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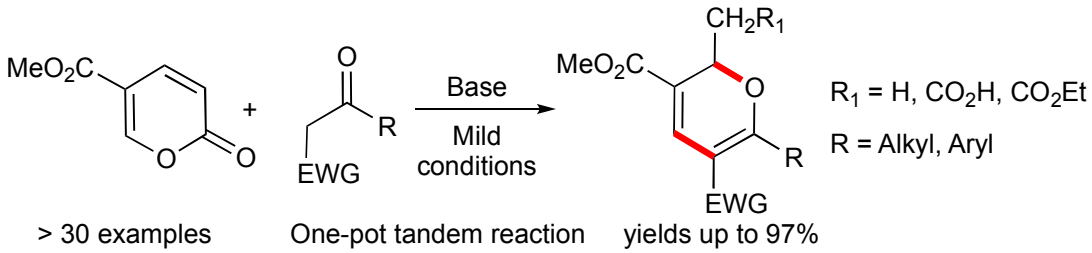
Supporting Information Placeholder

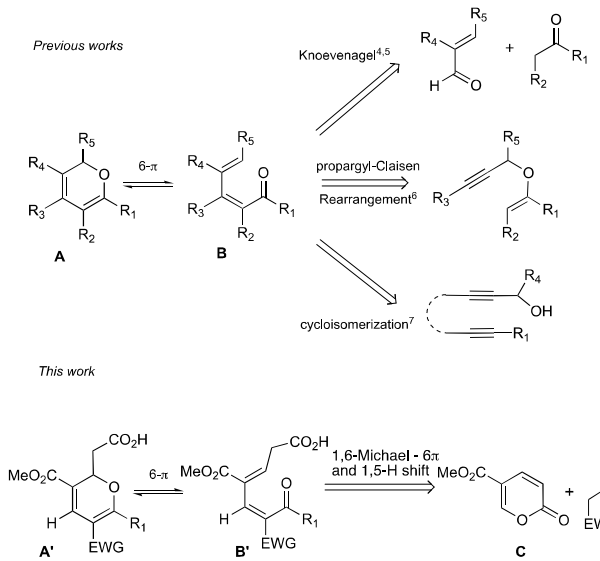


ABSTRACT: The reaction of methyl coumalate with a wide range of methylene active compounds such as keto-esters or keto-sulfones and cyclic or acyclic diketones afforded more than thirty 2,3,5,6-tetrasubstituted 2*H*-pyrans. The reaction proceeds via a cascade reaction involving a Michael addition - 6π-electrocyclic ring opening - Proton transfer and 6π Electrocyclization in which a variety of functional groups were tolerated.

The 2*H*-pyran core is widely encountered in natural products[1] and is often used as a key intermediate in total synthesis of natural products.[2] Since 2*H*-pyrans are in equilibrium with 1-oxatrienes by a 6π electrocyclic process, 1-oxatrienes generally afford an entry into the 2*H*-pyran skeleton (Figure 1). The 6π disrotatory process has been already discussed at different levels of theory.[3] The equilibrium between 2*H*-pyrans **A** and 1-oxatrienes **B** depends on many factors such as the presence of electron-withdrawing substituents or increased steric interactions. The most common entry into the 1-oxatriene core is the Knoevenagel reaction (most generally condensation between an enal and a cyclic 1,3-dicarbonyl compound). From a synthetic point of view, the tandem Knoevenagel / 6π-electrocyclization (Figure 1) can be considered as a formal [3+3] cycloaddition.[4,5] Conjugated 1-oxatrienes can also be obtained through a Claisen rearrangement of propargyl vinyl ethers[6] or cycloisomerization of diynols.[7] Other strategies towards 2*H*-pyrans that do not involve the "1-oxatriene pathway" but rather rely on formal [4+2]- or [3+3]-cycloaddition have been reported.[8,9]

We present a study enabling a general synthesis of tetrasubstituted 2*H*-pyrans by addition of methylene active nucleophiles **D** to methyl coumalate (**MC**). We have recently demonstrated that Grignard reagents add regioselectively on the C6 of **MC**.[10] Our hypothesis was that **MC** should react with the same regiochemistry with stabilized nucleophiles **D** like keto-esters or diketones in a tandem 1,6-Michael addition - 6π-electrocyclic ring opening – 1,5 H shift reaction offering an entry to 1-oxatrienes **B'**. This highly strained 1-oxatriene bearing two electron-withdrawing groups should through a final 6π-electrocyclization, deliver the 2*H*-pyran systems **A'** (Figure 1).

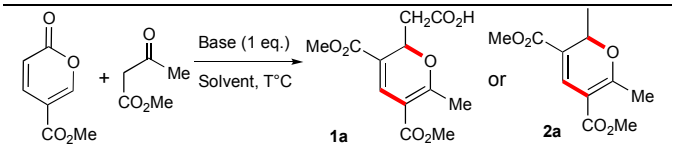
Figure 1. Approaches to 2*H*-Pyrans



This hypothesis was also based on a report of the literature[11] in which the aceto-phenylsulfone reacted with **MC** at high temperature to give the corresponding decarboxylated 2*H*-pyran in 67% yield. Only one example was described and we decided to reinvestigate the reaction conditions and to study the scope and limitations. We demonstrate here that careful control of the temperature is crucial and, in addition to the previously reported 2*H*-pyran, that 2-(2*H*-pyran-2-yl)acetic acids are also available in good yields. We also proposed a modified mechanism that takes into account some of our previous results.

We started our investigation with methyl acetoacetate (MAA) as a model nucleophile in the cascade reaction (Table 1). The first attempt was carried out with 20 mol % of cesium carbonate in DCM at room temperature for 15 h. The expected 2*H*-pyran **1a** was obtained in low yield due to low conversion (**MC** recovered in 75 mol %, see SI, Table S1). A stoichiometric amount of cesium carbonate gave compound **1a** with moderate yield (60%) (Table 1, entry 1).

