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New Regiospecific Synthesis of Tri- and Tetra-Substituted Furans

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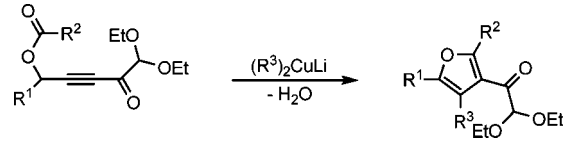


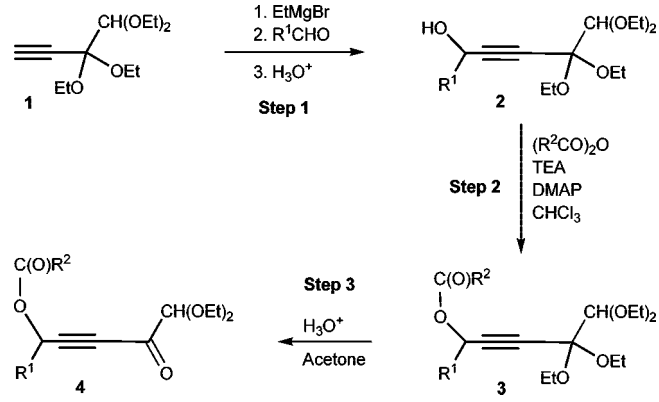
β-Acyloxy α,β-unsaturated acetylenic ketones have been shown to react with organocuprate reagents and undergo cyclization followed by dehydration to give substituted furans as the final products. The transformation appeared to be versatile, and tri- and tetra-substituted furans were obtained with regiochemical control in moderate to good yields. The best yields were generally obtained when the reactions were performed around −60 °C with substrates and cuprates containing sterically demanding substituents. The proposed mechanism for furan formation has been supported by experiments.

Introduction

We have reported a simple and efficient synthesis of 3,3,4,4-tetraethoxybutyne (TEB) (**1**), using ethyl vinyl ether as starting material and taking advantage of the serendipitous discovery that 1,1,2-trihalocyclopropanes undergo ring-opening under phase-transfer conditions in the presence of ethanol.[1] Easy access to TEB has made the preparation of 1-substituted 4,4,5,5-tetraethoxypent-2-yn-1-ols (**2**) straightforward (Scheme 1).[2−4] These alcohols are highly functionalized, and by selectively exploiting their reactive moieties, syntheses of a range of interesting compounds can be envisaged and are being investigated.

Among the compounds easily obtained from TEB in good yields are 1-alkyl- and 1-aryl-4,4,5,5-tetraethoxy-pent-2-yn-1-yl esters (**3**), which, like **1**, appear to be labile under acidic, aqueous conditions and undergo deketalization to give the corresponding ketoesters (**4**) (Scheme 1 and Experimental Section). These ketoesters contain an electron-deficient, activated triple bond which should be prone to react with nucleophilic reagents, but due to the presence of other electrophilic functional groups the outcome of the reactions is not necessarily obvious. That appears in fact to be the case; with some nucleophiles, very complex reaction mixtures are obtained whereas in other cases clean reactions are observed.[5]

SCHEME 1. Synthesis of Ketoesters 4 from TEB (1)



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(3) Some results were presented at the Petra International Chemistry Conference in Petra, Jordan, June 2007; see: Sydnes, L. K.; Holmelid, B.; Valdersnes, S.; Sengee, M.; Boman, K. *Jordanian J. Chem.* **2007**, *2*, 105.

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(5) Sydnes, L. K.; Sengee, M. To be published.

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Exploratory experiments with lithium dimethylcuprate,[6] which is well-known to react with conjugated, unsaturated ketones,[7−9] revealed that several ketoesters consistently gave fairly simple product mixtures when treated with this reagent and afforded substituted furans in variable yields. This observation is quite interesting considering the growing attention this class of compounds has received in recent years. Not only are furans important structural motifs in natural products and pharmaceutical substances,[10,11] such heterocycles have also turned out to be quite valuable intermediates in organic synthesis.[12] As a result development of syntheses of highly functionalized furans has emerged as an increasingly active field of research.[13] In this paper, we describe our successful regiospecific synthesis of tri- and tetra-substituted furans.

Results and Discussion

The ketoesters **4** used in this study were prepared from TEB by the three-step synthesis outlined in Scheme 1. The yield in each step was in most cases very good, and the total yield was in almost every case well above 50% (Table 1) whether the reactions were performed on a small or a large scale.

TABLE 1. Isolated Yields of Alcohols 2, Esters 3, and Ketoesters 4, Synthesized from TEB (1) as Summarized in Scheme 1[a]

		stepwise results; compound/yield (%)			
R^1	R^2	S1	S2	S3	total yield of **4** from **1** (%)
H	CH_3	**2a**/94	**3a**/95	**4a**/90	80
H	*i*-Pr		**3b**/87	**4b**/95	78
H	Ph		**3c**/76	**4c**/90	64
CH_3	CH_3	**2b**/92	**3d**/96	**4d**/91	80
CH_3	*i*-Pr		**3e**/82	**4e**/88	66
CH_3	Ph		**3f**/85	**4f**/91	71
i-Pr	CH_3	**2c**/78	**3g**/90	**4g**/95	67
i-Pr	*i*-Pr		**3h**/84	**4h**/92	60
i-Pr	Ph		**3i**/84	**4i**/92	60
t-Bu	CH_3	**2d**/55[b]	**3j**/90	**4j**/89	44
t-Bu	*i*-Pr		**3k**/80	**4k**/88	39
t-Bu	Ph		**3l**/82	**4l**/85	38
Ph	CH_3	**2e**/70[b]	**3m**/81	**4m**/94	53
Ph	*i*-Pr		**3n**/80	**4n**/98	55
Ph	Ph		**3o**/75	**4o**/95	50
C_6H_{13}	CH_3	**2f**/87	**3p**/90	**4p**/92	72
C_6H_{13}	*i*-Pr		**3q**/84	**4q**/90	66
C_6H_{13}	Ph		**3r**/85	**4r**/91	67

[a] Stepwise yields are for compounds **2**, **3**, and **4** obtained in steps 1−3 (S1 − S3), respectively. [b] Isolated yield after reductive workup as described in ref.[4]

Exploratory experiments using some ketones and Me_2CuLi (prepared as described by Gilman et al.[6]) showed that **4** reacted at room temperature and below to give essentially two products, a 2-alkenone and a substituted furan. The yield of the former was low and temperature sensitive in the sense that it dropped when the reaction temperature approached 0 °C; the furan formation, on the other hand, became gradually more important as the temperature dropped, and when it reached −50 °C this transformation was completely predominant.

In order to uncover the scope of the reaction acetylenic ketoesters **4a** − **4r** were treated with one molar equivalent of Me_2CuLi at temperatures ranging from room temperature to −78 °C. The ketoesters were completely consumed and, as the results compiled in Table 2 show, all substrates gave a 3-(2,2-diethoxyacetyl)-4-methyl-2-R^2-5-R^1-furan (**5**) in fair to good yield with a predictable substitution pattern. In accordance with the results from the exploratory experiments the yield was sensitive to the temperature prevailing during the reaction; the yield increased significantly, in the best cases more than 2.5 times (e.g., entries 1, 11 and 16), when the temperature was lowered from 0 °C to the −60 °C and below. However, running the reactions below −60 °C did not really improve the outcome; on the contrary, in some cases the yield even dropped, e.g. entries 7 and 16. It is also noteworthy that the yield dropped somewhat when cyanocuprate $Me_2Cu(CN)Li_2$ was applied.[14] Conjugated alkenones were formed from some substrates when reactions were run at and above 0 °C, but the yields were so low that isolation was not worthwhile.

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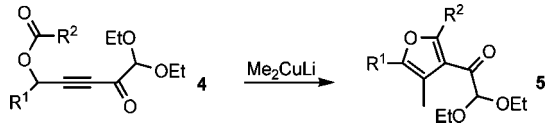
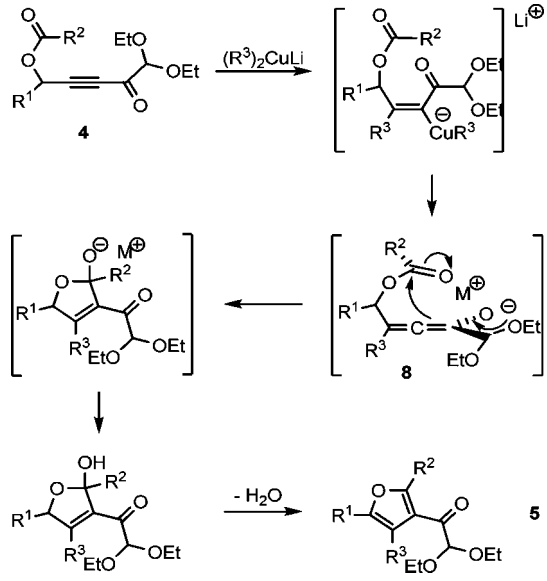
TABLE 2. Isolated Yields of Furans 5 Synthesized by Treating Ketoesters 4 with Me_2CuLi between rt and −78 °C



			isolated yield (%)			
entry	**4**	furan	−78 °C	−60 °C	0 °C	rt
1	**4a**	**5a**		50	10	
2	**4b**	**5b**	45	45		
3	**4c**	**5c**		40	25	
4	**4d**	**5d**	46	48	20	
5	**4e**	**5e**	47	50	26	
6	**4f**	**5f**		53	40	
7	**4g**	**5g**	74	81[a]	70	56
8	**4h**	**5h**		75	51	
9	**4i**	**5i**		47	45	
10	**4j**	**5j**	72	70	30	
11	**4k**	**5k**	68	68	25	
12	**4l**	**5l**		52		
13	**4m**	**5m**		52	24	
14	**4n**	**5n**		60	41	
15	**4o**	**5o**		53	35	
16	**4p**	**5p**	50	70	18	26
17	**4q**	**5q**	67	69	28	
18	**4r**	**5r**		50	32	

[a] Yield was 74% when a higher-order cuprate was used.

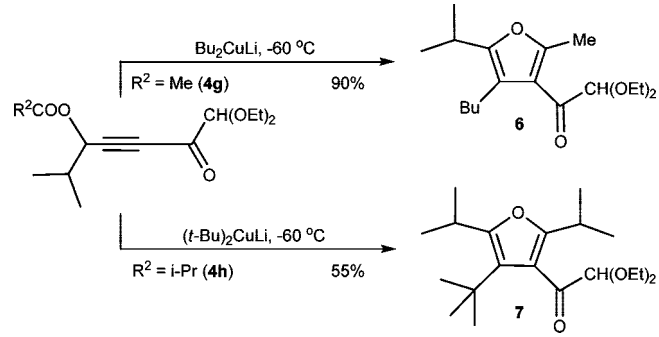
SCHEME 2. Suggested Reaction Mechanism for Cuprate Addition to 4[a]



[a] M^+denotes an unknown cationic species, formed from Li^+, CuR^3, and one or several cuprate species.[16]

A conceivable reaction mechanism for furan formation is outlined in Scheme 2. The initial step is attack of the electron-deficient conjugated carbon−carbon triple bond in a 1,4-fashion (conjugate addition) or a 1,2-fashion (carbocupration), two reactions with solid literature precedence.[15] In all the cases studied, the carbon atom attacked by the alkyl group in the copper reagent is directly attached to a sp^3-hybridized carbon atom. The bulkiness of this substituent varies quite a bit among the ketoesters, so it was expected that the outcome of the addition reaction would vary to a significant extent and be most successful for the ketoesters with the sterically least demanding group attached to C-β. Based on the furan yields, which reflect how successful the first step is, this was indeed the case, albeit

SCHEME 3. Synthesis of Congested Furans from Ketoesters 4g and 4h



only partly. Thus, a drop in the yield of **5** was observed for several ketoesters as the hydrocarbon part of the acyloxy moiety, that is, R^2, became sterically more demanding whereas the 5,5-diethoxy-1-R^1-pent-2-ynyl group remained the same; compare, for example, entries 7 (R^2 = Me; 81%), 8 (R^2 = *i*-Pr; 75%), and 9 (R^2 = Ph; 47%) for reactions run at −60 °C. For some other series, on the other hand, the yield increased instead (compare entries 4 (R^2 = Me; 48%), 5 (R^2 = *i*-Pr; 50%), and 6 (R^2 = Ph; 53%) for reactions run at −60 °C). However, when different esters of the same acid were reacted, *the furan yield generally increased as the steric crowding increased*. Particularly noteworthy is the series of substrates comprised of isobutyrates **4b**, **4e**, **4h**, and **4k** which at −60 °C gave the corresponding furans in 45, 50, 75, and 68% yield, respectively, as R^1 changes from H via Me and *i*-Pr to *t*-Bu (see Table 2, entries 2, 5, 8, and 11, respectively). This trend is further underlined when ketoesters **4g** and **4h** are treated with the butyl and *t*-butyl equivalents of the Gilman cuprate and furnish the expected and sterically quite congested furans **6** and **7**, respectively, in quite acceptable yields (Scheme 3).

It is known that cuprate addition to acyclic α,β-unsaturated ketones in general gives acyclic products, also when other functional groups are present.[8b,17] The course of reaction reported here therefore raises the question as to why cyclization occurs when **4** reacts.[18] One plausible explanation is based on the fact that copper is known to form complexes with oxygen-containing ligands,[19] including conjugated enones and enolates.[20] As outlined in Scheme 2, cuprate addition to **4** affords

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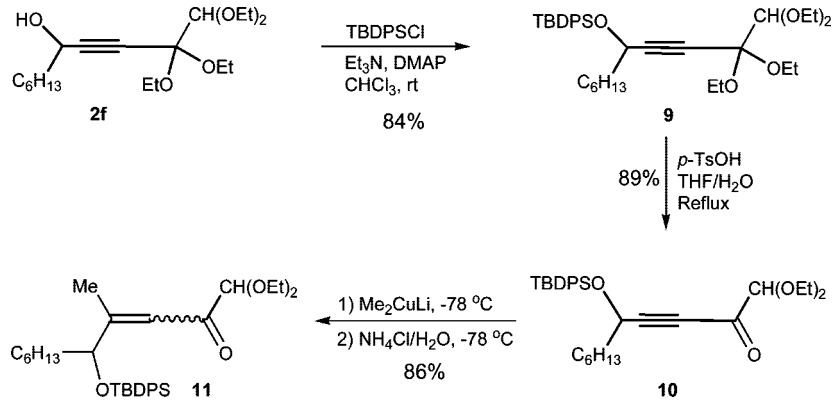
(20) (a) Krauss, S. R.; Smith, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 141. (b) Corey, E. J.; Boaz, N. W. *Tetrahedron Lett.* **1985**, *26*, 6015. (c) Hallnemo, G.; Olsson, T.; Ullenius, C. *J. Organomet. Chem.* **1984**, *265*, C22; **1985**, *282*, 133.

SCHEME 4



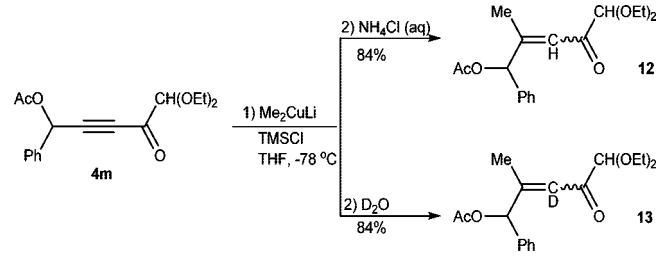
an allenoate (**8**) which, along with the carboxyl group and the acetal moiety, can act as a ligand to the copper species formed. If such complexation takes place the distance between the allenoate moiety and the carboxyl group is reduced enough to make cyclization feasible. This line of reasoning is supported by the outcome of reactions between similar ketoesters and other Michael donors *under copper-free conditions*; conjugate addition occurs but in no case was there any trace of furan whatsoever.[21,22]

But copper complexation is not the only reason; another factor must be the steric bulk of R^1 and R^3 since furans with sterically demanding substituents are formed in higher yields than furans with small substituents. When the size of R^1 and R^3 increases, the central carbon atom of the allenoate moiety will be pushed closer to the carboxyl carbon atom which will favor enolate attack and cyclization. This rationale is in keeping with what happens when γ-acyloxybutynoates are exposed to triarylphosphines under copper-free conditions and form intermediates, which undergo reductive condensation to give furans.[23]

On the basis of the mechanism depicted in Scheme 2 it is posssible to draw at least three obvious conculsions that can be tested experimentally. First, by replacing the acyloxy moiety in **4** with a silyloxy group no cyclization should occur, and that change was indeed observed. Thus, treatment of 5-{(*tert*-butyl)diphenylsiloxy}−1,1-diethoxyundec-3-yn-2-one (**10**), prepared from 1,1,2,2-tetraethoxyundec-3-yn-5-ol (**2f**) via (*tert*-butyl)(4,4,5,5-tetraethoxy-1-hexyl-2-pentynoxy) diphenylsilane (**9**) as shown in Scheme 4, with the Gilman reagent under standard conditions gave two acyclic compounds as the only products, viz. the (*E*) and the (*Z*) isomers of 5-{(*t*-butyl)diphenylsiloxy}−1,1-diethoxy-4-methylundec-3-en-2-one (**11**).

