

4. A New General Synthesis of 2,2-Dialkyl-2,3-dihydro-4*H*-pyran-4-ones and Their Application for the *in situ* Preparation of Electron-Rich Dienes in Carbonyl-Alkyne Exchange Reactions with Acetylenes¹⁾

by Daniel Obrecht

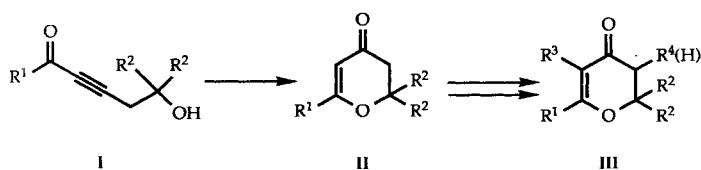
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(19.X. 90)

The substituted 2,2-dialkyl-2,3-dihydro-4*H*-pyran-4-ones of type **II** and **III** have been prepared by acid-catalyzed cyclization of the corresponding substituted acetylenic ketones **I** in good to excellent yields (*Scheme 1*). These 2,2-dialkyl-2,3-dihydro-4*H*-pyran-4-ones **II** and **III** have been used for the *in situ* preparation of highly reactive dienes of type **IV–VI** (*Scheme 2*) in carbonyl-alkyne exchange reactions with electron-poor alkynes **VII** to yield the highly substituted aromatic compounds **VIII** and **IX**. These reactions proceed in good yields and with excellent degree of regioselectivity. Aryl-substituted 2,2-dialkyl-2,3-dihydro-4*H*-pyran-4-ones **III** ($R^1 = \text{Ar}$) subsequently yield highly substituted biaryls. Reaction mechanisms are presented for the formation of the 2,2-dialkyl-2,3-dihydro-4*H*-pyran-4-ones as well as for the carbonyl-alkyne exchange reactions with electron-poor acetylenes.

1. Introduction. – Substituted 2,2-dialkyl-2,3-dihydro-4*H*-pyran-4-ones of type **III** (*Scheme 1*) are well known compounds which have been described with a number of different substituents R^1 , R^2 , R^3 , and R^4 . Such compounds are readily accessible by two different strategies. *Gelin* and coworkers have described the condensation of 2-acylacetic acids with 3,3-dialkyl-acryloyl chloride [1] and *Vereshchagin* and coworkers have pioneered the acid-catalyzed cyclization of substituted acetylenic ketones [2]. Recently, we have improved the cyclization method [2] by the use of aq. HBr as acid catalyst [3].

Scheme 1



Although the syntheses of 2,2-dialkyl-2,3-dihydro-4*H*-pyran-4-ones **II** and **III** (*Scheme 1*) have been studied quite extensively, relatively little is known about their chemistry and use as synthetic building blocks. *Gelin*, *e.g.*, has studied the base-catalyzed ring openings [1], whereas *Dreux* has described the addition of *Grignard* reagents [4].

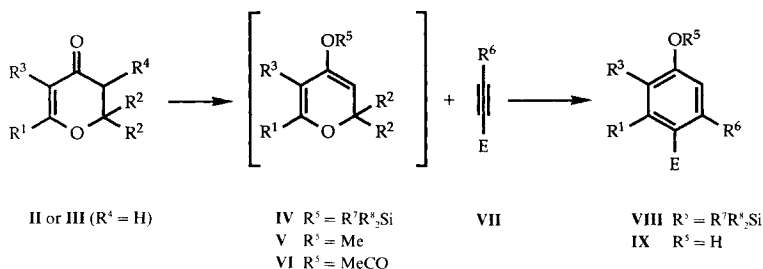
We describe in this paper a further improvement of the cyclization of substituted acetylenic ketones of type **I** [2] [3] to **II** using 33% HBr/AcOH in CH_2Cl_2 at room

¹⁾ Presented in part at the autumn meeting of the Swiss Chemical Society in Bern on October 20, 1989.

temperature (Scheme 1). Using this protocol, the 2,2-dialkyl-2,3-dihydro-4*H*-pyran-4-ones **II** are obtained under very mild conditions in good-to-excellent yields (Table 2). In addition, we present a convenient bromination of **II** at C(5) (Scheme 4, Table 2).

Furthermore, we describe the use of 2,2-dialkyl-2,3-dihydro-4*H*-pyran-4-ones as precursors for the *in situ* preparation of electron-rich dienes of type **IV–VI** and the carbonyl-alkyne exchange reaction (CAE reaction) with electron-poor acetylenes **VII** to yield the highly substituted aromatic compounds of type **VIII** and **IX** (Scheme 2). This

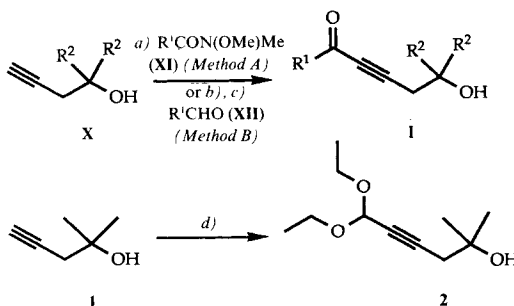
Scheme 2



CAE reaction, well known for 2*H*-pyran-2-ones [5–7] and 2*H*-pyrans [5], proceeds with the *in situ* prepared silyl enol ethers **IV** ($R^5 = R^7R^8Si$), methyl enol ethers **V** ($R^5 = Me$), and enol acetates **VI** ($R^5 = MeCO$; Scheme 2) with high degree of regioselectivity and under very mild conditions. In cases where $R^1 = Ar$, this novel transformation yields highly substituted biaryls, compounds which have recently attracted very much attention [8]. In addition, results of mechanistic investigations of the acid-catalyzed cyclizations and the CAE reactions are presented and discussed.

2. Substituted Acetylenic Ketones of Type I. – Ketones of type **I** (Scheme 1) were readily prepared from the known 1,1-dialkylbut-3-ynols **X** (**1** ($R^2 = Me$) and **4** ($R^2 = i-Pr$)). These compounds were conveniently prepared from propargyl bromide and the corresponding ketones [9], following our earlier described route [3] (Scheme 3). The

Scheme 3



a) (*i*-Pr) $MgCl$, THF, $R^1CON(OMe)Me$ (XI). b) (*i*-Pr) $MgCl$, THF, R^1CHO (XII). c) MnO_2 , CH_2Cl_2 , $0^\circ \rightarrow r.t.$
d) (*i*-Pr) $MgCl$, THF, $(EtO)_2CHOPh$ (12), 50° (72%).

Table 1. *Synthesis of the Substituted Acetylenic Ketones of Type I. See Scheme 3.*

Acetylenic alcohol X	R ¹ CON(OMe)Me XI	R ¹ CHO XII	Method	Acetylenic ketone I	R ¹	R ²	Yield [%]
1	5		<i>A</i>	13	Me	Me	61.1
1	6		<i>A</i>	14	Ph	Me	90.4
1		7	<i>B</i>	14	Ph	Me	85.0
4	6		<i>A</i>	15	Ph	i-Pr	88.4
1	8		<i>A</i>	16	<i>t</i> -Bu	Me	75.0
1		9	<i>B</i>	17	COOMe	Me	61.0
1	10^{a)}		<i>A</i>	18	CH ₂ COOEt	Me	43.7
1		11	<i>B</i>	19	2-(MeO)C ₆ H ₄	Me	67.0
1		12^{b)}	<i>B</i>	2^{c)}	H	Me	71.9

^{a)} Instead of amide **XI**, the corresponding commercially available acyl chloride **10** was used.

^{b)} Corresponding diethyl acetal **12** was used.

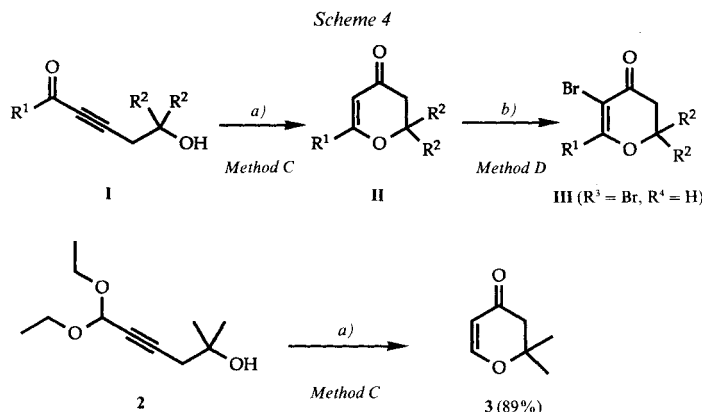
^{c)} Corresponding diethyl acetal (R¹ = H).

acetylenic alcohols **X** were treated with 2.2 equiv. of (i-Pr)MgCl in THF at room temperature for 4 h, followed either by addition of the *N*-methoxy-*N*-methylamides of type **XI** (**5**, **6**, and **8**) and mild hydrolysis (*Method A*) to yield the acetylenic ketones **I** (**13–16**, *Table 1*) or by addition of the corresponding aldehydes **XII** (**7**, **9**, and **11**) and oxidation with MnO₂ in CH₂Cl₂ (*Method B*) to yield **I** (**14**, **17**, and **19**, *Table 1*). The yields were 60–90% using *Method A* and 61–85% using *Method B*, based on isolated and purified products (*Table 1*). The corresponding starting material for R¹ = H was conveniently prepared as the diethyl acetal **2** using a modified procedure of Barbot [10] (*Scheme 3*), and acetylenic ketone **18** (R¹ = CH₂COOEt) was prepared following *Method A* but using the commercially available (ethoxycarbonyl)acetyl chloride (**10**; *Table 1*).

3. 2,2-Dialkyl-2,3-dihydro-4H-pyran-4-ones of Type II and III. – 3.1. *Acid-catalyzed Cyclization of Acetylenic Ketones I to II and Bromination at C(5)*. As mentioned in *Chapt. 1*, we found a general and efficient modification of the earlier described conditions [2] [3] for the acid-catalyzed cyclizations of the acetylenic ketones **I** to the 2,2-dialkyl-2,3-dihydro-4H-pyran-4-ones of type **II**. Replacement of aq. HBr/toluene (80°) [3] by HBr/AcOH in CH₂Cl₂ at 0° to room temperature yielded **II** (**3**, **20**, **22**, **24**, **26–29**) in good to excellent yields (67–96%; *cf. Table 2*). During our search to find efficient methods for

Table 2. *Synthesis of the 2,2-Dialkyl-2,3-dihydro-4H-pyran-4-ones of Type II and III. See Scheme 1.*

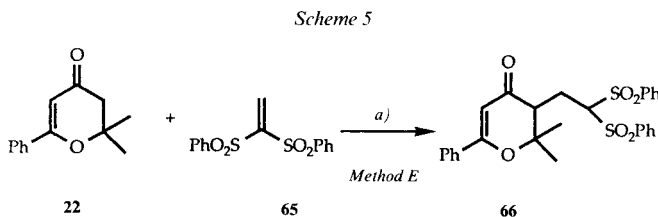
Acetylenic ketone I	Method	Pyranone II	Pyranone III	R ¹	R ²	R ³	Yield [%]
2	<i>C</i>	3 [18]		H	Me	H	89.0
13	<i>C</i>	20 [1]		Me	Me	H	86.8
	<i>D</i>		21	Me	Me	Br	86.4
14	<i>C</i>	22 [2] [3]		Ph	Me	H	87.3
	<i>D</i>		23	Ph	Me	Br	92.6
15	<i>C</i>	24		Ph	i-Pr	H	91.8
	<i>D</i>		25	Ph	i-Pr	Br	94.8
16	<i>C</i>	26 [10]		<i>t</i> -Bu	Me	H	91.0
17	<i>C</i>	27		COOMe	Me	H	66.9
18	<i>C</i>	28		CH ₂ COOEt	Me	H	72.6
19	<i>C</i>	29		2-(MeO)C ₆ H ₄	Me	H	96.3



a) 33% HBr/AcOH, CH_2Cl_2 , $0^\circ \rightarrow \text{r.t.}$ b) NBS, CHCl_3 , $0^\circ \rightarrow \text{r.t.}$

introducing further substituents R^3 and R^4 , we discovered that compounds of type **II** could be easily brominated with *N*-bromosuccinimide (NBS) in CHCl_3 (Scheme 4). The isolated yields for this transformation of **II** (**20**, **22**, **24**) into **III** (**21**, **23**, **25**) were excellent (86–95%; cf. Table 2).

Substituents R^4 at C(3) of the 2,2-dialkyl-2,3-dihydro-4*H*-pyran-4-ones **II** are most conveniently introduced by reaction of the corresponding silyl enol ether (prepared by reaction of **II** with 1.2 equiv. of (*tert*-butyl)dimethylsilyl trifluoromethanesulfonate ((*t*-Bu) Me_2SiOTf) and 1.3 equiv. of 2,6-di(*tert*-butyl)pyridine ((*t*-Bu) $\text{C}_5\text{H}_3\text{N}$) in CHCl_3 [11]) with an appropriate electrophile. Using this method, reaction of **22** with 1,1-bis(phenylsulfonyl)ethene (**65**) afforded the C(3)-substituted derivative **66** in 96% yield (Scheme 5).

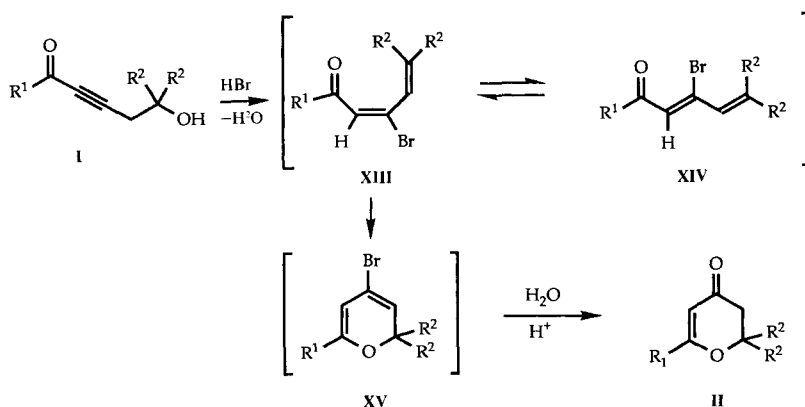


a) (*t*-Bu) $\text{C}_5\text{H}_3\text{N}$, (*t*-Bu) Me_2SiOTf , CHCl_3 , $0^\circ \rightarrow \text{r.t.}$ (96%).

