

# Reactions of 1,2-Diketones with Vinyllithium: Addition Reactions and Dianionic Oxy Cope Rearrangements of Cyclic and Acyclic Substrates

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*Dedicated to Professor Henning Hopf on the occasion of his 60th birthday*

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Dianionic oxy Cope rearrangements have been shown to take place at low temperature upon *syn* double addition of alkenyllithium derivatives to cyclobutanedione compounds such as benzocyclobutanedione chromium complex **1** or squaric acid esters. In order to obtain some insight into the more general applicability of this type of reaction sequence beyond these special cases, a number of 1,2-diketones were treated with vinyllithium. The diketones tested include benzil derivatives, aliphatic acyclic 1,2-diketones, *ortho*-quinones, and cyclic aliphatic 1,2-diketones. With benzil and heterobenzil derivatives, the desired double addition/dianionic oxy Cope rearrangement was found to take place at low temperature, leading to 1,6-diketones and their intramolecular aldol adducts in up to 80% overall yield. With acyclic aliphatic 1,2-diketones as substrates, this reaction sequence

was also found, albeit with somewhat lower yields and requiring higher temperatures than in the benzil cases. A brief investigation of the intramolecular aldol adduct/1,6-hexanedione equilibrium indicated that the preferential formation of intramolecular aldol adducts at lower temperatures and at shorter reaction times appears to be the result of kinetic reaction control, whereas the preference for 1,6-diketones at higher temperatures is caused by thermodynamic reaction control. *ortho*-Quinones reacted with vinyllithium only by addition; no dianionic oxy Cope rearrangement was observed. This was also the case for most aliphatic cyclic diketones; however, in the case of 1,2-indanedione, rearrangement products were obtained in moderate yield at elevated reaction temperatures.

## Introduction

Pericyclic reactions have proven to be of prime importance in organic chemistry, thanks to their predictable stereoselectivity. However, high reaction temperatures are often required, which limits their practical value, particularly in cases involving highly functionalized substrates. It has been found that it is in some cases possible to accelerate the reactions and to use lower reaction temperatures. Hence, strained systems and systems in which electronic effects of certain substituents cause a decrease in transition state energy usually require comparatively low reaction temperatures.

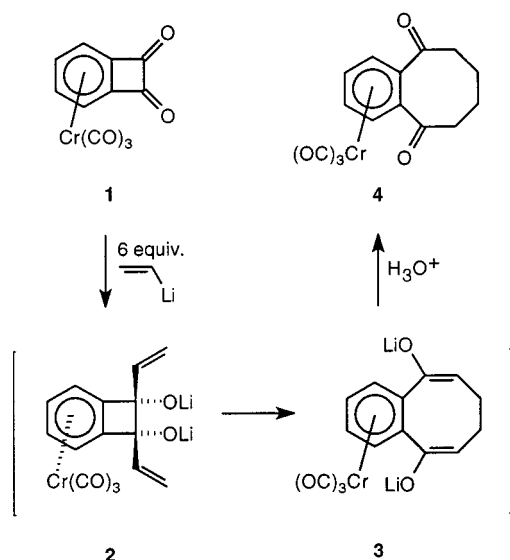
The alkoxide functionality has turned out to be particularly valuable in this context. This anionic substituent can accelerate some pericyclic reactions significantly if it is situated at such a position in the substrate as to result in a resonance-stabilized alkoxide function in the product, usually an enolate. This often allows the reaction to take place at room temperature or slightly above; in some cases reaction temperatures as low as  $-78\text{ }^{\circ}\text{C}$  have been reported. While this type of acceleration is not possible for a Diels–Alder cycloaddition, Hart reported an anion-driven

retro Diels–Alder cycloaddition in 1967,<sup>[2]</sup> and Grimme investigated this reaction type more systematically in 1980.<sup>[3]</sup> More recently, Nicolaou reported the use of this reaction in the synthesis of an enediyne, which underwent a Bergman cyclization at room temperature.<sup>[4,5]</sup> Danheiser showed that vinylcyclopropane–cyclopentene rearrangements could be significantly accelerated by an alkoxide substituent.<sup>[6,7]</sup> Anion-accelerated vinylcyclobutane–cyclohexene rearrangements have been reported for a number of different substitution patterns.<sup>[6]</sup> Anion-accelerated rearrangements of 1-hydroxy-1-vinylcyclobutenes are rare and are believed to proceed stepwise.<sup>[8,9]</sup> Anionic ring-opening reactions of benzocyclobutenols<sup>[10]</sup> and benzocyclobutenol complexes<sup>[11–16]</sup> have been found both by ourselves and by others, and were reviewed recently.<sup>[17]</sup> The anion-accelerated Claisen rearrangement, first reported by Ireland in 1972, is another example in this context.<sup>[18,19]</sup> In 1975, Evans reported the first case of an anionic oxy Cope rearrangement, which since then has frequently been applied in organic syntheses.<sup>[20–22]</sup> Dianionic oxy Cope rearrangements are rare. In some cases they have been induced by deprotonation of 1,2-divinyl-1,2-diols.<sup>[23,24]</sup> However, one cannot say beyond any doubt that these reactions took place only after the second deprotonation, as rearrangement after the first one would lead to the same result. Alder et al., in 1990, reported the first rearrangement that does not allow such an argument.<sup>[25]</sup> These authors created a 1,2-divinyl-1,2-diolate by addition of two equivalents of an alkenyllithium to acenaphthenequinone. The reaction took place at room

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temperature. In 1993 we reported the first case of a dianionic oxy Cope rearrangement taking place at  $-78^{\circ}\text{C}$ . Treatment of (benzocyclobutenedione)tricarboxylchromium(0) (**1**) with an excess of vinyl lithium resulted in the formation of bis(enolate) **3** (via diadduct **2**), which was hydrolyzed to the benzocyclooctenedione complex **4**. In some cases, when other alkenyllithium reagents were used, the rearrangement was followed by an intramolecular aldol addition, resulting in the formation of anellated cyclopentane rings.<sup>[26–29]</sup>



The role of the tricarboxylchromium fragment in this reaction is a double one. On one hand, its electron-withdrawing capability facilitates nucleophilic attack at the oxo groups; on the other, the steric bulk of the  $\text{Cr}(\text{CO})_3$  group forces both alkenyllithium nucleophiles to attack from the face opposite to the chromium center, resulting in a 1,2-*cis* configuration. According to Salaün, this is mandatory for a Cope rearrangement to take place with divinylcyclobutanes.<sup>[30]</sup>

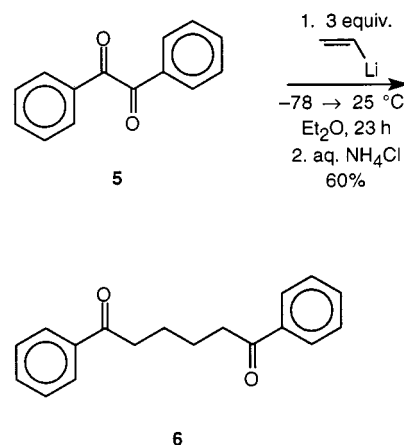
A short time after our communication about this reaction, Paquette reported on reaction sequences in which alkenylmetal reagents added to squaric acid esters.<sup>[22,31]</sup> In most cases, a *trans* double addition dominated: Only in chelation-assisted examples was a *cis* double addition observed. After the dominant *trans* double addition, products similar to those of dianionic oxy Cope rearrangements resulted from anion-driven electrocyclic ring-opening reactions, conformational changes, subsequent electrocyclizations to cyclooctane derivatives, and, finally, intramolecular aldol additions. Although the reaction mechanisms are different, the alkenylmetal additions to **1** and to squaric acid esters have in common that they are unquestionably dianionic and – in contrast to the other reactions mentioned – take place at temperatures as low as  $-78^{\circ}\text{C}$ .<sup>[31–40]</sup>

In the light of these reactions, which in most cases involved strained substrates, we were interested in the question of how general this type of reaction sequences is. Is the tricarboxylchromium group really necessary? Can one

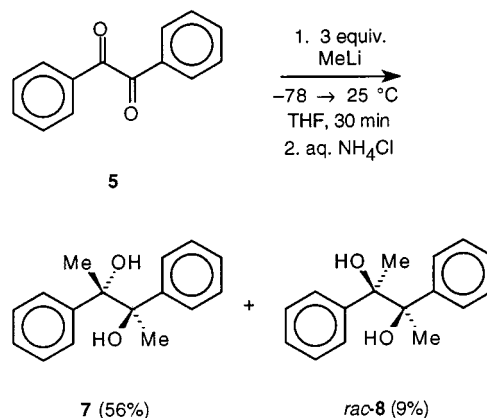
perform such reaction sequences starting from 1,2-diketones other than strained ones such as **1** or squaric acid esters? Are acyclic 1,2-diketones feasible starting materials? Here we present results of investigations along these lines. As the results were in all cases rather poor when vinylmagnesium bromide was used, the use of vinyl lithium was investigated.

### Reactions of Aromatic Ethanediones with Vinyl lithium

Treatment of benzil (**5**) with 3 equiv. of vinyl lithium at  $-78^{\circ}\text{C}$ , followed by warming to  $25^{\circ}\text{C}$  over 23 h and hydrolysis at  $-78^{\circ}\text{C}$ , gave 1,6-diphenyl-1,6-hexanedione (**6**) in 60% yield. The diadduct – 3,4-diphenyl-1,5-hexadiene-3,4-diol – was not observed.



The formation of **6** can be explained by a double addition of vinyl lithium, followed by a dianionic oxy Cope rearrangement. Either intermediate – *meso*- or *rac*-3,4-diphenyl-1,5-hexadiene-3,4-diolate – may undergo this rearrangement, leading to identical products. To obtain some impression of which type of intermediate might be formed preferentially, benzil (**5**) was treated with methyl lithium, to give a 56% yield of *meso* diadduct **7** and a 9% yield of *rac*-**8**. This suggests that, in the case of vinyl lithium addition, both intermediates can take part in a dianionic oxy Cope rearrangement.



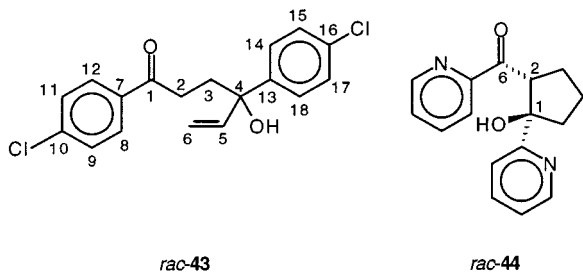
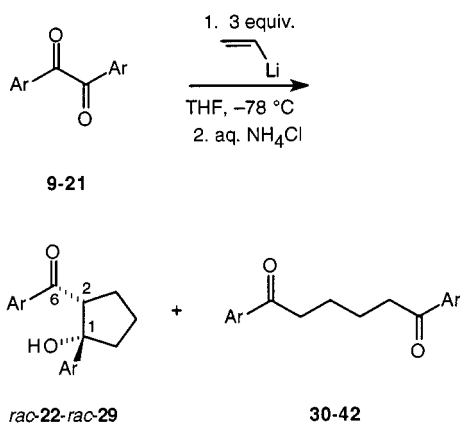
Possible effects of substituents on benzil were investigated, with some derivatives listed in Table 1. Most of the

Table 1. Reaction of aromatic ethanedione derivatives **9–21** with vinylolithium

Entry	Ar	Starting material	Intramolecular aldol adduct (yield)	1,6-Diaryl-1,6-hexanedione (yield)
1	<i>p</i> -methylphenyl	<b>9</b>	<i>rac</i> - <b>22</b> (20%)	<b>30</b> <sup>[49,50]</sup> (46%)
2	<i>p</i> -isopropylphenyl	<b>10</b>	<i>rac</i> - <b>23</b> (36%)	<b>31</b> (35%)
3	<i>p</i> - <i>tert</i> -butylphenyl	<b>11</b>	<i>rac</i> - <b>24</b> (40%)	<b>32</b> (30%)
4	$\beta$ -naphthyl	<b>12</b>	<i>rac</i> - <b>25</b> (71%)	<b>33</b> (9%)
5	<i>p</i> -methoxyphenyl	<b>13</b>	<i>rac</i> - <b>26</b> (33%)	<b>34</b> <sup>[70]</sup> (35%)
6	<i>p</i> -(difluoromethoxy)phenyl	<b>14</b>	<i>rac</i> - <b>27</b> (46%)	<b>35</b> (9%)
7	<i>p</i> -(trifluoromethoxy)phenyl	<b>15</b>	<i>rac</i> - <b>28</b> (10%)	<b>36</b> (40%)
8	<i>p</i> -chlorophenyl	<b>16</b>	<sup>[a]</sup>	<b>37</b> <sup>[79]</sup> (33%)
9	<i>p</i> -(trifluoromethyl)phenyl	<b>17</b>		<b>38</b> (58%)
10	2-furyl	<b>18</b>		<b>39</b> <sup>[81]</sup> (49%)
11	2-thienyl	<b>19</b>		<b>40</b> <sup>[81]</sup> (39%)
12	2-( <i>N</i> -methylbenzimidazolyl)	<b>20</b>	<i>rac</i> - <b>29</b> (5%)	<b>41</b> (6%)
13	2-pyridyl	<b>21</b>	<sup>[b]</sup>	<b>42</b> (10%)

<sup>[a]</sup> Rearranged product *rac*-**43** was obtained in 11% yield. — <sup>[b]</sup> *trans* diastereomer *rac*-**44** was obtained in 6% yield.

selected derivatives are *para*-substituted, in order to obtain clearer NMR spectra and to avoid the steric interactions which might be possible in *ortho*-substituted systems. The reactions were performed in THF, because most of the substrates are only unsatisfactorily soluble in diethyl ether at  $-78\text{ }^{\circ}\text{C}$ . In most cases, mixtures of intramolecular aldol adducts *rac*-**22** to *rac*-**29** and 1,6-hexanediones **30–42** were obtained in moderate to good overall yields.



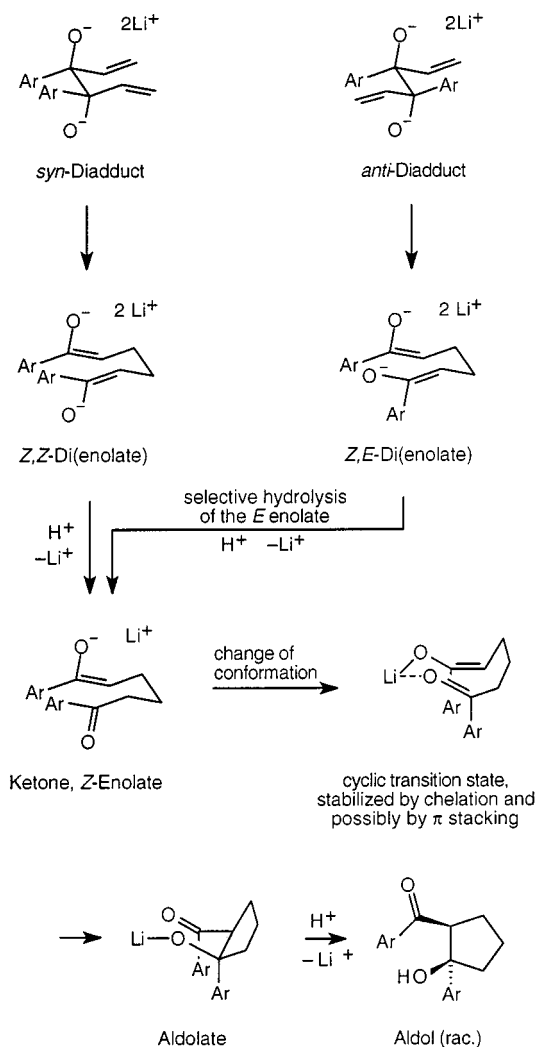
Alkyl-substituted benzil derivatives **9–11** reacted in approximately 70% overall yield to give mixtures of the rearranged 1,6-hexanediones **30–32** and their intramolecular aldol adducts *rac*-**22** to *rac*-**24**, the proportion of the latter increasing with the steric bulk of the alkyl substituent (Entries 1–3). The highest yield was obtained when  $\beta$ -naphthyl derivative **12** was used, resulting mainly in the aldol adduct (Entry 4). Alkoxy derivatives **13–15** do not show any clear trend: overall yields are between 50 and 68% (Entries 5–7). When the chlorophenyl derivative was used, 11% of *rac*-**43**

was obtained as well as the 1,6-hexanedione **37** (33%), most probably as the result of a 1,3-rearrangement (Entry 8). With the electron-poor trifluoromethyl derivative **17**, only 1,6-hexanedione **38** was obtained, in 58% yield (Entry 9). The product ratio is solvent-dependent: When the reaction of **13** was performed in diethyl ether, *rac*-**26** was obtained in only 6% yield, whereas hexanedione **34** was isolated in 56% yield.

Heteroaromatic benzil analogs **18–21** gave corresponding products *rac*-**29** and **39–42** in lower yields. Only in the case of the 2-pyridyl derivative was formation of the *trans*-configured aldol adduct *rac*-**44** observed (6% yield).

To establish the relative configurations in the aldol adducts, *rac*-**24** was subjected to an NOE investigation. Irradiation at the resonance frequency of 2-H caused a 10.7% NOE at the *ortho*-protons of the aryl substituent at C-1. Irradiation at the resonance frequency of these protons gave a 3.8% NOE at 2-H. These results are in agreement with the relative configuration of *rac*-**24**. NOE measurements with methoxy derivative *rac*-**26** gave similar results. The relative configurations of the other aldol adducts were assigned by comparison of their NMR spectra with those of *rac*-**24** and *rac*-**26**.

The diastereoselectivity of the aldol addition can be explained by assuming a six-centered transition state, with the (*Z*)-enolate attacking the oxo group as depicted in Scheme 1. This transition state may be stabilized by some  $\pi$ -stacking interactions between the 1,3-diaxial aryl substituents. Its formation can be accounted for both by a *syn* and by an *anti* double addition of vinylolithium to the diketone. In the *syn* case, the dianionic oxy Cope rearrangement results in the (*Z,Z*)-bis(enolate), which upon partial hydrolysis gives the oxo functionality and the remaining (*Z*)-enolate. In the *anti* case, the dianionic oxy Cope rearrangement results in a (*Z,E*)-bis(enolate). Selective hydrolysis of the (*E*)-arylenolate moiety leads to the same intermediate. The preferred hydrolysis of the (*E*)-arylenolate moiety is in agreement with the known preference for the formation of (*Z*)-arylenolates.<sup>[41]</sup> A force field calculation (MM+<sup>[42]</sup>) showed *rac*-**26** to be thermodynamically more stable than its diastereomer (potential energy 9.8 vs. 10.5 kcal/mol).



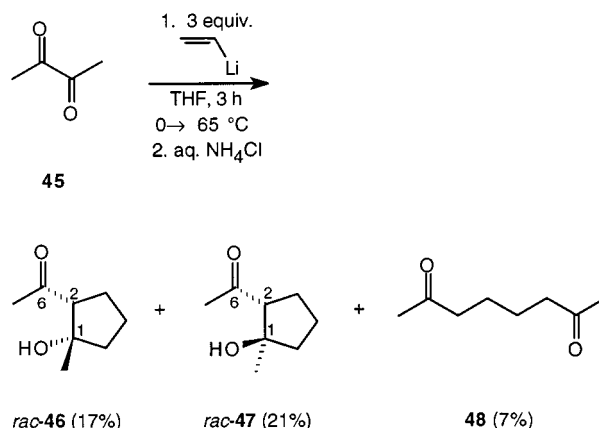
Scheme 1. Stereochemistry of aldol formation

The reaction of heterocyclic 2-pyridyl derivative **21** is an exception: *trans* diastereomer *rac-44* was obtained in 6% yield. Obviously, the transition state is not the same as in the alicyclic cases (Entries 1–7), possibly because the heteroatoms influence the extent of  $\pi$  stacking. Although this line of thought explains the observed stereoselectivity, it does not take into account all the complexity of the stereochemistry of enolates, such as aggregation phenomena, for example.<sup>[43]</sup> Therefore the observed stereoselectivity would merit further investigation.

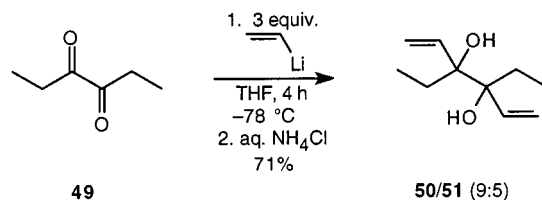
### Reactions of Acyclic Aliphatic Ethanediones with Vinyl lithium

Having shown that dianionic oxy Cope rearrangements are possible with aromatic ethanediones, we were interested in examining to what extent they might be possible with aliphatic ethanediones. Conia has shown that treatment of 2,3-butanedione (**45**) with vinylmagnesium chloride results in the formation of *meso*- and *rac*-3,4-dihydroxy-3,4-dimethyl-1,5-hexadienes.<sup>[44]</sup> When **45** was treated with 3 equiv. of vinyl lithium in THF at 0 °C, we also obtained these products, as a 1:1 mixture of diastereomers. However,

when **45** was added to vinyl lithium at 0 °C and the mixture heated at reflux for 3 h, dianionic oxy Cope rearrangement products *rac-46*–**48** were obtained in 45% overall yield. Remarkably, in contrast to all other experiments, *trans* product *rac-47* was obtained as the main product.

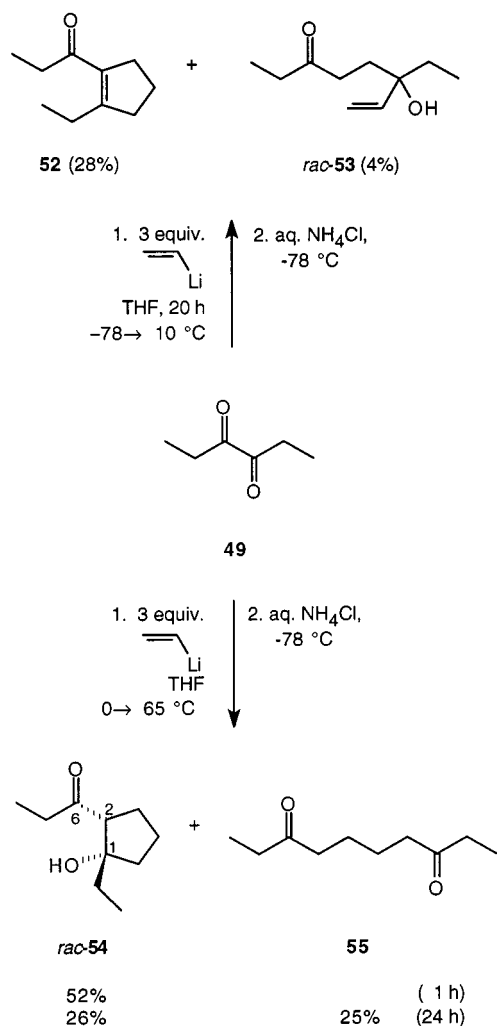


The diastereomers were assigned on the basis of their NMR spectra. The <sup>1</sup>H NMR spectrum of *rac-46*<sup>[45,46]</sup> is very similar to those of *rac-22* to *rac-29*. In addition, NOE measurements confirmed the assignments made. It is not surprising that the reaction of **45** requires a higher temperature than those of aromatic 1,2-diketones: In these cases, the bis(enolates) formed by rearrangement reactions are stabilized by resonance interaction with the aromatic system.



Treatment of 3,4-hexanedione (**49**) with 3 equiv. of vinyl lithium at –78 °C afforded only diadducts **50/51**<sup>[47]</sup> as a 9:5 mixture of diastereomers, which was not separated. However, when the reaction mixture was allowed to warm to 10 °C over 20 h, aldol condensation product **52**<sup>[47,48]</sup> was obtained in 28% yield, together with a second product – presumably *rac-53* (4%) – which was not completely characterized and appeared to be the product of a 1,3-rearrangement process.

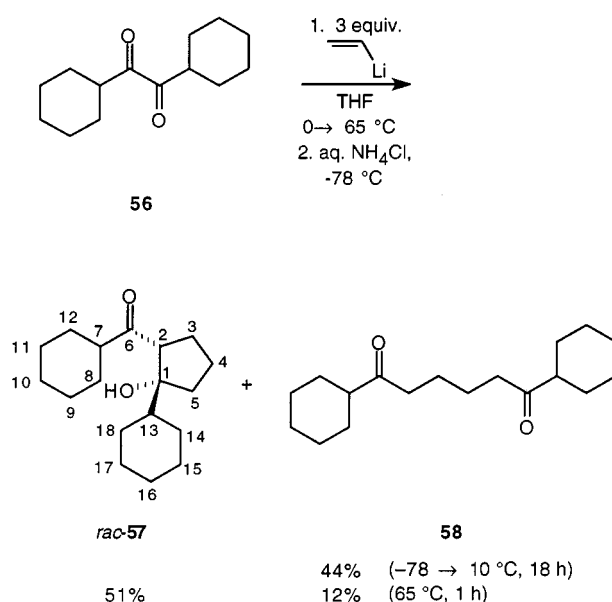
When vinyl lithium was added at 0 °C instead of –78 °C, with subsequent heating at reflux for only 1 h, a 52% yield of **54**<sup>[49,50]</sup> was isolated; the result of a dianionic oxy Cope rearrangement followed by an intramolecular aldol addition. Heating instead for 24 h under reflux resulted in a mixture of **54** (26%) and 3,8-decanedione (**55**, 25%), indicating similar thermodynamic stabilities of the two compounds.



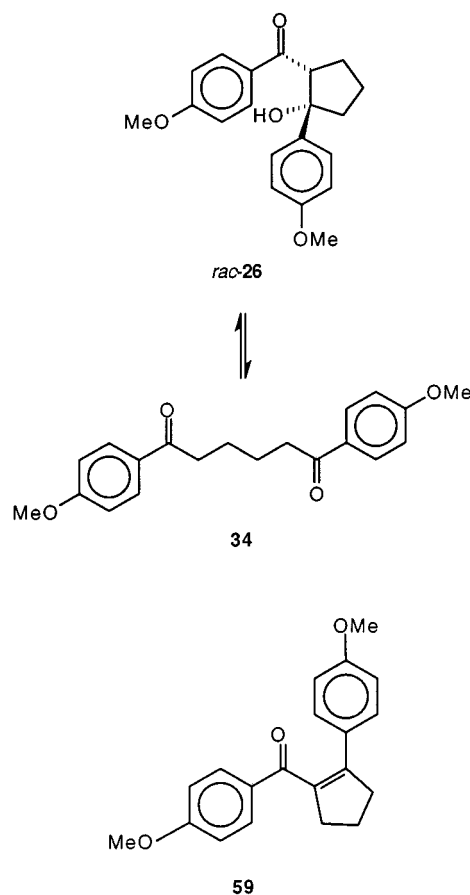
This was confirmed by the reaction of 1,2-dicyclohexylethanedione (56). Addition of 3 equiv. of vinyl lithium at -78 °C, followed by warming to 10 °C over 18 h, gave 1,6-dicyclohexyl-1,6-hexanedione (58) in 44% yield.<sup>[51]</sup> Addition at 0 °C, followed by heating at 65 °C for 1 h, gave cyclopentanol *rac*-57 in 51% yield, in addition to 58 (12%). Longer reaction times apparently result in some preference for the hexanediones. TLC monitoring revealed that the dianionic oxy Cope rearrangement took place at about 0 °C, while the relative configuration of *rac*-57 was confirmed by an NOE measurement.

