JOC The Journal of Organic Chemistry

Note

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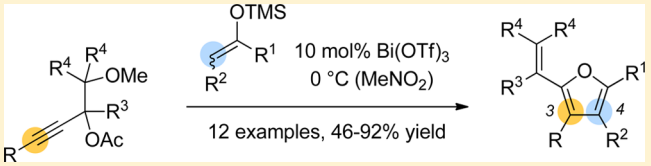
Bismuth(III) Triflate-Catalyzed Synthesis of Substituted 2-Alkenylfurans

Dominik Nitsch and Thorsten Bach*

Lehrstuhl für Organische Chemie I and Catalysis Research Center (CRC), Technische Universität München, Lichtenbergstr. 4, 85747 Garching, Germany

Supporting Information

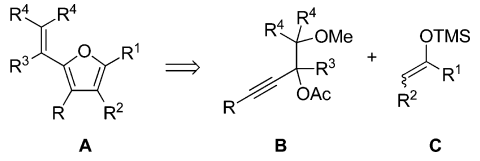
ABSTRACT: A convergent synthesis of the title compounds is reported, which relies on a successive 2-fold S_N'-type substitution reaction at methoxy-substituted propargylic acetates. The furan C3−C4 bond is presumably established by silyl enol ether attack at a propargylic cation intermediate. The resulting α-methoxyallene is intramolecularly substituted, leading to cyclization by displacement of the methoxy group (O−C2 bond formation) and to simultaneous formation of the exocyclic alkene double bond. Despite the relatively mild conditions, the reactions were complete within 5 min.



Substituted furans play an important role in organic chemistry due to their presence in many naturally occurring compounds[1] and pharmaceuticals.[2] Furthermore, they represent useful building blocks in synthetic chemistry.[3] The remarkable utility of furans has led to a broad spectrum of synthetic routes for the construction of their heterocyclic core structure. Besides classical reactions like the Paal−Knorr[4] and the Feist−Benary[5] furan synthesis, transition-metal catalysis often plays an essential role in the formation of multiply substituted furans.[6] These approaches include not only cycloisomerization-type reactions[7] but also formal [4 + 1][8] and [3 + 2][9] cycloaddition reactions of alkyne- and allene-containing compounds.

When searching more specifically for an access to 2-alkenylfurans of general structure **A** (Scheme 1), three main

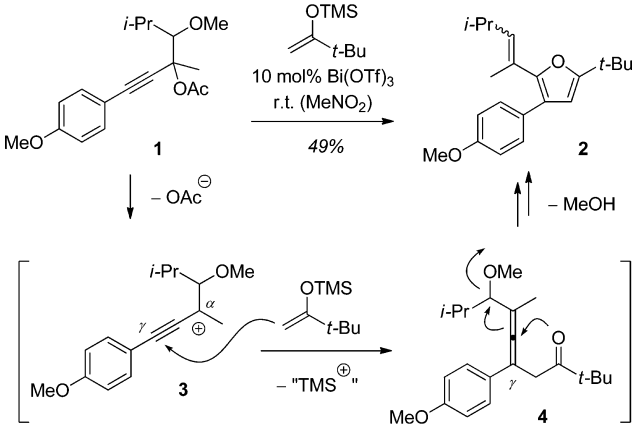
Scheme 1. General Structure A of the Title Compounds and Disconnection into Starting Materials of General Structure B and C



access strategies are found in the literature.[10] Starting from enyne-ketones or alcohols, an attack of the oxygen nucleophile at the triple bond leads to 2-alkenylfurans with simultaneous generation of the furan core.[11] Alternatively, the double bond can be installed at an existing furan ring, either by C−C bond formation at the 2-position of the furan nucleus[12] or by olefination reactions.[13] In this note, we describe an alternative access to the title compounds that is based on an acid-catalyzed domino reaction between propargylic acetates of general structure **B** and silyl enol ethers **C** (Scheme 1).

During our studies on S_N1-type reactions of propargylic carbocations[14] we observed that, in contrast to its secondary analogues, tertiary propargylic acetate **1** reacted with the silyl enol ether 2-trimethylsilyloxy-3,3-dimethylbutene not to the expected substitution product but to 2-alkenylfuran **2**. Typical reaction conditions included the use of 10 mol % bismuth(III) trifluoromethanesulfonate [$Bi(OTf)_3$][15] as the Lewis acid and nitromethane as the solvent (Scheme 2) at room temperature. Mechanistically, the reaction outcome was interpreted as an S_N1' attack of the nucleophile at the distal γ-position of the propargylic cation **3**. Indeed, in a previous example[14a] the γ-approach had been observed at a related secondary cation for a

Scheme 2. Formation of Furan 2 from Propargylic Acetate 1 upon Attempted $Bi(OTf)_3$-Catalyzed S_N1-type Substitution and Mechanistic Explanation Based on Intermediates 3 and 4



Received: May 8, 2014
Published: June 19, 2014

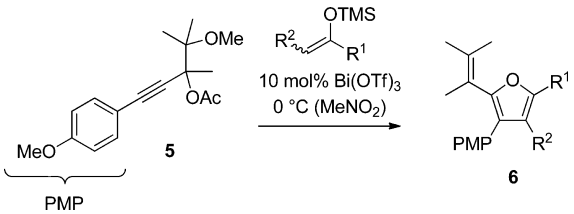
   dx.doi.org/10.1021/jo5009993 | J. Org. Chem. 2014, 79, 6372−6379

sterically encumbered silyl enol ether but it had not led to a consecutive reaction. In the present case, it is likely that the tertiary group adjacent to the α-position prevents the S_N1-type attack and guides the nucleophile to form allene intermediate **4**. Apparently, the Lewis acid is not only sufficiently strong to initiate formation of cation **3** but also induces another S_N1' substitution, which leads to oxygen−carbon formation at the central allene carbon atom upon displacement of the methoxy group. Deprotonation at the resulting cationic intermediate generates the observed product **2** (d.r. = 54/46). Further evidence for the suggested mechanism was obtained by isolation of the intermediate allene related to **4**, if the respective methyl- instead of the methoxy-substituted substrate was employed under identical reaction conditions.

Regarding the bond set, the reaction is reminiscent of a recently reported $FeCl_3$-catalyzed substitution reaction of secondary propargylic acetates with silyl enol ethers affording the corresponding γ-alkynyl ketones.[16] A subsequent acid-catalyzed cyclization provided tri- and tetrasubstituted furans. Nevertheless, high temperatures and strong Brønsted acids limit the scope of possible substrates for this transformation. A milder alternative was reported by the Kirsch group who used $AuCl(PPh_3)$ for a cascade reaction including a propargyl-Claisen rearrangement followed by an heterocyclyzation of propargyl vinyl ethers.[17] In neither of these reactions 2-alkenylketones are formed, however, because the reactions are terminated by addition to the triple bond.

It seemed as if the observed furan formation could be general as long as the respective propargylic acetates were tertiary and would carry a methoxy group as leaving group in the adjacent position. The reaction of substrate **5** with 2-trimethylsilyloxy-3,3-dimethylbutene was studied more closely and indeed led to the expected furan product **6a** (Table 1). It turned out that the reaction can be performed not only with $Bi(OTf)_3$ as catalyst (10 mol %) but also with other Lewis and Brønsted acids. Yields, which were comparable to the yield with $Bi(OTf)_3$ (67%), were recorded at identical catalyst loadings for $InCl_3$ (63%), AgOTf (62%), $Sc(OTf)_3$ (65%) and HOTf (61%) in nitromethane as solvent at ambient temperature (for further details see the Supporting Information). While the reaction under $Bi(OTf)_3$-catalysis was relatively slow at −78 °C, it was found to proceed rapidly (within 5 min) at 0 °C. TLC control indicated complete conversion and work-up was performed upon warming to room temperature. Under these conditions the yield rose to 77% (Table 1, entry 1), and the reaction could be performed with similar success on larger scale. Using the optimized conditions other silyl enol ethers were employed as nucleophiles and the multiply substituted furans **6b**−**6e** (entries 2−6) were obtained in moderate to high yields (46−92%).

