JOC The Journal of Organic Chemistry

Article

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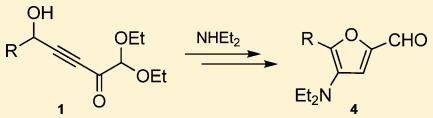
Synthesis and Reactivity of 4-Amino-Substituted Furfurals

Uranbaatar Erdenebileg, Inger Høstmark, Karina Polden, and Leiv K. Sydnes*

Department of Chemistry, University of Bergen, Allégaten 41, NO-5007 Bergen, Norway

Supporting Information

ABSTRACT: γ-Hydroxy α,β-unsaturated acetylenic ketones have been converted to 4-amino-substituted furfurals by reaction with secondary amines followed by treatment with acid in a mixture of THF and water. The stability of the furfurals depends to some extent on the nature of the amino group, whereas the reactivity has been shown to be reagent-dependent. When treated with phosphorus ylids, the expected alkenes are formed with *E* configuration in high yields, but when exposed to nitroalkanes under basic conditions (the Henry reaction) abnormal transformations appear to occur, and 2-acylated furans are obtained, albeit in low yield, instead of nitroalkanols.



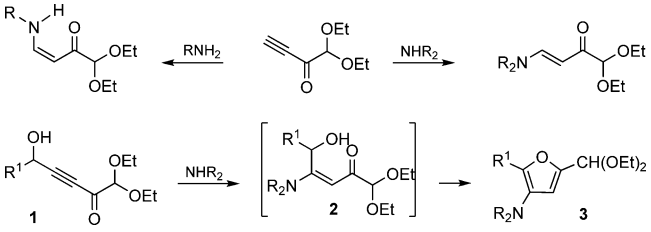
INTRODUCTION

Unsaturated, conjugated motifs constitute an important group of reactive substructures in organic synthesis. One such structure that has been relatively little utilized but now is gaining more attention is the α,β-unsaturated acetylenic ketones.[1−3] After having worked out several high-yield syntheses of a variety of such compounds, employing 3,3,4,4-tetraethoxybut-1-yne as starting material,[2] the study of synthetic transformations of such ketones has been a priority in our group.[3] This has led to a growing body of interesting results including several furan syntheses,[4,5] and here we report a new regiospecific synthesis of 4,5-disubstituted furfurals.

The basis for the synthesis was the discovery that when 1,1-diethoxybut-3-yn-2-one was reacted with primary and secondary amines, even in significant excess, only monoaddition occurred and gave the corresponding 4-amino-substituted 1,1-diethoxybut-3-en-2-ones.[5] Not only was the yield high, but also the reaction was stereospecific in the sense that ammonia and all the primary amines investigated afforded only the corresponding *Z* alkene, whereas the secondary amines furnished the *E* isomer (Scheme 1).

A reasonable consequence of this specificity should be that if secondary amines react with 1,1-diethoxy-5-hydroxyalk-3-yn-2-ones (**1**), the primary products should be the corresponding (3*E*)-1,1-diethoxy-4-dialkylamino-5-hydroxyalk-3-en-2-ones (**2**) because the carbonyl moiety is sterically repelled from the dialkylamino group but attracted by hydrogen bonding to the 1-hydroxyalkyl group. Hydroxyketones **2**, if formed, are expected to be labile and undergo cyclization and hemiketal formation and finally form furans (**3**) rather easily under the right conditions (Scheme 1). What will happen if **1** is treated with a primary amine, however, is less clear because in such a case the resulting secondary amino moiety and the hydroxyl group can become involved in intramolecular hydrogen bonding with the carbonyl group and end up *cis* to the carbonyl moiety.

Scheme 1. Michael Addition of Amines to α,β-Unsaturated Acetylenic Ketones



RESULTS AND DISCUSSION

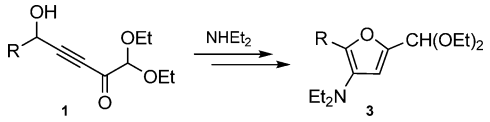
In order to test these predictions, exploratory experiments were performed by treating 1,1-diethoxy-5-hydroxyhex-3-yn-2-one (Scheme 1, R^1 = Me; **1b**) with methylamine and diethyl-amine under various conditions. Both amines reacted fairly quickly, but the outcome was quite different; whereas the latter gave one product only, viz. 2-diethoxymethyl-4-(diethyl-amino)furan (**3b**), methylamine afforded a 5:3 mixture of compounds, the structures of which were elucidated to be the *E* and *Z* isomers of a hydroxyketone, 1,1-diethoxy-5-hydroxy-4-(methylamino)-hex-3-en-2-one, on the basis of ^{1}H spectra of crude product mixtures from several reactions. Isolation of **3b** was straightforward by flash chromatography, but attempts to isolate the isomers of the hydroxyketone were totally unsuccessful; instead a single isomer of 1,1-diethoxy-4-(methylamino)hex-3-ene-2,5-dione, conceivably the *Z* isomer due to the chemical shift of the olefinic proton,[6] was obtained. On the basis of these observations, we decided to investigate reactions with secondary amines first, and the results from these studies are reported here.

Four other 5-substituted derivatives of **1a** were then reacted with diethylamine under conditions identical to those applied when **1b** was reacted, and without exception the substrates reacted quickly and furnished a single product, viz. the corresponding 5-*R*-substituted furan **3**, in quite good yields (Table 1). There were no traces of the anticipated intermediate

Received: November 28, 2013
Published: January 6, 2014

dx.doi.org/10.1021/jo4026308 | J. Org. Chem. 2014, 79, 1213−1221

Table 1. Synthesis of 4-Diethylaminofurfural Diethyl Acetals (3) from 1,1-Diethoxy-5-hydroxyalk-3-yn-2-ones (1)

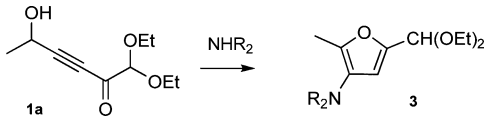


R	1,3	reaction time (h)	isolated yield (%)
H	**a**	1.0	70
Me	**b**	0.5	81
i-Pr	**c**	1.0	78
n-C_6H_{13}	**d**	1.0	77
Ph	**e**	1.0	75

products, the corresponding isomeric Michael adducts, in any of the reactions, and this indicates that the carbonyl group is activated toward nucleophilic attack by the diethoxymethyl group attached to it.

The scope of the transformation was further investigated by reacting **1b** with a few additional secondary amines. It appeared that piperidine, morpholine, and pyrrolidine were almost as efficient as diethylamine and furnished the expected 4-aminosubstituted furfural diethyl acetals, **3f**, **3g**, and **3h**, respectively, in fairly good yields (Table 2, entries 1–3). However, when less nucleophilic secondary amines were employed, e.g., diphenylamine, no reaction occurred at all (Table 2, entry 4).

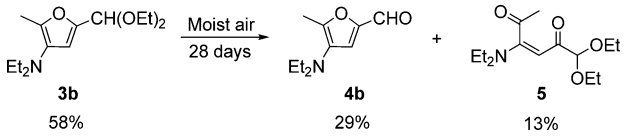
Table 2. Preparation of 4-Amino-Substituted 5-Methylfurfural Diethyl Acetals (3; R = Me) from 1,1-Diethoxy-5-hydroxyhex-3-yn-2-one (1a)



entry	NR_2	3	reaction time (h)	isolated yield (%)
1	piperidin-1-yl	**f**	1.0	69
2	morpholin-4-yl	**g**	1.0	66
3	pyrrolidin-1-yl	**h**	1.0	60
4	diphenylamino		3.0	0

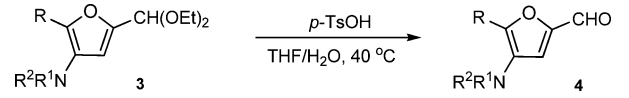
The stability of acetals **3** appeared to be amine-dependent in the sense that all the furans except pyrrolidine derivative **3h** were stable when kept dry in closed vials at and below room temperature. Why **3h** is so special is still not clear, but a key point is probably that the interaction between the nitrogen electron pair and the π system in the furan ring is different for this compound because of conformational constraints imposed by the butylene chain in the pyrrolidine ring. However, several other 4-aminofurfural diethyl acetals stored at room temperature with access to air and moisture turned out to be unstable and appeared to be gradually converted to at least two products, the corresponding furfural **4** and a diketone. For instance, the two compounds formed in the case of 5-diethoxymethyl-3-diethylamino-2-methylfuran (**3b**) were 4-diethylamino-5-methylfuran-2-carbaldehyde (**4b**) and a compound believed to be 1,1-diethoxy-4-diethylaminohex-3-ene-2,5-dione (**5**) (Scheme 2). Both compounds can be envisaged to have been formed by transformations with significant literature precedence, deacetalization of the acetal moiety, and oxidative ring cleavage of the furan ring, respectively.

