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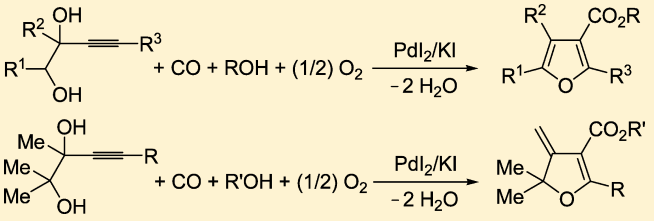
Synthesis of Furan-3-carboxylic and 4-Methylene-4,5-dihydrofuran-3-carboxylic Esters by Direct Palladium Iodide Catalyzed Oxidative Carbonylation of 3-Yne-1,2-diol Derivatives

Bartolo Gabriele,*[,†] Raffaella Mancuso,[‡] Vito Maltese,[‡] Lucia Veltri,[‡] and Giuseppe Salerno[‡]

[†]Dipartimento di Scienze Farmaceutiche and [‡]Dipartimento di Chimica, Università della Calabria, 87036 Arcavacata di Rende (CS), Italy

Supporting Information

ABSTRACT: A variety of 3-yne-1,2-diol derivatives **1**, bearing a primary or secondary alcoholic group at C-1, have been efficiently converted into high value added furan-3-carboxylic esters **2** in one step by PdI_2/KI-catalyzed direct oxidative carbonylation, carried out in alcoholic media under relatively mild conditions (100 °C under 40 atm of a 4/1 mixture of CO and air). Carbonylated furans **2** were obtained in fair to excellent isolated yields (56−93%) through a sequential 5-*endo-dig* heterocyclization−alkoxycarbonylation−dehydration process, using only oxygen as the external oxidant. Under similar conditions, 2-methyl-3-yne-1,2-diols **3**, bearing a tertiary alcoholic group, afforded 4-methylene-4,5-dihydrofuran-3-carboxylates **4** in satisfactory yields (58−70%).



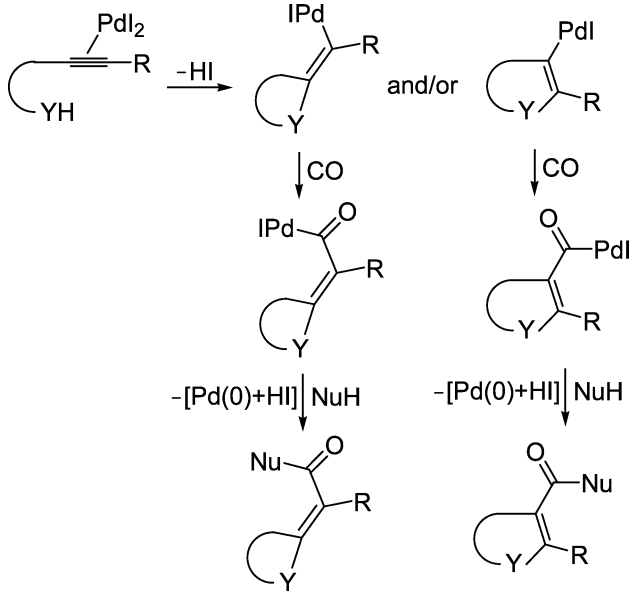
INTRODUCTION

PdI_2/KI-catalyzed heterocyclization−alkoxycarbonylation or heterocyclization−aminocarbonylation of acetylenic substrates bearing a suitably placed nucleophilic group is a powerful methodology for the direct synthesis of important carbonylated heterocycles.[1−3] The heterocyclization−carbonylation sequence is promoted by PdI_2, which is then reduced to Pd(0) at the end of the cycle (Scheme 1; in this and in the following schemes anionic iodide ligands are omitted for clarity).

Therefore, the presence of an oxidant is needed in order to make the process catalytic. In some particular cases, an external oxidant is not needed if the product initially ensuing from the carbonylation process still possesses a reducible functional group able to reoxidize Pd(0) to Pd(II), as exemplified in Scheme 2.[1,2] Usually, however, the reaction is carried out under oxidative conditions,[1,3] in the presence of oxygen as the external oxidant, which is able to reconvert Pd(0) to PdI_2 through the oxidation of HI (also ensuing from the carbonylation process) to I_2 followed by oxidative addition of the latter to Pd(0) (Scheme 3).[2]

In this paper, we report a full account of the PdI_2/KI-catalyzed oxidative 5-*endo-dig* heterocyclodehydration−alkoxycarbonylation of readily available 3-yne-1,2-diol derivatives **1** and **3** to give furan-3-carboxylic and methylenedihydrofuran-3-carboxylic esters **2** and **4**, respectively (Scheme 4). In these reactions, the heterocyclization−alkoxycarbonylation process is accompanied by dehydration, either from the $R^1CHC(2)OH$ moiety of **1** (resulting in aromatization and leading to **2**) or from the MeC(2)OH moiety of **3** (leading to **4**). To our knowledge, this is the first example of synthesis of these important classes of heterocycles via a direct carbonylation approach of acyclic precursors.[4−8]

Scheme 1. Mechanism of PdI_2-Promoted Heterocyclization−Carbonylation of Acetylenic Substrates Bearing a Suitably Placed Nucleophilic Group (Y = O, NR′; NuH = OH, NR″)



RESULTS AND DISCUSSION

2-Methyloct-3-yne-1,2-diol (**1a**; R^1 = H, R^2 = Me, R^3 = Bu), readily available by alkynylation of hydroxyacetone (see the

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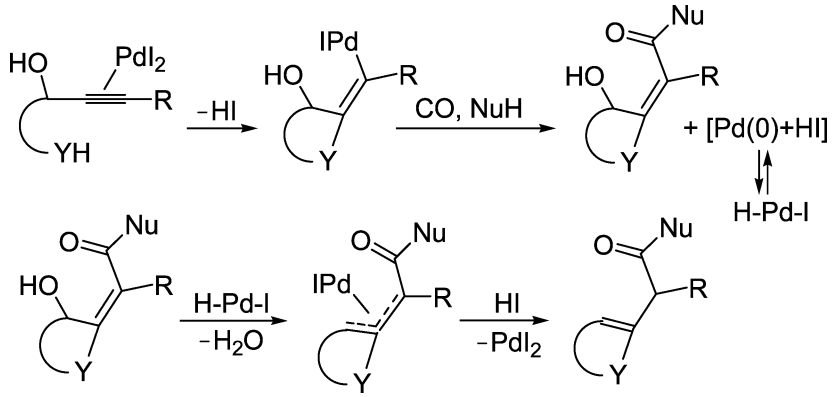
Scheme 2. Mechanism of PdI_2-Catalyzed Heterocyclization−Carbonylation of Acetylenic Substrates Bearing a Suitably Placed Nucleophilic Group and a Reducible Function (Y = O, NR′; NuH = OH, NR″)



Scheme 3. Mechanism of Reoxidation of Pd(0) to PdI_2 in the Presence of O_2 as External Oxidant

$$2\ HI + (1/2)\ O_2 \longrightarrow I_2 + H_2O$$

$$Pd(0) + I_2 \longrightarrow PdI_2$$

Experimental Section for details), was chosen as a model substrate for assessing the reactivity of 3-yne-1,2-diol derivatives **1** bearing a primary alcoholic group at C-1 under oxidative carbonylation conditions in the presence of catalytic amounts of PdI_2/KI. The reaction was initially conducted at 80 °C in MeOH as the solvent (**1a** concentration 0.25 mmol per mL of MeOH, **1a**/KI/PdI_2 molar ratio 1/10/100) under 20 atm of a 4/1 mixture of CO and air. A mixture of the desired furan-carboxylic methyl ester derivative **2a** (28% GLC yield) and 2-hydroxy-2-methyloct-3-ynyl 2-butyl-4-methylfuran-3-carboxylate (**5a**) (clearly deriving from nucleophilic displacement by substrate **1a** rather than MeOH, 13% GLC yield) at a substrate conversion of 70% was obtained under these conditions, as shown in Table 1, entry 1. Although **5a** could not be isolated in a pure state by conventional chromatographic techniques, its formation was strongly suggested by the GC-MS analysis of the crude reaction mixture (see the Experimental Section for details).

In order to improve this initial result, we then screened the reaction parameters; the results obtained are shown in Table 1, entries 2−7. As can be seen from Table 1, entry 2, an increase of the temperature to 100 °C caused an improvement of both the total yield and the selectivity of the process toward the formation of **2a**. A similar effect was observed when the substrate concentration was decreased (entry 3) and when the KI/PdI_2 ratio was lowered to 5 (entry 5). A significant augment of the total yield (81%, by GLC) was obtained when the total pressure was increased to 40 atm (entry 7). When the reaction was carried out under the conditions thus optimized (**1a**/KI/PdI_2 molar ratio 1/5/100, 100 °C, 32 atm of CO, 8 atm of air, **1a** concentration 0.05 mmol/mL of MeOH), methyl 2-butyl-4-methylfuran-3-carboxylate (**2a**) was selectively obtained in 76% GLC yield (69% isolated; Table 2, entry 1). An even higher yield (81% isolated) could be obtained using a higher catalyst loading (2 mol %; Table 2, entry 2).

The generality of the process was then verified by testing the reactivity of other differently substituted 3-yne-1,2-diols **1b−r**, bearing a primary or secondary alcoholic group at C-1, as well as different substituents at C-2 and C-4. As can be seen from the results reported in Table 2, entries 2−19, the process was quite general, the corresponding furan-3-carboxylic esters **2b−r** being consistently obtained in satisfactory isolated yields (56−93%). It is worth noting that the reaction also worked nicely with dialkynyl substrates, such as 2-(hex-1-ynyl)oct-3-yne-1,2-diol (**1d**) and (*S*)-3-(hex-1-ynyl)non-4-yne-2,3-diol (**1f**), which were converted into the corresponding furan-3-carboxylic esters **2d,f** without affecting the alkynyl substituent at C-3 (Table 2, entries 5 and 7), which would allow further functionalization at the furan ring. As can be seen from entries 20 and 21 (Table 2), a higher alcohol, such as EtOH, could also be used instead of MeOH, still with satisfactory results.[9]

Scheme 4. Formation of Furan-3-carboxylic and 4-Methylene-5,6-dihydrofuran-3-carboxylic Esters 2 and 4 by Direct Palladium Iodide Catalyzed Oxidative Carbonylation of 3-Yne-1,2-diol Derivatives 1 and 3, Respectively

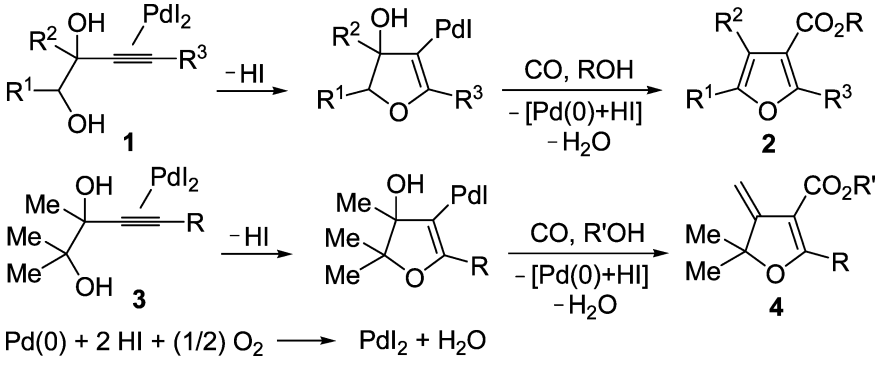


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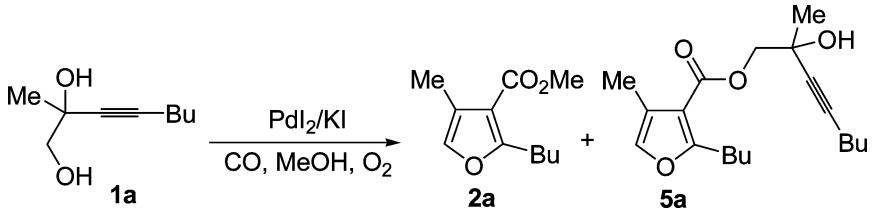
Table 1. PdI_2/KI-Catalyzed Oxidative Carbonylation Reactions of 2-Methyloct-3-yne-1,2-diol (1a) Under Different Conditions[a]



entry	KI/PdI_2 molar ratio	T (°C)	substrate concn[b]	P_{CO}/P_{air} (atm)	yield of **2a**[c] (%)	yield of **5a**[c] (%)	total yield (%)
1[d]	10	80	0.25	16/4	28	13	41
2	10	100	0.25	16/4	55	9	64
3	10	80	0.05	16/4	60	2	62
4	10	80	0.02	16/4	45	1	46
5	5	80	0.25	16/4	52	15	67
6	2	80	0.25	16/4	37	9	46
7	10	80	0.25	32/8	49	32	81

[a]All reactions were carried out in MeOH for 2 h in the presence of 1 mol % of PdI_2. Unless otherwise noted, substrate conversion was quantitative. [b]In units of mmol of starting **1a**/mL of MeOH. [c]Based on starting **1a**, by GLC. The formation of unidentified heavy products (chromatographically immobile materials) accounted for the difference between the substrate conversion and the product yield. [d]Substrate conversion was ca. 70% (determined by GLC).

