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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

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Accepted author version posted online: 02 Jan 2012. Version of record first published: 29 May 2012.

To cite this article: Sakineh Asghari & Ahmad Khabbazi Habibi (2012): Reactivity of Various α -Halo Ketones in One-Pot Synthesis of γ -Iminolactones, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:19, 2894-2906

To link to this article: <u>http://dx.doi.org/10.1080/00397911.2011.571806</u>

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Synthetic Communications[®], 42: 2894–2906, 2012 Copyright © Taylor & Francis Group, LLC ISSN: 0039-7911 print/1532-2432 online DOI: 10.1080/00397911.2011.571806

REACTIVITY OF VARIOUS α -HALO KETONES IN ONE-POT SYNTHESIS OF γ -IMINOLACTONES

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GRAPHICAL ABSTRACT



Abstract The highly reactive 1:1 intermediate generated in the reaction of text-butyl isocyanide and dialkyl acetylenedicarboxylate is trapped by α -halo ketones to produce halogenated iminolactones as the sole product in good yields.

Keywords α -Bromo ketones; α -chloro ketones; acetylenic esters; halogenated γ -iminolactones; *tert*-butyl isocyanide

INTRODUCTION

The importance of isocyanides in the synthesis of heterocyclic compounds is evident by the diversity of available products. They are known to form zwitterionic intermediates during reactions with acetylenic esters in which the third component can be added to the system to produce the new heterocyclic target molecules that have been reported by several groups.^[1–9] Iminolactones have been the subject of interest because of their use as antibacterial agents, aldosterone inhibitors, and precursors for preparation of a wide spectrum of the natural compounds.^[10a] For example, iminolactones can be hydrolyzed to corresponding butenolides^[10b-e] with various pharmacological activities.^[10f,g] The most widely used approach to iminolactone synthesis is isocyanide-based reactions.^[4,5,7,8,11–13] The reactive 1:1 intermediate generated in the reaction of isocyanide and acetylenic ester is trapped by an electron-deficient ketone such as isatin,^[5a,7b] 1,2-diketone,^[5,12c] α -ketoester,^[4e,7a] and di(2-pyridyl) ketone.^[12a]

Received January 3, 2011.

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Recently Shaabani et al. reported the synthesis of the γ -iminolactones through a three-component condensation using 2-bromo-1-(4-bromophenyl)ethanone, and a mechanism was also proposed by the authors.^[8b] Although the supposition mechanism seems to be reasonable, utilization of different α -haloketones could alter the mechanism, especially those α -halo ketones containing electron-withdrawing groups, which enhance the acidity strength of H_{α} of the halo ketones and virtually bring it into the reaction with zwitterionic intermediate that is generated in the reaction of *tert*-butyl isocyanide and dialkyl acetylenedicarboxylate. Thus, to investigate the generalization of the mechanism, a series of α -halo ketone derivatives with a variety of electronic properties were prepared and their reactivities toward a threecomponent condensation were studied.

Herein, we report the reaction of *tert*-butyl isocyanide with dialkyl acetylenedicarboxylate 1 in the presence of α -haloketone derivatives 2 that leads to the halogenated γ -iminolactones 3a-v as the sole product in good yields (Scheme 1).

Initially the reaction of tert-butyl isocyanide and dialkyl acetylenedicarboxylate with acetophenone was examined at room temperature. The reaction was very slow and yielded an unidentified mixture without formation of any iminolactone. When phenacylchloride was used under similar reaction conditions, compound 3e was obtained as the sole product in good yield after only 3 h. This implies the effects of the halogens at the α -position of the carbonyl group, which probably enhance the electrophilicity of the carbonyl carbon atom. Based on this interesting preliminary result, the reaction of isocyanide and dialkyl acetylenedicarboxylate with various α -halo ketones was examined and the obtained results are tabulated in Table 1. As is clear from the table, the α -chloro and α -bromo ketones reacted smoothly and chemoselectively with *tert*-butyl isocyanide and acetylenic esters to give the corresponding iminolactones in good yields. The α -chloro ketones were more reactive than the α -bromo analogous (entries **3j** and **3m**). The α, α -dichloro ketone reacted faster and afforded the expected products in excellent yield (compare 3c and 3d with **3a** and **3b** or **3k** and **3l** with **3i** and **3j**, respectively). Moreover, the aryl substituted α halo ketones afforded the expected iminolactones similarly in good yields under the reaction conditions (entries 30-3r). An interesting feature of this procedure is that all the reactions chemoselectively afforded the desired iminolactone derivatives and no ketenimine or 4*H*-pyran derivative was observed.

On the basis of the established chemistry of isocyanide, $[^{14-16}]$ it is reasonable to assume that the initial event is the Michael addition of *tert*-butyl isocyanide to



Scheme 1. Synthesis of compound 3.

3	R	Z	Х	Y	Yield (%)	Time (h)
a	CH ₃	CH ₃	Н	Cl	80	3
b	C_2H_5	CH ₃	Н	Cl	77	3
с	CH ₃	CH ₃	Cl	Cl	95	2
d	C_2H_5	CH_3	Cl	Cl	92	2
e	CH ₃	CH ₂ Cl	Н	Cl	70	3
f	C_2H_5	CH ₂ Cl	Н	Cl	65	3
g	CH_3	CH_3	CH_3	Cl	40	5
h	C_2H_5	CH_3	CH_3	Cl	36	5
i	CH_3	C_6H_5	Н	Cl	70	3
j	C_2H_5	C_6H_5	Н	Cl	70	3
k	CH_3	C_6H_5	Cl	Cl	90	1
1	C_2H_5	C_6H_5	Cl	Cl	92	1
m	CH_3	C_6H_5	Н	Br	60	4
n	C_2H_5	C_6H_5	Н	Br	58	4
0	CH_3	$O_2N-C_6H_5$	Н	Br	80	3
р	C_2H_5	$O_2N-C_6H_5$	Н	Br	75	3
q	CH_3	Cl-C ₆ H ₅	Н	Br	70	4
r	C_2H_5	Cl-C ₆ H ₅	Н	Br	68	4
s	CH_3	CF_3	Н	Br	50	4
t	C_2H_5	CF_3	Н	Br	48	5
u	CH_3	CH ₂ Br	Η	Br	60	5
V	C_2H_5	CH ₂ Br	Н	Br	55	5

