The Reactions of *α*-Ylidene (Vinylidene, Benzylidene, Styrylmethylidene) Bis[carbonyls] with Copper Mono/Bis[carbonylcarbenoids]

by **Gökçe Merey***, **Mustafa Kaya**, and **Olcay Anaç***

Istanbul Technical University, Faculty of Science and Letters, Department of Chemistry, 34460 Maslak, TR-Istanbul (phone: +90-212-2853229; fax: +90-212-2856386; e-mail: anac@itu.edu.tr)

The [Cu(acac)$_2$]-catalyzed reactions of various *α*,*β*,*γ*,*δ*-unsaturated bis-ketones/bis-esters/bis-keto esters with dimethyl diazomalonate and ethyl diazoacetate were studied. Total steric/electronic convenience of the present reaction paths was investigated. Methoxy/nitro substituents in *m*-/*p*-positions on benzylidene biscarbonyls did not alter the general routes of the reactions, supporting concerted mechanism. Dihydrobenzoxepine/oxepine formation was sterically sensitive to the related pre-ring conformation, and dihydrofurans were effected by both charge control and steric factors.

Introduction. – The metal-catalyzed reactions of diazo compounds became promising for a diverse array of transformations with the advent of new catalysts. The recognition of different classes of carbenoids can open up new vistas of reactivity, moreover, there are still several attempts to react new substrates with old-generation metallocarbenes to investigate reaction probabilities with/without stereochemical concern [1–15].

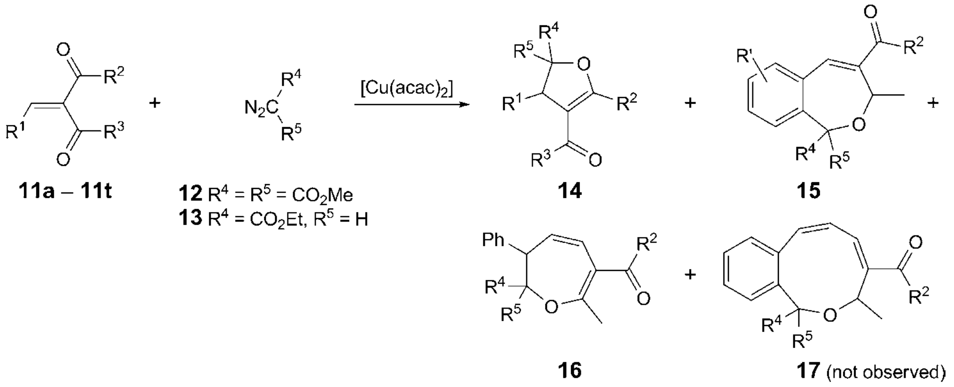
We recently reported the reactions of (dimethoxycarbonylcarbenoid)copper(II) with anilino derivatives of *tert*-enaminophenones [16] and *α*,*β*-unsaturated carboxamides [17]. In both studies, the conjugated carbonyl compounds offered three reaction sites (N, C(*α*), and O) for attack by electrophiles, beside carbenoid additions to the present double bonds, and several novel derivatives were obtained.

We also reported the (dimethoxycarbonylcarbenoid)copper(II) reactions of 2-vinylidene-/benzylidene mono/bis-ketones/esters [18] as pilot studies. In the reactions with 2-benzylidene monoketones/esters [18b], we did not observe any dihydrobenzoxepine derivative by a 1,7-electrocyclization from the related conjugated carbonyl ylides because of the restricted rotation around the double bond which hindered the necessary pre-ring conformation. In these reactions, we only found dihydrofurans, and its derivatives such as furofuran and *β*-vinylic dimethyl malonyl compounds. However, dihydrobenzoxepine formation by 1,7-electrocyclization was observed almost equal to dihydrofuran formation by 1,5-electrocyclization, when we investigated the reaction of 2-benzylidene-1,3-bisketones and bisketoesters [18c] with dimethyl diazomalonate. It should be mentioned that various researchers obtained either cyclopropanes [4a][19][20] or different products under similar conditions.

Considering that the factors controlling the chemoselectivity were more subtle than thought, we planned to extend this chemistry to more elaborate systems. Accordingly, we decided to conduct a systematic study to better understand the controlling factors behind the selectivity of this chemistry, which would allow a broader application of this methodology in total synthesis.

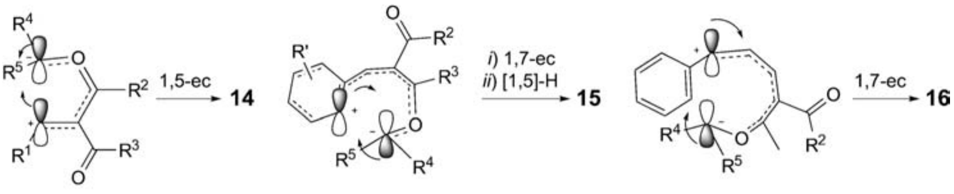
Results and Discussion. – In this study, several different substituted ene-biscarbonyls, **11a**–**11t**, were reacted with two different diazo carbonyl compounds, dimethyl diazomalonate (**12**) and ethyl diazoacetate (**13**), in the presence of [Cu(acac)$_2$] catalyst (*Scheme 1*). As the chemoselectivity problem has been a recurrent theme on transition metal-catalyzed carbene-transfer reactions over the last three decades, we aimed to search for the formation of dihydrofuran **14**, dihydrobenzoxepines **15**, dihydrooxepines **16**, and probably dihydrobenzooxonine derivatives **17** by 1,5-/1,7-, and perhaps 1,9-electrocyclic reactions beside other possible reaction pathways.

Scheme 1



The results are compiled in the *Table*, the related mechanisms are outlined in *Scheme 2*.

Scheme 2



ec = electrocyclization

In the first series of experiments, we studied both the electronic and steric effects of the ene-biscarbonyl structure on the chemoselectivity of the reaction. First, we used benzylidene and *m*-/*p*-MeO/NO$_2$ benzylidene-bis[phenyl ketones] **11a**–**11d** in the reaction with dimethyl diazomalonate (**12**). With these bulky ene-diones, reactions were so clean that only dihydrofuran derivatives **14a$_{12}$**–**14d$_{12}$** were obtained. Addi-

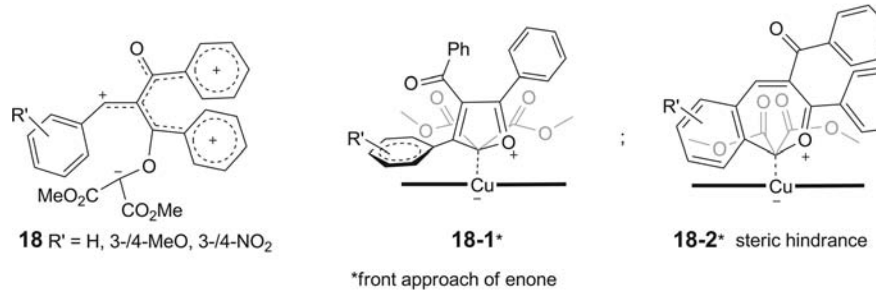
Table. *Product Distrubition of Cu^{II}-Catalyzed Reactions of Conjugated Biscarbonyls with Diazobiscarbonyls*

Entry	**11**	R^1	R^2	R^3	Diazo compound	**14/15** or **14/16**
1	**a**	Ph	Ph	Ph	**12**	100 : 0
2	**b**	3-MeO–C_6H_4	Ph	Ph	**12**	100 : 0
3	**c**	4-MeO–C_6H_4	Ph	Ph	**12**	100 : 0
4	**d**	3-NO_2–C_6H_4	Ph	Ph	**12**	100 : 0
5	**e**	Ph–CH=CH	Me	Me	**12**	76 : 24
6	**f**	Ph	Me	Me	**12**	40 : 60 [18c]
7	**g**	3-MeO–C_6H_4	Me	Me	**12**	40 : 60[a])
8	**h**	4-MeO–C_6H_4	Me	Me	**12**	44 : 56
9	**i**	3-NO_2–C_6H_4	Me	Me	**12**	29 : 71[a])
10	**j**	4-NO_2–C_6H_4	Me	Me	**12**	38 : 62
11	**k**	Ph	EtO	Me	**12**	50 : 50 [18c]
12	**l**	3-NO_2–C_6H_4	EtO	Me	**12**	47 : 53[a])
13	**m**	4-NO_2–C_6H_4	EtO	Me	**12**	43 : 57
14	**n**	Ph–CH=CH	EtO	Me	**12**	55 : 45
15	**o**	Ph	EtO	EtO	**12**	100 : 0 [18b]
16	**p**	3-MeO–C_6H_4	EtO	EtO	**12**	100 : 0
17	**q**	3-NO_2–C_6H_4	EtO	EtO	**12**	100 : 0
18	**r**	4-NO_2–C_6H_4	EtO	EtO	**12**	100 : 0
19	**s**	Ph–CH=CH	EtO	EtO	**12**	100 : 0
20	**t**	Me	EtO	EtO	**12**	N/A[b])
21	**a**	Ph	Ph	Ph	**13**	N/A[b])
22	**b**	3-MeO–C_6H_4	Ph	Ph	**13**	N/A[b])
23	**c**	4-MeO–C_6H_4	Ph	Ph	**13**	N/A[b])
24	**d**	3-NO_2–C_6H_4	Ph	Ph	**13**	N/A[b])
25	**e**	Ph–CH=CH	Me	Me	**13**	58 : 42
26	**f**	Ph	Me	Me	**13**	63 : 37
27	**g**	3-MeO–C_6H_4	Me	Me	**13**	62 : 38[a])
28	**h**	4-MeO–C_6H_4	Me	Me	**13**	59 : 41
29	**i**	3-NO_2–C_6H_4	Me	Me	**13**	58 : 42
30	**j**	4-NO_2–C_6H_4	Me	Me	**13**	53 : 47
31	**k**	Ph	EtO	Me	**13**	60 : 40
32	**l**	3-NO_2–C_6H_4	EtO	Me	**13**	55 : 45
33	**m**	4-NO_2–C_6H_4	EtO	Me	**13**	58 : 42
34	**n**	Ph–CH=CH	EtO	Me	**13**	74 : 26[a])
35	**o**	Ph	EtO	EtO	**13**	N/A[b])
36	**p**	3-MeO–C_6H_4	EtO	EtO	**13**	N/A[b])
37	**q**	3-NO_2–C_6H_4	EtO	EtO	**13**	N/A[b])
38	**r**	4-NO_2–C_6H_4	EtO	EtO	**13**	N/A[b])
39	**s**	Ph–CH=CH	EtO	EtO	**13**	N/A[b])
40	**t**	Me	EtO	EtO	**13**	N/A[b])

[a]) Compound **15** was obtained as a 1 : 1 mixture of stereoisomers. [b]) N/A: Not available.

tional resonance caused by carbonyl-phenyl rings stabilized completely the pre-ring carbonyl-ylide structure **18** for a 1,5-dipole (*Scheme 3*). Moreover, the configuration of a Cu-associated carbonyl ylide intermediate **18-1** might be responsible for this excellent chemoselectivity leading to only dihydrofuran formation **14a$_{12}$**–**14d$_{12}$**. *m*-/*p*-MeO/NO_2

Scheme 3



Substituents on phenyl ring did not alter these preferences. In contrast to the steric conformity in the hypothetic model **18-1** for dihydrofuran formation, the steric hindrance in the hypothetic model **18-2** caused by phenyl groups presumably prevented a 1,7-electrocyclization to yield dihydrobenzoxepines.