We also tested the reactivity of 2-methyl-3-yne-1,2-diols **3**, bearing a tertiary alcoholic group, for which aromatization is clearly not possible. Interestingly, when we reacted 2,3-dimethyl-5-phenylpent-4-yne-2,3-diol (**3a**) under the conditions already optimized for substrates **1**, using 1 mol % of PdI_2 for 5 h, methyl 5,5-dimethyl-4-methylene-2-phenyl-4,5-dihydrofuran-3-carboxylate (**4a**) was obtained in 65% isolated yield, resulting from 5-*endo-dig* cyclization−alkoxycarbonylation with simultaneous dehydration from the MeC(3)OH moiety (Table 3, entry 1). This yield remained practically the same on working with a higher catalyst loading (Table 3, entry 2). Since this kind of reactivity could represent a convenient entry to an important class of functionalized heterocycles starting from simple and available building blocks, we then applied our method to other similar substrates **3b−e**, bearing different substituents on the triple bond. As shown in Table 3, entries 3−6, the corresponding 4-methylene-4,5-dihydrofuran-3-carboxylates **4b−e** were obtained in good yields with all the substrates tested. In the case of 2,3-dimethylnon-4-yne-2,3-diol (**3b**), better results were obtained working at 80 °C under more concentrated conditions (Table 3, entry 2). The reaction could also be carried out successfully in EtOH as the solvent, as shown by entry 7 (Table 3).

The proposed catalytic cycle for the overall transformation from 3-yne-1,2-diols **1** and **3** to give furan-3-carboxylic esters **2** and methylenedihydrofuran-3-carboxylic esters **4**, respectively, is shown in Scheme 5 (anionic iodide ligands are omitted for clarity). It involves the coordination of the substrate to PdI_2, followed by intramolecular 5-*endo-dig* nucleophilic attack by the hydroxyl group at C-1 at the coordinate triple bond to give the vinylpalladium intermediate **I**. Carbon monoxide insertion, to give acylpalladium complex **II**, followed by nucleophilic displacement by the external alcohol and dehydration (or vice versa) eventually leads to the final product and Pd(0). The latter is then reoxidized back to PdI_2 according to the mechanism shown in Scheme 3.

CONCLUSIONS

In conclusion, we have reported a general, convenient, and atom-economical method for the one-step synthesis of furan-3-carboxylic esters **2** and 4-methylene-4,5-dihydrofuran-3-carboxylic esters **4** starting from very simple building blocks (3-yne-1,2-diol derivatives **1** or **3**, respectively, CO, O_2, and ROH), which are sequentially assembled under the promoting action of the metal catalyst. The catalytic system employed is very simple (PdI_2 + 5 KI), and the reaction conditions, corresponding to an oxidative carbonylation process with only O_2 as the external oxidant, are relatively mild. The generality of the process has been assessed with a variety of differently substituted 3-yne-1,2-diols **1** and **3**, with the corresponding heterocyclic derivatives **2** and **4**, respectively, being consistently obtained in fair to excellent yields.

EXPERIMENTAL SECTION

General Experimental Methods. Melting points are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded at 25 °C in $CDCl_3$ or DMSO-d_6 solutions at 300 and 75 MHz, respectively, with Me_4Si as internal standard. Chemical shifts (δ) and coupling constants (J) are given in ppm and in Hz, respectively. IR spectra were taken with an FT-IR spectrometer. Mass spectra were obtained using a GC-MS apparatus at 70 eV ionization voltage or a mass spectrometer equipped with a turbo ion spray ionization source in the positive mode (ion spray voltage (IS) 4500 V; curtain gas 10 psi; temperature 25 °C; ion source gas (1) 20 psi; declustering and focusing potentials 50 and 400 V, respectively). Microanalyses were carried out at our analytical laboratory. All reactions were analyzed by TLC on silica gel 60 F_{254} or on neutral alumina and by GLC using a gas chromatograph and capillary columns with polymethylsilicone +5% phenylsilicone as the stationary phase. Column chromatography was performed on silica gel 60 (70−230 mesh). Evaporation refers to the removal of solvent under reduced pressure.

Preparation of Substrates 1. Substrates **1** were prepared by alkynylation of the appropriate α-hydroxy aldehyde, α-hydroxy ketone or α-hydroxy ester using an excess of $R^3C{\equiv}CLi$ or $R^3C{\equiv}CMgBr$, as described below.

General Procedure for the Preparation of 3-Yne-1,2-diols 1a,b,e,h,i,k−m,o−r. To a solution of BuLi in hexane (1.6 M; 25 mL, 40 mmol) was added anhydrous THF (6 mL) and hexane (25 mL) under nitrogen. The resulting mixture was cooled to −40 °C and maintained with stirring. A solution of the 1-alkyne (44.5 mmol: 1-hexyne, 3.66 g; *tert*-butylacetylene, 3.66 g; phenylacetylene, 4.54 g; 3-ethynylthiophene, 4.81 g; 1-ethynylcyclohex-1-ene, 4.72 g; *p*-bromophenylacetylene, 8.06 g; *p*-methylphenylacetylene, 5.17 g) in anhydrous THF (6 mL) was added dropwise under nitrogen to the cooled mixture followed by a solution of LiBr (1.56 g, 18.0 mmol) in

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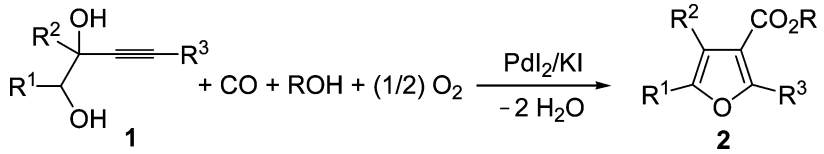
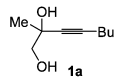
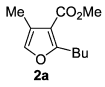
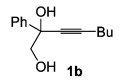
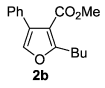
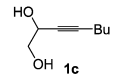
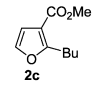
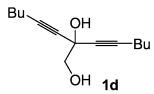
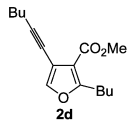
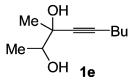
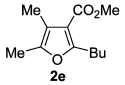
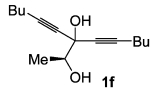
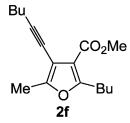
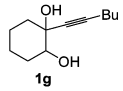
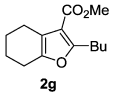
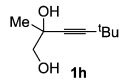
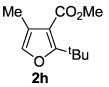
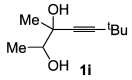
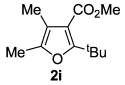
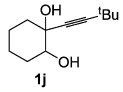
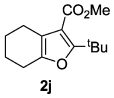
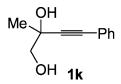
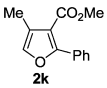
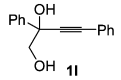
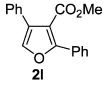
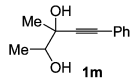
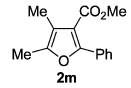
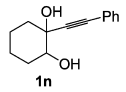
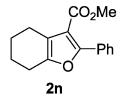
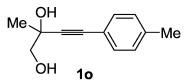
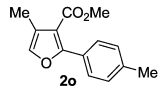
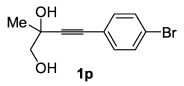
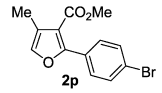
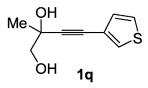
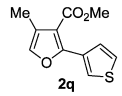
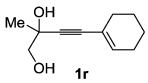
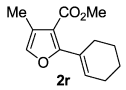
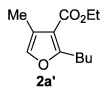
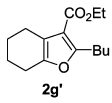
Table 2. Synthesis of Furan-3-carboxylic Esters 2 by PdI_2/KI-Catalyzed Oxidative Carbonylation of 3-Yne-1,2-diols 1 Bearing a Primary or Secondary Alcoholic Group at C-1[a]



entry	1	R	2	yield of 2[b] (%)
1[c]	 1a	Me	 2a	69[d]
2	1a	Me	2a	81
3	 1b	Me	 2b	74
4	 1c	Me	 2c	85
5	 1d	Me	 2d	80
6	 1e	Me	 2e	78
7	 1f	Me	 2f	73
8	 1g	Me	 2g	75
9	 1h	Me	 2h	60
10	 1i	Me	 2i	58
11	 1j	Me	 2j	75
12	 1k	Me	 2k	71
13	 1l	Me	 2l	65
14	 1m	Me	 2m	56
15	 1n	Me	 2n	70
16	 1o	Me	 2o	76
17	 1p	Me	 2p	81
18	 1q	Me	 2q	88
19	 1r	Me	 2r	93
20	1a	Et	 2a′	78
21	1g	Et	 2g′	69

[a]Unless otherwise noted, all carbonylation reactions were carried out at 100 °C for 2 h under 40 atm (at 25 °C) of a 4/1 mixture of CO and air, in ROH as the solvent (0.05 mmol of starting **1**/mL of solvent) in the presence of PdI_2 (2 mol %) and KI (KI/PdI_2 molar ratio of 5). Conversion of **1** was quantitative in all cases. [b]Isolated yield based on starting **1**. [c]The reaction was carried out with 1 mol % of PdI_2. [d]The GLC yield of **2a** was 76%.

anhydrous THF (6 mL). After the mixture was stirred for 0.5 h at −40 °C, a solution of the appropriate α-hydroxy ketone (17 mmol) (α-hydroxyacetone (purity 90%), 1.40 g; 3-hydroxybutan-2-one, 1.50 g; α-hydroxyacetophenone, 2.31 g) in anhydrous THF (5 mL) was added under nitrogen. The mixture was stirred at the same temperature for 2 h, and then it was warmed to room temperature. Saturated aqueous NH_4Cl (40 mL) was added, followed by Et_2O (50 mL). Phases were separated, and the aqueous phase was extracted with Et_2O (50 mL × 3). The collected organic phases were washed with brine to neutral pH and dried over Na_2SO_4. After filtration and evaporation of the solvent, products **1b,e,i,k−m,p,q** were purified by column chromatography on silica gel using the following mixtures as eluent: 6/4 hexane/AcOEt (**1b,l**), 7/3 hexane/AcOEt (**1e,m**), 8/2 hexane/acetone (**1i,q**), 9/1 hexane/acetone (**1k**), 95/5 hexane/

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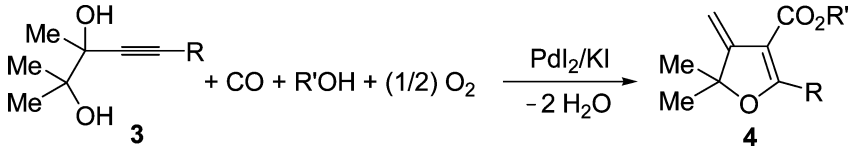
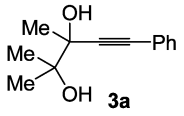
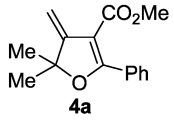
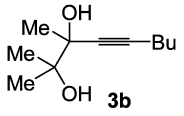
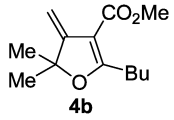
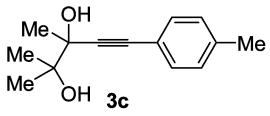
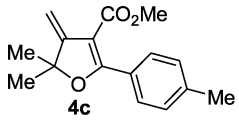
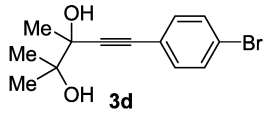
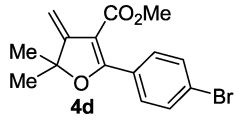
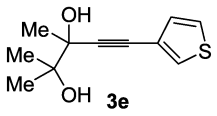
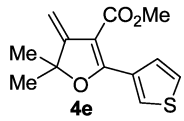
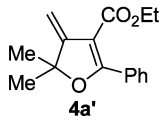
Table 3. Synthesis of 4-Methylene-4,5-dihydrofuran-3-carboxylates 4 by PdI_2/KI-Catalyzed Oxidative Carbonylation of 2-Methyl-3-yne-1,2-diols 3 Bearing a Tertiary Alcoholic Group at C-1[a]



entry	3	R′	4	yield of 4[b] (%)
1	 **3a**	Me	 **4a**	67
2[c]	**3a**	Me	**4a**	66
3[d]	 **3b**	Me	 **4b**	58
4	 **3c**	Me	 **4c**	64
5	 **3d**	Me	 **4d**	63
6	 **3e**	Me	 **4e**	70
7	**3a**	Et	 **4a′**	55

[a]Unless otherwise noted, all carbonylation reactions were carried out at 100 °C for 2 h under 40 atm (at 25 °C) of a 4/1 mixture of CO and air, in ROH as the solvent (0.05 mmol of starting **3**/mL of MeOH) and with a substrate/KI/PdI_2 molar ratio of 100/5/1. Conversion of **3** was quantitative in all cases. [b]Isolated yield based on starting **3**. [c]The reaction was carried out with 2 mol % of catalyst. [d]The reaction was carried out at 80 °C with a substrate concentration of 0.2 mmol of **3b**/mL of MeOH.

acetone (**1p**). Crude products **1a,h,o,r** were sufficiently pure to be used as such for the subsequent carbonylation reaction.