Scheme 2



Furfurals are useful compounds in synthesis,[7] and the formation of **4** when **3** is stored under moist conditions encouraged us to prepare the furfurals from **3**. A number of methods are available for this transformation,[8] and after some exploratory experiments with **3b** we settled for treating **3** with *p*-TsOH in a mixture of THF and water at 40 °C, which appeared to give **4b** in good yield (77%). All the other aminofuran acetals were then reacted under these conditions, and with two exceptions the corresponding furfural was obtained in 76–80% isolated yield (Table 3). One of the

Table 3. Preparation of 4-Amino-Substituted Furfurals (4) from 4-Amino-Substituted Furfural Diethyl Acetals (3)



R	3	R^1,R^2	reaction time (h)	4	isolated yield (%)
H	**a**	Et,Et	1.0	**a**	0
Me	**b**	Et,Et	1.0	**b**	77
i-Pr	**c**	Et,Et	1.0	**c**	89
n-C_6H_{13}	**d**	Et,Et	1.5	**d**	80
Ph	**e**	Et,Et	1.0	**e**	78
Me	**f**	$(CH_2)_5$	1.0	**f**	76
Me	**g**	$(CH_2)_2O(CH_2)_2$	1.0	**g**	76
Me	**h**	$(CH_2)_4$	1.0	**h**	55

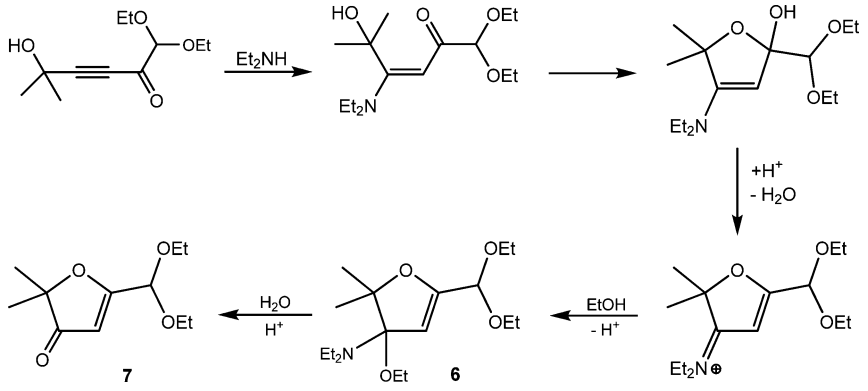
exceptions was again pyrrolidinyl acetal (**3f**), which suffered partial decomposition and furnished the corresponding furfural **4f** in 55% yield only. The other exception was 2-diethoxymethyl-4-diethylaminofuran (**3a**), which underwent complete destruction under acidic conditions and gave an intractable product mixture, from which not even a small amount of furfural **4a** could be isolated (Table 3). Not surprisingly, the yield of the furfurals could be improved by performing the two-step preparation in a one-pot synthesis from **1**. For instance, when **4b** was prepared in this way from **1b**, the overall yield increased from 62 to 73%.

A likely consequence of the mechanistic sketch in Scheme 1 is that if the propargylic alcohol is tertiary, no furan formation will take place because dehydration becomes unlikely. And indeed, when 1,1-diethoxy-5-hydroxy-5-methylhex-3-yn-2-one (**1f**) was treated with diethylamine, only cyclization and no aromatization occurred, and 4-ethoxy-2-diethoxymethyl-4-diethylamino-4,5-dihydro-5,5-dimethylfuran (**6**) was obtained in 86% yield. This compound appeared not to be stable unless it was dried thoroughly, so if exposed to air under ambient conditions **6** was gradually converted to the corresponding ketone, 5-(diethoxymethyl)-2,2-dimethylfuran-3(2*H*)-one (**7**). A conceivable reaction pathway for the formation of **7** is outlined in Scheme 3.

Structurally aminofurfurals **4** are interesting compounds because there are both electron-withdrawing and electron-donating substituents attached to the aromatic ring. Overall this will give a push–pull system, which conceivably could lead to

dx.doi.org/10.1021/jo4026308 | J. Org. Chem. 2014, 79, 1213–1221

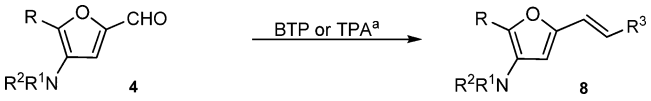
Scheme 3



chemical properties different from those exhibited by furfural itself. In order to explore if this is the case, selected 4-aminofurfurals are being used as substrates in various reactions with carbanions. So far the Wittig and Henry reactions, known to furnish the corresponding 2-(1-alkenyl)furans and 1-furfuryl-2-nitroalkan-1-ols, respectively, when furfural itself is reacted,[9,10] have been most extensively investigated.

The Wittig-type reactions were performed by treating selected 4-aminofurfurals with benzylidenetriphenylphosphorane and the phosphonate carbanion from triethyl phosphonoacetate under standard conditions. In all cases the reactions proceeded smoothly and gave the expected alkenyl-substituted furans **8** in good to excellent yield (Table 4). It is noteworthy that the best yield with both reagents was obtained when **4g** was reacted. This furfural contains a morpholine moiety that is much less basic than both piperidine and diethylamine, the other bases attached to the furan ring in **4** (pK_b is 5.70 for morpholine compared to 3.02 for piperidine and 2.71 for diethylamine).[11] On the basis of these pK_b values, it is conceivable that the electron density of the formyl group increases less in **4g** than in the other furfurals, rendering its carbonyl group more electrophilic and more reactive in Wittig reactions. It is also interesting to note that all reactions were stereospecific and furnished the expected alkenes with *E* configuration; the stereochemistry was borne out by the size of the coupling constant for the vicinal H−H coupling across the C−C double bond, which was 16.2 or 16.3 Hz for the styrenyl-substituted furans (**8a**−**8d**) and 15.6 or 15.7 Hz for the acrylate derivatives (**8e**−**8h**).[12]

Table 4. Preparation of 2-Ethenylfuran Derivatives 8 by Treating 4-Amino-Substituted Furfurals 4 with Phosphorous Reagents[a]



4	R	R^1,R^2	reagent	R^3	8	isolated yield (%)
b	Me	Et,Et	BTP	Ph	**a**	89
f	Me	$(CH_2)_5$	BTP	Ph	**b**	60
g	Me	$(CH_2)_2O(CH_2)_2$	BTP	Ph	**c**	90
e	Ph	Et,Et	BTP	Ph	**d**	50
b	Me	Et,Et	TPA	CO_2Et	**e**	60
f	Me	$(CH_2)_5$	TPA	CO_2Et	**f**	84
g	Me	$(CH_2)_2O(CH_2)_2$	TPA	CO_2Et	**g**	85
e	Ph	Et,Et	TPA	CO_2Et	**h**	84

[a]Reactions were performed with benzylidenetriphenylphosphorane (BTP) and the phosphonate carbanion from triethyl phosphonoacetate (TPA).

Two of the 4-aminofurfurals, **4b** and **4e**, were then reacted with some nitroalkanes under basic conditions (the Henry reaction), and on the basis of literature precedence,[10] formation of the corresponding 2-nitroalkan-1-ols and/or 2-nitroalk-1-enes was the anticipated outcome (Scheme 4, path A). However, to our surprise such products were not obtained; in every case except one a complex reaction mixture was obtained, and only one product, an alkyl furan-2-yl ketone (**9**), could be structure elucidated and isolated in moderate yield (Table 5). The only exception to this rule was **4b**, which when reacted with nitromethane under basic conditions gave one product in addition to the alkyl furan-2-yl ketone, viz. 3-diethylamino-5-hydroxy-iminoacetyl-2-methylfuran (**10**) (Scheme 4, path B).

Formation of **9** has little literature precedence, but a similar transformation was reported by Nomland and Hills, who obtained 2-acylquinoline instead of the Henry product when quinoline-2-carbaldehyde was treated with nitroalkanes under basic conditions.[13] The total oxidation state of the carbon atoms in the acyl groups is identical to that of the carbon atoms in their precursors, the nitroalkanol moieties, and this indicates that the acyl groups is formed from the Henry products by HNO_2 elimination. When this rationale is applied to explain the formation of **9**, transition state **11** and enol **12** are invoked as intermediates when **4b** is used as an example (Scheme 5). The much lower yields obtained when nitroethane and 1-nitrobutane are applied is probably due to conformational effects caused by steric interactions between neighboring groups; these effects will make it more difficult to achieve the gauche-like relationship required between the hydrogen atom and the nitro group, and this slows down the nitrous-acid elimination.

Oxime **10**, however, results from a much more deep-seated transformation since both carbon atoms in the likely 2-nitroethanol intermediate **11** are oxidized, whereas the nitrogen atom is reduced. The ability of the nitro group to function as an oxidizing agent is well established.[14] A conceivable reaction mechanism for formation of **10** is depicted in Scheme 6.