We needed additional data to explain the excess formation of dihydrobenzoxepine **15f**$_{12}$ in our previous study [18c] with benzylidene acetone and dimethyl diazomalonate. Therefore, a series of benzylidene-bisacetyls **11f** – **11j** and benzylidene-bis[keto esters] **11k** – **11m** were reacted with dimethyl diazomalonate (**12**). With the exception of **11k**, which gave equal amounts of **14** and **15**, all reactions yielded the corresponding dihydrofurans **14** and dihydrobenzoxepines **15** in favor of **15**. This preference might be explained rather by the orbital coefficients of the 1,7-dipole, which are smaller (less centralized) than those of the 1,5-dipole. These results supported the reports [20] [21], which indicated the preference of 1,7-ring closures because of the larger orbital coefficients at the termini of the conjugated system involving 8π electrons (*Scheme 2*).

It is also of interest to note that two different 1,7-ring closures occurred in the case of *m*-methoxy- and *m*-nitrobenzylidene biscarbonyls **11g**, **11i**, and **11l** due to the presence of two possible positions. The ratio of these two 1,7-cyclization products was almost 1 : 1, showing no selectivity despite the presence of electron-donating/withdrawing groups. This result also supported a concerted mechanism [22 – 24] for a 1,7-electrocyclization reaction of the corresponding conjugated carbonyl-ylide, thus questioning the argument of charge control in chemo-/regioselectivity to a certain extent.

In the experiments with conjugated bis[keto esters] **11k** – **11n**, an additional chemoselectivity on ketone or ester carbonyls was observed1). Our previous result concerning the reaction of **11k** [11], and the novel results with **11l** – **11n** showed that 1,7-electrocyclizations took place only from ketone sides and 1,5-electrocyclizations only from ester sides. Being analogous to the resonance stability of **18**, the O-atom of the ester alkoxy group might facilitate the centralization of 1,5-dipole as shown on the intermediate conjugated ester ylide **19** (*Scheme 4*). In addition to the availability of more centralized charge-controlled structure with respect to ester **19** ($R^2 = Me$), the

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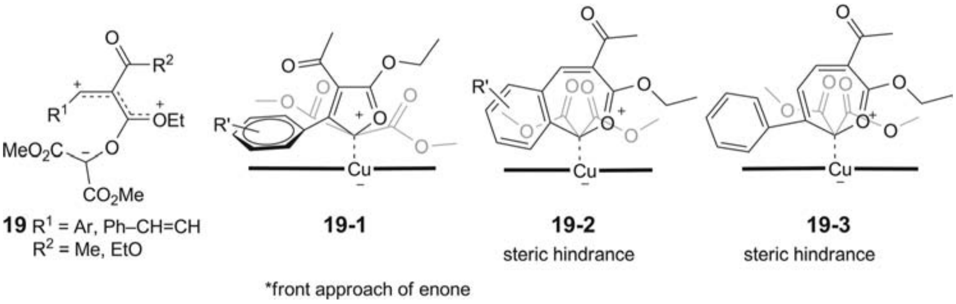
1) The available rotation around formal C=C bonds allows either keto or ester function to adopt pre-ring 1,5-/1,7-conformations in these fully conjugated, highly polarized bis[keto esters] under our experimental conditions.

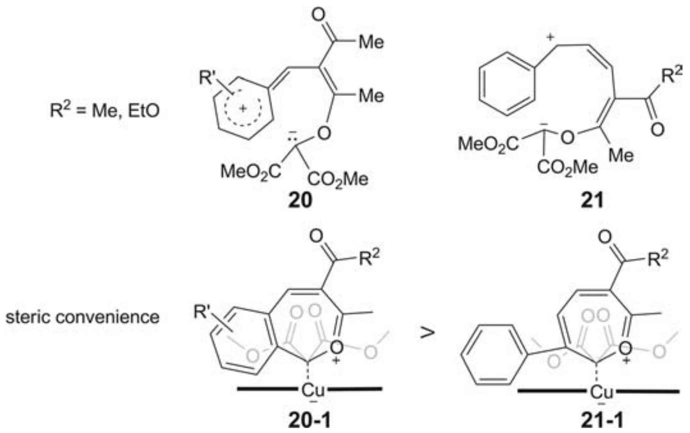
hypothetical model **19-1** also showed that 1,5-cyclization was sterically more attractive in the case of ester carbonyl ylide than 1,7-cyclizations *via* **19-2** or **19-3** (*Scheme 4*).

Scheme 4



By the same approach, the expanded conjugation/charge control over styrylmethylidene/benzylidene was more feasible on the intermediate conjugated keto-ylides **20**/**21** (*Scheme 5*, $R^2 = EtO$) derived from the keto side of the related bis[keto ester]. Predictive Cu-associated carbonyl ylide intermediate models **20-1**/**21-1**, derived from the keto- carbonyl-ylide side, for 1,7-cyclizations were also sterically feasible. It was also noticed that *m*-/*p*-NO_2 substituents on phenyl ring did not change the preferences apparently in the reactions with ene-bis[keto esters].

Scheme 5



On the other hand, in the reactions of styrylmethylidene-bis[carbonyls] **11e**, **11n**, and **11s**, the chemoselectivity was reversed in favor of the corresponding dihydrofurans in comparison to benzylidene-bis[carbonyls] **11f**–**11m** [18c]. It should be remembered that $\sigma_{\beta-\gamma}$ bonds of styrylmethylidene-bis[carbonyls] are mainly *transoid* thus causing less dihydrooxepine formation, while $\sigma_{\beta-\gamma}$ bonds of benzylidene-bis[carbonyls] are certainly *cisoid* giving rise to dihydrobenzoxepines. Furthermore, hypothetic model **20-1**, for the related 1,7-cyclizations from benzylidene-bis[carbonyls], was sterically more available than **21-1** from styrylmethylidene-bis[carbonyls]. As a result, in the reaction of **11e**, **11n**, and **11s**, dihydrofuran formation was preferred over dihydrooxepine formation.

To check if any dihydrooxepine was formed from an ester side, conjugated diesters **11p** – **11s** were reacted with dimethyl diazomalonate (**12**), similarly to our recent reaction with diethyl benzylidenediester (**11o**) [18c]. All reactions yielded only the corresponding dihydrofuran derivatives $\mathbf{14o_{12}}$ – $\mathbf{14s_{12}}$ because of the restricted expansion of conjugation/orbital system (model **19**) similar to benzylidene bis[phenyl ketones] (model **18**).

Although a vinylidene mono ester (ethyl crotonate) yielded dihydrofuran derivatives [18b], ethylidenebis[ester] **11t** did not yield any distinguishable product in the mixture of products. This result emphasized the inadequacy of a β-alkyl group in conjugated diesters for a 1,5-dipole generation.

As known, electrocyclization of a conjugated carbonyl ylide is a process that starts with a carbenoid formation derived from the corresponding diazo decomposition by catalysis. At this step, diazoacetates are known as more reactive species than diazomalonates [25]. The next step is the generation of a metal-conjugated carbonyl ylide from metallocarbene and substrate. In this second step, steric effects based on conformational influences of both ene-carbonyl, and carbene and ligated catalyst may be superior to the present electronic influences. So, in each reaction, the neat periselectivity may be a balance between individual electronic and steric factors within the related metal-conjugated carbonyl-ylide intermediates.

The next series of reactions were conducted to determine the effect of diazo substituents on the course of the reaction. In other words, we tried to find out whether sterically more crowded diazo conformers provided higher periselectivity. Therefore, ethyl diazoacetate (**13**) was also used as carbenoid source to determine its chemo/stereoselectivities on the formation of dihydrofuran and dihydrobenzoxepine.

In the reactions of **11a** – **11d** (conjugated bis[phenyl ketones]) with **13**, no reaction product could be determined because of the steric mismatch of the related intermediate containing bisphenyls and ethyl ester groups all together. On the other hand, in the reactions of **11e** – **11k** (benzylidene bis[ketones/keto esters]) and **11n** (styrymethylidene-bis[keto ester]) with **13**, reactions were so rapid that formal poly-adducts were also found in appreciable amounts close to those of dihydrofurans and small amounts of dihydrobenzoxepines. But, in the reactions with **11l** and **11m**, *m*-/*p*-NO_2 groups of the phenyl part in benzylidene bis[keto esters], sterically inhibited poly-adduct formation and gave the best results with respect to formal $[1+1]$ products.

The reactions of **11o** – **11s** (conjugated bis[diethyl esters]) with ethyl diazoacetate (**13**) led to no product at all. These results demonstrated that the total steric consistency of the related intermediate metallo-conjugated carbonyl ylide was dominant for the subsequent electrocyclizations: if the global steric consistency was proper, related metallo-conjugated carbonyl ylides from diazoacetates are more suitable species for dihydrofuran formation, when compared with those from diazomalonates. As a result, in the reactions of **11e** – **11n**, periselectivity was reversed in favor of dihydrofuran formation in comparison to dihydrobenzoxepines.

Finally, styrylmethylidene-bis[carbonyls] having certainly *cisoid* $\sigma_{\delta-\varepsilon}$ bonds did not yield any 1,9-electrocyclization products even in minor amounts. As known, rings with nine members are notoriously difficult to construct.

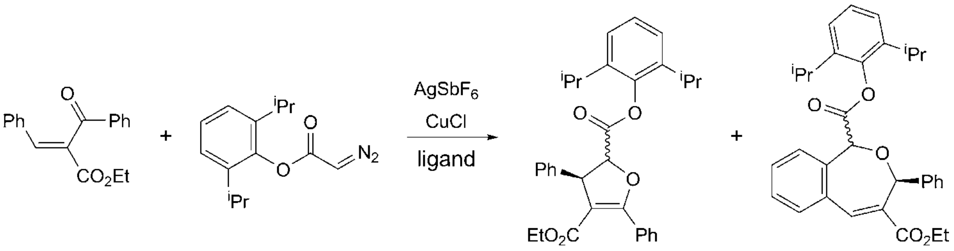
Conclusions. – In conclusion, we have broadened the scope of the reactions with conjugated bisketones/conjugated bisesters/conjugated bis[keto esters] and dimethyl diazomalonate/ethyl diazocetate to obtain dihydrofuran and dihydrobenzoxepine/dihydrooxepine derivatives by 1,5-/1,7-electrocyclic reactions of related conjugated carbonyl ylides with the absence of any 1,9-electrocyclic product. The steric/electronic structures of both ene-bis[carbonyls] and diazo compounds had significant effects on the regioselectivities of these two pericyclic reactions in the presence of [Cu(acac)$_2$]: dihydrobenzoxepine/oxepine formation was sterically more sensitive to the related prering conformation. On the other hand, dihydrofurans were more effected by the 1,5-charge control of the related ylides.