*2-Methyloct-3-yne-1,2-diol (**1a**).* Yield: 2.39 g, starting from 1.40 g of α-hydroxyacetone (90%). Colorless amorphous solid. Mp: 33−35 °C (lit.[10] mp 32−34 °C). IR (KBr): ν 3367 (m, br), 2937 (m), 2247 (w), 1469 (m), 1380 (m), 1256 (m), 1147 (m), 1200 (m), 1059 (m), 950 (m), 919 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.61 (distorted d, J = 11.0, 1 H), 3.47 (distorted d, br, J = 11.0, 1 H), 3.30 (s, br, 2 H), 2.20 (t, J = 6.7, 2 H), 1.54−1.33 (m, 4 H), 1.43 (s, 3 H), 0.91 (t, J = 7.3, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 85.3, 82.1, 71.0, 68.7, 30.9, 25.9, 22.0, 18.4, 13.5. GC-MS (EI, 70 eV): *m/z* 156 (absent) [M^+], 125 (100), 95 (10), 91 (14), 81 (21), 79 (24), 69 (50), 67 (25), 55 (42). Anal. Calcd for $C_9H_{16}O_2$ (156.22): C, 69.19; H, 10.32. Found: C, 69.13; H, 10.35.

*2-Phenyloct-3-yne-1,2-diol (**1b**).* Yield: 3.33 g, starting from 2.31 g of α-hydroxyacetophenone (90%). Yellow oil. IR (film): ν 3341 (m, br), 2931 (m), 2247 (w), 1588 (m), 1495 (m), 1386 (m), 1245 (s), 1074 (m), 1034 (m), 903 (m), 758 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.65−7.58 (m, 2 H), 7.40−7.26 (m, 3 H), 3.69 (distorted dd, J = 10.9, 4.2, 1 H), 3.61 (distorted dd, J = 10.9, 6.3, 1 H), 3.23 (s, 1 H), 2.48−2.38 (m, 1 H), 2.29 (t, J = 6.9, 2 H), 1.60−1.36 (m, 4 H), 0.92 (t, J = 7.3, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.5, 128.3, 128.0, 125.9, 87.8, 80.7, 73.9, 72.3, 30.7, 22.0, 18.5, 13.6. GC-MS (EI, 70 eV): *m/z* 218 (absent) [M^+], 188 (52), 187 (100), 141 (11), 128 (26), 115 (53), 109 (58), 105 (67), 91 (37), 79 (46), 77 (52), 66 (38). Anal. Calcd for $C_{14}H_{18}O_2$ (218.29): C, 77.03; H, 8.31. Found: C, 77.12; H, 8.29.

*3-Methylnon-4-yne-2,3-diol (**1e**).* Yield: 1.71 g, starting from 1.50 g of 3-hydroxybutan-2-one (59%). Mixture of diastereomers A + B, A/B

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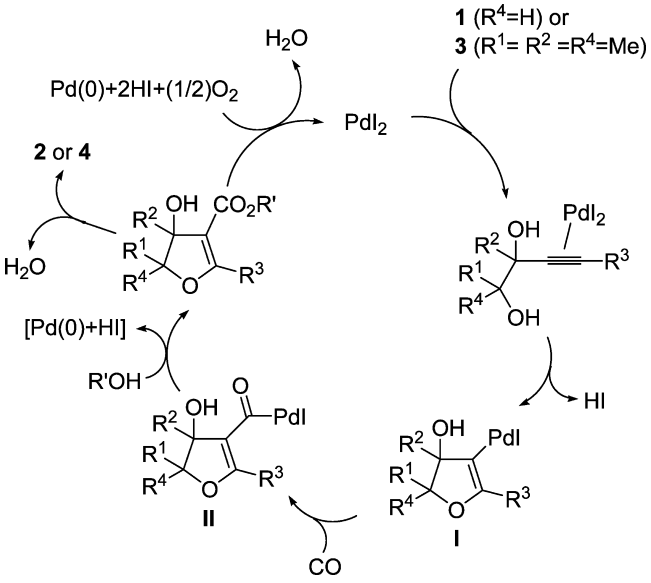
Scheme 5. Proposed Catalytic Cycle for the PdI_2/KI-Catalyzed Oxidative Carbonylation of 3-Yne-1,2-diol Derivatives 1 and 3 Leading to Furan-3-carboxylic and 4-Methylene-5,6-dihydrofuran-3-carboxylic Esters 2 and 4, Respectively



ratio ca. 3/1, determined by ^{1}H NMR. Yellow oil. IR (film): ν 3388 (s, br), 2873 (m), 2244 (m), 1458 (m), 1372 (m), 1107 (m), 1076 (m), 929 (w), 904 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.77 [A (q, 1 H, J = 6.5)], 3.59 [B (q, 1 H, J = 6.5)], 3.13 [B, (s, br, 1 H)], 2.78 [A (s, br, 1 H)], 2.66 [A (s, br, 1 H)], 2.42 [B (s, br, 1 H)], 2.23 [B (t, J = 7.1, 2 H)], 2.20 [A (t, J = 7.1, 2 H)], 1.56−1.35 [A (m, 4 H), + B (m, 4 H)], 1.40 [B (s, 3 H)], 1.39 [A (s, 3 H)], 1.27 [B (d, J = 6.5, 3 H)], 1.22 [A (d, J = 6.5, 3 H)], 0.91 [A (t, J = 7.3, 3 H) + B (t, J = 7.3, 3 H)]. ^{13}C NMR (75 MHz, $CDCl_3$): δ 86.1 (B), 85.5 (A), 82.5 (A + B), 74.5 (B), 74.0 (A), 72.1 (B), 71.3 (A), 30.9 (B), 30.8 (A), 26.1 (A + B), 23.7 (B), 22.0 (A), 18.3 (B), 16.7 (A), 13.6 (B), 13.5 (A). MS (ESI +, direct infusion) m/z 193 [(M + Na)$^+$]. Anal. Calcd for $C_{10}H_{18}O_2$ (170.25): C, 70.55; H, 10.66. Found: C, 70.61; H, 10.64.

*2,5,5-Trimethylhex-3-yne-1,2-diol (**1h**).* Yield: 2.12 g, starting from 1.40 g of α-hydroxyacetone (80%). Colorless amorphous solid. Mp: 90−91 °C (lit.[11] mp 95.5−96 °C). IR (KBr): ν 3362 (m, br), 3222 (m, br), 2968 (m), 2226 (vw), 1458 (m), 1422 (m), 1360 (m), 1267 (m), 1188 (m), 1147 (m), 1059 (s), 960 (m), 716 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.61 (distorted d, J = 11.0, 1 H), 3.46 (distorted d, J = 11.0, 1 H), 3.39 (s, br, 1 H), 3.05 (s, br, 1 H), 1.43 (s, 3 H), 1.21 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 93.6, 80.3, 70.9, 68.6, 31.1, 27.3, 25.8. GC-MS (EI, 70 eV): m/z 156 (M$^+$, absent), 125 (100), 107 (14), 95 (18), 91 (20), 79 (24), 69 (22), 67 (20), 57 (16). Anal. Calcd for $C_9H_{16}O_2$ (156.22): C, 69.19; H, 10.32. Found: C, 69.12; H, 10.34.

*3,6,6-Trimethylhept-4-yne-2,3-diol (**1i**).* Mixture of diastereomers A + B, A/B ratio ca. 2.5/1, determined by ^{1}H NMR. Yield: 1.88 g, starting from 1.50 g of 3-hydroxybutan-2-one (65%). Colorless amorphous solid. Mp: 50−52 °C. IR (KBr): ν 3427 (s, br), 3231 (m, br), 2968 (m), 2220 (vw), 1631 (m), 1456 (m), 1384 (m), 1268 (m), 1099 (m), 1011 (w), 974 (m), 927 (m), 894 (w), 842 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.76 [A (q, J = 6.1, 1 H)], 3.58 [B (q, J = 6.1, 1 H)], 3.10 [B (s, br, 1 H)], 2.78 [A (s, br, 1 H)], 2.65 [A (s, br, 1 H)], 2.35 [B (s, br, 1 H)], 1.39 [B (s, 3 H)], 1.38 [A (s, 3 H)], 1.26 [B (d, J = 6.1, 3 H)], 1.22 [B (s, 9 H)], 1.21 [A (s, 9 H)], 1.21 [A (d, J = 6.1, 3 H)]. ^{13}C NMR (75 MHz, $CDCl_3$): δ 94.4 (B), 93.9 (A), 80.9 (A + B), 74.4 (B), 74.0 (A), 71.8 (B), 71.2 (A), 31.1 (B), 31.0 (A), 27.3 (B), 26.2 (A), 23.6 (A + B), 18.4 (B), 16.8 (A). MS (ESI+, direct infusion): m/z 193 [(M + Na)$^+$]. Anal. Calcd for $C_{10}H_{18}O_2$ (170.25): C, 70.55; H, 10.66. Found: C, 70.61; H, 10.63.

*2-Methyl-4-phenylbut-3-yne-1,2-diol (**1k**).* Yield: 2.55 g, starting from 1.40 g of α-hydroxyacetone (85%). Colorless amorphous solid. Mp: 105−106 °C (lit.[12] mp 105−106 °C). IR (KBr): ν 3398 (s, br), 2977 (w), 2932 (m), 2232 (vw), 1491 (m), 1403 (m), 1376 (m), 1341 (m), 1283 (m), 1136 (m), 1090 (m), 1050 (s), 1028 (m), 986 (w), 900 (m), 764 (s), 696 (m), 677 (m) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.45−7.33 (m, 5 H), 5.42 (s, 1 H), 5.02 (t, J = 6.3, 1 H), 3.52−3.26 (m, 2 H), 1.42 (s, 3 H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 131.2, 128.5, 128.2, 122.7, 94.2, 81.9, 69.6, 67.7, 26.2. GC-MS (EI, 70 eV): m/z 176 (3) [M$^+$], 146 (18), 145 (100), 129 (11), 115 (11), 102 (8), 77 (10). Anal. Calcd for $C_{11}H_{12}O_2$ (176.21): C, 74.98; H, 6.86. Found: C, 75.12; H, 6.84.

*2,4-Diphenylbut-3-yne-1,2-diol (**1l**).* Yield: 3.44 g, starting from 2.31 g of α-hydroxyacetophenone (85%). Colorless amorphous solid. Mp: 104−105 °C (lit.[13] mp 106 °C). IR (KBr): ν 3352 (s, br), 3222 (s, br), 2215 (w), 1489 (m), 1412 (m), 1100 (m), 1069 (s), 1033 (m), 903 (m), 758 (s), 690 (m) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.70−7.64 (m, 2 H), 7.51−7.45 (m, 2 H), 7.42−7.26 (m, 6 H), 3.89−3.67 (m, 2 H), 3.54 (s, br, 1 H), 2.65 (s, br, 1 H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 141.04, 141.01, 131.9, 128.8, 128.43, 128.38, 128.26, 126.0, 89.5, 86.7, 74.2, 72.2. GC-MS (EI, 70 eV): m/z 238 (<0.5) [M$^+$], 208 (49), 207 (100), 191 (13), 189 (15), 178 (18), 130 (24), 129 (93), 105 (66), 77 (54). Anal. Calcd for $C_{16}H_{14}O_2$ (238.28): C, 80.65; H, 5.92. Found: C, 80.71; H, 5.90.

*3-Methyl-5-phenylpent-4-yne-2,3-diol (**1m**).* Mixture of diastereomers A + B, A/B ratio ca. 1.5/1, determined by ^{1}H NMR. Yield: 1.91 g, starting from 1.50 g of 3-hydroxybutan-2-one (59%). Colorless amorphous solid. Mp: 61−62 °C. IR (KBr): ν 3568 (m, br), 3301 (m, br), 2986 (m), 2231 (w), 1598 (w), 1490 (m), 1443 (m), 1370 (m), 1123 (s), 1077 (m), 961 (m), 939 (m), 846 (w), 756 (s), 691 (s) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.48−7.39 [A (m, 2 H) + B (m, 2 H)], 7.35−7.28 [A (m, 3 H) + B (m, 3 H)], 3.92 [A (q, J = 6.2, 1 H)], 3.71 [B (q, J = 6.2, 1 H)], 2.93 [B (s, br, 1 H)], 2.44 [A (s, br, 1 H)], 2.34 [A (s, br, 1 H)], 2.03 [B (s, br, 1 H)], 1.53 [B (s, 3 H)], 1.52 [A (s, 3 H)], 1.38 [B (distorted d, J = 6.2, 3 H), 1.31 [A (distorted d, J = 6.2)]. ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.86 (B), 131.82 (A), 128.61 (A), 128.56 (B), 128.4 (A + B), 122.6 (A or B), 122.5 (B or A), 91.2 (A), 89.9 (B), 85.5 (B), 84.9 (A), 74.6 (B), 73.9 (A), 72.5 (B), 71.8 (A), 25.9 (B), 23.6 (A), 18.6 (B), 16.8 (A). MS (ESI+, direct infusion): m/z 213 [(M + Na)$^+$]. Anal. Calcd for $C_{12}H_{14}O_2$ (190.24): C, 75.76; H, 7.42. Found: C, 75.83; H, 7.40.

