Mercury(II)-Catalyzed Synthesis of Spiro[4.5]decatrienediones from Allenyl Ketones and Comparison with Silver(I)-, Palladium(II)- and Brønsted Acid-Catalyzed Reactions

A. Stephen K. Hashmi*, Lothar Schwarz, and **J. W. Bats**

Frankfurt am Main, Institut für Organische Chemie der Johann Wolfgang Goethe-Universität

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Abstract. The allenyl *p*-methoxybenzyl ketone **3a** and allenyl *p*-siloxybenzyl ketones **6b** selectively delivered three different products with three different transition metal-catalysts. With Hg(II)-catalysts a spiro[4.5]decene **9**, with Ag(I)-catalysts a 2-substituted furan (**10**/**11**) and with Pd(II)-catalysts a 2,4-disubstituted furan (**8**/**12**) was formed. Only with perchloric acid the intermolecular addition of water to the allene, leading to 1,3-dicarbonyl compounds **7**, was observed. While with the corresponding allenyl *o*-methoxybenzyl ketone **3b** the Ag(I)- and Pd(II)-catalysts provided the expected products, the mercury-catalyst led to a new and interesting side-product rac-**17** which combined both the furan moiety and the spiro[4.5]decene moiety. Efforts to prepare allenyl hydroxybenzyl ketones failed, in one case a small amount of a 5*H*-benzo[b]oxepin-4-one **21** was isolated. It also was not possible to extend the spirocyclization to allenyl *p*-siloxyphenyl ketone **6a** or allenyl 2-(*p*-siloxyphenyl)ethyl ketone **6c**.

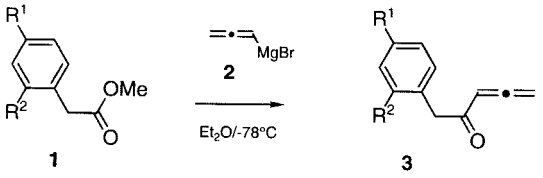
The synthesis of the spiro[4.5]decane terpene skeleton from methoxy [1] and hydroxy [2] substituted arenes has been stimulated by the interest in naturally occuring sesquiterpenes like spirovetivanes, acorones or alaskanes [1b,3] and their analogues. Among these methods is Nagao's approach [4] that utilizes easily available allenyl benzyl ketones and *stoichiometric* amounts of Lewis acids (LA) like $BF_3 \cdot Et_2O$, ZnI_2 or $AlCl_3$. One major synthetic limitation of this method was the need of *at least two* methoxy substituents on the aromatic system. With only one methoxy group, the yield dropped from more than 80% to 8%.

We were interested in overcoming both limitations *i.e.* to use *catalytical* amounts of lewis acids and *only one* methoxy substituent. We also wanted to address the question of selectivity, since it was known from work of Marshall's and our groups [5, 6] that silver or palladium catalysts are able to cause a cycloisomerization of the allenyl ketone to a furan.

Recently, we published preliminary results concerning the spirocyclization [7]. Here, we now want to report the mercury-catalyzed reactions in full detail and compare them with silver-, palladium-, and Brønsted acid-catalyzed reactions.

Synthesis of the Substrates

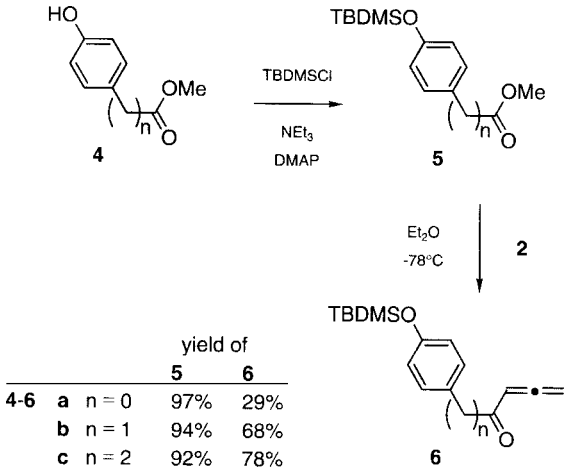
One class of substrates used in this investigation were the allenyl methoxybenzyl ketones **3a**–**b**. They were prepared by the addition of allenylmagnesium bromide (**2**) to the esters **1a**–**b** at –78 °C.



1a,**3a**	R^1 = OMe, R^2 = H	49%
1b,**3b**	R^1 = H, R^2 = OMe	57%

Scheme 1 Synthesis of allenyl methoxybenzyl ketones **3**

Starting from phenols **4a**–**c**, the TBDMS-protected **5a**–**c** delivered **6a**–**c** by the same low temperature addition of **2**.



			yield of 5	yield of 6
4-6	**a**	n = 0	97%	29%
	b	n = 1	94%	68%
	c	n = 2	92%	78%

Scheme 2 Synthesis of allenyl ketones **6** containing *p*-(*t*-butyldimethylsilanyloxy)phenyl groups

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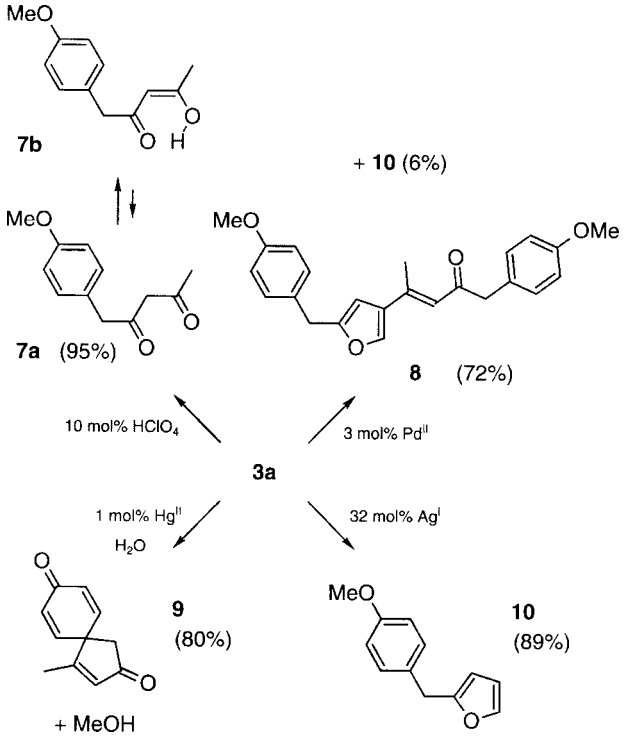
Catalysis Reactions

The substrate **3a** was first subjected to 10 mol% perchloric acid in aqueous acetonitrile (MeCN). Under these conditions only the 1,3-dicarbonyl compound **7a** (in equilibrium with the corresponding enol **7b**) was formed. This mode of reaction is not unexpected, it is well known that strong acids catalyze the addition of water to allenes (as well as to the isomeric alkynes) [8]. On the other hand, under similar conditions $PdCl_2(MeCN)_2$ mainly led to **8** (accompanied by small amounts of **10** as reported previously), and $AgNO_3$ delivered **10** as the exclusive product. With $Hg(ClO_4)_2$, again under similar conditions, 80% of **9** and only 6% of **7a**/**b** were isolated. The mercury-catalyzed addition of water to allenes and the isomeric alkynes is well documented in the literature [9]. Both, the structure of **8** (Figure1) [10] and **9** [7] have been proven by X-ray crystal structure analyses.



Scheme 3 Reactions of allenyl ketone **3a** with different catalysts

In the solid state the middle part of **8** (the furan ring, the double bond and the carbonyl group) is essentially coplanar [tilts of 8.2(3)° and 9.7(2)°], and the outer phenyl groups are almost orthogonal to that middle part [81.2(1)° and 60.2(1)°]. The conformation of the α,β-unsaturated system is, like in other related derivatives [6c,d], *s-cis*. And also the relative arrangement of the vinyl group and the furyl group is identical with the conformations observed in related derivatives before: The hydrogen at the 3-position of the furan points toward the hydrogen atom of the trisubstituted double bond and the methyl group toward the hydrogen atom at the 5-position. The NOE-data are in accordance with this being the main conformer, the minor conformer is the one with the opposite arrangement. There is only one significant short intermolecular distance, O1 and H4 of neighbouring molecules are separated by 2.44(1)Å.

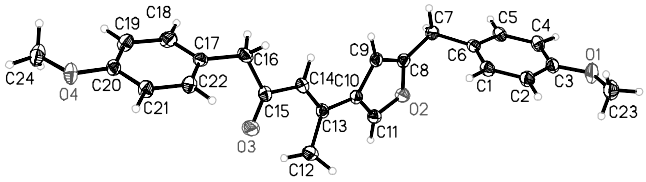


Fig. 1 ORTEP diagram of 1-(4-methoxybenzyl)-3-[5-(4-methoxybenzyl)furan-3-yl]but-2-en-1-one (**8**)

NMR studies on **8** ($^1H,^1H$-COSY, HSQC and NOESY, see Figure 2) revealed that a similar conformation seems to be the major conformer in solution. But a second set of weak cross-peaks indicated that the other conformer is also populated.

