Synthesis of Allenyl Ketones and their Palladium-Catalyzed Cycloisomerization/Dimerization: Approaching the Limits

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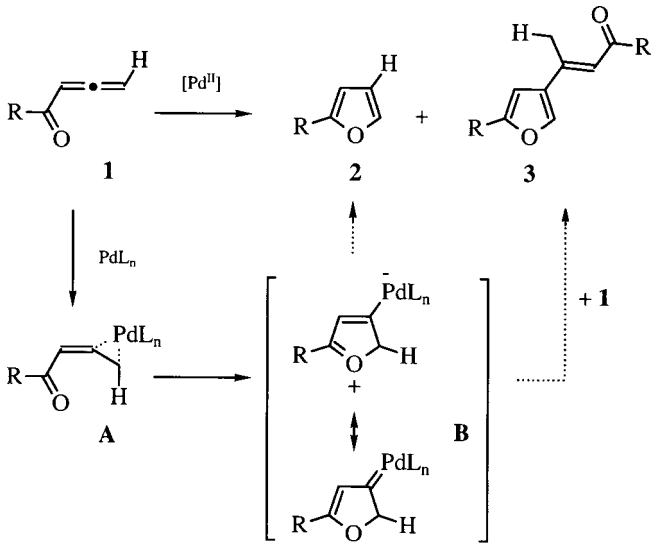
Abstract. The preparation of several new allenyl ketones **1a**–**j** and **1o**–**q** is reported. In the case of allenyl ketones with nucleophilic groups in the side-chain like **1k**–**m**, the material polymerized during the purification procedure; with the dialkyl thioether **1n** the product of a Pummerer isomerization, the acetoxymethyl alkyl thioether, **11** was formed. Depending on the route to **1** sometimes either the acetate adducts **8** and the 1-propynyl ketones **9** or the dipropargyl and propargyl allenyl carbinol **14** and **15** were observed as side-products. Good yields of the sensitive aryl γ-halogen-allenyl ketones **23a** and **23b** were obtained by a new synthetic route, on the other hand the aryl γ-silylallenyl ketone **23c** was readily desilylated. Subjecting the new allenyl ketones to the $PdCl_2(MeCN)_2$ catalyst provided the 2-substituted furans **2** and the 2,4-disubstituted furans **3** in most cases. The yields and ratios of these products strongly depended on the nature of the groups being present. With the aryl thioether and the γ-halogen allenyl ketones the palladium-catalyzed reaction failed. Detailed structural information about the new products was provided by the X-ray structure analyses of the *p*-acetamidophenyl propargyl carbinol **6g** and the 2-aryl-4-(1-methyl-3-aryl-3-oxo-propen-1-yl furan **3h**.

The furan moiety is frequently found in natural products and in important pharmaceuticals as well as in flavouring, aroma and fragrance compounds [1]. Furans are also often used as building blocks in organic synthesis [2]. One relatively new method for the preparation of furans is the silver-catalyzed cycloisomerization of the easily available allenyl ketones [3] discovered by Marshall [4]. He successfully applied this methodology to the synthesis of macrocyclic marine natural products [5].



1,**2**,**3**: substituents specified in Table 1

Scheme 1

We recently reported on the palladium-catalyzed cycloisomerization/dimerization of terminal allenyl ketones **1** leading to furans **2** as minor and 2,4-disubstituted furans **3**, the latter derived from an additional C–C-bond formation, as major products [6, 7].

Although the detailed mechanism is still unknown, we assume that the reaction proceeds as follows: Coordination of the electrophilic $Pd(II)L_n$ to the electron-rich C=C-double bond of **1** bends the allene as shown in **A**. This allows the C–O-bond formation leading to the heterocyclic intermediate **B**. From **B** then either **2** is formed by the migration of one hydrogen and liberation of the metal or **3** is formed by the addition to a second molecule of **1** and a hydrogen migration.

This interesting C–C-bond forming reaction tolerates numerous functional groups, most exciting being substrates in which functional groups that are known to react with palladium or other transition metals as well, remained untouched. Even the selective transformation of an allenyl ketone in the presence of an allenyl carbinol could be achieved.

To establish this previously published methodology, it was important to test (a) the limits of the synthesis of allenyl ketones with certain, possibly problematic substituents and (b) their ability to form **2** and/or **3** in the presence of the palladium catalyst.

Synthesis of the Allenyl Ketones

In most of the cases we prepared allenyl ketones **1** by a two-step sequence: the addition of allenylmagnesium

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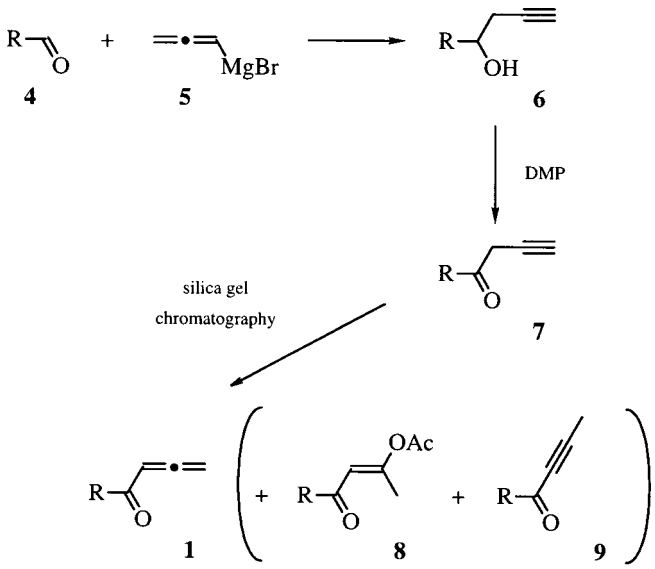


1,**4**,**6**-**9**: substituents specified in Table 1

Scheme 2

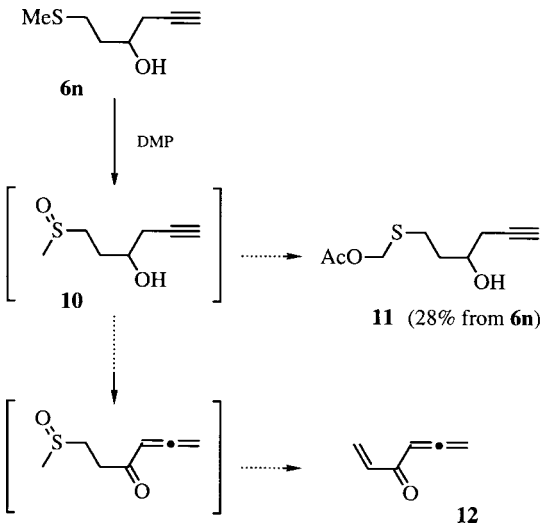
Table 1 Synthesis and Palladium-Catalyzed Transformation of Allenyl Ketones **1a**–**r**

entry	substituent R		**6** (%)	**1** (%)	**2** (%)	**3** (%)
1	**a**	CH_2OCH_2Ph	78	83	5	89
2	**b**	adamantyl	–[a])	41[a])	7	81
3	**c**	cyclopropyl	–[a])	38[a])	–	63
4	**d**		86[b])	69	–	78
5	**e**	3-(MeO)C_6H_4	99	67	8	46
6	**f**	3,4-(O–CH_2–O)C_6H_3	71	60	1	13
7	**g**	4-(AcNH)C_6H_4	58	80	3	87
8	**h**	2-(O_2N)C_6H_4	59	73	3	90
9	**i**	4-(O_2N)C_6H_4	24	58	4	82
10	**j**	4-(NC)C_6H_4	53	72	–	77
11	**k**	4-pyridyl	47	–	–	–
12	**l**	4-(Me_2N)C_6H_4	78	–	–	–
13	**m**	*N*–Me-pyrrol-2-yl	92	–	–	–
14	**n**	CH_2CH_2SMe	46	–	–	–
15	**o**	4-(MeS)C_6H_4	66	60	–[c])	–[c])
16	**p**	4-[MeC(=O)-CH=C=CH]C_6H_4	59 (**22**)	60	–[c])	–[c])
17	**q**	see formula of **6q** and **1q** above	86	81	–[c])	–[c])
18	**r**	$CH_2C{\equiv}CH$	62	–	–	–

[a]) **1** prepared from carboxylates. [b]) prepared by epoxidation of the corresponding allyl homopropargyl alcohol. [c]) no selective reaction.

bromide **5** to aldehydes **4** followed by a Dess-Martin oxidation of the homopropargyl alcohols **6**. The Dess-Martin oxidation first forms the propargyl ketone **7** which isomerizes to **1** during the chromatographic working up [8]. The results are shown in Table 1.

Usually the Dess-Martin oxidation was successful, as previously described, the only side products being **8** and/or **9** [8]. There are three major exceptions: (a) Substrates containing nucleophilic groups (entries 11 and 12). Here the direct chromatographic working up of the crude reaction mixture (containing the propargyl ketone **7**) yields **1** but the latter represents a highly reactive Michael-acceptor and starts to undergo nucleophilic polymerisation on concentration of the fractions obtained from chromatography. (b) Substrates containing groups that can also be oxidized. The electron-rich pyrrole in entry 13 led to tary material only. The thioether **6n** in entry 14 was also oxidized at sulfur, a subsequent Pummerer isomerization of the sulfoxide **10** led to **11**. This is the second time that such a Pummerer isomerization was observed [9] and the first time that the primary (here **11**) product has been isolated in Dess-Martin oxidations. Probably some of the desired **1n** is formed but decomposes by elimination (leading to the highly reactive and volatile **12**). Placing one aryl group in the thioether eliminated these problems, the sulfur is less readily oxidized by the DMP (**1o**, entry 15). (c) The allenyl ketone expected in entry 18 appears to be highly reactive and volatile, all efforts to isolate this product failed.



Scheme 3

The propargyl alcohols and allenyl ketones from entries 7, 8 and 9 possess a low solubility, making their handling quite inconvenient. On the other hand, this enabled us to grow crystals and perform an X-ray structure analysis of **6g** (Figure 1).

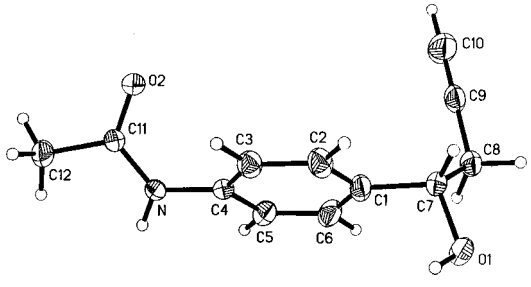


Fig. 1 ORTEP diagram of *N*-[4-(1-hydroxybut-3-ynyl)phenyl]acetamide (**6g**)

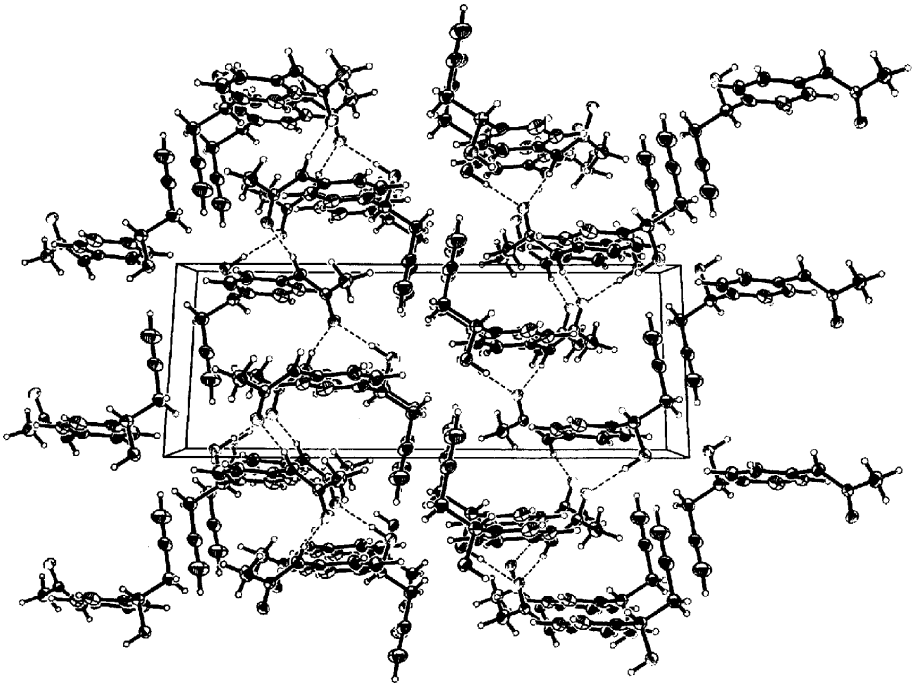
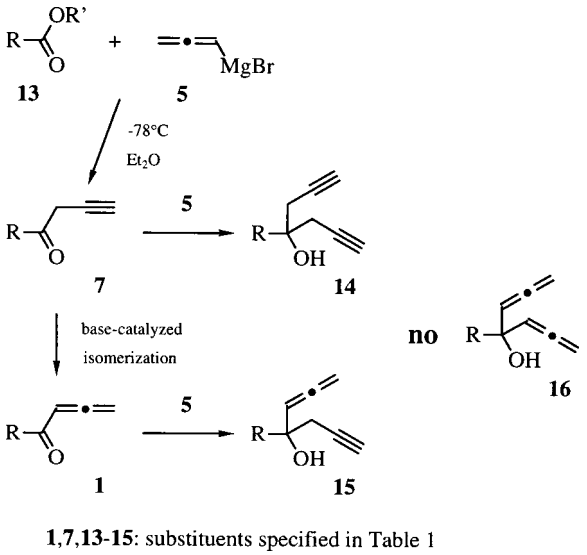


Fig. 2 Layers in the solid-state structure of *N*-[4-(1-hydroxybut-3-ynyl)phenyl]acetamide (**6g**)

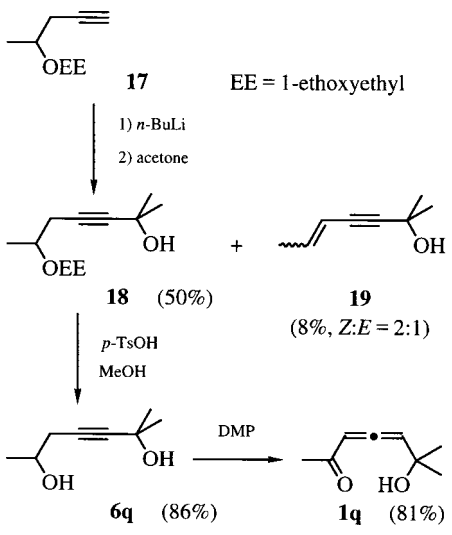
In **6g** the angle between the plane of the benzene ring and that of the amide group is 47.2(1)°. The molecules show no short intramolecular contacts. The crystal packing shows two intermolecular hydrogen bonds which connect the molecules in layers in the crystallographic a,c-direction (Figure 2, probably the low solubility originates from this structural feature). The keto oxygen atom O2 is an acceptor for two hydrogen bonds, consequently the observed C11–O2 distance of 1.242(1) Å is rather long. Weak electrostatic interactions between O1 and H atoms of neighbouring molecules with O···H distances of about 2.5 Å connect the hydrogen bonded layers in the crystallographic b-direction.