*2-Methyl-4-p-tolylbut-3-yne-1,2-diol (**1o**).* Yield: 2.72 g, starting from 1.40 g of α-hydroxyacetone (84%). Colorless amorphous solid. Mp: 89−90 °C (lit.[14] mp 88−90 °C). IR (KBr): ν 3386 (s, br), 3312 (s, br), 2235 (vw), 1637 (m), 1510 (m), 1384 (m), 1265 (m), 1122 (m), 1057 (m), 951 (w), 815 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35−7.26 (m, 2 H), 7.11−7.03 (m, 2 H), 3.75 (distorted d, J = 11.2, 1 H), 3.57 (distorted d, J = 11.2, 1 H), 3.39 (s, br, 2 H), 2.31 (s, 3 H), 1.52 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.6, 131.7, 129.0, 119.2, 89.9, 84.5, 70.6, 69.0, 25.4, 21.5. GC-MS (EI, 70 eV): m/z 190 (6) [M$^+$], 172 (3), 159 (100), 143 (9), 128 (10), 115 (25), 91 (6), 89 (6), 77 (5). Anal. Calcd for $C_{12}H_{14}O_2$ (190.24): C, 75.76; H, 7.42. Found: C, 75.81; H, 7.41.

*4-(4-Bromophenyl)-2-methylbut-3-yne-1,2-diol (**1p**).* Yield: 3.47 g, starting from 1.40 g of α-hydroxyacetone (80%). Yellow amorphous solid. Mp: 84−85 °C. IR (KBr): ν 3304 (s, br), 2930 (m), 2233 (vw), 1490 (m), 1384 (m), 1139 (m), 1064 (s), 952 (m), 755 (s), 669 (s) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.50−7.23 (m, 4 H), 5.40 (s, 1 H), 5.00 (t, br, J = 6.2, 1 H), 3.49−3.34 (m, 2 H), 1.40 (s, 3 H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 131.2, 128.5, 125.8, 122.6, 94.2, 81.8, 69.5, 67.7, 26.2. GC-MS (EI, 70 eV): m/z 254 (absent) [M$^+$], 176 (2), 145 (100), 129 (11), 115 (11), 102 (8), 89 (4), 77 (11). Anal. Calcd for $C_{11}H_{11}BrO_2$ (255.11): C, 51.79; H, 4.35; Br, 31.32. Found: C, 51.81; H, 4.31; Br, 31.30.

*2-Methyl-4-thiophen-3-ylbut-3-yne-1,2-diol (**1q**).* Yield: 2.63 g, starting from 1.40 g of α-hydroxyacetone (85%). Yellow amorphous solid. Mp: 81.0−83.0 °C. IR (KBr): ν 3334 (s, br), 3237 (s, br), 2232 (vw), 1384 (m), 1357 (w), 1168 (m), 1127 (m), 1053 (s), 952 (w), 780 (s), 627 (m) cm^{-1}. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.74−7.64 (m, 1 H), 7.58 (dd, J = 4.9, 3.2, 1 H), 7.11 (d, br, J = 4.9, 1 H), 5.37 (s, 1 H), 4.98 (t, J = 6.1, 1 H), 3.50−3.31 (m, 2 H), 1.38 (s, 3 H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 129.5, 128.9, 126.4, 121.5, 93.4, 77.3,

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69.5, 67.7, 26.2. GC-MS (EI, 70 eV): m/z 182 (7) [M^+], 151 (100), 135 (9), 121 (5), 109 (11), 89 (5), 77 (6), 63 (14). Anal. Calcd for $C_9H_{10}O_2S$ (182.24): C, 59.32; H, 5.53; S, 17.59. Found: C, 59.39; H, 5.51; S; 17.58.

*4-Cyclohex-1-enyl-2-methylbut-3-yne-1,2-diol (**1r**).* Yield: 2.57 g, starting from 1.40 g of α-hydroxyacetone (84%). Yellow amorphous solid. Mp: 33−34 °C. IR (KBr): ν 3447 (s, br), 2933 (w), 2218 (vw), 1631 (m), 1384 (s), 1056 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 6.16−6.04 (m, 1 H), 3.81−3.21 (m, 2 H), 3.66 (distorted d, J = 11.3, 1 H), 3.50 (distorted d, J = 11.3, 1 H), 2.17−2.01 (m, 4 H), 1.69−1.52 (m, 4 H), 1.46 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.5, 119.9, 87.9, 86.1, 70.6, 68.8, 29.2, 25.6, 25.5, 22.2, 21.4. GC-MS (EI, 70 eV): m/z 180 (9) [M^+], 150 (18), 149 (100), 115 (3), 105 (9), 91 (19), 79 (15), 77 (16), 65 (7). Anal. Calcd for $C_{11}H_{16}O_2$ (180.24): C, 73.30; H, 8.95. Found: C, 73.38; H, 8.93.

Preparation of Oct-3-yne-1,2-diol (1c). To a suspension of Mg turnings (1.88 g, 77.4 mmol) in anhydrous THF (16 mL), maintained under nitrogen and under reflux, was added pure ethyl bromide (1.4 mL) to start the formation of the Grignard reagent. The remaining bromide was added dropwise in THF solution (4.0 mL of EtBr in 44 mL of THF; total amount of EtBr added 7.88 g, 72.3 mmol). The mixture was then refluxed for an additional 20 min. After cooling, the resulting solution of EtMgBr was transferred under nitrogen to a dropping funnel and added dropwise under nitrogen to a solution of 1-hexyne (5.91 g, 71.9 mmol) in anhydrous THF (21.6 mL) at 0 °C with stirring. After additional stirring at 0 °C for 15 min, the mixture was warmed to room temperature and then maintained at 50 °C for 2 h. While warm (ca. 40−45 °C), the solution of 1-hexynylmagnesium bromide thus obtained was then added dropwise under nitrogen to a preheated (50 °C) solution of glycolaldehyde (36 mmol) in anhydrous THF (obtained from glycolaldehyde dimer (2.16 g) in anhydrous THF (44 mL)). The resulting mixture was stirred at 50 °C for an additional 2 h. After the mixture was cooled to room temperature, saturated NH_4Cl (100 mL) and AcOEt (40 mL) were sequentially added. Phases were separated, and the aqueous phase was extracted with AcOEt (3 × 100 mL). The collected organic layers were washed with brine and dried over Na_2SO_4. After filtration and evaporation of the solvent, the product was purified by column chromatography on silica gel using 6/4 hexane/acetone as the eluent to give pure oct-3-yne-1,2-diol (**1c**). Yield: 2.10 g, starting from 2.16 g of glycolaldehyde dimer (41%). Colorless oil. IR (film): ν 3397 (m, br), 2957 (m), 2239 (w), 1647 (m), 1464 (w), 1149 (m), 1087 (m), 1039 (m), 876 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.48−4.41 (m, 1 H), 3.71 (distorted dd, J = 11.3, 3.4, 1 H), 3.61 (distorted dd, J = 11.3, 7.3, 1 H), 3.51 (s, br, 1 H), 3.29 (s, br, 1 H), 2.21 (td, J = 7.1, 2.0, 2 H), 1.55−1.32 (m, 4 H), 0.91 (t, J = 7.3, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 87.2, 78.0, 67.0, 63.6, 30.7, 22.0, 18.4, 13.5. GC-MS (EI, 70 eV): m/z 142 (absent) [M^+], 125 (77), 111 (43), 110 (11), 107 (16), 95 (20), 93 (47), 91 (37), 83 (27), 79 (27), 77 (29), 71 (40). Anal. Calcd for $C_8H_{14}O_2$ (142.20): C, 67.57; H, 9.92. Found: C, 67.53; H, 9.90.

Preparation of 3-Yne-1,2-diols 1g,j,n. To a cooled (0 °C), stirred solution of the 1-alkyne (30.8 mmol: 1-hexyne, 3.66 g; *tert*-butylacetylene, 3.66 g; phenylacetylene, 4.54 g; 3-ethynylthiophene, 4.81 g; 1-ethynylcyclohex-1-ene, 4.72 g; *p*-bromophenylacetylene, 8.06 g; *p*-methylphenylacetylene, 5.17 g) in anhydrous THF (75 mL) maintained under nitrogen was added dropwise a solution of BuLi in hexane (1.6 M; 19.3 mL, 30.9 mmol). The resulting mixture was stirred at 0 °C for 0.5 h. Dodecahydrodibenzo[*b*,*e*][1,4]dioxine-4a,9a-diol (2-hydroxycyclohexanone dimer; 1.60 g, 7.0 mmol, corresponding to 14.0 mmol of 2-hydroxycyclohexanone) was added under nitrogen in portions. After additional stirring at 0 °C for an additional 0.5 h, the mixture was warmed to room temperature and then saturated aqueous NH_4Cl was added followed by Et_2O (50 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (50 mL × 3). The collected organic phases were washed with brine to neutral pH and dried over Na_2SO_4. After filtration and evaporation of the solvent, crude products **1g,j,n** were sufficiently pure to be used as such for the carbonylation reaction.

*1-Hex-1-ynylcyclohexane-1,2-diol (**1g**).* Mixture of diastereomers A + B, A/B ratio ca. 1.1:1, determined by ^1H NMR. Yield: 2.39 g, starting from 1.60 g of 2-hydroxycyclohexanone dimer (87%). Yellow oil. IR (film): ν 3410 (m, br), 2934 (s), 2854 (m), 2238 (w), 1449 (s), 1250 (w), 1172 (w), 1063 (s), 1000 (m), 866 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.70 [A (dd, J = 7.3, 4.0, 1 H)], 3.39 [B (dd, J = 11.3, 4.4, 1 H)], 2.89 [A (s, br, 2 H) + B (s, br, 2 H)], 2.26 [B (t, J = 6.9, 2 H)], 2.21 [B (t, J = 6.7, 2 H)], 2.06−1.85 [A (m, 2 H) + B (m, 2 H)], 1.83−1.23 [A (m, 10 H) + B (m, 10 H)], 0.92 [B (t, J = 7.3, 3 H)], 0.91 [A (t, J = 7.3, 3 H)]. ^{13}C NMR (75 MHz, $CDCl_3$): δ 88.1 (A or B), 85.5 (B or A), 82.6 (A or B), 79.6 (B or A), 77.0 (A or B), 74.2 (B or A), 74.0 (A or B), 70.3 (B or A), 38.0 (A or B), 35.6 (B or A), 32.1 (A or B), 30.9 (B or A), 30.8 (A or B), 28.7 (B or A), 24.2 (A or B), 23.3 (B or A), 22.02 (A or B), 21.98 (B or A), 21.61 (A or B), 21.56 (B or A), 18.4 (A + B), 13.6 (A + B). GC-MS (EI, 70 eV): A: m/z 196 (absent) [M^+], 168 (3), 154 (86), 149 (9), 137 (46), 136 (30), 121 (27), 118 (44), 108 (71), 107 (60), 97 (31), 95 (56), 94 (39), 93 (57), 91 (52), 81 (54), 79 (98), 68 (71), 67 (70), 55 (100); B: m/z 196 (absent) [M^+], 168 (3) 154 (91), 149 (7), 137 (42), 136 (28), 121 (28), 118 (48), 108 (68), 107 (60), 97 (37), 95 (55), 94 (34), 93 (56), 91 (47), 81 (54), 79 (90), 77 (48), 69 (55), 68 (75), 67 (69), 55 (100). Anal. Calcd for $C_{12}H_{20}O_2$ (196.29): C, 73.43; H, 10.27. Found: C, 73.51; H, 10.25.

