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Synthesis of functionalized iminolactones via an isocyanide-based three-component reaction

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ABSTRACT

A three-component reaction of the zwitterions generated from isocyanides and dialkyl acetylenedicarboxylate with 1-(4-bromophenyl)-2-thiocyanatoethanone or 1-phenyl-2-thiocyanatoethanone is described. The reaction afforded the corresponding special type of functionalized iminolactone derivatives in good yields at room temperature without using a catalyst.

1. Introduction

Thiocyanates are versatile synthetic starting materials for the preparation of a variety of organosulfur and heterocyclic compounds.[1–4] These compounds possess a broad range of bioactivities and applications as anticancer agents, insecticides, antiasthmatic drugs, and DNA topoisomerase inhibitors.[5,6]

Iminolactones have been the subject of great consideration because of their effects as antibacterial agents, aldosterone inhibitors, and proper precursors for the preparation of a wide spectrum of natural compounds.[7] Iminolactones could be hydrolyzed with aqueous hydrochloric acid to produce butenolides.[8] This core unit is the key structure to induce a wide range of biological activities like antimicrobial,[9] antifungal,[10] anti-inflamatory,[11] anticancer,[12] and anti-viral HIV-1.[13]

Recently, the synthesis of these compounds has been of great interest in literature. A number of the synthetic methods for the synthesis of iminolactones have been developed during the past two decades. The most widely used approach to iminolactones synthesis is the isocyanide-based reactions.[14–20] The reactions of α,β-unsaturated carbonyl compounds with isocyanide via Et_2AlCl[14] and $GaCl_3$[15] catalysis have attracted much attention. Moreover, $GaCl_3$ catalyzes the double insertion of aryl isocyanides into terminal and disubstituted epoxides leads to α,β-unsaturated α-amino iminolactones.[16] Trapping of zwitterions intermediate derived from electron deficient acetylenic compounds and isocyanides with activated carbonyl compounds, such as hexachloroacetone,[17] 2-bromo-1-(4-bromophenyl)-ethanone,[18] benzoyl cyanide,[19] ethyl bromopyruvate,[20] and alkyl phenylglyoxylate[21] afforded iminolactones. Furthermore, the reaction of 4,4-disubstituted 2,3-allenamides and organic iodides afforded iminolactones.[22] Finally the haloiminolactonization of 4,4-disubstituted 2,3-alkadienamides with copper(II) halide or I_2 also proceeded to produce unsaturated iminolactones.[23]

2. Results and discussion

As a part of our ongoing research program on the isocyanides chemistry,[24,25] herein we describe an efficient synthesis of fully substituted iminolactones derivatives **4a**–**s** via a three-component reaction (Scheme 1).

In a model reaction, 1-(4-bromophenyl)-2-thiocyanatoethanone (**1a**), dimethyl acetylenedicarboxylate (**3a**), and cyclohexyl isocyanide (**2a**) in CH_2Cl_2 were stirred at room temperature. After completion of the reaction (after 5 h), the solvent was removed under vacuum and the residue was crystallized from *n*-hexane/ether (2:1) mixture and the product **4a** was obtained.

Next, various 1-phenyl-2-thiocyanatoethanone derivatives (**1a**–**d**, Scheme 2), alkyl or aryl isocyanides (**2a**–**d**, Scheme 3) and different dialkyl acetylenedicarboxylates (**3a**–**c**, Scheme 4) were treated under this reaction conditions. All of these reactions work fine to afford desired iminolactone products (**4a**–**o**) in good yields.

In order to investigate the scope and limitations of this reaction further, we decided to extend it to 1-(4-nitrophenyl)ethanone (**1e**), instead of 1-phenyl-2-thiocyanatoethanone derivatives (**1a**–**e**). In this regard **1e**, **3a**, and **2a** in CH_2Cl_2 were stirred at room temperature.

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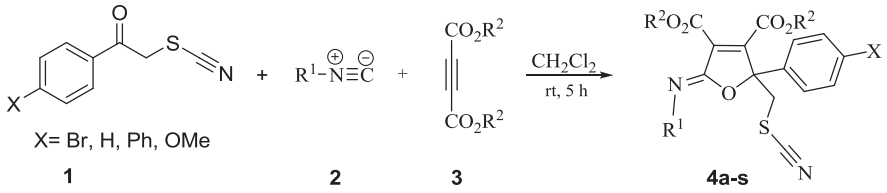
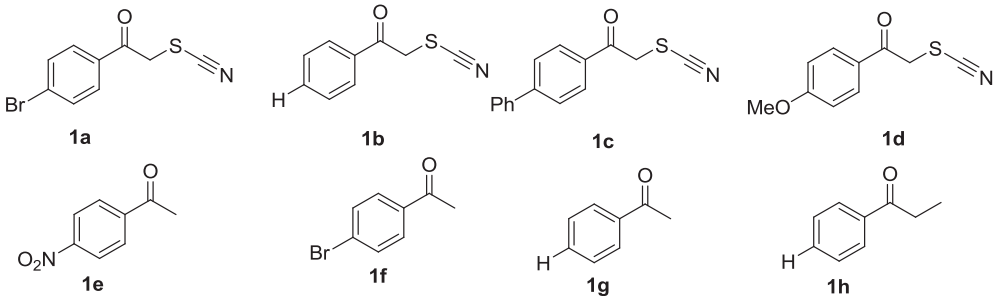
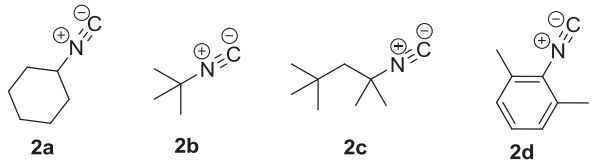


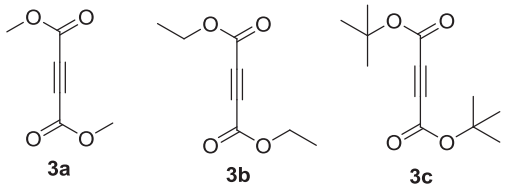
Scheme 1. Synthesis of fully substituted iminolactone compounds.



Scheme 2. Carbonyl compound starting materials.



Scheme 3. Isocyanide starting materials.



Scheme 4. Dialkyl acetylenedicarboxylate starting materials.