In some entries (2 and 3) **1** was synthesized in one step by the addition of **5** to esters **13** at –78 °C. The major side reaction was the addition of a second molecule of **5** to the ketone, leading to a tertiary alcohol. This could either happen at the stage of the intermediate **7** or after base-catalyzed (by magnesium alkoxides) rearrangement of **7** at the stage of **1**, thus the dipropargyl carbinol **14** and the allenyl propargyl carbinol **15** were the side products. Since in our hands the addition

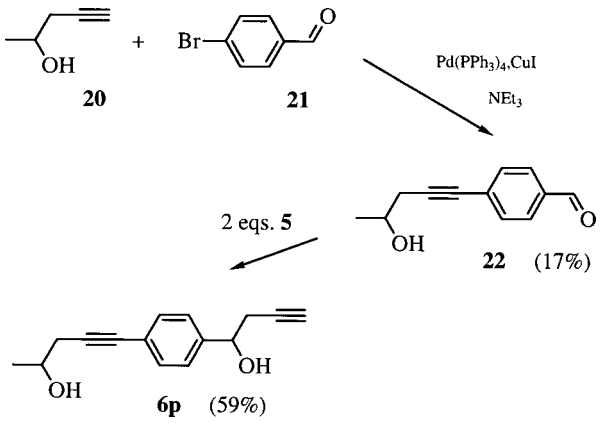


1,7,13-15: substituents specified in Table 1

Scheme 4



Scheme 5

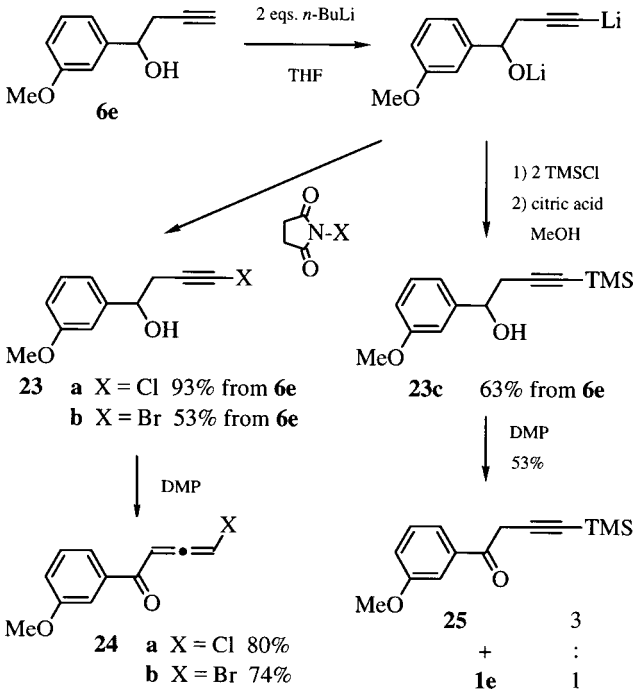


Scheme 6

of **5** to carbonyl compounds initially led to propargyl compounds **7** exclusively, the formation of the isomeric diallenyl carbinols **16** as side products was not observed.

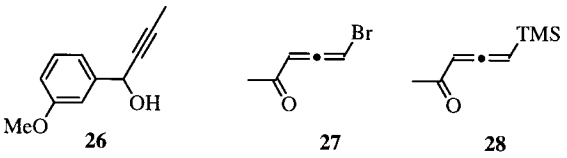
The homopropargylic alcohol **6q** was accessible through the addition of the 1-ethoxyethyl protected, deprotonated 4-pentin-2-ol **17** to acetone and subsequent deprotection. The preparation of **6p** started with the cross coupling of **20** and 4-bromobenzaldehyde **21** followed by the usual addition of the Grignard reagent **5**. Compound **6r** was formed in the reaction of ethyl formiate with an excess of **5**.

Starting from **6e** the chloro-, bromo- and trimethylsilylhomopropargyl alcohols **23a**–**c** could be prepared in analogy to literature procedures [10]. The only side



Scheme 7

product was the propargylic alcohol **26**, an isomer of **6e** (6% in the formation of **23a**, 2% in the formation of **23b**). The Dess-Martin oxidations of **23a** and **23b** led to the desired γ-chloro- and γ-bromoallenyl ketones **24a** and **24b**. In the case of **23c** only a mixture of the γ-trimethylsilylpropargyl ketone **25** (no isomerization to the allene!) and the desilylation product **1e** could be obtained.



Allenyl halides even occur in nature as exemplified by the bromoallenes found as secondary metabolit in red algae *Laurencia pannosa* [11a]. In the literature one can find the synthesis of several allenyl halides, but they readily (yet, unselectively) dimerize to dimethylenecyclobutanes [11b]. As far as γ-haloallenyl ketones are concerned, only one single derivative is known, the 5-bromo-3,4-pentadien-2-one **27** was prepared by dehydrohalogenation [12]. As neat substrates our γ-haloallenyl ketones also oligomerized unspecifically at room temperature within a few hours. Therefore, they were immediately taken up in the solvent for the next step and stored in the freezer at –30 °C.

Compound **28** is the only known γ-silylated allenyl ketone also bearing a hydrogen atom in the γ-position which is necessary for the cycloisomerization to a furan. Interestingly, it was prepared by photochemical isomerization of the corresponding furan [13].

Palladium-Catalyzed Transformations

After their preparation the individual allenyl ketones **1** were treated with the $PdCl_2(MeCN)_2$ catalyst in MeCN [7]. The results are also listed in Table 1.

As one would expect, **1a** and **1b** led to the dimers **3a** and **3b** in high yields, the monosubstituted furans **2a** and **2b** were only side products. In the case of **1c** it was interesting to observe that more of **2c** was formed; probably the electron-donating properties of the cyclopropyl group reduce the reactivity of the allenyl ketone, so less C–C-bond formation was observed [7]. The allenyl ketone **1d** behaves quite normal, here it is interesting to mention that the 2,2-dimethyloxirane can in principle be used as a proton scavenger as demonstrated by Utimoto et al. [14], so our observation makes the participation of free protons even less likely and is in accordance with the suggestions made before [7]. If one compares **1e** to **1f**, the poor yield of the latter may be explained by the sensitivity of the phenolic formyl acetal

– we lost a lot of material during chromatography (the reaction was monitored by NMR and was quite selective). With the nitrogen-containing substrates **1g–j** things were quite normal again. Due to the low solubility of the dimers **3g–j** the reaction products precipitated directly. For **3h** an X-ray structure determination was possible (Figure 3).

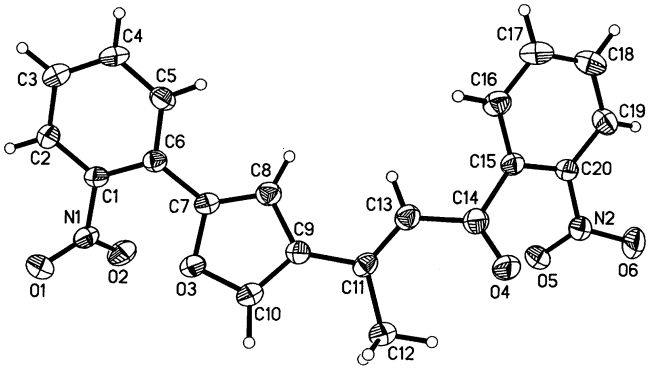
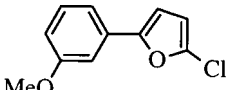


Fig. 3 ORTEP diagram of 1-(2-nitrophenyl)-3-[5-(2-nitrophenyl)furan-3-yl]but-2-en-1-one (**3h**)

The elemental cell contains two crystallographically independent molecules. The planar five-membered ring is almost coplanar with the plane of the C11–C13 double bond and its four substituents (angle between the planes 7.4(4)°). The angle between the C11–C13 double bond and the keto-group C14–O4 is only 15.9(2)°, close to a s-*cis*-conformation. Full coplanarity is not possible because of the steric interaction between O4 and the methyl group C12. The intramolecular O4···H12a distance of 2.23(3) Å is slightly shorter than the sum of the van der Waals radii of 2.4 Å. The angle between the phenyl group C1 to C6 and the furan ring is 26.9(1)° and is required to avoid a short contact between O3 and the N1–O2 bond. The angle between the plane of the keto group and the phenyl group C15 to C20 is 45.4(1)° and is required to avoid a short contact between O4 and the N2–O5 bond. The angles between the phenyl group and the nitro group attached to it are 52° and 39°. Planarity of the nitrophenyl groups is prohibited by the *ortho*-substitution on the phenyl groups. The main difference between molecule I and II is the rotational angle between the phenyl group labeled C1 to C6 and the five-membered ring which is –27° for molecule I and +35° for molecule II. A number of intermolecular O···H distances (O2···H8: 2.46(2) Å; O5···H2: 2.42 (2) Å; O6···H2': 2.39 (3) Å) approach the van der Waals contact distance of 2.4 Å and may be characterized as electrostatic interactions.

With **1o** as well as **1p** the reaction failed, only insoluble, probably polymeric materials, were formed. Compound **1q** immediately reduced the Pd catalyst, Pd metal precipitated and no catalytic conversion was observed. In the reactions of the γ-haloallenyl ketones all starting materials were consumed, but the reactions were quite unspecific, only in the case of **24a** a small amount of the halofuran **29** could be isolated – no dimers of the type **3** were detected. In the case of a successful conversion interesting one-pot reactions, cycloisomerization followed e.g. by cross coupling, would have been possible.



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Conclusion

The synthesis of allenyl ketones failed in the cases of compounds containing substituents with nucleophilic groups. In the palladium-catalyzed cycloisomerization/dimerization it is not possible to use substrates that contain thioethers, groups reducing palladium(II) or 1,n-di(allenylketones) that polymerize.

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. Furthermore we are grateful to the Degussa AG for the generous donation of palladium salts.

Experimental

All operations were carried out under N_2 and in anhydrous solvents; transfers were effected by means of Schlenk-tube techniques. **5** [15a, 16], Dess-Martin periodinane (DMP) [9b, 17], $Pd(PPh_3)_4$ [18] and $PdCl_2(MeCN)_2$ [19] were prepared according to literature procedures. All other chemicals were commercially available and used as received. – IR: Perkin-Elmer 1600. – NMR: Bruker AM 250 (250 and 62.9 MHz for ^1H and ^{13}C, respectively) and Bruker AM 270 (270 and 67.9 MHz for ^1H and ^{13}C, respectively) Bruker DRX 600 (600 MHz for ^1H). $CDCl_3$ as solvent δ_H/ppm = 7.25; δ_C/ppm = 77.0. The degree of substitution of the C atoms was determined by a combination of DEPT 135 and DEPT 90 spectra. – 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 > 20 000, peak match). – *m.p.* (uncorrected): Kofler hot-stage. – Column chromatography: Merck Kieselgel 60 using hexane/ethyl acetate (H/EA), hexane/acetone (H/A) or pentane/diethyl ether (P/E) as eluent. – Elemental analyses were performed on a Foss-Heraus CHN–O-Rapid elemental analyser.

General Procedures

(a) Homopropargylic Alcohols **6** *from Aldehydes* **4** and **5** [15b] A solution of **4** (1.0 equiv.) in diethyl ether (2 ml/mmol of **6**) was cooled in an ice bath. Then a solution of **5** in diethyl ether (1.64M, 1.0 equiv.) was added with stirring. 30 minutes

after the addition the reaction was quenched by the addition of saturated aqueous ammonium chloride solution to the mixture. The organic layer was separated, after three further extractions of the aqueous layer with diethyl ether the combined organic phases were dried over magnesium sulfate, filtered, and the solvent was removed *in vacuo*. The crude product was purified as described below.

(b) Oxidation of Homopropargylic Alcohols **6** *with DMP* [16, 20]

6 (1.0 eq.) was dissolved in DCM (2 ml/10 mmol of **6**) in a flask cooled in a bath of cold water. Then the DMP (1.1 eqs.) was added in small portions, afterwards stirring was continued for 20 minutes. Then the reaction mixture was directly put on a silica gel column, and the product isolated by chromatography as described below. In the case of products **1** with electron-rich substituents the addition of acetic acid (from the Dess-Martin periodinane) to the allene was observed as a side reaction as exemplified by **8e**, **8f**, **8j** and **8o**. In the case of products **1** with electron withdrawing substituents the isomeric 1-alkynones were observed as side products, see the formation of **9e**, **9h**, **9i** and **9o**.

(c) Allenyl Ketones **1** *from Carboxylic Acid Esters* **13** [21]

A well-stirred solution of **5** in diethyl ether (1.64M, 1.0 eq.) was diluted with the same volume of diethyl ether and cooled to −78 °C. Then a solution of **13** (1.0 eq.) in diethyl ether (10 ml/16 mmol of **13**) was added within 10–15 minutes. Stirring was continued at that temperature for 10 minutes, then a few milliliters of a saturated aqueous ammonium chloride solution were added. The solution was allowed to warm to 0 °C, then more aqueous ammonium chloride was added. Further working up as mentioned in (a). As described in the literature, the desired product **1** was always accompanied by the product of a second addition of the grignard reagent as exemplified by **14b**, **15b**, and **14c**. Not commercially available esters **13** were obtained by acid catalyzed esterification of the corresponding carboxylic acids [22].

(d) Cyclization/Dimerization Reactions of **1**

The substrate **1** was dissolved in acetonitrile under an atmosphere of nitrogen (approximately 1M solution), and the containment was placed in a bath with cold water. Then the $PdCl_2(MeCN)_2$ catalyst was added, and the reaction was monitored by ^1H NMR or TLC. The crude reaction mixture was directly purified by column chromatography using Merck silica gel 60.

1-Benzyloxypent-4-yn-2-ol (**6a**)

From 10.0 ml (16.4 mmol) of a solution of **5** in diethyl ether and 2.46 g (16.4 mmol) of **4a** 2.43 g (78%) of **6a** were obtained according to the general procedure (a). R_f (H/EA, 3:1) = 0.42. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3433, 3295, 2914, 2864, 2120, 1496, 1453, 1365, 1206, 1117, 1028, 739. – ^1H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.04 (t, J = 2.7 Hz, 1H), 2.42–2.45 (m, 2H), 3.04 (br s, 1H), 3.47–3.53 (m, 1H), 3.57–3.62 (m, 1H), 3.91–4.01 (m, 1H), 4.55 (s, 2H), 7.29–7.37 (m, 5H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 23.4 (t), 68.6 (d), 70.5 (d), 72.8 (t), 73.3 (t), 80.4 (s), 127.7 (d, 2C and d), 128.3 (d, 2C and d), 137.8 (s). – ^{13}C NMR ([D]$_6$acetone, 62.9 MHz): δ/ppm = 24.3 (t), 69.6 (d), 71.1 (d), 73.6 (t), 74.1 (t), 81.8 (s), 128.0 (d), 128.2 (d, 2 C), 128.9 (d, 2 C), 139.6 (s). – MS (70 eV); *m/z* (%): 190 (8)[M$^+$], 189 (9), 147 (5), 105 (9), 91 (100).

$C_{12}H_{14}O_2$	Calcd.:	C 75.76 H 7.42
(190.2)	Found:	C 75.54 H 7.47.

