Unexpected Thermal Transformation of Aryl 3-Arylprop-2-ynoates: Formation of 3-(Diarylmethylidene)-2,3-dihydrofuran-2-ones

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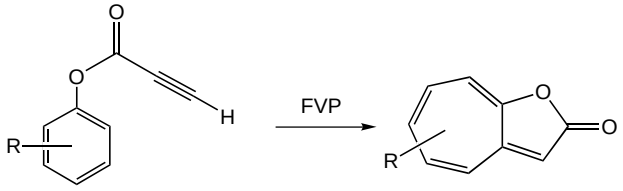
Dedicated to *Conrad Hans Eugster* on the occasion of his 80th birthday

A number of aryl 3-arylprop-2-ynoates **3** has been prepared (*cf. Table 1* and *Schemes 3–5*). In contrast to aryl prop-2-ynoates and but-2-ynoates, 3-arylprop-2-ynoates **3** (with the exception of **3b**) do not undergo, by flash vacuum pyrolysis (FVP), rearrangement to corresponding cyclohepta[*b*]furan-2(2*H*)-ones **2** (*cf. Schemes 1* and *2*). On melting, however, or in solution at temperatures $>150°$, the compounds **3** are converted stereospecifically to the dimers 3-[(*Z*)-diarylmethylidene]-2,3-dihydrofuran-2-ones (*Z*)-**11** and the cyclic anhydrides **12** of 1,4-diarylnaphthalene-2,3-dicarboxylic acids, which also represent dimers of **3**, formed by loss of one molecule of the corresponding phenol from the aryloxy part (*cf. Scheme 6*). Small amounts of diaryl naphthalene-2,3-dicarboxylates **13** accompanied the product types (*Z*)-**11** and **12**, when the thermal transformation of **3** was performed in the molten state or at high concentration of **3** in solution (*cf. Tables 2* and *4*). The structure of the dihydrofuranone (*Z*)-**11c** was established by an X-ray crystal-structure analysis (*Fig. 1*). The structures of the dihydrofuranones **11** and the cyclic anhydrides **12** indicate that the 3-arylprop-2-ynoates **3**, on heating, must undergo an aryl O → C(3) migration leading to a reactive intermediate, which attacks a second molecule of **3**, finally under formation of (*Z*)-**11** or **12**. Formation of the diaryl dicarboxylates **13**, on the other hand, are the result of the well-known thermal *Diels-Alder*-type dimerization of **3** without rearrangement (*cf. Scheme 7*). At low concentration of **3** in decalin, the decrease of **3** follows up to *ca.* 20% conversion first-order kinetics (*cf. Table 5*), which is in agreement with a monomolecular rearrangement of **3**. Moreover, heating the highly reactive 2,4,6-trimethylphenyl 3-(4-nitrophenyl)prop-2-ynonate (**3f**) in the presence of a twofold molar amount of the much less reactive phenyl 3-(4-nitrophenyl)prop-2-ynonate (**3g**) led, beside (*Z*)-**11f**, to the cross products (*Z*)-**11fg**, and, due to subsequent thermal isomerization, (*E*)-**11fg** (*cf. Scheme 10*), the structures of which indicated that they were composed, as expected, of rearranged **3f** and structurally unaltered **3g**. Finally, thermal transposition of [^{17}O]-**3i** with the ^{17}O-label at the aryloxy group gave (*Z*)- and (*E*)-[$^{17}O_2$]-**11i** with the ^{17}O-label of rearranged [^{17}O]-**3i** specifically at the oxo group of the two isomeric dihydrofuranones (*cf. Scheme 8*), indicating a highly ordered cyclic transition state of the aryl O → C(3) migration (*cf. Scheme 9*).

1. Introduction. – Recently, we have demonstrated that flash vacuum pyrolysis (FVP) of highly substituted phenyl prop-2-ynoates **1**, according to the original procedure of *Trahanovsky et al.* [1], represents an excellent method for the synthesis of polyalkylated cyclohepta[*b*]furan-2(2*H*)-ones **2** [2] (*Scheme 1*).

Brown and *Eastwood* [3] have found that FVP of phenyl but-2-ynoate (**3a**) at 650° leads in a maximum yield of only 5% to the corresponding cyclohepta[*b*]furan-2(2*H*)-one **4a** (*Scheme 2*). Nonetheless, this experiment is in agreement with the hypothesis that the high-temperature rearrangements **1** → **2** is connected with the alkyne ⇌ alkenylidene equilibrium (−C≡C−H ⇌ −CH=C:), which favors, below 600°, completely the alkyne structures, but is shifted towards the alkenylidene structure above 600°. Intramolecular addition of the unsaturated carbene part to the adjacent C=C bond of the PhO residue induces then the formation of **2**. In the case of **3a**, the discussed equilibrium is less pronounced at 650° due to the bad migratory aptitude of the Me

Scheme 1

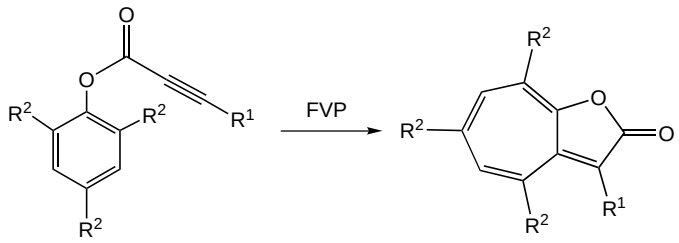


1 **2**

group in the alkyne–alkenylidene rearrangement[1]). In our experiments, we were interested in the high-temperature behavior of phenyl 3-phenylprop-2-ynoate (**3b**) with the hope that the migratory aptitude of a Ph substituent might be better than that of a Me group. However, the yield of the expected 3-phenylcyclohepta[*b*]furan-2(2*H*)-one (**4b**)[2]) did not exceed 2%, even under optimal FVP conditions (*Scheme 2*). Moreover, when we performed FVP experiments with 2,4,6-trimethylphenyl 3-phenylprop-2-ynoate (**3c**), the formation of the corresponding cyclohepta[*b*]furan-2(2*H*)-one **4c** was not observed at all. However, in the preheating phase of **3c** for its evaporation for FVP we observed a thermal transformation of **3c** already in the molten state at temperatures $>150°$. Below, we will report on this unprecedented thermal transformation of aryl 3-arylprop-2-ynoates.

2. Synthesis of Aryl 3-Arylprop-2-ynoates. – We synthesized a number of highly substituted phenyl prop-2-ynoates **3** with the sodium salts **5′** of the corresponding prop-2-ynoic acids **5** and highly substituted phenyl carbonochloridates **6**, according to a procedure described in [2] (*Table 1*). The procedure is not applicable to phenyl carbonochloridates that carry no *o*-substituents (*cf.* [2]) as shown once more by the

Scheme 2



R^1 = Me, R^2 = H: **3a**
R^1 = Ph, R^2 = H: **3b**
R^1 = Ph, R^2 = Me: **3c**

4a (4 - 5 %)
4b (2 %)
4c (none)

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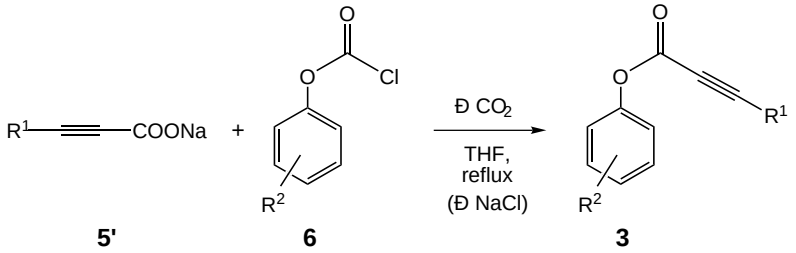
[1]) Calculations on isodesmic reactions show that the transition-state energies of the ethyne–ethenylidene and propyne–propenylidene transformation differ by 90–120 kJ/mol. We thank Dr. *R. W. Kunz* for these calculations.

[2]) For an efficient synthesis of **4b**, see [4].

Table 1. *Synthesis of Highly Substituted Aryl Pro-2-ynoates* **3**



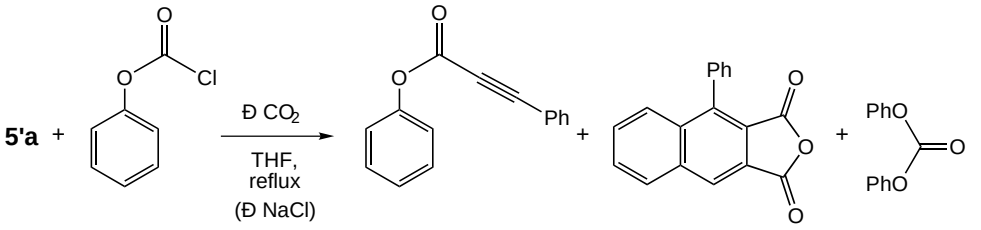
5' **6** **3**

R^1	No.	R^2	No.	Prop-2-ynoates	
				No.	Yield [%][a])
Ph	**5′a**	2,4,6-Me_3	**6a**	**3c**	73
Ph	**5′a**	2,3,4,5,6-Me_5	**6b**	**3d**	69
4-$NO_2C_6H_4$	**5′b**	2,3,4,5,6-Br_5	**6c**	**3e**	92
4-$NO_2C_6H_4$	**5′b**	2,4,6-Me_3	**6a**	**3f**	80
4-$NO_2C_6H_4$	**5′b**	H	**6d**	**3g**	41 [b])
Me	**5′c**	2,4,6-Me_3	**6a**	**3h**	50

[a]) Yield have not been optimized. [b]) Side products are formed.

reaction of **5′a** with phenyl carbonochloridate (**6d**; *Scheme 3*). The expected propynoate **3b** is formed in a yield of only 41% due to the fact that the mixed anhydride of **5a** and **6b** is attacked by the nucleophiles PhO^- and $Ph-C\equiv C-COO^-$ at both C=O groups. The *Diels-Alder*-like cyclization of 3-arylpropynoic acid anhydrides with concomitant H-migration to the corresponding cyclic anhydride of naphthalene-2,3-dicarboxylic acids is a well-known reaction (*cf.* [5] and refs. cit. therein). The esterification of 3-(4-nitrophenyl)prop-2-ynoic acid could be realized with the carbonochloridates **6a** and **6c** in excellent yields, whereas the established procedure with the acid chloride **9b**, which is easily available from the acid and oxalyl chloride in the presence of a catalytic amount of DMF at ambient temperature in CH_2Cl_2, and the corresponding sodium phenolates in THF resulted in the formation of a number of products (*cf. Scheme 4*). Also **3b** could not be synthesized in pure form from **9c** and PhONa. Fortunately, *Okajima* had already synthesized **3b** by reacting **9c** with phenol in

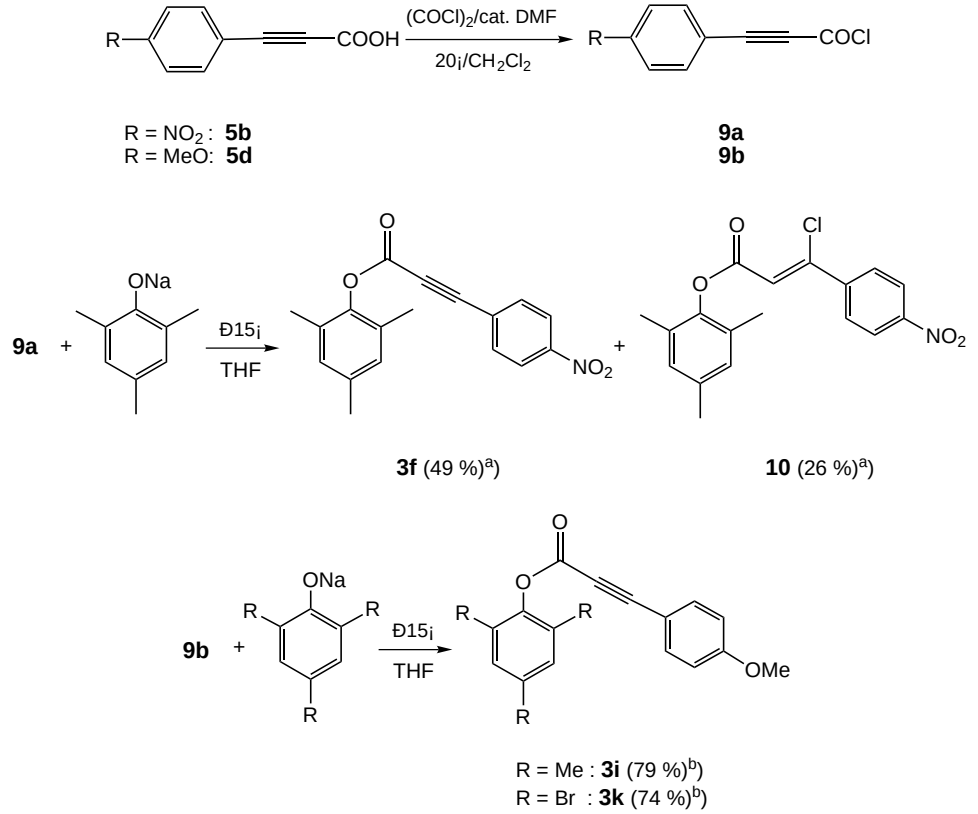
Scheme 3



6d **3b** (41 %) **7b** (73 %)[a]) **8** (93 %)[a])

[a]) Yield with respect to the expected amount, based on 41% yield of **3b**.

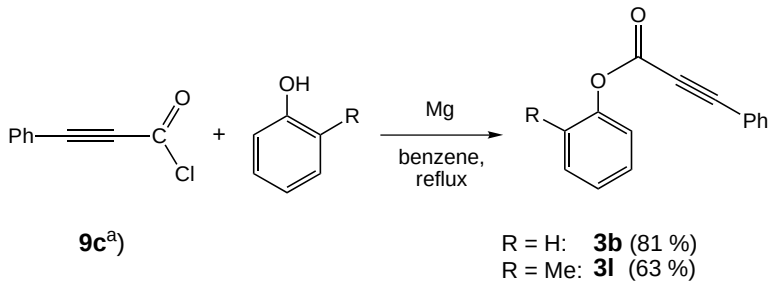
Scheme 4



a) Yield over both steps aqueous workup. b) Yield over both steps after chromatography on silica gel.

boiling benzene in the presence of Mg turnings [6]. Indeed, by following this protocol, we obtained **3b** in a yield of 81% (*Scheme 5*). The method was also applicable to the synthesis of (2-methylphenyl) 3-phenylprop-2-ynoate (**3l**), which was isolated in 63%

Scheme 5



a) See *Scheme 4*.

yield. On the other hand, the acid chloride/PhONa procedure is well-suited for the synthesis of the highly substituted phenyl 3-(4-methoxyphenyl)prop-2-ynoates **3i** and **3k** (*Scheme 4*).

3. Thermal Transformation of the Aryl 3-Arylprop-2-ynoates 3. – When the more or less colorless esters **3** are heated in the molten state or in concentrated solutions in solvents such as decalin at temperatures $\geq 150°$, an intense yellow color develops slowly, which can be attributed to the formation of the 3-(diarylmethylidene)-2,3-dihydrofuran-4-carboxylates (*Z*)-**11** (*Scheme 6*). In all cases, the lactones (*Z*)-**11** are accompanied by smaller amounts of the cyclic anhydrides **12**, the diaryl naphthalene-2,3-dicarboxylates **13**, and some (*E*)-**11**, which is formed by thermal isomerization of (*Z*)-**11** during the reaction. The product balance of the reactions in the molten state does not account for 100%, since a certain amount of polymeric material is also formed, which was not further investigated. The results of the realized thermal transformations are collected in *Table 2*. The furan-carboxylates **11** and the diaryl naphthalene-dicarboxylates **13** represent dimers of **3**, whereas the cyclic anhydrides **12** indicate the loss of one molecule of the corresponding phenols in the course of the dimerization of **3**. A first inspection of *Scheme 6* and *Table 2* reveals that the formation of (*Z*)-**11** and **12** is accompanied by an O → C migration of the aryl group of the aryloxy part in one molecule of **3**. The COO group of the second molecule of **3** enters the dimers (*Z*)-**11** unchanged and is found as (aryloxy)carbonyl group at C(4)[3]) of the furan ring. The loss of one molecule of the corresponding phenol must occur after O → C migration from the second molecule of **3** that enters into the reaction leading to **12**. On the other hand, the formation of **13** takes place without change of the ester part of **3**, since it is found unaltered in the naphthalene-2,3-dicarboxylate part of **13**. The formation of 1-phenylnaphthalene-2,3-dicarboxylates on heating of 3-phenylprop-2-ynoates at 200° has already been described by *Pfeiffer* and *Möller* in 1907 [7][4]) and, later, it was found that the dimerization of 3-phenylprop-2-ynoates slowly takes place already in solution at ambient temperature in the presence of an acid (*cf.* [8] and earlier refs. cit. therein). Moreover, *Michael* and *Bucher* reported even ten years earlier that 3-phenylprop-2-ynoic acid, on treatment with Ac_2O, forms the cyclic anhydride of 1-phenylnaphthalene-2,3-dicarboxylic acid [9] (*cf.* also [10]).

The formation of (*Z*)-**11** and **12** is dependent on the number of *o*-substituents in the aryloxy part of the esters **3**, but seems not to be influenced by the electronic nature of the substituents, since the reaction occurs both with the 2,4,6-trimethylphenoxy and with the 2,4,6-tribromophenoxy residue in **3**. However, when the 2,4,6-trimethylphenoxy group is replaced with a 2-methylphenoxy moiety, as realized in the ester **3l**, the product formation declines distinctly, and higher temperatures for the conversion of **3l** are necessary; and ester **3b**, which bears no substituent at its phenoxy part, provides, up to 200°, neither furanone (*Z*)-**11b** nor anhydride **12b**.

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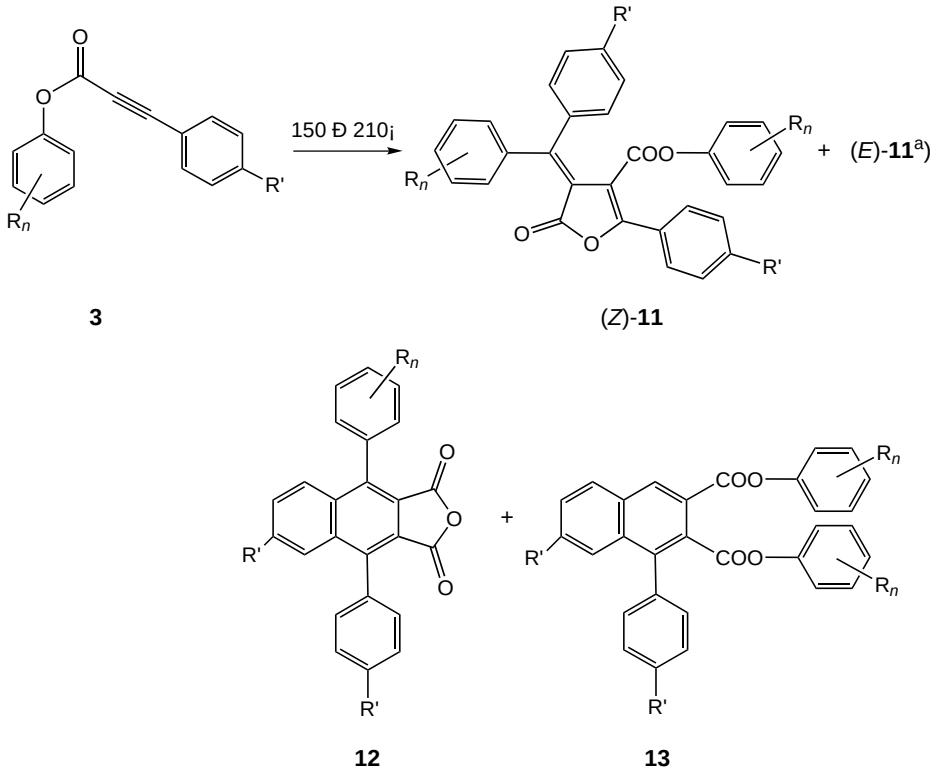
[3]) The C-atom numberings for **11** and **12** correspond to the systematic nomenclature (see *Table 3* and *Exper. Part*).

[4]) As a Zurich reminiscence, it is worthwhile to mention that *Paul Pfeiffer* and his co-worker performed the investigation '*Zur Polymerisation des Phenylpropiolsäureesters*' in the old '*Universitätslaboratorium*' in Zurich shortly before the new chemistry building at the Rämistrasse, founded by *Alfred Werner*, was ready for use (summer term 1909).

Scheme 6



[a]) Formed thermally from (*Z*)-**11**.

Table 2. *Product Composition of the Thermal Transformation of Aryl 3-Arylprop-2-ynoates* **3**[a])

	Propynoate **3**		Temp.	Time	Furanones **11**[b])		Anhydrides **12**	Diester **13**	Recovered **3**
No.[c])	R′	R_n	[°]	[h]	(*Z*) [%]	(*E*) [%]	[%]	[%]	[%]
c	H	2,4,6-Me_3	150	18	38	< 0.5[d])	n.d.[e])[f])	n.d.[f])	37
d	H	2,3,4,5,6-Me_5	150	24	30	14	n.d.	n.d.	9
e	NO_2	2,3,4,5,6-Br_5	220	1	–[g])	–	–	–	–
f	NO_2	2,4,6-Me_3	150	16	68	6	n.d.	n.d.	0
g	NO_2	H	185	17	1.8	0.8	n.d.	24	0
i	MeO	2,4,6-Me_3	200	12	25	4	19	n.d.	0
k	MeO	2,4,6-Br_3	210	5	48	< 0.5[d])	n.o.[h])	n.o.	0
l	H	2-Me	200	15	4	2	8	7	n.d.