The progress of the reaction was monitored by TLC. After 5 h, the reaction was completed and (5*Z*)-dimethyl 5-(cyclohexylimino)-2,5-dihydro-2-methyl-2-(4-nitrophenyl)furan-3,4-dicarboxylate (**4p**) was obtained in 76% yield. To evaluate the use of this approach, a variety of 1-phenylethanone derivatives (**1f**–**h**) were used under similar circumstances; however the reaction did not proceed. These result, indicate that reactive zwitterionic intermediate has been trapped by carbonyl compounds that involving electron withdrawing substituent in the *para* position of phenyl group (**1e**) or electron withdrawing group in α position of carbonyl group (**1a**–**d**). As well as the yields range shown that carbonyl compounds that involving electron withdrawing (EW) substituent in the *para* position of phenyl group and EW group in α position of carbonyl group (**1a** and **1c**) have highly yields (Table 1, **4a**–**f** and **4m**–**n**). Whereas carbonyl compound that involving electron donating (ED) substituent in the *para* position (**1d**) has low yield (Table 1, **4o**). So carbonyl compounds that involving EW substituent in the *para* position of phenyl group (**1e**) or EW group in α position of carbonyl group (**1b**) have average yields (Table 1, **4g**–**k** and **4p**–**s**). On the other hand electron withdrawing group moiety has an important role in the reaction pathway and presence of this moiety is essential for reaction proceeding.

The synthesis of these functionalized iminolactones can be rationalized by initial formation of a highly reactive 1:1 zwitterionic intermediate **6**[24,25g,26] by the Michael type addition reaction of isocyanide **2** with dialkyl acetylenedicarboxylate **3** followed by a two-step dipolar species **7** formation with carbonyl compound **1** and then intramolecular cyclization reaction (path **A**) or a one-step [2+3] dipolar type cycloaddition reaction with carbonyl compound **1** (path **B**) to afford iminolactones **4a**–**s** (Scheme 5). The efficient conversion of the carbonyl compounds that involving EW substituents in the *para* position of phenyl group and EW groups in α position of carbonyl group (**1a** and **1c**) supported the two-step mechanism reaction sequence (path **A**).

As indicated in Table 1, isocyanides **2** react with dialkyl acetylenedicarboxylate **3** and 1-phenyl-2-thiocyanatoethanone derivatives **1** to undergo a smooth 1:1:1 addition reaction in CH_2Cl_2 at room temperature to produce fully substituted iminolactones **4**. The structures of the products were deduced from their IR, mass, ^{1}H NMR, and ^{13}C NMR spectra. The mass spectra of these compounds displayed molecular ion peaks at the appropriate *m*/*z* values.

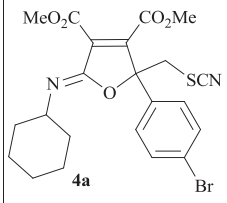
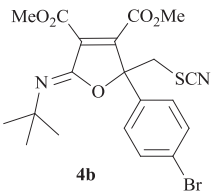
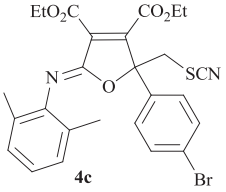
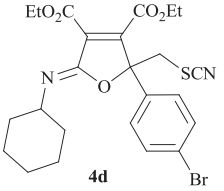
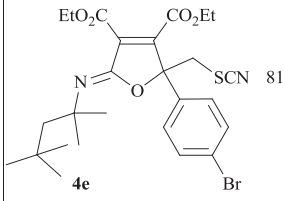
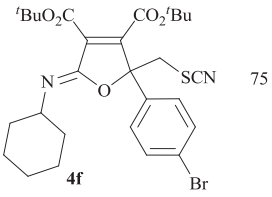
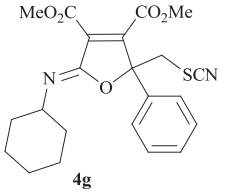
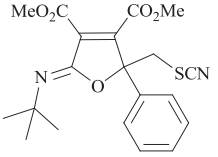
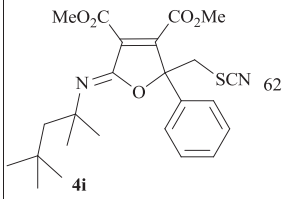
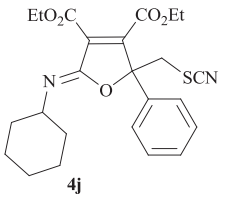
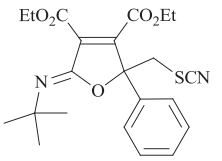
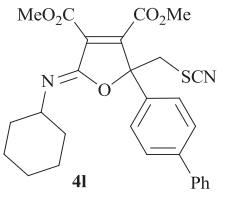
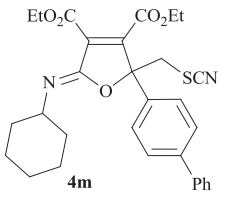
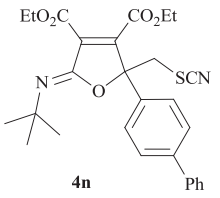
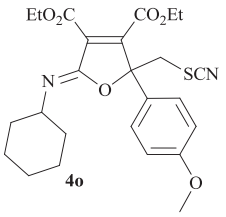
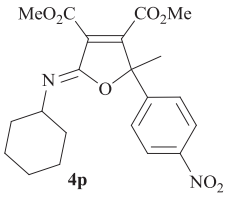
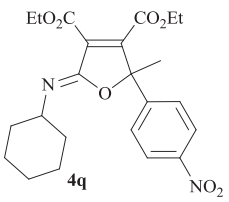
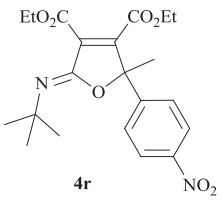
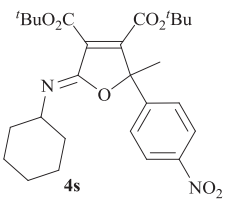
Finally, the structure of the product **4b** was confirmed unambiguously by single-crystal X-ray analysis (Fig. 1).

