Switch from Palladium-Catalyzed Cycloisomerization/Dimerization of Terminal Allenyl Ketones to Preferential Formation of Monomers by a 5-Palladatricyclo[4.1.0.0^{2,4}]heptane Catalyst: Synthesis of Furans from Substrates Incompatible with the Commonly used Silver Catalysts

A. Stephen K. Hashmi* and Lothar Schwarz

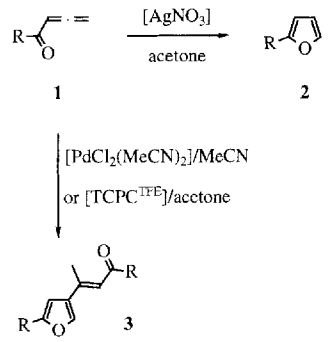
Institut für Organische Chemie der Johann Wolfgang Goethe-Universität,
Marie-Curie-Straße 11, D-60439 Frankfurt am Main, Germany
Fax: (internat.) + 49(0)69/798-29464
E-mail: hashmi@chemie.uni-frankfurt.de

Received March 12, 1997

Keywords: Alkynes / Allenes / Furans / Palladium / Catalysis

By making the choice of either $PdCl_2(MeCN)_2$ or PTH *rac*-**4** as catalyst, the allenyl ketones **1** could be preferentially cycloisomerized/dimerized to either 2,4-disubstituted furans **3** or preferentially cycloisomerized to the monosubstituted furans **2**. Since the PTH catalyst tolerates functional groups like terminal alkynes, α-halogen ketones, and alkyl halides that inhibit the silver catalysis, the latter method is an important extension of Marshall's Ag^I-catalyzed isomerization of **1** to **2**. Some of these latter reactions also showed exciting chemoselectivities, e.g. with allenyl ketones, such as **1c** and **1d**, which also possess a 1,6-enyne substructure, no enyne-cyclization was observed. This is also the first reported example of catalysis by a PTH.

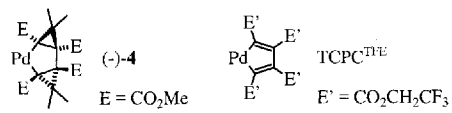
In 1990 Marshall reported in the literature on the silver(I)-catalyzed cycloisomerization of allenyl ketones **1** to furans **2**[1]. We recently reported the cyclization/dimerization of **1** to the 2,4-disubstituted furans **3** by means of palladium catalysts[2].



1 **2** **3**

1,2,3:	R
a	$-CH_3$
b	$-CH(OCH_2C{\equiv}CH)CH_3$
c	$-C(CH_2C{\equiv}CH)(OCH_2C{\equiv}CH)CH_3$
d	$-C(OH)(CH_2C{\equiv}CH)CH_3$
e	$-CH_2CH(OCH_2C{\equiv}CH)CH_3$
f	-3-[CH(OH)($CH_2C{\equiv}CH$)]C_6H_4
g	$-CH_2Cl$
h	$-(CH_2)_3Cl$
i	$-(CH_2)_4Br$
j	$-(CH_2)_4I$

In the palladium-catalyzed reactions the ratio of **2**/**3** depends on the choice of the solvent and the catalyst[2]. In some exploratory experiments we discovered that with dichlorobis(acetonitrile)palladium(II) $[PdCl_2(MeCN)_2]$ in acetonitrile (MeCN), instead of $TCPC^{TFE}$[3] in acetone[2], **3** was formed almost exclusively. This observation was very important since $PdCl_2(MeCN)_2$ is probably the most easily[4] available soluble Pd^{II} compound, while $TCPC^{TFE}$ is not readily available. Under the same conditions our newly developed 5-palladatricyclo[4.1.0.0^{2,4}]heptane catalyst (PTH, **4**[5]) produced, in addition to **3**, appreciable amounts of **2** (see below). This observation suggested that when **4** is used in solvents which, with $TCPC^{TFE}$, favor the formation of **2**, the latter should be preferentially formed. The Pd^{II} catalysts tolerate numerous functionalities in the substituent group R that would be interesting for applications in organic synthesis but are known to react with Marshall's silver Ag^I catalyst and thus inhibit catalysis. Therefore such a selective formation of **2**, through the use of the catalyst **4**, would be of general interest.



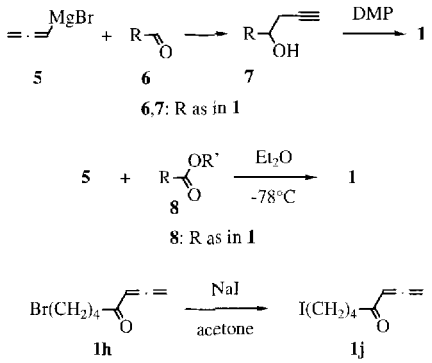
Synthesis of the Test Substrates

In order to investigate this point we chose terminal alkynes, an α-halogen ketone and unactivated alkyl halides as additional functional groups in the substrate **1**; all of which are incompatible with Ag^I ions.

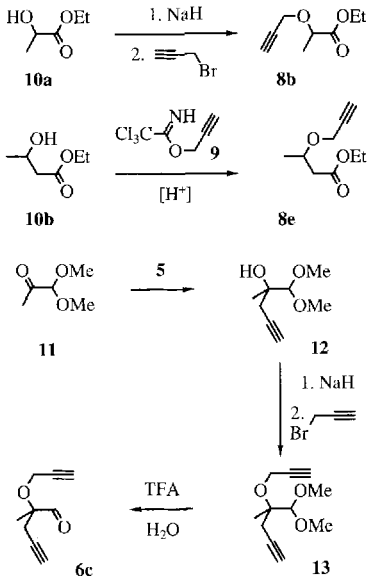
The different substrates **1a**–**1j** used in this investigation were synthesized by two methods. (1) The addition of allenylmagnesium bromide **5** to aldehydes **6**[6a]. The resulting secondary homopropargylic alcohols **7** were then oxidized

  0009–2940/97/1010–1449 S 17.50+.50/0

to **1** by the Dess-Martin periodinane (DMP) reagent[7]. (2) The direct addition of **5** to carboxylic acid esters **8** at low temperatures as described by Gaudemar et al.[8]. **1j** was prepared from **1h** by Finkelstein reaction.



The aldehyde **6f'** (dialdehyde, addition of two equivalents of **5**) and the esters **8d'** (α-oxo ester, addition of two equivalents of **5**), **8g**, **8h**, and **8i** were commercially available. **8b** and **8e** were obtained by etherification of esters **10a** (with NaH/propargyl bromide) and **10b** (with propargyl trichloroacetimidate **9**). **6c** was synthesized from **11** by the addition of **5**, followed by propargylation of the tertiary alcohol **12** with NaH/propargyl bromide and deprotection of the acetal in **13** with aqueous triflouroacetic acid.



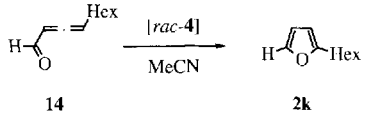
Results and Discussion

First **1a** was used as a test substrate. With $PdCl_2(MeCN)_2$/MeCN **3** was the main product (Table 1, entry 1). This result is quite similar to that obtained with the $TCPC^{TFE}$/acetone system[2]. But when $PdCl_2(MeCN)_2$ was substituted by *rac*-**4** the ratio of **2**/**3** dropped to 1:2.1 (entry 2). With a terminal alkyne moiety in the molecule (**1b**), even under the $PdCl_2(MeCN)_2$/MeCN conditions, only a molar ratio of 1.9:1 was achieved (entry 3[9]). PTH *rac*-**4** in benzene gave a ratio of better than 20:1 (entry 4), and in dichloromethane (DCM) a similar ratio was achieved (entry 5). Only traces of **3** were visible in the ^{1}H-NMR spectra taken from the crude reaction mixture. With $AgNO_3$/acetone **1b**, as well as the other substrates with a terminal alkyne group, precipitates (probably the silver acetylides) formed, and the formation of **2** or **3** was not observed (these experiments are not listed in Table 1).

Table 1. Palladium catalyzed conversions of allenyl ketones **1**

Entry	Allenyl ketone	Condition[a]	**2**	: **3**[b]	Isolated yields **2**	**3**
1	**1a**	$PdCl_2(MeCN)_2$/CD_3CN	<1	: 20	–[c]	89%
2	**1a**	*rac*-**4**/CD_3CN	1	: 2.1	–[c]	70%
3	**1b**	$PdCl_2(MeCN)_2$/CD_3CN	1.9	: 1	44%	46%
4	**1b**	*rac*-**4**/C_6D_6	>20	: 1	80%	8%
5	**1b**	*rac*-**4**/CD_2Cl_2	>20	: 1		
6	**1c**	$PdCl_2(MeCN)_2$/CD_3CN	1.3	: 1	32%	49%
7	**1c**	*rac*-**4**/C_6D_6	>20	: 1		
8	**1c**	*rac*-**4**/CD_2Cl_2	>20	: 1		
9	**1d**	$PdCl_2(MeCN)_2$/CD_3CN	1	: 3.3	10%	68%
10	**1d**	*rac*-**4**/CD_2Cl_2	17	: 1	65%	7%
11	**1e**	$PdCl_2(MeCN)_2$/CD_3CN	1.5	: 1	34%	47%
12	**1e**	*rac*-**4**/CD_2Cl_2	8.9	: 1	64%	14%
13	**1f**	*rac*-**4**/CD_2Cl_2	12	: 1	80%	13%
14	**1g**	*rac*-**4**/CD_2Cl_2	3.6	: 1[d]	–[c]	29%
15	**1h**	$PdCl_2(MeCN)_2$/CD_3CN	1	: 3.7		
16	**1h**	*rac*-**4**/C_6D_6	4.3	: 1	73%	17%
17	**1h**	*rac*-**4**/CD_2Cl_2	2.9	: 1	60%	27%
18	**1h**	$AgNO_3$/[D_3]acetone	1	: 0[d,e]		
19	**1i**	$PdCl_2(MeCN)_2$/CD_3CN	1	: 5.3		
20	**1i**	*rac*-**4**/C_6D_6	2.5	: 1		
21	**1i**	*rac*-**4**/CD_2Cl_2	2.5	: 1	44%	32%
22	**1i**	$AgNO_3$/[D_3]acetone	1	: 0[d,e]		
23	**1j**	$PdCl_2(MeCN)_2$/CD_3CN	1	: 3.4		
24	**1j**	*rac*-**4**/CD_2Cl_2	2.2	: 1	41%	37%
25	**1j**	$AgNO_3$/[D_3]acetone	–	: –[f]		
26	**14**	*rac*-**4**/CD_2Cl_2	1	: 0		

[a] Further reaction conditions see Experimental Section. – [b] By ^{1}H NMR. – [c] Too volatile to be isolated. – [d] Slow reaction. – [e] Reaction does not run to completion. – [f] No reaction, precipitate is formed.