With this set of reactions, a wide range of new highly substituted 2,2-dialkyl-2,3-dihydro-4*H*-pyran-4-ones of type **III** (Schemes 2 and 4) has become readily accessible (cf. Table 2).

3.2. Mechanistic Studies. Under the cyclization conditions used by Vereshchagin [2] (aq. $\text{H}_2\text{SO}_4/\text{EtOH}$, 100°), the reaction mechanism probably involves hydrolysis of the acetylenic ketones **I** to the corresponding β -diketones, cyclization, and dehydration to **II**. For the acid-catalyzed cyclizations with HBr, however, we propose that ketones **I** are first transformed, by addition of HBr and elimination of H_2O , to a mixture of (*Z*)- and (*E*)-bromo-dienones **XIII** and **XIV**, which rapidly interconvert under the reaction condi-

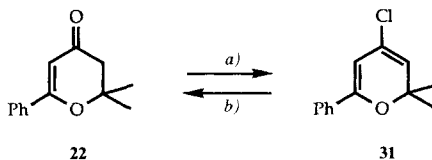
Scheme 6



tions (Scheme 6). The (*E*)-isomers **XIII**, thus, react in a 6 π -electrocyclization to the bromo-2*H*-pyran derivatives **XV**, which are transformed under the reaction conditions into the corresponding 2,2-dialkyl-2,3-dihydro-4*H*-pyran-4-ones **II**.

The following observations provide strong support for this mechanism. First, the isolable chloro-2*H*-pyran **31** (Scheme 7), prepared by treatment of **22** with 1.5 equiv. of oxalyl chloride and a catalytic amount of DMF in CH₂Cl₂ in 96% yield, provides **22** under the standard cyclization conditions. Second, the 4-chloro-2*H*-pyran **31** shows similar TLC properties with the most apolar spot from the cyclization reaction mixture (e.g. **14** → **22**) which slowly disappears during the course of the reaction.

Scheme 7



a) (COCl)₂, cat. DMF, CH₂Cl₂ (96%). b) HBr/AcOH, CH₂Cl₂, r.t. (Method C).

4. Carbonyl-Alkyne Exchange (CAE) Reactions of *in situ*-Prepared Electron-Rich Dienes IV–VI Derived from II and III with Electron-Poor Acetylenes VII. – 4.1. *General.* While the CAE reactions have been extensively studied for 2*H*-pyran-2-ones of type **XXII** (see below, Scheme 14) [6] [7], there are only a few examples in the case of 2*H*-pyrans of type **XXIII** [5]. *Danishefsky* and coworkers have shown, that the acyclic electron-rich dienes of type **XXV** [12] undergo *Diels-Alder* reactions with electron-poor acetylenes **VII** (Scheme 2) to yield, after elimination of ROH, highly substituted aromatic compounds of type **VIII**. Although the regioselectivities of these acyclic dienes in the CAE reactions are usually excellent (in contrast to those of **XXII** and **XXIII**), there is only a little variation of R¹ and R³ described in the literature so far. To our knowledge,

Table 3. CAE Reactions of **II** or **III** with Acetylenes **VII**. See Scheme 8.

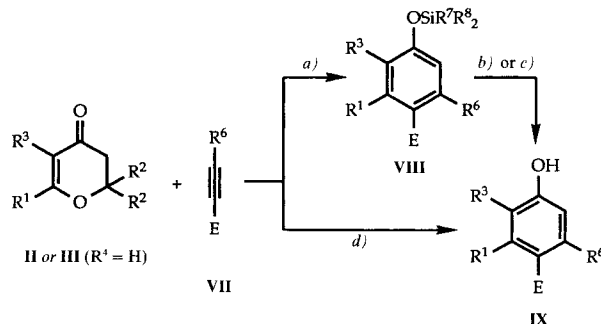
4H-Pyran-4-one II or III	Acetylene VII	Method	Silylated phenol VIII	Phenol IX	R ¹	R ²	R ³	R ⁶	E	R ⁷	R ⁸	Yield [%]
22	32	<i>E</i>	33		Ph	Me	H	H	PhCO	<i>t</i> -Bu	Me	96.8
22	32	<i>E</i>	34		Ph	Me	H	H	PhCO	<i>i</i> -Pr	<i>i</i> -Pr	90.4
22	32	HCl/MeOH		35	Ph	Me	H	H	PhCO			93.0
22	36	<i>F</i>		35	Ph	Me	H	H	PhCO			83.7
22	36	<i>E</i>	37		Ph	Me	H	Me	PhCO	<i>i</i> -Pr	<i>i</i> -Pr	95.0
22	39	HCl/EtOH	40	38	Ph	Me	H	Me	PhCO			93.4
22	42	HCl/MeOH	43	41	Ph	Me	H	COOMe	COOMe	<i>i</i> -Pr	<i>i</i> -Pr	68.7
22	45	HCl/EtOH	46	44 [13]	Ph	Me	H	H	COOMe			93.6
22	48	<i>E</i>	49	47	Ph	Me	H	COOMe	COOMe	<i>i</i> -Pr	<i>i</i> -Pr	56.8
23	32	HCl/EtOH		50	Ph	Me	H	H	PhCO			99.0
26	36	<i>F</i>		51	Ph	Me	H	CHO	PhCO	<i>t</i> -Bu	Me	98.0
26	39	<i>E</i>	52		<i>t</i> -Bu	Me	H	Me	PhCO			91.0
26	39	HCl/EtOH	54	53	<i>t</i> -Bu	Me	H	Me	PhCO	<i>t</i> -Bu	Me	74.0
29	32	HCl/MeOH	56	55	<i>t</i> -Bu	Me	H	COOMe	COOMe	<i>i</i> -Pr	<i>i</i> -Pr	94.0
29	39	HCl/EtOH	58	57	2-(MeO)C ₆ H ₄	Me	H	H	PhCO	thexyl	Me	91.4
30	36	Bu ₄ NF		59	2-(MeO)C ₆ H ₄	Me	H	COOMe	COOMe	<i>i</i> -Pr	<i>i</i> -Pr	87.5
30	39	<i>E</i>	61	60	2-(MeO)C ₆ H ₄	Me	H	COOMe	COOMe	thexyl	Me	93.0
		Bu ₄ NF		62	Ph	Me	COOEt	COOMe	COOMe			79.2
					Ph	Me	COOEt	COOMe	COOMe			90.0
					Ph	Me	COOEt	COOMe	COOMe			47.0
					Ph	Me	COOEt	COOMe	COOMe			58.0
					Ph	Me	COOEt	COOMe	COOMe			90.7

a) During the aq. workup and FC, the acetal group was hydrolyzed to R⁶ = CHO.

2,2-dialkyl-2,3-dihydro-4*H*-pyran-4-ones **II** (or **III**) have never been described in connection with CAE reactions, such as shown in *Scheme 2*.

4.2. Via *Silyl Enol Ethers of II or III*. The best conditions for the *in situ* preparation of the silyl enol ethers of type **IV** from **II** or **III** (see *Scheme 2*) were either the use of 2.5 equiv. of $(t\text{-Bu})_2\text{C}_5\text{H}_3\text{N}$ and 2.2 equiv. of a bulky trialkylsilyl trifluoromethanesulfonate $\text{R}^7\text{R}^8\text{SiOTf}$ ($\text{R}^7 = \text{R}^8 = i\text{-Pr}$; $\text{R}^7 = t\text{-Bu}$, $\text{R}^8 = \text{Me}$; $\text{R}^7 = \text{thexyl}$, $\text{R}^8 = \text{Me}$) in CHCl_3 at room temperature to 60° (*Method E*; cf. *Table 3*) or the use of 2.5 equiv. of Me_3SiOTf and 2.2 equiv. of $(t\text{-Bu})_2\text{C}_5\text{H}_3\text{N}$ in CHCl_3 (*Method F*; cf. *Table 3*) at room temperature. When $\text{R}^7\text{R}^8\text{SiOTf}$ was used, the highly substituted silylated phenols of type **VIII** were obtained from **II** or **III** and **VII** in excellent yields (*Scheme 8*), after purification by flash chromatography (FC) [15]. These compounds **VIII** could then be hydrolyzed to the crystalline phenols **IX**. When Me_3SiOTf (*Method F*) was used, phenols **IX** were directly obtained after quenching the reaction mixture with HCl/MeOH (*Scheme 8*).

Scheme 8



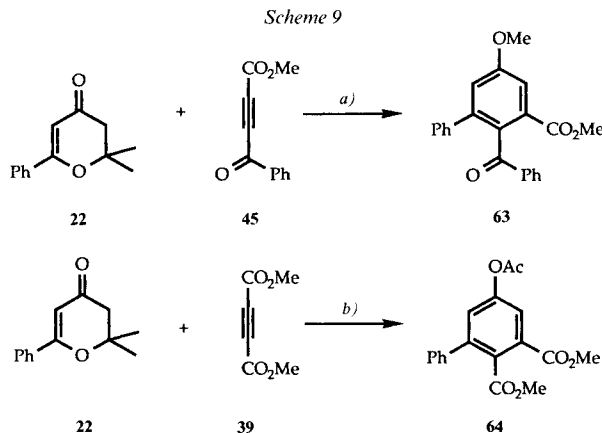
a) $(t\text{-Bu})_2\text{C}_5\text{H}_3\text{N}$ (2.5 equiv.), $\text{R}^7\text{R}^8\text{SiOTf}$ (2.2 equiv.), CHCl_3 $0^\circ \rightarrow 60^\circ$ (*Method E*). b) ROH ($\text{R} = \text{Me}$ or Et), 2N aq. HCl soln., $60\text{--}80^\circ$. c) Bu_4NF , THF , r.t. d) $(t\text{-Bu})_2\text{C}_5\text{H}_3\text{N}$ (2.2 equiv.), Me_3SiOTf (2.5 equiv.), CHCl_3 , $0^\circ \rightarrow \text{r.t.}$, then MeOH , 2N aq. HCl (*Method F*).

As depicted in *Table 3*, the 2,3-dihydro-2,2-dimethyl-4*H*-pyran-4-ones **II** or **III** ($\text{R}^2 = \text{Me}$; **22**, **23**, **26**, **29**, and **30**) were chosen as models for the CAE reactions with electron-poor acetylenes **VII** (**32**, **36**, **39**, **42**, **45**, and **48**). When **VII** was unsymmetrical (**32**, **36**, **42**, **45**, **48**), the reactions were completely regioselective. The observed regiochemistry is in accordance with simple FMO considerations and with earlier published work [5]. It is interesting to note, that the CAE reactions work especially well for **22** ($\text{R}^1 = \text{Ph}$), **29** ($\text{R}^1 = 2\text{-(MeO)C}_6\text{H}_4$), and even for **26** ($\text{R}^1 = t\text{-Bu}$), which demonstrates the high reactivity of the *in situ*-prepared electron-rich dienes of type **IV** (*Scheme 2*). Furthermore, even the very acid-labile acetal group of acetylene **48** ($\text{R}^6 = (\text{OEt})_2\text{CH}$) is compatible with the mild reaction conditions (*Method E*), yielding, after hydrolytic workup, the highly functionalized biphenylcarbaldehyde **50** ($\text{R}^6 = \text{CHO}$) in 90% overall yield.

Substituents (Br , COOEt) at C(5) of the 2,3-dihydro-2,2-dimethyl-4*H*-pyran-4-ones **III** ($\text{R}^2 = \text{Me}$; **23** and **30**) generally decrease the reactivity towards the CAE reactions. The additional substituent R^3 presumably slows down the formation of the intermediate silyl enol ether **IV** due to steric reasons. These dienes, however, once formed, are thermo-

dynamically more stable and thus less susceptible towards the undesired electrocyclic ring opening (see below (*Scheme 10*) and *Chapt. 4.5*). For these reasons, the use of the much more reactive silylating agent Me_3SiOTf (*Method F*) is preferred when $\text{R}^3 \neq \text{H}$. The excess of Me_3SiOTf presumably serves as a *Lewis*-acid catalyst.

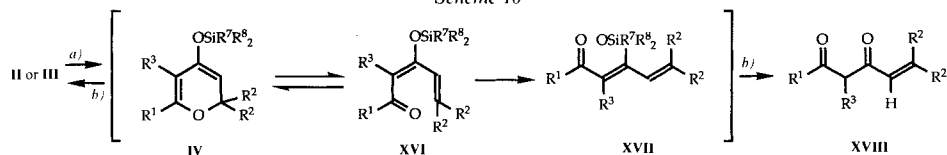
4.3. Via *Enol Ethers and Enol Acetates of II*. In analogy to the *in situ*-prepared silyl enol ethers **IV** from **II** or **III**, compounds **II** or **III** can also be transformed into the corresponding methyl enol ethers **V** ($\text{R}^5 = \text{Me}$) and enol acetates **VI** ($\text{R}^5 = \text{MeCO}$; *Scheme 2*). Such enol ethers and enol acetates also undergo the CAE reactions with electron-poor acetylenes of type **VII** as exemplified in *Scheme 9*. The enol ether of 4*H*-pyran-4-one **22**, generated *in situ* by reaction with 2.2 equiv. Me_3OBF_4 and 2.5 equiv. of $(t\text{-Bu})_2\text{C}_5\text{H}_3\text{N}$ in CHCl_3 , yields with acetylene **45** the highly substituted aromatic compound **63** in 57% isolated yield (87% based on recovered starting material), whereas the enol acetate, generated *in situ* by reaction of **22** with excess of isopropenyl acetate and a catalytic amount of TsOH in toluene, yields with acetylene **39** the corresponding aromatic compound **64** in 90.5% isolated yield (*Scheme 9*). The latter process is especially promising, considering the ease of handling, the low cost of the reagents, and the high yield of isolated product.



a) $(t\text{-Bu})_2\text{C}_5\text{H}_3\text{N}$, Me_3OBF_4 , CHCl_3 , r.t. (87%). *b)* Isopropenyl acetate, TsOH , CHCl_3 , 75° (90.5%).

