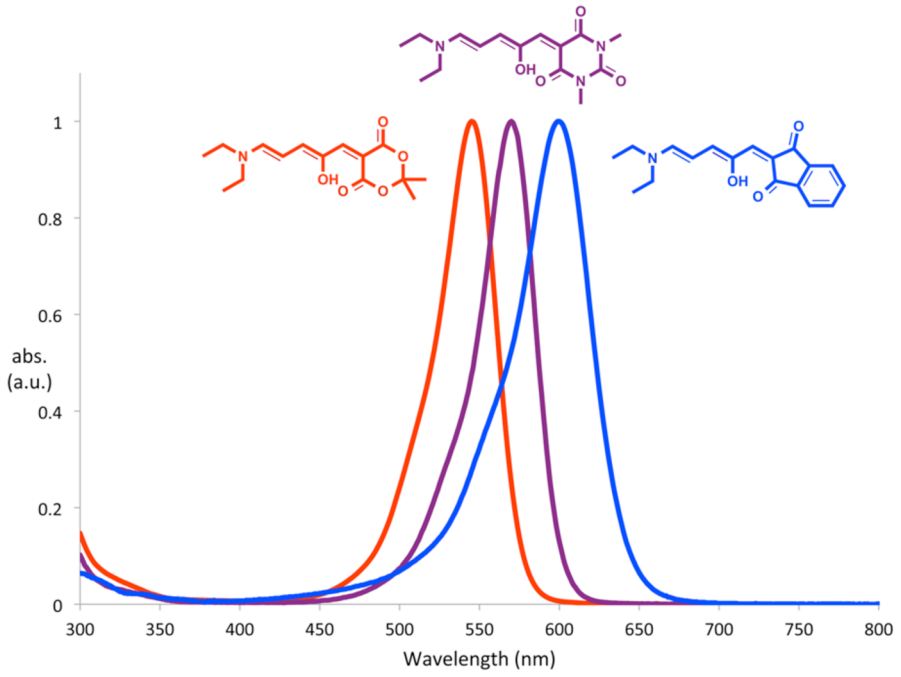

Figure 6. Absorption spectra of **22**, **34**, and **36** in toluene.

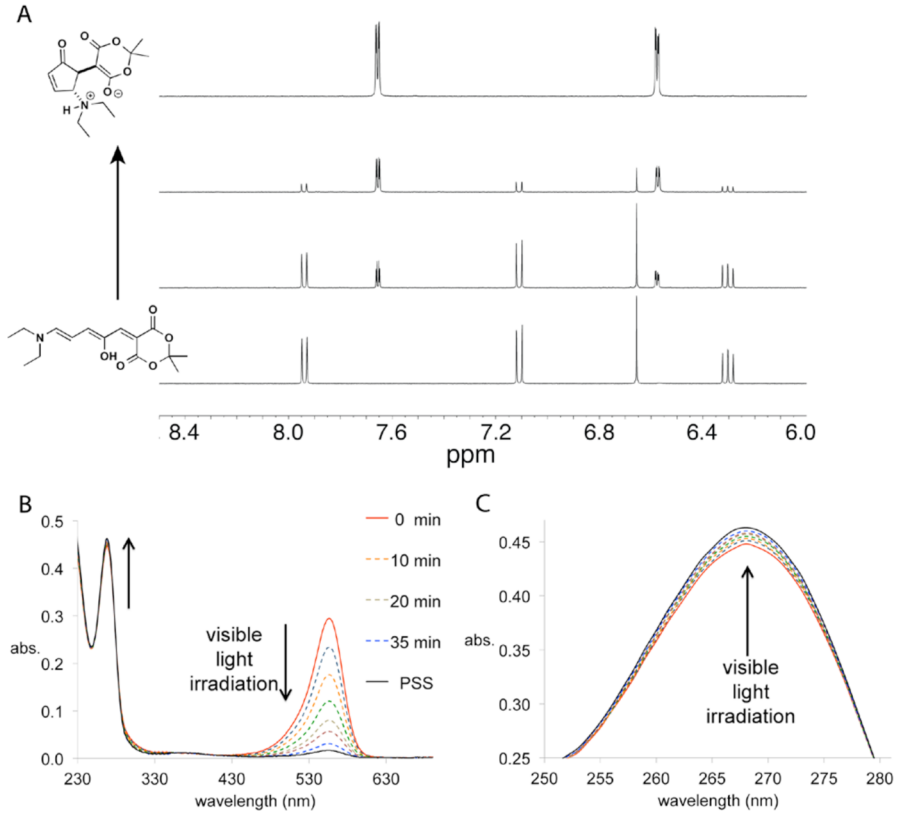

Figure 7. (A) The conversion of **22** to **73** by ^{1}H NMR in CD_3OD over 4 h. (B) Absorption spectra of **34** to **78** on irradiation with visible light (λ = 570 nm) in methanol. (C) Expanded view of absorption spectra between 250−280 nm.

To probe the potential of this avenue, we layered toluene solutions of Meldrum's acid derived adducts **22**, **24**, and **26** over water (Figure 9). Upon irradiation of these biphasic systems with visible light, the DASAs were observed to cyclize with transfer of the DASA to the aqueous layer being quantified by UV−vis and NMR spectroscopy. We found that the amine donor plays a dramatic role in the efficacy of transfer to the aqueous phase. Employing short alkyl chain amine donors (derivatives **22** and **24**) results in near quantitative transfer of the DASA to the aqueous phase. Conversely, a long alkyl chain donor (derivative **26**) results in DASA cyclization; however, this derivative fails to transfer to the aqueous phase. Efforts to

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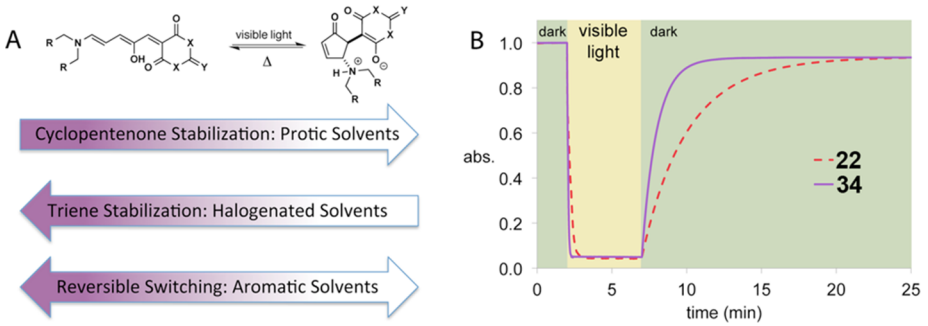

Figure 8. (A) Solution-state switching behavior of DASAs. (B) In situ kinetic plot of the switching cycle of **22** and **34** in PhMe, monitored at λ_{max} of 545 and 570 nm, respectively.

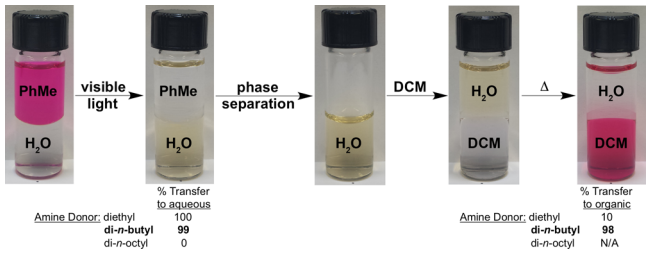

Figure 9. Schematic representation of DASA dynamic phase transfer and results.

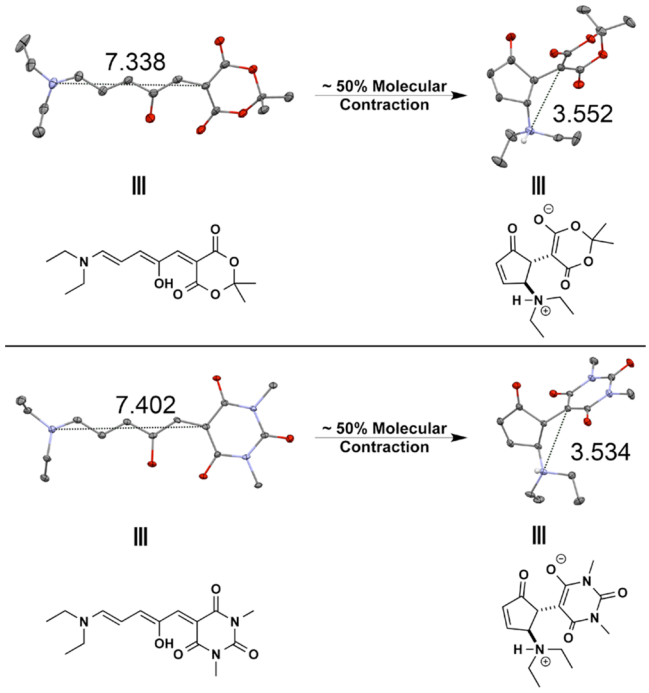

Figure 10. ORTEP renderings of **22** and **73** (top) and **34** and **78** (bottom) (distances in angstroms, 50% probability ellipsoids, hydrogen atoms omitted for clarity).

thermally revert the cyclopentenone to the triene and transfer the adduct from the aqueous layer back to the aromatic organic layer were unsuccessful. However, separation of the resultant aqueous solution and extraction with DCM enabled recovery of the triene forms of derivatives **22** and **26** in 10% and quantitative yield, respectively, again highlighting the critical role of the amine donor in this process. Application of this procedure toward catalyst separation and recycling are underway in our laboratory and will be reported in due course.

Finally, further structural characterization of the two isomeric DASA states was provided by single-crystal X-ray diffraction, which revealed the triene form to be a conjugated, linear, hydrophobic material with an amine "donor" and a 1,3-dicarbonyl "acceptor". Our assignment of the cyclopentenone form as a zwitterion comes from the observation that these materials are water-soluble and further from bond length measurements in their crystal structures. We have found that one of the ester (or amide) functionalities in the 1,3-dicarbonyl moiety displays bond lengths more appropriate for a β-enolic ester (or amide) than a β-dicarbonyl (see the Supporting Information for further details). The large volume change these materials exhibit upon switching is clearly evident in their crystal structures (Figure 10). Atomic distance measurements identify a 52% molecular contraction of the DASA upon switching as measured from the nitrogen donor to the carbon at the 5 position of the acceptor (7.34/7.40 Å for the open derivative, 3.55/3.53 Å for the closed). This distance is significantly greater than that observed for other privileged photoswitches whose molecular contraction has been exploited for a number of applications, including the spiropyran[23] or azobenzene[24] systems, (~20% and 30% molecular contraction based on distance (Å) in published crystal structures, respectively).

