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Gold Catalysis: Efficient 1,3-Induction with Diastereotopic Homopropargyl Alcohols in the Phenol Synthesis

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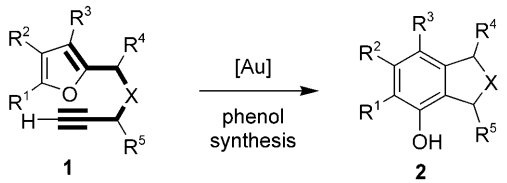
Abstract: Furans with diastereotopic alkynyl groups were prepared and then converted to anellated phenols in gold-catalyzed reactions. In all cases a highly diastereoselective reaction was observed. The stereochemical outcome of the 1,3-induction could be assigned by two independent crystal structure analyses, showing a *cis*-arrangement of the two alkyl substituents on the benzoanellated cyclohexene ring.

Keywords: alkynes; arenes; cobalt; furans; gold; stereoselectivity

Introduction

In homogeneous gold catalysis[1] the cycloisomerization of ω-alkynylfurans **1** to anellated phenols **2**, the first example of a substrate with the 1,6-enyne substructure (shown in bold in Scheme 1) in a gold-catalyzed cycloisomerization reaction, has proven to be one of the most reliable and broadly applicable methods in this area. After the discovery of this useful transformation in 2000,[2] mechanistic investigations[3] and exploration of the synthetic scope of the reaction in the synthesis of different carbo- and heterocycles[4] have dominated.

So far, stereoselective reactions have not been investigated. Since the reacting *sp* and sp^2 centers of the alkyne and the furan do not form new stereocenters in the product **2** (with respect to the carbon atoms, all new bonds involve only sp^2 centers), such stereoselective conversions would demand heterotopic reacting groups in the substrate. A substrate like **3**, with identical length of the tether between the branching point and the alkyne unit would fulfil this condition (Figure 1).



X = O, OCR_2, NR, CR_2NR, CR_2, ...
R^1 = H, alkyl, aryl, alkynyl
R^2 = H, alkyl, Br
R^3 = H, alkyl
R^4, R^5 = H, alkyl, aryl

Scheme 1. The gold-catalyzed phenol synthesis.

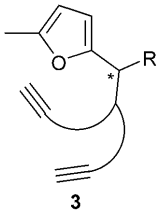


Figure 1. Substrates with diastereotopic alkynyl groups.

Here we describe the synthesis and the gold-catalyzed conversion of such substrates possessing two diastereotopic alkynyl groups.

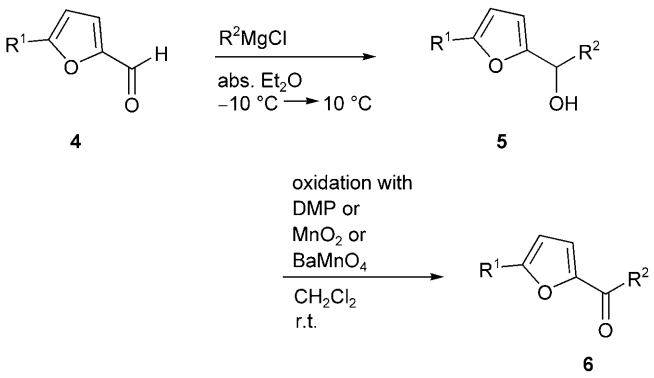
Results and Discussion

For the substrate synthesis we started with the furfurals **4**, the addition of Grignard compounds delivered **5**, the latter was oxidized to the acylfurans **6** (Scheme 2).

As shown in Table 1, these reactions often gave excellent yields of the furfurols **5**, but the yield of the subsequent oxidation step could be as low as 34% (entry 5). The oxidation of **5** to **6** was successful with either MnO_2 or Dess–Martin periodinane (DMP).

Table 1. Two-step route to the acylfurans **6**.

Entry	4	5	Yield [%]	Oxidant	6	Yield [%]
1	**4a**: R^1 = Me	**5a**: R^1 = Me, R^2 = *c*-Pr	100	MnO_2	**6a**	73
				DMP		–
2		**5b**: R^1 = Me, R^2 = *i*-Pr	99	DMP	**6b**	95
				$BaMnO_4$		–
				MnO_2		–
3		**5c**: R^1 = Me, R^2 = *t*-Bu	99	DMP	**6c**	88
				MnO_2		–
4		**5d**: R^1 = Me, R^2 = *n*-Bu	100	MnO_2	**6d**	54
5	**4b**: R^1 = Ph	**5e**: R^2 = Me	58	DMP	**6e**	34



Scheme 2. Synthesis of **6** from furfurals **4**.

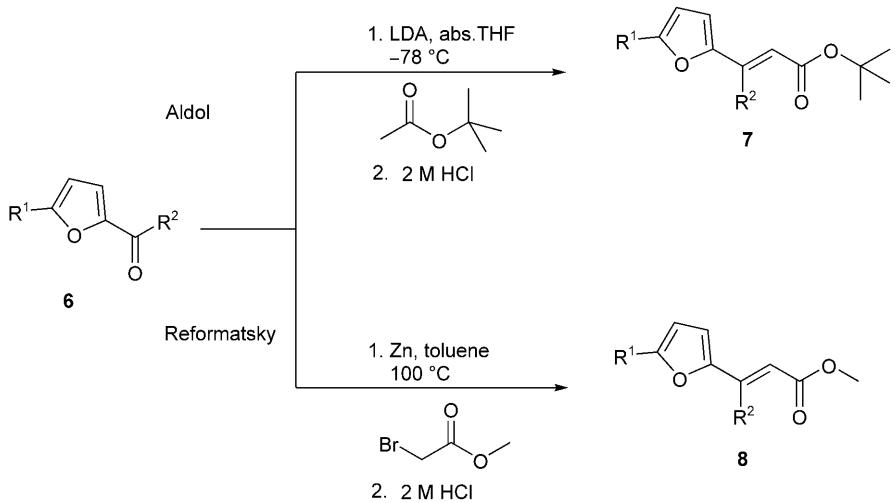
Table 2. Aldol condensation leading to **7** and Reformatsky reaction providing **8**.

Entry	6	7	Yield [%]	8	Yield [%]
1	**6a**: R^1 = Me, R^2 = *c*-Pr			**8a**	56
2	**6b**: R^1 = Me, R^2 = *i*-Pr	**7b**	64		
3	**6c**: R^1 = Me, R^2 = *t*-Bu	–		–	–
4	**6d**: R^1 = Me, R^2 = *n*-Bu			**8d**	47
5	**6e**: R^1 = Ph, R^2 = Me	**7e**	78		
6	**6f**: R^1 = Ph, R^2 = H			**8f**	80
7	**6g**: R^1 = Me, R^2 = Me	**7g**	48	**8g**	97
8	**6h**: R^1 = Me, R^2 = H	**7h**	36		

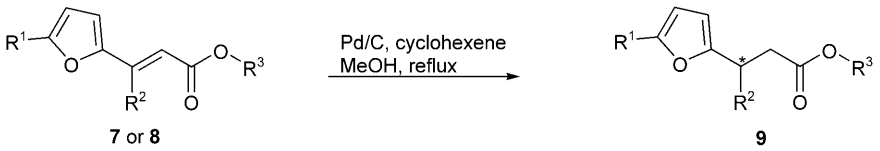
Nevertheless, this short sequence is a fast synthetic route to **6**.

For the further conversion of **6** we investigated two different routes. The aldol condensation with *tert*-butyl acetate provided the *tert*-butyl esters **7**, the Reformatsky reaction with methyl bromoacetate gave the corresponding methyl esters **8** (Scheme 3).

The results from Table 2 show that the Reformatsky reaction might give better results (entry 7), but with the aldol condensation also good yields could be obtained (entry 5). Due to the different ester groups (Me or *t*-Bu), the results cannot be compared directly. For the substrate **6c**, where the initial nucleophilic attack must occur at a neopentylic carbonyl group, both reaction types failed completely (entry 3). The low yield of **7h** resulted from a significant portion of aldol addition product which had not eliminated to **7h**.



Scheme 3. Aldol and Reformatsky route to the α,β-unsaturated esters **7** and **8**.



Scheme 4. Transfer hydrogenation delivers **9**.

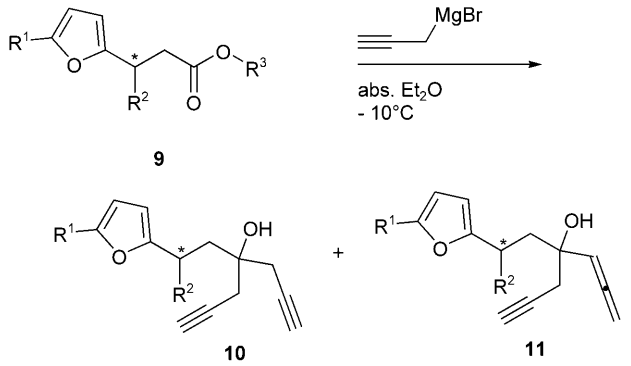
Table 3. Hydrogenation of **7** and **8**.

Entry	Substrate	Product	Yield [%]
1	**8a**: R^1=Me, R^2=*c*-Pr, R^3=Me	**9a**: R^2=*n*-Pr[a]	99
2	**7b**: R^1=Me, R^2=*i*-Pr, R^3=*t*-Bu	**9b**	94
3	**8d**: R^1=Me, R^2=*n*-Bu, R^3=Me	**9d**	97
4	**7e**: R^1=Ph, R^2=Me, R^3=*t*-Bu	**9e**	96
5	**8f**: R^1=Ph, R^2=H, R^3=Me	**9f**	42
6	**7g**: R^1=Me, R^2=Me, R^3=*t*-Bu	**9g**	87
7	**7h**: R^1=Me, R^2=H, R^3=*t*-Bu	**9h**	83

[a] Additional hydrogenative ring opening.

The substrates **7** and **8** were then reduced to the esters **9** with cyclohexene as the hydrogen transfer reagent and a heterogeneous palladium catalyst (Scheme 4).

Table 3 shows that with the exception of **9f** (entry 5) very good yields were obtained. In **8a** the Pd catalyst does not only hydrogenate the alkene, the strained cyclopropyl ring is also opened by a hydrogenative C–C bond cleavage to deliver **9a** with an *n*-propyl side chain.



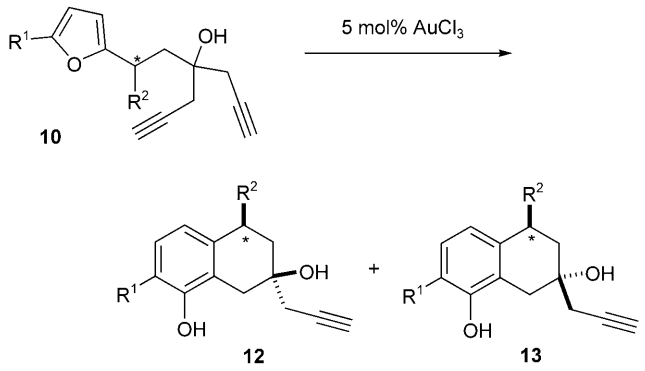
Scheme 5. Tertiary alcohols **10** and **11** by Grignard addition to the ester group of **9**.