Table 1. $Bi(OTf)_3$-Catalyzed Reaction of Propargylic Acetate 5 with Various Silyl Enol Ethers to 2-(1,2-Dimethyl-1-propenyl)furans 6

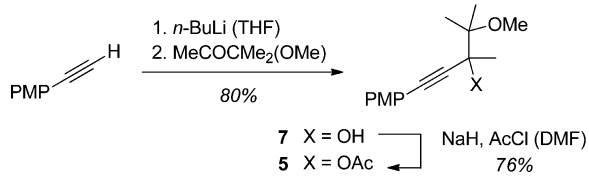


entry[a]	R^1	R^2	product	yield [%]
1	*t*-Bu	H	**6a**	77
2	Ph	H	**6b**	69
3	−$(CH_2)_4$−		**6c**	92
4	−$(CH_2)_3$−		**6d**	63
5[b]	Me	Et	**6e**	86
6	Me	Ac	**6f**	46

[a]Reactions were performed in dry $MeNO_2$ (c = 125 mM). After 5 min at 0 °C the reaction mixture was warmed to ambient temperature. [b]The silyl enol ether was used as an E/Z mixture (E/Z = 20/80).

The synthesis of the propargylic acetates was straightforward and commenced with the respective acetylene, i.e., with *para*-methoxyphenylaceteylene in the case of acetate **5**. Deprotonation with butyl lithium at −78 °C delivered a suitable nucleophile for attack at the respective α-methoxyketone. The intermediate alcohol **7** was subsequently acylated with acetyl chloride employing sodium hydride as the base (Scheme 3). Attempts to take alcohol **7** directly into the furan synthesis failed under a variety of conditions.

Scheme 3. Synthesis of Substrate 5 from *para*-Methoxyphenylaceteylene via Alcohol 7

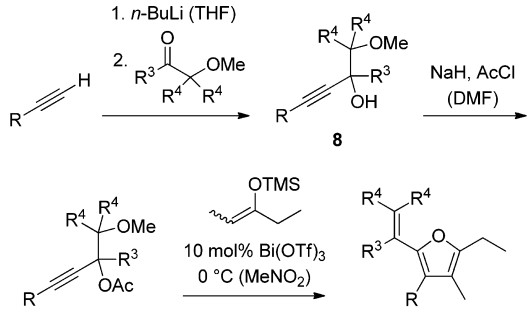


To avoid the formation of olefin diastereoisomers, we tested in further experiments only substrates with identical substituents R^4 at the methoxy-substituted carbon atom. As for acetate **5**, the reaction sequence commenced with the respective alkyne (Table 2) and went via the respective alcohol **8** to acetates **9**. Gratifyingly, we noted that the furan formation was also general regarding different substituents R, R^3 and R^4. Furans **10** were isolated in yields of 51 to 92% with the lowest yield recorded for the butyl-substituted propargyl acetate **9b** (entry 2). The latter result indicates that stabilization of the intermediate propargylic cation plays an important role for the outcome of the reaction. The synthesis of the isopropyl-substituted acetate **9g** (entry 7) turned out to be not possible under standard acetylation conditions. Instead, the alcohol **8g** could in this specific case be directly converted to the desired furan **10g** in moderate yield (55%). While the furan forming reactions with other substituents R^4 = alkyl went smoothly (entries 1−6), the reaction for the respective substrate **9h** with R^4 = H did not produce a furan (entry 8). In this case, the silyl enol ether attacked the substrate at the α-position (Scheme 2) in a direct S_N1 but not in an S_N1' reaction forming an alkynylketone. The addition product was obtained in 71% yield. Apparently, the γ-attack of the silyl enol ether requires significant steric shielding at the α-position to occur.

In summary, a new route for the synthesis of various 2-alkenylfurans was established, which is based on a simultaneous construction of the furan core and of the alkenyl side chain. It requires readily available starting materials (propargylic acetates, silyl enol ethers), which can be easily varied. The reaction appears general for several substitution patterns at both substrates and should allow for the construction of a diverse array of 2-alkenylfurans.

dx.doi.org/10.1021/jo5009993 | J. Org. Chem. 2014, 79, 6372−6379

Table 2. Preparation of Various Propargylic Acetates 9 and Their $Bi(OTf)_3$-Catalyzed Reaction with 3-Trimethylsilyloxy-3,3-dimethylbutene to Furans 10



entry (# code)[a]	R	R^3	R^4	yield (8) [%]	yield (9) [%]	yield (10) [%]
1 (**a**)	cyclopropyl	Me	Me	74	63	77
2 (**b**)	*n*-Bu	Me	Me	72	58	51
3 (**c**)	1-cyclohexenyl	Me	Me	77	51	60
4 (**d**)	PhS	Me	Me	89	67	84
5 (**e**)	Ph	Me	Me	87	69	92
6 (**f**)	PMP	Me	$-(CH_2)_5-$	64	62	88
7 (**g**)[b]	PMP	*i* Pr	Me	54	——	55
8 (**h**)	PMP	Me	H	71	93	——[c]

[a]The latin letter refers to the substitution pattern at the propargylic substrate. The silyl enol ether in the furan forming reaction was used as an *E*/*Z* mixture (*E*/*Z* = 20/80). [b]Instead of the acetate, the free alcohol **8g** was used in the furan synthesis. [c]No furan formation was observed. The S_N1 substitution product was formed in 71% yield.

EXPERIMENTAL SECTION

General Methods. All reactions, sensitive to air or moisture, were carried out in flame-dried glassware under positive pressure of argon using standard Schlenk techniques. Flash chromatography was performed on silica gel 60 (230−400 mesh) with the eluent mixtures given for the corresponding procedures. Thin layer chromatography (TLC) was performed on silica coated glass plates (silca gel 60 F 254). Compounds were detected by UV (λ = 254 nm, 366 nm) and CAM (cerium ammonium molybdate solution). Technical solvents (*n*-pentane, ethyl acetate) employed for preparative column chromatography were purified by distillation prior to use. Chemical shifts are reported relative to the solvent ($CHCl_3$ $\delta(^1H)$ = 7.26 ppm, $\delta(^{13}C)$ = 77.0 ppm) as reference. HRMS data were recorded by electron ionization (EI) on a transmission quadrupole mass spectrometer. Commercially available, anhydrous $Bi(OTf)_3$ was handled in a glovebox. All other chemicals were used as received from commercial suppliers. The silyl nucleophiles were synthesized by following known procedures: [(3,3-dimethylbut-1-en-2-yl)oxy]trimethylsilane,[18] trimethyl[(1-phenylvinyl)oxy]silane,[19] (cyclohex-1-en-1-yloxy)-trimethylsilane,[20] (cyclopent-1-en-1-yloxy)trimethylsilane,[21] trimethyl-(pent-2-en-3-yloxy)silane,[19] 4-[(trimethylsilyl)oxy]pent-3-en-2-one.[22] 3-Methoxy-3-methylbutan-2-one,[23] 2-methoxy-2,4-dimethylpentan-3-one[24] and 1-(1-methoxycyclohexyl)ethanone[25] were prepared according to literature procedures.

General Procedure for the Preparation of Tertiary Propargylic Acetates 5 and 9. *n*-BuLi (1.0 equiv, 2.5 M in hexane) was added to a solution of the corresponding alkyne (1.00 equiv) in dry THF (*c* = 0.5 M) at −78 °C. The solution was stirred for 30 min and a solution of the ketone (1.00 equiv) in THF (*c* = 2.0 M) was added. After complete addition the reaction mixture was stirred for additional 30 min at −78 °C and was subsequently warmed to room temperature. Water (2.5 mL/mmol) was added to the reaction mixture, and the aqueous layer was then extracted with ethyl acetate (3 × 2.5 mL/mmol). The combined organic extracts were washed with an aqueous saturated NaCl-solution (5.0 mL/mmol), dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography on silica gel to afford the tertiary propargylic alcohols **7** and **8**.