■ CONCLUSION

In summary, we have developed general conditions for the ring opening of furfural derivatives activated with cyclic β-dicarbonyls by a wide variety of secondary amines to provide 1-dicarbonylmethylene-2-hydroxy-5-(dialkylamino)pentadienes. This strategy provides unprecedented synthetic modularity and tunability in the preparation of visible light activated photoswitches. We have further demonstrated that this process can be performed in a one-pot fashion in water from commercially available starting materials, leading to materials that undergo reversible photochromism to give stable, colorless 4-aminocyclopentenone zwitterions. We believe this work is a powerful addition to the field of organic photochromes, providing a versatile platform with unique properties that are synthetically accessible to a wide range of researchers.

■ EXPERIMENTAL SECTION

General Methods. Unless stated otherwise, reactions were conducted in flame-dried glassware under an atmosphere of air using

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reagent-grade solvents. All commercially obtained reagents were used as received. Reaction temperatures were controlled using automated temperature modulator, and unless stated otherwise, reactions were performed at room temperature (rt, approximately 23 °C). Thin-layer chromatography (TLC) was conducted with E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by exposure to UV light (254 nm) or stained with anisaldehyde or potassium permanganate. Flash column chromatography was performed using normal-phase silica gel (60 Å, 230−240 mesh, Merck KGA). ^{1}H NMR spectra were recorded at 500 or 600 MHz and are reported relative to deuterated solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration; ^{13}C NMR spectra were recorded at 125 or 150 MHz. Data for ^{13}C NMR spectra are reported as follows: shift (δ ppm). High-resolution mass spectra (HRMS) were obtained using a TOF mass spectrometer, whereas infrared (IR) spectra were obtained using a Fourier transform infrared spectrometer. Compounds **6**,[16] **22**,[7] **33**,[25] **34**,[7] **35**,[26] **60**,[7] **73**,[7] and **78**[7] were prepared by literature procedures.

General Procedure A: Preparation of Stenhouse Adducts. The activated furan (1.0 equiv) was added to tetrahydrofuran (0.4 M). To this solution at 23 °C was added 1.0 equiv of secondary amine. The reaction mixture was stirred at 23 °C for 10 min followed by cooling at 0 °C for 20 min. The reaction mixture was then filtered to collect the precipitated solid; the solid iswas washed with cold diethyl ether and dried in vacuo to afford the title compounds.

5-((2*Z*,4*E*)-2-Hydroxy-5-(pyrrolidin-1-yl)penta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (8). Following general procedure A, the title compound was obtained as a red solid (1.25g, 95%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 11.36 (s, 1H), 7.53 (d, J = 12.0 Hz, 1H), 6.95 (s, 1H), 6.77 (d, J = 12.6 Hz, 1H), 5.97 (t, J = 12.3 Hz, 1H), 3.71 (t, J = 6.5 Hz, 2H), 3.54 (t, J = 6.6 Hz, 2H), 2.14−2.08 (m, 2H), 2.05−1.98 (m, 2H), 1.68 (s, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 167.0, 164.6, 155.0, 150.7, 144.7, 137.7, 103.6, 103.0, 89.8, 54.1, 48.7, 26.4, 24.9, 24.9; IR (KBr) 2986, 2874, 1689, 1643, 1640, 1574, 1521, 1453, 1391, 1371, 1344, 1308, 1263, 1228, 1200, 1152, 1104, 1004 cm^{-1}; HRMS (ESI+) m/z 316.1154 (316.1161 calcd for $C_{15}H_{19}NO_5Na^+$ [M + Na]$^+$).

5-((2*Z*,4*E*)-2-Hydroxy-5-(piperidin-1-yl)penta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (17). Following general procedure A, the title compound was obtained as a red solid (1.10g, 80%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 11.38 (s, 1H), 7.32 (d, J = 12.2 Hz, 1H), 6.93 (s, 1H), 6.85−6.79 (m, 1H), 6.14 (t, J = 12.3 Hz, 1H), 3.58 (d, J = 23.3 Hz, 4H), 1.75 (s, 6H), 1.68 (s, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 167.0, 164.7, 157.5, 151.6, 144.5, 137.0, 102.9, 101.7, 57.0, 47.9, 26.7, 26.4, 25.4, 23.5; IR (KBr) 3855, 3841, 3678, 3446, 3075, 2987, 2941, 1720, 1681, 1639, 1599, 1571, 1524, 1469, 1452, 1412, 1372, 1263, 1244, 1201, 1149, 1024 cm^{-1}; HRMS (ESI+) m/z 330.1318 (330.1317 calcd for $C_{16}H_{21}NO_5Na^+$ [M + Na]$^+$).

5-((2*Z*,4*E*)-2-Hydroxy-5-morpholinopenta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (18). Following general procedure A, the title compound was obtained as a red solid (1.19g, 85%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 11.27 (s, 1H), 7.22 (d, J = 12.4 Hz, 1H), 7.10 (s, 1H), 6.76 (d, J = 12.2 Hz, 1H), 6.09 (t, J = 12.3 Hz, 1H), 3.80−3.78 (m, 4H), 3.58 (s, 4H), 1.69 (s, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 161.7, 156.1, 156.1, 149.8, 140.5, 140.5, 140.5, 134.3, 100.9, 69.3, 67.0, 49.6, 46.1, 44.7, 28.0, 26.8, 26.5; IR (KBr) 2988, 2934, 2857, 1688, 1633, 1604, 1569, 1520, 1442, 1392, 1371, 1354, 1301, 1278, 1258, 1244, 1204, 1162, 1139, 1114, 1067, 1025, 1009 cm^{-1}; HRMS (ESI+) m/z 332.1105 (332.1110 calcd for $C_{15}H_{19}NO_6Na^+$ [M + Na]$^+$). Crystal structure data for **5-((2Z,4E)-2-hydroxy-5-morpholinopenta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (18)** can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif CCDC 844844.

5-((2*Z*,4*E*)-2-Hydroxy-5-(4-phenylpiperazin-1-yl)penta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (19). Following general procedure A, the title compound was obtained as a red solid (273 mg, 71%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 11.22 (s, 1H), 7.24−7.14 (m, 4H), 7.00 (s, 1H), 6.89−6.83 (m, 4H), 6.73−6.66 (m, 1H), 6.06 (t, J = 12.3 Hz, 1H), 3.65 (s, 4H), 3.24 (t, J = 5.2 Hz, 4H), 1.61 (s, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 164.4, 156.0, 150.2, 150.0, 140.1, 134.2, 129.3, 129.0, 121.0, 119.6, 116.8, 116.0, 103.3, 101.1, 93.9, 69.0, 49.4, 49.2, 46.3, 44.8, 28.0, 26.8, 26.5; IR (KBr) 3055, 2995, 2930, 2829, 1689, 1634, 1601, 1568, 1523, 1503, 1443, 1389, 1374, 1362, 1283, 1258, 1249, 1230, 1208, 1163, 1095, 1051, 1015 cm^{-1}; HRMS (ESI+) m/z 407.1581 (407.1583 calcd for $C_{21}H_{24}N_2O_5Na^+$ [M + Na]$^+$).

5-((2*Z*,4*E*)-2-Hydroxy-5-((*R*)-2-methylpyrrolidin-1-yl)penta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (20). Following general procedure A, the title compound was obtained as a red solid (1.21g, 87%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 11.28 (s, 1H), 7.42 (d, J = 12.0 Hz, 1H), 6.85 (s, 1H), 6.72 (d, J = 12.6 Hz, 1H), 5.90 (t, J = 12.3 Hz, 1H), 3.83 (d, J = 6.5 Hz, 1H), 3.56−3.47 (m, 2H), 2.17−1.87 (m, 4H), 1.59 (s, 6H), 1.28 (d, J = 6.5 Hz, 3H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 167.0, 164.7, 153.9, 150.9, 144.6, 137.3, 103.9, 102.9, 89.6, 60.4, 49.2, 32.7, 26.4, 26.4, 22.8, 20.1; IR (KBr) 3065, 2996, 2877, 1676, 1599, 1509, 1466, 1441, 1369, 1345, 1311, 1259, 1232, 1191, 1135, 1004 cm^{-1}; HRMS (ESI+) m/z 330.1320 (330.1317 calcd for $C_{16}H_{21}NO_5Na^+$ [M + Na]$^+$).

(*S*)-Methyl-1-((1*E*,3*Z*)-5-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-4-hydroxypenta-1,3-dien-1-yl) pyrrolidine-2-carboxylate (21). Following general procedure A, the title compound was obtained as a green solid (1.33g, 84%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 11.14 (s, 1H), 7.29 (d, J = 12.5 Hz, 1H), 7.05 (s, 1H), 6.63 (d, J = 12.3 Hz, 1H), 5.89 (t, J = 12.3 Hz, 1H), 4.37−4.32 (m, 1H), 3.70 (s, 3H), 2.24−2.17 (m, 2H), 2.07−1.98 (m, 2H), 1.74 (d, J = 3.6 Hz, 2H), 1.61 (d, J = 2.0 Hz, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 166.8, 164.2, 161.6, 153.6, 149.0, 141.8, 134.5, 110.0, 103.4, 103.1, 65.0, 62.9, 51.8, 48.8, 46.5, 29.7, 29.5, 26.5, 26.5, 23.9, 23.7, 23.5; IR (KBr) 3068, 2990, 2953, 2880, 1742, 1688, 1627, 1485, 1450, 1407, 1391, 1362, 1340, 1274, 1244, 1234, 1200, 1141, 1118, 1043, 1006 cm^{-1}; HRMS (ESI+) m/z 374.1212 (374.1216 calcd for $C_{17}H_{21}NO_7Na^+$ [M + Na]$^+$). Crystal structure data for **(*S*)-methyl 1-((1*E*,3*Z*)-5-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-4-hydroxypenta-1,3-dien-1-yl)pyrrolidine-2-carboxylate (21)** can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif CCDC 844843.

5-((2*Z*,4*E*)-5-(Diethylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (22).[7] Following general procedure A, the title compound was obtained as a red solid (1.13g, 85%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 11.37−11.34 (m, 1H), 7.33 (d, J = 12.2 Hz, 1H), 6.96 (s, 1H), 6.80 (dd, J = 12.5, 1.3 Hz, 1H), 6.08 (t, J = 12.4 Hz, 1H), 3.54−3.45 (m, 4H), 1.68 (s, 6H), 1.31 (dt, J = 18.1, 7.3 Hz, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 167.0, 164.6, 157.6, 151.4, 144.5, 137.8, 103.0, 102.2, 89.8, 52.0, 44.2, 26.4, 14.2, 12.1; IR (KBr) 3071, 2996, 2938, 1681, 1634, 1603, 1573, 1510, 1463, 1414, 1369, 1340, 1264, 1235, 1196, 1172, 1139, 1128, 1096, 1083, 1059, 1015 cm^{-1}; HRMS (ESI+) m/z 318.1313 (318.1317 calcd for $C_{15}H_{21}NO_5Na^+$ [M + Na]$^+$). Crystal structure data for **5-((2Z,4E)-5-(diethylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (22)** has been previously reported[7] and can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif CCDC 865315.

