

Reaction of Isocyanides, Dialkyl Acetylenedicarboxylates, and α -Keto Lactones: Unexpected Participation of an Ester Carbonyl Group in the Isocyanide-Based Three-Component Reaction

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Abstract: The reaction of benzofuran-2,3-dione derivatives with dialkyl acetylenedicarboxylates and alkyl isocyanides results in a three-component addition reaction in which the ester carbonyl group is incorporated into a two-atom assembling unit to give highly functionalized γ -spiroiminolactones in good yield. This reaction provides the first example of an ester carbonyl group participating in an isocyanide-based multicomponent reaction.

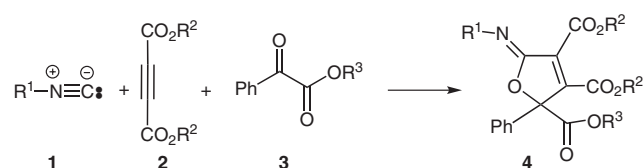
Key words: ketones, dialkyl acetylenedicarboxylates, alkyl isocyanides, spiro compounds, lactones

Multicomponent reactions (MCRs), by virtue of their convergence, productivity, facile execution, and generally high yields, have attracted much attention from the viewpoint of combinatorial chemistry.^{1,2} Of pivotal importance in this area are the isocyanide-based MCRs such as the versatile Ugi and Passerini reactions.^{3,4} The reactivity of nucleophilic carbenes such as isocyanides towards dimethyl acetylenedicarboxylate (DMAD) is well documented.^{5,6} The initially formed zwitterionic intermediate from DMAD and isocyanide has been shown to undergo further reactions with different electrophilic reagents, leading to a variety of complex heterocyclic compounds. These reactions have been the subject of detailed investigations by a number of research groups.^{7–10}

Recently, γ -spiroiminolactones have become interesting because of their properties as antibacterial agents, aldosterone inhibitors, and proper precursors for the preparation of a wide spectrum of natural compounds.¹¹ Iminolactones could be hydrolyzed with aqueous hydrochloric acid to produce butenolides¹² [also known as furan-2(5*H*)-ones], an important class of biologically active natural products, which have been used in medicine and agriculture.^{13–17} So far, several synthetic methods have been reported for the preparation of iminolactones.^{18–24} The most widely used approach to iminolactone synthesis is based on isocyanides.^{18–22}

On the basis of our previous success with isocyanide-based MCRs, we investigated the reactions of alkyl phenylglyoxylates **3** as the α -keto ester components with dialkyl acetylenedicarboxylates (DAAD) **2** and alkyl isocyanides **1**; the addition products **4** were obtained by par-

ticipation of the keto carbonyl group²⁵ (Scheme 1). We were not able to obtain the annulated product at the ester carbonyl group.

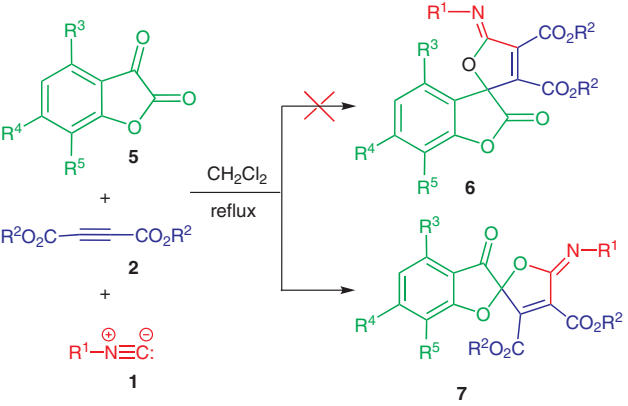


Scheme 1

Impressed by the success of the reaction, we turned our attention to trapping the zwitterions with α -keto lactones such as benzofuran-2,3-diones **5**, as this would furnish γ -spiroiminolactone derivatives **6** if the reaction proceeded similarly to that of alkyl phenylglyoxylates (Table 1). However, the reaction followed an unexpected course, affording γ -spiroiminolactone derivatives **7** instead of **6** in fairly high yields (Table 1). This is the first example of a new type of isocyanide-based MCR in which the ester carbonyl group is incorporated as the carbon–oxygen unit.