The substrates **9** were subsequently converted to the tertiary alcohols **10**. Since the two-fold addition is a step-wise process, a propargyl ketone is the intermediate, and this intermediate might partially isomerize to the corresponding allenyl ketone prior to addition of the second equivalent of propargylmagnesium bromide – this ultimately can deliver the allenyl-propargyl carbinol **11** as a side-product (Scheme 5, Table 4).[5]

A significant amount of this side-product is obtained only in two cases (Table 4: **11d**, entry 3 and **11h**, entry 7), in one case a small amount (3%) could be detected (**11g**, entry 6). For these three cases the propargyl compound was difficult to separate from allene **6**, **10d**/**11d** could not be separated but were used as a mixture in the next step in which the allenic substrate only delivered oligomeric/polymeric material which could easily be separated. The pair **10g**/**11g** behaved similarly, but due to the small percentage of **11g**, the spectroscopic data for **10g** could be assigned.

Table 4. Grignard addition to the ester group of **9**.

Entry	**9**	**10**	Yield [%]	**11**	Yield [%]
1	**9a**: R^1=Me, R^2=*n*-Pr, R^3=Me	**10a**: R^1=Me, R^2=*n*-Pr	33	**11a**	–
2	**9b**: R^1=Me, R^2=*i*-Pr, R^3=*t*-Bu	**10b**: R^1=Me, R^2=*i*-Pr	36	**11b**	–
3	**9d**: R^1=Me, R^2=*n*-Bu, R^3=Me	**10d**: R^1=Me, R^2=*n*-Bu	32	**11d**	32
4	**9e**: R^1=Ph, R^2=Me, R^3=*t*-Bu	**10e**: R^1=Ph, R^2=Me	61	**11e**	–
5	**9f**: R^1=Ph, R^2=H, R^3=Me	**10f**: R^1=Ph, R^2=H	66	**11f**	–
6	**9g**: R^1=Me, R^2=Me, R^3=*t*-Bu	**10g**: R^1=Me, R^2=Me	31	**11g**	3
7	**9h**: R^1=Me, R^2=H, R^3=*t*-Bu	**10h**: R^1=Me, R^2=H	44	**11h**	30



Scheme 6. Gold-catalyzed conversion of substrates **10**.

In the case of **10h**/**11h** the constitutional isomers could be separated. The other conversions of **9** provided clean **10**.

The gold-catalyzed conversion of **10** now delivered only one single diastereoisomer (Scheme 6). Neither in the NMR spectra taken *in situ* during the transformation nor during the work-up or by GC, did we find any evidence for the other diastereoisomer. Thus a diastereoselectivity better than 99:1 can be assumed.

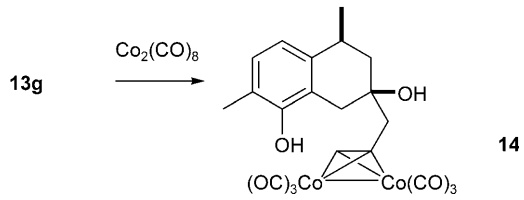
The yields are moderate to good and seem to depend on a complicated interplay of both R^1 (probably influencing the electronic properties of the furan ring and intermediates) and R^2 (influencing the conformation of the tether), a comparison of entries 4 and 6 from Table 5 shows that even the remote phenyl group in **10e** deminishes the yield, with the related methyl derivative **10g** a significantly higher yield was obtained.

The assignment of the product to one of the two possible structures **12** or **13**, which is already provided in Table 5, was not easy. Intensive NMR studies gave no clear results, and initially none of the products was crystalline. Thus we converted the product **13g** to the dicobalt hexacarbonyl complex, which indeed delivered a crystalline product **14** (Scheme 7). Single crystals for a X-ray crystal structure analysis could be obtained (Figure 2).[6]

The methyl substitutent at C-6 and the side-chain at C-1 (the former propargyl group) are *cis* on the cyclohexane ring. In the solid state they occupy a pseudo-equatorial position, placing the hydroxy group at C-1 in an axial position.

Table 5. Diastereoselective gold-catalyzed cycloisomerization of **10**.

Entry	**10**	Product	Yield [%]
1	**10a**: R^1 = Me, R^2 = *n*-Pr	**13a**	46
2	**10b**: R^1 = Me, R^2 = *i*-Pr	**13b**	87
3	**10d**: R^1 = Me, R^2 = *n*-Bu	**13d**	67
4	**10e**: R^1 = Ph, R^2 = Me	**13e**	50
5	**10f:** R^1 = Ph, R^2 = H	**13f**	87
6	**10g**: R^1 = Me, R^2 = Me	**13g**	67
7	**10h:** R^1 = Me, R^2 = H	**13h**	66



Scheme 7. Preparation of a crystalline derivative of **13g**.

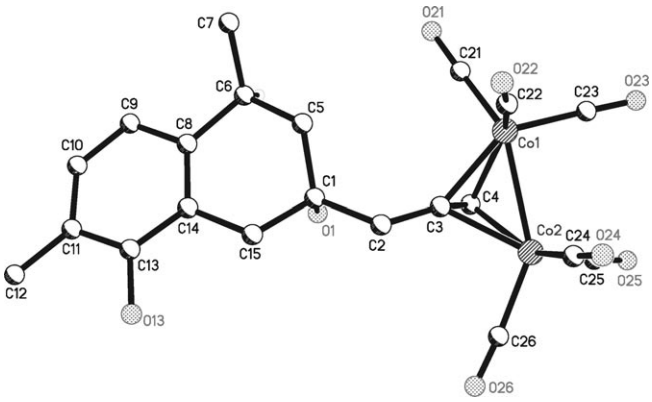


Figure 2. X-Ray crystal structure analysis of the dicobalthexacarbonyl complex **1 4** .

Once we had obtained the crystal structure of **14** by functionalization of **13g**, one of the products **13**, namely **13a**, also crystallised over time (Figure 3).

For **13a** the same relative configuration and a similar conformation as in **14** is observed in the solid state. Again the *n*-propyl group at C-10 and the propargyl group at C-8 are *cis* and in a pseudo-equatorial position, the hydroxy group at C-8 is axial.

These two structures independently show that this 1,3-induction results in a *cis*-arrangement of the substitutent and the unreacted propargyl group. On this basis the products from Table 5 were assigned to the diastereoisomer **13**, the NMR spectroscopic data of the products are in good agreement with the data of the two products **13a** and **13g**, there is no evidence for another relative configuration in any of the other (non-crystalline) products **13b**–**13e**. Only the substrates **10f** and **10h** lack the furylic stereocenter and thus deliver only racemic products **13f** and **13h**. These simply provide another proof of the reaction principle and the chemoselectivity for the phenol synthesis even in the presence of the free hydroxy group and the second alkyne.

The stereoselectivity-determining step is the formation of the first C–C bond after coodination of the catalyst to a triple bond. The two transition states of this selectivity-determining step, a 6-*exo*-*dig* cycliza-

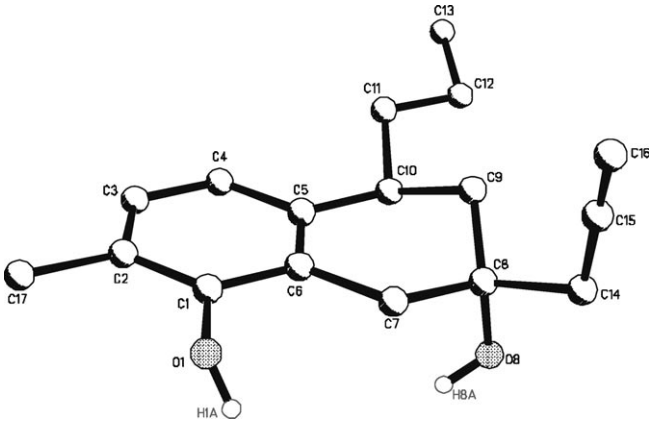


Figure 3. X-Ray crystal structure analysis of **13a**.

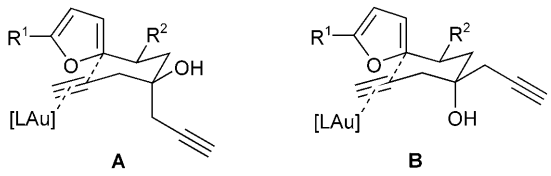
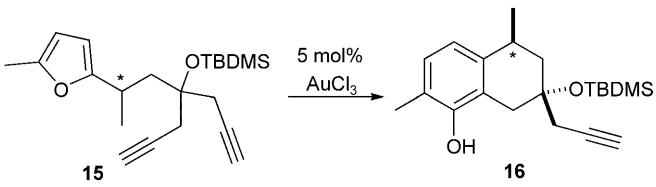


Figure 4. Competing transition states in the cyclization of **10**.

tion, ultimately leading to the two diastereomers **12** and **13**, are shown in Figure 4. Transition state **A** would deliver the diastereomer **12**, but the propargyl group would be placed in an axial position. This probably is the reason for the selectivity for transition state **B**, leading to diastereomer **13**.

Another question is the possible participation of the hydroxy group as an active volume, also coordinating to the catalyst. In order to address this question, we prepared substrate **15** with a TBDMS protecting group on the tertiary alcohol by protecting **10g** with TBDMSOTf. The gold-catalyzed cyclization of **15** (Scheme 8) still delivered the same diastereomer of **16**, but with slightly reduced diastereoselectivity (87:13).

The stereochemical assignment again was not trivial, the deprotection of **16** to **13** failed even with Bu_4NF or CsF. Only the TBDMS-protection of **13a**, delivering **16**, after two-fold silylation and subsequent deprotection of the reactive silyl group on the phenolic oxygen atom, finally proved that the same relative configuration was formed in the conversion of both



Scheme 8. Preferred diastereomer formed with protected **15**.

the unprotected and protected substrate. This suggests that the direct influence of the hydroxy group by coordination is only a minor one.

Conclusions

Highly diastereoselective ring-closure reactions with simple $AuCl_3$ are possible when using diastereotopic alkynyl groups in the phenol synthesis. The 1,3-*cis* position of the two side chains at the newly formed cyclohexenyl ring suggests a bis-equatorial position of these groups in the transition state of the ring closure step.

Experimental Section

General Procedure A: For the Grignard Reaction with Aldehydes

All reactions were carried out under a nitrogen atmosphere in oven-dried glassware. The Grignard reagent (0.5–2 M, 2 equiv.) was diluted in 20–30 mL Et_2O, cooled to about −10 °C. Aldehyde (1 equiv.) was then added slowly over 20 min with vigorous stirring. Then the temperature was allowed to rise to +10 °C. A suspension formed which was hydrolyzed by pouring it into a solution of saturated cold ammonium chloride. After phase separation the aqueous phase was extracted with Et_2O. The organic phase was dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. Then the product was isolated by column chromatography.

General Procedure B: For Oxidation with DMP or MnO_2

a) With DMP: The secondary alcohol (1 equiv.) was dissolved in 20 mL of dichloromethane and DMP (1.1 equiv.) was added. The reaction was stirred at room temperature for 3–5 h. The resulting suspension was filtered, the filtrate was washed with dichloromethane. The solvent was removed, the residue was purified by column chromatography.
b) With MnO_2: The secondary alcohol (1 equiv.) was dissolved in 20 mL of dichloromethane or acetone, manganese dioxide (15.5–20 equiv.) was added. The mixture was stirred at room temperature for 3–5 h, then the suspension was then filtered and the filtrate was washed with dichloromethane or acetone. The solvent was removed and the residue was purified by chromatography column.

General Procedure C: For the Reformatsky Reaction

Activated zinc (1.7 equiv.) was dissolved in 20–30 mL of absolute toluene and a mixture of the ketone (1 equiv.) and methyl bromoacetate (1.5 equiv.) in 10 mL toluene was slowly added. After refluxing for 24 h, the reaction mixture was hydrolyzed with 3 N HCl. The organic layer was separated, the aqueous phase was extracted with toluene and the combined organic phasees were washed with water, dried over $MgSO_4$, filtered and the solvent removed under re-

duced pressure. The crude product was purified by column chromatography.