All reactions with dimethyl diazomalonate yielded products from different periselectivity. Benzylidene-bis[phenylketones] and bis-esters gave only dihydrofurans because of the steric/electronic effects. Additionally, chemospecificity was determined between keto and ester sides of conjugated bis[keto esters] due to both charge control and steric availability of hypothetic Cu-associated carbonyl-ylide intermediate. Consequently, dihydrooxepines/dihydrobenzoxepines were derived only from ketone reactants, and dihydrofurans only from ester reactants. While reactions with benzylidene conjugated bis[keto ester]/conjugated bis-ketones preferably lead to dihydrobenzoxepines, the reactions with styrylmethylidene conjugated bis[keto ester]/conjugated bis-ketone afford dihydrofurans. The presence of *m*-/*p*-MeO/NO$_2$ substituents on benzylidene-bis[carbonyls] did not sterically/electronically effect the general routes of the reactions, in supporting a concerted mechanism.

The EtO group of ethyl diazoacetate was sterically less convenient together with the crowded phenyl/ethyl ester groups of the studied ene-carbonyls, especially for the formation of dihydrobenzoxepines. Just the contrary is true, if ene-carbonyls were sterically proper, the more reactive diazo-acetate increased the reaction rate. So, benzylidene-bis[phenyl ketones] and bis-esters inhibited all the reaction pathways with ethyl diazoacetate. But, benzylidene/styrylmethylidene-bis[keto esters] underwent rapid reactions.

These new results with several different types of substrates and two diazo compounds support our recent reports. Our conditions are appearently different from those of recent results of *Tang* and co-workers [21]. They neither identified any product over substrate's ester function nor argued the absence the related products by DFT calculations in their study with the unique model of α-benzylidene-β-dicarbonyl and 2,6-diisopropylphenyl diazoacetate, changing benzylidene substituents, catalyst, and ligands (*Scheme 6*).

Scheme 6



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Experimental Part

General. M.p.: *Gallenkamp* apparatus; uncorrected. IR Spectra: *Perkin-Elmer Spectrum One*; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Varian Unity INOVA 500* and *Bruker AC 250*; δ in ppm rel. to Me_4Si as internal standard, J in Hz. GC/MS: *6890 Hewlett-Packard* GC instrument, with *HP-1* cap. column (24 m) packed with cross-linked (phenylmethyl)siloxane; *5973 HP* mass dedector; column temp. program: isothermal at 100° for 5 min, heating to 290° with ramp of 20°/min and staying isothermal for 10 min; t_R in min; in m/z (rel. %). HR-EI-MS: *JEOL AccuTOF-CS* (ESI pos., needle voltage 1800–2400 eV); in m/z.

General Procedure for the Synthesis of Starting Bis[carbonyls] 11a–11t. All bis[carbonyl] compounds were prepared according to literature procedure [26]. Dicarbonyl starting materials (0.03 mol) were used in each reaction.

2-Benzylidene-1,3-diphenylpropane-1,3-dione (**11a**). Yield: 89% (8.3 g). Dark yellow solid. M.p. 87°. IR (neat): 3044, 2927, 1598, 1530, 1220, 748. ^1H-NMR (250 MHz, $CDCl_3$): 8.02–7.94 (*m*, 2 H); 7.92–7.83 (*m*, 2 H); 7.61–7.22 (*m*, 12 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 192.1; 185.5; 148.0; 136.2; 135.3; 134.2; 133.5 (2 C); 132.3 (2 C); 130.0 (2 C); 129.5 (2 C); 128.8 (2 C); 128.6 (2 C); 128.5 (2 C); 126.9 (2 C). GC/MS: t_R 16.16. EI-MS: 312 (51, M^+), 284 (43), 267 (2), 233 (1), 207 (71), 178 (20), 129 (7), 105 (100), 77 (84), 51 (14). HR-EI-MS: 312.3612 (M^+, $C_{22}H_{16}O_2^+$; calc. 312.1150).

2-(3-Methoxybenzylidene)-1,3-diphenylpropane-1,3-dione (**11b**). Yield: 92% (9.4 g). Yellow oil. IR (neat): 1707, 1505, 1272, 1098. ^1H-NMR (250 MHz, $CDCl_3$): 7.98 (*d*, $J = 7.7$, 2 H); 7.87 (*d*, $J = 7.6$, 2 H); 7.69–7.22 (*m*, 8 H); 7.13 (*t*, $J = 7.8$, 1 H); 6.94–6.79 (*m*, 2 H); 3.59 (*s*, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 191.5; 190.8; 161.0; 145.7; 138.2; 137.9; 135.4; 134.6; 134.4; 132.1; 129.5 (2 C); 129.3; 129.1; 128.7; 128.6 (2 C); 128.3; 128.1; 119.5; 112.5; 111.7; 57.2. GC/MS: t_R 17.55. EI-MS: 342 (86, M^+), 311 (49), 283 (8), 237 (78), 235 (5), 212 (34), 207 (15), 165 (17), 139 (4), 107 (5), 105 (100), 77 (93), 51 (15). HR-EI-MS: 342.3872 (M^+, $C_{23}H_{18}O_3^+$; calc. 342.1256).

2-(4-Methoxybenzylidene)-1,3-diphenylpropane-1,3-dione (**11c**). Yield: 85% (8.7 g). Dark yellow oil. IR (neat): 1676, 1610, 1231, 1026. ^1H-NMR (250 MHz, $CDCl_3$): 7.99 (*d*, $J = 7.3$, 2 H); 7.82 (*d*, $J = 7.0$, 2 H); 7.55–7.36 (*m*, 7 H); 7.28 (*d*, $J = 8.6$, 2 H); 6.73 (*d*, $J = 8.6$, 2 H); 3.70 (*s*, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 191.7; 191.2; 160.7; 143.9; 138.3; 137.9; 135.7; 134.6; 134.1; 132.0; 129.7; 129.6; 129.3; 129.1; 128.7; 128.6 (2 C); 128.3; 128.1; 125.4; 113.7; 112.7; 55.8. GC/MS: t_R 18.36. EI-MS: 342 (50, M^+), 313 (9), 283 (3), 265 (1), 237 (77), 206 (16), 165 (13), 139 (1), 105 (100), 77 (75), 51 (9). HR-EI-MS: 342.3874 (M^+, $C_{23}H_{18}O_3^+$; calc. 342.1256).

2-(4-Nitrobenzylidene)-1,3-diphenylpropane-1,3-dione (**11d**). Yield: 96% (10.3 g). Yellow solid. M.p. 100°. IR (neat): 3059, 1669, 1263, 733. ^1H-NMR ($CDCl_3$, 250 MHz): 8.09 (*d*, $J = 8.7$, 2 H); 7.92 (*t*, $J = 8.0$, 4 H); 7.64–7.39 (*m*, 9 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 191.3; 190.8; 147.2; 138.2; 137.9; 135.4; 134.6; 134.4; 134.1; 129.5; 129.3 (2 C); 129.1; 128.7 (2 C); 128.4 (2 C); 128.3 (2 C); 128.1; 123.5; 122.9. GC/MS: t_R 17.54. EI-MS: 358 (M^+, 21), 329 (50), 328 (12), 311 (3), 282 (3), 280 (2), 252 (10), 251 (14), 236 (33), 235 (5), 207 (12), 176 (9), 151 (3), 105 (100), 77 (97), 51 (19). HR-EI-MS: 357.3585 (M^+, $C_{22}H_{15}NO_4^+$; calc. 357.1001).

*3-[(2*E*)-3-Phenylprop-2-en-1-ylidene]pentane-2,4-dione*; **11e**). Yield: 65% (4.2 g). Yellow solid. M.p. 96°. IR (neat): 2923, 1688, 1644, 1610, 1281, 1233, 976, 756. ^1H-NMR (250 MHz, $CDCl_3$): 7.45–7.48 (*m*, 2 H); 7.31–7.37 (*m*, 3 H), 6.98–7.18 (*m*, 3 H); 2.38 (*s*, 6 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 202.9; 197.1; 144.9; 142.8; 141.3; 135.3; 129.9; 128.8; 127.8; 123.3; 31.7; 26.3. GC/MS: t_R 13.43. EI-MS: 214 (99, M^+), 199 (73), 171 (100), 128 (86), 115 (38), 77 (19). HR-EI-MS: 214.2581 (M^+, $C_{14}H_{14}O_2^+$; calc. 214.0994).

3-Benzylidenepentane-2,4-dione (**11f**). Yield: 89% (5.0 g). Dark yellow oil. IR (neat): 3100, 1710, 1680, 1350, 1240. ^1H-NMR (250 MHz, $CDCl_3$): 7.47 (*s*, 1 H); 7.38 (*m*, 5 H); 2.41 (*s*, 3 H); 2.27 (*s*, 3 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 200.3; 200.2; 142.4; 139.4; 132.9; 128.7 (2 C), 128.5; 128.3; 127.9; 29.4; 29.1. GC/MS: t_R 10.22. EI-MS: 188 (92, M^+), 173 (23), 131 (100), 103 (39), 77 (13). HR-EI-MS: 188.2223 (M^+, $C_{12}H_{12}O_2^+$; calc. 188.0837).

3-(3-Methoxybenzylidene)pentane-2,4-dione (**11g**). Yield: 81% (5.3 g). Orange liquid. ^1H-NMR ($CDCl_3$, 250 MHz) 7.45 (*s*, 1 H); 7.29 (*t*, $J = 7.9$, 1 H); 6.98–6.90 (*m*, 3 H); 3.79 (*s*, 3 H); 2.41 (*s*, 3 H); 2.28

(*s*, 3 H). ^{13}C-NMR (125 MHz, CDCl$_3$): 200.1; 199.9; 160.4; 145.0; 139.3; 136.2; 129.5; 120.4; 114.2; 114.0; 56.2; 29.7; 28.0. GC/MS: t_R 12.04. EI-MS: 218 (70, M^+), 203 (45), 175 (30), 161 (100), 133 (25), 89 (10), 63 (7). HR-EI-MS: 218.2490 (M^+, $C_{13}H_{14}O_3^+$; calc. 218.0943).

3-(4-Methoxybenzylidene)pentane-2,4-dione (**11h**). Yield: 89% (5.8 g). Yellow liquid. IR (neat): 2925, 2835, 1709, 1654, 1600, 1570, 1513, 1423, 1307, 1260, 1172, 1028, 830. ^{1}H-NMR (250 MHz, CDCl$_3$): 7.40 (*s*, 1 H); 7.34 (*d*, $J = 8.6$, 2 H); 6.88 (*d*, $J = 8.6$, 2 H); 3.82 (*s*, 3 H); 2.38 (*s*, 3 H); 2.30 (*s*, 3 H). ^{13}C-NMR (125 MHz, CDCl$_3$): 206.4; 196.7; 162.0; 141.0; 140.0; 132.1; 125.6 (2 C); 114.8 (2 C); 55.7; 31.9; 26.6. GC/MS: t_R 12.16. EI-MS: 218 (88, M^+), 203 (67), 187 (27), 175 (45), 161 (100), 133 (38), 118 (10), 89 (17), 63 (9). HR-EI-MS: 218.2491 (M^+, $C_{13}H_{14}O_3^+$; calc. 218.0943).