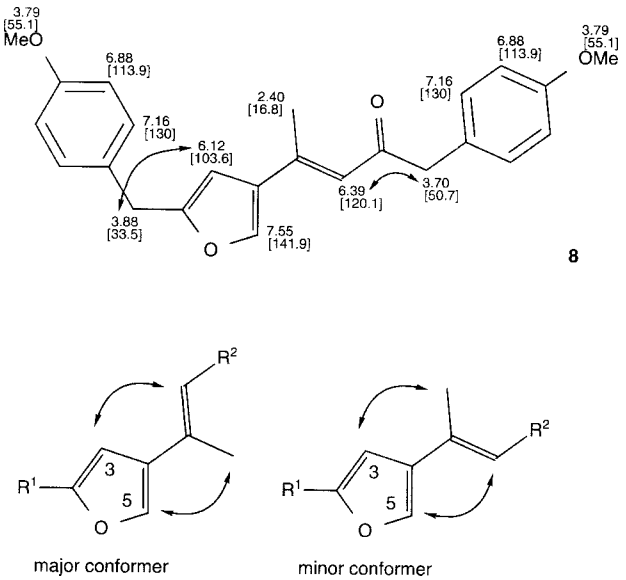


Fig. 2 Assignment of the ^1H (numbers without brackets) and ^{13}C (numbers in brackets) NMR signals of **8** obtained from $^1H,^1H$-COSY, HSQC and important cross-peaks obtained from NOESY spectra (arrows)

With $Hg(ClO_4)_2$ the optimal solvent was MeCN containing 2 eqs. of water. In wet ethyl acetate, acetone and dichloromethane the reaction was slower and lower yields were obtained. In *n*-hexane no reaction was observed. Several other mercury salts and Lewis acids that tolerate water were also tested. The results are shown

in Table 1. As one can see, $Hg(NO_3)_2$, $Hg(OAc)_2$ and $HgSO_4$ also show some catalytic activity, but $Hg(ClO_4)_2$ was the optimal catalyst. Obviously a weakly coordinating ligand at Hg^{2+} was necessary. In the absence of water the reaction failed.

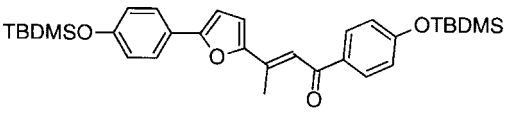
Table 1 Reactions of **3a** with different Lewis-acids that tolerate water

Lewis-acid	solvent	yield (%) of **9**
5 mol% $Hg(ClO_4)_2$	MeCN	80
6 mol% $Hg(ClO_4)_2$	acetone	45
10 mol% $Hg(ClO_4)_2$	CH_2Cl_2	66
10 mol% $Hg(ClO_4)_2$	Et_2O	– [a])
10 mol% $Hg(ClO_4)_2$	ethyl acetate	– [b])
10 mol% $Hg(ClO_4)_2$	*n*-hexane	– [a])
10 mol% $Hg(NO_3)_2$	MeCN	47 [c])
10 mol% $HgCl_2$	MeCN	– [a])
10 mol% $Hg(OAc)_2$	MeCN	– [a])
10 mol% $Hg(SCN)_2$	MeCN	– [a])
10 mol% $HgSO_4$	MeCN	55 [c])
10 mol% $InCl_3$	MeCN	– [a])
10 mol% $Tl(ClO_4)_3$	MeCN	– [a])
10 mol% $Sc(SO_2CF_3)_3$	MeCN	– [a])

[a]) no reaction. [b]) starting material completely consumed, but only polymeric material was formed. [c]) slow reaction.

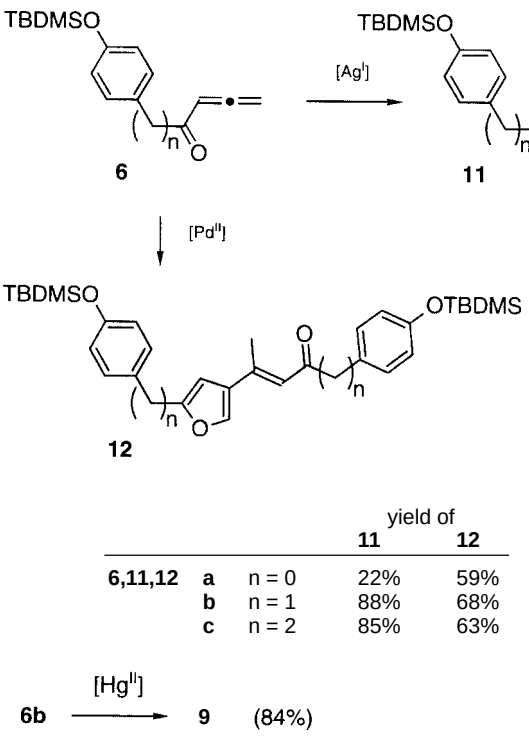
The allenyl ketones **6a**–**c** reacted with the Ag(I)- and Pd(II)-catalysts in the expected manner, leading either to **11a**–**c** or to **12a**–**c**. When **6b** was subjected to Hg(II) under the optimal conditions mentioned above, an even higher yield of **9** was observed (84%). This might be explained by the higher kinetic lability of the O–Si-bond that might be broken during the reaction. Efforts to extend this reaction to the synthesis of four- or six-membered rings, failed. Neither from **6a** nor from **6c** any spirocycles were obtained.

An interesting aspect of the Ag(I)-catalyzed reaction of **6a** is the side product **13** which was isolated in 14% yield. It is a constitutional isomer of **12a**, the product of the Pd(II)-catalyzed reaction. The formation of **13** is still under investigation.

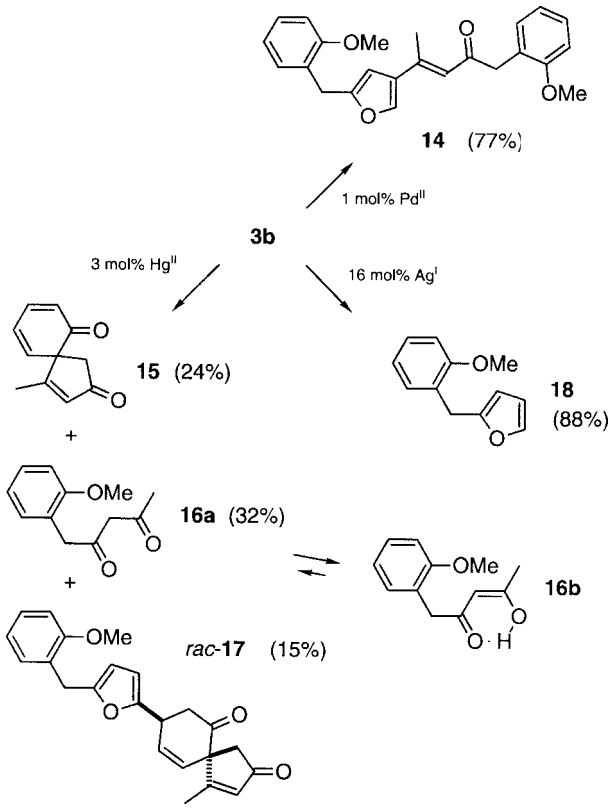


13 (14%)

Then we investigated the reactivity of **3b**. Again with Pd(II) and Ag(I), the expected furans **14** and **18** were obtained. With Hg(II) the reaction was slow (120 h instead of 1 h for **3a**) and only 24% of the spirocycle could be isolated. The major product was **16a** (32%, again in equilibrium with small amounts of the corresponding enol **16b**). Quite unexpected was another side product that combined both structural motives, a spiro[4.5]decane and a furan, the compound *rac*-**17**, which was formed in 15% yield.



Scheme 4 Reactions of allenyl ketones **6** with different catalysts



Scheme 5 Reactions of allenyl ketone **3b** with different catalysts

The structural assignment for *rac*-**17** is based on ^{1}H, ^{13}C, $^{1}H,^{1}H$-COSY, $^{13}C,^{1}H$-COSY, $^{13}C,^{1}H$-HMBC and NOESY spectra [11]. The ^{1}H and ^{13}C assignments and crucial NOESY-crosspeaks for the assignment of the relative configuration of the two stereogenic centers in *rac*-**17** are summarized in Figure 3.

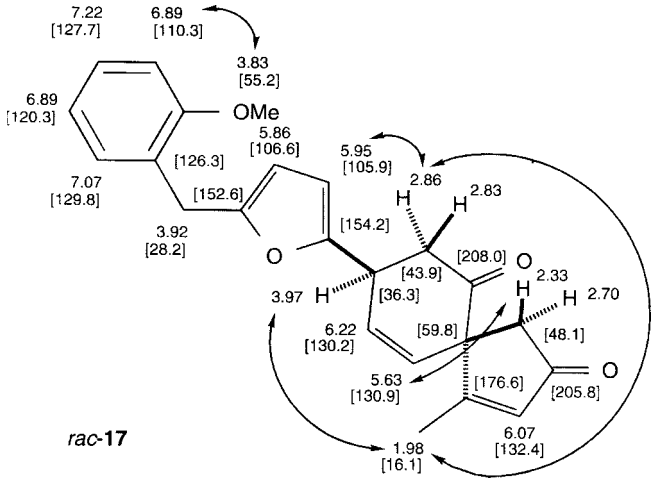
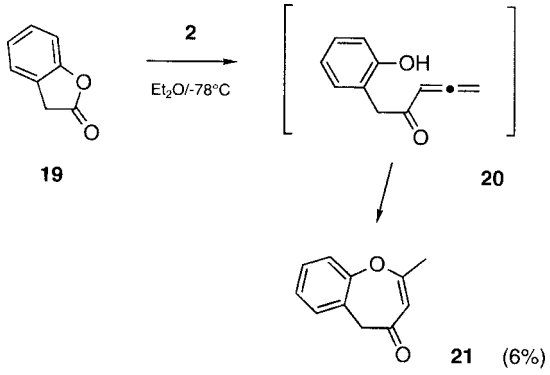


Fig. 3 Assignment of the ^{1}H (numbers without brackets) and ^{13}C (numbers in brackets) NMR signals of *rac*-**17** obtained from $^{1}H,^{1}H$-COSY, $^{13}C,^{1}H$-COSY, HMBC and important cross-peaks obtained from NOESY spectra (arrows)

In order to test a free hydroxyl-group with a proton as an even better leaving group for the spirocyclization, we tried to synthesize allenyl *p*-hydroxybenzyl ketones. Efforts to deprotect **6b** failed, only the formation of oligomeric or polymeric material was observed. Then we tried to obtain the allenyl *o*-hydroxybenzyl ketone **20** following our standard route from **19** and **2**. Apart from polymeric material only 6% of the seven-membered cyclic vinyl ether **21** were obtained. The structure of **21** has also been proven by an X-ray crystal structure analysis [7]. Comparable formations of a seven-membered heterocycle by the intramolecular addition of an *O*-nucleophile to an allene have been reported before [12].