Table 1. Reactions of *tert*-butyl isocyanide with dialkyl acetylenedicarboxylates in the presence of α -halo ketone

dialkyl acetylenedicarboxylate to form the zwitterionic intermediate **4**. The intermediate **4** either can attack the carbonyl group of α -halo ketone that leads to the dipolar species **5**, which cyclizes subsequently to form the iminolactone derivative **3** (route a in Scheme 2), or can be protonated by α -halo ketone as a CH acid to give positively charged ion **6**. Reaction of the enolate anion of the α -halo ketone with **6** forms the ketenimine **7**, which can isomerize to produce the enol tautomer **8** under the reaction conditions. An intramolecular attack of the enole **8** to the sp-hybridized carbon atom of the ketenimine moiety and a subsequent proton transfer can form 4*H*-pyran derivative **9** (route b in Scheme 2). As is clear from the results in Table 1, the reactions did not give any ketenimine or 4*H*-pyran derivatives. This is probably a result of the inductive effects of the α -halogenes in the α -halo ketones, which make the carbonyl group more electrophile. The α -hydrogenes in α -halo ketones are not acidic enough to protonate the zwitterion **4** through route b in Scheme 2 to afford ketenimine or 4*H*-pyran derivatives, as was observed for the β -diketones.^[4b,6b,6c,17]

The structures of **3a–v** were deduced from their ¹H and ¹³C NMR and infrared (IR) spectra as well as elemental analyses. The mass spectra of these compounds displayed molecular ion peaks at the appropriate m/z values (M⁺ and M⁺ + 2). The ¹H NMR spectrum of **3a** in CDCl₃ displayed a singlet at $\delta = 1.24$ ppm for the *tert*-butyl group, another singlet at $\delta = 1.61$ ppm for the methyl group, and two singlets at $\delta = 3.79$ ppm and 3.86 ppm for two methoxy groups. The methylene protons of the CH₂Cl moiety are diastereotopic and showed a characteristic AB quartet system at $\delta = 3.81$ and 3.96 ppm (²J_{HH} = 11.2–11.6 Hz). The ¹³C NMR spectrum of **3a**



Scheme 2. Proposed mechanism for the formation of compound 3 and 4H-pyran derivatives 9.

displayed 12 sharp lines in agreement with the proposed structure. The partial assignment of these resonances is given in the experimental section. The mass spectrum of **3a** exhibited molecular ion peaks at m/z 318 (M⁺ + 1) (63) and 320 (M⁺ + 3) (23) due to the existence of the isotopes of the chlorine atom (³⁵Cl and ³⁷Cl). The ¹H and ¹³C NMR spectra of **3b–v** were similar to those of **3a** except those the

substituents in positions 2, 3, and 4, which showed characteristic resonances in appropriate regions of the spectrum.

It can be concluded that a series of α -halo ketones were prepared under neutral conditions without the use of a catalyst, and their reactivities in a three-component condensation of *tert*-butyl isocyanide and dialkyl acetylenedicarboxylates with α -halo ketones were investigated. The prepared halogenated γ -iminolactone reveals that although two different routes are possible for this type of the reaction, the sole and high-yielding products confirm the generalization of the mechanism using a variety of α -halo ketones with different electronic properties. The simplicity of the present procedure also makes it an interesting alternative to the other approaches.

EXPERIMENTAL

Dialkyl acetylenedicarboxylates, tert-butyl isocyanide, chloroacetone, 1,1-dichloroacetone, 1,3-dichloroacetone, 3-chloro-2-butanone, 1-chloro-acetophenone, 1,1dichloroacetophenone. 1,3-dibromoacetone, 2-bromo-acetophenone, 2-bromo-4nitroacetophenone, 2-bromo-4-chloroacetophenone, and 1,1,1-trifluoroacetone were purchased from Fluka and Merck and used without further purification. Melting points were measured on an Electrothermal 9100 apparatus. NMR spectra were recorded with a Bruker DRX-400 Avance instrument (400.1 MHz for ¹H, 100.6 MHz for ¹³C, and 376.5 MHz for ¹⁹F) with CDCl₃ as solvent. Chemical shifts are given in parts per million (ppm, δ) relative to tetramethylsilane (TMS), and coupling constants (J) are reported in hertz (Hz). IR spectra were recorded on a Fourier transform (FT-IR) Bruker vector 22 spectrometer. Mass spectra were recorded on a Finnigan-Matt 8430 mass spectrometer operating at an ionization potential of 70 eV. Elemental analyses were performed using a Heraeus CHN-O Rapid analyzer.

General Procedure for the Preparation of Compound 3

tert-butyl isocyanide (0.24 ml, 2.0 mmol) was added to a stirred solution of dialkyl acetylenedicarboxylate (2.0 mmol) and α -halo ketone derivatives (2.0 mmol) in 10 ml of dry dichloromethane at room temperature. The mixture was allowed to stir for 1–5 h. The solvent was removed under reduced pressure. The powder products **3e–g**, **3i–s**, **3u**, and **3v** were isolated and purified by recrystallization in ethanol from the mixture of the reactions. The oil products **3a–d**, **3h**, and **3t** were purified by silica gel (Merck silica gel, 230–400 mesh) column chromatography using hexane–ethyl acetate (4:1) as eluent. The solvent was removed under reduced pressure, and the products **3a–d**, **3h**, and **3t** were obtained as yellow oils.

Dimethyl 5-(*tert*-butylimino)-2-(chloromethyl)-2-methyl-2,5-dihydrofuran-3,4-dicarboxylate (3a). Yellow oil, yield 80%. IR (KBr) (v_{max}/cm^{-1}): 1750 and 1729 (C=O), 1686 (C=N), 1616 (C=C) cm⁻¹. ¹H NMR (400.1 MHz, CDCl₃): $\delta = 1.24$ (9H, s, CMe₃), 1.61 (3H, s, CH₃), 3.79 and 3.86 (6H, 2 s, 2OCH₃), 3.88 (2H, AB system, ² $J_{AB} = 11.6$ Hz, $\Delta v_{AB} = 60$ Hz, CH₂Cl) ppm. ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 22.3$ (CH₃), 29.3 (CMe₃), 48.6 (CH₂Cl₂), 52.8 and 52.9 (2OCH₃), 54.6 (NCMe₃), 88.8 (C), 139.9 (C), 140.9 (C), 152.5 (C=N), 160.9 and 162.6 (2C=O). MS: m/z (%) = 318 (M⁺ + 1, 63), 320 (M⁺ + 3, 23), 302 (100), 304 (34), 262 (9), 264 (3), 246 (3), 244 (9), 213 (9), 57 (24). Anal. calcd. for $C_{14}H_{20}CINO_5$ (317.77): C, 52.92; H, 6.34; N, 4.41%. Found: C, 53.03; H, 6.36; N, 4.42%.