1-Benzyloxypenta-3,4-dien-2-one (**1a**)

From 1.40 g (3.30 mmol) DMP and 571 mg (3.00 mmol) **6a**, 469 mg (83%) of **1a** were obtained according to the general procedure (b). R_f (H/EA, 5:1) = 0.23. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3064, 3031, 2988, 2866, 1958, 1931, 1695, 1497, 1454, 1414, 1188, 1123, 1028, 861. – ^1H NMR ($CDCl_3$, 250 MHz): δ/ppm = 4.32 (s, 2H), 4.57 (s, 2H), 5.17 (d, J = 6.6 Hz, 2H), 5.85 (t, J = 6.6 Hz, 1H), 7.24–7.34 (m, 5H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 72.5 (t), 73.1 (t), 79.7 (t), 93.1 (d), 127.8 (d, 2C), 128.3 (d, 2C), 137.2 (s), 196.2 (s), 215.7 (s). – MS (70 eV); *m/z* (%): 188 (1)[M$^+$], 187 (1), 157 (1), 145 (1), 129 (2), 107 (6), 91 (100), 82 (67), 67 (25).

$C_{12}H_{12}O_2$	Calcd.:	C 76.57 H 6.43
(188.2)F	Found:	C 76.30 H 6.52.

Reaction of **1a** *with* $PdCl_2(MeCN)_2$

From 376 mg (2.00 mmol) **1a** and 2.6 mg (0.5 mol-%) $PdCl_2(MeCN)_2$ according to the general procedure (d), 18.7 mg (5%) 2-benzyloxymethylfuran (**2a**) and 335 mg (89%) 1-benzyloxy-4-(5-benzyloxymethylfuran-3-yl)-pent-3-en-2-one (**3a**) were obtained.

a) **2a**: R_f (H/EA, 8:1) = 0.46. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3031, 2901, 2859, 1499, 1454, 1357, 1224, 1150, 1090, 1070, 1015, 919, 814. – ^1H NMR ($CDCl_3$, 250 MHz): δ/ppm = 4.50 (s, 2H), 4.57 (s, 2H), 6.33–6.38 (m, 2H), 7.29–7.38 (m, 5H), 7.44 (br s, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 63.7 (t), 71.8 (t), 109.3 (d), 110.1 (d), 127.6 (d), 127.8 (d, 2C), 128.3 (d, 2C), 137.8 (s), 142.7 (d), 151.7 (s). – MS (70 eV); *m/z* (%): 188 (19)[M$^+$], 97 (20), 91 (81), 81 (100).

$C_{12}H_{12}O_2$	Calcd.:	C 76.57 H 6.43
(188.2)	Found:	C 76.32 H 6.54.

b) **3a**: R_f (H/EA, 2:1) = 0.43. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3031, 2914, 2860, 1696, 1677, 1594, 1454, 1146, 1095, 1070. – ^1H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.50 (d, J = 1.1 Hz, 3H), 4.15 (s, 2H), 4.48 (s, 2H), 4.58 (s, 2H), 4.64 (s, 2H), 6.54 (s, 1H), 6.63 (br s, 1H), 7.28–7.42 (m, 10H), 7.71 (br s, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 17.2 (q), 63.7 (t), 72.1 (t), 73.2 (t), 76.0 (t), 106.8 (d), 116.8 (d), 127.7 (d, 1+2C), 127.8 (d,1+ 2C), 128.3 (d, 2C), 128.4 (d, 2C), 129.1 (s), 137.3 (s), 137.5 (s), 143.2 (d), 146.8 (s), 153.4 (s), 198.1 (s). (2 C hidden) – MS (70 eV); *m/z* (%): 376 (2)[M$^+$], 285 (4), 270 (23), 255 (69), 91 (100).

$C_{24}H_{24}O_4$	Calcd.:	C 76.57 H 6.43
(376.5)	Found:	C 76.39 H 6.56.

Adamantane-1-carboxylic acid hexyl ester (**13b**)

From 5.77 g (32.0 mmol) adamantane-1-carboxylic acid, 5.11 g (50.0 mmol) 1-hexanol and 110 mg (578 μmol, 1.8 mol-%) *p*-toluenesulphonic acid monohydrate (*p*-TsOH·H_2O) in 35 ml CCl_4 were obtained 5.50 g (65%) **13b** in analogy to the literature procedure for related substrates [22]. Column with H/EA (40:1). – R_f (H/EA, 40:1) = 0.15. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 2931, 2908, 2853, 1728, 1453, 1325, 1268, 1236, 1184, 1103, 1079. – ^1H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.89 (t, J = 5.9 Hz, 3H), 1.22–1.42 (m, 6H), 1.56–1.70 (m, 2H), 1.72 (br s, 6H), 1.89 (br d, J = 2.9

Hz, 6H), 2.00 (br s, 3H), 4.04 (t, J = 6.6 Hz, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 13.8 (q), 22.3 (t), 25.4 (t), 27.8 (d, 3 C), 28.4 (t), 31.2 (t), 36.4 (t, 3C), 38.7 (t, 3 C), 40.5 (s), 63.9 (t), 177.4 (s). – MS (70 eV); *m/z* (%): 264 (0.5)[M^+], 215 (0.7), 181 (90), 135 (100).

$C_{17}H_{28}O_2$	Calcd.:	C 77.22 H 10.67
(264.4)	Found:	C 77.46 H 10.84.

1-Adamantan-1-ylbuta-2,3-dien-1-one (**1b**)

From 10.0 ml (16.4 mmol) of **5** and 4.34 g (16.4 mmol) **13b**, 1.36 g (41%) **1b**, 319 mg (8%) 4-adamantan-1-ylhepta-1,6-diyn-4-ol (**14b**) and 438 mg (11%) 4-adamantan-1-ylhepta-1,2-dien-6-yn-4-ol (**15b**) were obtained according to the general procedure (c).

a) **1b**: Column with H/EA (30:1). – R_f (H/EA, 5:1) = 0.49. – *m.p.* 38–43 °C. – IR (KBr): $\tilde{\nu}$/cm^{-1} = 3028, 2905, 2848, 1953, 1934, 1666, 1452, 1415, 1344, 1309, 1197, 1164, 1005, 842. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.60–1.80 (m, 6H), 1.86 (d, J = 2.6 Hz, 6H), 2.06 (m, 3H), 5.18 (d, J = 6.5 Hz, 2H), 6.20 (t, J = 6.5 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 27.8 (d, 3C), 36.4 (t, 3C), 38.0 (t, 3C), 46.4 (s), 78.8 (t), 90.0 (d), 203.3 (s), 215.5 (s). – MS (70 eV); *m/z* (%): 202 (2)[M^+], 163 (9), 135 (100), 107 (8), 93 (17).

$C_{14}H_{18}O$	Calcd.:	C 83.12 H 8.97
(202.3)	Found:	C 83.22 H 8.97.

b) **14b**: Column with H/EA (30:1). – R_f (H/EA, 5:1) = 0.43. – IR (KBr): $\tilde{\nu}$/cm^{-1} = 3533, 3283, 3232, 2905, 2847, 1450, 1425, 1362, 1068, 1008, 638. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.61–1.73 (m, 6H), 1.76 (d, J = 3.0 Hz, 6H), 2.01 (br s, 3H), 2.10 (m, 2H), 2.59 (dd, J = 16.8 Hz, 2.7 Hz, 2H), 2.69 (dd, J = 16.8 Hz, 2.7 Hz, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 25.2 (t, 2C), 28.3 (d, 3C), 36.5 (t, 3C), 36.7 (t, 3C), 39.8 (s), 71.7 (d, 2C), 75.1 (s), 81.3 (s, 2C). – MS (70 eV): *m/z* (%): 242 (0.1)[M^+], 227 (0.1), 203 (18), 135 (100), 93 (13).

$C_{17}H_{22}O$	Calcd.:	C 84.25 H 9.15
(242.4)	Found:	C 84.03 H 9.37.

c) **15b**: Column with H/EA (30:1). – R_f (H/EA, 5:1) = 0.52. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3562, 3307, 2930, 2905, 2849, 1958, 1451, 1346, 1074, 1058, 995, 939, 926, 847. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.56–1.72 (m, 12H), 2.00 (br s, 3H), 2.04 (t, J = 2.6 Hz, 1H), 2.27 (s, 1H), 2.31 (dd, J = 16.3 Hz, 2.6 Hz, 1H), 2.64 (dd, J = 16.3 Hz, 2.6 Hz, 1H), 4.95 (d, J = 6.6 Hz, 2H), 5.28 (t, J = 6.6 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 25.6 (t), 28.3 (d, 3C), 36.2 (t, 3C), 36.8 (t, 3C), 39.6 (s), 71.3 (d), 75.6 (s), 78.6 (t), 81.2 (s), 94.8 (d), 206.4 (s). – MS (70 eV): *m/z* (%): 242 (2)[M^+], 227 (4), 203 (28), 185 (2), 135 (100), 107 (20), 93 (36).

$C_{17}H_{22}O$	Calcd.:	C 84.25 H 9.15
(242.4)	Found:	C 83.99 H 9.42.

Reaction of **1b** *with* $PdCl_2(MeCN)_2$

From 405 mg (2.00 mmol) **1b** and 2.6 mg (0.5 mol-%) $PdCl_2(MeCN)_2$ according to the general procedure (d), 28.1 mg (7%) 2-adamantan-1-ylfuran (**2b**) and 327 mg (81%) 1-adamantan-1-yl-3-(5-adamantan-1-ylfuran-3-yl)but-2-en-1-one (**3b**) were obtained.

a) **2b**: Column with H/EA (40:1). – R_f (H/EA, 40:1) = 0.63. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 2905, 2850, 1586, 1504, 1452, 1151, 1010, 727. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.76 (br s, 6H), 1.91 (br s, 6H), 2.04 (br s, 3H), 5.91 (dd, J = 3.2 Hz, 0.7 Hz, 1H), 6.27 (dd, J = 3.2 Hz, 1.8 Hz, 1H), 7.29 (dd, J = 1.8 Hz, 0.7 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 28.1 (d, 3C), 34.3 (s), 36.6 (t, 3C), 41.0 (t, 3C), 101.1 (d), 109.5 (d), 140.1 (d), 164.5 (s). – MS (70 eV); *m/z* (%): 202 (100)[M^+], 145 (73). – $C_{14}H_{18}O$: calcd. 202.13577, found 202.13573 (MS).

$C_{14}H_{18}O$	Calcd.:	C 83.12 H 8.97
(202.3)	Found:	C 83.39 H 8.98.

b) **3b**: Product precipitates. – Column with H/EA (40:1). – R_f (H/EA, 40:1) = 0.13. – IR (KBr): $\tilde{\nu}$/cm^{-1} = 2902, 2849, 1670, 1597, 1583, 1452, 1163, 1145, 1027, 923, 809. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.68–1.82 (m, 12H), 1.85 (br s, 6H), 1.93 (br s, 6H), 2.06 (br s, 6H), 2.36 (d, J = 1.2 Hz, 3H), 6.13 (br s, 1H), 6.66 (br s, 1H), 7.53 (br s, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 17.0 (q), 28.0 (6 d), 34.4 (s), 36.5 (t, 3C), 36.6 (t, 3C), 38.3 (t, 3C), 40.8 (t, 3C), 46.1 (s), 99.1 (d), 116.5 (d), 129.0 (s), 140.5 (d), 145.3 (s), 165.9 (s), 206.0 (s). – MS (70 eV); *m/z* (%): 404 (53)[M^+], 269 (100), 135 (44). – $C_{28}H_{36}O_2$: calcd. 404.27153, found 404.27139 (MS).

$C_{28}H_{36}O_2$	Calcd.:	C 83.12 H 8.97
(404.6)	Found:	C 83.29 H 9.08.

1-Cyclopropylbuta-2,3-dien-1-one (**1c**)

From 10.0 ml (16.4 mmol) of **5** and 1.64 g (16.4 mmol) methyl cyclopropylcarboxylate, 675 g (38%) **1c** and 170 mg (14%) 4-cyclopropylhepta-1,6-diyn-4-ol (**14c**) were obtained according to the general procedure (c).

a) **1c**: Column with P/E (40:1). – R_f (P/E, 10:1) = 0.32. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3065, 3010, 2991, 1959, 1935, 1669, 1442, 1418, 1387, 1194, 1171, 1067, 905, 888, 853. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.85–0.93 (m, 2H), 1.02–1.09 (m, 2H), 2.37–2.47 (m, 1H), 5.31 (dd, J = 6.5 Hz, 1.6 Hz, 2H), 5.87 (td, J = 6.5 Hz, 2.0 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 10.9 (t, 2C), 17.4 (d), 79.4 (t), 97.2 (d), 199.6 (s), 216.9 (s). – MS (70 eV); *m/z* (%): 108 (15)[M^+], 69 (100), 41 (79), 39 (64).

C_7H_8O	Calcd.:	C 77.75 H 7.46
(108.1)	Found:	C 77.47 H 7.64.

b) **14c**: Column with P/E (40:1). – R_f (P/E, 10:1) = 0.22. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3550, 3470, 3298, 3087, 3010, 2914, 2118, 1426, 1053, 1018, 926, 825. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.38–0.48 (m, 2H), 0.50–0.55 (m, 2H), 1.13–1.24 (m, 1H), 1.86 (d, J = 0.5 Hz, 1H), 2.10 (t, J = 2.7 Hz, 2H), 2.52–2.67 (m, 4H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 0.1 (t), 18.0 (d), 30.1 (t, 2C), 70.2 (s), 71.0 (d, 2C), 79.8 (s, 2C). – MS (70 eV): *m/z* (%): 109 (25)[$M^+ - C_3H_3$], 69 (100), 41 (50), 39 (33).

$C_{10}H_{12}O$	Calcd.:	C 81.04 H 8.16
(148.2)	Found:	C 80.80 H 8.27.

Reaction of **1c** *with* $PdCl_2(MeCN)_2$

From 216 mg (2.00 mmol) **1c** and 2.6 mg (0.5 mol-%) $PdCl_2(MeCN)_2$ according to the general procedure (d), 137 mg (63%) 1-cyclopropyl-3-(5-cyclopropylfuran-3-yl)-but-2-en-1-one (**3c**) were obtained. – **3c**: IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3091, 3010, 1763, 1667, 1591, 1442, 1378, 1137, 1025, 954, 942, 895, 886, 814. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.74–0.80 (m, 2H), 0.83–0.93 (m, 4H), 1.03–1.09 (m, 2H), 1.81–1.92 (m, 1H), 1.94–2.04 (m, 1H), 2.38 (d, J = 1.3 Hz, 3H), 6.18 (br s, 1H), 6.53 (br s, 1H), 7.48 (br s, 1H). –

^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 6.5 (t, 2C), 8.5 (d), 10.8 (t, 2C), 16.7 (q), 22.6 (d), 101.0 (d), 121.3 (d), 129.1 (s), 140.8 (d), 144.0 (s), 158.9 (s), 200.6 (s). – MS (70 eV); *m/z* (%): 216 (100)[M^+], 201 (25), 187 (17), 175 (61). – $C_{14}H_{16}O_2$: calcd. 216.11503, found 216.11501 (MS).

$C_{14}H_{16}O_2$	Calcd.:	C 77.75 H 7.46
(216.3)	Found:	C 77.75 H 7.51.

