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3-BENZOYL-4-HYDROXYISOCHROMEN-1-ONE DERIVATIVES, THEIR SYNTHESIS AND SYNTHETIC APPLICATION

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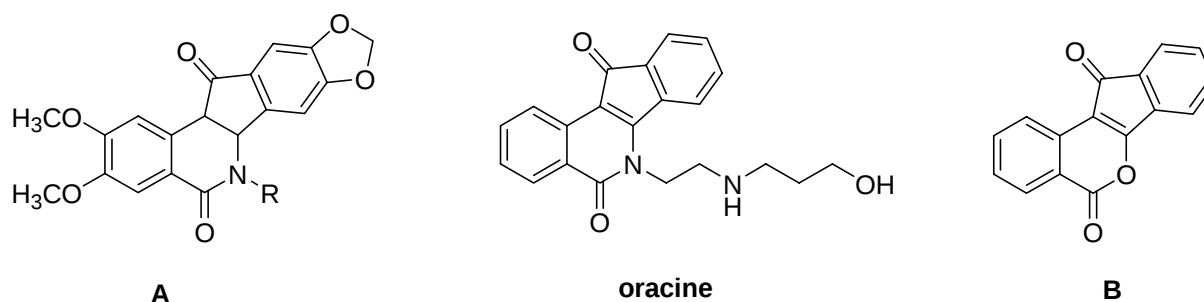
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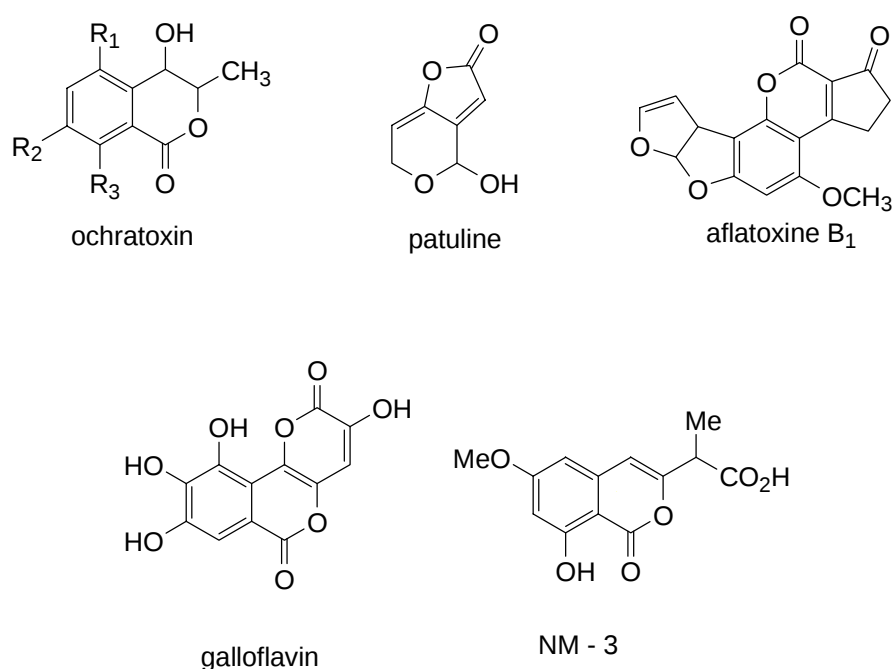
Abstract – 3-Benzoyl-1,4-isochromandione derivatives were prepared by cyclization of phenacyl phthalates (**2**). The cyclization was done in the presence of *N*-methylpyrrolidone and potassium hydroxide. These compounds served as intermediates for the synthesis of more complicated isocoumarine derivatives. A Wittig reaction with (carbethoxymethylene)triphenyl phosphorane was conducted in a microwave reactor and resulted in the formation of substituted 4-phenylpyrano[3,2-*c*]isochromene-2,6-dione.

INTRODUCTION

A number of derivatives of indenoisoquinolines (**A**) were prepared and subsequently found to be cytotoxic in human cancer cells (Figure 1).^{1,2} These compounds were synthesized by reaction of the corresponding lactone with various primary amines.^{1,2} For example, the cytostatic compound oracine was prepared from commercially available benz [*d*]indeno[1,2-*b*]pyran-5,11-dione (**B**) (Figure 1).³

**Figure 1**

Further, from the literature, it is also known that compounds containing the lactone ring frequently exhibit a broad spectrum of biological activities – antimicrobial, cytostatic, and so on.⁴ Their frequent occurrence in, for example mycotoxins, is also well-documented (Figure 2). Related analogs of these compounds were developed as potential drugs. Some of them are shown in Fig. 2. For example, the oncologically active compound NM-3 is in clinical trial, or the compound galloflavin which targets HIV-1 integrase⁵ could be a useful drug for the treatment of HIV disease. Based on this knowledge we decided to prepare substituted 1,4-isochromandiones (**3**) and substituted pyrano[3,2-*c*]isochromene-2,6-dione (**4**) (Scheme 1) as analogs of compound (**B**) and also galloflavin. This group of compounds is readily available, has not yet been described and provides many opportunities for structure modification. They may serve as key intermediates for the synthesis of various biologically active heterocyclic compounds.