*1-(3,3-Dimethylbut-1-ynyl)cyclohexane-1,2-diol (**1j**).* Mixture of diastereomers A + B, A/B ratio ca. 1/1, determined by ^1H NMR. Yield: 2.28 g, starting from 1.60 g of 2-hydroxycyclohexanone dimer (83%). Colorless amorphous solid. Mp: 67−68 °C. IR (KBr): ν 3387 (s, br), 2966 (m), 2939 (m), 2861 (m), 2233 (vw), 1633 (m), 1384 (m), 1361 (w), 1263 (m), 1079 (m), 997 (w), 866 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.70 [A (dd, J = 6.5, 4.0, 1 H)], 3.38 [B (dd, J = 11.1, 4.2, 1 H)], 2.90 [A (s, br, 2 H) + B (s, br, 2 H)], 2.07−1.85 [A (m, 2 H) + B (m, 2 H)], 1.83−1.23 [A (m, 6 H) + B (m, 6 H)], 1.25 [A or B (s, 9 H)], 1.22 [B or A (s, 9 H)]. ^{13}C NMR (75 MHz, $CDCl_3$): δ 96.7 (A or B), 94.1 (B or A), 80.8 (A or B), 77.9 (B or A), 77.5 (A or B), 74.0 (B or A), 73.8 (A or B), 70.1 (B or A), 38.0 (A or B), 35.3 (B or A), 32.2 (A or B), 31.1 (B or A), 31.0 (A or B), 28.7 (B or A), 27.4 (A or B), 27.3 (B or A), 24.2 (A or B), 23.3 (B or A), 21.9 (A or B), 21.1 (B or A). GC-MS (EI, 70 eV): A or B: m/z 196 (absent) [M^+], 181 (3), 163 (6), 145 (4), 135 (14), 126 (22), 111 (100), 109 (24), 107 (21), 95 (20), 93 (29), 91 (28), 83 (25), 81 (22), 79 (31), 77 (24), 67 (36), 57 (37), 55 (37); B or A: m/z 196 (absent) [M^+], 181 (4), 163 (8), 145 (5), 137 (13), 135 (16), 126 (22), 111 (100), 109 (28), 107 (25), 95 (21), 93 (30), 91 (30), 83 (24), 81 (24), 79 (33), 77 (25), 67 (37), 57 (35), 55 (38). Anal. Calcd for $C_{12}H_{20}O_2$ (196.29): C, 73.43; H, 10.27. Found: C, 73.52; H, 10.25.

*1-Phenylethynylcyclohexane-1,2-diol (**1n**).* Mixture of diastereomers A + B, A/B ratio ca. 1/1, determined by ^1H NMR. Yield: 2.39 g, starting from 1.60 g of 2-hydroxycyclohexanone dimer (79%). Yellow oil. IR (film): ν 3369 (m, br), 2937 (s), 2860 (m), 2225 (vw), 1598 (w), 1489 (m), 1443 (m), 1385 (m), 1353 (m), 1268 (m), 1059 (s), 1008 (m), 972 (w), 949 (w), 867 (m), 755 (s), 691 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.51−7.39 [A (m, 2 H), + B (m, 2 H)], 7.35−7.20 [A (m, 3 H), + B (m, 3 H)], 3.85 [A (dd, J = 7.3, 4.0, 1 H)], 3.52 [B (dd, J = 11.3, 4.4, 1 H)], 3.37 [A (s, br, 2 H) + B (s, br, 2 H)], 2.21−1.15 [A (m, 8 H) + B (m, 8 H)]. ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.1 (A or B), 131.8 (B or A), 131.7 (A or B), 128.41 (B or A), 128.37 (A or B), 128.28 (B or A), 128.23 (A or B), 122.5 (B or A), 91.6 (A or B), 88.8 (B or A), 87.3 (A or B), 84.8 (B or A), 77.2 (A or B), 74.4 (B or A), 73.9 (A or B), 70.6 (B or A), 37.9 (A or B), 35.4 (B or A), 32.0 (A or B), 28.9 (B or A), 24.2 (A or B), 23.3 (B or A), 21.56 (A or B), 21.47 (B or A). GC-MS (EI, 70 eV): A or B: m/z 216 (13) [M^+], 198 (5), 187 (12), 170 (20), 157 (42), 154 (20), 146 (100), 145 (57), 141 (39), 131 (78), 129 (93), 115 (85), 103 (37), 102 (45), 97 (28), 91 (42), 77 (45), 75 (23), 55 (43); B: m/z 216 (16) [M^+], 198 (6), 187 (15), 170 (24), 157 (49), 146 (97), 145 (56), 142 (31), 141 (45), 131 (79), 129 (100), 115 (97), 103 (38), 102 (50), 97 (34), 91 (46), 77 (50), 55 (48). Anal. Calcd for $C_{14}H_{16}O_2$ (216.28): C, 77.75; H, 7.46. Found: C, 77.82; H, 7.44.

Preparation of 1,1-Dialkynyl-1,2-diols 1d,f. A solution of 1-hexyne (4.19 g, 51.0 mmol) in anhydrous THF (8 mL) was added

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dropwise under nitrogen to a stirred, cooled (−78 °C) mixture of BuLi (34 mL of a 1.6 M solution in hexanes, 54.4 mmol) in anhydrous THF (22 mL) and anhydrous hexane (34 mL). To the resulting mixture, maintained at −78 °C, was added, with stirring, a solution of LiBr (2.13 g, 24.5 mmol) in THF (7 mL). After 0.5 h, the appropriate α-hydroxyacetic acid ester (17 mmol: α-hydroxyacetic acid methyl ester, 1.53 g; (*S*)-α-hydroxypropionic acid ethyl ester, 2.01 g) diluted in anhydrous THF (5 mL) was slowly added under nitrogen at the same temperature. The resulting mixture was stirred for an additional 2 h and then warmed to room temperature. After quenching with a saturated solution of NH_4Cl (20 mL), the mixture was extracted with Et_2O (3 × 50 mL). The combined organic layers were washed with water (40 mL) and then dried oven Na_2SO_4. After filtration and evaporation of the solvent, the crude products were purified by column chromatography using 8/2 hexane/AcOEt as eluent.

*2-Hex-1-ynyloct-3-yne-1,2-diol (**1d**).* Yield: 2.80 g, starting from 1.53 g of α-hydroxyacetic acid methyl ester (74%). Yellow solid. Mp: 30−32 °C. IR (KBr): ν 3339 (m, br), 2934 (m), 2241 (w), 1465 (w), 1382 (w), 1263 (m), 1175 (m), 1084 (m), 912 (w), 679 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.70 (s, 2 H), 3.00 (s, br, 2 H), 2.24 (t, *J* = 6.9, 4 H), 1.60−1.30 (m, 8 H), 0.91 (t, *J* = 7.1, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 85.4, 78.5, 71.0, 64.5, 30.5, 22.0, 18.4, 13.6. GC-MS (EI, 70 eV): *m*/*z* 222 (absent) [M^+], 192 (15), 191 (100), 135 (3), 115 (4), 105 (7), 91 (17), 79 (20), 77 (12). Anal. Calcd for $C_{14}H_{22}O_2$ (222.32): C, 75.63; H, 9.97. Found: C, 75.55; H, 9.99.

*(S)-3-Hex-1-ynylnon-4-yne-2,3-diol (**1f**).* Yield: 3.21 g, 80% based on (*S*)-α-hydroxypropionic acid ethyl ester. Yellow oil. $[\alpha]^{25}_D$(MeOH, $c = 9.1 \times 10^{-3}$ g mL^{-1}) = −22°. IR (film): ν 3399 (m, br), 2933 (m), 2237 (w), 1466 (w), 1378 (w), 1363 (w), 1270 (w), 1119 (m), 1012 (m), 889 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.90−3.77 (m, 1 H), 3.37 (s, br, 1 H), 2.70 (s, br, 1 H), 2.29−2.19 (m, 4 H), 1.58−1.33 (m, 8 H), 1.37 (d, *J* = 6.5, 3 H), 0.96−0.87 (m, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 85.9, 85.4, 79.1, 77.8, 74.4, 68.0, 30.5, 30.4, 22.00, 21.97, 18.44, 18.40, 17.5, 13.6. GC-MS (EI, 70 eV): *m*/*z* 236 (absent) [M^+], 191 (73), 150 (16), 131 (28), 121 (75), 117 (50), 108 (100), 107 (61), 91 (99), 79 (81). Anal. Calcd for $C_{15}H_{24}O_2$ (236.35): C, 76.23; H, 10.24. Found: C, 76.13; H, 10.25.

PdI_2/KI-Catalyzed Oxidative Carbonylation of 2-Methyloct-3-yne-1,2-diol (1a) Leading to a Mixture of Methyl 2-Butyl-4-methylfuran-3-carboxylate (2a) and 2-Hydroxy-2-methyloct-3-ynyl 2-Butyl-4-methylfuran-3-carboxylate (5a) (Table 1, Entry 7). A 50 mL stainless steel autoclave was charged in the presence of air with PdI_2 (5.0 mg, 1.39×10^{-2} mmol), KI (23.0 mg, 0.14 mmol), anhydrous MeOH (5.6 mL), and 2-methyloct-3-yne-1,2-diol (**1a**; 217 mg, 1.39 mmol). The autoclave was sealed and, while the mixture was stirred, the autoclave was pressurized with CO (32 atm) and air (up to 40 atm). After the mixture was stirred at 80 °C for 2 h, the autoclave was cooled, degassed, and opened. GLC-MS analysis of the crude reaction mixture was consistent with the formation of methyl 2-butyl-4-methylfuran-3-carboxylate (**2a**; 49% GLC yield) and 2-hydroxy-2-methyloct-3-ynyl 2-butyl-4-methylfuran-3-carboxylate (**5a**; 32% GLC yield). After evaporation of the solvent, only compound **2a** could be isolated in a pure state by column chromatography on silica gel using 99/1 hexane/Et_2O as eluent. Compound **2a** was then fully characterized by spectroscopic techniques and elemental analysis (see below). The GC-MS spectrum of **5a** (EI, 70 eV) was in agreement with the proposed structure: *m*/*z* 302 (14) [M^+], 259 (14), 245 (100), 217 (14), 203 (27), 189 (8), 175 (28), 135 (40), 123 (34), 91 (11), 77 (14), 65 (19). Additional evidence for the proposed structure for **5a** was the observation that, when the carbonylation reaction was carried out for a longer reaction time (8−15 h), partial conversion of **5a** into **2a** was observed, deriving from methanolysis of the estereal linkage of **5a**.

General Procedure for the Synthesis of Furan-3-carboxylic Esters 2a−r. A 250 mL stainless steel autoclave was charged in the presence of air with PdI_2 (5.0 mg, 1.39×10^{-2} mmol or 10.0 mg, 2.78×10^{-2} mmol; see Table 2), KI (11.5 mg, 6.93×10^{-2} mmol or 23.0 mg, 0.14 mmol; see Table 2), anhydrous ROH (R = Me, Et, 28 mL), and the 3-yne-1,2-diol **1a−r** (1.39 mmol). The autoclave was sealed and, while the mixture was stirred, the autoclave was pressurized with CO (32 atm) and air (up to 40 atm). After the mixture was stirred at 100 °C for the required time (see Table 2), the autoclave was cooled, degassed, and opened. The solvent was evaporated, and the products **2a−r** were purified by column chromatography on silica gel using the following mixtures as eluent: 9/1 hexane/acetone (**2a**,**e**,**k**,**p**,**r**), 98/2 hexane/AcOEt (**2a′**), 95/5 hexane/AcOEt (**2b**,**h**,**l**), 6/4 hexane/acetone (**2c**), 99/1 hexane/AcOEt (**2d**,**f**), 9/1 hexane/AcOEt (**2g**,**n**,**o**), 8/2 hexane/acetone (**2i**,**j**), 8/2 hexane/AcOEt (**2m**), 7/3 hexane/acetone (**2q**).

*Methyl 2-Butyl-4-methylfuran-3-carboxylate (**2a**).* Yield: 220 mg, starting from 217.0 mg of **1a** (81%) (Table 2, entry 2). Yellow oil. IR (film): ν 2957 (m), 1739 (s), 1442 (m), 1391 (w), 1256 (m), 971 (w), 763 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.04 (s, br, 1 H), 3.82 (s, 3 H), 2.98−2.90 (m, 2 H), 2.13 (s, br, 3 H), 1.69−1.57 (m, 2 H), 1.42−1.28 (m, 2 H), 0.92 (t, *J* = 7.3, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.2, 164.3, 137.9, 121.2, 113.2, 50.8, 30.2, 27.9, 22.4, 13.7, 9.9. GC-MS (EI, 70 eV): *m*/*z* 196 (25) [M^+], 167 (11), 165 (12), 154 (32), 153 (100), 139 (32), 137 (16), 135 (44), 123 (47), 122 (16), 121 (29), 95 (15), 79 (11), 77 (18), 65 (45). Anal. Calcd for $C_{11}H_{16}O_3$ (196.24): C, 67.32; H, 8.22. Found: C, 67.23; H, 8.24.