Table 1. Optimization of the Reaction Conditions[a]



Entry	Base	Solvent	Temp	Time (h)	Products (yield)
1	Cs_2CO_3	DCM	RT	3	**1a** (60%)
2	Cs_2CO_3	EtOH	RT	3	**1a** (80%)
3	Na_2CO_3	EtOH	RT	1	**1a** (90%)
4	Et_3N	EtOH	RT	3	**1a** (46%)[b]
5	Et_3N	DCM	RT	3	**1a** (55%)
6	Et_3N	DCM	reflux	15	**2a** (87%)
7	Et_3N	EtOH	reflux	15	**2a** (58%)
8	Et_3N	THF	reflux	6	**2a** (54%)[c]
9	Et_3N	Toluene	reflux	6	**2a** (80%)
10	DBU	DCM	reflux	1	**2a** (32%)[c]
11	Et_3N[d]	DCM	reflux	24	**2a** (77%)[e]
12	Et_3N[d]	DCM	reflux	48	**2a** (86%)
13	Et_3N	Neat	50°C	15	**2a** (60%)

[a] Reaction conditions: All reactions were performed with MC (1 mmol) and MAA (1 mmol), in 5 mL of organic solvent. [b] 54% of MC was observed in the crude reaction mixture, determined by ^{1}H NMR. [c] Degradation was observed. [d] 20 mol % of Et_3N. [e] 18% of MC was observed in the crude reaction mixture, determined by ^{1}H NMR

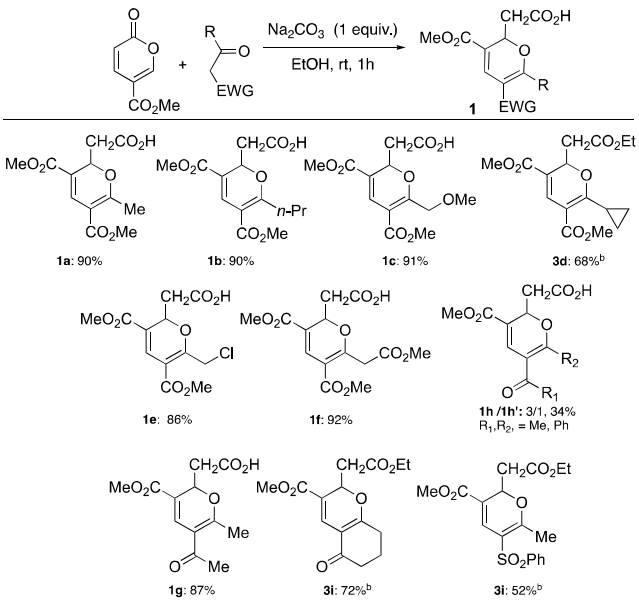
2*H*-Pyran **1a** was obtained with better yield when the reaction was performed in EtOH with either cesium or sodium carbonate (entries 2-3). At rt NEt_3 gave moderate conversions and yields using either EtOH or DCM as solvents (entries 4-5). Interestingly, after prolonged reaction time, some traces of the decarboxylated 2*H*-pyran **2a** were observed (see SI, Table S1). In order to favour the complete decarboxylation, the reaction mixture was heated to reflux for 15h in DCM. Product **2a** was thus isolated in good yield (87%, entry 6). Changing DCM for toluene, EtOH or THF did not improve the yield of **2a** (entries 7-9) and the use of DBU instead of NEt_3 in DCM gave only modest results (entry 10). Interestingly, the reaction was successfully tested with a catalytic amount of Et_3N. Complete conversion of **MC** into the expected decarboxylated 2*H*-pyran **2a** was reached in 48 h with 86% yield (entry 12, see also SI, Table S1 for shorter reaction times). A solvent-free reaction led to the formation of the expected compound **2a**, however in a moderate 60% yield after 15 hours at 50°C (entry 13).

Having in hand the best conditions to synthesize either 2*H*-pyran **1a** (entry 3) or its corresponding decarboxylated analogue **2a** (entry 6), we explored the scope and limitations of these reactions.

The data in Table 2 illustrate the reaction with Na_2CO_3 in EtOH for 1h at room temperature. 1,3-Ketoesters gave the expected 2*H*-pyrans **1a-c,e,f** in yields ranging from 86% to 92%. Diverse functions such as methylether (**1c**), halogen (**1e**) or a second ester function (**1f**) gave the expected products whereas 1,3-diketones gave moderate to good yields. For example, the symmetrical 1,3-pentanedione gave the 2*H*-pyran **1g** in 87% yield whereas the non-symmetrical acetoacetophenone gave the 2*H*-pyrans **1h** and **1h'** in a 3/1 mixture, which could not be purified by flash chromatography, reflecting the two diastereoisomeric 1-oxatriene intermediates **5h** (EWG=COPh R=Me) and **5h'** (EWG=COMe and R=Ph) (see Scheme 1).

The purifications of some of 2*H*-pyrans **1** were not satisfying. We surmised that direct esterification of the carboxylic acid function following Steglich procedure[12] could solve the problem. Compounds **3d,3i,3j** were efficiently prepared in a one-pot manner with yields from 52% to 72% (Table 2).

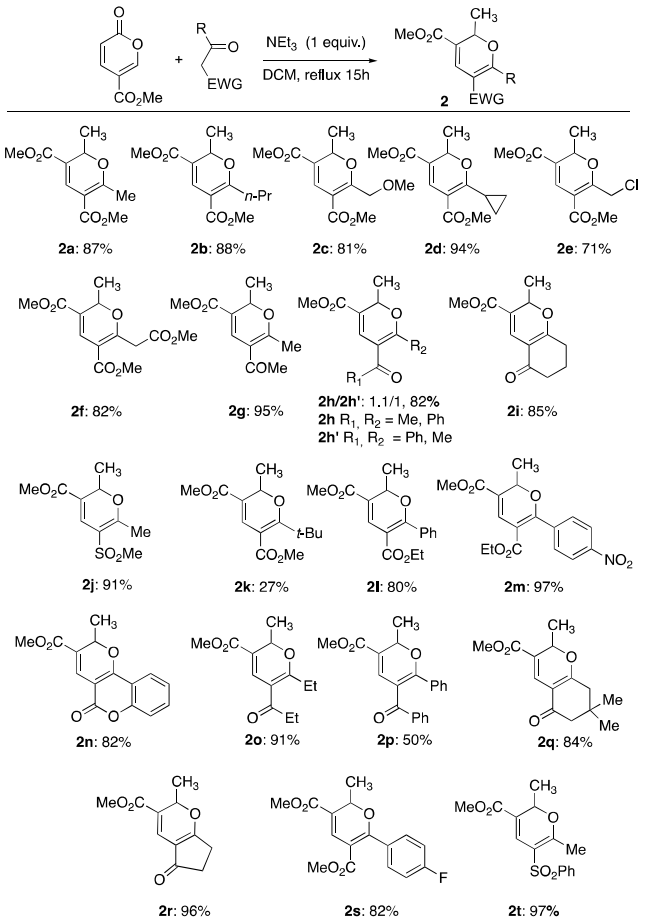
Table 2. Substrate Scope of the Tandem Michael / 6π / 1,5H shift / 6π Reaction at Room Temperature[a]



[a] Reaction conditions : MC/Methylene active nucleophile/Na_2CO_3 (1/1/1) in EtOH for 1 h. [b] 5mL of DCM, 1 equiv. of EDC.HCl and 20 mol% of DMAP were directly added to the reaction mixture after 1h and stirred 15h.