■ EXPERIMENTAL SECTION

Unless otherwise noted all reagents were commercially available and used as received. THF was dried and distilled from Na/benzophenone under nitrogen. TLC analyses were performed with silica gel (60 F_{254}) on aluminum sheets, and an ethanol solution of phosphor

dx.doi.org/10.1021/jo4026308 | J. Org. Chem. 2014, 79, 1213−1221

Scheme 4

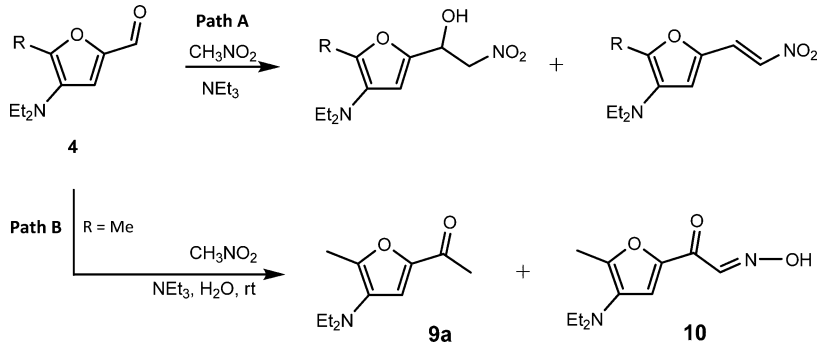
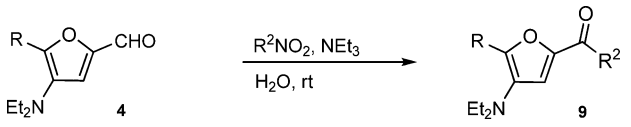


Table 5. Preparation of Alkyl Furan-2-yl Ketones by Treating 4-Amino-Substituted Furfurals 4 with Nitroalkanes under Basic Conditions



4	R	R^2	reaction time (h)	9	isolated yield (%)
b	Me	Me	6	**a**	66[a]
b	Me	Et	12	**b**	38
e	Ph	Et	24	**c**	37
b	Me	Bu	24	**d**	18

[a]In addition 3-diethylamino-5-(*N*-hydroxyiminoacetyl)-2-methylfuran (**10**) was isolated in 18% yield.

polymolybdic acid was used as visualizing agent. Flash chromatography (FC) was carried out with silica gel (230–400 mesh) as the stationary phase and mixtures of either hexanes and ethyl acetate or dichloromethane and methanol as the mobile phase. The eluent composition is given in each case. IR absorptions are given in wave numbers (cm^{-1}), and intensities are characterized as (s) for strong, (m) for medium, (w) for weak. ^1H NMR spectra were recorded at ambient temperature at 400 MHz with TMS as the internal reference (δ_H = 0.00 ppm). Chemical shifts are reported downfield from TMS, and coupling constants are given in Hz. Multiplicity is given as (s) for singlet, (d) for doublet, (t) for triplet, (q) for quartet, (dd) for doublet of doublets, and (m) for multiplet. ^{13}C NMR spectra were recorded at ambient temperature at 100 MHz with the central peak of $CDCl_3$ triplet (δ_C = 77.23 ppm) as the internal reference. Mass spectra were obtained on a TOF MS high-resolution mass spectrometer operated in the DART/ESI+ mode with ionization potential 70 eV.

Synthesis of Hydroxyketones 1 from the Corresponding 4,4,5,5-Tetraethoxyalk-3-yn-1-ols; General Procedure. The 4,4,5,5-tetraethoxyalk-3-yn-1-ol derivative (2.0 g) was dissolved in a 7:3 mixture of THF and water (100 mL). *p*-Toluenesulfonic acid monohydrate (0.2 equiv) was added, and the mixture was refluxed until all the starting material had been consumed (followed by TLC). Most of the THF was then evaporated under reduced pressure on a rotary evaporator. To the residue was added brine (30 mL) and DCM (30 mL). The phases were separated, and the aqueous phase was extracted with DCM (3 × 20 mL). The combined extracts were washed with a saturated aqueous solution of $NaHCO_3$ (80 mL), dried over $MgSO_4$, filtered and evaporated under reduced pressure, affording a crude product, which was essentially pure **1**. Following this procedure **1a–e** were prepared.

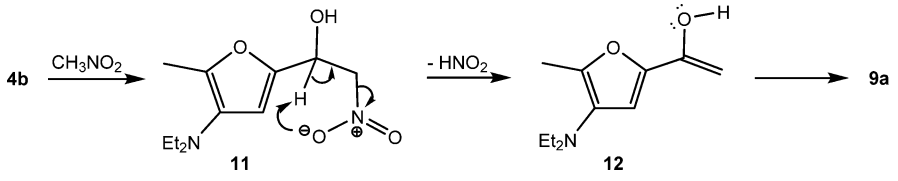
*1,1-Diethoxy-5-hydroxypent-3-yn-2-one (**1a**).* 4,4,5,5-Tetraethoxypent-2-yn-1-ol (2.0 g, 7.7 mmol) was refluxed for 3.0 h and gave essentially pure **1a** (1.33 g, 93%) as a yellowish liquid without purification: IR (film) 3449 (s), 2211 (s), 1693 (s), 1480 (w), 1444 (m), 1394 (m), 1373 (m), 1321 (m), 1250 (s), 1167 (s), 1112 (s), 1058 (s), 961 (w), 906 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.72 (s, 1H), 4.48 (s, 2H), 3.78–3.60 (m, 4H), 2.00 (bs, 1H), 1.28 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.6, 101.8, 94.2, 82.8, 63.6, 51.0, 15.2; HRMS Calcd for $C_9H_{14}O_4^+$ $[M + H]^+$ 187.09703, found 187.09852.

*1,1-Diethoxy-5-hydroxyhex-3-yn-2-one (**1b**).* 5,5,6,6-Tetraethoxyhex-3-yn-2-ol (2.0 g, 7.3 mmol) was refluxed for 3.0 h and gave esentially pure **1b** (1.31 g, 90%) as a yellowish liquid without purification: IR (film) 3443 (s), 2216 (s), 1689 (s), 1480 (w), 1446 (m), 1394 (m), 1372 (m), 1325 (m), 1247 (m), 1167 (s), 1122 (s), 1102 (s), 1068 (s), 952 (w), 913 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.74 (s, 1H), 4.71 (q, J = 6.7 Hz, 1H), 3.77–3.60 (m, 4H), 2.09 (bs, 1H), 1.53 (d, J = 6.7 Hz, 3H), 1.28 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.8, 101.8, 97.2, 81.2, 63.5, 58.3, 23.4, 15.3; HRMS Calcd for $C_{10}H_{17}O_4^+$ $[M + H]^+$ 201.11268, found 201.11204.

*1,1-Diethoxy-5-hydroxy-6-methylhept-3-yn-2-one (**1c**).* 6,6,7,7-Tetraethoxy-2-methyl-hept-4-yn-3-ol[4] (2.0 g, 6.6 mmol) was refluxed for 3.0 h and gave essentially pure **1c** (1.37 g, 91%) as a yellowish liquid without purification: IR (film) 3437 (s), 2210 (s), 1693 (s), 1469 (m), 1446 (m), 1387 (m), 1371 (m), 1347 (m), 1320 (m), 1245 (m), 1164 (s), 1108 (s), 1067 (s), 960 (w), 926 (w), 900 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.74 (s, 1H), 4.36 (t, J = 5.8 Hz, 1H), 3.76–3.60 (m, 4H), 2.04–1.94 (m, 2H) 1.27 (t, J = 7.0 Hz, 6H), 1.06 (d, J = 6.6 Hz, 3H), 1.04 (d, J = 6.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.9, 101.7, 95.9, 82.9, 67.9, 63.3, 34.5, 18.2, 17.7, 15.3; HRMS Calcd for $C_{12}H_{20}O_4^+$ $[M + H]^+$ 229.14398, found 229.14386.

*1,1-Diethoxy-5-hydroxyundec-3-yn-2-one (**1d**).* 1,1,2,2-Tetraethoxyundec-3-yn-5-ol (2.0 g, 5.8 mmol) was refluxed for 3 h and gave **1d** (1.49 g, 95%) as a reddish liquid without any purification: IR (film) 3436 (s), 2211 (s), 1760 (w), 1690 (s), 1479 (w), 1467 (m), 1457 (m), 1445 (m), 1393 (m), 1374 (m), 1319 (m), 1245 (m), 1162 (s), 1110 (s), 1066 (s), 907 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.73 (s, 1H), 4.55 (q, J = 6.7 Hz, 1H), 3.76–3.60 (m, 4H), 1.98 (bs, 1H), 1.82–1.26 (m, 16H), 0.89 (t, J = 6.7 Hz, 3H); ^{13}C NMR (100

Scheme 5



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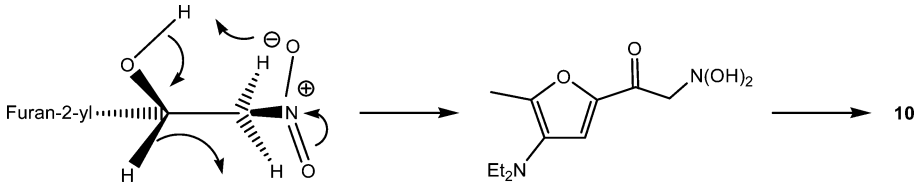
Scheme 6



MHz, $CDCl_3$) δ 182.9, 101.8, 96.6, 82.2, 63.4, 62.6, 37.1, 31.8, 29.0, 25.1, 22.7, 15.3, 14.2; HRMS Calcd for $C_{15}H_{26}O_4^+$ $[M + H]^+$ 271.19093, found 271.19193.

*1,1-Diethoxy-5-hydroxy-5-phenylpent-3-yn-2-one (**1e**).* 4,4,5,5-Tetraethoxy-1-phenyl-pent-2-yn-1-ol (2.0 g, 5.9 mmol) was refluxed for 5.0 h and afforded **1e** (1.51 g, 95%) as a yellow liquid: IR (film) 3429 (s), 3088 (w), 3064 (m), 3032 (m), 2978 (s), 2931 (s), 2896 (s), 2210 (s), 1694 (s), 1601 (w), 1494 (s), 1480 (m), 1453 (s), 1393 (m), 1373 (m), 1321 (m), 1293 (m), 1244 (m), 1160 (s), 1109 (s), 1065 (s), 919 (m), 837 (m), 818 (m) 763 (m), 700 (s), 655 (m), 600 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.57- 7.35 (m, 5H), 5.65 (s, 1H), 4.76 (s, 1H), 3.77−3.60 (m, 4H), 2.47 (bs, 1H), 1.27 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.8, 138.8, 129.1, 127.7, 127.1, 101.8, 94.6, 83.4, 64.7, 63.4, 15.3, 15.1; HRMS Calcd for $C_{13}H_{13}O_3^+$ $[M - OEt]^+$ 217.08647, found 217.08856.