*Ethyl 2-Butyl-4-methylfuran-3-carboxylate (**2a′**).* Yield: 228 mg, starting from 217.0 mg of **1a** (78%) (Table 2, entry 20). Colorless oil. IR (film): ν 2960 (m), 2932 (m), 1720 (s), 1608 (w), 1557 (w), 1383 (w), 1267 (m), 1073 (m), 1029 (w), 787 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.04 (q, *J* = 1.3, 1 H), 4.29 (q, *J* = 7.2, 2 H), 2.98−2.91 (m, 2 H), 2.14 (d, *J* = 1.3, 3 H), 1.69−1.58 (m, 2 H), 1.42−1.26 (m, 2 H), 1.35 (t, *J* = 7.2, 3 H), 0.92 (t, *J* = 7.5, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.8, 164.1, 137.8, 121.2, 113.2, 59.8, 30.3, 28.0, 22.4, 14.4, 13.8, 10.0. GC-MS (EI, 70 eV): *m*/*z* 210 (29) [M^+], 181 (18), 168 (14), 167 (13), 165 (12), 140 (11), 139 (100), 135 (15), 123 (13), 121 (10), 95 (6), 77 (6), 65 (9). Anal. Calcd for $C_{12}H_{18}O_3$ (210.27): C, 68.54; H, 8.63. Found: C, 68.53; H, 8.64.

*Methyl 2-Butyl-4-phenylfuran-3-carboxylate (**2b**).* Yield: 265 mg, starting from 303.5 mg of **1b** (74%) (Table 2, entry 3). Colorless oil. IR (film): ν 2963 (m), 1718 (s), 1438 (m), 1391 (m), 1292 (m), 1121 (m), 1038 (w), 758 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.38−7.29 (m, 5 H), 7.27 (s, 1 H), 3.70 (s, 3 H), 3.04−2.96 (m, 2 H), 1.76−1.64 (m, 2 H), 1.47−1.33 (m, 2 H), 0.95 (t, *J* = 7.3, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.6, 164.2, 138.4, 132.2, 129.2, 127.9, 127.3, 112.3, 51.0, 30.2, 27.9, 22.4, 13.8. GC-MS (EI, 70 eV): *m*/*z* 258 (41) [M^+], 226 (17), 215 (39), 197 (100), 183 (54), 155 (23), 141 (12), 128 (34), 127 (49), 115 (28), 77 (19). Anal. Calcd for $C_{16}H_{18}O_3$ (258.31): C, 74.39; H, 7.02. Found: C, 74.29; H, 7.03.

*Methyl 2-Butylfuran-3-carboxylate (**2c**).* Yield: 215 mg, starting from 197.5 mg of **1c** (85%) (Table 2, entry 4). Colorless oil. IR (film): ν 2962 (m), 1720 (s), 1605 (m), 1442 (m), 1307 (m), 1201 (m), 1123 (w), 1039 (m), 736 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.24 (d, *J* = 2.0, 1 H), 6.63 (d, *J* = 2.0, 1 H), 3.82 (s, 3 H), 3.00 (t, *J* = 7.7, 2 H), 1.72−1.59 (m, 2 H), 1.42−1.29 (m, 2 H), 0.93 (t, *J* = 7.3, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.5, 163.5, 140.4, 113.0, 110.7, 51.2, 30.1, 27.3, 22.3, 13.7. GC-MS (EI, 70 eV): *m*/*z* 182 (56) [M^+], 153 (42), 151 (25), 140 (8), 139 (87), 125 (47), 121 (74), 109 (100), 81 (23). Anal. Calcd for $C_{10}H_{14}O_3$ (182.22): C, 65.91; H, 7.74. Found: C, 65.79; H, 7.72.

*Methyl 2-Butyl-4-hex-1-ynylfuran-3-carboxylate (**2d**).* Yield: 290 mg, starting from 309.5 mg of **1d** (80%) (Table 2, entry 5). Yellow oil. IR (film): ν 2958 (m), 2873 (w), 2221 (vw), 1719 (s), 1438 (m), 1320 (w), 1231 (m), 970 (w), 764 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.40 (s, 1 H), 3.84 (s, 3 H), 2.95 (t, *J* = 7.7, 2 H), 2.42 (t, *J* = 6.9, 2 H), 1.70−1.25 (m, 8 H), 0.94 (t, *J* = 7.3, 3 H), 0.91 (t, *J* = 7.3, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.9, 163.8, 143.9, 113.4, 108.5, 93.8, 70.4, 51.3, 30.8, 29.9, 27.6, 22.2, 21.9, 19.3, 13.7, 13.6 . GC-MS (EI, 70 eV): *m*/*z* 262 (77) [M^+], 233 (26), 231 (26), 220 (77), 219 (50), 201 (100), 191 (54), 188 (62), 176 (26), 173 (33), 161 (23), 160 (36), 145 (40), 131 (42), 117 (42), 116 (24), 115 (49), 105 (32), 91 (84), 89 (40), 77 (57). Anal. Calcd for $C_{16}H_{22}O_3$ (262.34): C, 73.25; H, 8.45. Found: C, 73.23; H, 8.44.

*Methyl 2-Butyl-4,5-dimethylfuran-3-carboxylate (**2e**).* Yield: 228 mg, starting from 237 mg of **1e** (78%) (Table 2, entry 6). Yellow oil. IR (film): ν 2969 (m), 2931 (m), 2864 (w), 1715 (s), 1577 (m), 1439

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(m), 1382 (w), 1294 (m), 1211 (m), 1077 (m), 736 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 3 H), 2.90 (t, J = 7.5, 2 H), 2.16 (s, 3 H), 2.05 (s, 3H), 1.68−1.55 (m, 2 H), 1.43−1.28 (m, 2 H), 0.92 (t, J = 7.5, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.5, 161.5, 145.8, 114.4, 113.1, 50.8, 30.4, 27.7, 22.4, 13.8, 11.0, 9.9. GC-MS (EI, 70 eV): m/z 210 (55) [M^+], 179 (17), 167 (100), 153 (33), 151 (38), 137 (27), 135 (57), 109 (14), 97 (6), 77 (13), 65 (16), 55 (18). Anal. Calcd for $C_{12}H_{18}O_3$ (210.27): C, 68.54; H, 8.63. Found: C, 68.64; H, 8.61.

*Methyl 2-Butyl-4-hex-1-ynyl-5-methylfuran-3-carboxylate (**2f**).* Yield: 280 mg, starting from 329.0 mg of **1f** (73%) (Table 2, entry 7). Yellow oil. IR (film): ν 2960 (m), 2932 (m), 2217 (vw), 1712 (s), 1439 (m), 1216 (s), 1147 (w), 1060 (w), 754 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.82 (s, 3 H), 2.90 (t, J = 7.4, 2 H), 2.44 (t, J = 6.9, 2 H), 2.30 (s, 3 H), 1.67−1.24 (m, 8 H), 0.95 (t, J = 7.1, 3 H), 0.91 (t, J = 7.3, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.1, 161.5, 154.4, 113.4, 103.9, 94.4, 71.5, 51.1, 31.0, 30.2, 27.4, 22.3, 21.9, 19.4, 13.8, 13.7, 12.3. GC-MS (EI, 70 eV): m/z 276 (51) [M^+], 245 (15), 233 (73), 219 (17), 215 (25), 205 (17), 202 (24), 191 (16), 187 (15), 175 (24), 173 (22), 159 (13), 147 (11), 131 (13), 115 (16), 91 (16), 77 (14). Anal. Calcd for $C_{17}H_{24}O_3$ (276.37): C, 73.88; H, 8.75. Found: C, 73.83; H, 8.73.

*Methyl 2-Butyl-4,5,6,7-tetrahydrobenzofuran-3-carboxylate (**2g**).* Yield: 246 mg, starting from 273 mg of **1g** (75%) (Table 2, entry 8). Yellow oil. IR (film): ν 2935 (m), 2857 (m), 1719 (s), 1577 (m), 1440 (m), 1345 (w), 1273 (m), 1213 (m), 1056 (m), 956 (w), 869 (w), 784 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.79 (s, 3 H), 2.93 (t, J = 7.7, 2 H), 2.62−2.49 (m, 4 H), 1.86−1.56 (m, 6 H), 1.44−1.29 (m, 2 H), 0.92 (t, J = 7.3, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.4, 161.9, 149.2, 117.2, 112.2, 50.8, 30.5, 27.6, 22.9, 22.7, 22.43, 22.36, 13.8. GC-MS (EI, 70 eV): m/z 236 (M^+, 26), 221 (3), 205 (7), 193 (100), 179 (16), 177 (24), 161 (17), 147 (4), 133 (9), 119 (3), 105 (12), 91 (16), 79 (11), 77 (12). Anal. Calcd for $C_{14}H_{20}O_3$ (236.31): C, 71.16; H, 8.53. Found: C, 71.20; H, 8.51.

*Ethyl 2-Butyl-4,5,6,7-tetrahydrobenzofuran-3-carboxylate (**2g′**).* Yield: 240 mg, starting from 273 mg of **1g** (69%) (Table 2, entry 21). Yellow oil. IR (film): ν 2934 (m), 2853 (m), 1713 (s), 1576 (m), 1444 (m), 1367 (w), 1325 (m), 1273 (m), 1212 (m), 1104 (m), 1056 (m), 957 (w), 869 (w), 783 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 4.25 (q, J = 7.1, 2 H), 2.93 (t, J = 7.5, 2 H), 2.63−2.48 (m, 4 H), 1.85−1.56 (m, 6 H), 1.44−1.29 (m, 2 H), 1.33 (t, J = 7.1, 3 H), 0.92 (t, J = 7.3, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9, 161.7, 149.2, 117.3, 112.5, 59.6, 30.5, 27.7, 23.0, 22.8, 22.5, 22.4, 14.4, 13.8. GC-MS (EI, 70 eV): m/z 250 (M^+, 39), 221 (33), 207 (81), 193 (5), 179 (100), 177 (28), 161 (17), 147 (3), 133 (9), 119 (5), 105 (10), 91 (14), 79 (10), 77 (10). Anal. Calcd for $C_{15}H_{22}O_3$ (250.33): C, 71.97; H, 8.86. Found: C, 72.04; H, 8.84.

*Methyl 2-tert-Butyl-4-methylfuran-3-carboxylate (**2h**).* Yield: 165 mg, starting from 217.0 mg of **1h** (60%) (Table 2, entry 9). Yellow oil. IR (film): ν 2958 (m), 1720 (s), 1531 (m), 1435 (w), 1364 (w), 1283 (m), 1228 (m), 1084 (s), 939 (w), 750 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.00 (q, J = 1.3, 1 H), 3.83 (s, 3 H), 2.07 (d, J = 1.3, 3 H), 1.38 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.5, 165.6, 136.4, 121.7, 112.9, 51.0, 34.7, 28.5, 9.9. GC-MS (EI, 70 eV): m/z 196 (13) [M^+], 181 (38), 165 (9), 149 (100), 122 (6), 107 (5), 93 (8), 91 (19), 79 (12), 77 (24). Anal. Calcd for $C_{11}H_{16}O_3$ (196.24): C, 67.32; H, 8.22. Found: C, 67.28; H, 8.23.

*Methyl 2-tert-Butyl-4,5-dimethylfuran-3-carboxylate (**2i**).* Yield: 170 mg, starting from 237 mg of **1i** (58%) (Table 2, entry 10). Yellow oil. IR (film): ν 2960 (w), 2932 (w), 1714 (s), 1643 (w), 1436 (m), 1364 (m), 1222 (m), 1083 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.81 (s, 3 H), 2.16 (q, J = 1.0, 3 H), 1.98 (q, J = 1.0, 3 H), 1.36 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.0, 164.3, 144.4, 115.1, 113.3, 51.0, 34.4, 28.7, 11.0, 9.8. GC-MS (EI, 70 eV): m/z 210 (16) [M^+], 195 (42), 179 (8), 163 (100), 135 (4), 121 (2), 107 (3), 91 (9), 77 (8), 65 (5). Anal. Calcd for $C_{12}H_{18}O_3$ (210.27): C, 68.54; H, 8.63. Found: C, 68.59; H, 8.61.

*Methyl 2-tert-Butyl-4,5,6,7-tetrahydrobenzofuran-3-carboxylate (**2j**).* Yield: 246 mg, starting from 273 mg of **1j** (75%) (Table 2, entry 11). Colorless amorphous solid. Mp: 39−40 °C. IR (KBr): ν 2939 (s), 2851 (m), 1718 (s), 1537 (m), 1435 (w), 1384 (m), 1316 (m), 1282 (m), 1244 (m), 1218 (m), 1117 (m), 1051 (m), 1027 (w), 936 (w), 803 (w), 789 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 3.79 (s, 3 H), 2.58−2.48 (m, 4 H), 1.84−1.65 (m, 4 H), 1.40 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.1, 165.5, 147.6, 118.2, 111.6, 51.0, 34.5, 28.4, 23.0, 22.9, 22.7, 22.6. GC-MS (EI, 70 eV): m/z 236 (22) [M^+], 221 (77), 205 (9), 189 (100), 161 (5), 147 (2), 134 (3), 119 (3), 105 (8), 91 (16), 77 (9), 65 (6). Anal. Calcd for $C_{14}H_{20}O_3$ (236.31): C, 71.16; H, 8.53. Found: C, 71.23; H, 8.52.

