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Synthesis of 1-azaxanthones by condensation of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 3-(cyano)benzopyrylium triflates and subsequent domino ‘retro-Michael/nitrile-addition/heterocyclization’ reaction

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A B S T R A C T

Functionalized 1-azaxanthones (5-oxo-5*H*-[1]-benzopyrano[2,3-*b*]pyridines) were prepared by TMSOTf-mediated condensation of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 3-cyanochromones and subsequent base-mediated domino ‘retro-Michael/nitrile-addition/heterocyclization’ reaction.

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1. Introduction

1-Azaxanthones (i.e., 5-oxo-5*H*-[1]-benzopyrano[2,3-*b*]pyridines) are of considerable pharmacological relevance. For example, they show anti-inflammatory activity and represent inhibitors of the passive cutaneous anaphylaxis.[1] 1-Azaxanthones are available, based on pioneering work of Ghosh and co-workers,[2a] by base-mediated reaction of 3-cyanochromones with active methylene compounds.[2] Despite its preparative utility, the scope of this approach is limited to specific substrates and substitution patterns. 4-(Trimethylsilyloxy)benzopyrylium triflates can be readily generated by addition of trimethylsilyl-trifluoromethanesulfonate (TMSOTf) to chromones. Their reaction with nucleophiles allows the regioselective functionalization of carbon atom C-2 of the chromone moiety. The formal [4+2]-cycloaddition of 1,3-butadienes with 4-(trimethylsilyloxy)benzopyrylium triflates was first reported by Akiba and co-workers.[3] Later, the TMSOTf-mediated [4+2]-cycloaddition of 1,3-butadienes with 3-cyanochromone, via its 4-(trimethylsilyloxy)benzopyrylium triflate, has been reported.[4] In the course of our interest in the development of new domino reactions[5] of 4-(silyloxy)benzopyrylium triflates,[6] we recently reported[7] the TMSOTf-mediated reaction of 3-cyanochromones with 1,3-bis(trimethylsilyloxy)-1,3-butadienes.[8] These reactions allow a convenient synthesis of functionalized 1-azaxanthones, which are not readily available by other methods. Herein, full details of our methodology and a comprehensive study related to its preparative scope are reported.

2. Results and discussion

The TMSOTf-mediated reaction of **1a** with 1,3-bis(trimethylsilyloxy)-1,3-butadiene **2a**, readily available in two steps from methyl acetoacetate,[9] afforded the condensation product **3a** by regioselective attack of the terminal carbon atom of **2a** onto carbon atom C-2 of **1a** and subsequent hydrolysis. Treatment of an ethanol solution of crude **3a** with triethylamine afforded 1-azaxanthone **4a** (Scheme 1). The base-mediated retro-Michael reaction of **3a** gave open-chained intermediate **B**. The attack of the hydroxy group onto the nitrile gave intermediate **C**. The attack of the imino nitrogen atom onto the carbonyl group (intermediate **D**) and subsequent aromatization by extrusion of water afforded **4a**. The transformation of **3a** into **4a** can be regarded as a domino ‘retro-Michael/nitrile-addition/heterocyclization’ reaction.

The reaction of 1,3-bis(trimethylsilyloxy)-1,3-butadienes **2a**–**c**, prepared from methyl, ethyl and isopropyl acetoacetate, with parent 3-cyanochromone (**1a**) and with the alkyl- and halogen-substituted 3-cyanochromones **1b**–**g** afforded products **3a**–**j**, which were transformed, by reaction with NEt_3, into the 1-azaxanthones **4a**–**j** (Scheme 2, Table 1). The reaction of parent 3-cyanochromone (**1a**) with 1,3-bis(trimethylsilyloxy)-1,3-butadiene **2d**, prepared from methyl 3-oxopentanoate, afforded **3a**. Treatment of **3a** with triethylamine afforded dibenzo[*b*,*d*]pyran-6-one **5a** rather than the expected methyl-substituted azaxanthone **4k**. The formation of **5a** can be explained by a competing domino ‘retro-Michael/aldol/lactonization’ reaction (Scheme 3).[10] In contrast, the reaction of **2e** (derived from ethyl 3-oxopentanoate) with chlorinated 3-cyanochromone **1e** afforded azaxanthone **4l** (via **3l**). The reaction of parent cyanochromone **1a** with 1,3-bis(silyl enol ether) **2f**, prepared from ethyl 3-oxohexanoate, afforded **3m**. Treatment of the

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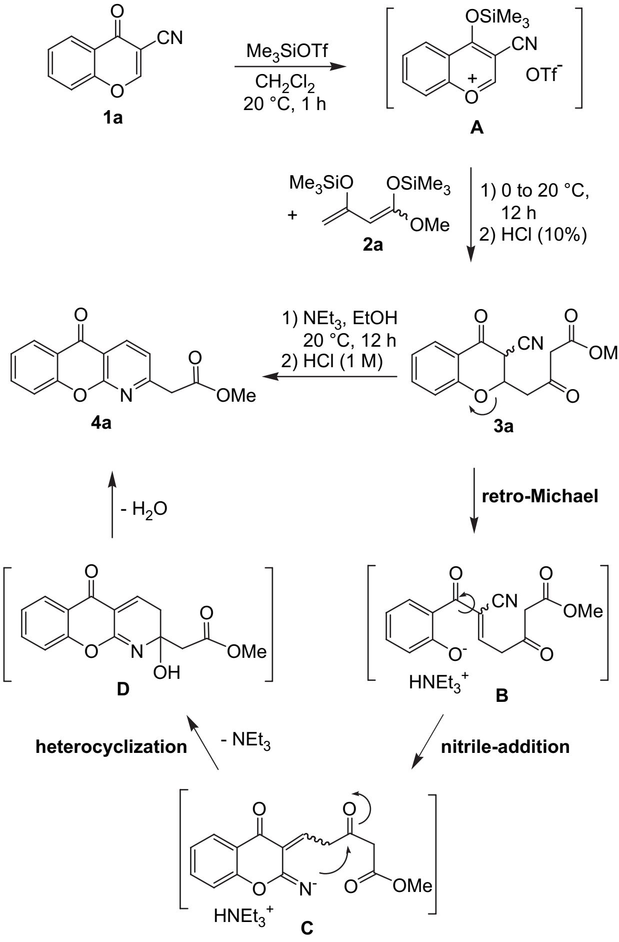


Scheme 1. Mechanism of the formation of **4a**.

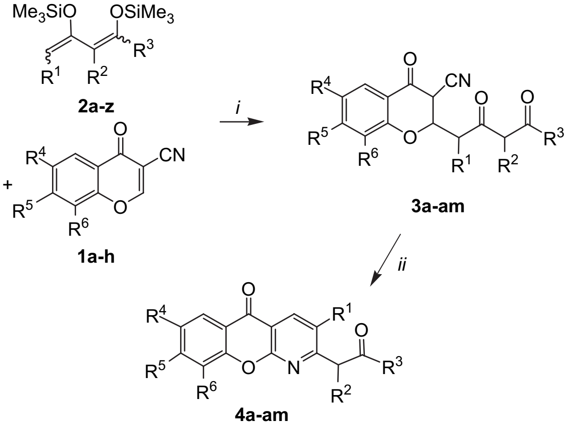
Table 1
Products and yields

1	2	4	5	R^1	R^2	R^3	R^4	R^5	R^6	% (**4**,**5**)[a]
a	**a**	**a**		H	H	OMe	H	H	H	41
a	**b**	**b**		H	H	OEt	H	H	H	46
a	**c**	**c**		H	H	O^{i}Pr	H	H	H	42
b	**a**	**d**		H	H	OEt	Me	H	H	40
c	**c**	**e**		H	H	O^{i}Pr	Et	H	H	31
d	**a**	**f**		H	H	OEt	^{i}Pr	H	H	41
e	**a**	**g**		H	H	OEt	Cl	H	H	37
f	**a**	**h**		H	H	OEt	Cl	H	Cl	48
g	**a**	**i**		H	H	OEt	Br	H	H	34
g	**c**	**j**		H	H	O^{i}Pr	Br	H	H	32
a	**d**	**k**	**a**	Me	H	OMe	H	H	H	0 (34)[b]
e	**e**	**l**		Me	H	OEt	Cl	H	H	41
a	**f**	**m**	**b**	Et	H	OEt	H	H	H	17 (34)[b]
e	**f**	**n**		Et	H	OEt	Cl	H	H	46
h	**f**	**o**		Et	H	OEt	Me	Me	H	38
a	**g**	**p**	**c**	^{n}Pr	H	OMe	H	H	H	0 (37)[b]
a	**h**	**q**	**d**	^{n}Bu	H	OMe	H	H	H	0 (42)[b]
a	**i**	**r**		^{n}Hept	H	OEt	H	H	H	25
e	**i**	**s**		^{n}Hept	H	OEt	Cl	H	H	38
a	**j**	**t**		Allyl	H	OMe	H	H	H	38
e	**j**	**u**		Allyl	H	OMe	Cl	H	H	30
a	**k**	**v**		Ph	H	OMe	H	H	H	62
a	**l**	**w**		4-Me(C$_6$H$_4$)	H	OMe	H	H	H	63
a	**m**	**x**		4-Cl(C$_6$H$_4$)	H	OMe	H	H	H	50
e	**n**	**y**		2-MeO(C$_6$H$_4$)	H	OMe	Cl	H	H	40
b	**n**	**z**		2-MeO(C$_6$H$_4$)	H	OMe	Me	H	H	32
a	**o**	**aa**		MeO	H	OMe	H	H	H	31
a	**p**	**ab**		PhO	H	OEt	H	H	H	66
f	**p**	**ac**		PhO	H	OEt	Cl	H	Cl	44
h	**q**	**ad**		4-Cl(C$_6$H$_4$)O	H	OMe	Me	Me	H	33
f	**r**	**ae**		4-Me(C$_6$H$_4$)O	H	OMe	Cl	H	Cl	42
a	**s**	**af**		PhS	H	OEt	H	H	H	51
h	**t**	**ag**		4-Cl(C$_6$H$_4$)S	H	OEt	Me	Me	H	56
b	**u**	**ah**		4-Me(C$_6$H$_4$)S	H	OEt	Me	H	H	63
f	**v**	**ai**		4-MeO(C$_6$H$_4$)S	H	OEt	Cl	H	Cl	45
a	**w**	**aj**		H	Me	OEt	H	H	H	31
a	**x**	**ak**		H	Et	OMe	H	H	H	34
a	**y**	**al**		–(CH$_2$)$_3$–		OEt	H	H	H	36
a	**z**	**am**		–CH$_2$CHMeCH$_2$–		OMe	H	H	H	32[c]
a	**aa**	**an**		–(CH$_2$)$_4$–		OMe	H	H	H	0
a	**ab**	**ao**		–(CH$_2$)$_9$–		OMe	H	H	H	0
a	**ac**	**ap**		H	H	Ph	H	H	H	0
a	**ad**	**aq**		H	H	Me	H	H	H	0

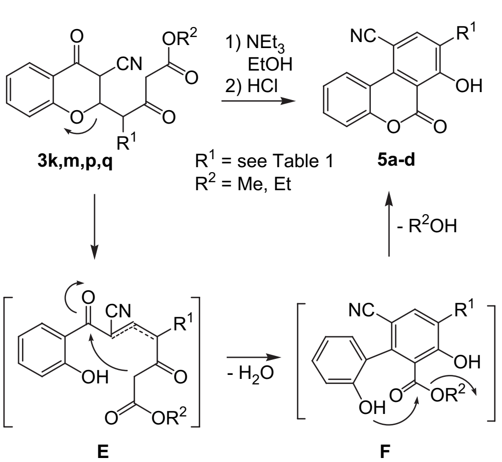
[a] Yields of isolated products **4** over two steps (based on **1**).
[b] Yields in brackets refer to **5a–d** (for structures see Scheme 3).
[c] dr=2:3.

latter with base resulted in formation of a separable mixture of ethyl-substituted azaxanthone **4m** and dibenzo[*b*,*d*]pyran-6-one **5b**. In contrast, the exclusive formation of azaxanthones **4n**,**o** was observed when substituted cyanochromones **1e** and **1h** were employed. The propyl- and butyl-substituted dibenzo[*b*,*d*]pyran-6-ones **5c** and **5d** were isolated from the reaction of parent cyanochromone **1a** with 1,3-bis(trimethylsilyloxy)-1,3-butadienes **2g** and **2h**. The reaction of **2i** with **1a** and **1e** exclusively afforded the heptyl-substituted azaxanthones **4r** and **4s**, respectively. The allyl-substituted azaxanthones **4t** and **4u** were prepared from **2j**.

The reaction of 4-aryl-1,3-bis(trimethylsilyloxy)-1,3-butadienes **2k–n** with 3-cyanochromones **1a**,**b**,**e** gave the products **3v–z**, which were transformed into the 3-aryl-1-azaxanthones **4v–z**. 3-Methoxy-



Scheme 2. Synthesis of 1-azaxanthones **4a–am**: (i) (1) **1a–h**, Me$_3$SiOTf, 1 h, 20 °C, (2) **2a–z**, CH$_2$Cl$_2$, 0→20 °C, 12 h, (3) HCl (10%); (ii) (1) NEt$_3$, EtOH, 20 °C, 12 h, (2) HCl (1 M).



Scheme 3. Mechanism of the formation of **5a–d**.