### The Cyclopentanol/1,6-Hexanedione Equilibrium

As the cyclopentanol/1,6-hexanedione ratio of the reaction products varied considerably, even though the reaction conditions were in most cases fairly similar, some experiments were undertaken to examine this aldol/retro-aldol equilibrium. For closer study, the reaction of 1,2-bis(*p*-methoxyphenyl)ethanedione (13) was chosen; this yielded *rac*-26 and 34 as the products of a dianionic oxy Cope rearrangement and subsequent intramolecular aldol addition (Table 1).



When *rac*-26 was dissolved in a 1:1 mixture of THF and a saturated, aqueous solution of ammonium chloride for 5 h at 25 °C, a 59:41 mixture of *rac*-26 and 34 was obtained.



When a CDCl<sub>3</sub> solution of *rac*-26 was allowed to stand at 25 °C for a number of days, cyclopentanol *rac*-26 was found to react almost completely with formation of 1,6-



Table 2. Reaction of **13** with vinylolithium in THF

Entry	Reaction temp. [°C]	Reaction time <sup>[95]</sup>	Acid (hydrolysis)	Hydrolysis temp. [°C]	Hydrolysis time <sup>[95]</sup>	Yield of <i>rac</i> - <b>26</b> [%]	Yield of <b>34</b> [%]	Yield of <b>59</b> [%]
1	−78	0.5	aq NH <sub>4</sub> Cl	−78	27	47	22	
2	−78	0.5	aq NH <sub>4</sub> Cl	−78	2	33	35	
3	−78	0.5	aq NH <sub>4</sub> Cl	−78	1 <sup>[a]</sup>	18	56	
4	0	0.5	aq NH <sub>4</sub> Cl	0	0.5	13	62	
5	−78→0	23	aq NH <sub>4</sub> Cl	−78	2		28	18
6	−78	2	F <sub>3</sub> CSO <sub>3</sub> H	−78	2		38	15

<sup>[a]</sup> Followed by stirring at 25 °C for 26 h.

hexanedione **34**. Only traces of *rac*-**26** could be detected. When **34** was stirred in a 1:1 mixture of THF and a saturated, aqueous solution of ammonium chloride for 23 h at 25 °C, no reaction was observed. Even the addition of an equimolar amount of (*S*)-proline, used to catalyze enantioselective aldol additions,<sup>[52,53]</sup> did not cause any reaction to take place, even under reflux conditions. To rule out these observations as specific to the case of *rac*-**26/34**, 1,2-bis(*p*-chlorophenyl)ethanedione (**37**) was also stirred in a 1:1 mixture of THF and a saturated, aqueous solution of ammonium chloride for 23 h at 25 °C, with no observed reaction. These observations indicate that the equilibrium between *rac*-**26** and **34** is far on the 1,6-hexanedione side. This is in agreement with the fact that only two cases of intramolecular aldol additions of 1,6-diketones are reported in the literature: in both cases, medium-sized rings reacted to give bicyclic systems in 16% and in 30% yield,<sup>[54,55]</sup> respectively.

In contrast to the intramolecular aldol addition of 1,6-diketones, a number of aldol condensations under acidic reaction conditions, leading to the corresponding conjugated acylcyclopentenones, are known.<sup>[56]</sup> Accordingly, upon treatment of *rac*-**26** with 3 equiv. of trifluoroacetic acid at 25 °C, cyclopentene **59**<sup>[57]</sup> was formed in 38% yield, along with 19% of starting material *rac*-**26**. This aldol condensation was also possible under basic reaction conditions. Treatment of *rac*-**26** with 5 equiv. of sodium methoxide gave a 75% yield of **59** and 6% of *rac*-**26**. In addition, ca. 9% of an unidentified product was formed.

Despite the observation that the 1,6-hexanedione derivatives are thermodynamically favored, aldol adducts were frequently obtained as the isolated reaction products. To obtain a deeper insight into this, the conditions for the reaction of **13** with vinylolithium were varied. Results are summarized in Table 2.

Entries 1–3 relate to variation in the workup temperatures. Addition of aqueous NH<sub>4</sub>Cl at −78 °C results in immediate freezing of the added solution. From the frozen aqueous layer, only a few of the water molecules would be available for hydrolysis. This would result in predominant hydrolysis of only one of the two enolate moieties, converting it into a ketone, which would be attacked by the remaining enolate function to give the aldol adduct *rac*-**26**

before the second hydrolysis step could take place. If the reaction mixture was heated to 25 °C after only 2 h (Entry 2), rather than 27 h (Entry 1), the aqueous layer melted and water concentration in the organic layer increased, allowing a comparatively rapid hydrolysis of all enolate functions: Significant quantities of 1,6-hexanedione **34** were formed. Stirring at 25 °C for a longer period of time after the hydrolysis step (Entry 3) allowed a retro-aldol process to take place, to increase further the yield of **34** relative to *rac*-**26**. Reaction and hydrolysis at 0 °C (Entry 4) did not cause the aqueous solution to freeze, all enolate functions were immediately quenched, with formation of **34** at the highest yield, with only 13% of aldol adduct *rac*-**26** formed. When the reaction mixture was allowed to warm up before the addition of the NH<sub>4</sub>Cl solution (Entry 5), a substantial quantity of cyclopentene **59** was obtained in addition to a moderate yield of **34**. Hydrolysis with trifluoromethanesulfonic acid, which is soluble in THF, immediately hydrolyzed all enolate functions, with formation of **34** and – as a result of an acid-catalyzed aldol condensation – some **59** as a side product. In conclusion, the preferential formation of the cyclopentanol products at low temperatures and with shorter hydrolysis times appears to be the result of a kinetic reaction control of the hydrolysis. Longer times and temperatures above 0 °C result in formation of the thermodynamically favored 1,6-hexanedione.

### Reactions of *ortho*-Quinones with Vinylolithium

In most of the cases investigated, *ortho*-quinones did not undergo rearrangement upon treatment with vinylolithium. In addition to decomposed material, adducts *rac*-**60** to *rac*-**64** were isolated in moderate yields (32–62%). Here, 3 equiv. of vinylolithium were added to the respective *ortho*-quinone at −78 °C. In the case of *rac*-**60**, the mixture was allowed to warm to 25 °C over 20 h; with the reaction of *rac*-**63**, even heating at 65 °C for 21 h did not result in the desired rearrangement. Compound *rac*-**62** was characterized by an X-ray structure analysis, which confirmed the relative configuration (Figure 1). The NMR-spectroscopic data for this compound were used as the basis of comparisons for the characterizations of other 1,2-divinyl-1,2-diols.

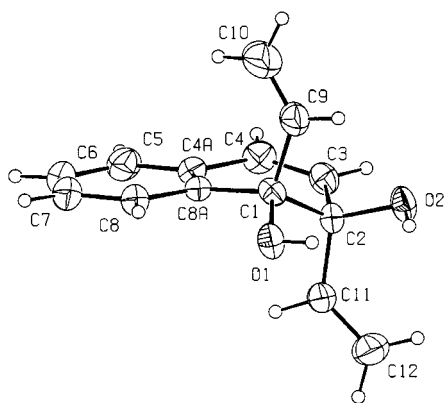
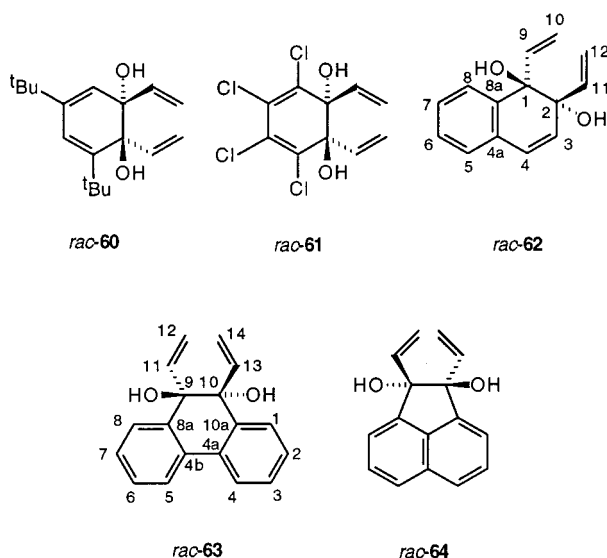
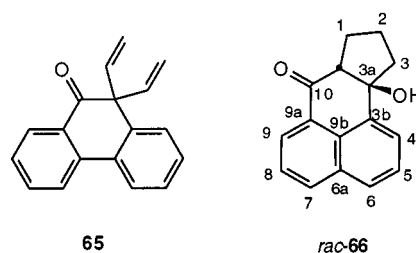


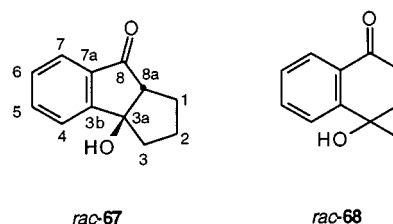
Figure 1. Structure of *rac*-62 in the crystal; bond lengths [Å]: C1–C2 1.566(5), C1–C8a 1.503(5), C2–C3 1.486(5), C3–C4 1.330(5), C4–C4a 1.452(5), C4a–C5 1.402(5), C5–C6 1.390(6), C6–C7 1.384(5), C7–C8 1.377(5), C8–C8a 1.383(5), C4a–C8a 1.398(5), C1–C9 1.517(5), C9–C10 1.113(7), C2–C11 1.541(5), C11–C12 1.285(5), C1–O1 1.434(4), C2–O2 1.422(4); the abnormal bond length C9–C10 is a result of disorder of the terminal vinyl group



When phenanthrenequinone was treated with 5 equiv. of vinyl lithium after 2 h at  $-78^{\circ}\text{C}$ , instead of diadduct *rac*-63, a 68% yield of **65** was obtained. This was presumably a result of a pinacol rearrangement, which possibly occurred during the course of the acidic workup. It is noteworthy that pinacol rearrangements of 1,2-divinyl-1,2-diols usually take place in the presence of strong Lewis acids or at elevated temperatures.<sup>[58–61]</sup> Treatment of acenaphthenequinone with 3 equiv. of vinyl lithium at  $0\rightarrow 65^{\circ}\text{C}$  gave *rac*-66 in only 14% yield, in addition to ca. 20% of an unidentified product. Compound *rac*-66 is the product of a dianionic oxy Cope rearrangement, followed by an intramolecular aldol addition. In conclusion, it is our impression that five-membered ring quinones are more prone to the desired dianionic oxy Cope rearrangement than their six-membered counterparts.



With chromium complex **1** undergoing the dianionic oxy-Cope rearrangement at low temperature in high yield, and with five-membered ring compounds being more successful than six-membered ones, it was obviously attractive to examine uncomplexed benzocyclobutenedione. When benzocyclobutenedione<sup>[62]</sup> was treated with 8 equiv. of vinyl lithium at  $-78\rightarrow 25^{\circ}\text{C}$ , *rac*-67 and *rac*-68 were obtained in 15% and 12% yield. With a smaller excess of vinyl lithium, a little more *rac*-67 and only traces of *rac*-68 were obtained. Compound *rac*-67 is the product of a dianionic oxy Cope rearrangement followed by an intramolecular aldol addition and had been prepared previously by Proctor by intramolecular aldol addition of benzocyclooctene-1,6-dione.<sup>[55]</sup> No benzocyclooctene-1,6-dione was observed. Compound *rac*-68 is the result of a 1,3-sigmatropic rearrangement.



### Reactions of Cyclic Aliphatic Diketones with Vinyl lithium

When cyclic aliphatic diketones were examined, only vinyl lithium addition was observed in a number of cases, without any rearrangement. Treatment of bicyclo[2.2.1]hept-5-ene-2,3-dione with 3 equiv. of vinyl lithium at  $-78^{\circ}\text{C}$  selectively gave *syn* diadduct **69** in 66% yield. Similarly, *rac*-70 and **71** (33%, 37%) were obtained from dibenzocyclo[2.2.2]octa-5,7-diene-2,3-dione. Presumably as a result of the steric shielding effect of the methyl substituents, only a single addition was observed upon treatment of 3,3,5,5-tetramethyl-1,2-cyclopentanedione with 3 equiv. of vinyl lithium at  $-78^{\circ}\text{C}$ , giving a 78% yield of *rac*-72 after hydrolytic workup. With the less sterically hindered, nonenolizable 3,3-dimethylindane-1,2-dione, an *anti* double addition was achieved, to give *rac*-73 in 74% yield. As attempts to determine the relative configuration of *rac*-73 by NOE experiment were unsuccessful, an X-ray structure analysis was performed (Figure 2).

In contrast with the preceding examples, it proved possible to accomplish the desired rearrangement when the enolizable 1,2-indanedione (**74**) was used. Upon treatment of **74** with 3 equiv. of vinyl lithium at  $-78^{\circ}\text{C}$ , a mixture of monoadduct *rac*-75 (11%) and *trans* diadduct *rac*-76<sup>[63]</sup>

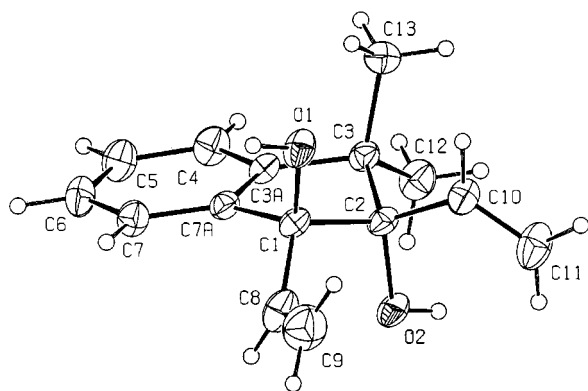
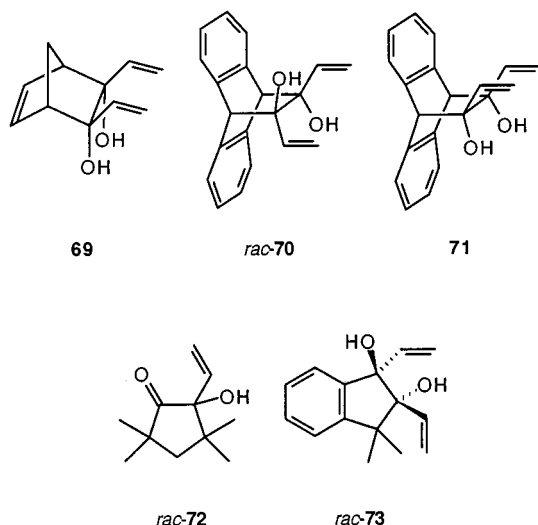


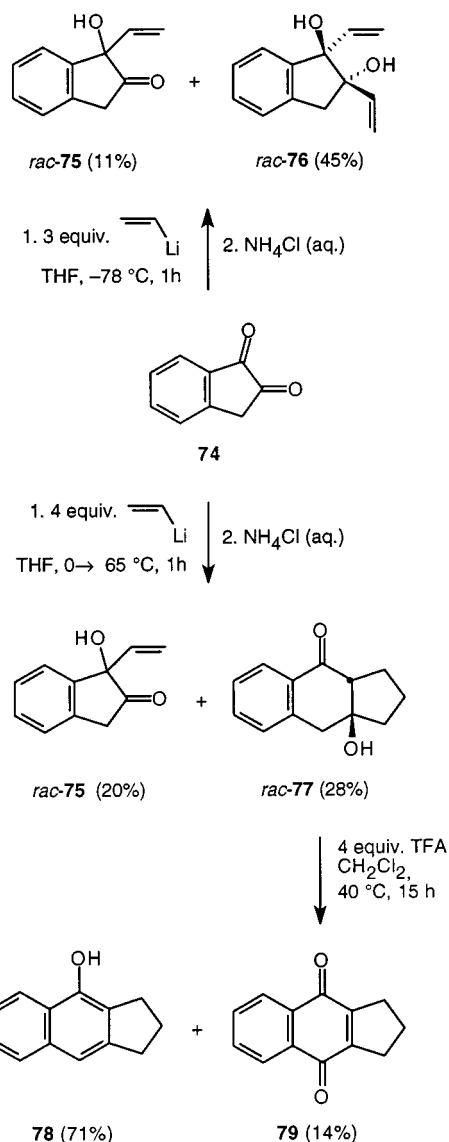
Figure 2. Structure of *rac*-73 in the crystal; selected bond lengths [Å]: C1–C2 1.562(4), C2–C3 1.563(3), C3–C3a 1.518(4), C3a–C4 1.389(4), C4–C5 1.385(4), C5–C6 1.376(4), C6–C7 1.378(4), C7–C7a 1.376(4), C3a–C7a 1.387(3), C1–C7a 1.519(4), C1–C8 1.513(3), C8–C9 1.265(4), C2–C10 1.509(4), C10–C11 1.302(4), C3–C12 1.524(4), C3–C13 1.545(3), C1–O1 1.434(3), C2–O2 1.447(3).



(45%) was obtained, the latter diastereomerically pure ( $^1\text{H}$  NMR: *de* > 95%). A similar result was obtained when the reaction was carried out at 0 °C. However, when the reaction mixture was heated at 65 °C for 1 h, a 28% yield of tricycle *rac*-77 was obtained in addition to 20% of *rac*-75. Upon treatment with trifluoroacetic acid (TFA), elimination of water resulted in the formation of naphthol **78**<sup>[64]</sup> in 71% yield, along with a small portion of oxidation product naphthoquinone **79** (14%).

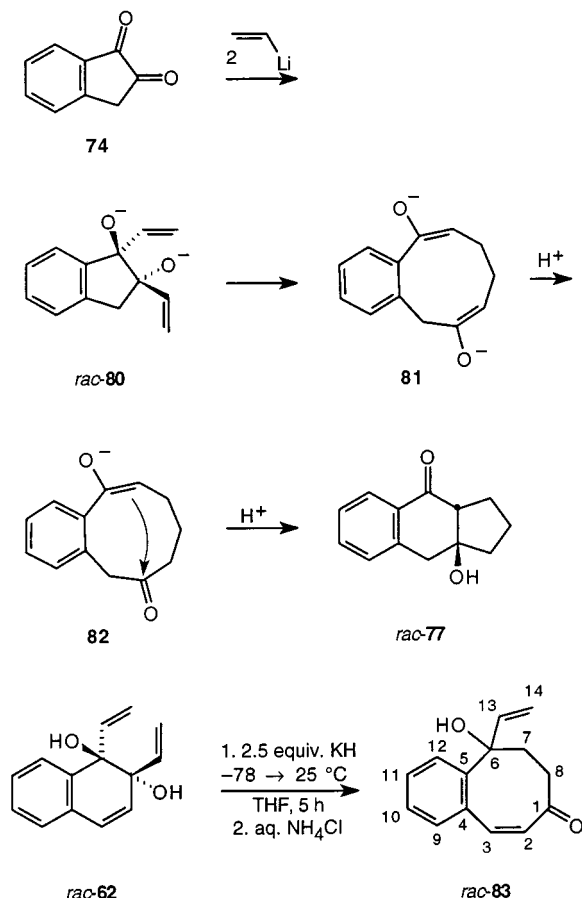
The formation of *rac*-77 may be regarded as the result of a dianionic oxy Cope rearrangement via the *anti* diadduct *rac*-80 and the bis(enolate) **81**. Selective hydrolysis at the more reactive, nonconjugated enolate moiety presumably gave **82**, followed by an intramolecular aldol addition to give *rac*-77. Remarkably, the reaction sequence involves a benzocyclononane intermediate.

In conclusion, it has been shown that, with a variety of 1,2-diketones, dianionic oxy Cope rearrangements are pos-



sible upon addition of vinyl lithium. In many cases, the rearrangement took place at low temperature; however, some substrates required heating at up to 65 °C. These included rearrangements of both linear and cyclic 1,2-diketones. As the divinyl diolates undergoing the rearrangement reaction had been generated by addition of vinyl lithium to 1,2-diketones, and not by deprotonation of 1,2-divinyl diols, monoanionic pathways can be ruled out. *ortho*-Quinones yielded solely the vinyl lithium adducts: No rearrangement was observed in these cases. Bicyclic and sterically hindered monocyclic diketones also did not rearrange. In certain cases, small yields of 1,3-rearranged products were observed, indicating the possible existence of stepwise reaction pathways. In this context it is interesting that, in a preliminary experiment, treatment of *rac*-62 with 2.5 equiv. of potassium hydride at  $-78 \rightarrow 25$  °C resulted in a 56% yield of *rac*-83 after hydrolytic workup. Further investigations concerning the possibility of an anionic 1,3-rearrangement are in progress.





## Experimental Section

**General:** All operations involving air-sensitive materials were performed in flame-dried reaction vessels under argon using the Schlenk technique. Diethyl ether (DEE) and THF were distilled from sodium-potassium alloy/benzophenone. –  $^1\text{H}$  NMR: Bruker WP 80 (80 MHz), WP 200 SY (200.1 MHz), AM 400 (400.1 MHz).  $^{13}\text{C}$  NMR: Bruker WP 200 SY (50.3 MHz), AM 400 (100.1 MHz). Signal multiplicities were determined with APT and DEPT techniques. Chemical shifts refer to  $\delta_{\text{TMS}} = 0$  or to residual solvent signals.<sup>[65][66]</sup> – IR: Perkin–Elmer FT-IR 580 and 1710. – MS: Finnigan MAT 112, 312 at 70 eV. – HRMS: Finnigan MAT 312, VG Autospec, peak matching with PFK. – Combustion analyses: Heraeus CHN Rapid. – Melting points (uncorrected) were determined in sealed glass tubes with a Tottoli apparatus. – Column chromatography: silica gel (J. T. Baker, 40  $\mu\text{m}$ ). Separations were performed by flash chromatography.<sup>[67]</sup> Column length ( $l$ ) and diameter ( $\varnothing$ ) are given. Unless otherwise mentioned, starting materials were purchased and used without further purification. Vinyl lithium was prepared as published.<sup>[68]</sup> 1,2-Bis[2-(*N*-methylbenzimidazolyl)]ethanedione (**20**) was donated by Bayer AG, Wuppertal (Germany).

**1,6-Diphenyl-1,6-hexanedione (6):** Benzil (**5**) (1.000 g, 4.8 mmol) in DEE (10 mL) was added at  $-78^\circ\text{C}$  to a solution of vinyl lithium in DEE (1.11 M, 13.0 mL, 14.4 mmol), which had been diluted by addition of 30 mL of DEE. The mixture was warmed to  $25^\circ\text{C}$  over 23 h, and then hydrolyzed at  $-78^\circ\text{C}$  by addition of an aq. sat.

solution of  $\text{NH}_4\text{Cl}$  (40 mL). After warming to  $25^\circ\text{C}$ , the mixture was extracted with 5 portions of DEE (each 40 mL), and the collected organic layers were dried with  $\text{MgSO}_4$ . Column chromatography ( $l$  17 cm,  $\varnothing$  4 cm, PE/DEE 5:1) gave 0.754 g (2.8 mmol, 59%) of **6**.<sup>[69][70]</sup>

**(*R,S*)-2,3-Diphenylbutane-2,3-diol (7) and (*R,R/S,S*)-2,3-Diphenylbutane-2,3-diol (*rac*-8):** Benzil (**5**) (294 mg, 1.4 mmol) in THF (20 mL) was added at  $-78^\circ\text{C}$  to a mixture of a solution of methyl-lithium in DEE (1.6 M, 2.6 mL, 4.2 mmol) and THF (20 mL). After 30 min, an aq. sat. solution of  $\text{NH}_4\text{Cl}$  (25 mL) was added, and after 1 h, the mixture was warmed to  $25^\circ\text{C}$ . The mixture was extracted three times with DEE (each 50 mL), and the collected organic layers were dried with  $\text{MgSO}_4$ . Column chromatography ( $l$  16 cm,  $\varnothing$  3 cm, PE/DEE 3:1) gave 195 mg (0.8 mmol, 56%) of **7** and 31 mg (0.1 mmol, 9%) of *rac*-8 as an unseparated solid mixture, identified spectroscopically.<sup>[71–74]</sup>

**General Procedure for Treatment of Benzil Derivatives with Vinyl-lithium (GP1):** Vinyl lithium (3 equiv.) in DEE was diluted with THF and cooled to  $-78^\circ\text{C}$ . The benzil derivative (1 equiv.) in THF was added. The mixture was stirred at  $-78^\circ\text{C}$  and then hydrolyzed by addition of an aq. sat. solution of  $\text{NH}_4\text{Cl}$  (25 mL). The mixture was stirred at  $-78^\circ\text{C}$  for 1 h and then warmed to  $25^\circ\text{C}$ . Precipitated  $\text{NH}_4\text{Cl}$  was dissolved by addition of water. The solution was extracted 3 times with DEE (each 30 mL). The collected organic layers were dried with  $\text{Na}_2\text{SO}_4$  and purified by column chromatography.

