

## Synthesis of functionalized furans through the reaction of isocyanides

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**Abstract:** In this work, electropolymerization of N,N-dimethylaniline (DMA) onto a carbon paste electrode (CPE) has been done in the presence of sodium dodecyl sulfate (SDS) in an acidic solution. It was a novel matrix for the deposition of silver (Ag) particles. Then, the electrochemical oxidation of formaldehyde (CH<sub>2</sub>O) is studied at the surface of this modified electrode in an alkaline solution. The electrochemical behavior and electrocatalytic activity of the electrode were studied using cyclic voltammetry studies. Several parameters such as the number of potential cycles for preparation of the polymeric film, and variables such as Ag<sup>+</sup> concentration, accumulation time of Ag<sup>+</sup> ions, and CH<sub>2</sub>O concentration were also investigated for obtaining optimal conditions. Under these conditions, the peak current response increased linearly with CH<sub>2</sub>O concentration over the range of 0.05–0.8 mM.

**Keywords:** isocyanide, ethyl bromopyruvate, dibenzoylacetylene, three-component reaction, acetylenic ester, iminolactone.

### Introduction

Isocyanides are the only class of stable organic compounds with a formally divalent carbon. Owing to its reactivity the isocyanide group differs fundamentally from other functional groups [1-4]. One of the classic themes in the chemistry of isocyanides is heterocyclic synthesis [5]. Multi-component reactions (MCRs), by virtue of their convergence, facile execution, and generally high yields of products, have attracted much attention from the point of combinatorial chemistry. Of pivotal importance in this area are the isocyanide-based MCRs such as the versatile Ugi and Passerini reactions [1-6]. The reactivity of nucleophilic carbenes such as isocyanides towards dimethyl acetylenedicarboxylate (DMAD) is well recognized [6-9]. The initially formed zwitterionic intermediate, from DMAD and isocyanide, has been shown to undergo further reaction with

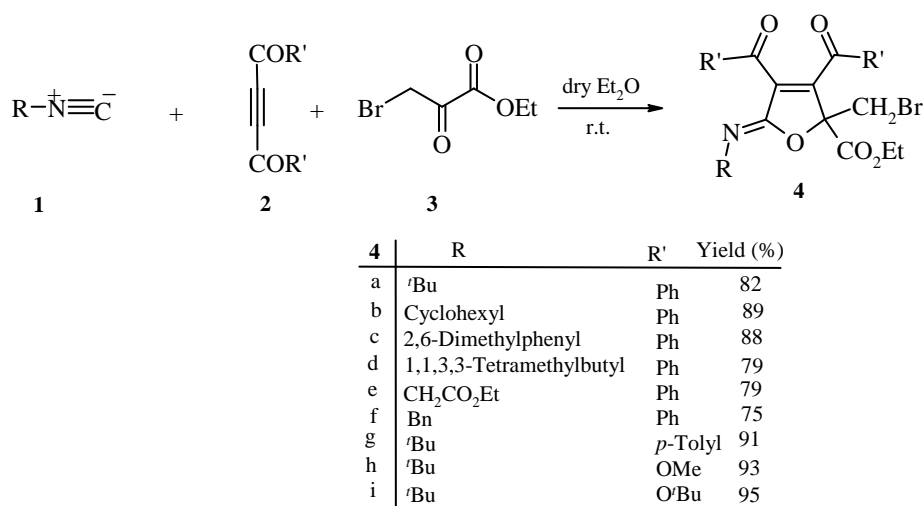
different electrophilic reagents, leading to a variety of complex heterocyclic compounds.

These reactions have been the subject of detailed investigation by a number of research groups [10-12]. The reaction of alkyl(aryl) isocyanides and activated acetylenes in the presence of ethyl bromopyruvate was investigated and the results are presented here.

### Results and discussion

*tert*-Butyl isocyanide (**1a**) and dibenzoylacetylene (**2a**) undergo a smooth reaction in the presence of ethyl bromopyruvate (**3**), in dry diethyl ether at room temperature to produce ethyl 3,4-dibenzoyl-2-bromomethyl-5-*tert*-butylimino-2,5-dihydro-furan-2-carboxylate (**4a**) in 82% yield (Scheme 1). Using the isocyanides **1b-1f**, compounds **4b-4i** are obtained in 75-89% yields (see Scheme 1). The structures of compounds **4a-4i** were deduced from their elemental analyses and their IR, <sup>1</sup>H and <sup>13</sup>C NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at the appropriate *m/z* values.

