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Diversity-oriented general protocol for the synthesis of privileged oxygen scaffolds: pyrones, coumarins, benzocoumarins and naphthocoumarins†

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A new general methodology for the synthesis of various functionalized privileged oxygen heterocyclic scaffolds, *viz.* pyrones, coumarins, and benzannulated coumarins, is developed. The synthesis proceeds through carbanion-induced ring transformation of lactones with various methylene carbonyl compounds followed by DDQ-mediated unprecedented oxidative cleavage of oxaylidenes intermediates. Studies of the mechanism of the conversions of oxaylidene intermediates into corresponding carbonyl compounds in the presence of DDQ revealed that the reactions took place *via* the formation of a Michael adduct instead of an intermolecular charge transfer complex. The methodology offers the fabrication of diverse privileged scaffolds with tolerance for many functional groups onto the oxygen heterocyclic molecular framework.

Introduction

α-Pyrone, coumarin and their benzannulated scaffolds are key structural motifs found in a large number of biologically important natural alkaloids, isolated from an eclectic array of plant and marine sources.[1,2] Owing to their interesting photophysical properties[3] and the broad range of pharmacological activities[4] associated with them, they come under the category of privileged scaffolds in medicinal chemistry. As a consequence; numerous approaches to the synthesis of pyrones, coumarins and benzocoumarins have been reported either by the conventional approaches[5] or by procedures involving transition metal-catalyzed reactions.[6,7]

Undoubtedly these classical approaches play a crucial role in the realm of natural and medicinal chemistry; however in the era of high throughput screening and the rapid generation of libraries of small molecules, chemists need to keep up their pace to fulfil the demands of current research. Therefore new efficient and general synthetic methods, which produce privileged scaffolds such as α-pyrones, coumarins and benzocoumarins under one set of reaction protocols, would be what is needed today, especially when the reported procedures usually require expensive organometallic catalysts (Pd, Ru or Au), harsh reaction conditions and often lead to substances with traces of toxic metal impurities.[6,7] Herein we report a new protocol for the synthesis of various privileged heterocyclic scaffolds through carbanion-induced ring transformation of flexible or rigid lactones followed by DDQ-promoted unprecedented oxidative cleavage of oxaylidenes to their corresponding carbonyl compounds.

Results and discussion

Over the last decade we have been exploring the reactivity of 2*H*-pyran-2-ones towards various C- and N-nucleophiles for generating diverse molecular architectures suitable for biological and material applications.[8] We have recently demonstrated an efficient synthesis of the partially hydrogenated oxa[5]helicenes **1a**, **2a** and investigated their stereochemical behaviour in collaboration with Bringmann and co-workers.[9] In our further efforts directed towards the oxidation of 9,10-dihydro-7-oxa[5]helicene-8-ylidenylacetonitrile **2a** to produce oxa[5]helicene **3a** with a higher inversion barrier, we reacted **2a** (inversion barrier 78.2 kJ mol^{-1}) with 2 equiv. of 2,3-dichloro-5,6-dicyano-1,4-quinone (DDQ) using benzene as a solvent. Under this condition, we failed to obtain **3a**. When we attempted the reaction of 5,6,9,10-tetrahydro-7-oxa[5]helicene-8-ylidenylacetonitrile **1a** in dioxane using 4 equiv. of DDQ, we observed the formation of two new products **4a** and **5a** on TLC under UV exposure at 254 nm (Scheme 1). The structures of both the compounds were assigned by analyzing the spectroscopic data. The structure of **4a** was unambiguously confirmed by single-

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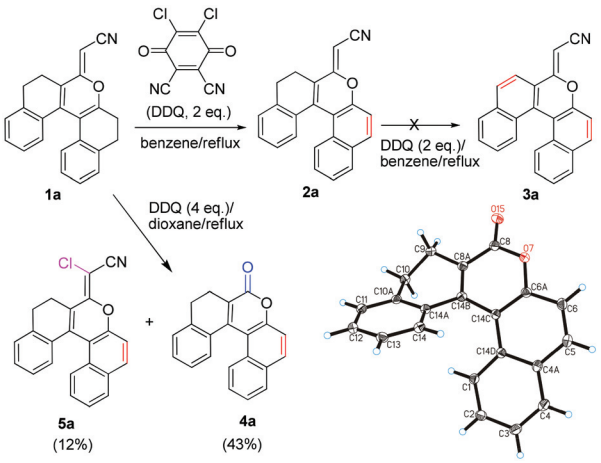
†Electronic supplementary information (ESI) available: Copies of ^{1}H and ^{13}C NMR of the compounds prepared, X-ray data (CIF, **4a** and **12**). CCDC 877580 and 877581. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ob40859k



Scheme 1 Synthesis of dinaphthopyranone **4a**.

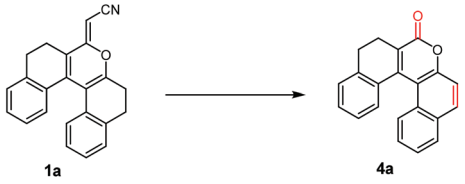
crystal X-ray analysis (**4a**: CCDC no. 877580; Scheme 1). An unusual chlorination of the ylidenic proton in **1a** led to the formation of **5a** in minor yield. Few unexpected chlorinations on different substrates have been reported earlier for DDQ-mediated oxidation reactions.[10] Interestingly the unexpected chlorination of the ylidenic proton is possible, however, the conversion of such an ylidenic group into corresponding carbonyl functionality promoted by DDQ has not been reported in the literature prior to this study. These new observations prompted us to investigate the possibility of using the DDQ for the cleavage of the ylidenic double bond.

Considering the fact that there are limited synthetic methods for the preparation of dinaphthopyranones,[11] we thus focused our attention on optimizing the reaction conditions for this unexpected transformation (Table 1). In order to improve the yield of **4a**, we investigated the reaction using 5,6,9,10-tetrahydro-7-oxa[5]helicene-8-ylidenylacetonitrile **1a** (0.2 mmol) and DDQ (0.8 mmol) by changing the reaction conditions as mentioned in Table 1. No product was observed in THF and MeOH (Table 1, entries 7 and 8) while only traces of cleaved products were formed in acetonitrile and acetone at room temp (Table 1, entries 5 and 6). When dioxane was used as a solvent we isolated **4a** in moderate yield (entries 1 and 2), together with a minor product **5a** (see the ESI; Scheme S1†).

However switching the solvent from dioxane to acetic acid significantly increased the yield of **4a** (entries 3 and 4) and only **4a** was isolated as the sole product. The best result was obtained with 4 equiv. of DDQ in AcOH at room temperature producing a 58% yield of **4a** (entry 4). It is worth noting that in the absence of DDQ, no reaction occurred suggesting the role of DDQ in the given transformation (entries 3 and 6).

With the optimized conditions in hand, a series of substituted (*Z*)-2-(5,6-dihydro-1*H*-benzo[*f*]naphtho-[2,1-*c*]chromen-4-(2*H*)-ylidene)acetonitriles[9] (**1a–f**) was subjected to oxidative cleavage using DDQ (4 equiv.) as an oxidant in acetic acid to afford partially hydrogenated 4*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-ones (**4a–f**) in good yields (Scheme 2).

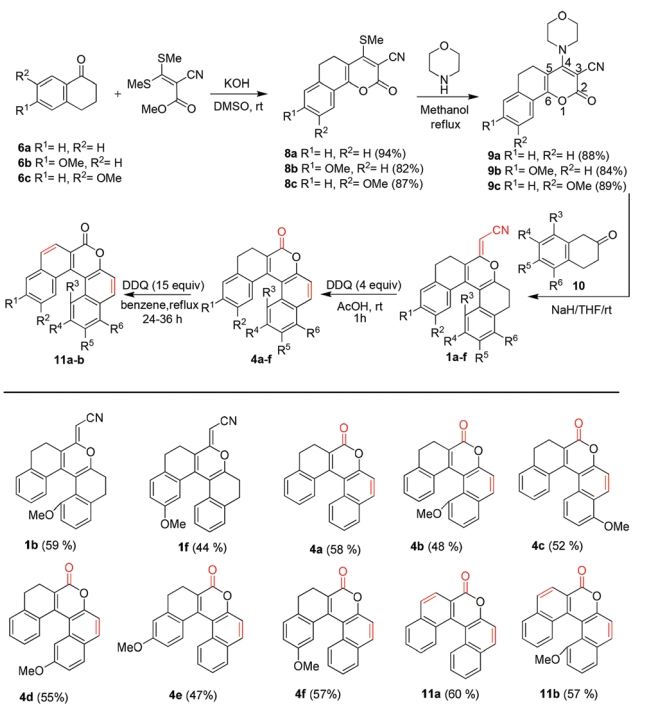
Table 1 Optimization of unusual transformation



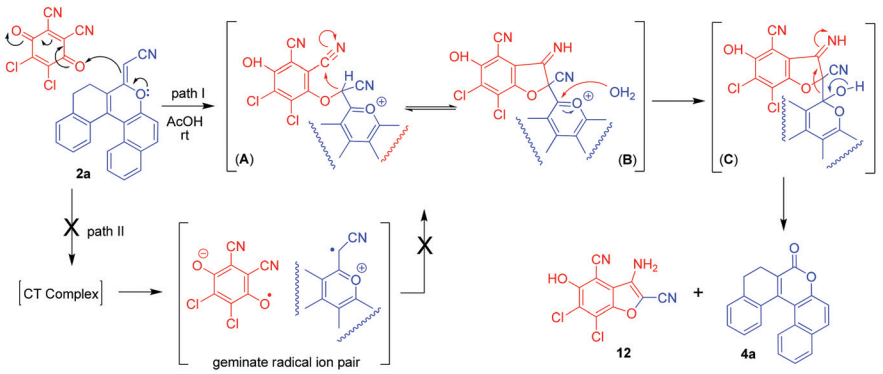
Entry	Solvent	DDQ (equiv.)	Temp (°C)	Time (h)	Yield[a] (%) 4a	5a
1	Dioxane	4	rt	24	15	5
2	Dioxane	4	rx	4	43	12
3	Dioxane	0	rx	4	—	—
4	AcOH	4	rt	1	58	—
5	AcOH	4	rx	2	42	—
6	AcOH	0	rx	2	—	—
7	MeCN	4	rt	24	Trace	—
8	Acetone	4	rt	24	Trace	—
9	THF	4	rt	24	—	—
10	MeOH	4	rt	24	—	—

[a] Isolated yield, rt means room temperature, rx means reflux.

The compounds **4a,b** were further converted into their fully aromatized products 4*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-ones (**11a,b**) using an excess amount of DDQ (15 equiv.) in refluxing benzene. Such dinaphthopyranones exist in configurationally labile helimeric equilibrium and they are important chemical scaffolds for the atroposelective synthesis of a broad range of naturally occurring biaryls and axially chiral auxiliaries.[11] The classical approaches for the synthesis of dinaphthopyranones



Scheme 2 Synthesis of 4*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-ones **4** and **11**.



Scheme 3 Proposed mechanism for the oxidative cleavage of the ylidenic bond of **2a**.

mainly involve palladium-catalyzed intramolecular Heck arylation using harsh reaction conditions and limited only to less sterically hindered substrates.[11] Our approach provides an easy access to these interesting compounds under mild reaction conditions and without using any transition metal catalysts. In order to examine the reaction mechanism, a survey of the literature reveals examples of carbon–oxygen adduct formation through charge transfer complex between DDQ and aromatic hydrocarbons, heterocycles, and olefins.[12] Based on these literature reports, we proposed two possible pathways for the formation of **4a** as depicted in Scheme 3, which revealed that the formation of **4a** may be explained *via* a nonradical mechanism (path I) or through a radical mechanism (path II). In the nonradical mechanism (path I), a carbon–oxygen adduct (**A**) may be formed by Michael addition of the 5,6,9,10-tetrahydro-7-oxa[5]-helicene-8-ylidenyl-acetonitrile **2a** to the 2,3-dichloro-5,6-dicyano-1,4-quinone (DDQ) followed by intramolecular cyclization involving methyne carbon and the nitrile group of DDQ to produce intermediate B. This intermediate B under acidic conditions may lead to intermediate C, which on further internalization would afford the final product **4a** together with the formation of 3-amino-benzofuran **12**. Our presumption for the path I is supported by the isolation and characterization of a final product **4a** together with the benzofuran derivative **12**, whose structure was unambiguously confirmed using X-ray analysis of the air-sensitive single-crystals of **12** in acetonitrile (Fig. 1). It is worth noting that the formation of diffraction quality crystals of **12** was largely dependent on the acetonitrile solvent molecules, which formed intermolecular hydrogen bonding with the NH_2 group of the furan ring. As soon as the solvent evaporates during the crystal growth, the crystals become opaque revealing the importance of strong non-covalent interactions with acetonitrile solvent in the crystal formation.