1-azaxanthone **4aa** was prepared from 4-methoxy-1,3-bis(trimethylsilyloxy)-1,3-butadiene **2o**, which is available from methyl 4-methoxyacetoacetate. The reaction of 4-aryloxy-1,3-bis(trimethylsilyloxy)-1,3-butadienes **2p**–**r** with **1a**,**f**,**h** afforded the condensation products **3ab**–**ae**, which were transformed into the 3-aryloxy-1-azaxanthones **4ab**–**ae**. Starting with 4-thioaryloxy-1,3-bis(trimethylsilyloxy)-1,3-butadienes **2s**–**v**, the 3-thioaryloxy-1-azaxanthones **4af**–**ai** were prepared. 1-Azaxanthones **4aj** and **4ak** were prepared from **1a** and from 2-methyl- and 2-ethyl-1,3-bis(trimethylsilyloxy)-1,3-butadienes **2w** and **2x**, respectively. The reaction of **1a** with cyclohexanone-derived 1,3-bis(trimethylsilyloxy)-1,3-butadienes **2y** and **2z** gave **3al** and **3am**, which were transformed into the tetracyclic azaxanthones **4al** and **4am**, respectively. The employment of 7- and 12-membered cyclic 1,3-bis(trimethylsilyloxy)-1,3-butadienes **2aa** and **2ab** proved to be unsuccessful. The reaction of 3-cyanochromones with 1,3-diketone-derived 1,3-bis(silyl enol ethers), such as 1-phenyl-1,3-bis(trimethylsilyloxy)-1,3-butadiene (**2ac**) or 2,4-bis(trimethylsilyloxy)-1,3-pentadiene (**2ad**), resulted in the formation of complex mixtures.

The structures of all products were proved by spectroscopic methods. The structure of **4t** was independently confirmed by X-ray crystal structure analysis (Fig. 1).[11]

The overall yields of 1-azaxanthones **4a**–**am** are, in most cases, only moderate. However, it has to be taken into account that the yields refer to *two* steps. In fact, a 50% overall yield is obtained when each individual step proceeds in ca. 70% yield. The moderate yields can be explained by the fact that, for the first step, the conversion is often not complete. However, the yields could not be increased by employment of an excess of the 1,3-bis(trimethylsilyloxy)-1,3-butadiene or by longer reaction times.

The yields depend on the type of 1,3-bis(trimethylsilyloxy)-1,3-butadiene and 3-cyanaochromone employed. The synthesis of 3-alkyl-1-azachromones from parent 3-cyanochromone is problematic, due to the competing formation of dibenzo[*b*,*d*]pyran-6-ones, which might be related to the steric influence of the alkyl group. In contrast, the synthesis of 3-alkyl-1-azachromones derived from substituted 3-cyanochromones proved to be possible. Relatively good yields are observed for 1-azaxanthones **4v**–**x** prepared from the phenyl- and 4-chlorophenyl-substituted dienes **2k**–**m**. The yields dropped for products **4y**,**z**, which were prepared from diene **2n** (containing the sterically more demanding 2-methoxyphenyl group). The yields of 1-azaxanthones **4ab**–**ai**, containing an aryloxy- or thioaryloxy-substituent, are again relatively good. These results can be explained by the assumption that, despite their steric effect, all these substituents exert an advantageous electronic effect in the first step (the addition of the diene onto the pyrylium salt) or in the second step (formation of intermediate **B** in Scheme 1). The yields of tetracyclic products **4al** and **4am** are rather low and the synthesis of analogues containing larger annulated rings was not possible at all. This might be explained by steric effects. The failure of the synthesis of **3ap** and **3aq** (and, thus, of the corresponding 1-azaxanthones) can be explained by the generally lower reactivity of 1,3-diketone- compared to β-ketoester-derived 1,3-bis(trimethylsilyloxy)-1,3-butadienes.

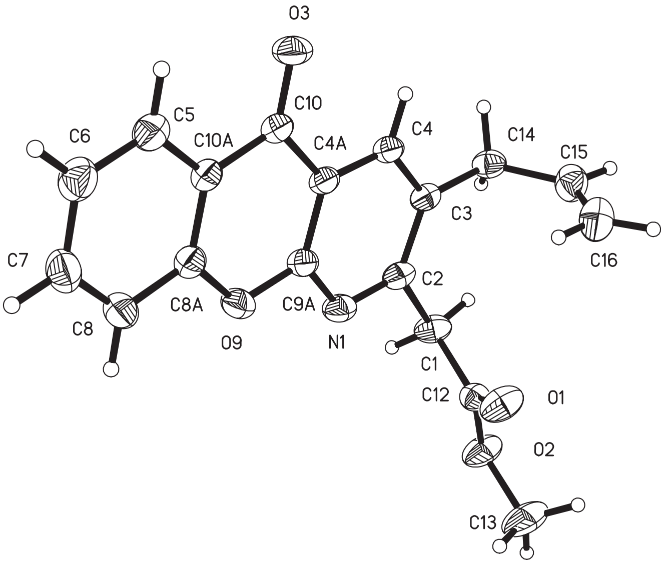


Figure 1. ORTEP plot of **4t** (50% probability level).

In conclusion, a variety of 1-azaxanthones were prepared by TMSOTf-mediated condensation of 1,3-bis(trimethylsilyloxy)-1,3-butadienes with 3-cyanochromones and subsequent base-mediated domino 'retro-Michael/lactonization/aldol' reaction. Noteworthy, the syntheses can be carried out under mild conditions and the reactions proceed in acceptable yields with very good regio- and chemoselectivity. The products are not readily available by other methods.

3. Experimental section

3.1. General comments

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^{1}H and ^{13}C NMR spectra the deuterated solvents indicated were used. Mass spectrometric data (MS) were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, H_2O) or electrospray ionization (ESI). For preparative scale chromatography, silica gel (60–200 mesh) was used. Melting points are uncorrected.

3.2. General procedure for the synthesis of azaxanthones 4a–am and dibenzo[*b*,*d*]pyran-6-ones 5a–d

To neat 3-cyanochromone **1** (1.0 equiv) was added Me_3SiOTf (1.3 equiv) and CH_2Cl_2 (1 mL) at 20 °C. After stirring for 1 h, CH_2Cl_2 and 1,3-bis(trimethylsilyloxy)-1,3-butadiene 2 (1.3 equiv) were added at 0 °C. The mixture was stirred for 12 h at 20 °C and subsequently poured into hydrochloric acid (10%). The organic and the aqueous layer were separated and the latter was extracted with CH_2Cl_2 (3×100 mL). The combined organic layers were washed with water, dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was filtered through a pad of silica gel (EtOAc/hexane=5:1) to give crude **3a**–**am**. To an ethanol solution (10 mL) of **3a**–**am** was added NEt_3 (2.0 equiv) and the solution was stirred for 12 h at 20 °C. To the solution were subsequently added an aqueous solution of hydrochloric acid (1 M) and ether (50 mL). The organic and the aqueous layer were separated and the latter was extracted with ether (3×100 mL). The combined organic layers were washed with water, dried (Na_2SO_4), filtered and the filtrate was concentrated in vacuo. The residue was purified by column chromatography (silica gel, EtOAc/hexane).

3.2.1. *Methyl 2-(4-azaxanthon-3-yl)acetate (**4a**)*

Starting with 3-cyanochromone (**1a**) (300 mg, 1.75 mmol), Me_3SiOTf (0.41 mL, 2.28 mmol), **2a** (593 mg, 2.28 mmol), CH_2Cl_2 (15 mL), methanol (20 mL) and triethylamine (885 mg, 1.21 mL, 8.75 mmol), **4a** was isolated as a yellow solid (193 mg, 41%), mp=138 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.77 (s, 3H, OCH_3), 4.01 (s, 2H, CH_2), 7.44 (m, 2H, Ar), 7.61 (d, ^3J=8.4 Hz, 1H, Ar), 7.79 (m, 1H, Ar), 8.31 (dd, ^3J=7.9 Hz, ^4J=1.6 Hz, 1H, Ar), 8.69 (d, ^3J=7.9 Hz, 1H, Ar). ^{13}C NMR (DEPT, 75.5 MHz, $CDCl_3$): δ=34.9 (CH_2), 52.5 (OCH_3), 115.4 (C), 118.5, 121.5 (CH), 121.7 (C), 124.8, 126.7, 135.7, 138.1 (CH), 155.7, 159.9 (C), 160.0 (C), 169.8 (C=O, ester), 177.4 (C=O, ketone).

IR (KBr, cm^{-1}): $\tilde{\nu}$=3438 (m), 2955 (m), 1739 (s), 1662 (s), 1645 (s), 1553 (m), 1463 (s), 1436 (m), 1401 (s), 1345 (m), 1274 (m), 1202 (s), 1164 (s), 1106 (s), 987 (w), 778 (m), 467 (w). UV–vis (CH_3CN, nm): λ_{max}: 332, 285, 264. Fluorescence (CH_3CN, nm): $F\lambda_{max}$ (λ_{Ex}): 420 (352). MS (EI, 70 eV): *m*/*z* (%)=269 (M^+, 100), 238 (16), 225 (21), 211 (68), 182 (42), 127 (11), 59 (13). HRMS (FT-ICR) calcd for $C_{15}H_{12}NO_4$ ($[M+1]^+$): 270.07608; found: 270.07605.

3.2.2. Ethyl 2-(4-azaxanthon-3-yl)acetate (**4b**)

Starting with 3-cyanochromone (**1a**) (300 mg, 1.75 mmol), Me_3SiOTf (506 mg, 0.41 mL, 2.28 mmol), **2b** (626 mg, 2.28 mmol), CH_2Cl_2 (15 mL), EtOH (20 mL) and triethylamine (891 mg, 1.22 mL, 8.77 mmol), **4b** was isolated as a yellow solid (229 mg, 46%), mp=127 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.29 (t, ^3J=7.0 Hz, 3H, CH_3), 3.99 (s, 2H, CH_2), 4.23 (q, ^3J=7.0 Hz, 2H, OCH_2CH_3), 7.44 (m, 2H, Ar), 7.62 (d, ^3J=8.3 Hz, 1H, Ar), 7.79 (m, 1H, Ar), 8.31 (dd, ^3J=7.9 Hz, ^4J=1.7 Hz, 1H, Ar), 8.69 (d, ^3J=7.9 Hz, 1H, Ar). ^{13}C NMR (DEPT, 75.5 MHz, $CDCl_3$): δ=14.2 (CH_3), 44.2 (CH_2), 61.5 (OCH_2), 115.3 (C), 118.5, 121.5 (CH), 121.7 (C), 124.7, 126.7, 135.6, 137.9 (CH), 155.7, 159.9, 160.2 (C), 169.3 (C=O, ester), 177.34 (C=O, ketone). IR (KBr, cm^{-1}): $\tilde{\nu}$=2985 (m), 2928 (m), 1728 (s), 1669 (s), 1602 (s), 1564 (s), 1472 (s), 1406 (s), 1372 (m), 1323 (m), 1282 (s), 1191 (s), 1207 (s), 1104 (s), 1024 (m), 767 (s), 750 (m). UV–vis (CH_3CN, nm): λ_{max} (lg ε): 236 (4.36), 285 (4.20), 331 (3.92). MS (EI, 70 eV): *m*/*z* (%)=283 (M^+, 85), 238 (16), 212 (12), 211 ($[M-CO_2, H_2C{=}CH_2]^+$ 100), 182 (10), 127 (5). HRMS (EI, 70 eV) calcd for $C_{16}H_{13}NO_4$ ($[M]^+$): 283.0845; found: 283.0845±2 ppm.

3.2.3. Isopropyl 2-(4-azaxanthon-3-yl)acetate (**4c**)

Starting with 3-cyanochromone (**1a**) (130 mg, 0.76 mmol), Me_3SiOTf (219 mg, 0.18 mL, 0.98 mmol), **2c** (285 mg, 0.98 mmol), CH_2Cl_2 (10 mL), EtOH (20 mL) and triethylamine (506 mg, 0.69 mL, 5.00 mmol), **4c** was isolated as a yellow solid (76 mg, 42%), mp=148 °C. ^1H NMR (300 MHz, DMSO-d_6): δ=1.22 (d, ^3J=6.3 Hz, 6H, CH_3), 4.02 (s, 2H, CH_2), 4.96 (sept, ^3J=6.3 Hz, 1H, $OCH(CH_3)_2$), 7.55 (m, 2H, Ar), 7.73 (dd, ^3J=8.6 Hz, ^4J=1.1 Hz, 1H, Ar), 7.90 (m, 1H, Ar), 8.15 (dd, ^3J=8.0 Hz, ^4J=1.6 Hz, 1H, Ar), 8.58 (d, ^3J=7.9 Hz, 1H, Ar). ^{13}C NMR (DEPT, 75.5 MHz, DMSO-d_6): δ=21.5 (CH_3), 43.5 (CH_2), 68.2 ($OCH(CH_3)_2$), 114.7 (C), 118.4 (CH), 121.1 (C), 122.1, 124.9, 126.0, 136.0, 137.3 (CH), 155.1, 159.2, 160.6 (C), 168.9 (C=O, ester), 176.57 (C=O, ketone). IR (KBr, cm^{-1}): $\tilde{\nu}$=3436 (m), 2984 (m), 2962 (m), 1722 (s), 1672 (s), 1615 (s), 1583 (m), 1563 (s), 1465 (s), 1400 (s), 1323 (m), 1206 (s), 1109 (s), 954 (w), 766 (s), 749 (m). UV–vis (CH_3CN, nm): λ_{max} (lg ε): 332 (3.95), 285 (4.22), 227 (4.46). MS (EI, 70 eV): *m*/*z* (%)=297 (M^+, 75), 238 ($[M-OCH(CH_3)_2]^+$, 100), 182 (25), 155 (5), 127 (7), 43 ($[CH(CH_3)_2]^+$, 40). Anal. Calcd (%) for $C_{17}H_{15}NO_4$: C, 68.68; H, 5.09; N, 4.71. Found: C, 68.60; H, 5.30; N, 4.58.