Diethyl 5-(*tert***-butylimino)-2-(chloromethyl)-2-methyl-2,5-dihydrofuran-3,4-dicarboxylate (3b).** Yellow oil, yield 77%. IR (KBr) (v_{max}/cm^{-1}): 1741 and 1719 (C=O), 1686 (C=N), 1614 (C=C) cm⁻¹. ¹H NMR (400.1 MHz, CDCl₃): $\delta = 1.20$ (9H, s, CMe₃), 1.22 (3H, t, ³J_{HH} = 7.2 Hz, CH₃), 1.27 (3H, t, ³J_{HH} = 7.2 Hz, CH₃) 1.56 (3H, s, CH₃), 3.84 (2H, AB system, ²J_{HH} = 11.6 Hz, $\Delta v_{AB} = 56$ Hz, CH₂Cl), 4.19 (2H, q, ³J_{HH} = 7.2 Hz, OCH₂), 4.27 (2H, q, ³J_{HH} = 7.2 Hz, OCH₂). ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 13.8$ (CH₃), 14.0 (CH₃), 22.3 (CH₃), 29.3 (CMe₃), 48.6 (CH₂Cl), 54.4 (NCMe₃), 61.7 and 61.8 (2CH₂), 88.7 (C), 139.7 (C), 145.6 (C), 152.5 (C=N), 160.4 and 162.1 (2C=O). MS: m/z (%) = 346 (M⁺ + 1, 81), 348 (M⁺ + 3, 28), 330 (100), 332 (34), 290 (19), 292 (6), 244 (10), 246 (3), 199 (9), 201 (3), 65 (5) 57 (20). Anal. calcd. for C₁₆H₂₄ClNO₅ (345.83): C, 55.57; H, 7.00; N, 4.05%. Found: C, 55.68; H, 7.02; N, 4.06%.

Dimethyl 5-(*tert*-butylimino)-2-(dichloromethyl)-2-methyl-2,5-dihydrofuran-**3,4-dicarboxylate (3c).** Yellow powder, mp 50–53 °C, yield 95%. IR (KBr) ($\nu_{max}/$ cm⁻¹): 1752 and 1725 (C=O), 1687 (C=N), 1655 (C=C) cm⁻¹. ¹HNMR (400.1 MHz, CDCl₃): $\delta = 1.34$ (9H, s, CMe₃), 1.77 (3H, s, CH₃), 3.85 and 3.92 (6H, 2 s, 2OCH₃), 6.23 (1H, s, CHCl₂). ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 22.0$ (CH₃), 29.3 (CMe₃), 53.0 and 53.1 (2OCH₃), 55.2 (NCMe₃), 74.7 (CHCl₂), 91.1 (C), 139.6 (C), 140.9 (C), 151.9 (C=N), 160.8 and 162.2 (2C=O). MS: m/z (%) = 352 (M⁺ + 1, 29), 354 (M⁺ + 3, 19), 356 (M⁺ + 5, 3), 336 (100), 338 (70), 340 (12), 296 (8), 298 (6), 300 (1), 253 (20), 181 (8), 57 (34). Anal. calcd. for C₁₄H₁₉Cl₂NO₅ (352.22): C, 47.74; H, 5.44; N, 3.98%. Found: C, 47.84; H, 5.45; N, 3.99%.

Diethyl 5-(*tert***-butylimino)-2-(dichloromethyl)-2-methyl-2,5-dihydrofuran-3,4-dicarboxylate (3d).** Yellow viscous oil, yield 92%. IR (KBr) (v_{max}/cm^{-1}): 1752 and 1729 (C=O), 1693 (C=N), 1654 (C=C) cm⁻¹. ¹H NMR (400.1 MHz, CDCl₃): $\delta = 1.28$ (3H, t, ${}^{3}J_{HH} = 7.2$ Hz, CH₃), 1.30 (9H, s, CMe₃), 1.33 (3H, t, ${}^{3}J_{HH} = 7.2$ Hz CH₃), 1.73 (3H, s, CH₃), 4.25 (2H, q, ${}^{3}J_{HH} = 7.2$ Hz, OCH₂), 4.33 (2H, q, ${}^{3}J_{HH} = 7.2$ Hz, OCH₂), 6.21 (1H, s, CHCl₂). ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 13.8$ (CH₃), 14.0 (CH₃), 22.0 (CH₃), 29.3 (CMe₃), 55.0 (NCMe₃), 62.1 and 62.2 (2OCH₂), 74.8 (CHCl₂), 91.0 (C), 139.5 (C) 140.6 (C), 152.0 (C=N), 160.4 and 161.7 (2C=O). MS: m/z (%) = 380 (M⁺ + 1, 37), 382 (M⁺ + 3, 26), 384 (M⁺ + 5, 4), 364 (100), 366 (68), 368 (12), 324 (18), 326 (12), 328 (2), 281 (10), 57 (23). Anal. calcd. for C₁₆H₂₃Cl₂NO₅ (380.27): C, 50.54; H, 6.10; N, 3.68%. Found: C, 50.64; H, 6.11; N, 3.69%.

Dimethyl 5-(*tert***-butylimino)-2,2-bis(chloromethyl)-2,5-dihydrofuran-3,4-dicarboxylate (3e).** White powder, mp 130–132 °C, yield 70%. IR (KBr) ($v_{\text{max}}/\text{cm}^{-1}$): 1750 and 1734 (C=O), 1686 (C=N), 1660 (C=C) cm⁻¹. ¹H NMR (400.1 MHz, CDCl₃): $\delta = 1.33$ (9H, s, CMe₃), 3.86 and 3.93 (6H, 2 s, 20CH₃), 4.00 (4H, AB system, ²J_{HH} = 11.6 Hz, $\Delta v_{AB} = 11.12$ Hz, 2CH₂Cl). ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 29.4$ (CMe₃), 45.8 (CH₂Cl), 53.0 and 53.1 (20CH₃), 55.2 (NCMe₃), 89.9 (C), 137.4 (C) 142.0 (C), 151.7 (C=N), 160.8 and 162.1 (2C=O). MS: m/z (%) = 352 (M⁺ + 1, 27), 354 (M⁺ + 3, 18), 356 (M⁺ + 5, 3), 336 (100),

338 (67), 340 (11), 296 (9), 298 (6), 300 (1), 257 (8), 57 (20). Anal. calcd. for $C_{14}H_{19}Cl_2NO_5$ (350.22): C, 47.74; H, 5.44; N, 3.98%. Found: C, 47.85; H, 5.46; N, 3.99%.