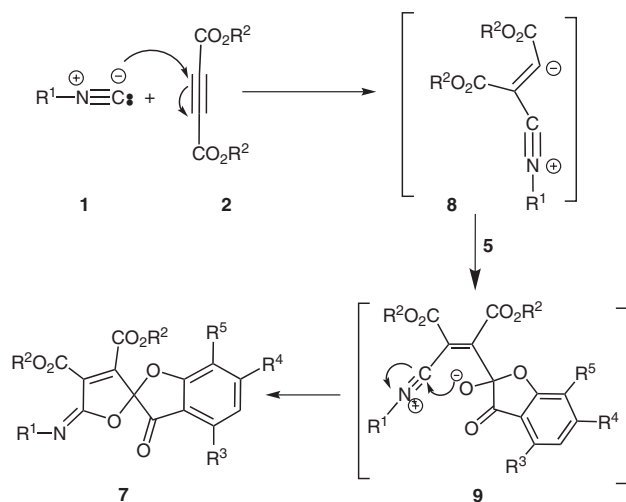
The structures of the products were deduced from their IR, 1H NMR, and ^{13}C NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at the appropriate m/z values. For example, the 1H NMR spectrum of **7a** contained multiplet signals for a cyclohexyl ring (δ = 1.12–1.71), two singlets for the aryl methyl groups (δ = 2.36, 2.52), a multiplet for N–CH of the cyclohexyl ring (δ = 3.65), two singlets for two methoxy groups (δ = 3.65 and 3.90), a singlet for an aryl proton (δ = 6.69, R^5 = H), and a singlet for the other aryl proton (δ = 6.72). The assignment is supported by the IR absorptions at 1752, 1736, 1730 (3 C=O), and 1684 (C=N) cm^{-1} . The proton-decoupled ^{13}C NMR spectrum of **7a** showed 23 distinct resonances, and partial assignment of these resonances is given in the experimental section. The characteristic ^{13}C NMR signal due to the spiro carbon appeared at δ = 106.64, that of the two ester carbonyls at δ = 161.1 and 171.13, and the ketone carbonyl at δ = 191.12.

Although the mechanism of the reaction between the isocyanide and dialkyl acetylenedicarboxylate in the presence of carbonyl groups has not been established experimentally, a possible pathway is proposed in Scheme 2. On the basis of the well-established chemistry of isocyanides,^{26,27} it is reasonable to assume that a highly

Table 1 Reactions of Benzofuran-2,3-diones **5** with Dialkyl Acetylenedicarboxylates **2** and Isocyanides **1**


7	R ¹	R ²	R ³	R ⁴	R ⁵	Yield (%)
7a	Cy	Me	Me	Me	H	65
7b	Cy	Et	Me	Me	Me	60
7c	Cy	<i>i</i> -Pr	Me	H	Me	65
7d	<i>t</i> -Bu	Et	Me	Me	H	70
7e	<i>t</i> -Bu	Et	Me	Me	Me	55
7f	CMe ₂ CH ₂ <i>t</i> -Bu	Et	Me	Me	H	70
7g	CMe ₂ CH ₂ <i>t</i> -Bu	Me	Me	Me	H	75
7h	CMe ₂ CH ₂ <i>t</i> -Bu	Me	Me	Me	Me	70
7i	CMe ₂ CH ₂ <i>t</i> -Bu	Et	Me	Me	Me	65

reactive 1:1 zwitterionic intermediate **8** initially forms by a Michael-type addition reaction of isocyanide **1** with dialkyl acetylenedicarboxylate **2**; subsequent addition of **8** to the ester carbonyl group of benzofuran-2,3-dione **5** results in the formation of **9**, which undergoes intramolecular cyclization to deliver γ -spiroiminolactone **7**.

**Scheme 2**

In summary, we have demonstrated the first example of the participation of an ester carbonyl group in a multicomponent reaction with DAAD and isocyanides to synthesize γ -spiroiminolactone backbones. Although the ester carbonyl group is known to be generally less reactive than a ketone carbonyl group, the ester carbonyl group in α -keto lactones **5** is sufficiently reactive to compete with the ketone carbonyl group. The reason for the difference in reactivity between the keto carbonyl group and the ester carbonyl group is not clear to us, but steric hindrance around the keto moiety may retard the reactivity of the ketone portion of the benzofuran-2,3-diones **5** in this reaction. Fairly good yields of the products and the use of simple starting materials are the main advantages of this method. The reactions were performed under neutral conditions, and the starting materials and reagents can be mixed without any activation or modification.

