# Synthesis of the Naphthalenone, Dihydroquinoline, and Dihydrofuran Derivatives

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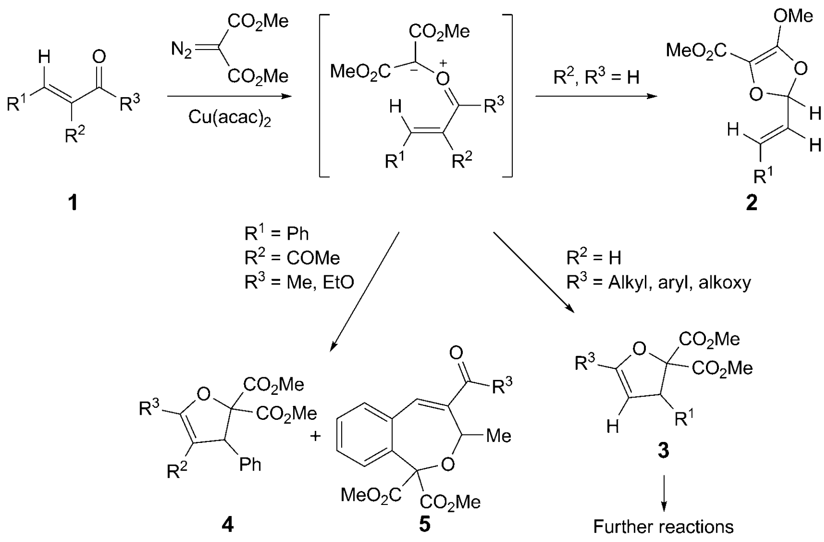
The reactions of enaminones with dimethyl diazomalonate were investigated in the presence of copper(II) acetylacetonate. From the reaction of (*E*)-3-[methyl(phenyl)amino]-1-phenylprop-2-en-1-one (**6c**), dimethyl 2-[methyl(phenyl)amino]-4-oxonaphthalene-1,1-(4*H*)-dicarboxylate, was unexpectedly obtained as the major product. Quinoline derivatives were formed as the major products in the case of *N*-methyl-*p*-anisidino and *N*-methyl-*p*-toluidino enaminones. The reactions of acetyl enaminones were also realized, and quinoline derivatives were isolated as the major products. 3*H*- and 5*H*-dihydrofurans were also formed as side products in these reactions. These results differ from those reported earlier on the reactions of tertiary enaminones with carbenes/metal carbenes.

**Introduction.** – During the past decade, we have studied the formal 1,5-electrocyclic reaction of carbonyl ylides derived from $\alpha,\beta$-unsaturated ketones, esters, diesters, and enaminones [1–7]. The reactions of $\alpha,\beta$-unsaturated ketones and esters with diazo dicarbonyl compounds such as dimethyl diazomalonate (= dimethyl 2-diazopropanedioate) yielded in the presence of copper(II) acetylacetonate ($Cu(acac)_2$) mainly dihydrofuran derivatives. On the other hand, the reactions of $\alpha,\beta$-enals were found to yield dioxolanes, instead. Furthermore, $\alpha$-benzylidene-$\beta$-dicarbonyl compounds with at least one ketone group yielded by 1,7-electrocyclizations of intermediate keto carbonyl ylides dihydrobenzoxepines **5** as the main products along with dihydrofurans **4** in varying ratios (*Scheme 1*) [6]. Analogous 1,5-electrocyclizations reported by *Hamaguchi* and *Matsubara* [8], and *Sliwinska* and *Warkentin* [9] yielded only dihydrofurans under different reaction conditions and with different starting compounds.

Enaminones, which are '*push-pull*' olefins, are versatile synthetic intermediates. *Kascheres* and co-workers have studied the reactions of primary and secondary enaminones with diazocarbonyl compounds in the presence of copper catalysts [10–13]. They obtained H–C($\alpha$) or H–N carbene insertion products, depending on the structure of the enaminones. On the other hand, the Cu-catalyzed reactions of acyclic tertiary enaminones with diazoacetates were reported by *Maas* and *Müller* to yield '*push-pull*' cyclopropanes and their rearrangement products [14]. In this study, dihydrofuran derivatives were only detected in a few reactions in trace amounts. *Maas* and co-workers have also investigated the reactions of semicyclic enaminones with vinyl diazoacetate, and they obtained betaines and dienamines [15][16].

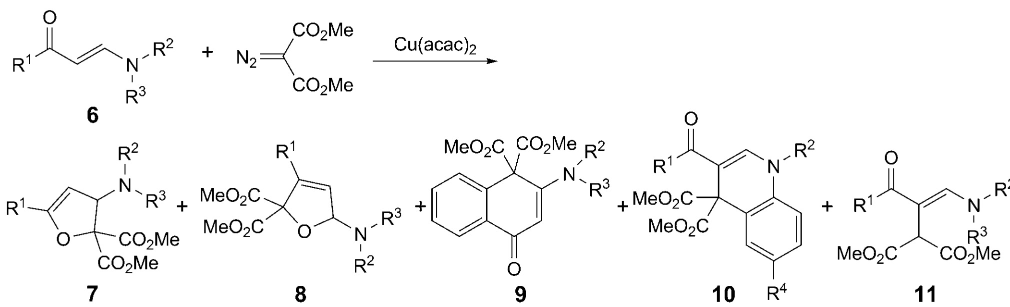
*Anaç* and co-workers recently reported their initial findings on the reactions of tertiary enaminones with dimethyl diazomalonate ($E_2C{=}N_2$, $E = CO_2Me$) in the presence of $Cu(acac)_2$ [5], which, in contrast to the literature, revealed the presence of

Scheme 1. *The Reaction of α,β-Unsaturated Carbonyl Compounds with $E_2C{=}N_2$*




significant amounts of dihydrofuran products, along with naphthalenone derivatives **9** and H–C(α) insertion products **11** (*Scheme 2*). Here, we present further results on the reactions of several tertiary enaminones and $E_2C{=}N_2$ with $Cu(acac)_2$ as the catalyst.

Scheme 2. *The Reactions of Enaminones and $E_2C{=}N_2$*




**Results and Discussion.** – We repeated the reaction of (*E*)-3-[methyl(phenyl)-amino]-1-phenylprop-2-en-1-one (**6c**) with dimethyl diazomalonate with different catalysts in addition to $Cu(acac)_2$. Although we had studied this reaction with $Cu(acac)_2$ before [5], the unexpected naphthalenone product prompted us to re-investigate the reaction with copper(II) triflate ($Cu(OTf)_2$), copper(II) hexafluoro-acetylacetonate ($Cu(hfacac)_2$), dirhodium tetraacetate ($Rh_2(AcO)_4$), rhodium(II) trifluoroacetate dimer ($Rh_2(CF_3CO_2)_4$) as catalysts. The results are shown in *Table 1*.

Table 1. *Reaction of (2*E*)-3-[Methyl(phenyl)amino]-1-phenylprop-2-en-1-one* (**6c**) *with Dimethyl Diazomalonate*[a])

| Catalyst | **7c** | **8c** | **9c** | **10c** | **11c** |
|---|---|---|---|---|---|
| $Cu(acac)_2$ [5] | 1 | – | 3.52 | – | – |
| $Cu(OTf)_2$ | 1 | – | 0.35 | – | – |
| $Cu(hfacac)_2$ | 1 | – | 0.09 | – | – |
| $Rh_2(AcO)_4$ | 1 | – | 0.05 | – | – |
| $Rh_2(CF_3CO_2)_4$ | 1 | – | – | – | – |

[a]) Reaction conditions: 2.1 mmol of **6c** and catalyst (0.01 mmol) in 10 ml of benzene, and $E_2C{=}N_2$ (1.4 mmol) in 1 ml of benzene, reflux, under $N_2$; GC analysis, relative product ratios with respect to **7c**.

As can be seen from *Table 1*, naphthalenone **9c** was distinctly preferred with $Cu(acac)_2$ as a catalyst. To obtain different derivatives and to better understand naphthalenone formation, we continued our experiments with only $Cu(acac)_2$ as catalyst with further enaminones and $E_2C{=}N_2$. Along with the new enaminones, we also repeated the reaction of **6a** [5], and this allowed us to isolate new products. The new results are depicted in *Scheme 2* and compiled in *Table 2*.

Table 2. *$Cu(acac)_2$-Catalyzed Reactions of Enaminones and $E_2C{=}N_2$*[a])

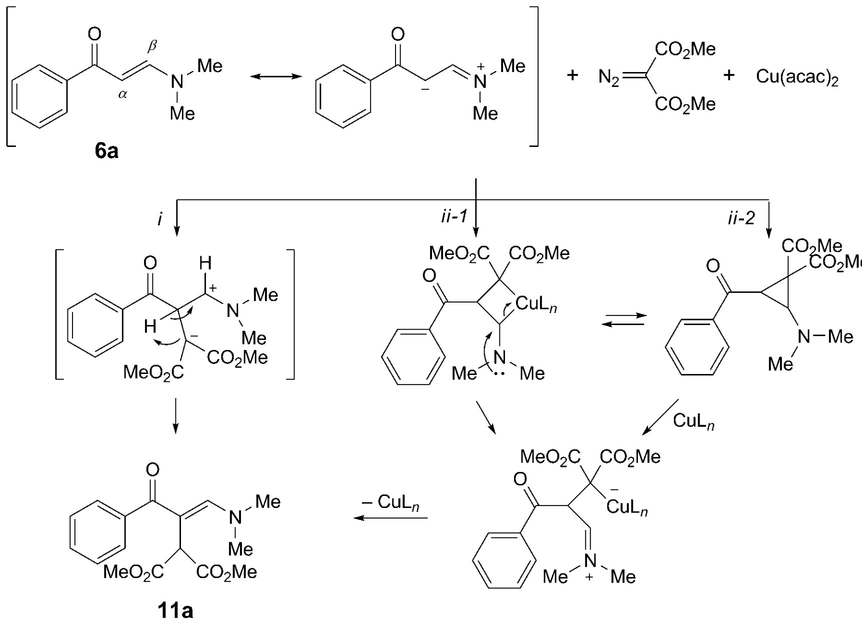
| *Entry* | $R^1$ | $R^2$ | $R^3$ | $R^4$ | **7** | **8** | **9** | **10** | **11** |
|---|---|---|---|---|---|---|---|---|---|
| **a** | Ph | Me | Me | – | 1[b]) | 0.33 | – | – | 0.56[b]) |
| **b** | Ph | $-(CH_2)_5-$ | | – | 1[b]) | 0.35[c]) | – | – | – |
| **c** | Ph | Me | Ph | – | 1[b]) | 0.53[d]) | 3.52[b]) | – | – |
| **d** | Ph | Ph | Ph | – | 1[b])[d]) | – | 2.47[b]) | – | – |
| **e** | Ph | Me | $4\text{-}O_2N\text{–}C_6H_4$ | – | 1 | – | – | – | – |
| **f** | Ph | Me | $4\text{-}MeO\text{–}C_6H_4$ | MeO | 1[e]) | 1[e]) | – | 3.52 | – |
| **g** | Ph | Me | $4\text{-}Me\text{–}C_6H_4$ | Me | 1 | [c]) | – | 1.27 | – |
| **h** | $4\text{-}O_2N\text{–}C_6H_4$ | Me | Ph | H | 1 | – | – | 11.73 | – |
| **i** | $4\text{-}MeO\text{–}C_6H_4$ | Me | Ph | H | 1[d]) | 0.72 | – | 14.30 | – |
| **j** | $4\text{-}Me\text{–}C_6H_4$ | Me | Ph | H | 1 | 0.98 | – | 1.20 | – |
| **k** | $3\text{-}O_2N\text{–}C_6H_4$ | Me | Me | – | 1 | – | – | – | – |
| **l** | $3\text{-}MeO\text{–}C_6H_4$ | Me | Me | – | – | 1 | – | – | 0.30 |
| **m** | Naphthalen-2-yl | Me | Ph | H | 1 | 1 | 0.84 | – | – |
| **n** | Me | Me | Ph | H | – | – | – | 1[f]) | – |
| **o** | Me | Me | $4\text{-}MeO\text{–}C_6H_4$ | MeO | 1[g]) | 5.08 | – | 5.36 | – |
| **p** | Me | Me | $4\text{-}Me\text{–}C_6H_4$ | Me | 1 | 1 | – | 1.13 | – |