5-((2*Z*,4*E*)-5-(Dipropylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (23). Following general procedure A, the title compound was obtained as a red solid (252 mg, 78%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 11.35 (s, 1H), 7.31 (d, J = 12.2 Hz, 1H), 6.96 (s, 1H), 6.78 (d, J = 12.4 Hz, 1H), 6.06 (t, J = 12.3 Hz, 1H), 3.38 (q, J = 7.4 Hz, 4H), 1.72 (dq, J = 9.6, 7.5 Hz, 4H), 1.67 (s, 6H), 0.96 (dt, J = 25.4, 7.4 Hz, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 167.6, 165.3, 159.0, 152.0, 145.2, 138.5, 103.6, 102.9, 59.9, 51.8, 27.0, 22.8, 21.1, 11.6, 11.2; IR (KBr) 3150, 2993, 2917, 2696, 1644, 1589, 1548, 1501, 1447, 1403, 1359, 1315, 1278, 1232, 1196, 1145, 1122 cm^{-1}; HRMS (ESI+) m/z 346.1620 (346.1630 calcd for $C_{17}H_{25}NO_5Na^+$ [M + Na]$^+$).

5-((2*Z*,4*E*)-5-(Dibutylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (24). Following general procedure A, the title compound was obtained as a red solid (288 mg, 82%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 11.34 (s, 1H), 7.31 (d, J =

12.3 Hz, 1H), 6.95 (s, 1H), 6.78 (dd, J = 12.5, 1.5 Hz, 1H), 6.06 (t, J = 12.3 Hz, 1H), 3.41 (q, J = 7.0 Hz, 4H), 1.67 (s, 10H), 1.37 (dh, J = 29.9, 7.4 Hz, 4H), 0.97 (q, J = 7.5 Hz, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 167.6, 165.2, 159.0, 152.0, 145.2, 138.2, 103.6, 103.0, 58.1, 50.1, 31.4, 29.7, 27.0, 20.7, 20.2, 14.0, 140; IR (KBr) 3157, 2991, 2923, 1691, 1645, 1592, 1544, 1498, 1446, 1404, 1357, 1311, 1274, 1228, 1191, 1136, 1116 cm^{-1}; HRMS (ESI+) m/z 374.1947 (374.1943 calcd for $C_{19}H_{29}NO_5Na^+$ [M + Na]$^+$).

5-((2*Z*,4*E*)-5-(Dihexylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (25). Following general procedure A, the title compound was obtained as a red solid (371 mg, 91%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 11.34 (s, 1H), 7.31 (d, J = 12.2 Hz, 1H), 6.94 (s, 1H), 6.78 (dd, J = 12.5, 1.5 Hz, 1H), 6.06 (t, J = 12.3 Hz, 1H), 3.41 (q, J = 6.7 Hz, 5H), 1.67 (s, 10H), 1.38−1.25 (m, 16H), 0.90 (ddt, J = 10.8, 7.6, 4.4 Hz, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 167.6, 165.3, 159.0, 152.0, 145.2, 138.2, 103.6, 103.0, 58.3, 50.3, 31.9, 31.9, 31.9, 29.4, 27.6, 27.1, 27.0, 26.6, 23.1, 23.1, 23.0, 14.3; IR (KBr) 3163, 2996, 2921, 1694, 1639, 1585, 1537, 1487, 1435, 1395, 1344, 1297, 1260, 1223, 1183, 1125, 1109 cm^{-1}; HRMS (ESI+) m/z 430.2573 (430.2569 calcd for $C_{23}H_{37}NO_5Na^+$ [M + Na]$^+$).

5-((2*Z*,4*E*)-5-(Dioctylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (26). Following general procedure A, the title compound was obtained as a red solid (1.75g, 83%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 11.36 (s, 1H), 7.30 (d, J = 12.2 Hz, 1H), 6.96 (s, 1H), 6.78 (d, J = 12.4 Hz, 1H), 6.07 (t, J = 12.3 Hz, 1H), 3.41 (q, J = 7.2 Hz, 4H), 1.68 (s, 6H), 1.41−1.18 (m, 24H), 0.90 (t, J = 6.8 Hz, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 167.0, 164.6, 158.3, 151.3, 144.6, 137.7, 103.0, 102.3, 89.8, 57.7, 49.7, 31.7, 31.7, 29.1, 29.1, 29.0, 28.8, 27.3, 27.0, 26.9, 26.4, 26.4, 22.6, 13.8; IR (KBr) 2924, 2855, 1719, 1676, 1575, 1503, 1462, 1416, 1391, 1346, 1287, 1262, 1231, 1199, 1142, 1117, 1047, 1029 cm^{-1}; HRMS (ESI+) m/z 486.3181 (486.3195 calcd for $C_{27}H_{45}NO_5Na^+$ [M + Na]$^+$).

5-((2*Z*,4*E*)-5-(Diallylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (27). Following general procedure A, the title compound was obtained as a purple solid (968 mg, 68%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 11.17 (s, 1H), 7.23 (d, J = 12.4 Hz, 1H), 7.00 (s, 1H), 6.65 (d, J = 12.3 Hz, 1H), 5.96 (t, J = 12.3 Hz, 1H), 5.75 (dt, J = 13.8, 7.6 Hz, 2H), 5.32−5.15 (m, 4H), 3.94 (dd, J = 16.9, 5.0 Hz, 4H), 1.60 (s, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 166.9, 164.4, 157.1, 150.1, 145.1, 140.5, 131.2, 129.4, 120.5, 119.1, 119.0, 103.3, 102.0, 91.9, 59.1, 51.3, 26.5; IR (KBr) 3071, 3003, 2943, 1698, 1646, 1612, 1561, 1499, 1446, 1368, 1299, 1283, 1242, 1207, 1164 cm^{-1}; HRMS (ESI+) m/z 342.1324 (342.1317 calcd for $C_{17}H_{21}NO_5Na^+$ [M +Na]$^+$).

5-((2*Z*,4*E*)-5-(Benzyl(methyl)amino)-2-hydroxypenta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (28). Following general procedure A, the title compound was obtained as a purple solid (1.31g, 85%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 11.32 (d, J = 1.6 Hz, 1H), 7.53 (d, J = 12.2 Hz, 1H), 7.42 (qd, J = 7.8, 7.2, 3.7 Hz, 3H), 7.31−7.18 (m, 2H), 7.08 (s, 1H), 6.82 (dd, J = 12.5, 1.6 Hz, 1H), 6.14 (dt, J = 93.0, 12.3 Hz, 1H), 4.61 (d, J = 18.0 Hz, 2H), 3.13 (d, J = 122.7 Hz, 3H), 1.68 (d, J = 5.1 Hz, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 166.9, 164.5, 158.8, 158.0, 150.7, 150.4, 145.1, 139.9, 139.5, 134.0, 129.2, 129.1, 128.8, 128.7, 128.5, 128.4, 127.8, 127.4, 103.2, 102.1, 102.0, 62.9, 53.8, 53.6, 53.4, 53.3, 53.1, 36.3, 26.5; IR (KBr) 3082, 3028, 2990, 2940, 1695, 1610, 1565, 1502, 1447, 1401, 1386, 1356, 1276, 1260, 1239, 1200, 1150, 1065, 1032, 1003 cm^{-1}; HRMS (ESI+) m/z 366.1320 (366.1317 calcd for $C_{19}H_{21}NO_5Na^+$ [M +Na]$^+$).

5-((2*Z*,4*E*)-5-(3,4-Dihydroisoquinolin-2(1*H*)-yl)-2-hydroxypenta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (29). Following general procedure A, the title compound was obtained as a red solid (1.32 g, 82%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 11.24 (s, 1H), 7.36 (d, J = 12.4 Hz, 1H), 7.25−6.90 (m, 7H), 6.71 (d, J = 12.3 Hz, 1H), 6.06 (d, J = 12.5 Hz, 1H), 4.64 (s, 2), 3.75−3.64 (m, 2H), 2.96 (d, J = 18.9 Hz, 2H), 1.60 (s, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 166.9, 164.4, 156.7, 156.6, 150.1, 150.0, 140.1, 128.7, 128.6, 127.3, 127.1, 127.1, 127.0, 126.5, 126.4, 125.6, 101.5, 101.4, 52.4, 48.3, 29.3, 26.5; IR (KBr) 3469, 3062, 2992, 2937, 1690, 1632, 1609, 1561, 1500, 1458, 1440, 1364, 1283, 1267, 1234, 1203, 1153, 1051 cm^{-1}; HRMS (ESI+) m/z 378.1314 (378.1317 calcd for $C_{20}H_{21}NO_5Na^+$ [M +Na]$^+$).

5-((2*Z*,4*E*)-2-Hydroxy-5-(isoindolin-2-yl)penta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (30). Following general procedure A, the title compound was obtained as a red solid (870 mg, 91%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 11.21 (s, 1H), 7.48 (d, J = 12.2 Hz, 1H), 7.27 (d, J = 26.5 Hz, 4H), 7.05 (s, 1H), 6.69 (d, J = 12.2 Hz, 1H), 5.96 (t, J = 12.3 Hz, 1H), 4.97 (s, 2H), 4.78 (s, 2H), 1.61 (s, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 153.6, 149.0, 141.1, 128.4, 128.2, 122.8, 122.5, 103.3, 103.0, 58.3, 54.5, 26.5; IR (KBr) 3063, 2985, 2958, 1688, 1637, 1611, 1565, 1505, 1468, 1451, 1368, 1349, 1284, 1268, 1235, 1223, 1198, 1180, 1151, 1114, 1025, 1006 cm^{-1}; HRMS (ESI+) m/z 364.1163 (364.1161 calcd for $C_{19}H_{19}NO_5Na^+$ [M +Na]$^+$). Crystal structure data for **5-((2*Z*,4*E*)-2-hydroxy-5-(isoindolin-2-yl)penta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (30)** can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif CCDC 846378.

5-((2*Z*,4*E*)-5-(Dibenzylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (31). Following general procedure A, the title compound was obtained as a green solid (1.42g, 75%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 11.25 (s, 1H), 7.59 (d, J = 12.4 Hz, 1H), 7.40 (tt, J = 14.8, 6.6 Hz, 6H), 7.22 (dd, J = 12.8, 7.3 Hz, 4H), 7.13 (s, 1H), 6.83 (d, J = 12.2 Hz, 1H), 6.23 (t, J = 12.3 Hz, 1H), 4.56 (d, J = 5.5 Hz, 4H), 1.68 (s, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 166.9, 164.4, 157.7, 150.2, 145.2, 140.8, 134.1, 133.8, 129.2, 129.1, 128.8, 128.8, 128.4, 128.3, 128.1, 127.5, 127.3, 103.4, 102.0, 92.2, 60.0, 54.5, 51.7, 26.6, 26.5; IR (KBr) 3469, 3058, 3027, 2992, 2932, 1696, 1626, 1553, 1489, 1476, 1449, 1391, 1365, 1346, 1291, 1261, 1231, 1197, 1139, 1111, 1030, 1016, 1003 cm^{-1}; HRMS (ESI+) m/z 442.1637 (442.1630 calcd for $C_{25}H_{25}NO_5Na^+$ [M + Na]$^+$). Crystal structure data for **5-((2*Z*,4*E*)-5-(dibenzylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (31)** can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif CCDC 844842.