Second, cyclization would also be prevented if allenoate **8** could be trapped before it attacks the acyloxy moiety. In order to try to achieve this cuprate addition was carried out in the presence of trimethylsilyl chloride (TMSCl), which is known to be both compatible with and capable of trapping enolates under the conditions prevailing when α,β-unsaturated ketones are reacted with cuprate reagents.[24] To our satisfaction it appeared that the allenoate attack of the acyloxy group was completely intercepted under these conditions; instead, conjugate addition took place and furnished the corresponding and expected β-methylated α,β-unsaturated alkenone after standard hydrolytic workup. In all the reactions carried out under these conditions the yield was excellent as illustrated by the results obtained when 5,5-diethoxy-4-oxo-1-phenylpent-2-ynyl acetate (**4m**) was treated with lithium dimethylcuprate under standard conditions at −78 °C; hydrolysis furnished a 1:1 mixture of (*E*)- and (*Z*)-5,5-diethoxy-2-methyl-4-oxo-1-phenylpent-2-enyl acetate (**12*E*** and **12*Z***, respectively) in 84% yield when aqueous ammonium chloride was used and the 3-deuterated analogue 3-deuterio-5,5-diethoxy-2-methyl-4-oxo-1-phenylpent-2-enyl acetate (**13**) when deuterium oxide was applied (Scheme 5).

SCHEME 5



A third consequence of the proposed reaction mechanism is that if the alkynyl group in ketoester **4** comes from a tertiary propargylic alcohol, no furan can be formed because dehydration becomes impossible. In order to check out this corollary 5,5,6,6-tetraethoxy-2-methylhex-3-yn-2-ol (**14**) was prepared and converted to 5,5-diethoxy-1,1-dimethyl-4-oxopent-2-ynyl acetate (**16**), which was treated with the Gilman reagent under the same conditions that led to furan formation (Scheme 6). Notably, one product only was obtained, viz. 2,2-diethoxy-1-(2,5-dihydro-2-hydroxy-2,4,5,5-tetramethylfuran-3-yl)ethanone (**17**), which is exactly the compound expected from the mechanism in Scheme 2.

In summary, we have developed a new method for the synthesis of tri- and tetra-substituted furans. Under the best conditions (around −60 °C) the cyclization proceeds in 40−80% yield. The highest yields were generally obtained with substrates containing the more bulky substituents. The ease with which our starting materials, acylated γ-hydroxy α,β-unsaturated acetylenic ketones, can be prepared makes the method a good

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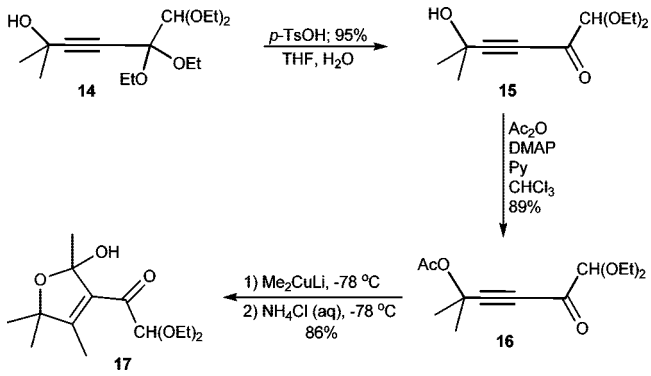
SCHEME 6



alternative to other syntheses used to prepare the same sort of compounds, for instance based on conjugated allenyl ketones.[13a,d,25] The reaction is somewhat similar to the phosphine-mediated synthesis of furans by reductive condensation of γ-acyloxy butynoates,[23] but a major difference is apparent: whereas the phosphine-based method can only give di- and trisubstituted furans, our method furnishes tri- and tetra-substituted furans.

Experimental Section

General. IR spectra were run on a Nicolet Impact 410 infrared spectrophotometer or a Spectrum One FT-IR ATR spectrometer. NMR spectra were recorded on a Bruker Spectrospin AC 200 F or a Bruker Spectrospin DPX-400 MHz spectrometer. Chemical shifts are reported in ppm downfield from TMS. TLC analyses of the reaction mixtures were performed with Silica gel (60 F254) on aluminum sheets with mixtures of hexanes (a commercial mixture of isomeric hexanes) and ethyl acetate as the mobile phase. Flash chromatography was carried out with Silica gel (230−400 mesh) as the stationary phase and mixtures of ethyl acetate and hexanes (a commercial mixture of isomeric hexanes) as the mobile phase. The eluent composition is given in each case. Mass spectra were obtained on a VG 7070 Micromass spectrometer, an Autospec Ultima spectrometer, a three-sector instrument with EBE geometry from Micromass, and a JEOL AccuTOF T100GC spectrometer. The instruments were operated in the EI mode at 70 eV or the DART/ESI+ mode.

Synthesis of Propargylic Alcohols (2) from TEB (1). 4,4,5,5-Tetraethoxypent-2-yn-1-ol (**2a**), 5,5,6,6-tetraethoxyhex-3-yn-2-ol (**2b**), 6,6,7,7-tetraethoxy-2,2-dimethylhept-4-yn-3-ol (**2d**), 4,4,5,5-tetraethoxy-1-phenylpent-2-yn-1-ol (**2e**), and 1,1,2,2-tetraethoxyundec-3-yn-5-ol (**2f**) were synthesized as described in the literature[4] whereas 6,6,7,7-tetraethoxy-2-methylhept-4-yn-3-ol (**2c**) was prepared as follows.

An EtMgBr solution in Et_2O (2.1 mL, 3.0 M, 6.3 mmol) was added dropwise through a septum to a stirred solution of TEB (1.38 g, 6.0 mmol) in dry THF (9.0 mL) kept under nitrogen atmosphere at room temperature. The resulting mixture was refluxed for 80 min before it was cooled to room temperature. Isobutyraldehyde (0.45 g, 6.3 mmol) was then added dropwise and the resulting solution was stirred and refluxed for 3 h. The reaction mixture was cooled to room temperature, quenched with saturated aqueous NH_4Cl (15 mL), and extracted with DCM (3 × 20 mL). The combined organic extracts were dried over $MgSO_4$ (anhd.) and then concentrated under vacuum on a rotary evaporator. The crude product was purified by flash chromatography (hexanes-ethyl acetate, 80:20) and gave **2c** (1.41 g, 78%) as a clear liquid. IR (film) 3443 (s), 2976 (s), 2931 (s), 2897 (s), 2875 (s), 2240 (w), 1469 (m), 1458 (m), 1444 (m), 1388 (m), 1370 (m), 1329 (m), 1293 (w), 1245 (m), 1117 (s), 1077 (s), 919 (w), 878 (m), 805 (w), 759 (w), 702 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.38 (s, 1H), 4.28−4.24 (m, 1H), 3.79−3.70 (m, 8H), 2.03−1.85 (m, 1H), 1.78 (bs, 1H), 1.27−1.18 (m, 12H), 1.05−0.99 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 103.9, 98.6, 86.7, 80.1, 67.7, 64.5, 59.6, 34.3, 17.9, 17.4, 15.3, 15.2; MS (ESI) *m/z* 285 (100), 257 (50), 246 (20), 211 (10); HRMS Calcd for $C_{14}H_{25}O_4^+$ [$M^{+\cdot}$ − EtO·] 257.1753, found 257.1732.

Synthesis of Propargylic Esters (3) from 2; General Procedure. Carboxylic anhydride (3.0 mol equiv), triethylamine (TEA) (2.0 mol equiv.), and 4-(*N*,*N*-dimethylamino)pyridine (DMAP) (0.15 mol equiv) were added to a stirred solution of propargylic alcohol **2** in $CHCl_3$ (for volume see the description for the individual esters below) and left stirring at room temperature until all the starting material was consumed (TLC). The reaction mixture was cooled to 0 °C and hydrolyzed with saturated aqueous $NaHCO_3$ (equal the volume of $CHCl_3$). The resulting mixture was stirred for 15 min, the phases were separated, and the aqueous layer was extracted with DCM (3 × the volume of the $NaHCO_3$ solution). The combined organic layers were dried over $MgSO_4$ (anhd.) and then concentrated under vacuum on a rotary evaporator to give a crude product, which was purified by flash chromatography.

4,4,5,5-Tetraethoxypent-2-ynyl Acetate (3a). Acetic anhydride (0.92 g, 9.0 mmol), TEA (0.61 g, 6.0 mmol), and DMAP (0.037 g, 0.30 mmol) were added to a solution of **2a** (0.78 g, 3.0 mmol) in $CHCl_3$ (10 mL) and reacted for 15 min to give the title compound (0.86 g, 95%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (90:10). IR (film) 2980 (s), 2932 (s), 2894 (s), 2250 (w), 1750 (s), 1481 (w), 1443 (m), 1378 (s), 1333 (m), 1225 (s), 1184 (s), 1117 (s), 1078 (s), 1033 (s), 961 (m), 913 (w), 881 (w), 827 (w), 754 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.76 (s, 2H), 4.39 (s, 1H), 3.84−3.62 (m, 8H), 2.08 (s, 3H), 1.23 (q, J = 7.0 Hz, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.9, 103.6, 98.4, 81.1, 80.5, 64.7, 59.4, 52.1, 20.4, 15.0; MS (EI) *m/z* 257 (85), 229 (40), 212 (45), 200 (55), 199 (65), 187 (35), 172 (85), 170 (35), 169 (75), 155 (85), 143 (15), 142 (48), 141 (65), 140 (80), 129 (55), 126 (70), 125 (40), 124 (35), 114 (45), 112 (80), 111 (75), 104 (70), 97 (80), 85 (70), 84 (100), 83 (80), 76 (70); HRMS Calcd for $C_{13}H_{21}O_5^+$ [$M^{+\cdot}$ − EtO·] 257.1389, found 257.1384.

4,4,5,5-Tetraethoxypent-2-ynyl Isobutyrate (3b). Isobutyric anhydride (2.46 g, 15.6 mmol), TEA (1.05 g, 10.4 mmol) and DMAP (0.097 g, 0.8 mmol) were added to a solution of **2a** in $CHCl_3$ (10 mL) and reacted for 30 min to give the title compound (1.50 g, 87%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (90:10). IR (film) 2976 (s), 2932 (s), 2891 (s), 2737 (w), 2628 (w), 2255 (w), 1929 (w), 1744 (s), 1471 (m), 1445 (m), 1389 (m), 1372 (m), 1339 (m), 1295 (w), 1245 (m), 1185 (s), 1144 (s), 1118 (s), 1079 (s), 1022 (s), 966 (m), 920 (w), 888 (m), 815 (w), 752 (m), 665 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.76 (s, 2H), 4.38 (s, 1H), 3.84−3.62 (m, 8H), 2.58 (se, J = 7.0 Hz, 1H), 1.28−1.15 (m, 18H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 176.1, 103.7, 98.5, 81.0 (2C), 64.7, 59.6 ($2CH_2$), 52.0 ($2CH_2$), 33.6, 18.7 ($2CH_3$), 15.2 ($2CH_3$), 15.1 ($2CH_3$); MS (ESI) m/z 285 (100), 257 (10), 239 (5), 211 (12); HRMS Calcd for $C_{15}H_{25}O_5^+$ [$M^{+\cdot}$ − EtO·] 285.1702, found 285.1724.

4,4,5,5-Tetraethoxypent-2-ynyl Benzoate (3c). Benzoic anhydride (3.53 g, 15.6 mmol), TEA (1.05 g, 10.4 mmol) and DMAP (0.097 g, 0.8 mmol) were added to a solution of **2a** (1.36 g, 5.2 mmol) in $CHCl_3$ (10 mL) and reacted for 15 min to give the title compound (1.45 g, 76%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (95:5). IR (film) 3063 (w), 3034 (w), 2976 (s), 2929 (s), 2898 (s), 2874 (s), 2737 (w), 2250 (w), 1970 (w), 1913 (w), 1729 (s), 1601 (m), 1585 (w), 1452 (m), 1371 (m), 1315 (m), 1268 (s), 1177 (s), 1113 (s), 1097 (s), 1079 (s), 1027 (s), 947 (m), 877 (w), 805 (w), 751 (w), 713

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(s), 687 (m), 665 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.07−8.03 (d, 2H), 7.62−7.41 (m, 3H), 5.01 (s, 2H), 4.40 (s, 1H), 3.88−3.63 (m, 8H), 1.28−1.18 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.6, 133.1, 129.7, 129.5 (2C), 128.3 (2C), 103.7, 98.5, 81.5, 80.7, 64.8 ($2CH_2$), 59.6 ($2CH_2$), 52.7, 15.2 ($2CH_3$), 15.1 ($2CH_3$); MS (ESI) *m/z* 319 (100), 291 (10), 273 (5), 245 (10); HRMS Calcd for $C_{18}H_{23}O_5^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 319.1545, found 319.1558.

4,4,5,5-Tetraethoxy-1-methylpent-2-ynyl Acetate (3d). Acetic anhydride (0.92 g, 9.0 mmol), TEA (0.61 g, 6.0 mmol) and DMAP (0.037 g, 0.3 mmol) were added to a solution of **2b** (0.82 g, 3.0 mmol) in $CHCl_3$ (10 mL) and reacted for 45 min to give the title compound (0.91 g, 96%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (90:10). IR (film) 2977 (s), 2933 (s), 2892 (s), 1746 (s), 1281 (w), 1445 (m), 1389 (s), 1372 (s), 1338 (m), 1306 (w), 1232 (s), 1184 (s), 1117 (s), 1081 (s), 1022 (s), 959 (m), 918 (w), 875 (w), 730 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.53 (q, J = 6.7 Hz, 1H), 4.39 (s, 1H), 3.88−3.65 (m, 8H), 2.04 (s, 1H), 1.51 (d, J = 6.7 Hz, 3H), 1.32−1.18 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.2, 103.5, 98.1, 84.8, 79.3, 64.3, 59.8, 59.3, 20.8, 20.6, 15.0, 14.9; MS (EI) *m/z* 316 (2), 273 (50), 272 (40), 257 (45), 243 (50), 228 (20), 226 (25), 214 (90), 201 (90), 184 (55), 171 (60), 155 (60), 139 (80), 137 (80), 127 (60), 111 (100), 109 (55), 104 (50), 97 (50), 89 (30), 83 (70), 76 (65), 69 (50); HRMS Calcd for $C_{16}H_{28}O_6^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 316.1886, found 316.1888.

4,4,5,5-Tetraethoxy-1-methylpent-2-ynyl Isobutyrate (3e). Isobutyric anhydride (1.42 g, 9.0 mmol), TEA (0.61 g, 6.0 mmol) and DMAP (0.037 g, 0.3 mmol) were added to a solution of **2b** (0.82 g, 3.0 mmol) in $CHCl_3$ (10 mL) and reacted for 30 min to give the title compound (0.85 g, 82%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (90:10). IR (film) 2977 (s), 2933 (m), 2897 (m), 2250 (w), 1742 (s), 1470 (w), 1457 (w), 1446 (w), 1388 (m), 1372 (m), 1333 (m), 1249 (m), 1188 (m), 1148 (s), 1118 (s), 1081 (s), 1021 (m), 950 (m), 907 (w), 850 (w), 754 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.55 (q, J = 6.0 Hz, 1H), 4.39 (s, 1H), 3.87−3.63 (m, 8H), 2.54 (septet, J = 7.0 Hz, 1H), 1.50 (d, J = 6.0 Hz, 3H), 1.29−1.15 (m, 18H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 175.6, 103.7, 98.3, 85.3, 79.3, 64.5, 64.4, 59.8, 59.6, 33.7, 20.9, 18.7, 18.6, 15.2, 15.1; MS (EI) m/*z* 299 (100), 273 (30), 201 (5), 103 (5); HRMS Calcd for $C_{16}H_{27}O_5^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 299.18585, found 299.18608.

4,4,5,5-Tetraethoxy-1-methylpent-2-ynyl Benzoate (3f). Benzoic anhydride (1.49 g, 6.6 mmol), TEA (0.44 g, 4.4 mmol) and DMAP (0.04 g, 0.3 mmol) were added to a solution of **2b** (0.60 g, 2.2 mmol) in $CHCl_3$ (20 mL) and reacted for 45 min to give the title compound (0.70 g, 85%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (90:10). IR (film) 3063 (w), 3035 (s), 2977 (s), 2931 (s), 2896 (s), 2250 (w), 1971 (w), 1913 (w), 1725 (s), 1602 (m), 1586 (m), 1481 (m), 1452 (m), 1390 (m), 1372 (m), 1338 (m), 1315 (s), 1267 (s), 1176 (s), 1109 (s), 1097 (s), 1079 (s), 1026 (s), 946 (m), 922 (w), 872 (w), 853 (w), 806 (w), 714 (s), 688 (m), 665 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.07−8.03 (m, 2H), 7.61−7.40 (m, 3H), 5.80 (q, J = 6.7 Hz, 1H), 4.40 (s, 1H), 3.87−3.61 (m, 8H), 1.65 (d, J = 6.7 Hz, 3H), 1.26−1.17 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.5, 133.0, 130.1, 129.6 (2C), 128.2 (2C), 103.7, 98.4, 85.1, 79.9, 64.6, 64.5, 60.8, 59.7, 59.6, 21.2, 15. ($2CH_3$), 15.1 ($2CH_3$); MS (ESI) *m/z* 333 (100), 305 (7); HRMS Calcd for $C_{19}H_{25}O_5^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 333.1702, found 333.1706.