Similar results were obtained with the substrates **1c** (entries 6–8) and **1d** (entries 9, 10). With the substrates **1c** (entries 11, 12) and **1f** (entry 13) the switch in selectivity is still relevant, but not as dramatic as in the examples above. The α-chloro ketone **1g** shows an even greater reduction in selectivity (entry 14), and this trend holds for the alkyl chloride, bromide, and iodide; **1h**, **1i**, and **1j** respectively (entries 15–25). **1g** was also incompatible with the Ag^I catalyst, but **1h** and **1i** reacted well with $AgNO_3$/acetone. Only in the case of **1j** did the silver catalysis fail, and again a precipitate (probably AgI) was formed; when *rac*-**4** was added to this mixture, the conversion to **2** and **3** started immediately and ran to completion without a problem.

An allenyl aldehyde like **14** (synthesized from the commercially available 3-decyn-1-ol by Dess-Martin oxidation) is also compatible with the **4**/DCM conditions, and the formation of solely **2k** is in accordance with our earlier observation that non-terminal allenyl ketones form only monomeric cycloisomers[2].

Some of these reactions show fascinating chemoselectivities. Terminal alkynes are known to add to acceptor-substituted allenes in palladium-catalyzed reactions[10], but this was not observed here (substrates **1b**–**1f**). Furthermore the substrates **1c** and **1d** (and also the products **3c** and **3d** derived from them) are 1,6-enynes which one could also expect to be cycloisomerized by palladium catalysts[11] (**1b** and **1c** also contain an 1,7-enyne subunit which can effectively be cycloisomerized by ruthenium[12] rather than by a palladium catalyst; **1e** also contains an 1,8-enyne, **1c** also a 1,7-diyne).

In **1e**, and the product **3e**, a β-alkoxy ketone is maintained, and no elimination to form the α,β-unsaturated ketone was observed.

1d and **1f** are substrates with unprotected hydroxyl groups. These are known to add to allenes in both inter- and intramolecular reactions catalyzed by Hg^{II} [13][14], Ag^{I} [15][16], and Pd^{II} catalysts[14][17]. We did not detect such products.

We assign the observed selectivity to a combination of two effects. (1) Steric effects: PTHs are sterically crowded systems, with sterically demanding ligands[5], which show a strong deviation from the ideal square-planar coordination. So the approach of a second allenyl ketone becomes difficult. (2) Blocking of coordination sites on the catalyst by the alkyne: The alkyne is a good ligand and thus competes with the allene in coordination to the palladium but, unlike the more reactive allenyl ketone, the alkyne is not incorporated into the product. For the possible reaction mechanism see ref.[2].

Conclusion

In conclusion the most selective formation of **2** was possible with the substrates containing terminal alkynes. The reaction of activated alkyl halides and alkyl iodides still had the advantage of tolerating substrates incompatible with the Ag catalyst, but here only a small excess of the monomer **2** was formed (small if one takes into consideration the fact that the dimer **3** has twice the molecular weight of **2**). In the case of alkyl chlorides and bromides **4** showed no advantage over $AgNO_3$ (the only advantage was a faster reaction, but since **4** is not readily available and $AgNO_3$ is cheap, and thus more Ag catalyst can be used, this is probably irrelevant to synthetic chemists). Nevertheless all these reactions showed for the first time the catalytic properties of PTHs **4**.

We thank the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie* and the *Degussa AG* for generous support of this work.

Experimental Section

General: All operations were carried out under N_2 and in dry solvents; transfers were effected by means of Schlenk tube techniques. Allenylmagnesium bromide (**5**[6b]), DMP[7], $PdCl_2(MeCN)_2$[4], PTH *rac*-**4**[5], 3,4-pentadien-2-one (**1a**[18]) and 1-chloro-3,4-pentadien-2-one (**1g**[8a]) were prepared according to literature procedures. – IR: Perkin-Elmer 1600, 257, and 580B. – NMR: Bruker AM 250, AM 270, and AMX 600 (250, 270, 600, 62.9, and 67.9 MHz for ^1H and ^{13}C, respectively). $CDCl_3$ as solvent $\delta_H = 7.25$; $\delta_C = 77.0$. The degree of substitution of the C atoms was determined by a combination of DEPT-135 and DEPT-90. – MS: VG-Instruments-Micro-Mass Tris 2000, EI 70 eV, quadrupole analyser and Finnigan CH7A (80 eV). – HRMS: Finnigan MAT 711 (EI, 80 eV, 8 kV ion acceleration, resolution above $R = 20000$, peak match). – Melting points (uncorrected): Kofler hot-stage. – HPLC Merck Septech, UV and RI detection, 0.1 l/min, 2 cartridges Waters prepPak Silica 500. – Column chromatography: Merck Kieselgel 60 using hexane/ethyl acetate (H/EA) or pentane/ether (P/E) as eluent.

Synthesis of the Allenyl Ketones **1**

1. *2-(2-Propynyloxy)-4,5-hexadien-3-one* (**1b**). – a) *Ethyl 2-(2-Propynyloxy)propionate* (**8b**): Ethyl (–)-2-hydroxypropionoate (**10a**, 20.0 mmol, 2.36 g) was added at 0°C to a well-stirred suspension of NaH (19.2 mmol, 461 mg) in THF (50 ml). After 30 min, the resulting solution was added to propargyl bromide (22.4 mmol, 2.50 ml, 80% toluene solution) in THF (40 ml) at 0°C within 2 min. Stirring at 0°C was continued for 45 min, then the ice bath was removed and the mixture was allowed to reach room temperature. After hydrolysis with water (20 ml) the organic layer was separated, the aqueous layer was extracted with diethyl ether (3 × 80 ml), the combined organic layers were dried with $MgSO_4$, filtered and concentrated in vacuo. Purification of the crude product by column chromatography (H/EA, 10:1) gave 2.06 g (13.2 mmol, 69%) of **8b** as an oil. – R_f (H/EA, 5:1) = 0.40. – IR (neat): $\tilde{\nu}$ = 3275 cm^{-1} (≡C–H), 2986, 2940, 2908, 2874, 2117 (C≡C), 1745 (C=O). – ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.26 (t, J = 7.1 Hz, 3 H), 1.39 (d, J = 6.1 Hz, 3 H), 2.42 (t, J = 2.4 Hz, 1 H), 4.12–4.34 (m, 5 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 14.00 (q), 18.30 (q), 56.85 (t), 60.78 (t), 72.90 (d), 74.80 (d), 78.82 (s), 172.46 (s). – MS (70 eV); *m/z* (%): 157 (9) [MH^+], 83 (100), 55 (18). – $C_8H_{12}O_3$ (156.2): calcd. C 61.52, H 7.74; found C 61.31, H 7.77.

b) **1b**: Prepared by a procedure analgous to that in ref.[8] from 1.38 g (8.84 mmol) of **8b** in diethyl ether (215 ml) and **5** (8.84 mmol, 5.46 ml, 1.62 M). Purification of the crude product by column chromatography (H/EA, 10:1) gave 1.01 g (6.72 mmol, 76%) of **1b** as a colourless oil. – R_f (H/EA, 5:1) = 0.25. – IR (neat): $\tilde{\nu}$ = 3281 cm^{-1} (≡C–H), 3066, 2987, 2936, 2868, 2117 (C≡C), 1959 (C=C=C), 1931 (C=C=C), 1688 (C=O). – ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.34 (d, J = 6.8 Hz, 3 H), 2.42 (t, J = 2.4 Hz, 1 H), 4.07 (dd, J = 15.9 Hz, 2.4 Hz, 1 H), 4.22 (dd, J = 15.9 Hz, 2.4 Hz, 1 H), 4.51 (q, J = 6.9 Hz, 1 H), 5.25 (d, J = 6.1 Hz, 2 H), 5.97 (t, J = 6.5 Hz, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 18.11 (q), 56.60 (t), 74.91 (d), 76.94 (d), 78.93 (s), 79.38 (t), 92.49 (d), 199.75 (s), 216.31 (s). – MS (70 eV); *m/z* (%): 151 (0.5) [MH^+], 135 (4) [$M^+ - CH_3$], 83 (100), 67 (21), 55 (14). – $C_9H_{10}O_2$ (150.2): calcd. C 71.98, H 6.71; found C 71.74, H 6.84.