[a]) All reactions were performed in molten phase. [b]) Yields of purified compounds with respect to reacted **3**. [c]) Identification letter for **3** and **11**–**13**. [d]) Limit of detection by HPLC. [e]) n.d.: Compound observed by TLC and/or HPLC, but amount not determined; see also *Table 5*. [f]) After 100 h at 150°, relative ratio **11c**/**12c**/**13c** 6.5 : 2.5 : 1. [g]) Mostly decomposition was observed. [h]) n.o. = not observed.

On the other side, the electronic effect of *p*-substituents at the 3-arylprop-2-ynoic part of the esters **3** on the rate and also on the cleanness of the transformations is most markedly. A π-acceptor substituent favors the reaction. We obtained the best results with the 3-(4-nitrophenyl)prop-2-ynoate **3f**, which underwent complete transformation already after 16 h heating at 150° with an isolated yield of 74% of (*Z*)-**11f** and (*E*)-**11f**. The unsubstituted 3-phenylprop-2-ynoate **3c** led, under similar conditions, to starting material, and only 38% of (*Z*)-**11c** in the presence of **12c** and some **13c** were formed. Furthermore, whereas the propynoate **3b** exhibits no thermal reactivity at all up to 200°, its analog **3g**, derived from 3-(4-nitrophenyl)prop-2-ynoic acid (**5g**), gave, at 185°, 2.6% of (*E*)-**11g** and (*Z*)-**11g**, but mainly the naphthalene-2,3-dicarboxylate **13g** (24%; *Table 2*). A π-donor substituent such as a MeO group retards the reaction of the esters **3**. The thermal transformation of the *p*-MeO-substituted prop-2-ynoate **3i** did not proceed to a visible extent at 150°. The temperature had to be raised to 200° so that completion of product formation was realized within 12 h, leading to 25% of (*Z*)-**11i** and 4% of (*E*)-**11i** besides 19% of the cyclic anhydride **12i**. Diester **13i** was also present, but its amount was not determined. The thermal reaction of the corresponding Br-substituted ester **3k** was complete after 5-h heating at 210° and led to the formation of 48% of the furanone (*Z*)-**11k**.

The described thermal transformation of the esters **3** into the lactones **11** seems to be bound to 3-aryl substituents at the propynoic-acid part, since we were not able to thermally react 2,4,6-trimethylphenyl but-2-ynoate (**3h**). We also recognized that the transformations observed can only be realized thermally, since irradiation of our model ester **3c** in toluene gave no reaction at all.

3. Characterization of the New Products. – 3.1. *3-(Diarylmethylidene)-2,3-dihydrofuran-2-ones* **11**. Since the furan ring of **11** is only surrounded by aryl groups, a purely spectroscopic structure assignment, especially with respect to the presence of (*Z*)- and (*E*)-isomers, was impossible. The structure of the yellow main product from the thermal transformation of the ester **3c** was, therefore, solved by an X-ray crystal-structure determination (*Fig. 1*). It established the presence of an unsaturated five-membered lactone ring and also revealed the (*Z*)-configuration at the methylidene group. In *Table 3*, some of the torsion angles Θ are listed. The five-membered lactone ring is almost planar (mean deviation from a least-squares plane: 2.0 pm). However, C(3′) of the methylidene substituent as well as C(4′) of the carbonyl group at C(4) deviate markedly from this plane (above (19.6 pm) and below (43.0 pm), resp.). As a consequence, the corresponding torsion angles Θ(O(1)–C(2)–C(3)–C(3′)) and Θ(C(5)–C(4)–C(3)–C(3′)) are deflected, with 170.0(5)° and – 171.3(6)°, respectively, markedly from 180°. Similarly, Θ(C(2)–C(3)–C(4)–C(4′)) and Θ(O(1)–C(5)–C(4)–C(4′)) amount to – 157.6(5)° and 161.1(5)°, respectively, leading to an average deviation of 20° from an ideal antiperiplanar arrangement. In turn, the torsion angle between C(3′) and C(4′), *i.e.*, Θ(C(3′)–C(3)–C(4)–C(4′)), amounts to 28.0(9)°. C(1^a)-Atom of the Ph substituent at C(5) of the endocyclic C=C bond is also turned out of the plane of the lactone ring by 7.8 pm, which is also indicated by Θ(C(2)–O(1)–C(5)–C(1^a)) = 174.9(4)° as well as by Θ(C(4′)–C(4)–C(5)–C(1^a)) = – 17(1)°. The 2,4,6-trimethylphenyl substituent in (*Z*)-position at C(3′) is – as expected – heavily turned out of conjugation with the methylidene group (*cf.*

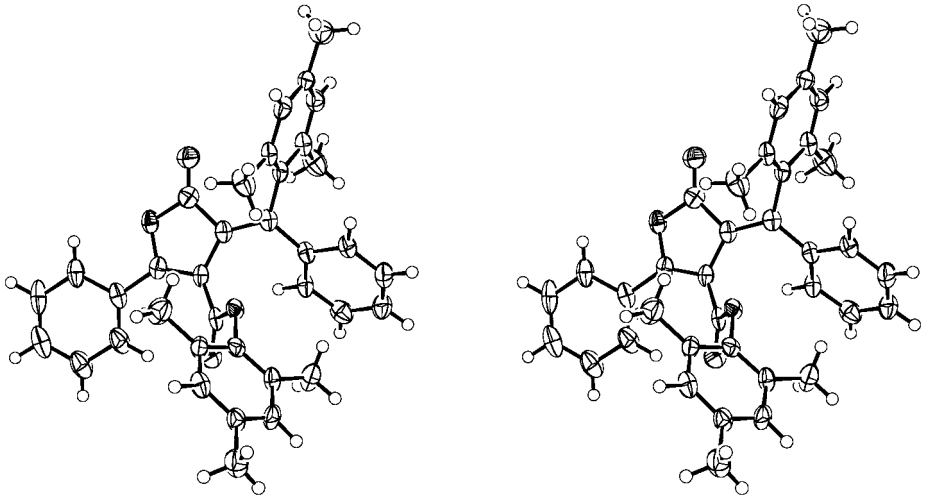


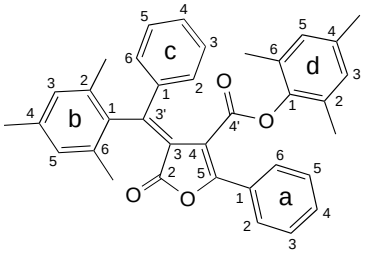
Fig. 1. *Stereoscopic view of the X-ray crystal structure of (2,4,6-trimethylphenyl) 2,3-dihydro-2-oxo-5-phenyl-3-[(Z)-(phenyl)(2,4,6-trimethylphenyl)methylidene]furan-4-carboxylate* ((*Z*)-**11c**)

Θ(C(3)–C(3′)–C(1^b)–C(2^b)), whereas the Ph substituent at the methylidene group is tilted with respect to the π-plane to a much smaller extent (*cf.* Θ(C(3)–C(3′)–C(1^c)–C(2^c)).

Table 3. *Selected Torsions Angles Θ from the X-Ray Crystal Structure of 2,3-Dihydrofuran-2-one (Z)-***11c** [a])

Atoms	Θ [°]	Atoms	Θ [°]
O=C(2)–C(3)–C(3′)	– 5(1)	O(1)–C(2)–C(3)–C(4)	– 5.0(6)
C(2)–C(3)–C(3′)–C(1^b)	21.1(9)	O(1)–C(5)–C(4)–C(3)	0.0(6)
C(4)–C(3)–C(3′)–C(1^c)	16.2(9)	O=C(2)–C(3)–C(4)	179.8(7)
C(3)–C(3′)–C(1^b)–C(2^b)	70.5(7)	O=C(2)–O(1)–C(5)	178.5(5)
C(3)–C(3′)–C(1^c)–C(2^c)	36.0(9)	O(1)–C(2)–C(3)–C(3′)	170.0(5)
C(4′)–C(4)–C(5)–C(1^a)	– 17(1)	C(5)–C(4)–C(3)–C(3′)	– 171.3(6)
C(4)–C(5)–C(1^a)–C(2^a)	– 17(1)	C(2)–C(3)–C(4)–C(4′)	– 157.6(5)
O=C(4′)–C(4)–C(5)	52.6(9)	O(1)–C(5)–C(4)–C(4′)	161.1(5)
C(2)–C(3)–C(4)–C(5)	3.2(6)	C(3′)–C(3)–C(4)–C(4′)	28.0(9)

[a]) Numbering, which is also valid for the NMR data (including the *Exper. Part*), is shown below:



The (*E*)-configuration can be attributed to the second yellow compound that accompanied (*Z*)-**11c**. When a solution of pure (*Z*)-**11c** in decalin was heated at 160–165° during 24 h, (*E*)-**11c** was obtained in 30% yield together with 70% of (*Z*)-**11c**. The (*E*)-isomer was also formed, when pure (*Z*)-**11c** was irradiated in $CDCl_3$ solution in a NMR tube with (366 ± 25)-nm light, to give, after 33 h, without any decomposition a photostationary state with 84% of (*E*)-**11c** and 16% of (*Z*)-**11c**. These observations and comparison of the UV/VIS (*cf. Fig. 2*), and the ^{1}H- and ^{13}C-NMR spectra, and especially ^{1}H-NOE measurements (*cf. Fig. 3*) of (*Z*)-**11c** and (*E*)-**11c** indicated unequivocally that both forms are indeed stereoisomers with opposite configurations at the 3-methylidene group. The pure (*E*)-isomers, beside the (*Z*)-isomers, were also isolated and fully characterized in the case of **11d**, **11f**, **11g**[5]) and **11i**.

The UV/VIS spectra (hexane) of the (*Z*)- and (*E*)-configured furanones **11** are characterized by a broad absorption band around 400 nm (log ε 4.20) with an average value of (401 ± 10) nm for the (*Z*)-forms and (398 ± 10) nm for the (*E*)-forms (*cf.*

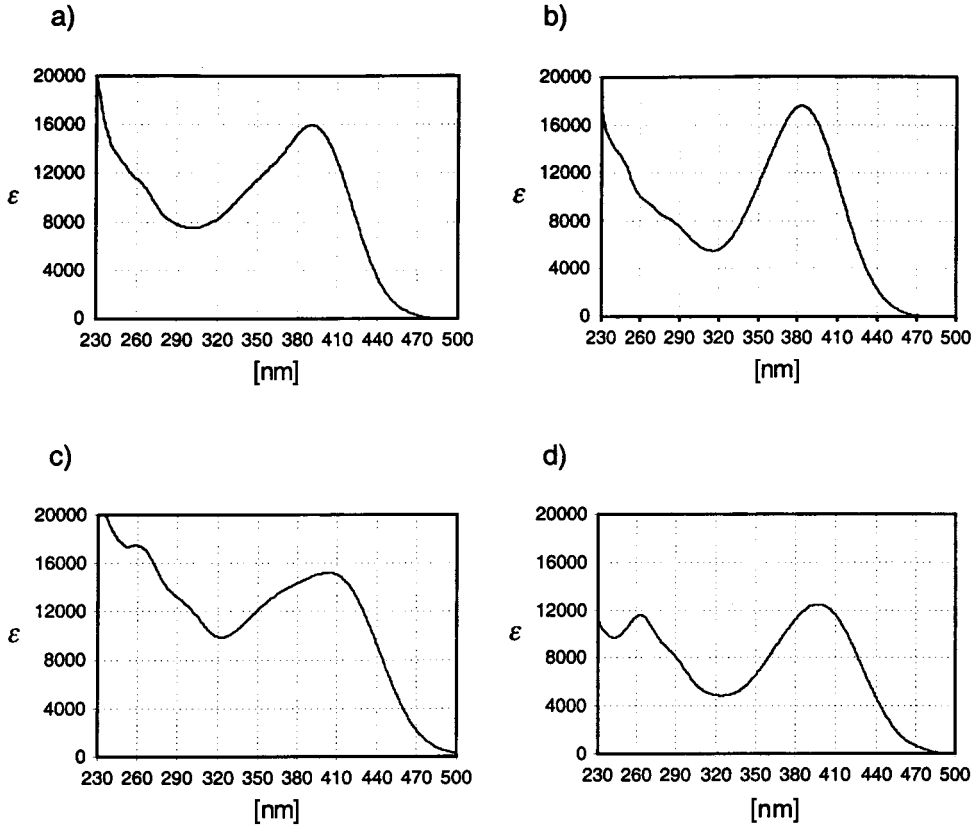


Fig. 2. *UV/VIS Spectra* (hexane) *of* a) *(*Z*)*-**11c**, b) *(*E*)*-**11c**, c) *(Z)*-**11f** *and* d) *(*E*)*-**11f**

[5]) The stereochemical descriptors are reversed in this case due to the priority rules, *i.e.*, (*E*)-**11g** and (*Z*)-**11g** correspond to the (*Z*)- and (*E*)-configuration, respectively, of the other furanones **11**.

Exper. Part). As examples, the spectra of (*Z*)-**11c**, (*E*)-**11c**, (*Z*)-**11f**, and (*E*)-**11f** are displayed in *Fig. 2*. The absorption band of the (*Z*)-isomers (*Fig. 2, a* and *c*) exhibits at its short-wavelength flank a shoulder at *ca.* 350–360 nm, which is not visible in the more or less symmetric band of the (*E*)-isomers (*Fig. 2, b* and *d*). This small difference is observable in all spectra of the (*Z*)- and (*E*)-isomers (*cf. Exper. Part*) and may be used for an assignment of the configuration at the exocyclic C=C bond.

The IR spectra ($CHCl_3$) of (*Z*)-**11** and (*E*)-**11** show two strong C=O absorption bands at (1780 ± 9) and (1734 ± 7) cm^{-1}, which can be attributed to the C=O vibrations of the unsaturated lactone function and of the ester group at C(4), respectively. The lactone band for the (*Z*)-isomers appears at higher wave-numbers than that for the (*E*)-isomers (average values: (1782 ± 9) cm^{-1} for (*Z*)-forms and (1777 ± 9) cm^{-1} for (*E*)-forms). However, the difference is not significant enough to allow, in all cases, an unambiguous assignment of the configuration at the methylidene group (*cf. Exper. Part*).

Compounds (*Z*)-**11** and (*E*)-**11** exhibit similar chemical shifts so that the ^{1}H- and ^{13}C-NMR spectra do not allow an unequivocal configurational assignment. However, based on the established furanone ring of (*Z*)-**11c** (*Fig. 1*), ^{1}H-NOE measurements allow the correct assignment of the configuration of (*Z*)-**11** and (*E*)-**11**. As an example, the signal-enhancement effects for (*Z*)-**11c** and (*E*)-**11c** are depicted in *Fig. 3*. The observed effects between the two 2,4,6-trimethylphenyl moieties are only compatible with the (*E*)-configured diastereoisomer of **11c**. This observation allows also the assignment of all other signals to the H-atoms and Me groups at the phenyl rings (*cf. Exper. Part*).

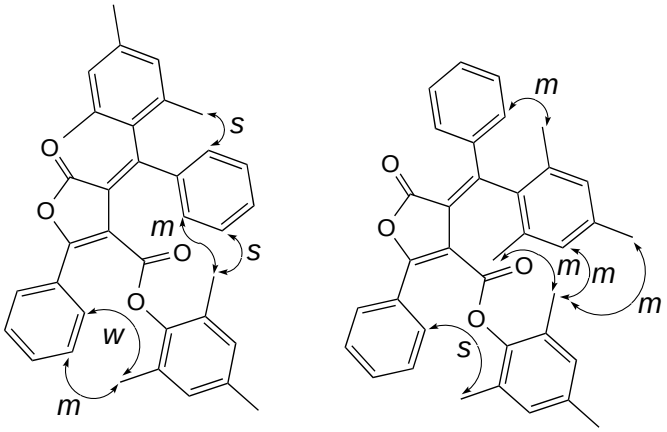


Fig. 3. *Observed ^{1}H-NOE effects of* (Z)-**11c** *and* (E)-**11c** ($CDCl_3$)

3.2. *Cyclic Anhydrides* **12**. Since compounds of this type are principally well-known (see, *e.g.*, [5]) and exhibit characteristic UV spectra, we isolated only anhydrides **12i** and **12l** in 19% and 8% yield, respectively, from the corresponding reaction mixtures (*Table 2*), in order to determine the position of the substituents at the naphthalene ring by ^{1}H-NOE measurements. For example, the signal of H–C(8)[3]) appears in the ^{1}H-NMR spectrum ($CDCl_3$) of **12i** at 7.59 ppm as *d* with $^3J(8,7) = 9.0$ Hz. It interferes in

^{1}H-NOE experiments strongly with the *s* of Me–C(2″,6″) of the 2,4,6-trimethylphenyl group at C(9). In agreement with this finding, the *d* of H–C(5) with $^4J(5,7) = 2.5$ Hz at 7.29 ppm shows a strong reciprocal enhancement effect with the signal of H–C(2′,6′) of the MeO-substituted Ph ring at C(4), which appear as *d* ($J_o = 6.5$ Hz) with fine structure (f.s.) at 7.44 ppm.

The cyclic anhydride **12l** showed two *d*'s with f.s. and $J \approx 8$ Hz at 7.97 and 7.77 ppm, followed by two *t*'s with f.s. and $J \approx 8$ Hz at 7.70 and 7.68 ppm, which can be attributed to H–C(5–8) at the naphthalene ring. Because the *d* with f.s. at 7.77 ppm induced, on irradiation, a strong enhancement effect on the *s* at 2.05 ppm of Me–C(2″) of the *o*-toluyl group at C(9), it had to be attributed to H–C(8). The identification of the other signals follows from further ^{1}H-NOE and ^{1}H-COSY measurements. They are in full agreement with the anticipated structure of **12l**.

The cyclic anhydride structure of **12i** and **12l** was further verified by their IR spectra ($CHCl_3$), which exhibited $\tilde{\nu}_{as}$ at 1842 and 1835 cm^{-1}, and $\tilde{\nu}_s$ at 1773 and 1777 cm^{-1}, respectively, due to the vibrationally coupled C=O groups.

All the other cyclic anhydrides **12** were solely identified by their UV spectra, recorded during HPLC analyses, as well as by their R_f values and fluorescence quenching properties in TLC analyses.

3.3. *Diaryl Naphthalene-2,3-dicarboxylates* **13**. Again, we isolated and characterized only two compounds of this type, namely, those from the thermal reaction of ester **3g** and **3l**. They were obtained in 24 and 7% yield, respectively. The ^{1}H- and ^{13}C-NMR spectra as well as ^{1}H-NOE measurements allowed complete elucidation of the structures. Whereas the UV spectra of the cyclic anhydrides **12** and the diaryl naphthalene-2,3-dicarboxylates **13** are, with the exception of one absorption band in the 250-nm region, quite similar (*cf. Exper. Part*), they can be nicely differentiated by their IR spectra ($CHCl_3$), since they exhibit only one C=O vibrational band at 1745 (**13g**) and 1740 cm^{-1} (**13l**).

All other diaryl naphthalene-2,3-dicarboxylates **13** were mostly identified by their UV spectra, recorded during HPLC analyses, as well as by their R_f values and fluorescence quenching properties in TLC analyses.

4. Mechanistical Studies. – That the main products (*Z*)-**11**, **12**, and **13** of the thermal reaction of the esters **3** represent dimers of **3**, whereby **12** is formed by loss of the corresponding phenol of the aryloxy part of one molecule of **3**, indicates that bimolecular reactions play the decisive role. Since some further uncontrolled side reactions such as polymerizations also took place, clean kinetic experiments could not be performed. Nonetheless, the product composition of the thermal reaction of **3c** in dependence of the initial concentration of **3c** after 13.5-h heating at 185–190°, as summarized in *Table 4*, is in agreement with a bimolecular reaction pathway of **3c**. As we have already mentioned, (*Z*)-**11c** is thermodynamically favored, but its formation is kinetically controlled. Indeed, AM1 calculation of the structure of (*Z*)-**11c** as well as of (*E*)-**11c**, with the crystal conformation of (*Z*)-**11c** as start geometry (*cf. Fig. 1*), led to $\Delta\Delta H_f^\circ = 0.92$ kcal · mol^{-1}. The equilibrium mixture of (*Z*)-**11c**/(*E*)-**11c** in hexane in the presence of I_2 at ambient temperature consists of 84% of (*Z*)-**11c** and 16% of (*E*)-**11c**. By the assumption that $\Delta\Delta H_f^\circ \approx \Delta\Delta G_f^\circ$, *i.e.*, $\Delta\Delta S_f^\circ \approx 0$, the calculated composition of 83% of (*Z*)-**11e** and 17% of (*E*)-**11c** is in excellent agreement with the observed

composition[6]). Also in cases where (*Z*)-**11** is accompanied by small amounts of (*E*)-**11**, the latter isomer is formed thermally from (*Z*)-**11**. As an example, *Fig. 4* represents the course of the reaction of the most reactive 1-(4-nitrophenyl)prop-2-ynoate **3f** at 175° in $PhNO_2$. At the beginning of the transformation, only (*Z*)-**11f** is recognizable. The amount of (*E*)-**11f** generated depends upon (*Z*)-**11f** provided by the reaction of **3f**. This fact leads to a typical convexity of the curve of the formation of (*Z*)-**11f** and, in turn, a concavity of the curve of the appearance of (*E*)-**11f**.