4,4,5,5-Tetraethoxy-1-isopropylpent-2-ynyl Acetate (3g). Acetic anhydride (1.22 g, 12.0 mmol), TEA (0.81 g, 8.0 mmol) and DMAP (0.07 g, 0.6 mmol) were added to a solution of **2c** (1.21 g, 4.0 mmol) in $CHCl_3$ (15 mL) and reacted for 30 min to give the title compound (1.24 g, 90%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (85:15). IR (film) 2976 (s), 2931 (s), 2898 (s), 2877 (s), 2737 (w), 2250 (w), 1747 (s), 1444 (s), 1389 (s), 1371 (s), 1357 (s), 1331 (m), 1228 (s), 1117 (s), 1078 (s), 1021 (s), 984 (s), 902 (m), 604 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.33 (d, J = 5.4 Hz, 1H), 4.39 (s, 1H), 3.79−3.67 (m, 8H), 2.30−2.15 (m, 1H), 2.07 (s, 3H), 1.26−1.17 (m, 12H), 1.02 (t, J = 6.2 Hz 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 169.7, 103.8, 98.5, 83.0, 80.7, 68.7, 64.3 ($2CH_2$), 59.8 ($2CH_2$), 32,3, 20.8, 18.0, 17.3, 15.2 ($2CH_3$), 15.1 ($2CH_3$); MS (EI) *m/z* 299 (6), 257 (12), 241 (28), 182 (19), 167 (17), 153 (23), 139 (14), 125 (19), 103 (48), 75 (51); HRMS Calcd for $C_{16}H_{27}O_5^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 299.1858, found 299.1852.

4,4,5,5-Tetraethoxy-1-isopropylpent-2-ynyl Isobutyrate (3h). Isobutyric anhydride (2.37 g, 15.0 mmol), TEA (1.01 g, 10.0 mmol) and DMAP (0.10 g, 0.8 mmol) were added to a solution of **2c** (1.51 g, 5.0 mmol) in $CHCl_3$ (15 mL) was added and reacted for 30 min to give the title compound (1.56 g, 84%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (90:10). IR (film) 2975 (s), 2933 (s), 2898 (s), 2878 (s), 2737 (w), 2255 (w), 1743 (s), 1470 (m), 1455 (m), 1388 (m), 1370 (m), 1349 (m), 1331 (m), 1246 (m), 1188 (s), 1080 (s), 1020 (m), 986 (m), 914 (w), 873 (w), 811 (w), 754 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.29 (d, J = 6.9 Hz, 1H), 4.38 (s, 1H), 3.86−3.60 (m, 8H), 2.57 (septet, J = 7.0 Hz, 1H), 2.11−1.95 (m, 1H), 1.32−1.15 (m, 18H), 1.05−1.00 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 175.7, 103.9, 98.5, 83.5, 80.5, 68.4, 64.2 ($2CH_2$), 59.9 ($2CH_2$), 33.9, 32.4, 18.8, 18.7, 18.0, 17.4, 15.3 ($2CH_3$), 15.2 ($2CH_3$); MS (ESI) *m/z* 327 (100), 316 (35), 299 (82), 257 (4), 229 (5); HRMS Calcd for $C_{18}H_{31}O_5^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 327.2171, found 327.2159.

4,4,5,5-Tetraethoxy-1-isopropylpent-2-ynyl Benzoate (3i). Benzoic anhydride (3.46 g, 15.3 mmol), TEA (1.03 g, 10.2 mmol) and DMAP (0.10 g, 0.8 mmol) were added to a solution of **2c** (1.54 g, 5.1 mmol) in $CHCl_3$ (20 mL) and reacted for 45 min to give the title compound (1.74 g, 84%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (95:5). IR (film) 3090 (w), 3063 (w), 3034 (w), 2975 (s), 2931 (s), 2898 (s), 2877 (s), 2736 (w), 2623 (w), 2250 (w), 1976 (w), 1919 (w), 1820 (w), 1727 (s), 1601 (m), 1585 (m), 1469 (m), 1452 (s), 1389 (s), 1370 (s), 1335 (s), 1315 (s), 1264 (s), 1176 (s), 1094 (s), 1026 (s), 978 (s), 959 (m), 937 (m), 916 (m), 877 (m), 804 (w), 760 (w), 713 (s), 687 (m), 673 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.08−8.04 (m, 2H), 7.62−7.41 (m, 3H), 5.58 (d, J = 6.5 Hz, 1H), 4.40 (s, 1H), 3.93−3.63 (m, 8H), 2.24−2.14 (m, 1H), 1.27−1.09 (m, 18H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.2, 132.9, 130.0, 129.6 (2CH), 128.2 (2CH), 103.8, 98.5, 83.1, 81.1, 69.2, 64.3 ($2CH_2$), 59.9 ($2CH_2$), 32.6, 18.1, 17.5, 15.3 ($2CH_3$), 15.1 ($2CH_3$); MS (ESI) *m/z* 361 (100); HRMS Calcd for $C_{21}H_{29}O_5^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 361.2015, found 361.1999.

1-(t-Butyl)-4,4,5,5-tetraethoxypent-2-ynyl Acetate (3j). Acetic anhydride (0.92 g, 9.0 mmol), TEA (0.61 g, 6.0 mmol) and DMAP (0.037 g, 0.3 mmol) were added to a solution of **2d** (0.95 g, 3.0 mmol) in $CHCl_3$ (10 mL) and reacted for 45 min to give the title compound (0.97 g, 90%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (90:10). IR (film) 2975 (s), 2932 (m), 2899 (m), 2873 (m), 1746 (s), 1481 (w), 1444 (w), 1391 (m), 1370 (s), 1235 (s), 1182 (m), 1235 (s), 1182 (m), 1118 (s), 1081 (s), 1019 (s), 980 (m), 909 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.21 (s, 1H), 4.38 (s, 1H), 3.85−3.62 (m, 8H), 2.10 (s, 3H), 1.23 (t, J = 7.1 Hz, 6H), 1.22 (t, J = 7.1 Hz, 6H), 1.03 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.1, 103.8, 83.2, 80.5, 71.4, 64.1, 59.8, 35.2, 25.3, 20.6, 15.2; MS (EI) *m/z* 358 (M^+, 2), 313 (45), 272 (20), 271 (50), 256 (60), 255 (70), 225 (55), 200 (40), 197 (60), 196 (65), 182 (45), 181 (70), 168 (70), 153 (70), 127 (35), 125 (70), 111 (90), 103 (100), 95 (70), 93 (60), 83 (58), 75 (98), 67 (60); HRMS Calcd for $C_{17}H_{29}O_5^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 313.2015, found 313.2023.

1-(t-Butyl)-4,4,5,5-tetraethoxypent-2-ynyl Isobutyrate (3k). Isobutyric anhydride (1.42 g, 9.0 mmol), TEA (0.61 g, 6.0 mmol) and DMAP (0.037 g, 0.3 mmol) were added to a solution of **2d** (0.95 g, 3.0 mmol) in $CHCl_3$ (10 mL) and reacted for 200 min to give the title compound (0.93 g, 80%) as a colorless liquid after isolation by flash chromatography using hexanes−-ethyl acetate (90:10). IR (film) 2976 (s), 2933 (m), 2900 (s), 2896 (s), 1743 (s),

1480 (m), 1471 (m), 1445 (m), 1388 (m), 1368 (m), 1329 (m), 1247 (m), 1186 (s), 1150 (s), 1118 (s), 1082 (s), 1020 (m), 977 (m), 919 (w), 907 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.20 (s, 1H), 4.38 (s, 1H), 3.81−3.62 (m, 8H), 2.59 (septet, $J = 7.0$ Hz, 1H), 1.27 (t, $J = 7.1$ Hz, 6H), 1.24 (t, $J = 7.1$ Hz, 6H), 1.03 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 175.6, 103.9, 98.5, 83.6, 80.4, 71.2, 64.1, 60.0, 35.3, 34.0, 25.4, 18.9, 18.6, 15.3, 15.2; MS (ESI) *m/z* 386 (M^+, 45), 341 (80), 103 (100); HRMS: calcd for $C_{19}H_{33}O_5^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 341.2335, found 341.2341.

1-(t-Butyl)-4,4,5,5-tetraethoxypent-2-ynyl Benzoate (3l). Benzoic anhydride (2.04 g, 9.0 mmol), TEA (0.61 g, 6.0 mmol), and DMAP (0.037 g, 0.3 mmol) were added to a solution of **2d** (0.95 g, 3.0 mmol) in $CHCl_3$ (10 mL) and reacted for 5 h to give the title compound (1.03 g, 82%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (90:10). IR (film) 3090 (w), 3063 (w), 3033 (w), 2975 (s), 2932 (s), 2898 (s), 2873 (s), 2250 (w), 1727 (s), 1601 (m), 1585 (w), 1480 (m), 1452 (s), 1395 (m), 1367 (s), 1337 (s), 1315 (s), 1267 (s), 1177 (s), 1106 (s), 1082 (s), 1026 (s), 964 (s), 937 (m), 914 (w), 878 (w), 805 (w), 767 (w), 713 (s), 687 (w), 671 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.10−8.03 (m, 2H), 7.62−7.40 (m, 3H), 5.45 (s, 1H), 4.39 (s, 1H), 3.87−3.61 (m, 8H), 1.19 (t, $J = 7.0$ Hz, 3H), 1.17 (t, $J = 7.0$ Hz, 3H), 1.13 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.2, 132.9, 130.0, 129.6, 128.2, 103.9, 98.5, 83.3, 80.9, 72.1, 64.1, 60.0, 35.6, 25.6, 15.3, 15.1; MS (ESI) *m/z* 375 (100), 161 (25); HRMS Calcd for $C_{22}H_{31}O_5^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 375.21715, found 375.21690.

4,4,5,5-Tetraethoxy-1-phenylpent-2-ynyl Acetate (3m). Acetic anhydride (1.38 g, 13.5 mmol), TEA (0.91 g, 9.0 mmol) and DMAP (0.09 g, 0.7 mmol) were added to a solution of **2e** (1.50 g, 4.5 mmol) in $CHCl_3$ (10 mL) and reacted for 30 min to give the title compound (1.36 g, 81%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (90:10). IR (film) 3090 (w), 3065 (m), 3035 (m), 2976 (s), 2930 (s), 2897 (s), 2245 (w), 1744 (s), 1600 (w), 1570 (w), 1496 (m), 1481 (m), 1456 (s), 1445 (m), 1370 (s), 1342 (m), 1274 (m), 1224 (s), 1178 (s), 1117 (s), 1078 (s), 1019 (s), 955 (s), 902 (m), 832 (w), 757 (m), 698 (s), 604 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.60−7.51 (m, 2H), 7.44−7.30 (m, 3H), 6.57 (s, 1H), 4.43 (s, 1H), 3.87−3.60 (m, 8H), 2.08 (s, 3H), 1.26−1.17 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.6, 137.5, 129.6, 129.2 (2CH), 128.7 (2CH), 104.4, 99.1, 83.6, 82.8, 65.7, 64.8 ($2CH_2$), 60.1 ($2CH_2$), 21.0, 15.2 ($2CH_3$), 15.1 ($2CH_3$); MS (EI) *m/z* 333 (5), 291 (24), 275 (25), 217 (25), 216 (100), 187 (14), 160 (15), 143 (13), 131 (12), 115 (47), 103 (86), 75 (39); HRMS Calcd for $C_{19}H_{25}O_5$ [$M^{+\cdot}$ − EtO$^\cdot$] 333.1702, found 333.1717.

4,4,5,5-Tetraethoxy-1-phenylpent-2-ynyl Isobutyrate (3n). Isobutyric anhydride (1.71 g, 10.8 mmol), TEA (0.73 g, 7.2 mmol) and DMAP (0.07 g, 0.7 mmol) were added to a solution of **2e** (1.20 g, 3.6 mmol) in $CHCl_3$ (10 mL) and reacted for 30 min to give the title compound (1.17 g, 80%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (95:5). IR (film) 3090 (w), 3065 (m), 3035 (m), 2976 (s), 2932 (s), 2896 (s), 2737 (w), 2623 (w), 2255 (w), 1955 (w), 1740 (s), 1603 (w), 1587 (w), 1496 (m), 1473 (m), 1456 (s), 1388 (s), 1370 (m), 1345 (m), 1295 (m), 1274 (m), 1242 (m), 1183 (s), 1143 (s), 1116 (s), 1081 (s), 1028 (s), 946 (m), 908 (m), 876 (m), 815 (w), 757 (m), 698 (s), 675 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.57−7.51 (m, 2H), 7.42−7.26 (m, 3H), 6.56 (s, 1H), 4.42 (s, 1H), 3.86−3.60 (m, 8H), 2.58 (septet, $J = 7.0$ Hz, 1H), 1.28−1.10 (m, 18H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 175.5, 136.8, 128.6, 128.3 (2CH), 127.7 (2CH), 103.8, 98.6, 83.4, 82.2, 65.1, 64.3 ($2CH_2$), 59.9 ($2CH_2$), 33.8, 18.6 ($2CH_3$), 15.2 ($2CH_3$), 15.1 ($2CH_3$); MS (ESI) *m/z* 361 (85), 333 (100), 319 (12), 291 (10), 263 (30), 216 (13); HRMS Calcd for $C_{21}H_{29}O_5^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 361.2015, found 361.2018.

4,4,5,5-Tetraethoxy-1-phenylpent-2-ynyl Benzoate (3o). Benzoic anhydride (3.80 g, 16.8 mmol), TEA (1.13 g, 11.2 mmol) and DMAP (0.10 g, 0.8 mmol) were added to **2e** (1.88 g, 5.6 mmol) in $CHCl_3$ (25 mL) and reacted for 45 min to give the title compound (1.85 g, 75%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (95:5). IR (film) 3090 (m), 3065 (m), 3035 (m), 2976 (s), 2929 (s), 2896 (s), 2735 (w), 2255 (w), 1965 (w), 1913 (w), 1725 (s), 1601 (m), 1585 (m), 1495 (m), 1481 (m), 1453 (s), 1390 (m), 1371 (m), 1317 (s), 1259 (s), 1176 (s), 1093 (s), 1026 (s), 941 (m), 913 (m), 803 (m), 759 (m), 713 (s), 698 (s) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.08−8.03 (m, 2H), 7.67−7.36 (m, 8H), 6.83 (s, 1H), 4.44 (s, 1H), 3.85−3.60 (m, 8H), 1.26−1.16 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.1, 136.7, 133.1, 129.8 (2CH), 129.7, 128.8, 128.4 (2CH), 128.2 (2CH), 127.9 (2CH), 103.8, 98.6, 83.1, 82.7, 65.9, 64.3 ($2CH_2$), 59.9 ($2CH_2$), 15.3 ($2CH_3$), 15.1 ($2CH_3$); MS (ESI) *m/z* 395 (100); HRMS Calcd for $C_{24}H_{27}O_5$ [$M^{+\cdot}$ − EtO$^\cdot$] 395.1858, found 395.1875.

4,4,5,5-Tetraethoxy-1-hexylpent-2-ynyl Acetate (3p). Acetic anhydride (0.92 g, 9.0 mmol), TEA (0.61 g, 6.0 mmol) and DMAP (0.037 g, 0.3 mmol) were added to a solution of **2f** (1.03 g, 3.0 mmol) in $CHCl_3$ (10 mL) and reacted for 15 min to give the title compound (1.04 g, 90%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (90:10). IR (film) 2977 (s), 2932 (m), 2895 (m), 1747 (s), 1481 (w), 1445 (w), 1389 (s), 1372 (s), 1337 (m), 1306 (w), 1233 (s), 1184 (m), 1117 (s), 1080 (s), 1021 (s), 960 (m), 909 (w), 876 (w), 754 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.43 (s, 1H), 4.36 (s, 1H), 3.83−3.58 (m, 8H), 2.04 (s, 3H), 1.81−1.15 (m, 22H), 0.86 (t, $J = 6.1$ Hz, 1H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 170.0, 103.7, 98.6, 84.4, 80.1, 64.5, 63.9, 59.7, 34.5, 31.6, 28.7, 24.9, 22.5, 21.0, 15.3, 15.1, 14.0; MS (EI) *m/z* 341 (60), 327 (15), 300 (40), 299 (65), 284 (60), 283 (70), 269 (15), 252 (20), 253 (55), 241 (5), 229 (5), 225 (55), 214 (40), 197 (50), 196 (65), 182 (30), 179 (70), 167 (60), 153 (55), 149 (55), 139 (50), 125 (35), 125 (60), 107 (55), 103 (95), 97 (80), 95 (65), 93 (60), 83 (40), 81 (100), 75 (90); HRMS Calcd for $C_{19}H_{33}O_5$ [$M^{+\cdot}$ − EtO$^\cdot$] 341.2328, found 341.2323.