Scheme 6 Formation of *5H*-benzo[b]oxepin-4-one **21**

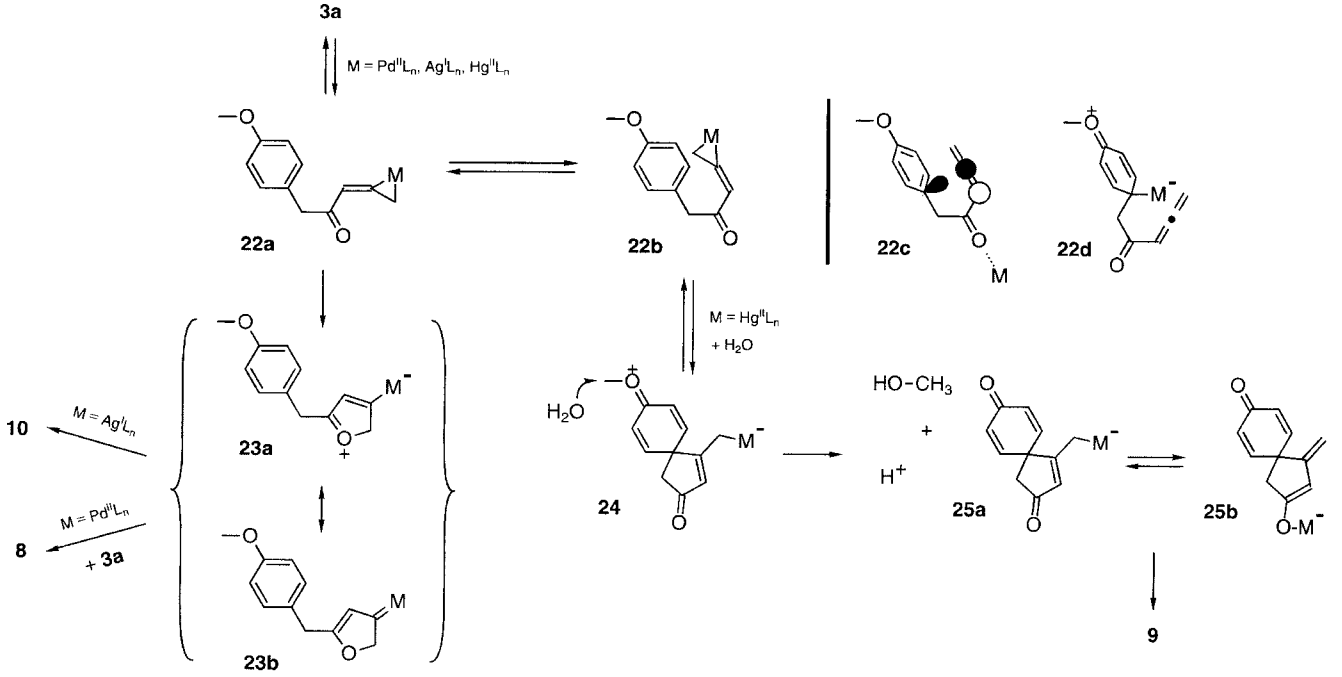
Mechanistic Considerations

Now the question arose, why these quite simple salts or complexes of different transition metals led to different products. This shall be discussed for the reaction of **3a**. The Ag(I)- and Pd(II)-systems have been compared before [6c], one suggestion for the selective formation of either **10** or **8** was that only in the case of metal M = Pd(II) the intermediate **23** lives long enough to react with a second molecule of **3a**, for M = Ag(I) a fast formation of **10** takes place. In both these reactions, the electrophilic metal first coordinates to the electron-rich and less substituted terminal double bond of the allene as shown in **22**. This coordination will allow a nucleophilic attack by the carbonyl-oxygen only if it takes place from the face opposite to the carbonyl-substituent on the allene. Furthermore, the conformation **22a** (*s-cis* for the enone) is necessary. For the spirocyclization things look similar, it is exactly the same face of the terminal double bond that was mentioned above to react with the nucleophilic oxygen after coordination to the metal that now will have to react with the (nucleophilic) aromatic system by an electrophilic attack. Here only the *s-trans* conformer **23b** can react in the desired manner (connecting the central carbon of the allene to the *ipso*-carbon of the arene). For geometrical reasons we favor the model of a coordination of the soft Hg(II) to the terminal double bond of the allene as shown in **22b** which will yield **24**. A coordination to the carbonyl group (as in **22c**) would activate a π-orbital with lobes orthogonal to those of the aromatic ring. A third possibility would be an *ipso*-mercuration of the electron-rich aromatic ring (**22d**), followed by a 1,4-addition to the Michael-acceptor substructure of the allenylketone, but for simple geometric reasons such an 5-*endo-trig* cyclization (carbomercuration of the enone) is not favourable (Scheme 7).

Then a nucleophilic substitution at the methyl-group or a nucleophilic attack at the arene-carbon of **24** with water as the nucleophile will ultimately form methanol, a proton and the mercury dienolate **25**. The proton finally sets free the product **9** and the transition catalyst.

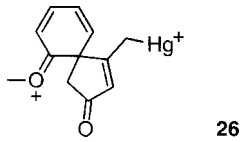
With the various metals the rates for these processes seem to be quite different. So with Ag(I) and Pd(II) no **9** was formed. On the other hand, when the spirocyclization was slow, as with the *o*-methoxybenzyl derivative **3b**, the formation of *rac*-**17** suggests that some of the furan **27** was also produced with Hg(II).

We now would like to suggest that the different abilities for back-bonding and the charge of the metal ion are responsible for this behaviour. In the case of Pd(II) back-donation is feasible, the intermediate **23** is easily accessible and profits a lot from **23b**. In the case of Ag(I) the intermediate **23** is still accessible, but here **23a** might be more important, the intermediate does not live long



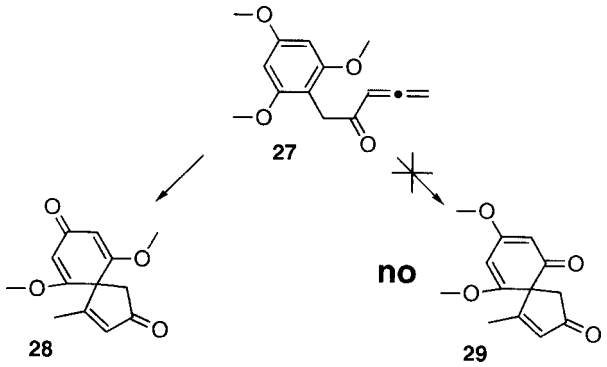
Scheme 7 Possible pathways for the formation of the different products

enough to react with a second molecule of **3a**. With the doubly charged Hg^{2+}-ion an electrophilic attack at the arene becomes the main pathway, due to the bad ability for back-donation **23** would be quite unfavourable. If now, like with **3b**, in the subsequent transformations the σ-complex **26** reacts only slowly with the nucleophile, the reversibility of the electrophilic attack at the arene allows the formation of some **10** *via* **22a** and **23**. **27** might then react with the 2,4-dien-1-one system in the other product **15** and give *rac*-**17**. This reaction stereoselectively takes place from the less hindered face of **15** (opposite to the methyl group shielding the diene) and is regioselective (no C–C bond formation next to the spiro-carbon), thus the relative configuration of the stereocenters in the product can be explained. The formation of **13** mentionend above is another evidence for the ability of furans to react with α,β-unsaturated ketones under the influence of electrophilic metal-catalysts. These reactions are still under investigation.



26

The slow reaction of **3b** (compared to **3a**) also explains why Nagao only saw the product **28** and no **29** in the reactions of **27**. The origin of this positional selectivity is yet unknown, sterical reasons might be part of it. The back-side attack at the methyl groups with small nucleophiles like Cl^- or H_2O should not be so sensitive to sterical hindrance three bonds away but an attack of H_2O at the arene-carbon should be (see **26**) .



Scheme 8 Positional selectivity of the loss of the substituent on the arene

The formation of slightly higher amounts of **16** in the reaction of **3b** (compared to **3a**) with Hg(II) also shows that only when the other reactions, in which the first step always is intramolecular, are slow, the intermolecular addition of water to the allene also becomes visible.

Conclusion

By the choice of the transition metal-catalyst it is possible to obtain selectively one out of three possible prod-

ucts from the allenyl ketones **3a** and **6a**–**c**. While with Ag(I)- and Pd(II)- this is also true for **3b**, the Hg(II)-catalysis was very slow and delivered several products. This explains why Nagao in his *o,p*-disubstituted derivatives observed only the product resulting from the loss of the *p*-MeO group but never of the *o*-MeO group. The side products **13** and *rac*-**17** suggest that, at least in electron-rich furans, there exists the possibility to form new C–C-bonds also in the 5-position of the furan (and not only in the 4-position as observed in the Pd(II)-catalyzed reactions).

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Experimental

All operations with Grignard-reagents were carried out under N_2 and in anhydrous solvents; transfers were effected by means of Schlenk-tube techniques. **2** [13] and $PdCl_2(MeCN)_2$ [14] were prepared by 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 AMX 400 (400 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 *n*-hexane/ethyl acetate (H/EA) as eluent. – Elemental analyses were performed on a Foss-Heraeus CHN-O-Rapid elemental analyser.