3-(3-Nitrobenzylidene)pentane-2,4-dione (**11i**). Yield: 75% (5.2 g). Yellow oil. IR (neat): 1708, 1667, 1528, 1359. ^{1}H-NMR (250 MHz, CDCl$_3$): 8.24 (*s*, 2 H); 7.69–7.47 (*m*, 3 H); 2.45 (*s*, 3 H); 2.30 (*s*, 3 H). GC/MS: t_R 12.72. EI-MS: 233 (57, M^+), 216 (91), 176 (100), 191 (19), 131 (17), 101 (23), 75 (16), 51 (7). HR-EI-MS: 233.2204 (M^+, $C_{12}H_{11}NO_4^+$; calc. 233.0688).

3-(4-Nitrobenzylidene)pentane-2,4-dione (**11j**). Yield: 89% (6.2 g). Dark yellow oil. IR (neat): 3105, 3069, 1712, 1661, 1597, 1520, 1418, 1347, 1237, 1175, 862, 752, 691. ^{1}H-NMR (250 MHz, CDCl$_3$): 8.24–8.20 (*m*, 2 H); 7.55 (*d*, $J = 8.0$, 2 H); 7.47 (*s*, 1 H), 2.44 (*s*, 3 H); 2.27 (*s*, 3 H). GC/MS: t_R 12.82. EI-MS: 233 (8, M^+), 216 (100), 190 (17), 187 (18), 176 (62), 145 (10), 130 (13), 115 (12), 101 (10), 75 (12), 51 (7). HR-EI-MS: 233.2204 (M^+, $C_{12}H_{11}NO_4^+$; calc. 233.0688).

*Ethyl (2*E*/*Z*)-2-Benzylidene-3-oxobutanoate* (**11k**). Yield: 72% (4.7 g). Yellow liquid. IR (neat): 2922, 2853, 1730, 1664, 1460, 1376, 1207. (*E*)-Isomer: ^{1}H-NMR (CDCl$_3$, 250 MHz): 7.66 (*s*, 1 H); 7.46–7.32 (*m*, 5 H); 4.36–4.27 (*m*, 2 H); 2.34 (*s*, 3 H); 1.25 (*t*, $J = 7.2$, 3 H). (*Z*)-Isomer: ^{1}H-NMR (CDCl$_3$, 250 MHz): 7.55 (*s*, 1 H); 7.46–7.32 (*m*, 5 H); 4.36–4.27 (*m*, 2 H); 2.41 (*s*, 3 H); 1.25 (*t*, $J = 7.2$, 3 H). ^{13}C-NMR (125 MHz, CDCl$_3$): 193.9; 167.1; 139.2; 136.3; 134.5; 130.9; 130.3 (2 C); 128.9 (2 C); 61.4; 26.2; 13.4. GC/MS: t_R 11.05. EI-MS: 218 (100, M^+), 203 (24), 197 (22), 173 (29), 147 (16), 144 (12), 136 (23), 131 (53), 126 (10), 107 (21), 103 (30), 91 (9), 77 (18), 63 (5), 51 (7). HR-EI-MS: 218.2487 (M^+, $C_{13}H_{14}O_3^+$; calc. 218.0943).

*Ethyl (2*E*/*Z*)-2-(3-Nitrobenzylidene)-3-oxobutanoate* (**11l**). Yield: 78% (6.1 g). White solid. M.p. 102°. IR (neat): 1728.4, 1660.9, 1628.1, 1529.7, 780, 735. (*E*)- or (*Z*)-Isomer: ^{1}H-NMR (250 MHz, CDCl$_3$): 8.25 (*s*, 1 H); 8.23 (*s*, 1 H); 7.76–7.49 (*m*, 3 H); 4.33 (*q*, $J = 7.2$, 2 H); 2.43 (*s*, 3 H); 1.21 (*t*, $J = 7.1$, 3 H). GC/MS: t_R 13.13. EI-MS: 263 (52, M^+), 248 (98), 246 (100), 220 (29), 218 (48), 202 (34), 176 (60), 129 (29), 101 (35), 75 (19), 51 (10). (*Z*)- or (*E*)-Isomer: ^{1}H-NMR (250 MHz, CDCl$_3$): 8.32 (*s*, 1 H); 8.23 (*s*, 1 H); 7.76–7.49 (*m*, 3 H); 4.33 (*q*, $J = 7.1$, 2 H); 2.38 (*s*, 3 H); 1.34 (*t*, $J = 7.0$, 3 H). ^{13}C-NMR (125 MHz, CDCl$_3$): 198.7; 165.0; 148.6; 147.1; 139.0; 132.1; 132.0; 130.7; 123.8; 123.7; 61.4; 29.6; 14.2. GC/MS: t_R 13.22. EI-MS: 263 (52, M^+), 248 (98), 246 (100), 220 (27), 218 (36), 202 (30), 176 (45), 129 (21), 101 (22), 75 (9), 51 (4). HR-EI-MS: 263.2457 (M^+, $C_{13}H_{13}NO_5^+$; calc. 263.0794).

*Ethyl (2*E*/*Z*)-2-(4-Nitrobenzylidene)-3-oxobutanoate* (**11m**). Yield: 77% (6.1 g). Light yellow solid. M.p. 172°. IR (neat): 1732.3, 1711.1, 1608.8, 1529.7, 1464.1, 844.9. (*Z*)- or (*E*)-Isomer: ^{1}H-NMR (250 MHz, CDCl$_3$): 8.25–8.20 (*m*, 2 H); 7.67–7.53 (*m*, 3 H), 4.33 (*q*, $J = 4.0$, 2 H); 2.44 (*s*, 3 H); 1.34 (*t*, $J = 7.2$, 3 H). GC/MS: t_R 13.18. EI-MS: 263 (6, M^+), 246 (100), 216 (23), 189 (6), 176 (24), 152 (11), 101 (9), 75 (80, 51 (4). (*E*)- or (*Z*)-Isomer: ^{1}H-NMR (250 MHz, CDCl$_3$): 8.25–8.20 (*m*, 2 H), 7.67–7.53 (*m*, 3 H); 4.30 (*q*, $J = 4.0$, 2 H); 2.35 (*s*, 3 H); 1.25 (*t*, $J = 7.1$, 3 H). ^{13}C-NMR (125 MHz, CDCl$_3$): 200.3; 175.0; 165.2; 145.3; 139.3; 130.0; 128.2 (2 C); 125.5 (2 C); 45; 30; 15. GC/MS: t_R 13.25. EI-MS: 263 (6, M^+), 246 (100), 216 (23), 189 (6), 176 (24), 152 (11), 101 (9), 75 (80, 51 (4). HR-EI-MS: 263.2460 (M^+, $C_{13}H_{13}NO_5^+$; calc. 263.0794).

*Ethyl (2*E*,4*E*)-2-Acetyl-5-phenylpenta-2,4-dienoate* (**11n**). Yield: 67% (4.9 g). Yellow liquid. (*E*)- or (*Z*)-isomer. GC/MS: t_R 12.81. EI-MS: 244 (48, M^+), 215 (100), 199 (12), 155 (20), 128 (25), 115 (15), 77 (5). Mixture of (*E*)- and (*Z*)-isomers: ^{1}H-NMR (CDCl$_3$, 250 MHz): 7.02–7.50 (*m*, 12 H); 6.88–6.64 (4 H); 4.39 (*q*, $J = 7.2$, 2 H); 4.29 (*q*, $J = 7.1$, 2 H); 2.45 (*s*, 3 H); 2.40 (*s*, 3 H); 1.40 (*t*, $J = 7.3$, 3 H); 1.34 (*t*, $J = 7.4$, 3 H). GC/MS: t_R 12.94. EI-MS: 244 (52, M^+), 215 (100),199 (18), 155 (35), 128 (49), 115 (33), 77 (6).

Diethyl 2-Benzylidenepropanedioate (**11o**). Yield: 87% (6.5 g). Colorless liquid. IR (neat): 2923, 2853, 1708, 1659, 1616, 1490, 1241, 1093, 823. ^{1}H-NMR (250 MHz, CDCl$_3$): 7.68 (*s*, 1 H); 7.40–7.30 (*m*, 5 H); 4.27 (*q*, *J* = 7.0, 4 H); 1.26 (*t*, *J* = 7.0, 3 H); 1.22 (*t*, *J* = 7.0, 3 H). ^{13}C-NMR (125 MHz, CDCl$_3$): 166.5; 163.9; 141.9; 132.8; 130.4; 129.6; 128.6 (2 C); 126.2; 61.6; 61.5; 14.0; 13.9. GC/MS: t_R 11.78. EI-MS: 248 (66, M^+), 219 (19), 203 (87), 173 (35), 158 (76), 147 (17), 130 (71), 102 (100), 91 (17), 77 (36), 51 (16). HR-EI-MS: 248.2737 (M^+, $C_{14}H_{14}O_4^+$; calc. 248.1049).

Diethyl 2-(3-Methoxybenzylidene)propanedioate (**11p**). Yield: 89% (7.4 g). IR (neat): 2906, 2982, 1754, 1254, 1308. ^{1}H-NMR (250 MHz, CDCl$_3$): 7.69 (*s*, 1 H); 7.31 – 6.92 (*m*, 4 H); 4.32 (*q*, *J* = 7.2, 2 H); 4.29 (*q*, *J* = 7.3, 2 H); 3.78 (*s*, 3 H); 1.32 (*t*, *J* = 7.1, 3 H); 1.28 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR (125 MHz, CDCl$_3$): 163.8; 166.3; 140.0; 132.9; 130.4; 130.3; 129.0; 125.4 (2 C); 60.1; 61.4; 14.0, 13.7. GC/MS: t_R 12.90. EI-MS: 278 (100, M^+), 233 (73), 249 (5), 188 (74), 160 (46), 132 (69), 102 (21), 89 (20), 63 (10). HR-EI-MS: 278.3006 (M^+, $C_{15}H_{18}O_5^+$; calc. 278.1154).

Diethyl 2-(3-Nitrobenzylidene)propanedioate (**11q**). Yield: 87% (7.6 g). ^{1}H-NMR (250 MHz, CDCl$_3$): 8.19 (*s*, 1 H); 8.12 (*d*, *J* = 7.8, 1 H); 7.96 – 7.89 (*m*, 3 H), 4.32 (*q*, *J* = 7.0, 2 H); 4.30 (*q*, *J* = 7.0, 2 H); 1.34 (*t*, *J* = 7.1, 3 H); 1.29 (*t*, *J* = 7.1, 3 H). GC/MS: t_R 13.61. EI-MS: 293 (39, M^+), 264 (30),248 (100), 203 (81), 201 (36), 147 (48), 101 (35), 75 (15), 51 (5). HR-EI-MS: 293.2717 (M^+, $C_{14}H_{15}NO_6^+$; calc. 293.0899).

Diethyl 2-(4-Nitrobenzylidene)propanedioate (**11r**). Yield: 89% (7.8 g). ^{1}H-NMR (250 MHz, CDCl$_3$): 8.22 (*d*, *J* = 8.6, 2 H); 7.74 (*s*,1 H); 7.60 (*d*, *J* = 8.5, 2 H); 4.33 (*q*, *J* = 6.9, 4 H); 1.34 (*t*, *J* = 7.1, 3 H); 1.26 (*t*, *J* = 7.0, 3 H). GC/MS: t_R 13.65. EI-MS: 293 (34, M^+), 248 (100), 220 (43), 203 (96), 175 (48), 147 (52), 101 (22), 75 (32), 51 (9). HR-EI-MS: 293.2715 (M^+, $C_{14}H_{15}NO_6^+$; calc. 293.0899).