Reaction of 1,1-Diethoxy-5-hydroxyhex-3-yn-2-one (1b) with Methylamine. Hydroxy-ketone **1b** (0.200 g, 1.0 mmol) was dissolved in ethanol (5 mL), and a 40% (w/w) aqueous solution of methylamine (0.080 g, 1.0 mmol) was added under stirring at rt in the presence of air. The mixture was then stirred at rt until all the starting material had been consumed as judged from TLC (15 min). After drying ($MgSO_4$) and filtration the solvent was evaporated on a rotary evaporator, and a ^1H NMR spectrum of the residue was recorded before isomer separation by FC was attempted: ^1H NMR (400 MHz, $CDCl_3$) δ 10.90 and 6.00 (2 bs in a 5:3 ratio, 1H, NH), 5.67 and 5.35 (2 bs in a 5:3 ratio, 1H), 5.20 and 4.63 (2 m in a 5:3 ratio, 1H), 3.8−3.5 (m, 4H), 3.01 (d, J = 5.6 Hz, 3H), 2.43 (s, 3H), 1.3−1.2 (m, 6H). Separation by FC (hexanes/ethyl acetate 80:20) gave only one product, 1,1-diethoxy-4-(methylamino)hex-3-ene-2,5-dione, (0.121 g, 53%), as an orange liquid: IR (film) 3273 (s), 3082 (m), 1712 (s), 1616 (s), 1573 (s), 1535 (s), 1429 (s), 1358 (s), 1317 (s), 1164 (s), 1102 (s), 1063 (s), 969 (m), 901 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.25 (bs, 1H), 5.68 (s, 1H), 4.67 (s, 1H), 3.74−3.56 (m, 4H), 3.01 (d, J = 5.6 Hz, 3H), 2.43 (s, 3H), 1.25 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 194.6, 160.5, 102.3, 89.8, 62.8, 31.7, 29.1, 15.4; HRMS Calcd for $C_{11}H_{20}NO_4^+$ $[M + H^+]$ 230.13923, found 230.14050.

Synthesis of Furfural Diethyl Acetals (3) from 1; General Procedure. γ-Hydroxy-α,β-unsaturated acetylenic ketone (**1**) (1−2 mmol) was dissolved in ethanol (5 mL), and amine (1.0 mol equiv) was added under stirring at rt in the presence of air. The reaction mixture was subsequently stirred at rt until all the starting material had been consumed as judged from TLC (0.5−1.0 h, see Table 1). The solvent was then evaporated, and from the residue the product was isolated by FC.

*2-Diethoxymethyl-4-(diethylamino)furan (**3a**).* Compound **1a** (0.373 g, 2.00 mmol) was reacted with diethylamine (0,146 g, 2.00 mmol) for 1 h. Isolation by FC (hexanes/ethyl acetate 90:10) provided the title compound (0.337 g, 70%) as an orange liquid. The spectroscopic data are in accordance with those reported in the literature: IR (film) 3100 (w), 1763 (s), 1620 (s), 1545 (s), 1447 (s), 1374 (s), 1342 (s), 1277 (s), 1226 (m), 1176 (s), 1139 (s), 1107 (s), 1058 (s), 1030 (s), 980 (m), 964 (m), 941 (w), 902 (m), 861 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 1H), 6.24 (s, 1H), 5.44 (s, 1H), 3.67−3.54 (m, 4H), 3.06−3.01 (m, 4H), 1.23 (t, J = 7.1 Hz, 6H), 1.07 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 139.1, 125.1, 102.8, 96.7, 61.4, 45.1, 15.4, 11.8; HRMS Calcd for $C_{13}H_{24}NO_3^+$ $[M + H]^+$ 242.17562, found 242.17495.

*5-Diethoxymethyl-3-diethylamino-2-methylfuran (**3b**).* Compound **1b** (0.201 g, 1.00 mmol) was reacted with diethylamine (0,073 g, 1.0 mmol). Isolation by FC (hexanes/ethyl acetate 90:10) provided the title compound (0.207 g, 81%) as a yellow liquid: IR (film) 1709 (w), 1639 (m), 1633 (m), 1579 (m), 1526 (m), 1477 (m), 1445 (s), 1404 (m), 1372 (s), 1338 (s), 1294 (m), 1277 (m), 1238 (s), 1228 (s), 1184 (m), 1174 (m), 1161 (m), 1121 (s), 1091 (s), 1055 (s), 1007 (s), 988 (m), 954 (m), 904 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.31 (s, 1H), 5.43 (s, 1H), 3.67−3.54 (m, 4H), 2.79 (q, J = 7.1 Hz, 4H), 2.21 (s, 3H), 1.24 (t, J = 7.1 Hz, 6H), 0.93 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 146.4, 131.1, 105.2, 96.8, 61.4, 50.3, 15.4, 13.4, 11.5; HRMS Calcd for $C_{14}H_{26}NO_3^+$ $[M + H^+]$ 256.19127, found 256.18940.

*5-Diethoxymethyl-3-diethylamino-2-isopropylfuran (**3c**).* Compound **1c** (0.227 g, 1.00 mmol) was reacted with diethylamine (0,073 g, 1.0 mmol). Isolation by FC (hexanes/ethyl acetate 90:10) provided the title compound (0.220 g, 78%) as a yellow liquid: IR (film) 1628 (w), 1576 (w), 1476 (m), 1446 (m), 1404 (m), 1371 (s), 1339 (s), 1240 (s), 1160 (m), 1122 (s), 1091 (s), 1054 (s), 1025 (m), 1006 (m), 979 (m), 906 (m), 873 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.31 (s, 1H), 5.46 (s, 1H), 3.64−3.52 (m, 4H), 3.12 (septet, J = 7.0 Hz, 1H), 2.75 (q, J = 7.1 Hz, 4H), 1.23−1.18 (m, 12H) 0.92 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 148.7, 128.8, 104.8, 96.8, 61.1, 50.9, 25.3, 21.5, 15.4, 13.6; HRMS Calcd for $C_{16}H_{30}NO_3^+$ $[M + H^+]$ 284.22257, found 284.22481.

*5-Diethoxymethyl-3-diethylamino-2-hexylfuran (**3d**).* Compound **1d** (0.270 g, 1.00 mmol) was reacted with diethylamine (0,073 g, 1.0 mmol). Isolation by FC (hexanes/ethyl acetate 95:5) provided the title compound (0.250 g, 77%) as a yellow liquid: IR (film) 1637 (m), 1576 (m), 1455 (m), 1445 (m), 1403 (m), 1372 (m), 1358 (m), 1338 (m), 1239 (m), 1225 (m), 1172 (m), 1123 (s), 1092 (s), 1055 (s), 1010 (s), 977 (m), 913 (m), 889 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.32 (s, 1H), 5.45 (s, 1H), 3.66−3.53 (m, 4H), 2.78 (q, J = 7.1 Hz, 4H), 2.57 (t, J = 7.6 Hz, 2H), 1.61−1.57 (m, 2H), 1.35−1.25 (m, 6H), 1.22 (t, J = 7.1 Hz, 6H), 0.93 (t, J = 7.1 Hz, 6H), 0.89−0.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 148.7, 130.7, 105.0, 96.8, 61.2, 50.6, 31.9, 29.3, 28.5, 25.7, 22.8, 15.4, 14.3, 13.5; HRMS Calcd for $C_{19}H_{36}NO_3^+$ $[M + H^+]$ 326.26952, found 326.27266.

*5-Diethoxymethyl-3-diethylamino-2-phenylfuran (**3e**).* Compound **1e** (0.262 g, 1.00 mmol) was reacted with diethylamine (0,073 g, 1.0 mmol). Isolation by FC (hexanes/ethyl acetate 95:5) provided the title compound (0.237 g, 75%) as a yellow liquid: IR (film) 3057 (w), 3026 (w) 1614 (m), 1492 (m), 1474 (m), 1402 (m), 1372 (s), 1357 (s), 1337 (s), 1175 (m), 1158 (m), 1132 (s), 1117 (s), 1093 (s), 1056 (s), 1034 (s), 1005 (m), 992 (m), 985 (m), 907 (m), 881 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08−8.06 (m, 2H), 7.37−7.33 (m, 2H), 7.20−7.16 (m, 1H), 6.52 (s, 1H), 5.54 (s, 1H), 3.72−3.58 (m, 4H), 2.92 (q, J = 7.1 Hz, 4H), 1.25 (t, J = 7.0 Hz, 6H), 1.01 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 144.9, 134.6, 131.7, 128.3, 126.5, 124.6, 106.9, 96.8, 61.5, 49.1, 15.4, 13.0; HRMS Calcd for $C_{19}H_{28}NO_3^+$ $[M + H^+]$ 318.20692, found 318.20960.