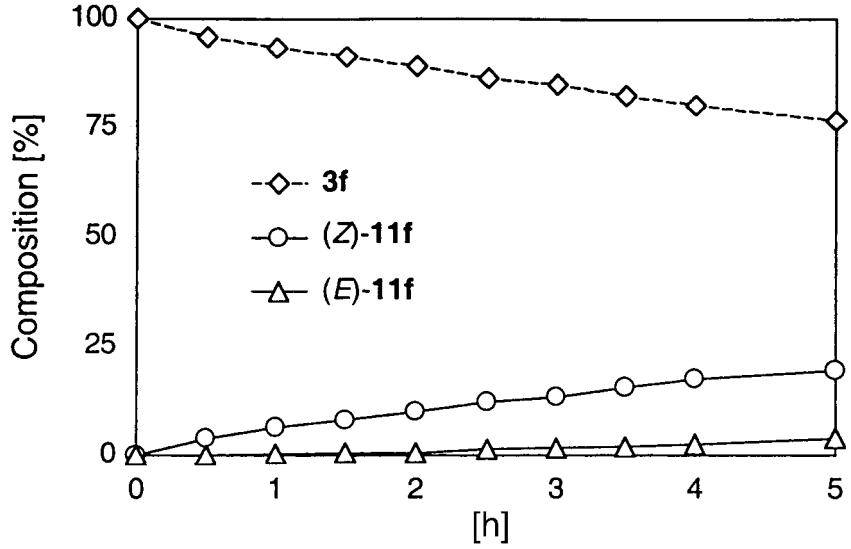


Fig. 4. *Progress of the thermal transformation of* **3f** (nitrobenzene, 175°)

Table 4. *Thermal Transformation of Propynoate* **3c** *in Various Media* [a])

Medium	Conc.	Time	Temp.	Amount [%] of				
	[mol/l]	[h]	[°]	**3c**	(*Z*)-**11c**	(*E*)-**11c**	**12c**	**13c**
Neat [b])	4.5	18	150	37	38	< 0.5	n.d.	n.d.
Neat [c])		13.5	185 – 190	3.8	25.9	21.8	41.1	11.2
Decalin [b])	0.5	24	160	30	43	< 0.5	n.d.	n.d.
Decalin [c])	0.25	13.5	185 – 190	52.3	39.1	22.1	35.8	3.0
	0.125	13.5	185 – 190	57.0	41.9	25.3	31.9	0.8
	0.063	75.3	185 – 190	75.3	45.6	27.8	26.6	0.1
Anisole [c])	0.5	24	160	56.8	41.8	3.2	49.9	5.1
Nitrobenzene [c])	0.5	24	160	60.2	47.9	3.9	42.7	5.5
	0.125	13.5	185 – 190	55.1	42.1	22.6	34.6	0.8
o-Xylene [c])	0.5	24	160	72.0	51.7	1.8	39.3	7.1

[a]) See also *Table 2*. [b]) Yields of isolated material. [c]) Product composition according to HPLC analysis; (*Z*)-**11c** + (*E*)-**11c** + **12c** + **13c** = 100%.

A closer inspection of *Table 4* reveals that the relative amount of **13c** drops significantly with the decrease of the initial concentration of **3c**. In contrast to (*Z*)-**11c**/(*E*)-**11c**

[6]) The AM1 calculations gave $\Delta H_f^\circ = -22.11$ kcal·mol^{-1} for (*Z*)-**11c** and -20.19 kcal·mol^{-1} for (*E*)-**11c**.

and **12c**, which are also formed in decreasing amounts, but with a more or less constant ratio, when the appearance of **13c** is no longer detectable at the given reaction time. One also recognizes that the transformation of **3c** exhibits almost no solvent effect. This is true for the overall rate as well as for the product composition after a given time.

As already mentioned in the preceding chapter, the furanones (*Z*)-**11** and the cyclic anhydrides **12** are formed by an O → C migration of the aryl group of the aryloxy part of the esters **3**, whereas the aryloxy group of **3** is found unchanged in the dimers **13**. Hence, we conclude that there exist two independent modes of thermal reactivity. One mode is quite obvious. The naphthalene-2,3-dicarboxylates **13** are formed in a *Diels-Alder*-type cycloaddition of two molecules of **3** with concomitant prototropic rearrangement. Such dimerization reactions have first been reported by *Pfeiffer* and *Möller* [7] (*Scheme 7*). The structure of the fully characterized **13g** ($R' = NO_2$, $R_n = H$) is in agreement with this assumption. Finally, it is a well-known reactivity of 3-arylprop-2-ynoic anhydrides that undergo such [4 + 2]-type reactions intramolecularly already at temperatures $< 100°$ [9][10] (see also the formation of **7b** in *Scheme 3*). In contrast to the formation of **13**, the formation of the furanones (*Z*)-**11** and the cyclic anhydrides **12** must take place *via* a common precursor **U**(1), formed thermally in a rate-determining monomolecular process of **3**, which leads to bonding between C(3) of the propynoic part and C(1) of the aryloxy group. Intermediate **U**(1) must then react rapidly in at least two or more independent steps with a second unchanged molecule of **3** to give (*Z*)-**11** and a second product, which, by further loss of the corresponding phenol, yields the cyclic anhydrides **12** (*Scheme 7*).

To gain more insight into the fate of the two O-atoms of the COO group of **3** after its rearrangement into the reactive intermediate **U**(1), we have synthesized 2,4,6-trimethyl[^{17}O]phenol with a [^{17}O] enrichment of 8 atom-% from 2,4,6-trimethylphenyldiazonium tetrafluoroborate [11] and $H_2[^{17}O]$ in the presence of CF_3COOH in analogy to the procedure described in [12]. Reaction of the Na salt of the 2,4,6-trimethyl[^{17}O]phenol with the acid chloride **9b** (*cf. Scheme 4*) gave [^{17}O]-**3i** with $\delta(^{17}O)$ in the expected range of 198 ppm for an aryloxy ^{17}O-atom ($CDCl_3$; external standard $H_2[^{17}O]$; *cf.* [13]) (*Scheme 8*). Heating of [^{17}O]-**3i** without solvent at 210° during 5 h gave (*Z*)-[$^{17}O_2$]-**11i** and (*E*)-[$^{17}O_2$]-**11i**[7]), in 25 and 5% yield, respectively. The ^{17}O-NMR spectra ($CDCl_3$) of both isomers are depicted in *Fig. 5*. The observed ^{17}O-shifts for (*Z*)-[$^{17}O_2$]-**11i** and (*E*)-[$^{17}O_2$]-**11i** reveal that one of the ^{17}O-atoms is now found exclusively in the oxo group at C(2) of (*Z*)-[$^{17}O_2$]-**11i** and (*E*)-[$^{17}O_2$]-**11i**, since $\delta(^{17}O)$ values of 340 and 314 ppm, respectively, are quite typical for ^{17}O-shifts of the oxo group of lactones (*cf.* [14]), whereas the other shifts observed (190 and 198 ppm, resp.) correspond to the aryloxy group of the starting ester, *i.e.*, they represent the unchanged 2,4,6-trimethylphenyl[^{17}O]oxycarbonyl group at C(4) in (*Z*)-[$^{17}O_2$]-**11i** and (*E*)-[$^{17}O_2$]-**11i**[8]).

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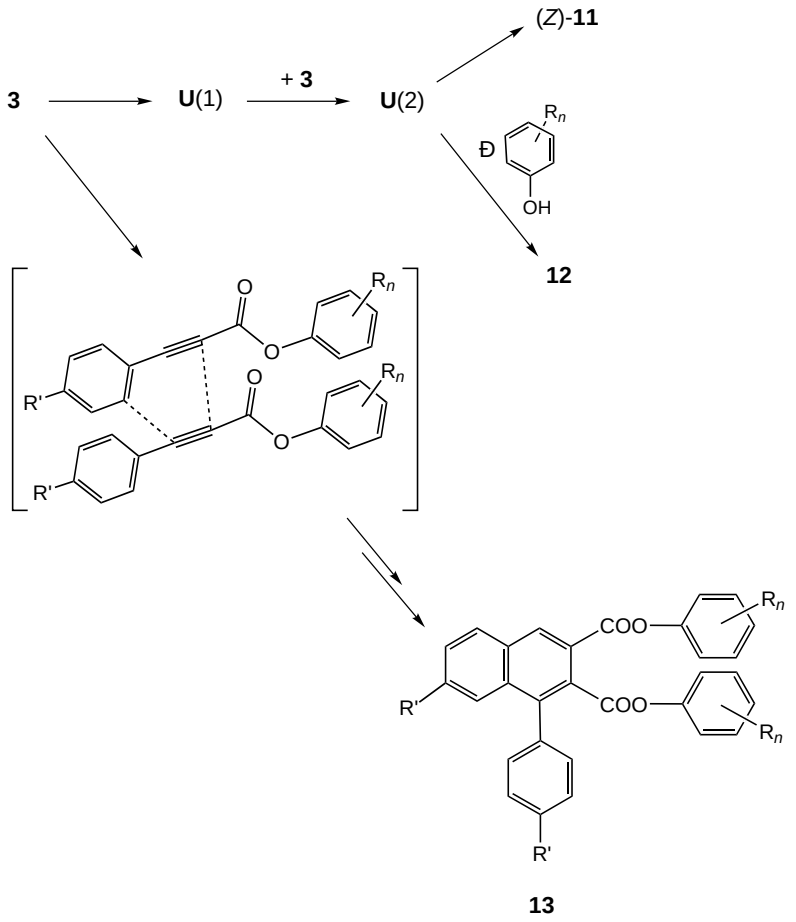
[7]) The cyclic anhydride **12i** was also formed. Unfortunately, it decomposed when we tried to purify it by column chromatography.

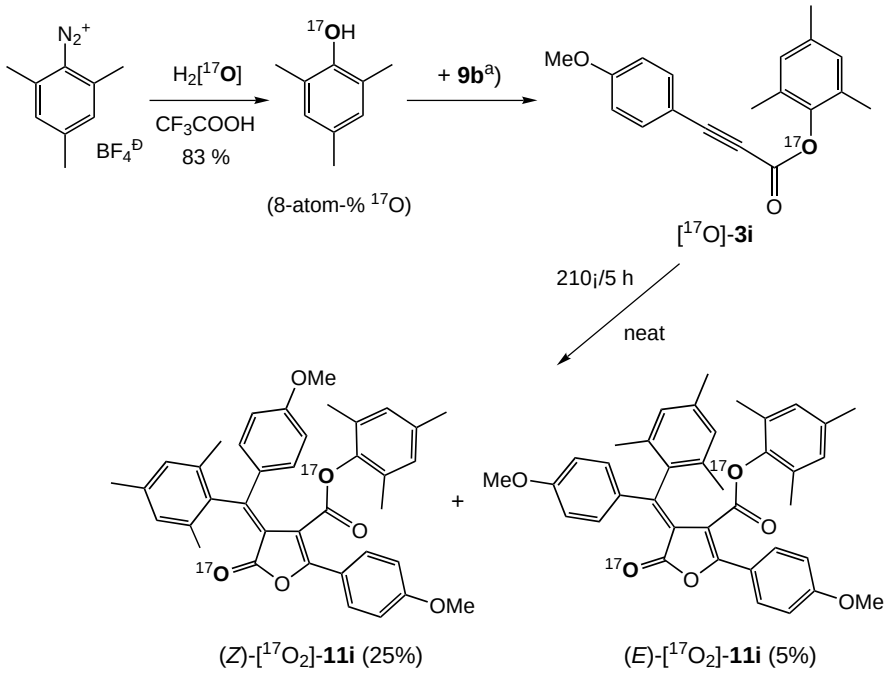
[8]) Our experiment also excludes O → O aryl migration in analogy to the *Chapman* rearrangement (*cf.* [15] and refs. cit. therein) prior to the monomolecular rearrangement of **3i**. Similarly, O → O aryl migration in the exocyclic ester part of (*Z*)-**11i** and (*E*)-**11i** can be excluded.

Scheme 7



These findings indicate that there exists, for the aryl propynoates **3**, a defined thermal bond-reorganization process whereby the O-atom of their aryloxy groups is finally converted, by O → C(3) aryl group migration, to the oxo group of the (*Z*)-configured furanones **11**. In other words, the observed *cis*-relation of the migrating aryl residue with respect to the formed oxo group provides an evidence for the formation of a highly reactive intermediate (= **U**(1)) with a fixed geometry, which is immediately trapped by a second unchanged molecule of **3** under preservation of the *cis*-relation. According to the 'principle of least motion', the postulated intermediate **U**(1) might have the structure of a σ,π-diradical **14** or any other related structure in which the identity of the two O-atoms of the thermally transformed **3** is preserved (*Scheme 9*). The intermediate σ,π-diradicals could be trapped at their reactive σ-radical site by a second molecule of **3** under formation of the π_2-diradicals **15a** and **15b**. Cyclization of **15a** under concomitant cleavage of the O–aryl bond would yield stereospecifically (*Z*)-**11**, whereas cyclization of **15b** leads to the π_2-diradicals **16**, which, after cleavage of

Scheme 8



[a]) See *Scheme 4*.

the O–aryl bond, form the cyclic anhydrides **12** under loss of the corresponding phenols.

The proposed mechanism should allow cross-reactions between two esters **3**, varying in reactivity. Indeed, when the most reactive nitro ester **3f**, which mainly forms (*Z*)-**11f** and, by thermal isomerization, some (*E*)-**11f** at 150° (*cf. Table 2*), was heated in decalin ($c = 0.65$M) in the presence of 2 mol-equiv. of the ester **3g**, which mostly reacts to **13g** (*cf. Table 2*), (*Z*)-**11f** and the mixed forms (*Z*)-**11fg** and (*E*)-**11fg** were obtained in the orange-colored furanone fraction in 23, 10, and 4% yield, respectively (*Scheme 10*). The structure of (*Z*)-**11fg** and (*E*)-**11fg** were established by their ^{1}H- and ^{13}C-NMR, and mass spectra. The mixed furanones (*E*)- and (*Z*)-**11gf** with the reverse combination of both esters were not present in detectable amounts in the reaction mixture of the cross experiment, in agreement with the finding that ester **3g** forms only reluctantly (*E*)-**11g** and (*Z*)-**11g** (*cf. Table 2*). On the other hand, that (*Z*)-**11fg** and (*E*)-**11fg** are formed in the cross-experiment demonstrates that it is indeed the first step to **U**(1) (=**14**) that determines the course of the further reaction. This fact can also be deduced from a kinetic experiment with ester **3f** in the absence or presence of a twofold molar amount of ester **3g** in $PhNO_2$ at $(175 \pm 1)^\circ$. In the case where **U**(1) is formed in the rate-determining step, the decrease of **3f** should follow first order kinetics at low conversions. *Fig. 6* demonstrates that this is indeed the case. Moreover, k_{-1}(**3f**) for **3f** + 2 **3g** is approximately three times as large as k_{-1}(**3f**) for **3f** alone, as one would expect

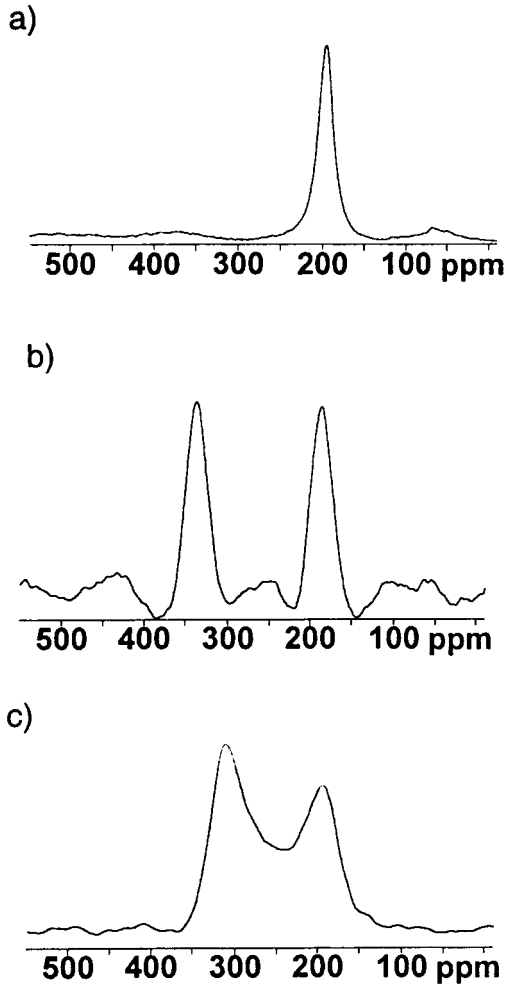
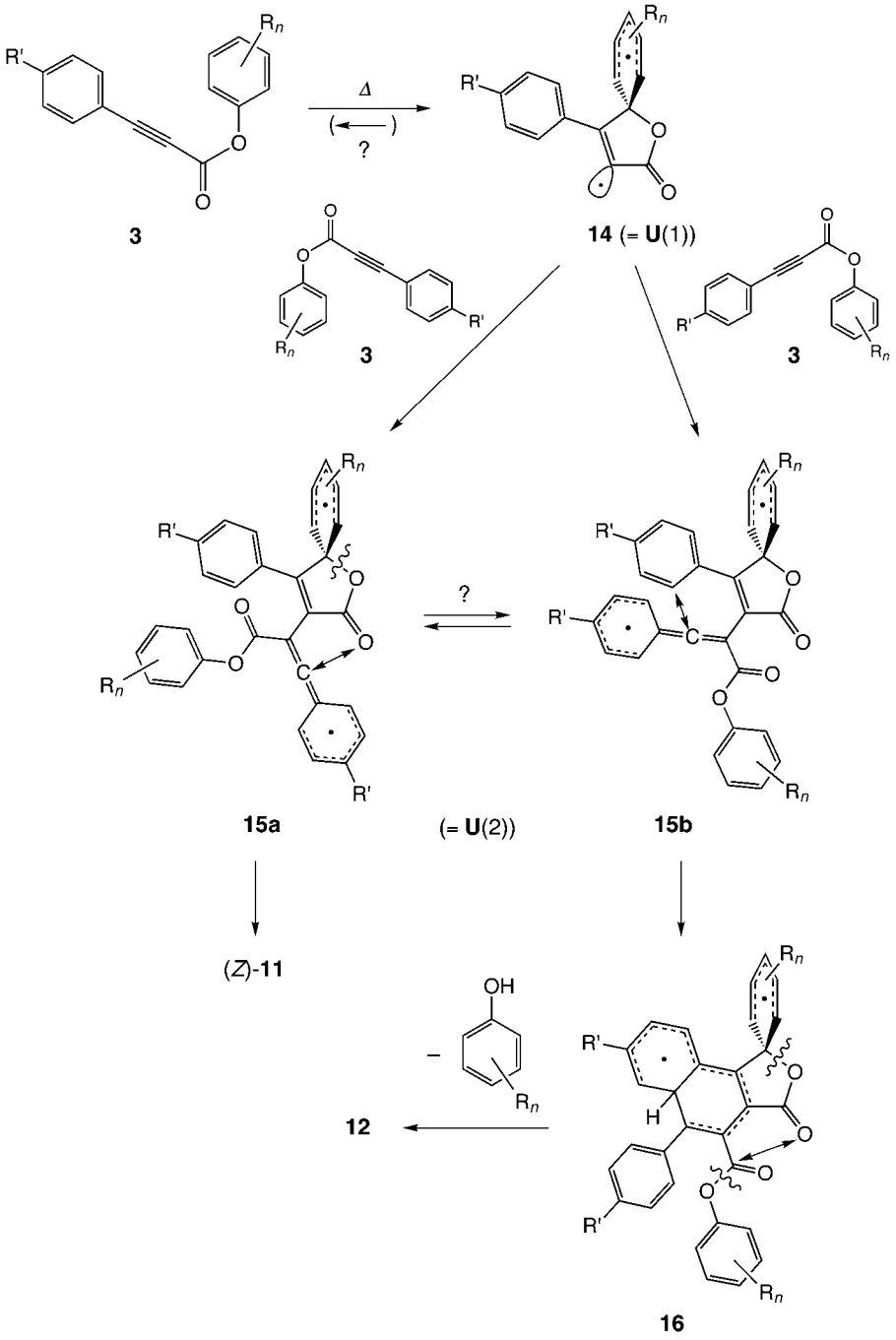


Fig. 5. *^{17}O-NMR Spectra* ($CDCl_3$; external ref. $H_2[^{17}O]$): a) *[^{17}O]-***3i**; b) *(*Z*)-[$^{17}O_2$]-***11i** *and* c) *(*E*)-[$^{17}O_2$]-***11i** *from the thermal transformation of [^{17}O]-***3i** (molten phase, 210°/5 h)

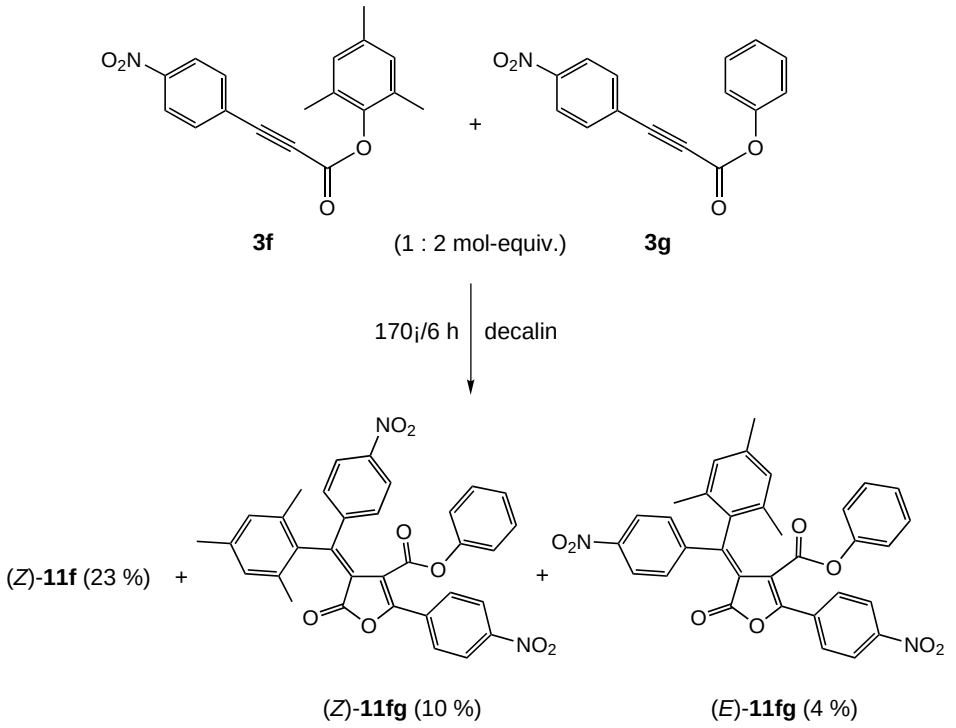
for the formation of a highly reactive intermediate **U**(1) from **3f**, which should exhibit similar second-order rate constants with **3f** and **3g**, *i.e.*, $k_2[\mathbf{U}(1)][\mathbf{3f}] \approx k_2[\mathbf{U}(1)][\mathbf{3g}]$.