***cis*-2-*p*-Methylbenzoyl-1-(*p*-methylphenyl)cyclopentanol (*rac*-22) and 1,6-Bis(*p*-methylphenyl)-1,6-hexanedione (**30**):** GP1, vinyl lithium in DEE (0.62 M, 10.5 mL, 6.5 mmol), THF (20 mL), 1,2-bis(*p*-methylphenyl)ethanedione (**9**) (500 mg, 2.1 mmol) in THF (15 mL), 1.5 h at  $-78^\circ\text{C}$ . Column chromatography ( $l$  15 cm,  $\varnothing$  5.0 cm, PE/DEE 4:1). I: 126 mg (0.4 mmol, 20%) of *rac*-22 as a colorless oil, which crystallized at  $6^\circ\text{C}$  over some months (m.p.  $119^\circ\text{C}$ ). II: 283 mg (1.0 mmol, 46%) of **30**.<sup>[49,50]</sup>

***rac*-22:** IR (film):  $\tilde{\nu} = 3396\text{ cm}^{-1}$  (m, OH), 3028 (w, arom. CH), 2960 (w, CH), 2944 (w, CH), 2920 (w, CH), 2864 (w, CH), 1652 (s, CO), 1604 (s, arom. C=C), 1568 (w, C=C), 1512 (w, arom. C=C), 1440 (w), 1388 (m), 1304 (w), 1244 (m), 1228 (m), 1188 (w), 1164 (w), 1116 (w), 1080 (w), 1060 (w), 1040 (m, C–O), 1016 (w), 996 (w), 932 (w), 888 (w), 820 (m), 776 (w), 732 (w), 684 (w), 604 (w), 504 (w), 472 (w). –  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.90\text{--}2.44$  (m, 6 H, 3-H, 4-H, 5-H), 2.27 (s, 3 H, 20-H), 2.38 (s, 3 H, 13-H), 4.05 (dd,  $^3J_{2,\text{cis-3}} = 8.9\text{ Hz}$ ,  $^3J_{2,\text{trans-3}} = 10.8\text{ Hz}$ , 1 H, 2-H), 5.50 (d,  $^4J_{\text{OH},5} = 1.5\text{ Hz}$ , 1 H, OH), 7.08 + 7.22 [AA'BB'-line system, 2  $\times$  2 H, 15(19)-H, 16(18)-H], 7.37 + 7.78 [AA'BB'-line system, 2  $\times$  2 H, 9(11)-H, 8(12)-H]. –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta = 20.9$  ( $\text{CH}_3$ , C-20), 21.6 ( $\text{CH}_3$ , C-13), 22.7 ( $\text{CH}_2$ , C-4), 30.5 ( $\text{CH}_2$ , C-3), 42.7 ( $\text{CH}_2$ , C-5), 54.2 (CH, C-2), 84.4 ( $\text{C}_q$ , C-1), 124.9 [CH, C-15(19)], 128.4 (CH), 128.8 (CH), 129.3 (CH), 134.4 ( $\text{C}_q$ , C-7), 136.1 ( $\text{C}_q$ , C-17), 142.3 ( $\text{C}_q$ , C-20), 144.7 ( $\text{C}_q$ , C-10), 205.1 ( $\text{C}_q$ , C-6). – MS (70 eV,  $90^\circ\text{C}$ ):  $m/z$  (%) = 295 (3) [ $\text{M}^+ + 1$ ], 294 (12) [ $\text{M}^+$ ], 161 (14), 160 (87) [ $\text{MePh}(\text{CO})\text{C}_3\text{H}_5^+$ ], 159 (8), 147 (16), 146 (9), 145 (71) [ $\text{MePh}(\text{CO})\text{C}_2\text{H}_4^+$ ], 134 (25) [ $\text{MePh}(\text{CO})\text{CH}_3^+$ ], 120 (13), 119 (100) [ $\text{MePh}(\text{CO})^+$ ], 92 (7), 91 (26) [ $\text{MePh}^+$ ], 65 (18) [ $\text{C}_5\text{H}_5^+$ ]. – HRMS ( $\text{C}_{20}\text{H}_{22}\text{O}_2$ ): calcd. 294.161980; found 294.162811. –  $\text{C}_{20}\text{H}_{22}\text{O}_2$  (294.39): calcd. C 81.60, H 7.53; found C 81.32, H 7.39.

***cis*-2-*p*-Isopropylbenzoyl-1-(*p*-isopropylphenyl)cyclopentanol (*rac*-23) and 1,6-Bis(*p*-methylphenyl)-1,6-hexanedione (**31**):** GP1, vinyl lithium in DEE (0.62 M, 8.5 mL, 5.3 mmol), THF (20 mL), 1,2-bis(*p*-isopropylphenyl)ethanedione (**10**)<sup>[75]</sup> (500 mg, 1.7 mmol) in THF

(15 mL), 1.5 h at  $-78^{\circ}\text{C}$ . Column chromatography ( $l$  15 cm,  $\varnothing$  3.5 cm, PE/DEE 5:1). I: 216 mg (0.6 mmol, 36%) of **rac-23** as a colorless oil, which crystallized at  $6^{\circ}\text{C}$  over some months (m.p.  $76^{\circ}\text{C}$ ). II: 208 mg (0.6 mmol, 35%), of **31**, colorless solid (m.p.  $93^{\circ}\text{C}$ ).

**rac-23**: IR (film):  $\tilde{\nu}$  =  $3436\text{ cm}^{-1}$  (m, br, OH),  $3084$  (w, arom. CH),  $3048$  (w, arom. CH),  $3024$  (w, arom. CH),  $2960$  (s, CH),  $2868$  (m, CH),  $1656$  (s, CO),  $1604$  (s, arom. C=C),  $1568$  (w, C=C),  $1508$  (w, arom. C=C),  $1460$  (m),  $1416$  (m),  $1380$  (m),  $1364$  (s),  $1300$  (m),  $1224$  (m),  $1184$  (m),  $1140$  (w),  $1084$  (w),  $1056$  (m, C–O),  $1036$  (m),  $1016$  (m),  $1000$  (w),  $884$  (w),  $828$  (m),  $760$  (w),  $692$  (w). –  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.19 (d,  $^3J_{22,21}$  = 6.8 Hz, 6 H, 22-H), 1.25 (d,  $^3J_{14,13}$  = 7.0 Hz, 6 H, 14-H), 1.90–2.40 (m, 6 H, 3-H, 4-H, 5-H), 2.83 (sept, 1 H, 21-H), 2.94 (sept, 1 H, 13-H), 4.06 (dd,  $^3J_{2,trans-3}$  = 10.7 Hz,  $^3J_{2,cis-3}$  = 8.8 Hz, 1 H, 2-H), 5.51 (d,  $^4J_{OH,5}$  = 1.7 Hz, 1 H, OH), 7.13 + 7.28 [AA'BB' line system,  $2 \times 2$  H, 17(19)-H, 16(20)-H], 7.39 + 7.83 [AA'BB' line system,  $2 \times 2$  H, 9(11)-H, 8(12)-H]. –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta$  = 22.7 ( $\text{CH}_2$ , C-4), 23.6 ( $\text{CH}_3$ , CHCH $_3$ ), 23.9 ( $\text{CH}_3$ , CHCH $_3$ ), 30.4 ( $\text{CH}_2$ , C-3), 33.6 (CH, C-21), 34.2 (CH, C-13), 42.6 ( $\text{CH}_2$ , C-5), 54.2 (CH, C-2), 84.5 ( $\text{C}_q$ , C-1), 124.9 [CH, C-17(19)], 126.2 [CH, C-9(11) or C-16(20)], 126.8 [CH, C-9(11) or C-16(20)], 128.7 [CH, C-8(12)], 134.7 ( $\text{C}_q$ , C-7), 142.6 ( $\text{C}_q$ , C-15), 147.1 ( $\text{C}_q$ , C-18), 155.3 ( $\text{C}_q$ , C-10), 205.0 ( $\text{C}_q$ , C-6). – MS (70 eV,  $70^{\circ}\text{C}$ ):  $m/z$  (%) = 351 (2) [ $\text{M}^+ + 1$ ], 350 (7) [ $\text{M}^+$ ], 289 (3), 252 (3), 209 (4), 189 (10), 188 (51) [ $i\text{PrPh}(\text{CO})\text{C}_3\text{H}_5^+$ ], 175 (5), 162 (34), 148 (13), 147 (100) [ $i\text{PrPh}(\text{CO})^+$ ], 146 (8), 145 (58), 133 (13), 119 (8), 117 (10), 115 (8), 105 (15), 104 (10), 103 (9), 92 (26) [ $\text{PhCH}_3^+$ ], 77 (14) [ $\text{C}_6\text{H}_5^+$ ]. – HRMS ( $\text{C}_{24}\text{H}_{30}\text{O}_2$ ): calcd. 350.224580; found 350.224030. –  $\text{C}_{24}\text{H}_{30}\text{O}_2$  (350.50): calcd. C 82.24, H 8.63; found C 82.29, H 8.33.

**30**: IR (KBr):  $\tilde{\nu}$  =  $2956\text{ cm}^{-1}$  (m, CH), 2892 (w, CH), 2872 (w, CH), 1676 (s, CO), 1604 (m, arom. C=C), 1568 (w, C=C), 1464 (w), 1412 (m), 1364 (m), 1304 (w), 1264 (m), 1176 (m), 1108 (w), 1060 (m), 1012 (w), 968 (m), 856 (w), 820 (m), 724 (w), 580 (m). –  $^1\text{H}$  NMR (200.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.27 (d,  $^3J_{8',7'}$  = 6.9 Hz, 12 H, 8'-H), 1.83 [m, 4 H, 3(4)-H], 2.89–3.08 [m, 6 H, 2(5)-H, 7'-H], 7.31 + 7.90 [AA'BB' line system,  $2 \times 2$  H,  $2 \times 2$  H, 3'(5')-H, 2'(6')-H]. –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta$  = 23.6 ( $\text{CH}_3$ , C-8'), 24.0 [ $\text{CH}_2$ , C-3(4)], 34.2 (CH, C-7'), 38.3 [ $\text{CH}_2$ , C-2(5)], 126.6 [CH, C-2'(6') or C-3'(5')], 128.3 [CH, C-2'(6') or C-3'(5')], 134.8 ( $\text{C}_q$ , C-1'), 154.4 ( $\text{C}_q$ , C-4'), 199.7 [ $\text{C}_q$ , C-1(6)]. – MS (70 eV,  $100^{\circ}\text{C}$ ):  $m/z$  (%) = 351 (1) [ $\text{M}^+ + 1$ ], 350 (3) [ $\text{M}^+$ ], 360 (2) [ $\text{M}^+ - \text{CO}$ ], 306 (2), 289 (2), 189 (8), 188 (24) [ $i\text{PrPh}(\text{CO})\text{C}_3\text{H}_5^+$ ], 163 (6), 162 (45) [ $i\text{PrPh}(\text{CO})\text{CH}_3^+$ ], 148 (11), 147 (100) [ $i\text{PrPh}(\text{CO})^+$ ], 145 (18), 119 (7), 104 (8), 103 (7), 91 (21) [ $\text{PhCH}_2^+$ ], 83 (5), 77 (7), 71 (6), 69 (5). – HRMS ( $\text{C}_{24}\text{H}_{30}\text{O}_2$ ): calcd. 350.224580; found 350.224823. –  $\text{C}_{24}\text{H}_{30}\text{O}_2$  (350.50): calcd. C 82.24, H 8.63; found C 82.29, H 8.61.

**cis-2-*p*-tert-Butylbenzoyl-1-(*p*-tert-butylphenyl)cyclopentanol (rac-24) and 1,6-Bis(*p*-tert-butylphenyl)-1,6-hexanedione (32)**: GP1, vinylolithium in DEE (0.85 M, 5.5 mL, 4.7 mmol), THF (20 mL), 1,2-bis(*p*-tert-butyl)ethanedione (**11**)<sup>[75][76]</sup> (500 mg, 1.6 mmol) in THF (20 mL), 3 h at  $-78^{\circ}\text{C}$ . Column chromatography ( $l$  10 cm,  $\varnothing$  5.0 cm, PE/DEE 6:1). I: 237 mg (0.6 mmol, 40%) of **rac-24**, colorless solid (m.p.  $94^{\circ}\text{C}$ ). II: 176 mg (0.5 mmol, 30%) of **32**, colorless solid (m.p.  $109^{\circ}\text{C}$ ).

**rac-24**: IR (KBr):  $\tilde{\nu}$  =  $3428\text{ cm}^{-1}$  (m, OH), 3088 (w, arom. CH), 3052 (w, arom. CH), 3028 (w, arom. CH), 2964 (s, CH), 2904 (m, CH), 2868 (m, CH), 1652 (s, CO), 1604 (s, arom. C=C), 1564 (w, C=C), 1504 (w, arom. C=C), 1464 (m), 1408 (s), 1392 (m), 1360 (s), 1300 (w), 1268 (s), 1224 (s), 1192 (m), 1168 (w), 1108 (s, C–O), 1060 (w), 1036 (m), 1012 (m), 996 (m), 936 (w), 888 (w), 824 (m),

720 (w), 692 (w), 572 (m), 544 (m). –  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.26 (s, 9 H,  $\text{CH}_3$ ), 1.32 (s, 9 H,  $\text{CH}_3$ ), 1.90–2.40 (m, 6 H, 3-H, 4-H, 5-H), 4.06 (dd,  $^3J_{2,trans-3}$  = 10.5 Hz,  $^3J_{2,cis-3}$  = 8.8 Hz, 1 H, 2-H), 5.47 (d,  $^4J_{OH,5}$  = 1.5 Hz, 1 H, OH), 7.28 + 7.39 [AA'BB' line system,  $2 \times 2$  H, 16(20)-H, 17(19)-H], 7.44 + 7.82 [AA'BB' line system,  $2 \times 2$  H, 9(11)-H, 8(12)-H]. NOE: Irr. at 2-H, obs. at 16(20)-H (10.7%), 8(12)-H (23.6%); irr. at OH, obs. at 16(20)-H (6.5%); irr. at 17(19)-H, obs. at 16(20)-H (7.5%); irr. at 16(20)-H, obs. at 17(19)-H (8.9%), 2-H (3.8%), OH (3.0%); irr. at 9(11)-H, obs. at 8(12)-H (11.4%); irr. at 8(12)-H, obs. at 9(11)-H (15.6%), 2-H (7.8%). –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta$  = 22.6 ( $\text{CH}_2$ , C-4), 30.5 ( $\text{CH}_2$ , C-3), 31.0 ( $\text{CH}_3$ ), 31.3 ( $\text{CH}_3$ ), 34.3 ( $\text{C}_q$ , CCH $_3$ ), 35.1 ( $\text{C}_q$ , CCH $_3$ ), 42.6 ( $\text{CH}_2$ , C-5), 54.2 (CH, C-2), 84.4 ( $\text{C}_q$ , C-1), 124.7 (CH), 125.0 (CH), 125.6 (CH), 128.3 [CH, C-8(12)], 134.3 ( $\text{C}_q$ , C-7), 142.3 ( $\text{C}_q$ , C-15), 149.4 ( $\text{C}_q$ , C-18), 157.6 ( $\text{C}_q$ , C-10), 205.0 ( $\text{C}_q$ , C-6). – MS (70 eV,  $90^{\circ}\text{C}$ ):  $m/z$  (%) = 379 (1) [ $\text{M}^+ + 1$ ], 378 (3) [ $\text{M}^+$ ], 360 (2) [ $\text{M}^+ - \text{CO}$ ], 251 (11), 203 (8), 202 (26) [ $i\text{BuPh}(\text{CO})\text{C}_3\text{H}_5^+$ ], 181 (11), 177 (6), 176 (31) [ $i\text{BuPh}(\text{CO})\text{CH}_3^+$ ], 174 (5), 162 (13), 161 (100) [ $i\text{BuPh}(\text{CO})^+$ ], 154 (7), 146 (12), 145 (27) [ $i\text{BuPh}(\text{CO})^+$ ], 131 (6), 118 (10), 117 (7), 115 (7), 105 (18) [ $\text{Ph}(\text{CO})^+$ ], 102 (5), 92 (14) [ $\text{PhCH}_3^+$ ], 84 (13), 77 (15) [ $\text{C}_6\text{H}_5^+$ ], 74 (18), 70 (13). – HRMS ( $\text{C}_{26}\text{H}_{34}\text{O}_2$ ): calcd. 378.255881; found 378.256104. –  $\text{C}_{26}\text{H}_{34}\text{O}_2$  (378.55): calcd. C 82.49, H 9.05; found C 82.23, H 9.00.

**32**: IR (KBr):  $\tilde{\nu}$  =  $2964\text{ cm}^{-1}$  (m, CH), 2888 (w, CH), 2868 (w, CH), 1684 (s, CO), 1604 (m, arom. C=C), 1460 (w), 1404 (w), 1364 (m), 1264 (m), 1180 (m), 1104 (w), 1052 (w), 1020 (w), 968 (m), 824 (m), 724 (w), 584 (w). –  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.34 (s, 18 H, 8'-H), 1.83 [m, 4 H, 3(4)-H], 3.02 [m, 4 H, 2(5)-H], 7.47 + 7.91 [AA'BB' line system,  $2 \times 2$  H +  $2 \times 2$  H, 3'(5')-H, 2'(6')-H]. –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta$  = 24.0 [ $\text{CH}_2$ , C-3(4)], 31.1 ( $\text{CH}_3$ , C-8'), 35.0 ( $\text{C}_q$ , C-7'), 38.3 [ $\text{CH}_2$ , C-2(5)], 125.5 [CH, C-3'(5')], 128.0 [CH, C-2'(6')], 134.4 ( $\text{C}_q$ , C-1'), 156.6 ( $\text{C}_q$ , C-4'), 198.6 [ $\text{C}_q$ , C-1(6)]. – MS (70 eV,  $100^{\circ}\text{C}$ ):  $m/z$  (%) = 379 (1) [ $\text{M}^+ + 1$ ], 378 (2) [ $\text{M}^+$ ], 360 (3) [ $\text{M}^+ - \text{CO}$ ], 303 (5), 203 (8), 202 (23) [ $\text{M}^+ - i\text{BuPh}(\text{CO}) - \text{CH}_3$ ], 177 (8), 176 (39), 162 (13), 161 (100) [ $i\text{BuPh}(\text{CO})^+$ ], 146 (10), 145 (22), 133 (4), 118 (11) [ $\text{PhCH}_3\text{H}_6^+$ ], 115 (6), 105 (6), 91 (14) [ $\text{PhCH}_2^+$ ], 77 (6). – HRMS ( $\text{C}_{26}\text{H}_{34}\text{O}_2$ ): calcd. 378.255881; found 378.256843. –  $\text{C}_{26}\text{H}_{34}\text{O}_2$  (378.55): calcd. C 82.49, H 9.05; found C 81.81, H 8.97.

**cis-2-(2-Naphthoyl)-1-(2-naphthyl)cyclopentanol (rac-25) and 1,6-Bis(2-naphthyl)-1,6-hexanedione (33)**: GP1, vinylolithium in DEE (0.92 M, 3.3 mL, 3.0 mmol), THF (20 mL), 1,2-bis(2-naphthyl)ethanedione (**12**)<sup>[77]</sup> (300 mg, 1.0 mmol) in THF (20 mL), 1 h at  $-78^{\circ}\text{C}$ . Column chromatography ( $l$  14 cm,  $\varnothing$  3.5 cm, PE/DEE 3:1). I: 253 mg (0.7 mmol, 71%) of **rac-25**, colorless solid (m.p.  $142^{\circ}\text{C}$ ). II: 31 mg (0.1 mmol, 9%) of **33**, colorless solid (m.p.  $147^{\circ}\text{C}$ ).

**rac-25**: IR ( $\text{CHCl}_3$ ):  $\tilde{\nu}$  =  $3432\text{ cm}^{-1}$  (m, br, OH), 3060 (m, arom. CH), 3028 (w, arom. CH), 2976 (m, CH), 2952 (m, CH), 2872 (m, CH), 1656 (s, CO), 1628 (m, C=C), 1596 (m, arom. C=C), 1508 (w, arom. C=C), 1468 (w), 1436 (w), 1376 (m), 1304 (w), 1276 (m), 1248 (w), 1192 (m), 1176 (m), 1124 (s, C–O), 1036 (m), 948 (w), 932 (w), 896 (w), 860 (m), 816 (m), 600 (w). –  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.01–2.50 (m, 6 H, 3-H, 4-H, 5-H), 4.37 (dd,  $^3J_{2,trans-3}$  = 10.9 Hz,  $^3J_{2,cis-3}$  = 8.7 Hz, 1 H, 2-H), 5.61 (d, 1 H, OH), 7.38 (m, 2 H, 21-H, 22-H), 7.48–7.83 (m, 10 H, arom. H), 8.02 (d,  $^4J_{18,26}$  = 1.4 Hz, 1 H, 18-H), 8.36 (s, br, 1 H, 8-H). –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta$  = 22.9 ( $\text{CH}_2$ , C-4), 30.8 ( $\text{CH}_2$ , C-3), 42.8 ( $\text{CH}_2$ , C-5), 54.7 (CH, C-2), 84.9 ( $\text{C}_q$ , C-1), 123.4 (CH), 123.6 (CH), 123.8 (CH), 125.6 (CH), 126.0 (CH), 126.9 (CH), 127.3 (CH), 127.7 (CH), 127.9 (CH), 128.1 (CH), 128.5 (CH), 128.8 (CH), 129.6 (CH), 130.4 (CH), 132.33 ( $\text{C}_q$ , C-9 or C-

19 or C-24), 132.35 (C<sub>q</sub>, C-9 or C-19 or C-24), 133.1 (C<sub>q</sub>, C-9 or C-19 or C-24), 134.2 (C<sub>q</sub>, C-7), 135.8 (C<sub>q</sub>, C-14), 142.6 (C<sub>q</sub>, C-17), 205.2 (C<sub>q</sub>, C-6). – MS (70 eV, 130 °C): *m/z* (%) = 367 (5) [M<sup>+</sup> + 1], 366 (14) [M<sup>+</sup>], 348 (4) [M<sup>+</sup> – H<sub>2</sub>O], 347 (4), 197 (10), 196 (60), 195 (9), 183 (5), 179 (4), 171 (10), 170 (69) [C<sub>10</sub>H<sub>7</sub>(CO)CH<sub>3</sub><sup>+</sup>], 156 (12), 155 (100) [C<sub>10</sub>H<sub>7</sub>(CO)<sup>+</sup>], 141 (4), 128 (16), 127 (100) [C<sub>10</sub>H<sub>7</sub><sup>+</sup>], 126 (8), 101 (4), 77 (6). – HRMS (C<sub>26</sub>H<sub>22</sub>O<sub>2</sub>): calcd. 366.161980; found 366.161743. – C<sub>26</sub>H<sub>22</sub>O<sub>2</sub> (366.46): calcd. C 85.22, H 6.05; found C 84.88, H 6.00.

**33:** IR (KBr):  $\tilde{\nu}$  = 3056 cm<sup>−1</sup> (w, arom. CH), 2940 (w, CH), 2888 (w, CH), 2868 (w, CH), 1676 (s, CO), 1624 (m, C=C), 1596 (w, C=C), 1504 (w, C=C), 1468 (w), 1404 (w), 1372 (m), 1276 (m), 1236 (w), 1216 (w), 1168 (m), 1124 (m), 1016 (w), 940 (w), 856 (w), 816 (m), 748 (m), 700 (w), 476 (m). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.95 [m, 4 H, 3(4)], 3.20 [m, 4 H, 2(5)-H], 7.49–7.65 + 7.84–8.08 (m, 12 H, arom. H), 8.48 (s, br, 2 H, 2'-H). – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 24.1 [CH<sub>2</sub>, C-3(4)], 38.5 [CH<sub>2</sub>, C-2(5)], 123.9 (CH), 126.7 (CH), 127.8 (CH), 128.38 (CH), 128.43 (CH), 129.6 (CH), 129.7 (CH), 132.5 (C<sub>q</sub>, C-3'), 134.3 (C<sub>q</sub>, C-1'), 135.5 (C<sub>q</sub>, C-8'), 200.0 [C<sub>q</sub>, C-1(6)]. – MS (70 eV, 170 °C): *m/z* (%) = 367 (2) [M<sup>+</sup> + 1], 366 (7) [M<sup>+</sup>], 348 (3), 338 (2), 309 (2), 233 (7), 197 (7), 196 (33) [C<sub>10</sub>H<sub>7</sub>(CO)C<sub>3</sub>H<sub>5</sub><sup>+</sup>], 183 (9), 171 (8), 170 (51) [C<sub>10</sub>H<sub>7</sub>(CO)CH<sub>3</sub><sup>+</sup>], 156 (15), 155 (100) [C<sub>10</sub>H<sub>7</sub>(CO)<sup>+</sup>], 141 (5), 128 (17), 127 (80) [C<sub>10</sub>H<sub>7</sub><sup>+</sup>], 105 (5), 77 (11), 69 (6). – HRMS (C<sub>26</sub>H<sub>22</sub>O<sub>2</sub>): calcd. 366.161980; found 366.162689. – C<sub>26</sub>H<sub>22</sub>O<sub>2</sub> (366.46): calcd. C 85.22, H 6.05; found C 85.38, H 6.09.

**cis-2-*p*-Methoxybenzoyl-1-(*p*-methoxyphenyl)cyclopentanol (*rac*-26) and 1,6-Bis(*p*-methoxyphenyl)-1,6-hexanedione (34):** GP1, vinyllithium in DEE (0.89 M, 4.0 mL, 3.6 mmol), THF (20 mL), 1,2-bis(*p*-methoxyphenyl)ethanedione (**13**) (300 mg, 1.1 mmol) in THF (15 mL), 30 min at −78 °C. Column chromatography (*l* 14 cm, Ø 3.5 cm, PE/DEE 5:1→1:1). I: 119 mg (0.4 mmol, 33%) of *rac*-26, colorless solid (m.p. 80 °C). II: 126 mg (0.4 mmol, 35%) of **34**, colorless solid (m.p. 142 °C).<sup>[70]</sup>

***rac*-26:** IR (cap.-film):  $\tilde{\nu}$  = 3415 cm<sup>−1</sup> (m, OH), 2949 (m, CH), 2871 (w, CH), 2839 (m, CH), 1651 (s, CO), 1600 (s, arom. C=C), 1573 (s, arom. C=C), 1511 (s, arom. C=C), 1462 (m), 1443 (m), 1421 (m), 1367 (m), 1308 (m), 1245 (s, br, OH), 1176 (s, C–O), 1116 (m), 1085 (w), 1030 (s, C–O), 999 (w), 970 (w), 945 (w), 886 (w), 832 (s), 781 (w), 741 (w), 718 (w), 688 (w), 598 (m). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.90–2.35 (m, 6 H, 3-H, 4-H, 5-H), 3.75 (s, 3 H, 20-H), 3.85 (s, 3 H, 13-H), 4.00 (dd, <sup>3</sup>*J*<sub>2,trans-3</sub> = 10.9 Hz, <sup>3</sup>*J*<sub>2,cis-3</sub> = 10.5 Hz, 1 H, 2-H), 5.57 (d, <sup>3</sup>*J*<sub>OH,5</sub> = 1.47 Hz, 1 H, OH), 6.80 + 7.39 [AA'BB'-system, 2 × 2 H, 16(18)-H, 15(19)-H], 6.90 + 7.86 [AA'BB'-system, 2 × 2 H, 9(11)-H, 8(12)-H]. NOE: Irr. at 2-H, obs. at 15(19)-H (10.6%), 8(12)-H (17.7%); irr. at OH, obs. at 15(19)-H (6.7%), irr. at 15(19)-H, obs. at 16(18)-H (15.7%), 2-H (0.9%), OH (0.9%); irr. at 8(12)-H, obs. at 9(11)-H (15.0%), 2-H (6.4%). – <sup>13</sup>C NMR (50.3 MHz, CDCl<sub>3</sub>, APT):  $\delta$  = 22.6 (+, C-4), 30.5 (+, C-3), 42.6 (+, C-5), 53.9 (−, C-2), 55.2 (−, C-13 or C-20), 55.5 (−, C-13 or C-20), 84.3 (+, C-1), 113.5 [−, C-9(11) or C-16(18)], 113.9 [−, C-9(11) or C-16(18)], 126.1 [−, C-15(19)], 130.0 (+, C-7), 130.7 [−, C-8(12)], 137.5 (+, C-14), 158.3 (+, C-17), 164.1 (+, C-10), 204.0 (+, C-6). – MS (70 eV, 60 °C): *m/z* (%) = 327 (2) [M<sup>+</sup> + 1], 326 (7) [M<sup>+</sup>], 308 (2) [M<sup>+</sup> – H<sub>2</sub>O], 298 (2) [M<sup>+</sup> – CO], 223 (3), 213 (3), 177 (6), 176 (36) [H<sub>3</sub>COPh(CO)CH<sub>2</sub>CH<sub>2</sub>CH<sup>+</sup>], 175 (8), 164 (3), 163 (11), 161 (4), 159 (5), 151 (4), 150 (33) [H<sub>3</sub>COPh(CO)CH<sub>2</sub><sup>+</sup>], 145 (11), 137 (3), 136 (10), 135 (100) [H<sub>3</sub>COPh(CO)<sup>+</sup>], 121 (3), 115 (3), 108 (3), 107 (8) [H<sub>3</sub>COPh<sup>+</sup>], 92 (12), 91 (4), 78 (3), 77 (16) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>], 65 (6). – HRMS (C<sub>20</sub>H<sub>22</sub>O<sub>4</sub>): calcd. 326.1518222; found 326.1511947. – C<sub>20</sub>H<sub>22</sub>O<sub>4</sub> (326.39): calcd. C 73.60, H 6.79; found C 73.45, H 6.65.