[a]) Normalized by GC values. [b]) Values taken from [5]. [c]) Not isolated in pure state. Structure assignment based on $^1$H-NMR of an impure sample and GC/MS. [d]) Not isolated in pure state. [e]) Two products give a single peak in GC. The ratio **7**/**8** is unknown. [f]) No other product was isolated. [g]) The product was isolated as a mixture with **8o**.

Contrary to the data of *Maas* and co-workers, our new results also supported that all these reactions gave 3*H*-dihydrofuran derivatives **7** (except for *Entries* **l** and **n**). The reaction of **6e** and **6k** afforded 3*H*-dihydrofurans as the only products, representing a method of the synthesis of these polyfunctional derivatives as valuable building blocks. When dimethylamino- (*i.e.*, **6a** and **6l**) and piperidino- (*i.e.*, **6b**) substituted starting materials were used, H–C(α) insertion products were also observed as by-products. According to literature, these H–C(α) insertion products may be formed by two general pathways as summarized below.

*i*) As enaminones are known to have different nucleophilic sites (N, C(α), and O) [10][13], the electrophilic attack of a carbene at C(α) may be conceived as depicted in *Scheme 3* (pathway *i*).

Scheme 3. *Formation of H–C(α) Insertion Products*

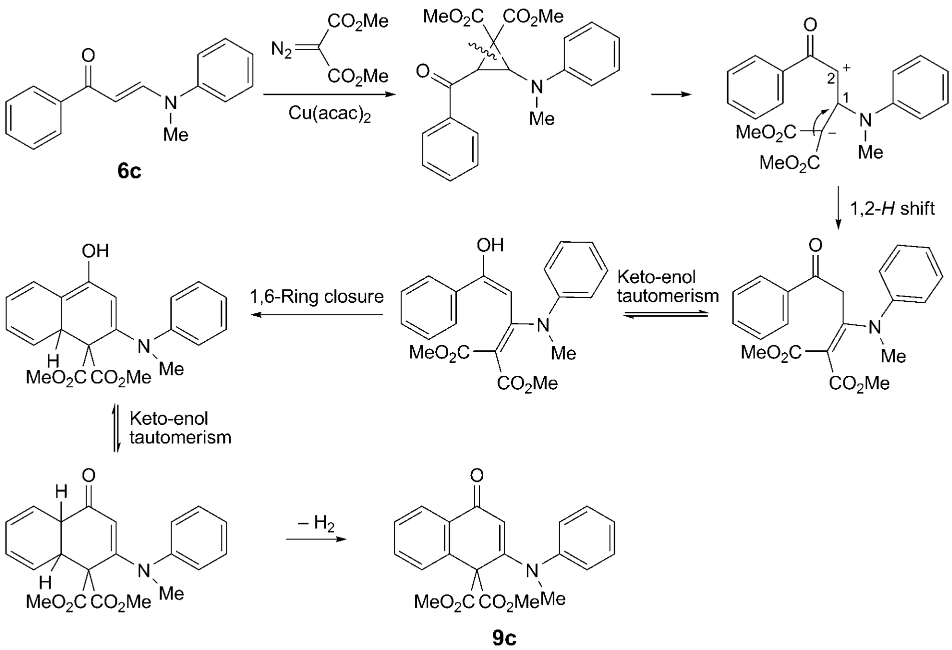



*ii*) A metallacyclobutane intermediate, either formed directly (pathway *ii*-1) or formed by transition-metal-catalyzed rearrangement of an intermediate donor–acceptor substituted cyclopropane (pathway *ii*-2), can lead to the H–C(α) insertion product **11a** [17].

As can be seen from *Table 2*, the reaction of enaminones **6c**, **6d**, and **6m**, give the naphthalenone derivatives **9c**, **9d**, and **9m** as major products. These products can be formed *via* two pathways:

*i*) A donor–acceptor-substituted cyclopropane intermediate is initially formed, which then undergoes ring opening and subsequent rearrangement to a benzoylpropenedicarboxylate system. Finally, naphthalenone derivative is obtained by 1,6-electrocyclization, followed by aromatization (*Scheme 4*). Since this mechanism involves the same cyclopropane intermediate as the previously discussed H–C(α) insertion mechanisms (*Scheme 3*, pathway *ii*-2) and shows similarity with the quinoline-formation mechanisms, which will be discussed below, it seems to be a more probable route for the formation of the naphthalenone derivatives.

Scheme 4. *Formation of Naphthalenone Derivatives: Pathway 1*



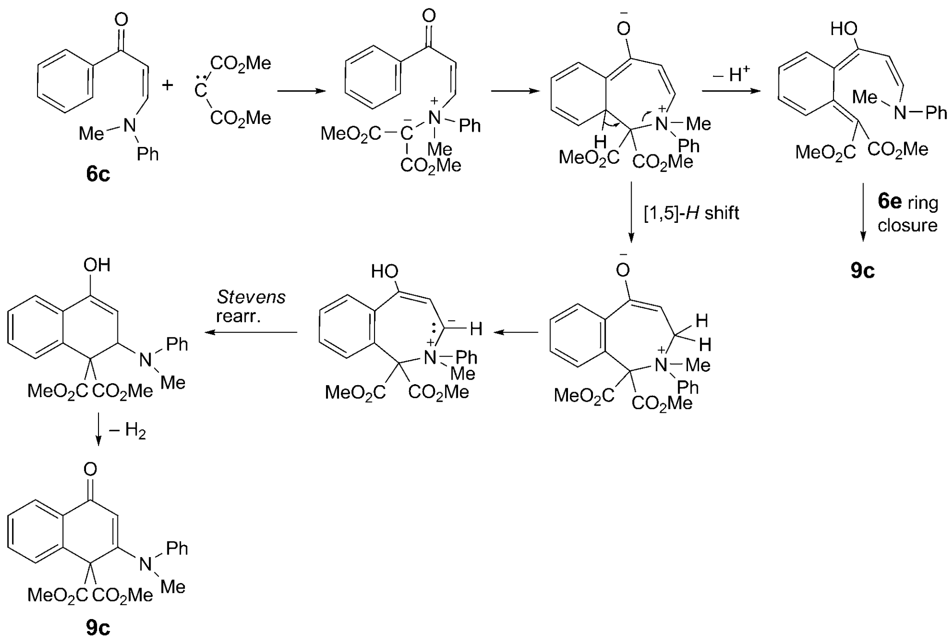

*ii*) Electrophilic carbene attacks the amine group to form a nitrogen ylide intermediate, whose C-atom attacks the Ph ring. The intermediate then undergoes further rearrangements to give compound **9c** (*Scheme 5*).

In the reaction of **6h**, **6i**, **6j**, and **6n**, quinoline derivatives **10** were obtained as major products, the structures of which were determined by their $^{1}$H- and $^{13}$C-NMR spectra as well as the crystallographic analysis of **10n** (*Fig. 1*).

The quinoline derivatives are formed probably *via* the ring opening and subsequent dehydrogenation, and finally 1,6-ring closure of an initially formed '*push-pull*' cyclopropane derivative (*Scheme 6*, pathway *i*). The initial intermediate may be a betain derivative formed by the attack of a carbenoid at C($\alpha$) (*Scheme 6*, pathway *ii*). The last probable route (*Scheme 6*, pathway *iii*) may proceed *via* the initial carbene attack at the *ortho*-position of the aniline ring and further necessary transformations. The absence of a quinoline product with the *p*-nitroanilino enaminone **6e** supports this last route, which appears reasonable taking into account the high electrophilicity of $E_2C$. However, our inability to detect any products resulting from a *para*- instead of *ortho*-attack raises questions about the validity of pathway *iii*.