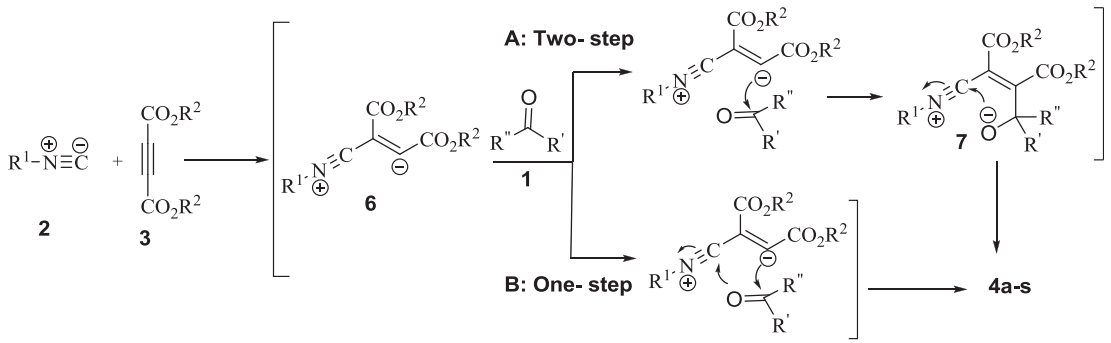
The reaction did not require any optimization, and we explored the use of various alkyl and aryl isocyanides with 1-phenyl-2-thiocyanatoethanone derivatives in CH_2Cl_2 at room temperature, which led to the formation of the corresponding fully substituted iminolactones derivatives in high yields. The reaction proceeds under mild reaction conditions and is compatible with a wide range of functional groups. Owing to the great diversity of substitution patterns, this reaction may be used in the production of combinatorial libraries (Table 1).

The synthetic scope of this new reaction is highly increased by the potential of the hydrolysis of iminolactones involving imines. Besides the obvious hydrolysis, more interesting heterocycle formations could be reached using these iminolactones as reactive intermediates. For instance, hydrolysis of iminolactones with aqueous hydrochloric acid[8] at room temperature provides butenolides in good yields (Table 2). The structures of the products were deduced from their IR, ^{1}H NMR, and ^{13}C NMR spectra.

In summary we have described a highly efficient approach to the synthesis of fully substituted iminolactones involving thiocyanate group from various isocyanides and dialkyl acetylenedicarboxylates in the presence of 1-phenyl-2-thiocyanatoethanone derivatives in absence of catalyst. Scope and limitation of the reaction are described. The reaction has been shown to display relatively good

Table 1
Synthesis of fully substituted iminolactones (**4a**–**s**)

Structure	Yield (%)	Structure	Yield (%)	Structure	Yield (%)	Structure	Yield (%)
 **4a**	81	 **4b**	78	 **4c**	85	 **4d**	80
 **4e**	81	 **4f**	75	 **4g**	65	 **4h**	63
 **4i**	62	 **4j**	60	 **4k**	57	 **4l**	83
 **4m**	85	 **4n**	80	 **4o**	60	 **4p**	76
 **4q**	74	 **4r**	69	 **4s**	78		



Scheme 5. Proposed pathway.

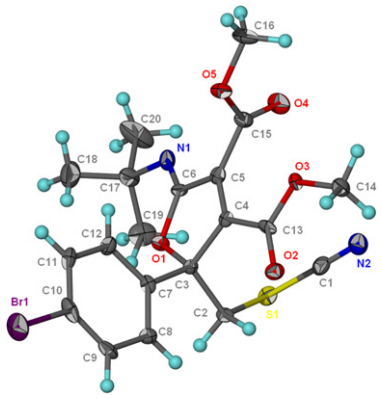


Fig. 1. ORTEP diagram of **4b** (CCDC reference number 816044).

functional group tolerance and is high yielding and product isolation is very straightforward. The diversity offered by this process is further enhanced by hydrolysis of iminolactones with aqueous hydrochloric acid, which provides butenolide derivatives. We hope that this approach may be of value to others seeking novel synthetic fragments with unique properties for medicinal chemistry.

3. Experimental

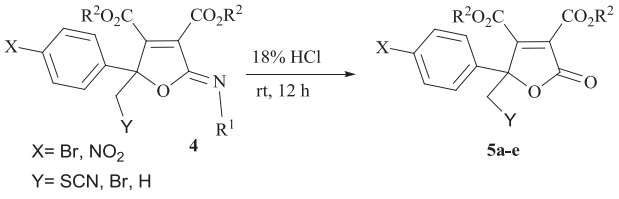
3.1. General

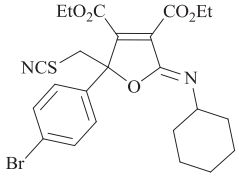
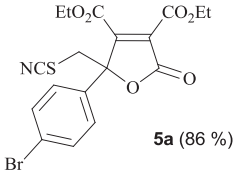
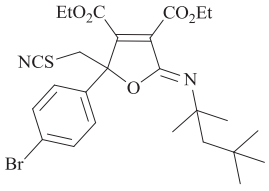
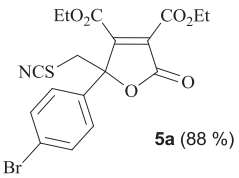
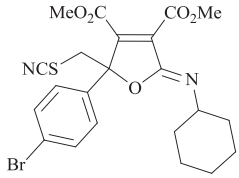
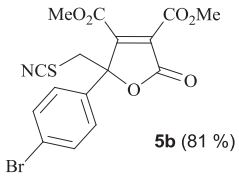
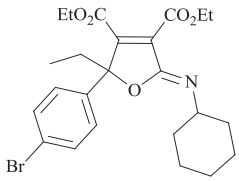
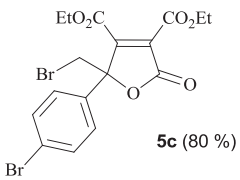
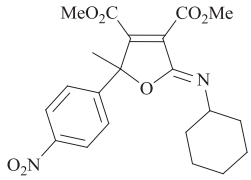
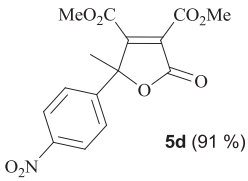
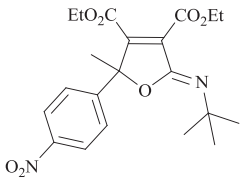
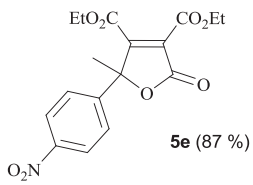
Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Mass spectra were recorded on a FINNIGAN-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 and 75.47 MHz. NMR spectra were obtained on solution in $CDCl_3$ using TMS as internal standard. The chemicals used in this work were purchased from Merck and Fluka Chemical Companies. Compounds (**1a**–**d**) have previously been described[3] and their physical properties were in agreement with those reported.