Similarly a radical mechanism (path II) may be proposed *via* the formation of an intermolecular charge transfer (ICT) complex between **2a** and DDQ followed by a single electron transfer (SET),[12] which on recombination may form a carbon–oxygen adduct (**A**). To check the possibility of a single electron transfer (SET) mechanism (path II), we carried out an independent experiment by reacting **2a** and DDQ in acetic acid at room

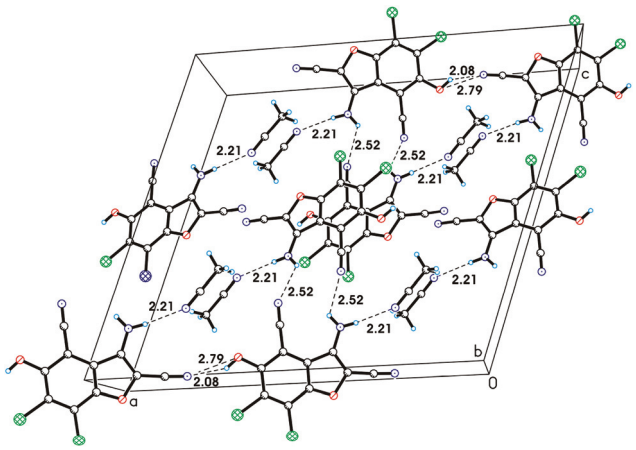


Fig. 1 The crystal structure of **12** showing the network of intermolecular N–H···N and O–H···N interactions.

temperature. The absorption spectra of the reaction mixtures ($\sim 10^{-6}$ μM) in acetic acid were monitored at different time intervals (Fig. 2).

Neither a coloured ICT complex nor any band in the range of 500–700 nm was observed during the reaction.[12] These results clearly suggested that the reaction follows non-ICT path I to produce compounds **4a** and **12**.

To further extend the scope of the above ring transformation and considering that 4-aryl-coumarins (neoflavones) are ubiquitous structural units in a plethora of natural products with interesting biological activities,[13] we designed a new protocol utilizing the reactivity of substituted resorcinols **13** towards 2*H*-pyran-2-ones **14** in the presence of a base (Scheme 4). Thus reaction of commercially available substituted resorcinols **13** (R^1, R^2 = H, Me, Cl) and 6-aryl-4-(methylthio)-2-oxo-2*H*-pyran-3-carboxylate[14] **14** in NaH/DMF afforded methyl 2-(7-hydroxy-2*H*-chromen-2-ylidene)acetates **15** in good yields (up to 60–70%) as a mixture of geometrical isomers. As depicted in Scheme 4, the reaction is possibly initiated by a Michael addition of a conjugate base of resorcinol generated *in situ* in the presence of a base, at C6 of the 6-aryl-4-(methylthio)-2-oxo-2*H*-pyran-3-carboxylates **14** followed by ring opening to give intermediate **I**.

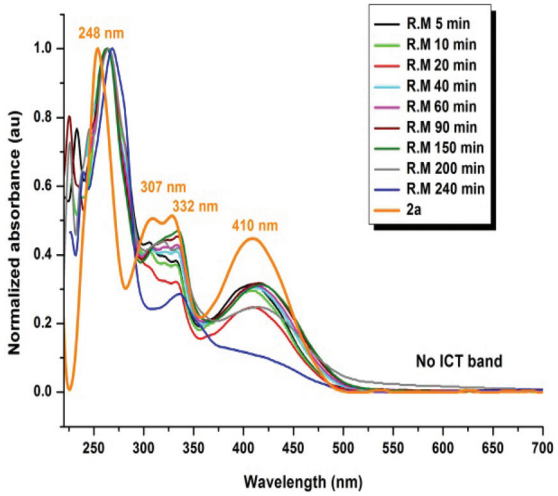
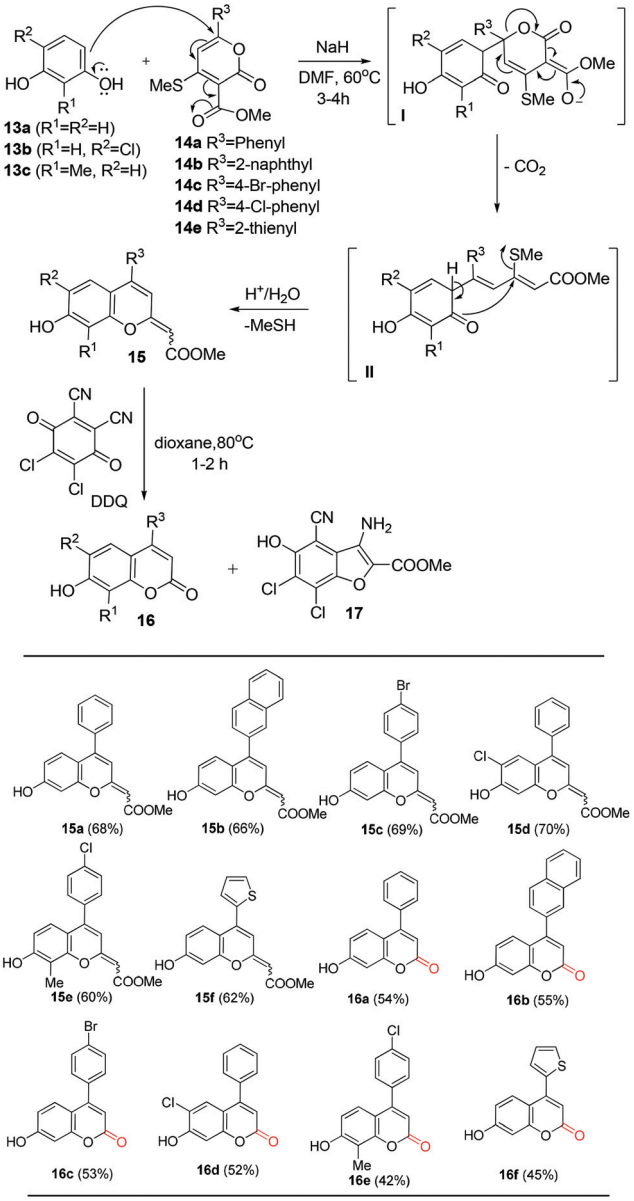


Fig. 2 Absorption spectra of the reaction mixtures (~10^{-6} μM) in acetic acid at different time intervals.

This Michael intermediate **I** may undergo an intramolecular cyclization involving the carbonyl functionality and C4 center of **14** with the elimination of carbon dioxide and methyl mercaptan to yield the (*Z*/*E*)-methyl 2-(7-hydroxy-2*H*-chromen-2-ylidene)acetates **15** in good yields. Furthermore these ylidenes **15a–f** were converted to 4-aryl-7-hydroxy-coumarins **16a–f** through oxidative cleavage using DDQ (2 equiv.) in dioxane at 80 °C for 1–2 h. The formation of carbomethoxy-substituted benzofuran **17** as a side product similar to the product **12** confirmed the possible route I for obtaining the coumarins **16a–f**. Although numerous synthetic methodologies for 4-aryl/heteroaryl-coumarins are reported, most of them depend on organometal-catalyzed reactions *via* C–H or C–X activation on a preformed coumarin nucleus.[15] Our novel methodology provides an easy access to 4-aryl-7-hydroxy-coumarin derivatives under a transition-metal free environment using easily available precursors in good yields. After successful demonstration of this methodology for the preparation of 4-aryl-7-hydroxy-coumarins **16a–f**, we extended the methodology to the synthesis of benzocoumarins *viz.* 5,6-dihydro-2*H*-benzo[*h*]chromen-2-ones (**19**) and 2*H*-benzo[*h*]-chromen-2-ones (**20**) (Scheme 5). To synthesize these compounds, the requisite precursor methyl 2-(4-aryl-5,6-dihydro-2*H*-benzo[*h*]chromen-2-ylidene)acetates **18a–c** were prepared according to improved methodology.[16] Treatment of **18a–c** with DDQ (2 equiv.)/AcOH afforded the 4-aryl-5,6-dihydro-2*H*-benzo[*h*]chromen-2-one **19a–c** in moderate yields (46–52%). The partially hydrogenated benzocoumarin **19a** was aromatized using DDQ in benzene at reflux temperature to afford 4-(4-bromophenyl)-8-methoxy-2*H*-benzo[*h*]chromen-2-one (**20a**) in a 52% yield.

Finally, the synthesis of highly substituted α-pyrones (**24a–f**) was explored as shown in Scheme 6. The precursors functionalized 2*H*-pyran-2-ylidene-acetonitriles **23a–f** were prepared by reacting substituted 2*H*-pyran-2-ones **21a–f** with substituted methylene carbonyl compounds **22a–f** (see the Experimental section) and converted to highly substituted α-pyrones **24a–f** through oxidative cleavage using DDQ (2 equiv.)/AcOH at room temperature in 5–6 h (Scheme 6).

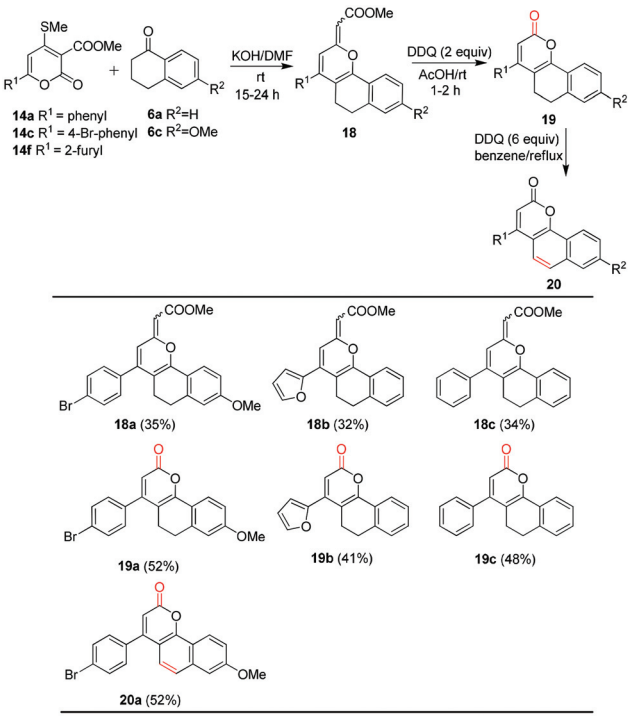


Scheme 4 Synthesis of 4-arylcoumaryl-2-ylidenes **15** and 4-arylcoumarins **16**.

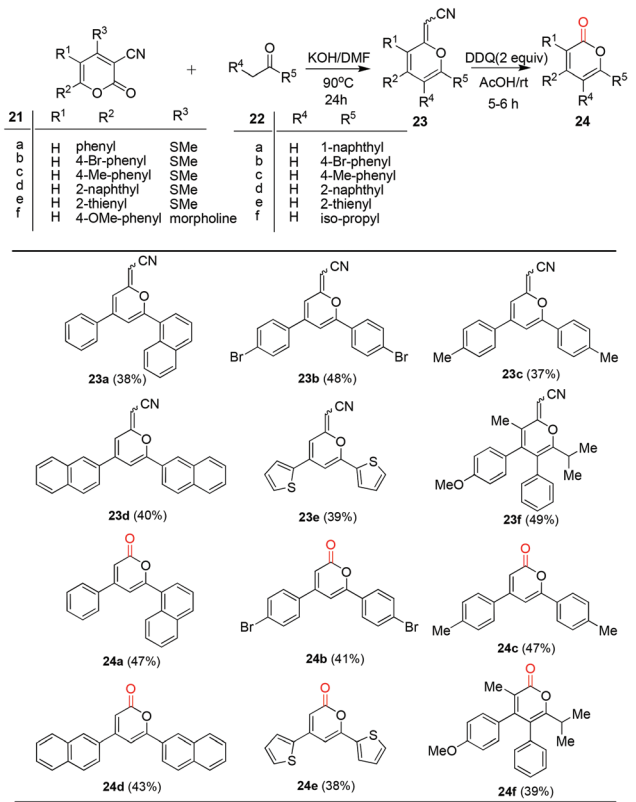
It is important to note that highly hindered 2-(6-isopropyl-4-(4-methoxyphenyl)-3-methyl-5-phenyl-2*H*-pyran-2-ylidene)-acetonitrile (**23f**) was successfully converted to the corresponding carbonyl compound 6-isopropyl-4-(4-methoxyphenyl)-3-methyl-5-phenyl-2*H*-pyran-2-one (**24f**) under the same reaction conditions. This new methodology offers a general synthesis of α-pyrones with four point diversity.

Conclusion

In summary, we have demonstrated a novel and general synthesis of highly functionalized α-pyrones, coumarins and



Scheme 5 Synthesis of benzocoumarinyl-2-ylidenes **18** and benzocoumarins **19** and **20**.



21	R1	R2	R3
a	H	phenyl	SMe
b	H	4-Br-phenyl	SMe
c	H	4-Me-phenyl	SMe
d	H	2-naphthyl	SMe
e	H	2-thienyl	SMe
f	H	4-OMe-phenyl	morpholine

22	R4	R5
a	H	1-naphthyl
b	H	4-Br-phenyl
c	H	4-Me-phenyl
d	H	2-naphthyl
e	H	2-thienyl
f	H	iso-propyl

Scheme 6 Synthesis of pyran-2-ylidenes **23** and α-pyrones **24**.

benzannulated coumarins through the ring transformation of easily accessible lactones with various methylene carbonyl compounds followed by unprecedented DDQ-mediated oxidative cleavage of oxaylidene intermediates under mild reaction conditions. Studies of the synthesis mechanism of a benzonaphthocoumarin revealed that the reaction was initiated through Michael addition as examined using UV-vis absorption experiments. This methodology can be used for the synthesis of a variety of oxygen heterocycles with flexibility of substituents variation on to the molecular scaffolds. Interestingly, this diversity-oriented synthetic protocol may be useful to generate a small library of compounds for drug discovery perspectives.