4.4. *Mechanistic Considerations.* 4.4.1. *Stability of the in situ-Prepared Silyl Enol Ethers, Enol Ethers, and Enol Acetates Derived from II or III.* As mentioned earlier, the 2,2-dialkyl-2,3-dihydro-4*H*-pyran-4-ones **II** or **III** can be transformed into the corresponding β -diketones of type **XVIII** by a base-catalyzed, probably electrocyclic ring opening [1]. Under acidic conditions, these β -diketones **XVIII** yield **II** or **III** [1]. A similar electrocyclic equilibrium of ring-opened and -closed forms is known for the parent 2*H*-pyrans [5]. Based on these facts, we reasoned that such an equilibrium might also exist in the case of the *in situ*-prepared silyl enol ethers **IV** ($\text{R}^5 = \text{SiR}^7\text{R}^8_2$), enol ethers **V** ($\text{R}^5 = \text{Me}$), and enol acetates **VI** ($\text{R}^5 = \text{MeCO}$, *Scheme 2*). Careful analysis of the hydrolysis products **II** or **III** and **XVII**, generated from the mixture of silyl enol ethers **IV**, **XVI**, and **XVII** (*Scheme 10*), revealed the expected lability of the intermediates **IV**

Scheme 10



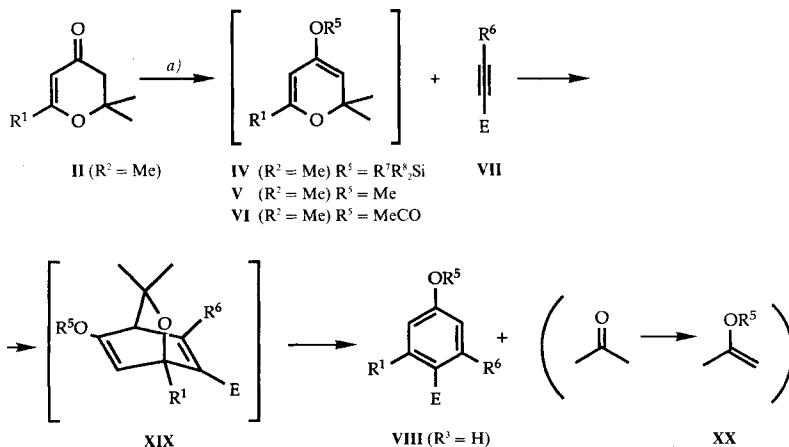
a) Base (2.2–2.5 equiv.), $R^7R^8_2SiOTf$ (2.2–2.5 equiv.), $CHCl_3$. b) 2N aq. HCl soln.

towards certain bases (e.g. Et_3N , NaOH) and their stability towards acids (TsOH, Me_3SiOTf). It was finally found, that the use of $(t-Bu)_2C_5H_3N$ instead of Et_3N [11] for the *in situ* preparation of the silyl enol ethers of type IV completely suppressed the formation of XVI and XVII and thus of XVIII after hydrolysis. These observations led to the development of the conditions described in *Methods E* and *F* (see *Chapt. 4.4.2*). As noted previously, the silyl enol ethers IV bearing substituents at C(5) were generally more stable and less susceptible towards electrocyclic ring opening, but their preparation required higher temperatures (60° instead of room temperature, *Method E*) or the more reactive Me_3SiOTf as silylating reagent (*Method F*).

4.4.2. *Mechanistic Studies of the CAE Reactions.* In the cases of the 2H-pyran-2-ones of type XXII [6] [7] and the 2H-pyrans of type XXIII [5] (see below, *Scheme 14*), it is generally accepted, that the CAE reactions proceed *via* two sequential concerted processes, namely a [4 + 2] cycloaddition followed by a [4 + 2] cycloreversion with extrusion of CO_2 or acetone. In the case of open-chain silyl enol ethers, *Mukaiyama* has produced experimental evidence for two sequential *Lewis* acid catalyzed *Michael* additions [14], whereas in the case of the ‘*Danishefsky* dienes’, the concerted mechanism was favored [12].

We believe that the silyl enol ethers of type IV ($R^5 = R^7R^8_2Si$), generated from II by *Method E*, the enol ether V ($R^1 = Ph$, $R^2 = R^5 = Me$), and the enol acetate VI ($R^1 = Ph$,

Scheme 11

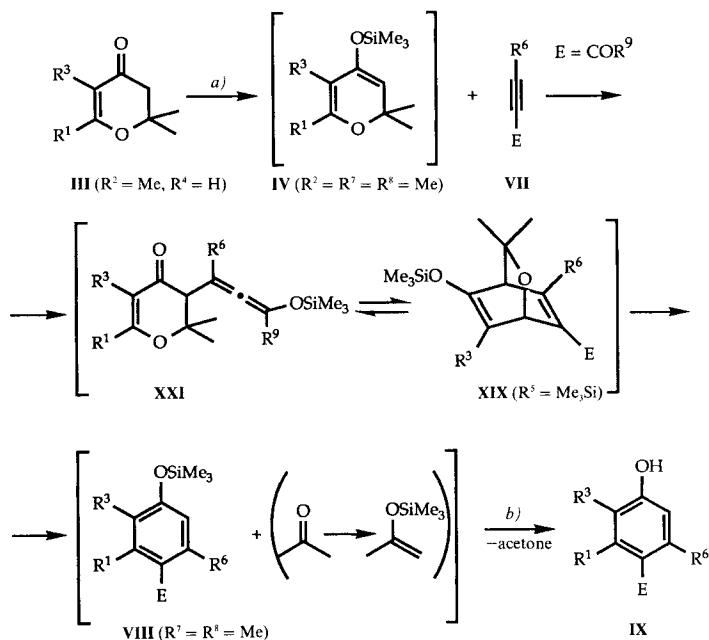


a) $(t-Bu)_2C_5H_3N$ (2.5 equiv.), $R^7R^8_2SiOTf$ (2.2 equiv.), $CHCl_3$ ($R^5 = R^7R^8_2Si$), or $(t-Bu)_2C_5H_3N$ (2.5 equiv.), Me_3OBF_4 , $CHCl_3$ ($R^5 = Me$), or isopropenyl acetate, TsOH, toluene ($R^5 = Ac$).

$R^2 = \text{Me}$, $R^5 = \text{MeCO}$) derived from **22**, follow the mechanism presented in *Scheme 11*. These *in situ*-prepared dienes of type **IV–VI** would react in *Diels-Alder* fashion with electron-poor acetylenes **VII** to the non-isolable intermediates **XIX**, which upon extrusion of acetone ($R^2 = \text{Me}$) yield the highly substituted aromatic compounds **VIII** and the ketone derivative **XX²**.

In the cases where Me_3SiOTf was used as the silylating agent (*Method F*), we can not exclude a 'Mukaiyama'-type reaction pathway as depicted in *Scheme 12*. In these cases, the *in situ*-formed silyl enol ethers **IV** (from **III**) would react with acetylene **VII** in two sequential *Lewis* acid catalyzed *Michael* additions *via* **XXI** to the bicyclic intermediates **XIX** (*Scheme 12*), which upon extrusion of acetone yield **VIII** and the highly substituted phenols **IX** after hydrolysis.

Scheme 12



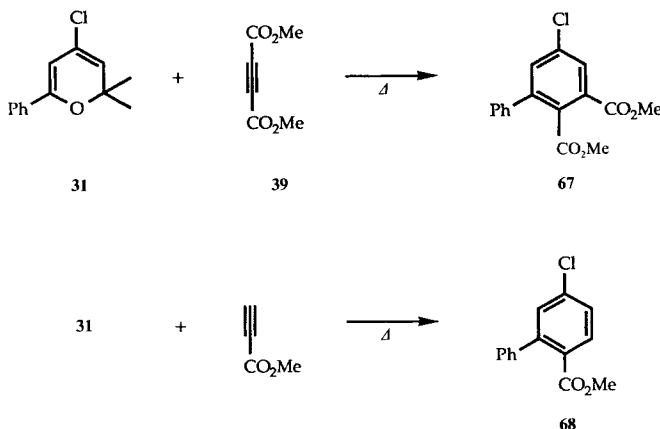
a) $(t\text{-Bu})_2\text{C}_5\text{H}_3\text{N}$ (2.2 equiv.), Me_3SiOTf (2.5 equiv.), CHCl_3 , $0^\circ \rightarrow \text{r.t.}$ (*Method F*). *b*) 2N aq. HCl, MeOH.

Strong support for the concerted mechanism is furnished by the fact, that 4-chloro-2*H*-pyran **31** (*Scheme 7*) cleanly undergoes the CAE reaction with acetylene **39** or methyl propiolate in purely thermal reactions upon heating at 80° (*Scheme 13*).

On the other hand it was mentioned earlier (*Chapt. 3.1*) that the silyl enol ether derived from **22** ($R^1 = \text{Ph}$, $R^2 = \text{Me}$) reacts in 'Mukaiyama' fashion with *Michael* acceptors such as, *e.g.*, with 1,1-bis(benzenesulfonyl)ethene (**65**) to yield the 3-substituted 2,3-dihydro-2,2-dimethyl-4*H*-pyran-4-one **66** in 96% yield (*Scheme 5*).

²⁾ The use of 2.5 equiv. of $(t\text{-Bu})_2\text{C}_5\text{H}_3\text{N}$ and excess of enolizing reagent ($R^7R^8_2\text{SiOTf}$, Me_3OBf_4 , or isopropenyl acetate) accelerates the formation of **VIII** by trapping the liberated acetone as its enol ethers or enol acetate **XX**, thus prohibiting an undesired transesterification from **IV–VI** to acetone.

Scheme 13



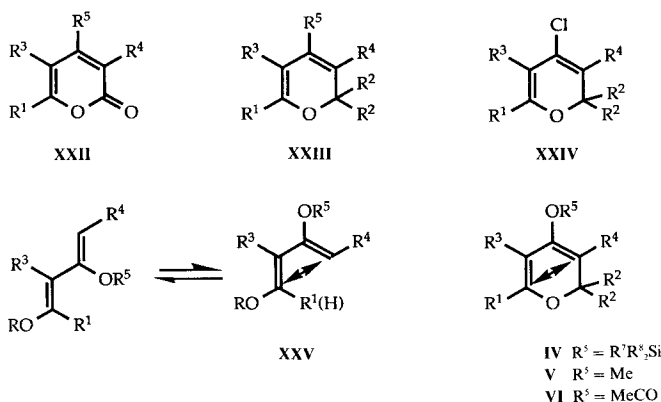
Furthermore, it should be noted, that the CAE reactions of **II** seem to be restricted to $R^2 = \text{Me}$, since **24** ($R^1 = \text{Ph}$, $R^2 = i\text{-Pr}$) did not undergo the expected CAE reaction, presumably for steric reasons. In addition, it should be noted that the corresponding diene of **3** ($R^1 = \text{H}$, $R^2 = \text{Me}$) prepared by *Method E* was not stable at 0° .

5. Conclusions. – In this paper, we described a general high-yield synthesis of substituted 2,2-dialkyl-2,3-dihydro-4*H*-pyran-ones of type **II** and **III** (Scheme 1) by acid-catalyzed cyclization of the corresponding acetylenic ketones **I**. Moreover, we have investigated the scope and limitations of the highly regioselective CAE reactions of the *in situ*-prepared electron-rich silyl enol ethers **IV** ($R^5 = R^7R^8\text{Si}$), enol ethers **V** ($R^5 = \text{Me}$), and enol acetates **VI** ($R^5 = \text{MeCO}$) (Scheme 2) of **II** and **III** with electron-poor acetylenes **VII**. In these reactions, the highly substituted aromatic compounds of type **VIII** and **IX** (Schemes 2, 8, 10, and 11) are formed in good-to-excellent yields (Table 3). This reaction is especially interesting for $R^1 = \text{Ar}$, where highly substituted biaryls **VIII** and **IX** ($R^1 = \text{Ar}$) are obtained. This methodology thus offers a novel route to biologically interesting biaryl-derived natural products [8]. In addition, we present reaction mechanisms for the formation of the compounds of type **II** (or **III**; Scheme 6) and their CAE reactions with electron-poor acetylenes **VII** (Schemes 11 and 12).

A comparison of the reactivities of the corresponding 2*H*-pyran-2-ones **XXII** [6] [7], 2*H*-pyrans **XXIII** [5], 4-chloro-2*H*-pyrans **XXIV**, and the *in situ*-prepared electron-rich dienes **IV**–**VI** in the CAE reactions with electron-poor acetylenes of type **VII** reveals roughly the following order: **IV** > **V** $\approx$ **VI** > **XXIV** > **XXIII** > **XXII** (Scheme 14).

In conclusion, the *in situ*-prepared electron-rich dienes of type **IV**–**VI** derived from the readily available 2,2-dialkyl-2,3-dihydro-4*H*-pyran-4-ones **II** or **III** should be regarded as cyclic, conformationally restricted analogues of the ‘Danishefsky dienes’ **XXV** [12] (Scheme 14). Their increased reactivities in *Diels-Alder*-type reactions with electron-poor acetylenes **VII** can be attributed to the facts, that in the cyclic dienes **IV** the *s-cis*-conformation is fixed and the distance between the terminal sp^2 C-atoms of the diene system is shortened compared to the acyclic dienes **XXV**, and for these reasons, they are more ‘transition state like’. Finally, since the CAE reactions of **IV** work best when there are bulky substituents R^1 (e.g. $R^1 = \text{Ar}$, *t*-Bu) and the ‘Danishefsky dienes’ **XXV**

Scheme 14



work best when $R^1 = H, OR$, these dienes are complementary. The use of the *in situ*-prepared electron-rich dienes of type IV–VI and XXIV in natural product synthesis will be reported in due course.