3.2. Typical procedure for preparation of (*Z*)-dimethyl 2-(4-bromophenyl)-5-(cyclohexylimino)-2-(thiocyanatomethyl)-2,5-dihydrofuran-3,4-dicarboxylate (4a)

To a magnetically stirred solution of 1-(4-bromophenyl)-2-thiocyanatoethanone (0.26 g, 1.0 mmol) and dimethyl acetylenedicarboxylate (0.14 g, 1.0 mmol) in 10 mL CH_2Cl_2 was added, dropwise, cyclohexyl isocyanide (0.11 g, 1 mmol) at 0 °C over 10 min. The mixture was allowed to warm up to room temperature and was finally stirred for 5 h. The solvent was removed under vacuum and the residue was crystallized from *n*-hexane/ether (2:1) mixture and the products were thus obtained as colorless crystals, yield 0.51 g (81%); mp 123–126 °C; R_f (25% AcOEt/*n*-hexane) 0.68; IR (KBr) ν_{max}=2919, 2841, 2157, 1752, 1729, 1680, 1429, 1296 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.22–2.00 (10H, m, 5CH_2 of cyclohexyl), 3.78 (4H, br s, OCH_3 and CH–N), 3.86 (1H, d, $^2J_{AB}$=14.2 Hz, CH_2SCN), 3.92 (3H, s, OCH_3), 4.17 (1H, d, $^2J_{AB}$=14.2 Hz, CH_2SCN), 7.28 (2H, d, $^3J_{HH}$=8.6 Hz, H–Ar), 7.52 (2H, d, $^3J_{HH}$=8.6 Hz, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.6, 24.7, 25.6, 31.0, 33.3, 41.2, 53.2, 53.3, 57.1, 89.8, 111.3, 123.8, 127.3, 132.5, 135.9, 137.9, 141.7, 153.0, 161.1, 161.7 ppm. Anal. Calcd for $C_{22}H_{23}BrN_2O_5S$: C, 52.08; H, 4.57; N, 5.52. Found: C, 51.97; H, 4.60; N, 5.47.

Table 2
Hydrolysis of iminolactones to butenolides (**5a**–**e**)



Iminolactone	Product	Iminolactone	Product
	 **5a** (86 %)		 **5a** (88 %)
	 **5b** (81 %)		 **5c** (80 %)
	 **5d** (91 %)		 **5e** (87 %)

*3.2.1. (5Z)-Dimethyl 5-(tert-butylimino)-2-(4-bromophenyl)-2,5-dihydro-2-(thiocyanatomethyl)furan-3,4-dicarboxylate (**4b**).* Colorless crystals, yield 0.37 g (78%); mp 120–122 °C; R_f (25% AcOEt/*n*-hexane) 0.63; IR (KBr) ν_{max}=2930, 2869, 2146, 1755, 1720, 1672, 1650 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.36 (9H, s, $C(CH_3)_3$), 3.79 (3H, s, OCH_3), 3.87 (1H, d, $^2J_{AB}$=14.3 Hz, CH_2SCN), 3.92 (3H, s, OCH_3), 4.26 (1H, d, $^2J_{AB}$=14.3 Hz, CH_2SCN), 7.30 (2H, d, $^3J_{HH}$=8.3 Hz, H–Ar), 7.53 (2H, d, $^3J_{HH}$=8.3 Hz, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=29.7, 41.5, 53.1, 53.3, 55.3, 90.2, 111.2, 123.7, 127.4, 132.2, 135.9, 139.4, 140.5, 150.8, 160.9, 161.8 ppm. Anal. Calcd for $C_{20}H_{21}BrN_2O_5S$: C, 49.90; H, 4.40; N, 5.82. Found: C, 50.03; H, 4.35; N, 5.94; CCDC reference number 816044.

*3.2.2. (5Z)-Dimethyl 5-(2,6-dimethylphenylimino)-2-(4-bromophenyl)-2,5-dihydro-2-(thiocyanatomethyl)furan-3,4-dicarboxylate (**4c**).* White crystals, yield 0.45 g (85%); mp 178–182 °C; R_f (25% AcOEt/*n*-hexane) 0.64; IR (KBr) ν_{max}=2952, 2924, 2168, 1733, 1691, 1645, 1277 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=2.16 (6H, s, $2CH_3$), 3.68 (1H, d, $^2J_{AB}$=14.1 Hz, CH_2SCN), 3.87 (3H, s, OCH_3), 4.03 (3H, s, OCH_3), 4.32 (1H, d, $^2J_{AB}$=14.1 Hz, CH_2SCN), 6.95–7.05 (3H, m, H–Ar), 7.24 (2H, d, $^3J_{HH}$=7.8 Hz, H–Ar), 7.53 (2H, d, $^3J_{HH}$=7.8 Hz, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=18.2, 40.7, 53.5, 53.6, 90.7, 110.8, 124.1, 124.2, 127.0, 127.3, 127.7, 132.3, 135.1, 137.6, 143.0, 143.4, 160.7, 161.3 ppm. Anal. Calcd for $C_{24}H_{21}BrN_2O_5S$: C, 54.45; H, 4.00; N, 5.29. Found: C, 54.67; H, 4.07; N, 5.41.

*3.2.3. (5Z)-Diethyl 2-(4-bromophenyl)-5-(cyclohexylimino)-2,5-dihydro-2-(thiocyanatomethyl)furan-3,4-dicarboxylate (**4d**).* Colorless crystals, yield 0.43 g (80%); R_f (25% AcOEt/*n*-hexane) 0.67; mp 102–105 °C; IR (KBr) ν_{max}=2928, 2847, 2152, 1750, 1722, 1681, 1485 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.22–1.77 (16H, m, $2OCH_2CH_3$, $5CH_2$ of cyclohexyl), 3.80–4.43 (7H, m, $2OCH_2CH_3$, CH_2SCN and CH–N), 7.31 (2H, d, $^3J_{HH}$=8.5 Hz, H–Ar), 7.54 (2H, d, $^3J_{HH}$=8.5 Hz, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.9, 14.0, 24.5, 24.6, 25.7, 33.3, 41.3, 56.9, 62.5, 62.6, 89.7, 111.3, 123.7, 127.3, 132.2, 136.0, 137.9, 141.4, 153.0, 160.8, 161.3 ppm. Anal. Calcd for $C_{24}H_{27}BrN_2O_5S$: C, 53.83; H, 5.08; N, 5.23. Found: C, 53.70; H, 4.89; N, 5.35.