General Procedures

a) Preparation of allenyl ketones from esters. 1.1 eqs. of a solution of **2** in Et_2O (1.6M) were diluted with dry Et_2O (amount given in the individual experiment) and cooled to –78 °C. 1.0 eq. of the ester was dissolved in Et_2O (amount given in the individual experiment), precooled to –78 °C and slowly added to the well-stirred solution of **2**. After 15 minutes of stirring the reaction was quenched with saturated, NH_4Cl solution (still at –78 °C). Then the reaction mixture was warmed to room temperature, the organic layer separated and the aqueous solution was extracted with ether twice. The combined organic layers were dried over $MgSO_4$, the solvent was removed *in vacuo*, and the crude product was purified by column chromatography or HPLC as described in the individual experiments.

b) Silylation of phenols. To a solution of 1.0 eq. of phenol in dry THF (10 ml/g phenol) 2.3 eqs. of Et_3N and 0.1 eqs. 4-*N,N*-dimethylaminopyridine (DMAP) were added with stirring. Then the reaction mixture was cooled to 0 °C and 1.2 eqs. of *tert*-butyldimethylchlorosilane (TBDMSCl) were added. After warming to room temperature, stirring was continued for one hour. The precipitate was filtered off, the filtrate was washed with water, and the aqueous layer was extracted with Et_2O three times. The combined organic layers were treated as mentioned above (general procedure a).

c) Cycloisomerisation to furans by Ag^I-catalysts. The allenyl ketone was dissolved in acetone (amount given in the individual experiment). 10–30 mol% $AgNO_3$ were added. Then the reaction mixture was stirred at room temperature over night or refluxed for 1 hour. After removing the solvent *in vacuo*, the crude product was purified by column chromatography as described below.

d) Cycloisomerization/Dimerization by Pd^{II}-catalysts. The starting material was dissolved in MeCN (amount given in the individual experiment) and $PdCl_2(MeCN)_2$ was added at room temperature. When the reaction was finished (checked by TLC), the solvent was removed in vacuo and the crude product was purified by column chromatography as described below.

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

Following the general procedure a), from 24.3 g (135 mmol) methyl (*p*-methoxyphenyl)acetate (**1a**) in 170 ml Et_2O, 94.0 ml (1.6M, 150 mmol) allenylmagnesium bromide (**2**) in 94 ml of Et_2O after HPLC (H/EE, 20:3), 12.5 g (49%) of **3a** were obtained. R_f (H/EE, 5:1) = 0.24. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3 064, 3 033, 2 990, 2 967, 2 935, 2 907, 2 836, 1 958 (C=C=C), 1 933 (C=C=C), 1 678 (C=O), 1 611, 1 513, 1 248, 1 154, 1 035, 857, 804, 774. – ^1H NMR ($CDCl_3$, 250 MHz): δ/ppm = 3.78 (s, 3H), 3.84 (s, 2H), 5.28 (d, J = 6.5 Hz, 2H), 5.81 (t, J = 6.5 Hz, 1H), 6.82–6.88 (m, 2H), 7.11–7.17 (m, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 44.97 (t), 55.08 (q), 79.60 (t), 96.21 (d), 113.90 (d, 2C), 126.47 (s), 130.32 (d, 2C), 158.43 (s), 197.81 (s), 216.98 (s). – MS (70 eV): *m/z* (%) = 188 (30)[M^+], 157 (8), 121 (100).

$C_{12}H_{12}O_2$	Calcd.:	C 76.57 H 6.43
(188.22)	Found:	C 76.70 H 6.57.

1-(2-Methoxyphenyl)penta-3,4-dien-2-one (**3b**)

7.44 g (41.3 mmol) methyl 2-methoxyphenylacetate (**1b**) in 80 ml of Et_2O and 31.0 ml (49.6 mmol, 1.6M) **2** in 31 ml of Et_2O were treated according to the general procedure a). Purification by HPLC (H/MeOAc, 10:0.35+30% DCM) provided 4.41 mg (57%) of **3b**. R_f (H/EE, 2:1) 0.44. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3 064, 2 988, 2 940, 2 837, 1 957 (C=C=C), 1 934 (C=C=C), 1 690 (C=O), 1 602, 1 496, 1 464, 1 439, 1 336, 1 290, 1 247, 1 156, 1 112, 1 029, 858, 754. – ^1H NMR ($CDCl_3$, 250 MHz): δ/ppm = 3.79 (s, 3H), 3.92 (s, 2H), 5.23 (d, J = 6.5 Hz, 2H), 5.86 (t, J = 6.5 Hz, 1H), 6.85–6.95 (m, 2H), 7.11–7.15 (m, 1H), 7.22–7.29 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 40.93 (t), 55.22 (q), 79.35 (t), 96.04 (d), 110.35 (d), 120.37 (d), 123.51 (s), 128.23 (d), 131.04 (d), 157.27 (s), 197.62 (s), 216.37 (s). – MS (80 eV): *m/z* (%) = 188 (62)[M^+], 121 (100), 91 (69).

$C_{12}H_{12}O_2$	Calcd.:	C 76.57 H 6.43
(188.22)	Found:	C 76.33 H 6.48.

Methyl 4-(t-butyldimethylsilanyloxy)benzoate (**5a**)

3.96 g (26.0 mmol) methyl *p*-hydroxybenzoate (**4a**), 9.40 g (31.2 mmol) of a solution containing 50% TBDMSCl in *n*-hexane, 6.03 g (8.3 ml, 59.5 mmol) Et_3N, 320 mg (2.62 mmol) DMAP and 400 ml THF were treated according to the general procedure b). Purification by column chromatography (H/EE, 25:1) provided 6.69 g (97%) of **5a**. R_f (H/EE, 2:1) 0.64. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2954, 2931, 2887, 2859, 1723 (C=O), 1604, 1509, 1435, 1271, 1163, 912, 839, 783. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.21 (s, 6H), 0.97 (s, 9H), 3.85 (s, 3H), 6.81–6.87 (m, 2H), 7.90–7.96 (m, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = –4.58 (q, 2C), 18.06 (s), 25.42 (q, 3C), 51.62 (q), 119.65 (d, 2C), 123.09 (s), 131.37 (d, 2C), 159.86 (s), 166.64 (s). – MS (70 eV): *m/z* (%) = 266 (17)[M$^+$], 235 (15), 209 (100), 84 (76), 59 (14), 51 (79).

$C_{14}H_{22}O_3Si$	Calcd.:	C 63.12	H 8.32
(266.41)	Found:	C 62.88	H 8.42.

Methyl [4-(t-butyldimethylsilanyloxy)phenyl]acetate (**5b**)

10.0 g (60.2 mmol) methyl *p*-hydroxyphenylacetate (**4b**), 19.7 g (65.5 mmol) of a solution containing 50% TBDMSCl in *n*-hexane, 13.9 g (19.1 ml, 137 mmol) Et_3N, 825 mg (6.75 mmol) DMAP and 100 ml of THF were treated according to the general procedure b). Purification by column chromatography (H/EE, 25:1) provided 15.9 g (94%) of **5b**. R_f (H/EE, 20:1) 0.22. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2955, 2931, 2888, 2858, 1742 (C=O), 1610, 1511, 1464, 1257, 1156, 916, 840, 781. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.17 (s, 6H), 0.96 (s, 9H), 3.53 (s, 2H), 3.67 (s, 3H), 6.75–6.78 (m, 2H), 7.03–7.13 (m, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = –4.58 (q, 2C), 18.03 (s), 25.53 (q, 3C), 40.23 (t), 51.80 (q), 119.96 (d, 2C), 126.50 (s), 130.06 (d, 2C), 154.61 (s), 172.20 (s). – MS (70 eV): *m/z* (%) = 280 (31)[M$^+$], 223 (100), 163 (50). – $C_{15}H_{24}O_3Si$ (280.43): calcd. 280.14947; found: 280.14920 (MS).

Methyl 3-[4-(t-butyldimethylsilanyloxy)phenyl]propionate (**5c**)

5.00 g (27.7 mmol) methyl *p*-hydroxyphenylpropionate (**4c**), 9.50 g (31.5 mmol) of a solution containing 50% TBDMCl in *n*-hexane, 6.53 g (9.00 ml, 65.6 mmol) Et_3N, 396 mg (3.24 mol) DMAP and 100 ml THF were treated according to the general procedure b). Purification by column chromatography (H/EE, 25:1), provided 7.50 g (92%) of **5c**. R_f (H/EE, 2:1) 0.58. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2954, 2930, 2887, 2858, 1741 (C=O), 1610, 1511, 1436, 1256, 1170, 916, 840, 781. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.19 (s, 6H), 0.99 (s, 9H), 2.57–2.63 (m, 2H), 2.86–2.92 (m, 2H), 3.66 (s, 3H), 6.73–6.79 (m, 2H), 7.02–7.08 (m, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = –4.58 (q, 2C), 18.03 (s), 25.55 (q, 3C), 30.07 (t), 35.84 (t), 51.36 (q), 119.87 (d, 2C), 129.00 (d, 2C), 133.04 (s), 153.88 (s), 173.25 (s). – MS (70 eV): *m/z* (%) = 294 (51)[M$^+$], 237 (62), 221 (25), 195 (54), 163 (87), 161 (100), 107 (56), 89 (81), 73 (49), 57 (55).

$C_{16}H_{26}O_3Si$	Calcd.:	C 65.26	H 8.90
(294.47)	Found:	C 65.13	H 8.90.

1-[4-(t-Butyldimethylsilanyloxy)phenyl]buta-2,3-dien-1-one (**6a**)

6.30 g (23.6 mmol) **5a** in 390 ml of Et_2O and 23.0 ml (36.8 mmol, 1.6M) **2** in 23 ml Et_2O were treated according to the general procedure a). Purification by HPLC (H/EE, 5:1) provided 1.88 g (29%) of **6a**. R_f (H/EE, 5:1) = 0.36. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2956, 2930, 2886, 2858, 1963, 1935 (C=C=C), 1654, 1597, 1508, 1272, 1216, 1167, 911, 840, 783. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.23 (s, 6H), 0.98 (s, 9H), 5.24 (d, *J* = 6.5 Hz, 2H), 6.44 (t, *J* = 6.5 Hz, 1H), 6.83–6.89 (m, 2H), 7.83–7.89 (m, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = –4.51 (q, 2C), 18.09 (s), 25.43 (q, 3C), 78.89 (t), 92.68 (d), 119.64 (d, 2C), 130.76 (d, 2C), 130.76 (s), 160.09 (s), 189.01 (s), 216.34 (s). – ^{13}C NMR (DMSO, 67.9 MHz): δ/ppm = –4.62 (q, 2C), 17.90 (s), 25.39 (q, 3C), 79.35 (t), 91.79 (d), 119.71 (d, 2C), 130.55 (s), 130.77 (d, 2C), 159.57 (s), 187.90 (s), 216.02 (s). – MS (70 eV): *m/z* (%) = 274 (6)[M$^+$], 235 (100), 217 (44), 150 (9), 73 (72), 67 (88), 57 (39).