Diethyl 5-(*tert*-butylimino)-2,2-bis(chloromethyl)-2,5-dihydrofuran-3,4dicarboxylate (3f). White powder, mp 78–79 °C, yield 65%. IR (KBr) (v_{max}/cm^{-1}): 1740 and 1729 (C=O), 1686 (C=N), 1660 (C=C) cm⁻¹. ¹H NMR (400.1 MHz, CDCl₃): $\delta = 1.33$ (9H, s, CMe₃), 1.34 (3H, t, ³J_{HH} = 7.2 Hz, CH₃), 1.38 (3H, t, ³J_{HH} = 7.2 Hz, CH₃), 4.01 (4H, AB quartet system, ²J_{HH} = 11.6 Hz, $\Delta v_{AB} = 20.0$ Hz, 2CH₂Cl), 4.30 (2H, q, ³J_{HH} = 7.2 Hz, OCH₂), 4.40 (2H, q, ³J_{HH} = 7.2 Hz, OCH₂). ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 13.8$ (CH₃), 14.1 (CH₃), 29.4 (CMe₃), 45.9 (CH₂Cl), 55.1 (NCMe₃), 62.2 and 62.3 (2OCH₂), 89.8 (C), 137.3 (C) 141.9 (C), 151.8 (C=N), 160.4 and 161.8 (2C=O). MS: m/z (%) = 380 (M⁺ + 1, 9), 382 (M⁺ + 3, 6), 384 (M⁺ + 5, 1), 364 (100), 366 (67), 368 (11), 280 (5), 233 (9), 235 (6), 237 (1), 57 (29). Anal. calcd. for C₁₆H₂₃Cl₂NO₅ (380.27): C, 50.54; H, 6.15; N, 3.68%. Found: C, 50.64; H, 6.12; N, 3.69%.

Dimethyl 5-(*tert***-butylimino)-2-(1-chloroethyl)-2-methyl-2,5-dihydrofuran-3,4-dicarboxylate (3g).** Yellow powder, mp 35–38 °C, yield 40%. IR (KBr) (ν_{max} / cm⁻¹): 1751 and 1728 (C=O), 1682 (C=N), 1655 (C=C) cm⁻¹. ¹H NMR (400.1 MHz, CDCl₃): $\delta = 1.33$ (9H, s, CMe₃), 1.39 (3H, d, ³J_{HH} = 6.8 Hz, CH₃), 1.74 (3H. s, CH₃), 3.84 and 3.91 (6H, 2 s, 2 OCH₃), 4.54 (1H, q, ³J_{HH} = 6.8 Hz, CHCl). ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 19.6$ (CH₃), 23.0 (CH₃), 29.3 (CMe₃), 52.9 and 60.5 (2OCH₃), 54.9 (NCMe₃), 59.8 (CHCl), 91.4 (C), 138.6 (C), 143.1(C), 152.6 (C=N), 161.2 and 162.4 (2C=O). MS: m/z (%) = 332 (M⁺ + 1, 37), 334 (M⁺ + 3, 12), 316 (100), 318 (33), 276 (8), 278(3), 222 (13), 57 (20). Anal. calcd. for C₁₅H₂₂Cl₂NO₅ (331.80): C, 54.30; H, 6.68; N, 4.22%. Found: C, 54.41; H, 6.69; N, 4.23%.

Diethyl 5-(*tert*-butylimino)-2-(1-chloroethyl)-2-methyl-2,5-dihydrofuran-**3,4-dicarboxylate** (**3**h). Yellow oil, yield 36%. IR (KBr) (v_{max}/cm^{-1}): 1740 and 1721(C=O), 1682 (C=N), 1651 (C=C) cm⁻¹. ¹H NMR (400.1 MHz,CDCl₃): δ = 1.32 (3H, t, ³J_{HH} = 7.2 Hz, CH₃), 1.33 (9H, s, CMe₃),1.36 (3H, t, ³J_{HH} = 7.2 Hz, CH₃), 1.38 (3H, d, ³J_{HH} = 6.80 Hz, CH₃),1.74 (3H, s, CH₃), 4.28 (2H, q, ³J_{HH} = 7.2 Hz, OCH₂), 4.37 (2H, q, ³J_{HH} = 7.2 Hz, OCH₂), 4.55 (1H, q, ³J_{HH} = 6.8 Hz, CHCl). ¹³C NMR (100.6 MHz, CDCl₃): δ = 13.9 (CH₃), 14.1 (CH₃), 19.6 (CH₃), 22.0 (CH₃), 29.3 (*CMe*₃), 54.7 (*NCMe*₃), 60.6 (CHCl), 62.0 and 62.1 (2OCH₂), 91.3 (C), 138.5 (C), 142.8 (C), 152.7 (C=N), 160.8 and 162.0 (2C=O). MS: *m*/*z* (%) = 360 (M⁺ + 1, 44), 362 (M⁺ + 3, 15), 344 (100), 346 (33), 304 (8), 306 (3), 236 (8), 57 (17). Anal. calcd. for C₁₇H₂₆CINO₅ (359.85): C, 56.74; H, 7.28; N, 3.89%. Found: C, 56.85; H, 7.30; N, 3.90%.