2. *5-Methyl-5-(2-propynyloxy)-1,2-octadien-7-yn-4-one* (**1c**). – a) *1,1-Dimethoxy-2-methyl-4-pentyn-2-ol* (**12**): Compound **5** (60.0 mmol, 36.6 ml, 1.64 M) was added in the usual manner[19] to 1,1-dimethoxy-2-propanone (**11**) (50 mmol, 5.91 g) in diethyl ether (115 ml). Purification of the crude product by column chromatography

(H/EA, 2:1) gave 7.82 g (49.4 mmol, 99%) of **12** as an colourless oil. – R_f (H/EA, 2:1) = 0.20. – IR (neat): $\tilde{\nu}$ = 3484 cm^{-1} (OH), 3288 (≡C–H), 2983, 2937, 2835, 2118 (C≡C). – ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.22 (s, 3 H), 2.02 (t, *J* = 2.7 Hz, 1 H), 2.28 (s, 1 H), 2.40 (m, 2 H), 3.52 (d, *J* = 2.9 Hz, 6 H), 4.19 (s, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.41 (q), 27.53 (t), 57.83 (q), 58.05 (q), 70.54 (d), 73.64 (s), 80.37 (s), 108.97 (d). – MS (70 eV); *m/z* (%): 157 (1) [M^+ – H], 119 (5) [M^+ – C_3H_3], 87 (28), 83 (11), 75 (100), 43 (35). – $C_8H_{14}O_3$ (158.2): calcd. C 60.74, H 8.92; found C 60.68, H 8.93.

b) *5,5-Dimethoxy-4-methyl-4-(2-propynyloxy)-1-pentyne* (**13**): In an analogous procedure to that for **8b**, **13** was prepared from **12** (12.1 mmol, 1.92 g), NaH (12.7 mmol, 305 mg), and propargyl bromide (14.4 mmol, 1.60 ml, 80% in toluene) in THF (150 ml). The alkylation step was very slow and worked up after 7 d at room temp. when the conversion still was not complete. Purification of the crude product by column chromatography (H/EA, 10:1) gave 958 mg (4.88 mmol, 40%) of **13** as an colourless oil. – R_f (H/EA, 2:1) = 0.44. – IR (neat): $\tilde{\nu}$ = 3291 cm^{-1} (≡C–H), 2986, 2936, 2834, 2119 (C≡C). – ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.24 (s, 3 H), 1.97 (t, *J* = 2.7 Hz, 1 H), 2.33 (t, *J* = 2.4 Hz, 1 H), 2.45 (d, *J* = 2.7 Hz, 2 H), 3.46 (s, 3 H), 3.48 (s, 3 H), 4.21 (s, 1 H), 4.25 (d, *J* = 2.4 Hz, 2 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 17.53 (q), 25.45 (t), 51.74 (t), 57.57 (q), 58.01 (q), 70.53 (d), 73.13 (d), 79.25 (s), 80.25 (s), 81.14 (s), 108.84 (d). – MS (70 eV); *m/z* (%): 157 (6) [M^+ – C_3H_3], 95 (1), 87 (6), 75 (100), 67 (2), 59 (8). – $C_{11}H_{16}O_3$ (196.2): calcd. C 67.32, H 8.22; found C 67.10, H 8.18.

c) *2-Methyl-2-(2-propynyloxy)-4-pentynal* (**6c**): Compound **13** (4.74 mmol, 931 mg) was added to a 4:1 mixture of F_3CCO_2H and water (2 ml) and heated to 100°C for 30 min. After neutralization with $NaHCO_3$ (saturated solution), the product was extracted with diethyl ether (5 × 60 ml). The combined organic layers were dried with $MgSO_4$ filtered and concentrated in vacuo. Purification of the crude product by column chromatography (H/EA, 10:1) gave 574 mg (3.82 mmol, 81%) of **6c** as a colourless oil. – R_f (H/EA, 2:1) = 0.54. – IR (neat): $\tilde{\nu}$ = 3291 cm^{-1} (≡C–H), 2987, 2935, 2821, 2709, 2120 (C≡C), 1733 (C=O). – ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.38 (s, 3 H), 2.06 (t, *J* = 2.7 Hz, 1 H), 2.46 (t, *J* = 2.4 Hz, 1 H), 2.58 (d, *J* = 2.7 Hz, 2 H), 4.23 (d, *J* = 2.5 Hz, 2 H), 9.67 (s, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 18.28 (q), 24.54 (t), 52.86 (t), 71.90 (d), 75.57 (d), 77.76 (s), 79.56 (s), 81.29 (s), 202.02 (d). – MS (70 eV); *m/z* (%): 150 (1) [M^+], 121 (100), 111 (14) [M^+ – C_3H_3]. – $C_9H_{10}O_2$ (150.2): calcd. C 71.98, H 6.71; found C 71.83, H 6.88.

d) *5-Methyl-5-(2-propynyloxy)-1,7-octadiyn-4-ol* (**7c**): Compound **7c** was prepared from **6c** (2.71 mmol, 407 mg) in diethyl ether (60 ml) and **5** (5.41 mmol, 3.30 ml, 1.64 M) in the usual manner[19]. Purification of the crude product by column chromatography (H/EA, 10:1) gave 361 mg (1.90 mmol, 70%) of **7c** as a 6:1 mixture of diastereomers (colourless oil). – R_f (H/EA, 2:1) = 0.43. – IR (neat): $\tilde{\nu}$ = 3540, 3454 cm^{-1} (OH), 3292 (≡C–H), 2983, 2924, 2118 (C≡C). – ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.31–1.33 (m, 3 H), 2.03–2.07 (m, 2 H), 2.31–2.66 (m, 6 H), 3.89–3.96 (m, 1 H), 4.23–4.26 (m, 2 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 17.58 (q), 21.62 (t), 26.00 (t), 51.16 (t), 70.32 (d), 71.28 (d), 73.15 (d), 73.67 (d), 78.76 (s), 79.74 (s), 80.63 (s), 81.58 (s). – MS (70 eV); *m/z* (%): 191 (0.5) [MH^+], 151 (11) [M^+ – C_3H_3], 135 (4), 121 (100). – $C_{12}H_{14}O_2$ (190.2) calcd. C 75.76, H 7.42; found C 75.79, H 7.54.

e) **1c**: Compound **1c** was prepared from **7c** (1.89 mmol, 360 mg) in dichloromethane (DCM, 5 ml) and DMP (2.36 mmol, 1.00 g) according to the general procedure[7]. Column chromatography (H/EA, 10:1) gave 323 mg (1.72 mmol, 91%) of **1c** as a colourless oil. – R_f (H/EA, 5:1) = 0.30. – IR (neat): $\tilde{\nu}$ = 3291 cm^{-1} (≡C–H), 3066, 2989, 2934, 2864, 2122 (C≡C), 1959 (C=C=C), 1931 (C=C=C), 1685 (C=O). – ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.46 (s, 3 H), 2.05 (t, *J* = 2.7 Hz, 1 H), 2.44 (t, *J* = 2.4 Hz, 1 H), 2.65 (d, *J* = 2.7 Hz, 2 H), 4.07 (dd, *J* = 2.4 Hz, 15.1 Hz, 1 H), 4.16 (dd, *J* = 2.4 Hz, 15.1 Hz, 1 H), 5.23 (d, *J* = 6.4 Hz, 2 H), 6.40 (t, *J* = 6.4 Hz, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.03 (q), 25.89 (t), 53.20 (t), 71.74 (d), 74.93 (d), 78.43 (s), 79.07 (t), 79.17 (s), 83.30 (s), 89.91 (d), 200.13 (s), 216.46 (s). – MS (70 eV); *m/z* (%): 189 (1) [MH^+], 149 (3) [M^+ – C_3H_3], 133 (9), 121 (100), 67 (19). – $C_{12}H_{12}O_2$ (188.2): calcd. C 76.57, H 6.43; found C 76.44, H 6.61.

3. *5-Hydroxy-5-methyl-1,2-octadien-7-yn-4-one* (**1d**): Ethyl pyruvate (**8d'**, 1.86 g, 16.0 mmol) in diethyl ether (20 ml) and **5** (20.0 ml, 32.0 mmol, 1.60 M) were treated in according to the general procedure[8]. A complex product mixture resulted; 407 mg (2.59 mmol, 16%) of the desired product **1d** were obtained as an colourless oil by HPLC. – HPLC with H/MeOAc (6.7:1) + 20% DCM. – R_f (H/EA, 3:1) = 0.23. – IR (neat, KBr): $\tilde{\nu}$ = 3452 cm^{-1} (OH), 3293 (≡C–H), 2984, 2934, 1960 (C=C=C), 1933 (C=C=C), 1692 (C=O), 1599. – ^1H NMR (CD_3CN, 250 MHz): δ = 1.36 (s, 3 H), 2.22 (t, *J* = 2.7 Hz, 1 H), 2.54 (dd, *J* = 17.0 Hz, 2.7 Hz, 1 H), 2.66 (dd, *J* = 17.0 Hz, 2.7 Hz, 1 H), 3.95 (s, 1 H), 5.32 (d, *J* = 6.6 Hz, 2 H), 6.37 (t, *J* = 6.6 Hz, 1 H). – ^{13}C NMR (CD_3CN, 62.9 MHz): δ = 24.7 (q), 30.1 (t), 72.0 (d), 78.3 (s), 79.6 (t), 80.3 (s), 90.0 (d), 201.6 (s), 216.8 (s). – MS (70 eV); *m/z* (%): 150 (100) [M^+], 135 (9) [M^+ – CH_3], 122 (29), 111 (24). – $C_9H_{10}O_2$ (150.2): calcd. C 71.98, H 6.71; found C 72.00, H 6.79.