We next examined the outcome of the cascade reactions in the presence of NEt_3 in DCM under reflux. Under these conditions, more than 20 examples of 2*H*-pyrans **2** were synthesized. Results are reported in Table 3. The decarboxylated 2*H*-pyrans **2a-f** were prepared from the 1,3-ketoesters in excellent yields. Again, ether, halogen or ester moieties were tolerated in this cascade reaction. Satisfyingly and in contrast to the first conditions, the crowded 2*H*-pyran **2k** and the aromatic 2*H*-pyrans **2l,m,s** were synthesized with up to 97% yield (*vide supra* for mechanistic explanations). The 4-hydroxycoumarin gave the expected tricyclic product **2n** in 82% yield. In these conditions, β-oxosulfones led to 2*H*-pyrans **2j,t** in almost quantitative yield.[11]

Table 3. Substrates Scope of the Decarboxylative Tandem Reaction[a]

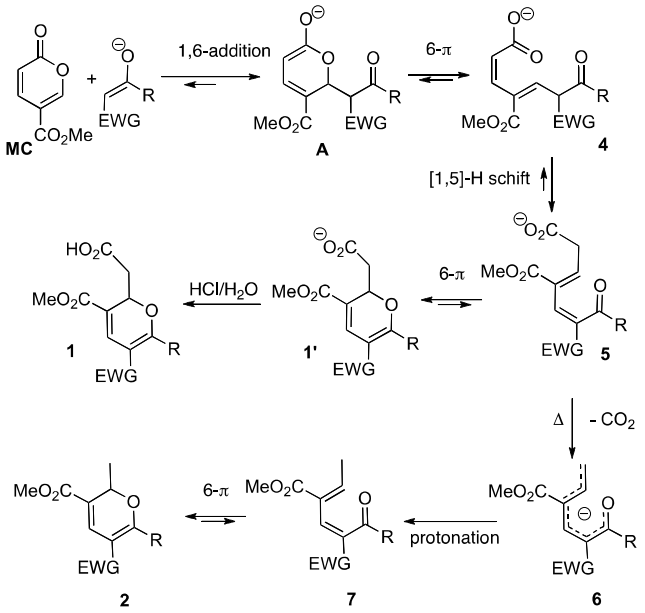


[a] Reaction conditions : MC/Methylene active nucleophile/Et_3N (1/1/1) in DCM reflux for 15 h.

Various 1.3-diketones could also lead to the expected 2*H*-Pyrans in moderate to excellent yields. Even aromatic diketones, which were unproductive at rt produced the expected pyrans **2p** albeit in moderate yields. Again, acetoacetophenone gave a 1.1/1 mixture of isomers **2h** and **2h'** in good yield (82%). This result seems to indicate that there is no stereoselectivity in the proton shift step (see *vide supra* for mechanism). Finally 2*H*-pyrans **2i,q,r** resulting from the addition of 5- and 6-membered cyclic diketones were isolated in good yields (84-96 %).

Our proposal for the mechanism of this cascade reaction might involve a 1,6-addition of the enolate on **MC** followed by a 6-π-electrocyclic ring opening[13] leading to the dienoic carboxylates **4** (Scheme 1) followed by a [1,5]-H shift through a deprotonation-reprotonation sequence. We ruled out a [1,5]-H sigmatropic shift due to high steric constraint in the required planar transition state due to the *cis,cis* configuration of the dienoic system **4**.[14] A further rapid 6π electrocyclization would lead to the 2*H*-pyran **1'** from oxatriene **5**. This last electrocyclic reaction seemed to be a rapid process since oxatriene intermediate **5** was never detected. This observation suggests that even during the formation of 2*H*-pyran **2,** the mechanism involves intermediate **1'**. This proposition is confirmed by the fact that 2*H*-pyran **1a**, treated with NEt_3 in DCM delivered, after 15h at reflux, the corresponding decarboxylated 2*H*-pyran **2a** in 95 %. The mechanistic pathway to 2*H*-pyrans **2** implies that decarboxylation may operate on the transient 1-oxatriene **5** giving the stabilized enolate **6** which, after reprotonation from ammonium, gives the oxatriene **7** and regenerates NEt_3 (Table 1, entry 12). The mechanistic pathway ends with the rapid 6π electrocyclization delivering the stable 2*H*-pyran **2**.

Scheme 1. Proposed Unified Mechanism for Cascade Reaction Leading to *2H*-pyrans 1 and 2



A possible rationale for the modest yields obtained with aromatic di-ketones at rt could be explained by steric factors. The planarity of the substituents of the double bonds (EWG=COAr and R=Ar) in the 6π transition state is required for the transformation of 1-oxatriene **5** to 2*H*-pyran **1'**. Since the 6π electrocyclization was inhibited and all the steps are reversible, starting materials were recovered accompanied by complex mixture of by-products. In contrast, by heating the reaction mixture, intermediate **5** was irreversibly converted to enolate **6** which after reprotonation and 6-π electrocyclization gave the stable 2*H*-pyran **2**.

In summary, we described here a rapid and efficient synthesis of more than thirty stable tetrasubstituted 2*H*-pyrans **1**, **2** and **3**. The reactions to **1** or **2** proceed through a cascade 1,6-Michael / 6π electrocyclic ring opening / [1,5]-H transfer / (decarboxylation) / 6π electrocyclization reaction. In addition to the broad substrate scope, this methodology has the advantage of using readily available starting materials and mild conditions. The resulting 2*H*-pyrans bear functional groups, which should allow chemoselective transformations useful in total synthesis.[2] Secoiridoid monoterpenes such as secologanin or gentiopicroside are also potential targets with biological activities of interest.[15]

EXPERIMENTAL SECTION

General. All reactions were carried out under argon atmosphere with magnetic stirring in dry and distillated solvents. ^1H and ^{13}C NMR spectra were recorded at 400 MHz for ^1H nuclei, 100 MHz for ^{13}C nuclei. Chemical shifts are reported in δ units, parts per million (ppm) using, for ^1H and ^{13}C, solvent residual peak as internal standard references: chloroform (7.26 ppm for

^{1}H NMR and 77.16 ppm for ^{13}C NMR). Coupling constants (*J*) are given in Hz, multiplicities are abbreviated as: s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublets), ddd (doublet of doublets of doublets), t (triplet), m (multiplet). High resolution mass spectra (HR-MS) were recorded on a LTQ-Orbitrap Mass Spectrometer [Thermo Scientific]. IR: Shimadzu IRAffinity-1CE spectrometer, wavenumbers in cm^{-1}. Reactions were monitored by thin-layer chromatography carried out on silica plates (silica gel 60 F254, Merck) using UV-light for visualization. Column chromatography was performed on silica gel 60 (0.040−0.063 mm, Merck) using the indicated eluent given in volume ratio. All starting materials were purchased at the highest commercial quality and used without further purification unless otherwise stated.