As we reported before [1][3][4][6], the formation of 3*H*-dihydrofuran derivatives **7** has to be attributed to a 1,5-electrocyclization of carbonyl ylide intermediates (*Scheme 7*, pathway *iii*). In this study, some of our reactions, however, yielded additionally novel 5*H*-dihydrofuran derivatives **8**. A comparison of the $^{1}$H-NMR spectra of the dihydrofurans **7f** and **8f** are displayed in *Fig. 2,a*. The 3*H*-dihydrofuran

Scheme 5. *Formation of Naphthalenone Derivatives: Pathway 2*



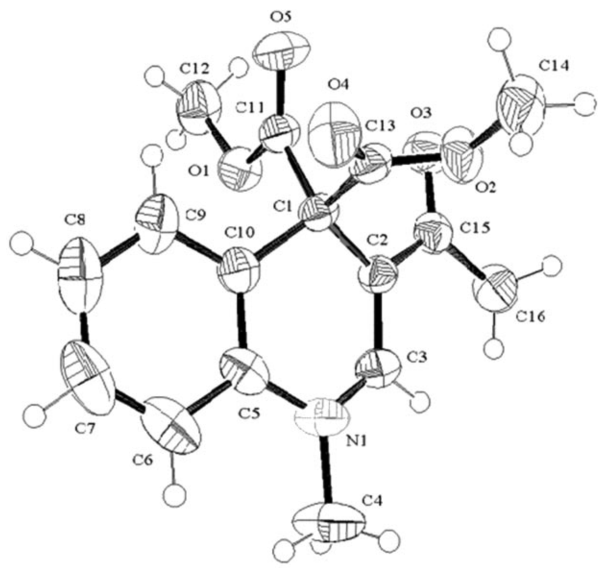
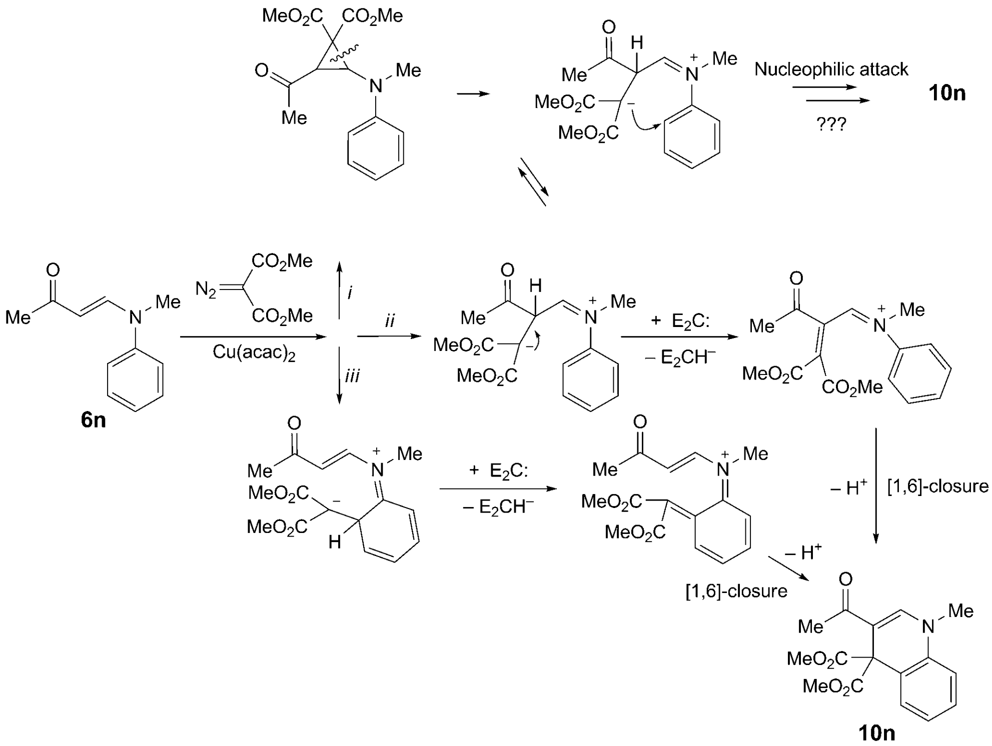




Fig. 1. *X-Ray crystal structure of* **10n**

Scheme 6. *Formation of Quinoline Derivatives*



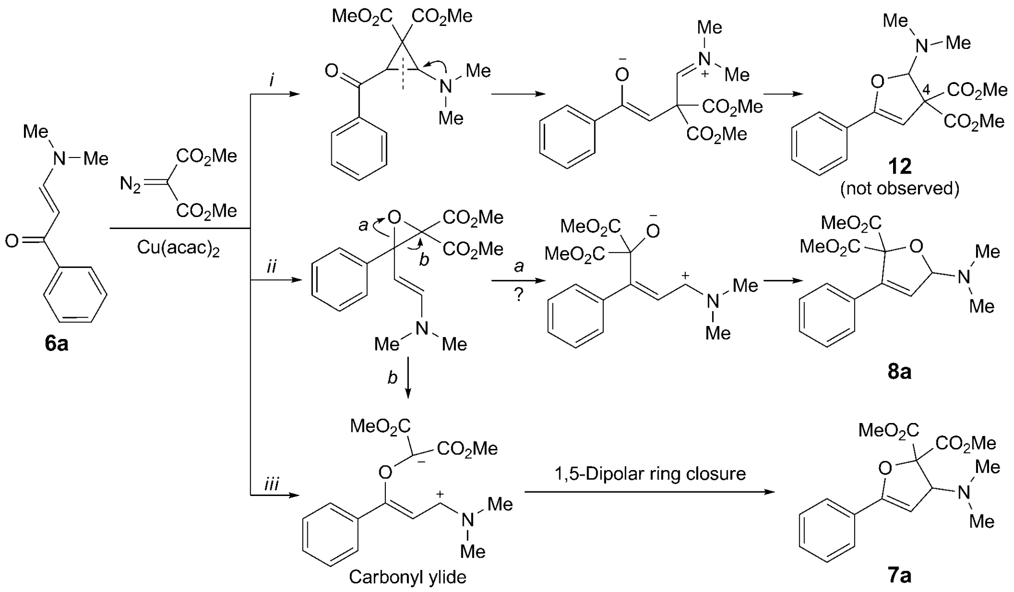

structure of **7f** ($\delta$(H) 5.92 ($d, J = 2.7$), 5.41 ($d, J = 2.9$); *Fig. 2,b*) was further verified by crystallographic analysis (*Fig. 3*).

Of the two possible structures assignable to the second dihydrofuran isomer, namely **8** or **12**, we established that the actual structure was that of a 5*H*-dihydrofuran **8** (*Scheme 7*, pathway *ii*). The other dihydrofuran derivative **12** may have been formed by ring opening of a donor–acceptor cyclopropane intermediate (*Scheme 7*, pathway *i*). In the $^{13}$C-NMR spectra of the new dihydrofuran isomers, a signal between $\delta$(C) 118 and 126 ppm was recognizable, which is not attributable to C(4) of the hypothetical 2*H*-dihydrofuran **12**. All spectral data fit best the 5*H*-dihydrofuran structure **8**. The chemical shifts and coupling constants of compounds **7** and **8** are listed in *Tables 3* and *4*, respectively.

The formation of 3*H*-dihydrofurans **7** has been attributed to 1,5-electrocyclization of carbonyl ylide intermediates. Now that the 3*H*-dihydrofurans are observed along with their 5*H*-isomers, the epoxide route in *Scheme 7*, pathway *ii*, can be alternative mechanism, whereas the 1,5-electrocyclization might still be valid for the 3*H*-isomers.

**Conclusions.** – Cu(acac)$_2$-Catalyzed reactions of tertiary enaminones and dimethyl diazomalonate ($E_2C{=}N_2$, $E = CO_2Me$) lead to significant amounts of 3*H*- and 5*H*-dihydrofuran derivatives. Tertiary enaminones with benzoyl, and *N*-methyl and/or *N*-

Scheme 7. *Formation of Dihdyrofuran Derivatives* **7** *and* **8**



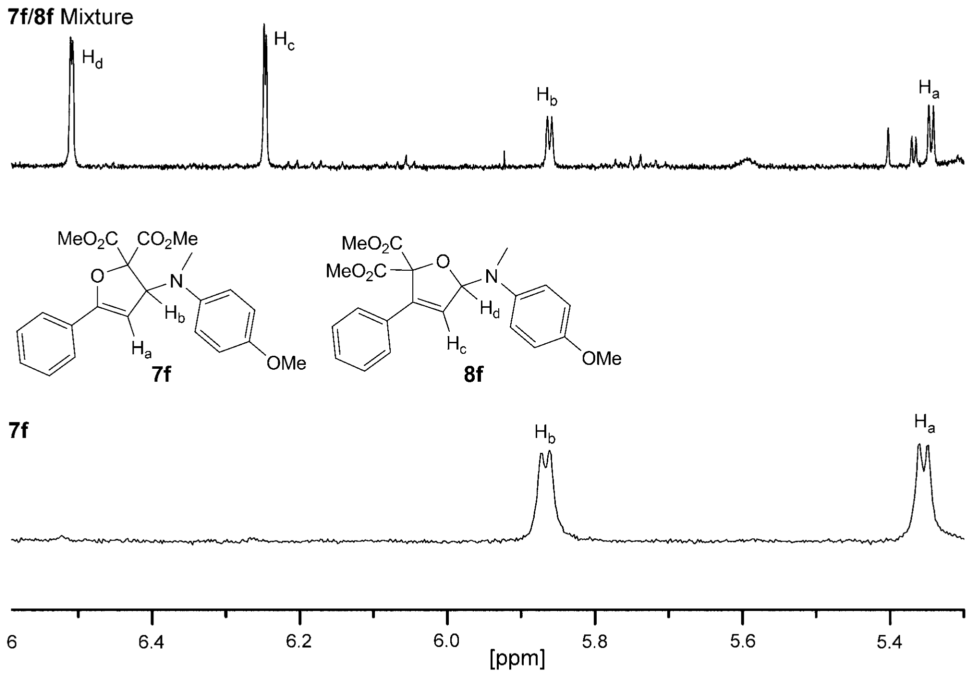




Fig. 2. *$^{1}$H-NMR Spectra of dihydrofuran derivatives* **7f** *and mixture* **7f**/**8f**

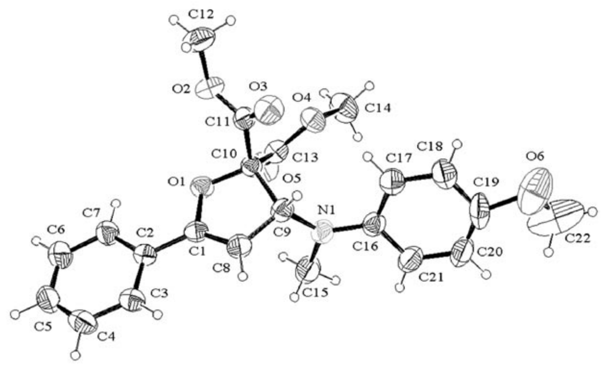



Fig. 3. *X-Ray crystal structure of* **7f**

Table 3. *Chemical Shifts and Coupling Constants for 3*H-*Dihydrofuran Derivatives* **7**

| | **7a** | **7b** | **7c** | **7e** | **7f** | **7g** | **7h** | **7j** | **7k** | **7m** | **7o** | **7p** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\delta$(H) for H–C(3) | 4.77 | 4.73 | 5.43 | 5.40 | 5.41 | 5.33 | 5.57 | 5.33 | 4.76 | 5.47 | 4.63 | 4.69 |
| $\delta$(H) for H–C(4) | 5.50 | 5.52 | 6.12 | 6.20 | 5.92 | 5.94 | 6.06 | 6.05 | 5.62 | 6.07 | 5.66 | 5.81 |
| $^3J$(3,4) [Hz] | 2.9 | 2.8 | 3.1 | 3.1 | 2.8 | 3.2 | 3.2 | 2.5 | 2.7 | 2.7 | 2.9[a]) | [b]) |

[a]) Only from H–C(3); H–C(4) appeared as a broad *singlet*. [b]) Both H–C(3) and H–C(4) appeared as broad *singlet*s.