3.2.4. Ethyl 2-(4-aza-8-methylxanthon-3-yl)acetate (**4d**)

Starting with 3-cyano-6-methylchromone (**1b**) (152 mg, 0.82 mmol), Me_3SiOTf (238 mg, 0.19 mL, 1.07 mmol), **2a** (294 mg, 1.07 mmol), CH_2Cl_2 (16 mL), EtOH (20 mL) and triethylamine (536 mg, 0.73 mL, 5.30 mmol), **4d** was isolated as a yellow solid (97 mg, 40%), mp=128 °C. ^1H NMR (300 MHz, DMSO-d_6): δ=1.21 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 2.52 (s, 3H, CH_3), 4.04 (s, 2H, CH_2), 4.14 (q, ^3J=7.1 Hz, 2H, OCH_2CH_3), 7.57 (d, ^3J=7.9 Hz, 1H, Ar), 7.63 (d, ^3J=8.5 Hz, 1H, Ar), 7.74 (dd, ^3J=8.5 Hz, ^4J=2.5 Hz, 1H, Ar), 7.96 (d, ^4J=1.5 Hz, 1H, Ar), 8.61 (d, ^3J=7.9 Hz, 1H, Ar). ^{13}C NMR (APT, 75.5 MHz, DMSO-d_6): δ=14.1 (OCH_2CH_3), 20.4 (CH_3), 43.3 (CH_2), 60.8 (OCH_2), 114.7 (C), 118.3 (CH), 120.8 (C), 122.1, 125.3 (CH), 134.5 (C), 137.1, 137.5 (CH), 153.4, 159.3, 160.5 (C), 169.5 (C=O, ester), 176.58 (C=O, ketone). IR (KBr, cm^{-1}): $\tilde{\nu}$=3439 (m), 2979 (s), 2935 (s), 1727 (s), 1670 (s), 1616 (s), 1587 (s), 1490 (s), 1432 (s), 1394 (s), 1371 (s), 1340 (s), 1305 (s), 1278 (s), 1203 (s), 1173 (s), 1144 (m), 1108 (m), 1028 (s), 998 (w), 882 (w), 814 (m), 783 (m). UV–vis (CH_3CN, nm): λ_{max} (lg ε): 334 (3.86), 290 (4.23), 240 (4.39), 229 (4.46). MS (EI, 70 eV): *m*/*z* (%)=297 (M^+, 84), 252 ($[M-OCH_2CH_3]^+$, 14), 225 ($[M-CO_2CH_2CH_3]^+$, 100), 196 (18). Anal. Calcd (%) for $C_{17}H_{15}NO_4$ (297): C, 68.68; H, 5.09; N, 4.71. Found: C, 68.93; H, 5.91; N, 4.48.

3.2.5. Isopropyl 2-(4-aza-8-ethylxanthon-3-yl)acetate (**4e**)

Starting with 3-cyano-6-ethylchromone (**1c**) (141 mg, 0.71 mmol), Me_3SiOTf (205 mg, 0.17 mL, 0.92 mmol), **2c** (266 mg, 0.92 mmol), CH_2Cl_2 (20 mL), EtOH (20 mL) and triethylamine (465 mg, 0.64 mL, 4.60 mmol), **4e** was isolated as a yellow solid (58 mg, 31%), mp=127 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.29 (m, 9H, CH_2CH_3, $OCH(CH_3)_2$), 2.79 (q, ^3J=7.6 Hz, 2H, CH_2CH_3), 3.95 (s, 2H, CH_2), 5.09 (sept, ^3J=6.3 Hz, 1H, $OCH(CH_3)_2$), 7.43 (d, ^3J=7.9 Hz, 1H, Ar), 7.53 (d, ^3J=8.6 Hz, 1H, Ar), 7.62 (dd, ^3J=8.6 Hz, ^4J=2.2 Hz, 1H, Ar), 8.12 (d, ^4J=2.2 Hz, 1H, Ar), 8.69 (d, ^3J=7.9 Hz, 1H, Ar). ^{13}C NMR (DEPT, 75.5 MHz, $CDCl_3$): δ=15.5 (CH_2CH_3), 21.8 ($OCH(CH_3)_2$), 28.3 (CH_2CH_3), 44.4 (CH_2), 69.1 ($OCH(CH_3)_2$), 115.2 (C), 118.4 (CH), 121.3, 121.4 (C), 124.8, 135.8, 137.9, 141.0 (CH), 154.0, 159.1, 160.2 (C), 168.9 (C=O, ester), 177.5 (C=O, ketone). IR (KBr, cm^{-1}): $\tilde{\nu}$=3436 (m), 2977 (m), 2934 (m), 1724 (s), 1669 (s), 1612 (s), 1586 (s), 1563 (m), 1491 (m), 1444 (s), 1398 (s), 1307 (m), 1282 (m), 1208 (m), 1180 (s), 1107 (s), 780 (m). UV–vis (CH_3CN, nm): λ_{max} (lg ε): 335 (3.84), 290 (4.26), 240 (4.42), 229 (4.48). MS (EI, 70 eV): *m*/*z* (%)=326 (M^+, 67), 268 ($[M-CH(CH_3)_2]^+$, 15), 239 ($[M-CO_2CH(CH_3)_2)]^+$, 100), 211 (16), 196 (7), 133 (8), 43 ($[CH(CH_3)_2)]^+$, 95). HRMS (FT-ICR) calcd for $C_{19}H_{20}NO_4$ ($[M+1]^+$): 326.13868; found: 326.13826.

3.2.6. Ethyl 2-(4-aza-8-isopropylxanthon-3-yl)acetate (**4f**)

Starting with 3-cyano-6-isopropylchromone **1d** (145 mg, 0.68 mmol), Me_3SiOTf (196 mg, 0.16 mL, 0.88 mmol), **2a** (242 mg, 0.88 mmol), CH_2Cl_2 (20 mL), EtOH (25 mL) and triethylamine (526 mg, 0.72 mL, 5.20 mmol), **4f** was isolated as a yellow solid (91 mg, 41%), mp=140 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.28 (m, 9H, CH_3), 3.12 (sept, 1H, $CH(CH_3)_2$), 3.98 (s, 2H, CH_2), 4.22 (q, ^3J=7.2 Hz, OCH_2CH_3), 7.45 (d, ^3J=7.9 Hz, 1H, Ar), 7.53 (d, ^3J=8.6 Hz, 1H, Ar), 7.66 (dd, ^3J=8.6 Hz, ^4J=2.3 Hz, 1H, Ar), 8.15 (d, ^4J=2.3 Hz, 1H, Ar), 8.70 (d, ^3J=7.9 Hz, 1H, Ar). ^{13}C NMR (DEPT, 75.5 MHz, $CDCl_3$): δ=14.2 (OCH_2CH_3), 23.9 ($CH(CH_3)_2$), 33.7 ($CH(CH_3)_2$), 44.2 (CH_2), 61.5 (OCH_2CH_3), 115.3 (C), 118.4, 121.3 (CH), 121.4 (C), 123.5, 134.6, 138.0 (CH), 145.6, 154.1, 159.9, 160.0 (C), 169.4 (C=O, ester), 177.6 (C=O, ketone). IR (KBr, cm^{-1}): $\tilde{\nu}$=3428 (m), 3340 (m), 3190 (m), 2962 (m), 2933 (m), 1724 (m), 1666 (s), 1623 (s), 1616 (s), 1536 (s), 1459 (s), 1329 (m), 1266 (m), 1227 (m), 1156 (m), 1095 (m), 1034 (m), 808 (w). UV–vis (CH_3CN, nm): λ_{max} (lg ε): 334 (3.79), 291 (4.08), 280 (3.99), 248 (4.39). GC–MS (EI, 70 eV): *m*/*z* (%)=325 (M, 46), 310 (100), 267 (11), 238 (23). HRMS (EI, 70 eV) calcd for $C_{19}H_{19}NO_4$: 325.1314; found: 325.1314±2 ppm.

3.2.7. Ethyl 2-(4-aza-8-chloroxanthon-3-yl)acetate (**4g**)

Starting with 6-chloro-3-cyanochromone (**1e**) (148 mg, 0.72 mmol), Me_3SiOTf (209 mg, 0.17 mL, 0.94 mmol), **2a** (258 mg, 0.94 mmol), CH_2Cl_2 (16 mL), EtOH (20 mL) and triethylamine (476 mg, 0.65 mL, 4.70 mmol), **4g** was isolated as a yellow solid (85 mg, 37%), mp=118 °C. ^1H NMR (300 MHz, DMSO-d_6): δ=1.21 (t, ^3J=7.2 Hz, 3H, OCH_2CH_3), 4.05 (s, 2H, CH_2), 4.13 (q, ^3J=7.2 Hz, 2H, OCH_2CH_3), 7.61 (d, ^3J=7.9 Hz, 1H, Ar), 7.80 (d, ^3J=8.9 Hz, 1H, Ar), 7.96 (dd, ^3J=8.9 Hz, ^4J=2.6 Hz, 1H, Ar), 8.10 (d, ^4J=2.6 Hz, 1H, Ar), 8.62 (d, ^3J=6.9 Hz, 1H, Ar). ^{13}C NMR (APT, 75.5 MHz, DMSO-d_6): δ=13.9 (CH_3), 43.2 (CH_2), 60.6 (OCH_2), 114.4 (C), 120.8 (CH), 122.2 (C), 122.3, 124.7 (CH), 129.0 (C), 135.5, 137.3 (CH), 153.7, 160. 0, 160.8 (C), 169.1 (C=O, ester), 175.6 (C=O, ketone). IR (KBr, cm^{-1}): $\tilde{\nu}$=2978 (m), 2931 (m), 1727 (s), 1673 (s), 1610 (s), 1559 (m), 1472 (s), 1434 (s), 1395 (s), 1338 (m), 1258 (s), 1210 (s), 1186 (s), 1108 (m), 1027 (m), 839 (w), 784 (w). UV–vis (CH_3CN, nm): λ_{max} (lg ε): 334 (3.85), 292 (4.11), 230 (4.45). MS (EI, 70 eV): *m*/*z* (%)=319 (M^+, ^{37}Cl, 21), 317 (M^+, ^{35}Cl, 67), 272 (19), 245 (100), 216 (21), 189 (5), 153 (7), 126 (10), 64 (12).

3.2.8. *Ethyl 2-(4-aza-6,8-dichloroxanthon-3-yl)acetate (**4h**)*

Starting with 6,8-dichloro-3-cyanochromone (**1f**) (162 mg, 0.67 mmol), Me_3SiOTf (194 mg, 0.16 mL, 0.87 mmol), **2a** (239 mg, 0.87 mmol), CH_2Cl_2 (15 mL), EtOH (20 mL) and triethylamine (365 mg, 0.50 mL, 3.60 mmol), **4h** was isolated as a yellow solid (113 mg, 48%), mp=155 °C. ^1H NMR (300 MHz, DMSO-d_6): δ=1.31 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 3.74 (s, 2H, CH_2), 4.30 (q, ^3J=7.1 Hz, 2H, OCH_2CH_3), 6.92 (dd, ^3J=6.9 Hz, ^4J=2.2 Hz, 1H, Ar), 7.64 (dd, ^3J=6.9 Hz, ^4J=2.1 Hz, 1H, Ar), 7.87 (d, ^4J=2.6 Hz, 1H, Ar), 8.06 (d, ^4J=2.6 Hz, 1H, Ar). ^{13}C NMR (DEPT, 75.5 MHz, DMSO-d_6): δ=13.9 (CH_3), 55.2 (CH_2), 62.3 (OCH_2), 113.9, 121.9 (CH), 122.1 (C), 123.3 (CH), 124.8, 129.5 (C), 133.3 (CH), 147.8, 155.1, 156.2, 160.8 (C), 164.9 (C=O, ester), 173.4 (C=O, ketone). IR (KBr, cm^{-1}): $\tilde{\nu}$=3423 (m), 3352 (s), 3260 (m), 3134 (m), 1724 (s), 1675 (s), 1613 (s), 1572 (s), 1543 (s), 1512 (s), 1459 (s), 1387 (m), 1323 (m), 1293 (s), 1243 (s), 1176 (s), 1021 (m), 858 (m), 777 (m), 707 (m). UV–vis (CH_3CN, nm): λ_{max} (lg ε): 431 (2.85), 271 (4.19), 221 (3.80). MS (EI, 70 eV): m/z (%)=356 ($[M]^+$, $[2\times{}^{37}Cl]$, 3), 354 ($[M]^+$, $[^{37}Cl]$, $[^{35}Cl]$, 11), 352 ($[M]^+$, $[2\times{}^{35}Cl]$, 22), 307 (12), 279 (16), 258 (22), 224 (74), 189 (77), 149 (100), 122 (83), 97 (11), 69 (14).