Procedure A: General procedure for the synthesis of compounds 1a-c, 1e-j. The corresponding methylene active compound (1 mmol, 1 equiv) was added at r.t. to a solution of methyl coumalate (154 mg, 1 mmol, 1 equiv) in EtOH (5 mL). After Na_2CO_3 (105 mg, 1 mmol, 1 equiv) was added to this colorless solution, it turned to orange. Thus prepared solution was stirred for 1 h at r.t. under Argon. Then the reaction mixture was diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). Then the aqueous layer, containing the product as sodium salt, was acidified with 1M HCl (5 mL, until pH = 2) and extracted with DCM (3 × 20 mL). Collected organic layers were dried over anhydrous $MgSO_4$, filtrated and evaporated under reduced pressure to afford the target products.

Procedure B: General procedure for the synthesis of compounds 2a-u. To a solution of methyl coumalate (154 mg, 1 mmol, 1 equiv) in CH_2Cl_2 (5 mL) at r.t. was added the corresponding methylene active compound (1 mmol, 1 equiv) followed by triethylamine (101 mg, 1 mmol, 1 equiv). The solution was stirred for 15 h under reflux, cool to r.t. then quenched with 1M HCl (10 mL). The mixture was extracted with DCM (3 × 20 mL). The organic layers were washed with brine and dried over anhydrous $MgSO_4$, filtrated and evaporated and the residue was subjected to column chromatography on silica yielding the respective title compounds.

Procedure C: General procedure for the synthesis of compounds 3d, 3i, 3j. The corresponding methylene active compound (1 mmol, 1 equiv) was added at r.t. to a solution of methyl coumalate (154 mg, 1 mmol, 1 equiv) in EtOH (5 mL). After Na_2CO_3 (105 mg, 1 mmol, 1 equiv) was added to this colorless solution, it turned to orange. Thus prepared solution was stirred for 1h at r.t. under Argon. Then N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (192 mg, 1 mmol, 1 equiv) and DMAP (24 mg, 0.2 mmol, 0.2 equiv) was added in CH_2Cl_2 (5mL) solution, Once reaction was completed, the reaction mixture was quenched with 1M HCl (10 mL) and mixture was extracted into CH_2Cl_2 (3 × 20 mL) Collected organic layers were washed with brine and dried over anhydrous $MgSO_4$, filtrated and evaporated and the residue was subjected to column chromatography on silica yielding the respective title compounds.

2-(3,5-bis(methoxycarbonyl)-6-methyl-2*H*-pyran-2-yl) acetic acid (1a) : The title compound was prepared according to procedure A, 243 mg; 90% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.65 (br s, 1H), 7.56 (s, 1H), 5.73 (dd, *J* = 10.1, 3.1 Hz, 1H), 3.77 (s, 6H), 2.84 (dd, *J* = 15.2, 10.1 Hz, 1H), 2.56 (dd, *J* = 15.2, 3.1 Hz, 1H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.9, 170.6, 165.4, 164.6, 132.3, 114.8, 104.4, 72.2, 51.9, 51.6, 37.9, 20.2; **IR** (film, cm^{-1}): ~3600-2600 (br), 2976, 2868, 1716, 1436, 1362, 1244, 1182, 1112, 933, 790; **HRMS** (ESI) Found *m/z* 293.0632 calcd for [M+Na^+] $C_{12}H_{14}NaO_7$ 293.0632.

2-(6-butyl-3,5-bis(methoxycarbonyl)-2*H*-pyran-2-yl)acetic acid (1b): The title compound was prepared according to procedure A, 268 mg; 90% yield; yellow oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.43 (br s, 1H), 7.57 (s, 1H), 5.75 (dd, *J* = 10.1, 3.0 Hz, 1H), 3.77 (s, 3H), 3.77 (s, 3H), 2.98 – 2.76 (m, 2H), 2.55-2.57 (m, 2H), 1.66 – 1.52 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 175.2, 174.0, 165.3, 164.7, 132.6, 114.6, 104.1, 72.0, 51.9, 51.6, 37.7, 34.6, 20.7, 14.0; **IR** (film, cm^{-1}): ~3600-2600 (br), 2960, 2873, 1714, 1558, 1436, 1232, 1112, 1060, 977, 756; **HRMS** (ESI) Found *m/z* 321.0957 calcd for [M+Na^+] $C_{14}H_{18}NaO_7$ 321.0945

2-(3,5-bis (methoxycarbonyl) -6- (methoxymethyl)-2H-pyran-2-yl) acetic acid (1c): The title compound was prepared according to procedure A, 273 mg; 91% yield: colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.63 (br s, 1H), 7.53 (s, 1H), 5.83 (dd, J = 9.9, 3.2 Hz, 1H), 4.65 (d, *J* = 14.0 Hz, 1H), 4.44 (d, *J* = 14.0 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.40 (s, 3H), 2.90 (dd, *J* = 15.6, 9.9 Hz, 1H), 2.57 (dd, *J* = 15.6, 3.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.9, 167.4, 164.8, 164.3, 131.5, 116.6, 105.9, 72.3, 69.3, 59.3, 52.1, 51.9, 37.6; **IR** (film, cm^{-1}): ~3700-2500 (br), 2953, 1710, 1641, 1570, 1242, 1112, 1064, 977, 756; **HRMS** (ESI) Found *m/z* 323.0748 calcd for [M+Na^+] $C_{13}H_{16}NaO_8$ 323.0737.