Experimental section

^{1}H and ^{13}C NMR spectra were taken on a NMR spectrophotometer at 400, 300 and 200 MHz. $CDCl_3$ and DMSO-d_6 were used as the solvents. Chemical shifts are reported in parts per million (δ-value) from Me_4Si (δ = 0 ppm for 1H) as an internal standard or based on the middle peak of the solvent (for $CDCl_3$, 7.26 ppm for ^{1}H and 77.1 (±0.1) ppm for ^{13}C NMR; for DMSO-d_6, 2.5 ppm for ^{1}H and 40.0 ppm for ^{13}C NMR). Signal patterns are indicate as s, singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet. Coupling constants (J) are given in hertz. Infrared (IR) spectra were recorded on an IR spectrophotometer using KBr discs and reported in wave number (cm^{-1}). MS (ESI) and HRMS (ESI) were recorded on a Mass Spectrophotometer with a Q-ToF mass analyzer.

General procedure for the synthesis of 5,6-dihydro-1*H*-benzo-[*f*]naphtho[2,1-*c*]chromen-4(2*H*)-ylidene)acetonitrile 1a–f[9]

A mixture of the 4-morpholino-2-oxo-5,6-dihydro-2*H*-benzo[*h*]-chromene-3-carbonitriles **9a–c** (1.0 mmol), the respective 2-tetralones **10** (1.2 mmol), and NaH (1.5 mmol) in THF was stirred for 1–2.5 h at ambient temperature. The reaction was monitored using TLC until completion. Excess THF was removed under reduced pressure and the reaction mixture was poured into ice-cool water with constant stirring followed by neutralization with 10% HCl. The precipitate thus obtained was filtered, washed with water, dried and purified with a neutral alumina column using 20% $CHCl_3$ in hexane as the eluent to afford **1a–f**.

(*Z*)-2-(11-Methoxy-5,6-dihydro-1*H*-benzo[*f*]naphtho[2,1-*c*]-chromen-4(2*H*)-ylidene)acetonitrile (1b)

A mixture of 4-morpholino-2-oxo-5,6-dihydro-2*H*-benzo[*h*]-chromene-3-carbonitrile (**9a**, 308 mg, 1.0 mmol, 1 equiv.), 8-methoxy-2-tetralone (**10**, 211 mg, 1.2 mmol, 1.2 equiv.) and NaH (60% dispersion in oil, 60 mg, 1.5 mmol, 1.5 equiv.) in dry THF (5 ml) was stirred at room temperature for 1.5 h. Using the general procedure described above, 208 mg (59%) of **1b** was obtained as a yellow solid: R_f = 0.44 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 146–148 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2927 (m), 2847 (w), 2190 (s), 1628 (s); ^{1}H NMR

(300 MHz, $CDCl_3$): δ = 2.42–3.11 (m, 11H), 4.43 (s, 1H), 6.54 (d, J = 8.2 Hz, 1H), 6.84–6.98 (m, 4H), 7.08–7.17 (m, 2H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 22.5, 27.2, 27.8, 29.0, 53.9, 63.7, 108.8, 110.2, 118.8, 120.1, 121.3, 123.1, 123.4, 125.9, 127.1, 127.6, 134.1, 135.6, 136.6, 137.6, 154.4, 159.2, 165.2 ppm; m/z (ESI): 354 [M + H$^+$]; HRMS (ESI) calcd for $C_{24}H_{19}NO_2$ [M$^+$ + 1] 354.1494, found 354.1491.

(*Z*)-2-(9-Methoxy-5,6-dihydro-1*H*-benzo[*f*]naphtho[2,1-*c*]-chromen-4(2*H*)-ylidene)acetonitrile (1e)

A mixture of 9-methoxy 4-morpholino-2-oxo-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitrile (**9e**, 338 mg, 1.0 mmol, 1 equiv.), 2-tetralone (**10**, 0.146 ml, 1.2 mmol, 1.2 equiv.) and NaH (60% dispersion in oil, 60 mg, 1.5 mmol, 1.5 equiv.) in dry THF (5 ml) was stirred at room temperature for 1 h. Using the general procedure described above, 155 mg (44%) of **1e** was obtained as a yellow solid: R_f = 0.47 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 162–164 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2932 (m), 2848 (w), 2199 (s), 1728 (w); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.08–2.27 (m, 1H), 2.40–2.53 (m, 1H), 2.72–2.86 (m, 5H), 3.01–3.18 (m, 1H), 3.44 (s, 3H), 4.49 (s, 1H), 6.54 (d, J = 1.7 Hz, 1H), 6.73–6.86 (m, 2H), 6.93–7.24 (m, 4H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 23.0, 26.8, 27.3, 28.3, 55.1, 64.6, 110.8, 113.9, 115.2, 118.6, 125.6, 126.2, 126.3, 127.3, 127.6, 128.3, 129.6, 131.4, 131.6, 134.1, 135.3, 157.3, 159.1, 164.8 ppm; m/z (ESI): 354 [M + H$^+$]; HRMS (ESI) calcd for $C_{24}H_{19}NO_2$ [M$^+$ + 1] 354.1494, found 354.1480.

General procedure for the synthesis of 4a–f

(*Z*)-2-(5,6-Dihydro-1*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4(2*H*)-ylidene)acetonitriles (**1a–f**) were treated with 4.0 mmol of DDQ in AcOH at room temp. for 1 h. After completion, the reaction mixture was filtered and the filtrate was collected and evaporated to dryness. Thereafter, the crude obtained was purified through neutral alumina using 60% $CHCl_3$ in hexane as eluent to afford **4a–f**.

5,6-Dihydro-4*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-one (4a)

The (*Z*)-2-(5,6-dihydro-1*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4(2*H*)-ylidene)acetonitrile (**1a**, 323 mg, 1.0 mmol, 1 equiv.) was treated with DDQ (908 mg, 4.0 mmol, 4 equiv.) in glacial acetic acid for 1 h. Using the general procedure described above, 172 mg (58%) of **4a** was obtained as a light yellow solid: R_f = 0.57 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 204–206 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2931 (w), 2744 (w), 1704 (s), 1609 (m); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.23–2.41 (m, 1H), 2.90–3.00 (m, 2H), 3.16–3.29 (m, 1H), 7.05–7.15 (m, 1H), 7.20–7.30 (m, 2H), 7.31–7.53 (m, 4H), 7.81–7.96 (m, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 22.8, 28.1, 112.4, 117.3, 125.4, 125.5, 125.8, 126.7, 127.2, 127.9, 128.6, 128.9, 129.0, 130.0, 131.1, 132.0, 132.4, 138.5, 145.9, 152.6, 161.5 ppm; m/z (ESI): 299 [M$^+$ + H]; HRMS (ESI) calcd for $C_{21}H_{14}O_2$ [M$^+$ + 1] 299.1072, found 299.1081.

The crystal data of **4a** (CCDC deposit no: 877580): $C_{21}H_{14}O_2$, M = 298.32, Orthorhombic, *Pbca*, a = 15.050(5) Å, b = 8.960(3) Å, c = 21.187(7) Å, V = 2857(2) Å^3, Z = 8, D_c = 1.387 g cm^{-3}, μ (Mo-Kα) = 0.09 mm^{-1}, F(000) = 1248, rectangular block, reddish, 17 307 reflections measured (R_{int} = 0.0861), 3513 unique, wR_2 = 0.2040 for all data, conventional R_1 = 0.0630 for 2408 $F_o > 4\sigma(F_o)$ and 0.1060 for all 3513 data, S = 1.083 for all data and 209 parameters.

11-Methoxy-5,6-dihydro-4*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-one (4b)

The (*Z*)-2-(11-methoxy-5,6-dihydro-1*H*-benzo[*f*]naphtho[2,1-*c*]-chromen-4(2*H*)-ylidene)acetonitrile (**1b**, 353 mg, 1.0 mmol, 1 equiv.) was treated with DDQ (908 mg, 4.0 mmol, 4 equiv.) in glacial acetic acid for 1 h. Using the general procedure described above, 157 mg (48%) of **4b** was obtained as a light yellow solid: R_f = 0.47 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 191–193 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3020 (m), 2932 (w), 1725 (s), 1610 (m); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.26–2.42 (m, 1H), 2.93–3.01 (m, 2H), 3.02 (s, 3H), 3.16–3.30 (m, 1H), 6.72 (d, J = 7.6 Hz, 1H), 6.84 (d, J = 7.6 Hz, 1H), 6.94–7.03 (m, 1H), 7.17–7.51 (m, 5H), 7.88 (d, J = 8.8 Hz, 1H) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$) δ = 22.4, 27.9, 53.6, 107.6, 117.5, 120.5, 121.3, 123.5, 124.0, 126.0, 126.2, 127.6, 128.7, 131.3, 132.4, 136.1, 152.5, 155.1, 161.7 ppm; m/z (ESI): 329 [M$^+$ + H]; HRMS (ESI) calcd for $C_{22}H_{16}O_3$ [M$^+$ + 1] 329.1178, found 329.1177.

14-Methoxy-5,6-dihydro-4*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-one (4c)

The (*Z*)-2-(14-methoxy-5,6-dihydro-1*H*-benzo[*f*]naphtho[2,1-*c*]-chromen-4(2*H*)-ylidene)acetonitrile (**3c**, 353 mg, 1.0 mmol, 1 equiv.) was treated with DDQ (908 mg, 4.0 mmol, 4 equiv.) in glacial acetic acid for 1 h. Using the general procedure described above, 170 mg (52%) of **4c** was obtained as a light yellow solid: R_f = 0.50 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 149–151 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2942 (m), 2841 (w), 1711 (s); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.23–2.42 (m, 1H), 2.91–3.02 (m, 2H), 3.17–3.30 (m, 1H), 4.03 (s, 3H), 6.79 (d, J = 7.7 Hz, 1H), 7.06–7.51 (m, 7H), 8.45 (d, J = 9.1 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 22.7, 28.0, 55.7, 103.6, 112.1, 116.2, 119.9, 123.0, 125.7, 125.9, 126.1, 126.6, 127.8, 129.0, 129.9, 130.2, 132.5, 138.4, 146.2, 152.9, 155.6, 161.6 ppm; m/z (ESI): 329 [M$^+$ + H]; HRMS (ESI) calcd for $C_{22}H_{16}O_3$ [M$^+$ + 1] 329.1178, found 329.1180.

12-Methoxy-5,6-dihydro-4*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-one (4d)

The (*Z*)-2-(12-methoxy-5,6-dihydro-1*H*-benzo[*f*]naphtho[2,1-*c*]-chromen-4(2*H*)-ylidene)acetonitrile (**1d**, 353 mg, 1.0 mmol, 1 equiv.) was treated with DDQ (908 mg, 4.0 mmol, 4 equiv.) in glacial acetic acid for 1 h. Using the general procedure described above, 181 mg (55%) of **4d** was obtained as a light yellow solid: R_f = 0.52 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 176–178 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3022 (m), 1629 (m); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.16–2.33 (m, 1H), 2.84–3.14 (m, 2H), 3.12 (s, 1H), 3.37 (s, 3H), 6.96–7.04 (m, 1H), 7.05–7.39 (m, 6H), 7.67 (d, J = 8.9 Hz, 1H), 7.78 (d, J = 8.8 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 22.6, 28.1, 54.7,

107.4, 111.5, 114.7, 117.6, 125.6, 126.3, 126.4, 128.0, 129.3, 129.9, 130.0, 130.3, 131.7, 132.1, 138.7, 145.9, 153.2, 157.1, 161.5 ppm; *m*/*z* (ESI): 329 [M^+ + H]; HRMS (ESI) calcd for $C_{22}H_{16}O_3$ [M^+ + 1] 329.1178, found 329.1176.

9-Methoxy-5,6-dihydro-4*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-one (4e)

The (*Z*)-2-(9-methoxy-5,6-dihydro-1*H*-benzo[*f*]naphtho[2,1-*c*]-chromen-4(2*H*)-ylidene)acetonitrile (**1e**, 353 mg, 1.0 mmol, 1 equiv.) was treated with DDQ (908 mg, 4.0 mmol, 4 equiv.) in glacial acetic acid for 1 h. Using the general procedure described above, 187 mg (57%) of **4e** was obtained as a light yellow solid: R_f = 0.45 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 163–165 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2930 (m), 2851 (w), 1708 (s); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.23–2.42 (m, 1H), 2.87–2.95 (m, 2H), 3.16–3.29 (m, 1H), 3.52 (s, 3H), 6.81 (d, *J* = 2.4 Hz, 1H), 6.92 (dd, *J* = 8.2, 2.6 Hz, 1H), 7.27–7.36 (m, 2H), 7.40–7.55 (m, 2H), 7.83–7.99 (m, 3H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 22.7, 27.1, 55.3, 112.2, 114.1, 114.2, 116.3, 117.3, 125.4, 125.4, 127.0, 127.4, 128.6, 128.7, 128.8, 130.6, 131.2, 132.0, 133.1, 139.2, 145.8, 152.5, 157.5, 161.4 ppm; *m*/*z* (ESI): 329 [M^+ + H]; HRMS (ESI) calcd for $C_{22}H_{16}O_3$ [M^+ + 1] 329.1178, found 329.1175.