General Procedure D: For the Transfer Hydrogenation

All reactions were carried out under a nitrogen atmosphere in oven-dried glassware. The unsaturated ester (1 equiv.) was taken up in 10–20 mL of absolute methanol. Freshly distilled cyclohexene (20–40 equiv.) and Pd/C (5% of Pd or l0% Pd) were added. The mixture was heated to reflux for 24 h. Then the reaction mixture was filtered over celite and the solvent was removed under reduced pressure.

General Procedure E: For the Grignard Reaction with Propargylmagnesium Bromide

All reactions were carried out under a nitrogen atmosphere in oven-dried glassware. Propargylmagnesium bromide (4 equiv., 2.04 M in diethyl ether) was dissolved in 5–10 mL diethyl ether and cooled to −10 °C. The ester (1 equiv.) was added over 15 min with vigorous stirring to the Grignard reagent, the temperature was controlled to be in the range −10 °C to 0 °C. Then the cooling bath was removed and the mixture was allowed to warm to room temperature. A suspension was formed, after stirring overnight, the mixture was hydrolyzed by pouring the reaction mixture in a cold saturated solution of NH_4Cl (30–50 mL). The layers were separated, the aqueous phase was extracted with diethyl ether (2×20 mL), the combined organic phases were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude product was purified by column chromatography.

General Procedure F: For Gold Catalysis

To a solution of dipropargyl Alcohol derivative in acetonitrile-d_3 (650 μL) was added 5 mol% $AuCl_3$. The progress of the reaction was monitored by ^{1}H NMR spectroscopy. Upon completion, the reaction mixture was concentrated under vacuum and the crude product was purified by column chromatography on silica gel.

Cyclopropyl(5-methylfuran-2-yl)methanol (5a): Prepared according to the general procedure **A** using 5-methylfurfural (1.00 g, 0.91 mL, 9.08 mmol,) in 10 mL absolute Et_2O and cyclopropylmagnesium bromide (1.98 g, 27.2 mL, 13.6 mmol). After the solvent was removed under vacuum the desired product **5a** was obtained and used without further purification; yield: 1.81 g. IR (film): $\tilde{\nu}$ = 3375, 3085, 3006, 2923, 2880, 1564, 1433, 1220, 1021, 785 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.28–0.46 (m, 2H), 0.51–0.67 (m, 2H), 1.25–1.36 (m, 1H), 2.27 (s, 3H), 3.95 (d, J = 8.3 Hz, 1H), 5.89 (d, J = 3.0 Hz, 1H), 6.16 (d, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 2.5 (t), 3.3 (t), 13.6 (q), 16.0 (d), 72 (d), 106.0 (d), 106.8 (d), 151.8 (s), 154.3 (s); MS (EI, 70 eV): m/z (%) = 152 (70) [M$^+$], 124 (100), 111 (90) [M$^+$−cyclopropyl], 71 [M$^+$−C_4H_7O].

2-Methyl-1-(5-methylfuran-2-yl)propan-1-ol (5b): Prepared according to the general procedure **A** using 5-methylfurfural (2.00 g, 19.8 mmol) in 10 mL absolute Et_2O and isopropylmagnesium bromide (3.05 g, 14.8 mL, 29.7 mmol). After removal of the solvent under vacuum the desired product **5b** was obtained; yield: 3.04 g (99%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.87 (d, J = 6.9 Hz, 3H), 1.04 (d, J = 6.9 Hz, 3H), 2.08 (m, J = 6.9 Hz, 1H), 2.30 (s, 3H), 4.28 (m, 1H), 5.94 (d, J = 3.0 Hz, 1H), 6.12 (d, J = 3.0 Hz, 1H). These data are in agreement with the literature.[7]

2,2-Dimethyl-1-(5-methylfuran-2 yl)propan-1-ol (5c): Prepared according to the general procedure **A** using 5-methylfurfural (1.00 g, 900 μL, 9.08 mmol,) in 10 mL absolute THF and *tert*-BuLi (5.34 mL, 9.08 mmol). After the removal of the solvent under vacuum the desired product **5c** was obtained; yield: 1.51 g (99%). IR (film): $\tilde{\nu}$ = 3449, 2995, 2871, 1666, 1561, 1479, 1464, 1365, 1219, 1062, 1018, 964, 785 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.91 (s, 9H), 2.23 (s, 3H), 4.24 (s, 1H), 5.86 (d, J = 3.0 Hz, 1H), 6.03 (d, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 13.5 (q), 25.6 (q), 35.6 (s), 76.5 (d), 105.8 (d), 107.8 (d), 150.9 (s), 153.8 (s); MS (EI, 70 eV): m/z (%) = 168 (10) [M$^+$], 111 (100) [M$^+$−11 $C_6H_7O_2$], 57 (10) [M$^+$−11 C_4H_9]; anal. calcd. for $C_{10}H_{16}O_2$ (168.12): C 71.39, H 9.59; found: C 68.47, H 9.23; HR-MS (EI+): m/z = 168.1158, calcd. for M$^+$ = $C_{10}H_{16}O_2$: 168.1224.

1-(5-Methylfuran-2-yl)pentan-1-ol (5d): Prepared according to the general procedure **A** using the 5-methylfurfural (1.40 mL, 13.6 mmol) in 2 mL absolute Et_2O and butylmagnesium chloride (1.60 mL, 27.3 mmol). After removal of the solvent under vacuum the desired product **5d** was obtained; yield: 3.36 g (100%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.92 (t, J = 7.3 Hz, 3H), 1.36 (m, J = 7.3 Hz, 2H), 1.62 (m, 2H), 1.82 (m, 2H), 2.41 (s, 3H), 3.47 (q, 1H), 6.15 (dq, J = 3.1 Hz, 1H), 7.08 (d, J = 3.1 Hz, 1H). These data are in agreement with the literature.[8]

1-(5-Phenylfuran-2-yl)ethanol (5e): Prepared according to the general procedure **A** using 5-phenylfurfural (2.00 g, 11.6 mmol) in 10 mL absolute Et_2O and methylmagnesium bromide (1.98 g, 9.70 mL, 29.1 mmol). After removal of the solvent under vacuum **5e** was obtained; yield: 1.22 g (58%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.57 (d, J = 7.5 Hz, 3H), 4.15 (q, J = 7.5 Hz, 1H), 6.20 (dd, J = 3.1 Hz, 0.7 Hz, 1H), 6.61 (d, J = 3.1 Hz, 1H), 7.25 (m, 1H), 7.37 (m, 2H), 7.66 (m, 2H). These data are in agreement with the literature.[8]

Cyclopropyl(5-methylfuran-2-yl)methanone (6a): Prepared according to the general procedure **Bb** using alcohol **5a** (1.68 g, 11.0 mmol) in 25 mL absolute dichloromethane and MnO_2 (14.9 g, 171 mmol). After 3 days the solvent was removed under vacuum and **6a** was obtained; yield: 1.21 g (73%). IR (film): $\tilde{\nu}$ = 3500, 3124, 3013, 2921, 2876, 1661, 1517, 1396, 1054, 799 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.91–0.97 (m, 2H), 1.15–1.20 (m, 2H), 2.38 (s, 3H), 2.43–2.52 (m, 1H), 6.14 (d, J = 3.4 Hz, 1H), 7.12 (d, J = 3.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 10.9 (t, 2C), 14.0 (q), 16.9 (d), 108.8 (d), 118.4 (d), 152.0 (s), 157.5 (s), 188.5 (s); MS (EI+): m/z (%) = 150 (80) [M$^+$], 109 (100) [M$^+$−cyclopropyl].

2-Methyl-1-(5-methylfuran-2-yl)propan-1-one (6b): Prepared according to the general procedure **Ba** using alcohol **5b** (1.40 g, 9.05 mmol) in 25 mL absolute dichloromethane and DMP (5.00 g, 11.8 mmol). After 24 h the solvent was removed under vacuum and after work-up **6b** was obtained; yield: 1.30 g (95%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.21 (d, J = 6.8 Hz, 6H), 2.41 (s, 3H), 3.29 (m, J = 6.9 Hz, 1H), 6.16 (dd, J = 3.5 Hz, 0.9 Hz, 1H), 7.12 (d, J = 3.4 Hz, 1H). These data are in agreement with the literature.[9]

2-Methyl-1-(5-methylfuran-2-yl)propan-1-one (6c): Prepared according to the general procedure **Ba** using alcohol

5c (1.50 g, 8.92 mmol) in 25 mL absolute dichloromethane and DMP (4.90 g, 11.7 mmol). After 24 h the solvent was removed under vacuum and after work-up **6c** was obtained; yield: 1.30 g (88%). IR (film): $\tilde{\nu}$ = 2971, 2932, 2875, 1661, 1508, 1480, 1459, 1367, 1200, 1006, 905, 797 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.37 (s, 9H), 2.37 (s, 3H), 6.14 (dd, J = 3.5 Hz, 0.9 Hz, 1H), 7.15 (d, J = 3.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.0 (q), 27.2 (q, 3C), 42.9 (s), 108.3 (d), 119.6 (d), 151.0 (s), 156.0 (s), 194.4 (s); MS (EI+): m/z (%) = 166 (21) [M^+], 110 (22), 109 (100) [$M^+-C_6H_5O_2$.]; HR-MS: (EI$^+$): m/z = 166.0981, calcd. for $M^+ = C_{10}H_{14}O_2$: 166.0994.

1-(5-Methylfuran-2-yl)pentan-1-one (6d): Prepared according to the general procedure **Bb** using alcohol **5d** (3.36 g, 19.9 mmol) in 50 mL absolute dichloromethane and MnO_2 (15.0 g, 172 mmol). After removal of the solvent under vacuum and the purification by column chromatography **6d** was obtained; yield: 1.81 g (54%). R_f (petrol ether: ethyl acetate, 20:1) = 0.15; ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.94 (t, J = 7.3 Hz, 3H), 1.39 (m, J = 7.3 Hz, 2H), 1.67 (m, 2H), 2.39 (s, 3H), 2.75 (t, 2H), 6.15 (dq, J = 3.1 Hz, 1H), 7.08 (d, J = 3.1 Hz, 1H). These data are in agreement with the literature.[10]

1-(5-Phenylfuran-2-yl)ethanone (6e): Prepared according to the general procedure **Ba** using alcohol **5e** (1.22 g, 6.47 mmol) in 25 mL absolute dichloromethane and DMP (3.02 g, 7.11 mmol). After 24 h the solvent was removed under vacuum and **6e** was obtained; yield: 405 mg (34%). ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.56 (s, 3H), 6.81 (d, J = 3.2 Hz, 1H), 7.29 (d, J = 3.1 Hz, 1H), 7.39–7.52 (m, 3H), 7.79–7.82 (m, 2H). These data are in agreement with the literature.[11]

Methyl (2*E*)-3-cyclopropyl-3-(5-methylfuran-2-yl)prop-2-enoate (8a): Prepared according to the general procedure **C** using **6a** (1.13 g, 7.53 mmol), methyl bromoacetate (1.73 g, 11.3 mmol) and zinc (840 mg, 12.8 mmol) in toluene 20 mL. After removal of the solvent under vacuum **8a** was obtained; yield: 810 mg (56%). IR (film): $\tilde{\nu}$ = 3012, 2953, 2928, 2855, 1721, 1437, 1255, 1199, 1171, 1023, 736 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.73–0.78 (m, 2H), 0.93–0.99 (m, 2H), 2. 28 (s, 3H), 2.31–2.41 (m, 1H), 3.72 (s, 3H), 6.00 (d, J = 3.3 Hz, 1H,), 6.32 (d, J = 1.4 Hz, 1H,), 6.57 (d, J = 3.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 8.1 (t, 2C), 11.4 (d), 15.8 (q), 51.1 (q), 108.2 (d), 113.2 (d), 113.7 (d), 147.5 (s), 151.3 (s), 153.8 (s), 167.3 (s); MS (EI+): m/z (%) = 206 (100) [M^+], 178 (93) [M^+-CH_3O], 163 (37), 147 (41), 91 (54); HR-MS: (EI+): m/z = 206.0943, calcd. for $M^+ = C_{12}H_{14}O_3$: 206.0924.