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Experimental Part

General. All reactions with air- or moisture-sensitive reactants and solvents were carried out in oven- or flame-dried glassware under a positive pressure of dry Ar. Reaction solvents and liquid reagents were purified by distillation shortly before use. THF was distilled under Ar from Na with benzophenone ketyl as indicator. CH_2Cl_2 was distilled from powdered CaH_2 . All other reactants were 'reagent-grade' unless described otherwise. Di(*tert*-butyl)pyridine ((*t*-Bu) $_2C_5H_3N$), dimethyl(thexyl)silyl trifluoromethanesulfonate ($Me_2(Th)SiOTf$), (*tert*-butyl)-dimethylsilyl trifluoromethanesulfonate ((*t*-Bu) Me_2SiOTf), triisopropylsilyl trifluoromethanesulfonate ((*i*-Pr) $_3SiOTf$), trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf), and *N*-bromosuccinimide (NBS) were all from *Fluka*. Anal. TLC: 2.5×10 cm precoated TLC plates, SiO_2 60F-254, layer thickness 0.25 mm (*E. Merck & Co.*, Darmstadt, FRG). Flash chromatography (FC): *E. Merck* SiO_2 60 (230–400 mesh ASTM); according to [15]. M.p.: *Büchi-SMP-20* apparatus; uncorrected. IR: *Nicolet-7199-FT-IR* spectrometer; solids in KBr pellets, liquids as thin films; characteristic bands in cm^{-1} . 1H -NMR: *Bruker-AC-250* apparatus, at 250 MHz; in $CDCl_3$; TMS as internal standard; chemical shifts of signal centres and ranges in ppm (δ), *J* in Hz.

1. General Methods. – **Method A.** To a stirred soln. of acetylenic alcohol **X** (10.0 mmol) in THF (30 ml) was added (*i*-Pr) $MgCl$ (2M in THF; 10.5 ml, 21.0 mmol) at 0°. The mixture was stirred under Ar at r.t. for 5 h, a soln. of *N*-methoxy-*N*-methylamide **XI** (10.0 mmol) in THF (10 ml) added at -40° , and the mixture stirred for 12 h at r.t. and poured into a mixture of ice (20 g), 1M aq. NaH_2PO_4 (50 ml), and AcOEt (50 ml). After vigorous stirring for 30 min, the aq. layer was extracted with AcOEt (2×50 ml), the combined org. fraction washed with sat. brine (100 ml) and evaporated, and the residue purified by FC (150 g, SiO_2 , Et_2O /hexane 1:1) and dried under reduced pressure, affording acetylenic ketone **I** as slightly yellow oil.

Method B. To a stirred soln. of acetylenic alcohol **X** (10.0 mmol) in THF (30 ml) was added at 0° (*i*-Pr) $MgCl$ (2M in THF; 10.5 ml, 21.0 mmol). The mixture was stirred under Ar at r.t. for 5 h, a soln. of aldehyde **XII** (10.0 mmol) in THF (10 ml) added at -40° , and the mixture stirred for 30 min at -40° and for 2 h at 0° and poured

into a mixture of ice (20 g), sat. NH_4Cl soln. (50 ml) and AcOEt (50 ml). The aq. layer was extracted with AcOEt (2×50 ml) and the combined org. fraction washed with sat. brine (100 ml), dried (MgSO_4), and evaporated. The residue was dissolved in CH_2Cl_2 (15 ml) and added to a mechanically stirred suspension of MnO_2 (26 g) in CH_2Cl_2 (50 ml) at 0° . The mixture was stirred for 1 h at 0° and for 30 min at r.t. and filtered through MgSO_4 , the filtrate evaporated, and the resulting residue purified as described in *Method A*.

Method C. To a stirred soln. of acetylenic ketone **I** (10.0 mmol) in CH_2Cl_2 (50 ml) was slowly added at 0° 33% HBr/AcOH soln. (2.75 ml). The mixture was stirred for 30 min at 0° and for 4–10 h at r.t. and poured into ice (50 g), H_2O (100 ml), and CH_2Cl_2 (50 ml). The aq. phase was extracted with CH_2Cl_2 (2×50 ml), the combined org. fraction dried (MgSO_4) and evaporated, the residue purified by FC (150 g, SiO_2 , $\text{Et}_2\text{O}/\text{hexane}$ 1:1), and the pyranone **II** crystallized or further purified by bulb-to-bulb distillation as indicated.

Method D. To a stirred soln. of pyranone **II** (10.0 mmol) in CHCl_3 (50 ml) was added slowly NBS (2.37 g, 10.5 mmol) at 0° . The mixture was stirred for 6 h at r.t. and poured into H_2O (100 ml) and CH_2Cl_2 (50 ml), the org. layer dried (MgSO_4) and evaporated, and the residue purified by FC (150 g, SiO_2 , $\text{Et}_2\text{O}/\text{hexane}$ 2:3) affording **III** ($\text{R}^3 = \text{Br}$) as colourless crystals after recrystallization from $\text{AcOEt}/\text{hexane}$.

Method E. To a stirred soln. of **II** or **III** (1.0 mmol), $(t\text{-Bu})_2\text{C}_5\text{H}_3\text{N}$ (0.48 g, 2.5 mmol), and acetylene **VII** (1.0–6.0 mmol) in CHCl_3 (2.5 ml) was slowly added $\text{R}^7\text{R}^8\text{SiOTf}$ (2.2–2.3 mmol) under Ar. The mixture was stirred for 2 h at 0° and at r.t. as indicated and poured into a mixture of ice (10 g), sat. NaHCO_3 soln. (5 ml), and Et_2O (10 ml). The aq. layer was extracted with Et_2O (2×10 ml), the combined org. fraction extracted with sat. brine (10 ml), dried (MgSO_4), and evaporated, and the excess of **VII** (where possible) removed by bulb-to-bulb distillation under reduced pressure. The residue was purified by FC (30 g SiO_2) as indicated: **VIII** as colourless oils.

Method F. To a stirred soln. of **III** (1.0 mmol), $(t\text{-Bu})_2\text{C}_5\text{H}_3\text{N}$ (0.42 g, 2.2 mmol), and acetylene **VII** (1.0–3.0 mmol) in CHCl_3 (2.5 ml) was added at -30° freshly distilled Me_3SiOTf (0.46 ml, 2.5 mmol). The mixture was stirred for 30 min at 0° and at r.t. as indicated and poured into a mixture of MeOH (0.5 ml), 2N aq. HCl (5 ml), ice (5 g) and Et_2O (10 ml). The aq. layer was extracted with AcOEt (2×50 ml), the combined org. fraction dried (MgSO_4) and evaporated, the excess of **VII** and $(t\text{-Bu})_2\text{C}_5\text{H}_3\text{N}$ removed by bulb-to-bulb distillation under reduced pressure, the residue purified by FC (35 g SiO_2) as indicated, and the product **IX** crystallized from $\text{AcOEt}/\text{hexane}$.

2. Substituted Acetylenic Ketones of Type I. – 2.1. *5-Hydroxy-5-methylhex-2-ynal Diethyl Acetal (2)* [16]. A stirred soln. of **1** [9] (3.0 g, 30.56 mmol) in THF (150 ml) was treated according to *Method A* with diethyl phenyl orthoformate [16] (**12**; 7.68 ml, 1.3 equiv.) and stirred for 12 h at 45° . The mixture was poured into a mixture of ice (50 g), 2N aq. NaOH (100 ml), and Et_2O (200 ml). The org. layer was extracted with 2N aq. NaOH (2×75 ml), dried (MgSO_4), and evaporated. The residue was purified by FC (SiO_2 400 g), $\text{Et}_2\text{O}/\text{hexane}$ 3:2 to yield, after bulb-to-bulb distillation under reduced pressure, 4.40 g (71.9%) of **2**. Colorless liquid. B.p. $150^\circ/0.07$ mbar. IR (film): 2976m, 2886w, 2242m, 1449w, 1361w, 1329w, 1150m, 1082w, 1051s, 1006w, 908w. $^1\text{H-NMR}$ (CDCl_3 , 250 MHz): 5.29 (t, $J = 1.6$, $\text{H}-\text{C}(1)$); 3.8–3.55 (m, $(\text{CH}_3\text{CH}_2\text{O})_2\text{CH}$); 2.45 (d, $J = 1.6$, 2 $\text{H}-\text{C}(4)$); 1.86 (br. s, OH); 1.43 (s, 2 $\text{CH}_3-\text{C}(5)$); 1.24 (t, $J = 7.1$, $(\text{CH}_3\text{CH}_2\text{O})_2\text{CH}$). MS: 199 (< 1 , $[\text{M} - \text{H}]^+$), 155 (18), 97 (56), 98 (58), 69 (39), 68 (50), 59 (100), 43 (61). Anal. calc. for $\text{C}_{11}\text{H}_{20}\text{O}_3$ (200.28): C 65.97, H 10.07; found: C 65.98, H 10.20.

2.2. *6-Hydroxy-6-methylhept-3-yn-2-one (13)*. From **1** (5.0 g, 50.94 mmol) and **5** [17] (5.25 g, 50.94 mmol) according to *Method A*: 4.36 g (61.1%) of **13**. Colourless oil. IR (film): 3429m (br.), 2975m, 2212s, 1672s, 1418w, 1361m, 1361m, 1235s, 1149w, 967w, 906w. $^1\text{H-NMR}$ (CDCl_3 , 250 MHz): 2.56 (s, 2 $\text{H}-\text{C}(5)$); 2.36 (s, 3 $\text{H}-\text{C}(1)$); 2.02 (s, OH); 1.35 (s, 2 $\text{CH}_3-\text{C}(6)$). MS: 125 (2, $[\text{M} - \text{CH}_3]^+$), 82 (47), 59 (100), 43 (75).

2.3. *5-Hydroxy-5-methylhex-2-ynophenone (14)* [2] [3]. From **1** (5.94 g, 60.54 mmol) and **6** [17] (10.0 g, 60.54 mmol) according to *Method A*: 11.08 g (90.4%) of **14**. Colourless oil [3].

2.4. *5-Hydroxy-5-isopropyl-6-methylhept-2-ynophenone (15)*. From **4** (5.0 g, 32.4 mmol; prepared analogously to [9]) and **6** [17] (5.35 g, 32.4 mmol) according to *Method A*: 7.40 g (88.4%) of **15**. Slightly yellow oil. IR (film): 3500w (br.), 2968m, 2879w, 2199m, 1640s, 1599w, 1448w, 1314m, 1267s, 1175w, 702s. $^1\text{H-NMR}$ (CDCl_3 , 250 MHz): 8.2–8.1, 7.65–7.45 (2m, 5 arom. H); 2.73 (s, 2 $\text{H}-\text{C}(4)$); 2.25–2.05 (m, 2 $(\text{CH}_3)_2\text{CH}_2$); 1.47 (br. s, OH); 1.07, 1.03 (2d, $J = 6.9$, 2 $(\text{CH}_3)_2\text{CH}$). MS: 258 (< 1 , M^+), 215 (31), 145 (37), 144 (100), 115 (49), 105 (30), 71 (57), 43 (47). Anal. calc. for $\text{C}_{17}\text{H}_{22}\text{O}_2$ (258.36): C 79.03, H 8.58; found: C 78.37, H 8.75.

2.5. *7-Hydroxy-2,2,7-trimethyloct-4-yn-3-one (16)*. From **1** (3.0 g, 30.6 mmol) and **8** [17] (4.45 g, 30.6 mmol) according to *Method A*: 4.18 g (75%) of **16**. Slightly yellow oil. IR (film): 3424w (br.), 2990s, 2934w, 2210m, 1668s, 1478m, 1365w, 1277w, 1156s, 945m, 904w. $^1\text{H-NMR}$ (CDCl_3 , 250 MHz): 2.59 (s, 2 $\text{H}-\text{C}(4)$); 2.0–1.5 (br. s, OH); 1.37 (s, 2 $\text{CH}_3-\text{C}(7)$); 1.21 (s, $(\text{CH}_3)_3\text{C}$). MS: 167 (2, $[\text{M} - \text{CH}_3]^+$), 124 (20), 81 (23), 67 (40), 59 (100), 57 (61), 43 (32), 41 (29). Anal. calc. for $\text{C}_{11}\text{H}_{18}\text{O}_2$ (182.26): C 72.49, H 9.95; found: C 72.18, H 9.85.

2.6. *Methyl 6-Hydroxy-6-methyl-2-oxohept-3-ynoate (17)*. From **1** (7.80 g, 79.5 mmol) and a freshly prepared soln. of methyl glyoxylate (**9**; 10.5 g, 0.119 mol) in THF (100 ml) according to *Method B*. FC (SiO_2 400 g),

Et₂O/hexane 1:1) gave 8.93 g (61%) of **17**. Slightly yellow oil. IR (film): 3523m, 3426m, 2977m, 2214s, 1745s, 1684s, 1438w, 1276m, 1198m, 1162s, 1002m, 906w, 800w. ¹H-NMR (CDCl₃, 250 MHz): 3.93 (s, COOCH₃); 2.68 (s, 2 H–C(5)); 2.00 (br. s, OH); 1.40 (s, 2 CH₃–C(6)). MS: 125 (11, [M – (CH₃)₂CO]⁺), 67 (54), 59 (100), 43 (34), 41 (12), 39 (12), 31 (18).

2.7. *Ethyl 7-Hydroxy-7-methyl-3-oxooct-4-ynoate (18)*. From **1** (3.92 g, 39.9 mmol) and *ethyl 3-chloro-3-oxopropanoate (10; Fluka; 2.5 ml, 19.15 mmol)* according to *Method A*. FC (SiO₂ (250 g), AcOEt/hexane 1:3 → 1:1) gave 1.85 g (43.7%) of **18**. Slightly yellow oil. IR (film): 3452w, 2979m, 2214m, 1741s, 1678s, 1615m, 1467w, 1373m, 1324m, 1252s, 1176m, 1145m, 1032m. ¹H-NMR (CDCl₃, 250 MHz): 11.89 (s, OH, ca. 10% enol form); 5.32 (s, H–C(2), ca. 10% enol form); 4.22 (q, *J* = 7.9, CH₃CH₂O); 3.58 (s, 2 H–C(2)); 2.58 (s, 2 H–C(6)); 1.36 (s, 2 CH₃–C(7)); 1.27 (t, *J* = 7.9, CH₃CH₂O). MS: 154 (9, [M – (CH₃)₂CO]⁺), 126 (41), 67 (38), 66 (38), 59 (100), 43 (42).