8-Methoxy-5,6-dihydro-4*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-one (4f)

The (*Z*)-2-(9-methoxy-5,6-dihydro-1*H*-benzo[*f*]naphtho[2,1-*c*]-chromen-4(2*H*)-ylidene)acetonitrile (**1f**, 353 mg, 1.0 mmol, 1 equiv.) was treated with DDQ (908 mg, 4.0 mmol, 4 equiv.) in glacial acetic acid for 1 h. Using the general procedure described above, 154 mg (47%) of **4f** was obtained as a light yellow solid: R_f = 0.44 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 156–158 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2942 (m), 2842 (w), 1653 (m); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.25–2.44 (m, 1H), 2.86–3.07 (m, 2H), 3.17–3.28 (m, 1H), 3.87 (s, 3H), 6.61–6.69 (m, 1H), 6.91 (s, 1H), 7.17–7.32 (m, 2H), 7.39–7.53 (m, 2H), 7.82–7.99 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 22.5, 28.5, 55.4, 111.3, 112.4, 113.2, 117.3, 124.5, 125.2, 125.3, 125.4, 127.1, 128.5, 129.1, 130.6, 131.1, 131.9, 140.7, 145.9, 152.5, 160.9, 161.6 ppm; *m*/*z* (ESI): 329 [M^+ + H]; HRMS (ESI) calcd for $C_{22}H_{16}O_3$ [M^+ + 1] 329.1178, found 329.1207.

2-Chloro-2-(5,6-dihydro-4*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-ylidene)acetonitrile (5a)

The (*Z*)-2-(5,6-dihydro-1*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-(2*H*)-ylidene)acetonitrile (**1a**, 323 mg, 1.0 mmol, 1 equiv.) was treated with DDQ (908 mg, 4.0 mmol, 4 equiv.) in dioxane for 4 h at reflux temperature. After completion, reaction mixture was filtered and filtrate was collected and evaporated to dryness. Thereafter, the crude mixture was purified through neutral alumina using 10% $CHCl_3$ in hexane as the eluent to afford 43 mg (12%) of **5a** {along with 128 mg (43%) of **4a**}as a light yellow solid: R_f = 0.71 ($CHCl_3$–*n*-hexane, 7 : 3 v/v); mp 178–180 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2924 (s), 2855 (m), 2193 (s), 1540 (s); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.32–2.55 (m, 1H), 2.92–3.03 (m, 2H), 3.65–3.76 (m, 1H), 7.04–7.09 (m, 2H), 7.20–7.51 (m, 5H), 7.66 (d, *J* = 8.6 Hz, 1H), 7.80–7.94 (m, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 24.0, 27.8, 113.5, 116.4, 118.2, 125.3, 125.7, 126.0, 127.0, 127.4, 127.9, 128.4, 128.6, 129.5, 131.2, 131.8, 132.5, 137.1, 137.3, 151.8, 158.1 ppm; *m*/*z* (ESI): 356 [M^+ + H]; HRMS (ESI) calcd for $C_{23}H_{14}ClNO$ [M^+ + 1] 356.0842, found 356.0850.

General procedure for the synthesis of 8a–c[17]

A mixture of methyl 2-cyano-3,3-dimethylthioacrylate **7** (10.1 g, 0.05 mol), the respective 1-tetralone **6a–c** (7.3 ml, 0.05 mol) was stirred in the presence of powdered KOH (3.3 g, 0.06 mol) in DMSO (50 ml) for 5–6 h at ambient temperature. Completion of the reaction was monitored using TLC and on completion the reaction mixture was poured into ice-cool water with constant stirring and the resulting precipitate was filtered, washed with water, dried, and purified through a silica gel column using 2% MeOH in $CHCl_3$ as the eluent to afford **8a–c**.

Synthesis of 9-methoxy-4-(methylthio)-2-oxo-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitrile (8c)

A mixture of methyl 2-cyano-3,3-dimethylthioacrylate **7** (10.1 g, 0.05 mol) and 7-methoxy-1-tetralone **6c** (8.8 g, 0.05 mol) was stirred in the presence of powdered KOH (3.3 g, 0.06 mol) in DMSO (50 ml) for 6 h. Using the general procedure described above, 13 g (87%) of **8c** was obtained as a yellow solid: R_f = 0.56 (MeOH–$CHCl_3$, 1 : 25 v/v); mp 188–190 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3339 (m), 2212 (w), 1713 (m); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.74–2.83 (m, 2H), 2.84–2.93 (m, 2H), 2.99 (s, 3H), 3.84 (s, 3H), 6.92–7.02 (m, 1H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.34–7.41 (m, 1H) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 17.6, 22.0, 26.1, 55.7, 108.6, 119.3, 129.0, 130.6, 131.0, 138.4, 159.1 ppm; *m*/*z* (ESI): 300 [M^+ + H]; HRMS (ESI) calcd for $C_{16}H_{13}NO_3S$ [M^+ + 1] 300.0694, found 300.0695.

General procedure for the synthesis of 9a–c[17]

A mixture of **8** (2.7 g, 0.01 mol) and morpholine (1.3 ml, 0.012 mol) in methanol (25 ml) was refluxed for 5 h. The reaction mixture was cooled to room temperature, and the precipitate obtained was filtered, washed with methanol, dried, and crystallized from methanol to afford **9a–c**.

Synthesis of 9-methoxy-4-morpholino-2-oxo-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitrile (9c)

A mixture of **8c** (3.0 g, 0.01 mol) and morpholine (1.3 ml, 0.012 mol) in methanol (25 ml) was refluxed for 5 h. The reaction mixture was cooled to room temperature, and the precipitate obtained was filtered, washed with methanol, dried, and crystallized from methanol to afford 3.01 g (89%) of **9c** as a yellow solid: R_f = 0.49 (MeOH–$CHCl_3$, 1 : 25 v/v); mp 174–176 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3021 (w), 2215 (w), 1635 (m); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.56–2.72 (m, 2H), 2.75–2.91 (m, 2H), 3.52–3.69 (m, 4H), 3.82 (s, 3H), 3.85–3.98 (m, 4H), 6.87–7.01 (m, 1H), 7.13 (d, *J* = 8.3 Hz, 1H), 7.28–7.39 (m, 1H) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 23.8, 26.9, 51.7, 55.7, 67.1, 81.5, 108.7, 116.5, 118.7, 128.5, 129.9,

157.7, 159.1, 166.6 ppm; *m*/*z* (ESI): 339 [M^+ + H]; HRMS (ESI) calcd for $C_{19}H_{18}N_2O_4$ [M^+ + 1] 339.1345, found 339.1336.

General procedure for the synthesis of 11a,b

5,6-Dihydro-4*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-ones (**4a,b**) were treated with 15 mmol of DDQ in benzene and refluxed for 24 h. After completion, reaction mixture was filtered and filtrate was collected and evaporated to dryness. Thereafter, the crude obtained was purified through neutral alumina using 40% $CHCl_3$ in hexane as the eluent.

4*H*-Benzo[*f*]naphtho[2,1-*c*]chromen-4-one (11a)

The 5,6-dihydro-4*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-one (**4a**, 298 mg, 1.0 mmol, 1 equiv.) was treated with DDQ (3405 mg, 15.0 mmol, 15 equiv.) in refluxing benzene for 24 h. Using the general procedure described above, 177 mg (60%) of **11a** was obtained as an off-white solid: R_f = 0.71 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 237–239 °C {lit.[18] 236–238 °C} ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2924 (m), 2855 (w), 1730 (s); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.32–7.55 (m, 3H), 7.57–7.73 (m, 2H), 7.88–8.16 (m, 6H), 8.37 (d, *J* = 8.5 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 112.9, 117.2, 121.6, 124.2, 125.4, 125.5, 125.8, 127.2, 128.3, 128.4, 129.1, 129.4, 129.8, 131.2, 131.7, 134.9, 136.7, 150.5, 161.8 ppm; *m*/*z* (ESI): 297 [M^+ + H]; HRMS (ESI) calcd for $C_{21}H_{12}O_2$ [M^+ + 1] 297.0916, found 297.0900.

11-Methoxy-4*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-one (11b)

The 11-methoxy-5,6-dihydro-4*H*-benzo[*f*]naphtho[2,1-*c*]-chromen-4-one (**4b**, 328 mg, 1.0 mmol, 1 equiv.) was treated with DDQ (3405 mg, 15.0 mmol, 15 equiv.) in refluxing benzene for 24 h. Using the general procedure described above, 185 mg (57%) of **11b** was obtained as an off-white solid: R_f = 0.60 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 214–216 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2946 (m), 2835 (m), 1654 (m); ^{1}H NMR (200 MHz, $CDCl_3$) δ = 2.98 (s, 3H), 6.81 (d, *J* = 7.4 Hz, 1H), 7.28–7.38 (m, 1H), 7.52–7.64 (m, 4H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.91–8.02 (m, 3H), 8.30 (d, *J* = 8.6 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 53.9, 106.6, 110.7, 117.5, 120.7, 123.3, 125.3, 126.0, 126.3, 128.0, 128.2, 128.7, 131.3, 134.7, 155.6 ppm; *m*/*z* (ESI): 327 [M^+ + H]; HRMS (ESI) calcd for $C_{22}H_{14}O_3$ [M^+ + 1] 327.1021, found 327.1016.

3-Amino-6,7-dichloro-5-hydroxybenzofuran-2,4-dicarbonitrile (12)

The (*Z*)-2-(5,6-dihydro-4*H*-benzo[*f*]naphtho[2,1-*c*]chromen-4-ylidene)acetonitrile (**2a**, 321 mg, 1.0 mmol, 1 equiv.) was treated with DDQ (554 mg, 2.0 mmol, 2 equiv.) in glacial acetic acid for 4 h. After completion, the reaction mixture was filtered and filtrate was collected and evaporated to dryness. Thereafter, the crude obtained was purified with a neutral alumina column using 10% MeOH in chloroform as the eluent to afford 88 mg (33%) **12** (along with **4a**) as an off-white solid: R_f = 0.31 (MeOH–$CHCl_3$, 1 : 4, v/v); mp > 250 °C (CH_3CN); IR (KBr) ν_{max}/cm^{-1} = 3489 (w), 3374 (m), 3151 (m), 2222 (s); ^{1}H NMR (300 MHz, DMSO-d_6) δ = 6.12 (brs, 2H) ppm; ^{13}C NMR (100.6 MHz, DMSO-d_6) δ = 90.8, 111.7, 112.9, 114.3, 119.7, 122.3, 124.5, 141.0, 144.6, 155.2 ppm; *m*/*z* (ESI): 267 [M^+ + H]; HRMS (ESI) calcd for $C_{10}H_3Cl_2N_3O_2$ [M^+ + 1] 267.9681, found 267.9641.

The crystal data for **12** (CCDC deposit no: 877581): $C_{12}H_6Cl_2N_4O_2$, *M* = 309.11, monoclinic, *C*2/*c*, *a* = 20.542(2) Å, *b* = 7.512(1) Å, *c* = 18.182(2) Å, β = 109.593(1)°, *V* = 2643.2(5) Å^3, *Z* = 8, D_c = 1.554 g cm^{-3}, μ (Mo-Kα) = 0.50 mm^{-1}, *F*(000) = 1248, rectangular block, yellow, 8334 reflections measured (R_{int} = 0.0537), 4295 unique, wR_2 = 0.1660 for all data, conventional R_1 = 0.0594 for 2448 $F_o > 4\sigma(F_o)$ and 0.1133 for all 4295 data, *S* = 0.993 for all data and 183 parameters.

General procedure for the synthesis of 15a–f

A mixture of the methyl 4-(methylthio)-2-oxo-6-aryl-2*H*-pyran-3-carboxylates **14** (1.0 mmol), the respective resorcinol **13** (2.0 mmol) and NaH (60% dispersion in oil, 200 mg, 5.0 mmol, 5 equiv.) in dry DMF (5 ml) was stirred at a temperature of 60 °C for 3–4 h. Completion of the reaction was monitored using TLC and on completion the reaction mixture was poured into crushed ice with vigorous stirring and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified on a silica gel column using 10% ethyl acetate in *n*-hexane as the eluent to afford **15a–f** as a mixture of *cis*- and *trans*-isomers.

(*Z*/*E*)-Methyl 2-(7-hydroxy-4-phenyl-2*H*-chromen-2-ylidene)-acetate (15a)

A mixture of methyl 4-(methylthio)-2-oxo-6-phenyl-2*H*-pyran-3-carboxylate (**14a**, 276 mg, 1.0 mmol, 1 equiv.), resorcinol (**13a**, 220 mg, 2.0 mmol, 2 equiv.) and NaH (60% dispersion in oil, 200 mg, 5.0 mmol, 5 equiv.) in dry DMF (5 ml) was stirred at a temperature of 60 °C for 3 h. Using the general procedure described above, 200 mg (68%) of **15a** was obtained as a mixture of *cis*- and *trans*-isomers, as a yellow solid: R_f = 0.47 (ethyl acetate–*n*-hexane, 1 : 9, v/v); mp 210–212 °C (ethyl acetate–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3584 (s), 1636 (w); ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 4.43 (s, 3H, *cis*), 4.47 (s, 3H, *trans*), 5.72 (s, 1H, *trans*), 6.09 (s, 1H, *cis*), 6.83 (s, 1H, *trans*), 7.31–7.38 (m, 2H, *cis* + *trans*), 7.42 (d, *J* = 2.2 Hz, 1H, *cis*), 7.61 (d, *J* = 2.2 Hz, 1H, *trans*), 7.82–7.92 (m, 2H, *cis* + *trans*), 8.10–8.21 (m, 12H, *cis* + *trans*), 10.37 (s, 1H, *trans*), 10.38 (s, 1H, *cis*) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 50.0, 89.8, 102.0, 111.2, 111.7, 112.6, 126.7, 127.8, 128.4, 128.6, 135.7, 143.8, 153.3, 160.3, 162.1, 166.5; *m*/*z* (ESI): 295 [M + H^+]; HRMS (ESI) calcd for $C_{18}H_{14}O_4$ [M^+ + 1] 295.0970; found 295.0965.