*1-(5-Diethoxymethyl-2-methylfuran-3-yl)piperidine (**3f**).* Compound **1b** (0.201 g, 1.00 mmol) was reacted with piperidine (0,085 g, 1.0 mmol). Isolation by FC (hexanes/ethyl acetate 95:5) provided the title compound (0.185 g, 69%) as a yellow liquid: IR (film) 2792 (s), 2744 (m), 1634 (m), 1572 (m), 1452 (m), 1442 (s), 1403 (m), 1381 (s), 1372 (s), 1342 (m), 1294 (m), 1271 (m), 1261 (m), 1225 (s), 1163 (m), 1154 (m), 1114 (s), 1098 (s), 1056 (s), 1008 (m), 988 (m), 955 (m), 905 (m), 866 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.31 (s, 1H), 5.40 (s, 1H), 3.67−3.53 (m, 4H), 2.79−2.76 (m, 4H), 2.25 (s, 3H), 1.68−1.62 (m, 4H), 1.51−1.46 (m, 2H), 1.23 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.0, 141.0, 135.7, 104.3,

dx.doi.org/10.1021/jo4026308 | J. Org. Chem. 2014, 79, 1213−1221

96.8, 61.5, 54.3, 26.5, 24.3, 15.4, 12.2; HRMS Calcd for $C_{15}H_{26}NO_3^+$ [M + H$^+$] 268.19127, found 268.19248.

*4-(5-Diethoxymethyl-2-methylfuran-3-yl)morpholine (**3g**).* Compound **1b** (0.201 g, 1.00 mmol) was reacted with morpholine (0,087 g, 1.0 mmol). Isolation by FC (hexanes/ethyl acetate 90:10) provided the title compound (0.177 g, 66%) as an orange liquid: IR (film) 1742 (m), 1634 (m), 1573 (m), 1526 (w), 1451 (s), 1404 (m), 1390 (m), 1374 (s), 1360 (s), 1342 (m), 1284 (m), 1263 (s), 1227 (s), 1162 (m), 1117 (s), 1098 (s), 1056 (s), 1009 (m), 988 (m), 956 (m), 917 (s), 850 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.32 (s, 1H), 5.40 (s, 1H), 3.65−3.62 (m, 4H), 3.59−3.53 (m, 4H), 2.83−2.80 (m, 4H), 2.25 (s, 3H), 1.23 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 141.8, 134.5, 103.9, 96.8, 67.4, 61.6, 53.2, 15.4, 12.0; HRMS Calcd for $C_{14}H_{24}NO_4^+$ [M + H$^+$] 270.17053, found 270.17177.

*1-(5-Diethoxymethyl-2-methylfuran-3-yl)pyrrolidine (**3h**).* Compound **1b** (0.200 g, 1.00 mmol) was reacted with pyrrolidine (0,071 g, 1.0 mmol). Isolation by FC (hexanes/ethyl acetate 90:10) provided the title compound (0.152 g, 60%) as an orange liquid: IR (film) 3117 (w), 1742 (m), 1713 (m), 1637 (s), 1566 (s), 1523 (s), 1480 (s), 1443 (s), 1430 (s), 1404 (s), 1374 (s), 1359 (s), 1343 (s), 1295 (m), 1265 (s), 1198 (s), 1163 (s), 1118 (s), 1055 (s), 1011 (s), 990 (s), 956 (m), 940 (m), 904 (s), 873 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.20 (s, 1H), 5.40 (s, 1H), 3.6−3.53 (m, 4H), 3.11−3.08 (m, 4H), 2.36 (s, 3H), 1.90−1.87 (m, 4H), 1.23 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 135.6, 133.1, 103.9, 96.8, 61.5, 52.0, 24.8, 15.4, 13.1; HRMS Calcd for $C_{14}H_{24}NO_3^+$ [M + H$^+$] 254.17562, found 254.17758.

Stability Study. A sample of **3b** was kept at rt with open access to moist air, and the compound was analyzed by TLC at intervals. Gradually two products appeared to be formed, and after 28 days the two compounds were isolated by FC (hexanes/ethyl acetate 90:10) after proton NMR spectra of the product mixture had been recorded. The main product was 4-diethylamino-5-methylfuran-2-carbaldehyde (**4b**), which was isolated pure as a reddish liquid, whereas the minor product, a yellowish liquid, tentatively was given the structure 1,1-diethoxy-4-diethylaminohex-3-ene-2,5-dione (**5**) on the basis of NMR and IR spectra of an impure sample of the compound. The composition of the product mixture was determined from its proton NMR spectra and the individual spectra of **3b**, **4b** and **5**. Data for **4b**: IR (film) 3341 (w), 3100 (w), 1680 (s), 1604 (s), 1522 (s), 1477 (s), 1448 (s), 1374 (s), 1356 (m), 1315 (s), 1248 (m), 1117 (s), 1088 (s), 1067 (m), 1031 (w), 1000 (m), 947 (m), 887 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.15 (s, 1H), 2.88 (q, J = 7.1 Hz, 4H), 2.34 (s, 3H), 0.97 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 154.0, 150.2, 135.2, 118.9, 49.5, 13.0, 12.3; HRMS Calcd for $C_{10}H_{16}NO_2^+$ [M + H$^+$] 182.11810, found 182.11676.

Conversion of Furfural Diethyl Acetals 3 to Furfurals 4; General Procedure. Aminofuran **3** (0.5−1.0 mmol) was dissolved in a 7:3 mixture of THF and H_2O (5 mL). *p*-Toluenesulfonic acid monohydrate (0.019 g, 0.10 mmol) was added, and the mixture was stirred at 40 °C for 1 h. Most of the THF was then evaporated under reduced pressure, and to the residue was added a saturated aqueous solution of NaCl (2 mL) and DCM (2 mL). The phases were separated, and the aqueous phase was extracted with DCM (3 × 3 mL). The combined extracts were washed with a saturated aqueous solution of $NaHCO_3$ (5 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure. The crude product was isolated by FC (hexanes/ethyl acetate) to give the corresponding furfural **4**.

*4-Diethylamino-5-methylfuran-2-carbaldehyde (**4b**).* Furfural acetal **3b** (0.256 g, 1.00 mmol) was used. Isolation by FC (hexanes/ethyl acetate 90:10) provided the title compound (0.140 g, 77%) as a reddish liquid. The spectroscopic and spectrometric data were identical to those reported above.

*4-Diethylamino-5-isopropylfuran-2-carbaldehyde (**4c**).* Furfural acetal **3c** (0.267 g, 0.940 mmol) was used. Isolation by FC (hexanes/ethyl acetate 90:10) provided the title compound (0.175 g, 89%) as a deep orange liquid: IR (film) 3099 (w), 1683 (s), 1600 (m), 1525 (s), 1477 (m), 1450 (m), 1378 (s), 1330 (s), 1307 (m), 1285 (m), 1244 (m), 1232 (m), 1133 (m), 1104 (m), 1080 (s), 1063 (m), 1044 (w), 964 (m), 867 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 7.18 (s, 1H), 3.23 (septet, J = 7.0 Hz, 1H), 2.83 (q, J = 7.1 Hz, 4H), 1.27 (d, J = 7.0 Hz, 6H), 0.95 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 163.1, 150.4, 133.2, 119.1, 50.3, 26.0, 20.9, 13.2; HRMS Calcd for $C_{12}H_{20}NO_2^+$ [M + H$^+$] 210.14940, found 210.14942.

*4-Diethylamino-5-hexylfuran-2-carbaldehyde (**4d**).* Furfural acetal **3d** (0.163 g, 0.500 mmol) was used. Isolation by FC (hexanes/ethyl acetate 90:10) provided the title compound (0.100 g, 80%) as a reddish liquid: IR (film) 1682 (s), 1601 (m), 1522 (s), 1475 (m), 1466 (m), 1449 (m), 1377 (m), 1360 (m), 1320 (m), 1293 (m), 1120 (m), 1085 (m), 969 (w), 901 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 1H), 7.17 (s, 1H), 2.86 (q, J = 7.1 Hz, 4H), 2.68 (t, J = 7.7 Hz, 2H), 1.70−1.65 (m, 2H), 1.38−1.26 (m, 6H), 0.96 (t, J = 7.1 Hz, 6H), 0.90−0.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 158.5, 150.4, 134.9, 119.1, 49.9, 31.7, 29.3, 27.7, 26.3, 22.7, 14.2, 13.1; HRMS Calcd for $C_{15}H_{26}NO_2^+$ [M + H$^+$] 252.19635, found 252.19785.

*4-Diethylamino-5-phenylfuran-2-carbaldehyde (**4e**).* Furfural acetal **3e** (0.159 g, 0.50 mmol) was used. Isolation by FC (hexanes/ethyl acetate 90:10) provided the title compound (0.094 g, 78%) as an orange liquid: IR (film) 3341 (w), 3063 (m), 3024 (m), 2756 (m), 1742 (m), 1678 (s), 1602 (s), 1589 (s), 1571 (s), 1520 (s), 1486 (s), 1473 (s), 1445 (s), 1423 (s), 1379 (s), 1360 (s), 1331 (s), 1306 (s), 1291 (s), 1245 (s), 1201 (s), 1181 (m), 1140(s), 1118 (s), 1086 (s), 1036 (s), 1020 (m), 995 (m), 922 (w), 873 (m), 842 (m), 782 (s), 770 (s), 717 (s), 695 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.19 (d, J = 7.3 Hz, 2H), 7.44−7.31 (m, 4H), 2.98 (q, J = 7.1 Hz, 4H), 1.03 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 150.6, 150.0, 136.9, 130.1, 128.9, 128.7, 126.0, 118.8, 48.5, 12.6; HRMS Calcd for $C_{15}H_{18}NO_2^+$ [M + H$^+$] 244.13375, found 244.13344.