2.8. *5-Hydroxy-1-(2-methoxyphenyl)-5-methylhex-2-yn-1-one (19)*. From **1** (3.5 g, 35.66 mmol) and *2-methoxybenzaldehyde (11; Fluka; 4.86 g, 35.66 mmol)* according to *Method B*. FC (SiO₂, Et₂O/hexane 2:1) gave 5.55 g (67%) of **19**. Pale yellow oil. IR (film): 3433m (br.), 2973m, 2936w, 2213m, 1635s, 1594s, 1486s, 1463m, 1434m, 1380w, 1303m, 1243s, 1164m, 1134m, 1020m, 920m, 758m. ¹H-NMR (CDCl₃, 250 MHz): 8.0–7.95, 7.55–7.5, 7.1–7.0 (3m, 4 arom. H); 3.93 (s, CH₃O); 2.65 (s, 2 H–C(4)); 1.39 (2 CH₃–C(5)). MS: 232 (2, M⁺), 174 (55), 77 (19), 59 (100), 43 (14).

3. 2,2-Dialkyl-2,3-dihydro-4H-pyran-4-ones of Type II and III. – 3.1. *2,3-Dihydro-2,2-dimethyl-4H-pyran-4-one (3)* [18]. From **2** (1.0 g; 4.99 mmol) according to *Method C*. Bulb-to-bulb distillation under reduced pressure gave 560 mg (89%) of **3**. Slightly red liquid. B. p. 110°/18 Torr. IR (film): 3054w, 2980m, 1675s, 1595s, 1466w, 1410m, 1371m, 1324w, 1281s, 1173m, 1038s, 984w, 886m, 781w. ¹H-NMR (CDCl₃, 250 MHz): 7.23 (*d*, *J* = 6.1, H–C(6)); 5.39 (*d*, *J* = 6.1, H–C(5)); 2.53 (s, 2 H–C(3)); 1.44 (s, 2 CH₃–C(2)). MS: 126 (33, M⁺), 111 (21), 71 (83), 56 (100), 41 (69). Anal. calc. for C₇H₁₀O₂ (126.16): C 66.64, H 7.99; found: C 66.81, H 8.30.

3.2. *2,3-Dihydro-2,2,6-trimethyl-4H-pyran-4-one (20)* [1]. From **13** (4.32 g, 30.8 mmol) according to *Method C*. Bulb-to-bulb distillation under reduced pressure gave 3.75 g (86.8%) of **20**. Colorless liquid. B. p. 70°/0.05 mbar. IR (film): 2979w, 2903w, 1667s, 1611s, 1437w, 1393s, 1359m, 1250m, 1156m, 1097w, 1016m, 990m, 882w, 800w. ¹H-NMR (CDCl₃, 250 MHz): 5.30 (s, H–C(5)); 2.43 (s, 2 H–C(3)); 1.97 (s, CH₃–C(6)); 1.42 (s, 2 CH₃–C(2)). MS: 140 (27, M⁺), 125 (37), 85 (100), 69 (22), 56 (71), 43 (74), 41 (55). Anal. calc. for C₈H₁₂O₂ (140.18): C 68.55, H 8.63; found: C 68.31, H 8.84.

3.3. *5-Bromo-2,3-dihydro-2,2,6-trimethyl-4H-pyran-4-one (21)*. From **20** (300 mg, 2.14 mmol) according to *Method D*. After recrystallization, 405 mg (86.4%) of **21**. M.p. 60–62°. IR (KBr): 2967w, 1673s, 1576s, 1374m, 1332m, 1272w, 1235m, 1168m, 1094w, 1002m, 570m. ¹H-NMR (CDCl₃, 250 MHz): 2.67 (s, 2 H–C(3)); 2.26 (s, CH₃–C(6)); 1.44 (s, 2 CH₃–C(2)). MS: 220, 218 (19, M⁺), 205, 203 (60), 165, 163 (28), 56 (59), 43 (100). Anal. calc. for C₈H₁₁BrO₂ (219.08): C 43.86, H 5.06, Br 36.47; found: C 43.75, H 5.01, Br 36.92.

3.4. *2,3-Dihydro-2,2-dimethyl-6-phenyl-4H-pyran-4-one (22)* [2] [3]. From **14** (11.00 g, 53.32 mmol) according to *Method C*. FC (SiO₂, AcOEt/hexane 1:1) gave 9.60 g (87.3%) of **22**. White solid. M.p. 36–37°. Spectra: identical to those described in [3].

3.5. *5-Bromo-2,3-dihydro-2,2-dimethyl-6-phenyl-4H-pyran-4-one (23)*. From **22** (2.05 g, 10.14 mmol) according to *Method D*. After recrystallization, 2.64 g (92.6%) of **23**. M.p. 98–99°. IR (KBr): 2990w, 1674s, 1604w, 1559w, 1488w, 1447w, 1374w, 1335m, 1233w, 1070m, 995m, 760m, 695m. ¹H-NMR (CDCl₃, 250 MHz): 7.7–7.65, 7.5–7.4 (2 m, 5 arom. H); 2.83 (s, 2 H–C(3)); 1.56 (s, 2 CH₃–C(2)). MS: 282, 280 (9, M⁺), 267, 265 (22), 227, 225 (12), 105 (100), 77 (38). Anal. calc. for C₁₃H₁₃BrO₂ (281.15): C 55.54, H 4.66, Br 28.42; found: C 55.33, H 4.80, Br 28.38.

3.6. *2,3-Dihydro-2,2-diisopropyl-6-phenyl-4H-pyran-4-one (24)*. From **15** (3.68 g, 14.25 mmol) according to *Method C*: 3.38 g (91.8%) of **24** as pale yellow oil, which solidified upon standing. M.p. 36–37°. IR (KBr): 3057w, 2975m, 2878w, 1648s, 1599s, 1570m, 1448m, 1381s, 1264m, 1060w, 1015w, 981m, 871m. ¹H-NMR (CDCl₃, 250 MHz): 7.8–7.7, 7.55–7.4 (2 m, 5 arom. H); 5.93 (s, H–C(5)); 2.62 (s, 2 H–C(3)); 2.29 (*sept.* *J* = 6.9, 2 (CH₃)₂CH); 1.05, 0.98 (2 *d*, *J* = 6.9, 2 (CH₃)₂CH). MS: 258 (12, M⁺), 215 (16), 147 (51), 138 (100), 105 (72), 77 (23), 71 (43), 69 (60), 43 (42), 41 (44). Anal. calc. for C₁₇H₂₂O₂ (258.36): C 79.03, H 8.58; found: C 79.10, H 8.54.

3.7. *5-Bromo-2,3-dihydro-2,2-diisopropyl-6-phenyl-4H-pyran-4-one (25)*. From **24** (2.78 g, 10.76 mmol) according to *Method D*. After recrystallization, 3.44 g (94.8%) of **25**. M.p. 71.5–72.5°. IR (KBr): 2982w, 2935w, 2876w, 1665s, 1652s, 1498w, 1443w, 1350m, 1324w, 1095w, 1025m, 989m, 681m. ¹H-NMR (CDCl₃, 250 MHz): 7.75–7.65, 7.55–7.4 (2 m, 5 arom. H); 2.88 (s, 2 H–C(3)); 2.28 (*sept.* *J* = 6.9, 2 (CH₃)₂CH); 1.04, 1.02 (2 *d*, *J* = 6.9, 2 (CH₃)₂CH). MS: 336 (3, M⁺), 295, 293 (30), 257 (52), 227, 225 (33), 105 (100), 71, 69 (43), 55 (37), 43 (95). Anal. calc. for C₁₇H₂₁BrO₂ (337.26): C 60.54, H 6.28, Br 23.69; found: C 60.45, H 6.25, Br 23.57.

3.8. *6-(tert-Butyl)-2,3-dihydro-2,2-dimethyl-4H-pyran-4-one (26)* [10]. From **16** (3.08 g, 16.90 mmol) according to *Method C*: 2.80 g (91%) of **26** as pale yellow oil, which solidified upon standing. M.p. 36–37°. IR (KBr):

2958m, 1666w, 1587m, 1492s, 1454m, 1436m, 1282s, 1244s, 1177s, 1072m, 1029m, 830m. ¹H-NMR (CDCl₃, 250 MHz): 5.40 (s, H-C(5)); 2.43 (s, 2 H-C(3)); 1.41 (s, 2 CH₃-C(2)); 1.14 (s, (CH₃)₃C). MS: 182 (15, M⁺), 127 (38), 69 (40), 57 (100), 43 (53), 41 (12). Anal. calc. for C₁₁H₁₈O₂ (182.26): C 72.49, H 9.95; found: C 72.40, H 10.11.

3.9. *Methyl 3,4-Dihydro-2,2-dimethyl-4-oxo-2H-pyran-6-carboxylate (27)* [19]. From **17** (1.30 g, 7.06 mmol) according to *Method C* (18 h at r.t.). FC (SiO₂ (50 g), Et₂O/hexane 1:1) and crystallization from Et₂O/hexane gave 870 mg (66.9%) of **27**. Pale yellow crystals. M.p. 67° ([19]: 68°). IR (KBr): 2981w, 2955w, 1733s, 1674s, 1610m, 1441m, 1393m, 1373m, 1279s, 1173w, 1078m, 993m, 866m. ¹H-NMR (CDCl₃, 250 MHz): 6.21 (s, H-C(5)); 3.88 (s, COOCH₃); 2.55 (s, 2 H-C(3)); 1.50 (s, 2 CH₃-C(2)). MS: 184 (8, M⁺), 129 (21), 125 (36), 69 (100), 57 (27), 56 (65), 41 (31).

3.10. *Ethyl 3,4-Dihydro-2,2-dimethyl-4-oxo-2H-pyran-5-acetate (28)*. From **18** (980 mg, 4.61 mmol) according to *Method C*. FC (SiO₂ (50 g), AcOEt/hexane 1:2) gave 710 mg (72.6%) of **28**. Pale yellow oil. IR (film): 2981m, 2905w, 1740s, 1670s, 1615s, 1465w, 1391m, 1324m, 1251m, 1177m, 1151m, 1030m, 992m. ¹H-NMR (CDCl₃, 250 MHz): 5.40 (s, H-C(5)); 4.19 (q, J = 7.5, CH₃CH₂O); 3.23 (s, CH₂COOCH₂CH₃); 2.48 (s, 2 H-C(3)); 1.44 (s, 2 CH₃-C(2)); 1.28 (t, J = 7.5, CH₃CH₂O). MS: 212 (4, M⁺), 197 (12), 157 (12), 115 (16), 69 (100), 56 (46), 55 (56), 43 (50), 41 (58), 39 (54).

3.11. *2,3-Dihydro-2,2-dimethyl-6-(2-methoxyphenyl)-4H-pyran-4-one (29)*. From **19** (5.40 g, 23.2 mmol) according to *Method C*. FC (SiO₂ (150 g), Et₂O/hexane 2:1) gave 5.25 g (96.3%) of **29** as pale yellow oil which solidified upon standing. M.p. 30–31°. IR (film): 2977w, 1657s, 1604s, 1568m, 1491m, 1462m, 1366s, 1280m, 1244s, 1167s, 1040m, 1020m, 760m. ¹H-NMR (CDCl₃, 250 MHz): 7.7–7.65 (m, 1 arom. H); 7.45–7.35 (m, 1 arom. H); 7.05–6.9 (m, 2 arom. H); 6.23 (s, H-C(5)); 3.87 (s, CH₃O); 2.59 (s, 2 H-C(3)); 1.53 (s, 2 CH₃-C(2)). MS: 232 (16, M⁺), 217 (10), 137 (100), 105 (12), 77 (14). Anal. calc. for C₁₄H₁₆O₃ (232.28): C 72.39, H 6.94; found: C 72.18, H 6.99.

3.12. *Ethyl 3,4-Dihydro-2,2-dimethyl-4-oxo-6-phenyl-2H-pyran-5-carboxylate (30)* [1]. To a stirred soln. of ethyl 2-benzoylacetate (*Aldrich*; 10.0 g, 52.08 mmol) in THF (150 ml) was added a soln. of (i-Pr)MgCl (2 M in THF; 28.6 ml) at –60°. The mixture was stirred for 1 h at 0°, 3,3-dimethylacryloyl chloride (*Aldrich*; 6.17 g, 52.02 mmol) added at 0°, and the mixture stirred for 6 h at 40°, cooled to r.t., and quenched with sat. NH₄Cl soln. (100 ml), ice (100 g), and Et₂O (200 ml). The aq. phase was extracted with Et₂O (2 × 100 ml), the comb. org. fraction extracted with sat. brine (150 ml), dried (MgSO₄), and evaporated, and the residue chromatographed (SiO₂ (450 g), AcOEt/hexane 1:1) and recrystallized from AcOEt/hexane: 10.80 g (75.7%) of **30**. Colorless crystals. M.p. 78.5–79.5°. IR (KBr): 2975w, 2902w, 1722s, 1675m, 1571m, 1374s, 1258m, 1141m, 1086s, 704w. ¹H-NMR (CDCl₃, 250 MHz): 7.6–7.35 (m, 5 arom. H); 4.07 (q, J = 7.2, CH₃CH₂O); 2.67 (s, 2 H-C(3)); 1.58 (s, 2 CH₃-C(2)); 0.99 (t, J = 7.2, CH₃CH₂O). MS: 274 (4, M⁺), 105 (100), 83 (18), 77 (50), 56 (19), 51 (18), 41 (20). Anal. calc. for C₁₆H₁₈O₄ (274.32): C 70.06, H 6.61; found: C 69.85, H 6.36.

3.13. *4-Chloro-2,2-dimethyl-6-phenyl-2H-pyran (31)*. To a stirred soln. of 650 mg (3.21 mmol) of **22** in CH₂Cl₂ (8 ml) was added at 0° 1 drop of DMF and 0.41 ml (4.87 mmol) of freshly distilled oxalyl chloride. The mixture was stirred under Ar for 45 min at 0° and then evaporated and the residue purified by FC (SiO₂ (40 g), Et₂O/hexane 1:5): 680 mg (96%) of **31**. Pale yellow oil (which turned slightly red in the freezer). IR (film): 3088w, 3062w, 2978w, 2930w, 1634s, 1569m, 1492m, 1442m, 1360m, 1303m, 1197w, 1148m, 1048s, 1024m, 784m, 749s. ¹H-NMR (CDCl₃, 250 MHz): 7.65–7.6 (m, 2 arom. H); 7.4–7.35 (m, 3 arom. H); 5.78, 5.30 (2 d, J = 1.6, H-C(3), H-C(5)); 1.48 (s, 2 CH₃-C(2)). MS: 220 (5, M⁺), 207 (34), 205 (100), 105 (48), 77 (47), 51 (16), 43 (21).