**1,2-Bis(*p*-difluoromethoxyphenyl)-2-hydroxyethanone:** Triethylamine (0.58 mL, 0.407 g, 4.0 mmol) was added to *N*-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride (0.453 g, 1.7 mmol) in ethanol (10.0 mL), with formation of a pale yellow solution. *p*-Difluoromethoxybenzaldehyde (5.0 mL, 6.860 g, 39.8 mmol) was added, and the mixture was stirred at 25 °C for 24 h. The mixture was extracted three times with DEE (each 25 mL). Purification by column chromatography (*l* 14 cm, Ø 3.5 cm, PE/DEE 3:1) gave 5.700 g (15.0 mmol, 75%) of 1,2-bis(*p*-difluoromethoxyphenyl)-2-hydroxyethanone, pale green oil. – IR (KBr):  $\tilde{\nu}$  = 3448 (br, s, OH) cm<sup>−1</sup>, 3108 (m, arom. CH), 3076 (m, arom. CH), 3044 (m, arom. CH), 3004 (m, arom. CH), 2928 (w, CH), 1684 (s, C=O), 1604 (s, arom. C=C), 1508 (s, arom. C=C), 1384 (s, C–F), 1228 (br, s, C–F), 1176 (s, C–F), 1116 (br, s), 1044 (br, s, OH), 828 (s), 780 (m), 736 (m), 692 (m). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.53 (br, s, 1 H, OH), 5.94 (s, 1 H, 2-H), 6.47 (t, 1 H, <sup>2</sup>*J*<sub>H,F</sub> = 73.5 Hz, *CHF*<sub>2</sub>), 6.47 (t, 1 H, <sup>2</sup>*J*<sub>H,F</sub> = 73.5 Hz, *CHF*<sub>2</sub>), 7.08 + 7.33 [AA'BB' line system, 2 × 2 H, arom. H], 7.12 + 7.93 [AA'BB' line system, 2 × 2 H, arom. H]. – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 75.7 (CH, C-2), 115.1 (t, CH, <sup>1</sup>*J*<sub>C,F</sub> = −262.4 Hz, *CHF*<sub>2</sub>), 115.6 (t, CH, <sup>1</sup>*J*<sub>C,F</sub> = −262.4 Hz, *CHF*<sub>2</sub>), 118.8 [t, CH, <sup>4</sup>*J*<sub>C,F</sub> = −0.8 Hz, C-3'(5') or C-3''(5'')], 120.1 [t, CH, <sup>4</sup>*J*<sub>C,F</sub> = −0.8 Hz, C-3'(5') or C-3''(5'')], 129.3 [CH, C-2'(6') or C-2''(6'')], 130.0 (C<sub>q</sub>, C-1'), 131.3 [CH, C-2'(6') or C-2''(6'')], 136.0 (C<sub>q</sub>, C-1''), 151.3 (t, C<sub>q</sub>, <sup>3</sup>*J*<sub>4',7'-F</sub> = −3.0 Hz, C-4''), 155.3 (t, C<sub>q</sub>, <sup>3</sup>*J*<sub>4',7'-F</sub> = −2.8 Hz, C-4'), 197.1 (C<sub>q</sub>, C-1). – MS (70 eV, 25 °C): *m/z* (%) = 325 (1) [M<sup>+</sup> – F], 297 (1) [M<sup>+</sup> – F – CO], 278 (2) [M<sup>+</sup> – 2F – CO], 174 (6), 173 (70) [CHF<sub>2</sub>OPhCHOH<sup>+</sup>], 172 (12), 171 (100) [CHF<sub>2</sub>OPh(CO)<sup>+</sup>], 147 (4), 143 (3) [CHF<sub>2</sub>OPh<sup>+</sup>], 122 (33) [CFOPh<sup>+</sup>], 105 (3), 95 (21), 92 (7), 77 (20) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>]. – C<sub>16</sub>H<sub>12</sub>F<sub>4</sub>O<sub>4</sub> (344.27): calcd. C 55.82, H 3.51; found C 55.80, H 3.40.

**1,2-Bis(*p*-difluoromethoxyphenyl)ethanedione (14):** 1,2-Bis(*p*-difluoromethoxyphenyl)-2-hydroxyethanone (4.620 g, 13.4 mmol), ammonium nitrate (1.350 g, 16.9 mmol), and copper(II) acetate monohydrate (0.303 g, 1.5 mmol) in 80% acetic acid (50 mL) were heated at reflux, the color changing from blue to dark brown and to dark green. When no more gas evolution was observed, the solution was cooled to 25 °C with precipitation of yellow material. The precipitation was completed by addition of water. The precipitate was filtered off and dried at 0.01 mbar to give 4.330 g (12.2 mmol, 81%) of **14**, bright yellow solid (m.p. 120 °C). – IR (KBr):  $\tilde{\nu}$  = 1668 cm<sup>−1</sup> (s, C=O), 1604 (s, arom. C=C), 1584 (m, arom. C=C), 1508 (m, arom. C=C), 1424 (w), 1396 (m), 1312 (w), 1248 (s, C–F), 1224 (m), 1172 (s, C–O), 1148 (s), 1108 (s), 1028 (s, C–O), 888 (m), 864 (w), 844 (m), 772 (m), 696 (w), 668 (w), 600 (w), 512 (w). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.63 (t, 2 H, <sup>2</sup>*J*<sub>7',7'-F</sub> = 72.6 Hz, *CHF*<sub>2</sub>), 7.23 + 8.01 [AA'BB'-system, 2 × 2 H, arom. H]. – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 115.2 (t, CH, <sup>1</sup>*J*<sub>7',7'-F</sub> = −262.6 Hz, *CHF*<sub>2</sub>), 119.1 [CH, C-3'(5')], 129.7 (C<sub>q</sub>, *ipso*-C), 132.3 [CH, C-2'(6')], 156.1 (t, C<sub>q</sub>, <sup>3</sup>*J*<sub>4',7'-F</sub> = −2.8 Hz, *COCHF*<sub>2</sub>), 192.2 [C<sub>q</sub>, C-1(2)]. – MS (70 eV, 60 °C): *m/z* (%) = 342 (1) [M<sup>+</sup>], 323 (1) [M<sup>+</sup> – F], 173 (2), 172 (8), 171 (100) [CHF<sub>2</sub>OPhCO<sup>+</sup>], 143 (2) [CHF<sub>2</sub>OPh<sup>+</sup>], 121 (31), 105 (2), 95 (9), 93 (6), 92 (6) [PhO<sup>+</sup>], 85 (2), 83 (2), 76 (3) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>], 75 (2). – HRMS (C<sub>8</sub>H<sub>5</sub>F<sub>2</sub>O<sub>2</sub>): calcd. 171.025761; found 171.025146. – C<sub>16</sub>H<sub>10</sub>F<sub>4</sub>O<sub>4</sub> (342.25): calcd. C 56.15, H 2.95; found C 56.14, H 3.06.

**cis-2-*p*-Difluoromethoxybenzoyl-1-(*p*-difluoromethoxyphenyl)cyclopentanol (*rac*-27) and 1,6-Bis(*p*-difluoromethoxyphenyl)-1,6-hexanedione (35):** GP1, vinyllithium in DEE (0.92 M, 4.0 mL, 3.6 mmol), THF (20 mL), 1,2-bis(*p*-difluoromethoxyphenyl)ethanedione (**14**) (400 mg, 1.2 mmol) in THF (20 mL), 1.5 h at −78 °C. Column chromatography (*l* 18 cm, Ø 3.5 cm, PE/DEE 3:1). I: 212 mg



(0.5 mmol, 46%) of **rac-27**, colorless solid (m.p. 128 °C). II: 41 mg (0.1 mmol, 9%) of **35**, colorless solid (m.p. 144 °C).

**rac-27**: IR (KBr):  $\tilde{\nu}$  = 3428 cm<sup>-1</sup> (m, br, OH), 3084 (w, arom. CH), 3068 (w, arom. CH), 2952 (w, CH), 2872 (m, CH), 1672 (s, CO), 1604 (s, arom. C=C), 1508 (m, arom. C=C), 1464 (w), 1420 (m), 1392 (m), 1300 (w), 1204 (m), 1232 (s), 1176 (s, C–O), 1108 (s), 1044 (s), 972 (m), 864 (w), 832 (m), 740 (w), 684 (w), 636 (w), 600 (w), 568 (w), 476 (w). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.93–2.39 (m, 6 H, 3-H, 4-H, 5-H), 4.00 (dd, <sup>3</sup>J<sub>2,trans-3</sub> = 10.6 Hz, <sup>3</sup>J<sub>2,cis-3</sub> = 8.9 Hz, 1 H, 2-H), 5.31 (d, J<sub>OH,5-H</sub> = 1.3 Hz, 1 H, OH), 6.45 (t, J<sub>20,20-F</sub> = –74.0 Hz, 1 H, 20-H), 6.58 (t, <sup>1</sup>J<sub>13,13-F</sub> = –72.8 Hz, 1 H, 13-H), 7.03 + 7.46 [AA'BB' line system, 2 × 2 H, 16(18)-H, 15(19)-H], 7.15 + 7.89 [AA'BB' line system, 2 × 2 H, 9(11)-H, 8(12)-H]. – MS (70 eV, 25 °C): *m/z* (%) = 398 (1) [M<sup>+</sup>], 258 (2), 249 (2), 212 (3), 199 (6), 188 (4), 187 (4), 186 (5), 171 (19) [F<sub>2</sub>HCOPh(CO)<sup>+</sup>], 148 (3), 139 (4), 138 (5), 124 (4), 122 (6), 121 (16) [HOPh(CO)<sup>+</sup>], 120 (8), 111 (5), 110 (7), 99 (9), 95 (12), 92 (12), 91 (100) [OPh<sup>+</sup>], 83 (6), 79 (5), 77 (6), 73 (6), 69 (16), 65 (6). – HRMS (C<sub>20</sub>H<sub>18</sub>O<sub>4</sub>F<sub>4</sub>): calcd. 398.114122; found 398.114197. – C<sub>24</sub>H<sub>30</sub>O<sub>2</sub> (398.36): calcd. C 60.30, H 4.55; found C 59.81, H 4.57.

IR (KBr):  $\tilde{\nu}$  = 3112 cm<sup>-1</sup> (w, arom. CH), 3084 (w, arom. CH), 3056 (w, arom. CH), 2948 (m, CH), 2896 (w, CH), 2872 (w, CH), 1672 (s, CO), 1600 (s, C=C), 1508 (m, C=C), 1464 (w), 1388 (m), 1300 (m), 1264 (m), 1228 (s, C–F), 1172 (s, C–F), 1108 (s, br, C–F), 1060 (s), 972 (s), 864 (m), 836 (m), 800 (w), 740 (m), 684 (w), 640 (w), 604 (w), 572 (w), 484 (w). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.83 [m, 4 H, 3(4)-H], 3.02 [m, 4 H, 2(5)-H], 6.60 (t, J<sub>7,7-F</sub> = –73.1 Hz, 2 H, 7'-H), 7.18 + 7.99 [AA'BB' line system, 2 × 2 H + 2 × 2 H, 3'(5')-H, 2'(6')-H]. – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 23.8 [CH<sub>2</sub>, C-3(4)], 38.3 [CH<sub>2</sub>, C-2(5)], 115.3 (t, <sup>1</sup>J<sub>7,7-F</sub> = –261.4 Hz, C<sub>q</sub>, C-7'), 118.8 [t, <sup>4</sup>J<sub>3'(5'),7'-F</sub> = –0.8 Hz, CH, C-3'(5')], 130.2 [CH, C-2'(6')], 133.9 (q, C<sub>q</sub>, C-1'), 154.7 (t, <sup>3</sup>J<sub>1',7'-F</sub> = –2.8 Hz, C<sub>q</sub>, C-4'), 198.4 [C<sub>q</sub>, C-1(6)]. – MS (70 eV, 110 °C): *m/z* (%) = 398 (2) [M<sup>+</sup>], 380 (5), 365 (3), 212 (18) [F<sub>2</sub>HCOPh(CO)C<sub>3</sub>H<sub>5</sub><sup>+</sup>], 199 (14), 186 (33) [F<sub>2</sub>HCOPh(CO)CH<sub>3</sub><sup>+</sup>], 172 (8), 171 (100) [F<sub>2</sub>HCOPh(CO)<sup>+</sup>], 145 (12), 121 (35), 111 (15), 97 (19), 95 (11), 85 (16), 83 (19), 81 (18), 71 (24), 69 (29). – HRMS (C<sub>20</sub>H<sub>18</sub>O<sub>4</sub>F<sub>4</sub>): calcd. 398.114122; found 398.114868. – C<sub>20</sub>H<sub>18</sub>O<sub>4</sub>F<sub>4</sub> (398.35): calcd. C 60.30, H 4.55; found C 59.93, H 4.57.

**1,2-Bis(*p*-trifluoromethoxyphenyl)-2-hydroxyethanone**: Triethylamine (0.51 mL, 0.375 g, 3.7 mmol) was added to *N*-benzyl-5-(2-hydroxyethyl)-4-methylthiazolium chloride (0.437 g, 1.6 mmol) in ethanol (10.0 mL), with formation of a pale yellow solution. *p*-Trifluoromethoxybenzaldehyde (5.0 mL, 6.980 g, 36.7 mmol) was added, and the mixture was stirred at 25 °C for 24 h. The mixture was extracted three times with DEE (each 25 mL). Purification by column chromatography (*l* 14 cm, Ø 6.0 cm, PE/DEE 5:1→3:1). I: 0.880 g (2.3 mmol, 13%) of 1,2-bis(*p*-trifluoromethoxyphenyl)ethanedione (**15**), yellow solid (m.p. 108 °C). II: 3.480 g (9.1 mmol, 50%) of 1,2-bis(*p*-trifluoromethoxy)-2-hydroxyethanone, colorless solid (m.p. 64 °C). – IR (KBr):  $\tilde{\nu}$  = 3426 cm<sup>-1</sup> (m, OH), 3392 (m, OH), 1680 (s, C=O), 1604 (w, arom. C=C), 1508 (m, arom. C=C), 1320 (s, C–F), 1260 (br, s, C–F), 1216 (br, s, C–F), 1160 (br, s, C–F), 1076 (w, OH), 976 (w), 824 (w). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 4.57 (br, s, 1 H, OH), 5.96 (s, 1 H, 2-H), 7.19 + 7.25 [AA'BB' line system, 2 × 2 H, 3'(5')-H + 2'(6')-H], 7.37 + 7.97 [AA'BB'-System, 2 × 2 H, 3'(5')-H + 2'(6')-H]. – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 75.4 (CH, C-2), 120.2 (q, C<sub>q</sub>, <sup>1</sup>J<sub>C,F</sub> = –259.4 Hz, CF<sub>3</sub>), 120.39 (q, C<sub>q</sub>, <sup>1</sup>J<sub>C,F</sub> = –259.4 Hz, CF<sub>3</sub>), 120.45 [q, CH, C-3'(5') or C-3''(5'')], <sup>4</sup>J<sub>C,F</sub> = –1.2 Hz], 121.7 [q,

CH, C-3'(5') or C-3''(5''), <sup>4</sup>J<sub>C,F</sub> = –1.2 Hz], 129.3 [CH, C-2''(6'')], 131.3 [CH, C-2'(6')], 131.4 (C<sub>q</sub>, C-1'), 137.2 (C<sub>q</sub>, C-1''), 149.5 (q, C<sub>q</sub>, <sup>3</sup>J<sub>4',7'-F</sub> = –1.8 Hz, C-4''), 153.3 (q, C<sub>q</sub>, <sup>3</sup>J<sub>4',7'-F</sub> = –1.8 Hz, C-4'), 197.8 (C<sub>q</sub>, C-1). – MS (70 eV, 25 °C): *m/z* (%) = 380 (1) [M<sup>+</sup>], 294 (2) [M<sup>+</sup> – CF<sub>3</sub>OPh], 192 (6), 191 (58) [CF<sub>3</sub>OPhCHOH<sup>+</sup>], 190 (11), 189 (100) [CF<sub>3</sub>OPh(CO)<sup>+</sup>], 161 (8) [CF<sub>3</sub>OPh<sup>+</sup>], 105 (2), 95 (19), 77 (24) [C<sub>6</sub>H<sub>5</sub><sup>+</sup>]. – HRMS (C<sub>16</sub>H<sub>10</sub>F<sub>6</sub>O<sub>4</sub>): calcd. 380.048328; found 380.048035. – C<sub>16</sub>H<sub>10</sub>F<sub>6</sub>O<sub>4</sub> (380.24): calcd. C 50.54, H 2.65; found C 50.49, H 2.73.

**1,2-Bis(*p*-trifluoromethoxyphenyl)ethanedione (**15**)**: 1,2-Bis(*p*-trifluoromethoxyphenyl)-2-hydroxyethanone (3.070 g, 8.1 mmol), ammonium nitrate (0.816 g, 10.2 mmol), and copper(II) acetate monohydrate (0.183 g, 0.9 mmol) in 80% acetic acid (50 mL) were heated at reflux, the color changing from blue to dark brown and to dark green. When no more gas evolution was observed, the solution was cooled to 25 °C with precipitation of yellow material. The precipitation was completed by addition of water. The precipitate was filtered off and dried at 0.01 mbar to give 2.650 g (7.0 mmol, 87%) of **15**, bright yellow solid (m.p. 108 °C). – IR (KBr):  $\tilde{\nu}$  = 3112 cm<sup>-1</sup> (w, arom. CH), 3080 (w, arom. CH), 1672 (s, C=O), 1600 (s, arom. C=C), 1504 (m, arom. C=C), 1416 (w), 1312 (s), 1288 (br, s, C–F), 1220 (br, s), 1168 (br, s, C–O), 1016 (w), 928 (w), 892 (m), 848 (m), 760 (m), 696 (w), 508 (w). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.35 + 8.06 [AA'BB' line system, 2 × 2 H, 3'(5')-H + 2'(6')-H]. – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 120.9 (q, C<sub>q</sub>, <sup>1</sup>J<sub>7',7'-F</sub> = –259.8 Hz, C-7'), 121.4 [t, C<sub>q</sub>, <sup>4</sup>J<sub>3'(5'),7'-F</sub> = –1.2 Hz, C-3'(5')], 130.9 (C<sub>q</sub>, C-1'), 132.2 [t, CH, C-2'(6')], 154.1 (q, C<sub>q</sub>, <sup>3</sup>J<sub>4',7'-F</sub> = –1.6 Hz, C-4'), 191.9 [C<sub>q</sub>, C-1(2)]. – MS (70 eV, 25 °C): *m/z* (%) = 378 (1) [M<sup>+</sup>], 293 (2) [M<sup>+</sup> – F<sub>3</sub>CO], 206 (4), 190 (9), 189 (100) [CF<sub>3</sub>OPhCO<sup>+</sup>], 161 (11) [CF<sub>3</sub>OPh<sup>+</sup>], 104 (2), 95 (29), 92 (5) [PhO<sup>+</sup>], 75 (4). – HRMS (C<sub>16</sub>H<sub>8</sub>F<sub>6</sub>O<sub>4</sub>): calcd. 378.032678; found 378.031769. – C<sub>16</sub>H<sub>8</sub>F<sub>6</sub>O<sub>4</sub> (378.23): calcd. C 50.81, H 2.13; found C 50.71, H 2.33.

**cis-2-*p*-Trifluoromethoxybenzoyl-1-(*p*-trifluoromethoxyphenyl)cyclopentanol (**rac-28**) and 1,6-Bis(*p*-trifluoromethoxyphenyl)-1,6-hexanedione (**36**)**: GP1, vinyl lithium in DEE (0.62 M, 5.3 mL, 3.3 mmol), THF (20 mL), 1,2-bis(*p*-trifluoromethoxyphenyl)ethanedione (**15**) (400 mg, 1.1 mmol) in THF (15 mL), 1.5 h at –78 °C. Column chromatography (*l* 14 cm, Ø 3.5 cm, PE/DEE 4:1). Mixture of 44 mg (0.1 mmol, 10%) of **rac-28** and 183 mg (0.4 mmol, 40%) of **36**, from which pure **36** was isolated as a colorless solid (m.p. 130 °C) by recrystallization from DEE.

**rac-28**: <sup>1</sup>H NMR (200.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.96–2.48 (m, 6 H, 3-H + 4-H + 5-H), 4.01 (dd, 2-H, <sup>3</sup>J<sub>2,trans-3</sub> = 10.6 Hz, <sup>3</sup>J<sub>2,cis-3</sub> = 9.0 Hz, 1 H), 5.22 (s, 1 H, OH), 7.12 + 7.49 [AA'BB' line system, 2 × 2 H, 16(18)-H + 15(19)-H], 7.25 + 7.90 [AA'BB' line system, 2 × 2 H, 9(11)-H + 8(12)-H, <sup>3</sup>J = 8.9 Hz].

**36**: IR (KBr):  $\tilde{\nu}$  = 3124 cm<sup>-1</sup> (w, arom. CH), 2948 (m, CH), 2896 (w, CH), 2872 (w, CH), 1676 (s, CO), 1600 (m, C=C), 1508 (w, C=C), 1460 (w), 1404 (w), 1400 (w), 1368 (m), 1304 (m), 1256 (s, C–F), 1204 (s, C–F), 1168 (s, C–F), 1112 (w), 1048 (w), 1016 (w), 972 (m), 928 (m), 848 (m), 825 (m), 740 (w), 568 (w), 492 (w). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.84 [m, 4 H, 3(4)-H], 3.04 [m, 4 H, 2(5)-H], 7.29 + 8.02 [AA'BB' line system, 2 × 2 H + 2 × 2 H, 3'(5')-H, 2'(6')-H]. – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 23.7 [CH<sub>2</sub>, C-3(4)], 38.4 [CH<sub>2</sub>, C-2(5)], 120.3 (q, <sup>1</sup>J<sub>7',7'-F</sub> = –258.6 Hz, C<sub>q</sub>, C-7'), 120.5 [q, <sup>4</sup>J<sub>3'(5'),7'-F</sub> = –1.2 Hz, CH, C-3'(5')], 130.1 [CH, C-2'(6')], 135.2 (q, C<sub>q</sub>, C-1'), 152.6 (q, <sup>3</sup>J<sub>1',7'-F</sub> = –1.8 Hz, C<sub>q</sub>, C-4'), 198.3 [C<sub>q</sub>, C-1(6)]. – MS (70 eV, 80 °C): *m/z* (%) = 434 (3) [M<sup>+</sup>], 415 (2) [M<sup>+</sup> – F], 232 (7), 231 (20)

[F<sub>3</sub>COPh(CO)C<sub>3</sub>H<sub>6</sub><sup>+</sup>], 217 (5), 205 (5), 204 (38) [F<sub>3</sub>COPh(CO)CH<sub>3</sub><sup>+</sup>], 190 (9), 189 (100) [F<sub>3</sub>COPh(CO)<sup>+</sup>], 161 (12) [F<sub>3</sub>CPh<sup>+</sup>], 145 (11), 95 (31), 92 (7), 85 (5). – HRMS (C<sub>20</sub>H<sub>16</sub>O<sub>4</sub>F<sub>6</sub>): calcd. 434.095279; found 434.094788. – C<sub>20</sub>H<sub>16</sub>O<sub>4</sub>F<sub>6</sub> (434.34): calcd. C 55.31, H 3.71; found C 55.21, H 3.73.

**1,6-Bis(*p*-chlorophenyl)-1,6-hexanedione (37) and 1,4-Bis(*p*-chlorophenyl)-4-hydroxyhex-5-en-1-one (*rac*-43):** GP1, vinylolithium in DEE (0.92 M, 6.0 mL, 5.5 mmol), THF (20 mL), 1,2-bis(*p*-chlorophenyl)ethanedione (**16**)<sup>[78]</sup> (500 mg, 1.8 mmol) in THF (20 mL), 2 h at –78 °C. **37**<sup>[79]</sup> (199 mg, 0.6 mmol, 33%) crystallized as a colorless solid (m.p. 175 °C), which was characterized spectroscopically. After workup (GP1), the filtrate was purified by column chromatography (*l* 14 cm, Ø 3.5 cm, PE/DEE 3:1), giving 66 mg (0.2 mmol, 11%) of *rac*-43 as a yellow oil.

***rac*-43:** IR (CHCl<sub>3</sub>):  $\tilde{\nu}$  = 3592 cm<sup>–1</sup> (w, OH), 3088 (w, arom. CH), 3000 (w, arom. CH), 2976 (w, CH), 2936 (w, CH), 2876 (w, CH), 1684 (m, CO), 1592 (m, arom. C=C), 1488 (m), 1448 (w), 1400 (m), 1364 (w), 1264 (m), 1228 (m), 1172 (w), 1092 (s, C–O), 1040 (m), 1012 (s), 932 (w), 872 (w), 832 (m), 628 (w), 528 (w). – <sup>1</sup>H NMR (200.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.35 (t, <sup>3</sup>J<sub>3,2</sub> = 7.1 Hz, 2 H, 3-H), 2.85–3.13 (m, 2 H, 1-H), 5.20 (dd, <sup>2</sup>J = 0.9 Hz, <sup>3</sup>J<sub>6,cis-5</sub> = 10.6 Hz, 1 H, 6-H), 5.35 (dd, <sup>3</sup>J<sub>6,trans-5</sub> = 17.3 Hz, 1 H, 6-H), 6.16 (dd, 1 H, 5-H), 7.28–7.46 [m, 6 H, 9(11)-H, 14(18)-H, 15(17)-H], 7.84 [m, <sup>3</sup>J = 8.8 Hz, 2 H, 8(12)-H]. – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 33.2 (CH<sub>2</sub>, C-3), 35.3 (CH<sub>2</sub>, C-2), 76.1 (C<sub>q</sub>, C-4), 113.5 (CH<sub>2</sub>, C-6), 126.9 [CH, C-9(11)], 128.5 (CH), 128.9 (CH), 129.5 (CH), 132.9 (C<sub>q</sub>, C-16), 135.0 (C<sub>q</sub>, C-7), 139.7 (C<sub>q</sub>, C-10), 143.5 (CH, C-5), 143.6 (C<sub>q</sub>, C-13), 199.7 (C<sub>q</sub>, C-1). – MS (70 eV, 25 °C): *m/z* (%) = 317 (2) [M – OH], 290 (2), 193 (2), 191 (4), 177 (3), 167 (7), 156 (9), 154 (5), 145 (4), 141 (47), 139 (100) [CPh(CO)<sup>+</sup>], 129 (4), 113 (8), 111 (24) [CPh<sup>+</sup>], 77 (5), 75 (10). – C<sub>18</sub>H<sub>16</sub>Cl<sub>2</sub>O<sub>2</sub> (335.23): calcd. C 64.49, H 4.81; found C 64.12, H 4.98.