To transform the alcohol to the corresponding acetates **5** and **9**, a solution of the alcohol (1.0 equiv) in DMF (1.0 mL/mmol alcohol) was added to a suspension of NaH (60% in mineral oil, 10.0 equiv) in dry DMF (0.5 mL/mmol NaH) at 0 °C. The mixture was warmed to room temperature and stirred for additional 30 min before it was cooled to 0 °C again. Acetyl chloride (10.0 equiv) was added within 30 min; the reaction was warmed to room temperature and was stirred for 60 min. Water (4 mL/mmol) was added to the reaction mixture, and the mixture was saturated with NaCl. The aqueous layer was then extracted with diethyl ether (4 × 4 mL/mmol). The combined organic extracts were washed subsequently with water (4 mL/mmol) and an aqueous saturated NaCl-solution (4 mL/mmol), dried over Na_2SO_4, filtered and concentrated. The crude product was purified by flash chromatography on silica gel to afford the tertiary propargylic acetate **5** and **9**.

*4-Methoxy-1-(4-methoxyphenyl)-3,4-dimethylpent-1-yn-3-ol (**7**).* Synthesized according to the general procedure, using 1-ethynyl-4-methoxybenzene (1.32 g, 10.0 mmol, 1.0 equiv) in THF (20 mL), *n*-BuLi (4.0 mL, 10.0 mmol, 1.0 equiv) and 3-methoxy-3-methylbutan-2-one (1.16 g, 10.0 mmol, 1.0 equiv) in THF (5 mL). Work up and purification by column chromatography (*n*-pentane/EtOAc: 5/1) yielded product **7** (1.99 g, 80%) as a colorless oil: TLC R_f = 0.42 (P:EtOAc 5:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 3448, 2979, 2939, 2833, 2237, 1508, 1247, 1109, 1028, 832, 738 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 248 (6) $[C_{15}H_{20}O_3]^+$, 73 (100) $[C_4H_9O]^+$; ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.27 (s, 3H), 1.40 (s, 3H), 1.53 (s, 3H), 3.05 (s, 1H), 3.33 (s, 3H), 3.80 (s, 3H), 6.79−6.84 (m, 2H), 7.34−7.39 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 19.4, 19.9, 24.7, 50.2, 55.3, 74.3, 79.5, 83.7, 90.5, 113.8, 115.2, 133.1, 159.4; HRMS (EI, 70 eV) ($C_{15}H_{20}O_3$) calcd. 248.1407, found 248.1404.

*4-Methoxy-1-(4-methoxyphenyl)-3,4-dimethylpent-1-yn-3-yl acetate (**5**).* Synthesized according to the general procedure, using alcohol **7** (1.11 g, 4.47 mmol, 1.0 equiv) in DMF (4.5 mL), NaH (1.80 g, 45.0 mmol, 10.0 equiv) in DMF (22 mL) and acetyl chloride (3.2 mL, 3.5 g, 45.0 mmol, 10.0 equiv). Work up and purification by column chromatography (*n*-pentane/EtOAc: 5/1) yielded product **5** (0.99 g, 76%) as a colorless oil: TLC R_f = 0.48 (P:EtOAc 5:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 2981, 2950, 2835, 2233, 1741, 1509, 1241, 1126, 1085, 1030, 832 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 290 (3) $[C_{17}H_{22}O_4]^+$, 230 (19) $[C_{15}H_{18}O_2]^+$, 200 (35) $[C_{14}H_{16}O_2]^+$, 73 (100) $[C_4H_9O]^+$, 43 (98) $[C_2H_3O]^+$; ^1H NMR (360 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.39 (s, 6H), 1.81 (s, 3H), 2.06 (s, 3H), 3.36 (s, 3H), 3.79 (s, 3H), 6.78−6.83 (m, 2H), 7.34−7.39 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 19.7, 20.4, 21.4, 22.2, 50.9, 55.3, 79.4, 81.0, 85.8, 87.2, 113.7, 114.9, 133.2, 159.6, 169.0; HRMS (EI, 70 eV) ($C_{17}H_{22}O_4$) calcd. 290.1513, found 290.1515.

*1-Cyclopropyl-4-methoxy-3,4-dimethylpent-1-yn-3-ol (**8a**).* Synthesized according to the general procedure, using cyclopropylacetylene (664 mg, 10.0 mmol, 1.0 equiv) in THF (20 mL), *n*-BuLi (4.0 mL, 10.0 mmol, 1.0 equiv) and 3-methoxy-3-methylbutan-2-one (1.16 g, 10.0 mmol, 1.0 equiv) in THF (5 mL). Work up and purification by column chromatography (*n*-pentane/EtOAc: 20/1) yielded product **8a** (1.35 g, 74%) as a colorless oil: TLC R_f = 0.37 (P:EtOAc 10:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 3446, 2980, 2943, 2831, 2243, 1363, 1160, 1088, 905, 876, 814 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 182 (1) $[C_{11}H_{18}O_2]^+$, 167 (1) $[C_{10}H_{15}O_2]^+$, 109 (3) $[C_7H_9O]^+$, 73 (100) $[C_4H_9O]^+$, 43 (21) $[C_2H_3O]^+$; ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ [ppm] = 0.63−0.66 (m, 2H), 0.71−0.75 (m, 2H), 1.18 (s, 3H), 1.23 (tt, ^3J = 8.3, 5.0 Hz, 1H), 1.29 (s, 3H), 1.39 (s, 3H), 2.85 (s, 1H), 3.27 (s, 3H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = −0.5, 8.2, 19.3, 19.8, 24.9, 50.2, 73.8, 77.9, 79.4, 87.3. The compound was too labile to obtain an EI-HRMS.

*1-Cyclopropyl-4-methoxy-3,4-dimethylpent-1-yn-3-yl acetate (**9a**).* Synthesized according to the general procedure, using **8a** (1.35 g, 7.40 mmol, 1.0 equiv) in DMF (7.5 mL), NaH (2.96 g, 74.0 mmol,

dx.doi.org/10.1021/jo5009993 | J. Org. Chem. 2014, 79, 6372−6379

10.0 equiv) in DMF (40 mL) and acetyl chloride (5.3 mL, 5.8 g, 74.0 mmol, 10.0 equiv). Work up and purification by column chromatography (*n*-pentane/EtOAc: 30/1) yielded product **9a** (1.05 g, 63%) as a colorless oil: TLC R_f = 0.41 (P:EtOAc 10:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 2981, 2949, 2829, 2237, 1741, 1364, 1234, 1128, 1071, 1013, 885, 817 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 224 (1) $[C_{13}H_{20}O_3]^+$, 209 (1) $[C_{12}H_{17}O_3]^+$, 73 (100) $[C_4H_9O]^+$, 43 (21) $[C_2H_3O]^+$; ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ [ppm] = 0.64−0.68 (m, 2H), 0.72−0.76 (m, 2H), 1.26 (tt, ^3J = 8.2, 5.1 Hz, 1H), 1.28 (s, 3H), 1.30 (s, 3H), 1.68 (s, 3H), 2.02 (s, 3H), 3.31 (s, 3H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = −0.4, 8.2, 8.3, 19.6, 20.5, 21.2, 22.3, 50.8, 74.3, 79.3, 80.9, 89.6, 169.0. The compound was too labile to obtain an EI-HRMS.

*2-Methoxy-2,3-dimethylnon-4-yn-3-ol (**8b**).* Synthesized according to the general procedure, using 1-hexyne (822 mg, 10.0 mmol, 1.0 equiv) in THF (20 mL), *n*-BuLi (4.0 mL, 10.0 mmol, 1.0 equiv) and 3-methoxy-3-methylbutan-2-one (1.16 g, 10.0 mmol, 1.0 equiv) in THF (5 mL). Work up and purification by column chromatography (*n*-pentane/EtOAc: 20/1) yielded product **8b** (1.43 g, 72%) as a colorless oil: TLC R_f = 0.48 (P:EtOAc 10:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 3465, 2978, 2956, 2934, 2832, 2244, 1465, 1363, 1154, 1116, 1091, 904, 768, 739 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 141 (1) $[C_8H_{13}O_2]^+$, 125 (3) $[C_8H_{13}O]^+$, 73 (100) $[C_4H_9O]^+$, 43 (21) $[C_2H_3O]^+$; ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ [ppm] = 0.89 (t, ^3J = 7.3 Hz, 3H), 1.20 (s, 3H), 1.31 (s, 3H), 1.35−1.41 (m, 2H), 1.41 (s, 3H), 1.44−1.51 (m, 2H), 2.19 (t, ^3J = 7.0 Hz, 2H), 2.86 (s, 1H), 3.27 (s, 3H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 13.6, 18.4, 19.4, 19.8, 21.9, 25.0, 30.8, 50.2, 73.9, 79.4, 82.8, 84.4; HRMS (EI, 70 eV) ($C_{12}H_{22}O_2$) calcd. 198.1614, found 198.1607.