*Diethyl 2-[(2*E*/*Z*)-3-Phenylprop-2-en-1-ylidene]propanedioate*; **11s**). Yield: 42% (3.5 g). Major isomer: IR (neat): 2982, 1716, 1619, 1373, 1245, 1152, 1098, 1056, 1024. ^{1}H-NMR (CDCl$_3$, 500 MHz): 7.44 – 7.30 (*m*, 5 H); 7.00 (*d*, *J* = 11.2, 1 H); 6.65 (*t*, *J* = 11.6, 1 H); 4.36 (*q*, *J* = 7.2, 2 H); 4.24 (*q*, *J* = 7.2, 2 H); 1.36 (*t*, *J* = 7.2, 3 H); 1.28 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR (CDCl$_3$, 125 MHz): 165.4; 164.6; 141.4; 139.9; 135.7; 129.6; 128.7; 128.6; 127.5; 124.0; 61.4 (2 C); 61.3; 14.2; 14.1. HR-EI-MS: 274.3115 (M^+, $C_{16}H_{18}O_4^+$; calc. 274.1205).

Diethyl 2-Ethylidenepropanedioate (**11t**). Yield: 72% (12.0 g). Yellow liquid. ^{1}H-NMR (250 MHz, CDCl$_3$): 7.19 (*q*, *J* = 6.9, 1 H), 4.22 (*q*, *J* = 7.2, 4 H); 1.78 (*d*, *J* = 6.9, 3 H); 1.34 (*t*, *J* = 7.2, 6 H). ^{13}C-NMR (75 MHz, CDCl$_3$): 166.0; 147.1; 127.3; 62.1 (2 C); 16.2; 14.4; 9.3. HR-EI-MS: 186.2055 (M^+, $C_9H_{14}O_4^+$; calc. 186.0892).

General Procedure for the Catalytic Reactions of Bis[carbonyls] **11a** – **11t** *with Dimethyl Diazomalonate* (**12**). To a soln. of **11a** – **11t** (3 mmol) in benzene (10 ml) was added [Cu(acac)$_2$] (0.01 mmol), and the mixture was heated under reflux. A soln. of **12** or **13** (5 mmol) in benzene (5 ml) was added dropwise over 3 h. When the IR spectrum indicated total consumption of **12** or **13** (absence of characteristic diazo band at 2130 cm^{-1}), the mixture was concentrated under reduced pressure and subjected to flash chromatography on silica gel.

*Dimethyl 4-Benzoyl-3,5-diphenylfuran-2,2(3*H*)-dicarboxylate* (**14a$_{12}$**). Yield: 56% (0. 74 g). ^{1}H-NMR (250 MHz, CDCl$_3$): 7.52 (*d*, *J* = 7.2, 2 H); 7.41 (*d*, *J* = 7.1, 2 H); 7.30 – 7.09 (*m*, 11 H); 5.66 (*s*, 1 H); 3.91 (*s*, 3 H); 3.23 (*s*, 3 H). ^{13}C-NMR (125 MHz, CDCl$_3$): 190.6; 166.4; 164.7; 162.0; 137.1; 135.7 (2 C); 130.8; 129.6 (2 C); 128.6 (2 C); 128.1 (2 C); 127.8 (2 C); 127.6 (2 C); 127.3 (2 C); 126.8 (2 C); 113.5; 90.8; 56.7 (2 C); 28.7. GC/MS: t_R 19.05. EI-MS: 442 (5, M^+), 383 (90), 351 (100), 337 (40), 305 (20), 273 (20), 189 (15), 105 (92), 77 (55), 59 (5). HR-EI-MS: 442.4600 (M^+, $C_{27}H_{22}O_6^+$; calc. 442.1416).

*Dimethyl 4-Benzoyl-3-(3-methoxyphenyl)-5-phenylfuran-2,2(3*H*)-dicarboxylate* (**14b$_{12}$**). Yield: 47% (0.66 g). ^{1}H-NMR (250 MHz, CDCl$_3$): 7.47 (*dd*, *J* = 8.0, 1.8, 2 H); 7.36 (*dd*, *J* = 8.0, 1.8, 2 H); 7.21 – 7.09 (*m*, 7 H); 6.86 (*s*, 1 H); 6.68 (*dd*, *J* = 8.0, 1.8, 1 H); 6.63 (*dd*, *J* = 8.0, 1.8, 1 H); 5.64 (*s*, 1 H); 3.85 (*s*, 3 H); 3.65 (*s*, 3 H); 3.25 (*s*, 3 H). ^{13}C-NMR (CDCl$_3$, 125 MHz): 196.0; 167.1; 167.0; 162.5; 160.0; 141.2; 138.0; 132.0 (2 C); 130.7 (2 C); 129.8 (2 C); 129.5; 129.3 (2 C); 128.0 (2 C); 119.9; 126.1; 114.9; 114.2; 92.5; 57.7; 54.9; 54.0; 52.6. GC/MS: t_R 20.47. EI-MS: 472 (5, M^+), 454 (10), 412 (18), 381 (100), 335 (10), 303 (8), 221 (5), 105 (80), 77 (30), 59 (2). HR-EI-MS: 472.4844 (M^+, $C_{28}H_{24}O_7^+$; calc. 472.1522).

*Dimethyl 4-Benzoyl-3-(4-methoxyphenyl)-5-phenylfuran-2,2(3*H*)-dicarboxylate* (**14c$_{12}$**). Yield: 62% (0.88 g). Yellow oil. ^{1}H-NMR (250 MHz, CDCl$_3$): 7.53 (*d*, *J* = 7.3, 1 H); 7.43 (*d*, *J* = 7.2, 1 H); 7.25 – 7.08 (*m*, 12 H); 5.60 (*s*, 1 H); 3.92 (*s*, 3 H); 3.74 (*s*, 3 H); 3.32 (*s*, 3 H). ^{13}C-NMR (125 MHz, CDCl$_3$): 189.6; 168.2; 166.5; 161.6; 148.2; 136.7; 134.4 (2 C); 132.5; 129.6 (2 C); 128.3 (2 C); 127.9 (2 C); 126.8 (2 C);

126.2 (2 C); 125.9 (2 C); 119.7; 117.2; 110.2; 97.8; 62.8; 52.4 (2 C). GC/MS: t_R 21.83. EI-MS: 472 (5, M^+), 454 (3), 412 (48), 381 (100), 387 (30), 335 (7), 303 (10), 221 (15), 105 (70), 77 (45), 59 (10). HR-EI-MS: 472.4867 (M^+, $C_{28}H_{24}O_7^+$; calc. 472.1522).

*Dimethyl 4-Benzoyl-3-(4-nitrophenyl)-5-phenylfuran-2,2(3*H*)-dicarboxylate* (**14d$_{12}$**). The product could not be isolated from the crude mixture. GC/MS: t_R 21.75. EI-MS: 487 (3, M^+), 441 (12), 427 (55), 410 (10), 396 (100), 382 (75), 122 (22), 105 (25), 77 (15), 59 (7).

*Dimethyl 4-Acetyl-5-methyl-3-[(*E*)-2-phenylethenyl]furan-2,2(3*H*)-dicarboxylate* (**14e$_{12}$**). Yield: 54% (0.56 g). Yellow oil. ^{1}H-NMR (250 MHz, CDCl$_3$): 7.26–7.18 (*m*, 5 H); 6.54 (*d*, $J = 15.9$, 1 H); 5.95 (*dd*, $J = 16.1, 9.3$, 1 H); 4.67 (*d*, $J = 9.3$, 1 H); 3.79 (*s*, 3 H); 3.59 (*s*, 3 H); 2.31 (*s*, 3 H); 2.11 (*s*, 3 H). GC/MS: t_R 14.30. EI-MS: 344 (4, M^+), 312 (8), 301 (9), 285 (17), 253 (100), 224 (37), 153 (11), 59 (5). HR-EI-MS: 344.3576 (M^+, $C_{19}H_{20}O_6^+$; calc. 344.1260).

*Dimethyl 4-Acetyl-3-(3-methoxyphenyl)-5-methylfuran-2,2(3*H*)-dicarboxylate* (**14g$_{12}$**). Yield: 28% (0.29 g). Yellow oil. ^{1}H-NMR (CDCl$_3$, 250 MHz): 7.23–7.20 (*m*, 2 H); 6.82–6.76 (*m*, 2 H); 5.18 (*s*, 1 H); 3.86 (*s*, 3 H); 3.76 (*s*, 3 H); 3.23 (*s*, 3 H); 1.92 (*s*, 3 H); 1.90 (*s*, 3 H). ^{13}C-NMR (CDCl$_3$, 125 MHz): 193.3; 166.4; 165.7; 164.1; 158.7; 137.7; 128.5 (2 C); 120.1; 113.9; 112.6; 91.5; 54.3; 53.7; 52.8; 51.5; 28.6;13.6. GC/MS: t_R 12.78. EI-MS: 348 (2, M^+), 300 (45), 289 (40), 257 (100), 241 (10), 215 (25), 193 (30), 159 (10), 115 (10), 59 (5). HR-EI-MS: 348.3462 (M^+, $C_{18}H_{20}O_7^+$; calc. 348.1209).

*Dimethyl 4-Acetyl-3-(4-methoxyphenyl)-5-methylfuran-2,2(3*H*)-dicarboxylate* (**14h$_{12}$**). Yield: 27% (0.28 g). Yellow oil. ^{1}H-NMR (CDCl$_3$, 250 MHz): 7.07 (*d*, $J = 7.9$, 2 H); 6.79 (*d*, $J = 8.1$, 2 H); 5.15 (*s*, 1 H); 3.84 (*s*, 3 H); 3.75 (*s*, 3 H); 3.22 (*s*, 3 H); 2.41 (*s*, 3 H);1.87 (*s*, 3 H). ^{13}C-NMR (CDCl$_3$, 125 MHz): 194.7; 167.7; 167.8; 165.5; 159.6; 130.2; 129.1 (2 C); 114.1 (2 C); 110.2; 92.6; 55.5; 54.2; 52.7 (2 C); 29.8; 14.9. GC/MS: t_R 14.09. EI-MS: 348 (55, M^+), 317 (10), 305 (15), 288 (75), 257 (100), 215 (15), 159 (10), 115 (7), 59 (3). HR-EI-MS: 348.3487 (M^+, $C_{18}H_{20}O_7^+$; calc. 348.1209).