4. Carbonyl-Alkyne Exchange Reactions of *in situ*-Prepared Dienes of Type IV–VI. – 4.1. 5-{[tert-Butyl]dimethylsilyl}oxy}biphenyl-2-yl Phenyl Ketone (**33**). From **22** (500 mg, 2.47 mmol), **32** (420 mg, 3.23 mmol); prepared according to [3], and (t-Bu)Me₂SiOTf (1.36 ml, 5.92 mmol) according to *Method E* (1.5 h at r.t.). FC (SiO₂ (80 g), Et₂O/hexane 1:8), gave 930 mg (96.8%) of **33**. Colorless oil. IR (film): 3028w, 2931m, 2857w, 1683m, 1597s, 1558w, 1480m, 1045w, 1310m, 1259s, 1215m, 910s, 833s, 693s. ¹H-NMR (CDCl₃, 250 MHz): 7.65–7.6 (m, 2 arom. H); 7.5–7.35 (m, 2 arom. H); 7.3–7.1 (m, 7 arom. H); 6.95–6.85 (m, 2 arom. H); 1.01 (s, tBuSi); 0.26 (s, Me₂Si). MS: 388 (20, M⁺), 331 (53), 105 (100), 77 (27).

4.2. 5-{[Triisopropylsilyl]oxy}biphenyl-2-yl Phenyl Ketone (**34**). From **22** (300 mg, 1.48 mmol), **32** (250 mg, 1.92 mmol), and (i-Pr)₃SiOTf (0.42 ml, 3.40 mmol) according to *Method E* (2 h at r.t.). FC (SiO₂ (50 g), Et₂O/hexane 1:10) gave 560 mg (90.4%) of **34**. Colorless oil. IR (film): 3029m, 2944m, 2867m, 1663m, 1597s, 1555m, 1482m, 1402w, 1312m, 1280s, 1216s, 941m, 882m, 789m, 695s. ¹H-NMR (CDCl₃, 250 MHz): 7.65–7.55 (m, 2 arom. H); 7.5–7.35 (m, 2 arom. H); 7.3–7.1 (m, 7 arom. H); 7.0–6.9 (m, 2 arom. H); 1.4–1.2 (m, J = 6.7, ((CH₃)₂CH)Si); 1.14 (d, J = 6.7, ((CH₃)₂CH)Si). MS: 430 (9, M⁺), 387 (30), 105 (100), 77 (19).

4.3. 5-Hydroxybiphenyl-2-yl Phenyl Ketone (**35**). a) A soln. of **34** (400 mg, 0.96 mmol) in MeOH (3 ml) and 2N aq. HCl (1 ml) was stirred for 3 h at 80° in a sealed tube, cooled to r.t., and mixed with H₂O (5 ml) and AcOEt

(10 ml). The aq. phase was extracted with AcOEt (2 × 5 ml), the comb. org. fraction dried (MgSO₄) and evaporated, and the residue crystallized from Et₂O/hexane: 245 mg (93%) of **35**. Colorless crystals. M.p. 179–180°. IR (KBr): 3292m (br.), 3024w, 1635s, 1595s, 1481w, 1437w, 1318w, 1289s, 1219w, 887m, 746m, 698s. ¹H-NMR (CDCl₃, 250 MHz): 7.7–7.55 (m, 2 arom. H); 7.5–7.35 (m, 2 arom. H); 7.35–7.05 (m, 7 arom. H); 6.9–6.8 (m, 2 arom. H); 6.41 (s, OH). MS: 274 (58, M⁺), 273 (45), 197 (100), 105 (21), 77 (31). Anal. calc. for C₁₉H₁₄O₂ (274.32): C 83.29, H 5.14; found: C 83.15, H 5.08.

b) From **22** (700 mg, 3.46 mmol), **32** (585 mg, 4.50 mmol), and Me₃SiOTf (1.60 ml, 8.65 mmol) according to *Method F* (24 h at r.t.). Recrystallization from AcOEt/hexane gave 794 mg (83.7%) of **35**. Colorless crystals. M.p. 179–180°.

4.4. 3-Methyl-5-[(triisopropylsilyl)oxy]biphenyl-2-yl Phenyl Ketone (**37**). From **22** (300 mg, 1.48 mmol), *but-2-ynophenone* (**36**; prepared according to *Method A*; 336 mg, 2.33 mmol), and (i-Pr)₃SiOTf (0.92 ml, 3.41 mmol) according to *Method E*. Chromatography (SiO₂ (50 g), Et₂O/hexane 1:10) gave 625 mg (95%) of **37**. Colorless oil. IR (film): 3031w, 2944m, 2867m, 1666m, 1595s, 1467m, 1335s, 1266m, 1195s, 995w, 926w, 881m, 792m, 693m. ¹H-NMR (CDCl₃, 250 MHz): 7.6–7.5, 7.4–7.3, 7.3–7.05, 6.85–6.75 (4m, 12 arom. H); 2.21 (s, CH₃); 1.4–1.2 (m, J = 6.6, 3 (CH₃)₂CH); 1.14 (d, J = 6.6, 3 (CH₃)₂CH). MS: 444 (10, M⁺), 401 (20), 105 (100), 77 (22).

4.5. 5-Hydroxy-3-methylbiphenyl-2-yl Phenyl Ketone (**38**). A soln. of **37** (580 mg, 1.30 mmol) in EtOH (4.5 ml) and 2N aq. HCl (1 ml) was treated for 4.5 h at 80° in a sealed tube, cooled to r.t., and mixed with ice (5 g) H₂O (5 ml), and Et₂O (10 ml). The org. phase was dried (MgSO₄) and evaporated and the residue purified by FC (SiO₂ (50 g), Et₂O/hexane 1:1) and recrystallization from AcOEt/hexane: 350 mg (93.4%) of **38**. Colorless crystals. M.p. 148.0–148.5°. IR (KBr): 3309m (br.), 3024w, 2932w, 1638s, 1595m, 1576m, 1497w, 1447w, 1319m, 1279s, 1187m, 1099w, 916w, 858w, 748m, 699m. ¹H-NMR (CDCl₃, 250 MHz): 7.6–6.55 (m, 2 arom. H); 7.45–7.3 (m, 1 arom. H); 7.3–7.05 (m, 7 arom. H); 6.8–6.7 (m, 2 arom. H); 5.44 (s, OH); 2.20 (s, CH₃). MS: 288 (70, M⁺) 287 (100, [M – 1]⁺), 211 (73). Anal. calc. for C₂₀H₁₆O₂ (288.35): C 83.31, H 5.59; found: C 83.15, H 5.68.

4.6. Dimethyl 5-[(triisopropylsilyl)oxy]biphenyl-2,3-dicarboxylate (**40**). From **22** (300 mg, 1.48 mmol), dimethyl acetylenedicarboxylate (**39**; Fluka; 0.55 ml, 4.48 mmol) and (i-Pr)₃SiOTf (0.92 ml, 3.41 mmol) according to *Method E* (30 h at r.t.). FC (SiO₂ (50 g), Et₂O/hexane 1:5) gave 450 mg (68.7%) of **40**. Pale yellow oil. IR (film): 2947m, 2868m, 1735s, 1595m, 1466m, 1432m, 1344s, 1267s, 1239s, 1168s, 1112w, 1066w, 1011m, 884w, 781w. ¹H-NMR (CDCl₃, 250 MHz): 7.44 (d, J = 2.5, 1 arom. H); 7.45–7.3 (m, 5 arom. H); 7.03 (d, J = 2.5, 1 arom. H); 3.90, 3.64 (2s, 2 COOCH₃); 1.4–1.2 (m, J = 6.7, 3 (CH₃)₂CH); 1.11 (d, J = 6.7, 3 (CH₃)₂CH). MS: 442 (11, M⁺), 411 (10), 399 (28), 367 (100), 339 (28). Anal. calc. for C₂₅H₃₄O₅Si (442.63): C 67.84, H 7.74; found: C 67.46, H 8.00.

4.7. Dimethyl 5-Hydroxybiphenyl-2,3-dicarboxylate (**41**). A soln. of 370 mg (0.84 mmol) of **40** in MeOH (2.5 ml) and 2N aq. HCl (0.5 ml) was stirred for 3 h at 80° in a sealed tube, cooled to r.t., and mixed with ice (5 g), H₂O (5 ml), and AcOEt (10 ml). The org. layer was dried (MgSO₄) and evaporated and the residue purified by FC (SiO₂ (30 g), AcOEt/hexane 1:1) and recrystallization from Et₂O: 225 mg (93.6%) of **41**. Colorless crystals. M.p. 105–107°. IR (KBr): 3306m (br.), 3057w, 3021w, 2908w, 1720s, 1700s, 1600m, 1428m, 1339m, 1301m, 1268m, 1232m, 1121w, 1064w, 999w, 948w, 870w, 779w, 760w, 702m. ¹H-NMR (CDCl₃, 250 MHz): 7.35–7.25 (m, 5 arom. H); 7.32, 6.91 (2d, J = 2.5, 2 arom. H); 6.69 (s, OH); 3.84, 3.64 (2s, 2 COOCH₃). MS: 286 (34, M⁺), 256 (19), 255 (100), 223 (10), 139 (14). Anal. calc. for C₁₆H₁₄O₅ (286.28): C 67.13, H 4.93; found: C 66.83, H 5.09.

4.8. Ethyl 5-[(triisopropylsilyl)oxy]biphenyl-2-carboxylate (**43**). From **22** (300 mg, 1.48 mmol), ethyl propionate (**42**; Fluka; 1.5 ml, 14.8 mmol), and (i-Pr)₃SiOTf (1.0 ml, 3.71 mmol) according to *Method E* (18 h at 60°). FC (SiO₂ (50 g), Et₂O/hexane 1:20) gave 335 mg (56.8%) of **43**. Pale yellow oil. IR (film): 3060w, 3038w, 2944m, 2868m, 1711s, 1598s, 1561w, 1484m, 1386w, 1364w, 1313m, 1280s, 1245m, 1217s, 1127m, 1099w, 1020w, 940m, 882m, 778w, 696m. ¹H-NMR (CDCl₃, 250 MHz): 7.80 (d, J = 7.9, 1 arom. H); 7.45–7.25 (m, 5 arom. H); 6.95–6.85 (m, 2 arom. H); 4.05 (q, J = 7.1, COOCH₂CH₃); 1.4–1.2 (m, 3 (CH₃)₂CH); 1.10 (d, J = 6.7, 3 (CH₃)₂CH); 0.96 (t, J = 7.1, COOCH₂CH₃). MS: 398 (13, M⁺), 356 (27), 355 (100), 327 (30), 299 (52), 211 (28), 127 (26).

4.9. Ethyl 5-Hydroxybiphenyl-2-carboxylate (**44**) [13]. A stirred soln. of **43** (300 mg, 0.75 mmol) in EtOH (5 ml) and 2N aq. HCl (1 ml) was treated for 7 h at 75° in a sealed tube, cooled to r.t., and mixed with ice (5 g), H₂O (5 ml), and AcOEt (10 ml). The org. phase was dried (MgSO₄) and evaporated and the residue purified by FC (SiO₂ (40 g), Et₂O/hexane 1:2) and recrystallization from Et₂O: 180 mg (99%) of **44**. M.p. 72.5–73.5°. IR (KBr): 3389s, 3056w, 2987w, 2900w, 1672s, 1600s, 1472w, 1437w, 1390w, 1364w, 1295s, 1221s, 1135m, 1023w, 865w, 768m, 704m. ¹H-NMR (CDCl₃, 250 MHz): 7.82 (d, J = 7.8, 1 arom. H); 7.4–7.2 (m, 5 arom. H); 6.85–6.75 (m, 2 arom. H); 5.89 (br. s, OH); 4.05 (q, J = 7.1, COOCH₂CH₃); 0.98 (t, J = 7.1, COOCH₂CH₃). MS: 242 (31, M⁺), 197 (100), 141 (13), 139 (11), 115 (12). Anal. calc. for C₁₅H₁₄O₃ (242.27): C 74.36, H 5.82; found: C 74.43, H 5.96.

4.10. Methyl 2-Benzoyl-5-[(tert-butyl)dimethylsilyl]oxy}biphenyl-3-carboxylate (**46**). From **22** (500 mg, 2.47 mmol), methyl 4-oxo-4-phenylbut-2-ynoate [20] (**45**; 490 mg, 2.60 mmol), and (t-Bu)Me₂SiOTf (1.25 ml, 5.43 mmol) according to *Method E* (2 h at r.t.). FC (SiO₂ (70 g), Et₂O/hexane 1:3) and crystallization from Et₂O gave

1.08 g (98%) of **46**. White solid. M.p. 83–85°. IR (KBr): 3063w, 3003w, 2930m, 2857m, 1726s, 1671m, 1598m, 1440m, 1342s, 1285m, 1165m, 1011m, 945m, 835s, 699m. ¹H-NMR (CDCl₃, 250 MHz): 7.65–7.5 (m, 2 arom. H); 7.50 (d, *J* = 2.4, 1 arom. H); 7.45–7.35 (m, 1 arom. H); 7.35–7.2 (m, 2 arom. H); 7.16 (s, 5 arom. H); 7.04 (d, *J* = 2.4, 1 arom. H); 3.66 (s, COOCH₃); 1.02 (s, *t*-BuSi); 0.27 (s, Me₂Si). MS: 466 (45, *M*⁺), 389 (74), 357 (100), 313 (30), 226 (19), 105 (54), 89 (49), 77 (55), 75 (38), 59 (31), 57 (22). Anal. calc. for C₂₇H₂₀O₄Si (446.62): C 72.61, H 6.77; found: C 72.44, H 6.91.