5-((2*Z*,4*E*)-2-Hydroxy-5-(methyl(phenyl)amino)penta-2,4-dien-1-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (32). Following general procedure A, the title compound was obtained as a purple solid (74 mg, 22%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 7.67 (d, J = 5.5 Hz, 1H), 7.24 (t, J = 7.8 Hz, 2H), 6.84 (d, J = 8.1 Hz, 2H), 6.78 (t, J = 7.3 Hz, 1H), 6.43 (d, J = 4.6 Hz, 1H), 5.52 (s, 1H), 4.00 (s, 1H), 3.50−3.43 (d, J = 3.4 Hz, 1H), 2.79 (s, 3H), 1.70 (s, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 163.8, 149.9, 134.7, 130.4, 130.0, 118.9, 114.1, 106.2, 63.6, 48.4, 45.0, 32.8, 28.4, 27.2, 27.2. IR (ATR) 3060, 2999, 2921, 1780, 1742, 1710, 1596, 1503, 1470, 1382, 1324, 1269, 1197, 1147, 1104, 1015, 990, 927, 871, 791, 749, 694 cm^{-1}; HRMS (ESI+) m/z 352.1147 (352.1161 calcd for $C_{18}H_{19}NO_5Na^+$ [M + Na]$^+$).

5-((2*Z*,4*E*)-5-(Diethylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (34).[7] Following general procedure A, the title compound was obtained as a purple solid (260 mg, 85%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 12.50 (s, 1H), 7.30 (d, J = 12.2 Hz, 1H), 7.06 (s, 1H), 6.82 (dd, J = 12.3, 1.5 Hz, 1H), 6.10 (t, J = 12.3 Hz, 1H), 3.50 (dq, J = 25.4, 7.2 Hz, 4H), 3.29 (s, 3H), 3.27 (s, 3H), 1.31 (dt, J = 13.0, 7.2 Hz, 6H); ^{13}C NMR (151 MHz, CD_2Cl_2) δ 165.7, 163.6, 157.8, 151.8, 146.7, 138.2, 103.3, 98.1, 52.6, 44.8, 28.6, 28.5, 14.8, 12.7; IR (KBr) 3365, 2944, 2486, 1685, 1618, 1592, 1566, 1509, 1460, 1418, 1373, 1328, 1309, 1286, 1270 cm^{-1}; HRMS (ESI+) m/z 330.1433 (330.1430 calcd for $C_{15}H_{21}N_3O_4Na^+$ [M +Na]$^+$). Crystal structure data for **5-((2*Z*,4*E*)-5-(diethylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (34)** can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif CCDC 1026490.

2-((2*Z*,4*E*)-5-(Diethylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-1*H*-indene-1,3(2*H*)-dione (36). Following general procedure A, the title compound was obtained as a dark blue solid (259 mg, 87%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 11.51 (s, 1H), 7.60 (dt, J = 19.4, 2.6 Hz, 2H), 7.57−7.52 (m, 2H), 7.24 (d, J = 12.2 Hz, 1H), 6.71

(d, J = 12.3 Hz, 1H), 6.64 (s, 1H), 6.04 (t, J = 12.3 Hz, 1H), 3.46 (dq, J = 28.1, 7.2 Hz, 4H), 1.27 (dt, J = 7.9, 4.5 Hz, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 193.2, 190.8, 156.4, 147.8, 147.3, 141.2, 140.9, 133.5, 133.2, 132.0, 121.3, 121.1, 114.5, 102.6, 52.3, 44.5, 14.8, 12.6. IR (ATR): 3007, 2971, 2924, 2869, 1674, 1613, 1583, 1483, 1439, 1373, 1353, 1331, 1262, 1163, 1146, 1110, 974, 905, 765 cm^{-1}; HRMS (ESI+) m/z 320.1262 (320.1263 calcd for $C_{18}H_{19}NO_3Na^+$ $[M + Na]^+$).

5-((2*Z*,4*E*)-2-Hydroxy-5-(pyrrolidin-1-yl)penta-2,4-dien-1-ylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (42). Following general procedure A, the title compound was obtained as a purple solid (275 mg, 90%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.53 (s, 1H), 7.43 (d, J = 12.2 Hz, 1H), 7.14 (s, 1H), 6.72 (d, J = 12.4 Hz, 1H), 5.98 (t, J = 12.3 Hz, 1H), 3.70 (t, J = 6.8 Hz, 3H), 3.52 (t, J = 7.0 Hz, 3H), 3.35 (d, J = 6.2 Hz, 7H), 3.21 (s, 2H), 2.13 (p, J = 6.8 Hz, 4H), 2.04 (p, J = 6.6 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.3, 153.6, 150.0, 146.7, 139.4, 104.0, 70.0, 53.8, 48.4, 28.4, 28.3, 25.0, 22.7; IR (KBr) 2961, 2915, 2763, 1693, 1617, 1580, 1559, 1491, 1454, 1419, 1370, 1343, 1266, 1226, 1177, 1105, 1043, 967, 941, 924, 829, 754 cm^{-1}; HRMS (ESI+) m/z 328.1263 (328.1273 calcd for $C_{15}H_{19}N_3O_4Na^+$ $[M + Na]^+$).

5-((2*Z*,4*E*)-2-Hydroxy-5-(piperidin-1-yl)penta-2,4-dien-1-ylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (43). Following general procedure A, the title compound was obtained as a purple solid (297 mg, 93%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 12.52 (s, 1H), 7.32 (d, J = 12.1 Hz, 1H), 7.01 (s, 1H), 6.85 (d, J = 12.5 Hz, 1H), 6.16 (t, J = 12.3 Hz, 1H), 3.71−3.65 (m, 2H), 3.61−3.58 (m, 2H), 3.55 (bs, 2H), 3.29 (s, 3H), 3.26 (s, 3H), 3.17 (bs, 2H), 1.84−1.79 (m, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 165.0, 163.0, 157.3, 151.6, 146.1, 136.7, 102.4, 67.7, 57.0, 27.9, 25.5, 23.6; IR (KBr) 2964, 2915, 2832, 1694, 1616, 1578, 1557, 1488, 1452, 1419, 1369, 1345, 1260, 1217, 1164, 1105, 1043, 967, 941, 924, 829, 754 cm^{-1}; HRMS (ESI+) m/z 342.1426 (342.1430 calcd for $C_{16}H_{21}N_3O_4Na^+$ $[M + Na]^+$).

5-((2*Z*,4*E*)-2-Hydroxy-5-((*R*)-2-methylpyrrolidin-1-yl)penta-2,4-dien-1-ylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (46). Following general procedure A, the title compound was obtained as a purple solid (278 mg, 87%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 12.53 (s, 1H), 7.38 (d, J = 12.2 Hz, 1H), 7.15 (s, 1H), 6.75 (d, J = 12.6 Hz, 1H), 5.99 (t, J = 12.3 Hz, 1H), 3.89 (q, J = 6.5 Hz, 1H), 3.58 (q, J = 6.7 Hz, 2H), 3.35 (d, J = 5.8 Hz, 7H), 2.32−1.95 (m, 5H), 1.71 (dq, J = 12.9, 6.6 Hz, 1H), 1.37 (d, J = 6.5 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.1, 152.3, 152.0, 150.2, 146.7, 139.2, 104.2, 59.9, 49.0, 32.9, 28.4, 28.3, 22.9, 20.5; IR (KBr) 2965, 2913, 2821, 1694, 1616, 1576, 1557, 1487, 1452, 1421, 1369, 1346, 1260, 1219, 1166, 1109, 1050, 976, 968, 924, 829, 754 cm^{-1}; HRMS (ESI+) m/z 342.1430 (342.1430 calcd for $C_{16}H_{21}N_3O_4Na^+$ $[M + Na]^+$).

(*S*)-Methyl-1-((1*E*,3*Z*)-5-(1,3-dimethyl-2,4,6-trioxotetrahydropyrimidin-5(2*H*)-ylidene)-4-hydroxypenta-1,3-dien-1-yl)pyrrolidine-2-carboxylate (47). Following general procedure A, the title compound was obtained as a purple solid (189 mg, 52%: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 12.35 (s, 1H), 7.37 (d, J = 12.1 Hz, 1H), 7.18 (s, 1H), 6.72 (d, J = 12.5 Hz, 1H), 5.96 (t, J = 12.3 Hz, 1H), 4.43 (dd, J = 7.7, 4.3 Hz, 1H), 3.76 (s, 3H), 3.71−3.58 (m, 2H), 3.28 (s, 3H), 3.25 (s, 3H), 2.32−2.18 (m, 2H), 2.07 (tdd, J = 12.8, 8.0, 5.9 Hz, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 171.3, 165.8, 163.3, 153.9, 152.2, 149.4, 147.5, 141.9, 135.0, 104.3, 65.6, 53.5, 49.4, 30.1, 28.7, 28.6, 24.1; IR (KBr) 2966, 2912, 2813, 1694, 1615, 1573, 1557, 1486, 1452, 1425, 1369, 1347, 1260, 1222, 1180, 1126, 1071, 1004, 968, 924, 829, 754 cm^{-1}; HRMS (ESI+) m/z 386.1321 (386.1328 calcd for $C_{17}H_{21}N_3O_6Na^+$ $[M + Na]^+$).

5-((2*Z*,4*E*)-5-(Dipropylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (48). Following general procedure A, the title compound was obtained as a purple solid (278 mg, 83%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 12.50 (s, 1H), 7.31 (d, J = 12.2 Hz, 1H), 7.05 (s, 1H), 6.83 (d, J = 12.5 Hz, 1H), 6.09 (t, J = 12.3 Hz, 1H), 3.39 (dt, J = 11.8, 7.8 Hz, 4H), 3.29 (s, 3H), 3.26 (s, 3H), 1.72 (dh, J = 16.8, 9.6, 8.1 Hz, 4H), 0.97 (dt, J = 28.8, 7.4 Hz, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 165.6, 163.6, 158.8, 151.9, 146.8, 138.1, 103.4, 59.8, 51.8, 28.6, 28.5, 22.8, 21.1, 11.7, 11.5, 11.2; IR (KBr) 2972, 2920, 2813, 1695, 1614, 1569, 1558, 1485, 1451, 1424, 1386, 1346, 1260, 1221, 1176, 1122, 1078, 1009, 977, 936, 836, 757 cm^{-1}; HRMS (ESI+) m/z 358.1740 (358.1743 calcd for $C_{17}H_{25}N_3O_4Na^+$ $[M + Na]^+$).