1-(3,3-Dimethyloxiranyl)-but-3-yn-1-ol (**6d**)

a) *6-Methylhept-5-en-1-yn-4-ol*: From 10.0 ml (16.4 mmol) of a solution of **5** in diethyl ether and 1.38 g (16.4 mmol) of 3-methyl-2-butenal, 1.91 g (94%) of 6-methylhept-5-en-1-yn-4-ol were obtained according to the general procedure (a). – Column with H/EA (20:1). – R_f (H/EA, 3:1) = 0.29. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3297, 2972, 2915, 2861, 2120, 1676, 1447, 1377, 1035, 836. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.71 (d, *J* = 1.4 Hz, 3H), 1.74 (d, *J* = 1.4 Hz, 3H), 2.04 (t, *J* = 2.6 Hz, 1H), 2.37–2.41 (m, 3H), 4.47–4.56 (m, 1H), 5.23–5.28 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 18.2 (q), 25.5 (q), 27.5 (t), 66.6 (d), 70.2 (d), 80.8 (s), 125.9 (d), 136.3 (s). – MS (70 eV): *m/z* (%): 124 (63)[M^+], 109 (2), 85 (100), 41 (81).

$C_8H_{12}O$	Calcd.:	C 77.38 H 9.74
(124.2)	Found:	C 77.15 H 9.51.

b) **6d**: From 1.24 g (10.0 mmol) of 6-methylhept-5-en-1-yn-4-ol and 6.18 g (10.0 mmol, 80%) of MMPP in 20 ml methanol were obtained 1.21 g (86%) **6d** in analogy to the literature procedure for other substrates [23]. R_f (H/EA, 1:1) = 0.37. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3422, 3292, 2965, 2930, 2120, 1459, 1426, 1380, 1250, 1133, 1053, 1035, 918, 862, 804. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.35 (br s, 6H), 2.07 (t, *J* = 2.7 Hz, 1H), 2.46 (ddd, *J* = 16.7 Hz, 5.3 Hz, 2.7 Hz, 1H), 2.57 (ddd, *J* = 16.7 Hz, 5.3 Hz, 2.7 Hz, 1H), 2.84 (d, *J* = 8.0 Hz, 1H), 3.37 (d, *J* = 3.6 Hz, 1H), 3.63–3.73 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 19.5 (q), 23.9 (t), 24.5 (q), 60.0 (s), 66.8 (d), 68.3 (d), 70.3 (d), 79.3 (s). – MS (70 eV); *m/z* (%): 140 (0.1)[M^+], 123 (0.7), 111 (0.5), 101 (43), 59 (100), 55 (94).

$C_8H_{12}O_2$	Calcd.:	C 68.55 H 8.63
(140.2)	Found:	C 67.89 H 8.53.

1-(3,3-Dimethyloxiranyl)buta-2,3-dien-1-one (**1d**)

From 1.40 g (3.30 mmol) DMP and 421 mg (3.00 mmol) **6d**, 286 mg (69%) of **1d** were obtained according to the general procedure (b). R_f (H/EA, 3:1) = 0.33. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3066, 2988, 2929, 1957, 1931, 1689, 1402, 1379, 1189, 1119, 1039, 929, 863, 817. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.28 (s, 3H), 1.44 (s, 3H), 3.76 (s, 1H), 5.27–5.43 (m, 2H), 5.99 (t, *J* = 6.5 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 18.0 (q), 24.1 (q), 61.1 (s), 64.0 (d), 79.7 (t), 94.9 (d), 193.2 (s), 216.9 (s). – MS (70 eV); *m/z* (%): 138 (0.8)[M^+], 123 (11), 67 (100), 43 (70), 39 (90).

$C_8H_{10}O_2$	Calcd.:	C 69.55 H 7.30
(138.2)	Found:	C 69.56 H 7.49.

Reaction of **1d** *with* $PdCl_2(MeCN)_2$

From 276 mg (2.00 mmol) **1d** and 2.6 mg (0.5 mol-%) $PdCl_2(MeCN)_2$ according to the general procedure (d), 214 mg (78%) 1-(3,3-dimethyloxiranyl)-3-[5-(3,3-dimethyloxi-ranyl)furan-3-yl]but-2-en-1-one (**3d**) were obtained. R_f (H/EA, 6:1) = 0.25. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 2970, 2929, 1769, 1679, 1591, 1453, 1380, 1249, 1142, 1110, 1037, 922, 809, 757. – ^{1}H NMR (CD_3CN, 250 MHz): δ/ppm = 1.19 (s, 3H), 1.30 (s, 3H), 1.39 (2 s, 3H each), 2.40 (d, *J* = 1.2 Hz, 3H), 3.51 (s, 1H), 3.74 (s, 1H), 6.61 (br s, 1H), 6.69 (br s, 1H), 7.85 (br s, 1H). – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.23 (s, 3H), 1.27 (s, 3H), 1.37 (s, 3H), 1.39 (s, 3H), 2.41 (d, *J* = 1.2 Hz, 3H), 3.33 (d, *J* = 3.2 Hz, 1H), 3.65 (s, 1H), 6.45 (br s, 1H), 6.56 (br s, 1H), 7.63 (br s, 1H). – ^{13}C NMR (CD_3CN, 62.9 MHz): δ/ppm = 16.8 (q), 18.0 (q), 18.4 (q), 23.7 (q), 24.3 (q), 58.3 (d), 61.2 (s), 61.7 (s), 66.8 (d), 106.2 (d), 119.4 (d), 129.6 (s), 144.4 (d), 146.3 (s), 153.4 (s), 196.0 (s). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 17.2 (q), 18.5 (q), 18.6 (q), 24.0 (q), 24.8 (q), 58.2 (d), 61.0 (s), 61.4 (s), 66.4 (d), 105.7 (d), 117.8 (d), 129.1 (s), 143.0 (d), 147.0 (s), 152.7 (s), 196.0 (s). – MS (70 eV); *m/z* (%): 276 (76)[M^+], 205 (62), 147 (100), 119 (52). – $C_{16}H_{20}O_4$: calcd. 276.13616, found 276.13604 (MS).

$C_{16}H_{20}O_4$	Calcd.:	C 69.55 H 7.30
(276.3)	Found:	C 69.78 H 7.29.

1-(3-Methyoxyphenyl)but-3-yn-1-ol (**6e**)

From 13.4 ml (22.0 mmol) of a solution of **5** in diethyl ether and 3.00 g (22.0 mmol) of 3-methoxybenzaldehyde, 3.84 g (99%) **6e** were obtained according to the general procedure (a). Column with H/EA (5:1). – R_f (H/EA, 2:1) = 0.33. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3420, 3289, 1602, 1587, 1489, 1262, 1154, 1042, 787, 699. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.08 (t, *J* = 2.7 Hz, 1H), 2.55 (s, 1H), 2.63 (dd, *J* = 2.6 Hz, 2H), 3.81 (s, 3H), 4.83 (t, *J* = 6.3 Hz, 1H), 6.94–6.96 (m, 3H), 7.23–7.31 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 29.2 (t), 55.1 (q), 70.8 (d), 72.1 (d), 80.6 (s), 111.2 (d), 113.3 (d), 117.9 (d), 129.3 (d), 144.1 (s), 159.6 (s).

$C_{11}H_{12}O_2$	Calcd.:	C 74.98 H 6.86
(176.2)	Found:	C 74.35 H 6.84.

1-(3-Methoxyphenyl)buta-2,3-dien-1-one (**1e**)

From 2.63 g (6.20 mmol) DMP and 1.00 g (5.67 mmol) **6e**, 660 mg (67%) of **1e** were obtained according to the general procedure (b). Side products were acetic acid 3-(3-methoxyphenyl)-1-methyl-3-oxopropenyl ester (**8e**, 70.3 mg, 300 µmol, 5%) and 1-(3-methoxyphenyl)but-2-yn-1-ol (**9e**, 119 mg, 680 µmol, 12%).

a) **1e**: Column with H/EA (10 + 0.7) + 30% DCM. – R_f (H/EA, 2:1) = 0.39. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 1959 (C=C=C), 1932 (C=C=C), 1651, 1487, 1581, 1487, 1429, 1347, 1260, 1037, 755. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 3.75 (s, 3H), 5.16 (d, *J* = 4.4 Hz, 2H), 6.34 (t, *J* = 6.5 Hz, 1H), 6.98–7.03 (m, 1H), 7.19–7.42 (m, 3H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 55.2 (q), 79.0 (t), 93.1 (d), 112.9 (d), 119.1 (d), 121.1 (d), 129.2 (d), 138.6 (s), 159.5 (s), 190.4 (s), 216.8 (s).

$C_{11}H_{10}O_2$	Calcd.:	C 75.84 H 5.79
(174.2)	Found:	C 75.56 H 5.83.

b) **8e**: Column with H/EA (10 + 0.7) + 30% DCM. – R_f (H/EA, 2:1) = 0.39. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 1762, 1672, 1594, 1488, 1267, 1204, 1138. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.13 (s, 3H), 2.32 (s, 3H), 3.78 (s, 3H), 6.68 (s, 1H), 6.99–7.02 (m, 1H), 7.19–7.39 (m, 3H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 18.8 (q), 21.1 (q), 55.3 (q), 112.2 (d), 113.5 (d), 119.3 (d), 120.5 (d), 129.4 (d), 139.9 (s), 159.7 (s), 163.5 (s), 168.0 (s), 189.9 (s). – MS (70 eV); *m/z* (%): 234

(18)[M$^+$], 192 (100), 177 (42), 174 (33), 161 (18). – $C_{13}H_{14}O_4$: calcd. 234.08921, found 234.08916 (MS).

c) **9e**: Column with H/EA (10:1). – R_f (H/EA, 2:1) = 0.37. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2230 (C≡C), 1644, 1596, 1485, 1432, 1275, 1225, 1042, 811, 739. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.15 (s, 3H), 3.85 (s, 3H), 7.11–7.16 (m, 1H), 7.38 (dd, J = 7.8 Hz, 1H), 7.61–7.62 (m, 1H), 7.74–7.78 (dm, J = 7.7 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 4.2 (q), 55.3 (q), 78.9 (s), 92.2 (s), 112.7 (d), 120.5 (d), 122.7 (d), 129.4 (d), 138.0 (s), 159.5 (s), 177.8 (s).

$C_{11}H_{10}O_2$	Calcd.:	C 75.84 H 5.79
(174.2)	Found:	C 76.02 H 5.86.

Reaction of **1e** *with* $PdCl_2(MeCN)_2$

From 131 mg (750 µmol) **1e** and 1.2 mg (0.6 mol-%) $PdCl_2(MeCN)_2$ according to the general procedure (d), 10.0 mg (8%) 2-(3-methoxyphenyl)furan (**2e**) and 60.0 mg (46%) 1-(3-methoxyphenyl)-3-[5-(3-methoxyphenyl)furan-3-yl]but-2-en-1-one (**3e**) were obtained.

a) **2e**: Column with H/EA (100:1). – R_f (H/EA, 3:1) = 0.55. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2835, 1606, 1573, 1408, 1290, 1226, 1155, 1038, 778. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 3.86 (s, 3H), 6.48 (dd, J = 1.8 Hz, 1H), 6.68 (d, J = 4.7 Hz, 1H), 6.81–6.87 (m, 1H), 7.24–7.34 (m, 3H), 7.47–7.48 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 55.1 (q), 105.1 (d), 109.0 (d), 111.5 (d), 113.0 (d), 116.3 (d), 129.6 (d), 132.0 (s), 141.9 (d), 153.7 (s), 159.8 (s).

$C_{11}H_{10}O_2$	Calcd.:	C 75.84 H 5.79
(174.2)	Found:	C 75.66 H 6.01.

b) **3e**: Column with H/EA (10:1). – R_f (H/EA, 8:1) = 0.04. – *m.p.* 70–71°C. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2958, 2835, 1651, 1574, 1532, 1488, 1434, 1286, 784. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.53 (s, 3H), 3.86 (s, 3H), 3.89 (s, 3H), 6.86–6.91 (m, 2H), 7.08–7.18 (m, 2H), 7.24–7.41 (m, 4H), 7.52–7.59 (m, 2H), 7.74 (s, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 17.3 (q), 55.1 (q), 55.3 (q), 102.4 (d), 109.3 (d), 112.5 (d), 113.7 (d), 116.5 (d), 118.6 (d), 118.9 (d), 120.5 (d), 129.3 (d), 129.7 (d), 130.5 (s), 131.2 (s), 140.9 (s), 141.9 (d), 145.9 (s), 155.1 (s), 159.7 (s), 159.8 (s), 191.1 (s).

$C_{22}H_{20}O_4$	Calcd.:	C 75.84 H 5.79
(348.4)	Found:	C 75.77 H 5.92.

1-Benzo[1,3]dioxol-5-ylbut-3-yn-1-ol (**6f**)

From 20.3 ml (33.3 mmol) of a solution of **5** in diethyl ether and 5.00 g (33.3 mmol) of **4f**, 4.50 g (71%) of **6f** were obtained according to the general procedure (a). **6f** was accompanied by 623 mg (11%) of 1,5-bis(benzo[1,3]dioxol-5-yl)pent-2-yne-1,5-diol, probably the product from an *in situ* deprotonation of the magnesium salt of **6f** by **5** and a subsequent addition of this nucleophile to a second molecule of **4f**.

a) **6f**: Column with H/EA (5:1). – R_f (H/EA, 2:1) = 0.48. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3535, 3415, 3292, 2898, 2120, 1503, 1488, 1444, 1246, 1096, 1039, 932, 865, 813. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.07 (t, J = 2.6 Hz, 1H), 2.53 (br s, 1H), 2.57–2.61 (m, 2H), 4.74–4.79 (m, 1H), 5.94 (s, 2H), 6.75–6.89 (m, 3H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 29.3 (t), 70.9 (d), 72.1 (d), 80.6 (s), 100.9 (t), 106.2 (d), 108.0 (d), 119.1 (d), 136.4 (s), 147.1 (s), 147.6 (s). – MS (70 eV): *m/z* (%): 190 (19)[M$^+$], 151 (100), 93 (45), 65 (24).

$C_{11}H_{10}O_3$	Calcd.:	C 69.46 H 5.30
(190.2)	Found:	C 69.42 H 5.45.

b) 1,5-Bis(benzo[1,3]dioxol-5-yl)pent-2-yne-1,5-diol: Column with H/EA (5:1). – R_f (H/EA, 2:1) = 0.20. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3395, 2898, 1503, 1488, 1444, 1247, 1040, 932, 866, 811, 737. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.60–2.63 (m, 2H), 3.25–3.38 (br s, 1H), 3.51–3.62 (br t, 1H), 4.70–4.76 (br t, 1H), 5.28 (br s, 1H), 5.91 (s, 2H), 5.92 (s, 2H), 6.70–6.96 (m, 6H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 29.5 (t), [64.1 (d), 72.1 (d)], 82.5 (s), 83.3 (s), 100.9 (t), 101.0 (t), 106.2 (d), 107.3 (d), 107.8 (d), 107.9 (d), 119.2 (d), 120.2 (d), 134.9 (s), 136.6 (s), 147.0 (s), 147.3 (s), 147.6 (2s). – MS (70 eV): *m/z* (%): 340 (11)[M$^+$], 188 (24), 172 (100), 151 (85), 93 (42).

$C_{19}H_{16}O_6$	Calcd.:	C 67.06 H 4.74
(340.3)	Found:	C 66.80 H 4.97.