*2-Methoxy-2,3-dimethylnon-4-yn-3-yl acetate (**9b**).* Synthesized according to the general procedure, using **8b** (1.43 g, 7.20 mmol, 1.0 equiv) in DMF (7.0 mL), NaH (2.88 g, 72.0 mmol, 10.0 equiv) in DMF (40 mL) and acetyl chloride (5.1 mL, 5.7 g, 72.0 mmol, 10.0 equiv). Work up and purification by column chromatography (*n*-pentane/EtOAc: 30/1) yielded product **9b** (1.00 g, 58%) as a colorless oil: TLC R_f = 0.54 (P:EtOAc 10:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 2984, 2935, 2837, 2243, 1744, 1365, 1231, 1128, 1086, 1012, 947, 840 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 73 (100) $[C_4H_9O]^+$, 43 (16) $[C_2H_3O]^+$; ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ [ppm] = 0.89 (t, ^3J = 7.3 Hz, 3H), 1.31 (s, 3H), 1.32 (s, 3H), 1.36−1.43 (m, 2H), 1.45−1.52 (m, 2H), 1.70 (s, 3H), 2.02 (s, 3H), 2.21 (t, ^3J = 7.0 Hz, 2H), 3.32 (s, 3H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 13.6, 18.5, 19.5, 20.5, 21.2, 21.9, 22.3, 30.6, 50.8, 79.3, 79.4, 80.9, 86.6, 169.0; HRMS (EI, 70 eV) [($C_{12}H_{22}O_2$(M-Ac)] calcd. 198.1614, found 198.1607.

*1-(Cyclohex-1-en-1-yl)-4-methoxy-3,4-dimethylpent-1-yn-3-ol (**8c**).* Synthesized according to the general procedure, using 1-ethynylcyclohexene (533 mg, 5.0 mmol, 1.0 equiv) in THF (10 mL), *n*-BuLi (2.0 mL, 5.0 mmol, 1.0 equiv) and 3-methoxy-3-methylbutan-2-one (518 mg, 5.0 mmol, 1.0 equiv) in THF (2.5 mL). Work up and purification by column chromatography (*n*-pentane/EtOAc: 20/1) yielded product **8c** (853 mg, 77%) as a colorless oil: TLC R_f = 0.34 (P:EtOAc 10:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 3404, 2979, 2939, 2832, 2209, 1716, 1672, 1364, 1182, 1087 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 222 (2) $[C_{14}H_{22}O_2]^+$, 73 (100) $[C_4H_9O]^+$, 43 (76) $[C_2H_3O]^+$; ^1H NMR (360 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.21 (s, 3H), 1.32 (s, 3H), 1.45 (s, 3H), 1.52−1.67 (m, 4H), 2.04−2.14 (m, 4H), 2.94 (s, 1H), 3.29 (s, 3H), 6.05−6.09 (m, 1H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 19.4, 19.9, 21.5, 22.3, 24.7, 25.5, 29.2, 50.2, 74.1, 79.4, 85.6, 89.2, 120.3, 134.6; HRMS (EI, 70 eV) ($C_{14}H_{22}O_2$) calcd. 222.1614, found 222.1615.

*1-(Cyclohex-1-en-1-yl)-4-methoxy-3,4-dimethylpent-1-yn-3-yl acetate (**9c**).* Synthesized according to the general procedure, using **8c** (694 mg, 3.07 mmol, 1.0 equiv) in DMF (3.0 mL), NaH (1.23 g, 30.7 mmol, 10.0 equiv) in DMF (15 mL) and acetyl chloride (2.2 mL, 2.4 g, 31.0 mmol, 10.0 equiv). Work up and purification by column chromatography (*n*-pentane/EtOAc: 30/1) yielded product **9c** (418 mg, 51%) as a colorless oil: TLC R_f = 0.44 (P:EtOAc 10:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 2980, 2939, 2833, 2209, 1717, 1365, 1086 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 73 (100) $[C_4H_9O]^+$, 43 (89) $[C_2H_3O]^+$; ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.33 (s, 3H), 1.34 (s, 3H), 1.53−1.63 (m, 4H), 1.73 (s, 3H), 2.03 (s, 3H), 2.04−2.13 (m, 4H), 3.33 (s, 3H), 6.07−6.11 (m, 1H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 19.7, 20.4, 21.4, 21.5, 22.2, 22.2, 25.6, 29.0, 50.9, 79.4, 81.0, 85.8, 87.7, 120.2, 135.1, 168.9. The compound was too labile to obtain an EI-HRMS.

*4-Methoxy-3,4-dimethyl-1-(phenylthio)pent-1-yn-3-ol (**8d**).* Synthesized according to the general procedure, using ethynyl(phenyl)-sulfane (1.07 g, 8.0 mmol, 1.0 equiv) in THF (16 mL), *n*-BuLi (3.2 mL, 8.0 mmol, 1.0 equiv) and 3-methoxy-3-methylbutan-2-one (929 mg, 8.0 mmol, 1.0 equiv) in THF (4 mL). Work up and purification by column chromatography (*n*-pentane/EtOAc: 20/1) yielded product **8d** (1.79 g, 89%) as a colorless oil: TLC R_f = 0.39 (P:EtOAc 9:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 3432, 3052, 2979, 2948, 2833, 2318, 1715, 1439, 1200, 1088, 1024, 740, 688 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 250 (6) $[C_{14}H_{18}O_2S]^+$, 177 (100) $[C_{10}H_9OS]^+$, 141 (34) $[C_8H_{13}O_2]^+$; ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.25 (s, 3H), 1.36 (s, 3H), 1.53 (s, 3H), 3.14 (s, 1H), 3.32 (s, 3H), 7.18−7.23 (m, 1H), 7.30−7.35 (m, 2H), 7.41−7.45 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 18.7, 20.1, 24.4, 50.1, 70.0, 75.0, 79.6, 102.0, 125.9, 126.3, 129.1, 133.1; HRMS (EI, 70 eV) ($C_{14}H_{18}O_2S$) calcd. 250.1022, found 250.1042.

*4-Methoxy-3,4-dimethyl-1-(phenylthio)pent-1-yn-3-yl acetate (**9d**).* Synthesized according to the general procedure, using **8d** (1.13 g, 4.50 mmol, 1.0 equiv) in DMF (4.5 mL), NaH (1.80 g, 45.0 mmol, 10.0 equiv) in DMF (23 mL) and acetyl chloride (3.2 mL, 3.5 g, 45.0 mmol, 10.0 equiv). Work up and purification by column chromatography (*n*-pentane/EtOAc: 7/1) yielded product **9d** (0.88 g, 67%) as a colorless oil: TLC R_f = 0.40 (P:EtOAc 9:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 3062, 2981, 2949, 2837, 2177, 1741, 1365, 1240, 1126, 1085, 789, 688 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 292 (2) $[C_{16}H_{20}O_3S]^+$, 73 (100) $[C_4H_9O]^+$, 43 (22) $[C_2H_3O]^+$; ^1H NMR (360 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.35 (s, 3H), 1.37 (s, 3H), 1.82 (s, 3H), 2.07 (s, 3H), 3.35 (s, 3H), 7.18−7.22 (m, 1H), 7.31−7.35 (m, 2H), 7.47−7.50 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 19.8, 20.7, 21.1, 22.1, 50.7, 72.7, 79.3, 81.1, 98.5, 126.1, 126.3, 129.1, 133.1, 169.0; HRMS (EI, 70 eV) ($C_{16}H_{20}O_3S$) calcd. 292.1128, found 292.1137.