*5-Methyl-4-(piperidin-1-yl)furan-2-carbaldehyde (**4f**).* Furfural acetal **3f** (0.148 g, 0.55 mmol) was used. Isolation by FC (hexanes/ethyl acetate 90:10) provided the title compound (0.081 g, 76%) as a brownish red liquid: IR (film) 3341 (w), 3095 (w), 3024 (w), 1739 (m), 1677 (s), 1602 (s), 1517 (s), 1467 (m), 1452 (s), 1442 (s), 1384 (s), 1367 (s), 1329 (s), 1300 (w), 1284 (s), 1274 (m), 1260 (m), 1242 (m), 1231 (m), 1174 (m), 1130 (s), 1110 (s), 1063 (m), 1039 (m), 1026 (m), 1000 (m), 950 (m), 908 (m), 861 (m), 837 (m), 781 (s), 712 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 7.11 (s, 1H), 2.82−2.79 (m, 4H), 2.37 (s, 3H), 1.72−1.66 (m, 4H), 1.56−1.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 150.2, 149.8, 139.2, 116.9, 54.0, 26.3, 24.1, 12.8; HRMS Calcd for $C_{11}H_{16}NO_2^+$ [M + H$^+$] 194.11810, found 194.11694.

*5-Methyl-4-(morpholine-4-yl)furan-2-carbaldehyde (**4g**).* Furfural acetal **3g** (0.134 g, 0.500 mmol) was used. Isolation by FC (hexanes/ethyl acetate 90:10) provided the title compound (0.074 g, 76%) as an orange liquid: IR (film) 3341 (w), 3099 (m), 2688 (m), 1732 (m), 1673 (s), 1603 (s), 1519 (s), 1452 (s), 1392 (m), 1375 (s), 1329 (s), 1304 (s), 1288 (m), 1275 (s), 1265 (s), 1242 (m), 1222 (m), 1210 (m), 1182 (m), 1116 (s), 1071 (m), 1044 (m), 1030 (m), 1001 (m), 951 (m), 918 (s), 848 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.13 (s, 1H), 3.83−3.81 (m, 4H), 2.88−2.86 (m, 4H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 150.4, 150.0, 137.8, 116.3, 67.1, 52.8, 12.6; HRMS Calcd for $C_{10}H_{14}NO_3^+$ [M + H$^+$] 196.09737, found 196.09791.

*5-Methyl-4-(pyrrolidin-1-yl)furan-2-carbaldehyde (**4h**).* Furfural acetal **3h** (0.101 g, 0.400 mmol) was used. Isolation by FC (hexanes/ethyl acetate 80:20) provided **4h** (0.046 g, 55%) as a red liquid: IR (film) 3431 (w), 3325 (w), 3185 (w), 3100 (w), 2706 (w), 1763 (m), 1738 (s), 1672 (s), 1606 (s), 1513 (s), 1489 (s), 1445 (s), 1394 (m), 1368 (s), 1335 (s), 1271 (m), 1247 (m), 1214 (s), 1170 (s), 1108 (s), 1059 (m), 1002 (m), 956 (m), 914 (w) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.40 (s, 1H), 6.91 (s, 1H), 3.19−3.15 (t, J = 6.4 Hz, 4H), 2.48 (s, 3H), 1.98−1.91 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 149.3, 143.7, 136.6, 114.8, 51.4, 25.1, 13.9; HRMS Calcd for $C_{10}H_{14}NO_2^+$ [M + H$^+$] 180.10245, found 180.10193.

One-Pot Synthesis of 4b. A solution of **1b** (2.13 g, 10.6 mmol) in ethanol (50 mL) was mixed with diethylamine (0.78 g, 10.6 mmol), and the mixture was stirred for 1 h at rt. The ethanol was removed on a rotary evaporator, and to the residue a solution of *p*-TsOH hydrate (0.40 g, 2.11 mmol) in a 3:1 mixture of THF and water (100 mL) was

added. The resulting mixture was stirred at 40 °C for 1 h. Most of the THF was then evaporated under reduced pressure on a rotary evaporator, and to the residue was added DCM (20 mL) and a saturated aqueous solution of NaCl (20 mL). The phases were separated, and the aqueous phase was extracted with DCM (3 × 30 mL). The extracts were washed with a saturated aqueous solution of $NaHCO_3$ (50 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure on a rotary evaporator. From the residue **4b** (1.36 g, 73%) was isolated pure by FC (hexanes/ethyl acetate 90:10) as a reddish liquid. The spectroscopic data were identical to those reported above.

3-Ethoxy-5-diethoxymethyl-*N,N*-diethyl-2,3-dihydro-2,2-dimethylfuran-3-amine (6) and 5-Diethoxymethyl-2,2-dimethylfuran-3(2*H*)-one (7). 1,1-Diethoxy-5-hydroxy-5-methyl-hex-3-yn-2-one[4] (0.214 g, 1.00 mmol) was dissolved in ethanol (5 mL), and diethylamine (0.073 g, 1.0 mmol) was added under stirring at rt in the presence of air. The mixture was stirred at rt for 1 h, and the solvent was then evaporated, and essentially pure **6** (0.272 g, 86%) was obtained as an orange liquid.

The compound remained unchanged when stored in a vial at rt and below. When spread over a glass plate and exposed to laboratory air, it was gradually converted to 5-(diethoxymethyl)-2,2-dimethylfuran-3(2*H*)-one (**7**) in quantitative yield. The rate was of course dependent on how thin the liquid layer was. Data for **6**: IR (film) 3392 (s), 1759 (s), 1708 (s), 1621 (s), 1594 (s), 1456 (s), 1375 (s), 1334 (m), 1280 (m), 1246 (m), 1163 (s), 1111 (s), 1068 (s), 988 (s), 952 (m), 913 (m), 895 (m), 822 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.23 (s, 1H), 4.11 (s, 1H), 3.80−3.62 (m, 4H), 3.52−3.44 (m, 2H), 3.18−3.00 (m, 4H), 1.66−1.49 (m, 6H), 1.27−1.06 (m, 15H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 111.9, 106.0, 89.1, 84.6, 65.4, 65.3, 56.9, 43.9, 28.8, 28.0, 15.9, 15.6, 15.5, 12.7; HRMS Calcd for $C_{15}H_{28}NO_3^+$ [M − OEt]$^+$ 270.20692, found 270.20806. Data for **7**: IR (film) 3483 (s), 1757 (s), 1709 (s), 1605 (s), 1457 (s), 1377 (s), 1334 (m), 1301 (s), 1268 (s), 1170 (s), 1154 (s), 1110 (s), 1064 (s), 974 (s), 952 (m), 904 (m), 864 (m), 840 (m), 820 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.70 (s, 1H), 5.24 (s, 1H), 3.72−3.60 (m, 4H), 1.4(s, 6H), 1.26 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.3, 185.5, 102.8, 96.4, 89.5, 62.0, 22.9, 15.2; HRMS Calcd for $C_{11}H_{19}NO_4^+$ [M + H$^+$] 215.12833, found 215.12662.

Synthesis of Styrene Derivatives 8 from Furfural 4 by Wittig Reaction; General Procedure. To a flask equipped with magnetic stirrer and condenser were transferred furfural **4** (1.0−0.10 mmol), DCM (4 mL), benzyltriphenylphosphonium bromide (BTPB) (1.0 equiv) and water (2 mL). The mixture was stirred vigorously for some 5 min, and then a 50% aqueous solution of NaOH (0.1−0.4 mL) was added dropwise. The reaction mixture was stirred for 20 min at rt in all cases except one. After addition of DCM (3 mL) and H_2O (5 mL), the phases were separated, and the aqueous phase was extracted with DCM (3 × 5 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated under reduced pressure on the rotary evaporator (40 °C). Purification by FC with mixtures of hexanes and ethyl acetate as eluent provided the following compounds.

*3-Diethylamino-2-methyl-5-(2-phenylethen-1E-yl)furan (**8a**).* Furfural **4b** (0.181 g, 1.00 mmol) was reacted with BTPB (0.433 g, 1.00 mmol) and a 50% aqueous solution of NaOH (0.4 mL). The reaction mixture was stirred for 20 min. Isolation by FC (hexanes/ethyl acetate 80:20) gave **8a** (0.227 g, 89%) as an orange liquid: IR (ATR) 3024 (w), 1711 (m), 1596 (s), 1576 (w), 1514 (s), 1464 (m), 1445 (m), 1375 (m), 1355 (m), 1196 (m), 1139 (m), 1108 (s), 1026 (m), 997 (m), 953 (m), 790 (m), 748 (s), 697 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, 2H), 7.32 (t, 2H), 7.21 (t, 1H), 6.93 (d, J = 16.2 Hz, 1H), 6.78 (d, J = 16.2 Hz, 1H), 6.28 (s, 1H), 2.85−2.80 (m, 4H), 2.28 (s, 3H), 0.97 (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 145.5, 136.5, 131.9, 127.8, 126.3, 125.3, 124.2, 116.1, 105.4, 49.2, 12.2, 10.6; MS (DART+) m/z 256 (100, M$^+$+H); HRMS Calcd for $C_{17}H_{22}NO^+$ [M + H$^+$] 256.17014, found 256.17000.