***tert*-Butyl (2*E*)-4-Methyl-3-(5-methylfuran-2-yl)pent-2-enoate (7b)**

***a) tert*-Butyl 3-hydroxy-4-methyl-3-(5-methylfuran-2-yl)pentanoate (7b′):** Under nitrogen *tert*-butylacetic acid (840 mg, 7.23 mmol) was added dropwise to LDA (4.30 mL, 8.55 mmol) in absolute THF (20 mL) at −78 °C. After 1 h, **6b** (1.00 g, 6.58 mmol) was added and the mixture was stirred for 1 h at −78 °C. Then the reaction mixture was allowed to gradually warm to room temperature and stirred at that temperature for another hour. The reaction mixture was quenched with 50 mL 2 M HCl and diluted with 30 mL ether. After two extractions with ether (30 mL each) the combined organic phases were dried with $MgSO_4$, filtered, and the solvent was removed under vacuum. Column chromatography on silica gel furnished the alcohol **7b′** as an orange oil; yield: 1.50 g (78%). R_f (petrol ether:ethyl acetate, 10:1) = 0.25; IR (film): $\tilde{\nu}$ = 3484, 2969, 2935, 2879, 1707, 1604, 1347, 1252, 1229, 1152, 1026 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.86 (t, J = 7.1 Hz, 6H), 1.34 (s, 9H), 1.99 (m, J = 7.1 Hz, 1H), 2.23 (d, J = 0.9 Hz, 3H), 2.58 (d, J = 15.2 Hz, 1H,), 2.82 (d, J = 15.2 Hz, 1H), 5.84 (dd, J = 3.03 Hz, 0.9 Hz, 1H), 6.07 (d, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.6 (q), 16.8 (q), 17.3 (q), 27.9 (q, 3C), 37.3 (d), 41.1 (t), 75.1 (s), 81.6 (s), 105.9 (d), 106.9 (d), 150.7 (s), 155.9 (s), 172.7 (s); MS (FAB+): m/z (%) = 268 (29) [M^+], 251 (100), 250 (65); HR-MS (FAB$^+$): m/z = 268.1642, calcd. for $M^+ = C_{15}H_{24}O_4$: 268.1675.

***b) Elimination to* 7b:** The racemic alcohol **7b′** (500 mg, 1.86 mmol) was dissolved in 15 mL THF, 25 mL of 3 N HCl were added and the mixture was stirred for 30 min at room temperature. The mixture was diluted with 20 mL of Et_2O, the layers were separated and the organic layer was dried with $MgSO_4$. After filtration the solvent was removed under reduced pressure. Purification by column chromatography delivered **7b**; yield: 298 mg (64%). R_f (petroleum ether:ethyl acetate; 100:1) = 0.52; IR (film): $\tilde{\nu}$ = 2974, 2933, 1703, 1609, 1589, 1523, 1458, 1392, 1368, 1273, 1224, 1205, 1147, 1127, 1029, 878, 785, 750, 699 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.29 (d, J = 7.0 Hz, 6H), 1.52 (s, 9H), 2.33 (s, 2H), 4.25 (m, J = 7.0 Hz, 1H), 6.04 (d, J = 3.1 Hz, 1H), 6.18 (s, 1H), 6.56 (d, J = 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.7 (q), 21.4 (q), 27.1 (d), 28.3 (q, 3C), 79.8 (s), 107.8 (d), 112.6 (d), 113.7 (d), 150.8 (s), 151.7 (s), 153.0 (s), 166.5 (s); HR-MS: (FAB$^+$): m/z = 250.1579, calcd. for $M^+ = C_{15}H_{22}O_3$: 250.1569.

Methyl (2*E*)-3-(5-methylfuran-2-yl)hept-2-enoate (8d): Prepared according to the general procedure **C** using the ketone **6d** (433 mg, 2.61 mmol), methyl bromoacetate (399 mg, 2.93 mmol) and zinc dust (170 mg, 2.61 mmol) in toluene (20 mL). After removal of the solvent under vacuum and purification by column chromatography the desired product **8d** was obtained; yield: 273 mg (47%). R_f (petrol ether:ethyl acetate, 50:1) = 0.11; IR (film): $\tilde{\nu}$ = 2953, 2927, 2871, 2768, 1708, 1651, 1586, 1524, 1457, 1432, 1377, 1340, 1306, 1275, 1223, 1188, 1161, 1124, 1025, 963, 870, 631 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.94 (t, J = 7.3 Hz, 3H), 1.39 (m, J = 7.3 Hz, 2H), 1.50 (m, 2H), 2.31 (s, 3H), 2.86 (t, 2H), 3.72 (s, 3H), 6.05 (dq, J = 3.1 Hz, 1H), 6.25 (s, 1H), 6.54 (d, J = 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.9 (q), 17.5 (q), 23.1 (t), 28.4 (t), 32.5 (t), 50.9 (t), 108.4 (d), 109.7 (d), 112.8 (d), 147.9 (s), 152.3 (s), 154.5 (s), 167.4 (s); MS: (EI+, 70 eV): m/z (%) = 222 (35) [M^+], 191 (31), 180 (100), 161 (27), 122 (52), 105 (9), 77 (9), 43 (18); HR-MS (EI+, 70 eV): m/z = 222.1236, calcd. for $C_{13}H_{18}O_3$: 222.1256.

***tert*-Butyl (2*E*)-3-(5-phenylfuran-2-yl)but-2-enoate (7e):** To LDA (1.73 mL, 2.99 mmol) in absolute THF (20 mL) under an atmosphere of nitrogen at −78 °C *tert*-butylacetic acid (290 mg, 2.5 mmol) was added dropwise. After 1 h 5-phenyl-2-acetylfuran **6e** (429 mg, 2.30 mmol) was added and the mixture was stirred for 1 h at −78 °C. Then the reaction mixture was allowed to gradually warm to room temperature and stirred for another hour. The reaction mixture was quenched with 50 mL 2 M HCl and diluted with 30 mL ether. After two extractions with ether (30 mL each) the combined organic phases were dried with $MgSO_4$, filtered,

and the solvent was removed under vacuum. Column chromatography on silica gel furnished **7e** as an orange solid; yield: 512 mg (78%); mp 80–85 °C. R_f (petrol ether:ethyl acetate,10:1) = 0.52; IR (film): $\tilde{\nu}$ = 2958, 2930, 2859, 1702, 1619, 1482, 1450, 1392, 1367, 1288, 1207, 1148, 1101, 1073, 1028, 761, 691 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.50 (s, 9H), 2.47 (d, J = 1.1 Hz, 3H), 6.1 (d, J = 1.3 Hz, 1H), 6.77 (d, J = 1.3 Hz, 1H), 7.31–7.75 (m, 6H, Ph, 1Furan); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.6 (q), 28.2 (q, 3C), 80.1 (s), 107.1 (d), 113.6 (d), 114.5 (d), 140.4 (d), 124.1 (d), 124.5 (d), 128.5 (d), 129.2 (d, 2C), 130.5 (s), 140.9 (s), 154.6 (s), 155.3 (s), 166.6 (s); HR-MS (EI$^+$): m/z = 284.1390, calcd. for $M^+ = C_{18}H_{20}O_3$: 284.1412.

Methyl (2*E*)-3-(5-phenylfuran-2-yl)prop-2-enoate (8f): Prepared according to the general procedure **C** using **6f** (2.00 g, 11.6 mmol), methyl bromoacetate (2.13 g, 13.9 mmol) and zinc (840 mg, 12.8 mmol) in toluene (20 mL). After removal of the solvent under vacuum and purification by column chromatography **8f** was obtained; yield: 2.10 g (80%). R_f (petrol ether:ethyl acetate, 10:1) = 0.21; ^1H NMR ($CDCl_3$, 300 MHz): δ = 3.81 (s, 3H), 6.05 (d, J = 2.5 Hz, 1H), 6.39 (d, J = 15.5 Hz, 1H), 6.5 (d, J = 2.5 Hz, 1H), 7.24–7.41 (m, 6H, Ph and HC=C). These data are in agreement with the literature.[12]

(*E*)-*tert*-Butyl 3-(5-methylfuran-2-yl)but-2-enoate (7g): To LDA (3.76 g, 20.9 mmol) in absolute THF (30 mL) under an atmosphere of nitrogen at −78 °C *tert*-butylacetic acid (2.06 g, 17.7 mmol) was added dropwise. After 1 h **6g** (2.00 g, 16.1 mmol) was added and stirring was continued for 1 h at −78 °C. Then the reaction mixture was allowed to gradually warm to room temperature and stirred for another hour. The reaction mixture was quenched with 50 mL 2M HCl and diluted with 30 mL ether. After two extractions with ether (30 mL each) the combined organic phases were dried with $MgSO_4$, filtered, and the solvent was removed under vacuum. Column chromatography on silica gel furnished **7g** as a yellow oil; yield: 1.70 g (48%). R_f (petrol ether:ethyl acetate, 50:1and then 10:1) = 0.26; IR (film): $\tilde{\nu}$ = 2978, 1704, 1624, 1367, 1349, 1283, 1255, 1207, 1128, 885, 799, 741, 676 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.50 (s, 9H), 2.31 (s, 3H), 2.38 (d, J = 1.3 Hz, 3H), 6.03 (dq, J = 3.3 Hz, 1.3 Hz, 1H), 6.23 (d, J = 1.3 Hz, 1H), 6.50 (d, J = 3.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.5 (q), 28.3 (q, 3C), 79.8 (s), 110.7 (d), 111.8 (d), 114.5 (d), 140.8 (s), 143.6 (d), 154.6 (s), 166.6 (s); MS (EI+, 70 eV): m/z (%) = 208 (16) [M$^+$], 152 (100), 135 (46), 124 (19), 108 (20), 77 (15), 57 (20), 41 (14), 29 (10).

Methyl (2*E*)-3-(5-methylfuran-2-yl)but-2-enoate (8g): Prepared according to the general procedure **C** using **6g** (1.00 g, 8.06 mmol), methyl bromoacetate (1.37 g, 8.94 mmol) and zinc (530 mg, 8.06 mmol) in toluene (20 mL). After the residual solvent was concentrated under vacuum the desired product **8g** was obtained; yield: 1.40 g (97%); mp 85 °C. IR (film): $\tilde{\nu}$ = 2948, 2362, 1708, 1618, 1587, 1526, 1433, 1364, 1288, 1165, 1100, 1026, 750, 633 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.35 (s, 3H), 2.42 (s, 3H), 3.73 (s, 3H), 6.06 (dq, J = 3.1 Hz, 0.9 Hz, 1H), 6.31 (s, 1H), 6.54 (d, J = 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.9 (q), 14.6 (q), 51.0 (q), 108.4 (d), 110.4 (d), 112.9 (d), 142.6 (s), 152.8 (s), 154.5 (s), 167.9 (s); MS (EI+, 70 eV): m/z (%) = 180 (100) [M$^+$], 165 (17), 150 (10), 149 (88), 138 (14), 122 (16), 105 (6), 91 (12), 77 (16), 43 (35); anal. calcd. for $C_{10}H_{12}O_3$ (180.20): C 66.65, H 6.71; found: C 66.63, H 6.68.