*4-Methoxy-3,4-dimethyl-1-phenylpent-1-yn-3-ol (**8e**).* Synthesized according to the general procedure, using phenylacetylene (818 mg, 8.0 mmol, 1.0 equiv) in THF (16 mL), *n*-BuLi (3.2 mL, 8.0 mmol, 1.0 equiv) and 3-methoxy-3-methylbutan-2-one (929 mg, 8.0 mmol, 1.0 equiv) in THF (4 mL). Work up and purification by column chromatography (*n*-pentane/EtOAc: 20/1) yielded product **8e** (1.52 g, 87%) as a colorless oil: TLC R_f = 0.39 (P:EtOAc 9:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 3447, 2980, 2942, 2831, 2230, 1364, 1121, 1106, 1089, 755, 690 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 218 (2) $[C_{14}H_{18}O_2]^+$, 102 (78), 73 (100) $[C_4H_9O]^+$; ^1H NMR (360 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.28 (s, 3H), 1.41 (s, 3H), 1.55 (s, 3H), 3.09 (s, 1H), 3.33 (s, 3H), 7.27−7.32 (m, 3H), 7.41−7.46 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 19.3, 19.9, 24.6, 50.2, 74.3, 79.5, 83.8, 92.0, 123.0, 128.1, 128.1, 131.6; HRMS (EI, 70 eV) ($C_{14}H_{18}O_2$) calcd. 218.1301, found 218.1296.

*4-Methoxy-3,4-dimethyl-1-phenylpent-1-yn-3-yl acetate (**9e**).* Synthesized according to the general procedure, using **8e** (982 mg, 4.50 mmol, 1.0 equiv) in DMF (4.5 mL), NaH (1.80 g, 45.0 mmol, 10.0 equiv) in DMF (23 mL) and acetyl chloride (3.2 mL, 3.5 g, 45.0 mmol, 10.0 equiv). Work up and purification by column chromatography (*n*-pentane/EtOAc: 20/1) yielded product **9e** (804 mg, 69%) as a colorless oil: TLC R_f = 0.48 (P:EtOAc 9:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 2981, 2949, 2826, 2240, 1741, 1365, 1233, 1126, 1085, 756, 691 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 260 (3) $[C_{16}H_{20}O_3]^+$, 73 (100) $[C_4H_9O]^+$, 43 (54) $[C_2H_3O]^+$; ^1H NMR (360 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.40 (s, 6H), 1.82 (s, 3H), 2.07 (s, 3H), 3.36 (s, 3H), 7.27−7.31 (m, 3H), 7.41−7.46 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 19.7, 20.3, 21.3, 22.2, 50.9, 79.4, 80.9, 85.9, 88.6, 122.8, 128.1, 128.3, 131.8, 168.9; HRMS (EI, 70 eV) ($C_{16}H_{20}O_3$) calcd. 260.1407, found 260.1412.

*2-(1-Methoxycyclohexyl)-4-(4-methoxyphenyl)but-3-yn-2-ol (**8f**).* Synthesized according to the general procedure, using 1-ethynyl-4-methoxybenzene (1.98 g, 15.0 mmol, 1.0 equiv) in THF (30 mL), *n*-

dx.doi.org/10.1021/jo5009993 | J. Org. Chem. 2014, 79, 6372−6379

BuLi (6.0 mL, 15.0 mmol, 1.0 equiv) and 1-(1-methoxycyclohexyl)-ethanone (2.34 g, 15.0 mmol, 1.0 equiv) in THF (7 mL). Work up and purification by column chromatography (*n*-pentane/EtOAc: 20/1) yielded product **8f** (2.77 g, 64%) as a colorless oil: TLC R_f = 0.33 (P:EtOAc 9:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 3446, 2934, 2856, 2835, 2230, 1605, 1508, 1245, 1071, 1031, 830, 795 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 288 (2) $[C_{18}H_{24}O_3]^+$, 113 (100) $[C_7H_{13}O]^+$; ^1H NMR (360 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.36−1.73 (m, 8H), 1.54 (s, 3H), 1.80−1.89 (m, 1H), 2.25−2.33 (m, 1H), 2.81 (s, 1H), 3.56 (s, 3H), 3.80 (s, 3H), 6.81−6.85 (m, 2H), 7.32−7.36 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 21.8, 22.1, 25.4, 25.6, 27.2, 30.8, 51.7, 55.3, 73.6, 79.4, 84.9, 91.7, 113.9, 115.0, 132.8, 159.6; HRMS (EI, 70 eV) ($C_{18}H_{24}O_3$) calcd. 288.1720, found 288.1721.

*2-(1-Methoxycyclohexyl)-4-(4-methoxyphenyl)but-3-yn-2-yl acetate (**9f**).* Synthesized according to the general procedure, using **8f** (865 mg, 3.00 mmol, 1.0 equiv) in DMF (3 mL), NaH (1.20 g, 30.0 mmol, 10.0 equiv) in DMF (15 mL) and acetyl chloride (1.7 mL, 1.9 g, 24.0 mmol, 10.0 equiv). Work up and purification by column chromatography (*n*-pentane/EtOAc: 20/1) yielded product **9f** (615 mg, 62%) as a colorless oil: TLC R_f = 0.37 (P:EtOAc 9:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 2935, 2861, 2840, 2233, 1743, 1509, 1240, 1077, 831 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 330 (1) $[C_{20}H_{26}O_4]^+$, 113 (86) $[C_7H_{13}O]^+$, 85 (64), 43 (100) $[C_2H_3O]^+$; ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.13−1.28 (m, 2H), 1.39−1.56 (m, 3H), 1.67−1.77 (m, 3H), 1.79 (s, 3H), 1.84−1.90 (m, 1H), 2.05 (s, 3H), 2.21−2.27 (m, 1H), 3.47 (s, 3H), 3.80 (s, 3H), 6.80−6.83 (m, 2H), 7.34−7.37 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 20.2, 21.8, 21.8, 22.3, 25.6, 26.9, 30.9, 51.7, 55.3, 79.9, 82.2, 86.5, 87.5, 113.8, 114.9, 133.1, 159.7, 168.5; HRMS (EI, 70 eV) ($C_{20}H_{26}O_4$) calcd. 330.1826, found 330.1829.

*3-Isopropyl-4-methoxy-1-(4-methoxyphenyl)-4-methylpent-1-yn-3-ol (**8g**).* Synthesized according to the general procedure, using 1-ethynyl-4-methoxybenzene (1.98 g, 15.0 mmol, 1.0 equiv) in THF (30 mL), *n*-BuLi (6.0 mL, 15.0 mmol, 1.0 equiv) and 2-methoxy-2,4-dimethylpentan-3-one (2.16 g, 15.0 mmol, 1.0 equiv) in THF (7 mL). Work up and purification by column chromatography (*n*-pentane/EtOAc: 20/1) yielded product **8g** (2.23 g, 54%) as a colorless oil: TLC R_f = 0.43 (P:EtOAc 9:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 3520, 2963, 2837, 2216, 1605, 1500, 1250, 1020 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 276 (5) $[C_{17}H_{24}O_3]^+$, 203 (10) $[C_{13}H_{15}O_2]^+$, 73 (100) $[C_4H_9O]^+$; ^1H NMR (360 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.11 (d, ^3J = 6.7 Hz, 3H), 1.13 (d, ^3J = 6.7 Hz, 3H), 1.29 (s, 3H), 1.45 (s, 3H), 2.08 (hept, ^3J = 6.7 Hz, 1H), 3.32 (s, 3H), 3.47 (s, 1H), 3.80 (s, 3H), 6.80−6.84 (m, 2H), 7.35−7.39 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 18.9, 19.8, 20.0, 21.6, 34.6, 49.7, 55.3, 79.5, 80.2, 85.5, 88.7, 113.8, 115.4, 133.0, 159.4; HRMS (EI, 70 eV) ($C_{17}H_{24}O_3$) calcd. 276.1720, found 276.1715.

General Procedure for the Synthesis of Substituted 2-Alkenylfurans 2, 6 and 10. To a solution of the propargylic acetate (250 μmol, 1.0 equiv), silyl enol ether (1.00 mmol, 4.0 equiv) and nitromethane (c = 125 mM) in a flame-dried flask was added $Bi(OTf)_3$ (25 μmol, 0.1 equiv) at 0 °C. After 5 min the reaction mixture was warmed to room temperature. The solvent was removed under reduced pressure, and the crude mixture was purified by flash column chromatography to afford the substituted 2-alkenylfuran.