1-Benzo[1,3]dioxol-5-ylbuta-2,3-diene-1-one (**1f**)

From 4.67 g (11.0 mmol) DMP and 1.90 g (10.0 mmol) **6f**, 1.13 g (60%) of **1f** were obtained according to the general procedure (b). The side-product was acetic acid 3-benzo-[1,3]dioxol-5-yl-1-methyl-3-oxopropenyl ester (**8f**, 521 mg, 21%).

a) **1f**: Column with H/EA/DCM (20:1:4). – R_f (H/EA, 3:1) = 0.30. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2968, 1934 (C=C=C), 1638, 1600, 1500, 1444, 1334, 1258, 1036, 936, 878, 759. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 5.25 (d, J = 6.5 Hz, 2H), 6.05 (s, 2H), 6.42 (t, J = 6.5 Hz, 1H), 6.85 (d, J = 8.1 Hz, 1H), 7.41 (d, J = 1.8 Hz, 1H), 7.54 (dd, J = 8.1 Hz, 1.8 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 79.1 (t), 92.8 (d), 101.8 (t), 107.8 (d), 108.6 (d), 124.9 (d), 132.1 (s), 148.1 (s), 151.8 (s), 188.8 (s), 216.5 (s).

$C_{11}H_8O_3$	Calcd.:	C 70.21 H 4.29
(188.2)	Found:	C 70.31 H 4.32.

b) **8f**: Column with H/EA/DCM (20:1:4). – R_f (H/EA, 3:1) = 0.25. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2909, 1759, 1668, 1622, 1489, 1444, 1255, 1206, 1161, 1105, 1037, 931. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.21 (s, 3H), 2.36 (d, J = 0.9 Hz, 3H), 6.03 (s, 2H), 6.68 (q, J = 0.9 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 7.41 (d, J = 1.7 Hz, 1H), 7.50 (dd, J = 8.2 Hz, 1.7 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 18.7 (q), 21.1 (q), 101.7 (t), 107.7 (d), 107.8 (d), 113.5 (d), 124.3 (d), 133.3 (s), 148.1 (s), 151.5 (s), 162.8 (s), 168.1 (s), 188.3 (s).

$C_{13}H_{12}O_5$	Calcd.:	C 62.90 H 4.87
(248.2)	Found:	C 62.71 H 4.92.

Reaction of **1f** *with* $PdCl_2(MeCN)_2$

From 753 mg (4.00 mmol) **1f** and 6.2 mg (0.6 mol-%) $PdCl_2(MeCN)_2$ according to the general procedure (d), 8.3 mg (1%) 5-furan-2-ylbenzo[1,3]dioxole (**2f**) and 98.9 mg (13%) 1-benzo[1,3]dioxol-5-yl-3-(5-benzo[1,3]dioxol-5-yl-furan-3-yl)but-2-en-1-one (**3f**) were obtained.

a) **2f**: Column with H/EA (12:1). – R_f (H/EA, 3:1) = 0.52. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2892, 2360, 1507, 1479, 1451, 1337, 1257, 1227, 1161, 1041, 1009, 922, 811, 731. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 5.98 (s, 2H), 6.44 (dd, J = 1.8 Hz, 1H), 6.51 (dd, J = 0.7 Hz, 1H), 6.83 (t, J = 4.0 Hz, 1H), 7.15–7.21 (m, 2H), 7.42–7.43 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 100.9 (t), 103.7 (d), 104.5 (d),

108.4 (d), 111.4 (d), 117.5 (d), 125.3 (s), 141.3 (d), 146.8 (s), 147.8 (s), 153.7 (s).
$C_{11}H_8O_3$ Calcd.: C 70.21 H 4.29
(188.2) Found: C 70.01 H 4.47.

b) **3f**: Column with H/EA (5:1). – R_f (H/EA, 5:1) = 0.16. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2900, 1648, 1583, 1483, 1444, 1357, 1251, 1110, 1038, 930, 806. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.48 (d, J = 1.0 Hz, 3H), 6.03 (s, 2H), 6.06 (s, 2H), 6.77 (s, 1H), 6.87 (dd, J = 5.0 Hz, 2H), 7.07 (s, 1H), 7.18 (d, J = 1.7 Hz, 1H), 7.22 (dd, J = 1.7 Hz, 1H), 7.49 (d, J = 1.7 Hz, 1H), 7.60 (dd, J = 1.7 Hz, 1H), 7.70 (s, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 17.3 (q), 101.0 (d), 101.1 (t), 101.6 (t), 104.6 (d), 107.7 (d), 108.0 (d), 108.5 (d), 117.9 (d), 118.9 (d), 124.1 (d), 124.5 (s), 130.5 (s), 134.4 (s), 141.2 (d), 145.2 (s), 147.6 (s), 148.1 (s), 151.3 (s), 155.2 (s), 159.7 (s), 189.8 (s).
$C_{22}H_{16}O_6$ Calcd.: C 70.21 H 4.29
(376.4) Found: C 70.70 H 4.35.

N-[4-(1-Hydroxybut-3-ynyl)phenyl]acetamide (**6g**)

From 10.0 ml (16.4 mmol) of a solution of **5** in diethyl ether and 2.68 g (16.4 mmol) of **4g**, 1.93 g (58%) of **6g** were obtained according to the general procedure (a). R_f (H/EA, 1:1.5) = 0.21. *m.p.* 128–131°C. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3300, 3123, 3060, 2922, 2851, 1632, 1598, 1539, 1515, 1423, 1371, 1319, 1043, 1019, 976, 951, 805, 845. – ^{1}H NMR ([D$_6$]DMSO, 250 MHz): δ/ppm = 2.04 (s, 3H), 2.47–2.52 (m, 2H), 2.67 (t, J = 2.6 Hz, 1H), 4.64 (t, J = 6.4 Hz, 1H), 5.42 (v br s, 1H), 7.29 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.5 Hz, 2H), 9.88 (s, 1H). – ^{13}C NMR ([D$_6$]DMSO, 62.9 MHz): δ/ppm = 24.1 (q), 29.1 (t), 70.9 (d), 72.5 (d), 82.1 (s), 118.7 (d, 2 C), 126.5 (d, 2 C), 138.4 (s), 139.1 (s), 168.3 (s). – MS (70 eV); *m/z* (%): 203 (9)[M$^+$], 164 (100), 122 (52), 94 (17).
$C_{12}H_{13}NO_2$ Calcd.: C 70.92 H 6.45 N 6.89
(203.2) Found: C 70.74 H 6.53 N 6.74.

Crystal Structure Determination of 6g

X-ray crystal data for $C_{12}H_{13}NO_2$: monoclinic, P21/n, a = 7.494 (1) Å, b = 19.801 (4) Å, c = 8.1301 (8) Å, b = 114.67(1)°, V = 1096.3 (3) Å^3, Z = 4, Dcalc = 1.231 g cm^{-3}, MoKα radiation (l = 0.71073 Å), m = 0.08 mm^{-1}, T = –140 °C. 17481 reflections were collected on a SIEMENS CCD three-circle diffractometer for 2° < 2q < 61°. The data were corrected for absorption effects using the program SADABS [24]. The structure was solved by direct methods and refined by full-matrix least-square against F to R(F) = 0.062 (wR(F) = 0.057) and S = 1.70 for 3065 (Rint = 0.024) unique reflections [25].

N-(4-Buta-2,3-dienoylphenyl)acetamide (**1g**)

From 1.40 g (3.30 mmol) DMP and 610 mg (3.00 mmol) **6g**, 482 mg (80%) of **1g** were obtained according to the general procedure (b). R_f (H/EA, 1:1) = 0.36. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3340, 3029, 1970, 1936 (C=C=C), 1697, 1631, 1594, 1530, 1422, 1407, 1357, 1245, 1228, 1180, 984, 850, 825. – ^{1}H NMR ([D$_6$]acetone, 250 MHz): δ/ppm = 2.11 (s, 3H), 5.32 (d, J = 6.6 Hz, 2H), 6.56 (t, J = 6.6, 1H), 7.75 (d, J = 8.8 Hz, 2H), 7.93 (d, J = 8.8 Hz, 2H), 9.46 (br s, 1H). – ^{13}C NMR ([D$_6$]acetone, 62.9 MHz): δ/ppm = 24.7, 24.8 (2 q), 79.5 (t), 93.3 (d), 119.3 (d), 119.4 (d), 131.0 (d, 2 C), 133.5 (s), 145.0, 145.1 (2 s), 169.7, 169.8 (2 s), 189.3 (s), 217.7 (s). – MS (70 eV); *m/z* (%): 201 (30)[M$^+$], 162 (100), 120 (77), 92 (14).
$C_{12}H_{11}NO_2$ Calcd.: C 71.63 H 5.51 N 6.96
(201.2) Found: C 71.61 H 5.59 N 6.87.

Reaction of **1g** *with* $PdCl_2(MeCN)_2$

From 302 mg (1.50 mmol) **1g** and 1.9 mg (0.5 mol-%) $PdCl_2(MeCN)_2$ according to the general procedure (d), 9.1 mg (3%) *N*-(4-furan-2-ylphenyl)acetamide (**2g**) and 262 mg (87%) *N*-(4-{4-[3-(4-acetylaminophenyl)-1-methyl-3-oxopropenyl]furan-2-yl}phenyl)acetamide (**3g**) were obtained.

a) **2g**: R_f (H/EA, 1:1) = 0.53. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3295, 2923, 2852, 1667, 1599, 1534, 1514, 1482, 1413, 1372, 1319, 1262, 1232, 1177, 1009, 834. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.19 (s, 3H), 6.46 (dd, J = 3.3 Hz, 1.8 Hz, 1H), 6.59 (d, J = 3.3 Hz, 1H), 7.20 (br s, 1H), 7.45 (d, J = 1.8 Hz, 1H), 7.53 (d, J = 8.7 Hz, 2H), 7.63 (d, J = 8.7 Hz, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 24.1 (q), 104.3 (d), 111.5 (d), 119.7 (d), 123.0 (s), 124.4 (d, 2 C), 129.6 (d), 136.9 (s), 141.7 (d), 168.0 (s). (1 s hidden) – MS (70 eV); *m/z* (%): 201 (96)[M$^+$], 159 (100), 130 (45).
$C_{12}H_{11}NO_2$ Calcd.: C 71.63 H 5.51 N 6.96
(201.2) Found: C 71.83 H 5.49 N 7.02.

b) **3g**: R_f (H/EA, 6:1) = 0.26. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3292, 1668, 1644, 1599, 1526, 1410, 1366, 1318, 1260, 1220, 1178, 1050, 1012, 914, 849, 827. – ^{1}H NMR ([D$_6$]DMSO, 250 MHz): δ/ppm = 2.07 (s, 3H), 2.10 (s, 3H), 2.46 (s, 3H), 7.41 (br s, 1H), 7.51 (br s, 1H), 7.69 (br s, 4H), 7.76 (d, J = 8.7 Hz, 2H), 8.02 (d, J = 8.7 Hz, 2H), 8.17 (br s, 1H), 10.05 (br s, 1H), 10.26 (br s, 1H). – ^{13}C NMR ([D$_6$]DMSO, 62.9 MHz): δ/ppm = 16.9 (q), 24.0 (q), 24.1 (q), 102.4 (d), 118.2 (2 d), 118.4 (d), 119.2 (2 d), 124.2 (2 d), 124.7 (s), 129.4 (2 d), 130.5 (s), 133.6 (s), 139.2 (s), 143.1 (d), 143.3 (s), 145.1 (s), 154.4 (s), 168.4 (s), 168.4 (s), 1891 (s). – MS (70 eV); *m/z* (%): 402 (59)[M$^+$], 177 (27), 162 (100), 120 (68). – $C_{24}H_{22}N_2O_4$: calcd. 402.15796, found 402.15776 (MS).
$C_{24}H_{22}N_2O_4$ Calcd.: C 71.63 H 5.51 N 6.96
(402.5) Found: C 71.71 H 5.63 N 6.94.

1-(2-Nitrophenyl)but-3-yn-1-ol (**6h**)

From 10.0 ml (16.4 mmol) of a solution of **5** in diethyl ether and 2.48 g (16.4 mmol) of **4h**, 1.84 g (59%) of **6h** were obtained according to the general procedure (a). R_f (H/EA, 5:1) = 0.11. – IR (KBr): $\tilde{\nu}$/cm^{-1} = 3287, 3265, 1522, 1346, 1195, 1085, 1058, 858, 821, 793, 743. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.10 (t, J = 2.6 Hz, 1H), 2.61–2.72 (m, 1H), 2.83–2.95 (m, 2H), 5.44–5.48 (m, 1H), 7.45 (td, J = 7.8 Hz, 1.5 Hz, 1H), 7.66 (td, J = 7.7 Hz, 1.3 Hz, 1H), 7.88 (dd, J = 8.0 Hz, 1.3 Hz, 1H), 7.95 (dd, J = 8.0 Hz, 1.3 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 28.3 (t), 67.3 (d), 71.6 (d), 79.6 (s), 124.3 (d), 128.1 (d), 128.5 (d), 133.4 (d), 137.6 (s), 147.6 (s). – MS (70 eV); *m/z* (%): 191 (0.1)[M$^+$], 190 (0.1), 172 (0.2), 152 (100), 104 (65), 77 (63).
$C_{10}H_9NO_3$ Calcd.: C 62.82 H 4.75 N 7.33
(191.2) Found: C 62.98 H 4.85 N 7.20.

1-(2-Nitrophenyl)buta-2,3-dien-1-one (**1h**)

From 1.40 g (3.30 mmol) DMP and 574 mg (3.00 mmol) **6h** 417 mg (73%) of **1h** and 130 mg (23%) of 1-(2-nitro-

phenyl)but-2-yn-1-one (**9h**) were obtained according to the general procedure (b).

a) **1h**: R_f (H/EA, 4:1) = 0.15. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3070, 2992, 1958, 1931, 1672, 1529, 1349, 1279, 1250, 856, 789, 745, 702. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 5.03 (d, J = 6.4 Hz, 2H), 6.14 (t, J = 6.4 Hz, 1H), 7.40–7.44 (m, 1H), 7.55–7.62 (m, 1H), 7.66 (m, 1H), 8.05–8.09 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 80.2 (t), 97.0 (d), 123.8 (d), 128.4 (d), 130.4 (d), 133.7 (d), 135.5 (s), 146.6 (s), 192.2 (s), 217.6 (s). – MS (70 eV); *m/z* (%): 189 (0.1)[M$^+$], 172 (0.5), 161 (2), 150 (100), 104 (27), 76 (90).

$C_{10}H_7NO_3$	Calcd.:	C 63.49	H 3.73	N 7.40
(189.2)	Found:	C 63.74	H 3.78	N 7.35.

b) **9h**: Column with H/EA (10:3). – R_f (H/EA, 3:1) = 0.21. *m.p.* 60–61 °C. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2221 (C≡C), 1656, 1534, 1349, 1265, 908. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.10 (s, 3H), 7.61–7.89 (m, 4H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 4.3 (q), 78.9 (s), 94.7 (s), 123.9 (d), 129.8 (d), 132.1 (d), 132.8 (d), 133.9 (s), 175.8 (s). (one s hidden)

$C_{10}H_7NO_3$	Calcd.:	C 63.49	H 3.73	N 7.40
(189.2)	Found:	C 63.21	H 3.87	N 7.29.