(*E*)-*tert*-Butyl 3-(5-methylfuran-2-yl)acrylate (7h): To LDA (9.00 g, 51.5 mmol) in absolute THF (70 mL) under an atmosphere of nitrogen at −78 °C *tert*-butylacetic acid (5.06 g, 43.6 mmol) was added dropwise. After 1 h 5-methyl-2-furfural (4.36 g, 39.6 mmol) was added and stirred was continued for 1 h at −78 °C. Then the reaction mixture was allowed to gradually warm to room temperature and stirred for another hour. The reaction mixture was quenched with 50 mL 2M HCl solution and diluted with 30 mL ether. After two extractions with ether (30 mL each) the combined organic phases were dried with $MgSO_4$, filtered, and the solvent was removed under vacuum. Column chromatography on silica gel furnished **7h** as a yellow oil; yield: 3.05 g (36%). R_f (petrol ether:ethyl acetate, 20:1and then 3:1) = 0.50; IR (film): $\tilde{\nu}$ = 2975, 2356, 1701, 1635, 1307, 1150, 631 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.50 (s, 9H), 2.31 (s, J = 0.8 Hz, 3H), 6.04 (dd, J = 3.2 Hz, 0.8 Hz, 1H), 6.16 (dd, J = 15.7 Hz, 0.8 Hz, 1H), 6.45 (dd, J = 3.2 Hz, 0.8 Hz, 1H), 7.25 (d, J = 15.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.8 (q), 28.2 (q, 3C), 80.0 (s), 108.6 (d), 115.7 (d), 116.1 (d), 130.1 (d), 149.7 (s), 155.0 (s), 166.7 (s); MS (70 eV): m/z (%) = 208 (19) [M$^+$], 152 (100), 135 (38), 110 (21), 77 (10), 57 (10), 43 (17).

Methyl 3-(5-methylfuran-2-yl)hexanoate (9a): Prepared according to the general procedure **D** using of **8a** (540 mg, 2.61 mmol) in absolute MeOH (10 mL) and cyclohexene (10.6 mL, 104 mmol) and 5% Pd/C (320 mg). After 24 h the solution was filtered over celite and the solvent was removed under vacuum. After purification **9a** was obtained; yield: 540 mg (99%). R_f (petrol ether:ethyl acetate, 10:1) = 0.52; IR (film): $\tilde{\nu}$ = 2957, 2913, 2973, 1739, 1437, 1274, 781, 746, 669 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.86 (t, J = 7.3 Hz, 3H), 1.18–1.39 (m, 2H), 1.51–1.63 (m, 2H), 2.21 (s, 3H), 2.55 (dq, J = 15.3 Hz, 7.4 Hz, 1H), 3.10–3.20 (m, 1H), 3.62 (s, 3H), 5.79 (d, J = 3.0 Hz, 1H), 5.85 (d, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.5 (q), 13.9 (q), 20.2 (t), 35.4 (d), 36.0 (t), 39.2 (t), 51.5 (q), 105.5 (d), 106.0 (d), 150.5 (s), 155.4 (s), 172.8 (s); MS (EI+): m/z (%) = 210 (50) [M$^+$], 167 (100) [M$^+$−C_3H_7], 151 (19), 137 (87), 125 (53), 95 (51), 91 (21); HR-MS: (EI+): m/z = 210.1256, calcd. for $M^+ = C_{12}H_{18}O_3$: 210.1263.

***tert*-Butyl 4-methyl-3-(5-methylfuran-2-yl)pentanoate (9b):** Prepared according to the general procedure **D** using **7b** (90 mg, 359 μmol) in absolute MeOH (10 mL) and cyclohexene (0.7 mL, 7.19 mmol) and 5% Pd/C (38.3 mg). After 24 h the solution was filtered over celite and the solvent was removed under vacuum. After purification **9b** was obtained; yield: 85.0 mg (94%). R_f (petrol ether:ethyl acetate, 10:1) = 0.42; IR (film): $\tilde{\nu}$ = 3626, 3105, 3006, 2958, 2934, 2874, 1726, 1707, 1606, 1568, 1433, 1329, 1207, 1256, 1224, 1208, 1183, 1142, 1024, 842 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.82 (d, J = 7.0 Hz, 3H), 0.87 (d, J = 7.0 Hz ,3H), 1.33 (s, 9H), 1.87 (m, J = 6.8 Hz, 1H), 2.21 (s, 3H), 2.47 (m, 2H), 2.97 (m, 1H), 5.79 (s, 1H), 5.83 (d, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.5 (q), 19.5 (q), 20.2 (q), 27.9 (q, 3C), 31.2 (d), 37.2 (t), 42.1 (d), 80.1 (s), 105.5 (d), 106.5 (d), 150.1 (s), 172.1 (s); HR-MS (FAB$^+$): m/z = 252.1716, calcd. for $M^+ = C_{15}H_{24}O_3$: 252.1725.

Methyl 3-(5-methylfuran-2-yl)heptanoate (9d): Prepared according to the general procedure **D** using **8d** (100 mg, 449

μmol) in absolute MeOH (10 mL) and cyclohexene (1.00 mL, 8.99 mmol) and 10% Pd/C (30.6 mg). After 24 h the solution was filtered over celite and the solvent was removed under vacuum to deliver **9d**; yield: 130 mg (97%). IR (film): $\tilde{\nu}$ = 2953, 2927, 2871, 2768, 1708, 1651, 1586, 1524, 1506, 1457, 1432, 1377, 1340, 1310, 1276, 1249, 1188, 1161, 1124, 1025, 963, 909, 870, 849, 707, 631 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.70 (t, J = 7.3 Hz, 3H), 1.07 (m, J = 7.3 Hz, 2H), 1.13 (m, 2H), 1.41 (m, 2H), 2.08 (s, 3H), 2.38 (dd, J = 15.3 Hz, 7.1 Hz, 1H), 2.44 (dd, J = 15.3 Hz, 7.1 Hz, 1H), 2.99 (m, 1H), 3.48 (s, 3H), 5.66 (dq, J = 3.0 Hz, 1.0 Hz, 1H), 5.71 (d, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.6 (q), 14.0 (q), 22.5 (t), 29.2 (t), 33.4 (t), 35.5 (d), 39.0 (t), 51.6 (q), 105.6 (d), 105.7 (d), 155.4 (s), 154.5 (s), 172.9 (s).

***tert*-Butyl 3-(5-phenylfuran-2-yl)butanoate (9e):** Prepared according to the general procedure **D** using **7e** (452 mg, 1.51 mmol) in absolute MeOH (10 mL) and cyclohexene (3.23 mL, 31.8 mmol) and 5% Pd/C (96 mg). After 24 h the solution was filtered over celite and the solvent was removed under vacuum to afford **9e**; yield: 560 mg (97%). IR (film): $\tilde{\nu}$ = 2976, 1729, 1452, 1368, 1288, 1257, 1208, 1151, 1023, 789, 760, 692 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.32 (d, J = 7.0 Hz, 3H), 1.40 (s, 9H), 2.39 (dd, J = 15.0 Hz, 8.0 Hz, 1H), 2.66 (dd, J = 15.0 Hz, 8.0 Hz, 1H), 3.34 (m, J = 7.0 Hz, 1H), 6.09 (dd, J = 3.4 Hz, 1.2 Hz, 1H), 6.56 (d, J = 3.4 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.4 (t, J = 7.7 Hz, 1.6 Hz, 2H), 7.62 (d, J = 7. 5 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 19.1 (q), 28.2 (q, 3C), 30.8 (d), 42.0 (t), 80.6 (s), 105.9 (d), 106.4 (d), 123.7 (d, 2C), 127.3 (d), 129.0 (d, 2C), 131.5 (s), 152.6 (s), 159.3 (s), 171.5 (s); HR-MS (FAB+): m/z = 286.1574, calcd. for $M^+ = C_{18}H_{22}O_3$: 286.1569.

Methyl 3-(5-phenylfuran-2-yl)propanoate (9f): Prepared according to the general procedure **D** using **8f** (2.07 g, 9.06 mmol) in absolute MeOH (10 mL) and cyclohexene (18.5 mL, 181 mmol) and 5% Pd/C (670 mg). After 24 h the solution was filtered over celite and the solvent was removed under vacuum to afford **9f**; yield: 877 mg (42%). IR (film): $\tilde{\nu}$ = 2949, 2171, 2042, 1995, 1739, 1595, 1548, 1487, 1437, 1202, 1023 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.76 (t, J = 7.8 Hz, 2H), 3.07 (t, J = 7.9 Hz, 2H), 3.74 (s, 3H), 6.14 (d, J = 3.2 Hz, 1.18 Hz, 1H), 6.57 (d, J = 3.2 Hz, 1H), 7.27 (t, J = 6.3 Hz, 1H), 7.38 (m, 2H), 7.64 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.1(t), 32.6 (t), 51.8 (q), 105.7 (d), 107.6 (d), 123.4 (d), 127.0 (d), 128.6 (d), 129.0 (d), 131.0 (s), 152.7 (s), 153.8 (s), 173.0 (s); anal. calcd. for $C_{14}H_{14}O_3$ (230.26): C 73.03, H 6.13; found: C 74.18 , H 6.34; HR-MS (ESI+): m/z = 253.0835, calcd. for $[M^+ + Na] = C_{14}H_{14}O$: 230.0841.

***tert*-Butyl-3-(5-methylfuran-2-yl)butanoate (9g):** Prepared according to the general procedure **D** using of **7g** (1.00 g, 4.52 mmol) in absolute MeOH (50 mL) and cyclohexene (9.10 mL, 89.9 mmol) and 5% Pd/C (310 mg). After 24 h, the solution was filtered over celite and the solvent was removed under vacuum to deliver **9g**; yield: 884 mg (87%). IR (film): $\tilde{\nu}$ = 2973, 2929, 1727, 1569, 1456, 1362, 1286, 1251, 1220, 1149, 1027, 952, 843, 782 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.26 (d, J = 6.5 Hz, 1H), 1.43 (s, 9H), 2.24 (s, 3H), 2.33 (dd, J = 14.9 Hz, 8.2 Hz, 1H), 2.60 (dd, J = 14.9 Hz, 8.2 Hz, 1H), 3.24 (m, 1H), 5.82 (dq, J = 3.1 Hz, 1H), 5.85 (d, J = 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.5 (q), 18.8 (q), 28.1 (q, 3C), 30.3 (d), 41.9 (t), 80.3 (s), 104.3 (d), 105.6 (d), 150.4 (s), 157.1 (s), 171.5 (s); anal. calcd. for $C_{13}H_{20}O_3$ (224.30): C 69.61, H 8.99; found: C 70.09, H 9.14.

***tert*-Butyl-3-(5-methylfuran-2-yl)propanoate (9h):** Prepared according to the general procedure D using of the unsaturated ester **7h** (500 mg, 2.40 mmol) in absolute MeOH (10 mL) and cyclohexene (5.00 mL, 48.0 mmol) and 5% Pd/C (150 mg). After 24 h the solution was filtered over celite and the residual solvent was concentrated under vacuum to afford the desired product **9h**; yield: 420 mg (83%). IR (film): $\tilde{\nu}$ = 2997, 2924, 1728, 1570, 1453, 1391, 1366, 1254, 1217, 1148, 1022, 958, 847, 781 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.44 (s, 9H), 2.24 (d, J = 1.0 Hz, 3H), 2.53 (t, J = 7.5 Hz, 2H), 2.86 (t, J = 7.5 Hz, 2H), 5.83 (dd, J = 3.1 Hz, 1.0 Hz, 1H), 5.86 (dd, J = 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.5 (q), 23.7 (t), 28.1 (q, 3C), 34.4 (t), 82.1 (s), 104.3 (d), 105.7 (d), 150.5 (s), 152.6 (s), 171.9 (s); MS (EI+, 70 eV): m/z (%) = 210 (13) [M^+], 211 (5), 157 (5), 154 (35), 111 (9), 95 (100), 57 (22), 28 (16); anal. calcd. for $C_{12}H_{18}O_3$ (210.28): C 68.54, H 8.63; found. C 68.42, H 8.46.