Melting points were determined on an Electro thermal 9100 apparatus and are uncorrected. IR spectra were obtained on a Perkin–Elmer 783 infrared spectrophotometer. ¹H and ¹³C NMR spectra were measured with a Bruker DRX-500 Avance spectrometer at 500.1 and 125.77 MHz, respectively. Mass spectra were recorded on a Shimadzu GCMS-QP5050 mass spectrometer operating at an ionization potential of 70 eV. Benzofuran-2,3-diones were prepared by known methods.²⁸ Isocyanides and acetylenic esters were obtained from Merck (Germany) and Fluka (Buchs, Switzerland) and all materials were used without further purification.

Dialkyl 5'-(Alkylimino)-3-oxospiro[benzofuran-2(3*H*),2'-(5'*H*)-furan]-3',4'-dicarboxylates **7**; General Procedure

A soln of isocyanide **1** (1.1 mmol) in anhyd CH₂Cl₂ (2 mL) was added over 10 min by syringe to a stirred soln of benzofuran-2,3-dione **5** (1.0 mmol) and dialkyl acetylenedicarboxylate **2** (1.1 mmol) in anhyd CH₂Cl₂ (5 mL) at –10 °C. The reaction mixture was allowed to warm to r.t. and was then refluxed for about 12 h. On completion of the reaction, the solvent was removed under vacuum, and cold Et₂O (5 mL; for **7a–e**) or cold hexane (5 mL; for **7f–i**) was added to the residue. This produced a solid precipitate, which was collected by filtration and washed with cold EtOH (2 mL); this gave pure product **7**.

Dimethyl 5'-(Cyclohexylimino)-4,6-dimethyl-3-oxospiro[benzofuran-2(3*H*),2'-(5'*H*)-furan]-3',4'-dicarboxylate (**7a**)

Yield: 0.276 g (65%); mp 148–149 °C.

IR (KBr): 2966 (C–H_{st}), 1752, 1736, 1730 (3 C=O), 1684 (C=N) cm^{–1}.

¹H NMR (500 MHz, CDCl₃): δ = 1.12–1.71 [m, 10 H, CH(CH₂)₅], 2.36 (s, 3 H, Ar-CH₃), 2.52 (s, 3 H, Ar-CH₃), 3.60 (m, 1 H, NCH), 3.65 (s, 3 H, OMe), 3.90 (s, 3 H, OMe), 6.69 (s, 1 H, H₅), 6.72 (s, 1 H, H₇).

¹³C NMR (125 MHz, CDCl₃): δ = 17.68, 22.55 (2 Ar-CH₃), 24.49, 24.53, 25.58, 32.99, 33.18 (5 CH₂), 52.96, 53.2 (2 OCH₃), 57.31 (N-CH), 106.64 (C_{spiro}), 110.56, 114.94, 125.15, 136.71, 140.19, 140.55, 150.95, 151.46, 159.80 (C=N), 161.10, 171.13, 191.12 (3 C=O).

MS (EI, 70 eV): m/z (%) = 427 [M⁺] (12), 330 [M⁺ – C₆H₁₁N] (4), 286 [M⁺ + 1 – C₆H₆O₄] (4), 279 [M⁺ – 2CO₂Me – 2 CH₃] (38), 149 [C₉H₈O₂] (78), 91 [C₇H₈⁺] (17), 59 [CO₂Me⁺] (9).

Diethyl 5'-(Cyclohexylimino)-4,6,7-trimethyl-3-oxospiro[benzofuran-2(3*H*),2'-(5'*H*)-furan]-3',4'-dicarboxylate (**7b**)

Yield: 0.281 g (60%); mp 153–155 °C.

IR (KBr): 2987 (C–H_{st}), 1760, 1740, 1735 (3 C=O), 1685 (C=N) cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 1.00 (t, ³J_{HH} = 7.1 Hz, 3 H, CH₂CH₃), 1.35 (t, ³J_{HH} = 7.1 Hz, 3 H, CH₂CH₃), 1.15–1.72 [m, 10 H, CH(CH₂)₅], 2.12, 2.28, 2.50 (3 s, 9 H, 3 Ar-CH₃), 3.63 (m, 1 H, NCH), 4.08 (m, 2 H, OCH₂), 4.4 (q, ³J_{HH} = 7.1 Hz, 2 H, OCH₂), 6.7 (s, 1 H, H₅).