**Figure 2**

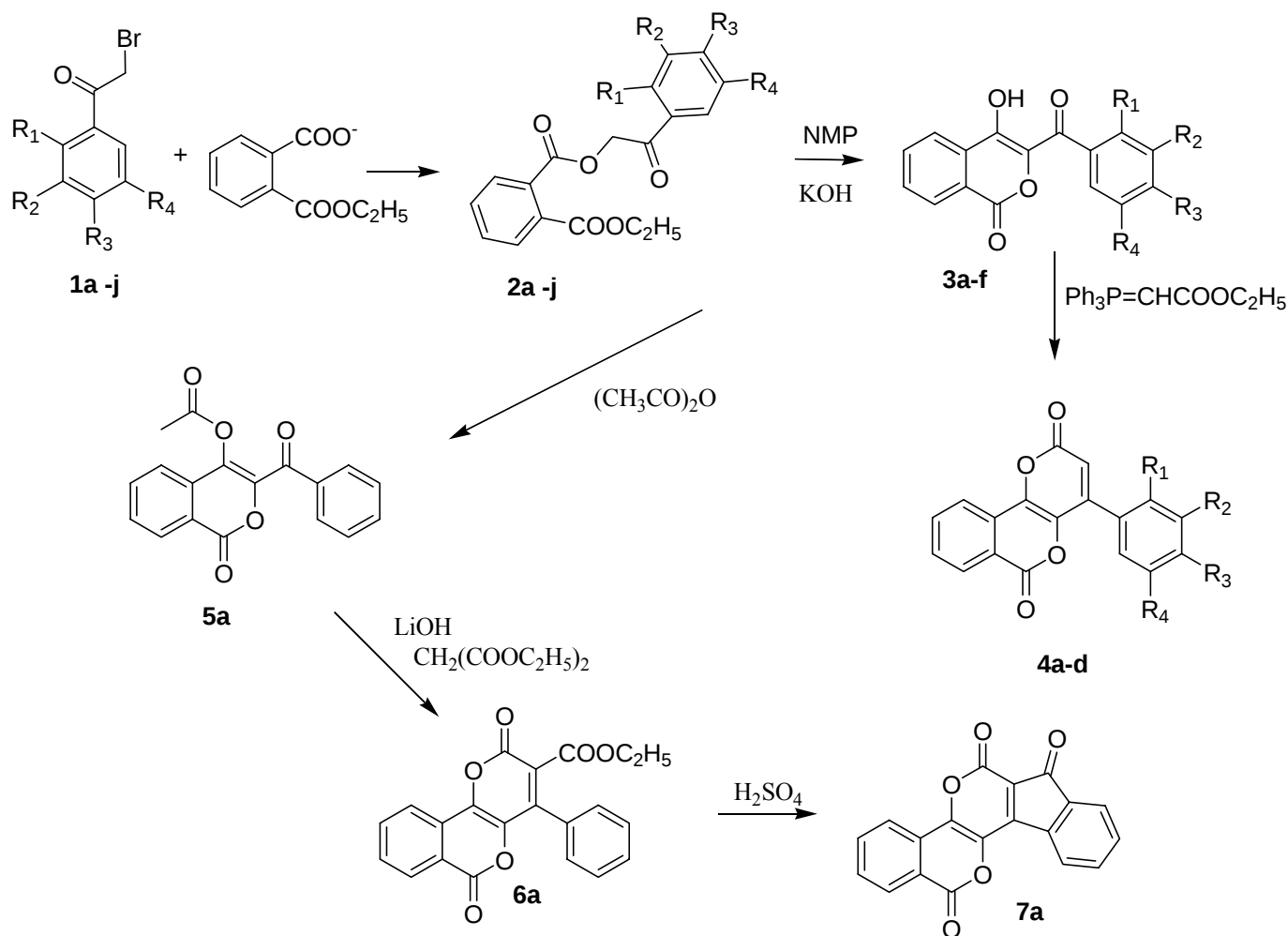
RESULTS AND DISCUSSION

Only few 1,4-isochromandiones substituted by the carbonyl group in the position 3 are known. In general 3-carbethoxy derivatives have been known for some time⁶⁻⁸ though only one compound with substitution by the carbonyl group in the same position⁹ has been described. Carbethoxy compounds were prepared by Claisen condensation from phthalide and diethyloxalate. A compound with the 2-naphthoyl group was prepared by acid catalyzed cyclization of 2-(3-naphthalen-1-yl-3-oxo-propionyl)benzoic acid ethyl ester in dichloromethane. For the preparation of the key intermediates, 3-acyl-1,4-isochromandiones, a synthesis similar to the Gabriel Isoquinoline synthesis was selected. Instead of phenacyl phthalimides, phenacyl phthalates (**2**) were chosen. These compounds are simply available by reaction of phthalic acid monoester salt and phenacyl bromide in acetone and they were subjected to reactions with various catalysts. Acids were completely inefficient. The use of bases like potassium carbonate, sodium hydride, and sodium or potassium methoxide, potassium *t*-butoxide and so on, was also unsuccessful. The reaction was successfully performed in dimethyl sulfoxide or amides like dimethylformamide, dimethylacetamide, 1,3-dimethylimidazolidinone or *N*-methylpyrrolidone (NMP) by potassium hydroxide or sodium hydroxide. The reaction takes several hours and the yield was 20 to 80 % depending on substitution and temperature. The optimal course of reaction was observed in the temperature range from 25 to 45 °C. The course of substitution strongly depended on the substitution of the phenacyl part of the ester but we did not find a simple dependence between substitution and capability to cyclize.

For example, cyclization of mono chloro derivative (**2c**) afforded the required product (**3c**). The reaction time was longer and the yield was not too high. The cyclization was not observed for dichloro derivatives (**2g**) and (**2i**). On the other hand, derivative (**2e**) smoothly afforded **3e** with very high yield. The progress of the reaction was checked by TLC. As soon as starting material could no longer be observed, diluted hydrochloric acid was added to the reaction mixture and the products (**3**) were isolated as yellow needles. Compounds (**3**) were then used as a starting material for the next stage of the synthesis.

In the initial step a Wittig reaction was carried out in toluene or xylene. However, the reaction proceeded very slowly and even after 20 hours only a small part of the starting material had been consumed resulting in the compound (**4**). This being case, we resorted to the use of a microwave reactor. The microwave reactor is a prototype specially constructed by the Romil company (Brno, Czech Republic). The maximum power of the microwave source is 250W and microwaves are focused on the reaction area, and energetic input is regulated. The reaction was done in a melt and only a small amount of *N*-methyl pyrrolidone was added. The reaction mixture absorbs microwaves better under these conditions. After several minutes the reaction was completed. The starting material was not observed by TLC. The required

products (**4**) precipitated after addition of ethyl acetate. Some product remained in the mother liquor due to its solubility in triphenyl phosphine oxide (Scheme 1). The isolated product was generally very pure. The structure of the products (**4a**) and (**4b**) was confirmed by X-Ray diffraction. (Figure 3 and 4) In the cyclization of compounds (**3e**) and (**3f**), the desired products (**4e**) and (**4f**) did not arise and the reaction mixture contained multifarious unknown compounds.



a	$\text{R}_1 = \text{H}, \text{R}_2 = \text{H},$	$\text{R}_3 = \text{H}, \text{R}_4 = \text{H}.$
b	$\text{R}_1 = \text{H}, \text{R}_2 = \text{H},$	$\text{R}_3 = \text{CH}_3, \text{R}_4 = \text{H}.$
c	$\text{R}_1 = \text{H}, \text{R}_2 = \text{H},$	$\text{R}_3 = \text{Cl}, \text{R}_4 = \text{H}.$
d	$\text{R}_1 = \text{H}, \text{R}_2 = \text{H},$	$\text{R}_3 = \text{F}, \text{R}_4 = \text{H}.$
e	$\text{R}_1 = \text{H}, \text{R}_2 = \text{Cl},$	$\text{R}_3 = \text{NH}_2, \text{R}_4 = \text{Cl}.$
f	$\text{R}_1 = \text{H}, \text{R}_2 = \text{OCH}_3,$	$\text{R}_3 = \text{OCH}_3, \text{R}_4 = \text{H}.$
g	$\text{R}_1 = \text{Cl}, \text{R}_2 = \text{H},$	$\text{R}_3 = \text{Cl}, \text{R}_4 = \text{H}.$
h	$\text{R}_1 = \text{H}, \text{R}_2 = \text{H},$	$\text{R}_3 = \text{NO}_2, \text{R}_4 = \text{H}.$
i	$\text{R}_1 = \text{H}, \text{R}_2 = \text{Cl},$	$\text{R}_3 = \text{H}, \text{R}_4 = \text{Cl}.$
j	$\text{R}_1 = \text{H}, \text{R}_2 = \text{NO}_2,$	$\text{R}_3 = \text{Cl}, \text{R}_4 = \text{H}.$

Scheme 1

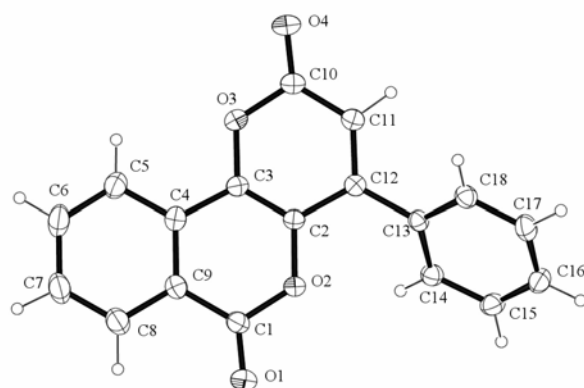


Figure 3. ORTEP view of compound (4a) showing the thermal ellipsoids at 30% level of probability