We measured $k_{obs}(150 \pm 1°)$ in 0.1M decalin solution in the range of 0–20% conversion for a number of differently substituted propynoates **3**, which all followed first-order kinetics (see *Table 5* and *Fig. 7*). The fastest reaction is observed for the 4-NO_2-substituted ester **3f**, whereas the 4-MeO-substituted ester **3i** exhibits only a moderate rate enhancement with respect to the unsubstituted ester **3c**. These observations may indicate a certain charge transfer from the 2,4,6-trimethylphenoxy moiety to the aryl group at C(3) of the propynoates in the transition state. This assumption is supported by the slight rate enhancement observed, when the 2,4,6-trimethylphenoxy group of **3c** is replaced with a 2,4,6-tribromophenoxy group as in **3k**, whereas an

Scheme 9



Scheme 10



unsubstituted PhO group as in **3b** does not lead to any rearrangement at 150° and above. Therefore, we assume that the transition state for the formation of **U**(1) from the propynoates **3** is characterized by bond formation between C(3) of the ethynyl part and C(1) of the aryloxy group of **3**, favored by an electron density flux from the aryloxy to the aryl substituent and ending with the aryl O → C migration observed. Its also of interest to note that the bimolecular step between **U**(1) and **3**, which leads finally to (*Z*)-**11** and **12**, is strongly influenced by the nature of the 4-substituent of the aryl group at C(3) (*cf. Table 5*). This would mean according to our proposed mechanism (*Scheme 9*), that the π_2-diradicals **15a** and **15b** are long-lived enough to be converted to each other, whereby the NO_2-substitued diradicals favor the formation of (*Z*)-**11** and the MeO-substituted diradicals the formation of **12**.

The starting conformation for the described rearrangement of the propynoates **3** must be s-*cis*. The X-ray crystal-structure analysis of the model ester **3c** shows the 2,4,6-trimethylphenyl residue is in a perfect s-*trans* and parallel arrangement with respect to the C≡C bond of the acid part (see *Exper. Part*). In addition, the Ph ring at C(3) of the acid part is in an periplanar orientation to the C=O group. Just the same arrangement is found by AM1 calculations as the energetically most favorable one of **3c** (*Fig. 8*). However, only 0.7 kcal · mol^{-1} higher in ΔH_f° lies the calculated s-*cis* conformation of **3c**, again with a perfect parallel arrangement of the mesityl residue with respect to the

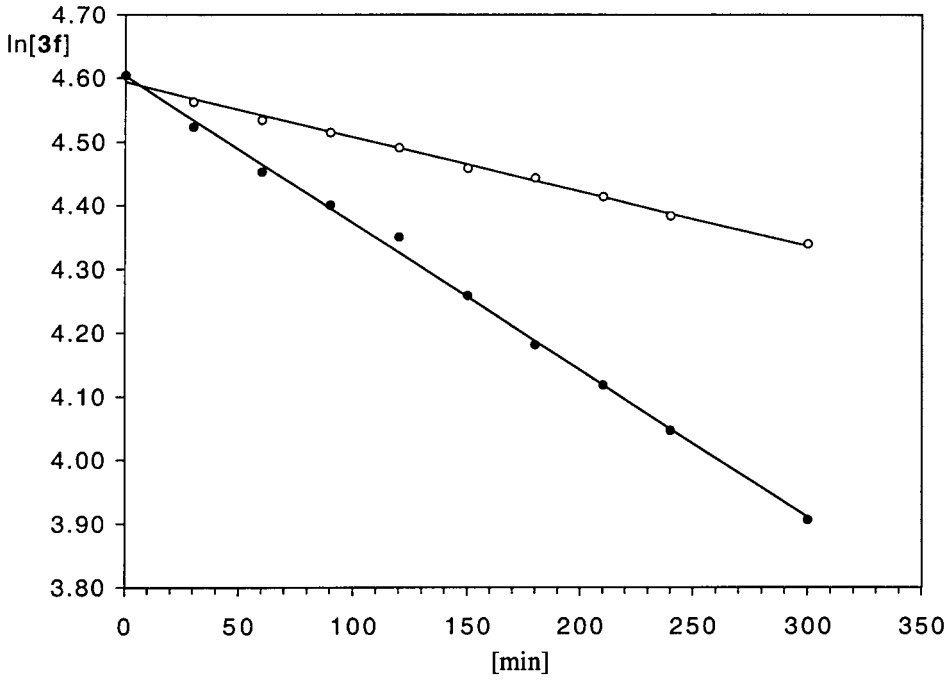


Fig. 6. *Kinetics of the thermal transformation of* **3f** (—○—) *and of a 1:2 molar mixture of* **3f** *and* **3g** (—●—; $PhNO_2$, $175 \pm 1°$; $c_{init.}$ of **3f** = 0.1M). k_{-1} (**3f**) = $(8.52 \pm 0.48) \cdot 10^{-4}$ min^{-1} ($r^2 = 0.995$) for **3f**, and k_{-1} (**3f**) = $(2.31 \pm 0.09) \cdot 10^{-3}$ min^{-1} ($r^2 = 0.998$) for **3f** + 2 **3g**).

triple bond, and the Ph group at C(3) of the propynoic part exhibits once more a periplanar orientation with the C=O group, causing an edge-to-face interaction with the 2,4,6-trimethylphenyl residue. This latter conformation with a $d(C(3) \cdots C_{aryloxy}(1))$ value of 355 pm must be responsible for the formation of **U**(1). At 150°, it should be present in the s-*trans*/s-*cis* equilibrium mixture of **3c** to an extent of *ca.* 30%, if we assume that $\Delta\Delta S_f^\circ \approx 0$[9]). It is of interest to note that the IR spectrum of **3c** in $CHCl_3$ solution shows in the stretching region of the C≡C bond two frequencies at 2235 and 2207 cm^{-1} of nearly equal intensities (see *Fig. 9*). At first sight, we thought that these bands might represent $\tilde{\nu}$(C≡C) of s-*trans* and s-*cis* **3c** at thermal equilibrium[10]). However, since we observed this band splitting also in the IR spectrum of crystalline **3c** in a fixed s-*trans* conformation, it must have another origin. Indeed, two bands in the 2240–2210-cm^{-1} region have already been found for a number of 4-substituted ethyl 3-

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[9]) Microwave and IR spectra of methyl prop-2-ynoate are in accordance with an almost exclusive s-*trans* conformation of this ester in the temperature range of −70 to 20° [16]. Irradiation of s-*trans* methyl prop-2-ynoate in an Ar matrix at 20.4 K generates a new species to which the s-*cis* conformation has been assigned [17].

[10]) Indeed, the calculated IR frequencies of s-*trans*- and s-*cis* phenyl prop-2-ynoate give $\Delta\nu = 12$ cm^{-1} with the lower wave-number for the s-*cis* conformation. We thank Prof. *J. Hutter* from our Institute for these calculations.

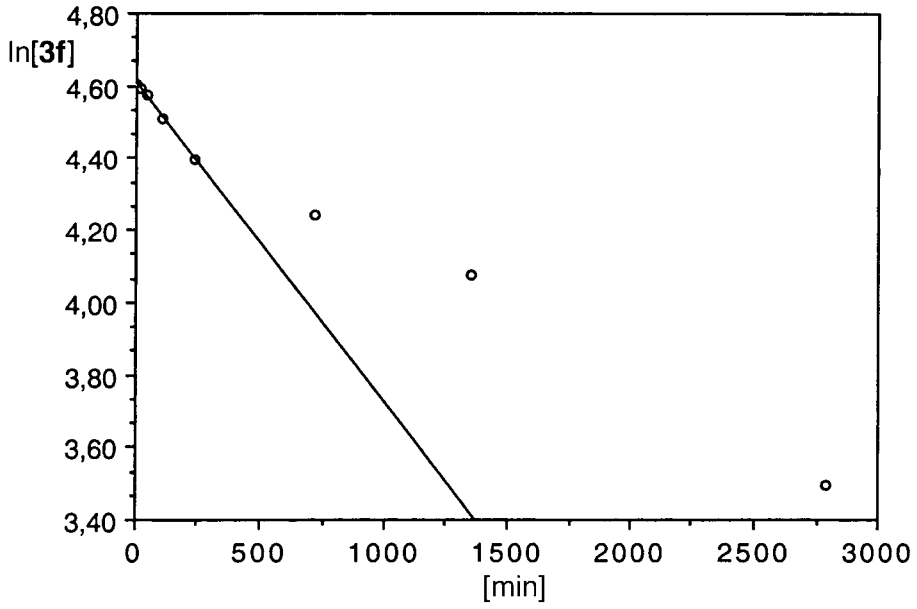


Fig. 7. *Kinetics of the thermal tranformation of propynoate* **3f** (decalin, $150 \pm 1°$; $c_{init.} = 0.1$M). $k_{obs} = k_{-1}$ [**3f**] = $(8.84 \pm 0.89) \cdot 10^{-4}$ min^{-1} ($r^2 = 0.996$; up to 19% conversion of **3f**).

Table 5. *Initial Rate Constants of the Transformation of Some Aryl 3-Arylpropynoates* **3** *in Decalin* [a])

Propynoates **3**			Decrease of **3**			Product ratio [b])
R^1	R^2	No.	Range [%]	k_{obs} [10^{-5} min^{-1}][c])	k_{rel} (150°)	Furanones **11**/ Anhydrides **12**
Ph	2,4,6-Me_3	**3c**	100–93	1.72 ± 0.18	1	1.1 : 1
4-NO_2–C_6H_4	2,4,6-Me_3	**3f**	100–81	88.4 ± 8.9	50	> 200 : 1 [d])
4-MeO–C_6H_4	2,4,6-Me_3	**3i**	100–92	2.88 ± 0.26	1.7	1 : 18
Ph	2,4,6-Br_3	**3k**	100–86	12.0 ± 0.7	7	1.4 : 1

[a]) Initial concentration: 0.1M; temperature: $(150 \pm 1)°$; diaryl naphthalene-2,3-dicarboxylates **13** were formed in undetectable amounts under these conditions. [b]) Average value of the indicated range of transformation of **3** (for details, see *Exper. Part*). [c]) Correlation coefficients (r^2) for linear regression analysis: 0.999–0.996. [d]) Anhydride **12f** was not detectable within the indicated range of transformation.

phenylprop-2-ynoates, and they have been attributed to a *Fermi* interaction with a combination or overtone band in this region [18] (see also [19]).

The calculated lowest-energy conformation of 3-phenylprop-2-ynoic acid displays an s-*cis* arrangement of the OH group with all atoms in one plane. The calculated IR frequencies of this conformation show, in the low-frequency region (202 cm^{-1}), a *transoid* in-plane vibration that brings C(3) closer to the O-atom of the OH group [10][11])

[11]) One may consider mesityl cinnamate (=2,4,6-trimethylphenyl 3-phenylprop-2-enoate) in its s-*cis* conformation as a model for this mode of vibration. The AM1 calculation of this conformation provides an interatomic distance between C(3) and $C_{Mes}(1)$ of 265 pm, *i.e.*, both C-atoms are close enough for bond formation.

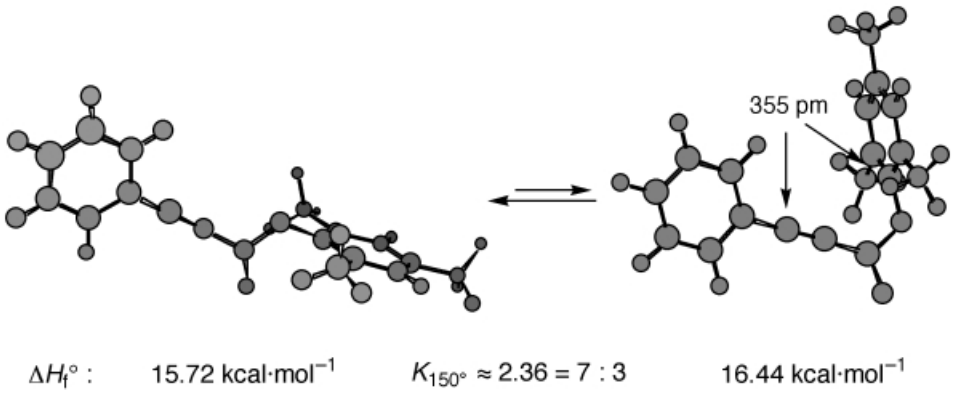
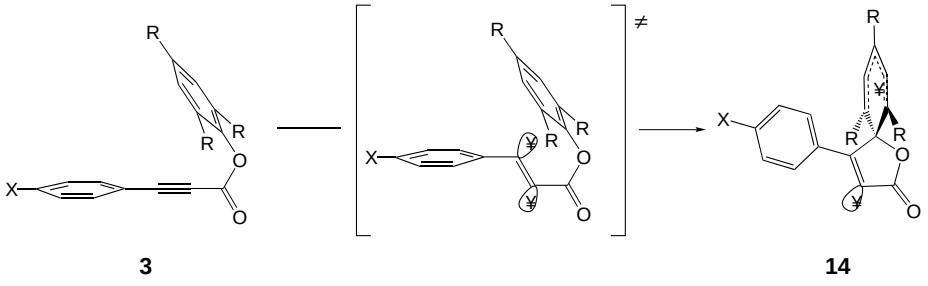


Fig. 8. *AM1-Calculated s-*cis *and s-*trans *conformation of propynoate* **3c**

(*cf.* also [20]). We assume that the unimolecular thermal rearrangement of the aryl 3-arylprop-2-ynoates **3** to **U**(1) follow a vibrational mode as discussed (*Scheme 11*).

Scheme 11



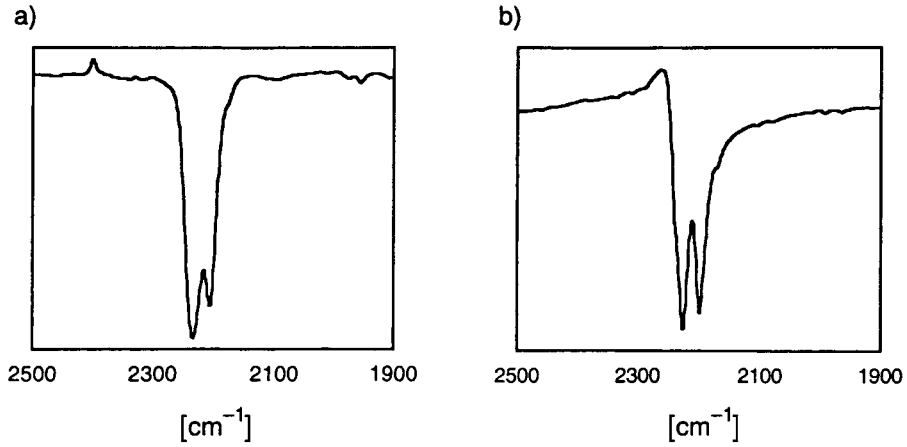


Fig. 9. *C≡C Stretching region of the IR spectra of* **3c**: a) *in* $CDCl_3$; b) *as crystals in KBr*

We thank Prof. *M. Hesse* and his co-workers for mass spectra, our NMR Laboratory and, especially, *Nadja Walch* for specific NMR measurements, Dr. *A. Linden* for the two X-ray crystal-structure analyses, and our Analytical Laboratory for elemental analyses. The financial support of this work by the *Swiss National Science Foundation* is gratefully acknowledged.

Experimental Part

General. High-performance liquid chromatography (HPLC): *Bischoff* HPLC pump model *2200* with an anal. column *Spherisorb Nitrile* (250 × 3 mm), with a photodiode array detector (*Waters 991*). Prep. HPLC: *Du Pont Instruments 830* liquid chromatograph, with a prep. column (250 × 20 mm) and a stationary phase *Spherisorb S5 CN*. Flash vacuum pyrolysis (FVP): was performed on an apparatus equipped with a *Tube Furnace Type F 21100* (*Barnstead/Thermolyne Corp.*), a 30-cm long *Pyrex* tube filled with *Pyrex* O-rings. The material was slowly evaporated from an air-bath-heated flask and collected, after pyrolysis at 650°/8 Pa, on a cold finger, cooled with liq. N_2. 2,4,6-Trimethylphenyl and 2,3,4,5,6-pentamethylphenyl carbonochloridates were synthesized according to [2]. The 4-NO_2 and 4-MeO derivatives of 3-phenylprop-2-ynoic acid were prepared according to [21]. UV Spectra: *Perkin-Elmer Lambda 19* spectrometer. IR Spectra: *Perkin-Elmer Spectrum One* spectrometer. NMR Spectra: *Bruker* instruments *ARX 300* (300/75 MHz), *Avance DRX 500* (500/125 MHz), and *Avance DRX 600* (600/150 MHz); chemical shifts (δ [ppm] relative to $CD(H)Cl_3$ (7.27/77.00 ppm). ^{17}O-NMR Spectra: *Bruker* spectrometer *Avance DRX 500* (67.8 MHz) and *Avance DRX 600* (81.37 MHz); chemical shifts relative to external H_2O at 300 K. For complete assignments of ^{1}H-NMR signals, COSY, TOCSY, NOESY, ROESY 2D- or 1D-NMR methods were applied. For complete assignments of ^{13}C-NMR signals, HSQC and HMBC 2D-NMR methods were employed. The degree of ^{17}O-labeling in the ^{17}O-enriched 2,4,6-trimethylphenol was determined by mass spectrometry, with the calculated natural-abundance correction of $[M+1]$ and $[M+2]$ peaks. Electron-impact mass spectra (EI-MS): *Finnigan SSQ 700* and *Varian MAT 90* mass spectrometer. Chemical-ionization mass spectra (CI-MS): *Varian MAT 90* mass spectrometer; ionization *via* CH_4. Electrospray-ionization mass spectra (ESI-MS): *Finnigan TSQ 700* instrument.

1. General Procedures. – 1.1. *3-Arylprop-2-ynoyl Chlorides* **9**. Oxalyl chloride (5 equiv.) and several drops of dry DMF were added dropwise to a 0.5M soln. of the acids **5** in CH_2Cl_2. After 5 h stirring, the excess of oxalyl chloride and CH_2Cl_2 were removed *in vacuo*, and the residue was dried at 35°/250 kPa for 1 h. The crude acid chlorides **9** were immediately used in the next step.

1.2. *Aryl 3-Arylprop-2-ynoates and Aryl But-2-ynoates* **3**. *Procedure A* (with the acid chlorides): To the stirred suspension of NaH (1 equiv.) in dry THF at 0° was added dropwise a 0.5M THF soln. of the phenol (1 equiv.) so that a 0.25M soln. of PhONa was formed. It was cooled to – 15°, and 1 equiv. of a 0.5M soln. of **9** in dry THF was added dropwise under stirring. After 5 h, the mixture was allowed to warm to r.t. Stirring was continued for 15 h. Then, the solvent was removed *in vacuo*, and the residue was further purified by CC (silica gel; hexane/Et_2O 9:1).

Procedure B (with the Na salts **5′** of the acids): The Na salts of the 3-arylprop-2-ynoic or but-2-ynoic acids **5** was prepared from the acid, dissolved in MeOH, by titration with 5% aq. NaOH soln. Before use, the salt was dried several h in high vacuum at 50°. A suspension of **5′** (1.05 equiv.) and the carbonochloridates **6** (1 equiv.) in dry THF was stirred and heated at 40° for 1 h. Then, the temp. of the stirred suspension was slowly increased within 5 h to reflux temp. After 10 h, the mixture was cooled to r.t. and filtered. The solvent was removed *in vacuo*, and the residue was further purified by CC (silica gel; hexane/Et_2O 1:1).

1.2.1. *Phenyl 3-Phenylprop-2-ynoate* (**3b**). According to [6], acid **5a** was converted, *via* its chloride **9c**, to **3b**; yield 81%.

Data of **3b**: M.p. 40.1–40.8° (hexane/Et_2O). IR ($CHCl_3$): 2238*s*/2213*s* (C≡C), 1720*s* (C=O), 1285*s* (C–O). ^{1}H-NMR ($CDCl_3$): 7.69 (*m*, 2 arom. H); 7.55 (*m*, 1 arom. H); 7.43–7.53 (*m*, 4 arom. H); 7.34 (*m*, 1 arom. H); 7.25 (*m*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 152.25 (*s*); 150.14 (*s*); 133.11 (*d*); 130.95 (*d*); 129.51 (*d*); 128.61 (*d*); 126.31 (*d*); 121.40 (*d*); 119.22 (*s*); 88.63 (*s*); 80.21 (*s*). EI-MS: 222 (5, $M^{+\cdot}$), 129 (100, $[Ph-C\equiv C-CO]^+$). Anal. calc. for $C_{15}H_{10}O_2$ (222.24): C 81.07, H 4.54; found: C 80.77, H 4.66.

1.2.2. *2,4,6-Trimethylphenyl 3-Phenylprop-2-ynoate* (**3c**). According to *Procedure B*, **5′a** and **6a** (2.25 g, 11.33 mmol) yielded colorless crystals of **3c** (2.20 g, 73%).