6-(5-Methylfuran-2-yl)-4-prop-2-yn-1-ylnon-1-yn-4-ol (10a): Prepared according to the general procedure **E** using **9a** (480 mg, 228 μmol) and the Grignard reagent (4.50 mL, 9.12 mmol). After removal of the solvent under vacuum and after purification it was possible to obtain **10a**; yield: 188 mg (33%). R_f (petrol ether:ethyl acetate, 10:1) = 0.29; IR (film): $\tilde{\nu}$ = 3295, 2958, 2934, 2871, 2120, 1769, 1052, 985, 854, 648. cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.85 (t, J = 7.3 Hz, 3H), 1.12–1.29 (m, 2H), 1.43–1.65 (m, 2H), 1.91–1.09 (m, 6H), 2.23 (s, 3H), 2.38 (m, 2H), 2.81–2.91 (m, 1H), 5.82 (d, J = 3.0 Hz, 1H), 5.90 (d, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.5 (q), 13.9 (q), 20.3 (t), 29.6 (t), 29.8 (t), 34.2 (d), 38.4 (t), 41.9 (t), 71.1 (d), 71.3 (d), 72.9 (s), 80.2 (s), 80.3 (s), 105.9 (d), 106.3 (d), 150.6 (s), 156.1 (s); MS (EI+, 70 eV): m/z (%) = 230 (18) [M^+], 191 (29), 173 (24), 109 (100), 43 (21), 39 (9); HR-MS (ESI+): m/z = 281.1512, calcd. for $[M + Na^+] = C_{17}H_{22}ONa$: 281.1517.

7-Methyl 6-(5-methylfuran-2-yl)-4-prop-2-yn-1-yloct-1-yn-4-ol (10b): Prepared according to the general procedure **E** using **9b** (80.0 mg, 320 μmol) and propargylmagnesium bromide (600 μL, 950 μmol). After removal of the solvent under vacuum and purification by column chromatography **10b** was obtained; yield: 30 mg (36%). R_f (petrol ether:ethyl acetate, 10:1) = 0.26; IR (film): $\tilde{\nu}$ = 3548, 3530, 3299, 2959, 2323, 2873, 1562, 1466, 1436, 1386, 1370, 1337, 1278, 1221, 1164, 1066, 1022, 951, 783 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.81 (d, J = 6.9 Hz, 3H), 0.95 (d, J = 6.9 Hz, 3H), 2.0–2.1 (m, 2H), 2.24 (s, 3H), 2.34 (m, 2H), 2.39 (t, J = 2.8 Hz, 2H), 2.68 (m, 1H), 5.84 (d, J = 2.9 Hz, 1H), 5.92 (d, J = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.6 (q), 19.6 (q), 20.6 (q), 29.66 (t), 29.7 (d), 32.0 (d), 33.2 (t), 40.3 (d), 71.3 (d, 2C), 72.9 (s), 80.3 (s), 80.3 (s), 105.8 (d), 107.1 8d), 150.6 (s), 155.4 (s); HR-MS: (EI+): m/z = 258.1602, calcd. for $M^+ = C_{17}H_{22}O_2$: 258.1620.

6-(5-Methylfuran-2-yl)-4-prop-2-yn-1-yldec-1-yn-4-ol (10d): Prepared according to the general procedure **E** using **9d** (120 mg, 535 μmol) and Grignard reagent (1.05 mL, 2.14 mmol). After removal of the solvent in vacuum it was possible to obtain a 1:1 mixture of **10d** and **11d**; yield: 92 mg (63%). These could not be separated. R_f (petrol ether:ethyl acetate, 3:1) = 0.36; IR (film): $\tilde{\nu}$ = 3299, 2925, 2857, 2359, 1956, 1567, 1524, 1506, 1457, 1432, 1377, 1340,

1310, 1219, 1188, 1161, 1124, 1021, 963, 909, 889, 849, 707, 631 cm^{-1}.

4-[2-(5-Phenylfuran-2-yl)propyl]hepta-1,6-diyn-4-ol (10e): Prepared according to the general procedure **E** using **10e** (561 mg, 1.96 mmol) and propargylmagnesium bromide (5.40 mL, 5.88 mmol). After removal of the solvent under vacuum and purification by column chromatography **10e** was obtained; yield: 352 mg (61%). R_f (petrol ether:ethyl acetate, 5:1) = 0.25; IR (film): $\tilde{\nu}$ = 3302, 3053, 2974, 1546, 1265, 1021, 790, 738, 704, 651 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.35 (d, J = 6.9 Hz, 3H), 1.94 (dd, J = 15.2 Hz, 4.74 Hz, 1H), 2.06 (t, 2H), 2.26 (dd, J = 15.2 Hz, 4.7 Hz, 1H), 2. 50 (m, 4H), 3.16 (m, J = 7.0 Hz, 1H), 6.11 (s, 1H), 6.5 (s, 1H), 7.20 (t, J = 7. 7 Hz, 1H), 7.33 (t, J = 7.7 Hz, 2H), 7.60 (d, J = 7.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.9 (q), 29.0 (d), 29.5 (t), 29.7 (t), 43.4 (t), 71.4 (d), 71.5 (d), 72.9 (s), 96.8 (s), 97.3 (s), 105.7 (d), 106.3 (d), 123.3 (d), 123.4 (d), 126.9 (d), 126.9 (d), 128. 6 (d, 2C), 131. 0 (s), 152.3 (s), 159.5 (s); HR-MS (FAB$^+$): m/z = 292.1467, calcd. for [M^+] = $C_{20}H_{20}O_2$: 292.1463.

4-(2-(5-Phenylfuran-2-yl)ethyl)hepta-1,6-diyn-4-ol (10f): Prepared according to the general procedure **E** using **9f** (870 mg, 3.78 mmol) and propargylmagnesium bromide (5.80 mL, 11.3 mmol). After removal of the solvent under vacuum and purification by column chromatography **10f** was obtained; yield: 701 mg (66%). R_f (petrol ether:ethyl acetate, 5:1) = 0.16; IR (film): $\tilde{\nu}$ = 3543, 3292, 2920, 2120, 1967, 1594, 1486, 1447, 1285, 1075, 1019, 964, 891, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.05 (m, 2H), 2.09 (m, 2H), 2.53 (m, 4H), 2.78 (m, 2H), 6.04 (d, 1H, J = 3.1 Hz), 6.47 (d, 1H, J = 3.1 Hz), 7.15 (m, 1H), 7.29 (m, 2H), 7.57 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 22.4 (t), 35.9 (t, 2C), 36.22 (t), 71.9 (d, 2C), 72.5 (s), 79.78 (s, 2C), 105.89 (d), 107.14 (d), 123.40 (d, 2C), 126.7 (d), 128.62 (d, 2C), 131.08 (s), 152.48 (s), 154.43 (s); anal. calcd. for $C_{19}H_{18}O_2$ (278.13): C 81.99, H 6.52; found: C 80.53 , H 6.52; HR-MS (ESI$^+$): m/z = 301.1199, calcd. for [M^+] = $C_{19}H_{18}NaO_2$: 301.1204.

4-[2-(5-Methylfuran-2-yl)propyl]hepta-1,6-diyn-4-ol (10g): Prepared according to the general procedure **E** using **9g** (554 mg, 2.47 mmol) and propargylmagnesium bromide (3.61 mL, 7.40 mmol). After removal of the solvent under vacuum and purification by column chromatography **10g** (yield:158 mg, 31%) and **11g** (yield:17 mg) were obtained.

10g: R_f (petrol ether:ethyl acetate, 7:1) = 0.25; IR (film): $\tilde{\nu}$ = 3293, 2965, 2921, 2858, 1957, 1710, 1614, 1566, 1435, 1362, 1280, 1219, 1069, 1019, 940, 852, 781, 633 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.32 (d, J = 7.2 Hz, 3H), 1.94 (dd, J = 14.7 Hz, 4.5 Hz, 1H), 2.09 (t, J = 2.4 Hz, 2H), 2.18 (dd, J = 14.7 Hz, 4.5 Hz, 1H), 2.25 (s, 3H), 2.55 (dd, J = 15.7 Hz, 2.4 Hz, 4H), 3.0 (m, J = 7.2 Hz, 4.5 Hz, 1H), 5.84 (dq, J = 3.1 Hz, 1.2 Hz, 1H), 5.88 (d, J = 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.5 (q), 21.9 (q), 28.9 (t), 29.6 (t), 29.9(t), 71.4 (d, 2C), 73.0 (s), 80.2 (d, 2C), 104.9 (d), 105.9 (d), 150.5 (s), 157.7 (s); MS (EI+, 70 eV): m/z (%) = 230 (18) [M^+], 191 (29), 173 (24), 109 (100), 43 (21), 39 (9); anal. calcd. for $C_{15}H_{18}O_2$ (230.30): C 78.23, H 7.88; found: C 77.76, H 8.00.

4-[2-(5-Methylfuran-2-yl)ethyl]hepta-1,6-diyn-4-ol (10h): Prepared according to the general procedure **E** using **9h** (400 mg, 1.90 mmol) and Grignard reagent (7.00 mL, 7.60 mmol). After removal of the solvent in vacuum **10h** (yield: 182 mg, 44%) and a mixture of **10h** and **11h** (yield: 24.2 mg, 3:7 mixture, thus the spectroscopic data of **11h** could be obtained when substracting the signals of pure **10h**) was obtaimed.

10h: R_f (petrol ether:ethyl acetate, 7:1) = 0.23; IR (film): $\tilde{\nu}$ = 3292, 2921, 2858, 1615, 1569, 1430, 1383, 1270, 1217, 1074, 1020, 995, 983, 947, 862, 781, 632 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.05 (m, 2H), 2.09 (t, J = 2.6 Hz, 2H), 2.25 (d, J = 1.2 Hz, 3H), 2.55 (dd, J = 16.6 Hz, 2.6 Hz, 4H), 2.73 (m, 2H), 5.84 (dq, J = 3.1 Hz, 1.2 Hz, 1H), 5.88 (d, J = 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.5 (q), 22.2 (t), 29.6 (t, 2C), 36.4 (t), 71.6 (s), 71.8 (d, 2C), 80.0 (s, 2C), 105.5 (d), 105.9 (d), 150.5 (s), 153.7 (s); MS (EI+, 70 eV): m/z (%) = 216 (7) [M^+], 177 (18), 159 (15), 135 (4), 96 (8), 95 (100), 77 (4), 43 (27), 32 (13), 28 (54), 18 (9); HR-MS (EI+, 70 eV): m/z = 216.1151, calcd. for $C_{14}H_{16}O_2$: 216.1144.