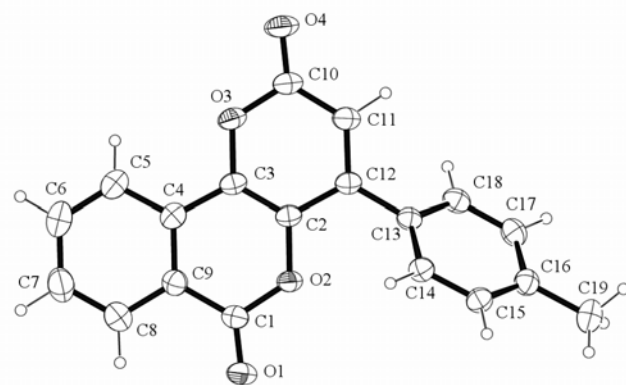


Figure 4. ORTEP view of compound (4b) showing the thermal ellipsoids at 30% level of probability

After reaction of derivative (3a) with acetic anhydride, acetyl derivative (5a) was prepared. If the same reaction was done with ethyl 3-chloro-3-oxopropionate and triethylamine in acetone, a different course of reaction was observed and the compound (6a) was isolated. But yield of the compound (6a) was very low and did not exceed 15% even if a ten-fold excess of acyl chloride was used. It was noted that the same compound (6a) is formed by reaction of acetyl derivative (5a) with malonic acid diethyl ester in alkaline medium. After addition of hydroxide, the slightly yellow reaction mixture turned to an intensively violet one. Cyclization of the compound (6a) progresses smoothly in sulfuric or polyphosphoric acid and the compound (7a) is formed.

X-Ray crystal structure determinations.

X-Ray diffraction data for compounds (4a) and (4b) were collected on a Nonius Kappa CCD diffractometer, at room temperature ($T = 295$ K), with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å) and corrected for Lorentz and polarization effects. The structures were solved by direct methods (SIR97)¹⁰ and refined (SHELXL-97)¹¹ by full matrix least squares with anisotropic non-H atoms

and isotropic hydrogens. All other calculations were accomplished using the system of programs PARST.¹² ORTEP 11 views of compounds (**4a**) and (**4b**) are shown in Figures 3 and 4.

Crystal data: **4a**, C₁₈H₁₀O₄; monoclinic, space group *P2₁/n*, *a* = 12.9485(4), *b* = 7.5251(2), *c* = 14.9469(4) Å, β = 115.578(2)°, *V* = 1313.68(7) Å³, *Z* = 4, *D_c* = 1.468 g cm⁻³. Intensity data collected with θ ≤ 30°; 3733 independent reflections measured; 2318 reflections observed [*I* > 2σ(*I*)]. Final *R* = 0.0469 (observed reflections), *R_w* = 0.1376 (all reflections), and *S* (goodness of fit) = 1.026.

4b, C₁₉H₁₂O₄; monoclinic, space group *P2₁/n*, *a* = 7.1121(1), *b* = 7.7001(1), *c* = 26.5088(6) Å, β = 96.064(1)°, *V* = 1443.60(4) Å³, *Z* = 4, *D_c* = 1.400 g cm⁻³. Intensity data collected with θ ≤ 30°; 4134 independent reflections measured; 2571 reflections observed [*I* > 2σ(*I*)]. Final *R* = 0.0468 (observed reflections), *R_w* = 0.1389 (all reflections), and *S* (goodness of fit) = 1.053.

EXPERIMENTAL

Melting points were measured in the Kofler apparatus and are uncorrected. TLC was performed on Polygram Sil G/UV₂₅₄ with UV light detection and mobile phase *n*-hexane : ethylacetate 7: 3. Infrared spectra (KBr discs) were taken with an ATI Unicam Genesis FTIR instrument. MS characterization was carried out using the DEP-CI-MS-MS (direct exposure probe-chemical ionization-tandem mass spectrometry) technique with quadrupole ion trap mass analyzer and methane as a CI reagent gas. NMR spectra were measured with a Bruker Avance 300 spectrometer operating at 300 MHz (¹H) and 75 MHz (¹³C). The compounds were dissolved in DMSO-*d*₆ and measured at 300 K.

General method of preparation of phthalic acid 1-ethyl ester 2-(2-oxo-2-phenylethyl) ester (**2**)

Monoethyl ester of phthalic acid (35 g, 0.236 mol) was dissolved in acetone (300 mL) and triethylamine (23 mL, 0.166 mol) was added. The reaction mixture was stirred and bromoacetophenone derivative (0.13 mol) was added and the reaction mixture was refluxed with stirring. When substituted bromoacetophenone was not observed on TLC, solid triethyl ammonium bromide was filtered off and the filtrate was evaporated to dryness. The oily residue was dissolved in EtOH (70 mL) and the solution was cooled at 0°C. Crystalline material was filtered off, dried and recrystallized from EtOH.

Phthalic acid 1-ethyl ester 2-(2-oxo-2-phenylethyl) ester (**2a**)

Yellow solid (23.5 g, 58%) mp 75-77 °C; reaction time 3 h.

Anal. Calcd for C₁₈H₁₆O₅ (312.32): C, 69.22; H, 5.16. Found: C, 69.21; H, 5.24.

Full MS, *m/z* (relative intensity) 341 [M+C₂H₅]⁺, 313 (<1) [M+H]⁺, 267 [M+H-C₂H₅OH]⁺, 177 [C₆H₄COOC₂H₅(CO)]⁺, 163, 149 (100) [C₆H₄COOH(CO)]⁺, 133, 121, 119, 105, 91.

^1H NMR (DMSO- d_6 , 300 MHz) δ 8.03 (2H, dd, $J = 7.5, 1.3$ Hz), 7.94-7.88 (1H, m), 7.79-7.69 (4H, m), 7.59 (2H, dd, $J = 8.1, 7.4$ Hz), 5.75 (2H, s), 4.27 (2H, q, $J = 7.1$ Hz), 1.27 (3H, t, $J = 7.1$ Hz); ^{13}C NMR (DMSO- d_6 , 75 MHz) δ 192.9, 167.4, 166.6, 134.6, 134.3, 132.7, 132.6, 132.0, 130.9, 129.6, 129.4, 129.2, 128.3, 67.9, 61.9, 14.3.

Phthalic acid 1-ethyl ester 2-(2-oxo-2-p-tolyloethyl) ester (**2b**)

Slight yellow solid (26.7 g, 63 %) mp 86-88 °C; reaction time 2 h.

Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{O}_5$ (326.34): C, 69.94; H, 5.52. Found: C, 69.82; H, 5.63.

Full MS, m/z (relative intensity) 355 $[\text{M}+\text{C}_2\text{H}_5]^+$, 327 (<1) $[\text{M}+\text{H}]^+$, 281 $[\text{M}+\text{H}-\text{C}_2\text{H}_5\text{OH}]^+$, 177 $[\text{C}_6\text{H}_4\text{COOC}_2\text{H}_5(\text{CO})]^+$, 149 (100) $[\text{C}_6\text{H}_4\text{COOH}(\text{CO})]^+$, 133, 119, 105, 91.