Data of **3c**: M.p. 62.8–64.8° (hexane/Et_2O). UV (hexane): λ_{max} 264 (4.29); λ_{min} 228 (3.96). IR ($CHCl_3$): 2234*s*/2206*s* (C≡C), 1720*vs* (C=O), 1606*w* (arom. C–H), 1285*s*/1182*vs* (C–O). ^{1}H-NMR ($CDCl_3$): 7.67 (*d*-like, $J = 7.7$, 2 arom. H); 7.50 (*t*-like, $J = 7.4$, 1 arom. H); 7.43 (*t*-like, $J = 7.7$, 2 arom. H); 6.93 (*s*, 2 arom. H); 2.31 (*s*, Me); 2.23 (*s*, 2 Me). ^{13}C-NMR ($CDCl_3$): 152.06 (*s*); 145.36 (*s*); 135.88 (*s*); 133.20 (*d*); 131.88 (*s*); 130.96 (*d*);

129.70 (*d*); 129.33 (*d*); 128.63 (*d*); 119.29 (*s*); 88.18 (*s*); 80.16 (*s*); 20.16 (*q*); 16.21 (*q*). EI-MS: 264 (5, $M^{+\bullet}$), 129 (100, $[Ph-C\equiv C-CO]^+$). Anal. calc. for $C_{18}H_{16}O_2$ (264.32): C 81.79, H 6.10; found: C 81.84, H 6.20.

1.2.3. *2,3,4,5,6-Pentamethylphenyl 3-Phenylprop-2-ynoate* (**3d**). According to *Procedure B*, **5a′** (0.445 g, 2.64 mmol) and **6b** (0.588 g, 2.59 mmol) yielded colorless crystals of **3d** (0.522 g, 69%) after recrystallization from hexane/Et_2O.

Data of **3d**: M.p. 146.0–147.0° (hexane/Et_2O). IR ($CHCl_3$): 2233*s*/2213*m* (C≡C), 1717*s* (C=O), 1287*s*/1182*s* (C–O). ^{1}H-NMR ($CDCl_3$): 7.73 (*dd*, $J_m = 1.3$, $J_o = 8.4$, 2 arom. H); 7.56 (*m*, 1 arom. H); 7.49 (*m*, 2 arom. H); 2.31 (*s*, Me–C(3,4,5)); 2.24 (*s*, Me–C(2,6)). ^{13}C-NMR ($CDCl_3$): 152.50 (*s*); 145.19 (*s*); 133.54 (*s*); 133.18 (*d*); 130.87 (*d*); 128.58 (*d*); 125.22 (*s*); 119.39 (*s*); 87.98 (*s*); 80.31 (*s*); 16.57 (*q*); 16.38 (*q*); 13.38 (*q*). EI-MS: 292.0 (80, $M^{+\bullet}$), 277.0 (75, $[M-Me]^+$), 162.9 (50, $[M-Ph-C\equiv C-CO]^+$), 128.8 (100, $[Ph-C\equiv C-CO]^+$). Anal. calc. for $C_{20}H_{20}O_2$ (292.37): C 82.16, H 6.89; found: C 81.93, H 6.92.

1.2.4. *2,3,4,5,6-Pentabromophenyl 3-(4-Nitrophenyl)prop-2-ynoate* (**3e**). 1.2.4.1. *2,3,4,5,6-Pentabromophenyl Carbonochloridate* (**6c**). A 500-ml flask was charged with toluene (30 ml), CH_2Cl_2 (40 ml), and 2,3,4,5,6-pentabromophenol (36.88 g, 75.5 mmol). A soln. of phosgene in toluene was added to the stirred suspension, which was then cooled to 0°. *N,N*-Dimethylaniline (10 ml, 79 mmol) was cautiously added through a dropping funnel within 15 min, while maintaining the temp. at 0°. Within a few min, the mixture became a clear soln. After 2 h, the mixture was allowed to warm to r.t. and stirred for additional 15 h. Toluene (300 ml) and, after cooling to 0° again, cold H_2O was cautiously added, and the org. layer was separated. The org. layer was washed successively with dil. HCl, NaOH, and H_2O, and then dried ($MgSO_4$). The solvent was removed, and **6c** crystallized from toluene (39.4 g, 95%).

Data of **6c**: M.p. 122.0–123.7° (toluene). IR ($CHCl_3$): 1801*s*/1790*s*/1775*s* (C=O), 1088v*s* (C–O). ^{13}C-NMR ($CDCl_3$): 147.42 (*s*); 146.62 (*s*); 128.87 (*s*); 128.70 (*s*); 120.11 (s). EI-MS: 545.5/547.5/549.4/551.4/553.4/555.6 (0.2/2.1/4.6/5.2/3.3/0.5, $M^{+\bullet}$). Anal. calc. for $C_7Br_5ClO_2$ (551.05): C 15.26, Cl 6.43; found: C 15.31, Cl 6.45.

1.2.4.2. *Formation of* **3e**. According to *Procedure B*, **5′b** (0.123 g, 0.575 mmol) and **6c** (0.302 g, 0.548 mmol) gave beige crystals of **3e** (0.333 g, 92%).

Data of **3e**: M.p. 197.3–200.0° (THF). IR ($CHCl_3$): 2240*m* (C≡C), 1749*s* (C=O), 1527*s*/1349v*s* (NO_2), 1279*s*/1134v*s* (C–O). ^{1}H-NMR ($CDCl_3$): 8.31 (*dt*, $J_o = 8.9$, $J_m = 2.0$, 2 arom. H); 7.87 (*dt*, $J_o = 8.9$, $J_m = 2.0$, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 149.07 (*s*); 148.57 (*s*); 145.64 (*s*); 134.24 (*d*); 128.79 (*s*); 128.00 (*s*); 125.14 (*s*); 123.87 (*d*); 120.78 (*s*); 86.98 (*s*); 82.31 (*s*). Anal. calc. for $C_{15}H_4Br_5NO_4 \cdot 0.25$ THF (679.74): C 28.27, H 0.89, N 2.06; found: C 28.20, H 0.87, N 2.07 (The elemental analysis was repeated two times with identical results, after drying a few days at 60°/0.02 Torr).

1.2.5. *2,4,6-Trimethylphenyl 3-(4-Nitrophenyl)prop-2-ynoate* (**3f**). According to *Procedure B*, **5′b** (0.223 g, 1.05 mmol) and **6a** (0.249 g, 1.25 mmol) gave, after CC (hexane/Et_2O 9:1) and crystallization from hexane/Et_2O pale beige crystals of **3f** (0.248 g, 80%). *Procedure A* gave, after repetitive CC and crystallization, a maximum yield of 49% of **3f**.

Data of **3f**: M.p. 146.0–147.0° (hexane/Et_2O). UV (hexane): λ_{max} 293 (sh, 4.26), 284 (4.35), 280 (sh, 4.34), 213 (sh, 4.38); λ_{min} 241 (3.74). IR ($CHCl_3$): 2240*m* (C≡C), 1722*s* (C=O), 1526*s*/1349v*s* (NO_2), 1287*s*/1169v*s* (C–O). ^{1}H-NMR ($CDCl_3$): 8.29 (*dt*, $J_o = 8.9$, $J_m = 2.0$, 2 arom. H); 7.82 (*dt*, $J_o = 8.9$, $J_m = 2.0$, 2 arom. H); 6.93 (*s*, 2 arom. H); 2.30 (*s*, Me–C(4)); 2.21 (*s*, Me–C(2,6)). ^{13}C-NMR ($CDCl_3$): 151.26 (*s*); 148.66 (*s*); 145.09 (*s*); 136.15 (*s*); 133.85 (*d*); 129.48 (*s*); 129.37 (*d*); 125.87 (*s*); 123.71 (*d*); 84.58 (*s*); 83.41 (*s*); 20.67 (*q*); 16.14 (*q*). EI-MS ($C_{18}H_{15}NO_4$, 309.32): 309.0 (40, $M^{+\bullet}$), 174.0 (100, $[NO_2C_6H_4-C\equiv C-CO]^+$), 127.9 (100, $[C_9H_4O]^+$). Anal. calc. for $C_{18}H_{15}NO_4$ (309.32): C 69.89, H 4.89, N 4.53; found: C 69.69, H 4.87, N 4.42.

1.2.6. *Phenyl 3-(4-Nitrophenyl)prop-2-ynoate* (**3g**). According to *Procedure B*, **5′b** (2.50 g, 11.73 mmol) and **6d** (1.62 ml, 12.9 mmol) gave yellowish crystals of **3g** (1.285 g, 41%).

Data of **3g**: M.p. 150.2–150.8° (hexane/CH_2Cl_2). UV (hexane): λ_{max} 300 (sh, 4.19), 284 (4.35), 281 (sh, 4.34), 215 (sh, 4.19); λ_{min} 241 (3.83). IR ($CHCl_3$): 2242*m*/2219*m* (C≡C), 1728*s* (C=O), 1526*s*/1349v*s* (NO_2), 1286*s*/1169v*s* (C–O). ^{1}H-NMR ($CDCl_3$): 8.27 (*dt*, $J_o = 8.9$, $J_m = 2.1$, 2 arom. H); 7.80 (*dt*, $J_o = 8.9$, $J_m = 2.1$, 2 arom. H); 7.44 (*tt*, $J_o = 7.7$, $J_m = 2.1$, 2 arom. H); 7.31 (*tt*, $J_o = 8.0$, $J_m = 2.3$, 1 arom. H); 7.20 (*dq*, $J_o = 7.5$, $J_m = 2.5$, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 151.46 (*s*); 149.86 (*s*); 133.77 (*d*); 129.59 (*d*); 126.56 (*d*); 125.77 (*s*); 123.71 (*d*); 121.16 (*s*); 84.96 (*s*); 83.51 (*s*). EI-MS ($C_{15}H_9NO_4$; 267.24): 267.0 (25, $M^{+\bullet}$), 239.0 (25, $[M-CO]^{+\cdot}$), 173.9 (100, $[NO_2C_6H_4-C\equiv C-CO]^+$), 127.9 (95, $[C_9H_4O]^+$). Anal. calc. for $C_{15}H_9NO_4 \cdot 0.1\ H_2O$ (269.04): C 66.97, H 3.45, N 5.21; found: C 66.97, H 3.36, N 5.03.

1.2.7. *2,4,6-Trimethylphenyl But-2-ynoate* (**3h**). From **5′c** (0.058 g, 0.545 mmol) and **6a** (0.110 g, 0.545 mmol), **3h** (0.055 g, 50%) was obtained as a glassy mass, according to *Procedure B*.

Data of **3h**: IR ($CHCl_3$): 2291*s*/2237*s* (C≡C), 1720*s* (C=O), 1251*s* (C–O). ^{1}H-NMR ($CDCl_3$): 6.80 (*s*, 2 arom. H); 2.19 (*s*, Me–C(4′)); 2.08 (*s*, Me–C(2′,6′)); 1.99 (*s*, Me–C(3)). ^{13}C-NMR ($CDCl_3$): 151.60 (*s*); 145.19

(*s*); 135.73 (*s*); 129.57 (*s*); 129.21 (*d*); 87.45 (*s*); 71.88 (*s*); 20.65 (*q*); 16.08 (*q*); 3.83 (*q*). EI-MS ($C_{13}H_{14}O_2$; 202.25) 202.1 (20, $M^{+\cdot}$), 187.1 (10, $[M-CH_3]^+$), 136.1 (50, $[M-CH_3-C\equiv C-CO]^+$), 67.1 (100, $[CH_3-C\equiv C-CO]^+$).

1.2.8. *2,4,6-Trimethylphenyl 3-(4-Methoxyphenyl)prop-2-ynoate* (**3i**). Following 1.1 and then procedure A, acid **5b** (0.190 g, 1.08 mmol) and mesitol (0.147 g, 1.08 mmol) gave light beige crystals of **3i** (0.251 g, 79%).

Data of **3i**: M.p. 54.7–59.0° (hexane/Et_2O). UV (hexane): λ_{max} 296 (4.29), 282 (4.32), 277 (sh, 4.28), 211 (sh, 4.36); λ_{min} 292 (4.26), 232 (3.68). IR ($CHCl_3$): 2210*s*/2203*s* (C≡C), 1713*s* (C=O), 1605*s* (arom.), 1256*s* (C–O). ^{1}H-NMR ($CDCl_3$): 7.47 (*d*, J_o = 8.9, 2 arom. H); 6.80 (*d*, J_o = 8.9, 2 arom. H); 6.79 (*s*, 2 arom. H); 3.73 (*s*, MeO); 2.18 (*s*, Me–C(4)); 2.09 (*s*, Me–C(2,6)). ^{13}C-NMR ($CDCl_3$): 161.78 (*s*); 152.30 (*s*); 145.41 (*s*); 135.74 (*s*); 135.18 (*d*); 129.75 (*s*); 129.26 (*d*); 114.33 (*d*); 111.03 (*d*); 89.16 (*s*); 79.61 (*s*); 55.33 (*q*); 20.70 (*q*); 16.19 (*q*). EI-MS ($C_{19}H_{18}O_3$; 294,34): 294.1 (1, $M^{+\cdot}$), 159.0 (100, $[CH_3OC_6H_4-C\equiv C-CO]^+$). Anal. calc. for $C_{19}H_{18}O_3 \cdot 0.125\ H_2O$ (296.59): C 76.94, H 6.20; found: C 76.88, H 6.49.

1.2.9. *2,4,6-Tribromophenyl 3-(4-Methoxyphenyl)prop-2-ynoate* (**3k**). According to *1.1* and then *Procedure A*, acid **5b** (0.200 g, 1.14 mmol) and 2,4,6-tribromophenol (0.394 g, 1.14 mmol) gave light beige crystals of **3k** (0.408 g, 74%) after crystallization from MeOH.

Data of **3k**: M.p. 106.7–109.2° (MeOH). UV (hexane): λ_{max} 303 (4.43), 292 (sh, 3.78), 287 (4.48), 277 (sh, 3.21); λ_{min} 298 (4.32), 241 (3.91). IR ($CHCl_3$): 2221*s*/2200*s* (C≡C), 1734*s* (C=O), 1604*s* (arom.), 1256*s* (C–O). ^{1}H-NMR ($CDCl_3$): 7.75 (*s*, 2 arom. H); 7.63 (*d*, J_o = 8.8, 2 arom. H); 6.94 (*d*, J_o = 8.8, 2 arom. H); 3.87 (*s*, MeO–C(4)). ^{13}C-NMR ($CDCl_3$): 162.11(*s*); 149.67(*s*); 144.95 (*s*); 135.46 (*d*); 134.83 (*d*); 120.24 (*s*); 118.40 (*s*); 114.39 (*d*); 110.44 (*s*); 91.40 (*s*); 78.92 (*s*); 55.37 (*q*). CI-MS: 503.7/505.7/507.7/509.7 (30/97/100/33, $[M+NH_4]^+$). Anal. calc. for $C_{16}H_9Br_3O_3$ (488.95): C 39.30, H 1.86; found: C 39.37, H 1.99.

1.2.10. *2-Methylphenyl 3-Phenylprop-2-ynoate* (**3l**). According to [6], **5a** and 2-methylphenol were converted *via* chloride **9c** to **3l**; yield 63%.

Data of **3l**: M.p. 60.3–62.2° (hexane). IR ($CHCl_3$): 2236*s*/2206*s* (C≡C), 1722v*s* (C=O), 1285*s*/1153v*s* (C–O). ^{1}H-NMR ($CDCl_3$): 7.87 (*dt*, J_o = 6.8, J_m = 1.5, arom. H); 7.73 (*tt*, J_o = 7.4, J_m = 1.4, arom. H); 7.64 (*tt*, J_o = 7.3, J_m = 1.7, 2 arom. H); 7.52–7.39 (m, 3 arom. H); 7.34 (*dd*, J_o = 7.5, J_m = 1.6, arom H); 2.51 (*s*, Me–C(2)). ^{13}C-NMR ($CDCl_3$): 152.19 (*s*); 148.80 (*s*); 133.21 (*d*); 131.30 (*d*); 131.00 (*s*); 130.22 (*d*); 128.65 (*d*); 121.79 (*d*); 119.31 (*s*); 88.57 (*s*); 80.14 (*s*); 16.17 (*q*). EI-MS ($C_{16}H_{12}O_2$, 236.27): 236.1 (5, $M^{+\cdot}$), 158.1 (100, $[M-C_6H_6]^{+\cdot}$), 129.0 (100, $[Ph-C\equiv C-CO]^+$). Anal. calc. for $C_{16}H_{12}O_2 \cdot 0.125\ H_2O$ (238.52): C 80.57, H 5.18; found: C 80.83, H 5.17.

2. Thermolysis of the Aryl 3-Arylprop-2-ynoates 3. – 2.1. *2,4,6-Trimethylphenyl 3-Phenylprop-2-ynoate* (**3c**). A stirred 0.5M soln. of **3c** (0.060 g, 0.227 mmol) in decalin was heated at 160° during 24 h. Decalin was distilled off, and the residual orange-colored solid was purified by CC (silica gel; toluene). Crystallization from hexane gave pure (*Z*)-**11c** (0.020 g, 33%) and recovered **3c** (0.008 g, 13%). Heating molten **3c** gave, after 18 h and chromatography, 24% of (*Z*)-**11c** and 22% of recovered **3c**. Heating a 2M soln. of **3c** in *o*-xylene during 260 h led to 15% of (*Z*)-**11c** and 1% of (*E*)-**11c**, which were again isolated by chromatography.

Data of 2,4,6-Trimethylphenyl 2,3-Dihydro-2-oxo-5-phenyl-3-[(Z)-(phenyl)(2,4,6-trimethylphenyl)methylidene]furan-4-carboxylate ((*Z*)-**11c**). Yellow crystals. M.p. 152.1–153.4°. UV (hexane; see *Fig. 2*, *a*): λ_{max} 391 (4.20), 356 (sh, 4.11), 261 (sh, 4.13), 249 (sh, 4.11); λ_{min} 302 (3.88). IR ($CHCl_3$): 1774*m* (C=O, five-ring lactone), 1731*m* (C=O, aryl ester), 1010*s* (C–O). ^{1}H-NMR (600 MHz, $CDCl_3$): 8.01 (*dd*, J_o = 7.9, J_m = 1.4, H–C(2^a,6^a)); 7.48 (*td*, J_o = 7.3, J_m = 2.0, H–C(4^a)); 7.41–7.44 (*m*, H–C(3^a,5^a)), H–C(2^c,6^c)); 7.27–7.36 (*m*, H–C(3^c,4^c,5^c)); 6.97 (*s*, H–C(3^b,5^b)); 6.68 (*s*, H–C(3^d,5^d)); 2.36 (*s*, Me–C(4^b)); 2.23 (*s*, Me–C(4^d)); 2.10 (*s*, Me–C(2^b,6^b)); 1.52 (*s*, Me–C(2^d,6^d)). ^{13}C-NMR (150 MHz, $CDCl_3$): 163.83 (*s*, C(2)); 160.59 (*s*, *C*O–C(4)); 159.81 (*s*, C(5)); 158.11 (*s*, C(3′)); 145.61 (*s*, C(1^d)); 139.98 (*s*, C(1^c)); 138.07 (*s*, C(4^b)); 136.57 (*s*, C(1^b)); 135.30 (*s*, C(4^d)); 135.12 (*s*, C(2^b,6^b)); 131.36 (*d*, C(4^a)); 130.23 (*d*, C(4^c)); 130.19 (*d*, C(2^c,6^c)); 129.92 (*d*, C(2^a,6^a)); 129.86 (*s*, C(2^d,6^d)); 129.00 (*d*, C(3^d,5^d)); 128.87 (*d*, C(3^b,5^b) and C(3^c,5^c)); 128.24 (*s*, C(1^a)); 128.07 (*d*, C(3^a,5^a)); 121.45 (*s*, C(3)); 111.40 (*s*, C(4)); 21.29 (*q*, *Me*–C(4^b)); 20.58 (*q*, *Me*–C(4^d)); 20.00 (*q*, *Me*–C(2^b,6^b)); 15.95 (*q*, *Me*–C(2^d,6^d)). CI-MS ($C_{36}H_{32}O_4$; 528.64): 546.1 (100, $[M+NH_4]^+$); 529.1 (67, $[M+H]^+$); 393.0 (15, $[M-Me_3C_6H_2O]^+$). EI-MS: 393.1 (100, $[M-Me_3C_6H_2O]^+$). Anal. calc. for $C_{36}H_{32}O_4 \cdot 0.125\ H_2O$ (530.89): C 81.43, H 6.12; found: C 81.40, H 6.31.

Data of (E)-**11c**. Yellow solid. M.p. 120.1–125.4°. UV (hexane; see *Fig. 2*, *b*): λ_{max} 383 (4.20), 281 (sh, 3.79), 266 (sh, 3.87), 243 (sh, 4.07); λ_{min} 316 (3.56). IR ($CHCl_3$): 1769v*s* (C=O; five-ring lactone), 1729v*s* (C=O, aryl ester), 1010*s* (C–O). ^{1}H-NMR (600 MHz, $CDCl_3$): 7.81 (*dt*, J_o = 7.2, J_m = 1.6, H–C(2^a,6^a)); 7.44 (*tt*, J_o = 7.4, J_m = 2.0, H–C(4^a)); 7.42 (*tt*, J_o = 7.2, J_m = 1.4, H–C(4^b)); 7.36–7.39 (*m*, H–C(3^a,5^a), and H–C(2^b,6^b)); 7.33 (*t*, J_o = 7.8, H–C(3^b,5^b)); 6.83 (*s*, H–C(3^c,5^c)); 6.65 (*s*, H–C(3^d,5^d)); 2.33 (*s*, Me–C(4^c)); 2.15 (*s*, Me–C(4^d)); 2.10 (*s*, Me–C(2^c,6^c)); 1.41 (*s*, Me–C(2^d,6^d)). ^{13}C-NMR (150 MHz, $CDCl_3$): 163.96 (*s*, C(2)); 161.10 (*s*, C(5)); 160.45 (*s*,

C(3′)); 158.48 (*s*, *C*O–C(4)); 144.89 (*s*, C(1^{d})); 138.48 (*s*, C(4^{c})); 137.67 (*s*, C(1^{c})); 137.34 (*s*, C(1^{b})); 136.29 (*s*, C(2^{c},6^{c})); 135.24 (*s*, C(4^{d})); 131.20 (*d*, C(4^{a})); 131.11 (*d*, C(2^{b},6^{b})); 130.65 (*d*, C(4^{b})); 130.34 (*d*, C(2^{a},6^{a})); 129.91 (*s*, C(2^{d},6^{d})); 129.17 (*d*, C(3^{c},5^{c})); 129.04 (*d*, C(3^{d},5^{d})); 128.86 (*s*, C(1^{a})); 127.90 (*d*, C(3^{b},5^{b})); 127.65 (*d*, C(3^{a},5^{a})); 121.99 (*s*, C(3)); 111.52 (*s*, C(4)); 21.03 (*q*, *Me*–C(4^{c})); 20.61 (*q*, *Me*–C(4^{d})); 20.51 (*q*, *Me*–C(2^{c},6^{c})); 14.10 (*q*, *Me*–C(2^{d},6^{d})). CI-MS ($C_{36}H_{32}O_4$; 528.64): 546.4 (100, $[M+NH_4]^+$); 529.4 (97, $[M+H]^+$); 393.2 (19, $[M-Me_3C_6H_2O]^+$).