4. *6-(2-Propynyloxy)-1,2-heptadien-4-one* (**1e**). – a) *2-Propynyl 2,2,2-Trichloroacetimidate* (**9**): The preparation is described in the literature[20], but the NMR data have not yet been reported. – ^1H NMR ($CDCl_3$, 250 MHz): δ = 2.54 (t, *J* = 2.4 Hz, 1 H), 4.90 (d, *J* = 2.4 Hz, 2 H), 8.48 (br s, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 56.41 (t), 75.50 (d), 76.84 (s), 90.54 (s), 161.64 (s).

b) *Ethyl 3-(2-Propynyloxy)butanoate* (**8e**): 2.50 ml of F_3CSO_3H was added to a stirred solution of ethyl (±)-3-hydroxybutanoate (**10b**, 189 mmol, 25.0 g) and **9** (249 mmol, 50.0 g) in a mixture of cyclohexane (250 ml) and DCM (120 ml). Subsequently, the resulting reaction mixture was stirred at 40°C for 46 h. The precipitated trichloroacetamide was filtered off and the organic solution was washed with saturated $NaHCO_3$ solution (50 ml) and with water (50 ml). The organic layer was dried with Na_2SO_4 filtered off and concentrated in vacuo. Purification of the crude product by HPLC (H/methyl acetate, 60:1) gave 10.4 g (61.1 mmol, 32%) of **8e** as a colourless oil. – R_f (H/EA, 5:1) = 0.30. – IR (neat): $\tilde{\nu}$ = 3287 cm^{-1} (≡C–H), 2980, 2980, 2935, 2908, 2117 (C≡C), 1734 (C=O) – ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.20–1.26 (m, 6 H), 2.36 (dd, *J* = 5.9 Hz, 15.3 Hz, 1 H), 2.38 (t, *J* = 2.4 Hz, 1 H), 2.58 (dd, *J* = 7.0 Hz, 15.3 Hz, 1 H), 4.02–4.16 (m, 5 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 14.12 (q), 19.54 (q), 41.77 (t), 55.99 (t), 60.36 (t), 71.54 (d), 73.93 (d), 79.91 (s), 171.06 (s). – MS (70 eV); *m/z* (%): 171 (3) [MH^+], 131 (16) [M^+ – C_3H_3], 125 (17), 83 (100), 55 (19). – $C_9H_{14}O_3$ (170.2): calcd. C 63.51, H 8.29; found C 63.23, H 8.26.

c) **1e**: Compound **1e** was prepared by a procedure analagous to that in ref.[8] from **8e** (11.8 mmol, 2.00 g) in diethyl ether (215 ml) and **6** (13.1 mmol, 8.00 ml, 1.64 M). Purification by column chromatography (H/EA, 7:1) gave 1.06 mg (6.46 mmol, 55%) of **1e** as a colourless oil. – R_f (H/EA, 5:1) = 0.22. – IR (neat): $\tilde{\nu}$ = 3282 cm^{-1} (≡C–H), 3066, 2976, 2933, 2860, 2116 (C≡C), 1958 (C=C=C), 1932 (C=C=C), 1681 (C=O). – ^1H NMR ($CDCl_3$, 250 MHz): δ = 1.19 (d, *J* = 6.2 Hz, 3 H), 2.39 (t, *J* = 2.4 Hz, 1 H), 2.60 (dd,

J = 6.2 Hz, 15.7 Hz, 1 H), 2.98 (dd, J = 6.4 Hz, 15.7 Hz, 1 H), 4.04–4.16 (m, 3 H), 5.25 (d, J = 6.5 Hz, 2 H), 5.78 (t, J = 6.5 Hz, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.55 (q), 45.71 (t), 55.85 (t), 71.32 (d), 73.82 (d), 79.57 (t), 79.92 (s), 97.04 (d), 197.85 (s), 216.81 (s). – MS (70 eV); *m/z* (%): 165 (6) [MH^+], 125 (38) [$M^+ - C_3H_3$], 83 (100), 67 (42), 55 (19). – $C_{10}H_{12}O_2$ (164.2): calcd. C 73.15, H 7.37; found H 72.93, C 7.54.

5. *1-[3-(1-Hydroxy-3-butynyl)phenyl]-2,3-butadien-1-one* (**1f**). – a) *1-[3-(1-Hydroxy-3-butynyl)phenyl]-3-butyn-1-ol* (**7f**): Isophthaldialdehyde (2.68 g, 20.0 mmol) was added to **5** (25.0 ml, 40.0 mmol, 1.60 M) in diethyl ether (25 ml). A thick slurry formed, which was then refluxed in an ultrasonic bath for 5 h. After the usual workup[19], the crude product was purified by column chromatography (H/EA, 1.6:1) and gave 2.96 g (13.8 mmol, 69%) of **7f** as a highly viscous oil. From this 1:1 mixture of diastereomers the C_s-symmetrical isomer crystallized (relative configuration proven by X-ray analysis; colourless crystals, m.p. 76–78°C). – R_f (H/EA, 1:1) = 0.25. – IR (neat, KBr): $\tilde{\nu}$ = 3378 cm^{-1}, 3289 (≡C–H), 2911, 2118 (C≡C), 1691, 1608, 1422, 1312, 1257, 1152, 1051. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.06 (t, J = 2.6 Hz, 2 H), 2.52–2.65 (m, 4 H), 2.85 (d, J = 3.5 Hz, 1 H), 4.79–4.84 (m, 2 H), 7.26–7.38 (m, 4 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 29.2 (t, 2 C), 71.0 (d, 2 C), 72.1 (d, 2 C), 80.7 (s, 2 C), 123.1 (d), 123.2 (d), 125.4 (d, 2 C), 128.4 (d), 142.6 (s, 2 C); crystalline-diastereomer ^{13}C-NMR signal at δ = 123.1, no signal at δ = 123.2. – MS (70 eV); *m/z* (%): 214 (0.2) [M^+], 175 (100) [$M^+ - C_3H_3$], 135 (95), 129 (25), 79 (23). – $C_{14}H_{14}O_2$ (214.3): calcd. C 78.48, H 6.59; found C 77.81, H 6.59. – $C_{14}H_{14}O_2$: calcd. 214.09938, found 214.09956 (MS).

b) **1f**: Compound **1f** was prepared from **7f** (2.33 mmol, 500 mg) in DCM (3 ml) and DMP (2.33 mmol, 564 mg) according to the general procedure[7]. Column chromatography (H/EA, 4:1) gave 223 mg (1.05 mmol, 45%) of **1f** as a colourless oil. – R_f (H/EA, 2:1) = 0.19. – IR (neat): $\tilde{\nu}$ = 3439 cm^{-1}, 3295 (≡C–H), 3064, 2987, 2911, 2119 (C≡C), 1958 (C=C=C), 1931 (C=C=C), 1758, 1649. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.06 (t, J = 2.6 Hz, 1 H), 2.61–2.65 (m, 2 H), 2.96 (br s, 1 H), 4.87–4.93 (m, 1 H), 5.24 (d, J = 6.5 Hz, 2 H), 6.41 (t, J = 6.5 Hz, 1 H), 7.37–7.43 (m, 1 H), 7.56–7.59 (m, 1 H), 7.76–7.80 (m, 1 H), 7.89 (br s, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 29.3 (t), 71.2 (d), 71.7 (d), 79.2 (t), 80.1 (s), 93.1 (d), 126.0 (d), 128.1 (d), 128.4 (d), 130.2 (d), 137.3 (s), 142.9 (s), 190.9 (s), 217.1 (s). – MS (70 eV); *m/z* (%): 212 (1) [M^+], 191 (3), 173 (100), 133 (43). – $C_{14}H_{12}O_2$ (212.2): calcd. C 79.23, H 5.70; found C 78.94, H 5.75.

6. *7-Chloro-1,2-heptadien-4-one* (**1h**): Compound **1h** was prepared by a procedure analagous to that in ref.[8] from **5** (49.2 mmol, 30.0 ml, 1.64 M) in diethyl ether (200 ml) and methyl 4-chlorobutanoate (**8h**, 42.5 mmol, 5.80 g) in diethyl ether (15 ml). Purification of the crude product by HPLC (H/EA, 20:3) gave 2.76 g (19.1 mmol, 45%) of **1h** as a colourless oil. – R_f (H/EA, 5:1) = 0.35. – IR (neat): $\tilde{\nu}$ = 3067 cm^{-1}, 2990, 2963, 2925, 2872, 1959 (C=C=C), 1932 (C=C=C), 1678 (C=O). – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.05 (m, 2 H), 2.79 (t, J = 7.0 Hz, 2 H), 3.56 (t, J = 6.3 Hz, 2 H), 5.26 (d, J = 6.6 Hz, 2 H), 5.77 (t, J = 6.6 Hz, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 26.72 (t), 35.75 (t), 44.28 (t), 79.62 (t), 96.48 (d), 199.11 (s), 216.50 (s). – MS (70 eV); *m/z* (%):147/145 (7/21) [MH^+], 109 (15) [M^+ – Cl], 107/105 (46/100) [$M^+ - C_3H_3$], 95 (5), 79/77 (8/21), 67 (21). – C_7H_9ClO (144.6): calcd. C 58.14, H 6.27; found C 58.36, H 6.37.