4.11. *Methyl 2-Benzoyl-5-hydroxybiphenyl-3-carboxylate (47)*. A suspension of **46** (550 mg, 1.23 mmol) in MeOH (5 ml) and 2N aq. HCl (1 ml) was stirred for 2 h at 75° (clear soln.), cooled to r.t., and mixed with ice (5 g), H₂O (5 ml), and AcOEt (10 ml). The org. phase was dried (MgSO₄) and evaporated and the residue crystallized from AcOEt/hexane: 370 mg (90.5%) of **47**. Colorless crystals. M.p. 152–153°. IR (KBr): 3368m (br.), 3089w, 3020w, 2956w, 1696s, 1671s, 1602m, 1580m, 1448w, 1351m, 1312m, 1263s, 1234s, 1186m, 1073w, 1002w, 925w, 772w, 708m. ¹H-NMR (CDCl₃, 250 MHz): 7.65–7.55 (m, 2 arom. H); 7.45 (d, *J* = 2.5, 1 arom. H); 7.45–7.35 (m, 1 arom. H); 7.3–7.25 (m, 2 arom. H); 7.12 (s, 5 arom. H); 7.0–6.95 (br. s, OH); 6.98 (d, *J* = 2.5, 1 arom. H); 3.58 (s, COOCH₃). MS: 332 (25, *M*⁺), 255 (100), 105 (29), 77 (22). Anal. calc. for C₂₁H₁₆O₄ (332.36): C 75.89, H 4.85; found: C 75.61, H 5.03.

4.12. *2-Benzoyl-5-[(tert-butyl)dimethylsilyl]oxybiphenyl-3-carbaldehyde (49)*. From **22** (180 mg, 0.89 mmol), *4,4*-diethoxybut-2-ynophenone [20] (**48**; 250 mg, 1.08 mmol), and (*t*-Bu)Me₂SiOTf (0.45 ml, 1.96 mmol) according to *Method E* (2 h at r.t.). FC (SiO₂ (40 g), Et₂O/hexane 1:1.5) gave 365 mg (98%) of **49**. Pale yellow oil. IR (film): 3060w, 2955w, 2930w, 2858w, 1665m, 1597s, 1463w, 1341m, 1263s, 1177m, 1128m, 1059s, 882w, 835s. ¹H-NMR (CDCl₃, 250 MHz): 9.90 (s, CHO); 7.6–7.1 (m, 12 arom. H); 1.03 (s, *t*-BuSi); 0.29 (s, Me₂Si). MS: 416 (33, *M*⁺), 415 (100, [*M* – 1]⁺), 105 (27), 73 (33).

4.13. *2-Benzoyl-5-hydroxybiphenyl-3-carbaldehyde (50)*. A soln. of **49** (310 mg, 0.74 mmol) in EtOH (4 ml) and 2N aq. HCl (2 ml) was stirred for 2 h at 65° in a sealed tube, cooled to r.t., and mixed with ice (5 g), H₂O (5 ml), and AcOEt (10 ml). The org. phase was dried (MgSO₄) and evaporated and the residue crystallized from AcOEt/hexane: 205 mg (91%) of **50**. Colorless crystals. M.p. 193.5–194.5°. IR (KBr): 3213m (br.), 3061w, 2925w, 2888w, 1675s, 1603m, 1575m, 1446w, 1330m, 1247s, 1176m, 1114w, 928m, 697s. ¹H-NMR (CDCl₃, 250 MHz): 9.87 (s, CHO); 7.65–7.55 (m, 2 arom. H); 7.5–7.35 (m, 2 arom. H); 7.3–7.1 (m, 8 arom. H); 6.06 (br. s, OH). MS: 302 (100, *M*⁺), 273 (47), 257 (29), 197 (22), 105 (24), 77 (50). Anal. calc. for C₂₀H₂₄O₃ (302.33): C 79.46, H 4.67; found: C 79.64, H 4.64.

4.14. *6-Bromo-5-hydroxybiphenyl-2-yl Phenyl Ketone (51)*. From **23** (350 mg, 1.24 mmol) and **32** (486 mg, 3.73 mmol) according to *Method F* (24 h at r.t.). FC (SiO₂ (40 g), Et₂O/hexane 3:2) gave 85 mg (24%) of recovered **23** and 197 mg (45%; 59% based on recovered **23**) of **51**. Pale yellow solid. M.p. 155–156°. IR (KBr): 3449m (br.), 3059w, 1652s, 1595m, 1551m, 1435w, 1313s, 1267s, 1236m, 1136w, 1073w, 702m. ¹H-NMR (CDCl₃, 250 MHz): 7.6–7.5, 7.5–7.35, 7.3–7.05 (3m, 12 arom. H); 6.03 (br. s, OH). MS: 354, 352 (60, *M*⁺), 277, 275 (100), 196 (65), 168 (31), 113 (23), 105 (88), 77 (98), 51 (24). Anal. calc. for C₁₉H₁₃BrO₂ (353.22): C 64.61, H 3.71, Br 22.62; found: C 64.65, H 3.65, Br 22.32.

4.15. *2-(tert-Butyl)-4-[(tert-butyl)dimethylsilyl]oxy-6-methylbenzophenone (52)*. From **26** (400 mg, 2.19 mmol), **36** (633 mg, 4.39 mmol), and (*t*-Bu)Me₂SiOTf (1.11 ml, 4.82 mmol) according to *Method E* (4 h at r.t.). FC (SiO₂ (50 g), AcOEt/hexane 1:20) gave 310 mg (49%) of recovered **36** and 620 mg (74%) of **52**. Pale yellow oil. IR (film): 3060w, 2930w, 2859w, 1671m, 1597s, 1469m, 1307s, 1251s, 1212w, 1157m, 1120w, 841s, 781m, 717m. ¹H-NMR (CDCl₃, 250 MHz): 8.3–7.6 (br. m, 2 arom. H); 7.6–7.35 (br. m, 3 arom. H); 6.87, 6.56 (2d, *J* = 2.3, 2 arom. H); 1.94 (s, CH₃); 1.21 (s, *t*-BuC); 1.02 (s, *t*-BuSi); 0.25 (s, Me₂Si). MS: 382 (17, *M*⁺), 325 (31), 105 (100), 77 (16).

4.16. *2-(tert-Butyl)-4-hydroxy-6-methylbenzophenone (53)*. A soln. of **52** (400 mg, 1.05 mmol) in EtOH (5 ml) and 2N aq. HCl (2 ml) was stirred for 1 h at 75° in a sealed tube, cooled to r.t., and mixed with ice (5 g), H₂O (5 ml), and AcOEt (10 ml). The org. phase was dried (MgSO₄) and evaporated and the residue purified by FC (SiO₂ (40 g), Et₂O/hexane 2:3) and recrystallization from Et₂O/hexane: 265 mg (94%) of **53**. Colorless crystals. M.p. 150–152°. IR (KBr): 3380m, 3060w, 2959m, 2867m, 1651s, 1605s, 1585s, 1448m, 1365w, 1302s, 1267s, 1248s, 1210m, 1116w, 984w, 859w, 719m. ¹H-NMR (CDCl₃, 250 MHz): 8.3–7.6 (br. m, 2 arom. H); 7.6–7.35 (m, 3 arom. H); 6.89, 6.55 (2d, *J* = 2.4, 2 arom. H); 5.21 (br. s, OH); 1.94 (s, CH₃); 1.22 (s, *t*-Bu). MS: 268 (14, *M*⁺), 253 (16), 191 (100), 105 (38), 77 (41). Anal. calc. for C₁₈H₂₀O₂ (268.36): C 80.56, H 7.51; found: C 80.45, H 7.23.

4.17. *Dimethyl 3-(tert-Butyl)-5-[(triisopropylsilyl)oxy]benzene-1,2-dicarboxylate (54)*. From **26** (300 mg, 1.65 mmol) **39** (Fluka; 1.22 ml, 9.93 mmol), and (*i*-Pr)₃SiOTf (1.02 ml, 3.80 mmol) according to *Method E* (24 h at 60°). FC (SiO₂ (50 g), Et₂O/hexane 1:4) gave 420 mg (60.2%) of **54**. Pale yellow oil. IR (film): 2948s, 2868m, 1738s, 1596s, 1463m, 1433m, 1318s, 1229s, 1125m, 1010m, 883m. ¹H-NMR (CDCl₃, 250 MHz): 7.31, 7.18 (2d, *J* = 2.5, 2

arom. H); 3.87, 3.86 (2s, 2 COOCH₃); 1.37 (s, *t*-Bu); 1.35–1.15 (m, ((CH₃)₂CH)₃Si); 1.10 (d, *J* = 8.7, ((CH₃)₂CH)₃Si). MS: 422 (7, *M*⁺), 391 (9), 379 (16), 347 (100), 319 (16), 59 (20).

4.18. *Dimethyl 3-(tert-Butyl)-5-hydroxybenzene-1,2-dicarboxylate (55)*. A soln. of **54** (320 mg, 0.76 mmol) in MeOH (3 ml) and 2N aq. HCl (1 ml) was stirred for 3.5 h at 80° in a sealed tube, cooled to r.t., and mixed with ice (5 g), H₂O (5 ml), and AcOEt (10 ml). The org. layer was dried (MgSO₄) and evaporated and the residue crystallized from AcOEt/hexane: 185 mg (91.4%) of **55**. Colorless crystals. M.p. 119–120°. IR (KBr): 3381*m* (br.), 2960*w*, 1727*s*, 1702*s*, 1581*m*, 1430*m*, 1321*m*, 1261*s*, 1218*s*, 1130*m*, 1081*m*, 1000*w*, 951*w*, 881*w*. ¹H-NMR (CDCl₃, 250 MHz): 7.28, 7.16 (2*d*, *J* = 2.6, 2 arom. H); 5.46 (br. *s*, OH); 3.87, 3.85 (2*s*, 2 COOCH₃); 1.37 (s, *t*-Bu). MS: 266 (19, *M*⁺), 235 (65), 219 (100), 203 (23). Anal. calc. for C₁₄H₁₈O₅ (266.29): C 63.15, H 6.81; found: C 62.85, H 6.54.

4.19. *5-{[Dimethyl(1,1,2-trimethylpropyl)silyloxy]-2'-methoxybiphenyl-2-yl Phenyl Ketone (56)}*. From **29** (500 mg, 2.15 mmol), **32** (364 mg, 2.80 mmol), and Me₂(Th)SiOTf (1.25 ml, 4.95 mmol) according to *Method E* (2 h at r.t.). FC (SiO₂ (50 g), Et₂O/hexane 1:10) and crystallization from EtOH/H₂O gave 840 mg (87.5%) of **56**. White needles. M.p. 94.5–95.5°. IR (KBr): 3063*w*, 3007*w*, 2960*m*, 2864*w*, 1663*s*, 1600*s*, 1557*m*, 1491*m*, 1450*w*, 1313*s*, 1258*s*, 1214*s*, 1026*w*, 940*m*, 827*s*, 709*m*. ¹H-NMR (CDCl₃, 250 MHz): 7.8–7.7 (*m*, 2 arom. H); 7.5–7.15 (*m*, 6 arom. H); 7.0–6.8 (*m*, 3 arom. H); 6.64 (*d*, *J* = 8.0, 1 arom. H); 3.39 (*s*, CH₃O); 1.74 (*sept.*, *J* = 6.6, [(CH₃)₂CHC(CH₃)₂Si]); 0.96 (*d*, *J* = 6.6, [(CH₃)₂CHC(CH₃)₂Si]); 0.97 (*s*, [(CH₃)₂CHC(CH₃)₂Si]); 0.29 (*s*, Me₂Si). MS: 446 (1, *M*⁺), 415 (36), 361 (22), 331 (15), 105 (100), 77 (22). Anal. calc. for C₂₂H₃₄O₃Si (446.66): C 75.29, H 7.67; found: C 75.38, H 7.56.

4.20. *5-Hydroxy-2'-methoxybiphenyl-2-yl Phenyl Ketone (57)*. A soln. of **56** (670 mg, 1.50 mmol) in EtOH (5 ml) and 2N aq. HCl (2 ml) was stirred for 2.5 h at 80° in a sealed tube, cooled to r.t., and mixed with ice (5 g), H₂O (5 ml), and AcOEt (10 ml). The org. layer was dried (MgSO₄) and evaporated and the residue crystallized from Et₂O/hexane: 425 mg (93%) of **57**. Colorless crystals. M.p. 177.5–178.5°. IR (KBr): 3212*m* (br.), 3069*w*, 2965*m*, 2935*w*, 1624*w*, 1595*s*, 1585*m*, 1490*w*, 1431*m*, 1318*s*, 1290*w*, 1239*s*, 1179*w*, 939*w*, 750*w*, 750*m*, 705*m*. ¹H-NMR (CDCl₃, 250 MHz): 7.8–7.7 (*m*, 2 arom. H); 7.5–7.1 (*m*, 6 arom. H); 7.0–6.8 (*m*, 3 arom. H); 6.65 (*d*, *J* = 8.0, 1 arom. H); 5.52 (*s*, OH); 3.39 (*s*, CH₃O). MS: 304 (2, *M*⁺), 274 (20), 273 (100), 105 (10), 77 (15). Anal. calc. for C₂₀H₁₆O₃ (304.35): C 78.93, H 5.10; found: C 78.79, H 5.44.

4.21. *Dimethyl 2'-Methoxy-5-[(triisopropylsilyl)oxy]biphenyl-2,3-dicarboxylate (58)*. From **29** (360 mg, 1.55 mmol), **39** (Fluka; 0.95 ml, 7.73 mmol), and (i-Pr)₃SiOTf (0.96 ml, 3.57 mmol) according to *Method E* (16 h at 60°). FC (SiO₂ (50 g), Et₂O/hexane 1:3) gave 580 mg (79.2%) of **58**. Pale yellow oil. IR (film): 2947*m*, 2868*m*, 1735*s*, 1498*w*, 1463*m*, 1432*m*, 1342*s*, 1264*s*, 1246*s*, 1164*m*, 1122*m*, 1011*m*, 761*w*. ¹H-NMR (CDCl₃, 250 MHz): 7.4–7.25 (*m*, 2 arom. H); 7.2–7.15 (*m*, 1 arom. H); 7.0–6.9 (*m*, 3 arom. H); 3.86, 3.72 (2*s*, 2 COOCH₃); 3.59 (*s*, CH₃O); 1.4–1.2 (*m*, ((CH₃)₂CH)₃Si); 1.10 (*d*, *J* = 6.7, ((CH₃)₂CH)₃Si). MS: 472 (6, *M*⁺), 397 (100), 369 (17), 59 (17).