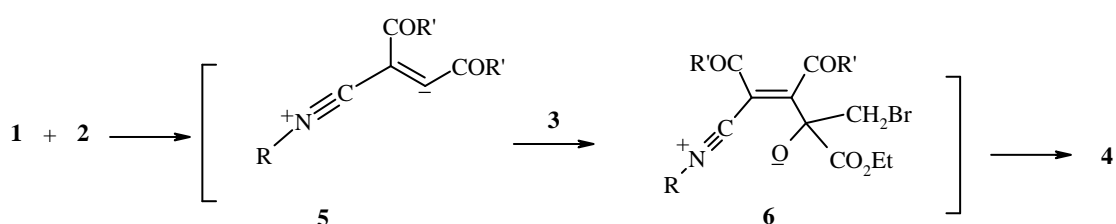
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**Scheme 1:** Synthesis of furan derivatives **4**

The <sup>1</sup>H NMR spectrum of **4a** in CDCl<sub>3</sub> showed a triplet at  $\delta = 1.26$  ( $^3J_{\text{HH}} = 7.2$  Hz) for the methyl group and a singlet at 1.27 ppm for the *tert*-butyl group. The methylene protons of CH<sub>2</sub>Br and OCH<sub>2</sub> moieties are diastereotopic and showed characteristic AB quartet systems at  $\delta = 4.18$  and 4.32 ppm. Three single resonances at  $\delta = 165.9$ , 188.7, and 190.4 ppm are observed in the <sup>13</sup>C NMR spectrum of **4a**, which are attributed to the carbonyl groups. The <sup>1</sup>H and <sup>13</sup>C NMR spectra of **4b-4i** are similar to those for **4a** except for the imino moieties and the substituents in positions 3 and 4, which show characteristic resonances in appropriate regions of the spectrum.

Mechanistically, it is conceivable that the reaction involves the initial formation of a 1,3-

dipolar intermediate **5** between isocyanide and the acetylenic compound [7], which reacts with ethyl bromopyruvate to produce **6**. Cyclization of this zwitterionic intermediate leads to the 2-bromomethyl-5-alkyl(aryl)imino-2,5-dihydro-furan derivative **4** (Scheme 2).

**Scheme 2:** Proposed mechanism for the synthesis of **4**

In conclusion, this method is simple and efficient to obtain 2-bromomethyl-5-alkyl(aryl)imino-2,5-dihydro-furan derivatives. The presented one-pot reaction carries the advantage that not only is the reaction performed under neutral conditions, but the substances can be mixed without any prior activation or modification.

## Experimental

### Materials and methods

1,4-Diaryl-but-2-yne-1,4-diones were prepared by a known procedure [13, 14]. Other chemicals used in this work were purchased from Fluka and used without further purification. Melting points were measured on an Electrothermal 9100 apparatus. NMR spectra were recorded with a Bruker DRX-500 AVANCE instrument (500.1 MHz for <sup>1</sup>H and 125.7 MHz for <sup>13</sup>C) with CDCl<sub>3</sub> as solvent. Chemical shifts are given in ppm ( $\delta$ ) relative to internal TMS, and coupling constant (*J*) are reported in Hertz (Hz). Elemental analyses

for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. These results agreed favorably with the calculated values. Mass spectra were recorded with a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were measured with a Shimadzu IR-460 spectrometer.

### General procedure

To a stirred solution of dibenzoylacetylene (0.23 g, 1 mmol) and bromopyruvate (0.19 g, 1 mmol) in 10 mL dry ether was added *tert*-butyl isocyanide (0.12 mL, 1 mmol) at room temperature. The reaction mixture was then stirred for 24 h. The solvent was removed under reduced pressure and the viscous residue was purified by column chromatography on silica gel (Merck 230-400 mesh) using *n*-hexane-EtOAc (3:1) as eluent.