*3.2.4. (5Z)-Diethyl 5-(2,4,4-trimethylpentan-2-ylimino)-2-(4-bromophenyl)-2,5-dihydro-2-(thiocyanatomethyl)furan-3,4-dicarboxylate (**4e**).* Yellow oil, yield 0.43 g (81%); R_f (25% AcOEt/*n*-hexane) 0.65; IR (KBr) ν_{max}=2983, 2926, 2146, 1755, 1735, 1663, 1658, 1585 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=0.99 (9H, s, $C(CH_3)_3$) 1.24 (3H, t, $^3J_{HH}$=7.1 Hz, OCH_2CH_3), 1.33 (3H, t, $^3J_{HH}$=7.1 Hz, OCH_2CH_3), 1.40 (6H, s, $C(CH_3)_2$), 1.61 (2H, br s, CH_2), 3.87 (1H, d, $^2J_{AB}$=14.0 Hz, CH_2SCN) 4.11–4.36 (5H, $2OCH_2CH_3$ and CH_2SCN), 7.34 (2H, d, $^3J_{HH}$=8.5 Hz, H–Ar), 7.50 (2H, d, $^3J_{HH}$=8.5 Hz, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.7, 14.1, 29.7, 29.8, 31.7, 31.9, 41.7, 55.7, 58.7, 62.2, 62.5, 90.1, 111.2, 123.5, 127.6, 132.1, 136.2, 139.7, 139.8, 149.6, 160.6, 161.5 ppm. Anal. Calcd for $C_{26}H_{33}BrN_2O_5S$: C, 55.22; H, 5.88; N, 4.95. Found: C, 55.38; H, 5.76; N, 5.03.

*3.2.5. (5Z)-Di-tert-butyl 2-(4-bromophenyl)-5-(cyclohexylimino)-2,5-dihydro-2-(thiocyanatomethyl)furan-3,4-dicarboxylate (**4f**).* White crystals, yield 0.44 g (75%); mp 123–126 °C; R_f (25% AcOEt/*n*-hexane) 0.65; IR (KBr) ν_{max}=2930, 2863, 2157, 1744, 1722, 1683, 1479 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.35–2.17 (28H, m, $5CH_2$ of cyclohexyl and $2OC(CH_3)_3$), 3.82 (1H, br s, CH–N), 3.85 (1H, d, $^2J_{AB}$=14.0 Hz, CH_2SCN), 4.13 (1H, d, $^2J_{AB}$=14.0 Hz, CH_2SCN), 7.29 (2H, d, $^3J_{HH}$=8.4 Hz, H–Ar), 7.53 (2H, d, $^3J_{HH}$=8.4 Hz, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.1, 24.2, 25.9, 27.9, 28.2, 30.9, 33.4, 41.9, 55.9, 84.0, 84.6, 89.4, 111.4, 123.4, 127.3, 132.0, 136.5, 137.4, 141.6, 152.8, 160.4, 160.5 ppm. Anal. Calcd for $C_{28}H_{35}BrN_2O_5S$: C, 56.85; H, 5.96; N, 4.74. Found: C, 56.97; H, 5.84; N, 4.90.

*3.2.6. (5Z)-Dimethyl 5-(cyclohexylimino)-2,5-dihydro-2-phenyl-2-(thiocyanatomethyl)furan-3,4-dicarboxylate (**4g**).* Colorless crystals, yield 0.28 g (65%); R_f (25% AcOEt/*n*-hexane) 0.71; mp 105–108 °C; IR (KBr) ν_{max}=2931, 2852, 2152, 1753, 1728, 1683, 1438 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.18–2.02 (10H, m, $5CH_2$ of cyclohexyl), 3.77–4.23 (9H, m, $2OCH_3$, CH–N and CH_2SCN), 7.39 (5H, br s, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.6, 24.7, 25.7, 33.3, 33.4, 41.4, 53.1, 53.2, 56.9, 90.2, 111.5, 125.5, 129.1, 129.4, 136.8, 137.6, 142.3, 153.4, 161.2, 161.8 ppm. Anal. Calcd for $C_{22}H_{24}N_2O_5S$: C, 61.67; H, 5.65; N, 6.54. Found: C, 61.87; H, 5.49; N, 6.71.

*3.2.7. (5Z)-Dimethyl 5-(tert-butylimino)-2,5-dihydro-2-phenyl-2-(thiocyanatomethyl)furan-3,4-dicarboxylate (**4h**).* Colorless crystals, yield 0.25 g (78%); R_f (25% AcOEt/*n*-hexane) 0.70; mp 102–105 °C; IR (KBr) ν_{max}=2968, 2924, 2161, 1752, 1726, 1680, 1432 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.38 (9H, s, $C(CH_3)_3$), 3.74–3.90 (7H, m, $2OCH_3$, CH_2SCN), 4.31 (1H, d, $^2J_{AB}$=14.0 Hz, CH_2SCN), 7.38–7.41 (5H, m, H–Ar), ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=29.7, 41.7, 53.1, 53.2, 55.2, 90.6, 111.5, 125.6, 129.0, 129.4, 136.9, 139.2, 141.1, 151.2, 161.1, 162.0 ppm. Anal. Calcd for $C_{20}H_{22}N_2O_5S$: C, 59.69; H, 5.51; N, 6.96. Found: C, 59.48; H, 5.43; N, 7.12.

*3.2.8. (5Z)-Dimethyl 5-(2,4,4-trimethylpentan-2-ylimino)-2,5-dihydro-2-phenyl-2-(thiocyanatomethyl)furan-3,4-dicarboxylate (**4i**).* Colorless crystals, yield 0.29 g (62%); R_f (25% AcOEt/*n*-hexane) 0.68; mp 80–82 °C; IR (KBr) ν_{max}=2951, 2866, 2160, 1748, 1727, 1690, 1648 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.05(9H, s, $(CH_3)_3$), 1.43 (6H, s, $(CH_3)_2$), 1.63 (2H, br s, CH_2), 3.79 (3H, s, OCH_3), 3.89 (3H, s, OCH_3), 3.94 (1H, d, $^2J_{AB}$=13.9 Hz, CH_2SCN), 4.28 (1H, d, $^2J_{AB}$=13.9 Hz, CH_2SCN),7.39–7.43 (5H, br s, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=29.6, 31.0, 31.6, 32.0, 41.9, 52.9, 53.1, 55.8, 58.8, 90.6, 111.5, 125.7, 128.9, 129.3, 137.0, 139.6, 140.3, 149.8, 161.2, 162.1 ppm. Anal. Calcd for $C_{24}H_{30}N_2O_5S$: C, 62.86; H, 6.59; N, 6.11. Found: C, 63.04; H, 6.60; N, 6.14.