11h: R_f (petrol ether:ethyl acetate, 7:1) = 0.23; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.05 (m, 2H), 2.09 (t, 1H), 2.24 (s, 3H), 2.52 (dd, 2H), 2.73 (m, 2H), 4.98 (d, J = 6.7 Hz, 2H), 5.36 (t, J = 6.7 Hz, 1H), 5.83 (dq, J = 3.1 Hz, 1H), 5.86 (d, J = 3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.5 (q), 22.7 (t), 32.0 (t), 38.3 (t), 72.5 (d), 80.01 (s), 96.71 (s), 105.9 (d), 105.4 (d), 150.4 (s), 153.8 (s), 206.03 (s); $C_{14}H_{16}O_2$ (216. 28).

2-Methyl-5-propyl-7-prop-2-yn-1-yl-5,6,7,8-tetrahydronaphthalene-1,7-diol (13a): Prepared according to the general procedure **F** using **10a** (50.0 mg, 119 μmol) in acetonitrile-d_3 and $AuCl_3$ (2.93 mg, 9.39 μmol, 5 mol%). After removal of the solvent under vacuum **13a** was obtained as an orange oil; yield: 23.0 mg (46%). R_f (pentane:ethyl acetate = 10:3) = 0.25; IR (film): $\tilde{\nu}$ = 3412, 3271, 2955, 2932, 2870, 1631, 1493, 1464, 1303, 1226, 1037, 803, 647 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.93 (t, J = 7.3 Hz, 3H), 1.22–1.45 (m, 2H), 1.49–1.62 (m, 2H), 1.68 (s, 1H), 1.84–2.11 (m, 2H), 1.92–1.95 (m, 1H), 2.12 (t, J = 2.6 Hz, 2H), 2.18 (s, 3H), 2.54 (t, J = 2.5 Hz,1H), 2.80 (dd, J = 16.9 Hz, 1H), 3.05 (s, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.4 (q), 15.5 (q), 19.4 (t), 33.6 (d), 33.7 (t) 35.1 (t), 37.7 (t), 38.6 (t), 69.7 (d), 71.7 (s), 80.4 (s), 118.1 (d), 119.6 (s), 120.3 (s), 128.1 (d), 138.6 (s), 151.75 (s); HR-MS (ESI$^+$): m/z = 281.1512, calcd. for [M + Na$^+$] = $C_{17}H_{22}ONa$: 281.1514.

5-Isopropyl-2-methyl-7-(propyl-2-ynyl)-5,6,7,8-tetrahydronaphthalene-1,7-diol (13b): Prepared according to the general procedure **F** using **10b** (30.0 mg, 120 μmol) in acetonitrile-d_3 and $AuCl_3$ (1.8 mg, 12 μmol, 5 mol%). After removal of the solvent under vacuum **13b** was obtained as a brown oil; yield: 27 mg (87%). R_f (petrol ether:ethyl acetate = 10:1) = 0.05; IR (film): $\tilde{\nu}$ = 3416, 3303, 2958, 2928, 2871, 1462, 1422, 1308, 1227, 1194, 1091, 1057, 954 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 0.59 (d, J = 6.7 Hz, 3H), 1.04 (d, J = 6.7 Hz, 3H), 1.59 (m, 2H), 1.89 (m, 1H), 2.18 (s, 3H), 2.29 (t, J = 2.6 Hz, 1H), 2.47 (m, 1H), 2.50 (d, J = 2.6 Hz, 2H), 2.90 (dd, J = 16.5 Hz, 2.80 Hz, 1H), 2.99 (dd, J = 16.5 Hz, 2.8 Hz, 1H), 6.8 (d, J = 7.7 Hz, 1H), 6.96 (d, J = 7.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 15.7 (q), 20.9 (q), 29.3 (t), 30.8 (q), 34.3 (d), 35.3 (d), 36.1 (t), 39.8 (t), 70.0 (d), 71.8 (s), 80.9 (s), 119.0 (d), 119.4 (s), 121.5 (d), 128.4 (s), 138.5 (s), 152.2 (s); MS (FAB+, 70 eV): m/z (%) = 258 (24) [M^+], 241 (31), 217 (27), 201 (19), 176 (23), 154 (100), 137, 136 (100), 107 865); HR-MS (FAB$^+$): m/z = 258.1606, calcd. for [M^+] = $C_{17}H_{27}O_2$: 258.1620.

5-Butyl-2-methyl-7-prop-2-yn-1-yl-5,6,7,8-tetrahydronaphthalene-1,7-diol (13d): Prepared according to the general procedure **F** using **10d** (40.0 mg, 147 μmol as a 1:1 mixture with 40 mg **11d**) in acetonitrile-d_3 and $AuCl_3$ (2.23 mg, 7.39 μmol, 5 mol%). After removal of the solvent under vacuum and purification **13d** was obtained as a brown oil; yield: 27.0 mg (67%). R_f (pentane:ethyl acetate:dichloromethane = 3:1:2) = 0.29; IR (film): $\tilde{\nu}$ = 3534, 3291, 2929, 2859, 2218, 2142, 1578, 1492, 1460, 1421, 1378, 1310, 1226, 1101, 1051, 814, 698 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 0.94 (t, J = 7.0 Hz, 3H), 1.26–1.40 (m, 4H), 1.55 (m, 1H), 1.66 (m, 1H), 1.92 (m, 2H), 2.11 (dd, J = 5.7 Hz, 2.7 Hz, 1H), 2.14 (dd, J = 5.7 Hz, 2.7 Hz, 1H), 2.23 (s, 3H), 2.54 (t, J = 2.7 Hz, 1H), 2.73 (d, J = 16.9 Hz, 1H), 2.98 (d, J = 16.9 Hz, 1H), 3.09 (m, 1H), 6.91 (d, J = 8.0 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.1 (t), 15.6 (q), 23.1 (t), 28.4 (d), 33.7 (t), 33.8 (t), 35.1 (t), 35.2 (t), 38.6 (t), 69.8 (d), 71.8 (s), 80.4 (s), 118.8 (s), 119.6 (d), 120.4 (s), 128.2 (d), 138.7 (s), 151.8 (s).

5-Methyl-2-phenyl-7-prop-2-yn-1-yl-5,6,7,8-tetrahydronaphthalene-1,7-diol (13e): Prepared according to the general procedure **F** using **10e** (50.0 mg, 170 μmol) in acetonitrile-d_3 and $AuCl_3$ (2.6 mg, 17 μmol, 5 mol%). After removal of the solvent under vacuum and purification **13e** was obtained as a brown oil; yield: 25.2 mg (50%). R_f (pentane:ethyl acetate:dichloromethane = 3:1:2) = 0.25; IR (film): $\tilde{\nu}$ = 3547, 3299, 2928, 1562, 1424, 1229, 1132, 1020, 811, 747, 703 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.36 (d, J = 6.8 Hz, 3H), 1.52 (s, 1H), 1.88 (bs, OH), 2.06 (dd, J = 5.8, 2.6 Hz, 1H), 2.17 (t, J = 2.5 Hz, 1H), 2.54 (t, J = 2.7 Hz, 2H), 2.73 (dd, J = 17.9, 2.60 Hz, 2H), 2.98 (dd, J = 17.9, 2.6 Hz, 1H), 3.15 (m, J = 6.8 Hz, 1H), 6.99 (d, J = 7.5 Hz, 1H), 7.08 (d, J = 7.8 Hz, 1H), 7.33–7.51 (m, 5H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.15 (q), 22.8 (d), 34.3 (t), 36.0 (t), 42.3 (t), 69.8 (d), 71.9 (s), 80.8 (s), 119.0 (d), 121.4 (s), 125. 3 (s), 127.6 (d), 128.2 (d), 129.5 (d, 2C), 129.9 (d, 2C), 137.9 (s), 142.3 (s), 150.6 (s); MS (FAB+, 70 eV): m/z (%) = 292 (52) [M^+], 275 (70), 249 (37), 235 (100), 233 (38), 221 (39), 202 (19), 178 (20); HR-MS (FAB$^+$): m/z = 292.1440, calcd. for [M^+] = $C_{20}H_{20}O_2$: 292.1463.

2-Phenyl-7-prop-2-yn-1-yl-5,6,7,8-tetrahydronaphthalene-1,7-diol (13f): Prepared according to the general procedure **F** using **10f** (20.0 mg, 72.5 μmol) in acetonitrile-d_3 and $AuCl_3$ (1.1 mg, 3.63 μmol, 5 mol%). After removal of the solvent under vacuum and purification **13f** was obtained as a brown oil; yield: 17.2 mg (87%). R_f (pentane:ethyl acetate:dichloromethane = 3:1:2) = 0.27; ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.82 (m, 1H), 1.94 (m, 1H), 2.07 (t, J = 2.5 Hz, 1H), 2.48 (dd, J = 2.5 Hz, 2H), 2.65–3.0 (m, 4H), 4.50 (bs, 1H), 5.27 (bs, 1H), 6.74 (d, J = 7.8 Hz, 1H), 7.03 (d, J = 7.8 Hz, 1H), 7.33 (m, 2H), 7.40 (m, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 26.1 (t), 32.4 (t), 32.7 (t), 35.5 (t), 69.7 (d), 71.82 (s), 80.3 (s), 120.7 (d), 121.3 (d), 123.4 (d), 125.0 (d), 127.9 (d), 128.6 (s), 129.5 (d), 136.5 (s), 137.2 (s), 150.4 (s); HR-MS (ESI$^+$): m/z = 301.1199, calcd. for [M + Na^+] = $C_{19}H_{18}O_2Na$: 301.1204.

2,5-Dimethyl-7-prop-2-yn-1-yl-5,6,7,8-tetrahydronaphthalene-1,7-diol (13g): Prepared according to the general procedure **F** using **10g** and **11g** (50.0 mg, 217 μmol containing additional 10% **11g**) in acetonitrile-d_3 and $AuCl_3$ (3.30 mg, 10.9 μmol, 5 mol%). After removal of the solvent under vacuum and purification the desired phenol **13g** was obtained as brown oil; yield: 33.3 mg (67%). R_f (pentane:ethyl acetate:dichloromethane = 3:1:2) = 0.25; IR (film): $\tilde{\nu}$ = 3534, 3294, 2996, 2926, 2871, 2360, 2244, 2117, 1577, 1493, 1461, 1420, 1380, 1328, 1226, 1133, 1096, 1021, 909, 893, 870, 807, 732, 696, 650, 635, 591 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.35 (d, J = 7.1 Hz, 3H), 1.5 (t, J = 2.7 Hz, 1H), 1.94 (bs, OH), 2.03 (dd, J = 5.7 Hz, 2.7 Hz, 1H), 2.07 (dd, J = 5.7 Hz, 2.7 Hz, 1H), 2.13 (t, J = 2.7 Hz, 1H), 2.20 (s, 3H), 2.54 (t, J = 2.7 Hz, 2H), 2.73 (d, J = 16.9 Hz, 1H), 2.90 (d, J = 16.9 Hz, 1H), 3.15 (m, 1H), 6.88 (d, J = 8.0 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 15.6 (q), 21.1 (q), 28.9 (d), 33.8 (t), 35.4 (t), 42.0 (t), 69.7 (d), 71.8 (s), 80.4 (s), 118.5 (s), 120.2 (d), 120.6 (s), 128.2 (d), 139.7 (s), 151.7 (s); MS (EI+, 70 eV): m/z (%) = 230 (30) [M^+], 191 (30), 173 (100), 158 (13), 148 (14), 121 (9), 77 (5), 53 (6); HR-MS (EI+, 70 eV): m/z = 230.1304, calcd. for $C_{15}H_{18}O_2$: 230.1307.