*Ethyl 3,4-dibenzoyl-2-bromomethyl-5-tert-butylimino-2,5-dihydro-furan-2-carboxylate (4a):*

Pale yellow crystals, yield: 0.42 g (82%), m.p. 115-117 °C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1726, 1680, and 1652 (C=O), 1583 (C=N), 1263 (C-O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  = 7.63 (2 H, d,  $^3J_{\text{HH}} = 7.6$  Hz, 2  $\text{CH}_{\text{ortho}}$ ), 7.54 (2 H, d,  $^3J_{\text{HH}} = 7.5$  Hz, 2  $\text{CH}_{\text{ortho}}$ ), 7.47 (1 H, t,  $^3J_{\text{HH}} = 7.3$  Hz,  $\text{CH}_{\text{para}}$ ), 7.41 (1 H, t,  $^3J_{\text{HH}} = 7.2$  Hz,  $\text{CH}_{\text{para}}$ ), 7.25 (2 H, t,  $^3J_{\text{HH}} = 7.8$  Hz, 2  $\text{CH}_{\text{meta}}$ ), 7.14 (2 H, t,  $^3J_{\text{HH}} = 7.7$  Hz, 2  $\text{CH}_{\text{meta}}$ ), 4.32 (2 H, ABX<sub>3</sub> system,  $\text{OCH}_2$ ), 4.18 (2 H, AB system,  $^2J_{\text{AB}} = 11.4$  Hz,  $\Delta\nu_{\text{AB}} = 13.2$  Hz,  $\text{CH}_2\text{Br}$ ), 1.27 (9 H, s,  $\text{CMe}_3$ ), 1.26 (3 H, t,  $^3J_{\text{HH}} = 7.2$  Hz,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR:  $\delta$  = 190.4 (C=O), 188.7 (C=O), 165.9 (C=O), 153.0 (C=N), 146.2 (C), 141.7 (C), 136.5 ( $\text{C}_{\text{ipso}}$ ), 136.4 ( $\text{C}_{\text{ipso}}$ ), 134.0 (CH), 133.9 (CH), 129.2 (2 CH), 129.0 (2 CH), 128.7 (2 CH), 128.4 (2 CH), 89.9 (C), 63.1 ( $\text{OCH}_2$ ), 55.3 (C-N), 33.7 ( $\text{CH}_2\text{Br}$ ), 29.6 ( $\text{CMe}_3$ ), 14.0 ( $\text{CH}_3$ ) ppm.

*Ethyl 3,4-dibenzoyl-2-bromomethyl-5-cyclohexylimino-2,5-dihydro-furan-2-carboxylate (4b):*

Pale yellow powder, yield: 0.48 g (89%), m.p. 127-129 °C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1740, 1681, and 1658 (C=O), 1587 (C=N), 1254 (C-O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  = 7.63 (2 H, d,  $^3J_{\text{HH}} = 7.4$  Hz, 2  $\text{CH}_{\text{ortho}}$ ), 7.52 (2 H, d,  $^3J_{\text{HH}} = 7.5$  Hz, 2  $\text{CH}_{\text{ortho}}$ ), 7.44 (1 H, t,  $^3J_{\text{HH}} = 7.3$  Hz,  $\text{CH}_{\text{para}}$ ), 7.39 (1 H, t,  $^3J_{\text{HH}} = 7.2$  Hz,  $\text{CH}_{\text{para}}$ ), 7.30 (2 H, t,  $^3J_{\text{HH}} = 7.5$  Hz, 2  $\text{CH}_{\text{meta}}$ ), 7.16 (2 H, t,  $^3J_{\text{HH}} = 7.2$  Hz, 2  $\text{CH}_{\text{meta}}$ ), 4.33 (2 H, ABX<sub>3</sub> system,  $\text{OCH}_2$ ), 4.22 (2 H, AB system,  $^2J_{\text{AB}} = 11.8$  Hz,  $\Delta\nu_{\text{AB}} = 19.3$  Hz,  $\text{CH}_2\text{Br}$ ), 3.79 (1 H, m, N-CH), 1.84 (2 H, m,  $\text{CH}_2$ ), 1.66