¹³C NMR (125 MHz, CDCl₃): δ = 10.37, 13.45 (2 CH₂CH₃), 14.02, 17.32, 20.34 (3 Ar-CH₃), 24.47, 24.52, 25.64, 32.98, 33.21 (5 CH₂), 57.13 (N-CH), 61.93, 62.49 (2 OCH₂), 106.77 (C_{spiro}), 114.98, 118.36, 126.38, 136.98, 137.04, 140.20, 149.01, 151.70, 159.28 (C=N), 160.83, 169.36, 192.17 (3 C=O).

MS (EI, 70 eV): *m/z* (%) = 469 [M⁺] (19), 372 [M⁺ – C₆H₁₁N] (7), 341 [M⁺ – 1 – C₆H₁₁N – 2CH₃] (4), 307 [M⁺ – 1 – 2CO₂CH₂CH₃ – CH₃] (47), 269 [M⁺ – C₈H₁₀O₄ – 2CH₃] (7), 225 [M⁺ – 1 – C₆H₁₁N – 2CO₂CH₂CH₃] (100), 163 [C₁₀H₁₀O₂⁺] (87).

Diisopropyl 5'-(Cyclohexylimino)-4,7-dimethyl-3-oxo-spiro[benzofuran-2(3H),2'(5'H)-furan]-3',4'-dicarboxylate (7c)
Yield: 0.314 g (65%); mp 147–148 °C.

IR (KBr): 2990 (C–H_{st}), 1765, 1750, 1740 (3 C=O), 1680 (C=N) cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 0.91 (d, ³J_{HH} = 6.16 Hz, 6 H, CH(CH₃)₂), 0.95 (d, ³J_{HH} = 6.21 Hz, 6 H, CH(CH₃)₂), 1.20–1.54 [m, 10 H, CH(CH₂)₅], 2.22, 2.53 (2 s, 6 H, 2 Ar-CH₃), 3.63 (m, 1 H, NCH), 4.91, 5.30 (2 m, 2 H, 2 OCH(CH₃)₂), 6.79 (d, ³J_{HH} = 7.5 Hz, 1 H, H₅), 7.30 (d, ³J_{HH} = 7.49 Hz, 1 H, H₇).

¹³C NMR (125 MHz, CDCl₃): δ = 13.81, 17.36 (2 Ar-CH₃), 21.19, 21.30, 21.56, 21.72 (4 Me of 2 CH(CH₃)₂), 24.31, 24.35, 25.70, 32.98, 33.20, (5 CH₂), 56.83 (N-CH), 69.92, 70.56 (2 OCH(CH₃)₂), 106.31 (C_{spiro}), 117.10, 119.96, 124.14, 136.83, 137.71, 139.16, 140.55, 151.47, 158.53 (C=N), 160.35, 169.30, 192.94 (3 C=O).

MS (EI, 70 eV): *m/z* (%) = 483 [M⁺] (13), 397 [M⁺ + 1 – CO₂i-Pr] (3), 386 [M⁺ – C₆H₁₁N] (13), 336 [M⁺ – 1 – CO₂i-Pr – Oi-Pr] (10), 284 [M⁺ – 1 – C₁₀H₁₄O₄] (10), 255 [M⁺ – C₁₀H₁₄O₄ – 2CH₃] (14), 211 [M⁺ + 1 – C₆H₁₁N – CO₂i-Pr – Oi-Pr – 2CH₃] (63), 149 [C₉H₈O₂⁺] (95), 91 [C₇H₈⁺] (16), 43 [CH(CH₃)₂⁺] (100).

Diethyl 5'-(tert-Butylimino)-4,6-dimethyl-3-oxospiro[benzofuran-2(3H),2'(5'H)-furan]-3',4'-dicarboxylate (7d)

Yield: 0.300 g (70%); mp 142–144 °C.