*3.2.9. (5Z)-Diethyl 5-(cyclohexylimino)-2,5-dihydro-2-phenyl-2-(thiocyanatomethyl)furan-3,4-dicarboxylate (**4j**).* Colorless crystals, yield 0.27 g (60%); R_f (25% AcOEt/*n*-hexane) 0.72; mp 100–102 °C; IR (KBr) ν_{max}=2930, 2847, 2152, 1746, 1718, 1687, 1650, 1446 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.24–1.83 (16H, m, $5CH_2$ of cyclohexyl and $2OCH_2CH_3$), 3.89–4.40 (7H, m, $2OCH_2CH_3$, CH–N and CH_2SCN), 7.41 (5H, br s, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8, 14.0, 24.5, 24.7, 25.7, 33.4, 41.6, 56.8, 62.4, 62.5, 90.1, 111.5, 125.5, 129.0, 129.3, 136.9, 137.5, 142.1, 153.3, 160.9, 161.4 ppm. Anal. Calcd for $C_{24}H_{28}N_2O_5S$: C, 63.14; H, 6.18; N, 6.14. Found: C, 63.05; H, 6.19; N, 6.21.

*3.2.10. (5Z)-Diethyl 5-(tert-butylimino)-2,5-dihydro-2-phenyl-2-(thiocyanatomethyl)furan-3,4-dicarboxylate (**4k**).* Yellow oil, yield 0.24 g (57%); R_f (25% AcOEt/*n*-hexane) 0.69; IR (KBr) ν_{max}=2968, 2897, 2152, 1744, 1719, 16891651 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.23–1.42 (15H, 3, $(CH_3)_3$ and $2OCH_2CH_3$), 3.91–476 (6H, $2OCH_2CH_3$, CH_2SCN), 7.37–7.45 (5H, br s, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8, 14.1, 29.7, 41.9, 55.1, 62.2, 62.4, 90.5, 111.5, 125.7, 129.1, 129.3, 137.0, 139.1, 140.8, 151.2, 160.7, 161.4 ppm. Anal. Calcd for $C_{22}H_{26}N_2O_5S$: C, 61.38; H, 6.09; N, 6.51. Found: C, 61.36; H, 6.13; N, 6.46.

*3.2.11. (5Z)-Dimethyl 2-(4-phenylophenyl)-5-(cyclohexylimino)-2-(thiocyanatomethyl)-2,5-dihydrofuran-3,4-dicarboxylate (**4l**).* White crystals, yield 0.42 g (83%); mp 165–167 °C; R_f (25% AcOEt/*n*-hexane) 0.58; IR (KBr) ν_{max}=2930, 2849, 2156, 1751, 1724, 1679, 1642, 1440 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.23–1.88 (10H, m, $5CH_2$ of cyclohexyl), 3.83 (4H, br s, OCH_3 and CH–N), 3.92 (3H, s, OCH_3), 3.96 (1H, d, $^2J_{AB}$=14.2 Hz, CH_2SCN), 4.27 (1H, d, $^2J_{AB}$=14.2 Hz, CH_2SCN), 7.28–7.66 (9H, m, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.6, 24.8, 25.7, 33.4, 33.5, 41.4, 53.2, 57.1, 90.1, 111.5, 127.1, 127.7, 127.9, 128.9, 129.1, 135.7, 137.7, 142.2, 142.3, 153.3, 161.3, 161.8 ppm. Anal.

Calcd for $C_{28}H_{28}N_2O_5S$: C, 66.65; H, 5.59; N, 5.55. Found: C, 66.91; H, 5.73; N, 5.51.

*3.2.12. (5Z)-Diethyl 2-(4-phenylophenyl)-5-(cyclohexylimino)-2,5-dihydro-2-(thiocyanatomethyl)furan-3,4-dicarboxylate (**4m**).* White crystals, yield 0.45 g (85%); mp 149–151 °C; R_f (25% AcOEt/*n*-hexane) 0.57; IR (KBr) ν_{max}=2931, 2829, 2161, 1745, 1740, 1666, 1598 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.20–1.79 (16H, m, $2OCH_2CH_3$ and $5CH_2$ of cyclohexyl), 3.98–4.43 (7H, m, $2OCH_2CH_3$, CH_2SCN and CH–N), 7.39–7.66 (9H, m, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8, 14.1, 24.6, 24.7, 25.7, 33.4, 41.5, 56.9, 62.4, 62.5, 90.1, 111.5, 126.1, 127.1, 127.7, 128.9, 129.1, 135.8, 137.6, 139.9, 142.2, 153.4, 161.0, 161.4 ppm. Anal. Calcd for $C_{30}H_{32}N_2O_5S$: C, 67.65; H, 6.06; N, 5.26. Found: C, 67.63; H, 5.98; N, 5.35.

*3.2.13. (5Z)-Diethyl 5-(tert-butylimino)-2-(4-phenylophenyl)-2,5-dihydro-2-(thiocyanatomethyl)furan-3,4-dicarboxylate (**4n**).* White crystals, yield 0.4 g (80%); mp 120–121 °C; R_f (25% AcOEt/*n*-hexane) 0.60; IR (KBr) ν_{max}=2967, 2931, 2156, 1752, 1721, 1685, 1637 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.21–1.42 (15H, m, $C(CH_3)_3$ and $2OCH_2CH_3$), 3.98 (1H, d, $^2J_{AB}$=13.9 Hz, CH_2SCN), 4.17–4.45 (5H, m, $2OCH_2CH_3$ and CH_2SCN), 7.28–7.77 (9H, m, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8, 14.1, 29.8, 41.9, 55.2, 62.3, 62.4, 90.5, 111.5, 126.2, 127.1, 127.6, 127.8, 128.9, 135.8, 139.2, 139.9, 140.7, 142.1, 151.2, 160.8, 161.7 ppm. Anal. Calcd for $C_{28}H_{30}N_2O_5S$: C, 66.38; H, 5.97; N, 5.53. Found: C, 66.52; H, 5.92; N, 5.50.