5-((2*Z*,4*E*)-5-(Dibutylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (49). Following general procedure A, the title compound was obtained as a purple solid (276 mg, 76%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ: 12.49 (s, 1H), 7.29 (d, J = 12.2 Hz, 1H), 7.04 (s, 1H), 6.81 (d, J = 12.4 Hz, 1H), 6.08 (t, J = 12.3 Hz, 1H), 3.42 (dt, J = 12.2, 7.7 Hz, 4H), 3.29 (s, 3H), 3.26 (s, 3H), 1.71−1.62 (m, 4H), 1.37 (dh, J = 30.1, 7.4 Hz, 4H), 0.97 (dt, J = 11.4, 7.4 Hz, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 165.1, 163.0, 158.0, 151.2, 146.2, 137.4, 102.9, 57.4, 49.5, 30.9, 29.1, 28.0, 27.9, 20.2, 19.6, 13.4, 13.3; IR (KBr) 2971, 2919, 2813, 1695, 1613, 1586, 1558, 1484, 1451, 1423, 1370, 1339, 1257, 1221, 1176, 1122, 1063, 1007, 977, 936, 836, 759 cm^{-1}; HRMS (ESI+) m/z 386.2049 (386.2056 calcd for $C_{19}H_{29}N_3O_4Na^+$ $[M + Na]^+$).

5-((2*Z*,4*E*)-5-(Dihexylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (50). Following general procedure A, the title compound was obtained as a purple solid (394 mg, 94%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 12.49 (s, 1H), 7.30 (d, J = 12.2 Hz, 1H), 7.03 (s, 1H), 6.82 (d, J = 12.1 Hz, 1H), 6.08 (t, J = 12.3 Hz, 1H), 3.41 (dt, J = 10.8, 7.8 Hz, 4H), 3.29 (s, 3H), 3.26 (s, 3H), 1.69−1.65 (m, 4H), 1.34−1.30 (m, 12H), 0.91−0.89 (m, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 165.0, 163.0, 158.0, 151.3, 146.2, 137.3, 103.0, 57.7, 49.7, 31.3, 31.3, 28.8, 28.0, 27.9, 27.0, 26.5, 26.4, 26.0, 22.5, 22.4, 13.7; IR (KBr) 2971, 2919, 2818, 1699, 1613, 1568, 1553, 1484, 1457, 1423, 1369, 1343, 1264, 1220, 1173, 1123, 1075, 1009, 979, 944, 848, 766 cm^{-1}; HRMS (ESI+) m/z 442.2681 (442.2682 calcd for $C_{23}H_{37}N_3O_4Na^+$ $[M + Na]^+$).

5-((2*Z*,4*E*)-5-(Dioctylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (51). Following general procedure A, the title compound was obtained as a purple solid (414 mg, 87%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 12.49 (s, 1H), 7.29 (d, J = 12.2 Hz, 1H), 7.03 (s, 1H), 6.82 (d, J = 12.5 Hz, 1H), 6.08 (t, J = 12.3 Hz, 1H), 3.41 (dt, J = 11.0, 7.7 Hz, 4H), 3.29 (s, 3H), 3.26 (s, 3H), 1.70−1.65 (m, 4H), 1.32−1.27 (m, 20H), 0.90−0.87 (m, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 165.0, 163.0, 158.0, 151.3, 146.2, 137.3, 102.9, 57.7, 49.7, 31.7, 31.7, 31.7, 29.1, 29.1, 29.1, 29.1, 28.9, 28.0, 27.9, 27.1, 26.9, 26.4, 22.6, 13.8; IR (KBr) 2969, 2917, 2806, 1693, 1616, 1576, 1557, 1487, 1453, 1425, 1360, 1342, 1267, 1226, 1180, 1124, 1073, 1006, 978, 941, 851, 761 cm^{-1}; HRMS (ESI+) m/z 498.3296 (498.3308 calcd for $C_{27}H_{45}N_3O_4Na^+$ $[M + Na]^+$).

5-((2*Z*,4*E*)-5-(Diallylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (52). Following general procedure A, the title compound was obtained as a purple solid (315 mg, 95%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 12.40 (s, 1H), 7.31 (d, J = 12.4 Hz, 1H), 7.15 (s, 1H), 6.78−6.75 (m, 2H), 6.06 (t, J = 12.3 Hz, 1H), 5.40−5.33 (m, 2H), 5.31−5.24 (m, 2H), 4.07−3.96 (m, 4H), 3.36 (m, 2H), 3.29 (s, 3H), 3.27 (s, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 165.8, 163.5, 157.4, 152.2, 150.6, 147.2, 140.7, 131.9, 130.1, 121.1, 119.6, 103.2, 59.7, 50.8, 30.3, 28.7, 28.6; IR (KBr) 2967, 2911, 2809, 1694, 1610, 1552, 1459, 1428, 1361, 1348, 1263, 1222, 1174, 1116, 1060, 991, 965, 931, 836, 758 cm^{-1}; HRMS (ESI+) m/z 354.1426 (354.1430 calcd for $C_{17}H_{21}N_3O_4Na^+$ $[M + Na]^+$).

5-((2*Z*,4*E*)-5-(Benzyl(methyl)amino)-2-hydroxypenta-2,4-dien-1-ylidene)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (53). Following general procedure A, the title compound was obtained as a purple solid (327 mg, 92%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 12.44 (s, 1H), 7.46 (d, J = 12.3 Hz, 1H), 7.40 (dd, J = 13.8, 7.2 Hz, 3H), 7.24 (d, J = 7.4 Hz, 2H), 7.18 (s, 1H), 6.82 (d, J = 12.3 Hz, 1H), 6.06 (t, J = 12.3 Hz, 1H), 4.58 (s, 2H), 3.30 (s, 3H), 3.27 (s, 3H), 3.03 (s, 3H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 165.8, 163.5, 157.8, 152.3, 150.4, 147.3, 140.7, 134.7, 129.7, 129.4, 128.3, 128.0, 102.9, 63.4, 36.9, 28.7, 28.6; IR (KBr) 2961, 2918, 2816, 1692, 1614, 1573, 1559, 1486, 1456, 1421, 1369, 1341, 1261, 1221, 1179, 1118, 1062, 994, 968, 932, 841, 752 cm^{-1}; HRMS (ESI+) m/z 378.1428 (378.1430 calcd for $C_{19}H_{21}N_3O_4Na^+$ $[M + Na]^+$).

5-((2*Z*,4*E*)-5-(3,4-Dihydroisoquinolin-2(1*H*)-yl)-2-hydroxypenta-2,4-dien-1-ylidene)-1,3-dimethylpyrimidine-2,4,6-(1*H*,3*H*,5*H*)-trione (54). Following general procedure A, the title compound was obtained as a purple solid (301 mg, 82%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 12.48 (s, 1H), 7.45 (d, J = 12.9 Hz, 1H), 7.30−

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7.10 (m, 6H), 6.84 (d, J = 12.3 Hz, 1H), 6.17 (d, J = 11.9 Hz, 1H), 4.73 (s, 2H), 3.81 (s, 2H), 3.30 (s, 3H), 3.26 (s, 3H), 3.09−2.99 (m, 2H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 165.7, 163.6, 157.0, 152.3, 150.6, 140.3, 129.5, 129.3, 128.5, 127.7, 127.1, 102.7, 68.3, 52.6, 45.4, 42.4, 29.9, 28.7, 28.6, 26.1, 25.9; IR (KBr) 2965, 2913, 2814, 1697, 1619, 1573, 1556, 1481, 1456, 1426, 1362, 1345, 1269, 1228, 1175, 1120, 1065, 998, 972, 933, 838, 759 cm^{-1}; HRMS (ESI) m/z 390.1425 (390.1430 calcd for $C_{20}H_{21}N_3O_4Na^+$ [M + Na]$^+$).

1,3-Dibutyl-5-((2*Z*,4*E*)-5-(diethylamino)-2-hydroxypenta-2,4-dien-1-ylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (59). Following general procedure A, the title compound was obtained as a purple solid (341 mg, 87%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 12.56 (s, 1H), 7.28 (d, J = 12.3 Hz, 1H), 7.06 (s, 1H), 6.80 (d, J = 11.5 Hz, 1H), 6.07 (t, J = 12.3 Hz, 1H), 3.87 (dt, J = 14.9, 7.5 Hz, 4H), 3.49 (dq, J = 24.8, 7.2 Hz, 4H), 1.55 (m, 4H), 1.40−1.23 (m, 10H), 0.93 (q, J = 7.3 Hz, 6H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 165.5, 163.3, 157.4, 151.9, 151.3, 146.8, 138.7, 103.0, 98.7, 52.5, 44.7, 41.8, 41.7, 30.9, 30.9, 20.8, 20.8, 14.8, 14.2, 14.2, 12.7. IR (ATR): 2958, 2932, 2873, 1691, 1622, 1596, 1556, 1497, 1405, 1373, 1339, 1261, 1205, 1143, 1076, 990, 907, 779 cm^{-1}; HRMS (ESI+) m/z 414.2379 (414.2369 calcd for $C_{21}H_{33}N_3O_4Na^+$ [M + Na]$^+$)

5-((2*Z*,4*E*)-5-(Diethylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-1,3-dioctylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (61). Following general procedure A, the title compound was obtained as a purple solid (453 mg, 90%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 12.56 (s, 1H), 7.28 (d, J = 12.2 Hz, 1H), 7.06 (s, 1H), 6.79 (d, J = 12.4 Hz, 1H), 6.07 (t, J = 12.3 Hz, 1H), 3.92−3.81 (m, 4H), 3.49 (dq, J = 24.7, 7.2 Hz, 4H), 1.57 (dt, J = 18.5, 7.4 Hz, 4H), 1.28 (m, 26H), 0.87 (td, J = 7.0, 2.1 Hz, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 165.5, 163.3, 157.4, 151.8, 151.3, 146.8, 138.7, 103.0, 98.8, 52.5, 42.1, 32.4, 30.0, 29.9, 28.8, 27.6, 23.2, 14.4. IR (ATR) 2956, 2923, 2854, 1691, 1620, 1595, 1556, 1492, 1454, 1403, 1370, 1337, 1260, 1198, 1074, 989, 907, 779 cm^{-1}; HRMS (ESI+) m/z 526.3612 (526.3621 calcd for $C_{29}H_{49}N_3O_4Na^+$ [M + Na]$^+$).