*5-(tert-Butyl)-3-(4-methoxyphenyl)-2-(4-methylpent-2-en-2-yl)-furan (**2**).* Synthesized according to the general procedure, using **1** (76.1 mg, 250 μmol, 1.0 equiv), [(3,3-dimethylbut-1-en-2-yl)oxy]-trimethylsilane (172 mg, 1.00 mmol, 4.0 equiv), $Bi(OTf)_3$ (16.4 mg, 25.0 μmol, 0.1 equiv) and nitromethane (2.0 mL). Purification by column chromatography (*n*-pentane) yielded product **2** (61.7 mg, 49%) as a colorless oil (d.r. = 54/46): TLC R_f = 0.81 (P:EtOAc 10:1 [CAM]); MS (EI, 70 eV) *m*/*z* (%) = 312 (80) $[C_{21}H_{28}O_2]^+$, 297 (100) $[C_{20}H_{25}O_2]^+$; Major diastereoisomer, ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ [ppm] = 0.96 (d, ^3J = 6.6 Hz, 6H), 1.32 (s, 9H), 1.85 (d, ^4J = 1.5 Hz, 3H), 2.63 (dhept, ^3J = 9.8, 6.6 Hz, 1H), 3.83 (s, 3H), 5.61 (dd, ^4J = 1.5 Hz, ^3J = 9.8 Hz, 1H), 5.99 (s, 1H), 6.85−6.90 (m, 2H), 7.30−7.35 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 14.5, 22.5, 27.3, 29.1, 32.5, 55.2, 105.8, 113.5, 120.6, 123.6, 127.9, 129.7, 136.6, 149.0, 158.1, 161.4; Minor diastereoisomer, ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ [ppm] = 0.89 (d, ^3J = 6.6 Hz, 6H), 1.32 (s, 9H), 1.86 (d, ^4J = 1.5 Hz, 3H), 2.45 (dhept, ^3J = 9.8, 6.6 Hz, 1H), 3.82 (s, 3H), 5.37 (dd, ^4J = 1.5 Hz, ^3J = 9.8 Hz, 1H), 6.10 (s, 1H), 6.85−6.90 (m, 2H), 7.30−7.35 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 14.5, 22.3, 23.0, 29.1, 32.5, 55.2, 103.7, 113.7, 121.4, 124.4, 127.1, 128.5, 140.7, 147.0, 158.1, 162.3.

*5-(tert-Butyl)-3-(4-methoxyphenyl)-2-(3-methylbut-2-en-2-yl)-furan (**6a**).* Synthesized according to the general procedure, using **5** (72.6 mg, 250 μmol, 1.0 equiv), [(3,3-dimethylbut-1-en-2-yl)oxy]-trimethylsilane (172 mg, 1.00 mmol, 4.0 equiv), $Bi(OTf)_3$ (16.4 mg, 25.0 μmol, 0.1 equiv) and nitromethane (2.0 mL). Purification by column chromatography (*n*-pentane) yielded product **6a** (57.4 mg, 77%) as a colorless oil: TLC R_f = 0.20 (Pentane [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 2964, 2931, 2906, 2835, 1509, 1246, 1176, 1130, 1036, 833, 801 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 298 (59) $[C_{20}H_{26}O_2]^+$, 283 (100) $[C_{19}H_{23}O_2]^+$, 44 (66); ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.32 (s, 9H), 1.53 (s, 3H), 1.81 (s, 3H), 1.92 (s, 3H), 3.82 (s, 3H), 6.13 (s, 1H), 6.85−6.88 (m, 2H), 7.30−7.33 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 17.8, 20.5, 22.3, 29.1, 32.6, 55.2, 103.0, 113.7, 120.4, 120.6, 127.4, 127.9, 134.1, 148.9, 157.8, 162.1; HRMS (EI, 70 eV) ($C_{20}H_{26}O_2$) calcd. 298.1927, found 298.1925.

*3-(4-Methoxyphenyl)-2-(3-methylbut-2-en-2-yl)-5-phenylfuran (**6b**).* Synthesized according to the general procedure, using **5** (72.6 mg, 250 μmol, 1.0 equiv), trimethyl[(1-phenylvinyl)oxy]silane (192 mg, 1.00 mmol, 4.0 equiv), $Bi(OTf)_3$ (16.4 mg, 25.0 μmol, 0.1 equiv) and nitromethane (2.0 mL). Purification by column chromatography (*n*-pentane) yielded product **6b** (54.9 mg, 69%) as a colorless oil: TLC R_f = 0.78 (P:EtOAc 10:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 3058, 3035, 2970, 2930, 2836, 1607, 1508, 1246, 1176, 1034, 833, 760, 690 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 318 (8) $[C_{22}H_{22}O_2]^+$, 115 (100), 77 (40) $[C_6H_5]^+$; ^1H NMR (360 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.57 (s, 3H), 1.85 (s, 3H), 2.01 (s, 3H), 3.84 (s, 3H), 6.85 (s, 1H), 6.90−6.94 (m, 2H), 7.23−7.28 (m, 1H), 7.37−7.42 (m, 4H), 7.70−7.74 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 17.9, 20.6, 22.5, 55.2, 106.1, 113.9, 120.1, 122.7, 123.5, 126.7, 127.0, 128.0, 128.6, 131.0, 135.0, 150.7, 151.6, 158.2; HRMS (EI, 70 eV) ($C_{22}H_{22}O_2$) calcd. 318.1614, found 318.1615.

*3-(4-Methoxyphenyl)-2-(3-methylbut-2-en-2-yl)-4,5,6,7-tetrahydrobenzofuran (**6c**).* Synthesized according to the general procedure, using **5** (72.6 mg, 250 μmol, 1.0 equiv), (cyclohex-1-en-1-yloxy)-trimethylsilane (170 mg, 1.00 mmol, 4.0 equiv), $Bi(OTf)_3$ (16.4 mg, 25.0 μmol, 0.1 equiv) and nitromethane (2.0 mL). Purification by column chromatography (*n*-pentane) yielded product **6c** (68.2 mg, 92%) as a colorless oil: TLC R_f = 0.88 (P:EtOAc 10:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 2931, 2853, 1509, 1244, 1173, 1034, 834, 731 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 296 (27) $[C_{20}H_{24}O_2]^+$, 281 (37) $[C_{19}H_{21}O_2]^+$, 84 (100); ^1H NMR (360 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.44 (s, 3H), 1.72−1.78 (m, 5H), 1.85−1.89 (m, 2H), 1.91 (s, 3H), 2.48 (tt, ^3J = 6.2, 2.0 Hz, 2H), 2.64 (tt, ^3J = 6.4, 1.8 Hz, 2H), 3.82 (s, 3H), 6.86−6.90 (m, 2H), 7.19−7.23 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 18.1, 20.5, 22.2, 22.4, 22.9, 23.3, 23.3, 55.1, 113.6, 116.8, 120.0, 120.8, 129.2, 127.1, 133.4, 148.9, 149.4, 157.8; HRMS (EI, 70 eV) ($C_{20}H_{24}O_2$) calcd. 296.1771, found 296.1767.