3.2.9. *Ethyl 2-(4-aza-8-bromoxanthon-3-yl)acetate (**4i**)*

Starting with 6-bromo-3-cyanochromone (**1g**) (170 mg, 0.68 mmol), Me_3SiOTf (196 mg, 0.16 mL, 0.88 mmol), **2a** (243 mg, 0.88 mmol), CH_2Cl_2 (15 mL), EtOH (20 mL) and triethylamine (455 mg, 0.62 mL, 4.50 mmol), **4i** was isolated as a yellow solid (84 mg, 34%), mp=127 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.26 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 3.98 (s, 2H, CH_2), 4.22 (q, ^3J=7.1 Hz, 2H, OCH_2CH_3), 7.44 (d, ^3J=7.9 Hz, 1H, Ar), 7.45 (d, ^3J=8.5 Hz, 1H, Ar), 7.57 (dd, ^3J=8.5 Hz, ^4J=2.2 Hz, 1H, Ar), 8.08 (d, ^4J=2.2 Hz, 1H, Ar), 8.67 (d, ^3J=7.9 Hz, 1H, Ar). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ=14.2 (CH_3), 20.9, 44.1 (CH_2), 61.5 (OCH_2), 115.3 (C), 118.3 (CH), 121.3 (C), 121.3, 126.0 (CH), 134.7 (C), 136.9, 137.9 (CH), 153.9, 159.9, 160.0 (C), 169.4 (C=O, ester), 177.44 (C=O, ketone). IR (KBr, cm^{-1}): $\tilde{\nu}$=2981 (m), 2934 (m), 1728 (s), 1669 (s), 1614 (s), 1409 (m), 1433 (s), 1397 (s), 1339 (m), 1305 (m), 1278 (m), 1206 (s), 1174 (s), 1137 (m), 1029 (m), 816 (m), 782 (m). UV–vis (CH_3CN, nm): λ_{max} (lg ε): 335 (3.89), 290 (4.28), 240 (4.44), 228 (4.51). MS (EI, 70 eV): m/z (%)=363 (M^+, ^{81}Br, 2), 361 (M^+, ^{79}Br, 3), 252/250 (10/12), 225 (100), 196 (34), 148 (23), 86 (32).

3.2.10. *Isopropyl 2-(4-aza-8-bromoxanthon-3-yl)acetate (**4j**)*

Starting with 6-bromo-3-cyanochromone (**1g**) (162 mg, 0.65 mmol), Me_3SiOTf (187 mg, 0.15 mL, 0.84 mmol), **2c** (242 mg, 0.84 mmol), CH_2Cl_2 (15 mL), EtOH (20 mL) and triethylamine (425 mg, 0.58 mL, 4.20 mmol), **4j** was isolated as a yellow solid (66 mg, 32%), mp=128 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.35 (d, ^3J=6.3 Hz, 6H, $CH(CH_3)_2$), 3.96 (s, 2H, CH_2), 5.09 (sept, ^3J=6.3 Hz, 1H, $CH(CH_3)_2$), 7.48 (m, 2H, Ar), 7.83 (dd, ^3J=8.9 Hz, ^4J=2.6 Hz, 1H, Ar), 8.39 (d, ^4J=2.4 Hz, 1H, Ar), 8.65 (d, ^3J=7.9 Hz, 1H, Ar). ^{13}C NMR (DEPT, 75.5 MHz, $CDCl_3$): δ=21.8 ($OCH(CH_3)_2$), 44.4 (CH_2), 69.2 ($OCH(CH_3)_2$), 115.0, 117.9 (C), 120.4, 121.9 (CH), 122.9 (C), 129.2, 137.9, 138.4 (CH), 154.4, 159.4, 160.8 (C), 168.8 (C=O, ester), 176.1 (C=O, ketone). IR (KBr, cm^{-1}): $\tilde{\nu}$=2931 (m), 2249 (m), 1650 (m), 1492 (s), 1458 (s), 1423 (m), 1403 (s), 752 (s). MS (EI, 70 eV): m/z (%)=377 (M^+, ^{81}Br, 33), 375 (M^+, ^{79}Br, 34), 319/317 ($[M-O^iPr]^+$, 6/6), 292/290 ($[M-CO_2{}^iPr]^+$, 34/36), 266 (33), 251 (54), 182 (7), 121 (15), 86 (9), 43 ($^iPr^+$, 100). HRMS (EI) calcd for $C_{17}H_{14}BrNO_4$ (M^+, ^{79}Br): 375.0106; found: 375.0106±2 ppm.

3.2.11. *Methyl 2-(4-aza-2-methylxanthon-3-yl)acetate (**4k**) and 10-cyano-7-hydroxy-8-methyldibenzo[b,d]pyran-6-one (**5a**)*

Starting with **1a** (171 mg, 1.0 mmol), Me_3SiOTf (289 mg, 1.3 mmol) and **2d** (357 mg, 1.3 mmol), **5a** (85 mg, 34%) was isolated as a yellow solid, mp=238 °C. The synthesis of **5a** has been previously reported.[10] ^1H NMR (300 MHz, $CDCl_3$): δ=2.38 (s, 3H, CH_3), 7.44 (m, 2H, Ar), 7.61 (m, 1H, Ar), 7.87 (s, 1H, Ar), 9.18 (dd, ^3J=2.3 Hz, ^4J=1.4 Hz, 1H, Ar), 12.66 (s, 1H, OH). ^{13}C NMR (DEPT, 75.5 MHz, $CDCl_3$): δ=15.5 (CH_3), 96.1 (*C*–CN), 106.2 (CN), 116.7 (C), 117.9 (CH), 119.5 (C), 125.0, 125.7 (CH), 127.5 (C), 132.1 (CH), 135.3 (C), 143.8 (CH), 150.3, 164.7, 165.0 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3420 (w), 2970 (w), 2830 (w), 2212 (s), 1684 (s), 1600 (s), 1459 (s), 1412 (m), 1388 (m), 1326 (m), 1262 (s), 1219 (m), 1170 (s), 1147 (s), 1112 (s), 811 (m), 764 (s), 666 (m). UV–vis (CH_3CN, nm): λ_{max} (lg ε): 350 (3.81), 338 (3.34), 311 (4.02), 299 (3.95), 288 (3.96), 254 (4.48), 206 (4.52). Fluorescence (CH_3CN, nm): $F\lambda_{max}$ (λ_{Ex}): 489 (345). MS (EI, 70 eV): m/z (%)=251 (M^+, 100), 222 (18), 194 (14), 177 (8), 140 (10), 71 (6). Anal. Calcd (%) for $C_{15}H_9NO_3$ (250.7): C, 71.98; H, 3.61; N, 5.60. Found: C, 71.71; H, 4.20; N, 5.70. In a second fraction, **4k** was detected, which could not be isolated in pure form. Signals of **4k** in the mixture with **5a**: ^1H NMR (300 MHz, $CDCl_3$): δ=2.47 (s, 3H, CH_3), 3.76 (s, 3H, OMe), 3.82 (s, 2H, CH_2), 7.38 (m, 2H, Ar), 7.76 (m, 2H, Ar), 8.47 (s, 1H, Ar). MS (EI, 70 eV): m/z (%)=283 (M^+, 72), 268 (38), 251 (223, 100), 224 (21), 197 (14), 121 (12).

3.2.12. *Ethyl 2-(7-chloro-3-methyl-5-oxo-5H-chromeno[2,3-b]pyrid-2-yl)acetate (**4l**)*

Starting with 6-chlorocyanochromone (**1e**) (150 mg, 0.60 mmol), **2e** (288 mg, 0.78 mmol), Me_3SiOTf (0.14 mL, 0.78 mmol) and NEt_3 (0.16 mL, 1.20 mmol), **4l** was isolated as a colourless solid (98 mg, 41%), mp=190 °C. ^1H NMR (250 MHz, $CDCl_3$): δ=1.27 (t, 3H, ^3J=7.1 Hz, CH_3), 2.46 (s, 3H, CH_3), 3.99 (s, 2H, CH_2), 4.28 (q, 2H, ^3J=6.9 Hz, OCH_2CH_3), 7.55 (d, 1H, ^3J=8.9 Hz, ArH), 7.71 (dd, 1H, ^3J=7.91 Hz, ^4J=2.5 Hz, ArH), 8.26 (d, 1H, ^4J=2.5 Hz, ArH), 8.46 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.1, 18.1 (CH_3), 42.3, 61.4 (CH_2), 115.6 (C), 120.2 (CH), 122.5 (2C, C), 125.9 (CH), 130.0 (C), 135.5, 138.1 (CH), (C), 154.0, 157.1, 159.5 (C), 169.0, 176.5 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3092 (w), 2977 (m), 2921 (w), 1724 (s), 1667 (s), 1603 (m), 1439 (s), 1270 (s), 1180 (s), 843 (s), 788 (m). GC–MS (EI, 70 eV): m/z (%)=333 (M^+, ^{37}Cl, 27), 331 (M^+, ^{35}Cl, 87), 285 (70), 257 (100), 230 (29), 194 (4), 126 (15), 63 (10). HRMS (ESI) calcd for $C_{18}H_{16}NO_4Cl$ (M^{++}, ^{35}Cl): 331.06059; found: 331.060408.

3.2.13. *Ethyl 2-(4-aza-2-ethylxanthon-3-yl)acetate (**4m**) and 10-cyano-8-ethyl-7-hydroxydibenzo[b,d]pyran-6-one (**5b**)*

Starting with **1a** (171 mg, 1.0 mmol), Me_3SiOTf (289 mg, 1.3 mmol) and **1f** (393 mg, 1.3 mmol), **4m** (53 mg, 17%) was isolated as a yellow solid and **5b** was isolated as a colourless solid (90 mg, 34%). The synthesis of **5b** has been previously reported.[10]

Compound **4m**: mp=125 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.25 (t, ^3J=8.9 Hz, 3H, CH_2CH_3), 1.33 (t, ^3J=7.5 Hz, 3H, OCH_2CH_3), 2.80 (q, ^3J=8.9 Hz, 2H, CH_2CH_3), 4.02 (s, 2H, CH_2), 4.21 (q, ^3J=7.5 Hz, 2H, OCH_2CH_3), 7.42 (m, 1H, Ar), 7.61 (dd, ^3J=8.8 Hz, ^4J=0.6 Hz, 1H, Ar), 7.76 (m, 1H, Ar), 8.32 (dd, ^3J=8.0 Hz, ^4J=1.7 Hz, 1H, Ar), 8.53 (s, 1H, Ar). ^{13}C NMR (DEPT, 75.5 MHz, $CDCl_3$): δ=14.0 (OCH_2CH_3), 14.2 (CH_2CH_3), 24.5 (CH_2CH_3), 41.8 (CH_2), 61.4 (OCH_2CH_3), 115.6 (C), 118.5 (CH), 121.6 (C), 124.5, 126.9, 135.4 (CH), 135.9 (C), 136.4 (CH), 155.8, 158.1, 158.6 (C), 169.4 (CO, ester), 177.7 (C=O, ketone). IR (KBr, cm^{-1}): $\tilde{\nu}$=3390 (m), 3150 (m), 2984 (m), 2932 (m), 1733 (s), 1663 (s), 1612 (s), 1561 (s), 1471 (s), 1424 (s), 1316 (s), 1266 (s), 1229 (m), 1184 (m), 1149 (s), 1119 (s), 1028 (m), 909 (w), 734 (m). UV–vis (CH_3CN, nm): λ_{max} (lg ε): 339 (3.93), 289 (4.09), 229 (4.47). MS (EI, 70 eV): m/z (%)=311 (M^+, 100), 265 (42), 237 (97), 210 (15), 175 (13), 153 (12), 86 (19), 57 (76). HRMS (EI) calcd for $C_{18}H_{17}NO_4$ (M^+): 311.1158; found: 311.1158±2 ppm.

Compound **5b**: mp=183 °C. ^1H NMR (300 MHz, $CDCl_3$): δ=1.30 (t, ^3J=7.2 Hz, 3H, CH_2CH_3), 2.78 (q, ^3J=7.2 Hz, 2H, CH_2CH_3), 7.45 (m, 2H, Ar), 7.60 (m, 1H, Ar), 7.88 (s, 1H, Ar), 9.19 (dd, ^3J=2.3 Hz, ^4J=1.4 Hz, 1H, Ar), 12.71 (s, 1H, OH). ^{13}C NMR (DEPT, 75.5 MHz, $CDCl_3$): δ=13.0 (CH_3), 22.5 (CH_2), 96.3, 106.3, 116.8 (C), 117.9 (CH), 119.8 (C), 125.1, 125.8, 132.2 (CH), 133.2, 135.3 (C), 142.3 (CH), 150.3, 164.2, 165.2 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3150 (w), 2971 (w), 2939 (w), 2877 (w), 2219 (m), 1675 (s), 1600 (s), 1459 (s), 1440 (m), 1422 (s), 1361 (w), 1338 (m), 1316 (m), 1273 (s), 1250 (m), 1221 (m), 1169 (s), 1155 (m), 1115 (m), 817 (s), 796 (m), 764 (s). UV–vis (CH_3CN, nm): λ_{max} (lg ε): 383

(3.11), 351 (3.78), 338 (3.79), 311 (3.97), 300 (3.92), 289 (3.93), 255 (4.45), 208 (4.44). MS (EI, 70 eV): *m*/*z* (%)=265 (M^+, 64), 251 (94), 211 (3), 58 (7), 32 (23). HRMS (EI) calcd for $C_{16}H_{11}NO_3$ (M^+): 265.0739; found: 265.0739±2 ppm.