*Dimethyl 4-Acetyl-5-methyl-3-(3-nitrophenyl)furan-2,2(3*H*)-dicarboxylate* (**14i$_{12}$**). Yield: 18% (0.20 g). Yellow oil. ^{1}H-NMR (CDCl$_3$, 250 MHz): 8.12 (*d*, $J = 7.3$, 1 H); 8.05 (*s*, 1 H); 7.55–7.48 (*m*, 2 H); 5.34 (*s*, 1 H); 3.88 (*s*, 3 H); 3.23 (*s*, 3 H); 3.22 (*s*, 3 H); 2.04 (*s*, 3 H). ^{13}C-NMR (CDCl$_3$, 125 MHz): 191.7; 166.3; 165.8; 163.8; 147.3; 138.7; 128.4 (2 C); 122.1 (2 C); 114.3; 90.9; 53.3; 53.1; 51.7; 28.6; 14.0. GC/MS: t_R 14.69. EI-MS: 363 (35, M^+), 346 (45), 304 (43), 288 (50), 272 (100), 256 (10), 230 (8), 167 (6), 128 (10), 59 (6). HR-EI-MS: 363.3178 (M^+, $C_{17}H_{17}NO_8^+$; calc. 363.0954).

*Dimethyl 4-Acetyl-5-methyl-3-(4-nitrophenyl)furan-2,2(3*H*)-dicarboxylate* (**14j$_{12}$**). The product was isolated together with the product **15j$_{12}$** and the starting material **11j**. ^{1}H-NMR (250 MHz, CDCl$_3$): 7.59 (*d*, $J = 8.4$, 2 H); 7.23–7.15 (*m*, 2 H); 5.33 (*s*, 1 H); 4.00 (*s*, 3 H); 3.72 (*s*, 3 H); 2.33 (*s*, 3 H); 2.28 (*s*, 3 H). GC/MS: t_R 14.88. EI-MS: 363 (8, M^+), 348 (3), 320 (10), 304 (100), 288 (40), 272 (42), 260 (4), 230 (5), 199 (3), 167 (3), 128 (5), 59 (5).

*Dimethyl 4-Acetyl-5-ethoxy-3-(3-nitrophenyl)furan-2,2(3*H*)-dicarboxylate* (**14l$_{12}$**). The product could not be isolated from the crude mixture. GC/MS: t_R 14.73. EI-MS: 393 (45, M^+), 376 (100), 348 (35), 302 (37), 288 (90), 273 (25), 230 (15), 183 (7), 128 (9), 59 (7).

*Dimethyl 4-Acetyl-5-ethoxy-3-(4-nitrophenyl)furan-2,2(3*H*)-dicarboxylate* (**14m$_{12}$**). The product could not be isolated from the crude mixture. GC/MS: t_R 14.93. EI-MS: 393 (28, M^+), 361 (18), 348 (32), 334 (100), 333 (97), 319 (70), 288 (90), 246 (10), 230 (12), 183 (7), 128 (10), 59 (12).

*Dimethyl 4-Acetyl-5-ethoxy-3-[(*E*)-2-phenylethenyl]furan-2,2(3*H*)-dicarboxylate* (**14n$_{12}$**). The product was isolated as a mixture with **16n$_{12}$**. ^{1}H-NMR (250 MHz, CDCl$_3$): 7.42–7.13 (*m*, 5 H), 6.58 (*d*, $J = 14.9$, 1 H); 5.99 (*dd*, $J = 14.9, 9.3$, 1 H); 4.68 (*d*, $J = 9.3$, 1 H); 4.22 (*q*, $J = 7.1$, 2 H); 3.83 (*s*, 3 H); 3.66 (*s*, 3 H); 2.85 (*s*, 3 H); 1.17 (*t*, $J = 7.1$, 3 H). GC/MS: t_R 14.48. EI-MS: 374 (5, M^+), 342 (18), 329 (18), 283 (62), 269 (100), 240 (77), 209 (26), 153 (26), 115 (18), 77 (8), 59 (10).

*4-Ethyl 2,2-Dimethyl 5-Ethoxy-3-(3-methoxyphenyl)furan-2,2,4(3*H*)-tricarboxylate* (**14p$_{12}$**). Yield: 67% (0.82 g). Dark yellow oil. ^{1}H-NMR (250 MHz, CDCl$_3$): 7.39–7.25 (*m*, 1 H); 6.83–6.77 (*m*, 3 H); 5.07 (*s*, 1 H); 4.58–4.45 (*m*, 4 H); 3.86 (*s*, 3 H); 3.78 (*s*, 3 H); 3.24 (*s*, 3 H); 1.02 (*t*, $J = 7.2$, 3 H); 0.87 (*t*, $J = 7.2$, 3 H). ^{13}C-NMR (CDCl$_3$, 125 MHz): 179.3; 167.9; 166.1; 164.8; 159.6; 141.3; 128.9; 119.8; 113.2; 110.5; 89.8; 69.7; 62.1; 59.7; 58.0; 51.4; 50.7; 37.2; 18.9; 14.1. GC/MS: t_R 12.69. EI-MS: 408 (21, $[M+1]^+$), 348 (22), 334 (71), 274 (75), 159 (64), 59 (32), 29 (100). HR-EI-MS: 408.3984 (M^+, $C_{20}H_{24}O_9^+$; calc. 408.1420).

4-Ethyl 2,2-Dimethyl 5-Ethoxy-3-(3-nitrophenyl)furan-2,2,4(3H)-tricarboxylate ($\mathbf{14q_{12}}$). The product could not be isolated from the crude mixture. GC/MS: t_R 14.31. EI-MS: 423 (14, $[M+1]^+$), 391 (95), 332 (100), 300 (48), 228 (90), 214 (58), 59 (24).

4-Ethyl 2,2-Dimethyl 5-Ethoxy-3-(4-nitrophenyl)furan-2,2,4(3H)-tricarboxylate ($\mathbf{14r_{12}}$). Yield: 71% (0.90 g). Yellow oil. ^{1}H-NMR (250 MHz, CDCl$_3$): 8.20–8.11 (*m*, 2 H); 7.47–7.34 (*m*, 2 H); 5.23 (*s*, 1 H); 4.58–4. 47 (*m*, 2 H); 4.36–4.22 (*m*, 2 H); 3.69 (*s*, 3 H); 3.66 (*s*, 3 H); 1.31 (*t*, $J=7.0$, 3 H); 1.01 (*t*, $J=7.1$, 3 H). GC/MS: t_R 12.69. EI-MS: 423 (1, $[M+1]^+$), 407 (60), 364 (44), 347 (51), 300 (60),275 (40), 255 (55), 59 (33). HR-EI-MS: 423.3718 (M^+, $C_{19}H_{21}NO_{10}^+$; calc. 423.1165).

4-Ethyl 2,2-Dimethyl 5-Ethoxy-3-[(E)-2-phenylethenyl]furan-2,2,4(3H)-tricarboxylate ($\mathbf{14s_{12}}$). Yield: 65% (0.79 g). Yellow oil. ^{1}H-NMR (250 MHz, CDCl$_3$): 7.35–7.28 (*m*, 5 H); 6.80 (*d*, $J=15.7$, 1 H); 6.36 (*dd*, $J=15.7, 9.7$, 1 H); 5.02 (*d*, $J=9.7$, 1 H); 4.36–4.15 (*m*, 4 H); 3.85 (*s*, 3 H); 3.76 (*s*, 3 H), 1.31 (*t*, $J=7.2$, 3 H); 1.26 (*t*, $J=6.8$, 3 H). GC/MS: t_R 14.78. EI-MS: 404 (5, M^+), 373 (40), 358 (100), 298 (32), 280 (34), 267 (70), 253 (85), 184 (83), 156 (90),128 (84), 123 (50), 115 (48), 59 (35). HR-EI-MS: 404.4119 (M^+, $C_{21}H_{24}O_8^+$; calc. 404.1471).

Dimethyl 6-Acetyl-7-methyl-3-phenyloxepine-2,2(3H)-dicarboxylate ($\mathbf{16e_{12}}$). Yield: 49% (0.51 g). Yellow oil. ^{1}H-NMR (250 MHz, CDCl$_3$): 7.06–7.26 (*m*, 5 H); 6.03 (*d*, $J=12.2$, 1 H); 5.96 (*dd*, $J=12.2$, 6.3, 1 H); 4.58 (*d*, $J=6.3$, 1 H); 3.70 (*s*, 3 H); 3.44 (*s*, 3 H); 2.28 (*s*, 3 H); 2.18 (*s*, 3 H). GC/MS: t_R 13.89. EI-MS: 344 (48, M^+), 312 (13), 301 (15), 280 (100), 253 (72), 225 (30), 210 (48), 153 (32), 59 (14). HR-EI-MS: 344.3376 (M^+, $C_{19}H_{20}O_6^+$; calc. 344.1260).

Dimethyl 4-Acetyl-9-methoxy-3-methyl-2-benzoxepine-1,1(3H)-dicarboxylate ($\mathbf{15g_{12}}$). The product was isolated as a mixture with $\mathbf{15g_{12'}}$. ^{1}H-NMR (CDCl$_3$, 250 MHz): 7.37–6.92 (*m*, 3 H); 7.34 (*s*, 1 H); 5.50 (*q*, $J=6.5$, 1 H); 3.82 (*s*, 3 H); 3.74 (*s*, 3 H); 3.76 (*s*, 3 H); 2.38 (*s*, 3 H); 1.29 (*d*, $J=6.5$, 3 H). GC/MS: t_R 13.51. EI-MS: 348 (18, M^+), 300 (50), 289 (16), 257 (48), 232 (22), 193 (42), 148 (15), 135 (10), 84 (10), 59 (8), 43 (100).

Dimethyl 4-Acetyl-7-methoxy-3-methyl-2-benzoxepine-1,1(3H)-dicarboxylate ($\mathbf{15g'_{12}}$). Yield: 12% (0.13 g). Dark yellow oil. ^{1}H-NMR (CDCl$_3$, 250 MHz): 7.37 (*s*, 1 H); 6.95 (*d*, $J=8.8$, 1 H); 6.79–6.76 (*m*, 2 H); 5.44 (*q*, $J=6.5$, 1 H); 3.91 (*s*, 3 H); 3.82 (*s*, 3 H); 3.71 (*s*, 3 H); 2.40 (*s*, 3 H); 1.30 (*d*, $J=6.5$, 3 H).^{13}C-NMR (CDCl$_3$, 125 MHz): 196.9; 167.7; 167.4; 158.6; 144.6; 137.9; 133.8; 130.2; 127.1; 116.9; 113.0; 85.0; 72.0; 54.5; 52.3; 51.1; 25.6; 20.8. GC/MS: t_R 13.77. EI-MS: 348 (2, M^+), 316 (4), 305 (12), 289 (50), 275 (30), 256 (35), 242 (38), 229 (85), 217 (20), 187 (100), 159 (38), 144 (30), 115 (38), 59 (20). HR-EI-MS: 348.3494 (M^+, $C_{18}H_{20}O_7^+$; calc. 348.1209).

Dimethyl 4-Acetyl-8-methoxy-3-methyl-2-benzoxepine-1,1(3H)-dicarboxylate ($\mathbf{15h_{12}}$). Yield: 22% (0.23 g). Yellow oil. ^{1}H-NMR (CDCl$_3$, 250 MHz): 7.37 (*s*, 1 H); 7.19 (*d*, $J=6.1$, 1 H); 6.89 (*d*, $J=6.3$, 1 H); 6.56 (*s*, 1 H); 5.47 (*d*, $J=6.4$, 1 H); 3.89 (*s*, 3 H); 3.77 (*s*, 3 H); 3.68 (*s*, 3 H); 2.36 (*s*, 3 H); 1.30 (*d*, $J=6.4$, 3 H). ^{13}C-NMR (CDCl$_3$, 125 MHz): 198.1; 168.3; 160.3; 143.4; 139.4; 134.8; 129.9; 125.8; 114.2; 113.1; 86.4; 74.2; 55.7; 53.6; 53.4; 26.6; 22.1. GC/MS: t_R 14.72. EI-MS: 348 (5, M^+), 333 (10), 305 (100), 273 (40), 257 (75), 245 (73), 242 (72), 214 (70), 187 (50), 159 (12), 115 (15), 59 (7). HR-EI-MS: 348.3479 (M^+, $C_{18}H_{20}O_7^+$; calc. 348.1209).