$C_{16}H_{22}O_2Si$	Calcd.:	C 70.03	H 8.08
(274.44)	Found:	C 69.75	H 8.07.

1-[4-(t-Butyl-dimethyl-silanyloxy)phenyl]penta-3,4-dien-2-one (**6b**)

5.62 g (20.0 mmol) methyl [4-(*t*-butyldimethylsilanyloxy) phenyl]acetate (**5b**) in 190 ml of Et_2O and 22.0 ml (35.2 mmol, 1.6M) **2** in 22 ml of Et_2O were treated according to the general procedure a). Purification by HPLC (H/MeOAc, 10:0.7), delivered 3.92 mg (68%) of **6b**. R_f (H/EE, 5:1) = 0.38. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 1956, 2930, 2895, 2858, 1959, 1933 (C=C=C), 1681 (C=O), 1608, 1509, 1261, 1170, 1152, 916, 840, 781. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.17 (s, 6H), 0.96 (s, 9H), 3.80 (s, 2H), 5.24 (d, *J* = 6.4 Hz, 2H), 5.78 (t, *J* = 6.5 Hz, 1H), 6.72–6.78 (m, 2H), 7.02–7.08 (m, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = –4.57 (q, 2C), 18.03 (s), 25.53 (q, 3C), 45.11 (t), 79.54 (t), 96.26 (d), 119.96 (d, 2C), 127.09 (s), 130.26 (d, 2C), 154.43 (s), 197.86 (s), 217.02 (s). – MS (70 eV): *m/z* (%) = 288 (45)[M$^+$], 231 (26), 221 (64), 203 (48), 73 (100).

$C_{17}H_{24}O_2Si$	Calcd.:	C 70.78	H 8.39
(288.46)	Found:	C 70.56	H 8.40.

1-[4-(t-Butyldimethylsilanyloxy)phenyl]hexa-4,5-dien-3-one (**6c**)

7.30 g (24.8 mmol) **5c** in 400 ml of Et_2O and 24.0 ml (38.4 mmol, 1.6M) **2** in 24 ml of Et_2O were treated according to 2.4. Purification by HPLC (H/EE, 10:1) provided 5.86 g (78%) of **6c**. R_f (H/EE, 5:1) = 0.42. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2956, 2930, 2895, 2858, 1960, 1934 (C=C=C), 1682 (C=O), 1610, 1510, 1257, 1155, 916, 840, 781. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.18 (s, 6H), 0.98 (s, 9H), 2.85–2.89 (m, 4H), 5.20 (d, *J* = 6.5 Hz, 2H), 5.77 (t, *J* = 6.5 Hz, 1H), 6.71–6.77 (m, 2H), 7.00–7.06 (m, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = –4.57 (q, 3C), 18.04 (s), 25.54 (q, 2C), 29.55 (t), 40.92 (t), 79.36 (t), 96.59 (d), 119.81 (d, 2C), 129.08 (d, 2C), 133.51 (s), 153.76 (s), 199.75 (s), 216.64 (s). – MS (70 eV): *m/z* (%) = 302 (32)[M$^+$], 245 (88), 221 (25), 139 (66), 97 (45), 73 (100), 67 (38), 57 (77).

$C_{18}H_{26}O_2Si$	Calcd.:	C 71.47	H 8.66
(302.49)	Found:	C 71.29	H 8.72.

1-(4-Methoxyphenyl)pentan-2,4-dione (**7a**) and *4-Hydroxy-1-(4-methoxyphenyl)pent-3-en-2-one* (**7b**)

To 102 mg (542 µmol) **3a** and 12.4 mg (688 µmol) H_2O in 1.34 g (32.6 mmol) MeCN were added 7.60 mg (71.3%,

53.9 μmol, 9.9 mol%) $HClO_4$ and stirred for 3 h. Purification of the crude material by column chromatography (H/EE, 5:1) provided 106 mg (95%) **7a** (in equilibrium with a small amount of **7b**).

a) **7a**+**b**: R_f (H/EE, 5:1) = 0.25. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3002, 2955, 2837, 1706, 1613, 1513, 1460, 1359, 1300, 1248, 1179, 1130, 1034, 918, 819, 788. – MS (80 eV): *m/z* (%) = 206 (35)[M$^+$], 122 (100), 85 (89).

$C_{12}H_{14}O_3$	Calcd.:	C 69.89	H 6.84
(206.24)	Found:	C 70.07	H 6.96.

b) **7a**: ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.08 (s, 3H), 3.49 (s, 2H), 3.64 (s, 2H), 3.73 (s, 3H), 6.77–6.83 (m, 2H), 7.03–7.12 (m, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 30.60 (q), 49.68 (t), 55.07 (q), 56.33 (t), 114.19 (d, 2C), 130.47 (d, 2C).

b) **7b**: ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.94 (s, 3H), 3.45 (s, 2H), 3.73 (s, 3H), 5.35 (m, 1H), 6.77–6.83 (m, 2H), 7.03–7.12 (m, 2H), 15.33 (br s, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 24.64 (q), 44.09 (t), 55.09 (q), 99.56 (d), 113.96 (d, 2C), 126.96 (s), 130.20 (d, 2C), 158.55 (s), 191.03 (s), 192.65 (s).

(E)-4-[5-(4-Methoxybenzyl)furan-3-yl]-1-(4-methoxyphenyl) pent-3-en-2-one (**8**)

From 57.0 mg (303 μmol) **3a** and 2.0 mg (7.7 μmol, 2.5 mol%) $Pd(MeCN)_2Cl_2$ in 400 mg MeCN, 41.2 mg (72%) of **8** were obtained according to the general procedure d). – Column with (H/EE, 5:1). – R_f (H/EE, 2:1) = 0.38. – *m.p.* 89 °C. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3032, 3000, 2954, 2934, 2908, 2835, 1676, 1610, 1588, 1512, 1463, 1248, 1178, 1034, 819, 770. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.40 (d, *J* = 1.1 Hz, 3H), 3.71 (s, 2H), 3.80 (s, 3H), 3.81 (s, 3H), 3.89 (s, 2H), 6.12 (d, *J* = 0.9 Hz, 1H), 6.39 (d, *J* = 1.1 Hz, 1H), 6.85–6.92 (m, 4H), 7.12–7.18 (m, 4H), 7.55 (d, *J* = 0.8 Hz, 1H). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ/ppm = 2.40 (d, *J* = 1.1 Hz, 3H), 3.70 (s, 2H), 3.79 (s, 3H), 3.80 (s, 3H), 3.88 (s, 2H), 6.12 (d, *J* = 0.9 Hz, 1H), 6.39 (d, *J* = 1.0 Hz, 1H), 6.86–6.89 (m, 4H), 7.13–7.18 (m, 4H), 7.55 (d, *J* = 0.6 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 16.81 (q), 33.48 (t), 50.66 (t), 55.12 (q, 2C), 103.63 (d), 113.91 (d), 113.99 (d, 2C), 120.05 (d, 2C), 126.91 (s), 129.10 (s), 129.22 (s), 129.58 (d, 2C), 130.32 (d, 2C), 141.90 (d), 145.92 (s), 156.72 (s), 158.33 (s), 158.40 (s), 198.31 (s). – MS (70 eV): *m/z* (%) = 376 (18)[M$^+$], 255 (100), 212 (69).

$C_{24}H_{24}O_4$	Calcd.:	C 76.57	H 6.43
(376.45)	Found:	C 76.30	H 6.46.

Crystal Structure Determination of (*E*)-4-[5-(4-Methoxybenzyl)furan-3-yl]-1-(4-methoxyphenyl)pent-3-en-2-one (**8**)

X-ray crystal data for $C_{24}H_{24}O_4$: triclinic, P (–1), a = 5.4743 (6) Å, b = 12.685 (2) Å, c = 15.210 (2) Å, α = 108.29 (2)°, β = 97.35 (1)°, γ = 98.33 (1)°, V = 975.2 (3) Å^3, Z = 2, D_{calc} = 1.282 g cm^{-3}, $Mo_{K\alpha}$ radiation (λ = 0.71073 Å), μ = 0.086 mm^{-1}, T = –140 °C. 15773 reflections were collected on a SIEMENS CCD three-circle diffractometer for 3° < 2θ < 65°. The data were corrected for absorption effects using the program SADABS [15]. The structure was solved by direct methods and refined by full-matrix least-square against F^2 to R(F) = 0.045 (wR(F^2) = 0.134) and S = 1.52 for 5621 (R_{int} = 0.024) unique reflections [10].