Table 4. *Chemical Shifts and Coupling Constants for 5*H-*Dihydrofuran Derivatives* **8**

| | **8a** | **8f** | **8g** | **8i** | **8j** | **8l** | **8m** | **8o** | **8p** |
|---|---|---|---|---|---|---|---|---|---|
| $\delta$(H) for H–C(4) | 5.95 | 6.24 | 6.24 | 6.15 | 6.21 | 5.88 | 6.38 | 5.62 | 5.63 |
| $\delta$(H) for H–C(5) | 6.19 | 6.51 | 6.61 | 6.65 | 6.65 | 6.11 | 6.72 | 6.31 | 6.42 |
| $^3J$(4,5) [Hz] | 1.4 | 1.5 | 1.5 | 1.5[a]) | 1.5[a]) | 1.5 | 1.5 | 1.5 | 1.5 |

[a]) Only from H–C(4); H–C(5) appeared as a broad *singlet*.

aryl groups yield naphthalenone derivatives as major products. In case of *p*-substituted benzoyl and/or *N*-methyl *p*-substituted anilino groups (except for *N*-methyl-4-nitro-aniline), quinoline derivatives were obtained almost as a sole product. These 5*H*-dihydrofuran, naphthalenone, and quinoline derivatives are novel products which, to the best of our knowledge, have not been observed in carbene reactions so far.

## Experimental Part

*General.* All reactions of diazo compounds and enaminones were carried out under an atmosphere of $N_2$. A rotary evaporator equipped with a $H_2O$ condenser and attached to a vacuum system was used to evaporate *in vacuo*. All solvents and reactants are commercially available. Dimethyl diazomalonate ($E_2C{=}N_2$, $E = CO_2Me$) was prepared by literature procedure [18]. FT-IR Spectra: *Perkin-Elmer FT-IR*

*Spectrum One* spectrometer. $^1$H- and $^{13}$C-NMR spectra: in $CDCl_3$; chemical shifts ($\delta$) in ppm downfield from TMS, at ambient temp., on 250- or 500-MHz and 60- or 125-MHz *Bruker AC*, resp. GC/MS: *Hewlett-Packard* instrument equipped with a flame ionization detector; cross-linked (phenylmethyl)siloxane cap. column (30 m × 0.32 mm × 0.25 μm) with He as the carrier gas (25 psi column head pressure); temp. program: start 100°; then 5 min isothermal; ramp 20°/min; final 290°, and then 10 min isothermal; retention times ($t_R$) in min.

*Synthesis of Enaminones.* Compounds **6a**–**6i**, and **6m**–**6p** were prepared by *Procedure 1* (see below), and **6k** and **6l** were prepared by a literature procedure [19].

*Preparation of β-Keto Aldehyde Sodium Enolate.* To soln. of NaH 80% (0.8 mol) in $Et_2O$ (400 ml) was added MeOH (0.8 mol) at reflux temp. After addition, the mixture was refluxed for 10 min and cooled at 0°. The mixture of methyl ketone (0.8 mol) and methyl formate (0.84 mol) was added to the mixture at 5–10° in 40 min. After addition of $Et_2O$ (200 ml), the mixture was stirred overnight. Then, the mixture was filtered, and the precipitate was washed with $Et_2O$ (200 ml). β-Keto aldehyde sodium enolate was dried *in vacuo*.

*Preparation of β-Acylethenyl Chloride.* β-Keto aldehyde sodium enolate (1 equiv.) was dissolved in cold $H_2O$ and extracted with $CH_2Cl_2$. To the aq. layer was added 2N AcOH (1 equiv.), and the mixture was extracted with $CH_2Cl_2$. The org. layer was washed with $H_2O$ and brine, and dried ($MgSO_4$). The solvent was removed *in vacuo*. The residue (β-keto aldehyde; 0.1 mol) was dissolved in benzene (100 ml), and $SOCl_2$ (0.11 mol) was added to this soln. The mixture was refluxed until HCl was no longer evolved. The solvent was removed under reduced pressure, and the residue was distilled *in vacuo*. Yield 65%.

*Procedure 1.* To a soln. of a β-acylethenyl chloride (14 mmol) in benzene (50 ml) was added the secondary amine (14 mmol) at r.t., and the mixture was refluxed until HCl was no longer evolved. Benzene was removed *in vacuo* and the residue purified by recrystallization or distillation.

*(2E)-3-[Methyl(4-nitrophenyl)amino]-1-phenylprop-2-en-1-one* (**6e**). Recrystallized from benzene. Yellow solid. Yield 65%. M.p. 132–134°. $t_R$ 18.38. IR (neat): 1642, 1543, 1503. $^1$H-NMR[1]): 8.31 (*d*, *J* = 12.8, 1 H); 8.25 (*d*, *J* = 9.2, 2 H); 7.95 (*d*, *J* = 8.3, 2 H); 7.56–7.42 (*m*, 3 H); 7.30 (*d*, *J* = 9.2, 2 H); 6.34 (*d*, *J* = 12.8, 1 H). $^{13}$C-NMR (60 MHz): 189.3; 148.9; 146.2; 138.9; 133.6; 131.0; 129.9; 127.2; 126.7; 124.2; 119.9; 99.0; 37.6. EI-MS: 282 ($M^+$, 50), 265 (100), 236 (10), 205 (15), 177 (27), 159 (27), 131 (62), 105 (32), 77 (39). HR-MS: 283.1080 ($C_{16}H_{15}N_2O_3^+$; calc. 283.1083).

*(2E)-3-[(4-Methoxyphenyl)(methyl)amino]-1-phenylprop-2-en-1-one* (**6f**). Recrystallized from hexane. Light yellow solid. M.p. 146–148°. $t_R$ 16.1. IR (neat): 3012, 2967, 1641, 1552, 1232. $^1$H-NMR: 8.12 (*d*, *J* = 12.5, 1 H); 7.92 (*d*, *J* = 6.5, 2 H); 7.48–7.42 (*m*, 3 H); 7.13 (*d*, *J* = 8.8, 2 H); 6.90 (*d*, *J* = 8.8, 2 H); 6.00 (*d*, *J* = 12.5, 1 H); 3.81 (*s*, 3 H); 3.36 (*s*, 3 H). $^{13}$C-NMR[2]): 188.3; 156.3; 149.8; 139.3; 130.2; 127.2; 126.6; 121.6; 113.7; 108.8; 95.0; 54.6; 31.1. EI-MS: 267 (100, $M^+$), 251 (95), 190 (27), 162 (94), 147 (54), 105 (48), 77 (44). HR-MS: 268.1340 ($C_{17}H_{18}NO_2^+$; calc. 268.1338).

*(2E)-3-[Methyl(4-methylphenyl)amino]-1-phenylprop-2-en-1-one* (**6g**). Recrystallized from hexane. Yellow-orange solid. M.p. 109–111°. $t_R$ 15.3. IR (neat): 3057, 2982, 1634, 1545, 1254, 1313. $^1$H-NMR: 8.19 (*d*, *J* = 12.7, 1 H); 7.93 (*d*, *J* = 6.6, 2 H); 7.48–7.43 (*m*, 3 H); 7.18 (*d*, *J* = 8.2, 2 H); 7.09 (*d*, *J* = 8.3, 2 H); 6.05 (*d*, *J* = 12.7, 1 H); 3.37 (*s*, 3 H); 2.34 (*s*, 3 H). $^{13}$C-NMR: 188.4; 149.3; 139.2; 133.9; 130.2; 129.1; 127.2; 126.7; 119.6; 95.5; 30.7; 19.7. EI-MS: 251 (70, $M^+$), 234 (90), 174 (54), 146 (100), 131 (43), 105 (41), 77 (34). HR-MS: 252.1385 ($C_{17}H_{17}NO^+$; calc. 252.1388).

*(2E)-1-(4-Methoxyphenyl)-3-[methyl(phenyl)amino]prop-2-en-1-one* (**6i**). Recrystallized from AcOEt. Yellow solid. M.p. 194–198°. $t_R$ 16.4. IR (neat): 3005, 2667, 1641, 1552, 1240. $^1$H-NMR: 8.21 (*d*, *J* = 12.7, 1 H); 7.94 (*d*, *J* = 8.7, 2 H); 7.39–7.33 (*m*, 2 H); 7.21–7.12 (*m*, 3 H); 6.92 (*d*, *J* = 8.7, 2 H); 6.09 (*d*, *J* = 12.7, 1 H); 3.85 (*s*, 3 H); 3.38 (*s*, 3 H). $^{13}$C-NMR: 187.1; 161.4; 148.4; 145.5; 131.7; 130.2; 122.7; 119.4; 112.9; 112.5; 95.6; 58.5; 37.2. EI-MS: 267 (53, $M^+$), 250 (100), 236 (5), 160 (23), 132 (75), 77 (32). HR-MS: 268.1344 ($C_{17}H_{17}NO_2^+$; calc. 268.1338).

*(2E)-1-(4-Methylphenyl)-3-[methyl(phenyl)amino]prop-2-en-1-one* (**6j**). Recrystallized from hexane. Orange solid. M.p. 134–136°. $t_R$ 14.3. $^1$H-NMR (500 MHz): 8.14 (*d*, *J* = 12.7, 1 H); 7.78 (*d*, *J* = 7.8,

[1]) If not stated otherwise at 250 MHz.

[2]) If not stated otherwise at 125 MHz.