7. *8-Bromo-1,2-octadien-4-one* (**1i**): Compound **1i** was prepared by the procedure given in ref.[8] from ethyl 5-bromopentanoate (**8i**, 23.9 mmol, 5.00 g) in diethyl ether (215 ml) and **5** (27.6 mmol, 16.8 ml, 1.64 M). Purification of the crude product by HPLC [(H/EA, 20:1) + 30% DCM] gave 2.39 g (11.8 mmol, 49%) of **1i** as a colourless oil. – R_f (H/EA, 5:1) = 0.31. – IR (neat): $\tilde{\nu}$ = 3064 cm^{-1}, 2988, 2960, 2941, 2869, 1959 (C=C=C), 1932 (C=C=C), 1681 (C=O). – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.70–1.92 (m, 4 H), 2.63 (t, J = 7.1 Hz, 2 H), 3.39 (t, J = 6.5 Hz, 2 H), 5.23 (d, J = 6.5 Hz, 2 H), 5.77 (t, J = 6.5 Hz, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 22.80 (t), 31.92 (t), 33.04 (t), 37.85 (t), 79.40 (t), 96.48 (d), 199.78 (s), 216.50 (s). – MS (70 eV); *m/z* (%): 203/205 (23) [MH^+], 165/163 (67) [$M^+ - C_3H_3$], 137/135 (32), 123 (45) [M^+ – Br], 67 (29), 55 (100). – $C_8H_{11}BrO$ (203.1): calcd. C 47.32, H 5.46; found C 47.45, H 5.55.

8. *8-Iodo-1,2-octadien-4-one* (**1j**): A solution of **1h** (500 mg, 2.46 mmol) in dry acetone (5 ml) was added to a stirred solution of NaI (3.60 g, 24.0 mmol) in dry acetone (20 ml) at room temp. and protected from light. After 20 h the precipitated NaBr was separated by filtration. The organic solution was concentrated in vacuo, and the remaining NaI was precipitated by the addition of DCM and filtered off. Purification of the crude product by column chromatography (H/EA, 5:1) gave 513 mg (2.17 mmol, 88%) of **1j** as a yellow oil. – R_f (H/EA, 5:1) = 0.33. – IR (neat): $\tilde{\nu}$ = 3062 cm^{-1}, 2985, 2937, 2866, 2836, 1958 (C=C=C), 1932 (C=C=C), 1681 (C=O). – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.63–1.86 (m, 4 H), 2.59 (t, J = 7.1 Hz, 2 H), 3.14 (t, J = 6.8 Hz, 2 H), 5.22 (d, J = 6.5 Hz, 2 H), 5.74 (t, J = 6.5 Hz, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 6.03 (t), 25.11 (t), 32.69 (t), 37.67 (t), 79.48 (t), 96.50 (d), 199.81 (s), 216.51 (s). – MS (70 eV); *m/z* (%): 251 (8) [MH^+], 211 (28) [$M^+ - C_3H_3$], 183 (25), 155 (8), 123 (100) [M^+ – I], 95 (20), 81 (13), 67 (42), 55 (90). – $C_8H_{11}IO$ (250.1): calcd. C 38.42, H 4.43; found C 38.47, H 4.42.

9. *2,3-Decadienal* (**14**): 3-Decyn-1-ol (1.55 g, 10.0 mmol) was oxidized with DMP (4.67 g, 11.0 mmol) in DCM (8 ml) according to the general procedure[7]. Purification of the crude product by column chromatography (H/EA, 40:1) gave 1.27 g (8.34 mmol, 83%) of **14** as a yellow oil. – R_f (H/EA, 40:1) = 0.27. – IR (neat, KBr): $\tilde{\nu}$ = 2955 cm^{-1}, 2929, 2857, 1943 (C=C=C), 1691, 1467, 1089, 876. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.84–0.89 (m, 3 H), 1.11–1.52 (m, 8 H), 2.12–2.22 (m, 2 H), 5.69–5.83 (m, 2 H), 9.47 (d, J = 7.0 Hz, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 13.8 (q), 22.4 (t), 27.3 (t), 28.4 (t), 28.6 (t), 31.3 (t), 96.2 (d), 98.4 (d), 192.1 (d), 218.9 (s). MS (70 eV); *m/z* (%): 152 (1) [M^+], 151 (1), 137 (1), 123 (16), 109 (10), 81 (100). – $C_{10}H_{16}O$ (152.2): calcd. C 78.90, H 10.59; found C 78.67, H 10.58.

Palladium-Catalyzed Reactions. – General Procedure: All reactions were performed in NMR tubes. The allenyl ketones (30–40 mg) were weighed directly into the NMR tube then the deuterated solvent (0.5 ml) was added. A ^{1}H-NMR spectrum was taken before the catalyst (0.7 mg) was added and then the progress of the reaction was monitored by ^{1}H NMR at 22°C. All products were isolated by direct chromatographic workup of the reaction mixture. Yields are given in Table 1 and below.

1. 47.2 mg (575 μmol) of **1a** gave the following products (Table 1, entry 2). a) *2-Methylfuran* (**2a**): Distilled off with CD_3CN. For NMR data see ref.[21]

b) *(E)-4-(5-Methyl-3-furanyl)-3-penten-2-one* (**3a**): 33.0 mg (201 μmol, 70%). For NMR data see ref.[2]

2. 35.6 mg (237 μmol) of **1b** gave the following products (Table 1, entry 3). – a) *2-[1-(2-Propynyloxy)ethyl]furan* (**2b**[22]): 15.7 mg (105 μmol, 44%). – Column with P/E (10:1). – R_f (H/EA, 5:1) = 0.45. – IR (neat): $\tilde{\nu}$ = 3296 cm^{-1} (≡C–H), 3147, 3120, 2985, 2936, 2897, 2856, 2117 (C≡C), 1503. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.54 (d, J = 6.6 Hz, 3 H), 2.41 (t, J = 2.4 Hz, 1 H), 3.98 (dd,

J = 2.3 Hz, 15.8 Hz, 1 H), 4.14 (dd, J = 2.4 Hz, 15.8 Hz, 1 H), 4.71 (q, J = 6.6 Hz, 1 H), 6.34–6.30 (m, 2 H), 7.39 (dd, J = 0.8 Hz, 1.6 Hz, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.50 (q), 55.38 (t), 69.10 (d), 74.13 (d), 79.67 (s), 107.83 (d), 109.98 (d), 142.39 (d), 154.19 (s). – MS (70 eV); *m/z* (%): 150 (100) [M^+], 122 (27), 120 (83), 118 (84). – $C_9H_{10}O_2$ (150.2).

b) *(E)-2-(2-Propynyloxy)-5-{5-[1-(2-propynyloxy)ethyl]-3-furanyl}-4-hexen-3-one* (**3b**): 16.4 mg (54.6 µmol, 46%). – Column with H/EA (10:1). – R_f (H/EA, 5:1) = 0.20. – IR (neat): $\tilde{\nu}$ = 3292 cm^{-1} (≡C–H), 3144, 2983, 2933, 2856, 2117 (C≡C), 1679 (C=O), 1590. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.37 (d, J = 6.9 Hz, 3 H), 1.54 (d, J = 6.6 Hz, 3 H), 2.45–2.47 (m, 5 H), 3.99–4.30 (m, 5 H), 4.71 (q, J = 6.6 Hz, 1 H), 6.57 (s, 1 H), 6.73 (d, 1 H), 7.69 (s, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 17.15 (q), 17.75 (q), 19.31 (q), 55.54 (t), 56.88 (t), 68.98 (d), 74.38 (d), 74.76 (d), 79.12 (s), 79.57 (s), 80.61 (d), 105.27 (d), 116.11 (d), 129.05 (s), 142.84 (d), 147.63 (s), 156.11 (s), 201.36 (s). – MS (70 eV); m/z (%): 300 (16) [M^+], 249 (10), 165 (18), 83 (100). – $C_{18}H_{20}O_4$: calcd. 300.13616, found 300.13618 (MS).

3. 40.6 mg (216 µmol) of **1c** gave the following products (Table 1, entry 6). – a) *2-[1-Methyl-1-(2-propynyloxy)-3-butynyl]furan* (**2c**): 13.1 mg (69.5 µmol, 32%). – Column with H/EA (10:1). – R_f (H/EA, 5:1) = 0.36. – IR (neat): $\tilde{\nu}$ = 3295 cm^{-1} (≡C–H), 3146, 3119, 2987, 2938, 2920, 2864, 2121 (C≡C), 1584. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.64 (s, 3 H), 1.91 (t, J = 2.7 Hz, 1 H), 2.28 (t, J = 2.5 Hz, 1 H), 2.72 (dd, J = 2.7 Hz, 16.6 Hz, 1 H), 2.84 (dd, J = 2.6 Hz, 16.6 Hz, 1 H), 3.79 (dd, J = 2.5 Hz, 15.3 Hz, 1 H), 3.87 (dd, J = 2.4 Hz, 15.3 Hz, 1 H), 6.28 (dd, J = 1.8 Hz, 3.3 Hz, 1 H), 6.32 (dd, J = 0.8 Hz, 3.3 Hz, 1 H), 7.36 (dd, J = 0.8 Hz, 1.8 Hz, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 21.82 (q), 29.75 (t), 51.71 (t), 70.73 (d), 73.31 (d), 75.46 (s), 79.57 (s), 80.33 (s), 109.03 (d), 109.91 (d), 142.55 (d), 153.93 (s). – MS (70 eV); *m/z* (%): 188 (79) [M^+], 120 (93), 118 (97), 115 (100). – $C_{12}H_{12}O_2$: calcd. 188.08373, found 188.08359 (MS).