IR (KBr): 3000 (C–H_{st}), 1740, 1730, 1720 (3 C=O), 1680 (C=N) cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 0.99 (t, ³J_{HH} = 6.9 Hz, 3 H, CH₂CH₃), 1.26 (s, 9 H, C(CH₃)₃), 1.33 (t, ³J_{HH} = 6.9 Hz, 3 H, CH₂CH₃), 2.36, 2.52 (2 s, 6 H, 2 Ar-CH₃), 4.06 (q, ³J_{HH} = 4.4 Hz, 2 H, OCH₂), 4.36 (q, ³J_{HH} = 6.9 Hz, 2 H, OCH₂), 6.91 (s, 1 H, H₅), 6.71 (s, 1 H, H₇).

¹³C NMR (125 MHz, CDCl₃): δ = 13.42, 14.03 (2 CH₂CH₃), 17.64, 22.53 (2 Ar-CH₃), 29.49, 29.61, 29.75 [C(CH₃)₃], 55.78 [C(CH₃)₃], 61.95, 62.34 (2 OCH₂), 107.12 (C_{spiro}), 110.48, 115.18, 125.88, 135.74, 140.38, 141.53, 149.21, 150.72, 159.27 (C=N), 160.92, 171.17, 191.43 (3 C=O).

MS (EI, 70 eV): *m/z* (%) = 429 [M⁺] (4), 373 [M⁺ + 1 – C(CH₃)₃] (6), 327 [M⁺ + 1 – NC(CH₃)₃ – 2 CH₃] (11), 255 [M⁺ – 1 – NC(CH₃)₃ – CO₂CH₂CH₃ – CH₂CH₃] (5), 225 [M⁺ – NC(CH₃)₃ – CO₂CH₂CH₃ – OCH₂CH₃ – CH₃] (14), 149 [C₉H₈O₂⁺] (100), 91 [C₇H₈⁺] (6).

Diethyl 5'-(tert-Butylimino)-4,6,7-trimethyl-3-oxospiro[benzofuran-2(3H),2'(5'H)-furan]-3',4'-dicarboxylate (7e)

Yield: 0.244 g (55%); mp 141–143 °C.

IR (KBr): 2995 (C–H_{st}), 1735, 1725, 1720 (3 C=O), 1685 (C=N) cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 0.99 (t, ³J_{HH} = 7.0 Hz, 3 H, CH₃), 1.27 (s, 9 H, C(CH₃)₃), 1.34 (t, ³J_{HH} = 7.0 Hz, 3 H, CH₃), 2.11, 2.87, 2.5 (3 s, 9 H, 3 Ar-CH₃), 4.05 (m, 2 H, OCH₂CH₃), 4.38 (q, ³J_{HH} = 7.04 Hz, 2 H, OCH₂CH₃), 6.7 (s, 1 H, H₅).

¹³C NMR (125 MHz, CDCl₃): δ = 10.34, 13.44 (2 CH₂CH₃), 14.05, 17.31, 20.33 (3 Ar-CH₃), 29.62, [C(CH₃)₃], 55.74, [C(CH₃)₃], 61.87, 62.36 (2 OCH₂), 107.21 (C_{spiro}), 115.00, 118.35, 126.30, 135.95, 136.97, 141.47, 148.89, 149.37, 159.33 (C=N), 161.09, 169.39, 192.21 (3 C=O).

MS (EI, 70 eV): *m/z* (%) = 443 [M⁺] (4), 387 [M⁺ + 1 – C(CH₃)₃] (6), 341 [M⁺ – C(CH₃)₃ – 3 CH₃] (10), 240 [M⁺ + 1 – CO₂CH₂CH₃ – C(CH₃)₃] (2), 225 [M⁺ + 1 – 2CO₂CH₂CH₃ – NC(CH₃)₃] (13), 163 [C₁₀H₁₀O₂⁺] (100), 91 (C₇H₈⁺, 14).

Diethyl 4,6-Dimethyl-3-oxo-5'-[(1,1,3,3-tetramethylbutyl)imino]spiro[benzofuran-2(3H),2'(5'H)-furan]-3',4'-dicarboxylate (7f)

Yield: 0.340 g (70%); mp 145–146 °C.