(*E*/*Z*)-5-((2*Z*,4*E*)-5-(Diethylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-1-methyl-3-octylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (63). Following general procedure A, the title compound was obtained as a dark purple solid (90 mg, 65%): ^{1}H NMR (500 MHz, CD_2Cl_2) δ 12.53 (dd, J = 28.6, 1.3 Hz, 1H), 7.29 (dd, J = 12.2, 1.2 Hz, 1H), 7.06 (s, 1H), 6.81 (ddd, J = 12.3, 2.8, 1.5 Hz, 1H), 6.08 (t, J = 12.3 Hz, 1H), 3.93−3.81 (m, 2H), 3.49 (dq, J = 21.1, 7.2 Hz, 4H), 3.27 (d, J = 14.2 Hz, 3H), 1.63−1.52 (m, 2H), 1.30 (m, 16H), 0.88 (td, J = 7.0, 2.0 Hz, 3H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 165.7, 165.4, 163.6, 163.2, 157.6, 152.1, 151.6, 146.7, 146.7, 138.4, 103.2, 98.4, 52.5, 44.7, 42.1, 42.0, 32.4, 30.0, 29.9, 29.9, 29.8, 28.8, 28.7, 28.5, 28.4, 27.6, 27.5, 23.2, 14.8, 14.4, 12.7. IR (ATR) 2925, 2854, 1692, 1621, 1596, 1557, 1495, 1461, 1425, 1406, 1371, 1352, 1261, 1229, 1203, 1150, 1074, 989, 909, 838, 777, 729, 685; HRMS (ESI+) m/z 428.2524 (428.2525 calcd for $C_{22}H_{35}N_3O_4Na^+$ [M + Na]$^+$).

5-((2*Z*,4*E*)-5-(Diethylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-1,3-diphenylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (65). Following general procedure A, the title compound was obtained as a purple solid (371 mg, 86%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 12.19 (s, 1H), 7.52−7.24 (m, 11H), 7.02 (s, 1H), 6.92 (dd, J = 12.6, 1.5 Hz, 1H), 6.16 (t, J = 12.4 Hz, 1H), 3.50 (dq, J = 36.5, 7.3 Hz, 4H), 1.30 (dt, J = 10.2, 7.2 Hz, 6H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 165.1, 163.2, 158.7, 153.2, 151.2, 146.3, 136.7, 136.3, 135.6, 129.0, 129.0, 128.9, 128.8, 128.5, 128.2, 128.0, 103.9, 96.5, 52.2, 44.5, 14.1, 12.2. IR(ATR) 3398, 2976, 2927, 1691, 1623, 1583, 1491, 1453, 1430, 1367, 1348, 1254, 1223, 1181, 1115, 1071, 986, 958, 883, 751, 692 cm^{-1}; HRMS (ESI+) m/z 454.1735 (454.1743 calcd for $C_{25}H_{25}N_3O_4Na^+$ [M + Na]$^+$).

5-((2*Z*,4*E*)-5-(Diethylamino)-2-hydroxypenta-2,4-dien-1-ylidene)-1,3-bis(4-methoxyphenyl)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (67). Following general procedure A, the title compound was obtained as a purple solid (398 mg, 81%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 12.21 (s, 1H), 7.35 (d, J = 12.1 Hz, 1H), 7.17 (dd, J = 19.5, 8.8 Hz, 4H), 7.03 (s, 1H), 6.97 (t, J = 9.1 Hz, 4H), 6.90 (dd, J = 12.7, 1.5 Hz, 1H), 6.14 (t, J = 12.3 Hz, 1H), 3.83 (d, J = 3.4 Hz, 6H), 3.51 (dq, J = 28.3, 7.2 Hz, 4H), 1.34−1.27 (m, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 165.3, 163.3, 159.3, 159.1, 158.2, 152.7, 151.6, 146.3, 136.4, 129.9, 129.2, 128.8, 114.1, 103.6, 96.9, 55.4, 52.2, 44.4, 14.1, 12.2. IR(ATR) 3444, 2984, 2928, 2837, 1697, 1587, 1508, 1462, 1432, 1368, 1349, 1244, 1181, 1143, 1117, 1073, 1026, 987, 961, 828, 769, 748 cm^{-1}; HRMS (ESI+) m/z 514.1949 (514.1954 calcd for $C_{27}H_{29}N_3O_6Na^+$ [M + Na]$^+$).

1,3-Bis(4-chlorophenyl)-5-((2*Z*,4*E*)-5-(diethylamino)-2-hydroxypenta-2,4-dien-1-ylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (69). Following general procedure A, the title compound was obtained as a purple solid (445 mg, 89%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 12.08 (s, 1H), 7.44 (dd, J = 11.2, 8.5 Hz, 4H), 7.40 (d, J = 12.1 Hz, 1H), 7.24 (dd, J = 18.5, 8.6 Hz, 4H), 6.97 (s, 1H), 6.93 (dd, J = 12.8, 1.4 Hz, 1H), 6.20 (t, J = 12.4 Hz, 1H), 3.54 (dq, J = 25.9, 7.3 Hz, 4H), 1.32 (dt, J = 18.1, 7.2 Hz, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 163.4, 159.6, 154.4, 151.5, 146.9, 135.5, 134.3, 131.1, 131.0, 129.6, 129.6, 104.9, 96.6, 54.4, 53.0, 45.3, 14.7, 12.8. IR(ATR) 3468, 3007, 2986, 2928, 1701, 1625, 1589, 1489, 1461, 1430, 1366, 1347, 1275, 1258, 1224, 1181, 1142, 1116, 1073, 1014, 959, 824, 810, 765, 750 cm^{-1}; HRMS (ESI+) m/z 522.0953 (522.0963 calcd for $C_{25}H_{23}N_3O_4Cl_2Na^+$ [M + Na]$^+$).

General Procedure B: Photoisomerization of Stenhouse Adducts to Cyclopentenones. Stenhouse adduct was suspended in methanol (0.04 M). The reaction mixture was irradiated with a GE Crystal Clear 200 bulb (200 W, 3780 lm) placed approximately 10 in. from the reaction vessel at ambient temperature with stirring for 12 h. The reaction mixture was cooled to 0 °C for 20 min and then filtered to collect the precipitated solid; the solid was washed with cold diethyl ether and dried *in vacuo* to afford the title compounds.

2,2-Dimethyl-4-oxo-5-(2-oxo-5-(pyrrolidin-1-ium-1-yl)-cyclopent-3-en-1-yl)-4*H*-1,3-dioxin-6-olate (9). Following general procedure B, the title compound was obtained as a white solid (87.8 mg, 82%): ^{1}H NMR (600 MHz, D_2O) δ 7.87 (d, J = 6.1 Hz, 1H), 6.67 (d, J = 6.0 Hz, 1H), 4.57 (s, 1H), 3.66−3.41 (b, 4H), 3.56 (d, J = 3.1 Hz, 1H), 2.12 (b, 4H), 1.68 (s, 6H); ^{13}C NMR (150 MHz, D_2O) δ 208.4, 155.1, 137.6, 103.7, 72.3, 69.1, 52.6, 46.6, 24.5, 22.7; IR (KBr) 3410, 3090, 3036, 2985, 2908, 2584, 2411, 1715, 1667, 1574, 1490, 1471, 1412, 1393, 1371, 1346, 1323, 1289, 1263, 1216, 1198, 1162, 1134, 1116, 1066, 1035, 1006 cm^{-1}; HRMS (ESI+) m/z 316.1154 (316.1161 calcd for $C_{15}H_{19}NO_5Na^+$ [M + Na]$^+$).

2,2-Dimethyl-4-oxo-5-(2-oxo-5-(piperidin-1-ium-1-yl)-cyclopent-3-en-1-yl)-4*H*-1,3-dioxin-6-olate (72). Following general procedure B, the title compound was obtained as a white solid (108 mg, 88%): ^{1}H NMR (500 MHz, D_2O) δ 7.86 (dd, J = 6.1, 1.8 Hz, 1H), 6.65 (dd, J = 6.1, 1.4 Hz, 1H), 4.62−4.52 (m, 1H), 3.58−2.94 (m, 4H), 2.24−1.71 (m, 6H), 1.67 (s, 6H); ^{13}C NMR (125 MHz, D_2O) δ 208.4, 154.5, 137.6, 103.7, 73.0, 70.7, 44.3, 24.5, 23.1, 21.1; IR (KBr) 3420, 3049, 2989, 2968, 2940, 2877, 2645, 2327, 2274, 1717, 1682, 1576, 1521, 1469, 1446, 1413, 1375, 1365, 1345, 1330, 1321, 1291, 1261, 1235, 1215, 1201, 1190, 1179, 1149, 1116, 1081, 1048, 1038, 1005 cm^{-1}; HRMS (ESI+) m/z 330.1318 (330.1317 calcd for $C_{16}H_{21}NO_5Na^+$ [M + Na]$^+$). Because of it sparing solubility in D_2O and reversion to **17** in organic solvents, the structure of **72** was confirmed by single-crystal X-ray analysis. The crystal structure data for **2,2-dimethyl-4-oxo-5-(2-oxo-5-(piperidin-1-ium-1-yl)cyclopent-3-en-1-yl)-4*H*-1,3-dioxin-6-olate** (**72**) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif CCDC 844845.

5-(2-(Diethylammonio)-5-oxocyclopent-3-en-1-yl)-2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-olate (73). Following general procedure B, the title compound was obtained as a white solid (101 mg, 68%): ^{1}H NMR (600 MHz, D_2O) δ 7.68 (dd, J = 6.1, 1.9 Hz, 1H), 6.55 (dt, J = 6.1, 1.4 Hz, 1H), 4.72−4.69 (m, 1H), 3.49 (d, J = 3.6 Hz, 1H), 3.24 (b, J = 72.0 Hz, 4H), 1.54 (s, 6H), 1.22 (t, J = 7.3 Hz, 6H); ^{13}C NMR (150 MHz, D_2O) δ 208.2, 155.1, 138.0, 103.7, 72.6, 66.6, 44.1, 24.5, 9.3; IR (KBr) 3409, 3071, 2992, 2956, 2916, 2589, 2439, 1714, 1673, 1572, 1513, 1487, 1475, 1460, 1416, 1376, 1339, 1287, 1261, 1233, 1215, 1198, 1182, 1161, 1148, 1121, 1047, 1030 cm^{-1}; HRMS (ESI+) m/z 318.1313 (318.1317 calcd for $C_{15}H_{21}NO_5Na^+$ [M + Na]$^+$). The crystal structure data for **5-(2-(diethylammonio)-5-oxocyclopent-3-en-1-yl)-2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-olate**

(**73**) has been previously reported[7] and can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif CCDC 977459.