Reaction of **1h** *with* $PdCl_2(MeCN)_2$

From 284 mg (1.50 mmol) **1** and 1.9 mg (0.5 mol-%) $PdCl_2(MeCN)_2$ according to the general procedure (d), 8.9 mg (3%) 2-(2-nitrophenyl)furan (**2h**) and 255 mg (90%) 1-(2-nitrophenyl)-3-[5-(2-nitrophenyl)furan-3-yl]but-2-en-1-one (**3h**) were obtained.

a) **2h**: R_f (H/EA, 3:1) = 0.40. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 2922, 1530, 1501, 1363, 1158, 1010, 908, 850, 778, 747. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 6.50 (dd, J = 3.5 Hz, 1.9 Hz, 1H), 6.67 (d, J = 3.5 Hz, 1H), 7.40 (td, J = 7.7 Hz, 1.5 Hz, 1H), 7.51 (d, J = 1.9 Hz, 1H), 7.57 (td, J = 7.6 Hz, 1.3 Hz, 1H), 7.66–7.73 (m, 2H). – MS (70 eV); *m/z* (%): 189 (56)[M$^+$], 172 (14), 161 (21), 144 (37), 116 (78), 89 (74), 77 (100).

$C_{10}H_7NO_3$	Calcd.:	C 63.49	H 3.73	N 7.40
(189.2)	Found:	C 62.85	H 3.66	N 7.35.

b) **3h**: Product precipitates. *m.p.* 128–131 °C. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 1655, 1583, 1525, 1360, 1223, 1146, 918, 850, 781. – ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm = 2.55 (d, J = 1.2 Hz, 3H), 6.63 (q, J = 1.2 Hz, 1H), 6.79 (d, J = 0.9 Hz, 1H), 7.45–7.48 (m, 1H), 7.51 (dd, J = 7.6 Hz, 1.4 Hz, 1H), 7.57–7.66 (m, 2H), 7.69 (dd, J = 7.9 Hz, 1.4 Hz, 1H), 7.72 (td, J = 7.5 Hz, 1.2 Hz, 1H), 7.74 (dd, J = 8.1 Hz, 1.2 Hz, 1H), 7.80 (d, J = 0.8 Hz, 1H), 8.08 (dd, J = 8.2 Hz, 1.1 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 17.4 (q), 106.8 (d), 120.5 (d), 123.4 (s), 124.0 (d), 124.2 (d), 127.9 (d), 129.0 (d), 129.2 (d), 130.0 (s), 130.2 (d), 132.1 (d), 133.8 (d), 138.6 (s), 143.9 (d), 146.3 (s), 146.8 (s), 147.5 (s), 150.0 (s), 191.3 (s). – MS (70 eV); *m/z* (%): 378 (0.9)[M$^+$], 348 (0.3), 333 (2), 244 (100). – $C_{20}H_{14}N_2O_6$: calcd. 378.085119, found 378.08499 (MS).

$C_{20}H_{14}N_2O_6$	Calcd.:	C 63.49	H 3.73	N 7.40
(378.3)	Found:	C 63.65	H 3.71	N 7.37.

Crystal Structure Determination of 3h

X-ray crystal data for $C_{20}H_{14}N_2O_6$: monoclinic, C2/c, a = 32.212 (4) Å, b = 7.6355 (7) Å, c = 24.866 (2) Å, β = 122.344 (9)°, V = 5167 (1) Å^3, Z = 12 (two independent molecules), D_{calc} = 1.459 g cm^{-3}, $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), μ = 0.10 mm^{-1}, T = –139 °C. 39397 reflections were collected on a SIEMENS CCD three-circle diffractometer for 2° < 2θ < 60°. The data were corrected for absorption effects using the program SADABS [24]. The structure was solved by direct methods and refined by full-matrix least-square against F to R(F) = 0.094 (wR(F) = 0.084) and S = 1.79 for 6554 (R_{int} = 0.039) unique reflections [25].

1-(4-Nitrophenyl)but-3-yn-1-ol (**6i**)

From 12.4 ml (19.9 mmol) of a solution of **5** in diethyl ether and 3.00 g (19.9 mmol) of **4i** in DCM, 914 mg (24%) of **6i** were obtained according to the general procedure (a). Column with H/EA (5:1). – R_f (H/EA, 3:1) = 0.20. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.10 (t, J = 2.6 Hz, 1H), 2.57–2.72 (m, 3H), 4.99 (t, J = 6.2 Hz, 1H), 7.59 (d, J = 4.2 Hz, 2H), 8.22 (d, J = 4.2 Hz, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 29.3 (t), 71.1 (d), 71.8 (s), 79.2 (s), 123.5 (d, 2C), 126.5 (d, 2C), 149.3 (s).

1-(4-Nitrophenyl)buta-2,3-diene-1-one (**1i**)

From 920 mg (2.17 mmol) DMP and 373 mg (1.95 mmol) **6i**, 214 mg (58%) of **1i** and 81.2 mg (22%) 1-(4-nitrophenyl)but-2-yn-1-one (**9i**) were obtained according to the general procedure (b).

a) **1i**: Column with H/EA/DCM (25:1:5). – R_f (H/EA/DCM, 20:1:5) = 0.17. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 5.30 (d, J = 4.4 Hz, 2H), 6.38 (t, J = 6.5 Hz, 1H), 8.01 (d, J = 8.7 Hz, 2H), 8.30 (d, J = 8.7 Hz, 2H).

$C_{10}H_7NO_3$	Calcd.:	C 63.49	H 3.73	N 7.40
(189.2)	Found:	C 63.75	H 3.80	N 7.32.

b) **9i**: Column with H/EA/DCM (25:1:5). – R_f (H/EA/DCM, 20:1:5) = 0.17. *m.p.* 162–165 °C. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3101, 2241, 2202 (C≡C), 1650, 1600, 1521, 1344, 1260, 850. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.21 (s, 3H), 8.31 (d, J = 2.2 Hz, 4H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 4.3 (q), 78.6 (s), 94.8 (s), 123.5 (d, 2C), 130.3 (d, 2C), 140.8 (s), 150.7 (s), 175.8 (s).

$C_{10}H_7NO_3$	Calcd.:	C 63.49	H 3.73	N 7.40
(189.2)	Found:	C 63.22	H 3.85	N 7.23.

Reaction of **1i** *with* $PdCl_2(MeCN)_2$

From 144 mg (760 µmol) **1** and 4.0 mg (2.0 mol-%) $PdCl_2(MeCN)_2$ according to the general procedure (d), 5.8 mg (4%) 2-(4-nitrophenyl)furan (**2i**) and 118 mg (82%) 1-(4-nitrophenyl)-3-[5-(4-nitrophenyl)furan-3-yl]but-2-en-1-one (**3i**) were obtained.

a) **2i**: Column with H/EA/DCM (20:2:1). – R_f (H/EA/DCM, 5:1:2) = 0.58. *m.p.* 131–133 °C. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 1600, 1509, 1336, 1018, 855, 753. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 6.56 (dd, J = 0.9 Hz, 1H), 6.88 (d, J = 3.4 Hz, 1H), 7.58 (d, J = 0.7 Hz, 1H), 7.79 (d, J = 6.6 Hz, 2H), 8.25 (d, J = 6.6 Hz, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 108.8 (d), 112.3 (d), 123.8 (d, 2 C), 124.2 (d, 2C), 136.3 (s), 144.0 (d), 146.0 (s), 151.6 (s).

$C_{10}H_7NO_3$	Calcd.:	C 63.49	H 3.73	N 7.40
(189.2)	Found:	C 63.21	H 3.75	N 7.16.

b) **3i**: product precipitates, low solubility. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.60 (d, J = 1.1 Hz, 3H), 7.15 (s, 1H), 7.17 (s, 1H), 7.86 (d, J = 9.0 Hz, 2H), 7.92 (s, 1H), 8.12 (d,

J = 8.8 Hz, 2H), 8.30 (d, *J* = 9.0 Hz, 2H), 8.35 (d, *J* = 8.9 Hz, 2H).

$C_{20}H_{14}N_2O_6$	Calcd.:	C 63.49	H 3.73	N 7.40
(378.3)	Found:	C 63.72	H 3.76	N 7.36.

4-Hydroxybut-3-ynyl)benzonitrile (**6j**)

From 10.0 ml (16.4 mmol) of a solution of **5** in diethyl ether and 2.15 g (16.4 mmol) of **4j** in DCM, 1.49 g (53%) of **6j** as colorless crystals were obtained according to the general procedure (a). Column with H/EA (4:1). – R_f (H/EA, 4:1) = 0.13. *m.p.* 114 °C. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3055, 2908, 2229 (C≡C), 1608, 1504, 1402, 1255, 1207, 1072, 1016, 869, 850, 815. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.09 (t, *J* = 2.6 Hz, 1 H), 2.61–2.66 (m, 3 H), 4.90–4.96 (m, 1H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 29.3 (t), 71.3 (d), 71.7 (d), 79.4 (s), 111.5 (s), 118.5 (s), 126.4 (d, 2C), 132.1 (d, 2C), 147.5 (s). – MS (70 eV): *m/z* (%): 171 (2)[M$^+$], 132 (100), 104 (47), 77 (20).

$C_{11}H_9NO$	Calcd.:	C 77.17	H 5.30	N 8.18
(171.2)	Found:	C 77.45	H 5.32	N 8.23.

4-Buta-2,3-dienoylbenzonitrile (**1j**)

From 1.40 g (3.30 mmol) DMP and 514 mg (3.00 mmol) **6j**, 364 mg (72%) of **1j** and 41.2 mg (6%) of acetic acid 3-(4-cyanophenyl)-1-methyl-3-oxopropenyl ester (**8j**) were obtained according to the general procedure (b).

a) **1j**: Column with H/EA (4:1). – R_f (H/EA, 4:1) = 0.21. *m.p.* 64–67 °C. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3061, 2984, 2230, 1956, 1921, 1658, 1419, 1358, 1338, 1309, 1288, 1217, 991, 867, 852, 729. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 5.27 (d, *J* = 6.5 Hz, 2H), 6.35 (t, *J* = 6.5 Hz, 1H), 7.70–7.74, 7.90–7.94 (2 m, AA'BB'-system, 2H each). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 79.8 (t), 93.4 (d), 115.7 (s), 117.8 (s), 128.9 (d, 2 C), 132.0 (d, 2 C), 140.5 (s), 189.9 (s), 217.6 (s). – MS (70 eV): *m/z* (%): 169 (11)[M$^+$], 130 (100), 102 (49). – $C_{11}H_7NO$: calcd. 169.052764, found 169.05282 (MS).

b) **8j**: Column with H/EA (10:1). – R_f (H/EA, 10:1) = 0.08. *m.p.* 101–104 °C. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2234, 1761, 1674, 1616, 1414, 1372, 1294, 1248, 1194, 1146, 1018, 899, 846, 804. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.24 (s, 3H), 2.42 (d, *J* = 0.9 Hz, 3H), 6.78 (q, *J* = 0.9 Hz, 1H), 7.72–7.81 and 7.88–8.03 (AA'BB', 4H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 19.1 (q), 21.2 (q), 112.5 (d), 115.9 (s), 117.8 (s), 128.3 (d, 2C), 132.6 (d, 2C), 141.6 (s), 165.5 (s), 167.9 (s), 188.6 (s). – MS (70 eV); *m/z* (%): 229 (5)[M$^+$], 187 (100), 172 (54), 130 (21), 102 (24).

Reaction of **1j** *with* $PdCl_2(MeCN)_2$

From 300 mg (1.77 mmol) **1j** and 4.6 mg (18 μmol, 1 mol-%) $PdCl_2(MeCN)_2$ according to the general procedure (d), 232 mg (77%) 4-[4-(1-methyl-3-oxo-3-phenylpropenyl)furan-2-yl]benzonitrile (**3j**) were obtained. Column with H/EA/DCM (10:0.6:10). – R_f (H/EA/DCM, 10:1:10) = 0.21. *m.p.* 252–254 °C. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2228, 1660, 1608, 1585, 1218, 1146, 1059, 820. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.57 (d, *J* = 1.1 Hz, 3H), 7.08 (br s, 1H), 7.13 (br s, 1H), 7.69–7.82 (m, 6H), 7.87 (br s, 1H), 8.03–8.08 (m, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 17.6 (q), 104.9 (d), 111.2 (s), 115.6 (s), 117.9 (s), 118.3 (d), 118.4 (s), 124.2 (d, 2 C), 128.3 (d, 2C), 130.6 (s), 132.3 (d, 2C), 132.6 (d, 2C), 133.5 (s), 142.5 (s), 143.6 (d), 147.7 (s), 153.4 (s). – MS (70 eV); *m/z* (%): 338 (50)[M$^+$], 323 (16), 210 (44), 208 (39), 130 (100), 102 (28). – $C_{22}H_{14}N_2O_2$: calcd. 338.10553, found 338.10591 (MS).

1-Pyridin-4-ylbut-3-yn-1-ol (**6k**)

From 10.0 ml (16.4 mmol) of a solution of **5** in diethyl ether and 1.76 g (16.4 mmol) of **4k** in DCM, 1.13 g (47%) of **6k** were obtained according to the general procedure (a). Column with H/EA (1:4). – R_f (H/EA, 1:4) = 0.15. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3297, 2911, 1605, 1416, 1065, 1004, 823, 732, 640. – ^{1}H NMR ($CDCl_3$, 270 MHz): δ/ppm = 2.00 (t, *J* = 2.6 Hz, 1H), 2.59 (dd, *J* = 6.3 Hz, 2.6 Hz, 2H), 4.82 (t, *J* = 6.3 Hz, 1H), 5.70 (br s, 1H), 7.30 (dd, *J* = 4.6 Hz, 1.6 Hz, 2H), 8.35 (dd, *J* = 4.6 Hz, 1.6 Hz, 2H). – ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ/ppm = 28.9 (t), 70.4 (d), 71.2 (d), 79.9 (s), 121.1 (d, 2 C), 148.9 (d, 2 C), 152.7 (s). – MS (70 eV); *m/z* (%): 147 (7)[M$^+$], 108 (100), 80 (21).

1-(4-Dimethylaminophenyl)but-3-yn-1-ol (**6l**)

From 10.0 ml (16.4 mmol) of a solution of **5** in diethyl ether and 2.45 g (16.4 mmol) of **4l** in DCM, 2.41 g (78%) of **6l** were obtained according to the general procedure (a). Column with H/EA (4:1). – R_f (H/EA, 4:1) = 0.12. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3398, 3290, 2909, 1616, 1524, 1351, 819. – ^{1}H NMR ($CDCl_3$, 270 MHz): δ/ppm = 2.05 (t, *J* = 2.6 Hz, 1H), 2.58–2.63 (m, 2H), 2.93 (s, 7H), 2.93 (s, 6H), 4.73 (t, *J* = 6.5 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 8.8 Hz, 2H). – ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ/ppm = 28.7 (t), 40.4 (d), 70.3 (d), 71.8 (d), 81.2 (s), 112.3 (d, 2C), 126.5 (d, 2C), 130.5 (s), 150.1 (s). – MS (70 eV); *m/z* (%): 189 (15)[M$^+$], 150 (100), 120 (10). – $C_{12}H_{15}NO$: calcd. 189.11536, found 189.11523 (MS).

$C_{12}H_{15}NO$	Calcd.:	C 76.16	H 7.99	N 7.40
(189.3)	Found:	C 76.08	H 8.05	N 7.48.