4,4,5,5-Tetraethoxy-1-hexylpent-2-ynyl Isobutyrate (3q). Isobutyric anhydride (1.42 g, 9.0 mmol), TEA (0.61 g, 6.0 mmol) and DMAP (0.037 g, 0.3 mmol) were added **2f** (1.03 g, 3.0 mmol) in $CHCl_3$ (10 mL) and reacted for 45 min to give the title compound (1.04 g, 84%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (90:10). IR (film) 2976 (s), 2931 (s), 2897 (s), 2250 (w), 1742 (s), 1470 (m), 1459 (m), 1445 (m), 1388 (m), 1370 (m), 1333 (m), 1246 (m), 1187 (s), 1152 (s), 1118 (s), 1081 (s), 1021 (m), 970 (m), 910 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.46 (t, $J = 6.5$ Hz, 1H), 4.38 (s, 1H), 3.87−3.60 (m, 8H), 2.55 (septet, $J = 6.9$ Hz, 1H), 1.48−1.10 (m, 22H), 0.90 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 175.7, 103.8, 98.4, 84.6, 79.9, 71.2, 64.3, 63.5, 59.8, 34.4, 33.8, 31.5, 28.6, 24.7, 22.3, 18.7, 18.6, 15.2, 15.1, 13.9; MS (ESI) *m/z*) 414 (M^+, 5), 369 (60), 312 (10), 299 (20), 103 (100); HRMS: calcd for $C_{21}H_{37}O_5^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 369.2641, found 369.255.

4,4,5,5-Tetraethoxy-1-hexylpent-2-ynyl Benzoate (3r). Benzoic anhydride (2.71 g, 12.0 mmol), TEA (0.81 g, 8.0 mmol) and DMAP (0.07 g, 0.6 mmol) were added **2f** (1.40 g, 4.0 mmol) in $CHCl_3$ (20 mL) and reacted for 45 min to give the title compound (1.53 g, 85%) as a colorless liquid after isolation by flash chromatography using hexanes−ethyl acetate (90:10). IR (film) 3062 (m), 2975 (s), 2956 (s), 2930 (s), 2871 (s), 2250 (w), 1971 (w), 1913 (w), 1725 (s), 1603 (m), 1586 (m), 1452 (s), 1395 (m), 1371 (m), 1342 (m), 1267 (s), 1176 (s), 1105 (s), 1070 (s), 1026 (s), 969 (m), 938 (m), 880 (m), 806 (w), 713 (s), 669 (m), 642 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.14−8.03 (m, 2H), 7.62−7.40 (m, 3H), 5.72 (t, $J = 6.5$ Hz, 1H), 4.40 (s, 1H), 3.86−3.63 (m, 8H), 1.99−1.87 (m, 2H), 1.30−1.17 (m, 20H), 0.88 (t, $J = 6.5$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 165.2, 132.9, 130.1, 129.6 (2CH), 128.2 (2CH), 103.8, 98.5, 84.4, 80.5, 64.5, 64.4 ($2CH_2$), 59.8 ($2CH_2$), 34.6, 31.5, 28.7, 24.8, 22.4, 15.2 ($2CH_3$), 15.1 ($2CH_3$), 13.9; MS (ESI) *m/z* 403 (100), 375 (30); HRMS Calcd for $C_{24}H_{35}O_5^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 403.2485, found 403.2490.

Synthesis of Propargylic Ketoesters 4 from Ketals 3; General Procedure. Ester **3** was dissolved in a mixture of acetone and water (2:1/v:v) containing some *p*-TsOH and refluxed for 3−8 h. The reaction mixture was then cooled to room temperature before DCM

(volume equal to that of the reaction mixture) and H_2O (volume equal to that of the reaction mixture) were added. The phases were separated and the aqueous layer was extracted with DCM (3 × volume of the aqueous layer). The organic phases were combined, washed with an equal volume of a saturated aqueous $NaHCO_3$ solution, and dried over $MgSO_4$ (anhd.). Filtration and concentration on a rotary evaporator *in vacuo* gave ketoester **4**, which, if not pure enough for subsequent reactions, was purified by flash chromatography.

5,5-Diethoxy-4-oxopent-2-ynyl Acetate (4a). 4,4,5,5-Tetraethoxypent-2-ynyl acetate (**3a**) (0.60 g, 2.0 mmol) and *p*-TsOH (0.038 g, 0.2 mmol) in a mixture of acetone and water (20 mL) were refluxed for 2 h and gave the title compound (0.41 g, 90%) as a colorless liquid. IR (film) 2980 (m), 2934 (m), 2888 (m), 2220 (m), 1754 (s), 1692 (s), 1560 (m), 1444 (m), 1376 (m), 1319 (w), 1221 (s), 1168 (m), 1117 (s), 1065 (s), 964 (w), 906 (w), 828 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.89 (s, 2H), 4.74 (s, 1H), 3.81−3.56 (m, 4H), 2.12 (s, 3H), 1.25 (t, J = 7.0 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 181.9, 169.5, 101.2, 88.9, 83.0, 63.0, 51.2, 20.2, 15.0, 14.8; MS (EI) *m/z* 183 (24), 156 (5), 155 (18), 141 (25), 140 (18), 125 (20), 113 (52), 104 (50), 103 (90), 83 (15), 76 (20), 75 (100), 67 (58), 66 (80); HRMS Calcd for $C_9H_{11}O_4^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 183.0657, found 183.0660.

5,5-Diethoxy-4-oxopent-2-ynyl Isobutyrate (4b). 4,4,5,5-Tetraethoxypent-2-ynyl isobutyrate (**3b**) (1.04 g, 3.1 mmol) and *p*-TsOH (0.15 g, 0.8 mmol) in a mixture of acetone and water (25 mL) were refluxed for 3 h and gave the title compound (0.99 g, 95%) as a yellowish liquid after purification by flash chromatography (hexanes−ethyl acetate, 90:10). IR (film) 2979 (s), 2937 (s), 2881 (s), 2220 (m), 1747 (s), 1697 (s), 1621 (w), 1471 (s), 1446 (m), 1428 (m), 1389 (s), 1372 (m), 1339 (s), 1246 (s), 1186 (s), 1145 (s), 1119 (s), 1069 (s), 969 (m), 909 (m), 837 (w), 815 (m), 754 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.87 (s, 2H), 4.74 (s, 1H), 3.77−3.56 (m, 4H), 2.62 (se, J = 7.0 Hz, 1H), 1.31−1.18 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.1, 175.8, 101.3, 89.3, 83.1, 63.1 ($2CH_2$), 51.3, 33.6, 18.7 ($2CH_3$), 15.0 ($2CH_3$); MS (ESI) *m/z* 256 ($M^{+\cdot}$, 6), 211 (100); HRMS Calcd for $C_{11}H_{15}O_4^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 211.0970, found 211.0954.

5,5-Diethoxy-4-oxopent-2-ynyl Benzoate (4c). 4,4,5,5-Tetraethoxypent-2-ynyl benzoate (**3c**) (1.35 g, 3.7 mmol) and *p*-TsOH (0.17 g, 0.9 mmol) in a mixture of acetone and water (25 mL) were refluxed for 4 h and gave the title compound (0.97 g, 90%) as a yellowish liquid after purification by flash chromatography (hexanes−ethyl acetate, 95:5). IR (film) 3074 (w), 2979 (s), 2954 (m), 2904 (m), 2897 (m), 2221 (m), 1730 (s), 1693 (s), 1601 (m), 1452 (s), 1425 (m), 1370 (s), 1316 (s), 1267 (s), 1177 (s), 1107 (s), 1096 (s), 1070 (s), 1027 (s), 956 (w), 902 (w), 806 (w), 712 (s), 687 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.10−8.04 (m, 2H), 7.64−7.42 (m, 3H), 5.12 (s, 2H), 4.76 (s, 1H), 3.78−3.59 (m, 4H), 1.31−1.22 (t, J = 7.0 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.1, 165.4, 133.5, 130.1, 129.8 (2CH), 128.4 (2CH), 101.4, 89.1, 83.5, 63.2 ($2CH_2$), 52.0, 15.0 ($2CH_3$); MS (ESI) *m/z* 291 (28), 245 (100); HRMS Calcd for $C_{16}H_{19}O_5^+$ [M + H]$^+$ 291.1232, found 291.1241.

5,5-Diethoxyl-1-methyl-4-oxopent-2-ynyl Acetate (4d). 4,4,5,5-Tetraethoxy-1-methylpent-3-ynyl acetate (**3d**) (0.63 g, 2.0 mmol) and *p*-TsOH (0.038 g, 0.2 mmol) in a mixture of acetone and water (20 mL) were refluxed for 2 h and gave the title compound (0.44 g, 91%) as a colorless liquid. IR (film) 2980 (s), 2937 (m), 2898 (m), 2222 (m), 1758 (s), 1693 (s), 1619 (m), 1447 (m), 1372 (s), 1336 (m), 1300 (m), 1229 (s), 1194 (s), 1167 (s), 1135 (s), 1106 (s), 1071 (s), 1042 (s), 962 (m), 906 (m), 828 (w), 757 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.59 (q, J = 6.9 Hz, 1H), 4.75 (s, 1H), 3.77−3.55 (m, 4H), 2.11 (s, 3H), 1.57 (d, J = 6.9 Hz, 3H), 1.30−1.24 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.2, 169.3, 101.2, 92.8, 81.4, 62.9, 59.4, 20.6, 20.1, 14.9; MS (EI) *m/z* 242 (M^+, 5), 197 (50), 183 (10), 171 (60), 155 (100), 139 (75), 127 (90), 75 (50); HRMS Calcd for $C_{12}H_{18}O_5^+$ [M^+] 242.1154, found 242.1151.

5,5-Diethoxy1−1-methyl-4-oxopent-2-ynyl Isobutyrate (4e). 4,4,5,5-Tetraethoxy-1-methylpent-3-ynyl isobutyrate (**3e**) (0.69 g, 2.0 mmol) and *p*-TsOH (0.038 g, 0.2 mmol) in a mixture of acetone and water (20 mL) were refluxed for 2 h and gave the title compound (0.48 g, 88%) as a yellowish liquid. IR (film) 2979 (s), 2938 (m), 2880 (m), 2222 (m), 1742 (s), 1697 (s), 1471 (m), 1447 (m), 1388 (m), 1373 (m), 1331 (m), 1300 (m), 1244 (s), 1187 (s), 1151 (s), 1134 (s), 1106 (s), 1067 (s), 956 (w), 910 (w), 846 (w), 822 (w), 753 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.61 (q, J = 6.8 Hz, 1H), 4.75 (s, 1H), 3.73−3.59 (m, 4H), 2.57 (septet, J = 7.0 Hz, 1H), 1.56 (d, J = 6.8 Hz, 3H), 1.26 (t, J = 7.0 Hz, 6H), 1.18 (d, J = 7.0 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.3, 175.4, 101.2, 93.1, 81.3, 62.9, 59.2, 33.6, 20.1, 18.7, 14.9; MS (EI) *m/z* 270 (M^+, 10), 225 (70), 199 (40), 183 (55), 167 (30), 155 (30), 103 (100); HRMS Calcd for $C_{14}H_{22}O_5^+$ [M^+] 270.14672, found 270.14659.

5,5-Diethoxy1−1-methyl-4-oxopent-2-ynyl Benzoate (4f). 4,4,5,5-Tetraethoxy-1-methylpent-3-ynyl benzoate (**3f**) (0.70 g, 1.8 mmol) and *p*-TsOH (0.10 g, 0.5 mmol) in a mixture of acetone and water (20 mL) were refluxed for 3 h and gave the title compound (0.51 g, 91%) as a yellowish liquid after purification by flash chromatography (hexanes−ethyl acetate, 90:10). IR (film) 3064 (m), 3034 (m), 2979 (s), 2936 (s), 2896 (s), 2223 (s), 1970 (w), 1913 (w), 1727 (s), 1694 (s), 1602 (m), 1585 (m), 1492 (m), 1480 (m), 1452 (s), 1393 (m), 1337 (s), 1315 (s), 1304 (s), 1265 (s), 1176 (s), 1135 (s), 1106 (s), 1097 (s), 1070 (s), 1026 (s), 948 (m), 907 (m), 866 (m), 850 (m), 805 (m), 713 (s), 688 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.09−8.03 (m, 2H), 7.63−7.42 (m, 3H), 5.86 (q, J = 6.8 Hz, 1H), 4.76 (s, 1H), 3.79−3.54 (m, 4H), 1.70 (d, J = 6.8 Hz, 3H), 1.25 (t, J = 7.0 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.4, 165.0, 133.3, 129.7 (2CH), 129.2, 128.3 (2CH), 101.2, 93.0, 81.7, 63.0 ($2CH_2$), 60.1, 20.3, 14.9 ($2CH_3$); MS (ESI) *m/z* 305 (100), 259 (84); HRMS Calcd for $C_{17}H_{21}O_5$ [M + H]$^+$ 305.1389, found 305.1390.

5,5-Diethoxy-1-isopropyl-4-oxopent-2-ynyl Acetate (4g). 4,4,5,5-Tetraethoxy-1-isopropylpent-2-ynyl acetate (**3g**) (1.17 g, 3.4 mmol) and *p*-TsOH (0.15 g, 0.8 mmol) in a mixture of acetone and water (25 mL) were refluxed for 3 h and gave the title compound (0.87 g, 95%) as a yellowish liquid after purification by flash chromatography (hexanes−ethyl acetate, 90:10). IR (film) 2976 (s), 2933 (s), 2879 (s), 2217 (m), 1747 (s), 1694 (s), 1618 (w), 1467 (m), 1447 (m), 1373 (s), 1326 (m), 1228 (s), 1112 (s), 1070 (s), 1025 (s), 991 (m), 903 (m), 720 (m), 602 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.37 (d, J = 5.8 Hz, 1H), 4.75 (s, 1H), 3.76−3.55 (m, 4H), 2.16−2.02 (m, 1H), 2.11 (s, 3H), 1.26 (t, J = 7.0 Hz, 6H), 1.08−0.97 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 188.4, 169.5, 101.3, 91.7, 82.8, 68.2, 62.9 ($2CH_2$), 32.2, 20.6, 18.0, 17.4, 15.0 ($2CH_3$); MS (EI) *m/z* 225 (3), 183 (13), 182 (17), 167 (10), 141 (9), 140 (90), 139 (25), 137 (20), 125 (12), 112 (20), 107 (31), 104 (64), 103 (75), 47 (85), 43 (100); HRMS Calcd for $C_{12}H_{17}O_4^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 225.1127, found 225.1120.

5,5-Diethoxy-1-isopropyl-4-oxopent-2-ynyl Isobutyrate (4h). 4,4,5,5-Tetraethoxy-1-isopropylpent-2-ynyl isobutyrate (**3h**) (1.46 g, 3.9 mmol) and *p*-TsOH (0.19 g, 1.0 mmol) in a mixture of acetone and water (25 mL) were refluxed for 3 h and gave the title compound (1.07 g, 92%) as a yellowish liquid after purification by flash chromatography (hexanes−ethyl acetate, 90:10). IR (film) 2976 (s), 2935 (s), 2899 (s), 2878 (s), 2218 (s), 1744 (s), 1693 (s), 1618 (w), 1470 (s), 1389 (s), 1371 (s), 1350 (m), 1322 (m), 1297 (m), 1244 (s), 1186 (s), 1151 (s), 1112 (s), 1066 (s), 993 (s), 962 (m), 930 (m), 911 (m), 839 (w), 800 (w), 752 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.38 (d, J = 5.8 Hz, 1H), 4.75 (s, 1H), 3.79−3.55 (m, 4H), 2.60 (septet, J = 6.6 Hz, 1H), 2.19−1.95 (m, 1H), 1.35−1.18 (m, 12H), 1.08−1.03 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.4, 175.5, 101.2, 91.9, 82.6, 67.9, 62.8 ($2CH_2$), 33.8, 32.3, 18.8, 18.6, 18.0, 17.5, 15.0 ($2CH_3$); MS (ESI) *m/z* 299 (93), 283 (20), 271 (25), 253 (100), 225 (10), 211 (5), 183 (5); HRMS Calcd for $C_{16}H_{27}O_5^+$ [M + H]$^+$ 299.1858, found 299.1856.