3.2.14. *Ethyl 2-(7-chloro-3-ethyl-5-oxo-5H-chromeno[2,3-b]pyrid-2-yl)acetate (**4n**)*

Starting with 6-chlorocyanochromone (**1e**) (150 mg, 0.60 mmol), 1,3-bis(silyl enol ether) **2f** (305 mg, 0.78 mmol), Me_3SiOTf (0.14 mL, 0.78 mmol) and NEt_3 (0.16 mL, 1.20 mmol), **4n** was isolated as a highly viscous yellowish oil (150 mg, 46%). ^1H NMR (250 MHz, $CDCl_3$): δ=1.25 (t, 3H, ^3J=7.3 Hz, CH_3), 1.33 (t, 3H, ^3J=7.5 Hz, CH_3), 2.81 (q, 2H, ^3J=6.9 Hz, CH_2CH_3), 4.00 (s, 2H, CH_2), 4.20 (q, 2H, ^3J=7.1 Hz, OCH_2CH_3), 7.55 (d, 1H, ^3J=8.9 Hz, ArH), 7.70 (dd, 1H, ^3J=7.91 Hz, ^4J=1.5 Hz, ArH), 8.28 (d, 1H, ^4J=2.5 Hz, ArH), 8.51 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=13.9, 14.1 (CH_3), 29.6, 41.7, 61.4 (CH_2), 115.2 (C), 120.2 (CH), 122.5 (C), 125.9 (CH), 130.0 (C), 135.5 (CH), 136.3 (C), 136.4 (CH), 154.0, 157.2, 159.0 (C), 169.2, 176.5 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=2956 (w), 2921 (m), 2935 (w), 1726 (s), 1699 (s), 1583 (m), 1428 (s), 1180 (s), 1024 (s), 789 (s), 710 (m). GC–MS (EI, 70 eV): *m*/*z* (%)=347 (M^+, ^{37}Cl, 24), 345 (M^+, ^{35}Cl), 299 (34), 271 (100), 257 (29), 208 (4), 139 (15), 63 (10). HRMS (ESI) calcd for $C_{18}H_{16}NO_4Cl$ (M^+, ^{35}Cl): 345.0764; found: 345.07626.

3.2.15. *Ethyl 2-(3-ethyl-7,8-dimethyl-5-oxo-5H-chromeno[2,3-b]-pyrid-2-yl)acetate (**4o**)*

Starting with 6,7-dimethylcyanochromone (**1h**) (150 mg, 0.75 mmol), 1,3-bis(silyl enol ether) **2f** (302 mg, 0.97 mmol), Me_3SiOTf (0.17 mL, 0.97 mmol) and NEt_3 (0.20 mL, 1.5 mmol), **4o** was isolated as a colourless solid (100 mg, 38%), mp=149 °C. ^1H NMR (250 MHz, $CDCl_3$): δ=1.25 (t, 3H, ^3J=7.1 Hz, CH_3), 1.34 (t, 3H, ^3J=7.5 Hz, CH_3), 2.37 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.79 (q, 2H, ^3J=7.4 Hz, CH_2CH_3), 4.0 (s, 2H, CH_2), 4.21 (q, 2H, ^3J=7.2 Hz, OCH_2CH_3), 7.34 (s, 1H, ArH), 8.00 (s, 1H, ArH), 8.51 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.0, 14.1, 19.2, 20.6 (CH_3), 24.4, 41.7, 61.3 (CH_2), 115.6 (C), 118.5 (CH), 119.4 (C), 126.2 (CH), 133.7, 135.5 (C), 136.3 (CH), 146.2, 154.2, 157.9, 158.0 (C), 169.4, 177.4 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=2970 (w), 2921 (m), 2856 (w), 1727 (s), 1663 (s), 1607 (m), 1425 (s), 1181 (s), 1158 (s), 1026 (s), 789 (s), 739 (m). GC–MS (EI, 70 eV): *m*/*z* (%)=339 (M^+, 96), 293 (61), 265 (100), 250 (16), 222 (7), 1194 (15), 91 (10). HRMS (ESI) calcd for $C_{20}H_{21}NO_4$ $[M]^+$: 339.14651; found: 339.14641.

3.2.16. *10-Cyano-7-hydroxy-8-n-propyldibenzo[b,d]pyran-6-one (**5c**)*

Starting with **1a** (205 mg, 1.2 mmol), Me_3SiOTf (347 mg, 0.28 mL, 1.56 mmol) and **2g** (428 mg, 1.56 mmol), **5c** (124 mg, 37%) was isolated as a yellow solid, mp=172 °C. The synthesis of **5c** has been previously reported.[10] ^1H NMR (300 MHz, $CDCl_3$): δ=1.01 (t, ^3J=7.4 Hz, 3H, CH_3), 1.69 (m, 2H, CH_2CH_3), 2.74 (t, ^3J=7.3 Hz, 2H, $ArCH_2$), 7.45 (m, 2H, Ar), 7.61 (m, 1H, Ar), 7.86 (s, 1H, Ar), 9.20 (dd, ^3J=8.1 Hz, ^4J=1.3 Hz, 1H, Ar), 12.69 (s, 1H, Ar). ^{13}C NMR (DEPT, 75.5 MHz, $CDCl_3$): δ=13.8 (CH_3), 21.9 (CH_2CH_3), 31.2 ($ArCH_2$), 96.1, 106.2, 116.6 (C), 117.8 (CH), 119.6 (C), 124.9, 125.7 (CH), 131.7 (C), 132.1 (CH), 135.2 (C), 143.1 (CH), 150.2, 164.5, 165.0 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3434 (m), 2961 (m), 2875 (m), 2219 (m), 1678 (s), 1602 (s), 1459 (s), 1416 (s), 1357 (m), 1325 (s), 1270 (s), 1224 (m), 1168 (s), 1115 (m), 814 (m), 791 (w), 761 (m). UV–vis (CH_3CN, nm): λ_{max} (lg ε): 351 (3.83), 339 (3.86), 311 (4.03), 299 (3.96), 289 (3.96), 255 (4.48), 208 (4.47). MS (EI, 70 eV): *m*/*z* (%)=279 (M^+, 43), 264 (12), 250 (100), 222 (4), 206 (2), 164 (4), 139 (5), 77 (50), 43 (4). HRMS (EI) calcd for $C_{17}H_{13}NO_3$ (M^+): 279.0895; found: 279.0895±2 ppm.

3.2.17. *8-n-Butyl-10-cyano-7-hydroxydibenzo[b,d]pyran-6-one (**5d**)*

Starting with **1a** (257 mg, 1.5 mmol), Me_3SiOTf (433 mg, 1.95 mmol) and **2h** (645 mg, 1.95 mmol), **5d** (185 mg, 42%) was isolated as a colourless solid, mp=132 °C. The synthesis of **5d** has been previously reported.[10] ^1H NMR (300 MHz, $CDCl_3$): δ=0.98 (t, ^3J=7.3 Hz, 3H, CH_3), 1.42 (m, 2H, CH_2), 1.65 (m, 2H, CH_2), 2.74 (t, ^3J=7.6 Hz, 2H, $ArCH_2$), 7.39–7.47 (br m, 2H, Ar), 7.60 (m, 1H, Ar), 7.84 (s, 1H, Ar), 9.15 (dd, ^3J=8.3 Hz, ^4J=1.4 Hz, 1H, Ar), 12.67 (s, 1H, OH). ^{13}C NMR (DEPT, 75.5 MHz, $CDCl_3$): δ=13.9 (CH_3), 22.5, 29.0, 30.9 (CH_2), 96.2, 106.3, 116.7 (C), 117.9 (CH), 119.7 (C), 125.0, 125.7 (CH), 132.0 (C), 132.2 (CH), 135.2 (C), 143.1 (CH), 150.3, 164.5, 165.1 (C). IR (KBr, cm^{-1}): $\tilde{\nu}$=3126 (w), 2958 (w), 2929 (w), 2866 (w), 2219 (m), 1679 (s), 1602 (s), 1458 (s), 1414 (s), 1352 (m), 1326 (s), 1268 (s), 1213 (m), 1169 (s), 1114 (m), 805 (m), 791 (m), 765 (s), 739 (m), 668 (m). UV–vis (CH_3CN, nm): λ_{max} (lg ε): 351 (3.86), 339 (3.88), 311 (4.04), 299 (3.95), 289 (3.96), 255 (4.50), 207 (4.53). Fluorescence (CH_3CN, nm): $F\lambda_{max}$ (λ_{Ex}): 479 (345). MS (EI, 70 eV): *m*/*z* (%)=293 (M^+, 100), 250 (26), 222 (3), 210 (3), 164 (79), 161 (18), 70 (3). HRMS (EI) calcd for $C_{18}H_{15}NO_3$ (M^+): 293.1052; found: 293.1052±2 ppm.

3.2.18. *Ethyl 2-(3-heptyl-5-oxo-5H-chromeno[2,3-b]pyrid-2-yl)acetate (**4r**)*

Starting with **1a** (343 mg, 2.0 mmol), **2i** (967 mg, 2.61 mmol), Me_3SiOTf (0.47 mL, 2.61 mmol) and NEt_3 (1.4 mL, 10.0 mmol), **4r** was isolated as a colourless solid (195 mg, 25%), mp=117 °C. ^1H NMR (250 MHz, $CDCl_3$): δ=0.86 (t, ^3J=6.7 Hz, 3H, CH_2CH_3), 1.25 (t, ^3J=7.2 Hz, 3H, CH_2CH_3), 1.34 (m, 8H, $CH_2CH_2C_4H_8CH_3$), 1.66 (m, 2H, $CH_2CH_2C_5H_{11}$), 2.72 (t, ^3J=8.0 Hz, 2H, $CH_2C_6H_{13}$), 3.99 (s, 2H, CH_2COO), 4.19 (q, ^3J=7.16 Hz, 2H, OCH_2CH_3), 7.39 (m, 1H, Ar), 7.56 (d, ^3J=8.5 Hz, 1H, Ar), 7.74 (ddd, ^3J=8.7 Hz, ^4J=1.7 Hz, 1H, Ar), 8.28 (dd, ^3J=1.5, 8.0 Hz, 1H, Ar), 8.47 (s, 1H, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=14.0 (CH_3), 14.1 (CH_3), 22.6, 29.0, 29.3, 30.0, 31.5, 31.7, 41.7 (CH_2), 61.4 (OCH_2CH_3), 115.4 (C), 118.4 (CH), 121.6 (C), 124.4, 126.6 (CH), 134.8 (C), 135.4, 137.1 (CH), 155.7, 158.0, 158.6, 169.4 (C), 177.6 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3453 (br, w), 3051 (w), 2976 (m), 2951 (m), 2922 (s), 2849 (m), 1733 (s), 1669 (s), 1613 (s), 1560 (w), 1447 (s), 1428 (s), 1367 (m), 1340 (m), 1320 (m), 1277 (m), 1231 (m), 1205 (m), 1176 (m), 1115 (m), 1035 (m), 961 (w), 943 (w), 875 (w), 764 (m). MS (EI, 70 eV): *m*/*z* (%)=381 (M^+, 12), 294 (100), 336 (8), 310 (79), 264 (29), 236 (84), 224 (61). HRMS (EI) calcd for $C_{23}H_{27}NO_4$ (M^+): 381.19346; found: 381.19345.

3.2.19. *Ethyl 2-(7-chloro-3-heptyl-5-oxo-5H-chromeno[2,3-b]-pyrid-2-yl)acetate (**4s**)*

Starting with 3-chloro-3-cyanochromone **1e** (150 mg, 0.7 mmol), **2i** (340 mg, 0.91 mmol), Me_3SiOTf (0.21 mL, 0.91 mmol) and NEt_3 (0.45 mL, 3.5 mmol), **4s** was isolated as a colourless solid (110 mg, 38%), mp=146 °C. ^1H NMR (250 MHz, $CDCl_3$): δ=0.86 (t, ^3J=6.7 Hz, 3H, CH_2CH_3), 1.25 (t, ^3J=7.1 Hz, 3H, CH_2CH_3), 1.35 (m, 8H, $CH_2CH_2C_4H_8CH_3$), 1.66 (m, 2H, $CH_2CH_2C_5H_{11}$), 2.72 (t, ^3J=8.0 Hz, 2H, $CH_2C_6H_{13}$), 3.99 (s, 2H, CH_2COO), 4.19 (q, ^3J=7.16 Hz, 2H, OCH_2CH_3), 7.53 (d, ^3J=8.8 Hz, 1H, Ar), 7.68 (dd, ^4J=2.6 Hz, ^3J=8.9 Hz, 1H, Ar), 8.25 (d, ^3J=2.5 Hz, 1H, Ar), 8.46 (s, 1H, Ar). ^{13}C NMR (250 MHz, $CDCl_3$): δ=14.0, 14.1 (CH_3), 22.6, 29.0, 29.4, 30.0, 31.5, 31.7, 41.8 (CH_2), 61.4 (OCH_2CH_3), 115.1 (C), 120.2 (CH), 122.5 (C), 126.0 (CH), 130.3, 135.2 (C), 135.5, 137.2 (CH), 154.1, 157.8, 159.1, 169.3 (C), 176.6 (C=O). IR (ATR, cm^{-1}): $\tilde{\nu}$=2923 (br, w), 1730 (m), 1667 (s), 1556 (w), 1431 (s), 1337 (m), 1314 (w), 1271 (m), 1173 (m), 1089 (m), 968 (w), 891 (w), 791 (m), 712 (m), 578 (m), 542 (w). MS (EI, 70 eV): *m*/*z* (%)=417 (M^+, ^{37}Cl, 4), 415 (M^+, ^{35}Cl, 13), 328 (100), 370 (8), 344 (61), 298 (25), 270 (64), 207 (7). HRMS (EI) calcd for $C_{23}H_{26}ClNO_4$ (M^+, ^{35}Cl): 415.155487; found: 415.15449.