1-(1-Methyl-1H-pyrrol-2-yl)but-3-yn-1-ol (**6m**)

From 10.0 ml (16.4 mmol) of a solution of **5** in diethyl ether and 1.79 g (16.4 mmol) of **4m** in DCM, 2.25 g (92%) of **6m** were obtained according to the general procedure (a). Column with H/EA (3:1). – R_f (H/EA, 3:1) = 0.25. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3407, 3288, 2943, 2917, 2119, 1491, 1302, 1090, 1052, 1018, 993, 853, 721, 648. – ^{1}H NMR ($CDCl_3$, 270 MHz): δ/ppm = 2.10 (t, *J* = 2.7 Hz, 1H), 2.51 (d, *J* = 6.3 Hz, 1H), 2.77–2.80 (m, 2H), 3.67 (s, 3H), 4.77–4.84 (m, 1H), 6.06–6.09 (m, 1H), 6.16–6.18 (m, 1H), 6.61–6.62 (m, 1H). – ^{13}C NMR ($CDCl_3$, 67.9 MHz): δ/ppm = 26.4 (t), 33.9 (q), 64.6 (d), 71.0 (d), 80.9 (s), 106.3 (d), 106.6 (d), 123.3 (d), 132.7 (s). – MS (70 eV): *m/z* (%): 149 (30)[M$^+$], 110 (100).

$C_9H_{11}NO$	Calcd.:	C 72.46	H 7.43	N 9.39
(149.2)	Found:	C 71.77	H 7.51	N 9.22.

1-Methylsulfanylhex-5-yn-3-ol (**6n**)

From 30.0 ml (49.2 mmol) of a solution of **5** in diethyl ether and 5.00 g (48.0 mmol) of **4n** in DCM, 3.18 g (46%) of **6n** were obtained according to the general procedure (a). Column with H/EA (7:1). – R_f (H/EA, 5:1) = 0.12. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3414, 3290, 2916, 1429, 1274, 1062, 961. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.80–1.90 (m, 2H), 2.02–2.08 (m, 1H), 2.10 (s, 3H), 2.38 (s, 1H), 2.39–2.42 (m, 2H), 2.63 (t, *J* = 7.2, 2H), 3.87–3.96 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 15.3 (q), 27.2 (t), 30.4 (t), 34.8 (t), 68.8 (d), 70.8 (d), 80.3 (s).

$C_7H_{12}OS$ Calcd.: C 58.29 H 8.39
(144.2) Found: C 58.03 H 8.55.

Acetic acid 3-hydroxyhex-5-ynylsulfanylmethyl ester (**11**)

From 1.99 g (4.69 mmol) DMP and 616 mg (4.27 mmol) **6n**, 241 mg (28%) of **11** were obtained according to the general procedure (b). Column with H/EA (3:1). – R_f (H/EA, 2:1) = 0.17. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3450, 3289, 2933, 1742, 1421, 1371, 1217, 1020. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.82–1.91 (m, 2H), 2.08 (m, 4H), 2.30–2.50 (m, 2H), 2.72–2.91 (m, 2H), 3.86–3.96 (m, 1H), 5.16 (s, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 20.9 (q), 27.3 (t), 28.5 (t), 35.8 (t), 66.4 (t), 68.3 (d), 71.0 (d), 80.1 (s), 170.5 (s).
$C_9H_{14}O_3S$ Calcd.: C 53.44 H 6.98
(202.3) Found: C 50.85 H 6.31.

1-(4-Methylsulfanylphenyl)but-3-yn-1-ol (**6o**)

From 20.5 ml (32.8 mmol) of a solution of **5** in diethyl ether and 5.00 g (32.8 mmol) of **4o** in DCM, 4.18 g (66%) of **6o** were obtained according to the general procedure (a). Column with H/EA (5:1). – R_f (H/EA, 3:1) = 0.23. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3406, 3290, 2920, 2366, 1600, 1493, 1425, 1093, 1053, 821. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.06–2.07 (m, 1H), 2.41–2.45 (m, 1H), 2.48 (s, 3H), 2.60–2.67 (m, 2H), 4.80–4.86 (m, 1H), 7.22–7.32 (m, 4H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 15.7 (q), 29.2 (t), 70.9 (s), 71.8 (d), 80.4 (s), 126.1 (d, 2C), 126.5 (d, 2C).
$C_{11}H_{12}OS$ Calcd.: C 68.71 H 6.29
(192.3) Found: C 68.33 H 6.18.

1-(4-Methylsulfanylphenyl)buta-2,3-dien-1-one (**1o**)

From 2.43 g (5.72 mmol) DMP and 959 mg (4.99 mmol) **6n**, 565 mg (60%) of **1o** were obtained according to the general procedure (b). Side-products were acetic acid 3-(4-methylsulfanylphenyl)-1-methyl-3-oxopropenyl ester (**8o**) (124 mg, 10%) and 1-(4-methylsulfanylphenyl)but-2-yn-1-one (**9o**, 47.5 mg, 5%).

a) **1o**: Column with H/EA (10:1). – R_f (H/EA, 3:1) = 0.38. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2921, 1960 (C=C=C), 1933, 1646, 1589, 1554, 1417, 1346, 1284, 1219, 1186, 1093, 980, 838, 757. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.51 (s, 3H), 5.25 (d, J = 6.5 Hz, 2H), 6.42 (t, J = 6.5 Hz, 1H), 7.21–7.28 (m, 2H), 7.81–7.85 (m, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 14.6 (q), 79.1 (t), 92.8 (d), 124.7 (d, 2C), 129.0 (d, 2C), 133.5 (s), 145.6 (s), 189.5 (s), 216.6 (s).
$C_{11}H_{10}OS$ Calcd.: C 69.44 H 5.30
(190.3) Found: C 69.40 H 5.40.

b) **8o**: Column with H/MeOAc (10 + 0.5) + 100% DCM. – *m.p.* 47–48 °C. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2923, 1759, 1672, 1620, 1556, 1370, 1206, 1093, 1024, 912, 864, 743, 682. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.21 (s, 3H), 2.40 (s, 3H), 2.51 (s, 3H), 6.75 (s, 1H), 7.18–7.27 (m, 2H), 7.76–7.85 (m, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 14.6 (q), 18.7 (q), 21.1 (q), 113.2 (d), 124.8 (d, 2C), 128.4 (d, 2C), 134.7 (s), 145.5 (s), 163.2 (s), 168.1 (s), 189.0 (s).
$C_{13}H_{14}O_3S$ Calcd.: C 62.38 H 5.64
(250.3) Found: C 62.63 H 5.62.

c) **9o**: Column with H/MeOAc (10+0.5) + 100% DCM. – *m.p.* 84–86 °C. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2215 (C≡C), 1736, 1633, 1593, 1557, 1404, 1279, 1091, 905, 830, 743, 679. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.13 (s, 3H), 2.51 (s, 3H), 7.25 (d, J = 6.9 Hz, 2H), 8.02 (d, J = 6.8 Hz, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 4.2 (q), 14.5 (q), 78.8 (s), 92.0 (s), 124.5 (d, 2C), 129.7 (d, 2C), 133.2 (s), 147.2 (s), 177.0 (s).
$C_{11}H_{10}OS$ Calcd.: C 69.44 H 5.30
(190.3) Found: C 68.40 H 5.43.

5-(4-Buta-2,3-dienoylphenyl)penta-3,4-dien-2-one (**1p**)

*a) 4-(4-Hydroxypent-1-ynyl)benzaldehyde (**22**)*: From 9.00 g (107 mmol) pent-4-yn-2-ol (**20**), 19.8 g (107 mmol) 4-bromobenzaldehyde (**21**), 1.23 g (1.07 mmol, 1%) tetrakis(triphenylphosphane)palladium, 408 mg (2.14 mmol, 2%) CuI and 100 ml triethylamine according to the reference [15c], 3.41 g (17%) **22** were obtained. Column with H/EA (1:3). – R_f (H/EA, 1:3) = 0.10. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3400, 2972, 2929, 2937, 2224, 1701, 1602, 1561, 1413, 1388, 1377, 1303, 1285, 1208, 1167, 1114, 1086, 1063, 938, 831, 713. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.32 (d, J = 6.1 Hz, 3H), 2.27 (br s, 1H), 2.60–2.63 (m, 2H), 4.00–4.12 (m, 1H), 7.51–7.54 (m, 2H), 7.76–7.80 (m, 2H), 9.96 (s, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 22.4 (d), 29.9 (t), 66.3 (d), 82.1 (s), 90.9 (s), 129.4 (d, 2C), 129.7 (s), 132.0 (2 d), 135.0 (s), 191.4 (d). – MS (70 eV): *m/z* (%): 188 (11)[M$^+$], 144 (97), 115 (100).
$C_{12}H_{12}O_2$ Calcd.: C 76.57 H 6.43
(188.2) Found: C 76.32 H 6.66.

b) 5-[4-(1-Hydroxybut-3-ynyl)phenyl]pent-4-yn-2-ol (**6p**): From 10.0 ml (16.4 mmol) of a solution of **5** in diethyl ether and 3.09 g (16.4 mmol) of **22** in DCM, 2.21 g (59%) of **6p** were obtained according to the general procedure (a). Column with H/EA (3:1). – R_f (H/EA, 1:1) = 0.13. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3370, 3297, 2972, 2929, 2909, 2246, 2220, 1507, 1454, 1418, 1376, 1351, 1289, 1204, 1111, 1085, 1061, 1016, 937, 911, 837, 734. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.27 (d, J = 6.2 Hz, 3H), 2.03 (t, J = 2.6 Hz, 1H), 2.48 (d, J = 3.7 Hz, 1H), 2.52–2.59 (m, 4H), 3.10 (d, J = 3.7 Hz, 1H), 3.94–4.03 (m, 1H), 4.76–4.82 (m, 1H), 7.26 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 22.2 (q), 29.1 (t), 29.8 (t), 66. 4 (d), 71.0 (d), 71.8 (d), 80.4 (s), 82.6 (s), 86.3 (s), 122.8 (s), 125.6 (d, 2C), 131.5 (d, 2C), 142.2 (s). – MS (70 eV): *m/z* (%): 228 (10)[M$^+$], 189 (100), 165 (11), 145 (28), 115 (56), 91 (15), 84 (56).
$C_{15}H_{16}O_2$ Calcd.: C 78.92 H 7.06
(228.3) Found: C 79.07 H 7.13.

c) **1p**: From 2.80 g (6.60 mmol) DMP and 685 mg (3.00 mmol) **6p**, 401 mg (60%) of **1p** were obtained according to the general procedure (b). Column with H/EA (5:1). – R_f (H/EA, 1:1) = 0.60. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3064, 3012, 2991, 2921, 2243, 2204, 1960, 1933, 1759, 1711, 1683, 1648, 1602, 1420, 1357, 1277 1219, 1179, 1145, 1015, 982, 905, 882, 853, 787, 757. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.26 (s, 3H), 5.25 (d, J = 6.6 Hz, 2H), 6.17 (d, J = 6.3 Hz, 1H), 6.41 (t, J = 6.6 Hz, 1H), 6.67 (d, J = 6.3 Hz, 1H), 7.37 (d, J = 8.3 Hz, 2H), 7.89 (d, J = 8.3 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 26.9 (q), 79.2 (t), 93.1 (d), 97.9 (d), 101.1 (d), 127.0 (d, 2C), 129.3 (d, 2C), 135.6 (s), 136.8 (s), 189.9 (s), 197.1 (s), 216.3 (s), 216.9 (s). – MS (70 eV): *m/z* (%): 224 (21)[M$^+$], 200 (8), 185 (56), 182 (58), 153 (17), 143 (34), 114 (39), 84 (100).

$C_{15}H_{12}O_2$ (224.3) Calcd.: C 80.34 H 5.39 Found: C 80.11 H 5.58.

6-Hydroxy-6-methylhepta-3,4-dien-2-one (**1q**)

a) 4-(1-Ethoxyethoxy)pent-1-yne (**17**): From 10.0 g (119 mmol) **20**, 17.3 g (240 mmol, 2 eqs.) ethyl vinyl ether and 120 mg (631 µmol) *p*-TsOH·H_2O, according to reference [15d], 18.2 g (98%) **17** were obtained. IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3297, 2977, 2934, 2883, 2121 (C≡C), 1446, 1377, 1335, 1228, 1131, 1099, 1058, 980, 956, 924, 866, 845. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.94–1.10 (m, 9H), 1.77 (t, J = 2.7 Hz, 1H), 2.01–2.49 (m, 2H), 3.22–3.49 (m, 2H), 3.58–3.72 (m, 1H), 4.51–4.61 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 15.0, 15.1 (2q), 19.7, 20.2 (2q), 20.3, 20.6 (2q), 26.3, 26.8 (2t), 59.7 (2t), 69.7 (2 separate t), 69.8, 70.2 (2d), 81.0, 81.9 (2s), 98.2, 98.8 (2d). – MS (70 eV): *m/z* (%): 141 (12)[M$^+$], 117 (8), 111 (6), 80 (8), 73 (100).
$C_9H_{16}O_2$ (156.2) Calcd.: C 69.19 H 10.32 Found: C 68.94 H 10.27.

b) 6-(1-Ethoxyethoxy)-2-methylhept-3-yn-2-ol (**18**): From 2.00 g (12.8 mmol) **17** in 11 ml diethyl ether, 8.00 ml (12.8 mmol, 1.6M) *n*-BuLi in hexane and 1.25 ml dry acetone, according to reference [15e], 1.37 g (50%) **18** and 120 mg (8%) of a 2:1 mixture of the elimination products (*Z*)-2-methylhept-5-en-3-yn-2-ol ((*Z*)-**19**) and (*E*)-2-methylhept-5-en-3-yn-2-ol ((*E*)-**19**) were obtained.

α) **18**: Column with H/EA (5:1). – R_f (H/EA, 8:1) = 0.07. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3401, 2980, 2933, 2237 (C≡C), 1457, 1377, 1241, 1164, 1120, 1087, 1062, 979, 951, 856. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.10–1.28 (m, 9H), 1.43 (br s, 6H), 2.14–2.46 (m, 2H), 2.78 (v br s, 1H), 3.36–3.91 (m, 3H), 4.62–4.79 (m, 1H). – MS (70 eV): *m/z* (%): 199 (1)[M$^+$], 169 (3), 153 (5), 141 (2), 125 (13), 109 (17), 80 (99), 73 (100).
$C_{12}H_{22}O_3$ (214.3) Calcd.: C 67.26 H 10.35 Found: C 67.36 H 10.12.

β) **19**: Column with H/EA (5:1). – R_f (H/EA, 8:1) = 0.17. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3374, 2981, 2934, 2861, 2212 (C≡C), 1725, 1671, 1455, 1442, 1363, 1247, 1220, 1165, 952, 920, 853. – MS (70 eV): *m/z* (%): 124 (15)[M$^+$], 109 (70), 97 (21), 43 (100).
$C_8H_{12}O$ (124.2) Calcd.: C 77.38 H 9.74 Found: C 77.16 H 9.82.