^1H NMR (DMSO- d_6 , 300 MHz) δ 7.93 (2H, dd, $J = 8.1, 1.4$ Hz), 7.91-7.87 (1H, m), 7.80-7.70 (3H, m), 7.40 (2H, d, $J = 8.3$ Hz), 5.70 (2H, s), 4.27 (2H, q, $J = 7.1$ Hz), 2.41 (3H, s), 1.27 (3H, t, $J = 7.1$ Hz); ^{13}C NMR (DMSO- d_6 , 75 MHz) δ 192.3, 167.4, 166.6, 145.1, 132.7, 132.5, 132.0, 131.8, 131.0, 129.9, 129.6, 129.1, 128.4, 67.8, 61.9, 21.7, 14.3.

Phthalic acid 1-[2-(4-chloro-phenyl)-2-oxoethyl] ester 2-ethyl ester (**2c**)

Yellow solid (34.6 g, 77 %) mp 55-57 °C; reaction time 0.5 h.

Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{O}_5\text{Cl}$ (346.77): C, 62.35; H, 4.33. Found: C, 61.49; H, 4.27.

Full MS, m/z 375 $[\text{M}(^{35}\text{Cl})+\text{C}_2\text{H}_5]^+$, 347, 349 ($<1, <1$) $[\text{M}(^{35}\text{Cl}, ^{37}\text{Cl})+\text{H}]^+$, 301 $[\text{M}(^{35}\text{Cl})+\text{H}-\text{C}_2\text{H}_5\text{OH}]^+$, 177 $[\text{C}_6\text{H}_4\text{COOC}_2\text{H}_5(\text{CO})]^+$, 153, 155 (21, 7), 149 (100) $[\text{C}_6\text{H}_4\text{COOH}(\text{CO})]^+$, 141, 139, 127, 125, 121, 105, 91.

^1H NMR (DMSO- d_6 , 300 MHz) δ 8.05 (2H, dd, $J = 8.5, 1.7$ Hz), 7.93-7.87 (1H, m), 7.79-7.71 (3H, m), 7.67 (2H, dd, $J = 8.6, 1.9$ Hz), 5.73 (2H, s), 4.27 (2H, q, $J = 7.1$ Hz), 1.27 (3H, t, $J = 7.1$ Hz); ^{13}C NMR (DMSO- d_6 , 75 MHz) δ 192.1, 167.4, 166.6, 139.4, 132.9, 132.7, 132.6, 132.0, 130.8, 130.3, 129.6, 129.2, 67.9, 61.9, 14.3.

Phthalic acid 1-ethyl ester 2-[2-(4-fluorophenyl)-2-oxoethyl] ester (**2d**)

Yellow solid (29.2 g, 68 %) mp 59-61 °C; reaction time 0.5 h.

Anal. Calcd for $\text{C}_{18}\text{H}_{15}\text{O}_5\text{F}$ (330.31): C, 65.45; H, 4.55. Found: C, 65.11; H, 4.53.

Full MS, m/z 359 $[\text{M}+\text{C}_2\text{H}_5]^+$, 331 (<1) $[\text{M}+\text{H}]^+$, 311 $[\text{M}+\text{H}-\text{HF}]^+$, 285 $[\text{M}+\text{H}-\text{C}_2\text{H}_5\text{OH}]^+$, 177 $[\text{C}_6\text{H}_4\text{COOC}_2\text{H}_5(\text{CO})]^+$, 149 (100) $[\text{C}_6\text{H}_4\text{COOH}(\text{CO})]^+$, 137, 123, 109, 91.

^1H NMR (DMSO- d_6 , 300 MHz) δ 8.14 (1H, dd, $J = 8.9, 2.1$ Hz), 8.11 (1H, dd, $J = 8.9, 2.1$ Hz), 7.93-7.87 (1H, m), 7.79-7.71 (3H, m), 7.43 (2H, ddd, $J = 8.9, 8.8, 2.0$ Hz), 5.75 (2H, s), 4.27 (2H, q, $J = 7.1$ Hz), 1.27 (3H, t, $J = 7.1$ Hz); ^{13}C NMR (DMSO- d_6 , 75 MHz) δ 167.6, 167.4, 166.6, 132.7, 132.6, 132.0, 131.6, 131.4, 131.1, 131.0, 130.9, 129.6, 129.2, 116.7, 116.4, 67.9, 61.9, 14.3.

Phthalic acid 1-[2-(4-amino-3,5-dichlorophenyl)-2-oxoethyl] ester 2-ethyl ester (**2e**)

Orange solid (26.8 g, 52 %) mp 115-116 °C; reaction time 0.5 h.

Anal. Calcd for $C_{18}H_{15}O_5NCl_2$ (396.22): C, 54.56; H, 3.79; N, 3.54. Found: C, 54.73; H, 3.57; N, 3.49.

Full MS, m/z 424 $[M(^{35}Cl)+C_2H_5]^+$, 396, 398, 400 (3, 2, <1) $[M(^{35}Cl, ^{37}Cl)+H]^+$, 350 $[M(^{35}Cl)+H-C_2H_5OH]^+$, 248, 234, 204, 188, 174, 177 $[C_6H_4COOC_2H_5(CO)]^+$, 174, 149 (100) $[C_6H_4COOH(CO)]^+$, 121, 105, 91.

1H NMR (DMSO- d_6 , 300 MHz) δ 7.90 (2H, s), 7.90-7.85 (1H, m), 7.78-7.70 (3H, m), 6.61 (1H, s), 5.61 (2H, s), 4.27 (2H, q, $J = 7.1$ Hz), 1.27 (3H, t, $J = 7.1$ Hz); ^{13}C NMR (DMSO- d_6 , 75 MHz) δ 167.4, 166.6, 146.6, 132.7, 132.5, 131.9, 131.0, 129.6, 129.1, 128.8, 122.6, 117.9, 117.8, 67.9, 61.9, 14.3.

Phthalic acid 1-[2-(3,4-dimethoxyphenyl)-2-oxoethyl] ester 2-ethyl ester (**2f**)

Pale yellow solid (36.8 g, 76 %) mp 77-79 °C; reaction time 0.5 h.

Anal. Calcd for $C_{20}H_{20}O_7$ (372.38): C, 64.52; H, 5.38. Found: C, 64.52; H, 5.38.

Full MS, m/z 401 $[M+C_2H_5]^+$, 373 (2) $[M+H]^+$, 327 $[M+H-C_2H_5OH]^+$, 179, 177 $[C_6H_4COOC_2H_5(CO)]^+$, 165, 151, 149 (100) $[C_6H_4COOH(CO)]^+$, 139, 121, 105, 91.

1H NMR (DMSO- d_6 , 300 MHz) δ 7.93-7.86 (1H, m), 7.80-7.69 (4H, m), 7.49 (1H, d, $J = 1.8$ Hz), 7.13 (1H, d, $J = 8.5$ Hz), 5.70 (2H, s), 4.27 (2H, q, $J = 7.1$ Hz), 3.88 (3H, s), 3.84 (3H, s), 1.28 (3H, t, $J = 7.1$ Hz); ^{13}C NMR (DMSO- d_6 , 75 MHz) δ 191.2, 167.4, 166.7, 154.2, 149.2, 132.6, 132.5, 132.0, 131.1, 129.6, 129.1, 127.1, 123.1, 111.5, 110.5, 67.7, 61.9, 56.3, 56.1, 14.3.