Reactions of Different Lewis-acids with 3a (from Table 1)

a) $Hg(ClO_4)_2$ in Acetone. 132 mg (701 μmol) **3a** were dissolved in 500 μl [D_6]-acetone containing 15.2 mg (844 μmol, 1.2 eqs.) in a NMR tube and 16.8 mg (42.1 μmol, 6 mol%) $Hg(ClO_4)_2$ were added. The reaction was monitored by ^{1}H NMR. When complete, the mixture was directly purified by column chromatography as described above. Thus 55.0 mg (45%) of **9** were obtained.

b) $Hg(ClO_4)_2$ in DCM. 132 mg (701 μmol) **3a** were dissolved in 500 μl [D_2]-DCM containing 15.2 mg (844 μmol, 1.2 eqs.) in a NMR tube and 28.0 mg (70.1 μmol, 10 mol%) $Hg(ClO_4)_2$ were added. The reaction was monitored by ^{1}H NMR. When complete, the mixture was directly purified by column chromatography as described above. Thus 80.5 mg (66%) of **9** were obtained.

c) $Hg(ClO_4)_2$ in Et_2O. 132 mg (701 μmol) **3a** were dissolved in 500 μl Et_2O containing 15.2 mg (844 μmol, 1.2 eqs.) and 28.0 mg (70.1 μmol, 10 mol%) $Hg(ClO_4)_2$ were added. The progress of the reaction was checked by ^{1}H NMR of small aliquotes of the Et_2O in $CDCl_3$. Even after the addition of more water and heating to 30 °C no reaction was observed.

d) $Hg(ClO_4)_2$ in Ethyl Acetate. 132 mg (701 μmol) **3a** were dissolved in 500 μl ethyl acetate containing 15.2 mg (844 μmol, 1.2 eqs.) and 28.0 mg (70.1 μmol, 10 mol%) $Hg(ClO_4)_2$ were added. The progress of the reaction was checked by ^{1}H NMR of small aliquots of the Et_2O in $CDCl_3$. The starting material was completely consumed, but in the spectra only broad signals were visible and the TLC showed a baseline spot.

e) $Hg(ClO_4)_2$ in n-Hexane. 132 mg (701 μmol) **3a** were dissolved in 500 μl *n*-hexane containing 15.2 mg (844 μmol, 1.2 eqs.) and 28.0 mg (70.1 μmol, 6 mol%) $Hg(ClO_4)_2$ were added. The progress of the reaction was checked by ^{1}H NMR of small aliquotes of the Et_2O in $CDCl_3$. No reaction was observed, even when heated to 40 °C.

f) $Hg(NO_3)_2$ in MeCN. 132 mg (701 μmol) **3a** were dissolved in 500 μl [D_3]-MeCN containing 15.2 mg (844 μmol, 1.2 eqs.) in a NMR tube and 22.8 mg (70.1 μmol, 10 mol%) $Hg(NO_3)_2$ were added. The reaction was monitored by ^{1}H NMR. When complete (approximately 40 h), the mixture was directly purified by column chromatography as described above. Thus 57.3 mg (47%) of **9** were obtained.

g) $HgCl_2$ in MeCN. 132 mg (701 μmol) **3a** were dissolved in 500 μl [D_3]-MeCN containing 15.2 mg (844 μmol, 1.2 eqs.) in a NMR tube and 19.0 mg (70.1 μmol, 10 mol%) $HgCl_2$ were added. The reaction was monitored by ^{1}H NMR. But only starting material was visible.

h) $Hg(OAc)_2$ in MeCN. 132 mg (701 μmol) **3a** were dissolved in 500 μl [D_3]-MeCN containing 15.2 mg (844 μmol, 1.2 eqs.) in a NMR tube and 22.3 mg (70.1 μmol, 10 mol%) $Hg(OAc)_2$ were added. The reaction was monitored by ^{1}H NMR. But only starting material was visible.

i) $Hg(SCN)_2$ in MeCN. 132 mg (701 μmol) **3a** were dissolved in 500 μl [D_3]-MeCN containing 15.2 mg (844 μmol, 1.2 eqs.) in a NMR tube and 22.2 mg (70.1 μmol, 10 mol%)

$Hg(SCN)_2$ were added. The reaction was monitored by ^1H NMR. But only starting material was visible.

j) $HgSO_4$ in MeCN. 132 mg (701 µmol) **3a** were dissolved in 500 µl [D_3]-MeCN containing 15.2 mg (844 µmol, 1.2 eqs.) in a NMR tube and 18.6 mg (70.1 µmol, 10 mol%) $HgSO_4$ were added. The reaction was monitored by ^1H NMR. When complete (approximately 26 h), the mixture was directly purified by column chromatography as described above. Thus 67.3 mg (45%) of **9** were obtained.

k) $InCl_3$ in MeCN. 132 mg (701 µmol) **3a** were dissolved in 500 µl [D_3]-MeCN containing 15.2 mg (844 µmol, 1.2 eqs.) in a NMR tube and 15.5 mg (70.1 µmol, 10 mol%) $InCl_3$ were added. The reaction was monitored by ^1H NMR. But only starting material was visible, even after the addition of a large excess of water.

l) $Tl(ClO_4)_3$ in MeCN. 132 mg (701 µmol) **3a** were dissolved in 500 µl [D_3]-MeCN containing 15.2 mg (844 µmol, 1.2 eqs.) in a NMR tube and 35.2 mg (70.1 µmol, 10 mol%) $Tl(ClO_4)_3$ were added. The reaction was monitored by ^1H NMR. But only starting material was visible, even after the addition of a large excess of water.

m) $Sc(SO_2CF_3)_2$ in MeCN. 132 mg (701 µmol) **3a** were dissolved in 500 µl [D_3]-MeCN containing 15.2 mg (844 µmol, 1.2 eqs.) in a NMR tube and 31.1 mg (70.1 µmol, 10 mol%) $Sc(SO_2CF_3)_3$ were added. The reaction was monitored by ^1H NMR. But only starting material was visible, even after the addition of a large excess of water.

4-Methyl-spiro[4.5]deca-3,6,9-trien-2,8-dione (**9**) *from* **3a**

To 203 mg (1.17 mmol) **3a** in 265 mg MeCN containing 21.6 mg (1.20 mmol) H_2O at 0 °C under stirring 2.4 mg (6.0 µmol, 0.5 mol%) $Hg(ClO_4)_2$ were added, and stirring was continued at room temperature for 6h. Then the solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel. Thus 163 mg (80%) of **9** were obtained. – Column with (H/EE, 1:1). – R_f (H/EE, 1:1) 0.20. – *m.p.* 269 °C. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3069, 3043, 2970, 1720, 1698, 1661, 1621, 1434, 1404, 1289, 1253, 1200, 1083, 860. – ^1H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.90 (d, *J* = 1.3 Hz, 3H), 2.64 (s, 2H), 6.20 (q, *J* = 1.3 Hz, 1H), 6.41–6.47 (m, 2H), 6.61–6.67 (m, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 15.01 (q), 45.11 (t), 52.37 (s), 130.68 (d, 2C), 132.37 (d), 149.51 (d, 2C), 176.63 (s), 184.54 (s), 204.27 (s). – MS (80 eV): *m/z* (%) = 147 (100)[M^+], 146 (94), 131 (36), 117 (28), 78 (53).

$C_{11}H_{10}O_2$	Calcd.:	C 75.84	H 5.79
(174.19)	Found:	C 75.53	H 5.83.

9 *from* **6b.** To 2.01 mg (6.97 mmol) **6b** in 4.0 ml MeCN containing 130 mg (7.22 mmol) H_2O at 0 °C under stirring 13.9 mg (34.7 µmol, 0.5 mol%) $Hg(ClO_4)_2$ were added and stirring was continued at room temperature for 6 h. Then the solvent was removed *in vacuo* and the residue was purified by column chromatography on silica gel. Thus 1.02 g (84%) of **9** were obtained.

2-(4-Methoxybenzyl)furan (**10**)

From 28.0 mg (149 µmol) **3a**, 8.00 mg (47.1 µmol, 32 mol%) $AgNO_3$ and 3 ml of acetone 24.8 mg (89%) of **10** were obtained according to the general procedure c). – Column with (H/EE, 5:1). – R_f (H/EE, 5:1) = 0.48. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3032, 3000, 2955, 2934, 2907, 2835, 1611, 1513, 1463, 1248, 1176, 1035, 1010, 931, 804, 761. – ^1H NMR ($CDCl_3$, 250 MHz): δ/ppm = 3.81 (s, 3H), 3.93 (s, 2H), 6.00 (dd, *J* = 3.1 Hz, 0.8 Hz, 1H), 6.30 (dd, *J* = 3.2 Hz, 1.8 Hz, 1H), 6.84–6.90 (m, 2H), 7.15–7.20 (m, 2H), 7.34 (dd, *J* = 1.8 Hz, 0.7 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 33.48 (t), 55.12 (q), 105.82 (d), 110.07 (d), 113.80 (d, 2C), 129.54 (d, 2C), 130.09 (s), 141.27 (d), 154.92 (s), 158.15 (s). – MS (70 eV): *m/z* (%) = 188 (100)[M^+], 159 (25), 157 (19), 144 (21), 115 (22).

$C_{12}H_{12}O_2$	Calcd.:	C 76.57	H 6.43
(188.22)	Found:	C 76.33	H 6.56.

Reaction of 6a with Ag(I)

65.0 mg (237 µmol) **6a** and 1.9 mg (11.2 µmol, 5 mol%) $AgNO_3$ in 305 mg acetone were treated according to the general procedure *c)*. Purification by column chromatography (H/EE, 50:1) provided 14.5 mg (22%) *t*-butyl-(4-furan-2-ylphenoxy)dimethylsilane (**11a**) and 9.3 mg (14%) 4-{5-[4-(*t*-butyldimethylsilanyloxy)benzyl]furan-2-yl}-1-[4-(*t*-butyldimethylsilanyloxy)phenyl]pentan-2-one (**13**).

a) **11a**: R_f (H/EE, 20:1) = 0.54. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2956, 2930, 2886, 2858, 1613, 1589, 1514, 1484, 1266, 1169, 1007, 912, 841, 781. – ^1H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.22 (s, 6H), 1.00 (s, 9H), 6.44 (dd, *J* = 1.8 Hz, 3.3 Hz, 1H), 6.52 (d, *J* = 3.3 Hz, 1H), 6.85–6.89 (m, 2H), 7.42–7.43 (m, 1H), 7.52–7.58 (m, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = –4.54 (q, 2C), 18.11 (s), 25.54 (q, 3C), 103.32 (d), 111.38 (d), 120.21 (d, 2C), 124.45 (s), 125.02 (d, 2C), 141.24 (d), 153.97 (s), 155.04 (s). – MS (70 eV): *m/z* (%) = 274 (55)[M^+], 217 (100), 161 (4), 115 (7). – $C_{16}H_{22}O_2Si$: calcd. 274.13891, found 274.13884 (MS).