*3-(4-Methoxyphenyl)-2-(3-methylbut-2-en-2-yl)-5,6-dihydro-4H-cyclopenta[b]furan (**6d**).* Synthesized according to the general procedure, using **5** (72.6 mg, 250 μmol, 1.0 equiv), (cyclopent-1-en-1-yloxy)trimethylsilane (156 mg, 1.00 mmol, 4.0 equiv), $Bi(OTf)_3$ (16.4 mg, 25.0 μmol, 0.1 equiv) and nitromethane (2.0 mL). Purification by column chromatography (*n*-pentane) yielded product **6d** (44.5 mg, 63%) as a colorless oil: TLC R_f = 0.85 (P:EtOAc 10:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 2955, 2931, 2853, 1708, 1598, 1509, 1249, 1175, 1029, 832, 732 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 282 (12) $[C_{19}H_{22}O_2]^+$, 225 (52) $[C_{15}H_{13}O_2]^+$, 84 (100); ^1H NMR (360 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.50 (s, 3H), 1.78 (s, 3H), 1.94 (s, 3H), 2.48 (p, ^3J = 6.9 Hz, 2H), 2.73 (t, ^3J = 6.9 Hz, 4H), 3.81 (s, 3H), 6.84−6.88 (m, 2H), 7.28−7.33 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 18.0, 20.5, 22.4, 24.5, 24.9, 27.7, 55.2, 113.8, 119.0, 121.0, 125.6, 127.1, 127.9, 134.3, 154.4, 157.4, 157.8; HRMS (EI, 70 eV) ($C_{19}H_{22}O_2$) calcd. 282.1614, found 282.1617.

dx.doi.org/10.1021/jo5009993 | *J. Org. Chem.* 2014, 79, 6372−6379

*2-Ethyl-4-(4-methoxyphenyl)-3-methyl-5-(3-methylbut-2-en-2-yl)furan (**6e**).* Synthesized according to the general procedure, using **5** (72.6 mg, 250 μmol, 1.0 equiv), trimethyl(pent-2-en-3-yloxy)silane (158 mg, 1.00 mmol, 4.0 equiv), $Bi(OTf)_3$ (16.4 mg, 25.0 μmol, 0.1 equiv) and nitromethane (2.0 mL). Purification by column chromatography (*n*-pentane) yielded product **6e** (61.1 mg, 86%) as a colorless oil: TLC R_f = 0.88 (P:EtOAc 10:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 2972, 2933, 2837, 1509, 1245, 1173, 1035, 909, 833, 781 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 284 (84) $[C_{19}H_{24}O_2]^+$, 269 (100) $[C_{18}H_{21}O_2]^+$, 44 (84); ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.25 (t, ^3J = 7.6 Hz, 3H), 1.44 (s, 3H), 1.72 (s, 3H), 1.84 (s, 3H), 1.95 (s, 3H), 2.64 (q, ^3J = 7.6 Hz, 2H), 3.83 (s, 3H), 6.88−6.91 (m, 2H), 7.15−7.18 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 9.1, 13.1, 18.0, 19.6, 20.5, 22.4, 55.1, 113.0, 113.6, 119.9, 122.5, 127.3, 129.9, 133.2, 149.4, 150.6, 157.8; HRMS (EI, 70 eV) ($C_{19}H_{24}O_2$) calcd. 284.1771, found 284.1767.

*1-[4-(4-Methoxyphenyl)-2-methyl-5-(3-methylbut-2-en-2-yl)-furan-3-yl]ethanone (**6f**).* Synthesized according to the general procedure, using **5** (72.6 mg, 250 μmol, 1.0 equiv), 4-[(trimethylsilyl)-oxy]pent-3-en-2-one (172 mg, 1.00 mmol, 4.0 equiv), $Bi(OTf)_3$ (16.4 mg, 25.0 μmol, 0.1 equiv) and nitromethane (2.0 mL). Purification by column chromatography (*n*-pentane) yielded product **6f** (34.3 mg, 46%) as a colorless oil: TLC R_f = 0.53 (P:EtOAc 10:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 2931, 2839, 1670, 1509, 1245, 1174, 1031, 951, 832 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 298 (94) $[C_{19}H_{22}O_3]^+$, 283 (100) $[C_{18}H_{19}O_3]^+$; ^1H NMR (360 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.40 (s, 3H), 1.67 (s, 3H), 1.77 (s, 3H), 1.99 (s, 3H), 2.53 (s, 3H), 3.82 (s, 3H), 6.86−6.90 (m, 2H), 7.09−7.13 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 14.3, 18.2, 20.3, 22.5, 30.8, 55.1, 113.7, 118.5, 120.8, 123.2, 126.1, 130.6, 135.4, 150.8, 156.0, 158.7, 196.7; HRMS (EI, 70 eV) ($C_{19}H_{22}O_3$) calcd. 298.1563, found 298.1555.

*3-Cyclopropyl-5-ethyl-4-methyl-2-(3-methylbut-2-en-2-yl)furan (**10a**).* Synthesized according to the general procedure, using **9a** (56.1 mg, 250 μmol, 1.0 equiv), trimethyl(pent-2-en-3-yloxy)silane (158 mg, 1.00 mmol, 4.0 equiv), $Bi(OTf)_3$ (16.4 mg, 25.0 μmol, 0.1 equiv) and nitromethane (2.0 mL). Purification by column chromatography (*n*-pentane) yielded product **10a** (42.0 mg, 77%) as a colorless oil: TLC R_f = 0.40 (P [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 2979, 2935, 1760, 1716, 1376, 1025, 933 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 218 (5) $[C_{15}H_{22}O]^+$, 177 (20) $[C_{12}H_{17}O]^+$, 69 (81) $[C_5H_9]^+$, 43 (100), 41 (61) $[C_3H_5]^+$; ^1H NMR (360 MHz, $CDCl_3$, 300 K) δ [ppm] = 0.34−0.39 (m, 2H), 0.63−0.69 (m, 2H), 1.17 (t, ^3J = 7.5 Hz, 3H), 1.36 (tt, ^3J = 8.4, 5.3 Hz, 1H), 1.70 (s, 3H), 1.81 (s, 3H), 1.88 (s, 3H), 1.94 (s, 3H), 2.53 (q, ^3J = 7.5 Hz, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 5.0, 6.1, 8.4, 13.1, 18.2, 19.5, 20.4, 22.7, 114.8, 120.4, 121.5, 132.9, 149.7, 150.1; HRMS (EI, 70 eV) ($C_{15}H_{22}O$) calcd. 218.1665, found 218.1669.

*3-n-Butyl-5-ethyl-4-methyl-2-(3-methylbut-2-en-2-yl)furan (**10b**).* Synthesized according to the general procedure, using **9b** (60.1 mg, 250 μmol, 1.0 equiv), trimethyl(pent-2-en-3-yloxy)silane (158 mg, 1.00 mmol, 4.0 equiv), $Bi(OTf)_3$ (16.4 mg, 25.0 μmol, 0.1 equiv) and nitromethane (2.0 mL). Purification by column chromatography (*n*-pentane) yielded product **10b** (29.9 mg, 51%) as a colorless oil: TLC R_f = 0.55 (P [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 2958, 2932, 2872, 1716, 1457, 1377, 1084, 936 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 234 (63) $[C_{16}H_{26}O]^+$, 219 (69) $[C_{15}H_{23}O]^+$, 205 (63) $[C_{14}H_{21}O]^+$, 191 (67) $[C_{13}H_{19}O]^+$, 57 (93) $[C_4H_9]^+$, 43 (100) $[C_3H_7]^+$; ^1H NMR (360 MHz, $CDCl_3$, 300 K) δ [ppm] = 0.89 (t, ^3J = 7.2 Hz, 3H), 1.17 (t, ^3J = 7.5 Hz, 3H), 1.24−1.34 (m, 2H), 1.36−1.45 (m, 2H), 1.64 (s, 3H), 1.79 (s, 3H), 1.87 (s, 3H), 1.89 (s, 3H), 2.17−2.23 (m, 2H), 2.55 (q, ^3J = 7.6 Hz, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 8.5, 13.1, 13.9, 18.5, 19.5, 20.3, 22.5, 22.6, 23.9, 31.7, 113.5, 120.3, 120.7, 133.0, 149.0, 150.1; HRMS (EI, 70 eV) ($C_{16}H_{26}O$) calcd. 234.1978, found 234.1975.

*3-(Cyclohex-1-en-1-yl)-5-ethyl-4-methyl-2-(3-methylbut-2-en-2-yl)furan (**10c**).* Synthesized according to the general procedure, using **9c** (66.1 mg, 250 μmol, 1.0 equiv), trimethyl(pent-2-en-3-yloxy)silane (158 mg, 1.00 mmol, 4.0 equiv), $Bi(OTf)_3$ (16.4 mg, 25.0 μmol, 0.1 equiv) and nitromethane (2.0 mL). Purification by column chromatography (*n*-pentane) yielded product **10c** (38.8 mg, 60%) as a colorless oil: TLC R_f = 0.40 (P [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 2970, 2926, 2856, 1716, 1448, 1374, 1089, 919 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 258 (41) $[C_{18}H_{26}O]^+$, 243 (100) $[C_{17}H_{23}O]^+$; ^1H NMR (360 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.18 (t, ^3J = 7.5 Hz, 3H), 1.59−1.67 (m, 7H), 1.77 (s, 3H), 1.87 (s, 3H), 1.88 (s, 3H), 2.05−2.15 (m, 4H), 2.55 (q, ^3J = 7.5 Hz, 2H), 5.53−5.57 (m, 1H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 9.3, 13.1, 18.1, 19.6, 20.6, 22.3, 22.6, 23.3, 25.7, 28.5, 112.9, 120.9, 124.9, 126.1, 131.1, 132.7, 148.7, 150.0; HRMS (EI, 70 eV) ($C_{18}H_{26}O$) calcd. 258.1978, found 258.1979.