Dimethyl 5-(*tert***-butylimino)-2-(chloromethyl)-2-phenyl-2,5-dihydrofuran-3,4-dicarboxylate (3i).** White powder, mp = 110–112 °C, yield 70%. IR (KBr) (ν_{max}/cm^{-1}): 1747 and 1731 (C=O), 1683 (C=N), 1661 and 1439 (C=C) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): $\delta = 1.40$ (9H, s, CMe₃), 3.79 and 3.92 (6H, 2 s, 20CH₃), 4.23 (1H, d, ²J_{HH} = 11.6 Hz, CH), 4.66 (1H, d, ²J_{HH} = 11.6 Hz, CH), 7.37–7.47 (5H, m, C₆H₅). ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 29.6$ (CMe₃), 48.1 (CH₂Cl), 52.9 and 53.0 (20Me), 55.0 (NCMe₃), 91.4 (C), 125.8 128.8, 129.0 and

136.8 (aromatic carbons), 139.1 and 141.2 (olefinic carbons), 152.2 (C=N), 161.2 and 162.4 (2C=O). MS: m/z (%) = 380 (M⁺ + 1, 3), 382 (M⁺ + 3, 1), 394(100), 366 (30), 332 (34), 334 (12), 275 (10), 277 (3), 238(9), 105 (40), 57 (29). Anal. calcd. for C₁₉H₂₂CINO₅ (379.74): C, 60.08; H, 5.84; N, 3.69%. Found: C, 59.92; H, 5.80; N, 3.65%.

Diethyl 5-(*tert***-butylimino)-2-(chloromethyl)-2-phenyl-2,5-dihydrofuran-3,4-dicarboxylate (3j).** White powder, mp = 58–60 °C, yield 70%. IR (KBr) (ν_{max} / cm⁻¹): 1742 and 1726 (C=O), 1688 (C=N), 1666 and 1455 (C=C) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): $\delta = 1.27$ (3H, ³ $J_{HH} = 7.2$ Hz, CH₃), 1.37 (3H, ³ $J_{HH} = 7.2$ Hz, CH₃), 1.40 (9H, s, CMe₃), 4.16–4.31 (2H, m, OCH₂), 4.24 (1H, d, ² $J_{HH} = 11.6$ Hz, CH), 4.35–4.41 (2H, m, OCH₂), 4.63 (1H, d, ² $J_{HH} = 11.6$ Hz, CH), 7.35–7.48 (5H, m, C₆H₅). ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 13.8$ and 14.1 (2CH3), 29.6 (CMe₃), 48.2 (CH₂Cl), 54.9 (NCMe₃), 62.0 and 62.1 (2OCH₂), 91.3(C), 125.9, 128.8, 129.0, and 137.0 (aromatic carbons), 139.0 and 141.0 (olefinic carbons), 152.4 (C=N), 160.8 and 162.0 (2C=O). MS: m/z (%) = 408 (M⁺ + 1, 10), 410 (M⁺ + 3, 3), 392 (100), 394 (38), 346 (20), 348 (7), 306 (10), 308 (3), 238 (14), 155 (10), 105 (41), 57 (47). Anal. calcd. for C₂₁H₂₆CINO₅ (407.79): C, 61.84; H, 6.42; N, 3.43%. Found: C, 61.78; H, 6.38; N, 3.40%.

Dimethyl 5-(*tert***-butylimino)-2-(dichloromethyl)-2-phenyl-2,5-dihydro-furan-3,4-dicarboxylate (3k).** White powder, mp 140–142 °C, yield 90%. IR (KBr) (v_{max}/cm^{-1}): 1761 and 1729 (C=O), 1686 (C=N), 1644 (C=C) cm⁻¹. ¹H NMR (400.1 MHz, CDCl₃): $\delta = 1.49$ (9H, s, CMe_3), 3.81 and 3.90 (6H, 2 s, 2OCH₃), 6.96 (1H, s, CHCl₂), 7.40–7.42 (3H, m, 2H meta and H para), 7.50–7.53 (2H, m, 2H meta). ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 29.6$ (CM e_3), 53.0 and 53.1 (2OCH₃), 55.5 (NCMe₃), 74.3 (CHCl₂), 94.1 (C), 125.8, 128.9, 129.2, and 135.7 (aromatic carbons), 138.0 (C), 141.8 (C), 151.6 (C=N), 161.2 and 161.9 (2C=O). MS: m/z (%) = 414 (M⁺ +1, 9), 416 (M⁺ +3, 6), 418 (M⁺ +5, 1), 398 (100), 400 (67), 402 (11), 315 (36), 283 (32), 242 (9), 77 (33), 57 (33). Anal. calcd. for C₁₉H₂₁Cl₂NO₅ (414.29): C, 51.09; H, 5.11; N, 3.38%. Found: C, 51.19; H, 5.13; N, 3.39%.

Diethyl 5-(*tert*-butylimino)-2-(dichloromethyl)-2-phenyl-2,5-dihydrofuran-3,4-dicarboylate (3l). White powder, mp 115–117 °C, yield 92%. IR (KBr) (v_{max}/cm^{-1}) : 1755 and 1724 (C=O), 1692 (C=N), 1649 (C=C) cm⁻¹. ¹HNMR (400.1 MHz, CDCl₃): $\delta = 1.27$ (3H, t, ³ $J_{HH} = 7.2$ Hz, CH₃), 1.36 (3H, t, ³ $J_{HH} = 7.2$ Hz, CH₃), 1.49 (9H, s, CMe₃), 4.19–4.38 (2H, m, 2OCH₂), 7.38–7.44 (3H, m, 2H ortho and H para), 7.52–7.54 (2H, m, 2H meta). ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 13.7$ (CH₃), 14.1 (CH₃), 29.6 (CMe₃), 55.3 (NCMe₃), 62.2 and 62.4 (2O CH₂), 74.4 (CHCl₂), 94.1 (C), 125.8, 128.8, 129.11, and 135.9 (aromatic carbons), 138.0 (C), 141.5 (C), 151.7 (C=N), 160.8 and 161.5 (2C=O). MS: m/z (%) = 441 (M⁺ + 1, 18), 443 (M⁺ + 3, 12), 445 (M⁺ + 5, 2), 426 (100), 428 (66), 430 (11), 343 (30), 297 (20), 77 (9), 57 (28). Anal. calcd. for C₂₁H₂₅Cl₂NO₅ (442.34): C, 57.02; H, 5.70; N, 3.17%. Found: C, 57.13; H, 5.72; N, 3.18%.