IR (KBr): 3000 (C–H_{st}), 1765, 1760, 1730 (3 C=O), 1688 (C=N) cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 0.96 (s, 9 H, CMe₃), 1.01 (t, ³J_{HH} = 7.0 Hz, 3 H, CH₂CH₃), 1.29, 1.31 (2 s, 6 H, CMe₂), 1.34 (t, ³J_{HH} = 7.7 Hz, 3 H, CH₂CH₃), 1.54, 1.59 (AB system, ²J_{HH} = 14.3 Hz, 2 H, CH₃), 2.37, 2.54 (2 s, 6 H, 2 Ar-CH₃), 4.07 (q, ³J_{HH} = 5.5 Hz, 2 H, OCH₂), 4.35 (dq, ³J_{HH} = 4.4 Hz, ²J_{HH} = 4.5 Hz, 2 H, OCH₂), 6.70 (s, 1 H, H₅), 6.72 (s, 1 H, H₇).

¹³C NMR (125 MHz, CDCl₃): δ = 13.43, 14.03 (2 CH₂CH₃), 17.65, 22.52 (2 Ar-Me), 29.79 (CMe₂), 31.55 (CMe₃), 31.90 (CH₂), 55.38 (CMe₃), 59.26 (N-CMe₂), 61.89, 62.26 (2 OCH₂), 107.21 (C_{spiro}), 110.47, 115.25, 125.82, 135.34, 140.37, 141.74, 148.14, 150.60, 159.35 (C=N), 161.00, 171.17, 191.48 (3 C=O).

MS (EI, 70 eV): *m/z* (%) = 486 [M⁺ + 1] (5), 470 [M⁺ – CH₃] (3), 439 [M⁺ – 1 – OCH₂CH₃] (4), 429 [M⁺ + 1 – C(CH₃)₃] (3), 414 [M⁺ – CH₂ – C(CH₃)₃] (10), 358 [M⁺ – C₈H₁₇N] (6), 327 [M⁺ – C₈H₁₇N – 2CH₃] (21), 308 [M⁺ – 1 – 2CO₂CH₂CH₃ – 2CH₃] (9), 149 [C₉H₈O₂⁺] (100).

Dimethyl 4,6-Dimethyl-3-oxo-5'-[(1,1,3,3-tetramethylbutyl)imino]spiro[benzofuran-2(3H),2'(5'H)-furan]-3',4'-dicarboxylate (7g)

Yield: 0.344 g (75%); mp 202–204 °C.

IR (KBr): 2990 (C–H_{st}), 1750, 1735, 1720 (3 C=O), 1685 (C=N) cm⁻¹.

¹H NMR (500 MHz, CDCl₃): δ = 0.95 (s, 9 H, CMe₃), 1.29, 1.31 (2 s, 6 H, CMe₂), 1.55, 1.59 (AB system, ²J_{HH} = 14.3 Hz, 2 H, CH₂), 2.38, 2.54 (2 s, 6 H, 2 Ar-CH₃), 3.66, 3.89 (2 s, 6 H, 2 OCH₃), 6.71 (s, 1 H, H₅), 6.73 (s, 1 H, H₇).

¹³C NMR (125 MHz, CDCl₃): δ = 17.53, 22.53 (2 Ar-CH₃), 29.79, (CMe₂), 31.51 (CMe₃), 31.94 (CH₂), 52.83, 52.90 (2 OCH₃), 55.42 (CMe₃), 59.39 (N-CMe₂), 107.17 (C_{spiro}), 110.52, 115.05, 125.98, 135.28, 140.43, 141.63, 148.02, 150.69, 159.93 (C=N), 161.40, 171.16, 191.23 (3 C=O).

MS (EI, 70 eV): *m/z* (%) = 458 [M⁺ + 1] (9), 442 [M⁺ – CH₃] (3), 425 [M⁺ – 1 – OCH₃] (3), 398 [M⁺ + 1 – CO₂CH₃] (3), 386 [M⁺ – CH₂ – C(CH₃)₃] (11), 345 [M⁺ – C(CH₃)₂ – CH₂ – C(CH₃)₃] (5), 330 [M⁺ – NC(CH₃)₂ – CH₂ – C(CH₃)₃] (5), 309 [M⁺ – 2CO₂CH₃ – 2CH₃] (19), 149 [C₉H₈O₂⁺] (100).