(*Z*)-Isomer: ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.56 (s, 6H), 1.84 (dd, J = 6.8 Hz, 1.7 Hz, 3H), 2.07 (br s, 1H), 5.44–5.53 (m, 2H), 5.98 (dq, J = 10.7 Hz, 6.8 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 15.7 (q), 31.4 (q, 2C), 65.5 (s), 78.6 (s), 98.3 (s), 109.3 (d), 138.4 (d). – (*E*)-Isomer: ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.52 (s, 6H), 1.77 (dd, J = 6.8 Hz, 1.8 Hz, 3H), 2.07 (br s, 1H), 5.44–5.53 (m, 2H), 6.12 (dq, J = 15.8 Hz, 6.8 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 18.4 (q), 31.3 (q, 2C), 65.4 (s), 80.7 (s), 92.1 (s), 110.0 (d), 139.6 (d).

c) 2-Methylhept-3-yn-2,6-diol (**6q**): From 1.33 g (6.21 mmol) **18** and 10 mg (52.6 µmol) *p*-TsOH·H_2O in 20 ml methanol, in analogy to reference [26], 761 mg (86%) **6q** were obtained. Column with H/EA (1:2). – R_f (H/EA, 1:2) = 0.27. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 2311, 3204, 2983, 2933, 2892, 2239, 1464, 1435, 1409, 1378, 1358, 1282, 1239, 1170, 1115, 1084, 955, 944, 861. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.22 (d, J = 6.2 Hz, 3H), 1.45 (s, 3H), 1.46 (s, 3H), 2.25 (dd, J = 16.5 Hz, 6.4 Hz, 1H), 2.36 (dd, J = 16.5 Hz, 4.9 Hz, 1H), 3.56 (br s, 2H), 3.86–3.98 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 22.1 (q), 28.8 (t), 31.3 (q), 31.4 (q), 64.8 (s), 66.1 (d), 78.6 (s), 87.5 (s). – MS (70 eV): *m/z* (%): 127 (12)[M$^+$], 109 (14), 80 (100), 59 (26), 43 (59).
$C_8H_{14}O_2$ (142.2) Calcd.: C 67.57 H 9.92 Found: C 67.30 H 9.92.

d) **1q**: From 2.40 g (5.67 mmol) DMP and 732 mg (5.15 mmol) **6q**, 584 mg (81%) **1q** were obtained according to the general procedure (b). – **1q**: Column with H/EA (2:1). – R_f (H/EA, 2:1) = 0.43. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3421, 2977, 2932, 1947 (C=C=C), 1721, 1682, 1459, 1421, 1362, 1237, 1159, 1019, 1000, 971, 897, 881. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.40 (s, 6H), 2.20 (s, 3H), 3.70 (v br s, 1H), 5.79–5.86 (m, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 26.6 (q), 29.7 (q), 29.8 (q), 69.9 (s), 99.9 (d), 104.9 (d), 198.7 (s), 210.9 (s). – MS (70 eV): *m/z* (%): 140 (1)[M$^+$], 125 (14), 82 (83), 59 (86), 43 (100).
$C_8H_{12}O_2$ (140.2) Calcd.: C 68.55 H 8.63 Found: C 68.32 H 8.62.

Hepta-1,6-diyn-4-ol (**6r**)

From 3.00 g (40.5 mmol) ethyl formiate and 51.3 ml (84.1 mmol) **5**, according to the general procedure (c), 2.71 g (62%) **6r** were obtained. Column with H/EA (5:1). – R_f (H/EA, 5:1) = 0.15. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3294, 2939, 2916, 2120, 1429, 1076, 1057, 883. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.11 (t, J = 2.7 Hz, 2H), 2.43–2.61 (m, 4H), 2.71 (d, J = 5.4 Hz, 1H), 3. 96 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 25.8 (t, 2C), 68.1 (d), 71.0 (d, 2C), 79.9 (s, 2C). – MS (70 eV): *m/z* (%): 107 (5)[M$^+$], 79 (43), 69 (77), 39 (100).
C_7H_8O (108.1) Calcd.: C 77.75 H 7.46 Found: C 77.49 H 7.54.

4-Chloro-1-(3-methoxyphenyl)but-3-yn-1-ol (**23a**)

In analogy to the literature procedure of Verboom *et al*. for related substrates [10a] at –50 °C 3.50 ml *n*-BuLi in hexane (1.6M, 5.60 mmol) were added to a solution of 530 mg (3.01 mmol) **6e** in THF. The clear, yellow solution was stirred at –55 °C to –50 °C for 30 min. Then *N*-chlorosuccinimid (2.99 mmol, 399 mg) were added, a white precipitate formed. The reaction mixture was allowed to warm to room temperature and stirred for another two hours. After aqueous working up as described above 588 mg (93%) **23a** and 33.3 mg (6%) of 1-(3-methoxyphenylbut-2-yn-1-ol (**26**) were isolated by column chromatography.

a) **23a**: Column with H/EA (10+2) + 30% DCM. – R_f (H/EA, 3:1) = 0.31. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3417, 2938, 2836, 2363, 2244 (C(124.2)C), 1602, 1489, 1456, 1436, 1263, 1154, 1042, 786, 669. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.25 (s, 1H), 2.63 (d, J = 6.2 Hz, 2H), 3.84 (s, 3H), 4.83 (t, J = 6.2 Hz, 1H), 6.82–6.95 (m, 3H), 7.24–7.31 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 29.5 (t), 55.1 (q), 59.8 (s), 65.9 (s), 72.2 (d), 111.0 (d), 113.4 (d), 117.8 (d), 129.4 (d), 144.0 (s), 159.6 (s).
$C_{11}H_{11}ClO_2$ (210.7) Calcd.: C 62.72 H 5.26 Found: C 62.46 H 5.34.

b) **26**: Column with H/EA (10 + 2) + 30% DCM. – R_f (H/EA, 3:1) = 0.24. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3406, 2920, 2837, 2229 (C(124.2)C), 1601, 1488, 1436, 1259, 1132, 1039. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.91 (s, 3H), 2.17 (s, 1H), 3.82 (s, 3H), 5.39–5.40 (m, 1H), 6.83–6.88 (m, 1H), 7.09–7.15 (m, 2H), 7.25–7.32 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 3.5 (q), 55.1 (q), 64.6 (d), 78.9 (s), 82.9 (s), 111.9 (d), 113.7 (d), 118.7 (d), 129.4 (d), 142.7 (s), 159.6 (s).

$C_{11}H_{12}O_2$	Calcd.:	C 74.98	H 6.86
(176.2)	Found:	C 74.96	H 6.99.

4-Chloro-1-(3-methylphenyl)buta-2,3-dien-1-one (**24a**)

From 1.44 g (3.39 mmol) DMP and 649 mg (3.08 mmol) **23a**, 512 mg (80%) of **24a** were obtained according to the general procedure (b). The neat substance decomposed rapidly at room temperature. Column with H/EA (8:1). – R_f (H/EA, 3:1) = 0.47. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3050, 2835, 1954 (C=C=C), 1660, 1596, 1487, 1429, 1266, 1037. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.86 (s, 3H), 6.42 (d, J = 5.4 Hz, 1H), 6.56 (d, J = 6.0 Hz, 1H), 7.14 (m, 1H), 7.35–7.50 (m, 3H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 55.3 (q), 92.2 (d), 100.2 (d), 112.8 (d), 120.1 (d), 121.4 (d), 129.4 (d), 137.7 (s), 159.6 (s), 189.1 (s), 211.6 (s).

$C_{11}H_9ClO_2$	Calcd.:	C 63.32	H 4.35
(208.6)	Found:	C 63.36	H 4.55.

2-Chloro-5-(3-methoxyphenyl)furan (**29**)

Reaction of **24a** *with* $PdCl_2(MeCN)_2$: From 337 mg (1.61 mmol) **24a** and 8.3 mg (2.0 mol-%) $PdCl_2(MeCN)_2$ according to the general procedure (d), 6.9 mg (2%) **29** were obtained. Column with H/EA (15:1). – R_f (H/EA, 3:1) = 0.55. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2939, 2836, 1596, 1514, 1488, 1293, 1216, 1154, 1041, 942, 774. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 3.86 (s, 3H), 6.25 (d, J = 3.4 Hz, 1H), 6.62 (d, J = 3.4 Hz, 1H), 6.81–6.85 (m, 1H), 7.15–7.33 (m, 3H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 55.2 (q), 107.0 (d), 108.1 (d), 108.6 (d), 113.4 (d), 115.8 (d), 129.7 (d), 131.0 (s), 135.8 (s), 153.2 (s), 159.8 (s).

$C_{11}H_9ClO_2$	Calcd.:	C 63.32	H 4.35
(208.6)	Found:	C 63.55	H 4.47.

4-Bromo-1-(3-methoxyphenyl)but-3-yn-1-ol (**23b**)

In analogy to **23a** from 18.0 ml *n*-BuLi in hexane (28.8 mmol), 2.50 g (14.2 mmol) **6e** and 2.73 g (15.3 mmol) *N*-bromsuccinimid, 1.91 g (53%) **23b** and 42.9 mg (2%) of **26** were obtained. Another side-product was 5-hydroxy-1,5-bis(3-methoxyphenyl)pent-2-yn-1-on (21.8 mg, less than 0.5%), probably formed by an oxidation of an impurity in **6e** (compare 1,5-bis(benzo[1,3]dioxol-5-yl)pent-2-yne-1,5-diol above).

a) **23b**: Column with H/EA (6:1). – R_f (H/EA, 3:1) = 0.28. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3416, 1602, 1488, 1455, 1435, 1262, 1154, 1040, 786. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.39 (d, J = 3.5 Hz, 1H), 2.65 (d, J = 6.3 Hz, 2H), 3.82 (s, 3H), 4.81–4.87 (m, 1H), 6.82–6.87 (m, 1H), 6.92–6.95 (m, 2H), 7.24–7.31 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 30.4 (t), 40.7 (s), 55.1 (q), 72.1 (d), 76.5 (s), 111.0 (d), 113.5 (d), 117.8 (d), 129.4 (d), 143.9 (s), 159.6 (s).

$C_{11}H_{11}BrO_2$	Calcd.:	C 51.79	H 4.35
(255.1)	Found:	C 51.70	H 4.35.

b) 5-Hydroxy-1,5-bis(3-methoxyphenyl)pent-2-yn-1-on: Column with H/EA (8:1). – R_f (H/EA, 3:1) = 0.39. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2940, 2836, 2228 (C≡C), 1722, 1644, 1587, 1488, 1454, 1275, 1102, 1044, 755, 699. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.89 (dd, J = 4.8 Hz, 2H), 3.82–3.87 (m, 8H), 6.06 (t, J = 6.4 Hz, 1H), 6.84–6.89 (m, 1H), 7.01–7.15 (m, 2H), 7.33–7.42 (m, 2H), 7.60–7.64 (m, 1H), 7.72–7.75 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 27.7 (t), 40.9 (s), 55.1 (q), 55.3 (q), 73.7 (d), 75.3 (s), 112.0 (d), 113.6 (d), 114.2 (d), 118.4 (d), 119.4 (d), 122.0 (d), 129.3 (d), 129.5 (d), 131.1 (s), 140.4 (s), 159.5 (s), 165.2 (s), 190.5 (s).

4-Bromo-1-(3-methylphenyl)buta-2,3-dien-1-one (**23b**)

From 751 mg (1.77 mmol) DMP and 411 mg (1.61 mmol) **23b**, 301 mg (74%) of **24b** were obtained according to the general procedure (b). The neat substance decomposed rapidly at room temperature. Column with H/EA (8:1). – R_f (H/EA, 3:1) = 0.31. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 1654, 1596, 1581, 1429, 1264, 1224, 1035, 760. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 3.85 (s, 3H), 6.30 (d, J = 5.8 Hz, 1H), 6.35 (d, J = 5.8 Hz, 1H), 7.11–7.14 (m, 1H), 7.33–7.49 (m, 3H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 55.4 (q), 75.3 (d), 98.7 (d), 112.7 (d), 120.0 (d), 121.4 (d), 129.4 (d), 137.8 (s), 159.6 (s), 189.0 (s), 210.1 (s).

$C_{11}H_9BrO_2$	Calcd.:	C 52.20	H 3.58
(253.1)	Found:	C 52.14	H 3.72.

1-(3-Methoxyphenyl)-4-trimethylsilanylbut-3-yn-1-ol (**23c**)

a) *1-Methoxy-3-(4-trimethylsilyl-1-trimethylsiloxybut-3-ynyl)benzene*: In analogy to **23a** from 23.3 ml (37.3 mmol, 2eqs.) *n*-BuLi in hexane, 3.28 g (18.6 mmol) **6e** and 4.04 g (37.2 mmol, 2 eqs.) TMSCl we obtained 4.78 g (80%) 1-methoxy-3-(4-trimethylsilyl-1-trimethylsiloxybut-3-ynyl)benzene. Column with H/EA (100:1). – R_f (H/EA, 3:1) = 0.54. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2958, 2178 (C≡C), 1602, 1487, 1251, 1102, 1047, 938, 843, 760. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.10 (s, 9H), 0.12 (s, 9H), 2.46–2.65 (m, 2H), 3.81 (s, 3H), 4.77–4.82 (m, 1H), 6.77–6.82 (m, 1H), 6.89–6.93 (m, 2H), 7.19–7.26 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 0.0 (q, 3C), 0.1 (q, 3C), 32.3 (t), 55.1 (q), 73.6 (d), 86.1 (s), 104.5 (s), 111.1 (d), 112.8 (d), 118.1 (d), 129.0 (d), 145.7 (s), 159.5 (s).

$C_{17}H_{28}O_2Si_2$	Calcd.:	C 63.69	H 8.80
(320.6)	Found:	C 63.73	H 9.00.

b) **23c**: To a solution of 4.34 g (13.5 mmol) **33** in methanol at room temperature 280 mg (1.46 mmol) citric acid were added [10b]. The reaction was monitored by TLC, after 15 min. the reaction mixture was poured on a water/DCM mixture. After aqueous working up and chromatography 2.67 g (79%) of **23c** were obtained. Column with H/EA (5:1). – R_f (H/EA, 3:1) = 0.33. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3418, 2958, 2176 (C≡C), 1602, 1488, 1250, 1153, 1040, 843, 760, 698. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.14 (s, 9H), 2.48 (d, J = 3.4 Hz, 1H), 2.63–2.66 (m, 2H), 3.81 (s, 3H), 4.80–4.86 (m, 1H), 6.81–6.85 (m, 1H), 6.93–6.96 (m, 2H), 7.23–7.29 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 0.0 (q, 3C), 31.2 (t), 55.2 (q), 72.2 (d), 88.0 (s), 102.9 (s), 111.2 (d), 113.4 (d), 118.0 (d), 129.4 (d), 144.2 (s), 159.7 (s).

$C_{14}H_{20}O_2Si$	Calcd.:	C 67.70	H 8.12
(248.4)	Found:	C 67.44	H 8.19.

Reaction of **23c** *with DMP*

From 1.20 g (2.83 mmol) DMP and 634 mg (2.55 mmol) **23c**, 307 mg (53%) of a 3:1 mixture of **25** and **1e** were obtained according to the general procedure (b). Since the NMR data of **1e** was known, the data of **23c** could be extracted from the spectrum of this mixture. **23c**: ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.15 (s, 9H), 3.85 (s, 3H), 3.87 (s, 2H), 7.07–7.15 (m, 1H), 7.32–7.60 (m, 3H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = –0.1 (q, 3C), 32.1 (t), 55.5 (q), 91.0 (s), 98.5 (s), 112.8 (d), 120.2 (d), 121.4 (d), 129.6 (d), 136.7 (s), 159.9 (s), 192.8 (s).

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