2 H); 7.30 (*t*, *J* = 7.8, 2 H); 7.18 – 7.14 (*m*, 4 H); 7.09 (*td*, *J* = 7.3, 1, 1 H); 6.03 (*d*, *J* = 12.7, 1 H); 3.32 (*s*, 3 H); 2.33 (*s*, 3 H). $^{13}$C-NMR: 188.1; 148.7; 145.5; 140.8; 136.4; 128.5; 127.9; 126.8; 123.8; 119.4; 95.9; 36.8; 20.5. EI-MS: 251 (40, $M^+$), 234 (59), 160 (30), 132 (100), 91 (46), 77 (37). HR-MS: 252.1390 ($C_{17}H_{17}NO^+$; calc. 252.1388).

*(2*E*)-3-[Methyl(phenyl)amino]-1-(naphthalen-2-yl)prop-2-en-1-one* (**6m**). Dissolved in benzene and precipitated in hexane. Grey solid. M.p. 107 – 109°. $t_R$ 16.7. IR (neat): 3050, 2960, 1641, 1530, 1247, 1083. $^1$H-NMR (500 MHz): 8.36 (br. *s*, 1 H); 8.21 (*d*, *J* = 12.7, 1 H); 7.97 (*dd*, *J* = 8.5, 1.7, 1 H); 7.88 (*d*, *J* = 7.8, 1 H); 7.81 (*d*, *J* = 8.8, 1 H); 7.79 (*d*, *J* = 8.5, 1 H); 7.45 (*dquint.*, *J* = 7.3, 1.6, 2 H); 7.31 (*td*, *J* = 7.0, 1.6, 2 H); 7.16 (*td*, *J* = 8.0, 1.2, 2 H); 7.10 (*t*, *J* = 7.3, 1 H); 6.18 (*d*, *J* = 12.7, 1 H); 3.36 (*s*, 3 H). $^{13}$C-NMR: 188.2; 149.0; 145.5; 136.4; 133.9; 131.8; 128.5; 128.2; 127.3; 127.0; 126.7; 126.5; 125.3; 124.0; 123.6; 119.5; 96.1; 36.4. EI-MS: 287 (70, $M^+$), 270 (100), 182 (8), 160 (34), 132 (75), 77 (30). HR-MS: 288.1380 ($C_{20}H_{17}NO^+$; calc. 288.1388).

*(3*E*)-4-[Methyl(phenyl)amino]but-3-en-2-one* (**6n**). Synthesized by a literature procedure [20]. $^1$H-NMR: 7.83 (*d*, *J* = 13.1, 1 H); 7.30 (*t*, *J* = 7.8, 3 H); 7.08 (*d*, *J* = 8.3, 2 H); 5.36 (*d*, *J* = 13.1, 1 H); 3.20 (*s*, 3 H); 2.13 (*s*, 3 H).

*(3*E*)-4-[(4-Methoxyphenyl)(methyl)amino]but-3-en-2-one* (**6o**). Recrystallized from hexane. Yellow solid. M.p. 146 – 148°. $t_R$ 12.8. IR (neat): 3057, 2967, 1664, 1552, 1500, 1240. $^1$H-NMR: 7.74 (*d*, *J* = 13.0, 1 H); 7.03 (*d*, *J* = 8.9, 2 H); 6.84 (*d*, *J* = 8.9, 2 H); 5.29 (*d*, *J* = 13.0, 1 H); 3.76 (*s*, 3 H); 3.19 (*s*, 3 H); 2.12 (*s*, 3 H). $^{13}$C-NMR (60 MHz): 185.4; 153.3; 149.0; 140.2; 116.2; 114.1; 106.6; 46.9; 46.8; 29.0. EI-MS: 205 (95, $M^+$), 190 (100), 162 (60), 147 (97), 121 (24), 77 (12). HR-MS: 206.1175 ($C_{12}H_{15}NO_2^+$; calc. 206.1181).

*(3*E*)-4-[Methyl(4-methylphenyl)amino]but-3-en-2-one* (**6p**). Recrystallized from hexane. Orange solid. M.p. 109 – 111°. $t_R$ 11.2. IR (neat): 3027, 2915, 1664, 1596, 1552, 1508, 1336, 1254. $^1$H-NMR: 7.79 (*d*, *J* = 13.1, 1 H); 7.08 (*d*, *J* = 8.0, 2 H); 6.96 (*d*, *J* = 8.0, 2 H); 5.31 (*d*, *J* = 13.1, 1 H); 3.17 (*s*, 3 H); 2.25 (*s*, 3 H); 2.11 (*s*, 3 H). $^{13}$C-NMR (60 MHz): 196.0; 148.7; 144.1; 134.6; 130.0; 120.4; 101.2; 37.2; 28.1; 20.7. EI-MS: 205 (95, $M^+$), 190 (100), 162 (60), 147 (97), 121 (24), 77 (12). HR-MS: 190.1234 ($C_{12}H_{15}NO^+$; calc. 190.1232).

*(2*E*)-3-(Dimethylamino)-1-(3-nitrophenyl)prop-2-en-1-one* (**6k**). Recrystallized from hexane. Brown solid. M.p. 70 – 73°. $t_R$ 14.3. $^1$H-NMR: 8.68 (br. *s*, 1 arom. H); 8.27 (*ttt*, *J* = 9.1, *ca*. 2, 2 H); 7.88 (*d*, *J* = 12.2, 1 H); 7.58 (*t*, *J* = 7.9, 1 H); 5.70 (*d*, *J* = 12.2, 1 H); 3.19 (*s*, 3 H); 2.98 (*s*, 3 H). $^{13}$C-NMR (60 MHz): 185.4; 155.2; 148.2; 142.1; 133.4; 129.2; 125.3; 122.3; 91.3; 45.2; 37.5. EI-MS: 220 (43, $M^+$), 203 (100), 157 (12), 98 (73), 70 (13). HR-MS: 221.0100 ($C_{11}H_{12}N_2O_3^+$; calc. 221.0926).

*(2*E*)-3-(Dimethylamino)-1-(3-methoxyphenyl)prop-2-en-1-one* (**6l**). $^1$H-NMR: 7.77 (*d*, *J* = 12.3, 1 H); 7.45 (br. *s*, 2 H); 7.29 (*t*, *J* = 8.1, 1 H); 6.98 (*d*, *J* = 7.8, 1 H); 5.67 (*d*, *J* = 12.3, 1 H); 3.83 (*s*, 3 H); 3.10 (br. *s*, 3 H); 2.90 (br. *s*, 3 H).

*General Procedure for the Reaction of Enaminones with Dimethyl Diazomalonate.* To a soln. of **6** (2.1 mmol) in benzene (10 ml) was added Cu(acac)$_2$ ($9 \times 10^{-3}$ mmol), and the mixture was heated at reflux temp. A soln. of $E_2C{=}N_2$ (1.4 mmol) in benzene (4 ml) was added to this soln. over 2.5 h under $N_2$. When the IR spectrum of the mixture indicated total consumption of $E_2C{=}N_2$ (absence of the characteristic diazo band at 2130 cm$^{-1}$), the mixture was filtered, evaporated, and purified by CC or prep. TLC. The crude mixture contained varying amounts of unidentified compounds (max. 20% by GC).

*Dimethyl 3-[Methyl(4-nitrophenyl)amino]-5-phenylfuran-2,2(3*H*)-dicarboxylate* (**7e**). Isolated by CC (neutral alumina; hexane/AcOEt 4 :1). Colorless solid. M.p. 167 – 170°. $t_R$ 21.63. IR (neat): 1730, 1592, 1383, 1229. $^1$H-NMR: 8.15 (*dd*, *J* = 7.3, 2.2, 2 H); 7.73 – 7.69 (*m*, 2 H); 7.44 – 7.37 (*m*, 3 H); 6.97 (*dd*, *J* = 7.4, 2.1, 2 H); 6.20 (*d*, *J* = 3.1, 1 H); 5.40 (*d*, *J* = 3.1, 1 H); 3.88 (*s*, 3 H); 3.46 (*s*, 3 H); 2.85 (*s*, 3 H). $^{13}$C-NMR: 167.8; 165.5; 158.2; 153.6; 137.4; 131.5; 129.5; 128.8; 127.2; 124.6; 113.3; 95.8; 92.9; 69.7; 52.8; 51.7; 32.2. EI-MS: 412 (1, $M^+$), 261 (100), 217 (61), 202 (38), 171 (23), 115 (16), 59 (7). HR-MS: 413.1351 ($C_{21}H_{20}N_2O_7^+$; calc. 413.1349).

*Dimethyl 3-[(4-Methoxyphenyl)(methyl)amino]-5-phenylfuran-2,2(3*H*)-dicarboxylate* (**7f**). Purified by CC (neutral alumina; hexane/AcOEt 4 :1). Yellowish solid. $t_R$ 16.94. IR (neat): 2982, 2960, 1738, 1508, 1083. $^1$H-NMR: 7.69 – 7.68 (*m*, 2 H); 7.39 – 7.37 (*m*, 3 H); 6.92 (*d*, *J* = 9.2, 2 H); 6.84 (*d*, *J* = 9.1, 2 H); 5.92 (*d*, *J* = 2.7, 1 H); 5.41 (*d*, *J* = 2.9, 1 H); 3.85 (*s*, 3 H); 3.76 (*s*, 3 H); 3.55 (*s*, 3 H); 2.71 (*s*, 3 H). $^{13}$C-NMR: 167.2; 165.0; 155.6; 151.3; 143.0; 128.6; 128.2; 127.4; 125.0; 114.2; 113.5; 94.6; 90.7; 69.9; 54.7; 52.5; 52.4;

32.3. EI-MS: 397 (37, $M^+$), 338 (44), 261 (100), 217 (72), 185 (76), 171 (32), 129 (31), 115 (23), 59 (13). HR-MS: 398.1601 ($C_{22}H_{23}NO_6^+$; calc. 398.1604). The structure of **7f** was finally established by an X-ray crystal-structure analysis (*Fig. 3*)[3]).