**1,6-Bis(*p*-trifluoromethylphenyl)-1,6-hexanedione (38):** GP1, vinylolithium in DEE (0.67 M, 6.5 mL, 4.4 mmol), THF (20 mL), 1,2-bis(*p*-trifluoromethylphenyl)ethanedione (**17**)<sup>[80]</sup> (500 mg, 1.4 mmol) in THF (15 mL), 1.5 h at –78 °C. Column chromatography (*l* 18 cm, Ø 3.5 cm, PE/DEE 5:1) gave 337 mg (0.8 mmol, 58%) of **38**, colorless solid (m.p. 167 °C). – IR (KBr):  $\tilde{\nu}$  = 2961 cm<sup>–1</sup> (w, CH), 2937 (w, CH), 2904 (w, CH), 2876 (w, CH), 1689 (s, CO), 1581 (w, C=C), 1511 (w, C=C), 1464 (w), 1411 (m), 1371 (w), 1322 (s, C–F), 1260 (m), 1177 (s) 1164 (s), 1138 (m), 1123 (m), 1110 (m), 1065 (s), 1014 (m), 976 (m), 860 (m), 836 (m), 766 (w), 723 (w), 683 (w), 604 (w), 500 (w). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.87 [m, 4 H, 3(4)-H], 3.09 [m, 4 H, 2(5)-H], 7.47 + 8.07 [AA'BB' line system, 2 × 2 H + 2 × 2 H, 3'(5')-H + 2'(6')-H]. – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 23.5 [CH<sub>2</sub>, C-3(4)], 38.7 [CH<sub>2</sub>, C-2 (5)], 123.6 (q, C<sub>q</sub>, C-7'), <sup>1</sup>J<sub>7',7'-F</sub> = –272.6 Hz), 125.7 [q, CH, C-3'(5')], <sup>3</sup>J<sub>3'(5'),7'-F</sub> = –3.8 Hz), 128.4 [CH, C-2'(6')], 134.4 (q, C<sub>q</sub>, C-4'), <sup>2</sup>J<sub>4',7'-F</sub> = –32.7 Hz), 139.6 (q, C<sub>q</sub>, C-1'), <sup>5</sup>J<sub>1',7'-F</sub> = –1.2 Hz), 199.7 [C<sub>q</sub>, C-1(6)]. – MS (70 eV, 100 °C): *m/z* (%) = 402 (2) [M<sup>+</sup>], 384 (2), 383 (7) [M<sup>+</sup> – F], 215 (11), 214 (25), 201 (3), 188 (26) [F<sub>3</sub>CPh(CO)CH<sub>3</sub><sup>+</sup>], 174 (9), 173 (100) [F<sub>3</sub>CPh(CO)<sup>+</sup>], 145 (56) [F<sub>3</sub>CPh<sup>+</sup>], 126 (4), 125 (5), 95 (7), 71 (4). – HRMS (C<sub>20</sub>H<sub>16</sub>O<sub>2</sub>F<sub>6</sub>): calcd. 402.105449; found 402.105530. – C<sub>20</sub>H<sub>16</sub>O<sub>2</sub>F<sub>6</sub> (402.34): calcd. C 59.71, H 4.01; found C 59.63, H 4.08.

**1,6-Bis(2-furyl)-1,6-hexanedione (39):**<sup>[81]</sup> GP1, vinylolithium in DEE (0.85 M, 9.3 mL, 7.9 mmol), THF (20 mL), 1,2-bis(2-furyl)ethanedione (**18**)<sup>[82][83]</sup> (500 mg, 2.6 mmol) in THF (20 mL), 2 h. Column chromatography (*l* 14 cm, Ø 4.0 cm, PE/DEE 3:1) gave 277 mg (1.3 mmol, 49%) of **39**.<sup>[81]</sup>

**1,6-Bis(2-thienyl)-1,6-hexanedione (40):**<sup>[81]</sup> GP1, vinylolithium in DEE (0.67 M, 10 mL, 6.7 mmol), THF (20 mL), 1,2-bis(2-thienyl)-

ethanedione (**19**)<sup>[84]</sup> (500 mg, 2.2 mmol) in THF (10 mL), 3 h at –78 °C. Column chromatography (20 cm, Ø 3 cm, PE/DEE 2:1) gave 245 mg (0.9 mmol, 39%) of **40**.<sup>[81]</sup>

***cis*-2-[2-(*N*-Methylbenzimidazolyl)]-1-[2-(*N*-methylbenzimidazolyl)]cyclopentanol (*rac*-29) and 1,6-Bis[2-(*N*-methylbenzimidazolyl)]-1,6-hexanedione (41):** GP1, vinylolithium in DEE (0.86 M, 5.5 mL, 4.7 mmol), THF (30 mL), 1,2-bis[2-(*N*-methylbenzimidazolyl)]ethanedione (**20**) (500 mg, 1.6 mmol) in THF (20 mL), 3.5 h at –78 °C. Extraction with dichloromethane until the organic layer remained colorless. Column chromatography (*l* 14 cm, Ø 5.0 cm, PE/DEE 3:1). I: 29 mg (0.1 mmol, 5%) of *rac*-29 as a yellow solid (m.p. 176 °C). II: 34 mg (0.1 mmol, 6%) of **41** as a colorless solid (m.p. 145 °C).

***rac*-29:** IR (KBr):  $\tilde{\nu}$  = 3444 cm<sup>–1</sup> (w, br, OH), 3064 (w, arom. CH), 2948 (m, CH), 2872 (w, CH), 1684 (s, CO), 1612 (w, C=C), 1588 (w, arom. C=C), 1464 (s), 1444 (w), 1388 (m), 1328 (m), 1284 (m), 1252 (w), 1204 (m), 1156 (w), 1128 (w), 1108 (w), 1060 (w), 1028 (m, C–O), 1004 (w), 960 (w), 924 (w), 900 (w), 880 (w), 828 (w), 762 (m), 740 (s), 544 (w). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.60 (s, 1 H, OH), 1.62–1.74 (m, 1 H, 4-H), 1.88–2.00 (m, 1 H, 4-H), 2.27–2.66 (m, 4 H, 3-H + 5-H), 3.87 (s, 3 H, 22-H), 3.93 (dd, <sup>3</sup>J<sub>2,trans-3</sub> = 9.8 Hz, <sup>3</sup>J<sub>2,cis-3</sub> = 8.7 Hz, 1 H, 2-H), 4.13 (s, 3 H, 14-H), 7.04–7.15 (m, 4 H, 10-H + 11-H + 18-H + 19-H), 7.19–7.29 (m, 2 H, 10-H + 17-H), 7.47 (d, <sup>3</sup>J<sub>20,19</sub> = 7.9 Hz, 1 H, 20-H), 7.65 (d, <sup>3</sup>J<sub>13,12</sub> = 8.1 Hz, 1 H, 13-H). – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 22.3 (CH<sub>2</sub>, C-4), 27.3 (CH<sub>2</sub>, C-3), 31.1 (CH<sub>3</sub>), 31.7 (CH<sub>3</sub>), 41.7 (CH<sub>2</sub>, C-5), 64.2 (CH, C-2), 80.7 (C<sub>q</sub>, C-1), 109.1 (CH, C-9 or C-17), 110.5 (CH, C-9 or C-17), 119.2 (CH), 120.6 (CH), 121.5 (CH), 122.2 (CH), 123.4 (CH), 125.0 (CH), 135.9 (C<sub>q</sub>, C-16), 136.9 (C<sub>q</sub>, C-8), 139.9 (C<sub>q</sub>, C-21), 141.0 (C<sub>q</sub>, C-13), 148.8 (C<sub>q</sub>, C-7), 156.4 (C<sub>q</sub>, C-15), 192.5 (C<sub>q</sub>, C-6). – MS (70 eV, 160 °C): *m/z* (%) = 376 (3) [M<sup>+</sup> + 2], 375 (9) [M<sup>+</sup> + 1], 374 (27) [M<sup>+</sup>], 358 (4), 357 (8), 356 (14) [M<sup>+</sup> – H<sub>2</sub>O], 347 (9), 346 (29) [M<sup>+</sup> – CO], 328 (6), 327 (7), 319 (10), 318 (36) [M<sup>+</sup> – 2 CO], 312 (6), 264 (6), 243 (11), 226 (6), 225 (6), 224 (9), 216 (10), 215 (55) [M<sup>+</sup> – C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>3</sub>(CO)], 214 (7), 213 (9), 202 (15), 201 (88) [M<sup>+</sup> – C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>3</sub>(CO) – CH<sub>2</sub>], 199 (15), 197 (20), 188 (26), 187 (62) [M<sup>+</sup> – C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>3</sub>(CO) – C<sub>2</sub>H<sub>4</sub>], 175 (73) [C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>3</sub>C(OH)CH<sub>3</sub><sup>+</sup>], 172 (31), 160 (31), 159 (100) [C<sub>7</sub>H<sub>4</sub>N<sub>2</sub>CH<sub>3</sub>(CO)<sup>+</sup>], 146 (52) [C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>(CO)<sup>+</sup>], 133 (78) [C<sub>7</sub>H<sub>6</sub>N<sub>2</sub>CH<sub>3</sub><sup>+</sup>], 132 (47), 131 (39), 104 (16), 92 (19), 77 (26). – HRMS (C<sub>22</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub>): calcd. 374.174276; found 374.174011. – C<sub>22</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub> (374.44): calcd. C 70.57, H 5.92, N 14.96; found C 70.36, H 5.90, N 14.76.

**41:** <sup>1</sup>H NMR (200.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.92 (m, 4 H, 3-H + 4-H), 3.41 (m, 4 H, 2-H + 5-H), 4.10 (s, 6 H, 8'-H), 7.35–7.50 (m, 4 H, 3'-H + 4'-H + 5'-H), 7.92 (d, <sup>3</sup>J<sub>7',6'</sub> = 7.7 Hz, 2 H, 7'-H). – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 23.5 [CH<sub>2</sub>, C-3(4)], 32.3 (CH<sub>3</sub>, C-8'), 39.7 [CH<sub>2</sub>, C-2(5)], 110.5 (CH, C-3'), 121.8 (CH, C-6'), 123.7 (CH, C-4'), 125.8 (CH, C-5'), 136.9 (C<sub>q</sub>, C-2), 141.6 (C<sub>q</sub>, C-7), 146.0 (C<sub>q</sub>, C-1') 195.5 [C<sub>q</sub>, C-1 (6)].

***trans*-2-(2-Pyridylcarbonyl)-1-(2-pyridyl)cyclopentanol (*rac*-44) and 1,6-Bis(2-pyridyl)-1,6-hexanedione (42):** GP1, vinylolithium in DEE (0.67 M, 11.0 mL, 7.4 mmol), THF (20 mL), 1,2-bis(2-pyridyl)ethanedione (**21**) (500 mg, 2.4 mmol) in THF (10 mL), 3 h at –78 °C. Column chromatography (*l* 14 cm, Ø 3.5 cm, PE/dichloromethane 5:1). Mixture of 35 mg (0.1 mmol, 6%) of *rac*-44 and 59 mg (0.2 mmol, 9%) of **42**, from which **42** was obtained as a colorless solid (m.p. 112 °C) by recrystallization from DEE.

***rac*-44:** <sup>1</sup>H NMR (200.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.98–2.47 (m, 6 H, 3-H + 4-H + 5-H), 4.97 (dd, <sup>3</sup>J<sub>2,cis-3</sub> = 8.7 Hz, <sup>3</sup>J<sub>2,trans-3</sub> = 10.3 Hz,



1 H, 2-H), 5.45 (s, 1 H, OH), 7.05 (ddd,  $^3J_{14,13} = 4.8$  Hz,  $^3J_{14,15} = 6.9$  Hz,  $^4J_{14,16} = 1.7$  Hz, 1 H, 14-H), 7.37 (ddd,  $^3J_{9,8} = 4.7$  Hz,  $^3J_{9,10} = 7.6$  Hz,  $^4J_{9,11} = 1.4$  Hz, 1 H, 9-H), 7.60–7.95 (m, 4 H, 10-H + 11-H + 15-H + 16-H), 8.33 (ddd,  $^4J_{13,15} = 1.7$  Hz,  $^5J_{13,16} = 1.0$  Hz, 1 H, 13-H), 8.49 (ddd,  $^4J_{8,10} = 1.7$  Hz,  $^5J_{8,11} = 0.9$  Hz, 1 H, 8-H).

**42:** IR (KBr):  $\tilde{\nu} = 3092$  cm $^{-1}$  (w, arom. CH), 3064 (w, arom. CH), 2948 (m, CH), 2904 (w, CH), 2872 (w, CH), 1692 (s, CO), 1580 (m, C=C), 1456 (m), 1436 (m), 1404 (m), 1372 (m), 1276 (m), 1240 (m), 1192 (m), 1056 (w), 1040 (w), 996 (m), 972 (m), 780 (m), 744 (m), 724 (w), 684 (w), 616 (w), 572 (w). –  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.86$  [m, 4 H, 3(4)-H], 3.30 [m, 4 H, 2(5)-H], 7.47 (ddd,  $^3J_{3',2'} = 4.8$  Hz,  $^3J_{3',4'} = 7.5$  Hz,  $^4J_{3',5'} = 1.3$  Hz, 2 H, 3'-H), 7.84 (m,  $^3J_{4',5'} = 7.9$  Hz,  $^4J_{4',2'} = 1.8$  Hz, 2 H, 4'-H), 8.04 (m,  $^5J_{5',2'} = 0.9$  Hz, 2 H, 5'-H), 8.68 (ddd, 2 H, 2'-H). –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta = 23.6$  [ $\text{CH}_2$ , C-3(4)], 37.5 [ $\text{CH}_2$ , C-2(5)], 121.8 (CH, C-5'), 127.0 (CH, C-3'), 136.9 (CH, C-4'), 148.9 (CH, C-2'), 153.5 ( $\text{C}_q$ , C-1'), 201.8 [ $\text{C}_q$ , C-1(6)]. – MS (70 eV, 90 °C):  $m/z$  (%) = 269 (4) [ $\text{M}^+ + 1$ ], 268 (17) [ $\text{M}^+$ ], 250 (13), 240 (10) [ $\text{M}^+ - \text{CO}$ ], 223 (5), 222 (5), 212 (24) [ $\text{M}^+ - 2 \text{ CO}$ ], 190 (15), 172 (11), 162 (20), 148 (39) [ $\text{M}^+ - \text{C}_5\text{H}_4\text{N} - \text{CO} - \text{CH}_2$ ], 147 (20), 146 (13), 144 (26), 135 (40), 134 (99) [ $\text{M}^+/2$ ], 122 (30), 121 (26), 118 (10), 117 (10), 107 (13), 106 (48) [ $\text{C}_5\text{H}_4\text{N}(\text{CO})^+$ ], 93 (10), 80 (15), 79 (55), 78 (100) [ $\text{C}_5\text{H}_4\text{N}^+$ ]. – HRMS ( $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$ ): calcd. 268.121178; found 268.122162. –  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_2$  (268.32): calcd. C 71.62, H 6.01, N 10.44; found C 71.32, H 5.93, N 10.25.

**General Procedure for Reactions of Aliphatic Diones with Vinylithium (GP2a and GP2b):** A solution of vinylolithium in DEE (3 equiv.) was diluted with THF and cooled at  $-78$  °C (GP2a) or  $0$  °C (GP2b). The dione (1 equiv.) in THF was added, the mixture was stirred at  $-78$  °C (GP2a) or at  $0$  °C (GP2b), and then warmed to  $25$  °C. After cooling to  $-78$  °C (GP2a) or  $0$  °C (GP2b), an aq. sat. solution of  $\text{NH}_4\text{Cl}$  (25 mL) was added. After stirring for 1 h at  $-78$  °C (GP2a) or at  $0$  °C (GP2b), the mixture was warmed to  $25$  °C. Solid  $\text{NH}_4\text{Cl}$  was dissolved by addition of water. The mixture was extracted three times with DEE (each 30 mL). The collected organic layers were dried with  $\text{Na}_2\text{SO}_4$ , followed by product purification by column chromatography.

**Treatment of 2,3-Butanedione (45) with Vinylithium:** GP2b, vinylolithium in DEE (0.89 M, 19.5 mL, 17.4 mmol), THF (20 mL), 2,3-butanedione (**45**) (486 mg, 5.6 mmol) in THF (15 mL), 1 h at  $0$  °C, 5 h heating at reflux, sat. aq.  $\text{NH}_4\text{Cl}$  (35 mL). Column chromatography ( $l$  18 cm,  $\varnothing$  3.5 cm, PE/DEE 3:1 $\rightarrow$ 1:3). I: 136 mg (1.0 mmol, 17%) of *cis*-2-acetyl-1-methylcyclopentanol (*rac*-**46**) as a bright yellow oil. II: 58 mg (0.4 mmol, 7%) of 2,7-octanedione (**48**).<sup>[45,46]</sup> III: 168 mg (1.2 mmol, 21%) of *trans*-2-acetyl-1-methylcyclopentanol (*rac*-**47**) as a bright yellow oil.

**rac-46:** IR (film):  $\tilde{\nu} = 3384$  cm $^{-1}$  (m, br, OH), 2964 (s, CH), 2872 (m, CH), 1692 (m, CO), 1492 (w), 1448 (m), 1412 (m), 1372 (s), 1300 (w), 1216 (m), 1180 (m), 1064 (m), 1028 (m), 1000 (m), 920 (s), 848 (w), 760 (m), 700 (s), 664 (m). –  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.37$  (s, 3 H, 8-H), 1.50–2.10 (m, 6 H, 3-H + 4-H + 5-H), 2.20 (s, 3 H, 7-H), 2.67 (dd,  $^3J_{2,\text{cis-3}} = 8.7$  Hz,  $^3J_{2,\text{trans-3}} = 10.4$  Hz, 1 H, 2-H), 3.71 (s, 1 H, OH). NOE: Irr. at 8-H, obs. at 2-H (1.1%). –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta = 21.8$  ( $\text{CH}_2$ , C-4), 26.9 ( $\text{CH}_3$ , C-8), 28.4 ( $\text{CH}_2$ , C-3), 31.3 ( $\text{CH}_3$ , C-8), 40.9 ( $\text{CH}_2$ , C-5), 59.9 (CH, C-2), 80.1 ( $\text{C}_q$ , C-1), 213.6 ( $\text{C}_q$ , C-6). – MS (70 eV,  $25$  °C):  $m/z$  (%) = 142 (3) [ $\text{M}^+$ ], 127 (4) [ $\text{M}^+ - \text{CH}_3$ ], 121 (6), 113 (5), 94 (5), 86 (12), 84 (100) [ $\text{M}^+ - \text{CO} - 2 \text{ CH}_3$ ], 81 (14), 79 (7), 72 (15), 71 (52), 69 (30), 67 (18).

**rac-47:** IR (film):  $\tilde{\nu} = 3420$  cm $^{-1}$  (s, br, OH), 2968 (s, CH), 2880 (m, CH), 1700 (s, CO), 1460 (m), 1420 (m), 1368 (s), 1304 (m),

1212 (m), 1172 (m), 1124 (m), 1088 (m), 1016 (w), 936 (m), 872 (w), 700 (w). –  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.19$  (s, 3 H, 8-H), 1.60–2.00 (m, 6 H, 3-H + 4-H + 5-H), 1.77 (s, 1 H, OH), 2.24 (s, 3 H, 7-H), 2.94 (m, 1 H, 2-H). NOE: Irr. at 8-H, obs. at OH (2.4%); irr. at OH, obs. at 2-H (1.1%); irr. at 2-H, obs. at OH (2.3%). –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta = 20.7$  ( $\text{CH}_2$ , C-4), 24.0 ( $\text{CH}_3$ , C-8), 25.6 ( $\text{CH}_2$ , C-3), 31.4 ( $\text{CH}_3$ , C-8), 41.8 ( $\text{CH}_2$ , C-5), 62.2 (CH, C-2), 80.9 ( $\text{C}_q$ , C-1), 211.1 ( $\text{C}_q$ , C-6). – MS (70 eV,  $25$  °C):  $m/z$  (%) = 142 (2) [ $\text{M}^+$ ], 127 (3) [ $\text{M}^+ - \text{CH}_3$ ], 113 (3), 109 (5), 97 (3), 85 (14), 84 (100) [ $\text{M}^+ - \text{CO} - 2 \text{ CH}_3$ ], 81 (13), 79 (4), 72 (16), 71 (53), 69 (35), 68 (4), 67 (8).

#### Treatment of 3,4-Hexanedione (49) with Vinylolithium

**a)** GP1, vinylolithium in DEE (0.85 M, 11.6 mL, 9.9 mmol), THF (30 mL), 3,4-hexanedione (**49**) (376 mg, 3.3 mmol) in THF (15 mL), 5 h. Column chromatography ( $l$  13 cm,  $\varnothing$  4.0 cm, PE/DEE 4:1). 397 mg (2.3 mmol, 71% of an unseparated mixture of diastereomeric *meso*- and *rac*-3,4-diethylhexa-1,5-diene-3,4-diols **50** and **51** (9:5 or 5:9)).<sup>[47]</sup>

**50 or 51:**  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.83$  (t,  $^3J_{8(10),7(9)} = 7.4$  Hz, 6 H, 8-H + 10-H), 1.48–1.86 (m, 4 H, 7-H + 9-H), 2.02 (s, 2 H, OH), 5.25–5.37 (m, 4-H, 1-H + 6-H), 5.83 (dd,  $^3J_{2(5),\text{trans-1(6)}} = 17.3$  Hz,  $^3J_{2(5),\text{cis-1(6)}} = 10.4$  Hz, 2-H, 2-H + 5-H). –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta = 7.53$  ( $\text{CH}_3$ , C-8 + C-10), 25.7 ( $\text{CH}_2$ , C-7 + C-9), 80.0 ( $\text{C}_q$ , C-3 + C-4), 115.4 ( $\text{CH}_2$ , C-1 + C-6), 139.9 (CH, C-2 + C-5).

**51 or 50:**  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.81$  (t,  $^3J_{8(10),7(9)} = 7.5$  Hz, 6 H, 8-H + 10-H), 1.48–1.86 (m, 4 H, 7-H + 9-H), 2.02 (s, 2 H, OH), 5.25–5.37 (m, 4-H, 1-H + 6-H), 5.76 (dd,  $^3J_{2(5),\text{trans-1(6)}} = 17.3$  Hz,  $^3J_{2(5),\text{cis-1(6)}} = 10.3$  Hz, 2-H, 2-H + 5-H). –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta = 7.46$  ( $\text{CH}_3$ , C-8 + C-10), 27.2 ( $\text{CH}_2$ , C-7 + C-9), 79.9 ( $\text{C}_q$ , C-3 + C-4), 115.6 ( $\text{CH}_2$ , C-1 + C-6), 139.8 (CH, C-2 + C-5).

**b)** GP2a, vinylolithium in DEE (0.67 M, 14.0 mL, 9.4 mmol), THF (25 mL), 3,4-hexanedione (**49**) (415 mg, 3.6 mmol) in THF (10 mL), 2.5 h at  $-78$  °C, warming to  $10$  °C over 14 h. Column chromatography ( $l$  15 cm,  $\varnothing$  4.0 cm, PE/DEE 3:1 $\rightarrow$ 1:3). I: 152 mg (1.0 mmol, 28%) of 2-ethyl-1-propanoylcyclopentene (**52**), colorless liquid.<sup>[47,48]</sup> II: 23 mg (0.1 mmol, 4%) of *rac*-6-ethyl-6-hydroxyoct-7-en-3-one (*rac*-**53**), colorless oil.

**52:**  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta = 1.05$  (t,  $^3J_{8 \text{ or } 10,7 \text{ or } 9} = 7.5$  Hz, 3 H,  $\text{CH}_3$ ), 1.07 (t,  $^3J_{8 \text{ or } 10,7 \text{ or } 9} = 7.2$  Hz, 3 H,  $\text{CH}_3$ ), 1.82 (m, 2 H, 4-H), 2.44–2.72 (m, 8 H, 3-H + 5-H + 7-H + 9-H). –  $^{13}\text{C}$  NMR (50.3 MHz,  $\text{CDCl}_3$ , APT):  $\delta = 7.4$  (–, C-10), 12.2 (–, C-8), 21.5 (+, C-4), 23.3 (+, C-9), 33.9 (+, C-3 or C-5 or C-7), 35.1 (+, C-3 or C-5 or C-7), 37.4 (+, C-3 or C-5 or C-7), 134.1 (+, C-1), 159.2 (+, C-2), 201.0 (C-6).

**rac-53:** IR ( $\text{CHCl}_3$ ):  $\tilde{\nu} = 3464$  cm $^{-1}$  (w, br, OH), 2968 (s, CH), 2936 (s, CH), 2880 (m, CH), 2852 (w, CH), 1704 (s, CO), 1668 (m, C=C), 1604 (m, C=C), 1460 (m), 1408 (w), 1380 (m), 1260 (m), 1228 (w), 1100 (s, br, C–O), 1032 (m), 932 (w), 872 (w), 808 (w), 612 (w). –  $^1\text{H}$  NMR (200.1 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.84$  (t,  $^3J_{10,9} = 7.4$  Hz, 3 H, 10-H), 1.10 (t,  $^3J_{1,2} = 7.2$  Hz, 3 H, 1-H), 1.71–1.92 (m, 4 H, 5-H + 9-H), 2.42–2.69 (m, 4 H, 2-H + 4-H), 4.04 (s, 1 H, OH), 5.23 (dd,  $^2J = 1.4$  Hz,  $^3J_{8,\text{cis-7}} = 10.5$  Hz, 1 H, 8-H), 5.48 (dd,  $^3J_{8,\text{trans-7}} = 17.0$  Hz, 1 H, 8-H), 5.94 (dd, 1 H, 7-H). – MS (70 eV,  $25$  °C):  $m/z$  (%) = 154 (10), 153 (5), 152 (19) [ $\text{M}^+ - \text{H}_2\text{O}$ ], 142 (4), 135 (34) [ $\text{M}^+ - \text{H}_2\text{O} - \text{OH}$ ], 133 (8), 124 (10), 123 (100) [ $\text{M}^+ - \text{H}_2\text{O} - \text{C}_2\text{H}_5$ ], 115 (6), 110 (6), 109 (6), 105 (11), 95 (19) [ $\text{M}^+ -$

$\text{H}_2\text{O} - \text{C}_2\text{H}_5 - \text{CO}$ ], 93 (7), 91 (11), 85 (70), 79 (11), 77 (22), 67 (37), 65 (11).