5,5-Diethoxy-1-isopropyl-4-oxopent-2-ynyl Benzoate (4i). 4,4,5,5-Tetraethoxy-1-isopropylpent-2-ynyl benzoate (**3i**) (1.70 g, 4.2 mmol) and *p*-TsOH (0.19 g, 1.0 mmol) in a mixture of acetone and water (25 mL) were refluxed for 5 h and gave the title compound (1.28 g, 92%) as a yellowish liquid after purification by flash chromatography (hexanes−ethyl acetate, 95:5). IR (film) 3062 (w), 2976 (s), 2932 (s), 2898 (m), 2878 (s), 2217 (m), 1727 (s), 1693 (s), 1602 (m), 1586 (w), 1452 (s), 1371 (m), 1333 (m), 1315 (s), 1274 (s), 1261 (s), 1177 (s), 1163 (s), 1106 (s), 1095 (s), 1069 (s), 1026 (s), 984 (s), 911 (w), 843 (w), 806 (w), 712 (s) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.10−8.05 (m, 2H), 7.64−7.42 (m, 3H), 5.63 (d, J = 5.7 Hz, 1H), 4.76 (s, 1H), 3.79−3.54 (m, 4H), 2.34−2.18 (m, 1H), 1.28−1.02 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.4, 165.1, 133.3, 129.7 (2CH), 129.3, 128.4 (2CH), 101.2, 91.7, 83.0, 68.7, 62.9 ($2CH_2$), 32.5, 18.1, 17.6, 15.0 ($2CH_3$); MS (ESI) *m/z* 333 (100), 305 (12), 287 (65), 259 (50); HRMS Calcd for $C_{19}H_{25}O_5^+$ $[M + H]^+$ 333.1702, found 333.1689.

1-(t-Butyl)-5,5-diethoxy-4-oxopent-2-ynyl Acetate (4j). 1-(*t*-Butyl)-4,4,5,5-tetraethoxypent-2-ynyl acetate (**3j**) (0.72 g, 2.0 mmol) and *p*-TsOH (0.038 g, 0.2 mmol) in a mixture of acetone and water (20 mL) were refluxed for 5 h and gave the title compound (0.51 g, 89%) as a yellowish liquid. IR (film) 2976 (s), 2935 (m), 2904 (m), 2875 (m), 2216 (m), 1746 (s), 1694 (s), 1481 (w), 1445 (w), 1445 (w), 1398 (w), 1371 (s), 1332 (w), 1233 (s), 1223 (s), 1166 (m), 1118 (s), 1067 (s), 1020 (s), 985 (m), 910 (w), 840 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.28 (s, 1H), 4.75 (s, 1H), 3.76−3.38 (m, 4H), 2.12 (s, 3H), 1.25 (t, J = 7.1 Hz, 6H), 1.05 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.4, 169.7, 101.2, 92.0, 82.6, 71.0, 62.7, 35.4, 25.4, 20.5, 14.9; MS (EI) *m/z* 239 (10), 228 (15), 223 (20), 211 (20), 197 (30), 182 (60), 168 (50), 153 (60), 140 (80), 139 (60), 125 (55), 121 (55), 112 (75), 111 (100), 103 (95), 95 (60), 89 (50), 83 (75), 75 (90), 67 (60); HRMS Calcd for $C_{13}H_{19}O_4$ $[M^{+\cdot} - EtO^{\cdot}]$ 239.1283 found, 239.1283.

1-(t-Butyl)-5,5-diethoxy-4-oxopent-2-ynyl Isobutyrate (4k). 1-(*t*-Butyl)-4,4,5,5-tetraethoxypent-2-ynyl isobutyrate (**3k**) (0.77 g, 2.0 mmol) and *p*-TsOH (0.038 g, 0.2 mmol) in a mixture of acetone and water (20 mL) were refluxed for 6 h and gave the title compound (0.55 g, 88%) as a yellowish liquid. IR (film) 2976 (m), 2936 (m), 2877 (m), 2216 (m), 1743 (s), 1694 (s), 1480 (m), 1470 (m), 1448 (m), 1418 (w), 1397 (w), 1369 (m), 1327 (m), 1241 (m), 1185 (s) 1147 (s), 1116 (s), 1065 (s), 983 (m), 937 (w), 919 (m), 838 (w), 752 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.28 (s, 1H), 4.74 (s, 1H), 3.70−3.58 (m, 4H), 2.62 (septet, J = 6.9 Hz, 1H), 1.23 (d, J = 6.9 Hz, 6H), 1.21 (t, J = 7.0 Hz, 3H), 1.19 (t, J = 7.0 Hz, 3H), 1.06 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.5, 175.5, 101.2, 92.2, 82.6, 70.7, 62.7, 35.6, 33.9, 25.5, 18.9, 18.6, 15.0; MS (ESI) *m/z* 312 (M^+, 90), 267 (75), 209 (25), 179 (15); HRMS Calcd for $C_{15}H_{23}O_4^+$ $[M^{+\cdot} - EtO^{\cdot}]$ 267.15963, found 267.16214.

1-(t-Butyl)-5,5-diethoxy-4-oxopent-2-ynyl Benzoate (4l). 1-(*t*-Butyl)-4,4,5,5-tetraethoxypent-2-ynyl benzoate (**3l**) (0.84 g, 2.0 mmol) and *p*-TsOH (0.038 g, 0.2 mmol) in a mixture of acetone and water (20 mL) was refluxed for 8 h and gave the title compound (0.59 g, 85%) as a yellowish liquid. IR (film) 3066 (w), 3034 (w), 2975 (s), 2934 (m), 2875 (m), 2899 (m), 2217 (m), 1727 (s), 1694 (s), 1601 (w), 1585 (w), 1480 (w), 1452 (m), 1397 (m), 1369 (m), 1335 (m), 1315 (m), 1303 (m), 1264 (s), 1176 (m), 1097 (s), 1069 (s), 1026 (m), 970 (m), 937 (w), 907 (w), 838 (w), 767 (w), 713 (s), 687 (w), 672 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.09 (t, J = 1.5 Hz, 1H), 8.05 (d, J = 1.5 Hz, 1H), 7.64−7.42 (m, 3H), 5.54 (s, 1H), 4.75 (s, 1H), 3.78−3.53 (m, 4H), 1.23 (t, J = 7.0 Hz, 3H), 1.22 (t, J = 7.0 Hz, 3H), 1.16 (s, 9H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.4, 165.1, 133.3, 129.7, 129.3, 128.4, 101.2, 91.9, 82.9, 71.6, 64.1, 35.9, 25.6, 15.1; MS (EI) *m/z* 347 (85), 301 (50), 273 (50), 225 (25), 179 (10) 103 (5); HRMS Calcd for $C_{20}H_{27}O_5^+$ $[M + H]^+$ 347.18585, found 347.18245.

5,5-Diethoxy-4-oxo-1-phenylpent-2-ynyl Acetate (4m). 4,4,5,5-Tetraethoxy-1-phenylpent-2-ynyl acetate (**3m**) (1.10 g, 2.91 mmol) and *p*-TsOH (0.13 g, 0.7 mmol) in a mixture of acetone and water (20 mL) were refluxed for 3 h and gave the title compound (0.83 g, 94%) as a yellowish liquid after purification by flash chromatography (hexanes−ethyl acetate, 90:10). IR (film) 3064 (w), 2979 (s), 2933 (s), 2890 (s), 2219 (s), 1961 (w), 1898 (w), 1746 (s), 1694 (s), 1601 (m), 1492 (m), 1372 (s), 1319 (m), 1222 (s), 1113 (s), 1071 (s), 1023 (s), 962 (m), 906 (m), 835 (m), 757 (m), 700 (m), 648 (w), 603 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.56−7.36 (m, 5H), 6.62 (s, 1H), 4.77 (s, 1H), 3.80−3.54 (m, 4H), 2.13 (s, 3H), 1.26 (t, J = 7.0 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.2, 169.2, 134.8, 129.2, 128.6 (2CH), 127.6 (2CH), 101.1, 90.7, 83.2, 64.7, 62.9 ($2CH_2$), 20.6, 14.8 ($2CH_3$); MS (EI) *m/z* 304 (M^+, 1), 291 (24), 275 (25), 217 (25), 216 (100), 187 (14), 160 (15), 143 (13), 131 (12), 115 (47), 103 (86), 75 (39); HRMS Calcd for $C_{17}H_{20}O_5^+$ $[M^+]$ 304.1311, found 304.1291.

5,5-Diethoxy-4-oxo-1-phenylpent-2-ynyl Isobutyrate (4n). 4,4,5,5-Tetraethoxy-1-phenylpent-2-ynyl isobutyrate (**3n**) (1.15 g, 2.8 mmol) and *p*-TsOH (0.13 g, 0.7 mmol) in a mixture of acetone and water (20 mL) were refluxed for 3 h and gave the title compound (0.92 g, 98%) as a yellowish liquid. IR (film) 3066 (w), 3035 (w), 2978 (s), 2934 (s), 2879 (s), 2220 (m), 1744 (s), 1695 (s), 1603 (w), 1496 (m), 1470 (m), 1456 (s), 1388 (m), 1370 (m), 1352 (m), 1272 (m), 1240 (s), 1184 (s), 1142 (s), 1112 (s), 1066 (s), 953 (m), 909 (m), 877 (w), 842 (w), 811 (w), 758 (m), 698 (s), 665 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.54−7.26 (m, 5H), 6.62 (s, 1H), 4.77 (s, 1H), 3.79−3.55 (m, 4H), 2.62 (septet, J = 7.0 Hz, 1H), 1.30−1.13 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.3, 175.3, 135.2, 129.2, 128.7 (2CH), 127.4 (2CH), 101.2, 91.1, 83.3, 64.6, 62.9 ($2CH_2$), 33.7, 18.6 ($2CH_3$), 14.9 ($2CH_3$); MS (ESI) *m/z* 333 (100), 305 (20), 287 (12), 263 (15), 245 (40), 217 (9); HRMS Calcd for $C_{19}H_{25}O_5^+$ $[M + H]^+$ 333.1702, found 333.1709.

5,5-Diethoxy-1-phenyl-4-oxopent-2-ynyl Benzoate (4o). 4,4,5,5-Tetraethoxy-1-phenylpent-2-ynyl benzoate (**3o**) (1.60 g, 3.6 mmol) and *p*-TsOH (0.15 g, 0.8 mmol) in a mixture of acetone and water (25 mL) were refluxed for 3 h and gave the title compound (1.23 g, 95%) as a yellowish liquid after purification by flash chromatography (hexanes−ethyl acetate, 95:5). IR (film) 3063 (m), 3033 (m), 2980 (s), 2932 (s), 2897 (s), 2220 (s), 1727 (s), 1693 (s), 1601 (m), 1585 (m), 1495 (m), 1452 (s), 1392 (m), 1316 (s), 1250 (s), 1176 (s), 1091 (s), 1068 (s), 916 (m), 838 (w), 803 (w), 760 (m), 712 (s), 698 (s), 665 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.10−8.05 (m, 2H), 7.64−7.26 (m, 8H), 6.87 (s, 1H), 4.78 (s, 1H), 3.75−3.58 (m, 4H), 1.27−1.17 (m, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.3, 164.9, 135.1, 133.4, 129.8 (2CH), 129.3, 129.0, 128.8 (2CH), 128.4 (2CH), 127.7 (2CH), 101.3, 90.9, 83.6, 65.4, 63.0 ($2CH_2$), 14.9 ($2CH_3$); MS (ESI) *m/z* 367 (100), 321 (8), 245 (25); HRMS Calcd for $C_{22}H_{23}O_5^+$ $[M + H]^+$ 367.1545, found 367.1556.

5,5-Diethoxy-1-hexyl-4-oxopent-2-ynyl acetate (4p). 4,4,5,5-Tetraethoxy-1-hexylpent-2-ynyl acetate (**3p**) (0.77 g, 2.0 mmol) and *p*-TsOH (0.038 g, 0.2 mmol) in a mixture of acetone and water (20 mL) was refluxed for 3 h and gave the title compound (0.57 g, 92%) as a yellowish liquid. IR (film) 2975 (m), 2938 (m), 2907 (m), 2875 (m), 2217 (m), 1746 (s), 1698 (s), 1481 (m), 1466 (w), 1446 (w), 1398 (w), 1372 (s), 1332 (m), 1299 (m), 1234 (s), 1117 (s), 1067 (s), 1022 (s), 986 (m), 910 (w), 837 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.50 (t, J = 6.9 Hz, 1H), 4.73 (s, 1H), 3.78−3.54 (m, 4H), 2.08 (s, 3H), 1.88−1.21 (m, 22H), 0.88 (t, J = 6.6 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.4, 170.5, 102.2, 93.7, 89.8, 64.3, 64.0, 34.7, 32.4, 29.5, 25.6, 23.3, 21.6, 15.8, 14.8; MS (EI) *m/z* 267 (5), 253 (10), 225 (25), 209 (25), 197 (15), 179 (20), 149 (30), 135 (20), 125 (30), 122 (40), 112 (30), 103 (100), 95 (40), 93 (40), 81 (75), 75 (95), 67 (60), 61 (40), 55 (70); HRMS Calcd for $C_{15}H_{23}O_4$ $[M^{+\cdot} - EtO^{\cdot}]$ 267.1596, found 267.1592.

5,5-Diethoxy-1-hexyl-4-oxopent-2-ynyl Isobutyrate (4q). 4,4,5,5-Tetraethoxy-1-hexyl-pent-2-ynyl isobutyrate (**3q**) (0.83 g, 2.0 mmol) and *p*-TsOH (0.038 g, 0.2 mmol) in a mixture of acetone and water (20 mL) were refluxed for 6 h and gave the title compound (0.61 g, 90%) as a yellowish liquid. IR (film) 2977 (s), 2957 (s), 2932 (m), 2874 (m), 2862 (m), 2218 (m), 1744 (s), 1696 (s), 1469 (m),

1388 (m), 1372 (m), 1337 (m), 1296 (w), 1243 (m), 1186 (s) 1149 (s), 1113 (s), 1065 (s), 985 (m), 916 (w), 842 (w), 752 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.52 (t, $J = 6.8$ Hz, 1H), 4.74 (s, 1H), 3.80−3.55 (m, 4H), 2.58 (septet, $J = 6.8$ Hz, 1H), 1.90−1.17 (m, 17H), 0.89 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 181.7, 174.9, 100.6, 92.2, 81.4, 62.3, 62.2, 33.2, 33.1, 30.8, 27.9, 24.0, 21.7, 18.1, 17.9, 14.3, 13.2; MS (ESI) *m/z* 340 ($M^{+\cdot}$, 90), 295 (100), 267 (85), 253 (55), 225 (15); HRMS Calcd for $C_{17}H_{27}O_4^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 295.19093, found 295.19072.

5,5-Diethoxy-1-hexyl-4-oxopent-2-ynyl Benzoate (4r). 4,4,5,5-Tetraethoxy-1-hexyl-pent-2-ynyl benzoate (**3r**) (1.55 g, 3.5 mmol) and *p*-TsOH (0.15 g, 0.8 mmol) in a mixture of acetone and water (25 mL) were refluxed for 4 h and gave the title compound (1.17 g, 91%) as a yellowish liquid after purification by flash chromatography (hexanes−ethyl acetate, 90:10). IR (film) 3063 (m), 2977 (s), 2955 (s), 2930 (s), 2860 (s), 2218 (s), 1970 (w), 1919 (w), 1727 (s), 1694 (s), 1602 (m), 1587 (m), 1452 (s), 1372 (m), 1340 (s), 1316 (s), 1265 (s), 1177 (s), 1105 (s), 1095 (s), 1069 (s), 1026 (s), 1002 (m), 976 (m), 909 (m), 842 (w), 805 (w), 713 (s), 687 (m), 671 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.08−8.04 (m, 2H), 7.64−7.42 (m, 3H), 5.78 (t, $J = 6.6$ Hz, 1H), 4.75 (s, 1H), 3.79−3.54 (m, 4H), 2.04−1.93 (m, 2H), 1.37−1.14 (m, 14H), 0.88 (t, $J = 6.4$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.4, 165.1, 133.3, 129.7 (2CH), 129.3, 128.3 (2CH), 101.2, 92.6, 82.4, 63.8, 62.9 ($2CH_2$), 34.0, 31.4, 28.6, 24.8, 22.4, 14.9 ($2CH_3$), 13.9; MS (ESI) *m/z* 375 (100), 347 (15), 329 (92), 301 (35), 279 (19), 253 (25), 225 (13); HRMS Calcd for $C_{22}H_{31}O_5^+$ [M + H]$^+$ 375.2171, found 375.2172.

Synthesis of Furans 5 from Ketoesters 4; General Procedure. CuI (0.19 g, 1.0 mmol) [CuCN (0.090 g, 1.0 mmol) when the higher-order cyanocuprate $Me_2Cu(CN)Li_2$ was made[14]] was dispersed in dried THF (10 mL) [distilled from sodium-benzophenone ketyl prior to use] and cooled to −30 °C. MeLi (1.25 mL, 1.6 M, 2.0 mmol) was added dropwise during 15 min (BuLi and Bu^{t}Li were used instead of MeLi in syntheses of **6** and **7** respectively). When the addition was complete the reaction mixture was allowed to stir at −30 °C for 30 min before it was cooled to either −78 or −60 °C or heated to 0 °C or room temperature (see Table 2 and subsequent descriptions). Ketoester **4** (1.0 mmol), dissolved in dried THF (2 mL), was then added dropwise during 15 min at the selected temperature, and the resulting mixture was stirred for an additional 60 min at the same temperature before a saturated aqueous solution of NH_4Cl (10 mL) was added in one portion, also at the same temperature. The hydrolysate was allowed to reach room temperature, the phases were separated, and the water phase was extracted with diethyl ether (3 × 10 mL). The combined organic extracts were washed with an equal volume of a saturated aqueous NaCl solution, dried over $MgSO_4$ (anhd.), and then concentrated under vacuum on a rotary evaporator to give a crude product, which was purified by flash chromatography.