2.2. *2,3,4,5,6-Pentamethylphenyl 3-Phenylprop-2-ynoate* (**3d**). Molten **3d** (0.220 g, 0.751 mmol) was stirred at 150° during 24 h. At first, the formed orange solid was purified by CC (silica gel; hexane/CH_2Cl_2 1:1). Subsequent prep. HPLC (hexane/i-PrOH 95:5) gave pure (*Z*)-**11d** (0.060 g, 27%) and (*E*)-**11d** (0.028 g, 13%). The same reaction, carried out at 180°, yielded, after 18 h, 27% of (*Z*)-**11d** and 3% of (*E*)-**11d**.

Data of 2,3,4,5,6-Pentamethylphenyl 2,3-Dihydro-2-oxo-5-phenyl-3-[(Z)-(phenyl)(2,3,4,5,6-pentamethylphenyl)methylidene]furan-4-carboxylate ((*Z*)-**11d**): Yellow crystals. M.p. 251.2–253.9° (hexane/i-PrOH 95:5). UV (hexane): λ_{max} 384 (4.08), 346 (sh, 3.98), 268 (sh, 3.96), 241 (sh, 4.27); λ_{min} 308 (3.79). IR ($CHCl_3$): 1778*s* (C=O; five-ring lactone), 1735*s* (br.; C=O, aryl ester), 1149*s* (C–O). ^{1}H-NMR (600 MHz, $CDCl_3$): 8.02 (*d*, J_o = 7.2, H–C(2^{a},6^{a})); 7.47 (*t*, J_o = 7.3, H–C(4^{a})); 7.41–7.44 (*m*, H–C(3^{a},5^{a}), H–C(2^{c},6^{c})); 7.27–7.36 (*m*, H–C(3^{c},4^{c},5^{c})); 2.31 (*s*, Me–C(4^{b})); 2.24 (*s*, Me–C(3^{b},5^{b})); 2.13 (*s*, Me–C(4^{d}), Me–C(2^{b},6^{b})); 2.05 (*s*, Me–C(3^{d},5^{d})); 1.49 (*s*, Me–C(2^{d},6^{d})). ^{13}C-NMR (150 MHz, $CDCl_3$): 163.88 (*s*, C(2)); 161.11 (*s*, *C*O–C(4)); 160.59 (*s*, C(5)); 159.61 (*s*, C(3′)); 145.61 (*s*, C(1^{d})); 140.50 (*s*, C(1^{c})); 137.10 (*s*, C(1^{b})); 135.12 (*s*, C(4^{b})); 133.16 (*s*, C(3^{d},5^{d})); 132.78 (*s*, C(3^{b},5^{b})); 132.71 (*s*, C(4^{d})); 131.26 (*d*, C(4^{a})); 130.33 (*d*, C(2^{c},6^{c})); 130.07 (*d*, C(4^{c})); 130.02 (*d*, C(2^{a},6^{a})); 129.99 (*s*, C(2^{b},6^{b})); 128.86 (*d*, C(3^{c},5^{c})); 128.37 (*s*, C(1^{a})); 128.05 (*d*, C(3^{a},5^{a})); 125.52 (*s*, C(2^{d},6^{d})); 121.43 (*s*, C(3)); 110.53 (*s*, C(4)); 17.66 (*q*, *Me*–C(2^{b},6^{b})); 17.01 (*q*, *Me*–C(4^{b})); 16.47 (*q*, *Me*–C(3^{b},5^{b}), *Me*–C(4^{d})); 16.28 (*q*, *Me*–C(3^{d},5^{d})); 13.07 (*q*, *Me*–C(2^{d},6^{d})). EI-MS ($C_{40}H_{40}O_4$; 584.74): 584.0 (0.2, $M^{+\bullet}$); 421.0 (100, $[M-Me_5C_6O]^+$). Anal. calc. for $C_{40}H_{40}O_4 \cdot 0.25H_2O$ (589.2): C 81.53, H 6.93; found: C 81.50, H 6.87.

Data of (*E*)-**11d**. Yellow crystals. M.p. 247.2–249.9° (hexane/i-PrOH 95:5). UV (hexane): λ_{max} 383 (4.18), 273 (sh, 3.95), 243 (sh, 4.16); λ_{min} 318 (3.73). IR ($CHCl_3$): 1777*s* (C=O; five-ring lactone), 1724*s* (br.; C=O, aryl ester). ^{1}H-NMR (600 MHz, $CDCl_3$): 7.84 (*d*, J_o = 7.8, H–C(2^{a},6^{a})); 7.44 (*t*, J_o = 7.2, H–C(4^{a})); 7.41 (*t*, J_o = 7.2, H–C(4^{b})); 7.39 (*d*, J_o = 7.2, H–C(2^{b},6^{b})); 7.38 (*t*, J_o = 7.8, H–C(3^{a},5^{a})); 7.34 (*t*, J_o = 7.8, H–C(3^{b},5^{b})); 2.25 (*s*, Me–C(4^{c})); 2.16 (*s*, Me–C(3,5)); 2.11 (*s*, Me–C(4^{d})); 2.09 (*s*, Me–C(2^{c},6^{c})); 2.04 (*s*, Me–C(3^{d},5^{d})); 1.29 (*s*, Me–C(2^{d},6^{d})). ^{13}C-NMR (150 MHz, $CDCl_3$): 164.13 (*s*, C(2)); 162.54 (*s*, C(3′)); 160.76 (*s*, C(5)); 159.13 (*s*, *C*O–C(4)); 144.84 (*s*, C(1^{d})); 138.41 (*s*, C(1^{c})); 137.98 (*s*, C(1^{b})); 135.63 (*s*, C(4^{c})); 133.09 (*s*, C(3^{d},5^{d})); 132.94 (*s*, C(3^{c},5^{c})); 132.61 (*s*, C(4^{d})); 131.40 (*s*, C(2^{c},6^{c})); 131.23 (*d*, C(2^{b},6^{b})); 131.09 (*d*, C(4^{a})); 130.36 (*d*, C(2^{a},6^{a})); 130.32 (*d*, C(4^{b})); 128.90 (*s*, C(1^{a})); 127.88 (*d*, C(3^{a},5^{a})); 127.46 (*d*, C(3^{b},5^{b})); 125.48 (*s*, C(2^{d},6^{d})); 122.47 (*s*, C(3)); 111.62 (*s*, C(4)); 18.37 (*q*, *Me*–C(2^{c},6^{c})); 16.87 (*q*, *Me*–C(4^{c})); 16.56 (*q*, *Me*–C(3^{c},5^{c})); 16.53 (*q*, *Me*–C(4^{d})); 16.29 (*q*, *Me*–C(3^{d},5^{d})); 12.39 (*q*, *Me*–C(2^{d},6^{d})). EI-MS ($C_{40}H_{40}O_4$; 584.74): 584.0 (0.4, $M^{+\bullet}$); 421.0 (100, $[M-Me_5C_6O]^+$). Anal. calc. for $C_{40}H_{40}O_4 \cdot H_2O$ (602.75): C 79.71, H 7.02; found: C 79.50, H 6.75.

2.3. *2,4,6-Trimethylphenyl 3-(4-Nitrophenyl)prop-2-ynoate* (**3f**). Molten **3f** (0.185 g, 0.598 mmol) was heated for 16 h at 150°. CC (silica gel; hexane/ Et_2O 1:1) gave a pure mixture (*Z*)-**11f**/(*E*)-**11f** (0.137 g, 74%) in a ratio of 92:8. For the analyses, the isomers were separated by HPLC (hexane/CH_2Cl_2/MeOH 80:20:0.5).

Data of 2,4,6-Trimethylphenyl 2,3-Dihydro-5-(4-nitrophenyl)-3-[(Z)-(4-nitrophenyl)(2,4,6-trimethylphenyl)methylidene]-2-oxofuran-4-carboxylate ((*Z*)-**11f**): Orange solid. M.p. 134.9–138.5° (hexane/(*t*-Bu)$_2$O). UV (hexane; see *Fig. 2*, *c*): λ_{max} 403 (4.18), 378 (sh, 4.16), 292 (sh, 4.11), 258 (4.24); λ_{min} 322 (4.00), 252 (4.24). IR ($CHCl_3$): 1794*m* (C=O, five-ring lactone), 1729*m* (C=O, aryl ester), 1525*s*/1347*vs* (NO_2). ^{1}H- NMR (600 MHz, $CDCl_3$): 8.29 (*d*, J_o = 8.4, H–C(3^{a},5^{a})); 8.19 (*d*, J_o = 8.4, H–C(2^{a},6^{a}) and H–C(3^{c},5^{c})); 7.54 (*d*, J_o = 8.4, H–C(2^{c},6^{c})); 7.00 (*s*, H–C(3^{b},5^{b})); 6.71 (*s*, H–C(3^{d},5^{d})); 2.36 (*s*, Me–C(4^{b})); 2.16 (*s*, Me–C(4^{d})); 2.11 (*s*, Me–C(2^{b},6^{b})); 1.62 (*s*, Me–C(2^{d},6^{d})). ^{13}C-NMR (150 MHz, $CDCl_3$): 162.39 (*s*, C(2)); 159.52 (*s*, C(5)); 159.16 (*s*, *C*O–C(4)); 157.53 (*s*, C(3′)); 149.28 (*s*, C(4^{a})); 148.19 (*s*, C(4^{c})); 146.06 (*s*, C(1^{c})); 144.82 (*s*, C(1^{d})); 139.19 (*s*, C(4^{b})); 136.05 (*s*, C(4^{d})); 135.24 (*s*, C(1^{b})); 134.85 (*d*, C(2^{b},6^{b})); 133.94 (*s*, C(1^{a})); 131.30 (*d*, C(2^{a},6^{a})); 130.55 (*d*, C(2^{c},6^{c})); 129.39 (*d*, C(3^{d},5^{d})); 129.33 (*d*, C(3^{b},5^{b})); 129.05 (*s*, C(2^{d},6^{d})); 123.86 (*d*, C(3^{c},5^{c})); 123.20 (*s*, C(3)); 123.13 (*d*, C(3^{a},5^{a})); 111.40 (*s*, C(4)); 21.20 (*q*, *Me*–C(4^{b})); 20.50 (*q*, *Me*–C(4^{d})); 20.03 (*q*, *Me*–C(2^{b},6^{b})); 16.00 (*q*, *Me*–C(2^{d},6^{d})). EI-MS ($C_{36}H_{30}N_2O_8$; 618.63): 618.2 (1, $M^{+\bullet}$), 483.1 (100, $[M-Me_3C_6H_2O]^+$). Anal. calc. for $C_{36}H_{30}N_2O_8$ (618.62): C 69.89, H 4.89, N 4.53; found: C 69.94, H 5.01, N 4.33.

Data of (*E*)-**11f**: Yellow crystals. M.p. 253.5–255.3° (hexane/CH_2Cl_2). UV (hexane; see *Fig. 2*, *d*): λ_{max} 396 (4.11), 283 (sh, 3.95), 262 (4.07), 216 (sh, 4.32); λ_{min} 323 (3.71), 242 (4.00). IR ($CHCl_3$): 1783*s* (C=O; five-ring lactone), 1735*s* (C=O; aryl ester), 1525vs/1347v*s* (NO_2). ^{1}H-NMR (600 MHz, $CDCl_3$): 8.26 (*dt*, J_o = 8.7, J_m = 1.6, H–C(3^{a},5^{a})); 8.20 (*dt*, J_o = 8.9, J_m = 1.8, H–C(3^{b},5^{b})); 8.05 (*dt*, J_o = 9.0, J_m = 2.0, H–C(2^{a},6^{a})); 7.53 (*dt*, J_o = 8.9, J_m = 1.9, H–C(2^{b},6^{b})); 6.87 (*s*, H–C(3^{c},5^{c})); 6.69 (*s*, H–C(3^{d},5^{d})); 2.28 (*s*, Me–C(4^{c})); 2.17 (*s*, Me–C(4^{d}));

2.11 (*s*, Me–C(2^c,6^c)); 1.45 (*s*, Me–C(2^d,6^d)). ^{13}C-NMR (150 MHz, $CDCl_3$): 162.94 (*s*, C(2)); 159.16 (*s*, C(5)); 158.92 (*s*, C(3′)); 157.58 (*s*, *C*O–C(4)); 149.23 (*s*, C(4^a)); 148.70 (*s*, C(4^b)); 144.50 (*s*, C(1^d)); 143.25 (*s*, C(1^b)); 139.65 (*s*, C(4^c)); 136.48 (*s*, C(1^c)); 135.96 (*s*, C(2^c,6^c)); 135.88 (*s*, C(4^d)); 134.34 (*s*, C(1^a)); 131.80 (*d*, C(2^b,6^b)); 131.42 (*d*, C(2^b,6^b)); 129.60 (*d*, C(3^c,5^c)); 129.41 (*s*, C(2^d,6^d)); 129.34 (*d*, C(3^d,5^d)); 123.61 (*s*, C(3)); 123.19 (*d*, C(3^a,5^a)); 122.97 (*d*, C(3^b,5^b)); 113.27 (*s*, C(4)); 21.04 (*q*, *Me*–C(4^c)); 20.59 (*q*, *Me*–C(4^d), *Me*–C(2^c,6^c)); 15.69 (*q*, *Me*–C(2^b,6^b)). CI-MS ($C_{36}H_{30}N_2O_8$; 618.63): 636.3 (100, $[M+NH_4]^+$), 619.3 (7, $[M+H]^+$), 483.2 (21, $[M-$2,4,6-$Me_3C_6H_2O]^+$). Anal. calc. for $C_{36}H_{30}N_2O_8$ (618.62): C 69.89, H 4.89, N 4.53; found: C 69.67, H 4.84, N 4.46.

2.4. *Phenyl 3-(4-Nitrophenyl)prop-2-ynoate* (**3g**). Molten ester **3g** (0.800 g, 2.99 mmol) was heated under Ar during 17 h at 180°. Prep. TLC on silica gel (hexane/CH_2Cl_2 7:3) gave an orange colored fraction (0.240 g), which contained (*Z*)-**11g** and (*E*)-**11g** as well as diester **13g**. Dimer **13g** (0.190 g, 24%) was fractionally crystallized from cold CH_2Cl_2. The mother liquor was evaporated. The residue was submitted to prep. HPLC. Repetitive runs (hexane/CH_2Cl_2/MeOH 80:20:0.5) yielded finally pure (*E*)-**11g** (0.014 g, 1.8%) and (*Z*)-**11g** (0.006 g, 0.8%).

*Data of Phenyl 2,3-Dihydro-5-(4-nitrophenyl)-3-[(*E*)-(4-nitrophenyl)(phenyl)methylidene]-2-oxofuran-4-carboxylate* ((*E*)-**11g** [5]). Orange crystals. M.p. 193.3–197.4° (hexane/CH_2Cl_2). UV (hexane/i-PrOH 9:1): λ_{max} 408 (4.11), 265 (4.16); λ_{min} 348 (3.77), 245 (4.12). IR ($CHCl_3$): 1785*m* (C=O: five-ring lactone), 1741*m* (C=O; aryl ester), 1525*s*/1349v*s* (NO_2). ^{1}H-NMR (600 MHz, $CDCl_3$): 8.31 (*dt*, $J_o=9.0$, $J_m=1.9$, H–C(3^a,5^a)); 8.18 (*dt*, $J_o=8.7$, $J_m=2.0$, H–C(3^c,5^c)); 8.10 (*dt*, $J_o=9.0$, $J_m=2.1$, H–C(2^a,6^a)); 7.56 (*t*, $J_o=7.5$, H–C(4^b)); 7.44–7.48 (*m*, H–C(2^c,6^c) and H–C(3^b,5^b)); 7.35 (*dd*, $J_o=7.9$, $J_m=0.8$, H–C(2^b,6^b)); 7.20 (*tt*, $J_o=7.3$, $J_m=2.0$, H–C(3^d,5^d)); 7.14 (*tt*, $J_o=7.3$, $J_m=1.7$, H–C(4^d)); 6.50 (*dd*, $J_o=7.6$, $J_m=1.1$, H–C(2^d,6^d)). ^{13}C-NMR (150 MHz, $CDCl_3$): 163.05 (*s*, C(2)); 160.63 (*s*, *C*O–C(4)); 157.43 (*s*, C(3′)); 155.30 (*s*, C(5)); 149.52 (*s*, C(1^d)); 149.18 (*s*, C(4^a)); 148.65 (*s*, C(4^c)); 147.14 (*s*, C(1^c)); 137.29 (*s*, C(1^b)); 133.03 (*s*, C(1^a)); 131.74 (*d*, C(4^b)); 131.48 (*d*, C(2^c,6^c)); 131.44 (*d*, C(2^b,6^b)); 129.69 (*d*, C(2^a,6^a)); 129.39 (*d*, C(3^d,5^d)); 128.55 (*d*, C(3^b,5^b)); 126.49 (*d*, C(4^d)); 123.91 (*d*, C(3^c,5^c)); 123.78 (*d*, C(3^a,5^a)); 122.19 (*s*, C(3)); 119.83 (*d*, C(2^d,6^d)); 113.32 (*s*, C(4)). CI-MS ($C_{30}H_{18}N_2O_8$; 534.47): 552.2 (100, $[M+NH_4]^+$), 505.2 (37, $[M-CHO]^+$), 414.2 (68, $[M-(C_6H_5O+CHO)]^+$).

Data of (*Z*)-**11g** [5]): Orange crystals. M.p. 205.4–212.8° (hexane/CH_2Cl_2). UV (CH_2Cl_2): λ_{max} 412 (4.32), 296 (sh, 4.18), 264 (4.32); λ_{min} 343 (3.93), 244 (4.25). IR ($CHCl_3$): 1786*s* (C=O, five-ring lactone), 1741*s* (C=O, aryl ester), 1524*s*/1348v*s* (NO_2). ^{1}H-NMR (600 MHz, $CDCl_3$): 8.31 (*dt*, $J_o=8.9$, $J_m=1.8$, H–C(3^a,5^a)); 8.28 (*dt*, $J_o=9.0$, $J_m=1.8$, H–C(3^b,5^b)); 8.15 (*dt*, $J_o=8.9$, $J_m=1.9$, H–C(2^a,6^a)); 7.52–7.54 (*m*, H–C(2^b,6^b), H–C(4^c)); 7.45 (*t*, $J_o=7.7$, H–C(3^c,5^c)); 7.31 (*d*, $J_o=7.4$, H–C(2^c,6^c)); 7.20 (*t*, $J_o=7.7$, H–C(3^d,5^d)); 7.14 (*t*, $J_o=7.3$, H–C(4^d)); 6.34 (*d*, $J_o=7.4$, H–C(2^d,6^d)). ^{13}C-NMR (150 MHz, $CDCl_3$): 163.37 (*s*, C(2)); 161.09 (*s*, *C*O–C(4)); 157.24 (*s*, C(3′)); 155.00 (*s*, C(5)); 149.49 (*s*, C(1^d)); 149.13 (*s*, C(4^a)); 148.94 (*s*, C(4^b)); 144.67 (*s*, C(1^b)); 140.06 (*s*, C(1^c)); 132.99 (*s*, C(1^a)); 132.13 (*d*, C(2^b,6^b)); 131.41 (*d*, C(4^c)); 130.85 (*d*, C(2^c,6^c)); 129.64 (*d*, C(2^a,6^a)); 129.34 (*d*, C(3^c,5^c)); 129.23 (*d*, C(3^d,5^d)); 126.30 (*d*, C(4^d)); 123.77 (*d*, C(3^a,5^a)); 123.44 (*d*, C(3^b,5^b)); 122.19 (*s*, C(3)); 120.56 (*d*, C(2^d,6^d)); 113.74 (*s*, C(4)). CI-MS ($C_{30}H_{18}N_2O_8$, 534.47): 552.2 (100, $[M+NH_4]^+$), 505.2 (8, $[M-CHO]^+$), 441.1 (35, $[M-C_6H_5O]^+$).