b) **13**: R_f (H/EE, 10:1) = 0.26. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2955, 2930, 2885, 2858, 1648, 1598, 1507, 1486, 1420, 1363, 1268, 1219, 1165, 1043, 911, 841, 806. – ^1H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.24 (s, 6H), 0.26 (s, 6H), 1.01 (s, 18H), 2.53 (d, *J* = 1.0 Hz, 3H), 6.64 (d, *J* = 3.6 Hz, 1H), 6.81 (d, *J* = 3.6 Hz, 1H), 6.88–6.96 (m, 4H), 7.51 (d, *J* = 1.1 Hz, 1H), 7.62–7.68 (m, 2H), 7.95–8.01 (m, 2H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = –4.54 (q, 2C), –4.51 (q, 2C), 15.37 (s), 18.01 (s), 25.41 (q), 25.46 (q, 3C), 25.50 (q, 3C), 106.28 (d), 114.45 (d), 115.66 (d), 119.73 (d, 2C), 120.38 (d, 2C), 123.49 (s), 125.60 (d, 2C), 130.08 (d, 2C), 133.36 (s), 141.00 (s), 153.54 (s), 155.38 (s), 155.95 (s), 159.49 (s), 189.96 (s).

t-Butyl-(4-furan-2-ylmethylphenoxy)dimethylsilane (**11b**)

50.0 mg (173 µmol) **6b**, 5 mg (29.4 µmol, 17 mol%) $AgNO_3$, 2 ml of acetone were treated according to the general procedure c). Purification by column chromatography (H/EE, 20:1) provided 44 mg (88%) of **11b**. R_f (H/EE, 5:1) = 0.66. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2956, 2930, 2896, 2858, 1609, 1510, 1472, 1261, 1169, 1010, 916, 839, 781. – ^1H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.19 (s, 6H), 0.99 (s, 9H), 3.90 (s, 2H), 5.96 (dd, *J* = 0.8 Hz, 3.1 Hz, 1H), 6.28 (dd, *J* = 1.9 Hz, 3.1 Hz, 1H), 6.75–6.81 (m, 2H), 7.06–7.11 (m, 2H), 7.32 (dd, *J* = 0.8 Hz, 1.9 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = –4.55 (q, 2C), 18.07 (s), 25.57 (q, 3C), 33.56 (t),

105.85 (d), 110.07 (d), 119.89 (d, 2C), 129.49 (d, 2C), 130.65 (s), 141.23 (d), 154.11 (s), 154.96 (s). – MS (70 eV): *m/z* (%) = 288 (24)[M^+], 231 (36), 81 (100).

$C_{17}H_{24}O_2Si$	Calcd.:	C 70.78 H 8.39
(288.46)	Found:	C 70.56 H 8.42.

t-Butyl-[4-(2-furan-2-ylethyl)phenoxy]dimethylsilane (**11c**)

30.0 mg (99.2 µmol) **6c**, 4.00 mg (23.5 µmol, 24 mol%) $AgNO_3$, 400 mg of acetone were treated according to the general procedure c). Purification by column chromatography (H/EE, 20:1) provided 25.4 mg (85%) of **11c**. R_f (H/EE, 5:1) = 0.62. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2956, 2930, 2896, 2858, 1610, 1510, 1463, 1257, 1170, 1013, 917, 840, 780. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.20 (s, 6H), 0.99 (s, 9H), 2.90 (s, 4H), 5.95 (d, J = 3.2 Hz, 1H), 6.28 (dd, J = 1.9 Hz, 3.1 Hz, 1H), 6.75–6.79 (m, 2H), 7.00–7.06 (m, 2H), 7.32 (dd, J = 0.8 Hz, 1.9 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = –4.57 (q, 2C), 18.06 (s), 25.56 (q, 3C), 30.02 (t), 33.46 (t), 104.96 (d), 109.95 (d), 119.75 (d, 2C), 129.05 (d, 2C), 133.81 (s), 140.65 (d), 153.70 (s), 155.40 (s). – MS (70 eV): *m/z* (%) = 302 (5)[M^+], 245 (2), 221 (100), 81 (20), 73 (43).

$C_{18}H_{26}O_2Si$	Calcd.:	C 71.47 H 8.66
(302.48)	Found:	C 71.28 H 8.97.

(E)-1-[4-(t-Butyldimethylsilanyloxy)phenyl]-3-{5-[4-(t-butyldimethylsilanyloxy)phenyl]furan-3-yl}-but-2-en-1-one (**12a**)

110 mg (401 µmol) **6a**, 0.8 mg (3.1 µmol, 1 mol%) $Pd(MeCN)_2Cl_2$ and 360 mg MeCN were treated according to 2.9. Purification by column chromatography (H/EE, 50:1) provided 65.0 mg (59%) **12a**. R_f (H/EE, 10:1) = 0.34. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2956, 2930, 2886, 2858, 1651, 1599, 1495, 1257, 1221, 1165, 1049, 912, 840, 805. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.23 (s, 6H), 0.25 (s, 6H), 1.00 (s, 18H), 2.49 (d, J = 1.1 Hz, 3H), 6.78 (d, J = 0.7 Hz, 1H), 6.86–6.93 (m, 4H), 7.14 (d, J = 1.1 Hz, 1H), 7.55–7.61 (m, 2H), 7.69 (s, 1H), 7.91–7.96 (m, 2H). – ^{13}C NMR ($CDCl_t$, 62.9 MHz): δ/ppm = –4.49 (q, 2C), –4.52 (q, 2C), 17.25 (q), 18.10 (s), 18.12 (s), 25.48 (q, 3C), 25.53 (q, 3C), 100.74 (d), 119.01 (d), 119.77 (d, 2C), 120.29 (d, 2C), 123.62 (s), 125.34 (d, 2C), 130.21 (d, 2C), 130.49 (s), 133.00 (s), 141.16 (d), 144.95 (s), 155.30 (s), 155.64 (s), 159.65 (s), 190.35 (s). – MS (70 eV): *m/z* (%) = 548 (51)[M^+], 491 (14), 341 (13), 301 (12), 299 (13), 235 (100), 217 (16), 195 (27). – $C_{32}H_{44}O_4Si_2$: calcd. 548.27781, found 548.27761 (MS).

(E)-4-{5-[4-(t-Butyldimethylsilanyloxy)benzyl]furan-3-yl}-1-[4-(t-butyl-dimethylsilanyloxy)phenyl]pent-3-en-2-one (**12b**)

110 mg (381 µmol) **6b**, 5.00 mg (19.3 µmol, 5 mol%) $Pd(MeCN)_2Cl_2$ and 5 ml MeCN were treated according to the general procedure d). Purification by column chromatography (H/EE, 20:1) provided 74.9 mg (68%) of **12b**. R_f (H/EE, 10:1) = 0.36. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2956, 2300, 2895, 2858, 1678, 1608, 1591, 1509, 1472, 1261, 1169, 916, 839, 781. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.19 (s, 6H), 0.20 (s, 6H), 0.98 (s, 9H), 1.00 (s, 9H), 2.39 (d, J = 1.1 Hz, 3H), 3.68 (s, 2H), 3.86 (s, 2H), 6.09 (d, J = 0.9 Hz, 1H), 6.37 (d, J = 1.1 Hz, 1H), 6.77–6.81 (m, 4H), 7.07–7.10 (m, 4H), 7.55 (d, J = 0.8 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = –4.54 (q, 4C), 16.80 (s, 2C), 18.06 (q), 25.56 (q, 6C), 33.54 (t), 50.82 (t), 103.64 (d), 120.00 (d, 2C), 120.05 (d), 120.10 (d, 2C), 127.58 (s), 129.11 (s), 129.52 (d, 2C), 129.83 (s), 130.29 (d, 2C), 141.88 (d), 145.83 (s), 154.31 (s), 154.41 (s), 156.71 (s), 198.37 (s). – MS (70 eV): *m/z* (%) = 576 (10)[M^+], 355 (100), 221 (26), 73 (9). – $C_{34}H_{48}O_4Si$: calcd. 576.30911, found 576.30953 (MS).

(E)-1-[4-(t-Butyldimethylsilanyloxy)phenyl]-5-(5-{2-[4-(t-butyldimethylsilanyloxy)phenyl]ethyl}furan-3-yl)hex-4-en-3-one (**12c**)

50.7 mg (167.6 µmol) **6c**, 1.20 mg (4.63 µmol, 3 mol%) $Pd(MeCN)_2Cl_2$ and 400 mg of MeCN were treated according to the general procedure d). Purification by column chromatography (H/EE, 20:1) provided 31.9 mg (63%) of **12c** R_f (H/EE, 5:1) = 0.44. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 2955, 2929, 2895, 2858, 1682, 1608, 1593, 1510, 1472, 1257, 1169, 916, 840, 781. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 0.18 (s, 6H), 0.19 (s, 6H), 0.98 (s, 18H), 2.41 (d, J = 1.1 Hz, 3H), 2.75–2.92 (m, 8H), 6.13 (s, 1H), 6.34 (d, J = 1.1 Hz, 1H), 6.72–6.78 (m, 4H), 6.79–7.08 (m, 4H), 7.56 (d, J = 0.7 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = –4.57 (q, 4C), 16.79 (q), 18.05 (s, 2C), 25.55 (q, 6C), 29.35 (t), 29.97 (t), 33.16 (t), 46.43 (t), 102.87 (d), 119.82 (d, 4C), 120.60 (d), 129.04 (d, 4C), 133.36 (s), 133.87 (s), 141.37 (d), 144.97 (s), 153.64 (s), 153.81 (s, 2C), 157.07 (s), 200.18 (s). – MS (70 eV): *m/z* (%) = 604 (5)[M^+], 221 (100), 73 (31). – $C_{36}H_{52}O_4Si_2$: Calcd. 604.34041, found 604.34012 (MS).