2,2-Diethoxy-1-(2,4-dimethylfuran-3-yl)ethanone (5a). 5,5-Diethoxy-4-oxopent-2-ynyl acetate (**4a**) (0.23 g) was reacted at −60 °C and gave the title compound (0.11 g, 50%) as a colorless liquid after purification by flash chromatograph using hexanes−ethyl acetate (97.5:2.5). IR (film) 2978 (s), 2931 (s), 2875 (m), 1665 (s), 1617 (m), 1594 (m), 1551 (m), 1457 (m), 1445 (w), 1405 (m), 1386 (w), 1368 (m), 1311 (m), 1282 (m), 1232 (s), 1188 (m), 1101 (s), 1055 (s), 1017 (s), 965 (m), 941 (w), 837 (w), 709 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.02 (s, 1H), 5.06 (s, 1H), 3.75−3.53 (m, 4H), 2.58 (s, 3H), 2.18 (s, 3H), 1.24 (t, $J = 7.0$ Hz, 3H), 1.23 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 192.4, 160.8, 137.8, 121.1, 119.4, 101.3, 62.4 ($2CH_2$), 29.6, 15.5, 15.0, 10.4; MS (EI) *m/z* 226 (M^+, 3), 181 (20), 153 (30), 131 (5), 123 (80), 103 (95), 95 (5), 75 (90), 65 (30), 47 (100); HRMS Calcd for $C_{12}H_{18}O_4^+$ [M^+] 226.1205, found 226.1196.

2,2-Diethoxy-1-(2-isopropyl-4-methylfuran-3-yl)ethanone (5b). 5,5-Diethoxy-4-oxopent-2-ynyl isobutyrate (**4b**) (0.25 g) was reacted at −60 °C and gave the title compound (0.11 g, 45%) as a colorless liquid after purification by flash chromatograph using hexanes−ethyl acetate (97.5:2.5). IR (film) 2975 (s), 2930 (s), 2874 (m), 1680 (s), 1662 (s), 1555 (m), 1467 (m), 1458 (m), 1448 (m), 1409 (m), 1374 (m), 1289 (m), 1264 (w), 1186 (m), 1137 (m), 1114 (m), 1067 (s), 966 (w), 927 (m), 913 (m), 892 (w), 833 (w), 733 (w), 683 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.04 (s, 1H), 5.07 (s, 1H), 3.71−3.60 (m, 5H), 2.16 (s, 3H), 1.26 (t, $J = 7.0$ Hz, 3H), 1.25 (d, $J = 6.8$ Hz, 6H), 1.24 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 191.9, 168.6, 138.0, 120.1, 117.6, 101.4, 62.5 ($2CH_2$), 28.0, 20.8 (2 CH_3), 15.2 (2 CH_3), 10.6; MS (ESI) *m/z* 255 (40), 216 (8), 169 (13), 139 (22), 117 (75), 85 (9), 59 (100); HRMS Calcd for $C_{14}H_{23}O_4^+$ [M + H]$^+$ 255.15885, found 255.15963.

2,2-Diethoxy-1-(4-methyl-2-phenylfuran-3-yl)ethanone (5c). 5,5-Diethoxy-4-oxopent-2-ynyl benzoate (**4c**) (0.29 g) was reacted at −60 °C and gave the title compound (0.11 g, 40%) as a colorless liquid after purification by flash chromatography (hexanes−ethyl acetate, 97.5:2.5). IR (film) 3062 (m), 3039 (m), 2977 (s), 2930 (s), 2896 (s), 1775 (s), 1686 (s), 1595 (m), 1547 (m), 1485 (s), 1446 (s), 1372 (s), 1339 (m), 1269 (s), 1177 (s), 1159 (s), 1118 (s), 1067 (s), 966 (m), 917 (m), 839 (m), 771 (s), 698 (s), 600 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.58−7.53 (m, 2H), 7.46−7.41 (m, 3H), 7.27 (s, 1H), 4.97 (s, 1H), 3.59−3.31 (m, 4H), 2.16 (s, 3H), 1,12 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 193.8, 156.8, 139.4, 130.7, 129.2, 128.4 (2CH), 128.0 (2CH), 122.1, 121.0, 99.2, 62.0 ($2CH_2$), 14.9 ($2CH_3$), 9.3; MS (ESI) *m/z* 289 (33), 243 (100), 197 (30), 117 (38); HRMS Calcd for $C_{17}H_{21}O_4^+$ [M + H]$^+$ 289.1440, found 289.1436.

2,2-Diethoxy-1-(2,4,5-trimethylfuran-3-yl)ethanone (5d). 5,5-Diethoxy1−1-methyl-4-oxopent-2-ynyl acetate (**4d**) (0.24 g) was reacted at −60 °C and gave the title compound (0.12 g, 48%) as a colorless liquid after purification by flash chromatograph using hexanes−ethyl acetate (97.5:2.5). IR (film) 2976 (s), 2929 (s), 2873 (m), 1664 (s), 1612 (m), 1594 (w), 1454 (w), 1444 (w), 1405 (m), 1386 (w), 1371 (w), 1368 (m), 1280 (m), 1232 (s), 1188 (m), 1174 (s), 1099 (s), 1017 (s), 965 (m), 944 (w), 837 (w), 709 (m), 703 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.04 (s, 1H), 3.72−3.54 (m, 4H), 2.58 (s, 3H), 2.22 (s, 3H), 2.18 (s, 3H), 1.23 (t, $J = 7.0$ Hz, 3H), 1.22 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 192.1, 160.6, 137.8, 121.0, 118.2, 101.2, 62.4 ($2CH_2$), 15.5 ($2CH_3$), 10.7, 10.4, 10.2; MS (ESI) *m/z* 241 (10), 240 (M^+, 5), 195 (70), 103 (100); HRMS Calcd for $C_{13}H_{20}O_4^+$ [M^+] 240.13616, found 240.13583.

2,2-Diethoxy-1-(2-isopropyl-4,5-dimethylfuran-3-yl)ethanone (5e). 5,5-Diethoxy1−1-methyl-4-oxopent-2-ynyl isobutyrate (**4e**) (0.27 g) was reacted at −60 °C and gave the title compound (0.13 g, 50%) as a colorless liquid after purification by flash chromatograph using hexanes-ethyl acetate (97.5:2.5). IR (film) 2975 (s), 2930 (s), 2874 (m), 1681 (s), 1662 (s), 1555 (s), 1467 (m), 1448 (m), 1409 (m), 1389 (m), 1374 (m), 1322 (m), 1289 (m), 1264 (w), 1188 (m), 1114 (m), 1068 (s), 1014 (m), 966 (m), 948 (w), 912 (m), 833 (w), 732 (w), 683 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.07 (s, 1H), 3.71−3.60 (m, 5H), 2.17 (s, 3H), 2.07 (s, 3H), 1.25 (d, $J = 6.8$ Hz, 6H), 1.24 (t, $J = 7.0$ Hz, 3H), 1.23 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 191.9, 165.7, 145.8, 118.2, 113.8, 101.1, 62.1 ($2CH_2$), 27.9, 20.9 ($2CH_3$), 15.0 ($2CH_3$), 10.8, 10.2; MS (EI) *m/z* 268 (M^+, 20), 223 (50), 165 (20), 131 (30), 103 (100) 75 (60); HRMS Calcd for $C_{15}H_{24}O_4^+$ [M^+] 268.16745, found 268.16740.

2,2-Diethoxy-1-(4,5-dimethyl-2-phenylfuran-3-yl)ethanone (5f). 5,5-Diethoxy1−1-methyl-4-oxopent-2-ynyl benzoate (**4f**) (0.30 g) was reacted at −60 °C and gave the title compound (0.16 g, 53%) as a colorless liquid after purification by flash chromatography (hexanes−ethyl acetate, 95:5). IR (film) 3059 (m), 3032 (m), 2976 (s), 2926 (s), 2898 (s), 2359 (w), 2338 (w), 1960 (w), 1893 (w), 1686 (s), 1633 (m), 1604 (m), 1556 (s), 1487 (s), 1446 (s), 1389 (s), 1370 (s), 1304 (s), 1285 (m), 1247 (w), 1096 (s), 1073 (s), 969 (s), 921 (s), 840 (s), 769 (s), 698 (s), 656 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.55−7.36 (m, 5H), 4.96 (s, 1H), 3.61−3.27 (m, 4H), 2.27 (s, 3H), 2.07 (s, 3H), 1.12 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 194.0, 154.3, 148.1, 130.8, 128.9, 128.4 (2CH),

127.8 (2CH), 125.1, 116.0, 99.0, 61.9 ($2CH_2$), 15.0 ($2CH_3$), 11.1, 9.2; MS (ESI) *m/z* 303 (100), 257 (35); HRMS Calcd for $C_{18}H_{23}O_4^+$ $[M + H]^+$ 303.1596, found 303.1601.

2,2-Diethoxy-1-(5-isopropyl-2,4-dimethylfuran-3-yl)ethanone (5 g). 5,5-Diethoxy-1-isopropyl-4-oxopent-2-ynyl acetate (**4g**) (0.27 g) was reacted at −60 °C and gave the title compound (0.21 g, 81% when Me_2CuLi was used; 0.19 g, 74% when $Me_2Cu(CN)Li_2$ was applied) as a colorless liquid after purification by flash chromatography (hexanes−ethyl acetate, 90:10). IR (film) 2973 (s), 2930 (s), 2874 (s), 1681 (s), 1663 (s), 1561 (m), 1447 (m), 1411 (m), 1380 (m), 1266 (m), 1124 (m), 1057 (s), 950 (w), 885 (w), 800 (w), 670 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.06 (s, 1H), 3.77−3.54 (m, 4H), 2.97 (septet, $J = 7.0$ Hz, 1H), 2.55 (s, 3H), 2.10 (s, 3H), 1.28−1.18 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 192.0, 154.2, 152.9, 120.0, 112.7, 101.3, 62.3 ($2CH_2$), 25.3, 21.1 ($2CH_3$), 15.4, 15.0 ($2CH_3$), 9.9; MS (EI) *m/z* 268 (M^+,1), 195 (5), 165 (19), 103 (100), 75 (82); HRMS Calcd for $C_{15}H_{24}O_4^+$ $[M^+]$ 268.1675, found 268.1684.

2,2-Diethoxy-1-(2,5-diisopropyl-4-methylfuran-3-yl)ethanone (5 h). 5,5-Diethoxy-1-isopropyl-4-oxopent-2-ynyl isobutyrate (**4h**) (0.30 g) was reacted at −60 °C and gave the title compound (0.22 g, 75%) as a colorless liquid after purification by flash chromatography (hexanes−ethyl acetate, 95:5). IR (film) 2971 (s), 2932 (s), 2874 (s), 2756 (m), 2618 (w), 2360 (m), 1732 (m), 1681 (s), 1660 (s), 1619 (m), 1556 (s), 1468 (s), 1409 (m), 1377 (s), 1364 (m), 1322 (s), 1267 (s), 1157 (s), 1122 (s), 1073 (s), 1013 (s), 955 (m), 912 (m), 892 (m), 832 (m), 793 (m), 765 (m), 730 (m), 701 (m), 679 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.07 (s, 1H), 3.72−3.54 (m, 5H), 2.98 (septet, $J = 7.0$ Hz, 1H), 2.09 (s, 3H), 1.27−1.19 (m, 18H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 192.0, 165.3, 153.8, 118.1, 111.8, 101.2, 62.2 ($2CH_2$), 28.0, 25.5, 21.0 ($2CH_3$), 20.8 ($2CH_3$), 15.0 ($2CH_3$), 9.9; MS (ESI) *m/z* 297 (100), 223 (10), 119 (5); HRMS Calcd for $C_{17}H_{29}O_4^+$ $[M + H]^+$ 297.2066, found 297.2075.

2,2-Diethoxy-1-(5-isopropyl-4-methyl-2-phenylfuran-3-yl)-ethanone (5i). 5,5-Diethoxy-1-isopropyl-4-oxopent-2-ynyl benzoate (**4i**) (0.33 g) was reacted at −60 °C and gave the title compound (0.15 g, 47%) as a colorless liquid after purification by flash chromatography (hexanes−ethyl acetate, 95:5). IR (film) 3062 (m), 3030 (m), 2972 (s), 2930 (s), 2899 (s), 2873 (s), 1960 (w), 1815 (w), 1686 (s), 1603 (m), 1556 (m), 1485 (s), 1459 (m), 1446 (m), 1381 (m), 1371 (m), 1315 (w), 1295 (m), 1265 (m), 1161 (m), 1119 (s), 1073 (s), 1058 (s), 1051 (s), 1007 (m), 960 (m), 922 (m), 909 (m), 840 (m), 832 (m), 769 (s), 698 (s), 669 (w), 647 (w), 625 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.55−7.33 (m, 5H), 4.97 (s, 1H), 3.63−3.29 (m, 4H), 3.13−2.99 (m, 1H), 2.08 (s, 3H), 1.28 (d, $J = 7.0$ Hz, 6H), 1.12 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 194.1, 156.1, 153.7, 130.9, 128.8, 128.3 (2CH), 127.7 (2CH), 121.6, 114.0, 98.9, 61.8 ($2CH_2$), 25.8, 21.0 ($2CH_3$), 14.9 ($2CH_3$), 8.8; MS (ESI) *m/z* 331 (50), 285 (100); HRMS Calcd for $C_{20}H_{27}O_4^+$ $[M + H]^+$ 331.1909, found 331.1911.

1-(5-*tert*-Butyl-2,4-dimethylfuran-3-yl)-2,2-diethoxyethanone (5j). 7,7-Diethoxy-2,2-dimethyl-6-oxohept-4-yn-3-yl acetate (**4j**) (0.28 g) was reacted at −78 °C and gave the title compound (0.21 g, 72%) as a colorless liquid after purification by flash chromatograph using hexanes-ethyl acetate (97.5:2.5). IR (film) 2963 (s), 2930 (s), 2872 (s), 1680 (s), 1660 (s), 1622 (w), 1552 (m), 1466 (m), 1409 (m), 1377 (m), 1322 (m), 1283 (m), 1175 (s), 1118 (s), 1071 (s), 954 (w), 913 (m), 891 (w), 832 (w), 770 (w), 732 (w), 680 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.05 (s, 1H), 3.80−3.54 (m, 4H), 2.52 (s, 3H), 2.22 (s, 3H), 1.32 (s, 9H), 1.24 (t, $J = 7.0$ Hz, 3H), 1.23 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 192.1, 158.8, 136.3, 120.4, 113.3, 101.3, 62.4 ($2CH_2$), 29.4 ($3CH_3$), 26.1, 15.2 ($2CH_3$), 14.2, 10.6; MS (EI) *m/z* 282 (M^+, 5), 237 (5), 179 (25), 103 (100), 75 (90); HRMS Calcd for $C_{16}H_{26}O_4^+$ $[M^+]$ 282.1831, found 282.1833.

1-(5-*tert*-Butyl-2-isopropyl-4-methylfuran-3-yl)-2,2-diethoxyethanone (5k). 7,7-Diethoxy-2,2-dimethyl-6-oxohept-4-yn-3-yl isobutyrate (**4k**) (0.31 g) was reacted at −60 °C and gave the title compound (0.21 g, 68%) as a colorless liquid after purification by flash chromatograph using hexanes−ethyl acetate (97.5:2.5). IR (film) 2975 (s), 2932 (s), 2874 (m), 1676 (s), 1661 (s), 1598 (w), 1554 (m), 1466 (m), 1394 (w), 1375 (m), 1365 (m), 1323 (m), 1272 (w), 1220 (w), 1128 (s), 1065 (s), 958 (w), 821 (w), 832 (w), 702 (w), 676 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.05 (s, 1H), 3.73−3.50 (m, 5H), 2.20 (s, 3H), 1.31 (s, 9H), 1.24 (d, $J = 6.6$ Hz, 6H), 1.23 (2 almost overlapping t, $J = 7.0$ Hz for each, 3H for each); ^{13}C NMR (50 MHz, $CDCl_3$) δ 192.8, 163.4, 155.2, 119.1, 112.3, 101.6, 62.4 ($2CH_2$), 33.7, 29.4 ($3CH_3$), 28.1, 21.2 ($2CH_3$), 15.2 ($2CH_3$), 10.6; MS (EI) *m/z* 310 (M^+, 20), 265 (40), 207 (30), 103 (100); HRMS Calcd for $C_{18}H_{30}O_4^+$ $[M^+]$ 310.21440, found 310.21446.