(2 H, m,  $\text{CH}_2$ ), 1.47 (2 H, m,  $\text{CH}_2$ ), 1.40 (2 H, m,  $\text{CH}_2$ ), 1.34 (2 H, m,  $\text{CH}_2$ ), 1.26 (3 H, t,  $^3J_{\text{HH}} = 7.2$  Hz,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR:  $\delta$  = 190.4 (C=O), 188.5 (C=O), 165.9 (C=O), 155.2 (C=N), 146.9 (C), 140.6 (C), 136.5 ( $\text{C}_{\text{ipso}}$ ), 136.4 ( $\text{C}_{\text{ipso}}$ ), 134.0 (CH), 133.9 (CH), 129.2 (2 CH), 129.1 (2 CH), 128.4 (2 CH), 128.3 (2 CH), 89.5 (C), 63.6 ( $\text{OCH}_2$ ), 56.9 (C-N), 33.8 ( $\text{CH}_2\text{Br}$ ), 33.5 ( $\text{CH}_2$ ), 33.3 ( $\text{CH}_2$ ), 25.5 ( $\text{CH}_2$ ), 24.5 ( $\text{CH}_2$ ), 24.3 ( $\text{CH}_2$ ), 13.9 ( $\text{CH}_3$ ) ppm.

*Ethyl 3,4-dibenzoyl-2-bromomethyl-5-(2,6-dimethyl-phenylimino)-2,5-dihydro-furan-2-carboxylate (4c):*

Orange powder, yield: 0.49 g (88%), m.p. 110-112 °C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1743, 1695, and 1664 (C=O), 1586 (C=N), 1249 (C-O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  = 7.66 (2 H, d,  $^3J_{\text{HH}} = 7.4$  Hz, 2  $\text{CH}_{\text{ortho}}$ ), 7.51 (2 H, d,  $^3J_{\text{HH}} = 7.3$  Hz, 2  $\text{CH}_{\text{ortho}}$ ), 7.46 (1 H, dd,  $^3J_{\text{HH}} = 7.5$  Hz,  $\text{CH}_{\text{para}}$ ), 7.37 (1 H, t,  $^3J_{\text{HH}} = 7.4$  Hz,  $\text{CH}_{\text{para}}$ ), 7.33 (2 H, t,  $^3J_{\text{HH}} = 7.1$  Hz, 2  $\text{CH}_{\text{meta}}$ ), 7.23 (2 H, t,  $^3J_{\text{HH}} = 7.4$  Hz, 2  $\text{CH}_{\text{meta}}$ ), 7.16 (1 H, d,  $^3J_{\text{HH}} = 7.4$  Hz, CH of Aryl), 7.11 (1 H, d,  $^3J_{\text{HH}} = 7.0$  Hz, CH of Aryl), 7.04 (1 H, t,  $^3J_{\text{HH}} = 7.1$  Hz, CH of Aryl), 4.35 (2 H, ABX<sub>3</sub> system,  $\text{OCH}_2$ ), 4.08 (2 H, AB system,  $^2J_{\text{AB}} = 12.4$  Hz,  $\Delta\nu_{\text{AB}} = 23.1$  Hz,  $\text{CH}_2\text{Br}$ ), 2.22 (3 H, s,  $\text{CH}_3$ ), 2.21 (3 H, s,  $\text{CH}_3$ ), 1.35 (3 H, t,  $^3J_{\text{HH}} = 7.2$  Hz,  $\text{CH}_3$ ) ppm.  $^{13}\text{C}$  NMR:  $\delta$  = 189.8 (C=O), 188.1 (C=O), 165.3 (C=O), 155.9 (C=N), 149.1 (C), 143.9 (C-N), 140.1 (C), 136.1 ( $\text{C}_{\text{ipso}}$ ), 136.0 ( $\text{C}_{\text{ipso}}$ ), 134.4 (CH), 134.3 (CH), 129.4 (2 CH), 129.3 (2 CH), 128.4 (2 CH), 128.4 (2 CH of Aryl), 127.5 (2 CH), 127.3 (2 C of Aryl), 123.8 (CH of Aryl), 90.5 (C), 63.5 ( $\text{OCH}_2$ ), 32.4 ( $\text{CH}_2\text{Br}$ ), 18.4 ( $\text{CH}_3$ ), 18.3 ( $\text{CH}_3$ ), 13.8 ( $\text{CH}_3$ ) ppm.