Data of Diphenyl 7-Nitro-1-(4-Nitrophenyl)naphthalene-2,3-dicarboxylate (**13g**). Yellowish crystals. M.p. 256.4–257.8° (CH_2Cl_2). UV (CH_2Cl_2): λ_{max} 359 (3.49), 285 (sh, 4.02), 257 (4.48); λ_{min} 333 (3.32), 240 (4.32). IR ($CHCl_3$): 1745*s* (C=O, aryl ester), 1528*s* (NO_2), 1351v*s* (NO_2), 1190*s* (C–O). ^{1}H-NMR (500 MHz, $CDCl_3$): 9.06 (*s*, H–C(4)); 8.49 (*d*, $J_o=8.5$, H–C(3′,5′)); 8.47 (*dd*, $J(6,5)=9.0$, $J(6,8)=2.1$, H–C(6)); 8.42 (*d*, $J(8,6)=1.7$, H–C(6)); 8.32 (*d*, $J(5,6)=9.0$, H–C(5)); 7.74 (*d*, $J_o=8.6$, H–C(2′,6′)); 7.48 (*t*, $J_o=7.9$, H–C(3‴,5‴)); 7.34 (*t*, $J_o=7.4$, H–C(4‴)); 7.29 (*d*, $J_o=7.4$, H–C(2‴,6‴)); 7.25 (*t*, $J_o=7.8$, H–C(3″,5″)); 7.17 (*t*, $J_o=7.4$, H–C(4″)); 6.71 (*d*, $J_o=7.6$, H–C(2″,6″)). ^{13}C-NMR ($CDCl_3$): 165.55, 163.28 (2*s*, 2 C=O); 150.47 (*s*); 150.05 (*s*); 148.49 (*s*); 148.14 (*s*); 141.64 (*s*); 138.68 (*s*); 134.94 (*s*); 132.75 (*s*); 132.62 (*d*); 131.73 (*d*); 131.65 (*d*); 129.75 (*d*); 129.53 (*d*); 127.71 (*s*); 126.60 (*d*); 126.37 (*d*); 123.95 (*d*); 122.52 (*d*); 121.81 (*d*); 121.46 (*d*); 120.93 (*d*). CI-MS: 552.0 (100, $[M+NH_4]^+$), 505.2 (8, $[M-CHO]^+$), 441.1 (35, $[M-C_6H_5O]^+$). Anal. calc. for $C_{30}H_{18}N_2O_8$ (534.47): C 67.42, H 3.39, N 5.24; found: C 67.64, H 3.53, N 5.18.

2.5. *2,4,6-Trimethylphenyl 3-(4-Methoxyphenyl)prop-2-ynoate* (**3i**). Molten ester **3i** (0.140 g, 0.476 mmol) was stirred during 12 h at 200°. CC (silica gel, hexane/CH_2Cl_2 1:1) of the orange colored solid gave as a first fraction (*Z*)-**11i** (0.035 g, 25%). Subsequent prep. HPLC (hexane/i-PrOH 95:5) of the second orange colored fraction led to pure (*E*)-**11i** (0.006 g, 4%) and **12i** (0.020 g, 19%).

Data of 2,4,6-Trimethylphenyl 2,3-Dihydro-5-(4-methoxyphenyl-3-[(Z)-(4-methoxyphenyl)(2,4,6-trimethylphenyl)methylidene]-2-oxofuran-4-carboxylate ((*Z*)-**11i**). Yellow-orange crystals. M.p. 209.2–214.5° (EtOH). UV (hexane): λ_{max} 406 (4.40), 361 (sh, 4.10), 313 (4.07), 291 (4.08), 239 (sh, 4.25); λ_{min} 334 (3.99), 304 (4.06), 269 (4.03). IR ($CHCl_3$): 1772*m* (C=O, five-ring lactone), 1735*s* (C=O, aryl ester), 1605*s* (arom.). ^{1}H NMR (600 MHz, $CDCl_3$): 8.01 (*d*, $J_o=9.0$, H–C(2^a,6^a)); 7.36 (*d*, $J_o=9.0$, H–C(2^c,6^c)); 6.95 (*s*, H–C(3^b,5^b)); 6.92

(*d*, J_o = 9.0, H–C(3^a,5^a)); 6.87 (*d*, J_o = 9.0, H–C(3^c,5^c)); 6.70 (*s*, H–C(3^d,5^d)); 3.85 (*s*, MeO–C(4^a)); 3.82 (*s*, MeO–C(4^c)); 2.35 (*s*, Me–C(4^b)); 2.18 (*s*, Me–C(4^d)); 2.08 (*s*, Me–C(2^b,6^b)); 1.58 (*s*, Me–C(2^d,6^d)). ^{13}C-NMR (150 MHz, $CDCl_3$): 164.16 (*s*, C(2)); 161.99 (*s*, C(4^a)); 161.39 (*s*, C(3′)); 161.37 (*s*, C(4^c)); 159.04 (*s*, C(4)); 156.63 (*s*, *C*O–C(4)); 145.87 (*s*, C(1^d)); 137.86 (*s*, C(4^b)); 136.75 (*s*, C(1^b)); 135.32 (*s*, C(2^b,6^b)); 135.26 (*s*, C(4^d)); 132.73 (*s*, C(1^c)); 132.00 (*d*, C(2^c,6^c)); 131.70 (*d*, C(2^a,6^a)); 129.97 (*s*, C(2^d,6^d)); 129.04 (*d*, C(3^d,5^d)); 128.78 (*d*, C(3^b,5^b)); 120.59 (*s*, C(1^a)); 119.92 (*s*, C(2)); 114.43 (*d*, C(3^c,5^c)); 113.58 (*d*, C(3^a,5^a)); 109.04 (*s*, C(3)); 55.35 (*q*, *Me*O–C(4^a)); 55.35 (*q*, *Me*O–C(4^c)); 21.27 (*q*, *Me*–C(4^b)); 20.57 (*q*, *Me*–C(4^d)); 19.89 (*q*, *Me*–C(2^b,6^b)); 15.94 (*q*, *Me*–C(2^d,6^d)). CI-MS ($C_{38}H_{36}O_6$; 588.69): 589.0 (100, $[M+H]^+$). Anal. calc. for $C_{38}H_{36}O_6 \cdot 0.125\ H_2O$ (590.94): C 76.94, H 6.20; found: C 77.17, H 6.31.

Data of (*E*)-**11i**. Yellow crystals. M.p. 206.6–208.4° (hexane/CH_2Cl_2). UV (hexane): λ_{max} 408 (4.39), 300 (sh, 4.05), 286 (4.07), 241 (4.22); λ_{min} 344 (3.86), 279 (4.06). IR ($CHCl_3$): 1763*s* (C=O, five-ring lactone), 1725*s* (C=O, aryl ester), 1603*s* (arom.). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.82 (*dt*, J_o = 9.0, J_m = 2.4, H–C(2^a,6^a)); 7.34 (*dt*, J_o = 8.9, J_m = 2.4, H–C(2^b,6^b)); 6.89 (*dt*, J_o = 9.0, J_m = 2.4, H–C(3^a,5^a)); 6.84 (*d*, J_o = 8.9, J_m = 2.5, H–C(3^b,5^b)); 6.84 (*s*, H–C(3^c,5^c)); 6.68 (*s*, H–C(3^d,5^d)); 3.85 (*s*, MeO–C(4^b)); 3.82 (*s*, MeO–C(4^a)); 2.28 (*s*, Me–C(4^c)); 2.18 (*s*, Me–C(4^d)); 2.08 (*s*, Me–C(2^c,6^c)); 1.47 (*s*, Me–C(2^d,6^d)). ^{13}C-NMR (150 MHz, $CDCl_3$): 164.42 (*s*, C(2)); 161.85 (*s*, C(4^a), C(4^b)); 160.33 (*s*, C(4)); 159.53 (*s*, C(3′)); 158.81 (*s*, *C*O–C(4)); 144.98 (*s*, C(1^d)); 138.32 (*s*, C(4^d)); 137.83 (*s*, C(1^c)); 136.60 (*s*, C(2^c,6^c)); 135.13 (*s*, C(4^c)); 133.17 (*d*, C(2^b,6^b)); 132.12 (*d*, C(2^a,6^a)); 130.01 (*s*, C(2^d,6^d)); 129.96 (*s*, C(1^b)); 129.07 (*d*, C(3^c,5^c)); 129.00 (*d*, C(3^d,5^d)); 121.10 (*s*, C(1^a)); 120.63 (*s*, C(2)); 113.34 (*d*, C(3^a,5^a)); 113.13 (*d*, C(3^b,5^b)); 110.50 (*s*, C(3)); 55.35 (*q*, *Me*O–C(4^a)); 55.35 (*q*, *Me*O–C(4^b)); 21.03 (*q*, *Me*–C(4^c)); 20.63 (*q*, *Me*–C(4^d)); 20.45 (*q*, *Me*–C(2^c,6^c)); 15.61 (*q*, *Me*–C(2^d,6^d)). EI-MS: 588.1 (6, $M^{+\bullet}$); 452.9 (100, $[M - Me_3C_6H_2O]^+$), 168.9 (80). Anal. calc. for $C_{38}H_{36}O_6$ (588.69): C 77.53, H 6.16; found: C 77.54, H 6.14.

*Data of 6-Methoxy-4-(4-methoxyphenyl)-9-(2,4,6-trimethylphenyl)-1*H,*3*H-*naphtho[2,3-*c*]furan-1,3-dione* (**12i**). Light beige crystals. M.p. 224.0–226.1° (hexane/CH_2Cl_2). UV (hexane): λ_{max} 369 (3.35), 330 (3.66), 323 (3.66), 268 (sh, 4.35), 265 (4.36); λ_{min} 365 (3.33), 329 (3.66), 311 (3.63), 239 (3.79). IR ($CHCl_3$): 1842*m* ($\tilde{\nu}_{asym}$(C=O), cyclic anhydride), 1773*s* ($\tilde{\nu}_{sym}$(C=O), cyclic anhydride), 1614*m* (arom.). ^{1}H-NMR (500 MHz, $CDCl_3$): 7.59 (*d*, *J*(8,7) = 9.0, H–C(8)); 7.44 (*dt*, J_o = 6.5, J_m = 1.5, H–C(2′,6′)); 7.29 (*d*, *J*(5,7) = 2.5, H–C(5)); 7.26 (*dt*, *J*(7,8) = 9.0, *J*(7,5) = 2.5, H–C(7)); 7.14 (*dt*, J_o = 6.5, J_m = 1.5, H–C(3′,5′)); 7.07 (*s*, H–C(3)); 3.96 (*s*, MeO–C(4′)); 3.79 (*s*, MeO–C(6)); 2.43 (*s*, Me–C(4″)); 1.89 (*s*, Me–C(2″,6″)). ^{13}C-NMR (125 MHz, $CDCl_3$): 162.53, 161.98 (2*s*, C(2,3)); 160.87 (*s*, C(6)); 160.09 (*s*, C(4′)); 141.62 (*s*, C(1)); 140.53 (*s*, C(4)); 138.58 (*s*, C(4a)); 138.29 (*s*, C(4″)); 135.76 (*s*, C(2″,6″)); 131.21 (*d*, C(2′,6′)); 131.04 (*s*, C(8a)); 130.30 (*s*, C(1″)); 129.49 (*d*, C(8)); 128.61 (*d*, C(3″,5″)); 125.67 (*s*, C(1′)); 123.23 (*s*, C(2) or C(3)); 122.26 (*d*, C(5)); 120.75 (*s*, C(3) or C(2)); 114.02 (*d*, C(3′,5′)); 107.67 (*d*, C(7)); 55.49 (*q*, *Me*O–C(6)); 55.33 (*q*, *Me*O–C(4′)); 21.29 (*q*, *Me*–C(4″)); 20.11 (*q*, *Me*–C(2″,6″)). EI-MS ($C_{29}H_{24}O_5$; 452.50): 453,1 (30, $[M+1]^+$), 452.1 (100, $M^{+\bullet}$). Anal. calc. for $C_{29}H_{24}O_5 \cdot 0.25\ H_2O$ (457.00): C 76.22, H 5.40; found: C 76.24, H 5.68.

2.6. *2,4,6-Tribromophenyl 3-(4-Methoxyphenyl)prop-2-ynoate* (**3k**). Molten ester **3k** (0.075 g, 0.153 mmol) was stirred during 5 h at 210°. CC (hexane/CH_2Cl_2 1:1) gave pure (*Z*)-**11k** (0.036 g, 48%). The product was recrystallized from hexane/CH_2Cl_2 (0.033 g).

*Data of 2,4,6-Tribromophenyl 2,3-Dihydro-5-(4-methoxyphenyl)-3-[(*Z*)-(4-methoxyphenyl)(2,4,6-tribromophenyl)methylidene]-2-oxofuran-4-carboxylate* ((*Z*)-**11k**). Orange crystals. M.p. 135.6–137.9° (hexane/CH_2Cl_2). UV (hexane): λ_{max} 407 (4.42), 325 (3.98), 276 (4.04), 242 (sh, 4.28), 223 (sh, 4.71); λ_{min} 349 (3.92), 306 (3.94), 275 (4.04). IR ($CHCl_3$): 1782*s* (C=O, five-ring lactone); 1740*s* (C=O, aryl ester); 1604*s* (arom.). ^{1}H-NMR (600 MHz, $CDCl_3$): 7.98 (*d*, J_o = 9.0, H–C(2^a,6^a)); 7.82 (*s*, H–C(3^b,5^b)); 7.56 (*s*, H–C(3^d,5^d)); 7.36 (*d*, J_o = 9.0, H–C(2^c,6^c)); 6.94 (*d*, J_o = 9.0, H–C(3^a,5^a)); 6.87 (*d*, J_o = 9.0, H–C(3^c,5^c)); 3.88 (*s*, MeO–C(4^a)); 3.81 (*s*, MeO–C(4^c)). ^{13}C-NMR (150 MHz, $CDCl_3$): 164.45 (*s*, C(2)); 163.71 (*s*); 162.91 (*s*); 161.61 (*s*); 157.46 (*s*); 152.49 (*s*); 145.41 (*s*); 140.84 (*s*); 135.00 (*d*); 134.98 (*d*); 132.74 (*d*); 132.68 (*d*); 129.90 (*s*); 123.99 (*s*); 122.99 (*s*); 120.64 (*s*); 120.58 (*s*); 119.96 (*s*); 118.67 (*s*); 114.44 (*d*); 113.76 (*d*); 106.58 (*s*); 55.66 (*q*); 55.57 (*q*). CI-MS: 982.2 (28, $[M+H+10]^+$), 980.6 (78, $[M+H+8]^+$), 978.7 (100, $[M+H+6]^+$), 976.5 (60, $[M+H+4]^+$), 974.6 (18, $[M+2]^+$). Anal. calc. for $C_{32}H_{18}Br_6O_6 \cdot 0.67\ H_2O$ (989.90): C 38.83, H 1.97; found: C 38.60, H 2.01.

2.7. *2-Methylphenyl 3-Phenylprop-2-ynoate* (**3l**). Molten ester **3l** (2.80 g, 11.8 mmol) was heated in a sealed glass tube during 15 h at 200°. Repeated CC (silica gel, hexane/Et_2O 9:1) gave a 2:1 mixture (*Z*)-**11l**/(*E*)-**11l** (0.155 g, 6%), **12l** (0.180 g, 8%), and **13l** (0.188 g, 7%).

*Data of 2-Methylphenyl 2,3-Dihydro-3-[(*Z*)- and (*E*)-(2-methylphenyl)(phenyl)methylidene]-2-oxo-5-phenylfuran-4-carboxylate* ((*E*)-**11f**/(*Z*)-**11l**): Orange solid (2:1 mixture). M.p. 76.5–78.0° (hexane/Et_2O). UV (hexane): λ_{max} 385 (4.09), 300 (sh, 3.87), 241 (sh, 4.26); λ_{min} 327 (3.82). IR ($CHCl_3$): 1778*s* (C=O, five-ring lactone), 1737*s* (C=O, aryl ester), 1168v*s* (C–O). ^{1}H-NMR of the (*Z*)-isomer (600 MHz, $CDCl_3$): 8.04 (*dd*,

J_o = 7.8, J_m = 1.2, H–C(2^a,6^a)); 7.48 (*tt*, J_o = 7.3, J_m = 1.2, H–C(4^a)); 7.47–7.43 (*m*, H–C(3^a,5^a), H–C(2^c,6^c)); 7.40–7.37 (*m*, H–C(5^b), H–C(3^c,4^c,5^c)); 7.30 (*d*, J_o = 7.3, H–C(6^b)); 7.29 (*t*, J_o = 7.3, H–C(4^b)); 7.18 (*d*, J_o = 7.5, H–C(3^b)); 7.07 (*d*, J_o = 7.5, H–C(3^d)); 7.01 (*td*, J_o = 7.5, J_m = 1.0, H–C(4^d)); 6.93 (*td*, J_o = 7.7, J_m = 1.3, H–C(5^d)); 5.68 (*d*, J_o = 7.8, H–C(6^d)); 2.16 (*s*, Me–C(2^b)); 2.19 (*s*, Me–C(2^d)). ^{1}H-NMR of the (*E*)-isomer (600 MHz, $CDCl_3$): 7.89 (*d*-like, J_o = 7.8, H–C(2^a,6^a)); 7.45 (*t*, J_o = 7.2, H–C(4^a)); 7.43–7.38 (*m*, H–C(3^a,5^a), H–C(2^b,3^b,4^b,5^b,6^b), H–C(6^c)); 7.36 (*td*, J_o = 7.5, J_m = 1.6, H–C(4^c)); 7.32 (*td*, J_o = 7.5, J_m = 1.3, H–C(5^c)); 7.16 (*d*, J_o = 7.5, H–C(3^c)); 7.07 (*d*, J_o = 7.5, H–C(^{d}3)); 7.03 (*td*, J_o = 7.4, J_m = 1.0, H–C(4^d)); 6.97 (*td*, J_o = 7.9, J_m = 1.4, H–C^d(5^d)); 5.94 (*d*, J_o = 7.8, H–C(6^d)); 1.92 (*s*, Me–C(2^c)); 1.84 (*s*, Me–C(2^d)). EI-MS: 472.0 (20, $M^{+\bullet}$), 365.0 (95, $[M - CH_3C_6H_4O]^+$), 104.8 (100, $[CH_3C_6H_4O]^+$). ESI-MS: 373.2 (100, $[M+H]^+$). Anal. calc. for $C_{32}H_{24}O_4$ (472.53): C 81.34, H 5.12; found: C 81.59, H 5.39.

*Data of 4-(2-Methylphenyl)-9-phenyl-1*H*,3*H*-naphtho[2,3-c]furan-1,3-dione* (**12l**). Yellowish crystals. M.p. 224.8–228.5° (hexane/Et_2O). UV (hexane): λ_{max} 357 (3.79), 340 (3.77), 317 (4.02), 260 (4.71), 252 (4.71), 205 (sh, 4.66); λ_{min} 351 (3.65), 337 (3.76), 289 (3.82), 257 (4.70), 232 (4.26). IR ($CHCl_3$): 1835*m* ($\tilde{\nu}_{asym}$(C=O), cyclic anhydride), 1777*s* ($\tilde{\nu}_{sym}$(C=O), cyclic anhydride), 1611*w* (arom.). ^{1}H-NMR (600 MHz, $CDCl_3$): 7.97 (*m*, H–C(5)); 7.77 (*m*, H–C(8)); 7.70 (*m*, H–C(6)); 7.68 (*m*, H–C(7)); 7.63–7.61 (*m*, H–C(3′,4′,5′)); 7.53 (*m*, H–C(2′))[12]; 7.51 (*td*, J_o = 7.6, J_m = 1.4, H–C(4′)); 7.49 (*m*, H–C(6′))[12]; 7.46 (*d*, J_o = 7.6, H–C(3′)); 7.41 (*t*, J_o = 7.5, H–C(5′)); 7.24 (*dd*, J_o = 7.4, J_m = 1.0, H–C(6′)); 2.05 (*s*, Me–C(2′)). ^{13}C-NMR ($CDCl_3$): 161.91, 161.73 (2*s*, C=O); 142.55 (*s*); 142.08 (*s*); 136.26 (*s*); 135.99 (*s*); 133.46 (*s*); 133.37 (*s*); 130.27 (*d*); 129.98 (*d*); 129.93 (*d*); 129.76 (*d*); 129.30 (*d*); 129.07 (*d*); 128.98 (*d*); 128.93 (*d*); 128.48 (*d*); 128.39 (*d*); 125.93 (*d*); 122.54 (*s*); 122.11 (*s*); 19.77 (*q*). EI-MS: 365.0 (60, $[M+1]^+$), 364.0 (95, $M^{+\bullet}$), 289.0 (100, $[M-75]^+$). Anal. calc. for $C_{25}H_{16}O_3$ (364.39): C 82.40, H 4.43; found: C 82.33, H 4.54.

Data of 2-Methylphenyl 1-Phenylnaphthalene-2,3-dicarboxylate (**13l**). Yellowish crystals. M.p. 224.8–228.5° (hexane/Et_2O). UV (hexane): λ_{max} 340 (3.45), 326 (3.39), 285 (3.95), 275 (3.93), 244 (4.85), 243 (sh, 4.84), 204 (sh); λ_{min} 331 (3.34), 315 (3.25), 279 (3.92), 272 (3.92). IR ($CHCl_3$): 1740v*s* (C=O), 1172*s*/1116*s* (C–O). ^{1}H-NMR (600 MHz, $CDCl_3$): 8.95 (*s*, H–C(4)); 8.12 (*d*, *J*(5,4) = 7.8, H–C(5)); 7.66–7.69 (*m*, H–C(6)); 7.59–7.51 (*m*, H–C(7,8)); 7.53 (*s*, H–C(2′,3′,4′,5′,6′)); 7.31 (*d*, *J* = 7.8, H–C(3‴)); 7.28 (*td*, J_o = 6.7, J_m = 1.6, H–C(5‴)); 7.24–7.20 (*m*, H–C(4‴,6‴)); 7.07 (*dd*, *J* = 5.7, 3.6, H–C(3″)); 7.01–7.03 (*m*, H–C(4″, 5″)); 6.60 (*dd*, *J* = 5.7, *J* = 3.6, H–C(6″)); 2.32 (*s*, Me–C(2‴)); 1.81 (*s*, Me–C(2″)). ^{13}C-NMR (150 MHz, $CDCl_3$): 166.60 (*s*, *C*O–C(2)); 164.04 (*s*, *C*O–C(3)); 149.50 (*s*, C(1‴)); 149.24 (*s*, C(1″)); 139.27 (*s*, C(1)); 136.40 (*s*, C(1′)); 134.64 (*s*, C(8a)); 132.44 (*s*, C(4a)); 132.23 (*d*, C(4)); 131.22 (*d*, C(3‴)); 130.93 (*d*, C(3′)); 130.79 (*d*, C(3″)); 130.58 (*s*, C(2)); 130.47 (*s*, C(2‴)); 130.30 (*s*, C(2″)); 129.44 (*d*, C(5,7)); 128.33 (*d*, C(2′,4′)); 127.87 (*d*, C(6)); 127.19 (*d*, C(8)); 127.03 (*d*, C(5‴)); 126.47 (*d*, C(4″)); 126.27 (*d*, C(6‴)); 125.63 (*d*, C(5″)); 124.11 (*d*, C(3)); 122.05 (*d*, C(4‴)); 121.81 (*d*, C(6″)); 16.34 (*q*, *Me*–C(2‴)); 15.66 (*q*, *Me*–C(2″)). EI-MS: 472.1 (3, $M^{+\bullet}$), 365.0 (100, $[M - CH_3C_6H_4O]^+$). Anal. calc. for $C_{32}H_{24}O_4$ (472.53): C 81.34, H 5.12; found: C 81.39, H 5.23.