2-(6-(chloromethyl)-3,5-bis(methoxycarbonyl)-2*H*-pyran-2-yl) acetic acid (1e): The title compound was prepared according to procedure A , 255 mg; 84% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (br s, 1H), 7.52 (s, 1H), 5.81 (dd, *J* = 9.9, 3.1 Hz, 1H), 4.90 (d, *J* = 11.3 Hz, 1H), 4.29 (d, *J* = 11.3 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 2.93 (dd, *J* = 16.2, 9.9 Hz, 1H), 2.56 (dd, *J* = 16.2, 3.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.7, 164.2, 164.2, 164.1, 131.1, 117.9, 106.1, 72.0, 52.2 (2C), 39.8, 37.4; **IR** (film, cm^{-1}): ~3700-2400 (br), 2978, 1716, 1436, 1384, 1251, 1238, 1193, 1180, 1097, 1070, 1002, 933, 833, 756; **HRMS** (ESI) Found m/z 303.0266, calcd for [M-H^+] $C_{12}H_{12}ClO_7$ 303.0277.

2-(6-(2-methoxy-2-oxoethyl)-3,5-bis(methoxycarbonyl)-2*H*-pyran-2-yl) acetic acid (1f): The title compound was prepared according to procedure A, 302 mg; 92% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.16 (br s, 1H), 7.55 (s, 1H); 5.80 (dd, *J* = 10.1, 2.7 Hz, 1H); 4.14 (d, *J* = 16.2 Hz, 1H); 3.79 (s, 3H); 3.77 (s, 3H); 3.71 (s, 3H); 3.48 (d, *J* = 16.2 Hz, 1H´); 3.07 (dd, *J* = 16.4, 10.1 Hz, 1H); 2.53 (dd, *J* = 16.4, 2.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.8; 168.7; 164.9; 164.6; 164.4; 131.4; 116.5; 106.4; 72.4; 52.6; 52.1; 52.0; 39.0; 37.4; **IR** (film, cm^{-1}): ~3500-2400 (br), 2960, 1714, 1697, 11435, 1357, 1247, 1093, 997, 877, 775; **HRMS** (ESI) Found *m/z* 351.0687, calcd for [M+Na^+] $C_{14}H_{16}NaO_9$ 351.0691.

2-(5-acetyl-3-(methoxycarbonyl)-6-methyl-2*H*-pyran-2-yl)acetic acid (1g): The title compound was prepared according to procedure A, 228 mg; 90% yield; colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.42 (br s, 1H), 7.46 (s, 1H), 5.74 – 5.54 (m, 1H), 3.73 (s, 3H), 2.77 (m, 1H), 2.50 (m, 1H), 2.28 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.6, 174.4, 171.1, 164.5, 132.3, 114.8, 112.9, 72.3, 52.0, 37.9, 28.9, 21.0; **IR** (film, cm^{-1}): ~3500-2400 (br), 2976, 2870, 1712, 1624, 1436, 1382, 1238, 1105, 1070, 1018, 935, 840; **HRMS** (ESI) Found *m/z* 277.0784, calcd for [M+Na^+] $C_{12}H_{14}NaO_6$ 277.0683.

Dimethyl-2,6-dimethyl-2*H*-pyran-3,5-dicarboxylate (2a): The title compound was prepared according to procedure B,

196 mg; 87% yield; colorless oil; R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 5.34 (q, J = 6.5 Hz, 1H), 3.74 (s, 3H), 3.74 (s, 3H), 2.34 (s, 3H), 1.30 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.8, 165.8, 165.0, 130.8, 117.2, 103.5, 72.5, 51.6, 51.4, 20.5, 19.2; **IR** (film, cm^{-1}): 2951, 2918, 1716, 1689, 1637, 1433, 1379, 1309, 1226, 1128, 1045, 910, 752; **HRMS** (ESI) Found *m/z* 233.0996, calcd for $[M+Li^+]$ $C_{11}H_{14}LiO_5$ 233.0996.

Dimethyl-2-methyl-6-propyl-2*H*-pyran-3,5-dicarboxylate (2b): The title compound was prepared according to procedure B, 224 mg; 88% yield; white solid, m.p.123-126^{o}C; R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 5.34 (q, *J* = 6.5 Hz, 1H), 3.73 (s, 3H), 3.73 (s, 3H), 3.04 – 2.84 (m, 1H), 2.51 – 242 (m, 1H), 1.67 – 1.50 (m, 2H), 1.27 (d, *J* = 6.5 Hz, 3H), 0.95 (t, *J* = 7.4 Hz, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.1, 165.6, 165.0, 131.0, 117.2, 103.4, 72.2, 51.6, 51.3, 34.7, 20.6, 19.0, 13.9; **IR** (film, cm^{-1}): 2974, 2872, 1701, 1639, 1556, 1435, 1307, 1224, 1122, 1068, 914, 756; **HRMS** (ESI) Found *m/z* 277.1051, calcd for $[M+Na^+]$ $C_{13}H_{18}NaO_5$ 277.1046

Dimethyl-6-(methoxymethyl)-2-methyl-2*H*-pyran-3,5-dicarboxylate (2c): The title compound was prepared according to procedure B, 208 mg, 81% yield, white solid, m.p.140-141^{o}C, R_f = 0.3 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (s, 1H), 5.46 (q, *J* = 6.5 Hz, 1H), 4.67 (d, *J* = 14.3 Hz, 1H), 4.40 (d, *J* = 14.3 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.39 (s, 3H), 1.35 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 165.1, 164.7, 130.1, 118.8, 104.9, 72.8, 69.6, 59.1, 51.8, 51.6, 19.0; **IR** (film, cm^{-1}): 2951, 2931, 1699, 1639, 1566, 1435, 1309, 1226, 1124, 1076, 991, 912, 752; **HRMS** (ESI) Found *m/z* 279.0835 calcd for $[M+Na^+]$ $C_{12}H_{16}NaO_6$ 279.0839.

Dimethyl-6-cyclopropyl-2-methyl-2*H*-pyran-3,5-dicarboxylate (2d): The title compound was prepared according to procedure B, 237 mg; 94% yield; white solid, m.p.101-103^{o}C; R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 5.27 (q, *J* = 6.5 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.17 – 3.10 (m, 1H), 1.35 – 1.24 (m, 1H), 1.21 (d, *J* = 6.5 Hz, 3H), 1.09 – 0.97 (m, 1H), 0.97 – 0.88 (m, 1H), 0.88 – 0.74 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.8, 166.2, 165.1, 131.4, 116.3, 103.5, 72.0, 51.5, 51.4, 18.6, 13.1, 10.1, 7.1; **IR** (film, cm^{-1}): 2951, 2929, 1687, 1635, 1539, 1301, 1222, 1062, 1043, 931, 875, 815; **HRMS** (ESI) Found *m/z* 275.0885, calcd for $[M+Na^+]$ $C_{13}H_{16}NaO_5$ 275.0890.