*Ethyl 3,4-dibenzoyl-2-bromomethyl-5-(1,1,3,3-tetramethyl-butylimino)-2,5-dihydro-furan-2-carboxylate (4d):*

Pale yellow powder, yield: 0.45 g (79%), m.p. 120-122 °C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1735, 1684, and 1631 (C=O), 1587 (C=N), 1281 (C-O)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  = 7.62 (2 H, d,  $^3J_{\text{HH}} = 7.7$  Hz, 2  $\text{CH}_{\text{ortho}}$ ), 7.50 (2 H, d,  $^3J_{\text{HH}} = 7.6$  Hz, 2  $\text{CH}_{\text{ortho}}$ ), 7.44 (1 H, t,  $^3J_{\text{HH}} = 7.3$  Hz,  $\text{CH}_{\text{para}}$ ), 7.39 (1 H, t,  $^3J_{\text{HH}} = 7.4$  Hz,  $\text{CH}_{\text{para}}$ ), 7.24 (2 H, t,  $^3J_{\text{HH}} = 7.9$  Hz, 2  $\text{CH}_{\text{meta}}$ ), 7.16 (2 H, t,  $^3J_{\text{HH}} = 7.8$  Hz, 2  $\text{CH}_{\text{meta}}$ ), 4.32 (2 H, ABX<sub>3</sub> system,  $\text{OCH}_2$ ), 4.17 (2 H, AB system,  $^2J_{\text{AB}} = 12.7$  Hz,  $\Delta\nu_{\text{AB}} = 17.5$  Hz,  $\text{CH}_2\text{Br}$ ), 1.83 (2 H, s,  $\text{CH}_2$ ), 1.56 (3 H, s,  $\text{CH}_3$ ), 1.55 (3 H, s,  $\text{CH}_3$ ), 1.24 (3 H, t,  $^3J_{\text{HH}} = 7.2$  Hz,  $\text{CH}_3$ ), 1.03 (9 H, s,  $\text{CMe}_3$ ) ppm.  $^{13}\text{C}$  NMR:  $\delta$  = 190.4 (C=O), 188.8 (C=O), 166.1 (C=O), 151.8 (C=N), 145.6 (C), 142.3 (C), 136.4 ( $\text{C}_{\text{ipso}}$ ), 136.3 ( $\text{C}_{\text{ipso}}$ ), 133.9

(CH), 133.8 (CH), 129.2 (2 CH), 129.1 (2 CH), 128.3 (2 CH), 128.1 (2 CH), 89.9 (C), 63.0 (C-N), 58.9 (OCH<sub>2</sub>), 55.0 (CH<sub>2</sub>), 33.6 (CH<sub>2</sub>Br), 31.9 (CH<sub>3</sub>), 31.6 (CMe<sub>3</sub>), 29.8 (CH<sub>3</sub>), 29.7 (C), 13.9 (CH<sub>3</sub>) ppm.

*Ethyl 3,4-dibenzoyl-2-bromomethyl-5-ethoxycarbonylmethylimino-2,5-dihydro-furan-2-carboxylate (4e):*