Dimethyl 2-(bromomethyl)-5-(*tert*-butylimino)-2-phenyl-2,5-dihydrofuran-3,4-dicarboxylate (3m). White powder, mp = 100–102 °C, yield 92%. IR (KBr) (ν_{max} /cm⁻¹): 1740 (C=O), 1687 (C=N), 1656 (C=C) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): $\delta = 1.40$ (9H, s, CMe₃), 3.79 and 3.92 (6H, 2 s, 2OCH₃), 4.14 (1H, d, ${}^{2}J_{\rm HH} = 11.2$ Hz, CH), 4.54 (1H, d, ${}^{2}J_{\rm HH} = 11.2$ Hz, CH), 7.36–7.48 (5H, m, C₆H₅). 13 C NMR (100.6 MHz, CDCl₃): $\delta = 29.6$ (CMe₃), 36.8 (CH₂Br), 52.9 and 53.0 (2 OMe), 55.0 (NCMe₃), 90.7 (C), 125.9 128.8, 129.1 and 136.9 (aromatic carbons), 138.9 and 141.9 (olefinic carbons), 152.2 (C=N), 161.1 and 162.4 (2C=O). MS: m/z (%) = 423 (M⁺, 3), 425 (M⁺ + 2, 3), 408 (100), 410 (100), 376 (34), 378 (M⁺ + 2, 34), 351 (M⁺ + 1, 4), 353 (4), 272 (3), 238 (10), 213 (7), 105 (18), 77 (11), 57 (13). Anal. calcd. for C₁₉H₂₂BrNO₅ (424.29): C, 53.79; H, 5.23; N, 3.30%. Found: C, 53.73; H, 5.19; N, 3.27%.

Diethyl 2-(bromomethyl)-5-(*tert***-butylimino)-2-phenyl-2,5-dihydrofuran-3,4-dicarboxylate (3n).** White powder, mp = 73–75 °C, yield 90%. IR (KBr) (ν_{max}/cm^{-1}): 1735 (C=O), 1677 (C=N), 1614 (C=C) cm⁻¹. ¹H NMR (400.13 MHz, CDC₁₃): $\delta = 1.27$ (3H, ³ $J_{HH} = 7.2$ Hz, CH₃), 1.37 (3H, ³ $J_{HH} = 7.2$ Hz, CH3), 1.41 (9H, s, C Me_3), 4.15 (1H, d, ² $J_{HH} = 11.2$ Hz,CH₃), 4.18–4.32 (2H, m, OCH₂), 4.38 (2H, q, ³ $J_{HH} = 7.2$ Hz,OCH₂), 4.52, (1H, d, ² $J_{HH} = 11.2$ Hz, CH), 7.36–7.50 (5H, m, C₆H₅). ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 13.8$ and 14.1 (2CH₃), 29.6 (C Me_3), 35.9 (CH₂Br), 54.9 (NCMe₃), 62.0 and 62.1 (2OCH₂), 90.6 (C), 125.9, 128.8, 129.0, and 137.2 (aromatic carbons), 138.8 and 141.6 (olefinic carbons), 152.2 (C=N), 160.8 and 162.0 (2C=O). MS: m/z (%) = 452 (M⁺ + 1, 3), 454 (M⁺ + 3, 3), 436 (90), 438 (90), 396 (100), 398 (100), 350 (98), 352 (98), 294 (50), 296 (50), 277 (52), 279 (52), 238 (23), 225 (17), 209 (10), 211 (10), 199 (13), 181 (11), 158 (13), 105 (38), 77 (21), 57 (38). Anal. calcd. for C₂₁H₂₆BrNO₅ (452.34): C, 55.76; H, 5.79; N, 3.10%. Found: C, 55.71; H, 5.74; N, 3.07%.

Dimethyl 2-(bromomethyl)-5-(*tert*-butylimino)-2-(4-nitrophenyl)-2,5dihydrofuran–3,4-dicarboxylate (30). White powder, mp = 105–107 °C, yield 80%. IR (KBr) (ν_{max}/cm^{-1}): 1746 and 1724 (C=O), 1693 (C=N), 1656 (C=C) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): $\delta = 1.41$ (9H, s, CMe₃), 2.81 and 3.92 (6H, 2 s, 2OCH₃), $\delta = 4.17$ (1H, d, ² $J_{HH} = 11.2$ Hz, CH), 4.46 (1H, d, ² $J_{HH} = 11.2$ Hz, CH), 7.69 (2H, d, ³ $J_{HH} = 8.8$ Hz, 2CH),8.26 (2H, d, ³ $J_{HH} = 8.8$ Hz, 2CH). ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 29.6$ (CMe₃), 35.9 (CH₂Br), 53.1 and 53.2 (2OCH₃), 55.3 (NCMe₃), 90.1 (C), 123.9, 127.3, 140.7 and 143.8 (aromatic carbons), 139.6 and 148.1 (olefinic carbons), 151.1 (C=N), 160.8 and 162.0 (2C=O). MS: m/z (%) = 469 (M⁺ + 1, 2), 471 (M⁺ + 3, 2), 453 (100), 455 (100), 421 (12), 423 (12), 396 (4), 398 (4), 368 (5), 370 (5), 317 (8), 283 (12), 215 (6), 150 (13), 104 (7), 84 (20), 57 (50). Anal. calcd. for C₁₉H₂₁BrN₂O₇ (469.28): C, 48.63; H, 4.51; N, 5.97%. Found: C,48.69; H, 4.48; N, 5.95%.

Diethyl 2-(bromomethyl)-5-(*tert***-butylimino)-2-(4-nitrophenyl)-2,5dihydrofuran-3,4-dicarboxylate (3p).** Yellow powder, mp = 68–70 °C, yield 75%. IR (KBr) (ν_{max} /cm⁻¹): 1735 and 1698 (C=O), 1698 (C=N), 1660 (C=C) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): $\delta = 1.27$ (3H, t, ${}^{3}J_{HH} = 7.2$ Hz, CH₃), 1.37(3H, t, ${}^{3}J_{HH} = 7.2$ Hz, CH₃), 1.40 (9H, s, CMe₃), 4.19 (1H, d, ${}^{2}J_{HH} = 11.2$ Hz, CH), 4.22–4.30 (2H, m, OCH₂), 4.35–4.39 (2H, m, OCH₂), 4.42 (1H, d, ${}^{2}J_{HH} = 11.2$ Hz, CH), 7.70 (2H, d, ${}^{3}J_{HH} = 8.8$ Hz, 2CH), 8.25 (2H, ${}^{3}J_{HH} = 8.8$ Hz, 2CH). 13 C NMR (100.6 MHz, CDCl₃): $\delta = 13.8$ and 14.1 (2CH₃), 29.6 (CMe₃), 36.0 (CH₂Br), 55.2 (NCMe₃), 62.3 and 62.4 (2 OCH₂), 90.0 (C), 123.8, 127.3, 140.4 and 144.0 (aromatic carbons), 139.5 and 148.1 (olefinic carbons), 151.2 (C=N), 160.5 and 161.6 (2C=O). MS: m/z (%) = 497 (M⁺ + 1, 13), 499 (M⁺ + 3, 13), 481 (100), 483 (100), 441 (7), 443 (7), 395 (3), 397 (3), 363 (5), 365 (5), 352 (7), 354 (7), 283 (24), 272 (7), 243 (6), 225 (11), 150 (24), 104 (9), 84 (13), 57 (49). Anal. calcd. for C₂₁H₂₅BrN₂O₇ (497.34): C, 50.72; H, 5.07; N, 5.63%. Found: C, 50.68; H, 5.04; N, 5.59%.