b) *(E)-5-Methyl-2-{5-[1-methyl-1-(2-propynyloxy)-3-butynyl]-3-furanyl}-5-(2-propynyloxy)-2-octen-7-yn-4-one* (**3c**): 19.8 mg (52.5 µmol, 49%). – Column with H/EA (10:1). – R_f (H/EA, 5:1) = 0.21. – IR (neat): $\tilde{\nu}$ = 3292 cm^{-1} (≡C–H), 3143, 2986, 2918, 2863, 2121 (C≡C), 1679 (C=O), 1587. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.43 (s, 3 H), 1.66 (s, 3 H), 1.94 (t, J = 2.7 Hz, 1 H), 2.01 (t, J = 2.7 Hz, 1 H), 2.31 (t, J = 2.4 Hz, 1 H), 2.39 (d, J = 1.1 Hz, 3 H), 2.42 (t, J = 2.4 Hz, 1 H), 2.63 (d, J = 2.6 Hz, 2 H), 2.71 (dd, J = 2.7 Hz, 16.6 Hz, 1 H), 2.85 (dd, J = 2.6 Hz, 16.6 Hz, 1 H), 3.84 (dd, J = 2.4 Hz, 15.3 Hz, 1 H), 3.92 (dd, J = 2.4 Hz, 15.3 Hz, 1 H), 4.03 (dd, J = 2.4 Hz, 15.1 Hz, 1 H), 4.14 (dd, J = 2.4 Hz, 15.1 Hz, 1 H), 6.63 (d, J = 0.8 Hz, 1 H), 6.97 (d, J = 1.1 Hz, 1 H), 7.67 (d, J = 0.6 Hz, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 17.15 (q), 21.15 (q), 21.61 (q), 26.01 (t), 29.74 (t), 51.89 (t), 53.32 (t), 71.10 (d), 71.45 (d), 73.64 (d), 74.65 (d), 75.54 (s), 78.98 (s), 79.18 (s), 79.62 (s), 80.04 (s), 83.71 (s), 106.90 (d), 115.82 (d), 129.17 (s), 143.12 (d), 148.02 (s), 155.75 (s), 201.56 (s). – MS (70 eV); *m/z* (%): 376 (2) [M^-], 337 (4), 255 (30), 121 (61), 43 (100). – $C_{24}H_{24}O_4$: calcd. 376.167, found 376.167 (MS).

4. 39.5 mg (263 µmol) of **1d** gave the following products (Table 1, entry 9). – a) *2-(2-Furanyl)-4-pentyn-2-ol* (**2d**): 4.1 mg (27.3 µmol, 10%). – Column with H/EA (3:1). – R_f (H/EA, 2:1) = 0.50. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.65 (s, 3 H), 2.06 (t, J = 2.6 Hz, 1 H), 2.40 (br s, 1 H), 2.65–2.87 (m, 2 H), 6.28–6.33 (m, 2 H), 7.36–7.37 (m, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 26.1 (q), 32.1 (t), 70.1 (s), 71.5 (d), 79.6 (s), 105.0 (d), 110.0 (d), 141.7 (d), 157.7 (s). – MS (70 eV); *m/z* (%): 150 (12) [M^+], 149 (27), 111 (100). – $C_9H_{10}O_2$ (150.2): calcd. C 71.98, H 6.71; found C 71.74, H 6.81. – $C_9H_{10}O_2$: calcd. 150.06808, found 150.06812 (MS).

b) *(E)-5-Hydroxy-2-[5-(1-hydroxy-1-methyl-3-butynyl)-3-furanyl]-5-methyl-2-octen-7-yn-4-one* (**3d**): 26.9 mg (89.5 µmol, 68%). – Column with H/EA (3:1). – R_f (H/EA, 2:1) = 0.29. – IR (neat, KBr): $\tilde{\nu}$ = 3438 cm^{-1}, 3295 (≡C–H), 2982, 2934, 2120 (C≡C), 1671 (C=O), 1588, 1371, 1145, 1106, 1076, 936. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.49 (s, 3 H), 1.66 (s, 3 H), 2.07 (t, J = 2.7 Hz, 1 H), 2.11 (t, J = 2.7 Hz, 1 H), 2.49 (d, J = 1.2 Hz, 3 H), 2.50 (s, 1 H), 2.56–2.88 (m, 4 H), 4.21 (s, 1 H), 6.55 (br s, 1 H), 6.72 (br s, 1 H), 7.68 (br s, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 17.5 (q), 24.5 (q), 26.2 (q), 30.1 (t), 32.0 (t), 70.2 (s), 71.2 (d), 72.1 (d), 79.1 (s), 79.4 (s), 102.8 (d), 114.8 (d), 129.0 (s), 142.6 (d), 149.4 (s), 159.8 (s), 201.1 (s) (one signal hidden). – MS (70 eV); *m/z* (%): 300 (1) [M^+], 277 (1), 261 (8), 243 (4), 217 (100). – $C_{18}H_{20}O_4$ (300.4): calcd. C 71.98, H 6.71; found C 71.95, H 6.75. – $C_{18}H_{20}O_4$: calcd. 300.13616, found 300.13618 (MS).

5. 43.2 mg (263 µmol) of **1e** gave the following products (Table 1, entry 11). – a) *2-[2-(2-Propynyloxy)propyl]furan* (**2e**): 14.6 mg (88.9 µmol, 34%). – Column with H/EA (10:1). – R_f (H/EA, 2:1) = 0.55. – IR (neat): $\tilde{\nu}$ = 3296 cm^{-1} (≡C–H), 3148, 3118, 2974, 2930, 2859, 2116 (C≡C), 1597. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.19 (d, J = 6.1 Hz, 3 H), 2.39 (t, J = 2.4 Hz, 1 H), 2.72 (dd, J = 6.7 Hz, 15.0 Hz, 1 H), 2.96 (dd, J = 5.9 Hz, 15.0 Hz, 1 H), 3.88–4.01 (m, 1 H), 4.14 (d, J = 2.4 Hz, 2 H), 6.08–6.09 (m, 1 H), 6.28–6.29 (m, 1 H), 7.31 (m, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 19.31 (q), 34.92 (t), 55.73 (t), 73.31 (d), 73.74 (d), 80.01 (s), 106.59 (d), 110.12 (d), 141.01 (d), 152.48 (s). – MS (70 eV); *m/z* (%): 149 (100) [$M^+ - CH_3$]. – $C_9H_9O_2$: calcd. 149.06026, found 149.06046 (MS).

b) *6-(2-Propynyloxy)-2-{5-[2-(2-propynyloxy)propyl]-3-furanyl}-2-hepten-4-one* (**3e**): 20.4 mg (62.1 µmol, 47%). – Column with H/EA (10:1). – R_f (H/EA, 2:1) = 0.38. – IR (neat): $\tilde{\nu}$ = 3289 cm^{-1} (≡C–H), 3145, 2972, 2929, 2860, 2115 (C≡C), 1764, 1677, 1590. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.14 (d, J = 6.2 Hz, 3 H), 1.18 (d, J = 6.2 Hz, 3 H), 2.32–2.35 (m, 5 H), 2.47 (dd, J = 5.6 Hz, 15.7 Hz, 1 H), 2.66 (dd, J = 6.3 Hz, 15.1 Hz, 1 H), 2.74–2.87 (m, 2 H), 3.81–3.96 (m, 1 H), 4.03–4.21 (m, 5 H), 6.27 (s, 1 H), 6.35 (s, 1 H), 7.51 (s, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.83 (q), 19.21 (q), 19.75 (q), 34.91 (t), 51.48 (t), 55.75 (t), 55.93 (t), 71.64 (d), 72.88 (d), 73.79 (d), 73.89 (d), 79.85 (s), 80.06 (s), 104.54 (d), 121.16 (d), 129.11 (s), 141.70 (d), 145.22 (s), 154.27 (s), 198.65 (s).

6. 58.3 mg (275 µmol) of **1f** gave the following products (Table 1, entry 13). – a) *1-[3-(2-Furanyl)phenyl]-3-butyn-1-ol* (**2f**): 46.7 mg (220 µmol, 80%). – Column with H/EA (3:1). – R_f (H/EA, 1:1) = 0.57. – IR (neat, KBr): $\tilde{\nu}$ = 3420 cm^{-1}, 3295 (≡C–H), 2916, 2119 (C≡C), 1717, 1610, 1503, 1424, 1292, 1061, 1013, 793, 739, 699, 641. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.09 (t, J = 2.6 Hz, 1 H), 2.40 (br s, 1 H), 2.66–2.70 (m, 2 H), 4.92 (t, J = 6.4 Hz, 1 H), 6.47 (dd, J = 3.4 Hz, 1 H), 6.67 (dd, J = 3.4 Hz, 0.7 Hz, 1 H), 7.25–7.31 (m, 1 H), 7.38 (t, J = 7.6 Hz, 1 H), 7.47 (dd, J = 1.8 Hz, 0.7 Hz, 1 H), 7.61 (dt, J = 7.6 Hz, 1.5 Hz, 1 H), 7.71 (t, J = 1.7 Hz, 1 H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 29.3 (t), 71.0 (d), 72.1 (d), 80.4 (s), 105.1 (d), 111.5 (d), 121.0 (d), 123.3 (d), 124.5 (d), 128.7 (d), 131.0 (s), 142.0 (d), 142.8 (s), 153.6 (s). – MS (70 eV); *m/z* (%): 212 (51) [M^+], 173 (100), 145 (20), 127 (19), 117 (30), 115 (33). – $C_{14}H_{12}O_2$ (212.2): calcd. C 79.23, H 5.70; found C 79.33, H 5.76.