3.2.20. *Methyl 2-(3-allyl-5-oxo-5H-chromeno[2,3-b]pyrid-2-yl)-acetate (**4t**)*

Starting with 3-cyanochromone (**1a**) (400 mg, 2.33 mmol), **2j** (917 mg, 3.0 mmol), Me_3SiOTf (0.54 mL, 3.0 mmol) and NEt_3 (0.6 mL, 4.66 mmol), **4t** was isolated as a colourless solid (275 mg, 38%), mp=124 °C. ^1H NMR ($CDCl_3$, 250 MHz): δ=3.48 (d, ^3J=6.1 Hz, 2H, CH_2CHCH_2), 3.68 (s, 3H, OCH_3), 3.96 (s, 2H, CH_2), 4.98–5.16 (m, 2H, $CHCH_2$), 5.86–5.96 (m, 1H, $CHCH_2$), 7.32–7.38 (m, 1H, ArH), 7.53 (dd, ^3J=8.5 Hz, ^4J=0.6 Hz, 1H, ArH), 7.67–7.74 (m, 1H, ArH), 8.23 (dd, ^3J=7.8 Hz, ^4J=1.5 Hz, 1H, ArH), 8.44 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=35.8, 41.5 (CH_2), 52.4 (CH_3), 115.5 (C), 117.8 (CH_2), 118.4 (CH), 121.5 (C), 124.5, 126.6 (CH), 132.0 (C), 134.5, 135.5, 138.1 (CH), 155.6, 158.3, 158.8 (C), 169.6, 177.4 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3065 (w), 2995 (w), 2841 (w), 1738 (s), 1668 (s), 1609 (s), 1559 (m), 1429 (s), 1344 (s), 1269 (m), 1190 (s), 1165 (m), 997 (m), 916 (w), 766 (s), 670 (w). GC–MS (EI, 70 eV): m/z (%)=309 (M^+, 85), 278 (11), 249 (100), 236 (35), 220 (16), 191 (5), 152 (5), 124 (6), 77 (8), 51 (3). Anal. Calcd (%) for $C_{18}H_{15}NO_4$: C, 69.89; H, 4.89; N, 4.53. Found: C, 6980; H, 4.97; N, 4.30.

3.2.21. *Methyl 2-(3-allyl-7-chloro-5-oxo-5H-chromeno[2,3-b]-pyrid-2-yl)acetate (**4u**)*

Starting with **1e** (200 mg, 0.97 mmol), **2j** (380 mg, 1.26 mmol), Me_3SiOTf (0.22 mL, 1.26 mmol) and NEt_3 (0.27 mL, 1.94 mmol), **4u** was isolated as a colourless solid (100 mg, 30%), mp=177 °C. ^1H NMR ($CDCl_3$, 250 MHz): δ=3.64 (d, ^3J=6.3 Hz, 2H, CH_2CHCH_2), 3.84 (s, 3H, OCH_3), 4.12 (s, 2H, CH_2), 5.14–5.34 (m, 2H, $CHCH_2$), 5.98–6.12 (m, 1H, $CHCH_2$), 7.65 (d, ^3J=8.9 Hz, 1H, ArH), 7.81 (dd, ^3J=8.5 Hz, ^4J=2.5 Hz, 1H, ArH), 8.36 (d, ^4J=2.3 Hz, 1H, ArH), 8.59 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=35.8, 41.5 (CH_2), 52.4 (CH_3), 115.2 (C), 117.9 (CH_2), 120.0 (CH), 122.5 (C), 126.0 (CH), 130.4, 132.4 (C), 134.3, 135.6, 138.1 (CH), 154.0, 158.2, 159.2 (C), 169.5, 176.4 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3052 (w), 2999 (w), 2950 (w), 1738 (s), 1667 (s), 1608 (s), 1475 (s), 1348 (s), 1311 (m), 1272 (s), 1169 (s), 1137 (m), 1000 (m), 639 (w). GC–MS (EI, 70 eV): m/z (%)=345 (M^+, ^{37}Cl, 20), 343 (M^+, ^{35}Cl, 60), 285 (^{37}Cl, 43), 283 (^{35}Cl, 100), 270 (29), 248 (10), 219 (7), 178 (10), 149 (13), 97 (19), 69 (55), 57 (50). Anal. Calcd (%) for $C_{18}H_{14}ClNO_4$: C, 62.89; H, 4.10; N, 4.07. Found: C, 62.86; H, 4.31; N, 3.60.

3.2.22. *Ethyl 2-(5-oxo-3-phenyl-5H-chromeno[2,3-b]pyrid-2-yl)-acetate (**4v**)*

Starting with 3-cyanochromone **1a** (256 mg, 1.5 mmol), **2k** (656 mg, 1.95 mmol), Me_3SiOTf (0.35 mL, 1.95 mmol) and Et_3N (0.45 mL, 3.0 mmol), **4v** was isolated as a colourless solid (320 mg, 62%), mp=152 °C. ^1H NMR ($CDCl_3$, 250 MHz): δ=3.85 (s, 3H, CH_3), 4.65 (s, 2H, CH_2), 7.11–7.27 (m, 5H, ArH), 7.38 (m, 2H, ArH), 7.54 (m, 1H, ArH), 7.72 (m, 1H, 7-H), 8.21 (dd, ^3J=7.9 Hz, ^4J=1.5 Hz, 1H, Ar–H), 9.13 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=42.5 (CH_3), 52.6 (CH_2), 114.3 (C), 118.6 (CH), 121.6, 123.2 (C), 125.1, 126.5, 126.8 (CH), 128.4, 129.2 (2C, CH), 135.9 (CH), 138.1 (C), 141.1 (CH), 155.5, 160.5, 165.1 (C), 167.7, 176.8 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3048 (w), 3061 (w), 3028 (w), 3007 (w), 2948 (w), 2929 (w), 1725 (s), 1669 (s), 1595 (s), 1547 (m), 1466 (s), 1413 (s), 1314 (m), 1270 (s), 1214 (s), 1069 (m), 968 (m), 765 (s), 742 (s), 690 (s). GC–MS (EI, 70 eV): m/z (%)=345 (M^+, 100), 313 (56), 286 (28), 256 (8), 228 (12). HRMS (EI) calcd for $C_{21}H_{15}O_4N$ (M^+, ^{35}Cl): 345.09956; found: 345.09971.

3.2.23. *Methyl 2-[3-(4-methylphenyl)-5-oxo-5H-chromeno[2,3-b]-pyrid-2-yl]acetate (**4w**)*

Starting with **1a** (0.256 mg, 1.5 mmol), Me_3SiOTf (219 mg, 0.18 mL, 0.98 mmol), CH_2Cl_2 (13.5 mL) and 1,3-bis(trimethylsilyloxy)-1,3-butadiene **2l** (0.683 mg, 0.98 mmol), **4w** was isolated as a yellow solid (333 mg, 63%), mp=173–174 °C. ^1H NMR ($CDCl_3$, 250 MHz): δ=2.23 (s, 3H, CH_3), 3.85 (s, 3H, CH_3), 4.60 (s, 2H, CH_2), 6.98 (d, J=7.8 Hz, 2H, ArH), 7.15 (d, 2H, ArH), 7.33–7.39 (m, 1H, ArH), 7.53 (d, J=7.87 Hz, 1H, ArH), 7.67–7.74 (m, 1H, ArH), 8.20 (m, 1H, ArH), 9.10 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=21.0 (CH_3), 42.1 (CH_2), 52.5 (OCH_3), 114.3 (C), 118.6 (CH), 121.6, 123.2 (C), 125.1, 126.8 (CH), 129.0 (2C, CH), 129.1 (2C, CH), 135.0 (C), 135.8 (CH), 136.1 (C), 141.1 (CH), 155.6, 160.5, 165.3 (C), 168.0, 176.8 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3084 (w), 3058 (w), 3009 (w), 2948 (w), 1720 (s), 1671 (s), 1613 (m), 1600 (s), 1597 (s), 1548 (m), 1467 (s), 1442 (m), 1412 (s), 1314 (m), 1271 (s), 1253 (s), 1216 (s), 1150 (s), 1069 (s), 793 (m), 755 (s), 615 (m). GC–MS (EI, 70 eV): m/z (%)=359 (M^+, 100), 327 (M^+, 70), 298 (17), 285 (5), 256 (5), 228 (4), 150 (7). HRMS (EI) calcd for $C_{22}H_{17}O_4N$ (M^+): 359.114605; found: 359.11521.

3.2.24. *Ethyl 2-[3-(4-chlorophenyl)-5-oxo-5H-chromeno[2,3-b]-pyrid-2-yl]acetate (**4x**)*

Starting with **1a** (256 mg, 1.5 mmol), **2m** (723 mg, 1.95 mmol), Me_3SiOTf (0.36 mL, 1.95 mmol) and NEt_3 (0.45 mL, 3.0 mmol), **4x** was isolated as a colourless solid (284 mg, 50%), mp=182 °C. ^1H NMR ($CDCl_3$, 250 MHz): δ=3.78 (s, 3H, CH_3), 4.52 (s, 2H, CH_2), 7.06–7.17 (m, 4H, ArH), 7.30 (m, 1H, ArH), 7.45 (m, 1H, ArH), 7.61 (m, 1H, ArH), 8.13 (dd, ^3J=7.8 Hz, ^4J=1.4 Hz, 1H, Ar–H), 9.06 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=41.8 (CH_3), 52.6 (CH_2), 114.5 (C), 118.6 (CH), 121.6, 123.0 (C), 125.8, 126.8 (CH), 128.5, 130.6 (2C, CH), 132.4 (C), 135.9 (CH), 136.5 (C), 141.3 (CH), 155.5, 160.5, 165.1 (C), 167.2, 177.3 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3076 (w), 3048 (w), 2952 (w), 2918 (w), 1729 (s), 1664 (s), 1613 (m), 1600 (s), 1547 (m), 1492 (w), 1483 (s), 1414 (s), 1338 (w), 1310 (m), 1271 (s), 1247 (s), 1216 (s), 1139 (m), 1065 (m), 943 (m), 765 (s). GC–MS (EI, 70 eV): m/z (%)=381 (M^+, ^{37}Cl, 34), 379 (M^+, ^{35}Cl, 100), 347 (46), 320 (15), 312 (59), 284 (13), 256 (14), 228 (9). HRMS (EI) calcd for $C_{21}H_{14}O_4NCl$ (M^+, ^{35}Cl): 379.06059; found: 379.06052.

3.2.25. *Methyl 2-[7-chloro-3-(2-methoxyphenyl)-5-oxo-5H-chromeno[2,3-b]pyrid-2-yl]acetate (**4y**)*

Starting with **1e** (200 mg, 0.97 mmol), **2n** (465 mg, 1.26 mmol), Me_3SiOTf (0.22 mL, 1.26 mmol) and NEt_3 (0.27 mL, 1.94 mmol), **4y** was isolated as a colourless solid (144 mg, 40%), mp=172 °C. ^1H NMR ($CDCl_3$, 250 MHz): δ=3.55 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.79 (s, 2H, CH_2), 6.91–7.02 (m, 2H, ArH), 7.15 (dd, ^3J=7.4 Hz, ^4J=1.8 Hz, 1H, ArH), 7.33–7.39 (m, 1H, ArH), 7.49 (d, ^3J=8.8 Hz, 1H, ArH), 7.64 (dd, ^3J=8.8 Hz, ^4J=2.5 Hz, 1H, ArH), 8.19 (d, ^4J=2.3 Hz, 1H, ArH), 8.45 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=42.2 (CH_2), 52.1, 52.3 (CH_3), 110.8 (CH), 114.9 (C), 120.2, 121.0 (CH), 122.5, 125.5 (C), 125.9, 130.4, 131.3 (CH), 132.8 (C), 135.5, 139.0 (CH), 154.0, 156.2, 158.7, 159.6 (C), 169.8, 176.4 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3067 (w), 2985 (w), 2939 (w), 1727 (s), 1662 (s), 1597 (s), 1471 (s), 1432 (s), 1309 (m), 1259 (s), 1025 (m), 828 (m), 631 (w), 538 (w). GC–MS (EI, 70 eV): m/z (%)=411 (M^+, ^{37}Cl, 8), 409 (M^+, ^{35}Cl, 26), 338 (^{37}Cl, 27), 336 (^{35}Cl, 100), 306 (9), 243 (2), 168 (3), 97 (10), 83 (13), 71 (11), 69 (20), 57 (21), 44 (25). HRMS (EI) calcd for $C_{22}H_{16}ClNO_5$ (M^{++}, ^{35}Cl): 409.07189; found: 409.07115.

3.2.26. *Methyl 2-[7-methyl-3-(2-methoxyphenyl)-5-oxo-5H-chromeno[2,3-b]pyrid-2-yl]acetate (**4z**)*

Starting with **1b** (200 mg, 1.08 mmol), **2n** (516 mg, 1.4 mmol), Me_3SiOTf (0.25 mL, 1.4 mmol) and NEt_3 (0.3 mL, 2.16 mmol), **4z** was isolated as a colourless solid (134 mg, 32%), mp=165 °C. ^1H NMR ($CDCl_3$, 250 MHz): δ=2.41 (s, 3H, CH_3), 3.54 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.78 (s, 2H, CH_2), 6.90–7.01 (m, 2H, ArH), 7.15 (dd, ^3J=7.4 Hz, ^4J=1.7 Hz, 1H, ArH), 7.32–7.39 (m, 1H, ArH), 7.43–7.53 (m, 2H, ArH), 8.02 (s, 1H, ArH), 8.46 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=20.8 (CH_3), 42.0 (CH_2), 52.0, 52.3 (CH_3), 110.7 (CH), 115.2 (C), 118.2, 120.9 (CH), 121.3, 125.8 (C), 126.0, 130.2, 131.4 (CH), 132.2, 134.4 (C), 136.7, 138.9 (CH), 153.9, 156.2, 159.0 (C), 169.9, 177.6 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3058 (w), 3046 (w), 2923 (w), 1742 (s), 1655 (s), 1488 (s), 1432 (s), 1253 (m), 1147 (s), 1020 (s), 834 (m), 794 (m), 630 (w), 542 (w). GC–MS (EI, 70 eV): m/z (%)=389 (M^+, 35), 357 (9), 316 (100), 286 (11), 149 (8), 111 (18), 97 (32), 83 (41), 57 (65), 44 (90). HRMS (EI) calcd for $C_{23}H_{19}NO_5$ $[M]^+$: 389.12597; found: 389.12577.