*3-(Piperidin-1-yl)-2-methyl-5-(2-phenylethen-1E-yl)furan (**8b**).* Furfural **4f** (0.10 g, 0.50 mmol) was reacted with BTPB (0.22 g, 0.50 mmol) and a 50% aqueous solution of NaOH (0.2 mL). The reaction mixture was stirred for 20 min. Isolation by FC (hexanes/ethyl acetate 70:30) gave **8b** (0.080 g, 60%) as a yellow liquid: IR (ATR) 1762 (m), 1710 (m), 1593 (m), 1575 (w), 1509 (s), 1445 (s), 1360 (m), 1320 (s), 1252 (m), 1134 (m), 1105 (m), 1024 (m), 977 (m), 953 (m), 908 (w), 853 (m), 777 (w), 734 (s) 692 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, 2H), 7.36−7.30 (m, 3H), 6.91 (d, J = 16.3 Hz, 1H), 6.76 (d, J = 16.3 Hz, 1H), 6.28 (s, 1H), 2.82−2.79 (m, 4H), 2.32 (s, 3H), 1.69−1.68 (m, 4H), 1.56−1.53 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.8, 128.7, 128.3, 126.8, 126.1, 125.2, 117.0, 54.3, 26.3, 12.3; MS (DART+) m/z 268 (95, [M+H]$^+$); HRMS Calcd for $C_{18}H_{22}NO^+$ [M + H$^+$] 268.17014, found 268.17035.

*3-(Morpholine-4-yl)-2-methyl-5-(2-phenylethen-1E-yl)furan (**8c**).* Furfural **4g** (0.020 g, 0.10 mmol) was reacted with BTPB (0.041 g, 0.10 mmol) and a 50% aqueous solution of NaOH (0.1 mL). The reaction mixture was stirred for 20 min. Isolation by FC (hexanes/ethyl acetate 70:30) gave **8c** (0.03 g, 90%) as an orange liquid: IR (ATR) 3026 (w), 1710 (m), 1596 (s), 1576 (m), 1517 (s), 1494 (m), 1446 (s), 1415 (m), 1318 (m), 1300 (m), 1264 (s), 1155 (m), 1102 (s), 1070 (m), 1043 (m), 985 (w), 952 (s), 916 (s), 845 (m), 786 (m), 748 (s) 691 (s), 580 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, 2H), 7.35−7.31 (m, 2H), 7.25−7.20 (m, 1H), 6.93 (d, J = 16.2 Hz, 1H), 6.77 (d, J = 16.3 Hz, 1H), 6.28 (s, 1H), 3.82−3.80 (m, 4H), 2.87−2.85 (m, 4H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.0, 128.8, 128.2, 127.4, 126.3, 125.7, 116.6, 104.5, 67.4, 53.3, 12.2; MS (ESI+) m/z 270 (25, [M+H] $^+$); HRMS Calcd for $C_{17}H_{20}NO_2^+$ [M + H$^+$] 270.14940, found 270.14958.

*3-Diethylamino-2-phenyl-5-(2-phenylethen-1E-yl)furan (**8d**).* Furfural **4e** (0.12 g, 0.50 mmol) was reacted with BTPB (0.44 g, 1.0 mmol) and a 50% aqueous solution of NaOH (0.4 mL). The reaction mixture was stirred for 2 h. Isolation by FC (hexanes/ethyl acetate 90:10) to obtain the title compound **8d** (0.080 g, 50%) as a yellowish liquid: IR (ATR) 3056 (w), 3030 (w), 1949, (w), 1882 (w), 1808 (w), 1678 (m), 1630 (m), 1596 (m), 1585 (s), 1565 (m), 1522 (m), 1487 (m), 1474 (m), 1414 (m), 1327 (m), 1291 (m), 1200 (m), 1178 (m), 1119 (m), 1064 (m), 1023 (m), 984 (m), 976 (m), 958 (m), 912 (m), 873 (m), 850 (m), 801 (s), 787 (w), 765 (m), 749 (s), 702 (m), 692 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, 2H), 7.48 (d, 2H), 7.40−7.32 (m, 4H), 7.25−7.18 (m, 2H), 7.10 (d, J = 16.3 Hz, 1H), 6.85 (d, J = 16.3 Hz, 1H), 6.47 (s, 1H), 2.95−2.91 (m, 4H), 1.06−1.02 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 144.6, 137.3, 136.3, 131.6, 128.9, 128.4, 127.6, 126.9, 126.4, 124.6, 124.4, 116.8, 107.9, 48.9, 12.8; MS (ESI+) m/z 318 (18, [M + H]$^+$); HRMS Calcd for $C_{22}H_{24}NO^+$ [M + H$^+$] 318.18579, found 318.18578.

Synthesis of Ethyl Acrylate Derivatives 8 from Furfural 4 by Emmons−Horner−Wadsworth Reaction; General Procedure. A dried 25-mL, two-necked, round-bottom flask equipped with magnetic stirrer and condenser was charged with triethyl phosphonoacetate (TPA) (0.11 g, 0.50 mmol) and dry THF (8 mL). The mixture was cooled to −78 °C before a 1.6 M solution of BuLi in hexane (0.25 mL, 0.40 mmol) was added under N_2. The reaction mixture was stirred at −78 °C for some 20 min, and furfural **4** (0.070 g, 0.40 mmol) in dry THF (3 mL) was then added dropwise. When the addition was complete the cooling was removed, and the mixture was stirred for approximately 4 h while the temperature reached rt. The reaction was quenched with a saturated aqueous solution of NH_4Cl (12 mL) and was then worked up by extraction with DCM (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated under reduced pressure on a rotary evaporator (40 °C). Purification of the crude product using FC with mixtures of hexanes and ethyl acetate as eluent provided the following products.

*Ethyl (2E)-3-(4-Diethylamino-5-methylfuran-2-yl)prop-2-enoate (**8e**).* TPA (0.11 g, 0.50 mmol) was reacted with furfural **4b** (0.070 g, 0.40 mmol). Isolation by FC (hexane/ethyl acetate 80:20) gave **8e** (0.060 g, 60%) as a yellow liquid: IR (ATR) 1706 (s), 1631 (s), 1585 (s), 1567 (m), 1467 (m), 1445 (m), 1379 (m), 1294 (m), 1261 (s), 1159 (s), 1111 (m), 1066 (m), 1035 (m), 995 (w), 967 (m), 920 (w), 856 (m), 818 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 15.6 Hz, 1H), 6.52 (s, 1H), 6.20 (d, J = 15.6 Hz, 1H), 4.25−4.20 (m, 2H), 2.85 (m, 4H), 2.27 (s, 3H), 1.83−1.29 (m, 3H), 0.97−0.93 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 149.5, 147.9, 134.0, 131.4, 113.7, 112.7, 60.4, 49.9, 14.5, 13.1, 11.8; MS (DART+) m/z 252

dx.doi.org/10.1021/jo4026308 | J. Org. Chem. 2014, 79, 1213−1221

(100, M^++H); HRMS Calcd for $C_{14}H_{22}NO_3^+$ [M + H^+] 252.15997, found 252.15969.

*Ethyl (2E)-3-(5-Methyl-4-(piperidin-1-yl)furan-2-yl)prop-2-enoate (**8f**).* TPA (0.11 g, 0.50 mmol) was reacted with furfural **4f** (0.10 g, 0.50 mmol). Isolation by FC (hexane/ethyl acetate 80:20) gave the title compound **8f** (0.11 g, 84%) as a yellow/orange liquid: IR (ATR) 1771 (w), 1702 (s), 1638 (m), 1594 (s), 1519 (m), 1443 (m), 1365 (m), 1320 (m), 1299 (m), 1256 (s), 1227 (m), 1162 (s), 1127 (s), 1107 (s), 1030 (m), 1026 (m), 1000 (w), 968 (m), 943 (w), 908 (m), 856 (m) 807 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 15.6 Hz, 1H), 6.50 (s, 1H), 6.18 (d, J = 15.6 Hz, 1H), 4.25−4.19 (m, 2H), 2.79−2.77 (m, 4H), 2.30 (s, 3H), 1.68−1.64 (m, 6 H), 1.32−1.29 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 167.6, 147.4, 144.9, 138.4, 131.3, 113.4, 111.0, 60.5, 60.3, 54.1, 26.3, 24.1, 21.2, 14.5, 14.3, 12.5; MS (DART+) m/z 264 (100, M^++H); HRMS Calcd for $C_{15}H_{22}NO_3^+$ [M + H^+] 264.15997, found 264.15969.

*Ethyl (2E)-3-(5-Methyl-4-(morpholin-4-yl)furan-2-yl)prop-2-enoate (**8g**).* TPA (0.040 g, 0.20 mmol) was reacted with furfural **4g** (0.040 g, 0.20 mmol). Isolation by FC (hexane/ethyl acetate 80:20) gave **8g** (0.050 g, 85%) as an orange liquid: IR (ATR) 1768 (m), 1712 (s), 1639 (m), 1597 (m), 1516 (s), 1442 (m), 1366 (m), 1298 (m), 1256 (m), 1230 (m), 1156 (s), 1110 (s), 1015 (m), 971 (m), 918 (m), 880 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 15.7 Hz, 1H), 6.50 (s, 1H), 6.21 (d, J = 15.7 Hz, 1H), 4.25−4.20 (m, 2H), 3.82−3,79 (m, 4H), 2.85−2.83 (m, 4H), 2.31 (s, 3H), 1.33−1.29 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 147.8, 145.4, 137.1, 131.1, 114.1, 110.5, 67.2, 60.4, 52.9, 30.8, 14.4, 12.8; MS (DART+) m/z 266 (100, M^++H); HRMS Calcd for $C_{14}H_{20}NO_4^+$ [M + H^+] 266.13923, found 266.13945.