(*Z*/*E*)-Methyl 2-(7-hydroxy-4-(naphthalen-2-yl)-2*H*-chromen-2-ylidene)acetate (15b)

A mixture of methyl 4-(methylthio)-6-(naphthalen-2-yl)-2-oxo-2*H*-pyran-3-carboxylate (**14b**, 326 mg, 1.0 mmol, 1 equiv.), resorcinol (**13a**, 220 mg, 2.0 mmol, 2 equiv.) and NaH (60% dispersion in oil, 200 mg, 5.0 mmol, 5 equiv.) in dry DMF (5 ml) was stirred at a temperature of 60 °C for 4 h. Using the general procedure described above, 227 mg (66%) of **15b** was obtained as a mixture of *cis*- and *trans*-isomers, as a yellow

solid: R_f = 0.56 (ethyl acetate–*n*-hexane, 1 : 9, v/v); mp 224–226 °C (ethyl acetate–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3201 (w), 2857 (m), 1647 (m), 1562 (w); ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6): δ = 4.09 (s, 3H, *cis*), 4.13 (s, 3H, *trans*), 5.42 (s, 1H, *trans*), 5.77 (s, 1H, *cis*), 6.62 (s, 1H, *trans*), 6.98–7.05 (m, 2H, *cis* + *trans*), 7.10 (d, J = 1.74 Hz, 1H, *trans*), 7.27 (s, 1H, *trans*), 7.54–7.63 (m, 2H, *cis* + *trans*), 7.91–7.99 (m, 8H, *cis* + *trans*), 8.31–8.38 (m, 8H, *cis* + *trans*), 10.22 (s, 1H, *trans*), 10.22 (s, 1H, *cis*) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 50.9, 90.9, 102.9, 112.3, 112.7, 113.9, 126.4, 127.2, 127.4, 127.8, 127.9, 128.0, 128.7, 128.8, 133.3, 133.4, 134.2, 144.7, 154.3, 161.3, 163.0, 167.5; *m*/*z* (ESI): 345 [M + H^+]; HRMS(ESI) calcd for $C_{22}H_{16}O_4$ [M^+ + 1] 345.1126, found 345.1188.

(*Z*/*E*)-Methyl 2-(4-(4-bromophenyl)-7-hydroxy-2*H*-chromen-2-ylidene)acetate (15c)

A mixture of methyl 6-(4-bromophenyl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carboxylate (**14c**, 354 mg, 1.0 mmol, 1 equiv.), resorcinol (**13a**, 220 mg, 2.0 mmol, 2 equiv.) and NaH (60% dispersion in oil, 200 mg, 5.0 mmol, 5 equiv.) in dry DMF (5 ml) was stirred at a temperature of 60 °C for 4 h. Using the general procedure described above, 257 mg (69%) of **15c** was obtained as a mixture of *cis*- and *trans*-isomers, as a yellow solid: R_f = 0.56 (ethyl acetate–*n*-hexane, 1 : 9, v/v); mp 284–252 °C (ethyl acetate–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3201 (w), 2857 (m), 1647 (m), 1562 (w); ^{1}H NMR (300 MHz, DMSO-d_6+$CDCl_3$): δ = 3.59 (s, 1H, *cis*), 3.60 (s, 1H, *trans*), 5.15 (s, 1H, *trans*), 5.32 (s, 1H, *cis*), 6.41 (s, 1H, *trans*), 6.60–6.65 (m, 2H, *cis* + *trans*), 7.05–7.10 (m, 1H, *cis* + *trans*), 7.37–7.46 (m, 2H, *cis* + *trans*), 7.51 (s, 1H, *cis*), 7.70–7.75 (m, 2H, *cis* + *trans*), 10.44 (s, 1H, OH, D_2O exchange); ^{13}C NMR (75 MHz, DMSO-d_6): δ = 50.9, 79.6, 91.2, 102.9, 111.8, 112.7, 113.7, 123.0, 127.5, 130.1, 132.3, 135.9, 143.5, 154.2, 161.4, 162.8, 167.4; HRMS (ESI) calcd for $C_{18}H_{13}BrO_4$ [M^+ + 1] 373.0075, found 373.0066.

(*Z*/*E*)-Methyl 2-(6-chloro-7-hydroxy-4-phenyl-2*H*-chromen-2-ylidene)acetate (15d)

A mixture of methyl 4-(methylthio)-2-oxo-6-phenyl-2*H*-pyran-3-carboxylate (**14a**, 276 mg, 1.0 mmol, 1 equiv.), 4-chloro-resorcinol (**13b**, 286 mg, 2.0 mmol, 2 equiv.) and NaH (60% dispersion in oil, 200 mg, 5.0 mmol, 5 equiv.) in dry DMF (15 ml) was stirred at a temperature of 60 °C for 3 h. Using the general procedure described above, 230 mg (70%) of **15d** was obtained as a mixture of *cis*- and *trans*-isomers, as a yellow solid: R_f = 0.58 (ethyl acetate–*n*-hexane, 1 : 9, v/v); mp 234–236 °C (ethyl acetate–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3600 (s), 1650 (m); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.59 (s, 3H, *cis*), 3.60 (s, 3H, *trans*), 5.20 (s, 1H, *trans*), 5.36 (s, 1H, *cis*), 6.49 (s, 1H, *trans*), 6.84 (s, 2H, *cis* + *trans*), 7.09 (s, 1H, *trans*), 7.11 (s, 1H, *cis*), 7.42–7.57 (m, 12H, *cis* + *trans*), 11.30 (brs, 2H, *cis* + *trans*) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 51.1, 91.9, 104.1, 113.2, 114.6, 116.4, 126.7, 128.7, 129.4, 129.6, 129.8, 129.5, 136.0, 143.4, 152.5, 156.4, 162.4, 167.3; HRMS (ESI) calcd for $C_{18}H_{13}ClO_4$ [M^+ + 1] 329.0581, found 329.0574.

(*Z*/*E*)-Methyl 2-(4-(4-chlorophenyl)-7-hydroxy-8-methyl-2*H*-chromen-2-ylidene)acetate (15e)

A mixture of methyl 6-(4-chlorophenyl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carboxylate (**14d**, 310 mg, 1.0 mmol, 1 equiv.), 2-methyl-resorcinol (**13c**, 248 mg, 2.0 mmol, 2 equiv.) and NaH (60% dispersion in oil, 200 mg, 5.0 mmol, 5 equiv.) in dry DMF (5 ml) was stirred at a temperature of 60 °C for 3 h. Using the general procedure described above, 205 mg (60%) of **15e** was obtained as a mixture of *cis*- and *trans*-isomers, as a yellow solid: R_f = 0.56 (ethyl acetate–*n*-hexane, 1 : 9, v/v); mp 226–228 °C (ethyl acetate–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3458 (w), 1728 (s), 1670 (s), 1586 (s); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 2.14 (s, 3H, *cis*), 2.26 (s, 3H, *trans*), 3.59 (s, 3H, *cis*), 3.62 (s, 3H, *trans*), 5.14 (s, 1H, *trans*), 5.37 (s, 1H, *cis*), 6.40 (s, 1H, *trans*), 6.69 (d, J = 8.2 Hz, 2H, *cis* + *trans*), 6.92 (d, J = 8.4 Hz, 2H, *cis* + *trans*), 7.45–7.63 (m, 10H, *cis* + *trans*), 10.25 (s, 1H, *trans*), 10.35 (s, 1H, *cis*) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 7.9, 50.4, 90.4, 111.0, 111.4, 112.8, 123.8, 128.8, 130.2, 133.8, 135.2, 143.5, 151.5, 158.7, 162.5, 167.0; HRMS (ESI) calcd for $C_{19}H_{15}ClO_4$ [M^+ + 1] 343.0737, found 343.0729.

(*Z*/*E*)-Methyl 2-(7-hydroxy-4-(thiophen-2-yl)-2*H*-chromen-2-ylidene)acetate (15f)

A mixture of methyl 4-(methylthio)-2-oxo-6-(thiophen-2-yl)-2*H*-pyran-3-carboxylate (**14e**, 282 mg, 1.0 mmol, 1 equiv.), resorcinol (**13a**, 220 mg, 2.0 mmol, 2 equiv.) and NaH (60% dispersion in oil, 200 mg, 5.0 mmol, 5 equiv.) in dry DMF (15 ml) was stirred at a temperature of 60 °C for 4 h. Using the general procedure described above, 186 mg (62%) of **15f** was obtained as a mixture of *cis*- and *trans*-isomers, as a yellow solid: R_f = 0.58 (ethyl acetate–*n*-hexane, 1 : 9, v/v); mp 234–236 °C (ethyl acetate–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3600 (s), 1650 (m); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.62 (s, 3H, *cis* + *trans*), 5.20 (s, 1H, *trans*), 5.31 (s, 1H, *cis*), 6.57 (s, 1H, *trans*), 6.63–6.75 (m, 2H, *cis* + *trans*), 7.24–7.31 (m, 1H, *cis* + *trans*), 7.44–7.62 (m, 2H, *cis* + *trans*), 7.70–7.83 (m, 2H, *cis* + *trans*), 10.50 (s, 1H, OH, D_2O exchange); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ = 51.0, 91.2, 103.1, 111.3, 112.8, 113.7, 127.5, 128.6, 128.8, 128.8, 129.4, 137.1, 137.5, 154.3, 161.5, 162.5, 167.4; HRMS (ESI) calcd for $C_{16}H_{12}O_4S$ [M^+ + 1] 301.0535, found 301.0528.

General procedure for the synthesis of 16a–f

(*Z*/*E*)-Methyl 2-(7-hydroxy-2*H*-chromen-2-ylidene)-acetates (**15a–f**) were treated with 2.0 mmol of DDQ in dioxane at 80 °C for 1–2 h. After completion, the reaction mixture was filtered and the filtrate was collected and evaporated to dryness. Thereafter, the crude obtained was purified through neutral alumina using 10% acetone–*n*-hexane as the eluent to afford **16a–f**.

7-Hydroxy-4-phenyl-2*H*-chromen-2-one (16a)

The methyl 2-(7-hydroxy-4-phenyl-2*H*-chromen-2-ylidene)-acetate (**15a**, 147 mg, 0.5 mmol, 1 equiv.) was treated with DDQ (227 mg, 1.0 mmol, 2 equiv.) in dioxane (5 ml) at 80 °C for 2 h. Using the general procedure described above, 66 mg

(54%) of **16a** was obtained as a yellow solid: R_f = 0.56 (acetone–*n*-hexane, 1 : 10, v/v); mp 234–236 °C {lit.[15] 210–211 °C} (acetone–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3102 (m), 1695 (s), 1595 (s); ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6) δ = 6.03 (s, 1H), 6.65–6.79 (m, 2H), 7.24 (d, J = 13.0 Hz, 1H), 7.36–7.52 (m, 5H), 10.27 (s, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$ + DMSO-d_6) δ = 102.6, 110.0, 110.7, 112.9, 127.7, 127.9, 128.4, 129.1, 135.1, 155.5, 155.6, 160.5, 161.3; HRMS (ESI) calcd for $C_{15}H_{10}O_3$ [M^+ + 1] 239.0708, found: 239.0706.

7-Hydroxy-4-(naphthalen-2-yl)-2*H*-chromen-2-one (16b)

The methyl 2-(7-hydroxy-4-(naphthalen-2-yl)-2*H*-chromen-2-ylidene)acetate (**15b**, 172 mg, 0.5 mmol, 1 equiv.) was treated with DDQ (227 mg, 1.0 mmol, 2 equiv.) in dioxane (5 ml) at 80 °C for 2 h. Using the general procedure described above, 80 mg (55%) of **16b** was obtained as a yellow solid: R_f = 0.48 (acetone–*n*-hexane, 1 : 10, v/v); mp 214–216 °C (acetone–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3402 (m), 1629 (s); ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6) δ = 6.20 (s, 1H), 6.75 (dd, J = 8.6, 2.2 Hz, 1H), 6.86 (d, J = 2.2 Hz, 1H), 7.34 (d, J = 8.7 Hz, 1H), 7.51–7.62 (m, 3H), 7.94–8.03 (m, 4H), 10.18 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ = 102.7, 110.3, 110.9, 112.9, 125.2, 126.4, 126.7, 127.3, 127.4, 127.7, 127.8, 128.0, 132.4, 132.7, 132.9, 155.5, 155.6, 160.7, 161.2; HRMS (ESI) calcd for $C_{19}H_{12}O_3$ [M^+ + 1] 289.0865, found: 289.0859.

4-(4-Bromophenyl)-7-hydroxy-2*H*-chromen-2-one (16c)

The methyl 2-(4-(4-bromophenyl)-7-hydroxy-2*H*-chromen-2-ylidene)acetate (**15c**, 185 mg, 0.5 mmol, 1 equiv.) was treated with DDQ (227 mg, 1.0 mmol, 2 equiv.) in refluxing dioxane (5 ml) at 90 °C for 1 h. Using the general procedure described above, 84 mg (53%) of **16c** was obtained as a yellow solid: R_f = 0.46 (acetone–*n*-hexane, 1 : 10, v/v); mp 246–248 °C (acetone–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3231 (m), 1705 (s), 1621 (s); ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6) δ = 6.18 (s, 1H), 6.74–6.82 (m, 2H), 7.25 (d, J = 8.6 Hz, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 8.3 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$ + DMSO-d_6) δ = 103.2, 110.9, 111.0, 113.8, 123.6, 128.5, 131.0, 132.3, 134.8, 154.7, 156.0, 160.5, 162.0; HRMS (ESI) calcd for $C_{15}H_9BrO_3$ [M^+ + 1] 316.9813, found: 316.9802.