1-(5-*tert*-Butyl-4-methyl-2-phenylfuran-3-yl)-2,2-diethoxyethanone (5 L). 7,7-Dieth-oxy-2,2-dimethyl-6-oxohept-4-yn-3-yl benzoate (**4l**) (0.35 g) was reacted at −60 °C and gave the title compound (0.18 g, 52%) as a colorless liquid after purification by flash chromatograph using hexanes-ethyl acetate (95:5). IR (film) 3059 (w), 3028 (w), 2975 (s), 2931 (s), 2905 (m), 2875, 1686 (s), 1611 (w), 1597 (w), 1578 (w), 1556 (m), 1487 (m), 1461 (m), 1446 (m), 1392 (m), 1366 (m), 1342 (w), 1317 (w), 1306 (w), 1268 (w), 1224 (w), 1202 (w), 1132 (m), 1117 (s), 1071 (s), 1006 (m), 967 (m), 960 (m), 923 (m), 843 (m), 824 (w), 770 (m), 698 (s) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.50−7.37 (m, 5H), 4.94 (s, 1H), 3.57−3.51 (m, 2H), 3.42−3.36 (m, 2H), 2.17 (s, 3H), 1.38 (s, 9H), 1.12 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 194.7, 157.5, 152.0, 130.7, 128.6, 128.3 (2CH), 127.4 (2CH), 122.6, 114.1, 99.1, 61.9 ($2CH_2$), 33.8, 29.3 ($2CH_3$), 14.9 ($2CH_3$), 9.6; MS (ESI) *m/z* 299 (100), 253 (35); HRMS Calcd for $C_{19}H_{23}O_3^+$ $[M^{+\cdot} - EtO^{\cdot}]$ 299.16472, found 299.16648.

2,2-Diethoxy-1-(2,4-dimethyl-5-phenylfuran-3-yl)ethanone (5m). 5,5-Diethoxy-4-oxo-1-phenylpent-2-ynyl acetate (**4m**) (0.30 g) was reacted at −60 °C and gave the title compound (0.15 g, 52%) as a colorless liquid after purification by flash chromatography (hexanes−ethyl acetate, 90:10). IR (film) 3054 (w), 2977 (s), 2928 (s), 2879 (s), 1681 (s), 1666 (s), 1614 (m), 1575 (w), 1553 (m), 1494 (m), 1444 (m), 1494 (m), 1409 (m), 1376 (m), 1322 (m), 1303 (m), 1252 (w), 1157 (m), 1117 (s), 1062 (s), 1016 (s), 969 (w), 911 (w), 765 (s), 696 (s), 665 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.59−7.56 (m, 2H), 7.46−7.20 (m, 3H), 5.09 (s, 1H), 3.82−3.55 (m, 4H), 2.65 (s, 3H), 2.39 (s, 3H), 1.26 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 192.0, 158.7, 147.9, 130.4, 129.2 (2CH), 128.0, 127.1 (2CH), 121.6, 117.7, 102.2, 62.6 ($2CH_2$), 15.1, 15.0 ($2CH_3$), 11.2; MS (EI) *m/z* 302 (M^+, 33), 257 (10), 229 (45), 201 (14), 200 (35), 199 (52), 171 (95), 143 (18), 130 (18), 129 (55), 128 (71), 127 (28), 115 (15), 105 (96), 104 (64), 103 (50), 77 (100), 75 (53); HRMS Calcd for $C_{18}H_{22}O_4^+$ $[M^+]$ 302.1518, found 302.1522.

2,2-Diethoxy-1-(2-isopropyl-4-methyl-5-phenylfuran-3-yl)-ethanone (5n). 5,5-Diethoxy-4-oxo-1-phenylpent-2-ynyl isobutyrate (**4n**) (0.33 g) was reacted at −60 °C and gave the title compound (0.20 g, 60%) as a colorless liquid after purification by flash chromatography (hexanes−ethyl acetate, 95:5). IR (film) 3083 (w), 3055 (m), 2975 (s), 2931 (s), 2874 (s), 1714 (m), 1688 (s), 1664 (s), 1611 (m), 1549 (m), 1493 (m), 1466 (m), 1445 (m), 1376 (m), 1316 (m), 1259 (w), 1222 (m), 1113 (s), 1063 (s), 1013 (s), 955 (m), 911 (m), 831 (w), 766 (s), 728 (w), 696 (s) 666 (m), 655 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.60−7.56 (m, 2H), 7.46−7.26 (m, 3H), 5.10 (s, 1H), 3.81−3.56 (m, 5H), 2.37 (s, 3H), 1.34−1.18 (m, 12H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 192.4, 166.1, 147.5, 130.9, 128.4 (2CH), 127.2, 126.3 (2CH), 119.7, 116.2, 101.6, 62.5 ($2CH_2$), 28.0, 21.0 ($2CH_3$), 15.0 (2 CH_3), 11.2; MS (ESI) *m/z* 331 (100), 317 (8), 285 (10), 257 (7), 186 (10); HRMS Calcd for $C_{20}H_{27}O_4^+$ $[M + H]^+$ 331.1909, found 331.1906.

2,2-Diethoxy-1-(4-methyl-2,5-diphenylfuran-3-yl)ethanone (5o). 5,5-Diethoxy-1-phenyl-4-oxopent-2-ynyl benzoate (**4o**) (0.37 g) was reacted at −60 °C and gave the title compound (0.19 g, 53%) as a colorless liquid after purification by flash chromatography (hexanes−ethyl acetate, 95:5). IR (film) 3057 (w), 3031 (w), 2975 (s),

2956 (s), 2926 (s), 2871 (m), 2856 (m), 1688 (s), 1613 (m), 1595 (m), 1555 (m), 1486 (m), 1445 (m), 1381 (m), 1316 (m), 1265 (w), 1158 (m), 1112 (s), 1070 (s), 965 (m), 912 (m), 839 (m), 766 (s), 695 (s), 667 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.71−7.59 (m, 4H), 7.49−7.29 (m, 6H), 5.00 (s, 1H), 3.66−3.32 (m, 4H), 2.36 (s, 3H), 1.11 (t, J = 7.0 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 194.5, 154.3, 149.3, 130.6, 130.4, 129.2, 128.5 (4CH), 127.8 (2CH), 127.5, 126.1 (2CH), 123.1, 117.9, 99.3, 62.2 ($2CH_2$), 14.9 ($2CH_3$), 10.3; MS (ESI) m/z 364 (M^+, 40), 335 (20), 319 (42), 293 (30), 279 (20), 215 (20), 187 (100), 158 (10); HRMS Calcd for $C_{23}H_{24}O_4^+$ [M^+] 364.1675, found 364.1662.

2,2-Diethoxy-1-(5-hexyl-2,4-dimethylfuran-3-yl)ethanone (5p). 5,5-Diethoxy-1-hexyl-4-oxopent-2-ynyl acetate (**4p**) (0.31 g) was reacted at −60 °C and gave the title compound (0.22 g, 70%) as a colorless liquid after purification by flash chromatograph using hexanes−ethyl acetate (90:10). IR (film) 2972 (s), 2930 (s), 2873 (s), 1681 (s), 1663 (s), 1560 (m), 1457 (m), 1447 (m), 1414 (m), 1380 (m), 1323 (w), 1295 (w), 1271 (m), 1259 (m), 1159 (m), 1124 (m), 1061 (s), 968 (m), 914 (w), 785 (w), 699 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.06 (s, 1H), 3.76−3.59 (m, 4H), 2.54 (s, 3H), 2.10 (s, 3H), 1.64−1.59 (m, 10H), 1.31−1.22 (m, 6H), 0.88 (t, J = 7.0 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 191.5, 158.0, 150.1, 119.9, 114.3, 101.1, 62.3 (2 CH_2), 31.5, 29.7, 28.8, 28.4, 25.3, 22.5, 15.4 (2 CH_3), 14.0, 10.3; MS (EI) m/z 310 (M^+, 10), 265 (10), 237 (40), 207 (70), 137 (20), 103 (100), 75 (90), 43 (80); HRMS Calcd for $C_{18}H_{30}O_4^+$ [M^+] 310.2144, found 310.2141.

2,2-Diethoxy-1-(5-hexyl-2-isopropyl-4-methylfuran-3-yl)ethanone (5q). 5,5-Dieth-oxy-1-hexyl-4-oxopent-2-ynyl isobutyrate (**4q**) (0.34 g) was reacted at −60 °C and gave the title compound (0.23 g, 69%) as a colorless liquid after purification by flash chromatograph using hexanes−ethyl acetate (90:10). IR (film) 2963 (s), 2930 (s), 2872 (m), 2860 (s), 1742 (w), 1681 (s), 1660 (s), 1623 (m), 1555 (s), 1467 (s), 1409 (m), 1377 (m), 1361 (m), 1339 (m), 1322 (m), 1283 (m), 1175 (m), 1118 (s), 1071 (s), 1013 (m), 954 (m), 927 (m), 891 (w), 832 (w), 732 (w), 680 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.08 (s, 1H), 3.72−3.56 (m, 4H), 2.49 (se, J = 7.0 Hz, 1H), 2.04 (s, 3H), 1.56−1.21 (m, 22H), 0.90 (t, J = 6.6 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 191.8, 165.6, 150.0, 118.1, 113.5, 101.1, 62.2 (2 CH_2), 31.4, 28.6, 28.1, 27.9, 27.8, 25.2, 22.4, 20.9 (2 CH_3), 15.8 (2 CH_3), 10.1; MS (ESI) m/z 339 (100), 310 (40), 293 (60); HRMS Calcd for $C_{18}H_{29}O_3^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 293.21167, found 293.21172.

2,2-Diethoxy-1-(5-hexyl-4-methyl-2-phenylfuran-3-yl)ethanone (5r). 5,5-Diethoxy-1-hexyl-4-oxopent-2-ynyl benzoate (**4r**) (0.37 g) was reacted at −60 °C and gave the title compound (0.19 g, 50%) as a colorless liquid after purification by flash chromatography (hexane−ethyl acetate, 90:10). IR (film) 3064 (w), 3034 (w), 2956 (s), 2925 (s), 2871 (s), 2855 (s), 1686 (s), 1605 (m), 1584 (w), 1559 (m), 1459 (s), 1378 (m), 1265 (s), 1176 (m), 1098 (s), 1070 (s), 1027 (m), 964 (w), 917 (w), 768 (m), 711 (m), 666 (s) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 7.55−7.50 (m, 2H), 7.43−7.37 (m, 3H), 4.97 (s, 1H), 3.59−3.32 (m, 4H), 2.61 (t, J = 7.0 Hz, 2H), 2.04 (s, 3H), 1.43−0.98 (m, 17H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 194.1, 154.0, 152.2, 130.9, 128.8, 128.4 (2CH), 127.8 (2CH), 121.8, 115.8, 99.0, 61.9 ($2CH_2$), 31.5, 29.3, 28.7, 26.8, 22.6, 14.9, 14.0 ($2CH_3$), 9.1; MS (ESI) m/z 373 (100), 359 (6); HRMS Calcd for $C_{23}H_{33}O_4$ [M + H]$^+$ 373.2379, found 373.2373.

1-(4-Butyl-5-isopropyl-2-methylfuran-3-yl)-2,2-diethoxyethanone (6). 5,5-Diethoxy-1-isopropyl-4-oxopent-2-ynyl acetate (**4g**) (0.27 g, 1.0 mmol) and *in situ* formed Bu_2CuLi (1.0 mmol) were reacted at −60 °C and gave the title compound (0.28 g, 90%) as a colorless liquid after purification by flash chromatography (hexanes−ethyl acetate, 95:5). IR (film) 2968 (s), 2931 (s), 2873 (s), 1685 (s), 1661 (s), 1560 (s), 1466 (m), 1410 (m), 1381 (m), 1323 (m), 1300 (w), 1259 (m), 1159 (m), 1125 (s), 1054 (s), 968 (m), 911 (m), 841 (w), 798 (w), 691 (m), 666 (m) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 5.07 (s, 1H), 3.77−3.53 (m, 4H), 2.95 (septet, J = 7.0 Hz, 1H), 2.56 (s, 3H), 2.51 (t, J = 7.4 Hz, 2H), 1.40−1.18 (m, 16H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 191.4, 157.1, 154.3, 119.1, 118.3, 101.0, 62.2 ($2CH_2$), 33.1, 25.3, 23.7, 22.6, 21.4 ($2CH_3$), 15.6, 15.0 ($2CH_3$), 13.9; MS (ESI) m/z 311 (70), 309 (100), 281 (48), 263 (10), 235 (7), 117 (34); HRMS Calcd for $C_{18}H_{31}O_4^+$ [M + H]$^+$ 311.2222, found 311.2218.

1-(4-*tert*-Butyl-2,5-diisopropylfuran-3-yl)-2,2-diethoxyethanone (7). 5,5-Diethoxy-1-isopropyl-4-oxopent-2-ynyl isobutyrate (**4h**) (0.30 g, 1.0 mmol) and *in situ* formed Bu^t_2CuLi (1.0 mmol) were reacted at −60 °C and gave the title compound (0.19 g, 55%) as a colorless liquid after purification by flash chromatography (hexanes−ethyl acetate, 95:5). IR (film) 2970 (s), 2932 (s), 2873 (s), 1699 (s), 1600 (w), 1560 (m), 1483 (m), 1468 (s), 1394 (m), 1364 (s), 1276 (m), 1261 (m), 1205 (m), 1157 (s), 1111 (s), 1080 (s), 1064 (s), 1011 (s), 929 (m), 845 (w), 762 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.96 (s, 1H), 3.85−3.54 (m, 4H), 3.23 (septet, J = 6.9 Hz, 1H), 2.93 (septet, J = 6.9 Hz, 1H), 1.29−1.13 (m, 27H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 199.1, 156.0, 153.1, 124.8, 118.9, 101.8, 63.0 ($2CH_2$), 31.9 ($3CH_3$), 27.9, 27.3, 22.3, 21.6 ($2CH_2$), 21.3 ($2CH_3$), 15.0 ($2CH_3$); MS (ESI) m/z 339 (70), 338 (20), 337 (100), 293 (28), 271 (15) 213 (21), 143 (10), 59 (17); HRMS Calcd for $C_{20}H_{35}O_4^+$ [M + H]$^+$ 339.2535, found 339.2526.

(*tert*-Butyl)(4,4,5,5-tetraethoxy-1-hexyl-2-pentynoxy)diphenylsilane (9). 1,1,2,2-Tetraethoxyundec-3-yn-5-ol (0.69 g, 2.0 mmol) was dissolved in $CHCl_3$ (20 mL) under N_2 at 20 °C. After addition of Et_3N (0.40 g, 4.0 mmol) and DMAP (0.037 g, 0.3 mmol) (*t*-butyl)(chloro)-diphenylsilane (0.60 g, 2.2 mmol) was added dropwise during 5 min. The reaction mixture was allowed to stir for an additional 30 min before the reaction was quenched by a saturated aqueous solution of $NaHCO_3$ (20 mL). The phases were separated, the aqueous phase was extracted with DCM (3 × 20 mL), and the organic extracts were combined and dried over $MgSO_4$ (anhd.). Filtration and evaporation of the solvent followed by isolation by flash chromatography using hexanes−ethyl acetate (95:5) as eluent, gave the title compound (0.98 g, 84%) as a clear liquid. IR (film) 3071 (m), 3049 (w), 3028 (w), 3014 (w), 2961 (s), 2930 (s), 2894 (s), 2858 (s), 1587 (w), 1473 (m), 1463 (m), 1448 (s), 1427 (m), 1390 (w), 1332 (w), 1258 (w), 1186 (m), 1113 (s), 1082 (s), 1020 (m), 1010 (m), 998 (w), 963 (w), 938 (w), 854 (m), 823 (m), 741 (m), 709 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70−7.65 (m, 4H), 7.41−7.33 (m, 6H), 4.43 (t, J = 6.6 Hz, 1H), 4.35 (s, 1H), 3.66−3.52 (m, 8H), 1.72−1.55 (m, 10H), 1.23 (t, J = 7.0 Hz, 6H), 1.21 (t, J = 7.0 Hz, 6H), 1.19 (s, 9H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 135.5, 133.1, 132.8, 129.8, 129.7, 127.6, 127.5, 101.1, 95.8, 83.6, 63.9, 62.6, 37.4, 31.7, 28.8, 26.7, 24.4, 22.4, 15.0, 14.9, 13.9; MS (ESI) m/z 537 (45), 479 (20), 327 (50), 255 (20), 103 (100); HRMS Calcd for $C_{33}H_{49}O_4Si^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 537.3400, found 537.3402.