*3.2.14. (5Z)-Diethyl 5-(cyclohexylimino)-2,5-dihydro-2-(4-methoxyphenyl)-2-(thiocyanatomethyl)furan-3,4-dicarboxylate (**4o**).* Yellow oil, yield 0.29 g (60%); R_f (25% AcOEt/*n*-hexane) 0.62; IR (KBr) ν_{max}=2933, 2844, 2151, 1748, 1724, 1678, 1601, 1513 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.1.18–1.75 (16H, m, $2OCH_2CH_3$ and $5CH_2$ of cyclohexyl), 3.71–4.31 (10H, m, OCH_3, $2OCH_2CH_3$, CH_2SCN and CH–N), 6.84 (2H, d, $^3J_{HH}$=7.9 Hz, H–Ar), 7.26 (2H, d, $^3J_{HH}$=7.9 Hz, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.7, 13.9, 24.5, 24.6, 25.7, 33.3, 41.4, 55.2, 56.6, 62.2, 62.3, 90.0, 111.5, 114.2, 126.9, 128.7, 137.3, 142.2, 153.5, 160.1, 160.7, 161.4 ppm. Anal. Calcd for $C_{25}H_{30}N_2O_6S$: C, 61.71; H, 6.21; N, 5.76. Found: C, 61.90; H, 6.17; N, 5.84.

*3.2.15. (5Z)-Dimethyl 5-(cyclohexylimino)-2,5-dihydro-2-methyl-2-(4-nitrophenyl)furan-3,4-dicarboxylate (**4p**).* White crystals, yield 0.32 g (76%); R_f (25% AcOEt/*n*-hexane) 0.40; mp 167–170 °C; IR (KBr) ν_{max}=2929, 2849, 1753, 1731, 1676, 1521 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.19–1.85 (10H, m, $5CH_2$ of cyclohexyl), 2.09 (3H, s, CH_3), 3.61 (1H, br s, CH–N), 3.73 (3H, s, OCH_3), 3.92 (3H, s, OCH_3), 7.61 (2H, d, $^3J_{HH}$=8.6 Hz, H–Ar), 8.23 (2H, d, $^3J_{HH}$=8.6 Hz, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=4.2, 24.7, 25.7, 33.3, 52.8, 53.1, 56.8, 88.9, 123.7, 127.1, 135.9, 145.5, 146.4, 147.8, 154.2, 160.8, 162.3 ppm. Anal. Calcd for $C_{21}H_{24}N_2O_7$: C, 60.57; H, 5.81; N, 6.73. Found: C, 60.60; H, 5.81; N, 6.92.

*3.2.16. (5Z)-Diethyl 5-(cyclohexylimino)-2,5-dihydro-2-methyl-2-(4-nitrophenyl)furan-3,4-dicarboxylate (**4q**).* White crystals, yield 0.33 g (74%); mp 138–140 °C; R_f (25% AcOEt/*n*-hexane) 0.48; IR (KBr) ν_{max}=2936, 2839, 1745, 1723, 1676, 1519 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.21–1.76 (16H, m, $2OCH_2CH_3$ and $5CH_2$ of cyclohexyl), 2.10 (3H, s, CH_3), 3.65 (1H, m, CH–N), 4.16 (2H, q, $^3J_{HH}$=6.9 Hz, OCH_2CH_3), 4.39 (2H, q, $^3J_{HH}$=7.0 Hz, OCH_2CH_3), 7.62 (2H, d, $^3J_{HH}$=8.6 Hz, H–Ar), 8.23 (2H, d, $^3J_{HH}$=8.6 Hz, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8, 14.1, 24.3, 24.7, 25.7, 33.4, 56.6, 62.1, 62.3, 89.0, 123.6, 127.1, 135.9, 145.3, 146.7, 147.8, 154.3, 160.4, 161.9 ppm. Anal. Calcd for $C_{23}H_{28}N_2O_7$: C, 62.15; H, 6.35; N, 6.30. Found: C, 62.32; H, 6.21; N, 6.39.

*3.2.17. (5Z)-Diethyl 5-(tert-butylimino)-2,5-dihydro-2-methyl-2-(4-nitrophenyl)furan-3,4-dicarboxylate (**4r**).* Yellow oil, yield 0.29 g (69%); R_f (25% AcOEt/*n*-hexane) 0.43; IR (KBr) ν_{max}=2980, 2865, 1745, 1724, 1678, 1528 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.13–1.44 (15H, m, $C(CH_3)_3$ and $2OCH_2CH_3$), 2.03 (3H, s, CH_3), 4.09 (2H, q, $^2J_{AB}$=7.0 Hz, OCH_2CH_3), 4.29 (2H, q, $^2J_{AB}$=7.1 Hz, OCH_2CH_3), 7.57 (2H, d, $^3J_{HH}$=8.8 Hz, H–Ar), 8.13 (2H, d, $^3J_{HH}$=8.8 Hz, H–Ar)ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.6, 13.8, 24.2, 29.4, 54.6, 61.9, 62.0, 89.5, 123.5, 127.1, 129.3, 137.3, 144.2, 146.8, 147.6, 152.3, 160.3, 162.0 ppm. Anal. Calcd for $C_{21}H_{26}N_2O_7$: C, 60.28; H, 6.26; N, 6.69. Found: C, 60.46; H, 6.19; N, 6.81.

*3.2.18. (5Z)-Di-tert-butyl 5-(cyclohexylimino)-2,5-dihydro-2-methyl-2-(4-nitrophenyl)furan-3,4-dicarboxylate (**4s**).* White crystals, yield 0.39 g (78%); mp 124–126 °C; R_f (25% AcOEt/*n*-hexane) 0.45; IR (KBr) ν_{max}=2989, 2933, 2863, 1725, 1682, 1521 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=093–2.04 (28H, m, $5CH_2$ of cyclohexyl and $2OC(CH_3)_3$), 3.63 (1H, br s, CH–N), 7.58 (2H, d, $^3J_{HH}$=8.3 Hz, H–Ar), 8.20 (2H, d, $^3J_{HH}$=8.4 Hz, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.3, 25.8, 27.1, 27.8, 28.2, 33.3, 55.6, 83.7, 83.8, 88.7, 123.3, 123.5, 125.8, 127.0, 129.2, 147.1, 147.6, 159.9, 160.9 ppm. Anal. Calcd for $C_{27}H_{36}N_2O_7$: C, 64.78; H, 7.25; N, 5.60. Found: C, 64.97; H, 7.41; N, 5.78.