Dimethyl-6-(chloromethyl)-2-methyl-2*H*-pyran-3,5-dicarboxylate (2e): The title compound was prepared according to procedure B, 179 mg; 71% yield; colorless oil; R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 0.4 Hz, 1H), 5.43 (q, *J* = 6.5 Hz, 1H), 4.97 (d, *J* = 11.2 Hz, 1H), 4.24 (d, *J* = 11.2 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 1.36 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 164.1, 129.6, 120.4, 105.5, 72.6, 52.0, 51.9, 40.1, 18.9; **IR** (film, cm^{-1}): 2953, 2926, 1703; 1643, 1573, 1435, 1307, 1228, 1124, 1076, 939, 796, 754; **HRMS** (ESI) Found *m/z* 267.0610, calcd for $[M+Li^+]$ $C_{11}H_{13}ClLiO_5$ 267.0606.

Dimethyl-6-(2-methoxy-2-oxoethyl)-2-methyl-2*H*-pyran-3,5-dicarboxylate (2f): The title compound was prepared according to procedure B, 233 mg, 82% yield, colorless oil, R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 5.35 (q, *J* = 6.5 Hz, 1H), 4.05 (d, *J* = 16.2 Hz, 1H), 3.71 (s, 3H), 3.71 (s, 3H), 3.67 (s, 3H), 3.44 (d, *J* = 16.2 Hz, 1H), 1.32 (d, *J* = 6.5 Hz, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.7, 165.2, 164.8, 164.7, 129.8, 118.8, 105.4, 73.0, 52.2, 51.7, 51.6, 39.0, 19.1; **IR** (film, cm^{-1}): 3001, 2954, 1739, 1712, 1689, 1641, 1573, 1463, 1332, 1122, 1047, 948, 871; **HRMS** (ESI) Found *m/z* 307.0784, calcd for $[M+Na^+]$ $C_{13}H_{16}NaO_7$ 307.0788.

Methyl-5-acetyl-2,6-dimethyl-2*H*-pyran-3-carboxylate (2g): The title compound was prepared according to procedure B, 199 mg; 95% yield, colorless oil, R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 5.32 (q, *J* = 6.5 Hz, 1H), 3.73 (s, 3H), 2.29 (s, 3H), 2.28 (s, 3H), 1.27 (d, *J* = 6.5 Hz, 3H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.2, 171.1, 164.9, 131.0, 117.1, 112.3, 72.5, 51.6, 28.9, 21.3, 19.2; **IR** (film, cm^{-1}): 2976, 1703, 1633, 1558, 1436, 1274, 1228, 1147, 1122, 954, 756; **HRMS** (ESI) Found *m/z* 233.0783 calcd for $[M+Na^+]$ $C_{11}H_{14}NaO_4$ 233.0784.

Methyl-5-acetyl-2-methyl-6-phenyl-2*H*-pyran-3-carboxylate (2h): The title compound was prepared according to procedure B, 117 mg, 43% yield, yellow oil, R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.60 – 7.30 (m, 5H), 5.53 (q, *J* = 6.5 Hz, 1H), 3.78 (s, 3H), 1.88 (s, 3H), 1.48 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.8, 165.6, 165.0, 133.7, 131.7, 131.1, 129.9, 128.5, 119.0, 115.8, 72.6, 51.8, 29.8, 18.3; **IR** (film, cm^{-1}): 2976, 1705, 1625, 1435, 1363, 1283, 1119, 875, 771, 793; **HRMS** (ESI) Found *m/z* 295.0942, calcd for $[M+Na^+]$ $C_{16}H_{16}NaO_4$ 295.0941.

Methyl-5-benzoyl-2,6-dimethyl-2*H*-pyran-3-carboxylate (2h'): The title compound was prepared according to procedure B, 106 mg, 39% yield, colorless oil, R_f = 0.3 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 – 7.38 (m, 5H), 7.32 (s, 1H), 5.43 (q, *J* = 6.5 Hz, 1H), 3.72 (s, 3H), 2.09 (s, 3H), 1.44 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.7, 169.2, 165.1, 139.1, 132.3, 131.6, 128.9, 128.6, 116.8, 112.2, 72.4, 51.6, 26.9, 20.7, 19.3; **IR** (film, cm^{-1}): 2976, 1703, 1624, 1435, 1381, 1238, 1147, 1043, 939, 877, 725; **HRMS** (ESI) Found *m/z* 311.0675, calcd for $[M+K^+]$ $C_{16}H_{16}KO_4$ 311.0680.

Methyl-2-methyl-5-oxo-5,6,7,8-tetrahydro-2H-chromene-3-carboxylate (2i): The title compound was prepared according to procedure B, 188 mg, 85% yield, colorless oil, R_f = 0.3 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 5.39 (q, *J* = 6.5 Hz, 1H), 3.72 (s, 3H), 2.49 – 2.43 (m, 2H), 2.43 – 2.36 (m, 2H), 2.05 – 1.88 (m, 2H), 1.33 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.1, 175.0, 165.1, 126.7, 119.4, 110.9, 73.5, 51.6, 36.4, 28.8, 20.3, 20.2; **IR** (film, cm^{-1}): 2954, 2927, 1703, 1633, 1556, 1435, 1381, 1274, 1145, 1122, 1076, 954, 754; **HRMS** (ESI) Found *m/z* 245.0789, calcd for $[M+Na^+]$ $C_{12}H_{14}NaO_4$ 245.0784.

Methyl-2,6-dimethyl-5-(methylsulfonyl)-2*H*-pyran-3-carboxylate (2j): The title compound was prepared according to procedure B, 223 mg, 91% yield, colorless oil, R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 5.36 (q, *J* = 6.5 Hz, 1H), 3.73 (s, 3H), 2.95 (s, 3H), 2.33 (s, 3H), 1.34 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 164.3, 128.0 (2C), 118.4, 113.8, 73.1, 51.9, 44.2, 19.3; **IR** (film, cm^{-1}): 2980, 2954, 1703, 1633, 1556, 1435, 1381, 1274, 1228, 1145, 1122, 1043, 954, 754; **HRMS** (ESI) Found *m/z* 269.0458, calcd for $[M+Na^+]$ $C_{10}H_{14}NaO_5S$ 269.0454.