**c)** GP2b, vinyllithium in DEE (0.62 M, 20.0 mL, 12.4 mmol), THF (20 mL), 3,4-hexanedione (**49**) (481 mg, 4.2 mmol) in THF (15 mL), 1.5 h at 0 °C, 2 h at 50 °C. Column chromatography (*l* 10 cm,  $\varnothing$  5.0 cm, PE/DEE 4:1) gave 370 mg (2.2 mmol, 52%) of *rac-cis*-1-ethyl-2-propanoylcyclopentanol (*rac*-**54**), bright yellow liquid.

*rac*-**54**: IR (film):  $\tilde{\nu}$  = 3400  $\text{cm}^{-1}$  (m, br, OH), 2968 (s, CH), 2940 (s, CH), 2880 (m, CH), 1692 (s, CO), 1460 (m), 1396 (m), 1316 (m), 1300 (w), 1268 (w), 1228 (w), 1164 (w), 1120 (m, C–O), 1068 (w), 1024 (w), 976 (m), 884 (w), 828 (w), 756 (m), 692 (m). –  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.93 (t,  $^3J_{10,9}$  = 7.5 Hz, 3 H, 10-H), 1.06 (t,  $^3J_{8,7}$  = 7.3 Hz, 3 H, 8-H), 1.48–2.04 (m, 8 H, 3-H + 4-H + 5-H + 9-H), 2.51 (m, 2 H, 7-H), 2.70 (dd,  $^3J_{2,cis-3}$  = 8.7 Hz,  $^3J_{2,trans-3}$  = 10.4 Hz, 1 H, 2-H), 4.14 (s, 1 H, OH). –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta$  = 7.4 ( $\text{CH}_3$ , C-8), 9.2 ( $\text{CH}_3$ , C-10), 21.9 ( $\text{CH}_2$ , C-4), 29.2 ( $\text{CH}_2$ , C-3), 33.0 ( $\text{CH}_2$ , C-9), 37.5 ( $\text{CH}_2$ , C-5 or C-7), 37.9 ( $\text{CH}_2$ , C-5 or C-7), 57.2 (CH, C-2), 83.7 ( $\text{C}_q$ , C-1), 217.5 ( $\text{C}_q$ , C-6). – MS (70 eV, 25 °C): *m/z* (%) = 170 (4) [ $\text{M}^+$ ], 152 (5) [ $\text{M}^+ - \text{H}_2\text{O}$ ], 141 (29) [ $\text{M}^+ - \text{C}_2\text{H}_5$ ], 137 (16), 123 (12), 113 (3), 99 (11), 98 (100) [ $\text{M}^+ - \text{CO} - \text{C}_2\text{H}_5 - \text{CH}_3$ ], 96 (8), 95 (62) [ $\text{M}^+ - \text{H}_2\text{O} - 2 \text{C}_2\text{H}_5$ ], 94 (41), 86 (17), 85 (38), 83 (11), 72 (7), 69 (72), 67 (26), 66 (16), 65 (12). – HRMS ( $\text{C}_{10}\text{H}_{18}\text{O}_2$ ): calcd. 170.130680; found 170.130859.

**d)** GP2b, vinyllithium in DEE (0.67 M, 15.0 mL, 10.1 mmol), THF (20 mL), 3,4-hexanedione (**49**) (360 mg, 3.2 mmol) in THF (15 mL), 2 h at 0 °C, 24 h heating at reflux. Column chromatography (*l* 12 cm,  $\phi$  3.5 cm, PE/DEE 5:1). I: 140 mg (0.8 mmol, 26%) of *rac-cis*-1-ethyl-2-propanoylcyclopentanol (*rac*-**54**). II: 132 mg (0.8 mmol, 25%) of 3,8-decanedione, colorless solid (m.p. 63 °C).<sup>[49,50]</sup>

#### *cis*-2-(Cyclohexylcarbonyl)-1-cyclohexylcyclopentanol (*rac*-**57**) and 1,6-dicyclohexyl-1,6-hexanedione (**58**)

**a)** GP2a, vinyllithium in DEE (1.00 M, 4.2 mL, 4.2 mmol), THF (20 mL), 1,2-dicyclohexylethanedione (**56**)<sup>[85,86]</sup> (300 mg, 1.3 mmol) in THF (15 mL), 1 h at –78 °C, warming to 10 °C over 18 h. Column chromatography (*l* 14 cm,  $\varnothing$  3.5 cm, PE/TBME 8:1) gave 167 mg (0.6 mmol, 44%) of **58**, colorless solid (m.p. 38 °C).<sup>[51]</sup>

**b)** GP2b, vinyllithium in DEE (1.6 M, 2.8 mL, 4.5 mmol), THF (20 mL), **56** (300 mg, 1.3 mmol) in THF (15 mL), 1 h at 0 °C, 3 h heating at reflux. Column chromatography (*l* 12 cm,  $\phi$  3.5 cm, PE/TBME 7:1). I: 191 mg (0.7 mmol, 51%) of *rac*-**57**, colorless solid (m.p. 40 °C). II: 46 mg (0.2 mmol, 12%) of **58**.<sup>[51]</sup>

*rac*-**57**: IR (film):  $\tilde{\nu}$  = 3444  $\text{cm}^{-1}$  (w, br, OH), 2932 (s, CH), 2856 (m, CH), 1680 (m, CO), 1448 (m), 1392 (w), 1344 (w), 1304 (w), 1240 (w), 1144 (w), 1060 (w), 1008 (w), 892 (w). –  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.95–1.97 (m, 26 H,  $\text{CH}_2$ ), 2.03 (m, 1 H, 13-H), 2.40 (m, 1 H, 7-H), 2.88 (dd,  $^3J_{2,cis-3}$  = 8.6 Hz,  $^3J_{2,trans-3}$  = 10.4 Hz, 1 H, 2-H), 4.61 (d,  $^4J_{2,5-H}$  = 1.7 Hz, 1 H, OH). NOE: Irr. at 13-H, obs. at 2-H (6.5%); irr. at 2-H, obs. at 13-H (5.5%), 7-H (5.0%). –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta$  = 22.0 ( $\text{CH}_2$ , C-4), 25.65 ( $\text{CH}_2$ ), 25.68 ( $\text{CH}_2$ ), 25.8 ( $\text{CH}_2$ ), 26.5 ( $\text{CH}_2$ ), 26.68 ( $\text{CH}_2$ ), 26.73 ( $\text{CH}_2$ ), 28.2 ( $\text{CH}_2$ ), 28.45 ( $\text{CH}_2$ ), 28.46 ( $\text{CH}_2$ ), 28.8 ( $\text{CH}_2$ ), 30.3 ( $\text{CH}_2$ , C-3), 36.4 ( $\text{CH}_2$ , C-5), 46.9 (CH, C-13), 52.2 (CH, C-7), 53.3 (CH, C-2), 86.6 ( $\text{C}_q$ , C-1), 221.2 ( $\text{C}_q$ , C-6). – MS (70 eV, 25 °C): *m/z* (%) = 278 (4) [ $\text{M}^+$ ], 260 (2) [ $\text{M}^+ - \text{CO}$ ], 217 (3), 196 (12), 195 (65) [ $\text{M}^+ - \text{C}_6\text{H}_{11}$ ], 194 (10), 181 (7), 177 (8), 153 (8), 152 (47), 149 (23), 133 (64), 111 (61) [ $\text{C}_6\text{H}_{11}(\text{CO})^+$ ], 105 (12), 96 (16), 84 (14), 83 (100)

[ $\text{C}_6\text{H}_{11}^+$ ], 81 (18), 67 (16). – HRMS ( $\text{C}_{18}\text{H}_{30}\text{O}_2$ ): calcd. 278.224580; found 278.224854. –  $\text{C}_{18}\text{H}_{30}\text{O}_2$  (278.44): calcd. C 77.65, H 10.86; found C 77.52, H 10.89.

**58**: IR<sup>[51]</sup> ( $\text{CHCl}_3$ ):  $\tilde{\nu}$  = 2932  $\text{cm}^{-1}$  (s, CH), 2856 (s, CH), 1700 (s, CO), 1448 (m), 1404 (w), 1372 (m), 1308 (w), 1288 (w), 1200 (m), 1144 (m), 1096 (w), 1068 (w), 996 (w), 892 (w). –  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.13–1.37 (m, 12 H), 1.52 [m, 4 H, 3(4)-H], 1.62–1.85 (m, 10 H), 2.32 (m, 2 H, 1'-H), 2.44 [m, 4 H, 2(5)-H]. –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta$  = 23.3 [ $\text{CH}_2$ , C-3(4)], 25.6 [ $\text{CH}_2$ , C-2'(6) or C-3'(5')], 25.8 ( $\text{CH}_2$ , C-4'), 28.8 [ $\text{CH}_2$ , C-2'(6) or C-3'(5')], 40.4 [ $\text{CH}_2$ , C-2(5)], 50.8 (CH, C-1'), 213.9 [ $\text{C}_q$ , C-1(6)]. – MS (70 eV, 110 °C): *m/z* (%) = 279 (9) [ $\text{M}^+ + 1$ ], 278 (18) [ $\text{M}^+$ ], 195 (16) [ $\text{M}^+ - \text{C}_6\text{H}_{11}$ ], 177 (18), 168 (10), 165 (10), 159 (11), 152 (60) [ $\text{C}_6\text{H}_{11}(\text{CO})\text{C}_3\text{H}_5^+$ ], 149 (53), 139 (10), 126 (14), 111 (41) [ $\text{C}_6\text{H}_{11}(\text{CO})^+$ ], 108 (16), 99 (12), 95 (16), 83 (100) [ $\text{C}_6\text{H}_{11}^+$ ], 81 (24), 67 (25). – HRMS ( $\text{C}_{18}\text{H}_{30}\text{O}_2$ ): calcd. 278.224580; found 278.223450. –  $\text{C}_{18}\text{H}_{30}\text{O}_2$  (278.44): calcd. C 77.65, H 10.86; C 77.56, H 10.76.

#### The Cyclopentanol/1,6-Hexanedione Equilibrium

**Treatment of *rac*-26 with Ammonium Chloride:** A mixture of *rac*-**26** (56 mg, 0.2 mmol) in THF (15 mL) and an aq. sat. solution of  $\text{NH}_4\text{Cl}$  (10 mL) was stirred for 5 h at 25 °C. The precipitate formed was dissolved by addition of as little water as possible. The mixture was extracted three times with MTBE (each 30 mL). After drying of the collected organic layers, filtration, and solvent removal at reduced pressure, a mixture of 59% of *rac*-**26** and 41% of **34** (NMR) was isolated.

**Treatment of *rac*-26 with Trifluoroacetic Acid:** Compound *rac*-**26** (130 mg, 0.4 mmol) in dichloromethane (5 mL) was treated with trifluoroacetic acid (0.01 mL, 11 mg, 0.1 mmol) and stirred for 21 h at 25 °C. Additional trifluoroacetic acid (0.09 mL, 101 mg, 0.9 mmol) was then added; the solution became yellow. After 76 h, water (20 mL) was added, and the mixture was extracted with 20 mL portions of dichloromethane until the organic extracts remained colorless. The collected organic layers were dried with  $\text{Na}_2\text{SO}_4$  and filtered. After solvent removal at reduced pressure, 94 mg of a mixture of 47 mg (0.15 mmol, 38%) of 1-(*p*-methoxybenzoyl)-2-(*p*-methoxyphenyl)cyclopentene (**59**),<sup>[57]</sup> 25 mg (0.08 mmol, 19%) of **34**, and 22 mg of an unidentified compound.

**59**: IR ( $\text{CHCl}_3$ ):  $\tilde{\nu}$  = 3000  $\text{cm}^{-1}$  (w, arom. CH), 2960 (m, CH), 2936 (m, CH), 2840 (w, CH), 1640 (m, CO), 1596 (s, arom. C=C), 1572 (m, arom. C=C), 1512 (s, C=C), 1464 (m), 1440 (w), 1420 (w), 1344 (m), 1308 (m), 1256 (s), 1168 (s), 1140 (w), 1108 (w), 1032 (s), 956 (w), 864 (w), 832 (m), 612 (w). –  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.10 (m, 2 H, 4-H), 2.89 (m, 2 H, 3-H or 5-H), 2.97 (m, 2 H, 3-H or 5-H), 3.71 (s, 3 H, 13-H or 20-H), 3.80 (s, 3 H, 13-H or 20-H), 6.66 + 7.13 [AA'BB' line system,  $2 \times 2$  H, 16(18)-H + 15(19)-H], 6.77 + 7.78 [AA'BB' line system,  $2 \times 2$  H, 9(11)-H + 8(12)-H]. –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta$  = 22.6 ( $\text{CH}_2$ , C-4), 37.5 ( $\text{CH}_2$ , C-3 or C-5), 38.0 ( $\text{CH}_2$ , C-3 or C-5), 55.1 ( $\text{CH}_3$ ), 55.3 ( $\text{CH}_3$ ), 113.4 [CH, C-9(11) or C-16(18)], 113.5 [CH, C-9(11) or C-16(18)], 128.6 ( $\text{C}_q$ , C-14), 129.0 [CH, C-15(19)], 130.2 ( $\text{C}_q$ , C-7), 131.7 [CH, C-8(12)], 136.0 ( $\text{C}_q$ , C-1), 143.4 ( $\text{C}_q$ , C-2), 158.9 ( $\text{C}_q$ , C-17), 163.4 ( $\text{C}_q$ , C-10), 197.7 ( $\text{C}_q$ , C-6). – MS (70 eV, 110 °C): *m/z* (%) = 309 (21) [ $\text{M}^+ + 1$ ], 308 (100) [ $\text{M}^+$ ], 307 (71), 294 (19), 281 (15), 279 (15), 277 (22) [ $\text{M}^+ - \text{OMe}$ ], 265 (12), 249 (6), 212 (5), 201 (16) [ $\text{M}^+ - \text{MeOPh}$ ], 183 (8), 173 (29) [ $\text{M}^+ - \text{MeOPh}(\text{CO})$ ], 172 (14), 165 (24), 158 (12), 137 (22), 135 (92) [ $\text{MeOPh}(\text{CO})^+$ ], 128 (11), 121 (17), 115 (13), 108 (20), 92 (20), 91 (15), 84 (30), 77 (40) [ $\text{C}_6\text{H}_5^+$ ], 71 (13), 69 (21). – HRMS ( $\text{C}_{20}\text{H}_{20}\text{O}_3$ ): calcd. 308.141245; found 308.140411.

**Treatment of 34 with Sodium Methoxide:** Sodium methoxide (151 mg, 2.8 mmol) and **34** (181 mg, 0.6 mmol) were dissolved in THF (20 mL). The orange solution was heated at reflux for 24 h. At 25 °C, an aq. sat solution of NH<sub>4</sub>Cl (25 mL) was added, and the mixture was extracted with 30 mL portions of MTBE until the organic extract remained colorless. The collected organic layers were dried with NaSO<sub>4</sub>, filtered, and the solvent was removed at reduced pressure. An oil (155 mg) was obtained, consisting (NMR) of 128 mg (0.42 mmol, 75%) of **59**, 10 mg (0.03 mmol, 6%) of **34**, and 17 mg of an unidentified compound.

**Variation of the Reaction Conditions for Treatment of 13 with Vinyl-lithium:** Vinylolithium in DEE (3 equiv.) was diluted with THF (20 mL) and cooled to the given reaction temperature (Table 2). **13** (300 mg, 1.1 mmol) in THF (15 mL) was added. The mixture was kept at the given reaction temperature for the given reaction time (Table 2). At the given hydrolysis temperature, either an aq. sat. solution of NH<sub>4</sub>Cl (25 mL) or trifluoromethanesulfonic acid (0.7 mL) was added, and the mixture was warmed to 25 °C over the given hydrolysis time. A precipitate was dissolved by addition of as little water as possible. The mixture was extracted three times with DEE or TBME (each 50 mL), the collected organic layers were dried with Na<sub>2</sub>SO<sub>4</sub> and filtered. Purification by column chromatography Results are summarized in Table 2.

**rac-trans-3,5-Di-tert-butyl-1,2-divinyl-3,5-cyclohexadiene-1,2-diol (rac-60):** GP2a, vinylolithium in DEE (1.69 M, 13.4 mL, 23.0 mmol, 10 equiv.) was diluted by addition of DEE (50 mL). 3,5-Di-tert-butyl-ortho-benzoquinone (500 mg, 2.3 mmol) in DEE (15 mL), 6 h at –78 °C, warming to 25 °C over 14 h. Column chromatography (*l* 14 cm, Ø 3.5 cm, PE/DEE 6:1) gave 224 mg (0.8 mmol, 35%) of **rac-60**, colorless solid (m.p. 58 °C). – IR (KBr):  $\tilde{\nu}$  = 3547 cm<sup>–1</sup> (s, OH), 3522 (s, OH), 3088 (w, vinyl CH), 3078 (w, arom. CH), 3059 (w, arom. CH), 2959 (s, CH), 2869 (m, CH), 1645 (w, C=C), 1585 (w, arom. C=C), 1484 (m), 1396 (m), 1364 (m, CH), 1336 (w), 1300 (w), 1265 (m), 1184 (w), 1160 (m, OH), 1150 (m, OH), 1099 (w), 1017 (m), 994 (m), 955 (m), 924 (s), 885 (m), 821 (m), 772 (w), 727 (w), 694 (w), 676 (w), 653 (m), 612 (w). – <sup>1</sup>H NMR (200.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.06 (s, 9 H, CH<sub>3</sub>), 1.19 (s, 9 H, CH<sub>3</sub>), 2.10 (s, 2 H, OH), 5.27 (d, <sup>4</sup>*J*<sub>4,6</sub> = 1.9 Hz, 1 H, 4-H or 6-H), 5.23 (dd, <sup>2</sup>*J* = 1.9 Hz, <sup>3</sup>*J*<sub>8(10),cis-7(9)</sub> = 10.6 Hz, 1 H, 8-H or 10-H), 5.31 (dd, <sup>2</sup>*J* = 1.8 Hz, <sup>3</sup>*J*<sub>8(10),cis-7(9)</sub> = 10.6 Hz, 1 H, 8-H or 10-H), 5.51 (dd, <sup>2</sup>*J* = 1.9 Hz, <sup>3</sup>*J*<sub>8(10),trans-7(9)</sub> = 17.3 Hz, 1 H, 8-H or 10-H), 5.52 (dd, <sup>2</sup>*J* = 1.8 Hz, <sup>3</sup>*J*<sub>8(10),trans-7(9)</sub> = 17.3 Hz, 1 H, 8-H or 10-H), 5.80 (d, 1 H, 4-H or 6-H), 6.09 (dd, 1 H, 7-H or 9-H), 6.17 (dd, 1 H, 7-H or 9-H). – <sup>13</sup>C NMR (50.3 MHz, CDCl<sub>3</sub>, APT):  $\delta$  = 28.5 (–, CH<sub>3</sub>), 30.2 (–, CH<sub>3</sub>), 33.9 (+, CCH<sub>3</sub>), 37.2 (+, CCH<sub>3</sub>), 80.1 (+, C-1 or C-2), 82.1 (+, C-1 or C-2), 115.8 (+, C-8 or C-10), 117.0 (+, C-8 or C-10), 117.6 (–, C-4 or C-6), 123.9 (–, C-4 or C-6), 136.3 (–, C-7 or C-9), 139.0 (–, C-7 or C-9), 144.3 (+, C-3 or C-5), 151.7 (+, C-3 or C-5). – MS (70 eV): *m/z* (%) = 277 (1) [M<sup>+</sup> + 1], 276 (4) [M<sup>+</sup>], 274 (2), 261 (4), 260 (10), 258 (100) [M<sup>+</sup> – H<sub>2</sub>O], 244 (8), 243 (30) [M<sup>+</sup> – H<sub>2</sub>O – CH<sub>3</sub>], 230 (3), 220 (3), 219 (14) [M<sup>+</sup> – CCH<sub>3</sub>], 216 (11), 203 (8), 192 (12), 187 (9), 173 (18), 164 (8), 159 (11), 147 (5), 145 (6), 133 (10), 118 (5), 105 (12), 92 (4), 77 (9). – C<sub>18</sub>H<sub>28</sub>O<sub>2</sub> (276.42): calcd. C 78.20, H 10.22; found C 77.95, H 10.19.

**rac-3,4,5,6-Tetrachloro-trans-1,2-divinyl-3,5-cyclohexadiene-1,2-diol (rac-61):** GP1, vinylolithium in DEE (1.11 M, 6.0 mL, 6.7 mmol), tetrachloro-ortho-benzoquinone (500 mg, 2.0 mmol) in DEE (10 mL), 2 h at –78 °C. Column chromatography (*l* 14 cm, Ø 3.5 cm, PE/DEE 1:2) gave 193 mg (0.6 mmol, 32%) of **rac-61**, dark brown oil, purity ca. 95% (NMR). – IR (CHCl<sub>3</sub>):  $\tilde{\nu}$  = 3536 cm<sup>–1</sup> (br, m, OH), 3424 (br, w, OH), 3000 (w, vinyl CH), 2932 (w), 1636

(w, vinyl C=C), 1596 (m, C=C), 1488 (w), 1460 (m), 1432 (m), 1404 (s), 1320 (m), 1288 (s, OH), 1252 (m), 1196 (s, C–O), 1108 (m), 1076 (m), 988 (m), 940 (w), 892 (w). – <sup>1</sup>H–NMR (200.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.55 (s, br, 2 H, OH), 5.49 (dd, <sup>2</sup>*J* = 2.0 Hz, <sup>3</sup>*J*<sub>8(10),cis-7(9)</sub> = 11.0 Hz, 2 H, 8-H + 10-H), 5.63 (dd, <sup>3</sup>*J*<sub>8(10),trans-7(9)</sub> = 17.0 Hz, 2 H, 8-H + 10-H), 6.07 (dd, 2 H, 7-H + 9-H). – <sup>13</sup>C NMR (50.3 MHz, CDCl<sub>3</sub>, APT):  $\delta$  = 80.6 (+, C-1 + C-2), 118.8 (+, C-3 or C-6), 119.5 (+, C-8 + C-10), 124.5 (+, C-3 or C-6), 132.3 (–, C-7 + C-9), 135.2 (+, C-4 or C-5), 140.2 (+, C-4 or C-5). – MS (70 eV, 50 °C): *m/z* (%) = 271 (9), 267 (12), 265 (13) [M<sup>+</sup> – Cl], 251 (21), 250 (50), 249 (55), 248 (100) [M<sup>+</sup> – Cl – OH], 247 (54), 246 (77), 231 (31), 229 (45) [M<sup>+</sup> – Cl – HCl], 214 (31), 212 (56) [M<sup>+</sup> – 2 Cl – H<sub>2</sub>O], 211 (38), 209 (30), 194 (35), 193 (28), 184 (22), 183 (24), 175 (18), 165 (22), 149 (53), 147 (42), 137 (21), 131 (20), 122 (24), 111 (38), 107 (50), 105 (48), 84 (41), 78 (57), 77 (70), 73 (54).

**rac-trans-1,2-Dihydro-1,2-divinyl-1,2-naphthalenediol (rac-62):** GP1, vinylolithium in DEE (1.00 M, 6.0 mL, 6.0 mmol), THF (20 mL), 1,2-naphthoquinone (300 mg, 1.9 mmol) in THF (15 mL), 1.5 h at –78 °C. Extraction with TBME. Column chromatography (*l* 14 cm, Ø 3.5 cm, PE/TBME 7:1→3:1) gave 171 mg (0.8 mmol, 42%) of **rac-62**, colorless crystals (from petroleum ether, m.p. 71 °C). – IR (CHCl<sub>3</sub>):  $\tilde{\nu}$  = 3564 cm<sup>–1</sup> (s, OH), 3092 (w, vinyl CH), 3068 (w, arom. CH), 3028 (w, arom. CH), 1672 (w, C=C), 1632 (w, vinyl C=C), 1596 (w, arom. C=C), 1480 (w), 1452 (w), 1408 (s), 1320 (m), 1196 (m), 1152 (s), 1108 (w), 1048 (w), 992 (s), 936 (s), 908 (m), 840 (w), 616 (w), 524 (w). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.22 (s, 1 H, OH), 2.29 (s, 1 H, OH), 5.23 (dd, <sup>2</sup>*J* = 1.5 Hz, <sup>3</sup>*J*<sub>12 or 14, cis-11 or cis-13</sub> = 10.7 Hz, 1 H, 12-H or 14-H), 5.27 (dd, <sup>2</sup>*J* = 1.5 Hz, <sup>3</sup>*J*<sub>12 or 14, cis-11 or cis-13</sub> = 10.7 Hz, 1 H, 12-H or 14-H), 5.48 (dd, <sup>3</sup>*J*<sub>12 or 14,trans-11 or -13</sub> = 17.1 Hz, 1 H, 12-H or 14-H), 5.58 (dd, <sup>3</sup>*J*<sub>12 or 14,trans-11 or -13</sub> = 17.1 Hz, 1 H, 12-H or 14-H), 5.79 (d, <sup>3</sup>*J*<sub>3,4</sub> = 9.7 Hz, 1 H, 3-H), 5.90 (dd, 1 H, 11-H or 13-H), 6.35 (dd, 1 H, 11-H or 13-H), 6.40 (d, 1 H, 4-H), 7.05–7.08 (m, 1 H, 8-H), 7.20–7.27 (m, 2 H, 7-H + 9-H), 7.47–7.50 (m, 1 H, 6-H). – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 79.2 (C<sub>q</sub>, C-1 or C-2), 79.9 (C<sub>q</sub>, C-1 or C-2), 115.6 (CH<sub>2</sub>, C-12 or C-14), 117.0 (CH<sub>2</sub>, C-12 or C-14), 124.4 (CH, C-3), 126.6 (CH), 126.8 (CH), 128.0 (CH), 128.6 (CH), 131.7 (C<sub>q</sub>, C-5), 133.8 (CH, C-4), 136.3 (CH, C-11 or C-13), 137.7 (CH, C-11 or C-13), 139.4 (C<sub>q</sub>, C-10). – MS (70 eV, 25 °C): *m/z* (%) = 214 (4) [M<sup>+</sup>], 196 (15) [M<sup>+</sup> – H<sub>2</sub>O], 195 (9), 181 (8), 168 (10), 167 (10), 165 (9), 159 (34) [M<sup>+</sup> – C<sub>2</sub>H<sub>4</sub> – C<sub>2</sub>H<sub>3</sub>], 158 (10), 157 (18), 152 (9), 145 (21), 144 (100) [M<sup>+</sup> – H<sub>2</sub>O – 2 C<sub>2</sub>H<sub>3</sub>], 141 (30), 139 (8), 131 (21), 129 (12), 128 (16), 116 (16), 115 (41) [PhC<sub>3</sub>H<sub>3</sub><sup>+</sup>], 103 (8), 91 (11), 77 (14). – HRMS (C<sub>14</sub>H<sub>14</sub>O<sub>2</sub>): calcd. 214.099380; found 214.098618. – C<sub>14</sub>H<sub>14</sub>O<sub>2</sub> (214.26): calcd. C 78.48, H 6.59; found C 78.15, H 6.47.