*Methyl 4-Methyl-2-phenylfuran-3-carboxylate (**2k**).* Yield: 214 mg, starting from 245.0 mg of **1k** (71%) (Table 2, entry 12). Yellow oil. IR (film): ν 3030 (m), 2957 (m), 1728 (s), 1448 (m), 1386 (w), 1225 (m), 960 (w), 758 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.79−7.74 (m, 1 H), 7.45−7.36 (m, 4 H), 7.24 (q, J = 0.9, 1 H), 3.80 (s, 3 H), 2.20 (d, J = 0.9, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9, 158.0, 139.2, 129.4, 129.1, 128.4, 128.1, 128.0, 122.6, 51.2, 10.0. GC-MS (EI, 70 eV): m/z 216 (82) [M^+], 185 (100), 156 (16), 129 (23), 128 (53), 127 (33), 115 (10), 102 (15), 77 (38). Anal. Calcd for $C_{13}H_{12}O_3$ (216.23): C, 72.21; H, 5.59. Found: C, 72.30; H, 5.60.

*Methyl 2,4-Diphenylfuran-3-carboxylate (**2l**).* Yield: 250 mg, starting from 331.2 mg of **1l** (65%) (Table 2, entry 13). Yellow solid. Mp: 27−28 °C. IR (KBr): ν 3051 (m), 2942 (m), 1717 (s), 1541 (m), 1482 (m), 1386 (m), 1266 (m), 1152 (m), 924 (m), 768 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.83−7.77 (m, 2 H), 7.50 (s, 1 H), 7.47−7.30 (m, 8 H), 3.68 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.1, 156.6, 139.2, 131.7, 130.1, 129.2, 128.6, 128.33, 128.26, 127.7, 127.6, 113.7, 51.6. GC-MS (EI, 70 eV): m/z 278 (100) [M^+], 247 (92), 191 (43), 189 (55), 165 (15), 139 (12), 105 (42), 94 (20), 77 (43), 63 (20). Anal. Calcd for $C_{18}H_{14}O_3$ (278.30): C, 77.68; H, 5.07. Found: C, 77.60; H, 5.07.

*Methyl 4,5-Dimethyl-2-phenylfuran-3-carboxylate (**2m**).* Yield: 180 mg, starting from 265 mg of **1m** (56%) (Table 2, entry 14) Yellow oil. IR (film): ν 2957 (w), 1717 (s), 1603 (w), 1449 (m), 1242 (m), 1112 (w), 757 (m), 697 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.76−7.71 (m, 2 H), 7.42−7.28 (m, 3 H,), 3.77 (s, 3 H), 2.25 (s, 3 H), 2.10 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.2, 155.2, 147.7, 130.6, 128.6, 128.1, 128.0, 116.3, 114.4, 51.1, 11.2, 10.0. GC-MS (EI, 70 eV): m/z 230 (100) [M^+], 215 (4), 199 (62), 170 (15), 159 (6), 143 (4), 128 (17), 115 (7), 105 (21), 77 (27). Anal. Calcd for $C_{14}H_{14}O_3$ (230.26): C, 73.03; H, 6.13. Found: C, 73.14; H, 6.11.

*Methyl 2-Phenyl-4,5,6,7-tetrahydrobenzofuran-3-carboxylate (**2n**).* Yield: 250 mg, starting from 300 mg of **1n** (70%) (Table 2, entry 15). Colorless amorphous solid. Mp: 49−50 °C. IR (KBr): ν 2939 (m), 2851 (w), 1714 (s), 1636 (w), 1547 (m), 1497 (m), 1437 (m), 1384 (w), 1326 (w), 1282 (m), 1218 (s), 1090 (s), 1021 (w), 920 (w), 774 (m), 758 (m), 688 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.87−7.78 (m, 2 H), 7.45−7.31 (m, 3 H), 3.79 (s, 3 H), 2.70−2.58 (m, 4 H), 1.91−1.71 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.0, 155.9, 150.9, 130.6, 128.7, 128.2, 128.0, 119.1, 113.2, 51.2, 23.1, 22.9, 22.62, 22.55. GC-MS (EI, 70 eV): m/z 256 (100) [M^+], 241 (4), 228 (26), 196 (16), 170 (38), 141 (15), 128 (11), 115 (19), 105 (34), 91 (11), 77 (37). Anal. Calcd for $C_{16}H_{16}O_3$ (256.30): C, 74.98; H, 6.29. Found: C, 75.07; H, 6.27.

*Methyl 2-tert-Butyl-4,5,6,7-tetrahydrobenzofuran-3-carboxylate (**2o**).* Yield: 243 mg, starting from 264 mg of **1o** (76%) (Table 2, entry 16). Yellow oil. IR (film): ν 2953 (w), 1717 (s), 1615 (w), 1500 (w), 1436 (m), 1291 (m), 1120 (m), 1076 (m), 822 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.70−7.61 (m, 2 H), 7.28−7.13 (m, 3 H), 3.78 (s, 3 H), 2.36 (s, 3 H), 2.17 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.0, 158.4, 139.1, 138.9, 128.7, 128.3, 127.7, 122.4, 113.5, 51.1, 21.4, 10.1. GC-MS (EI, 70 eV): m/z 230 (100) [M^+], 199 (80), 170 (19), 159 (4), 141 (26), 128 (36), 115 (35), 91 (13). Anal. Calcd for $C_{14}H_{14}O_3$ (230.26): C, 73.03; H, 6.13. Found: C, 73.15; H, 6.12.

*Methyl 2-(4-Bromophenyl)-4-methylfuran-3-carboxylate (**2p**).* Yield: 332 mg, starting from 355 mg of **1p** (81%) (Table 2, entry 17). Yellow oil. IR (film): ν 2951 (w), 1719 (s), 1547 (w), 1490 (w), 1290 (m), 1213 (m), 1085 (m), 1066 (w), 766 (m), 693 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.65−7.25 (m, 5 H), 3.73 (s, 3 H), 2.23 (s, 3 H). GC-MS (EI, 70 eV): m/z 294 (absent) [M^+], 216 (81), 185 (100), 156 (16), 129 (24), 128 (57), 127 (34), 115 (9), 102 (15),

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77 (31). Anal. Calcd for $C_{13}H_{11}BrO_3$ (295.13): C, 52.91; H, 3.76; Br, 27.07. Found: C, 52.99; H, 3.75; Br, 27.09.

*Methyl 4-Methyl-2-(thiophen-3-yl)furan-3-carboxylate (**2q**).* Yield: 272 mg, starting from 253 mg of **1q** (88%) (Table 2, entry 18). Yellow oil. IR (film): ν 2953 (m), 1718 (s), 1619 (w), 1521 (w), 1438 (m), 1242 (m), 1075 (m), 864 (w), 806 (m), 784 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.19 (d, J = 3.2, 1 H), 7.62 (d, J = 5.3, 1 H), 7.30 (dd, J = 5.3, 3.2, 1 H), 7.16 (s, 1 H), 3.85 (s, 3 H), 2.17 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.9, 154.6, 138.3, 131.2, 127.3, 125.9, 124.9, 122.3, 113.0, 51.2, 10.4. GC-MS (EI, 70 eV): m/z 222 (100) [M^+], 207 (4), 191 (87), 179 (4), 165 (15), 162 (29), 151 (6), 135 (34), 134 (27), 121 (4), 111 (12), 91 (34), 89 (18). Anal. Calcd for $C_{11}H_{10}O_3S$ (222.26): C, 59.44; H, 4.53; S, 14.43. Found: C, 59.51; H, 4.54; S, 14.44.

*Methyl 2-Cyclohex-1-enyl-4-methylfuran-3-carboxylic Acid Methyl Ester (**2r**).* Yield: 285 mg, starting from 250 mg of **1r** (93%) (Table 2, entry 19). Yellow oil. IR (film): ν 2936 (s), 2862 (m), 1719 (s), 1602 (w), 1534 (m), 1436 (s), 1379 (w), 1286 (w), 1205 (w), 1087 (s), 805 (w), 787 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.06 (s, 1 H), 6.42−6.34 (m, 1 H), 3.81 (s, 3 H), 2.42−2.29 (m, 2 H), 2.28−2.16 (m, 2 H), 2.11 (s, 3 H), 1.80−1.58 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.3, 160.3, 137.5, 131.5, 128.4, 121.7, 112.7, 51.2, 26.3, 25.6, 22.5, 21.8, 10.0. GC-MS (EI, 70 eV): m/z 220 (100) [M^+], 205 (17), 188 (77), 187 (57), 173 (12), 166 (31), 161 (25), 160 (27), 159 (24), 145 (15), 133 (24), 132 (18), 131 (21), 117 (20), 115 (23), 105 (24), 103 (14), 91 (45), 79 (22), 77 (38), 65 (19). Anal. Calcd for $C_{13}H_{16}O_3$ (220.26): C, 70.89; H, 7.32. Found: C, 70.95; H, 7.30.

General Procedure for the Preparation of 2-Methyl-3-yne-1,2-diols 3a−e. To a solution of BuLi in hexane (1.6 M; 25 mL, 40 mmol) was added anhydrous THF (6 mL) and hexane (25 mL) under nitrogen. The resulting mixture was cooled to −40 °C and maintained with stirring. A solution of the 1-alkyne (44.5 mmol: 1-hexyne, 3.66 g; phenylacetylene, 4.54 g; 3-ethynylthiophene, 4.81 g; *p*-bromophenylacetylene, 8.06 g; *p*-methylphenylacetylene, 5.17 g) in anhydrous THF (6 mL) was added dropwise under nitrogen to the cooled mixture followed by a solution of LiBr (1.56 g, 18.0 mmol) in anhydrous THF (6 mL). After the mixture was stirred for 0.5 h at −40 °C, a solution of 3-hydroxy-3-methylbutan-2-one (1.74 g, 17 mmol) in anhydrous THF (5 mL) was added under nitrogen. The mixture was stirred at the same temperature for 2 h, and then it was warmed to room temperature. Saturated aqueous NH_4Cl (40 mL) was added, followed by Et_2O (50 mL). The phases were separated, and the aqueous phase was extracted with Et_2O (50 mL × 3). The collected organic phases were washed with brine to neutral pH and dried over Na_2SO_4. After filtration and evaporation of the solvent, products **3a−e** were purified by column chromatography on silica gel using the following mixtures as eluent: 85/15 hexane/AcOEt (**3a**), 9/1 hexane/AcOEt (**3b**,**d**), 95/5 hexane/AcOEt (**3c**), 8/2 hexane/AcOEt (**3e**).

*2,3-Dimethyl-5-phenylpent-4-yne-2,3-diol (**3a**).* Yield: 2.64 g, starting from 1.74 g of 3-hydroxy-3-methylbutan-2-one (76%). Yellow oil. IR (film): ν 3568 (m, br), 3301 (m, br), 2986 (m), 2231 (vw), 1598 (w), 1490 (w), 1443 (w), 1370 (m), 1338 (m), 1266 (w), 1123 (m), 1077 (m), 961 (w), 939 (w), 903 (w), 846 (w), 756 (m), 691 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.44−7.38 (m, 2 H), 7.32−7.26 (m, 3 H), 3.16 (s, br, 1 H), 2.42 (s, br, 1 H), 1.56 (s, 3 H), 1.45 (s, 3 H), 1.33 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 131.7, 128.4, 128.3, 122.6, 91.6, 84.8, 75.5, 74.4, 25.8, 24.5, 23.3. GC-MS (EI, 70 eV): m/z 204 (absent) [M^+], 171 (8), 146 (93), 145 (84), 131 (100), 128 (42), 115 (13), 103 (29), 102 (19), 77 (17), 59 (53). Anal. Calcd for $C_{13}H_{16}O_2$ (204.26): C, 76.44; H, 7.90. Found: C, 76.51; H, 7.89.

*2,3-Dimethylnon-4-yne-2,3-diol (**3b**).* Yield: 2.16 g, starting from 1.74 g of 3-hydroxy-3-methylbutan-2-one (69%). Colorless oil. IR (film): ν 3420 (s, br), 2963 (m), 2935 (m), 2242 (vw), 1636 (m), 1461 (m), 1368 (m), 1175 (m), 1084 (m), 960 (w), 917 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 2.87 (s, br, 1 H), 2.27 (s, br, 1 H), 2.22 (t, J = 7.0, 2 H), 1.56−1.32 (m, 4 H), 1.44 (s, 3 H), 1.37 (s, 3 H), 1.27 (s, 3 H), 0.91 (t, J = 7.3, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 85.4, 82.4, 75.3, 74.0, 30.7, 25.7, 24.6, 22.9, 22.0, 18.3, 13.6. GC-MS (EI, 70 eV): m/z 184 (absent) [M^+], 151 (1), 125 (10), 109 (3), 97 (12), 84 (100), 79 (11), 69 (59), 59 (52). Anal. Calcd for $C_{11}H_{20}O_2$ (184.28): C, 71.70; H, 10.94. Found: C, 71.79; H, 10.93.