Dimethyl-6-(tert-butyl)-2-methyl-2*H*-pyran-3,5-dicarboxylate (2k): The title compound was prepared according to Procedure B, 71 mg, 27% yield, colorless oil, R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ

7.36 (s, 1H), 5.36 (q, *J* = 6.5 Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 1.27 (d, *J* = 6.5 Hz, 3H), 1.25 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.8, 167.4, 164.9, 132.7, 116.6, 105.2, 71.3, 51.7, 51.6, 38.2, 27.6, 17.5; **IR** (film, cm^{-1}): 2951, 1701,1637, 1529, 1435, 1384, 1301, 1230, 1215, 1107, 933, 914, 756; **HRMS** (ESI) Found *m/z*, 291.1214, calcd for $[M+Na^+]$ $C_{14}H_{20}NaO_5$ 291.1203

5-ethyl-3-methyl-2-methyl-6-phenyl-2*H*-pyran-3,5-dicarboxylate (2l): The title compound was prepared according to procedure B, 262 mg, 80% yield, yellow oil, R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.53 – 7.30 (m, 5H), 5.53 (q, *J* = 6.5 Hz, 1H), 4.07 (q, *J* = 7.1, 2H), 3.78 (s, 3H), 1.49 (d, *J* = 6.5 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.8, 165.7, 164.9, 133.9, 131.6, 130.8(2C), 129.5(2C), 127.7, 118.5, 105.3, 72.7, 60.4, 51.7, 18.5, 13.8; **IR** (film, cm^{-1}): 2978, 1697, 1637, 1548, 1487, 1436, 1375, 1300, 1230, 1124, 1080, 989, 920, 754; **HRMS** (ESI) Found *m/z* 325.1071, calcd for $[M+Na^+]$ $C_{17}H_{18}NaO_5$ 325.1052.

5-ethyl-3-methyl-2-methyl-6-(4-nitrophenyl)-2*H*-pyran-3,5-dicarboxylate (2m): The title compound was prepared according to procedure B, 336 mg, 97% yield, yellow oil, R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.9 Hz, 2H), 7.62 (s, 1H), 7.61 (d, *J* = 8.9 Hz, 2H), 5.56 (q, *J* = 6.5 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 1.52 (d, *J* = 6.5 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.7, 164.6, 163.0, 148.8, 140.1, 130.6, 130.5, 123.0, 120.0, 106.7, 73.1, 60.9, 52.0, 18.9, 13.9; **IR** (film, cm^{-1}): 2989, 1693, 1633, 1546, 1435, 1371, 1298, 1236, 1134, 1018, 1991, 856, 752; **HRMS** (ESI) Found *m/z* 370.0910, calcd for $[M+Na^+]$ $C_{17}H_{17}NNaO_7$ 370.0903.

Methyl-2-methyl-5-oxo-2,5-dihydropyrano-[3,2-c]-chromene-3-carboxylate (2n) : The title compound was prepared according to procedure B, 222 mg, 82% yield, yellow oil; R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 1H), 7.66 (s, 1H), 7.64 – 7.55 (m, 1H), 7.36 – 7.28 (m, 2H), 5.71 (q, *J* = 6.5 Hz, 1H), 3.82 (s, 3H), 1.50 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.5, 161.4, 160.1, 153.9, 133.7, 127.4, 124.4, 123.6, 122.3, 117.1, 114.8, 100.4, 74.0, 52.0, 20.5; **IR** (film, cm-1): 2926, 2854, 1722, 1699, 1637, 1606, 1556, 1490, 1296, 1242, 1205, 1029, 975, 935, 752; **HRMS** (ESI) Found *m/z* 295.0584, calcd for $[M+Na^+]$ $C_{15}H_{12}NaO_5$ 295.0577.

Methyl-6-ethyl-2-methyl-5-propionyl-2*H*-pyran-3-carboxylate (2o): The title compound was prepared according to procedure B, 216 mg, 91% yield, colorless oil; R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 5.32 (q, *J* = 6.5 Hz, 1H), 3.72 (s, 3H), 2.98 – 2.77 (m, 1H), 2.73 – 2.50 (m, 2H), 2.48 – 2.29 (m, 1H), 1.25 (d, *J* = 6.5 Hz, 3H), 1.10 (t, *J* = 7.5 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 174.7, 164.9, 130.7, 117.1, 111.4, 71.9, 51.6, 33.5, 26.9, 18.7, 11.1, 8.1. **IR** (film, cm-1): 2980, 2941, 1707, 1678, 1624, 1531, 1436, 1377, 1290, 1220, 1195, 1068, 898, 761; **HRMS** (ESI) Found *m/z* 277.0840, calcd for $[M+K^+]$ $C_{13}H_{18}KO_4$ 277.0837.

Methyl-5-benzoyl-2-methyl-6-phenyl-2*H*-pyran-3-carboxylate (2p): The title compound was prepared according to procedure B, 166 mg, 50% yield, yellow oil, R_f = 0.3 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.53 – 7.46 (m, 2H), 7.26 – 7.14 (m, 3H), 7.15 – 6.97 (m, 5H), 5.57 (q, *J* = 6.5 Hz, 1H), 3.73 (s, 3H), 1.57 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.9, 165.0, 164.0, 138.1, 133.0, 132.2, 132.1, 131.1, 130.1(2C), 129.3(2C), 128.0(2C), 127.9(2C), 119.0, 113.4, 72.4, 51.8, 18.6; **IR** (film, cm-1): 2974, 2852, 1695, 1672, 1543, 1446, 1435, 1240, 1176, 1053, 1020 941, 904, 771; **HRMS** (ESI) Found *m/z* 357.1107, calcd for $[M+Na^+]$ $C_{21}H_{18}NaO_4$ 357.1097.

Methyl-2,7,7-trimethyl-5-oxo-5,6,7,8-tetrahydro-2*H*-chromene-3-carboxylate (2q): The title compound was prepared according to procedure B, 210 mg, 84% yield, colorless oil, R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 5.41 (q, *J* = 6.5 Hz, 1H), 3.72 (s, 3H), 2.43 – 2.31 (m, 2H), 2.30 – 2.11 (m, 2H), 1.33 (d, *J* = 6.5 Hz, 3H), 1.08 (s, 3H), 1.00 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.8, 173.7, 165.1, 126.6, 119.1, 109.9, 73.6, 51.6, 50.3, 42.5, 32.3, 29.4, 27.2, 20.2; **IR** (film, cm-1): 2965, 2872, 1703, 1660, 1571, 1398, 1307, 1217, 1145, 1068, 939, 761; **HRMS** (ESI) Found *m/z* 273.1099, calcd for $[M+Na^+]$ $C_{14}H_{18}NaO_4$ 273.1097.