Dimethyl 2-(bromomethyl)-5-(*tert***-butylimino)-2-(4-chlorophenyl)-2,5**dihydrofuran-3,4-dicarboxylate (3q). White powder, mp = 73–75 °C, yield 70%. IR (KBr) (ν_{max} /cm⁻¹): 1747 and 1720 (C=O), 1690 (C=N), 1660 (C=C) cm⁻¹. ¹H NMR(400.13 MHz, CDCl₃): $\delta = 1.39$ (9H, s, CMe₃), 3.79 and 3.92 (6H, 2 s, 20CH₃), 4.11 (1H, d, ²J_{HH} = 11.2 Hz, CH), 4.47 (1H, d, ²J_{HH} = 11.2 Hz, CH), 7.36 (2H, d, ³J_{HH} = 8.8 Hz, 2CH), 7.41 (2H, d, ³J_{HH} = 8.8 Hz, 2CH). ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 29.6$ (CMe₃), 36.4 (CH₂Br), 53.0 and 53.1 (20CH₃), 55.1 (NCMe₃),90.2 (C), 127.4, 129.0, 135.2 and 135.4 (aromatic carbons), 139.0 and 141.4 (olefinic carbons), 151.8 (C=N), 161.0 and 162.2 (2C=O). MS: *m*/*z* (%) = 457 (M⁺, 3), 459 (M⁺ + 2, 4), 461 (M⁺ + 4,1), 442 (74), 444 (100), 446 (24), 410 (43), 412 (60), 414 (15), 385 (3), 387 (4), 389 (1), 357 (6), 359 (8), 361 (2), 327 (5), 272 (16), 247 (9), 249 (3), 189 (9), 191 (3), 139 (33), 141 (11), 111 (12), 113 (4), 84 (15), 57 (31). Anal. calcd. for C₁₉H₂₁BrClNO₅(458.73): C, 49.75; H, 4.61; N, 3.05%. Found: C, 49.70; H, 4.57; N, 3.01%.

Diethyl 2-(bromomethyl)-5-(tert-butylimino)-2-(4-chlorophenyl)-2,5**dihydrofuran-3,4-dicarboxylate (3r).** White powder, mp = 90-92 °C, yield 68%. IR (KBr) (ν_{ma}/cm^{-1}):1731 (C=O), 1687 (C=N), 1650 and 1484 (C=C) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): $\delta = 1.27$ (3H, t, ${}^{3}J_{HH} = 7.2$ Hz, CH₃), 1.37(3H, t, ${}^{3}J_{\rm HH} = 7.2 \,{\rm Hz}, \,{\rm CH}_{3}$, 1.39 (9H, s, CMe₃), 4.12 (1H, d, ${}^{2}J_{\rm HH} = 11.2 \,{\rm Hz}, \,{\rm CH}$), 4.18–4.29 (2H, m, OCH₂), 4.38 (2H, q, ${}^{3}J_{HH} = 7.2$ Hz, OCH₂), 4.44 (1H, d,=11.2 Hz, CH), 7.36 (2H, d, ${}^{3}J_{HH} = 8.8$ Hz, 2CH), 7.42 (2H, d, ${}^{3}J_{HH} = 8.8$ Hz, 2CH), ¹³C NMR(100.6 MHz, CDCl₃): $\delta = 13.8$ and 14.1 (2CH₃), 29.6 (CMe₃), 36.5 (CH₂Br), 55.0 (NCMe₃), 62.1 (20CH₂), 90.2 (C), 127.5, 128.9,134.0 and 135.7 (aromatic carbons), 139.0 and 141.1 (olefinic carbons), 151.8 (C=N), 160.6 and 161.8 (2C=O). MS: m/z (%) = 486 (M⁺ + 1, 3), 488 (M⁺ + 3, 4), 490 (1), 470 (78), 472 (100), 474 (27), 424 (30), 426 (38), 428 (10), 339 (9), 341 (12), 343 (3), 261 (16), 263 (6), 189 (11), 191 (4), 139 (30), 141 (10), 111 (9), 113 (3), 84 (16), 57 (51). Anal. calcd. for C₂₁H₂₅BrClNO₅ (486.78): C, 51.81; H, 5.18; N, 2.88%. Found: C, 51.76; H, 5.14; N, 2.85%.

Dimethyl 2-(bromomethyl)-5-(*tert***-butylimino)-2-(***trifluoromethyl***)-2,5dihydrofuran-3,4-dicarboxylate (3s).** White powder, mp = 50–52 °C, yield 50%. IR (KBr) (ν_{max} /cm⁻¹): 1747 (C=O), 1698 (C=N), 1650 (C=C) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): $\delta = 1.34$ (9H, s, CMe₃), 3.88 and 3.94 (6H, 2 s,2OCH₃), 3.91 (1H, d, ⁴J_{HH} = 11.2 Hz, CH), 4.33 (1H, d, ²J_{HH} = 11.2 Hz, CH). ¹³C NMR (100.6 MHz, CDCl₃): 29.3 (CH₂Br), $\delta = 29.4$ (CMe₃), 53.2 and 53.3 (2OCH₃), 55.7 (NCMe₃), 88.2 (q, ²J_{FC} = 31.9 Hz, CCF₃), 121.9 (q, ¹J_{FC} = 287.7 Hz, CF₃), 135.1 and 143.4 (olefinic carbons), 149.7 (C=N), 159.7 and 161.3 (2C=O). ¹⁹F NMR (376.50, CDCl₃): $\delta = -75.68$. MS: m/z (%) = 416 (M⁺ + 1, 60), 418 (M⁺ + 3, 60), 400 (14), 402 (14), 277 (17), 265 (16), 250 (9), 192 (20), 136 (11), 69 (38), 57 (100). Anal. calcd. for C₁₄H₁₇ Br F₃ NO₅ (416.19): C, 40.40; H, 4.76; N, 3.15%. Found: C, 40.34; H, 4.72; N, 3.11%.