Dimethyl 4-Acetyl-3-methyl-9-nitro-2-benzoxepine-1,1(3H)-dicarboxylate ($\mathbf{15i_{12}}$). Yield: 23% (0.25 g). Yellow oil. ^{1}H-NMR (CDCl$_3$, 250 MHz): 7.83 (*d*, $J=7.2$, 1 H); 7.61 (*d*, $J=6.9$, 1 H); 7.54–7.48 (*m*, 1 H); 7.32 (*s*, 1 H); 5.64 (*q*, $J=6.4$, 1 H); 3.81 (*s*, 3 H); 3.75 (*s*, 3 H); 2.40 (*s*, 3 H); 1.27 (*d*, $J=6.4$, 3 H). ^{13}C-NMR (CDCl$_3$, 125 MHz): 196.2; 167.5; 165.9; 148.5; 146.2; 135.7; 135.5; 135.3; 133.9; 127.9; 123.9; 82.8; 73.5; 52.9; 52.1; 25.7; 20.6. GC/MS: t_R 15.41. EI-MS: 346 (3), 320 (90), 304 (15), 288 (50), 272 (100), 257 (80), 229 (30), 202 (8), 156 (6), 128 (15), 59 (6). HR-EI-MS: 363.3172 (M^+, $C_{17}H_{17}NO_8^+$; calc. 363.0954).

Dimethyl 4-Acetyl-3-methyl-7-nitro-2-benzoxepine-1,1(3H)-dicarboxylate ($\mathbf{15i'_{12}}$). The product could not be isolated from the crude mixture. GC/MS: t_R 15.31. EI-MS: 346 (2), 320 (90), 304 (15), 288 (55), 272 (100), 257 (80), 229 (35), 202 (8), 156 (6), 128 (15), 59 (6).

Dimethyl 4-Acetyl-3-methyl-8-nitro-2-benzoxepine-1,1(3H)-dicarboxylate ($\mathbf{15j_{12}}$). The product could be isolated together with $\mathbf{14j_{12}}$ and the starting material **11j**. ^{1}H-NMR (250 MHz, CDCl$_3$): 7.89 (*s*, 1 H); 7.23–7.15 (*m*, 2 H); 7.16 (*s*, 1 H); 5.56 (*q*, $J=6.5$, 1 H); 3.90 (*s*, 3 H); 3.74 (*s*, 3 H); 2.46 (*s*, 3 H); 1.35 (*d*, $J=6.4$, 3 H). GC/MS: t_R 15.26. EI-MS: 346 (2), 320 (90), 304 (35), 288 (50), 272 (100), 257 (55), 229 (20), 202 (10), 156 (7), 128 (12), 59 (7).

*4-Ethyl 1,1-Dimethyl 3-Methyl-9-nitro-2-benzoxepine-1,1,4(3*H*)-tricarboxylate* (**15l**$_{12}$) *or 4-Ethyl 1,1-Dimethyl 3-Methyl-7-nitro-2-benzoxepine-1,1,4(3*H*)-tricarboxylate* (**15l′**$_{12}$). The products could not be isolated in pure form, both isomers were observed by GC/MS analysis, and both gave the same mass spectra. GC/MS: t_R 15.61 and 15.69. EI-MS: 393 (2, M^+), 350 (30), 319 (28), 302 (100), 288 (25), 273 (45), 260 (55), 215 (15), 202 (12), 128 (20), 59 (15).

*4-Ethyl 1,1-Dimethyl 3-Methyl-8-nitro-2-benzoxepine-1,1,4(3*H*)-tricarboxylate* (**15m**$_{12}$). Yield: 33% (0.39 g). Dark yellow oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.23 (*d*, $J = 8.7$, 1 H); 8.18 (*s*, 1 H); 7.70 (*d*, $J = 8.6$, 1 H); 7.50 (*s*, 1 H); 4.47 – 4.05 (*m*, 3 H); 3.87 (*s*, 3 H); 3.76 (*s*, 3 H); 1.70 – 1.55 (*m*, 3 H); 1.24 (*d*, $J = 6.5$, 3 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 173.9; 172.0; 165.3; 149.5; 138.6; 138.3; 134.2; 129.4; 128.7; 125.0; 123.0; 91.4; 65.0; 61.5; 52.5; 51.6; 19.1; 13.1. GC/MS: t_R 15.60. EI-MS: 393 (1, M^+), 350 (35), 304 (88), 302 (100), 273 (45), 260 (65), 215 (15), 185 (15), 128 (15), 59 (12). HR-EI-MS: 393.3434 (M^+, $C_{18}H_{19}NO_9^+$; calc. 393.1060).

*6-Ethyl 2,2-Dimethyl 7-Methyl-3-phenyloxepine-2,2,6(3*H*)-tricarboxylate* (**16n**$_{12}$). The product was isolated as a mixture with **14n**$_{12}$. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.42 – 7.13 (*m*, 5 H); 6.29 (*d*, $J = 12.4$, 1 H); 5.98 (*dd*, $J = 12.3, 6.6$, 1 H); 4.64 (*d*, $J = 6.6$, 1 H); 4.09 (*q*, $J = 7.1$, 2 H); 3.74 (*s*, 3 H); 3.60 (*s*, 3 H); 2.28 (*s*, 3 H); 1.30 (*t*, $J = 7.1$, 3 H). GC/MS: t_R 14.30. EI-MS: 374 (48, M^+), 342 (8), 329 (26), 310 (100), 282 (59), 269 (53), 253 (30), 153 (38), 115 (24), 77 (9), 59 (14). HR-EI-MS: 374.3831 (M^+, $C_{20}H_{22}O_7^+$; calc. 374.1366).

*Ethyl 4-Acetyl-2,3-dihydro-5-methyl-3-[(*E*)-2-phenylethenyl]furan-2-carboxylate* (**14e**$_{13}$). Yield: 41% (0.37 g). Yellow oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.35 – 7.25 (*m*, 5 H); 6.51 (*d*, $J = 15.8$, 1 H); 6.03 (*d*, $J = 15.9, 9.4$, 1 H); 5.15 (*d*, $J = 9.9$, 1 H); 4.22 – 4.09 (*m*, 3 H); 2.35 (*s*, 3 H); 2.16 (*s*, 3 H); 1.13 (*t*, $J = 7.1$, 3 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 193.1; 171.4; 167.1; 138.1; 129.6 (2 C); 129.4; 129.3; 128.4 (2 C); 127.8; 117.0; 73.1; 60.6; 29.6; 21.2; 15.4; 13.9. GC/MS: t_R 13.93. EI-MS: 300 (30, M^+), 257 (40), 254 (100), 227 (95), 211 (60), 185 (35), 141 (50), 115 (48), 91 (45), 77 (25). HR-EI-MS: 300.3495 (M^+, $C_{18}H_{20}O_4^+$; calc. 300.1362).

Ethyl 4-Acetyl-2,3-dihydro-5-methyl-3-phenylfuran-2-carboxylate (**14f**$_{13}$). Yield: 7% (0.06 g). Yellow oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.35 – 7.13 (*m*, 5 H); 5.31 (*d*, $J = 10.4$, 1 H); 4.60 (*d*, $J = 10.5$, 1 H); 4.37 – 4.13 (*m*, 2 H); 2.44 (*s*, 3 H); 1.90 (*s*, 3 H); 0.85 (*t*, $J = 7.0$, 3 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 205.7; 196.6; 143.1; 140.0; 133.2; 130.9; 129.9 (2 C); 129.3 (2 C); 73.2; 61.8; 31.8; 26.7; 22.9; 14.3. GC/MS: t_R 12.47. EI-MS: 274 (27, M^+), 259 (5), 231 (25), 201 (100), 185 (35), 158 (10), 128 (15), 115 (14), 77 (7). HR-EI-MS: 274.3130 (M^+, $C_{16}H_{18}O_4^+$; calc. 274.1205).

Ethyl 4-Acetyl-2,3-dihydro-3-(3-methoxyphenyl)-5-methylfuran-2-carboxylate (**14g**$_{13}$). The product was isolated together with **15g′**$_{13}$. ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.29 – 6.66 (*m*, 4 H), 5.27 (*d*, $J = 10.3$, 1 H), 4.56 (*d*, $J = 10.3$, 1 H); 4.31 – 4.16 (*m*, 2 H); 3.74 (*s*, 3 H); 2.41 (*s*, 3 H); 1.90 (*s*, 3 H); 1.27 (*t*, $J = 7.2$, 3 H). GC/MS: t_R 13.40. EI-MS: 304 (55, M^+), 289 (2), 261 (15), 215 (20), 231 (100), 188 (12) 159 (10), 145 (9), 115 (18), 77 (7).

Ethyl 4-Acetyl-2,3-dihydro-3-(4-methoxyphenyl)-5-methylfuran-2-carboxylate (**14h**$_{13}$). Yield: 31% (0.28 g). Yellow oil. ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.25 – 6.66 (*m*, 4 H); 5.26 (*d*, $J = 10.3$, 1 H); 4.55 (*d*, $J = 10.3$, 1 H); 4.31 – 4.20 (*m*, 2 H); 3.75 (*s*, 3 H); 2.42 (*s*, 3 H); 1.89 (*s*, 3 H); 1.35 – 1.24 (*m*, 3 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 194.9; 168.7; 167.8; 1595; 139.8; 130.1; 129.8; 120.2; 116.1; 114.0 (2 C); 84.0; 61.4; 55.5; 51.5; 15.1; 13.9. GC/MS: t_R 13.71. EI-MS: 304 (55, M^+), 261 (60), 231 (100), 214 (35), 188 (30), 159 (10), 115 (11), 77 (4). HR-EI-MS: 304.3386 (M^+, $C_{17}H_{20}O_5^+$; calc. 304.1311).

Ethyl 4-Acetyl-2,3-dihydro-5-methyl-3-(3-nitrophenyl)furan-2-carboxylate (**14i**$_{13}$). Yield: 18% (0.17 g). Yellow oil. ^{1}H-NMR ($CDCl_3$, 250 MHz): 8.29 – 7.42 (*m*, 4 H); 5.33 (*d*, $J = 10.5$, 1 H); 4.74 (*d*, $J = 10.6$, 1 H); 4.30 – 4.15 (*m*, 2 H); 2.47 (*s*, 3 H); 2.06 (*s*, 3 H); 1.27 (*t*, $J = 7.0$, 3 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 191.9; 168.0; 165.9; 147.2; 139.5; 133.4; 128.4; 122.4; 121.8; 115.5; 82.1; 60.5; 40.7; 28.5; 14.2; 12.7. GC/MS: t_R 14.45. EI-MS: 319 (45, M^+), 302 (90), 276 (8), 246 (100), 230 (50), 200 (10), 157 (6), 128 (12), 77 (3). HR-EI-MS: 319.3093 (M^+, $C_{16}H_{17}NO_6^+$; calc. 319.1056).