2-Methyl-7-prop-2-yn-1-yl-5,6,7,8-tetrahydronaphthalene-1,7-diol (13h): Prepared according to the general procedure **F** using **10h** (20.0 mg, 92.5 μmol) in acetonitrile-d_3 and $AuCl_3$ (1.47 mg, 4.63 μmol, 5 mol%). After removal of the solvent under vacuum and purification the desired phenol **13h** was obtained as brown solid; yield: 13.2 mg (66%); mp 85 °C. R_f (pentane:ethyl acetate:dichloromethane = 3:1:2) = 0.10; IR (film): $\tilde{\nu}$ = 3290, 2927, 2360, 2341, 1581, 1494, 1462, 1422, 1381, 1322, 1226, 1183, 1041, 1008, 964, 874, 755, 744, 605 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.80 (m, 2H), 2.06 (t, J = 2.5 Hz, 1H), 2.14 (s, 3H), 2.45 (dd, J = 2.5 Hz, 2H), 2.72 (m, 1H), 2.75 (m, 2H), 2.96 (m, 1H), 4.50 (bs, 1H), 6.60 (d, J = 8.1 Hz, 1H), 6.85 (d, J = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 15.5 (q), 26.0 (t), 32.1 (t), 32.8 (t), 35.3 (t), 69.8 (d), 71.8 (s), 80.2 (s), 119.6 (s), 120.2 (d), 120.6 (s), 128.1 (d), 134.3 (s), 151.9 (s); MS (EI+, 70 eV): m/z (%) = 216 (63)[M^+], 217 (10), 198 (32), 178 (2), 177 (75), 159 (100), 135 (4), 91 (18), 77 (9), 39 (2), 28 (2); anal. calcd. for $C_{14}H_{16}O_2$ (216.28): C 77.75, H 7.46; found: C 77.52, H 7.55.

***tert*-Butyldimethyl{4-[2-(5-methylfuran-2-yl)propyl]hepta-1,6-diyn-4-yloxy}silane (15):** 260 mg (1.13 mmol) **10g** were dissolved in 5 mL DCM and cooled to 0 °C. After the addition of 520 μL (2.26 mmol) TBDMSOTf and 526 μL (4.52 mmol) lutidine, the solution was stirred for 2 d at room temperature. After the addition of 5 mL H_2O, the aqueous phase was extracted three times with 5 mL dichloromethane. The combined organic phases were dried over $MgSO_4$, filtered and the solvent was removed under vacuum. After purification by column chromatography (SiO_2, hexanes), **15** was obtained as a colourless oil; yield: 317 mg (920 μmol, 81%). R_f (PE) = 0.11. IR (film): $\tilde{\nu}$ = 3310, 2957, 2929, 2886, 2857, 2249, 2121, 1472, 1462, 1255, 1222, 1111, 1061, 1018, 990, 940, 910, 836, 815, 776, 736, 643 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = 0.15 (s, 3H), 0.17 (s, 3H), 0.91 (s, 9H), 1.26 (d, ^3J = 7.0 Hz, 3H), 1.86 (dd, ^2J = 14.4 Hz, ^3J = 4.4 Hz, 1H), 1.99 (t, ^4J = 2.7 Hz, 1H), 2.03 (t, ^4J = 2.7 Hz, 1H), 2.20–2.29 (m, 4H), 2.38 (d, ^4J = 2.7 Hz, 2H), 2.38 (dd, ^2J = 16.4 Hz, ^4J = 2.7 Hz, 1H), 2.51 (dd, ^2J = 16.4 Hz, ^4J = 2.7 Hz, 1H), 2.99–3.11 (m, 1H), 5.79–5.86 (m, 2H). ^{13}C NMR ($CDCl_3$, 126 MHz): δ = −1.99 (q), −1.97 (q), 13.65 (q), 18.66 (s), 22.70 (q), 26.08 (q, 3 C), 28.89 (d), 29.70 (t), 31.42 (t), 44.84 (t), 70.95 (d), 71.38 (d), 76.61 (s), 81.29 (s), 81.39 (s), 104.64 (d), 105.87 (d), 150.16 (s), 158.39 (s); HR-MS (ESI+): m/z = 383.1809, calcd. for $C_{21}H_{32}KO_2Si$: 383.1809.

7-(*tert*-Butyldimethylsilyloxy)-2,5-dimethyl-7-(prop-2-ynyl)-5,6,7,8-tetrahydronaphthalen-1-ol (16): 110 mg (319 μmol) **15** were dissolved in 3 mL CH_3CN and the solution was cooled to 0 °C. After the addition of 2.90 mg (9.57 μmol) $AuCl_3$ the starting material was fully converted after 10 min. Analysis of the crude mixture by GCMS, showed a *dr* of 87:13 (the same *dr* was measured during a test reaction at room temperature as well). Purification of the crude product by column chromatography (SiO_2, PE:EA, 100:1) afforded the major diastereoisomer **16a** (yield: 62.0 mg, 180 μmol, 56%) and the minor diastereoisomer **16b** (yield: 10.1 mg, 29.0 μmol, 9%), both as yellow oils.

Major diastereoisomer 16a: R_f (PE:EA, 50:1) = 0.11. IR (film): $\tilde{\nu}$ = 3559, 3310, 2955, 2929, 2856, 2249, 2120, 1463, 1359, 1328, 1308, 1254, 1224, 1178, 1112, 1067, 979, 908, 836, 807, 774, 735, 637 cm^{-1}; ^1H NMR ($CDCl_3$, 250 MHz): δ = −0.24 (s, 3H), 0.11 (s, 3H), 0.74 (s, 9H), 1.33 (d, J = 6.9 Hz, 3H), 1.52–1.62 (m, 1H), 1.96–2.04 (m, 1H), 2.06 (t, J = 2.7 Hz, 1H), 2.23 (s, 3H), 2.56–2.57 (m, 2H), 2.83 (d, J = 17.3, 1H), 2.92 (d, J = 17.3 Hz, 1H), 3.06–3.18 (m, 1H), 4.57 (s, 1H), 6.85 (d, J = 7.9 Hz, 1H), 6.96 (d, J = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = −3.18 (q), −2.18 (q), 15.68 (q), 18.43 (s), 21.13 (q), 25.84 (q, 3 C), 29.26 (d), 34.27 (t), 35.13 (t), 43.44 (t), 71.14 (d), 73.08 (s), 81.51 (s), 118.52 (d), 119.18 (s), 120.86 (s), 127.93 (d), 140.55 (s), 151.51 (s); HR-MS (ESI+): m/z = 367.2064, calcd. for $C_{21}H_{32}NaO_2Si$: 367.2069.

Minor diastereoisomer 16b: R_f (PE:EA, 50:1) = 0.07. IR (film): $\tilde{\nu}$ = 3541, 3310, 2956, 2928, 2856, 2249, 2120, 1714, 1490, 1462, 1359, 1257, 1113, 1067, 1008, 979, 909, 836, 822, 807, 774, 735 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz): δ = −0.26 (s, 3H), 0.09 (s, 3H), 0.71 (s, 9H), 1.30 (d, J = 6.9 Hz, 3H), 1.52–1.54 (m, 1H), 1.95–1.99 (m, 1H), 2.05 (t, J = 2.5 Hz, 1H), 2.12 (s, 3H), 2.49–2.57 (m, 2H), 2.77 (d, J = 17.2 Hz, 1H), 2.89 (d, J = 17.2 Hz, 1H), 3.04–3.12 (m, 1H), 4.51 (s, 1H), 6.64 (d, 8.5 Hz, 1H), 7.05 6 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = −3.11 (q), −2.14 (q), 11.38 (q), 18.34 (s), 21.40 (q), 25.79 (q, 3 C), 29.09 (d), 34.33 (t), 39.11 (t), 43.45 (t), 71.09 (d), 73.52 (s), 81.54 (s), 112.91 (d), 121.52 (s), 124.56 (d), 133.78 (s), 134.58 (s), 151.26 (s); HR-MS (ESI+): m/z = 383.1803, calcd. for $C_{21}H_{32}KO_2Si$: 383.1809.

[2,5-Dimethyl-7-(prop-2-ynyl)-5,6,7,8-tetrahydronaphthalene-1,7-diyl]bis(oxy)bis(*tert*-butyldimethylsilane) (17): 50.0 mg of **10g** were dissolved in 5 mL of dichloromethane and the solution was cooled to 0 °C. After the addition of 202 μL (1.74 mmol) lutidine and 199 μL (868 μmol) TBDMSOTf, the reaction mixture was stirred for 3 d at room temperature. After the addition of 5 mL water, the mixture was extracted three times with 5 mL of dichloromethane, the combined organic phases were dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (SiO_2, PE). The disilylated compound was obtained as a colourless oil; yield: 89.1 mg (194 μmol, 89%). R_f (PE) = 0.21. IR (film): $\tilde{\nu}$ = 3313, 2955, 2930, 2886, 2858, 1472, 1462, 1416, 1325, 1256,1211, 1137,1113, 1066, 1006, 979, 937, 924, 835, 808, 777 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): δ = −0.27 (s, 3H), 0.10 (s, 3H), 0.23 (s, 3H), 0.24 (s, 3H), 0.74 (s, 9H), 1.08 (s, 9H), 1.35 (d, J = 6.8 Hz, 3H), 1.52–1.57 (m, 1H), 1.98 (ddd, J = 13.2, 5.8, 2.7, 1H), 2.06 (t, J = 2.7 Hz, 1H), 2.21 (s, 3H), 2.50 (dd, J = 16.4, 2.7 Hz, 1H), 2.55 (dd, J = 16.4, 2.7 Hz, 1H), 2.82 (d, J = 17.0, 1H), 2.98 (dd, J = 17.0, 2.7 Hz, 1H), 3.05–3.13 (m, 1H), 6.89 (d, J = 7.9 Hz, 1H), 6.97 (d, J = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = −3.36 (q), −2.56 (q), −2.41 (q), −2.25 (q), 17.73 (q), 18.29 (s), 18.31 (s), 21.46 (q), 25.86 (q, 3 C), 26.39 (q, 3C), 29.69 (d), 34.31 (t), 36.90 (t) ,43.67 (t), 70.94 (d), 73.44 (s), 81.67 (s), 119.66 (d), 125.10 (s), 125.91 (s), 128.36 (d), 140.09 (s), 151.65 (s); HR-MS (ESI+): m/z = 481.2939, calcd. for $C_{27}H_{46}NaO_2Si_2$: 481.2934.

The compound from the previous experiment was deprotected to furnish **16a** as follows: 51.5 mg (116 μmol) **17** were dissolved in 3 mL THF and cooled to 0 °C. After the addition of 73.2 mg (232 μmol) TBAF·3 H_2O, the reaction was stirred for 5 min. 5 mL H_2O were added and the solution was extracted three times with dichloromethane (5 mL). After drying over $MgSO_4$ and filtration, the solvent was removed under vacuum. Column chromatography on silica (PE:EA, 50:1) afforded **16a** as a yellow oil; yield: 38.3 mg (111 μmol, 96%). R_f (PE:EA, 50:1) = 0.11; ^1H NMR ($CDCl_3$, 250 MHz): δ = −0.24 (s, 3H), 0.11 (s, 3H), 0.74 (s, 9H), 1.33 (d, J = 6.9 Hz, 3H), 1.52–1.62 (m, 1H), 1.96–2.04 (m, 1H), 2.06 (t, J = 2.7 Hz, 1H), 2.23 (s, 3H), 2.56–2.57 (m, 2H), 2.83 (d, J = 17.3, 1H), 2.92 (d, J = 17.3 Hz, 1H), 3.06–3.18 (m, 1H), 4.57 (s, 1H), 6.85 (d, J = 7.9 Hz, 1H), 6.96 (d, J = 7.9 Hz, 1H). These data are in accordance with the data of **16a** obtained in the cyclization of **15**.

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