6-Chloro-7-hydroxy-4-phenyl-2*H*-chromen-2-one (16d)

The methyl 2-(6-chloro-7-hydroxy-4-phenyl-2*H*-chromen-2-ylidene)acetate (**15d**, 164 mg, 0.5 mmol, 1 equiv.) was treated with DDQ (227 mg, 1.0 mmol, 2 equiv.) in dioxane (5 ml) at 80 °C for 1 h. Using the general procedure described above, 71 mg (52%) of **16d** was obtained as a yellow solid: R_f = 0.48 (acetone–*n*-hexane, 1 : 10, v/v); mp 226–228 °C {Llit.[19] 281 °C (ethyl acetate–heptane)} (acetone–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3201 (w), 1691 (s); ^1H NMR (300 MHz, DMSO-d_6) δ = 6.24 (s, 1H), 7.00 (s, 1H), 7.28 (s, 1H), 7.48–7.60 (m, 5H), 11.52 (brs, 1H, OH, D_2O exchange); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 104.4, 111.9, 112.0, 117.5, 127.4, 128.8, 129.4, 130.3, 135.0, 154.2, 154.8, 157.0, 160.1; HRMS (ESI) calcd for $C_{15}H_9ClO_3$ [M^+ + 1] 273.0318; found: 273.0311.

4-(4-Chlorophenyl)-7-hydroxy-8-methyl-2*H*-chromen-2-one (16e)

The methyl 2-(4-(4-chlorophenyl)-7-hydroxy-8-methyl-2*H*-chromen-2-ylidene)acetate (**15e**, 171 mg, 0.5 mmol, 1 equiv.) was treated with DDQ (227 mg, 1.0 mmol, 2 equiv.) in dioxane (5 ml) at 80 °C for 1 h. Using the general procedure described above, 60 mg (42%) of **16e** was obtained as a yellow solid: R_f = 0.48 (acetone–*n*-hexane, 1 : 10, v/v); mp 248–250 °C (acetone–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3398 (w), 1682 (s); ^1H NMR (300 MHz, DMSO-d_6) δ = 2.20 (s, 3H), 6.16 (s, 1H), 6.84 (d, J = 8.6 Hz, 1H), 7.09 (d, J = 8.4 Hz, 1H), 7.48–7.64 (m, 4H), 10.58 (s, 1H); ^{13}C NMR (75.5 MHz, DMSO-d_6) δ = 8.0, 110.0, 110.5, 111.4, 112.0, 124.7, 128.8, 130.3, 134.0, 134.3, 153.3, 154.8, 159.2, 160.4; HRMS (ESI) calcd for $C_{16}H_{11}ClO_3$ [M^+ + 1] 287.0475; found: 287.0477.

7-Hydroxy-4-(thiophen-2-yl)-2*H*-chromen-2-one (16f)

The methyl 2-(7-hydroxy-4-(thiophen-2-yl)-2*H*-chromen-2-ylidene)acetate (**15f**, 150 mg, 0.5 mmol, 1 equiv.) was treated with DDQ (227 mg, 1.0 mmol, 2 equiv.) in refluxing dioxane (5 ml) at 90 °C for 2 h. Using the general procedure described above, 110 mg (45%) of **16f** was obtained as a yellow solid: R_f = 0.63 (acetone–*n*-hexane, 1 : 10, v/v); mp 236–238 °C (acetone–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3413 (s), 1730 (w); ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6) δ = 6.27 (s, 1H), 6.87 (d, J = 7.2 Hz, 2H), 7.28–7.35 (m, 1H), 7.53 (d, J = 2.3 Hz, 1H), 7.69–7.74 (m, 1H), 7.81 (d, J = 9.3 Hz, 1H), 7.98 (s, 1H), 10.40 (s, 1H, OH, D_2O exchange); ^{13}C NMR ($CDCl_3$ + DMSO-d_6) δ = 103.2, 110.3, 113.4, 127.8, 128.2, 128.7, 129.4, 136.2, 148.2, 155.9, 160.5, 161.9; HRMS (ESI) calcd for $C_{13}H_8O_3S$ [M^+ + 1] 245.0272; found: 245.0266.

Methyl 3-amino-6,7-dichloro-4-cyano-5-hydroxybenzofuran-2-carboxylate (17)

The methyl 2-(7-hydroxy-4-phenyl-2*H*-chromen-2-ylidene) acetate (**15a**, 147 mg, 0.5 mmol, 1 equiv.) was treated with DDQ (227 mg, 1.0 mmol, 2 equiv.) in dioxane (5 ml) at 80 °C for 2 h. Using the general procedure described above, 47 mg (31%) of **17** was obtained as an off-white solid: R_f = 0.52 (MeOH–$CHCl_3$, 1 : 4, v/v); mp > 250 °C ($CHCl_3$–MeOH); IR (KBr) ν_{max}/cm^{-1} = 3374 (m), 3206 (w), 2229 (m), 1684 (s); ^1H NMR (300 MHz, DMSO-d_6) δ = 3.87 (s, 3H), 5.65 (s, 1H) ppm; ^{13}C NMR (50.3 MHz, DMSO-d_6) δ = 51.5, 90.7, 101.9, 113.8, 119.6, 128.9, 137.3, 150.8, 154.0 ppm; *m*/*z* (ESI): 301 [M^+ + H]; HRMS (ESI) calcd for $C_{11}H_6Cl_2N_2O_4$ [M^+ + 1] 300.9783, found 300.9760.

General procedure for the synthesis of 18a–c

A mixture of the methyl 4-(methylthio)-2-oxo-6-aryl-2*H*-pyran-3-carboxylates **14** (1 mmol), the respective 1-tetralone (1.2 mmol) and KOH (2.0 mmol) in dry DMF (10 ml) was stirred at 90 °C for 12–24 h. Completion of the reaction was monitored using TLC and on completion the reaction mixture was poured into crushed ice with vigorous stirring and finally neutralized with 10% HCl. The precipitate obtained was

filtered and purified on a silica gel column using 20% $CHCl_3$ in *n*-hexane as the eluent to afford **18a–c** as a mixture of *cis*- and *trans*-isomers.

(*Z*/*E*)-Methyl 2-(4-(4-bromophenyl)-8-methoxy-5,6-dihydro-2*H*-benzo[*h*]chromen-2-ylidene)acetate (18a)

A mixture of methyl 6-(4-bromophenyl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carboxylate (**14c**, 353 mg, 1.0 mmol, 1 equiv.), 6-methoxy 1-tetralone (**6c**, 211 mg, 1.2 mmol, 1.2 equiv.) and KOH (112 mg, 2.0 mmol, 2 equiv.) in dry DMF (10 ml) was stirred at 90 °C for 12 h. Using the general procedure described above, 153 mg (35%) of **18a** was obtained as a mixture of *cis*- and *trans*-isomers, as a red oil: R_f = 0.54 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); IR (KBr) ν_{max}/cm^{-1} = 2952 (m), 2861 (w), 2337 (m), 1605 (m); ^1H NMR (300 MHz, $CDCl_3$): δ = 2.42–2.51 (m, 4H, *cis* + *trans*), 2.71–2.80 (m, 4H, *cis* + *trans*), 3.68 (s, 3H, *cis*), 3.74 (s, 3H, *trans*), 3.84 (s, 6H, *cis* + *trans*), 4.93 (s, 3H, *trans*), 5.31 (s, 1H, *cis*), 6.71 (s, 2H, *cis* + *trans*), 6.78–6.92 (m, 1H, *cis* + *trans*), 7.12–7.24 (m, 2H, *cis* + *trans*), 7.51–7.68 (m, 4H, *cis* + *trans*) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 26.6, 28.1, 51.8, 55.3, 87.3, 112.1, 112.1, 113.5, 116.2, 124.3, 127.2, 129.5, 129.7, 130.2, 130.6, 131.4, 131.6, 140.0, 144.8, 146.4, 157.6, 159.3, 168.4 ppm; *m*/*z* (ESI): 439 [M + H^+]; HRMS (ESI) calcd for $C_{23}H_{19}BrO_4$ [M^+ + 1] 439.0545, found 439.0507.

(*Z*/*E*)-Methyl 2-(4-(furan-2-yl)-5,6-dihydro-2*H*-benzo[*h*]chromen-2-ylidene)acetate (18b)

A mixture of methyl 6-(furan-2-yl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carboxylate (**14f**, 266 mg, 1.0 mmol, 1 equiv.), 1-tetralone (**6a**, 0.146 ml, 1.2 mmol, 1.2 equiv.) and KOH (112 mg, 2.0 mmol, 2 equiv.) in dry DMF (10 ml) was stirred at 90 °C for 15 h. Using the general procedure described above, 102 mg (32%) of **18b** was obtained as a mixture of *cis*- and *trans*-isomers, as a red oil: R_f = 0.52 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); IR (KBr) ν_{max}/cm^{-1} = 2932 (m), 2854 (w), 1734 (m), 1632 (w); ^1H NMR (300 MHz, $CDCl_3$): δ = 2.89 (s, 8H, *cis* + *trans*), 3.72 (s, 3H, *trans*), 3.75 (s, 3H, *cis*), 5.01 (s, 1H, *trans*), 5.32 (s, 1H, *cis*), 6.48–6.61 (m, 2H, *cis* + *trans*), 6.68 (d, *J* = 3.4 Hz, 1H, *trans*), 6.74 (d, *J* = 3.4 Hz, 1H, *cis*), 7.14–7.38 (m, 6H, *cis* + *trans*), 7.54 (d, *J* = 1.3 Hz, 2H, *cis* + *trans*), 7.64–7.71 (m, 1H, *cis*), 8.13 (d, *J* = 5.1 Hz, 2H, *cis* + *trans*) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 23.0, 27.4, 50.5, 87.8, 109.9, 111.9, 112.4, 113.8, 122.4, 126.9, 127.3, 128.5, 129.5, 134.4, 136.7, 143.8, 150.1, 151.1, 164.4, 168.4 ppm; *m*/*z* (ESI): 321 [M + H^+]; HRMS (ESI) calcd for $C_{20}H_{16}O_4$ [M^+ + 1] 321.1127, found 321.1119.

(*Z*/*E*)-Methyl 2-(4-phenyl-5,6-dihydro-2*H*-benzo[*h*]chromen-2-ylidene)acetate (18c)

A mixture of methyl 4-(methylthio)-2-oxo-6-phenyl-2*H*-pyran-3-carboxylate (**14a**, 276 mg, 1.0 mmol, 1 equiv.), 1-tetralone (**6a**, 0.146 ml, 1.2 mmol, 1.2 equiv.) and KOH (112 mg, 2.0 mmol, 2 equiv.) in dry DMF (10 ml) was stirred at 90 °C for 24 h. Using the general procedure described above, 113 mg (34%) of **18c** was obtained as a mixture of *cis*- and *trans*-isomers, as a red oil: R_f = 0.57 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); IR (KBr) ν_{max}/cm^{-1} = 2926 (s), 2857 (m), 1647 (m), 1562 (w); ^1H NMR (300 MHz, $CDCl_3$): δ = 2.47–2.58 (m, 4H, *cis* + *trans*), 2.75–2.84 (m, 2H, *cis* + *trans*), 3.68 (s, 3H, *cis*), 3.76 (s, 3H, *trans*), 4.96 (s, 1H, *trans*), 5.34 (s, 1H, *cis*), 7.14–7.44 (m, 8H, *cis* + *trans*), 7.70–7.78 (m, 1H, *cis* + *trans*) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 23.1, 27.6, 50.5, 87.5, 112.0, 117.0, 122.5, 126.9, 127.5, 127.8, 128.0, 128.4, 128.5, 128.6, 129.6, 137.1, 137.2, 147.2, 151.0, 165.3, 168.9 ppm; *m*/*z* (ESI): 331 [M + H^+]; HRMS (ESI) calcd for $C_{22}H_{18}O_3$ [M^+ + 1] 331.1334, found 331.1372.

General procedure for the synthesis of 19a–c

(*Z*/*E*)-Methyl 2-(4-aryl-5,6-dihydro-2*H*-benzo[*h*]chromen-2-ylidene)acetates (**18a–c**) were treated with 2.0 mmol of DDQ in AcOH at room temp for 1–2 h. After completion, the reaction mixture was filtered and the filtrate was collected and evaporated to dryness. Thereafter, the crude obtained was purified through a silica gel column using 40% $CHCl_3$ in hexane as the eluent to afford **19a–c**.

4-(4-Bromophenyl)-8-methoxy-5,6-dihydro-2*H*-benzo[*h*]-chromen-2-one (19a)

The (*Z*/*E*)-methyl 2-(4-(4-bromophenyl)-8-methoxy-5,6-dihydro-2*H*-benzo[*h*]chromen-2-ylidene)-acetate (**18a**, 219 mg, 0.5 mmol, 1 equiv.) was treated with DDQ (227 mg, 1.0 mmol, 2 equiv.) in glacial acetic acid (5 ml) for 2 h. Using the general procedure described above, 99 mg (52%) of **19a** was obtained as a yellow solid: R_f = 0.70 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 176–178 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2925 (w), 2856 (w), 1712 (m); ^1H NMR (300 MHz, $CDCl_3$) δ = 2.51–2.60 (m, 2H), 2.76–2.85 (m, 2H), 3.85 (s, 3H), 6.09 (s, 1H), 6.73 (s, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 7.14–7.24 (m, 2H), 7.56–7.63 (m, 2H) 7.85 (d, *J* = 8.6 Hz, 1H) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$) δ = 23.0, 27.9, 55.4, 109.3, 111.2, 112.2, 113.6, 121.1, 123.5, 125.6, 129.3, 131.9, 135.4, 139.6, 155.9, 157.5, 161.5 ppm; *m*/*z* (ESI): 383 [M^+ + H]; HRMS (ESI) calcd for $C_{20}H_{15}BrO_3$ [M^+ + 1] 383.0283, found 383.0250.