*Dimethyl 3-[Methyl(4-methylphenyl)amino]-5-phenylfuran-2,2(3*H*)-dicarboxylate* (**7g**). The product was isolated by CC on neutral alumina (hexane/AcOEt 8:1) as a dark yellow oil. $t_R$ 16.14 min. IR (neat): 3027, 2960, 1738, 1515. $^1$H-NMR (500 MHz): 7.63 (*dd*, *J* = 7.6, 2.2, 2 H); 7.33–7.30 (*m*, 3 H); 6.91 (*d*, *J* = 8.3, 2 H); 6.80 (*d*, *J* = 8.8, 2 H); 5.94 (*d*, *J* = 3.4, 1 H); 5.33 (*d*, *J* = 2.9, 1 H); 3.79 (*s*, 3 H); 3.47 (*s*, 3 H); 2.66 (*s*, 3 H); 2.19 (*s*, 3 H). $^{13}$C-NMR: 167.2; 165.0; 155.7; 146.3; 128.6; 128.5; 128.2; 127.4; 126.0; 125.0; 112.8; 94.6; 90.5; 69.2; 52.5; 51.6; 32.0; 19.3. EI-MS: 381 (16, $M^+$), 322 (41), 261 (100), 217 (66), 185 (70), 171 (33), 129 (29), 115 (23), 91 (26), 59 (15). HR-MS: 382.1652 ($C_{22}H_{23}NO_5^+$; calc. 382.1654).

*Dimethyl 3-[Methyl(phenyl)amino]-5-(4-nitrophenyl)furan-2,2(3*H*)-dicarboxylate* (**7h**). Purification by prep. TLC (alumina plate; hexane/AcOEt 6:1). Red oil. $t_R$ 16.47. $^1$H-NMR (500 MHz): 8.19 (*dd*, *J* = 8.8, 2.0, 2 H); 7.79 (*dd*, *J* = 8.8, 2.0, 2 H); 7.23–7.22 (*m*, 2 H); 6.91 (*d*, *J* = 8.3, 2 H); 6.74 (*t*, *J* = 7.3, 1 H); 6.06 (*d*, *J* = 2.9, 1 H); 5.57 (*d*, *J* = 3.4, 1 H); 3.82 (*s*, 3 H); 3.46 (*s*, 3 H); 2.69 (*s*, 3 H). $^{13}$C-NMR: 166.7; 164.5; 153.6; 148.0; 147.3; 133.9; 128.0; 125.8; 122.8; 117.3; 112.7; 108.8; 99.0; 68.8; 51.9; 28.7. EI-MS: 412 (4, $M^+$), 394 (12), 353 (47), 306 (45), 262 (100), 231 (42), 106 (46), 77 (48), 59 (36). HR-MS: 413.1352 ($C_{21}H_{20}N_2O_7^+$; calc. 413.1349).

*Dimethyl 5-(4-Methylphenyl)-3-[methyl(phenyl)amino]furan-2,2(3*H*)-dicarboxylate* (**7j**). Purification by prep. TLC (alumina plate; hexane/AcOEt 5:1). Yellow oil. $t_R$ 14.98. $^1$H-NMR: 7.59 (*d*, *J* = 7.9, 2 H); 7.28–7.18 (*m*, 3 H); 6.97 (*d*, *J* = 8.1, 2 H); 6.76 (*t*, *J* = 7.1, 2 H); 6.05 (*d*, *J* = 2.4, 1 H); 5.33 (*d*, *J* = 2.7, 1 H); 3.85 (*s*, 3 H); 3.49 (*s*, 3 H); 2.74 (*s*, 3 H); 2.37 (*s*, 3 H). $^{13}$C-NMR: 167.2; 165.0; 156.0; 148.3; 138.9; 128.1; 128.0; 125.4; 125.0; 116.7; 112.5; 93.7; 90.4; 68.7; 52.5; 51.6; 31.8; 20.4. EI-MS: 381 (2, $M^+$), 275 (100), 231 (70), 216 (74), 185 (43), 129 (54), 77 (95), 59 (47). HR-MS: 382.1652 ($C_{22}H_{23}NO_5^+$; calc. 382.1654).

*Dimethyl 3-(Dimethylamino)-5-(3-nitrophenyl)furan-2,2(3*H*)-dicarboxylate* (**7k**). Isolated by CC (neutral alumina; hexane/AcOEt 9:1). Red-brown oil. $t_R$ 14.50. $^1$H-NMR (500 MHz): 8.41 (*t*, *J* = 1.71, 1 H); 8.12 (*ddd*, *J* = 8.3, 2.4, 1, 1 H); 7.91 (*dt*, *J* = 8.3, 1.3, 1 H); 7.48 (*t*, *J* = 8.1, 1 H); 5.62 (*d*, *J* = 2.9, 1 H); 4.76 (*d*, *J* = 2.4, 1 H); 3.77 (*s*, 3 H); 3.74 (*s*, 3 H); 2.27 (*s*, 6 H). $^{13}$C-NMR: 166.9; 165.0; 153.0; 130.5; 130.1; 128.5; 122.8; 119.9; 108.8; 96.3; 91.6; 72.5; 52.5; 51.8; 40.9. EI-MS: 350 (8, $M^+$), 306 (16), 291 (100), 262 (46), 231 (24), 157 (8), 115 (12), 59 (7). HR-MS: 351.1189 ($C_{16}H_{18}N_2O_7^+$; calc. 351.1192).

*Dimethyl 5-Methyl-3-[methyl(4-methylphenyl)amino]furan-2,2(3*H*)-dicarboxylate* (**7p**) *and Dimethyl (Methylamino)(4-methylphenyl)propanedioate* (**13**). Purified by CC ($SiO_2$; hexane/AcOEt 80:20). Compounds **7p** and **13** were obtained as a mixture (1:1 from $^1$H-NMR).

*Data of* **7p**. $t_R$ 13.3 (from the mixture of **7p** and **13**). $^1$H-NMR (from the mixture of **7p** and **13**): 6.81 (*d*, *J* = 7.9, 1 H); 6.71 (*d*, *J* = 7.9, 1 H); 5.81 (br. *s*, 1 H); 4.69 (br. *s*, 1 H); 3.84 (*s*, 3 H); 3.48 (*s*, 3 H); 2.65 (*s*, 3 H); 2.23 (*s*, 3 H); 1.98 (*s*, 3 H). $^{13}$C-NMR: 167.19; 167.18; 155.4; 146.4; 128.8; 128.4; 112.9; 95.6; 90.6; 69.1; 51.6; 51.5; 34.8; 19.2; 12.6. EI-MS: 319 (29, $M^+$), 199 (18), 155 (100), 121 (92), 91 (28), 59 (18).

*Data of* **13**. $t_R$ 11.7 (from the mixture of **7p** and **13**). $^1$H-NMR (from the mixture of **7p** and **13**): 7.06–7.01 (*m*, 4 H); 5.10 (br. *s*, 1 H); 3.78 (*s*, 6 H); 3.00 (*s*, 3 H); 2.23 (*s*, 3 H). $^{13}$C-NMR: 165.2; 145.8; 127.2; 125.8; 112.7; 65.2; 52.4; 31.7; 19.3. EI-MS: 251 (21, $M^+$), 192 (100), 132 (11), 118 (14), 91 (14), 59 (3).

*Dimethyl 5-(Dimethylamino)-3-phenylfuran-2,2(5*H*)-dicarboxylate* (**8a**). Purification by CC (neutral alumina; hexane/AcOEt 72:28). A fraction from the column was further chromatographed on a prep. alumina TLC plate (hexane/AcOEt 72:28). Compound **8a** was obtained as a light red oil. $t_R$ 12.75. IR (neat): 2982, 1731, 1440, 1075. $^1$H-NMR: 7.42 (*dd*, *J* = 6.6, 3.2, 2 H); 7.33–7.29 (*m*, 3 H); 6.19 (*d*, *J* = 1.4, 1 H); 5.95 (*d*, *J* = 1.4, 1 H); 3.77 (*s*, 3 H); 3.73 (*s*, 3 H); 2.41 (*s*, 6 H). $^{13}$C-NMR: 168.0; 166.2; 141.7; 132.5; 128.10; 127.3; 127.7; 126.8; 102.9; 102.1; 52.6; 51.1; 38.4. EI-MS: 305 (13, $M^+$), 261 (89), 246 (100), 185 (60), 172 (31), 158 (53), 115 (38), 59 (8). HR-MS: 306.1343 ($C_{16}H_{19}NO_5^+$; calc. 306.1341).

*Dimethyl 5-[(4-Methoxyphenyl)(methyl)amino]-3-phenylfuran-2,2(5*H*)-dicarboxylate* (**8f**). Purified by CC (neutral alumina; hexane/AcOEt 85:15). Compound **8f** was obtained as a mixture with **7f**

[3]) CCDC-774461 (for **7f**) and -774462 (for **10n**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the *Cambridge Crystallographic Data Center via* www.ccdc.cam.ac.uk/data_request/cif.

(1.58 : 0.68 from $^1$H-NMR). $t_R$ 17.4. $^1$H-NMR: 7.40 – 7.39 (*m*, 1 H); 7.27 – 7.26 (*m*, 2 H); 6.99 (*d*, *J* = 8.3, 2 H); 6.85 (*d*, *J* = 7.6, 2 H); 6.78 (*d*, *J* = 8.8, 2 H); 6.51 (*d*, *J* = 1.5, 1 H); 6.24 (*d*, *J* = 1.5, 1 H); 3.79 (*s*, 3 H); 3.70 (*s*, 3 H); 3.69 (*s*, 3 H); 2.77 (*s*, 3 H). EI-MS: 397 (36, $M^+$), 338 (47), 261 (100), 217 (69), 185 (71), 171 (36), 129 (33), 115 (27), 77 (16), 59 (8).

*Dimethyl 5-[Methyl(4-methylphenyl)amino]-3-phenylfuran-2,2(5*H*)-dicarboxylate* (**8g**). Purification of the mixture was realized on neutral alumina CC (hexane/AcOEt 80 : 20). A fraction from the column was further chromatographed on a prep. alumina TLC plate (hexane/AcOEt 80 : 20). Compound **8g** was obtained as a mixture with **7g** (**8g**/**7g** 1 : 9 from $^1$H-NMR). This mixture gave only one peak in GC.

*Data of* **8g**. $t_R$ 16.1 (from the mixture). $^1$H-NMR (500 MHz): 7.42 – 7.40 (*m*, 3 H); 7.27 – 7.26 (*m*, 2 H); 7.01 (*d*, *J* = 8.8, 2 H); 6.92 (*d*, *J* = 8.3, 2 H); 6.61 (*d*, *J* = 1.5, 1 H); 6.24 (*d*, *J* = 1.5, 1 H); 3.69 (*s*, 3 H); 3.68 (*s*, 3 H); 2.79 (*s*, 3 H); 2.21 (*s*, 3 H). EI-MS: 381 (16, $M^+$), 322 (41), 261 (100), 217 (66), 185 (70), 171 (33), 129 (29), 115 (23), 91 (26), 59 (15).