Phthalic acid 1-[2-(2,4-dichlorophenyl)-2-oxoethyl] ester 2-ethyl ester (**2g**)

Off white solid (33.6 g, 68 %) mp 93-95 °C; reaction time 0.5 h.

Anal. Calcd for $C_{18}H_{14}O_5Cl_2$ (381.21): C, 56.66; H, 3.70. Found: C, 57.36; H, 3.72.

Full MS, m/z 409 $[M(^{35}Cl)+C_2H_5]^+$, 381, 383, 385 (<1, <1, <1) $[M(^{35}Cl, ^{37}Cl)+H]^+$, 335 $[M(^{35}Cl)+H-C_2H_5OH]^+$, 191, 189, 187, 177 $[C_6H_4COOC_2H_5(CO)]^+$, 173, 159, 149 (100) $[C_6H_4COOH(CO)]^+$, 121, 105, 91.

1H NMR (DMSO- d_6 , 300 MHz) δ 7.91 (1H, d, $J = 8.4$ Hz), 7.83 (1H, d, $J = 2.0$ Hz), 7.82-7.78 (1H, m), 7.78-7.70 (3H, m), 7.64 (1H, dd, $J = 8.3, 2.1$ Hz), 5.54 (2H, s), 4.27 (2H, q, $J = 7.1$ Hz), 1.27 (3H, t, $J = 7.1$ Hz); ^{13}C NMR (DMSO- d_6 , 75 MHz) δ 194.1, 167.3, 166.5, 137.8, 133.8, 132.7, 132.6, 132.5, 132.0, 131.9, 130.9, 130.7, 129.4, 129.2, 128.2, 69.1, 61.9, 14.3.

Phthalic acid 1-ethyl ester 2-[2-(4-nitrophenyl)-2-oxoethyl] ester (**2h**)

Brown solid (26.0 g, 56 %) mp 55-58 °C; reaction time 1.5 h.

Anal. Calcd for $C_{18}H_{15}O_7N$ (357.31): C, 60.50; H, 4.20; N, 3.92. Found: C, 60.11; H, 4.28; N, 4.15.

Full MS, m/z 386 $[M+C_2H_5]^+$, 358 (<1) $[M+H]^+$, 312 $[M+H-C_2H_5OH]^+$,

177 [C₆H₄COOC₂H₅(CO)]⁺, 164, 149 (100) [C₆H₄COOH(CO)]⁺, 137, 121, 106, 91.

¹H NMR (DMSO-*d*₆, 300 MHz) δ 8.40 (2H, ddd, *J* = 8.8, 2.3, 1.9 Hz), 8.27 (2H, ddd, *J* = 8.9, 2.1, 1.9 Hz), 7.93-7.86 (1H, m), 7.80-7.71 (3H, m), 5.81 (2H, s), 4.28 (2H, q, *J* = 7.1 Hz), 1.28 (3H, t, *J* = 7.1 Hz); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 192.4, 167.4, 166.6, 150.9, 138.8, 132.7, 132.6, 132.0, 130.7, 129.9, 129.6, 129.2, 124.5, 68.2, 61.9, 14.3.

Phthalic acid 1-[2-(3,5-dichlorophenyl)-2-oxoethyl] ester 2-ethyl ester (**2i**)

Pale yellow solid (31.7 g, 64 %) mp 89-91 °C; reaction time 0.5 h.

Anal. Calcd for C₁₈H₁₄O₅Cl₂ (381.21): C, 56.66; H, 3.70. Found: C, 57.10; H, 3.72.

Full MS, *m/z* 409 [M(³⁵Cl)+C₂H₅]⁺, 381, 383, 385 (<1, <1, <1) [M(³⁵Cl, ³⁷Cl)+H]⁺, 335 [M(³⁵Cl)+H-C₂H₅OH]⁺, 191, 189, 187, 177 [C₆H₄COOC₂H₅(CO)]⁺, 173, 159, 149 (100) [C₆H₄COOH(CO)]⁺, 121, 105, 91.

¹H NMR (DMSO-*d*₆, 300 MHz) δ 7.91 (1H, d, *J* = 8.4 Hz), 7.83 (1H, d, *J* = 2.3 Hz), 7.82-7.78 (1H, m), 7.78-7.70 (3H, m), 7.64 (1H, dd, *J* = 8.9, 1.7 Hz), 5.54 (2H, s), 4.27 (2H, q, *J* = 7.1 Hz), 1.27 (3H, t, *J* = 7.1 Hz); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 194.1, 167.3, 166.5, 137.8, 133.8, 132.7, 132.6, 132.5, 132.0, 131.9, 130.9, 130.6, 129.4, 129.2, 128.2, 69.1, 61.9, 14.3.

Phthalic acid 1-[2-(4-chloro-3-nitrophenyl)-2-oxoethyl] ester 2-ethyl ester (**2j**)

Yellow solid (31.6 g, 62 %) mp 73-75 °C; reaction time 0.5 h.

Anal. Calcd for C₁₈H₁₄O₇NCI (391.77): C, 55.18; H, 3.58; N, 3.58. Found: C, 55.13; H, 3.54; N, 3.60.

Full MS, *m/z* 420 [M(³⁵Cl)+C₂H₅]⁺, 392, 394 (<1, <1) [M(³⁵Cl, ³⁷Cl)+H]⁺, 346 [M(³⁵Cl)+H-C₂H₅OH]⁺, 200, 198, 183, 177 [C₆H₄COOC₂H₅(CO)]⁺, 170, 163, 149 (100) [C₆H₄COOH(CO)]⁺, 121, 105, 91.

¹H NMR (DMSO-*d*₆, 300 MHz) δ 8.66 (1H, d, *J* = 1.9 Hz), 8.29 (1H, dd, *J* = 8.5, 2.0 Hz), 8.02 (1H, d, *J* = 8.4 Hz), 7.92-7.85 (1H, m), 7.80-7.72 (3H, m), 5.79 (2H, s), 4.27 (2H, q, *J* = 7.1 Hz), 1.28 (3H, t, *J* = 7.1 Hz); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 191.1, 167.3, 166.6, 148.4, 133.9, 133.1, 132.9, 132.6, 132.0, 130.7, 130.6, 129.5, 129.2, 125.4, 68.0, 61.9, 14.3.

General Method of the preparation of 3-Acyl-4-hydroxy-isochromen-1-ones (**3**)

Phenacyl phthalates (**2**) (25 mmol) were dissolved in NMP (30 mL) and KOH (2.8 g; 50 mmol) was added. The reaction mixture was stirred for 3.5 h at temperature 25 to 50 °C. Then the reaction mixture was poured into water (70 mL). The solution was acidified with hydrochloric acid to pH 5 and the solid product was filtered off after 6 h of stirring. The isolated product was crystallized from EtOH. Yield, reaction time and melting points are summarized as follows:

3-Benzoyl-4-hydroxyisochromen-1-one (3a)

Yellow solid (4.8 g, 72 %) mp 168-172 °C; reaction time 3.5 h; reaction temperature 25°C.

Anal. Calcd for C₁₆H₁₀O₄ (266.25): C, 72.18; H, 3.79. Found: C, 71.78; H, 4.07.