*2-Ethyl-3-methyl-5-(3-methylbut-2-en-2-yl)-4-(phenylthio)furan (**10d**).* Synthesized according to the general procedure, using **9d** (73.1 mg, 250 μmol, 1.0 equiv), trimethyl(pent-2-en-3-yloxy)silane (158 mg, 1.00 mmol, 4.0 equiv), $Bi(OTf)_3$ (16.4 mg, 25.0 μmol, 0.1 equiv) and nitromethane (2.0 mL). Purification by column chromatography (*n*-pentane) yielded product **10d** (60.2 mg, 84%) as a colorless oil: TLC R_f = 0.90 (P:EtOAc 9:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 3059, 2978, 2923, 2877, 1667, 1440, 1084, 1023, 739, 689 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 286 (100) $[C_{18}H_{22}OS]^+$, 271 (22) $[C_{17}H_{19}OS]^+$, 209 (64) $[C_{12}H_{17}OS]^+$; ^1H NMR (360 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.25 (t, ^3J = 7.5 Hz, 3H), 1.69 (s, 3H), 1.80 (s, 3H), 1.82 (s, 3H), 1.93 (s, 3H), 2.64 (q, ^3J = 7.5 Hz, 2H), 7.05−7.13 (m, 3H), 7.18−7.24 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 8.3, 13.0, 18.3, 19.9, 20.6, 22.8, 109.5, 116.6, 119.5, 124.6, 125.7, 128.6, 135.7, 138.2, 151.4, 157.5; HRMS (EI, 70 eV) ($C_{18}H_{22}OS$) calcd. 286.1386, found 286.1390.

*2-Ethyl-3-methyl-5-(3-methylbut-2-en-2-yl)-4-phenylfuran (**10e**).* Synthesized according to the general procedure, using **9e** (65.1 mg, 250 μmol, 1.0 equiv), trimethyl(pent-2-en-3-yloxy)silane (158 mg, 1.00 mmol, 4.0 equiv), $Bi(OTf)_3$ (16.4 mg, 25.0 μmol, 0.1 equiv) and nitromethane (2.0 mL). Purification by column chromatography (*n*-pentane) yielded product **8e** (58.5 mg, 92%) as a colorless oil: TLC R_f = 0.93 (P:EtOAc 9:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 3057, 3027, 2975, 2933, 2877, 1762, 1715, 1682, 1445, 1071, 769, 699 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 254 (80) $[C_{18}H_{22}O]^+$, 239 (100) $[C_{17}H_{19}O]^+$; ^1H NMR (360 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.26 (t, ^3J = 7.5 Hz, 3H), 1.43 (s, 3H), 1.72 (s, 3H), 1.86 (s, 3H), 1.98 (s, 3H), 2.65 (q, ^3J = 7.5 Hz, 2H), 7.20−7.27 (m, 3H), 7.32−7.36 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 9.1, 13.1, 18.1, 19.6, 20.5, 22.4, 112.9, 119.8, 123.0, 126.0, 128.1, 128.9, 133.3, 134.9, 149.8, 150.8; HRMS (EI, 70 eV) ($C_{18}H_{22}O$) calcd. 254.1665, found 254.1665.

*2-(1-Cyclohexylideneethyl)-5-ethyl-3-(4-methoxyphenyl)-4-methylfuran (**10f**).* Synthesized according to the general procedure, using **9f** (82.6 mg, 250 μmol, 1.0 equiv), trimethyl(pent-2-en-3-yloxy)silane (158 mg, 1.00 mmol, 4.0 equiv), $Bi(OTf)_3$ (16.4 mg, 25.0 μmol, 0.1 equiv) and nitromethane (2.0 mL). Purification by column chromatography (*n*-pentane/EtOAc: 40/1) yielded product **8f** (71.4 mg, 88%) as a colorless oil: TLC R_f = 0.77 (P:EtOAc 9:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 2931, 2845, 1509, 1246, 1173, 1032, 834 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 324 (42) $[C_{22}H_{28}O_2]^+$, 309 (23) $[C_{21}H_{25}O_2]^+$, 135 (100); ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ [ppm] = 1.08−1.13 (m, 2H), 1.23 (t, ^3J = 7.6 Hz, 3H), 1.39−1.45 (m, 2H), 1.46−1.51 (m, 2H), 1.85 (s, 3H), 1.86−1.89 (m, 2H), 1.93 (s, 3H), 2.17−2.22 (m, 2H), 2.62 (q, ^3J = 7.6 Hz, 2H), 3.82 (s, 3H), 6.86−6.90 (m, 2H), 7.14−7.18 (m, 2H); ^{13}C {^1H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 9.1, 13.0, 17.5, 19.6, 26.6, 27.3, 27.5, 30.5, 32.3, 55.2, 112.9, 113.6, 116.7, 122.3, 127.3, 130.1, 141.1, 149.4, 150.6, 158.0; HRMS (EI, 70 eV) ($C_{22}H_{28}O_2$) calcd. 324.2084, found 324.2083.

*2-(2,4-Dimethylpent-2-en-3-yl)-5-ethyl-3-(4-methoxyphenyl)-4-methylfuran (**10g**).* Synthesized according to the general procedure, using **9g** (69.1 mg, 250 μmol, 1.0 equiv), trimethyl(pent-2-en-3-yloxy)silane (158 mg, 1.00 mmol, 4.0 equiv), $Bi(OTf)_3$ (16.4 mg, 25.0 μmol, 0.1 equiv) and nitromethane (2.0 mL). Purification by column chromatography (*n*-pentane/EtOAc: 40/1) yielded product **8g** (43.0 mg, 55%) as a colorless oil: TLC R_f = 0.75 (P:EtOAc 9:1 [UV/CAM]); IR (ATR) $\tilde{\nu}$ = 2964, 2932, 2871, 1509, 1245, 1172, 1035, 831 cm^{-1}; MS (EI, 70 eV) *m*/*z* (%) = 312 (30) $[C_{21}H_{28}O_2]^+$, 269 (36) $[C_{18}H_{21}O_2]^+$, 173 (100); ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ [ppm] = 0.86 (d, ^3J = 6.9 Hz, 6H), 1.22 (t, ^3J = 7.6 Hz, 3H), 1.43 (s,

dx.doi.org/10.1021/jo5009993 | J. Org. Chem. 2014, 79, 6372−6379

3H), 1.74 (s, 3H), 1.93 (s, 3H), 2.61 (q, ^3J = 7.6 Hz, 2H), 2.92 (hept, ^3J = 6.9 Hz, 1H), 3.81 (s, 3H), 6.84−6.88 (m, 2H), 7.12−7.17 (m, 2H); ^{13}C {^{1}H} NMR (91 MHz, $CDCl_3$, 300 K) δ [ppm] = 9.3, 13.1, 19.6, 19.7, 21.6, 23.1, 30.6, 55.1, 112.5, 113.4, 123.7, 127.7, 129.9, 130.9, 133.7, 147.3, 150.7, 157.8; HRMS (EI, 70 eV) ($C_{21}H_{28}O_2$) calcd. 312.2084, found 312.2090.

■ ASSOCIATED CONTENT

Supporting Information

Complete set of conditions for the reaction optimization, ^{1}H and ^{13}C NMR spectra of compounds **2**, **5**, **6**, **7**, **8**, **9** and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: thorsten.bach@ch.tum.de.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft (Ba 1372/12-2) and by the Fonds der Chemischen Industrie (Kekulé scholarship to D.N.).

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dx.doi.org/10.1021/jo5009993 | *J. Org. Chem.* 2014, 79, 6372−6379