*Dimethyl 3-(4-Methoxyphenyl)-5-[methyl(phenyl)amino]furan-2,2(5*H*)-dicarboxylate* (**8i**). Purified by CC (neutral alumina; hexane/AcOEt 80 : 20). Compound **8i** was obtained as a mixture with **6i** (**8i**/**6i** 3 : 1 from $^1$H-NMR).

*Data of* **8i**. $t_R$ 17.4. $^1$H-NMR (500 MHz): 7.38 (*d*, *J* = 8.8, 2 H); 7.22 – 7.18 (*m*, 3 H); 6.99 (*d*, *J* = 8.3, 2 H); 6.81 – 6.79 (*m*, 2 H); 6.65 (br. *s*, 1 H); 6.15 (*d*, *J* = 1.5, 1 H); 3.79 (*s*, 3 H); 3.74 (*s*, 3 H); 3.69 (*s*, 3 H); 2.81 (*s*, 3 H). $^{13}$C-NMR: 168.0; 166.9; 159.0; 148.3; 140.2; 128.7; 128.2; 128.1; 124.9; 119.1; 115.7; 112.7; 97.1; 90.4; 54.3; 52.0; 51.8; 31.7. EI-MS: 397 (1, $M^+$), 338 (17), 291 (100), 250 (20), 215 (30), 187 (15), 159 (12), 145 (8), 77 (11), 59 (5).

*Dimethyl 3-(4-Methylphenyl)-5-[methyl(phenyl)amino]furan-2,2(5*H*)-dicarboxylate* (**8j**). Purification by prep. TLC (alumina plate; hexane/AcOEt 80 : 20). Compound **8j** was obtained as a mixture with **7j** (**8j**/**7j** 1.79 : 1 from $^1$H-NMR).

*Data of* **8j**. $t_R$ 14.9. $^1$H-NMR (500 MHz): 7.31 (*d*, *J* = 7.8, 2 H); 7.22 – 7.20 (*m*, 2 H); 7.08 (*d*, *J* = 7.8, 2 H); 7.00 (*d*, *J* = 8.3, 2 H); 6.82 (*t*, *J* = 7.0, 1 H); 6.65 (br. *s*, 1 H); 6.21 (*d*, *J* = 1.46, 1 H); 3.70 (*s*, 3 H); 3.60 (*s*, 3 H); 2.82 (*s*, 3 H); 2.28 (*s*, 3 H). $^{13}$C-NMR: 169.2; 168.1; 149.5; 141.9; 139.1; 129.3; 129.2; 128.6; 128.0; 126.2; 120.38; 116.93; 98.3; 91.8; 53.2; 53.0; 33.0; 21.5. EI-MS: 381 (1, $M^+$), 322 (7), 275 (28), 198 (19), 143 (14), 119 (100), 91 (35), 77 (23).

*Dimethyl 5-(Dimethylamino)-3-(3-methoxyphenyl)furan-2,2(5*H*)-dicarboxylate* (**8l**). Isolated by CC (neutral alumina; hexane/AcOEt 85 : 15). $t_R$ 13.7. IR (neat): 2975, 1738, 1596. $^1$H-NMR (500 MHz): 7.16 (*t*, *J* = 8.0, 1 H); 6.95 (*d*, *J* = 7.6, 1 H); 6.94 (*d*, *J* = 1.5, 1 H); 6.79 (*dtd*, *J* = 8.7, 2.4, 1.2, 1 H); 6.11 (*d*, *J* = 1.5, 1 H); 5.88 (*d*, *J* = 1.5, 1 H); 3.73 (*s*, 3 H); 3.71 (*s*, 3 H); 3.68 (*s*, 3 H); 2.35 (*s*, 6 H). $^{13}$C-NMR: 168.1; 166.9; 158.3; 141.0; 140.0; 128.2; 128.1; 119.4; 113.1; 112.8; 102.4; 54.2; 51.9; 51.7; 38.4. EI-MS: 335 (21, $M^+$), 291 (90), 276 (100), 247 (40), 187 (46), 159 (19), 115 (11), 82 (20), 59 (7). HR-MS: 336.1450 ($C_{17}H_{21}NO_6^+$; calc. 336.1447).

*Dimethyl 5-[Methyl(phenyl)amino]-3-(naphthalen-2-yl)furan-2,2(5*H*)-dicarboxylate* (**8m**). Purification by prep. TLC (alumina plate; hexane/AcOEt 80 : 20). Compound **8m** was obtained as a mixture with **7m** (**8m**/**7m** 4 : 1, from $^1$H-NMR). This mixture gave one peak on GC. $t_R$ 17.37. $^1$H-NMR (500 MHz, 4 : 1 mixture with **7m**): 7.89 (br. *s*, 1 H); 7.78 – 7.73 (*m*, 3 H); 7.54 (*dd*, *J* = 8.5, 1.7, 1 H); 7.43 – 7.41 (*m*, 2 H); 7.22 (*td*, *J* = 8.0, 1.0, 2 H); 7.03 (*dd*, *J* = 8.8, 1.0, 2 H); 6.84 (*t*, *J* = 6.4, 1 H); 6.72 (*d*, *J* = 1.5, 1 H); 6.38 (*d*, *J* = 1.5, 1 H); 3.713 (*s*, 3 H); 3.711 (*s*, 3 H); 2.86 (*s*, 3 H). $^{13}$C-NMR: 168.0; 166.9; 148.3; 140.8; 140.6; 132.3; 132.0; 128.1; 127.6; 127.4; 126.9; 126.6; 126.5; 125.8; 125.4; 124.3; 119.3; 115.8; 97.2; 90.6; 52.0; 51.9; 31.9. EI-MS: 417 (2, $M^+$), 399 (9), 368 (19), 311 (100), 270 (33), 235 (43), 207 (35), 179 (30), 77 (14), 59 (8).

*Dimethyl 3-[(4-Methoxyphenyl)(methyl)amino]-5-methylfuran-2,2(3*H*)-dicarboxylate* (**7o**) *and Dimethyl 5-[(4-Methoxyphenyl)(methyl)amino]-3-methylfuran-2,2(5*H*)-dicarboxylate* (**8o**). The mixture was purified by CC (neutral alumina; hexane/AcOEt 80 : 20). Compounds **7o** and **8o** were obtained as a mixture (**7o**/**8o** 1 : 2, from $^1$H-NMR) as a yellow oil.

*Data of* **7o**. $t_R$ 13.95. $^1$H-NMR (500 MHz, 1 : 2 mixture with **8o**): 6.79 (*dt*, *J* = 6.8, 2.9, 2 H); 6.74 (*dt*, *J* = 8.1, 2.9, 2 H); 5.66 (br. *s*, 1 H); 4.63 (*dq*, *J* = 2.9, 1.4, 1 H); 3.77 (*s*, 3 H); 3.67 (*s*, 3 H); 3.44 (*s*, 3 H); 2.58 (*s*, 3 H); 1.90 (*t*, *J* = 1.7, 3 H). $^{13}$C-NMR: 167.2; 165.2; 155.3; 151.2; 143.1; 114.0; 113.4; 91.0; 90.7; 69.8; 54.7; 52.4; 51.5; 32.0; 12.6. EI-MS: 335 ($M^+$, 36), 276 (32), 155 (81), 137 (100), 109 (40), 59 (33).

*Data of* **8o**. $t_R$ 14.1. $^1$H-NMR (500 MHz, 2:1 mixture with **7o**): 6.93 (*dd*, *J* = 6.83, 1.96, 2 H); 6.74 (*dt*, *J* = 8.1, 2.9, 2 H); 6.31 (*d*, *J* = 1.5, 1 H); 5.62 (*d*, *J* = 1.5, 1 H); 3.71 (*s*, 3 H); 3.70 (*s*, 3 H); 3.67 (*s*, 3 H); 2.65 (*s*, 3 H); 1.90 (*t*, *J* = 1.7, 3 H). $^{13}$C-NMR: 167.8; 166.8; 153.3; 142.5; 137.1; 126.1; 118.9; 113.4; 98.7; 95.5; 54.6; 51.8; 51.6; 32.6; 11.9. EI-MS: 335 (56, $M^+$), 276 (75), 155 (100), 137 (44), 109 (42), 59 (17).

*Dimethyl 3-Methyl-5-[methyl(4-methylphenyl)amino]furan-2,2(5*H*)-dicarboxylate* (**8p**). Purified by CC ($SiO_2$; hexane/AcOEt 85:15). Yellow oil. $t_R$ 12.69 min. IR (neat): 2982, 2878, 1746, 1523, 1269. $^1$H-NMR (500 MHz): 6.98 (*d*, *J* = 8.8, 2 H); 6.87 (*d*, *J* = 8.8, 2 H); 6.42 (*d*, *J* = 1.5, 1 H); 5.63 (*d*, *J* = 1.5, 1 H); 3.73 (*s*, 3 H); 3.70 (*s*, 3 H); 2.68 (*s*, 3 H); 2.19 (*s*, 3 H); 1.92 (*s*, 3 H). $^{13}$C-NMR: 167.7; 166.8; 146.1; 137.2; 128.6; 128.5; 126.0; 116.3; 97.7; 91.0; 51.8; 51.7; 31.7; 19.4; 11.9. EI-MS: 319 (24, $M^+$), 260 (44), 199 (36), 155 (100), 121 (57), 91 (33), 59 (36). HR-MS: 320.1503 ($C_{17}H_{21}NO_5^+$; calc. 320.1498).

*Dimethyl 2-[Methyl(phenyl)amino]-4-oxoanthracene-1,1(4*H*)-dicarboxylate* (**9m**). Isolated by prep. TLC (alumina plate; hexane/AcOEt 85:15). Light yellow oil. $t_R$ 20.56. $^1$H-NMR (500 MHz): 8.02 (br. *s*, 1 H); 7.85–7.81 (*m*, 2 H); 7.65 (*d*, *J* = 8.8, 1 H); 7.49 (*dquint.*, *J* = 7.6, 1.5, 2 H); 7.27 (*td*, *J* = 7.4, 1.5, 2 H); 7.16 (*s*, 1 H); 7.10 (*t*, *J* = 7.5, 1 H); 6.89 (*d*, *J* = 8.3, 1 H); 3.72 (*s*, 6 H); 3.24 (*s*, 3 H). $^{13}$C-NMR: 192.2; 169.5; 145.9; 135.9; 135.4; 133.3; 131.5; 129.4; 128.0; 127.8; 127.5; 127.2; 126.8; 126.2; 123.1; 120.2; 112.2; 109.0; 56.0; 52.16; 52.15; 38.8. HR-MS: 416.1495 ($C_{25}H_{21}NO_5^+$; calc. 416.1498).