Full MS, m/z (relative intensity) 295 [M+C₂H₅]⁺, 267 (40) [M+H]⁺, 189 [M+H-C₆H₆]⁺, 161 [M+H-C₆H₅COH]⁺, 133 [C₆H₄CO(CO)]⁺, 105 (100) [C₆H₅CO]⁺, 91; MS²(267,w5,EV1.5), m/z 237, 221, 209, 189, 181, 161, 152, 133, 105.

¹H NMR (DMSO-*d*₆, 300 MHz) δ 8.28 (1H, ddd, *J* = 7.9, 1.9, 0.7 Hz), 8.17 (1H, ddd, *J* = 7.9, 1.9, 0.7 Hz), 8.11-8.04 (4H, m), 7.93 (1H, ddd, *J* = 7.7, 7.5, 1.5 Hz), 7.71 (1H, ddd, *J* = 7.5, 7.3, 2.4 Hz), 7.61 (1H, ddd, *J* = 7.6, 7.2, 1.5 Hz); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 189.9, 158.4, 135.9, 135.2, 133.7, 133.6, 133.0, 131.8, 130.0, 128.9, 124.5, 124.3.

4-Hydroxy-3-(4-methylbenzoyl)isochromen-1-one (3b)

Yellow solid (3.7 g, 53 %) mp 148-150 °C; reaction time 2.5 h; reaction temperature 25°C.

Anal. Calcd for C₁₇H₁₂O₄ (280.27): C, 72.86; H, 4.29. Found: C, 72.58; H, 4.38.

Full MS, m/z 309 [M+C₂H₅]⁺, 281 (50) [M+H]⁺, 189 [M+H-C₆H₅CH₃]⁺, 161 [M+H-C₆H₄CH₃(COH)]⁺, 133 [C₆H₄CO(CO)]⁺, 119 (100) [C₆H₄CH₃(CO)]⁺, 105 [C₆H₅CO]⁺, 91; MS²(281,w5,EV1.5), m/z 265, 251, 235, 223, 195, 189, 161, 133, 119, 105.

¹H NMR (DMSO-*d*₆, 300 MHz) δ 8.27 (1H, ddd, *J* = 7.9, 1.9, 0.7 Hz), 8.16 (1H, ddd, *J* = 7.9, 1.1, 0.6 Hz), 8.07 (1H, ddd, *J* = 7.9, 7.3, 1.1 Hz), 8.01 (2H, dd, *J* = 8.4, 1.1 Hz), 7.92 (1H, ddd, *J* = 7.8, 7.4, 1.2 Hz), 7.42 (2H, d, *J* = 8.3 Hz), 2.43 (3H, s); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 188.6, 158.4, 144.4, 135.9, 133.5, 133.1, 132.8, 131.8, 130.2, 130.0, 129.5, 124.4, 124.2, 21.7.

3-(4-Chlorobenzoyl)-4-hydroxyisochromen-1-one (3c)

Yellow solid (3.9 g, 52 %) mp 177-178 °C; reaction time 100 min; reaction temperature 45°C.

Anal. Calcd for C₁₆H₉O₄Cl (300.7): C, 63.91; H, 3.02. Found: C, 63.51; H, 2.93.

Full MS, m/z 329,331 [M(³⁵Cl,³⁷Cl)+C₂H₅]⁺, 301,303 (54,18) [M(³⁵Cl,³⁷Cl)+H]⁺, 265 [M+H-HCl]⁺, 189 [M+H-C₆H₅Cl]⁺, 161 [M+H-C₆H₄Cl(COH)]⁺, 139,141 (100,33) [C₆H₄Cl(CO)]⁺, 133 [C₆H₄CO(CO)]⁺, 119, 105 [C₆H₅CO]⁺, 91; MS²(302,w5,EV1.5), m/z 189, 161, 141, 139.

¹H NMR (DMSO-*d*₆, 300 MHz) δ 8.29 (1H, ddd, *J* = 7.9, 1.0, 0.7 Hz), 8.17 (1H, ddd, *J* = 7.9, 1.1, 0.7 Hz), 8.09 (2H, dd, *J* = 8.4, 1.5 Hz), 8.08 (1H, ddd, *J* = 7.6, 7.5, 0.8 Hz), 7.94 (1H, ddd, *J* = 7.6, 7.4, 0.8 Hz), 7.70 (2H, dd, *J* = 8.5, 1.6 Hz); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 158.4, 138.6, 135.9, 134.2, 133.7, 133.0, 131.9, 131.7, 130.0, 129.1, 124.5, 124.3.

3-(4-Fluorobenzoyl)-4-hydroxyisochromen-1-one (3d)

Yellow solid (3.6 g, 50 %) mp 195-198 °C; reaction time 1.5 h; reaction temperature 25°C.

Anal. Calcd for C₁₆H₉O₄F (284.24): C, 67.61; H, 3.17. Found: C, 67.25; H, 3.09.

Full MS, m/z 313 [M+C₂H₅]⁺, 285 (50) [M+H]⁺, 265 [M+H-HF]⁺, 189 [M+H-C₆H₅F]⁺, 161 [M+H-C₆H₄F(COH)]⁺, 133 [C₆H₄CO(CO)]⁺, 123 (100) [C₆H₄F(CO)]⁺, 119, 109, 105 [C₆H₅CO]⁺, 91; MS²(285,w5,EV1.5), m/z 123.

¹H NMR (DMSO-*d*₆, 300 MHz) δ 8.29 (1H, ddd, *J* = 7.8, 1.2, 0.7 Hz), 8.21-8.14 (3H, m), 8.08 (1H, ddd, *J* = 7.6, 7.5, 0.8 Hz), 7.93 (1H, ddd, *J* = 7.6, 7.5, 0.7 Hz), 7.48 (1H, dd, *J* = 9.0, 2.0 Hz), 7.45 (1H, dd, *J* = 8.9, 1.9 Hz); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 187.6, 167.1, 163.7, 158.4, 135.9, 133.6, 133.2, 133.1, 133.0, 132.1, 131.8, 130.0, 124.4, 124.3, 116.3, 116.0.

3-(4-Amino-3,5-dichlorobenzoyl)-4-hydroxyisochromen-1-one (**3e**)

Orange solid (7.2 g, 82 %) mp 244-248 °C; reaction time 2 h; reaction temperature 45°C.

Anal. Calcd for C₁₆H₉O₄NCl₂ (350.15): C, 54.87; H, 2.57; N, 4.00. Found: C, 54.82; H, 2.27; N, 3.66.

Full MS, m/z 378,380,382 [M(³⁵Cl,³⁷Cl)+C₂H₅]⁺, 350,352,354 (90,60,10) [M(³⁵Cl,³⁷Cl)+H]⁺, 188,190,192 (100,65,11) [C₆H₂NH₂(Cl)(Cl)(CO)]⁺, 149, 133 [C₆H₄CO(CO)]⁺, 123, 119, 105 [C₆H₅CO]⁺, 91; MS²(352,w5,EV1.5), m/z 192, 190, 188, 165, 163, 161, 133.