3.2.27. *Methyl 2-(4-aza-2-methoxyxanthon-3-yl)acetate (**4aa**)*

Starting with **1a** (171 mg, 1.0 mmol), Me_3SiOTf (289 mg, 1.3 mmol) and **2o** (377 mg, 1.3 mmol), **4aa** (92 mg, 31%) was isolated as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ=3.74 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 4.03 (s, 2H, CH_2), 7.43 (m, 1H, Ar), 7.54 (d, ^{3}J=8.1 Hz, 1H, Ar), 7.78 (m, 1H, Ar), 8.33 (dd, ^{3}J=8.2 Hz, ^{4}J=1.8 Hz, 1H, Ar), 8.06 (s, 1H, Ar). ^{13}C NMR (DEPT, 75.5 MHz, $CDCl_3$): δ=39.1 (CH_2), 52.3, 56.5 (OCH_3), 115.1 (CH), 115.7 (C), 118.4 (CH), 120.9 (C), 124.4, 126.5, 135.3 (CH), 151.0, 152.1, 153.8, 155.6 (C), 169.7 (C=O, ester), 177.6 (C=O, ketone). MS (EI, 70 eV): m/z (%)=299 (M^+, 100), 267 (28), 240 (41), 210 (46), 171 (12), 120 (13).

3.2.28. Ethyl 2-(5-oxo-3-phenoxy-5H-chromeno[2,3-b]pyrid-2-yl)-acetate (4ab)

Starting with **1a** (400 mg, 2.62 mmol), **2p** (1.25 g, 3.41 mmol), Me_3SiOTf (0.62 mL, 3.41 mmol), NEt_3 (0.72 mL, 5.24 mmol), **4ab** was isolated as a colourless solid (595 mg, 66%), mp=144 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ=1.13 (t, ^{3}J=7.0 Hz, 3H, CH_3), 4.01 (s, 2H, CH_2), 4.09 (q, ^{3}J=7.0 Hz, 2H, OCH_2CH_3), 6.98–7.00 (m, 2H, ArH), 7.08–7.15 (m, 1H, ArH), 7.26–7.33 (m, 3H, ArH), 7.49 (dd, ^{3}J=8.5 Hz, ^{4}J=0.7 Hz, 1H, ArH), 7.63–7.70 (m, 1H, ArH), 7.95 (s, 1H, ArH), 8.15 (dd, ^{3}J=8.0 Hz, ^{4}J=1.4 Hz, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.1 (CH_3), 39.5 (CH_2), 61.3 (OCH_2), 116.1 (C), 118.3 (CH), 119.2 (2C, CH), 120.9 (C), 123.1, 124.5, 124.8, 126.5 (CH), 130.2 (2C, CH), 135.5 (CH), 150.6, 152.5, 154.9, 155.5, 155.7 (C), 169.0, 177.1 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3072 (w), 2985 (w), 2937 (w), 1730 (s), 1664 (s), 1470 (s), 1309 (s), 1220 (s), 1119 (m), 1024 (m), 771 (s), 757 (m), 689 (m), 498 (w). GC–MS (EI, 70 eV): m/z (%)=375 (M^+, 100), 302 (10), 282 (12), 254 (88), 177 (44), 153 (13), 127 (54), 91 (10), 51 (7). Anal. Calcd (%) for $C_{22}H_{17}NO_5$: C, 70.39; H, 4.56; N, 3.73. Found: C, 69.78; H, 4.46; N, 3.55.

3.2.29. Ethyl 2-(7,9-dichloro-5-oxo-3-phenoxy-5H-chromeno-[2,3-b]pyrid-2-yl)acetate (4ac)

Starting with **1f** (125 mg, 0.52 mmol), **2p** (247 mg, 0.67 mmol), Me_3SiOTf (0.12 mL, 0.67 mmol) and NEt_3 (0.14 mL, 1.04 mmol), **4ac** was isolated as a colourless solid (102 mg, 44%), mp=147 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=1.17 (t, ^{3}J=7.0 Hz, 3H, CH_3), 4.07 (s, 2H, CH_2), 4.09 (q, ^{3}J=7.0 Hz, 2H, OCH_2CH_3), 7.01 (m, 2H, ArH), 7.17 (m, 1H, ArH), 7.35 (m, 2H, ArH), 7.74 (d, ^{4}J=2.6 Hz, 1H, ArH), 7.90 (s, 1H, ArH), 8.05 (d, ^{4}J=2.6 Hz, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.1 (CH_3), 38.6 (CH_2), 60.4 (OCH_2), 114.5 (C), 118.6 (2C, CH), 121.1 (CH), 121.7 (C), 123.5 (CH), 123.6 (C), 124.2 (CH), 129.0 (C), 129.4 (2C, CH), 134.4 (CH), 149.0, 150.6, 152.4, 153.2, 154.3 (C), 167.9, 174.7 (C=O). IR (ATR, cm^{-1}): $\tilde{\nu}$=3073 (w), 2983 (w), 2916 (w), 1720 (s), 1671 (s), 1423 (s), 1225 (s), 1192 (s), 1120 (m), 1024 (m), 991 (m), 802 (m), 785 (s), 692 (m). GC–MS (EI, 70 eV): m/z (%)=447 ($[M]^+$, [2×^{37}Cl], 1), 445 ($[M]^+$, [^{37}Cl], [^{35}Cl], 2), 443 ($[M]^+$, [2×^{35}Cl], 4), 400 (3), 398 (4), 352 (25), 350 (38), 324 (64), 322 (100), 294 (15), 266 (5), 174 (2), 94 (5), 65 (7). HRMS (EI) calcd for $C_{22}H_{15}Cl_2NO_5$ ($[M]^+$, [2×^{35}Cl]): 443.03114; found: 343.03218.

3.2.30. Methyl 2-[3-(4-chlorophenoxy)-7,8-dimethyl-5-oxo-5H-chromeno[2,3-b]pyrid-2-yl]acetate (4ad)

Starting with **1h** (400 mg, 2.0 mmol), **2q** (1.00 g, 2.61 mmol), Me_3SiOTf (0.47 mL, 2.61 mmol) and NEt_3 (0.55 mL, 4.0 mmol), **4ad** was isolated as a colourless solid (280 mg, 33%), mp=155 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ=2.26 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 3.61 (s, 3H, OCH_3), 3.99 (s, 2H, CH_2), 6.91 (d, ^{3}J=7.5 Hz, 2H, ArH), 7.26 (d, ^{3}J=7.3 Hz, 2H, ArH), 7.86 (s, 1H, ArH), 7.95 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=19.1, 20.6 (CH_3), 39.2 (CH_2), 52.3 (OCH_3), 61.5 (OCH_2), 116.3, 118.4 (C), 118.7 (CH), 120.4 (2C, CH), 123.6, 126.1 (CH), 129.9 (C), 130.0 (2C, CH), 133.9, 146.6, 149.9, 151.8, 153.9, 154.0, 154.5 (C), 169.5, 176.7 (C=O). IR (ATR, cm^{-1}): $\tilde{\nu}$=3051 (w), 2956 (w), 2847 (w), 1730 (s), 1607 (s), 1471 (s), 1410 (s), 1318 (s), 1209 (s), 1145 (s), 1087 (s), 994 (m), 873 (m), 672 (w). GC–MS (EI, 70 eV): m/z (%)=425 (M^+, ^{37}Cl, 1), 423 (M^+, ^{35}Cl, 3), 392 (1), 364 (1), 296 (100), 266 (7), 238 (4), 127 (1), 99 (2). HRMS (EI) calcd for $C_{23}H_{18}ClNO_5$ (M^{++}, ^{35}Cl): 423.08620; found: 423.08680.

3.2.31. Methyl 2-[7,9-dichloro-3-(4-methylphenoxy)-5-oxo-5H-chromeno[2,3-b]pyrid-2-yl]acetate (4ae)

Starting with **1f** (400 mg, 1.66 mmol), **2r** (797 mg, 2.16 mmol), Me_3SiOTf (0.39 mL, 2.16 mmol) and NEt_3 (0.6 mL, 4.32 mmol), **4ae** was isolated as a colourless solid (294 mg, 42%), mp=194 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ=2.31 (s, 3H, CH_3), 3.65 (s, 3H, OCH_3), 4.09 (s, 2H, CH_2), 6.89 (d, ^{3}J=8.5 Hz, 2H, ArH), 7.14 (d, ^{3}J=8.1 Hz, 2H, ArH), 7.74 (d, ^{4}J=2.6 Hz, 1H, ArH), 7.85 (s, 1H, ArH), 8.05 (d, ^{4}J=2.5 Hz, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=20.1 (CH_3), 39.3 (CH_2), 52.4 (OCH_3), 115.5 (C), 119.6 (2C, CH), 121.5 (CH), 122.6 (C), 124.5 (CH), 124.5, 130.0 (C), 130.9 (2C, CH), 135.1 (C), 135.3 (CH), 150.0, 152.1, 152.8, 152.9, 154.0 (C), 169.4, 175.7 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3068 (w), 2964 (w), 2924 (w), 1728 (s), 1666 (s), 1508 (s), 1429 (s), 1396 (s), 1272 (m), 1172 (m), 1016 (m), 787 (m), 718 (w), 527 (w). GC–MS (EI, 70 eV): m/z (%)=447 ($[M]^+$, [2×^{37}Cl], 7), 445 ($[M]^+$, [^{37}Cl], [^{35}Cl], 47), 443 ($[M]^+$, [2×^{35}Cl], 7, 77), 386 (17), 384 (26), 311 (13), 266 (12), 239 (4), 149 (7), 105 (12), 97 (17), 84 (10), 71 (25), 44 (100). HRMS (EI) calcd for $C_{22}H_{15}Cl_2NO_5$ ($[M]^+$, [2×^{35}Cl]): 443.03085; found: 343.03218.

3.2.32. Ethyl 2-[5-oxo-3-(phenylsulfanyl)-5H-chromeno-[2,3-b]pyrid-2-yl]acetate (4af)

Starting with **1a** (400 mg, 2.33 mmol), **2s** (1.18 g, 3.11 mmol), Me_3SiOTf (0.56 mL, 3.11 mmol) and NEt_3 (0.64 mL, 4.66 mmol), **4af** was isolated as a colourless solid (465 mg, 51%), mp=88 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ=1.30 (t, ^{3}J=7.1 Hz, 3H, CH_3), 4.27 (q, ^{3}J=7.1 Hz, 2H, OCH_2CH_3), 4.65 (s, 2H, CH_2), 7.04–7.13 (m, 3H, ArH), 7.24–7.32 (m, 3H, ArH), 7.47 (dd, ^{3}J=8.3 Hz, ^{4}J=0.6 Hz, 1H, ArH), 7.62–7.69 (m, 1H, ArH), 8.16 (dd, ^{3}J=7.8 Hz, ^{4}J=1.5 Hz, 1H, ArH), 9.05 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.1 (CH_3), 40.0 (CH_2), 62.0 (OCH_2), 114.6 (C), 118.6 (CH), 121.6, 123.1 (C), 125.1, 126.7, 127.0 (CH), 128.8 (2C, CH), 131.0 (2C, CH), 134.4, 134.9 (C), 135.9, 141.0 (CH), 155.5, 164.6 (C), 165.4, 176.9 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3074 (w), 2982 (w), 2930 (w), 1725 (s), 1674 (s), 1600 (s), 1551 (m), 1310 (m), 1264 (s), 1159 (m), 765 (m), 689 (m), 528 (w), 508 (w). GC–MS (EI, 70 eV): m/z (%)=391 (M^+, 100), 58 (10), 345 (40), 282 (13), 254 (94), 226 (17), 196 (12), 170 (4), 109 (13), 65 (8). HRMS (EI) calcd for $C_{22}H_{17}NO_4S$ $[M]^+$: 391.08738; found: 391.08728.

3.2.33. Ethyl 2-{3-[(4-chlorophenyl)sulfanyl]-7,8-dimethyl-5-oxo-5H-chromeno[2,3-b]pyrid-2-yl}acetate (4ag)

Starting with **1h** (400 mg, 2.0 mmol), **2t** (418 mg, 2.6 mmol), Me_3SiOTf (0.46 mL, 2.6 mmol) and NEt_3 (0.55 mL, 4.0 mmol), **4ag** was isolated as a colourless solid (515 mg, 56%), mp=147 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.14 (t, 3H, ^{3}J=7.1 Hz, CH_3), 2.09 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 4.10 (q, 2H, ^{3}J=6.9 Hz, OCH_2CH_3), 4.43 (s, 2H, CH_2), 6.92 (m, 2H, ArH), 7.05 (s, 1H, ArH), 7.09 (m, 2H, ArH), 7.73 (s, 1H, ArH), 8.90 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.2, 19.2, 20.7 (CH_3), 40.1, 60.9 (CH_2), 114.8 (C), 118.7 (CH), 119.4, 122.6 (C), 126.4 (CH), 129.0 (2C, CH), 132.3 (2C, CH), 133.1, 133.6, 134.6, 141.1, 147.0, 153.9, 160.0, 164.6 (C), 164.9, 176.5 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3054 (w), 2975 (w), 2895 (w), 1703 (s), 1605 (s), 1463 (m), 1439 (s), 1240 (s), 1162 (s), 833 (s), 793 (m). GC–MS (EI, 70 eV): m/z (%)=455 (M^+, ^{37}Cl, 17), 453 (M^+, ^{35}Cl, 46), 407 (20), 311 (30), 282 (100), 266 (23), 144 (20), 109 (15), 44 (78). HRMS (ESI) calcd for $C_{24}H_{20}NO_4ClS$ (M^+, ^{35}Cl): 453.07961; found: 453.07890.