2.8 *Cross Experiment* with **3f** and **3g**. A molten mixture of **3f** (0.100 g, 0.323 mmol) and **3g** (0.173 g, 0.646 mmol) was stirred under Ar during 6 h at 170°. CC (silica gel; hexane/CH_2Cl_2 1:1) gave an orange colored fraction, which was submitted to prep. HPLC. A first run (hexane/i-PrOH 95:5) delivered the pure dimer (*Z*)-**11f** (0.023 g, 23%) and a mixture (*Z*)-**11fg**/(*E*)-**11fg**. Subsequent prep. HPLC (hexane/ CH_2Cl_2/MeOH 80:20:0.5) of the mixed fraction led to pure (*Z*)-**11fg** (0.019 g, 10%) and (*E*)-**11fg** (0.007 g, 4%).

Data of Phenyl 2,3-Dihydro-5-(4-nitrophenyl)-3-[(Z)-(4-nitrophenyl)(2,4,6-trimethylphenyl)methylidene]-2-oxofuran-4-carboxylate ((*Z*)-**11fg**). Orange solid. M.p. 131.2–136.5° (hexane/CH_2Cl_2). UV (hexane): λ_{max} 406 (4.21), 382 (sh, 4.14), 263 (4.15); λ_{min} 318 (3.80), 251 (4.14). IR ($CHCl_3$): 1787*m* (C=O, five-ring lactone), 1740*m* (C=O, aryl ester), 1525*s* (NO_2), 1349v*s* (NO_2). ^{1}H-NMR (600 MHz, $CDCl_3$): 8.32 (*dt*, J_o = 8.9, J_m = 1.9, H–C(3^a,5^a)); 8.21 (*dt*, J_o = 9.0, J_m = 1.9, H–C(2^a,6^a)); 8.16 (*dt*, J_o = 8.8, J_m = 1.8, H–C(3^c,5^c)); 7.52 (*dt*, J_o = 8.8, J_m = 1.8, H–C(2^c,6^c)); 7.20 (*tt*, J_o = 8.1, J_m = 1.9, H–C(3^d,5^d)); 7.14 (*t*, J_o = 7.4, H–C(4^d)); 7.01 (*s*, H–C(3^b,5^b)); 6.52 (*dt*, J_o = 8.7, J_m = 1.9, H–C(2^d,6^d)); 2.36 (*s*, Me–C(4^b)); 2.14 (*s*, Me–C(2^b,6^b)). ^{13}C-NMR (150 MHz, $CDCl_3$): 162.24 (*s*, C(2)); 160.80 (*s*, *C*O–C(4)); 156.14 (*s*, C(5)); 155.80 (*s*, C(3′)); 149.61 (*s*, C(1^d)); 149.27 (*s*, C(4^a)); 148.33 (*s*, C(4^c)); 145.60 (*s*, C(1^c)); 139.37 (*s*, C(4^b)); 134.89 (*s*, C(2,6^b)); 134.75 (*s*, C(1^b)); 132.95 (*s*, C(1^a)); 130.31 (*d*, C(2^c,6^c)); 129.99 (*d*, C(2^a,6^a)); 129.43 (*d*, C(3^d,5^d)); 129.35 (*d*, C(3^b,5^b)); 126.43 (*d*, C(4^d));

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12) The two Ph groups exhibit hindered rotation, which leads to a differentiation of H–C(2″) and H–C(6″) of Ph–C(9), because one H-atom is in a *cis* relation and the other one in a *trans* relation to the Me group of *o*-MeC_6H_4–C(4).

124.31 (*s*, C(3)); 124.02 (*d*, C(3^c,5^c)); 123.71 (*d*, C(3^a,5^a)); 119.71 (*d*, C(2^d,6^d)); 112.11 (*s*, C(4)); 21.27 (*q*, *Me*–C(4^b)); 20.12 (*q*, *Me*–C(2^b,6^b)). CI-MS ($C_{33}H_{24}N_2O_8$, 576.56): 594.1 (100, $[M+NH_4]^+$).

Data of (*E*)-**11fg**. Yellow crystals. M.p. 258.8–260.6° (hexane/CH_2Cl_2). UV (hexane): λ_{max} 404 (4.05), 265 (3.95); λ_{min} 322 (3.50), 248 (3.90). IR ($CHCl_3$): 1784*m* (C=O, five-ring lactone), 1745*m* (C=O, aryl ester), 1524*s* (NO_2), 1347v*s* (NO_2). ^{1}H-NMR (600 MHz, $CDCl_3$): 8.30 (*d*, J_o = 8.8, H–C(3^a,5^a)); 8.20 (*d*, J_o = 8.6, H–C(3^b,5^b)); 7.97 (*d*, J_o = 8.7, H–C(2^a,6^a)); 7.57 (*d*, J_o = 8.5, H–C(2^b,6^b)); 7.27 (*t*, J_o = 7.9, H–C(3^d,5^d)); 7.21 (*t*, J_o = 7.6, H–C(4^d)); 6.88 (*s*, H–C(3^c,5^c)); 6.51 (*d*, J_o = 7.9, H–C(2^d,6^d)); 2.36 (*s*, Me–C(4^c)); 2.11 (*s*, Me–C(2^c,6^c)). ^{13}C-NMR (150 MHz, $CDCl_3$): 162.76 (*s*, C(2)); 160.54 (*s*, *C*O–C(4)); 156.11 (*s*, C(3′)); 152.98 (*s*, C(5)); 149.52 (*s*, C(1^d)); 149.06 (*s*, C(4^a)); 148.63 (*s*, C(4^b)); 142.49 (*s*, C(1^b)); 140.09 (*s*, C(4^c)); 136.50 (*s*, C(2^c)); 135.10 (*s*, C(1^c)); 132.78 (*s*, C(1^a)); 131.56 (*d*, C(2^b,6^b)); 129.57 (*d*, C(3^c,5^c)); 129.09 (*d*, C(3^d,5^d)); 128.77 (*d*, C(2^a,6^a)); 126.26 (*d*, C(4^d)); 124.28 (*s*, C(3)); 123.96 (*d*, C(3^a,5^a)); 123.07 (*d*, C(3^b,5^b)); 120.49 (*s*, C(2^d,6^d)); 114.33 (*s*, C(4)); 21.03 (*q*, *Me*–C(4^c)); 20.33 (*q*, *Me*–C(2^c,6^c)). CI-MS ($C_{33}H_{24}N_2O_8$, 576.56): 594.0 (100, $[M+NH_4]^+$), 577.0 (12, $[M+H]^+$), 547.1 (26, $[M-CHO]^+$), 483.0 (66, $[M-C_6H_5O]^+$).

3. Synthesis of ^{17}O-Labeled Compounds. – 3.1. *2,4,6-Trimethyl-[^{17}O]phenol.* (2,4,6-Trimethylphenyl)diazonium tetrafluoroborate was prepared in quant. yield from 2,4,6-trimethylaniline (*cf.* [11]). The dry diazonium salt (0.590 g, 2.52 mmol) and dry AcONa (0.248 g, 2.52 mmol) were dissolved in $H_2[^{17}O]$ (0.454 ml, 25.2 mmol; ^{17}O-enrichment: 19%; source: *Isotec Inc.*). After the addition of CF_3COOH (3.86 ml, 50.4 mmol), the soln. was heated under Ar at reflux during 3 d (for a similar procedure, see [12]). The solvent mixture was distilled off, and the residue was submitted to CC (hexane/Et_2O 1:1). The isolated 2,4,6-trimethylphenyl [^{17}O]phenol was recrystallized from hexane (0.285 g, 83%). MS Analysis of the signals at *m/e* 136 ($M^{+\bullet}$), 137 ($[M+1]^{+\bullet}$), and 138 ($[M+2]^{+\bullet}$) indicated 8–9% ^{17}O-incorporation. ^{17}O-NMR (81.4 MHz, $CDCl_3$): 65 ($\Delta\nu_{1/2}$ = 240).

3.2. *^{17}O-(2,4,6-Trimethylphenyl) 3-(4-Methoxyphenyl)-[$^{17}O_1$]prop-2-ynoate* ([^{17}O]-**3i**). According to the procedure described in 1.2.8, [^{17}O]-**3i** was prepared from **5d** (0.194 g, 1.10 mmol) and 2,4,6-trimethylphenyl-[^{17}O]phenol (0.150 g, 1.10 mmol). Yield of [^{17}O]-**3i**: 0.249 g (77%). ^{17}O-NMR (81.4 MHz, $CDCl_3$; *cf. Fig. 5*): 198 ($\Delta\nu_{1/2}$ = 1660).

3.3. *Thermolysis of [^{17}O]-***3i**. The molten, labeled ester (0.210 g, 0.713 mmol) was heated during 5 h at 210°. CC (silica gel, hexane/CH_2Cl_2 1:1) of the orange colored solid gave as a first fraction (*Z*)-**11i** (0.052 g, 25%). Subsequent prep. HPLC (hexane/i-PrOH 95:5) of the second orange colored fraction led to pure (*E*)-**11i** (0.0113 g, 5%). Unfortunately, labeled **12i** had been destroyed in the course of the purification procedures.

Data of ^{17}O-*(2,4,6-Trimethylphenyl) 2,3-Dihydro-5-(4-methoxyphenyl-3-[(Z)-(4-methoxyphenyl)(2,4,6-trimethylphenyl)methylidene]-2-[$^{17}O_1$]oxofuran-4-[$^{17}O_1$]carboxylate* ((*Z*)-[$^{17}O_2$]-**11i**). ^{17}O-NMR (81.4 MHz, $CDCl_3$; *cf. Fig. 5*): 340 ($\Delta\nu_{1/2}$ = 2290); 190 ($\Delta\nu_{1/2}$ = 2290).

Data of ((*E*)-[$^{17}O_2$]-**11i**). ^{17}O-NMR (67.8 MHz, $CDCl_3$; *cf. Fig. 5*): 314 ($\Delta\nu_{1/2}$ = 7400); 198 ($\Delta\nu_{1/2}$ = 8600).

4. Kinetic Investigations. – 4.1. *Thermal Rearrangement of* **3c**. 4.1.1. *Influence of Solvent on Reactivity of* **3c**. A 0.5-ml glass tube was filled with a soln. of **3c** (0.2 ml; for solvent and concentration, see *Table 4*), the solvent was flushed with Ar, and the glass tube was sealed. At a fixed time (for time and temp., see *Table 4*) of the reaction the tube was opened, the solvent was evaporated (60°/0.04 mm), the residue redissolved in hexane/CH_2Cl_2 (80:20), and then subjected to HPLC (*Spherisorb CN*; hexane/CH_2Cl_2/MeOH 80:20:0.5). UV detection was performed at the isosbestic point of (*Z*)-**11c**, **12c**, and **13c** at (280 nm). The ratio between the ε values of **3c**, (*Z*)-**11c**, (*E*)-**11c**, **12c**, and **13c** at 280 nm is 1.7:1.0:0.8:1.0:1.0 (data for **12c** and **13c** were taken from the almost identical UV spectra of **12l** and **13l**). Therefore, the per cent ratio, which was obtained from HPLC analyses, was recalculated for the real molar ratio. The results are listed in *Table 4*.

4.1.2. *Kinetics of the Thermal Rearrangement of* **3c** *in Decalin.* A 0.1M soln. of **3c** in decalin was heated under Ar at 150 ± 1°. At regular time intervals, samples (10 µl) were taken, dissolved in hexane/CH_2Cl_2 (80:20), then subjected to HPLC, and analyzed as described in *4.1.1*. The results are listed below (*cf. Table 5*):*Scheme 4*

Entry	Time [min]	**3c**	(*Z*)-**11c**	**12c**
1	0	97.0	1.8	1.3
2	870	95.5	2.4	2.1
3	1380	94.6	2.8	2.6
4	2610	92.8	3.7	3.4

The decrease of **3c** followed first order kinetics with $k_{-1}([\mathbf{3c}]) = (1.72 \pm 0.18) \cdot 10^{-5}$ min^{-1} (r^2 = 0.999).

4.2. *Thermal Rearrangement of* **3f**. 4.2.1. *In $PhNO_2$.* A 0.1M soln. of **3f** in $PhNO_2$ was heated under Ar at 175 ± 1°. At regular time intervals, samples (10 µl) were taken, the solvent was evaporated (60°/0.04 mm), the

residue redissolved in hexane/CH_2Cl_2 (80:20), and then subjected to HPLC (*Spherisorb CN*; hexane/CH_2Cl_2/MeOH 80:20:0.5). UV detection was performed at the isosbestic point of **3f**, (*Z*)-**11f**, and (*E*)-**11f** (305 nm). The results are listed below (*cf. Fig. 6*):

Entry	Time [min]	**3f**	(*Z*)-**11f**	(*E*)-**11f**
1	0	100	0	0
2	30	95.90	3.96	0.14
3	60	93.21	6.48	0.31
4	90	91.34	8.14	0.52
5	120	89.25	10.06	0.69
6	150	86.37	12.29	1.34
7	180	85.09	1.53	2.1
8	210	15.50	1.94	2.6
9	240	80.19	17.41	2.40
10	300	76.70	19.32	3.98

The decrease of **3f** followed first order kinetics with $k_{-1}([\mathbf{3f}]) = (8.52 \pm 0.48) \cdot 10^{-4}\ min^{-1}$ ($r^2 = 0.995$).

4.2.2. *In Decalin.* A 0.1M soln. of **3f** in decalin was heated under Ar at $150 \pm 1°$. At regular time intervals samples (10 µl) were taken, dissolved in hexane/CH_2Cl_2 (80:20), and then subjected to HPLC (*Spherisorb CN*; hexane/CH_2Cl_2/MeOH 80:20:0.5). UV Detection at the isosbestic point of **3f**, (*Z*)-**11f**, and (*E*)-**11f** (305 nm). The results are listed below (*cf. Table 5* and *Fig. 7*):

Entry	Time [min]	**3f**	(*Z*)-**11f**	(*E*)-**11f**
1	0	100	0	0
2	900	98.8	1.2	0.0
3	2700	97.1	2.9	0.0
4	6300	91.0	9.0	0.0
5	14400	81.1	18.9	0.0
6	43200	69.6	30.4	0.0
7	81000	59.0	40.0	1.0
8	167400	33.0	48.9	1.5

The decrease of **3f** (*Entry 1–5*) followed first order kinetics with $k_{-1}([\mathbf{3f}]) = (8.84 \pm 0.89) \cdot 10^{-4}\ min^{-1}$ ($r^2 = 0.996$).

4.3. *Thermal Rearrangement of Mixed Prop-2-ynoate* **3f** *and* **3g** *in* $PhNO_2$. The 0.1M soln. of **3f** with 2 mol-equiv. amount of **3g** was heated under Ar at $175 \pm 1°$. At regular time interval samples (5 µl) were taken, solvent was evaporated (60°/0.04 Torr), diluted with hexane/CH_2Cl_2 (80:20), and subjected to HPLC (analyses were performed on the two in-line *Spherisorb CN* columns: 3 µm 125 × 40 mm and 5 µm 250 × 40; hexane/CH_2Cl_2/MeOH 80:20:0.5). UV Detection at the isosbestic point 305 nm. The results are listed below (*cf. Fig. 6*):

Entry	Time [min]	**3f**	**11f**	**11fg**
1	0	100	0	0
2	30	92.22	3.54	4.24
3	60	85.85	5.96	8.19
4	90	81.50	7.36	11.14
5	120	77.59	8.71	13.70
6	150	70.77	10.69	18.55
7	180	65.47	11.68	22.84
8	210	61.53	12.03	26.44
9	240	57.21	12.86	29.93
10	300	49.69	14.28	36.03

The decrease of **3f** followed first-order kinetics with $k_{-1}([\mathbf{3f}]) = (2.31 \pm 0.09) \cdot 10^{-3}\ min^{-1}$ ($r^2 = 0.998$).

4.4. *Thermal Rearrangement of* **3i** *in Decalin*. A 0.1M soln. of **3i** in decalin was heated under Ar at $150 \pm 1°$. Analysis as described in *4.2.2.* UV detection was performed at the isosbestic point of **3i**, (*Z*)-**11i**, and **12i** (242 nm). The results are listed below (*cf. Table 5*):

Entry	Time [min]	**3i**	(*Z*)-**11i**	**12i**
1	0	100	0	0
2	240	99.6	0.0	0.4
3	720	97.9	0.1	2.0
4	1350	96.1	0.2	3.7
5	2790	92.4	0.4	7.2

The decrease of **3i** followed first order kinetics with $k_{-1}([\mathbf{3i}]) = (2.88 \pm 0.26) \cdot 10^{-5}$ min^{-1} ($r^2 = 0.999$)

4.5. *Thermal Rearrangement of* **3k** *in Decalin*. A 0.1M soln. of **3k** in decalin was heated under Ar at $150 \pm 1°$. Analysis as described in *4.2.2.* UV Detection was performed at the isosbestic point of **3k**, (*Z*)-**11k**, and **12k** (242 nm). The results are listed below (*cf. Table 5*):

Entry	Time [min]	**3k**[a])	(*Z*)-**11k**[a])	**12k**[a])
1	0	100	0	0
2	30	98.8	0.8	0.1
3	210	96.0	2.5	0.7
4	390	94.0	3.2	1.2
5	1260	86.0	4.5	4.5
6	1770	80.0	5.0	5.0
7	3000	69.0	10.0	7.0

[a]) From overall 100% undefined side products were taken into account.

The decrease of **3k** followed first order kinetics with $k_{-1}([\mathbf{3k}]) = (1.20 \pm 0.07) \cdot 10^{-4}$ min^{-1} ($r^2 = 0.998$).

5. X-Ray Crystal Structure Determination of 2,3-Dihydrofuranone (*Z*)-11c and Prop-2-ynoate 3c[13]). – All measurements performed were at 173 K on a *Rigaku AFC5R* diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71069$ Å) and a 12-kW rotating anode generator (for details, *cf. Table 6*).

The structure of (*Z*)-**11c** ($C_{36}H_{32}O_4 \cdot 0.5\ H_2O$) has been solved and refined successfully (*cf. Fig. 1*). The needle-like crystals were not of high quality and were weakly diffracting with broad reflection profiles. As a result, the structure is clearly defined, but the standard uncertainties in the geometric parameters are slightly elevated (*cf. Table 6*). The crystal lattice contains also H_2O molecules. Each H_2O molecule sits on a center of inversion and may be either disordered about this site or does not fully occupy the site. The displacement parameters for the H_2O O-atom are very large, but refinements with a lower site occupation factor produced less satisfactory results. The ratio of H_2O molecules to substrate is, therefore, *ca.* 1:2.

The structure of **3c** ($C_{18}H_{16}O_2$) has been solved and refined successfully with no unusual features. The ester molecules occupy in the crystal an s-*trans* conformation (as shown for the AM1 calculated conformations in *Fig. 8*).

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[13]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-167021 and 167020 for (*Z*)-**11c** and **3c**, respectively. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-(0)1223-336033; email: deposit@ccdc.cam.ac.uk).

Table 6. *Crystallographic Data of* **3c** *and (Z)-*__11c__.

Parameter	**3c**	(*Z*)-**11c**
Crystallized from	hexane/heptane	MeOH
Empirical formula	$C_{18}H_{16}O_2$	$C_{36}H_{32}O_4 \cdot ½\ H_2O$
Formula weight [g·mol^{-1}]	264.32	537.65
Crystal color, habit	colorless, prism	orange, needle
Crystal dimensions [mm]	$0.28 \times 0.30 \times 0.48$	$0.10 \times 0.15 \times 0.50$
Temp. [K]	173(1)	173(1)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
Z	2	2
Reflections for cell determination	25	25
2θ Range for cell determination [°]	38 – 40	25 – 30
Unit cell parameters a [Å]	10.447(3)	11.935(4)
b [Å]	9.480(2)	12.297(4)
c [Å]	8.599(2)	11.204(5)
α [°]	71.92(1)	96.03(3)
β [°]	65.82(2)	95.90(4)
γ [°]	82.68(2)	62.70(2)
V [Å^3]	738.6(3)	1450.5(9)
$F(000)$	280	570
D_x [g cm^{-3}]	1.188	1.231
$\mu(\mathrm{Mo}K_\alpha)$ [mm^{-1}]	0.076	0.0800
Scan type	$\omega/2\theta$	$\omega/2\theta$
$2\theta_{(\max)}$ [°]	55	50
Total reflections measured	3571	5365
Symmetry independent reflections	3386	5101
R_{int}	0.023	0.052
Reflections used [$I > 2\sigma(I)$]	2332	2531
Parameters refined	246	368
Reflection/parameter ratio	9.48	6.88
Final R	0.0439	0.0684
wR	0.0389	0.0615
Weights: p in $w = [\sigma^2(F_o) + (pF_o)^2]^{-1}$	0.005	0.005
Goodness-of-fit	1.941	2.101
Secondary extinction coefficient	$5.7(4) \times 10^{-6}$	$7(1) \times 10^{-7}$
Final $\Delta_{\max}/\sigma$	0.0002	0.0001
$\Delta\rho$ (max; min) [e Å^{-3}]	0.18; −0.16	0.25; −0.26
$\sigma(d(\mathrm{C-C})$ [Å]	0.002 – 0.003	0.007 – 0.009

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