¹H NMR (DMSO-*d*₆, 300 MHz) δ 8.26 (1H, ddd, *J* = 7.9, 0.8, 0.6 Hz), 8.16-8.09 (3H, m), 8.04 (1H, ddd, *J* = 7.7, 7.3, 1.5 Hz), 7.90 (1H, ddd, *J* = 7.7, 7.4, 1.5 Hz), 6.75 (1H, bs); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 158.4, 146.6, 135.9, 133.4, 133.1, 131.9, 130.9, 129.9, 124.1, 117.6.

3-(3,4-Dimethoxybenzoyl)-4-hydroxyisochromen-1-one (**3f**)

Yellow solid (1.7 g, 21 %) mp 180-220 °C; reaction time 4 h; reaction temperature 25°C.

Anal. Calcd for C₁₈H₁₄O₆ (326.31): C, 66.26; H, 4.29. Found: C, 66.09; H, 4.18.

Full MS, m/z 355 [M+C₂H₅]⁺, 327 (100) [M+H]⁺, 189 [M+H-C₆H₄(CH₃O)₂]⁺, 165 [C₆H₃(CH₃O)₂(CO)]⁺, 161 [M+H-C₆H₃(CH₃O)₂(COH)]⁺, 138, 133 [C₆H₄CO(CO)]⁺, 105 [C₆H₅CO]⁺, 91; MS²(327,w5,EV1.5), m/z 189, 165, 161, 138, 133, 123.

¹H NMR (DMSO-*d*₆, 300 MHz) δ 8.30 (1H, dd, *J* = 7.8, 1.3 Hz), 8.18 (1H, dd, *J* = 7.7, 1.2 Hz), 8.08 (1H, ddd, *J* = 7.7, 7.5, 1.5 Hz), 7.99-7.90 (2H, m), 7.93 (2H, dd, *J* = 7.4, 7.3 Hz), 3.91 (3H, s), 3.85 (3H, s); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 158.4, 138.6, 135.9, 134.2, 133.7, 133.0, 131.9, 131.7, 130.0, 129.1, 124.5.

General procedure for preparation of 4-substituted-pyrano[3,2-*c*]isochromene-2,6-diones (**4**)

The mixture of 3-acyl-4-hydroxyisochromen-1-one (**3**) (2 mmol), (carbethoxymethylene)triphenyl phosphorane (0.85 g, 2.44 mmol) and NMP (0.1 g) was heated in a microwave reactor. Until the reaction mixture had melted (*ca.* 40 to 60 sec), the reactor was heated with 70% of the microwave energy,

thereafter the energy was reduced to 33%. The total reaction time was 7 minutes at a reaction temperature of approx. 90 °C. The starting material was not observed in the reaction mixture by TLC. Then 10 mL of ethyl acetate was added and the reaction mixture was cooled to 0 °C for 1 h. Precipitated solid was filtered off and washed with EtOAc, water and dried. Yield and results are summarized as follows:

4-Phenylpyrano[3,2-c]isochromene-2,6-dione (4a)

Beige solid (0.41 g, 70 %) mp 219-225 °C; reaction time 7 min.

Anal. Calcd for C₁₈H₁₀O₄ (290.27): C, 74.48; H, 3.47. Found: C, 74.40; H, 3.53.

Full MS, m/z (relative intensity) 331 [M+C₃H₅]⁺, 319 [M+C₂H₅]⁺, 291 (100) [M+H]⁺, 263 [M+H-CO]⁺, 235 [M+H-CO-CO]⁺, 219, 206, 191; MS²(291,w5,EV1.5), m/z 263, 262, 245, 235, 234, 219, 218, 207, 191, 189, 179, 178.

¹H NMR (DMSO-*d*₆, 300 MHz) δ 8.27 (1H, ddd, *J* = 8.1, 0.7, 0.6 Hz), 8.12-8.05 (2H, m), 7.90-7.81 (1H, m), 7.80-7.72 (2H, m), 7.62-7.55 (3H, m), 6.66 (1H, s); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 159.0, 158.9, 149.6, 139.6, 136.4, 135.1, 132.0, 131.8, 131.0, 130.3, 129.9, 129.5, 129.1, 122.0, 121.7, 115.0.

4-p-Tolylpyrano[3,2-c]isochromene-2,6-dione (4b)

Beige solid (0.21 g, 34 %) mp 237-240 °C; reaction time 7 min.

Anal. Calcd for C₁₉H₁₂O₄ (304.03): C, 75.06; H, 3.98. Found: C, 75.30; H, 3.99.

Full MS, m/z 345 [M+C₃H₅]⁺, 333 [M+C₂H₅]⁺, 305 (100) [M+H]⁺, 277 [M+H-CO]⁺, 249 [M+H-CO-CO]⁺, 233, 220, 205, 191; MS²(305,w5,EV1.5), m/z 277, 276, 259, 249, 248, 233, 231, 221, 220, 218, 205, 203, 202, 193, 178.

¹H NMR (DMSO-*d*₆, 300 MHz) δ 8.27 (1H, ddd, *J* = 8.1, 0.7, 0.6 Hz), 8.11-8.05 (2H, m), 7.89-7.81 (1H, m), 7.67 (2H, dd, *J* = 8.2, 1.6 Hz), 7.40 (2H, d, *J* = 8.3 Hz), 6.62 (1H, s), 2.42 (3H, s); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 159.0, 149.5, 141.1, 139.5, 136.3, 135.2, 131.8, 130.3, 129.9, 129.7, 129.5, 129.1, 122.0, 121.7, 114.4, 21.4.

4-(4-Chlorophenyl)pyrano[3,2-c]isochromene-2,6-dione (4c)

Off white solid (0.32 g, 50 %) mp 314-320 °C; reaction time 15 min.

Anal. Calcd for C₁₈H₉O₄Cl (324.71): C, 66.58; H, 2.79. Found: C, 65.90; H, 2.90.

Full MS, m/z 365,367 [M(³⁵Cl,³⁷Cl)+C₃H₅]⁺, 353,355 [M(³⁵Cl,³⁷Cl)+C₂H₅]⁺, 325,327 (100,33) [M(³⁵Cl,³⁷Cl)+H]⁺, 297,299 [M(³⁵Cl,³⁷Cl)+H-CO]⁺, 269,271 [M(³⁵Cl,³⁷Cl)+H-CO-CO]⁺, 247, 233, 218, 205; MS²(326,w5,EV1.5), m/z 299, 298, 297, 296, 271, 269, 253, 251, 243, 241, 234, 233, 218, 206, 205, 189, 178, 176.

¹H NMR (DMSO-*d*₆, 300 MHz) δ 8.28 (1H, ddd, *J* = 8.1, 0.7, 0.6 Hz), 8.12-8.04 (2H, m), 7.89-7.82 (1H, m), 7.79 (2H, ddd, *J* = 8.5, 2.4, 1.9 Hz), 7.67 (2H, ddd, *J* = 8.6, 2.2, 2.0 Hz), 6.70 (1H, s); ¹³C NMR

(DMSO- d_6 , 75 MHz) δ 158.9, 158.8, 148.4, 139.6, 136.4, 136.0, 134.9, 131.9, 131.4, 130.8, 130.3, 129.8, 129.2, 122.0, 121.8, 115.2.

4-(4-Fluorophenyl)pyrano[3,2-*c*]isochromene-2,6-dione (**4d**)

Beige solid (0.27 g, 44 %) mp 289-292 °C; reaction time 10 min.