4.22. *Dimethyl 5-Hydroxy-2'-methoxybiphenyl-2,3-dicarboxylate (59)*. To a stirred soln. of **58** (530 mg, 1.12 mmol) in THF (5 ml) was added a soln. of Bu₄NF·3H₂O (Fluka; 389 mg, 1.23 mmol) in THF (5 ml) at 0°. The mixture was stirred for 30 min at 0° and for 30 min at r.t., mixed with ice (5 g), H₂O (5 ml), and Et₂O (10 ml), the aq. layer extracted with AcOEt (2 × 5 ml), the combined org. fraction dried (MgSO₄) and evaporated, and the residue purified by FC (SiO₂ (30 g), Et₂O/hexane) and recrystallization from Et₂O/hexane: 319 mg (90%) of **59**. Colorless crystals. M.p. 161.5–162.5°. IR (KBr): 3384*m* (br.), 3076*m*, 2995*w*, 2945*w*, 1713*s*, 1612*m*, 1578*m*, 1500*m*, 1430*m*, 1352*m*, 1280*s*, 1265*s*, 1239*s*, 1195*m*, 1125*m*, 1063*w*, 1020*w*, 997*w*, 765*m*. ¹H-NMR (CDCl₃, 250 MHz): 7.35–7.25 (*m*, 2 arom. H); 7.2–7.1 (*m*, 1 arom. H); 7.0–6.8 (*m*, 3 arom. H); 5.73 (*s*, OH); 3.86, 3.72 (2*s*, 2 COOCH₃); 3.58 (*s*, CH₃O). MS: 316 (25, *M*⁺), 285 (100), 256 (15), 241 (53), 225 (28), 197 (15), 69 (16). Anal. calc. for C₁₇H₁₆O₆ (316.31): C 64.55, H 5.10; found: C 64.58, H 5.04.

4.23. *Ethyl 6-Benzoyl-3-hydroxy-5-methylbiphenyl-2-carboxylate (60)*. From **30** (300 mg, 1.09 mmol) and **36** (0.31 g, 2.18 mmol) according to *Method F* (5 h at r.t.). Crystallization from AcOEt/hexane gave 185 mg (47%) of **60**. Pale yellow solid. M.p. 104–106°. IR (KBr): 3028*w*, 2930*w*, 2861*w*, 1656*s*, 1575*m*, 1447*w*, 1397*w*, 1354*m*, 1309*m*, 1272*m*, 1235*s*, 1196*m*, 1074*s*, 693*m*. ¹H-NMR (CDCl₃, 250 MHz): 11.15 (*s*, OH); 7.55–7.35, 7.3–7.15, 7.1–6.75 (3*m*, 10 arom. H); 6.95 (*s*, H–C(3)); 3.90 (*q*, *J* = 7.1, COOCH₂CH₃); 2.20 (*s*, CH₃–C(4)); 0.63 (*t*, *J* = 7.1, COOCH₂CH₃). MS: 360 (60, *M*⁺), 314 (100), 237 (43), 152 (20), 105 (69), 17 (67). Anal. calc. for C₂₃H₂₀O₄ (360.41): C 76.65, H 5.59; found: C 76.92, H 5.56.

4.24. *6-Ethyl 2,3-Dimethyl 5-{[Dimethyl(1,1,2-trimethylpropyl)silyloxy]biphenyl-2,3,6-tricarboxylate (61)}*. From **30** (500 mg, 1.82 mmol), **39** (Fluka; 2.23 ml, 18.16 mmol), and Me₂(Th)SiOTf (1.05 mmol, 4.19 mmol) according to *Method E* (60 h at 60°). FC (SiO₂ (80 g), Et₂O/hexane 1:5) gave 530 mg (58%) of **61**. Pale yellow oil. IR (film): 2955*m*, 2870*w*, 1735*s*, 1588*m*, 1463*m*, 1344*m*, 1299*m*, 1239*s*, 1179*m*, 1102*m*, 821*m*, 701*w*. ¹H-NMR (CDCl₃, 250 MHz): 7.44 (*s*, 1 arom. H); 7.4–7.2 (*m*, 5 arom. H); 3.95 (*q*, *J* = 7.1, COOCH₂CH₃); 3.90, 3.53 (2*s*, 2 COOCH₃); 1.71 (*sept.*, *J* = 6.8, [(CH₃)₂CHC(CH₃)₂Si]); 0.95–0.8 (*m*, [(CH₃)₂CHC(CH₃)₂Si]); 0.33 (*s*, Me₂Si). MS: 469 (6, [*M* – CH₃O]⁺), 415 (60), 355 (100), 75 (30), 43 (24).

4.25. *6-Ethyl 2,3-Dimethyl 5-Hydroxybiphenyl-2,3,6-tricarboxylate (62)*. To a stirred soln. of **61** (200 mg, 0.40 mmol) in THF (2 ml) was added a soln. of $\text{Bu}_4\text{NF} \cdot 3\text{H}_2\text{O}$ (Fluka; 139 mg, 0.44 mmol) in THF (1 ml) at 0°. The mixture was stirred for 30 min at 0° and for 30 min at r.t. and then mixed with ice (5 g), 2N aq. HCl (2 ml), and AcOEt (10 ml), the aq. phase extracted with AcOEt (2 × 5 ml), the combined org. fraction dried (MgSO_4) and evaporated, and the residue purified by FC (SiO_2 (15 g), Et_2O /hexane 2:1) and recrystallization from Et_2O /hexane: 130 mg (90.7%) of **62**. Colorless crystals. M.p. 100–102°. IR (KBr): 3295m (br.), 3090w, 3062w, 2980w, 2953w, 1726s, 1695s, 1589m, 1440m, 1418m, 1312m, 1227s, 1182m, 1107m, 1011w, 669m. $^1\text{H-NMR}$ (CDCl_3 , 250 MHz): 11.04 (s, OH); 7.61 (s, 1 arom. H); 7.35–7.3 (m, 3 arom. H); 7.2–7.1 (m, 2 arom. H); 3.95 (q, $J = 7.2$, $\text{COOCH}_2\text{CH}_3$); 3.91, 3.47 (2s, 2 COOCH_3); 0.69 (t, $J = 7.2$, $\text{COOCH}_2\text{CH}_3$). MS: 358 (41, M^+), 312 (100), 281 (85), 280 (46), 252 (56), 105 (10), 77 (10). Anal. calc. for $\text{C}_{19}\text{H}_{18}\text{O}_7$ (358.35): C 63.68, H 5.06; found: C 63.68, H 5.18.

4.26. *Methyl 2-Benzoyl-5-methoxybiphenyl-3-carboxylate (63)*. To a stirred suspension of Me_3OBF_4 (Fluka; 285 mg, 1.93 mmol) in dry CH_2Cl_2 (3 ml) was added under Ar (*t*-Bu) $_2\text{C}_5\text{H}_3\text{N}$ (425 mg, 2.22 mmol) and **22** (300 mg, 1.48 mmol) at 0°. The mixture was stirred for 3 h at r.t., followed by addition of **45** [20] (306 mg, 1.63 mmol) in small portions. The mixture was stirred for 18 h at r.t., mixed with ice (10 g), 2N aq. HCl (5 ml), and AcOEt (10 ml), the aq. layer extracted with AcOEt (2 × 5 ml), the combined org. fraction dried (MgSO_4) and evaporated, and the residue purified by FC (SiO_2 (50 g), Et_2O /hexane 2:5): 105 mg (35%) of recovered **22** and 290 mg (56.6%; 87% based on recovered **22**) of **63**. White solid. A sample was recrystallized from Et_2O /hexane. M.p. 124–125°. IR (KBr): 3060w, 3015w, 2948w, 1728s, 1672s, 1598w, 1443w, 1339s, 1262m, 1159w, 1074w, 1039w, 751w. $^1\text{H-NMR}$ (CDCl_3 , 250 MHz): 7.65–7.55 (m, 3 arom. H); 7.45–7.35 (m, 1 arom. H); 7.3–7.2 (m, 2 arom. H); 7.17 (s, 5 arom. H); 7.09 (d, $J = 2.6$, 1 arom. H); 3.93 (s, COOCH_3); 3.66 (s, CH_3O). MS: 346 (27, M^+), 269 (100), 139 (11), 105 (22), 77 (35). Anal. calc. for $\text{C}_{22}\text{H}_{18}\text{O}_4$ (346.38): C 76.29, H 5.24; found: C 76.24, H 5.35.

4.27. *Dimethyl 5-Acetoxybiphenyl-2,3-dicarboxylate (64)*. A stirred soln. of **22** (150 mg, 0.74 mmol), **39** (Fluka; 0.45 ml, 3.66 mmol), isopropenyl acetate (Fluka; 0.37 g, 3.70 mmol), and $\text{TsOH} \cdot \text{H}_2\text{O}$ (Fluka; 10 mg) in CHCl_3 (1 ml) was treated under Ar for 18 h at 75° in a sealed tube. The solvents were evaporated, and the residue was purified by FC (SiO_2 (20 g), AcOEt/hexane 1:4): 220 mg (90.5%) of **63**. Colorless oil. IR (KBr): 3060w, 3026w, 2952w, 1768s, 1731s, 1598m, 1435m, 1326s, 1268s, 1241s, 1200s, 1158m, 1112m, 1068m, 1017m, 702m. $^1\text{H-NMR}$ (CDCl_3 , 250 MHz): 7.75 (d, $J = 2.4$, 1 arom. H); 7.45–7.35 (m, 5 arom. H); 7.31 (d, $J = 2.4$, 1 arom. H); 3.91, 3.67 (2s, 2 COOCH_3); 2.33 (s, AcO). MS: 328 (6, M^+), 286 (44), 255 (100), 195 (10), 43 (37). Anal. calc. for $\text{C}_{18}\text{H}_{16}\text{O}_6$ (328.22): C 65.85, H 4.91; found: C 65.78, H 5.17.

4.28. *3-[2,2-Bis(phenylsulfonyl)ethyl]-2,3-dihydro-2,2-dimethyl-6-phenyl-4H-pyran-4-one (66)*. From **22** (400 mg, 1.98 mmol), *1,1-bis(phenylsulfonyl)ethene (65; Fluka; 792 mg, 2.57 mmol)* and (*t*-Bu) Me_2SiOTf (1.14 ml, 4.96 mmol) according to *Method E* (3 h at r.t.). FC (SiO_2 (80 g), AcOEt/hexane 1:1) and recrystallization from Et_2O /hexane gave 970 mg (96%) of **66**. White solid. M.p. 178.5–179.5°. IR (KBr): 3061w, 2980w, 2920w, 1650s, 1602s, 1570m, 1479w, 1370m, 1326m, 1156s, 1079m, 728m, 686m. $^1\text{H-NMR}$ (CDCl_3 , 250 MHz): 8.15–8.0 (m, 2 arom. H); 7.8–7.35 (m, 13 arom. H); 5.53 (s, H–C(5)); 5.25–5.15 (m, $(\text{PhSO}_2)_2\text{CHCH}_2$); 3.05–2.9 (m, H–C(3)); 2.7–2.55, 2.35–2.2 (2m, $(\text{PhSO}_2)_2\text{CHCH}_2$); 1.54, 1.52 (2s, 2 CH_3 –C(2)). MS: 495 (13, $[M - \text{CH}_3]^+$), 223 (89), 202 (83), 187 (87), 147 (62), 105 (89), 77 (100), 69 (46), 41 (36). Anal. calc. for $\text{C}_{27}\text{H}_{26}\text{O}_6\text{S}_2$ (510.62): C 63.51, H 5.13, S 12.56; found: C 63.43, H 5.14, S 12.35.

4.29. *Dimethyl 5-Chlorobiphenyl-2,3-dicarboxylate (67)*. A stirred soln. of freshly prepared **31** (220 mg, 1.00 mmol) and **39** (Fluka; 1 ml) was heated under Ar for 2.5 h at 60° in a sealed tube. The excess of **39** was evaporated and the residue purified by FC (SiO_2 (30 g), Et_2O /hexane 1:4): 235 mg (77.1%) of **67**. Colorless oil. IR (film): 3060w, 3027w, 2950w, 1728s, 1667w, 1591m, 1433m, 1287s, 1243m, 1132w, 1107m, 1042w, 835w, 762m. $^1\text{H-NMR}$ (CDCl_3 , 250 MHz): 7.98, 7.54 (2d, $J = 2.1$, 2 arom. H); 7.45–7.3 (m, 5 arom. H); 3.92, 3.66 (2s, 2 COOCH_3). MS: 304 (38, M^+), 275 (33), 273 (100), 241 (20). Anal. calc. for $\text{C}_{16}\text{H}_{13}\text{ClO}_4$ (304.73): C 63.06, H 4.03, Cl 11.63; found: C 62.85, H 4.29, Cl 11.51.

4.30. *Methyl 5-Chlorobiphenyl-2-carboxylate (68)*. A stirred soln. of freshly prepared **31** (210 mg, 0.95 mmol) and methyl propiolate (Fluka; 1 ml) was heated under Ar for 24 h at 60°. The excess methyl propiolate was evaporated and the residue purified by FC (SiO_2 (25 g), Et_2O /hexane 1:10): 40 mg (19%) of recovered **31** and 140 mg (59.7%; 73.7% based on recovered **31**) of **68**. Colorless oil. IR (film): 3063w, 3030w, 3000w, 2951w, 1733s, 1582m, 1497w, 1452w, 1434m, 1422m, 1308s, 1265s, 1237s, 1201m, 1176m, 1122m, 1069m, 978w, 791m. $^1\text{H-NMR}$ (CDCl_3 , 250 MHz): 7.85–7.8 (m, 1 arom. H); 7.45–7.35, 7.35–7.25 (2m, 7 arom. H); 3.63 (s, COOCH_3). MS: 246 (44, M^+), 213 (33), 215 (100), 152 (65), 76 (23). Anal. calc. for $\text{C}_{14}\text{H}_{11}\text{ClO}_2$ (246.69): C 68.16, H 4.49, Cl 14.37; found: C 67.83, H 4.30, Cl 14.25.

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