*Ethyl (2E)-3-(4-Diethylamino-5-phenylfuran-2-yl)prop-2-enoate (**8h**).* TPA (0.22 g, 1.0 mmol) was reacted with furfural **4e** (0.23 g, 0.95 mmol). Isolation by FC (hexane/ethyl acetate 80:20) furnished **8h** (0.25 g, 84%) as a yellowish liquid: IR (ATR) 1702 (s), 1632 (s), 1584 (m), 1567 (m), 1520 (m), 1488 (m), 1479 (w), 1450 (m), 1365 (m), 1294 (m), 1261 (s), 1236 (m), 1154 (s), 1133 (m), 1093 (w), 1034 (s), 995 (w), 967 (m), 917 (w), 877 (w), 856 (m), 818 (m), 766 (m), 714 (m), 692 (s), 671 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, 2H), 7.41−7.37 (m, 3H), 7.36−7.25 (3H), 6.70 (s, 1H), 6.38 (d, J = 15.6 Hz, 1H), 4.28−4.23 (m, 2H), 2.96−2.91 (m, 4H), 1.35−1.32 (m, 3H), 1.04−1.01 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 148.6, 136.8, 131.0, 128.7, 127.1, 125.1, 115.4, 113.8, 111.4, 60.3, 48.6, 26.3, 14.6, 13.0; MS (DART+) m/z 314 (100, [M + H^+]); HRMS Calcd for $C_{19}H_{24}NO_3^+$ [M + H^+] 314.17562, found 314.17586.

Henry Reactions with Furfurals 4b and 4e; General Procedure. Furfural **4** (0.5−1.0 mmol) in water (5 mL) was stirred at rt in a flask equipped with condenser. Nitroalkane (1.0−2.2 mmol) and Et_3N (1.0−1.2 mmol) were added, and the reaction mixture was kept stirring for about 6−24 h at rt. Water (10 mL) and Et_2O (10 mL) were added, the phases were separated, and the aqueous phase was extracted with Et_2O (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered and concentrated under reduced pressure on the rotary evaporator (40 °C). The product(s) were isolated by FC of the residue using mixtures of hexanes and ethyl acetate as eluents.

1-(4-Diethylamino-5-methylfuran-2-yl)ethanone (9a) and 3-Diethylamino-5-hydroxyiminoacetyl-2-methylfuran (10). Furfural **4b** (0.181 g, 1.0 mmol) was reacted with nitromethane (0.122 g, 2.0 mmol) in the presence of Et_3N (0.101 g, 1.0 mmol) for 6 h. Isolation by FC (hexanes/ethyl acetate 90:10) furnished **9a** (0.128 g, 66%) as a red liquid and **10** (0.041 g, 18%) as a dark red semisolid with no clear melting point. Data for **9a**: IR (film) 3326 (w), 3103 (w), 1746 (m), 1714 (s), 1673 (s), 1611 (a), 1526 (s), 1473 (s), 1448 (s), 1423 (s), 1360 (s), 1315 (s), 1286 (s), 1227 (s), 1195 (m), 1152 (s), 1120 (s), 1088 (s), 1022 (m), 994 (m), 941 (m), 919 (m), 890 (w), 843 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 1H), 2.86 (q, J = 7.1 Hz, 4H), 2.42 (s, 3H), 2.32 (s, 3H), 0.96 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.2, 152.0, 149.9, 134.5, 115.1, 49.7, 25.6, 13.0, 12.1; HRMS Calcd for $C_{11}H_{18}NO_2^+$ [M + H]$^+$ 196.13375, found 196.13449. Data for **10**: IR (film) 3267 (s), 3046 (s), 1965 (w), 1853 (w), 1840 (w), 1714 (m), 1644 (s), 1599 (s), 1555 (s), 1516 (s), 1453 (s), 1379 (s), 1337 (s), 1268 (s), 1229 (s), 1211 (s), 1155 (s), 1121 (s), 1084 (s), 1062 (s), 1006 (s), 950 (m), 921 (m), 882 (w), 832 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.44 (s, 1H), 2.90 (q, J = 7.1 Hz, 4H), 2.37 (s, 3H), 0.98 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 154.0, 148.2, 147.6, 134.4, 119.8, 49.8, 12.8, 12.5; HRMS Calcd for $C_{11}H_{17}N_2O_3^+$ [M + H^+] 225.12392, found 225.12374.

1-(4-Diethylamino-5-methylfuran-2-yl)propan-1-one (9b). Furfural **4b** (0.181 g, 1.0 mmol) was reacted with nitroethane (0.150 g, 2.0 mmol) in the presence of Et_3N (0.101 g, 1.0 mmol) for 12 h. Isolation by FC (hexanes/ethyl acetate 90:10) using Et_3N-washed SiO_2 as stationary phase gave unreacted **4b** (0.02 g, 11%) as a yellowish oil and **9b** (0.080 g, 38%) as a yellow liquid: IR (ATR) 3100 (w), 1714 (w), 1669 (s), 1609 (s), 1518 (s), 1447 (m), 1376 (w), 1354 (m), 1262 (m), 1116 (s), 1086 (m), 1032 (m), 902 (s), 799 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 1H), 2.86 (q, J = 7.1 Hz, 4H), 2.79 (q, J = 7.4 Hz, 2H), 2.31 (s, 3H), 1.20 (t, J = 7.4 Hz, 3H), 0.96 (t, J = 7.1, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.9, 151.8, 149.8, 134.4, 114.6, 49.9, 31.3, 13.2, 12.2, 8.8; MS (DART+) m/z 210 (M + H^+); HRMS Calcd for $C_{12}H_{20}NO_2^+$ [M + H]$^+$ 210.14940, found 210.15039.

1-(4-Diethylamino-5-phenylfuran-2-yl)propan-1-one (9c). Furfural **4e** (0.243 g, 1.00 mmol) was reacted with nitroethane (0.150 g, 2.00 mmol) in the presence of Et_3N (0.101 g, 1.00 mmol) for 24 h. Isolation by FC using Et_3N-washed SiO_2 as stationary phase and hexanes/ethyl acetate 90:10 as eluent gave unreacted **4e** (0.030 g, 12%) as a yellowish oil and **9c** (0.10 g, 37%) as an orange liquid: IR (ATR) 3319 (w), 3064 (w), 1669 (s), 1592 (m), 1571 (m), 1519 (s), 1485 (s), 1444 (s), 1415 (m), 1377 (m), 1359 (m), 1273 (m), 1204 (m), 1140 (s), 1084 (m), 1071 (m), 1027 (s), 918 (m), 900 (s), 844 (w), 799 (m), 768 (s), 712 (m), 692 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.6 Hz, 2H), 7.43−7.28 (m, 3H), 7.24 (s, 1H), 2.98−2.89 (m, 6H), 1.24 (t, J = 7.4 Hz, 3H), 1.02 (t, J = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 149.9, 148.4, 136.6, 130.7, 128.7, 128.4, 125.8, 115.0, 48.8, 31.6, 12.8, 8.6; MS (EI$^+$) m/z 271.2 (M^+), 256.1 (100, M − CH_3); HRMS Calcd for $C_{17}H_{22}NO_2^+$ [M + H^+] 272.16505, found 272.16588.

1-(4-Diethylamino-5-methylfuran-2-yl)pentan-1-one (9d). Furfural **4b** (0.097 g, 0.50 mmol) was reacted with 1-nitrobutane (0.110 g, 1.0 mmol) in the presence of Et_3N (0.054 g, 0.5 mmol) for 24 h. Isolation by FC using Et_3N-washed SiO_2 as stationary phase and hexanes/ethyl acetate 90:10 as eluent unreacted starting material **4b** (0.023 g, 13%) and **9d** (0.023 g, 18%): IR (ATR) 3103 (w), 1744 (w), 1718 (w), 1668 (s), 1610 (m), 1519 (s), 1446 (m), 1375 (m), 1355 (m), 1282 (m), 1231 (m), 1116 (s), 1082 (s), 1039 (s), 915 (m), 870 (w), 843 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 1H), 2.85 (q, J = 7.1 Hz, 4H), 2.75 (t, J = 7.5 Hz, 2H), 2.31 (s, 3H), 1.69 (m, 2H), 1.40 (m, 2H), 0.96 (t, J = 7.1 Hz, 6H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 152.0, 150.0, 134.4, 114.8, 49.9, 37.9, 27.1, 22.8, 14.2, 13.2, 12.3; MS (EI$^+$) m/z 237.2 (M^+), 222.2 (100, M − CH_3); HRMS Calcd for $C_{14}H_{24}NO_2^+$ [M + H^+] 238.18070, found 238.18088.

■ ASSOCIATED CONTENT

Supporting Information

^1H NMR and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: leiv.sydnes@kj.uib.no.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the Research Council of Norway, the University of Bergen and the Munin Foundation is highly

appreciated. Recording of mass spectra by Dr. Bjarte Holmelid is sincerely acknowledged. Thanks are also due to Professor Victor S. Martin and his research group at the Universidad de La Laguna, Tenerife, Spain, for excellent working conditions during a sabbatical stay.

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