Anal. Calcd for $C_{18}H_9O_4F$ (308.26): C, 70.13; H, 2.94. Found: C, 70.20; H, 3.10.

Full MS, m/z 349 $[M+C_3H_5]^+$, 337 $[M+C_2H_5]^+$, 309 (100) $[M+H]^+$, 289 $[M+H-HF]^+$, 281 $[M+H-CO]^+$, 253 $[M+H-CO-CO]^+$, 238, 224; $MS^2(309, w5, EV1.5)$, m/z 281, 280, 263, 253, 252, 237, 235, 225, 224, 209, 207, 205, 197, 196, 177, 176.

1H NMR (DMSO- d_6 , 300 MHz) δ 8.28 (1H, d, $J = 8.1$ Hz), 8.12-8.04 (2H, m), 7.90-7.81 (3H, m), 7.45 (2H, ddd, $J = 9.0, 8.9, 1.9$ Hz), 6.68 (1H, s); ^{13}C NMR (DMSO- d_6 , 75 MHz) δ 158.4, 147.9, 139.0, 135.8, 131.6, 131.5, 131.3, 129.8, 129.3, 127.8, 121.4, 121.2, 115.8, 115.5, 114.5.

Acetic acid 3-benzoyl-1-oxo-1*H*-isochromen-4-yl ester (**5a**)

Compound (**3a**) (2 g, 7.51 mmol) and acetic anhydride were mixed and *p*-toluenesulfonic acid (0.1 g) was added. The reaction mixture was refluxed for 3 h (compound (**3a**) was not observed on TLC). Acetic acid and acetic anhydride were evaporated in *vacuo* and the residue was crystallized from AcOEt. Yield was 2.3 g (99.3 % theory), mp 140-143.5 °C.

Anal. Calcd for $C_{18}H_{12}O_5$ (308.28): C, 70.13; H, 3.92. Found: C, 70.35; H, 3.89.

full MS, m/z (relative intensity) 349 $[M+C_3H_5]^+$, 337 $[M+C_2H_5]^+$, 309 (6) $[M+H]^+$, 295, 267 (100) $[M+H-COCH_3+H]^+$, 231, 189, 133, 105, 91; $MS^2(309, w5, EV1.5)$, m/z 293, 280, 267, 265, 262, 218, 189, 145, 133, 105.

1H NMR (DMSO- d_6 , 300 MHz) δ 8.30 (1H, dd, $J = 7.9, 0.8$ Hz), 8.04 (1H, ddd, $J = 7.2, 6.8, 1.3$ Hz), 7.97-7.82 (4H, m), 7.73 (1H, ddd, $J = 7.5, 7.4, 1.4$ Hz), 7.68 (2H, ddd, $J = 7.8, 7.4, 1.4$ Hz), 2.19 (3H, s); ^{13}C NMR (DMSO- d_6 , 75 MHz) δ 186.00, 168.32, 158.60, 140.94, 135.59, 133.95, 133.70, 132.31, 131.49, 129.50, 129.45, 128.53, 123.09, 121.92, 19.92.

2,6-Dioxo-4-phenyl-2,6-dihydropyrano[3,2-*c*]isochromene-3-carboxylic acid ethyl ester (**6a**)

Diethylmalonate (520 mg, 3.24 mmol) was dissolved in THF (3 mL) and a very fine powder of LiOH·H₂O (68 mg, 1.62 mmol) was added. A solution of acetyl derivative (**5**) (100 mg, 0.32 mmol) in THF (4 mL) was added to this suspension at temperature 20 – 25 °C. After 90 min no acetyl derivative (**5**) was observed on the TLC (*n*-hexane : AcOEt 7 : 5). The solvent was evaporated in *vacuo*, water was added and the water suspension extracted by AcOEt (2 x 25 mL). After drying by sodium sulfate and filtration the organic layer was evaporated to dryness: The residue was dissolved in MeOH and cyclohexane was added. The precipitate was filtered off and yielding 65 mg (55%), mp 170-172 °C.

Anal. Calcd for C₂₁H₁₄O₆ (362.33): C, 69.61; H, 3.92. Found: C, 69.60; H, 3.95.

full MS, *m/z* 403 [M+C₃H₅]⁺, 391 [M+C₂H₅]⁺, 363 (45) [M+H]⁺, 334 [M+H-C₂H₅]⁺, 317 (100) [M+H-C₂H₅OH]⁺, 306, 289, 261, 233; MS²(363,w5,EV1), *m/z* 334, 317, 306, 289, 261, 233, 221, 205, 193.

¹H NMR (DMSO-*d*₆, 300 MHz) δ 8.27 (1H, ddd, *J* = 7.8, 0.9, 0.8 Hz), 8.14-8.05 (2H, m), 7.88 (1H, ddd, *J* = 6.7, 6.4, 2.2 Hz), 7.61-7.55 (3H, m), 7.52-7.47 (2H, m), 4.05 (2H, q, *J* = 7.0 Hz), 0.91 (3H, t, *J* = 7.0 Hz); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 162.73, 158.37, 155.97, 147.68, 139.84, 135.93, 134.03, 131.92, 130.24, 129.84, 129.71, 128.75, 128.43, 128.39, 121.77, 121.53, 119.82, 61.54, 13.26.

5,12-Dioxaindeno[1,2-*a*]phenanthrene-6,7,13-trione (**7a**)

Ethyl ester (**6a**) (1.07 g, 2.95 mmol) was dissolved in sulfuric acid (5 mL) and the reaction mixture was heated to 130-140 °C for 75 min. At this stage the starting material was no longer observed in TLC. The reaction mixture was cooled to lab temperature and EtOH (30 mL) was added. The reaction mixture was stirred for 5 min and then diluted with water (20 mL). The red precipitate was filtered off, washed with a mixture of ethanol (1.5 mL) and water (1.5 mL) and then with ethanol (2 mL). The isolated compound (**7**) was crystallized from DMF. 0.66 g (71 %) of red needles were isolated, mp 318-326 °C.

Anal. Calcd for C₁₉H₈O₅ (316.26): C, 72.16; H, 2.55. Found: C, 72.00; H, 2.62.

full MS, *m/z* 357 [M+C₃H₅]⁺, 345 [M+C₂H₅]⁺, 317 (100) [M+H]⁺, 289 [M+H-CO]⁺, 261 [M+H-CO-CO]⁺, 233 [M+H-CO-CO-CO]⁺, 133, 105, 91; MS²(317,w5,EV1), *m/z* 289, 261, 245, 233, 217, 205, 189.

¹H NMR (DMSO-*d*₆, 300 MHz) δ 8.38 (1H, ddd, *J* = 7.6, 1.1, 0.6 Hz), 8.23-8.10 (3H, m), 7.99 (1H, ddd, *J* = 7.4, 7.2, 1.5 Hz), 7.87-7.79 (1H, m), 7.76-7.71 (2H, m); ¹³C NMR (DMSO-*d*₆, 75 MHz) δ 157.93, 154.84, 153.23, 152.77, 147.50, 136.11, 135.27, 134.95, 133.91, 133.52, 132.48, 130.28, 126.36, 123.83, 123.08, 122.77.

Supplementary material

Complete crystallographic data (excluding structural factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers CCDC 276393 - 276394. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033; e-mail: deposit@ccdc.cam.ac.uk, or <http://www.ccdc.cam.ac.uk/conts/retrieving.html>]

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