4-(Furan-2-yl)-5,6-dihydro-2*H*-benzo[*h*]chromen-2-one (19b)

The (*Z*/*E*)-methyl 2-(4-(furan-2-yl)-5,6-dihydro-2*H*-benzo[*h*]-chromen-2-ylidene)acetate (**18b**, 160 mg, 0.5 mmol, 1 equiv.) was treated with DDQ (227 mg, 1.0 mmol, 2 equiv.) in glacial acetic acid (5 ml) for 2 h. Using the general procedure described above, 54 mg (41%) of **19b** was obtained as a yellow solid: R_f = 0.39 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 144–146 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2924 (m), 1630 (m); ^1H NMR (300 MHz, $CDCl_3$) δ = 2.94–3.00 (m, 4H), 6.57 (s, 2H), 6.86 (d, *J* = 3.0 Hz, 1H), 7.21–7.35 (m, 3H), 7.60–7.64 (m, 1H), 7.90 (d, *J* = 4.6 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 23.1, 27.3, 108.3, 109.6, 112.3, 114.3, 123.7, 127.1, 127.5, 128.3, 130.3, 136.9, 144.9, 148.9, 155.4, 162.0 ppm; *m*/*z* (ESI): 265 [M^+ + H]; HRMS (ESI) calcd for $C_{17}H_{12}O_3$ [M^+ + 1] 265.0865, found 265.0868.

4-Phenyl-5,6-dihydro-2*H*-benzo[*h*]chromen-2-one (19c)

The(*Z*/*E*)-methyl 2-(4-phenyl-5,6-dihydro-2*H*-benzo[*h*]chromen-2-ylidene)acetate (**18c**, 165 mg, 0.5 mmol, 1 equiv.) was treated

with DDQ (227 mg, 1.0 mmol, 2 equiv.) in glacial acetic acid (5 ml) for 1 h. Using the general procedure described above, 65 mg (48%) of **19c** was obtained as a yellow solid: R_f = 0.50 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 154–156 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2922 (m), 2858 (w), 1750 (m); ^1H NMR (300 MHz, $CDCl_3$) δ = 2.56–2.65 (m, 2H), 2.79–2.88 (m, 2H), 6.20 (s, 1H), 7.16–7.49 (m, 8H), 7.88–7.94 (m, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 23.0, 27.6, 111.7, 112.8, 123.7, 127.2, 127.7, 128.3, 128.7, 129.2, 130.3, 136.4, 137.3, 155.1, 158.6, 161.9 ppm; *m*/*z* (ESI): 275 [M^+ + H]; HRMS (ESI) calcd for $C_{19}H_{14}O_2$ [M^+ + 1] 275.1072, found 275.1067.

4-(4-Bromophenyl)-8-methoxy-2*H*-benzo[*h*]chromen-2-one (20a)

4-(4-Bromophenyl)-8-methoxy-5,6-dihydro-2*H*-benzo[*h*]chromen-2-one (**19a**, 76 mg, 0.2 mmol, 1 equiv.) was refluxed with 6 mmol of DDQ (272 mg, 1.2 mmol, 6 equiv.) in benzene (5 ml) at 90 °C for 8 h. After completion, the reaction mixture was filtered and the filtrate was collected and evaporated to dryness. The crude **20a** obtained was purified by column chromatography on a silica gel using 30% $CHCl_3$ in *n*-hexane as the eluent to afford 40 mg (52%) of 4-(4-bromophenyl)-8-methoxy-2*H*-benzo[*h*]chromen-2-one (**20a**) was obtained as an off-white solid: R_f = 0.53 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 194–196 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3013 (w), 1718 (w), 1634 (m); ^1H NMR (300 MHz, $CDCl_3$) δ = 3.96 (s, 3H), 6.36 (s, 1H), 7.15 (d, *J* = 2.2 Hz, 1H), 7.27–7.33 (m, 1H), 7.34–7.41 (m, 3H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 8.51 (d, *J* = 9.2 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 55.4, 106.2, 112.2, 113.2, 118.2, 119.6, 122.7, 123.0, 124.0, 124.5, 130.1, 132.1, 134.6, 136.8, 151.8, 152.7, 155.5, 160.2, 160.7 ppm; *m*/*z* (ESI): 381 [M^+ + H]; HRMS (ESI) calcd for $C_{20}H_{13}BrO_3$ [M^+ + 1] 381.0126, found 381.0112.

General procedure for the synthesis of 23a–f

A mixture of the 4-(methylthio)-2-oxo-6-aryl-2*H*-pyran-3-carbonitriles **21** (1 mmol), substituted acetophenones **22** (1.2 mmol) and KOH (1.5 mmol) in dry DMF (15 ml) were stirred at 90 °C for 24 h. Completion of the reaction was monitored using TLC and on completion the reaction mixture was poured into crushed ice with vigorous stirring and finally neutralized with 10% HCl. The precipitate obtained was filtered and purified on a silica gel column using 30% $CHCl_3$ in *n*-hexane as the eluent to afford **23a–f** as a mixture of *cis*- and *trans*-isomers.

(*Z*/*E*)-2-(6-(Naphthalen-1-yl)-4-phenyl-2*H*-pyran-2-ylidene)-acetonitrile (23a)

A mixture of 4-(methylthio)-2-oxo-6-phenyl-2*H*-pyran-3-carbonitrile (**21a**, 243 mg, 1.0 mmol, 1 equiv.), 1-(naphthalen-1-yl) ethanone (**22a**, 170 mg, 1.0 mmol, 1 equiv.) and KOH (84 mg, 1.5 mmol, 1.5 equiv.) in dry DMF (15 ml) was stirred at 90 °C for 24 h. Using the general procedure described above, 122 mg (38%) of **23a** was obtained as a mixture of *cis*- and *trans*-isomers, as a red oil: R_f = 0.59 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); IR (KBr) ν_{max}/cm^{-1} = 2926 (w), 2215 (s), 1649 (s); ^1H NMR (300 MHz, $CDCl_3$): δ = 4.39 (s, 1H, *trans*), 4.61 (s, 1H, *cis*), 6.49 (s, 1H, *cis*), 6.52 (s, 1H, *trans*), 6.56 (s, 1H, *trans*), 7.05 (s, 1H, *cis*), 7.45–7.68 (m, 18H, *cis* + *trans*), 7.90–8.01 (m, 4H, *cis* + *trans*), 8.15 (d, *J* = 7.6 Hz, 1H, *trans*), 8.29 (d, *J* = 8.2 Hz, 1H, *trans*) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 66.4, 67.2, 105.9, 106.0, 112.1, 112.9, 113.2, 117.8, 119.1, 124.7, 124.7, 125.0, 125.9, 126.1, 126.4, 126.4, 126.5, 127.2, 127.4, 128.7, 129.1, 129.9, 130.0, 130.1, 130.2, 130.3, 130.4, 131.0, 133.7, 133.8, 135.5, 135.6, 142.9, 143.7, 158.0, 158.2, 166.3, 168.0 ppm; *m*/*z* (ESI): 322.2 [M + H^+]; HRMS (ESI) calcd for $C_{23}H_{15}NO$ [M^+ + 1] 322.1232, found 322.1237.

(*Z*/*E*)-2-(4,6-Bis(4-bromophenyl)-2*H*-pyran-2-ylidene) acetonitrile (23b)

A mixture of 6-(4-bromophenyl)-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitrile (**21b**, 320 mg, 1.0 mmol, 1 equiv.), 1-(4-bromophenyl)ethanone (**22b**, 199 mg, 1.0 mmol, 1 equiv.) and KOH (84 mg, 1.5 mmol, 1.5 equiv.) in dry DMF (15 ml) was stirred at 90 °C for 24 h. Using the general procedure described above, 204 mg (48%) of **23b** was obtained as a mixture of *cis*- and *trans*-isomers, as a red oil: R_f = 0.64 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); IR (KBr) ν_{max}/cm^{-1} = 2925 (w), 2872 (w), 2195 (m), 1649 (m); ^1H NMR (300 MHz, $CDCl_3$): δ = 4.38 (s, 1H, *cis*), 4.67 (s, 1H, *trans*), 6.48 (s, 1H, *cis*), 6.54 (s, 1H, *trans*), 6.58 (s, 1H, *cis*), 6.93 (s, 1H, *trans*), 7.41–7.63 (m, 14H, *cis* + *trans*), 7.73 (d, *J* = 8.6 Hz, 2H, *cis*) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 67.2, 68.1, 100.6, 100.9, 112.7, 113.7, 117.7, 118.8, 125.3, 126.6, 127.2, 127.4, 127.5, 127.6, 129.4, 129.8, 132.2, 132.2, 132.4, 134.0, 134.2, 141.9, 142.4, 155.9, 156.2, 165.5, 167.1 ppm; *m*/*z* (ESI): 427 [M^+ + H]; HRMS (ESI) calcd for $C_{19}H_{11}Br_2NO$ [M^+ + 1] 427.9286, found 427.9328.

(*Z*/*E*)-2-(4,6-Di-*p*-tolyl-2*H*-pyran-2-ylidene)acetonitrile (23c)

A mixture of 4-(methylthio)-2-oxo-6-(*p*-tolyl)-2*H*-pyran-3-carbonitrile (**21c**, 257 mg, 1.0 mmol, 1 equiv.), 1-(4-methylphenyl) ethanone (**22c**, 0.133 ml, 1.0 mmol, 1 equiv.) and KOH (84 mg, 1.5 mmol, 1.5 equiv.) in dry DMF (15 ml) was stirred at 90 °C for 24 h. Using the general procedure described above, 111 mg (37%) of **23c** was obtained as a mixture of *cis*- and *trans*-isomers, as a red oil: R_f = 0.64 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); IR (KBr) ν_{max}/cm^{-1} = 2923 (m), 2856 (w), 2193 (m), 1646 (w); ^1H NMR (300 MHz, $CDCl_3$): δ = 2.40 (s, 6H), 4.29 (s, 1H, *cis*), 4.57 (s, 1H, *trans*), 6.43 (s, 1H, *cis*), 6.58 (s, 1H, *trans*), 6.90 (s, 1H, *cis*), 6.91 (s, 1H, *trans*), 7.20–7.29 (m, 10H, *cis* + *trans*), 7.42–7.54 (m, 4H, *cis* + *trans*), 7.62 (d, *J* = 8.1 Hz, 2H, *cis*), 7.76 (d, *J* = 8.1 Hz, 2H, *trans*) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.3, 21.3, 21.4, 21.5, 65.3, 66.1, 100.0, 100.3, 111.2, 112.1, 118.5, 119.6, 125.1, 125.1, 125.9, 126.1, 128.4, 128.7, 129.5, 129.6, 129.6, 129.8, 132.9, 133.1, 140.4, 140.5, 141.1, 141.1, 143.3, 143.9, 156.8, 157.1, 166.4, 168.1 ppm; *m*/*z* (ESI): 300 [M^+ + H]; HRMS (ESI) calcd for $C_{21}H_{17}NO$ [M^+ + 1] 300.1388, found 300.1377.

(*Z*/*E*)-2-(4,6-Di(naphthalen-2-yl)-2*H*-pyran-2-ylidene)acetonitrile (23d)

A mixture of 4-(methylthio)-6-(naphthalen-2-yl)-2-oxo-2*H*-pyran-3-carbonitrile (**21d**, 293 mg, 1.0 mmol, 1 equiv.),

1-(naphthalen-2-yl)ethanone (**22d**, 170 mg, 1.0 mmol, 1 equiv.) and KOH (84 mg, 1.5 mmol, 1.5 equiv.) in dry DMF (15 ml) was stirred at 90 °C for 24 h. Using the general procedure described above, 149 mg (40%) of **23d** was obtained as a mixture of *cis*- and *trans*-isomers, as a red oil: R_f = 0.51 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); IR (KBr) ν_{max}/cm^{-1} = 2928 (w), 2860 (w), 2194 (s), 1647 (m); ^1H NMR (300 MHz, $CDCl_3$): δ = 4.36 (s, 1H, *cis*), 4.70 (s, 1H, *trans*), 6.55 (s, 1H, *cis*), 6.85 (s, 2H, *cis* + *trans*), 7.06 (s, 1H, *trans*), 7.48–7.65 (m, 10H, *cis* + *trans*), 7.79–8.10 (m, 16H, *cis* + *trans*), 8.23 (s, 1H, *trans*), 8.39 (s, 1H, *cis*) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 66.1, 67.0, 100.8, 101.0, 112.2, 113.2, 118.3, 119.3, 121.6, 121.7, 122.9, 123.0, 123.6, 124.2, 125.0, 125.3, 125.7, 125.8, 126.7, 126.9, 127.2, 127.4, 127.5, 127.7, 128.0, 128.2, 128.5, 128.5, 128.6, 128.7, 128.9, 129.0, 132.5, 132.7, 132.8, 133.1, 133.8, 133.9, 134.0, 142.7, 143.3, 156.3, 156.5, 165.9, 167.6 ppm; *m*/*z* (ESI): 372 [M^+ + H]; HRMS (ESI) calcd for $C_{27}H_{17}NO$ [M^+ + 1] 372.1388, found 372.1387.