**Crystal Structure Analysis of rac-62:** C<sub>14</sub>H<sub>14</sub>O<sub>2</sub>, crystal size 0.30 × 0.67 × 1.66 mm, *a* = 9.532(1), *b* = 24.457(3), *c* = 10.555(1) Å,  $\beta$  = 102.88(1)°, *V* = 2398.7(5) Å<sup>3</sup>, *d*<sub>calcd.</sub> = 1.187 g cm<sup>–3</sup>,  $\mu$  = 0.8 cm<sup>–1</sup>, *F*(000) = 912 e, *Z* = 8, crystal system monoclinic, space group *P*2<sub>1</sub>/*c* (No. 14), Stoe IPDS (Imaging Plate) diffractometer, Mo-*K* $\alpha$ ,  $\lambda$  = 0.71073 Å, *T* = 300 K,  $2\theta_{\min}$  = 4.3°,  $2\theta_{\max}$  = 47.9°, 190 exposures,  $\Delta\Phi$  = 1.0°, 14439 measured reflections ( $\pm 10$ ,  $\pm 27$ ,  $\pm 11$ ), 3607 unique and 1792 observed reflections [*I* > 2 $\sigma$ (*I*)], completeness of data 96.7%, *R*(*I*) = 0.097, no absorption correction, no extinction correction, refinement: SHELXL-93, *N*<sub>ref</sub> = 3607, *N*<sub>par</sub> = 289, *R* = 0.065, *R*<sub>w</sub> = 0.115 [*w* = 1/ $\sigma^2$ (*F*<sub>o</sub><sup>2</sup>)], *S* = 1.47, min./max. residual electron density: –0.23/0.33 e Å<sup>–3</sup>. The crystallographic data (without structure factors) of the structure were deposited at the Cambridge Crystallographic Data Centre (CCDC-144458). Copies of the data can be obtained from the following address in Great Bri-



tain: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

***rac-trans*-9,10-Dihydro-9,10-divinylphenanthrenediol (*rac*-63):**<sup>[87,88]</sup> GP2a, vinyllithium in DEE (0.99 M, 7.5 mL, 7.4 mmol), THF (20 mL), 9,10-phenanthrenequinone (500 mg, 2.4 mmol) in THF (15 mL), 30 min at  $-78^{\circ}\text{C}$ . Then, addition of another portion of vinyllithium in DEE (0.99 M, 7.5 mL, 7.4 mmol), 30 min at  $-78^{\circ}\text{C}$ , then warming to  $25^{\circ}\text{C}$  over 6 h. The mixture was stirred at  $25^{\circ}\text{C}$  for 14 h, then heated at reflux for 1 h. Hydrolysis at  $0^{\circ}\text{C}$ , followed by extraction with TBME. Column chromatography (*I* 14 cm,  $\varnothing$  3.5 cm, PE/TBME 3:1). I: 63 mg (0.2 mmol, 13%) of 9,10-phenanthrenequinone. II: 340 mg (1.3 mmol, 54%) of *rac*-63, colorless solid (m.p.  $85^{\circ}\text{C}$ ).<sup>[87][88]</sup>

***rac-trans*-1,2-Dihydro-1,2-divinyl-1,2-acenaphthenediol (*rac*-64):** GP1, vinyllithium in DEE (1.00 M, 8.5 mL, 8.5 mmol), THF (20 mL), 1,2-acenaphthenequinone (500 mg, 2.7 mmol) in THF (15 mL), 1.5 h at  $-78^{\circ}\text{C}$ . Extraction with TBME. Column chromatography (*I* 20 cm,  $\phi$  5.0 cm, PE/TBME 5:1 $\rightarrow$ 1:1) gave 406 mg (1.7 mmol, 62%) of *rac*-64, colorless solid (m.p.  $134^{\circ}\text{C}$ ). – IR (KBr):  $\tilde{\nu}$  = 3338  $\text{cm}^{-1}$  (OH), 3040 (w, arom. CH), 1636 (w, C=C), 1497 (w, arom. C=C), 1406 (m), 1303 (m), 1250 (w), 1234 (w), 1196 (s, C–O), 1183 (m, C–O), 1158 (m), 1141 (w), 1061 (m), 1034 (w), 997 (s), 968 (w), 926 (s), 905 (w), 873 (m), 855 (w), 821 (m), 779 (s), 692 (br, w), 663 (w), 627 (w). –  $^1\text{H}$  NMR (200.1 MHz,  $\text{CDCl}_3/\text{CD}_3\text{OD}$ ):  $\delta$  = 4.00 (s, br, 2 H, OH), 5.30 (dd,  $^2J$  = 2.0 Hz,  $^3J_{12,\text{cis-11}}$  = 11.0 Hz, 2 H, 12-H), 5.38 (dd,  $^3J_{12,\text{trans-11}}$  = 17.0 Hz, 2 H, 8-H), 6.26 (dd, 2 H, 11-H), 7.35 (d,  $^3J_{6(7),5(8)}$  = 6.0 Hz, 2 H, 6-H + 7-H), 7.54 (dd,  $^3J_{5(8),4(9)}$  = 7.0 Hz, 2 H, 5-H + 8-H), 7.74 (d, 2 H, 4-H + 9-H). –  $^{13}\text{C}$  NMR [50.3 MHz,  $\text{CDCl}_3/\text{CD}_3\text{OD}$  (1:1), APT]:  $\delta$  = 87.8 (+, C-1(2)), 114.6 (+, C-12), 120.2 (–, C-4 + C-9), 124.5 (–, C-5 + C-8), 128.0 (–, C-6 + C-7), 130.9 (+, C-6a), 135.5 (+, C-10a), 138.3 (–, C-11), 143.8 (+, C-3 + C-10). – MS (70 eV,  $25^{\circ}\text{C}$ ): *m/z* (%) = 239 (5) [ $\text{M}^+ + 1$ ], 238 (15) [ $\text{M}^+$ ], 221 (35) [ $\text{M}^+ - \text{OH}$ ], 220 (48) [ $\text{M}^+ - \text{H}_2\text{O}$ ], 219 (42), 211 (28) [ $\text{M}^+ - \text{CHCH}_2$ ], 205 (14), 203 (20), 197 (28), 196 (16), 194 (21), 193 (29) [ $\text{M}^+ - \text{H}_2\text{O} - \text{CHCH}_2$ ], 191 (22), 183 (39), 181 (64), 178 (16), 168 (37), 166 (19), 165 (100) [ $\text{M}^+ - \text{H}_2\text{O} - \text{CHCH}_2 - \text{CH}_2\text{CH}_2$ ], 164 (19), 163 (21), 155 (34), 153 (31), 152 (45) [ $\text{M}^+ - 2 \text{ OH} - 2 \text{ CHCH}_2$ ], 151 (19), 144 (16), 141 (15), 139 (20), 127 (41) [ $\text{C}_{10}\text{H}_7^+$ ], 115 (15), 102 (21), 99 (56), 88 (26), 77 (14) [ $\text{C}_6\text{H}_5^+$ ]. – HRMS ( $\text{C}_{16}\text{H}_{14}\text{O}_2$ ): calcd. 238.099380; found 238.098282.

**9,10-Dihydro-10,10-divinylphenanthren-9-one (65):** GP1, vinyllithium in DEE (1.00 M, 7.5 mL, 7.5 mmol), THF (20 mL), 9,10-phenanthrenequinone (500 mg, 2.4 mmol) in THF (15 mL), 1.5 h at  $-78^{\circ}\text{C}$ . Addition of another 5.0 mL (5.0 mmol) of 1.00 M vinyllithium in DEE. Hydrolysis after 30 min, extraction with TBME. Column chromatography (*I* 20 cm,  $\phi$  5.0 cm, PE/TBME 5:1 $\rightarrow$ 3:1) gave 400 mg (1.6 mmol, 68%) of 65, yellowish oil. – IR ( $\text{CHCl}_3$ ):  $\tilde{\nu}$  = 3072  $\text{cm}^{-1}$  (w, arom. CH), 3000 (w, arom. CH), 1684 (s, CO), 1624 (w, vinyl C=C), 1600 (m, arom. C=C), 1480 (w), 1448 (m), 1408 (w), 1296 (w), 1272 (m), 1228 (m), 1188 (w), 1160 (w), 1132 (w), 1112 (w), 1068 (w), 1040 (w), 992 (m), 928 (m), 880 (m), 616 (w), 528 (w). –  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 5.09 (dd,  $^2J$  = 0.9 Hz,  $^3J_{12,\text{trans-11}}$  = 17.3 Hz, 2 H, 12-H), 5.44 (dd,  $^3J_{12,\text{cis-11}}$  = 10.5 Hz, 2 H, 16-H), 6.10 (dd, 2 H, 11-H), 7.35–7.45 (m, 4 H, 1-H, 2-H, 3-H, 4-H), 7.63–7.69 (m, 1 H, 7-H), 7.97–8.05 (m, 3 H, 5-H, 6-H, 8-H). –  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta$  = 63.0 ( $\text{C}_q$ , C-10), 118.6 ( $\text{CH}_2$ , C-12), 122.9 ( $\text{CH}$ , C-1 or C-3), 124.0 ( $\text{CH}$ , C-1 or C-3), 127.9 ( $\text{CH}$ ), 128.0 ( $\text{CH}$ ), 128.3 ( $\text{CH}$ ), 128.8 ( $\text{CH}$ ), 129.2 ( $\text{C}_q$ , C-8a or C-10a), 130.2 ( $\text{CH}$ , C-8), 130.7 ( $\text{C}_q$ , C-8a or C-10a), 134.4 ( $\text{CH}$ , C-6), 137.0 ( $\text{C}_q$ , C-4a or C-4b), 137.3 ( $\text{C}_q$ , C-4a or C-4b), 138.5 ( $\text{CH}$ , C-11), 198.8 ( $\text{C}_q$ , C-9). – MS (70 eV,  $80^{\circ}\text{C}$ ):

*m/z* (%) = 247 (5) [ $\text{M}^+ + 1$ ], 246 (17) [ $\text{M}^+$ ], 231 (9), 219 (17), 218 (17), 218 (17), 215 (18), 205 (17), 204 (100), 203 (50), 202 (29), 191 (18), 189 (31), 176 (7), 165 (20), 163 (9), 152 (8), 139 (6), 109 (5), 101 (8), 95 (7). – HRMS ( $\text{C}_{18}\text{H}_{14}\text{O}$ ): calcd. 246.104465; found 246.103638. –  $\text{C}_{18}\text{H}_{14}\text{O}$  (246.31): calcd. C 87.78, H 5.73; found C 87.58, H 5.75.

***rac-cis*-1,2,3,3a,8,8a-Hexahydro-3a-hydroxycyclopenta[*a*]inden-8-one (*rac*-67) and *rac*-1,2,3,4-Tetrahydro-4-hydroxy-4-vinylnaphthalen-1-one (*rac*-68)**

**a)** GP2a, vinyllithium in DEE (1.69 M, 18.0 mL, 30.4 mmol, 8 equiv.), benzocyclobutenedione<sup>[62]</sup> (500 mg, 3.8 mmol) in DEE (40 mL), 7 h at  $-78^{\circ}\text{C}$ , warming to  $25^{\circ}\text{C}$  over 13 h. Column chromatography (*I* 32 cm,  $\varnothing$  3.0 cm, cyclohexane/DEE 10:1). I: 83 mg (0.4 mmol, 12%) of *rac*-68, yellow oil. II: 110 mg (0.6 mmol, 15%) of *rac*-67, yellow-brown oil.<sup>[55]</sup>

**b)** GP1, vinyllithium in DEE (1.11 M, 20.0 mL, 22.2 mmol), diluted by addition of DEE (30 mL), benzocyclobutenedione<sup>[62]</sup> (1.00 g, 7.6 mmol) in DEE (10 mL), 2 h at  $-78^{\circ}\text{C}$ . Sat. aq.  $\text{NH}_4\text{Cl}$  (30 mL). Column chromatography (*I* 17 cm,  $\phi$  4.0 cm, PE/DEE 1:1) gave 259 mg (1.4 mmol, 18%) of *rac*-67, yellow-brown oil.<sup>[55]</sup>

***rac*-67:** IR<sup>[55]</sup> (cap. film):  $\tilde{\nu}$  = 3408  $\text{cm}^{-1}$  (m, br, OH), 3073 (w, arom. CH), 2957 (m, CH), 2870 (m, CH), 1703 (s, br, CO), 1605 (m, arom. C=C), 1464 (m, CH), 1451 (w, arom. C=C), 1379 (w), 1289 (m, OH), 1250 (w), 1220 (m), 1168 (w), 1108 (w), 1045 (m), 996 (w), 951 (w), 934 (w), 875 (w), 851 (w), 804 (w), 769 (m), 747 (w), 703 (w), 689 (w). –  $^1\text{H}$  NMR (200.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.62–2.12 (m, 6 H, 1-H, 2-H, 3-H), 2.75 (dd,  $^3J_{8a,\text{cis-1}}$  = 3.0 Hz,  $^3J_{8a,\text{trans-1}}$  = 10.0 Hz, 1 H, 8a-H), 3.62 (br, s, 1 H, OH), 7.32–7.66 (m, 4 H, arom-H). –  $^{13}\text{C}$  NMR (50.3 MHz,  $\text{CDCl}_3$ , APT):  $\delta$  = 25.6 (+, C-2), 29.7 (+, C-1), 41.0 (+, C-3), 60.7 (–, C-8a), 86.2 (+, C-3a), 122.7 (–, C-4 or C-6), 124.4 (–, C-4 or C-6), 129.1 (–, C-7), 135.9 (–, C-5), 136.3 (+, C-7a), 157.6 (+, C-3b), 207.6 (+, C-8). – MS (70 eV,  $70^{\circ}\text{C}$ ): *m/z* (%) = 189 (4) [ $\text{M}^+ + 1$ ], 188 (24) [ $\text{M}^+$ ], 187 (2) [ $\text{M}^+ - \text{H}$ ], 171 (4), 170 (10) [ $\text{M}^+ - \text{H}_2\text{O}$ ], 169 (8), 161 (11), 160 (77) [ $\text{M}^+ - \text{CO}$ ], 159 (100) [ $\text{M}^+ - \text{H} - \text{CO}$ ], 153 (4), 152 (4), 147 (14), 146 (40) [ $\text{M}^+ - \text{C}_3\text{H}_6$ ], 145 (19) [ $\text{M}^+ - \text{C}_3\text{H}_7$ ], 142 (38), 141 (27), 132 (23), 131 (58), 115 (33), 105 (58), 103 (33), 91 (17), 89 (13), 86 (31), 84 (46), 82 (15), 78 (14), 76 (29), 65 (16).

***rac*-68:** IR ( $\text{CHCl}_3$ ):  $\tilde{\nu}$  = 3428  $\text{cm}^{-1}$  (m, OH), 3364 (w, br, OH), 3072 (w, arom. CH), 3000 (m, arom. CH), 2952 (m, CH), 2928 (m, CH), 2868 (w, CH), 1684 (s, CO), 1636 (w, C=C), 1600 (m, arom. C=C), 1452 (w, arom. C=C), 1408 (w), 1336 (w), 1288 (s, OH), 1236 (w), 1160 (w, OH), 1124 (m), 1048 (w), 1016 (w), 996 (w), 932 (m). –  $^1\text{H}$  NMR (200.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.22–2.33 (m, 2 H, 3-H), 2.62 (ddd,  $^2J$  =  $-17.5$  Hz,  $^3J_{2,\text{cis-3}}$  = 6.0 Hz,  $^3J_{2,\text{trans-3}}$  = 9.0 Hz, 1 H, 2-H), 2.84 (ddd,  $^3J_{2,\text{cis-3}}$  = 6.0 Hz,  $^3J_{2,\text{trans-3}}$  = 9.0 Hz, 1 H, 2-H), 5.09 (dd,  $^2J$  = 1.0 Hz,  $^3J_{10,\text{trans-9}}$  = 17.5 Hz, 1 H, 10-H), 5.29 (dd,  $^3J_{10,\text{cis-9}}$  = 11.0 Hz, 1 H, 10-H), 6.12 (dd, 1 H, 9-H), 7.37–7.65 (m, 3 H, 5-H + 6-H + 7-H), 8.01 (ddd,  $^3J_{8,7}$  = 8 Hz,  $^4J_{8,6}$  = 1.0 Hz,  $^5J_{8,5}$  = 0.5 Hz, 1 H, 8-H). –  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ , APT):  $\delta$  = 35.1 (+, C-2 or C-3), 36.6 (+, C-2 or C-3), 73.2 (+, C-4), 116.1 (+, C-10), 126.7 (–, C-5 or C-7 or C-8), 127.1 (–, C-5 or C-7 or C-8), 128.4 (–, C-6 or C-7 or C-8), 131.5 (+, C-8a), 134.1 (–, C-6), 146.0 (+, C-4a), 196.9 (+, C-1). – MS (70 eV,  $60^{\circ}\text{C}$ ): *m/z* (%) = 189 (6) [ $\text{M}^+ + 1$ ], 188 (25) [ $\text{M}^+$ ], 187 (7) [ $\text{M}^+ - \text{H}$ ], 173 (12), 171 (4), 170 (13) [ $\text{M}^+ - \text{H}_2\text{O}$ ], 162 (5), 161 (39) [ $\text{M}^+ - \text{C}_2\text{H}_3$ ], 160 (100) [ $\text{M}^+ - \text{CO}$ ], 147 (7), 145 (14), 141 (17), 133 (14), 132 (45), 131 (61) [ $\text{M}^+ - \text{CO} - \text{C}_2\text{H}_5$ ], 129 (16), 128 (54), 117 (15), 114 (38) [ $\text{M}^+ - \text{CO} - \text{C}_2\text{H}_5 - \text{OH}$ ], 105 (36) [ $\text{Ph}(\text{CO})^+$ ], 91 (12), 84 (8), 77 (46) [ $\text{C}_6\text{H}_5^+$ ], 76 (10), 66 (6).

**endo-cis-1,2-Divinylbicyclo[2.2.1]hept-5-ene-2,3-diol (69):** GP1, vinylolithium in DEE (0.89 M, 8.5 mL, 7.6 mmol), THF (20 mL), bicyclo[2.2.1]hept-5-ene-2,3-dione<sup>[89]</sup> (300 mg, 2.5 mmol) in THF (10 mL), 30 min. Column chromatography (*l* 15 cm,  $\phi$  3.5 cm, PE/DEE 3:1) gave 290 mg (1.6 mmol, 66%) of **69**, colorless oil. – IR (film):  $\tilde{\nu}$  = 3372 cm<sup>−1</sup> (s, br, OH), 3068 (w, olefin. CH), 3020 (w, olefin. CH), 2972 (s, CH), 2880 (w, CH), 1636 (w, C=C), 1456 (w), 1416 (m), 1356 (m), 1328 (s), 1260 (m), 1196 (m), 1160 (m), 1088 (s, C–O), 996 (s), 916 (s), 768 (s), 744 (s), 700 (m). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.61 (td, <sup>2</sup>*J* = −9.9 Hz, <sup>3</sup>*J*<sub>7,1(4)</sub> = 1.9 Hz, 1 H, 7-H), 1.69 (d, 1 H, 7-H), 2.53 (s, 2 H, OH), 2.94 [m, 2 H, 1(4)-H], 5.13 (dd, <sup>2</sup>*J* = 1.3 Hz, <sup>3</sup>*J*<sub>9,cis-8</sub> = 10.8 Hz, 2 H, 9-H), 5.33 (dd, <sup>3</sup>*J*<sub>9,trans-8</sub> = 17.1 Hz, 2 H, 9-H), 5.97 (dd, 2 H, 8-H), 6.36 [t, <sup>3</sup>*J*<sub>5(6),1(4)</sub> = 1.9 Hz, 2 H, 5(6)-H]. NOE: Irr. at 7-H, obs. at 8-H (5.3%); irr. at 8-H, obs. at 7-H (2.6%). – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 42.6 (CH<sub>2</sub>, C-7), 52.5 [CH, C-1(4)], 81.6 [C<sub>q</sub>, C-2(3)], 112.6 (CH<sub>2</sub>, C-9), 136.4 [CH, C-5(6)], 141.4 (CH, C-8). – MS (70 eV, 25 °C): *m/z* (%) = 178 (3) [M<sup>+</sup>], 123 (6), 122 (9), 121 (7), 112 (100) [M<sup>+</sup> − C<sub>5</sub>H<sub>6</sub>], 111 (21), 105 (26), 95 (19), 94 (53) [M<sup>+</sup> − C<sub>5</sub>H<sub>6</sub> − H<sub>4</sub>O], 93 (12), 91 (12), 84 (13), 83 (12), 79 (20), 77 (23), 66 (82) [C<sub>3</sub>H<sub>6</sub><sup>+</sup>], 65 (20). – C<sub>11</sub>H<sub>14</sub>O<sub>2</sub> (178.23): calcd. C 74.13, H 7.92; found C 73.59, H 7.53.

**rac-trans-Dibenzo-1,2-divinylbicyclo[2.2.2]octane-2,3-diol (rac-70) and cis-Dibenzo-1,2-divinylbicyclo[2.2.2]octane-2,3-diol (71):** GP1, vinylolithium in DEE (0.99 M, 4.0 mL, 4.0 mmol), THF (20 mL), 5,7-dibenzobicyclo[2.2.2]octane-2,3-dione<sup>[90]</sup> (300 mg, 1.3 mmol) in THF (15 mL). After 45 min, further vinylolithium in DEE (0.99 M, 1.3 mL, 1.3 mmol) was added, 2 h at −78 °C. Column chromatography (*l* 14 cm,  $\phi$  3.5 cm, PE/TBME 3:1). I: 122 mg (0.4 mmol, 33%) of **rac-70**, colorless solid (m.p. 168 °C). II: 139 mg (0.5 mmol, 37%) of **71**, colorless solid. Assignment of the diastereomers was made by comparison of the <sup>1</sup>H NMR spectra with those of other 1,2-divinyl-1,2-diols, including **rac-62**.

**rac-70:** IR (CHCl<sub>3</sub>):  $\tilde{\nu}$  = 3548 cm<sup>−1</sup> (m, br, OH), 3072 (m, arom. CH), 3000 (m, arom. CH), 2952 (m, CH), 1636 (w, vinyl C=C), 1464 (m), 1412 (m), 1336 (m), 1236 (m), 1180 (m), 1140 (s, C–O), 1116 (m), 1092 (w), 1052 (m), 996 (s), 928 (s), 568 (w). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 2.49 (s, 2 H, OH), 4.20 [s, 2 H, 1(4)-H], 5.01 (m, 2 H, 18(20)-H), 5.33–5.43 [m, 4 H, 17(19)-H + 18(20)-H], 7.18 [m, 2 H, 10(15)-H], 7.21 [m, 2 H, 11(14)-H], 7.30 [m, 2 H, 9(16)-H], 7.37 [m, 2 H, 12(13)-H]. – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 57.6 [CH, C-1(4)], 78.3 [C<sub>q</sub>, C-2(3)], 112.7 [CH<sub>2</sub>, C-18(20)], 125.6 (CH), 126.3 (CH), 126.68 (CH), 126.70 (CH), 139.6 (C<sub>q</sub>), 139.9 (C<sub>q</sub>), 141.1 [CH, C-17(19)]. – MS (70 eV, 25 °C): *m/z* (%) = 290 (2) [M<sup>+</sup>], 235 (3), 217 (3), 215 (3), 179 (24), 178 (100) [anthracene<sup>+</sup>], 153 (3), 152 (9), 138 (4), 137 (30), 122 (7), 121 (3), 112 (3), 108 (3), 107 (22), 105 (6), 92 (3), 91 (5), 89 (4), 85 (3), 84 (9), 83 (3), 79 (17), 78 (7), 77 (15), 69 (5), 66 (4). – HRMS (C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>): calcd. 290.130680; found 290.131012. – C<sub>20</sub>H<sub>18</sub>O<sub>2</sub> (290.36): calcd. C 82.73, H 6.25; found C 82.64, H 6.10.

**71:** IR (CHCl<sub>3</sub>):  $\tilde{\nu}$  = 3572 cm<sup>−1</sup> (m, OH), 3072 (w, arom. CH), 3008 (s, arom. CH), 2952 (w, CH), 2928 (w, CH), 1468 (m), 1412 (m), 1312 (w), 1296 (w), 1232 (w), 1172 (m, C–O), 1132 (m, C–O), 996 (s), 972 (m), 932 (m), 628 (m), 604 (w). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.52 (s, 2 H, OH), 4.18 [s, 2 H, 1(4)-H], 5.18 (dd, <sup>2</sup>*J* = 1.7 Hz, <sup>3</sup>*J*<sub>18,cis-17</sub> = 10.8 Hz, 2 H, 18-H), 5.42 (dd, <sup>3</sup>*J*<sub>18,trans-17</sub> = 17.3 Hz, 2 H, 18-H), 5.65 (dd, 2 H, 17-H), 7.17–7.23 [m, 4 H, 10(11)-H + 14(15)-H], 7.32–7.38 [m, 4 H, 9(12)-H + 13(16)-H]. – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 57.5 [CH, C-1(4)], 80.8 [C<sub>q</sub>, C-2(3)], 114.4 (CH<sub>2</sub>, C-18), 125.8 (CH), 126.0 (CH), 126.67 (CH), 126.71 (CH), 139.3 (C<sub>q</sub>), 139.8 (CH), 140.3 (C<sub>q</sub>). – MS (70 eV, 25 °C): *m/z* (%) = 290 (1) [M<sup>+</sup>], 235 (4),

217 (3), 215 (3), 202 (3), 179 (24), 178 (100) [anthracene<sup>+</sup>], 175 (6), 152 (4), 151 (3), 137 (3), 112 (3), 99 (3), 91 (3), 84 (8), 83 (3), 73 (4), 71 (3), 69 (4). – HRMS (C<sub>20</sub>H<sub>18</sub>O<sub>2</sub>): calcd. 290.130680; found 290.130554. – C<sub>20</sub>H<sub>18</sub>O<sub>2</sub> (290.36): calcd. C 82.73, H 6.25; found C 82.50, H 6.19.