Ethyl 4-Acetyl-2,3-dihydro-5-methyl-3-(4-nitrophenyl)furan-2-carboxylate (**14j**$_{13}$). Yield: 15% (0.14 g). Yellow oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.19 – 7.16 (*m*, 4 H); 5.33 (*d*, $J = 10.6$, 1 H); 4.72 (*d*, $J = 10.6$, 1 H); 4.28 – 4.23 (*m*, 2 H); 2.45 (*s*, 3 H); 2.04 (*s*, 3 H); 1.30 – 1.26 (*m*, 3 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 193.1; 171.2; 167.1; 147.7; 146.1; 129.6 (2 C); 123.7 (2 C); 117.0; 83.3; 62.5; 51.8; 29.6; 21.2; 14.3.

GC/MS: t_R 15.15. EI-MS: 319 (1, M^+), 304 (40), 276 (18), 260 (20), 246 (75), 232 (100), 204 (90), 185 (55), 158 (15), 128 (30), 115 (10), 77 (5). HR-EI-MS: 319.3101 (M^+, $C_{16}H_{17}NO_6^+$; calc. 319.1056).

Ethyl 4-Acetyl-5-ethoxy-2,3-dihydro-3-phenylfuran-2-carboxylate (**14k**$_{13}$). Yield: 7% (0.06 g). Yellow oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.40–7.24 (*m*, 5 H); 4.82 (*d*, *J* = 5.1, 1 H); 4.39 (*d*, *J* = 5.1, 1 H); 4.28 (*q*, *J* = 7.2, 2 H); 4.00 (*q*, *J* = 7.3, 2 H); 2.39 (*s*, 3 H); 1.31–1.24 (*m*, 3 H); 1.06 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 169.0; 167.4; 163.9; 141.6; 129.4; 128.7; 127.9; 127.6; 126.1; 84.8; 81.1; 60.7; 60.6; 58.6; 51.7; 13.1; 13.0. GC/MS: t_R 12.68. EI-MS: 304 (30, M^+), 258 (60), 230 (100), 202 (40), 185 (70), 158 (25), 128 (27), 115 (27), 77 (5). HR-EI-MS: 304.3385 (M^+, $C_{17}H_{20}O_5^+$; calc. 304.1311).

Ethyl 4-Acetyl-5-ethoxy-2,3-dihydro-3-(3-nitrophenyl)furan-2-carboxylate (**14l**$_{13}$). The product could not be isolated from the crude mixture. GC/MS: t_R 14.45. EI-MS: 349 (45, M^+), 332 (100), 304 (25), 275 (22), 247 (26), 230 (90), 204 (10), 128 (12), 77 (3).

Ethyl 4-Acetyl-5-ethoxy-2,3-dihydro-3-(4-nitrophenyl)furan-2-carboxylate (**14m**$_{13}$). The product could not be isolated from the crude mixture. GC/MS: t_R 15.49. EI-MS: 349 (15, M^+), 303 (85), 275 (100), 247 (75), 230 (76), 205 (10), 128 (13), 77 (3).

*Ethyl 4-Acetyl-5-ethoxy-2,3-dihydro-3-[(*E/Z*)-2-phenylethenyl]furan-2-carboxylate* (**14n**$_{13}$). The product was isolated as a mixture of two isomers together with **15n**$_{13}$ and **15n′**$_{13}$. ^{1}H-NMR (250 MHz, $CDCl_3$): of **14n**$_{13}$: 7.48–7.12 (*m*, 5 H); 6.60–6.43 (*m*, 1 H); 6.02–5.94 (*m*, 1 H); 5.14 (*d*, *J* = 8.8, 1 H); 4.40–4.05 (*m*, 4 H); 3.55–3.45 (*m*, 1 H); 2.45 (*s*, 3 H); 1.43–1.10 (*m*, 6 H); of: **14n′**$_{13}$: 7.48–7.12 (*m*, 5 H); 6.60–6.43 (*m*, 1 H); 6.02–5.94 (*m*, 1 H); 5.14 (*d*, *J* = 8.8, 1 H); 4.40–4.05 (*m*, 4 H); 3.55–3.45 (*m*, 1 H); 2.40 (*s*, 3 H); 1.43–1.10 (*m*, 6 H). GC/MS: t_R 14.07 and 14.10. EI-MS (same for two isomers): 330 (70, M^+), 284 (65), 211 (100), 183 (45), 167 (47), 141 (44), 115 (40), 91 (30),77 (28).

Ethyl 6-Acetyl-2,3-dihydro-7-methyl-3-phenyloxepine-2-carboxylate (**16e**$_{13}$). The product could not be isolated from the crude mixture. GC/MS: t_R 13.54. EI-MS: 300 (80, M^+), 257 (60), 227 (40), 211 (42), 199 (100), 185 (70), 155 (65), 141 (66), 137 (90), 127 (45), 115 (75), 91 (45), 77 (44).

Ethyl 4-Acetyl-1,3-dihydro-3-methyl-2-benzoxepine-1-carboxylate (**15f**$_{13}$). The product could not be isolated from the crude mixture. GC/MS: t_R 13.27. EI-MS: 274 (1, M^+), 259 (70), 231 (30), 201 (60), 185 (20), 159 (70), 141 (100), 128 (25), 115 (55), 77 (10).

Ethyl 4-Acetyl-1,3-dihydro-9-methoxy-3-methyl-2-benzoxepine-1-carboxylate (**15g**$_{13}$). The product was isolated together with **14g**$_{13}$. ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.43 (*s*, 1 H); 7.34–6.58 (*m*, 3 H); 5.11 (*q*, *J* = 6.4, 1 H); 5.05 (*s*, 1 H); 4.31–4.12 (*m*, 2 H); 3.75 (*s*, 3 H); 2.45 (*s*, 3 H); 1.29 (*d*, *J* = 7.2, 3 H); 0.86 (*t*, *J* = 7.1, 3 H). GC/MS: t_R 14.05. EI-MS: 289 (12), 261 (12), 231 (100), 189 (40) 171 (25), 145 (15), 115 (18), 91 (5).

Ethyl 4-Acetyl-1,3-dihydro-7-methoxy-3-methyl-2-benzoxepine-1-carboxylate (**15g′**$_{13}$). The product could not be isolated from the crude mixture. GC/MS: t_R 14.37. EI-MS: 304 (2, M^+), 289 (12), 261 (5), 231 (100), 189 (55) 171 (25), 161 (25), 145 (15), 115 (18), 91 (5).

Ethyl 4-Acetyl-1,3-dihydro-8-methoxy-3-methyl-2-benzoxepine-1-carboxylate (**15h**$_{13}$). The product could not be isolated from the crude mixture. GC/MS: t_R 14.42. EI-MS: 304 (10, M^+), 289 (90), 261 (65), 217 (50), 187 (70), 171 (100), 145 (68), 115 (13), 77 (3).

Ethyl 4-Acetyl-1,3-dihydro-3-methyl-9-nitro-2-benzoxepine-1-carboxylate (**15i**$_{13}$). Yield 12% (0.11 g). Yellow oil. ^{1}H-NMR ($CDCl_3$, 250 MHz): 7.80 (*d*, *J* = 7.9, 1 H); 7.65 (*d*, *J* = 7.3, 1 H); 7.51 (*dd*, *J* = 7.9, 7.3, 1 H); 7.40 (*s*, 1 H); 5.22 (*s*, 1 H); 4.23–4.15 (*m*, 3 H); 2.48 (*s*, 3 H); 1.40 (*d*, *J* = 6.4, 3 H); 1.28 (*t*, *J* = 7.1, 3 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 199.1; 167.9; 149.0; 137.7; 136.2; 135.9 (2 C); 133.6; 128.9; 124.8; 79.0; 75.4; 62.1; 27.3; 20.6; 14.1. GC/MS: t_R 14.69. EI-MS: 319 (1, M^+), 302 (3), 276 (5), 246 (100), 218 (10), 186 (40), 156 (45), 128 (20), 77 (6). HR-EI-MS: 319.3083 (M^+, $C_{17}H_{16}NO_6^+$; calc. 319.1056).

Ethyl 4-Acetyl-1,3-dihydro-3-methyl-8-nitro-2-benzoxepine-1-carboxylate (**15j**$_{13}$). The product could not be isolated from the crude mixture. GC/MS: t_R 15.15. EI-MS: 319 (1, M^+), 304 (40), 276 (18), 260 (20), 246 (75), 232 (100), 204 (90), 185 (55), 158 (15), 128 (30), 115 (10), 77 (5).

Diethyl 3-Methyl-1,3-dihydro-2-benzoxepine-1,4-dicarboxylate (**15k**$_{13}$). Yield: 10% (0.09 g). Yellow oil. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.65 (*s*, 1 H); 7.44 (*d*, *J* = 7.1, 1 H); 7.37–7.14 (*m*, 2 H); 7.02 (*d*, *J* = 7.3, 1 H); 5.22 (*q*, *J* = 6.4, 1 H); 5.13 (*s*, 1 H); 4.40–4.38 (*m*, 2 H); 4.30–4.26 (*m*, 2 H); 1.40–1.32 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$, 125 MHz): 164.3; 163.5; 138.2; 135.9; 131.8 (2 C); 128.7; 127.8; 127.5; 123.4; 77.8; 66.9; 60.4; 60.0; 28.2; 13.3; 13.1. GC/MS: t_R 13.75. EI-MS: 304 (10, M^+), 258 (24), 231 (100), 185 (25), 157 (90), 129 (75), 115 (30), 77 (8). HR-EI-MS: 304.3359 (M^+, $C_{17}H_{20}O_5^+$; calc. 304.1311).

Diethyl 1,3-Dihydro-3-methyl-9-nitro-2-benzoxepine-1,4-dicarboxylate or Diethyl 1,3-Dihydro-3-methyl-7-nitro-2-benzoxepine-1,4-dicarboxylate (**$15l_{13}$**). The product could not be isolated from the crude mixture. GC/MS: t_R 15.88. EI-MS: 349 (3, M^+), 301 (35), 276 (100), 262 (7), 216 (15), 158 (20), 128 (30), 77 (4).

Diethyl 1,3-Dihydro-3-methyl-8-nitro-2-benzoxepine-1,4-dicarboxylate (**$15m_{13}$**). The product could not be isolated from the crude mixture. GC/MS: t_R 15.49. EI-MS: 349 (2, M^+), 303 (25), 276 (100), 262 (7), 230 (50), 202 (95), 156 (25), 128 (28), 115 (8), 77 (4).

Diethyl 2,3-Dihydro-7-methyl-3-phenyloxepine-2,6-dicarboxylate (**$16n_{13}$**). The product could not be isolated from the crude mixture. GC/MS: t_R 14.18. EI-MS: 330 (5, M^+), 291 (35), 245 (40), 217 (65), 192 (100), 171 (30), 115 (43), 105 (50), 91 (30), 77 (28).

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