Dimethyl 4,6,7-Trimethyl-3-oxo-5'-[(1,1,3,3-tetramethylbutyl)imino]spiro[benzofuran-2(3H),2'(5'H)-furan]-3',4'-dicarboxylate (7h)

Yield: 0.330 g (70%); mp 161–163 °C.

IR (KBr): 2995 (C–H_{st}), 1745, 1735, 1725 (3 C=O), 1685 (C=N) cm⁻¹.¹H NMR (500 MHz, CDCl₃): δ = 0.96 (s, 9 H, CMe₃), 1.29, 1.31 (2 s, 6 H, CMe₂), 1.58, (s, 2 H, CH₂), 2.12, 2.29, 2.51 (3 s, 9 H, 3 Ar-CH₃), 3.66, 3.89 (2 s, 6 H, 2 OCH₃), 6.72 (s, 1 H, H₅).¹³C NMR (125 MHz, CDCl₃): δ = 10.30, 17.53, 22.53 (3 Ar-CH₃), 29.77 (CMe₂), 31.51 (CMe₃), 31.91 (CH₂), 52.81, 52.90 (2 OCH₃), 55.92 (CMe₃), 59.28 (N-CMe₂), 107.21 (C_{spiro}), 114.87, 118.38, 126.39, 135.45, 137.06, 141.55, 148.24, 148.89, 159.95 (C=N), 161.54, 169.35, 191.97 (3 C=O).MS (EI, 70 eV): *m/z* (%) = 471 [M⁺] (3), 456 [M⁺ – 1 – OCH₃] (3), 412 [M⁺ – CO₂CH₃] (3), 400 [M⁺ – C₅H₁₁] (5), 359 [M⁺ – C₈H₁₇] (5), 215 [M⁺ C₈H₁₇N] (6), 309 [M⁺ + 1 – 2CO₂CH₃ – 3CH₃] (16), 163 [C₁₀H₁₀O₂⁺] (100), 91 [C₇H₈⁺] (8).**Diethyl 4,6,7-Trimethyl-3-oxo-5'-[(1,1,3,3-tetramethylbutyl)imino]spiro[benzofuran-2(3H),2'(5'H)-furan]-3',4'-dicarboxylate (7i)**

Yield: 0.324 g (65%); mp 128–130 °C.

IR (KBr): 2995 (C–H_{st}), 1745, 1730, 1725 (3 C=O), 1680 (C=N) cm⁻¹.¹H NMR (500 MHz, CDCl₃): δ = 0.96 (s, 9 H, CMe₃), 1.00 (t, ³J_{HH} = 7.1 Hz, 3 H, CH₂CH₃), 1.30, 1.31 (2 s, 6 H, CMe₂), 1.35 (t, ³J_{HH} = 7.6 Hz, 3 H, CH₂CH₃), 1.58 (s, 2 H, CH₂), 2.11, 2.28, 2.50 (3 s, 9 H, 3 Ar-CH₃), 4.06 (dq, ³J_{HH} = 5.5 Hz, 2 H, ²J_{HH} = 4.5 Hz, OCH₂), 4.36 (dq, ³J_{HH} = 4.4 Hz, 2 H, ²J_{HH} = 4.5 Hz, OCH₂), 6.71 (s, 1 H, H₅).¹³C NMR (125 MHz, CDCl₃): δ = 10.28, 13.44 (CH₂CH₃), 14.04, 17.28, 20.28 (3 Ar-CH₃), 29.80 (CMe₂), 31.55 (CMe₃), 31.90 (CH₂), 55.31 (CMe₂), 59.20 (N-CMe₂), 61.90, 62.24 (2 OCH₂), 107.21 (C_{spiro}), 115.05, 117.64, 125.82, 126.64, 135.57, 136.34, 140.35, 148.35, 159.37 (C=N), 161.13, 169.37, 192.21 (3 C=O).MS (EI, 70 eV): *m/z* (%) = 499 [M⁺] (5), 484 [M⁺ – CH₃] (3), 453 [M⁺ – OCH₂CH₃] (11), 382 [M⁺ + 1 – CO₂CH₂CH₃ – 3CH₃] (16), 372 [M⁺ – C₈H₁₇N] (7), 337 [M⁺ + 1 – CO₂CH₂CH₃ – 3CH₃ – OCH₂CH₃] (13), 163 [C₁₀H₁₀O₂⁺] (100).**Acknowledgment**

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