3.2.34. Ethyl 2-{7-methyl-3-[(4-methylphenyl)sulfanyl]-5-oxo-5H-chromeno[2,3-b]pyrid-2-yl}acetate (4ah)

Starting with **1b** (400 mg, 2.16 mmol), **2u** (396 mg, 2.81 mmol), Me_3SiOTf (0.50 mL, 2.81 mmol) and NEt_3 (0.60 mL, 4.3 mmol), **4ah** was isolated as a colourless solid (572 mg, 63%), mp=148 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ=1.51 (t, 3H, ^{3}J=7.2 Hz, CH_3), 2.38 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 4.48 (q, 2H, ^{3}J=7.1 Hz, OCH_2CH_3), 4.83 (s, 2H, CH_2), 7.15 (d, 2H, ^{3}J=7.91 Hz, ArH), 7.37 (d, 2H, ^{3}J=7.6 Hz, ArH), 7.60

(d, 1H, ^3J=8.7 Hz, ArH), 7.70 (dd, 1H, ^3J=6.91 Hz, ^4J=2.5 Hz, ArH), 8.21 (d, 1H, ^4J=2.62 Hz, ArH), 9.30 (s, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.1, 20.8, 21.0 (CH_3), 40.6, 61.9 (CH_2), 114.5 (C), 118.0 (CH), 121.0, 123.2 (C), 126.1 (CH), 129.6 (2C, CH), 131.0 (C), 131.9 (2C, CH), 135.2 (C), 137.1 (CH), 137.3 (C), 140.9 (CH), 153.7, 160.1, 164.7 (C), 165.5, 176.8 (C=O). IR (neat, cm^{-1}): $\tilde{\nu}$=3075 (w), 2979 (w), 2810 (w), 1731 (s), 1695 (s), 1475 (m), 1339 (s), 1249 (s), 1062 (s), 803 (s), 796 (m). GC–MS (EI, 70 eV): *m*/*z* (%)=419 (M$^+$, 91), 404 (5), 373 (21), 268 (100), 240 (17), 210 (21), 105 (11). HRMS (ESI) calcd for $C_{24}H_{21}NO_4S$ $(M^+)^+$: 419.11858; found: 419.11936.

*3.2.35. Ethyl 2-{7,9-dichloro-3-[(4-methoxyphenyl)sulfanyl]-5-oxo-5H-chromeno[2,3-b]pyrid-2-yl}acetate (**4ai**)*

Starting with **1f** (400 mg, 1.66 mmol), **2v** (891 mg, 2.16 mmol), Me_3SiOTf (0.39 mL, 2.16 mmol) and NEt_3 (0.6 mL, 4.32 mmol), **4ai** was isolated as a colourless solid (366 mg, 45%), mp=153 °C. ^{1}H NMR ($CDCl_3$, 250 MHz): δ=1.28 (t, ^3J=7.0 Hz, 3H, CH_3), 3.83 (s, 3H, OCH_3), 4.17 (s, 2H, CH_2), 4.23 (q, ^3J=7.1 Hz, 2H, OCH_2), 6.91 (d, ^3J=8.9 Hz, 2H, ArH), 7.41 (d, ^3J=8.9 Hz, 2H, ArH), 7.77 (d, ^4J=2.5 Hz, 1H, ArH), 8.06 (d, ^4J=2.5 Hz, 1H, ArH), 8.20 (s, 1H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.1 (CH_3), 42.5 (CH_2), 55.4 (OCH_3), 61.5 (OCH_2), 115.3 (C), 115.6 (2C, CH), 121.5, 123.2 (C), 124.5 (CH), 130.1, 134.8, 135.1 (C), 135.4 (CH), 135.5 (2C, CH), 137.2 (CH), 149.9, 157.3, 159.0, 160.6 (C), 168.7, 175.2 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3070 (w), 2985 (w), 2836 (w), 1727 (s), 1668 (s), 1591 (s), 1413 (s), 1387 (s), 1253 (s), 1176 (s), 1024 (s), 830 (m), 787 (m), 523 (w). GC–MS (EI, 70 eV): *m*/*z* (%)=493 ([M]$^+$, [2×^{37}Cl], 7), 491 ([M]$^+$, [^{37}Cl], [^{35}Cl], 32), 489 ([M]$^+$, [2×^{35}Cl], 46), 419 (10), 417 (17), 384 (13), 311 (8), 266 (8), 207 (3), 97 (15), 85 (11), 84 (10), 57 (34), 44 (100). Anal. Calcd (%) for $C_{23}H_{17}Cl_2NO_5S$: C, 56.34; H, 3.49; N, 2.86. Found: C, 56.33; H, 3.46; N, 2.87.

*3.2.36. Ethyl 2-{7,9-dichloro-3-[(4-methoxyphenyl)sulfanyl]-5-oxo-5H-chromeno[2,3-b]pyrid-2-yl}propionate (**4aj**)*

Starting with **1a** (256 mg, 1.5 mmol), Me_3SiOTf (433 mg, 0.33 mL, 1.95 mmol), **2w** (560 mg, 1.95 mmol), CH_2Cl_2 (13.5 mL), EtOH (15 mL) and triethylamine (324 mg, 0.44 mL, 3.00 mmol), **4aj** was isolated as a yellow oil (149 mg, 34%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=1.12 (t, *J*=7.2 Hz, 3H, CH_3), 1.53 (d, *J*=7.2 Hz, 3H, CH_3), 3.92 (q, *J*=7.2 Hz, 1H, CH), 4.04–4.13 (m, 2H, CH_2), 7.32 (d, *J*=8.0 Hz, 2H, ArH), 7.50 (d, *J*=7.7 Hz, 1H, ArH), 7.64–7.70 (m, 1H, ArH), 8.18–8.21 (dd, *J*=1.4, 8.0 Hz, 1H, ArH), 8.58 (d, *J*=7.8 Hz, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=14.0, 16.9 (CH_3), 48.3 (CH), 61.3 (OCH_2), 115.3 (C), 118.4, 119.7 (CH), 121.6 (C), 124.6, 126.6, 135.5, 137.9 (CH), 155.7, 159.8, 165.6 (C), 172.3, 177.3 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3307 (w), 3069 (w), 2980 (m), 2874 (w), 1730 (s), 1662 (s), 1614 (m), 1598 (s), 1559 (m), 1461 (s), 1397 (s), 1318 (w), 1250 (m), 1149 (m), 1107 (m), 1027 (w), 958 (m), 852 (m), 763 (s), 688 (m). GC–MS (EI, 70 eV): *m*/*z* (%)=297 (M$^+$, 18), 252 (5), 225 (35), 224 (100). HRMS (EI) calcd for $C_{17}H_{15}O_4N$ (M$^+$): 297.09956; found: 297.099255.

*3.2.37. Methyl 2-{7,9-dichloro-3-[(4-methoxyphenyl)sulfanyl]-5-oxo-5H-chromeno[2,3-b]pyrid-2-yl}butyrate (**4ak**)*

Starting with **1a** (256 mg, 1.5 mmol), Me_3SiOTf (433 mg, 0.33 mL, 1.95 mmol), **2x** (560 mg, 1.95 mmol), CH_2Cl_2 (13.5 mL), EtOH (15 mL) and triethylamine (324 mg, 0.44 mL, 3.00 mmol), **4ak** was isolated as a yellow oil (136 mg, 31%). ^{1}H NMR ($CDCl_3$, 250 MHz): δ=0.88 (t, *J*=7.4 Hz, 3H, CH_3), 1.93–2.23 (m, 2H, CH_2), 3.46 (s, 3H, CH_3), 3.80 (t, *J*=7.7 Hz, 1H, CH), 7.31–7.40 (m, 2H, ArH), 7.52–7.55 (d, *J*=7.7 Hz, 1H, ArH), 7.66–7.73 (m, 1H, ArH), 8.20–8.24 (dd, *J*=1.4, 8.0 Hz, 1H, ArH), 8.58 (d, *J*=7.8 Hz, 1H, ArH). ^{13}C NMR (62 MHz, $CDCl_3$): δ=12.0 (CH_3), 25.5 (CH_2), 52.3 (OCH_3), 55.7 (CH), 115.4 (C), 118.4, 120.1 (CH), 121.6 (C), 124.6, 126.6, 135.5, 137.9 (CH), 155.6, 159.8, 164.4 (C), 172.2, 177.3 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3316 (w), 3068 (w), 2966 (m), 2875 (w), 2841 (w), 2705 (w), 1732 (s), 1661 (s), 1613 (m), 1597 (s), 1585 (m), 1599 (m), 1460 (s), 1397 (s), 1350 (w), 1194 (m), 1149 (m), 1103 (m), 1027 (w), 930 (m), 845 (m), 760 (s), 750 (m), 685 (m). GC–MS (EI, 70 eV): *m*/*z* (%)=297 (M$^+$, 0.7), 269 (83), 238 (90), 182 (7). HRMS (EI) calcd for $C_{17}H_{15}O_4N$ (M$^+$): 297.09956; found: 297.098859.

*3.2.38. Ethyl 6-aza-5-oxa-12-oxo-7,9,10,12-tetrahydronaphtacene-7-carboxylate (**4al**)*

Starting with **1a** (240 mg, 1.4 mmol), Me_3SiOTf (404 mg, 0.33 mL, 1.82 mmol) and **2y** (573 mg, 1.82 mmol), **4al** (163 mg, 36%) was isolated as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.29 (t, ^3J=7.1 Hz, 3H, OCH_2CH_3), 1.92 (m, 2H, CH_2), 2.27 (m, 2H, CH_2), 2.97 (m, 2H, CH_2), 4.04 (t, ^3J=6.1 Hz, 1H, CH), 4.26 (q, ^3J=7.3 Hz, 2H, OCH_2CH_3), 7.39 (m, 1H, Ar), 7.57 (dd, ^3J=8.0 Hz, ^4J=1.0 Hz, 1H, Ar), 7.75 (m, 1H, Ar), 8.28 (dd, ^3J=7.9 Hz, ^4J=1.6 Hz, 1H, Ar), 8.43 (s, 1H, Ar). ^{13}C NMR (DEPT, 75.5 MHz, $CDCl_3$): δ=14.2 (OCH_2CH_3), 20.0, 26.7, 27.8 (CH_2), 48.7 (CH), 61.2 (OCH_2CH_3), 115.5 (C), 118.5 (CH), 121.5 (C), 124.4, 126.6 (CH), 130.7 (C), 135.5, 137.6 (CH), 155.8, 158.0, 159.6 (C), 173.1 (C=O, ester), 177.6 (C=O, ketone). IR (KBr, cm^{-1}): $\tilde{\nu}$=3444 (m), 2980 (m), 2946 (m), 1734 (s), 1663 (s), 1608 (s), 1559 (m), 1471 (s), 1471 (s), 1439 (s), 1415 (s), 1369 (m), 1313 (m), 1264 (m), 1226 (m), 1171 (s), 1063 (m), 1032 (s), 766 (s). UV–vis (CH_3CN, nm): λ_{max} (lg ε): 341 (3.94), 292 (4.10), 232 (4.47). MS (EI, 70 eV): *m*/*z* (%)=323 (M$^+$, 98), 250 ([M−$CO_2CH_2CH_3$]$^+$, 100), 235 (16), 207 (7), 103 (5), 77 (8).

*3.2.39. Ethyl 6-aza-9-methyl-5-oxa-12-oxo-7,9,10,12-tetrahydronaphtacene-7-carboxylate (**4am**)*

Starting with **1a** (240 mg, 1.4 mmol), Me_3SiOTf (404 mg, 0.33 mL, 1.82 mmol) and **2z** (573 mg, 1.82 mmol), **4am** (145 mg, 32%) was isolated as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$, dr=3:2): δ=1.13, 1.16 (d, ^3J=6.3 Hz, 3H, CH_3), 1.37 (m, 1H, CH_2, CH_2), 1.79–1.91 (m, 1H, CH_2, CH_2), 2.20–2.35 (m, 1H, CH_2, CH_2), 2.72–2.48 (m, 1H, CH, CH), 2.95–3.10 (m, 1H, CH, CH), 3.73, 3.83 (s, 3H, OCH_3, OCH_3), 4.08–4.15 (m, 1H, CH, CH), 7.38–7.44 (m, 1H, Ar, Ar), 7.59 (d, ^3J=8.4 Hz, 1H, Ar, Ar), 7.73–7.79 (m, 1H, Ar, Ar), 8.28, 8.31 (t, ^2J=2.4 Hz, 1H, Ar, Ar), 8.41, 8.45 (s, 1H, Ar, Ar). ^{13}C NMR (DEPT, 75.5 MHz, $CDCl_3$, signals of main diastereomer): δ=21.2 (CH_3), 25.6 (CH), 34.2, 36.1 (CH_2), 48.1 (CH), 52.5 (CH_3), 115.6 (C), 118.5 (CH), 121.5 (C), 124.4, 126.7 (CH), 130.5 (C), 135.5, 137.1 (CH), 155.8, 159.0, 159.6 (C), 173.8, 177.6 (C=O). IR (KBr, cm^{-1}): $\tilde{\nu}$=3437 (m), 2952 (m), 2926 (m), 1737 (s), 1661 (s), 1609 (s), 1559 (m), 1471 (s), 1418 (s), 1319 (m), 1267 (m), 1223 (m), 1197 (m), 1161 (m), 767 (m). UV–vis (CH_3CN, nm): λ_{max} (lg ε): 341 (4.00), 292 (4.14), 232 (4.49). MS (EI, 70 eV): *m*/*z* (%)=323 (M$^+$, 28), 208 (34), 248 (43), 108 (7), 120 (100), 106 (34).

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