5-{(*tert*-Butyl)diphenylsiloxy}-1,1-diethoxyundec-3-yn-2-one (10). A mixture of silane **9** (0.58 g, 1.0 mmol) and *p*-TsOH (0.058 g, 0.3 mmol) in a 70:30 mixture of THF and H_2O (10 mL) was refluxed for 4 h. Most of the THF was then evaporated, leaving a residue which was mixed with CH_2Cl_2 (20 mL) and H_2O (10 mL). The phases were separated, the aqueous phase was extracted with DCM (3 × 20 mL), and the organic phases were combined and dried over $MgSO_4$ (anhd.). Filtration and evaporation of the solvent followed by isolation by flash chromatography using hexanes−ethyl acetate (95:5) as eluent, gave the title compound (0.45 g, 89%) as a clear oil. IR (film) 3072 (m), 3050 (w), 3013 (w), 2956 (s), 2931 (s), 2897 (s), 2859 (s), 2213 (s), 1690 (s), 1589 (w), 1472 (m), 1464 (m), 1428 (s), 1391 (w), 1318 (w), 1245 (w), 1187 (w), 1158 (m), 1113 (s), 1085 (s), 1008 (s), 999 (w), 932 (w), 823 (m), 741 (m), 702 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.71−7.66 (m, 4 H), 7.43−7.35 (m, 6H), 4.62 (s, 1H), 4.47 (t, J = 6.6 Hz, 1H), 3.66−3.52 (m, 4H), 1.72−1.55 (m, 10H), 1.23 (t, J = 7.0 Hz, 3H), 1.21 (t, J = 7.0 Hz, 3H), 1.19 (s, 9H), 0.88 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.4, 135.9, 135.7, 133.0, 132.9, 129.8, 129.7, 127.6, 127.5, 101.1, 96.8, 82.1, 63.9, 62.6, 37.4, 31.7, 28.8, 26.7, 24.4, 22.4, 14.9, 13.9; MS (ESI) m/z 465 (20), 464 (50), 463 (100), 269 (10), 239 (10); HRMS Calcd for $C_{29}H_{39}O_3Si^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 463.26711, found 463.26295.

5-{(*tert*-Butyl)diphenylsiloxy}-1,1-diethoxy-4-methylundec-3-en-2-one (11). CuI (0.051 g, 0.27 mmol) was dispersed in anhydrous THF (3 mL) and cooled to −30 °C. MeLi (0.33 mL, 1.6 M, 0.54 mmol) was added dropwise during 10 min. When the addition was complete the reaction mixture was allowed to stir at −30 °C for 30 min before it was cooled to −78 °C. Silyloxyketone **10** (0.136 g, 0.27 mmol), dissolved in anhydrous THF (2 mL), was then added dropwise during 2 min, and the resulting mixture was stirred for an additional 60 min at −78 °C before a saturated aqueous solution of NH_4Cl (5 mL) was added in one portion, also at −78 °C. The hydrolysate was allowed to reach room temperature, the phases were separated, and the aqueous phase was extracted with diethyl ether (3 × 10 mL). The combined organic extracts were washed with an equal volume of a saturated aqueous NaCl solution, dried over $MgSO_4$ (anhd.), and then concentrated under vacuum on a rotary evaporator to give a crude product, from which the products **11*E*** (0.062 g, 44%) and **11Z** (0.059 g, 42%) were isolated as clear liquids by flash chromatography using hexanes−ethyl acetate (97.5:2.5) as eluent. (*E*)-**11**: IR (film) 3071 (w), 3049 (w), 3013 (w), 2956 (s), 2931 (s), 2897 (s), 2858 (s), 1693 (m), 1615 (m), 1591 (w), 1472 (m), 1462 (m), 1428 (m), 1390 (m), 1372 (w), 1318 (w), 1311 (m), 1261 (w), 1158 (m), 1106 (s), 1065 (s), 1028 (m), 999 (m), 937 (w), 908 (w), 894 (w), 838 (m), 739 (m), 702 (s), 611 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.68−7.58 (m, 4H), 7.43−7.30 (m, 6H), 6.51 (s, 1H), 4.58 (s, 1H), 4.12 (t, J = 5.6 Hz, 1H), 3.64−3.51 (m, 4H), 2.05 (s, 3H), 1.46−1.26 (m, 10H), 1.22 (t, J = 7.0 Hz, 3H), 1.21 (t, J = 7.0 Hz, 3H), 1.08 (s, 9H), 0.89 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 162.1, 135.8, 134.0, 133.4, 129.6, 127.5, 118.3, 102.4, 78.0, 62.5, 35.2, 31.5, 29.0, 26.9, 24.0, 22.4, 19.2, 15.7, 15.0, 13.9; MS (ESI) *m*/*z* 481 (20), 480 (45), 479 (100), 421 (10), 269 (10); HRMS Calcd for $C_{30}H_{43}O_3Si^+$ [$M^{+\cdot}$ - EtO$^\cdot$] 479.29805, found 479.30529. (*Z*)-**11**: IR (film) 3071 (w), 3049 (w), 3012 (w), 2957 (s), 2931 (s), 2858 (s), 2897 (s), 1695 (m), 1621 (m), 1590 (w), 1472 (m), 1460 (m), 1428 (m), 1390 (m), 1372 (w), 1318 (w), 1311 (m), 1261 (w), 1158 (m), 1106 (s), 1065 (s), 1028 (m), 999 (m), 937 (w), 908 (w), 894 (w), 838 (m), 739 (m), 702 (s), 611 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64−7.56 (m, 4H), 7.41−7.28 (m, 6H), 5.72 (t, J = 6.2 Hz, 1H), 4.45 (s, 1H), 3.63−3.42 (m, 4H), 1.97 (s, 3H), 1.52−1.26 (m, 10H), 1.21 (t, J = 7.0 Hz, 6H), 1.06 (s, 9H), 0.83 (t, J = 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 165.5, 135.8, 134.3, 134.0, 129.5, 127.4, 118.4, 102.7, 71.3, 62.6, 62.5, 36.8, 31.6, 29.2, 26.9, 24.9, 22.5, 19.9, 15.0, 13.9; MS (ESI) *m*/*z* 481 (20), 480 (50), 479 (100), 269 (20); HRMS Calcd for $C_{30}H_{43}O_3Si^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 479.29805, found 479.30041.

5,5-Diethoxy-2-methyl-4-oxo-1-phenylpent-2-enyl Acetate (12). CuI (0.190 g, 1.0 mmol) was dispersed in anhydrous THF (10 mL) and cooled to −30 °C. MeLi (1.25 mL, 1.6 M, 2.0 mmol) was added dropwise during 10 min. When the addition was complete the reaction mixture was allowed to stir at −30 °C for 30 min before it was cooled to −78 °C. A solution of **4m** (0.304 g, 1.0 mmol) and trimethylsilyl chloride (0.130 g, 1.2 mmol) in anhydrous THF (5 mL) was then added dropwise to the reaction mixture during 5 min and the reaction was stirred for an additional 60 min at −78 °C before a saturated aqueous solution of NH_4Cl (5 mL) was added in one portion, also at −78 °C. The hydrolysate was allowed to reach room temperature, the phases were separated, and the aqueous phase was extracted with diethyl ether (3 × 10 mL). The combined organic extracts were dried over $MgSO_4$ (anhd.), filtered and then concentrated under vacuum on a rotary evaporator to give a crude product, from which was isolated, by flash chromatography with silica gel and hexane−ethyl acetate (95:5), 0.27 g (84%) of a 1:1 mixture (based on ^1H NMR-spectroscopy) of the (*E*) and the (*Z*) isomers of **12**. IR (film) 3083 (w), 3063 (w), 3032 (w), 2978 (s), 2932 (m), 2883 (m), 1745 (s), 1698 (s), 1624 (s), 1495 (w), 1450 (m), 1371 (s), 1317 (m), 1231 (s), 1181 (m), 1160 (m), 1112 (s), 1062 (s), 1027 (s), 982 (w), 912 (w), 894 (w), 822 (w), 751 (m), 700 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55−7.30 (m, 5H), 7.29 and 6.54 (2s, 1H, *E* and *Z* in a 1:1 ratio), 6.83 and 6.19 (2s, 1H, *E* and *Z* in a 1:1 ratio), 4.68 and 4.67 (2s, 1H, *E* and *Z* in a 1:1 ratio), 3.74−3.55 (m, 4H), 2.15 (s, 3H), 2.04 and 1.90 (2s, 3H, *E* and *Z* in a 1:1 ratio), 1.27 (t, J = 7.0 Hz, 3H), 1.25 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.4, 194.0, 169.5, 156.3, 137.9, 136.8, 128.6, 128.2, 127.7, 127.6, 126.1, 121.5, 117.7, 102.6, 102.3, 78.6, 72.7, 63.0, 62.8, 62.8, 62.7, 21.0, 20.8, 19.0, 16.5, 15.0; MS (ESI) *m*/*z* 275 (10), 261 (100); HRMS Calc. for $C_{16}H_{21}O_3^+$ [$M^{+\cdot}$ − AcO$^\cdot$] 261.14907, found 261.15154.

3-Deuterio-5,5-diethoxy-2-methyl-4-oxo-1-phenylpent-2-enyl Acetate (13). When the reaction with 0.304 g (1.0 mmol) of **4m** was repeated exactly as described under preparation of **12** except that the hydrolysis was performed with D_2O (5 mL) at −78 °C, 0.27 g (84%) of a 1:1 mixture (based on ^1H NMR-spectroscopy) of the (*E*) and the (*Z*) isomers of **13** was obtained. IR (film) 3082 (w), 3061 (w), 3031 (w), 2979 (s), 2931 (s), 2883 (m), 1744 (s), 1697 (s), 1624 (s), 1493 (w), 1452 (m), 1372 (s), 1319 (s), 1231 (s), 1180 (m), 1160 (m), 1112 (s), 1062 (s), 1025 (s), 982 (w), 912 (w), 891 (w), 822 (w), 751 (m), 700 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.55−7.30 (m, 5H), 7.28 and 6.54 (2s, 1H, *E* and *Z* in a 1:1 ratio), 4.68 and 4.67 (2s, 1H, *E* and *Z* in a 1:1 ratio), 3.74−3.55 (m, 4H), 2.14 (s, 3H), 2.04 and 1.92 (2s, 3H, *E* and *Z* in a 1:1 ratio), 1.27 (t, J = 7.0 Hz, 3H), 1.25 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 194.1, 169.3, 156.3, 137.8, 136.6, 128.6, 128.1, 127.7, 127.6, 126.1, 121.5, 117.7, 102.5, 102.3, 78.5, 72.4, 63.0, 62.8, 62.8, 62.7, 21.0, 20.8, 19.0, 16.5, 15.1; MS (ESI) *m*/*z* 276 (10), 262 (100), 218 (30); HRMS Calcd. for $C_{16}H_{20}DO_3^+$ [$M^{+\cdot}$ − AcO$^\cdot$] 262.15689, found 262.15712.

5,5,6,6-Tetraethoxy-2-methylhex-3-yn-2-ol (14). The compound was synthesized from TEB, using BuLi or EtMgBr as base and acetone as electrophile, following literature procedures.[4] The product was isolated as a pale yellow liquid employing silica gel flash chromatography (hexane−ethyl acetate, 70:30) and was obtained in 80 and 90% yield, respectively. IR (film) 3431 (m), 2978 (s), 2931 (s), 2896 (s), 2244 (w), 1480 (w), 1445 (m), 1388 (m), 1373 (m), 1336 (m), 1243 (m), 1169 (s), 1116 (s), 1017 (m), 969 (m), 933 (m), 879 (w), 808 (w), 760 (w), 736 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.38 (s, 1H), 3.88−3.62 (m, 8H), 3.34 (bs, 1H), 1.54 (s, 6H), 1.24 (t, J = 7.0 Hz, 6H), 1.23 (t, J = 7.0 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 103.6, 98.2, 91.5, 76.3, 64.4, 64.3, 59.2, 30.9, 15.0, 14.9; MS (EI) *m*/*z* 243 (9), 215 (2), 185 (21), 169 (5), 141 (4), 139 (4), 123 (6), 111 (9), 104 (4), 103 (100), 95 (19), 83 (5), 75 (59); HRMS Calcd for $C_{13}H_{23}O_4^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 243.1596, found 243.1592.

1,1-Diethoxy-5-hydroxy-5-methylhex-3-yn-2-one (15). Alcohol **14** (1.73 g, 6.0 mmol) was refluxed for 3 h in a THF-H_2O mixture (6:4) (60 mL) containing *p*-TsOH (0.11 g, 0.6 mmol, 0.1 equiv). Most of the THF was then evaporated on a rotary evaporator, and the residue was mixed with DCM (20 mL). The phases were separated, the aqueous phase was extracted with DCM (3 × 20 mL), and the combined organic phases were dried over $MgSO_4$ (anhd.). Filtration followed by concentration under vacuum on a rotary evaporator furnished a crude product, from which **15** (1.22 g, 95%) was isolated as a colorless liquid by flash chromatography using hexanes−ethyl acetate (85:15) as eluent. IR (film) 3433 (m), 2982 (s), 2934 (m), 2896 (m), 2215 (s), 1690 (s), 1446 (m), 1372 (m), 1322 (m), 1292 (w), 1254 (s), 1233 (s), 1173 (s), 1105 (s), 1068 (s), 968 (m), 933 (m), 900 (m), 840 (w), 754 (w) cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.76 (s, 1H), 3.81−3.56 (m, 4H), 3.18 (bs, 1H), 1.59 (s, 6H), 1.28 (t, J = 7.0 Hz, 6H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 182.6, 101.2, 99.6, 81.7, 79.2, 64.8, 62.9, 30.3, 14.9; MS (ESI) *m*/*z* 197 (10), 169 (60), 155 (10), 111 (65), 103 (40); HRMS Calcd for $C_{19}H_{13}O_3^+$ [$M^{+\cdot}$ − EtO$^\cdot$] 169.0865, found 169.0865.

5,5-Diethoxy-1,1-dimethyl-4-oxopent-2-ynyl Acetate (16). Hydroxyketone **15** (0.21 g, 1.0 mmol) was dissolved in $CHCl_3$ (10 mL) and added dropwise to a stirred solution of acetic anhydride (1.01 g, 10.0 mmol), pyridine (0.24 g, 3.0 mmol) and DMAP (0.018 g, 0.15 mmol) in $CHCl_3$ (3 mL) kept at rt. The reaction mixture was stirred at this temperature for 14 h and a saturated aqueous

solution of $NaHCO_3$ (20 mL) was then added. The phases were separated, the aqueous phase was extracted with DCM (3 × 20 mL), and the combined organic extracts were dried over $MgSO_4$ (anhd.). Filtration followed by concentration under vacuum on a rotary evaporator furnished a crude product, from which **16** (0.23 g, 89%) was isolated as a colorless liquid by flash chromatography using hexanes−ethyl acetate (95:5) as eluent. IR (film) 2980 (m), 2936 (m), 2916 (s), 2895 (s), 2222 (m), 1747 (s), 1698 (s), 1444 (w), 1370 (s), 1259 (m), 1239 (s), 1188 (m), 1138 (s), 1086 (s), 1079 (s), 1017 (m), 969 (w), 912 (w), 871 (w), 840 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.78 (s, 1H), 3.75−3.60 (m, 4H), 2.04 (s, 3H), 1.71 (s, 6H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.25 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.7, 169.0, 101.3, 96.1, 81.9, 70.8, 63.0, 28.1, 21.6, 15.0; MS (ESI) m/z 257 (25), 211 (55), 197 (100), 153 (35). HRMS Calcd for $C_{13}H_{21}O_5^+$ $[M + H]^+$ 257.13890, found 257.14186.

2,2-Diethoxy-1-(2,5-dihydro-2-hydroxy-2,4,5,5-tetramethylfuran-3-yl)ethanone (17). CuI (0.040 g, 0.21 mmol) was dispersed in anhydrous THF (3 mL) and cooled to −30 °C. MeLi (0.28 mL, 1.6 M, 0.44 mmol) was added dropwise in 5 min. When the addition was complete the reaction mixture was allowed to stir at −30 °C for 30 min before it was cooled to −78 °C. A solution of **16** (0.054 g, 0.21 mmol) in anhydrous THF (1 mL) was then added dropwise to the reaction mixture in 3 min and the mixture was stirred for additional 60 min at −78 °C before a saturated aqueous solution of NH_4Cl (5 mL) was added in one portion, also at −78 °C. The hydrolysate was allowed to reach room temperature, the phases were separated, and the aqueous phase was extracted with diethyl ether (3 × 10 mL). The combined organic extracts were dried over $MgSO_4$ (anhd.), filtered and then concentrated under vacuum on a rotary evaporator to give a crude product, from which 17 (0.049 g, 86%) was isolated as a colorless liquid by flash chromatography using hexanes−ethyl acetate (80:20) as eluent. IR (film) 3466 (m), 2977 (s), 2931 (m), 2899 (m), 2877 (m), 1662 (s), 1583 (s), 1445 (m), 1444 (m), 1393 (m), 1374 (m), 1324 (m), 1284 (s), 1170 (m), 1122 (s), 1090 (s), 1064 (s), 982 (m), 929 (w), 865 (w), 822 (w), 751 (m), 702 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.05 (s, 1H), 4.57 (s, 1H), 3.71−3.58 (m, 4H), 1.96 (s, 3H), 1.62 (s, 3H), 1.33 (s, 6H), 1.23 (t, $J = 7.0$ Hz, 3H), 1.22 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 152.4, 134.2, 101.0, 98.9, 89.7, 62.2, 28.2, 17.2, 15.1, 11.2; MS (ESI) *m/z* 273 (25), 255 (100), 227 (45); HRMS Calcd for $C_{14}H_{23}O_4^+$ $[M^{+\cdot} - HO^{\cdot}]$ 255.15963 found, 255.16275.

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Supporting Information Available: ^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.

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