Pale yellow powder, yield: 0.43 g (79%), m.p. 114-116 °C (dec.). IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1782, 1739, 1697, and 1661 (C=O), 1508 (C=N), 1262 (C-O)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR:  $\delta$  = 7.63 (2 H, d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2 CH<sub>ortho</sub>), 7.52 (2 H, d, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 2 CH<sub>ortho</sub>), 7.47 (1 H, t, <sup>3</sup>J<sub>HH</sub> = 7.3 Hz, CH<sub>para</sub>), 7.42 (1 H, t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, CH<sub>para</sub>), 7.26 (2 H, t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 2 CH<sub>meta</sub>), 7.16 (2 H, t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, 2 CH<sub>meta</sub>), 4.28 (2 H, ABX<sub>3</sub> system, OCH<sub>2</sub>), 4.25 (2 H, ABX<sub>3</sub> system, OCH<sub>2</sub>), 4.20 (2 H, AB system, <sup>2</sup>J<sub>AB</sub> = 13.1 Hz,  $\Delta\nu_{\text{AB}}$  = 11.4 Hz, CH<sub>2</sub>), 4.12 (2 H, AB system, <sup>2</sup>J<sub>AB</sub> = 12.2 Hz,  $\Delta\nu_{\text{AB}}$  = 18.2 Hz, CH<sub>2</sub>Br), 1.30 (3 H, t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, CH<sub>3</sub>), 1.23 (3 H, t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR:  $\delta$  = 189.1 (C=O), 187.8 (C=O), 165.2 (C=O), 164.1 (C=O), 156.5 (C=N), 148.6 (C), 136.2 (C<sub>ipso</sub>), 136.1 (C<sub>ipso</sub>), 134.8 (CH), 134.6 (CH), 128.8 (2 CH), 128.7 (2 CH), 128.5 (2 CH), 128.1 (2 CH), 86.8 (C), 64.1 (OCH<sub>2</sub>), 63.6 (OCH<sub>2</sub>), 50.3 (CH<sub>2</sub>-N), 33.1 (CH<sub>2</sub>Br), 14.1 (CH<sub>3</sub>), 13.9 (CH<sub>3</sub>) ppm.

*3,4-dibenzoyl-2-bromomethyl-5-benzylimino-2,5-dihydro-furan-2-carboxylate (4f):*

Pale yellow crystals, yield: 0.41 g (75%), m.p. 125-127 °C (dec.). IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1754, 1689 and 1655 (C=O), 1585 (C=N), 1269 (C-O)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR:  $\delta$  = 7.64 (2 H, d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2 CH<sub>ortho</sub>), 7.53 (2 H, d, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 2 CH<sub>ortho</sub>), 7.45 (1 H, t, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, CH<sub>para</sub>), 7.41 (2 H, t, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 2 CH<sub>para</sub>), 7.31 (2 H, t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 2 CH<sub>ortho</sub>), 7.25 (3 H, t, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 3 CH<sub>meta</sub>), 7.14 (3 H, t, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 2 CH<sub>meta</sub>), 4.71 (2 H, AB system, <sup>2</sup>J<sub>AB</sub> = 15.6 Hz,  $\Delta\nu_{\text{AB}}$  = 22.2 Hz, CH<sub>2</sub>Ph), 4.34 (2 H, ABX<sub>3</sub> system, OCH<sub>2</sub>), 4.20 (2 H, AB system, <sup>2</sup>J<sub>AB</sub> = 12.7 Hz,  $\Delta\nu_{\text{AB}}$  = 21.2 Hz, CH<sub>2</sub>Br), 1.24 (3 H, t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR:  $\delta$  = 190.1 (C=O), 188.2 (C=O), 165.5 (C=O), 157.7 (C=N), 147.7 (C), 140.1 (C), 139.3 (C<sub>ipso</sub>), 136.3 (C<sub>ipso</sub>), 136.2 (C<sub>ipso</sub>), 134.1 (CH), 134.0 (CH), 129.2 (2 CH), 129.1 (2 CH), 128.5 (2 CH), 128.4 (2 CH), 128.2 (2 CH), 127.6 (2 CH), 126.6 (CH), 90.2 (C), 63.4 (OCH<sub>2</sub>), 51.9 (CH<sub>2</sub>), 33.4 (CH<sub>2</sub>Br), 13.9 (CH<sub>3</sub>) ppm.

*Ethyl 2-bromomethyl-5-tert-butylimino-3,4-bis(4-methyl-benzoyl)-2,5-dihydro-furan-2-carboxylate (4g):*