5-(2-(Benzyl(methyl)ammonio)-5-oxocyclopent-3-en-1-yl)-2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-olate (74). Following general procedure B, the title compound was obtained as a white solid (137 mg, 80%): ^{1}H NMR (500 MHz, D_2O) δ 7.86 (s, 1H), 7.51 (m, 5H), 6.69 (dd, J = 6.1, 1.9 Hz, 1H), 4.22 (s, 1H), 3.76 (d, J = 3.6 Hz, 1H), 2.87 (s, 3H), 2.73 (s, 2H), 1.67 (m, 6H); ^{13}C NMR (125 MHz, D_2O) δ 208.1, 138.04, 130.6, 130.2, 129.6, 129.6, 129.4, 129.2, 129.0, 105.0, 103.8, 52.3, 32.0, 30.2, 25.1, 24.5; IR (KBr) 3080, 3037, 2988, 2938, 2901, 2646, 2461, 1726, 1717, 1673, 1576, 1498, 1476, 1458, 1415, 1375, 1349, 1290, 1262, 1212, 1199, 1173, 1159, 1120, 1040 cm^{-1}; HRMS (ESI+) m/z 366.1320 (366.1317 calcd for $C_{19}H_{21}NO_5Na^+$ [M + Na]$^+$). Because of its sparing solubility in D_2O and reversion to **28** in organic solvents, the structure of **74** was confirmed by single crystal X-ray analysis. The crystal structure data for **5-(2-(benzyl(methyl)ammonio)-5-oxocyclopent-3-en-1-yl)-2,2-dimethyl-4-oxo-4*H*-1,3-dioxin-6-olate** (**74**) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif CCDC 851860.

2,2-Dimethyl-4-oxo-5-(2-oxo-5-(1,2,3,4-tetrahydroisoquinolin-2-ium-2-yl)cyclopent-3-en-1-yl)-4*H*-1,3-dioxin-6-olate (75). Following general procedure B, the title compound was obtained as a white solid (151 mg, 85%): ^{1}H NMR (500 MHz, D_2O) δ 7.96 (dd, J = 6.1, 2.0 Hz, 1H), 7.37−7.27 (m, 3H), 7.21−7.15 (m, 1H), 6.68 (dd, J = 6.2, 1.9 Hz, 1H), 4.71 (s, 1H), 3.70 (d, J = 3.4 Hz, 1H), 3.62 (dq, J = 12.3, 6.3 Hz, 1H), 3.54 (t, J = 6.6 Hz, 1H), 3.21 (q, J = 6.4 Hz, 2H), 3.13 (t, J = 6.4 Hz, 1H), 3.02 (t, J = 6.7 Hz, 1H), 1.67 (s, 6H); ^{13}C NMR (125 MHz, D_2O) δ 207.3, 155.2, 137.6, 133.1, 128.7, 128.2, 128.0, 127.7, 127.0, 126.8, 126.6, 103.7, 69.5, 51.4, 47.9, 44.8, 41.6, 25.1, 24.5; IR (KBr) 3433, 3019, 2994, 2944, 2722, 2509, 2400, 1926, 1726, 1667, 1568, 1504, 1479, 1457, 1440, 1426, 1411, 1394, 1373, 1346, 1323, 1288, 1275, 1259, 1231, 1200, 1181, 1152, 1115, 1087, 1070, 1056, 1026, 1008 cm^{-1}; HRMS (ESI+) m/z 378.1314 (378.1317 calcd for $C_{20}H_{21}NO_5Na^+$ [M +Na]$^+$). Because of its sparing solubility in D_2O and reversion to **29** in organic solvents, the structure of **75** was confirmed by single crystal X-ray analysis. The crystal structure data for **2,2-dimethyl-4-oxo-5-(2-oxo-5-(1,2,3,4-tetrahydroisoquinolin-2-ium-2-yl)cyclopent-3-en-1-yl)-4*H*-1,3-dioxin-6-olate** (**75**) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif CCDC 844846.

1,3-Dimethyl-2,6-dioxo-5-(2-oxo-5-(pyrrolidin-1-ium-1-yl)-cyclopent-3-en-1-yl)-1,2,3,6-tetrahydropyrimidin-4-olate (76). Following general procedure B, the title compound was obtained as a white solid (235 mg, 77%): ^{1}H NMR (600 MHz, D_2O) δ 7.85 (dd, J = 5.8, 1.8 Hz, 1H), 6.67 (dd, J = 6.3, 1.6 Hz, 1H), 4.53 (d, J = 1.9 Hz, 1H), 3.78 (d, J = 3.4 Hz, 1H), 3.48 (s, 4H), 3.20 (d, J = 61.7 Hz, 6H), 2.06 (s, 4H); ^{13}C NMR (125 MHz, D_2O) δ 208.7, 164.4, 163.7, 154.8, 154.1, 137.7, 85.5, 69.1, 52.4, 46.9, 28.0, 27.2, 22.8; IR (ATR) 3006, 2990, 2747, 2619, 1716, 1667, 1567, 1435, 1361, 1275, 1260, 1189, 750 cm^{-1}; HRMS (ESI+) m/z 328.1273 (328.1273 calcd for $C_{15}H_{19}N_3O_4Na^+$ [M + Na]$^+$).

1,3-Dimethyl-2,6-dioxo-5-(2-oxo-5-(piperidin-1-ium-1-yl)-cyclopent-3-en-1-yl)-1,2,3,6-tetrahydropyrimidin-4-olate (77). Following general procedure B, the title compound was obtained as a white solid (259 mg, 81%): ^{1}H NMR (600 MHz, D_2O) δ 7.69 (dd, J = 6.2, 2.0 Hz, 1H), 6.50 (dd, J = 6.3, 1.9 Hz, 1H), 4.46−4.32 (m, 1H), 3.71 (d, J = 3.6 Hz, 1H), 3.49−2.85 (m, 10H), 1.93−1.24 (m, 6H); ^{13}C NMR (125 MHz, D_2O) δ 208.7, 164.4, 163.8, 154.3, 154.1, 137.5, 86.1, 70.7, 67.8, 50.8, 44.7, 23.0, 22.1, 21.4, 21.1. IR(ATR) 3006, 2989, 2918, 2861, 1718, 1673, 1604, 1575, 1473, 1440, 1370, 1319, 1275, 1260, 1191, 1153, 1117, 1016, 951, 707 cm^{-1}; HRMS (ESI+) m/z 342.1424 (324.1430 calcd for $C_{16}H_{21}N_3O_4Na^+$ [M + Na]$^=$).

5-(2-(Diethylammonio)-5-oxocyclopent-3-en-1-yl)-1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate (78).[7] Following general procedure B, the title compound was obtained as a white solid (142 mg, 92%): ^{1}H NMR (600 MHz, D_2O) δ 7.84 (dd, J = 6.1, 1.9 Hz, 1H), 6.71 (ddd, J = 6.1, 1.9, 0.8 Hz, 1H), 4.83 (d, J = 1.8 Hz, 1H), 3.88 (d, J = 3.6 Hz, 1H), 3.39 (dq, J = 14.6, 7.4 Hz, 2H), 3.36−3.21 (m, 6H), 3.18 (s, 2H), 1.30 (t, J = 7.3 Hz, 6H); ^{13}C NMR (150 MHz, D_2O) δ 208.5, 164.6, 163.7, 154.0, 138.0, 85.6, 66.5, 66.5, 46.4, 44.4, 44.4, 28.0, 27.2, 9.2; IR (KBr) 3052, 2986, 2972, 2919, 2742, 2660, 2502, 1727, 1674, 1667, 1614, 1599, 1578, 1517, 1477, 1435, 1397; HRMS (ESI+) m/z 330.1433 (330.1430 calcd for $C_{15}H_{21}N_3O_4Na^+$ [M +Na]$^+$). The crystal structure data for **5-(2-(diethylammonio)-5-oxocyclopent-3-en-1-yl)-1,3-dimethyl-2,6-dioxo-1,2,3,6-tetrahydropyrimidin-4-olate** (**78**) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif CCDC 1026491.

1,3-Dimethyl-2,6-dioxo-5-(2-oxo-5-(1,2,3,4-tetrahydroisoquinolin-2-ium-2-yl)cyclopent-3-en-1-yl)-1,2,3,6-tetrahydropyrimidin-4-olate (79). Following general procedure B, the title compound was obtained as a white solid (320 mg, 87%): ^{1}H NMR (600 MHz, D_2O) δ 7.84 (dd, J = 6.3, 1.9 Hz, 1H), 7.20−7.00 (m, 3H), 6.89−6.75 (m, 1H), 6.55 (dd, J = 6.2, 1.9 Hz, 1H), 4.59 (dt, J = 3.8, 2.0 Hz, 1H), 4.45−4.29 (m, 2H), 3.78 (d, J = 3.6 Hz, 1H), 3.67 (dt, J = 11.9, 5.7 Hz, 1H), 3.57 (dt, J = 5.5, 2.0 Hz, 1H), 3.19−2.78 (m, 8H); ^{13}C NMR (125 MHz, D_2O) δ 208.0, 164.4, 163.6, 153.9, 153.7, 137.8, 130.2, 128.9, 128.7, 128.4, 128.0, 126.8, 126.5, 85.5, 67.8, 51.3, 47.7, 45.8, 28.0, 27.1. IR (ATR) 3006, 2989, 1716, 1668, 1568, 1435, 1374, 1318, 1275, 1260, 1187, 1062, 967, 907, 824, 764, 750 cm^{-1}; HRMS (ESI+) m/z 390.1418 (390.1430 calcd for $C_{20}H_{21}N_3O_4Na^+$ [M + Na]$^+$).

2-(2-(Furan-2-ylmethylene)-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (37). Following the procedure outlined by Bello et al.,[27] the title compound was isolated as a bright orange solid (882 mg, 81%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.73−8.68 (m, 2H), 8.57 (s, 1H), 7.93 (dd, J = 7.5, 1.5 Hz, 1H), 7.84 (d, J = 1.6 Hz, 1H), 7.82−7.74 (m, 2H), 6.80−6.75 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.1, 160.5, 150.9, 150.2, 139.8, 137.3, 135.3, 134.8, 130.4, 127.3, 125.4, 124.4, 124.0, 115.5, 114.2, 113.8, 71.2. IR (ATR): 3166, 3147, 3129, 3079, 2218, 1708, 1595, 1576, 1543, 1451, 1357, 1231, 1146, 1091, 1025, 933, 764, 718 cm^{-1}; HRMS (EI+) m/z 272.0589 (272.0586 calcd for $C_{17}H_8N_2O_2$ [M]$^+$).