b) *(E)-1-[3-(1-Hydroxy-3-butynyl)phenyl]-3-{5-[3-(1-hydroxy-3-butynyl)phenyl]-3-furanyl}-2-buten-1-one* (**3f**): 7.7 mg (18.1 µmol, 13%). – Column with H/EA (3:1). – R_f (H/EA, 1:1) = 0.28. – IR

(neat, KBr): $\tilde{\nu}$ = 3404 cm^{-1}, 3340, 3283 (≡C−H), 1641 (C=O), 1593, 1571, 1433, 1336, 1270, 1243, 1180, 1152, 1048, 1020, 794, 700, 672, 642. − ^{1}H NMR ([D$_6$]DMSO, 600 MHz): δ = 2.50 (d, *J* = 0.8 Hz, 3 H), 2.53−2.63 (m, 4 H), 2.74 (br s, 2 H), 4.76 (q, *J* = 5.7 Hz, 1 H), 4.82 (q, *J* = 5.7 Hz, 1 H), 5.64 (d, *J* = 4.3 Hz, 1 H), 5.66 (d, *J* = 4.5 Hz, 1 H), 7.36 (d, *J* = 7.7 Hz, 1 H), 7.42 (d, *J* = 7.7 Hz, 1 H), 7.44 (d, *J* = 4.9 Hz, 1 H), 7.51 (t, *J* = 7.7 Hz, 1 H), 7.64−7.67 (m, 3 H), 7.81 (s, 1 H), 8.00 (d, *J* = 7.8 Hz, 1 H), 8.03 (s, 1 H), 8.31 (s, 1 H). − ^{13}C NMR ([D$_6$]DMSO, 62.9 MHz): δ = 17.1 (q), 28.9 (t, 2 C), 70.7 (d), 70.9 (d), 72.7 (d), 72.8 (d), 81.7 (s), 81.8 (s), 103.5 (d), 118.7 (d), 121.4 (d), 122.5 (d), 125.7 (d), 126.0 (d), 127.1 (d), 128.3 (d), 128.6 (d), 129.4 (s), 130.4 (s), 130.5 (d), 138.7 (s), 144.0 (d), 145.0 (s), 145.2 (s), 145.8 (s), 154.5 (s), 190.7 (s). − MS (70 eV); *m/z* (%): 424 (54) [M$^+$], 173 (100), 155 (17), 133 (29). − $C_{28}H_{24}O_4$ (424.5): calcd. C 79.22, H 5.70; found C 79.08, H 5.67.

7. 46.1 mg (396 μmol) of **1g** gave the following products (Table 1, entry 14). a) *2-(Chloromethyl)furan* (**2g**): Distilled off with CD_2Cl_2. For NMR data see ref.[23]

b) *(E)-1-Chloro-4-[5-(chloromethyl)-3-furanyl]-3-penten-2-one* (**3g**): 13.5 mg (57.9 μmol, 29%, after sublimation). − R_f (H/EA, 4:1) = 0.10. − M.p. 80−82°C. − IR (neat, KBr): $\tilde{\nu}$ = 2944 cm^{-1}, 1691, 1593, 1391, 1153, 1102, 701. − ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 2.45 (s, 3 H), 4.11 (s, 2 H), 4.54 (s, 2 H), 6.58 (s, 1 H), 6.60 (s, 1 H), 7.70 (s, 1 H). − ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ = 17.3 (q), 37.0 (t), 49.3 (t), 107.1 (d), 117.3 (d), 129.3 (s), 143.9 (d), 148.3 (s), 152.0 (s), 191.6 (s). − MS (70 eV); *m/z* (%): 232 (27) [M$^+$], 197 (35), 183 (100), 148 (9), 91 (32). − $C_{10}H_{10}Cl_2O_2$: calcd. 232.00579, found 232.00590 (MS).

8. 36.7 mg (254 μmol) of **1h** gave the following products (Table 1, entry 17). − a) *2-(3-Chloropropyl)furan* (**2h**[24]): Distillation with the CD_2Cl_2 at 13 mbar, room temp. − IR (neat): $\tilde{\nu}$ = 3116 cm^{-1}, 2960, 2920, 2840, 1598. − ^{1}H NMR (CD_2Cl_2, 250 MHz): δ = 2.06−2.14 (m, 2 H), 2.79 (t, *J* = 7.3 Hz, 2 H), 3.56 (t, *J* = 6.5 Hz, 2 H), 6.05 (dd, *J* = 0.8 Hz, 3.1 Hz, 1 H), 6.30 (dd, *J* = 1.9 Hz, 3.1 Hz, 1 H), 7.32 (dd, *J* = 0.8 Hz, 1.9 Hz, 1 H). − ^{13}C NMR (CD_2Cl_2, 62.9 MHz): δ = 25.51 (t), 31.40 (t), 44.72 (t), 105.89 (d), 110.55 (d), 141.57 (d), 154.99 (s).

b) *(E)-7-Chloro-2-[5-(3-chloropropyl)-3-furanyl]-2-hepten-4-one* (**3h**): 9.8 mg (33.8 μmol, 27%). − Column with H/EA (10:1). − R_f (H/EA, 5:1) = 0.33. − IR (neat): $\tilde{\nu}$ = 3147 cm^{-1}, 2960, 2921, 2849, 1680 (C=O), 1593. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.98−2.10 (m, 4 H), 2.34 (d, *J* = 0.8 Hz, 3 H), 2.64 (t, *J* = 7.0 Hz, 2 H), 2.73 (t, *J* = 7.2 Hz, 2 H), 3.50 (t, *J* = 6.4 Hz, 2 H), 3.54 (t, *J* = 6.3 Hz, 2 H), 6.20 (s, 1 H), 6.32 (d, *J* = 0.8 Hz, 1 H), 7.51 (s, 1 H). − ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.78 (q), 24.95 (t), 26.70 (t), 30.40 (t), 41.15 (t), 43.75 (t), 44.53 (t), 103.37 (d), 120.52 (d), 128.93 (s), 141.82 (d), 145.17 (s), 156.01 (s), 199.41 (s). − MS (70 eV); *m/z* (%), ^{35}Cl peaks: 288 (33) [M$^+$], 253 (38) [M$^+$ − Cl], 211 (100), 184 (25), 147 (24), 119 (20), 105 (79). − $C_{14}H_{18}Cl_2O_2$ (289.2): calcd. C 58.14, H 6.27; found C 57.85, H 6.30.

9. 39.3 mg (194 μmol) of **1i** gave the following products (Table 1, entry 21). − a) *2-(4-Bromobutyl)furan* (**2i**[24]): 17.2 mg (84.6 μmol, 44%). − Column with H/EA (10:1). − R_f (H/EA, 2:1) = 0.56. − IR (neat): $\tilde{\nu}$ = 3114 cm^{-1}, 2940, 2865, 1597. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.72−1.95 (m, 4 H), 2.65 (t, J = 7.1 Hz, 2 H), 3.40 (t, *J* = 6.5 Hz, 2 H), 5.98−5.99 (m, 1 H), 6.25−6.27 (m, 1 H), 7.28 (m, 1 H). − ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 26.47 (t), 26.90 (t), 31.94 (t), 33.22 (t), 104.93 (d), 109.95 (d), 140.79 (d), 155.28 (s). − MS (70 eV); *m/z* (%): 204/202 (13) [M$^+$], 123 (5), 81 (100).

b) *(E)-8-Bromo-2-[5-(4-bromobutyl)-3-furanyl]-2-octen-4-one* (**3i**): 12.6 mg (31.0 μmol, 32%). − Column with H/EA (10:1). − R_f (H/EA, 2:1) = 0.32. − IR (neat): $\tilde{\nu}$ = 2942 cm^{-1}, 2868, 1677 (C=O), 1591. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.74−1.95 (m, 8 H), 2.40 (s, 3 H), 2.53 (t, *J* = 7.5 Hz, 2 H), 2.64 (t, *J* = 7.1 Hz, 2 H), 3.39−3.44 (m, 4 H), 6.22 (s, 1 H), 6.37 (s, 1 H), 7.56 (s, 1 H). − ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 16.77 (q), 22.70 (t), 26.17 (t), 26.91 (t), 31.81 (t), 32.04 (t), 33.09 (t), 33.26 (t), 43.39 (t), 102.82 (d), 120.44 (d), 128.94 (s), 141.53 (d), 145.11 (s), 157.05 (s), 200.17 (s). − MS (70 eV); *m/z* (%): 406 (2), 165/163 (21), 137/135 (26), 82/80 (21), 55 (100). − $C_{16}H_{22}Br_2O_2$ (406.2): calcd. C 47.32, H 5.46; found C 47.03, H 5.53. − $C_{16}H_{22}Br_2O_2$: calcd. 403.99868, found 403.99826 (MS).