Yellow crystals, yield: 0.49 g (91%), m.p. 123-125 °C (dec.). IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1735, 1675, and 1655 (C=O), 1582 (C=N), 1260 (C-O)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR:  $\delta$  = 8.16 (2 H, d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 2 CH of Ar), 8.09 (2 H, d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, 2 CH of Ar), 7.94 (2 H, d, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, CH of Ar), 7.63 (2 H, d, <sup>3</sup>J<sub>HH</sub> = 7.5 Hz, CH of Ar), 4.30 (2 H, ABX<sub>3</sub> system, OCH<sub>2</sub>), 4.21 (2 H, AB system, <sup>2</sup>J<sub>AB</sub> = 11.9 Hz,  $\Delta\nu_{\text{AB}}$  = 18.0 Hz, CH<sub>2</sub>Br), 2.37 (3 H, s, Me), 2.35 (3 H, s, Me), 1.25 (9 H, s, CMe<sub>3</sub>), 1.16 (3 H, t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR:  $\delta$  = 193.5 (C=O), 191.8 (C=O), 167.3 (C=O), 155.2 (C=N), 144.7 (C), 143.7 (C), 143.6 (C<sub>ipso</sub>), 140.6 (C<sub>ipso</sub>), 136.9 (C<sub>ipso</sub>), 135.1 (C<sub>ipso</sub>), 130.7 (2 CH), 130.4 (2 CH), 129.6 (2 CH), 128.6 (2 CH), 85.2 (C), 60.8 (OCH<sub>2</sub>), 57.2 (C-N), 34.8 (CH<sub>2</sub>Br), 30.6 (CMe<sub>3</sub>), 21.7 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>), 14.3 (CH<sub>3</sub>) ppm.

*2-Ethyl 3,4-dimethyl 2-bromomethyl-5-tert-butylimino-2,5-dihydro-furan-2,3,4-tricarboxylate (4h)*

Pale yellow powder, yield: 0.39 g (93%), m.p. 98-100 °C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1726, 1715 and 1710 (C=O), 1553 (C=N), 1260 (C-O)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR:  $\delta$  = 4.36 (2 H, ABX<sub>3</sub> system, OCH<sub>2</sub>), 4.28 (2 H, AB system, <sup>2</sup>J<sub>AB</sub> = 15.3 Hz,  $\Delta\nu_{\text{AB}}$  = 20.2 Hz, CH<sub>2</sub>Br), 3.99 (3 H, s, OMe), 3.90 (3 H, s, OMe), 1.32 (9 H, s, CMe<sub>3</sub>), 1.28 (3 H, t, <sup>3</sup>J<sub>HH</sub> = 7.1 Hz, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR:  $\delta$  = 166.1 (C=O), 164.7 (C=O), 163.7 (C=O), 146.2 (C=N), 146.0 (C), 141.3 (C), 88.2 (C), 62.9 (OCH<sub>2</sub>), 55.3 (C-N), 53.1 (OMe), 53.0 (OMe), 33.5 (CH<sub>2</sub>Br), 29.9 (CMe<sub>3</sub>), 14.2 (CH<sub>3</sub>) ppm.

*3,4-Di-tert-butyl 2-ethyl 2-bromomethyl-5-tert-butylimino-2,5-dihydro-furan-2,3,4-tricarboxylate (4i)*

Pale yellow crystals, yield: 0.48 g (95%), m.p. 112-114 °C. IR (KBr) ( $\nu_{\max}/\text{cm}^{-1}$ ): 1724, 1714 and 1710 (C=O), 1549 (C=N), 1269 (C-O)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR:  $\delta$  = 4.41 (2 H, ABX<sub>3</sub> system, OCH<sub>2</sub>), 4.29 (2 H, AB system, <sup>2</sup>J<sub>AB</sub> = 14.3 Hz,  $\Delta\nu_{\text{AB}}$  = 22.1 Hz, CH<sub>2</sub>Br), 1.74 (9 H, s, CMe<sub>3</sub>), 1.71 (9 H, s, CMe<sub>3</sub>), 1.66 (9 H, s, CMe<sub>3</sub>), 1.26 (3 H, t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR:  $\delta$  = 165.0 (C=O), 163.8 (C=O), 163.5 (C=O), 153.0 (C=N), 146.0 (C), 142.5 (C), 89.0 (C), 84.0 (CMe<sub>3</sub>), 83.4 (CMe<sub>3</sub>), 62.1 (OCH<sub>2</sub>), 54.3 (C-N), 33.2 (CH<sub>2</sub>Br), 29.2 (CMe<sub>3</sub>), 28.4 (CMe<sub>3</sub>), 28.3 (CMe<sub>3</sub>), 13.9 (CH<sub>3</sub>) ppm.

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