(*Z*/*E*)-2-(4,6-Di(thiophen-2-yl)-2*H*-pyran-2-ylidene)acetonitrile (23e)

A mixture of 4-(methylthio)-2-oxo-6-(thiophen-2-yl)-2*H*-pyran-3-carbonitrile (**21e**, 248 mg, 1.0 mmol, 1 equiv.), 1-(thiophen-2-yl)ethanone (**22e**, 0.107 ml, 1.0 mmol, 1 equiv.) and KOH (84 mg, 1.5 mmol, 1.5 equiv.) in dry DMF (15 ml) was stirred at 90 °C for 24 h. Using the general procedure described above, 110 mg (39%) of **23e** was obtained as a mixture of *cis*- and *trans*-isomers, as a red oil: R_f = 0.48 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); IR (KBr) ν_{max}/cm^{-1} = 2922 (m), 2859 (w), 2191 (w), 1629 (m); ^1H NMR (300 MHz, $CDCl_3$): δ = 4.31 (s, 1H, *cis*), 4.58 (s, 1H, *trans*), 6.39–6.44 (m, 3H, *cis* + *trans*), 6.85 (d, *J* = 1.3 Hz, 1H, *trans*), 7.07–7.16 (m, 4H, *cis* + *trans*), 7.38–7.48 (m, 6H, *cis* + *trans*), 7.64 (d, *J* = 2.8 Hz, 2H, *trans*) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 66.2, 67.0, 98.7, 98.9, 109.0, 110.0, 126.6, 127.4, 128.3, 128.5, 128.6, 134.6, 139.1, 152.3, 165.1 ppm; *m*/*z* (ESI): 284 [M^+ + H]; HRMS (ESI) calcd for $C_{15}H_9NOS_2$ [M^+ + 1] 284.0204, found 284.0208.

6-(4-Methoxyphenyl)-5-methyl-4-morpholino-2-oxo-2*H*-pyran-3-carbonitrile (I)

In order to synthesize **23f**, the methylsulfanyl group of 6-(4-methoxyphenyl)-5-methyl-4-(methylthio)-2-oxo-2*H*-pyran-3-carbonitrile **21f**[20] was replaced by morpholine by reacting lactone **21f** (287 mg, 1.0 mmol) with morpholine (0.1 ml, 1.2 mmol) in methanol (10 ml) at reflux temperature for 8 h to give the precursor 6-(4-methoxyphenyl)-5-methyl-4-morpholino-2-oxo-2*H*-pyran-3-carbonitrile (**I**) in a quantitative yield of 310 mg (95%).

Yellow solid: R_f = 0.56 (MeOH–$CHCl_3$, 1 : 25 v/v); mp 164–166 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3024 (w), 2215 (w), 1703 (m); ^1H NMR (300 MHz, $CDCl_3$): δ = 2.10 (s, 3H), 3.58–3.75 (m, 4H), 3.82–3.94 (m, 7H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 17.7, 51.8, 55.5, 67.0, 80.8, 106.6, 113.9, 116.5, 124.0, 131.5, 161.9, 162.2, 168.1 ppm; *m*/*z* (ESI): 327 [M^+ + H]; HRMS (ESI) calcd for $C_{18}H_{18}N_2O_4$ [M^+ + 1] 327.1345, found 327.1344.

2-(6-Isopropyl-4-(4-methoxyphenyl)-3-methyl-5-phenyl-2*H*-pyran-2-ylidene)acetonitrile (23f)

A mixture of 6-(4-methoxyphenyl)-5-methyl-4-morpholino-2-oxo-2*H*-pyran-3-carbonitrile (**I**, 326 mg, 1.0 mmol, 1 equiv.), 3-methyl-1-phenyl-butan-2-one (**22f**, 0.162 ml, 1.0 mmol, 1 equiv.) and powdered KOH (84 mg, 1.5 mmol, 1.5 equiv.) in dry DMF (5 ml) was stirred at 90 °C for 24 h. Using the general procedure described above, 175 mg (49%) of **23f** was obtained as a yellow solid: R_f = 0.49 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 183–185 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 3022 (w), 2930 (w), 2199 (m); ^1H NMR (300 MHz, $CDCl_3$) δ = 1.21 (d, *J* = 6.8 Hz, 6H), 1.67 (s, 3H), 2.55–2.65 (m, 1H), 3.70 (s, 3H), 4.24 (s, 1H), 6.61–6.76 (m, 4H), 6.82–6.91 (m, 2H), 7.08–7.16 (m, 3H) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$) δ = 14.8, 18.4, 20.2, 30.2, 55.0, 62.9, 113.2, 116.9, 119.9, 126.9, 127.9, 128.9, 130.0, 130.3, 135.3, 158.6, 160.1, 167.4 ppm; *m*/*z* (ESI): 358 [M^+ + H]; HRMS (ESI) calcd for$C_{24}H_{23}NO_2$ [M^+ + 1] 358.1807, found 358.1800.

General procedure for the synthesis of 24a–f

The functionalized 2*H*-pyran-2-ylidene-acetonitriles (**23a–f**) were treated with 2.0 mmol of DDQ in AcOH at room temp for 5–6 h. After completion, the reaction mixture was filtered and the filtrate was collected and evaporated to dryness. Thereafter, the crude obtained was purified through column chromatography on silica gel using 50% $CHCl_3$ in hexane as the eluent to afford highly functionalized 2*H*-pyran-2-ones **24a–f.**

6-(Naphthalen-1-yl)-4-phenyl-2*H*-pyran-2-one (24a)

The (*Z*/*E*)-2-(6-(naphthalen-1-yl)-4-phenyl-2*H*-pyran-2-ylidene)-acetonitrile (**23a**, 161 mg, 0.5 mmol, 1 equiv.) was treated with DDQ (227 mg, 1.0 mmol, 2 equiv.) in glacial acetic acid (5 ml) for 6 h. Using the general procedure described above, 70 mg (47%) of **24a** was obtained as a yellow solid: R_f = 0.40 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 126–128 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2926 (m), 1715 (s), 1627 (m), 1538 (m); ^1H NMR (300 MHz, $CDCl_3$) δ = 6.58 (d, *J* = 1.3 Hz, 1H), 6.85 (d, *J* = 1.3 Hz, 1H), 7.48–7.79 (m, 9H), 7.88–8.01 (m, 2H), 8.22–8.29 (m, 1H) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$) δ = 106.5, 109.3, 124.9, 125.0, 126.5, 126.8, 127.4, 127.8, 128.7, 129.3, 130.4, 130.8, 131.2, 133.8, 135.8, 155.4, 161.8, 163.0 ppm; *m*/*z* (ESI): 299 [M^+ + H]; HRMS (ESI) calcd for $C_{21}H_{14}O_2$ [M^+ + 1] 299.1072, found 299.1078.

4,6-Bis(4-bromophenyl)-2*H*-pyran-2-one (24b)

The (*Z*/*E*)-2-(4,6-bis(4-bromophenyl)-2*H*-pyran-2-ylidene)acetonitrile (**23b**, 213 mg, 0.5 mmol, 1 equiv.) was treated with DDQ (227 mg, 1.0 mmol, 2 equiv.) in glacial acetic acid (5 ml) for 5 h. Using the general procedure described above, 83 mg (41%) of **24b** was obtained as a yellow solid: R_f = 0.48 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 216–218 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2920 (w), 1691 (s), 1535 (w); ^1H NMR (300 MHz, $CDCl_3$) δ = 6.45 (s, 1H), 6.88 (s, 1H), 7.45–7.68 (m, 6H), 7.75 (d, *J* = 8.6 Hz, 2H) ppm; ^{13}C NMR (50.3 MHz, $CDCl_3$) δ = 101.1, 109.7, 125.7, 127.2, 128.0, 128.2, 129.6, 130.3, 132.3, 132.6,

134.3, 137.2, 154.2, 159.6, 162.0 ppm; HRMS (ESI) calcd for $C_{17}H_{10}Br_2O_2$ [M^+ + 1] 404.9126, found 404.9313.

4,6-Di-*p*-tolyl-2*H*-pyran-2-one (24c)

The (*Z*/*E*)-2-(4,6-di-*p*-tolyl-2*H*-pyran-2-ylidene)acetonitrile (**23c**, 150 mg, 0.5 mmol, 1 equiv.) was treated with DDQ (227 mg, 1.0 mmol, 2 equiv.) in glacial acetic acid (5 ml) for 5 h. Using the general procedure described above, 65 mg (47%) of **24c** was obtained as a yellow solid: R_f = 0.38 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 163–165 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2928 (w), 1696 (m), 1630 (m), 1512 (m); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 2.41 (s, 3H), 2.43 (s, 3H), 6.43 (s, 1H), 6.92 (s, 1H), 7.22–7.35 (m, 4H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 21.4, 21.5, 100.6, 108.1, 125.7, 126.6, 128.9, 129.7, 129.9, 133.2, 141.1, 141.4, 155.5, 160.5, 163.0 ppm; *m*/*z* (ESI): 277 [M^+ + H]; HRMS (ESI) calcd for $C_{19}H_{16}O_2$ [M^+ + 1] 277.1229, found 277.1234.

4,6-Di(naphthalen-2-yl)-2*H*-pyran-2-one (24d)

The (*Z*/*E*)-2-(4,6-di(naphthalen-2-yl)-2*H*-pyran-2-ylidene)acetonitrile (**23d**, 186 mg, 0.5 mmol, 1 equiv.) was treated with DDQ (227 mg, 1.0 mmol, 2 equiv.) in glacial acetic acid (5 ml) for 6 h. Using the general procedure described above, 75 mg (43%) of **24d** was obtained as a yellow solid: R_f = 0.36 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 166–168 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2920 (m), 2853 (m), 1708 (m), 1531 (w); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.64 (d, *J* = 1.2 Hz, 1H), 7.24 (d, *J* = 1.2 Hz, 1H), 7.54–7.63 (m, 4H), 7.72–7.80 (m, 1H), 7.84–8.03 (m, 7H), 8.20 (s, 1H), 8.53 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 101.7, 107.9, 108.2, 116.0, 122.6, 129.9, 129.7, 130.1, 132.2, 138.2, 138.5, 139.7, 141.0, 152.5, 153.2, 153.3, 158.8, 159.5, 169.2 ppm.

4,6-Di(thiophen-2-yl)-2*H*-pyran-2-one (24e)

The (*Z*/*E*)-2-(4,6-di(thiophen-2-yl)-2*H*-pyran-2-ylidene)acetonitrile (**23e**, 142 mg, 0.5 mmol, 1 equiv.) was treated with DDQ (227 mg, 1.0 mmol, 2 equiv.) in glacial acetic acid (5 ml) for 6 h. Using the general procedure described above, 50 mg (38%) of **24e** was obtained as a yellow solid: R_f = 0.32 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 158–160 °C {lit.[21] 158 °C} ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2913 (m), 2139 (w), 1705 (m), 1651 (m); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.39 (d, *J* = 1.3 Hz, 1H), 6.76 (d, *J* = 1.3 Hz, 1H), 7.11–7.22 (m, 2H), 7.48 (d, *J* = 5.0 Hz, 1H), 7.51–7.59 (m, 2H), 7.64–7.69 (m, 1H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 99.1, 105.5, 127.7, 128.0, 128.4, 128.7, 129.1, 129.8, 135.1, 138.8, 148.1, 156.0, 161.8 ppm; *m*/*z* (ESI): 261 [M^+ + H]; HRMS (ESI) calcd for $C_{13}H_8O_2S_2$ [M^+ + 1] 261.0044, found 261.0046.

6-Isopropyl-4-(4-methoxyphenyl)-3-methyl-5-phenyl-2*H*-pyran-2-one (24f)

The (*Z*/*E*)-2-(6-isopropyl-4-(4-methoxyphenyl)-3-methyl-5-phenyl-2*H*-pyran-2-ylidene)acetonitrile (**23f**, 179 mg, 0.5 mmol, 1 equiv.) was treated with DDQ (227 mg, 1.0 mmol, 2 equiv.) in glacial acetic acid (5 ml) for 5 h. Using the general procedure described above, 65 mg (39%) of **24f** as a yellow solid: R_f = 0.40 ($CHCl_3$–*n*-hexane, 7 : 3, v/v); mp 172–174 °C ($CHCl_3$–*n*-hexane); IR (KBr) ν_{max}/cm^{-1} = 2974 (w), 2928 (w), 1707 (s); ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.19 (d, *J* = 6.8 Hz, 6H), 1.92 (s, 3H), 2.60–2.72 (m, 1H), 3.71 (s, 3H), 6.65–6.92 (m, 4H), 7.83–7.92 (m, 2H), 7.11–7.17 (m, 3H) ppm; ^{13}C NMR (50 MHz, $CDCl_3$) δ = 14.5, 20.3, 30.4, 30.9, 55.2, 113.1, 113.9, 117.9, 118.8, 127.0, 127.8, 128.0, 128.3, 128.9, 129.6, 130.4, 130.7, 137.4, 141.3, 152.2, 158.7 ppm; *m*/*z* (ESI): 335 [M^+ + H]; HRMS (ESI) calcd for $C_{22}H_{22}O_3$ [M^+ + 1] 335.1647, found 335.1642.

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