10. 43.2 mg (183 μmol) of **1j** gave the following products (Table 1, entry 24). − a) *2-(4-Iodobutyl)furan* (**2j**): 17.7 mg (74.9 μmol, 41%). − Column with H/EA (10:1). − R_f (H/EA, 5:1) = 0.30. − IR (neat): $\tilde{\nu}$ = 3113 cm^{-1}, 2935, 2861, 1596, 1507. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.70−1.94 (m, 4 H), 2.66 (t, *J* = 7.1 Hz, 2 H), 3.20 (t, *J* = 6.7 Hz, 2 H), 6.00−6.01 (m, 1 H), 6.29 (dd, *J* = 2.1 Hz, 2.8 Hz, 1 H), 7.30−7.31 (m, 1 H). − ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 6.26 (t), 26.72 (t), 28.78 (t), 32.68 (t), 104.93 (d), 109.97 (d), 140.80 (d), 155.29 (s). − MS (70 eV); *m/z* (%): 250 (22) [M$^+$], 123 (58) [M$^+$ − I], 81 (100), 67 (6). − $C_8H_{11}IO$ (250.1): calcd. C 38.42, H 4.43; found C 38.66, H 4.49.

b) *(E)-8-Iodo-2-[5-(4-iodobutyl)-3-furanyl]-2-octen-4-one* (**3j**): 16.1 mg (34.1 μmol, 37%). − Column with H/EA (10:1). − R_f (H/EA, 5:1) = 0.32. − IR (neat): $\tilde{\nu}$ = 3127 cm^{-1}, 2935, 2862, 1679 (C=O), 1591. − ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.61−1.93 (m, 8 H), 2.40 (d, *J* = 1.0 Hz, 3 H), 2.52 (t, *J* = 7.0 Hz, 2 H), 2.63 (t, *J* = 7.0 Hz, 2 H), 3.19 (t, *J* = 6.7 Hz, 4 H), 6.22 (d, *J* = 0.8 Hz, 1 H), 6.37 (d, *J* = 1.0 Hz, 1 H), 7.56 (d, *J* = 0.6, 1 H). − ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 6.15 (t), 6.34 (t), 16.81 (q), 25.01 (t), 26.72 (t), 28.49 (t), 32.52 (t), 32.79 (t), 43.22 (t), 102.82 (d), 120.43 (d), 128.93 (s), 141.57 (d), 145.12 (s), 157.05 (s), 200.17 (s). − MS (70 eV); *m/z* (%): 500 (3) [M$^+$], 373 (100) [M$^+$ − I], 317 (38), 211 (23), 183 (30), 161 (44), 55 (75). − $C_{16}H_{22}I_2O_2$ (500.2): calcd. C 38.42, H 4.43; found C 38.67, H 4.57.

11. 36.5 mg (240 μmol) **14** gave the following product (Table 1, entry 26). *2-Hexylfuran* (**2k**): For NMR data see ref.[25]

[1] [1a] J. A. Marshall, E. D. Robinson, *J. Org. Chem.* **1990**, *55*, 3450−3451. − [1b] J. A. Marshall, X. Wang, *J. Org. Chem.* **1991**, *56*, 960−969. − [1c] J. A. Marshall, X. Wang, *J. Org. Chem.* **1992**, *57*, 3387−3396. − [1d] J. A. Marshall, G. S. Bartley, *J. Org. Chem.* **1994**, *59*, 7169−7171. − [1e] J. A. Marshall, E. M. Wallace, P. S. Coan, *J. Org. Chem.* **1995**, *60*, 796−797. − [1f] J. A. Marshall, C. A. Schon, *J. Org. Chem.* **1995**, *60*, 5966−5968.

[2] A. S. K. Hashmi, *Angew. Chem.* **1995**, *107*, 1749−1751; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1581−1583.

[3] B. M. Trost, M. K. Trost, *J. Am. Chem. Soc.* **1991**, *113*, 1850−1852.

[4] See e.g.: L. S. Hegedus in *Organometallics in Synthesis* (Ed.: M. Schlosser), John Wiley & Sons, Chichester, **1994**, p. 448−448.

[5] A. S. K. Hashmi, F. Naumann, R. Probst, J. W. Bats, *Angew. Chem.* **1997**, *109*, 127−130; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 104−106.

[6] L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, **1988**. − [6a] p. 95−96. − [6b] p. 35−36.

[7] [7a] R. J. Boeckman, Jr. in *Encyclopedia of Reagents for Organic Synthesis* (Ed.: L. A. Paquette), John Wiley & Sons, Chichester, **1995**, vol. 7, p. 4982−4987. − [7b] A. Speicher, V. Bomm, T. Eicher, *J. Prakt. Chem./Chem.-Ztg.* **1996**, *338*, 588−590.

[8] [8a] R. Couffignal, M. Gaudemar, *Bull. Soc. Chim. Fr.* **1969**, 898−903. − [8b] R. Couffignal, M. Gaudemar, *Bull. Soc. Chim. Fr.* **1969**, 3218−3222. − [8c] R. Couffignal, M. Gaudemar, *Bull. Soc. Chim. Fr.* **1970**, 3157−3160.

[9] We already observed this effect with other substrates possessing terminal alkyne groups.

[10] B. M. Trost, G. Kottirsch, *J. Am. Chem. Soc.* **1990**, *112*, 2816–2818.
[11] B. M. Trost, *Acc. Chem. Res.* **1990**, *23*, 34–42.
[12] N. Chatani, T. Morimoto, T. Muto, S. Murai, *J. Am. Chem. Soc.* **1994**, *116*, 6049–6050.
[13] R. Gelin, S. Gelin, M. Albrand, *Bull. Soc. Chim. Fr.* **1972**, 1946–1949.
[14] [14a] R. D. Walkup, G. Park, *Tetrahedron Lett.* **1987**, *28*, 1023–1026. – [14b] R. D. Walkup, G. Park, *J. Am. Chem. Soc.* **1990**, *112*, 1597–1603. – [14c] R. D. Walkup, L. Guan, *Synth. Commun.* **1992**, *22*, 1007–1015. – [14d] R. D. Walkup, L. Guan, S. W. Kim, Y. S. Kim, *Tetrahedron Lett.* **1992**, *33*, 3969–3972.
[15] [15a] R. Gelin, M. Albrand, S. Gelin, *C. R. Acad. Sci., Ser. C* **1969**, *269*, 241–244. – [15b] L.-I. Olsson, A. Claesson, *Synthesis* **1979**, 743–745. – [15c] H. Saimoto, T. Hiyama, H. Nozaki, *J. Am. Chem. Soc.* **1981**, *103*, 4975–4977. – [15d] S. S. Nikam, K.-H. Chu, K. K. Wang, *J. Org. Chem.* **1986**, *51*, 745–747. – [15e] J. A. Marshall, X. Wang, *J. Org. Chem.* **1990**, *55*, 2995–2996. – [15f] J. A. Marshall, K. G. Pinney, *J. Org. Chem.* **1993**, *58*, 7180–7184. – [15g] J. A. Marshall, B. Yu, *J. Org. Chem.* **1994**, *59*, 324–331. – [15h] J. A. Marshall, R. H. Yu, J. F. Perkins, *J. Org. Chem.* **1995**, *60*, 5550–5555.
[16] [16a] P. Audin, A. Doutheau, L. Ruest, J. Goré, *Bull. Soc. Chim. Fr., Part II* **1981**, 313–318. – [16b] P. Audin, A. Doutheau, J. Gore, *Tetrahedron Lett.* **1982**, *23*, 4337–4340. – [16c] J.-J. Chilot, A. Doutheau, J. Gore, *Tetrahedron Lett.* **1982**, *23*, 4693–4696.
[17] [17a] H. Alper, F. W. Hartstock, B. Despeyroux, *J. Chem. Soc., Chem. Commun.* **1984**, 905–906. – [17b] R. D. Walkup, M. D. Mosher, *Tetrahedron* **1993**, *49*, 9285–9294. – [17c] R. D. Walkup, L. Guan, M. D. Mosher, S. W. Kim, Y. S. Kim, *Synlett* **1993**, 88–90. – [17d] R. D. Walkup, M. D. Mosher, *Tetrahedron Lett.* **1994**, *35*, 8545–8548. – [17e] R. D. Walkup, L. Guan, Y. S. Kim, S. W. Kim, *Tetrahedron Lett.* **1995**, *36*, 3805–3808.
[18] G. Buono, *Synthesis* **1981**, 872–872.
[19] K. Nützel, *Methoden Org. Chem. (Houben-Weyl)*, **1973**, vol. 13/2a, p. 285–326. See also ref.[6a]
[20] [20a] H. P. Wessel, T. Iversen, D. R. Bundle, *J. Chem. Soc., Perkin Trans. 1* **1985**, 2247–2250. – [20b] L. E. Overman, C. K. Marlowe, L. A. Clizbe, *Tetrahedron Lett.* **1979**, 599–600.
[21] [21a] A. Kiewiet, J. De Wit, W. D. Weringa, *Org. Magn. Reson.* **1974**, *6*, 461–465. – [21b] B. Wrackmeyer, H. Nöth, *Chem. Ber.* **1976**, *109*, 1075–1088. – [21c] J. F. Bertran, M. Rodriguez, *Org. Magn. Reson.* **1981**, *16*, 82–84.
[22] Y. Yamaguchi, N. Tatsuta, K. Hayakawa, K. Kanematsu, *J. Chem. Soc., Chem. Comm.* **1989**, 470–472.
[23] [23a] M. Altamura, E. Perrotta, *J. Org. Chem.* **1993**, *58*, 272–274. – [23b] G. Arena, R. Cali, E. Maccarone, A. Passerini, *J. Chem. Soc., Perkin Trans. 2* **1993**, 1941–1945.
[24] C. Rogers, B. A. Keay, *Can. J. Chem.* **1992**, *70*, 2929–2947.
[25] [25a] R. Iriye, T. Uno, I. Ohwa, A. Konishi, *Agric. Biol. Chem.* **1990**, *54*, 1841–1843. – [25b] N. B. McKeown, I. Chambrier, M. J. Cook, *J. Chem. Soc., Perkin Trans. 1* **1990**, 1169–1177. – [25c] J.-H. Sheu, C.-F. Yen, H.-C. Huang, Y.-L. V. Hong, *J. Org. Chem.* **1989**, *54*, 5126–5128.

[97058]