*Dimethyl 3-Benzoyl-6-methoxy-1-methylquinoline-4,4(1*H*)-dicarboxylate* (**10f**). Purified by CC (neutral alumina; hexane/AcOEt 85:15). $t_R$ 19.77. IR (neat): 2982, 2870, 1723, 1455, 1075. $^1$H-NMR (500 MHz): 7.52 (*dt*, *J* = 6.4, 1.7, 2 H); 7.39 (*tt*, *J* = 7.3, 1.5, 1 H); 7.35 (*tt*, *J* = 7.3, 1.5, 2 H); 7.08 (*s*, 1 H); 7.06 (*t*, *J* = 1.7, 1 H); 6.82 (*d*, *J* = 1.5, 2 H); 3.74 (*s*, 3 H); 3.68 (*s*, 6 H); 3.23 (*s*, 3 H). $^{13}$C-NMR: 192.0; 169.4; 145.0; 138.8; 129.3; 129.2; 127.5; 127.2; 121.4; 114.2; 114.1; 113.3; 107.5; 56.1; 54.7; 52.4; 38.9. EI-MS: 395 (2, $M^+$), 336 (100), 234 (5), 173 (4), 105 (3), 77 (4). HR-MS: 396.1450 ($C_{22}H_{21}NO_6^+$; calc. 396.1447).

*Dimethyl 3-Benzoyl-1,6-dimethylquinoline-4,4(1*H*)-dicarboxylate* (**10g**). Purified by CC (neutral alumina; hexane/AcOEt 80:20). $t_R$ 18.36. IR (neat): 3057, 2982, 1634, 1545, 1254. $^1$H-NMR (500 MHz): 7.52 (*dt*, *J* = 6.3, 1.5, 2 H); 7.39 (*tt*, *J* = 7.3, 1.5, 1 H); 7.35 (*tt*, *J* = 7.3, 1.5, 2 H); 7.28 (br. *s*, 1 H); 7.08 (*s*, 1 H); 7.06 (*dq*, *J* = 8.3, 1.0, 1 H); 6.77 (*d*, *J* = 8.3, 1 H); 3.69 (*s*, 6 H); 3.23 (*s*, 3 H); 2.27 (*s*, 3 H). $^{13}$C-NMR: 192.1; 169.6; 145.7; 138.7; 133.1; 132.9; 129.6; 129.3; 128.8; 127.5; 127.1; 120.0; 112.2; 108.4; 55.8; 52.4; 52.1; 38.8; 19.8. EI-MS: 379 (1, $M^+$), 320 (100), 260 (4), 157 (5), 105 (3), 77 (4). HR-MS: 379.1416 ($C_{22}H_{21}NO_5^+$; calc. 379.1420).

*Dimethyl 1-Methyl-3-(4-nitrobenzoyl)quinoline-4,4(1*H*)-dicarboxylate* (**10h**). Isolated by prep. TLC (alumina plate; hexane/AcOEt 80:20). White solid. M.p. 127–129°. $t_R$ 18.64. IR (neat): 3067, 3007, 2953, 1739, 1644, 1521, 1482, 1336. $^1$H-NMR (500 MHz): 8.28 (*d*, *J* = 8.5, 2 H); 7.73 (*d*, *J* = 8.5, 2 H); 7.55 (*d*, *J* = 7.8, 1 H); 7.35 (*t*, *J* = 7.7, 1 H); 7.18 (*t*, *J* = 7.5, 1 H); 7.03 (*s*, 1 H); 6.97 (*d*, *J* = 8.2, 1 H); 3.75 (*s*, 6 H); 3.34 (*s*, 3 H). $^{13}$C-NMR: 190.0; 169.2; 147.8; 146.1; 144.5; 135.0; 129.5; 128.3; 123.6; 122.5; 120.1; 112.5; 108.7; 55.7; 52.2; 39.1. EI-MS: 410 (1, $M^+$), 351 (100), 305 (14), 143 (5). HR-MS: 411.1194 ($C_{21}H_{18}N_2O_7^+$; calc. 411.1192).

*Dimethyl 3-(4-Methoxybenzoyl)-1-methylquinoline-4,4(1*H*)-dicarboxylate* (**10i**). Purified by CC (neutral alumina; hexane/AcOEt 80:20). Colorless solid. M.p. 198–200°. $t_R$ 21.59. $^1$H-NMR (500 MHz): 7.53 (*d*, *J* = 8.3, 2 H); 7.46 (*dd*, *J* = 7.8, 1.0, 1 H); 7.24 (*td*, *J* = 7.8, 1.0, 1 H); 7.11 (*s*, 1 H); 7.05 (*t*, *J* = 7.5, 1 H); 6.86 (*d*, *J* = 6.8, 1 H); 6.85 (*d*, *J* = 8.8, 1 H); 3.77 (*s*, 3 H); 3.65 (*s*, 6 H); 3.24 (*s*, 3 H). $^{13}$C-NMR: 191.4; 169.6; 160.7; 145.0; 135.5; 131.0; 129.7; 129.3; 128.0; 122.8; 120.1; 112.5; 112.2; 108.5; 56.1; 54.4; 52.0; 38.8. EI-MS: 395 (3, $M^+$), 336 (100), 143 (16), 77 (3). HR-MS: 396.1451 ($C_{22}H_{21}NO_6^+$; calc. 396.1447).

*Dimethyl 3-Acetyl-1-methylquinoline-4,4(1*H*)-dicarboxylate* (**10n**). Purified by CC (neutral alumina; hexane/AcOEt 85:15). Colorless solid. M.p. 216–218°. $t_R$ 14.77. IR (neat): 3087, 2982, 2945, 1731, 1626, 1567, 1478. $^1$H-NMR: 7.47 (*d*, *J* = 6.9, 1 H); 7.40 (*s*, 1 H); 7.30 (*t*, *J* = 7.8, 1 H); 7.10 (*t*, *J* = 7.7, 1 H); 6.93 (*d*, *J* = 8.3, 1 H); 3.69 (*s*, 6 H); 3.41 (*s*, 3 H); 2.32 (*s*, 3 H). $^{13}$C-NMR (60 MHz): 190.0; 170.5; 143.5; 136.4; 130.2; 129.0; 123.8; 121.0; 113.1; 110.7; 53.0; 39.8; 24.3. EI-MS: 303 (4, $M^+$), 244 (100), 210 (4), 184 (6), 143 (14). HR-MS: 304.1180 ($C_{16}H_{17}NO_5^+$; calc. 304.1185). The structure of **10n** was finally established by an X-ray crystal structure analysis (*Fig. 1*)[3]).

*Dimethyl 3-Acetyl-6-methoxy-1-methylquinoline-4,4(1*H*)-dicarboxylate* (**10o**). Purified by CC (neutral alumina; hexane/AcOEt 70:30). Light yellow solid. M.p. 203–205°. $t_R$ 15.66. IR (neat): 3094, 2938, 1753, 1596, 1485. $^1$H-NMR (500 MHz): 7.32 (*s*, 1 H); 6.99 (*dd*, *J* = 2.0, 1.0, 1 H); 6.81 (*s*, 1 H); 6.80 (*s*, 1 H); 3.71 (*s*, 3 H); 3.62 (*s*, 6 H); 3.33 (*s*, 3 H); 2.24 (*s*, 3 H). $^{13}$C-NMR: 193.1; 170.6; 156.4; 143.6; 130.6; 122.4; 115.28; 115.26; 114.5; 109.5; 56.8; 55.9; 53.2; 40.2; 24.5. EI-MS: 333 (4, $M^+$), 274 (100), 216 (3), 173 (8), 50 (1). HR-MS: 334.1293 ($C_{17}H_{19}NO_6^+$; calc. 334.1291).

*Dimethyl 3-Acetyl-1,6-dimethylquinoline-4,4(1*H*)-dicarboxylate* (**10p**). Isolated by CC ($SiO_2$; hexane/AcOEt 80:20). $t_R$ 13.84. IR ($CH_2Cl_2$): 2975, 2863, 1746, 1478, 1485. $^1$H-NMR: 7.38–7.10 (*m*, 2 H); 7.08 (*s*, 1 H); 6.82–6.80 (*m*, 1 H); 3.69 (*s*, 6 H); 3.39 (*s*, 3 H); 2.31 (*s*, 3 H); 2.20 (*s*, 3 H). $^{13}$C-NMR: 140.0; 136.3; 128.7; 124.9; 117.9; 112.1; 69.4; 52.4; 30.9; 26.2; 21.7. EI-MS: 317 (4, $M^+$), 258 (100), 198 (4), 157 (15), 115 (3), 59 (1). HR-MS: 318.1344 ($C_{17}H_{19}NO_5^+$; calc. 318.1341).

*Dimethyl [(1*Z*)-1-(Dimethylamino)-3-(3-methoxyphenyl)-3-oxoprop-1-en-2-yl]propanedioate* (**11l**). Purified by CC (neutral alumina; hexane/AcOEt 85:15). $t_R$ 14.5. $^1$H-NMR (500 MHz): 7.46 (*dt*, *J* = 8.0, 1.0, 1 H); 7.42 (*t*, *J* = 2.0, 1 H); 7.31 (*t*, *J* = 8.3, 1 H); 7.26 (*s*, 1 H); 7.06 (*ddd*, *J* = 8.3, 2.9, 1.0, 1 H); 3.79 (*s*, 3 H); 3.75 (*s*, 6 H); 3.59 (*s*, 1 H); 2.38 (*s*, 6 H). $^{13}$C-NMR: 188.7; 166.7; 159.0; 141.1; 137.8; 128.6; 128.4; 120.4; 118.8; 112.0; 58.6; 54.5; 51.7; 39.8. EI-MS: $M^+$ not observed, 276 (100), 217 (33), 135 (14), 107 (7), 72 (14), 59 (2). HR-MS: 336.1442 ($C_{17}H_{21}NO_6^+$; calc. 336.1447).

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