3-(Diethylamino)-1-(furan-2-yl)-9-oxo-2,9-dihydro-1*H*-indeno[2,1-*c*]pyridine-4-carbonitrile (38). Following general procedure A, the title compound was isolated as a dark blue solid (332 mg, 96%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.36 (d, J = 7.6 Hz, 1H), 7.61−7.40 (m, 4H), 7.31 (s, 1H), 6.95 (d, J = 12.8 Hz, 1H), 6.32 (s, 1H), 5.33 (s, 1H), 3.59 (dq, J = 29.4, 7.3 Hz, 4H), 1.36 (dt, J = 14.6, 7.3 Hz, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 191.7, 160.0, 159.8, 152.8, 148.4, 141.1, 136.6, 133.7, 132.2, 127.3, 123.8, 122.1, 118.2, 118.1, 113.4, 106.3, 53.2, 45.7, 14.6, 12.9. IR(ATR): 3325, 2979, 2935, 2874, 2196, 2179, 1666, 1616, 1602, 1579, 1498, 1436, 1367, 1344, 1243, 1185, 1111, 1068, 974, 912, 821, 759, 712 cm^{-1}; HRMS (EI+) m/z 345.1483 (345.1477 calcd for $C_{21}H_{19}N_3O_2$ [M]$^+$).

2,2′-(2-(Furan-2-ylmethylene)-1*H*-indene-1,3(2*H*)-diylidene)-dimalononitrile (39). Following the procedure outlined by Bello et al.,[27] the title compound was isolated as a bright orange solid (1.17 g, 91%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (d, J = 7.8 Hz, 1H), 8.51 (d, J = 7.8 Hz, 1H), 8.21 (s, 1H), 7.91−7.70 (m, 3H), 7.24 (d, J = 3.6 Hz, 1H), 6.72 (dd, J = 3.9, 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.7, 160.7, 149.7, 148.6, 138.3, 136.6, 135.3, 134.6, 127.8, 127.4, 126.7, 126.2, 125.3, 115.3, 113.3, 113.1, 112.1, 78.8, 71.9. IR(ATR): 3139, 3121, 2222, 1608, 1551, 1527, 1460, 1396, 1349, 1025, 880, 772. 715 cm^{-1}; HRMS (EI+) m/z 320.0693 (320.0698 calcd for $C_{20}H_8N_4O$ [M]$^+$).

2-(4-Cyano-3-(diethylamino)-1-(furan-2-yl)-1,2-dihydro-9*H*-indeno[2,1-*c*]pyridin-9-ylidene)malononitrile (40). Following general procedure A, the title compound was isolated as a dark blue solid (315 mg, 80%): ^{1}H NMR (600 MHz, CD_2Cl_2) δ 8.19−8.09 (m, 2H), 7.42−7.34 (m, 3H), 6.49 (s, 1H), 6.36−6.30 (m, 2H), 6.20 (d, J = 3.3 Hz, 1H), 3.63 (ddt, J = 42.7, 15.2, 7.5 Hz, 4H), 1.31 (t, J = 7.1 Hz, 6H); ^{13}C NMR (125 MHz, CD_2Cl_2) δ 158.1, 155.6, 155.2, 152.9, 144.0, 137.9, 137.6, 131.4, 130.8, 124.0, 123.1, 119.2, 117.5, 116.9, 111.0, 108.4, 48.0, 46.2, 30.3, 13.6. IR(ATR) 3312, 3108, 2937, 2206, 2188, 1581, 1546, 1504, 1396, 1380, 1347, 1242, 1219, 1164, 1143, 1079, 1015, 920, 882, 749 cm^{-1}; HRMS (EI+) m/z 393.1583 (393.1590 calcd for $C_{24}H_{19}N_5O$ [M]$^+$).

1,3-Dibutyl-5-(furan-2-ylmethylene)pyrimidine-2,4,6-(1*H*,3*H*,5*H*)-trione (58). Following the procedure outlined by Deb and Bhuyan,[25] the title compound was obtained as a pale yellow solid (10.93g, 63%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, J = 3.8 Hz, 1H), 8.41 (d, J = 0.7 Hz, 1H), 7.83 (dd, J = 1.7, 0.6 Hz, 1H), 6.72 (ddd, J = 3.8, 1.6, 0.8 Hz, 1H), 4.04−3.87 (m, 4H), 1.75−1.51 (m, 4H), 1.50−1.29 (m, 4H), 0.95 (td, J = 7.4, 3.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 160.8, 151.4, 151.1, 150.4, 141.0, 128.0, 115.2, 112.1, 42.5, 41.8, 30.4, 30.3, 20.4, 20.4, 14.0, 14.0. IR (ATR) 3120, 2957, 2933, 2873, 1724, 1659, 1578, 1445, 1428, 1409, 1376, 1308, 1250, 1203, 1157, 1128, 1091, 1036, 1022, 962, 915, 884, 791, 760, 734 cm^{-1}; HRMS (ESI+) m/z 341.1479 (341.1477 calcd for $C_{17}H_{22}N_2O_4Na^+$ [M + Na]$^+$).

5-(Furan-2-ylmethylene)-1-methyl-3-octylpyrimidine-2,4,6-(1*H*,3*H*,5*H*)-trione (62). 1-methyl-3-octylpyrimidine-2,4,6-(1*H*,3*H*,5*H*)-trione (S1): A solution of methylamine−HCl (0.12 g, 1.79 mmol) in anhydrous DCM (15 mL) was treated with *n*-octyl isocyanate (0.30 mL, 1.70 mmol) under argon. Triethylamine (0.35 mL, 2.56 mmol) was then added, and the mixture was heated to reflux. After 1 h, malonyl dichloride (0.17 mL, 1.70 mmol) was added under argon and heated to reflux for an additional 1 h. The mixture was cooled to rt and quenched with 1 N HCl. The crude product was extracted with DCM (3 × 10 mL), washed with H_2O (10 mL), dried over $MgSO_4$, and filtered. The solvent was removed in vacuo and the product was purified by column chromatography (hexane/EtOAc = 9:1 to 1:1) to afford clear oil (302 mg, 67%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.91−3.78 (m, 2H), 3.65 (s, 2H), 3.29 (s, 3H), 1.62−1.52 (m, 2H), 1.34−1.18 (m, 10H), 0.86 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.0, 164.7, 151.8, 42.4, 39.7, 32.0, 29.4, 29.3, 28.6, 28.2, 27.0, 22.8, 14.3. IR (ATR) 2956, 2924, 2855, 1685, 1519, 1433, 1409, 1389, 1364, 1334, 1268, 1168, 1121, 1005, 936, 758, 723, 685 cm^{-1}; HRMS (EI+) m/z 254.1641 (254.1630 calcd for $C_{13}H_{22}N_2O_3^+$ [M]$^+$). This material was subjected to the conditions of Deb and Bhuyan[25] to give the title compound as a pale yellow solid (228 mg, 83%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, J = 3.7 Hz, 1H), 8.42 (s, 1H), 7.84 (d, J = 1.5 Hz, 1H), 6.72 (ddd, J = 3.9, 1.8, 0.9 Hz, 1H), 3.98−3.92 (m, 2H), 3.40 (s, 3H), 1.68−1.61 (m, 2H), 1.39−1.24 (m, 10H), 0.89−0.85 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 160.7, 151.4, 151.3, 150.4, 141.1, 128.1, 115.3, 111.9, 42.1, 32.0, 29.5, 29.4, 29.1, 28.3, 27.2, 22.8, 14.3. IR (ATR) 3145, 2915, 2851, 1728, 1658, 1575, 1543, 1450, 1423, 1407, 1366, 1327, 1252, 1201, 1166, 1129, 1115, 1095, 1029, 988, 962, 921, 882, 789, 756, 719 cm^{-1}; HRMS (ESI+) m/z 355.1627 (355.1634 calcd for $C_{18}H_{24}N_2O_4Na^+$ [M + Na]$^+$)

5-(Furan-2-ylmethylene)-1,3-diphenylpyrimidine-2,4,6-(1*H*,3*H*,5*H*)-trione (64). Following the procedure out lined by Deb and Bhuyan,[25] the title compound was isolated as a bright yellow solid (1.22 g, 85%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, J = 3.9 Hz, 1H), 8.59 (s, 1H), 7.88 (d, J = 1.5 Hz, 1H), 7.56−7.41 (m, 6H), 7.36−7.30 (m, 4H), 6.71 (ddd, J = 3.9, 1.7, 0.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.5, 151.3, 151.1, 142.4, 135.0, 134.7, 129.5, 129.4, 129.2, 129.1, 128.8, 128.6, 115.6, 111.4. IR (ATR) 3348, 3146, 3124, 3070, 1736, 1668, 1570, 1490, 1455, 1416, 1356, 1326, 1236, 1199, 1149, 1030, 948, 882, 786, 691 cm^{-1}; HRMS (ESI+) m/z 381.0851 (381.0851 calcd for $C_{21}H_{14}N_2O_4Na^+$ [M + Na]$^+$).

5-(Furan-2-ylmethylene)-1,3-bis(4-methoxyphenyl)-pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (66). Following the procedure out lined by Deb and Bhuyan,[25] the title compound was isolated as a bright yellow solid (1.46 g, 87%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 (d, J = 3.9 Hz, 1H), 8.57 (s, 1H), 7.86 (d, J = 1.6 Hz, 1H), 7.25−7.20 (m, 4H), 7.04−6.98 (m, 4H), 6.70 (ddd, J = 4.0, 1.6, 0.8 Hz, 1H), 3.84 (d, J = 2.6 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.8, 161.3, 159.9, 159.8, 151.3, 151.2, 151.0, 142.3, 129.7, 129.6, 129.3, 127.6, 127.2, 115.5, 114.8, 114.7, 111.6, 55.6. IR (ATR) 3139, 3116, 3002, 2964, 2835, 1733, 1674, 1607, 1568, 1509, 1455, 1349, 1325, 1239, 1156, 1027, 951, 828, 808, 779, 752 cm^{-1}; HRMS (ESI+) m/z 441.1049 (441.1063 calcd for $C_{23}H_{18}N_2O_6Na^+$ [M + Na]$^+$).

1,3-Bis(4-chlorophenyl)-5-(furan-2-ylmethylene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (68). Following the procedure out lined by Deb and Bhuyan,[25] the title compound was isolated as a bright yellow solid (1.32 g, 77%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (d, J = 3.8 Hz, 1H), 8.49 (s, 1H), 7.81 (d, J = 1.5 Hz, 1H), 7.39 (dd, J = 13.3, 8.6 Hz, 4H), 7.17 (dd, J = 12.5, 8.6 Hz, 4H), 6.70−6.61 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.2, 160.7, 151.7, 151.2, 150.4, 142.8, 135.2, 135.1, 133.3, 133.0, 130.2, 130.0, 130.0, 129.8, 129.7, 115.8, 110.8; IR (ATR) 3136, 3118, 2925, 2855, 1735, 1672, 1564, 1489, 1454, 1418, 1399, 1346, 1324, 1233, 1154, 1087, 1028, 1014, 949, 920, 826, 801, 783, 751 cm^{-1}; HRMS (ESI+) m/z 449.0066 (449.0072 calcd for $C_{21}H_{12}N_2O_4Cl_2Na^+$ [M + Na]$^+$).

■ ASSOCIATED CONTENT

Supporting Information

Additional experimental details, spectroscopic data, XRD atomic distance measurements, and ORTEP plots of reported crystal structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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