Diethyl 2-(bromomethyl)-5-(*tert*-butylimino)-2-(trifluoromethyl)-2,5dihydrofuran-3,4-dicarboxylate (3t). Yellow oil, yield 48%. IR (KBr) (ν_{max} / cm⁻¹): 1741 (C=O), 1690 (C=N), 1655 (C=C) cm⁻¹¹. H NMR (400.13 MHz, CDCl₃):δ = 1.33 (9H, s, CMe₃), 1.34 (3H, t, ³J_{HH} = 7.2 Hz, CH₃), 1.38 (3H, t, ³J_{HH} = 7.2 Hz, CH₃), 3.90 (1H, d, ⁴J_{HH} = 11.2 Hz, CH), 4.29–4.38 (2H, m, OCH₂), 4.34 (1H, d, ²J_{HH} = 11.2 Hz, CH), 4.41 (2H, q, ³J_{HH} = 7.2 Hz, OCH₂). ¹³C NMR (100.6 MHz, CDCl₃): δ = 13.8 and 14.0 (2CH₃), 29.4 (CMe₃), 29.6 (CH₂Br), 55.6 (NCMe₃), 62.4 and 62.5 (2OCH₂), 88.1 (q, ²J_{FC} = 31.2 Hz, CCF₃), 122.0 (q, ¹J_{FC} = 287.7 Hz, CF₃), 134.9 and 143.4 (olefinic carbons), 149.8 (C=N), 159.3 and 160.9 (2C=O). ¹⁹F NMR (376.50, CDCl₃): δ = -75.64. MS: m/z (%) = 444 (M⁺ + 1, 48), 446 (M⁺ + 3, 48), 428 (17),430 (17), 416 (15), 418 (15), 360 (28), 362 (28), 308 (24), 275(27), 219 (22), 192 (52), 136 (24), 84 (30), 69 (44), 57 (100). Anal. calcd. for C₁₆H₂₁BrF₃NO₅ (416.19): C, 43.26; H, 4.76; N,3.15%. Found: C, 43.21; H, 4.73; N, 3.13%.

Dimethyl 2,2-bis (bromomethyl)-5-(*tert***-butylimino)-2,5-dihydrofuran-3,4-dicarboxylate (3u).** White powder, mp = 131–133 °C, yield 60%. IR (KBr) (ν_{max}/cm^{-1}): 1739 (C=O), 1681 (C=N), 1650 and 1448 (C=C) cm⁻¹. ¹HNMR (400.13 MHz, CDCl3): $\delta = 1.34$ (9H, s, CMe₃), 3.86 (3H, s,OCH₃), 3.90 (4H, s, 2CH₂Br), 3.93 (3H, s, OCH₃). ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 29.4$ (CMe₃), 33.8 (2CH₂Br), 53.1 and 53.2 (2OCH₃), 55.2 (NCMe₃), 88.3 (C), 138.5 and 141.6 (ole-finic carbons), 151.5 (C=N), 160.6 and 162.1 (2C=O). MS: m/z (%) = 439 (M⁺, 3), 441 (M⁺ + 2, 6), 443 (M⁺ + 4, 3), 424 (49), 426 (100), 428 (50), 408 (22), 410 (40), 412 (21), 392 (15), 394 (30), 396 (15), 393 (3), 395 (6), 397 (3), 384 (3), 386 (6), 388 (3), 367 (13), 369 (26), 371 (14), 95 (3), 93 (3), 84 (5), 57 (8). Anal. calcd. for C₁₄H₁₉Br₂NO₅(441.11): C, 38.12; H, 4.34; N, 3.18%. Found: C, 38.07; H, 4.31; N, 3.16%.

Diethyl 2,2-bis (bromomethyl)-5-(*tert***-butylimino)-2,5-dihydrofuran-3,4-dicarboxylate (3v).** White powder, mp = 83–85 °C, yield 55%. IR (KBr) (ν_{max}/cm^{-1}): 1735 (C=O), 1687 (C=N), 1650 and 1466 (C=C) cm⁻¹. ¹H NMR (400.13 MHz, CDCl₃): $\delta = 1.33$ (9H, s, CMe₃), 1.34 (3H, t, ³J_{HH} = 7.2 Hz, CH₃), 1.40 (3H, t, ³J_{HH} = 7.2 Hz, CH₃), 3.91 (4H, AB system, ²J_{HH} = 11.2 Hz, $\Delta \nu = 13.1$ Hz, 2CH₂Br), 4.31 (2H, q, ³J_{HH} = 7.2 Hz, OCH₂), 4.40 (2H, q, ³J_{HH} = 7.2 Hz, OCH₂). ¹³C NMR (100.6 MHz, CDCl₃): $\delta = 13.8$ and 14.1 (2CH₃) 29.4 (CMe₃), 34.0 (CH₂Br), 55.1 (NCMe₃), 62.2 and 62.3 (2OCH₂), 88.2 (C), 138.3 and 141.5 (olefinic carbons), 151.5 (C=N), 160.4 and 161.7 (2C=O). MS: *m/z* (%) = 467 (M⁺, 4), 469 (8), 471 (4), 452 (50),454 (100), 456 (50), 422 (2), 424 (4), 426 (2), 412 (4), 414 (8),416 (4), 346 (2), 348 (2), 321 (8), 323 (15), 325 (8), 84 (15), 57 (36). Anal. calcd. for C₁₆H₂₃Br₂NO₅ (469.17); C, 40.96; H, 4.94; 2.99; N, 2.98%. Found: C, 40.91; H, 4.91; N, 2.96%.

ACKNOWLEDGMENT

This research was supported by the Research Council of the University of Mazandaran in Iran.

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