3.3. Typical procedure for preparation of diethyl 2-(4-bromophenyl)-2,5-dihydro-5-oxo-2-(thiocyanatomethyl) furan-3,4-dicarboxylate (5a)

To a solution of hydrochloric acid (18%, 10 mL) was added powdered iminolactone **4d** (0.53 g, 1.0 mmol) and stirred at room temperature for 12 h. After completion of the reaction (monitored by TLC method), the reaction mixture was extracted with CH_2Cl_2 (2×10 mL). The combined extract solvent was removed under vacuum and the residue was crystallized from 1:3 CH_2Cl_2/*n*-hexane mixture to yield **5a** as a white crystals, yield 0.39 g (86%); mp 69–71 °C; R_f (25% AcOEt/*n*-hexane) 0.38; IR (KBr) ν_{max}=2162, 1749, 1729, 1656 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.31 (3H, t, $^3J_{HH}$=7.1 Hz, OCH_2CH_3), 1.39 (3H, t, $^3J_{HH}$=7.1 Hz, OCH_2CH_3), 3.89 (1H, d, $^2J_{AB}$=14.4 Hz, CH_2SCN), 4.21 (1H, d, $^2J_{AB}$=14.4 Hz, CH_2SCN),4.27–4.44 (4H, m, $2OCH_2CH_3$), 7.32 (2H, d, $^3J_{HH}$=8.7 Hz, H–Ar), 7.58 (2H, d, $^3J_{HH}$=8.7 Hz, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.7, 14.0, 41.0, 63.0, 63.5, 87.2, 110.5, 124.5, 127.2, 130.4, 132.6, 133.0, 153.2, 159.5, 160.2, 164.7 ppm. Anal. Calcd for $C_{18}H_{16}BrNO_6S$: C, 47.59; H, 3.55; N, 3.08. Found: C, 47.71; H, 3.49; N, 3.00.

*3.3.1. Dimethyl 2-(4-bromophenyl)-2,5-dihydro-5-oxo-2-(thiocyanatomethyl)furan-3,4-dicarboxylate (**5b**).* Colorless oil, yield 0.34 g (81%); R_f (25% AcOEt/*n*-hexane) 0.27; IR (KBr) ν_{max}=2168, 1793, 1734, 1663 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=3.87 (4H, br s, OCH_3 and CH_2SCN), 3.94 (3H, s, OCH_3), 4.20 (1H, d, $^2J_{AB}$=14.3 Hz, CH_2SCN), 7.28 (2H, d, $^3J_{HH}$=7.8 Hz, H–Ar), 7.56 (2H, d, $^3J_{HH}$=7.8 Hz, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=40.8, 53.6, 54.0, 87.3, 110.7, 124.6, 127.1, 129.9, 132.6, 132.8, 154.0, 159.8, 160.6, 164.6 ppm. Anal. Calcd for $C_{16}H_{12}BrNO_6S$: C, 45.09; H, 2.84; N, 3.29. Found: C, 44.87; H, 2.76; N, 3.35.

*3.3.2. Diethyl 2-(bromomethyl)-2-(4-bromophenyl)-2,5-dihydro-5-oxofuran-3,4-dicarboxylate (**5c**).* Colorless oil, yield 0.38 g (80%); R_f (25% AcOEt/*n*-hexane) 0.30; IR (KBr) ν_{max}=1795, 1731, 1663, 1486 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.23–1.36 (6H, m, $2OCH_2CH_3$), 4.06–4.44 (6H, m, CH_2Br and $2OCH_2CH_3$), 7.31 (2H, d, $^3J_{HH}$=7.4 Hz, H–Ar), 7.51 (2H, d, $^3J_{HH}$=7.4 Hz, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.8, 14.1, 35.1, 62.8, 63.2, 87.0, 124.2, 127.4, 130.1, 132.4, 133.1, 154.2, 159.8, 160.0, 165.1 ppm. Anal. Calcd for $C_{17}H_{16}Br_2O_6$: C, 42.89; H, 3.39. Found: C, 42.70; H, 3.45.

*3.3.3. Dimethyl 2,5-dihydro-2-methyl-2-(4-nitrophenyl)-5-oxofuran-3,4-dicarboxylate (**5d**).* White crystals, yield 0.30 g (91%); mp

97–100 °C; R_f (25% AcOEt/*n*-hexane) 0.25; IR (KBr) ν_{max}=1762, 1732, 1600, 1517 cm^{-1}; MS, *m*/*z* (%): 336 (M^++1, 1), 320 (3), 293 (5), 277 (10), 261 (10), 218 (5), 150 (20), 100 (5), 56 (100); ^1H NMR (300 MHz, $CDCl_3$): δ=2.14 (3H, s, CH_3), 3.81 (3H, s, OCH_3), 3.91 (3H, s, OCH_3), 7.58 (2H, d, $^3J_{HH}$=7.9 Hz, H–Ar), 8.22 (2H, d, $^3J_{HH}$=7.9 Hz, H–Ar) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.4, 53.4, 53.6, 86.6, 124.1, 126.8, 127.2, 143.1, 148.2, 159.2, 160.3, 160.6, 165.4 ppm. Anal. Calcd for $C_{15}H_{13}NO_8$: C, 53.74; H, 3.91; N, 4.18. Found: C, 53.47; H, 4.00; N, 4.27.

*3.3.4. Diethyl 2,5-dihydro-2-methyl-2-(4-nitrophenyl)-5-oxofuran-3,4-dicarboxylate (**5e**).* White crystals, yield 0.32 g (87%); R_f (25% AcOEt/*n*-hexane) 0.30; IR (KBr) ν_{max}=1788, 1734, 1656, 1527, 1346 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ=1.24–1.38 (6H, m, $2OCH_2CH_3$), 2.15 (3H, s, CH_3), 4.24–4.42 (4H, m, $2OCH_2CH_3$), 7.61 (2H, d, $^3J_{HH}$=8.9 Hz, H–Ar), 8.24 (2H, d, $^3J_{HH}$=8.9 Hz, H–Ar)ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ=13.7, 14.1, 24.4, 62.8, 63.0, 86.6, 124.0, 126.9, 127.6, 143.3, 148.2, 158.4, 159.9, 160.0, 165.7 ppm. Anal. Calcd for $C_{17}H_{17}NO_8$: C, 56.20; H, 4.72; N, 3.86. Found: C, 56.52; H, 4.90; N, 3.80.

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Supplementary data

Experimental procedures, spectra of products, IR, mass, ^1H and ^{13}C NMR for **4a**–**s** and **5e**–**d**, and crystallographic data for compound **4b**. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2011.03.100.

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