4-[5-(2-Methoxybenzyl)furan-3-yl]-1-(2-methoxyphenyl)pent-3-en-2-one (**14**)

150 mg (797 µmol) **3b**, 2.00 mg (7.71 µmol, 1 mol%) $Pd(MeCN)_2Cl_2$ and 207 mg MeCN were treated according to the general procedure d). Purification by column chromatography (H/EE, 7:1) provided 116 mg (77%) of **14**. R_f (H/EE, 2:1) = 0.40. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3065, 3003, 2939, 2836, 1768, 1681, 1590, 1494, 1463, 1439, 1369, 1325, 1290, 1247, 1176, 1129, 1111, 1050, 1029, 951, 754. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.38 (d, J = 1.2 Hz, 3H), 3.76 (s, 2H), 3.77 (s, 3H), 3.83 (s, 3H), 3.94 (s, 2H), 6.06 (d, J = 0.9 Hz, 1H), 6.43 (d, J = 1.1 Hz, 1H), 6.85–6.95 (m, 2H), 7.11–7.17 (m, 2H), 7.20–7.27 (m, 2H), 7.53 (d, J = 0.8 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 16.67 (q), 28.29 (t), 46.02 (t), 55.18 (q), 55.31 (q), 103.63 (d), 110.38 (d), 110.44 (d), 120.32 (d), 120.41 (d), 120.51 (d), 123.92 (s), 125.76 (s), 127.93 (d), 128.11 (d), 129.23 (s), 130.01 (d), 131.01 (d), 141.52 (d), 145.17 (s), 156.18 (s), 157.12 (s), 157.25 (s), 198.40 (s). – MS (70 eV): *m/z* (%) = 376 (38)[M^+], 255 (100), 147 (54), 121 (71), 91 (56). – $C_{24}H_{24}O_4$: Calcd. 376.16746, found 376.16345 (MS).

$C_{24}H_{24}O_4$	Calcd.:	C 76.57 H 6.43
(376.44)	Found:	C 76.34 H 6.46.

Reaction of 3b with Hg(II)

215 mg (1.14 mmol) **3b** and 20.5 mg (11.4 mg) H_2O were mixed with 1.3 g MeCN at 0 °C. 16.4 mg (41.0 µmol, 3.6 mol%) $Hg(ClO_4)_2$ were added. After 5 days at room temperature column chromatography (H/EE, 2:1) provided 47.3 mg (24%) of 4-methylspiro[4.5]deca-3,7,9-trien-2,6-dione (**15**), 75.4 mg (32%) of a mixture of 4-hydroxy-1-(2-

methoxyphenyl)pent-3-en-2-one (**16a**, major) and 1-(2-methoxyphenyl)pentan-2,4-dione (**16b**, minor) as well as 30.9 mg (15%) of 8-[5-(2-methoxybenzyl)furan-2yl]-4-methylspiro[4.5]deca-3,9-diene-2,6-dione (*rac*-**17**).

a) **15**: R_f (H/EE, 2:1) = 0.12. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3046, 2979, 2922, 2848, 2922, 1721, 1695, 1662, 1632, 1621, 1558, 1433, 1414, 1376, 1287, 1201, 1137, 966, 854. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.83 (s, 3H), 2.35 (d, J = 18.0 Hz, 1H), 2.73 (d, J = 18.1 Hz, 1H), 6.04–6.6 (m, 1H), 6.13–6.19 (m, 2H), 6.39–6.45 (m, 1H), 7.12–7.19 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 15.20 (q), 46.78 (q), 62.36 (q), 122.87 (q), 126.34 (q), 131.85 (q), 142.37 (q), 142.66 (q), 176.14 (q), 200.39 (q), 206.37 (q).

b) **16a**+**b**: R_f (H/EE, 2:1) = 0.44. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3065, 3004, 2940, 2837, 1727, 1707, 1602, 1538, 1495, 1464, 1247, 1112, 1050, 1029. – MS (80 eV): *m/z* (%) = 206 (40)[M$^+$], 148 (19), 122 (73), 91 (59), 85 (100).

$C_{12}H_{14}O_3$	Calcd.:	C 69.89 H 6.84
(206.24)	Found:	C 70.12 H 6.69.

c) **16b**: ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.89 (s, 3H), 3.53 (s, 2H), 3.72 (s, 3H), 5.31 (s, 1H), 6.78–6.87 (m, 2H), 7.02–7.18 (m, 1H), 7.20–7.22 (m, 1H), 15.35 (br, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 24.73 (q), 40.15 (t), 55.82 (q), 99.89 (d), 111.04 (d), 121.03 (d), 124.11 (s), 128.93 (d), 131.47 (d), 157.88 (s), 189.77 (s), 194.67 (s).

d) **16a**: ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.06 (s, 3H), 3.46 (s, 2H), 3.64 (s, 2H), 3.71 (s, 3H), 6.78–6.87 (m, 2H), 7.02–7.18 (m, 1H), 7.20–7.22 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 30.91 (q), 45.92 (t), 55.68 (q), 57.11 (t), 110.93 (d), 212.23 (d), 123.09 (s), 129.35 (d), 131.79 (d), 157.69 (s), 202.57 (s), 202.73 (s).

e) *rac*-**17**: R_f (H/EE, 2:1) = 0.20. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3067, 2962, 2939, 2915, 2837, 1721, 1715, 1697, 1623, 1601, 1558, 1494, 1464, 1439, 1376, 1292, 1247, 1176, 1106, 1050, 1028, 756. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 1.98 (d, J = 1.3 Hz, 3H), 2.33 (d, J = 18.3 Hz, 1H), 2.70 (d, J = 18.3 Hz, 1H), 2.83 (d, J = 1.7 Hz, 1H), 2.86 (s, 1H), 3.83 (s, 3H), 3.92 (s, 2H), 3.95–3.99 (m, 1H), 5.63 (dd, J = 2.0 Hz, 9.8 Hz, 1H), 5.85–5.87 (m, 1H), 5.95 (d, J = 3.0 Hz, 1H), 6.07 (q, J = 1.3 Hz, 1H), 6.22 (dd, J = 3.7 Hz, 9.8 Hz, 1H), 6.86–6.92 (m, 2H), 7.05–7.08 (m, 1H), 7.18–7.26 (m, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 16.05 (q), 28.18 (t), 36.33 (d), 43.86 (t), 48.10 (t), 55.25 (q), 59.84 (s), 105.88 (d), 106.59 (d), 110.31 (d), 120.32 (d), 126.25 (s), 127.67 (d), 129.77 (d), 130.24 (d), 130.95 (d), 132.39 (d), 152.63 (s), 154.18 (s), 157.05 (s), 176.60 (s), 205.75 (s), 208.00 (s). – MS (70 eV): *m/z* (%) = 362 (100)[M$^+$], 320 (44), 255 (10), 214 (30), 187 (29), 171 (26), 121 (43), 91 (40). – $C_{23}H_{22}O_4$: Calcd. 362.151809, found 362.15378 (MS).

2-(2-Methoxybenzyl)furan (**18**)

150 mg (797 µmol) **3b** in 1.99 g MeCN and 21.7 mg (128 µmol, 16 mol%) $AgNO_3$ in 97 mg MeCN were reacted according to the general procedure c). Purification by column chromatography (H/EE, 7:1) provided 132 mg (88%) of **18**. R_f (H/EE, 2:1) 0.60. – IR (film, NaCl): $\tilde{\nu}$/cm^{-1} = 3115, 3026, 3003, 2956, 2938, 2907, 2836, 1601, 1590, 1502, 1494, 1464, 1438, 1289, 1246, 1176, 1106, 1050, 1030, 1009, 935, 834, 805, 753, 730. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 3.84 (s, 3H), 3.99 (s, 2H), 5.97–6.00 (m, 1H), 6.29 (dd, J = 1.9 Hz, 3.2 Hz, 1H), 6.87–6.93 (m, 2H), 7.09–7.10 (m, 1H), 7.12–7.25 (m, 1H), 7.32 (dd, J = 0.8 Hz, 1.9 Hz, 1H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 28.20 (q), 55.29 (t), 105.90 (d), 110.09 (d), 110.35 (d), 120.37 (d), 126.63 (s), 127.62 (d), 129.90 (d), 140.98 (d), 154.36 (s), 157.12 (s). – MS (80 eV): *m/z* (%) = 188 (100)[M$^+$], 173 (21), 159 (18), 145 (15), 128 (18), 115 (15), 91 (10).

$C_{12}H_{12}O_2$	Calcd.:	C 76.57 H 6.43
(188.23)	Found:	C 76.58 H 6.43.

2-Methyl-5H-benzo[b]oxepin-4-one (**21**)

4.86 g (36.2 mmol) 2-cumaranone (**19**) in 410 ml of Et_2O and 36.0 ml (57.6 mmol, 1.6M) **2** in 36 ml Et_2O were reacted according to the general procedure a). Purification by column chromatography and HPLC provided 369 mg (6%) of **21**. R_f (H/EE, 2:1) = 0.38. – *m.p.* 57 °C. – IR (neat, KBr): $\tilde{\nu}$/cm^{-1} = 3046, 3008, 2952, 2913, 1666 (C=O), 1628. – ^{1}H NMR ($CDCl_3$, 250 MHz): δ/ppm = 2.13 (s, 3H), 3.70 (s, 2H), 5.46 (s, 1H), 7.05–7.22 (m, 4H). – ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ/ppm = 23.37 (q), 48.08 (t), 110.72 (d), 119.86 (d), 124.78 (s), 126.47 (d), 127.92 (d), 130.00 (d), 155.09 (s), 168.87 (s), 190.79 (s). – MS (70 eV): *m/z* (%) = 174 (48)[M$^+$], 145 (32), 131 (61), 115 (18), 89 (57), 78 (100), 63 (55), 51 (75).

$C_{11}H_{10}O_2$	Calcd.:	C 75.84 H 5.79
(174.20)	Found:	C 76.12 H 5.76.

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Address for correspondence:
Dr. A. Stephen K. Hashmi
Johann Wolfgang Goethe-Universität Frankfurt
Institut für Organische Chemie
Marie-Curie-Str. 11
D-60439 Frankfurt am Main
Fax: Internat. code (0) 69 798 29464
e-mail: hashmi@chemie.uni-frankfurt.de