Methyl-2-methyl-5-oxo-2,5,6,7-tetrahydrocyclopenta-[b]-pyran-3-carboxylate (2r): The title compound was prepared according to procedure B, 201 mg, 96% yield, colorless oil, R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 5.65 (q, *J* = 6.5 Hz, 1H), 3.76 (s, 3H), 2.81 – 2.57 (m, 2H), 2.54 (ddd, *J* = 12.1, 9.2, 6.4 Hz, 2H), 1.46 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.1, 187.9, 165.0, 125.2(2C), 120.3, 113.7, 51.9, 34.1, 26.7, 21.0; **IR** (film, cm-1): 2989, 2953, 1693, 1633, 1546, 1344, 991, 856, 752; **HRMS** (ESI) Found *m/z* 231.0637, calcd for $[M+Na^+]$ $C_{11}H_{12}NaO_4$ 231.0628.

Dimethyl-6-(4-fluorophenyl)-2-methyl-2*H*-pyran-3,5-dicarboxylate (2s): The title compound was prepared according to procedure B, 251 mg, 82% yield, yellow oil, R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.52 – 7.42 (m, 2H), 7.12 – 7.03 (m, 2H), 5.54 (q, *J* = 6.5 Hz, 1H), 3.80 (s, 3H), 3.64 (s, 3H), 1.47 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 165.6, 164.8, 131.9, 131.8, 131.4(2C), 118.7, 115.1(2C), 114.9, 104.7, 72.8, 51.8, 51.5, 18.5; **IR** (film, cm-1): 2976, 1699, 1637, 1602, 1595, 1367, 1083, 1049, 1024, 952, 914, 840, 754; **HRMS** (ESI) Found *m/z* 329.0807, calcd for $[M+Na^+]$ $C_{16}H_{15}FNaO_5$ 329.0796.

Methyl-2,6-dimethyl-5-(phenylsulfonyl)-2*H*-pyran-3-carboxylate (2t): The title compound was prepared according to procedure B, 300 mg, 97% yield, colorless oil, R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 – 7.79 (m, 2H), 7.63 – 7.48 (m, 3H), 7.41 (s, 1H), 5.34 (q, *J* = 6.5 Hz, 1H), 3.75 (s, 3H), 2.29 (s, 3H), 1.28 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.1, 164.4, 142.5, 133.0 (2C), 129.3, 128.3(2C), 126.5, 118.4, 114.4, 73.1, 51.9, 19.5, 19.5; **IR** (film, cm^{-1}): 2980, 1703, 1633, 1556, 1435, 1274, 999, 927, 756; **HRMS** (ESI) Found *m/z* 331.0600, calcd for $[M+Na^+]$ $C_{15}H_{16}NaO_5S$ 331.0611.

Dimethyl 6-cyclopropyl-2-(2-ethoxy-2-oxoethyl)-2*H*-pyran-3,5-dicarboxylate (3d): The title compound was prepared according to procedure C, 220 mg; 68% yield; colorless oil; R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 5.67 (dd, *J* = 10.2, 3.0 Hz, 1H), 4.27 – 4.09 (m, 2H), 3.79 (s, 3H), 3.77 (s, 3H), 3.12 (tt, *J* = 8.2, 4.9 Hz, 1H), 2.74 (dd, *J* = 15.4, 10.2 Hz, 1H), 2.43 (dd, *J* = 15.4, 3.0 Hz, 1H), 1.34 – 1.31 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.05 – 1.00 (m, 1H), 0.95 – 0.80 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.9, 169.4, 165.8, 164.7, 132.8, 113.7, 103.8, 72.2, 60.9, 51.7, 51.47, 37.6, 14.1, 13.2, 10.8, 7.7. **IR** (film, cm^{-1}): 2968, 2954, 1732, 1707, 1693, 1547, 1449, 1393, 1175, 1114, 985,

908, 877, 752; **HRMS** (ESI) Found *m/z* 347.1107 calcd for $[M+Na^+]$ $C_{16}H_{20}NaO_7$ 347.1101.

Methyl-2-(2-ethoxy-2-oxoethyl)-5-oxo-5,6,7,8-tetrahydro-2H-chromene-3-carboxylate (3i): The title compound was prepared according to procedure C, 211 mg; 72% yield; colorless oil; R_f = 0.2 [1:4 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 5.79 (dd, J = 9.8, 3.2 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.79 (s, 3H), 2.78 (dd, J = 15.0, 9.8 Hz, 1H), 2.61 (dd, J = 15.0, 3.2 Hz, 1H), 2.55 – 2.37 (m, 4H), 2.10 – 1.95 (m, 2H), 1.29 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.0, 174.8, 169.2, 164.7, 128.1, 117.1, 111.4, 73.4, 61.0, 51.9, 39.3, 36.4, 28.4, 20.2, 14.2; **IR** (film, cm^{-1}): 2983, 2871, 1726, 1709, 1633, 1592, 1445, 1383, 1271, 1229, 759, 726; **HRMS** (ESI) Found *m/z* 317.1005, calcd for $[M+Na^+]$ $C_{15}H_{18}NaO_6$: 317.0996.

Methyl-2-(2-ethoxy-2-oxoethyl)-6-methyl-5-(phenylsulfonyl)-2*H*-pyran-3-carboxylate (3j): The title compound was prepared according to procedure C, 193 mg; 52 % yield; yellow oil; R_f = 0.2 [1:5 (v/v) EA/cyclohexane]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 – 7.81 (m, 2H), 7.68 – 7.52 (m, 3H), 7.50 (d, J = 0.5 Hz, 1H), 5.72 (dd, J = 9.9, 3.3 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 3.80 (s, 3H), 2.73 (dd, J = 15.0, 9.9 Hz 1H), 2.50 (dd, J = 15.0, 3.3 Hz, 1H), 2.33 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.9, 168.0, 164.0, 142.2, 133.2, 129.6 (2C), 129.4 (2C), 126.7, 116.3, 115.2, 73.1, 61.0, 52.1, 38.5, 19.2, 14.2.; **IR** (film, cm^{-1}): 3061, 2847, 2360, 2341, 1663, 1645, 1620, 1459, 1386, 1276, 1150, 883, 759; **HRMS** (ESI) Found *m/z* 403.0823, calcd for $[M+Na^+]$ $C_{18}H_{20}NaO_7S$ 403.0822.

Supporting Information

Supporting Information with full analysis of products **1**, **2** and **3** is available free of charge on the ACS Publications website.

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ACKNOWLEDGMENT

We thank University P. et M. Curie (UPMC) and CNRS for fundings. The Fédération de Recherche (FR2769) provided technical access for analysis. Acknowledgements to the French Embassy in Slovakia and to China Scholarship Council (CSC) for financial supports to K.P. and L.C. respectively.

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