**rac-2-Hydroxy-3,3,5,5-tetramethyl-2-vinylcyclopentanone (rac-72):** GP1, vinylolithium in DEE (0.99 M, 6.0 mL, 5.9 mmol), THF (20 mL), 3,3,5,5-tetramethylcyclopentane-1,2-dione<sup>[91]</sup> (300 mg, 1.9 mmol) in THF (15 mL), 1.5 h at −78 °C. Extraction with MTBE. Column chromatography (*l* 14 cm,  $\phi$  3.5 cm, PE/TBME 3:1) gave 276 mg (1.5 mmol, 78%) of **rac-72**, colorless solid (m.p. 68 °C). – IR (film):  $\tilde{\nu}$  = 3528 cm<sup>−1</sup> (w, br, OH), 3096 (w, vinyl CH), 2972 (s, CH), 2940 (m, CH), 2904 (w, CH), 2872 (m, CH), 1740 (s, CO), 1628 (w, vinyl C=C), 1460 (m), 1388 (w), 1368 (w), 1336 (w), 1308 (w), 1280 (w), 1236 (w), 1184 (w), 1132 (w), 1100 (m), 1044 (m), 1012 (m), 992 (m), 968 (w), 932 (m), 820 (w). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.94 (s, 3 H, 10-H or 11-H), 1.03 (s, 3 H, 10-H or 11-H), 1.17 (s, 3 H, 8-H or 9-H), 1.22 (s, 3 H, 8-H or 9-H), 1.81 (d, <sup>2</sup>*J* = 13.6 or 16.2 Hz, 1 H, 4-H), 1.84 (d, 1 H, 4-H), 2.74 (s, 1 H, OH), 5.25 (dd, <sup>2</sup>*J* = 1.5 Hz, <sup>3</sup>*J*<sub>7,cis-6</sub> = 10.8, 1 H, 7-H), 5.50 (dd, <sup>3</sup>*J*<sub>7,trans-6</sub> = 16.9 Hz, 1 H, 7-H), 5.98 (dd, 1 H, 6-H). – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 24.0 (CH<sub>3</sub>, C-10 + C-11), 27.8 (CH<sub>3</sub>, C-8 or C-9), 28.1 (CH<sub>2</sub>, C-8 or C-9), 40.6 (C<sub>q</sub>, C-3 or C-5), 41.2 (C<sub>q</sub>, C-3 or C-5), 48.7 (CH<sub>2</sub>, C-4), 86.3 (C<sub>q</sub>, C-2), 116.0 (CH<sub>2</sub>, C-7), 134.4 (CH, C-6), 222.2 (C<sub>q</sub>, C-1). – MS (70 eV, 25 °C): *m/z* (%) = 183 (2) [M<sup>+</sup> + 1], 182 (16) [M<sup>+</sup>], 139 (2), 127 (3), 126 (3), 125 (2), 111 (3), 99 (8), 98 (100), 97 (10), 84 (3), 83 (31), 79 (4), 70 (5), 69 (5). – HRMS (C<sub>11</sub>H<sub>22</sub>O<sub>2</sub>): calcd. 182.130680; found 182.130692. – C<sub>11</sub>H<sub>22</sub>O<sub>2</sub> (182.26): calcd. C 72.49, H 9.95; found C 71.69, H 9.70.

**rac-trans-3,3-Dimethyl-1,2-divinyl-1,2-indanediol (rac-73):** GP1, vinylolithium in DEE (0.99 M, 5.3 mL, 5.2 mmol), THF (20 mL), 3,3-dimethyl-1,2-indanediol<sup>[92]</sup> (300 mg, 1.7 mmol) in THF (15 mL), 30 min at −78 °C, extraction with TBME. Column chromatography (*l* 14 cm,  $\phi$  3.5 cm, PE/TBME 3:1) gave 292 mg (1.3 mmol, 74%) of **rac-73**, colorless crystals (from petroleum ether, m.p. 70 °C). – IR (CHCl<sub>3</sub>):  $\tilde{\nu}$  = 3600 cm<sup>−1</sup> (m, OH), 3088 (w, vinyl CH), 3072 (w, arom. CH), 2992 (w, CH), 2964 (m, CH), 2928 (w, CH), 2868 (w), 1632 (w, vinyl C=C), 1604 (w, C=C), 1476 (m), 1456 (w), 1408 (w), 1384 (w), 1360 (w), 1320 (m), 1256 (m), 1228 (w), 1176 (w), 1128 (m, C–O), 1044 (w), 984 (s), 932 (m), 904 (m), 852 (w), 556 (w), 540 (w). – <sup>1</sup>H NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.26 (s, 3 H, CH<sub>3</sub>), 1.36 (s, 3 H, CH<sub>3</sub>), 1.58 (s, 1 H, OH), 1.86 (s, 1 H, OH), 5.39 (dd, <sup>2</sup>*J* = 1.8 Hz, *J*<sub>9,cis-8</sub> = 10.9 Hz, 1 H, 9-H), 5.43–5.50 (m, 3 H, 9-H + 11-H), 6.20 (dd, *J*<sub>8,trans-9</sub> = 17.4 Hz, 1 H, 8-H), 6.40 (dd, *J*<sub>10,cis-11</sub> = 10.9 Hz, *J*<sub>10,trans-11</sub> = 17.4 Hz, 1 H, 10-H), 7.22–7.28 (m, 2 H, 5-H + 6-H), 7.33–7.38 (m, 4-H + 7-H). – <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta$  = 21.5 (CH<sub>3</sub>), 29.4 (CH<sub>3</sub>), 50.3 (C<sub>q</sub>, C-3), 86.6 (C<sub>q</sub>, C-1 or C-2), 87.5 (C<sub>q</sub>, C-1 or C-2), 116.1 (CH<sub>2</sub>, C-9 or C-11), 118.3 (CH<sub>2</sub>, C-9 or C-11), 123.4 (CH, C-4 or C-6), 124.4 (CH, C-4 or C-6), 127.2 (CH, C-5 or C-7), 129.5 (CH, C-5 or C-7), 136.6 (CH, C-8 or C-10), 138.4 (CH, C-8 or C-10), 142.9 (C<sub>q</sub>, C-7a), 151.9 (C<sub>q</sub>, C-3a). – MS (70 eV, 50 °C): *m/z* (%) = 231 (3) [M<sup>+</sup> + 1], 230 (9) [M<sup>+</sup>], 215 (14) [M<sup>+</sup> − CH<sub>3</sub>], 212 (9) [M<sup>+</sup> − H<sub>2</sub>O], 198 (10), 197 (53) [M<sup>+</sup> − CH<sub>3</sub> − H<sub>2</sub>O], 188 (17), 187 (100) [M<sup>+</sup> − CH<sub>3</sub> − C<sub>2</sub>H<sub>4</sub>], 179 (14), 175 (17), 169 (34), 160 (44), 159 (57) [M<sup>+</sup> − CH<sub>3</sub> − C<sub>2</sub>H<sub>4</sub> − C<sub>2</sub>H<sub>4</sub>], 157 (49), 155 (23), 147 (29), 145 (68), 143 (52), 142 (61), 141 (46), 133 (30), 131 (35), 129 (49), 128 (42), 115 (63), 103 (19), 99 (19), 91 (36), 77 (33). – HRMS (C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>): calcd. 230.130680; found 230.130569. – C<sub>15</sub>H<sub>18</sub>O<sub>2</sub> (230.31): calcd. C 78.23, H 7.88, found C 77.58, H 7.69.



**Crystal Structure Analysis of *rac*-73:**  $C_{15}H_{18}O_2$ , crystal size  $0.67 \times 0.06 \times 0.20$  mm,  $a = 6.286(1)$ ,  $b = 8.928(2)$ ,  $c = 12.331(2)$  Å,  $\alpha = 107.26(2)$ ,  $\beta = 101.21(2)$ ,  $\gamma = 94.34(2)^\circ$ ,  $V = 641.7(2)$  Å<sup>3</sup>,  $d_{\text{calcd.}} = 1.192$  g cm<sup>-3</sup>,  $\mu = 0.8$  cm<sup>-1</sup>,  $F(000) = 248$  e,  $Z = 2$ , crystal system triclinic, space group  $P\bar{1}$  (No. 2), Stoe IPDS (Imaging Plate) diffractometer, Mo- $K_\alpha$ ,  $\lambda = 0.71073$  Å,  $T = 300$  K,  $2\theta_{\text{min}} = 4.8^\circ$ ,  $2\theta_{\text{max}} = 48.0^\circ$ , 146 exposures,  $\Delta\Phi = 1.3^\circ$ , 3827 measured reflections ( $\pm 7$ ,  $\pm 10$ ,  $-13:14$ ), 1871 unique and 1070 observed reflections [ $I > 2\sigma(I)$ ], completeness of data: 94.4%,  $R(I) = 0.050$ , no absorption correction, extinction correction:  $F_c'' = k \cdot F_c [1 + 0.001 \cdot x \cdot F_c^2 \cdot \lambda^{3/(\sin(2\theta))}]^{-0.25}$ ,  $x = 0.009$ , refinement: SHELXL-93,  $N_{\text{ref}} = 1871$ ,  $N_{\text{par}} = 155$ ,  $R = 0.0484$ ,  $wR2 = 0.098$  [ $w = 1/\sigma^2(F_o^2) + (0.02P)^2$ ;  $P = 1/3\{\max(F_o^2) + 2F_c^2\}$ ],  $S = 1.19$ , min./max. residual electron density:  $-0.32/0.33$  e Å<sup>-3</sup>. The crystallographic data (without structural factors) of the structure have been deposited at the Cambridge Crystallographic Data Centre (CCDC-144457). Copies of the data can be obtained from the following address in Great Britain: CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

### Reactions of 1,2-Indanedione (74)

**a)** GP1, vinylolithium in DEE (0.62 M, 13.5 mL, 8.4 mmol), THF (20 mL), 1,2-indanedione<sup>[93]</sup> (400 mg, 1.3 mmol) in THF (15 mL), 1 h at  $-78^\circ\text{C}$ . Column chromatography ( $l$  10 cm,  $\phi$  5.0 cm, PE/DEE 3:1). I: 53 mg (0.3 mmol, 11%) of *rac*-1-hydroxy-1-vinyl-2-indanone (*rac*-75), yellow oil. II: 251 mg (1.2 mmol, 45%) of *rac*-*trans*-1,2-divinyl-1,2-indanedione (*rac*-76)<sup>[94]</sup> colorless solid (m.p.  $77^\circ\text{C}$ ).

**b)** GP2b, vinylolithium in DEE (0.89 M, 9.5 mL, 2.7 mmol), 1,2-indanedione (400 mg, 2.7 mmol) in THF (15 mL). After 2 h, further vinylolithium in DEE (0.89 M, 3.0 mL, 2.7 mmol) was added. After 45 min at  $0^\circ\text{C}$ , the mixture was stirred at  $25^\circ\text{C}$  for 1 h, then heated at reflux for 2 h. Column chromatography ( $l$  18 cm,  $\phi$  3.5 cm, PE/DEE 3:1 $\rightarrow$ 2:3). I: 95 mg (0.5 mmol, 20%) of *rac*-75. II: 154 mg (0.8 mmol, 28%) of *rac*-*cis*-1,2,3,3a,4,9,9a-heptahydro-3a-hydroxycyclopenta[*b*]naphthalen-9-one (*rac*-77), yellow oil.

***rac*-75:** IR (film):  $\tilde{\nu} = 3416$  cm<sup>-1</sup> (s, br, OH), 3068 (w, arom. CH), 3028 (w, arom. CH), 2928 (w, CH), 1756 (s, CO), 1636 (w, C=C), 1596 (w, arom. C=C), 1476 (w), 1396 (m), 1296 (w), 1240 (w), 1220 (w), 1144 (w), 1100 (w), 1056 (m), 988 (m), 928 (m), 764 (s), 728 (m), 700 (m).  $^1\text{H}$  NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 3.17$  (s, br, 1 H, OH), 3.52 (d,  $^2J = -21.7$  Hz, 1 H, 3-H), 3.70 (d, 1 H, 3-H), 5.10 (d,  $^3J_{9,\text{trans-8}} = 17.1$  Hz, 1 H, 9-H), 5.26 (d,  $^3J_{9,\text{cis-8}} = 10.3$  Hz, 1 H, 9-H), 5.96 (dd, 1 H, 8-H), 7.32–7.46 (m, 4 H, 4-H, 5-H, 6-H, 7-H).  $^{13}\text{C}$  NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta = 40.1$  (CH<sub>2</sub>, C-3), 81.8 (C<sub>q</sub>, C-1), 117.1 (CH<sub>2</sub>, C-9), 124.9 (CH), 125.4 (CH), 128.3 (CH), 129.4 (CH), 135.5 (C<sub>q</sub>, C-3a), 137.5 (CH, C-8), 141.3 (C<sub>q</sub>, C-7a), 214.2 (C<sub>q</sub>, C-2).  $^{\text{MS}}$  (70 eV,  $25^\circ\text{C}$ ):  $m/z$  (%) = 175 (4) [ $M^+ + 1$ ], 174 (20) [ $M^+$ ], 159 (30), 147 (17), 146 (100) [ $M^+ - \text{CO}$ ], 145 (55), 131 (67) [ $M^+ - \text{CO} - \text{CH}_3$ ], 127 (21), 119 (22), 117 (21), 115 (20), 107 (19), 104 (25), 91 (43), 90 (16), 79 (15), 77 (29), 73 (20), 65 (15).  $^{\text{HRMS}}$  ( $C_{11}H_{10}O_2$ ): calcd. 174.068080; found 174.068069.

***rac*-76:** IR<sup>[63]</sup> (CHCl<sub>3</sub>):  $\tilde{\nu} = 3592$  cm<sup>-1</sup> (s, OH), 3432 (m, br, OH), 3076 (w, vinyl CH), 3072 (w, arom. CH), 3000 (w, arom. CH), 2952 (w, CH), 2920 (w, CH), 1636 (w, vinyl C=C), 1608 (w, C=C), 1476 (m), 1460 (m), 1412 (m), 1324 (m), 1296 (m), 1236 (m), 1136 (s, C=O), 1068 (m), 1000 (s), 932 (s), 904 (w), 880 (m).  $^1\text{H}$  NMR<sup>[63]</sup> (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 1.93$  (s, 2 H, OH), 2.91 (d,  $^2J = -5.8$  Hz, 1 H, 3-H), 3.37 (d, 1 H, 3-H), 5.33 (dd,  $^2J = 1.3$  Hz,  $J_{9,8} = 10.9$  Hz, 1 H, 9-H), 5.40–5.47 (m, 2 H, 9-H + 11-H), 5.47 (dd,  $^2J = 1.5$  Hz,

$J_{11,10} = 17.5$  Hz, 1 H, 11-H), 6.18 (dd, 2 H, 8-H + 10-H), 7.23–7.31 (m, 4 H, 4-H, 5-H, 6-H, 7-H).  $^{13}\text{C}$  NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta = 43.5$  (CH<sub>2</sub>, C-3), 85.9 (C<sub>q</sub>, C-1 or C-2), 86.5 (C<sub>q</sub>, C-1 or C-2), 116.3 (CH<sub>2</sub>, C-9 or C-11), 117.7 (CH<sub>2</sub>, C-9 or C-11), 124.4 (CH), 125.5 (CH), 127.2 (CH), 129.0 (CH, C-4), 136.9 (CH, C-8 or C-10), 138.5 (CH, C-8 or C-10), 141.2 (C<sub>q</sub>, C-3a), 144.5 (C<sub>q</sub>, C-7a).  $^{\text{MS}}$  (70 eV,  $25^\circ\text{C}$ ):  $m/z$  (%) = 202 (5) [ $M^+$ ], 185 (9), 184 (22) [ $M^+ - \text{H}_2\text{O}$ ], 183 (11), 174 (12), 173 (73) [ $M^+ - \text{COH}$ ], 160 (15), 157 (12), 155 (11), 147 (15), 146 (54), 145 (100) [ $M^+ - \text{COH} - \text{C}_2\text{H}_4$ ], 141 (12), 133 (24), 131 (21), 129 (45) [ $M^+ - \text{COH} - \text{C}_2\text{H}_3 - \text{OH}$ ], 128 (31), 127 (21), 119 (20), 117 (14), 115 (26), 91 (26), 77 (13).  $^{\text{HRMS}}$  ( $C_{13}H_{14}O_2$ ): calcd. 202.099380; found 202.098816.  $^{\text{C}_{13}H_{14}O_2}$  (202.25): calcd. C 77.20, H 6.98; found C 76.82, H 6.97.

***rac*-77:** IR (CHCl<sub>3</sub>):  $\tilde{\nu} = 3596$  cm<sup>-1</sup> (m, OH), 3004 (m, arom. CH), 2960 (m, CH), 2928 (m, CH), 2880 (w, CH), 1676 (s, CO), 1600 (m, arom. C=C), 1456 (m), 1408 (w), 1364 (w), 1284 (m), 1232 (m), 1156 (w), 1104 (m), 1052 (m), 1028 (w), 1008 (w), 988 (w), 932 (w).  $^1\text{H}$  NMR (400.1 MHz, CDCl<sub>3</sub>):  $\delta = 1.51$ –2.34 (m, 7 H, 1-H + 2-H + 3-H + OH), 2.80 (dd,  $^3J_{2,\text{trans-3}} = 8.8$  Hz,  $^3J_{2,\text{cis-3}} = 6.8$  Hz, 1 H, 9a-H), 3.15 (d,  $^2J = -16.4$  Hz, 1 H, 4-H), 3.24 (d, 1 H, 4-H), 7.26 (m, 1 H, 5-H), 7.33 (m,  $^4J_{7,5} = 0.6$  Hz, 1 H, 7-H), 7.51 (m,  $^4J_{6,8} = 1.5$  Hz, 1 H, 6-H), 7.98 (dd,  $^3J_{8,7} = 7.8$  Hz, 1 H, 8-H).  $^{13}\text{C}$  NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta = 21.7$  (CH<sub>2</sub>, C-2), 27.6 (CH<sub>2</sub>, C-1), 38.3 (CH<sub>2</sub>, C-3 or C-4), 38.3 (CH<sub>2</sub>, C-3 or C-4), 58.1 (CH, C-9a), 81.3 (C<sub>q</sub>, C-3a), 127.1 (CH, C-7 or C-8), 127.5 (CH, C-7 or C-8), 129.3 (CH, C-5), 130.9 (C<sub>q</sub>, C-7a), 134.0 (CH, C-6), 140.4 (C<sub>q</sub>, C-4a), 200.0 (C<sub>q</sub>, C-9).  $^{\text{MS}}$  (70 eV,  $25^\circ\text{C}$ ):  $m/z$  (%) = 203 (4) [ $M^+ + 1$ ], 202 (27) [ $M^+$ ], 187 (12), 185 (7), 184 (16) [ $M - \text{H}_2\text{O}$ ], 183 (7), 173 (7), 160 (7), 145 (7), 131 (7), 129 (7), 128 (9), 119 (53), 118 (100) [ $\text{Ph}(\text{CO})\text{CH}_2^+$ ], 115 (13), 91 (15), 90 (34) [ $\text{PhCH}_2^+$ ], 89 (14), 84 (14), 77 (8), 67 (9).  $^{\text{HRMS}}$  ( $C_{13}H_{14}O_2$ ): calcd. 202.099380; found 202.099182.

**Treatment of *rac*-76 with Trifluoroacetic Acid:** Compound *rac*-76 (64 mg, 0.3 mmol) in dichloromethane (5 mL) was treated with trifluoroacetic acid (0.14 mL, 157 mg, 1.4 mmol) and heated at reflux for 15 h. After solvent removal, a dark brown oil was obtained. Column chromatography ( $l$  10 cm,  $\phi$  1.0 cm, PE/TBME 1:1). I: 8 mg (0.04 mmol, 14%) of 1,2,3-trihydrocyclopenta[*b*]-4,9-naphthoquinone (79), yellow solid (m.p.  $162^\circ\text{C}$ ). II: 42 mg (0.20 mmol, 71%) of 1,2,3-trihydrocyclopenta[*b*]-4-naphthol (78), brown oil.<sup>[64]</sup>

**79:** IR (KBr):  $\tilde{\nu} = 3040$  cm<sup>-1</sup> (w, arom. CH), 2960 (w, CH), 2928 (w, CH), 1664 (s, C=O), 1620 (m, C=C), 1596 (m, arom. C=C), 1432 (w), 1388 (w), 1336 (s), 1316 (m), 1284 (m), 1260 (w), 1164 (w), 1080 (w), 1012 (w), 928 (w), 892 (w).  $^1\text{H}$  NMR (200.1 MHz, CDCl<sub>3</sub>):  $\delta = 2.10$  (quin,  $^3J_{2,1+3} = 7.7$  Hz, 2 H, 2-H), 2.95 [t, 4 H, 1(3)-H], 7.70 + 8.08 [AA'BB' line system,  $2 \times 2$  H, 5(8)-H + 6(7)-H].  $^{13}\text{C}$  NMR (100.6 MHz, CDCl<sub>3</sub>, DEPT):  $\delta = 21.5$  (CH<sub>2</sub>, C-2), 31.2 [CH<sub>2</sub>, C-1(3)], 126.2 [CH, C-5(8)], 133.2 [C<sub>q</sub>, C-4a(8a)], 133.4 [CH, C-6(7)], 151.3 [C<sub>q</sub>, C-3a(9a)], 189.9 [C<sub>q</sub>, C-4(9)].  $^{\text{MS}}$  (70 eV,  $25^\circ\text{C}$ ):  $m/z$  (%) = 200 (4) [ $M^+ + 2$ ], 199 (15) [ $M^+ + 1$ ], 198 (100) [ $M^+$ ], 190 (19), 181 (14), 169 (13), 159 (12), 142 (11), 141 (17), 139 (5), 133 (5), 116 (12), 105 (27) [ $\text{Ph}(\text{CO})^+$ ], 104 (18), 91 (6), 86 (6), 94 (10), 83 (5), 77 (11), 76 (16), 75 (6), 71 (6), 69 (6), 65 (5).

**Treatment of *rac*-*trans*-1,2-Dihydro-1,2-divinyl-1,2-naphthalenediol (*rac*-62) with Potassium Hydride:** Compound *rac*-62 (48 mg, 0.22 mmol) was added to a suspension of potassium hydride (18 mg, 0.45 mmol) in THF (5 mL). After 1 h at  $-78^\circ\text{C}$ , the mixture was allowed to warm to  $0^\circ\text{C}$  over 3 h, no reaction taking place. After further warming to  $25^\circ\text{C}$ , a reaction did take place.

After 1 h, the mixture was cooled to  $-20\text{ }^{\circ}\text{C}$  and hydrolyzed by addition of sat. aq.  $\text{NH}_4\text{Cl}$  (6 mL). The mixture was extracted with MTBE (10 mL portions) until the organic layer remained colorless. Column chromatography ( $l$  12 cm,  $\phi$  1.0 cm, PE/MTBE 2:1) gave an unseparated mixture of 27 mg (0.13 mmol, 56%) of *rac*-4,5-benzo-6-hydroxy-6-vinylcycloocta-2,4-dien-1-one (*rac*-**83**) and 13 mg of an unidentified compound.

***rac*-83** From the spectra of the mixture: IR ( $\text{CHCl}_3$ ):  $\tilde{\nu}$  = 3580  $\text{cm}^{-1}$  (m, OH), 3068 (w, arom. CH), 3000 (w, arom. CH), 2960 (m, CH), 2924 (w, CH), 2856 (w, CH), 1704 (m, CO), 1640 (w, vinyl C=C), 1484 (w), 1460 (w), 1444 (w), 1404 (w), 1342 (w), 1288 (m), 1152 (w), 1100 (s, C–O), 1068 (s), 1048 (s), 1016 (s), 976 (m), 928 (m), 864 (w).  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 2.09–2.18 (m, 1 H, 7-H), 2.31–2.44 (m, 3 H, 7-H + 8-H), 3.12 (s, br, 1 H, OH), 5.38 (dd,  $^2J$  = 1.3 Hz,  $^3J_{14,\text{cis-13}}$  = 10.7 Hz, 1 H, 14-H), 5.54 (dd,  $^3J_{14,\text{trans-13}}$  = 17.3 Hz, 1 H, 14-H), 6.03 (d,  $^8J_{2,3}$  = 11.8 Hz, 1 H, 2-H), 6.40 (dd, 1 H, 13-H), 6.41 (d, 1 H, 3-H), 7.13–7.25 (m, 4 H, 9-H, 10-H, 11-H, 12-H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta$  = 36.8 ( $\text{CH}_2$ , C-7), 43.6 ( $\text{CH}_2$ , C-8), 84.0 ( $\text{C}_q$ , C-6), 113.9 ( $\text{CH}_2$ , C-14), 121.0 (CH, C-9), 127.3 (CH, C-10 or C-11 or C-12), 127.3 (CH, C-2), 128.5 (CH, C-10 or C-11 or C-12), 131.3 (CH, C-10 or C-11 or C-12), 133.3 ( $\text{C}_q$ , C-4), 133.7 (CH, C-3), 140.0 ( $\text{C}_q$ , C-13), 142.7 ( $\text{C}_q$ , C-5), 209.4 ( $\text{C}_q$ , C-1). – MS (70 eV,  $25\text{ }^{\circ}\text{C}$ ):  $m/z$  (%) = 215 (4) [ $\text{M}^+ + 1$ ], 214 (21) [ $\text{M}^+$ ], 186 (4), 169 (18), 168 (15), 167 (9), 158 (26), 157 (100), 155 (12), 154 (117), 153 (15), 144 (17), 142 (10), 141 (23), 131 (10), 130 (9), 129 (23), 128 (23), 127 (9), 115 (30), 103 (10), 91 (7), 77 (13), 73 (33).

**Unidentified Compound** From the spectra of the mixture: IR ( $\text{CHCl}_3$ ):  $\tilde{\nu}$  = 3580  $\text{cm}^{-1}$  (w, OH), 3000 (w, arom. CH), 2960 (m, CH), 2924 (m, CH), 2852 (w, CH), 1704 (m, CO), 1460 (w), 1440 (w), 1412 (w), 1348 (w), 1260 (s), 1096 (s), 1044 (s), 1016 (s), 928 (w), 864 (w).  $^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 1.79–1.94 (m, 2 H), 2.04–2.09 (m, 1 H), 2.26–2.31 (m, 1 H), 2.80 (dd,  $J$  = 0.6 Hz,  $J$  = 15.8 Hz, 1 H), 3.27 (ddd,  $J$  = 0.4 Hz,  $J$  = 7.5 Hz,  $J$  = 15.8 Hz, 1 H), 5.30 (dd,  $^2J$  = 1.1 Hz,  $^3J$  = 10.9 Hz, 1 H), 5.48 (dd,  $^3J$  = 17.5 Hz, 1 H), 6.24 (dd, 1 H), 7.09–7.13 (m, 1 H), 7.28–7.32 (m, 1 H), 7.35–7.40 (m, 2 H).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CDCl}_3$ , DEPT):  $\delta$  = 36.6 ( $\text{CH}_2$ ), 39.6 ( $\text{CH}_2$ ), 52.4 ( $\text{CH}_2$ ), 76.3 (CH), 89.9 ( $\text{C}_q$ ), 106.4 ( $\text{C}_q$ ), 115.2 ( $\text{CH}_2$ ), 120.8 (CH), 127.6 (CH), 128.6 (CH), 134.4 (CH), 139.5 (CH), 142.9 ( $\text{C}_q$ ), 146.4 ( $\text{C}_q$ ).

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