*2,3-Dimethyl-5-p-tolylpent-4-yne-2,3-diol (**3c**).* Yield: 2.63 g, starting from 1.74 g of 3-hydroxy-3-methylbutan-2-one (71%). Pale yellow solid. Mp: 64−65 °C. IR (KBr): ν 3419 (s, br), 2985 (m), 2234 (w), 1665 (w), 1511 (m), 1370 (m), 1267 (w), 1121 (s), 940 (m), 903 (w), 816 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.35−7.27 (m, 2 H), 7.14−7.06 (m, 2 H), 2.93 (s, br, 1 H), 2.34 (s, 3 H), 2.25 (s, br, 1 H), 1.55 (s, 3 H), 1.45 (s, 3 H), 1.33 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.6, 131.6, 129.1, 119.4, 90.6, 84.9, 75.5, 74.4, 25.8, 24.4, 23.1, 21.5. GC-MS (EI, 70 eV): m/z 218 (1) [M^+], 185 (5), 160 (56), 159 (38), 145 (100), 142 (21), 141 (19), 128 (4), 117 (13), 115 (22), 91 (6), 59 (22). Anal. Calcd for $C_{14}H_{18}O_2$ (218.29): C, 77.03; H, 8.31. Found: C, 77.14; H, 8.30.

*5-(4-Bromophenyl)-2,3-dimethylpent-4-yne-2,3-diol (**3d**).* Yield: 2.84 g, starting from 1.74 g of 3-hydroxy-3-methylbutan-2-one (59%). Yellow oil. IR (film): ν 3399 (s, br), 3302 (m, br), 2932 (w), 2230 (vw), 1484 (m), 1384 (m), 1249 (m), 1124 (m), 1048 (s), 948 (w), 899 (m), 822 (m), 764 (m), 695 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.47−7.37 (m, 2 H), 7.33−7.25 (m, 2 H), 3.15 (s, br, 1 H), 2.38 (s, br, 1 H), 1.56 (s, 3 H), 1.46 (s, 3 H), 1.34 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.1, 131.7, 128.3, 122.5, 91.3, 84.7, 75.5, 74.4, 25.8, 24.4, 23.2. GC-MS (EI, 70 eV): m/z 282 (absent) [M^+], 251 (6), 249 (6), 226 (58), 224 (60), 211 (63), 209 (72), 183 (8), 181 (7), 145 (37), 127 (19), 115 (9), 102 (13), 101 (10), 75 (9), 59 (100). Anal. Calcd for $C_{13}H_{15}BrO_2$ (283.16): C, 55.14; H, 5.34, Br, 28.22. Found: C, 55.21; H, 5.33, 28.24.

*2,3-Dimethyl-5-thiophen-3-ylpent-4-yne-2,3-diol (**3e**).* Yield: 2.82 g, starting from 1.74 g of 3-hydroxy-3-methylbutan-2-one (79%). Yellow oil. IR (film): ν 3410 (s, br), 2984 (m), 2936 (w), 2234 (w), 1634 (w), 1459 (m), 1370 (m), 1182 (m), 1122 (m), 1080 (m), 963 (m), 919 (m), 866 (w), 841 (w), 782 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.43 (distorted dd, J = 3.0, 1.2, 1 H), 7.25 (distorted dd, J = 4.9, 3.0, 1 H), 7.09 (dd, J = 4.9, 1.2, 1 H), 2.42 (s, br, 2 H), 1.55 (s, 3 H), 1.45 (s, 3 H), 1.33 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.9, 129.0, 125.4, 121.5, 90.9, 80.0, 75.4, 74.5, 25.8, 24.4, 23.1. GC-MS (EI, 70 eV): m/z 210 (absent) [M^+], 195 (1), 177 (6), 152 (97), 151 (38), 137 (100), 134 (30), 109 (30), 89 (5), 77 (3), 69 (5), 59 (54). Anal. Calcd for $C_{11}H_{14}O_2S$ (210.29): C, 62.83; H, 6.71, S, 15.25. Found: C, 62.91; H, 6.70, S, 15.23.

General Procedure for the Synthesis of 4-Methylene-4,5-dihydrofuran-3-carboxylic Esters 4a−e. A 250 mL stainless steel autoclave was charged in the presence of air with PdI_2 (5.0 mg, 1.39 × 10^{-2} mmol), KI (11.5 mg, 6.93 × 10^{-2} mmol), anhydrous ROH (R = Me, Et, 28 mL), and the 2-methyl-3-yne-1,2-diol **3a−e** (1.39 mmol). The autoclave was sealed and, while the mixture was stirred, the autoclave was pressurized with CO (32 atm) and air (up to 40 atm). After the mixture was stirred at 100 °C for the required time (see Table 3), the autoclave was cooled, degassed, and opened. The solvent was evaporated, and the products **4a−e** were purified by column chromatography on silica gel using 95/5 hexane/AcOEt as eluent.

*Methyl 5,5-Dimethyl-4-methylene-2-phenyl-4,5-dihydrofuran-3-carboxylate (**4a**).* Yield: 228 mg, starting from 284 mg of **3a** (67%) (Table 3, entry 1). Pale yellow amorphous solid. Mp: 53−55 °C. IR (KBr): ν 1699 (s), 1589 (m), 1436 (w), 1384 (s), 1273 (m), 1193 (w), 1160 (w), 1098 (w), 1072 (m), 859 (m), 763 (m), 694 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.70−7.62 (m, 2 H), 7.47−7.34 (m, 3 H), 5.49 (s, 1 H), 4.68 (s, 1 H), 3.70 (s, 3 H), 1.50 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.2, 165.2, 153.1, 130.7, 130.6, 129.1, 127.7, 105.4, 99.7, 89.3, 50.9, 28.5. GC-MS (EI, 70 eV): m/z 244 (92) [M^+], 229 (42), 212 (19), 199 (18), 197 (23), 185 (24), 184 (20), 171 (15), 155 (13), 144 (23), 141 (20), 127 (17), 115 (18), 105 (84), 77 (100). Anal. Calcd for $C_{15}H_{16}O_3$ (244.29): C, 73.75; H, 6.60. Found: C, 73.82; H, 6.58.

*Ethyl 5,5-Dimethyl-4-methylene-2-phenyl-4,5-dihydrofuran-3-carboxylate (**4a'**).* Yield: 198 mg, starting from 284 mg of **3a** (55%) (Table 3, entry 7). Pale yellow amorphous solid. Mp: 82−83 °C. IR (KBr): ν 1687 (s), 1589 (m), 1405 (w), 1383 (s), 1275 (m), 1190 (w), 1167 (w), 1095 (m), 1073 (s), 863 (m), 765 (w), 699 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.70−7.63 (m, 2 H), 7.47−7.35

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(m, 3 H), 5.52 (s, 1 H), 4.67 (s, 1 H), 4.19 (q, J = 7.1, 2 H), 1.50 (s, 6 H), 1.20 (t, J = 7.1, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.9, 164.8, 153.4, 131.0, 130.4, 129.2, 127.7, 105.7, 99.6, 89.2, 59.9, 28.5, 14.0. GC-MS (EI, 70 eV): m/z 258 (58) [M^+], 243 (8), 229 (7), 215 (21), 197 (17), 186 (22), 185 (17), 184 (13), 171 (25), 144 (18), 136 (12), 115 (8), 105 (100), 77 (63). Anal. Calcd for $C_{16}H_{18}O_3$ (258.31): C, 74.39; H, 7.02. Found: C, 74.45; H, 7.01.

*Methyl 2-Butyl-5,5-dimethyl-4-methylene-4,5-dihydrofuran-3-carboxylate (**4b**).* Yield: 180 mg, starting from 256 mg of **3b** (58%) (Table 3, entry 3). Yellow oil. IR (film): ν 2957 (m), 2932 (m), 2872 (w), 1705 (s), 1598 (m), 1437 (m), 1383 (m), 1274 (m), 1198 (w), 1172 (w), 1077 (m), 1032 (w), 866 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.37 (s, 1 H), 4.51 (s, 1 H), 3.78 (s, 3 H), 2.75 (t, J = 7.6, 2 H), 1.66−1.31 (m, 2 H), 1.47−1.24 (m, 2 H), 1.39 (s, 6 H), 0.92 (t, J = 7.3, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.6, 165.7, 152.4, 104.6, 97.7, 89.6, 50.7, 29.0, 28.8, 28.3, 22.4, 13.8. GC-MS (EI, 70 eV): m/z 224 (47) [M^+], 209 (29), 195 (100), 177 (9), 167 (17), 149 (9), 135 (18), 107 (14), 79 (20). Anal. Calcd for $C_{13}H_{20}O_3$ (224.30): C, 69.61; H, 8.99. Found: C, 69.70; H, 8.97.

*Methyl 5,5-Dimethyl-4-methylene-2-p-tolyl-4,5-dihydrofuran-3-carboxylate (**4c**).* Yield: 230 mg, starting from 303 mg of **3c** (64%) (Table 3, entry 4). Yellow solid. Mp: 77−78 °C. IR (KBr): ν 2978 (w), 1699 (s), 1593 (m), 1505 (w), 1438 (m), 1383 (m), 1266 (m), 1192 (w), 1154 (w), 1093 (m), 1074 (m), 955 (w), 863 (m), 824 (m), 787 (m), 624 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.62−7.52 (m, 2 H), 7.24−7.12 (m, 2 H), 5.47 (s, 1 H), 4.65 (s, 1 H), 3.70 (s, 3 H), 2.37 (s, 3 H), 1.48 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.3, 165.3, 153.3, 140.9, 129.1, 128.4, 127.8, 104.9, 99.3, 89.1, 50.8, 28.5, 21.5. GC-MS (EI, 70 eV): m/z 258 (100) [M^+], 243 (41), 227 (10), 211 (32), 199 (10), 185 (11), 183 (8), 169 (6), 158 (10), 155 (9), 141 (9), 119 (57), 91 (35), 65 (12). Anal. Calcd for $C_{16}H_{18}O_3$ (258.31): C, 74.39; H, 7.02. Found: C, 74.45; H, 7.01.

*Methyl 2-(4-Bromophenyl)-5,5-dimethyl-4-methylene-4,5-dihydrofuran-3-carboxylate (**4d**).* Yield: 284 mg, starting from 394 mg of **3d** (63%) (Table 3, entry 5). Yellow oil. IR (film): ν 2978 (w), 1709 (s), 1589 (m), 1485 (w), 1437 (m), 1383 (m), 1366 (w), 1277 (m), 1195 (w), 1153 (w), 1094 (m), 1072 (m), 865 (m), 831 (w), 766 (m), 694 (m) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70−7.64 (m, 1 H), 7.57−7.51 (m, 1 H), 7.45−7.35 (m, 2 H), 5.49 (s, 1 H), 4.68 (s, 1 H), 3.70 (s, 3 H), 1.50 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.1, 165.2, 153.2, 130.8, 130.5, 129.1, 127.7, 100.3, 99.7, 89.3, 50.9, 28.5. GC-MS (EI, 70 eV): m/z 324 (99) [$(M + 2)^+$], 322 (100) [M^+], 309 (42), 307 (43), 291 (16), 277 (17), 264 (15), 224 (12), 222 (12), 211 (15), 202 (11), 185 (57), 183 (62), 169 (8), 157 (27), 155 (40), 143 (12), 141 (11), 126 (17), 76 (18). Anal. Calcd for $C_{15}H_{15}BrO_3$ (323.18): C, 55.75; H, 4.68; Br, 24.72. Found: C, 55.82; H, 4.69; Br, 24.69.

*Methyl 5,5-Dimethyl-4-methylene-2-thiophen-3-yl-4,5-dihydrofuran-3-carboxylate (**4e**).* Yield: 245 mg, starting from 292 mg of **3e** (70%) (Table 3, entry 6). Yellow oil. IR (film): ν 2978 (w), 1704 (s), 1579 (m), 1438 (m), 1364 (w), 1263 (m), 1192 (w), 1144 (w), 1098 (m), 1077 (m), 878 (m), 853 (m), 788 (m), 650 (w) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (d, J = 3.0, 1 H), 7.60 (distorted d, J = 5.5, 1 H), 7.29 (distorted dd, J = 5.5, 3.0, 1 H), 5.45 (s, 1 H), 4.66 (s, 1 H), 3.81 (s, 3 H), 1.48 (s, 6 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.5, 163.8, 153.1, 131.4, 130.7, 128.5, 124.5, 104.5, 99.7, 88.6, 51.0, 28.6. GC-MS (EI, 70 eV): m/z 250 (100) [M^+], 235 (35), 218 (12), 205 (13), 203 (21), 190 (11), 177 (11), 161 (9), 150 (11), 147 (11), 134 (9), 111 (64), 97 (8), 83 (13). Anal. Calcd for $C_{13}H_{14}O_3S$ (250.31): C, 62.38; H, 5.64; S, 12.81. Found: C, 62.44; H, 5.62; S, 12.80.

■ ASSOCIATED CONTENT

Supporting Information

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

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: b.gabriele@unical.it

Notes

The authors declare no competing financial interest.

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